Supporting Information

5-(Cyano)dibenzothiophenium Triflate: A Sulfur-Based Reagent for Electrophilic Cyanation and Cyanocyclizations
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# Supporting Information

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1. General methods

All dry solvents were obtained from a solvent purification system MBSPS7 from M.Braun. All reactions were carried out under nitrogen atmosphere unless stated otherwise. $^1$H and $^{13}$C NMR spectra were recorded at room temperature in CDCl₃, CD₃CN or DMSO-d₆ on Bruker AV 500, 400 or DPX 300 NMR spectrometer. $^1$H NMR spectra was recorded with CDCl₃ (tetramethylsilane, $\delta = 0.00$ ppm), CD₃CN ($\delta = 1.94$ ppm), Methylene Chloride-d₂ or DMSO-d₆ ($\delta = 2.50$ ppm) as internal reference; $^{13}$C NMR spectra was recorded with CDCl₃ ($\delta = 77.16$ ppm), CD₃CN ($\delta = 1.32$ ppm) or DMSO-d₆ ($\delta = 39.52$ ppm) as internal reference. Mass spectra were measured on a Finnigan MAT 8200 (70 eV) (EI), a Finnigan MAT 95 (ESI), or a Bruker APEX III FT-MS (7 T magnet) mass spectrometer. IR spectra were recorded on a JASCO FT/IR-4100 spectrometer at room temperature, the stretching frequencies are reported in wavenumbers (cm⁻¹). Column chromatography was performed either on Merck 60 (40-63 μm) silica gel or Biotage One automated column chromatography system on CHROMABOND® Flash BT 15g (or 25g) SiOH 40-63 μm from Macherey-Nagel. Thin-layer chromatography (TLC) analysis was performed using POLYGRAM® SIL G/UV254 TLC plates from Macherey-Nagel and visualized by UV irradiation and/or phosphomolybdic acid staining. All commercially available compounds (Acros, ABCR, Alfa Aesar, Aldrich, Fluorochem, TCI) were used as received unless stated otherwise.
2. Synthesis of 5-(cyano)dibenzothiophenium triflate 9

![Chemical structure]

Tf$_2$O (25 mmol, 1 equiv, 4.205 mL) was added dropwise within 5 minutes to a solution of dibenzo[b,d]thiophene 5-oxide 10$^{[1]}$ (1.0 equiv., 25 mmol, 5.007 g) in dry dichloromethane (350 mL) at -50°C under N$_2$. After stirring the resulting mixture for 1 hour, TMSCN (25 mmol, 1.0 equiv., 3.35 mL) was added dropwise and the mixture was further stirred at -50°C for 8 additional hours. Then, the cooling system was removed, and the formed suspension was allowed reaching room temperature. Filtration of the solvents afforded 9 as a white/beige solid, which was further washed with dichloromethane (2 x 50 mL), and finally dried under vacuum (5.39 g,15.0 mmol, 60%). $^1$H NMR (300 MHz, Acetonitrile-d$_3$) $\delta$ = 8.56 (d, $J$ = 8.4 Hz, 2H), 8.34 (dd, $J$ = 7.8, 1.2 Hz, 2H), 8.04 (td, $J$ = 7.8, 1.2 Hz, 2H), 7.89-7.83 (m, 2H). $^{13}$C NMR (75 MHz, Acetonitrile-d$_3$) $\delta$ 141.7, 137.2, 133.7, 130.0, 127.2, 126.4, 121.9 (q, $J$ = 320.4 Hz), 103.9. IR (neat): 3097, 2192, 1578, 1484, 1448, 1423, 1278, 1250, 1221, 1174, 1161, 1152, 1024, 780, 754, 700, 648, 631, 575, 514 cm$^{-1}$; HRMS calculated m/z for C$_{13}$H$_8$NS$^+$ [M-OTf]$^+$: 210.0372, found (ESI) 210.0365.

3. Preparation of substrates

Anilines S1, S2, S3, S4, S5, S6, S7, S8, S9, S10, S11, S27, carbazole S12, amine S13, thiols S14, S15, S16, S17, S18, silyl enol ether S20, alkene S21, pyrrole S22, indoles S25, 39, 42, 3H-benzo[e]indole 44, and arenes S26, S28 are commercially available and used as received. Silyl enol ether S19 is commercially available and was freshly distilled before use. Indoles S23,$^{[2]}$ S24$^{[3]}$ were prepared according to the previously reported literature procedures.
Tryptamine derivatives $S_{29}$, $S_{30}$, $S_{31}$, $S_{32}$, $S_{33}$, $S_{34}$, $S_{35}$, $S_{36}$, $S_{37}$, $S_{38}$, $S_{39}$ tryptophol derivatives $S_{40}$, $S_{41}$, $S_{42}$ and indole derivatives $S_{43}$, $S_{44}$, $S_{45}$, $S_{46}$, $S_{47}$, $S_{48}$, $S_{49}$ were prepared according to the previously reported literature procedures. Tryptophol $S_{39}$ is commercially available and used as received. Tryptamine derivatives $S_{33}$, $S_{34}$, $S_{37}$ and indole derivatives $S_{43}$, $S_{45}$, $S_{46}$, $S_{47}$, $S_{50}$, $S_{51}$ were prepared according to the following procedure:
Procedure for the preparation of S34

In a sealed tube, 5-chloropentan-2-one (20 mmol, 2.0 equiv, 2.29 mL) was added dropwise to a solution of phenylhydrazine (1.0 equiv., 10 mmol, 985 μL) in ethanol (30 mL) at room temperature. The resulting mixture was stirred at 110 °C for 10 h. After cooling to room temperature, the solvent was removed under vacuum. Then, DCM (20 mL) and NaOH aqueous (800 mg NaOH dissolved in 20 mL H₂O) was added. The resulting mixture was
stirred at 0 °C for 5 minutes. Then, ethyl chloroformiate (952 μL, 10 mmol, 1.0 equiv) was added to the mixture dropwise at 0 °C and the resulting mixture was stirred at room temperature for 5 h. The solution thus obtained was extracted with DCM, washed with brine and dried over anhydrous Na₂SO₄. Solvent evaporation from the organic phase under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 4:1) to afford S34 (1.53 g, 62% overall yield) as a colorless dense oil. ¹H NMR (400 MHz, DMSO-d₆, 100 °C) δ = 10.34 (bs, 1H), 7.45 – 7.38 (m, 1H), 7.25-7.22 (m, 1H), 7.01 – 6.89 (m, 2H), 6.52 (bs, 1H), 4.02 (q, J = 7.2 Hz, 2H), 3.25 – 3.13 (m, 2H), 2.85 – 2.76 (m, 2H), 2.34 (s, 3H), 1.17 (t, J = 7.2 Hz, 3H). ¹³C NMR (101 MHz, DMSO-d₆, 100 °C) δ = 155.7, 135.0, 131.5, 128.1, 119.3, 117.5, 116.7, 109.8, 107.2, 58.9, 40.9, 24.1, 14.0, 10.5. IR (neat): 3398, 3318, 2979, 2931, 1623, 1517, 1461, 1436, 1383, 1337, 1300, 1171, 1138, 1107, 1077, 1032, 1010, 955, 873, 778, 671, 584, 565, 507 cm⁻¹; HRMS calculated m/z for C₁₄H₁₉N₂O₂⁺ [M+H]⁺: 247.1441, found (ESI) 247.1444.

Procedure for the preparation of S33

To a stirred solution of S34 (665 mg, 2.70 mmol, 1.0 equiv) in DMF (20 mL), NaH (w/w 60% in mineral oil, 119 mg, 2.97 mmol, 1.1 equiv) was added under nitrogen flow. The resulting mixture was stirred at 0 °C for 0.5 h, Then, benzyl bromide (353 μL, 2.97 mmol, 1.1 equiv) was added to the mixture dropwise. The resulting mixture was stirred at room temperature for 4 h. The reaction was quenched with water, extracted with ethyl acetate and dried over Na₂SO₄. Evaporation of the organic solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 8:1) to afford S33 (375 mg, 41% yield) as a light yellow sticky oil. ¹H NMR (400 MHz, DMSO-d₆, 100 °C) δ = 7.55 – 7.50 (m, 1H), 7.31 – 7.24 (m, 3H), 7.24 – 7.18 (m, 1H), 7.06 – 6.97 (m, 4H), 6.56 (s, 1H), 5.36 (s, 2H), 4.01 (q, J = 7.2 Hz, 2H), 3.28 – 3.16 (m, 2H), 2.90-2.87 (m, 2H), 2.32 (s, 3H), 1.16 (t, J = 7.2 Hz, 3H). ¹³C NMR (101 MHz, DMSO-d₆, 100
\( \delta = 155.7, 138.0, 135.9, 132.9, 127.9, 127.4, 126.3, 125.6, 119.8, 118.1, 117.0, 108.7, 108.1, 58.9, 45.5, 40.9, 24.4, 14.0, 9.2. \) IR (neat): 3352, 2978, 2929, 1689, 1612, 1536, 1495, 1468, 1452, 1417, 1336, 1287, 1250, 1204, 1177, 1139, 1090, 1035, 980, 924, 878, 776, 737, 694, 608, 561, 520 cm\(^{-1}\); HRMS calculated m/z for C\(_{21}\)H\(_{25}\)N\(_2\)O\(_2\) \([\text{M+H}]^+\): 337.1911, found (ESI) 337.1917.

**Procedure for the preparation of S37**

\[
\begin{align*}
\text{S36} & \xrightarrow{\text{DMF, 0 °C-rt}} \text{NaH} & \xrightarrow{\text{Bn-Br}} \text{S37}
\end{align*}
\]

To a stirred solution of S36\(^{[9]}\) (2.22 g, 7.20 mmol, 1.0 equiv) in DMF (50 mL), NaH (w/w 60% in mineral oil, 317 mg, 7.92 mmol, 1.1 equiv) was added under nitrogen flow. The resulting mixture was stirred at 0 °C for 0.5 h. Then, benzyl bromide (856 μL, 7.20 mmol, 1.0 equiv) was added to the mixture dropwise. The resulting mixture was stirred at room temperature for 10 h. The reaction was quenched with water, extracted with ethyl acetate, dried over Na\(_2\)SO\(_4\). The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 20:1 to 10:1) to afford S37 (1.30 g, 45% yield) as a light yellow sticky oil. \(^1\)H NMR (400 MHz, DMSO-\(d_6\), 100 °C) \( \delta = 7.54 – 7.48 \) (m, 1H), 7.45 – 7.08 (m, 9H), 7.06 – 6.95 (m, 4H), 6.80 (s, 1H), 5.36 (s, 2H), 5.05 (s, 2H), 3.31 – 3.21 (m, 2H), 2.92-2.89 (m, 2H), 2.30 (s, 3H). \(^1\)C NMR (101 MHz, DMSO-\(d_6\), 100 °C) \( \delta = 155.5, 137.9, 136.9, 135.9, 132.9, 127.9, 127.6, 127.4, 127.0, 126.9, 126.3, 125.6, 119.8, 118.1, 117.0, 108.7, 108.1, 64.7, 45.5, 41.0, 24.4, 9.2. \) IR (neat): 3380, 2942, 1693, 1532, 1496, 1468, 1453, 1336, 1286, 1242, 1179, 1135, 1002, 737, 697, 608, 555 cm\(^{-1}\); HRMS calculated m/z for C\(_{26}\)H\(_{27}\)N\(_2\)O\(_2\) \([\text{M+H}]^+\): 399.2067, found (ESI) 399.2068.
Procedure for the preparation of S43

\[
\begin{align*}
\text{To a stirred solution of indole-3-acetic acid (876 mg, 5.0 mmol, 1.0 equiv) in DCM (25 mL) was added 4-dimethylaminepyridine (30.5 mg, 0.25 mmol, 0.05 equiv), dicyclohexylcarbodiimide (1.135 g, 5.5 mmol, 1.1 equiv) and 2-(trimethylsilyl)ethan-1-ol (1.43 mL, 10 mmol, 2.0 equiv), sequentially. The resulting mixture was stirred at room temperature for 28 h. Then, the reaction mixture was filtered through a pad of celite. The obtained organic phase was washed with water and dried over Na}_2\text{SO}_4. The solvent was evaporated under reduced pressure and the residue purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 10:1) to afford 2-(trimethylsilyl)ethyl 2-(1H-indol-3-yl)acetate.}
\end{align*}
\]

To a stirred solution of 2-(trimethylsilyl)ethyl 2-(1H-indol-3-yl)acetate (1.19 g, 4.33 mmol, 1.0 equiv) in DMF (25 mL), NaH (w/w 60% in mineral oil, 190 mg, 4.76 mmol, 1.1 equiv) was added under nitrogen. The resulting mixture was stirred at 0 °C for 0.5 h. Then, benzyl bromide (540 μL, 4.54 mmol, 1.05 equiv) was added to the mixture dropwise. The resulting reaction mixture was stirred at room temperature for 4 h and subsequently quenched with water and extracted with ethyl acetate. The organic phase was dried over Na}_2\text{SO}_4, the solvent evaporated under the reduced pressure and finally the residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 50:1) to afford S43 (656 mg, 41% yield) as a colorless oil.

\[
\begin{align*}
{^1}\text{H NMR (400 MHz, Chloroform-d) } &\delta = 7.68 (d, J = 8.0 Hz, 1H), 7.36-7.27 (m, 4H), 7.26 – 7.11 (m, 5H), 5.32 (s, 2H), 4.31 – 4.19 (m, 2H), 3.80 (s, 2H), 1.06-1.02 (m, 2H), 0.06 (s, 9H). \n{^{13}}\text{C NMR (101 MHz, Chloroform-d) } &\delta = 172.3, 137.6, 136.7, 128.9, 128.1, 127.7, 127.2, 127.0, 122.0, 119.5, 119.3, 109.8, 107.9, 63.1, 50.1, 31.7, 17.5, -1.4. \n\text{IR (neat): } &2952, 1727, 1614, 1496, 1467, 1454, 1357, 1334, 1248, 1147, 1041, 1014, 963, 857, 834, 735, 695, 608, 551 cm}^{-1}; \text{HRMS calculated m/z for C}_{22}\text{H}_{28}\text{NO}_{2}\text{Si}^+ [M+H]^+: 366.1884, \text{found (ESI) 366.1878.}
\end{align*}
\]

Procedure for the preparation of S45

\[\text{[15][16][17]}\]
To a stirred solution of formaldehyde (37 wt% in water, 1.65 mL, 22 mmol, 1.1 equiv.) in 1,4-dioxane (100 mL) water (1.54 mL) and glacial acetic acid (20 mL) were added sequentially. The resulting solution was stirred at 0 °C for 5 minutes. Then, dimethylamine (40 wt% in water, 2.73 mL, 22 mmol, 1.1 equiv.) and 2-methyl-1H-indole (2.624, 20 mmol, 1.0 equiv.) were added to the mixture, sequentially. The mixture was stirred at 0°C for 2 h, and for further 5 hours at room temperature. Then, the reaction was treated with NaOH aqueous (16 g NaOH dissolved in 200 mL H₂O) at 0 °C. The resulting mixture was extracted with ethyl acetate, and the organic phase was washed with brine and dried over anhydrous Na₂SO₄. Evaporation of the solvent under the reduced pressure afforded a residue, which was used directly for the next step without further purification.[15]

Diethyl malonate (3.04 mL, 20 mmol, 1.0 equiv.) and ethyl propiolate (2.03 mL, 20 mmol, 1.0 equiv.) were added sequentially to a stirred solution of the above residue in THF (100 mL). The resulting solution was stirred at room temperature for 12 h. Then, the reaction was quenched with water, extracted with ethyl acetate and the organic phase dried over anhydrous Na₂SO₄. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 8:1) to afford diethyl 2-((2-methyl-1H-indol-3-yl)methyl)malonate.[16]

NaH (w/w 60% in mineral oil, 120 mg, 3.0 mmol, 1.0 equiv) was added at 0 °C under nitrogen flow to a stirred solution of diethyl 2-((2-methyl-1H-indol-3-yl)methyl)malonate (910 mg, 3.0 mmol, 1.0 equiv) in THF (15 mL).[17] The resulting mixture was stirred at that temperature for 0.5 h. Then, 1-bromo-3-methylbut-2-ene (347 μL, 3.0 mmol, 1.0 equiv) was added to the mixture dropwise and the resulting solution was stirred at room temperature for 2 h. Then, it was quenched with saturated NH₄Cl (aq) and extracted with ethyl acetate. The organic phase was finally dried over anhydrous Na₂SO₄ and the solvent evaporated under reduced pressure. Compound S45 (931 mg, 84% yield) was obtained as a light yellow sticky
oil after purification by column chromatography on silica gel (eluents: hexane/ethyl acetate = 8:1 to 4:1).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ = 7.84 (bs, 1H), 7.44 (d, $J$ = 7.6, 1H), 7.19-7.16 (m, 1H), 7.07-6.98 (m, 2H), 5.27 – 5.19 (m, 1H), 4.17 – 4.00 (m, 4H), 3.40 (s, 2H), 2.59 (d, $J$ = 6.8 Hz, 2H), 2.30 (s, 3H), 1.74 (d, $J$ = 1.6 Hz, 3H), 1.57 (s, 3H), 1.17 (t, $J$ = 7.2 Hz, 6H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ = 172.0, 135.3, 135.2, 133.4, 129.6, 121.0, 119.1, 118.7, 118.7, 110.1, 106.4, 61.2, 59.1, 31.6, 27.9, 26.2, 18.3, 14.0, 12.2. IR (neat): 3350, 2979, 1750, 1713, 1493, 1462, 1444, 1366, 1233, 1297, 1248, 1211, 1175, 1117, 1096, 1071, 1053, 1026, 858, 816, 740, 665, 624, 567, 542, 517 cm$^{-1}$; HRMS calculated m/z for C$_{22}$H$_{30}$NO$_4$ $^{[M+H]^+}$: 372.2169, found (ESI) 372.2164.

Procedure for the preparation of S46

Diethyl malonate ($911 \mu$L, 6.0 mmol, 1.0 equiv.) and ethyl propiolate ($669 \mu$L, 6.6 mmol, 1.1 equiv.), were added sequentially to a stirred solution of 1-(5-methoxy-2-methyl-1H-indol-3-yl)-$N,N$-dimethylmethanamine (1.44 g, 6.6 mmol, 1.1 equiv.) in THF (30 mL). The resulting solution was stirred at room temperature for 18 h. Then, the reaction was quenched with water, extracted with ethyl acetate, washed with brine, and the organic phase was dried over anhydrous Na$_2$SO$_4$. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (hexane/ethyl acetate = 4:1) to afford diethyl 2-((5-methoxy-2-methyl-1H-indol-3-yl)methyl)malonate.$^{[16]}$

NaH (w/w 60% in mineral oil, 198 mg, 4.94 mmol, 1.1 equiv) was added to a stirred solution of diethyl 2-((5-methoxy-2-methyl-1H-indol-3-yl)methyl)malonate (1.50 g, 4.49 mmol, 1.0 equiv) in THF (15 mL) at 0 °C under nitrogen. The resulting mixture was stirred at 0 °C for 0.5 h; then, allyl bromide (427 μL, 4.94 mmol, 1.1 equiv) was added to the mixture dropwise and the resulting mixture stirred at room temperature for 3 h. Then, the reaction was quenched with water, extracted with ethyl acetate and the organic phase was dried over anhydrous
Na₂SO₄. Evaporation of the solvent under the reduced pressure let a residue, which was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 5:1) to afford S₄₆ (1.19 g, 71% yield) as a light yellow sticky oil.¹H NMR (400 MHz, Chloroform-d) δ = 7.77 (bs, 1H), 7.07 (d, J = 8.4 Hz, 1H), 6.96 (d, J = 2.4 Hz, 1H), 6.72 (dd, J = 8.4, 2.4 Hz, 1H), 5.98-5.88 (m, 1H), 5.20 – 5.04 (m, 2H), 4.21 – 3.98 (m, 4H), 3.82 (s, 3H), 3.37 (s, 2H), 2.66 (d, J = 7.2 Hz, 2H), 2.30 (s, 3H), 1.16 (s, 3H). ¹³C NMR (101 MHz, Chloroform-d) δ = 171.7, 153.9, 134.3, 133.5, 130.4, 130.0, 118.7, 110.8, 106.2, 101.5, 61.3, 59.4, 56.1, 37.9, 28.5, 14.1, 12.5. IR (neat): 3360, 2936, 1747, 1716, 1590, 1487, 1449, 1365, 1303, 1254, 1200, 1093, 1045, 1010, 967, 930, 891, 867, 843, 829, 792, 775, 745, 690, 670, 626, 583, 541 cm⁻¹; HRMS calculated m/z for C₂₁H₂₈NO₅⁺ [M+H]+: 374.1962, found (ESI) 374.1963.

Procedure for the preparation of S₄₇

Diethyl malonate (1.52 mL, 10 mmol, 1.0 equiv.) and ethyl propiolate (1.114 mL, 11 mmol, 1.1 equiv.) were subsequently added to a stirred solution of N-((1H-indol-3-yl)methyl)-N-ethylethanamine (2.225 g, 11 mmol, 1.1 equiv.) in THF (30 mL). The resulting solution was stirred at room temperature for 16 h, and then the reaction was quenched with water, extracted with ethyl acetate and the organic phase dried over anhydrous Na₂SO₄. The organic solvent was evaporated under reduced pressure and the residue obtained was used directly for the next step without further purification.

NaH (w/w 60% in mineral oil, 400 mg, 10.0 mmol, 1.0 equiv) was added at 0 °C under nitrogen to a stirred solution of the above residue in THF (50 mL). The resulting mixture was stirred at 0 °C for 0.5 h and then, allyl bromide (865 μL, 10.0 mmol, 1.0 equiv) was added to the mixture dropwise. The solution thus obtained was stirred at room temperature for 1 h and then quenched with water and extracted with ethyl acetate. The organic phase was subsequently dried over anhydrous Na₂SO₄ and the solvent evaporated under the reduced pressure. The residue obtained was purified by column chromatography on silica gel (eluent:
hexane/ethyl acetate = 10:1) to afford S47 (976 mg, 30% yield) as a light yellow sticky oil. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ = 8.10 (bs, 1H), 7.58-7.55 (m, 1H), 7.32-7.29 (m, 1H), 7.17-7.13 (m, 1H), 7.10-7.06 (m, 1H), 6.98 (d, $J$ = 2.8 Hz, 1H), 5.92 – 5.72 (m, 1H), 5.17 – 5.13 (m, 1H), 5.13 – 5.07 (m, 1H), 4.20 – 4.12 (m, 2H), 4.12 – 4.03 (m, 2H), 3.42 (d, $J$ = 0.8 Hz, 2H), 2.68 (dt, $J$ = 7.6, 1.6 Hz, 2H), 1.19 (t, $J$ = 7.2 Hz, 6H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ = 171.4, 135.9, 133.1, 128.3, 123.3, 122.0, 119.4, 119.1, 119.0, 111.2, 110.2, 61.4, 58.9, 37.4, 28.0, 14.1. IR (neat): 3347, 2976, 1752, 1714, 1641, 1459, 1444, 1361, 1290, 1245, 1193, 1151, 1097, 1066, 1039, 1017, 916, 860, 803, 745, 656, 614, 578, 563, 545 cm$^{-1}$; HRMS calculated m/z for C_{19}H_{24}NO_{4}^+ [M+H]^+: 330.1700, found (ESI) 330.1701.

Procedure for the preparation of S50

NaH (w/w 60% in mineral oil, 120 mg, 3.0 mmol, 1.0 equiv) was added at 0 °C under nitrogen to a stirred solution of diethyl 2-((2-methyl-1H-indol-3-yl)methyl)malonate (910 mg, 3.0 mmol, 1.0 equiv) in THF (15 mL). The resulting mixture was stirred at 0 °C for 0.5 h. and then allyl bromide (260 μL, 3.0 mmol, 1.0 equiv) was added dropwise and stirred at room temperature for two additional hours. Then, the reaction was quenched with saturated NH$_4$Cl solution, extracted with ethyl acetate and the organic phase was dried over anhydrous Na$_2$SO$_4$. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 10:1 to 5:1) to afford S50 (852 mg, 83% yield) as a light yellow sticky oil. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ = 7.82 (bs, 1H), 7.46 (d, $J$ = 7.6, 1H), 7.22-7.19 (m, 1H), 7.12 – 6.98 (m, 2H), 5.97-5.87 (m, 1H), 5.20 – 5.01 (m, 2H), 4.25 – 3.93 (m, 4H), 3.40 (s, 2H), 2.66-2.64 (m, 2H), 2.34 (s, 3H), 1.17 (t, $J$ = 7.2 Hz, 6H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ = 171.6, 135.3, 133.5, 133.4, 129.6, 121.1, 119.2, 118.7, 118.7, 110.1, 110.1, 106.4, 61.3, 59.4, 38.0, 28.4, 14.1, 12.5. IR (neat): 3372, 2981, 1743, 1713, 1491, 1462, 1440, 1392, 1366, 1297, 1198, 1158, 1120, 1096, 1062,
1046, 1020, 946, 862, 690, 667, 611, 579, 564, 515 cm\(^{-1}\); HRMS calculated m/z for C\(_{20}\)H\(_{26}\)NO\(_4\)^+ [M+H]^+: 344.1856, found (ESI) 344.1856.

**Procedure for the preparation of S51**

![Chemical structure](image)

To a stirred solution of formaldehyde (37 wt% in water, 825 μL, 11 mmol, 1.1 equiv.) in 1,4-dioxane (50 mL) water (770 μL) and glacial acetic acid (10 mL) were added sequentially. The resulting solution was stirred at 0 °C for 5 minutes. Then, dimethylamine (40 wt% in water, 1.365 mL, 11 mmol, 1.1 equiv.) and 2,5-dimethyl-1H-indole (1.452, 10 mmol, 1.0 equiv.) were added and the mixture stirred 2 h at 0°C and 10 additional hours at room temperature. Then, the reaction was treated with aqueous NaOH solution (8 g NaOH dissolved in 100 mL H\(_2\)O) at 0 °C and the resulting mixture extracted with ethyl acetate and washed with brine. The organic solvents were dried over anhydrous Na\(_2\)SO\(_4\) and evaporated under reduced pressure. The residue thus obtained was used directly for the next step without further purification.\(^{15}\)

Diethyl malonate (1.52 mL, 10 mmol, 1.0 equiv.) and ethyl propiolate (1.013 mL, 10 mmol, 1.0 equiv.), were sequentially added to a stirred solution of the above prepared residue in THF (30 mL). The resulting solution was stirred at room temperature for 12 h. Then, the reaction was quenched with water, extracted with ethyl acetate and the organic phase dried over anhydrous Na\(_2\)SO\(_4\). Evaporation of the solvents under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 8:1 to 4:1) to afford diethyl 2-((2,5-dimethyl-1H-indol-3-yl)methyl)malonate.\(^{16}\)

Finally, NaH (w/w 60% in mineral oil, 268 mg, 6.7 mmol, 1.0 equiv) was added at 0 °C to a stirred solution of diethyl 2-((2,5-dimethyl-1H-indol-3-yl)methyl)malonate (2.127 g, 6.7 mmol, 1.0 equiv) in THF (30 mL).\(^{17}\) The resulting mixture was stirred at 0 °C for 0.5 h. and then allyl bromide (580 μL, 6.7 mmol, 1.0 equiv) was added to the mixture dropwise. The resulting mixture was stirred at room temperature for 2 h. and then the reaction was quenched
with saturated NH₄Cl (aq), extracted with ethyl acetate, and the organic phase dried over anhydrous Na₂SO₄. Evaporation of the solvents in vacuo afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 10:1 to 5:1) to afford S51 (1.378 g, 58% yield) as a light yellow sticky oil. ¹H NMR (400 MHz, Chloroform-d) δ = 7.78 (bs, 1H), 7.22-7.217 (m, 1H), 7.05 (d, J = 8.0 Hz, 1H), 6.88 (dd, J = 8.0, 1.6 Hz, 1H), 5.96-5.86 (m, 1H), 5.19 – 5.05 (m, 2H), 4.20 – 4.01 (m, 4H), 3.37 (s, 2H), 2.65-2.63 (m, 2H), 2.40 (s, 3H), 2.27 (s, 3H), 1.19 (t, J = 7.2 Hz, 6H). ¹³C NMR (101 MHz, Chloroform-d) δ = 171.6, 133.6, 133.6, 129.7, 128.1, 122.5, 118.6, 118.4, 109.8, 105.7, 61.2, 59.3, 37.8, 28.4, 21.6, 14.1, 12.5. IR (neat): 3346, 2978, 1746, 1714, 1590, 1440, 1366, 1299, 1200, 1148, 1093, 1060, 1042, 1023, 928, 861, 790, 754, 694, 670, 639, 604, 558, 517 cm⁻¹; HRMS calculated m/z for C₂₁H₂₈NO₄⁺ [M+H]⁺: 358.2013, found (ESI) 358.2018.

4. Direct metal-free cyanation of nucleophiles using 9

**Procedure for the preparation of 11**

To a stirred solution of 4-(tert-butyl)aniline S1 (31.9 μL, 0.2 mmol, 1.0 equiv) in DCM (2 mL) was added K₃PO₄ (42.5 mg, 0.2 mmol, 1.0 equiv) and 9 (107.8 mg, 0.3 mmol, 1.5 equiv) at 0 °C under nitrogen flow, sequentially. The resulting mixture was stirred at 0 °C for 2 h. Then, the reaction was quenched with water, extracted with DCM and the organic phase was dried over anhydrous Na₂SO₄. Evaporation of the solvent under the reduced pressure produced a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) to afford 11 (25.2 mg, 72% yield) as a colorless oil. ¹H NMR (400 MHz, Chloroform-d) δ = 7.35 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 8.4 Hz, 2H), 6.61 (bs, 1H), 1.29 (s, 9H). ¹³C NMR (101 MHz, Chloroform-d) δ = 146.8, 134.7, 126.7, 115.3, 111.9, 34.4, 31.5. The spectroscopic data are in agreement with those previously reported.[18]
Procedure for the preparation of 12

![Image of 12](image)

To a stirred solution of [1,1'-biphenyl]-2-amine S2 (33.8 mg, 0.2 mmol, 1.0 equiv) in DCM (2 mL), K3PO4 (42.5 mg, 0.2 mmol, 1.0 equiv) and 9 (107.8 mg, 0.3 mmol, 1.5 equiv) were added sequentially at -10 °C. The resulting mixture was stirred at -10 °C for 4 h. and then the reaction was quenched with brine, extracted with DCM, and the organic phase dried over anhydrous Na2SO4. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 10:1) to afford 12 (37.7 mg, 97% yield) as a white solid. 1H NMR (300 MHz, Chloroform-d) δ = 7.54 – 7.45 (m, 2H), 7.45 – 7.26 (m, 5H), 7.24-7.21 (m, 1H), 7.18 – 7.09 (m, 1H), 5.96 (bs, 1H). 13C NMR (75 MHz, Chloroform-d) δ = 136.7, 134.2, 130.7, 129.6, 129.3, 129.2, 129.1, 128.5, 123.7, 115.2, 110.7. The spectroscopic data are in agreement with those previously reported.[19]

General procedure for the preparation of 13-21

Cs2CO3 (65.2 mg, 0.2 mmol, 1.0 equiv) and 9 (107.8 mg, 0.3 mmol, 1.5 equiv) were added sequentially at room temperature to a stirred solution of the desired aniline (0.2 mmol, 1.0 equiv) in DCM (2 mL). The resulting mixture was stirred at room temperature for 1.5-8 hours. Then, the reaction was quenched with brine, extracted with DCM, and the organic phase dried over anhydrous Na2SO4. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel.

![Image of 13](image)

A mixture of diphenylamine S3 (0.2 mmol, 33.8 mg), Cs2CO3 (0.02 mmol, 65.2 mg) and 9 (0.3 mmol, 107.8 mg) in DCM (2 mL) was stirred at room temperature for 6 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 9:1) afforded 13 in 98%
yield (38.0 mg) as a colorless oil. \(^1\)H NMR (300 MHz, Chloroform-\(d\)) \(\delta = 7.46 - 7.36\) (m, 4H), 7.33 – 7.18 (m, 6H). \(^1\)C NMR (75 MHz, Chloroform-\(d\)) \(\delta = 139.2, 130.0, 126.4, 121.4, 112.7\). The spectroscopic data are in agreement with those previously reported.\(^{[20]}\)

A mixture of \(N\)-methylaniline S4 (0.2 mmol, 21.7 \(\mu\)L), Cs\(_2\)CO\(_3\) (0.02 mmol, 65.2 mg) and 9 (0.3 mmol, 107.8 mg) in DCM (2 mL) was stirred at room temperature for 1.5 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded 14 in 90% yield (23.7 mg) as a colorless oil. \(^1\)H NMR (300 MHz, Chloroform-\(d\)) \(\delta = 7.45 - 7.31\) (m, 2H), 7.17 – 7.02 (m, 3H), 3.33 (s, 3H). \(^1\)C NMR (75 MHz, Chloroform-\(d\)) \(\delta = 140.4, 129.7, 123.4, 114.9, 114.2, 36.9\). The spectroscopic data are in agreement with those previously reported.\(^{[21]}\)

A mixture of \(N\)-benzylaniline S5 (0.2 mmol, 36.7 mg), Cs\(_2\)CO\(_3\) (0.02 mmol, 65.2 mg) and 9 (0.3 mmol, 107.8 mg) in DCM (2 mL) was stirred at room temperature for 3 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 9:1) afforded 15 in 91% yield (37.7 mg) as a colorless oil. \(^1\)H NMR (300 MHz, Chloroform-\(d\)) \(\delta = 7.42 - 7.26\) (m, 7H), 7.16 – 7.02 (m, 3H), 4.78 (s, 2H). \(^1\)C NMR (75 MHz, Chloroform-\(d\)) \(\delta = 139.8, 134.4, 129.7, 129.1, 128.6, 127.4, 123.8, 116.1, 114.0, 53.8\). The spectroscopic data are in agreement with those previously reported.\(^{[22]}\)

A mixture of indoline S6 (0.2 mmol, 22.4 \(\mu\)L), Cs\(_2\)CO\(_3\) (0.02 mmol, 65.2 mg) and 9 (0.3 mmol, 107.8 mg) in DCM (2 mL) was stirred at room temperature for 2 h. Column
chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded 16 in 95% yield (27.3 mg) as a colorless oil. $^1$H NMR (300 MHz, Chloroform-$d$) $\delta = 7.25 - 7.13$ (m, 2H), 7.04 - 6.92 (m, 2H), 4.05 (t, $J = 8.4$ Hz, 2H), 3.20 (t, $J = 8.4$ Hz, 2H). $^{13}$C NMR (75 MHz, Chloroform-$d$) $\delta = 142.3$, 128.2, 127.9, 125.3, 123.3, 112.6, 110.5, 50.8, 28.6. IR (neat): 3052, 2919, 2858, 2209, 1607, 1595, 1486, 1458, 1441, 1379, 1328, 1278, 1197, 1155, 1083, 1029, 935, 866, 825, 751, 602 cm$^{-1}$; HRMS calculated m/z for C$_9$H$_9$N$_2^+$ [M+H]$^+$: 145.0760, found (ESI) 145.0766.

A mixture of 1,2,3,4-tetrahydroquinoline S7 (0.2 mmol, 26.6 mg), Cs$_2$CO$_3$ (0.02 mmol, 65.2 mg) and 9 (0.3 mmol, 107.8 mg) in DCM (2 mL) was stirred at room temperature for 3 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded 17 in 92% yield (29.0 mg) as a colorless oil. $^1$H NMR (300 MHz, Chloroform-$d$) $\delta = 7.24 - 7.13$ (m, 2H), 7.09-7.05 (m, 1H), 7.01-6.93 (m, 1H), 3.81 – 3.69 (m, 2H), 2.87 – 2.71 (m, 2H), 2.10 – 1.94 (m, 2H). $^{13}$C NMR (75 MHz, Chloroform-$d$) $\delta = 135.6$, 129.8, 127.7, 124.0, 122.9, 115.7, 113.6, 48.6, 26.3, 22.0. IR (neat): 2938, 2212, 1605, 1587, 1495, 1455, 1385, 1347, 1290, 1251, 1229, 1198, 1183, 1167, 1113, 1059, 1017, 937, 909, 876, 848, 794, 747, 713, 690, 612, 532, 504 cm$^{-1}$; HRMS calculated m/z for C$_{10}$H$_{11}$N$_2^+$ [M+H]$^+$: 159.0917, found (ESI) 159.0918.

A mixture of 9,10-dihydroacridine S8 (0.2 mmol, 36.2 mg), Cs$_2$CO$_3$ (0.02 mmol, 65.2 mg) and 9 (0.3 mmol, 107.8 mg) in DCM (2 mL) was stirred at room temperature for 3 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 19:1) afforded 18 in 88% yield (36.4 mg) as a colorless oil. $^1$H NMR (300 MHz, Chloroform-$d$) $\delta = 7.41-7.37$ (m, 2H), 7.32-7.26 (m, 2H), 7.24 – 7.08 (m, 4H), 4.04 (s, 2H). $^{13}$C NMR (75 MHz,
Chloroform-$d$) $\delta = 134.6, 129.0, 128.9, 125.3, 123.3, 115.8, 109.4, 30.6$. IR (neat): 2920, 2218, 1721, 1653, 1604, 1581, 1489, 1455, 1426, 1344, 1316, 1298, 1255, 1196, 1168, 1150, 1097, 1045, 958, 933, 922, 857, 800, 743, 687, 667, 636 cm$^{-1}$; HRMS calculated m/z for C$_{14}$H$_{11}$N$_2^+$ [M+H]$^+$: 207.0917, found (ESI) 207.0917.

A mixture of 10$H$-phenoxazine S9 (0.2 mmol, 36.6 mg), Cs$_2$CO$_3$ (0.02 mmol, 65.2 mg) and 9 (0.3 mmol, 107.8 mg) in DCM (2 mL) was stirred at room temperature for 6 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 19:1) afforded 19 in 71% yield (29.6 mg) as a white solid. $^1$H NMR (300 MHz, Chloroform-$d$) $\delta = 7.12 – 6.94$ (m, 6H), 6.91 – 6.80 (m, 2H). $^{13}$C NMR (75 MHz, Chloroform-$d$) $\delta = 143.5, 126.3, 124.3, 123.9, 117.0, 115.7, 107.2$. IR (neat): 2227, 1594, 1488, 1321, 1293, 1273, 1204, 1152, 1137, 1095, 1039, 927, 867, 812, 746, 689, 634 cm$^{-1}$; HRMS calculated m/z for C$_{13}$H$_8$N$_2$ONa$^+$ [M+Na]$^+$: 231.0529, found (ESI) 231.0532.

A mixture of 10,11-dihydro-5$H$-dibenzo[b,f]azepine S10 (0.2 mmol, 39.1 mg), Cs$_2$CO$_3$ (0.02 mmol, 65.2 mg) and 9 (0.3 mmol, 107.8 mg) in DCM (2 mL) was stirred at room temperature for 8 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 9:1) afforded 20 in 94% yield (41.2 mg) as a colorless oil. $^1$H NMR (300 MHz, Chloroform-$d$) $\delta = 7.56-7.53$ (m, 2H), 7.30 – 7.10 (m, 6H), 3.16 (s, 4H). $^{13}$C NMR (75 MHz, Chloroform-$d$) $\delta = 139.5, 134.1, 130.7, 127.5, 127.0, 122.4, 114.2, 31.5$. IR (neat): 2908, 2202, 1578, 1488, 1448, 1427, 1332, 1286, 1251, 1219, 1177, 1135, 1110, 964, 941, 872, 854, 768,751, 742, 708, 680, 640, 596, 563, 548, 515 cm$^{-1}$; HRMS calculated m/z for C$_{15}$H$_{13}$N$_2^+$ [M+H]$^+$: 221.1073, found (ESI) 221.1075.
A mixture of 5H-dibenzo[b,f]azepine S11 (0.2 mmol, 38.6 mg), Cs₂CO₃ (0.02 mmol, 65.2 mg) and 9 (0.3 mmol, 107.8 mg) in DCM (2 mL) was stirred at room temperature for 6 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 9:1) afforded 21 in 99% yield (43.2 mg) as a white solid. ¹H NMR (300 MHz, Chloroform-d) δ = 7.49-7.46 (m, 2H), 7.41 – 7.32 (m, 2H), 7.28 – 7.14 (m, 4H), 6.74 (s, 2H). ¹³C NMR (75 MHz, Chloroform-d) δ = 140.8, 132.4, 131.1, 130.2, 130.1, 127.6, 122.9, 114.6. IR (neat): 3022, 2219, 1600, 1576, 1489, 1456, 1435, 1288, 1248, 1199, 1161, 1137, 1115, 941, 922, 803, 784, 754, 701, 681, 635, 556, 513 cm⁻¹; HRMS calculated m/z for C₁₅H₁₁N₂⁺ [M+H]⁺: 219.0917, found (ESI) 219.0918.

**Procedure for the preparation of 22**

Compound 9 (107.8 mg, 0.3 mmol, 1.5 equiv) was added to a stirred solution of 9H-carbazole S12 (33.4 mg, 0.2 mmol, 1.0 equiv) in DCE (2 mL) at room temperature. The resulting mixture was stirred at 50 °C for 14 h. and then the reaction was quenched with brine, extracted with DCM and the organic phase was dried over anhydrous Na₂SO₄. Evaporation of the solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) to afford 22 (26.0 mg, 68% yield) as a white solid. ¹H NMR (300 MHz, Chloroform-d) δ = 7.98-7.95 (m, 2H), 7.64-7.61 (m, 2H), 7.55-7.50 (m, 2H), 7.44-7.38 (m, 2H). ¹³C NMR (75 MHz, Chloroform-d) δ = 138.1, 127.8, 124.4, 124.3, 121.0, 111.7, 107.0. IR (neat): 3306, 2236, 1904, 1603, 1490, 1476, 1444, 1341, 1304, 1260, 1217, 1152, 1110, 1023, 935, 910, 856, 798, 741, 716, 650, 611, 551, 527 cm⁻¹; HRMS calculated m/z for C₁₃H₈N₂Na⁺ [M+Na]⁺: 215.0580, found (ESI) 215.0582.
Procedure for the preparation of 23

Compound 9 (107.8 mg, 0.3 mmol, 1.5 equiv) was added at -50 °C to a stirred solution of 1-phenylpiperazine S13 (30.6 μL, 0.2 mmol, 1.0 equiv) in DCM (2 mL). The resulting mixture was stirred at -50 °C for 6 h. Then, the reaction was quenched with brine, extracted with DCM, and the organic phase dried over anhydrous Na₂SO₄. Evaporation of the solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) to afford 23 (15.8 mg, 42% yield) as a colorless oil. ¹H NMR (300 MHz, Chloroform-d) δ = 7.36 – 7.22 (m, 2H), 6.99 – 6.86 (m, 3H), 3.44 – 3.34 (m, 4H), 3.29 – 3.18 (m, 4H). ¹³C NMR (75 MHz, Chloroform-d) δ = 150.9, 129.5, 121.3, 117.6, 117.3, 49.2, 49.0. The spectroscopic data are in agreement with those previously reported.²³

Procedure for the preparation of 24

Compound 9 (107.8 mg, 0.3 mmol, 1.5 equiv) was added at -10 °C under nitrogen to a stirred solution of naphthalene-1-thiol S14 (27.9 μL, 0.2 mmol, 1.0 equiv) in DCM (2 mL). The resulting mixture was stirred at -10 °C for 0.5 h. and then the reaction was quenched with brine, extracted with DCM, and the organic phase dried over anhydrous Na₂SO₄. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) to afford 24 (25.2 mg, 68% yield) as a colorless oil. ¹H NMR (300 MHz, Chloroform-d) δ = 8.22 (d, J = 8.7 Hz, 1H), 7.99 – 7.86 (m, 3H), 7.71-7.65 (m, 1H), 7.62-7.57 (m, 1H), 7.51-7.46 (m, 1H). ¹³C NMR (75 MHz, Chloroform-d) δ = 134.5, 132.5, 132.3, 131.7, 129.1, 128.3, 127.3, 126.0, 124.3, 120.9, 110.8. The spectroscopic data are in agreement with those previously reported.²⁴
Procedure for the preparation of 25

![Image of compound 25]

Compound 9 (107.8 mg, 0.3 mmol, 1.5 equiv) was added at -10 °C to a stirred solution of 2-bromobenzenethiol S15 (23.5 μL, 0.2 mmol, 1.0 equiv) in DCM (2 mL). The resulting mixture was stirred at -10 °C for 2.5 h. Then, the reaction was quenched with brine, extracted with DCM and the organic phase dried over anhydrous Na₂SO₄. Evaporation of the organic solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 50:1) to afford 25 (26.1 mg, 61% yield) as a colorless oil. ¹H NMR (300 MHz, Chloroform-d) δ = 7.73-7.70 (m, 1H), 7.63-7.60 (m, 1H), 7.47-7.41 (m, 1H), 7.31 – 7.21 (m, 1H). ¹³C NMR (75 MHz, Chloroform-d) δ = 133.7, 130.2, 129.6, 129.2, 127.3, 121.9, 109.7. The spectroscopic data is in agreement with that previously reported.[25]

Procedure for the preparation of 26

![Image of compound 26]

Compound 9 (107.8 mg, 0.3 mmol, 1.5 equiv) was added at -20 °C to a stirred solution of 2,4,6-trimethylbenzenethiol S16 (29.7 μL, 0.2 mmol, 1.0 equiv) in DCM (2 mL). The resulting mixture was stirred at -20 °C for 1 h. Then, the reaction was quenched with brine, extracted with DCM and the organic phase dried over anhydrous Na₂SO₄. Evaporation of the solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 50:1) to afford 26 (29.8 mg, 84% yield) as a colorless oil. ¹H NMR (300 MHz, Chloroform-d) δ = 7.00 (s, 2H), 2.55 (s, 6H), 2.29 (s, 3H). ¹³C NMR (75 MHz, Chloroform-d) δ = 142.8, 141.6, 130.2, 119.2, 111.0, 22.0, 21.2. The spectroscopic data are in agreement with those previously reported.[26]

Procedure for the preparation of 27
Compound 9 (107.8 mg, 0.3 mmol, 1.5 equiv) was added to a stirred solution of 3,4-dimethoxybenzenethiol S17 (29.0 μL, 0.2 mmol, 1.0 equiv) in DCM (2 mL) at -20 °C under nitrogen. The resulting mixture was stirred at -20 °C for 0.5 h. Then, the reaction was quenched with brine, extracted with DCM and the organic phase dried over anhydrous Na2SO4. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 1:4) to afford 27 (23.8 mg, 61% yield) as a colorless oil. 1H NMR (300 MHz, Chloroform-d) δ = 7.15 (dd, J = 8.4, 2.1 Hz, 1H), 7.05 (d, J = 2.1 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H). 13C NMR (75 MHz, Chloroform-d) δ = 151.0, 150.2, 125.4, 114.6, 114.0, 112.3, 111.6, 56.3, 56.2. The spectroscopic data are in agreement with those previously reported.[24]

Procedure for the preparation of 28

Compound 9 (107.8 mg, 0.3 mmol, 1.5 equiv) was added to a stirred suspension of (4-methoxyphenyl)methanethiol S18 (27.5 μL, 0.2 mmol, 1.0 equiv) and Cs2CO3 (65.2 mg, 0.2 mmol, 1.0 equiv) in DCM (2 mL) at -50 °C. The resulting mixture was stirred at -50 °C for 5 h. Then, the reaction was quenched with brine, extracted with DCM and the organic phase dried over anhydrous Na2SO4. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 10:1) to afford 28 (25.3 mg, 71% yield) as a colorless oil. 1H NMR (300 MHz, Chloroform-d) δ = 7.28 (d, J = 8.7 Hz, 2H), 6.90 (d, J = 8.7 Hz, 2H), 4.14 (s, 2H), 3.81 (s, 3H). 13C NMR (75 MHz, Chloroform-d) δ = 160.1, 130.5, 126.3, 114.6, 114.0, 112.3, 55.4, 38.4. The spectroscopic data are in agreement with those previously reported.[24]

Procedure for the preparation of 29
Compound 9 (71.9 mg, 0.2 mmol, 1.0 equiv) was added to a stirred solution of trimethyl(1-phenylvinyl)oxy)silane S19 (61.5 μL, 0.3 mmol, 1.5 equiv) in DCM (2 mL) at room temperature. The resulting mixture was stirred at room temperature for 15 minutes. Then, the reaction was quenched with brine, extracted with DCM and the organic phase dried over anhydrous Na₂SO₄. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 5:1) to afford 29 (27.4 mg, 94% yield) as a light yellow solid. ¹H NMR (300 MHz, Chloroform-d) δ = 7.98 – 7.87 (m, 2H), 7.73 – 7.60 (m, 1H), 7.59 – 7.46 (m, 2H), 4.12 (s, 2H).

¹³C NMR (75 MHz, Chloroform-d) δ 187.3, 134.8, 134.3, 129.2, 128.5, 114.0, 29.5. The spectroscopic data are in agreement with those previously reported.[27]

**Procedure for the preparation of 30**

![Image](attachment:image.png)

Compound 9 (71.9 mg, 0.2 mmol, 1.0 equiv) was added to a stirred solution of (cyclohex-1-en-1-yloxy)trimethylsilane 20 (58.4 μL, 0.3 mmol, 1.5 equiv) in DCM (2 mL) at room temperature. The resulting mixture was stirred for 10 minutes. Then, the reaction was quenched with brine, extracted with DCM, and the organic phase dried over anhydrous Na₂SO₄. Because 30 is volatile on high vacuum line, the solvent was evaporated under the reduced pressure and then a ¹H NMR analysis of the obtained mixture using CH₂Br₂ as internal standard was conducted, which indicated that the desired product 30 had been obtained in 92% NMR yield.

![Image](attachment:image.png)

To a stirred solution of the above recovered NMR sample in MeOH (3 mL), 4-methylbenzenesulfonohydrazide (55.9 mg, 0.3 mmol, 1.5 equiv.) was added and the
resulting solution stirred at 60 °C for 18 h. Then, the reaction was quenched with brine, extracted with DCM and the organic phase dried over anhydrous Na₂SO₄. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 1:1) to afford a white solid (26.0 mg, 0.0892 mmol, 45% overall yield). ¹H NMR (300 MHz, Chloroform-d) δ = 7.95 – 7.76 (m, 2H), 7.34 – 7.27 (m, 2H), 4.66 (bs, 2H), 2.58 – 2.45 (m, 2H), 2.41 (s, 3H), 2.27 – 2.12 (m, 2H), 1.70-1.65 (m, 4H). ¹³C NMR (75 MHz, Chloroform-d) δ = 156.4, 145.1, 144.7, 135.2, 129.9, 127.8, 99.2, 24.1, 22.8, 22.7, 21.8, 19.3. IR (neat): 3457, 3296, 2935, 2857, 1625, 1596, 1476, 1425, 1357, 1309, 1259, 1223, 1188, 1173, 1143, 1130, 1085, 1045, 956, 931, 856, 812, 730, 701, 687, 665, 614, 590, 542 cm⁻¹; HRMS calculated m/z for C₁₄H₁₈N₃O₂S⁺ [M+H]⁺: 292.1114, found (ESI) 292.1116.

**Procedure for the preparation of 31**

![Chemical structure of 31](image)

Compound 9 (107.8 mg, 0.3 mmol, 1.5 equiv) dissolved in CH₃CN (0.7 mL) was added to a stirred solution of ethene-1,1-diphenylethylene S₂₁ (36.1 mg, 0.2 mmol, 1.0 equiv) in DCE (1.4 mL) at room temperature. The resulting mixture was stirred at room temperature for 21 h. Then, the reaction was quenched with brine, extracted with DCM and the organic phase dried over anhydrous Na₂SO₄. Evaporation of the solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) to afford 31 (30.5 mg, 74% yield) as a colorless oil. ¹H NMR (300 MHz, Chloroform-d) δ = 7.48 – 7.33 (m, 8H), 7.32 – 7.26 (m, 2H), 5.73 (s, 1H). ¹³C NMR (75 MHz, Chloroform-d) δ = 163.2, 139.0, 137.2, 130.5, 130.1, 129.7, 128.8, 128.6, 118.0, 95.0. The spectroscopic data is in agreement with that previously reported.[28]

**Procedure for the preparation of 32**

![Chemical structure of 32](image)
Compound 9 (107.8 mg, 0.3 mmol, 1.5 equiv) was added to a stirred suspension of 1-phenyl-1\textit{H}-pyrrole S22 (28.6 mg, 0.2 mmol, 1.0 equiv) and Cs\textsubscript{2}CO\textsubscript{3} (65.2 mg, 0.2 mmol, 1.0 equiv) in DCM (2 mL) at 0 °C. The resulting mixture was stirred at that temperature for 12 h. Then, the reaction was quenched with brine, extracted with DCM and the organic phase dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}. Evaporation of the solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 10:1) to afford 32 (33.5 mg, 99% yield) as a colorless liquid. \textsuperscript{1}H NMR (300 MHz, Chloroform-\textit{d}) \(\delta = 7.49 – 7.27 \text{ (m, 5H)}, 7.00 \text{ (dd, } J = 2.8, 1.6 \text{ Hz, 1H}), 6.91 \text{ (dd, } J = 4.0, 1.6 \text{ Hz, 1H}), 6.27 \text{ (dd, } J = 4.0, 2.8 \text{ Hz, 1H}). \textsuperscript{13}C NMR (75 MHz, Chloroform-\textit{d}) \(\delta = 138.3, 129.8, 128.4, 127.1, 124.3, 122.3, 113.9, 110.7, 104.1.\) The spectroscopic data are in agreement with those previously reported.\textsuperscript{[29]}

**Procedure for the preparation of 33**

![Chemical structure of 33](image)

Compound 9 (143.7 mg, 0.4 mmol, 2.0 equiv) was added to a stirred suspension of 1-phenyl-1\textit{H}-indole S23 (38.7 mg, 0.2 mmol, 1.0 equiv) and K\textsubscript{3}PO\textsubscript{4} (63.7 mg, 0.3 mmol, 1.5 equiv) in DCM (2 mL) at 15 °C under nitrogen and the resulting mixture was stirred at that temperature for 20 h. Then, the reaction was quenched with brine, extracted with DCM and the organic phase dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}. Evaporation of the solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 10:1) to afford 33 (30.4 mg, 70% yield) as a light yellow solid. \textsuperscript{1}H NMR (300 MHz, Chloroform-\textit{d}) \(\delta = 7.86 – 7.80 \text{ (m, 1H)}, 7.78 \text{ (s, 1H)}, 7.62 – 7.53 \text{ (m, 2H)}, 7.53 – 7.42 \text{ (m, 4H)}, 7.37 – 7.29 \text{ (m, 2H}). \textsuperscript{13}C NMR (75 MHz, Chloroform-\textit{d}) \(\delta = 137.9, 135.7, 134.7, 130.1, 128.5, 128.0, 125.0, 124.6, 122.9, 120.1, 115.6, 111.6, 88.2.\) The spectroscopic data are in agreement with those previously reported.\textsuperscript{[30]}

**Procedure for the preparation of 34**
Compound 9 (143.7 mg, 0.4 mmol, 2.0 equiv) was added to a stirred suspension of 1-(4-methoxyphenyl)-1H-indole S24 (44.7 mg, 0.2 mmol, 1.0 equiv) and K3PO4 (42.5 mg, 0.2 mmol, 1.0 equiv) in DCM (2 mL) at 10 °C under nitrogen. The resulting mixture was stirred at that temperature for 5 h. Then, the reaction was quenched with brine, extracted with DCM, and the organic phase dried over anhydrous Na2SO4. Evaporation of the solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 10:1) to afford 34 (39.3 mg, 79% yield) as a white solid. 1H NMR (300 MHz, Chloroform-d) δ = 7.85 – 7.76 (m, 1H), 7.72 (s, 1H), 7.47 – 7.26 (m, 5H), 7.11 – 6.99 (m, 2H), 3.89 (s, 3H). 13C NMR (75 MHz, Chloroform-d) δ = 159.2, 136.1, 135.1, 130.7, 127.8, 126.5, 124.5, 122.7, 120.0, 115.8, 115.2, 111.6, 87.5, 55.8. The spectroscopic data are in agreement with those previously reported.[31]

Procedure for the preparation of 35

Compound 9 (71.9 mg, 0.2 mmol, 1.0 equiv) was added to a stirred solution of 1-methyl-2-phenyl-1H-indole S25 (62.2 mg, 0.3 mmol, 1.5 equiv) in DCM (2 mL) at room temperature and the resulting mixture was stirred at that temperature for 5 minutes. Then, the reaction was quenched with brine, extracted with DCM and the organic phase dried over anhydrous Na2SO4. Evaporation of the solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 10:1) to afford 35 (24.6 mg, 53% yield) as a colorless oil. 1H NMR (300 MHz, Chloroform-d) δ = 7.82 – 7.73 (m, 1H), 7.62 – 7.47 (m, 5H), 7.45 – 7.27 (m, 3H), 3.74 (s, 3H). 13C NMR (75 MHz, Chloroform-d) δ = 148.2, 137.0, 130.0, 129.9, 129.1, 128.8, 127.7, 124.0,
122.5, 119.6, 116.7, 110.6, 85.6, 31.8. The spectroscopic data are in agreement with those previously reported.[23]

**Procedure for the preparation of 36**

![Chemical Structure of 36](image)

Compound 9 (107.8 mg, 0.3 mmol, 1.5 equiv) was added to a stirred suspension of 1,3,5-trimethoxybenzene S26 (33.6 mg, 0.2 mmol, 1.0 equiv) and Cs2CO3 (65.2 mg, 0.2 mmol, 1.0 equiv) in DCM (2 mL) at room temperature. The resulting mixture was stirred at room temperature for 4 h and then, quenched with brine, extracted with DCM, and the organic phase dried over anhydrous Na2SO4. Evaporation of the solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) to afford 36 (30.8 mg, 80% yield) as a white solid. 1H NMR (300 MHz, Chloroform-\(d\)) \(\delta = 6.04\ (s, 2H), 3.85\ (s, 6H), 3.84\ (s, 3H).\) 13C NMR (75 MHz, Chloroform-\(d\)) \(\delta = 165.4, 163.8, 114.7, 90.4, 84.0, 56.2, 55.8.\) The spectroscopic data is in agreement with that previously reported.[32]

**Procedure for the preparation of 37**

![Chemical Structure of 37](image)

Salt 9 (143.7 mg, 0.4 mmol, 2.0 equiv) was added to a stirred solution of triphenylamine S27 (49.1 mg, 0.2 mmol, 1.0 equiv) in DCE (2 mL) at room temperature under nitrogen and the resulting mixture stirred at 50 °C for 14 h. Then, the reaction was quenched with brine, extracted with DCM and the organic phase dried over anhydrous Na2SO4. The solvent was evaporated under reduced pressure and the residue obtained purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) to afford 37 (17.8 mg, 33% yield) as a light yellow solid. 1H NMR (300 MHz, Chloroform-\(d\)) \(\delta = 7.45 – 7.38\ (m, 2H), 7.37 – 7.28\ (m, 4H), 7.21 – 7.08\ (m, 6H), 7.00 – 6.90\ (m, 2H).\) 13C NMR (75 MHz,
Chloroform- \textit{d}) \ \delta = 151.7, 146.1, 133.3, 129.9, 126.3, 125.3, 119.8, 102.6. The spectroscopic data are in agreement with those previously reported.\textsuperscript{[33]}

**Procedure for the preparation of 38**

Salt 9 (71.9 mg, 0.2 mmol, 1.0 equiv) was added to a stirred solution of tetracene S28 (45.7 mg, 0.2 mmol, 1.0 equiv) in DCE (2 mL) at room temperature. The resulting mixture was stirred at 50 °C for 7 h. After this another portion of 9 (71.9 mg, 0.2 mmol, 1.0 equiv) was added and the stirring continued for additional 11 h at the same temperature. Subsequently, the reaction was quenched with water, extracted with DCM and the organic phase dried over anhydrous Na$_2$SO$_4$. Evaporation of the solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 40:1) to afford 38 (13.8 mg, 27% yield) as a red solid. $^1$H NMR (400 MHz, Chloroform- \textit{d}) \ \delta = 8.95 (s, 1H), 8.83 (s, 1H), 8.66 (s, 1H), 8.35 (d, \textit{J} = 8.8 \text{ Hz}, 1H), 8.08 – 7.96 (m, 3H), 7.67 – 7.59 (m, 1H), 7.53 – 7.45 (m, 3H). $^{13}$C NMR (101 MHz, Chloroform- \textit{d}) \ \delta = 134.5, 133.5, 133.4, 132.0, 130.3, 130.3, 129.3, 128.9, 128.5, 128.3, 128.0, 127.2, 126.4, 126.0, 125.4, 123.9, 117.9, 104.9. IR (neat): 2918, 2849, 2220, 1674, 1483, 1457, 1259, 1098, 1019, 890, 801, 747, 697, 644, 626, 609, 577, 532 cm$^{-1}$; HRMS calculated m/z for C$_{19}$H$_{11}$N$^+$ [M]$^+$: 253.0886, found (ESI) 253.0885.

**Procedure for the preparation of 40 and 41**

Salt 9 (107.8 mg, 0.3 mmol, 1.5 equiv) was added to a stirred suspension of 3-methyl-$^1$H-indole 39 (26.2 mg, 0.2 mmol, 1.0 equiv) and Cs$_2$CO$_3$ (65.2 mg, 0.2 mmol, 1.0 equiv) in DCM (2 mL) at 0 °C under nitrogen. The resulting mixture was stirred at that temperature for 2 h. Then, the reaction was quenched with brine, extracted with DCM and the organic phase dried over anhydrous Na$_2$SO$_4$. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1) to afford 40 (14.4 mg, 50% yield) and 41 (9.3
mg, 30% yield), both as a white solids.

\[ \text{\textbf{40}} \]

\( ^1\text{H} \text{NMR (300 MHz, Dichloromethane-}d_2\text{)} \delta = 8.69 \text{ (bs, 1H), 7.63-7.60 (m, 1H), 7.40 – 7.32 (m, 1H), 7.32 – 7.09 (m, 4H), 7.00 – 6.91 (m, 1H), 6.89 – 6.79 (m, 1H), 5.06 – 4.92 (m, 1H), 4.31 (bs, 1H), 2.40 (s, 3H), 1.84 (s, 3H).} \]

\( ^{13}\text{C NMR (75 MHz, Dichloromethane-}d_2\text{)} \delta = 150.0, 135.9, 130.6, 129.7, 129.4, 128.6, 124.1, 123.1, 121.5, 121.2, 119.8, 119.2, 111.5, 111.4, 111.0, 67.3, 47.5, 22.8, 9.3. \)

IR (neat): 3441, 3334, 2922, 2226, 1607, 1479, 1463, 1385, 1336, 1314, 1304, 1252, 1214, 1154, 1131, 1036, 1012, 945, 876, 854, 819, 782, 758, 707, 694, 635, 607, 578, 566, 555, 528 cm\(^{-1}\); HRMS calculated m/z for C\(_{19}\)H\(_{18}\)N\(_3\)\(^+\) [M+H]\(^+\): 288.1495, found (ESI) 288.1496.

\[ \text{\textbf{41}} \]

\( ^1\text{H} \text{NMR (400 MHz, Chloroform-}d\text{)} \delta = 8.33 \text{ (bs, 1H), 7.65 – 7.58 (m, 1H), 7.50-7.46 (m, 1H), 7.43 – 7.33 (m, 2H), 7.31 – 7.22 (m, 2H), 7.21 – 7.12 (m, 2H), 5.35 (s, 1H), 2.43 (s, 3H), 1.88 (s, 3H).} \)

\( ^{13}\text{C NMR (101 MHz, Chloroform-}d\text{)} \delta = 141.3, 136.7, 131.4, 128.3, 127.3, 125.5, 124.3, 124.2, 122.7, 120.1, 119.5, 119.4, 115.4, 112.0, 111.8, 110.2, 69.6, 46.0, 23.4, 9.1. \)

IR (neat): 3304, 2919, 2222, 1597, 1481, 1464, 1336, 1316, 1241, 1172, 1099, 987, 934, 795, 745, 651, 597, 566 cm\(^{-1}\); HRMS calculated m/z for C\(_{20}\)H\(_{17}\)N\(_4\)\(^+\) [M+H]\(^+\): 313.1448, found (ESI) 313.1447.

**Procedure for the preparation of 43**

\[ \text{\textbf{43}} \]
Salt 9 (107.8 mg, 0.3 mmol, 1.5 equiv) was added to a stirred solution of 2,3,4,9-tetrahydro-1H-carbazole 42 (34.2 mg, 0.2 mmol, 1.0 equiv) in CH₃CN (2 mL) at room temperature and the resulting mixture stirred for 10 minutes. Then, the reaction was quenched with water, extracted with DCM, and the organic phase dried over anhydrous Na₂SO₄. Evaporation of the solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) to afford 43 (30.0 mg, 76% yield) as a white solid. ¹H NMR (400 MHz, Chloroform-d) δ = 7.65-7.63 (m, 1H), 7.57-7.54 (m, 1H), 7.47-7.43 (m, 1H), 7.33-7.29 (m, 1H), 3.08 – 2.96 (m, 1H), 2.93 – 2.75 (m, 2H), 2.36 – 2.23 (m, 1H), 2.12 – 1.97 (m, 1H), 1.98 – 1.86 (m, 1H), 1.60 – 1.43 (m, 1H), 1.32 – 1.17 (m, 1H). ¹³C NMR (101 MHz, Chloroform-d) δ = 178.6, 155.1, 137.2, 130.0, 126.6, 122.7, 121.3, 117.6, 51.9, 39.2, 30.2, 28.4, 22.4. IR (neat): 2941, 2854, 2236, 1731, 1618, 1592, 1440, 1347, 1273, 1231, 1187, 1139, 1093, 1043, 1012, 956, 934, 906, 867, 854, 772, 757, 689, 672, 635, 608, 563, 525 cm⁻¹; HRMS calculated m/z for C₁₃H₁₃N₂⁺ [M+H]⁺: 197.1073, found (ESI) 197.1074.

Procedure for the preparation of 45

Salt 9 (107.8 mg, 0.3 mmol, 1.5 equiv) was added to a stirred solution of 1,2-dimethyl-3H-benzo[e]indole 44 (39.1 mg, 0.2 mmol, 1.0 equiv) in CH₃CN (2 mL) at room temperature and the resulting mixture stirred for 10 minutes. Then, the reaction was quenched with water, extracted with DCM and the organic phase dried over anhydrous Na₂SO₄. Evaporation of the solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) to afford 45 (38.1 mg, 86% yield) as a light yellow oil. ¹H NMR (400 MHz, Chloroform-d) δ = 8.06-8.04 (m, 1H), 7.99 – 7.90 (m, 2H), 7.76 (d, J = 8.4 Hz, 1H), 7.66-7.62 (m, 1H), 7.54-7.50 (m, 1H), 2.60 (s, 3H), 1.85 (s, 3H). ¹³C NMR (101 MHz, Chloroform-d) δ = 178.3, 152.1, 132.7, 131.3, 131.3, 129.7, 128.0, 127.9, 125.8, 122.3, 119.9, 117.9, 50.2, 22.5, 16.1. IR (neat): 3054, 2236, 1626, 1602, 1574, 1520, 1443, 1380, 1261, 1228, 1215, 1201, 1103, 1078, 1022, 968,
908, 866, 771, 755, 691, 662, 598, 589, 569, 553, 525 cm\(^{-1}\); HRMS calculated m/z for C\(_{15}\)H\(_{13}\)N\(_2\)\(^+\) [M+H]\(^+\): 221.1073, found (ESI) 221.1072.

5. Metal-free cyano-cyclization of indole derivatives

General procedure of the cyano-cyclisation of indole derivatives: preparation of 46-62.

Compound 9 was added to a stirred solution of indole derivatives S\(_{29}\)-S\(_{45}\) (0.2 mmol, 1.0 equiv) in the appropriate solvent (2 mL) at room temperature under nitrogen flow and the resulting mixture was stirred at room temperature for the specified time (vide infra). Then, the reaction was quenched with water, extracted with DCM and the organic phase dried over anhydrous Na\(_2\)SO\(_4\). Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel to afford the desired products.

A mixture of S\(_{29}\) (0.2 mmol, 62.9 mg, 1.0 equiv) and 9 (0.3 mmol, 107.8 mg, 1.5 equiv) in CH\(_3\)CN (2 mL) was stirred at room temperature for 10 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded 46 in 69% yield (46.5 mg) as a colorless oil. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta = 7.83 – 7.70\) (m, 2H), 7.36 (d, \(J = 8.0\) Hz, 2H), 7.20-7.16 (m, 2H), 6.83 (t, \(J = 7.6\) Hz, 1H), 6.67 (d, \(J = 7.6\) Hz, 1H), 5.73 (s, 1H), 5.02 (bs, 1H), 3.58 – 3.44 (m, 1H), 3.30 – 3.13 (m, 1H), 2.54 – 2.24 (m, 5H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta = 148.5, 144.6, 135.1, 130.9, 130.3, 127.3, 123.79, 123.5, 120.4, 119.5, 110.5, 82.6, 49.7, 46.8, 37.4, 21.7. IR (neat): 3370, 2917, 2238, 1608, 1486, 1337, 1311, 1265, 1201, 1164, 1091, 1060, 1009, 931, 895, 848, 820, 707, 661, 592, 570, 543 cm\(^{-1}\); HRMS calculated m/z for C\(_{18}\)H\(_{18}\)N\(_3\)O\(_2\)S\(^+\) [M+H]\(^+\): 340.1114, found (ESI) 340.1117.
A mixture of S30 (0.2 mmol, 65.7 mg, 1.0 equiv) and 9 (0.3 mmol, 107.8 mg, 1.5 equiv) in CH3CN (2 mL) was stirred at room temperature for 15 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded 47 in 85% yield (59.9 mg) as a white solid. 1H NMR (400 MHz, Chloroform-d) δ = 7.63 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.20 – 7.08 (m, 2H), 6.79 (t, J = 7.6 Hz, 1H), 6.56 (d, J = 8.0 Hz, 1H), 5.36 (bs, 1H), 3.55 – 3.41 (m, 1H), 3.14 – 2.98 (m, 1H), 2.59 – 2.49 (m, 2H), 2.38 (s, 3H), 2.04 (s, 3H). 13C NMR (101 MHz, Chloroform-d) δ = 148.1, 143.8, 136.5, 130.7, 129.8, 127.2, 123.7, 123.7, 120.3, 118.6, 110.3, 90.6, 55.2, 47.0, 34.0, 25.1, 21.6. IR (neat): 3361, 2889, 2236, 1610, 1485, 1470, 1403, 1378, 1328, 1311, 1247, 1210, 1165, 1023, 1011, 959, 893, 816, 764, 706, 695, 617, 518 cm⁻¹; HRMS calculated m/z for C19H20N3O2S+ [M+H]+: 354.1271, found (ESI) 354.1274.

A mixture of S31 (0.2 mmol, 65.7 mg, 1.0 equiv) and 9 (0.3 mmol, 107.8 mg, 1.5 equiv) in CH3CN (2 mL) was stirred at room temperature for 15 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded 48 in 61% yield (42.9 mg) as a white solid. 1H NMR (300 MHz, Chloroform-d) δ = 7.87 – 7.74 (m, 2H), 7.44 – 7.35 (m, 2H), 7.23-7.18 (m, 1H), 7.16 – 7.06 (m, 1H), 6.75-6.69 (m, 1H), 6.45 (d, J = 7.8 Hz, 1H), 5.85 (s, 1H), 3.72-3.64 (m, 1H), 3.16-3.06 (m, 1H), 3.01 (s, 3H), 2.47 (s, 3H), 2.22-2.15 (m, 1H), 1.90-1.79 (m, 1H). 13C NMR (75 MHz, Chloroform-d) δ = 149.9, 144.8, 135.50, 131.0, 130.5, 127.4, 123.7, 123.5, 119.8, 118.7, 106.9, 88.7, 48.7, 47.4, 39.1, 31.1, 21.7. IR (neat): 2890, 2233, 1603, 1497, 1445, 1430, 1349, 1318, 1306, 1254, 1211, 1159, 1105, 1089, 1021, 969, 919, 876, 841, 815, 802, 751, 724, 660, 603, 574, 532 cm⁻¹; HRMS calculated m/z for C19H20N3O2S+ [M+H]+: 354.1271, found (ESI) 354.1278.
A mixture of S32 (0.2 mmol, 46.5 mg, 1.0 equiv) and 9 (0.3 mmol, 107.8 mg, 1.5 equiv) in CH$_3$CN (2 mL) was stirred at room temperature for 2 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded 49 in 68% yield (35.0 mg) as a colorless oil. $^1$H NMR (400 MHz, DMSO-$d_6$, 100 °C) $\delta$ = 7.34-7.31 (m, 1H), 7.17-7.13 (m, 1H), 6.78-6.74 (m, 1H), 6.70-6.68 (m, 1H), 6.54 (bs, 1H), 5.764-5.758 (m, 1H), 4.17-4.10 (m, 2H), 3.78-3.73 (m, 1H), 3.06-3.30 (m, 1H), 2.94 (s, 2H), 2.70-2.62 (m, 1H), 2.56 – 2.51 (m, 1H), 1.26 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$, 100 °C) $\delta$ = 153.1, 149.1, 129.6, 123.7, 123.1, 119.8, 118.3, 109.3, 79.5, 60.4, 48.3, 44.1, 35.4, 13.8. IR (neat): 3276, 2981, 2240, 1692, 1607, 1471, 1416, 1380, 1346, 1319, 1258, 1237, 1201, 1172, 1111, 1026, 1008, 894, 820, 747, 609, 527 cm$^{-1}$; HRMS calculated m/z for C$_{14}$H$_{16}$N$_3$O$_2$ $^{+}$ [M+H]$^+$: 258.1237, found (ESI) 258.1237.

A mixture of S33 (0.2 mmol, 67.3 mg, 1.0 equiv) and 9 (0.3 mmol, 107.8 mg, 1.5 equiv) in CH$_3$CN (2 mL) was stirred at room temperature for 10 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded 50 in 89% yield (64.5 mg) as a white solid. $^1$H NMR (400 MHz, DMSO-$d_6$, 100 °C) $\delta$ = 7.38-7.36 (m, 1H), 7.34 – 7.25 (m, 2H), 7.27 – 7.17 (m, 3H), 7.11-7.06 (m, 1H), 6.77-6.73 (m, 1H), 6.26 (d, $J$ = 8.0 Hz, 1H), 4.97 – 4.61 (m, 2H), 4.08-3.96 (m, 2H), 3.79-3.74 (m, 1H), 3.27 – 3.09 (m, 1H), 2.69 – 2.58 (m, 2H), 2.00 (s, 3H), 1.17 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$, 100 °C) $\delta$ = 153.1, 147.8, 138.5, 129.7, 127.8, 126.0, 125.6, 123.4, 122.8, 118.6, 117.8, 107.2, 89.7, 60.2, 54.8, 46.5, 45.8, 32.2, 19.3, 13.7. IR (neat): 3417, 2982, 2241, 1702, 1681, 1605, 1488, 1465, 1449, 1401, 1376, 1347, 1313, 1232, 1212, 1186, 1157, 1118, 1103, 1073, 1055, 1027, 1007, 919, 880, 838, 771, 751, 739, 726, 694, 653, 637, 608, 555, 545, 530 cm$^{-1}$; HRMS calculated m/z for C$_{22}$H$_{24}$N$_3$O$_2$ $^{+}$ [M+H]$^+$: 362.1863, found (ESI) 362.1867.
A mixture of S34 (0.2 mmol, 49.3 mg, 1.0 equiv) and 9 (0.3 mmol, 107.8 mg, 1.5 equiv) in CH3CN (2 mL) was stirred at room temperature for 10 minutes. Column chromatography on silica gel (eluent: hexane/ethyl acetate = 4:1) afforded 51 in 71% yield (38.5 mg) as a colorless oil. 1H NMR (400 MHz, DMSO- d6, 100 °C) δ = 7.36-7.33 (m, 1H), 7.17-7.12 (m, 1H), 6.79-6.75 (m, 1H), 6.73-6.71 (m, 1H), 6.50 (bs, 1H), 4.10 (q, J = 7.2 Hz, 2H), 3.64-3.59 (m, 1H), 3.08-3.01 (m, 1H), 2.70-2.55 (m, 2H), 1.86 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H). 13C NMR (101 MHz, DMSO- d6, 100 °C) δ = 152.6, 148.5, 129.6, 123.8, 123.2, 118.6, 118.4, 109.5, 86.5, 60.1, 53.7, 45.0, 31.7, 21.7, 13.8. IR (neat): 3369, 2981, 2239, 1687, 1609, 1485, 1470, 1407, 1377, 1333, 1233, 1205, 1160, 1103, 1075, 1055, 1028, 956, 881, 838, 820, 773, 750, 662, 608, 541 cm⁻¹; HRMS calculated m/z for C15H18N3O2⁺ [M+H]⁺: 272.1394, found (ESI) 272.1394.

A mixture of S35 (0.2 mmol, 58.9 mg, 1.0 equiv) and 9 (0.3 mmol, 107.8 mg, 1.5 equiv) in CH3CN (2 mL) was stirred at room temperature for 2 h. Column chromatography on silica gel (eluent: hexane/ethyl acetate = 4:1) afforded 52 in 56% yield (35.9 mg) as a colorless oil. 1H NMR (400 MHz, DMSO- d6, 100 °C) δ = 7.50 – 7.26 (m, 6H), 7.17-7.13 (m, 1H), 6.79-6.75 (m, 1H), 6.71-6.68 (m, 1H), 6.58 (bs, 1H), 5.823-5.817 (m, 1H), 5.26 – 5.09 (m, 2H), 3.86 – 3.73 (m, 1H), 3.11-3.04 (m, 1H), 2.72-2.64 (m, 1H), 2.58 – 2.51 (m, 1H). 13C NMR (101 MHz, DMSO- d6, 100 °C) δ = 152.9, 149.0, 136.2, 129.7, 127.8, 127.2, 127.0, 123.7, 123.1, 119.8, 118.4, 109.4, 79.6, 66.0, 48.4, 44.3, 35.4. IR (neat): 3254, 2953, 2240, 1698, 1606, 1485, 1471, 1411, 1353, 1318, 1258, 1236, 1200, 1108, 1027, 1008, 943, 888, 820, 747, 697, 585, 522 cm⁻¹; HRMS calculated m/z for C19H18N3O2⁺ [M+H]⁺: 320.1394, found (ESI) 320.1396.
A mixture of **S36** (0.2 mmol, 61.7 mg, 1.0 equiv) and **9** (0.3 mmol, 107.8 mg, 1.5 equiv) in CH$_3$CN (2 mL) was stirred at room temperature for 10 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **53** in 81% yield (53.9 mg) as a colorless oil. $^1$H NMR (400 MHz, DMSO-$d_6$, 100 °C) $\delta$ = 7.44 – 7.26 (m, 6H), 7.17-7.13 (m, 1H), 6.80-6.76 (m, 1H), 6.73-6.71 (m, 1H), 6.54 (bs, 1H), 5.14 (s, 2H), 3.70-3.64 (m, 1H), 3.19 – 3.03 (m, 1H), 2.74 – 2.55 (m, 2H), 1.88 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$, 100 °C) $\delta$ = 152.5, 148.4, 136.2, 129.7, 127.8, 127.20 126.9, 123.8, 123.2, 118.6, 118.5, 109.5, 86.7, 65.6, 53.7, 45.1, 31.7, 21.6. IR (neat): 3371, 2982, 2239, 1692, 1609, 1486, 1470, 1401, 1350, 1267, 1233, 1204, 1161, 1103, 1072, 1053, 1027, 955, 894, 820, 749, 697, 661, 608, 587, 542, 523 cm$^{-1}$; HRMS calculated m/z for C$_{20}$H$_{20}$N$_3$O$_2$ $^+$ [M+H]$^+$: 334.1550, found (ESI) 334.1552.

A mixture of **S37** (0.2 mmol, 79.7 mg, 1.0 equiv) and **9** (0.3 mmol, 107.8 mg, 1.5 equiv) in CH$_3$CN (2 mL) was stirred at room temperature for 10 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **54** in 93% yield (78.8 mg) as a white solid. $^1$H NMR (400 MHz, DMSO-$d_6$, 100 °C) $\delta$ = 7.46 – 7.25 (m, 8H), 7.24 – 7.16 (m, 3H), 7.11-7.07 (m, 1H), 6.83 – 6.69 (m, 1H), 6.26 (d, $J$ = 7.6 Hz, 1H), 5.07 (s, 2H), 4.87 (d, $J$ = 17.2 Hz, 1H), 4.63 (d, $J$ = 17.2 Hz, 1H), 3.85-3.80 (m, 1H), 3.36 – 3.14 (m, 1H), 2.73 – 2.58 (m, 2H), 2.02 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$, 100 °C) $\delta$ = 153.0, 147.8, 138.4, 135.9, 129.7, 127.8, 127.3, 127.1, 126.0, 125.6, 123.4, 122.8, 118.5, 117.8, 107.2, 89.9, 65.9, 54.8, 46.5, 45.9, 32.1, 19.2. IR (neat): 3031, 2239, 1699, 1606, 1488, 1452, 1397, 1349, 1266, 1211, 1185, 1148, 1101, 1071, 1053, 1026, 917, 887, 858, 819, 787, 769, 696, 636, 590, 554, 523 cm$^{-1}$; HRMS calculated m/z for C$_{27}$H$_{26}$N$_3$O$_2$ $^+$ [M+H]$^+$: 424.2020, found (ESI) 424.2019.
A mixture of S38 (0.2 mmol, 50.5 mg, 1.0 equiv) and 9 (0.3 mmol, 107.8 mg, 1.5 equiv) in CH3CN (2 mL) was stirred at room temperature for 30 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 2:1) afforded 55 in 68% yield (37.8 mg) as a white solid. 1H NMR (400 MHz, Chloroform-d) δ = 7.30 – 7.25 (m, 1H), 7.25-7.20 (m, 1H), 6.92-6.88 (m, 1H), 6.71-6.69 (m, 1H), 5.17 (bs, 1H), 3.66-3.61 (m, 1H), 3.17-3.11 (m, 1H), 2.80 (s, 3H), 2.70 – 2.55 (m, 2H), 2.02 (s, 3H). 13C NMR (101 MHz, Chloroform-d) δ = 148.0, 131.2, 124.2, 124.1, 121.0, 118.5, 110.6, 90.0, 55.5, 47.2, 38.9, 33.8, 25.6. IR (neat): 3366, 2876, 2234, 1609, 1484, 1472, 1400, 1386, 1346, 1329, 1244, 1205, 1165, 1110, 1035, 889, 863, 813, 732, 693, 652, 608, 555, 529 cm⁻¹; HRMS calculated m/z for C13H16N3O2S+ [M+H]+: 278.0956, found (ESI) 278.0956.

A mixture of S39 (0.2 mmol, 32.2 mg, 1.0 equiv) and 9 (0.3 mmol, 107.8 mg, 1.5 equiv) in CH3CN (2 mL) was stirred at room temperature for 15 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 5:1) afforded 56 in 55% yield (20.4 mg) as a colorless oil. 1H NMR (300 MHz, Chloroform-d) δ = 7.28 (d, J = 7.5 Hz, 1H), 7.17 (t, J = 7.5 Hz, 1H), 6.84 (t, J = 7.5 Hz, 1H), 6.63 (d, J = 7.8 Hz, 1H), 6.01 (d, J = 2.4 Hz, 1H), 4.75 (bs, 1H), 4.14-4.08 (m, 1H), 3.67-3.59 (m, 1H), 2.99 – 2.60 (m, 1H), 2.48-2.41 (m, 1H). 13C NMR (75 MHz, Chloroform-d) δ = 149.0, 130.5, 124.7, 124.5, 120.8, 120.2, 109.4, 97.6, 66.5, 49.8, 40.9. IR (neat): 3383, 2952, 2870, 2244, 1420, 1356, 1333, 1316, 1258, 1229, 1208, 1170, 1118, 1053, 945, 849, 778, 611, 585, 561, 544 cm⁻¹; HRMS calculated m/z for C11H11N2O+ [M+H]+: 187.0866, found (ESI) 187.0868.
A mixture of **S40** (0.2 mmol, 35.0 mg, 1.0 equiv) and **9** (0.24 mmol, 86.2 mg, 1.2 equiv) in CH$_3$CN (2 mL) was stirred at room temperature for 10 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **57** in 66% yield (26.3 mg) as a white solid. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta = 7.28-7.25$ (m, 1H), 7.17-7.13 (m, 1H), 6.84-6.80 (m, 1H), 6.58 (d, $J = 8.0$ Hz, 1H), 4.44 (bs, 1H), 4.07-4.02 (m, 1H), 3.65-3.59 (m, 1H), 2.78 – 2.54 (m, 1H), 2.46-2.42 (m, 1H), 1.81 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta =$ 148.5, 130.5, 125.2, 124.7, 120.2, 120.0, 109.1, 103.7, 65.9, 53.5, 41.7, 24.8. IR (neat): 3348, 2991, 2874, 2243, 1609, 1487, 1471, 1416, 1383, 1343, 1318, 1282, 1198, 1181, 1133, 1110, 1092, 991, 943, 911, 896, 861, 678, 608, 567, 542 cm$^{-1}$; HRMS calculated m/z for C$_{12}$H$_{13}$N$_2$O$^+$ [M+H]$^+$: 201.1022, found (ESI) 201.1022.

A mixture of **S41** (0.2 mmol, 47.5 mg, 1.0 equiv) and **9** (0.24 mmol, 86.2 mg, 1.2 equiv) in CH$_3$CN (2 mL) was stirred at room temperature for 10 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **58** in 89% yield (46.5 mg) as a white solid. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta = 7.67 – 7.55$ (m, 2H), 7.47 – 7.34 (m, 3H), 7.29 – 7.15 (m, 2H), 6.87-6.83 (m, 1H), 6.67 (d, $J = 8.0$ Hz, 1H), 4.79 (bs, 1H), 4.42 – 4.20 (m, 1H), 3.83-3.76 (m, 1H), 2.89 – 2.66 (m, 1H), 2.53-2.49 (m, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta =$ 149.2, 139.2, 130.6, 129.5, 128.6, 126.6, 124.8, 124.2, 120.1, 119.6, 108.7, 106.4, 67.0, 56.8, 41.1. IR (neat): 3390, 2895, 2232, 1610, 1486, 1470, 1445, 1392, 1354, 1324, 1281, 1232, 1133, 1094, 1070, 1035, 1022, 958, 942, 916, 889, 852, 762, 699, 662, 583, 536 cm$^{-1}$; HRMS calculated m/z for C$_{17}$H$_{15}$N$_2$O$^+$ [M+H]$^+$: 263.1179, found (ESI) 263.1183.

A mixture of **S42** (0.2 mmol, 35.0 mg, 1.0 equiv) and **9** (0.24 mmol, 86.2 mg, 1.2 equiv) in CH$_3$CN (2 mL) was stirred at room temperature for 10 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **59** in 64% yield (25.8 mg).
as a white solid. $^1$H NMR (400 MHz, Chloroform-$d$) δ = 7.25 (d, $J = 7.2$ Hz, 1H), 7.19 (t, $J = 7.6$ Hz, 1H), 6.88 (t, $J = 7.6$ Hz, 1H), 6.75 (d, $J = 8.0$ Hz, 1H), 5.35 (s, 1H), 4.45 (bs, 1H), 3.91 – 3.79 (m, 1H), 3.69 – 3.52 (m, 1H), 2.34-2.31 (m, 2H), 1.79 – 1.64 (m, 1H), 1.61 – 1.46 (m, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ = 148.1, 130.1, 125.7, 123.4, 121.2, 120.5, 110.9, 91.3, 61.7, 42.0, 29.1, 19.9. IR (neat): 3300, 2975, 2936, 2873, 2231, 1607, 1486, 1470, 1420, 1362, 1348, 1323, 1271, 1238, 1211, 1159, 1090, 1066, 1051, 1004, 970, 943, 909, 891, 868, 762, 747, 706, 665, 596, 558, 529, 506 cm$^{-1}$; HRMS calculated m/z for C$_{12}$H$_{13}$N$_2$O$^+$ [M+H]$^+$: 201.1022, found (ESI) 201.1022.

A mixture of S43 (0.2 mmol, 73.1 mg, 1.0 equiv) and 9 (0.24 mmol, 86.2 mg, 1.2 equiv) in DCM (2 mL) was stirred at room temperature for 12 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded 60 in 19% yield (11.0 mg) as a white solid. $^1$H NMR (400 MHz, Chloroform-$d$) δ = 7.44 – 7.22 (m, 7H), 6.99 – 6.89 (m, 1H), 6.61 (d, $J = 8.0$ Hz, 1H), 5.97 (s, 1H), 4.73 – 4.35 (m, 2H), 3.48 – 3.17 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ = 170.7, 147.9, 135.3, 131.8, 129.2, 128.3, 128.1, 124.6, 124.4, 121.3, 117.6, 109.3, 98.8, 49.2, 44.1, 40.1. IR (neat): 2918, 2849, 2248, 1783, 1706, 1600, 1485, 1454, 1417, 1384, 1338, 1303, 1284, 1249, 1205, 1188, 1144, 1100, 1066, 1043, 1026, 1006, 973, 920, 905, 852, 825, 805, 740, 696, 655, 599, 561, 547 cm$^{-1}$; HRMS calculated m/z for C$_{18}$H$_{15}$N$_2$O$_2$$^+$ [M+H]$^+$: 291.1128, found (ESI) 291.1128.

A mixture of S44 (0.2 mmol, 63.5 mg, 1.0 equiv) and 9 (0.3 mmol, 107.8 mg, 1.5 equiv) in CH$_3$CN (2 mL) was stirred at room temperature for 5 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded 61 in 86% yield (59.1 mg) as a colorless oil. $^1$H NMR (400 MHz, Chloroform-$d$) δ = 7.29 (d, $J = 7.6$ Hz, 1H), 7.13-7.09 (m,
1H), 6.83-6.79 (m, 1H), 6.57 (d, J = 8.0 Hz, 1H), 4.39 – 4.20 (m, 4H), 4.07 (bs, 1H), 3.01-2.93 (m, 1H), 2.45-2.36 (m, 1H), 2.33 – 2.24 (m, 1H), 2.22 – 2.07 (m, 1H), 1.79 (s, 3H), 1.41 – 1.22 (m, 6H). 13C NMR (101 MHz, Chloroform-d) δ = 170.2, 169.4, 147.6, 129.7, 128.7, 124.3, 121.1, 120.0, 110.0, 79.4, 69.1, 62.1, 61.5, 55.4, 39.8, 32.8, 21.7, 14.1, 14.0. IR (neat): 3350, 2980, 2239, 1721, 1605, 1487, 1469, 1445, 1366, 1316, 1262, 1223, 1174, 1147, 1107, 1061, 1037, 1016, 941, 912, 858, 745, 649, 569, 532 cm⁻¹; HRMS calculated m/z for C₁₉H₂₃N₂O₄⁺ [M+H]⁺: 343.1652, found (ESI) 343.1656.

![Image](image.png)

A mixture of S₄₅ (0.2 mmol, 74.3 mg, 1.0 equiv) and 9 (0.24 mmol, 86.2 mg, 1.2 equiv) in DCM (2 mL) was stirred at room temperature for 11 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 10:1) afforded 62-minor in 17% yield (13.4 mg) and 62-major in 79% yield (62.6 mg) both as a colorless oils.

![Image](image.png)

1H NMR (400 MHz, Chloroform-d) δ = 7.33 – 7.26 (m, 1H), 7.16-7.12 (m, 1H), 6.85-6.81 (m, 1H), 6.69 (d, J = 8.0 Hz, 1H), 5.14 – 4.94 (m, 2H), 4.48 – 4.35 (m, 1H), 4.33 – 4.19 (m, 1H), 4.23 – 4.03 (m, 2H), 3.59 (bs, 1H), 2.87-2.83 (m, 1H), 2.71-2.67 (m, 1H), 2.34 – 2.23 (m, 1H), 2.10 – 1.95 (m, 2H), 1.96 – 1.87 (m, 3H), 1.35 (t, J = 7.2 Hz, 3H), 1.31 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H). 13C NMR (101 MHz, Chloroform-d) δ = 170.8, 169.7, 146.9, 145.9, 130.3, 129.5, 123.3, 120.0, 119.6, 114.4, 111.5, 67.8, 62.0, 62.0, 52.7, 47.7, 44.4, 38.4, 32.4, 25.1, 24.5, 14.1, 14.0. IR (neat): 3357, 2977, 2240, 1641, 1608, 1482, 1466, 1444, 1376, 1318, 1239, 1218, 1175, 1147, 1127, 1077, 1056, 1020, 907, 859, 807, 749, 732, 635, 601, 561, 516 cm⁻¹; HRMS calculated m/z for C₂₃H₂₉N₂O₄⁺ [M+H]⁺: 397.2122, found (ESI) 397.2127.
$^1$H NMR (400 MHz, Chloroform-d) δ = 7.21 (d, $J = 7.6$ Hz, 1H), 7.14-7.10 (m, 1H), 6.79-6.75 (m, 1H), 6.63 (d, $J = 7.6$ Hz, 1H), 5.03 (t, $J = 1.6$ Hz, 1H), 4.80 – 4.62 (m, 1H), 4.42 (bs, 1H), 4.34 – 4.15 (m, 2H), 4.16 – 4.03 (m, 1H), 4.02 – 3.87 (m, 1H), 3.11-3.07 (m, 1H), 2.76 (d, $J = 15.2$ Hz, 1H), 2.72-2.68 (m, 1H), 2.30-2.25 (m, 1H), 1.85 (t, $J = 13.6$ Hz, 1H), 1.80 (s, 3H), 1.47 (s, 3H), 1.27 (t, $J = 7.2$ Hz, 3H), 1.16 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-d) δ = 170.8, 170.0, 148.6, 143.9, 130.3, 125.5, 124.7, 120.6, 119.4, 119.0, 110.9, 68.0, 62.3, 61.9, 52.6, 50.0, 44.3, 32.1, 30.6, 21.8, 18.5, 14.1, 13.8. IR (neat): 3362, 2980, 2231, 1727, 1607, 1482, 1467, 1385, 1368, 1328, 1299, 1248, 1197, 1156, 1093, 1050, 1020, 964, 908, 858, 797, 730, 647, 621, 591, 551 cm$^{-1}$; HRMS calculated m/z for C$_{23}$H$_{29}$N$_2$O$_4$ $^+$ [M+H]$^+$: 397.2122, found (ESI) 397.2126.

6. Metal-free cyanation/Povarov cycloaddition of indole derivatives

General procedure of the cyanation/Povarov cycloaddition of indole derivatives: preparation of 63-68.

Compound 9 was added to a stirred solution of indole derivatives S46-S51 (0.2 mmol, 1.0 equiv) in DCM (2 mL) at room temperature and the resulting mixture was stirred for the specified time (vide infra). Then, the reaction was quenched with water, extracted with DCM, and the organic phase dried over anhydrous Na$_2$SO$_4$. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel to afford the desired products.
A mixture of $\text{S46}$ (0.2 mmol, 74.7 mg, 1.0 equiv) and $\text{9}$ (0.3 mmol, 107.8 mg, 1.5 equiv) in DCM (2 mL) was stirred at room temperature for 4 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 2:1) afforded $\text{63}$ in 80% yield (63.9 mg) as a colorless oil. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta = 6.63 – 6.40$ (m, 2H), 5.36 (s, 1H), 4.42 – 4.11 (m, 4H), 3.72 (s, 3H), 3.03 (d, $J = 16.4$ Hz, 1H), 2.81-2.76 (m, 1H), 2.63-2.58 (m, 1H), 2.42 (d, $J = 16.4$ Hz, 1H), 1.72 (s, 3H), 1.70 – 1.60 (m, 1H), 1.37 – 1.21 (m, 7H), 1.08-1.03 (m, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta = 175.2, 172.3, 172.1, 156.0, 135.5, 122.9, 120.2, 94.6, 78.5, 67.1, 62.7, 62.6, 59.5, 55.0, 50.2, 35.0, 31.7, 30.5, 29.8, 16.8, 14.0, 14.0. IR (neat): 2963, 2254, 1724, 1642, 1568, 1463, 1386, 1239, 1189, 1141, 1086, 1029, 977, 913, 886, 860, 813, 784, 731, 649, 612, 541, 510 cm$^{-1}$; HRMS calculated m/z for C$_{22}$H$_{27}$N$_2$O$_5$ $^+$ [M+H]$^+$: 399.1914, found (ESI) 399.1918.

A mixture of $\text{S47}$ (0.2 mmol, 65.9 mg, 1.0 equiv) and $\text{9}$ (0.2 mmol, 71.9 mg, 1.0 equiv) in DCM (2 mL) was stirred at room temperature for 3 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 1:1) followed by preparative HPLC afforded $\text{64}$ in 67% yield (47.6 mg) as a colorless oil. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta = 6.79 – 6.67$ (m, 1H), 6.65 – 6.46 (m, 3H), 4.60 (d, $J = 3.6$ Hz, 1H), 4.37 – 4.15 (m, 4H), 2.99 (d, $J = 16.4$ Hz, 1H), 2.83-2.79 (m, 1H), 2.61 – 2.46 (m, 2H), 1.75 – 1.65 (m, 1H), 1.65 – 1.55 (m, 1H), 1.36 – 1.21 (m, 6H), 0.97-0.92 (m, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta = 176.9, 172.4, 171.6, 134.6, 130.1, 128.7, 122.3, 120.4, 72.8, 64.5, 62.7, 62.7, 59.4, 50.2, 32.9, 30.9, 25.9, 14.1. IR (neat): 2981, 2237, 1633, 1560, 1444, 1367, 1253, 1190, 1145, 1092, 1051, 1019, 934, 909, 858, 809, 746, 696, 648, 627, 589, 565 cm$^{-1}$; HRMS calculated m/z for C$_{20}$H$_{23}$N$_2$O$_4$ $^+$ [M+H]$^+$: 355.1652, found (ESI) 355.1654.
A mixture of S48 (0.2 mmol, 81.1 mg, 1.0 equiv) and 9 (0.3 mmol, 107.8 mg, 1.5 equiv) in DCM (2 mL) was stirred at room temperature for 36 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 2:1) afforded 65 in 78% yield (66.8 mg) as a white solid. \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta = 7.65\) (d, \(J = 8.0\) Hz, 2H), 7.44 (t, \(J = 7.6\) Hz, 2H), 7.41 – 7.32 (m, 1H), 6.81-6.77 (m, 1H), 6.72 – 6.53 (m, 3H), 4.42 – 4.09 (m, 4H), 3.05 (dd, \(J = 14.8, 3.6\) Hz, 1H), 2.86 (d, \(J = 17.2\) Hz, 1H), 2.67 (d, \(J = 17.2\) Hz, 1H), 2.44 – 2.27 (m, 2H), 1.90-1.87 (m, 1H), 1.39 – 1.15 (m, 7H). \(^13\)C NMR (101 MHz, Chloroform-d) \(\delta = 176.0, 172.6, 172.1, 136.2, 134.9, 130.8, 128.4, 128.4, 128.2, 128.0, 122.1, 119.7, 83.1, 69.6, 62.8, 62.7, 61.3, 49.3, 34.9, 31.4, 29.5, 28.9, 14.0. IR (neat): 2977, 2235, 1748, 1720, 1634, 1566, 1499, 1445, 1365, 1316, 1298, 1252, 1234, 1193, 1147, 1093, 1073, 1031, 1007, 902, 864, 813, 763, 747, 720, 695, 645, 632, 607, 584, 552 cm\(^{-1}\); HRMS calculated m/z for C\(_{26}\)H\(_{27}\)N\(_2\)O\(_4\)\(^+\) [M+H]\(^+\): 431.1965, found (ESI) 431.1966.

A mixture of S49 (0.2 mmol, 63.1 mg, 1.0 equiv) and 9 (0.2 mmol, 71.9 mg, 1.0 equiv) in DCM (2 mL) was stirred at room temperature for 4 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 1:1) afforded 66 in 76% yield (51.4 mg) as a colorless oil. \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta = 6.77 – 6.69\) (m, 1H), 6.64 – 6.55 (m, 2H), 6.52-6.49 (m, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 3.03 (d, \(J = 16.4\) Hz, 1H), 2.85-2.80 (m, 1H), 2.58-2.54 (m, 1H), 2.49 (d, \(J = 16.4\) Hz, 1H), 1.81 – 1.74 (m, 1H), 1.73 (s, 3H), 1.32-1.28 (m, 1H), 1.05-0.99 (m, 1H). \(^13\)C NMR (101 MHz, Chloroform-d) \(\delta = 175.5, 172.7, 172.2, 134.7, 130.4, 128.5, 122.0, 119.9, 78.2, 67.5, 60.1, 53.8, 53.7, 50.3, 34.8, 31.3, 30.7, 29.8, 16.7. IR (neat): 2956, 2239, 1719, 1635, 1560, 1457, 1431, 1383, 1340, 1269, 1234, 1201, 1179, 1148, 1106, 1086, 1004, 969, 911, 872, 861, 838, 797, 749, 731, 649, 632, 611, 572 cm\(^{-1}\)); HRMS calculated m/z for C\(_{19}\)H\(_{21}\)N\(_2\)O\(_4\)\(^+\) [M+H]\(^+\): 341.1496, found (ESI) 341.1500.
A mixture of S50 (0.2 mmol, 68.7 mg, 1.0 equiv) and 9 (0.2 mmol, 71.9 mg, 1.0 equiv) in DCM (2 mL) was stirred at room temperature for 3 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 1:1) afforded 67 in 85% yield (62.7 mg) as a colorless oil. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta =$ 6.75 – 6.71 (m, 1H), 6.62-6.56 (m, 2H), 6.50 (d, $J =$ 9.6 Hz, 1H), 4.40 – 4.16 (m, 4H), 3.02 (d, $J =$ 16.4 Hz, 1H), 2.83-2.78 (m, 1H), 2.60 – 2.51 (m, 1H), 2.51 – 2.40 (m, 1H), 1.74 (m, 4H), 1.30 (m, 7H), 1.04-0.99 (m, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta =$ 175.5, 172.3, 171.7, 134.6, 130.6, 128.4, 121.9, 120.0, 78.2, 67.4, 62.7, 62.7, 60.2, 50.3, 34.9, 31.2, 30.6, 29.7, 16.7, 14.1, 14.0. IR (neat): 2976, 2235, 1721, 1632, 1561, 1467, 1444, 1380, 1366, 1298, 1245, 1190, 1147, 1079, 1040, 1016, 909, 861, 819, 782, 749, 629, 608, 572, 511 cm$^{-1}$; HRMS calculated m/z for C$_{21}$H$_{25}$N$_2$O$_4^+$ [M+H]$^+$: 369.1809, found (ESI) 369.1812.

A mixture of S51 (0.2 mmol, 71.5 mg, 1.0 equiv) and 9 (0.2 mmol, 71.9 mg, 1.0 equiv) in DCM (2 mL) was stirred at room temperature for 3 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 1:1) afforded 68 in 81% yield (61.6 mg) as a colorless oil. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta =$ 6.59-6.56 (m, 1H), 6.47-6.45 (m, 1H), 6.26-6.24 (m, 1H), 4.43 – 3.99 (m, 4H), 3.01 (d, $J =$ 16.4 Hz, 1H), 2.80-2.75 (m, 1H), 2.58-2.54 (m, 1H), 2.44 (d, $J =$ 16.4 Hz, 1H), 2.05 (d, $J =$ 1.6 Hz, 3H), 1.73-1.69 (m, 4H), 1.34-1.26 (m, 7H), 1.04-0.98 (m, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta =$ 175.5, 172.3, 171.7, 139.1, 136.5, 124.5, 121.5, 120.2, 78.3, 67.3, 62.7, 62.6, 60.0, 50.3, 34.7, 31.5, 30.4, 29.7, 22.4, 16.7, 14.0, 14.0. IR (neat): 2980, 1727, 1563, 1441, 1383, 1234, 1196, 1176, 1142, 1083, 1065,
1022, 905, 857, 799, 723, 644, 607, 549, 512 cm$^{-1}$; HRMS calculated m/z for C$_{22}$H$_{27}$N$_2$O$_4$\(^{+}\) [M+H]$^+$: 383.1965, found (ESI) 383.1968.
7. Intermolecular cyanation-[4+2] cycloaddition

Procedure for the preparation of 69

Salt 9 (86.2 mg, 0.24 mmol, 1.2 equiv) was added to a stirred solution of 1,2-dimethyl-3H-benzo[e]indole 44 (39.1 mg, 0.2 mmol, 1.0 equiv) in DCM (2 mL) at room temperature and the resulting mixture was stirred for 10 minutes. Then, styrene (34.5 μL, 0.3 mmol, 1.5 equiv) was added and the resulting mixture stirred at room temperature for additional 11 h. Subsequently, the reaction was quenched with water, extracted with DCM and the organic phase dried over anhydrous Na2SO4. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) to afford 69 (57.7 mg, 89% yield) as a white solid. 1H NMR (400 MHz, Chloroform-d) δ = 7.99 (d, J = 7.6 Hz, 1H), 7.49 – 7.40 (m, 1H), 7.34 – 7.24 (m, 1H), 7.11 – 7.00 (m, 2H), 6.95 (t, J = 7.6 Hz, 2H), 6.72 – 6.61 (m, 2H), 6.55 (d, J = 9.6 Hz, 1H), 6.22 (d, J = 9.6 Hz, 1H), 4.08-4.04 (m, 1H), 2.75-2.69 (m, 1H), 1.85 – 1.73 (m, 4H), 0.97 (s, 3H). 13C NMR (101 MHz, Chloroform-d) δ = 173.0, 139.1, 137.1, 135.3, 133.5, 129.4, 129.1, 128.2, 128.0, 127.5, 127.1, 125.8, 122.3, 121.8, 77.9, 67.5, 63.1, 51.0, 34.8, 16.8, 13.6. IR (neat): 2976, 2225, 1614, 1571, 1498, 1451, 1373, 1294, 1173, 1160, 1093, 1035, 909, 870, 847, 805, 754, 729, 706, 601, 581, 555, 535, 510 cm⁻¹; HRMS calculated m/z for C23H21N2⁺ [M+H]⁺: 325.1699, found (ESI) 325.1703.

Procedure for the preparation of 70

Salt 9 (86.2 mg, 0.24 mmol, 1.2 equiv) and allylbenzene (39.8 μL, 0.3 mmol, 1.5 equiv) were successively added to a stirred solution of 1,2-dimethyl-3H-benzo[e]indole 44 (39.1 mg, 0.2 mmol, 1.0 equiv) in DCM (2 mL) at room temperature, and the resulting mixture was
stirred at room temperature for 37 h. Then, the reaction was quenched with water, extracted with DCM and the organic phase dried over anhydrous Na$_2$SO$_4$. Evaporation of the solvents under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) to afford 70 (58.7 mg, 87% yield, d.r. = 8:1 based on $^1$H NMR analysis). Separation of the isomers was only possible by preparative HPLC.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta = 7.89$ (d, $J = 7.6$ Hz, 1H), 7.49 – 7.33 (m, 3H), 7.23 – 7.06 (m, 4H), 6.98 – 6.83 (m, 2H), 6.65 – 6.48 (m, 1H), 3.21 – 3.02 (m, 1H), 2.42-2.38 (m, 1H), 2.34 – 2.22 (m, 1H), 2.01 – 1.89 (m, 1H), 1.63 (s, 3H), 1.07-1.02 (m, 1H), 0.94 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta = 173.4, 140.1, 139.5, 135.8, 133.7, 129.8, 129.5, 128.6, 128.4, 128.4, 126.3, 125.7, 122.2, 121.9, 65.5, 63.0, 48.2, 36.3, 34.0, 16.9, 13.5. IR (neat): 2974, 2933, 2227, 1612, 1571, 1497, 1450, 1388, 1376, 1296, 1212, 1166, 1119, 982, 943, 906, 867, 808, 753, 735, 705, 660, 623, 585, 544, 509 cm$^{-1}$; HRMS calculated m/z for C$_{24}$H$_{23}$N$_2^+$ [M+H]$^+$: 339.1856, found (ESI) 339.1857.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta = 7.87 – 7.78$ (m, 1H), 7.47 – 7.35 (m, 3H), 7.24 – 7.17 (m, 2H), 7.18 – 7.11 (m, 2H), 7.11 – 7.03 (m, 2H), 6.43 (d, $J = 9.6$ Hz, 1H), 3.36 (t, $J = 13.2$ Hz, 1H), 2.62-2.57 (m, 1H), 2.11-2.06 (m, 1H), 2.01 – 1.87 (m, 1H), 1.68 (s, 3H), 1.39-1.33 (m, 1H), 1.00 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta = 176.0, 140.0, 139.9, 134.8, 133.0, 130.0, 128.8, 128.7, 128.6, 128.4, 128.3, 126.3, 123.5, 119.4, 65.1, 58.0, 43.0, 37.0, 36.9, 16.6, 14.9. IR (neat): 3026, 2968, 2934, 2226, 1614, 1573, 1496, 1450, 1404, 1384, 1293, 1210, 1163, 1119, 1030, 988, 951, 909, 864, 813, 757, 730, 700, 660, 642, 611, 584, 548, 531, 515 cm$^{-1}$; HRMS calculated m/z for C$_{24}$H$_{23}$N$_2^+$ [M+H]$^+$: 339.1856, found (ESI) 339.1859.
8. Control experiments

Compound 7\textsuperscript{[25]} (81.9 mg, 0.3 mmol, 1.5 equiv) was added at room temperature under nitrogen flow to a stirred solution of S29 (62.9 mg, 0.2 mmol, 1.0 equiv) in CH\textsubscript{3}CN (2 mL). The resulting mixture was stirred at room temperature for 13 h. No trace of desired product 46 was observed. Then, the reaction was stirred at 70 °C for additional 28 h. without observing any change.

To a stirred solution of S29 (62.9 mg, 0.2 mmol, 1.0 equiv) in CH\textsubscript{3}CN (2 mL) 8\textsuperscript{[23]} (142.2 mg, 0.3 mmol, 1.5 equiv) was added at room temperature under nitrogen flow. The resulting mixture was stirred at room temperature for 5 h. No desired product 46 was observed. Stirring the reaction at 70 °C for additional 12 h. did not change the result.
9. X-ray crystal structure

X-ray crystal structure of 9

| Property                          | Value                      |
|----------------------------------|----------------------------|
| Empirical formula               | $\text{C}_{14}\text{H}_8\text{F}_3\text{NO}_3\text{S}_2$ |
| Formula weight                   | 359.33                     |
| Temperature/K                    | 101.44                     |
| Crystal system                   | monoclinic                 |
| Space group                      | $\text{P2}_1/\text{n}$    |
| $a/\text{Å}$                     | 6.7928(3)                  |
| $b/\text{Å}$                     | 14.0411(6)                 |
| $c/\text{Å}$                     | 15.2306(7)                 |
| $\alpha/°$                       | 90                         |
| $\beta/°$                        | 90.599(2)                  |
| $\gamma/°$                       | 90                         |
| Volume/Å$^3$                     | 1452.59(11)                |
| $Z$                              | 4                          |
| $\rho_{\text{calc}}/\text{g/cm}^3$ | 1.643                     |
| $\mu/\text{mm}^{-1}$             | 0.413                      |
| $F(000)$                         | 728.0                      |
| Crystal size/mm$^3$              | $0.416 \times 0.27 \times 0.263$ |
| Radiation                        | MoKα ($\lambda = 0.71073$) |
| $2\Theta$ range for data collection/° | 5.35 to 63.02         |
| Index ranges                     | $-9 \leq h \leq 9$, $-20 \leq k \leq 20$, $-22 \leq l \leq 22$ |
| Reflections collected            | 66179                      |
| Independent reflections          | 4789 [$R_{\text{int}} = 0.0186$, $R_{\text{sigma}} = 0.0104$] |
| Data/restraints/parameters       | 4789/0/208                 |
| Goodness-of-fit on $F^2$         | 1.079                      |
| Final R indexes [$I \geq 2\sigma (I)$] | $R_1 = 0.0251$, $wR_2 = 0.0680$ |
| Final R indexes [all data]       | $R_1 = 0.0252$, $wR_2 = 0.0682$ |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.50/-0.34               |
### X-ray crystal structure of 22

![22](image)

| Property                      | Value                                      |
|-------------------------------|--------------------------------------------|
| Empirical formula             | C\textsubscript{13}H\textsubscript{8}N\textsubscript{2} |
| Formula weight                | 192.21                                     |
| Temperature/K                 | 100.0                                      |
| Crystal system                | triclinic                                  |
| Space group                   | P-1                                        |
| a/Å                           | 8.0477(7)                                  |
| b/Å                           | 8.1521(7)                                  |
| c/Å                           | 14.5994(14)                                |
| α/°                           | 94.263(3)                                  |
| β/°                           | 93.278(3)                                  |
| γ/°                           | 93.638(3)                                  |
| Volume/Å\textsuperscript{3}   | 951.38(15)                                 |
| Z                             | 4                                          |
| ρ\textsubscript{calc}/g/cm\textsuperscript{3} | 1.342                                      |
| μ/mm\textsuperscript{-1}      | 0.081                                      |
| F(000)                        | 400.0                                      |
| Crystal size/mm\textsuperscript{3} | 0.421 × 0.22 × 0.219                     |
| Radiation                     | MoKα (λ = 0.71073)                         |
| 2θ range for data collection/°| 5.082 to 63.192                            |
| Index ranges                  | -11 ≤ h ≤ 11, -11 ≤ k ≤ 12, -21 ≤ l ≤ 21 |
| Reflections collected         | 34993                                      |
| Independent reflections       | 6331 [R\textsubscript{int} = 0.0279, R\textsubscript{sigma} = 0.0205] |
| Data/restraints/parameters    | 6331/0/271                                 |
| Goodness-of-fit on F\textsuperscript{2} | 1.153                                      |
| Final R indexes [I>2σ (I)]    | R\textsubscript{1} = 0.0476, wR\textsubscript{2} = 0.1259 |
| Final R indexes [all data]    | R\textsubscript{1} = 0.0503, wR\textsubscript{2} = 0.1277 |
| Largest diff. peak/hole / e Å\textsuperscript{-3} | 0.49/-0.21                                 |
X-ray crystal structure of 30a

| Property                        | Value                          |
|---------------------------------|-------------------------------|
| Empirical formula               | C_{14}H_{17}N_{3}O_{2}S        |
| Formula weight                  | 291.36                        |
| Temperature/K                   | 100                           |
| Crystal system                  | monoclinic                    |
| Space group                     | P2_1/c                        |
| a/Å                             | 13.7293(12)                   |
| b/Å                             | 8.4475(6)                     |
| c/Å                             | 12.0428(9)                    |
| α/°                             | 90                            |
| β/°                             | 100.898(4)                    |
| γ/°                             | 90                            |
| Volume/Å³                       | 1371.51(19)                   |
| Z                               | 4                             |
| ρ_{calc}/g/cm³                  | 1.411                         |
| μ/mm⁻¹                          | 0.241                         |
| F(000)                          | 616.0                         |
| Crystal size/mm³                | 0.45 \times 0.316 \times 0.214 | |
| Radiation                       | MoKα (λ = 0.71073)            |
| 2θ range for data collection/°  | 5.692 to 63.138               |
| Index ranges                    | -16 ≤ h ≤ 20, -12 ≤ k ≤ 12, -17 ≤ l ≤ 17 |
| Reflections collected           | 18342                         |
| Independent reflections         | 4579 [R_{int} = 0.0280, R_{sigma} = 0.0257] |
| Data/restraints/parameters      | 4579/0/209                    |
| Goodness-of-fit on F²           | 1.032                         |
| Final R indexes [I>=2σ (I)]    | R₁ = 0.0363, wR₂ = 0.1021     |
| Final R indexes [all data]     | R₁ = 0.0398, wR₂ = 0.1052     |
| Largest diff. peak/hole / e Å⁻³ | 0.83/-0.62                   |
**X-ray crystal structure of 40**

| Property                        | Value                      |
|---------------------------------|----------------------------|
| Empirical formula               | C_{19}H_{17}N_{3}          |
| Formula weight                  | 287.35                     |
| Temperature/K                   | 298                        |
| Crystal system                  | monoclinic                 |
| Space group                     | Cc                         |
| a/Å                             | 10.0946(8)                 |
| b/Å                             | 15.6754(11)                |
| c/Å                             | 10.9099(11)                |
| α/°                             | 90                         |
| β/°                             | 113.486(3)                 |
| γ/°                             | 90                         |
| Volume/Å³                       | 1583.3(2)                  |
| Z                               | 4                          |
| ρ_{calc}/g/cm³                  | 1.205                      |
| μ/µm⁻¹                          | 0.073                      |
| F(000)                          | 608.0                      |
| Crystal size/mm³                | 0.363 × 0.286 × 0.166      |
| Radiation                       | MoKα (λ = 0.71073)         |
| 2Θ range for data collection/° | 5.33 to 58.25              |
| Index ranges                    | -13 ≤ h ≤ 13, -21 ≤ k ≤ 21, -14 ≤ l ≤ 14 |
| Reflections collected           | 19130                      |
| Independent reflections         | 4229 [R_{int} = 0.0210, R_{sigma} = 0.0216] |
| Data/restraints/parameters      | 4229/2/207                 |
| Goodness-of-fit on F²           | 1.071                      |
| Final R indexes [I>=2σ (I)]    | R₁ = 0.0386, wR₂ = 0.1132  |
| Final R indexes [all data]      | R₁ = 0.0398, wR₂ = 0.1147  |
| Largest diff. peak/hole / e Å⁻³ | 0.18/-0.15                |
| Flack parameter                 | -0.1(4)                    |
### X-ray crystal structure of 41

| Property                          | Value                                      |
|-----------------------------------|--------------------------------------------|
| Empirical formula                | C<sub>20</sub>H<sub>16</sub>N<sub>4</sub>  |
| Formula weight                   | 312.37                                     |
| Temperature/K                    | 298                                        |
| Crystal system                   | orthorhombic                               |
| Space group                      | Pna<sub>2</sub><sub>1</sub>                |
| a/Å                              | 6.7642(4)                                  |
| b/Å                              | 25.5858(14)                                |
| c/Å                              | 9.4556(5)                                  |
| α/°                             | 90                                         |
| β/°                             | 90                                         |
| γ/°                             | 90                                         |
| Volume/Å³                        | 1636.46(16)                                |
| Z                                | 4                                          |
| ρ<sub>calc</sub>/g/cm³           | 1.268                                      |
| μ/mm⁻¹                           | 0.078                                      |
| F(000)                           | 656.0                                      |
| Crystal size/mm³                 | 0.363 × 0.354 × 0.136                      |
| Radiation                        | MoKα (λ = 0.71073)                         |
| 2Θ range for data collection/°   | 4.592 to 57.446                            |
| Index ranges                     | -9 ≤ h ≤ 9, -34 ≤ k ≤ 34, -12 ≤ l ≤ 12    |
| Reflections collected            | 44432                                      |
| Independent reflections          | 4209 [R<sub>int</sub> = 0.0252, R<sub>sigma</sub> = 0.0174] |
| Data/restraints/parameters       | 4209/38/222                                |
| Goodness-of-fit on F<sup>2</sup> | 1.062                                      |
| Final R indexes [I>=2σ (I)]     | R<sub>1</sub> = 0.0377, wR<sub>2</sub> = 0.1114 |
| Final R indexes [all data]      | R<sub>1</sub> = 0.0389, wR<sub>2</sub> = 0.1127 |
| Largest diff. peak/hole / e Å<sup>-3</sup> | 0.21/-0.20                                |
| Flack parameter                  | 0.0(3)                                     |
### X-ray crystal structure of 43

![Molecular structure of 43](image)

| Property                                               | Value                                      |
|--------------------------------------------------------|--------------------------------------------|
| **Empirical formula**                                   | C_{13}H_{12}N_{2}                         |
| **Formula weight**                                     | 196.25                                    |
| **Temperature/K**                                      | 100.01                                    |
| **Crystal system**                                     | monoclinic                                |
| **Space group**                                         | P2_{1}/c                                  |
| **a/A**                                                | 6.7185(13)                                |
| **b/A**                                                | 6.7629(15)                                |
| **c/A**                                                | 23.087(4)                                 |
| **α/°**                                                | 90                                        |
| **β/°**                                                | 90.519(7)                                 |
| **γ/°**                                                | 90                                        |
| **Volume/A^3**                                         | 1048.9(4)                                 |
| **Z**                                                  | 4                                         |
| **ρ_{calc}/g/cm^3**                                    | 1.243                                     |
| **μ/mm\(^{-1}\)**                                     | 0.075                                     |
| **F(000)**                                             | 416.0                                     |
| **Crystal size/mm\(^3\)**                             | 0.5 × 0.406 × 0.088                       |
| **Radiation**                                          | MoKα (λ = 0.71073)                        |
| **2θ range for data collection/°**                     | 6.064 to 54.348                           |
| **Index ranges**                                       | -8 ≤ h ≤ 8, -8 ≤ k ≤ 8, -28 ≤ l ≤ 29     |
| **Reflections collected**                              | 24225                                     |
| **Independent reflections**                            | 2344 [R_{int} = 0.0331, R_{sigma} = 0.0174] |
| **Data/restraints/parameters**                         | 2344/0/136                                |
| **Goodness-of-fit on F\(^2\)**                         | 1.093                                     |
| **Final R indexes [I>=2σ (I)]**                        | R₁ = 0.0439, wR₂ = 0.1107                 |
| **Final R indexes [all data]**                         | R₁ = 0.0471, wR₂ = 0.1126                 |
| **Largest diff. peak/hole / e Å\(^{-3}\)**             | 0.24/-0.19                               |
X-ray crystal structure of 48

| Property                        | Value                        |
|--------------------------------|------------------------------|
| Empirical formula              | C_{19}H_{19}N_{3}O_{2}S       |
| Formula weight                 | 353.43                       |
| Temperature/K                  | 199.98                       |
| Crystal system                 | monoclinic                   |
| Space group                    | P2_1/n                       |
| a/Å                            | 11.1603(18)                  |
| b/Å                            | 10.1311(13)                  |
| c/Å                            | 15.642(3)                    |
| α/°                            | 90                           |
| β/°                            | 96.422(8)                    |
| γ/°                            | 90                           |
| Volume/Å³                      | 1757.5(5)                    |
| Z                              | 4                            |
| ρ calcul./g/cm³                | 1.336                        |
| μ/Åmm⁻¹                        | 0.202                        |
| F(000)                         | 744.0                        |
| Crystal size/mm³               | 0.601 × 0.144 × 0.096        |
| Radiation                      | MoKα (λ = 0.71073)           |
| 2θ range for data collection/° | 5.446 to 57.424              |
| Index ranges                   | -15 ≤ h ≤ 15, -13 ≤ k ≤ 13, -21 ≤ l ≤ 21 |
| Reflections collected          | 40943                        |
| Independent reflections        | 4531 [R_{int} = 0.0201, R_{sigma} = 0.0126] |
| Data/restraints/parameters     | 4531/0/232                   |
| Goodness-of-fit on F²          | 1.041                        |
| Final R indexes [I>=2σ (I)]    | R₁ = 0.0377, wR₂ = 0.1064    |
| Final R indexes [all data]     | R₁ = 0.0404, wR₂ = 0.1091    |
| Largest diff. peak/hole / e Å⁻³| 0.30/-0.42                  |
X-ray crystal structure of 54

| Property                          | Value                                      |
|-----------------------------------|--------------------------------------------|
| Empirical formula                 | C_{27}H_{25}N_{3}O_{2}                     |
| Formula weight                    | 423.50                                     |
| Temperature/K                     | 99.96                                      |
| Crystal system                    | monoclinic                                 |
| Space group                       | P2_1/c                                     |
| a/Å                               | 18.5268(18)                                |
| b/Å                               | 7.8990(7)                                  |
| c/Å                               | 15.0062(15)                                |
| α/°                               | 90                                         |
| β/°                               | 90                                         |
| γ/°                               | 90                                         |
| Volume/Å³                         | 2196.1(4)                                  |
| Z                                 | 4                                          |
| ρ_{calc}/g/cm³                    | 1.281                                      |
| μ/µm⁻¹                            | 0.082                                      |
| F(000)                            | 896.0                                      |
| Crystal size/mm³                  | 0.67 × 0.634 × 0.586                       |
| Radiation                         | MoKα (λ = 0.71073)                         |
| 2Θ range for data collection/°   | 5.158 to 59.232                            |
| Index ranges                      | -25 ≤ h ≤ 25, -10 ≤ k ≤ 10, -20 ≤ l ≤ 18  |
| Reflections collected             | 33215                                      |
| Independent reflections           | 6071 [R_{int} = 0.0301, R_{sigma} = 0.0244]|
| Data/restraints/parameters        | 6071/0/291                                 |
| Goodness-of-fit on F²             | 1.035                                      |
| Final R indexes [I>=2σ (I)]      | R₁ = 0.0399, wR₂ = 0.1039                  |
| Final R indexes [all data]        | R₁ = 0.0417, wR₂ = 0.1065                  |
| Largest diff. peak/hole / e Å⁻³   | 0.30/-0.22                                 |
X-ray crystal structure of 55

| Property                          | Value                      |
|-----------------------------------|----------------------------|
| Empirical formula                | C_{13}H_{15}N_3O_2S        |
| Formula weight                    | 277.34                     |
| Temperature/K                     | 100.0                      |
| Crystal system                    | monoclinic                 |
| Space group                       | P2_{1}/c                   |
| a/Å                               | 13.2046(16)                |
| b/Å                               | 9.1200(10)                 |
| c/Å                               | 11.4034(15)                |
| α°                                | 90                         |
| β°                                | 110.802(4)                 |
| γ°                                | 90                         |
| Volume/Å³                         | 1283.7(3)                  |
| Z                                 | 4                          |
| ρ_{calc} g/cm³                    | 1.435                      |
| μ/Å⁻¹                             | 0.254                      |
| F(000)                            | 584.0                      |
| Crystal size/mm³                  | 0.936 × 0.364 × 0.08       |
| Radiation                         | MoKα (λ = 0.71073)         |
| 2Θ range for data collection/°    | 5.554 to 57.434            |
| Index ranges                      | -17 ≤ h ≤ 17, -11 ≤ k ≤ 12, -15 ≤ l ≤ 15 |
| Reflections collected             | 13200                      |
| Independent reflections           | 3291 [R_{int} = 0.0244, R_{sigma} = 0.0217] |
| Data/restraints/parameters        | 3291/0/177                 |
| Goodness-of-fit on F²             | 1.043                      |
| Final R indexes [I>2σ(I)]        | R₁ = 0.0301, wR₂ = 0.0765  |
| Final R indexes [all data]       | R₁ = 0.0323, wR₂ = 0.0785  |
| Largest diff. peak/hole / e Å⁻³   | 0.41/-0.44                 |
X-ray crystal structure of 59

| Property                        | Value                          |
|---------------------------------|--------------------------------|
| Empirical formula               | C\textsubscript{12}H\textsubscript{12}N\textsubscript{2}O               |
| Formula weight                  | 200.24                         |
| Temperature/K                   | 99.98                          |
| Crystal system                  | monoclinic                     |
| Space group                     | P2\textsubscript{1}/c          |
| a/Å                             | 9.9515(8)                      |
| b/Å                             | 7.1269(6)                      |
| c/Å                             | 14.6312(11)                    |
| α/°                             | 90                             |
| β/°                             | 97.573(3)                      |
| γ/°                             | 90                             |
| Volume/Å³                       | 1028.64(14)                    |
| Z                               | 4                              |
| ρ\text{calc}/g/cm\textsuperscript{3} | 1.293                          |
| μ/µm\textsuperscript{-1}       | 0.084                          |
| F(000)                          | 424.0                          |
| Crystal size/mm\textsuperscript{3} | 0.596 × 0.575 × 0.55           |
| Radiation                       | MoKα (\(\lambda = 0.71073\))  |
| 2Θ range for data collection/°  | 4.128 to 61.154                |
| Index ranges                    | -14 ≤ h ≤ 14, -10 ≤ k ≤ 10, -20 ≤ l ≤ 20 |
| Reflections collected           | 31056                          |
| Independent reflections         | 3122 [R\text{int} = 0.0254, R\text{sigma} = 0.0119] |
| Data/restraints/parameters      | 3122/0/140                     |
| Goodness-of-fit on F\textsuperscript{2} | 1.087                          |
| Final R indexes [I\textgeq 2σ (I)] | R\text{f} = 0.0362, wR\text{f} = 0.1008 |
| Final R indexes [all data]      | R\text{f} = 0.0375, wR\text{f} = 0.1032 |
| Largest diff. peak/hole / e Å\textsuperscript{-3} | 0.39/-0.24                   |
X-ray crystal structure of 60

Empirical formula C_{18}H_{14}N_{2}O_{2}
Formula weight 290.31
Temperature/K 100.0
Crystal system triclinic
Space group P-1
a/Å 8.3733(5)
b/Å 8.8124(6)
c/Å 9.8006(7)
α/° 92.376(3)
β/° 94.925(2)
γ/° 91.733(2)
Volume/Å³ 719.47(8)
Z 2
ρ_{calc} g/cm³ 1.340
μ/mm⁻¹ 0.089
F(000) 304.0
Crystal size/mm³ 0.308 × 0.225 × 0.22
Radiation MoKα (λ = 0.71073)
2Θ range for data collection/° 6.096 to 59.182
Index ranges -11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -13 ≤ l ≤ 13
Reflections collected 18340
Independent reflections 4034 [R_{int} = 0.0232, R_{sigma} = 0.0213]
Data/restraints/parameters 4034/403/374
Goodness-of-fit on F² 1.191
Final R indexes [I>2σ (I)] R₁ = 0.0555, wR₂ = 0.1200
Final R indexes [all data] R₁ = 0.0572, wR₂ = 0.1207
Largest diff. peak/hole / e Å⁻³ 0.30/-0.26
X-ray crystal structure of 65

| Property                        | Value                      |
|---------------------------------|----------------------------|
| Empirical formula               | C_{26}H_{26}N_{2}O_{4}     |
| Formula weight                  | 430.49                     |
| Temperature/K                   | 100.01                     |
| Crystal system                  | monoclinic                 |
| Space group                     | P2_1/n                     |
| a/Å                             | 10.4697(7)                 |
| b/Å                             | 20.5978(15)                |
| c/Å                             | 11.0885(7)                 |
| α/°                             | 90                         |
| β/°                             | 116.053(2)                 |
| γ/°                             | 90                         |
| Volume/Å³                       | 2148.3(3)                  |
| Z                               | 4                          |
| ρ_{calc}/g/cm³                  | 1.331                      |
| μ/mm⁻¹                          | 0.090                      |
| F(000)                          | 912.0                      |
| Crystal size/mm³                | 0.496 × 0.446 × 0.198      |
| Radiation                       | MoKα (λ = 0.71073)         |
| 2Θ range for data collection/°  | 4.76 to 59.232             |
| Index ranges                    | -14 ≤ h ≤ 14, -28 ≤ k ≤ 28, -15 ≤ l ≤ 15 |
| Reflections collected           | 41436                      |
| Independent reflections         | 5990 [R_{int} = 0.0270, R_{sigma} = 0.0174] |
| Data/restraints/parameters      | 5990/0/291                 |
| Goodness-of-fit on F²           | 1.037                      |
| Final R indexes [I≥2σ (I)]     | R₁ = 0.0360, wR₂ = 0.0933  |
| Final R indexes [all data]      | R₁ = 0.0400, wR₂ = 0.0978  |
| Largest diff. peak/hole / e Å⁻³ | 0.40/-0.23                |
X-ray crystal structure of 69

| Property                        | Value                        |
|--------------------------------|------------------------------|
| Empirical formula              | C_{23}H_{20}N_{2}            |
| Formula weight                 | 324.41                       |
| Temperature/K                  | 175                          |
| Crystal system                 | triclinic                    |
| Space group                    | P-1                          |
| a/Å                            | 6.9386(7)                    |
| b/Å                            | 10.8785(10)                  |
| c/Å                            | 12.1498(10)                  |
| α/°                            | 92.955(3)                    |
| β/°                            | 99.134(3)                    |
| γ/°                            | 107.607(3)                   |
| Volume/Å³                      | 858.20(14)                   |
| Z                              | 2                            |
| ρ_{calc}/g/cm³                 | 1.255                        |
| μ/mm⁻¹                         | 0.074                        |
| F(000)                         | 344.0                        |
| Crystal size/mm³               | 0.517 × 0.459 × 0.152        |
| Radiation                      | MoKα (λ = 0.71073)           |
| 2Θ range for data collection/°| 6.266 to 57.404              |
| Index ranges                   | -9 ≤ h ≤ 9, -14 ≤ k ≤ 14, -16 ≤ l ≤ 16 |
| Reflections collected          | 21504                        |
| Independent reflections        | 4423 [R_{int} = 0.0220, R_{sigma} = 0.0206] |
| Data/restraints/parameters     | 4423/0/229                   |
| Goodness-of-fit on F²          | 1.032                        |
| Final R indexes [I>=2σ (I)]    | R₁ = 0.0393, wR₂ = 0.1033    |
| Final R indexes [all data]     | R₁ = 0.0415, wR₂ = 0.1054    |
| Largest diff. peak/hole / e Å⁻³| 0.34/-0.19                  |
X-ray crystal structure of 70-major

| Property                           | Value                      |
|------------------------------------|----------------------------|
| Empirical formula                  | C₂₄H₂₂N₂                   |
| Formula weight                     | 338.43                     |
| Temperature/K                      | 99.97                      |
| Crystal system                     | orthorhombic               |
| Space group                        | Pna₂₁                      |
| a/Å                                | 15.504(2)                  |
| b/Å                                | 16.8542(18)                |
| c/Å                                | 7.0717(9)                  |
| α/°                                | 90                         |
| β/°                                | 90                         |
| γ/°                                | 90                         |
| Volume/Å³                          | 1847.9(4)                  |
| Z                                  | 4                          |
| ρ<sub>calc</sub>/g/cm³             | 1.217                      |
| μ/μm<sup>-1</sup>                  | 0.071                      |
| F(000)                             | 720.0                      |
| Crystal size/mm³                   | 0.27 × 0.236 × 0.182       |
| Radiation                          | MoKα (λ = 0.71073)         |
| 2θ range for data collection/°     | 5.254 to 57.502            |
| Index ranges                       | -20 ≤ h ≤ 20, -22 ≤ k ≤ 22, -9 ≤ l ≤ 9 |
| Reflections collected              | 41884                      |
| Independent reflections            | 4791 [R<sub>int</sub> = 0.0313, R<sub>sigma</sub> = 0.0184] |
| Data/restraints/parameters         | 4791/1/237                 |
| Goodness-of-fit on F²              | 1.065                      |
| Final R indexes [I>=2σ (I)]       | R<sub>1</sub> = 0.0343, wR<sub>2</sub> = 0.0922 |
| Final R indexes [all data]        | R<sub>1</sub> = 0.0352, wR<sub>2</sub> = 0.0932 |
| Largest diff. peak/hole / e Å⁻³   | 0.33/-0.20                |
| Flack parameter                    | -0.2(5)                    |
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11. NMR spectra

$^1$H NMR (300 MHz, CD$_3$CN)

$^{13}$C NMR (75 MHz, CD$_3$CN)
$^{13}$C NMR (101 MHz, DMSO-$d_6$, 100 °C)

$^1$H NMR (400 MHz, DMSO-$d_6$, 100 °C)
$^{13}$C NMR (101 MHz, DMSO-$d_6$, 100 $^\circ$C)
$^1$H NMR (400 MHz, Chloroform-\textit{d})

$^{13}$C NMR (101 MHz, Chloroform-\textit{d})
$^1$H NMR (400 MHz, Chloroform-$d$)

$^{13}$C NMR (101 MHz, Chloroform-$d$)
$^1$H NMR (400 MHz, Chloroform-$d$)

![Chemical Structure](image1)

$^{13}$C NMR (101 MHz, Chloroform-$d$)

![Chemical Structure](image2)
$^1$H NMR (400 MHz, Chloroform-$d$)

$^{13}$C NMR (101 MHz, Chloroform-$d$)
\(^1\)H NMR (400 MHz, Chloroform-\(d\))

\(^{13}\)C NMR (101 MHz, Chloroform-\(d\))
$^1$H NMR (400 MHz, Chloroform-$d$)

\[
\begin{array}{ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
\end{array}
\]

$^{13}$C NMR (101 MHz, Chloroform-$d$)
$^1$H NMR (400 MHz, Chloroform-$d$)

$\text{tBu}$

\[
\begin{align*}
\text{N} & \text{CN} \\
11
\end{align*}
\]

$^{13}$C NMR (101 MHz, Chloroform-$d$)

$\text{tBu}$

\[
\begin{align*}
\text{N} & \text{CN} \\
11
\end{align*}
\]
$^1$H NMR (300 MHz, Chloroform-$d$)

$^{13}$C NMR (75 MHz, Chloroform-$d$)
$^1$H NMR (300 MHz, Chloroform-$d$)

13C NMR (75 MHz, Chloroform-$d$)
$^1$H NMR (300 MHz, Chloroform-d)

$^{13}$C NMR (75 MHz, Chloroform-d)
$^1$H NMR (300 MHz, Chloroform-$d$)

15

$^{13}$C NMR (75 MHz, Chloroform-$d$)

15
$^1$H NMR (300 MHz, Chloroform-$d$)

$^{13}$C NMR (75 MHz, Chloroform-$d$)
$^1$H NMR (300 MHz, Chloroform-$d$)

17

$^{13}$C NMR (75 MHz, Chloroform-$d$)

17
$^1$H NMR (300 MHz, Chloroform-$d$)

18

$^{13}$C NMR (75 MHz, Chloroform-$d$)

18
$^1\text{H NMR (300 MHz, Chloroform-$d$)}$

$^{13}\text{C NMR (75 MHz, Chloroform-$d$)}$
$^1$H NMR (300 MHz, Chloroform-d)

![NMR Spectrum](image)

$^1$C NMR (75 MHz, Chloroform-d)

![NMR Spectrum](image)
$^{1}$H NMR (300 MHz, Chloroform-$d$)

$^{13}$C NMR (75 MHz, Chloroform-$d$)
$^1$H NMR (300 MHz, Chloroform-$d$)

$^{13}$C NMR (75 MHz, Chloroform-$d$)
$^1$H NMR (300 MHz, Chloroform-$d$)

$^{13}$C NMR (75 MHz, Chloroform-$d$)
$^1$H NMR (300 MHz, Chloroform-$d$)

$^{13}$C NMR (75 MHz, Chloroform-$d$)
$^1$H NMR (300 MHz, Chloroform-$d$)

$^{13}$C NMR (75 MHz, Chloroform-$d$)
$^1$H NMR (300 MHz, Chloroform-$d$)

![NMR spectrum](image)

13C NMR (75 MHz, Chloroform-$d$)

![NMR spectrum](image)
$^1$H NMR (300 MHz, Chloroform-$d$)

![1H NMR spectrum](image)

$^{13}$C NMR (75 MHz, Chloroform-$d$)

![$^{13}$C NMR spectrum](image)
$^1$H NMR (300 MHz, Chloroform-$d$)

$^{13}$C NMR (75 MHz, Chloroform-$d$)
$^1$H NMR (300 MHz, Chloroform-$d$)

$^{13}$C NMR (75 MHz, Chloroform-$d$)
\( ^1\text{H NMR} (300 \text{ MHz, Chloroform-}d) \)

\[
\begin{array}{c}
\text{Ts} \\
\text{N}^+ \text{N}^- \\
\text{NH}_2 \\
30a
\end{array}
\]

\( ^{13}\text{C NMR} (75 \text{ MHz, Chloroform-}d) \)

\[
\begin{array}{c}
\text{Ts} \\
\text{N}^+ \text{N}^- \\
\text{NH}_2 \\
30a
\end{array}
\]
$^1$H NMR (300 MHz, Chloroform-$d$)

$^{13}$C NMR (75 MHz, Chloroform-$d$)
**1H NMR (300 MHz, Chloroform-d)**

![1H NMR spectrum](image)

**13C NMR (75 MHz, Chloroform-d)**

![13C NMR spectrum](image)
$^1$H NMR (300 MHz, Chloroform-$d$)

$^{13}$C NMR (75 MHz, Chloroform-$d$)
$^1$H NMR (300 MHz, Chloroform-$d$)

$^{13}$C NMR (75 MHz, Chloroform-$d$)

35
$^1$H NMR (300 MHz, Chloroform-$d$)

$^{13}$C NMR (75 MHz, Chloroform-$d$)
$^1$H NMR (300 MHz, Chloroform-$d$)

$^{13}$C NMR (75 MHz, Chloroform-$d$)
$^1$H NMR (300 MHz, Methylene Chloride-$d_2$)

$^{13}$C NMR (75 MHz, Methylene Chloride-$d_2$)
$^1$H NMR (400 MHz, Chloroform-$d$)

$^{13}$C NMR (101 MHz, Chloroform-$d$)
$^1$H NMR (400 MHz, Chloroform-$d$)

$^{13}$C NMR (101 MHz, Chloroform-$d$)
$^1$H NMR (400 MHz, Chloroform-$d$)

$^{13}$C NMR (101 MHz, Chloroform-$d$)
$^1$H NMR (400 MHz, Chloroform-$d$)

![NMR spectrum for $^1$H NMR](image)

$^{13}$C NMR (101 MHz, Chloroform-$d$)

![NMR spectrum for $^{13}$C NMR](image)
$^1$H NMR (400 MHz, Chloroform-$d$)

\[
\begin{array}{c}
\text{NC} \\
\text{Me} \\
\text{Ts}
\end{array}
\]

$^{13}$C NMR (101 MHz, Chloroform-$d$)

\[
\begin{array}{c}
\text{NC} \\
\text{Me} \\
\text{Ts}
\end{array}
\]
$^1$H NMR (400 MHz, DMSO-$d_6$, 100 °C)

$^{13}$C NMR (101 MHz, DMSO-$d_6$, 100 °C)
$^1$H NMR (400 MHz, DMSO-$d_6$, 100 °C)

$^{13}$C NMR (101 MHz, DMSO-$d_6$, 100 °C)
$^1$H NMR (400 MHz, DMSO-$d_6$, 100 °C)

$^{13}$C NMR (101 MHz, DMSO-$d_6$, 100 °C)
$^1$H NMR (400 MHz, DMSO-\textit{d}_6, 100 \degree\text{C})

$^{13}$C NMR (101 MHz, DMSO-\textit{d}_6, 100 \degree\text{C})
$^1$H NMR (400 MHz, DMSO-$d_6$, 100 °C)

$^{13}$C NMR (101 MHz, DMSO-$d_6$, 100 °C)
$^1$H NMR (400 MHz, DMSO-$d_6$, 100 °C)

13C NMR (101 MHz, DMSO-$d_6$, 100 °C)
$^1$H NMR (400 MHz, Chloroform-$d$)

$^{13}$C NMR (101 MHz, Chloroform-$d$)
$^1$H NMR (300 MHz, Chloroform-d)

\[ \begin{array}{c}
\text{NC} \\
\text{56}
\end{array} \]

$^{13}$C NMR (75 MHz, Chloroform-d)

\[ \begin{array}{c}
\text{NC} \\
\text{56}
\end{array} \]
$^1$H NMR (400 MHz, Chloroform-$d$)

$^{13}$C NMR (101 MHz, Chloroform-$d$)
$^1$H NMR (400 MHz, Chloroform-$d$)

$^{13}$C NMR (101 MHz, Chloroform-$d$)
$^1$H NMR (400 MHz, Chloroform-$d$)

$^{13}$C NMR (101 MHz, Chloroform-$d$)
$^{1}H$ NMR (400 MHz, Chloroform-$d$)

$^{13}C$ NMR (101 MHz, Chloroform-$d$)

N
O
NC
H
Bn

N
O
NC
H
Bn

60

60
$^1$H NMR (400 MHz, Chloroform-$d$)

$^{13}$C NMR (101 MHz, Chloroform-$d$)
$^1$H NMR (400 MHz, Chloroform-$d$)

13C NMR (101 MHz, Chloroform-$d$)
**\(^1\)H NMR (400 MHz, Chloroform-\(d\))**

**\(^{13}\)C NMR (101 MHz, Chloroform-\(d\))**
$^1$H NMR (400 MHz, Chloroform-$d$)

$^{13}$C NMR (101 MHz, Chloroform-$d$)
$^{1}H$ NMR (400 MHz, Chloroform-$d$)

$^{13}C$ NMR (101 MHz, Chloroform-$d$)
$^1$H NMR (400 MHz, Chloroform-$d$)

$^{13}$C NMR (101 MHz, Chloroform-$d$)
$^1$H NMR (400 MHz, Chloroform-$d$)

$^{13}$C NMR (101 MHz, Chloroform-$d$)
$^1$H NMR (400 MHz, Chloroform-$d$)

\[ \text{N} \quad \text{CN} \quad \text{Me} \]

$^{13}$C NMR (101 MHz, Chloroform-$d$)

\[ \text{N} \quad \text{CN} \quad \text{Me} \]
$^1$H NMR (400 MHz, Chloroform-$d$)

$^{13}$C NMR (101 MHz, Chloroform-$d$)
$^1$H NMR (400 MHz, Chloroform-$d$)

$^{13}$C NMR (101 MHz, Chloroform-$d$)
$^1$H NMR (400 MHz, Chloroform-$d$)

$^{13}$C NMR (101 MHz, Chloroform-$d$)
$^1$H NMR (400 MHz, Chloroform-$d$)

$^{13}$C NMR (101 MHz, Chloroform-$d$)
