Photoinduced Co/Ni-cocatalyzed Markovnikov Hydroarylation of

Unactivated Olefins with Aryl Bromides

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1. General information

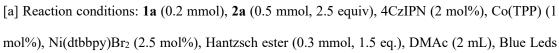
Unless otherwise noted, all these reactions were carried out under nitrogen atmosphere. For column chromatography, silica gel (200-300 mesh) was employed. Solvent was freshly distilled prior to use unless otherwise noted. Organic solvents were concentrated under reduced pressure using a rotary evaporator.

Instrumentation. Deuterated solvents were purchased from Cambridge Isotope Laboratories. ¹H NMR spectra were recorded on Bruker AVANCE III 400 or Bruker AVANCE III HD 400 with 400 MHz frequencies, and ¹³C NMR spectra were recorded on Bruker AVANCE III 400 or Bruker AVANCE III HD 400 with 101 MHz frequencies. ¹⁹F NMR spectra were recorded on a Bruker AVANCE III HD 400 spectrometer with a ¹⁹F operating frequency of 376 MHz. Chemical shifts (ppm) were recorded with TMS (tetramethylsilane) as the internal reference standard. Chemical shifts (δ) were reported in ppm relative to the residual solvent signal (TMS $\delta = 0$ for ¹H NMR and CDCl₃ $\delta = 77.0$ for ¹³C NMR). Multiplicities are given as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), td (triplet of doublets) or m (multiplet). HRMS obtained using a Q-TOF instrument equipped with an ESI source. All photochemical reactions were conducted using a blue light-emitting diode (LED) as the visible-light source (440 nm, Kessil LEDs lights).

Materials. Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available. Commercial reagents were used without further purification. The HE- d_2 and HE- d_3 were synthesized according to reported literatures.^{1, 2} The substrates of **3xr**, **3yr** and **3zr** were derived from 2,3-*O*-Isopropylidene-*D*-ribonic gamma-lactone (CAS number: 30725-00-9), Diacetone-D-glucose (CAS number: 14686-89-6) and Diacetonefructose (CAS number: 20880-92-6) respectively.

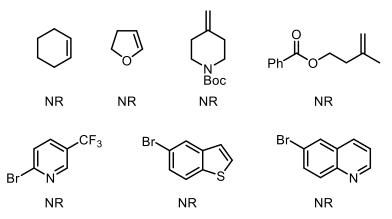
Br-CO ₂ Me 1a 0.2 mmol	+ + Hantzsch es DMAc 2a Blue Led 0.5 mmol r.t.,	(1 mol%) (2 (2.5 mol%) teter (1.5 eq.) (2 mL) s (10 W) (2 mL) (1 mol%) H
entry	modified conditions	s yield of 3aa (%) ^[b]
1	none	82%
2	Co-I	0
3	Co-II	0
4	Ir(dFCF3ppy)(dtbpy	82%
5	Eosin Y	0
6	PC-I	0
7	DMF	81%
8	1,4-dioxane	74%
9	Et ₃ N as reductant	0
10	No light	0
11	No 4CzIPN	0
12	No Co(TPP)	0
13	No Ni(dtbbpy)Br ₂	0
14	No Hantzsch ester	0
$Ph \qquad \qquad Ph \qquad \qquad $	t-Bu t-Bu t-Bu t-Bu t-Bu t-Bu t-Bu t-Bu	-Bu Co-II
$F \rightarrow CF_{3} \rightarrow PF_{6}$ $Ir[dF(CF_{3})ppy]_2(dtbbpy)PF_{6}$		$ \begin{array}{c} & & & & & \\ B^{T} \\ H^{T} \\ H^$

2. The optimization of the reaction^[a]



(10 W), r.t., Ar, 15 h, cooling with a fan. [b] Isolated yield. DMAc = *N*,*N*-Dimethylacetamide. Hantzsch ester = Diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate.

3. Unsuccessful substrates



4. Synthesis and characterization of products

4.1 General Procedures I (GPI)

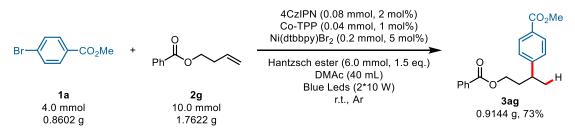
In an oven-dried 10 mL tube equipped with a stirring bar, aryl bromide compounds (0.2 mmol, 1.0 equiv.), unactivated olefins (0.5 mmol, 2.5 equiv.), diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate (Hantzsch ester, 0.3 mmol, 1.5 equiv.), 4CzIPN (0.004 mmol, 2 mol%), Ni(dtbbpy)Br₂ (0.005 mmol, 2.5 mol%), and Co(TPP) (0.002 mmol, 1 mol%) were added. The tube was charged with nitrogen (repeated three times), then *N*,*N*-Dimethylacetamide (DMAc, 2 mL) was injected. The resulting suspension was stirred at room temperature and irradiated with blue LEDs (440 nm, 10 W) by cooling with a fan for 15 h. After completion, the resulting mixture was quenched with H₂O (30 mL). Then the mixture was extracted with ethyl acetate (30 mL). The organic layer was washed with brine (30 mL × 2), dried over anhydrous Na₂SO₄, and concentrated in vacuum. The residue was purified by flash chromatography on silica gel to afford the desired products.

4.2 General Procedures II (GPII)

In an oven-dried 10 mL tube equipped with a stirring bar, aryl bromide compounds (0.2 mmol, 1.0 equiv.), unactivated olefins (0.5 mmol, 2.5 equiv.), Hantzsch ester (0.3 mmol, 1.5 equiv.), 4CzIPN (0.004 mmol, 2 mol%), Ni(dtbbpy)Br₂ (0.01 mmol, 5 mol%), and Co(TPP) (0.002 mmol, 1 mol%) were added. The tube was charged with nitrogen (repeated three times), then DMAc (2 mL) was injected. The resulting

suspension was stirred at room temperature and irradiated with blue LEDs (440 nm, 10 W) by cooling with a fan for 15 h. After completion, the resulting mixture was quenched with H₂O (30 mL). Then the mixture was extracted with ethyl acetate (30 mL). The organic layer was washed with brine (30 mL \times 2), dried over anhydrous Na₂SO₄, and concentrated in vacuum. The residue was purified by flash chromatography on silica gel to afford the desired products.

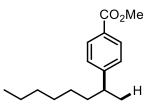
4.3 Gram-scale reaction procedures



In an oven-dried 100 mL tube equipped with a stirring bar, **1a** (4.0 mmol, 1 equiv.), **2g** (10 mmol, 2.5 equiv.), Hantzsch ester (6.0 mmol, 1.5 equiv.), 4CzIPN (0.08 mmol, 2 mol%), Ni(dtbbpy)Br₂ (0.2 mmol, 5 mol%), and Co(TPP) (0.04 mmol, 1 mol%) were added. The tube was charged with nitrogen (repeated three times), then DMAc (40.0 mL) was injected. The resulting suspension was stirred at room temperature and irradiated with blue LEDs (440 nm, 2*10 W) by cooling with a fan for 15 h. After completion, the resulting mixture was quenched with H₂O (100 mL). Then the mixture was extracted with ethyl acetate (100 mL). The organic layer was washed with brine (100 mL \times 2), dried over anhydrous Na₂SO₄, and concentrated in vacuum. The residue was purified by flash chromatography on silica gel to afford the desired product **3ag** (0.9144 g, 73%).

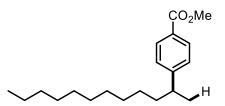
4.4 Characterization of products

methyl 4-(octan-2-yl)benzoate (3aa)



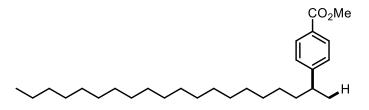
GPI, 41.0 mg, 82% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 3.89 (s, 3H), 2.78 – 2.68 (m, 1H), 1.62 – 1.52 (m, 2H), 1.29 - 1.19 (m, 10H), 1.16 - 1.07 (m, 1H), 0.85 (t, J = 6.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.1, 153.5, 129.6, 127.7, 127.0, 51.9, 40.0, 38.1, 31.7, 29.3, 27.5, 22.6, 22.0, 14.0. HRMS (ESI-TOF) (m/z): Calcd for C₁₆H₂₅O₂ ([M + H]⁺): 249.1849; found: 249.1848.

methyl 4-(dodecan-2-yl)benzoate (3ab)

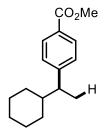


GPI, 48.2 mg, 79% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.93 (m, 2H), 7.26 – 7.22 (m, 2H), 3.90 (s, 3H), 2.78 – 2.68 (m, 1H), 1.60 – 1.51 (m, 2H), 1.28 – 1.18 (m, 18H), 1.16 – 1.08 (m, 1H), 0.87 (t, J = 6.9 Hz, 3H).¹³C NMR (101 MHz, CDCl₃) δ 167.2, 153.5, 129.6, 127.7, 127.0, 51.9, 40.0, 38.1, 31.9, 29.6, 29.6, 29.6, 29.5, 29.3, 27.6, 22.7, 22.0, 14.1. HRMS (ESI-TOF) (m/z): Calcd for C₂₀H₃₃O₂ ([M + H]⁺): 305.2475; found: 305.2475.

methyl 4-(icosan-2-yl)benzoate (3ac)

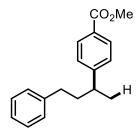


GPII, 42.9 mg, 51% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 3.90 (s, 3H), 2.78 – 2.68 (m, 1H), 1.62 – 1.51 (m, 3H), 1.28 – 1.19 (m, 34H), 0.88 (t, J = 6.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.2, 153.5, 129.7, 127.7, 127.0, 51.9, 40.1, 38.2, 31.9, 30.1 – 29.1 (m), 27.6, 22.7, 22.1, 14.1. HRMS (ESI-TOF) (m/z): Calcd for C₂₈H₄₉O₂ ([M + H]⁺): 417.3727; found: 417.3727. **methyl 4-(1-cyclohexylethyl)benzoate (3ad)**



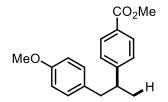
GPI, 37.6 mg, 76% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.99 – 7.90 (m, 2H), 7.24 – 7.16 (m, 2H), 3.90 (s, 3H), 2.55 – 2.44 (m, 1H), 1.87 (m, 1H), 1.78 – 1.70 (m, 1H), 1.67 – 1.55 (m, 2H), 1.47 – 1.35 (m, 2H), 1.26 – 1.19 (m, 4H), 1.14 – 1.04 (m, 2H), 0.99 – 0.87 (m, 1H), 0.85 – 0.73 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 167.2, 152.7, 129.4, 127.7, 127.7, 51.9, 46.0, 44.0, 31.4, 30.5, 26.4, 18.6. HRMS (ESI-TOF) (m/z): Calcd for C₁₆H₂₃O₂ ([M + H]⁺): 247.1693; found: 247.1693.

methyl 4-(4-phenylbutan-2-yl)benzoate (3ae)



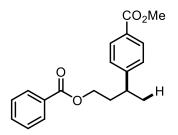
GPI, 46.5 mg, 86% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.96 (m, 2H), 7.29 – 7.22 (m, 4H), 7.19 – 7.14 (m, 1H), 7.13 – 7.08 (m, 2H), 3.90 (s, 3H), 2.83 – 2.72 (m, 1H), 2.55 – 2.42 (m, 2H), 1.97 – 1.87 (m, 2H), 1.28 (d, J = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.1, 152.7, 142.1, 129.8, 128.3, 127.9, 127.1, 125.7, 51.9, 39.6, 39.5, 33.7, 22.2. HRMS (ESI-TOF) (m/z): Calcd for C₁₈H₂₁O₂ ([M + H]⁺): 269.1536; found: 269.1537.

methyl 4-(1-(4-methoxyphenyl)propan-2-yl)benzoate (3af)



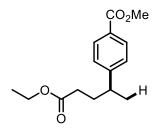
GPII, 43.1 mg, 75% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.95 – 7.91 (m, 2H), 7.23 – 7.17 (m, 2H), 6.96 – 6.90 (m, 2H), 6.78 – 6.72 (m, 2H), 3.89 (s, 3H), 3.75 (s, 3H), 3.06 – 2.95 (m, 1H), 2.88 – 2.70 (m, 2H), 1.25 (d, J = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.1, 157.8, 152.3, 132.2, 129.9, 129.6, 127.9, 127.1, 113.4, 55.1, 52.0, 43.8, 42.1, 21.0. HRMS (ESI-TOF) (m/z): Calcd for C₁₈H₂₀O₃Na ([M + Na]⁺): 307.1305; found: 307.1304.

methyl 4-(4-(benzoyloxy)butan-2-yl)benzoate (3ag)



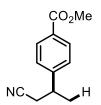
GPII, 44.1 mg, 70% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.94 (m, 4H), 7.58 – 7.52 (m, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 4.32 – 4.25 (m, 1H), 4.22 – 4.14 (m, 1H), 3.90 (s, 3H), 3.07 – 2.96 (m, 1H), 2.12 – 2.05 (m, 2H), 1.35 (d, J = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.0, 166.4, 151.7, 132.9, 130.2, 129.9, 129.5, 128.3, 128.2, 127.0, 63.2, 52.0, 37.1, 36.7, 22.1. HRMS (ESI-TOF) (m/z): Calcd for C₁₉H₂₀O₄Na ([M + Na]⁺): 335.1254; found: 335.1252.

methyl 4-(5-ethoxy-5-oxopentan-2-yl)benzoate (3ah)



GPII, 25.8 mg, 48% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, J = 8.3 Hz, 2H), 7.28 – 7.23 (m, 2H), 4.09 (q, J = 7.1 Hz, 2H), 3.91 (s, 3H), 2.84 – 2.73 (m, 1H), 2.24 – 2.10 (m, 2H), 2.02 – 1.85 (m, 2H), 1.28 (d, J = 6.8 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 173.4, 167.0, 151.8, 129.8, 128.2, 127.0, 60.3, 52.0, 39.4, 32.9, 32.4, 21.8, 14.2. HRMS (ESI-TOF) (m/z): Calcd for C₁₅H₂₀O₄Na ([M + Na]⁺): 287.1254; found: 287.1255.

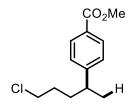
methyl 4-(1-cyanopropan-2-yl)benzoate (3ai)



GPII, 33.6 mg, 82% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.05 – 7.99 (m, 2H), 7.35 – 7.29 (m, 2H), 3.91 (s, 3H), 3.28 – 3.18 (m, 1H), 2.68 – 2.54 (m, 2H), 1.47 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.6, 148.1, 130.1, 129.3, 126.6, 118.1, 52.1, 36.5, 26.0, 20.5. HRMS (ESI-TOF) (m/z): Calcd for C₁₂H₁₃NO₂Na ([M + Na]⁺):

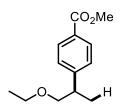
226.0839; found: 226.0838.

methyl 4-(5-chloropentan-2-yl)benzoate (3aj)



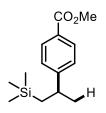
GPI, 41.0 mg, 85% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 3.90 (s, 3H), 3.50 – 3.45 (m, 2H), 2.82 – 2.72 (m, 1H), 1.79 – 1.68 (m, 3H), 1.65 – 1.55 (m, 1H), 1.28 (d, J = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.0, 152.3, 129.8, 128.1, 126.9, 52.0, 45.0, 39.5, 35.1, 30.6, 22.1. HRMS (ESI-TOF) (m/z): Calcd for C₁₃H₁₈ClO₂ ([M + H]⁺): 241.0990; found: 241.0990.

methyl 4-(1-ethoxypropan-2-yl)benzoate (3ak)



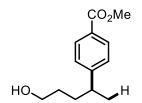
GPI, 35.5 mg, 79% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.0 (d, J = 8.1 Hz, 2H), 7.3 (d, J = 8.0 Hz, 2H), 3.9 (s, 3H), 3.6 – 3.5 (m, 1H), 3.5 – 3.4 (m, 3H), 3.1 – 3.0 (m, 1H), 1.3 (d, J = 7.0 Hz, 3H), 1.2 (t, J = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.1, 150.1, 129.6, 128.2, 127.4, 75.9, 66.4, 52.0, 40.1, 18.2, 15.1. HRMS (ESI-TOF) (m/z): Calcd for C₁₃H₁₉O₃ ([M + H]⁺): 223.1329; found: 223.1329.

methyl 4-(1-(trimethylsilyl)propan-2-yl)benzoate (3al)



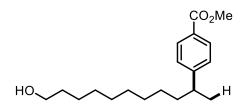
GPII, 36.7 mg, 73% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.92 (m, 2H), 7.30 – 7.25 (m, 2H), 3.90 (s, 3H), 2.97 – 2.88 (m, 1H), 1.28 (d, *J* = 6.9 Hz, 3H), 1.02 – 0.87 (m, 2H), -0.12 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 167.1, 155.3, 129.7, 127.7, 126.7, 51.9, 36.5, 26.7, 26.1, -1.0. HRMS (ESI-TOF) (m/z): Calcd for C₁₄H₂₃O₂Si ([M + H]⁺): 251.1462; found: 251.1462.

methyl 4-(5-hydroxypentan-2-yl)benzoate (3am)



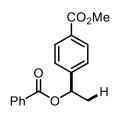
GPII, 29.7 mg, 66% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 3.90 (s, 3H), 3.59 (t, J = 6.5 Hz, 2H), 2.82 – 2.71 (m, 1H), 1.69 – 1.60 (m, 3H), 1.55 – 1.48 (m, 1H), 1.44 – 1.37 (m, 1H), 1.27 (d, J = 6.9 Hz, 3H)⁻¹³C NMR (101 MHz, CDCl₃) δ 167.1, 152.8, 129.7, 127.9, 127.0, 62.8, 52.0, 39.9, 34.1, 30.7, 22.1. HRMS (ESI-TOF) (m/z): Calcd for C₁₃H₁₈O₃Na ([M + Na]⁺): 245.1148; found: 245.1150.

methyl 4-(11-hydroxyundecan-2-yl)benzoate (3an)



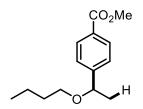
GPII, 40.2 mg, 65% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.93 (m, 2H), 7.26 – 7.21 (m, 2H), 3.90 (s, 3H), 3.62 (t, *J* = 6.6 Hz, 2H), 2.78 – 2.68 (m, 1H), 1.61 – 1.50 (m, 5H), 1.32 – 1.20 (m, 14H), 1.15 – 1.06 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 167.2, 153.4, 129.6, 127.7, 127.0, 63.0, 51.9, 40.0, 38.1, 32.7, 30.3 – 28.8 (m), 27.5, 25.7, 22.0. HRMS (ESI-TOF) (m/z): Calcd for C₁₉H₃₁O₃ ([M + H]⁺): 307.2268; found: 307.2267.

methyl 4-(1-(benzoyloxy)ethyl)benzoate (3ao)



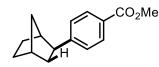
GPII, 44.9 mg, 78% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.11 – 8.02 (m, 4H), 7.60 – 7.54 (m, 1H), 7.53 – 7.43 (m, 4H), 6.16 (q, J = 6.6 Hz, 1H), 3.91 (s, 3H), 1.68 (d, J = 6.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.7, 165.6, 146.8, 133.1, 130.1, 129.9, 129.6, 128.4, 125.8, 72.3, 52.1, 22.4. HRMS (ESI-TOF) (m/z): Calcd for C₁₇H₁₆O₄Na ([M + Na]⁺): 307.0941; found: 307.0939.

methyl 4-(1-butoxyethyl)benzoate (3ap)



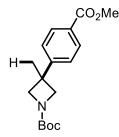
GPII, 39.3 mg, 83% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.04 – 7.99 (m, 2H), 7.41 – 7.36 (m, 2H), 4.43 (q, *J* = 6.5 Hz, 1H), 3.91 (s, 3H), 3.35 – 3.24 (m, 2H), 1.61 – 1.50 (m, 2H), 1.43 (d, *J* = 6.6 Hz, 3H), 1.40 – 1.31 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.0, 149.7, 129.7, 129.1, 126.0, 77.5, 68.7, 52.0, 32.0, 24.1, 19.3, 13.9. HRMS (ESI-TOF) (m/z): Calcd for C₁₄H₂₁O₃ ([M + H]⁺): 237.1485; found: 237.1485.

methyl 4-(bicyclo[2.2.1]heptan-2-yl)benzoate (3aq)



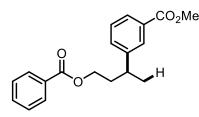
GPII, 40.6 mg, 88% yield, d.r. > 20: 1. ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 3.89 (s, 3H), 2.81 – 2.75 (m, 1H), 2.41 – 2.33 (m, 2H), 1.84 – 1.76 (m, 1H), 1.67 – 1.56 (m, 3H), 1.54 – 1.48 (m, 1H), 1.40 – 1.33 (m, 1H), 1.31 – 1.24 (m, 1H), 1.23 – 1.18 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 167.1, 153.1, 129.5, 127.2, 127.0, 51.9, 47.4, 42.7, 39.1, 36.8, 36.1, 30.5, 28.8. HRMS (ESI-TOF) (m/z): Calcd for C₁₅H₁₉O₂ ([M + H]⁺): 231.1380; found: 231.1380.

tert-butyl 3-(4-(methoxycarbonyl)phenyl)-3-methylazetidine-1-carboxylate (3ar)



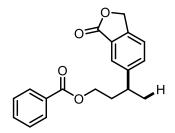
GPI, 52.2 mg, 85% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.04 – 7.99 (m, 2H), 7.29 – 7.24 (m, 2H), 4.20 (d, J = 8.1 Hz, 2H), 3.95 (d, J = 8.1 Hz, 2H), 3.92 (s, 3H), 1.64 (s, 3H), 1.45 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 166.7, 156.5, 152.0, 129.9, 128.3, 125.3, 79.6, 52.1, 38.1, 29.0, 28.4. HRMS (ESI-TOF) (m/z): Calcd for C₁₇H₂₃NO₄Na ([M + Na]⁺): 328.1519; found: 328.1519.

methyl 3-(4-(benzoyloxy)butan-2-yl)benzoate (3bg)



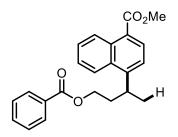
GPII, 41.3 mg, 66% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.99 – 7.95 (m, 2H), 7.94 – 7.91 (m, 1H), 7.89 – 7.85 (m, 1H), 7.58 – 7.52 (m, 1H), 7.45 – 7.40 (m, 3H), 7.39 – 7.34 (m, 1H), 4.31 – 4.24 (m, 1H), 4.22 – 4.15 (m, 1H), 3.90 (s, 3H), 3.07 – 2.96 (m, 1H), 2.09 (q, J = 6.8 Hz, 2H), 1.35 (d, J = 7.0 Hz, 3H)⁻¹³C NMR (101 MHz, CDCl₃) δ 167.1, 166.4, 146.6, 132.8, 131.7, 130.4, 130.2, 129.5, 128.6, 128.3, 128.0, 127.5, 63.2, 52.1, 36.8, 36.7, 22.3. HRMS (ESI-TOF) (m/z): Calcd for C₁₉H₂₁O₄ ([M + H]⁺): 313.1434; found: 313.1433.

3-(3-oxo-1,3-dihydroisobenzofuran-5-yl)butyl benzoate (3cg)



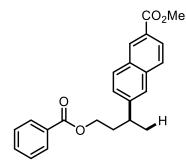
GPII, 46.1 mg, 74% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.87 (m, 2H), 7.84 (d, J = 8.0 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.44 – 7.38 (m, 3H), 7.32 (s, 1H), 5.22 (s, 2H), 4.35 – 4.28 (m, 1H), 4.26 – 4.19 (m, 1H), 3.15 – 3.04 (m, 1H), 2.13 (q, J = 6.7 Hz, 2H), 1.38 (d, J = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.9, 166.3, 153.7, 147.3, 133.0, 129.9, 129.3, 128.3, 128.2, 125.9, 123.9, 120.4, 69.4, 63.1, 37.7, 36.7, 22.4. HRMS (ESI-TOF) (m/z): Calcd for C₁₉H₁₉O₄ ([M + H]⁺): 311.1278; found: 311.1277.

methyl 4-(4-(benzoyloxy)butan-2-yl)-1-naphthoate (3dg)

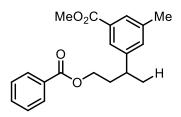


GPII, 54.6 mg, 75% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.99 – 8.94 (m, 1H), 8.22 (d, J = 8.6 Hz, 1H), 8.15 (d, J = 7.7 Hz, 1H), 7.99 – 7.94 (m, 2H), 7.62 – 7.50 (m, 3H), 7.47 (d, J = 7.7 Hz, 1H), 7.42 (t, J = 7.7 Hz, 2H), 4.45 – 4.38 (m, 1H), 4.32 – 4.25 (m, 1H), 3.98 (s, 3H), 3.95 – 3.86 (m, 1H), 2.36 – 2.27 (m, 1H), 2.21 – 2.11 (m, 1H), 1.48 (d, J = 6.9 Hz, 3H).¹³C NMR (101 MHz, CDCl₃) δ 168.0, 166.4, 148.1, 132.9, 131.7, 131.7, 130.1, 129.5, 129.3, 128.3, 127.1, 126.5, 126.2, 125.5, 123.3, 121.5, 63.2, 52.2, 52.0, 36.4, 21.5. HRMS (ESI-TOF) (m/z): Calcd for C₂₃H₂₂O₄Na ([M + Na]⁺): 385.1410; found: 385.1408.

methyl 6-(4-(benzoyloxy)butan-2-yl)-2-naphthoate (3eg)

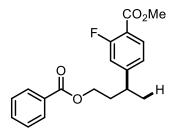


GPII, 51.4 mg, 70% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.56 (s, 1H), 8.05 – 8.01 (m, 1H), 7.94 – 7.87 (m, 3H), 7.80 (d, J = 8.6 Hz, 1H), 7.68 (s, 1H), 7.54 – 7.48 (m, 1H), 7.46 – 7.42 (m, 1H), 7.39 – 7.33 (m, 2H), 4.35 – 4.28 (m, 1H), 4.27 – 4.20 (m, 1H), 3.97 (s, 3H), 3.19 – 3.09 (m, 1H), 2.24 – 2.10 (m, 2H), 1.42 (d, J = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.3, 166.4, 146.5, 135.7, 132.8, 131.3, 130.7, 130.1, 129.7, 129.4, 128.2, 127.7, 126.8, 126.3, 125.4, 125.1, 63.4, 52.1, 37.3, 36.7, 22.2. HRMS (ESI-TOF) (m/z): Calcd for C₂₃H₂₃O₄ ([M + H]⁺): 363.1591; found: 363.1590. **methyl 3-(4-(benzoyloxy)butan-2-yl)-5-methylbenzoate (3fg)**



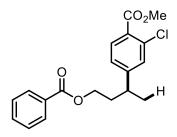
GPII, 48.7 mg, 74% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, J = 7.7 Hz, 2H), 7.70 (d, J = 11.9 Hz, 2H), 7.58 – 7.51 (m, 1H), 7.47 – 7.37 (m, 2H), 7.22 (s, 1H), 4.32 – 4.15 (m, 2H), 3.89 (s, 3H), 3.02 – 2.90 (m, 1H), 2.36 (s, 3H), 2.13 – 2.03 (m, 2H), 1.33 (d, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.3, 166.4, 146.6, 138.3, 132.8, 132.5, 130.2, 130.2, 129.4, 128.2, 128.1, 125.1, 63.3, 52.0, 36.8, 36.7, 22.3, 21.2. HRMS (ESI-TOF) (m/z): Calcd for C₂₀H₂₃O₄ ([M + H]⁺): 327.1591; found: 327.1590.

methyl 4-(4-(benzoyloxy)butan-2-yl)-2-fluorobenzoate (3gg)



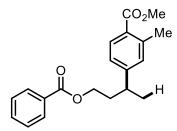
GPII, 39.7 mg, 60% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.93 (m, 2H), 7.89 – 7.83 (m, 1H), 7.58 – 7.53 (m, 1H), 7.46 – 7.39 (m, 2H), 7.09 – 6.97 (m, 2H), 4.33 – 4.26 (m, 1H), 4.23 – 4.16 (m, 1H), 3.92 (s, 3H), 3.05 – 2.94 (m, 1H), 2.11 – 2.02 (m, 2H), 1.33 (d, J = 6.9 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 166.4, 164.8 (d, J = 4.0 Hz), 162.1 (d, J = 260.1 Hz), 154.4 (d, J = 8.0 Hz), 132.9, 132.4 (d, J = 1.4 Hz), 130.0, 129.4, 128.3, 122.7, 116.4 (d, J = 10.0 Hz), 115.2 (d, J = 22.6 Hz), 62.9, 52.2, 36.9, 36.5, 21.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -109.34. HRMS (ESI-TOF) (m/z): Calcd for C₁₉H₂₀FO₄ ([M + H]⁺): 331.1340; found: 331.1340.

methyl 4-(4-(benzoyloxy)butan-2-yl)-2-chlorobenzoate (3hg)



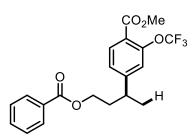
GPII, 43.7 mg, 63% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.97 – 7.92 (m, 2H), 7.78 (d, J = 8.1 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.46 – 7.40 (m, 2H), 7.32 (d, J = 1.7 Hz, 1H), 7.19 – 7.14 (m, 1H), 4.33 – 4.26 (m, 1H), 4.24 – 4.17 (m, 1H), 3.91 (s, 3H), 3.02 – 2.92 (m, 1H), 2.10 – 2.03 (m, 2H), 1.33 (d, J = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.4, 165.9, 152.0, 134.1, 132.9, 131.8, 130.0, 129.6, 129.4, 128.3, 127.6, 125.3, 63.0, 52.3, 36.8, 36.5, 21.9. HRMS (ESI-TOF) (m/z): Calcd for C₁₉H₂₀ClO₄ ([M + H]⁺): 347.1045; found: 347.1045.

methyl 4-(4-(benzoyloxy)butan-2-yl)-2-methylbenzoate (3ig)



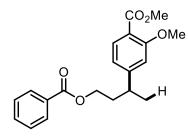
GPII, 50.3 mg, 77% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.97 – 7.93 (m, 2H), 7.86 (d, J = 7.8 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.45 – 7.39 (m, 2H), 7.12 – 7.07 (m, 2H), 4.31 – 4.24 (m, 1H), 4.23 – 4.16 (m, 1H), 3.87 (s, 3H), 2.99 – 2.89 (m, 1H), 2.57 (s, 3H), 2.11 – 2.04 (m, 2H), 1.33 (d, J = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.8, 166.4, 150.7, 140.6, 132.8, 131.1, 130.4, 130.2, 129.4, 128.3, 127.4, 124.2, 63.3, 51.7, 36.9, 36.6, 22.1, 21.9. HRMS (ESI-TOF) (m/z): Calcd for C₂₀H₂₂O₄Na ([M + Na]⁺): 349.1410; found: 349.1410.

methyl 4-(4-(benzoyloxy)butan-2-yl)-2-(trifluoromethoxy)benzoate (3jg)



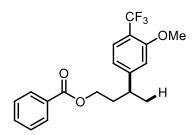
GPII, 54.5 mg, 68% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.97 – 7.93 (m, 2H), 7.91 – 7.88 (m, 1H), 7.58 – 7.52 (m, 1H), 7.45 – 7.39 (m, 2H), 7.27 – 7.22 (m, 1H), 7.20 – 7.17 (m, 1H), 4.35 – 4.28 (m, 1H), 4.24 – 4.16 (m, 1H), 3.91 (s, 3H), 3.08 – 2.97 (m, 1H), 2.14 – 2.03 (m, 2H), 1.35 (d, J = 6.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.3, 164.8, 153.3, 148.0 (q, *J* = 2.0 Hz), 132.9, 132.3, 130.0, 129.4, 128.3, 125.6, 122.7, 121.3 – 121.1 (m), 120.3 (q, J = 257.7 Hz), 62.9, 52.3, 36.9, 36.5, 21.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -57.35. HRMS (ESI-TOF) (m/z): Calcd for C₂₀H₂₀F₃O₅ ([M + H]⁺): 397.1257; found: 397.1258.

methyl 4-(4-(benzoyloxy)butan-2-yl)-2-methoxybenzoate (3kg)



GPII, 60.6 mg, 88% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.94 (m, 2H), 7.76 (d, J = 8.0 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.43 (t, J = 7.7 Hz, 2H), 6.88 – 6.84 (m, 1H), 6.82 – 6.79 (m, 1H), 4.32 – 4.25 (m, 1H), 4.24 – 4.17 (m, 1H), 3.87 (s, 6H), 3.02 – 2.91 (m, 1H), 2.13 – 2.01 (m, 2H), 1.34 (d, J = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.4, 166.4, 159.4, 152.8, 132.9, 132.1, 130.1, 129.4, 128.3, 118.5, 117.8, 110.8, 63.2, 55.9, 51.9, 37.4, 36.6, 22.0. HRMS (ESI-TOF) (m/z): Calcd for C₂₀H₂₃O₅ ([M + H]⁺): 343.1540; found: 343.1540.

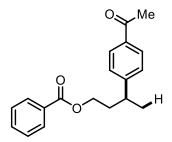
3-(3-methoxy-4-(trifluoromethyl)phenyl)butyl benzoate (3lg)



GPII, 51.8 mg, 73% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.97 – 7.92 (m, 2H), 7.58 – 7.53 (m, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.40 (m, 2H), 6.89 – 6.82 (m, 2H), 4.33 – 4.26 (m, 1H), 4.26 – 4.19 (m, 1H), 3.86 (s, 3H), 3.03 – 2.93 (m, 1H), 2.12 – 2.04 (m,

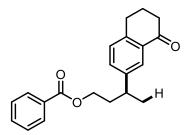
2H), 1.34 (d, J = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.4, 157.6, 152.4, 133.0, 130.1, 129.4, 128.3, 127.7 – 127.0 (m), 123.7 (q, J = 271.9 Hz), 118.3, 116.5, 111.0 – 110.5 (m), 63.2, 55.8, 37.5, 36.6, 22.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.08. HRMS (ESI-TOF) (m/z): Calcd for C₁₉H₁₉F₃O₃Na ([M + Na]⁺): 375.1179; found: 375.1178.

3-(4-acetylphenyl)butyl benzoate (3mg)



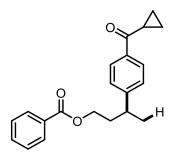
GPII, 43.7 mg, 73% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.97 – 7.93 (m, 2H), 7.91 – 7.87 (m, 2H), 7.57 – 7.52 (m, 1H), 7.44 – 7.39 (m, 2H), 7.34 – 7.29 (m, 2H), 4.33 – 4.25 (m, 1H), 4.23 – 4.15 (m, 1H), 3.08 – 2.97 (m, 1H), 2.56 (s, 3H), 2.13 – 2.06 (m, 2H), 1.35 (d, J = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.7, 166.4, 152.0, 135.4, 132.9, 130.1, 129.4, 128.7, 128.3, 127.1, 63.2, 37.1, 36.6, 26.5, 22.1. HRMS (ESI-TOF) (m/z): Calcd for C₁₉H₂₁O₃ ([M + H]⁺): 297.1485; found: 297.1486.

3-(8-oxo-5,6,7,8-tetrahydronaphthalen-2-yl)butyl benzoate (3ng)



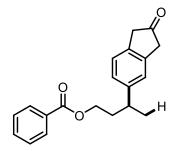
GPII, 36.8 mg, 57% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.95 (m, 2H), 7.92 (d, J = 2.0 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.45 – 7.40 (m, 2H), 7.35 – 7.31 (m, 1H), 7.18 (d, J = 7.9 Hz, 1H), 4.31 – 4.24 (m, 1H), 4.20 – 4.12 (m, 1H), 3.04 – 2.95 (m, 1H), 2.92 (t, J = 6.1 Hz, 2H), 2.66 – 2.61 (m, 2H), 2.15 – 2.04 (m, 4H), 1.33 (d, J = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 198.6, 166.4, 144.8, 142.5, 132.8, 132.6, 132.4, 130.2, 129.5, 129.0, 128.3, 125.1, 63.3, 39.2, 36.6, 36.6, 29.3, 23.3. HRMS (ESI-TOF) (m/z): Calcd for C₂₁H₂₃O₃ ([M + H]⁺): 323.1642; found: 323.1642.

3-(4-(cyclopropanecarbonyl)phenyl)butyl benzoate (3og)



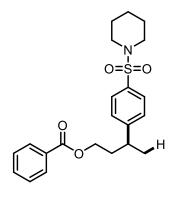
GPII, 41.3 mg, 64% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.92 (m, 4H), 7.57 – 7.52 (m, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 4.33 – 4.26 (m, 1H), 4.24 – 4.18 (m, 1H), 3.08 – 2.97 (m, 1H), 2.67 – 2.60 (m, 1H), 2.14 – 2.06 (m, 2H), 1.36 (d, *J* = 7.0 Hz, 3H), 1.24 – 1.20 (m, 2H), 1.05 – 0.99 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 200.1, 166.4, 151.6, 136.3, 132.9, 130.2, 129.5, 128.4, 128.3, 127.1, 63.2, 37.1, 36.7, 17.0, 11.5. HRMS (ESI-TOF) (m/z): Calcd for C₂₁H₂₃O₃ ([M + H]⁺): 323.1642; found: 323.1642.

3-(2-oxo-2,3-dihydro-1*H*-inden-5-yl)butyl benzoate (3pg)



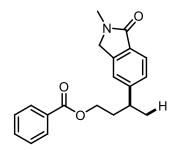
GPII, 50.5 mg, 81% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.88 (m, 2H), 7.69 (d, J = 7.9 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.41 (t, J = 7.8 Hz, 2H), 7.31 (s, 1H), 7.27 – 7.23 (m, 1H), 4.34 – 4.27 (m, 1H), 4.26 – 4.18 (m, 1H), 3.10 – 2.98 (m, 3H), 2.68 – 2.58 (m, 2H), 2.16 – 2.06 (m, 2H), 1.36 (d, J = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 206.5, 166.4, 155.9, 154.1, 135.6, 132.9, 130.1, 129.4, 128.2, 126.5, 125.0, 123.9, 63.2, 37.7, 36.7, 36.4, 25.7, 22.3. HRMS (ESI-TOF) (m/z): Calcd for C₂₀H₂₁O₃ ([M + H]⁺): 309.1485; found: 309.1485.

3-(4-(piperidin-1-ylsulfonyl)phenyl)butyl benzoate (3qg)



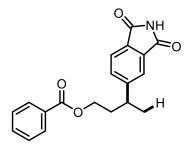
GPII, 67.4 mg, 83% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.95 (m, 2H), 7.69 (d, J = 8.2 Hz, 2H), 7.60 – 7.54 (m, 1H), 7.47 – 7.42 (m, 2H), 7.38 (d, J = 8.2 Hz, 2H), 4.33 – 4.25 (m, 1H), 4.24 – 4.15 (m, 1H), 3.09 – 3.01 (m, 1H), 2.98 (t, J = 5.5 Hz, 4H), 2.15 – 2.06 (m, 2H), 1.67 – 1.60 (m, 4H), 1.46 – 1.40 (m, 2H), 1.36 (d, J = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.4, 151.4, 134.1, 133.0, 130.0, 129.4, 128.3, 128.0, 127.5, 63.0, 46.8, 36.9, 36.6, 25.1, 23.4, 22.0. HRMS (ESI-TOF) (m/z): Calcd for C₂₂H₂₈NO₄S ([M + H]⁺): 402.1734; found: 402.1733.

3-(2-methyl-1-oxoisoindolin-5-yl)butyl benzoate (3rg)



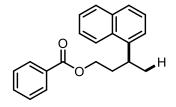
GPII, 51.3 mg, 79% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.89 (m, 2H), 7.76 (d, J = 7.8 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.40 (t, J = 7.7 Hz, 2H), 7.32 (d, J = 7.8 Hz, 1H), 7.26 (s, 1H), 4.32 – 4.17 (m, 4H), 3.16 (s, 3H), 3.08 – 3.00 (m, 1H), 2.10 (q, J = 6.7 Hz, 2H), 1.36 (d, J = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.5, 166.4, 150.2, 141.5, 132.8, 131.1, 130.0, 129.4, 128.2, 126.9, 123.7, 121.0, 63.2, 51.8, 37.4, 36.8, 29.4, 22.4. HRMS (ESI-TOF) (m/z): Calcd for C₂₀H₂₂NO₃ ([M + H]⁺): 324.1594; found: 324.1594.

3-(1,3-dioxoisoindolin-5-yl)butyl benzoate (3sg)



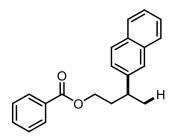
GPII, 37.2 mg, 57% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.95 – 7.90 (m, 2H), 7.78 – 7.73 (m, 2H), 7.61 – 7.53 (m, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 4.37 – 4.29 (m, 1H), 4.25 – 4.18 (m, 1H), 3.19 – 3.08 (m, 1H), 2.14 (q, *J* = 6.7 Hz, 2H), 1.68 (s, 1H), 1.39 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.9, 167.6, 166.3, 154.2, 133.3, 133.0, 130.7, 129.9, 129.4, 128.3, 123.9, 121.9, 62.9, 37.7, 36.7. HRMS (ESI-TOF) (m/z): Calcd for C₁₉H₁₈NO₄ ([M + H]⁺): 324.1230; found: 324.1231.

3-(naphthalen-1-yl)butyl benzoate (3tg)



GPII, 49.4 mg, 81% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.18 – 8.13 (m, 1H), 8.03 – 7.98 (m, 2H), 7.87 – 7.82 (m, 1H), 7.73 – 7.68 (m, 1H), 7.56 – 7.51 (m, 1H), 7.48 – 7.39 (m, 6H), 4.45 – 4.37 (m, 1H), 4.31 – 4.24 (m, 1H), 3.91 – 3.81 (m, 1H), 2.36 – 2.26 (m, 1H), 2.21 – 2.10 (m, 1H), 1.47 (d, J = 6.9 Hz, 3H).¹³C NMR (101 MHz, CDCl₃) δ 166.5, 142.4, 133.9, 132.8, 131.4, 130.3, 129.5, 129.0, 128.3, 126.6, 125.8, 125.6, 125.3, 122.9, 122.5, 63.5, 36.6, 30.5, 21.6. HRMS (ESI-TOF) (m/z): Calcd for C₂₁H₂₁O₂ ([M + H]⁺): 305.1536; found: 305.1536.

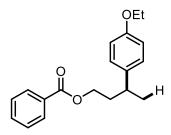
3-(naphthalen-2-yl)butyl benzoate (3ug)



GPII, 39.1 mg, 64% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.96 – 7.92 (m, 2H), 7.81 – 7.75 (m, 3H), 7.65 (d, *J* = 1.7 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.47 – 7.40 (m, 2H), 7.39

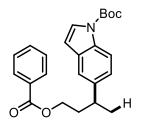
-7.34 (m, 3H), 4.33 - 4.27 (m, 1H), 4.26 - 4.19 (m, 1H), 3.16 - 3.06 (m, 1H), 2.19 - 2.09 (m, 2H), 1.41 (d, J = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.5, 143.7, 133.6, 132.8, 132.3, 130.3, 129.4, 128.2, 128.2, 127.5, 127.5, 125.9, 125.4, 125.2, 125.2, 63.5, 37.1, 36.8, 22.4. HRMS (ESI-TOF) (m/z): Calcd for C₂₁H₂₁O₂ ([M + H]⁺): 305.1536; found: 305.1536.

3-(4-ethoxyphenyl)butyl benzoate (3vg)



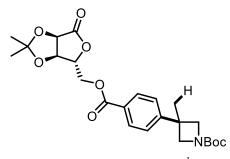
GPII, 21.2 mg, 35% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.03 – 7.95 (m, 2H), 7.57 – 7.51 (m, 1H), 7.46 – 7.39 (m, 2H), 7.15 – 7.08 (m, 2H), 6.86 – 6.79 (m, 2H), 4.30 – 4.22 (m, 1H), 4.20 – 4.13 (m, 1H), 4.00 (q, J = 6.9 Hz, 2H), 2.94 – 2.84 (m, 1H), 2.10 – 1.92 (m, 2H), 1.40 (t, J = 6.9 Hz, 3H), 1.30 (d, J = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.5, 157.3, 138.1, 132.8, 130.4, 129.5, 128.3, 127.8, 114.4, 63.5, 63.3, 37.1, 36.0, 22.5, 14.9. HRMS (ESI-TOF) (m/z): Calcd for C₁₉H₂₃O₃ ([M + H]⁺): 299.1642; found: 299.1642.

tert-butyl 5-(4-(benzoyloxy)butan-2-yl)-1H-indole-1-carboxylate (3wg)



GPII (Ni(dtbbpy)Br₂, 10 mol%), 34.5 mg, 43% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, J = 8.6 Hz, 1H), 7.99 – 7.95 (m, 2H), 7.59 – 7.49 (m, 2H), 7.44 – 7.37 (m, 3H), 7.21 – 7.15 (m, 1H), 6.52 – 6.49 (m, 1H), 4.33 – 4.15 (m, 2H), 3.10 – 2.98 (m, 1H), 2.15 – 2.06 (m, 2H), 1.66 (s, 9H), 1.37 (d, J = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.5, 149.8, 140.7, 132.7, 130.9, 130.4, 129.5, 128.2, 126.1, 123.3, 118.9, 115.2, 107.2, 83.5, 63.6, 37.3, 36.9, 28.2. HRMS (ESI-TOF) (m/z): Calcd for C₂₄H₂₇NO₄K ([M + K]⁺): 432.1572; found: 432.1572. tert-butyl

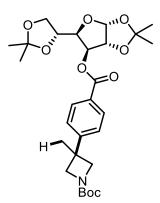
3-(4-(((((3*aR*,4*R*,6*aR*)-2,2-dimethyl-6-oxotetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)met hoxy)carbonyl)phenyl)-3-methylazetidine-1-carboxylate (3xr)



GPII, 70.7 mg, 76% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.88 (m, 2H), 7.33 – 7.27 (m, 2H), 4.92 – 4.88 (m, 1H), 4.84 – 4.76 (m, 2H), 4.68 – 4.61 (m, 1H), 4.56 – 4.49 (m, 1H), 4.19 (d, J = 8.1 Hz, 2H), 3.96 (d, J = 7.8 Hz, 2H), 1.64 (s, 3H), 1.51 (s, 3H), 1.46 (s, 9H), 1.39 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 173.4, 165.2, 156.4, 153.0, 129.9, 126.8, 125.7, 113.8, 79.8, 79.7, 77.8, 75.2, 63.7, 38.1, 28.9, 28.3, 26.7, 25.5. HRMS (ESI-TOF) (m/z): Calcd for C₂₄H₃₁NO₈Na ([M + Na]⁺): 484.1942; found: 484.1944.

tert-butyl

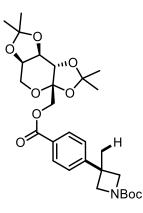
3-(4-(((((3*aR*,5*R*,6*S*,6*aR*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetra hydrofuro[2,3-*d*][1,3]dioxol-6-yl)oxy)carbonyl)phenyl)-3-methylazetidine-1-carb oxylate (3yr)



GPII, 83.2 mg, 77% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 5.88 (d, *J* = 4.1 Hz, 1H), 5.32 (t, *J* = 6.0 Hz, 1H), 4.93 (t, *J* = 5.0 Hz, 1H), 4.76 (q, *J* = 7.2 Hz, 1H), 4.23 – 4.12 (m, 4H), 3.97 (d, *J* = 8.1 Hz, 2H), 3.63 (t, *J* = 7.8 Hz, 1H), 1.65 (s, 3H), 1.54 (s, 3H), 1.48 – 1.44 (m, 12H), 1.42 (s, 3H), 1.34 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.1, 156.4, 152.8, 130.1, 127.1, 125.6, 114.8, 109.5, 105.1, 81.2, 79.7, 79.1, 75.2, 72.2, 66.3, 38.1, 28.3, 27.0, 26.6, 25.3. HRMS (ESI-TOF) (m/z): Calcd for C₂₈H₃₉NO₉K ([M + K]⁺): 572.2256; found: 572.2257.

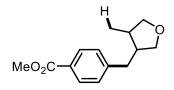
tert-butyl

3-methyl-3-(4-(((((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]d ioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methoxy)carbonyl)phenyl)azetidine-1-carboxyla te (3zr)



GPII, 80.3 mg, 75% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, J = 8.1 Hz, 2H), 7.29 – 7.25 (m, 2H), 4.70 – 4.62 (m, 2H), 4.46 (d, J = 2.6 Hz, 1H), 4.34 (d, J = 11.8 Hz, 1H), 4.27 (d, J = 7.9 Hz, 1H), 4.20 (d, J = 8.1 Hz, 2H), 3.99 – 3.92 (m, 3H), 3.81 (d, J = 13.0 Hz, 1H), 1.64 (s, 3H), 1.56 (s, 3H), 1.47 (s, 3H), 1.45 (s, 9H), 1.38 (s, 3H), 1.35 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.6, 152.2, 130.1, 128.0, 125.3, 109.1, 108.8, 101.6, 79.7, 70.8, 70.5, 70.1, 65.2, 61.3, 38.1, 28.4, 26.5, 25.9, 25.5, 24.0. HRMS (ESI-TOF) (m/z): Calcd for C₂₈H₃₉NO₉Na ([M + Na]⁺): 556.2517; found: 556.2517.

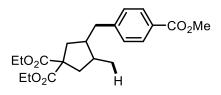
methyl 4-((4-methyltetrahydrofuran-3-yl)methyl)benzoate (5)



GPII, 28.1 mg, 59% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.95 (m, 2H), 7.27 – 7.24 (m, 2H), 3.98 – 3.93 (m, 1H), 3.91 (s, 3H), 3.79 – 3.74 (m, 1H), 3.55 – 3.48 (m, 2H), 2.87 – 2.79 (m, 1H), 2.62 – 2.49 (m, 2H), 2.41 – 2.31 (m, 1H), 1.04 (d, *J* = 7.0

Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.0, 146.4, 129.8, 128.6, 128.0, 75.0, 71.5, 52.0, 43.6, 35.9, 33.6, 13.1. HRMS (ESI-TOF) (m/z): Calcd for C₁₄H₁₉O₃ ([M + H]⁺): 235.1329; found: 235.1329.

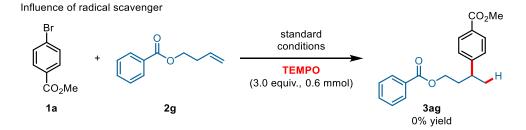
diethyl 3-(4-(methoxycarbonyl)benzyl)-4-methylcyclopentane-1,1-dicarboxylate (7)



GPII, 64.1 mg, 85% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.96 – 7.92 (m, 2H), 7.28 – 7.24 (m, 2H), 4.22 – 4.16 (m, 2H), 4.16 – 4.11 (m, 2H), 3.90 (s, 3H), 2.79 – 2.71 (m, 1H), 2.54 – 2.43 (m, 2H), 2.37 – 2.28 (m, 1H), 2.24 – 2.15 (m, 2H), 2.09 – 2.00 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H), 0.96 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.8, 167.1, 146.9, 129.6, 128.8, 127.8, 61.3, 58.7, 51.9, 44.1, 41.2, 37.7, 36.1, 35.7, 15.0, 13.9. HRMS (ESI-TOF) (m/z): Calcd for C₂₁H₂₉O₆ ([M + H]⁺): 377.1959; found: 377.1958.

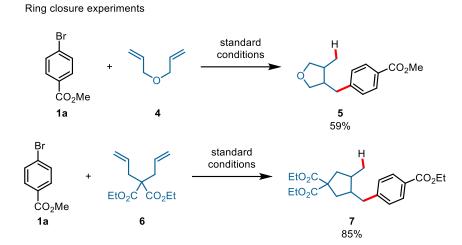
5. Mechanism study experiments

5.1 Influence of radical scavenger



In an oven-dried 10 mL tube equipped with a stirring bar, aryl bromide compounds (0.2 mmol, 1.0 equiv.), unactivated olefins (0.5 mmol, 2.5 equiv.), Hantzsch ester (0.3 mmol, 1.5 equiv.), 4CzIPN (0.004 mmol, 2 mol%), Ni(dtbbpy)Br₂ (0.01 mmol, 5 mol%), Co(TPP) (0.002 mmol, 1 mol%) and TEMPO (0.6 mmol, 3.0 equiv.) were added. The tube was charged with nitrogen (repeated three times), then DMAc (2 mL) was injected. The resulting suspension was stirred at room temperature and irradiated with blue LEDs (440 nm, 10W) by cooling with a fan for 15 h. After completion, the resulting mixture was monitored by TLC, and no desired product (**3ag**) was formed.

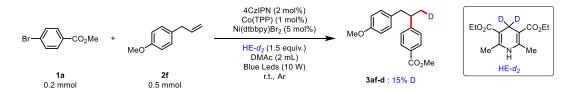
5.2 Procedure of ring closure experiments



In an oven-dried 10 mL tube equipped with a stirring bar, **1a** (0.2 mmol, 1.0 equiv), Olefins **4** or **6** (0.5 mmol, 2.5 equiv), Hantzsch ester (0.3 mmol, 1.5 equiv.), 4CzIPN (0.004 mmol, 2 mol%), Ni(dtbbpy)Br₂ (0.01 mmol, 5 mol%), and Co(TPP) (0.002 mmol, 1 mol%) were added. The tube was charged with nitrogen (repeated three times), then DMAc (2 mL) was injected. The resulting suspension was stirred at room temperature and irradiated with blue LEDs (440 nm, 10 W) by cooling with a fan for 15 h. After completion, the resulting mixture was quenched with H₂O (30 mL). Then the mixture was extracted with ethyl acetate (30 mL). The organic layer was washed with brine (30 mL \times 2), dried over anhydrous Na₂SO₄, and concentrated in vacuum. The residue was purified by flash chromatography on silica gel to afford the desired products.

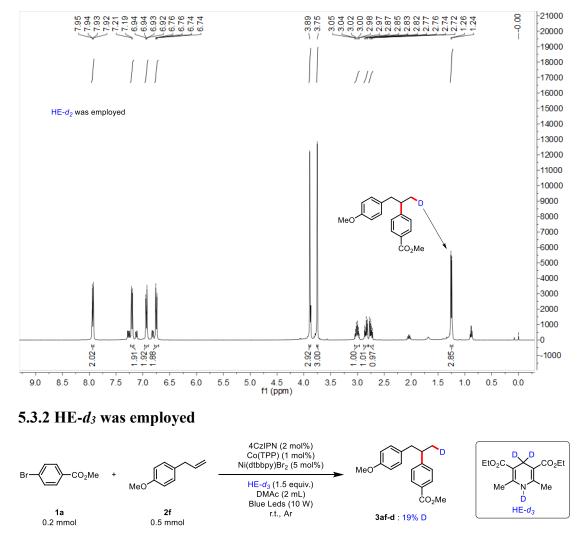
5.3 Deuterium-labelling experiments

5.3.1 HE-d2 was employed



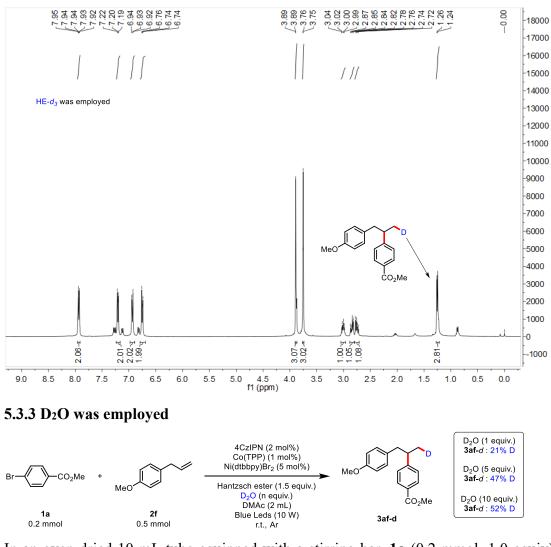
In an oven-dried 10 mL tube equipped with a stirring bar, **1a** (0.2 mmol, 1.0 equiv), HE- d_2 (0.3 mmol, 1.5 equiv.), 4CzIPN (0.004 mmol, 2 mol%), Ni(dtbbpy)Br₂ (0.01 mmol, 5 mol%), and Co(TPP) (0.002 mmol, 1 mol%) were added. The tube was charged with nitrogen (repeated three times), then DMAc (2 mL) and olefin **2f** (0.5

mmol, 2.5 equiv.) were injected. The resulting suspension was stirred at room temperature and irradiated with blue LEDs (440 nm, 10 W) by cooling with a fan for 6 h. After completion, the resulting mixture was quenched with H₂O (30 mL). Then the mixture was extracted with ethyl acetate (30 mL). The organic layer was washed with brine (30 mL \times 2), dried over anhydrous Na₂SO₄, and concentrated in vacuum. The residue was purified by flash chromatography on silica gel to afford the desired products (40.3 mg, 70% yield).



In an oven-dried 10 mL tube equipped with a stirring bar, **1a** (0.2 mmol, 1.0 equiv), HE- d_3 (0.3 mmol, 1.5 equiv.), 4CzIPN (0.004 mmol, 2 mol%), Ni(dtbbpy)Br₂ (0.01 mmol, 5 mol%), and Co(TPP) (0.002 mmol, 1 mol%) were added. The tube was charged with nitrogen (repeated three times), then DMAc (2 mL) and olefin **2f** (0.5 mmol, 2.5 equiv.) were injected. The resulting suspension was stirred at room temperature and irradiated with blue LEDs (440 nm, 10 W) by cooling with a fan for

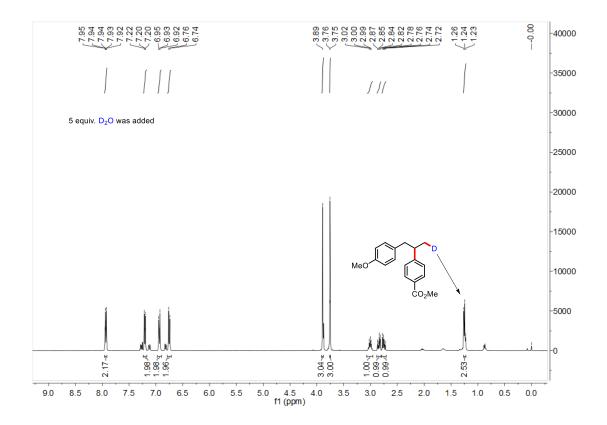
6 h. After completion, the resulting mixture was quenched with H₂O (30 mL). Then the mixture was extracted with ethyl acetate (30 mL). The organic layer was washed with brine (30 mL \times 2), dried over anhydrous Na₂SO₄, and concentrated in vacuum. The residue was purified by flash chromatography on silica gel to afford the desired products (41.5 mg, 72% yield).

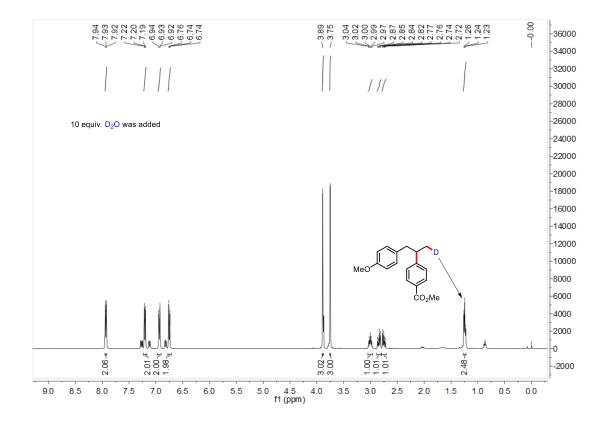


In an oven-dried 10 mL tube equipped with a stirring bar, **1a** (0.2 mmol, 1.0 equiv), Hantzsch ester (0.3 mmol, 1.5 equiv.), 4CzIPN (0.004 mmol, 2 mol%), Ni(dtbbpy)Br₂ (0.01 mmol, 5 mol%) and Co(TPP) (0.002 mmol, 1 mol%) were added. The tube was charged with nitrogen (repeated three times), then DMAc (2 mL), olefin **2f** (0.5 mmol, 2.5 equiv.) and D₂O (n equiv.) were injected. The resulting suspension was stirred at room temperature and irradiated with blue LEDs (440 nm, 10 W) by cooling with a fan for 15 h. After completion, the resulting mixture was quenched with H₂O (30 mL). Then the mixture was extracted with ethyl acetate (30 mL). The organic layer was

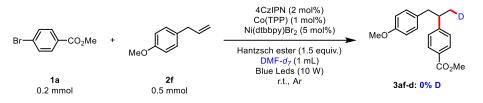
D Yield Entry n 42.5 mg/74% 21% D 1 1 equiv. 2 5 equiv. 47% D 41.7 mg/73% 42.5 mg/74% 3 10 equiv. 52% D -38000 --0.00 7.94 6.76 1.26 1.24 7.22 7.20 6.95 6.93 92 -36000 34000 -32000 *[||* -30000 -28000 1 equiv. D₂O was added -26000 -24000 -22000 20000 18000 16000 14000 12000 10000 MeC -8000 6000 I CO₂Me -4000 -2000 -0 3.02 -2.79*⊸* ຣ໌ຣ໌ສີ 2.9 858 -2000 4.5 f1 (ppm) 9.0 8.0 7.5 7.0 5.0 3.0 1.5 8.5 6.5 6.0 5.5 4.0 3.5 2.5 2.0 1.0 0.5 0.0

washed with brine (30 mL \times 2), dried over anhydrous Na₂SO₄, and concentrated in vacuum. The residue was purified by flash chromatography on silica gel to afford the desired products.

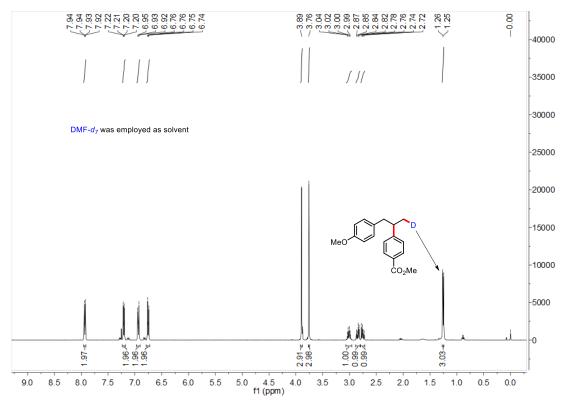




5.3.4 DMF-d7 was employed as solvent



In an oven-dried 10 mL tube equipped with a stirring bar, **1a** (0.2 mmol, 1.0 equiv), Hantzsch ester (0.3 mmol, 1.5 equiv.), 4CzIPN (0.004 mmol, 2 mol%), Ni(dtbbpy)Br₂ (0.01 mmol, 5 mol%) and Co(TPP) (0.002 mmol, 1 mol%) were added. The tube was charged with nitrogen (repeated three times), then DMF- d_7 (1 mL, here we used DMF- d_7 instead of DMAc- d_9) and olefin **2f** (0.5 mmol, 2.5 equiv.) were injected. The resulting suspension was stirred at room temperature and irradiated with blue LEDs (440 nm, 10 W) by cooling with a fan for 15 h. After completion, the resulting mixture was quenched with H₂O (30 mL). Then the mixture was extracted with ethyl acetate (30 mL). The organic layer was washed with brine (30 mL × 2), dried over anhydrous Na₂SO₄, and concentrated in vacuum. The residue was purified by flash chromatography on silica gel to afford the desired products (32.8 mg, 57% yield).



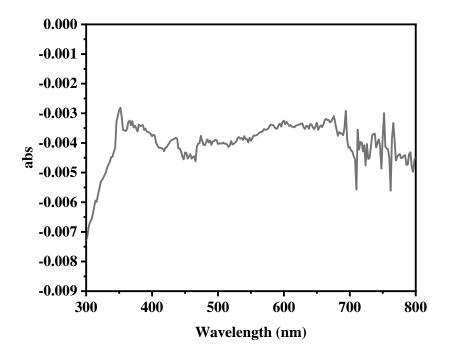


Figure S1 UV-Vis Absorption of 1a in DMAc (Concentration: 0.1 mM)

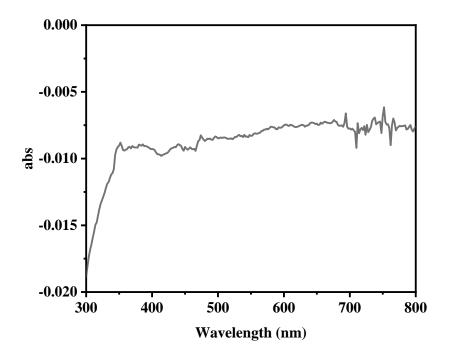


Figure S2 UV-Vis Absorption of 2a in DMAc (Concentration: 0.1 mM)

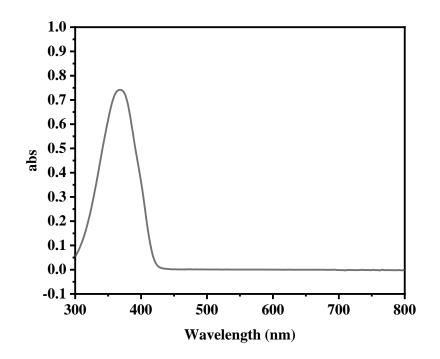


Figure S3 UV-Vis Absorption of Hantzsch ester in DMAc (Concentration: 0.1 mM)

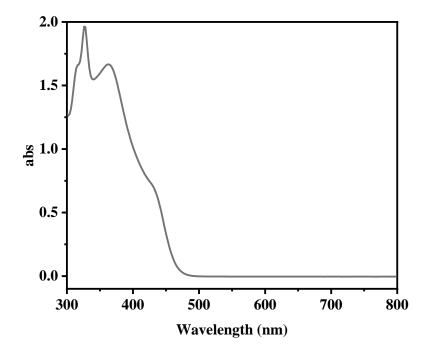


Figure S4 UV-Vis Absorption of 4CzIPN in DMAc (Concentration: 0.1 mM)

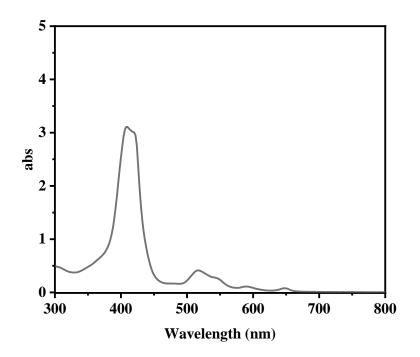


Figure S5 UV-Vis Absorption of Co(TPP) in DMAc (Concentration: 0.1 mM)

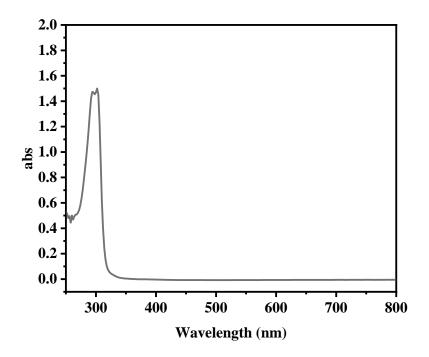


Figure S6 UV-Vis Absorption of Ni(dtbbpy)Br2 in DMAc (Concentration: 0.1 mM)

5.5 Stern-Volmer fluorescence quenching experiments

5.5.1 Quenching of 4CzIPN with Hantzsch ester

Excitation wavelength: 440 nm.

Excitation slit: 5 nm; emission slit: 5 nm.

To a standard solution of 4CzIPN in DMAc (0.1 mM) were added different amounts of a solution of Hantzsch ester in DMAc to afford the final concentrations reported in the figure below. The fluorescence of the solutions was then measured. DMAc was degassed with a stream of nitrogen for 30 min.

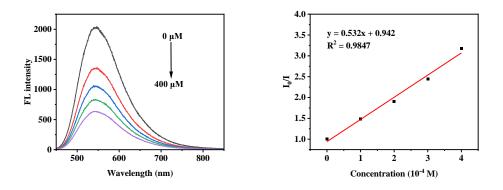


Figure S7 Emission spectra of the 4CzIPN with increasing concentrations of Hantzsch ester

5.5.2 Quenching of 4CzIPN with Ni(dtbbpy)Br₂

Excitation wavelength: 440 nm.

Excitation slit: 5 nm; emission slit: 5 nm.

To a standard solution of 4CzIPN in DMAc (0.1 mM) were added different amounts of a solution of Ni(dtbbpy)Br₂ in DMAc to afford the final concentrations reported in the figure below. The fluorescence of the solutions was then measured. DMAc was degassed with a stream of nitrogen for 30 min.

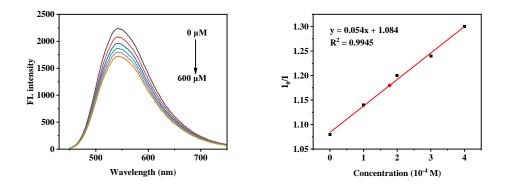


Figure S8 Emission spectra of the 4CzIPN with increasing concentrations of Ni(dtbbpy)Br₂

5.5.3 Quenching of 4CzIPN with Co(TPP)

Excitation wavelength: 440 nm.

Excitation slit: 5 nm; emission slit: 5 nm.

To a standard solution of 4CzIPN in DMAc (0.1 mM) were added different amounts of a solution of Co(TPP) in DMAc to afford the final concentrations reported in the figure below. The fluorescence of the solutions was then measured. DMAc was degassed with a stream of nitrogen for 30 min.

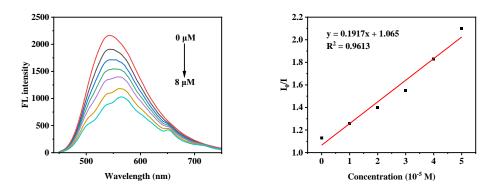


Figure S9 Emission spectra of the 4CzIPN with increasing concentrations of Co(TPP)

5.5.4 Quenching of Co(TPP) with Hantzsch ester

Excitation wavelength: 440 nm.

Excitation slit: 5 nm; emission slit: 5 nm.

To a standard solution of Co(TPP) in DMAc (0.1 mM) were added different amounts of a solution of Hantzsch ester in DMAc to afford the final concentrations reported in the figure below. The fluorescence of the solutions was then measured. DMAc was degassed with a stream of nitrogen for 30 min.

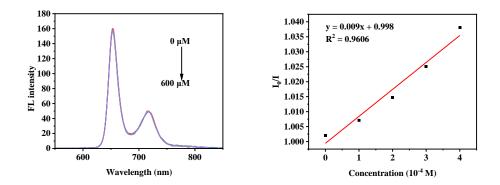


Figure S10 Emission spectra of the Co(TPP) with increasing concentrations of Hantzsch ester

6. An Alternative Mechanism

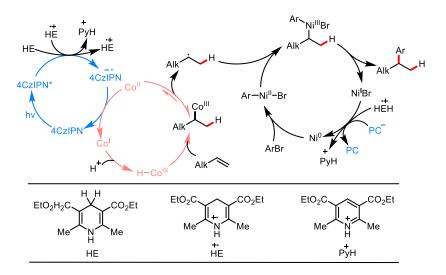


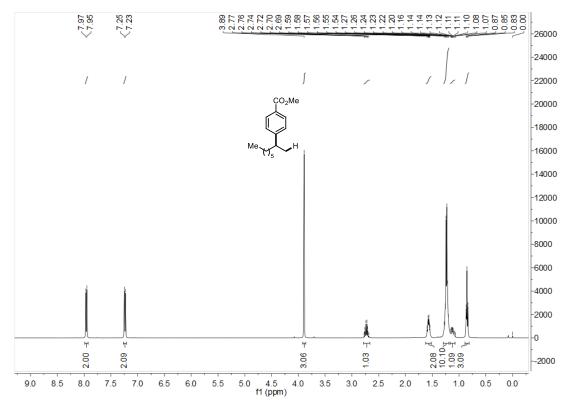
Figure S11 An alternative mechanism

7. References

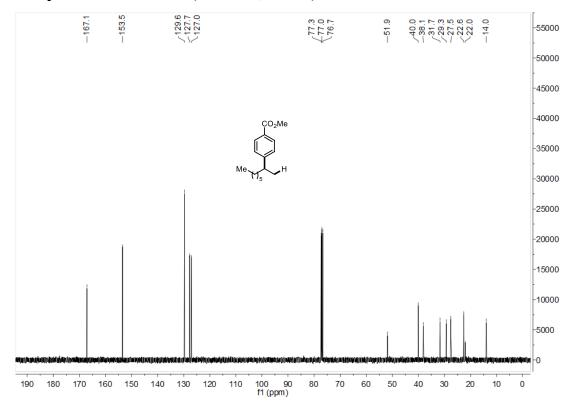
- 1 J. Qin, M. Barday, S. Jana, N. Sanosa, I. Funes-Ardoiz and C. J. Teskey, Angew. Chem. Int. Ed., 2023, 62, e202310639.
- 2 E. Bergamaschi, V. J. Mayerhofer and C. J. Teskey, ACS Catal., 2022, 12, 14806-14811.

8. ¹H, ¹³C and ¹⁹F NMR spectra of all products

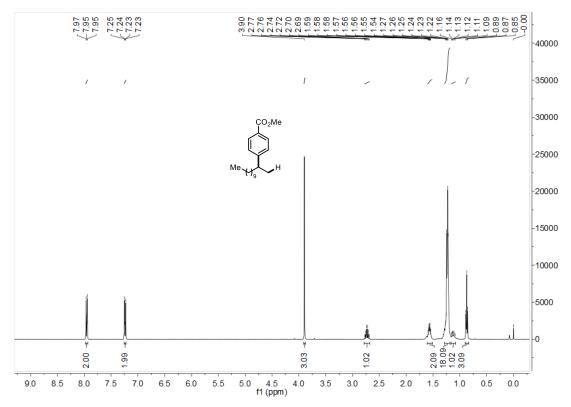
Compound 3aa ¹H NMR (400 MHz, CDCl₃)



Compound 3aa ¹³C NMR (101 MHz, CDCl₃)

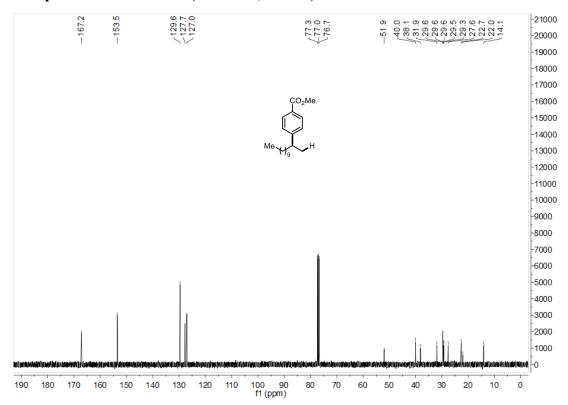


S36

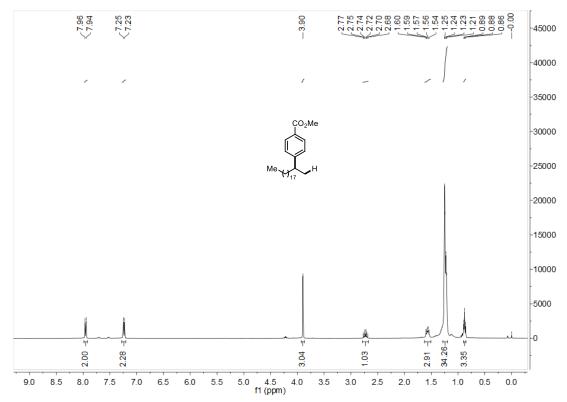


Compound 3ab ¹H NMR (400 MHz, CDCl₃)

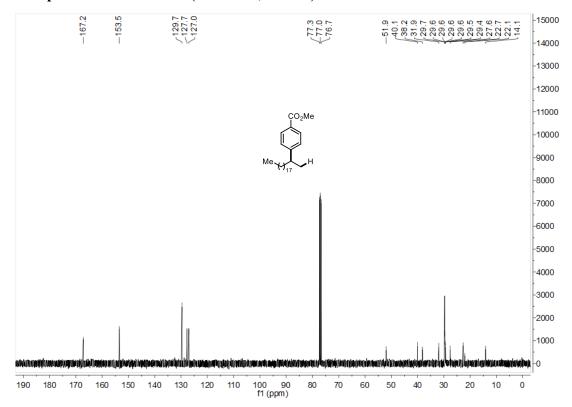
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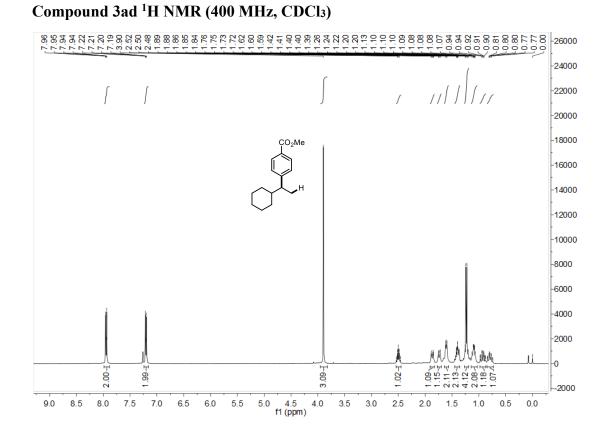




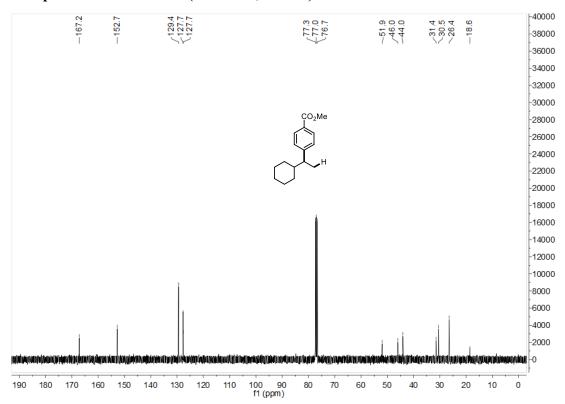


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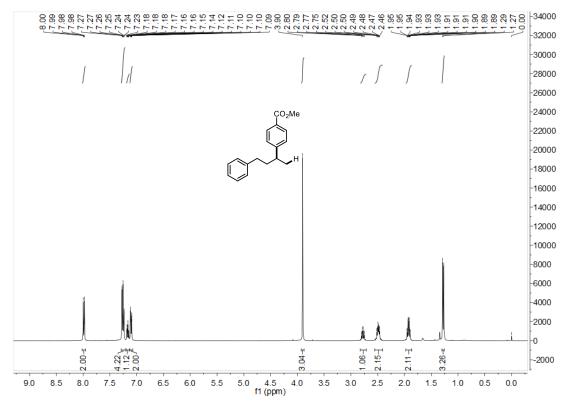




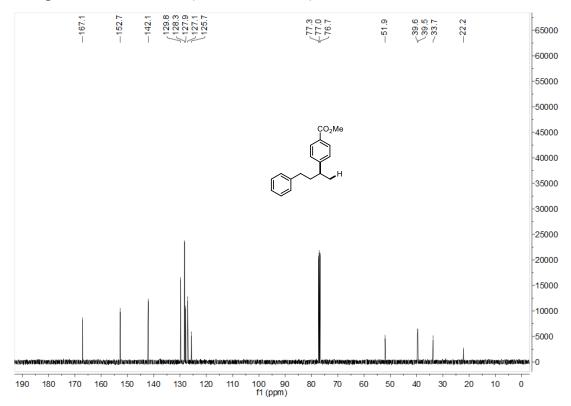
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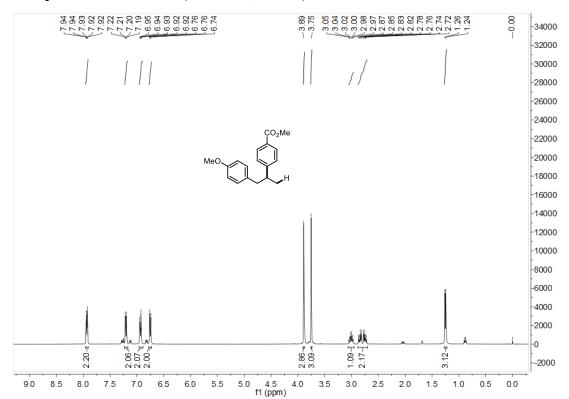






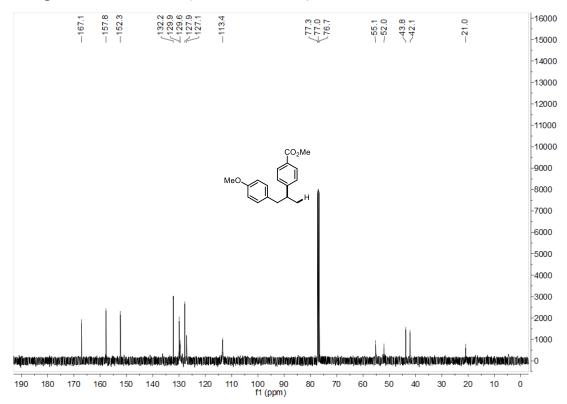
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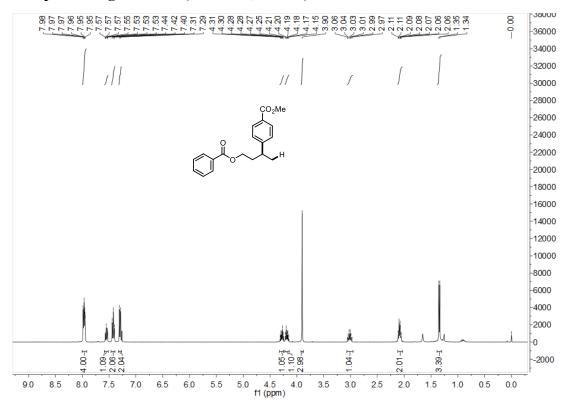




Compound 3af ¹H NMR (400 MHz, CDCl₃)

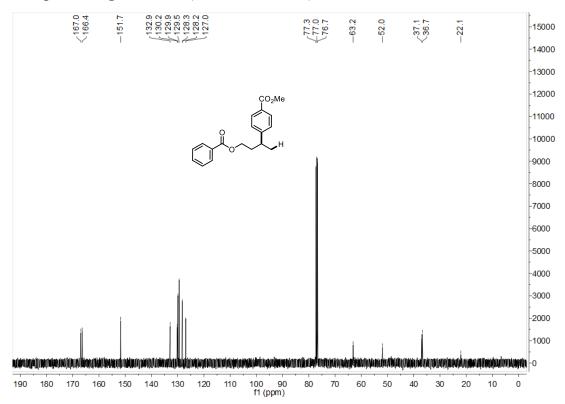
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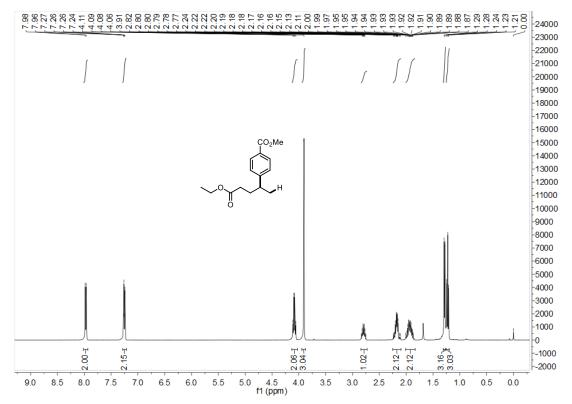


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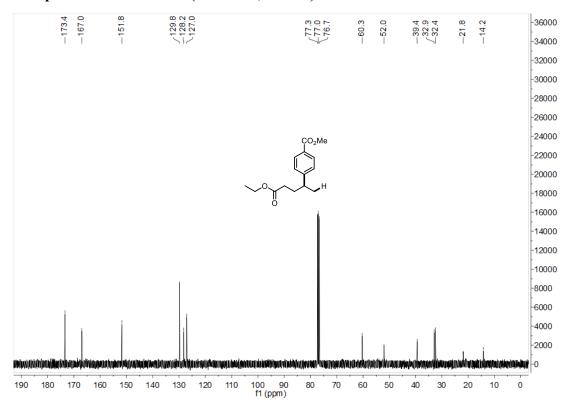
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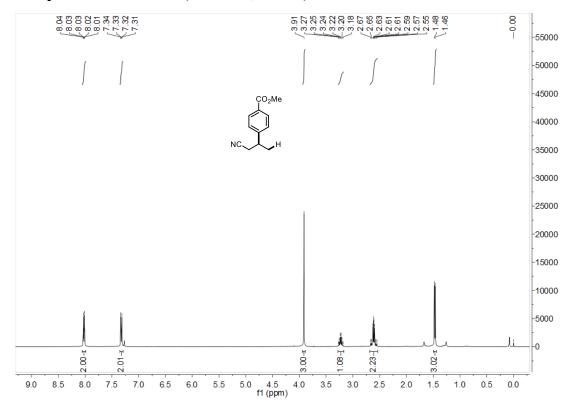






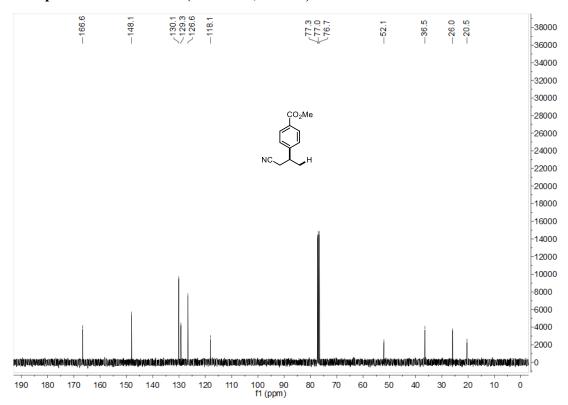
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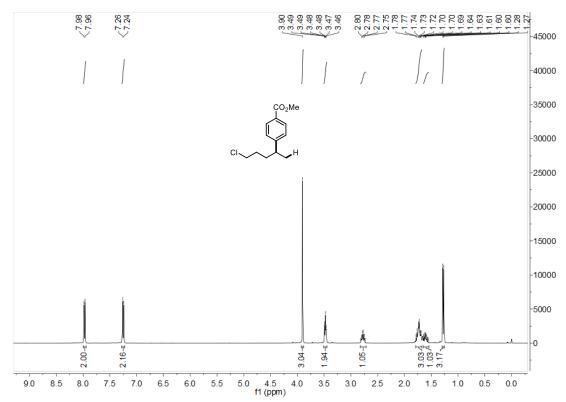




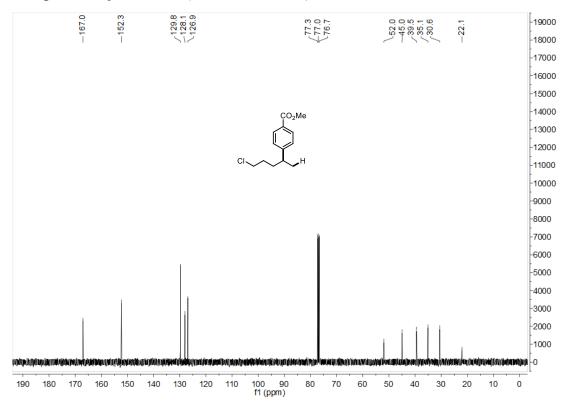
Compound 3ai ¹H NMR (400 MHz, CDCl₃)

Compound 3ai ¹³C NMR (101 MHz, CDCl₃)



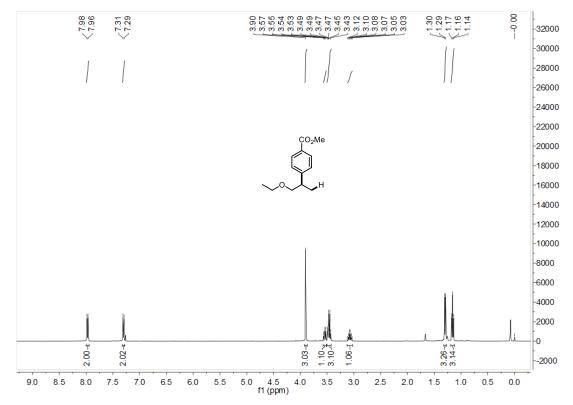


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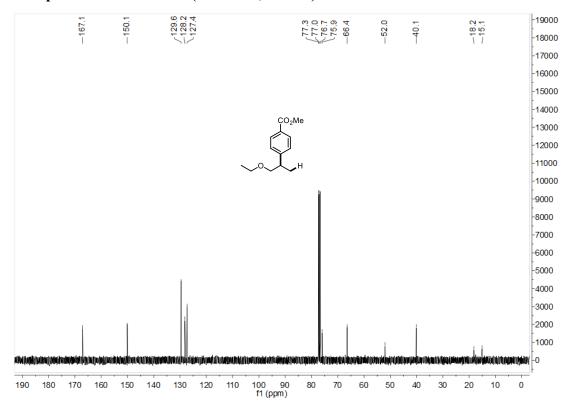


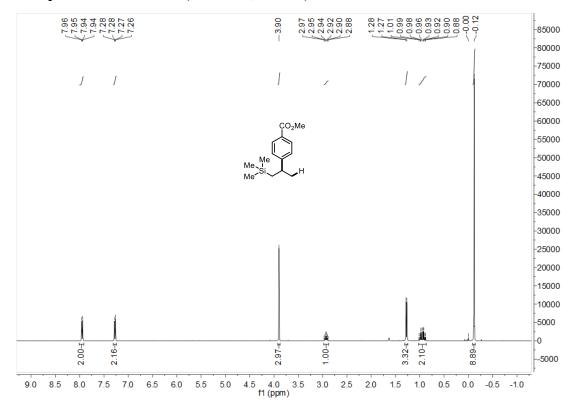
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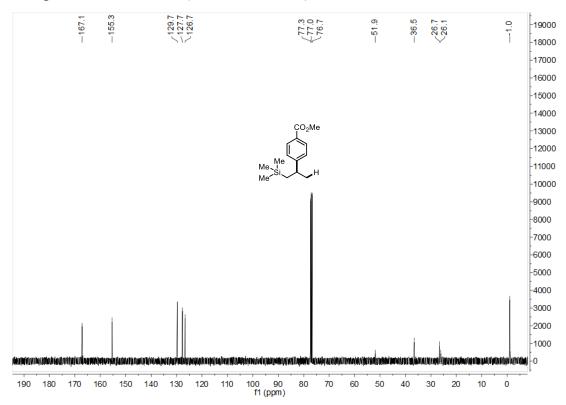
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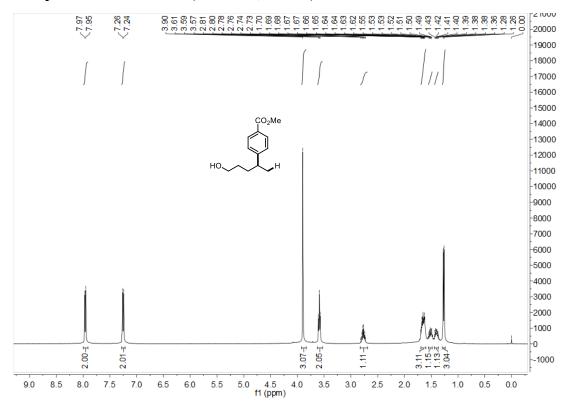




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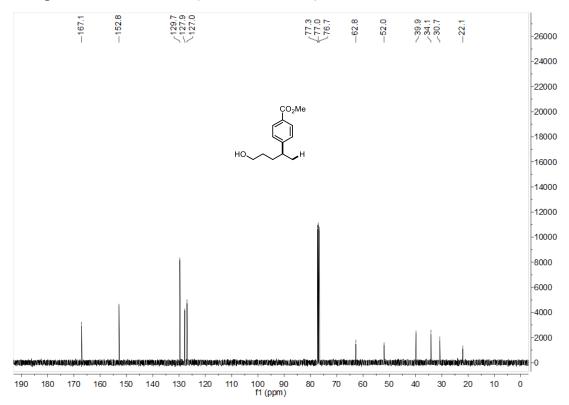
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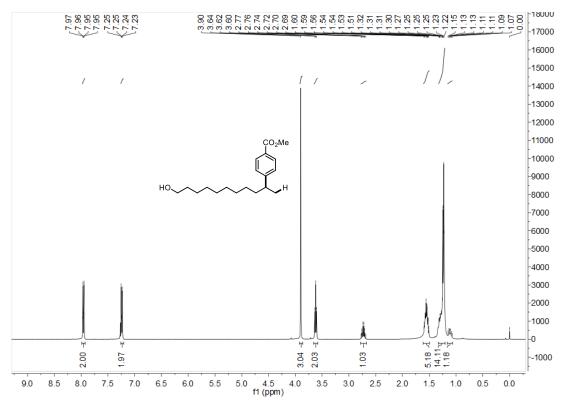




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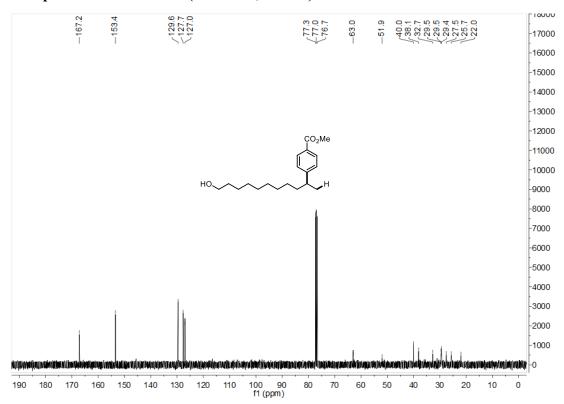
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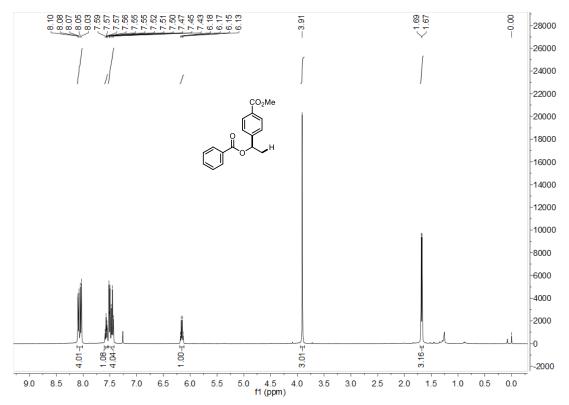


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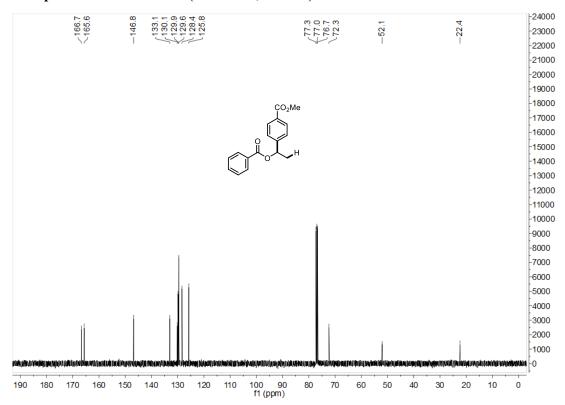
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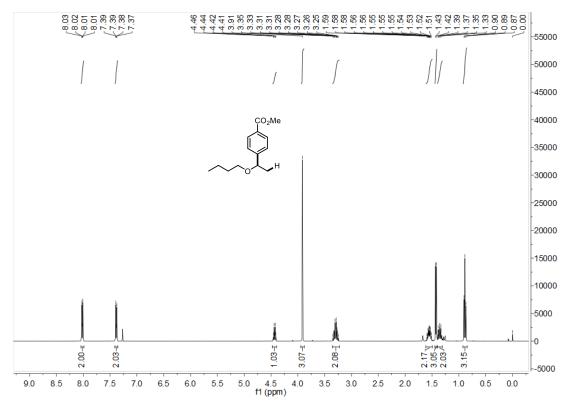






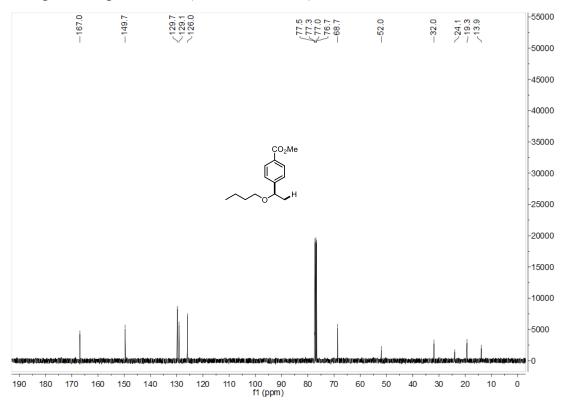
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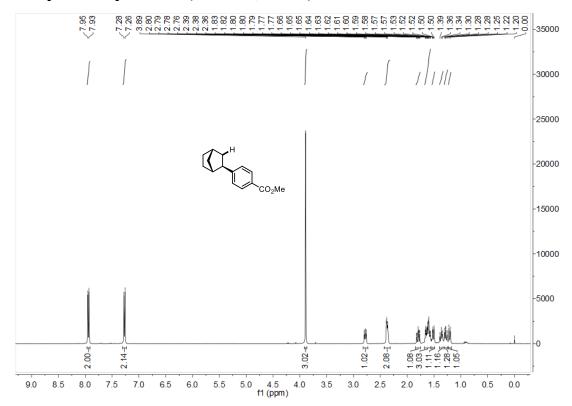




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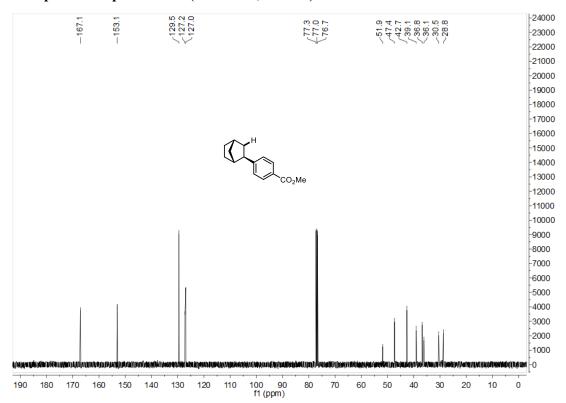
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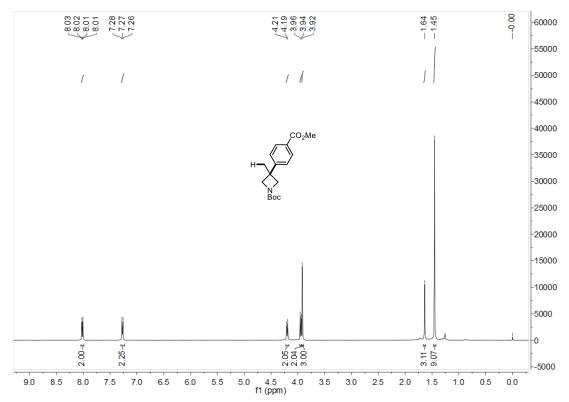


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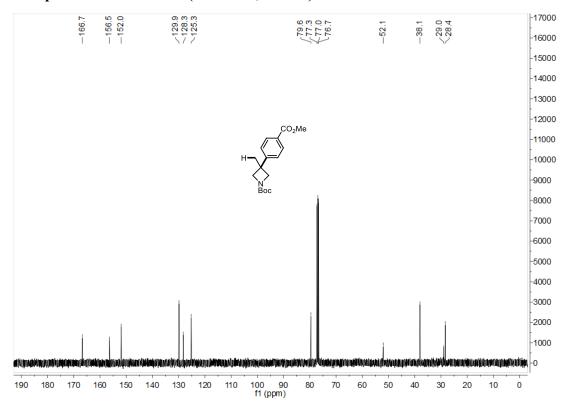
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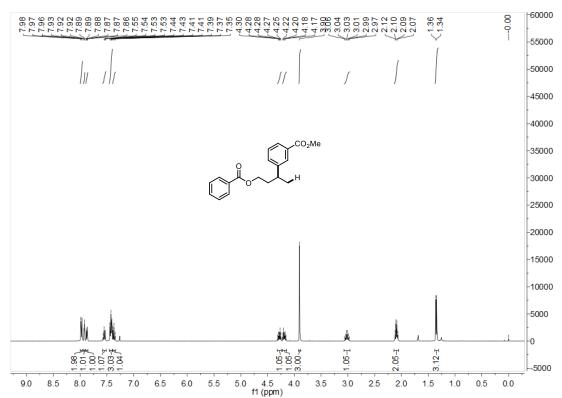




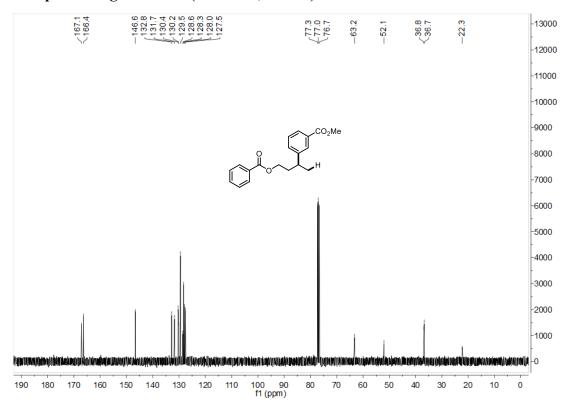


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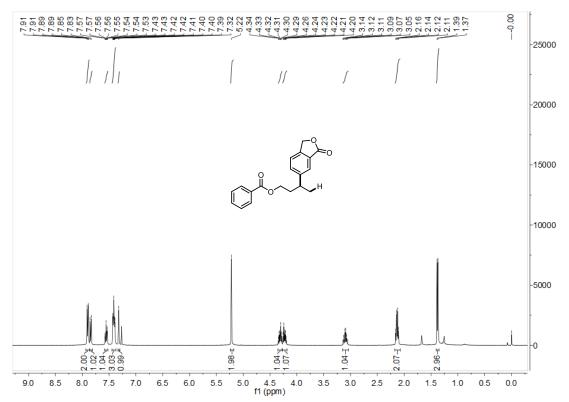


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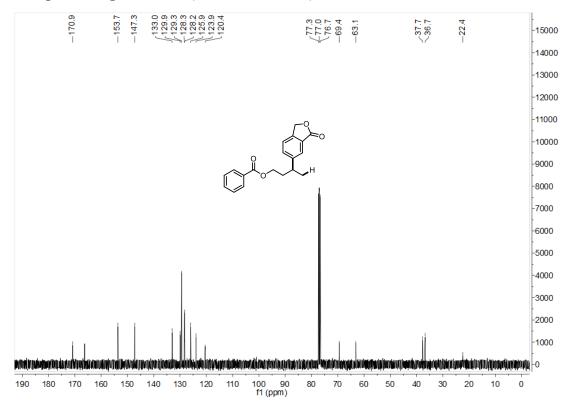


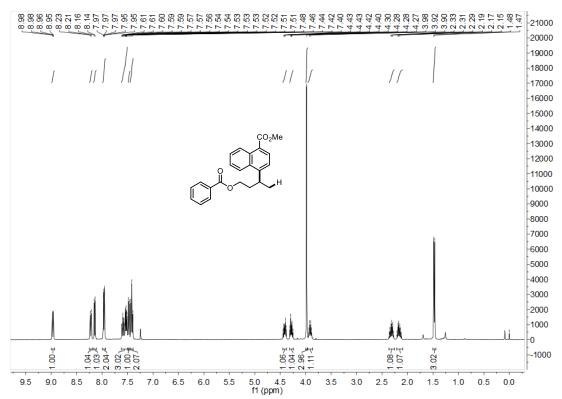
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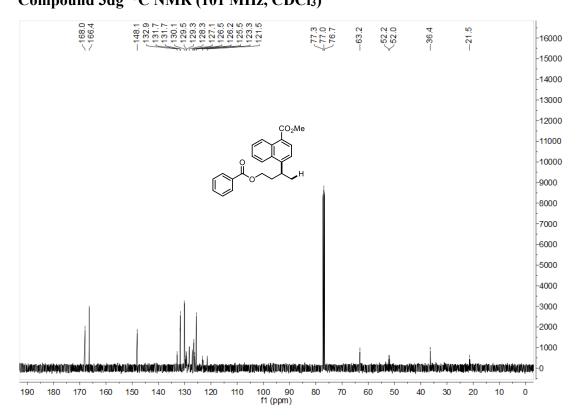


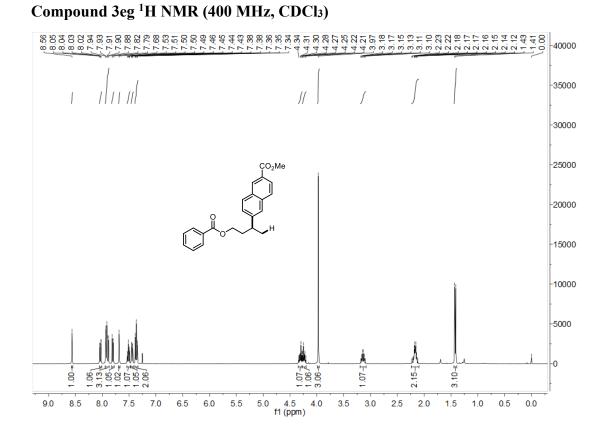
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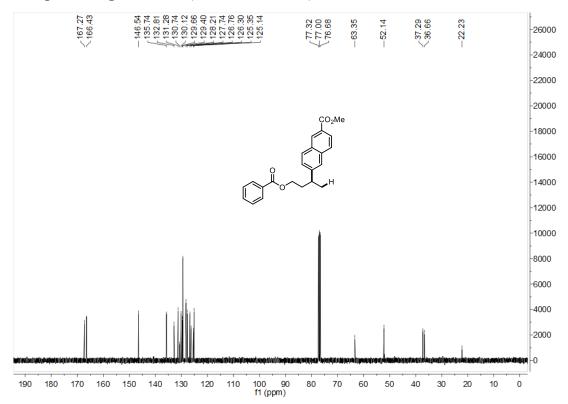


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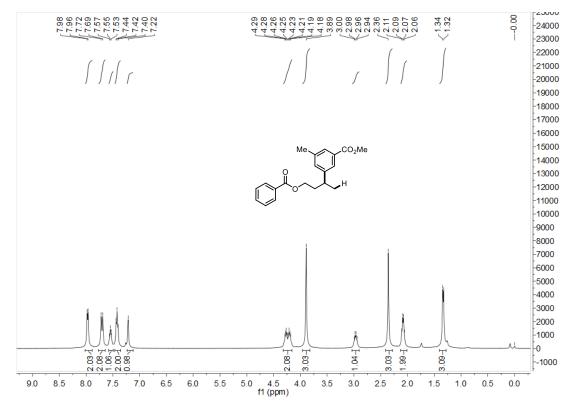




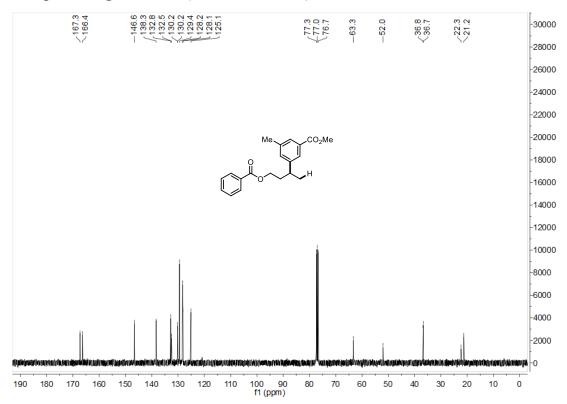
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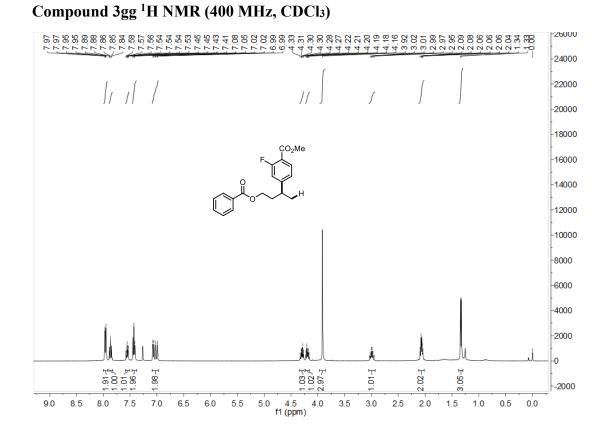


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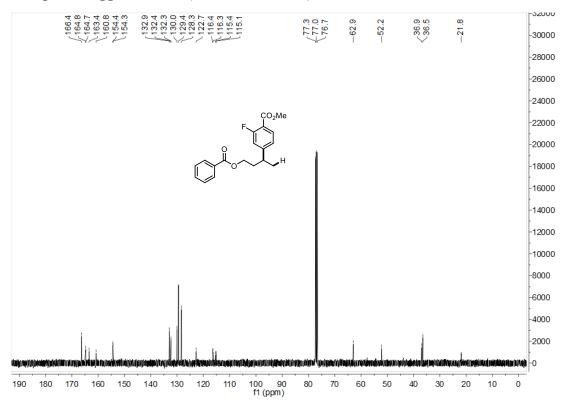


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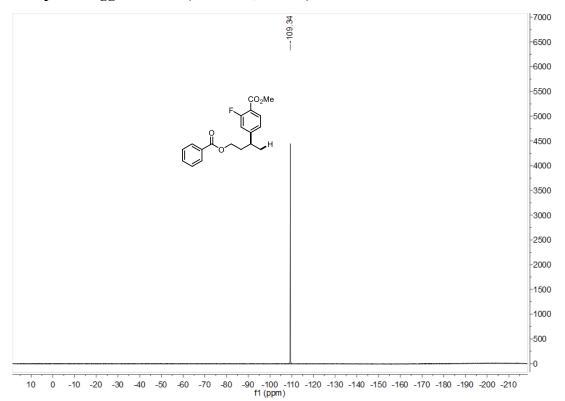




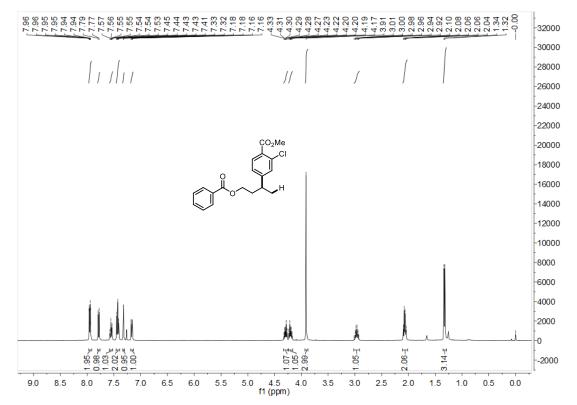
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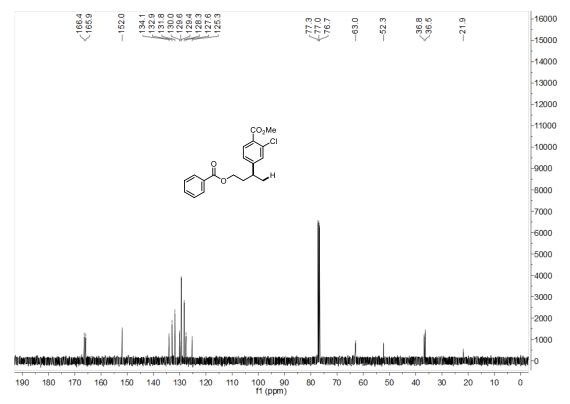
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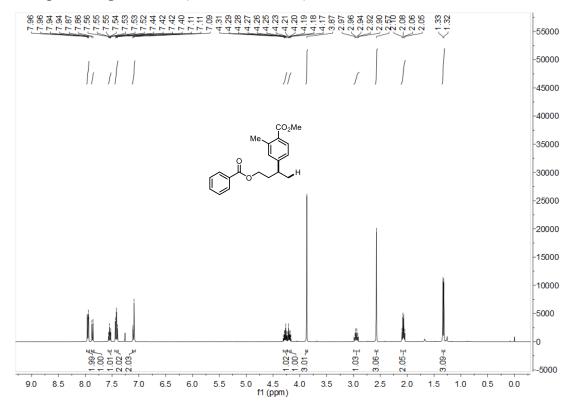
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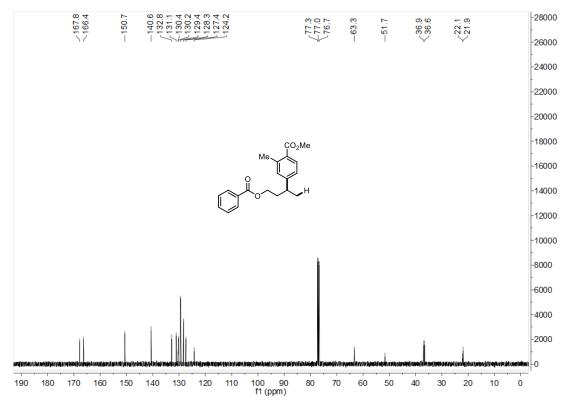


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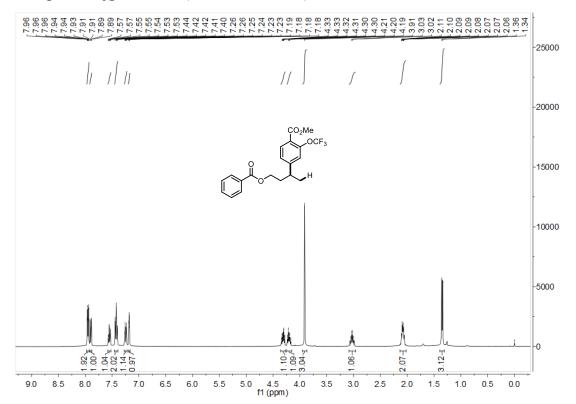
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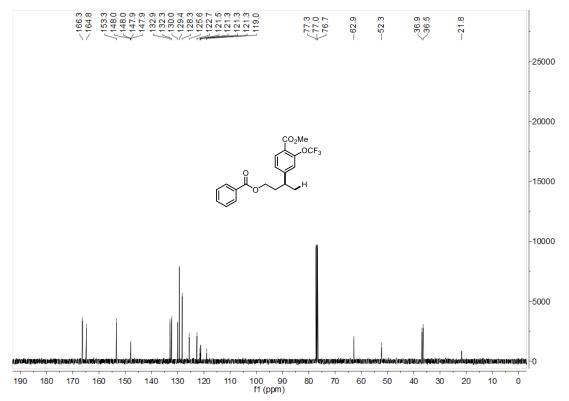


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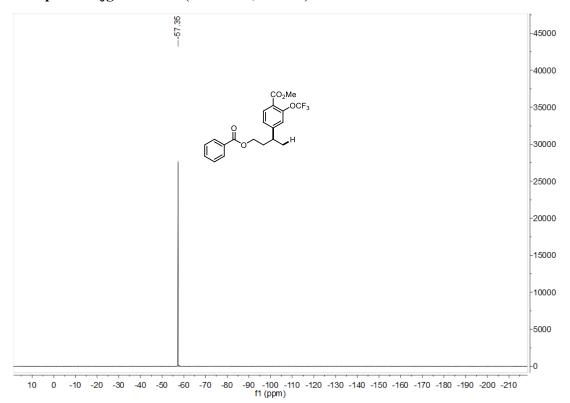
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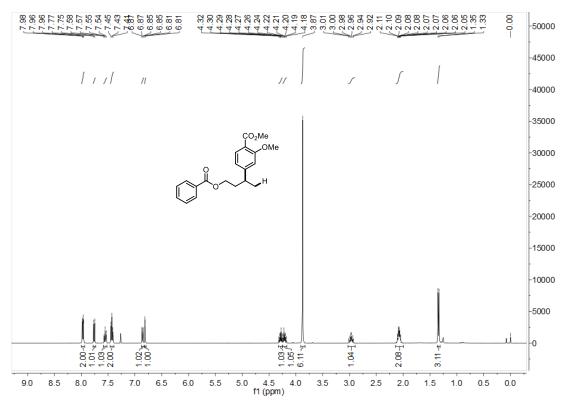






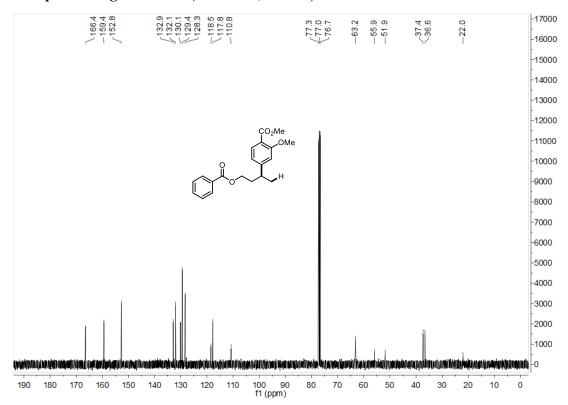
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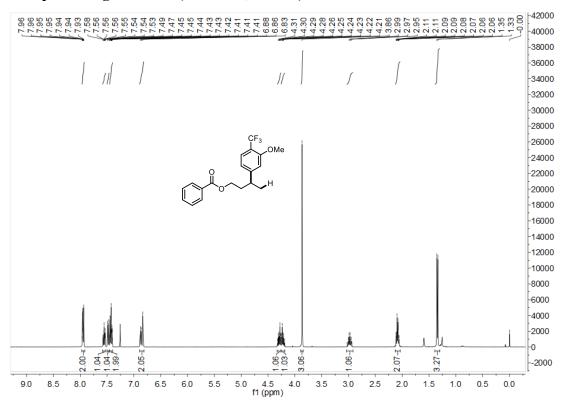




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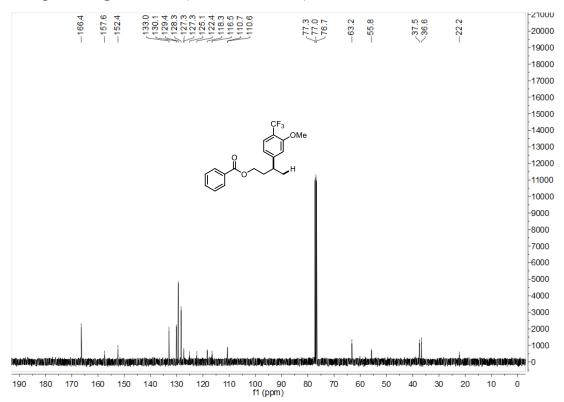
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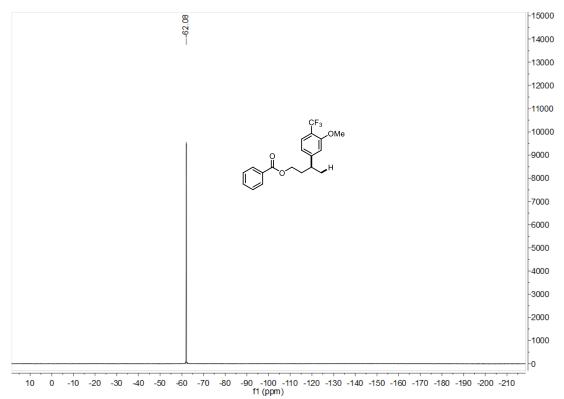


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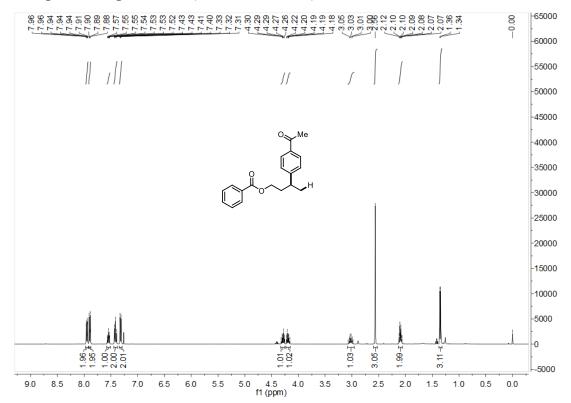
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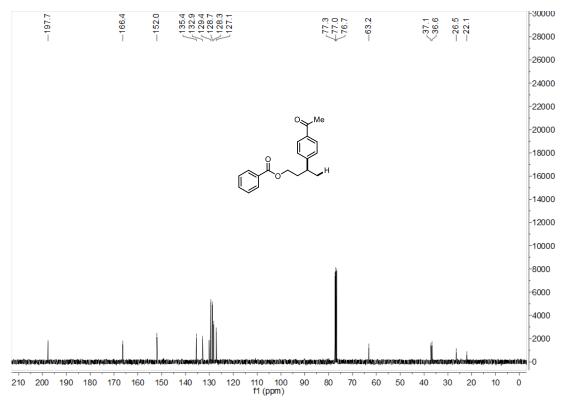
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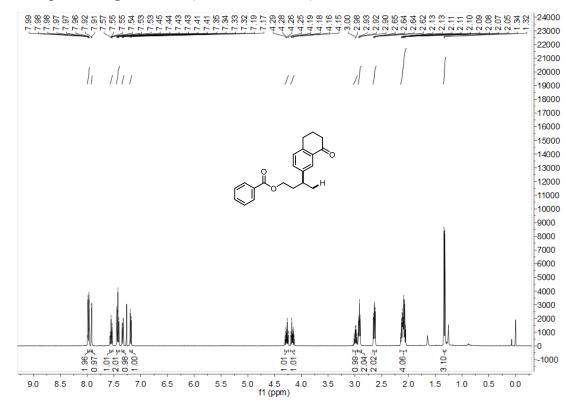
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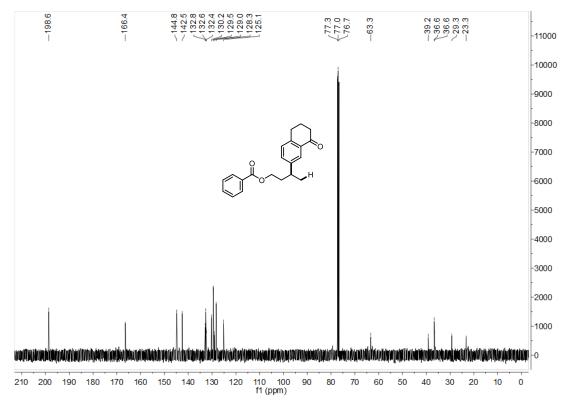




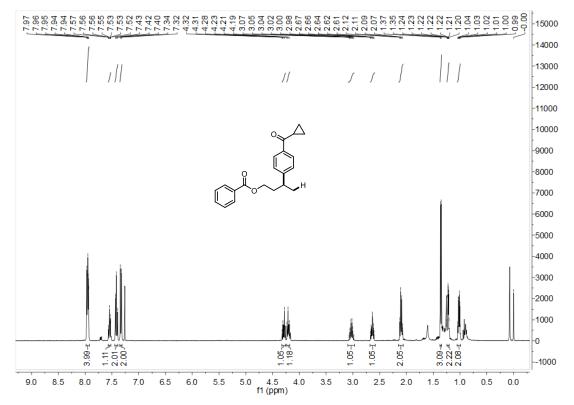
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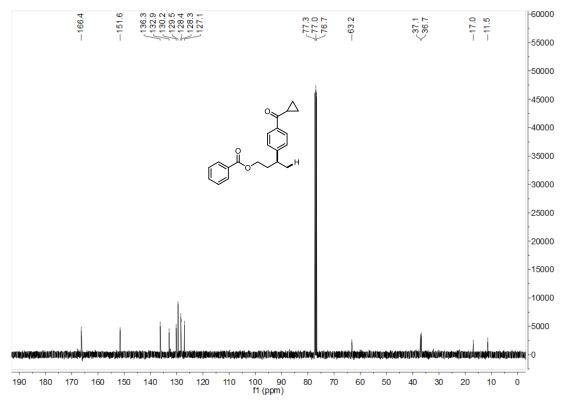
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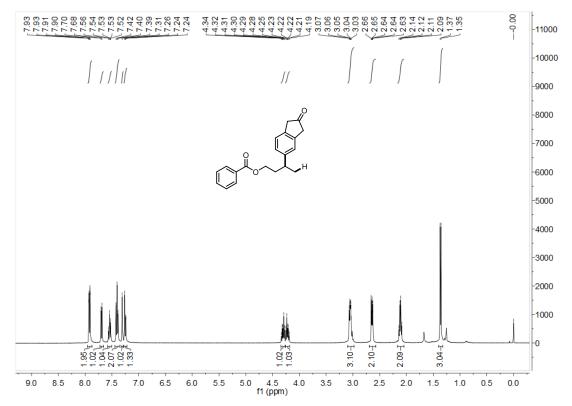
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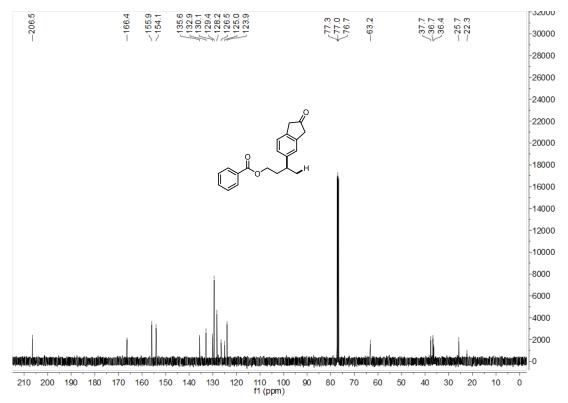
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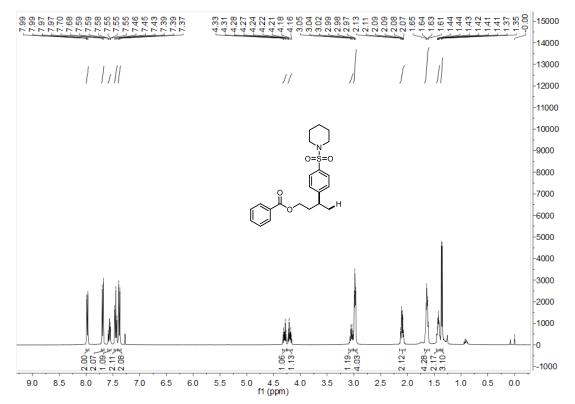
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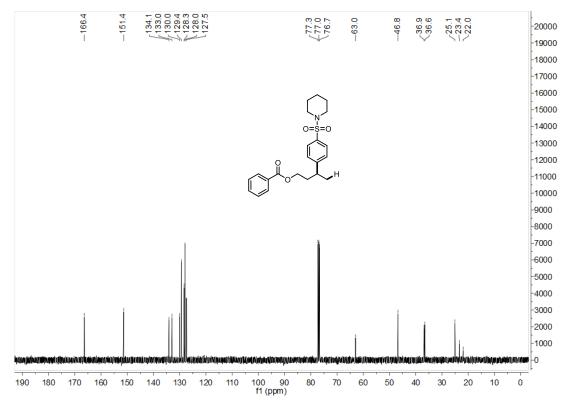
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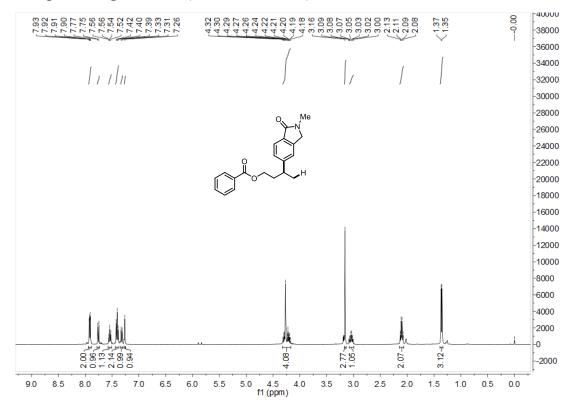
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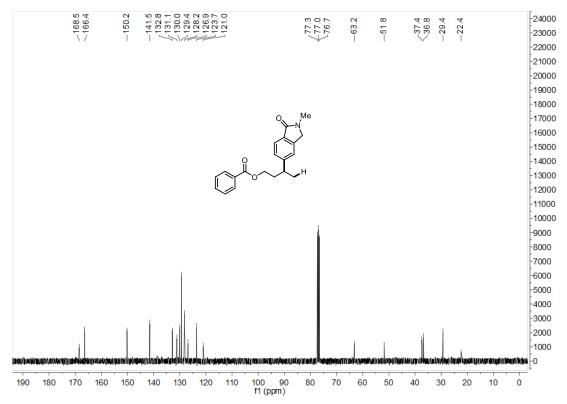
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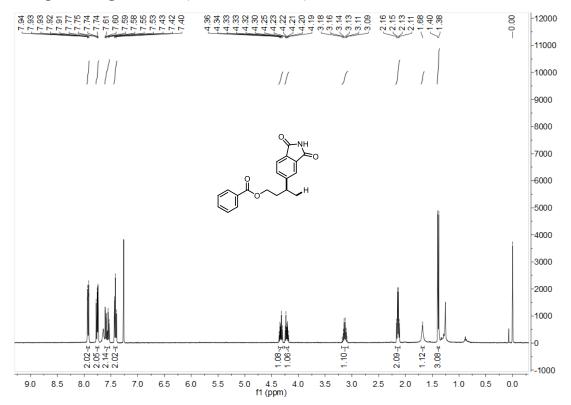
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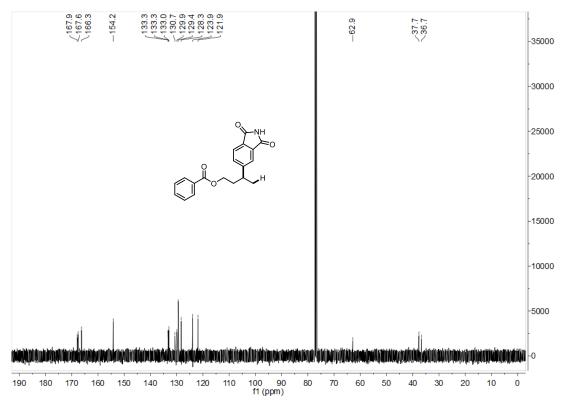




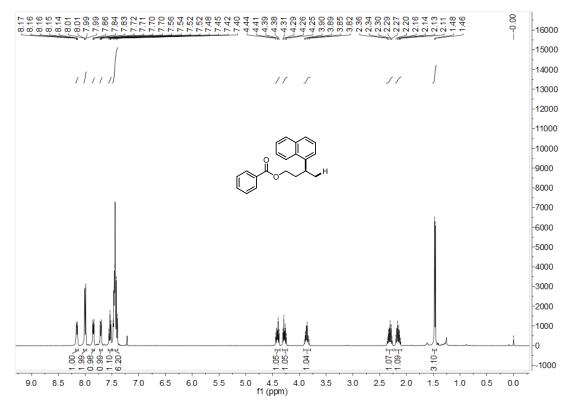
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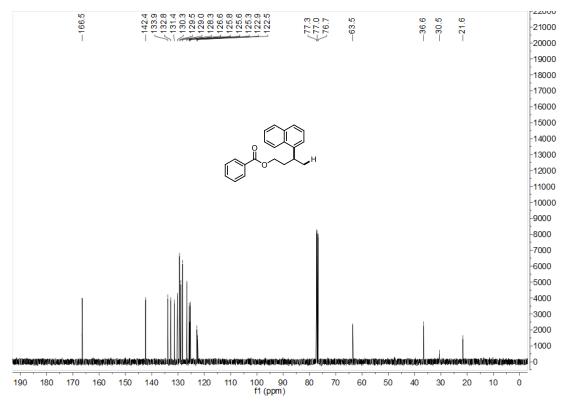
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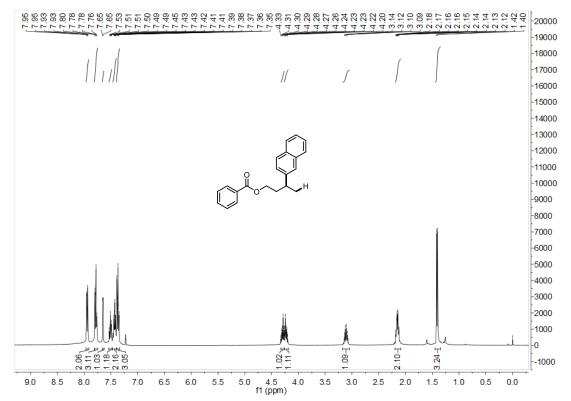
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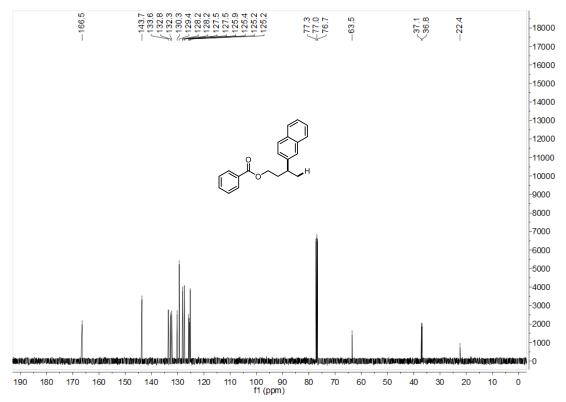
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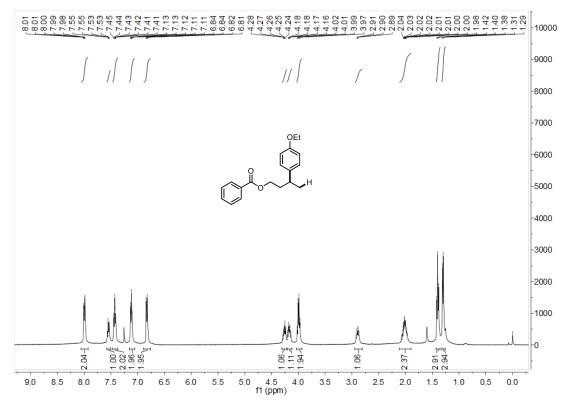
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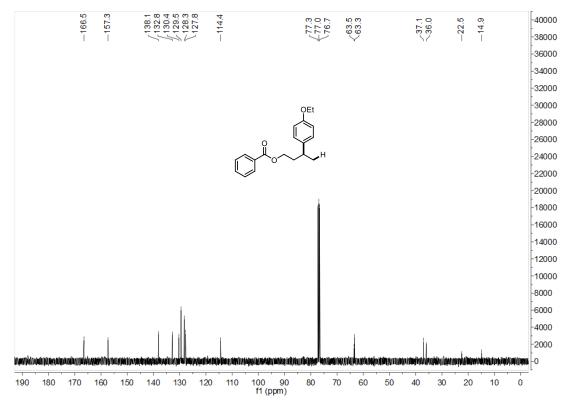
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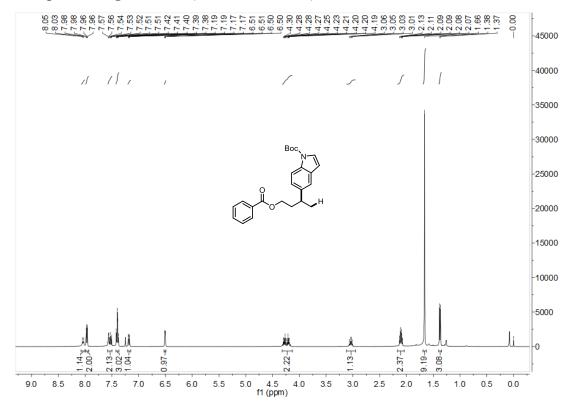
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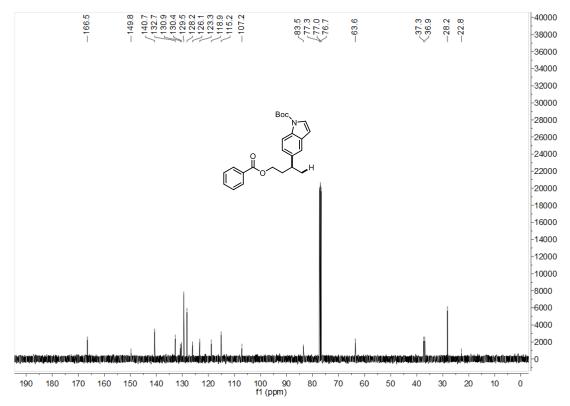
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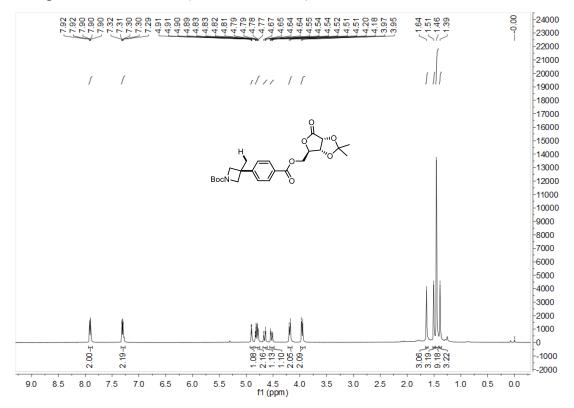
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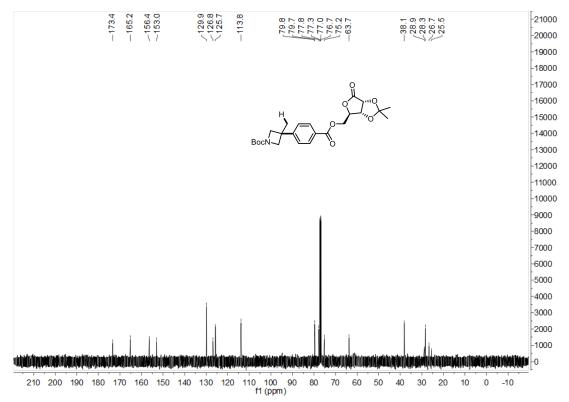
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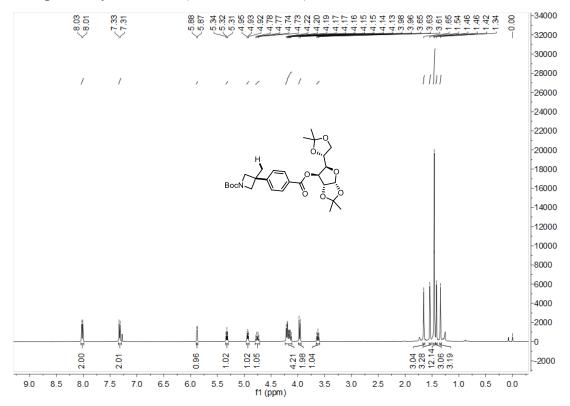
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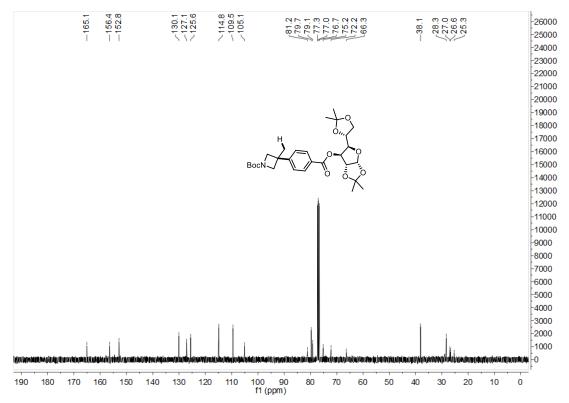
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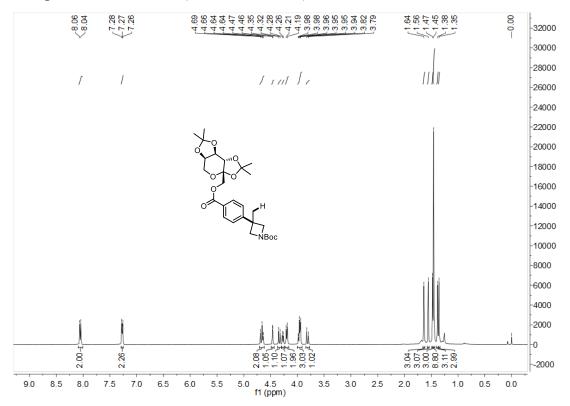
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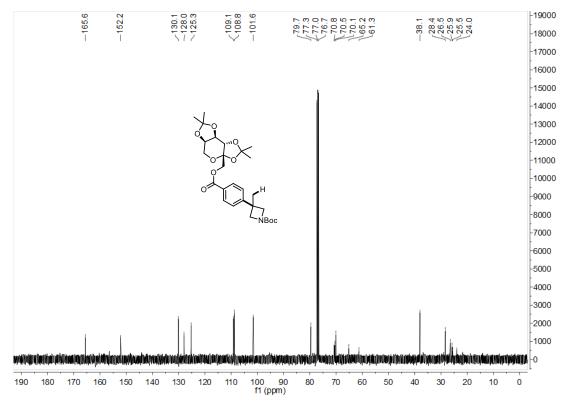
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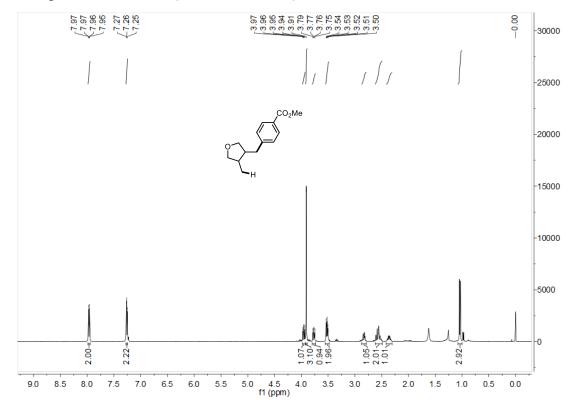
Compound 3zr ¹H NMR (400 MHz, CDCl₃)



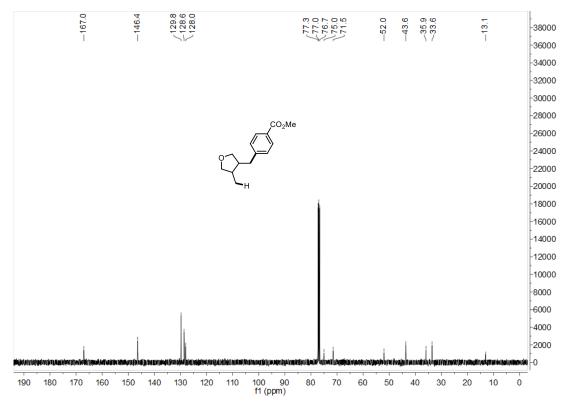




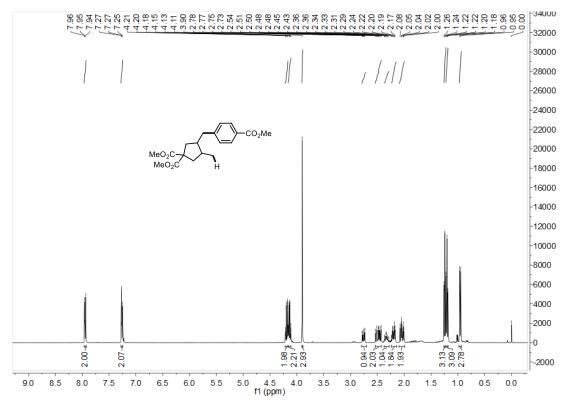
Compound 5¹H NMR (400 MHz, CDCl₃)



Compound 5¹³C NMR (101 MHz, CDCl₃)



Compound 7¹H NMR (400 MHz, CDCl₃)



Compound 7¹³C NMR (101 MHz, CDCl₃)

