# Supporting Information for

**Iron-Catalyzed α-C–H functionalization of π-Bonds: Cross-Dehydrogenative Coupling and Mechanistic Insights**

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General Information:

General Reagent Information: Anhydrous tetrahydrofuran, 1,2-dichloroethane, and trifluorotoluene were purchased from Acros (AcroSeal packaging), Sigma Aldrich (Sure/Seal packaging), and Frontier Scientific (J&KSeal packaging), respectively, and were transferred into an argon-filled glovebox and used as received. Other dry solvents were obtained by distillation and storage over 4Å molecular sieves. Triphenylcarbenium tetrafluoroborate (Ph₃C⁺BF₄⁻) was purchased from Alfa Aesar and stored in an argon-filled glove box. All other reagents were purchased from Oakwood, Acros, Alfa Aesar, or Sigma Aldrich and used as received. Compounds were purified by flash column chromatography using SiliCycle SiliaFlash® F60 silica gel, unless otherwise indicated.

General Analytical Information: New compounds were characterized by ¹H NMR, ¹³C NMR and HRMS. Copies of the ¹H NMR and ¹³C NMR spectra can be found at the end of the Supporting Information. ¹H and ¹³C NMR spectra were recorded on Bruker 400 MHz or 500 MHz instruments. All ¹H NMR data are reported in δ units, parts per million (ppm), and were measured relative to the residual proton signal in the deuterated solvent at 7.26 ppm (CDCl₃) or 5.32 ppm (CD₂Cl₂). All ¹³C NMR spectra are ¹H decoupled and reported in ppm relative to the solvent signal at 77.16 ppm (CDCl₃) or 53.84 ppm (CD₂Cl₂). Thin-layer chromatography (TLC) was performed on Silicycle 250 μm (analytical) or 1000 μm (preparative) silica gel plates. Compounds were visualized by irradiation with UV light, or by staining with iodine/silica gel, potassium permanganate, or phosphomolybdic acid (PMA). Yields refer to isolated compounds, unless otherwise indicated. High resolution mass spectra were recorded on a Thermo Scientific Q-Exactive mass spectrometer. NMR yield was determined by using 1,1,2,2-tetrachloroethane as internal standard for ¹H spectroscopy and using CDCl₃ as internal standard for ²H spectroscopy.
Mechanistic experiments

Stoichiometric experiments for Cp-based complexes.

In an argon-filled glovebox, an NMR tube was charged with 1l-I(Cp) (0.029 mmol, 10 mg) and CD$_2$Cl$_2$ (0.5 mL), then the base (1.0 equiv) was added into the above solution. The NMR tube was capped and removed from the glovebox and shaken by hand. $^1$H NMR spectra were then recorded after 5 min, 10 min, 20 min, 30 min, 1 h, and 2 h. The position of the equilibrium was determined by integration of the Cp signal of the cationic and neutral Fp-alkyne complexes. Equilibrium was established within 1 h for all bases examined.

Note: The $K_{eq}$ of sym-collidine is not determined because 1l-I(Cp) was transformed to the by-product for which we have so far not been able to assign a definitive structure.

In an argon-filled glovebox, 1l-II(Cp), prepared from 1l-I(Cp) (approx. 0.03 mmol), was dissolved in CD$_2$Cl$_2$ (0.5 mL) and added to an NMR tube charged with Ph$_3$C$^+$BF$_4^-$ (12 mg, 1.2 equiv). The NMR tube was capped and removed from the glovebox and shaken by hand. $^1$H NMR spectra were acquired after 5 min.
The Fe complex 1l-III (Cp) is stable to collect for $^1$H NMR and HRMS. To a solution of 1l-II(Cp) prepared from above (approx. 0.2 mmol) in dry CH$_2$Cl$_2$ (2 mL) was added Ph$_3$C$^+$BF$_4^-$ (66 mg, 0.2 mmol, 1.0 equiv.) as a solid in the argon-filled glove box. The mixture was stirred under N$_2$ at room temperature for 1.5 h. Then dry diethyl ether (5 mL) was added to the above solution. The desired product precipitated as an orange solid, which was collected on a frit, and further dried in vacuo (84 mg, 71% yield).

In an argon-filled glovebox, 1l-III(Cp) (0.012 mmol, 7 mg) was added to an NMR tube and dissolved in CD$_2$Cl$_2$ (0.5 mL). Then 3-hexyne (0.036 mmol, 4 µL, 3 equiv) was added to the above solution. The NMR tube was capped and removed from the glovebox and shaken by hand. A $^1$H NMR spectrum was acquired after 5 min. Then the NMR tube was placed in an oil bath, preheated to 40 °C, and another spectrum was acquired after 25 min, and then after 12 h. The alkyne exchange with Cp as the supporting ligand was still incomplete (80% conversion) after 12 hours. 1l-III(Cp)/6e or 1l-III(Cp)/ 1l-I(Cp) = 1:4.
An experiment in which 3-hexyne was added directly to an NMR tube containing \textit{in situ} generated 11-III(Cp) showed largely identical results (80% NMR yield of 6e after 12 h at 40 °C). The allenyl complex 11-II(Cp) was observed after addition of Et3N.

Stoichiometric experiments for Cp*-based complexes.

In an argon-filled glovebox, an NMR tube was charged with 11-I(Cp*) (0.024 mmol, 10 mg) and CD2Cl2 (0.5 mL), then the base (1.0 equiv) was added into the above solution. The NMR tube was capped and removed from the glovebox and shaken by hand. 1H NMR spectra were then recorded after 5 min, 10 min, 20 min, 30 min, 1 h, and 2h. The
position of the equilibrium was determined by integration of the Cp signal of the cationic and neutral Fp-alkyne complexes. Equilibrium was established within 2h for all bases examined, except in the case of TMPH.

**NOTE:** The equilibrium constant for the deprotonation of 1l-I(Cp*) by TMPH could not be determined, as equilibrium was not reached even after 24 h and the NMR sample had started to undergo decomposition.

In an argon-filled glovebox, 1l-II(Cp*) (0.03 mmol) was dissolved in CD$_2$Cl$_2$ (0.5 mL) and added to an NMR tube containing Ph$_3$C$^+$BF$_4^-$ (12 mg, 1.2 equiv). The NMR tube was removed from the glovebox and shaken by hand. $^1$H NMR spectra were acquired in 5 min. It showed the reaction was done determined by comparing the position of CH$_3$ groups in spectrum.

**NOTE:** The Fe complex 1l-III(Cp*) is not stable and will decompose to the product 6e slowly.
Because of the instability of Fe complex 11-III(Cp*), we conduct the alkyne-exchange experiments in one pot. The procedure is as following:

In an argon-filled glovebox, 11-II(Cp*) (0.03 mmol) was dissolved in CD₂Cl₂ (0.5 mL) and added to an NMR tube containing Ph₃C⁺BF₄⁻ (12 mg, 1.2 equiv) and 3-hexyne (10 µL, 0.09 mmol, 3.0 equiv). The NMR tube was removed from the glovebox and shaken by hand. ¹H NMR spectra were acquired after 5 min, 20 min, 50 min, 2 h and 3 h.

In contrast to the sluggish alkyne exchange for 11-III(Cp) (incomplete even after 12 h at 40 °C), the exchange of 3-hexyne with 11-III(Cp*) took place readily at room temperature, and was complete after 3 h.

These observations are consistent with rapid irreversible functionalization and rate-determining deprotonation observed for the optimized catalytic system.
In an argon-filled glovebox, 11-II(Cp*) (0.021 mmol) and 11-II(Cp) (0.023 mmol) was dissolved in CD$_2$Cl$_2$ (0.5 mL) and added to an NMR tube containing Ph$_3$C$^+$BF$_4^-$ (15 mg, 0.054 mmol, 1.2 equiv). The NMR tube was removed from the glovebox and shaken by hand. $^1$H NMR spectra were acquired in 5 min and 10 min. The CH$_3$ groups of 11-II(Cp*) and 11-II(Cp) are well-resolved as doublets in the $^1$H spectra. The spectrum of product is complicated because of the presence of rotamers and diastereomers. Thus, we are unable to determine the NMR yield of the products based on the spectrum. However, after 5 min, 11-II(Cp*) could no longer be observed, while a trace of 11-II(Cp) remained. After 10 min, 11-II(Cp) could no longer be observed.

**Kinetic isotope effect experiments**
In an argon-filled glovebox, \( \text{Cp}^\ast\text{Fe(CO)}_2\text{(thf)}^+\text{BF}_4^- \) (24.4 mg, 10 mol%, \( \text{Ph}_3\text{C}^+\text{BF}_4^- \) (300 mg, 0.9 mmol, 1.5 equiv), dry 1,2-dichloroethane (1.2 mL), \( 1\text{a} \) (39 µL, 0.3 mmol, 1.0 equiv), \( 1\text{a-d}_3 \) (36 mg, 0.3 mmol, 1.0 equiv) and 2,4,6-collidine (120 µL, 0.9 mmol, 1.5 equiv) were added to a flame-dried screw-cap reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) in rapid succession. The reaction tube was capped with a Teflon/silicone septum (Thermo/National part # C4015-66A) screw cap and removed from the glovebox. The reaction tube was then placed in an oil bath, preheated to 60 °C, where it was stirred for 2 h. The crude mixture was concentrated in vacuo and purified by flash column chromatography to provide a mixture of \( 6\text{a} \) and \( 6\text{a-d}_2 \) (20% NMR yield, 85:15 ratio, 31 mg, 14% yield).

In an argon-filled glovebox, \( \text{Cp}^\ast\text{Fe(CO)}_2\text{(thf)}^+\text{BF}_4^- \) (10 mol%, 12.2 mg), \( \text{Ph}_3\text{C}^+\text{BF}_4^- \) (150 mg, 0.45 mmol, 1.5 equiv), dry 1,2-dichloroethane (0.6 mL), \( 1\text{a} \) (39 µL, 0.3 mmol, 1.0 equiv) or \( 1\text{a-d}_3 \) (36 mg, 0.3 mmol, 1.0 equiv) and 2,4,6-collidine (60 µL, 0.45 mmol, 1.5 equiv) were added to a flame-dried screw-cap reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) in rapid succession. The reaction tube was capped with a Teflon/silicone septum (Thermo/National part # C4015-66A) screw cap and removed from the glovebox. The reaction tube was then placed in an oil bath, preheated to 60 °C, where it was stirred for 2 h or 12 h. The NMR yield was then determined by \(^1\text{H} \) and \(^2\text{H} \) NMR spectroscopy. We note that for \( 1\text{a-d}_3 \), the reaction was sluggish and low isolated yield was obtained after 48 h. This is due to formation of the by-product of \( 1\text{a-d}_3 \) and deactivation of the catalyst. Hence, absolute rate constant measurements could not be made. Nevertheless, the observation of a primary kinetic isotope effect by competition and by parallel experiments indicates that deprotonation is the turnover-limiting step of the catalytic cycle.
Isotope crossover/exchange experiments

In an argon-filled glovebox, Cp*Fe(CO)₂(thf)BF₄⁻ (4.1 mg, 10 mol%), Ph₃C⁺BF₄⁻ (50 mg, 0.15 mmol, 1.5 equiv), dry trifluorotoluene(0.5 mL), 1a-d₃ (0.1 mmol, 1.0 equiv) 2,6-lutidinium tetrafluoroborate (0.5 equiv or 1.0 equiv) and 2,4,6-collidine (20 µL, 0.15 mmol, 1.5 equiv) were added in rapid succession. The reaction tube was capped and removed from the glovebox. The reaction tube was then placed in an oil bath, preheated to 60 °C, where it was stirred for 48 h. The crude product was then analyzed by ¹H and ²H NMR spectroscopy. In both cases, only 6a-d₂ was observed, while 6a-d and 6a were not detected. Note: PhCF₃ was instead of 1,2-dichloroethane as the solvent in this experiment because signals for 6a and DCE both appear around 3.7 ppm.

In an argon-filled glovebox, Cp*Fe(CO)₂(thf)BF₄⁻ (8.2 mg, 10 mol %), Ph₃C⁺BF₄⁻ (100 mg, 0.3 mmol, 1.5 equiv), dry trifluorotoluene (1.0 mL), 1a-d₃ (0.1 mmol, 1.0 equiv), 1f (0.1 mmol, 1.0 equiv), and 2,4,6-collidine (40 µL, 0.3 mmol, 1.5 equiv) were added to a screw-cap reaction tube in rapid succession. The reaction tube was capped and removed from the glovebox. The reaction tube was then placed in an oil bath, preheated to 60 °C, where it was stirred for 48 h. After cooling down to room temperature, the internal standard CDCl₃ was used for ²H spectroscopy and the internal standard 1,1,2,2-tetrachloroethane was used for ¹H spectroscopy. None of the crossover products could be observed by ¹H or ²H NMR spectroscopy. Note: PhCF₃ was instead of 1,2-dichloroethane as the solvent in this experiment because signals for 6a and DCE both appear around 3.7 ppm.

The above two control experiments indicate that the deprotonation of alkyne is an irreversible process, consistent with the previous result that deprotonation is the turnover-limiting step.
Optimization of reaction conditions

1. Optimization of the protecting group.

\[
\begin{align*}
\text{1a} + \text{2,4,6-Collidine} & \rightarrow \text{3} \\
[\text{Cp}^*\text{Fe(CO)}_2(\text{thf})][\text{BF}_4^-] & + \text{Ph}_3\text{C}^+\text{BF}_4^- (1.5 \text{ equiv}) \\
\text{DCE (0.5 mL), 60 °C} & \\
\end{align*}
\]

| Entry | PG         | NMR Yield (%) \(^b\) |
|-------|------------|-----------------------|
| 1     | CO\textsubscript{2}Me | 55                    |
| 2     | CO\textsubscript{2}Bn | 40                    |
| 3     | Fmoc       | 43                    |
| 4     | Piv        | 31                    |
| 5     | P(\text{O})(\text{OEt})\textsubscript{2} | No Product            |
| 6     | Boc        | No Product            |
| 7     | CF\textsubscript{3}C(\text{O}) | No Product            |

\(^{a}\) All reactions were carried out with 1\(a\) (0.1 mmol), 2\(a\) (1.5 equiv), Ph\(_3\)C\(^+\)BF\(_4^-\) (1.5 equiv), 2,4,6-collidine (1.5 equiv), Cp\(^*\)Fe(CO\(_2\))(\text{thf})BF\(_4^-\) (30 mol\%) and dry DCE (0.5 mL) at 60 °C. \(^{b}\) NMR yield was determined by using 1,1,2,2-tetrachloroethane as internal standard.

2. Optimization of reagent ratio.

\[
\begin{align*}
\text{1a} + \text{2a} & \rightarrow \text{3a} \\
[\text{Cp}^*\text{Fe(CO)}_2(\text{thf})][\text{BF}_4^-] & + \text{Ph}_3\text{C}^+\text{BF}_4^- (1.5 \text{ equiv}) \\
\text{DCE (0.5 mL), 60 °C} & \\
\end{align*}
\]

| Entry | 1a: 2a: Ph\(_3\)CBF\(_4^-\): Collidine | NMR Yield (%) \(^b\) |
|-------|--------------------------------------|-----------------------|
| 1     | 1.0:1.5:1.5:1.8                      | 55                    |
| 2     | 1.0:1.8:1.8:1.8                      | No Product            |
| 3     | 1.0:2.0:2.0:2.5                      | 47                    |
| 4     | 1.0:1.5:1.7:1.8                      | 62                    |
| 5     | 1.0:1.5:1.5:2.5                      | 47                    |
| 6     | 2.0:1.0:1.0:1.0                      | 8                     |
| 7     | 2.0:1.0:1.0:1.2                      | 29                    |

\(^{a}\) All reactions were carried out with 1\(a\) (0.1 mmol), 2\(a\) (x equiv), Ph\(_3\)C\(^+\)BF\(_4^-\) (x equiv), 2,4,6-collidine (x equiv), Cp\(^*\)Fe(CO\(_2\))(\text{thf})BF\(_4^-\) (30 mol\%) and dry DCE (0.5 mL) at 60 °C. \(^{b}\) NMR yield was determined by using 1,1,2,2-tetrachloroethane as internal standard.
3. Optimization of the anion.

\[
\text{Ph} = \underset{\text{Me}}{\text{-}} \quad + \quad \text{N} \quad \text{Ph} \quad \text{Me} \quad \text{+ \text{CO}_{2}\text{Me}}
\]

\[
1a \quad + \quad 2a \quad \text{[Cp*Fe(CO)_2(thf)]}^{+}[\text{BF}_4^-] \quad \text{Ph}_3\text{C}^+X^- \quad [\text{Ph}_3\text{C}]^-[X]
\]

\[
\text{2,4,6-collidine (0.5 mL), 60 °C}
\]

| Entry | Ph₃C⁻X⁻ | NMR Yield (%) \(^b\) |
|-------|---------|----------------------|
| 1     | Ph₃C⁺BF₄⁻ | 62                  |
| 2     | Ph₃C⁺ClO₄⁻ | 17                  |
| 3     | Ph₃CCl + GaCl₃ | No Product         |
| 4     | Ph₃C⁺PF₆⁻ | trace               |
| 5     | Ph₃C⁺SbCl₆⁻ | No Product         |

\(^a\) All reactions were carried out with 1a (0.1 mmol), 2a (1.5 equiv), Ph₃C⁻X⁻ (1.7 equiv), 2,4,6-collidine (1.8 equiv), Cp*Fe(CO)₂(thf)BF₄ (30 mol%) and dry DCE (0.5 mL) at 60 °C. \(^b\) NMR yield was determined by using 1,1,2,2-tetrachloroethane as internal standard.

4. Optimization of solvent and catalyst loading.

\[
\text{Ph} = \underset{\text{Me}}{\text{-}} \quad + \quad \text{N} \quad \text{Ph} \quad \text{Me} \quad \text{+ \text{CO}_{2}\text{Me}}
\]

\[
1a \quad + \quad 2a \quad \text{[Cp*Fe(CO)_2(thf)]}^{+}[\text{BF}_4^-] \quad \text{Ph}_3\text{C}^+X^- \quad [\text{Ph}_3\text{C}]^-[X]
\]

\[
\text{2,4,6-collidine (1.8 eq.)} \quad \text{Sol. (0.5 mL), 60 °C}
\]

| Entry | Loading of [Fe] (%) | Solvents | NMR Yield (%) \(^b\) |
|-------|---------------------|----------|----------------------|
| 1     | 30                  | DCE      | 62                  |
| 2     | 30                  | CHCl₃    | 60                  |
| 3     | 30                  | C₆H₄F₂   | 70                  |
| 4     | 30                  | PhCl     | 76                  |
| 5     | 30                  | t-BuOMe  | No Product          |
| 6     | 30                  | PhCF₃    | 83                  |
| 7     | 20                  | PhCF₃    | 77                  |
| 8     | 10                  | PhCF₃    | 56                  |

\(^a\) All reactions were carried out with 1a (0.1 mmol), 2a (1.5 equiv), Ph₃C⁺BF₄⁻ (1.7 equiv), 2,4,6-collidine (1.8 equiv), Cp*Fe(CO)₂(thf)BF₄ (x mol%) and dry solvent (0.5 mL) at 60 °C. \(^b\) NMR yield was determined by using 1,1,2,2-tetrachloroethane as internal standard.
5. Optimization of the temperature.\textsuperscript{a}

\[
\begin{array}{ccc}
\text{Entry} & T (\degree C) & \text{NMR Yield} (\%) \text{\textsuperscript{b}} \\
1 & 25 & 12 \\
2 & 40 & 28 \\
3 & 60 & 43 \\
4 & 80 & 38 \\
\end{array}
\]

\textsuperscript{a} All reactions were carried out with \textit{1I} (0.1 mmol), Ph\textsubscript{3}C\textsuperscript{+}BF\textsubscript{4}\textsuperscript{-} (1.5 equiv), 2,4,6-collidine (1.5 equiv), Cp*Fe(CO)\textsubscript{2}(3-hexyne)\textsuperscript{+}BF\textsubscript{4}– (10 mol%) and dry DCE (0.5 mL). \textsuperscript{b} NMR yield was determined by using 1,1,2,2-tetrachloroethane as internal standard.

Characterization data for iron complexes.

\[
\begin{align*}
\text{\textsuperscript{1}H NMR} & (500 \text{ MHz, CDCl}_3) \delta 5.64 (\text{br s}, 5\text{H}), 2.71 (\text{br s}, 4\text{H}), 1.39 (\text{br s}, 6\text{H}) \\
\text{\textsuperscript{13}C NMR} & (125 \text{ MHz, CDCl}_3) \delta 207.9, 89.3, 50.3, 20.1, 15.2 \\
\text{\textsuperscript{19}F NMR} & (470 \text{ MHz, CDCl}_3) \delta -151.3 \\
\text{HRMS} & (\text{ESI}) \text{ calcd for C}_{13}\text{H}_{15}\text{O}_2\text{Fe [M–BF}_4^\text{-}]^+: 259.0416, \text{ found: 259.0424.}
\end{align*}
\]

To a solution of \textit{1I-I(Cp)} (69 mg, 0.2 mmol) in dry CH\textsubscript{2}Cl\textsubscript{2} (2 mL) was added triethylamine (28 \text{\mu L}, 1.0 equiv.) under N\textsubscript{2}. The mixture was stirred at room temperature
for 0.5 h. The solvent was removed under reduced pressure, and the residue was extracted with dry ether and filtered through Celite to remove the insoluble triethylammonium tetrafluoroborate. The filtrate was concentrated to give the crude product 1l-II(Cp) as a yellow oil. The major peaks of the $^1$H NMR spectrum could be assigned, but an analytically pure sample of 1l-II(Cp) could not be obtained.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 4.80 (s, 5H), 4.50-4.35 (m, 1H), 2.10-1.90 (m, 2H), 1.52 (d, $J = 6.4$ Hz, 3H), 1.00 (t, $J = 6.8$ Hz, 3H).

$^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ 216.5, 216.3, 199.5, 85.8, 84.6, 75.4, 36.1, 15.1, 15.0.

HRMS (ESI) calcd for C$_{13}$H$_{15}$O$_2$Fe [M+H]$^+$: 259.0416, found: 259.0419.

To a solution of 1l-II(Cp) prepared from above (approx. 0.2 mmol) in dry CH$_2$Cl$_2$ (2 mL) was added Ph$_3$C$^+$BF$_4^-$ (66 mg, 0.2 mmol, 1.0 equiv.) as a solid in the argon-filled glove box. The mixture was stirred under N$_2$ at room temperature for 1 h. Then dry ether (5 mL) was added to the above solution. The desired product precipitated as an orange solid, which was collected on a frit, and further dried in vacuo (84 mg, 71% yield).

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.35 (s, 15H), 5.45 (s, 5H), 4.65 (s, 1H), 2.33 (s, 2H), 1.41 (s, 3H), 0.87 (s, 3H).

HRMS (ESI) calcd for C$_{32}$H$_{29}$O$_2$Fe [M–BF$_4^-$]$^+$: 501.1511, found: 501.1501.

Dicarbonylpentamethylcyclopentadienyliiron(II)-alkyne complex 1l-I(Cp*) was synthesized according to a modification of a literature procedure. Under N$_2$, a solution of 3-hexyne (0.7 mL, 6 mmol, 3.0 equiv) in dry toluene (20 mL) was added to a 50 mL flame-dried round-bottom flask, charged with Cp*Fe(CO)$_2$I (748 mg, 2 mmol), AgBF$_4$ (400 mg, ~2 mmol), and a stir bar. The obtained suspension was stirred at 50 °C for 2-3 h. Subsequently, the reaction mixture was allowed to cool to room temperature and filtered through a pad of Celite. The filter cake was rinsed with CH$_2$Cl$_2$ until the filtrate turned colorless. The desired iron complex 1l-I(Cp*) was collected as brown solid (776 mg, 93%) upon concentration in vacuo.

$^1$H NMR (500 MHz, CDCl$_3$) δ 2.56 (q, $J = 7.0$ Hz, 4H), 1.89 (s, 15H), 1.42 (t, $J = 7.0$ Hz, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 211.1, 102.4, 60.3, 18.8, 16.1, 9.5.

$^{19}$F NMR (470 MHz, CDCl$_3$) δ –153.4.
To a solution of **1I-I(Cp*)** (12.5 mg, 0.03 mmol) in dry CH$_2$Cl$_2$ (0.5 mL) was added triethylamine (4 µL, 1.0 equiv.) under N$_2$. The mixture was stirred at room temperature for 0.5 h. The solvent was removed under reduced pressure, and the residue was extracted with dry ether, filtered through Celite to remove the insoluble triethylammonium tetrafluoroborate. The filtrate was concentrated to give the crude product **1I-II(Cp*)** as a yellow oil.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 4.56-4.43 (m, 1H), 2.10-1.97 (m, 2H), 1.80 (s, 15H), 1.63 (d, $J = 6.8$ Hz, 3H), 1.06 (t, $J = 7.2$ Hz, 3H).

The precatalyst was synthesized according to a modification of literature procedures. A mixture of (η$_5$-C$_5$Me$_5$)Fe(CO)$_2$I (1.53 g, 4 mmol) and AgBF$_4$ (800 mg, ~4.0 mmol) was stirred in THF (22 mL) overnight under N$_2$. The solvent was removed in vacuo, the residue was extracted with CH$_2$Cl$_2$, and the solution was filtered through Celite to remove AgI, and the filter cake was washed with CH$_2$Cl$_2$ until the filtrate became colorless. The filtrate was concentrated to 10 mL and diethyl ether (Et$_2$O) was added to precipitate the product as a red crystalline solid. After cooling the mixture at -20 °C for 2 h, the crystals were collected, washed with Et$_2$O, and dried in vacuo to give red crystals Fp*(thf)BF$_4$ (1.47 g, 91% yield).

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 3.42 (t, $J = 6.4$ Hz, 4H), 1.88-1.82 (m, 4H), 1.77 (s, 15H).

$^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ 210.8, 98.5, 80.8, 26.2, 9.4.

$^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) δ -152.1.

The spectroscopic data were identical in all respects to those previously reported.

HRMS (ESI) calcd for C$_{14}$H$_{18}$O$_2$NFe [M – C$_4$H$_8$O + C$_2$H$_3$N – BF$_4$]$^+$: 288.0681, found: 288.0683.

**General procedure A for propargylic C-H functionalization of alkynes.**

A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a
magnetic stir bar was capped with a Teflon/silicone septum (Thermo/National part # C4015-66A) screw cap and flame dried under vacuum. The reaction tube was cooled under argon and transferred into a nitrogen-filled glovebox. In the glovebox, the suspension of carbamate (2, 0.45 mmol, 1.5 equiv) and Ph₃C⁺BF₄⁻ (168 mg, 0.51 mmol, 1.7 equiv) in dry trifluorotoluene (1 mL) was stirred at room temperature for 3 hours to generate the iminium salt. Then [Cp*Fe(CO)₂(thf)]⁺[BF₄]⁻ (20 mol%, 24.6 mg), alkyne 1 (0.3 mmol, 1.0 equiv), trifluorotoluene (0.5 mL) and sym-collidine (72 µL, 0.54 mmol, 1.8 equiv) were added in rapid succession. The reaction tube was capped and removed from the glovebox. The reaction tube was placed in an oil bath, preheated to 60 °C, where it was stirred for 48 h. After completion of the reaction, the reaction mixture was cooled to room temperature. The crude mixture was concentrated in vacuo and purified by flash column chromatography to provide the desired product 3.

Characterization Data for Products 3:

Methyl 1-(3-phenylprop-2-yn-1-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (3aa): Prepared following general procedure A, using prop-1-yn-1-ylbenzene (1a, 39 µL, 0.3 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (2a, 86.1 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with pure DCM to provide the product 3aa as a colorless oil (66 mg, 72% yield).

1H NMR (500 MHz, CDCl₃, rotamers seen) δ 7.31-7.21 (m, 2H), 7.21-7.15 (m, 4H), 7.15-7.09 (m, 2H), 7.09-7.01 (m, 1H), 5.33 (t, J = 6.0 Hz, 0.5H), 5.26 (t, J = 6.5 Hz, 0.5H), 4.20-4.10 (m, 0.5H), 3.94-3.81 (m, 0.5H), 3.67 (s, 1.5H), 3.66 (s, 1.5H), 3.61-3.49 (m, 0.5H), 3.46-3.34 (m, 0.5H), 2.97-2.68 (m, 4H).

13C NMR (125 MHz, CDCl₃, rotamers seen) δ 156.0, 135.7, 135.5, 134.42, 134.37, 131.4, 129.0, 128.5, 128.2, 128.1, 127.8, 127.6, 127.4, 127.1, 127.0, 126.2, 126.1, 123.6, 123.4, 86.8, 86.5, 82.9, 53.7, 52.73, 52.67, 39.3, 38.2, 28.7, 28.4, 27.5, 27.2.

HRMS (ASAP) calcd for C₂₀H₂₀O₂N [M+H]⁺: 306.1494, found: 306.1480.

Methyl 1-(3-(4-fluorophenyl)prop-2-yn-1-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (3ba): Prepared following general procedure A, using 1-fluoro-4-(prop-1-
yn-1-yl)benzene (1b, 40.2 mg, 0.3 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (2a, 86.1 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with pure DCM to provide the product 3ba as a colorless oil (64 mg, 66% yield).

\[ \text{HNMR (500 MHz, CDCl}_3, \text{ rotamers seen)} \delta \ 7.38-7.18 (m, 5H), 7.18-7.10 (m, 1H), 7.02-6.96 (q, \ J = 8.5 Hz, 2H), 5.41 (t, \ J = 6.0 Hz, 0.5H), 5.33 (t, \ J = 6.5 Hz, 0.5H), 4.30-4.18 (m, 0.5H), 4.05-3.91 (m, 0.5H), 3.75 (s, 1.5H), 3.74 (s, 1.5H), 3.66-3.56 (m, 0.5H), 3.52-3.40 (m, 0.5H), 3.05-2.73 (m, 4H).

\[ \text{FNMR (470 MHz, CDCl}_3, \text{ rotamers seen)} \delta -111.6, -111.9.

\[ \text{CNMR (125 MHz, CDCl}_3, \text{ rotamers seen)} \delta 163.2, 163.1, 161.2, 161.1, 156.1, 135.6, 135.5, 134.4, 134.3, 133.3, 133.2, 131.4, 129.0, 128.5, 127.3, 127.1, 127.0, 126.2, 126.1, 119.7, 119.5, 115.5, 115.4, 115.3, 115.2, 86.1, 86.5, 81.83, 81.77, 53.7, 53.6, 52.73, 52.68, 39.2, 38.2, 28.7, 28.4, 27.5, 27.1 (the \text{CNMR spectrum is too complicated to distinguish the C-F coupling});

\[ \text{HRMS (ESI) calcd for C}_{20}\text{H}_{19}\text{O}_2\text{NF [M+H]}^+ : 324.1394, \text{ found: 324.1408.}

Methyl 1-(3-(4-bromophenyl)prop-2-yn-1-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (3ca): Prepared following general procedure A, using 1-bromo-4-(prop-1-yn-1-yl)benzene (1c, 58.2 mg, 0.3 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (2a, 86.1 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with pure DCM to provide the product 3ca as a brown oil (65 mg, 56% yield).

\[ \text{HNMR (500 MHz, CDCl}_3, \text{ rotamers seen)} \delta 7.48-7.36 (m, 2H), 7.32-7.08 (m, 6H), 5.44 (t, \ J = 6.0 Hz, 0.5H), 5.36 (t, \ J = 6.0 Hz, 0.5H), 4.32-4.20 (m, 0.5H), 4.03-3.93 (m, 0.5H), 3.78 (s, 1.5H), 3.76 (s, 1.5H), 3.68-3.56 (m, 0.5H), 3.54-3.40 (m, 0.5H), 3.07-2.75 (m, 4H).

\[ \text{CNMR (125 MHz, CDCl}_3, \text{ rotamers seen)} \delta 156.1, 135.6, 135.5, 134.5, 134.4, 133.0, 131.5, 131.4, 129.1, 128.6, 127.4, 127.2, 127.12, 127.08, 126.3, 126.2, 122.6, 122.4, 122.0, 121.9, 88.2, 87.9, 82.0, 81.9, 53.7, 53.6, 52.81, 52.77, 39.3, 38.2, 28.7, 28.4, 27.6, 27.3.

\[ \text{HRMS (ESI) calcd for C}_{20}\text{H}_{19}\text{O}_2\text{NBr [M+H]}^+ : 384.0594, \text{ found: 384.0612.}

Methyl 1-(3-(2-chlorophenyl)prop-2-yn-1-yl)-3,4-dihydroisoquinoline-2(1H)-
carboxylate (3da): Prepared following general procedure A, using 1-chloro-2-(prop-1-yn-1-yl)benzene (1d, 45 mg, 0.3 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (2a, 86.1 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with pure DCM to provide the product 3da as a colorless oil (65 mg, 64% yield).

\[ ^1H\text{NMR} \ (500 \text{ MHz, CDCl}_3, \text{rotamers seen}) \delta \ 7.45-7.27 \ (m, 3H), 7.25-7.10 \ (m, 5H), 5.44 \ (t, J = 5.5 \text{ Hz, 0.5H}), 5.37 \ (t, J = 6.0 \text{ Hz, 0.5H}), 4.33-4.19 \ (m, 0.5H), 4.06-3.93 \ (m, 0.5H), 3.754 \ (s, 1.5H), 3.749 \ (s, 1.5H), 3.70-3.64 \ (m, 0.5H), 3.56-3.43 \ (m, 0.5H), 3.12-2.75 \ (m, 4H).\]

\[ ^{13}C\text{NMR} \ (125 \text{ MHz, CDCl}_3, \text{rotamers seen}) \delta 156.0, 135.6, 135.5, 135.4, 134.5, 134.4, 133.4, 129.1, 129.02, 128.99, 128.8, 128.64, 128.58, 127.4, 127.1, 127.0, 126.3, 126.23, 126.17, 123.4, 123.3, 92.3, 92.0, 79.7, 53.5, 52.73, 52.67, 39.2, 38.2, 28.7, 28.4, 27.8, 27.3.\]

HRMS (ESI) calcd for C\(_{20}\)H\(_{19}\)O\(_2\)NCl [M+H]+: 340.1099, found: 340.1109.

Methyl 1-(3-(4-(tosyloxy)phenyl)prop-2-yn-1-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (3ea): Prepared following general procedure A, using 4-(prop-1-yn-1-yl)phenyl 4-methylbenzenesulfonate (1e, 86 mg, 0.3 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (2a, 86.1 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with 30% ethyl acetate in hexanes to provide the product 3ea as a colorless oil (79 mg, 55% yield).

\[ ^1H\text{NMR} \ (500 \text{ MHz, CDCl}_3, \text{rotamers seen}) \delta 7.71 \ (d, J = 8.0 \text{ Hz, 2H}), 7.32 \ (d, J = 8.0 \text{ Hz, 2H}), 7.30-7.13 \ (m, 6H), 6.91 \ (t, J = 8.5 \text{ Hz, 2H}), 5.42 \ (t, J = 6.5 \text{ Hz, 0.5H}), 5.37 \ (t, J = 6.5 \text{ Hz, 0.5H}), 4.31-4.18 \ (m, 0.5H), 4.03-3.93 \ (m, 0.5H), 3.76 \ (s, 1.5H), 3.75 \ (s, 1.5H), 3.67-3.55 \ (m, 0.5H), 3.53-3.41 \ (m, 0.5H), 3.07-2.80 \ (m, 4H), 2.47 \ (s, 3H).\]

\[ ^{13}C\text{NMR} \ (125 \text{ MHz, CDCl}_3, \text{rotamers seen}) \delta 156.0, 148.9, 148.8, 145.5, 135.6, 135.4, 134.41, 134.35, 132.7, 132.2, 129.8, 129.0, 128.6, 128.5, 127.3, 127.2, 127.1, 127.0, 126.22, 126.18, 122.4, 122.3, 88.1, 87.7, 81.6, 53.7, 53.6, 52.7, 39.2, 38.2, 28.7, 28.4, 27.5, 27.2, 21.7.\]

HRMS (ESI) calcd for C\(_{27}\)H\(_{26}\)O\(_5\)NS [M+H]+: 476.1526, found: 476.1535.

Methyl 1-(4-phenylbut-3-yn-2-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (3fa): Prepared following general procedure A, using but-1-yn-1-ylbenzene (1f, 42 µL, 0.3
mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (2a, 86.1 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with pure DCM to provide the product 3fa as a colorless oil (64 mg, 67% yield, 1:1 d.r.). The d.r. value was detected by crude NMR. The diastereoisomer could not be separated by column.

$^1$H NMR (500 MHz, CDCl$_3$, rotamers and diastereoisomer seen) δ 7.42-7.00 (m, 9H), 5.24 (d, $J$ = 5.5 Hz, 0.25H), 5.11-5.02 (m, 0.5 H), 4.97 (d, $J$ = 8.0 Hz, 0.25H), 4.18-4.08 (m, 0.25H), 4.06-3.98 (m, 0.25H), 3.98-3.91 (m, 0.25H), 3.90-3.81 (m, 0.25H), 3.81-3.71 (m, 0.25H), 3.73-3.61 (m, 0.25H), 3.66 (s, 1.5H), 3.65 (s, 0.75H), 3.64 (s, 0.75H), 3.59-3.51 (m, 0.25H), 3.42-3.33 (m, 0.25H), 3.25-2.65 (m, 3H), 1.38-1.22 (m, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$, rotamers and diastereoisomer seen) δ 156.8, 156.5, 156.4, 135.7, 135.4, 135.2, 134.8, 134.64, 134.56, 134.4, 131.4, 129.0, 128.9, 128.72, 128.67, 128.3, 128.2, 128.1, 128.0, 127., 127.83, 127.7, 127.6, 127.4, 127.3, 127.23, 127.18, 126.9, 126.1, 125.9, 125.5, 125.4, 92.1, 92.0, 91.5, 83.8, 83.5, 83.3, 83.2, 59.4, 58.9, 58.2, 57.9, 52.8, 52.7, 39.8, 39.5, 39.0, 38.8, 33.9, 33.2, 28.4, 28.2, 28.0, 27.8, 18.8, 18.6, 18.3, 18.1.

HRMS (ESI) calcd for C$_{21}$H$_{22}$NO$_2$ [M+H]$^+$: 320.1645, found: 320.1653.

Methyl 1-(5-(1,3-dioxoisindolin-2-yl)pent-2-yn-1-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (3ga): Prepared following general procedure A, using 2-(pent-3-yn-1-yl)isoindoline-1,3-dione (1g, 64 mg, 0.3 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (2a, 86.1 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with 20% ethyl acetate in hexane to provide the product 3ga as a colorless oil (74 mg, 61% yield).

$^1$H NMR (400 MHz, CDCl$_3$, rotamers seen) δ 7.91-7.77 (m, 2H), 7.77-7.62 (m, 2H), 7.20-7.00 (m, 4H), 5.22 (t, $J$ = 6.0 Hz, 0.5H), 5.12 (t, $J$ = 6.0 Hz, 0.5H), 4.16-4.02 (m, 0.5H), 3.91-3.82 (m, 0.5H), 3.81-3.73 (m, 2H), 3.71 (s, 1.5H), 3.70 (s, 1.5H), 3.54-3.40 (m, 0.5H), 3.40-3.25 (m, 0.5H), 3.05-2.73 (m, 2H), 2.73-2.40 (m, 4H).

$^{13}$C NMR (100 MHz, CDCl$_3$, rotamers seen) δ 167.9, 155.9, 135.7, 135.5, 134.23, 134.16, 133.9, 132.0, 128.8, 128.4, 127.2, 127.0, 126.9, 126.8, 126.0, 125.9, 123.2, 78.7, 78.6, 78.5, 78.4, 53.55, 53.49, 52.6, 38.9, 38.1, 36.8, 28.6, 28.2, 26.8, 26.3, 18.6.

HRMS (ESI) calcd for C$_{24}$H$_{23}$O$_4$N$_2$ [M+H]$^+$: 403.1652, found: 403.1655.
Diethyl 2-ethyl-2-(4-(2-(methoxycarbonyl)-1,2,3,4-tetrahydroisoquinolin-1-yl) but-2-yn-1-yl) malonate (3ha): Prepared following general procedure A, using diethyl 2-(but-2-yn-1-yl)-2-ethylmalonate (1h, 72 mg, 0.3 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (2a, 86.1 mg, 0.45 mmol, 1.5 equiv). The crude residue was diluted with CH$_2$Cl$_2$ and washed with 1N HCl to remove the sym-collidine. The extracts were combined and concentrated, purified by flash column chromatography, eluting with 20% ethyl acetate in hexane to provide the product 3ha as a colorless oil (77 mg, 60% yield).

$^{1}$H NMR (500 MHz, CDCl$_3$, rotamers seen) $\delta$ 7.22-7.14 (m, 3H), 7.14-7.06 (m, 1H), 5.22 (t, $J$ = 6.5 Hz, 0.5H), 5.13 (t, $J$ = 7.0 Hz, 0.5H), 4.22-4.04 (m, 4.5H), 4.00-3.87 (m, 0.5H), 3.73 (s, 3H), 3.60-3.47 (m, 0.5H), 3.45-3.31 (m, 0.5H), 3.00-2.50 (m, 6H), 2.00-1.80 (m, 2H), 1.29-1.10 (m, 6H), 0.83-0.65 (m, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$, rotamers seen) $\delta$ 170.4, 155.8, 135.6, 135.5, 134.4, 134.3, 128.9, 128.5, 127.2, 127.0, 126.9, 126.7, 126.1, 126.0, 79.5, 79.4, 77.20, 77.17, 61.2, 57.3, 53.45, 53.38, 52.61, 52.58, 39.1, 38.2, 28.7, 28.3, 26.9, 26.4, 24.7, 22.4, 14.0, 8.2.

HRMS (ESI) calcd for C$_{24}$H$_{32}$O$_6$N [M+H]$^+$: 430.2224, found: 430.2217.

Methyl 1-(3-cyclohexylprop-2-yn-1-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (3ia): Prepared following general procedure A, using prop-1-yn-1-ylcyclohexane (1i, 36.6 mg, 0.3 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (2a, 86.1 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with pure DCM to provide the product 3ia as a colorless oil (66 mg, 60% yield).

$^{1}$H NMR (500 MHz, CDCl$_3$, rotamers seen) $\delta$ 7.25-7.08 (m, 4H), 5.28 (t, $J$ = 6.0 Hz, 0.5H), 5.19 (t, $J$ = 6.5 Hz, 0.5H), 4.25-4.15 (m, 0.5H), 4.00-3.90 (m, 0.5H), 3.75 (s, 3H), 3.63-3.53 (m, 0.5H), 3.47-3.35 (m, 0.5H), 3.00-2.55 (m, 4H), 2.28 (s, 1H), 1.80-1.55 (m, 4H), 1.55-1.40 (m, 1H), 1.40-1.13 (m, 5H).

$^{13}$C NMR (125 MHz, CDCl$_3$, rotamers seen) $\delta$ 156.0, 155.9, 136.0, 135.8, 134.3, 134.2, 128.9, 128.4, 127.4, 127.1, 126.9, 126.8, 126.0, 125.9, 87.1, 87.0, 76.5, 76.2, 53.8, 52.6, 39.0, 38.0, 32.8, 32.7, 29.7, 29.1, 29.0, 28.7, 28.4, 26.9, 26.5, 25.9, 24.8, 24.7.

HRMS (ESI) calcd for C$_{20}$H$_{26}$O$_6$N [M+H]$^+$: 312.1958, found: 312.1960.
Methyl 1-(6-phenylhex-2-yn-1-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (3ja):
Prepared following general procedure A, using hex-4-yn-1-yl benzene (1j, 47.4 mg, 0.3 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (2a, 86.1 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with pure DCM to provide the product 3ja as a colorless oil (65 mg, 62% yield, 10:1 r.r.).

\[ ^1H\text{ NMR}\ (500\text{ MHz, CDCl}_3,\ \text{rotamers seen})\ \delta\ 7.50-7.00\ (m, 9H),\ 5.35\ (t, J = 6.0\ Hz, 0.5H),\ 5.25\ (t, J = 6.0\ Hz, 0.5H),\ 4.33-4.16\ (m, 0.5H),\ 4.10-3.94\ (m, 0.5H),\ 3.77\ (s, 1.5H),\ 3.76\ (s, 1.5H),\ 3.69-3.57\ (m, 0.5H),\ 3.57-3.41\ (m, 0.5H),\ 3.05-2.88\ (m, 1H),\ 2.88-2.69\ (m, 3H),\ 2.69-2.59\ (m, 2H),\ 2.25-2.07\ (m, 2H),\ 1.85-1.65\ (m, 2H).\]

\[ ^{13}C\text{ NMR}\ (125\text{ MHz, CDCl}_3,\ \text{rotamers seen})\ \delta\ 156.01,\ 155.96,\ 141.7,\ 141.6,\ 135.9,\ 135.7,\ 134.4,\ 134.3,\ 128.9,\ 128.52,\ 128.46,\ 128.2,\ 127.3,\ 127.05,\ 126.95,\ 126.8,\ 126.1,\ 126.0,\ 125.8,\ 125.7,\ 82.4,\ 82.2,\ 53.8,\ 52.6,\ 39.1,\ 38.2,\ 34.7,\ 34.6,\ 30.3,\ 28.7,\ 28.4,\ 26.9,\ 26.5,\ 18.1.\]

\[ \text{HRMS (ASAP) calcd for } C_{23}H_{26}NO_2 [M+H]^+: 348.1964, \text{ found: 348.1974.} \]

Methyl 1-(5-(benzoyloxy)pent-2-yn-1-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (3ka):
Prepared following general procedure A, using pent-3-yn-1-yl benzoate (1k, 56.4 mg, 0.3 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (2a, 86.1 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with pure DCM to provide the product 3ka as a colorless oil (58 mg, 51% yield, 4.3:1 r.r.).

\[ ^1H\text{ NMR}\ (500\text{ MHz, CDCl}_3,\ \text{rotamers seen})\ \delta\ 8.04\ (d, J = 10.0\ Hz, 2H),\ 7.61-7.53\ (m, 1H),\ 7.44\ (t, J = 9.5\ Hz, 2H),\ 7.25-7.02\ (m, 4H),\ 5.28\ (t, J = 7.5\ Hz, 0.5H),\ 5.19\ (t, J = 7.5\ Hz, 0.5H),\ 4.40-4.25\ (m, 2H),\ 4.21-4.08\ (m, 0.5H),\ 3.97-3.84\ (m, 0.5H),\ 3.75\ (s, 1.5H),\ 3.74\ (s, 1.5H),\ 3.62-3.50\ (m, 0.5H),\ 3.48-3.36\ (m, 0.5H),\ 2.98-2.63\ (m, 4H),\ 2.63-2.51\ (m, 2H).\]

\[ ^{13}C\text{ NMR}\ (125\text{ MHz, CDCl}_3,\ \text{rotamers seen})\ \delta\ 166.3,\ 156.0,\ 135.7,\ 135.6,\ 134.4,\ 134.3,\ 133.0,\ 130.1,\ 129.7,\ 128.9,\ 128.5,\ 128.4,\ 127.3,\ 127.1,\ 126.9,\ 126.14,\ 126.09,\ 78.6,\ 78.5,\ 78.3,\ 78.2,\ 63.1,\ 53.7,\ 52.7,\ 39.2,\ 38.3,\ 28.7,\ 28.4,\ 26.9,\ 26.5,\ 19.4.\]

\[ \text{HRMS (ESI) calcd for } C_{23}H_{24}O_4N [M+H]^+: 378.1700, \text{ found: 378.1701.} \]
Methyl 1-(hex-3-yn-2-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (3la): Prepared following general procedure A, using hex-3-yne (1l, 33 µL, 0.3 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (2a, 86.1 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with pure DCM to provide the product 3la as a colorless oil (57 mg, 70% yield, 1:1 d.r.). The d.r. value was detected by crude NMR.

One isomer:

$^1$H NMR (500 MHz, CDCl$_3$, rotamers seen) $\delta$ 7.42 (d, $J = 6.5$ Hz, 0.5H), 7.38 (J = 7.0 Hz, 0.5H), 7.24-7.06 (m, 3H), 5.01 (d, $J = 8.5$ Hz, 0.5H), 4.91 (d, $J = 9.0$ Hz, 0.5H), 4.12-4.02 (m, 0.5H), 3.80-3.70 (m, 0.5H), 3.73 (s, 3H), 3.60-3.52 (m, 0.5H), 3.43-3.34 (m, 0.5H), 3.06-2.76 (m, 3H), 2.19-2.06 (m, 2H), 1.26 (d, $J = 6.5$ Hz, 1.5H), 1.22 (d, $J = 6.5$ Hz, 1.5H), 1.09 (t, $J = 7.5$ Hz, 1.5H), 1.05 (t, $J = 7.5$ Hz, 1.5H).

$^{13}$C NMR (125 MHz, CDCl$_3$, rotamers seen) $\delta$ 156.7, 156.3, 135.51, 135.49, 134.4, 134.3, 129.0, 128.8, 128.6, 128.1, 127.2, 127.1, 125.2, 125.1, 85.0, 84.7, 81.5, 59.4, 58.9, 52.7, 52.6, 39.6, 38.6, 32.4, 28.1, 27.7, 19.1, 18.8, 13.8, 12.4.

HRMS (ESI) calcd for C$_{17}$H$_{22}$NO$_2$ [M+H]$^+$: 272.1645, found: 272.1648.

Another isomer:

$^1$H NMR (500 MHz, CDCl$_3$, rotamers seen) $\delta$ 7.23-7.06 (m, 4H), 5.17 (d, $J = 6.0$ Hz, 0.5H), 5.00 (d, $J = 6.0$ Hz, 0.5H), 4.22-4.12 (m, 0.5H), 4.04-3.95 (m, 0.5H), 3.95-3.85 (m, 0.5H), 3.85-3.75 (m, 0.5H), 3.72 (s, 3H), 3.09-2.74 (m, 3H), 2.10-1.96 (m, 2H), 1.26 (d, $J = 7.0$ Hz, 1.5H), 1.23 (d, $J = 7.0$ Hz, 1.5H), 1.03-0.92 (m, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$, rotamers seen) $\delta$ 156.7, 157.5, 136.0, 135.7, 134.8, 134.5, 128.9, 128.6, 127.4, 127.3, 126.9, 126.7, 125.9, 125.8, 84.6, 84.4, 81.3, 81.1, 58.2, 57.9, 52.7, 52.5, 39.3, 38.8, 33.14, 33.11, 28.4, 27.9, 18.64, 18.59, 13.93, 13.90, 12.4.

Methyl 6,7-dimethoxy-1-(3-phenylprop-2-yn-1-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (3ab): Prepared following general procedure A, using prop-1-yn-1-ylbenzene (1a, 39 µL, 0.3 mmol, 1.0 equiv) and methyl 6,7-dimethoxy-3,4-dihydroisoquinoline-2(1H)-carboxylate (2b, 113 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with 5% ethyl acetate in CH$_2$Cl$_2$ to provide the product 3ab as a white solid (81 mg, 74% yield).

Scale-up to 5 mmol:
In an argon-filled glovebox, to the 50 mL flame-dry flask, methyl 6,7-dimethoxy-3,4-dihydroisoquinoline-2(1H)-carboxylate (2b, 1883 mg, 7.5 mmol, 1.5 equiv) and Ph$_3$C$^+$BF$_4^-$ (2800 mg, 8.5 mmol, 1.7 equiv) was stirred in dry trifluorotoluene (15 mL) at room temperature for 3 hours to generate the iminium salt. Then Cp*Fe(CO)$_2$(thf)$^+$BF$_4^-$ (205 mg, 10 mol%), prop-1-yn-1-ylbenzene 1a (650 µL, 5 mmol, 1.0 equiv), trifluorotoluene (5 mL) and sym-collidine (1.2 mL, 9.0 mmol, 1.8 equiv) were added in rapid succession. The reaction tube was capped and removed from the glovebox. The reaction tube was placed in an oil bath, preheated to 60 °C, where it was stirred for 48 h. After completion of the reaction, the reaction mixture was cooled to room temperature. The crude mixture was concentrated in vacuo and purified by flash column chromatography to provide the desired product 3ab as a pale-yellow solid (1.008 g, 55% yield)

**m.p. = 50-51 °C.**

$^1$H NMR (500 MHz, CDCl$_3$, rotamers seen) δ 7.40-7.31 (m, 2H), 7.31-7.23 (m, 3H), 6.84 (d, $J = 25$ Hz, 1H), 6.64 (s, 1H), 5.35 (t, $J = 6.0$ Hz, 0.5H), 5.28 (t, $J = 6.5$ Hz, 0.5H), 4.31-4.20 (m, 0.5H), 4.04-3.94 (m, 0.5H), 3.88 (s, 3H), 3.81 (s, 1.5H), 3.79 (s, 1.5H), 3.76 (s, 3H), 3.64-3.52 (m, 0.5H), 3.50-3.35 (m, 0.5H), 3.05-2.80 (m, 3H), 2.80-2.67 (m, 1H).

$^{13}$C NMR (125 MHz, CDCl$_3$, rotamers seen) δ 156.0, 148.1, 148.0, 147.4, 131.5, 128.3, 128.2, 127.9, 127.8, 127.7, 127.5, 126.5, 126.3, 123.6, 123.4, 111.5, 111.2, 110.5, 110.2, 87.1, 86.8, 83.1, 55.95, 55.91, 53.4, 52.8, 52.7, 39.2, 38.2, 28.3, 28.0, 27.5, 27.1.

HRMS (ESI) calcd for C$_{22}$H$_{24}$O$_4$N [M+H]$^+$: 366.1700, found: 366.1707.

**Methyl 5-chloro-1-(3-phenylprop-2-yn-1-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (3ac):** Prepared following general procedure A, using prop-1-yn-1-ylbenzene (1a, 39 µL, 0.3 mmol, 1.0 equiv) and methyl 5-chloro-3,4-dihydroisoquinoline-2(1H)-carboxylate (2c, 101 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with pure DCM to provide the product 3ac as a light-yellow oil (75 mg, 74% yield).

$^1$H NMR (500 MHz, CDCl$_3$, rotamers seen) δ 7.42-7.26 (m, 6H), 7.26-7.14 (m, 2H), 5.47 (t, $J = 6.0$ Hz, 0.5H), 5.37 (t, $J = 6.5$ Hz, 0.5H), 4.44-4.32 (m, 0.5H), 4.20-4.04 (m, 0.5H), 3.78 (s, 1.5H), 3.77 (s, 1.5H), 3.65-3.55 (m, 0.5H), 3.50-3.38 (m, 0.5H), 3.05-2.80 (m, 4H).

$^{13}$C NMR (125 MHz, CDCl$_3$, rotamers seen) δ 155.9, 137.9, 137.8, 134.5, 134.1, 132.6, 132.5, 131.5, 128.3, 128.2, 128.0, 127.9, 127.0, 126.9, 125.9, 125.6, 123.5, 123.3, 86.3, 86.0, 83.3, 53.4, 53.3, 52.9, 38.2, 37.2, 27.4, 27.0, 26.5, 26.3.
Methyl 6-bromo-1-(3-phenylprop-2-yn-1-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (3ad): Prepared following general procedure A, using prop-1-yn-1-ylbenzene (1a, 39 µL, 0.3 mmol, 1.0 equiv) and methyl 6-bromo-3,4-dihydroisoquinoline-2(1H)-carboxylate (2d, 122 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with pure DCM to provide the product 3ad as a colorless oil (84 mg, 73% yield).

$^1$H NMR (500 MHz, CDCl$_3$, rotamers seen) $\delta$ 7.42-7.25 (m, 7H), 7.24-7.11 (m, 1H), 5.38 (t, $J = 6.0$ Hz, 0.5H), 5.30 (t, $J = 6.0$ Hz, 0.5H), 4.30-4.18 (m, 0.5H), 4.04-3.90 (m, 0.5H), 3.78 (s, 3H), 3.69-3.58 (m, 0.5H), 3.54-3.42 (m, 0.5H), 3.05-2.75 (m, 4H).

$^{13}$C NMR (125 MHz, CDCl$_3$, rotamers seen) $\delta$ 156.0, 136.83, 136.76, 134.7, 134.5, 131.8, 131.5, 131.4, 129.34, 129.29, 129.1, 128.8, 128.3, 128.2, 128.0, 127.9, 123.5, 123.3, 120.9, 120.8, 86.3, 86.1, 83.3, 53.4, 52.9, 52.8, 38.9, 37.9, 28.6, 28.3, 27.5, 27.1.

HRMS (ESI) calcd for C$_{20}$H$_{19}$O$_2$NBr [M+H]$^+$: 384.0594, found: 384.0602.

Methyl 7-fluoro-1-(3-phenylprop-2-yn-1-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (3ae): Prepared following general procedure A, using prop-1-yn-1-ylbenzene (1a, 39 µL, 0.3 mmol, 1.0 equiv) and methyl 7-fluoro-3,4-dihydroisoquinoline-2(1H)-carboxylate (2e, 94 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with pure DCM to provide the product 3ae as a colorless oil (73 mg, 75% yield).

$^1$H NMR (500 MHz, CDCl$_3$, rotamers seen) $\delta$ 7.43-7.20 (m, 5H), 7.19-7.10 (m, 1H), 7.10-6.99 (m, 1H), 6.99-6.89 (m, 1H), 5.40 (t, $J = 6.0$ Hz, 0.5H), 5.32 (t, $J = 6.0$ Hz, 0.5H), 4.33-4.19 (m, 0.5H), 4.05-3.93 (m, 0.5H), 3.78 (s, 3H), 3.69-3.56 (m, 0.5H), 3.54-3.41 (m, 0.5H), 3.07-2.74 (m, 4H).

$^{19}$F NMR (470 MHz, CDCl$_3$, rotamers seen) $\delta$ -116.23, -116.16.

$^{13}$C NMR (125 MHz, CDCl$_3$, rotamers seen) $\delta$ 162.1, 162.0, 160.15, 160.09, 156.0, 137.5, 137.4, 137.3, 137.2, 131.5, 130.44, 130.38, 130.1, 130.0, 128.3, 128.2, 128.0, 127.8, 123.5, 123.3, 114.4, 114.3, 114.1, 113.95, 113.86, 113.7, 86.4, 86.1, 83.32, 83.27, 53.60, 53.58, 52.9, 52.8, 39.3, 38.3, 28.1, 27.8, 27.5, 27.0. (the $^{13}$C spectrum is too complicated to distinguish the C-F coupling)
HRMS (ESI) calcd for C_{20}H_{19}O_{2}NF [M+H]^+: 324.1394, found: 324.1408.

**Methyl 7-bromo-1-(3-phenylprop-2-yn-1-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (3af):** Prepared following general procedure A, using prop-1-yn-1-ylbenzene (1a, 39 µL, 0.3 mmol, 1.0 equiv) and methyl 7-bromo-3,4-dihydroisoquinoline-2(1H)-carboxylate (2f, 122 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with pure DCM to provide the product 3af as a colorless oil (80 mg, 69% yield).

**1H NMR** (500 MHz, CDCl$_3$, rotamers seen) δ 7.50 (d, $J = 16.5$ Hz, 1H), 7.43-7.33 (m, 3H), 7.09-7.00 (m, 1H), 5.38 (t, $J = 5.5$ Hz, 0.5H), 5.30 (t, $J = 6.5$ Hz, 0.5H), 4.33-4.17 (m, 0.5H), 4.04-3.93 (m, 0.5H), 3.78 (s, 3H), 3.69-3.56 (m, 0.5H), 3.53-3.41 (m, 0.5H), 3.05-2.75 (m, 4H).

**13C NMR** (125 MHz, CDCl$_3$, rotamers seen) δ 156.0, 137.8, 137.6, 133.5, 131.5, 130.6, 130.4, 130.3, 130.2, 128.3, 128.2, 128.0, 127.9, 123.4, 123.3, 119.7, 119.6, 86.3, 86.0, 83.5, 53.3, 52.9, 52.8, 39.1, 38.1, 28.3, 28.0, 27.5, 27.1.

HRMS (ESI) calcd for C$_{20}$H$_{19}$O$_2$NBr [M+H]$^+$: 384.0593, found: 384.0602.

**Methyl 7-methyl-1-(3-phenylprop-2-yn-1-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (3ag):** Prepared following general procedure A, using prop-1-yn-1-ylbenzene (1a, 26 µL, 0.2 mmol, 1.0 equiv) and methyl 7-methyl-3,4-dihydroisoquinoline-2(1H)-carboxylate (2g, 61 mg, 0.3 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with pure DCM to provide the product 3ag as a colorless oil (43 mg, 67% yield).

**1H NMR** (500 MHz, CDCl$_3$, rotamers seen) δ 7.49-7.20 (m, 5H), 7.19-6.95 (m, 3H), 5.39 (s, 0.5H), 5.33 (s, 0.5H), 4.34-4.20 (m, 0.5H), 4.05-3.92 (m, 0.5H), 3.77 (s, 3H), 3.70-3.55 (m, 0.5H), 3.54-3.40 (m, 0.5H), 3.10-2.70 (m, 4H), 2.35 (s, 3H).

**13C NMR** (125 MHz, CDCl$_3$, rotamers seen) δ 156.1, 135.64, 135.61, 135.5, 135.4, 131.4, 131.3, 128.8, 128.3, 128.2, 128.1, 128.0, 127.9 127.83, 127.78, 127.7, 123.7, 123.5, 87.0, 86.6, 82.9, 53.7, 52.7, 52.6, 39.4, 38.3, 28.3, 28.0, 27.5, 27.2, 21.1.

HRMS (ESI) calcd for C$_{21}$H$_{22}$O$_2$N [M+H]$^+$: 320.1645, found: 320.1658.
Methyl 7-methyl-1-(3-phenylprop-2-yn-1-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (3ah): Prepared following general procedure A, using prop-1-yn-1-ylbenzene (1a, 39 µL, 0.3 mmol, 1.0 equiv) and (9H-fluoren-9-yl) methyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (2h, 159 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with pure DCM to provide the product 3ah as a colorless oil (78 mg, 55% yield).

$^1$H NMR (500 MHz, CDCl$_3$, rotamers seen) δ 7.85-7.70 (m, 2H), 7.70-7.50 (m, 2H), 7.47-7.40 (m, 2H), 7.40-7.23 (m, 10H), 7.23-7.16 (m, 1H), 5.46 (s, 0.5H), 5.22 (s, 0.5H), 4.64-4.42 (m, 2H), 4.36-4.24 (m, 1H), 4.23-4.14 (m, 0.5H), 4.06-3.94 (m, 0.5H), 3.78-3.66 (m, 0.5H), 3.60-3.48 (m, 0.5H), 3.06-2.74 (m, 4H).

$^{13}$C NMR (125 MHz, CDCl$_3$, rotamers seen) δ 155.4, 144.1, 144.0, 143.9, 141.33, 141.31, 135.6, 135.4, 134.4, 134.3, 131.5, 128.9, 128.5, 128.2, 128.1, 127.8, 127.64, 127.57, 127.4, 127.22, 127.19, 127.1, 127.0, 126.3, 126.1, 125.0, 124.9, 123.6, 123.5, 119.94, 119.90, 86.7, 86.5, 83.1, 82.9, 67.5, 67.4, 53.9, 53.8, 47.3, 39.4, 38.6, 28.7, 28.3, 27.6, 27.2.

HRMS (ESI) calcd for C$_{33}$H$_{28}$O$_2$N $[M+H]^+$: 470.2115, found: 470.2126.

Methyl 6-(3-(3-chlorophenyl)prop-2-yn-1-yl)-3,3-dimethyl-4-phenyl-3,6-dihydropyridine-1(2H)-carboxylate (3mi): Prepared following general procedure A, using 1-chloro-3-(prop-1-yn-1-yl)benzene (1m, 45 mg, 0.3 mmol, 1.0 equiv) and methyl 3,3-dimethyl-4-phenyl-3,6-dihydropyridine-1(2H)-carboxylate (2i, 110 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with pure DCM to provide the product 3mi as a colorless oil (72 mg, 61% yield).

$^1$H NMR (400 MHz, CDCl$_3$, rotamers seen) δ 7.42-7.37 (m, 1H), 7.37-7.25 (m, 5H), 7.25-7.16 (m, 3H), 5.66 (s, 1H), 4.83 (s, 0.5H), 4.73 (s, 0.5H), 4.10-3.96 (m, 0.5H), 3.75-3.85 (m, 0.5H), 3.81 (s, 3H), 3.18 (d, $J = 12.4$ Hz, 0.5H), 3.05 (d, $J = 12.8$ Hz, 0.5H), 2.80 (d, $J = 12.0$ Hz, 2H), 1.26 (s, 3H), 0.91 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$, rotamers seen) δ 156.2, 156.1, 148.3, 147.9, 141.0, 134.1, 131.4, 129.6, 129.5, 128.5, 128.1, 127.8, 126.9, 125.4, 125.3, 124.6, 124.1, 88.3, 87.9, 81.5, 52.8, 52.2, 51.5, 35.5, 25.8, 24.9, 24.7, 24.3.

HRMS (ESI) calcd for C$_{24}$H$_{25}$O$_2$NCl $[M+H]^+$: 394.1574, found: 394.1579.
Methyl 6-(3-(3-bromophenyl)prop-2-yn-1-yl)-3,3-dimethyl-4-phenyl-3,6-dihydropyridine-1(2H)-carboxylate (3ni): Prepared following general procedure A, using 1-bromo-3-(prop-1-yn-1-yl)benzene (1n, 59 mg, 0.3 mmol, 1.0 equiv) and methyl 3,3-dimethyl-4-phenyl-3,6-dihydropyridine-1(2H)-carboxylate (4i, 110 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with pure DCM to provide the product 3ni as a colorless oil (85 mg, 65% yield).

**1H NMR** (500 MHz, CDCl₃, rotamers seen) δ 7.58-7.52 (m, 1H), 7.43 (d, \( J = 8.0 \) Hz, 1H), 7.37-7.29 (m, 4H), 7.25-7.19 (m, 2H), 7.16 (t, \( J = 8.0 \) Hz, 1H), 5.66 (s, 0.5H), 5.65 (s, 0.5H), 4.83 (s, 0.5H), 4.72 (s, 0.5H), 4.03 (d, \( J = 13.0 \) Hz, 0.5H), 3.84 (d, \( J = 13.0 \) Hz, 0.5H), 3.81 (s, 3H), 3.18 (d, \( J = 13.0 \) Hz, 0.5H), 3.04 (d, \( J = 12.5 \) Hz, 0.5H), 2.90-2.68 (m, 2H), 1.26 (s, 1.5H), 1.24 (s, 1.5H), 0.91 (s, 3H).

**13C NMR** (125 MHz, CDCl₃, rotamers seen) δ 156.2, 156.0, 148.3, 147.9, 141.0, 134.3, 131.0, 130.1, 129.7, 128.5, 126.9, 125.5, 124.6, 124.1, 122.1, 88.5, 88.1, 81.4, 52.9, 52.7, 52.2, 51.4, 35.5, 25.7.

**HRMS** (ESI) calcd for C₂₄H₂₂O₂NBr [M+H]⁺: 438.1078, found: 438.1063.

Methyl 6-(5-(1,3-dioxoisindolin-2-yl)pent-2-yn-1-yl)-3,3-dimethyl-4-phenyl-3,6-dihydropyridine-1(2H)-carboxylate (3gi): Prepared following general procedure A, using 2-(pent-3-yn-1-yl)isoindoline-1,3-dione (1g, 64 mg, 0.3 mmol, 1.0 equiv) and methyl 3,3-dimethyl-4-phenyl-3,6-dihydropyridine-1(2H)-carboxylate (2i, 110 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with 20% ethyl acetate in hexane to provide the product 3gi as a pale-yellow oil (81 mg, 59% yield).

**1H NMR** (400 MHz, CDCl₃, rotamers seen) δ 7.84-7.74 (m, 2H), 7.74-7.64 (m, 2H), 7.36-7.26 (m, 3H), 7.22-7.12 (m, 2H), 5.56 (s, 1H), 4.64 (s, 0.5H), 4.52 (s, 0.5H), 3.98-3.66 (m, 6H), 3.02 (d, \( J = 11.6 \) Hz, 0.5H), 2.87 (d, \( J = 12.4 \) Hz, 0.5H), 2.66-2.65 (m, 2H), 2.54-2.32 (m, 2H), 1.19 (s, 3H), 0.86 (s, 3H).

**13C NMR** (100 MHz, CDCl₃, rotamers seen) δ 168.0, 156.2, 155.9, 147.7, 147.4, 141.0, 133.9, 132.0, 128.6, 127.7, 126.8, 124.8, 124.2, 123.3, 78.5, 52.7, 52.0, 51.6, 36.9, 35.4, 25.7, 24.7, 24.1, 23.5, 18.8;

**HRMS** (ESI) calcd for C₂₈H₂₉O₄N₂ [M+H]⁺: 457.2127, found: 457.2130.
Methyl 6-(3-cyclohexylprop-2-yn-1-yl)-3,3-dimethyl-4-phenyl-3,6-dihydropyridine-1(2H)-carboxylate (3ii): Prepared following general procedure A, using prop-1-yn-1-ylcyclohexane (1i, 36.6 mg, 0.3 mmol, 1.0 equiv) and methyl 3,3-dimethyl-4-phenyl-3,6-dihydropyridine-1(2H)-carboxylate (2i, 110 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with pure DCM to provide the product 3ii as a colorless oil (62 mg, 57% yield).

$^1$H NMR (500 MHz, CDCl$_3$, rotamers seen) δ 7.45-7.10 (m, 5H), 5.62 (s, 1H), 4.68 (s, 0.5H), 4.57 (s, 0.5H), 3.97 (d, $J$ = 12.5 Hz, 0.5H), 3.87-3.65 (m, 3.5H), 3.19 (d, $J$ = 12.0 Hz, 0.5H), 3.05 (d, $J$ = 12.0 Hz, 0.5H), 2.70-2.45 (m, 2H), 2.40-2.25 (m, 1H), 1.85-1.65 (m, 4H), 1.57-1.45 (m, 1H), 1.45-1.35 (m, 2H), 2.89 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$, rotamers seen) δ 156.3, 155.9, 147.7, 147.2, 141.3, 128.5, 127.7, 126.8, 125.2, 124.7, 87.1, 86.9, 76.5, 76.2, 52.7, 52.6, 52.3, 51.7, 51.6, 35.3, 33.0, 29.2, 25.9, 24.9, 24.7, 24.2, 23.6.

HRMS (ESI) calcd for C$_{24}$H$_{32}$O$_2$N [M+H]$^+$: 366.2428, found: 366.2439.

2-(5-(Isochroman-1-yl)pent-3-yn-1-yl)isoindoline-1,3-dione (3gj): Prepared following general procedure A, using 2-(pent-3-yn-1-yl)isoindoline-1,3-dione (1g, 64 mg, 0.3 mmol, 1.0 equiv) and isochroman (2j, 60.3 mg, 0.45 mmol, 1.5 equiv) in CHCl$_3$ (0.2 M). The crude residue was purified by flash column chromatography, eluting with pure DCM to provide the product 3gj as a colorless oil (53 mg, 51% yield, > 20:1 r.r.).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.90-7.80 (m, 2H), 7.75-7.65 (m, 2H), 7.17-7.03 (m, 4H), 4.85-4.75 (m, 1H), 4.12-4.05 (m, 1H), 3.82 (t, $J$ = 7.5 Hz, 2H), 3.77-3.68 (m, 1H), 3.00-2.89 (m, 1H), 2.76-2.54 (m, 5H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 168.0, 136.9, 134.0, 133.9, 132.1, 128.8, 126.6, 126.1, 124.8, 123.3, 79.2, 77.7, 74.6, 63.3, 37.0, 28.9, 26.8, 18.9.

HRMS (ESI) calcd for C$_{22}$H$_{20}$O$_3$N [M+H]$^+$: 346.1438, found: 346.1454.

1-(6-Phenylhex-2-yn-1-yl)isochromane (3jj): Prepared following general procedure A, using hex-4-yn-1-ylbenzene (1j, 47 mg, 0.3 mmol, 1.0 equiv) and isochroman (2j, 60.3
mg, 0.45 mmol, 1.5 equiv) in CHCl₃ (0.2 M). The crude residue was purified by flash column chromatography, eluting with 33% DCM in hexanes to provide the product 3jj as a colorless oil (39 mg, 45% yield, 15:1 r.r.).

**1H NMR** (500 MHz, CDCl₃) δ 7.22-7.15 (m, 2H), 7.15-6.98 (m, 7H), 4.86-4.78 (m, 1H), 4.18-4.08 (m, 1H), 4.80-4.69 (m, 1H), 3.00-2.87 (m, 1H), 2.78-2.58 (m, 3H), 2.55 (t, J = 7.5 Hz, 2H), 2.13-2.03 (m, 2H), 1.73-1.62 (m, 2H).

**13C NMR** (125 MHz, CDCl₃) δ 141.9, 137.1, 134.2, 128.9, 128.6, 128.3, 126.6, 126.2, 125.8, 125.0, 81.6, 77.4, 74.9, 63.5, 34.6, 30.5, 29.0, 26.8, 18.3.

**HRMS** (ESI) calcd for C₂₁H₂₃O [M+H]⁺: 291.1743, found: 291.1778.

O₃mj

1-(3-(3-Chlorophenyl)prop-2-yn-1-yl)isochromane (3mj): Prepared following general procedure C, using 1-chloro-3-(prop-1-yn-1-yl)benzene (1m, 45 mg, 0.3 mmol, 1.0 equiv) and isochroman (2j, 60.3 mg, 0.45 mmol, 1.5 equiv) in CHCl₃ (0.2 M). The crude residue was purified by flash column chromatography, eluting with pure DCM to provide the product 3mj as a colorless oil (34 mg, 40% yield).

**1H NMR** (500 MHz, CDCl₃) δ 7.37 (s, 1H), 7.30-7.14 (m, 7H), 5.04 (t, J = 5.0 Hz, 1H), 4.28-4.18 (m, 1H), 3.92-3.82 (m, 1H), 3.10-3.00 (m, 2H), 3.00-2.91 (m, 1H), 2.80-2.70 (m, 1H).

**13C NMR** (125 MHz, CDCl₃) δ 136.7, 134.2, 133.9, 131.6, 129.8, 129.3, 128.9, 128.0, 126.8, 126.3, 125.4, 124.9, 88.5, 80.9, 74.5, 63.4, 29.0, 27.6.

**HRMS** (ESI) calcd for C₁₈H₁₆OCl [M+H]⁺: 283.0884, found: 283.0905.

**General procedure B for propargylic C-H functionalization of alkenes.**

A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was capped with a Teflon/silicone septum (Thermo/National part # C4015-66A) screw cap and flame dried under vacuum. The reaction tube was cooled under argon and transferred into a nitrogen-filled glovebox. In the glovebox, the suspension of carbamate (2a, 0.45 mmol, 1.5 equiv) and Ph₃C⁺BF₄⁻ (168 mg, 0.51 mmol, 1.7 equiv) in dry trifluorotoluene (1 mL) was stirred at room temperature for 3 hours to generate the iminium salt. Then Cp*Fe(CO)₂(thf)⁺BF₄⁻ (20 mol%, 24.6 mg), alkene 4 (0.3 mmol, 1.0 equiv), trifluorotoluene (0.5 mL) and sym-collidine (72 µL, 0.54 mmol,
1.8 equiv) were added in rapid succession. The reaction tube was capped and removed from the glovebox. The reaction tube was placed in an oil bath, preheated to 60 °C, where it was stirred for 48 h. After completion of the reaction, the reaction mixture was cooled to room temperature. The crude mixture was concentrated in vacuo and purified by flash column chromatography to provide the desired product 5.

**Characterization Data for Products 5:**

**Methyl 1-(1-phenylallyl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (5aa):** Prepared following general procedure B, using prop-1-yn-1-ylbenzene (4a, 39 µL, 0.3 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (2a, 86.1 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with pure DCM to provide the product 5aa as a colorless oil (86 mg, 93% yield, 1:1 d.r.). The diastereoisomer could not be separated by column.

**1H NMR** (500 MHz, CDCl$_3$, rotamers and diastereoisomer seen) δ 7.40-6.65 (m, 8.5H), 6.27-5.90 (m, 1.5H), 5.43-5.15 (m, 1H), 5.08-4.76 (m, 2H), 4.03-3.30 (m, 6H), 2.93-2.45 (m, 2H).

**13C NMR** (125 MHz, CDCl$_3$, rotamers and diastereoisomer seen) δ 156.8, 156.4, 156.3, 155.9, 141.7, 141.5, 141.4, 141.3, 139.2, 138.4, 138.2, 138.1, 135.7, 135.3, 135.1, 135.0, 134.6, 134.4, 134.2, 134.1, 128.81, 128.75, 128.71, 128.67, 128.62, 128.58, 128.5, 128.4, 128.30, 128.28, 128.26, 128.23, 128.19, 127.9, 127.7, 127.2, 127.0, 126.91, 126.89, 126.78, 126.75, 126.5, 125.29, 125.26, 125.16, 125.11, 117.63, 117.56, 116.4, 115.9, 60.0, 59.73, 59.70, 59.6, 57.9, 57.6, 56.7, 56.5, 52.75, 52.67, 52.6, 52.4, 39.54, 39.46, 39.0, 38.7, 28.2, 27.9, 27.8, 27.7.

**HRMS** (ESI) calcd for C$_{20}$H$_{22}$O$_2$N [M+H]$^+$: 308.1645, found: 308.1636.

**Methyl 1-(1-(4-methoxyphenyl)allyl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (5ba):** Prepared following general procedure B, using 1-allyl-4-methoxybenzene (4b, 45 mg, 0.3 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (2a, 86.1 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with pure DCM to provide the product 5ba as a colorless oil (85 mg, 84% yield, 1.3:1 d.r.). The diastereoisomer could be separated by column. One isomer:
**$^1$H NMR** (500 MHz, CDCl$_3$, rotamers seen) $\delta$ 7.23-7.02 (m, 2H), 7.00 (t, $J$ = 8.0 Hz, 2H), 6.93-6.85 (m, 1H), 6.85-6.73 (m, 2H), 6.35 (d, $J$ = 8.0 Hz, 0.5H), 6.30 (d, $J$ = 8.0 Hz, 0.5H), 6.27-6.05 (m, 1H), 5.39 (d, $J$ = 9.0 Hz, 0.5H), 5.25 (d, $J$ = 9.0 Hz, 0.5H), 5.15-4.97 (m, 2H), 4.10-3.67 (m, 7H), 3.58 (t, $J$ = 9.0 Hz, 1H), 3.55-3.36 (m, 1H), 3.00-2.75 (m, 1H), 2.74-2.55 (m, 1H).

**$^{13}$C NMR** (125 MHz, CDCl$_3$, rotamers seen) $\delta$ 158.5, 158.4, 139.5, 138.7, 135.7, 135.4, 134.2, 134.1, 133.7, 133.5, 129.71, 129.66, 128.7, 128.2, 128.0, 127.8, 126.95, 126.86, 125.3, 125.2, 116.0, 115.5, 113.97, 113.89, 60.0, 59.8, 56.9, 56.7, 55.7, 55.27, 55.25, 52.73, 52.68, 39.4, 38.7, 27.9, 27.7.

Another isomer:

**$^1$H NMR** (500 MHz, CDCl$_3$, rotamers seen) $\delta$ 7.24-7.00 (m, 5H), 6.95-6.76 (m, 3H), 6.15-5.95 (m, 1H), 5.41 (d, $J$ = 7.0 Hz, 0.5H), 5.26 (d, $J$ = 7.5 Hz, 0.5H), 5.05 (t, $J$ = 9.0 Hz, 1H), 4.98 (d, $J$ = 17.0 Hz, 0.5H), 4.91 (d, $J$ = 17.0 Hz, 0.5H), 3.98-3.76 (m, 4H), 3.76-3.54 (m, 1H), 3.08-2.50 (m, 5H).

**$^{13}$C NMR** (125 MHz, CDCl$_3$, rotamers seen) $\delta$ 158.2, 158.1, 156.4, 155.9, 158.4, 138.3, 135.1, 135.0, 134.5, 134.4, 133.5, 133.2, 129.1, 129.0, 128.7, 128.6, 128.5, 128.3, 127.0, 126.8, 125.2, 125.0, 117.2, 117.1, 113.63, 113.59, 59.7, 59.6, 55.8, 55.5, 55.1, 52.5, 52.4, 39.5, 38.9, 28.1, 27.7.

**HRMS** (ESI) calcd for C$_{21}$H$_{24}$O$_3$N [M+H]$^+$: 338.1750, found: 338.1741.

**Methyl 1-(1-phenylbut-3-en-2-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (5ca):**
Prepared following general procedure B, using but-3-en-1-ylbenzene (4c, 45 µL, 0.3 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (2a, 86.1 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with pure DCM to provide the product 5ca as a colorless oil (34 mg, 35% yield, 1.2:1 d.r.). The diastereoisomer could not be separated by column.

**$^1$H NMR** (500 MHz, CDCl$_3$, rotamers and diastereoisomer seen) $\delta$ 7.28-7.00 (m, 9H), 5.80-5.48 (m, 1H), 5.28-4.98 (m, 1H), 4.93-4.82 (m, 1H), 4.72-4.50 (m, 1H), 4.10-3.66 (m, 4H), 3.66-3.46 (m, 1H), 3.08-2.50 (m, 5H).

**$^{13}$C NMR** (125 MHz, CDCl$_3$, rotamers and diastereoisomer seen) $\delta$ 156.96, 156.91, 156.48, 146.46, 140.42, 140.30, 140.11, 140.07, 138.62, 138.47, 138.30, 138.09, 136.70, 136.24, 135.80, 135.36, 134.80, 134.71, 134.58, 134.53, 129.24, 129.19, 129.14, 128.99, 128.70, 128.55, 128.31, 128.20, 128.09, 128.03, 127.69, 127.12, 127.09, 126.99, 125.96, 125.90, 125.84, 125.77, 125.42, 125.31, 117.94, 117.88, 117.45, 117.16, 59.28, 58.86, 58.68, 58.57, 53.35, 52.96, 52.74, 52.69, 52.66, 52.52, 52.35, 40.31, 39.85, 39.68, 38.52, 38.38, 38.36, 38.26, 28.16, 27.98, 27.89, 27.68.

**HRMS** (ESI) calcd for C$_{21}$H$_{24}$O$_2$N [M+H]$^+$: 322.1802, found: 322.1800.
Methyl 1-(5-(4-bromophenoxy)pent-1-en-3-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (5da): Prepared following general procedure B, using 1-bromo-4-(pent-4-en-1-yloxy)benzene (4d, 72 mg, 0.3 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (2a, 86.1 mg, 0.45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography, eluting with pure DCM to provide the product 5da as a colorless oil (43 mg, 33% yield, 1.2:1 d.r.). The diastereoisomer could not be separated by column.

$^1$H NMR (500 MHz, CDCl$_3$, rotamers and diastereoisomer seen) $\delta$ 7.40-7.27 (m, 2H), 7.23-7.03 (m, 4H), 6.80-6.65 (m, 2H), 5.81-5.50 (m, 1H), 5.20-4.75 (m, 3H), 4.10-3.75 (m, 3H), 3.75-3.67 (m, 3H), 3.63-3.43 (m, 1H), 3.00-2.80 (m, 2H), 2.77-2.63 (m, 1H), 2.20-2.00 (m, 1H), 1.87-1.70 (m, 1H).

$^{13}$C NMR (125 MHz, CDCl$_3$, rotamers and diastereoisomer seen) $\delta$ 158.06, 158.01, 156.96, 156.90, 156.40, 156.35, 138.54, 138.46, 138.31, 137.95, 136.25, 135.84, 135.75, 135.35, 134.72, 134.54, 134.39, 132.20, 132.18, 132.16, 129.00, 128.79, 128.64, 128.59, 128.30, 127.97, 127.73, 127.22, 127.10, 127.02, 126.50, 126.33, 126.00, 125.84, 125.38, 125.25, 118.40, 118.31, 117.78, 117.27, 116.40, 116.35, 116.29, 112.81, 112.73, 112.68, 112.66, 66.26, 65.99, 65.83, 58.73, 58.53, 58.50, 58.37, 52.78, 52.74, 52.69, 52.57, 47.53, 47.30, 47.28, 47.08, 40.15, 40.02, 39.63, 39.37, 30.95, 30.81, 30.49, 28.08, 27.93, 27.78, 27.57.

HRMS (ESI) calcd for C$_{22}$H$_{25}$O$_3$NBr [M+H]$^+$: 433.1012, found: 433.1017.

General procedure C for propargylic C-H functionalization of alkynes.

A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was capped with a Teflon/silicone septum (Thermo/National part # C4015-66A) screw cap and flame dried under vacuum. The reaction tube was cooled under argon and transferred into an argon-filled glovebox. In the glovebox, [Cp*Fe(CO)$_2$(thf)]$^{+}$[BF$_4$]$^{-}$ (12.2 mg, 10 mol%), Ph$_3$C$^+$BF$_4^-$ (150 mg, 0.45 mmol, 1.5 equiv.), dry 1,2-dichloroethane (0.6 mL), alkyne 1 (0.3 mmol, 1.0 equiv) and 2,4,6-
collidine (60 µL, 0.45 mmol, 1.5 equiv) were added in rapid succession. The reaction tube was capped and removed from the glovebox. The reaction tube was placed in an oil bath, preheated to 60 °C, where it was stirred for 48 h. After completion of the reaction, the reaction mixture was cooled to room temperature. The crude mixture was concentrated in vacuo and purified by flash column chromatography to provide the desired product.

\[
\begin{align*}
R^1 & \quad R^2 \\
\text{Cp*Fe(CO)}_2(\text{thf})\text{BF}_4 (10 \text{ mol%}) & \quad \text{sym-collidine (1.5 equiv)} \quad \text{DCE (0.5 M), 60 °C}
\end{align*}
\]

Characterization data for products 6:

**But-3-yne-1,1,1,4-tetrayltetraphenylene (6a):** Prepared following general procedure C using prop-1-yn-1-ylbenzene (1a, 39 µL, 0.3 mmol, 1.0 equiv). The reaction mixture was quenched after 48 h, and the crude residue was purified by flash column chromatography, eluting with a gradient of 5 to 6.3% DCM in hexanes to provide the title compound 6a as a white solid (86 mg, 80% yield). m.p. = 101–102 °C.

**1H NMR** (500 MHz, CDCl₃) δ 7.22-7.16 (m, 12H), 7.16-7.10 (m, 3H), 7.10-7.04 (m, 3H), 7.01-6.92 (m, 2H), 3.61 (s, 2H).

**13C NMR** (125 MHz, CDCl₃) δ 146.8, 131.3, 129.3, 128.0, 127.8, 127.5, 126.3, 123.8, 88.6, 84.3, 56.6, 33.5.

**HRMS (ASAP)** calcd for C₂₈H₂₃[M+H]⁺: 359.1800, found: 359.1812.
(4-(3-chlorophenyl) but-3-yne-1,1,1-triyl) tribenzene (6b): Prepared following general procedure C using 1-chloro-3-(prop-1-yn-1-yl) benzene (1m, 45 mg, 0.3 mmol, 1.0 equiv). The reaction mixture was quenched after 48 h, and the crude residue was purified by flash column chromatography, eluting with a gradient of 5 to 6.3% DCM in hexanes to provide the title compound 6b as a white solid (80 mg, 68% yield). **m.p.** = 99–100 °C. **1H NMR** (500 MHz, CDCl3) δ 7.50-7.22 (m, 15H), 7.21-7.16 (m, 1H), 7.15-7.08 (m, 1H), 7.05 (s, 1H), 6.98-6.91 (m, 1H), 3.72 (s, 2H).

**13C NMR** (125 MHz, CDCl3) δ 146.7, 133.8, 131.2, 129.4, 129.2, 127.83, 127.77, 126.4, 125.4, 90.1, 83.1, 56.6, 33.5.

**HRMS** (ASAP) calcd for C28H22Cl [M+H]+: 393.1404, found: 393.1418.

(4-(4-(trifluoromethyl)phenyl)but-3-yne-1,1,1-triyl)tribenzene (6c): Prepared following general procedure C using 1-(prop-1-yn-1-yl)-4-(trifluoromethyl)benzene (1o, 55.2 mg, 0.3 mmol, 1.0 equiv). The reaction mixture was quenched after 48 h, and the crude residue was purified by flash column chromatography, eluting with a gradient of 5 to 6.3% DCM in hexanes to provide the title compound 6c as a white solid (93 mg, 73% yield). **m.p.** = 67–68 °C. **1H NMR** (500 MHz, CDCl3) δ 7.47 (d, J = 8.0 Hz, 2H), 7.38-7.26 (m, 15H), 7.20-7.14 (m, 2H), 3.76 (s, 2H).

**19F NMR** (470 MHz, CDCl3, rotamers seen) δ –62.8.

**13C NMR** (125 MHz, CDCl3) δ 146.6, 131.5, 129.2, 128.9 (q, J_{C–F} = 145 Hz), 127.9, 126.9 (q, J_{C–F} = 150 Hz), 126.4, 124.9 (q, J_{C–F} = 3.8 Hz), 124.0 (q, J_{C–F} = 262.5 Hz), 91.5, 83.3, 56.6, 33.6.

**HRMS** (ASAP) calcd for C29H22F3 [M+H]+: 427.1674, found: 427.1681.

(2-methylbut-3-yne-1,1,1,4-tetrayl) tetrabenzene (6d): Prepared following general procedure C using but-1-yn-1-ylbenzene (1f, 42 µL, 0.3 mmol, 1.0 equiv). The reaction mixture was quenched after 48 h, and the crude residue was purified by flash column chromatography, eluting with a gradient of 5 to 6.3% DCM in hexanes to provide the title compound 6d as a white solid (61 mg, 55% yield). **m.p.** = 91–92 °C. **1H NMR** (500 MHz, CDCl3) δ 7.47 (d, J = 8.0 Hz, 6H), 7.30 (t, J = 7.5 Hz, 6H), 7.25-7.18 (m, 6H), 7.17-7.11 (m, 2H), 4.56 (q, J = 7.0 Hz, 1H), 1.22 (d, J = 7.0 Hz, 3H).

**13C NMR** (125 MHz, CDCl3) δ 145.2, 131.3, 130.0, 128.1, 127.44, 127.37, 126.0, 124.0, 93.3, 84.4, 61.0, 33.3, 18.2.

**HRMS** (ASAP) calcd for C29H25 [M+H]+: 373.1956, found: 373.1977.
(2-methylhex-3-yne-1,1,1-triyl) tribenzene (6e): Prepared following general procedure C using 3-hexyne (1l, 33 µL, 0.3 mmol, 1.0 equiv). The reaction mixture was quenched after 48 h, and the crude residue was purified by flash column chromatography (Hexanes) to provide the title compound 6e as a colorless liquid (61 mg, 62% yield).

\[ \text{1H NMR (400 MHz, CDCl}_3 \text{) } \delta 7.50-7.36 \text{ (m, 6H), 7.34-7.25 (m, 6H), 7.25-7.16 (m, 3H), 4.33 (qt, } J = 6.8, 2.0 \text{ Hz, 1H), 2.02 (qd, } J = 7.6, 2.0 \text{ Hz, 2H), 1.11 (d, } J = 6.8 \text{ Hz, 3H), 0.93 (t, } J = 7.6 \text{ Hz, 3H).} \]

\[ \text{13C NMR (100 MHz, CDCl}_3 \text{) } \delta 145.3, 130.0, 127.3, 125.8, 85.6, 82.5, 60.8, 32.4, 18.5, 13.9, 12.5. \]

HRMS (ESI) calcd for C\text{25}H\text{25} [M+H]⁺: 325.1951, found: 325.1963.

(4-cyclohexylbut-3-yne-1,1,1-triyl)tribenzene (6f): Prepared following general procedure C using prop-1-yn-1-ylcyclohexane (1i, 36.6 mg, 0.3 mmol, 1.0 equiv). The reaction mixture was quenched after 48 h, and the crude residue was purified by flash column chromatography, eluting with a gradient of 5 to 6.3% DCM in hexanes to provide the title compound 6f as a colorless liquid (55 mg, 50% yield, >20:1 r.r.).

\[ \text{1H NMR (400 MHz, CDCl}_3 \text{) } \delta 7.38-7.19 \text{ (m, 15H), 3.50 (d, } J = 2.0 \text{ Hz, 2H), 2.24 (s, 1H), 1.55-1.33 \text{ (m, 5H), 1.27-1.08 (m, 5H).} \]

\[ \text{13C NMR (100 MHz, CDCl}_3 \text{) } \delta 147.1, 129.4, 127.7, 126.1, 88.3, 78.7, 56.4, 32.9, 32.3, 28.7, 26.0, 24.3. \]

HRMS (ASAP) calcd for C\text{28}H\text{29} [M+H]⁺: 365.2269, found: 365.2289.

(5,5-dimethylhex-3-yne-1,1,1-triyl) tribenzene (6g): Prepared following general procedure C using 4,4-dimethylpent-2-yne (1r, 40 µL, 0.3 mmol, 1.0 equiv). The reaction mixture was quenched after 48 h, and the crude residue was purified by flash column chromatography, eluting with a gradient of 5 to 6.3% DCM in hexanes to provide the title compound 6g as a colorless liquid (34 mg, 33% yield).

\[ \text{1H NMR (500 MHz, CDCl}_3 \text{) } \delta 7.31-7.20 \text{ (m, 15H), 3.44 (s, 2H), 0.96 (s, 9H).} \]

\[ \text{13C NMR (125 MHz, CDCl}_3 \text{) } \delta 147.1, 129.4, 127.6, 126.1, 100.0, 92.9, 56.5, 32.8, 30.7, 27.2. \]

HRMS (ASAP) calcd for C\text{26}H\text{27} [M+H]⁺: 339.2113, found: 339.2131.

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Prepared following general procedure C using pent-2-yne (1p, 29 µL, 0.3 mmol, 1.0 equiv). The reaction mixture was quenched after 48 h, and the crude residue was purified by flash column chromatography, eluting with a gradient of 5 to 6.3% DCM in hexanes to provide the title compound 6h and 6h’ as a colorless oil (66 mg, 71% yield, 3.7:1 r.r.). The regioisomeric ratio was determined by 1H NMR of the crude material.

**hex-3-yne-1,1,1-triyltribenzene (6h):**

1H NMR (400 MHz, CDCl3) δ 7.38-7.18 (m, 15H), 3.49 (t, J = 2.4 Hz, 2H), 2.00 (qt, J = 7.6, 2.4 Hz, 2H), 0.90 (t, J = 7.6 Hz, 3H).

13C NMR (100 MHz, CDCl3) δ 147.1, 129.4, 127.7, 126.1, 85.6, 77.9, 56.4, 32.8, 13.9, 12.4.

HRMS (ESI) calcd for C24H22 [M+H]+: 311.1794, found: 311.1804.

**(2-methylpent-3-yne-1,1,1-triyl)tribenzene (6h’):**

1H NMR (400 MHz, CDCl3) δ 7.45-7.35 (m, 5H), 7.30-7.12 (m, 10H), 4.37-4.20 (m, 1H), 1.70-1.55 (m, 3H), 1.08 (d, J = 6.8 Hz, 3H).

13C NMR (100 MHz, CDCl3) δ 145.5, 129.9, 127.3, 125.8, 81.9, 79.6, 60.8, 32.3, 18.5, 3.6.

**Hept-3-yne-1,1,1,7-tetrayltetraphenyl (6i):** Prepared following general procedure C using hex-4-yn-1-ylbenzene (1j, 47 mg, 0.3 mmol, 1.0 equiv). The reaction mixture was quenched after 48 h, and the crude residue was purified by flash column chromatography, eluting with a gradient of 5 to 6.3% DCM in hexanes to provide the title compound 6i as a colorless oil (85 mg, 71% yield, 8.1:1 r.r.). The regioisomeric ratio was determined by 1H NMR of the crude material.

1H NMR (400 MHz, CDCl3) δ 7.35-7.24 (m, 18H), 7.08-7.03 (m, 2H), 3.55 (t, J = 2.4 Hz, 2H), 2.44 (t, J = 7.6 Hz, 2H), 2.07-1.98 (m, 2H), 1.63-1.53 (m, 2H).

13C NMR (100 MHz, CDCl3) δ 147.1, 141.9, 129.4, 128.6, 128.2, 127.8, 126.2, 125.7, 83.6, 79.1, 56.4, 34.3, 32.9, 30.2, 18.0.
HRMS (ESI) calcd for C$_{31}$H$_{29}$ [M+H]$^+$: 401.2264, found: 401.2278.

2-(6,6,6-triphenylhex-3-yn-1-yl) isoindoline-1,3-dione (6j): Prepared following general procedure C using 2-(pent-3-yn-1-yl)isoindoline-1,3-dione (1g, 64 mg, 0.3 mmol, 1.0 equiv). The reaction mixture was quenched after 48 h, and the crude residue was purified by flash column chromatography, eluting with a gradient of 6 to 12% ethyl acetate in hexanes to provide the title compound 6j as a light-yellow solid (100 mg, 73% yield, >20:1 r.r.). The regioisomeric ratio was determined by $^1$H NMR of the crude material. m.p. = 158-159 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.90-7.80 (m, 2H), 7.78-7.68 (m, 2H), 7.38-7.08 (m, 15H), 3.58 (t, $J$ = 7.6 Hz, 2H), 3.45 (t, $J$ = 2.4 Hz, 2H), 2.48-2.32 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.9, 146.8, 133.9, 132.1, 129.2, 127.7, 126.2, 123.3, 80.5, 79.8, 56.2, 36.8, 32.8, 18.6.

HRMS (ESI) calcd for C$_{32}$H$_{26}$O$_2$N [M+H]$^+$: 456.1958, found: 456.1955.

(5-cyclohexylpent-3-yn-1,1,1-triyl)tribenzene (6k): Prepared following general procedure C using but-2-yn-1-ylcyclohexane (1q, 40.8 mg, 0.3 mmol, 1.0 equiv). The reaction mixture was quenched after 48 h, and the crude residue was purified by flash column chromatography, eluting with a gradient of 5 to 6.3% DCM in hexanes to provide the title compound 6k as a colorless oil (58 mg, 51% yield, >20:1 r.r.).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.25-7.05 (m, 15H), 3.39 (t, $J$ = 2.4 Hz, 2H), 1.82-1.72 (m, 2H), 1.54-1.44 (m, 3H), 1.38-1.28 (m, 2H), 1.12-0.88 (m, 4H), 0.70-0.54 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 147.1, 129.3, 127.9, 127.7, 126.1, 82.9, 79.2, 56.3, 37.4, 32.9, 32.3, 26.6, 26.2.

HRMS (ESI) calcd for C$_{29}$H$_{31}$ [M+H]$^+$: 379.2420, found: 379.2432.

Pent-3-yn-1,1,1,2-tetrayltetraphene (6l'): Prepared following general procedure A using but-2-yn-1-ylbenzene (1s, 39 mg, 0.3 mmol, 1.0 equiv). The reaction mixture was quenched after 48 h, and the crude residue was purified by flash column chromatography, eluting with a gradient of 5 to 6.3% DCM in hexanes to provide the title compound 6l' as
a white solid (66 mg, 59% yield, 1:11 r.r.). The regioisomeric ratio was determined by $^1$H NMR of the crude material. **m.p.** = 173-174 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50-7.33 (m, 6H), 7.28-7.15 (m, 9H), 7.15-7.08 (m, 1 H), 7.07-6.95 (m, 2H), 6.93-6.75 (m, 2H), 5.49 (s, 1H), 1.73 (d, $J$ = 1.6 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.7, 138.8, 131.3, 130.8, 127.0, 126.8, 126.7, 125.9, 82.4, 80.4, 63.6, 45.1, 3.7.

**HRMS** (ESI) calcd for C$_{29}$H$_{25}$ [M+H]$^+$: 373.1951, found: 373.1959.

(10-chloro-2-methyldec-3-yne-1,1,1-triyl) tribenzene (6m): Prepared following general procedure C using 10-chlorodec-3-yne (1t, 57 µL, 0.3 mmol, 1.0 equiv). The reaction mixture was quenched after 48 h, and the crude residue was purified by flash column chromatography, eluting with a gradient of 5 to 6.3% DCM in hexanes to provide the title compound 6m as a colorless oil (56 mg, 45% yield, 3.8:1 r.r.). The regioisomeric ratio was determined by $^1$H NMR of the crude material.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.48-7.38 (m, 6H), 7.33-7.28 (m, 6H), 7.25-7.19 (m, 3H), 4.42-4.29 (m, 1H), 3.59-3.49 (m, 2H), 2.05 (td, $J$ = 7.0, 2.0 Hz, 2H), 1.78-1.67 (m, 2H), 1.40-1.26 (m, 4H), 1.22-1.14 (m, 2H), 1.11 (d, $J$ = 6.5 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.2, 130.2, 127.3, 125.8, 83.9, 83.3, 60.7, 45.0, 32.5, 28.4, 27.7, 26.4, 18.6, 18.5.

**HRMS** (ASAP) calcd for C$_{29}$H$_{32}$Cl [M+H]$^+$: 415.2193, found: 415.2212.

**Additional stoichiometric functionalization experiments**

![Stoichiometric functionalization experiments](image)
A reaction tube equipped with a magnetic stir bar was capped with a Teflon/silicone septum screw cap and flame dried under vacuum. The solution of 1l-II(Cp) (approx. 0.2 mmol) in CH₂Cl₂ (2 mL) was added dropwise to a stirred solution of 4-bromobenzaldehyde (40 mg, 0.24 mmol, 1.2 equiv) and triisopropylsilyl trifluoromethanesulfonate (TIPSOTf, 64 µL, 0.24 mmol, 1.2 equiv) in CH₂Cl₂ (2 mL). The reaction mixture was stirred at rt for 1 h. Then acetone (2 mL) and sodium iodide (30 mg, 0.2 mmol) were added in succession, and stirred at rt for another 10 min. The crude mixture was concentrated *in vacuo* and purified by preparative thin-layer chromatography to provide the desired product.

A reaction tube equipped with a magnetic stir bar was capped with a Teflon/silicone septum screw cap and flame dried under vacuum. The solution of 1l-II(Cp) (approx. 0.2 mmol) in CH₂Cl₂ (2 mL) was added dropwise to a stirred solution of 4,4'-bis(dimethoxy)benzhydrilium tetrafluoroborate (68 mg, 0.3 mmol, 1.5 equiv) in CH₂Cl₂ (1 mL) at rt for 1 h. Acetone (2 mL) and sodium iodide (30 mg, 0.2 mmol) were then added in succession, and stirred at rt for another 10 min. The crude mixture was concentrated *in vacuo* and purified by preparative thin-layer chromatography to provide the desired product.

A reaction tube equipped with a magnetic stir bar was capped with a Teflon/silicone septum screw cap and flame dried under vacuum. The reaction tube was cooled under argon and transferred into a nitrogen-filled glovebox. In the glovebox, the suspension of 2-(4-bromophenyl)-1,3-dioxolane (23 mg, 0.1 mmol) and Ph₃C⁺BF₄⁻ (33 mg, 0.1 mmol) in dry 1,2-dichloroethane (1 mL) was stirred at room temperature for 3 hours. Then the solution of 1l-II(Cp) (approx. 0.15 mmol) in 1,2-dichloroethane (1 mL) was added dropwise at rt, and the reaction mixture was stirred at 60 °C for 2 h. Subsequently, acetone (2 mL) and sodium iodide (30 mg, 0.2 mmol) were added in succession, and
stirred at rt for another 10 min. The crude mixture was concentrated in vacuo and purified by preparative thin-layer chromatography to provide the desired product.

**Synthesis of substrates and characterization data for new compounds:**

The alkyne substrates are list as following:

The alkynes 1a, 1f, 1j, 1l, 1p, 1r, 1s are commercial, and used directly without purification.

The alkynes were synthesized according to a known literature procedure and has been previously characterized.\(^5\)
The alkynes were synthesized according to a known literature procedure and has been previously characterized.\textsuperscript{6}

The alkyne was synthesized according to a known literature procedure and has been previously characterized.\textsuperscript{7}

The alkyne was synthesized according to a known literature procedure and has been previously characterized.\textsuperscript{8}

The diethyl 2-ethylmalonate (1.1 mL, 5.8 mmol) was added to the suspension of NaH (278 mg, 1.2 equiv) in THF (12 mL) at 0 °C. The mixture was stirred at room temperature for 0.5 h. Then 1-bromobut-2-yn (0.6 mL, 1.2 equiv) was added to the above suspension dropwise, stirred at room temperature for another 1 h. After completion, quenched with saturated NH\textsubscript{4}Cl solution, extracted with ethyl acetate for three times. The combined organic solution was washed with brine, dried (Na\textsubscript{2}SO\textsubscript{4}), filtered, and concentrated under reduced pressure. Purification by column chromatography (10% - 20% ethyl acetate in hexanes) afforded the product as colorless liquid (1.27 g, 91% yield).

**Diethyl 2-(but-2-yn-1-yl)-2-ethylmalonate (1h).**

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 4.25-4.12 (m, 4H), 2.77-2.68 (m, 2H), 2.12-2.00 (m, 2H), 1.78-1.68 (m, 3H), 1.30-1.17 (m, 6H), 0.88-0.77 (m, 3H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 170.6, 78.3, 73.5, 61.2, 57.5, 24.9, 22.4, 14.0, 8.3, 3.4.

HRMS (ESI) calcd for C\textsubscript{13}H\textsubscript{21}O\textsubscript{4} [M+H]\textsuperscript{+}: 241.1434, found: 241.1439.
Synthesis of carbamates.

The N-carbamate starting materials 2a-2g were synthesized according to the corresponding literatures and has been previously characterized. The chloroformate (1.1 equiv) was added dropwise to the solution of tetrahydroisoquinolines (1.0 equiv) and Et₃N (2.0 equiv) in CH₂Cl₂ (0.25 M) at 0 °C. The mixture was stirred at room temperature for 2 h. After completion, quenched with saturated NH₄Cl solution, extracted with CH₂Cl₂ for three times. The combined organic solution was washed with brine, dried (Na₂SO₄), filtered, and concentrated under reduced pressure. Purification by column chromatography (10% - 20% ethyl acetate in hexanes) afforded the product.

**1H NMR** (500 MHz, CDCl₃) δ 7.14 (d, J = 8.0 Hz, 1H), 7.03 (t, J = 8.0 Hz, 1H), 6.92 (s, 1H), 4.52 (s, 2H), 3.66 (s, 3H), 3.62 (s, 2H), 2.78 (t, J = 5.5 Hz, 2H);

**13C NMR** (125 MHz, CDCl₃) δ 155.9, 135.6, 134.3, 132.5, 127.2, 127.1, 124.7, 52.7, 45.7, 41.1, 26.6;

**1H NMR** (400 MHz, CDCl₃) δ 7.25-7.05 (m, 2H), 6.91 (d, J = 8.0 Hz, 1H), 4.49 (s, 2H), 3.66 (s, 3H), 3.58 (s, 2H), 2.69 (t, J = 4.8 Hz, 2H);

**13C NMR** (100 MHz, CDCl₃) δ 156.0, 135.3, 133.5, 130.4, 129.6, 129.1, 119.8, 52.8, 45.3, 41.4, 28.3;
Reference

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X-ray structures for products 3ab and 6d.

Figure S2. Molecular structure of 3ab (CCDC 1909840)

Datablock: wyd2_282

| Bond precision: C-C = 0.0024 Å | Wavelength=1.54178 |
|-----------------------------|---------------------|
| Cell: | a=17.0265(10) b=14.1187(8) c=8.9890(5) |
| alpha=90 beta=118.511(2) gamma=90 |
| Temperature: 150 K |
| Calculated | Reported |
| Volume | 1898.82(19) | 1898.82(19) |
| Space group | C c | C c |
| Hall group | C -2yc | C -2yc |
| Moiety formula | C22 H23 N O4 | ? |
| Sum formula | C22 H23 N O4 | C22 H23 N O4 |
| Mr | 365.41 | 365.41 |
| DX, g cm^{-3} | 1.278 | 1.278 |
| Z | 4 | 4 |
| Mr (mm-1) | 0.712 | 0.712 |
| F000 | 776.0 | 776.0 |
| F000’ | 778.40 |
| h,k,lmax | 20,17,10 | 20,17,10 |
| Nref | 3606[1807] | 3528 |
| Tmin, Tmax | 0.855,0.918 | 0.840,0.920 |
| Tmin’ | 0.855 |

Correction method= # Reported T Limits: Tmin=0.840 Tmax=0.920 |
AbsCorr - MULTI-SCAN |
Data completeness= 1.95/0.98 |
Theta(max)= 70.057 |
R(reflections)= 0.0257(3509) |
wR2(reflections)= 0.0773(3528) |
S = 1.074 |
Npar= 247
Figure S1. Molecular structure of 6d (CCDC 1909839)

Datablock: Yidong1_a

Bond precision: C-C = 0.0019 Å  Wavelength=1.54178

Cell:
\[ a=9.6092(4) \quad b=24.7359(10) \quad c=9.7874(4) \]
\[ \text{alpha}=90 \quad \text{beta}=116.350(2) \quad \text{gamma}=90 \]

Temperature: 150 K

| Calculated | Reported |
|------------|----------|
| Volume     | 2084.68 (15) | 2084.67 (15) |
| Space group | P 21/c     | P 21/c     |
| Hall group | -P 2ybc    | -P 2ybc    |
| Moiety formula | C29 H24 | C29 H24 |
| Sum formula | C29 H24    | C29 H24    |
| Mr         | 372.48     | 372.48     |
| Dx, g cm-3 | 1.187      | 1.187      |
| Z           | 4          | 4          |
| Mu (mm-1)  | 0.503      | 0.503      |
| F000       | 792.0      | 792.0      |
| F000'      | 794.00     |            |
| h,k,lmax   | 11,29,11   | 11,29,11   |
| Nref       | 3820       | 3689       |
| Tmin, Tmax | 0.947, 0.980 | 0.920, 0.980 |
| Tmin'      | 0.913      |            |

Correction method= # Reported  T Limits: Tmin=0.920  Tmax=0.960
AbsCorr = MULTI-SCAN

Data completeness= 0.966  Theta(max)= 60.240

R(reflections)= 0.0366 (3093)  wR2(reflections)= 0.1116 (3689)

S = 1.093  Npar = 263
Copies of $^1$H and $^{13}$C NMR spectra for catalyst, products and substrates.
\[ ^{19}\text{F NMR (470 MHz, CDCl}_3\text{)} \]
$^{1}H$ NMR (400 MHz, CD$_2$Cl$_2$)

$^{13}C$ NMR (100 MHz, CD$_2$Cl$_2$)
\[ {^1H \text{ NMR (400 MHz, CD}_2\text{Cl}_2) \]
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (470 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CD$_2$Cl$_2$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{13}C$ NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (470 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{13}C$ NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{1} \text{H NMR} (500 \text{ MHz, CDCl}_3)$

$^{13} \text{C NMR} (125 \text{ MHz, CDCl}_3)$
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{13}C$ NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl₃)

$^{13}$C NMR (125 MHz, CDCl₃)
$^{1}$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{13}C$ NMR (125 MHz, CDCl$_3$)
**$^1$H NMR (500 MHz, CDCl$_3$)**

![H NMR spectrum](image)

**$^{13}$C NMR (125 MHz, CDCl$_3$)**

![C NMR spectrum](image)
$^{1}H$ NMR (500 MHz, CDCl$_{3}$)

$^{13}C$ NMR (125 MHz, CDCl$_{3}$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}F$ NMR (470 MHz, CDCl$_3$)

$^{19}F$ NMR spectrum of compound 3ae. The spectrum shows a peak at approximately -121.0 ppm, typical for fluorine in aromatic systems.
$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{13}C$ NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
**1H NMR (400 MHz, CDCl₃)**

```
H NMR (400 MHz, CDCl₃)
```

**13C NMR (100 MHz, CDCl₃)**

```
H NMR (100 MHz, CDCl₃)
```
H NMR (500 MHz, CDCl₃)

13C NMR (125 MHz, CDCl₃)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
^1H NMR (500 MHz, CDCl₃)

^13C NMR (125 MHz, CDCl₃)
\[ ^1H \text{NMR (500 MHz, CDCl}_3\] \]

\[ ^{13}C \text{NMR (125 MHz, CDCl}_3\] \]
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{13}C$ NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
1H NMR (500 MHz, CDCl₃)

13C NMR (125 MHz, CDCl₃)
\[ ^1\text{H NMR} \ (500 \text{ MHz, CDCl}_3) \]

\[ ^{13}\text{C NMR} \ (125 \text{ MHz, CDCl}_3) \]
$^{1}$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}\text{F NMR (470 MHz, CDCl}_3\text{)}$
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{1} \text{H NMR (400 MHz, CDCl}_{3}\text{)}$

$^{13} \text{C NMR (100 MHz, CDCl}_{3}\text{)}$
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{1}$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)