# Supplementary Information

## Photoredox Cooperative N-Heterocyclic Carbene/Palladium-Catalysed Alkylacylation of Alkenes

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1. Supplementary Notes.

Unless otherwise indicated, all reactions were carried out under an N\textsubscript{2} atmosphere in oven-dried glassware with magnetic stirring. Anhydrous THF, Tol and 1,4-dioxane were distilled from sodium and benzophenone. Styrenes 1, aldehydes 2 were purchased from Innochem and Energy Chemical. 2-Bromo-2-methylbutane and (2-bromo-2-methylpropyl)benzene 3k-l were synthesized according to literature,\textsuperscript{1} and other alkyl halides 3 were purchased from Innochem and Energy Chemical. Column chromatograph was performed on silica gel 200~300 mesh. All \textsuperscript{1}H, \textsuperscript{13}C NMR spectra were recorded on a Bruker AV 300, 400 and 500 spectrometer. Chemical shifts were reported in parts per million (ppm, \(\delta\)), and the residual solvent peak was used as internal reference. \textsuperscript{1}HNMR Spectroscopy splitting patterns were designated as singlet (s), doublet (d) and triplet (t). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m). Coupling constants were reported in Herz (Hz). High-resolution mass spectra (HRMS) were obtained with the mass analyzer of an orbitrap. Infrared spectra were recorded on a JASCO FT/IR-480 spectrophotometer and reported as wave number (cm\textsuperscript{-1}). UV/vis absorption spectra were recorded on a Jasco V-650 spectrophotometer, equipped with a temperature control unit at 25 °C, and the samples were measured in Hellma fluorescence QS quartz cuvettes (chamber volume = 3.0 mL) fitted with a PTFE stopper.
2. Supplementary Methods.

2.1 Preparation of starting materials: tertiary alkyl bromides 3k-l

\[ \text{R–OH} \xrightarrow{\text{LiBr (2.0 equiv.)}} \text{R–Br} \]

\[ \text{48 wt% aqueous HBr (0.2 M)} \]

\[ 0 \, ^\circ \text{C to rt, overnight} \]

\[ 3k, \text{ R = Me} \]

\[ 3l, \text{ R = Ph} \]

The corresponding tertiary alcohol precursor (10 mmol, 1.0 equiv.) was added LiBr (1.80 g, 20 mmol, 2.0 equiv.) in 48 wt% aqueous HBr (0.2 M, 20 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for overnight. The reaction mixture was diluted with ethyl acetate, washed with water and saturated NaHCO₃. The organic layer was collected, washed with brine, dried over MgSO₄, and concentrated. The residue was purified by column chromatography to afford the desired tertiary bromides 3k-l, and the experimental data are in agreement with the previous reports.

2.2 Alkylacylation of alkenes (Fig. 2)

Typical procedure (Standard conditions). A 4 mL vial equipped with a stir bar was
charged with preNHC N1 (10.8 mg, 0.04 mmol), Pd(OAc)$_2$ (4.5 mg, 0.02 mmol), ligand L1 (11.9 mg, 0.024 mmol) and 1.0 mL of 1,4-dioxane. After stirring for 30 min in glove box, to the solution was added Cs$_2$CO$_3$ (97.8 mg, 0.3 mmol), additive A1 (4.4 mg, 0.04 mmol), alkenes 1 (0.2 mmol), aldehydes 2 (0.4 mmol), alkyl halides 3 (0.3 mmol), and 1.0 mL of 1,4-dioxane. The reaction mixture was removed from the glove box and stirred under 36W blue LED lights at room temperature until the complete consumption of 1 (generally 48 hours) by TLC analysis. The reaction mixture was filtered through a small pad of silica and eluted with EtOAc. The solution was concentrated under reduced pressure, and purified by column chromatography on silica gel to afford the desired ketones.

For the reaction with secondary and tertiary haloalkanes and benzylic bromide, two equivalent alkenes were used.

![Chemical Structure](image)

2-(naphthalen-2-yl)-1-(pyridin-2-yl)-4-(trimethylsilyl)butan-1-one (4)

Yield 54.0 mg, 78%. Light yellow oil, R$_f$ = 0.44 (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.68 – 8.67 (m, 1H), 8.02 (d, $J$ = 7.8 Hz, 1H), 7.86 – 7.68 (m, 5H), 7.57 (dd, $J$ = 8.5, 1.8 Hz, 1H), 7.48 – 7.32 (m, 3H), 5.50 (t, $J$ = 7.4 Hz, 1H), 2.31 – 2.18 (m, 1H), 2.04 – 1.91 (m, 1H), 0.62 – 0.41 (m, 2H), -0.02 (s, 9H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 201.9, 153.4, 149.0, 137.0, 136.9, 133.6, 132.6, 128.2, 127.9, 127.7, 127.4, 127.0, 126.0, 125.7, 122.8, 54.2, 27.7, 15.0, -1.7.

IR (KBr) $\nu$ 2950, 1693, 1247, 859, 834, 743 696.

HRMS (ESI) $m/z$: Calc. For C$_{22}$H$_{26}$O$_3$Si ([M+H]$^+$) 348.1778, Found 348.1777.
2-phenyl-1-(pyridin-2-yl)-4-(trimethylsilyl)butan-1-one (5)
Yield 50.5 mg, 85%. Light yellow oil, Rf = 0.48 (petroleum ether/ethyl acetate, 10:1).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.70 – 8.69 (m, 1H), 8.03 (d, \(J = 7.8\) Hz, 1H), 7.78 (td, \(J = 7.7, 1.8\) Hz, 1H), 7.44 – 7.40 (m, 3H), 7.32 – 7.27 (m, 2H), 7.23 – 7.20 (m, 1H), 5.37 (t, \(J = 7.5\) Hz, 1H), 2.26 – 2.14 (m, 1H), 1.96 – 1.83 (m, 1H), 0.60 – 0.41 (m, 2H), -0.00 (s, 9H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 202.0, 153.4, 149.0, 139.5, 136.9, 129.1, 128.6, 127.0, 126.8, 122.8, 54.0, 27.8, 14.9, -1.7.

IR (KBr) \(\nu\) 2951, 1694, 1501, 1249, 1177, 1036, 856, 836, 747.

HRMS (ESI) \(m/z\): Calc. For C\(_{18}\)H\(_{24}\)O\(_2\)N\(_2\)Si ([M+H]\(^+\)) 298.1621, Found 298.1621.

2-(4-methoxyphenyl)-1-(pyridin-2-yl)-4-(trimethylsilyl)butan-1-one (6)
Yield 46.7 mg, 71%. Light yellow oil, Rf = 0.31 (petroleum ether/ethyl acetate, 10:1).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.71 – 8.69 (m, 1H), 8.03 (d, \(J = 7.9\) Hz, 1H), 7.79 (td, \(J = 7.7, 1.8\) Hz, 1H), 7.44 – 7.40 (m, 1H), 7.34 (d, \(J = 8.7\) Hz, 2H), 6.83 (d, \(J = 8.7\) Hz, 2H), 5.31 (t, \(J = 7.5\) Hz, 1H), 3.77 (s, 3H), 2.23 – 2.10 (m, 1H), 1.92 – 1.79 (m, 1H), 0.58 – 0.41 (m, 2H), -0.00 (s, 9H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 202.1, 158.5, 153.5, 148.9, 136.9, 131.5, 130.1, 126.9, 122.8, 114.0, 55.3, 53.0, 27.6, 14.9, -1.7.

IR (KBr) \(\nu\) 2951, 1693, 1501, 1249, 1177, 1036, 856, 836, 747.

HRMS (ESI) \(m/z\): Calc. For C\(_{19}\)H\(_{26}\)O\(_2\)NSi ([M+H]\(^+\)) 328.1727, Found 328.1726.
2-(4-(tert-butyl)phenyl)-1-(pyridin-2-yl)-4-(trimethylsilyl)butan-1-one (7)

Yield 39.5 mg, 56%. Light yellow viscous oil, $R_f = 0.47$ (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.72 (d, $J = 4.8$ Hz, 1H), 8.04 (d, $J = 7.9$ Hz, 1H), 7.79 (td, $J = 7.7$, 1.8 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.36 – 7.28 (m, 4H), 5.39 (t, $J = 7.5$ Hz, 1H), 2.28 – 2.15 (m, 1H), 1.93 – 1.81 (m, 1H), 1.29 (s, 9H), 0.56 – 0.48 (m, 2H), 0.00 (s, 9H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 202.2, 153.6, 149.5, 149.0, 136.9, 136.4, 128.6, 127.0, 125.5, 122.8, 53.3, 34.5, 31.5, 27.9, 15.1, -1.7.

IR (KBr) $\nu$ 2955, 1694, 1247, 857, 835.

HRMS (ESI) $m/z$: Calc. For C$_{21}$H$_{32}$ONSi ([M+H]$^+$) 354.2248, Found 354.2247.

1-(pyridin-2-yl)-2-(p-tolyl)-4-(trimethylsilyl)butan-1-one (8)

Yield 37.1 mg, 60%. Light yellow oil, $R_f = 0.44$ (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.70 (d, $J = 4.8$ Hz, 1H), 8.03 (d, $J = 7.9$ Hz, 1H), 7.80 – 7.77 (m, 1H), 7.42 (t, $J = 5.9$ Hz, 1H), 7.32 – 7.29 (m, 2H), 7.10 (d, $J = 7.8$ Hz, 2H), 5.33 (t, $J = 7.4$ Hz, 1H), 2.30 (s, 3H), 2.22 – 2.14 (m, 1H), 1.91 – 1.85 (m, 1H), 0.57 – 0.45 (m, 2H), 0.00 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 202.1, 153.5, 149.0, 136.9, 136.4, 129.3, 129.0, 126.9, 122.8, 53.6, 27.7, 21.2, 14.9, -1.7.

IR (KBr) $\nu$ 2951, 1694, 1247, 857, 837, 802, 746.

HRMS (ESI) $m/z$: Calc. For C$_{19}$H$_{26}$NOSi ([M+H]$^+$) 312.1778, Found 312.1776.
2-([1,1'-biphenyl]-4-yl)-1-(pyridin-2-yl)-4-(trimethylsilyl)butan-1-one (9)

Yield 58.9 mg, 79%. Light yellow oil, R_f = 0.38 (petroleum ether/ethyl acetate, 10:1).

^1H NMR (500 MHz, CDCl_3) δ 8.74 – 8.70 (m, 1H), 8.08 – 8.03 (m, 1H), 7.83 – 7.77 (m, 1H), 7.59 – 7.47 (m, 6H), 7.43 – 7.39 (m, 3H), 7.35 – 7.27 (m, 1H), 5.44 – 5.40 (m, 1H), 2.25 – 2.18 (m, 1H), 1.95 – 1.89 (m, 1H), 0.59 – 0.50 (m, 2H), 0.00 (s, 9H).

^13C NMR (126 MHz, CDCl_3) δ 201.9, 153.4, 149.0, 141.0, 139.7, 138.6, 137.0, 129.5, 128.8, 127.3, 127.2, 127.1, 127.0, 122.8, 53.6, 27.8, 15.0, -1.7.

IR (KBr) ν 2951, 1694, 1485, 1247, 857, 836, 762, 697.

HRMS (ESI) m/z: Calc. For C_{24}H_{28}NOSi ([M+H]^+) 374.1935, Found 374.1932.

4-(1-oxo-1-(pyridin-2-yl)-4-(trimethylsilyl)butan-2-yl)phenyl acetate (10)

Yield 41.1 mg, 58%. Light yellow oil, R_f = 0.33 (petroleum ether/ethyl acetate, 5:1).

^1H NMR (400 MHz, CDCl_3) δ 8.69 (dd, J = 4.8, 1.8 Hz, 1H), 8.03 (d, J = 7.8 Hz, 1H), 7.79 (td, J = 7.7, 1.8 Hz, 1H), 7.45 – 7.41 (m, 3H), 7.01 – 6.99 (m, 2H), 5.39 (t, J = 7.5 Hz, 1H), 2.28 (s, 3H), 2.23 – 2.13 (m, 1H), 1.91 – 1.81 (m, 1H), 0.55 – 0.43 (m, 2H), -0.01 (s, 9H).

^13C NMR (126 MHz, CDCl_3) δ 201.8, 169.6, 153.2, 149.5, 149.0, 137.0, 130.1, 127.1, 122.8, 121.5, 53.2, 27.8, 21.3, 14.9, -1.7.

IR (KBr) ν 2951, 1764, 1694, 1504, 1369, 1167, 858, 837.

HRMS (ESI) m/z: Calc. For C_{20}H_{26}NO_3Si ([M+H]^+) 356.1677, Found 356.1675.
2-(4-fluorophenyl)-1-(pyridin-2-yl)-4-(trimethylsilyl)butan-1-one (11)

Yield 47.7 mg, 76%. Light yellow oil, R_f = 0.49 (petroleum ether/ethyl acetate, 10:1).

^1H NMR (500 MHz, CDCl_3) δ 8.70 – 8.69 (m, 1H), 8.03 (d, J = 7.9 Hz, 1H), 7.81 – 7.79 (m, 1H), 7.45 – 7.44 (m, 1H), 7.40 – 7.37 (m, 2H), 6.98 (t, J = 8.5 Hz, 2H), 5.35 (t, J = 7.5 Hz, 1H), 2.20 – 2.13 (m, 1H), 1.89 – 1.81 (m, 1H), 0.55 – 0.41 (m, 2H), 0.00 (s, 9H).

^13C NMR (126 MHz, CDCl_3) δ 201.9, 161.9 (d, J_{CF} = 245 Hz), 153.2, 149.0, 137.0, 135.1 (d, J_{CF} = 3 Hz), 130.6 (d, J_{CF} = 8 Hz), 127.1, 122.8, 115.4 (d, J_{CF} = 21 Hz), 53.0, 27.8, 14.8, -1.7.

IR (KBr) ν 2952, 1695, 1507, 1247, 1222, 857, 836, 747.

HRMS (ESI) m/z: Calc. For C_{18}H_{23}NOFSi ([M+H]^+) 316.1528, Found 316.1526.

2-(4-chlorophenyl)-1-(pyridin-2-yl)-4-(trimethylsilyl)butan-1-one (12)

Yield 53.6 mg, 81%. Light yellow oil, R_f = 0.42 (petroleum ether/ethyl acetate, 10:1).

^1H NMR (400 MHz, CDCl_3) δ 8.69 (d, J = 4.7 Hz, 1H), 8.03 (d, J = 7.8 Hz, 1H), 7.81 (t, J = 7.7 Hz, 1H), 7.46 – 7.43 (m, 1H), 7.36 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 5.34 (t, J = 7.5 Hz, 1H), 2.21 – 2.11 (m, 1H), 1.90 – 1.81 (m, 1H), 0.56 – 0.40 (m, 2H), 0.00 (s, 9H).

^13C NMR (101 MHz, CDCl_3) δ 201.6, 153.1, 149.0, 138.0, 137.0, 132.7, 130.5, 128.7, 127.2, 122.8, 53.3, 27.7, 14.8, -1.7.

IR (KBr) ν 1695, 1490, 1247, 1092, 1024, 856, 836, 744.

HRMS (ESI) m/z: Calc. For C_{18}H_{23}NOCl ([M+H]^+) 332.1232, Found 332.1228.
2-((4-bromophenyl)-1-(pyridin-2-yl)-4-(trimethylsilyl)butan-1-one (13)
Yield 65.3 mg, 87%. Light yellow oil, Rf = 0.38 (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.69 (d, $J = 4.9$ Hz, 1H), 8.03 (d, $J = 8.0$ Hz, 1H), 7.82 – 7.79 (m, 1H), 7.46 – 7.41 (m, 3H), 7.30 (d, $J = 8.6$ Hz, 2H), 5.33 (t, $J = 7.5$ Hz, 1H), 2.20 – 2.12 (m, 1H), 1.89 – 1.81 (m, 1H), 0.55 – 0.41 (m, 2H), 0.00 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 201.5, 153.1, 149.0, 138.5, 137.0, 131.7, 130.9, 127.2, 122.8, 120.8, 53.4, 27.6, 14.8, -1.7.

IR (KBr) $\nu$ 2951, 1695, 1486, 1247, 1011, 857, 836, 744, 695.

HRMS (ESI) $m/z$: Calc. For C$_{18}$H$_{23}$NOSi ([M+H]$^+$) 376.0727, Found 376.0723.

methyl 4-(1-oxo-1-(pyridin-2-yl)-4-(trimethylsilyl)butan-2-yl)benzoate (14)
Yield 62.5 mg, 88%. Light yellow oil, Rf = 0.22 (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.70 – 8.69 (m, 1H), 8.04 (d, $J = 7.9$ Hz, 1H), 7.97 (d, $J = 8.2$ Hz, 2H), 7.80 (td, $J = 7.7$, 1.7 Hz, 1H), 7.50 (d, $J = 8.0$ Hz, 2H), 7.45 – 7.43 (m, 1H), 5.43 (t, $J = 7.4$ Hz, 1H), 3.90 (s, 3H), 2.24 – 2.16 (m, 1H), 1.94 – 1.86 (m, 1H), 0.57 – 0.51 (m, 1H), 0.48 – 0.34 (m, 1H), 0.00 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 201.3, 167.1, 153.1, 149.0, 144.9, 137.0, 129.9, 129.2, 128.7, 127.2, 122.8, 54.1, 52.1, 27.7, 14.8, -1.7.

IR (KBr) $\nu$ 2951, 1695, 1486, 1247, 1011, 857, 836, 744, 695.

HRMS (ESI) $m/z$: Calc. For C$_{20}$H$_{26}$NO$_3$Si ([M+H]$^+$) 356.1676, Found 356.1682.
1-(pyridin-2-yl)-2-(4-(trifluoromethyl)phenyl)-4-(trimethylsilyl)butan-1-one (15)
Yield 53.5 mg, 73%. Light yellow oil, Rf = 0.51 (petroleum ether/ethyl acetate, 10:1).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.70 (d, \(J = 4.7\) Hz, 1H), 8.05 (d, \(J = 7.8\) Hz, 1H), 7.81 (td, \(J = 7.7, 1.7\) Hz, 1H), 7.55 (brs, 4H), 7.47 – 7.43 (m, 1H), 5.45 (t, \(J = 7.5\) Hz, 1H), 2.27 – 2.14 (m, 1H), 1.95 – 1.82 (m, 1H), 0.59 – 0.38 (m, 2H), 0.00 (s, 9H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 201.3, 153.0, 149.0, 143.6, 137.1, 129.5, 129.2, 127.3, 125.5 (d, \(J_{\text{CF}} = 4\) Hz), 124.3 (q, \(J_{\text{CF}} = 272\) Hz), 122.8, 53.8, 27.8, 14.9, -1.7.

IR (KBr) \(\nu\) 2953, 1697, 1325, 1248, 1165, 1125, 1068, 858, 837, 697.

HRMS (ESI) \(m/z\): Calc. For C\(_{19}\)H\(_{23}\)F\(_3\)ONSi ([M+H]\(^+\)) 366.1496, Found 366.1494.

4-(1-oxo-1-(pyridin-2-yl)-4-(trimethylsilyl)butan-2-yl)benzonitrile (16)
Yield 49.9 mg, 77%. Light yellow oil, Rf = 0.18 (petroleum ether/ethyl acetate, 10:1).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.70 (d, \(J = 4.7\) Hz, 1H), 8.05 (d, \(J = 7.8\) Hz, 1H), 7.83 (t, \(J = 7.7\) Hz, 1H), 7.57 (q, \(J = 8.2\) Hz, 4H), 7.49 – 7.46 (m, 1H), 5.44 (t, \(J = 7.4\) Hz, 1H), 2.24 – 2.15 (m, 1H), 1.92 – 1.82 (m, 1H), 0.52 (td, \(J = 13.6, 4.6\) Hz, 1H), 0.40 (td, \(J = 13.9, 13.5, 4.4\) Hz, 1H), 0.00 (s, 9H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 200.9, 152.8, 149.1, 145.1, 137.1, 132.4, 129.9, 127.5, 122.8, 119.1, 110.7, 54.1, 27.8, 14.9, -1.7.

IR (KBr) \(\nu\) 2952, 2228, 1696, 1247, 858, 837, 748, 562.

HRMS (ESI) \(m/z\): Calc. For C\(_{19}\)H\(_{23}\)N\(_2\)O\(_3\)Si ([M+H]\(^+\)) 323.1574, Found 323.1575.
4-(1-oxo-1-(pyridin-2-yl)-4-(trimethylsilyl)butan-2-yl)benzaldehyde (17)

Yield 43.5 mg, 67%. Light yellow oil, Rf = 0.38 (petroleum ether/ethyl acetate, 5:1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.97 (s, 1H), 8.70 (d, $J$ = 4.8 Hz, 1H), 8.05 (d, $J$ = 7.9 Hz, 1H), 7.83 – 7.81 (m, 3H), 7.51 – 7.59 (m, 2H), 7.47 – 7.43 (m, 1H), 5.47 (t, $J$ = 7.5 Hz, 1H), 2.22 – 2.17 (m, 1H), 1.95 – 1.87 (m, 1H), 0.58 – 0.40 (m, 2H), 0.00 (s, 9H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 201.1, 192.1, 152.9, 149.1, 146.8, 137.1, 135.2, 130.0, 129.8, 127.3, 122.8, 54.3, 27.8, 14.9, -1.7.

IR (KBr) ν 1699, 1603, 1247, 1212, 1168, 857, 838, 694.

HRMS (ESI) $m/z$: Calc. For C$_{19}$H$_{24}$NO$_2$Si ([M+H]$^+$) 326.1571, Found 326.1570.

2-(4-nitrophenyl)-1-(pyridin-2-yl)-4-(trimethylsilyl)butan-1-one (18)

Yield 38.5 mg, 56%. Light yellow oil, Rf = 0.29 (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.70 – 8.69 (m, 1H), 8.16 (d, $J$ = 8.8 Hz, 2H), 8.05 (d, $J$ = 7.9 Hz, 1H), 7.83 (td, $J$ = 7.7, 1.8 Hz, 1H), 7.60 (d, $J$ = 8.8 Hz, 2H), 7.49 – 7.45 (m, 1H), 5.50 (t, $J$ = 7.4 Hz, 1H), 2.28 – 2.15 (m, 1H), 1.96 – 1.82 (m, 1H), 0.59 – 0.35 (m, 2H), 0.00 (s, 9H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 200.7, 152.7, 149.1, 147.3, 147.0, 137.2, 130.0, 127.5, 123.8, 122.8, 53.9, 27.9, 14.9, -1.7.

IR (KBr) ν 2952, 1696, 1502, 1346, 1248, 857, 837, 744, 707.

HRMS (ESI) $m/z$: Calc. For C$_{18}$H$_{23}$O$_3$N$_2$Si ([M+H]$^+$) 343.1473, Found 343.1470.
1-(pyridin-2-yl)-4-(trimethylsilyl)-2-(4-((trimethylsilyl)ethynyl)phenyl)butan-1-one (19)

Yield 53.9 mg, 68%. Light yellow oil, R_f = 0.38 (petroleum ether/ethyl acetate, 10:1).

^1H NMR (400 MHz, CDCl₃) δ 8.68 (d, J = 4.8 Hz, 1H), 8.02 (d, J = 7.9 Hz, 1H), 7.82 – 7.78 (m, 1H), 7.45 – 7.34 (m, 5H), 5.33 (t, J = 7.5 Hz, 1H), 2.21 – 2.12 (m, 1H), 1.92 – 1.82 (m, 1H), 0.56 – 0.38 (m, 2H), 0.25 (s, 9H), 0.00 (s, 9H).

^13C NMR (101 MHz, CDCl₃) δ 201.5, 153.2, 149.0, 140.1, 136.9, 132.2, 129.1, 127.1, 122.7, 121.5, 105.2, 94.2, 54.0, 27.5, 14.8, 0.1, -1.7.

IR (KBr) ν 2954, 2157, 1696, 1248, 862, 841, 759.

HRMS (ESI) m/z: Calc. For C_{23}H_{32}NOSi₂ ([M+H]^+) 394.2017, Found 394.2015.

2-(naphthalen-1-yl)-1-(pyridin-2-yl)-4-(trimethylsilyl)butan-1-one (20)

Yield 42.5 mg, 61%. Light yellow oil, R_f = 0.49 (petroleum ether/ethyl acetate, 10:1).

^1H NMR (500 MHz, CDCl₃) δ 8.59 (s, 2H), 8.05 – 8.03 (m, 1H), 7.86 – 7.84 (m, 1H), 7.76 – 7.72 (m, 2H), 7.61 – 7.59 (m, 1H), 7.52 – 7.48 (m, 2H), 7.44 – 7.41 (m, 1H), 7.36 – 7.34 (m, 1H), 6.24 – 6.23 (m, 1H), 2.37 – 2.30 (m, 1H), 2.02 – 1.96 (m, 1H), 0.70 – 0.65 (m, 1H), 0.58 – 0.53 (m, 1H), 0.00 (s, 9H).

^13C NMR (126 MHz, CDCl₃) δ 202.4, 153.6, 149.0, 136.8, 136.3, 134.2, 132.3, 128.9, 127.4, 126.7, 126.1, 125.6, 125.5, 125.4, 124.4, 122.6, 49.0, 28.3, 15.4, -1.7.

IR (KBr) ν 2951, 1694, 1247, 859, 839, 795, 777.

HRMS (ESI) m/z: Calc. For C_{22}H_{26}NOSi ([M+H]^+) 348.1778, Found 348.1776.
11134E

1-(pyridin-2-yl)-2-(m-toly)-4-(trimethylsilyl)butan-1-one (21)

Yield 26.7 mg, 43%. Light yellow oil, R\text{f} = 0.54 (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.70 (d, $J = 4.9$ Hz, 1H), 8.03 (d, $J = 7.9$ Hz, 1H), 7.80 – 7.77 (m, 1H), 7.42 – 7.41 (m, 1H), 7.29 – 7.16 (m, 3H), 7.01 (d, $J = 7.7$ Hz, 1H), 5.36 – 5.32 (m, 1H), 2.33 (s, 3H), 2.27 – 2.16 (m, 1H), 1.90 – 1.84 (m, 1H), 0.57 – 0.44 (m, 2H), 0.00 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 202.1, 153.5, 149.0, 139.4, 138.1, 136.9, 129.6, 128.4, 127.6, 127.0, 126.3, 122.8, 53.9, 27.9, 21.6, 15.0, -1.7.

IR (KBr) ν 2951, 1694, 1247, 861, 834, 777, 705.

HRMS (ESI) $m/z$: Calc. For C$_{19}$H$_{26}$NOSi ([M+H]$^+$) 312.1778, Found 312.1780.

11132A

2-(3-bromophenyl)-1-(pyridin-2-yl)-4-(trimethylsilyl)butan-1-one (22)

Yield 50.7 mg, 67%. Light yellow oil, R\text{f} = 0.43 (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.71 – 8.70 (m, 1H), 8.04 (d, $J = 7.9$ Hz, 1H), 7.81 (t, $J = 7.8$ Hz, 1H), 7.58 (brs, 1H), 7.46 – 7.43 (m, 1H), 7.36 – 7.32 (m, 2H), 7.16 (t, $J = 7.8$ Hz, 1H), 5.34 (t, $J = 7.5$ Hz, 1H), 2.19 – 2.14 (m, 1H), 1.88 – 1.84 (m, 1H), 0.55 – 0.41 (m, 2H), 0.00 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 201.4, 153.0, 149.1, 141.9, 137.0, 132.1, 130.1, 130.0, 127.7, 127.2, 122.8, 122.6, 53.5, 27.8, 14.9, -1.7.

IR (KBr) ν 2951, 1695, 1566, 1247, 859, 837, 780, 689.

HRMS (ESI) $m/z$: Calc. For C$_{18}$H$_{23}$ONBrSi ([M+H]$^+$) 376.0727, Found 376.0722.
2-(2-bromophenyl)-1-(pyridin-2-yl)-4-(trimethylsilyl)butan-1-one (23)

Yield 52.2 mg, 69%. Light yellow oil, Rf = 0.40 (petroleum ether/ethyl acetate, 10:1).

\[ ^1H \text{ NMR } (500 \text{ MHz, CDCl}_3) \delta 8.68 (d, J = 4.8 \text{ Hz}, 1H), 8.03 (d, J = 7.8 \text{ Hz}, 1H), 7.79 (t, J = 7.7 \text{ Hz}, 1H), 7.58 (d, J = 8.0 \text{ Hz}, 1H), 7.42 - 7.40 (dd, J = 7.6, 4.6 \text{ Hz}, 1H), 7.28 - 7.26 (m, 1H), 7.24 - 7.21 (m, 1H), 7.06 (t, J = 7.7 \text{ Hz}, 1H), 5.77 (t, J = 7.2 \text{ Hz}, 1H), 2.19 - 2.11 (m, 1H), 1.86 - 1.78 (m, 1H), 0.67 (td, J = 13.7, 4.5 \text{ Hz}, 1H), 0.52 (td, J = 13.6, 4.5 Hz, 1H), 0.00 (s, 9H). \]

\[ ^{13}C \text{ NMR } (126 \text{ MHz, CDCl}_3) \delta 201.7, 153.3, 149.2, 139.4, 136.8, 133.2, 129.1, 128.2, 127.6, 127.0, 126.0, 122.5, 53.4, 27.6, 14.9, -1.7. \]

IR (KBr) ν 2951, 1696, 1469, 1247, 1022, 858, 836, 749.

HRMS (ESI) m/z: Calc. For C\textsubscript{18}H\textsubscript{23}NOSiBr ([M+H]\textsuperscript{+}) 376.0727, Found 376.0722.

2-(2-chlorophenyl)-1-(pyridin-2-yl)-4-(trimethylsilyl)butan-1-one (24)

Yield 60.6 mg, 91%. Light yellow oil, Rf = 0.54 (petroleum ether/ethyl acetate, 10:1).

\[ ^1H \text{ NMR } (500 \text{ MHz, CDCl}_3) \delta 8.68 (d, J = 4.7 \text{ Hz}, 1H), 8.03 (d, J = 7.8 \text{ Hz}, 1H), 7.79 (t, J = 7.7 \text{ Hz}, 1H), 7.42 - 7.38 (m, 2H), 7.31 - 7.29 (m, 1H), 7.21 - 7.13 (m, 2H), 5.80 (t, J = 7.1 \text{ Hz}, 1H), 2.20 - 2.13 (m, 1H), 1.87 - 1.80 (m, 1H), 0.68 - 0.62 (m, 1H), 0.55 - 0.49 (m, 1H), 0.00 (s, 9H). \]

\[ ^{13}C \text{ NMR } (126 \text{ MHz, CDCl}_3) \delta 201.8, 153.3, 149.2, 137.7, 136.8, 135.0, 129.8, 129.1, 127.9, 127.0, 126.9, 122.5, 50.7, 27.4, 14.8, -1.7. \]

IR (KBr) ν 2951, 1696, 1473, 1435, 1247, 1036, 858, 837, 751.

HRMS (ESI) m/z: Calc. For C\textsubscript{18}H\textsubscript{23}NOSiCl ([M+H]\textsuperscript{+}) 332.1232, Found 332.1229.
2-(perfluorophenyl)-1-(pyridin-2-yl)-4-(trimethylsilyl)butan-1-one (25)

Yield 59.7 mg, 77%. Light yellow oil, Rf = 0.42 (petroleum ether/ethyl acetate, 10:1).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.57 – 8.56 (m, 1H), 8.04 (d, \(J = 7.8\) Hz, 1H), 7.82 (td, \(J = 7.7, 1.7\) Hz, 1H), 7.44 – 7.41 (m, 1H), 5.25 – 5.22 (m, 1H), 2.31 – 2.24 (m, 1H), 1.92 – 1.84 (m, 1H), 0.59 (td, \(J = 13.6, 4.2\) Hz, 1H), 0.38 (td, \(J = 13.7, 4.5\) Hz, 1H), -0.00 (s, 9H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 197.7, 152.4, 148.9, 145.5(m), 139.8(m), 137.6(m), 137.1, 127.3, 122.8, 111.4(m), 46.4, 24.2, 14.7, -1.8.

IR (KBr) \(\nu\) 2953, 1708, 1521, 1501, 1249, 1029, 990, 863, 836.

HRMS (ESI) \(m/z\): Calc. For C\(_{18}\)H\(_{19}\)NOF\(_5\)Si ([M+H]\(^+\)) 388.1151, Found 388.1146.

1,2-di(pyridin-2-yl)-4-(trimethylsilyl)butan-1-one (26)

Yield 38.5 mg, 65%. Light yellow oil, Rf = 0.15 (petroleum ether/ethyl acetate, 10:1).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.66 (dd, \(J = 3.8, 1.0\) Hz, 1H), 8.62 – 8.45 (m, 1H), 8.08 (dd, \(J = 7.9, 1.2\) Hz, 1H), 7.80 (td, \(J = 7.7, 1.8\) Hz, 1H), 7.71 – 7.57 (m, 1H), 7.55 – 7.36 (m, 2H), 7.10 (ddd, \(J = 7.8, 5.0, 1.3\) Hz, 1H), 5.50 (t, \(J = 7.3\) Hz, 1H), 2.26 (tdd, \(J = 13.4, 7.2, 4.5\) Hz, 1H), 1.99 (tdd, \(J = 13.4, 7.4, 4.5\) Hz, 1H), 0.62 (dd, \(J = 14.0, 4.4\) Hz, 1H), 0.46 (ddd, \(J = 14.4, 12.9, 4.4\) Hz, 1H), 0.00 (s, 9H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 200.8, 159.7, 153.4, 149.5, 149.0, 136.8, 136.4, 126.8, 123.9, 122.7, 121.5, 56.9, 26.9, 14.9, -1.8.

IR (KBr) \(\nu\) 2951, 1699, 1587, 1433, 1247, 858, 837, 746.
HRMS (ESI) m/z: Calc. For C_{17}H_{23}ON_{2}Si ([M+H]^+) 299.1574, Found 299.1571.

1-(pyridin-2-yl)-2-(thiophen-2-yl)-4-(trimethylsilyl)butan-1-one (27)
Yield 51.8 mg, 85%. Light yellow oil, R_f = 0.31 (petroleum ether/ethyl acetate, 10:1).

^1H NMR (500 MHz, CDCl_3) δ 8.73 (d, J = 4.5 Hz, 1H), 8.08 (d, J = 7.8 Hz, 1H), 7.83 (t, J = 7.7 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.20 – 7.19 (m, 1H), 6.99 (s, 1H), 6.94 – 6.92 (m, 1H), 5.72 – 5.69 (m, 1H), 2.22 – 2.15 (m, 1H), 1.97 – 1.89 (m, 1H), 0.56 (t, J = 8.4 Hz, 2H), 0.00 (s, 9H).

^13C NMR (126 MHz, CDCl_3) δ 200.7, 152.9, 149.0, 142.1, 137.1, 127.3, 126.6, 126.1, 124.8, 123.0, 48.5, 29.1, 14.8, -1.7.

IR (KBr) ν 2951, 1697, 1247, 865, 835, 745, 697.

HRMS (ESI) m/z: Calc. For C_{16}H_{22}NOSi ([M+H]^+) 304.1186, Found 304.1186.

11134I

2-(benzofuran-2-yl)-1-(pyridin-2-yl)-4-(trimethylsilyl)butan-1-one (28)
Yield 56.5 mg, 84%. Light yellow oil, R_f = 0.21 (petroleum ether/ethyl acetate, 10:1).

^1H NMR (400 MHz, CDCl_3) δ 8.72 (d, J = 4.8 Hz, 1H), 8.09 (d, J = 7.8 Hz, 1H), 7.83 (td, J = 7.7, 1.8 Hz, 1H), 7.49 – 7.43 (m, 3H), 7.22 – 7.14 (m, 2H), 6.61 (s, 1H), 5.64 (t, J = 7.3 Hz, 1H), 2.34 – 2.04 (m, 2H), 0.61 – 0.57 (m, 2H), 0.00 (s, 9H).

^13C NMR (101 MHz, CDCl_3) δ 199.2, 156.2, 155.0, 152.9, 149.1, 137.1, 128.8, 127.4, 123.6, 122.8, 122.6, 120.7, 111.3, 104.6, 48.1, 25.7, 14.7, -1.7.

IR (KBr) ν 2927, 1693, 766, 743, 700.

HRMS (ESI) m/z: Calc. For C_{20}H_{24}NO_{2}Si ([M+H]^+) 338.1571, Found 338.1567.
2-methyl-2-phenyl-1-(pyridin-2-yl)-4-(trimethylsilyl)butan-1-one (29)

Yield 44.3 mg, 71%. Light yellow oil, R_f = 0.45 (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.44 – 8.43 (m, 1H), 7.89 (d, $J = 7.9$ Hz, 1H), 7.75 (t, $J = 7.8$ Hz, 1H), 7.34 – 7.33 (m, 4H), 7.29 – 7.27 (m, 1H), 7.25 – 7.23 (m, 1H), 2.70 (td, $J = 13.6$, 4.0 Hz, 1H), 2.08 (td, $J = 13.7$, 4.2 Hz, 1H), 1.76 (s, 3H), 0.44 (td, $J = 13.8$, 4.2 Hz, 1H), 0.29 (td, $J = 13.9$, 4.0 Hz, 1H), 0.00 (s, 9H).

$^{13}$C NMR 204.0, 154.2, 148.2, 145.2, 136.3, 128.3, 126.5, 126.0, 125.7, 123.7, 55.8, 33.0, 23.8, 10.8, -1.8.

IR (KBr) $\nu$ 2951, 1686, 1246, 973, 836, 758, 744, 699.

HRMS (ESI) $m/z$: Calc. For C$_{19}$H$_{26}$NOSi ([M+H]$^+$) 312.1778, Found 312.1777.

1-(furan-2-yl)-2-phenyl-4-(trimethylsilyl)butan-1-one (30)

Yield 29.6 mg, 52%. Colorless oil, R_f = 0.32 (petroleum ether/ethyl acetate, 20:1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (s, 1H), 7.38 – 7.20 (m, 6H), 6.50 (s, 1H), 4.33 (t, $J = 7.3$ Hz, 1H), 2.25 – 2.15 (m, 1H), 1.88 – 1.79 (m, 1H), 0.58 – 0.39 (m, 2H), 0.00 (s, 9H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 189.6, 152.9, 146.5, 139.4, 128.8, 128.5, 127.2, 117.8, 112.3, 57.3, 27.9, 15.0, -1.7

IR (KBr) $\nu$ 2951, 1673, 1565, 1466, 1248, 1030, 859, 836, 759, 698.

HRMS (ESI) $m/z$: Calc. For C$_{17}$H$_{23}$O$_2$Si ([M+H]$^+$) 287.1462, Found 287.1462.
**2-phenyl-1-(thiazol-4-yl)-4-(trimethylsilyl)butan-1-one (31)**

Yield 38.9 mg, 64%. Colorless Oil, R_f = 0.50 (petroleum ether/ethyl acetate, 20:1).

^1H NMR (400 MHz, CDCl_3) δ 8.80 (d, J = 2.1 Hz, 1H), 8.21 (d, J = 2.1 Hz, 1H), 7.42 – 7.41 (m, 2H), 7.33 – 7.29 (m, 2H), 7.24 – 7.23 (m, 1H), 4.95 (t, J = 7.4 Hz, 1H), 2.27 – 2.18 (m, 1H), 1.92 – 1.82 (m, 1H), 0.59 – 0.43 (m, 2H), 0.00 (s, 9H).

^13C NMR (101 MHz, CDCl_3) δ 195.4, 156.0, 152.6, 139.2, 129.0, 128.7, 127.0, 125.9, 57.9, 27.8, 14.9, -1.7.

IR (KBr) ν 2950, 1685, 1476, 1418, 1247, 858, 836, 740, 697.

HRMS (ESI) m/z: Calc. For C_{16}H_{22}NOSiS ([M+H]^+) 304.1186, Found 304.1184.

**1-(2-methylthiazol-4-yl)-2-phenyl-4-(trimethylsilyl)butan-1-one (32)**

Yield 42.2 mg, 66%. Colorless oil, R_f = 0.49 (petroleum ether/ethyl acetate, 10:1).

^1H NMR (400 MHz, CDCl_3) δ 7.99 (s, 1H), 7.42 (d, J = 7.6 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.25 – 7.23 (m, 1H), 4.86 (t, J = 7.4 Hz, 1H), 2.76 (s, 3H), 2.26 – 2.16 (m, 1H), 1.90 – 1.80 (m, 1H), 0.59 – 0.41 (m, 2H), 0.00 (s, 9H).

^13C NMR (101 MHz, CDCl_3) δ 195.3, 165.8, 154.9, 139.4, 129.0, 128.6, 127.0, 126.1, 57.7, 27.8, 19.5, 14.9, -1.7.

IR (KBr) ν 2951, 1684, 1476, 1247, 1155, 856, 836, 740, 697.

HRMS (ESI) m/z: Calc. For C_{17}H_{24}NOSiS ([M+H]^+) 318.1342, Found 318.1342.
1-(4-methylpyridin-2-yl)-2-phenyl-4-(trimethylsilyl)butan-1-one (33)
Yield 37.4 mg, 60%. Colorless oil, Rf = 0.27 (petroleum ether/ethyl acetate, 20:1).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.55 (d, \(J = 4.9\) Hz, 1H), 7.85 (s, 1H), 7.42 (d, \(J = 7.7\) Hz, 2H), 7.30 – 7.18 (m, 4H), 5.37 (t, \(J = 7.5\) Hz, 1H), 2.39 (s, 3H), 2.24 – 2.15 (m, 1H), 1.93 – 1.84 (m, 1H), 0.58 – 0.43 (m, 2H), 0.00 (s, 9H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 202.3, 153.4, 148.8, 148.2, 139.6, 129.1, 128.5, 127.9, 126.8, 123.6, 54.0, 27.7, 21.1, 14.9, 1.7.

IR (KBr) \(v\) 2951, 1693, 1599, 1474, 1304, 1249, 1034, 859, 834, 748, 702.

HRMS (ESI) \textit{m/z}: Calc. For C\(_{19}\)H\(_{26}\)NOSi ([M+H]\(^+\)) 312.1778, Found 312.1777.

1-((4-methoxypyridin-2-yl)-2-phenyl-4-(trimethylsilyl)butan-1-one (34)
Yield 39.7 mg, 61%. Colorless oil, Rf = 0.44 (petroleum ether/ethyl acetate, 10:1).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.50 (d, \(J = 5.7\) Hz, 1H), 7.56 (d, \(J = 2.5\) Hz, 1H), 7.42 (d, \(J = 7.6\) Hz, 2H), 7.29 (t, \(J = 7.5\) Hz, 2H), 7.22 – 7.20 (m, 1H), 6.94 – 6.93 (m, 1H), 5.37 (t, \(J = 7.5\) Hz, 1H), 3.88 (s, 3H), 2.24 – 2.14 (m, 1H), 1.93 – 1.83 (m, 1H), 0.57 – 0.44 (m, 2H), 0.00 (s, 9H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 202.0, 166.6, 155.4, 150.1, 139.5, 129.1, 128.6, 126.8, 113.9, 107.8, 55.5, 54.0, 27.8, 14.9, 1.7.

IR (KBr) \(v\) 2950, 1694, 1591, 1474, 1304, 1249, 1034, 860, 836, 747, 699.

HRMS (ESI) \textit{m/z}: Calc. For C\(_{19}\)H\(_{26}\)NO\(_2\)Si ([M+H]\(^+\)) 328.1727, Found 328.1726.

1-(4-chloropyridin-2-yl)-2-phenyl-4-(trimethylsilyl)butan-1-one (35)
Yield 26.9 mg, 41%. Colorless oil, \( R_f = 0.50 \) (petroleum ether/ethyl acetate, 20:1).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.58 (d, \( J = 5.2 \text{ Hz} \), 1H), 8.01 (m, 1H), 7.43 – 7.38 (m, 3H), 7.31 – 7.27 (m, 2H), 7.22 – 7.19 (m, 1H), 5.29 (t, \( J = 7.4 \text{ Hz} \), 1H), 2.23 – 2.14 (m, 1H), 1.93 – 1.83 (m, 1H), 0.57 – 0.41 (m, 2H), 0.00 (s, 9H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 200.7, 154.6, 149.9, 145.5, 139.0, 129.1, 128.7, 127.1, 127.0, 123.2, 54.3, 27.7, 14.9, -1.7.

IR (KBr) \( \nu \) 2951, 1696, 1569, 1247, 1216, 837, 727, 697.

HRMS (ESI) \( m/z \): Calc. For \( C_{18}H_{23}NOSi \) \([\text{[M+H]}^+]\) 332.1232, Found 332.1231.



2-phenyl-1-(pyridin-4-yl)-4-(trimethylsilyl)butan-1-one (36)

Yield 47.2 mg, 79%. Colorless oil, \( R_f = 0.18 \) (petroleum ether/ethyl acetate, 5:1).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.74 – 8.73 (m, 2H), 7.71 – 7.70 (m, 2H), 7.34 – 7.32 (m, 2H), 7.29 – 7.26 (m, 3H), 4.41 (t, \( J = 7.1 \text{ Hz} \), 1H), 2.24 – 2.17 (m, 1H), 1.87 – 1.79 (m, 1H), 0.53 (td, \( J = 13.6, 4.4 \text{ Hz} \), 1H), 0.42 (td, \( J = 13.6, 4.5 \text{ Hz} \), 1H), 0.00 (s, 9H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 199.9, 150.9, 143.2, 138.6, 129.3, 128.4, 127.5, 121.7, 57.9, 28.4, 14.9, -1.7.

IR (KBr) \( \nu \) 2951, 1692, 1407, 1246, 1219, 860, 836, 700.

HRMS (APCI) \( m/z \): Calc. For \( C_{18}H_{22}NOSi \) \([\text{[M-H]}^-]\) 296.1476, Found 296.1477.



4-(1-oxo-1-phenyl-4-(trimethylsilyl)butan-2-yl)benzonitrile (37)

Yield 35.6 mg, 55%. Light yellow oil, \( R_f = 0.20 \) (petroleum ether/ethyl acetate, 20:1).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.96 (d, \( J = 7.8 \text{ Hz} \), 2H), 7.62 (d, \( J = 8.2 \text{ Hz} \), 2H), 7.58 – 7.55 (m, 1H), 7.48 – 7.44 (m, 4H), 4.59 (t, \( J = 7.2 \text{ Hz} \), 1H), 2.24 – 2.17 (m, 1H),
1.86 – 1.79 (m, 1H), 0.56 – 0.50 (m, 1H), 0.41 – 0.36 (m, 1H), 0.00 (d, \( J = 2.1 \) Hz, 9H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 199.4, 145.1, 136.8, 133.5, 132.7, 129.3, 128.9, 128.7, 118.8, 111.1, 56.9, 29.0, 15.1, -1.8.

IR (KBr) \( \nu \) 2951, 2228, 1681, 1247, 855, 836, 692.

HRMS (EI) \( m/z \): Calc. For C\(_{20}\)H\(_{22}\)NOSi ([M\(^{+}\)]\(^{+}\)) 321.1543, Found 321.1546.

4-(1-(4-fluorophenyl)-1-oxo-4-(trimethylsilyl)butan-2-yl)benzonitrile (38)

Yield 35.0 mg, 52%. Colorless oil, \( R_f = 0.24 \) (petroleum ether/ethyl acetate, 20:1).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.00 – 7.97 (m, 2H), 7.63 (d, \( J = 8.3 \) Hz, 2H), 7.45 (d, \( J = 8.3 \) Hz, 2H), 7.12 (t, \( J = 8.6 \) Hz, 2H), 4.53 (t, \( J = 7.2 \) Hz, 1H), 2.23 – 2.16 (m, 1H), 1.85 – 1.78 (m, 1H), 0.55 – 0.49 (m, 1H), 0.41 – 0.35 (m, 1H), 0.00 (s, 9H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 197.8, 165.9 (d, \( J_{CF} = 256 \) Hz), 144.9, 133.2 (d, \( J_{CF} = 3 \) Hz), 132.8, 131.3 (d, \( J_{CF} = 9 \) Hz), 129.2, 118.8, 116.0 (d, \( J_{CF} = 22 \) Hz), 111.3, 56.9, 29.0, 15.1, -1.8.

IR (KBr) \( \nu \) 2951, 2228, 1682, 1597, 1504, 1246, 1156, 836.

HRMS (APCI) \( m/z \): Calc. For C\(_{20}\)H\(_{21}\)NOFSi ([M-H\(^-\)]) 338.1382, Found 338.1382.

4-(1-(4-chlorophenyl)-1-oxo-4-(trimethylsilyl)butan-2-yl)benzonitrile (39)

Yield 49.3 mg, 69%. Colorless oil, \( R_f = 0.23 \) (petroleum ether/ethyl acetate, 20:1).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.90 – 7.88 (m, 2H), 7.63 (d, \( J = 8.6 \) Hz, 2H), 7.45 – 7.42 (m, 4H), 4.53 – 4.51 (m, 1H), 2.23 – 2.15 (m, 1H), 1.85 – 1.78 (m, 1H), 0.55 – 0.49 (m, 1H), 0.41 – 0.34 (m, 1H), 0.00 (s, 9H).
**$^{13}$C NMR** (126 MHz, CDCl$_3$) $\delta$ 198.2, 144.8, 140.0, 135.1, 132.8, 130.1, 129.2, 129.2, 118.7, 111.3, 57.0, 28.9, 15.1, -1.8.

**IR** (KBr) $\nu$ 2952, 2228, 1683, 1588, 1247, 1093, 837.

**HRMS** (APCI) $m/z$: Calc. For C$_{20}$H$_{21}$NOCISi ([M-H]$^-$) 354.1086, Found 354.1087.

4-(1-(4-bromophenyl)-1-oxo-4-(trimethylsilyl)butan-2-yl)benzonitrile (40)

Yield 51.8 mg, 65%. Colorless oil, $R_f$ = 0.26 (petroleum ether/ethyl acetate, 20:1).

**$^1$H NMR** (500 MHz, CDCl$_3$) $\delta$ 7.81 (dd, $J$ = 8.4, 3.2 Hz, 2H), 7.64 – 7.58 (M, 4H), 7.44 (dd, $J$ = 8.3, 3.3 Hz, 2H), 4.53 – 4.50 (m, 1H), 2.22 – 2.15 (m, 1H), 1.85 – 1.77 (m, 1H), 0.52 (td, $J$ = 13.7, 4.1 Hz, 1H), 0.37 (td, $J$ = 13.6, 4.1 Hz, 1H), 0.00 (m, 9H).

**$^{13}$C NMR** (126 MHz, CDCl$_3$) $\delta$ 198.4, 144.8, 135.5, 132.8, 132.2, 130.1, 129.2, 128.8, 118.7, 111.3, 56.9, 28.9, 15.1, -1.8.

**IR** (KBr) $\nu$ 2951, 2228, 1682, 1584, 1247, 1070, 836.

**HRMS** (APCI) $m/z$: Calc. For C$_{20}$H$_{21}$NOBrSi ([M-H]$^-$) 398.0581, Found 398.0585.

4-(1-oxo-1-(3-(trifluoromethyl)phenyl)-4-(trimethylsilyl)butan-2-yl)benzonitrile (41)

Yield 65.8 mg, 84%. Light yellow oil, $R_f$ = 0.28 (petroleum ether/ethyl acetate, 20:1).

**$^1$H NMR** (500 MHz, CDCl$_3$) $\delta$ 8.04 (d, $J$ = 8.1 Hz, 2H), 7.71 (d, $J$ = 8.1 Hz, 2H), 7.64 (d, $J$ = 8.0 Hz, 2H), 7.44 (d, $J$ = 8.0 Hz, 2H), 4.56 (t, $J$ = 7.1 Hz, 1H), 2.24 – 2.17 (m, 1H), 1.87 – 1.80 (m, 1H), 0.52 (td, $J$ = 13.7, 4.3 Hz, 1H), 0.38 (td, $J$ = 13.6, 4.3 Hz, 1H), 0.00 (s, 9H).
**13C NMR** (126 MHz, CDCl₃) δ 198.5, 144.4, 139.4, 134.7 (qf, J CF = 33 Hz), 132.9, 129.2, 129.0, 126.0 (q, J CF J = 4 Hz), 123.4 (q, J CF = 273 Hz), 118.6, 111.5, 57.4, 28.9, 15.1, -1.8.

**IR** (KBr) ν 2229, 1689, 1325, 1170, 1132, 1067, 837.

**HRMS** (ESI) m/z: Calc. For C₂₁H₂₁NF₃OSi ([M-H]) 388.1350, Found 388.1358.

4,4’-(1-oxo-4-(trimethylsilyl)butane-1,2-diyl)dibenzonitrile (42)

Yield 66.6 mg, 96%. Colorless oil, Rf = 0.19 (petroleum ether/ethyl acetate, 5:1).

**1H NMR** (500 MHz, CDCl₃) δ 8.08 – 8.01 (m, 2H), 7.83 – 7.74 (m, 2H), 7.65 – 7.64 (m, 2H), 7.44 – 7.42 (m, 2H), 4.54 – 4.51 (m, 1H), 2.23 – 2.17 (m, 1H), 1.86 – 1.80 (m, 1H), 0.52 (td, J = 13.7, 3.6 Hz, 1H), 0.38 (td, J = 13.7, 3.1 Hz, 1H), 0.00 (s, 9H).

**13C NMR** (126 MHz, CDCl₃) δ 198.2, 144.1, 139.7, 132.9, 132.7, 129.2, 129.0, 118.6, 117.8, 116.7, 111.6, 57.4, 28.9, 15.0, -1.8.

**IR** (KBr) ν 2229, 1688, 1404, 1246, 1216, 836.

**HRMS** (APCI) m/z: Calc. For C₂₁H₂₁N₂OSi ([M-H]) 345.1429, Found 345.1431.

4-(1-(3-chlorophenyl)-1-oxo-4-(trimethylsilyl)butan-2-yl)benzonitrile (43)

Yield 53.6 mg, 75%. Light yellow oil, Rf = 0.21 (petroleum ether/ethyl acetate, 20:1).

**1H NMR** (500 MHz, CDCl₃) δ 7.92 (s, 1H), 7.81 (dt, J = 7.8 Hz, 1H), 7.64 (d, J = 8.1 Hz, 2H), 7.54 – 7.52 (m, 1H), 7.45 (d, J = 8.1 Hz, 2H), 7.39 (t, J = 7.9 Hz, 1H), 4.52 (t, J = 7.1 Hz, 1H), 2.22 – 2.15 (m, 1H), 1.85 – 1.77 (m, 1H), 0.52 (td, J = 13.7, 4.3 Hz, 1H), 0.38 (td, J = 13.6, 4.2 Hz, 1H), 0.00 (s, 9H).
$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 198.2, 144.6, 138.3, 135.3, 133.4, 132.9, 130.2, 129.2, 128.8, 126.7, 118.7, 111.4, 57.1, 29.0, 15.1, -1.8.

IR (KBr) $\nu$ 2951, 2228, 1685, 1247, 1214, 856, 837, 752.

HRMS (APCI) m/z: Calc. For C$_{20}$H$_{21}$NOClSi ([M-H]$^-$) 354.1086, Found 354.1089.

4-(1-(2-hydroxyphenyl)-1-oxo-4-(trimethylsilyl)butan-2-yl)benzonitrile (44)

Yield 35.7 mg, 53%. Colorless oil, $R_f = 0.20$ (petroleum ether/ethyl acetate, 20:1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 12.33 (s, 1H), 7.78 (d, $J = 8.1$ Hz, 1H), 7.64 (d, $J = 7.9$ Hz, 2H), 7.48 – 7.43 (m, 3H), 7.00 (d, $J = 8.4$ Hz, 1H), 6.93 – 6.86 (m, 1H), 4.61 (t, $J = 7.2$ Hz, 1H), 2.23 – 2.16 (m, 1H), 1.88 – 1.78 (m, 1H), 0.53 (td, $J = 13.6$, 4.3 Hz, 1H), 0.39 (td, $J = 13.5$, 4.3 Hz, 1H), -0.02 (s, 9H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 205.3, 163.4, 144.7, 136.9, 132.8, 130.0, 129.6, 129.1, 119.2, 119.1, 118.7, 111.5, 56.1, 28.8, 15.1, -1.8.

IR (KBr) $\nu$ 2951, 2228, 1636, 1605, 1446, 1247, 859, 837, 755.

HRMS (ESI) m/z: Calc. For C$_{20}$H$_{22}$NO$_2$Si ([M-H]$^-$) 336.1425, Found 336.1433.

4-(1-(4-fluoro-2-hydroxyphenyl)-1-oxo-4-(trimethylsilyl)butan-2-yl)benzonitrile (45)

Yield 50.1 mg, 70%. Colorless oil, $R_f = 0.17$ (petroleum ether/ethyl acetate, 20:1).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 12.66 (s, 1H), 7.79 (dd, $J = 9.0$, 6.2 Hz, 1H), 7.65 (d, $J = 8.2$ Hz, 2H), 7.46 (d, $J = 8.0$ Hz, 2H), 6.68 – 6.66 (m, 1H), 6.59 (td, $J = 8.5$, 2.6 Hz, 1H), 4.52 (t, $J = 7.1$ Hz, 1H), 2.23 – 2.15 (m, 1H), 1.86 – 1.79 (m, 1H), 0.51 (td, $J = 13.7$, 4.3 Hz, 1H), 0.38 (td, $J = 13.6$, 4.3 Hz, 1H), 0.00 (s, 9H).
\textbf{13C NMR} (126 MHz, CDCl$_3$) $\delta$ 204.2, 167.6 (d, $J_{CF} = 258$ Hz), 166.1 (d, $J_{CF} = 14$ Hz), 144.5, 132.9, 132.4 (d, $J_{CF} J = 12$ Hz), 129.1, 118.6, 116.4, 111.6, 107.6 (d, $J_{CF} = 23$ Hz), 105.6 (d, $J_{CF} = 24$ Hz), 56.3, 28.8, 15.1, -1.8.

\textbf{IR} (KBr) $\nu$ 2952, 2228, 1638, 1603, 1503, 1247, 1120, 855, 837.

\textbf{HRMS (APCI) $m/z$:} Calc. For C$_{20}$H$_{21}$NO$_2$FSi ([M-H]$^-$) 354.1331, Found 354.1332.

4-(1-(4-chloro-2-hydroxyphenyl)-1-oxo-4-(trimethylsilyl)butan-2-yl)benzonitrile (46)

Yield 53.3 mg, 72%. Colorless oil, $R_f = 0.17$ (petroleum ether/ethyl acetate, 20:1).

\textbf{1H NMR} (500 MHz, CDCl$_3$) $\delta$ 12.45 (d, $J = 4.2$ Hz, 1H), 7.69 (dd, $J = 8.7$, 4.1 Hz, 1H), 7.66 – 7.63 (m, 2H), 7.46 – 7.43 (m, 2H), 7.01 – 7.00 (m, 1H), 6.86 – 6.84 (m, 1H), 4.54 – 4.51 (m, 1H), 2.22 – 2.15 (m, 1H), 1.85 – 1.78 (m, 1H), 0.53 – 0.48 (m, 1H), 0.41 – 0.37 (m, 1H), 0.00 (s, 9H).

\textbf{13C NMR} (126 MHz, CDCl$_3$) $\delta$ 204.6, 164.1, 144.4, 142.8, 132.9, 131.0, 129.1, 119.9, 119.1, 118.6, 117.7, 111.6, 56.4, 28.8, 15.1, -1.8.

\textbf{IR} (KBr) $\nu$ 2952, 2229, 1637, 1605, 1487, 1409, 1247, 1203, 858, 837.

\textbf{HRMS (APCI) $m/z$:} Calc. For C$_{20}$H$_{21}$NO$_2$ClSi ([M-H]$^-$) 370.1036, Found 370.1038.

4-(1-oxo-1-(pyridin-2-yl)pentan-2-yl)benzonitrile (47)

Yield 30.5 mg, 58%. Light yellow oil, $R_f = 0.17$ (petroleum ether/ethyl acetate, 10:1).
$^1$H NMR (500 MHz, CDCl$_3$) δ 8.66 (d, $J = 4.8$ Hz, 1H), 8.01 (d, $J = 7.9$ Hz, 1H), 7.80 (t, $J = 7.7$ Hz, 1H), 7.56 – 7.43 (m, 5H), 5.49 (t, $J = 7.6$ Hz, 1H), 2.19 – 2.12 (m, 1H), 1.88 – 1.81 (m, 1H), 1.32 – 1.26 (m, 2H), 0.92 (t, $J = 7.3$ Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 200.6, 152.7, 149.1, 145.3, 137.1, 132.3, 129.9, 127.5, 122.9, 119.1, 110.7, 50.6, 35.2, 20.9, 14.1.

IR (KBr) ν 2958, 2227, 1696, 1330, 995, 747, 563.

HRMS (ESI) $m/z$: Calc. For C$_{17}$H$_{17}$N$_2$O ([M+H]$^+$) 265.1335, Found 265.1336.

4-(1-oxo-1-(pyridin-2-yl)heptan-2-yl)benzonitrile (48)

Yield 34.3 mg, 59%. Light yellow oil, R$_f$ = 0.22 (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.67 – 8.66 (m, 1H), 8.01 (d, $J = 7.9$ Hz, 1H), 7.80 (td, $J = 7.7$, 1.8 Hz, 1H), 7.56 – 7.51 (m, 4H), 7.45 – 7.43 (m, 1H), 5.46 (t, $J = 7.5$ Hz, 1H), 2.17 – 2.14 (m, 1H), 1.89 – 1.84 (m, 1H), 1.28 – 1.26 (m, 6H), 0.85 – 0.83 (m, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 200.7, 152.7, 149.1, 145.3, 137.1, 132.3, 129.9, 127.5, 122.9, 119.0, 110.7, 50.9, 33.0, 31.8, 27.4, 22.5, 14.1.

IR (KBr) ν 2955, 2227, 1697, 994, 750, 564.

HRMS (ESI) $m/z$: Calc. For C$_{19}$H$_{21}$N$_2$O ([M+H]$^+$) 293.1648, Found 293.1651.

4-(5-methyl-1-oxo-1-(pyridin-2-yl)hexan-2-yl)benzonitrile (49)

Yield 40.5 mg, 69%. Light yellow oil, R$_f$ = 0.30 (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.66 (d, $J = 4.8$ Hz, 1H), 8.02 (d, $J = 7.9$ Hz, 1H), 7.80 (td, $J = 7.7$, 1.7 Hz, 1H), 7.57 – 7.51 (m, 4H), 7.45 – 7.42 (m, 1H), 5.43 (t, $J = 7.5$ Hz, 1H), 2.17 – 2.14 (m, 1H), 1.89 – 1.86 (m, 1H), 1.28 – 1.26 (m, 6H), 0.85 – 0.83 (m, 3H).
1H, 2.20 – 2.14 (m, 1H), 1.90 – 1.82 (m, 1H), 1.61 – 1.52 (m, 1H), 1.22 – 1.15 (m, 1H), 1.12 – 1.04 (m, 1H), 0.85 (t, J = 7.0 Hz, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 200.7, 152.7, 149.1, 145.3, 137.1, 132.4, 129.9, 127.5, 122.9, 119.0, 110.7, 51.1, 36.8, 31.0, 28.1, 22.7, 22.5.

IR (KBr) ν 2932, 2850, 2227, 1696, 1447, 994, 750.

HRMS (ESI) m/z: Calc. For C$_{19}$H$_{21}$N$_2$O ([M+H]$^+$) 293.1648, Found 293.1650.

4-(5,5-dimethyl-1-oxo-1-(pyridin-2-yl)hexan-2-yl)benzonitrile (50)

Yield 50.6 mg, 81%. Light yellow oil, R$_f$ = 0.18 (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.67 – 8.66 (m, 1H), 8.02 (d, J = 7.8 Hz, 1H), 7.81 – 7.78 (m, 1H), 7.57 – 7.52 (m, 4H), 7.45 – 7.43 (m, 1H), 5.39 (td, J = 7.5, 2.6 Hz, 1H), 2.19 – 2.12 (m, 1H), 1.87 – 1.81 (m, 1H), 1.24 – 1.17 (m, 1H), 1.09 – 1.03 (m, 1H), 0.85 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 200.7, 152.6, 149.1, 145.3, 137.1, 132.4, 129.9, 127.5, 122.9, 119.0, 110.7, 51.5, 41.9, 30.4, 29.3, 28.3.

IR (KBr) ν 2955, 2227, 1697, 994, 750, 564.

HRMS (ESI) m/z: Calc. For C$_{20}$H$_{23}$N$_2$O ([M+H]$^+$) 307.1805, Found 307.1804.

4-(4-ethyl-1-oxo-1-(pyridin-2-yl)hexan-2-yl)benzonitrile (51)

Yield 40.1 mg, 65%. Light yellow oil, R$_f$ = 0.23 (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.67 (d, J = 4.7 Hz, 1H), 8.01 (d, J = 7.9 Hz, 1H), 7.80 (t, J = 7.7 Hz, 1H), 7.57 – 7.52 (m, 4H), 7.46 – 7.43 (m, 1H), 5.62 (t, J = 7.6 Hz, 1H), 4.76 (t, J = 7.7 Hz, 1H),
2.15 – 2.08 (m, 1H), 1.84 – 1.77 (m, 1H), 1.41 – 1.26 (m, 4H), 1.11 – 1.07 (m, 1H), 0.85 (t, J = 7.6 Hz, 3H), 0.78 (t, J = 7.5 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 200.7, 152.6, 149.1, 145.5, 137.1, 132.3, 130.0, 127.4, 122.9, 119.1, 110.6, 48.4, 38.2, 36.4, 25.5, 25.1, 10.7, 10.4.

IR (KBr) ν 2920, 2227, 1697, 1460, 994, 749.

HRMS (ESI) m/z: Calc. For C$_{20}$H$_{23}$N$_2$O ([M+H]$^+$) 307.1805, Found 307.1804.

4-(3-cyclohexyl-1-oxo-1-(pyridin-2-yl)propan-2-yl)benzonitrile (52)

Yield 41.4 mg, 65%. Light yellow oil, R$_f$ = 0.26 (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.67 (d, J = 4.8 Hz, 1H), 8.01 (d, J = 7.8 Hz, 1H), 7.79 (t, J = 7.7 Hz, 1H), 7.56 – 7.51 (m, 4H), 7.45 – 7.42 (m, 1H), 5.64 (t, J = 7.5 Hz, 1H), 2.13 – 2.06 (m, 1H), 1.81 – 1.92 (m, 6H), 1.15 – 1.10 (m, 4H), 0.97 – 0.89 (m, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 200.6, 152.6, 149.1, 145.6, 137.1, 132.3, 129.9, 127.4, 122.9, 119.1, 110.6, 48.0, 40.6, 35.7, 33.7, 33.2, 26.6, 26.24, 26.21.

IR (KBr) ν 2955, 2869, 2228, 1697.

HRMS (ESI) m/z: Calc. For C$_{21}$H$_{23}$N$_2$O ([M+H]$^+$) 319.1805, Found 319.1806.

3-cyclopentyl-2-phenyl-1-(pyridin-2-yl)propan-1-one (53)

Yield 42.6 mg, 76%. Light yellow oil, R$_f$ = 0.33 (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.67 – 8.66 (m, 1H), 7.99 (d, J = 7.9 Hz, 1H), 7.75 (td, J = 7.7, 1.7 Hz, 1H), 7.41 – 7.37 (m, 3H), 7.26 – 7.23 (m, 2H), 7.15 (t, J = 7.4 Hz, 1H), 5.48 (t, J = 7.6 Hz, 1H), 2.20 – 2.14 (m, 1H), 1.97 – 1.91 (m, 1H), 1.86 – 1.77 (m,
1H), 1.71 – 1.64 (m, 2H), 1.62 – 1.53 (m, 2H), 1.48 – 1.41 (m, 2H), 1.20 – 1.13 (m, 2H).

13C NMR (126 MHz, CDCl3) δ 201.8, 153.3, 149.0, 139.8, 136.9, 129.1, 128.5, 127.0, 126.8, 122.8, 49.8, 39.5, 38.3, 33.1, 32.7, 25.2.

IR (KBr) ν 2947, 2865, 1694, 859, 836, 701.

HRMS (ESI) m/z: Calc. For C19H22NO ([M+H]+) 280.1696, Found 280.1695.

1H NMR (500 MHz, CDCl3) δ 8.67 (d, J = 4.5 Hz, 1H), 8.01 (dd, J = 8.0, 2.4 Hz, 1H), 7.81 – 7.78 (m, 1H), 7.58 – 7.53 (m, 4H), 7.45 – 7.43 (m, 1H), 5.57 – 5.54 (m, 1H), 2.18 – 2.14 (m, 1H), 1.95 – 1.89 (m, 1H), 1.78 – 1.75 (m, 1H), 1.68 – 1.58 (m, 4H), 1.45 – 1.43 (m, 2H), 1.20 – 1.09 (m, 2H).

13C NMR (126 MHz, CDCl3) δ 200.7, 152.6, 149.1, 145.4, 137.1, 132.3, 129.9, 127.4, 122.9, 119.1, 110.7, 50.0, 39.3, 38.2, 33.1, 32.6, 25.2, 25.2.

IR (KBr) ν 2948, 2865, 2228, 1696, 1605, 1314.

HRMS (APCI) m/z: Calc. For C20H21N2O ([M+H]+) 305.1648, Found 305.1641

4-(3-cyclopentyl-1-oxo-1-(pyridin-2-yl)propan-2-yl)benzonitrile (54)

Yield 50.0 mg, 82%. Light yellow oil, Rf = 0.11 (petroleum ether/ethyl acetate, 10:1).

1H NMR (500 MHz, CDCl3) δ 8.66 (d, J = 4.8 Hz, 1H), 8.01 (d, J = 7.8 Hz, 1H), 7.79 (t, J = 7.6 Hz, 1H), 7.55 – 7.50 (m, 4H), 7.45 – 7.42 (m, 1H), 5.41 (t, J = 7.5 Hz, 1H),
2.25 – 2.21 (m, 1H), 2.17 – 2.14 (m, 1H), 2.00 – 1.96 (m, 2H), 1.89 – 1.86 (m, 1H), 1.78 – 1.67 (m, 3H), 1.59 – 1.55 (m, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 200.5, 152.6, 149.1, 145.3, 137.1, 132.3, 129.9, 127.4, 122.9, 119.1, 110.7, 49.0, 40.2, 34.4, 28.6, 28.3, 18.5.

IR (KBr) $\nu$ 2930, 2227, 1696, 1330.

HRMS (ESI) $m/z$: Calc. For C$_{19}$H$_{19}$N$_2$O ([M+H]$^+$) 291.1492, Found 291.1492.

![Chemical Structure](attachment:11154L.png)

4-(4,4-dimethyl-1-oxo-1-(pyridin-2-yl)pentan-2-yl)benzonitrile (56)
Yield 40.3 mg, 69%. Light yellow oil, $R_f$ = 0.23 (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.71 – 8.70 (m, 1H), 8.01 (d, $J$ = 7.8 Hz, 1H), 7.79 (td, $J$ = 7.7, 1.8 Hz, 1H), 7.55 – 7.51 (m, 4H), 7.46 – 7.44 (m, 1H), 5.73 (dd, $J$ = 8.9, 3.7 Hz, 1H), 2.55 (dd, $J$ = 13.9, 8.9 Hz, 1H), 1.63 (dd, $J$ = 13.9, 3.8 Hz, 1H), 0.88 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 200.6, 152.4, 149.1, 146.8, 137.1, 132.4, 129.8, 127.5, 123.1, 119.0, 110.5, 46.9, 46.8, 31.6, 29.9.

IR (KBr) $\nu$ 2954, 2228, 1698, 563.

HRMS (ESI) $m/z$: Calc. For C$_{19}$H$_{21}$N$_2$O ([M+H]$^+$) 293.1647, Found 293.1648.

![Chemical Structure](attachment:11166A.png)

4-(4,4-dimethyl-1-oxo-1-(pyridin-2-yl)hexan-2-yl)benzonitrile (57)
Yield 45.6 mg, 74%. Light yellow oil, $R_f$ = 0.23 (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.70 (d, $J$ = 4.8 Hz, 1H), 8.01 (d, $J$ = 7.8 Hz, 1H), 7.79 (t, $J$ = 7.7 Hz, 1H), 7.55 – 7.51 (m, 4H), 7.46 – 7.43 (m, 1H), 5.71 (dd, $J$ = 8.8, 3.6 Hz, 1H), 2.55 (dd, $J$ = 13.9, 8.9 Hz, 1H), 1.63 (dd, $J$ = 13.9, 3.8 Hz, 1H), 0.88 (s, 9H).
1H), 2.53 (dd, J = 14.0, 8.8 Hz, 1H), 1.62 (dd, J = 14.0, 3.6 Hz, 1H), 1.25 (q, J = 7.4 Hz, 2H), 0.81 – 0.77 (m, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 200.6, 152.4, 149.1, 146.9, 137.1, 132.4, 129.8, 127.4, 123.1, 119.0, 110.5, 46.3, 44.6, 34.7, 34.1, 27.1, 27.0, 8.5.

IR (KBr) ν 2961, 2227, 1697, 1463, 994, 564.

HRMS (ESI) m/z: Calc. For C$_{20}$H$_{23}$N$_2$O ([M+H]$^+$) 307.1805, Found 307.1805.

**4-(4,4-dimethyl-1-oxo-5-phenyl-1-(pyridin-2-yl)pentan-2-yl)benzonitrile (58)**
Yield 58.4 mg, 79%. Light yellow oil, R$_f$ = 0.18 (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.72 (d, J = 4.7 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.79 (t, J = 7.7 Hz, 1H), 7.56 – 7.51 (m, 4H), 7.47 – 7.44 (m, 1H), 7.26 – 7.17 (m, 3H), 7.08 (d, J = 7.1 Hz, 2H), 5.84 (dd, J = 9.2, 3.3 Hz, 1H), 2.63 (dd, J = 13.9, 9.0 Hz, 1H), 2.55 (s, 2H), 1.68 (dd, J = 13.9, 3.3 Hz, 1H), 0.83 (s, 3H), 0.81 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 200.5, 152.3, 149.1, 146.6, 138.8, 137.2, 132.4, 130.7, 129.8, 127.9, 127.5, 126.1, 123.2, 119.0, 110.6, 48.9, 46.3, 45.3, 35.3, 27.2, 27.0.

IR (KBr) ν 2958, 2227, 1697, 994, 702, 562.

HRMS (ESI) m/z: Calc. For C$_{25}$H$_{25}$N$_2$O ([M+H]$^+$) 369.1961, Found 369.1959.

**4-(6-chloro-1-oxo-1-(pyridin-2-yl)hexan-2-yl)benzonitrile (59)**
Yield 43.1 mg, 69%. Light yellow oil, R$_f$ = 0.17 (petroleum ether/ethyl acetate, 5:1).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.66 (d, J = 4.7 Hz, 1H), 8.02 (d, J = 7.9 Hz, 1H), 7.80 (t, J = 7.8 Hz, 1H), 7.57 – 7.51 (m, 4H), 7.46 – 7.43 (m, 1H), 5.48 (t, J = 7.5 Hz, 1H),
3.50 (t, $J = 6.6$ Hz, 2H), 2.22 – 2.18 (m, 1H), 1.92 – 1.77 (m, 3H), 1.46 – 1.37 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 200.3, 152.4, 149.1, 144.8, 137.2, 132.4, 129.8, 127.6, 122.9, 118.9, 110.9, 50.7, 44.7, 32.5, 32.2, 25.0.

IR (KBr) $\nu$ 2937, 2228, 1696, 1605, 1435, 1397, 1088, 1042, 995, 749, 565.

HRMS (EI) $m/z$: Calc. For C$_{18}$H$_{17}$N$_2$OCl ($[M]^{+}$) 312.1024, Found 312.1023.

11188C

4-(6-chloro-1-(4-chloro-2-hydroxyphenyl)-1-oxohexan-2-yl)benzonitrile (60)

Yield 54.8 mg, 76%. Oil, $R_f = 0.35$ (petroleum ether/ethyl acetate, 5:1).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 12.35 (s, 1H), 7.67 – 7.62 (m, 3H), 7.43 (d, $J = 8.0$ Hz, 2H), 6.99 (d, $J = 2.2$ Hz, 1H), 6.83 (dd, $J = 8.7$, 2.1 Hz, 1H), 4.57 (t, $J = 7.3$ Hz, 1H), 3.51 (q, $J = 7.0$, 6.5 Hz, 2H), 2.24 – 2.18 (m, 1H), 1.90 – 1.75 (m, 3H), 1.50 – 1.37 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 203.9, 164.1, 144.1, 142.9, 133.1, 130.9, 128.9, 120.0, 119.1, 118.5, 117.4, 111.8, 53.0, 44.6, 33.0, 32.4, 25.0.

IR (KBr) $\nu$ 2920, 2228, 1635, 1604, 1238.

HRMS (APCI) $m/z$: Calc. For C$_{19}$H$_{16}$NO$_2$Cl$_2$ ($[M-H]^{-}$) 360.0564, Found 360.0567.

11154F

4-(7-chloro-1-oxo-1-(pyridin-2-yl)heptan-2-yl)benzonitrile (61)

Yield 36.4 mg, 56%. Light yellow oil, $R_f = 0.20$ (petroleum ether/ethyl acetate, 5:1).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.66 (d, $J = 4.9$ Hz, 1H), 8.01 (d, $J = 7.8$ Hz, 1H), 7.80 (td, $J = 7.7$, 1.8 Hz, 1H), 7.57 – 7.51 (m, 4H), 7.46 – 7.43 (m, 1H), 5.47 (t, $J = 7.6$ Hz,
1H), 3.49 (t, $J = 6.6$ Hz, 2H), 2.22 – 2.18 (m, 1H), 1.89 – 1.85 (m, 1H), 1.76 – 1.70 (m, 2H), 1.49 – 1.45 (m, 2H), 1.32 – 1.24 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 200.4, 152.5, 149.1, 145.0, 137.2, 132.4, 129.8, 127.5, 122.9, 119.0, 110.8, 50.7, 45.0, 32.8, 32.4, 27.0, 26.8.

IR (KBr) $\nu$ 2920, 2870, 2195, 1712.

HRMS (ESI) $m/z$: Calc. For C$_{19}$H$_{20}$N$_2$OCl ([M+H]$^+$) 327.1259, Found 327.1258.

5,5,5-trifluoro-2-phenyl-1-(pyridin-2-yl)pentan-1-one (62)

Yield 47.9 mg, 82%. Light yellow oil, $R_f = 0.26$ (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.65 – 8.64 (m, 1H), 7.99 (d, $J = 7.8$ Hz, 1H), 7.76 (td, $J = 7.7$, 1.8 Hz, 1H), 7.41 – 7.36 (m, 3H), 7.27 (t, $J = 7.3$ Hz, 2H), 7.19 (t, $J = 7.3$ Hz, 1H), 5.41 (t, $J = 7.6$ Hz, 1H), 2.41 – 2.34 (m, 1H), 2.23 – 1.97 (m, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 200.3, 152.7, 149.0, 137.9, 137.0, 129.0, 128.9, 128.3, 127.4, 127.3, 127.1 (q, $J_{CF} = 276.6$ Hz), 126.1, 122.9, 49.7, 31.8 (q, $J_{CF} = 28.7$ Hz), 24.95 (d, $J_{CF} = 3.2$ Hz).

IR (KBr) $\nu$ 1696, 1389, 1301, 1256, 1213, 1139, 994, 702.

HRMS (ESI) $m/z$: Calc. For C$_{16}$H$_{15}$NOF$_3$ ([M+H]$^+$) 294.1100, Found 294.1100.

4-(6,6,6-trifluoro-1-oxo-1-(pyridin-2-yl)hexan-2-yl)benzonitrile (63)

Yield 54.6 mg, 82%. Light yellow oil, $R_f = 0.17$ (petroleum ether/ethyl acetate, 5:1).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.66 (d, $J = 4.8$ Hz, 1H), 8.02 (d, $J = 7.9$ Hz, 1H), 7.81 (td, $J = 7.7$, 1.8 Hz, 1H), 7.57 (d, $J = 8.1$ Hz, 2H), 7.51 (d, $J = 8.1$ Hz, 2H), 7.47 –
7.44 (m, 1H), 5.49 (t, $J = 7.5$ Hz, 1H), 2.28 – 2.22 (m, 1H), 2.16 – 2.07 (m, 2H), 1.96 – 1.92 (m, 1H), 1.60 – 1.48 (m, 2H).

**$^{13}$C NMR** (126 MHz, CDCl$_3$) δ 199.9, 152.3, 149.1, 144.3, 137.2, 132.6, 129.8, 127.7, 127.0 (q, $J_{CF} = 275$ Hz), 123.0, 118.8, 111.1, 50.5, 33.7 (q, $J_{CF} = 29$ Hz), 31.9, 20.3 (d, $J_{CF} = 3$ Hz).

**IR** (KBr) ν 2228, 1698, 1281, 1255, 1136, 1042, 1021, 995, 560.

**HRMS (ESI) m/z**: Calc. For C$_{18}$H$_{16}$F$_3$O ([M+H]$^+$) 333.1209, Found 333.1208.

![Structural formula of 4-(4-(4-bromophenyl)-1-oxo-1-(pyridin-2-yl)butan-2-yl)benzonitrile (64)](image)

**4-(4-(4-bromophenyl)-1-oxo-1-(pyridin-2-yl)butan-2-yl)benzonitrile (64)**

Yield 49.7 mg, 61%. Light yellow oil, $R_f = 0.19$ (petroleum ether/ethyl acetate, 5:1).

**$^1$H NMR** (400 MHz, CDCl$_3$) δ 8.64 (d, $J = 4.7$ Hz, 1H), 7.99 (d, $J = 7.8$ Hz, 1H), 7.80 (t, $J = 7.8$ Hz, 1H), 7.58 – 7.50 (m, 4H), 7.45 – 7.42 (m, 1H), 7.36 (d, $J = 8.0$ Hz, 2H), 6.99 (d, $J = 8.0$ Hz, 2H), 5.49 – 5.45 (m, 1H), 2.56 – 2.50 (m, 3H), 2.19 – 2.10 (m, 1H).

**$^{13}$C NMR** (101 MHz, CDCl$_3$) δ 200.0, 152.4, 149.1, 144.7, 140.3, 137.2, 132.5, 131.6, 130.3, 129.9, 127.6, 122.9, 120.0, 118.9, 111.0, 50.3, 34.3, 33.3.

**IR** (KBr) ν 2923, 2227, 1696, 1487, 1404, 1073, 1010, 818.

**HRMS (ESI) m/z**: Calc. For C$_{22}$H$_{16}$N$_2$OBr ([M-H]$^-$) 403.0452, Found 403.0458.

![Structural formula of 4-(1-oxo-1-(pyridin-2-yl)-3-(tetrahydro-2H-pyran-4-yl)propan-2-yl)benzonitrile (65)](image)

**4-(1-oxo-1-(pyridin-2-yl)-3-(tetrahydro-2H-pyran-4-yl)propan-2-yl)benzonitrile (65)**

Yield 44.8 mg, 70%. Light yellow oil, $R_f = 0.23$ (petroleum ether/ethyl acetate, 5:1).
**1H NMR (400 MHz, CDCl3)** δ 8.67 (d, J = 4.8 Hz, 1H), 8.01 (d, J = 7.9 Hz, 1H), 7.81 (t, J = 7.7 Hz, 1H), 7.54 (q, J = 8.1 Hz, 4H), 7.45 (dd, J = 7.5, 4.8 Hz, 1H), 5.66 (t, J = 7.6 Hz, 1H), 3.93 – 3.88 (m, 2H), 3.30 – 3.22 (m, 2H), 2.22 – 2.15 (m, 1H), 1.84 – 1.78 (m, 1H), 1.67 (d, J = 11.8 Hz, 1H), 1.59 (d, J = 12.6 Hz, 1H), 1.41 – 1.28 (m, 3H).

**13C NMR (101 MHz, CDCl3)** δ 200.2, 152.4, 149.1, 145.0, 137.2, 132.5, 129.8, 127.6, 123.0, 118.9, 110.9, 67.9, 67.9, 47.5, 40.0, 33.3, 33.1, 33.0.

**IR (KBr)** ν 2924, 2227, 1695, 1090, 994.

**HRMS (ESI) m/z**: Calc. For C20H21N2O2 ([M+H]+) 321.1598, Found 321.1596.

![](image)

**tert-butyl-4-(2-(4-cyanophenyl)-3-oxo-3-(pyridin-2-yl)propyl)piperidine-1-carboxylate (66)**

Yield 81.8 mg, 97%. Light yellow oil, Rf = 0.34 (petroleum ether/ethyl acetate, 5:1).

**1H NMR (400 MHz, CDCl3)** δ 8.67 (d, J = 4.8 Hz, 1H), 8.01 (d, J = 7.9 Hz, 1H), 7.80 (t, J = 7.7 Hz, 1H), 7.54 (q, J = 8.4 Hz, 4H), 7.47 – 7.44 (m, 1H), 5.65 (t, J = 7.6 Hz, 1H), 4.03 (brs, 2H), 2.57 (d, J = 12.5 Hz, 2H), 2.21 – 2.14 (m, 1H), 1.81 – 1.72 (m, 2H), 1.65 (d, J = 12.7 Hz, 1H), 1.43 (s, 9H), 1.32 – 1.26 (m, 1H), 1.16 – 1.13 (m, 2H).

**13C NMR (101 MHz, CDCl3)** δ 200.2, 154.9, 152.4, 149.1, 145.0, 137.2, 132.5, 129.8, 127.6, 123.0, 118.9, 110.9, 79.4, 47.7, 39.6, 34.1, 32.4, 28.6.

**IR (KBr)** ν 2928, 2228, 1423, 1244, 1166.

**HRMS (ESI) m/z**: Calc. For C25H28N3O3 ([M-H]−) 418.2136, Found 418.2146.
tert-butyl 5-oxo-4-phenyl-5-(pyridin-2-yl)pentanoate (67)

Yield 59.1 mg, 91%. Light yellow oil, Rf = 0.24 (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.63 (d, $J = 5.0$ Hz, 1H), 8.00 – 7.98 (m, 1H), 7.76 – 7.72 (m, 1H), 7.39 – 7.37 (m, 3H), 7.25 (t, $J = 7.5$ Hz, 2H), 7.18 – 7.15 (m, 1H), 5.43 (t, $J = 6.9$ Hz, 1H), 2.44 – 2.38 (m, 1H), 2.23 – 2.15 (m, 3H), 1.42 (s, 9H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 201.0, 172.7, 153.0, 149.0, 138.7, 136.9, 129.1, 128.7, 127.1, 122.8, 80.3, 49.9, 33.7, 28.3, 28.2.

IR (KBr) ν 1695, 1366, 1148, 701.

HRMS (ESI) $m/z$: Calc. For C$_{20}$H$_{24}$NO$_3$ ([M+H]$^+$) 326.1751, Found 326.1749.

ethyl 2,2-dimethyl-5-oxo-4-phenyl-5-(pyridin-2-yl)pentanoate (68)

Yield 45.2 mg, 68%. Light yellow oil, Rf = 0.13 (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.67 (d, $J = 4.8$ Hz, 1H), 7.98 (d, $J = 7.9$ Hz, 1H), 7.75 – 7.72 (m, 1H), 7.38 (d, $J = 8.1$ Hz, 3H), 7.23 – 7.20 (m, 2H), 7.13 (t, $J = 7.4$ Hz, 1H), 5.60 (dd, $J = 8.1, 4.6$ Hz, 1H), 3.98 – 3.92 (m, 1H), 3.88 – 3.83 (m, 1H), 2.71 (dd, $J = 14.1, 8.1$ Hz, 1H), 2.12 (dd, $J = 14.1, 4.6$ Hz, 1H), 1.19 (s, 3H), 1.17 (s, 3H), 1.13 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 200.8, 177.5, 152.8, 149.0, 140.0, 136.8, 129.2, 128.6, 127.0, 126.8, 122.9, 60.4, 47.1, 43.3, 42.4, 26.4, 25.2, 14.1.

IR (KBr) ν 1696, 1193, 1136, 701.

HRMS (EI) $m/z$: Calc. For C$_{20}$H$_{23}$NO$_3$ ([M]$^+$) 325.1672, Found 325.1671.
methyl 2,2-difluoro-5-oxo-4-phenyl-5-(pyridin-2-yl)pentanoate (69)

Yield 42.8 mg, 69%. Light yellow oil, Rf = 0. (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.67 – 8.66 (m, 1H), 8.00 (d, $J$ = 7.8 Hz, 1H), 7.75 (td, $J$ = 7.7, 1.8 Hz, 1H), 7.41 – 7.38 (m, 3H), 7.26 – 7.23 (m, 2H), 7.18 – 7.15 (m, 1H), 5.81 – 5.78 (m, 1H), 3.66 (s, 3H), 3.28 – 3.17 (m, 1H), 2.68 – 2.57 (m, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 198.7, 164.4 (t, $J_{CF} = 33$ Hz), 152.1, 149.1, 137.5, 136.9, 129.1, 128.8, 127.5, 127.3, 123.1, 115.6 (t, $J_{CF} = 251$ Hz), 53.3, 44.2 (t, $J_{CF} = 4$ Hz), 37.5 (t, $J_{CF} = 24$ Hz).

IR (KBr) v 1769, 1698, 1241, 1092.

HRMS (ESI) m/z: Calc. For C$_{17}$H$_{16}$NF$_2$O$_3$ ([M+H]$^+$) 320.1093, Found 320.1090.

2.3 Cascade alkylation/cyclopropanation (Fig. 3 and Fig. 4)

A 4 mL vial equipped with a stir bar was charged with preNHC N1 (10.8 mg, 0.04 mmol), Pd(OAc)$_2$ (4.5 mg, 0.02 mmol), ligand L1 (11.9 mg, 0.024 mmol) and 1.0 mL of 1,4-dioxane. After stirring for 30 min in glove box, to the solution was added Cs$_2$CO$_3$ (97.8 mg, 0.3 mmol), additive A1 (4.4 mg, 0.04 mmol), styrene 1m (25.8 mg, 0.2 mmol), aldehydes 2 (0.4 mmol), CHCl$_3$ 3w (238.8 mg, 2.0 mmol) or CCl$_4$ 3x (153.8 mg, 1.0 mmol), and 1.0 mL of 1,4-dioxane. The reaction mixture was removed from the glove box and stirred under 36W blue LED lights at room...
temperature until the complete consumption of 1m (generally 48 hours) by TLC analysis. The reaction mixture was filtered through a small pad of silica and eluted with EtOAc. The solution was concentrated under reduced pressure, and purified by column chromatography on silica gel to afford the desired cyclopropanes 70-79.

4-(1-benzoyl-2-chlorocyclopropyl)benzonitrile (70)

Yield 34.4 mg, 61%, > 20:1 dr. Light yellow oil, Rf = 0.12 (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.67 (d, $J = 7.4$ Hz, 2H), 7.61 (d, $J = 8.2$ Hz, 2H), 7.46 – 7.42 (m, 3H), 7.31 (t, $J = 7.8$ Hz, 2H), 4.18 (dd, $J = 7.7$, 5.0 Hz, 1H), 2.07 – 1.99 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 196.7, 140.7, 135.8, 133.2, 132.5, 131.0, 129.4, 128.6, 118.5, 111.9, 41.6, 38.3, 23.5.

IR (KBr) ν 2229, 1674, 1598, 1448, 1318, 1255, 653.

HRMS (APCI) m/z: Calc. For C$_{17}$H$_{13}$NO$_3$Cl ([M+H]$^+$) 282.0680, Found 282.0674.

4-(1-(2-naphthoyl)-2-chlorocyclopropyl)benzonitrile (71)

Yield 34.1 mg, 52%, 11:1 dr. Colorless oil, Rf = 0.14 (petroleum ether/ethyl acetate, 10:1).
$^1$H NMR (500 MHz, CDCl$_3$) δ 8.20 (s, 1H), 7.79 (dd, $J = 8.2$, 4.2 Hz, 2H), 7.74 – 7.73 (m, 2H), 7.61 – 7.55 (m, 3H), 7.52 – 7.48 (m, 3H), 4.26 – 4.24 (m, 1H), 2.14 – 2.07 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 196.5, 140.9, 135.4, 133.0, 132.5, 132.2, 131.4, 130.9, 129.6, 129.0, 128.5, 127.9, 127.2, 124.7, 118.5, 111.9, 41.7, 38.4, 23.6.

IR (KBr) ν 2920, 2229, 1670, 1403, 1276, 1196.

HRMS (APCI) $m/z$: Calc. For C$_{21}$H$_{15}$NO$_3$Cl ([M+H]$^+$) 332.0837, Found 332.0828.

4-(2-chloro-1-(4-fluorobenzoyl)cyclopropyl)benzonitrile (72)

Yield 31.4 mg, 52%, 13:1 dr. Light yellow oil, $R_f = 0.17$ (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.74 – 7.62 (m, 4H), 7.46 – 7.41 (m, 2H), 7.01 – 6.97 (m, 2H), 4.19 – 4.17 (m, 1H), 2.12 – 1.97 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 194.9, 165.5 (d, $J_{CF} = 258$ Hz), 140.5, 132.6, 132.1 (d, $J_{CF} = 9$ Hz), 130.8, 118.4, 115.8 (d, $J_{CF} = 22$ Hz), 112.1, 41.4, 38.2, 23.3.

IR (KBr) ν 2229, 1726, 1675, 1600, 1506, 1257, 1236, 1155, 848.

HRMS (EI) $m/z$: Calc. For C$_{17}$H$_{11}$NOCl ([M]$^+$) 299.0508, Found 299.0508.

4-(-2-chloro-1-(4-chlorobenzoyl)cyclopropyl)benzonitrile (73)

Yield 62.4 mg, 67%, > 20:1 dr. Light yellow oil, $R_f = 0.19$ (petroleum ether/ethyl acetate, 10:1).
\[ ^1H \text{NMR} \ (500 \text{ MHz, CDCl}_3) \delta 7.63 – 7.60 \ (\text{td}, J = 8.2, 2.3 \text{ Hz}, 4\text{H}), 7.41 – 7.40 \ (\text{m}, 2\text{H}), 7.29 – 7.26 \ (\text{m}, 2\text{H}), 4.19 – 4.17 \ (\text{m}, 1\text{H}), 2.07 – 1.98 \ (\text{m}, 2\text{H}). \]

\[ ^{13}C \text{NMR} \ (126 \text{ MHz, CDCl}_3) \delta 195.5, 140.4, 139.7, 134.1, 132.6, 130.9, 130.8, 128.9, 118.4, 112.1, 41.5, 38.3, 23.6. \]

\[ \text{IR (KBr)} v 2920, 2850, 2229, 1726, 1675, 1589, 1257, 1092. \]

\[ \text{HRMS (APCI) } m/z: \text{ Calc. For } \text{C}_{17}\text{H}_{12}\text{NOCl} ([\text{M+H}]^+) 316.0291, \text{ Found } 316.0282. \]

\[ \text{4-(2-chloro-1-(4-(trifluoromethyl)benzoyl)cyclopropyl)benzonitrile (74)} \]

Yield 49.7 mg, 71\%, > 20:1 dr. Light yellow oil, \( R_f = 0.13 \) (petroleum ether/ethyl acetate, 10:1).

\[ ^1H \text{NMR} \ (500 \text{ MHz, CDCl}_3) \delta 7.74 – 7.73 \ (\text{m}, 3\text{H}), 7.64 – 7.56 \ (\text{m}, 3\text{H}), 7.41 – 7.40 \ (\text{m}, 2\text{H}), 4.22 – 4.20 \ (\text{m}, 1\text{H}), 2.09 – 2.05 \ (\text{m}, 2\text{H}). \]

\[ ^{13}C \text{NMR} \ (126 \text{ MHz, CDCl}_3) \delta 196.2, 140.0, 139.0, 132.7, 131.1, 129.5, 129.5, 125.6, 123.3 \ (q, J_{CF} = 233 \text{ Hz}), 118.3, 112.3, 41.7, 38.6, 24.2. \]

\[ \text{IR (KBr)} v 2230, 1683, 1326, 1169, 1131, 1066. \]

\[ \text{HRMS (APCI) } m/z: \text{ Calc. For } \text{C}_{17}\text{H}_{10}\text{NOCl} ([\text{M-H}]^-) 348.0409, \text{ Found } 348.0399. \]

\[ \text{4-(1-benzoyl-2,2-dichlorocyclopropyl)benzonitrile (75)} \]

Yield 47.2 mg, 75\%. Light yellow oil, \( R_f = 0.19 \) (petroleum ether/ethyl acetate, 10:1).

\[ ^1H \text{NMR} \ (500 \text{ MHz, CDCl}_3) \delta 7.96 \ (d, J = 7.3 \text{ Hz}, 2\text{H}), 7.73 \ (d, J = 8.2 \text{ Hz}, 2\text{H}), 7.62 \ (d, J = 8.2 \text{ Hz}, 2\text{H}), 7.57 \ (t, J = 7.3 \text{ Hz}, 1\text{H}), 7.48 \ (t, J = 7.6 \text{ Hz}, 2\text{H}), 2.67 \ (d, J = 7.7 \text{ Hz}, 1\text{H}), 2.25 \ (d, J = 7.7 \text{ Hz}, 1\text{H}). \]
$^{13}$C NMR (126 MHz, CDCl$_3$) δ 192.1, 139.9, 134.5, 133.9, 132.5, 131.3, 129.8, 128.8, 118.3, 112.5, 60.8, 48.4, 32.0.

IR (KBr) ν 2230, 1681, 1323, 1259, 1066.

HRMS (APCI) m/z: Calc. For C$_{17}$H$_{12}$NOCl$_2$ ([M+H]$^+$) 316.0291, Found 316.0284.

4-(2,2-dichloro-1-(4-fluorobenzoyl)cyclopropyl)benzonitrile (76)

Yield 34.6 mg, 52%. Light yellow oil, R$_f$ = 0.21 (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.03 – 8.00 (m, 2H), 7.71 (d, $J$ = 8.7 Hz, 2H), 7.63 (d, $J$ = 8.4 Hz, 2H), 7.16 (t, $J$ = 8.7 Hz, 2H), 2.65 (dd, $J$ = 7.6, 1.4 Hz, 1H), 2.24 (d, $J$ = 7.6 Hz, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 190.5, 166.1 (d, $J_{CF}$ = 257 Hz), 139.7, 132.6, 132.5, 131.2, 130.8 (d, $J_{CF}$ = 3 Hz), 118.2, 116.2 (d, $J_{CF}$ = 22 Hz), 112.6, 60.7, 48.3, 32.1.

IR (KBr) ν 2220, 1681, 1598, 1260, 1238, 1154.

HRMS (EI) m/z: Calc. For C$_{17}$H$_{10}$NOClF$_2$ ([M]$^+$) 333.0118, Found 333.0118.

4-(2,2-dichloro-1-(4-chlorobenzoyl)cyclopropyl)benzonitrile (77)

Yield 54.1 mg, 77%. Light yellow oil, R$_f$ = 0.21 (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.91 (d, $J$ = 8.8 Hz, 2H), 7.70 (d, $J$ = 7.7 Hz, 2H), 7.63 (d, $J$ = 8.6 Hz, 2H), 7.45 (d, $J$ = 8.7 Hz, 2H), 2.66 (d, $J$ = 7.8 Hz, 1H), 2.23 (d, $J$ = 7.7 Hz, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 190.9, 140.6, 139.6, 132.8, 132.6, 131.24, 131.16, 129.3, 118.2, 112.7, 60.7, 48.3, 32.1.
**IR (KBr)** ν 2921, 2360, 1728, 1260, 1066.

**HRMS (El) m/z:** Calc. For C_{17}H_{10}NOCl (\([M]^+\)) 348.9822, Found 348.9822.

![Chemical Structure](image)

**4-(1-(4-bromobenzoyl)-2,2-dichlorocyclopropyl)benzonitrile (78)**

Yield 46.7 mg, 59%. Light yellow oil, R<sub>f</sub> = 0.18 (petroleum ether/ethyl acetate, 10:1).

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.83 (d, \(J = 8.2\) Hz, 2H), 7.70 (d, \(J = 8.2\) Hz, 2H), 7.63 (d, \(J = 8.3\) Hz, 4H), 2.66 (d, \(J = 7.7\) Hz, 1H), 2.22 (d, \(J = 7.7\) Hz, 1H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 191.1, 139.5, 133.2, 132.6, 132.3, 131.2, 129.3, 118.2, 112.7, 60.7, 48.3, 32.0.

**IR (KBr)** ν 2360, 2340, 1682, 1196, 1133.

**HRMS (APCI) m/z:** Calc. For C_{17}H_{9}NO_{3}Cl_{2}Br (\([M-H]^+\)) 391.9250, Found 391.9245.

![Chemical Structure](image)

**4-(2,2-dichloro-1-(4-(trifluoromethyl)benzoyl)cyclopropyl)benzonitrile (79)**

Yield 53.4 mg, 70%. Light yellow oil, R<sub>f</sub> = 0.16 (petroleum ether/ethyl acetate, 10:1).

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.06 (d, \(J = 8.0\) Hz, 2H), 7.81 – 7.72 (m, 2H), 7.70 (d, \(J = 8.4\) Hz, 2H), 7.63 (d, \(J = 8.4\) Hz, 2H), 2.71 (d, \(J = 7.6\) Hz, 1H), 2.25 (d, \(J = 7.7\) Hz, 1H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 191.4, 139.2, 137.5, 135.1 (q, \(J_{CF} = 33\) Hz), 132.7, 131.4, 130.0, 125.9 (d, \(J_{CF} = 4\) Hz), 123.4 (q, \(J_{CF} = 272\) Hz), 118.1, 112.9, 60.7, 48.5, 32.0.

**IR (KBr)** ν 2361, 1688, 1326, 1132, 1067.

**HRMS (APCI) m/z:** Calc. For C_{18}H_{9}NO_{3}F_{3}Cl_{2} (\([M-H]^+\)) 382.0019, Found 382.0022.
2.4 Gram-scale reaction and further transformations (Fig. 5)

Gram-scale reaction:

\[
\begin{align*}
\text{phenylethene} & \quad + \quad \text{pyridylaldehyde} & \quad + \quad \text{TMS-alkyl} & \quad \xrightarrow{\text{Standard conditions}} \quad \text{keto product} \\
5.0 \text{ mmol} & \quad & & \quad \text{5, 1.2 g, 81\%}
\end{align*}
\]

A 4 mL vial equipped with a stir bar was charged with preNHC N1 (270 mg, 1.0 mmol), Pd(OAc)$_2$ (112.5 mg, 0.5 mmol), ligand L1 (297.5 mg, 0.6 mmol) and 20 mL of 1,4-dioxane. After stirring for 30 min in glove box, to the solution was added Cs$_2$CO$_3$ (2.45 g, 7.5 mmol), additive A1 (110 mg, 1.0 mmol), styrene 1b (520 mg, 5.0 mmol), aldehyde 2a (1.07 g, 10.0 mmol), alkyl halide 3a (1.61 g, 7.5 mmol), and 20 mL of 1,4-dioxane. The reaction mixture was removed from the glove box and stirred under 36W blue LED lights at room temperature until the complete consumption of 1b by TLC analysis. The reaction mixture was filtered through a small pad of silica and eluted with EtOAc. The solution was concentrated under reduced pressure, and purified by column chromatography on silicagel to afford the desired ketones 5 (1.21 g, 81%).

Reaction a:

To a solution of NaBH$_4$ (9.8 mg, 0.22 mmol, 1.1 eq) in methanol (2.0 mL) in an ice/water bath was added dropwise the solution of ketone 5 (59.4 mg, 0.2 mmol) in THF (1.0 mL). The reaction mixture was allowed to warm to room temperature. After
stirring for 6 h, the reaction was quenched by addition of saturated aqueous NH₄Cl (2 mL) and extracted with ethyl acetate for three times. The combined organic layer was dried over anhydrous Na₂SO₄. After filtration, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel to give alcohol 80 as a colorless oil (51.4 mg, 86% yield) with 15:1 dr.

Rᵋ = 0.37 (petroleum ether/ethyl acetate, 2:1).

**¹H NMR** (400 MHz, CDCl₃) δ 8.44 (d, J = 5.0 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.31 – 7.14 (m, 5H), 7.09 – 7.05 (m, 2H), 5.06 (t, J = 5.2 Hz, 1H), 3.95 (d, J = 6.1 Hz, 1H), 3.02 – 2.97 (m, 1H), 1.94 – 1.87 (m, 2H), 0.55 – 0.41 (m, 2H), 0.00 (s, 9H).

**¹³C NMR** (101 MHz, CDCl₃) δ 160.9, 148.0, 140.2, 136.3, 129.3, 128.0, 126.5, 122.2, 121.1, 76.0, 56.5, 26.4, 14.8, -1.6.

**IR** (KBr) ν 2951, 1595, 1246, 1072, 860, 834, 702.

**HRMS** (APCI) m/z: Calc. For C₁₈H₂₆NOSi ([M+H]⁺) 300.1778, Found 300.1768.

**Reaction b:**

To a solution of ketone 5 (59.4 mg, 0.2 mmol) in THF (1.5 mL) at 0 °C under N₂ atmosphere was added a solution of ethynyl magnesium bromide (0.5 M in THF, 0.56 mL, 1.4 eq) dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 4 hours. After completion, the reaction was quenched by addition of saturated aqueous NH₄Cl (2.0 mL). The mixture was diluted with water (5.0 mL) and was extracted with ethyl acetate for three times. The combined organic layer was washed with brine and was dried over anhydrous Na₂SO₄. After filtration, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel to give alcohol 81 as a colorless oil (51.4 mg, 86% yield) with 15:1 dr.
chromatography on silica gel to give alcohol 81 as a colorless oil (63.8 mg, 99% yield) with 25:1 dr.

R_f = 0.18 (petroleum ether/ethyl acetate, 10:1).

**1H NMR** (400 MHz, CDCl₃) δ 8.25 (d, J = 4.9 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.65 – 7.63 (m, 1H), 7.14 – 7.10 (m, 4H), 7.01 – 7.00 (m, 2H), 5.51 (s, 1H), 3.07 (dd, J = 11.7, 3.0 Hz, 1H), 2.68 (s, 1H), 2.47 – 2.38 (m, 1H), 2.17 – 2.06 (m, 1H), 0.33 – 0.29 (m, 2H), 0.00 (s, 9H).

**13C NMR** (101 MHz, CDCl₃) δ 159.7, 146.7, 138.4, 136.8, 130.0, 127.6, 126.6, 122.6, 121.3, 86.4, 74.6, 73.4, 61.1, 24.4, 14.8, -1.6.

**IR** (KBr) ν 3304, 2850, 1434, 1247, 836.

**HRMS** (APCI) m/z: Calc. For C_{20}H_{26}NOSi ([M+H]^+) 324.1778, Found 324.1769

**Reaction c:**

![Chemical reaction](image)

To a flask charged with methyltriphenylphosphonium bromide (143 mg, 0.4 mmol) in 4.0 mL of anhydrous THF at 0 °C was added n-butyllithium (0.25 mL, 1.6 M in hexanes, 0.4 mmol). The reaction was allowed to warm to room temperature spontaneously and then stirred for 1 h. Ketone 5 (59.4 mg, 0.2 mmol) in anhydrous THF (1.0 mL) was added dropwise at room temperature. After stirring for 9 h, the reaction mixture was quenched with saturated aqueous NH₄Cl, and then extracted with ethyl acetate for three times. The combined organic layer was washed with brine and dried over anhydrous Na₂SO₄. After filtration, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel to afford olefin 82 as a colorless oil (39.5 mg, 67% yield).
$R_f = 0.34$ (petroleum ether/ethyl acetate, 20:1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.59 (d, $J = 4.8$ Hz, 1H), 7.57 (t, $J = 7.7$ Hz, 1H), 7.35 (d, $J = 7.9$ Hz, 1H), 7.32 – 7.26 (m, 4H), 7.20 – 7.14 (m, 1H), 7.13 – 7.11 (m, 1H), 5.88 (s, 1H), 5.38 (s, 1H), 4.23 (t, $J = 7.4$ Hz, 1H), 2.02 – 1.95 (m, 1H), 1.89 – 1.82 (m, 1H), 0.69 – 0.62 (m, 1H), 0.54 – 0.46 (m, 1H), 0.00 (s, 9H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.5, 151.5, 148.9, 143.9, 136.3, 128.5, 128.3, 126.1, 122.1, 121.3, 115.0, 51.1, 29.6, 15.1, -1.6.

IR (KBr) $\nu$ 2952, 2922, 1584, 1466, 1247, 862, 836.

HRMS (APCI) $m/z$: Calc. For C$_{19}$H$_{26}$NSi ([M+H]$^+$) 296.1829, Found 296.1821.

2.5 Control experiments

(a) Radical trapping experiment

A 4 mL vial equipped with a stir bar was charged with preNHC N1 (10.8 mg, 0.04 mmol), Pd(OAc)$_2$ (4.5 mg, 0.02 mmol), ligand L1 (11.9 mg, 0.024 mmol) and 1.0 mL of 1,4-dioxane. After stirring for 30 min in glove box, to the solution was added Cs$_2$CO$_3$ (97.8 mg, 0.3 mmol), additive A1 (4.4 mg, 0.04 mmol), alkenes 1 (0.2 mmol), aldehydes 2 (0.4 mmol), alkyl halides 3 (0.3 mmol), TEMPO (156.3 mg, 1.0 mmol) and 1.0 mL of 1,4-dioxane. The reaction mixture was removed from the glove box and stirred under 36W blue LED lights at room temperature for 48 hours. A portion of the reaction mixture was collected and analysed by HRMS without desired ketone 4 but with the adduct 83 trapped by TEMPO detected, HRMS (APCI) $m/z$: Calc. For
C_{12}H_{30}NOSi ([M+H])^+ 244.2091, Found 244.2087.

(b) Radical clock experiment with (bromomethyl)cyclopropane

\[
\begin{array}{cccc}
\text{NC} & \text{CHO} & \text{Br} & \text{Standard conditions} \\
\hline
& & & \\
\end{array}
\]

A 4 mL vial equipped with a stir bar was charged with preNHC N1 (10.8 mg, 0.04 mmol), Pd(OAc)$_2$ (4.5 mg, 0.02 mmol), ligand L1 (11.9 mg, 0.024 mmol) and 1.0 mL of 1,4-dioxane. After stirring for 30 min in glove box, to the solution was added Cs$_2$CO$_3$ (97.8 mg, 0.3 mmol), additive A1 (4.4 mg, 0.04 mmol), styrene 1m (25.8 mg, 0.2 mmol), aldehyde 2a (42.8 mg, 0.4 mmol), alkyl halide 3y (40.5 mg, 0.3 mmol), and 1.0 mL of 1,4-dioxane. The reaction mixture was removed from the glove box and stirred under 36W blue LED lights at room temperature for 48 hours. The reaction mixture was filtered through a small pad of silica and eluted with EtOAc. The solution was concentrated under reduced pressure, and purified by column chromatography on silica gel to afford the desired ketone 84 as a light yellow oil (27.2 mg, 47%).

\[R_f = 0.35\] (petroleum ether/ethyl acetate, 10:1).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.66 (s, 1H), 8.02 – 8.01 (m, 1H), 7.81 – 7.78 (m, 1H), 7.56 – 7.51 (m, 4H), 7.45 – 7.43 (m, 1H), 5.76 – 5.71 (m, 1H), 5.49 – 5.46 (m, 1H), 4.99 – 4.92 (m, 2H), 2.19 – 2.07 (m, 3H), 1.88 – 1.86 (m, 1H), 1.40 – 1.31 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 200.5, 152.6, 149.1, 145.1, 138.3, 137.2, 132.4, 129.9, 127.5, 122.9, 119.0, 115.0, 110.8, 50.7, 33.7, 32.5, 27.0.

IR (KBr) v 2925, 2228, 1697, 1435, 1087, 1042, 994.
HRMS (ESI) m/z: Calc. For C_{19}H_{19}N_{2}O ([M+H]^+) 291.1492, Found 291.1493.

(c) Radical probe experiment with 6-bromohex-1-ene

\[
\begin{align*}
\text{Ar} = 4-	ext{CN-C}_{6}	ext{H}_{4} & \quad + \quad \text{N}=\text{CH} \quad + \quad \text{CH}=	ext{CHBr} \\
\text{Standard conditions} & \quad \rightarrow \quad 85a \\
85a/85b & = 5:1, \text{ total yield 42%}
\end{align*}
\]

A 4 mL vial equipped with a stir bar was charged with preNHC N1 (10.8 mg, 0.04 mmol), Pd(OAc)$_2$ (4.5 mg, 0.02 mmol), ligand L1 (11.9 mg, 0.024 mmol) and 1.0 mL of 1,4-dioxane. After stirring for 30 min in glove box, to the solution was added Cs$_2$CO$_3$ (97.8 mg, 0.3 mmol), additive A1 (4.4 mg, 0.04 mmol), strene 1m (25.8 mg, 0.2 mmol), aldehyde 2a (42.8 mg, 0.4 mmol), alkyl halide 3z (48.9 mg, 0.3 mmol), and 1.0 mL of 1,4-dioxane. The reaction mixture was removed from the glove box and stirred under 36W blue LED lights at room temperature for 48 hours. The reaction mixture was filtered through a small pad of silica and eluted with EtOAc. The solution was concentrated under reduced pressure, and purified by column chromatography on silica gel to afford the mixture of 85a and 85b as a light yellow oil (85a/85b = 5.3:1, total 26.7 mg, 42%).

R$_f$ = 0.19 (petroleum ether/ethyl acetate, 10:1).

85a. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.66 (d, $J = 4.8$ Hz, 1H), 8.02 (d, $J = 7.8$ Hz, 1H), 7.80 (t, $J = 7.7$ Hz, 1H), 7.57 – 7.51 (m, 4H), 7.46 – 7.43 (m, 1H), 5.45 (t, $J = 7.3$ Hz, 1H), 2.20 – 2.15 (m, 1H), 1.88 – 1.74 (m, 4H), 1.55 – 1.48 (m, 3H), 1.34 – 1.19 (m, 3H), 1.105 – 1.00 (m, 2H).

13C NMR (101 MHz, CDCl$_3$) $\delta$ 200.5, 152.6, 148.9, 145.2, 137.0, 132.2, 129.8, 127.3, 122.8, 118.9, 110.6, 50.8, 38.7, 33.1, 27.7, 25.4, 22.6, 22.5.
IR (KBr) ν 2941, 2227, 1696, 994, 562.

HRMS (APCI) m/z: Calc. For C_{21}H_{21}N_{2}O ([M-H]) 317.1659, Found 317.1660.

(d) Radical clock experiment with (1-(2-phenylcyclopropyl)vinyl)benzene

A 4 mL vial equipped with a stir bar was charged with preNHC N1 (10.8 mg, 0.04 mmol), Pd(OAc)$_2$ (4.5 mg, 0.02 mmol), ligand L1 (11.9 mg, 0.024 mmol) and 1.0 mL of 1,4-dioxane. After stirring for 30 min in glove box, to the solution was added Cs$_2$CO$_3$ (97.8 mg, 0.3 mmol), additive A1 (4.4 mg, 0.04 mmol), styrene 1aa (44.0 mg, 0.2 mmol), aldehyde 2a (42.8 mg, 0.4 mmol), alkyl halide 3a (42.8 mg, 0.3 mmol), and 1.0 mL of 1,4-dioxane. The reaction mixture was removed from the glove box and stirred under 36W blue LED lights at room temperature for 48 hours. The reaction mixture was filtered through a small pad of silica and eluted with EtOAc. The solution was concentrated under reduced pressure, and purified by column chromatography on silica gel to afford the desired ketone 86 as a light yellow oil (40.9 mg, 49%).

$R_f = 0.50$ (petroleum ether/ethyl acetate, 20:1).

Major: $^1$H NMR (500 MHz, CDCl$_3$) δ 8.73 – 8.56 (m, 1H), 8.12 – 8.01 (m, 1H), 7.79 – 7.76 (m, 1H), 7.45 – 7.44 (m, 1H), 7.42 – 7.39 (m, 1H), 7.31 – 7.06 (m, 9H), 5.54 (q, J = 7.2 Hz, 2H), 3.05 (dt, J = 14.4, 7.2 Hz, 1H), 2.80 (dt, J = 14.9, 7.8 Hz, 1H), 2.43 (td, J = 11.4, 5.3 Hz, 2H), 0.60 – 0.45 (m, 1H), 0.45 – 0.28 (m, 1H), -0.00 (s, 9H).
$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 201.2, 153.1, 149.0, 144.6, 143.0, 139.1, 136.9, 129.1, 128.7, 128.2, 127.1, 127.0, 126.6, 126.6, 124.4, 122.8, 51.2, 32.3, 23.8, 16.1, -1.7.

IR (KBr) $\nu$ 2951, 1695, 1582, 1435, 1246, 860, 835.

HRMS (ESI) $m/z$: Calc. For C$_{27}$H$_{32}$NOSi ([M+H]$^+$) 414.2248, Found 414.2248.

2.6 UV-Visible absorption analysis

UV/Vis absorption spectra were recorded on a Jasco V-650 spectrophotometer, equipped with a temperature control unit at 25 °C. The samples were measured in Hellma fluorescence QS quartz cuvettes (chamber volume = 3.0 mL) fitted with a PTFE stopper. The UV-visible absorption of the substrates Pd(OAc)$_2$ and L1 ($10^{-4}$M), styrene (1m, $10^{-3}$M), benzaldehyde (2i, 2x10$^{-3}$M), trimethyl(iodomethyl) silane (3a, 1.5 x10$^{-3}$M), NHC-L1 (2x10$^{-4}$M), [L1 ($10^{-4}$M) and 3a (1.5x10$^{-3}$M)], NHC-2i (2x10$^{-3}$M), [Pd(OAc)$_2$, L1 ($10^{-4}$M), and NHC (2x10$^{-4}$M)], and standard reaction mixture were determined in 1,4-dioxane.

Supplementary Figure 1. UV-Visible absorption spectra.
2.7 Light on/off experiments

A 4 mL vials equipped with a stir bar separately were charged with preNHC N1 (10.8 mg, 0.04 mmol), Pd(OAc)$_2$ (4.5 mg, 0.02 mmol), ligand L1 (11.9 mg, 0.024 mmol) and 1.0 mL of 1,4-dioxane. After stirring for 30 min in glove box, to the solution was added Cs$_2$CO$_3$ (97.8 mg, 0.3 mmol), additive A1 (4.4 mg, 0.04 mmol), styrene 1a (30.8 mg, 0.2 mmol), aldehyde 2a (42.8 mg, 0.4 mmol), alkyl halide 3a (42.8 mg, 0.3 mmol), dodecane (internal standard, 25.8 mg, 0.15 mmol) and 1.0 mL of 1,4-dioxane. The reaction mixture was removed from the glove box and stirred under 36W blue LED lights at room temperature for 10 min, followed by 10 min in the dark, which was continued for a total reaction time of 80 min. After each sequence, an aliquot was taken and the reaction was analyzed via GC-MS analysis of the crude reaction mixture.

Supplementary Figure 2. Light on/off experiments
3. Supplementary Figures
3.1 NMR Spectra

Supplementary Figure 3. H-NMR of compound 4, recorded at 300MHz and 25 °C in CDCl₃
Supplementary Figure 4. $^{13}$C-NMR of compound 4, recorded at 75 MHz and 25 °C in CDCl$_3$. 

S53
Supplementary Figure 5. $^1$H-NMR of compound 5, recorded at 300 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters
NAME  11122B
EXPNO  1
PROCNO  1

F2 - Acquisition Parameters
Date_  20220130
Time   19.29
INSTRUM  spect
PROBHD  5 mm DUL 13C-1
PULPROG  zg30
TD   65536
SOLVENT  CDCl$_3$
NS  10
DS  2
SWH   6009.615 Hz
FIDRES  0.091699 Hz
AQ  5.4525952 sec
RG  209.09
DW  83.200 usec
DE   6.50 usec
TE  297.4 K
D1   1.00000000 sec
D11  0 sec
TD0   1

-------- CHANNEL f1 --------
SFO1  300.1318534 MHz
NUC1  1H
P1   8.00 usec
PLW1  18.00000000 W

-------- CHANNEL f2 --------
SFO2  300.1318534 MHz
NUC2  off
CPDPRG[2
PCPD2  0 usec
PLW2  0 W
PLW12  0 W
PLW13  0 W

F2 - Processing parameters
SI   65536
SF  300.1299987 MHz
WDW  EM
EBB  0
LB   0.30 Hz
PC   1.00

S54
Supplementary Figure 6. $^{13}$C-NMR of compound 5, recorded at 75 MHz and 25 °C in CDCl₃.

Current Data Parameters
NAME  11122B
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220130
Time 19.31
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 160
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 209.09
DW 27.733 usec
DE 6.50 usec
TE 297.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

-------- CHANNEL f1 --------
SFO1  75.4752949 MHz
NUC1  13C
P1  11.00 usec
PLW1  195.00000000 W

-------- CHANNEL f2 --------
SFO2  300.1312005 MHz
NUC2  1H
CPDPRG[2  waltz16
PCPD2  90.00 usec
PLW2  14.00000000 W
PLW12  0.17284000 W
PLW13  0.14000000 W

F2 - Processing parameters
SI  32768
SF  75.4677383 MHz
WDW EM
SSB 0
LB  1.00 Hz
GB  0
PC  1.40
Supplementary Figure 7. $^1$H-NMR of compound 6, recorded at 300 MHz and 25 °C in CDCl$_3$. 

S56
Supplementary Figure 8. $^{13}$C-NMR of compound 6, recorded at 75 MHz and 25 °C in CDCl$_3$. 

S57
Supplementary Figure 9. $^1$H-NMR of compound 7, recorded at 300 MHz and 25 °C in CDCl$_3$. 
Supplementary Figure 10. $^{13}$C-NMR of compound 7, recorded at 75 MHz and 25 °C in CDCl$_3$. 
S59
Supplementary Figure 11. $^1$H-NMR of compound 8, recorded at 500 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters

NAME  11132E
EXFNO  1
PROCNO  1

F2 - Acquisition Parameters
Date_  20220214
Time  9.50
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 31.72
DW 50.000 usec
DE 6.50 usec
TE 298.2 K
D1 1.0000000 sec
D11 0 sec
TD0 1

-------- CHANNEL f1 --------
SFO1 500.1330885 MHz
NUC1 1H
P1 11.25 usec
PLW1 20.0000000 W

-------- CHANNEL f2 --------
SFO2 500.1330885 MHz
NUC2 off
CPDPRG[2
PCPD2 0 usec
PLW2 0 W
PLW12 0 W
PLW13 0 W

F2 - Processing parameters
SI 65536
SF 500.1299974 MHz
WDW EM
SSB 0
LB 0.30 Hz
PC 1.00 /g27/g38/g39/g38/g79/g22/g15/g24/g19/g19/g48/g43/g93/g27
**Current Data Parameters**

**NAME** 11132E

**EXPNO** 2

**PROCNO** 1

**F2 - Acquisition Parameters**

**Date**  20220214

**Time**  9.53

**INSTRUM** spect

**PROBHD** 5 mm CPPBBO BB

**PULPROG** zgpg30

**TD**  65536

**SOLVENT** CDCl3

**NS**  60

**DS**  4

**SWH**  29761.904 Hz

**FIDRES**  0.454131 Hz

**AQ**  1.1010048 sec

**RG**  192.89

**DW**  16.800 usec

**DE**  18.00 usec

**TE**  298.2 K

**D1**  2.00000000 usec

**D11**  0.03000000 sec

**TD0**  1

--- CHANNEL f1 ---

**SFO1**  125.7703637 MHz

**NUC1**  13C

**P1**  10.50 usec

**PLW1**  57.00000000 W

--- CHANNEL f2 ---

**SFO2**  500.1320005 MHz

**NUC2**  1H

**CPDPRG[2** waltz16

**PCPD2**  80.00 usec

**PLW2**  20.00000000 W

**PLW12**  0.39550999 W

**PLW13**  0.25312999 W

**F2 - Processing parameters**

**SI**  32768

**SF**  125.7577729 MHz

**WDW** EM

**SSB**  0

**LB**  1.00 Hz

**GB**  0

**PC**  1.40

--- Supplementary Figure 12 ---

$^{13}$C-NMR of compound 8, recorded at 126 MHz and 25 °C in CDCl$_3$. S61
Current Data Parameters
NAME  11132H
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220214
Time   10.07
INSTRUM    spect
PROBHD 5 mm CPPBBO BB
PULPROG zg30
TD   65536
SOLVENT CDCl3
NS    16
DS    2
SWH  10000.000 Hz
FIDRES 0.152588 Hz
AQ  3.2767999 sec
RG  49.27
DW  50.000 usec
DE  8.50 usec
TE  298.2 K
D1    1.0000000 sec
D11  0 sec
TD0   1

-------- CHANNEL f1 --------
SFO1    500.1330885 MHz
NUC1  1H
P1  11.25 usec
PLW1  20.0000000 W

-------- CHANNEL f2 --------
SFO2  500.1330885 MHz
NUC2  off
CPDPGRG[2
PCPD2  0 usec
PLW2  0 W
PLW12  0 W
PLW13  0 W

F2 - Processing parameters
SI    65536
SF  500.1300076 MHz
WDW EM
GB  0
LB  0.30 Hz
PC  1.00

Supplementary Figure 13. $^1$H-NMR of compound 9, recorded at 500 MHz and 25 °C in CDCl$_3$. S62
Supplementary Figure 14. $^{13}$C-NMR of compound 9, recorded at 126 MHz and 25 °C in CDCl$_3$. 
Supplementary Figure 15. $^1$H-NMR of compound 10, recorded at 400 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters
NAME 11134K
EXFNO 3
PROCNO 1

F2 - Acquisition Parameters
Date 20220407
Time 18.17
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447233 sec
RG 206.33
DW 62.400 usec
DE 8.50 usec
TE 300.8 K
D1 2.0000000 sec
TD0 1

--------- CHANNEL f1 ---------
SFO1 400.2424716 MHz
NUC1 1H
P1 14.30 usec
PLW1 12.0000000 W

F2 - Processing parameters
SI 65536
SF 400.2400000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

AcO

TMS

10
Supplementary Figure 16. $^{13}$C-NMR of compound 10, recorded at 126 MHz and 25 °C in CDCl$_3$. S65
Supplementary Figure 17. ^1^H-NMR of compound 11, recorded at 500 MHz and 25 °C in CDCl₃.
Current Data Parameters
NAME  11132B
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220214
Time 9.30
INSTRUM  spect
PROBHD  5 mm CPPBBB BB
PULPRES zgpg30
TD  65536
SOLVENT CDCl3
NS  80
DS  4
SWH  29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 192.89
DW 16.800 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

-------- CHANNEL f1 --------
SFO1 125.7703637 MHz
NUC1 13C
P1 10.50 usec
PLW1 57.00000000 W

-------- CHANNEL f2 --------
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 20.00000000 W
PLW12 0.39550999 W
PLW13 0.25312999 W

F2 - Processing parameters
SI 32768
SF 125.7577719 MHz
WDW EM
SSB 0
LB  1.00 Hz
GB 0
PC 1.40

Supplementary Figure 18. $^{13}$C-NMR of compound 11, recorded at 126 MHz and 25 °C in CDCl$_3$. S67
Supplementary Figure 19. $^1$H-NMR of compound 12, recorded at 400 MHz and 25 °C in CDCl$_3$. 
Supplementary Figure 20. $^{13}$C-NMR of compound 12, recorded at 101 MHz and 25 °C in CDCl$_3$. 
Supplementary Figure 21. $^1$H-NMR of compound 13, recorded at 500 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters
NAME  11132C
EXPN0  1
PROCNO  1

F2 - Acquisition Parameters
Date_  20220214
Time  9.37
INSTRUM  spect
PROBHD  5 mm CPPBBO BB
PULPROG  zg30
TD  65536
SOLVENT  CDCl3
NS  16
DS  2
SWH  10000.000 Hz
FIDRES  0.152588 Hz
AQ  3.2767999 sec
RG  49.27
DW  50.000 usec
DE  8.50 usec
TE  298.2 K
D1  1.0000000 sec
D11  0 sec
TD0  1

--------------- CHANNEL f1 --------------
SFO1  500.1330885 MHz
NUC1  1H
P1  11.25 usec
PLW1  20.00000000 W

--------------- CHANNEL f2 --------------
SFO2  500.1330885 MHz
NUC2  off
CPDPRG[2
PCPD2  0 usec
PLW2  0 W
PLW12  0 W
PLW13  0 W

F2 - Processing parameters
SI  65536
SF  500.1299965 MHz
WDW  EM
SSB  0
LB  0.30 Hz
GB  0
PC  1.00
Supplementary Figure 22. $^{13}$C-NMR of compound 13, recorded at 126 MHz and 25 °C in CDCl₃.
## Supplementary Figure 23

$^1$H-NMR of compound 14, recorded at 500 MHz and 25 °C in CDCl$_3$. 

### Current Data Parameters

| Name     | 11134C |
|----------|--------|
| EXPNO    | 1      |
| PROCNO   | 1      |

### F2 - Acquisition Parameters

| Date     | 20220217 |
|----------|----------|
| Time     | 17.07    |
| INSTRUM  | spect    |
| PROBHD   | 5 mm CPPBBO BB |
| PULPROG  | zg30     |
| TD       | 65536    |
| SOLVENT  | CDCl3    |
| NS       | 12       |
| DS       | 2        |
| SWH      | 10000.000 Hz |
| FIDRES   | 0.152588 Hz |
| AQ       | 3.2767999 sec |
| RG       | 31.72    |
| DW       | 50.000 usec |
| DE       | 8.50 usec |
| TE       | 298.2 K  |
| D1       | 1.00000000 sec |
| D11      | 0 usec   |
| TD0      | 1        |

#### CHANNEL f1

| SFO1     | 500.1330885 MHz |
| NUC1     | 1H               |
| P1       | 11.25 usec       |
| PLW1     | 20.00000000 W    |

#### CHANNEL f2

| SFO2     | 500.1330885 MHz |
| NUC2     | off             |
| CPDPRG[2]| off             |
| PCPD2    | 0 usec          |
| PLW2     | 0 W             |
| PLW12    | 0 W             |
| PLW13    | 0 W             |

### F2 - Processing parameters

| SI       | 65536 |
| SF       | 500.1299945 MHz |
| WDW      | EM     |
| GB       | 0      |
| LB       | 0.30 Hz |
| GB       | 0      |
| PC       | 1.00   |
Supplementary Figure 24. $^{13}$C-NMR of compound 14, recorded at 126 MHz and 25 °C in CDCl$_3$. 
S73
Supplementary Figure 25. $^1$H-NMR of compound 15, recorded at 500 MHz and 25 °C in CDCl$_3$. 
Supplementary Figure 26. $^{13}$C-NMR of compound 15, recorded at 126 MHz and 25 °C in CDCl$_3$. S75
Current Data Parameters
NAME  11140C
EXFNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220222
Time 18.34
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447233 sec
RG 206.33
DW 62.400 usec
DE 6.50 usec
TE 298.7 K
D1 2.00000000 sec
D11 0 sec
TD0 1

-------- CHANNEL f1 --------
SFO1  400.2424716 MHz
NUC1  1H
P1 14.30 usec
PLW1 12.00000000 W

-------- CHANNEL f2 --------
SFO2  400.2424716 MHz
NUC2 off
CPDPRG[2
PCPD2 0 usec
PLW2 0 W
PLW12 0 W
PLW13 0 W

F2 - Processing parameters
SI  65536
SF  400.2399969 MHz
WDW EM
PC 1.00

Supplementary Figure 27. ¹H-NMR of compound 16, recorded at 500 MHz and 25 °C in CDCl₃.
### Current Data Parameters

| NAME        | 11140C |
|-------------|--------|
| EXPNO       | 2      |
| PROCNO      | 1      |

#### F2 - Acquisition Parameters

- **Date:** 20220222
- **Time:** 18.36
- **INSTRUM:** spect
- **PROBHD:** 5 mm PABBO BB/
- **PULPROG:** zgpg30
- **TD:** 65536
- **SOLVENT:** CDCl3
- **NS:** 260
- **DS:** 4
- **SWH:** 24038.461 Hz
- **FIDRES:** 0.366798 Hz
- **AQ:** 1.3631488 sec
- **RG:** 206.33
- **DW:** 20.800 usec
- **DE:** 6.50 usec
- **TE:** 299.0 K
- **D1:** 2.00000000 sec
- **D11:** 0.03000000 sec
- **TD0:** 1

---

#### CHANNEL f1

- **SFO1:** 100.6504916 MHz
- **NUC1:** 13C
- **P1:** 10.00 usec
- **PLW1:** 54.00000000 W

---

#### CHANNEL f2

- **SFO2:** 400.2416010 MHz
- **NUC2:** 1H
- **CPDPRG[2]:** waltz16
- **PCPD2:** 90.00 usec
- **PLW2:** 12.00000000 W
- **PLW12:** 0.30294999 W
- **PLW13:** 0.24539000 W

#### F2 - Processing parameters

- **SI:** 32768
- **SF:** 100.6404346 MHz
- **WDW:** EM
- **SSB:** 0
- **LB:** 1.00 Hz
- **GB:** 0
- **PC:** 1.40

---

**Supplementary Figure 28**. $^{13}$C-NMR of compound 16, recorded at 101 MHz and 25 °C in CDCl$_3$. 

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S77
Supplementary Figure 29. $^1$H-NMR of compound 17, recorded at 400 MHz and 25 °C in CDCl$_3$. 

17
**Current Data Parameters**

| NAME  | 11134L       |
|-------|--------------|
| EXPNO | 2            |
| PROCNO| 1            |

**F2 - Acquisition Parameters**

- **Date**: 20220217
- **Time**: 16.56
- **INSTRUM**: spect
- **PROBHD**: 5 mm PABBO BB/
- **PULPROM**: zgpg30
- **TD**: 65536
- **SOLVENT**: CDCl3
- **NS**: 150
- **DS**: 4
- **SWH**: 24038.461 Hz
- **FIDRES**: 0.366798 Hz
- **AQ**: 1.3631488 sec
- **RG**: 206.33
- **DW**: 20.800 usec
- **DE**: 6.50 usec
- **TE**: 298.0 K
- **D1**: 2.00000000 sec
- **D11**: 0.03000000 sec
- **TD0**: 1

**F2 - Processing parameters**

- **SI**: 32768
- **SF**: 100.6404154 MHz
- **WDW**: EM
- **SSB**: 0
- **LB**: 1.00 Hz
- **GB**: 0
- **PC**: 1.40

---

**Supplementary Figure 30.** $^{13}$C-NMR of compound 17, recorded at 101 MHz and 25 °C in CDCl$_3$. 

S79
Supplementary Figure 31. $^1$H-NMR of compound 18, recorded at 300 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters
NAME  11122F
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_  20220130
Time   20.29
INSTRUM    spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD   65536
SOLVENT CDCl3
NS 12
DS 2
SWH   6009.615 Hz
FIDRES  0.091699 Hz
AQ  5.4525952 sec
RG  209.09
DW  83.200 usec
DE  8.50 usec
TE  297.5 K
D1  1.00000000 sec
D11 0 sec
TD0 1

------- CHANNEL f1 -------
SFO1  300.1318534 MHz
NUC1  1H
P1  8.00 usec
PLW1  18.00000000 W

------- CHANNEL f2 -------
SFO2        300.1318534 MHz
NUC2                off
CPDPRG[2
PCPD2  0 usec
PLW2  0 W
PLW12  0 W
PLW13  0 W

F2 - Processing parameters
SI  65536
SF  300.1318534 MHz
WDM  EM
SSB  0
LB  0.30 Hz
GB  0
PC  1.00
Current Data Parameters
NAME  11122F
EXPNO  2
PROCNO  1

F2 - Acquisition Parameters
Date_ 20220130
Time   20.32
INSTRUM    spect
PROBHD  5 mm DUL 13C-1
PULPROG zgpg30
TD   65536
SOLVENT CDCl3
NS 250
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 209.09
DW 27.733 usec
DE 6.50 usec
TE 297.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

--------- CHANNEL f1 --------
SFO1  75.4752949 MHz
NUC1  13C
P1    11.00 usec
PLW1  195.00000000 W

--------- CHANNEL f2 --------
SFO2  300.1312005 MHz
NUC2  1H
CPDPDG[2 waltz16
PCPD2  90.00 usec
PLW2  14.00000000 W
PLW12 0.17284000 W
PLW13 0.14000000 W

F2 - Processing parameters
SI  32768
SF  75.4677387 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Supplementary Figure 32. 13C-NMR of compound 18, recorded at 75 MHz and 25 °C in CDCl3.
Supplementary Figure 33. $^1$H-NMR of compound 19, recorded at 400 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters
NAME  11140E
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220222
Time  18.53
INSTURM spect
PROBHD  5 mm PABBO BB/
PULPROG zg30
TD  32768
SOLVENT CDCl3
NS  16
DS  0
SWH  8012.820 Hz
FIDRES  0.244532 Hz
AQ  2.0447233 sec
RG  206.33
DW  62.400 usec
DE  6.50 usec
TE  298.3 K
D1  2.0000000 sec
D11  0 sec
TD0  1

-------- CHANNEL f1 --------
SFO1  400.2424716 MHz
NUC1  1H
P1  14.30 usec
PLW1  12.00000000 W

-------- CHANNEL f2 --------
SFO2  400.2424716 MHz
NUC2  off
CPDPRG[2
PCPD2  0 usec
PLW2  0 W
PLW12  0 W
PLW13  0 W

F2 - Processing parameters
SI  65536
SF  400.2399939 MHz
WDW EM
GSB  0
LB  0.30 Hz
GB  0
PC  1.00
Supplementary Figure 34. $^{13}$C-NMR of compound 19, recorded at 101 MHz and 25 °C in CDCl$_3$. 
Supplementary Figure 35. $^1$H-NMR of compound 20, recorded at 500 MHz and 25 °C in CDCl₃.
Supplementary Figure 36. $^{13}$C-NMR of compound 20, recorded at 126 MHz and 25 °C in CDCl$_3$. 
Supplementary Figure 37. $^1$H-NMR of compound 21, recorded at 500 MHz and 25 °C in CDCl$_3$. 
**Current Data Parameters**

**NAME**  
11134E

**EXPNO**  
2

**PROCNO**  
1

**F2 - Acquisition Parameters**

- **Date:** 20220217
- **Time:** 17.15
- **INSTRUM:** spect
- **PROBHD:** 5 mm CPPBBO BB
- **PULPROG:** zgpg30
- **TD:** 65536
- **SOLVENT:** CDCl3
- **NS:** 60
- **DS:** 4
- **SWH:** 29761.904 Hz
- **FIDRES:** 0.454131 Hz
- **AQ:** 1.1010048 sec
- **RG:** 192.89
- **DW:** 16.800 usec
- **DE:** 18.00 usec
- **TE:** 298.2 K
- **D1:** 2.0000000 sec
- **D11:** 0.03000000 sec
- **TD0:** 1

--- CHANNEL f1 ---

- **SFO1:** 125.7703637 MHz
- **NUC1:** 13C
- **P1:** 10.50 usec
- **PLW1:** 57.00000000 W

--- CHANNEL f2 ---

- **SFO2:** 500.1320005 MHz
- **NUC2:** 1H
- **CPDPRG[2]:** waltz16
- **PCPD2:** 80.00 usec
- **PLW2:** 20.00000000 W
- **PLW12:** 0.39550999 W
- **PLW13:** 0.25312999 W

**F2 - Processing parameters**

- **SI:** 32768
- **SF:** 125.7577728 MHz
- **WDW:** EM
- **SSB:** 0
- **LB:** 1.00 Hz
- **GB:** 0
- **PC:** 1.40

---

**Supplementary Figure 38.** $^{13}$C-NMR of compound 21, recorded at 126 MHz and 25 °C in CDCl$_3$.  

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S87
Supplementary Figure 39. $^1$H-NMR of compound 22, recorded at 500 MHz and 25 °C in CDCl$_3$. S88
Supplementary Figure 40. $^{13}$C-NMR of compound 22, recorded at 126 MHz and 25 °C in CDCl$_3$. 

S89
Supplementary Figure 41. $^1$H-NMR of compound 23, recorded at 500 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters
NAME  11134A
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220217
Time  16.52
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 10
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 62.06
DW 50.000 usec
DE 6.50 usec
TE 298.2 K
D1  1.00000000 sec
D11 0 sec
TD0 1

-------- CHANNEL f1 --------
SFO1  500.1330885 MHz
NUC1  1H
P1  11.25 usec
PLW1  20.00000000 W

-------- CHANNEL f2 --------
SFO2  500.1330885 MHz
NUC2  off
CPDPRG[2
PCPD2  0 usec
PLW2  0 W
PLW12  0 W
PLW13  0 W

F2 - Processing parameters
SI  65536
SF  500.1300024 MHz
WDW EM
SSB 0
LB  0.30 Hz
GB  0
PC  1.00
Supplementary Figure 42. $^{13}$C-NMR of compound 23, recorded at 126 MHz and 25 °C in CDCl$_3$. 
Current Data Parameters
NAME  11132D
EXPN0 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220214
Time 9.43
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 31.72
DW 50.000 usec
DE 8.50 usec
TE 298.2 K
D1 1.00000000 sec
D11 0 sec
TD0 1

---------- CHANNEL f1 ----------
SFO1 500.1330885 MHz
NUC1 1H
P1 11.25 usec
PLW1 20.00000000 W

---------- CHANNEL f2 ----------
SFO2 500.1330885 MHz
NUC2 off
CPDPRG[2
PCPD2 0 usec
PLW2 0 W
PLW12 0 W
PLW13 0 W

F2 - Processing parameters
SI 65536
SF 500.1300004 MHz
WDW EM
GB 0
LB 0.30 Hz
PC 1.00

Supplementary Figure 43. $^1$H-NMR of compound 24, recorded at 500 MHz and 25 °C in CDCl$_3$. 

S92
Supplementary Figure 44. $^{13}$C-NMR of compound 24, recorded at 126 MHz and 25 °C in CDCl$_3$. S93
Supplementary Figure 45. $^1$H-NMR of compound 25, recorded at 500 MHz and 25 °C in CDCl$_3$. 
Supplementary Figure 46. $^{13}$C-NMR of compound 25, recorded at 126 MHz and 25 °C in CDCl$_3$. 

S95
Supplementary Figure 47. $^1$H-NMR of compound 26, recorded at 400 MHz and 25 °C in CDCl$_3$. 

S96
Supplementary Figure 48. $^{13}$C-NMR of compound 26, recorded at 101 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters
NAME  11122G
EXPNO  2
PROCNO  1

F2 - Acquisition Parameters
Date_ 20220209
Time  19.40
INSTRUM  spect
PROBHD  5 mm PABBO BB/
PULPROG zgpg30
TD  65536
SOLVENT  CDCl3
NS  400
DS  4
SWH  24038.461 Hz
FIDRES  0.366798 Hz
AQ  1.3631488 sec
RG  206.33
DW  20.800 usec
DE  6.50 usec
TE  300.2 K
D1  2.00000000 sec
D11  0.03000000 sec
TD0  1

-------- CHANNEL f1 --------
SFO1  100.6504916 MHz
NUC1  13C
P1  10.00 usec
PLW1  54.00000000 W

-------- CHANNEL f2 --------
SFO2  400.2416010 MHz
NUC2  1H
CPDPREG[2  waltz16
PCPD2  90.00 usec
PLW2  12.00000000 W
PLW12  0.30294999 W
PLW13  0.24539000 W

F2 - Processing parameters
SI  32768
SF  100.6404146 MHz
WDW  EM
SSB  0
LB  1.00 Hz
GB  0
PC  1.40
Supplementary Figure 49. $^1$H-NMR of compound 27, recorded at 500 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters
NAME 11134I
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220217
Time 17.32
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 10
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 31.72
DW 50.000 usec
DE 8.50 usec
TE 298.2 K
D1 1.0000000 sec
D11 0 sec
TD0 1

---------- CHANNEL f1 ----------
SFO1 500.1330885 MHz
NUC1 1H
P1 11.25 usec
PLW1 20.0000000 W

---------- CHANNEL f2 ----------
SFO2 500.1330885 MHz
NUC2 off
CPDPRG[2
PCPD2 0 usec
PLW2 0 W
PLW12 0 W
PLW13 0 W

F2 - Processing parameters
SI 65536
SF 500.1300002 MHz
WDW EM
SSB 0
LB 0.30 Hz
PC 1.00

Supplementary Figure 50. $^{13}$C-NMR of compound 27, recorded at 126 MHz and 25 °C in CDCl₃.
Current Data Parameters
NAME  11140B
EXFNO  1
PROCNO  1

F2 - Acquisition Parameters
Date_ 20220222
Time   18.21
INSTRUM    spect
PROBHD  5 mm PABBO BB/
PULPROG  zg30
TD   32768
SOLVENT  CDCl3
NS  16
DS  0
SWH  8012.820 Hz
FIDRES  0.244532 Hz
AQ  2.0447233 sec
RG  206.33
DW  62.400 usec
DE  6.50 usec
TE  298.9 K
D1  2.0000000 sec
D11  0 sec
TD0  1

-------- CHANNEL f1 --------
SFO1  400.2424 MHz
NUC1  1H
P1  14.30 usec
PLW1  12.000000 W

-------- CHANNEL f2 --------
SFO2  400.2424 MHz
NUC2  off
CPDPDG[2
PCPD2  0 usec
PLW2  0 W
PLW12  0 W
PLW13  0 W

F2 - Processing parameters
SI  65536
SF  400.2400 eyes
WDW  EM
SB  0
LB  0.30 Hz
GB  0
PC  1.00

Supplementary Figure 51. 1H-NMR of compound 28, recorded at 400 MHz and 25 °C in CDCl3.
Supplementary Figure 52. $^{13}$C-NMR of compound 28, recorded at 101 MHz and 25 °C in CDCl$_3$. 

S101
Supplementary Figure 53. $^1$H-NMR of compound 29, recorded at 500 MHz and 25 °C in CDCl$_3$. 

S102
Supplementary Figure 54. $^{13}$C-NMR of compound 29, recorded at 126 MHz and 25 °C in CDCl$_3$. 

S103
Supplementary Figure 55. $^1$H-NMR of compound 30, recorded at 400 MHz and 25 °C in CDCl$_3$. S104
Supplementary Figure 56. $^{13}$C-NMR of compound 30, recorded at 101 MHz and 25 °C in CDCl$_3$. S105
Supplementary Figure 57. $^1$H-NMR of compound 31, recorded at 400 MHz and 25 °C in CDCl$_3$. 

S106
Supplementary Figure 58. $^{13}$C-NMR of compound 31, recorded at 101 MHz and 25 °C in CDCl$_3$. S107
Supplementary Figure 59. $^1$H-NMR of compound 32, recorded at 400 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters
NAME  11148G
EXFNO  1
PROCNO  1

F2 - Acquisition Parameters
Date_  20220226
Time    0.54
INSTRUM    spect
PROBHD  5 mm PABBO BB/
PULPROG  zg30
TD   32768
SOLVENT    CDCl3
NS    16
DS    0
SWH   8012.820 Hz
FIDRES  0.244532 Hz
AQ 2.0447233 sec
RG    102.73
DW   62.400 usec
DE    8.50 usec
TE    298.5 K
D1 2.00000000 sec
D11 0 sec
TD0   1

-------- CHANNEL f1 --------
SFO1  400.2424716 MHz
NUC1    1H
P1 14.30 usec
PLW1  12.00000000 W

-------- CHANNEL f2 --------
SFO2        400.2424716 MHz
NUC2                off
CPDPKG2
PCPD2 0 usec
PLW2 0 W
PLW12 0 W
PLW13 0 W

F2 - Processing parameters
SI    65536
SF  400.2399967 MHz
WDW    EM
SB    0
LB    0.30 Hz
GB    0
PC    1.00
Supplementary Figure 60. $^{13}$C-NMR of compound 32, recorded at 101 MHz and 25 °C in CDCl$_3$. 

S109
Supplementary Figure 61. $^1$H-NMR of compound 33, recorded at 400 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters
NAME  11148F
EXPNO  1
PROCNO  1

F2 - Acquisition Parameters
Date_ 20220226
Time  1.27
INSTRUM  spect
PROBHD  5 mm PABBO BB/
PULPROG  zg30
TD  32768
SOLVENT  CDCl3
NS  16
DS  0
SWH  8012.820 Hz
FIDRES  0.244532 Hz
AQ  2.0447233 sec
RG  206.33
DW  62.400 usec
DE  6.50 usec
TE  298.5 K
D1  2.00000000 sec
D11  0 sec
TD0  1

-------- CHANNEL f1 --------
SFO1  400.2424716 MHz
NUC1  1H
P1  14.30 usec
PLW1  12.00000000 W

-------- CHANNEL f2 --------
SFO2  400.2424716 MHz
NUC2  off
CPDPRG[2
PCPD2  0 usec
PLW2  0 W
PLW12  0 W
PLW13  0 W

F2 - Processing parameters
SI  65536
SF  400.2399968 MHz
WDW  EM
SSB  0
LB  0.30 Hz
GB  0
PC  1.00
Supplementary Figure 62. $^{13}$C-NMR of compound 33, recorded at 101 MHz and 25 °C in CDCl$_3$. S111
Supplementary Figure 63. $^1$H-NMR of compound 34, recorded at 400 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters
NAME 111481
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220226
Time 0.21
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447233 sec
RG 206.33
DW 62.400 usec
DE 6.50 usec
TE 298.5 K
D1 2.0000000 sec
D11 0 sec
TD0 1

---------- CHANNEL f1 ----------
SFO1 400.2424716 MHz
NUC1 1H
P1 14.30 usec
PLW1 12.00000000 W

---------- CHANNEL f2 ----------
SFO2 400.2424716 MHz
NUC2 off
CPDPRG[2
PCPD2 0 usec
PLW2 0 W
PLW12 0 W
PLW13 0 W

F2 - Processing parameters
SI 65536
SF 400.2399973 MHz
WDW EM
SB 0
LB 0.30 Hz
PC 1.00

S112
Supplementary Figure 64. $^{13}$C-NMR of compound 34, recorded at 101 MHz and 25 °C in CDCl$_3$. S113
Supplementary Figure 65. $^1$H-NMR of compound 35, recorded at 400 MHz and 25 °C in CDCl$_3$. 
Current Data Parameters
NAME  11148H
EXPNO  3
PROCNO  1

F2 - Acquisition Parameters
Date_ 20220225
Time   22.43
INSTRUM    spect
PROBHD  5 mm PABBO BB/
PULPROG zgpg30
TD   65536
SOLVENT CDCl3
NS    500
DS    4
SWH   24038.461 Hz
FIDRES  0.366798 Hz
AQ  1.3631488 sec
RG  206.33
DW  20.800 usec
DE    6.50 usec
TE  299.3 K
D1  2.00000000 sec
D11 0.03000000 sec
TD0 1

--------- CHANNEL f1 ---------
SFO1  100.6504916 MHz
NUC1  13C
P1     10.00 usec
PLW1  54.00000000 W

--------- CHANNEL f2 ---------
SFO2  400.2416010 MHz
NUC2  1H
CPDPRG[2  waltz16
PCPD2    90.00 usec
PLW2 12.00000000 W
PLW12 0.30294999 W
PLW13 0.24539000 W

F2 - Processing parameters
SI    32768
SF    100.6404344 MHz
WDW  EM
SSB    0
LB  1.00 Hz
GB    0
PC  1.40

Supplementary Figure 66. $^{13}$C-NMR of compound 35, recorded at 101 MHz and 25 °C in CDCl$_3$. S115
Current Data Parameters
NAME  11178A
EXFNO  1
PROCNO  1

F2 - Acquisition Parameters
Date_  20220311
Time   17.49
INSTRUM  spect
PROBHD  5 mm PABBO BB/
PULPROG  zg30
TD   32768
SOLVENT CDCl3
NS   16
DS   0
SWH   8012.820 Hz
FIDRES  0.244532 Hz
AQ  2.0447233 sec
RG  92.09
DW  62.400 usec
DE  6.50 usec
TE  298.0 K
D1  2.0000000 sec
D11  0 sec
TD0  1

--------- CHANNEL f1 ---------
SFO1  400.2424716 MHz
NUC1  1H
P1  14.30 usec
PLW1  12.00000000 W

--------- CHANNEL f2 ---------
SFO2  400.2424716 MHz
NUC2  off
CPDPRG[2
PCPD2  0 usec
PLW2  0 W
PLW12  0 W
PLW13  0 W

F2 - Processing parameters
SI   65536
SF  400.2399991 MHz
WDW  EM
GB  0
LB  0.30 Hz
PC  1.00

Supplementary Figure 67. $^1$H-NMR of compound 36, recorded at 400 MHz and 25 °C in CDCl$_3$. S116
Supplementary Figure 68. $^{13}$C-NMR of compound 36, recorded at 101 MHz and 25 °C in CDCl$_3$. S117
Supplementary Figure 69. $^1$H-NMR of compound 37, recorded at 500 MHz and 25 °C in CDCl$_3$. 
S118
Supplementary Figure 70. $^{13}$C-NMR of compound 37, recorded at 126 MHz and 25 °C in CDCl$_3$. 
S119
Current Data Parameters
NAME  11168A
EXFNO  1
PROCNO  1

F2 - Acquisition Parameters
Date_  20220306
Time   22.42
INSTRUM spect
PROBHD  5 mm CPPBBO BB
PULPROG zg30
TD  65536
SOLVENT CDCl3
NS  12
DS  2
SWH  10000.000 Hz
FIDRES  0.152588 Hz
AQ  3.2767999 sec
RG  55.37
DW  50.000 usec
DE  6.50 usec
TE  298.2 K
D1  1.0000000 sec
D11  0 sec
TD0  1

-------- CHANNEL f1 --------
SFO1  500.1330885 MHz
NUC1  1H
P1  11.25 usec
PLW1  20.00000000 W

-------- CHANNEL f2 --------
SFO2  500.1330885 MHz
NUC2  
CPDPRG2
PCPD2  0 usec
PLW2  0 W
PLW12  0 W
PLW13  0 W

F2 - Processing parameters
SI  65536
SF  500.1299977 MHz
WDW EM
SSB  0
LB  0.30 Hz
GB  0
PC  1.00

Supplementary Figure 71. $^1$H-NMR of compound 38, recorded at 500 MHz and 25 °C in CDCl$_3$. S120
Supplementary Figure 72. $^{13}$C-NMR of compound 39, recorded at 126 MHz and 25 °C in CDCl$_3$. 
S121
Supplementary Figure 73. $^1$H-NMR of compound 39, recorded at 500 MHz and 25 °C in CDCl$_3$. S122
Supplementary Figure 74. $^{13}$C-NMR of compound 39, recorded at 126 MHz and 25 °C in CDCl$_3$. 

S123
Supplementary Figure 75. $^1$H-NMR of compound 40, recorded at 400 MHz and 25 °C in CDCl$_3$. 
Current Data Parameters
NAME  11168G
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220306
Time  23.24
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zgpg30
TD  65536
SOLVENT CDCl3
NS  100
DS  4
SWH  29761.904 Hz
FIDRES  0.454131 Hz
AQ  1.1010048 sec
RG  192.89
DW  16.800 usec
DE  18.00 usec
TE  298.2 K
D1  2.0000000 sec
D11  0.0300000 sec
TD0  1

-------- CHANNEL f1 --------
SFO1  125.7703637 MHz
NUC1  13C
P1  10.50 usec
PLW1  57.00000000 W

-------- CHANNEL f2 --------
SFO2 500.1320005 MHz
NUC2  1H
CPDPRG[2 waltz16
PCPD2  80.00 usec
PLW2  20.00000000 W
PLW12  0.39550999 W
PLW13  0.25312999 W

F2 - Processing parameters
SI  32768
SF  125.7577729 MHz
WDW EM
SSB  0
LB  1.00 Hz
GB  0
PC  1.40

Supplementary Figure 76. $^{13}$C-NMR of compound 40, recorded at 126 MHz and 25 °C in CDCl$_3$. S125
Supplementary Figure 77. $^1$H-NMR of compound 41, recorded at 500 MHz and 25 °C in CDCl$_3$. 
S126
Supplementary Figure 78. $^{13}$C-NMR of compound 41, recorded at 126 MHz and 25 °C in CDCl$_3$. S127
Current Data Parameters
NAME  11172D
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220309
Time   22.00
INSTRUM    spect
PROBHD 5 mm CPPBBO BB
PULPROG zg30
TD   65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ  3.2767999 sec
RG 49.27
DW  50.000 usec
DE  6.50 usec
TE  298.2 K
D1  1.0000000 sec
D11 0 sec
TD0 1

--------- CHANNEL f1 ---------
SFO1  500.1330885 MHz
NUC1  1H
P1   11.25 usec
PLW1 20.00000000 W

--------- CHANNEL f2 ---------
SFO2        500.1330885 MHz
NUC2                off
CPDPRG[2
PCPD2 0 usec
PLW2 0 W
PLW12 0 W
PLW13 0 W

F2 - Processing parameters
SI  65536
SF  500.1299962 MHz
WDW EM
SSB 0
LB  0.30 Hz
GC 1.00
PC  1.00

Supplementary Figure 79. $^1$H-NMR of compound 42, recorded at 500 MHz and 25 °C in CDCl$_3$. S128
Supplementary Figure 80. $^{13}$C-NMR of compound 42, recorded at 126 MHz and 25 °C in CDCl$_3$. 
S129
Supplementary Figure 81. $^1$H-NMR of compound 43, recorded at 500 MHz and 25 °C in CDCl$_3$. S130
Supplementary Figure 82. $^{13}$C-NMR of compound 43, recorded at 126 MHz and 25 °C in CDCl$_3$. 

S131
Current Data Parameters
NAME  11157B
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220305
Time 17.49
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447233 sec
RG 102.73
DW 62.400 usec
DE 6.50 usec
TE 299.1 K
D1 2.00000000 sec
D11 0 sec
TD0 1

----------- CHANNEL f1 -----------
SFO1 400.2424716 MHz
NUC1 1H
P1 14.30 usec
PLW1 12.00000000 W

----------- CHANNEL f2 -----------
SFO2 400.2424716 MHz
NUC2 off
CPDPGR[2
PCPD2 0 usec
PLW2 0 W
PLW12 0 W
PLW13 0 W

F2 - Processing parameters
SI 65536
SF 400.2400015 MHz
WDW EM
PC 1.00
LB 0.30 Hz
GB 0

Supplementary Figure 83. 1H-NMR of compound 44, recorded at 400 MHz and 25 °C in CDCl3.
Supplementary Figure 84. $^{13}$C-NMR of compound 44, recorded at 101 MHz and 25 °C in CDCl$_3$. 

S133
Supplementary Figure 85. $^1$H-NMR of compound 45, recorded at 500 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters
NAME  11172A
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220309
Time  21.40
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zg30
TD  65536
SOLVENT CDCl3
NS  16
DS  2
SWH  10000.000 Hz
FIDRES  0.152588 Hz
AQ  3.2767999 sec
RG  49.27
DW  50.000 usec
DE  6.50 usec
TE  298.2 K
D1  1.0000000 sec
D11 0 sec
TD0  1

-------- CHANNEL f1 --------
SFO1  500.1330885 MHz
NUC1  1H
P1  11.25 usec
PLW1  20.00000000 W

-------- CHANNEL f2 --------
SFO2  500.1330885 MHz
NUC2  off
CPDPDG[2
PCPD2  0 usec
PLW2  0 W
PLW12  0 W
PLW13  0 W

F2 - Processing parameters
SI  65536
SF  500.1300020 MHz
WDW EM
SSB  0
LB  0.30 Hz
GB  0
PC  1.00
Supplementary Figure 86. $^{13}$C-NMR of compound 45, recorded at 126 MHz and 25 °C in CDCl$_3$. S135
Supplementary Figure 87. $^1$H-NMR of compound 46, recorded at 500 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters
NAME 11172B
EXFNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220309
Time 22.16
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 55.37
DW 50.000 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
D11 0 sec
TD0 1

-------- CHANNEL f1 --------
SFO1 500.1330885 MHz
NUC1 1H
P1 11.25 usec
PLW1 20.00000000 W

-------- CHANNEL f2 --------
SFO2 500.1330885 MHz
NUC2 off
CPDPRG[2
PCPD2 0 usec
PLW2 0 W
PLW12 0 W
PLW13 0 W

F2 - Processing parameters
SI 65536
SF 500.1300040 MHz
WDW EM
SSB 0
LB 0.30 Hz
PC 1.00
Supplementary Figure 88. $^{13}$C-NMR of compound 46, recorded at 126 MHz and 25 °C in CDCl$_3$. 

S137
Supplementary Figure 89. ¹H-NMR of compound 47, recorded at 500 MHz and 25 °C in CDCl₃.

S138
Supplementary Figure 90. $^{13}$C-NMR of compound 47, recorded at 126 MHz and 25 °C in CDCl$_3$. 
S139
Current Data Parameters
NAME 11154B
EXFNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220301
Time 19.36
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 55.37
DW 50.000 usec
DE 8.50 usec
TE 298.2 K
D1 1.00000000 sec
D11 0 sec
TD0 1

--------- CHANNEL f1 ---------
SFO1 500.1330885 MHz
NUC1 1H
P1 11.25 usec
PLW1 20.00000000 W

--------- CHANNEL f2 ---------
SFO2 500.1330885 MHz
NUC2 off
CPDPRG2
PCPD2 0 usec
PLW2 0 W
PLW12 0 W
PLW13 0 W

F2 - Processing parameters
SI 65536
SF 500.1300115 MHz
WDW EM
SSB 0
LB 0.30 Hz
PC 1.00

Supplementary Figure 91. ¹H-NMR of compound 48, recorded at 500 MHz and 25 °C in CDCl₃.
Supplementary Figure 92. $^{13}$C-NMR of compound 48, recorded at 126 MHz and 25 °C in CDCl$_3$. 

S141
### Current Data Parameters

**NAME**: 11150C  
**EXPNO**: 1  
**PROCNO**: 1

#### F2 - Acquisition Parameters

- **Date**: 20220227  
- **Time**: 18:21  
- **INSTRUM**: spect  
- **PROBHD**: 5 mm PABBO BB/  
- **PULPROG**: zg30  
- **TD**: 32768  
- **SOLVENT**: CDCl3

#### F2 - Processing parameters

- **SI**: 65536  
- **SF**: 400.2400080 MHz  
- **WDW**: EM  
- **SSB**: 0  
- **LB**: 0.30 Hz  
- **PC**: 1.00

---

**Supplementary Figure 93.** $^1$H-NMR of compound 49, recorded at 400 MHz and 25 °C in CDCl$_3$. S142
Supplementary Figure 94. $^{13}$C-NMR of compound 49, recorded at 101 MHz and 25 °C in CDCl$_3$. S143
Supplementary Figure 95. $^1$H-NMR of compound 50, recorded at 500 MHz and 25 °C in CDCl₃.
Supplementary Figure 96. $^{13}$C-NMR of compound 50, recorded at 126 MHz and 25 °C in CDCl$_3$. 

S145
Supplementary Figure 97. $^1$H-NMR of compound 51, recorded at 400 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters
NAME 11158D
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date 20220304
Time 15.08
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 10
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447233 sec
RG 206.33
DW 62.400 usec
DE 6.50 usec
TE 298.1 K
D1 2.00000000 sec
D11 0 sec
TD0 1

-------- CHANNEL f1 --------
SFO1 400.2424716 MHz
NUC1 1H
P1 14.30 usec
PLW1 12.00000000 W

-------- CHANNEL f2 --------
SFO2 400.2424716 MHz
NUC2 off
CPDPRG[2
PCPD2 0 usec
PLW2 0 W
PLW12 0 W
PLW13 0 W

F2 - Processing parameters
SI 65536
SF 400.2400092 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
**Current Data Parameters**

**NAME** 11158D-C  
**EXPN0** 2  
**PROCNO** 1  

**F2 - Acquisition Parameters**

- **Date:** 20220303  
- **Time:** 23.40  
- **INSTRUM:** spect  
- **PROBHD:** 5 mm CPPBBO BB  
- **PULPROG:** zgpg30  
- **TD:** 65536  
- **SOLVENT:** CDCl₃  
- **NS:** 150  
- **DS:** 4  
- **SWH:** 29761.904 Hz  
- **FIDRES:** 0.454131 Hz  
- **AQ:** 1.1010048 sec  
- **RG:** 192.89  
- **DW:** 16.800 usec  
- **DE:** 18.00 usec  
- **TE:** 298.2 K  
- **D1:** 2.00000000 sec  
- **D11:** 0.03000000 sec  
- **TD0:** 1  

**F2 - Processing parameters**

- **SI:** 32768  
- **SF:** 125.7577731 MHz  
- **WDW:** EM  
- **SSB:** 0  
- **LB:** 1.00 Hz  
- **GB:** 0  
- **PC:** 1.40

**Supplementary Figure 98.** $^{13}$C-NMR of compound 51, recorded at 126 MHz and 25 °C in CDCl₃.
Supplementary Figure 99. $^1$H-NMR of compound 52, recorded at 400 MHz and 25 °C in CDCl$_3$. S148
**Supplementary Figure 100.** $^{13}$C-NMR of compound 52, recorded at 101 MHz and 25 °C in CDCl$_3$. 

S149
Supplementary Figure 101. $^1$H-NMR of compound 53, recorded at 500 MHz and 25 °C in CDCl$_3$. S150
Supplementary Figure 102. $^{13}$C-NMR of compound 53, recorded at 126 MHz and 25 °C in CDCl$_3$. 

S151
Current Data Parameters
NAME 11193B
EXPN0 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220320
Time 11.31
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 69.95
DW 50.000 usec
DE 8.50 usec
TE 298.2 K
D1 1.0000000 sec
D11 0 sec
TD0 1

-------- CHANNEL f1 --------
SFO1 500.1330885 MHz
NUC1 1H
P1 11.25 usec
PLW1 20.00000000 W

-------- CHANNEL f2 --------
SFO2 500.1330885 MHz
NUC2 off
CPDPRG[2
PCPD2 0 usec
PLW2 0 W
PLW2 0 W
PLW2 0 W

F2 - Processing parameters
SI 65536
SF 500.1300128 MHz
WDW EM
SB 0
LB 0.30 Hz
PC 1.00

Supplementary Figure 103. ^1^H-NMR of compound 54, recorded at 500 MHz and 25 °C in CDCl_3.
Supplementary Figure 104. $^{13}$C-NMR of compound 54, recorded at 126 MHz and 25 °C in CDCl$_3$. S153
**Supplementary Figure 105.** $^1$H-NMR of compound 55, recorded at 500 MHz and 25 °C in CDCl$_3$. 

S154
Supplementary Figure 106. $^{13}$C-NMR of compound 55, recorded at 126 MHz and 25 °C in CDCl$_3$. S155
Supplementary Figure 107. $^1$H-NMR of compound 56, recorded at 500 MHz and 25 °C in CDCl$_3$. S156
Supplementary Figure 108. $^{13}$C-NMR of compound 56, recorded at 126 MHz and 25 °C in CDCl$_3$. 

S157
Supplementary Figure 109. $^1$H-NMR of compound 57, recorded at 500 MHz and 25 °C in CDCl$_3$. S158
Supplementary Figure 110. $^{13}$C-NMR of compound 57, recorded at 126 MHz and 25 °C in CDCl$_3$. 

S159
Supplementary Figure 111. $^1$H-NMR of compound 58, recorded at 400 MHz and 25 °C in CDCl₃.
Supplementary Figure 112. $^{13}$C-NMR of compound 58, recorded at 126 MHz and 25 °C in CDCl$_3$. S161
Supplementary Figure 113. $^1$H-NMR of compound 59, recorded at 500 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters
NAME     H-154J
EXFNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20220301
Time_    20.09
INSTRUM  spect
PROBHD   5 mm CPPBBO BB
PULPROG  zg30
TD       65536
SOLVENT  CDCl3
NS       16
DS       2
SWH      10000.000 Hz
FIDRES   0.152588 Hz
AQ       3.2767999 sec
RG       31.72
DW       50.000 usec
DE       6.50 usec
TE       298.2 K
D1       1.00000000 sec
D11      0 sec
TD0      1

---------- CHANNEL f1 ----------
SFO1     500.1330885 MHz
NUC1     1H
P1       11.25 usec
PLW1     20.00000000 W

---------- CHANNEL f2 ----------
SFO2     500.1330885 MHz
NUC2     off
CPDPRG[2
PCPD2    0 usec
PLW2     0 W
PLW12    0 W
PLW13    0 W

F2 - Processing parameters
SI       65536
SF       500.1300099 MHz
WDW      EM
SSB      0
LB       0.30 Hz
GB       0
PC       1.00
Supplementary Figure 114. $^{13}$C-NMR of compound 59, recorded at 126 MHz and 25 °C in CDCl$_3$. 

S163
Supplementary Figure 115. $^1$H-NMR of compound 60, recorded at 500 MHz and 25 °C in CDCl$_3$. S164
Supplementary Figure 116. $^{13}$C-NMR of compound 60, recorded at 126 MHz and 25 °C in CDCl$_3$. 

S165
Supplementary Figure 117. \(^1\)H-NMR of compound 61, recorded at 500 MHz and 25 °C in CDCl\(_3\),
Current Data Parameters
NAME             H-154F
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20220301
Time 20.18
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 40
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 192.89
DW 16.800 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

-------- CHANNEL f1 --------
SFO1 125.7703637 MHz
NUC1 13C
P1 10.50 usec
PLW1 57.00000000 W

-------- CHANNEL f2 --------
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 20.00000000 W
PLW12 0.39550999 W
PLW13 0.25312999 W

F2 - Processing parameters
SI 32768
SF 125.7577729 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Supplementary Figure 118. $^{13}$C-NMR of compound 61, recorded at 126 MHz and 25 °C in CDCl$_3$. S167
Supplementary Figure 119. $^1$H-NMR of compound 62, recorded at 500 MHz and 25 °C in CDCl₃.
Supplementary Figure 120. $^{13}$C-NMR of compound 62, recorded at 126 MHz and 25 °C in CDCl$_3$. S169
Supplementary Figure 121. $^1$H-NMR of compound 63, recorded at 500 MHz and 25 °C in CDCl$_3$. S170
Supplementary Figure 122. $^{13}$C-NMR of compound 62, recorded at 126 MHz and 25 °C in CDCl$_3$. 

S171
Supplementary Figure 123. $^1$H-NMR of compound 64, recorded at 400 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters
NAME  11158H
EXFNO  1
PROCNO  1

F2 - Acquisition Parameters
Date_  20220305
Time   18.36
INSTRUM    spect
PROBHD  5 mm PABBO BB/
PULPROG zg30
TD   32768
SOLVENT CDCl3
NS  16
DS
SWH  8012.820 Hz
FIDRES  0.244532 Hz
AQ  2.0447233 sec
RG  206.33
DW  62.400 usec
DE  8.50 usec
TE  299.3 K
D1    2.00000000 sec
D11  0 sec
TD0  1

-------- CHANNEL f1 --------
SFO1  400.2424716 MHz
NUC1  1H
P1     14.30 usec
PLW1  12.00000000 W

-------- CHANNEL f2 --------
SFO2        400.2424716 MHz
NUC2                off
CPDPRG[2
PCPD2  0 usec
PLW2  0 W
PLW12  0 W
PLW13  0 W

F2 - Processing parameters
SI  65536
SF  400.2400103 MHz
WDW EM
SSB  0
LB  0.30 Hz
GB
PC  1.00
Supplementary Figure 124. $^{13}$C-NMR of compound 64, recorded at 101 MHz and 25 °C in CDCl$_3$. 

S173
Supplementary Figure 125. $^1$H-NMR of compound 65, recorded at 400 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters
NAME 111158A
EXFNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220305
Time 18.07
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447233 sec
RG 206.33
DW 62.400 usec
DE 6.50 usec
TE 299.2 K
D1 2.0000000 sec
D11 0 sec
TD0 1

-------- CHANNEL f1 ---------
SFO1 400.2424716 MHz
NUC1 1H
P1 14.30 usec
PLW1 12.00000000 W

-------- CHANNEL f2 ---------
SFO2 400.2424716 MHz
NUC2 off
CPDPRG[2
CPD2 0 usec
PLW2 0 W
PLW12 0 W
PLW13 0 W

F2 - Processing parameters
SI 65536
SF 400.2400078 MHz
WDW EM
SB 0
LB 0.30 Hz
GB 0
PC 1.00
Supplementary Figure 126. $^{13}$C-NMR of compound 65, recorded at 101 MHz and 25 °C in CDCl$_3$. S175
Supplementary Figure 127. $^1$H-NMR of compound 66, recorded at 400 MHz and 25 °C in CDCl$_3$. S176
Supplementary Figure 128. $^{13}$C-NMR of compound 66, recorded at 101 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters
NAME  11158B
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220305
Time   18.25
INSTRUM    spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD   65536
SOLVENT CDCl3
NS 170
DS    4
SWH   24038.461 Hz
FIDRES 0.366798 Hz
AQ  1.3631488 sec
RG  206.33
DW   20.800 usec
DE   6.50 usec
TE   299.9 K
D1    2.00000000 sec
D11  0.03000000 sec
TD0   1

-------- CHANNEL f1 --------
SFO1  100.6504916 MHz
NUC1  13C
P1     10.00 usec
PLW1  54.00000000 W

-------- CHANNEL f2 --------
SFO2  400.2416010 MHz
NUC2    1H
CPDPRG[2 waltz16
PCPD2  90.00 usec
PLW2  12.00000000 W
PLW12 0.30294999 W
PLW13 0.24539000 W

F2 - Processing parameters
SI  32768
SF  100.6404388 MHz
WDW EM
SSB 0
LB    1.00 Hz
GB  0
PC  1.40
## Current Data Parameters

**NAME**  11151D  
**EXPNO**  1  
**PROCNO**  1  

### F2 - Acquisition Parameters

- **Date:** 20220227  
- **Time:** 18.33  
- **INSTRUM:** spect  
- **PROBHD:** 5 mm PABBO BB/  
- **PULPROG:** zg30  
- **TD:** 32768  
- **SOLVENT:** CDCl3  
- **NS:** 16  
- **DS:** 0  
- **SWH:** 8012.820 Hz  
- **FIDRES:** 0.244532 Hz  
- **AQ:** 2.0447233 sec  
- **RG:** 102.73  
- **DW:** 62.400 usec  
- **DE:** 8.50 usec  
- **TE:** 299.0 K  
- **D1:** 2.00000000 sec  
- **D11:** 0 sec  
- **TD0:** 1  

#### CHANNEL f1

- **SFO1:** 400.2424716 MHz  
- **NUC1:** 1H  
- **P1:** 14.30 usec  
- **PLW1:** 12.00000000 W  

#### CHANNEL f2

- **SFO2:** 400.2424716 MHz  
- **NUC2:** off  
- **CPDPDG[2:**  
- **PCPD2:** 0 usec  
- **PLW2:** 0 W  
- **PLW12:** 0 W  
- **PLW13:** 0 W  

### F2 - Processing parameters

- **SI:** 65536  
- **SF:** 400.2400099 MHz  
- **WDW:** EM  
- **SB:** 0  
- **LB:** 0.30 Hz  
- **GB:** 0  
- **PC:** 1.00  

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**Supplementary Figure 129.** $^1$H-NMR of compound 67, recorded at 400 MHz and 25 °C in CDCl$_3$. S178
Supplementary Figure 130. $^{13}$C-NMR of compound 67, recorded at 101 MHz and 25 °C in CDCl$_3$. 

S179
Supplementary Figure 131. $^1$H-NMR of compound 68, recorded at 500 MHz and 25 °C in CDCl$_3$. S180
Supplementary Figure 132. $^{13}$C-NMR of compound 68, recorded at 126 MHz and 25 °C in CDCl$_3$. S181
Supplementary Figure 133. $^1$H-NMR of compound 69, recorded at 500 MHz and 25 °C in CDCl$_3$. 
S182
Supplementary Figure 134. $^{13}$C-NMR of compound 69, recorded at 126 MHz and 25 °C in CDCl$_3$. S183
Supplementary Figure 135. $^1$H-NMR of compound 70, recorded at 500 MHz and 25 °C in CDCl$_3$. S184
Supplementary Figure 136. $^{13}$C-NMR of compound 70, recorded at 126 MHz and 25 °C in CDCl$_3$. S185
Supplementary Figure 137. $^1$H-NMR of compound 71, recorded at 500 MHz and 25 °C in CDCl$_3$. 

S186
Supplementary Figure 138. $^{13}$C-NMR of compound 71, recorded at 126 MHz and 25 °C in CDCl$_3$. S187
11193C-2
1D Selective Gradient NOESY
freq: 4.274ppm

Supplementary Figure 139. NOESY of compound 71, recorded at 400 MHz and 25 °C in CDC13
Supplementary Figure 140. $^1$H-NMR of compound 72, recorded at 500 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters
NAME 11200A
EXFNO 1
PROCNO 1

F2 - Acquisition Parameters
Date 20220325
Time 18.34
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zg30
TD 65536
SOLVENT CDCl$_3$
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 49.27
DW 50.000 usec
DE 6.50 usec
TE 298.2 K
D1 1.0000000 sec
D11 0 sec
TD0 1

-------- CHANNEL f1 --------
SFO1 500.1330885 MHz
NUC1 1H
P1 11.25 usec
PLW1 20.00000000 W

-------- CHANNEL f2 --------
SFO2 500.1330885 MHz
NUC2 off
CPDPRG[2
PCPD2 0 usec
PLW2 0 W
PLW12 0 W
PLW13 0 W

F2 - Processing parameters
SI 65536
SF 500.1300107 MHz
WDW EM
SSB 0
LB 0.30 Hz
PC 1.00

Supplementary Figure 140. $^1$H-NMR of compound 72, recorded at 500 MHz and 25 °C in CDCl$_3$. 

S189
Supplementary Figure 141. $^{13}$C-NMR of compound 72, recorded at 126 MHz and 25 °C in CDCl$_3$. S190
Current Data Parameters
NAME  11199F
EXFNO  1
PROCNO  1

F2 - Acquisition Parameters
Date_  20220323
Time   11.32
INSTRUM    spect
PROBHD  5 mm CPPBBO BB
PULPROG  zg30
TD   65536
SOLVENT    CDCl3
NS  12
DS  2
SWH  10000.000 Hz
FIDRES  0.152588 Hz
AQ  3.2767999 sec
RG  62.06
DW  50.000 usec
DE  8.50 usec
TE  298.2 K
D1  1.00000000 sec
D11  0 sec
TD0  1

-------- CHANNEL f1 --------
SFO1  500.1330885 MHz
NUC1  1H
P1  11.25 usec
PLW1  20.00000000 W

-------- CHANNEL f2 --------
SFO2        500.1330885 MHz
NUC2                off
CPDPRG[2
PCPD2  0 usec
PLW2  0 W
PLW12  0 W
PLW13  0 W

F2 - Processing parameters
SI  65536
SF  500.1300131 MHz
WDW  EM
SB  0
LB  0.30 Hz
GB  0
PC  1.00

Supplementary Figure 142. $^1$H-NMR of compound 73, recorded at 500 MHz and 25 °C in CDCl$_3$.  
S191
Current Data Parameters
NAME  11199F
EXPNO  2
PROCNO  1

F2 - Acquisition Parameters
Date_ 20220323
Time   11.34
INSTRUM    spect
PROBHD  5 mm CPPBBO BB
PULPROG zgpg30
TD   65536
SOLVENT CDCl3
NS    160
DS    4
SWH   29761.904 Hz
FIDRES 0.454131 Hz
AQ    1.1010048 sec
RG    192.89
DW   16.800 usec
DE    18.00 usec
TE    298.2 K
D1    2.00000000 sec
D11   0.03000000 sec
TD0    1

-------- CHANNEL f1 --------
SFO1  125.7703637 MHz
NUCl  13C
P1    10.50 usec
PLW1   57.00000000 W

-------- CHANNEL f2 --------
SFO2  500.1320005 MHz
NUC2  1H
CPDPDG[2 waltz16
PCPD2  80.00 usec
PLW2   20.00000000 W
PLW12  0.39550999 W
PLW13  0.25312999 W

F2 - Processing parameters
SI  32768
SF  125.7577729 MHz
WDW EM
SSB    0
LB   1.00 Hz
GB    0
PC    1.40

Supplementary Figure 143. $^1$C-NMR of compound 73, recorded at 126 MHz and 25 °C in CDCl$_3$. S192
Supplementary Figure 144. $^1$H-NMR of compound 74, recorded at 500 MHz and 25 °C in CDCl$_3$. S193
Supplementary Figure 145. $^{13}$C-NMR of compound 74, recorded at 126 MHz and 25 °C in CDCl$_3$. 

S194
Supplementary Figure 146. $^1$H-NMR of compound 75, recorded at 500 MHz and 25 °C in CDCl$_3$. 

S195
Supplementary Figure 147. $^{13}$C-NMR of compound 75, recorded at 126 MHz and 25 °C in CDCl$_3$. 

S196
Supplementary Figure 148. $^1$H-NMR of compound 76, recorded at 500 MHz and 25 °C in CDCl$_3$. S197
Supplementary Figure 149. $^{13}$C-NMR of compound 76, recorded at 126 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters

NAME  11200E
EXPNO  2
PROCNO  1

F2 - Acquisition Parameters
Date_  20220331
Time   6.45
INSTRUM   spect
PROBHD  5 mm CPPBBO BB
PULPROG zgpg30
TD   65536
SOLVENT CDCl3
NS  800
DS  4
SWH   29761.904 Hz
FIDRES  0.454131 Hz
AQ  1.1010048 sec
RG  192.89
DW   16.800 usec
DE  18.00 usec
TE  298.2 K
D1  2.0000000 sec
D11  0.0300000 sec
TD0  1

-------- CHANNEL f1 --------
SFO1  125.7703637 MHz
NUC1   13C
P1  10.50 usec
PLW1  57.00000000 W

-------- CHANNEL f2 --------
SFO2  500.1320005 MHz
NUC2   1H
CPDPDRG[2 waltz16
PCPD2  80.00 usec
PLW2  20.00000000 W
PLW12  0.39550999 W
PLW13  0.25312999 W

F2 - Processing parameters
SI  32768
SF  125.7577720 MHz
WDW  EM
SSB  0
LB  1.00 Hz
GB  0
PC  1.40
Supplementary Figure 150. $^1$H-NMR of compound 77, recorded at 500 MHz and 25 °C in CDCl$_3$. S199
Supplementary Figure 151. $^{13}$C-NMR of compound 77, recorded at 126 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters
NAME 11200F
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220401
Time_ 17.08
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPREG zgpg30
TD 65536
SOLVENT CDCl3
NS 300
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 192.89
DW 16.800 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 usec
D11 0.03000000 usec
TD0 1

-------- CHANNEL f1 --------
SFO1 125.7703637 MHz
NUC1 13C
P1 10.50 usec
PLW1 57.00000000 W

-------- CHANNEL f2 --------
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 20.00000000 W
PLW12 0.39550999 W
PLW13 0.25312999 W

F2 - Processing parameters
SI 32768
SF 125.7577729 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Supplementary Figure 152. $^1$H-NMR of compound 78, recorded at 500 MHz and 25 °C in CDCl$_3$.
Supplementary Figure 153. $^{13}$C-NMR of compound 78, recorded at 126 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters
NAME  11200G
EXPNO  4
PROCNO  1

F2 - Acquisition Parameters
Date_  20220401
Time  17.29
INSTRUM  spect
PROBHD  5 mm CPPBBO BB
PULPROG  zgpg30
TD  65536
SOLVENT  CDCl3
NS  300
DS  4
SWH  29761.904 Hz
FIDRES  0.454131 Hz
AQ  1.1010048 sec
RG  192.89
DW  16.800 usec
DE  18.00 usec
TE  298.2 K
D1  2.00000000 sec
D11  0.03000000 sec
TD0  1

-------- CHANNEL f1 --------
SFO1  125.7703637 MHz
NUC1  13C
P1  10.50 usec
PLW1  57.00000000 W

-------- CHANNEL f2 --------
SFO2  500.1320005 MHz
NUC2  1H
CPDPRG[2  waltz16
PCPD2  80.00 usec
PLW2  20.00000000 W
PLW12  0.39509999 W
PLW13  0.25312999 W

F2 - Processing parameters
SI  32768
SF  125.7577737 MHz
WDW  EM
SSB  0
LB  1.00 Hz
GB  0
PC  1.40
Supplementary Figure 154. $^1$H-NMR of compound 79, recorded at 500 MHz and 25 °C in CDCl$_3$, S203
Supplementary Figure 155. $^{13}$C-NMR of compound 79, recorded at 126 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters
NAME 11200H
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220401
Time 18.21
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPACR zgpg30
TD 65536
SOLVENT CDCl3
NS 900
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 192.89
DW 16.800 usec
DE 18.00 usec
TE 298.2 K
D1 2.0000000 sec
D11 0.03000000 sec
TD0 1

--------- CHANNEL f1 ---------
SFO1 125.7703637 MHz
NUC1 13C
P1 10.50 usec
PLW1 57.00000000 W

--------- CHANNEL f2 ---------
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 20.00000000 W
PLW12 0.39550999 W
PLW13 0.25312999 W

F2 - Processing parameters
SI 32768
SF 125.757773 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Supplementary Figure 156. $^1$H-NMR of compound 80, recorded at 400 MHz and 25 °C in CDCl$_3$. 

S205
Supplementary Figure 157. $^{13}$C-NMR of compound 80, recorded at 101 MHz and 25 °C in CDCl$_3$. 

S206
Supplementary Figure 158. $^1$H-NMR of compound 81, recorded at 400 MHz and 25 °C in CDCl$_3$. 

S207
Current Data Parameters
NAME  11195
EXPNO  2
PROCNO  1

F2 - Acquisition Parameters
Date_  20220316
Time   17.08
INSTRUM    spect
PROBHD  5 mm PABBO BB/
PULPROG zgpg30
TD   65536
SOLVENT CDCl3
NS  110
DS    4
SWH   24038.461 Hz
FIDRES  0.366798 Hz
AQ 1.3631488 sec
RG  206.33
DW  20.800 usec
DE   6.50 usec
TE    298.0 K
D1  2.00000000 sec
D11  0.03000000 sec
TD0  1

---------- CHANNEL f1 ----------
SFO1  100.6504916 MHz
NUC1  13C
P1     10.00 usec
PLW1  54.00000000 W

---------- CHANNEL f2 ----------
SFO2  400.2416010 MHz
NUC2  1H
CPDPRG[2  waltz16
PCPD2  90.00 usec
PLW2  12.00000000 W
PLW12  0.30294999 W
PLW13  0.24539000 W

F2 - Processing parameters
SI  32768
SF  100.6404361 MHz
WDW  EM
SSB  0
LB  1.00 Hz
GB  0
PC  1.40

Supplementary Figure 159. $^{13}$C-NMR of compound 81, recorded at 101 MHz and 25 °C in CDCl$_3$. S208
Supplementary Figure 160. $^1$H-NMR of compound 82, recorded at 400 MHz and 25 °C in CDCl$_3$. S209
### Current Data Parameters

| NAME  | 11196 |
|-------|-------|
| EXPNO | 2     |
| PROCNO| 1     |

F2 - Acquisition Parameters

| Date_  | 20220316 |
|--------|-----------|
| Time   | 17.25     |
| INSTRUM| spect     |
| PROBHD | 5 mm PABBO BB/ |
| PULPROG| zgpg30    |
| TD     | 65536     |
| SOLVENT| CDCl3    |
| NS     | 200       |
| DS     | 4         |
| SWH    | 24038.461 Hz |
| FIDRES | 0.366798 Hz |
| AQ     | 1.3631488 sec |
| RG     | 206.33    |
| DW     | 20.800 usec |
| DE     | 6.50     |
| TE     | 298.1 K   |
| D1     | 2.00000000 sec |
| D11    | 0.03000000 sec |
| TD0    | 1         |

--- CHANNEL f1 ---

| SFO1  | 100.6504916 MHz |
| NUC1  | 13C            |
| P1    | 10.00 usec     |
| PLW1  | 54.00000000 W  |

--- CHANNEL f2 ---

| SFO2  | 400.2416010 MHz |
| NUC2  | 1H             |
| CPDPDG[2 | waltz16     |
| PCPD2 | 90.00 usec     |
| PLW2  | 12.00000000 W  |
| PLW12 | 0.30294999 W   |
| PLW13 | 0.24539000 W   |

F2 - Processing parameters

| SI    | 32768 |
| SF    | 100.6404352 MHz |
| WDW   | EM     |
| SSB   | 0      |
| LB    | 1.00 Hz |
| GB    | 0      |
| PC    | 1.40   |

### Supplementary Figure 161

$^{13}$C-NMR of compound 82, recorded at 101 MHz and 25 °C in CDCl$_3$. 

[82]
Supplementary Figure 162. ¹H-NMR of compound 84, recorded at 500 MHz and 25 °C in CDCl₃.
Supplementary Figure 163. $^{13}$C-NMR of compound 84, recorded at 126 MHz and 25 °C in CDCl$_3$. 

S212
Supplementary Figure 164. $^1$H-NMR of compound 85, recorded at 400 MHz and 25 °C in CDCl$_3$. 

Current Data Parameters
NAME 11178D
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220314
Time 14.59
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447233 sec
RG 92.09
DW 62.400 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1

-------- CHANNEL f1 --------
SFO1 400.2424716 MHz
NUC1 1H
P1 14.30 usec
PLW1 12.00000000 W

-------- CHANNEL f2 --------
SFO2 400.2424716 MHz
NUC2 off
CPDPRG[2
PCPD2 0 usec
PLW2 0 W
PLW12 0 W
PLW13 0 W

F2 - Processing parameters
SI 65536
SF 400.2400077 MHz
WDW EM
SB 0
LB 0.30 Hz
PC 1.00
Supplementary Figure 165. $^{13}$C-NMR of compound 85, recorded at 126 MHz and 25 °C in CDCl$_3$.  

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Current Data Parameters
NAME  11178D-500
EXPNO  2
PROCNO  1

F2 - Acquisition Parameters
Date_ 20220311
Time_ 19.13
INSTRUM_ spect
PROBHD  5 mm CPPBBO BB
PULPROG zgpg30
TD  65536
SOLVENT CDCl3
NS  100
DS  4
SWH  29761.904 Hz
FIDRES  0.454131 Hz
AQ  1.1010048 sec
RG  192.89
DW  16.800 usec
DE  18.00 usec
TE  298.2 K
D1  2.0000000 sec
D11  0.0300000 sec
TD0  1

-------- CHANNEL f1 --------
SFO1  125.7703637 MHz
NUC1  13C
P1  10.50 usec
PLW1  57.0000000 W

-------- CHANNEL f2 --------
SFO2  500.1320005 MHz
NUC2  1H
CPDPDG[2  waltz16
PCPD2  80.00 usec
PLW2  20.00000000 W
PLW12  0.39550999 W
PLW13  0.25312999 W

F2 - Processing parameters
SI  32768
SF  125.7577738 MHz
WDW  EM
SSB  0
LB  1.00 Hz
GB  0
PC  1.40

---
Supplementary Figure 166. $^1$H-NMR of compound 86, recorded at 500 MHz and 25 °C in CDCl$_3$. S215
Supplementary Figure 167. $^{13}$C-NMR of compound 86, recorded at 126 MHz and 25 °C in CDCl$_3$. 

86, 3.6:1 E/Z
4. Supplementary References

1. Huang, H. M.; Bellotti, P.; Pfluger, P. M.; Schwarz, J. L.; Heidrich, B.; Glorius, F., Three-Component, Interrupted Radical Heck/Allylic Substitution Cascade Involving Unactivated Alkyl Bromides. *J. Am. Chem. Soc.* **2020**, *142* (22), 10173-10183.