Supporting Information

Regiocontrol in the Oxidative Heck Reaction of Indole by Ligand-Enabled Switch of the Regioselectivity-Determining Step

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1. General Information

Experimental. Air-sensitive or moisture-sensitive reactions were carried out in Schlenk tubes under a positive pressure of dry argon (balloon). Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled heating block. Organic solutions were concentrated using a rotary evaporator with a diaphragm vacuum pump. Analytical TLC was performed on silica gel GF254 plates. The TLC plates were visualized by either ultraviolet light (λ = 254 nm). Purification of products was accomplished by flash column chromatography on silica gel (Innochem SilicaFlashP60, 230-400 mesh).

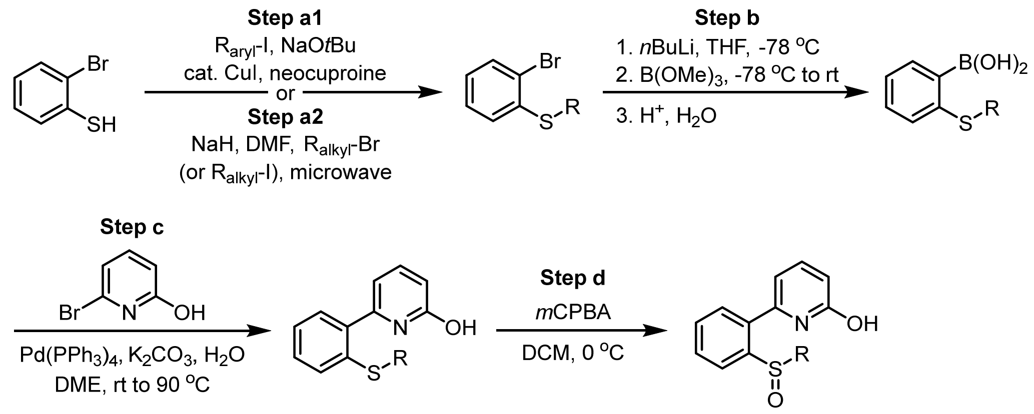
Chemicals. Dioxygen (99.999%) was supplied by Praxair. $Pd(OAc)_2$ (99%) was purchased from Energy Chemical, $PPd(MeCN)_2Cl_2$ (98%), $Cu(OTf)_2$ (98%), 1-methylindole (98%), *tert*-butyl acrylate (98%, stab. with MEHQ) was purchased from Innochem, $Cu(OH)_2CO_3$ (54-56% Cu) was purchased from Acros Organics. DMSO and DMF was purchased from J&K Scientific as anhydrous solvent and was used as received. Other chemicals were purchased from various commercial sources and were used as received.

Analytical. NMR spectra were recorded on a Bruker AVANCE III HD 400 (^{1}H at 400 MHz, ^{13}C at 100 MHz) nuclear magnetic resonance spectrometer. The ^{1}H NMR spectra were calibrated against the peak of tetramethylsilane (TMS, 0 ppm) and the ^{13}C NMR spectra were calibrated against the peak of $CDCl_3$ (77.16 ppm4). Infrared (IR) spectra were recorded on a Bruker FT-IR alpha (ATR mode) spectrophotometer. GC analysis was performed on a Shimadzu GC-2010 instrument equipped with a FID detector using nitrogen as the carrier gas. Initial rates were determined by high performance liquid chromatography (HPLC) analysis on a Shimadzu chromatograph Platisil Silica columns (4.6 × 250 mm). The single crystal X-ray diffraction analysis was performed on a SuperNova X-ray Diffraction System equipped with Atlas CCD detector and 4-circle kappa goniometer. Structure solution and refinement were accomplished with OLEX2.

2. Ligand Effect on the Model Reaction

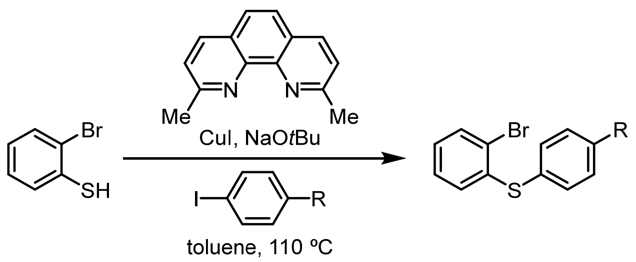
2.1 Synthesis and Characterization of New Ligands

(1) Synthetic route



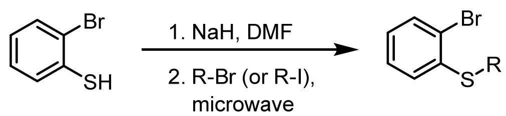
(2) General procedures

Step a1 for the synthesis of diaryl thioethers:



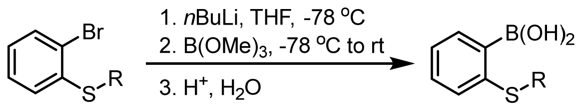
To a thick-walled reaction tube charged with a Teflon stir bar was added NaO*t*Bu (6.3 mmol, 1.5 equiv.), CuI (0.5 mmol, 12 mol%), neocuproine (0.5 mmol, 12 mol%), and toluene (5.0 mL) under Ar. Then 2-bromothiophenol (4.2 mmol, 1.0 equiv.) and aryl iodide (5.0 mmol, 1.2 equiv.) were added. The reaction mixture was then stirred at 110 °C for 24 hours. After cooled to room temperature, the reaction mixture was filtered to remove any insoluble residues. The filtrate was concentrated in vacuo and the crude product was purified by flash column chromatography on silica gel (petroleum ether as eluent) to obtain the desired sulfide.

Step a2 for the synthesis of aryl alkyl thioethers:



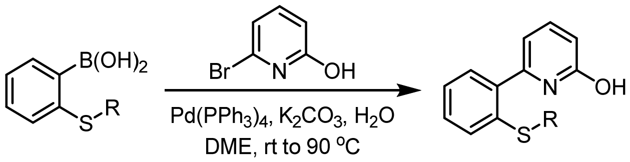
A 50 mL microwave reaction tube was charged with a Teflon stir bar, 2-bromobenzenethiol (0.4 mL, 3.3 mmol, 1.0 equiv.) and DMF (10.0 mL). Then, NaH (4.5 mmol, 1.4 equiv.) was slowly added in ice bath. After being stirred for 30 min, alkyl halide (5.1 mmol, 1.5 equiv.) was added. The reaction mixture was stirred in microwave reactor at 50 °C (max power = 200 W) for 2 h and then cooled to the room temperature. After being washed with water and extracted with diethyl ether, the organic layer was separated, then washed with saturated brine, dried over Na_2SO_4, concentrated and purified by flash column chromatography using petroleum ether as eluent on silica gel to afford the desired sulfide.

Step b:



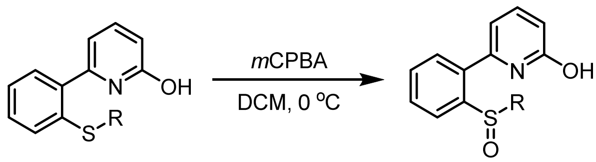
To a solution of thioether from **step a** (3.5 mmol, 1.0 equiv.) in dry THF (7.0 mL) under Ar was added *n*-BuLi (3.9 mmol, 1.1 equiv.) dropwise at -78 °C. The reaction mixture was then stirred for 1 h, followed by slow addition of $B(OMe)_3$ (4.5 mmol, 1.3 equiv.). The resulting solution was allowed to warm slowly to room temperature and stirred overnight. After the addition of deionized water, the mixture was acidified with diluted (1M) aqoeous HCl (12.0 mmol, 3.4 equiv.). After extraction with DCM, the organic layers were separated, combined, washed with brine, and dried over Na_2SO_4. Evaporation of the solvent afforded a solid which was recrystallized from hexane to give corresponding arylboric acid as white crystals.

Step c:



In a Schlenk flask charged with a magnetic stir bar, $Pd(PPh_3)_4$ (0.2 mmol, 5 mol%) was added to a stirred suspension of the arylboronic acid from **step b** (4.0 mmol, 1.0 equiv.) and 4-bromo-2-hydroxypyridine (4.1 mmol, 1.03 equiv.) in DME (8.0 mL). The reaction mixture was stirred under Ar for 90 min. Degassed aqueous (1.5 M) K_2CO_3 solution (12.0 mmol, 3.0 equiv.) was added and the reaction mixture was stirred at 90°C overnight. After cooled to room temperature, the solvent was evaporated and the residue was partitioned between DCM and water. After extraction with DCM, the organic layers were separated, combined, washed with brine, dried over Na_2SO_4, and evaporated using a rotavap. The residue was purified by flash column chromatography on silica gel (DCM and methanol as eluent) to afford the cross-coupling product.

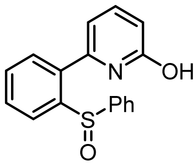
Step d:



A round-bottom flask was charged with a magnetic stir bar, cross-coupling product from **step c** (1.0 mmol, 1.0 equiv.), and DCM (25.0 mL). 3-Chloroperoxybenzoic acid (1.0 mmol, 1.0 equiv.) was slowly added in an ice-water bath. The reaction mixture was stirred at room temperature for 15 min, and then quenched with saturated aqueous $NaHCO_3$. After extraction with DCM, the organic layers were separated, combined, washed with brine, dried over Na_2SO_4, and evaporated using a rotavap. The residue was purified by flash column chromatography on silica gel (DCM and methanol as eluent) to afford the SOHP ligand.

(3) Characterization data for the new ligands

6-(2-(Phenylsulfinyl)phenyl)pyridin-2-ol (L7)



Following the general procedure (**step a1** was used), ligand **L7** was obtained as white solid in 57% overall yield from 2-bromothiophenol and iodobenzene.

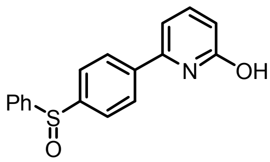
^{1}H NMR (400 MHz, $CDCl_3$): δ 12.44 (s, 1H), 8.17 (d, J = 7.8 Hz, 1H), 7.70 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 7.4 Hz, 1H), 7.44-7.34 (m, 2H), 7.27 (s, 5H), 6.46 (d, J = 9.1 Hz, 1H), 6.21 (d, J = 6.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 144.4, 144.4, 143.7, 140.7, 132.8, 131.3, 131.3, 130.9, 130.1, 129.2, 126.0, 125.4, 119.8, 108.4.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1647.

HRMS (ESI) calcd. for $C_{17}H_{13}NNaO_2S$ [M + Na]$^+$: 318.0559; found: 318.0548.

6-(4-(Phenylsulfinyl)phenyl)pyridin-2-ol (L8)



Following the general procedure (**step a1** was used), **L8** was obtained as white solid in 29% overall yield from 4-bromothiophenol and iodobenzene.

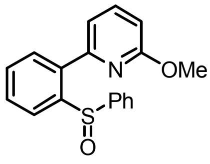
^{1}H NMR (400 MHz, $CDCl_3$): δ 12.86 (s, 1H), 7.85 (d, J = 8.5 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.70 (dd, J = 7.3, 2.2 Hz, 2H), 7.53-7.46 (m, 4H), 6.56 (d, J = 9.0 Hz, 1H), 6.51 (d, J = 6.9 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 147.3, 145.7, 145.2, 141.5, 136.1, 131.6, 129.7, 127.8, 125.5, 125.1, 119.6, 106.0.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1640.

HRMS (ESI) calcd. for $C_{17}H_{13}NNaO_2S$ [M + Na]$^+$: 318.0559; found: 318.0553.

2-Methoxy-6-(2-(phenylsulfinyl)phenyl)pyridine (L9)



Following the reported methylation procedure of pyridine-2-ol derivatives,[1] **L9** was obtained as white solid in 81% yield from **L7**.

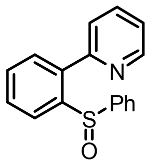
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 7.9 Hz, 1H), 7.63-7.50 (m, 4H), 7.44 (dd, J = 7.7, 1.7 Hz, 2H), 7.32 -7.25 (m, 3H), 7.04 (d, J = 7.3 Hz, 1H), 6.73 (d, J = 8.3 Hz, 1H), 3.82 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5, 154.2, 146.8, 144.9, 139.4, 139.1, 130.8, 130.4, 129.8, 129.2, 128.8, 126.2, 125.9, 116.4, 110.3, 54.3.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1674.

HRMS (ESI) calcd. for $C_{18}H_{15}NNaO_2S$ $[M + Na]^+$: 332.0716; found: 332.0712.

2-(2-(Phenylsulfinyl)phenyl)pyridine (L10)



Following the reported thiolation procedure[2] and oxidation step (**step d**), **L10** was obtained 57% yield from 2-phenylpyridine and diphenyl disulfide.

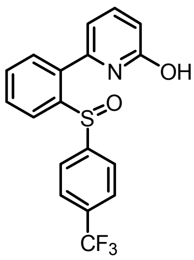
^1H NMR (400 MHz, $CDCl_3$): δ 8.63 (dd, J = 4.8, 0.6 Hz, 1H), 8.27 (dd, J = 7.9, 1.0 Hz, 1H), 7.76 (td, J = 7.8, 1.8 Hz, 1H), 7.73-7.70 (m, 2H), 7.67-7.60 (m, 3H), 7.54 (td, J = 7.5, 1.3 Hz, 1H), 7.36-7.31 (m, 3H), 7.30-7.25 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 148.3, 147.5, 145.5, 138.6, 137.0, 130.7, 130.2, 130.0, 128.9, 128.6, 126.2, 126.0, 122.9, 122.7.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1584.

HRMS (ESI) calcd. for $C_{17}H_{13}NNaOS$ $[M + Na]^+$: 302.0610; found: 302.0605.

6-(2-((4-(Trifluoromethyl)phenyl)sulfinyl)phenyl)pyridin-2-ol (L11)



Following the general procedure (**step a1** was used), **L11** was obtained as white solid in 37% overall yield from 2-bromothiophenol and 4-iodobenzotrifluoride.

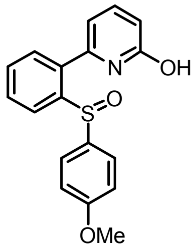
^1H NMR (400 MHz, $CDCl_3$): δ 12.85 (s, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.61 (t, J = 7.3 Hz, 1H), 7.54 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 8.1 Hz, 4H), 6.51 (d, J = 8.9 Hz, 1H), 6.26 (d, J = 6.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 148.9, 143.8, 140.9, 132.9 (q, J = 32.7 Hz), 133.1, 131.7, 131.1, 130.4, 126.1 (q, J = 3.7 Hz), 125.9, 125.4, 124.7, 123.4 (q, J = 272.8 Hz), 122.0, 119.7, 108.8.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1320, 1649.

HRMS (ESI) calcd. for $C_{18}H_{12}F_3NNaO_2S$ $[M + Na]^+$: 386.0433; found: 386.0425.

6-(2-((4-Methoxyphenyl)sulfinyl)phenyl)pyridin-2-ol (L12)



Following the general procedure (**step a1** was used), **L12** was obtained as white solid in 27% overall yield from 2-bromothiophenol and 4-iodoanisole.

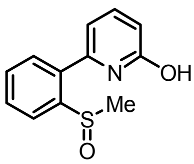
^{1}H NMR (400 MHz, $CDCl_3$): δ 12.37 (s, 1H), 8.22 (d, J = 7.8 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.57 (t, J = 7.3 Hz, 1H), 7.41-7.31 (m, 2H), 7.19 (d, J = 8.7 Hz, 2H), 6.74 (d, J = 8.7 Hz, 2H), 6.44 (d, J = 9.2 Hz, 1H), 6.13 (d, J = 6.7 Hz, 1H), 3.67 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6, 162.0, 144.7, 143.8, 140.6, 135.6, 132.6, 130.9, 130.7, 130.0, 128.3, 124.9, 119.7, 114.7, 108.2, 55.5.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1649.

HRMS (ESI) calcd. for $C_{18}H_{15}NNaO_3S$ [M + Na]$^+$: 348.0665; found: 348.0665.

6-(2-(Methylsulfinyl)phenyl)pyridin-2-ol (L13)



Following the general procedure (**step a2** was used), **L13** was obtained as white solid in 36% overall yield from 2-bromothiophenol and iodomethane.

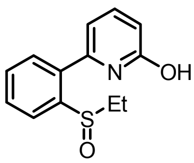
^{1}H NMR (400 MHz, $CDCl_3$): δ 12.44 (s, 1H), 8.17 (d, J = 7.8 Hz, 1H), 7.72 (t, J = 7.5 Hz, 1H), 7.61 (t, J = 7.4 Hz, 1H), 7.55-7.42 (m, 2H), 6.52 (d, J = 9.1 Hz, 1H), 6.36 (d, J = 6.7 Hz, 1H), 2.59 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 145.1, 144.2, 141.0, 132.0, 131.3, 131.2, 129.9, 124.4, 119.5, 108.5, 42.8.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1651.

HRMS (ESI) calcd. for $C_{12}H_{11}NNaO_2S$ [M + Na]$^+$: 256.0403; found: 256.0397.

6-(2-(Ethylsulfinyl)phenyl)pyridin-2-ol (L14)



Following the general procedure (**step a2** was used), **L14** was obtained as white solid in 71% overall yield from 2-bromothiophenol and iodoethane.

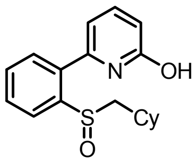
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.93 (s, 1H), 8.08 (d, J = 7.8 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H), 7.61 (t, J = 7.4 Hz, 1H), 7.51 (d, J = 7.5 Hz, 1H), 7.46 (dd, J = 9.0, 7.0 Hz, 1H), 6.50 (d, J = 9.1 Hz, 1H), 6.37 (d, J = 6.8 Hz, 1H), 2.76 (dq, J = 14.7, 7.4 Hz, 1H), 2.51 (dq, J = 14.6, 7.4 Hz, 1H), 1.06 (t, J = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 143.9, 142.3, 141.0, 132.0, 131.1, 130.7, 130.0, 125.3, 119.7, 108.2, 48.5, 6.1.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1649.

HRMS (ESI) calcd. for $C_{13}H_{13}NNaO_2S$ $[M + Na]^+$: 270.0559; found: 270.0552.

6-(2-((Cyclohexylmethyl)sulfinyl)phenyl)pyridin-2-ol (L15)



Following the general procedure (**step a2** was used), **L15** was obtained as white solid in 47% overall yield from 2-bromothiophenol and cyclohexylmethyl bromide.

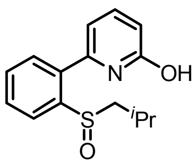
^{1}H NMR (400 MHz, $CDCl_3$): δ 11.96 (s, 1H), 8.15 (dd, J = 7.9, 0.8 Hz, 1H), 7.72 (td, J = 7.5, 0.9 Hz, 1H), 7.61 (td, J = 7.5, 0.9 Hz, 1H), 7.52-7.43 (m, 2H), 6.55 (d, J = 9.2 Hz, 1H), 6.36 (d, J = 6.8 Hz, 1H), 2.56 (dd, J = 13.1, 3.7 Hz, 1H), 2.40 (dd, J = 13.1, 9.9 Hz, 1H), 1.95-1.80 (m, 2H), 1.69-1.50 (m, 3H), 1.30-1.15 (m, 2H), 1.14-0.98 (m, 1H), 0.91 (qd, J = 12.4, 3.0 Hz, 1H), 0.74 (qd, J = 12.4, 3.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 144.1, 143.7, 140.9, 131.7, 131.1, 131.1, 129.8, 124.9, 119.9, 108.2, 65.3, 33.4, 33.1, 32.0, 26.0, 26.0, 25.6.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1651.

HRMS (ESI) calcd. for $C_{18}H_{21}NNaO_2S$ $[M + Na]^+$: 338.1185; found: 338.1177.

6-(2-(Isobutylsulfinyl)phenyl)pyridin-2-ol (L16)



Following the general procedure (**step a2** was used), **L16** was obtained as white solid in 46% overall yield from 2-bromothiophenol and 2-iodopropane.

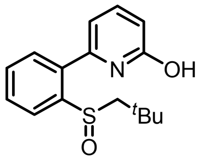
^{1}H NMR (400 MHz, $CDCl_3$): δ 12.95 (s, 1H), 8.14 (d, J = 7.8 Hz, 1H), 7.71 (td, J = 7.5, 0.9 Hz, 1H), 7.61 (td, J = 7.5, 0.9 Hz, 1H), 7.50 (d, J = 7.0 Hz, 1H), 7.46 (dd, J = 9.2, 6.9 Hz, 1H), 6.51 (d, J = 9.0 Hz, 1H), 6.36 (d, J = 6.6 Hz, 1H), 2.59 (dd, J = 13.1, 3.9 Hz, 1H), 2.39 (dd, J = 13.0, 10.1 Hz, 1H), 2.22-2.07 (m, 1H), 0.96-0.83 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 143.7, 143.7, 140.9, 131.6, 131.0, 129.9, 124.6, 119.7, 108.3, 66.6, 24.3, 22.8, 21.3.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1649.

HRMS (ESI) calcd. for $C_{15}H_{17}NNaO_2S$ [M + Na]$^+$: 298.0872; found: 298.0864.

6-(2-(Neopentylsulfinyl)phenyl)pyridin-2-ol (L17)



Following the general procedure (**step a2** was used), **L17** was obtained as white solid in 75% overall yield from 2-bromothiophenol and neopentyl bromide.

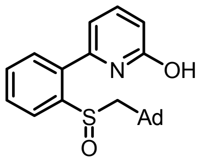
^{1}H NMR (400 MHz, CDCl$_3$): δ 12.93 (s, 1H), 8.17 (d, J = 7.8 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.60 (t, J = 7.4 Hz, 1H), 7.52-7.41 (m, 2H), 6.49 (d, J = 9.2 Hz, 1H), 6.34 (d, J = 6.7 Hz, 1H), 2.55 (s, 2H), 0.96 (s, 9H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 165.0, 144.5, 143.5, 141.0, 131.2, 131.0, 130.9, 130.0, 124.9, 119.9, 108.3, 72.7, 31.9, 29.6.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1649.

HRMS (ESI) calcd. for $C_{16}H_{19}NNaO_2S$ [M + Na]$^+$: 312.1029; found: 312.1029.

6-(2-((((3*S*)-adamantan-1-yl)methyl)sulfinyl)phenyl)pyridin-2-ol (L18)



Following the general procedure (**step a2** was adopted), **L17** was obtained as white solid in 39% overall yield from 2-bromothiophenol and adamantylmethyl bromide.

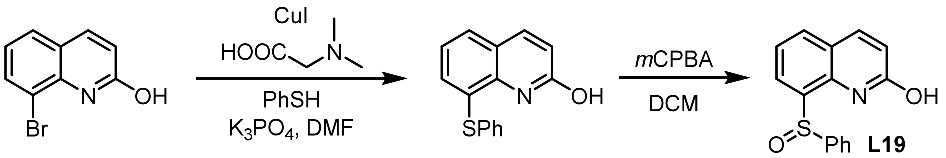
^{1}H NMR (400 MHz, CDCl$_3$): δ 12.89 (s, 1H), 8.17 (d, J = 7.6 Hz, 1H), 7.70 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 7.2 Hz, 1H), 7.51-7.42 (m, 2H), 6.51 (d, J = 9.2 Hz, 1H), 6.34 (d, J = 6.7 Hz, 1H), 2.46 (d, J = 13.8 Hz, 1H), 2.39 (d, J = 13.8 Hz, 1H), 1.91 (s, 3H), 1.65 (d, J = 12.1 Hz, 3H), 1.55 (d, J = 12.6 Hz, 6H), 1.48 (d, J = 12.2 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 165.0, 144.6, 143.5, 140.9, 131.1, 130.9, 130.8, 129.9, 125.0, 119.9, 108.3, 73.3, 42.3, 36.4, 33.7, 28.3.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1649.

HRMS (ESI) calcd. for $C_{22}H_{25}NNaO_2S$ [M + Na]$^+$: 390.1498; found: 390.1489.

8-(Phenylsulfinyl)quinolin-2-ol (L19)



L19

8-Bromoquinolin-2-ol[3] and PhSH were employed in the cross-coupling reaction for the synthesis of 8-phenylthioquinolin-2-ol.[4] After oxidation (**step d**), **L19** was obtained as white solid in 56% yield from 8-bromoquinolin-2-ol.

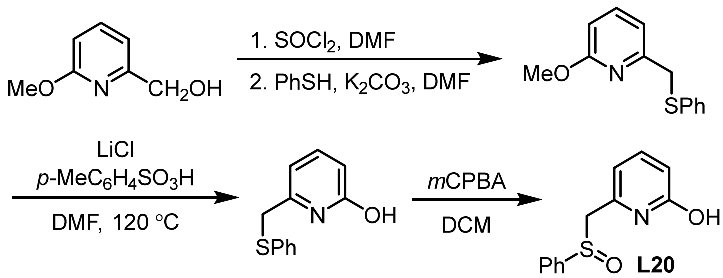
^{1}H NMR (400 MHz, $CDCl_3$): δ 11.29 (s, 1H), 7.60-7.72 (m, 5H), 7.52-7.41 (m, 3H), 7.22-7.30 (m, 1H), 6.61 (d, *J* = 9.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3, 142.8, 140.0, 138.5, 131.7, 131.3, 129.6, 128.5, 124.8, 124.3, 123.7, 121.7, 121.3.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1651.

HRMS (ESI) calcd. for $C_{15}H_{11}NNaO_2S$ [M + Na]$^+$: 292.0403; found: 292.0395.

6-((Phenylsulfinyl)methyl)pyridin-2-ol (L20)



L20

Starting from 6-methoxy-2-pyridinemethanol, following the reported thiolation[5] and demethylation[6] procedures and then oxidation (**step d**), ligand **L20** was obtained in 54% overall yield.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 12.77 (s, 1H), 7.65-7.59 (m, 2H), 7.50-7.42 (m, 3H), 7.39 (dd, *J* = 9.1, 6.8 Hz, 1H), 6.50 (d, *J* = 9.1 Hz, 1H), 6.18 (d, *J* = 6.8 Hz, 1H), 4.02 (d, *J* = 13.3 Hz, 1H), 3.82 (d, *J* = 13.3 Hz, 1H).

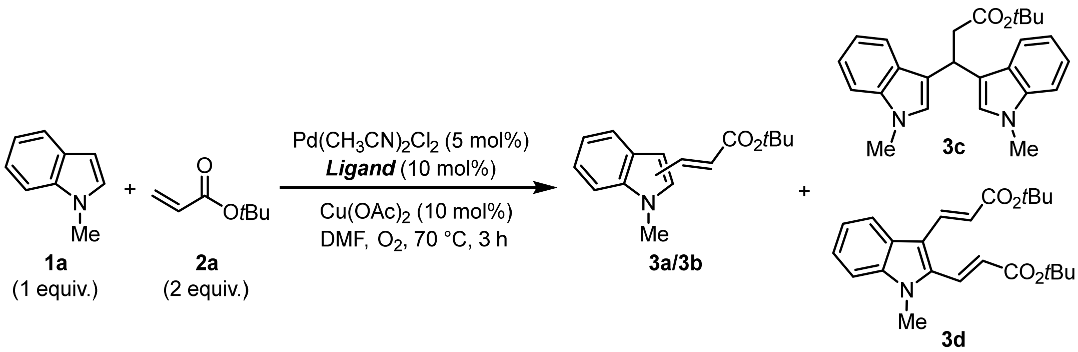
^{13}C NMR (100 MHz, $CDCl_3$): *δ* 165.5, 142.0, 141.5, 138.0, 131.6, 129.3, 124.3, 119.7, 109.2, 60.1.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1656.

HRMS (ESI) calcd. for $C_{12}H_{11}NNaO_2S$ [M + Na]$^+$: 256.0403; found: 256.0396.

2.2 General Procedure for Ligand Evaluation

(1) Experimental procedure



A 25 mL Schlenk tube equipped with magnetic stirrer was charged with $Pd(MeCN)_2Cl_2$ (10.4 mg, 0.0401 mmol), $Cu(OAc)_2$ (14.5 mg, 0.0798 mmol,), and the ligand (10 mol%). The tube was then filled with O_2 by three evacuation/O_2 backfill cycles. DMF (2.0 mL) was added and the reaction mixture was stirred at room temperature for 5 min before *tert*-butyl acrylate (205 mg, 1.60 mmol) and 1-methylindole (105 mg, 0.800 mmol) were added by syringe. After being heated to 70 °C and stirred for 3 h, the reaction mixture was quenched with brine (10 mL), and 1,3,5-trimethoxybenzene (44.8 mg, 0.266 mmol) was weighed into the tube as an internal standard (IS). After shaking, the reaction mixture was extracted with EtOAc (5.0 mL), and the organic phase was separated and analyzed by GC and NMR for the determination of the conversion and product yields, respectively. The results of ligand evaluation (**L1** to **L20**) were presented in Scheme 3 and **Table 1** in the main text.

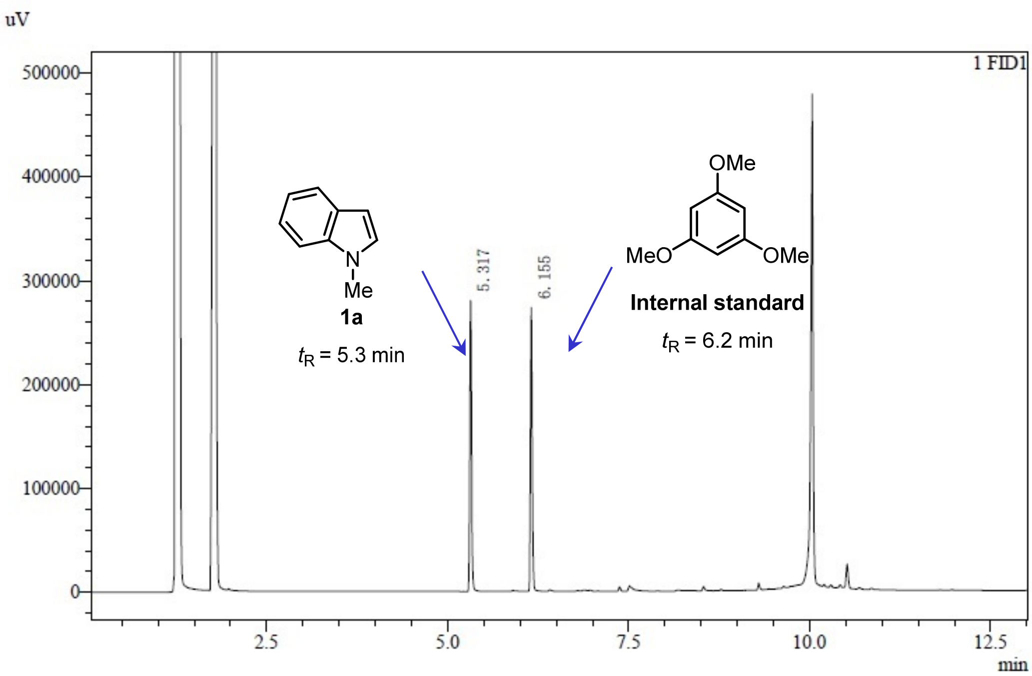


Figure S1. Representative GC trace of the reaction mixture. GC conditions: capillary column (0.25 mm × 30 m), constant pressure mode (160 kPa), inlet temperature 250 °C, split ratio 30:1, FID temperature 300 °C, initial temperature 80 °C, keep for 1.5 min, temperature elevation rate 25 °C/min, final temperature 280 °C, keep for 5 min.

(2) Data analysis for GC measurements

A representative GC trace of the reaction mixture is shown in Figure S1. The starting material *N*-methylindole (**1a**) and 1,3,5-trimethoxybenzene (IS) showed clear peaks, while the products were not stable under the GC conditions and the corresponding peaks are not suitable for quantification. The conversion of **1a** was calculated based on the peak area of **1a** (t_R = 5.3 min) relative to that of the IS (t_R = 6.2 min).

(3) Data analysis for NMR measurements

For the reaction producing both C2- and C3-alkenylation products, a representative ^{1}H NMR spectrum is shown in Figure S2. The yields of the products **3a**, **3b**, and **3d** were calculated based on the integration of their characteristic peaks relative to that of the IS (6.08 ppm).

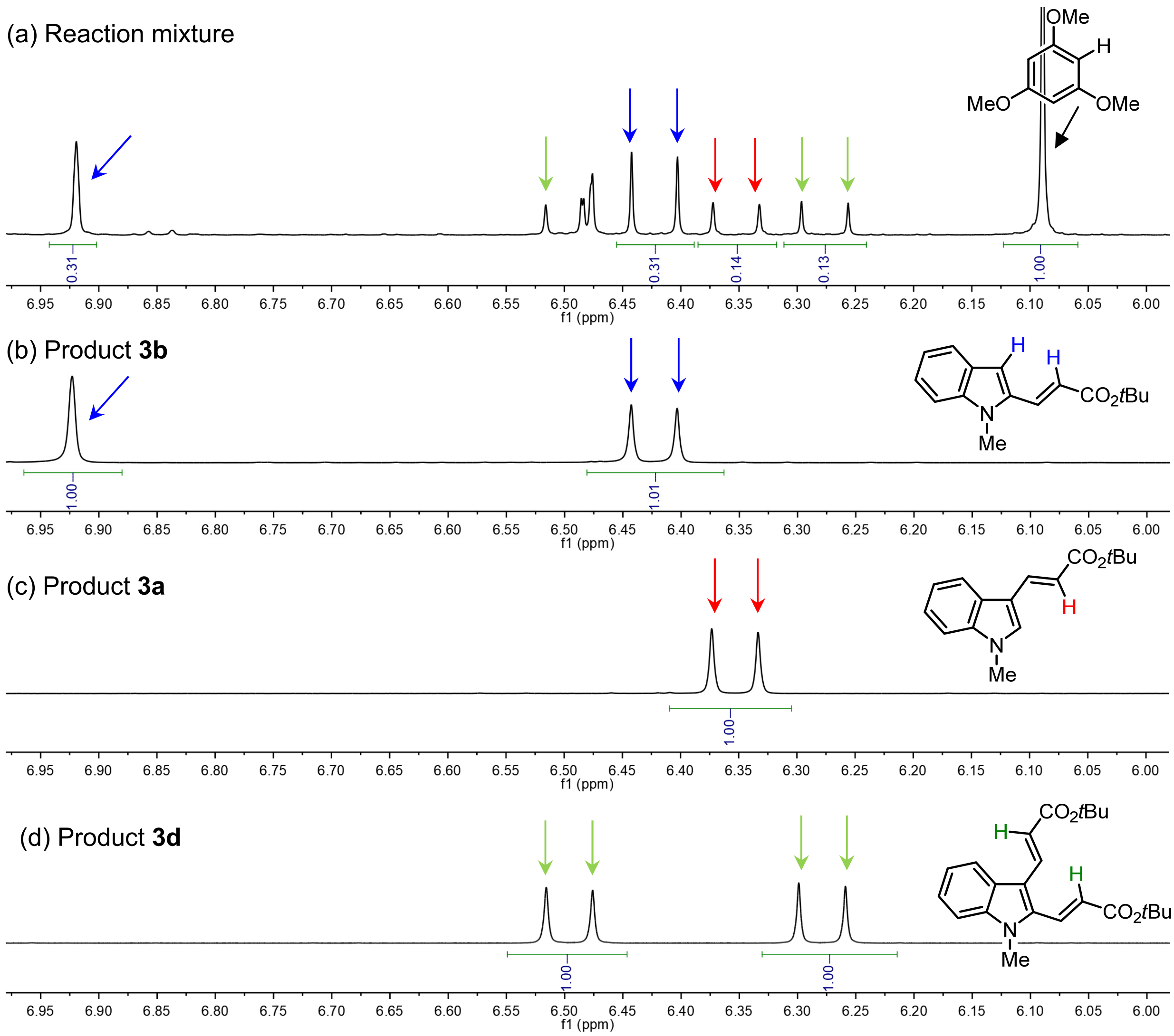


Figure S2. Representative ^{1}H NMR spectrum of the crude reaction mixture (a), ^{1}H NMR spectrum of isolated product **3b** (b), **3a** (c), and **3d** (d). Different products with characteristic peaks are marked by colored arrows.

For the reaction producing C3-alkenylation product as the major product, a representative ^{1}H NMR spectrum is shown in Figure S3. The yields of the products **3a** and **3c** were calculated based on the integration of their characteristic peaks relative to that of the IS (6.08 ppm).

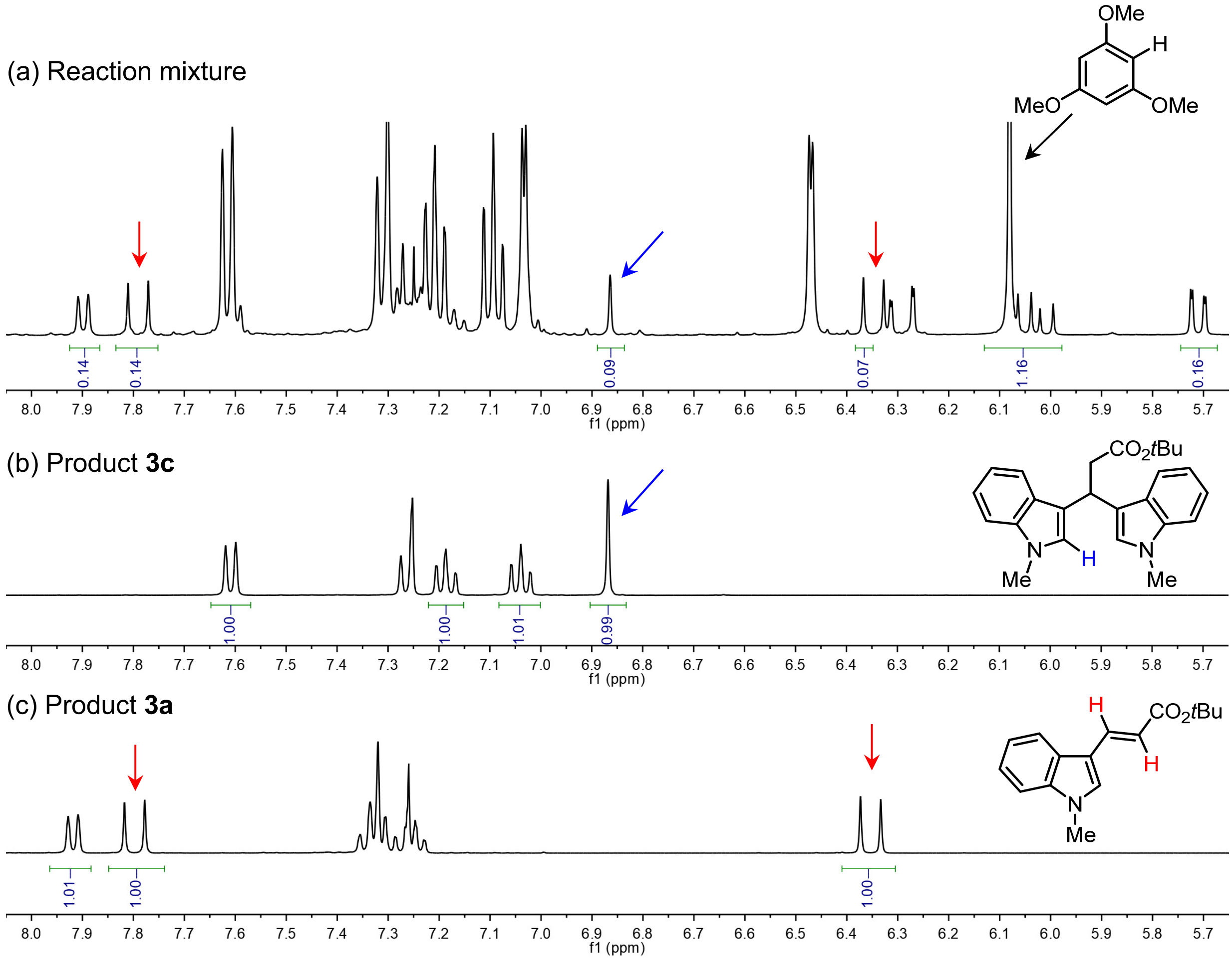
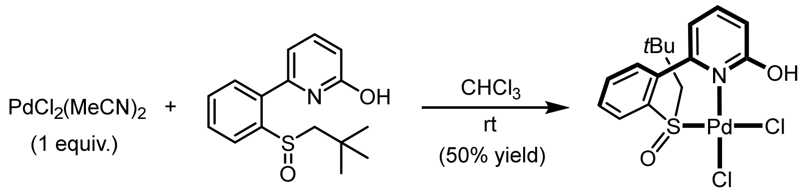


Figure S3. Representative ^{1}H NMR spectrum of the crude reaction mixture (a), ^{1}H NMR spectrum of isolated product **3c** (b) and **3a** (c). Different products with characteristic peaks are marked by colored arrows.

3. Mechanistic Studies

3.1 Structure and Activity of the Pd(II)-SOHP Complex

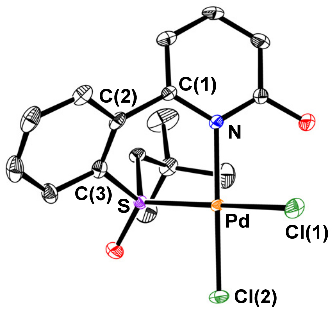
(1) Synthesis and structure of PdCl₂•L17•CHCl₃



A solution of $PdCl_2(MeCN)_2$ (51.8 mg, 0.200 mmol) and **L17** (57.9 mg, 0.200 mmol) in $CHCl_3$ (15.0 mL) was stirred at room temperature for 30 min. Evaporation of the solvent gave the crude complex, which was washed with Et_2O and then filtrated to afford the compex $PdCl_2$•**L17**•$CHCl_3$ as a yellow solid in 84% yield (78.6 mg).

^1H NMR (400 MHz, $CDCl_3$): δ 10.64 (s, 1H), 8.15 (dd, J = 7.5, 1.8 Hz, 1H), 7.97 (dd, J = 8.4, 7.4 Hz, 1H), 7.86 (ddt, J = 16.1, 1.6, 7.5 Hz, 2H), 7.76 (dd, J = 7.3, 1.7 Hz, 1H), 7.31 (dd, J = 7.4, 1.3 Hz, 1H), 7.18 (dd, J = 8.4, 1.2 Hz, 1H), 2.80 (d, J = 13.2 Hz, 1H), 2.28 (d, J = 13.2 Hz, 1H), 1.33 (s, 9H).

The structure of $PdCl_2$•**L17**•$CHCl_3$ was determined by X-ray diffraction analysis. A single crystal of this complex suitable for X-ray diffraction analysis was obtained by recrystallization from DCM-Et_2O.

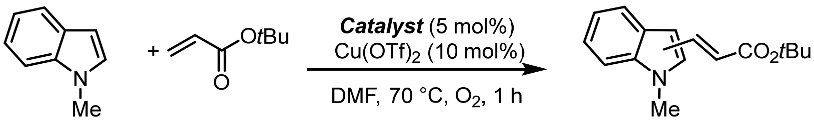


Crystal data for $PdCl_2$•**L17**•$CHCl_3$ (CCDC1978349)

Empirical formula	$C_{17}H_{20}Cl_5NO_2PdS$
Formula weight	586.05
Temperature/K	173.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.65140(10)
b/Å	16.4017(2)
c/Å	8.71580(10)
α/°	90
β/°	115.259(2)
γ/°	90
Volume/Å³	1118.50(3)
Z	2
$\rho_{calc}g/cm^3$	1.740

μ/mm^{-1}	13.177
F(000)	584.0
Crystal size/mm^3	0.4 × 0.2 × 0.15
Radiation	Cu K$_\alpha$ (λ = 1.54184)
2Θ range for data collection/°	10.788 to 149.194
Index ranges	-10 ≤ h ≤ 10, -15 ≤ k ≤ 20, -9 ≤ l ≤ 10
Reflections collected	7670
Independent reflections	3604 [R_{int} = 0.0301, R_{sigma} = 0.0318]
Data/restraints/parameters	3604/1/248
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0211, wR_2 = 0.0541
Final R indexes [all data]	R_1 = 0.0211, wR_2 = 0.0541
Largest diff. peak/hole / e Å^{-3}	0.87/-0.88
Flack parameter	-0.014(6)

(2) Activity test of $PdCl_2$•L17•$CHCl_3$



Catalyst	Conv. (%)	**3a** (%)	**3b** (%)	**3c** (%)
5 mol% $PdCl_2$•**L17**•$CHCl_3$	49%	8%	25%	4%
5 mol% $PdCl_2(CH_3CN)_2$ + 5 mol% **L17**	49%	8%	24%	4%

A 25 mL Schlenk tube equipped with magnetic stirrer was charged with $Pd(MeCN)_2Cl_2$ (10.4 mg, 0.0401 mmol) and **L17** (11.6 mg, 0.0401 mmol) [or $PdCl_2$•**L17**•$CHCl_3$ (18.7 mg, 0.0401 mmol)], and $Cu(OTf)_2$ (28.9 mg, 0.0799 mmol). Then the tube was filled with O_2 by three evacuation/O_2 backfill cycles. DMF (2.0 mL) was added and the reaction mixture was stirred at room temperature for 5 min before *tert*-butyl acrylate (206 mg, 1.60 mmol) and *N*-methylindole (105 mg, 0.800 mmol) were added by syringe. After heated to 70 °C for 3 h, the reaction mixture was quenched with brine (10 mL), and 1,3,5-trimethoxybenzene (44.8 mg, 0.266 mmol) was weighed into tube as IS. After shaking, the reaction mixture was extracted with EtOAc (5.0 mL), and the organic phase was analyzed by GC and NMR for the determination of the conversion and the product yields, respectively. The result shows that complex $PdCl_2$ •**L17**•$CHCl_3$ exhibit similar activity and selectivity with the $Pd(MeCN)_2Cl_2$ /**L17** combination.

(3) NMR study

To a solution of $Pd(MeCN)_2Cl_2$ dissolved in non-deuterated DMF, **L17** was added at room temperature under air. The resulting mixture was subjected to ^{1}H NMR analysis. The NMR spectra were recorded after ^{1}H gradient shimming without applying a ^{2}H-lock, and the undesired solvent signals were suppressed by the WET solvent suppression method.[7] The chemical shifts of the solvents utilized in the NMR experiments were calibrated against TMS (2.88, 2.96 and 8.02 ppm for DMF).

The ^{1}H NMR analysis (Figure S4) confirmed the homogeneity of the crystalline $PdCl_2$•**L17** and the complex prepared in situ in DMF (b and c), and showed that the excess ligand existed in free form without forming a PdL_2 type complex (d).

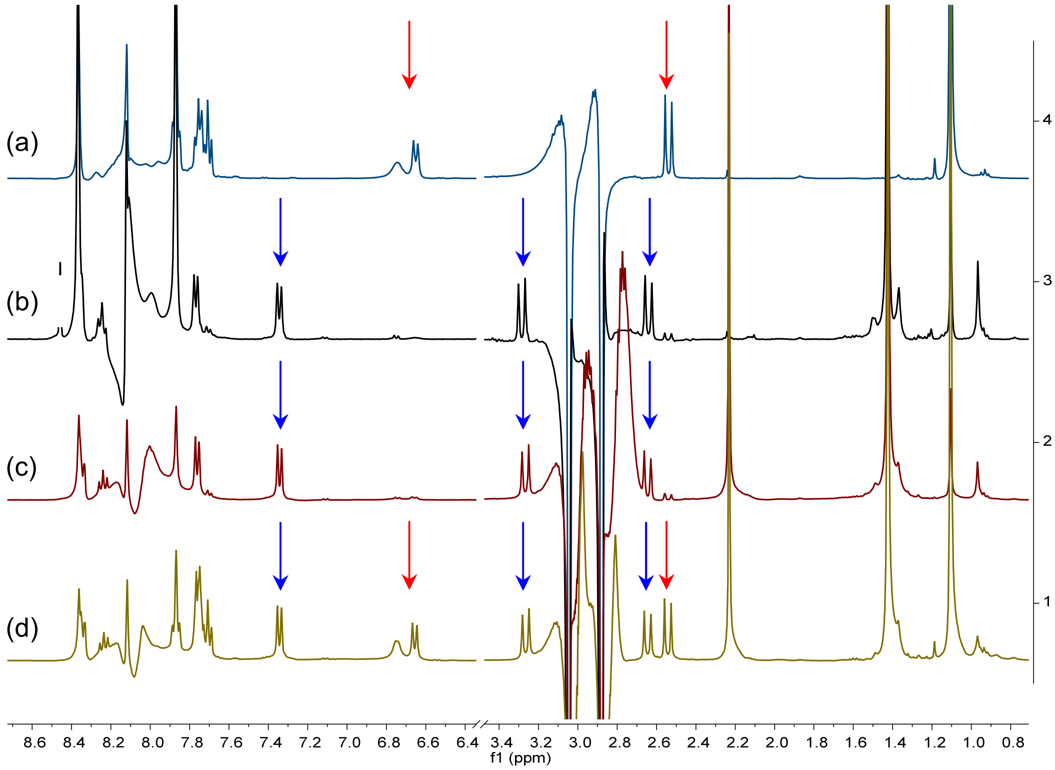


Figure S4. ^{1}H NMR study on the complexation between $Pd(MeCN)_2Cl_2$ and **L17**. ^{1}H NMR spectrum of **L17** (a), independently synthesized $PdCl_2$·**L17** (b), the mixture of $Pd(MeCN)_2Cl_2$ (40 mM) and **L17** (40 mM) (c), and the mixture of $Pd(MeCN)_2Cl_2$ (41 mM) and **L17** (81 mM). The characteristic peaks of **L17** and $PdCl_2$·**L17** are marked by red and blue arrows, respectively.

(4) Probing the interaction between Cu(II) and the SOHP ligand

Since $Cu(OTf)_2$ was used in the catalytic system, we wondered whether or not the coordination of the SOHP ligand **L17** to Cu(II) is favorable in DMF solvent. To address this issue, we performed an FT-IR measurement of $Cu(OTf)_2$ and **L17** in DMF using a Mettler-Toledo ReactIR 15 instrument equipped with a 9.5 mm diameter DiComp probe. It was found that, when a DMF solution of $Cu(OTf)_2$ was added to a DMF solution of **L17**, no new peaks emerged and the original peaks corresponding to $Cu(OTf)_2$ and the ligand persisted (Figure S5). This result indicated that in DMF solvent the formation of Cu(II)/**L17** complex was not favorable, and free ligand could exist in the reaction system in the presence of Cu(II).

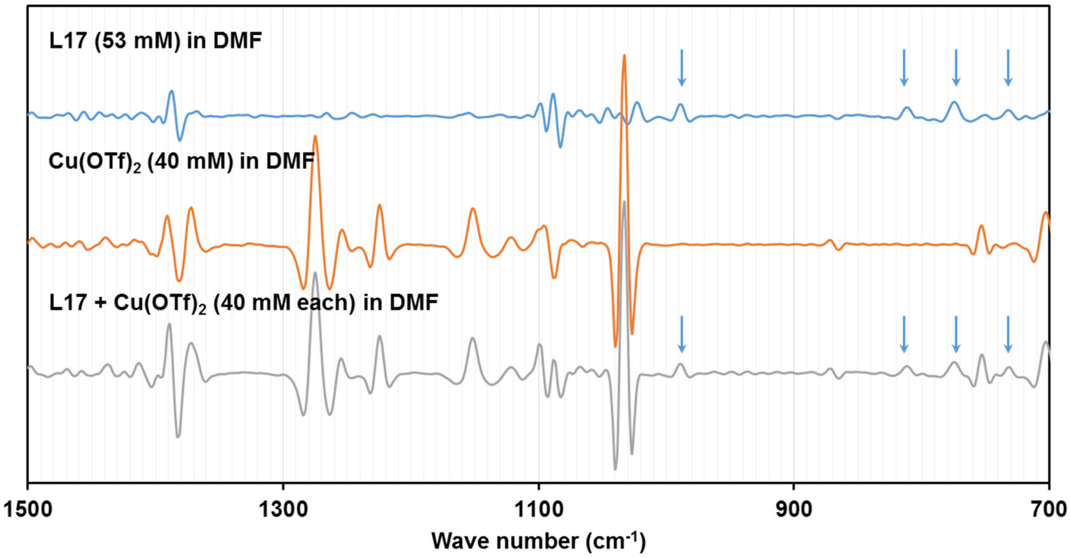
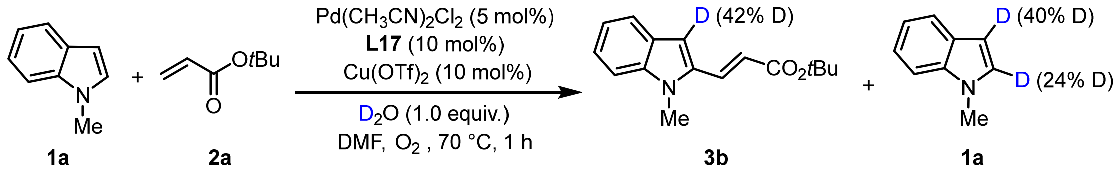


Figure S5. Secondary derivative FT-IR spectra of **L17**, $Cu(OTf)_2$, and **L17** + $Cu(OTf)_2$ in DMF (from top to bottom) acquired at rt, in which the DMF background has been subtracted. The characteristic peaks of ligand **L17** were marked by blue arrows.

3.2 Deuterium Labeling Experiments

(1) C2-deuteration of *N*-methylindole in the reaction



1a (1.0 equiv.) 2a (2.0 equiv.) 3b 40% yield 1a 41% recovered

A 25 mL Schlenk tube equipped with magnetic stirrer was charged with Pd(MeCN)$_2$Cl$_2$ (20.9 mg, 0.0806 mmol), **L17** (46.5 mg, 0.161 mmol) and Cu(OTf)$_2$ (57.9 mg, 0.160 mmol). The tube was filled with O_2 by three evacuation/O_2 backfill cycles. DMF (4.0 mL) was added and the reaction mixture was stirred at room temperature for 5 min, before D_2O (32.0 µL, 1.60 mmol), *tert*-butyl acrylate (411 mg, 3.21 mmol) and *N*-methylindole (211 mg, 1.60 mmol) were added by syringe. After heated to 70 °C for 1 h, the reaction mixture was quenched with brine (30 mL) and extracted with EtOAc (3 × 5 mL), and the organic extracts were combined, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (50:1 to 20:1) as eluent to afford the C2-alkenylation product **3b** (165 mg, 40% yield), together with recovered **1a** (86.8 mg, 41% recovery). The recovered *N*-methyindole (Figure S6) and the product **3b** (Figure S7) were submitted to ^{1}H NMR and ^{2}H NMR analysis to determine the deuterium incorporation.

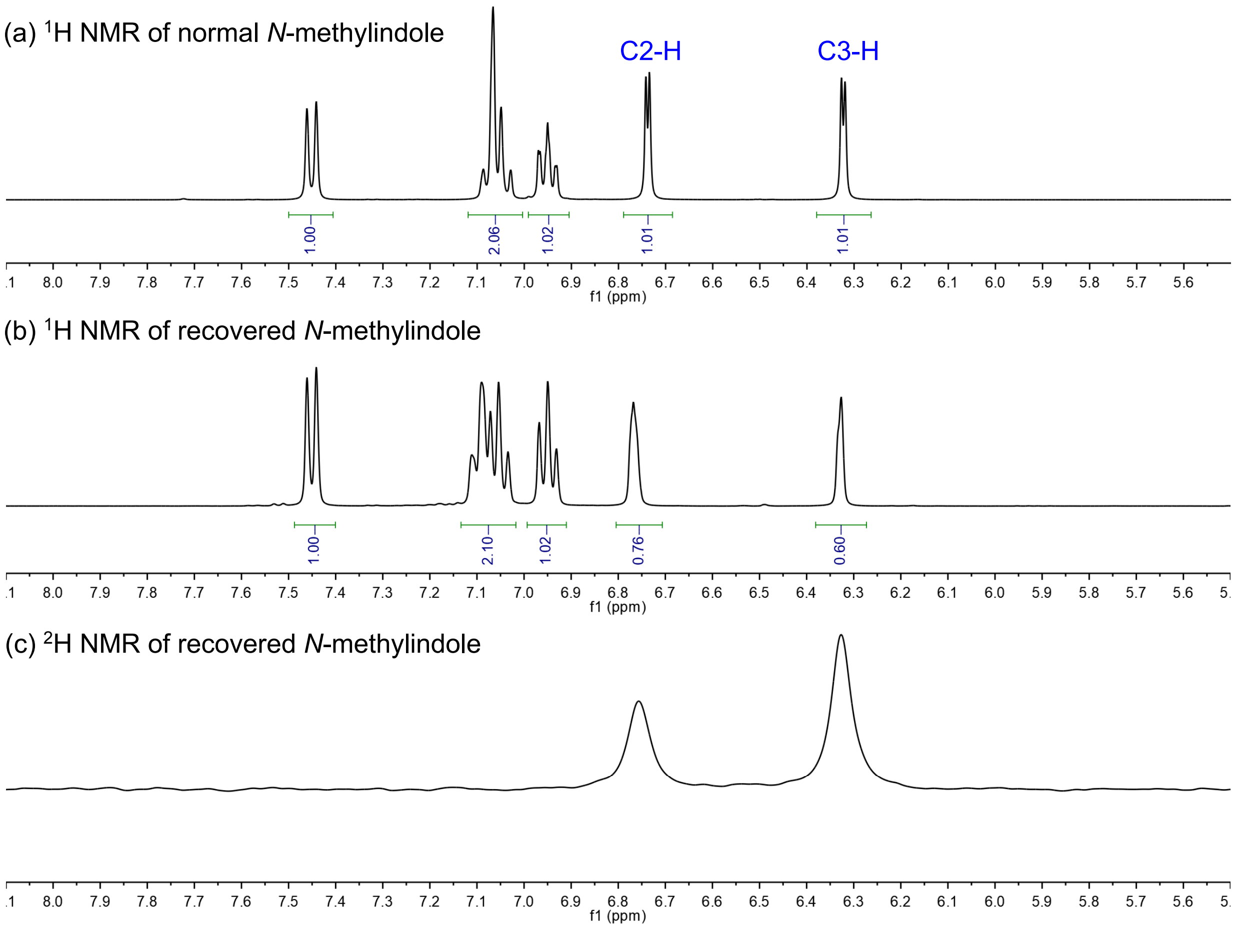


Figure S6. ^{1}H NMR (400 MHz) and ^{2}H NMR (61 MHz) spectra of *N*-methylindole **1a** recorded in cyclohexane.

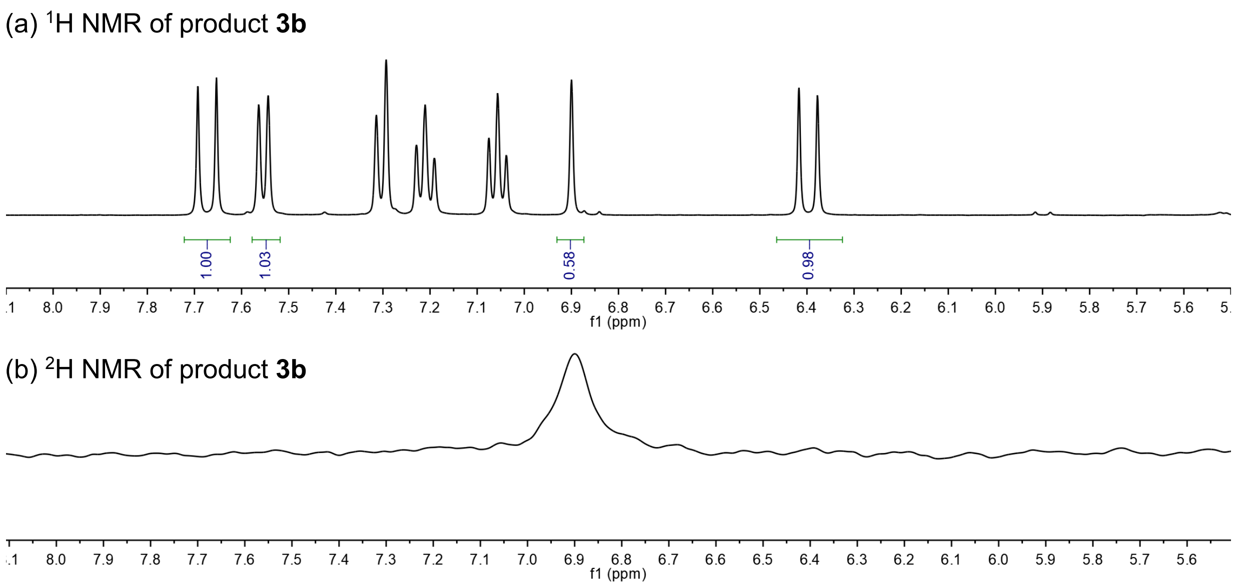
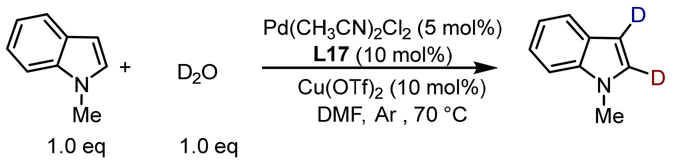


Figure S7. ^{1}H NMR (400 MHz) and ^{2}H NMR (61 MHz) spectra of product **3b** recorded in CH_2Cl_2.

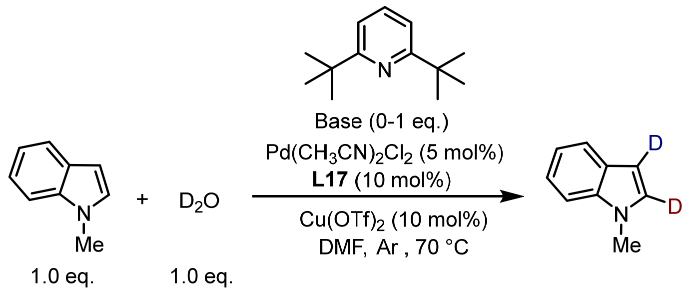
(2) Monitoring the deuteration progress of *N*-methylindole

a. The Pd(II)/L17 system:



	1 h	3 h	7 h	23 h	31 h
C2 (D)	5%	9%	19%	44%	49%
C3 (D)	55%	52%	52%	48%	47%

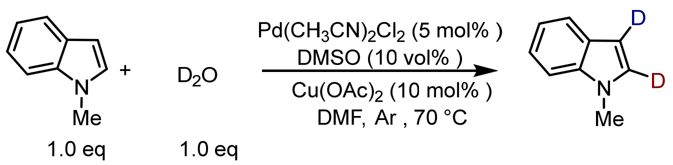
A 25 mL Schlenk flask equipped with magnetic stirrer was charged with $Pd(MeCN)_2Cl_2$ (20.8 mg, 0.0802 mmol), **L17** (46.2 mg, 0.160 mmol), and $Cu(OTf)_2$ (57.9 mg, 0.160 mmol) under Ar. DMF (4.0 mL) was added and the reaction mixture was stirred at room temperature for 5 min, before D_2O (32.0 μL, 1.60 mmol) and *N*-methylindole (210 mg, 1.60 mmol) were added by syringe. The reaction was stirred at 70 °C, and aliquots of the reaction mixture (ca. 0.5 mL each) was sampled by a syringe at 1 h, 3 h, 7 h, 23 h, and 31 h, respectively. The aliquots were immediately quenched by brine (5.0 mL) and extracted with cyclohexane (1.0 mL), and the organic layer was separated and submitted to ^{1}H and ^{2}H NMR analysis for determining the deuterium incorporation at C2- and C3-positions. Scheme 5a in the main text was plotted based on these data.



Equivalent of base	none	0.2 eq	1.0 eq	1.0 eq (wo/ **L17**)
C2-D incorporation in 1 h	5%	8%	10%	Not determined
C2-D incorporation in 3 h	9%	10%	18%	0%

Study on the effect of base addition was carried out employing 2,6-di-*tert*-butylpyridine as the base following the same procedure described above. The result showed that the presence of base could indeed accerlate the the C2-deuteration process, while in a longer period the base resulted in deactivation of the catalytic system. The observed acceleration effect is in agreement with the proposed reaction mechanism, and may serve as a tentative rationalization for the difference in the C2-deuteration rate of the catalytic reaction and the independent deuteration reaction.

b. The Pd(II)/DMSO system:



	1 h	3 h	7 h	23 h	31 h
C2 (D)	0	0	0	0	0
C3 (D)	35%	41%	52%	61%	71%

A 25 mL Schlenk flask equipped with magnetic stirrer was charged with $Pd(MeCN)_2Cl_2$ (21.5 mg, 0.0829 mmol) and $Cu(OAc)_2$ (30.6 mg, 0.168 mmol) under Ar. DMSO (0.4 mL, 10 vol%) and DMF (3.6 mL) was added and the reaction mixture was stirred at room temperature for 5 min, before D_2O (32.0 µL, 1.60 mmol) and *N*-methylindole (214 mg, 1.60 mmol) were added by syringe. The reaction was stirred at 70 °C, and aliquots of the reaction mixture (ca. 0.5 mL each) was sampled by a syringe at 1 h, 3 h, 7 h, 23 h, and 31 h, respectively. The aliquots were immediately quenched by brine (5.0 mL) and extracted with cyclohexane (1.0 mL), and the organic layer was separated and submitted to ^1H and ^2H NMR analysis for determining the deuterium incorporation at C2- and C3-positions. Scheme 5b in the main text was plotted based on these data.

3.3 Kinetic Isotope Effect (KIE) Study

(1) Full course catalytic rate profile of the model reaction

a. General methods:

The overall catalytic rate profile of the reaction catalyzed by the Pd/**L17** system was monitored. The yield of the products were determined by high performance liquid chromatography (HPLC) analysis, with 1,3,5-trimethoxybenzene as IS.

A 25 mL Schlenk tube equipped with a magnetic stirrer was charged with $Pd(MeCN)_2Cl_2$, $Cu(OTf)_2$, **L17**, and 1,3,5-trimethoxybenzene. The tube was filled with O_2 by three evacuation/O_2 backfill cycles. DMF was added and the reaction mixture was stirred at room temperature for 5 min, before *tert*-butyl acrylate and *N*-methylindole were added by syringe. The reaction solution was allowed to react at 70 °C, and the reaction aliquots (ca. 0.5 mL) were sampled by syringe. The sampled aliquots were immediately quenched with brine (5 mL) and extracted with EtOAc (2 mL). The organic layer was separated and filtrated through a pipette-filter filled with a thin pad of silica gel (eluted with petroleum ether/EtOAc 5:1), and then submitted to HPLC analysis.

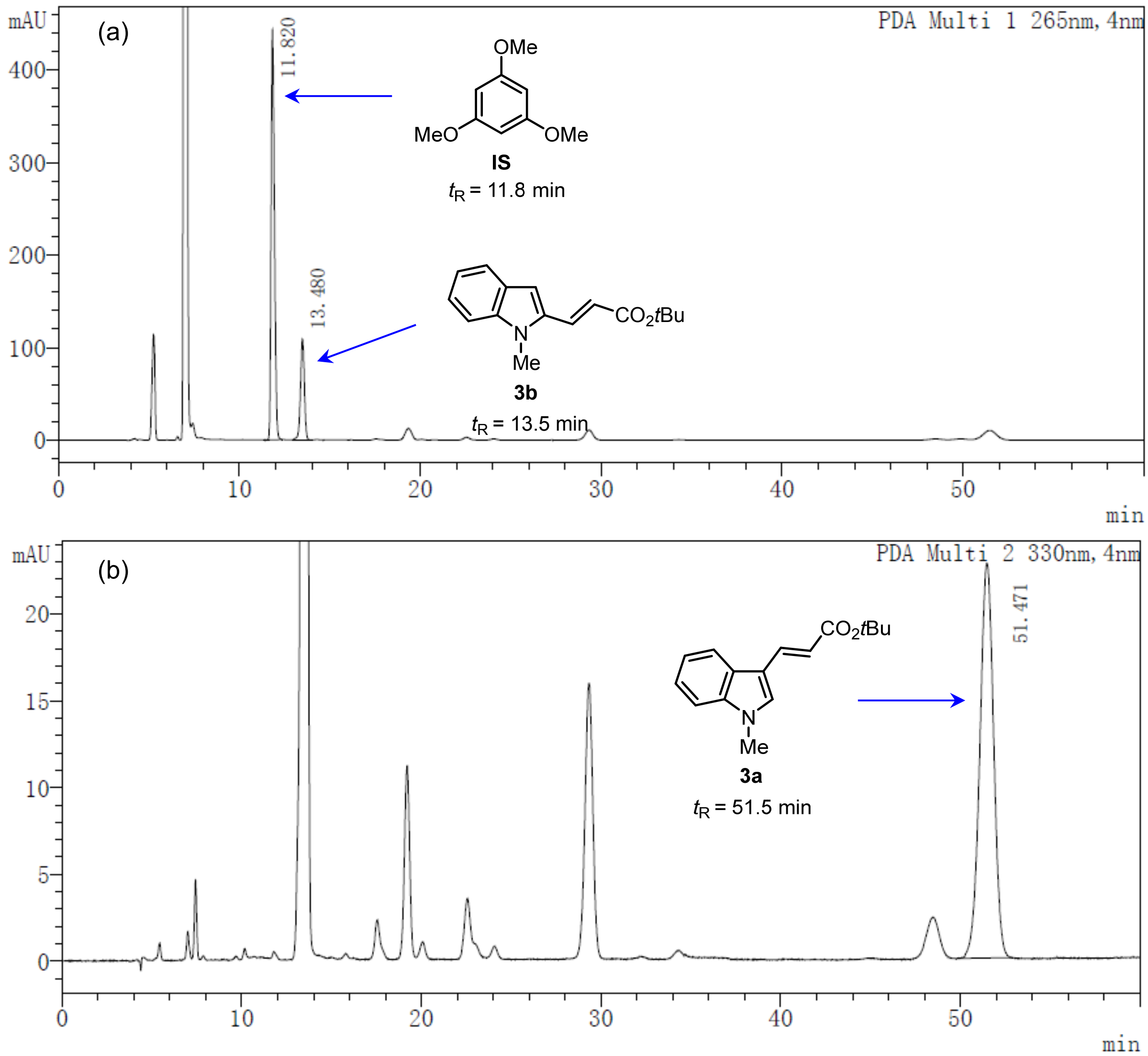
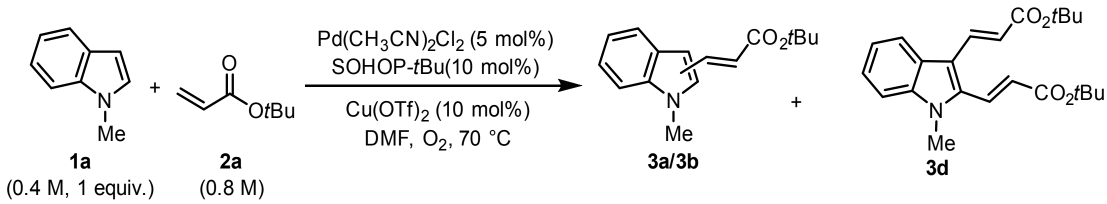


Figure S8. Representative HPLC traces of the reaction mixture monitored at 265 nm (a) and 330 nm (b).

Conditions for HPLC analysis: Platisil Silica column (4.6 × 250 mm), hexanes/EtOAc 95:5 as the mobility phase, flow rate 1.0 mL/min. The peaks of the IS, product **3b**, and product **3a** could be clearly identified: t_R(IS) = 11.8 min, t_R(**3b**) = 13.5 min, t_R(**3a**) = 51.5 min. The yields of products **3a** and **3b** in each sample were calculated by the areas of the corresponding peaks (product **3a** and **3b** was monitored at 330 and 265 nm, respectively) relative to that of the IS (monitored at 265 nm). The representative HPLC traces were shown in Figure S8.

b. Data for the full-course catalytic rate profile



sample	t(min)	**3b** yield	**3a** yield	**3d** yield	total yield
1	7	1.27%	0.19%	0	1.47%
2	12	3.50%	0.59%	0.01%	4.10%
3	15	5.80%	0.93%	0.02%	6.75%
4	22	8.26%	1.34%	0.04%	9.65%
5	27	9.74%	1.54%	0.06%	11.35%
6	42	15.57%	2.10%	0.15%	17.82%
7	60	22.62%	2.84%	0.35%	25.81%
8	90	30.13%	3.27%	0.72%	34.12%
9	120	36.10%	3.36%	1.17%	40.63%
10	180	41.96%	3.30%	1.92%	47.18%
11	240	45.32%	3.05%	2.68%	51.05%
12	300	47.95%	2.84%	3.32%	54.11%
13	720	49.27%	1.63%	6.77%	57.67%

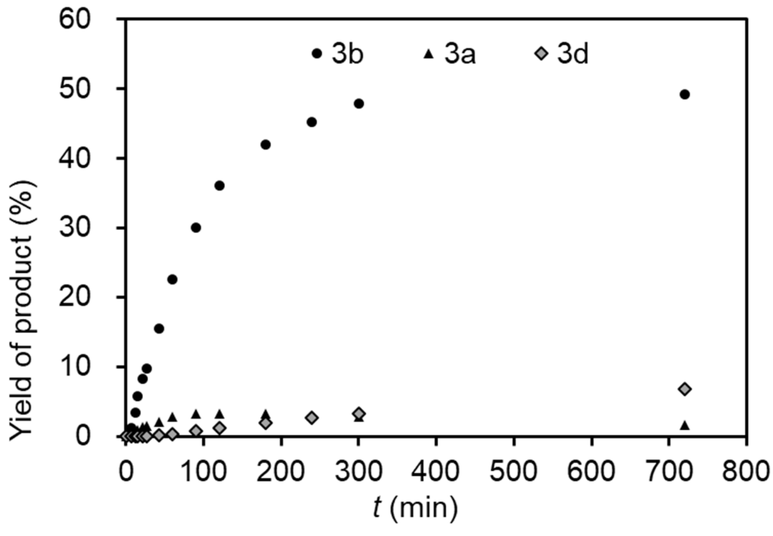


Figure S9. Overall catalytic rate profile of model reaction.

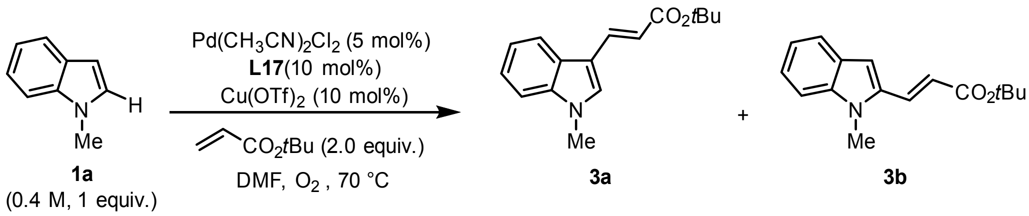
It was found that the reaction proceeded without an induction period (Figure S9), and the initial kinetic data could represent a steady-state situation and thus could be used to analyze the reaction mechanism.

(2) KIE determined by parallel kinetic experiments

a. General methods:

Kinetic isotope effect in this C-H alkenylation reaction was measured by parallel kinetic experiments employing *N*-methylindole and 2-deuterted *N*-methylindole, respectively. The initial rates of the reactions were determined by high performance liquid chromatography (HPLC) analysis, with 1,3,5-trimethoxybenzene as IS. For each kinetic measurement 5 data points were collected (for 2-H *N*-methylindole, reaction time = 20 min, conversion = ca. 15%; for 2-D *N*-methylindole, reaction time = 75 min, conversion = ca. 19%).

b. Kinetic measurement for 2-H *N*-methylindole



Time	4 min	8 min	12 min	16 min	20 min
Yield of **3b** (Run 1)	2.9%	5.9%	8.2%	10.5%	12.9%
Yield of **3a** (Run 1)	0.5%	1.0%	1.4%	1.8%	2.1%
Yield of **3b** (Run 2)	2.8%	5.5%	8.8%	10.2%	12.3%
Yield of **3a** (Run 2)	0.5%	0.9%	1.3%	1.6%	1.9%

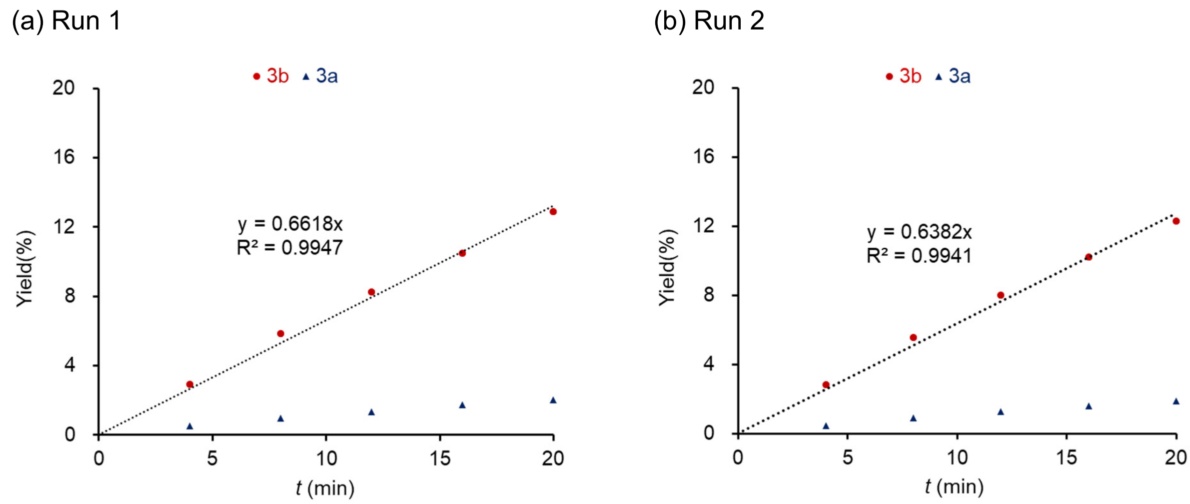
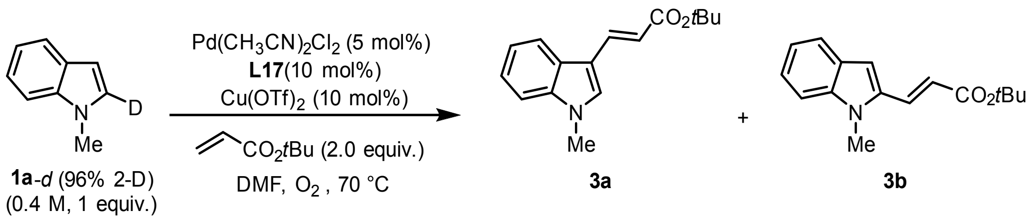


Figure S10. Plots of the yields of products **3a** and **3b** as a function of time employing 2-H *N*-methylindole. Initial rates for the formation of the C2-alkenylation product **3b**: (a) Run 1: 2.647 mM·min^{-1}; (b) Run 2: 2.553 mM·min^{-1}; average of two runs: 2.60 ± 0.05 mM·min^{-1}.

c. Kinetic measurement for 2-D *N*-methylindole



Time	15 min	30 min	45 min	60 min	75 min
Yield of 3b (Run 1)	3.2%	6.0%	8.8%	11.2%	13.4%
Yield of 3a (Run 1)	1.8%	2.9%	3.7%	4.3%	4.7%
Yield of 3b (Run 2)	2.9%	5.9%	8.7%	11.4%	13.8%
Yield of 3a (Run 2)	1.6%	2.8%	3.8%	4.4%	4.9%

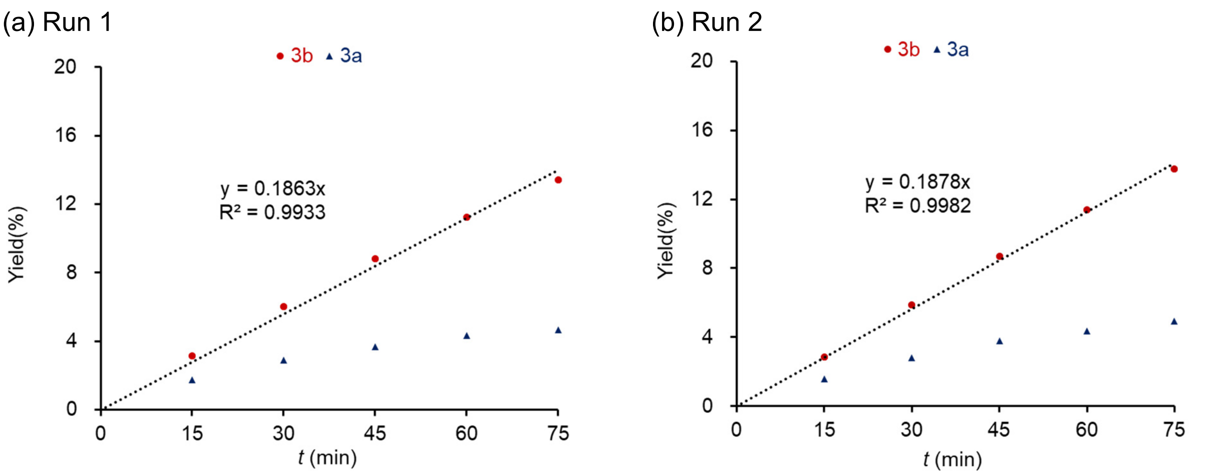


Figure S11. Plots of the yields of products **3a** and **3b** as a function of time employing 2-D *N*-methylindole. Initial rates for the formation of the C2-alkenylation product **3b**: (a) Run 1: 0.7452 mM·min^{-1}; (b) Run 2: 0.7512 mM·min^{-1}; average of two runs: 0.748 ± 0.003 mM·min^{-1}.

d. Calculation of KIE

KIE of this indole C-H alkenylation reaction was calculated based on the initial rates for product **3b** formation from 2-H and 2-D *N*-mehtylindole.

rate(2-H) = 2.60 ± 0.05 mM·min^{-1}

rate(2-D) =0.748 ± 0.003 mM·min^{-1}

KIE = rate(2-H)/rate(2-D) = 3.48 ± 0.03

(3) Isotope effect on synthetic scale reaction

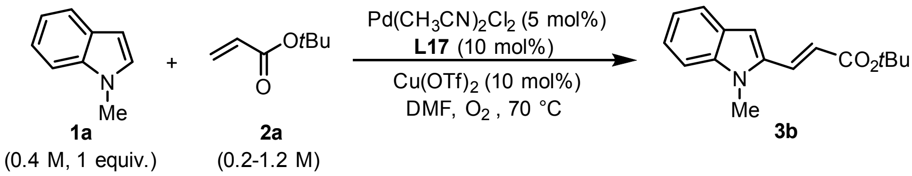
Study on the isotope effect on synthetic scale reaction was carried out employing 2-H 1a and 2-D *N*-methylindole following the procedure described in Section 3.1 (2), except that 10 mol% of the SOHP ligand **L17** was used. The results were summarized in Scheme 6 in the main text.

3.4 Effect of Acrylate Loading on the Model Reaction

(1) The Pd(II)/L17 system

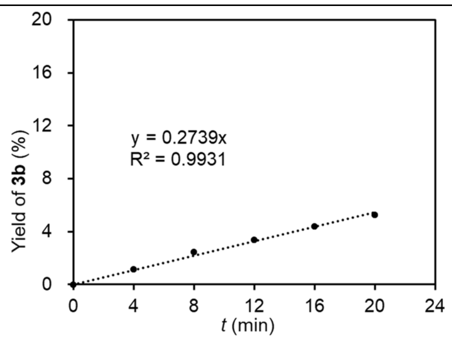
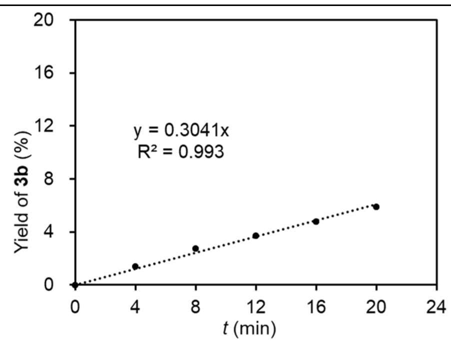
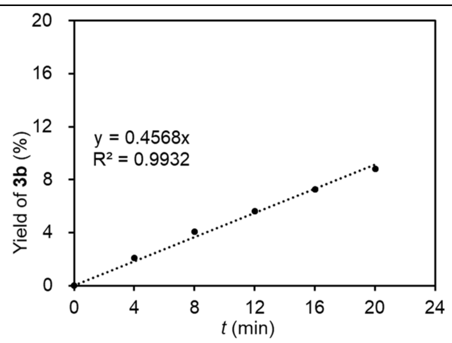
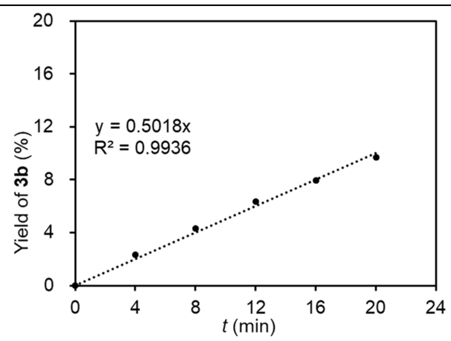
The effect of acrylate loading on the initial rate of C2-alkenylation reaction promoted by the Pd(II)/**L17** system was studied by performing a series of reactions following the procedure described in Section 3.3 (1), except that varying amounts of *tert*-butyl acrylate (0.2-1.2 M) were applied. Each experiment was conducted twice and the average of two results was used to plot the dependence of C2-alkenylation on acrylate loading shown in Scheme 7 (left part).

Table S1. Dependence of C2-alkenylation reaction initial rate on [acrylate].

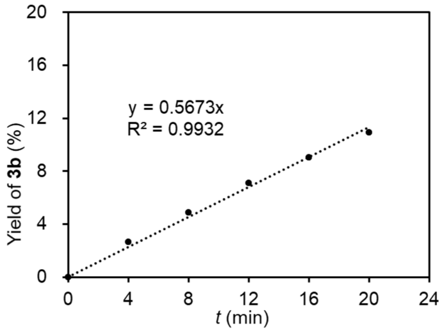


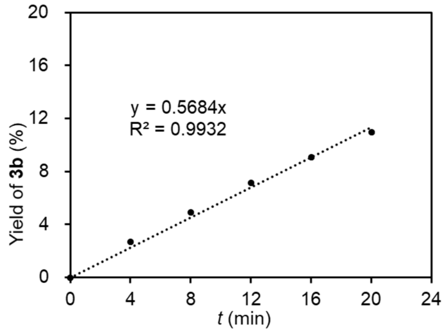
Entry	Acrylate (M)	Initial rate (mM/min)			SD
		Run 1	Run 2	Average	
1	0.2	1.0956	1.2164	1.1560	± 0.0604
2	0.4	1.8272	2.0072	1.9172	± 0.0900
3	0.6	2.2736	2.2692	2.2714	± 0.0022
4	0.8	2.7356	2.6472	2.6914	± 0.0442
5	1.0	2.5444	2.5416	2.543	± 0.0014
6	1.2	2.5860	2.6148	2.6004	± 0.0144

Raw data for this determination were shown below, and the initial rates were summarized in Table S1.

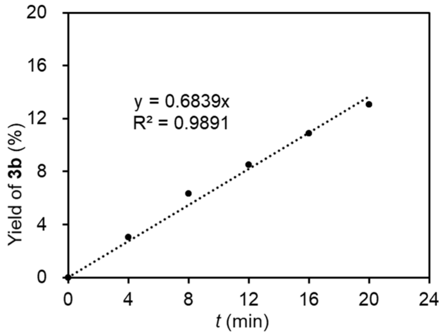
Condition	Plot for product formation run 1	Plot for product formation run 2
[**2a**] = 0.2 M		
[**2a**] = 0.4 M		

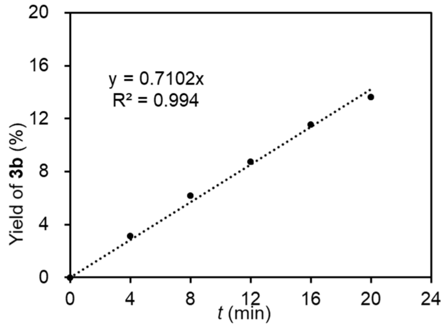
[**2a**] = 0.6 M



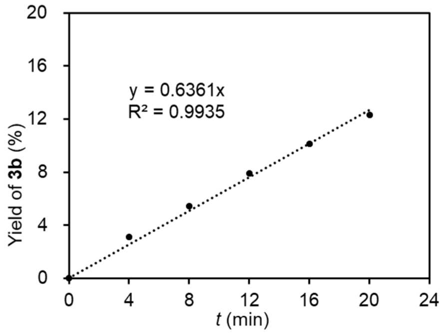


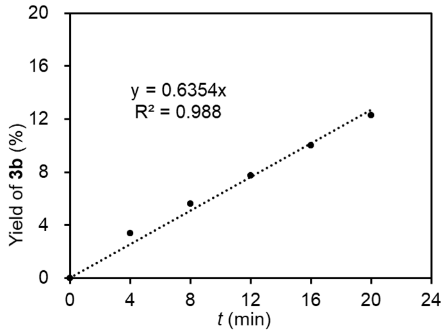
[**2a**] = 0.8 M



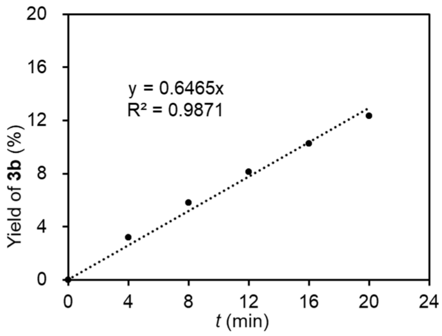


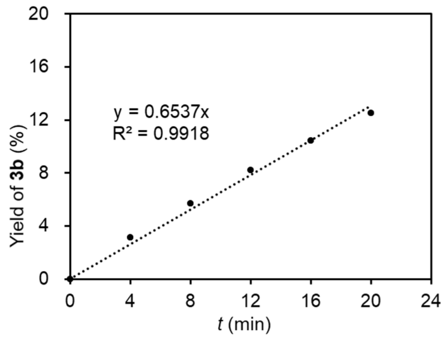
[**2a**] = 1.0 M





[**2a**] = 1.2 M

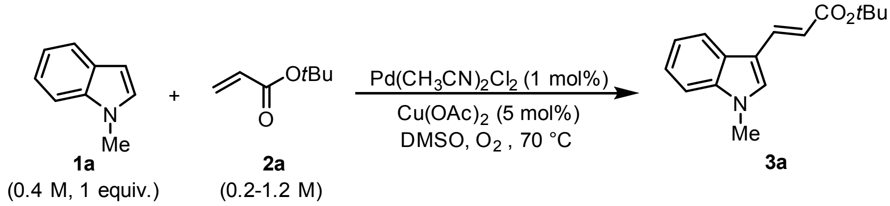




(2) The Pd(II)/DMSO system

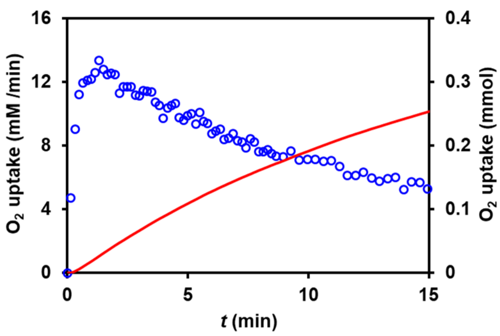
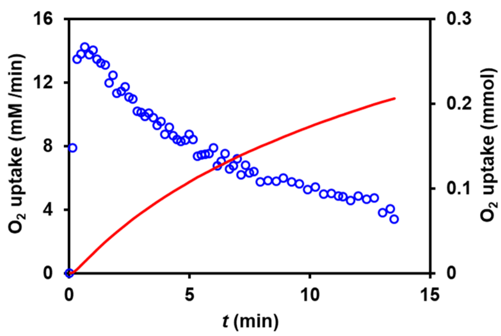
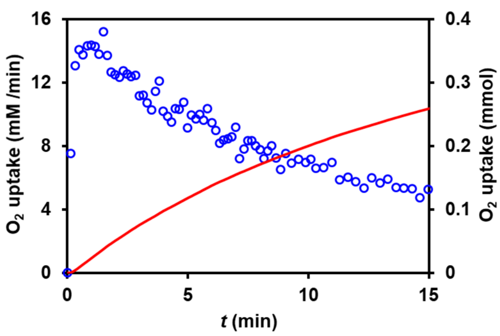
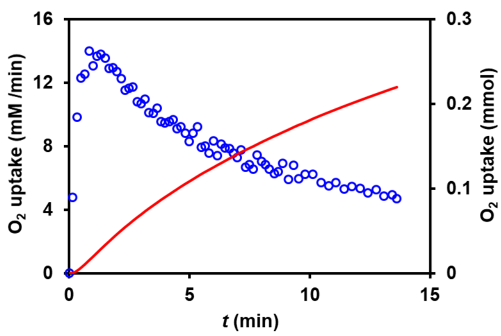
The effect of acrylate loading on the C3-alkenylation reaction promoted by the Pd(II)/DMSO system was studied by performing a series of reactions using gas uptake measurement method.[8] A 15 mL reaction vessel was charged with $PdCl_2(CH_3CN)_2$ (1 mol%) and $Cu(OAc)_2$ (5 mol%), after replacement with oxygen three times at a pressure of 103 kPa, DMSO (2.00 mL) and *tert*-butyl acrylate (0.5 to 3.0 equiv.) were added by syringe. The reaction vessel was allowed to reach thermo equilibrium in a 70 °C oil bath, and then the *N*-methylindole (0.8 mmol) was injected by syringe. The kinetic data of the initial period were acquired. Each experiment was conducted twice and the average of two results was used to plot the dependence of C3-alkenylation on acrylate loading shown in Scheme 7 (right part).

Table S2. Dependence of C3-alkenylation reaction initial rate on [acrylate].

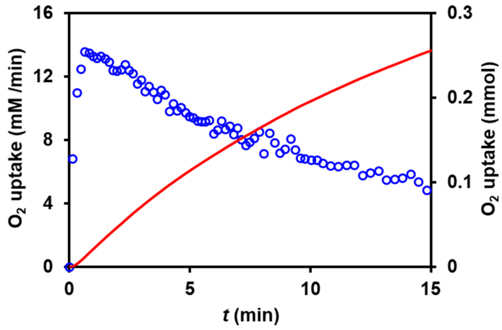


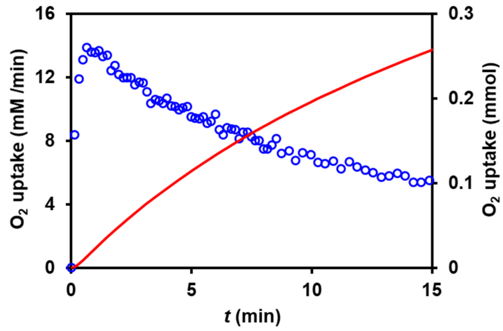
Entry	Acrylate (M)	Initial rate (mM/min)			SD
		Run 1	Run 2	Average	
1	0.2	25.42	27.26	26.34	± 0.92
2	0.4	28.42	26.92	27.66	± 0.74
3	0.6	27.22	27.02	27.12	± 0.10
4	0.8	22.7	22.84	22.78	± 0.06
5	1.0	20.62	20.12	20.36	± 0.24
6	1.2	16.54	18.88	17.7	± 1.2

Raw data for the determination of O_2 uptake initial rates were shown below, and the initial rates of the reaction were summarized in Table S2 (note that the rate of the reaction with respect to indole consumption or product formation is twice of the rate of O_2 uptake).

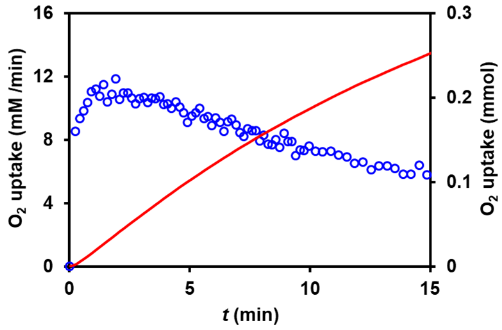
Condition	Plot for product formation run 1	Plot for product formation run 2
[**2a**] = 0.2 M		
[**2a**] = 0.4 M		

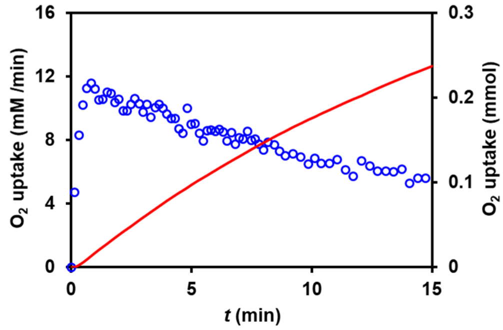
[**2a**] = 0.6 M



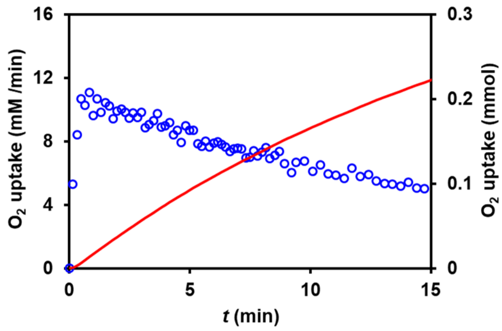


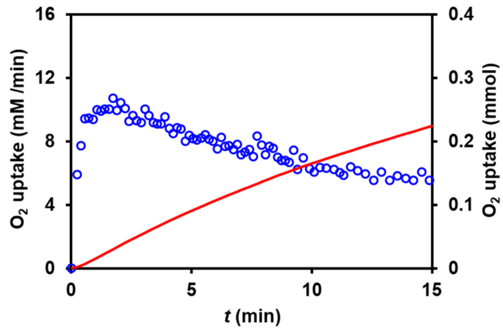
[**2a**] = 0.8 M



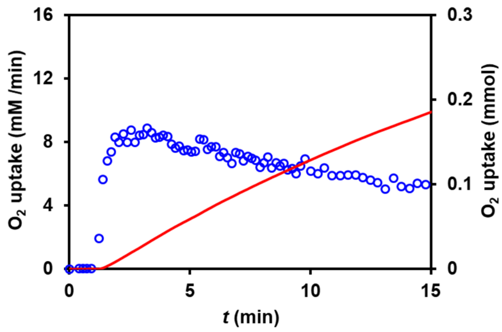


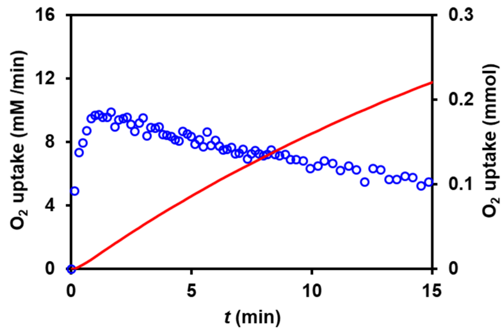
[**2a**] = 1.0 M





[**2a**] = 1.2 M

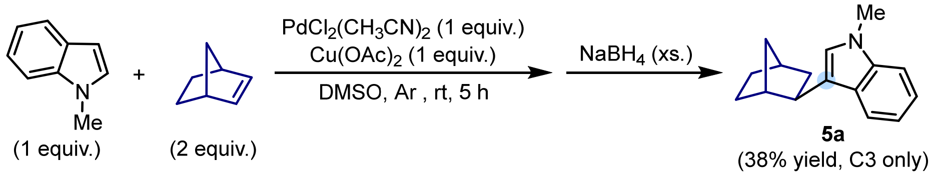




3.5 Trapping Experiments

(1) Direct reduction of the insertion intermediate

a. The Pd(II)/DMSO system



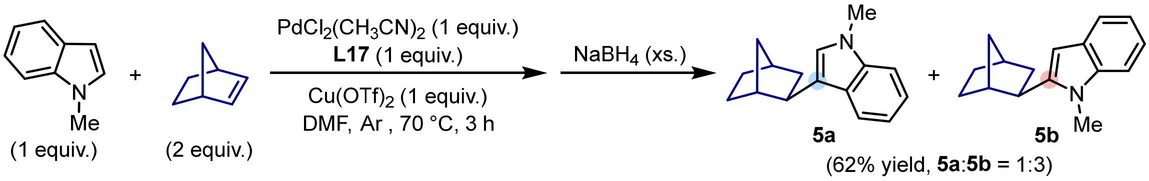
A solution of *N*-methylindole (25.5 mg, 0.194 mmol), norbornene (37.8 mg, 0.401 mmol), $PdCl_2(CH_3CN)_2$ (51.8 mg, 0.199 mmol), and $Cu(OAc)_2$ (36.2 mg, 0.199 mmol) in DMSO (2.0 mL) was stirred at room temperature under Ar for 5 h. Then $NaBH_4$ (38.1 mg, 1.01 mmol) was added and the resulting mixture was stirred for another 2 h before washed with water and extracted with CH_2Cl_2. The organic extracts were separated, washed with brine, dried over Na_2SO_4, and concentrated using a rotavap. The residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (1:0 to 20:1) as eluent to afford 3-norborylindole **5a** as white solid (16.4 mg, 38% yield).

Characterization data for **5a**:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J = 7.9 Hz, 1H), 7.30-7.15 (m, 2H), 7.08 (ddd, J = 8.0, 6.8, 1.3 Hz, 1H), 6.73 (d, J = 1.1 Hz, 1H), 3.72 (s, 3H), 2.96 (dd, J = 8.7, 5.3 Hz, 1H), 2.35 (dd, J = 18.8, 4.0 Hz, 2H), 1.79 (ddd, J = 11.3, 8.7, 2.2 Hz, 1H), 1.73-1.52 (m, 3H), 1.52-1.39 (m, 2H), 1.34-1.22 (m, 1H), 1.14 (dt, J = 9.5, 1.9 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5, 127.9, 124.5, 121.7, 121.6, 119.5, 118.5, 109.2, 42.6, 38.8, 38.2, 36.7, 36.1, 32.7, 30.1, 29.3.

b. The Pd(II)/L17 system



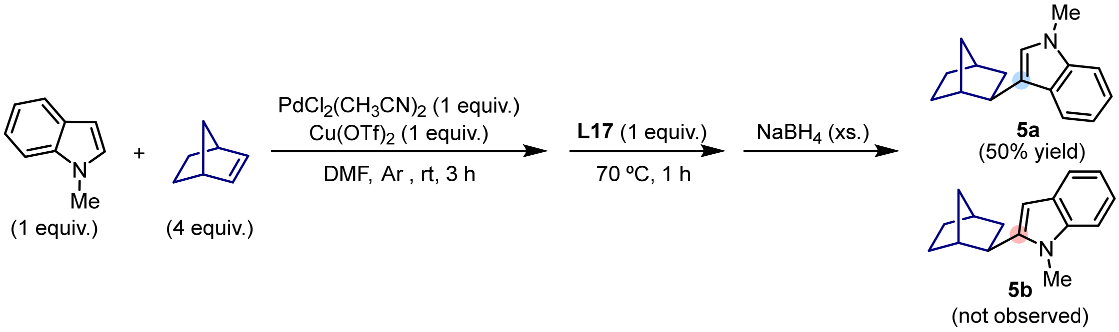
A solution of *N*-methylindole (52.5 mg, 0.400 mmol), norbornene (76.2 mg, 0.809 mmol), $PdCl_2$ $(CH_3CN)_2$ (51.8 mg, 0.200 mmol), **L17** (58.1 mg, 0.201 mmol), and $Cu(OTf)_2$ (72.5 mg, 0.200 mmol) in DMF (2.0 mL) was stirred at 70 °C under Ar for 3 h. The reaction mixture was cooled to room temperature, and $NaBH_4$ (60.7 mg, 1.60 mmol) was added. The resulting mixture was stirred for another 30 min before washed with water and extracted with CH_2Cl_2. The combined organic extracts were separated, washed with brine, dried over Na_2SO_4, and concentrated using a rotavap. The residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (1:0 to 20:1) as eluent to afford a mixture of **5a** and **5b** (in 1:3 ratio) as a white solid (28.0 mg, 62% yield).

Characterization data for **5b**:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (dt, J = 7.6, 1.0 Hz, 1H), 7.27-7.21 (m, 1H), 7.14 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.05 (ddd, J = 8.0, 7.1, 1.1 Hz, 1H), 6.21 (d, J = 0.9 Hz, 1H), 3.67 (s, 3H), 2.82 (dd, J = 8.4, 5.7 Hz, 1H), 2.47-2.33 (m, 2H), 1.85-1.54 (m, 5H), 1.47-1.24 (m, 2H), 1.20 (dp, J = 9.8, 1.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 137.7, 127.8, 120.7, 120.0, 119.3, 108.7, 97.2, 42.0, 39.9, 37.8, 36.8, 36.1, 30.1, 29.8, 29.2.

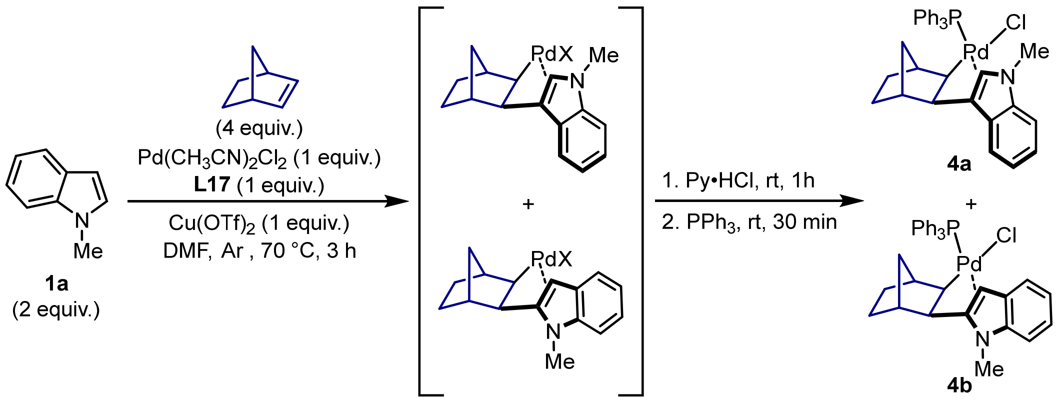
c. The effect of ligand on the generated C3-insertion intermediate



A solution of *N*-methylindole (26.0 mg, 0.198 mmol), norbornene (75.3 mg, 0.800 mmol), $PdCl_2(CH_3CN)_2$ (51.8 mg, 0.200 mmol), and $Cu(OTf)_2$ (72.4 mg, 0.200 mmol) in DMF (1.0 mL) was stirred at room temperature under Ar for 3 h. Then **L17** (58.0 mg, 0.200 mmol) was added and reaction mixture was heated to 70 °C for 1 h. After cooled to room temperature, $NaBH_4$ (40.2 mg, 1.06 mmol) was added. The resulting mixture was stirred for another 30 min, and then 1,3,5-trimethoxybenzene (9.3 mg, 0.055 mmol) was added as IS. The mixture was washed with water and extracted with CH_2Cl_2. The combined organic extracts were separated, washed with brine, dried over Na_2SO_4, concentrated using a rotavap, and subjected to ^1H NMR analysis. The ^1H NMR spectrum showed that only 3-norborylindole **5a** was produced (50% NMR yield), and 2-norborylindole **5b** was not produced.

(2) Characterization of the insertion intermediates

a. Preparation of the triphenylphosphine complexes



A solution of *N*-methylindole (403 mg, 3.07 mmol), norbornene (566 mg, 6.01 mmol), $PdCl_2(CH_3CN)_2$ (390 mg, 1.50 mmol), **L17** (434 mg, 1.50 mmol), and $Cu(OTf)_2$ (543 mg, 1.50 mmol) in DMF (15 mL) was stirred at 70 °C under Ar for 3 h. The reaction mixture was cooled to room temperature, washed with water, and extracted with CH_2Cl_2. The organic extracts were separated, washed with brine, dried over Na_2SO_4, and concentrated using a rotavap. The residue was filtered through a pad of silica gel using CH_2Cl_2 as eluent to afford the mixture of C2 and C3 insertion intermediate as a yellow solid. Pyridine hydrochloride (1.37 g, 11.8 mmol) was added to the solution of the above mixture in DCM (350 mL), and the mixture was stirred at room temperature for 1 h. Then PPh_3 (247 mg, 0.942 mmol) was added, and the resulting mixture was stirred at room temperature for 30 min. After evaporation of solvent, the residue was purified by flash column chromatography on silica gel using DCM and Et_2O (1:0 to 40:1) as eluent to afford C3-insertion intermediate-PPh_3 complex **4a** (148 mg, 16% yield) and trapped C2-insertion intermediate-PPh_3 complex **4b** (172 mg, 27% yield).

Characterization data for **4a**:

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.86-7.73 (m, 2H), 7.56 (dd, *J* = 11.3, 7.5 Hz, 3H), 7.47-7.22 (m, 6H), 4.04 (s, 3H), 3.60 (d, *J* = 7.2 Hz, 1H), 2.70 (d, *J* = 9.8 Hz, 1H), 2.19 (d, *J* = 4.0 Hz, 1H), 1.61 (s, 1H), 1.46-1.24 (m, 2H), 1.19-0.97 (m, 2H), 0.90-0.78 (m, 1H), 0.63-0.46 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): *δ* 140.3, 134.9 (d, *J* = 12.1 Hz), 132.2, 131.9, 131.4, 130.5, 130.3 (d, *J* = 2.6 Hz), 128.2 (d, *J* = 10.4 Hz), 123.8, 120.4, 119.5, 111.6, 46.7, 44.8, 42.0, 39.3, 34.0, 30.2 (d, *J* = 7.5 Hz), 29.1, 27.4 (d, *J* = 10.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): *δ* 34.07.

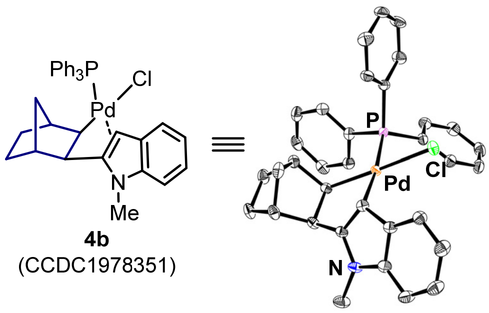
Characterization data for **4b**:

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.99 (d, *J* = 7.7 Hz, 1 H), 7.74 (ddt, *J* = 11.2, 6.6, 1.6 Hz, 6H), 7.48-7.35 (m, 10H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.28-7.22 (m, 2H), 3.74 (s, 3H), 2.98 (dd, *J* = 7.7, 3.1 Hz, 1H), 2.43 (d, *J* = 10.4 Hz, 1H), 2.15 (d, *J* = 3.9 Hz, 1H), 1.71 (t, *J* = 3.5 Hz, 1H), 1.44-1.31 (m, 1H), 1.22 (d, *J* = 10.4 Hz, 1H), 1.17 -0.97 (m, 2H), 0.83 (ddd, *J* = 16.8, 7.6, 1.9 Hz, 1H), 0.34 (ddt, *J* = 14.0, 10.5, 3.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 140.3 (d, *J* = 2.0 Hz), 135.3 (d, *J* = 11.6 Hz), 132.0 (d, *J* = 2.6 Hz), 131.6, 131.1, 130.5 (d, *J* = 2.6 Hz), 129.5 (d, *J* = 6.8 Hz), 128.3 (d, *J* = 10.5 Hz), 124.1, 123.7, 121.7, 110.1, 80.9 (d, *J* = 19.9 Hz), 45.1, 44.1(d, *J* = 1.9 Hz), 41.9(d, *J* = 2.2 Hz), 37.6, 31.2 (d, *J* = 7.4 Hz), 30.0 (d, *J* = 7.3 Hz), 19.5(d, *J* = 7.6 Hz).

^{31}P NMR (162 MHz, CDCl3): *δ* 35.50.

The structure of complex **4b** was determined by single crystal X-ray diffraction analysis. A single crystal of this complex suitable for XRD analysis was obtained by recrystallization from CH_2Cl_2-Et_2O.



Crystal data for **4b** (CCDC1978351)

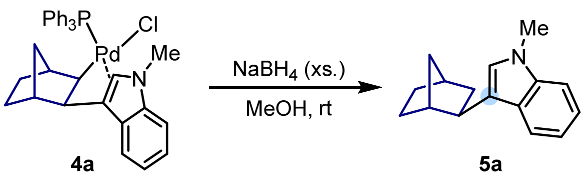
Empirical formula	$C_{36}H_{37}Cl_5NPPd$
Formula weight	798.28
Temperature/K	173.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.4499(4)
b/Å	11.5254(4)
c/Å	15.9550(5)

α/°	92.906(3)
β/°	104.074(3)
γ/°	111.149(3)
Volume/Å^3	1717.91(11)
Z	2
ρ_{calc}g/cm^3	1.543
μ/mm^{-1}	8.582
F(000)	812.0
Crystal size/mm^3	0.16 × 0.1 × 0.02
Radiation	Cu K$_\alpha$ (λ = 1.54184)
2Θ range for data collection/°	8.324 to 141.014
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 11, -19 ≤ l ≤ 18
Reflections collected	11582
Independent reflections	6368 [R_{int} = 0.0450, R_{sigma} = 0.0547]
Data/restraints/parameters	6368/0/398
Goodness-of-fit on F^2	1.080
Final R indexes [I>=2σ (I)]	R_1 = 0.0376, wR_2 = 0.1082
Final R indexes [all data]	R_1 = 0.0442, wR_2 = 0.1136
Largest diff. peak/hole / e Å^{-3}	0.94/-0.67

b. Reduction of the trapped insertion intermediates

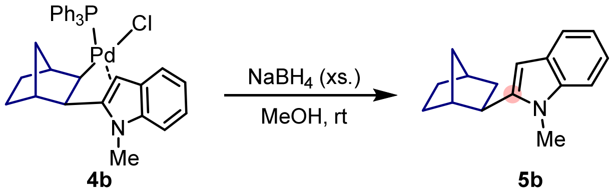
In order to further confirm the structure of the insertion intermediates and to obtain pure C2-insertion compound **5b**, the PPh_3 complexes **4a** and **4b** were reduced by treatment with $NaBH_4$.

Reduction of **4a** to **5a**:



To a solution of **4a** (39.9 mg, 0.0635 mmol) in MeOH (5.0 mL), $NaBH_4$ (30.1 mg, 0.796 mmol) was added and the resulting mixture was stirred at room temperature for 30 min. Then water (10 mL) was added to quench the excess reductant, and after stirred for 15 min, H_2O_2 (0.45 M, 0.2 mL, 0.09 mmol) was added to oxidize the released PPh_3. After stirred for another 30 min, the reaction mixture was washed with water and extracted with petroleum ether. The organic layer was separated, washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on silica gel using petroleum ether as eluent to afford product **5a** as white solid (11.5 mg, 85% yield).

Reduction of **4b** to **5b**:



Following the above experimental procedure, from complex **4b** (9.5 mg, 0.02 mmol), the C2-insertion product **5b** was obtained as white solid (2.6 mg, 77% yield).

4. DFT Computational Study

4.1 General Information

All calculations were performed using the Gaussian 09 program package.[9] The geometry optimizations were conducted using the B3LYP functional with 6-31G(d) basis set (the LANL2DZ pseudopotential was used for Pd atom). Frequency analysis was performed for each stationary points to confirm it as either a local minima or a saddle point. Single point energy calculations based on gas-phase optimized structures were conducted using the M06 functional with the 6-311+G(d,p) basis set (the SDD basis set was used for Pd atom), together with the application of the SMD continuum solvation model using DMF as the solvent. The solvent parameters for DMF solvent was taken from the Minnesota Solvent Descriptor Database.[10] Calculated Gibbs free energies in solution were used throughout the article for discussion.

4.2 $Pd(OAc)_2$-Catalyzed Oxidative Heck Reaction of *N*-methylindole

The potential energy surface of the oxidative Heck reaction of *N*-methylindole (**1a**) catalyzed by $Pd(OAc)_2$ without additional ligand was calculated (Figure S12). Two regiomeric pathways, the C3-alkenylation pathway (blue) and the C2-alkenylation pathway (red), were investigated and compared to figure out the origin of regioselectivity in this reaction. It was found that, the C-H palladation step is rate-limiting and irreversible in both pathways: $\Delta G^{\ddagger}$ for C3-palladation, calculated form $Pd_3(OAc)_6$ to **TS-S1a**, is 19.5 kcal/mol; and $\Delta G^{\ddagger}$ for C2-palladation, calculated form $Pd_3(OAc)_6$ to **TS-S1b**, is 24.4 kcal/mol. The following insertion step requires a much lower activation energy barrier: $\Delta G^{\ddagger}$ for C3-insertion, calculated from $Pd_3(OAc)_6$ to **TS-S2a**, is 16.0 kcal/mol; $\Delta G^{\ddagger}$ for C2-insertion, calculated from $Pd_3(OAc)_6$ to **TS-S2b**, is 15.2 kcal/mol. The final β-hydride elimination (BHE) step also has a low activation energy barrier: $\Delta G^{\ddagger}$ for BHE of the C3-insertion intermediate, calculated from **Int-2a** to **TS-S3a**, is 17.7 kcal/mol; $\Delta G^{\ddagger}$ for for BHE of the C2-insertion intermediate, calculated from **Int-2b** to **TS-S3b**, is 18.2 kcal/mol.

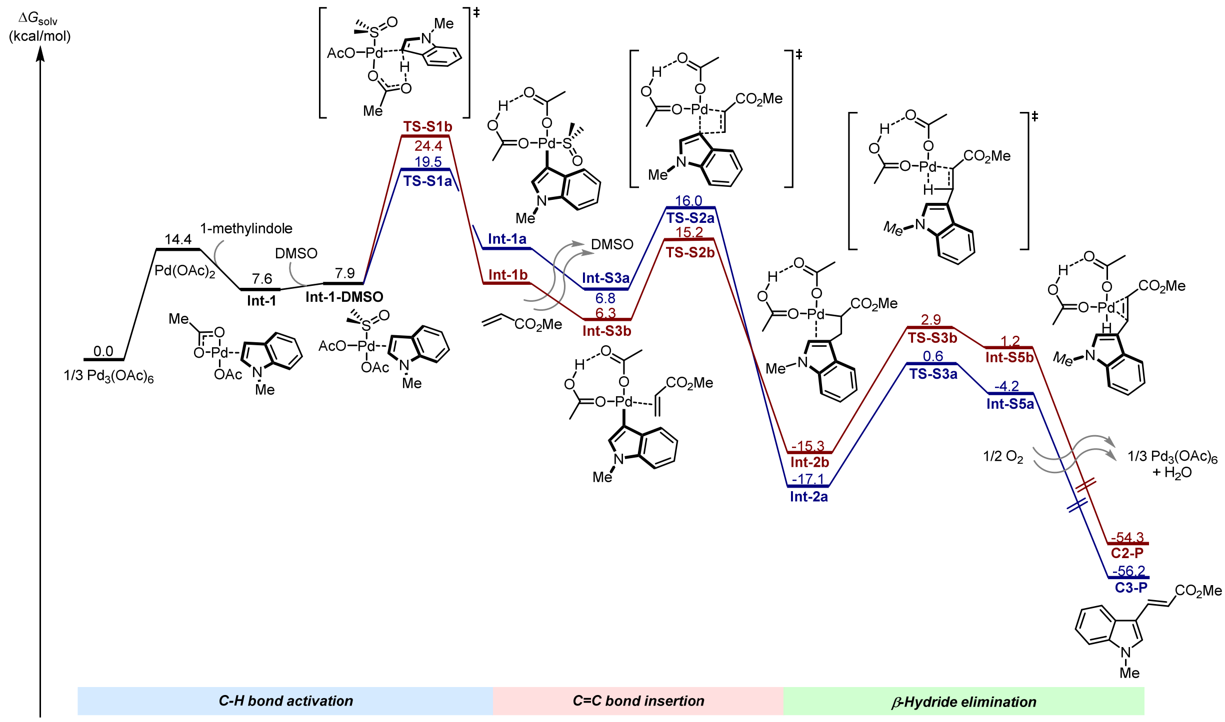
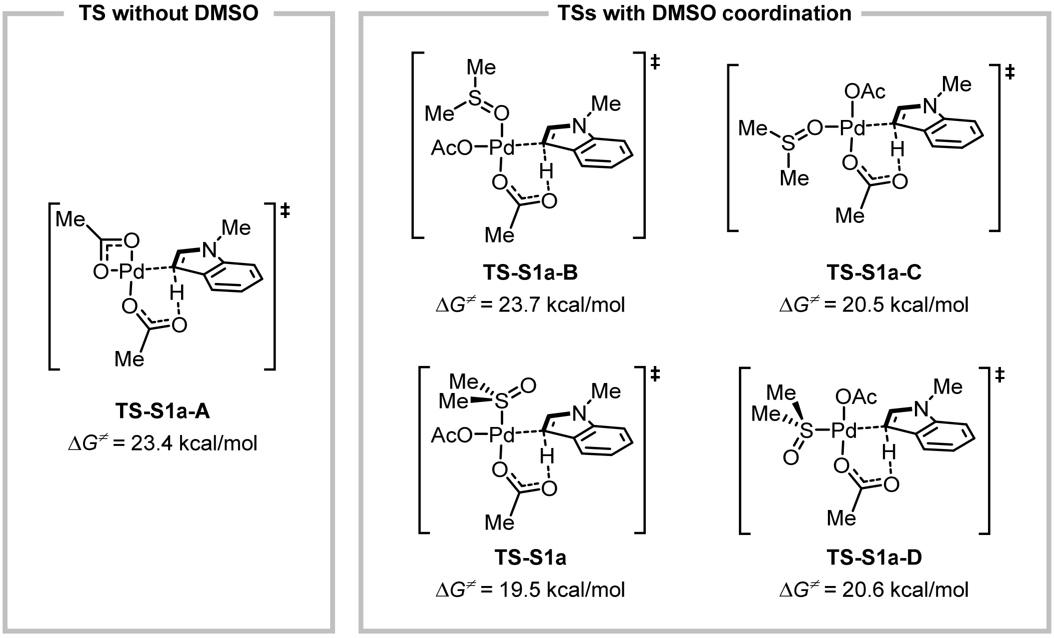


Figure S12. The potential energy surface of the C-H alkenylation reaction of *N*-methylindole (**1a**) catalyzed by Pd(OAc)2. Both C3- (blue) and C2-alkenylation (red) pathways are included. Only the intermediates and transition states in the C3-alkenylation pathway are shown for clarity.

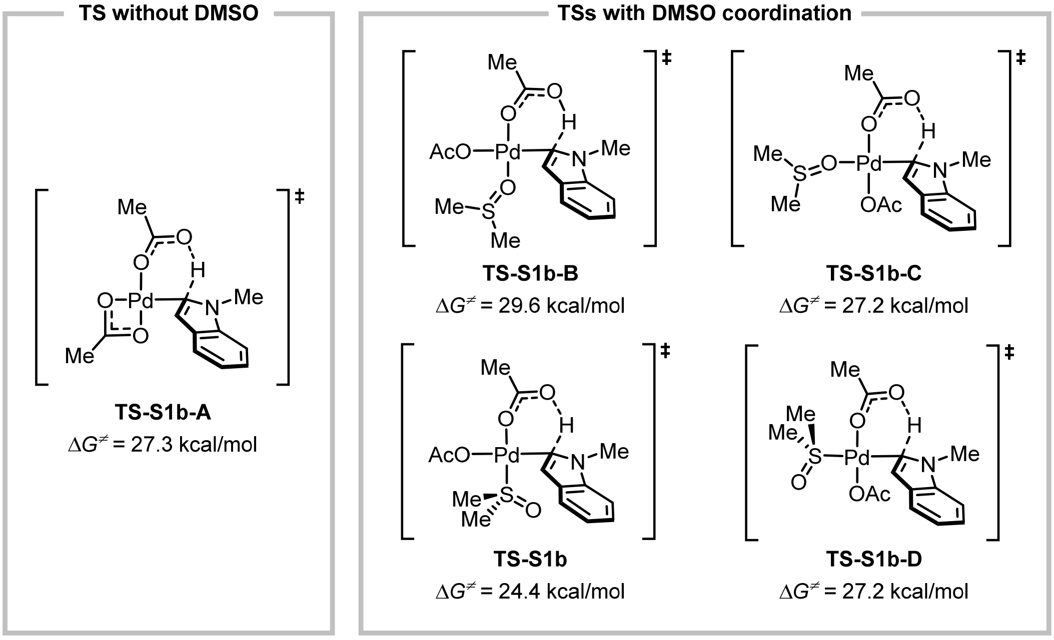
Given that the reaction was conducted in DMSO solvent and DMSO is a potential ligand, we have carefully assessed the energies of key TSs with different ligands to figure out the reasonable reaction pathways.

(a) For the C3-H activation step, five TSs with different ligands on Pd(**II**) center and different configurations were located:



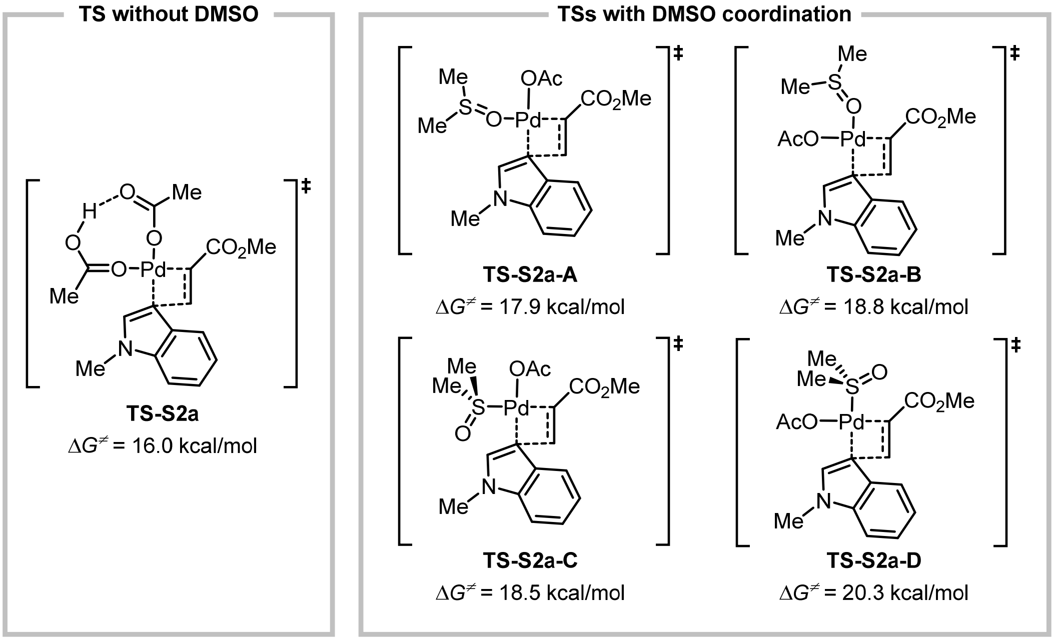
It was found that, the C3-H palladation transition state with a (DMSO-S) ligand (**TS-S1a**) was favored over other TSs. Therefore the potential energy surface for the C3-alkenylation pathway was constructed using **TS-S1a**.

(b) For the C2-H activation step, five TSs with different ligands on Pd(II) center and different configurations were located:



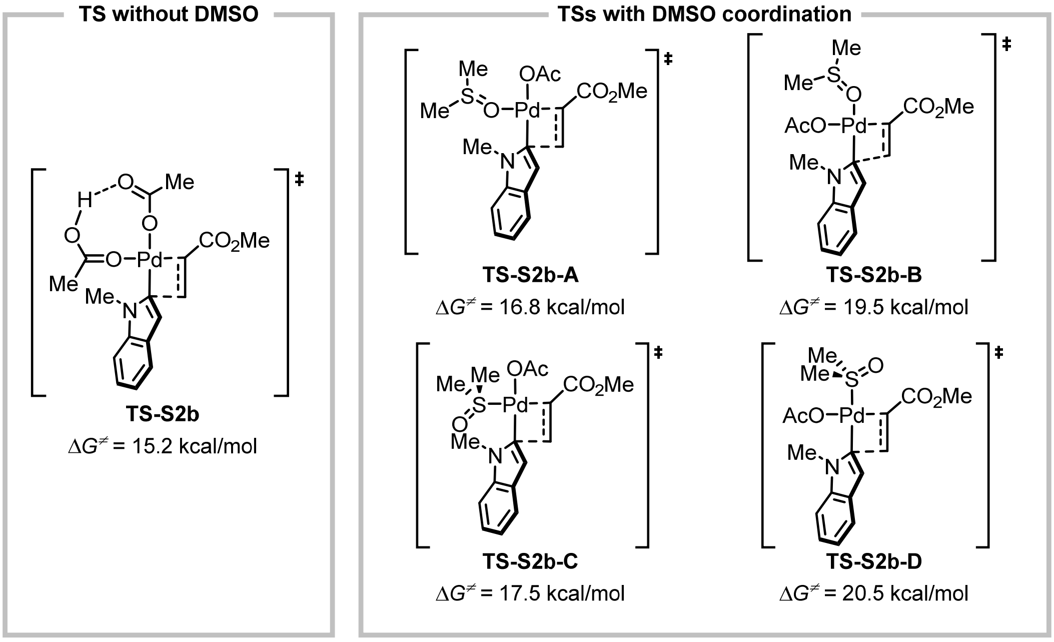
It was found that, the C2-H palladation transition state with a (DMSO-S) ligand (**TS-S1b**) was favored over other TSs. Therefore the potential energy surface for the C2-alkenylation pathway was constructed using **TS-S1b**.

(c) For the C3-insertion step, five TSs with different ligands on Pd(II) center and different configurations were located:



It was found that, the C3-insertion transition state without DMSO (**TS-S2a**) was favored over other TSs. Therefore the potential energy surface for the C3-insertion pathway was constructed using **TS-S2a**.

(d) For the C2-insertion step, five TSs with different ligands on Pd(II) center and different configurations were located:



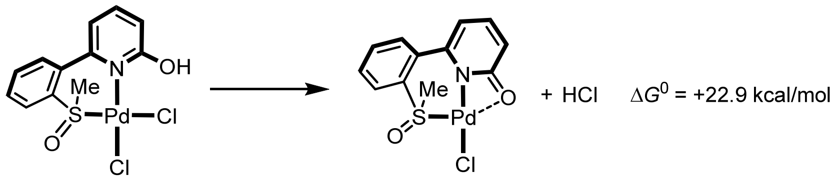
It was found that, the C2-insertion transition state without DMSO (**TS-S2b**) was favored over other TSs. Therefore the potential energy surface for the C2-insertion pathway was constructed using **TS-S2b**.

4.3 Pd(II)/SOHP-Catalyzed Oxidative Heck Reaction of *N*-methylindole

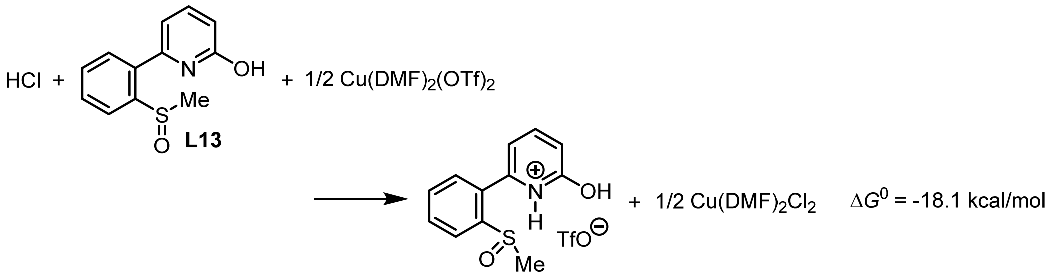
The potential energy surface of the oxidative Heck reaction of *N*-methylindole (**1a**) catalyzed by the Pd(II)/SOHP system was calculated. Two regiomeric pathways, the C3-alkenylation pathway (blue) and the C2-alkenylation pathway (red), were investigated, and the details are shown in Figure 2 of the main text. Here we present the computational details of the acid-base reaction.

(1) Consideration on the acid-base reaction of the Pd-complex for HCl elimination

It was found that, there are two acid-base reaction steps before the key insertion step. The first one is $PdCl_2$•**L13** to **Int-3**, and the other is **Int-5** to **Int-6**. Apparently, both steps involve the elimination of one molecule of HCl. Take the former for example, the step was found to be rather endogonic when a free HCl molecule is released:



Only when an appropriate acceptor of HCl, e.g. a base, was present, the overall Gibbs free energy change could be reduced. One of the possible HCl trapping processes is that, the free ligand acts as a base to trap a proton, and $Cu(OTf)_2$ serves as a Lewis acid to trap a chloride anion, achieving a largely exergonic HCl trapping reaction:



Given that the concentration of the free SOHP ligand **L13** is low in the actual reaction system (i.e., 20 mM), the Gibbs free energy change of the above reaction could be calibrated:

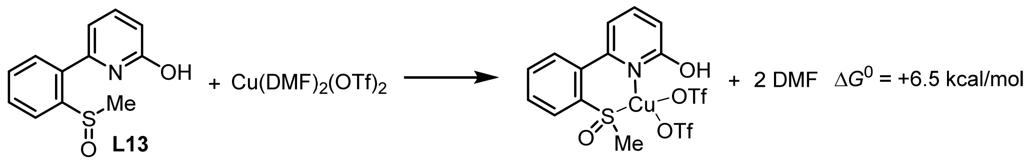
$$\Delta G(343\text{ K}) = \Delta G^0 - RT\ln(c/c^0) = (-18.1 + 2.7)\text{ kcal/mol} = -15.4\text{ kcal/mol}$$

By combining this HCl trapping reaction (ΔG = -15.4 kcal/mol) with the aforementioned HCl releasing processes, the overall Gibbs free energies are made reasonable. This indicated that the acid-base interaction has a significant impact on the potential energy surfaces. Although this correction method may introduce addition error into the overall Gibbs free energy of the reaction due to the complexity of the catalytic system, it gives a reasonable way to estimate the effect of HCl trapping on reactivity.

It is notable that, there are also other possible acid-base reactions that might be involved in the HCl trapping process. For example, the reaction between HCl and the basic oxide species generated from oxygen reduction (in the reoxidation process for Pd^0) is a possible pathway, however, it is difficult to be modeled in DFT calculation. Therefore, we employed the above ligand-trapping process in the calculation to build the potential energy surface in the present study.

(2) Consideration on the association of the SOHP ligand with $Cu(OTf)_2$

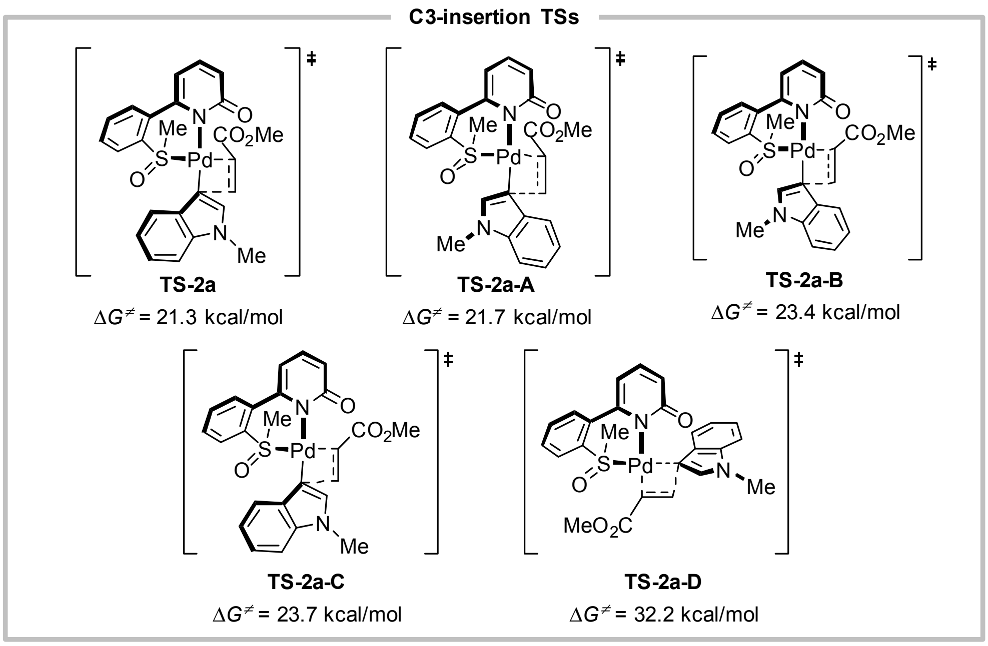
We calculated the thermodynamic parameter of the following reaction to evaluate the preference of the SOHP ligand to associate with the Cu(II) salt. It was found that, complexation of **L13** with $Cu(DMF)_2(OTf)_2$ in DMF solvent is an endergonic reaction with a Gibbs free energy change of +6.5 kcal/mol.



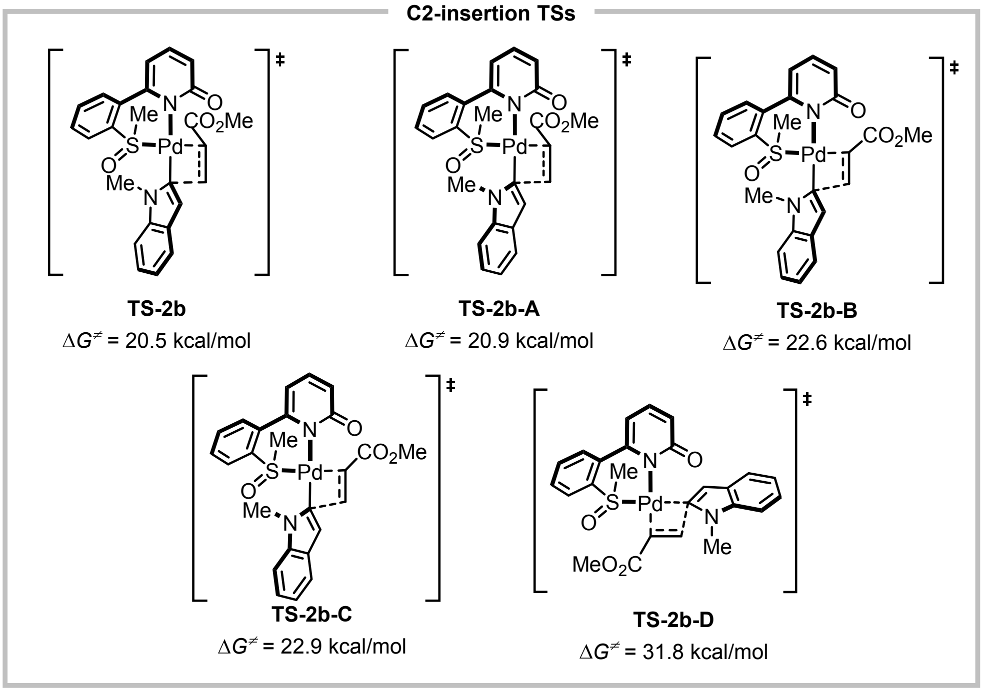
This indicated that the association of the SOHP ligand with Cu(II) is not favorable, and excess ligand may exist in the free form in the catalytic system.

(3) Consideration on the C=C insertion Transition States

In both C3- and C2-insertion pathways, four different insertion TSs with different conformations of the indole and acrylate moieties were located. For C3-insertion TSs, it was found that **TS-2a** was favored over other TSs:



For C2-insertion TSs, it was found that **TS-2b** was favored over other TSs:



Therefore, the potential energy surfaces for both pathways were constructed using the favorable TSs **TS-2a** and **TS-2b**.

4.4 Coordinates and Energies of Stationary Points

$Pd_3(OAc)_6$

G_{sol} = -584.737589 Hatree

Pd	-1.61291300	0.93068100	0.00105500
O	1.04964700	2.42951900	-1.28431100
O	-2.36933900	-0.01667300	1.64473000
C	-0.05112500	2.61227000	-1.88157600
O	-1.16010600	2.04213100	-1.65185600
C	-2.29378100	-1.25970700	1.88220500
O	-1.56821100	-2.11746600	1.29839200
C	-0.05489500	3.65795500	-2.98002000
H	-0.32412900	4.62528700	-2.53991500
H	0.93679800	3.74304100	-3.42800300
H	-0.80256400	3.40794700	-3.73561000
C	-3.20478300	-1.78784000	2.97371600
H	-4.12259800	-2.16592600	2.50830000
H	-2.72328500	-2.61380900	3.50125100
H	-3.47236500	-0.98739000	3.66586300
Pd	-0.00093900	-1.85444900	-0.00006500
O	-1.04724700	2.43052200	1.28454600
O	-1.21501300	-2.02734200	-1.63466400
C	0.05381000	2.61201000	1.88165900
O	1.16212000	2.04054300	1.65196500
C	-2.26293600	-1.35118200	-1.86246400
O	-2.65139200	-0.30215200	-1.26917900
C	0.05939000	3.65757100	2.98024800
H	0.79435600	3.39609100	3.74449300
H	0.34914500	4.62070500	2.54407200
H	-0.93598700	3.75701400	3.41680700
C	-3.17424000	-1.88019400	-2.95333500
H	-3.93182400	-2.52529000	-2.49311200
H	-3.68362800	-1.05458700	-3.45436000
H	-2.60300200	-2.47569300	-3.66803300
Pd	1.61366500	0.92874300	-0.00111600
O	2.65121000	-0.30490300	1.26912600
O	2.36913200	-0.01902200	-1.64492100
C	2.29249400	-1.26202200	-1.88230400
O	1.56628000	-2.11915800	-1.29837500
C	2.26158900	-1.35348900	1.86249400
O	1.21282900	-2.02836500	1.63481300
C	3.17221400	-1.88337200	2.95349500
H	3.68280200	-1.05831000	3.45416400
H	2.60024900	-2.47782700	3.66845200
H	3.92893200	-2.52963100	2.49347400
C	3.20296900	-1.79100500	-2.97383500
H	4.11955700	-2.17190100	-2.50831700
H	2.71985300	-2.61523400	-3.50263700
H	3.47279100	-0.99039000	-3.66490800

$Pd(OAc)_2$

G_{sol} = -584.714576 Hatree

Pd	-0.00007900	-0.00024300	-0.00938200
O	1.77065800	1.08814500	-0.01010400
O	1.77125300	-1.08831600	-0.00990200
O	-1.77053100	1.08828700	-0.00955300
O	-1.77109500	-1.08854900	-0.00967700
C	2.44311700	0.00006900	-0.00468500
C	-2.44303900	0.00000900	-0.00470100
C	-3.93895600	0.00074400	0.03573700
H	-4.32691200	0.90013200	-0.44820900
H	-4.32800600	-0.89824400	-0.44809100
H	-4.26899100	0.00098200	1.08142800
C	3.93905800	0.00070200	0.03610000
H	4.26914100	0.00089300	1.08168200
H	4.32793700	-0.89825000	-0.44799400
H	4.32710000	0.89996400	-0.44808200

***N*-methylindole**

G_{sol} = -402.798109 Hatree

C	0.38932000	0.98576900	-0.00000500
C	-0.15177100	-0.33247500	-0.00000300
C	0.65972700	-1.47337700	0.00009200
C	2.03748500	-1.28175500	0.00018500
C	2.59495000	0.01365400	0.00018300
C	1.78611600	1.14357200	0.00008900
C	-0.72646000	1.88952300	-0.00009800
C	-1.86075400	1.12125100	-0.00023600
H	0.23486300	-2.47341600	0.00009900
H	2.69562400	-2.14649900	0.00026400
H	3.67581300	0.12664400	0.00025900
H	2.22624200	2.13771900	0.00009400
H	-0.69049100	2.97030600	-0.00011300
H	-2.90145200	1.41722400	-0.00036400
C	-2.46035800	-1.33306100	-0.00008600
H	-2.32818700	-1.96021600	-0.89032700

H	-2.32840200	-1.96002900	0.89031900
H	-3.48083400	-0.94322800	-0.00025200
N	-1.53038700	-0.22387300	-0.00010100

Methyl acrylate

G_{sol} = -306.302402 Hatree

C	-2.49179600	-0.01261200	0.00016800
H	-2.52944700	1.07311300	0.00037400
H	-3.43325600	-0.55357900	0.00020200
C	-1.31713500	-0.64677800	-0.00012500
H	-1.24024500	-1.73000300	-0.00033000
C	-0.04332300	0.11701000	-0.00014200
O	0.06058100	1.32755600	-0.00010600
O	1.01717700	-0.72513200	0.00000000
C	2.30287300	-0.08830200	0.00012300
H	2.42225700	0.53715900	0.88919300
H	3.03235500	-0.89887600	0.00036600
H	2.42255800	0.53688600	-0.88910000

***N*,*N*-dimethylformamide (DMF)**

G_{sol} = -248.347797 Hatree

C	-0.86309800	-0.65101100	-0.00014900
H	-0.75143400	-1.75341500	-0.00037400
O	-1.95218800	-0.10158200	0.00023300
C	0.41240500	1.43214300	0.00002100
H	0.94074300	1.79824200	-0.89012800
H	-0.60972600	1.81248000	-0.00042300
H	0.93980600	1.79774500	0.89095700
C	1.59652700	-0.75509700	0.00020300
H	2.19668900	-0.51752500	-0.88869700
H	2.19548800	-0.51763900	0.88995600
H	1.38954000	-1.82931000	-0.00004900
N	0.34877100	-0.01916200	-0.00050800

O_2

G_{sol} = -150.314578 Hatree

O	0.00000000	0.00000000	0.60710800
O	0.00000000	0.00000000	-0.60710800

H_2O

G_{sol} = -76.419791 Hatree

O	0.00000000	0.00000000	0.11942600
H	0.00000000	0.76261700	-0.47770500
H	0.00000000	-0.76261700	-0.47770500

HCl

G_{sol} = -460.806391 Hatree

Cl	0.00000000	0.00000000	0.07163400
H	0.00000000	0.00000000	-1.21777200

Int-1

G_{sol} = -987.523515 Hatree

Pd	-0.85687800	0.37164600	-0.29573700
C	1.71075600	-1.20410600	-0.70930300
C	2.30157200	-0.86432600	0.53015300
C	3.64002500	-0.48700000	0.63846700
C	4.39699300	-0.48438100	-0.53231800
C	3.83386900	-0.84136400	-1.77056400
C	2.49164900	-1.19875700	-1.87043500
C	0.31080100	-1.49814000	-0.44102700
C	0.15353200	-1.38261600	0.96635700
H	4.08137900	-0.20807000	1.59012400
H	5.44481400	-0.20165500	-0.48520600
H	4.45572800	-0.83210800	-2.66093000
H	2.05506400	-1.46138100	-2.82993000
H	-0.34386400	-2.07863400	-1.07811600
H	-0.72516200	-1.62390500	1.55391000
C	1.48744700	-0.54487300	2.90199900
H	2.39986900	-0.96664200	3.33394700
H	1.53772400	0.54892000	2.93781600
H	0.62995000	-0.88377100	3.48619000
N	1.33085000	-0.99937500	1.53043900
C	-0.31395200	2.78727700	0.02297600
C	0.10837800	4.22135300	0.18328200
H	0.93570900	4.29865800	0.89296400
H	0.45013900	4.60375400	-0.78588800
H	-0.73872600	4.82857600	0.51097800
O	-1.49655400	2.47877400	-0.31040600
O	0.54391200	1.84326900	0.19664700
C	-3.17669900	-1.30684200	0.03416300
C	-4.51011400	-1.80289300	-0.51313800
H	-5.18369900	-0.94850500	-0.64525000
H	-4.37945900	-2.27139400	-1.49288100
H	-4.95838000	-2.50786300	0.18974400
O	-2.46863500	-0.68155500	-0.87714200

O	-2.84949900	-1.48499800	1.20711500

Int-1-DMSO

G_{sol} = -1540.604154 Hatree

Pd	0.79126700	0.14635400	-0.05233100
O	1.58786300	2.68283700	-1.45840800
O	1.95881800	1.70518500	0.54210300
O	2.55405000	-1.72337200	1.42999800
O	2.54688100	-0.79684900	-0.62699400
C	2.18063100	2.60848100	-0.38290400
C	3.11588000	-1.41536300	0.37658200
C	4.58432700	-1.74085000	0.12563200
H	4.93080500	-2.48577500	0.84510700
H	4.74209200	-2.09495000	-0.89745600
H	5.17395500	-0.82509800	0.24873000
C	3.27940700	3.59149000	0.00620100
H	3.17443100	3.90622800	1.04860400
H	4.25202200	3.09567500	-0.09099600
H	3.25235200	4.45808200	-0.65754000
C	-2.83347600	0.46474800	0.81751200
C	-2.26632900	1.21255500	-0.24135200
C	-3.00791100	1.42753400	-1.41254300
C	-4.28281600	0.87606200	-1.50426700
C	-4.81987400	0.11464800	-0.44727200
C	-4.10519100	-0.10591400	0.72646300
C	-0.80853900	1.14718400	1.51088600
C	-0.94821000	1.63401400	0.19335400
H	-2.59191500	2.01624900	-2.22578500
H	-4.87573000	1.03518200	-2.40045300
H	-5.81483600	-0.30932100	-0.54955100
H	-4.52163100	-0.70272900	1.53129600
H	-0.02767900	1.35968700	2.22834200
H	-0.37644100	2.43458300	-0.25698000
N	-1.92128100	0.44633800	1.87317400
C	-2.03532400	-0.40023700	3.05124600
H	-2.99540400	-0.22454800	3.54611100
H	-1.95241700	-1.45211700	2.76166400
H	-1.22985200	-0.15050800	3.74455800
S	-0.42155100	-1.80843300	-0.58451000
O	-1.57617900	-2.22661200	0.28055100
C	-0.98558500	-1.66271300	-2.30719700
H	-1.74664000	-0.87977500	-2.32868800
H	-0.13188800	-1.38012800	-2.92926700
H	-1.41345000	-2.61869400	-2.62205600
C	0.70578200	-3.22036500	-0.74543100
H	1.46613500	-2.98012700	-1.48985900
H	1.17112800	-3.35451600	0.23205800
H	0.10236500	-4.08625500	-1.03014900

TS-S1a

G_{sol} = -1540.585637 Hatree

Pd	1.04303900	0.21932700	0.14702000
C	-2.95002200	0.23356900	-1.10143600
C	-3.12047700	0.21476500	0.32065400
C	-4.35747100	-0.11623000	0.90753000
C	-5.40413500	-0.42988500	0.05839400
C	-5.25466300	-0.41474500	-1.35356800
C	-4.04683200	-0.08548600	-1.93643500
C	-1.60836300	0.61581600	-1.33314100
C	-0.97722700	0.84333600	-0.09451900
H	-4.48372000	-0.14057600	1.98521100
H	-6.36805300	-0.69906200	0.48187700
H	-6.10766600	-0.66597400	-1.97745700
H	-3.93427100	-0.06994700	-3.01735900
H	-1.13268000	0.75779600	-2.29598900
H	-0.51605300	2.08539500	0.02725600
C	-1.70757600	0.68334200	2.32989700
H	-2.54520900	1.19656100	2.81350500
H	-1.57601600	-0.31127200	2.76663500
H	-0.80003200	1.26915700	2.49018100
N	-1.94229900	0.58033700	0.90062000
C	3.58093100	-0.94499600	-0.61266700
C	5.10535200	-0.91928500	-0.59129900
H	5.44937500	0.09060000	-0.84180800
H	5.48180200	-1.15057700	0.40994700
H	5.50593800	-1.62674600	-1.32025200
O	2.96221500	-1.53338400	-1.51135400
O	3.03699700	-0.31477100	0.38500500
C	1.19735700	3.20142200	-0.03167700
C	1.96689200	4.50197400	-0.13160900
H	1.67713300	5.16224000	0.69093200
H	3.04143300	4.31711400	-0.11169700
H	1.69711000	5.00369000	-1.06735700
O	1.85187600	2.12282300	-0.13193500
O	-0.06263100	3.27874900	0.13203500
S	0.30325400	-1.97887000	0.46326100

O	-0.86740300	-2.23721600	1.36643800
C	1.67392700	-3.03922800	1.01217500
H	2.41397500	-3.09063600	0.21353600
H	2.10067000	-2.59162700	1.91032100
H	1.23417400	-4.01560300	1.23350900
C	-0.01520800	-2.69393000	-1.17397800
H	-0.88867300	-2.17620000	-1.57372900
H	0.87540500	-2.50557500	-1.77827000
H	-0.22373800	-3.76047000	-1.04984200

Int-1a

G_{sol} = -1540.603527 Hatree

Pd	0.72717200	0.08528000	-0.01479600
C	-2.34137700	0.22770500	-0.43766200
C	-3.52082300	0.15735600	0.36401500
C	-4.80107100	0.33801800	-0.17516300
C	-4.89745800	0.59119500	-1.53948900
C	-3.74648100	0.66663800	-2.35145900
C	-2.47746700	0.48911200	-1.81303200
C	-1.21885900	-0.01119500	0.43553600
C	-1.74579800	-0.20653300	1.68925700
H	-5.69069200	0.28503400	0.44685000
H	-5.87723000	0.73653600	-1.98662900
H	-3.85749200	0.87121000	-3.41300200
H	-1.59334000	0.55874200	-2.44294600
H	2.81569800	1.81560800	-0.51722200
H	-1.24791300	-0.38529000	2.63378900
C	-4.02301400	-0.21214600	2.80022700
H	-4.54983900	0.73313500	2.98219000
H	-4.76920200	-1.00230000	2.65017400
H	-3.43554800	-0.45673200	3.68829700
N	-3.13583100	-0.10967600	1.66173000
C	3.65440300	-0.34685100	0.30452700
C	5.12342300	-0.08106400	0.01632200
H	5.75216900	-0.61735200	0.72912800
H	5.35871100	-0.41076700	-1.00157300
H	5.33769400	0.99243600	0.06816700
O	2.82263800	0.32628200	-0.46380000
O	3.29388800	-1.13908400	1.17214000
C	1.45702900	3.07117200	0.04891200
C	1.14480500	4.53012200	0.25984400
H	1.88970800	4.97195800	0.92960500
H	1.21276100	5.05767100	-0.69739900
H	0.14525600	4.64537200	0.67903100
O	0.61196600	2.20311800	0.33713200
O	2.64153600	2.83693500	-0.44434400
S	0.76462200	-2.18315400	-0.46739500
O	1.85125300	-2.66499400	-1.37198900
C	-0.81169300	-2.81143000	-1.12378900
H	-1.61700000	-2.58553000	-0.42450000
H	-0.99369700	-2.30722000	-2.07394700
H	-0.68691400	-3.88641800	-1.28030400
C	0.82934800	-3.07686100	1.11111000
H	1.76582100	-2.76592400	1.57568900
H	-0.03066000	-2.77451600	1.71407900
H	0.81858600	-4.14980300	0.89927700

Int-S3a

G_{sol} = -1293.827301 Hatree

Pd	-0.50311600	0.27663100	-0.38360900
C	2.45857600	-0.54608800	0.19486500
C	3.74626000	-0.06728200	-0.19562300
C	4.92670400	-0.55231100	0.38078500
C	4.81153400	-1.54030900	1.35296900
C	3.55068900	-2.03768000	1.74169800
C	2.37788900	-1.55232300	1.17484200
C	1.49782500	0.18416100	-0.59061700
C	2.20601300	1.02427100	-1.41129600
H	5.90018300	-0.17274200	0.08186700
H	5.71003300	-1.93708200	1.81821300
H	3.49706200	-2.81649300	2.49772400
H	1.41181700	-1.95385300	1.46564200
H	-2.34278500	1.66663700	1.16930500
H	1.85855300	1.73822900	-2.14594600
C	4.62537300	1.64282700	-1.81658200
H	5.13751200	2.29785800	-1.10006000
H	5.36783800	0.97459300	-2.26921100
H	4.19292800	2.26229900	-2.60569800
N	3.57008000	0.88457300	-1.18022700
C	-3.50648600	0.83835100	-0.81287000
C	-4.80256400	1.43265300	-0.27609700
H	-5.50504300	1.59807800	-1.09454200
H	-5.24723400	0.75084700	0.45741900
H	-4.60564000	2.37981400	0.23898700
O	-2.58049100	0.65885600	0.11375800
O	-3.36829700	0.54103300	-1.99349300

C	-0.77188700	2.73743200	1.48182000
C	-0.20423100	3.90423500	2.24755500
H	-0.85593700	4.77586500	2.13135700
H	-0.17796000	3.65504000	3.31394900
H	0.80242000	4.13239200	1.89725900
O	-0.07748900	2.14686400	0.63336300
O	-1.99992800	2.42691900	1.79425300
C	-1.32279600	-1.63791900	-1.20148000
H	-2.18325100	-1.24770300	-1.73682200
C	-0.05485000	-1.53902900	-1.73136400
H	0.10010600	-1.09212100	-2.70718600
H	0.76311300	-2.10659100	-1.30433100
C	-1.58810900	-2.52462800	-0.02430500
O	-0.74265800	-3.03149300	0.68634000
O	-2.91084200	-2.71595700	0.12541400
C	-3.29096400	-3.55765900	1.22634500
H	-4.37864800	-3.61536900	1.18646100
H	-2.84657100	-4.55083000	1.12057500
H	-2.96194100	-3.11788300	2.17168800

TS-S2a

G_{sol} = -1293.812575 Hatree

C	-3.53167900	-0.61604400	0.35553100
C	-2.55543500	-0.26487500	-0.62077200
C	-2.98525100	0.29742900	-1.83365600
C	-4.34579100	0.49010000	-2.04689200
C	-5.29391000	0.13840400	-1.06510500
C	-4.90089000	-0.41567500	0.14949700
C	-1.51385200	-1.14430600	1.18443000
C	-1.26694000	-0.59977200	-0.06096200
N	-2.86790200	-1.15076300	1.44956900
Pd	0.53283600	0.18545200	-0.61086900
O	3.02027800	1.17314900	0.93024700
O	-0.25959100	2.12647700	-0.05839800
C	0.02112300	2.74274500	0.98404300
O	1.02304300	2.48670200	1.77663700
C	3.26404100	1.18708300	-0.30601500
O	2.40154600	0.99577000	-1.22764500
C	4.69155300	1.41991700	-0.77500900
C	-0.82877500	3.90884700	1.42608700
H	1.72952100	1.82582200	1.38928700
H	-0.81352500	-1.56625700	1.89286200
H	-5.63416900	-0.68123700	0.90605200
H	-6.35024500	0.30433100	-1.25812300
H	-4.68647000	0.92504000	-2.98254800
H	-2.25959600	0.58619300	-2.58974800
H	-1.08907300	3.79591200	2.48292900
H	-0.25129500	4.83484800	1.32930900
H	-1.73067100	3.97170800	0.81684500
H	5.30608000	1.81501300	0.03622300
H	5.11137100	0.46563900	-1.11385800
H	4.70282400	2.10377100	-1.62863800
C	1.31298600	-1.72653100	-1.15394600
H	1.87883500	-1.42840500	-2.03199900
C	-0.04548500	-2.07208000	-1.24505800
H	-0.44770900	-2.78888800	-0.54480600
H	-0.57541400	-1.95873300	-2.18392000
C	2.08226400	-2.21378900	0.02757600
O	1.58157200	-2.70477200	1.02404500
O	3.40522500	-2.03155000	-0.14209000
C	4.22200900	-2.30391100	1.01068200
H	3.99715400	-3.29144400	1.41930900
H	5.25187600	-2.25643000	0.65583100
H	4.04442800	-1.53679600	1.76903800
C	-3.49731100	-1.61658600	2.66896400
H	-4.24169900	-2.39082700	2.44959300
H	-2.73297100	-2.04276100	3.32208900
H	-3.99292600	-0.79390400	3.19855700

Int-2a

G_{sol} = -1293.865328 Hatree

C	-3.04792700	-0.41052500	0.53789500
C	-2.46100100	-1.27465000	-0.42116100
C	-3.19015600	-1.63073300	-1.56362900
C	-4.46899100	-1.10985600	-1.73235600
C	-5.02699300	-0.23682000	-0.77902900
C	-4.32651800	0.12808700	0.36754300
C	-1.00269900	-0.94559200	1.30333700
C	-1.13689600	-1.61646400	0.07104400
N	-2.15099100	-0.24729100	1.58659900
Pd	0.40023700	-0.03026000	-0.44869400
O	2.81953500	1.78724300	0.32456300
O	-0.70986400	1.88972500	-0.26755800
C	-0.36389500	2.98318300	0.20596600
O	0.80721300	3.26687900	0.70138900
C	2.95774700	1.31924600	-0.83434500

O	2.04248600	0.73514900	-1.51088300
C	4.31131500	1.41340100	-1.51946500
C	-1.33218800	4.14344100	0.23539800
H	1.53258300	2.52834700	0.57063700
H	-0.23409700	-1.09079700	2.05135900
H	-4.76365300	0.80038300	1.09967800
H	-6.02621900	0.15845700	-0.93919900
H	-5.04626900	-1.37594700	-2.61305800
H	-2.76240400	-2.29691600	-2.30786300
H	-1.29631900	4.64476500	1.20695400
H	-1.02930400	4.87673600	-0.52077800
H	-2.34316900	3.79888000	0.01400300
H	4.95553700	2.12932600	-1.00554700
H	4.78041100	0.42300000	-1.49938500
H	4.18772900	1.69573000	-2.56894800
C	1.16177400	-1.92842000	-0.59518700
H	1.64755400	-1.98297700	-1.56846200
C	-0.16480500	-2.67420400	-0.43740900
H	-0.09935700	-3.52419700	0.25225900
H	-0.50782100	-3.04479000	-1.40744000
C	2.10240200	-2.06771200	0.54735000
O	1.78038700	-2.37215600	1.68803500
O	3.38077200	-1.79896000	0.19421500
C	4.32567400	-1.77312500	1.27501000
H	4.30163900	-2.71140500	1.83487100
H	5.30043000	-1.62907500	0.80747500
H	4.10286700	-0.94193100	1.94997400
C	-2.32415600	0.66583200	2.69933300
H	-3.28279800	0.48091900	3.19485900
H	-1.52052300	0.50253400	3.42025400
H	-2.29114700	1.70837300	2.36223100

TS-S3a

G_{sol} = -1293.837113 Hatree

C	4.42002900	-0.02936600	0.48663200
C	3.45504100	-0.06038100	-0.55336800
C	3.83460900	0.33759800	-1.84510900
C	5.14564200	0.74508600	-2.06365900
C	6.08947900	0.76230600	-1.01710000
C	5.74161200	0.37493200	0.27284800
C	2.49087000	-0.75128900	1.37264400
C	2.22205100	-0.53472200	0.03332200
N	3.79835100	-0.45500600	1.65337100
Pd	-0.91176400	0.42718800	0.16930500
O	-3.93559900	-0.14951700	-0.08237900
O	-1.53276200	2.49787800	0.25176600
C	-2.56382600	2.95770600	-0.27012600
O	-3.55421800	2.26393500	-0.75165800
C	-3.52925000	-0.51081200	1.05444800
O	-2.38502400	-0.23654800	1.54806900
C	-4.43752300	-1.36666400	1.92391300
C	-2.75098500	4.45116600	-0.38573400
H	-3.54172800	1.24516600	-0.52491200
H	1.82975600	-1.08346900	2.16173800
H	6.47038800	0.38936700	1.07800800
H	7.10672100	1.08427400	-1.22080300
H	5.45070000	1.05623200	-3.05870300
H	3.11891500	0.32904200	-2.66291700
H	-2.98021100	4.71324100	-1.42345300
H	-3.60698600	4.75873000	0.22443400
H	-1.85289000	4.97290300	-0.05427000
H	-5.47084600	-1.31252900	1.57570900
H	-4.09589400	-2.40713200	1.87025600
H	-4.36969200	-1.05258000	2.96927500
C	-0.14378600	-1.48913300	-0.15609400
H	-0.07878900	-1.98059700	0.81071300
C	0.96680900	-0.74902200	-0.67254500
H	0.29943100	0.78005500	-0.83001100
H	1.02163200	-0.72895200	-1.75966500
C	-1.07827500	-2.09876100	-1.14713000
O	-1.04802100	-1.89798300	-2.34705800
O	-1.97388800	-2.90135900	-0.53604700
C	-3.03593200	-3.38875300	-1.37591200
H	-2.63441200	-3.82968700	-2.29082400
H	-3.55748000	-4.13922100	-0.78073600
H	-3.70772000	-2.56236600	-1.62295600
C	4.43858600	-0.56874900	2.95045600
H	5.24802300	-1.30710900	2.92276000
H	4.85133700	0.39712000	3.26159400
H	3.69765300	-0.88617900	3.68669600

Int-S5a

G_{sol} = -1293.844734 Hatree

C	3.86561300	-0.24775400	-0.08904500
C	2.93479400	0.61701300	0.53909500
C	3.27611100	1.20664900	1.76565900

C	4.51792500	0.92315500	2.32364300
C	5.42938100	0.06294800	1.67981600
C	5.11732600	-0.53561300	0.46312000
C	2.05099000	-0.13987000	-1.40624600
C	1.77116000	0.68270800	-0.32366000
N	3.29229100	-0.69705200	-1.27450900
Pd	-1.18130600	0.05879400	0.26624200
O	-2.09030300	-3.11907300	-0.77827100
O	-2.70342900	-0.38501600	3.07886800
C	-2.71842800	-1.39588600	2.39954000
O	-2.15103400	-1.51060100	1.20453300
C	-1.41901100	-2.47843800	-1.70402500
O	-0.92908100	-1.34871400	-1.56961100
C	-1.28570900	-3.25200900	-2.99337600
C	-3.39917000	-2.68133800	2.85497900
H	-2.16684400	-2.55732700	0.07805800
H	1.42146500	-0.39824700	-2.24566500
H	5.82047900	-1.19895100	-0.03208700
H	6.39198400	-0.13780900	2.14140600
H	4.79183100	1.37152900	3.27434600
H	2.58348800	1.87051000	2.27562800
H	-4.16744800	-2.97925400	2.13270300
H	-2.66769500	-3.49528000	2.90921300
H	-3.85553100	-2.53339600	3.83483400
H	-0.79744200	-4.21275800	-2.79989000
H	-2.28137800	-3.46973700	-3.39371900
H	-0.71228900	-2.67880900	-3.72267100
C	-0.48234000	1.71701800	-0.94572300
H	-0.49908900	1.31196000	-1.95387700
C	0.58921000	1.47351400	-0.07788400
H	-1.49629400	0.93784800	1.46964300
H	0.62212300	2.10972700	0.80336900
C	-1.35686100	2.89942800	-0.70721300
O	-1.25791800	3.68504700	0.21351800
O	-2.28462300	3.00450400	-1.68728400
C	-3.19586800	4.10460200	-1.54657700
H	-2.65528400	5.05517300	-1.54440200
H	-3.86258700	4.04404000	-2.40741600
H	-3.76148600	4.01611200	-0.61503500
C	3.91911800	-1.61255900	-2.20869100
H	4.84985600	-1.18863100	-2.60237700
H	4.14530700	-2.56752200	-1.72126200
H	3.23654500	-1.79492200	-3.04087200

C3-P

G_{sol} = -707.927530 Hatree

C	1.24565600	0.42577100	-0.00007000
C	2.58069900	-0.06288600	0.00012900
C	3.69619600	0.77926400	0.00016200
C	3.46338500	2.15078300	-0.00004200
C	2.15190200	2.66175300	-0.00022200
C	1.04690500	1.81649500	-0.00023200
C	0.37450800	-0.73725200	0.00001800
C	1.21843500	-1.83684200	0.00028300
H	4.70727200	0.38231600	0.00033300
H	4.30620200	2.83626300	-0.00006100
H	2.00051300	3.73757600	-0.00035200
H	0.04765900	2.23741800	-0.00031000
H	0.95732200	-2.88724000	0.00055700
C	3.68429100	-2.33021500	-0.00018500
H	4.30084700	-2.16373900	-0.89097200
H	4.30091000	-2.16448300	0.89070100
H	3.34129100	-3.36680500	-0.00061300
N	2.53172000	-1.45118900	0.00015200
C	-1.06050700	-0.86564700	0.00004100
H	-1.44002600	-1.88751600	-0.00032000
C	-2.00004800	0.10565400	0.00033500
H	-1.76577200	1.16304300	0.00057200
C	-3.42451900	-0.25590000	-0.00001100
O	-3.88681500	-1.38436400	-0.00056900
O	-4.20543500	0.85924500	0.00035300
C	-5.61536600	0.61270500	0.00001700
H	-5.91148200	0.04760800	0.88880300
H	-6.08713900	1.59655700	-0.00092200
H	-5.91085100	0.04618300	-0.88808000

TS-S1b

G_{sol} = -1540.577824 Hatree

Pd	1.04303900	0.21932700	0.14702000
C	-2.95002200	0.23356900	-1.10143600
C	-3.12047700	0.21476500	0.32065400
C	-4.35747100	-0.11623000	0.90753000
C	-5.40413500	-0.42988500	0.05839400
C	-5.25466300	-0.41474500	-1.35356800
C	-4.04683200	-0.08548600	-1.93643500
C	-1.60836300	0.61581600	-1.33314100
C	-0.97722700	0.84333600	-0.09451900

H	-4.48372000	-0.14057600	1.98521100
H	-6.36805300	-0.69906200	0.48187700
H	-6.10766600	-0.66597400	-1.97745700
H	-3.93427100	-0.06994700	-3.01735900
H	-1.13268000	0.75779600	-2.29598900
H	-0.51605300	2.08539500	0.02725600
C	-1.70757600	0.68334200	2.32989700
H	-2.54520900	1.19656100	2.81350500
H	-1.57601600	-0.31127200	2.76663500
H	-0.80003200	1.26915700	2.49018100
N	-1.94229900	0.58033700	0.90062000
C	3.58093100	-0.94499600	-0.61266700
C	5.10535200	-0.91928500	-0.59129900
H	5.44937500	0.09060000	-0.84180800
H	5.48180200	-1.15057700	0.40994700
H	5.50593800	-1.62674600	-1.32025200
O	2.96221500	-1.53338400	-1.51135400
O	3.03699700	-0.31477100	0.38500500
C	1.19735700	3.20142200	-0.03167700
C	1.96689200	4.50197400	-0.13160900
H	1.67713300	5.16224000	0.69093200
H	3.04143300	4.31711400	-0.11169700
H	1.69711000	5.00369000	-1.06735700
O	1.85187600	2.12282300	-0.13193500
O	-0.06263100	3.27874900	0.13203500
S	0.30325400	-1.97887000	0.46326100
O	-0.86740300	-2.23721600	1.36643800
C	1.67392700	-3.03922800	1.01217500
H	2.41397500	-3.09063600	0.21353600
H	2.10067000	-2.59162700	1.91032100
H	1.23417400	-4.01560300	1.23350900
C	-0.01520800	-2.69393000	-1.17397800
H	-0.88867300	-2.17620000	-1.57372900
H	0.87540500	-2.50557500	-1.77827000
H	-0.22373800	-3.76047000	-1.04984200

Int-1b

G_{sol} = -1540.606508 Hatree

Pd	0.79992500	0.08647100	0.06908000
C	-3.28519400	-0.18948600	-1.00493500
C	-3.36739300	0.36628300	0.30274100
C	-4.58954300	0.70770700	0.89265600
C	-5.74873800	0.47438200	0.15705600
C	-5.69045600	-0.08189200	-1.13619800
C	-4.47322200	-0.41363400	-1.72156500
C	-1.88749500	-0.39734200	-1.27298100
C	-1.18022700	0.02809800	-0.16709700
H	-4.63923100	1.14206900	1.88734900
H	-6.71371300	0.72803300	0.58763300
H	-6.61361600	-0.25012000	-1.68462900
H	-4.43972400	-0.83606500	-2.72298100
H	2.98282800	1.76180400	0.24225300
C	-1.74028300	1.10342800	2.06080700
H	-1.90430400	2.18812100	2.02597800
H	-2.34861900	0.68392400	2.87049300
H	-0.68663200	0.91790000	2.27981200
N	-2.07610300	0.47593600	0.79884000
C	3.65269300	-0.44160100	-0.58829300
C	5.15170600	-0.22411100	-0.46939600
H	5.67846800	-0.80046800	-1.23167600
H	5.39615700	0.83892200	-0.57509400
H	5.48642700	-0.53745000	0.52552100
O	2.93293000	0.27442300	0.25475900
O	3.16797100	-1.23169200	-1.39337300
C	1.58743700	3.05637300	-0.10794500
C	1.29167300	4.51754200	-0.32277700
H	1.65106700	5.09625400	0.53390100
H	1.83607300	4.86913900	-1.20585800
H	0.22165800	4.67066600	-0.46351400
O	0.67134300	2.21471100	-0.19017100
O	2.83459700	2.78688400	0.15506700
H	-1.45925700	-0.78056400	-2.19017600
S	0.82277600	-2.19858400	0.49724700
O	1.97776400	-2.70653100	1.29612100
C	0.70347300	-3.09391700	-1.07671700
H	-0.21220100	-2.77763200	-1.58184400
H	1.59041200	-2.80388300	-1.64075200
H	0.69389000	-4.16516800	-0.85643300
C	-0.70527000	-2.77010200	1.30393200
H	-0.75475500	-2.28623100	2.28101600
H	-1.56473300	-2.49046100	0.69275500
H	-0.62021300	-3.85337900	1.42575800

Int-S3b

G_{sol} = -1293.828012 Hatree

Pd	-0.93156700	0.04675500	-0.15140800

C	3.18277300	0.26127300	0.63874700
C	3.12573000	0.83528400	-0.66173400
C	4.25593600	1.36023900	-1.29702500
C	5.46743500	1.29408200	-0.61371900
C	5.54852100	0.72215400	0.67140500
C	4.42067500	0.20720800	1.30135700
C	1.84482000	-0.14982000	0.96730800
C	1.04620500	0.18143500	-0.10170700
H	4.19772700	1.80214300	-2.28783600
H	6.36521200	1.69012600	-1.08067100
H	6.50989200	0.68558000	1.17707700
H	4.49407300	-0.22794800	2.29513800
H	-3.20307900	1.48430100	0.67068600
C	1.33304800	1.38353800	-2.32227400
H	1.47848200	2.47103000	-2.30019900
H	1.86047500	0.97774200	-3.19379600
H	0.26612600	1.18049600	-2.43174500
N	1.81058800	0.76871800	-1.10088800
C	-4.04873000	-0.59224100	-0.43458400
C	-5.45315900	-0.10666800	-0.10167200
H	-6.19372100	-0.75671200	-0.57014100
H	-5.60162600	-0.10568100	0.98420500
H	-5.59351600	0.92283700	-0.45031400
O	-3.08796000	0.16117400	0.06473100
O	-3.84976100	-1.60185300	-1.10025600
C	-1.83607500	2.81882200	0.97762300
C	-1.55334100	4.20886600	1.48493900
H	-2.20062600	4.92727200	0.97211700
H	-1.79313700	4.25790400	2.55264000
H	-0.50484200	4.46329600	1.32976600
O	-0.90677700	2.11668700	0.52853400
O	-3.08044500	2.44908900	1.05955700
C	-0.88450500	-2.15813100	-0.46639300
H	-1.84580300	-2.41498800	-0.03053200
C	-0.84816700	-1.53943100	-1.70303600
H	-1.78301700	-1.34210800	-2.21756000
H	0.08819800	-1.49158600	-2.24997700
C	0.32682100	-2.85914300	0.07439700
O	1.28017500	-3.19543600	-0.59213200
O	0.17883300	-3.12803600	1.38652100
C	1.27718000	-3.83618400	1.98865200
H	0.99943300	-3.96989500	3.03420200
H	1.41965700	-4.80343000	1.49966100
H	2.19599300	-3.25110600	1.90045900
H	1.51854300	-0.63176000	1.87847200

TS-S2b

G_{sol} = -1293.813817 Hatree

C	-3.27296400	-0.53475300	0.56037700
C	-3.56161000	-0.41586800	-0.83106400
C	-4.90418200	-0.33656700	-1.24844100
C	-5.90912300	-0.36255700	-0.29207700
C	-5.60227200	-0.46372000	1.08241200
C	-4.28760100	-0.54629000	1.52729500
C	-1.30866300	-0.50348700	-0.54800900
C	-2.30405500	-0.41472600	-1.50746300
N	-1.89986700	-0.61622400	0.71039500
Pd	0.62637300	0.11567700	-0.79015100
O	2.87990100	1.18296400	1.01027800
O	-0.12479300	2.14209200	-0.57225500
C	-0.00137800	2.84433100	0.44586200
O	0.81553400	2.60739200	1.43588100
C	3.30437300	1.08647900	-0.17147100
O	2.58553500	0.79781100	-1.18753700
C	4.78265900	1.29934200	-0.45263800
C	-0.83197400	4.09116200	0.61636200
H	1.54504400	1.89814000	1.22548800
H	-4.06298100	-0.61694300	2.58734900
H	-6.41043800	-0.47567700	1.80875900
H	-6.94906300	-0.29941800	-0.60068700
H	-5.14565200	-0.24967400	-2.30475000
H	-0.17952000	4.96963700	0.56304400
H	-1.59289600	4.14835900	-0.16208400
H	-1.29870400	4.09141100	1.60609900
H	5.28418300	1.72762900	0.41708600
H	5.23955800	0.33431400	-0.69938300
H	4.90976800	1.95083500	-1.32232000
C	1.36675600	-1.87884000	-0.95419900
H	1.97428100	-1.80791000	-1.85235400
C	-0.00236700	-2.19758900	-1.04275500
H	-0.47491100	-2.70222400	-0.20781000
H	-0.45252100	-2.34254100	-2.01622100
C	2.08633300	-2.17282300	0.32132700
O	1.54403500	-2.47464000	1.36970300
O	3.41794200	-2.07659200	0.16540600
C	4.19126400	-2.22431900	1.37166000

H	3.93880800	-3.15795600	1.87916900
H	5.23267200	-2.22827800	1.04937000
H	3.99600900	-1.37715900	2.03397900
C	-1.20800300	-0.61345800	1.98993000
H	-1.77803600	-1.20974600	2.70829600
H	-0.22330500	-1.06914900	1.87625000
H	-1.09205400	0.40300600	2.38671500
H	-2.14272300	-0.36434800	-2.57629000

Int-2b

G_{sol} = -1293.862542 Hatree

C	-2.84672300	-1.13850300	0.34049300
C	-2.63655500	-0.12543100	-0.62156700
C	-3.49911400	0.97569000	-0.65853000
C	-4.53575800	1.04662600	0.27044200
C	-4.71868800	0.03606300	1.23046400
C	-3.87790400	-1.07519500	1.27853100
C	-1.09929200	-1.80206500	-0.91142100
C	-1.48325500	-0.53053200	-1.41061600
N	-1.88183900	-2.14111500	0.14260100
Pd	0.52354800	0.29288200	-0.87423300
O	2.41367100	1.45847500	1.33814700
O	-0.41676500	2.27689600	-0.64024300
C	-0.49738800	2.92230500	0.41849200
O	0.22056100	2.72427000	1.48806700
C	3.00574800	1.38032300	0.23306400
O	2.46851700	1.05180500	-0.87974600
C	4.49487900	1.68290000	0.16047900
C	-1.52153700	4.02287500	0.56018800
H	1.01578900	2.06874100	1.35928600
H	-4.03475100	-1.85922400	2.01247100
H	-5.53362200	0.11637700	1.94412900
H	-5.21669800	1.89318700	0.25262800
H	-3.35336200	1.76074700	-1.39417600
H	-1.17076200	4.79598800	1.24680000
H	-1.74906500	4.44835800	-0.41903300
H	-2.44121700	3.58782500	0.96927200
H	4.85967700	2.05491400	1.11969500
H	5.03304600	0.76920900	-0.11340800
H	4.68751900	2.42082300	-0.62479300
C	1.29680800	-1.63659800	-1.06541800
H	2.05632500	-1.55486500	-1.84338100
C	0.10638200	-2.53956100	-1.41841600
H	0.19350500	-3.54516200	-0.99683200
H	0.01752200	-2.63781500	-2.50651200
C	1.87501500	-1.97086700	0.26678500
O	1.26834300	-2.52782200	1.17307700
O	3.17323500	-1.61830300	0.37856700
C	3.75001500	-1.79776100	1.68296900
H	3.60021800	-2.82076000	2.03613600
H	4.81278000	-1.58395300	1.56245400
H	3.29874600	-1.09350200	2.38665000
C	-1.74046400	-3.31525400	0.99848300
H	-2.35252800	-4.14441000	0.62681800
H	-0.68870500	-3.59238700	1.05057500
H	-2.06722800	-3.05518100	2.00753800
H	-1.33101700	-0.24631100	-2.44928300

TS-S3b

G_{sol} = -1293.833501 Hatree

C	4.30898600	0.16769700	-0.30841000
C	2.69696200	-0.91812600	0.89728000
C	2.16861300	-0.53514900	-0.32087300
Pd	-0.92401500	0.43372500	0.14077300
O	-3.94170700	-0.17811700	0.16449800
O	-1.55015300	2.49837900	0.22151900
C	-2.63429000	2.94074300	-0.19947700
O	-3.65897900	2.23089400	-0.57315200
C	-3.44136700	-0.48784900	1.27868900
O	-2.25939000	-0.19163200	1.65961600
C	-4.26816800	-1.29934700	2.26305000
C	-2.84977800	4.43054800	-0.30781200
H	-3.61407600	1.21584200	-0.33765300
H	2.16530000	-1.44471200	1.67771500
H	-3.21632700	4.67845800	-1.30873000
H	-3.62129900	4.73701400	0.40686100
H	-1.92226800	4.96450500	-0.09991100
H	-5.32640100	-1.26953800	1.99655600
H	-3.92097500	-2.33899600	2.24029600
H	-4.11976700	-0.92711600	3.28057800
C	-0.18179400	-1.49723700	-0.18822300
H	0.00396600	-1.93338500	0.78870200
C	0.83819100	-0.76510600	-0.87034300
H	0.18175800	0.77360200	-0.97826000
H	0.74389200	-0.78716800	-1.95434700
C	-1.21342000	-2.16180000	-1.03956300

O	-1.31716100	-2.01140400	-2.24311200
O	-2.02343000	-2.94217600	-0.29998700
C	-3.15871500	-3.48673000	-0.99889700
H	-2.84263100	-3.98986400	-1.91523800
H	-3.61430800	-4.19448200	-0.30573200
H	-3.85636900	-2.67972200	-1.23729700
C	4.05363200	-0.48729000	0.93181200
N	3.14838700	0.13878600	-1.05413200
C	5.08719500	-0.58651100	1.88417600
C	6.32745800	-0.04529700	1.58654800
C	6.56346500	0.59427800	0.34847200
C	5.56749400	0.70722200	-0.61235300
H	4.90911300	-1.07994100	2.83584300
H	7.13415500	-0.11264600	2.31089300
H	7.54826400	1.00386700	0.14154000
H	5.76789200	1.19170400	-1.56313700
C	2.99953800	0.68125800	-2.39262200
H	3.71107400	1.49855600	-2.52763700
H	3.18216800	-0.07570700	-3.16585800
H	1.99536000	1.09150300	-2.52560800

Int-S5b

G_{sol} = -1293.836217 Hatree

C	5.81409200	-0.45074900	-0.24837900
C	5.70490900	-0.29526000	-1.64956900
C	4.53843900	0.18351800	-2.22053300
C	3.45492700	0.51714100	-1.38204500
C	3.58012300	0.35132600	0.02967800
C	4.76570900	-0.13339600	0.60430000
C	2.15403100	1.03195200	-1.61246700
C	1.51761000	1.15744800	-0.38352700
N	2.39558600	0.74328200	0.62279900
C	2.17896900	0.81596000	2.06042700
C	0.16236400	1.64394100	-0.23724800
C	-0.65670000	1.75753000	0.89422100
Pd	-1.29332500	-0.10455200	-0.06198000
O	-0.23164800	-1.39172800	1.54387500
C	-0.36094000	-2.60980600	1.73083700
O	-1.12608700	-3.39815000	1.01480100
C	0.38081300	-3.32964700	2.82926600
O	-3.43201000	-0.84018000	-2.31914600
C	-3.08212200	-1.83654200	-1.70903000
C	-3.62839400	-3.22329700	-2.02261000
O	-2.19877300	-1.84136700	-0.71944200
C	-1.82290400	2.68270700	0.96834700
O	-2.44353300	2.87883300	1.99427900
O	-2.09816500	3.29305800	-0.20437200
C	-3.25532400	4.14378700	-0.19756700
H	6.74067700	-0.83144600	0.17239200
H	6.54933900	-0.55746000	-2.28046300
H	4.45260400	0.30310800	-3.29715500
H	4.87113800	-0.26871900	1.67621300
H	1.70164700	1.26936200	-2.56627000
H	3.11939600	0.59376400	2.56577200
H	1.87278800	1.82497100	2.35389200
H	1.42435100	0.09166300	2.37778300
H	-0.19011500	2.15180700	-1.12961700
H	-0.32534300	1.44440700	1.87636500
H	-2.11943800	0.62817000	-1.11173800
H	-1.60671800	-2.87626500	0.27967100
H	0.91879000	-2.61807400	3.45618100
H	-0.32299500	-3.90898100	3.43454800
H	1.08832100	-4.03805200	2.38457200
H	-4.35385500	-3.16287900	-2.83507900
H	-2.81031900	-3.89342400	-2.30894000
H	-4.10568000	-3.65010500	-1.13365900
H	-3.31437100	4.56262200	-1.20226800
H	-4.15322700	3.56210000	0.02779300
H	-3.14499400	4.93645400	0.54693800

C2-P

G_{sol} = -707.924545 Hatree

C	1.20768500	0.37643600	-0.00104400
H	1.47851300	1.43015300	0.00141200
C	2.23947100	-0.49504300	-0.00175500
H	2.10187300	-1.57135400	-0.00392800
C	3.62158600	0.01078200	0.00050900
O	3.95634400	1.18306600	0.00294600
O	4.51165000	-1.01451400	-0.00055300
C	5.89029300	-0.62379500	0.00145300
H	6.12340900	-0.03209400	0.89139400
H	6.45981800	-1.55409800	0.00065500
H	6.12523000	-0.02947100	-0.88626800
C	-0.82241000	-1.19224800	-0.00130800
C	-2.22565000	-0.96974100	-0.00057300
C	-3.35039800	-1.81974000	0.00054600

C	-0.19501300	0.04466100	-0.00231800
H	-0.31919800	-2.14948100	-0.00091000
H	-3.21949300	-2.89865900	0.00065700
C	-4.61693300	-1.25920600	0.00182300
C	-2.41895900	0.44493400	-0.00102200
C	-3.70365800	1.00914800	0.00105600
C	-4.78941100	0.14380100	0.00218600
N	-1.17629700	1.04337700	-0.00370000
C	-0.92240200	2.47313500	-0.00018400
H	-1.87483800	3.00257700	-0.03570300
H	-0.39163200	2.78146500	0.90751700
H	-0.33302300	2.77216200	-0.87366700
H	-5.49298200	-1.90168500	0.00286600
H	-5.79487000	0.55563200	0.00386600
H	-3.85788600	2.08406100	0.00265100

TS-S1a-A

G_{sol} = -987.498448 Hatree

Pd	1.33229500	-0.04575000	-0.01237900
C	-1.71809900	0.19419200	-0.43529700
C	-2.80838200	-0.48815100	0.15622700
C	-4.02944400	-0.68007100	-0.49313900
C	-4.14509700	-0.17626900	-1.78675700
C	-3.07481200	0.50047400	-2.40055900
C	-1.86585800	0.69272200	-1.73639300
C	-0.63372300	0.24572500	0.54868800
C	-1.14018700	-0.46001400	1.65033300
H	-4.85773100	-1.19724500	-0.01723900
H	-5.07722900	-0.30780200	-2.32895200
H	-3.19681900	0.87852800	-3.41185500
H	-1.04310300	1.21297200	-2.21909700
H	-0.31181800	1.51394800	0.89478900
H	-0.65411100	-0.67740800	2.59310100
C	-3.25945500	-1.57789800	2.39109700
H	-4.13179600	-0.96991900	2.65585300
H	-3.60392700	-2.52629300	1.96549500
H	-2.68330600	-1.78566800	3.29474000
N	-2.41374000	-0.87875800	1.44023100
C	2.56593800	-2.18554300	-0.35305100
C	3.19183100	-3.53615600	-0.57961200
H	2.81257000	-4.25943300	0.14698600
H	2.92552500	-3.89144800	-1.58221300
H	4.27965800	-3.46111200	-0.51578800
O	3.19962800	-1.11467500	-0.57848100
O	1.34513600	-2.11992900	0.05371600
C	1.11190500	2.88425700	0.37778200
C	1.65938200	4.29170900	0.28015700
H	0.89920000	4.94782600	-0.15526200
H	1.87420500	4.66320000	1.28753400
H	2.56680600	4.31277200	-0.32425200
O	1.75732300	1.96071900	-0.20002900
O	0.03397600	2.72051600	1.03568500

TS-S1a-B

G_{sol} = -1540.578884 Hatree

Pd	0.80295500	0.34569400	0.05833800
C	-3.18298300	0.22033500	-1.09674700
C	-3.28104300	-0.20474200	0.26534500
C	-4.43552300	-0.84302100	0.75550500
C	-5.47647800	-1.05565400	-0.13424400
C	-5.39684700	-0.64268400	-1.48802000
C	-4.26777900	-0.00747600	-1.97212500
C	-1.90956200	0.82716800	-1.23116300
C	-1.25384300	0.79208400	0.00870700
H	-4.50846700	-1.16768200	1.78912800
H	-6.37771800	-1.55420700	0.21274300
H	-6.23880000	-0.83010600	-2.14841800
H	-4.20962900	0.31090100	-3.00971700
H	-1.50106400	1.27474000	-2.12873300
H	-0.90075800	2.04006000	0.43808600
C	-1.84047900	-0.11789200	2.30287100
H	-2.68782700	0.17838900	2.93130600
H	-1.62464000	-1.18010600	2.46926400
H	-0.96507500	0.46584800	2.59408100
N	-2.12679700	0.14370300	0.90782800
C	3.69920800	-0.19838100	-0.83442100
C	3.70435800	1.06169600	-1.68802500
H	2.82549800	1.06803000	-2.34482300
H	3.63693400	1.95396500	-1.06102400
H	4.60798900	1.08754800	-2.30029400
O	4.54810400	-1.07706100	-0.99760400
O	2.76132700	-0.32896700	0.07330700
C	0.70157400	3.27564700	0.48242800
C	1.34277800	4.63916700	0.61444400
H	1.13020500	5.04597200	1.60756500
H	2.41951200	4.57841100	0.45330200

H	0.89537200	5.31703000	-0.12031400
O	1.42807000	2.31778700	0.08578400
O	-0.53715700	3.18318800	0.76750900
S	0.93403700	-2.97860600	0.42030600
O	0.15126500	-1.65950600	0.14085300
C	2.16583500	-3.26548100	-0.89230800
H	2.46673200	-4.31519200	-0.80421000
H	1.63829600	-3.12273100	-1.83912500
H	3.02696600	-2.59313400	-0.81373800
C	2.06084600	-2.70000100	1.82419300
H	1.44099300	-2.50485600	2.70251500
H	2.63545200	-3.61984800	1.97248500
H	2.70385000	-1.85131000	1.57923000

TS-S1a-C

G_{sol} = -1540.584066 Hatree

Pd	0.76991400	0.24596000	-0.28335000
C	-3.34454900	0.32730500	-0.62845700
C	-3.18606700	-0.11432200	0.72485700
C	-4.25209200	-0.70509600	1.43174100
C	-5.45963100	-0.84574900	0.76974400
C	-5.63609200	-0.40843600	-0.56895900
C	-4.59734600	0.17602600	-1.26681400
C	-2.09585300	0.86237900	-1.01838000
C	-1.20452800	0.77954900	0.06837700
H	-4.13176200	-1.05285800	2.45293600
H	-6.29640100	-1.30801800	1.28663200
H	-6.60374300	-0.54007800	-1.04463500
H	-4.73225000	0.51060100	-2.29202500
H	-1.85487500	1.31138700	-1.97389100
H	-0.72757500	2.01306500	0.36536300
C	-1.33670900	-0.18744100	2.40762100
H	-2.08081900	-0.05652800	3.19921100
H	-0.97245300	-1.21943800	2.39738600
H	-0.49402200	0.47893800	2.60565400
N	-1.91165300	0.16501700	1.12309800
C	0.42946100	-2.65305000	-0.63314700
C	-0.05431400	-2.40575600	-2.05512300
H	-0.15173500	-3.35829900	-2.58073100
H	-1.00987900	-1.87262100	-2.05502400
H	0.67653700	-1.78311900	-2.58545100
O	0.35002100	-1.65653200	0.22755700
O	0.87641100	-3.74584300	-0.29031800
C	0.86290700	3.20679800	-0.12193400
C	1.51331200	4.56090600	-0.31109900
H	1.48731600	5.11906100	0.62895500
H	2.53947600	4.45218800	-0.66499200
H	0.93572700	5.13088300	-1.04748200
O	1.44907200	2.19462700	-0.60558000
O	-0.25029100	3.17933200	0.49885500
S	3.87388000	-1.03021700	-0.00914200
O	2.73403400	-0.48514700	-0.89788600
C	4.40554800	0.37084200	1.03134400
H	5.16352500	0.02610100	1.74106200
H	4.82885700	1.12570300	0.36528900
H	3.53587500	0.78075100	1.55268700
C	3.19064800	-2.08798300	1.31058300
H	2.59743100	-2.88064100	0.84065700
H	4.04762500	-2.50298100	1.85199000
H	2.54445000	-1.50721600	1.97194700

TS-S1a-D

G_{sol} = -1540.583839 Hatree

Pd	0.90346600	0.12777200	-0.01016700
C	-3.15005500	0.55659900	-0.82299600
C	-3.18651900	0.11342500	0.53744900
C	-4.37353500	-0.37163900	1.11944600
C	-5.50642100	-0.40897400	0.32461400
C	-5.49004200	0.03041900	-1.02458300
C	-4.33057400	0.51315900	-1.59980400
C	-1.81977600	0.97284000	-1.06683600
C	-1.07275100	0.81959300	0.11481900
H	-4.39971900	-0.72156000	2.14651500
H	-6.43414900	-0.79079600	0.74226500
H	-6.40533900	-0.01892800	-1.60741500
H	-4.31794100	0.84870100	-2.63344700
H	-1.43109300	1.38692100	-1.98907700
H	-0.49508800	2.05312100	0.44398000
C	-1.56381500	-0.10300000	2.42905300
H	-2.35814700	0.17224100	3.13009400
H	-1.35978500	-1.17615700	2.48823000
H	-0.65403600	0.43707200	2.69930800
N	-1.94254400	0.27669800	1.07901000
C	-0.16538800	-2.67637500	-0.18878100
C	-0.21549700	-2.43431800	-1.68907600
H	-0.56187500	-3.34084200	-2.18952000

H	-0.89722100	-1.60805300	-1.91720200
H	0.77864500	-2.16586100	-2.06501500
O	0.30908400	-1.69940800	0.58282100
O	-0.52087400	-3.72711900	0.32009900
C	1.18939800	3.08767200	0.00927300
C	1.92190200	4.39548400	-0.18713800
H	1.42651900	4.96069600	-0.98461500
H	1.86165800	4.99459700	0.72550100
H	2.96260200	4.22115700	-0.46372900
O	1.73817500	2.02259400	-0.40018500
O	0.04084100	3.14576100	0.56232200
S	3.11536700	-0.89485700	-0.19891900
O	3.40972800	-1.74654600	-1.40000200
C	3.37998400	-1.87608800	1.30749300
H	3.36841100	-1.21066100	2.17522500
H	2.54268000	-2.57370500	1.36814300
H	4.33450900	-2.40155600	1.21633500
C	4.44252100	0.33841400	-0.01724000
H	4.36170900	1.01546900	-0.86906100
H	4.29224300	0.89468800	0.91141400
H	5.40570400	-0.17875100	-0.02520000

TS-S1b**-A**

G_{sol} = -987.492222 Hatree

Pd	-1.35517900	0.19122300	-0.18894400
C	2.64391000	-0.48586500	-0.83191700
C	2.64726500	0.08367400	0.48192800
C	3.82667900	0.59724900	1.05483000
C	4.98459400	0.53622400	0.29780800
C	5.00061300	-0.02724400	-1.00449000
C	3.84875100	-0.53859500	-1.56993900
C	1.31579000	-0.89924800	-1.08245400
C	0.53231700	-0.62301100	0.05362800
H	3.83058400	1.03762900	2.04698500
H	5.90803400	0.93445900	0.70975800
H	5.93495700	-0.05257800	-1.55776800
H	3.86021300	-0.97081400	-2.56691200
H	0.94648700	-1.38651900	-1.97594700
H	-0.08909800	-1.74115200	0.49404100
C	0.96291300	0.50223000	2.28714000
H	1.73226400	0.30080200	3.03911400
H	0.76486700	1.57877400	2.24109700
H	0.04324100	-0.00845700	2.58006500
N	1.38471700	-0.00546300	0.99443400
C	-2.05207300	2.58226700	-0.18879500
C	-2.34619900	4.05669500	-0.22738500
H	-1.69796400	4.59338100	0.47006700
H	-2.14566300	4.43509100	-1.23679500
H	-3.39764700	4.23624600	0.00754500
O	-2.95213000	1.71670400	-0.38859500
O	-0.84391200	2.18455800	0.02447600
C	-1.86474000	-2.68674000	0.15620600
C	-2.76097500	-3.90483100	0.12421900
H	-2.99508400	-4.20324300	1.15133300
H	-3.68152000	-3.69346000	-0.42059100
H	-2.22582700	-4.73671900	-0.34424000
O	-2.28235100	-1.63309200	-0.41229500
O	-0.74357200	-2.79795800	0.74991100

TS-S1b**-B**

G_{sol} = -1540.569529 Hatree

Pd	0.80295500	0.34569400	0.05833800
C	-3.18298300	0.22033500	-1.09674700
C	-3.28104300	-0.20474200	0.26534500
C	-4.43552300	-0.84302100	0.75550500
C	-5.47647800	-1.05565400	-0.13424400
C	-5.39684700	-0.64268400	-1.48802000
C	-4.26777900	-0.00747600	-1.97212500
C	-1.90956200	0.82716800	-1.23116300
C	-1.25384300	0.79208400	0.00870700
H	-4.50846700	-1.16768200	1.78912800
H	-6.37771800	-1.55420700	0.21274300
H	-6.23880000	-0.83010600	-2.14841800
H	-4.20962900	0.31090100	-3.00971700
H	-1.50106400	1.27474000	-2.12873300
H	-0.90075800	2.04006000	0.43808600
C	-1.84047900	-0.11789200	2.30287100
H	-2.68782700	0.17838900	2.93130600
H	-1.62464000	-1.18010600	2.46926400
H	-0.96507500	0.46584800	2.59408100
N	-2.12679700	0.14370300	0.90782800
C	3.69920800	-0.19838100	-0.83442100
C	3.70435800	1.06169600	-1.68802500
H	2.82549800	1.06803000	-2.34482300
H	3.63693400	1.95396500	-1.06102400
H	4.60798900	1.08754800	-2.30029400

O	4.54810400	-1.07706100	-0.99760400
O	2.76132700	-0.32896700	0.07330700
C	0.70157400	3.27564700	0.48242800
C	1.34277800	4.63916700	0.61444400
H	1.13020500	5.04597200	1.60756500
H	2.41951200	4.57841100	0.45330200
H	0.89537200	5.31703000	-0.12031400
O	1.42807000	2.31778700	0.08578400
O	-0.53715700	3.18318800	0.76750900
S	0.93403700	-2.97860600	0.42030600
O	0.15126500	-1.65950600	0.14085300
C	2.16583500	-3.26548100	-0.89230800
H	2.46673200	-4.31519200	-0.80421000
H	1.63829600	-3.12273100	-1.83912500
H	3.02696600	-2.59313400	-0.81373800
C	2.06084600	-2.70000100	1.82419300
H	1.44099300	-2.50485600	2.70251500
H	2.63545200	-3.61984800	1.97248500
H	2.70385000	-1.85131000	1.57923000

TS-S1b**-C**

G_{sol} = -1540.573416 Hatree

Pd	0.76991400	0.24596000	-0.28335000
C	-3.34454900	0.32730500	-0.62845700
C	-3.18606700	-0.11432200	0.72485700
C	-4.25209200	-0.70509600	1.43174100
C	-5.45963100	-0.84574900	0.76974400
C	-5.63609200	-0.40843600	-0.56895900
C	-4.59734600	0.17602600	-1.26681400
C	-2.09585300	0.86237900	-1.01838000
C	-1.20452800	0.77954900	0.06837700
H	-4.13176200	-1.05285800	2.45293600
H	-6.29640100	-1.30801800	1.28663200
H	-6.60374300	-0.54007800	-1.04463500
H	-4.73225000	0.51060100	-2.29202500
H	-1.85487500	1.31138700	-1.97389100
H	-0.72757500	2.01306500	0.36536300
C	-1.33670900	-0.18744100	2.40762100
H	-2.08081900	-0.05652800	3.19921100
H	-0.97245300	-1.21943800	2.39738600
H	-0.49402200	0.47893800	2.60565400
N	-1.91165300	0.16501700	1.12309800
C	0.42946100	-2.65305000	-0.63314700
C	-0.05431400	-2.40575600	-2.05512300
H	-0.15173500	-3.35829900	-2.58073100
H	-1.00987900	-1.87262100	-2.05502400
H	0.67653700	-1.78311900	-2.58545100
O	0.35002100	-1.65653200	0.22755700
O	0.87641100	-3.74584300	-0.29031800
C	0.86290700	3.20679800	-0.12193400
C	1.51331200	4.56090600	-0.31109900
H	1.48731600	5.11906100	0.62895500
H	2.53947600	4.45218800	-0.66499200
H	0.93572700	5.13088300	-1.04748200
O	1.44907200	2.19462700	-0.60558000
O	-0.25029100	3.17933200	0.49885500
S	3.87388000	-1.03021700	-0.00914200
O	2.73403400	-0.48514700	-0.89788600
C	4.40554800	0.37084200	1.03134400
H	5.16352500	0.02610100	1.74106200
H	4.82885700	1.12570300	0.36528900
H	3.53587500	0.78075100	1.55268700
C	3.19064800	-2.08798300	1.31058300
H	2.59743100	-2.88064100	0.84065700
H	4.04762500	-2.50298100	1.85199000
H	2.54445000	-1.50721600	1.97194700

TS-S1b**-D**

G_{sol} = -1540.573383 Hatree

Pd	0.90346600	0.12777200	-0.01016700
C	-3.15005500	0.55659900	-0.82299600
C	-3.18651900	0.11342500	0.53744900
C	-4.37353500	-0.37163900	1.11944600
C	-5.50642100	-0.40897400	0.32461400
C	-5.49004200	0.03041900	-1.02458300
C	-4.33057400	0.51315900	-1.59980400
C	-1.81977600	0.97284000	-1.06683600
C	-1.07275100	0.81959300	0.11481900
H	-4.39971900	-0.72156000	2.14651500
H	-6.43414900	-0.79079600	0.74226500
H	-6.40533900	-0.01892800	-1.60741500
H	-4.31794100	0.84870100	-2.63344700
H	-1.43109300	1.38692100	-1.98907700
H	-0.49508800	2.05312100	0.44398000
C	-1.56381500	-0.10300000	2.42905300
H	-2.35814700	0.17224100	3.13009400

H	-1.35978500	-1.17615700	2.48823000
H	-0.65403600	0.43707200	2.69930800
N	-1.94254400	0.27669800	1.07901000
C	-0.16538800	-2.67637500	-0.18878100
C	-0.21549700	-2.43431800	-1.68907600
H	-0.56187500	-3.34084200	-2.18952000
H	-0.89722100	-1.60805300	-1.91720200
H	0.77864500	-2.16586100	-2.06501500
O	0.30908400	-1.69940800	0.58282100
O	-0.52087400	-3.72711900	0.32009900
C	1.18939800	3.08767200	0.00927300
C	1.92190200	4.39548400	-0.18713800
H	1.42651900	4.96069600	-0.98461500
H	1.86165800	4.99459700	0.72550100
H	2.96260200	4.22115700	-0.46372900
O	1.73817500	2.02259400	-0.40018500
O	0.04084100	3.14576100	0.56232200
S	3.11536700	-0.89485700	-0.19891900
O	3.40972800	-1.74654600	-1.40000200
C	3.37998400	-1.87608800	1.30749300
H	3.36841100	-1.21066100	2.17522500
H	2.54268000	-2.57370500	1.36814300
H	4.33450900	-2.40155600	1.21633500
C	4.44252100	0.33841400	-0.01724000
H	4.36170900	1.01546900	-0.86906100
H	4.29224300	0.89468800	0.91141400
H	5.40570400	-0.17875100	-0.02520000

TS-S2a-A

G_{sol} = -1617.887433 Hatree

C	-3.64218600	-0.75509500	0.35144600
C	-2.63536500	-0.28243800	-0.54015300
C	-3.02134000	0.51115700	-1.63236900
C	-4.36740100	0.81021700	-1.81355100
C	-5.34523300	0.33705900	-0.91527700
C	-4.99637200	-0.44837300	0.17953100
C	-1.66379800	-1.53260400	1.07250600
C	-1.37324900	-0.78010400	-0.04716900
N	-3.02164400	-1.51656000	1.32839400
Pd	0.47682400	0.02109800	-0.37210000
O	3.07968100	-0.11338800	1.18347800
C	3.25463300	0.65541700	0.23563600
O	2.34209500	1.00485500	-0.63177000
C	4.62435300	1.28152500	-0.02554000
H	-0.99483800	-2.11185700	1.69498400
H	-5.75241300	-0.80891000	0.87185300
H	-6.38939000	0.58978100	-1.07907400
H	-4.67363100	1.42259500	-2.65766300
H	-2.27058100	0.89127600	-2.32071200
H	5.28804900	1.11096500	0.82483700
H	5.06597100	0.82797200	-0.92082300
H	4.53401400	2.35569800	-0.21906600
C	1.19462400	-1.74378000	-1.33293800
H	1.77783900	-1.28854100	-2.12858600
C	-0.18424500	-1.97719400	-1.49073300
H	-0.62172900	-2.82025600	-0.97646300
H	-0.69679200	-1.63639700	-2.38308700
C	1.93585200	-2.57790300	-0.34264900
O	1.40861400	-3.23219600	0.53884100
O	3.25977600	-2.53439300	-0.57272300
C	4.08582300	-3.11885100	0.44827500
H	3.74198400	-4.12591800	0.69510800
H	5.09266600	-3.14618500	0.02918300
H	4.05411300	-2.47760200	1.33221200
C	-3.68662500	-2.15845500	2.44339900
H	-4.47288400	-2.83610500	2.09007100
H	-2.95327900	-2.74026400	3.00578500
H	-4.13845600	-1.41929400	3.11650300
S	0.75238800	2.98694200	0.79029500
O	-0.30248900	1.91331100	0.41156200
C	1.13064100	3.89162000	-0.74613900
H	1.71585700	4.78432500	-0.50349400
H	1.72113100	3.19613500	-1.34530200
H	0.19738100	4.15689500	-1.25100500
C	-0.28902500	4.25071200	1.58959500
H	-0.65955600	3.81565900	2.52029000
H	0.31478600	5.13722200	1.80562800
H	-1.12879200	4.49417600	0.93358700

TS-S2a-B

G_{sol} = -1617.886000 Hatree

C	3.76991900	0.25778000	0.26550500
C	2.72053700	-0.10584700	-0.62390900
C	3.02159300	-0.92073700	-1.72532700
C	4.33363600	-1.34040300	-1.91912200
C	5.35716100	-0.96778300	-1.02551400

C	5.08943500	-0.16655800	0.08118900
C	1.87765100	1.20047300	1.01963000
C	1.51102800	0.50783500	-0.12199300
N	3.22500200	1.05636500	1.26280800
Pd	-0.38497100	-0.09742500	-0.48074600
O	-1.17940600	-1.69807000	1.93569700
C	-0.31711300	-2.34086700	1.31038100
O	0.17677000	-2.01595600	0.16274800
C	0.25358300	-3.63503700	1.88692500
H	1.26948800	1.82662500	1.65826800
H	5.87925100	0.11425000	0.77260900
H	6.37226900	-1.31433500	-1.19958200
H	4.57482100	-1.97455200	-2.76803100
H	2.23233500	-1.22990500	-2.40520000
H	-0.30785100	-3.93952200	2.77295000
H	0.23058400	-4.43010100	1.13470700
H	1.30374100	-3.47936600	2.15927100
C	-0.84119900	1.86742400	-1.28180500
H	-1.51550300	1.52163300	-2.06031800
C	0.54911800	1.92639500	-1.49791100
H	1.11981900	2.69595400	-0.99911800
H	0.96879200	1.54153600	-2.42037200
C	-1.40898800	2.72696000	-0.21839500
O	-0.75882000	3.32237600	0.62521900
O	-2.76069500	2.78791800	-0.28622300
C	-3.38091500	3.60161700	0.71875700
H	-3.00137500	4.62622700	0.67693100
H	-4.44860800	3.58072500	0.49572200
H	-3.18941400	3.19587400	1.71643900
C	3.95403400	1.61002800	2.38567000
H	4.79426500	2.22311200	2.03915900
H	3.27994800	2.23954600	2.97024400
H	4.34354500	0.81558300	3.03377300
S	-3.24837500	-1.68469700	-0.15074400
O	-2.45754000	-0.63586200	-0.97539600
C	-3.98522900	-0.76762900	1.23844100
H	-4.75284900	-1.38732100	1.71228000
H	-3.15806700	-0.59228600	1.92689700
H	-4.40463600	0.16796600	0.85818400
C	-4.75860700	-1.87100100	-1.15877500
H	-4.45944200	-2.34196500	-2.09785300
H	-5.47239000	-2.51158100	-0.63198700
H	-5.18740900	-0.88508600	-1.35725600

TS-S2a-C

G_{sol} = -1617.886582 Hatree

C	-3.56295700	-0.77378100	0.27851400
C	-2.56370300	-0.26518800	-0.59833500
C	-2.96677200	0.43157900	-1.74828500
C	-4.32392600	0.60641900	-1.99496500
C	-5.29519600	0.10234700	-1.10731000
C	-4.92914300	-0.59208900	0.04170200
C	-1.56180000	-1.34922100	1.11409700
C	-1.28463100	-0.63252600	-0.03575100
N	-2.92248500	-1.43402100	1.31687400
Pd	0.54659500	0.20898300	-0.41098800
O	3.19198400	0.47808600	1.12848400
C	3.35725600	0.92533600	-0.01617200
O	2.41510800	1.09500800	-0.89454400
C	4.74802300	1.31391700	-0.50973400
H	-0.87671700	-1.84501100	1.78925200
H	-5.68074800	-0.97522800	0.72635400
H	-6.34861400	0.25972500	-1.32191800
H	-4.64405800	1.14712800	-2.88140400
H	-2.22364300	0.83583800	-2.43165500
H	5.43264900	1.43129100	0.33326200
H	5.12361800	0.51688500	-1.16243000
H	4.71486300	2.23240400	-1.10347200
C	1.26108900	-1.63792900	-1.34219400
H	1.78349000	-1.16684000	-2.16981000
C	-0.09745900	-1.95726600	-1.42752400
H	-0.47844800	-2.77099700	-0.82769100
H	-0.67294800	-1.68039100	-2.30312700
C	2.08052900	-2.33120400	-0.30864700
O	1.61710000	-2.95319300	0.63096700
O	3.39562700	-2.18914400	-0.55342600
C	4.27437300	-2.65400500	0.48740700
H	4.00690900	-3.66735000	0.79428800
H	5.27529600	-2.63178800	0.05486800
H	4.20782600	-1.96939500	1.33647900
C	-3.58012100	-2.05771800	2.44757100
H	-4.31742400	-2.79376100	2.10717700
H	-2.83156300	-2.57066000	3.05519000
H	-4.08941600	-1.31230900	3.07031200
S	-0.14959600	2.25876600	0.65656900
O	-1.58147200	2.63109300	0.90015100
C	0.67923800	3.63437400	-0.20053500

H	1.70373200	3.33247300	-0.42410800
H	0.12684800	3.79529400	-1.12900800
H	0.62783700	4.52754700	0.42771600
C	0.74505400	2.28463600	2.24071000
H	0.22211300	1.57789400	2.88924600
H	1.76931300	1.93856000	2.07413800
H	0.69075000	3.29245000	2.66223000

TS-S2a-D

G_{sol} = -1617.883612 Hatree

C	3.69541200	-0.85749200	-0.11339700
C	2.55306500	-0.30845500	0.53754700
C	2.74231700	0.56092400	1.62445300
C	4.03845700	0.84802100	2.04069500
C	5.15470000	0.28864900	1.38714900
C	4.99991400	-0.56617400	0.29950700
C	1.86855800	-1.62944800	-1.16345600
C	1.39585600	-0.81858600	-0.15534200
N	3.25110200	-1.66144800	-1.15019800
Pd	-0.47343500	0.02583200	-0.10353600
O	0.44328100	1.59648000	-1.14725600
C	0.60473300	2.63270100	-0.38244300
O	0.04636100	2.80273100	0.71488300
C	1.57494600	3.66874100	-0.93661000
H	1.32301800	-2.20647800	-1.89835700
H	5.86366500	-0.98600400	-0.20872300
H	6.15520400	0.53450500	1.73259800
H	4.19571200	1.52354400	2.87711100
H	1.88598000	1.02788600	2.10327700
H	2.59711000	3.33072500	-0.72894800
H	1.47260500	3.76437200	-2.02128100
H	1.42001300	4.63448400	-0.45020300
C	-1.33608200	-1.53793700	1.18306300
H	-1.62811300	-0.97042500	2.06353100
C	-0.03567600	-2.04152300	1.08983900
H	0.13533700	-2.89314300	0.44433200
H	0.67436400	-1.87694700	1.89025800
C	-2.43005800	-2.23007200	0.44318600
O	-2.27157800	-2.97864200	-0.50121500
O	-3.62219600	-1.93121700	0.99354200
C	-4.77532700	-2.43464600	0.29422200
H	-4.67388400	-3.50695900	0.11284800
H	-5.62342000	-2.23081000	0.94863500
H	-4.88218500	-1.89769400	-0.64991800
C	4.09868700	-2.37648200	-2.08207400
H	4.77361100	-3.05798200	-1.55089000
H	3.47065500	-2.96385100	-2.75537600
H	4.70094300	-1.68308300	-2.68162900
S	-2.67700000	1.17305400	-0.31144000
O	-3.85798000	0.42117800	-0.86789000
C	-2.51262800	2.71172600	-1.26946500
H	-1.86823600	3.40151300	-0.72392200
H	-2.07065200	2.45369200	-2.23265100
H	-3.52405100	3.10654100	-1.39856600
C	-3.11455900	1.89600000	1.30103400
H	-3.36719000	1.06276300	1.96039700
H	-2.23390500	2.43433400	1.66020000
H	-3.98126300	2.55209000	1.18041100

TS-S2b-A

G_{sol} = -1617.889149 Hatree

C	3.48315900	-0.76146100	-0.29560200
C	3.54513700	-0.09376700	0.96376000
C	4.80121200	0.27941800	1.47911200
C	5.94316600	0.00191400	0.74065600
C	5.85945200	-0.64337300	-0.51216800
C	4.63516700	-1.02878700	-1.04750500
C	1.36969500	-0.51896300	0.45841400
C	2.19884600	0.03074700	1.42295800
N	2.15667300	-1.03945700	-0.56876700
Pd	-0.59348200	-0.02727700	0.12693300
O	-2.56212500	0.54126100	-0.34713800
C	-3.30596300	0.90358600	0.65532700
O	-2.89743500	1.12638900	1.80418000
C	-4.78671400	1.03350500	0.30937100
H	4.58106000	-1.51821100	-2.01544500
H	6.77011500	-0.84200600	-1.07101500
H	6.91791300	0.28765200	1.12700800
H	4.87171400	0.78308500	2.44010500
H	-4.91912100	1.57624600	-0.63192200
H	-5.20566800	0.03040600	0.16820300
H	-5.32516300	1.53562800	1.11598500
C	-1.31384900	-1.80205900	1.04812000
H	-1.99001900	-1.40787600	1.80141700
C	0.05300000	-1.97789200	1.35641300
H	0.61132200	-2.74355800	0.82924700

H	0.39750500	-1.73035200	2.35173100
C	-1.91869600	-2.62315100	-0.03749000
O	-1.29515700	-3.23264100	-0.88984900
O	-3.26209000	-2.62905600	0.05119500
C	-3.94392300	-3.35835200	-0.98123700
H	-3.62224800	-4.40307300	-0.99190900
H	-5.00414800	-3.28469200	-0.73816600
H	-3.74210100	-2.91087200	-1.95814600
C	1.66525100	-1.58056900	-1.82508500
H	2.36104300	-2.34348700	-2.18734300
H	0.69203500	-2.04986800	-1.66663400
H	1.56636900	-0.79704200	-2.58673500
H	1.86996600	0.45732900	2.36167700
S	-0.82699600	2.98704900	-0.91269700
O	0.15581300	1.78377500	-0.82287600
C	-1.01082800	3.61343600	0.78884800
H	-1.57872200	4.54905500	0.75910700
H	-1.56498700	2.85059600	1.34764800
H	-0.01870200	3.76745000	1.22286500
C	0.26463600	4.29349300	-1.55949200
H	0.53181600	4.01418900	-2.58100900
H	-0.27317200	5.24619600	-1.56091200
H	1.16405400	4.34719500	-0.94064600

TS-S2b-B

G_{sol} = -1617.884989 Hatree

C	-3.37489400	-0.70395200	0.43490100
C	-3.50785200	0.02018500	-0.78836400
C	-4.79062900	0.41813400	-1.21498900
C	-5.88871100	0.10666500	-0.42739800
C	-5.73533100	-0.59801700	0.78749700
C	-4.48520700	-1.00802700	1.23562300
C	-1.31008900	-0.43578200	-0.43406600
C	-2.19307900	0.16829900	-1.31807900
N	-2.03758200	-0.99534600	0.61845100
Pd	0.66494800	-0.00471600	-0.20445000
O	0.01674300	1.69567400	0.86874500
C	-0.36275100	2.69857100	0.12809900
O	-0.06837100	2.86110600	-1.06296100
C	-1.24237700	3.70816000	0.86001400
H	-4.37969400	-1.54165700	2.17537100
H	-6.61379600	-0.82187500	1.38688200
H	-6.88306400	0.41112700	-0.74266500
H	-4.91177000	0.96795300	-2.14483300
H	-0.89251200	3.86984100	1.88428400
H	-1.27243000	4.65365900	0.31382300
H	-2.26003300	3.30458400	0.92204800
C	1.20817400	-1.82075700	-1.25757900
H	1.86672600	-1.43509700	-2.03085500
C	-0.17652500	-1.91437400	-1.50352500
H	-0.74929100	-2.67520400	-0.98493200
H	-0.55817300	-1.59698300	-2.46463000
C	1.82659600	-2.72609200	-0.25607400
O	1.22710100	-3.32431100	0.62243400
O	3.15558700	-2.83075200	-0.45220300
C	3.85333000	-3.65685000	0.49097300
H	3.46776400	-4.67980700	0.46851800
H	4.89860600	-3.63349300	0.18162900
H	3.74366500	-3.25685800	1.50269700
C	-1.47048000	-1.57165300	1.82687000
H	-2.17509300	-2.29603600	2.24541200
H	-0.54382500	-2.09565400	1.58361500
H	-1.26346000	-0.79665900	2.57473400
H	-1.91140000	0.66828200	-2.23443900
S	3.64886500	1.57187300	0.21315000
O	2.82353300	0.27052000	0.07020600
C	3.10158800	2.70899500	-1.09753500
H	3.57208900	3.68281100	-0.92675200
H	3.46789200	2.28954800	-2.03841000
H	2.00529000	2.78233400	-1.11622300
C	3.00771800	2.44908100	1.67671800
H	3.35365500	1.89153700	2.55078600
H	3.42398200	3.46096300	1.69525800
H	1.91484300	2.44766000	1.63553700

TS-S2b-C

G_{sol} = -1617.888099 Hatree

C	-3.34501300	-0.73479100	0.26874000
C	-3.42185200	-0.15381900	-1.03214400
C	-4.68637800	0.13262500	-1.58406100
C	-5.82245800	-0.14388300	-0.83899000
C	-5.72527500	-0.70180200	0.45561200
C	-4.49456600	-1.00008000	1.02668200
C	-1.23512500	-0.46463200	-0.48050300
C	-2.07755900	-0.00463800	-1.48629800
N	-2.01346200	-0.94413400	0.56941400

Pd	0.74569200	0.06019600	-0.21598200
O	2.77650800	0.52941500	0.02689300
C	3.18737900	1.53754800	-0.67842400
O	2.45173200	2.33056800	-1.28740500
C	4.70369400	1.70484000	-0.69252800
H	-4.43173300	-1.41739500	2.02685700
H	-6.63345200	-0.89863600	1.01888000
H	-6.80411000	0.07502300	-1.25018700
H	-4.76585800	0.56912200	-2.57655400
H	5.08023900	1.81030900	0.33094600
H	5.17014700	0.80848500	-1.11520300
H	4.98526200	2.57966000	-1.28176800
C	1.40386000	-1.80527400	-1.12254600
H	2.02357100	-1.46225100	-1.94584600
C	0.03211400	-2.03432400	-1.32261800
H	-0.48131800	-2.74222400	-0.68161900
H	-0.39091000	-1.87253000	-2.30453800
C	2.09853300	-2.51075100	-0.00988300
O	1.54533400	-2.99863700	0.96132200
O	3.42289700	-2.56840900	-0.22798300
C	4.19440500	-3.18508200	0.81512700
H	3.86944500	-4.21635400	0.97636800
H	5.22736000	-3.15652000	0.46809700
H	4.08656000	-2.62369300	1.74678000
C	-1.51051300	-1.37006100	1.86813300
H	-2.19634300	-2.10702300	2.29551100
H	-0.53388300	-1.84323800	1.74137400
H	-1.42142300	-0.51284000	2.54344800
H	-1.75513400	0.36079900	-2.45320200
S	-0.04505500	2.08212100	0.87367000
O	-1.14158300	1.95324800	1.89506000
C	-0.55495900	3.23663600	-0.43199800
H	0.28899100	3.33239900	-1.11903000
H	-1.41566000	2.78072500	-0.92525600
H	-0.83583200	4.18826900	0.02794600
C	1.31092200	3.04167800	1.61612900
H	1.80899400	2.39701500	2.34230100
H	1.99856100	3.34007200	0.82397600
H	0.85743800	3.90222800	2.11561300

TS-S2b-D

G_{sol} = -1617.883385 Hatree

C	-3.37586000	-0.91351900	0.44305700
C	-3.58011500	-0.24341700	-0.79946000
C	-4.89608100	0.00945700	-1.23209900
C	-5.95688600	-0.38971200	-0.43126800
C	-5.73326500	-1.03982000	0.80179800
C	-4.44666200	-1.30728300	1.25640200
C	-1.35443900	-0.45965600	-0.43634800
C	-2.28364800	0.02340300	-1.33875000
N	-2.01302900	-1.05983900	0.63295900
Pd	0.58961100	0.17555000	-0.22048600
O	-0.25282400	1.78603400	0.83209700
C	-0.53852700	2.79019300	0.04761100
O	-0.12661100	2.92153900	-1.11064200
C	-1.46431500	3.82199400	0.68082200
H	-4.28494800	-1.79967600	2.21072300
H	-6.58391800	-1.33451700	1.41044900
H	-6.97692500	-0.19686000	-0.75247800
H	-5.07422300	0.51651300	-2.17698200
H	-1.24215900	3.95841800	1.74317300
H	-1.39031400	4.77325300	0.14920600
H	-2.49515700	3.45618200	0.60458200
C	1.40071700	-1.57271000	-1.26036400
H	1.95175800	-1.17269900	-2.10759000
C	0.03219500	-1.85805800	-1.40994500
H	-0.41469400	-2.63424800	-0.79905300
H	-0.44538200	-1.65662200	-2.35907900
C	2.19969600	-2.33308100	-0.25731700
O	1.76514000	-2.77656500	0.79279400
O	3.46190200	-2.48396300	-0.68048100
C	4.37874200	-3.06536300	0.26233300
H	3.98624200	-4.00720900	0.65233400
H	5.30167900	-3.22891600	-0.29399000
H	4.54822600	-2.36114100	1.08002300
C	-1.39079100	-1.54409100	1.85405700
H	-1.97481600	-2.37914000	2.25271800
H	-0.38132100	-1.90101000	1.63568800
H	-1.33535700	-0.75242500	2.61126200
H	-2.05295200	0.51997200	-2.27137500
S	2.80915900	1.12868700	0.23395300
O	4.05948700	0.29097400	0.26703600
C	2.67659900	2.01544700	1.81645000
H	1.74864400	2.58791700	1.82273300
H	2.64196600	1.24801000	2.59297400
H	3.56422400	2.64102200	1.94157000

C	3.05867900	2.53029500	-0.89805800
H	3.29072300	2.09596700	-1.87334000
H	2.12489800	3.09589900	-0.96202600
H	3.90334700	3.12725800	-0.54308500

$PdCl_2$•L13

G_{sol} = -2115.218602 Hatree

C	2.95501100	-1.62713000	-0.24768000
C	1.98943300	-0.68460100	0.09740600
C	1.97211800	0.60774500	-0.46447500
C	2.98169300	0.91267900	-1.39143900
C	3.95378500	-0.02339100	-1.74508600
C	3.94875000	-1.29237100	-1.16842600
H	2.90476300	-2.61484100	0.19950000
H	2.98325900	1.89169800	-1.86012400
H	4.70753300	0.24103600	-2.48068000
H	4.70107600	-2.02576300	-1.44204200
C	1.01646000	1.68490700	-0.07708500
C	1.52670100	2.95301900	0.19008500
C	0.65913100	3.97978000	0.58236700
H	2.59412500	3.12327200	0.12341700
C	-1.15939600	2.42265100	0.39347600
C	-0.69054900	3.71957300	0.68427300
H	1.04724900	4.97053100	0.79956200
H	-1.41796200	4.47208000	0.96396300
N	-0.31864600	1.41871600	0.04468000
O	-2.46125100	2.21271100	0.50455300
S	0.66231700	-1.30317200	1.16998700
Pd	-1.13631200	-0.58146100	-0.14091300
O	0.97234000	-2.70989900	1.54965900
Cl	-1.98077800	-2.73083700	-0.20010400
C	0.84434900	-0.28720100	2.67196300
H	1.81670200	-0.52495500	3.11022500
H	0.76071300	0.77310600	2.43299400
H	0.03939600	-0.59368100	3.34393400
Cl	-2.81631700	0.15861400	-1.63721100
H	-2.75605700	1.46580700	-0.09294300

L13

G_{sol} = -1066.808903 Hatree

C	2.83747800	0.20068500	-0.22554600
C	1.46797700	-0.03367700	-0.12222500
C	0.55052700	1.04120800	-0.08714700
C	1.07643900	2.34342100	-0.16276300
C	2.44631300	2.57802700	-0.26204300
C	3.33341500	1.50333500	-0.28981700
H	3.49680000	-0.66264800	-0.24998300
H	0.39326600	3.18701500	-0.17630100
H	2.81370300	3.59828000	-0.32922700
H	4.40354000	1.67381700	-0.36956100
C	-0.92185600	0.86038600	0.01334700
C	-1.75154600	1.81444900	0.61568400
C	-3.13112200	1.58442700	0.64262600
H	-1.33461700	2.70290900	1.07474400
C	-2.74019900	-0.47721500	-0.47404500
C	-3.65551700	0.42676200	0.08623200
H	-3.79246800	2.31125000	1.10629500
H	-4.71634100	0.20442700	0.08173300
N	-1.42861800	-0.27529700	-0.50874400
O	-3.20670400	-1.62586600	-1.01254800
S	1.04349400	-1.83916600	-0.09604100
O	2.37458700	-2.56408900	-0.11510100
C	0.48262000	-1.88931400	1.66013600
H	1.31560700	-1.56873200	2.29066000
H	-0.39317800	-1.25581000	1.80813200
H	-2.42817900	-2.09946900	-1.35893000
H	0.23605800	-2.93263200	1.87486500

Cu(DMF)$_2$(OTf)$_2$

G_{sol} = -2616.906880 Hatree

Cu	0.00014800	0.00004500	-0.00030400
O	-2.28397900	0.64955700	1.67367900
S	-2.69029000	1.14830500	0.35005200
C	-4.18353700	0.15822500	-0.15326800
F	-3.95148500	-1.15270100	0.00881100
F	-5.22171700	0.50518300	0.61178400
F	-4.48314400	0.38872500	-1.43332000
O	-1.67044700	0.73812300	-0.72377300
O	-3.08766100	2.55325300	0.20910600
O	2.28405600	-0.65052100	-1.67376200
S	2.69038700	-1.14863200	-0.34991100
C	4.18351100	-0.15814100	0.15294700
F	5.22172100	-0.50532200	-0.61195800
F	3.95128000	1.15269000	-0.00973600
F	4.48316800	-0.38800200	1.43310400
O	3.08790900	-2.55345400	-0.20825700

O	1.67044800	-0.73804400	0.72365900
O	0.81599500	1.80930600	0.11183200
O	-0.81560900	-1.80929800	-0.11283700
C	0.27735500	2.89527300	-0.21060800
H	-0.74529700	2.93106600	-0.59227500
C	-0.27749400	-2.89510800	0.21095500
H	0.74484300	-2.93082100	0.59348500
N	0.89281300	4.07116500	-0.10127800
N	-0.89313800	-4.07095100	0.10206000
C	0.20024900	5.30953200	-0.44145400
H	0.16407900	5.97023300	0.43196900
H	0.72387800	5.82631300	-1.25362400
H	-0.82164700	5.08707900	-0.75531400
C	2.26039200	4.17455400	0.40222200
H	2.87318200	4.73005300	-0.31574700
H	2.26666900	4.70694800	1.36027800
H	2.66698300	3.17360000	0.53460600
C	-0.20103600	-5.30924800	0.44340600
H	-0.72552700	-5.82564600	1.25526100
H	-0.16406000	-5.97030700	-0.42971400
H	0.82056800	-5.08678000	0.75820400
C	-2.26028900	-4.17438200	-0.40258700
H	-2.66679600	-3.17343800	-0.53530300
H	-2.26579400	-4.70676200	-1.36066000
H	-2.87364000	-4.72989600	0.31488600

L13• HOTf

G_{sol} = -2028.805306 Hatree

C	1.84109500	-2.76643800	-0.44818100
C	1.70716500	-1.46333300	0.01995200
C	2.30659100	-0.38906700	-0.66409600
C	3.08223600	-0.66818100	-1.80076100
C	3.22679100	-1.97574000	-2.26303600
C	2.60005500	-3.02520700	-1.59077200
H	1.33867800	-3.55862700	0.10032100
H	3.54420800	0.15373700	-2.34035000
H	3.81556200	-2.16818700	-3.15498400
H	2.69938600	-4.04383000	-1.95479200
C	2.17648100	1.02726200	-0.23595800
C	3.26335400	1.84005900	0.02259100
C	3.04744500	3.18136100	0.39739100
H	4.26310600	1.42999800	-0.05140300
C	0.66865800	2.84035200	0.23728200
C	1.76992500	3.68333300	0.51323700
H	3.89870100	3.82334500	0.60470000
H	1.56296800	4.70631200	0.80238200
N	0.91519200	1.55299200	-0.12729800
O	-0.54057000	3.30379400	0.32252200
S	0.70190300	-1.27304200	1.55488000
O	0.14526100	-2.64158100	1.86013600
C	2.14443400	-1.04243200	2.67806900
H	2.79313200	-1.91923800	2.60790600
H	2.68909800	-0.13073300	2.41593400
H	-1.32185700	2.63282700	0.13766700
H	1.73941300	-0.95797000	3.69004800
H	0.09777500	0.94485300	-0.42586000
S	-2.47991600	0.53680400	-0.88698000
C	-3.29415300	-0.71371600	0.21830700
F	-4.55565100	-0.35087900	0.46653100
F	-2.63260800	-0.80018400	1.38012400
F	-3.28970200	-1.90933200	-0.37498800
O	-3.27399500	0.58188300	-2.10980400
O	-1.07729500	0.01990100	-1.03112600
O	-2.50554200	1.78230700	-0.03873300

$Cu(DMF)_2Cl_2$

G_{sol} = -1614.584496 Hatree

Cu	-0.00000100	-0.23076000	0.08637400
Cl	-0.00083400	-2.34882300	0.91713200
Cl	0.00020500	2.07555900	0.37726700
C	-2.81791500	0.46542600	-0.06249900
H	-2.55229500	1.39579400	0.45072900
N	-4.12415300	0.25528200	-0.25896800
O	-1.93623100	-0.33322500	-0.43960300
C	-5.11646300	1.23659900	0.15669900
H	-5.82010700	0.78777700	0.86740800
H	-4.62096900	2.08369000	0.63636700
H	-5.67977300	1.60163800	-0.71033000
C	-4.60264300	-0.95700500	-0.91700000
H	-3.75731200	-1.62561100	-1.07572400
H	-5.34804000	-1.44940000	-0.28299200
H	-5.06448600	-0.70912900	-1.88010300
C	2.81817500	0.46514400	-0.06231600
H	2.55248800	1.39616500	0.44969200
N	4.12442100	0.25505000	-0.25887700
O	1.93659000	-0.33425700	-0.43803700

C	5.11659300	1.23715600	0.15518900
H	4.62102500	2.08479700	0.63381100
H	5.82053500	0.78950300	0.86634700
H	5.67961200	1.60115300	-0.71247000
C	4.60298400	-0.95796000	-0.91555000
H	5.34893900	-1.44919500	-0.28130600
H	3.75780300	-1.62708500	-1.07288500
H	5.06417000	-0.71121600	-1.87926000

Cu(OTf)$_2$·L13

G_{sol} = -3187.009812 Hatree

C	-3.44802700	0.58579200	-2.45064100
C	-2.81414900	0.77646000	-1.22512300
C	-3.25990100	0.15264100	-0.04528900
C	-4.40068700	-0.65958600	-0.14554300
C	-5.05084300	-0.85061700	-1.36477900
C	-4.57971600	-0.22664300	-2.51926700
H	-3.04003400	1.07008500	-3.33221800
H	-4.75845700	-1.17349900	0.74097500
H	-5.91885900	-1.50140000	-1.41035600
H	-5.07928300	-0.37899400	-3.47106300
C	-2.64741800	0.33714600	1.30243900
C	-3.48459100	0.61620600	2.37842900
C	-2.94186100	0.75209300	3.66368600
H	-4.54627900	0.74551100	2.20739700
C	-0.79152200	0.25701200	2.73247300
C	-1.58978600	0.56060500	3.85150500
H	-3.58659700	0.98461300	4.50605700
H	-1.11405400	0.60576100	4.82370000
N	-1.29585100	0.21450700	1.47706600
O	0.49751700	0.02182000	2.94561100
S	-1.29053400	1.74657900	-1.26898600
O	-1.01955500	2.16720000	-2.67808700
C	-1.71972500	3.21826700	-0.28852000
H	-2.45462000	3.78708800	-0.86333000
H	-2.11998300	2.91499600	0.68049100
H	-0.78804000	3.77215400	-0.16142200
H	0.87254500	-0.57716500	2.24550500
Cu	0.14765700	0.20336300	-0.02341200
O	1.65893800	0.64954100	-1.17415900
O	1.10149100	-1.41177200	0.79226300
S	0.29674800	-2.60435400	0.21936100
S	2.28418200	1.97404900	-0.70531100
C	1.60138700	-3.46607300	-0.79352700
C	3.69093600	1.38190400	0.36309700
F	2.06301800	-2.64214300	-1.73137700
F	1.05622900	-4.53878200	-1.37235500
F	2.60277800	-3.84992700	-0.00141400
F	4.51927600	0.61867600	-0.34777600
F	4.35739400	2.43418200	0.84260800
F	3.20874800	0.66809500	1.39138700
O	2.88364500	2.75554600	-1.77716700
O	1.34250500	2.63130400	0.23934500
O	-0.68236700	-2.05592100	-0.74976900
O	-0.15409100	-3.54906400	1.23564100

Int-3

G_{sol} = -1654.375654 Hatree

C	2.67450200	-1.98368100	-0.23496300
C	1.73235000	-0.97244800	-0.02161100
C	2.10469600	0.39752200	-0.03859800
C	3.47000600	0.66356700	-0.26638100
C	4.41265300	-0.34232500	-0.45100900
C	4.01740100	-1.67784000	-0.43676400
H	2.33373400	-3.01351700	-0.25734800
H	3.79199300	1.69509900	-0.34261300
H	5.45031400	-0.07598100	-0.62920100
H	4.73684400	-2.47464400	-0.59843600
C	1.19400100	1.56966200	0.10166700
C	1.63273700	2.85075900	0.43997500
C	0.70682200	3.91393200	0.45079000
H	2.66397400	3.03575400	0.71014400
C	-1.05239400	2.40442500	-0.13578100
C	-0.63021500	3.72509600	0.15456700
H	1.05990600	4.90891400	0.70895300
H	-1.35620000	4.52958400	0.17417400
N	-0.11281200	1.41020800	-0.17437900
O	-2.24649600	1.96508100	-0.34458500
S	0.05409500	-1.68688400	0.23561800
Pd	-1.46131700	-0.07780200	-0.24804100
O	0.06957400	-3.07301400	-0.30720400
Cl	-3.26773300	-1.54508300	-0.14813100
C	-0.00865800	-1.77785800	2.05122000
H	0.78903800	-2.44738600	2.38374200
H	0.11134200	-0.77361500	2.46480300

H	-0.99277000	-2.18164800	2.30029700

Int-4

G_{sol} = -2057.179774 Hatree

C	-3.55009400	-2.19894700	-0.06268300
C	-2.86851400	-0.98846700	-0.17183900
C	-2.97556700	0.02537200	0.80342800
C	-3.80724100	-0.24313700	1.90364800
C	-4.49739100	-1.44920900	2.02227600
C	-4.37751000	-2.42902900	1.03657000
H	-3.41132700	-2.94658100	-0.83732900
H	-3.89390500	0.50626500	2.68398600
H	-5.12246100	-1.62406800	2.89348900
H	-4.91067000	-3.37088200	1.12597300
C	-2.33009900	1.36167400	0.67587800
C	-3.05869100	2.49264900	1.01174700
C	-2.47873700	3.76625000	0.80304300
H	-4.07493800	2.39681100	1.37349500
C	-0.49033700	2.69609700	-0.15567000
C	-1.23554100	3.87280700	0.24351500
H	-3.03814200	4.65924900	1.07288500
H	-0.76530300	4.83082600	0.04886800
N	-1.07218700	1.45534400	0.15480000
O	0.61102400	2.73878800	-0.72919300
S	-1.71335200	-0.88723800	-1.57350700
Pd	0.16968700	-0.16467100	-0.35051100
O	-1.82554300	-2.14927500	-2.36534100
Cl	1.42195300	-2.04153300	-1.03791300
C	-2.42537000	0.44755200	-2.59109800
H	-3.39310500	0.09306800	-2.95425500
H	-2.52007700	1.36128300	-2.00578200
H	-1.73465600	0.59623400	-3.42418600
C	3.01004900	0.72946500	0.45385500
C	3.75984600	-0.41375300	0.79961700
C	5.05339500	-0.63888300	0.33118200
C	5.60190200	0.34118700	-0.49401700
C	4.87585400	1.49598200	-0.83767100
C	3.57760200	1.70179000	-0.37618100
C	1.70816000	0.60071900	1.10801500
C	1.79675700	-0.59559100	1.86596300
H	5.61118000	-1.53455900	0.58619000
H	6.60781200	0.20651600	-0.88156400
H	5.33564100	2.23635300	-1.48636800
H	2.99291800	2.56842000	-0.66327100
H	1.11579400	1.44464500	1.43216600
H	1.06575500	-1.02642200	2.53688300
C	3.32817800	-2.54244600	2.09741400
H	3.27716800	-3.22627700	1.24528200
H	4.33719200	-2.54556200	2.51925400
H	2.62097800	-2.86713000	2.86312700
N	2.97950600	-1.19678000	1.66943000

TS-1a

G_{sol} = -2057.161473 Hatree

C	-3.54783000	-0.65488400	2.04758500
C	-2.86058200	-0.27254900	0.89811600
C	-2.53125700	1.07172100	0.63688100
C	-2.93609900	2.02102800	1.59066000
C	-3.62669000	1.65012600	2.74460600
C	-3.94037400	0.31139900	2.97430100
H	-3.75499900	-1.70967400	2.20000300
H	-2.68276600	3.06398700	1.42814100
H	-3.90930800	2.41081400	3.46667900
H	-4.47463800	0.01585800	3.87241300
C	-1.86031100	1.56187000	-0.60465700
C	-2.40669700	2.66751300	-1.24695700
C	-1.78974400	3.16424300	-2.40799300
H	-3.31399000	3.11724400	-0.86284300
C	-0.10621000	1.43628900	-2.19694900
C	-0.64715600	2.56512000	-2.87873500
H	-2.21398100	4.02186500	-2.92347300
H	-0.11895300	2.91556200	-3.75765000
N	-0.74626900	0.93452200	-1.08754500
O	0.98128600	0.89170600	-2.61726500
S	-2.28618200	-1.64284500	-0.14914000
Pd	0.02921100	-0.94073900	-0.37382500
O	-2.79189200	-2.92290800	0.44055100
Cl	0.81466000	-3.03669900	0.31362700
C	-3.23919300	-1.34183400	-1.67844900
H	-4.29927100	-1.45227900	-1.43742100
H	-3.02054400	-0.34915700	-2.07442900
H	-2.92856000	-2.11206900	-2.38829100
C	2.52385000	0.74457500	0.44742700
C	3.88225800	0.41218900	0.67689100
C	4.72490900	1.16384600	1.49599500
C	4.17485000	2.28295900	2.11839800

C	2.82811100	2.63237500	1.91584800
C	2.00160500	1.87732600	1.08615100
C	1.98266200	-0.23461900	-0.49807700
C	3.04531100	-1.12406700	-0.71915500
H	5.76611700	0.89365400	1.64741700
H	4.79613400	2.89184800	2.76911800
H	2.42599300	3.50782600	2.41869500
H	0.96168000	2.15460500	0.94232500
H	1.52014300	0.28120800	-1.66158700
H	3.05472400	-2.01559600	-1.33026300
C	5.45704300	-1.40329800	-0.10785300
H	6.21810300	-0.73798500	-0.53067700
H	5.76543500	-1.70249300	0.89940600
H	5.37690100	-2.29580900	-0.73090600
N	4.16510700	-0.74228800	-0.06196900

Int-5a

G_{sol} = -2057.17338 Hatree

C	-3.92444100	-1.14296200	1.44306200
C	-3.09899800	-0.49271100	0.52978700
C	-2.81170100	0.88257800	0.64248400
C	-3.40431600	1.57782600	1.70962300
C	-4.23289000	0.93365200	2.62881100
C	-4.50009100	-0.42778300	2.49421800
H	-4.09305100	-2.20826100	1.31695300
H	-3.19099300	2.63604700	1.82783300
H	-4.66059900	1.49820500	3.45220800
H	-5.14211400	-0.93623700	3.20744400
C	-1.99841000	1.66252000	-0.33614900
C	-2.52237000	2.85741900	-0.82627400
C	-1.78465000	3.61192400	-1.74653400
H	-3.50856900	3.17545900	-0.51065900
C	-0.05959700	1.95334100	-1.61406400
C	-0.54227900	3.16486800	-2.14519000
H	-2.18785500	4.54033200	-2.14048900
H	0.08442000	3.70579100	-2.84406400
N	-0.77621100	1.20571400	-0.74353000
O	1.13887600	1.54850400	-2.01084600
S	-2.30374800	-1.58220300	-0.70020700
Pd	0.01711200	-0.75147900	-0.21269600
O	-2.84559100	-2.96590100	-0.49972200
Cl	0.76948400	-2.88392200	0.29566000
C	-3.06106200	-0.94155500	-2.23980800
H	-4.13770300	-1.11864400	-2.18089900
H	-2.84019400	0.11922400	-2.36913800
H	-2.62749300	-1.52203800	-3.05771400
C	3.13980700	-0.36770400	0.05932900
C	3.99811900	0.48990000	0.80791900
C	5.39412200	0.42055400	0.71729200
C	5.93475200	-0.53163900	-0.13880700
C	5.10549900	-1.39519800	-0.88452500
C	3.72142200	-1.32257500	-0.79374000
C	1.78053600	0.01439000	0.38099200
C	1.87993800	1.03518300	1.30257900
H	6.03357800	1.08456500	1.29280700
H	7.01450300	-0.61395600	-0.23142400
H	5.56097300	-2.13594000	-1.53625900
H	3.08688300	-2.00636500	-1.34789000
H	1.47881200	0.86146800	-1.37461200
H	1.10092700	1.58465000	1.81428500
C	3.69134400	2.34854000	2.47495900
H	4.32422500	1.90938000	3.25549200
H	4.27369700	3.11041300	1.94161100
H	2.83843700	2.83473500	2.95423600
N	3.20606800	1.32956100	1.56926300

Int-6a

G_{sol} = -1596.32415 Hatree

C	-3.29580400	2.59439600	-0.20815800
C	-2.71130900	1.34578400	0.01521600
C	-3.46058100	0.14550300	-0.11552300
C	-4.81533500	0.29638100	-0.46825700
C	-5.40462900	1.54058000	-0.67347300
C	-4.64342700	2.69983300	-0.54664800
H	-2.67522000	3.47961000	-0.11629500
H	-5.40956500	-0.59672500	-0.62524500
H	-6.45290400	1.59700500	-0.95239400
H	-5.08365200	3.67731900	-0.71925700
C	-2.93054500	-1.24245600	0.01879500
C	-3.72765500	-2.35338800	0.30134500
C	-3.12551700	-3.62756000	0.29956700
H	-4.77973900	-2.24895900	0.53527900
C	-0.99350600	-2.63709000	-0.19250000
C	-1.77713600	-3.79847300	0.04121200
H	-3.74150900	-4.49801800	0.51184000
H	-1.30316400	-4.77354800	0.04323200

N	-1.62148300	-1.42229100	-0.21020200
O	0.28085600	-2.56839500	-0.37150500
S	-0.93626800	1.51345000	0.50732500
Pd	0.16022700	-0.33475400	-0.23028100
O	-0.55427500	2.95036300	0.31253000
C	-1.09242500	1.22871200	2.30161000
H	-1.75328200	1.99907800	2.70775300
H	-1.49110600	0.22599400	2.47119700
H	-0.08619400	1.31534000	2.71695000
C	3.21853500	-0.37744000	-0.06203600
C	4.30854600	0.54182000	-0.11234400
C	5.64262000	0.12523500	-0.02836600
C	5.88401500	-1.23735500	0.11384800
C	4.82201100	-2.16292900	0.16801800
C	3.49758800	-1.74851200	0.08135300
C	2.00867300	0.40709600	-0.18121400
C	2.40444100	1.71991000	-0.28509100
H	6.46275800	0.83717100	-0.07266800
H	6.90896600	-1.59294600	0.18206500
H	5.04572300	-3.22106800	0.27711800
H	2.68366500	-2.46624800	0.11484900
H	1.80489300	2.61587300	-0.37843600
C	4.56203300	3.03181600	-0.36185200
H	5.21498800	3.16546300	0.50967700
H	5.18580500	3.02565900	-1.26494400
H	3.87977400	3.88322400	-0.41696700
N	3.78768100	1.81548000	-0.24826300

Int-7a

G_{sol} = -1902.630546 Hatree

C	1.60691400	-0.39711600	-3.33007900
C	1.71024600	-0.71315500	-1.97546600
C	2.86738900	-0.42249000	-1.22187500
C	3.91893300	0.21119600	-1.90696200
C	3.82910500	0.52880200	-3.26118600
C	2.67420700	0.22114900	-3.98051200
H	0.68713300	-0.63971900	-3.85247800
H	4.81288700	0.47380400	-1.35073900
H	4.66174600	1.02655300	-3.75049800
H	2.59659700	0.46777800	-5.03529400
C	3.04457600	-0.79544100	0.20888000
C	4.27233400	-1.28190400	0.63662000
C	4.40695800	-1.68154100	1.98638700
H	5.09236600	-1.39554000	-0.06190900
C	2.05115900	-1.13357200	2.37268600
C	3.33747700	-1.60680300	2.83796800
H	5.36376600	-2.06077000	2.33897200
H	3.39988100	-1.91444700	3.87647200
N	1.97720400	-0.70134900	1.04537000
O	1.03067200	-1.08984600	3.09173600
S	0.19165700	-1.42743900	-1.26425700
Pd	-0.06074700	-0.01592000	0.60642600
O	-0.80381300	-1.58391900	-2.36950500
C	0.72594600	-3.10092100	-0.77428200
H	1.03295500	-3.62191800	-1.68436100
H	1.53451700	-3.03666100	-0.04654000
H	-0.15187900	-3.58118400	-0.33633300
C	-3.04791300	-0.61701700	0.24802900
C	-4.20578900	-0.04273500	-0.35786500
C	-5.43852200	-0.70509100	-0.38190800
C	-5.51248700	-1.95770700	0.21973100
C	-4.38547500	-2.53875200	0.83548800
C	-3.16118500	-1.87991100	0.85560000
C	-1.97578100	0.33084000	0.07810800
C	-2.50517500	1.40673600	-0.58799700
H	-6.31114900	-0.26059800	-0.85318600
H	-6.45723900	-2.49484800	0.21786800
H	-4.47936500	-3.51454900	1.30473100
H	-2.30098500	-2.32823600	1.34873300
H	-2.04409600	2.34098300	-0.87552400
C	-4.72682400	2.09182900	-1.58092400
H	-5.03160800	1.66469400	-2.54507800
H	-5.62833000	2.31383400	-0.99725400
H	-4.19787700	3.02939400	-1.76657500
N	-3.85274200	1.19488500	-0.85672000
C	-0.77971100	1.25754400	2.46680000
H	-1.74306600	1.69358500	2.23387800
H	-0.71058300	0.44926700	3.18656900
C	0.37038300	1.81555600	1.97522100
H	1.34063400	1.49135300	2.33147200
C	0.34467700	3.05087400	1.13688600
O	-0.65039200	3.65405100	0.78682300
O	1.60163000	3.43275600	0.82581100
C	1.70283600	4.62171300	0.02701300
H	1.23393400	5.46740500	0.53718500
H	2.77088800	4.79516300	-0.10466100

H	1.21504400	4.47438000	-0.94059600

TS-2a

G_{sol} = -1902.623332 Hatree

C	0.38121700	3.43694500	0.54551600
C	0.97336200	2.32717900	-0.05454700
C	2.20399800	1.79665900	0.39138600
C	2.80912100	2.44699900	1.48043300
C	2.22871400	3.56071700	2.08627700
C	1.01531400	4.06434400	1.61779300
H	-0.57487700	3.78530200	0.16756400
H	3.74436200	2.05171800	1.86399900
H	2.72334600	4.02745000	2.93357900
H	0.55605100	4.92805300	2.08946100
C	2.90371000	0.65616500	-0.26583500
C	4.27859800	0.71625900	-0.44524900
C	4.91676900	-0.33920500	-1.13757200
H	4.83831400	1.57959700	-0.10640200
C	2.74231800	-1.41309900	-1.49212200
C	4.18166900	-1.37765000	-1.64261400
H	5.99504200	-0.31020100	-1.27996900
H	4.63516300	-2.19551800	-2.19255300
N	2.16569800	-0.38430600	-0.73910100
O	2.01769200	-2.29848000	-1.99107600
S	-0.03367400	1.53845700	-1.35084000
Pd	0.04931000	-0.68679900	-0.51718900
O	-1.28384500	2.34531700	-1.54169100
C	0.99502500	1.79042900	-2.83756100
H	1.05803500	2.86807900	-3.00690500
H	1.97771900	1.34242800	-2.69415400
H	0.46953600	1.30371100	-3.66236200
C	-2.87552000	-0.24801100	0.56503600
C	-4.15607700	-0.09267700	-0.03773500
C	-5.24295300	0.46082600	0.64761600
C	-5.03866900	0.84802500	1.96828800
C	-3.78555300	0.68166300	2.59144000
C	-2.70445200	0.13856600	1.90511000
C	-2.00828500	-0.82972100	-0.43497200
C	-2.79259700	-1.02748500	-1.55299700
H	-6.21119200	0.58650900	0.17086600
H	-5.86227100	1.28112800	2.52962100
H	-3.66434800	0.98230400	3.62866600
H	-1.74742100	-0.00811500	2.39738200
H	-2.53139400	-1.45297100	-2.51342500
C	-5.15593800	-0.55814300	-2.30136500
H	-6.04725300	-1.05996500	-1.90726500
H	-5.42184700	0.47164100	-2.56965500
H	-4.83347800	-1.08220700	-3.20388100
N	-4.08215000	-0.58550100	-1.33003500
C	-1.04360200	-2.71983700	0.31342700
H	-1.72458200	-2.60602600	1.14805000
H	-1.39608500	-3.28231700	-0.54192000
C	0.33172300	-2.60048400	0.53246600
H	1.03917000	-3.04650600	-0.15980600
C	0.81582400	-2.23997800	1.89319100
O	0.13096300	-1.79118800	2.79540400
O	2.13459200	-2.49721700	2.01658100
C	2.70759100	-2.17392900	3.29133200
H	2.21941200	-2.74094100	4.08884000
H	3.76048000	-2.44632000	3.21493600
H	2.60073700	-1.10554600	3.49923300

Int-8a

G_{sol} = -1902.67238 Hatree

C	-0.31387200	3.22645300	1.01425100
C	0.46697700	2.32521500	0.29401900
C	1.71160900	1.85780300	0.77250300
C	2.12970000	2.35278300	2.01954300
C	1.35939600	3.25967300	2.74647900
C	0.13634000	3.70425400	2.24507900
H	-1.26913300	3.53324200	0.59982500
H	3.07106000	1.99794600	2.42684600
H	1.71371400	3.60898600	3.71232900
H	-0.47058300	4.40587200	2.80980800
C	2.60884200	0.94576300	0.00724900
C	3.97309500	1.19641500	-0.01572700
C	4.80063500	0.36328700	-0.80621100
H	4.38295900	2.04442400	0.51953000
C	2.82398300	-0.87819800	-1.56669100
C	4.25492700	-0.64339300	-1.55455000
H	5.87393600	0.54096400	-0.82604600
H	4.85818900	-1.29187900	-2.18114500
N	2.05904300	-0.06876200	-0.71396300
O	2.27157100	-1.73340400	-2.28052300
S	-0.29897500	1.69781600	-1.23704200
Pd	0.03795700	-0.68590300	-0.67434700

O	-1.62595800	2.40075100	-1.41979400
C	0.83276600	2.38933100	-2.49501200
H	0.76198000	3.47787100	-2.43117300
H	1.84950800	2.03964900	-2.31686800
H	0.47463600	2.03910500	-3.46596200
C	-2.71138600	-1.05780700	0.61782200
C	-3.53668200	-0.21080000	-0.16197500
C	-4.44464500	0.68290600	0.41242200
C	-4.53342600	0.69222700	1.80125700
C	-3.73239600	-0.15498300	2.59232900
C	-2.81592800	-1.02905600	2.01672800
C	-1.89302700	-1.82885500	-0.31080800
C	-2.28715200	-1.40224800	-1.59130300
H	-5.05246700	1.34598500	-0.19500700
H	-5.23202300	1.37019800	2.28392600
H	-3.82653300	-0.11566400	3.67399100
H	-2.16690700	-1.65260500	2.62267100
H	-1.98753700	-1.79845500	-2.55314100
C	-3.81697000	0.30352200	-2.61832900
H	-4.90989000	0.30935900	-2.55711400
H	-3.43481600	1.32829300	-2.59689800
H	-3.52321900	-0.17757600	-3.55410900
N	-3.26520800	-0.45553300	-1.50678200
C	-1.05336100	-3.07257200	-0.01215300
H	-1.40202800	-3.53959900	0.91430800
H	-1.16191100	-3.79706400	-0.82592700
C	0.38521300	-2.58987300	0.09492800
H	1.10952000	-3.01007900	-0.59874700
C	0.88996800	-2.43968300	1.48295600
O	0.19774900	-2.37574200	2.48912400
O	2.24293600	-2.39852300	1.53000800
C	2.80746800	-2.20521900	2.83145000
H	2.52078400	-3.01784700	3.50534000
H	3.88780700	-2.19414900	2.68251500
H	2.47084400	-1.25675000	3.26085300

TS-3a

G_{sol} = -1902.647763 Hatree

C	-3.76533700	-2.72113000	0.20917700
C	-3.09653800	-1.60890900	-0.29953000
C	-3.59818300	-0.29673200	-0.15253600
C	-4.81121000	-0.16804800	0.54719600
C	-5.49025500	-1.27316700	1.05791100
C	-4.97428200	-2.55693800	0.88441800
H	-3.31899500	-3.70131000	0.07357700
H	-5.21168500	0.82769100	0.70632600
H	-6.41922000	-1.12561300	1.60169600
H	-5.49597400	-3.42222700	1.28266800
C	-2.96511400	0.92264100	-0.73517800
C	-3.78071400	1.89807900	-1.29356400
C	-3.17554300	3.03690200	-1.87167000
H	-4.85534600	1.76578000	-1.32012300
C	-0.96604600	2.11230000	-1.35387100
C	-1.81228100	3.15348600	-1.89625900
H	-3.80133700	3.81347700	-2.30658400
H	-1.31081300	4.00720400	-2.33947600
N	-1.60816600	1.02924700	-0.74697100
O	0.27980200	2.15102900	-1.41630700
S	-1.47100700	-1.98418500	-1.03194400
Pd	-0.18887400	-0.36492100	0.09571900
O	-1.26252500	-3.47016600	-0.97416400
C	-1.74380400	-1.54425100	-2.78078600
H	-2.50645800	-2.22276800	-3.17115900
H	-2.04972700	-0.50099900	-2.85934200
H	-0.79212700	-1.70355800	-3.29300800
C	3.72101700	0.15251500	-0.21533100
C	5.04800900	-0.35421600	-0.22980300
C	5.95761800	-0.05741400	-1.24840300
C	5.51096600	0.76281400	-2.28006900
C	4.19503200	1.26264300	-2.29287500
C	3.29010000	0.96816000	-1.27641700
C	3.09639100	-0.37471100	0.98161800
C	4.04808100	-1.16699100	1.60008500
H	6.96960000	-0.45206700	-1.24143200
H	6.18914800	1.01631000	-3.09036900
H	3.87443500	1.89439400	-3.11647900
H	2.27579900	1.35477300	-1.32108400
H	3.96640400	-1.73650800	2.51703100
C	6.44127400	-1.84898800	1.25100200
H	6.72869500	-2.55568400	0.46424100
H	7.26226400	-1.13913500	1.40374000
H	6.27990100	-2.40344700	2.17772400
N	5.21926800	-1.15498700	0.89500400
C	1.77669400	-0.16949100	1.55134700
H	0.89442900	-1.35103500	0.76317000
H	1.58947900	-0.69354300	2.48864500

C	0.93716900	0.96775500	1.35606400
H	1.22047300	1.77011400	0.68459800
C	0.00903600	1.31046600	2.46729500
O	-0.24781200	0.59596600	3.42126400
O	-0.51263600	2.54351800	2.29760800
C	-1.44577900	2.95864900	3.30393000
H	-0.97078100	2.97401500	4.28897100
H	-1.76036000	3.96140800	3.01356100
H	-2.30364700	2.28091900	3.33520600

TS-1b

G_{sol} = -2057.156332 Hatree

C	-3.60948800	-1.65186400	1.60947900
C	-2.97499900	-0.76438100	0.74356700
C	-2.82945500	0.60270000	1.04805900
C	-3.36333700	1.04035600	2.27186100
C	-4.00258800	0.16157200	3.14665900
C	-4.13342000	-1.18638400	2.81587100
H	-3.67240500	-2.69783100	1.32577100
H	-3.25143100	2.08473600	2.54573200
H	-4.38837600	0.53372700	4.09135100
H	-4.62654200	-1.87602000	3.49443500
C	-2.22248100	1.62017600	0.13884500
C	-2.90586600	2.81628200	-0.05003500
C	-2.35501800	3.80056600	-0.88808000
H	-3.86591200	2.96639800	0.42813400
C	-0.45840400	2.34719300	-1.26891900
C	-1.13957900	3.57842600	-1.48820600
H	-2.88694800	4.73406100	-1.05123500
H	-0.65693400	4.30799900	-2.12766100
N	-1.03259600	1.37311800	-0.48690300
O	0.69967600	2.14819900	-1.79720700
S	-2.21635100	-1.52584200	-0.72013900
Pd	-0.02846000	-0.53034600	-0.53713900
O	-2.54509600	-2.98457300	-0.71260500
Cl	0.98157500	-2.63112900	-0.62842800
C	-3.17801000	-0.76235000	-2.07128600
H	-4.21789400	-1.07918800	-1.96022900
H	-3.08427300	0.32390500	-2.03799600
H	-2.75870500	-1.15328700	-3.00129700
C	2.10977800	0.81845600	1.06196900
C	3.47608600	0.59035900	1.34313500
C	4.31103200	0.83084400	2.45849300
C	1.84439800	0.39827900	-0.25363800
H	1.28325700	1.29359600	-1.09740200
H	1.37709400	1.25848500	1.72616600
H	3.90174000	1.27365900	3.36274900
C	5.64748000	0.49060400	2.37794400
C	4.03385200	0.00210900	0.16294000
C	5.39988000	-0.33012900	0.08218600
C	6.18393600	-0.08520200	1.19661900
N	3.04717500	-0.11614200	-0.77118000
C	3.23526400	-0.62311600	-2.11865700
H	4.10091600	-0.14017200	-2.58608900
H	3.37148400	-1.70843700	-2.10839400
H	2.34261200	-0.39645400	-2.70267400
H	6.30351500	0.66235600	3.22659600
H	7.23887700	-0.34513600	1.17036900
H	5.82084800	-0.77865400	-0.81220000

Int-5b

G_{sol} = -2057.173693 Hatree

C	-3.88284500	-0.76932200	1.73705500
C	-3.08519900	-0.21350100	0.74061700
C	-2.61813700	1.11395500	0.82009100
C	-3.00046300	1.86280500	1.94536200
C	-3.79966100	1.31378100	2.94842100
C	-4.24899300	-0.00151000	2.84351600
H	-4.19399000	-1.80428800	1.63200700
H	-2.64313000	2.88362600	2.04143400
H	-4.06096100	1.91540200	3.81399800
H	-4.86895600	-0.43544500	3.62234700
C	-1.82677000	1.80021400	-0.24245900
C	-2.24443900	3.05995800	-0.66812700
C	-1.52478100	3.73008600	-1.66444300
H	-3.13890300	3.49634100	-0.24068300
C	-0.02405600	1.86611000	-1.73150000
C	-0.40213600	3.13615400	-2.20329100
H	-1.84666900	4.70928200	-2.00652800
H	0.20829500	3.60646200	-2.96471700
N	-0.72774400	1.19974000	-0.79007700
O	1.06226500	1.31422300	-2.26086800
S	-2.55683900	-1.37668400	-0.56004000
Pd	-0.12303000	-0.84122500	-0.31812400
O	-3.23065500	-2.69093200	-0.30655000
Cl	0.38961200	-3.04041800	0.21389000

C	-3.36987800	-0.64039100	-2.02476700
H	-4.44958100	-0.67576600	-1.86075200
H	-3.02540700	0.38227700	-2.18543100
H	-3.09657100	-1.27091300	-2.87428100
C	2.06696000	0.69846700	1.04106100
C	3.49318900	0.76713300	1.14807500
C	4.39114200	1.55162300	1.89483100
C	1.75815300	-0.28121700	0.11581200
H	1.37370400	0.59214400	-1.65815200
H	1.34932000	1.28935900	1.59383600
H	4.01913300	2.30063400	2.58982300
C	5.75632000	1.35209400	1.73508400
C	4.01150600	-0.20691400	0.24904900
C	5.38842600	-0.40638900	0.08193100
C	6.24990700	0.38200100	0.83715200
N	2.94573400	-0.83394900	-0.37153900
C	3.10494900	-1.89235800	-1.35345900
H	3.80077800	-1.57185000	-2.13827100
H	3.48696500	-2.80561100	-0.88493800
H	2.13701000	-2.12344000	-1.79521700
H	6.45878500	1.94942200	2.31053400
H	7.32336300	0.24532800	0.73642700
H	5.77421900	-1.15613200	-0.60264000

Int-6b

G_{sol} = -1596.324778 Hatree

C	-2.92534300	2.91199300	-0.16067400
C	-2.53846500	1.58467000	0.03870600
C	-3.46011300	0.51635600	-0.12453000
C	-4.77310000	0.87800300	-0.48207000
C	-5.16544600	2.20122200	-0.66183300
C	-4.23831600	3.22802300	-0.50412400
H	-2.17857500	3.69080400	-0.04757700
H	-5.49417600	0.08964800	-0.66501800
H	-6.19034200	2.42210600	-0.94556500
H	-4.52300500	4.26460100	-0.65711200
C	-3.14840000	-0.93801900	-0.02277600
C	-4.10918700	-1.92237100	0.21822800
C	-3.71160700	-3.27300000	0.18483900
H	-5.13628200	-1.66445400	0.44359700
C	-1.45079300	-2.60840900	-0.25672500
C	-2.40148800	-3.64254700	-0.06597200
H	-4.45732600	-4.04332200	0.36476900
H	-2.08236900	-4.67828500	-0.09062000
N	-1.87857700	-1.31205600	-0.24162200
O	-0.17408000	-2.72995300	-0.42557800
S	-0.75891200	1.48065500	0.53936100
Pd	0.05353400	-0.52916800	-0.21430300
O	-0.17144700	2.84312300	0.34965300
C	-0.95704700	1.20859400	2.33088900
H	-1.50047700	2.06343600	2.74186900
H	-1.49676400	0.27293900	2.49404600
H	0.05118400	1.14999100	2.74649800
C	2.54289700	1.20218600	-0.42219400
C	3.96782100	1.06717200	-0.34365800
C	5.05317600	1.94449300	-0.51601200
C	1.98996300	-0.03430100	-0.15447600
H	1.99114400	2.10508400	-0.64395100
H	4.88021900	2.98601300	-0.77629100
C	6.34643900	1.46320900	-0.34847500
C	4.22862400	-0.29092900	-0.00565000
C	5.52991800	-0.77892100	0.16670100
C	6.58241700	0.11463800	-0.01004900
N	3.01493200	-0.94656400	0.10292700
C	2.89213900	-2.34198200	0.48161700
H	3.50014200	-2.96852200	-0.18191800
H	3.23467600	-2.49821600	1.51352600
H	1.85393000	-2.65962800	0.39525800
H	7.19169500	2.13407100	-0.47961100
H	7.60435200	-0.23392100	0.11535400
H	5.71718800	-1.81656300	0.42859300

Int-7b

G_{sol} = -1902.633146 Hatree

C	1.17513100	2.57574800	2.29108800
C	1.53755700	1.88283400	1.13688900
C	2.71472500	1.10775300	1.05698300
C	3.51483000	1.06554100	2.21129000
C	3.16683100	1.75675800	3.37119400
C	1.99885200	2.51847400	3.41505400
H	0.25109800	3.14509400	2.29226300
H	4.41508100	0.45976700	2.19463700
H	3.80778100	1.68981100	4.24581000
H	1.72171400	3.05520100	4.31735800
C	3.16218000	0.40963900	-0.18031600
C	4.50496600	0.43263300	-0.52885500

C	4.89681600	-0.16896500	-1.74783600
H	5.22629800	0.94511000	0.09595300
C	2.55865000	-0.72669300	-2.21637700
C	3.96165100	-0.73653900	-2.57135900
H	5.94660000	-0.16321300	-2.03293200
H	4.22480900	-1.19450100	-3.51895400
N	2.22583200	-0.17143900	-0.97779900
O	1.65516000	-1.18986200	-2.94431600
S	0.31608000	1.96980500	-0.20682500
Pd	0.07543400	-0.33227600	-0.63049300
O	-0.79395900	2.88340400	0.20717200
C	1.23564300	2.82321400	-1.53263300
H	1.45908300	3.82680600	-1.16264300
H	2.13866300	2.27042300	-1.78685700
H	0.56119400	2.87502900	-2.39008200
C	-0.62998600	-2.47849700	-1.35476700
H	-1.64878300	-2.64832500	-1.02748600
H	-0.41779600	-2.30834900	-2.40480500
C	0.41189700	-2.64488600	-0.48183600
H	1.43464300	-2.64175500	-0.83674100
C	0.18791800	-3.10437500	0.92262300
O	-0.88310000	-3.40993400	1.40424300
O	1.35949900	-3.16010500	1.59128300
C	1.26573300	-3.61001800	2.95271100
H	0.82704100	-4.61042700	2.99546100
H	2.28917000	-3.62106500	3.32759200
H	0.64748300	-2.92480200	3.53907800
C	-2.56429800	-0.63740300	0.88729300
C	-3.93636500	-0.23191300	0.75865100
C	-5.08111500	-0.36581500	1.56272900
C	-1.90313100	-0.21870800	-0.24482700
H	-2.13485100	-1.20719500	1.69836800
H	-5.02073700	-0.87296500	2.52258800
C	-6.28825800	0.16001600	1.11555400
C	-4.05147600	0.43148800	-0.49493200
C	-5.26236300	0.96805500	-0.94596800
C	-6.37788200	0.82192000	-0.12534600
N	-2.80319300	0.41408800	-1.09893100
C	-2.49989300	1.06296300	-2.35656700
H	-3.27887200	0.83863300	-3.09336300
H	-2.42935200	2.15294100	-2.24182600
H	-1.55048700	0.67895600	-2.74031300
H	-7.17836100	0.06271600	1.73183600
H	-7.33305500	1.22842100	-0.44730100
H	-5.33653700	1.48561500	-1.89837100

TS-2b

G_{sol} = -1902.624654 Hatree

C	0.72976500	3.31928100	1.25847000
C	1.20773900	2.31001600	0.42519900
C	2.44338100	1.66441700	0.65219500
C	3.17750800	2.09391800	1.77071300
C	2.71262500	3.10629300	2.60974400
C	1.48983800	3.72706000	2.35481800
H	-0.23582700	3.76378800	1.03805500
H	4.12171000	1.60507100	1.98876300
H	3.30574100	3.40166300	3.47073100
H	1.12142200	4.51231500	3.00821100
C	3.01714800	0.62960500	-0.25451000
C	4.36997500	0.66716200	-0.56017000
C	4.88133000	-0.27622200	-1.48170100
H	5.00604100	1.43601100	-0.13858700
C	2.62787400	-1.18502900	-1.79192000
C	4.04597400	-1.18201900	-2.07859500
H	5.94156300	-0.26489000	-1.72527000
H	4.40023700	-1.90836600	-2.80232400
N	2.18248900	-0.28425300	-0.82036000
O	1.80870900	-1.93981900	-2.35858200
S	0.05683300	1.80110700	-0.88995900
Pd	0.08901100	-0.53169200	-0.43519700
O	-1.16403000	2.67154600	-0.83018800
C	0.97695100	2.27516000	-2.39527500
H	1.07002600	3.36383800	-2.38132000
H	1.94973100	1.78466200	-2.41450100
H	0.37009900	1.95516700	-3.24526700
C	-1.08721600	-2.71296900	-0.03391600
H	-1.75001500	-2.89711600	0.79934600
H	-1.44961700	-2.97774500	-1.02116300
C	0.29416300	-2.63272800	0.19093400
H	0.98948200	-2.88700600	-0.60446200
C	0.77262200	-2.64740100	1.59926700
O	0.06564300	-2.50726600	2.58171700
O	2.10529700	-2.84996200	1.66008600
C	2.66452800	-2.86862600	2.98132600
H	2.20434500	-3.65660100	3.58374100
H	3.72889800	-3.06109100	2.84466600

H	2.50839600	-1.90628500	3.47722400
C	-2.51702400	-0.45627900	1.18302500
C	-3.88178100	-0.10184600	0.96036800
C	-4.96684900	0.21404900	1.80076300
C	-1.92283200	-0.65151600	-0.05563300
H	-2.02846500	-0.61806900	2.13467400
H	-4.83823100	0.22653900	2.87999300
C	-6.19504700	0.51459600	1.22961600
C	-4.08200900	-0.11963500	-0.45117500
C	-5.31781800	0.19722800	-1.02960800
C	-6.36675300	0.50977900	-0.17204300
N	-2.88837100	-0.47912400	-1.04877500
C	-2.64567000	-0.44244900	-2.47777700
H	-3.43110400	-0.99044600	-3.00965500
H	-2.62221000	0.58994100	-2.84997600
H	-1.68358500	-0.91528000	-2.68983200
H	-7.03960700	0.76304500	1.86659800
H	-7.33918100	0.75653500	-0.58968700
H	-5.45802200	0.20104100	-2.10658600

Int-8b

G_{sol} = -1902.670998 Hatree

C	2.36394800	2.90875300	1.12172500
C	2.00343700	1.93992100	0.18690400
C	2.90726400	0.94344600	-0.24144600
C	4.19382600	0.97113900	0.32296100
C	4.56430700	1.93706000	1.25772700
C	3.65208700	2.91368300	1.65723000
H	1.62245900	3.64519400	1.41589900
H	4.90253000	0.20298100	0.03012200
H	5.56570100	1.91869700	1.67901600
H	3.93390000	3.66817200	2.38601000
C	2.59122000	-0.06937600	-1.28728900
C	3.53044600	-0.35538200	-2.26803300
C	3.18326600	-1.27205600	-3.28682400
H	4.48897500	0.14944900	-2.27208100
C	0.94275900	-1.50296900	-2.31544700
C	1.93541700	-1.83606500	-3.31446100
H	3.91081700	-1.51497600	-4.05841100
H	1.63203900	-2.53169400	-4.08981600
N	1.35960300	-0.64325900	-1.29020600
O	-0.22615000	-1.94180400	-2.33201500
S	0.25227400	2.01334100	-0.34121600
Pd	-0.20741600	-0.36483900	0.10741200
O	-0.37708900	3.19184400	0.35519200
C	0.44981000	2.47107400	-2.09989800
H	0.94422400	3.44488300	-2.13559900
H	1.02795900	1.70651300	-2.62010600
H	-0.55792000	2.53947200	-2.51641900
C	-1.64275500	-2.74708600	0.79354600
H	-1.90844000	-3.23199500	1.74104200
H	-1.88350200	-3.42421200	-0.02771600
C	-0.16011700	-2.36398400	0.73377400
H	0.41453100	-2.88159600	-0.02730400
C	0.50784400	-2.31417900	2.05950700
O	-0.06048600	-2.18427400	3.13400800
O	1.85559800	-2.43489100	1.95646500
C	2.57393600	-2.34574800	3.19316800
H	2.24105300	-3.11738800	3.89300500
H	3.62321300	-2.49190600	2.93360200
H	2.42857800	-1.36431300	3.65453400
C	-2.08684300	-0.25865900	1.37498000
C	-3.02323100	0.74362200	0.88349700
C	-3.28789700	2.07214300	1.23491300
C	-2.37637900	-1.44323900	0.64529100
H	-1.63796000	-0.27514500	2.36189700
H	-2.72047400	2.55548100	2.02307900
C	-4.26647500	2.76964900	0.53066200
C	-3.76000800	0.14137300	-0.16426700
C	-4.73185800	0.83717200	-0.88431400
C	-4.97552100	2.16086400	-0.51827800
N	-3.34323400	-1.19605600	-0.28053000
C	-3.66006800	-2.07369000	-1.40534700
H	-4.50955600	-1.65783400	-1.94719200
H	-2.79588400	-2.14972000	-2.07362200
H	-3.94047500	-3.06672500	-1.04534000
H	-4.47790600	3.80334300	0.78841700
H	-5.72910600	2.72901200	-1.05653600
H	-5.29003100	0.37686600	-1.69368900

TS-3b

G_{sol} = -1902.644214 Hatree

C	3.82334700	-2.44970900	-1.06362300
C	3.11837600	-1.62560200	-0.18787700
C	3.63879000	-0.39463000	0.26951600
C	4.90995500	-0.03575400	-0.21226000

C	5.62540300	-0.85338700	-1.08581600
C	5.08834900	-2.06825500	-1.51027000
H	3.36265800	-3.37754900	-1.38814200
H	5.32835700	0.91697600	0.09554200
H	6.60039500	-0.53211700	-1.44158600
H	5.63866600	-2.70843000	-2.19345800
C	2.96095500	0.49293400	1.25792100
C	3.71814600	1.10537300	2.24705000
C	3.05860200	1.91392100	3.20074800
H	4.78515100	0.92992200	2.30865600
C	0.90777500	1.38521600	2.15221800
C	1.69854200	2.06283400	3.15661900
H	3.63941100	2.40686100	3.97743800
H	1.15753600	2.66594000	3.87791400
N	1.61021700	0.64270800	1.19705800
O	-0.33927400	1.43723600	2.11256800
S	1.43442500	-2.20801300	0.19921000
Pd	0.26624300	-0.20749100	-0.24004200
O	1.22117700	-3.52316300	-0.49293300
C	1.56638000	-2.54780600	1.98596400
H	2.28585500	-3.36120700	2.10892900
H	1.87889600	-1.64679400	2.51392900
H	0.57389100	-2.86115200	2.31782400
C	-1.66300000	0.64143200	-1.36814600
H	-0.83298700	-0.76491800	-1.29645100
H	-1.66775100	0.49718700	-2.44693100
C	-0.69719700	1.58960900	-0.91054400
H	-0.85423800	2.13978300	0.00995500
C	0.19427300	2.18587200	-1.93921200
O	0.26284900	1.82925500	-3.10309900
O	0.92347400	3.19740100	-1.42343100
C	1.83489100	3.82487700	-2.33655800
H	1.29693400	4.24760400	-3.18960400
H	2.32541800	4.61206800	-1.76347600
H	2.56894700	3.10167900	-2.70310600
C	-3.23854700	0.66623600	0.65688400
C	-4.55512100	0.16960400	0.87439300
C	-5.42957100	0.18304200	1.97949500
C	-2.89464100	0.35341400	-0.64526500
H	-2.58275700	1.14726900	1.37107100
H	-5.12103800	0.64719400	2.91223200
C	-6.67998900	-0.40011800	1.85403200
C	-4.97586500	-0.45002300	-0.34015200
C	-6.24643000	-1.03078100	-0.46898000
C	-7.08302000	-0.99928900	0.63878300
N	-3.94495600	-0.34490800	-1.25125000
C	-3.97900800	-0.81828500	-2.62282700
H	-4.77150000	-1.56186400	-2.72189800
H	-4.17180900	-0.00544600	-3.33459400
H	-3.03522900	-1.30518500	-2.88585900
H	-7.36547600	-0.39726600	2.69685200
H	-8.07199000	-1.44394000	0.56809000
H	-6.57631300	-1.48859700	-1.39680500

TS-2a-A

G_{sol} = -1902.622768 Hatree

C	-1.29875500	-3.25122500	1.28860700
C	-1.47992500	-2.22279300	0.36501900
C	-2.68746100	-1.49650700	0.27712200
C	-3.70491300	-1.85956800	1.17676800
C	-3.53617600	-2.88834300	2.10238400
C	-2.33389000	-3.59331000	2.15840800
H	-0.34271200	-3.76471100	1.31260700
H	-4.63690500	-1.30400600	1.15359400
H	-4.34476500	-3.13100000	2.78634400
H	-2.19517800	-4.39428000	2.87868800
C	-2.95067700	-0.43740800	-0.73744500
C	-4.19150400	-0.38712300	-1.35792500
C	-4.40656300	0.58608500	-2.36073300
H	-4.95850000	-1.11071400	-1.10986800
C	-2.09284700	1.34828600	-2.10415500
C	-3.39738900	1.43731400	-2.72343100
H	-5.37580300	0.64337200	-2.85166500
H	-3.52092400	2.18718300	-3.49765900
N	-1.94622900	0.41505100	-1.07327600
O	-1.11933000	2.05643100	-2.43958600
S	0.00342600	-1.82768600	-0.62046100
Pd	0.04792800	0.51703900	-0.26209500
O	1.09278100	-2.77608300	-0.21609800
C	-0.52916600	-2.29459100	-2.30231100
H	-0.74680300	-3.36533300	-2.29287400
H	-1.39967900	-1.70513000	-2.59053800
H	0.31525000	-2.08127300	-2.96169100
C	3.13564800	0.26716100	-0.52182000
C	4.20628600	-0.19130500	0.29770700
C	5.46146000	-0.51468000	-0.22737100

C	5.64348500	-0.36337300	-1.59915400
C	4.60063200	0.09667700	-2.42770300
C	3.35130900	0.41046500	-1.90229900
C	2.00255000	0.47926400	0.34759700
C	2.43239500	0.17238400	1.62275400
H	6.26758100	-0.87370500	0.40654300
H	6.60779000	-0.60475100	-2.03798200
H	4.77776300	0.20514300	-3.49431500
H	2.54986900	0.76437300	-2.54670900
H	1.89657300	0.24147100	2.56010700
C	4.51535300	-0.70236900	2.74445000
H	4.76200100	-1.76649600	2.64557600
H	5.44688800	-0.13348900	2.84572800
H	3.92263000	-0.56308900	3.65110300
N	3.75107200	-0.23552600	1.60586000
C	1.21894300	2.62550700	0.31668000
H	1.79984000	2.72654700	1.22173000
H	1.70546300	2.87233900	-0.62007600
C	-0.17404300	2.62203300	0.39338300
H	-0.76787700	2.92913100	-0.46129900
C	-0.79651500	2.59404500	1.74360000
O	-0.20620900	2.35634500	2.78370200
O	-2.11465300	2.87629300	1.68207200
C	-2.80677800	2.85714500	2.93841900
H	-2.37109900	3.58324800	3.63030700
H	-3.83943400	3.11916500	2.70667500
H	-2.75482600	1.86197400	3.38932100

TS-2a-B

G_{sol} = -1902.619992 Hatree

C	2.25184900	-3.49120400	-0.39113000
C	2.16196900	-2.18262200	0.08162600
C	3.14632500	-1.21361100	-0.21150800
C	4.22500400	-1.62866400	-1.01075700
C	4.32452300	-2.93495300	-1.48754800
C	3.34096900	-3.87341900	-1.17473100
H	1.46224500	-4.19139100	-0.13678900
H	4.98493600	-0.89899900	-1.27202300
H	5.16902100	-3.21493600	-2.11111500
H	3.41275400	-4.89264300	-1.54318200
C	3.12057100	0.17039100	0.33441400
C	4.29201200	0.74792600	0.80352000
C	4.21936600	2.02941500	1.39835400
H	5.22810200	0.20433000	0.76057200
C	1.79016300	2.02723800	1.09067800
C	3.01192800	2.66133300	1.53640400
H	5.12911100	2.50066000	1.76434000
H	2.91868100	3.63214600	2.01175300
N	1.92349200	0.80551900	0.42975100
O	0.64936300	2.50326000	1.26719500
S	0.62634900	-1.81210100	0.99996900
Pd	-0.01459700	0.15611400	-0.22725400
O	-0.17775800	-3.08065200	1.06405100
C	1.26407600	-1.49407700	2.68093400
H	1.71572100	-2.42254900	3.03843500
H	1.98401000	-0.67592400	2.65695500
H	0.39938900	-1.22579100	3.29219900
C	-3.09292800	0.01549600	0.14513800
C	-4.09201400	-0.99788900	0.09477800
C	-5.34988300	-0.83656500	0.68604300
C	-5.60731800	0.37302800	1.32388100
C	-4.63811500	1.39509800	1.36905700
C	-3.38502400	1.23030600	0.78830100
C	-1.93174700	-0.51323900	-0.53864900
C	-2.28517100	-1.76707100	-0.98990000
H	-6.09860200	-1.62334500	0.65268700
H	-6.57455200	0.53160000	1.79340400
H	-4.87564700	2.33046700	1.86824600
H	-2.64775600	2.02629200	0.81398700
H	-1.70453300	-2.49346500	-1.54186800
C	-4.24672000	-3.34021600	-0.81811100
H	-4.38322700	-3.87495300	0.12993800
H	-5.22852200	-3.18812000	-1.28101900
H	-3.64086500	-3.95979400	-1.48299900
N	-3.57797100	-2.07217900	-0.61479300
C	-1.23109300	0.80577600	-2.22474200
H	-1.09965200	-0.01583200	-2.91823800
H	-2.22692300	1.22054200	-2.13053300
C	-0.14195600	1.61277800	-1.87658300
C	-0.40460500	2.99238000	-1.37079200
O	-1.49255200	3.40752500	-1.02348900
O	0.71573200	3.73609300	-1.42063300
C	0.61011000	5.03213800	-0.80810900
H	0.42430500	4.90305400	0.26057000
H	1.57282200	5.51488700	-0.98088400
H	-0.19863100	5.60993000	-1.26278400

H	0.83703000	1.43437300	-2.31258900

TS-2a-C

G_{sol} = -1902.619578 Hatree

C	-0.64028300	3.84930800	-0.18266500
C	-1.17042000	2.60686700	0.16213600
C	-2.38646600	2.13484000	-0.38013400
C	-3.03852100	2.97819500	-1.29574800
C	-2.51741200	4.22299600	-1.64670200
C	-1.31952900	4.66691500	-1.08636500
H	0.30270400	4.15271400	0.26167800
H	-3.96278800	2.63375700	-1.74882700
H	-3.04674800	4.84152100	-2.36620600
H	-0.90852200	5.63533000	-1.35638800
C	-3.02029400	0.84970800	0.02400500
C	-4.39175700	0.79366800	0.22864300
C	-4.95342800	-0.41556100	0.70116100
H	-5.00607700	1.67325500	0.07892300
C	-2.71354500	-1.39721800	0.83170500
C	-4.14918700	-1.48609900	0.98996600
H	-6.02852900	-0.48100700	0.85469300
H	-4.54505800	-2.41784200	1.38015800
N	-2.21850700	-0.22188600	0.26311400
O	-1.91642200	-2.29484600	1.17443500
S	-0.09994800	1.60897100	1.25593700
Pd	-0.09800700	-0.40167200	-0.04382700
O	1.10170500	2.43672000	1.60671700
C	-1.11700200	1.48780300	2.76875600
H	-1.21349100	2.50003200	3.16884400
H	-2.08635800	1.04632400	2.54039500
H	-0.56126800	0.85287800	3.46236100
C	2.97599300	0.35668900	-0.41011200
C	4.18009000	-0.12968600	0.17545400
C	5.39276100	0.55991700	0.07483300
C	5.39809800	1.74959000	-0.64681600
C	4.22214500	2.24317100	-1.24617200
C	3.01611800	1.56170400	-1.12953900
C	1.94255100	-0.59959300	-0.09102000
C	2.55527700	-1.61151300	0.62462900
H	6.30001800	0.18375400	0.53949000
H	6.32483800	2.30780700	-0.74772800
H	4.26019900	3.17736700	-1.79993100
H	2.11044200	1.96135500	-1.57912900
H	2.13390400	-2.54284400	0.97841700
C	4.83640900	-2.13071200	1.56081400
H	5.71495200	-2.37256300	0.95182100
H	5.16867300	-1.60132500	2.46219700
H	4.35220300	-3.06282300	1.85929800
N	3.89384400	-1.33344900	0.80186300
C	1.00713200	-1.46265100	-1.94724100
H	1.18871000	-0.60815100	-2.58924400
H	1.80833700	-2.18136400	-1.85660300
C	-0.30139400	-1.87796900	-1.67179200
H	-1.14924600	-1.41038800	-2.16348300
C	-0.49672900	-3.25426300	-1.13345800
O	-1.74544300	-3.68991600	-1.36840500
C	-2.09956700	-4.92069800	-0.71649700
H	-3.08551100	-5.18257700	-1.10278900
H	-1.37369700	-5.70417100	-0.94723800
H	-2.13851500	-4.74531600	0.36101000
O	0.37950000	-3.91289100	-0.60306500

TS-2a-D

G_{sol} = -1902.606029 Hatree

C	4.48054800	-0.89607300	0.70857400
C	3.49575700	0.04979900	0.43536900
C	3.71052100	1.07689100	-0.51726300
C	4.95805400	1.11581800	-1.15733700
C	5.94922000	0.17544100	-0.87898600
C	5.71234200	-0.83526300	0.05226900
H	4.26664600	-1.66330000	1.44633700
H	5.14211000	1.88324100	-1.90333600
H	6.90247700	0.22968700	-1.39784700
H	6.47860000	-1.57388100	0.27068500
C	2.63028000	2.04326200	-0.82786000
C	2.77166500	3.27779200	-1.45940900
C	1.60649500	4.05793600	-1.59814300
H	3.73168100	3.64416800	-1.80561000
C	0.31449900	2.33740600	-0.49864700
C	0.38165800	3.61776100	-1.12643900
H	1.67417800	5.03165200	-2.07833500
H	-0.51839100	4.21649300	-1.21680000
N	1.44236200	1.61190800	-0.38902600
O	-0.77590900	1.82927800	-0.01586300
S	1.96076400	-0.18357300	1.45642100
Pd	-0.50080300	-0.23832900	0.42215100

O	2.25731500	-1.35140500	2.38001900
C	2.11012400	1.29941100	2.53134200
H	3.00688700	1.14595400	3.13628100
H	2.16726300	2.21434500	1.94541700
H	1.22271100	1.30642900	3.16851900
C	-3.56091800	0.22988600	0.51047700
C	-4.61676600	0.21885700	-0.44407400
C	-5.86306800	0.79844200	-0.18651900
C	-6.04950300	1.39501200	1.05713100
C	-5.01789900	1.41750000	2.01660000
C	-3.77851100	0.84473600	1.75258000
C	-2.44474500	-0.44957800	-0.10174600
C	-2.86003300	-0.83386200	-1.36322100
H	-6.65866100	0.78774000	-0.92636100
H	-7.00654300	1.85386500	1.28980600
H	-5.19408300	1.89865200	2.97477100
H	-2.98022600	0.88265700	2.48892100
H	-2.32853800	-1.40433800	-2.11255400
C	-4.92247300	-0.63722600	-2.79601400
H	-5.85443900	-1.17504800	-2.58657600
H	-5.16818100	0.32128100	-3.26863400
H	-4.32700700	-1.22941300	-3.49392100
N	-4.16071100	-0.43706200	-1.57956700
C	-1.74450300	-2.30986500	0.95402500
H	-2.40031900	-2.82813900	0.27006500
H	-2.14721700	-2.08511400	1.93525700
C	-0.35658300	-2.38479600	0.76403700
H	0.33360100	-2.34884200	1.60670800
C	0.13545800	-2.99490600	-0.50089000
O	-0.56784700	-3.31754500	-1.44384000
O	1.47689600	-3.13198100	-0.48967800
C	2.05706800	-3.66220700	-1.69059300
H	1.81695300	-3.02478900	-2.54596800
H	3.13224100	-3.67417300	-1.51189800
H	1.68563700	-4.67255300	-1.88313200

TS-2b-A

G_{sol} = -1902.623980 Hatree

C	0.97535800	3.42236400	0.77495900
C	1.31641000	2.28449900	0.04472500
C	2.55631500	1.63012300	0.20992800
C	3.43417800	2.18004400	1.16071700
C	3.10414000	3.31752200	1.89599700
C	1.87564200	3.94851100	1.70104200
H	0.00334400	3.87574800	0.60766100
H	4.38542400	1.68638800	1.33163000
H	3.80723100	3.70417600	2.62845100
H	1.61189500	4.83437800	2.27122900
C	2.99554000	0.45770200	-0.59762500
C	4.30597300	0.39946700	-1.05108200
C	4.69369800	-0.69159700	-1.86318900
H	5.00012000	1.19968500	-0.82498200
C	2.40507400	-1.56018600	-1.77750800
C	3.78194700	-1.65078600	-2.21281100
H	5.71956700	-0.75404000	-2.21988100
H	4.03987000	-2.49334000	-2.84558300
N	2.08590200	-0.50023500	-0.92098700
O	1.51468100	-2.36439600	-2.12200800
S	-0.01358200	1.65407900	-1.03220600
Pd	0.02210000	-0.62891600	-0.37654800
O	-1.20273200	2.55617900	-0.87047700
C	0.68230800	1.93836800	-2.69449400
H	0.80729700	3.01678300	-2.81837800
H	1.62905100	1.40573900	-2.79080400
H	-0.04996400	1.55141000	-3.40673400
C	-1.13619400	-2.59086800	0.62465200
H	-1.68813600	-2.43059500	1.54401200
H	-1.62469800	-3.17230000	-0.14563900
C	0.26712200	-2.55293800	0.65256300
H	0.83921500	-3.07981400	-0.10409800
C	0.94557900	-2.20302200	1.92894000
O	0.41133800	-1.68180500	2.89439800
O	2.24496800	-2.55843400	1.90038000
C	2.99526600	-2.25261800	3.08500800
H	2.56167300	-2.75198700	3.95565900
H	4.00366200	-2.61978100	2.89334700
H	3.00606400	-1.17345200	3.26221000
C	-2.91700300	-1.06254800	-1.12310400
C	-4.18985600	-0.52456000	-0.76827800
C	-5.46081200	-0.51886900	-1.37544000
C	-2.02133700	-0.73559900	-0.11432600
H	-2.68040500	-1.64890100	-2.00165400
H	-5.61163600	-1.00482700	-2.33605700
C	-6.50979800	0.12203000	-0.73307200
C	-4.02030200	0.11485200	0.49521800
C	-5.07732500	0.77475800	1.13696400

C	-6.31761300	0.76484500	0.50993600
N	-2.70576900	-0.04968800	0.88813000
C	-2.10375700	0.59273800	2.04421300
H	-1.85530900	1.63853900	1.82708300
H	-2.80352500	0.55931700	2.88483300
H	-1.19981000	0.05149900	2.33072200
H	-7.49473800	0.13711000	-1.19180600
H	-7.15716400	1.26509400	0.98518800
H	-4.93862300	1.27976200	2.08815400

TS-2b-B

G_{sol} = -1902.621337 Hatree

C	1.42777500	-3.79737900	-0.49708300
C	1.67441800	-2.51633500	-0.00596000
C	2.82736800	-1.78544000	-0.36777900
C	3.72087900	-2.41047100	-1.25363400
C	3.48461900	-3.69226800	-1.74924100
C	2.34005300	-4.39304900	-1.36870000
H	0.51937700	-4.30633400	-0.18992400
H	4.60481900	-1.86453800	-1.56813300
H	4.19382700	-4.13811700	-2.44102400
H	2.15001500	-5.39090100	-1.75303600
C	3.15434900	-0.44500600	0.18980000
C	4.45460100	-0.15303200	0.57544200
C	4.71167900	1.09744900	1.18468400
H	5.24058400	-0.88916700	0.45749700
C	2.32884100	1.64292500	1.06117300
C	3.68869500	1.97809600	1.41983400
H	5.72721100	1.34603300	1.48525400
H	3.84928500	2.93270300	1.90964300
N	2.14083300	0.44050200	0.37992500
O	1.33671900	2.35537900	1.32737600
S	0.33434400	-1.83482700	1.03300000
Pd	0.08242400	0.24487200	-0.14897700
O	-0.72468600	-2.88867300	1.16687800
C	1.16064000	-1.69151200	2.65594200
H	1.44274500	-2.70093400	2.96472300
H	2.02640000	-1.03354400	2.58040600
H	0.42009600	-1.27520600	3.34264600
C	-1.12244400	1.24178700	-2.04913900
H	-1.20469100	0.45823100	-2.79160700
H	-1.99226700	1.87180800	-1.90265500
C	0.14268000	1.76798900	-1.73374800
C	-2.62985600	-1.01430500	-1.03031100
C	-3.97718500	-0.97648100	-0.56339100
C	-5.12344700	-1.76150500	-0.79366900
C	-1.94224900	0.02969500	-0.42998900
H	-2.21007500	-1.71506400	-1.73975800
H	-5.07700800	-2.61683500	-1.46286200
C	-6.30548000	-1.43126000	-0.14689600
C	-4.06716300	0.14112500	0.31758200
C	-5.25709800	0.46571200	0.98349300
C	-6.36966000	-0.32968000	0.73489500
N	-2.83011900	0.75307200	0.36885800
C	-2.49116800	1.83703200	1.27941700
H	-3.21631700	2.65044500	1.17507400
H	-2.49592600	1.48789600	2.31981000
H	-1.50377400	2.22934600	1.03774100
H	-7.19693500	-2.02977200	-0.31384800
H	-7.30919800	-0.09910500	1.22997900
H	-5.31346600	1.30891600	1.66535600
C	0.21334900	3.15209700	-1.18244300
O	-0.73917700	3.76673900	-0.74066500
O	1.45301200	3.65550300	-1.30953500
C	1.66006200	4.92783600	-0.67275800
H	2.68341700	5.21328500	-0.91912500
H	0.95074100	5.66848300	-1.05044900
H	1.53750400	4.80669800	0.40590400
H	1.02515900	1.40805000	-2.25567600

TS-2b-C

G_{sol} = -1902.620793 Hatree

C	1.42777500	-3.79737900	-0.49708300
C	1.67441800	-2.51633500	-0.00596000
C	2.82736800	-1.78544000	-0.36777900
C	3.72087900	-2.41047100	-1.25363400
C	3.48461900	-3.69226800	-1.74924100
C	2.34005300	-4.39304900	-1.36870000
H	0.51937700	-4.30633400	-0.18992400
H	4.60481900	-1.86453800	-1.56813300
H	4.19382700	-4.13811700	-2.44102400
H	2.15001500	-5.39090100	-1.75303600
C	3.15434900	-0.44500600	0.18980000
C	4.45460100	-0.15303200	0.57544200
C	4.71167900	1.09744900	1.18468400
H	5.24058400	-0.88916700	0.45749700

C	2.32884100	1.64292500	1.06117300
C	3.68869500	1.97809600	1.41983400
H	5.72721100	1.34603300	1.48525400
H	3.84928500	2.93270300	1.90964300
N	2.14083300	0.44050200	0.37992500
O	1.33671900	2.35537900	1.32737600
S	0.33434400	-1.83482700	1.03300000
Pd	0.08242400	0.24487200	-0.14897700
O	-0.72468600	-2.88867300	1.16687800
C	1.16064000	-1.69151200	2.65594200
H	1.44274500	-2.70093400	2.96472300
H	2.02640000	-1.03354400	2.58040600
H	0.42009600	-1.27520600	3.34264600
C	-1.12244400	1.24178700	-2.04913900
H	-1.20469100	0.45823100	-2.79160700
H	-1.99226700	1.87180800	-1.90265500
C	0.14268000	1.76798900	-1.73374800
C	-2.62985600	-1.01430500	-1.03031100
C	-3.97718500	-0.97648100	-0.56339100
C	-5.12344700	-1.76150500	-0.79366900
C	-1.94224900	0.02969500	-0.42998900
H	-2.21007500	-1.71506400	-1.73975800
H	-5.07700800	-2.61683500	-1.46286200
C	-6.30548000	-1.43126000	-0.14689600
C	-4.06716300	0.14112500	0.31758200
C	-5.25709800	0.46571200	0.98349300
C	-6.36966000	-0.32968000	0.73489500
N	-2.83011900	0.75307200	0.36885800
C	-2.49116800	1.83703200	1.27941700
H	-3.21631700	2.65044500	1.17507400
H	-2.49592600	1.48789600	2.31981000
H	-1.50377400	2.22934600	1.03774100
H	-7.19693500	-2.02977200	-0.31384800
H	-7.30919800	-0.09910500	1.22997900
H	-5.31346600	1.30891600	1.66535600
C	0.21334900	3.15209700	-1.18244300
O	-0.73917700	3.76673900	-0.74066500
O	1.45301200	3.65550300	-1.30953500
C	1.66006200	4.92783600	-0.67275800
H	2.68341700	5.21328500	-0.91912500
H	0.95074100	5.66848300	-1.05044900
H	1.53750400	4.80669800	0.40590400
H	1.02515900	1.40805000	-2.25567600

TS-2b-D

G_{sol} = -1902.606610 Hatree

C	4.52620900	-0.98421500	0.49579500
C	3.52743800	-0.01733000	0.40581700
C	3.70739800	1.15148100	-0.37477100
C	4.93548600	1.30567200	-1.03540000
C	5.94010500	0.34367400	-0.94031200
C	5.73723800	-0.80598400	-0.17735200
H	4.34078300	-1.86171000	1.10766900
H	5.09259000	2.18433600	-1.65375000
H	6.87704600	0.49091100	-1.47056800
H	6.51448100	-1.56128600	-0.10164800
C	2.61525900	2.14567000	-0.49857200
C	2.74201700	3.46833600	-0.91943200
C	1.57392800	4.25568800	-0.90949600
H	3.69540200	3.89160700	-1.21498600
C	0.30768700	2.37217100	-0.08501500
C	0.35871500	3.73755300	-0.49526700
H	1.63170900	5.29560700	-1.22286100
H	-0.54400600	4.33834100	-0.46761600
N	1.43560700	1.64057500	-0.11685100
O	-0.77568000	1.78774200	0.32829800
S	2.02805600	-0.42977500	1.42265700
Pd	-0.46289200	-0.31156900	0.51826900
O	2.36197100	-1.72108600	2.14250800
C	2.19168100	0.87099500	2.70986100
H	3.11737200	0.65120900	3.24696600
H	2.20270900	1.86757500	2.27346500
H	1.33336000	0.75186100	3.37516500
C	-4.43404900	0.17312600	-0.60317800
C	-4.63762500	0.09937800	0.80693600
C	-5.91040200	0.39153600	1.33528800
C	-6.92837900	0.76170900	0.46959600
C	-6.70289300	0.84718700	-0.92220100
C	-5.46096900	0.55921400	-1.47573200
C	-2.48373300	-0.44038000	0.33741700
H	-6.08496600	0.33569100	2.40670600
H	-7.91372600	0.99554000	0.86330600
H	-7.51792500	1.14725500	-1.57533100
H	-5.29940000	0.63590700	-2.54657300
C	-1.70233900	-2.47302700	0.52589400
H	-2.31355900	-2.72434700	-0.33375700
H	-2.14059900	-2.64165500	1.50062400

C	-0.30245400	-2.47449700	0.39310200
H	0.33963500	-2.68597800	1.24664700
C	0.27047000	-2.72080000	-0.96175600
O	-0.37023200	-2.75814000	-1.99862600
O	1.60387300	-2.89955200	-0.90377800
C	2.25854000	-3.11352200	-2.16501300
H	2.06532600	-2.27779700	-2.84244800
H	3.32072300	-3.18043500	-1.93095600
H	1.90367200	-4.03867900	-2.62717300
C	-3.39198000	-0.29649000	1.37645200
H	-3.18421500	-0.47690500	2.42263700
N	-3.12523200	-0.18591800	-0.87024700
C	-2.47057000	-0.04481600	-2.16130100
H	-2.04943900	0.96016500	-2.27910200
H	-1.67603900	-0.78813700	-2.25011300
H	-3.19954400	-0.22879700	-2.95487400

5. Synthetic Studies

5.1 General Procedure for Indole Alkenylation

(1) General procedure for C3-alkenylation (Procedure A)

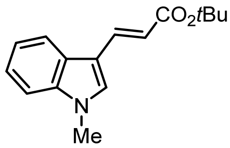
A 25 mL Schlenk tube was charged with a magnetic stir bar, $PdCl_2(MeCN)_2$ (0.04 mmol, 5 mol%), and $Cu(OAc)_2$ (0.08 mmol, 10 mol%), and the tube was filled with O_2 by three evacuation/O_2 backfill cycles. DMSO (0.2 mL, 10 vol%) and DMF (1.8 mL) were added successively, and the resulting mixture was stirred at room temperature for 5 min before the olefin substrate (1.6 mmol, 2 equiv.) and the indole substrate (0.8 mmol, 1 equiv.) were added by syringe. The reaction was stirred at 70 °C, and the progress was monitored by TLC. Upon completion, the reaction mixture was quenched with water, and extracted with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on silica gel to afford the desired C3-alkenylation product.

(2) General procedure for C2-alkenylation (Procedure B)

A 25 mL Schlenk tube was charged with a magnetic stir bar, $PdCl_2(MeCN)_2$ (0.04 mmol, 5 mol%), $Cu(OTf)_2$ (0.08 mmol, 10 mol%) or $Cu_2(OH)_2CO_3$ (0.4 mmol, 50 mol%), and **L17** (0.08 mmol, 10 mol%), and the tube was filled with O_2 by three evacuation/O_2 backfill cycles. DMF (2 mL) was added, and the resulting mixture was stirred at room temperature for 5 min before the olefin substrate (1.6 mmol, 2 equiv.) and the indole substrate (0.8 mmol, 1 equiv.) were added by syringe. The reaction was stirred at 70 °C, and the progress was monitored by TLC. Upon completion, the reaction mixture was quenched with water, and extracted with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on silica gel to afford the desired C2-alkenylation product.

5.2 Characterization Data for Synthesized Compounds

***Tert*-butyl (*E*)-3-(1-methyl-1*H*-indol-3-yl)acrylate (3a)**



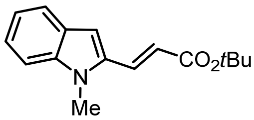
Following **Procedure A** (reaction time 3 h), **3a** was obtained as white solid (156 mg, 76% yield) from *tert*-butyl acrylate (240 uL, 1.60 mmol) and *N*-methylindole (100 uL, 0.80 mmol) using petroleum ether/EtOAc (15:1 to 10:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.91 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 15.9 Hz, 1H), 7.35-7.20 (m, 4H), 6.35 (d, *J* = 15.9 Hz, 1H), 3.79 (s, 3H), 1.55 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): *δ* 167.9, 138.2, 137.0, 132.8, 126.2, 123.0, 121.2, 120.8, 114.8, 112.3, 110.0, 79.8, 33.3, 28.5.

The NMR spectra were identical to those reported.[11]

***Tert*-butyl (*E*)-3-(1-methyl-1*H*-indol-2-yl)acrylate (3b)**



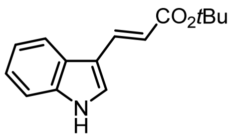
Following **Procedure B** (reaction time 12 h), **3b** was obtained as white solid (120 mg, 58% yield) from *tert*-butyl acrylate (103 mg, 0.806 mmol) and *N*-methylindole (210 mg, 1.60 mmol) using petroleum ether/EtOAc (50:1 to 20:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.71 (d, *J* = 15.8 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.22-7.28 (m, 1H), 7.15-7.07 (m, 1H), 6.93 (s, 1H), 6.43 (d, *J* = 15.8 Hz, 1H), 3.82 (s, 3H), 1.55 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): *δ* 166.6, 139.1, 135.3, 131.8, 127.6, 123.5, 121.4, 120.5, 120.4, 109.7, 103.4, 80.8, 30.2, 28.4.

The NMR spectra were identical to those reported.[12]

***Tert*-butyl (*E*)-3-(1*H*-indol-3-yl)acrylate (6a)**



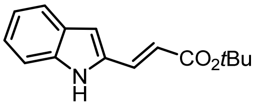
Following **Procedure A** (reaction time 3 h), **6a** was obtained as orange solid (56.3 mg, 28% yield) from *tert*-butyl acrylate (240 uL, 1.60 mmol) and 1*H*-indole (93.7 mg, 0.800 mmol) using petroleum ether/EtOAc (15:1 to 6:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.54 (s, 1H), 7.92 (d, *J* = 7.2 Hz, 1H), 7.83 (d, *J* = 16.0 Hz, 1H), 7.46 (d, *J* = 2.7 Hz, 1H), 7.41 (dd, *J* = 6.9, 1.4 Hz, 1H), 7.30-7.21 (m, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 1.56 (s, 9H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 167.9, 137.2, 137.2, 128.5, 125.5, 123.4, 121.5, 120.7, 115.6, 113.8, 111.8, 80.1, 28.5.

The NMR spectra were identical to those reported.[13]

Tert-butyl (_E_)-3-(1_H_-indol-2-yl)acrylate (6b)



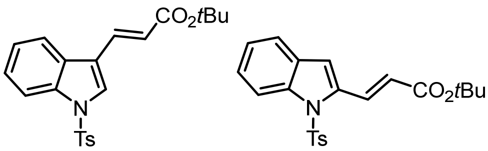
Following **Procedure B** (reaction time 12 h), **6b** was obtained as white solid (85.6 mg, 44% yield) from *tert*-butyl acrylate (103 mg, 0.800 mmol) and indole (188 mg, 1.61 mmol) using petroleum ether/EtOAc (50:1 to 25:1) as eluent.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.42 (s, 1H), 7.59 (dd, J = 11.8, 9.6 Hz, 2H), 7.35 (dd, J = 8.2, 0.6 Hz, 1H), 7.27-7.22 (m, 1H), 7.15-7.07 (m, 1H), 6.78 (d, J = 1.3 Hz, 1H), 6.19 (d, J = 16.0 Hz, 1H), 1.55 (s, 9H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 166.4, 137.9, 133.8, 133.5, 128.6, 124.6, 121.6, 120.7, 117.8, 111.2, 108.6, 80.9, 28.4.

The NMR spectra were identical to those reported.[13]

Tert-butyl (_E_)-3-(1-tosyl-1H-indol-3-yl)acrylate (7a) and
Tert-butyl (_E_)-3-(1-tosyl-1_H_-indol-2-yl)acrylate (7b)



7a **7b**

Following **Procedure B**, **7a** was obtained as a yellow solid (242 mg, 74% yield), together with a mixture of **7a** and **7b** (19.2 mg, 6% yield, **7a**:**7b** = 1:2.8), from *tert*-butyl acrylate (105 mg, 0.821 mmol) and *N*-tosyl-1*H*-indole (434 mg, 1.62 mmol) using petroleum ether/EtOAc (50:1 to 15:1) as eluent.

Characterization data for **7a**:

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.99 (d, J = 8.3 Hz, 1H), 7.86-7.73 (m, 4H), 7.68 (d, J = 16.1 Hz, 1H), 7.34 (dtd, J = 22.8, 7.4, 1.2 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 6.44 ji(d, J = 16.1 Hz, 1H), 2.34 (s, 3H), 1.54 (s, 9H).

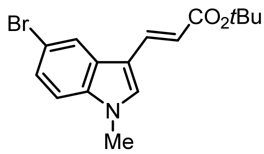
^{13}C NMR (100 MHz, CDCl$_3$): δ 166.5, 145.6, 135.8, 135.0, 134.6, 130.2, 128.4, 128.1, 127.1, 125.5, 124.2, 120.8, 120.5, 118.5, 114.0, 80.7, 28.4, 21.7.

The NMR spectra were identical to those reported.[14]

Characterization data for **7b**:

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.27 (d, J = 15.8 Hz, 1H), 8.22 (d, J = 8.4 Hz, 1H), 7.64 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 7.8 Hz, 1H), 7.40-7.20 (m, 2H), 7.16 (d, J = 8.1 Hz, 2H), 6.93 (s, 1H), 6.29 (d, J = 15.8 Hz, 1H), 2.31 (s, 3H), 1.57 (s, 9H).

***Tert*-butyl (*E*)-3-(5-bromo-1-methyl-1*H*-indol-3-yl)acrylate (8a)**



Following **Procedure A** (reaction time 12 h), **8a** was obtained as white solid (191 mg, 71% yield) from *tert*-butyl acrylate (240 uL, 1.60 mmol) and 5-bromo-1-methyl-1*H*-indole (168.2 mg, 0.801 mmol) using petroleum ether/EtOAc (15:1 to 6:1) as eluent.

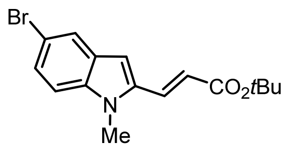
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 1.5 Hz, 1H), 7.70 (d, J = 16.0 Hz, 1H), 7.36 (dd, J = 8.7, 1.6 Hz, 1H), 7.27 (s, 1H), 7.17 (d, J = 8.7 Hz, 1H), 6.28 (d, J = 16.0 Hz, 1H), 3.76 (s, 3H), 1.55 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 136.8, 136.2, 133.5, 127.7, 125.8, 123.3, 115.5, 114.8, 111.8, 111.4, 80.1, 33.4, 28.5.

IR (ATR): $\tilde{v}$ (cm^{-1}) = 1692.

HRMS (ESI) calcd. for $C_{16}H_{18}BrNNaO_2$ [M + Na]$^+$: 358.0413; found: 358.0415.

***Tert*-butyl (*E*)-3-(5-bromo-1-methyl-1*H*-indol-2-yl)acrylate (8b)**



Following **Procedure B** (reaction time 6 h), **8b** was obtained as white solid (148 mg, 55% yield) from *tert*-butyl acrylate (104 mg, 0.808 mmol) and 5-bromo-1-methyl-1*H*-indole (236 mg, 1.60 mmol) using petroleum ether/EtOAc (20:1 to 15:1) as eluent.

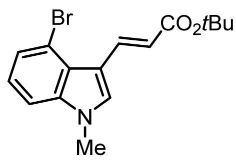
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 1.7 Hz, 1H), 7.64 (d, J = 15.8 Hz, 1H), 7.29 (dd, J = 8.8, 1.8 Hz, 1H), 7.13 (d, J = 8.8 Hz, 1H), 6.80 (s, 1H), 6.42 (d, J = 15.8 Hz, 1H), 3.75 (s, 3H), 1.55 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 137.5, 136.3, 131.2, 129.1, 126.2, 123.6, 121.5, 113.6, 111.1, 102.4, 80.9, 30.2, 28.3.

IR (ATR): $\tilde{v}$ (cm^{-1}) = 1699.

HRMS (ESI) calcd. for $C_{16}H_{19}BrNO_2$ [M + H]$^+$: 336.0594; found: 336.0598.

***Tert*-butyl (*E*)-3-(4-bromo-1-methyl-1*H*-indol-3-yl)acrylate (9a)**



Following **Procedure A** (reaction time 12 h, 10 mol% $PdCl_2(CH_3CN)_2$ was used), **9a** was obtained as white solid (231 mg, 85% yield) from *tert*-butyl acrylate (240 μL, 1.60 mmol) and 4-bromo-1-methyl-1*H*-indole (169 mg, 0.805 mmol) using petroleum ether/EtOAc (20:1 to 5:1) as eluent.

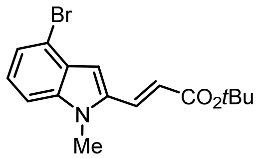
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, J = 15.9 Hz, 1H), 7.49 (s, 1H), 7.36 (d, J = 7.6 Hz, 1H), 7.26 (d, J = 8.2 Hz, 1H), 7.04-7.10 (m, 1H), 6.11 (d, J = 15.8 Hz, 1H), 3.80 (s, 3H), 1.54 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 138.6, 136.7, 129.2, 125.6, 125.3, 123.2, 115.3, 114.6, 113.0, 109.2, 79.9, 33.6, 28.5.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1691.

HRMS (ESI) calcd. for $C_{16}H_{18}BrNNaO_2$ $[M + Na]^+$: 358.0413; found: 358.0411.

Tert-butyl (_E_)-3-(6-chloro-1-methyl-1_H_-indol-2-yl)acrylate (9b)



Following **Procedure B** (reaction time 12 h), **9b** was obtained as white solid (202 mg, 75% yield) from *tert*-butyl acrylate (137mg, 1.07 mmol) and 4-bromo-1-methyl-1*H*-indole (170 mg, 0.810 mmol) using petroleum ether/EtOAc (80:1 to 20:1) as eluent.

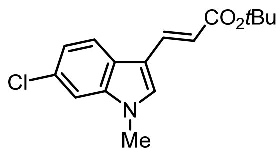
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 15.8 Hz, 1H), 7.30-7.23 (m, 2H), 7.09 (dd, J = 8.1, 7.7 Hz, 1H), 6.96 (s, 1H), 6.51 (d, J = 15.8 Hz, 1H), 3.81 (s, 3H), 1.55 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 139.1, 135.9, 131.1, 128.4, 124.1, 123.3, 121.8, 115.4, 108.9, 103.3, 81.0, 30.6, 28.4.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1703.

HRMS (ESI) calcd. for $C_{16}H_{18}BrNNaO_2$ $[M + Na]^+$: 358.0413; found: 358.0411.

Tert-butyl (_E_)-3-(6-chloro-1-methyl-1_H_-indol-3-yl)acrylate (10a)



Following **Procedure A** (reaction time 12 h), **10a** was obtained as white solid (200 mg, 86% yield) from *tert*-butyl acrylate (240 μL, 1.60 mmol) and 6-chloro-1-methyl-1*H*-indole (133 mg, 0.798 mmol) using petroleum ether/EtOAc (14:1 to 9:1) as eluent.

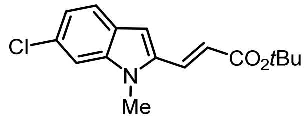
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.5 Hz, 1H), 7.72 (d, J = 16.0 Hz, 1H), 7.26-7.32 (m, 2H), 7.18 (dd, J = 8.5, 1.8 Hz, 1H), 6.29 (d, J = 16.0 Hz, 1H), 3.74 (s, 3H), 1.54 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 138.6, 136.3, 133.1, 129.0, 124.7, 121.8, 121.5, 115.5, 112.4, 110.1, 80.0, 33.3, 28.5.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1691.

HRMS (ESI) calcd. for $C_{16}H_{19}ClNO_2$ $[M + H]^+$: 292.1099; found: 292.1095.

***Tert*-butyl (*E*)-3-(6-chloro-1-methyl-1*H*-indol-2-yl)acrylate (10b)**



Following **Procedure B** (reaction time 9 h), **10b** was obtained as white solid (141 mg, 60% yield) from *tert*-butyl acrylate (104 mg, 0.811 mmol) and 6-chloro-1-methyl-1*H*-indole (265 mg, 1.60 mmol) using petroleum ether/EtOAc (40:1 to 30:1) as eluent.

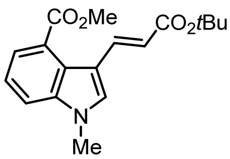
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 15.8 Hz, 1H), 7.48 (d, J = 8.5 Hz, 1H), 7.29 (s, 1H), 7.06 (dd, J = 8.5, 1.7 Hz, 1H), 6.86 (s, 1H), 6.41 (d, J = 15.8 Hz, 1H), 3.75 (s, 3H), 1.55 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 139.4, 136.1, 131.3, 129.4, 126.1, 122.2, 121.3, 121.0, 109.7, 103.4, 80.9, 30.3, 28.4.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1699.

HRMS (ESI) calcd. for $C_{16}H_{19}ClNO_2$ [M + H]$^+$: 292.1099; found: 292.1093.

Methyl (*E*)-3-(3-(*tert*-butoxy)-3-oxoprop-1-en-1-yl)-1-methyl-1*H*-indole-4-carboxylate (11a)



Following **Procedure A** (reaction time 12 h), **11a** was obtained as white solid in 63% yield (158 mg) from *tert*-butyl acrylate (240 uL, 1.60 mmol) and methyl 1-methyl-1*H*-indole-4-carboxylate (132 μL, 0.80 mmol) using petroleum ether/EtOAc (15:1 to 6:1) as eluent.

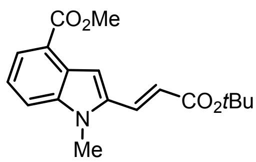
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 15.9 Hz, 1H), 7.76 (d, J = 7.4 Hz, 1H), 7.52-7.43 (m, 2H), 7.22-7.30(m, 1H), 6.04 (d, J = 15.8 Hz, 1H), 4.00 (s, 3H), 3.81 (s, 3H), 1.54 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 167.2, 139.0, 138.5, 130.7, 124.5, 124.3, 124.3, 121.6, 115.4, 114.0, 112.5, 79.8, 52.2, 33.5, 28.5.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1692.

HRMS (ESI) calcd. for $C_{18}H_{21}NNaO_4$ [M + Na]$^+$: 338.1363; found: 338.1362.

Methyl (*E*)-2-(3-(*tert*-butoxy)-3-oxoprop-1-en-1-yl)-1-methyl-1*H*-indole-4-carboxylate (11b)



Following **Procedure B** (reaction time 20 h), **11b** was obtained as white solid (188 mg, 75% yield) from *tert*-butyl acrylate (134 mg, 1.05 mmol) and methyl 1-methyl-1*H*-indole-4-carboxylate (150 mg, 0.793

mmol) using petroleum ether/EtOAc (50:1 to 15:1) as eluent.

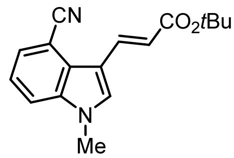
^{1}H NMR (400 *MHz*, $CDCl_3$): *δ* 7.95-7.87 (m, 1H), 7.72 (d, *J* = 15.8 Hz, 1H), 7.57-7.50 (m, 2H), 7.29 (t, *J* = 7.9 Hz, 1H), 6.56 (d, *J* = 15.7 Hz, 1H), 3.99 (s, 3H), 3.85 (s, 3H), 1.56 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): *δ* 167.9, 166.3, 139.7, 137.2, 131.2, 127.0, 124.2, 122.4, 122.2, 122.0, 114.4, 104.3, 81.0, 52.0, 30.3, 28.4.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1704.

HRMS (ESI) calcd. for $C_{18}H_{22}NO_4$ [M + H]$^+$: 316.1543; found: 316.1544.

Tert-butyl (_E_)-3-(4-cyano-1-methyl-1_H_-indol-3-yl)acrylate (12a)



Following **Procedure A** (reaction time 12 h), **12a** was obtained as white solid (125 mg, 55% yield) from *tert*-butyl acrylate (240 μL, 1.60 mmol) and 1-methyl-1*H*-indole-4-carbonitrile (125 mg, 0.800 mmol) using petroleum ether/EtOAc (15:1 to 3:1) as eluent.

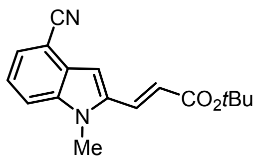
^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.34 (d, *J* = 15.9 Hz, 1H), 7.57-7.46 (m, 3H), 7.22-7.29 (m, 1H), 6.14 (d, *J* = 15.8 Hz, 1H), 3.87 (s, 3H), 1.55 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): *δ* 166.6, 137.4, 133.9, 130.5, 127.4, 126.2, 122.0, 119.0, 117.1, 114.8, 111.9, 102.5, 80.2, 33.6, 28.4.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1690, 2218.

HRMS (ESI) calcd. for $C_{17}H_{18}N_2NaO_2$ [M + Na]$^+$: 305.1260; found: 305.1260.

Tert-butyl (_E_)-3-(4-cyano-1-methyl-1_H_-indol-2-yl)acrylate (12b)



Following **Procedure B** (reaction time 20 h), **12b** was obtained as white solid (194 mg, 84% yield) from *tert*-butyl acrylate (134.3 mg, 1.05 mmol) and 1-methyl-1*H*-indole-4-carbonitrile (127 mg, 0.813 mmol) using petroleum ether/EtOAc (50:1 to 15:1) as eluent.

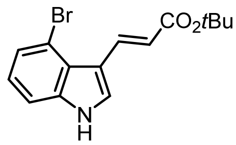
^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.69 (d, *J* = 15.8 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 7.0 Hz, 1H), 7.27 (dd, *J* = 8.3, 7.5 Hz, 1H), 7.10 (s, 1H), 6.55 (d, *J* = 15.8 Hz, 1H), 3.86 (s, 3H), 1.56 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): *δ* 165.9, 138.4, 137.9, 130.4, 128.8, 126.0, 123.6, 122.6, 118.5, 114.4, 103.6, 101.3, 81.3, 30.5, 28.3.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1701, 2226.

HRMS (ESI) calcd. for $C_{17}H_{19}N_2O_2$ [M + H]$^+$: 283.1441; found: 283.1441.

***Tert*-butyl (*E*)-3-(4-bromo-1*H*-indol-3-yl)acrylate (13a)**



Following **Procedure A** (reaction time 3 h), **13a** was obtained as colorless liquid (67.3 mg, 26% yield) from *tert*-butyl acrylate (240 μL, 1.60 mmol) and 4-bromo-1*H*-indole (100 μL, 0.80 mmol) using petroleum ether/EtOAc (14:1 to 5:1) as eluent.

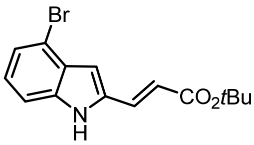
^{1}H NMR (400 MHz, CDCl$_3$): δ 8.72 (d, J = 15.9 Hz, 1H), 8.60 (s, 1H), 7.63 (d, J = 2.7 Hz, 1H), 7.35 (t, J = 7.7 Hz, 2H), 7.05 (t, J = 7.9 Hz, 1H), 6.17 (d, J = 15.8 Hz, 1H), 1.55 (s, 9H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 167.2, 137.7, 137.0, 125.9, 124.8, 124.6, 123.7, 116.3, 114.7, 114.6, 111.1, 80.1, 28.5.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1677, 3284.

HRMS (ESI) calcd. for $C_{15}H_{15}BrNO_2$ [M - H]$^-$: 322.0266; found: 322.0261.

***Tert*-butyl (*E*)-3-(4-bromo-1*H*-indol-2-yl)acrylate (13b)**

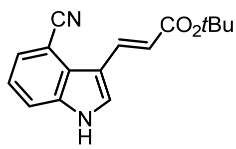


Following **Procedure B** (reaction time 6 h), an inseparable mixture of 4-bromo-1*H*-indole and product **13b** was obtained as a yellow oil (279 mg) from *tert*-butyl acrylate (103 mg, 0.800 mmol) and 4-bromo-1*H*-indole (317 mg, 1.62 mmol) using petroleum ether/EtOAc (30:1 to 15:1) as eluent.

After performing a methylation reaction of this mixture using NaH (72.0 mg, 60% dispersion in mineral oil, 1.80 mmol) and MeI (0.10 mL, 1.6 mmol) in THF, the methylated mixture can be separated by flash column chromatography on silica gel using petroleum ether/EtOAc (30:1 to 15:1) as eluent to afford pure *N*-methylated derivative of product **13b** (the same as **9b**) as a yellow solid (108.5 mg, 40% yield).

Characterization data of the methylation product of **13b** were identical to those of **9b**.

***Tert*-butyl (*E*)-3-(4-cyano-1*H*-indol-3-yl)acrylate (14a)**



Following **Procedure A** (reaction time 3 h), **14a** was obtained as white solid (33.3 mg,16% yield) from *tert*-butyl acrylate (240 μL, 1.60 mmol) and 1*H*-indole-4-carbonitrile (114 mg, 0.802 mmol) using petroleum ether/EtOAc (8:1 to 4:1) as eluent.

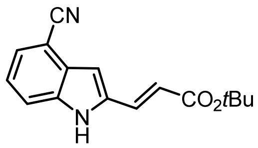
^{1}H NMR (400 MHz, DMSO-d_6): δ 12.36 (s, 1H), 8.48 (s, 1H), 8.36 (d, J = 16.0 Hz, 1H), 7.86 (dd, J = 8.2, 0.6 Hz, 1H), 7.70 (dd, J = 8.2, 0.6 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 6.50 (d, J = 15.7 Hz, 1H), 1.54 (s, 9H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 166.1, 136.8, 134.5, 129.8, 127.3, 125.0, 121.9, 119.1, 118.0, 115.5, 110.8, 100.2, 79.3, 28.0.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1682, 2218, 3296.

HRMS (ESI) calcd. for $C_{16}H_{16}N_2NaO_2$ [M + Na]$^+$: 291.1104; found: 291.1095.

Tert-butyl (_E_)-3-(4-cyano-1_H_-indol-2-yl)acrylate (14b)



Following **Procedure B** (reaction time 20 h), **14b** was obtained as yellow solid (82.4 mg, 39% yield) from *tert*-butyl acrylate (134 mg, 1.04 mmol) and 1*H*-indole-4-carbonitrile (112 mg, 0.790 mmol) using petroleum ether/EtOAc (50:1 to 15:1) as eluent.

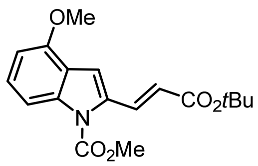
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (s, 1H), 7.63-7.56 (m, 2H), 7.49 (d, J = 7.1 Hz, 1H), 7.32-7.27 (m, 1H), 6.99 (s, 1H), 6.34 (d, J = 16.1 Hz, 1H), 1.57 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 137.2, 136.1, 132.5, 129.8, 126.2, 123.8, 120.8, 118.4, 115.9, 106.0, 103.9, 81.5, 28.4.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1706, 2219, 3350.

HRMS (ESI) calcd. for $C_{16}H_{16}N_2NaO_2$ [M + Na]$^+$: 291.1104; found: 291.1109.

Methyl (_E_)-2-(3-(_tert_-butoxy)-3-oxoprop-1-en-1-yl)-4-methoxy-1_H_-indole-1-carboxylate (15b)



Following **Procedure B** (reaction time 20 h), **15b** was obtained as yellow solid (218 mg, 82% yield) from *tert*-butyl acrylate (134 mg, 1.05 mmol) and methyl 4-methoxy-1*H*-indole-1-carboxylate (164 mg, 0.799 mmol) using petroleum ether/EtOAc (100:1 to 15:1) as eluent.

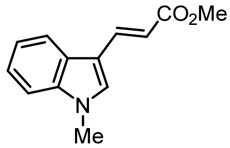
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (dd, J = 15.8, 0.6 Hz, 1H), 7.72 (d, J = 8.5 Hz, 1H), 7.24-7.30 (m, 1H), 7.13 (s, 1H), 6.67 (d, J = 8.0 Hz, 1H), 6.34 (d, J = 15.8 Hz, 1H), 4.08 (s, 3H), 3.94 (s, 3H), 1.54 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 153.2, 152.4, 138.8, 134.9, 134.7, 126.8, 121.4, 119.7, 108.9, 107.8, 103.7, 80.6, 55.6, 54.1, 28.4.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1738.

HRMS (ESI) calcd. for $C_{18}H_{21}NNaO_5$ [M + Na]$^+$: 354.1312; found: 354.1317.

Methyl (*E*)-3-(1-methyl-1*H*-indol-3-yl)acrylate (16a)



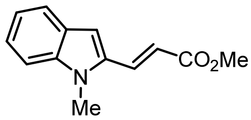
Following **Procedure A** (reaction time 3 h), **16a** was obtained as pale yellow solid (132 mg, 77% yield) from methyl acrylate (145 μL, 1.60 mmol) and 1-methyl-1*H*-indole (100 μL, 0.80 mmol) using petroleum ether/EtOAc (14:1 to 6:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.92-7.82 (m, 2H), 7.36-7.20 (m, 4H), 6.40 (d, *J* = 15.9 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): *δ* 168.8, 138.3, 138.2, 133.2, 126.2, 123.1, 121.4, 120.7, 112.3, 112.2, 110.1, 51.5, 33.3.

The NMR data were identical to those reported in literature.[15]

Methyl (*E*)-3-(1-methyl-1*H*-indol-2-yl)acrylate (16b)



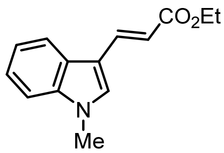
Following **Procedure B** (reaction time 3 h), **16b** was obtained as white solid (94.7 mg, 54% yield) from methyl acrylate (70.4 mg, 0.818 mmol) and *N*-methylindole (210 mg, 1.60 mmol) using petroleum ether/EtOAc (50:1 to 20:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.80 (d, *J* = 15.8 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.36-7.22 (m, 2H), 7.08-7.14 (m, 1H), 6.96 (s, 1H), 6.48 (d, *J* = 15.8 Hz, 1H), 3.82 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): *δ* 167.6, 139.2, 135.0, 133.0, 127.6, 123.8, 121.5, 120.6, 117.9, 109.8, 103.9, 51.9, 30.2.

The NMR data were identical to those reported in literature.[16]

Ethyl (*E*)-3-(1-methyl-1*H*-indol-3-yl)acrylate (17a)



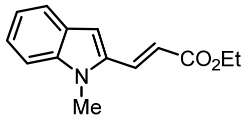
Following **Procedure A** (reaction time 3 h), **17a** was obtained as yellow solid (137 mg, 75% yield) from ethyl acrylate (175 μL, 1.61 mmol) and 1-methyl-1*H*-indole (100 μL, 0.80 mmol) using petroleum ether/EtOAc (14:1 to 6:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.85-7.93 (m, 2H), 7.35-7.20 (m, 4H), 6.41 (d, *J* = 15.9 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): *δ* 168.4, 138.2, 138.1, 133.2, 126.2, 123.0, 121.4, 120.7, 112.7, 112.2, 110.0, 60.1, 33.3, 14.6.

The NMR data were identical to those reported in literature. [17]

Ethyl (*E*)-3-(1-methyl-1*H*-indol-2-yl)acrylate (17b)



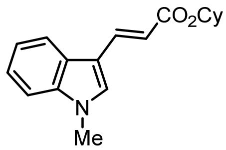
Following **Procedure B** (reaction time 3 h), **17b** was obtained as white solid (99.3 mg, 54% yield) from ethyl acrylate (79.7 mg, 0.796 mmol) and *N*-methylindole (211 mg, 1.61 mmol) using petroleum ether/EtOAc (50:1 to 15:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 15.8 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.33-7.22 (m, 2H), 7.08-7.14 (m, 1H), 6.95 (s, 1H), 6.48 (d, J = 15.8 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.82 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 139.2, 135.1, 132.8, 127.6, 123.7, 121.5, 120.6, 118.4, 109.7, 103.9, 60.7, 30.2, 14.5.

The NMR data were identical to those reported in literature. [12]

Cyclohexyl (*E*)-3-(1-methyl-1*H*-indol-3-yl)acrylate (18a)



Following **Procedure A** (reaction time 3 h), **18a** was obtained as white solid (141 mg, 62% yield) from cyclohexyl acrylate (267 μL, 1.60 mmol) and 1-methyl-1*H*-indole (100 μL, 0.80 mmol) using petroleum ether/EtOAc (15:1 to 6:1) as eluent.

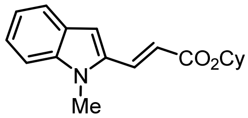
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 7.8 Hz, 1H), 7.87 (d, J = 15.9 Hz, 1H), 7.36-7.21 (m, 4H), 6.41 (d, J = 15.9 Hz, 1H), 4.99-4.81 (m, 1H), 3.78 (s, 3H), 2.01-1.73 (m, 4H), 1.62-1.20 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 138.2, 137.8, 133.1, 126.2, 123.0, 121.3, 120.8, 113.4, 112.3, 110.0, 72.3, 33.3, 32.1, 25.7, 24.1.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1693.

HRMS (ESI) calcd. for $C_{18}H_{21}NNaO_2$ [M + Na]$^+$: 306.1465; found: 306.1466.

Cyclohexyl (*E*)-3-(1-methyl-1*H*-indol-2-yl)acrylate (18b)



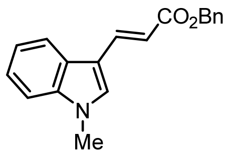
Following **Procedure B** (reaction time 20 h), **18b** was obtained as white solid (117 mg, 51% yield) from cyclohexyl acrylate (124 mg, 0.807 mmol) and 1-methylindole (211 mg, 1.61 mmol) using petroleum ether/EtOAc (50:1 to 15:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 15.8 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.31-7.21 (m, 2H), 7.07-7.14 (m, 1H), 6.92 (s, 1H), 6.46 (d, J = 15.8 Hz, 1H), 4.97-4.84 (m, 1H), 3.77 (s, 3H), 1.98-1.73 (m, 4H), 1.61-1.18 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 139.1, 135.1, 132.4, 127.6, 123.6, 121.4, 120.5, 118.9, 109.7, 103.7, 72.9, 31.9, 30.1, 25.6, 23.9.

The NMR data were identical to those reported in literature. [12]

Benzyl (*E*)-3-(1-methyl-1*H*-indol-3-yl)acrylate (19a)



Following **Procedure A** (reaction time 3 h), **19a** was obtained as white solid (124 mg, 53% yield) from benzyl acrylate (240 µL, 1.60 mmol) and 1-methyl-1*H*-indole (100 µL, 0.80 mmol) using petroleum ether/EtOAc (15:1 to 4:1) as eluent.

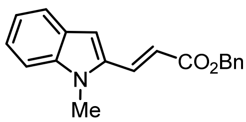
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.97 (m, 2H), 7.48-7.16 (m, 9H), 6.46 (d, J = 15.9 Hz, 1H), 5.26 (s, 2H), 3.77 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 138.7, 138.2, 136.7, 133.5, 128.7, 128.4, 128.2, 126.1, 123.1, 121.4, 120.7, 112.1, 110.1, 66.1, 33.3.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1693.

HRMS (ESI) calcd. for $C_{19}H_{17}NNaO_2$ $[M + Na]^+$: 314.1151; found: 314.1152.

Benzyl (*E*)-3-(1-methyl-1*H*-indol-2-yl)acrylate (19b)



Following **Procedure B** (reaction time 3 h), **19b** was obtained as white solid (115 mg, 50% yield) from benzyl acrylate (129 mg, 0.797 mmol) and *N*-methylindole (210 mg, 1.60 mmol) using petroleum ether/EtOAc (50:1 to 15:1) as eluent.

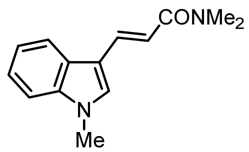
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 15.8 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.45-7.23 (m, 7H), 7.07-7.14 (m, 1H), 6.95 (s, 1H), 6.53 (d, J = 15.8 Hz, 1H), 5.27 (s, 2H), 3.81 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 139.2, 136.2, 135.0, 133.4, 128.8, 128.5, 128.4, 127.6, 123.8, 121.6, 120.6, 117.8, 109.8, 104.1, 66.6, 30.2.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1703.

HRMS (ESI) calcd. for $C_{19}H_{18}NO_2$ [M + H]$^+$: 292.1332; found: 292.1333.

(*E*)-*N,N*-dimethyl-3-(1-methyl-1*H*-indol-3-yl)acrylamide (20a)



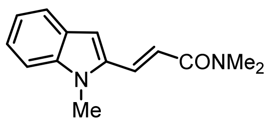
Following **Procedure A** (reaction time 3 h), **20a** was obtained as white solid (78.3 mg, 43% yield) from *N,N*-dimethylacrylamide (165 μL, 1.60 mmol) and *N*-methylindole (100 μL, 0.80 mmol) using DCM/MeOH (80:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (dd, J = 11.5, 6.5 Hz, 2H), 7.35-.21 (m, 4H), 6.86 (d, J = 15.3 Hz, 1H), 3.77 (s, 3H), 3.19 (s, 3H), 3.08 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 138.1, 135.8, 132.6, 126.1, 122.7, 120.9, 120.5, 112.7, 112.0, 110.0, 37.5, 36.0, 33.2.

The NMR data were identical to those reported in literature. [18]

(*E*)-*N,N*-dimethyl-3-(1-methyl-1*H*-indol-2-yl)acrylamide (20b)



Following **Procedure B** (reaction time 20 h), **20b** was obtained as yellow solid (131 mg, 73% yield) from *N*,*N*-dimethylacrylamide (78.0 mg, 0.787 mmol) and *N*-methylindole (211 mg, 1.60 mmol) using petroleum ether/EtOAc (2:1 to 1:2) as eluent.

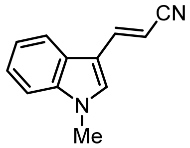
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 15.1 Hz, 1H), 7.58 (d, J = 7.9 Hz, 1H), 7.31-7.18 (m, 2H), 7.06-7.12 (m, 1H), 6.95 (d, J = 15.1 Hz, 1H), 6.91 (s, 1H), 3.78 (s, 3H), 3.14 (s, 3H), 3.06 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 138.7, 136.1, 130.6, 127.6, 123.0, 121.0, 120.3, 117.9, 109.6, 101.8, 37.4, 36.0, 29.9.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1644.

HRMS (ESI) calcd. for $C_{14}H_{17}N_2O$ [M + H]$^+$: 229.1335; found: 229.1340.

(*E*)-3-(1-methyl-1*H*-indol-3-yl)acrylonitrile (21a)



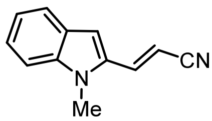
Following **Procedure A** (reaction time 3 h), **21a** was obtained as pale yellow solid (60.4 mg, 41% yield) from acrylonitrile (105 μL, 1.59 mmol) and *N*-methylindole (100 μL, 0.80 mmol) using petroleum ether/EtOAc (14:1 to 6:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.75 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 16.5 Hz, 1H), 7.39-7.24 (m, 4H), 5.72 (d, *J* = 16.5 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 143.6, 138.2, 133.0, 125.6, 123.5, 121.9, 120.2, 112.0, 110.4, 89.7, 33.4.

The NMR data were identical to those reported in literature.[19]

(*E*)-3-(1-methyl-1*H*-indol-2-yl)acrylonitrile (21b)



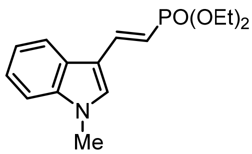
Following **Procedure B** (reaction time 3 h), **21b** was obtained as yellow solid (32.8 mg, 22% yield) from acrylonitrile (42.1 mg, 0.793 mmol) and *N*-methylindole (206 mg, 1.57 mmol) using petroleum ether/EtOAc (30:1 to 15:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.61 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.47 (dd, *J* = 16.3, 0.6 Hz, 1H), 7.35-7.27 (m, 2H), 7.14 (ddd, *J* = 7.9, 6.1, 1.7 Hz, 1H), 6.95 (s, 1H), 5.88 (d, *J* = 16.3 Hz, 1H), 3.80 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 139.4, 138.4, 134.1, 127.3, 124.5, 121.8, 121.0, 118.6, 109.9, 104.1, 95.6, 30.2.

The NMR data were identical to those reported in literature.[20]

Diethyl (*E*)-(2-(1-methyl-1*H*-indol-3-yl)vinyl)phosphonate (22a)



Following **Procedure A** (reaction time 3 h), **22a** was obtained as colorless liquid (48.6 mg, 21% yield) from diethyl vinylphosphonate (245 μL, 1.59 mmol) and *N*-methylindole (100 μL, 0.80 mmol) using DCM/MeOH (100:1 to 80:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.90 (d, *J* = 7.9 Hz, 1H), 7.68 (dd, *J* = 23.3, 17.5 Hz, 1H), 7.37-7.21 (m, 4H), 6.16-6.02 (app. t, *J* = 17.7 Hz, 1H), 4.18-4.08 (m, 4H), 3.81 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 6H).

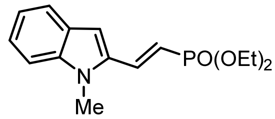
^{13}C NMR (100 MHz, $CDCl_3$): *δ* 142.4, 138.1, 132.6, 126.1, 123.1, 121.4, 120.5, 110.1, 108.2, 106.3, 61.7

(d, J = 5.3 Hz), 33.3, 16.6 (d, J = 6.5 Hz).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1239.

HRMS (ESI) calcd. for $C_{15}H_{20}NNaO_3P$ [M + Na]$^+$: 316.1073; found: 316.1074.

Diethyl (*E*)-(2-(1-methyl-1*H*-indol-2-yl)vinyl)phosphonate (22b)



Following **Procedure B** (reaction time 20 h), **22b** was obtained as yellow oil (97.8 mg, 41% yield) from diethyl vinylphosphonate (134 mg, 0.817 mmol) and *N*-methylindole (211 mg, 1.61 mmol) using petroleum ether/EtOAc (10:1 to 1:2) as eluent.

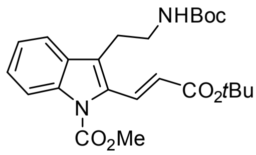
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68-7.54 (m, 2H) 7.23-7.35 (m, 2H), 7.12 (td, J = 7.4 Hz, 0.9 Hz,1H), 6.93 (s, 1H), 6.28 (app. t, J = 17.5 Hz, 1H), 4.20- 4.10 (m, 4H), 3.83 (s, 3H), 1.37 (t, J = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 137.0 (d, J = 7.9 Hz), 135.7, 135.4, 127.4, 123.6, 121.5, 120.5, 115.2, 113.3, 109.8, 103.2 (d, J = 1.8 Hz), 62.0 (d, J = 5.4 Hz), 30.2, 16.57 (d, J = 6.4 Hz).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1243.

HRMS (ESI) calcd. for $C_{15}H_{21}NO_3P$ [M + H]$^+$: 294.1254; found: 294.1256.

Methyl (*E*)-2-(3-(*tert*-butoxy)-3-oxoprop-1-en-1-yl)-3-(2-((*tert*-butoxycarbonyl)amino)ethyl)-1*H*-indole-1-carboxylate (23)



Following **Procedure B**, **23** was obtained as white solid (275 mg, 76% yield) from *tert*-butyl acrylate (240 µL, 1.60 mmol) and methyl 3-(2-((*tert*-butoxycarbonyl)amino)ethyl)-1*H*-indole-1-carboxylate (258 mg, 1.61 mmol) using petroleum ether/EtOAc (20:1 to 2:1) as eluent.

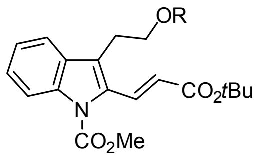
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, J = 8.3 Hz, 1H), 7.94 (d, J = 16.1 Hz, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.37 (ddd, J = 8.4, 7.2, 1.3 Hz, 1H), 7.29 (td, J = 7.5, 1.0 Hz, 1H), 6.08 (d, J = 16.1 Hz, 1H), 4.66 (s, 1H), 4.08, 3.44 (q, J = 6.9 Hz, 2H), 3.03 (t, J = 7.2 Hz, 2H), 1.55 (s, 9H), 1.45 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 155.9, 152.4, 136.3, 134.5, 132.5, 130.0, 126.1, 123.6, 122.8, 121.6, 119.9, 115.8, 80.9, 79.5, 54.1, 40.8, 28.6, 28.4, 25.8.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3360, 1702.

HRMS (ESI) calcd. for $C_{24}H_{32}N_2NaO_6$ [M + Na]$^+$:467.2153 ; found: 467.2153.

Methyl (*E*)-2-(3-(*tert*-butoxy)-3-oxoprop-1-en-1-yl)-3-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-1*H*-indole-1-carboxylate (24a) and methyl (*E*)-2-(3-(*tert*-butoxy)-3-oxoprop-1-en-1-yl)-3-(2-hydroxyethyl)-1H-indole-1-carboxylate (24b)



24a R = TBS
24b R = H

Following **Procedure B**, **24a** and **24b** were obtained in 64% overall yield (**24a**: 115 mg, 30% yield; **24b**: 97.6 mg, 34% yield) from *tert*-butyl acrylate (106 mg, 0.82 mmol) and methyl 3-(2-((*tert*-butoxycarbonyl)amino)ethyl)-1*H*-indole-1-carboxylate (532 mg, 1.60 mmol) using petroleum ether/EtOAc (20:1 to 1:1) as eluent.

Characterization data for **24a**:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, J = 8.3 Hz, 1H), 7.93 (d, J = 16.0 Hz, 1H), 7.58 (d, J = 7.7 Hz, 1H), 7.36 (ddd, J = 8.4, 7.2, 1.3 Hz, 1H), 7.31-7.24 (m, 1H), 6.30 (d, J = 16.0 Hz, 1H), 4.05 (s, 3H), 3.91 (t, J = 6.9 Hz, 2H), 3.05 (t, J = 6.9 Hz, 2H), 1.55 (s, 9H), 0.86 (s, 9H), -0.01 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 152.4, 136.3, 134.4, 132.9, 130.3, 125.9, 123.3, 123.0, 121.6, 119.8, 115.7, 80.7, 63.1, 54.0, 28.7, 28.4, 26.1, 18.5, -5.2.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1739, 1707.

HRMS (ESI) calcd. for $C_{25}H_{37}NNaO_5Si$ $[M + Na]^+$: 482.2333 ; found: 482.2332.

Characterization data for **24b**:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 8.3 Hz, 1H), 7.93 (d, J = 16.0 Hz, 1H), 7.63-7.57 (m, 1H), 7.37 (ddd, J = 8.4, 7.2, 1.3 Hz, 1H), 7.32-7.26 (m, 1H), 6.22 (d, J = 16.1 Hz, 1H), 4.05 (s, 3H), 3.96 (t, J = 6.7 Hz, 2H), 3.10 (t, J = 6.7 Hz, 2H), 1.55 (s, 9H).

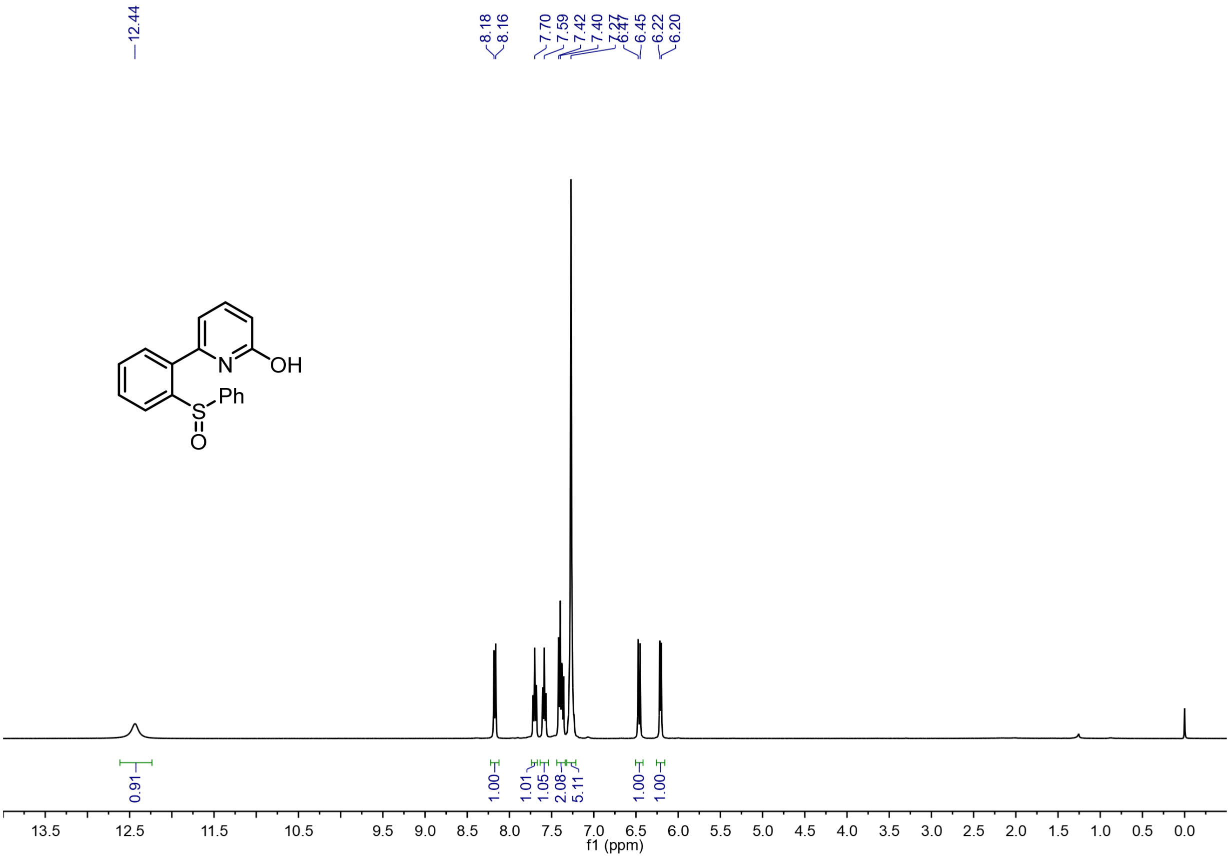
^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 152.3, 136.4, 134.4, 133.0, 130.1, 126.1, 123.5, 123.1, 120.9, 119.7, 115.8, 80.9, 62.6, 54.1, 28.4, 28.4.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3436, 1737, 1704.

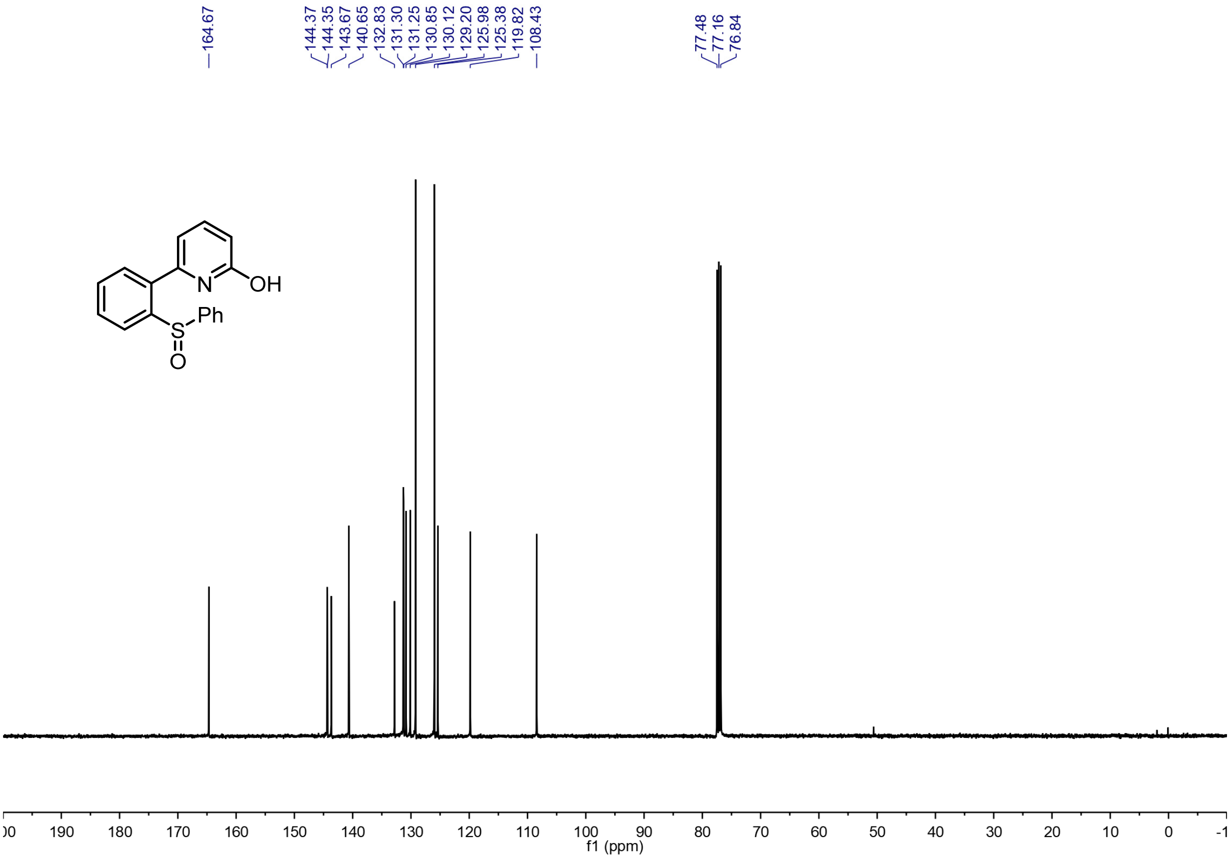
HRMS (ESI) calcd. for $C_{19}H_{23}NNaO_5$ $[M + Na]^+$: 368.1468; found: 368.1469.

6. NMR Spectra for Products

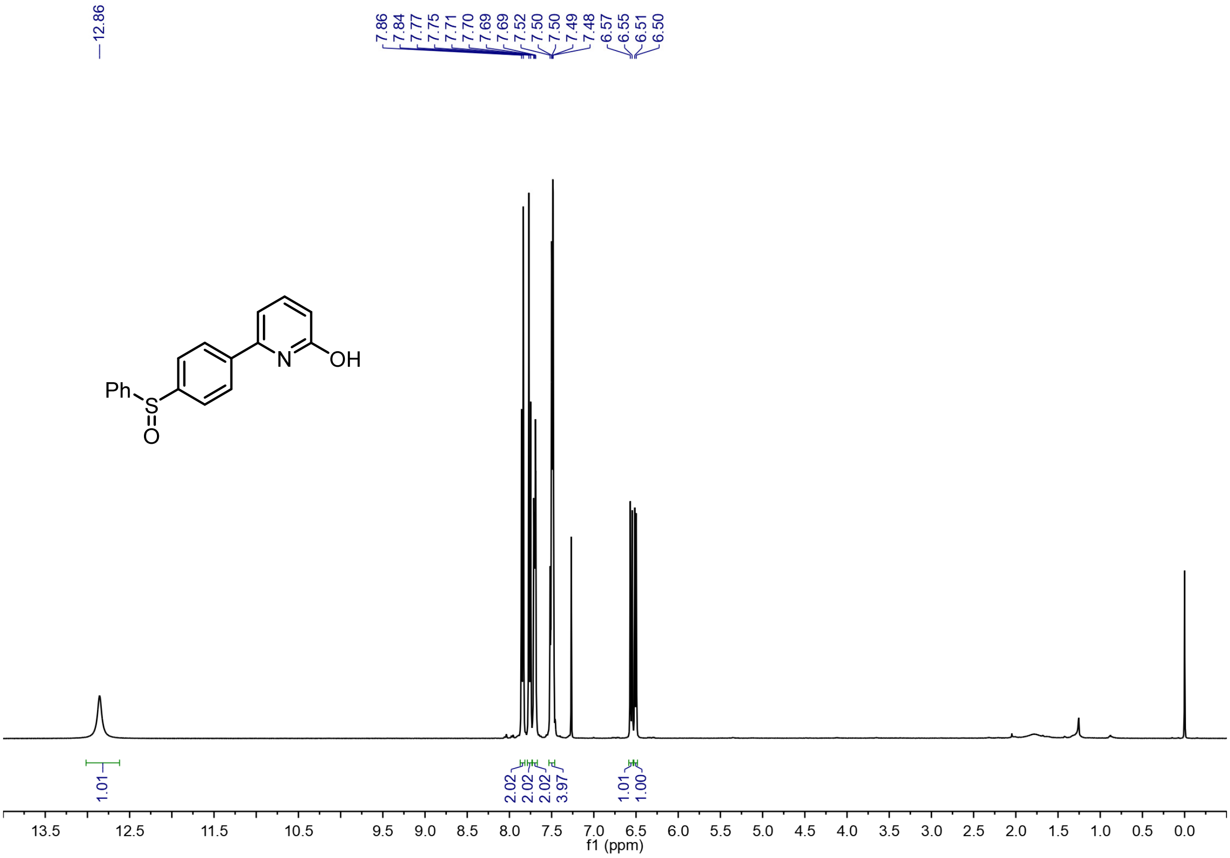
^{1}H NMR ($CDCl_3$, 400 MHz) of **L7**:



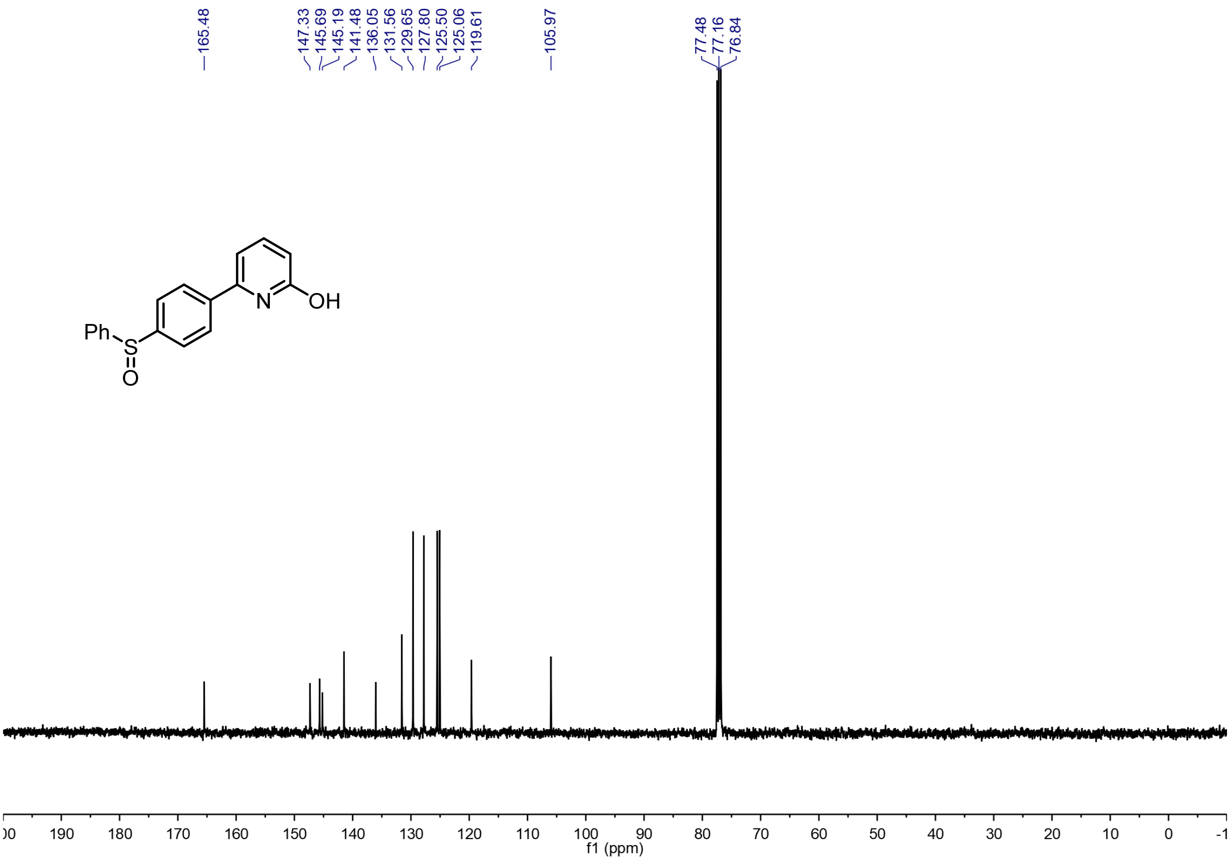
^{13}C NMR ($CDCl_3$, 100 MHz) of **L7**:



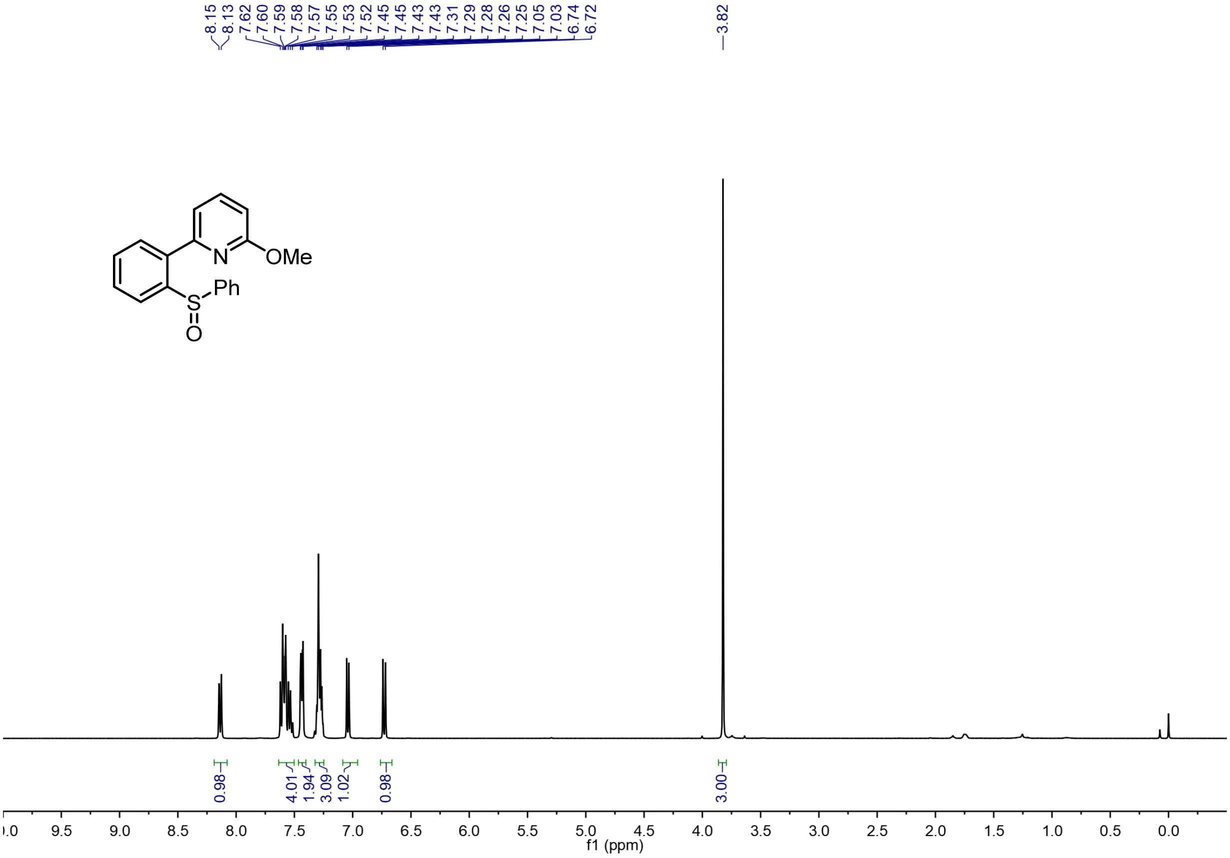
^1H NMR ($CDCl_3$, 400 MHz) of **L8**:



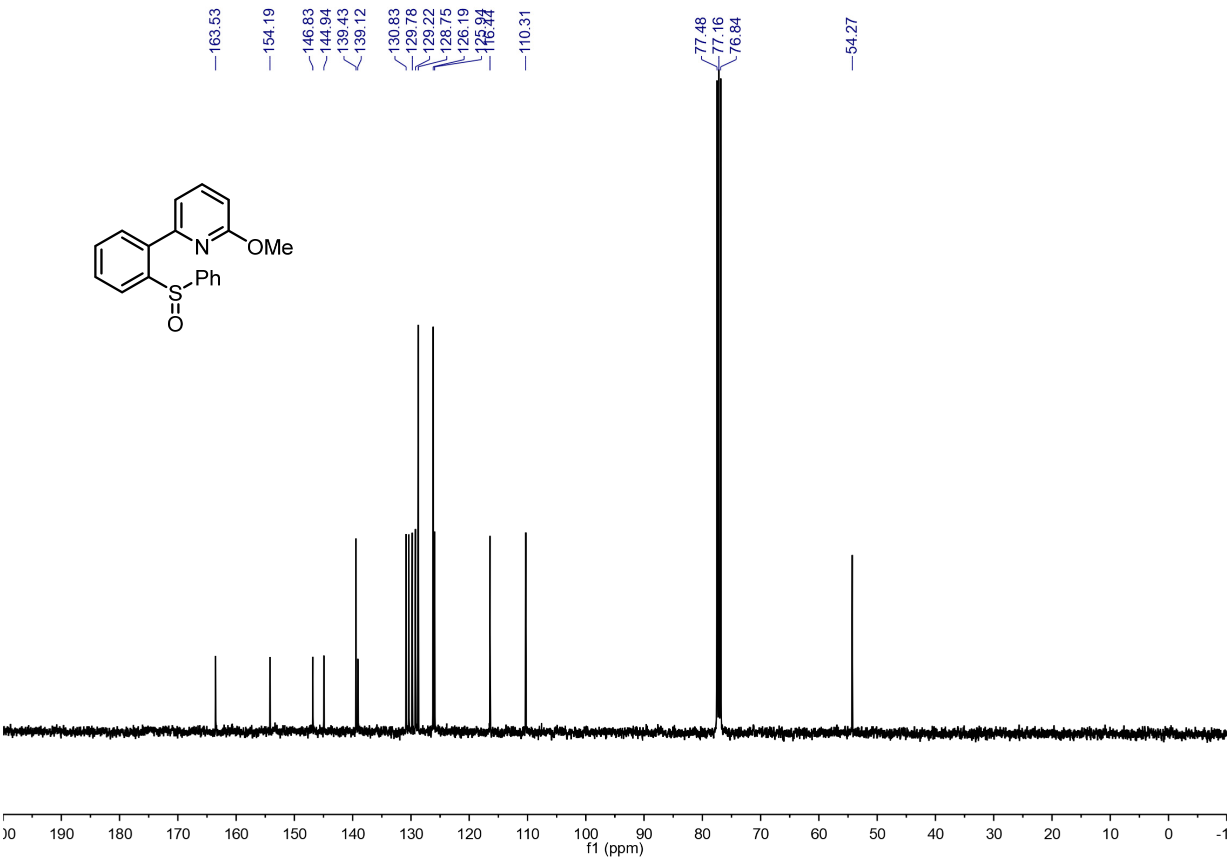
^{13}C NMR ($CDCl_3$, 100 MHz) of **L8**:



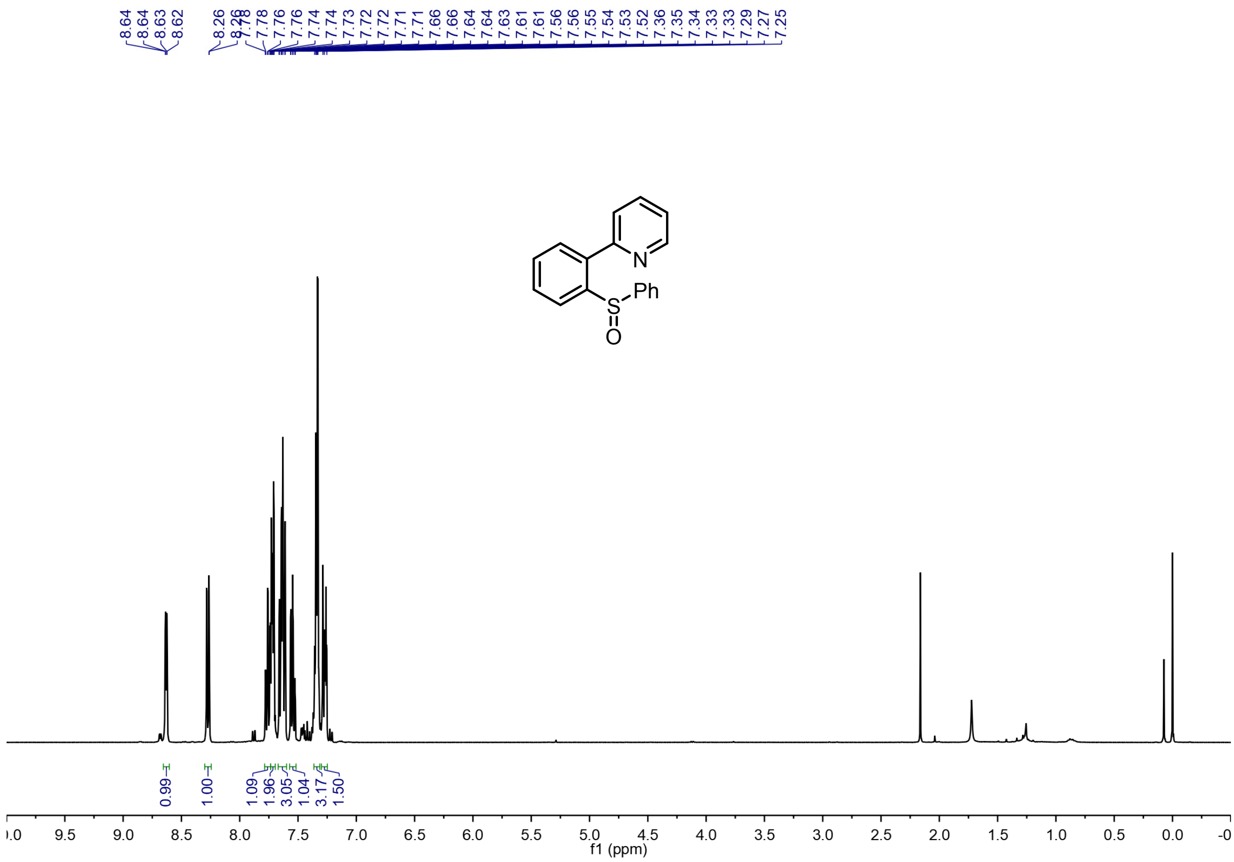
^1H NMR ($CDCl_3$, 400 MHz) of **L9**:



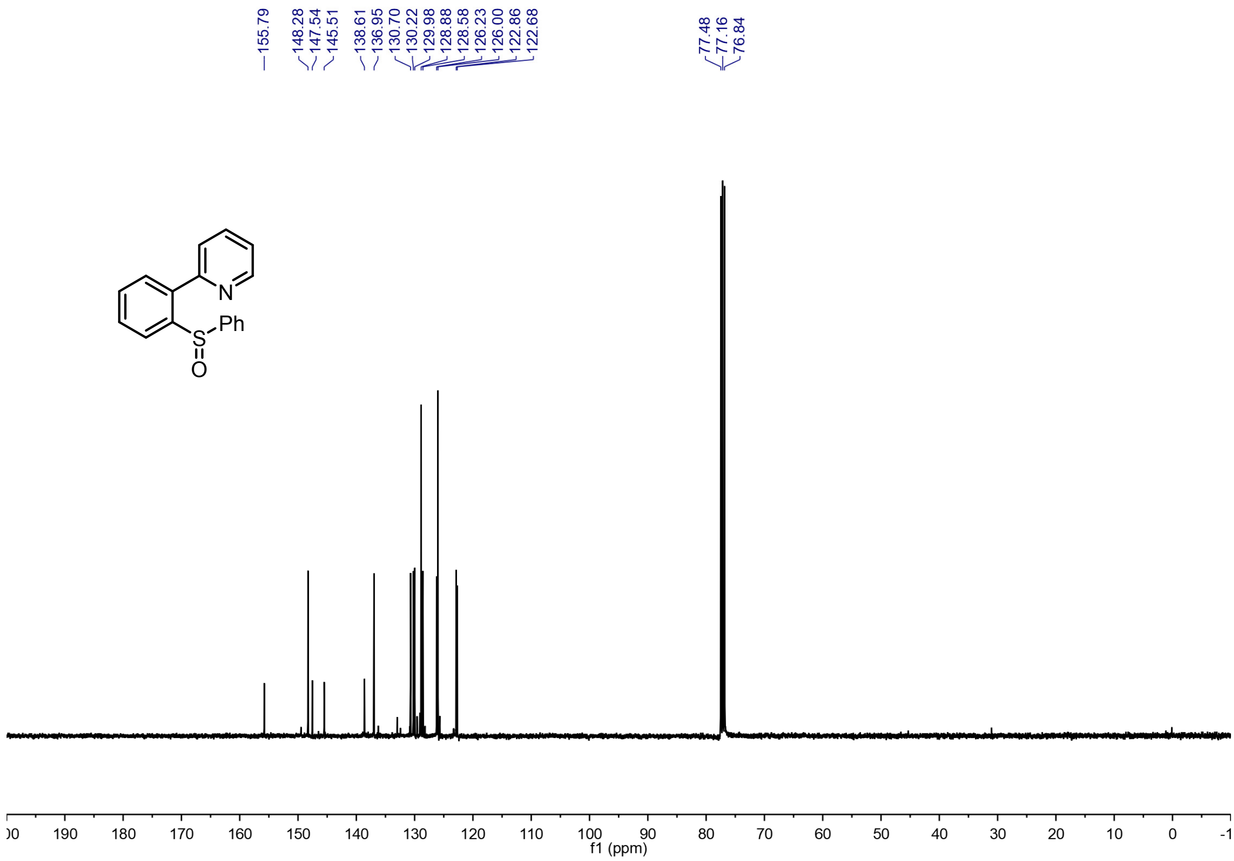
^{13}C NMR ($CDCl_3$, 100 MHz) of **L9**:



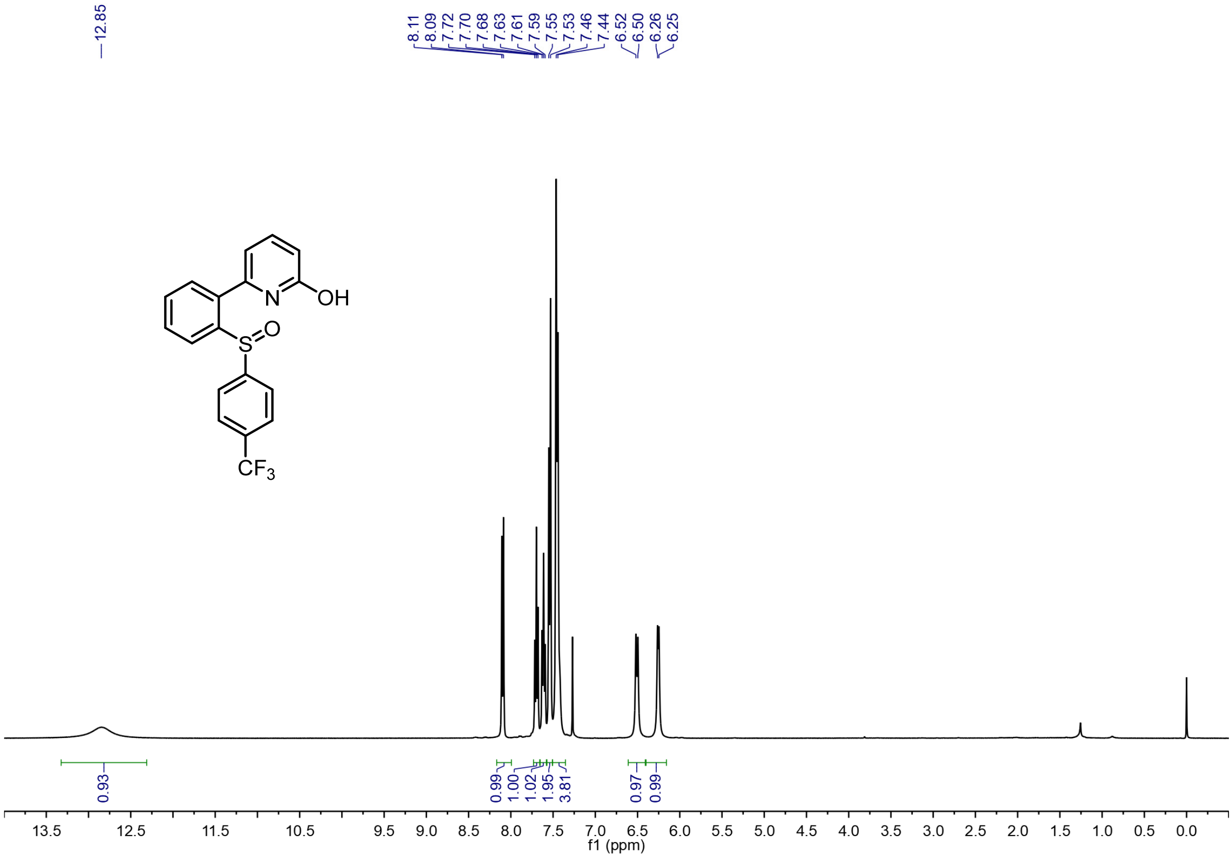
[1]H NMR ($CDCl_3$, 400 MHz) of **L10**:



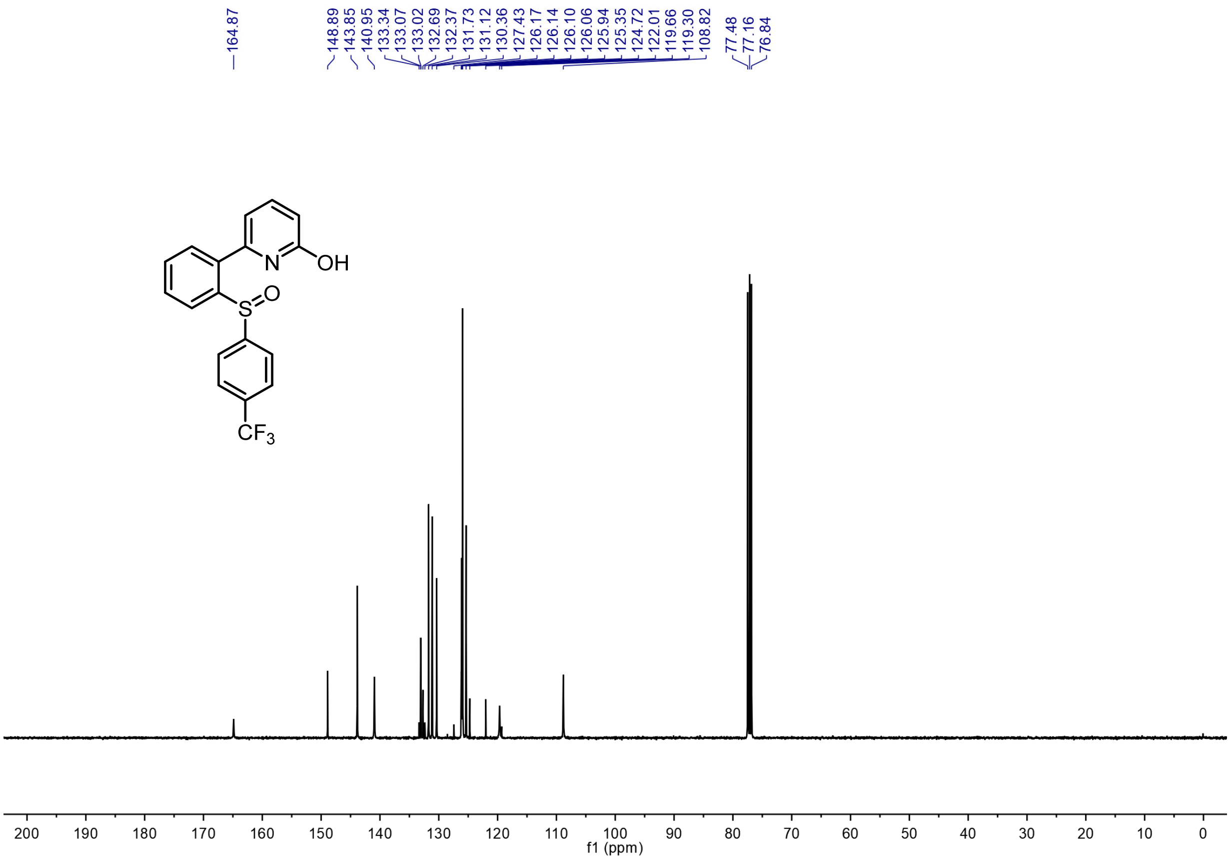
[13]C NMR ($CDCl_3$, 100 MHz) of **L10**:



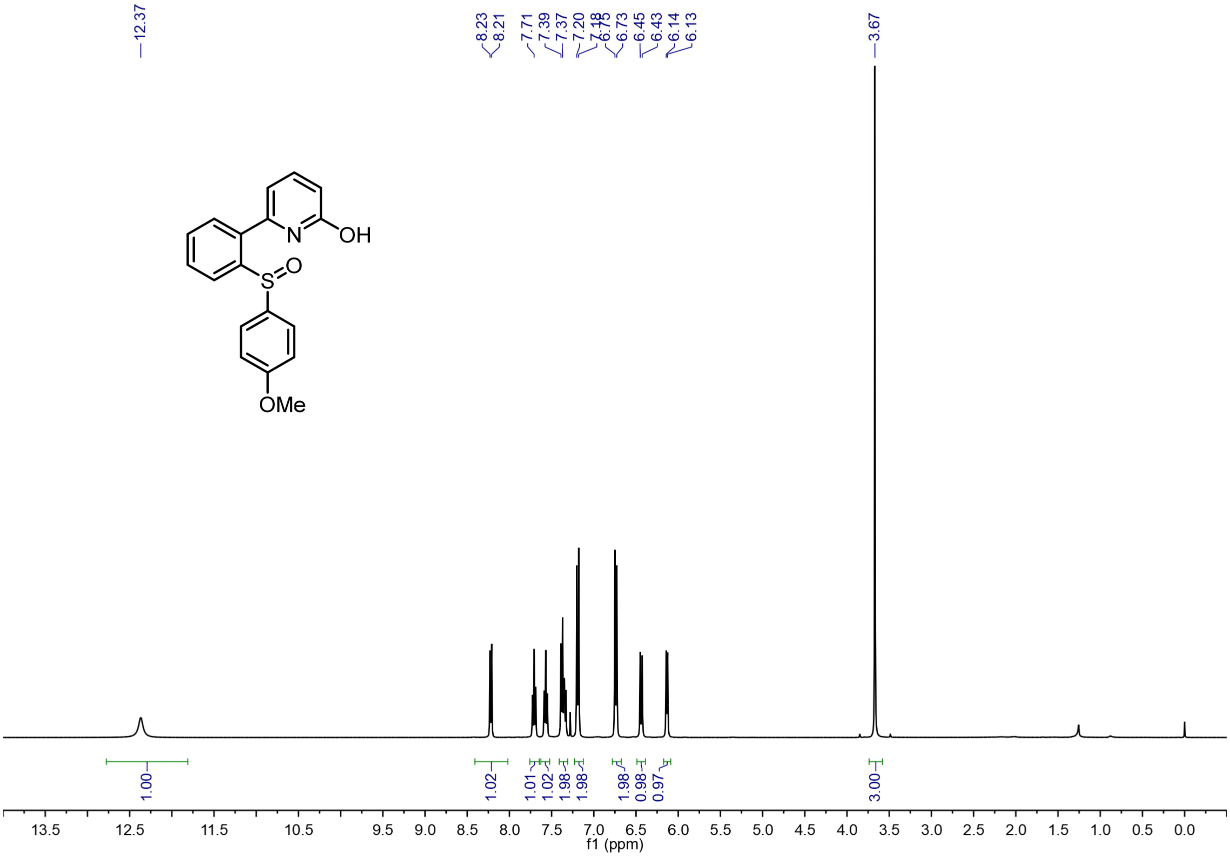
^{1}H NMR ($CDCl_3$, 400 MHz) of **L11**:



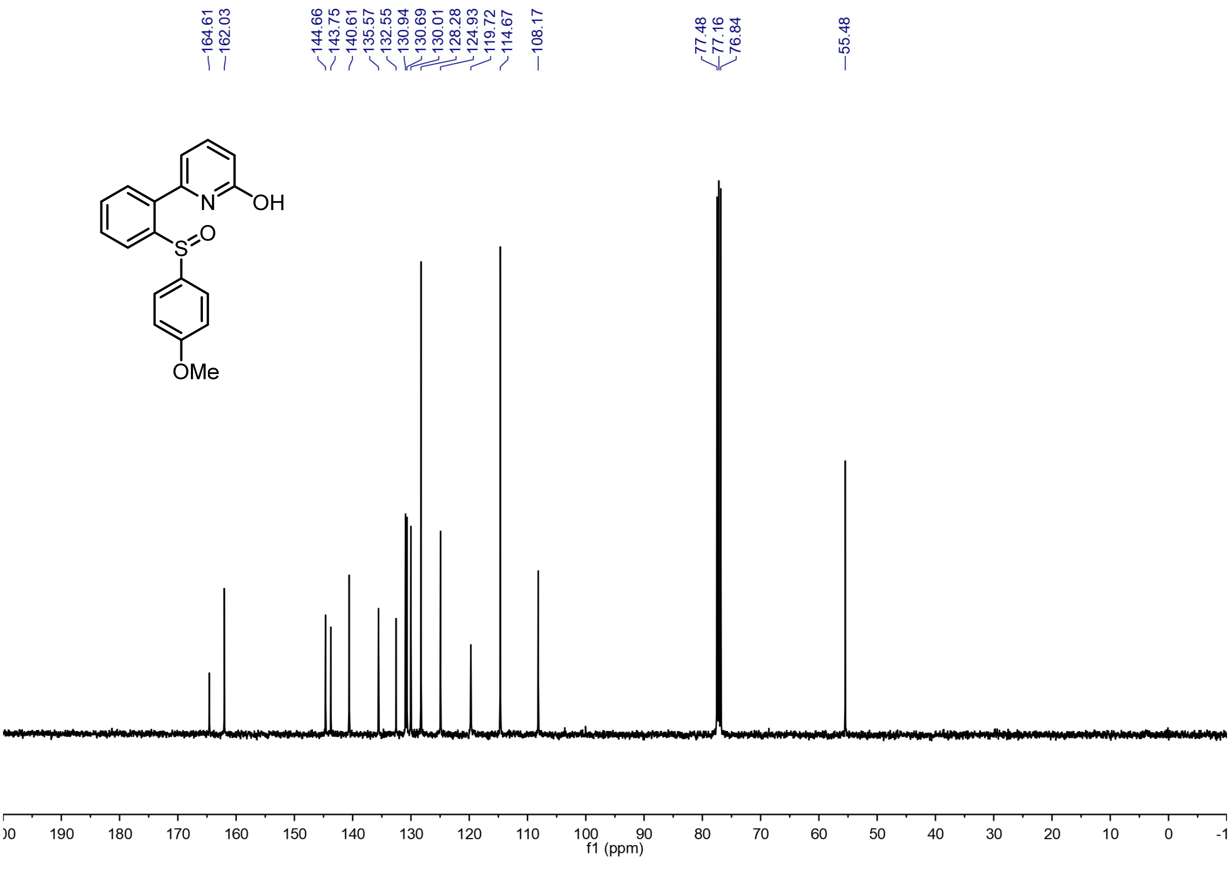
^{13}C NMR ($CDCl_3$, 100 MHz) of **L11**:



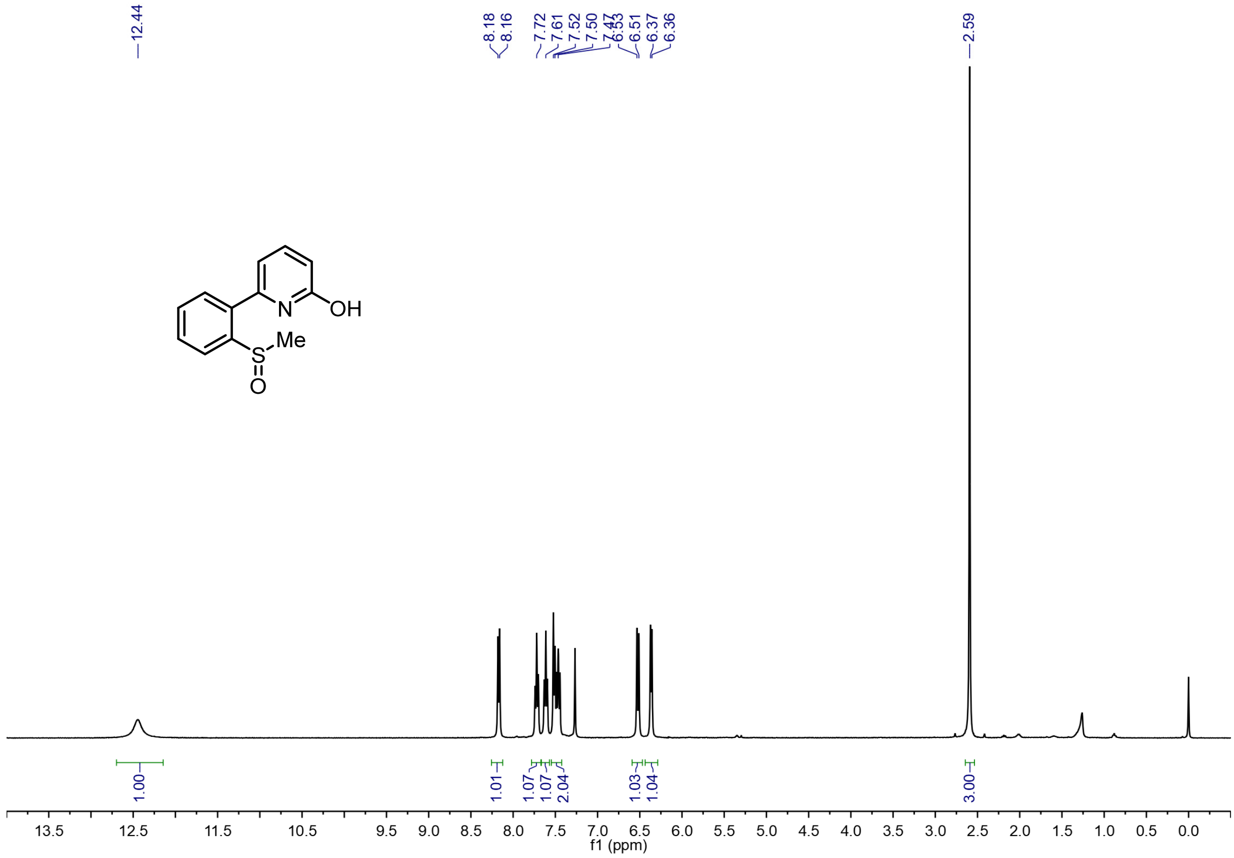
^{1}H NMR, $CDCl_3$, 400 MHz of **L12**:



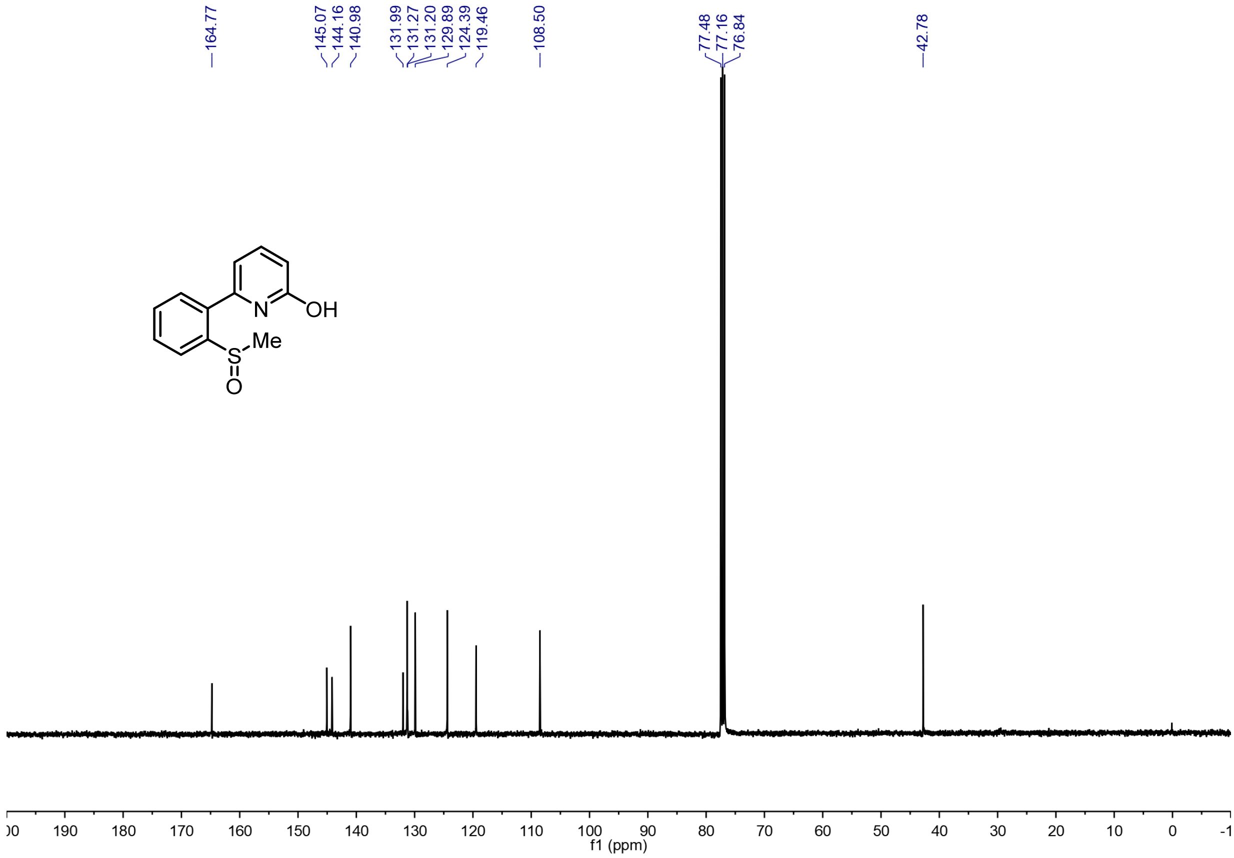
^{13}C NMR ($CDCl_3$, 100 MHz) of **L12**:



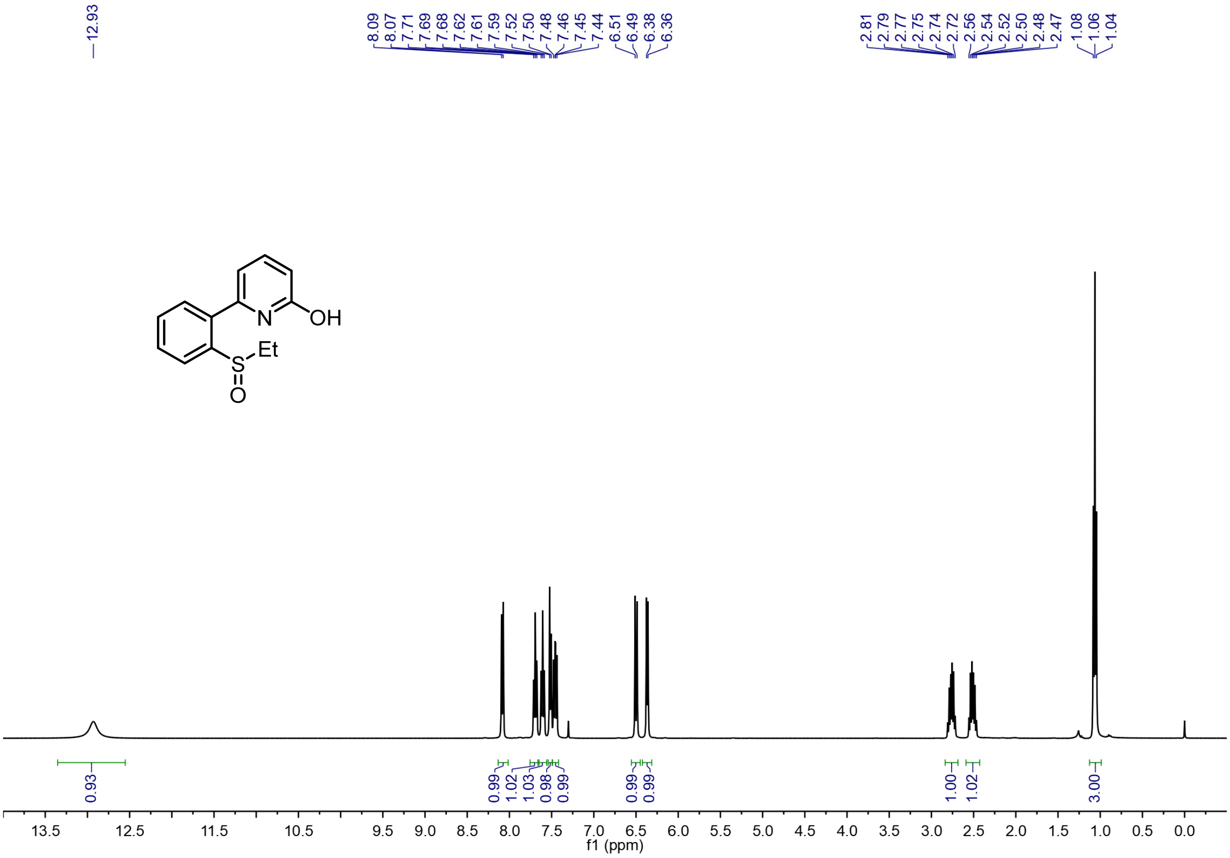
^{1}H NMR ($CDCl_3$, 400 MHz) of **L13**:



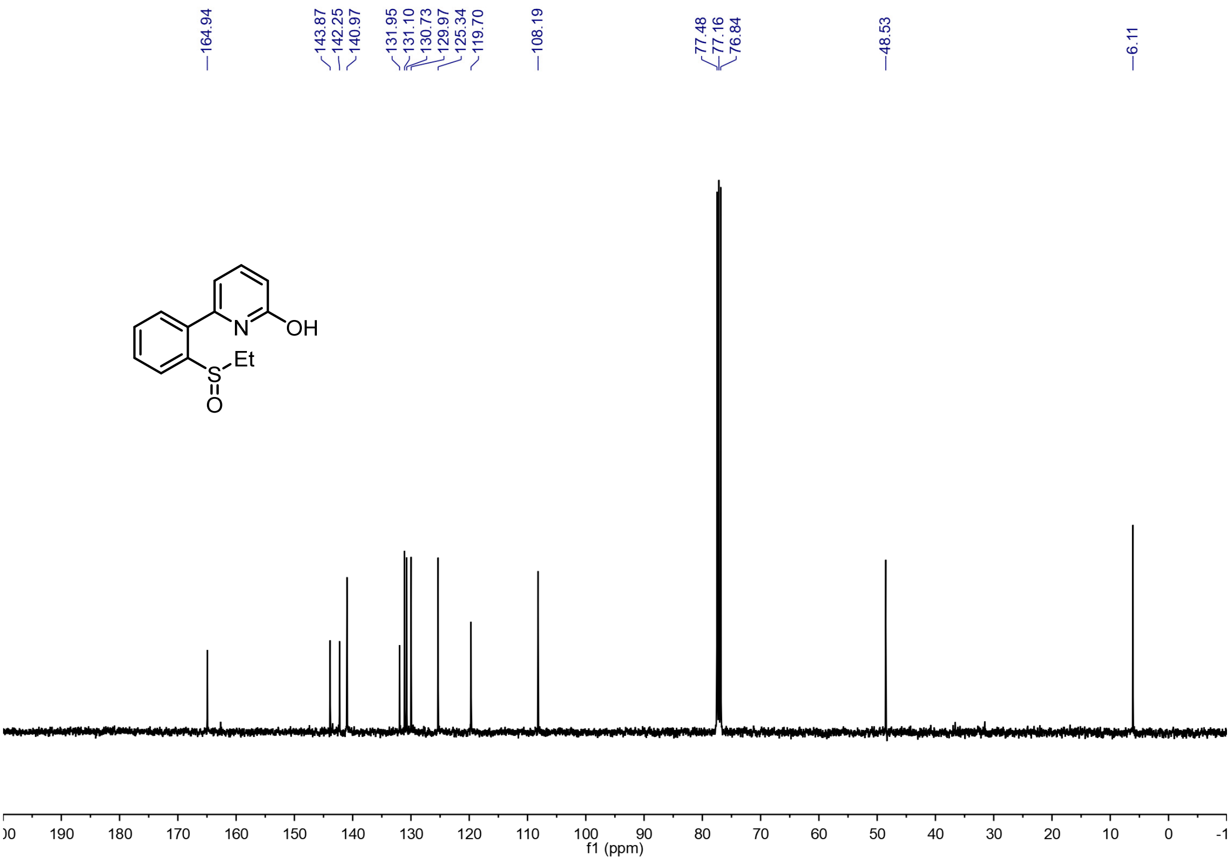
^{13}C NMR, $CDCl_3$, 100 MHz of **L13**:



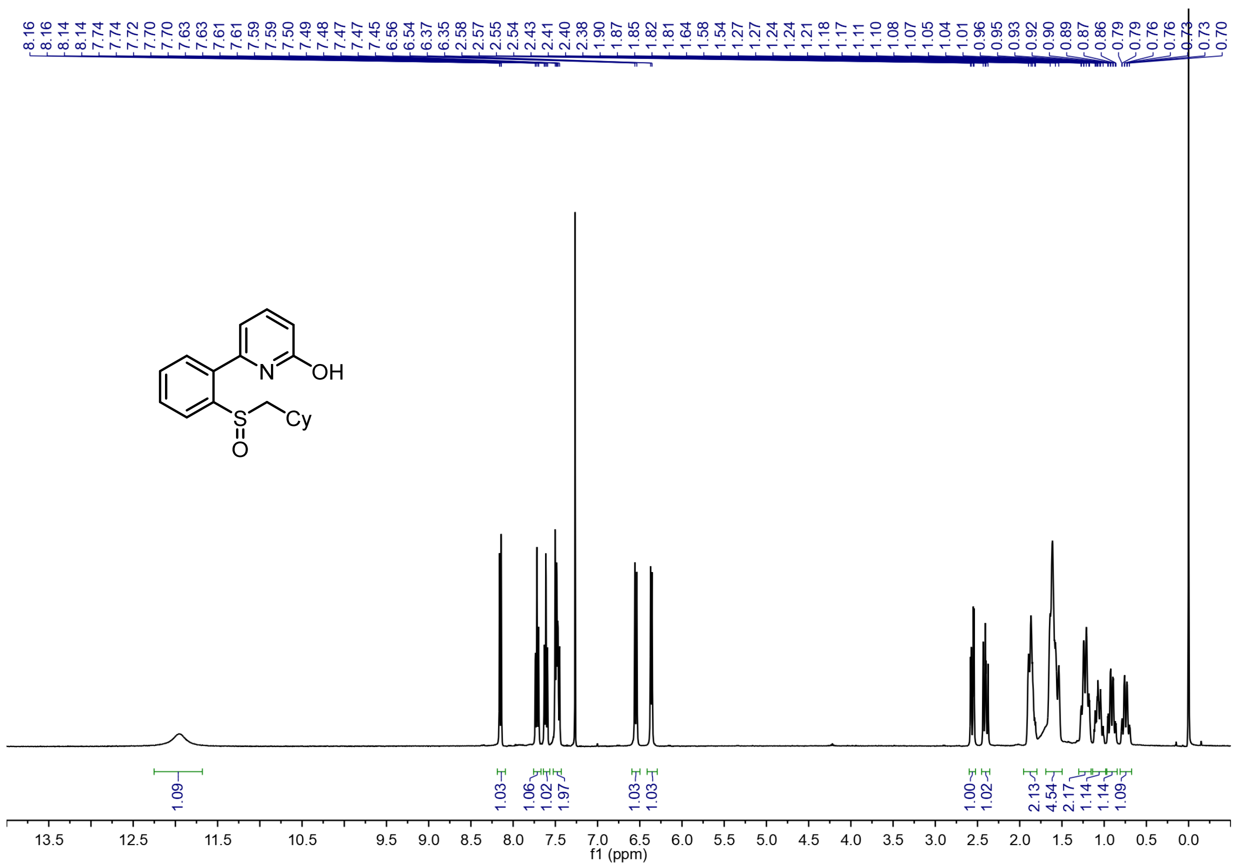
[1]H NMR ($CDCl_3$, 400 MHz) of **L14**:



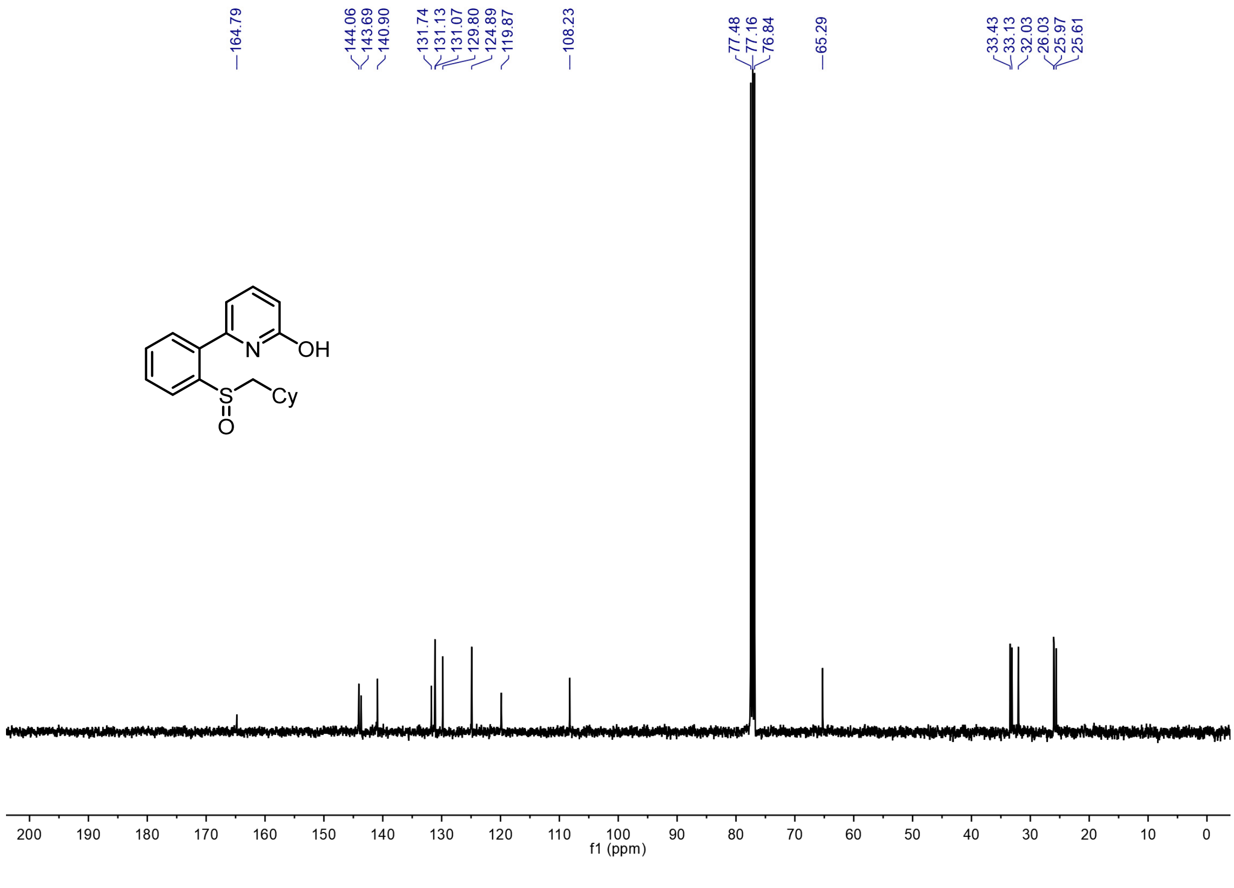
[13]C NMR ($CDCl_3$, 100 MHz) of **L14**:



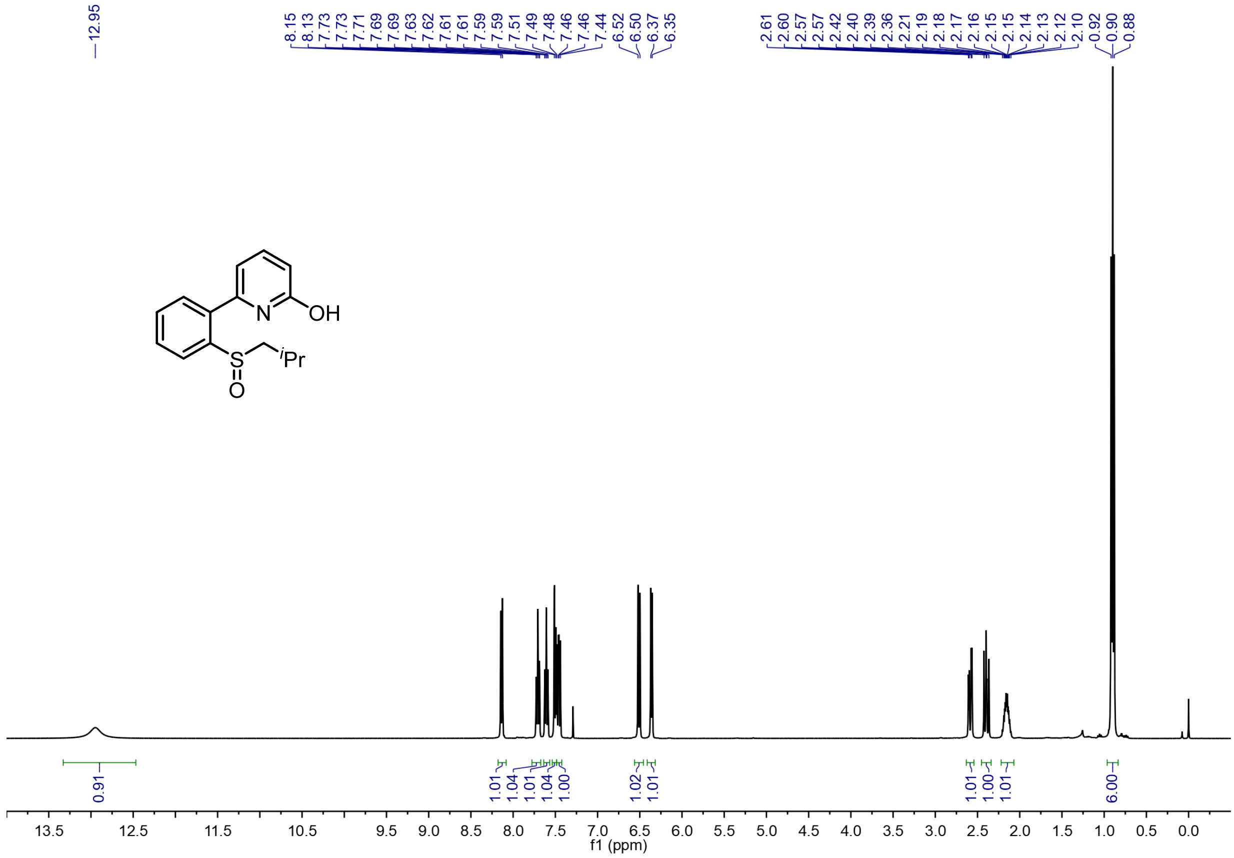
^{1}H NMR ($CDCl_3$, 400 MHz) of **L15**:



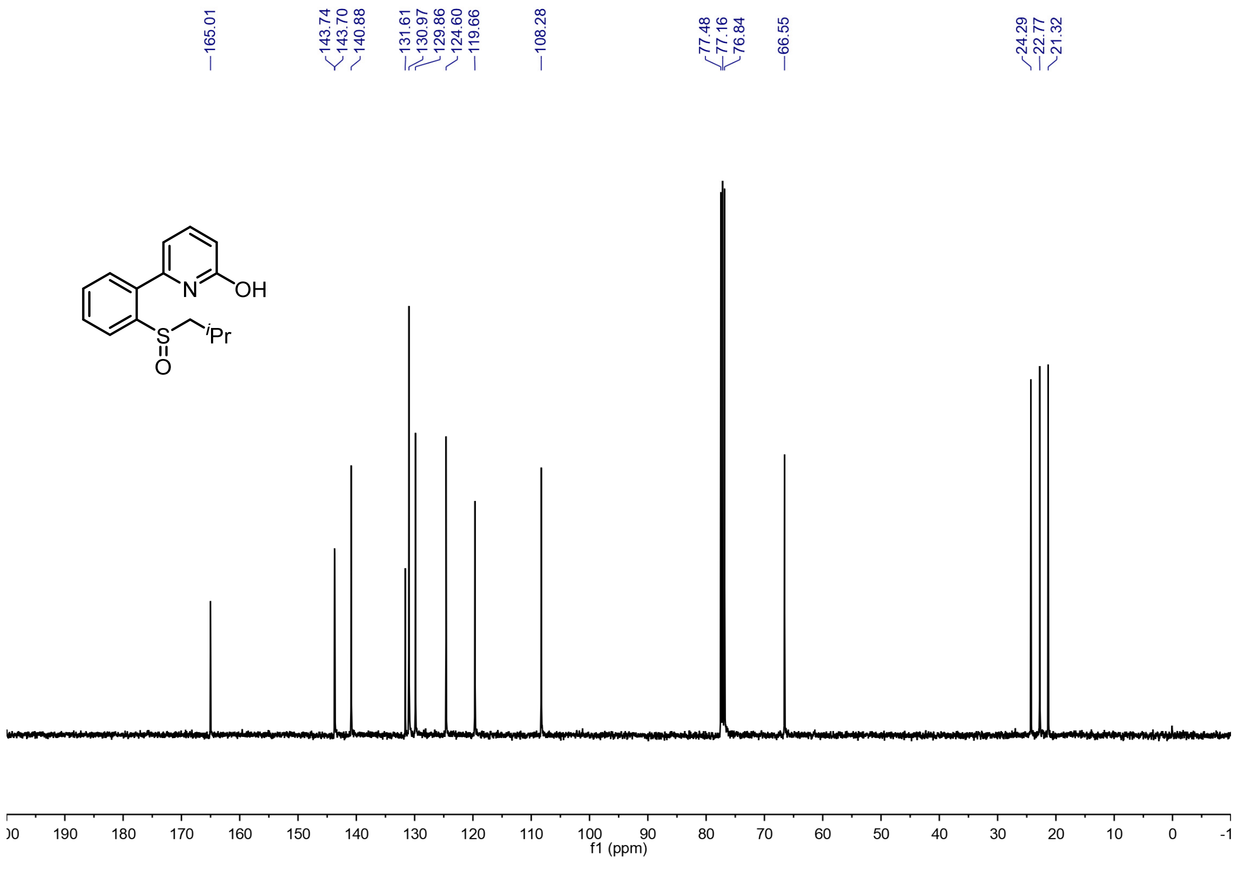
^{13}C NMR ($CDCl_3$, 100 MHz) of **L15**:



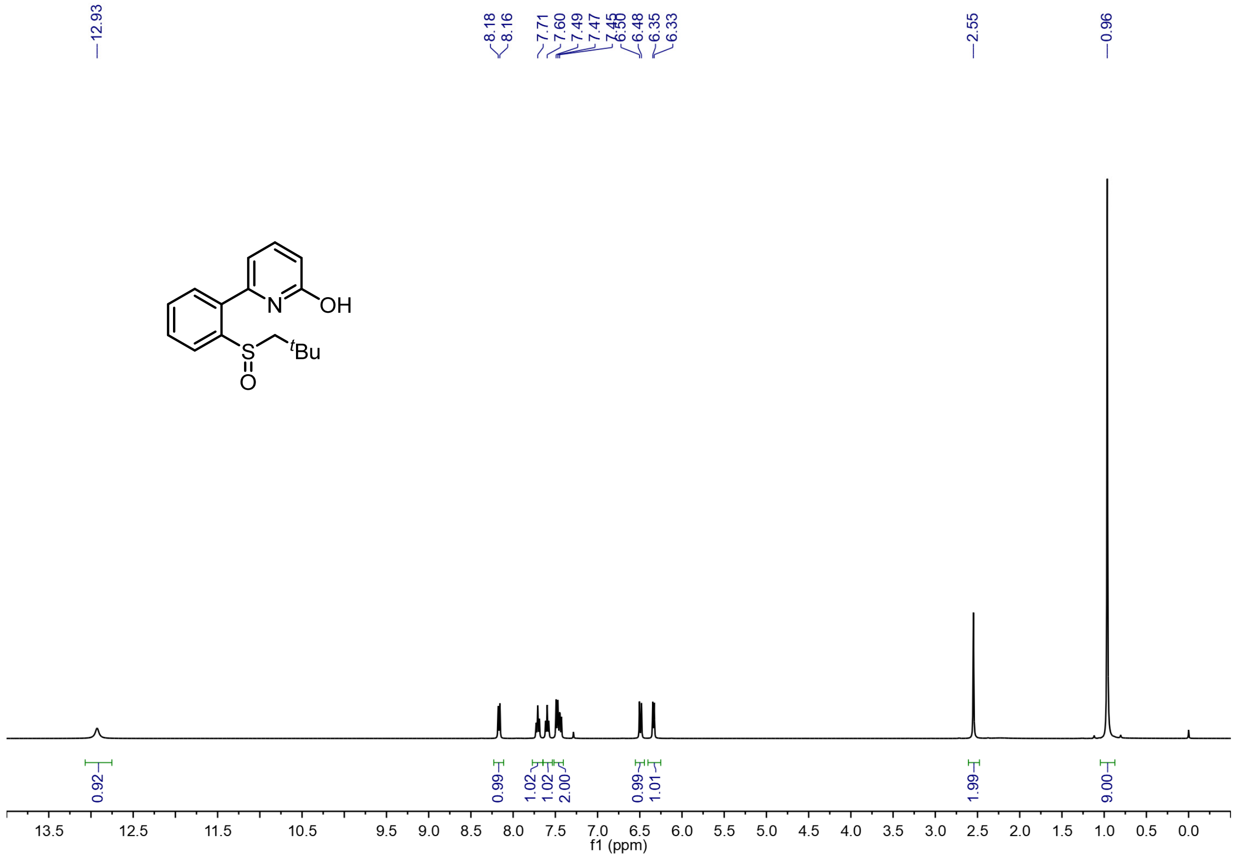
[1]H NMR ($CDCl_3$, 400 MHz) of **L16**:



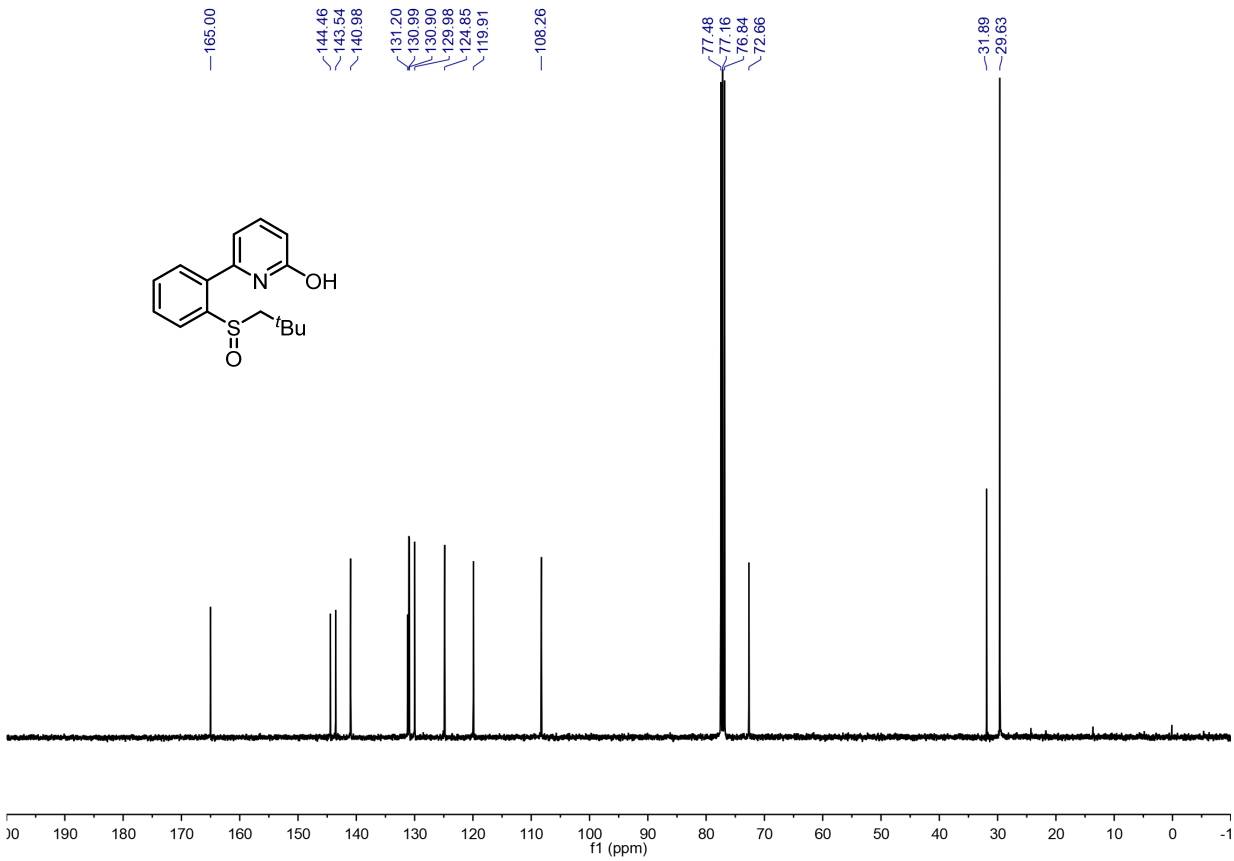
[13]C NMR ($CDCl_3$, 100 MHz) of **L16**:



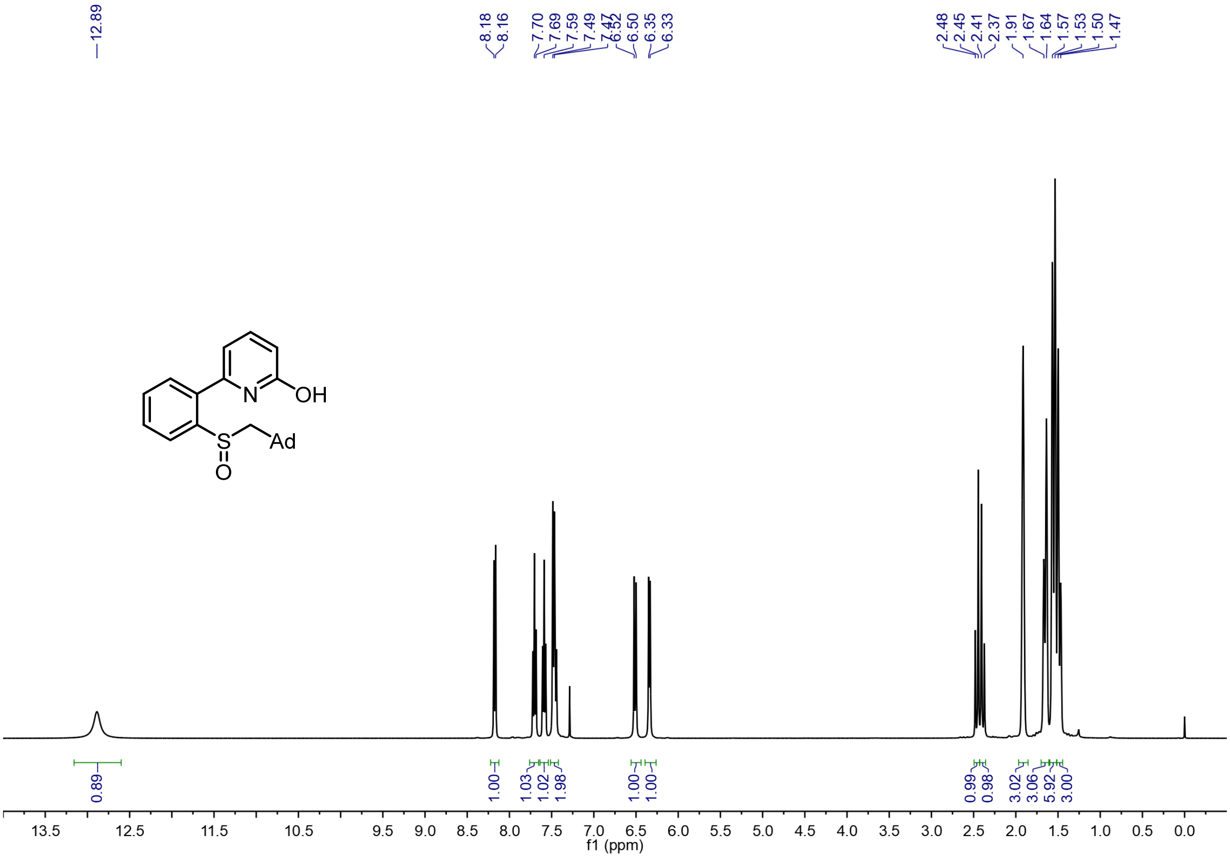
[1]H NMR ($CDCl_3$, 400 MHz) of **L17**:



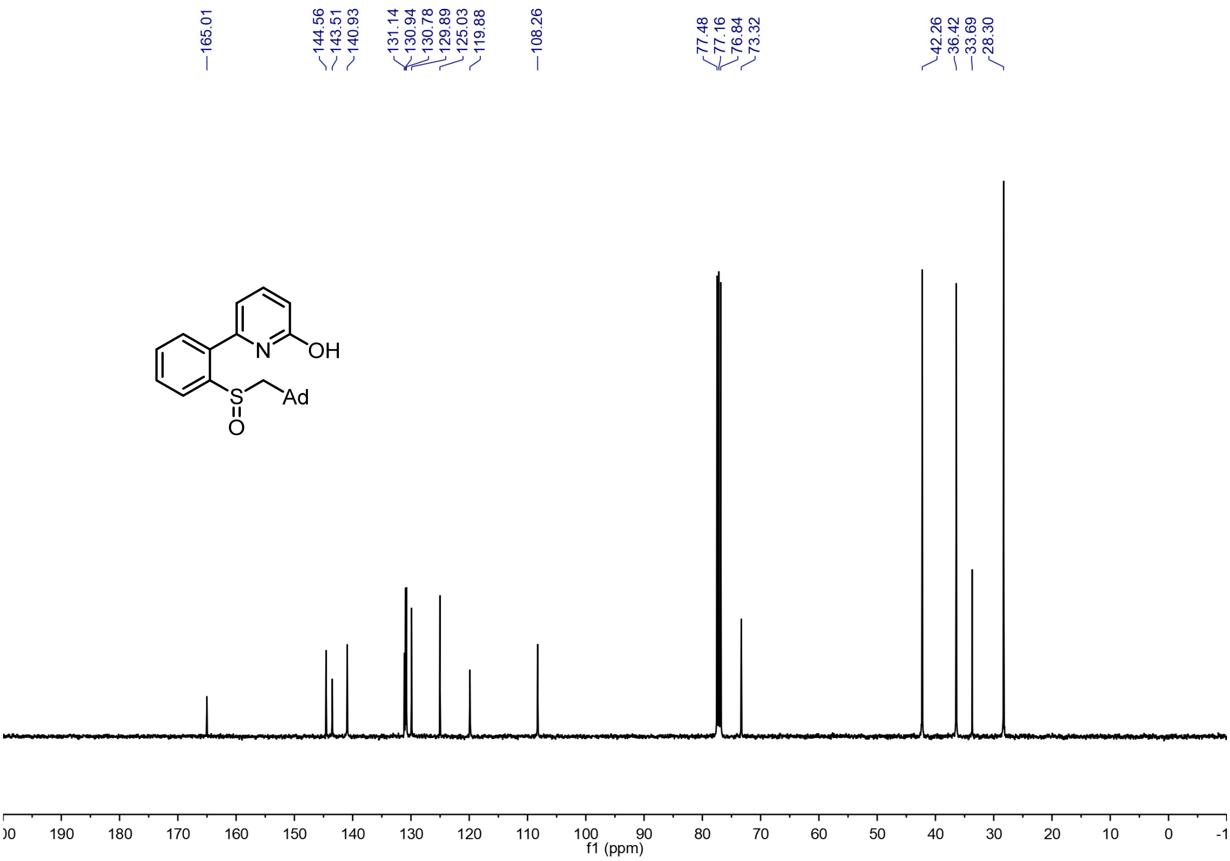
[13]C NMR ($CDCl_3$, 100 MHz) of **L17**:



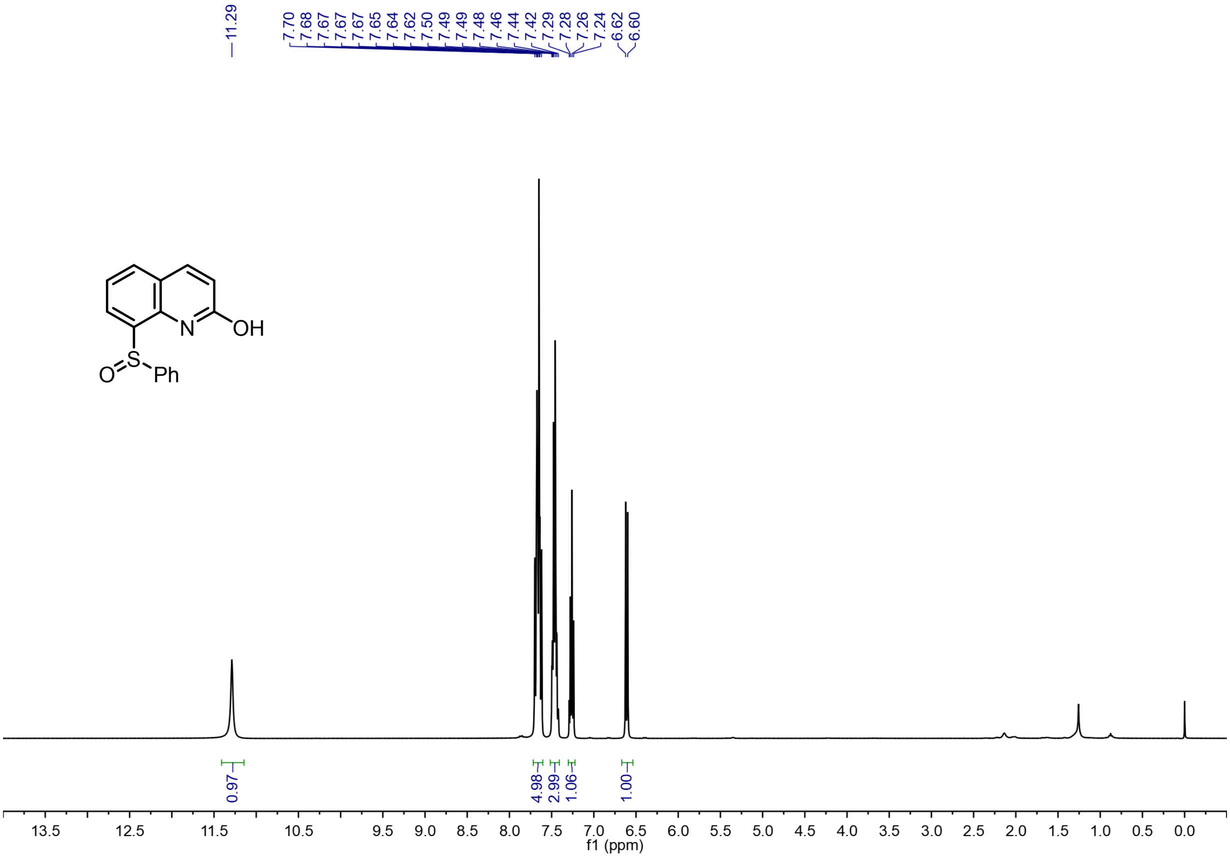
^{1}H NMR ($CDCl_3$, 400 MHz) of **L18**:



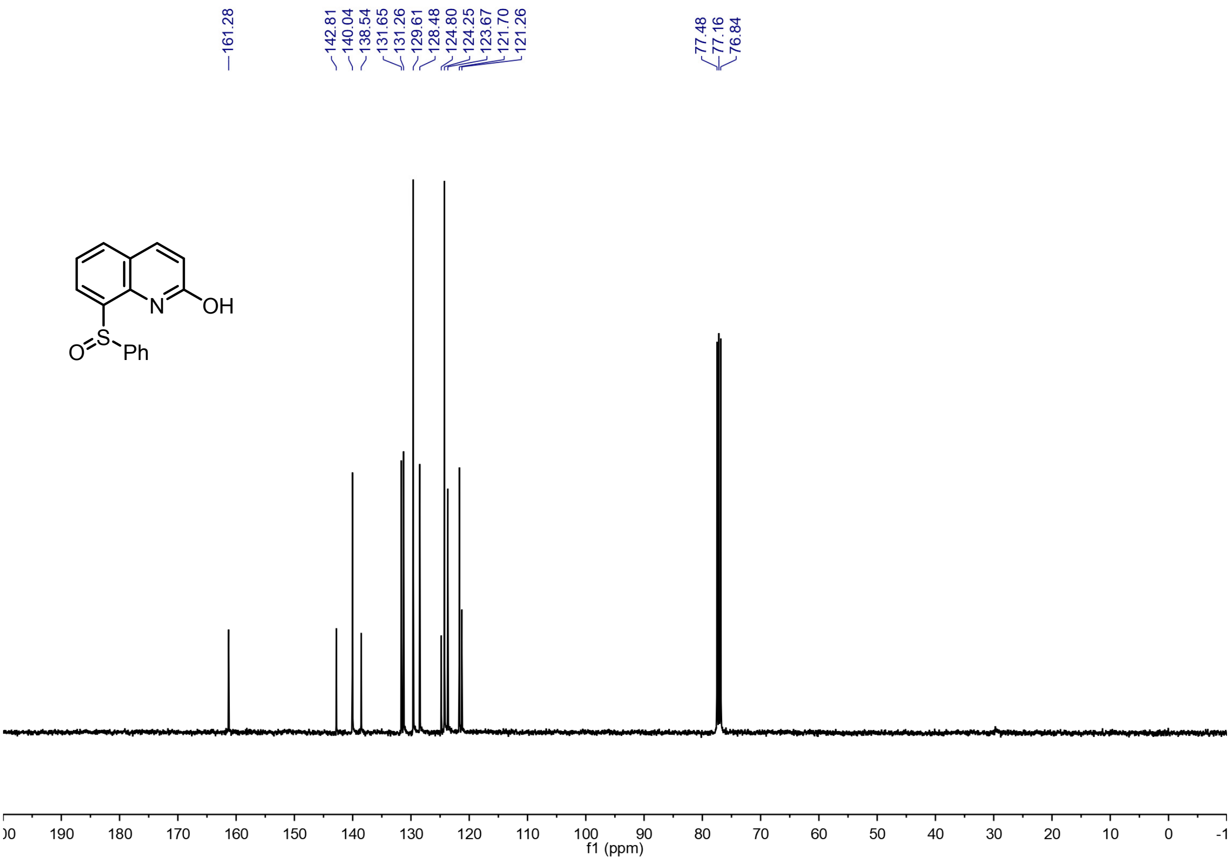
^{13}C NMR ($CDCl_3$, 100 MHz) of **L18**:



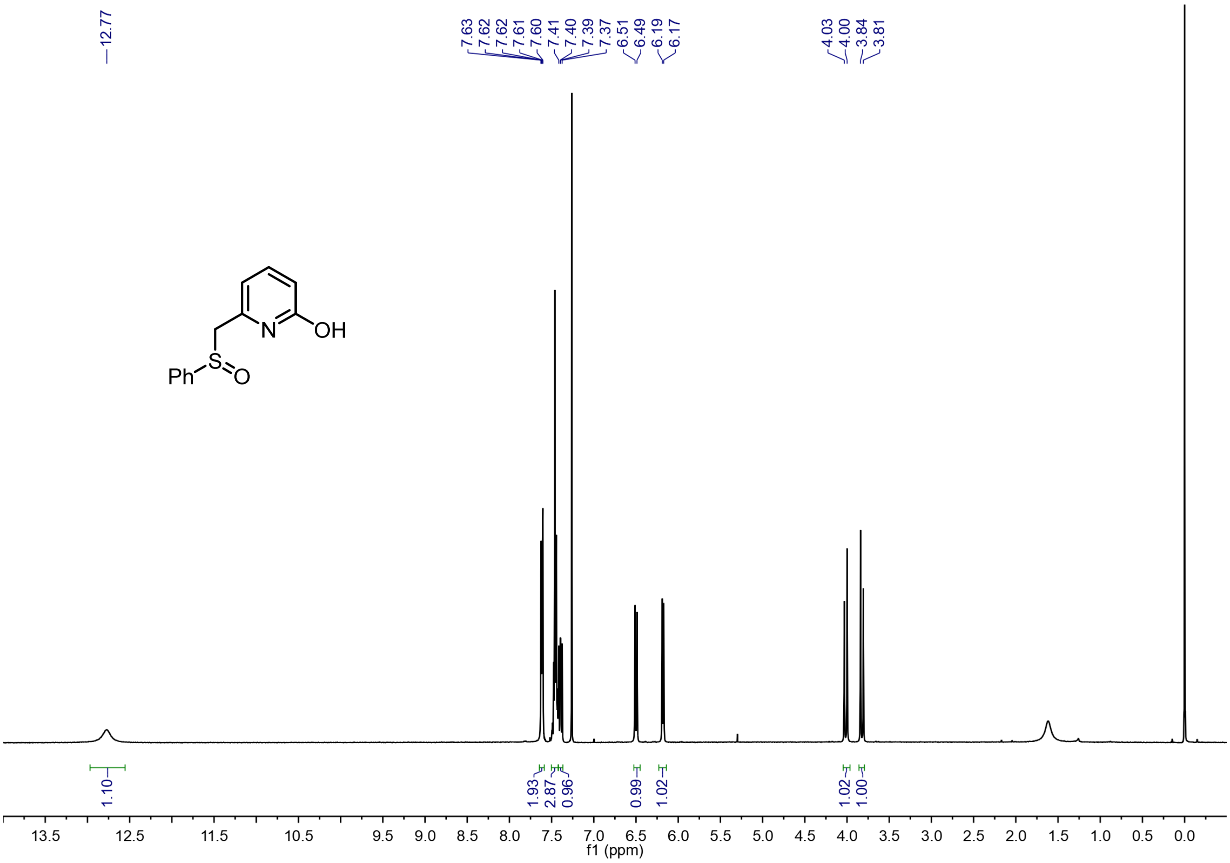
^{1}H NMR ($CDCl_3$, 400 MHz) of **L19**:



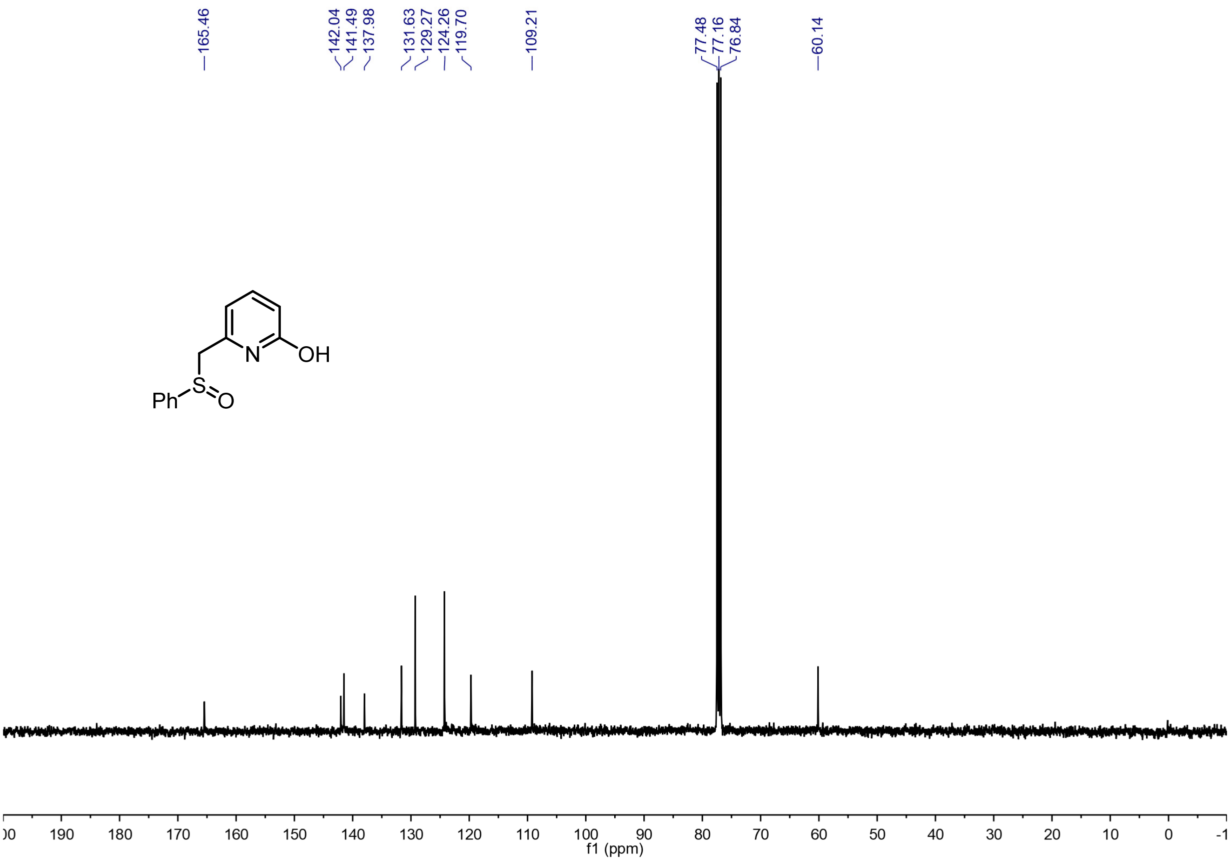
^{13}C NMR ($CDCl_3$, 100 MHz) of **L19**:



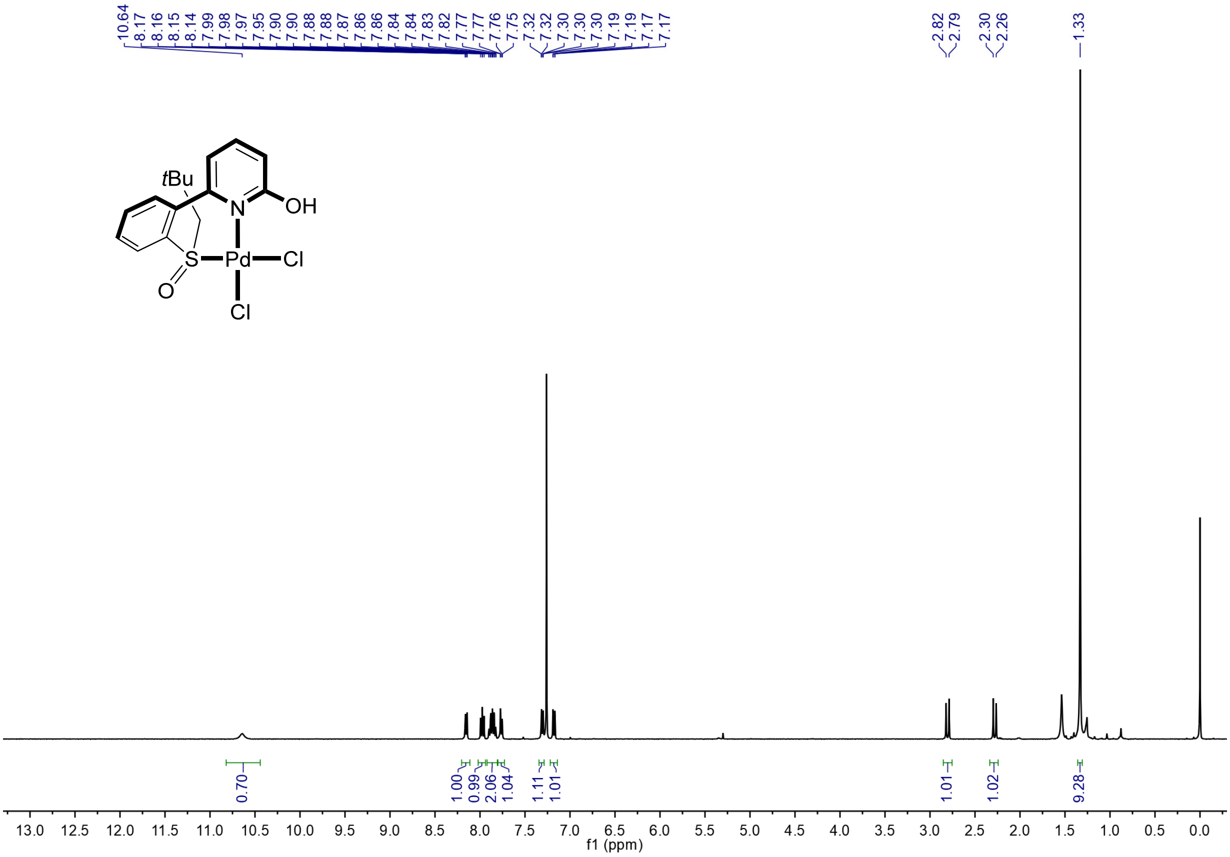
^{1}H NMR ($CDCl_3$, 400 MHz) of **L20**:



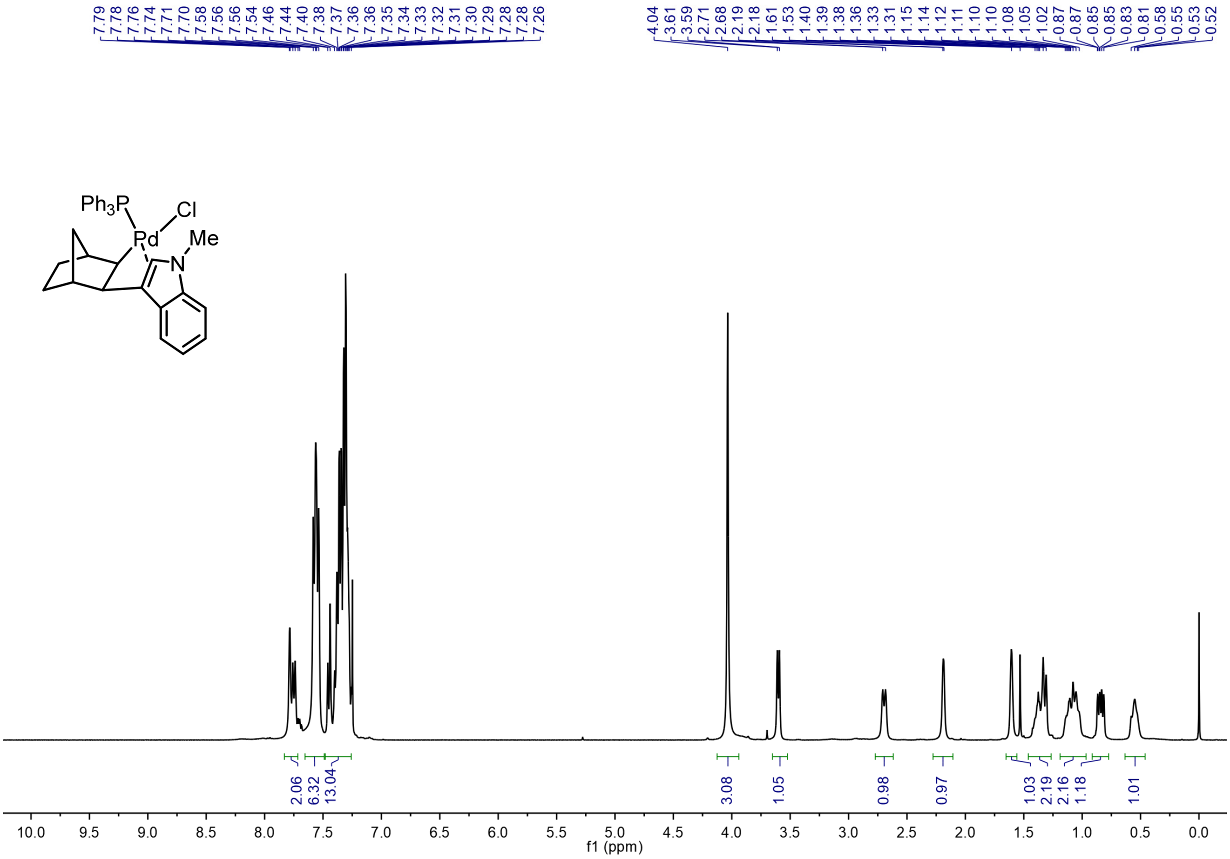
^{13}C NMR ($CDCl_3$, 100 MHz) of **L20**:



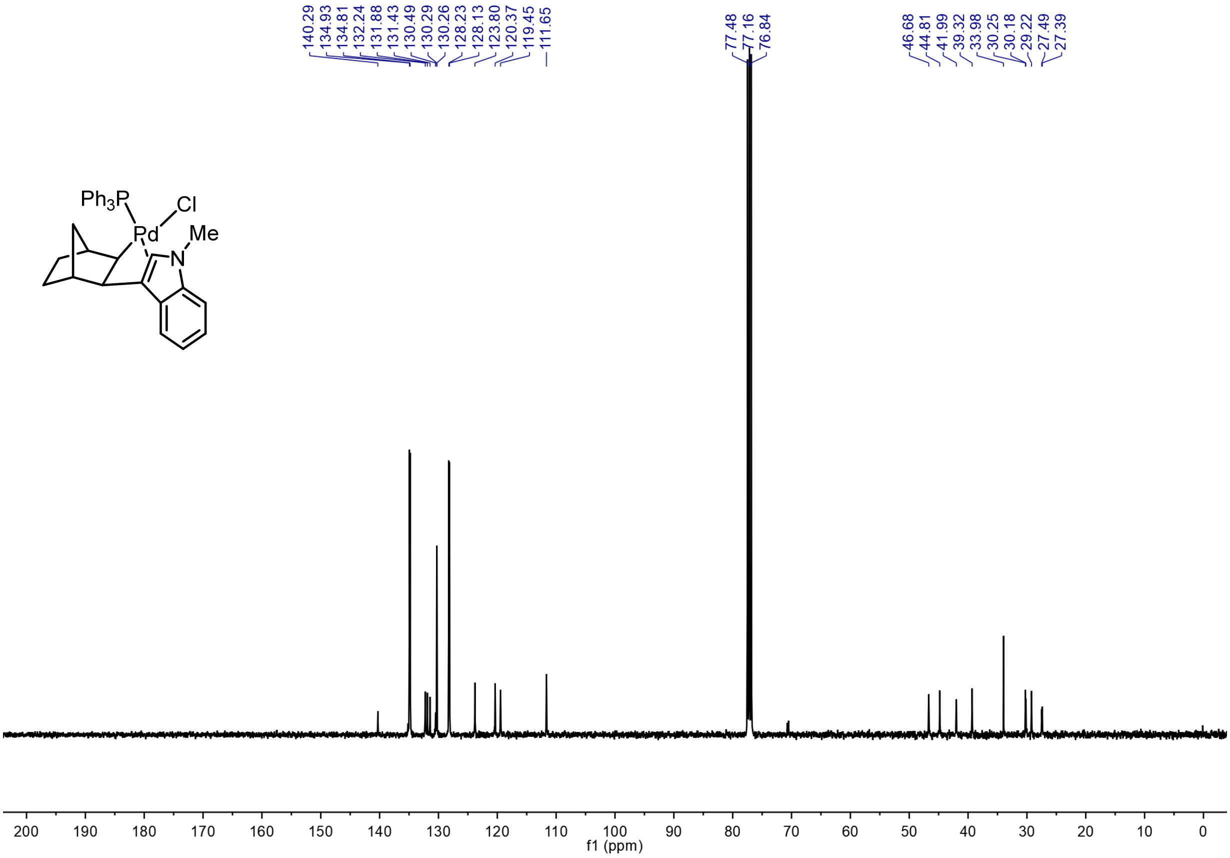
^{1}H NMR ($CDCl_3$, 400 MHz) of complex **Pd•L17**:



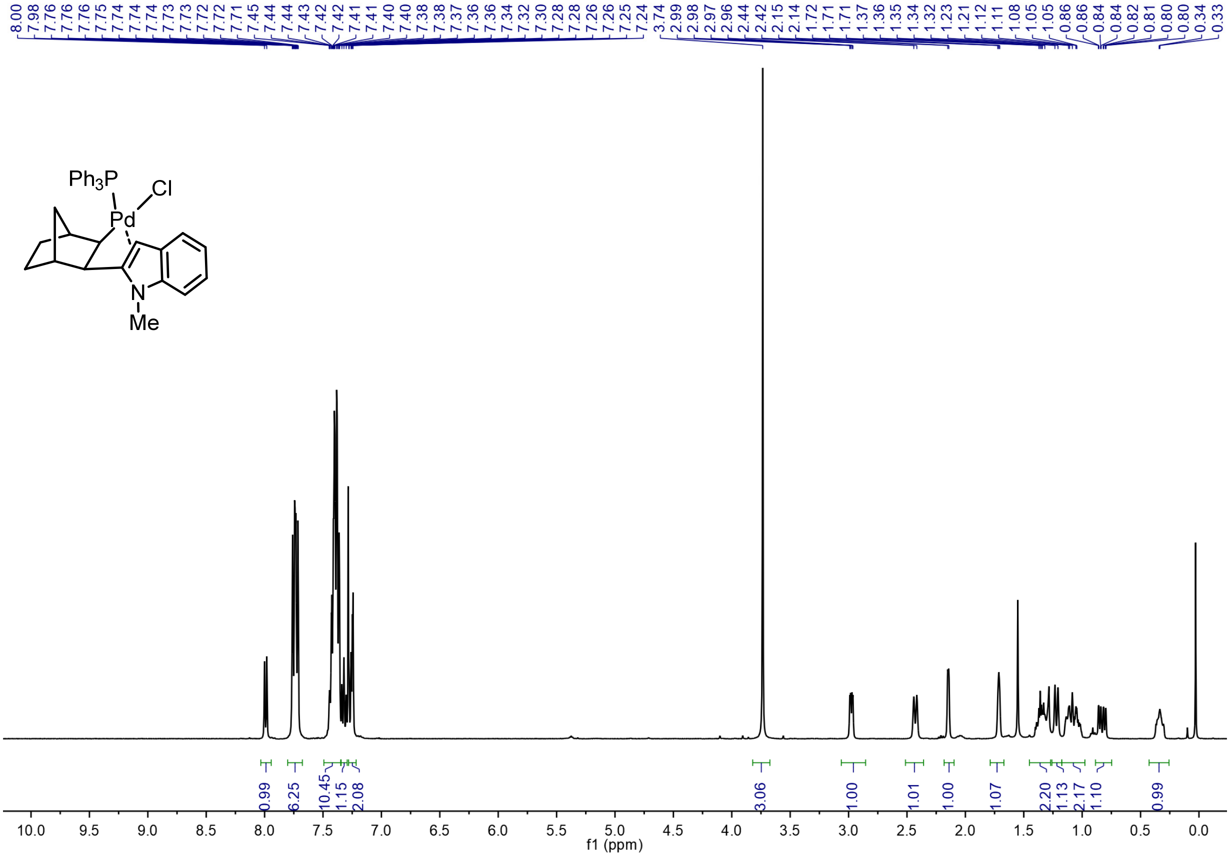
^{1}H NMR ($CDCl_3$, 400 MHz) of **4a**:



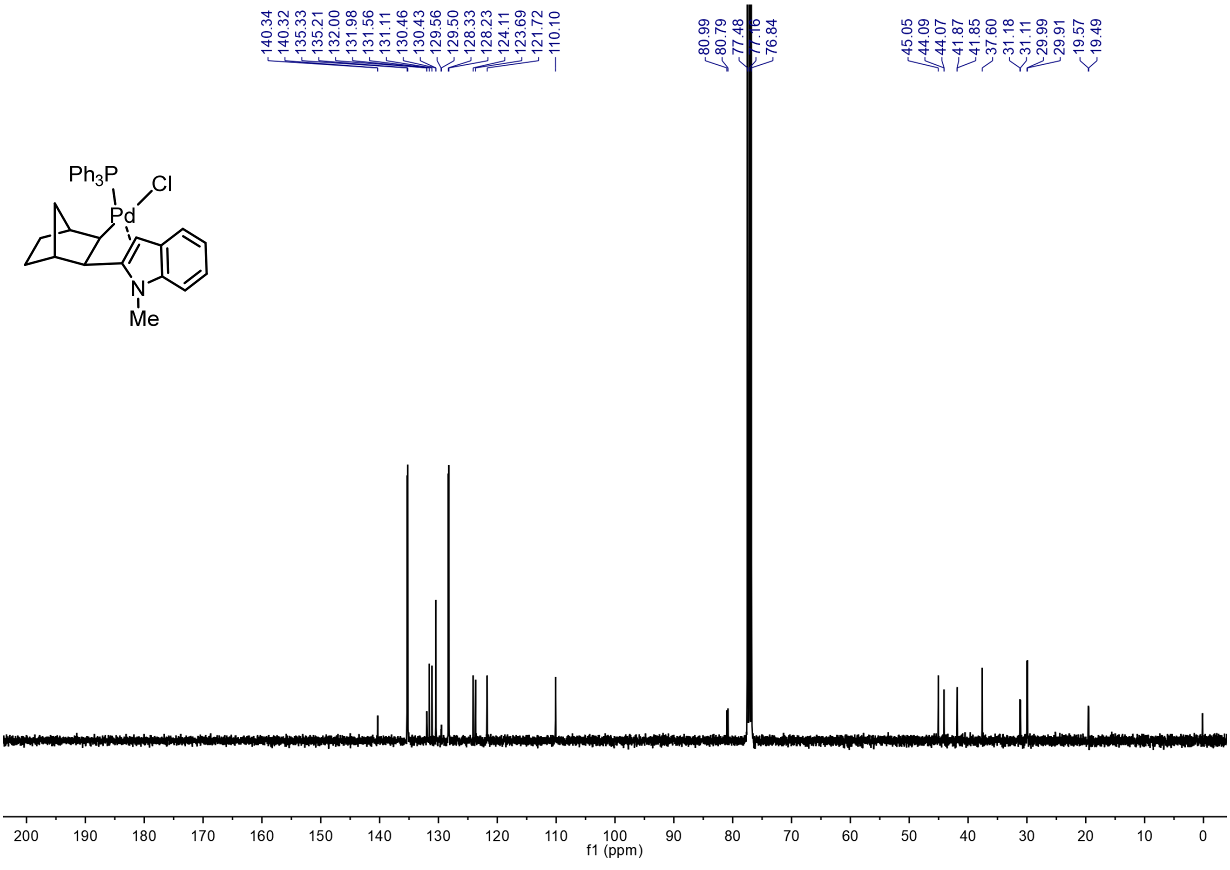
^{13}C NMR ($CDCl_3$, 100 MHz) of **4a**:



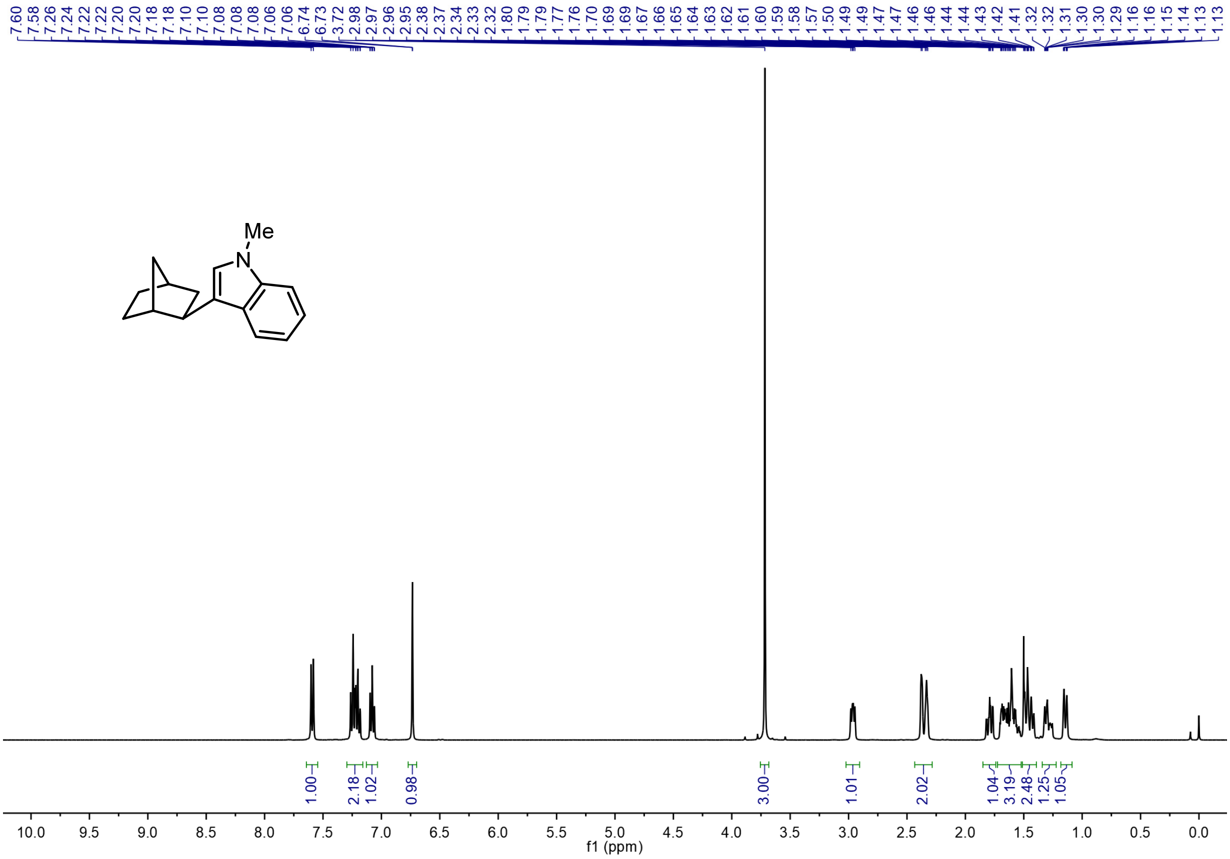
^{1}H NMR ($CDCl_3$, 400 MHz) of **4b**:



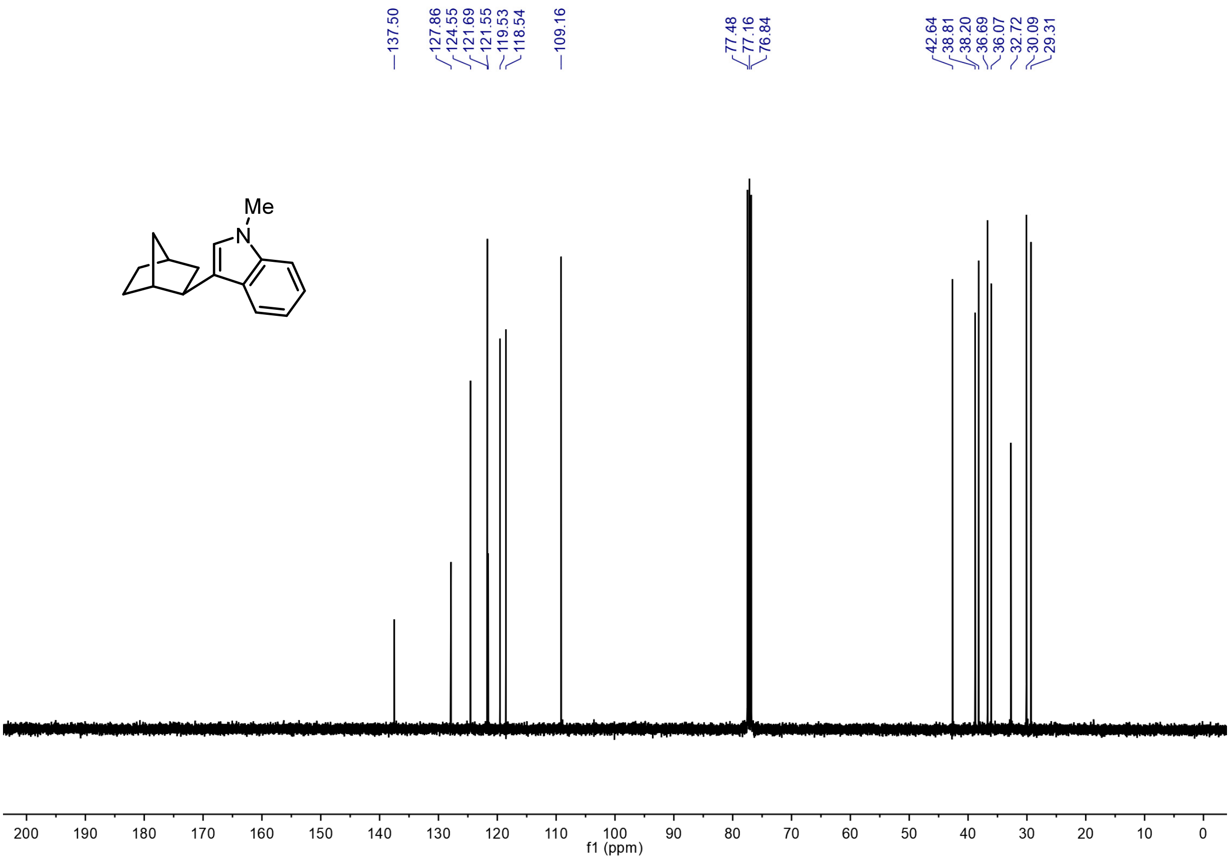
^{13}C NMR ($CDCl_3$, 100 MHz) of **4b**:



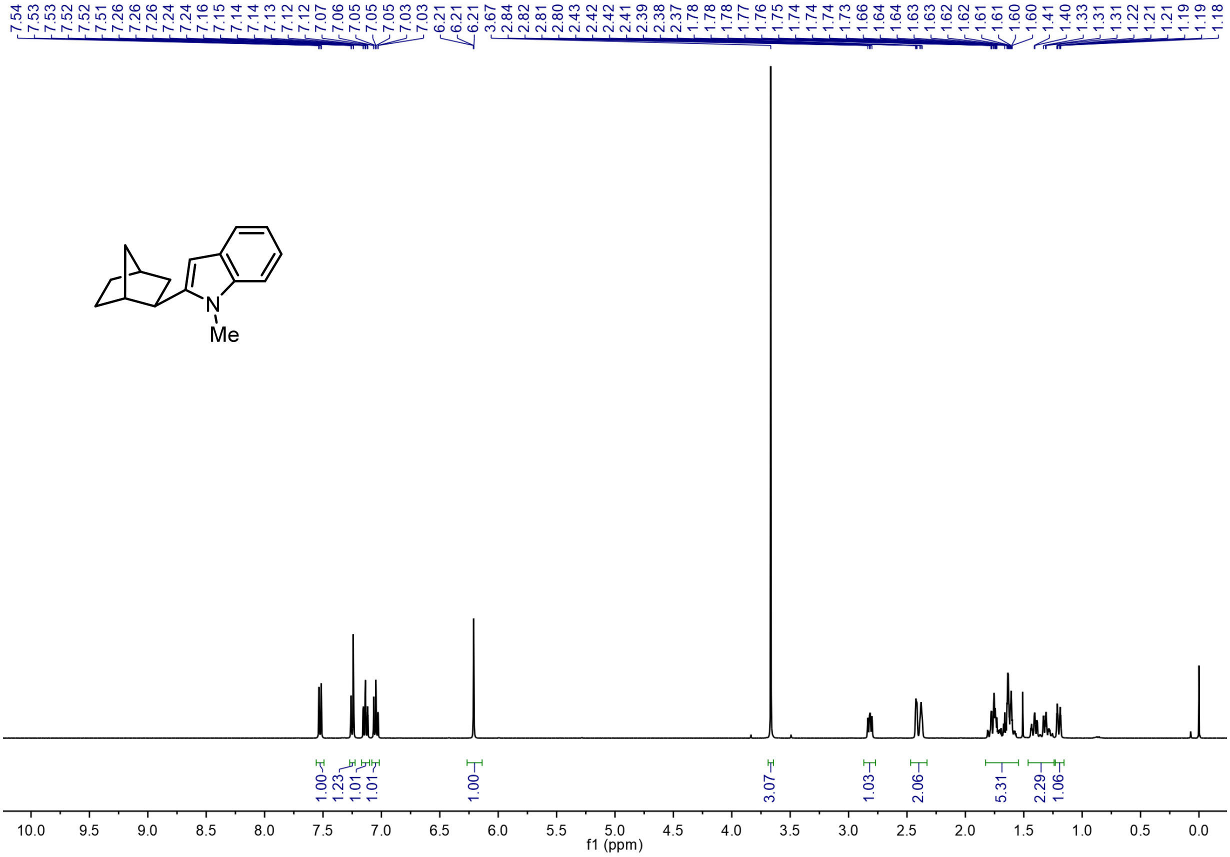
^1H NMR ($CDCl_3$, 400 MHz) of **5a**:



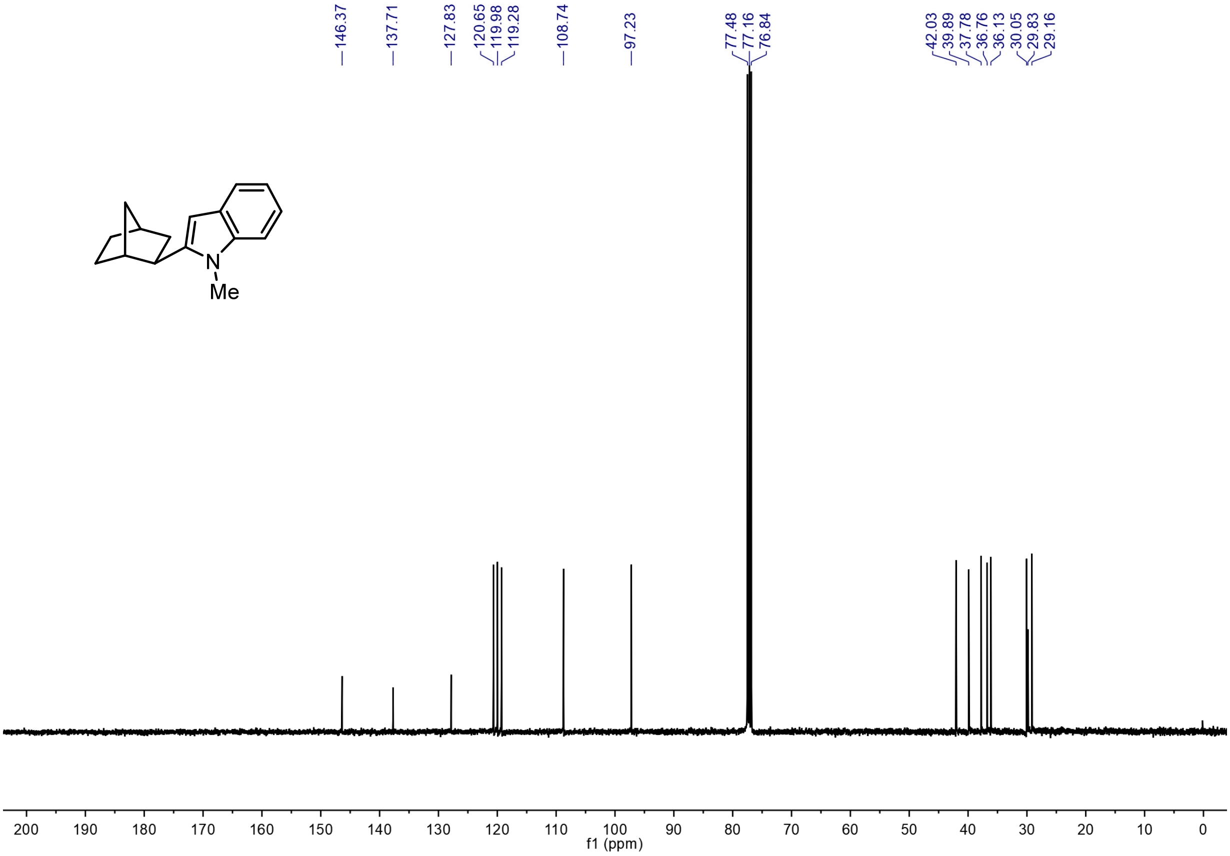
^{13}C NMR ($CDCl_3$, 100 MHz) of **5a**:



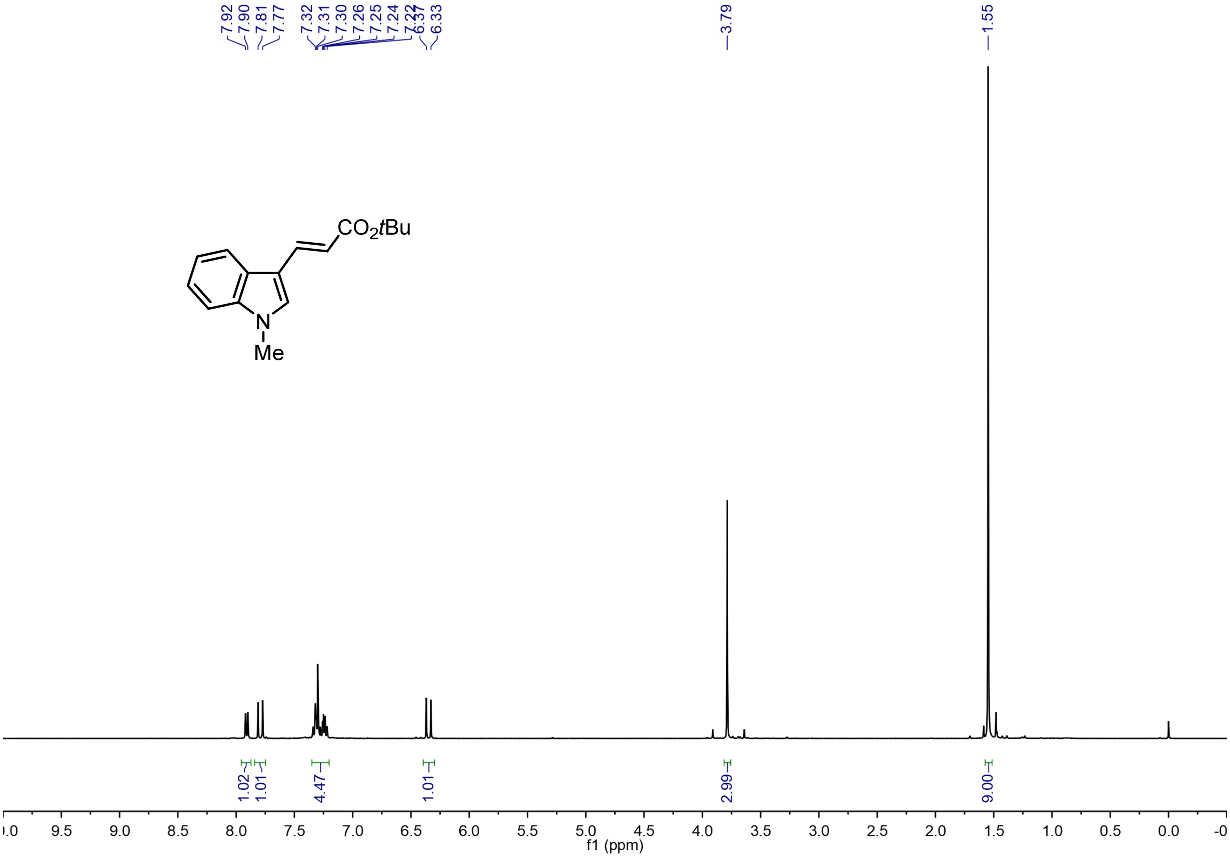
^{1}H NMR ($CDCl_3$, 400 MHz) of **5b**:



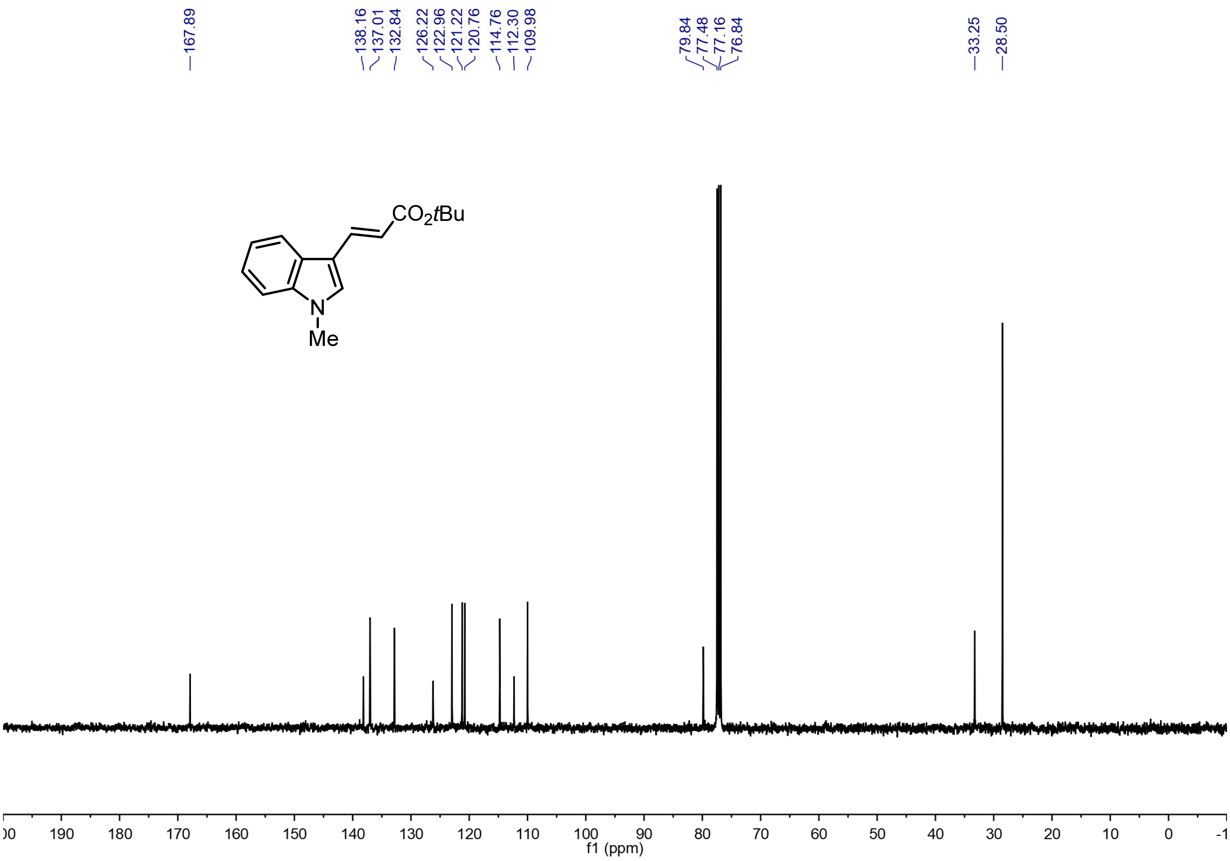
^{13}C NMR ($CDCl_3$, 100 MHz) of **5b**:



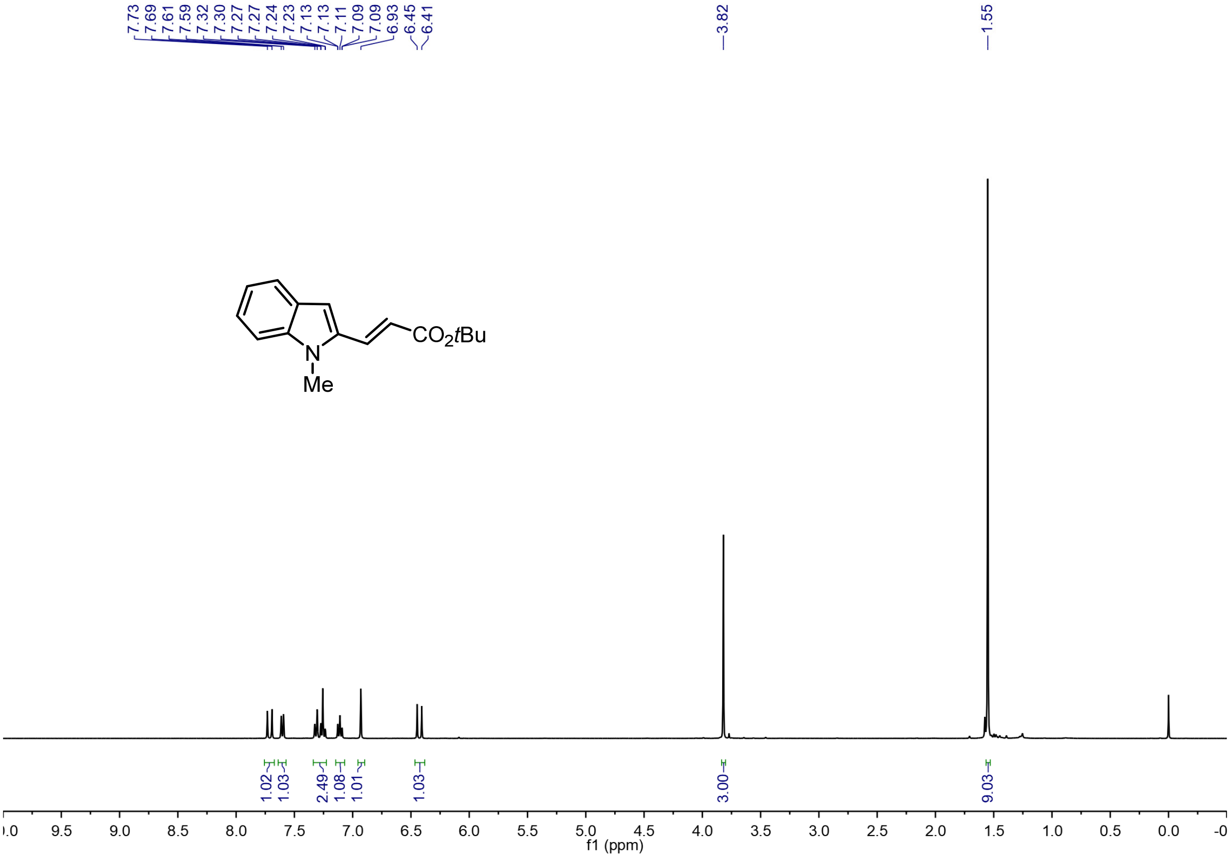
[1]H NMR ($CDCl_3$, 400 MHz) of **3a**:



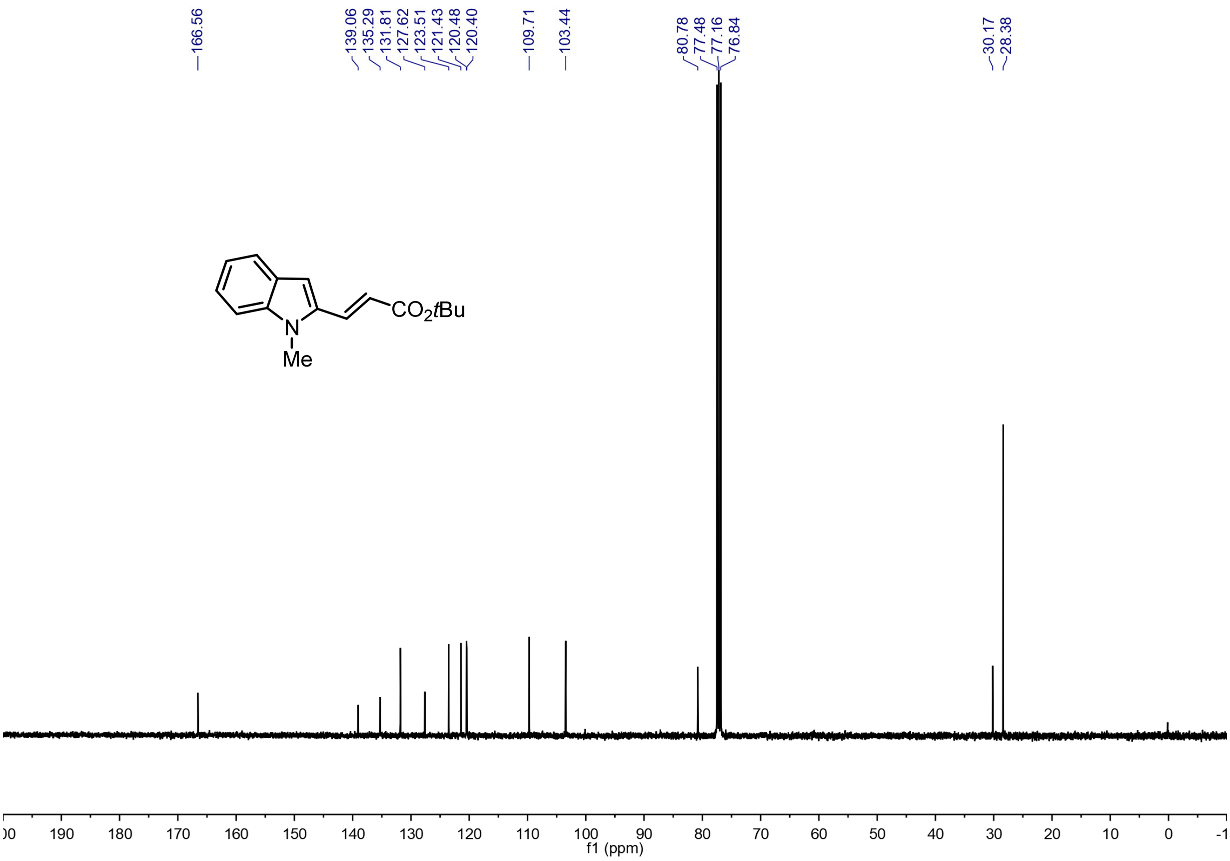
[13]C NMR ($CDCl_3$, 100 MHz) of **3a**:



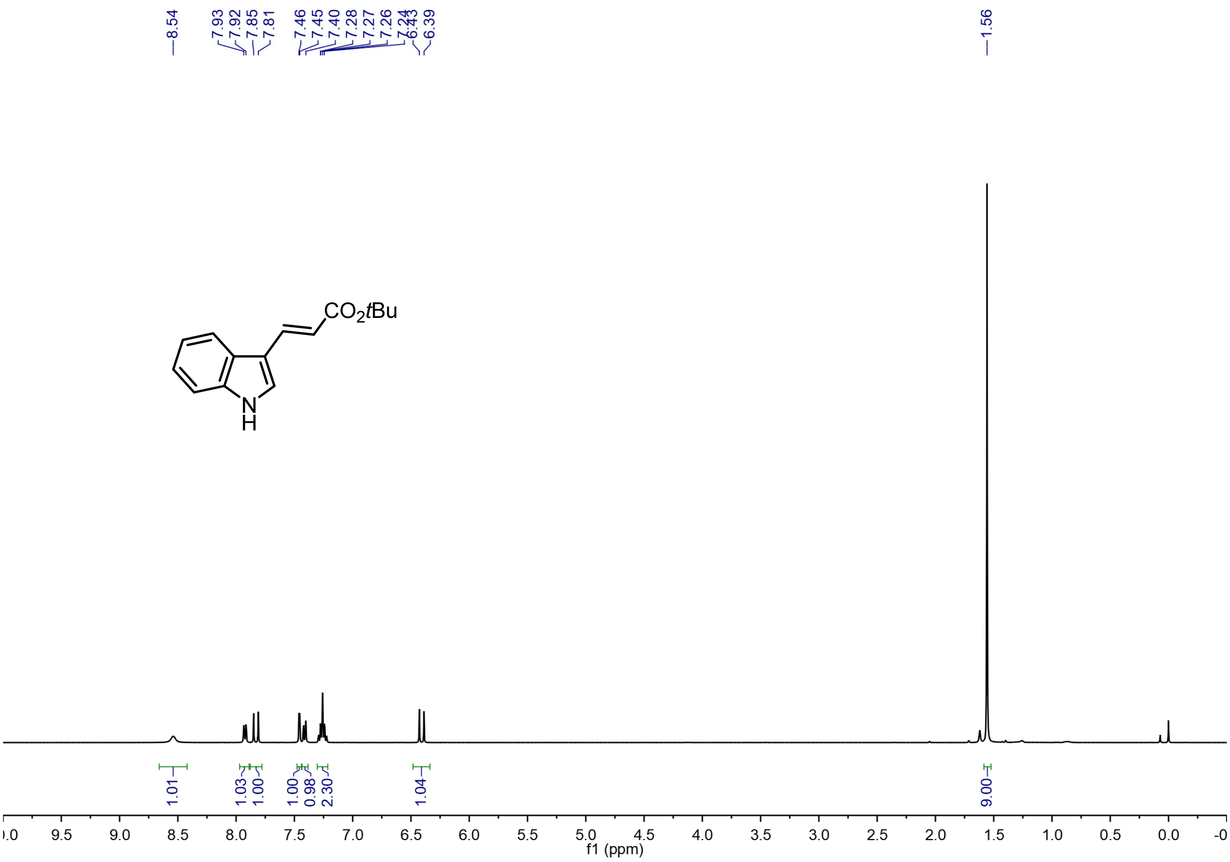
^1H NMR ($CDCl_3$, 400 MHz) of **3b**:



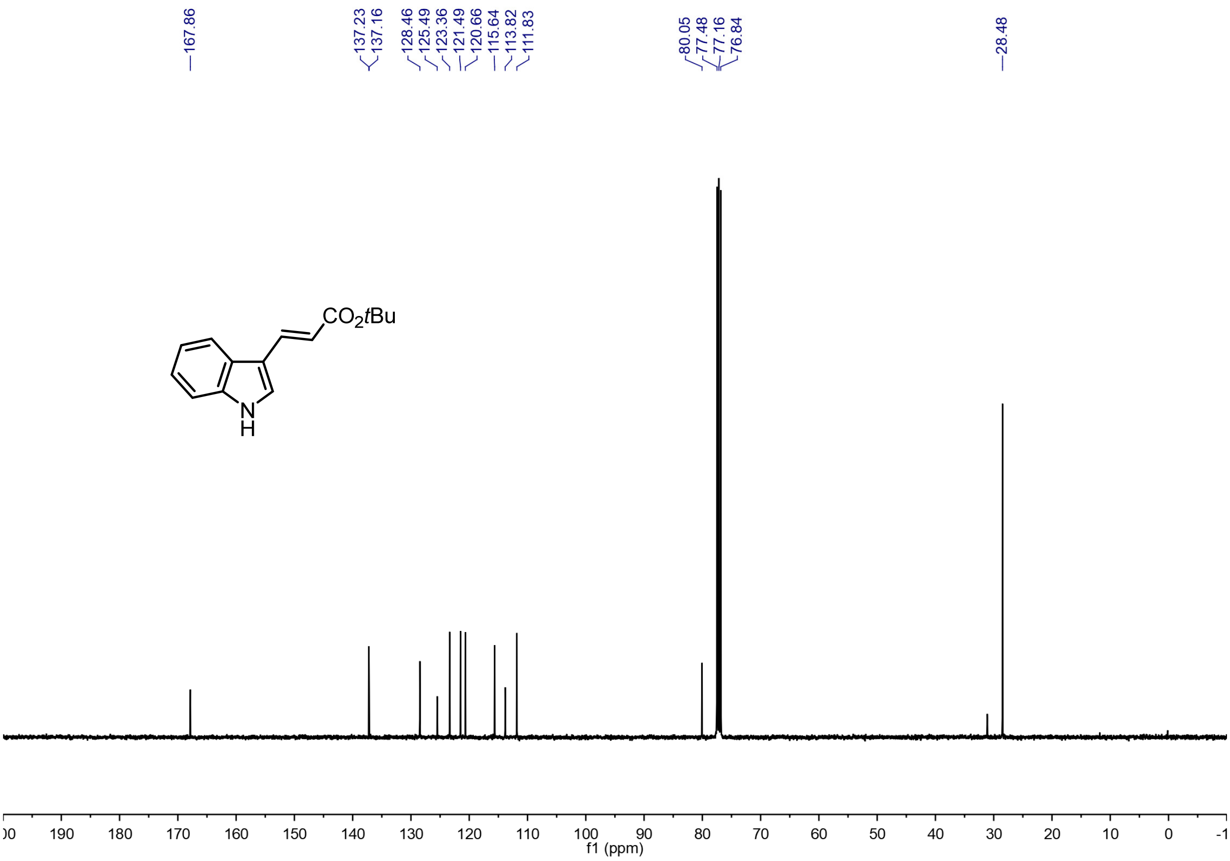
^{13}C NMR ($CDCl_3$, 100 MHz) of **3b**:



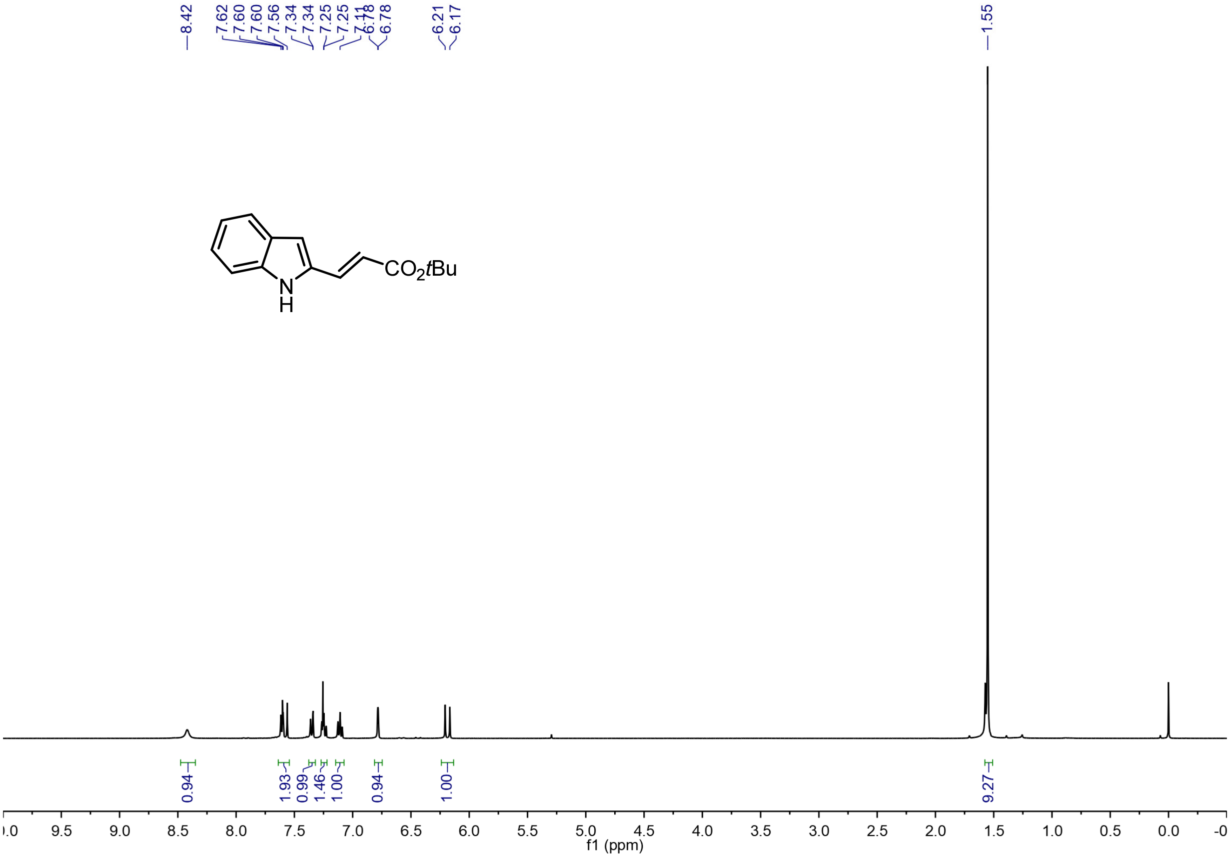
^{1}H NMR ($CDCl_3$, 400 MHz) of **6a**:



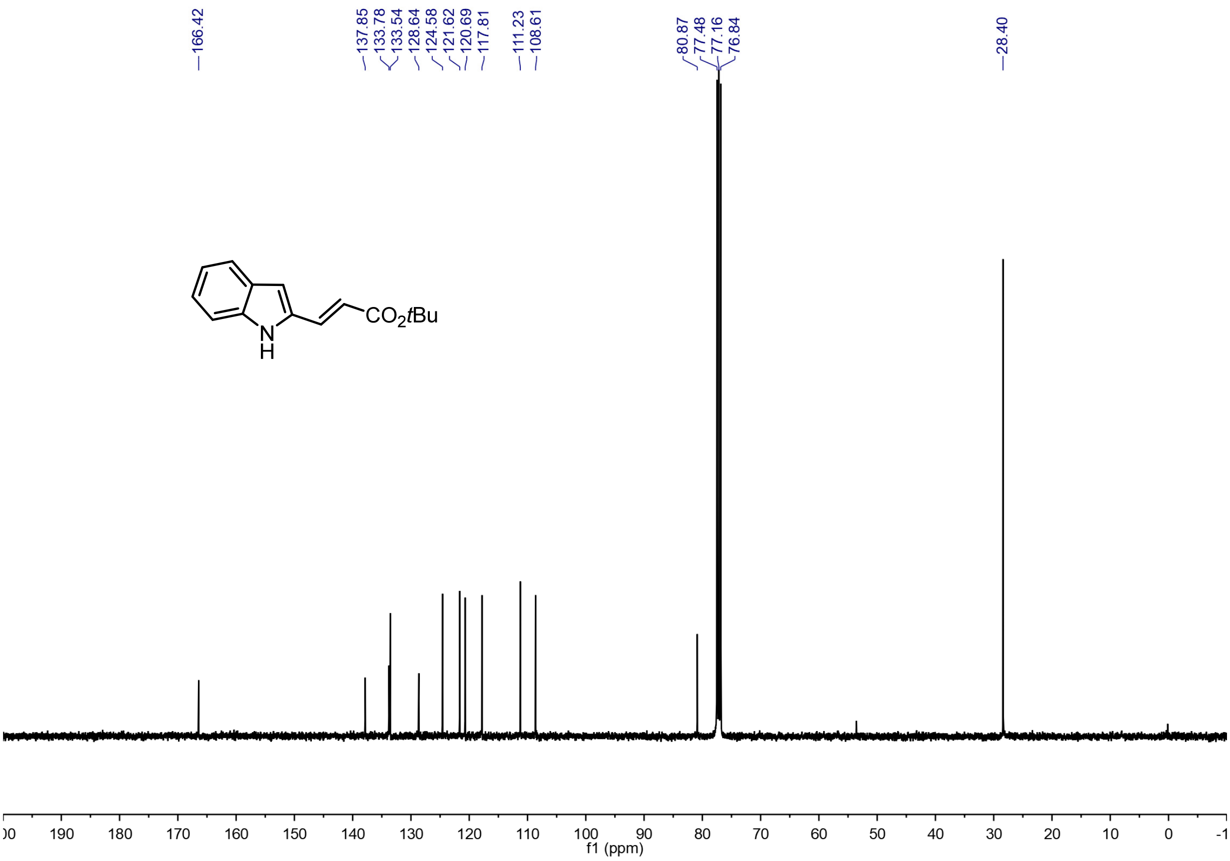
^{13}C NMR ($CDCl_3$, 100 MHz) of **6a**:



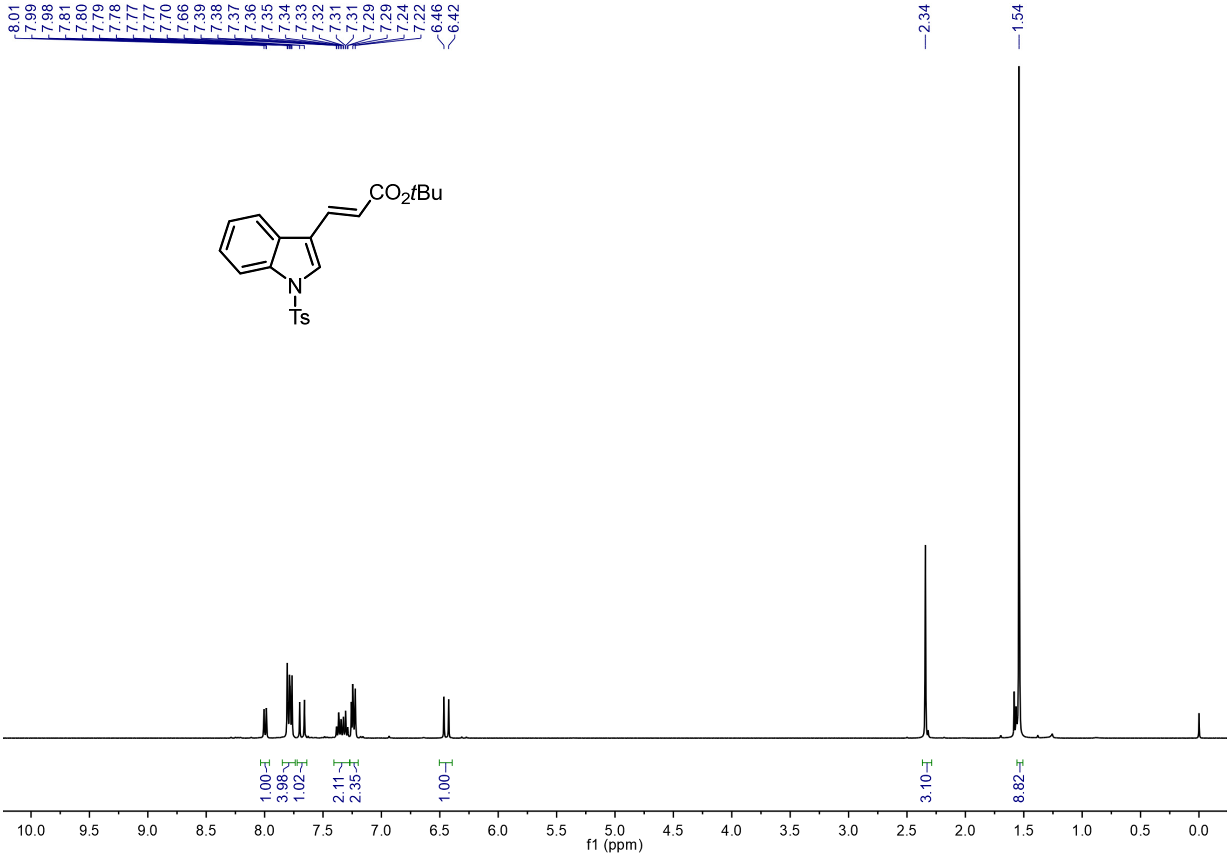
^1H NMR ($CDCl_3$, 400 MHz) of **6b**:



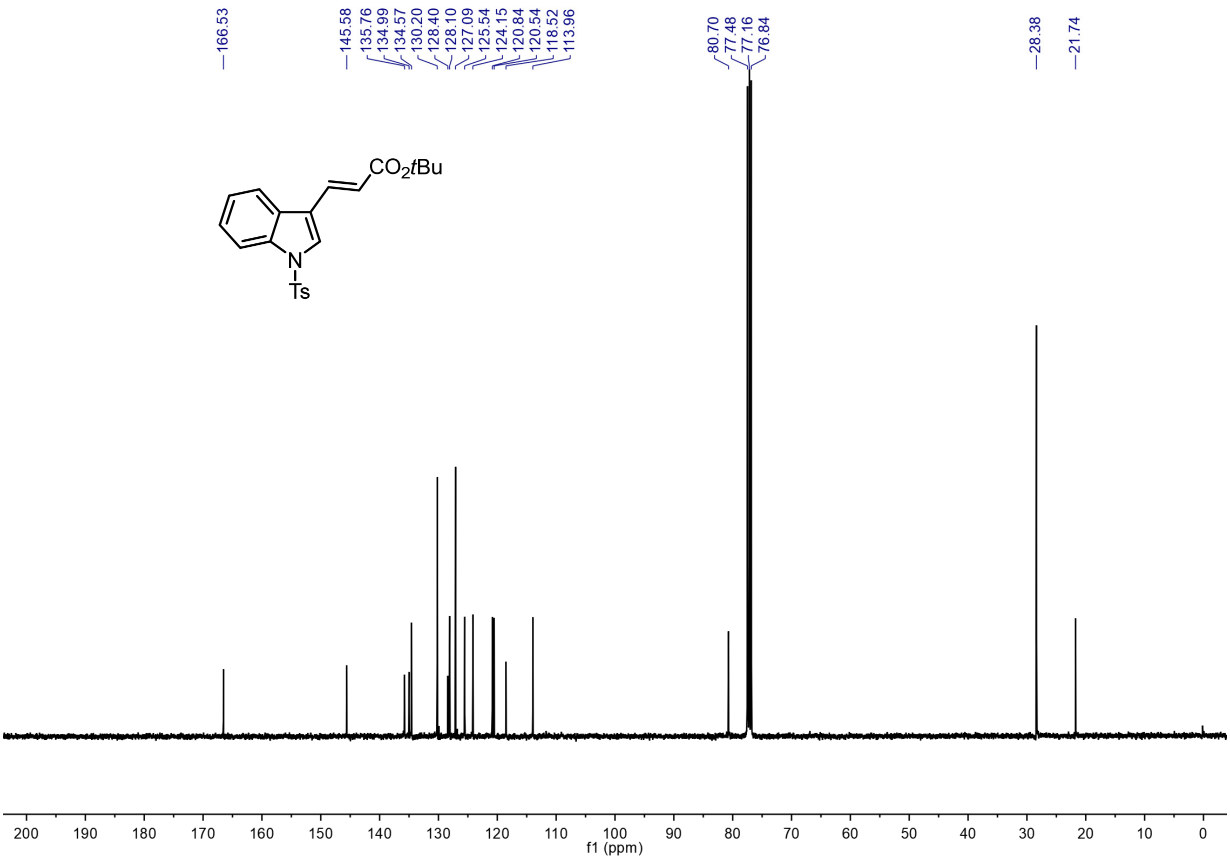
^{13}C NMR ($CDCl_3$, 100 MHz) of **6b**:



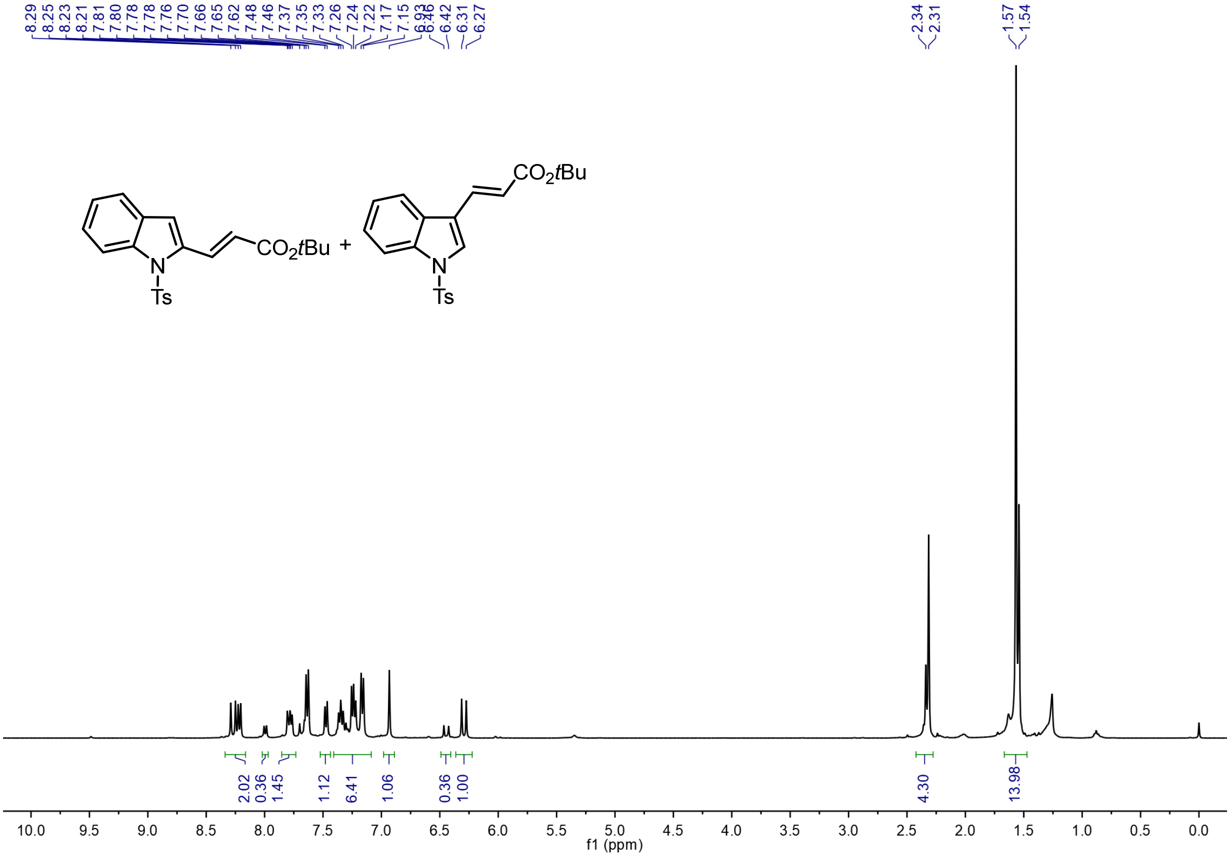
^1H NMR ($CDCl_3$, 400 MHz) of **7a**:



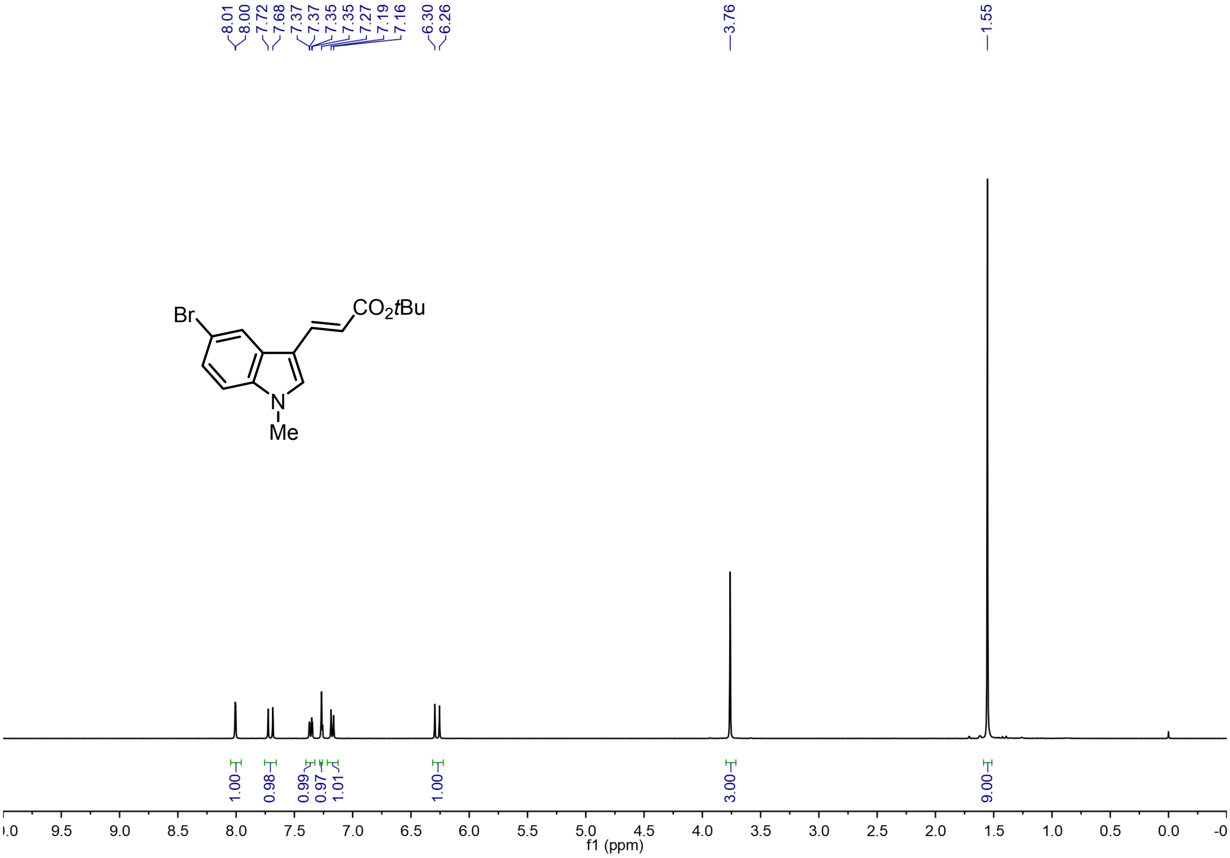
^{13}C NMR ($CDCl_3$, 100 MHz) of **7a**:



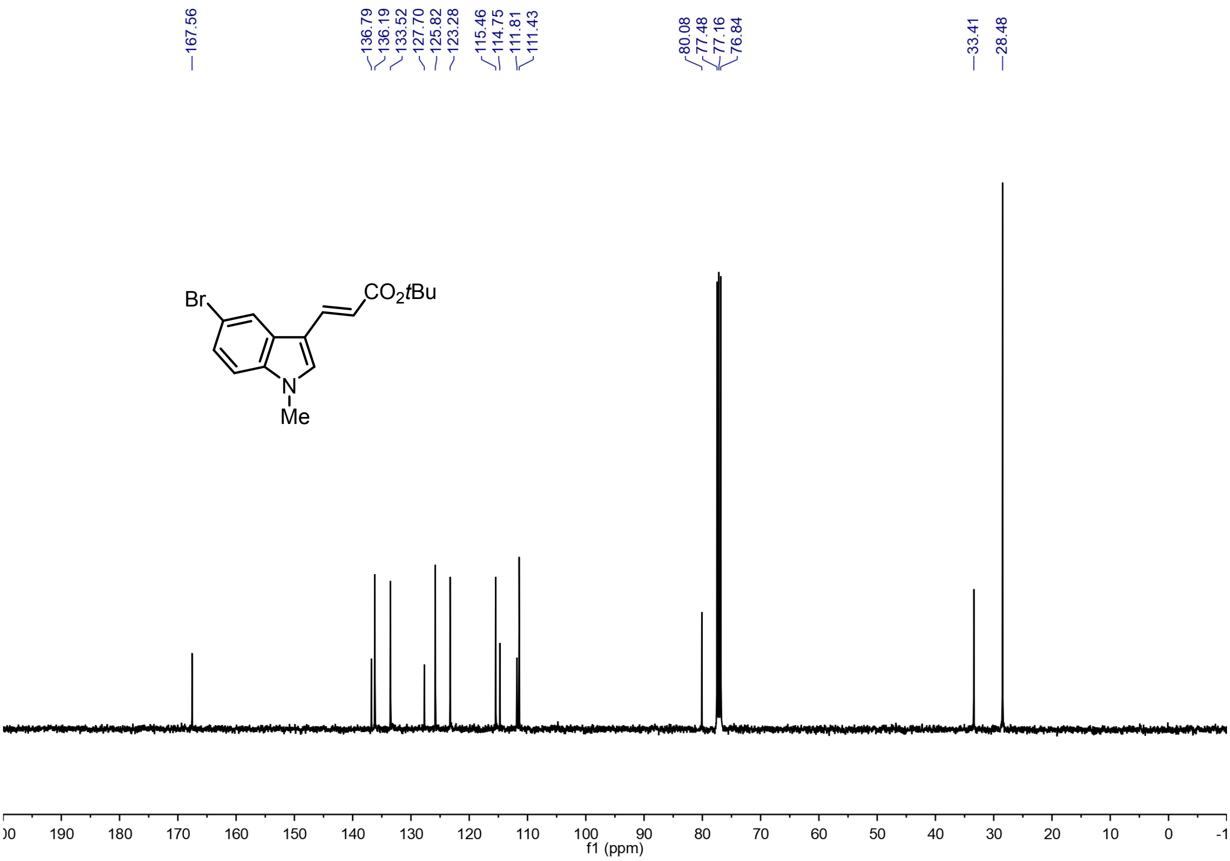
^{1}H NMR ($CDCl_3$, 400 MHz) of mixture of **7b** and **7a**:



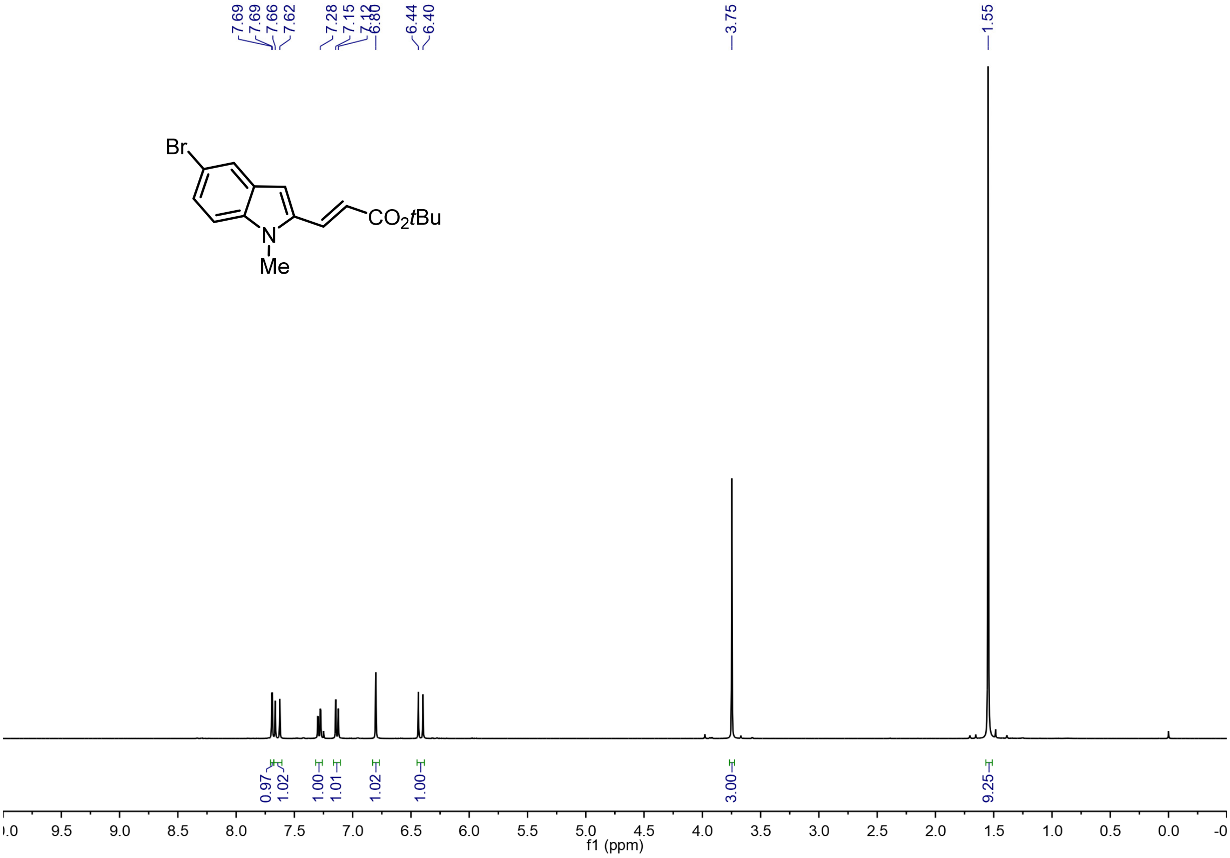
^{1}H NMR ($CDCl_3$, 400 MHz) of **8a**:



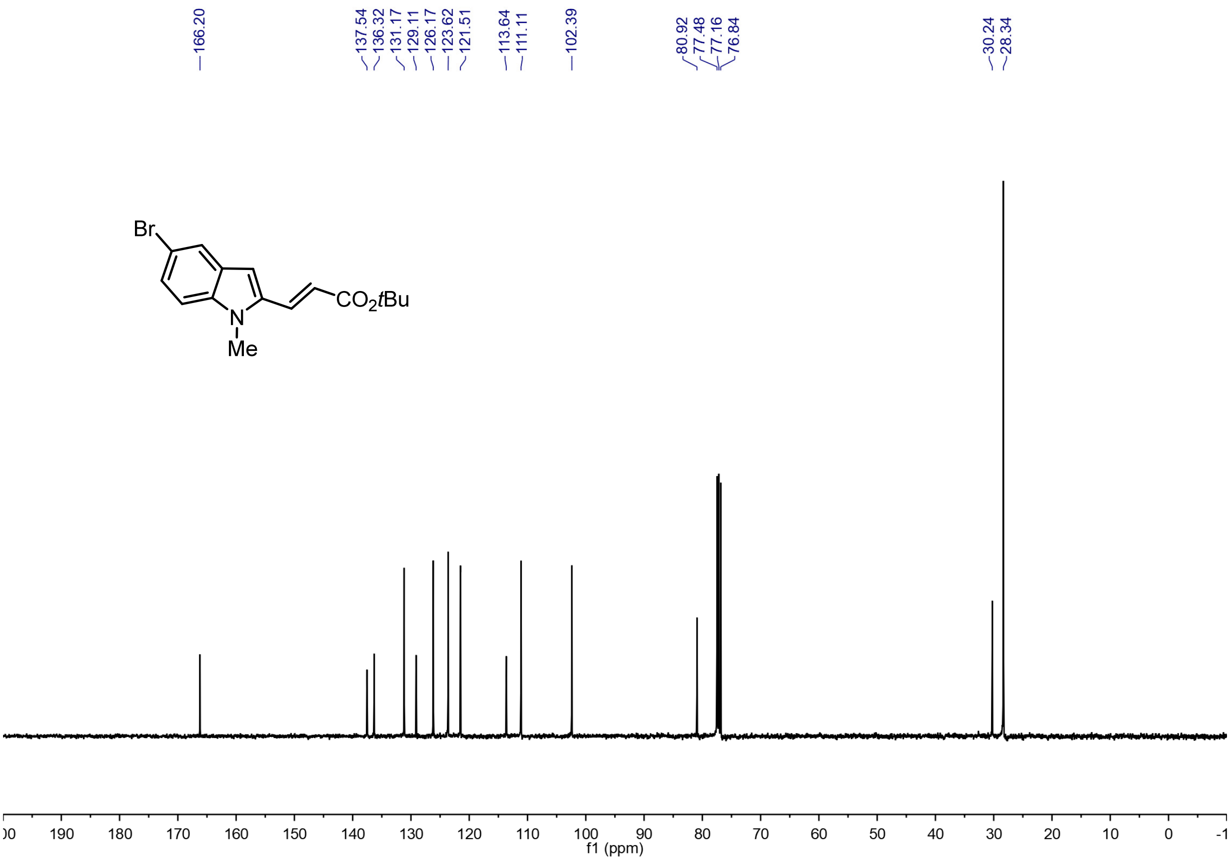
^{13}C NMR ($CDCl_3$, 100 MHz) of **8a**:



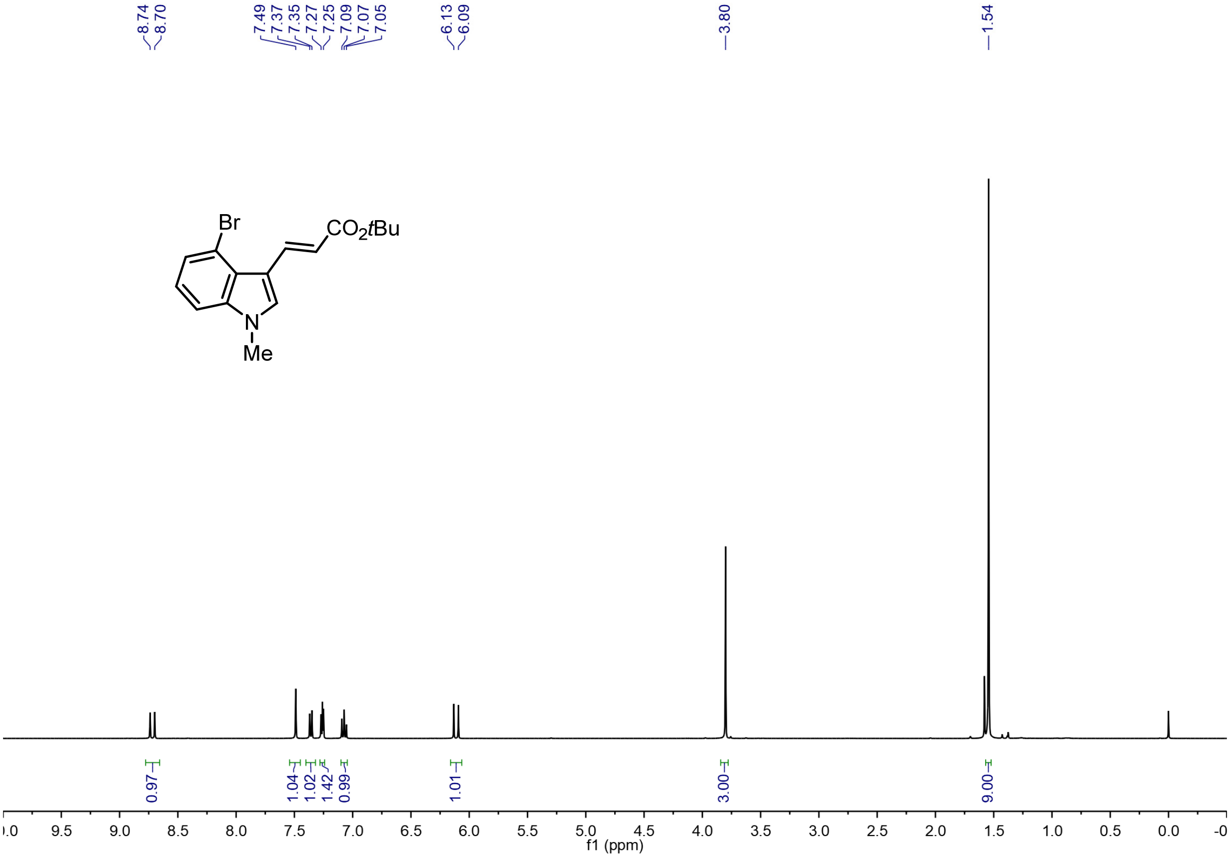
^{1}H NMR ($CDCl_3$, 400 MHz) of **8b**:



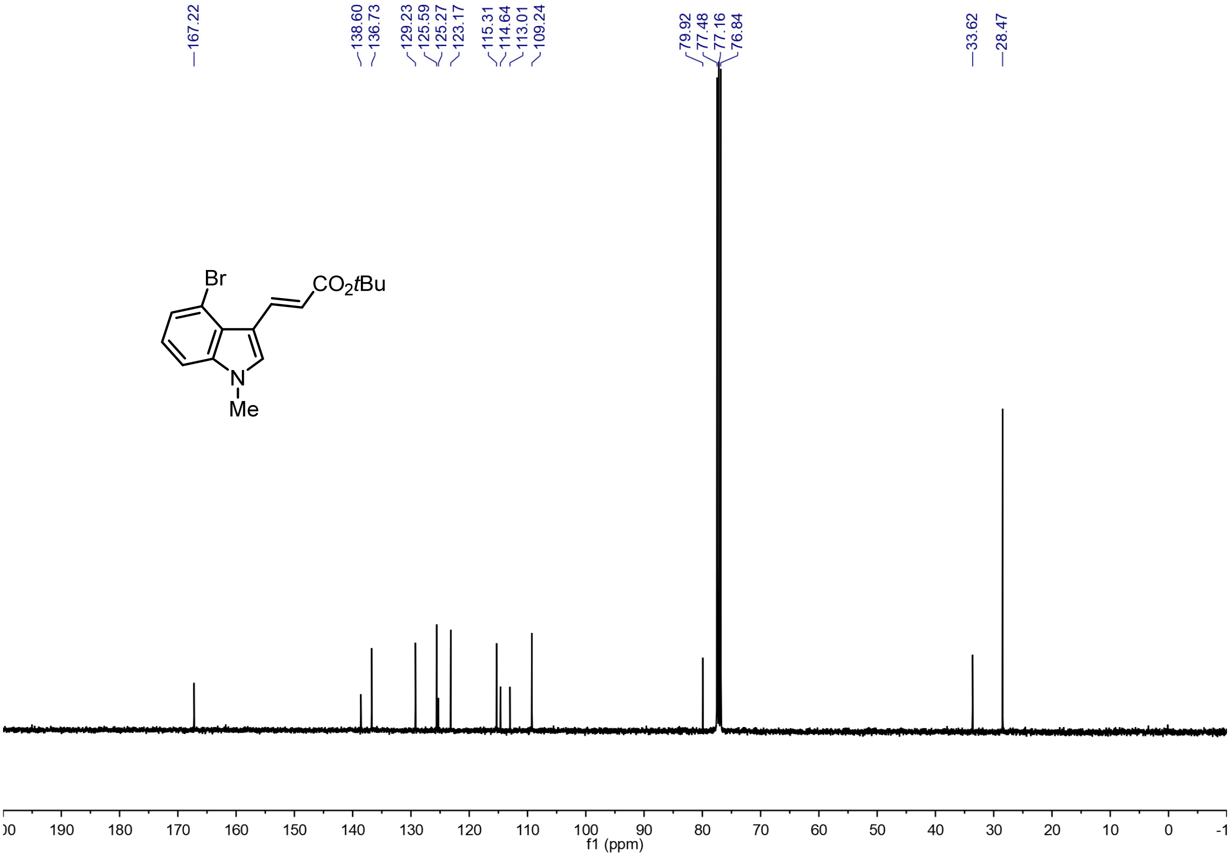
^{13}C NMR ($CDCl_3$, 100 MHz) of **8b**:



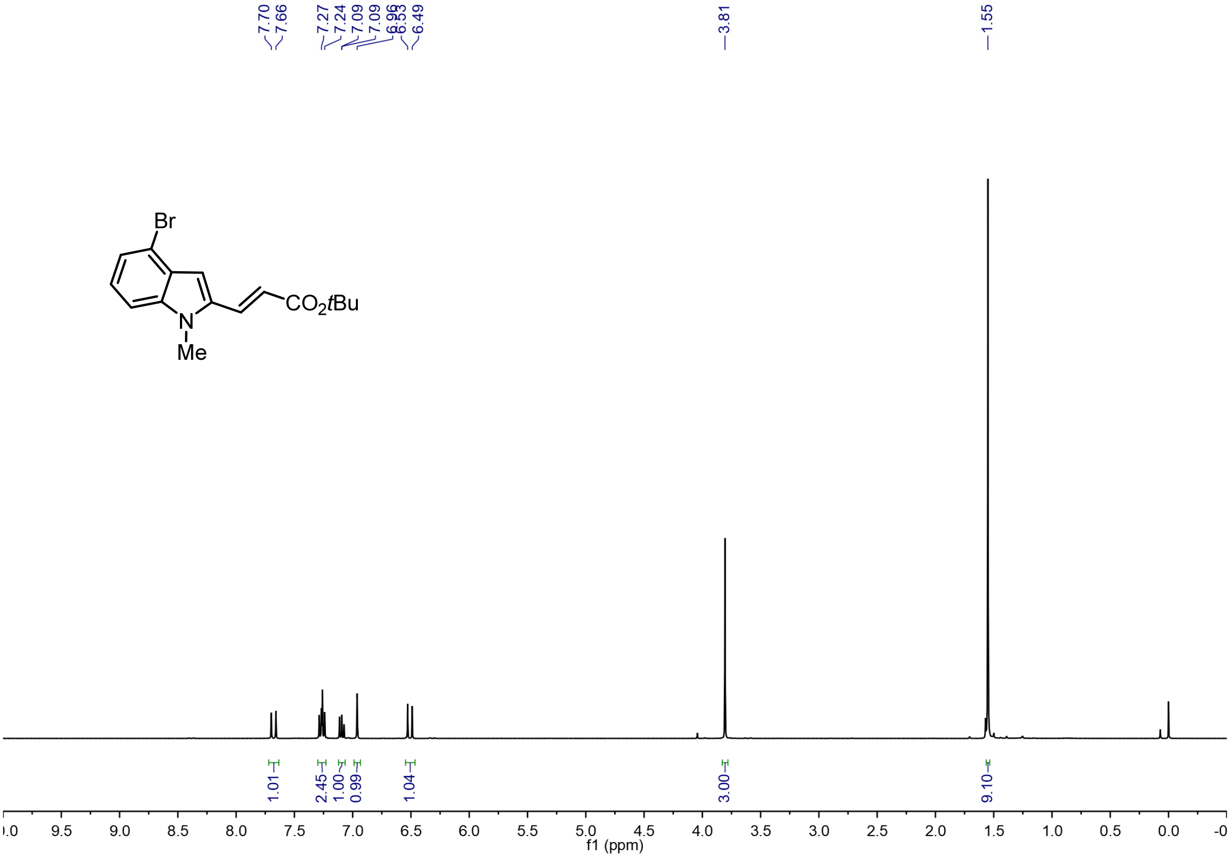
^{1}H NMR ($CDCl_3$, 400 MHz) of **9a**:



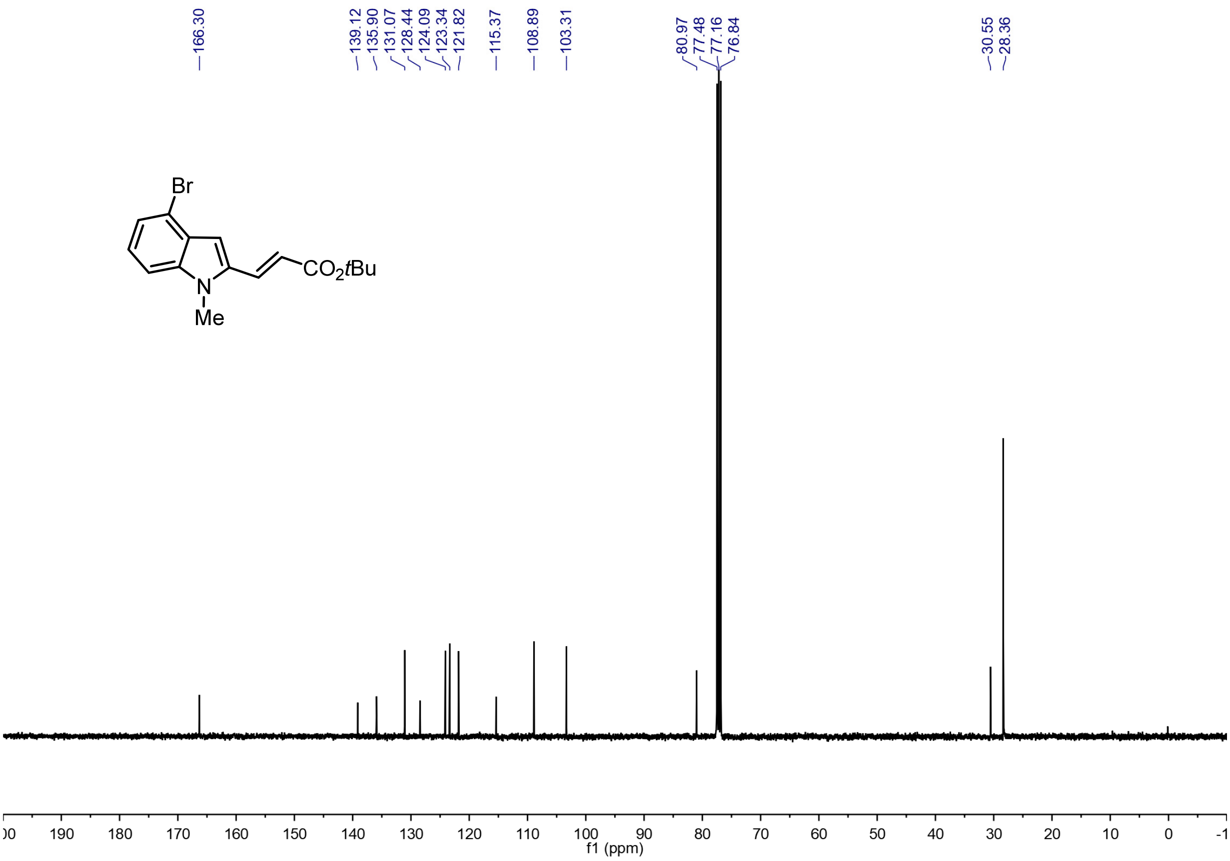
^{13}C NMR ($CDCl_3$, 100 MHz) of **9a**:



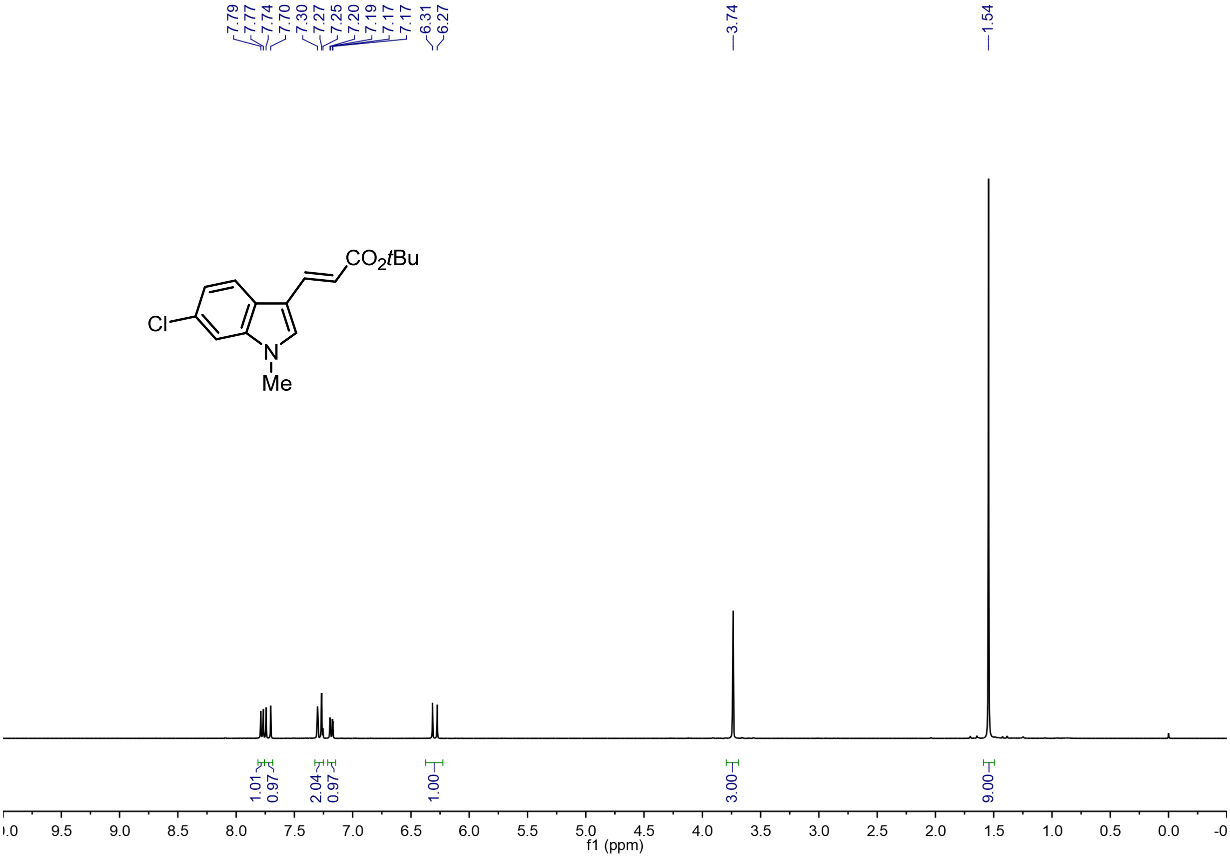
^{1}H NMR ($CDCl_3$, 400 MHz) of **9b**:



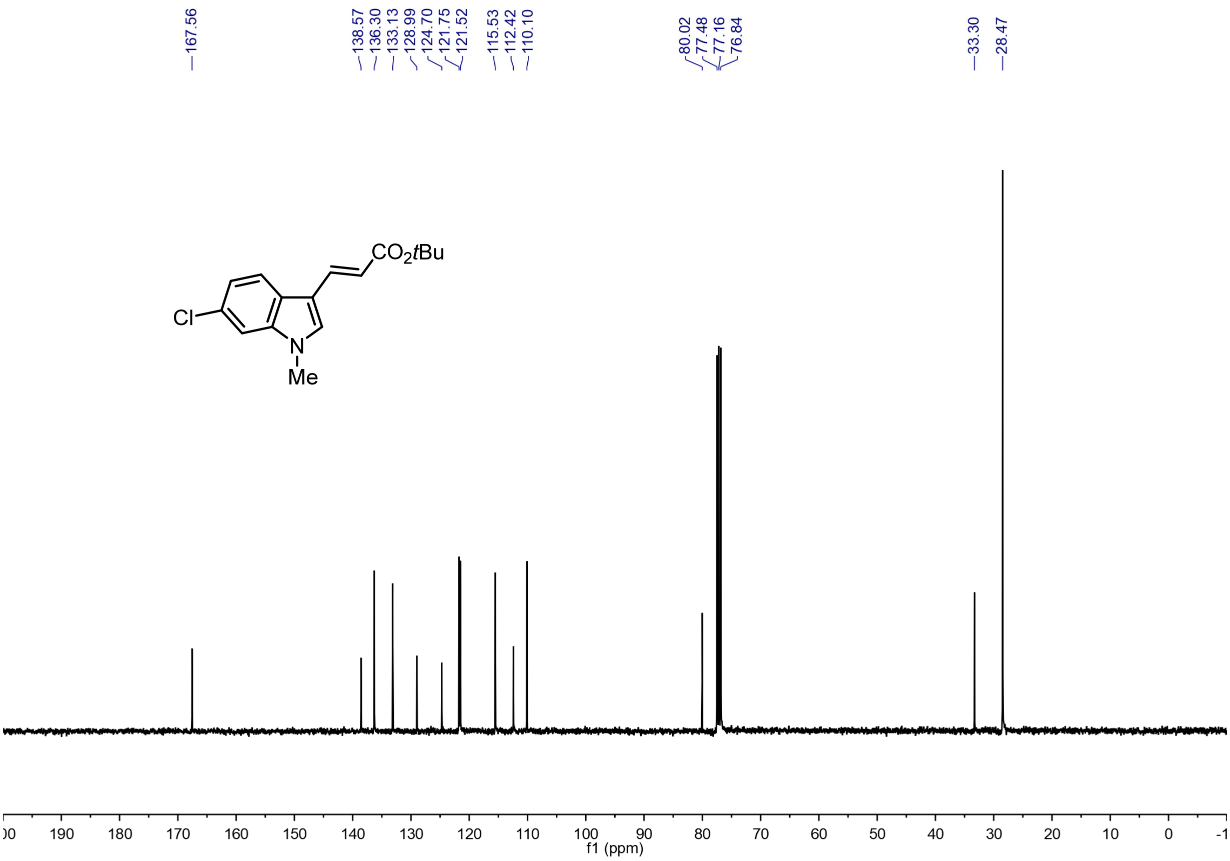
^{13}C NMR ($CDCl_3$, 100 MHz) of **9b**:



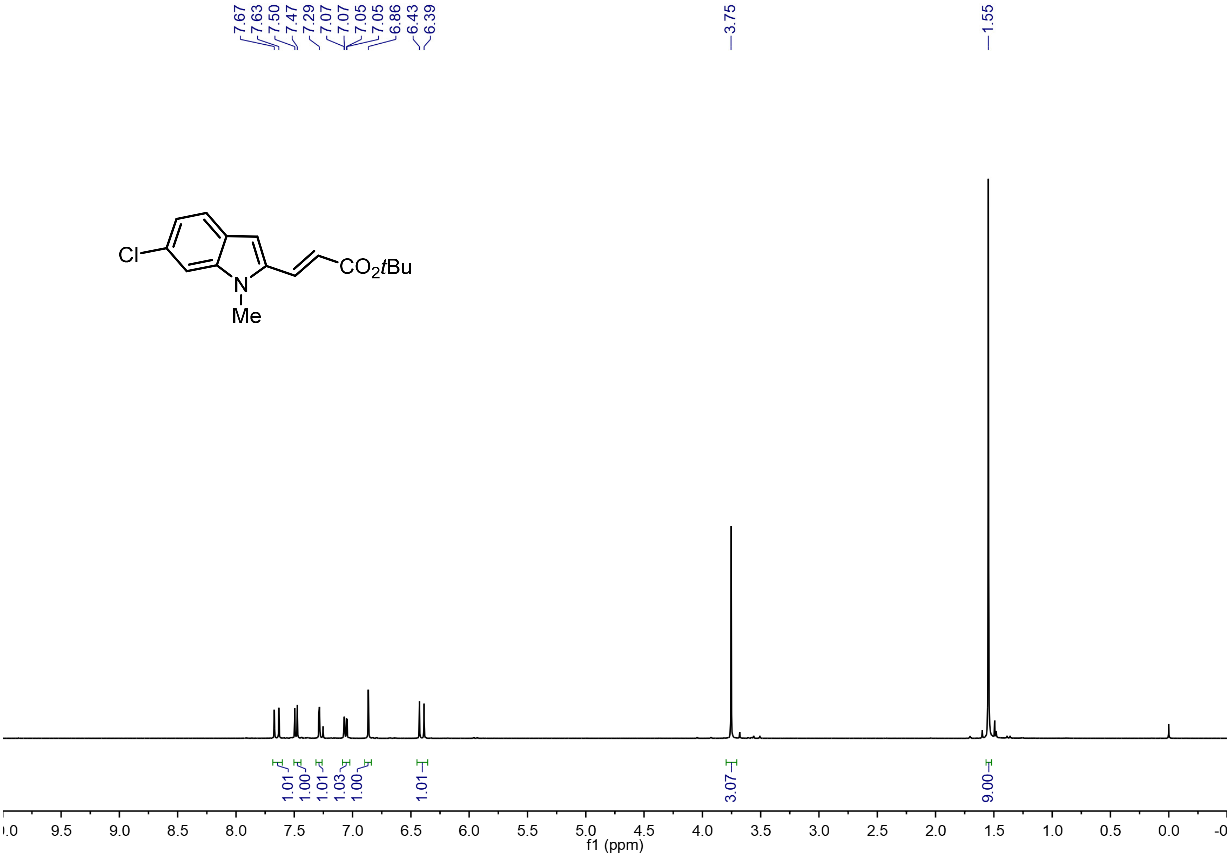
^1H NMR ($CDCl_3$, 400 MHz) of **10a**:



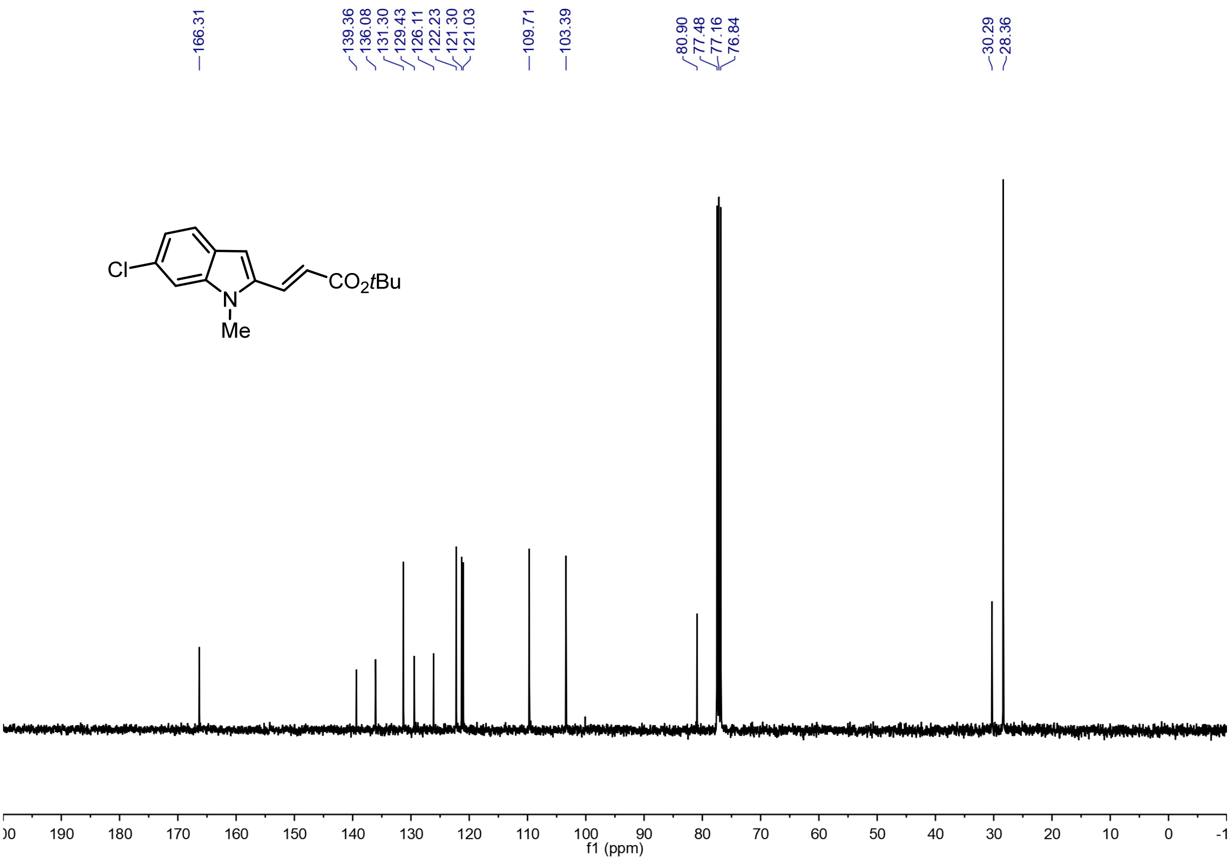
^{13}C NMR ($CDCl_3$, 100 MHz) of **10a**:



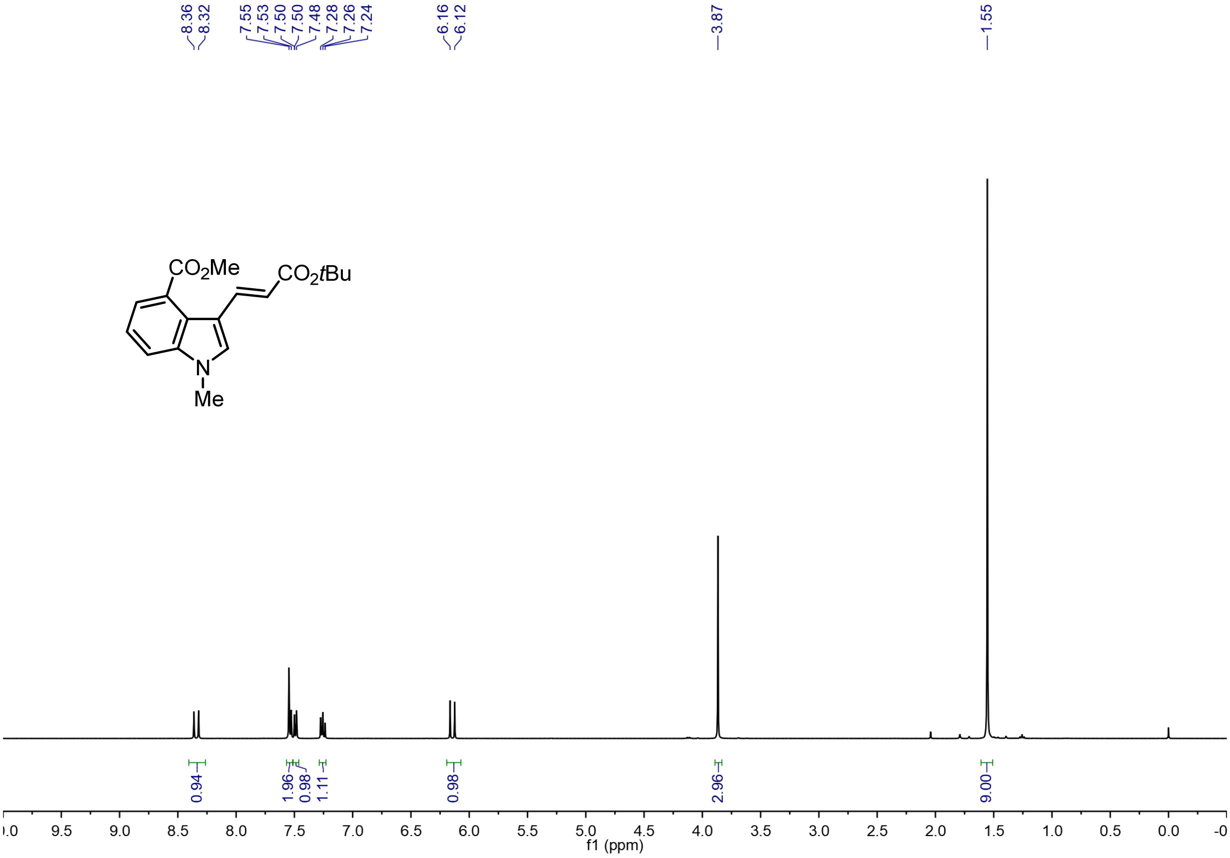
[1]H NMR ($CDCl_3$, 400 MHz) of **10b**:



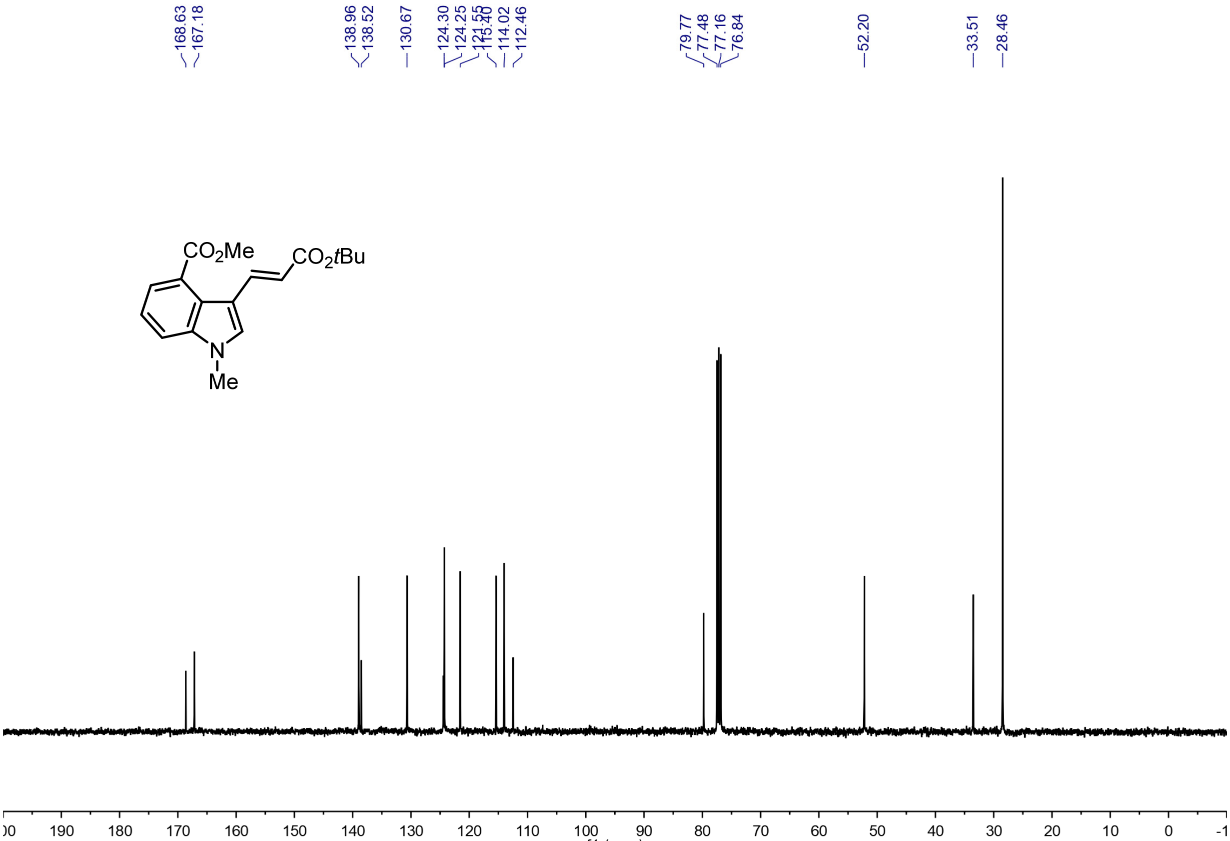
[13]C NMR ($CDCl_3$, 100 MHz) of **10b**:



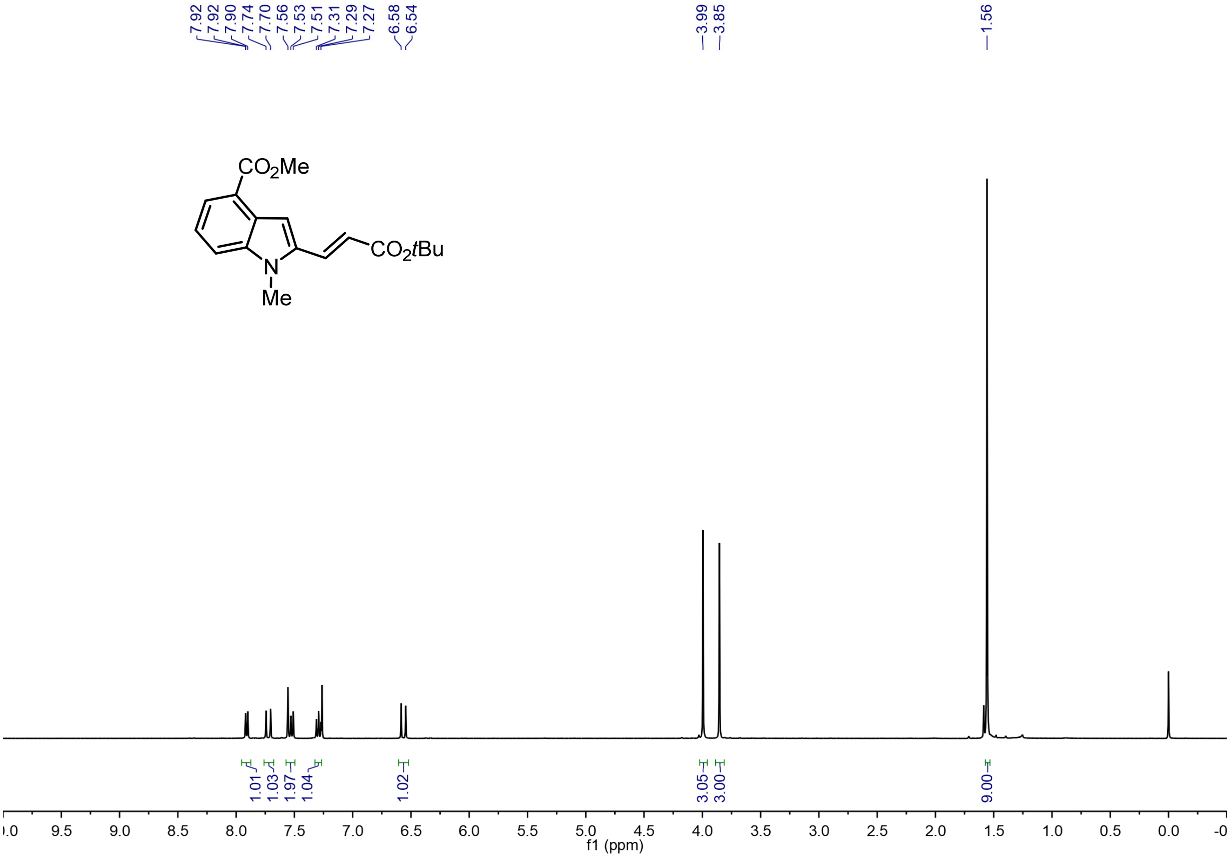
^1H NMR ($CDCl_3$, 400 MHz) of **11a**:



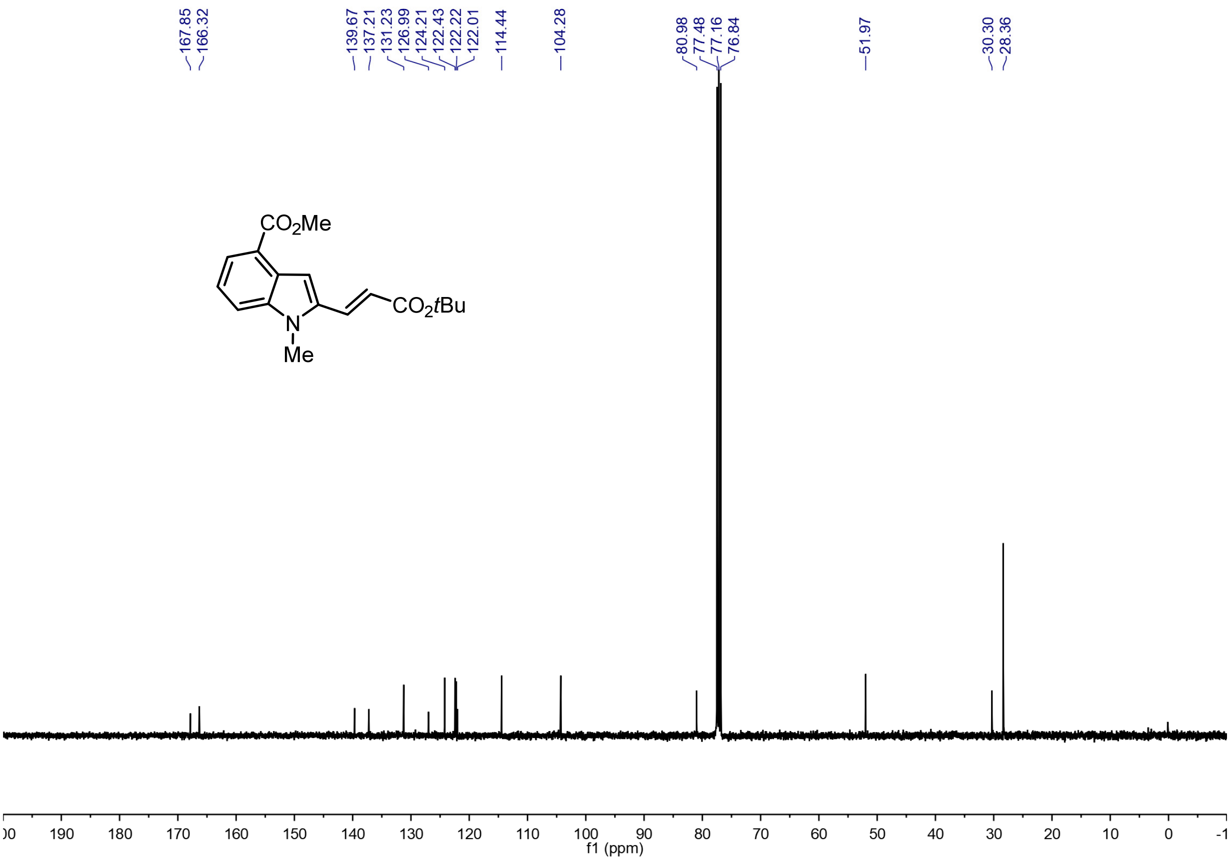
^{13}C NMR ($CDCl_3$, 100 MHz) of **11a**:



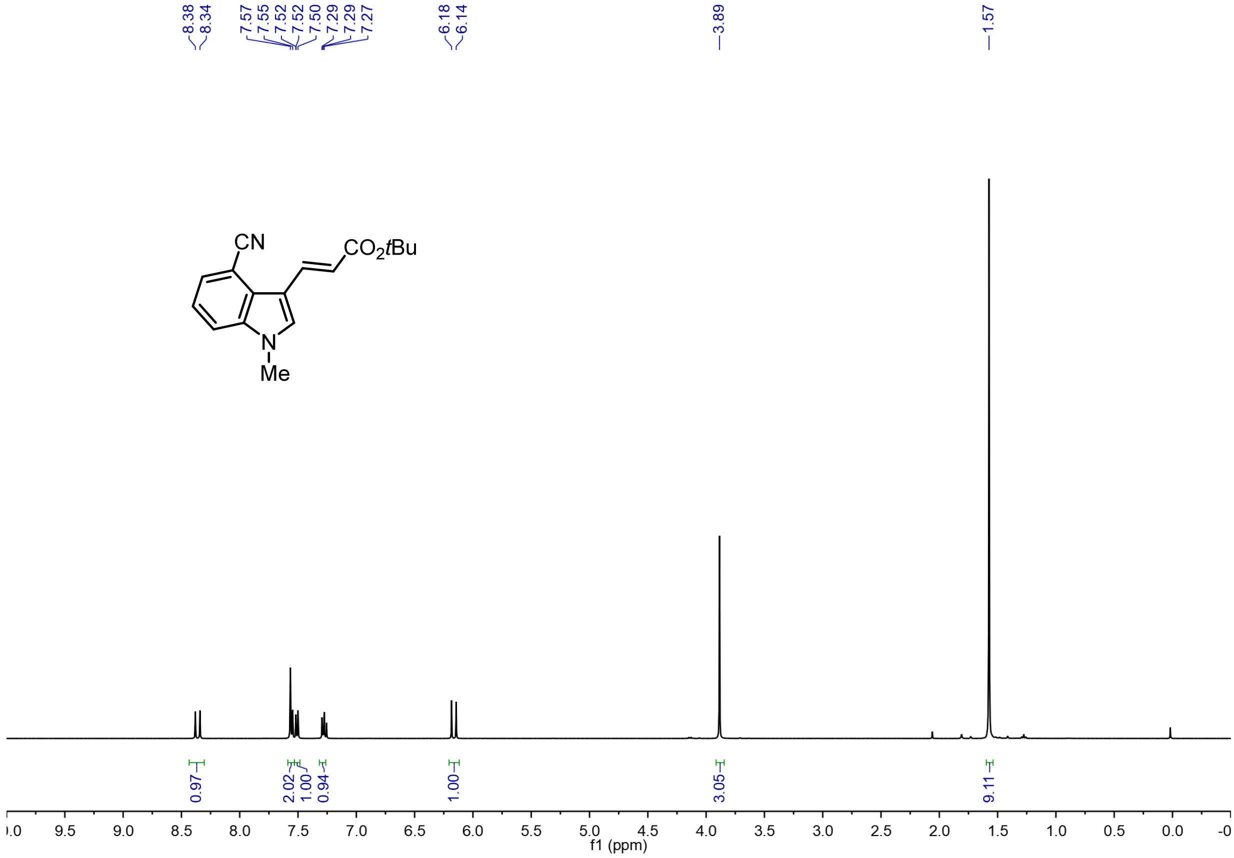
^1H NMR ($CDCl_3$, 400 MHz) of **11b**:



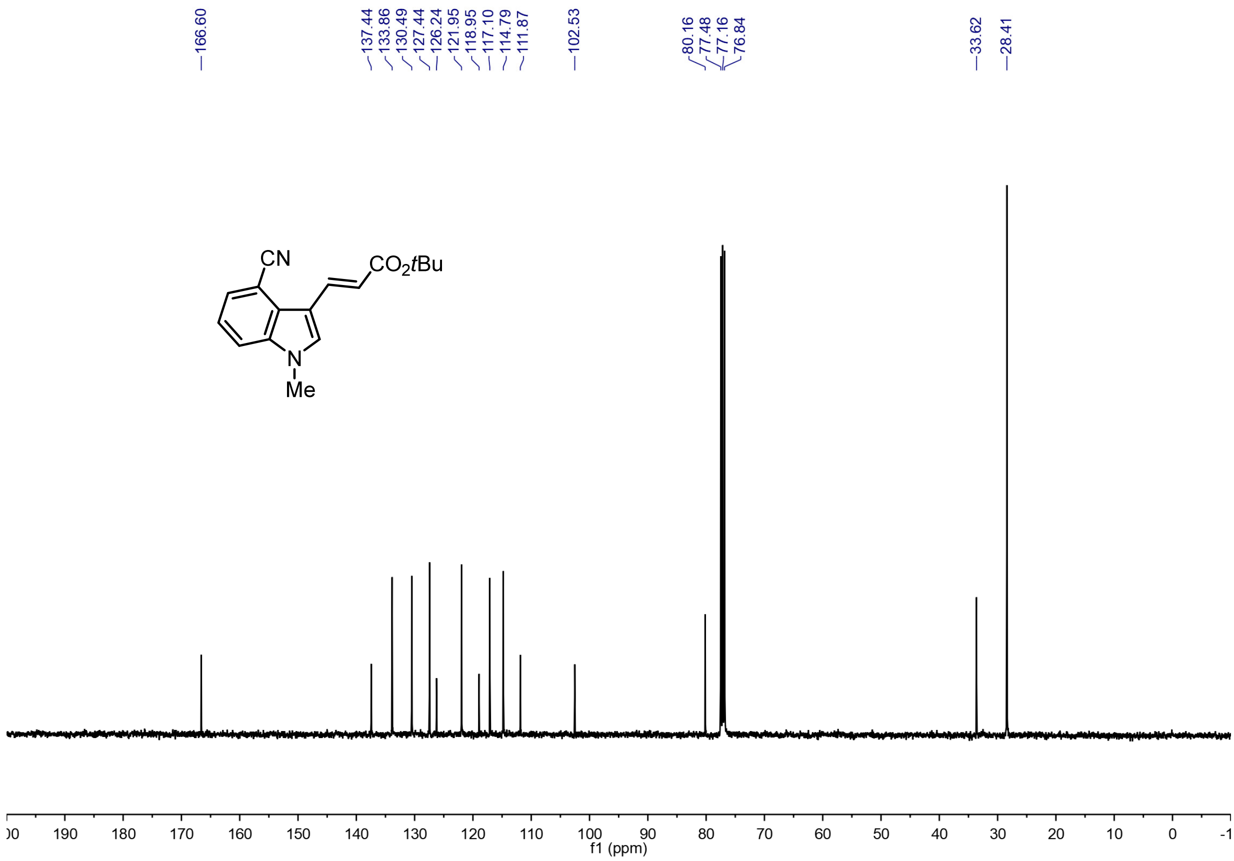
^{13}C NMR ($CDCl_3$, 100 MHz) of **11b**:



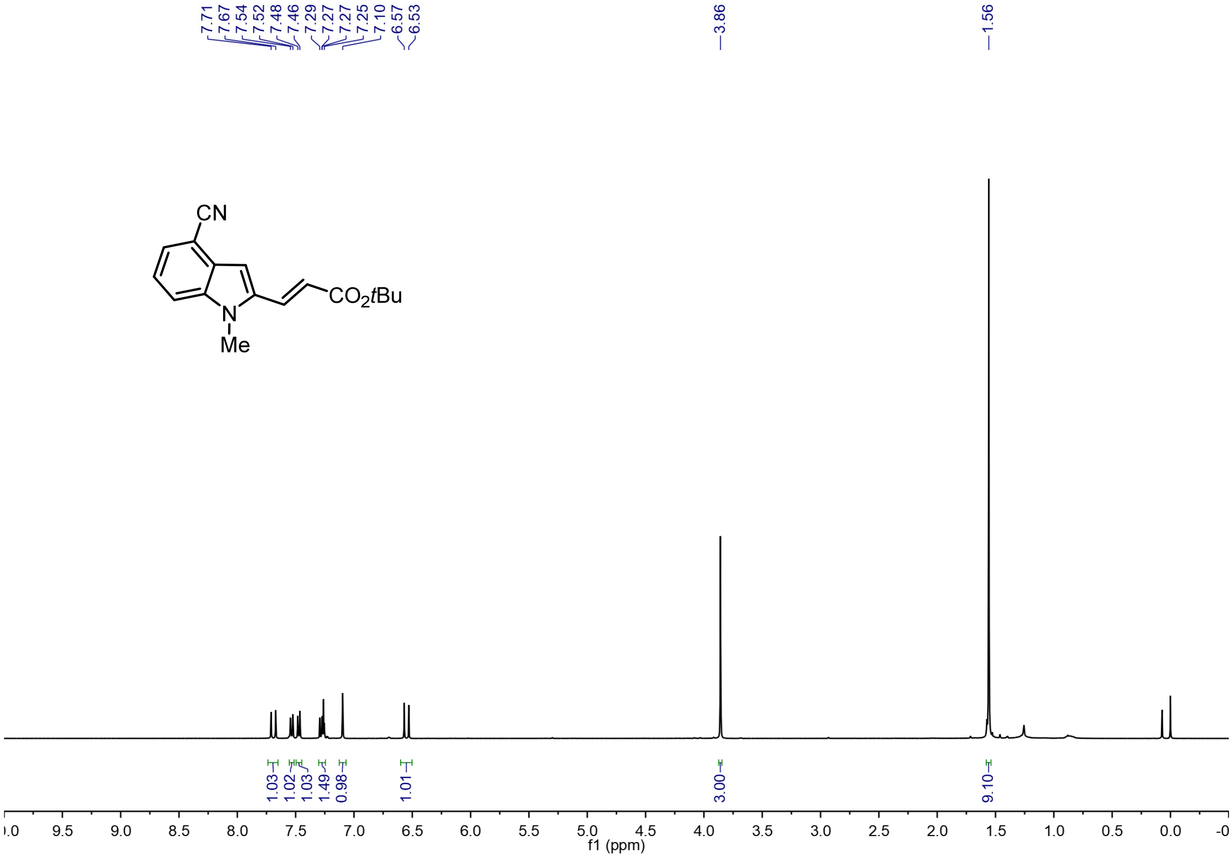
^{1}H NMR ($CDCl_3$, 400 MHz) of **12a**:



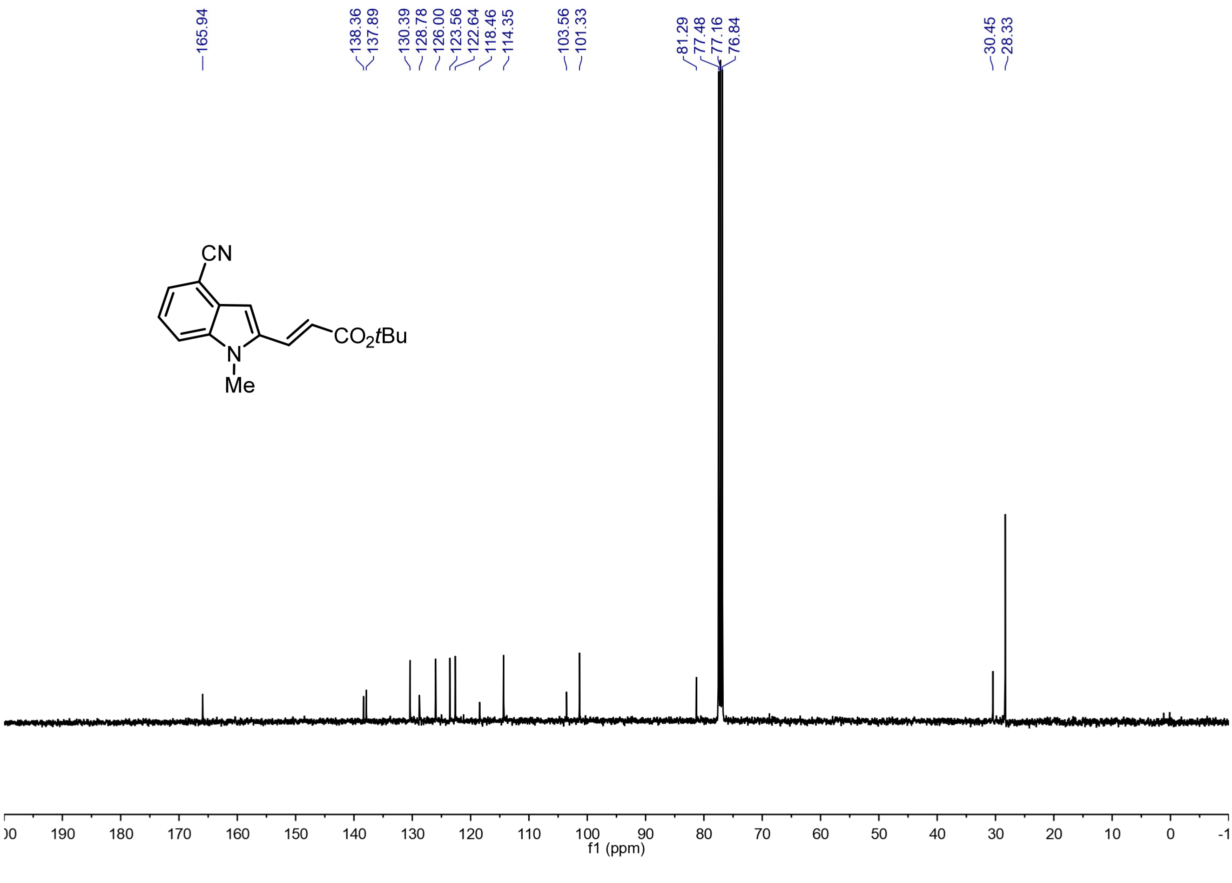
^{13}C NMR ($CDCl_3$, 100 MHz) of **12a**:



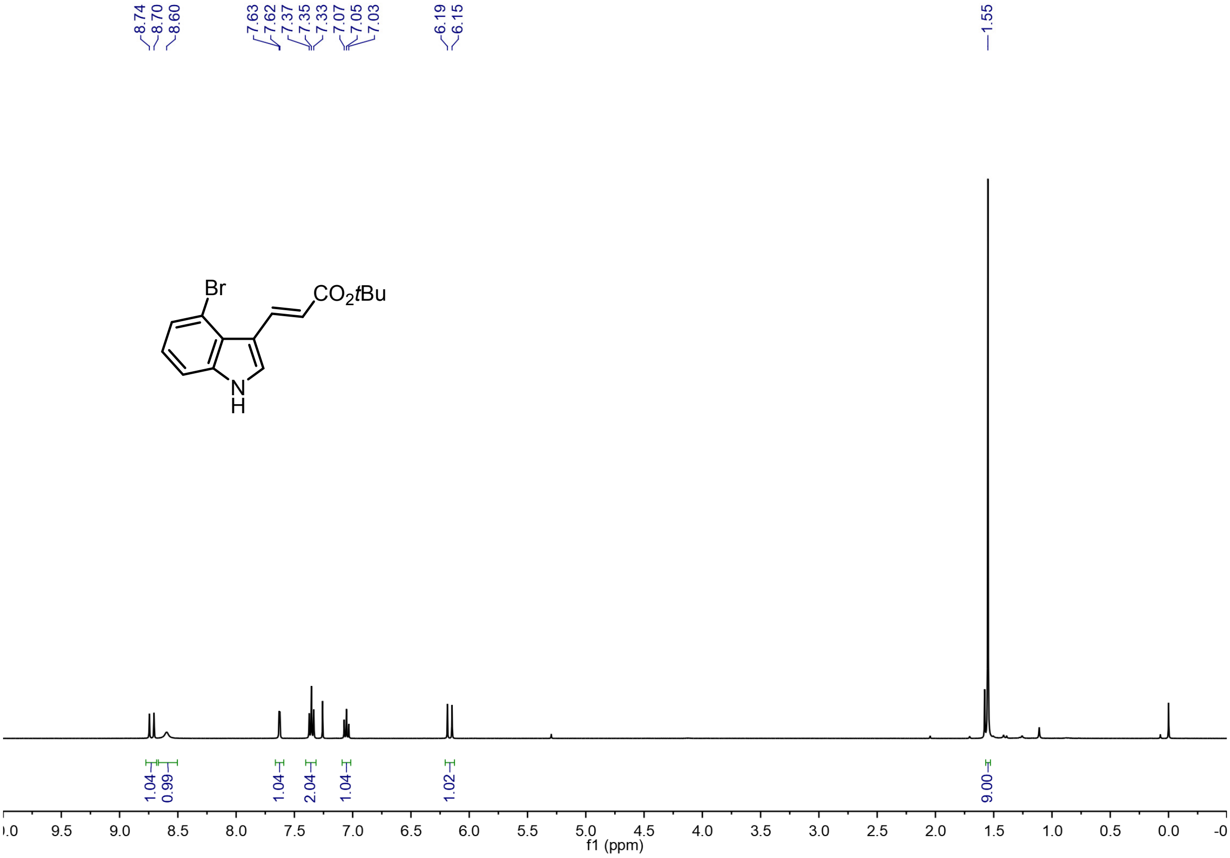
^{1}H NMR ($CDCl_3$, 400 MHz) of **12b**:



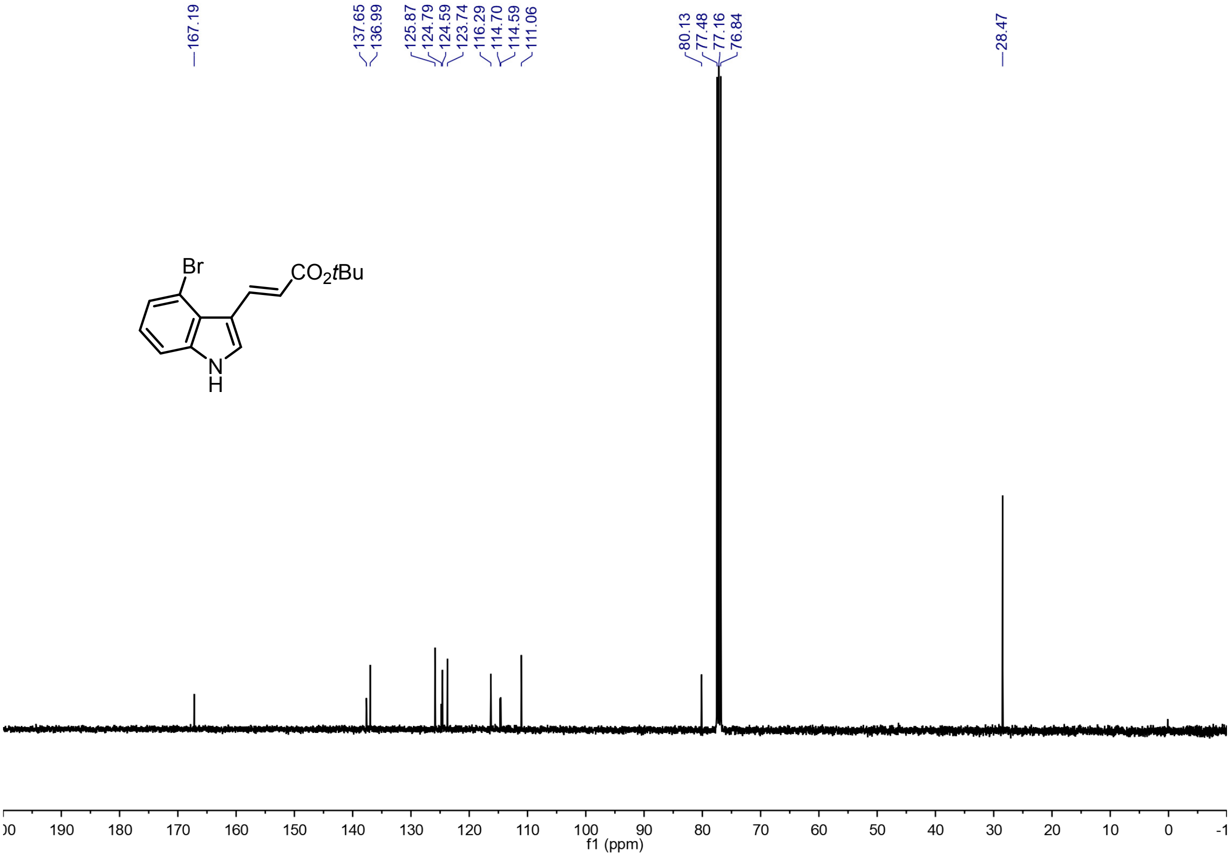
^{13}C NMR ($CDCl_3$, 100 MHz) of **12b**:



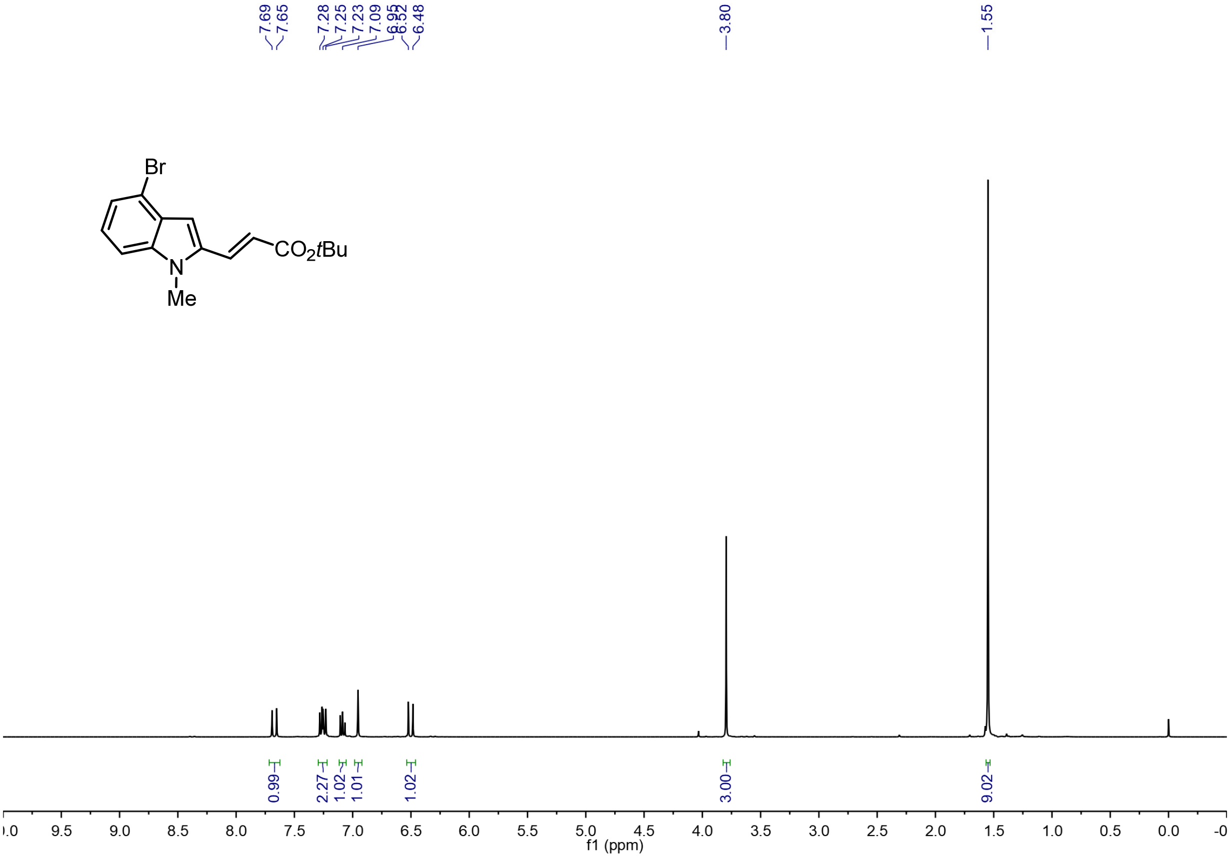
^{1}H NMR ($CDCl_3$, 400 MHz) of **13a**:



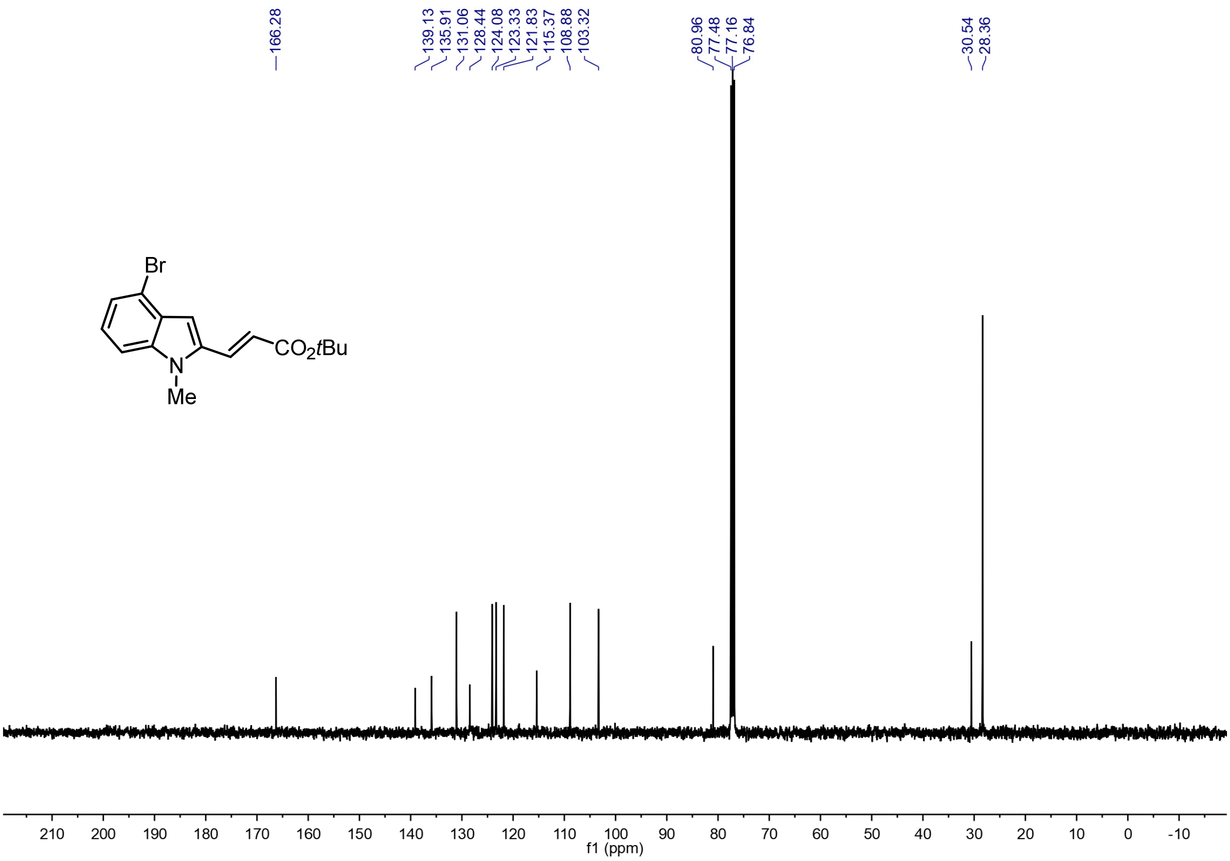
^{13}C NMR ($CDCl_3$, 100 MHz) of **13a**:



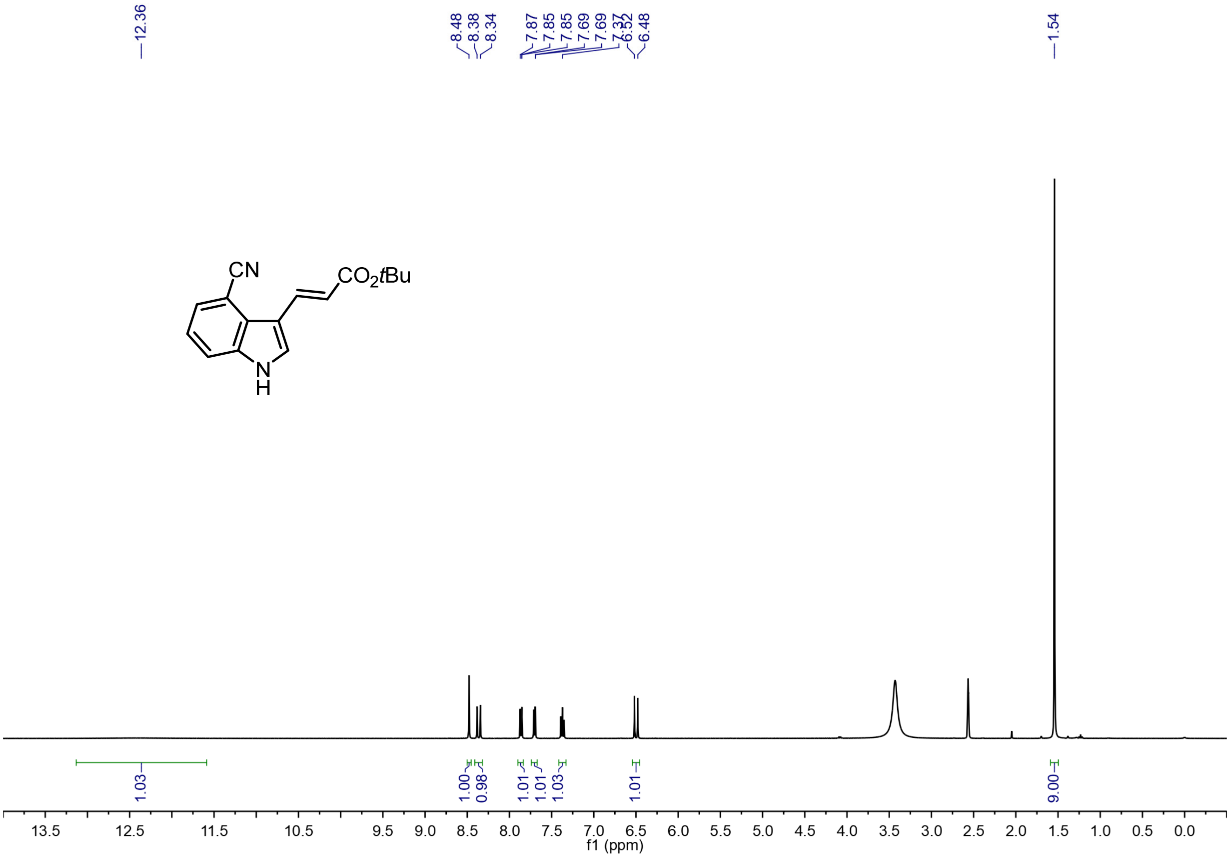
H NMR ($CDCl_3$, 400 MHz) of **13b** (after methylation):



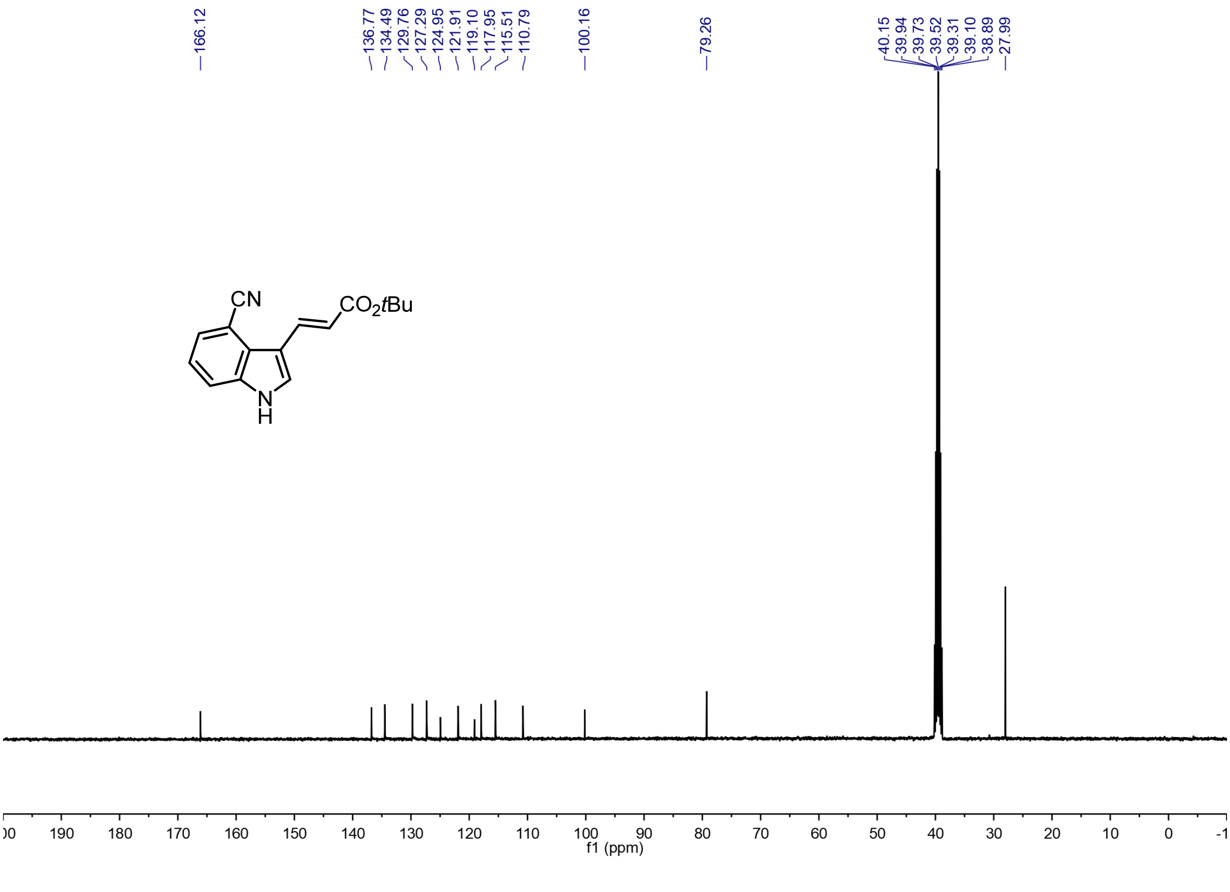
^{13}C NMR ($CDCl_3$, 100 MHz) of **13b** (after methylation):



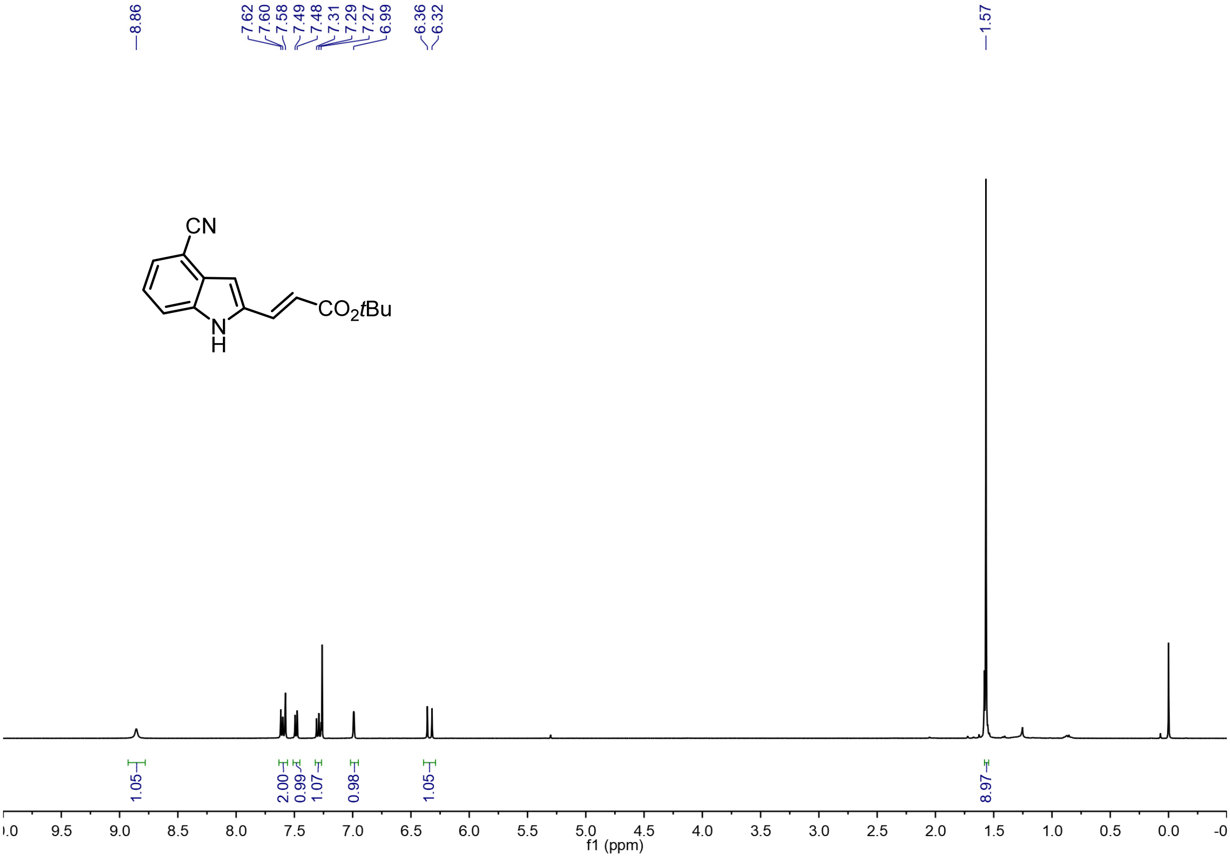
^{1}H NMR, DMSO-d^{6}, 400 MHz of **14a**:



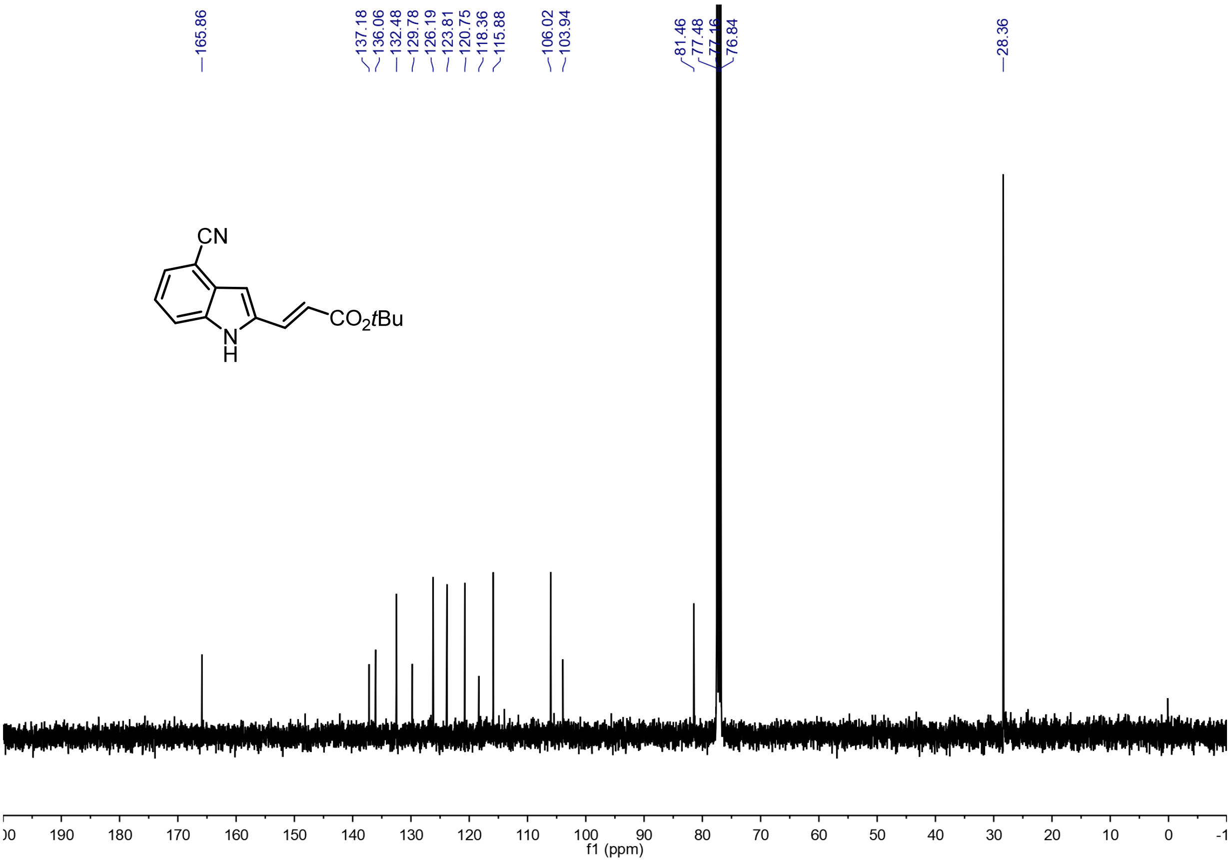
^{13}C NMR, DMSO-d^{6}, 100 MHz of **14a**:



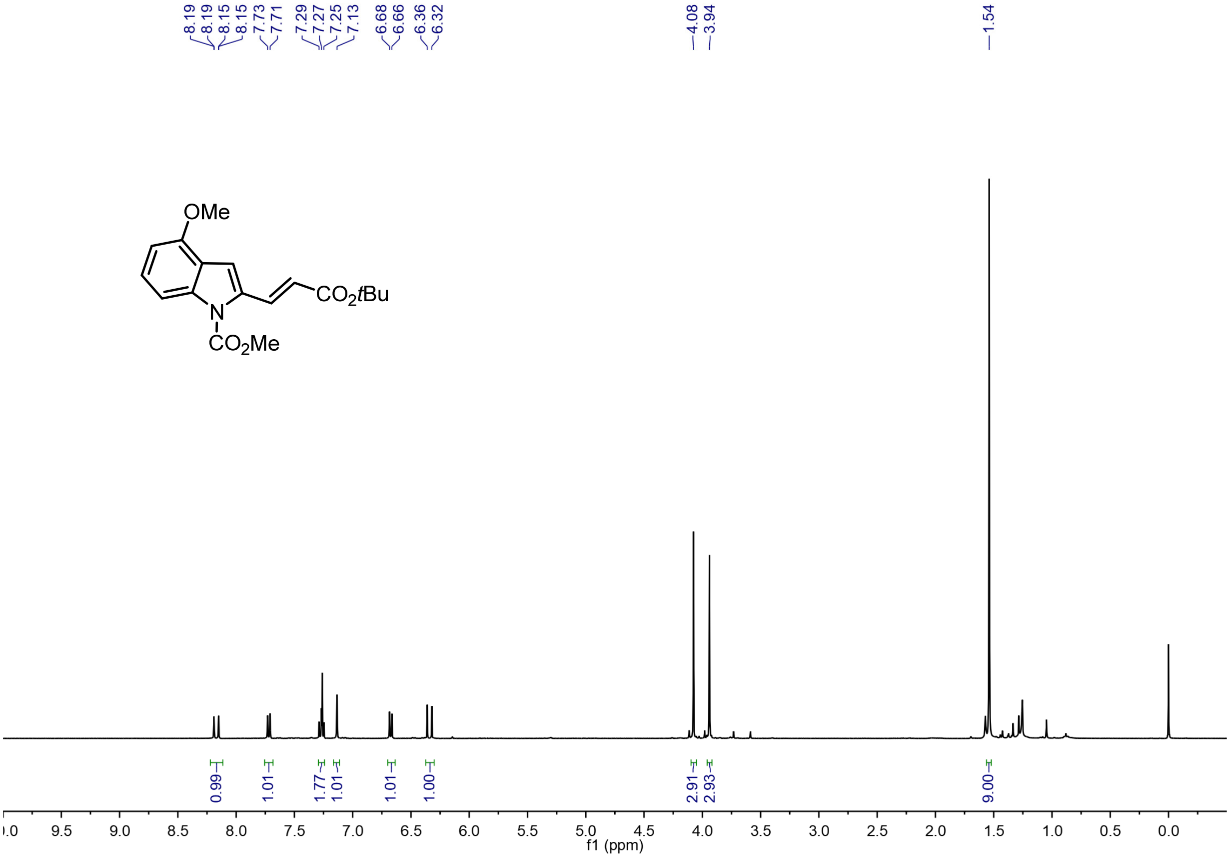
^{1}H NMR ($CDCl_3$, 400 MHz) of **14b**:



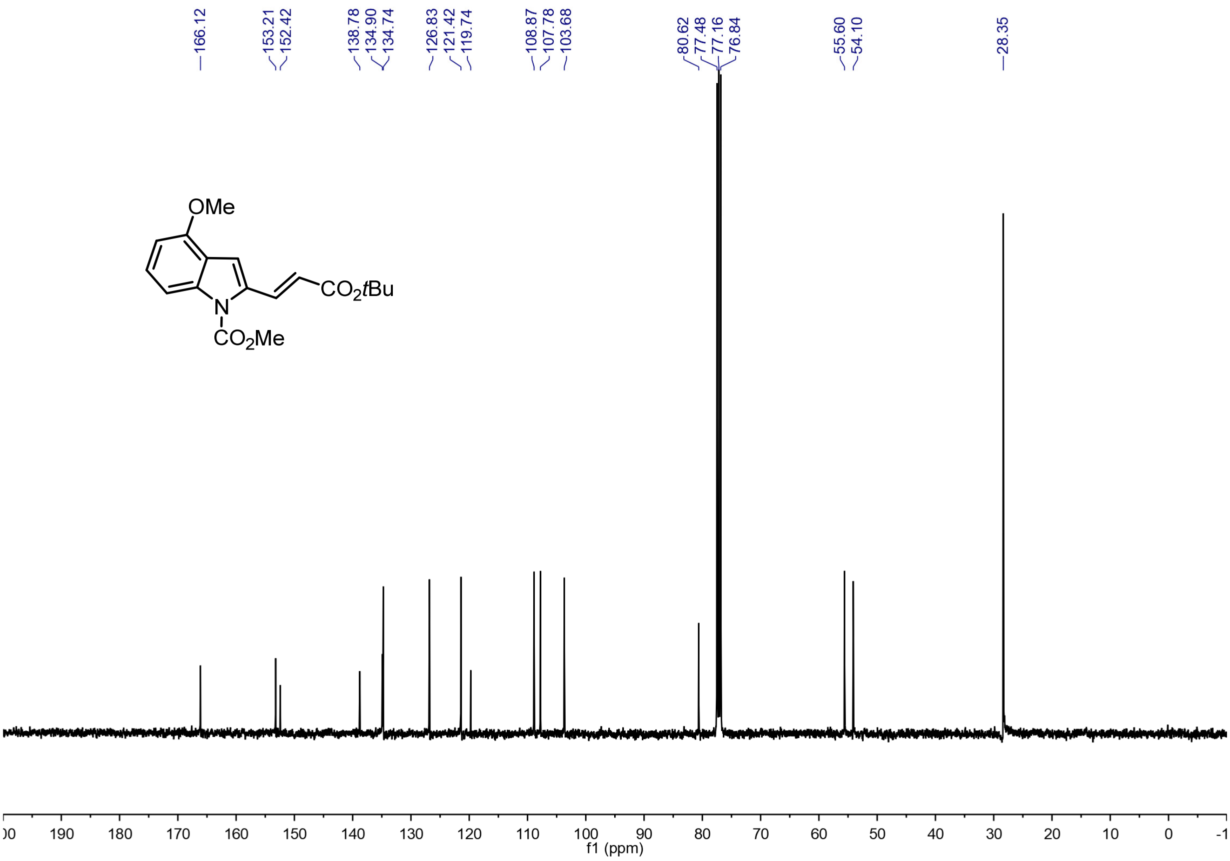
^{13}C NMR ($CDCl_3$, 100 MHz) of **14b**:



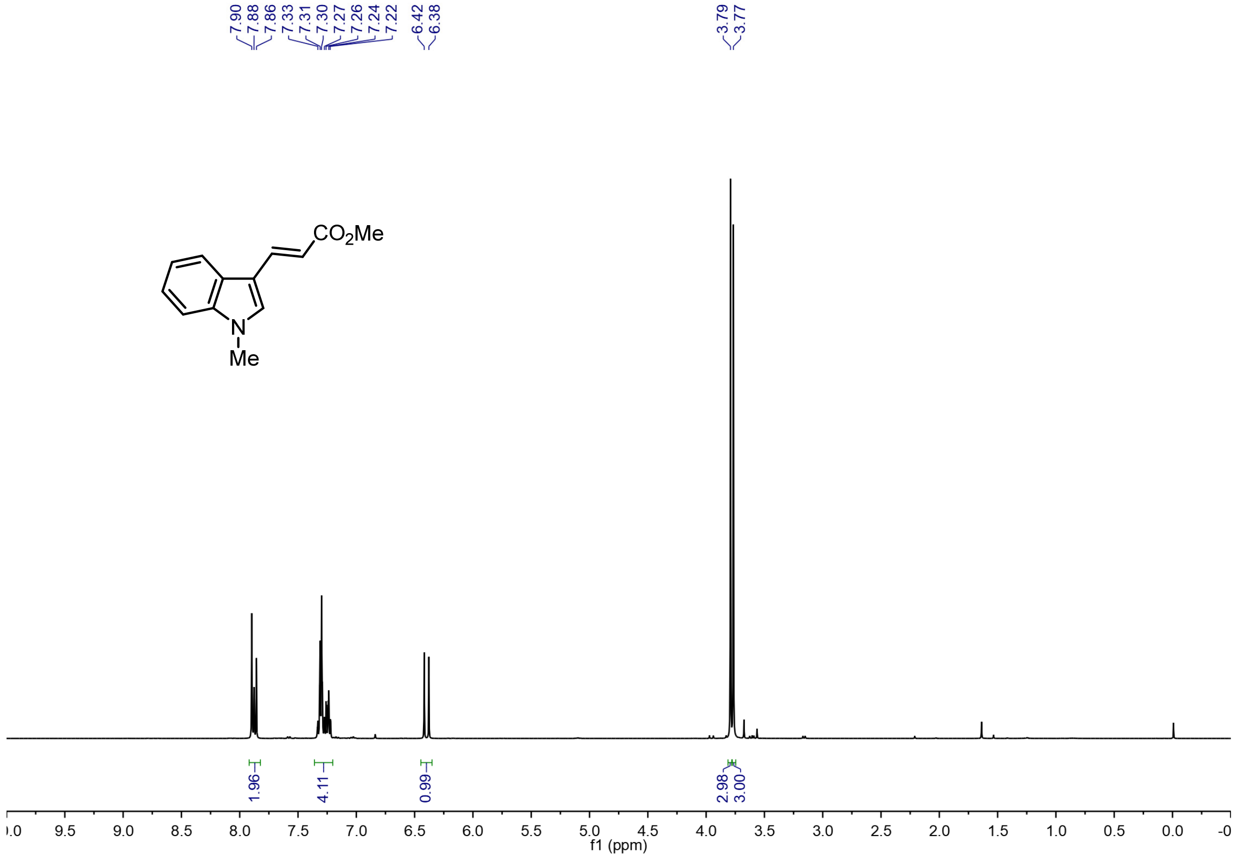
^{1}H NMR ($CDCl_3$, 400 MHz) of **15b**:



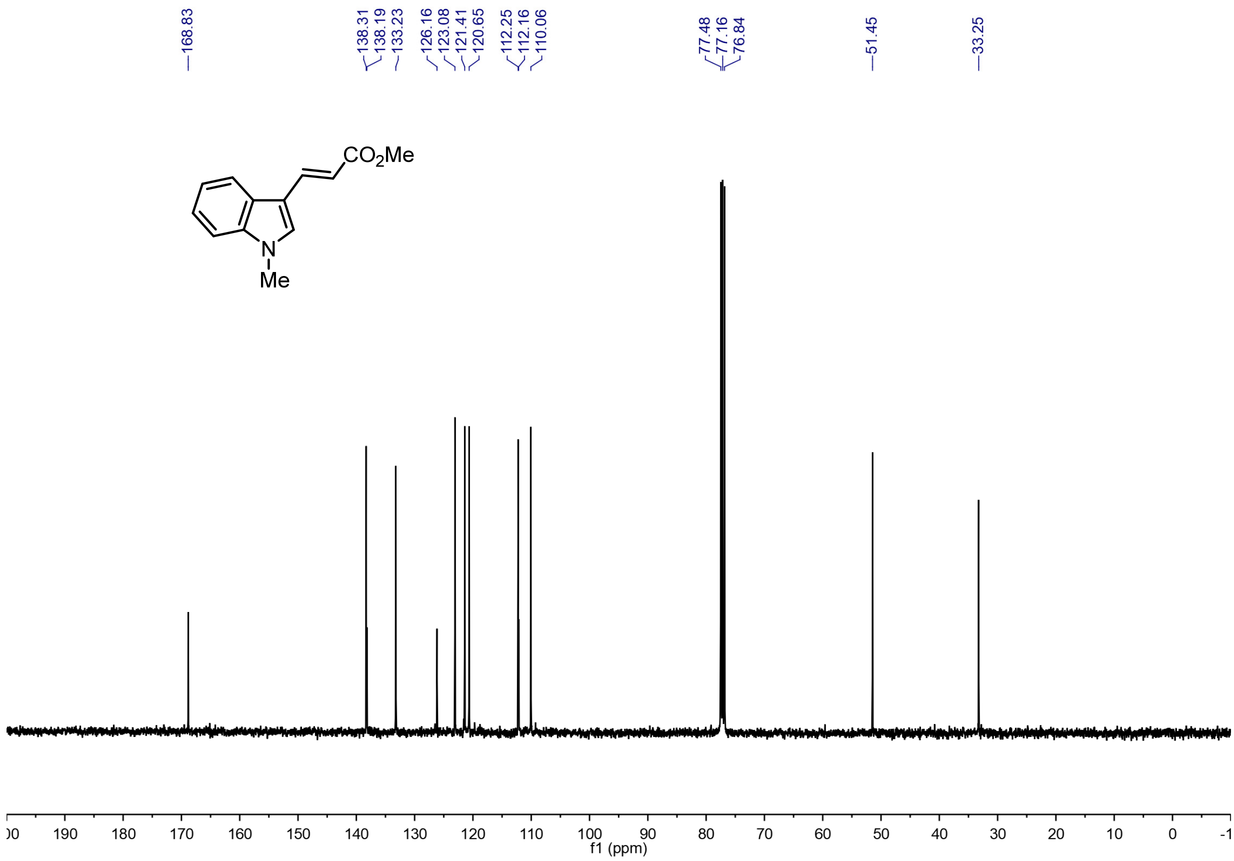
^{13}C NMR ($CDCl_3$, 100 MHz) of **15b**:



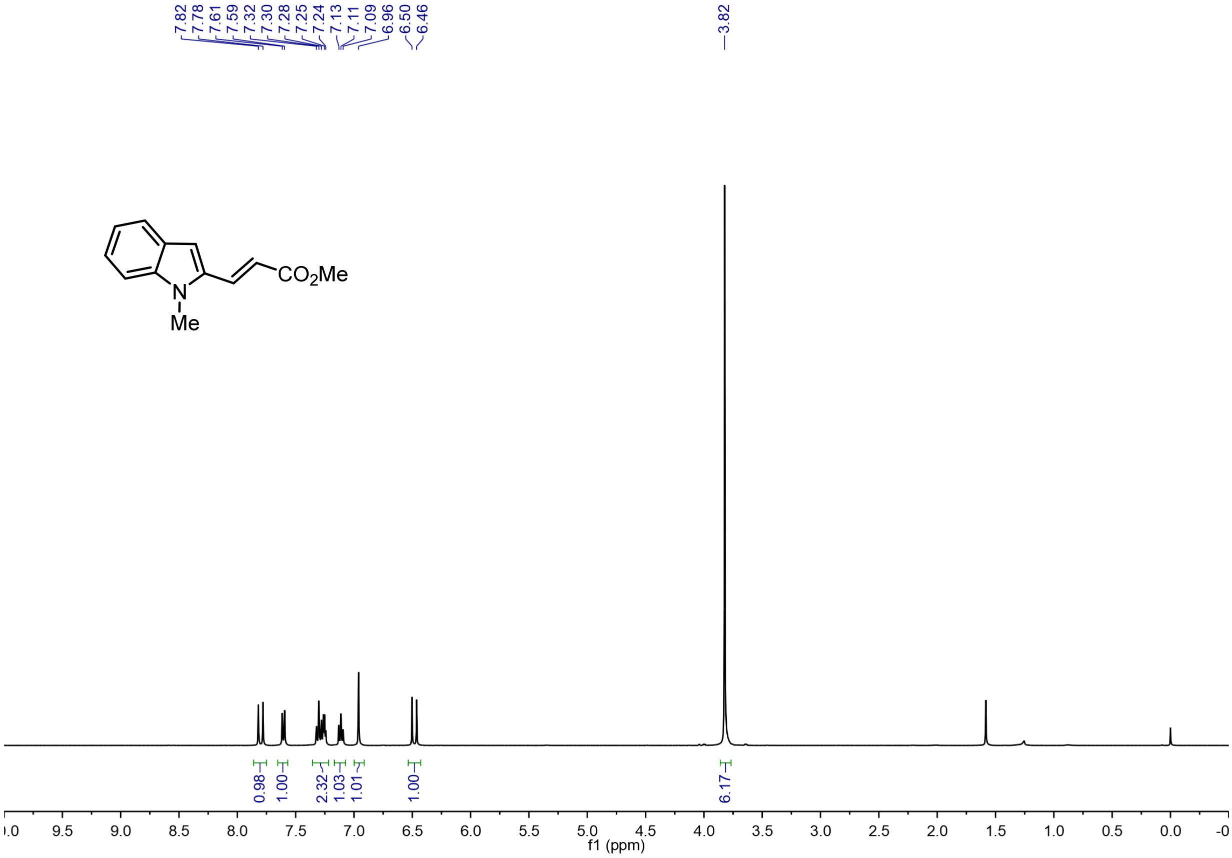
^{1}H NMR ($CDCl_3$, 400 MHz) of **16a**:



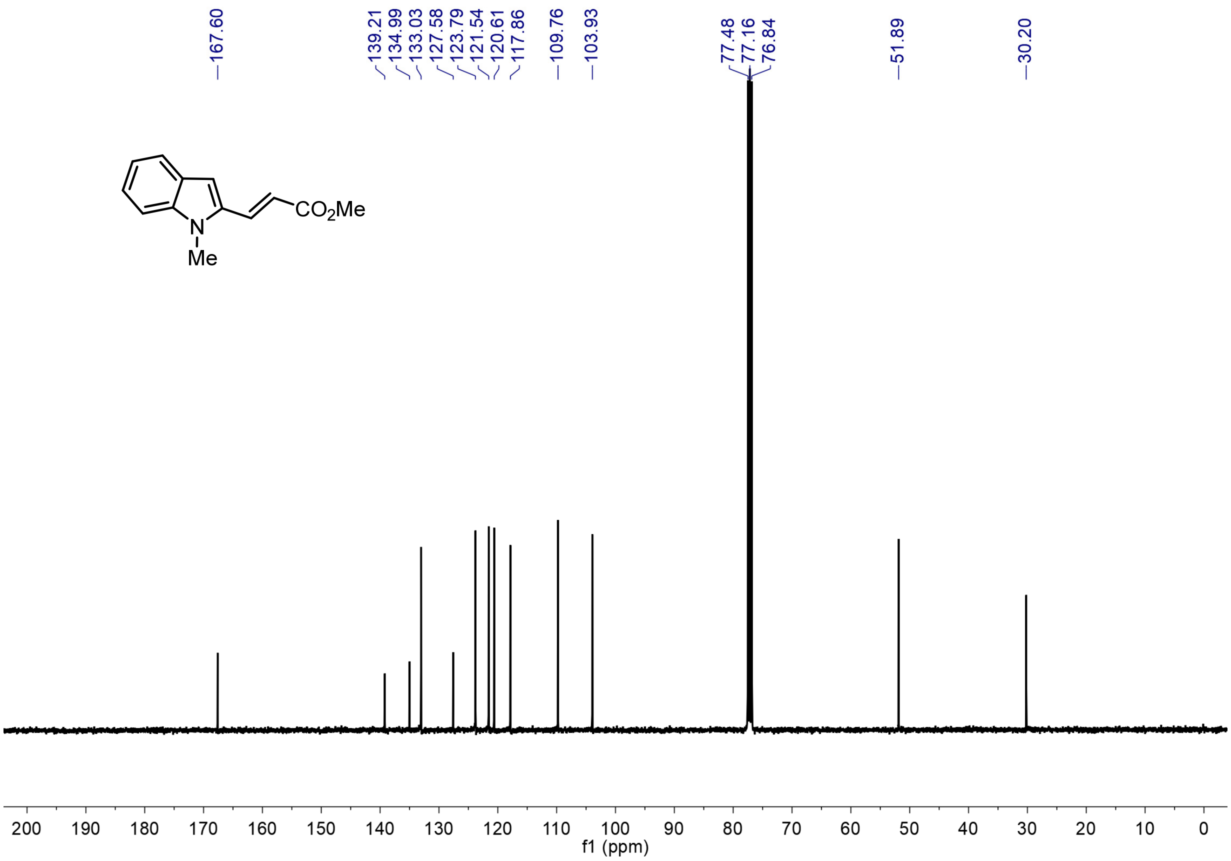
^{13}C NMR ($CDCl_3$, 100 MHz) of **16a**:



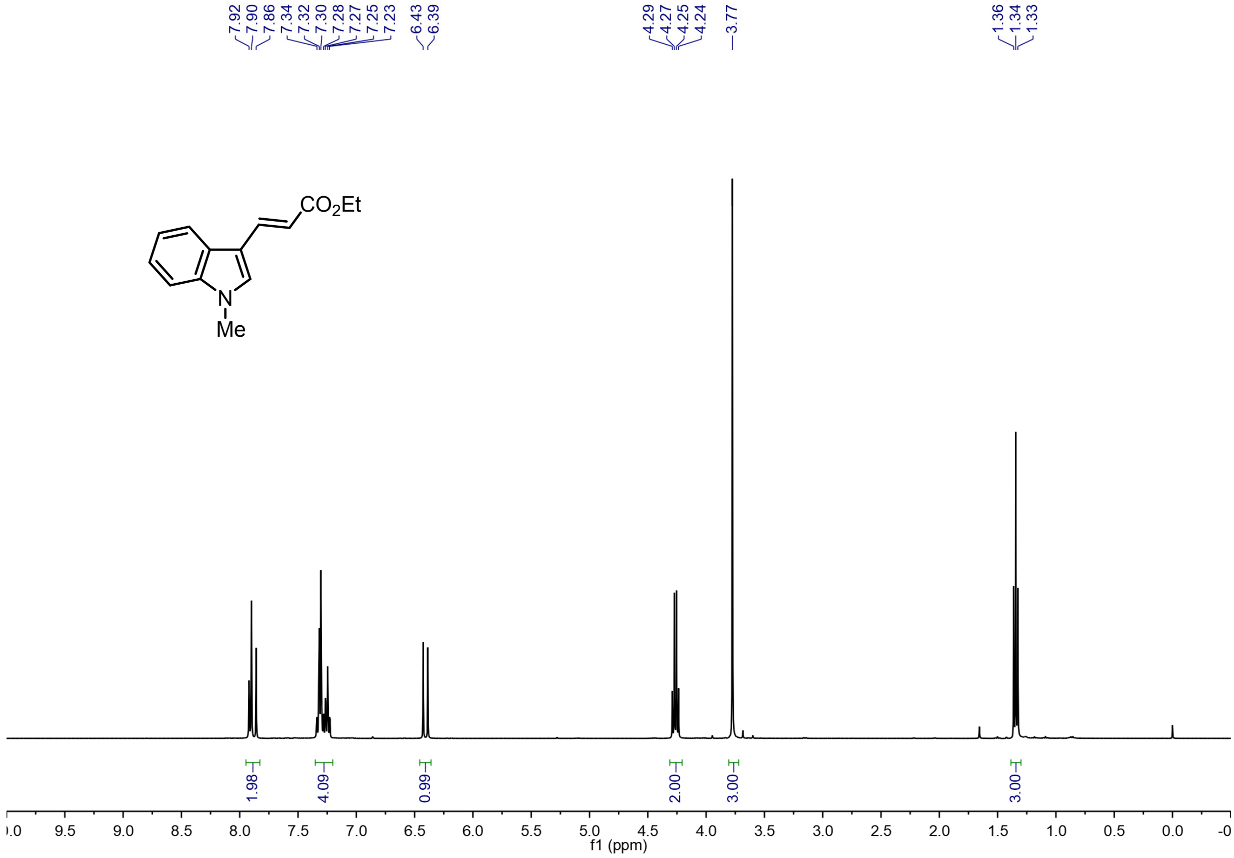
^{1}H NMR ($CDCl_3$, 400 MHz) of **16b**:



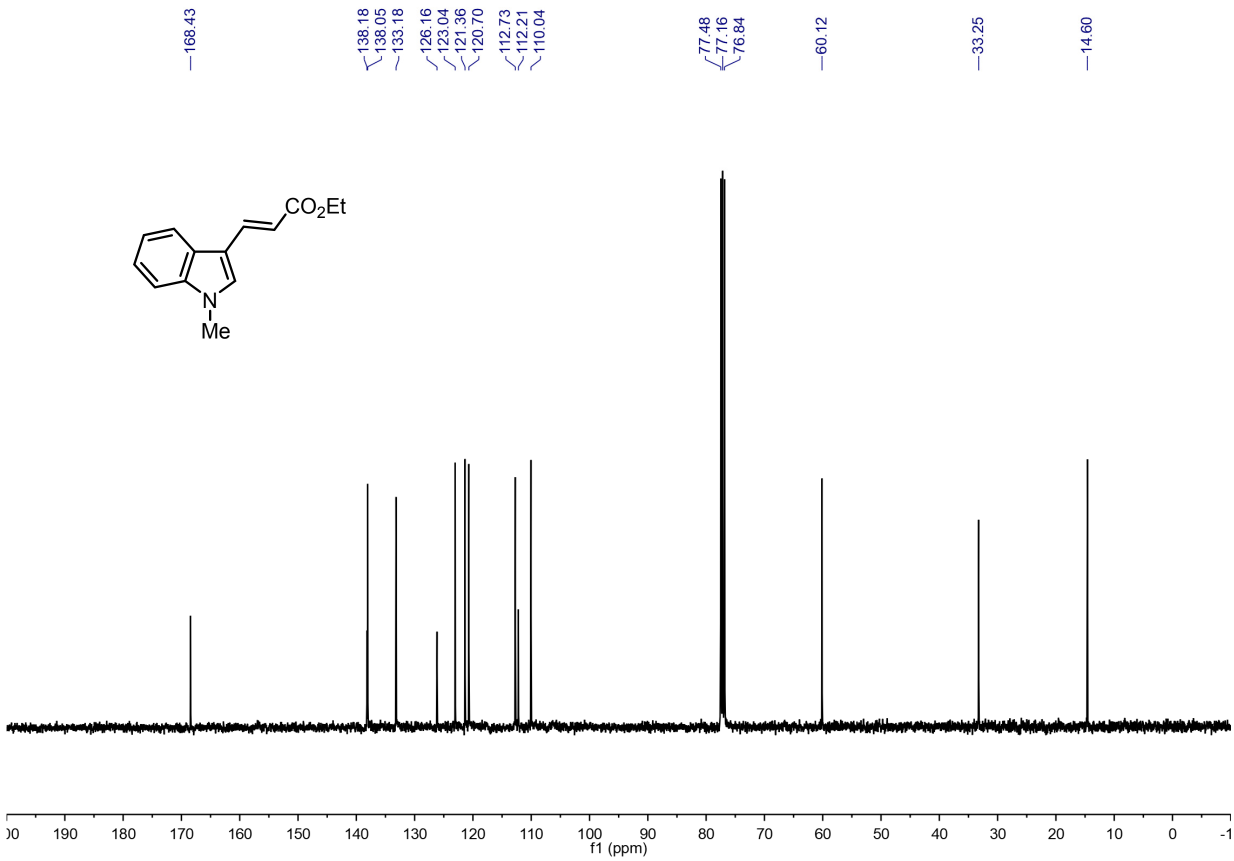
^{13}C NMR ($CDCl_3$, 100 MHz) of **16b**:



^1H NMR ($CDCl_3$, 400 MHz) of **17a**:



^{13}C NMR ($CDCl_3$, 100 MHz) of **17a**:



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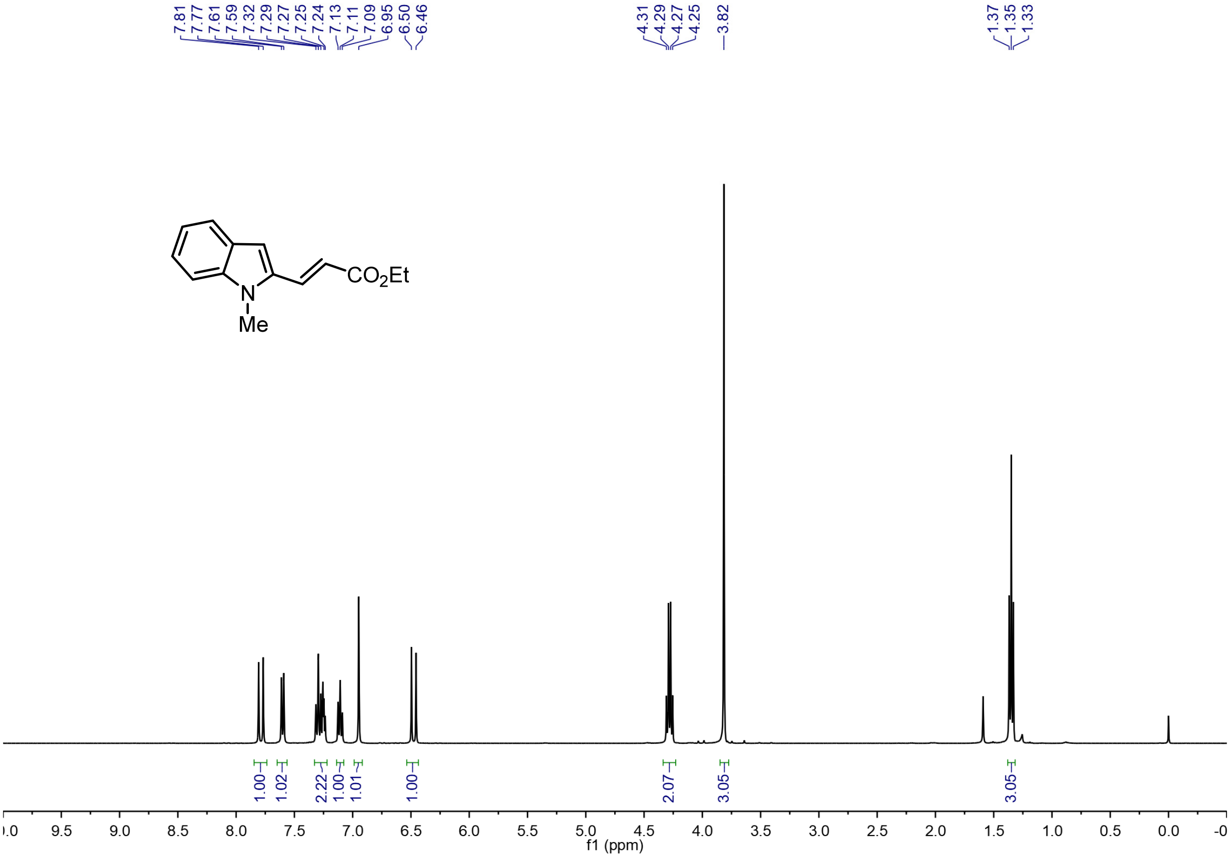

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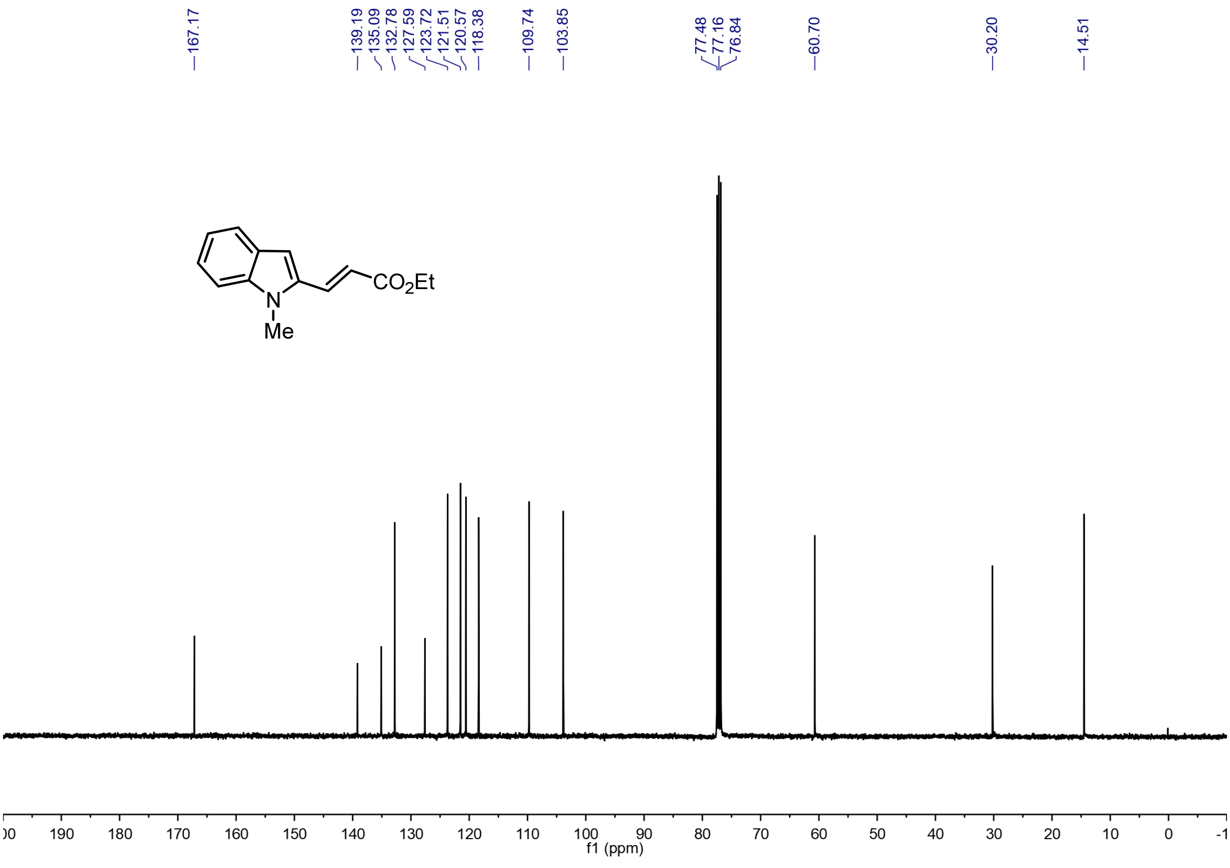

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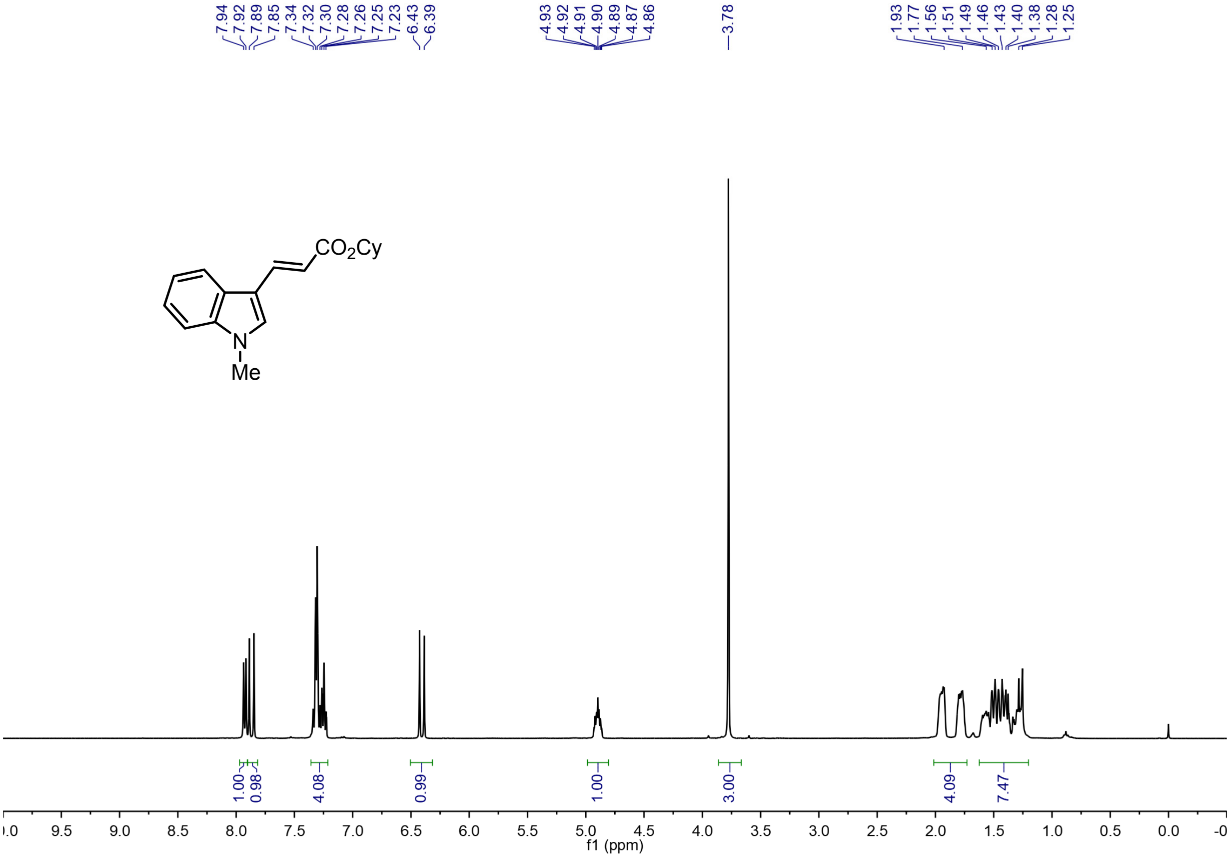

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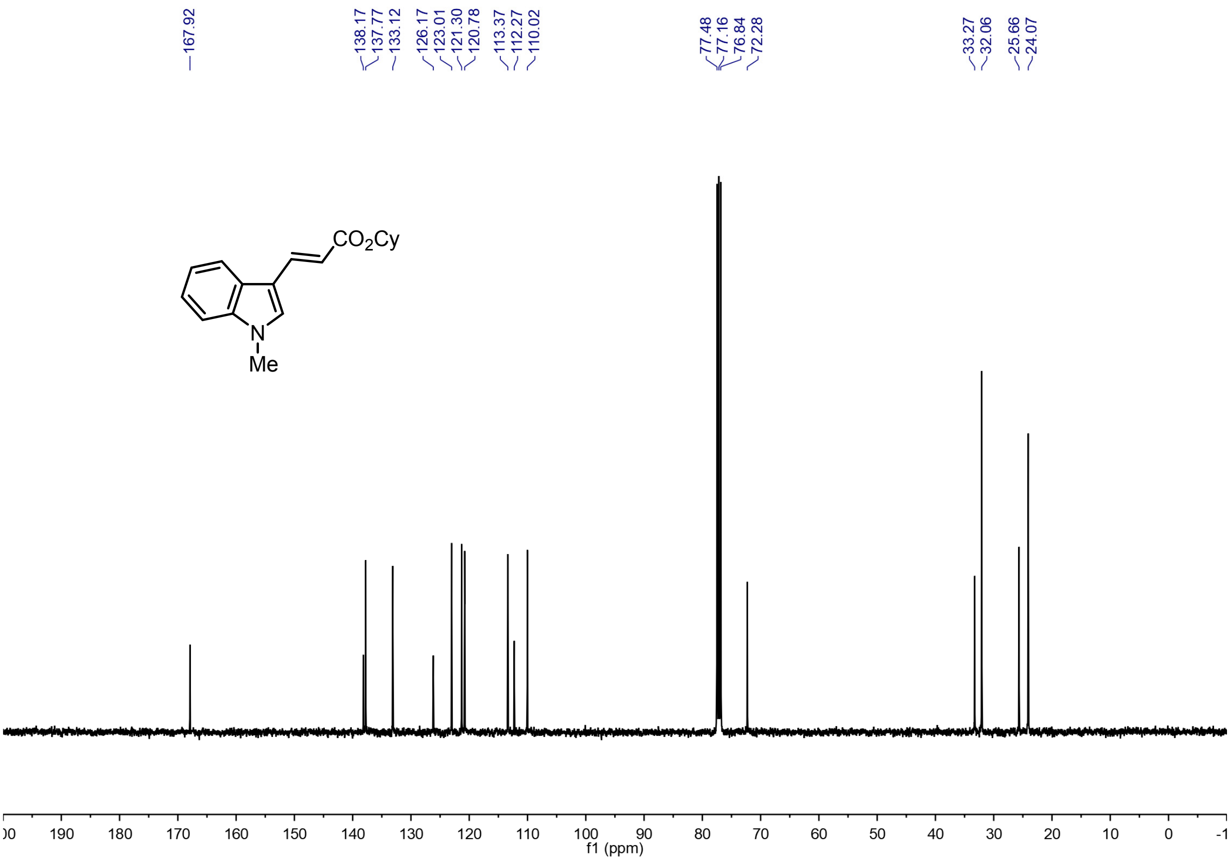

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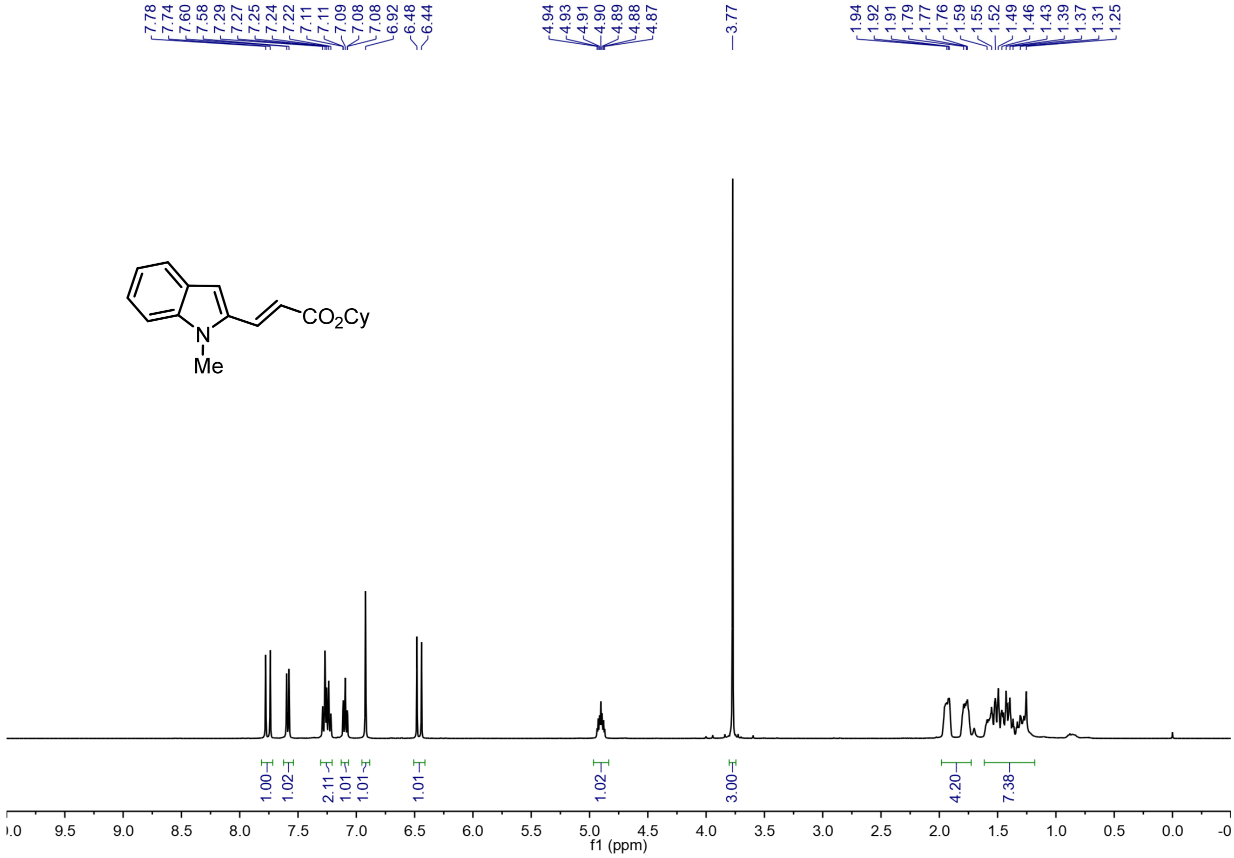

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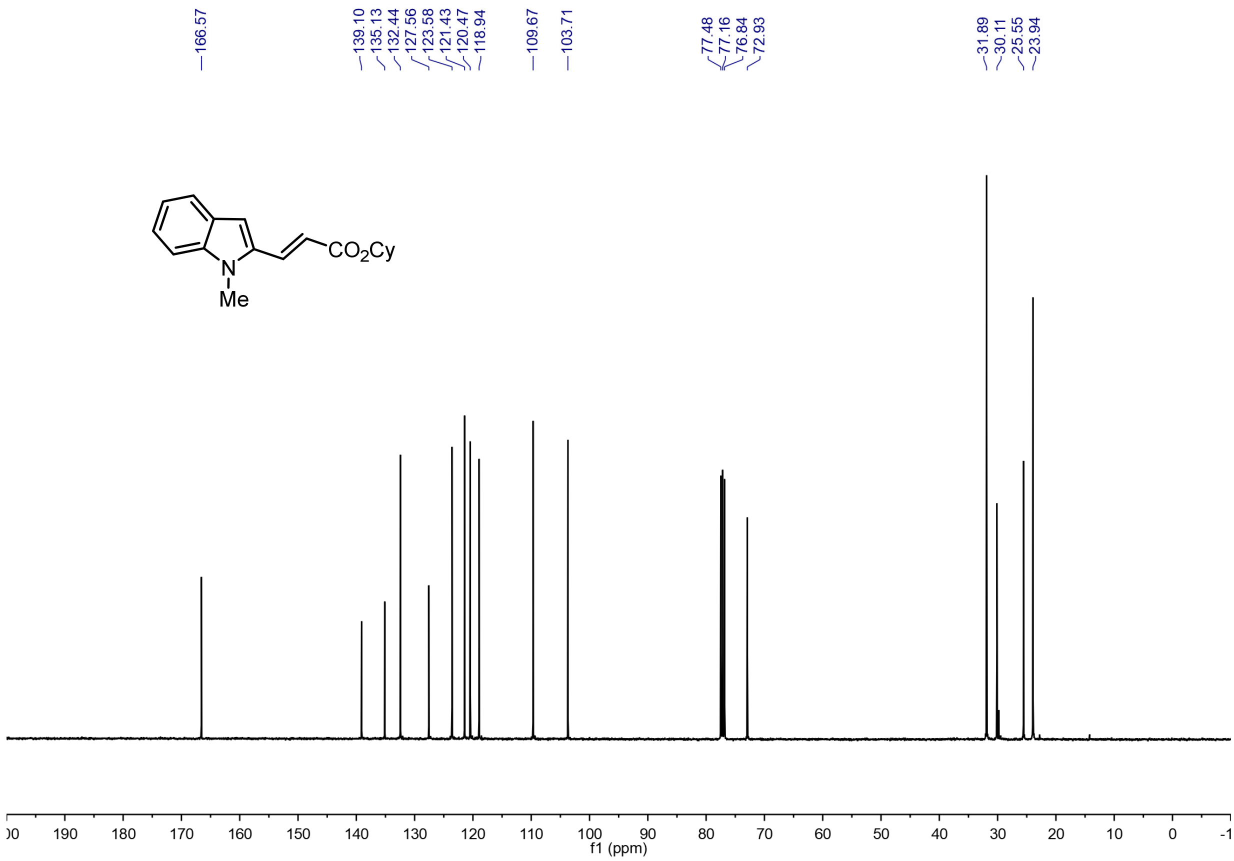

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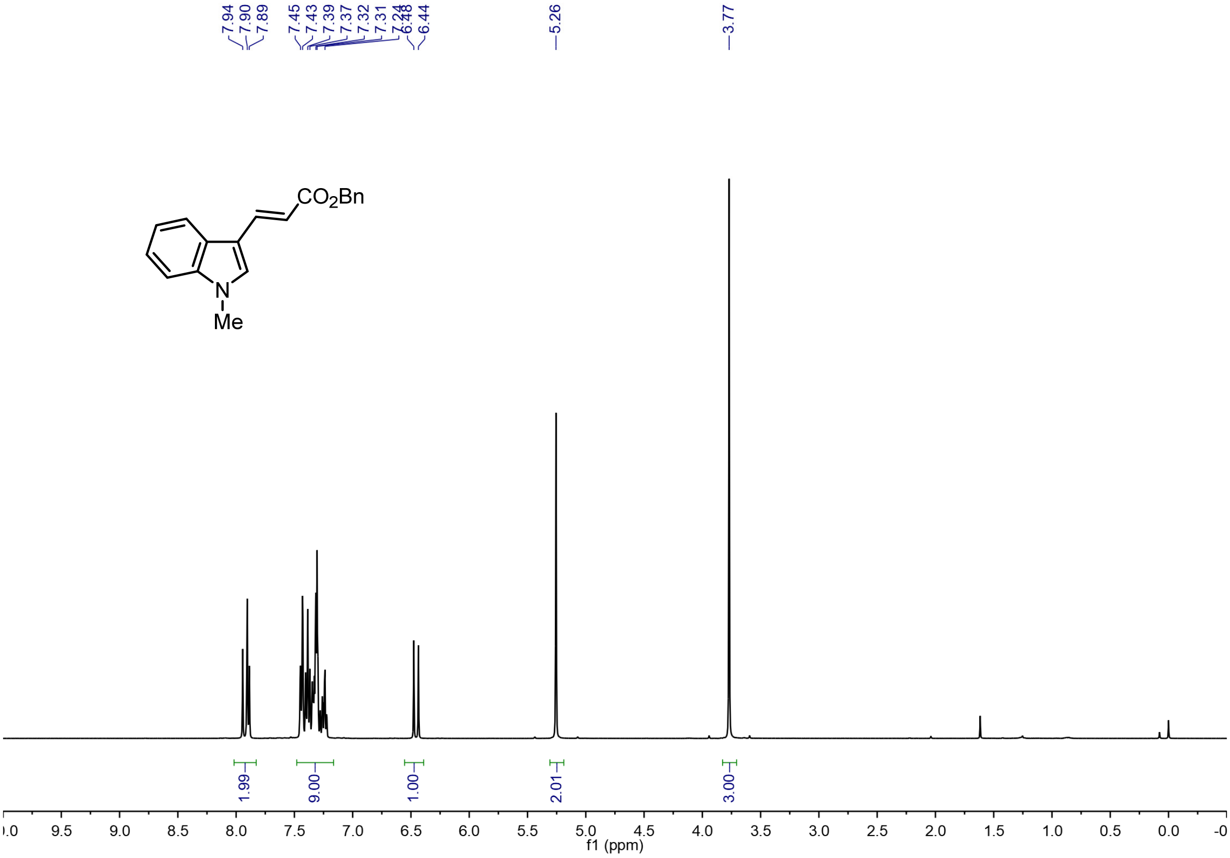
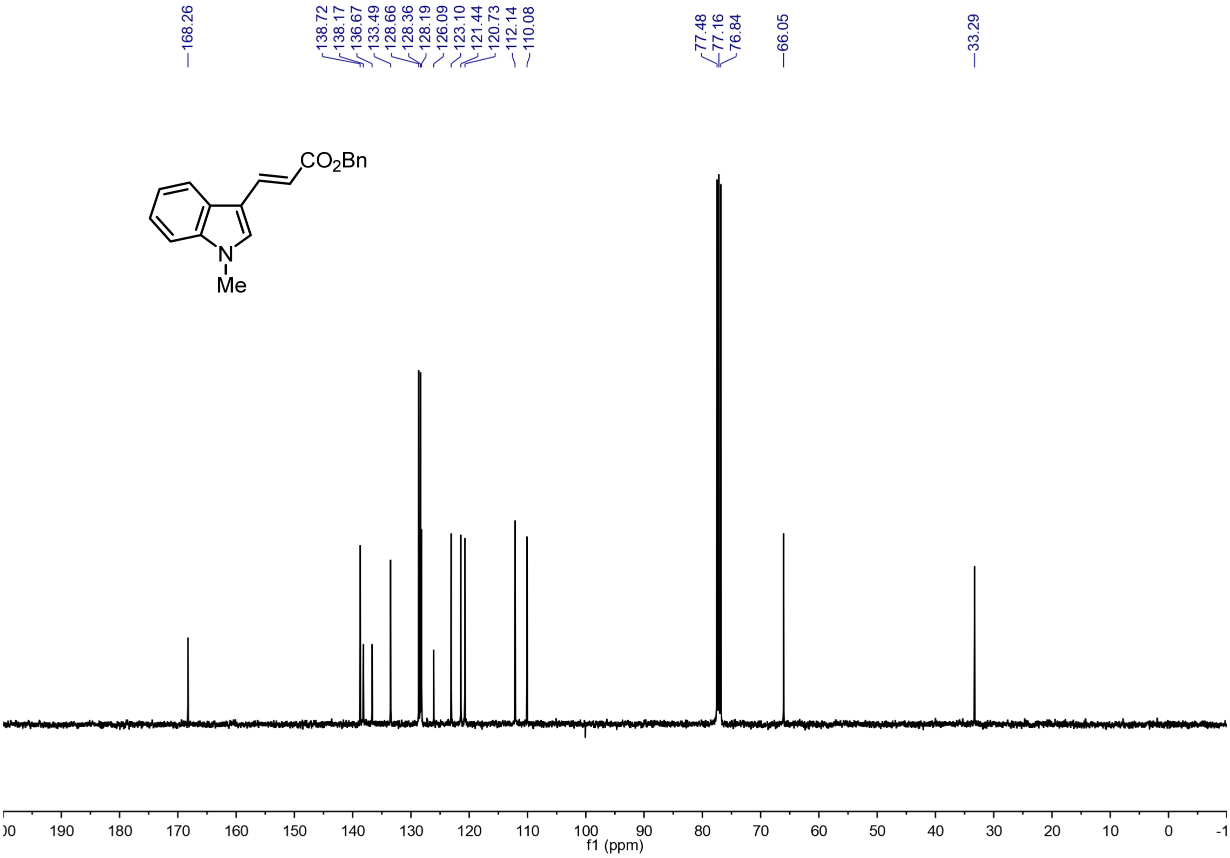
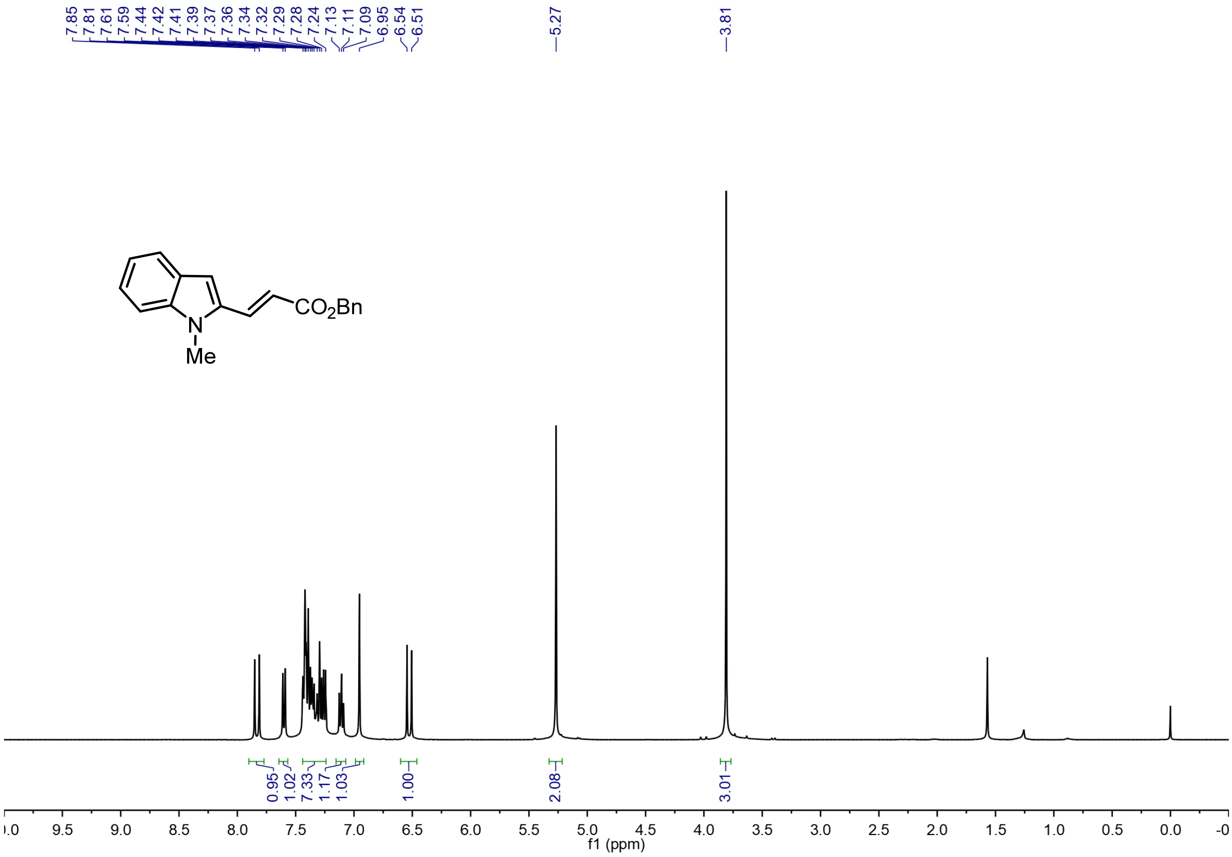


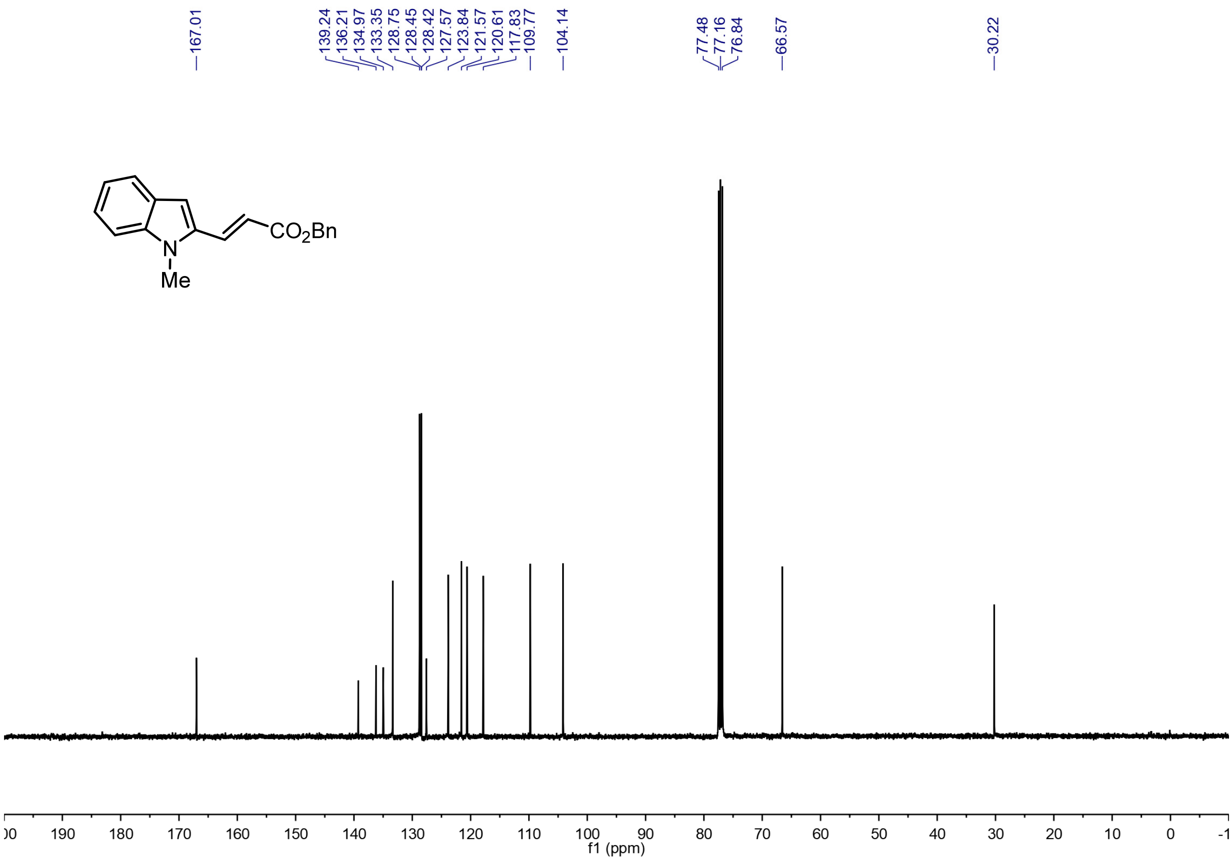
[13]C NMR ($CDCl_3$, 100 MHz) of **19a**:



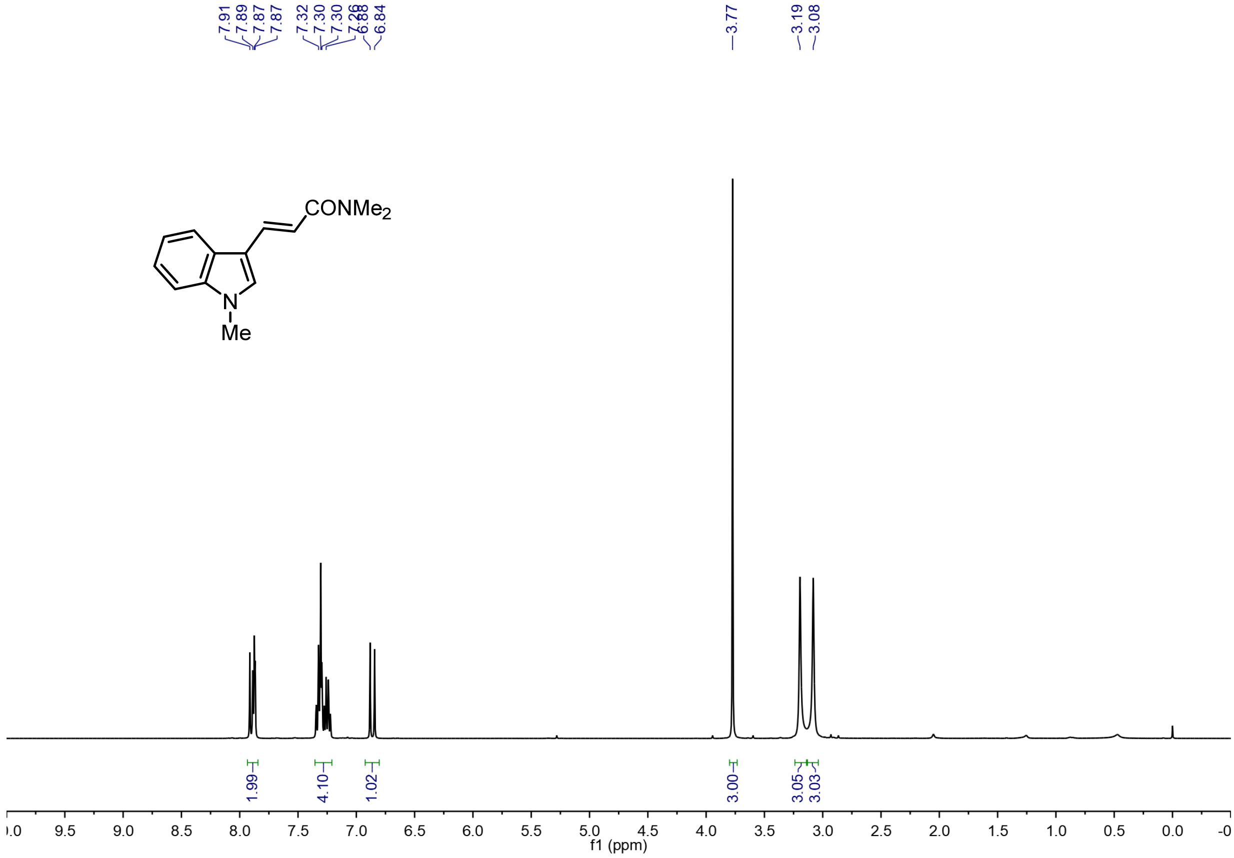
^{1}H NMR ($CDCl_3$, 400 MHz) of **19b**:



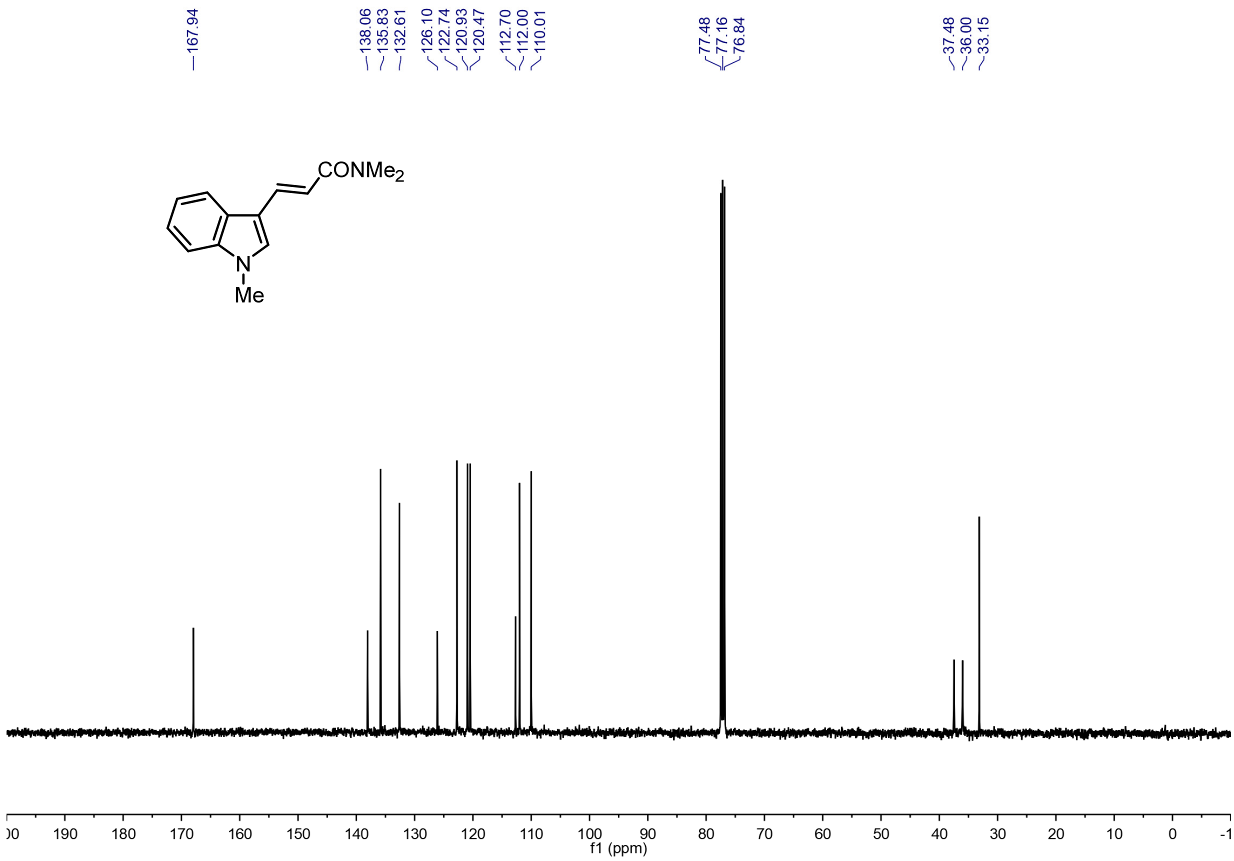
^{13}C NMR ($CDCl_3$, 100 MHz) of **19b**:



^{1}H NMR ($CDCl_3$, 400 MHz) of **20a**:



^{13}C NMR ($CDCl_3$, 100 MHz) of **20a**:



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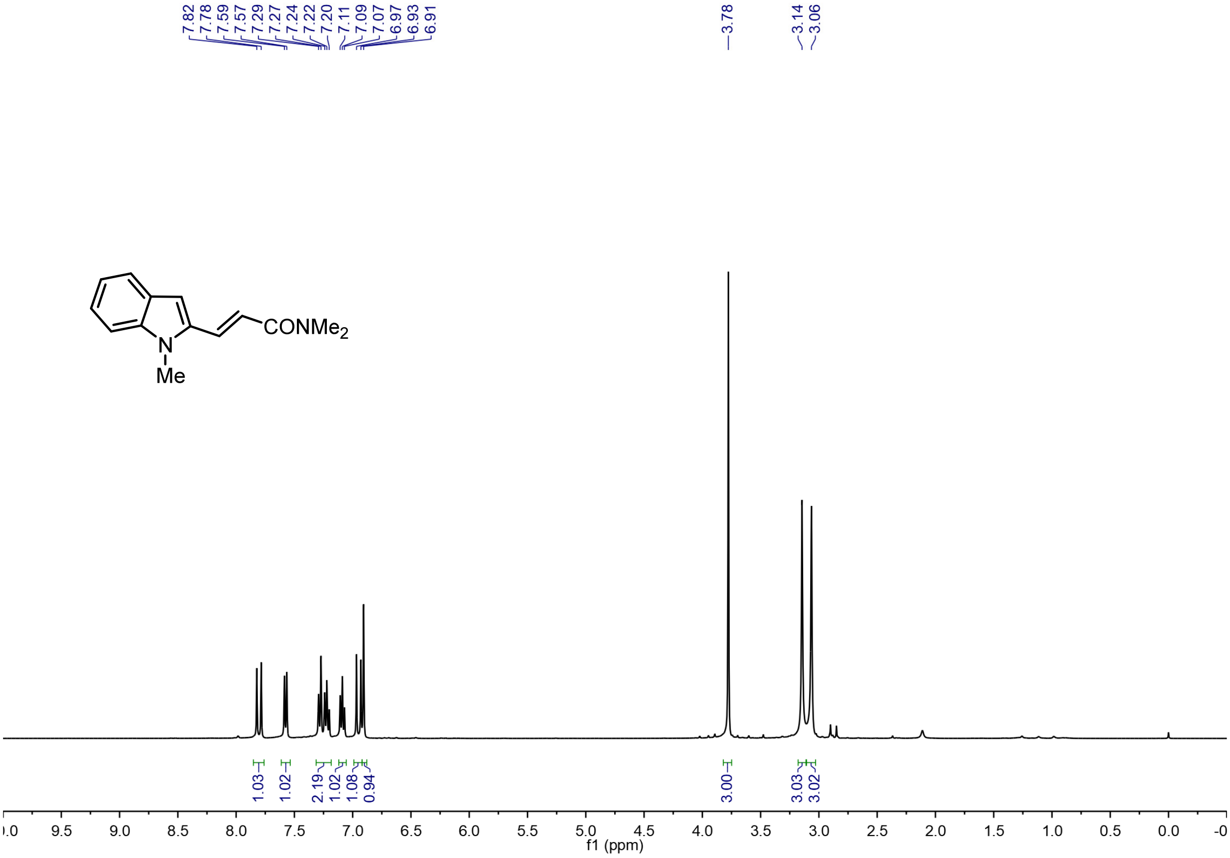
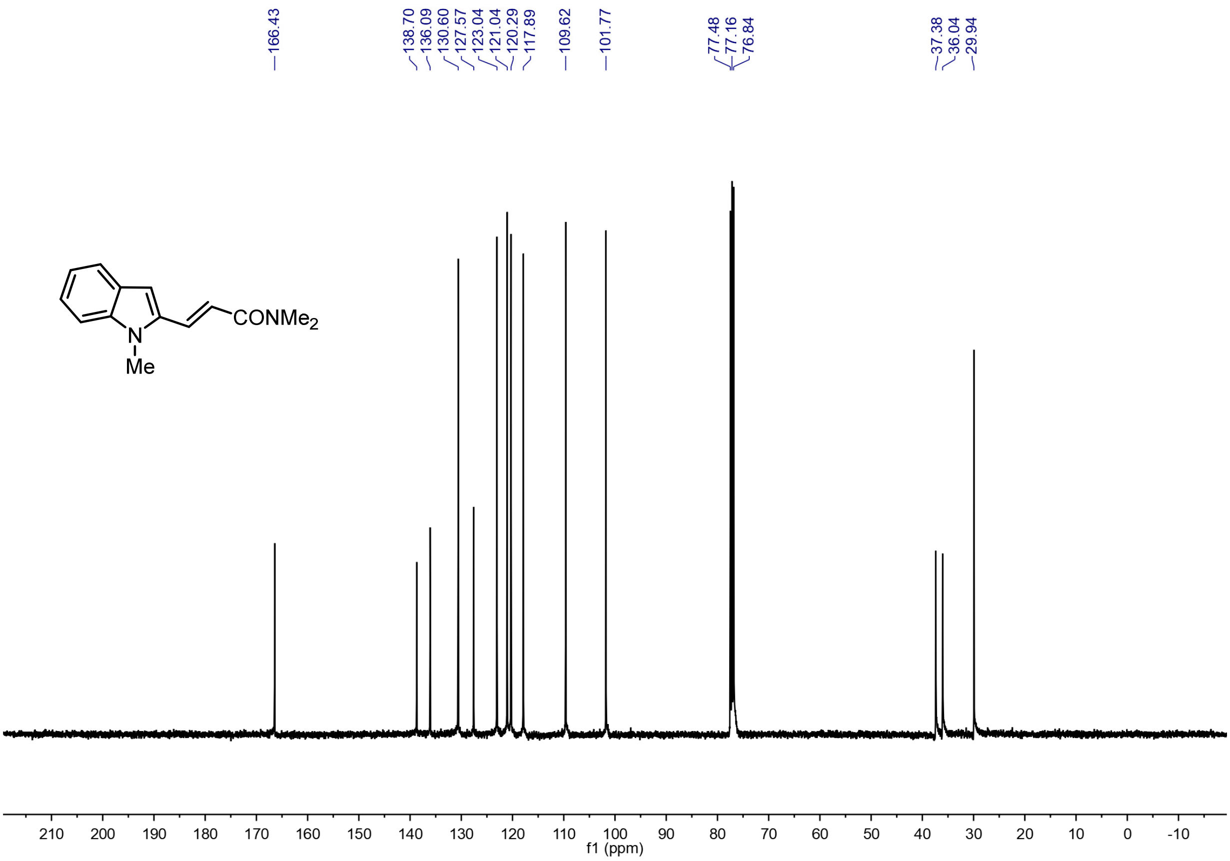
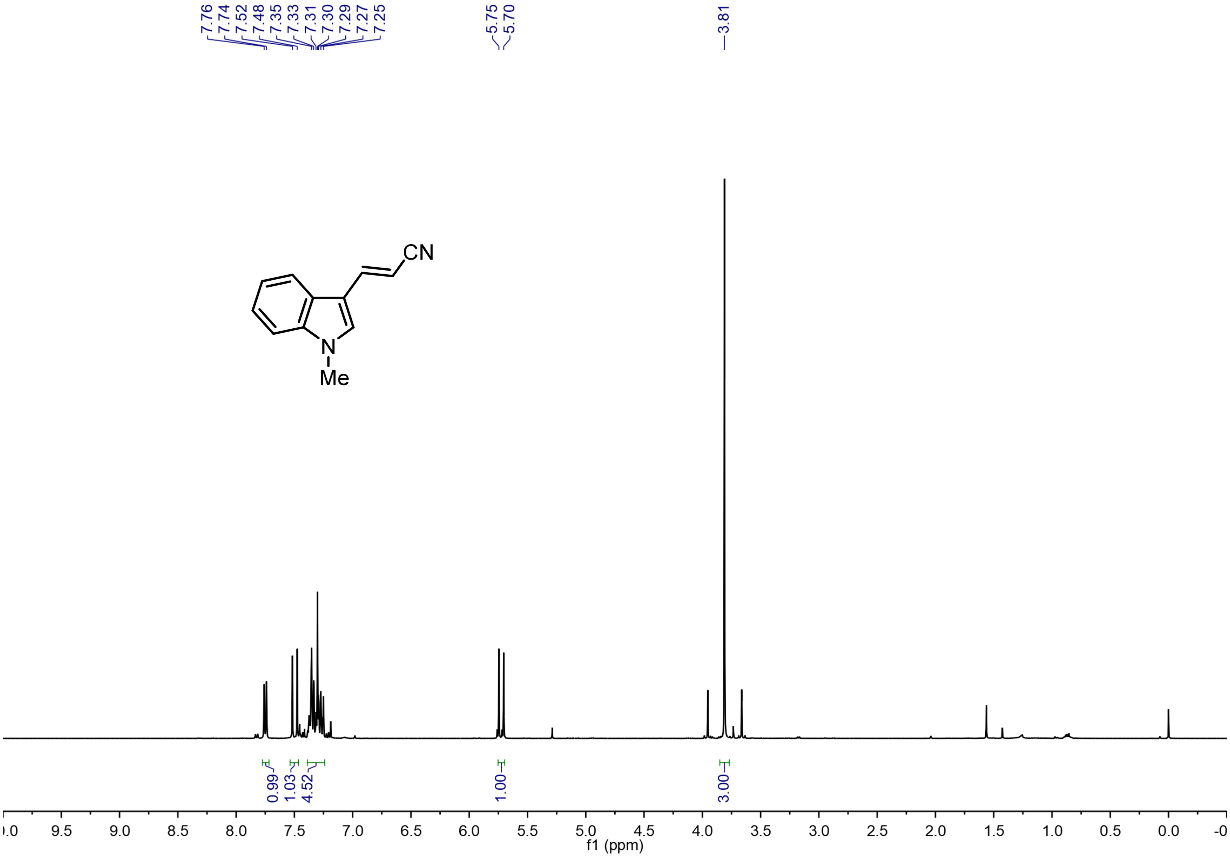


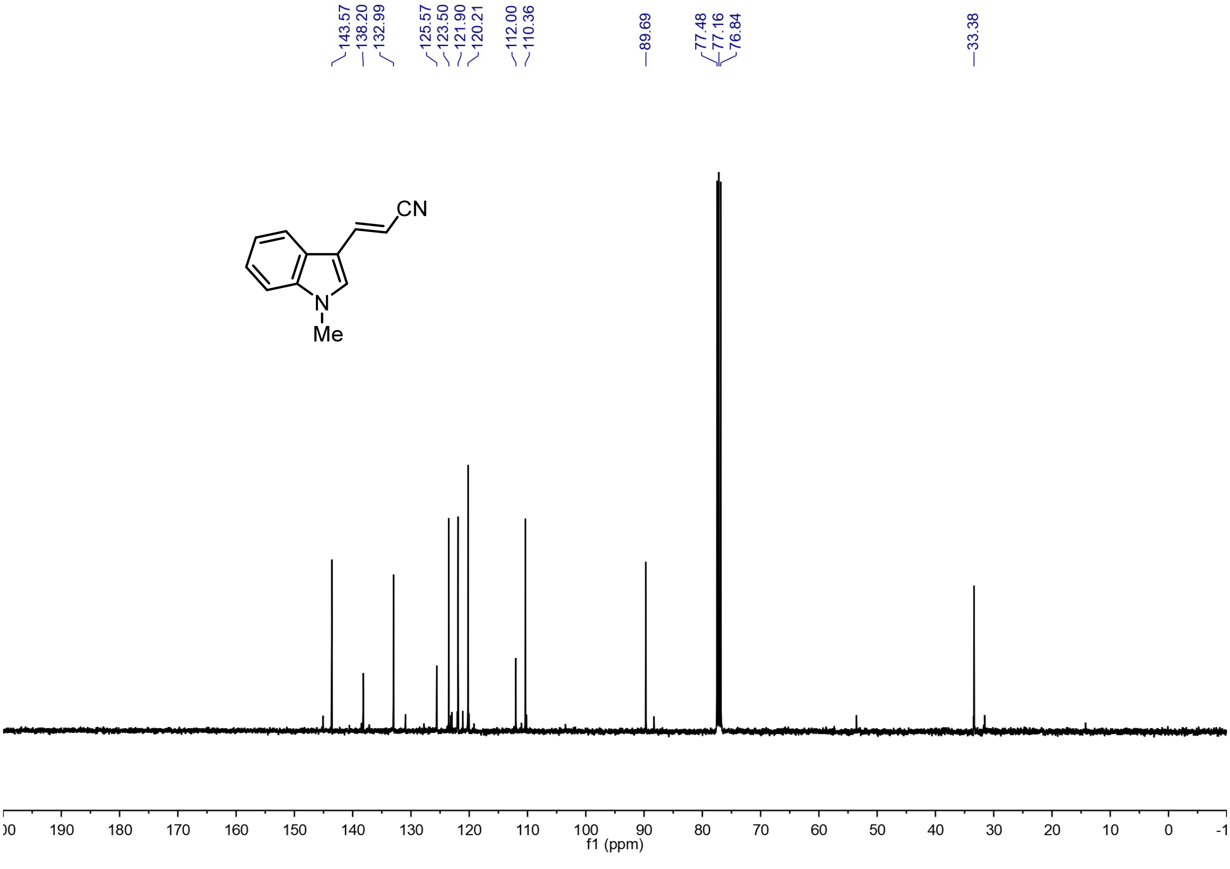
^{13}C NMR ($CDCl_3$, 100 MHz) of **20b**:



[1]H NMR ($CDCl_3$, 400 MHz) of **21a** (containing minor amounts of inseparable impurities):



[13]C NMR ($CDCl_3$, 100 MHz) of **21a** (containing minor amounts of inseparable impurities):



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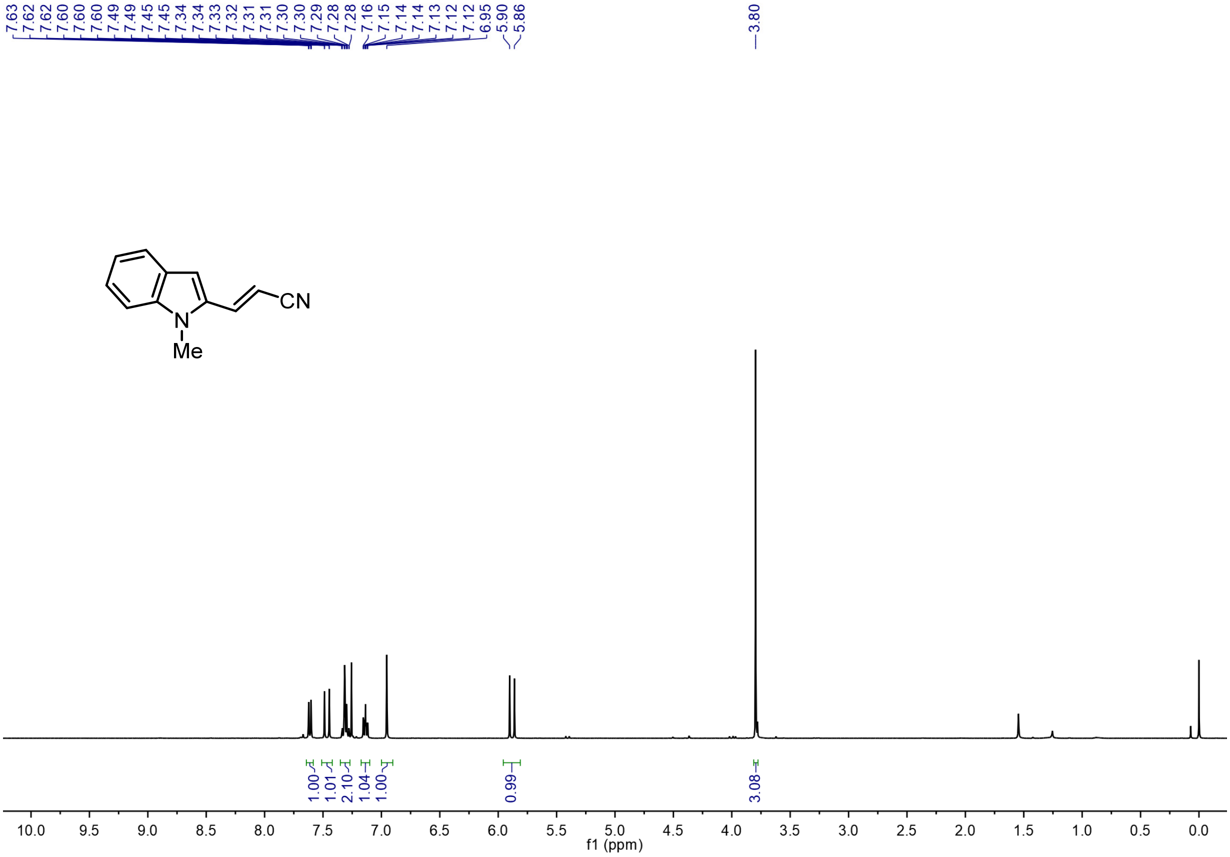
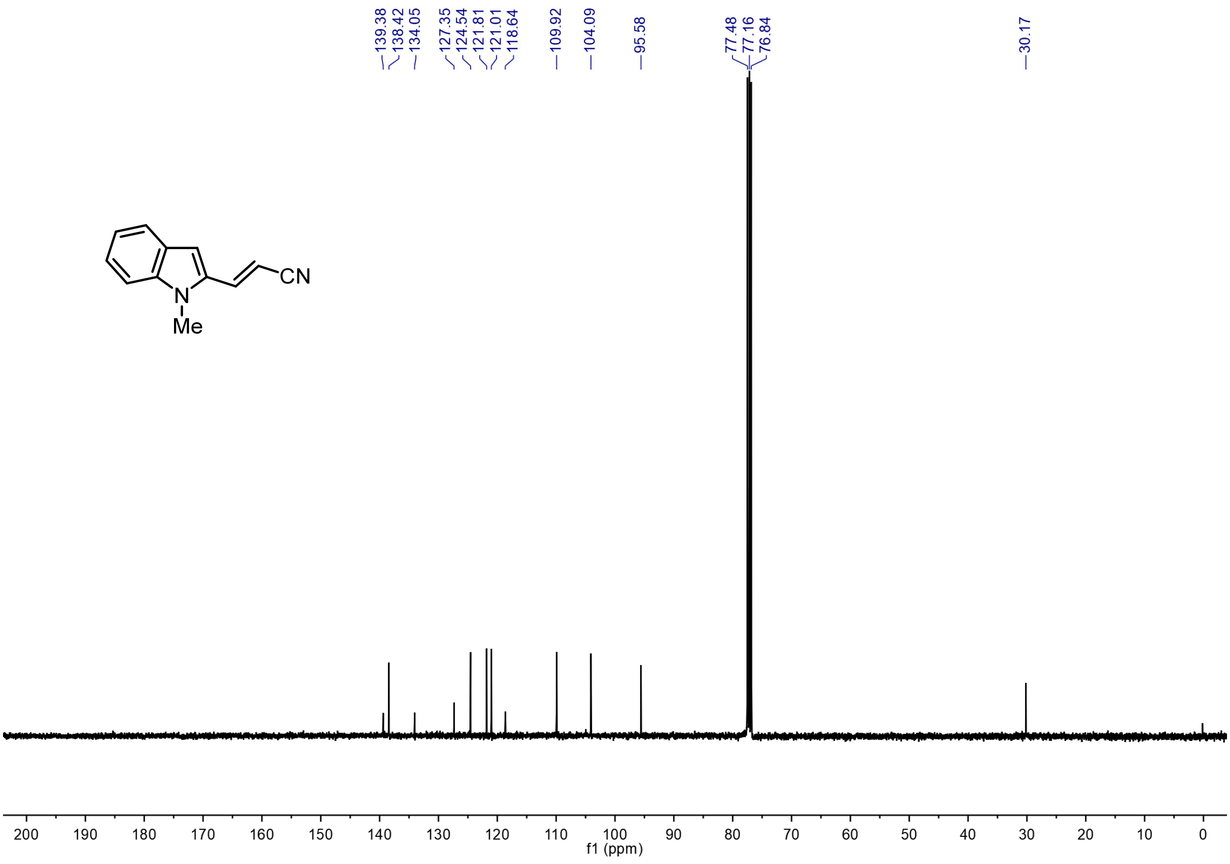
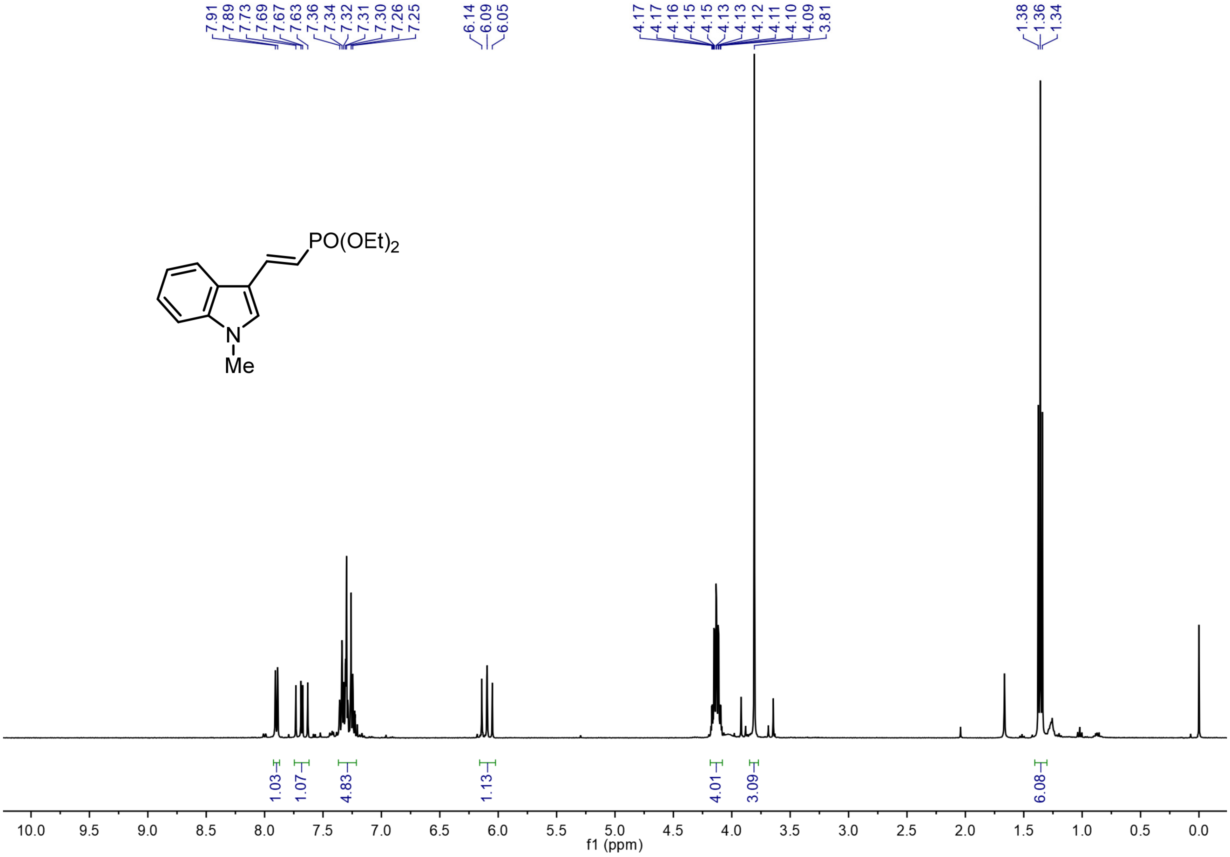


^{13}C NMR ($CDCl_3$, 100 MHz) of **21b**



^{1}H NMR ($CDCl_3$, 400 MHz) of **22a**:



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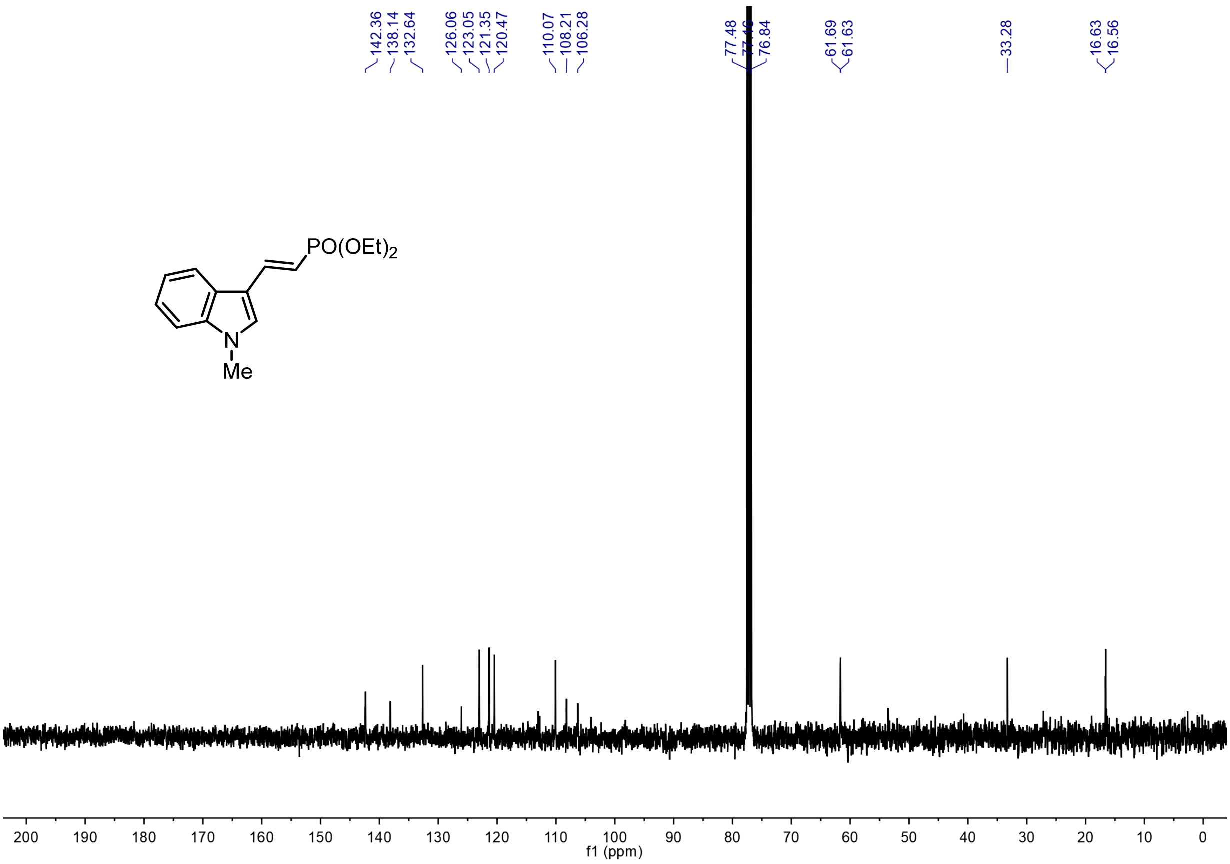

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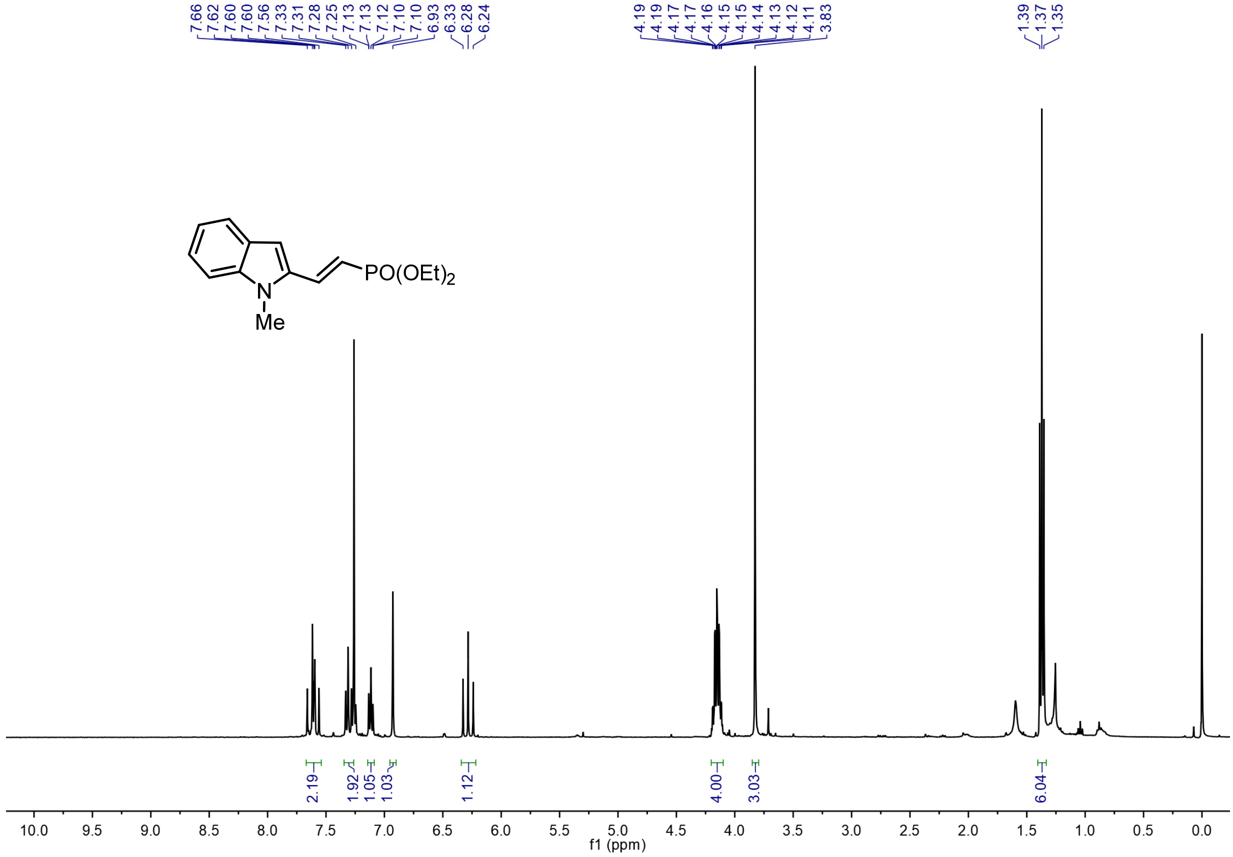

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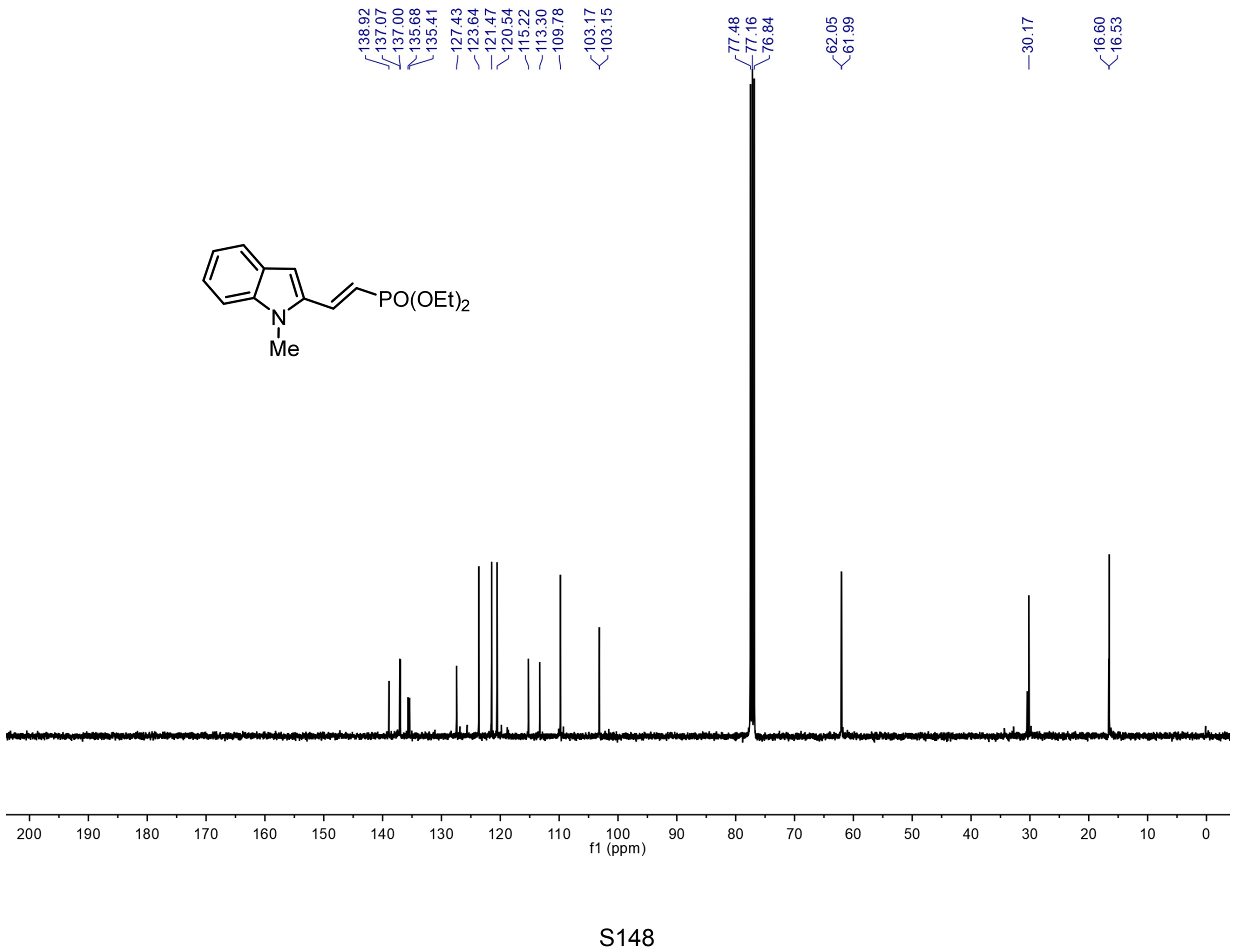

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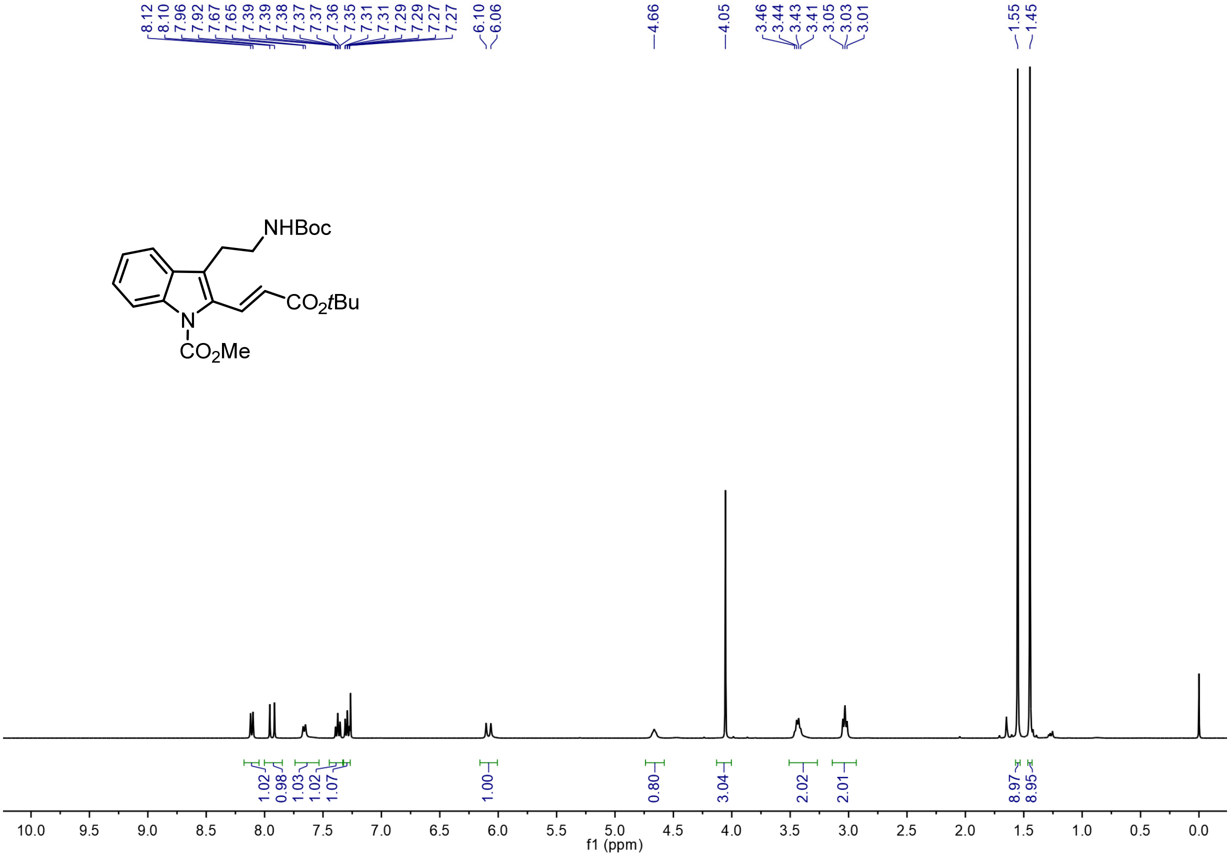

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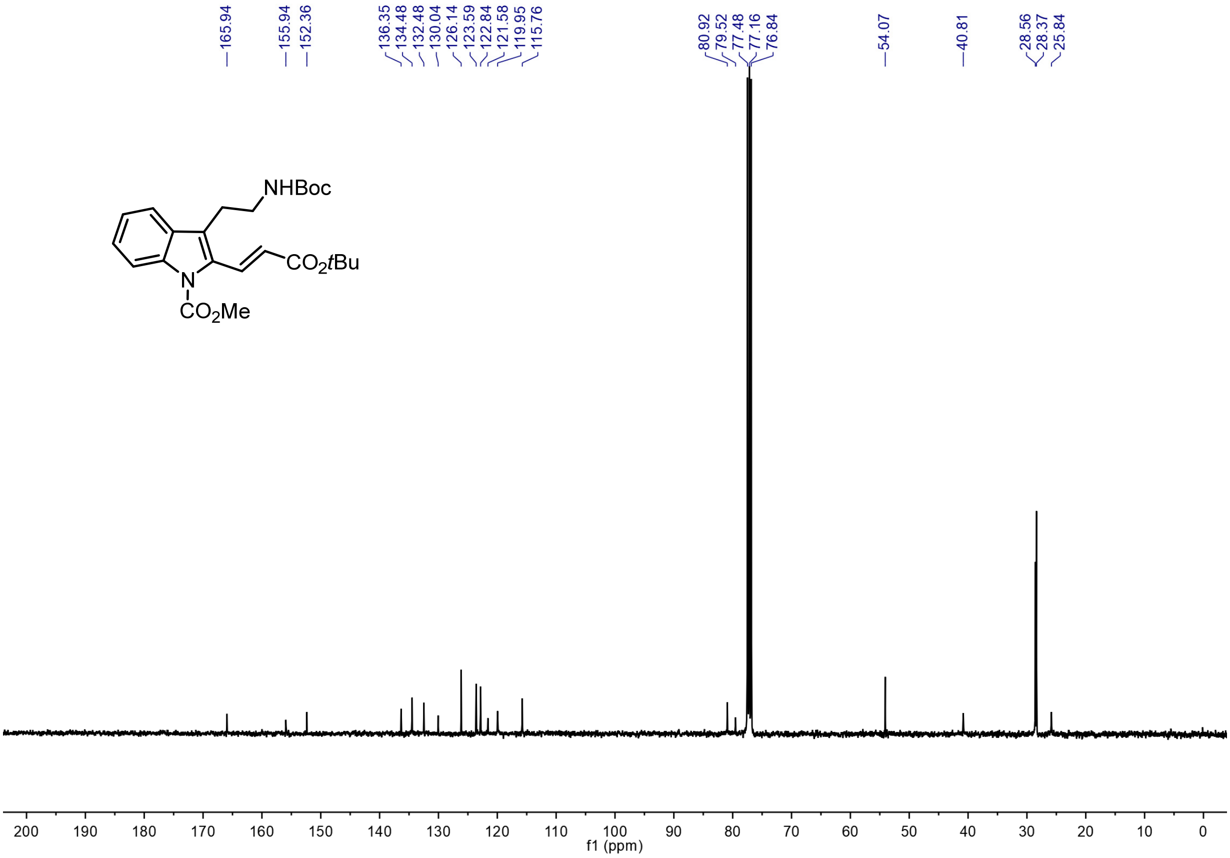
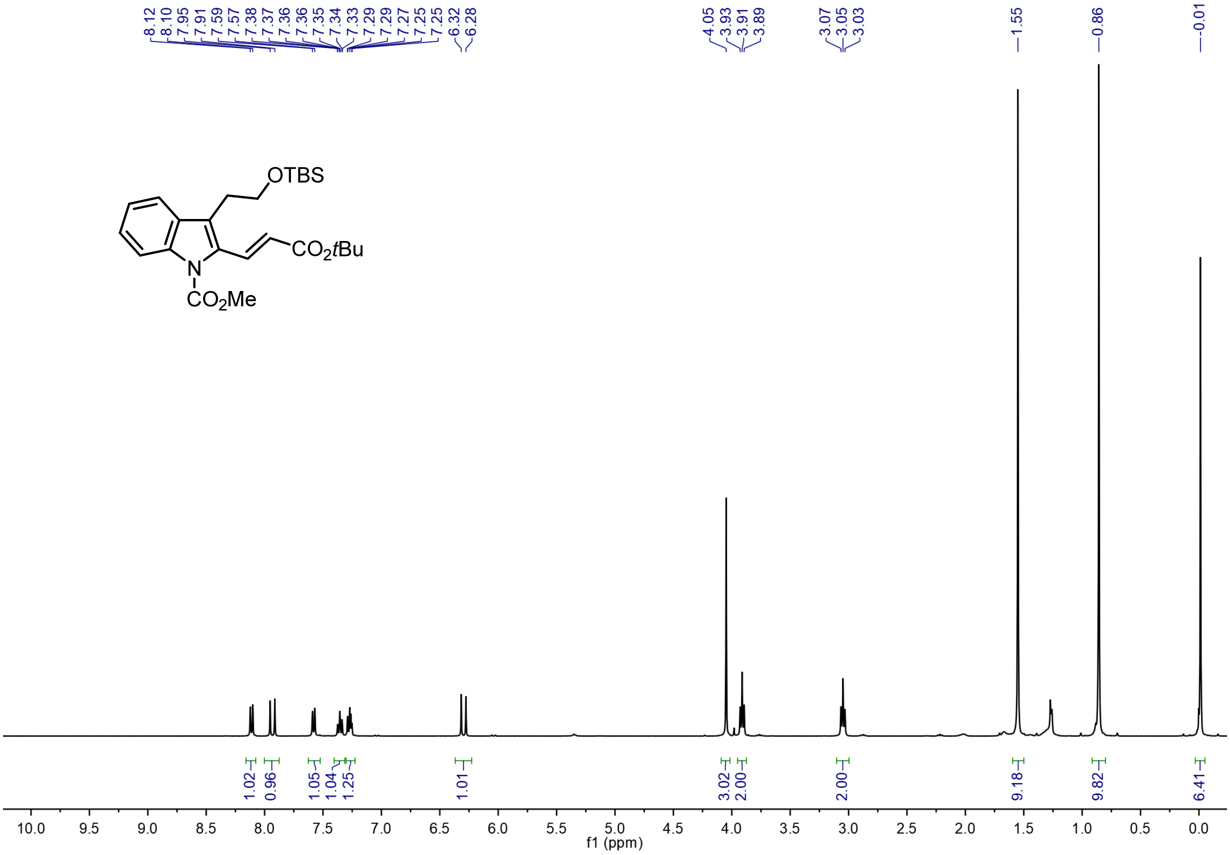
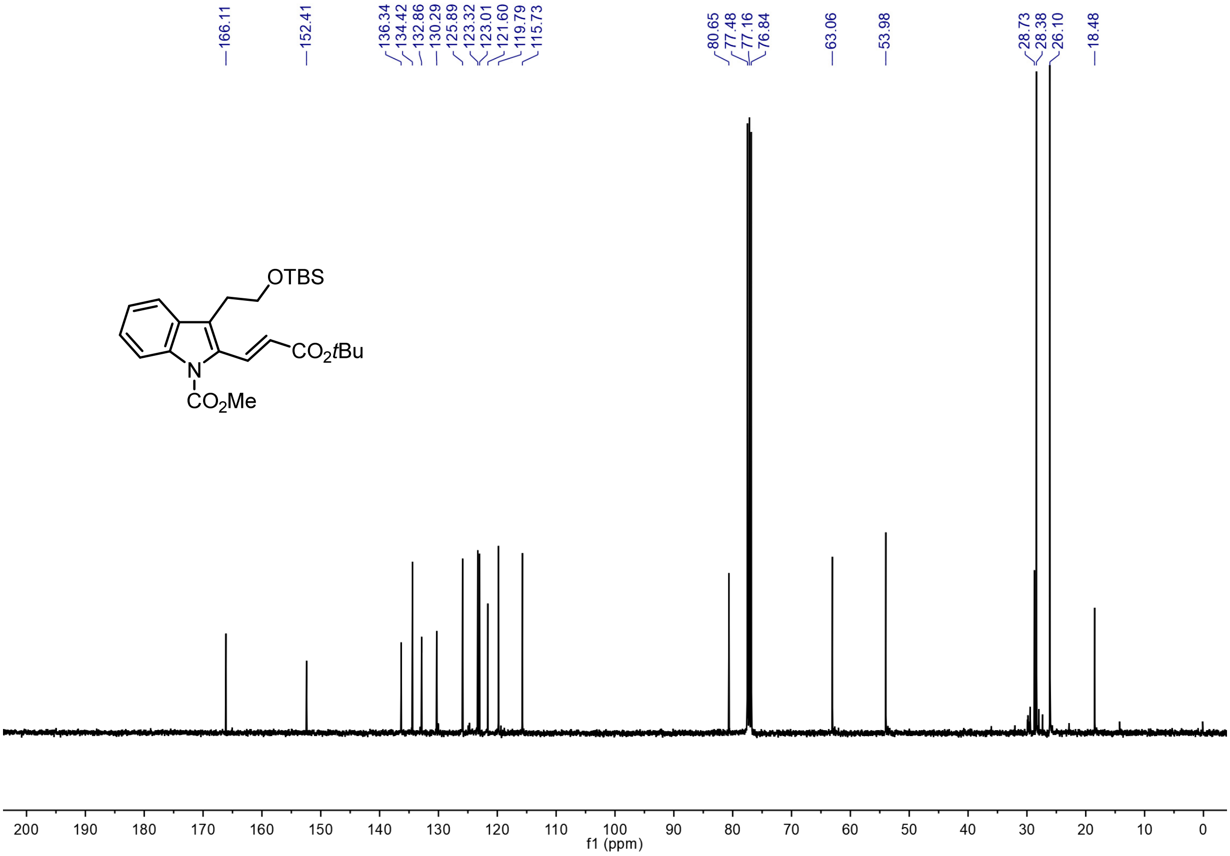


^{1}H NMR ($CDCl_3$, 400 MHz) of **24a**



^{13}C NMR ($CDCl_3$, 100 MHz) of **24a**



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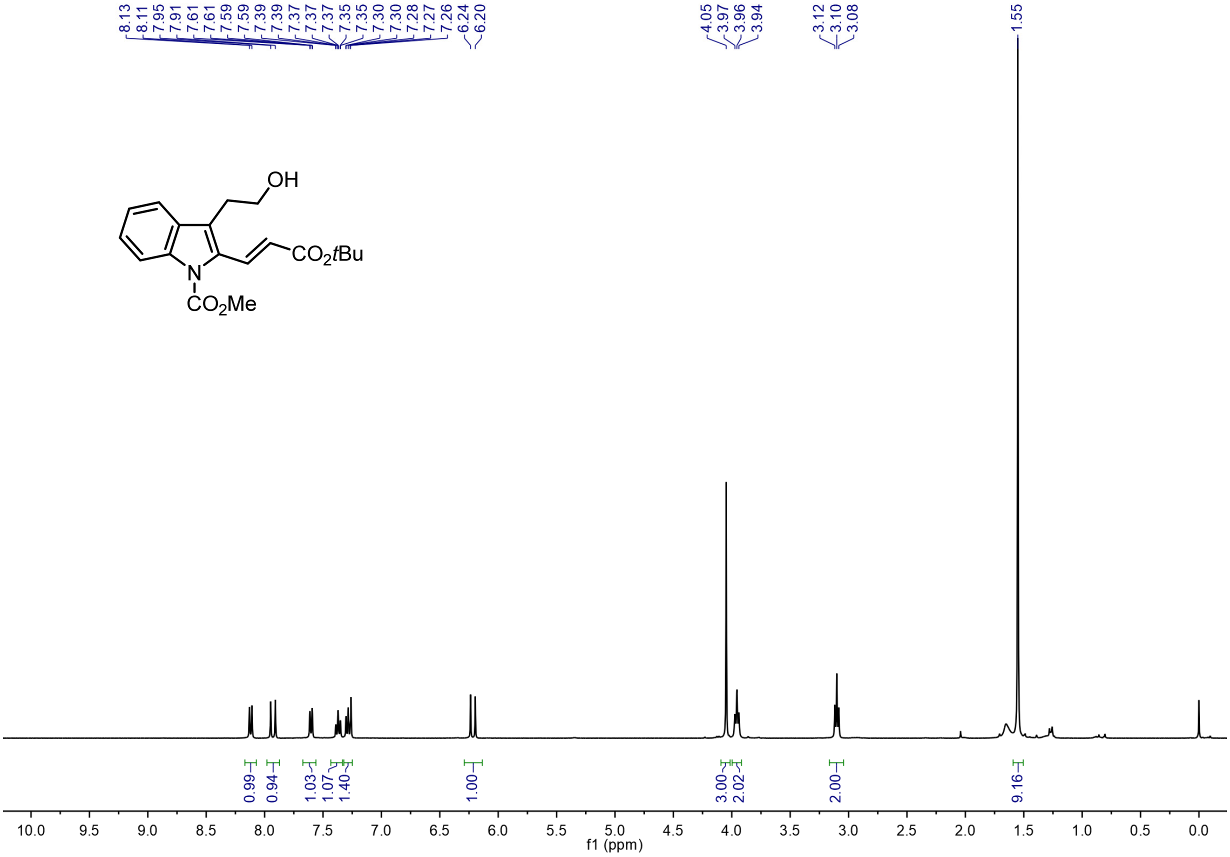

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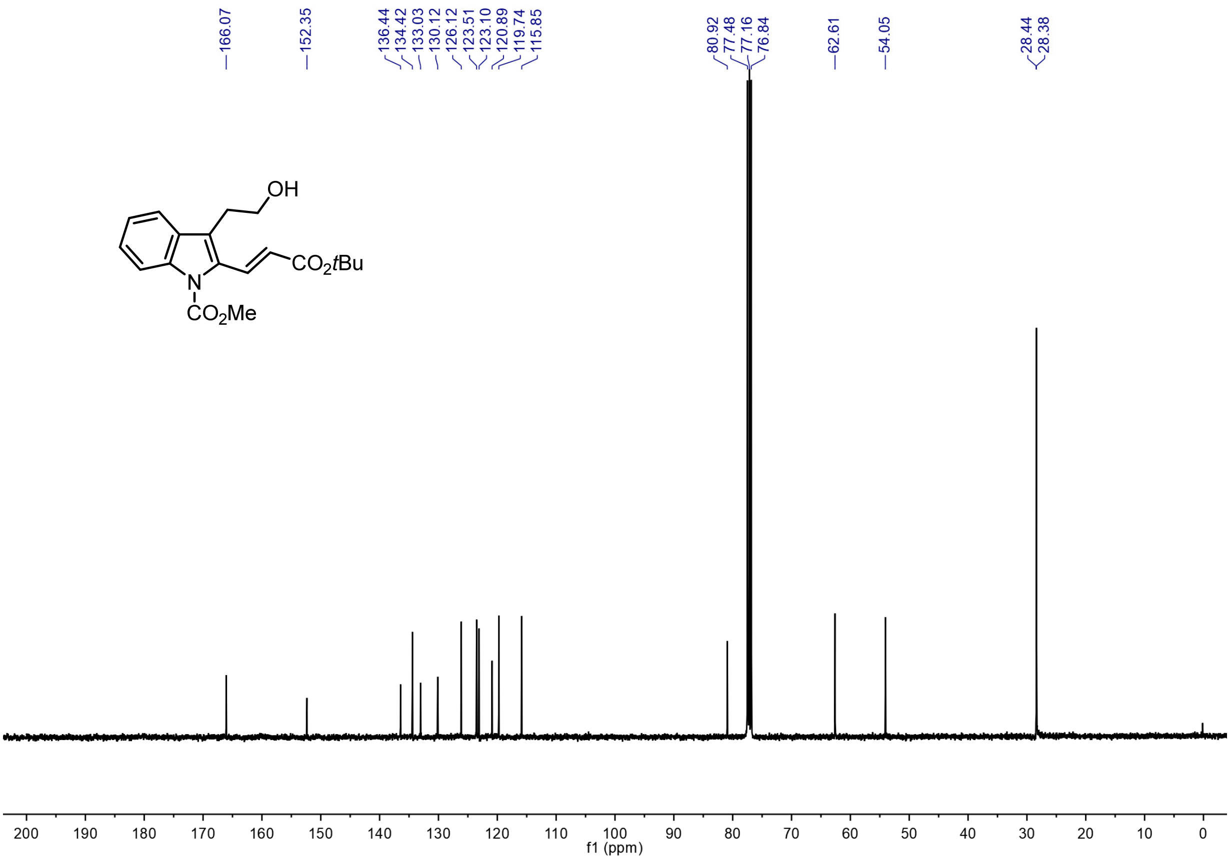

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