Electronic Supporting information

Access to functionalized luminescent Pt(II) complexes by photoredox-catalyzed Minisci alkylation of 6-aryl-2,2'-bipyridines

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1. General information

All reactions were carried out under argon atmosphere with standard Schlenk techniques. All reagents were obtained from commercial sources and used as supplied. All reactions were performed using dry and degassed solvents unless stated otherwise. Toluene was purified by passage through activated alumina using a Glass Contour Solvent Dispensing System. Technical grade heptane and ethyl acetate were used for column chromatography.

All reagents were weighed and handled in air.

^{1}H, and ^{13}C NMR spectra were recorded on Bruker AV III 400 MHz NMR spectrometer equipped with BBFO probehead. Chemical shifts (δ) were reported in parts per million relative to residual chloroform (7.28 ppm for ^{1}H; 77.23 ppm for ^{13}C), constants were reported in Hertz. 1H NMR assignment abbreviations were the following: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m).

UV/vis absorption spectra were recorded with a Jasco V-770 UV-Vis-NIR spectrophotometer using quartz cuvettes of 1 cm pathlength.

Steady-state luminescence spectra were measured using an Edinburgh FS920 Steady State Fluorimeter combined with a FL920 Fluorescence Lifetime Spectrometer. The spectra were corrected for the wavelength dependence of the detector, and the quoted emission maxima refer to the values after correction. Luminescence quantum yields were determined using $[Ru(bpy)_3]Cl_2$ (Φ = 0.042 in air-equilibrated aqueous solution)[1] as standard and correcting for the refractive index. Life-times measurements were conducted with 375 nm diode laser excitation (EPL-series) plugged to a TCSPC pulsed source interface.

Electronic circular dichroism spectra (ECD, in $M^{-1}.cm^{-1}$) were recorded on a Jasco J-815 Circular Dichroism Spectrometer (IFR140 facility - Biosit - Université de Rennes 1). Molar rotations are given in $deg.cm^2.mol^{-1}$.

Circularly polarized luminescence (CPL) measurements were performed using an in-house-developed CPL spectrofluoropolarimeter based on a Jasco J-701. The samples were excited using a 90°-geometry with a green InGaN (3 mm, 2 V) LED source (Luckylight Electronics Co., LTD, λmax= 517 nm, HWHM = 15 nm). The concentration of all the samples was ≈ 10^{-5} M.

GC-MS analyses were performed with a GCMS-QP2010S (Shimadzu) instrument with a GC-2010 equipped with a 30 m capillary column (Supelco, SLBTM- 5ms, fused silica capillary column, 30 m x 0.25 mm x 0.25 mm film thickness), which was used with helium as the vector

gas. The following GC conditions were used: initial temperature 80 ºC for 5 minutes, then rate 20 ºC/min until 280 ºC and 280 ºC for 28 minutes.

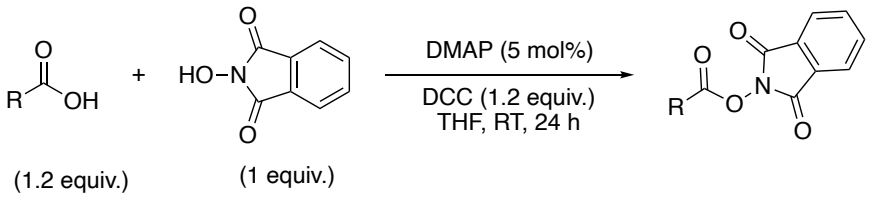
HRMS were recorded on a Waters Q-Tof 2 or Bruker Ultraflex III mass spectrometers at the corresponding facilities of the CRMPO (Centre Régional de Mesures Physiques de l'Ouest, Université de Rennes 1).

Elemental Analysis were recorded on a Thermo Fisher FLASH 1112 at the corresponding facilities of the CRMPO

fac-[Ir(ppy)$_3$] was prepared according to literature procedure.[2]

2. Procedure for the synthesis of NHPI redox-active esters & product characterizations

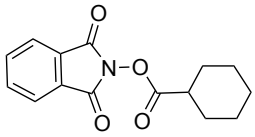
According to literature reports,[3] the redox active esters can be synthesized by condensation of corresponding carboxylic acids with N-hydroxyphthalimide.



Scheme S1. Synthesis of Redox Active Esters

General Procedure A: The corresponding alkyl carboxylic acid (12 mmol, 1.2 equiv.), N-hydroxyphthalimide (1.63 g, 10 mmol, 1.0 equiv.), and 4-dimethylaminopyridine (61mg, 0.5 mmol, 5 mol %) were mixed in a flask with a magnetic stirring bar. Dry THF (40 mL) was added. Then a solution of N,N´-dicyclohexylcarbodiimide (2.48 g, 12 mmol, 1.2 equiv.) in THF (15 mL) was added slowly at room temperature. The reaction mixture was stirred at room temperature for 24 h. After *N*-hydroxyphthalimide was completely converted, the white precipitate was filtered off and the solution was concentrated under vacuum. Corresponding redox active esters were purified by column chromatography on silica gel (petroleum ether/ethyl acetate as eluent).

1,3-Dioxoisoindolin-2-yl cyclohexanecarboxylate (**B1**): Following the general procedure **A**



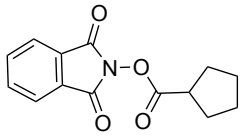
using cyclohexanecarboxylic acid (1.53 g, 12 mmol), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 95-5) to afford the desired compound **B1** (3.2 g, 85%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 2.76 (tt, *J* = 10.9, 3.7 Hz, 1H), 2.17 – 2.06 (m, 2H), 1.92 – 1.76 (m, 2H), 1.75 – 1.59 (m, 3H), 1.51 – 1.26 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 162.0, 134.6, 129.0, 123.8, 40.4, 28.8, 25.4, 25.0.

The NMR data are identical to those reported in the literature.[4]

1,3-Dioxoisoindolin-2-yl cyclopentanecarboxylate (B2): Following the general procedure **A**



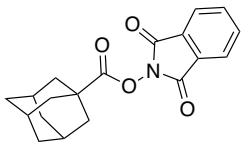
using cyclopentanecarboxylic acid (1.4 g, 12 mmol), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 95-5) to afford the desired compound **B2** (2.0 g, 78%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.82 (m, 2H), 7.78 – 7.75 (m, 2H), 3.09 (quint., *J* = 7.9 Hz, 1H), 2.07 – 1.99 (m, 4H), 1.81 – 1.72 (m, 2H), 1.69 – 1.63 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 162.0, 134.7, 128.9, 123.8, 40.6, 30.1, 25.9.

The NMR data are identical to those reported in the literature.[4]

1,3-Dioxoisoindolin-2-yl adamantane-1-carboxylate (B3): Following the general **A**



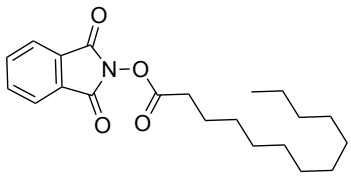
procedure using 1-adamantanecarboxylic acid (2.16 g, 12 mmol), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 95-5) to afford the desired compound **B3** (2.40 g, 74%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.80 (m, 2H), 7.76 – 7.73 (m, 2H), 2.17 – 2.03 (m, 9H), 1.76 – 1.75 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 162.0, 134.6, 129.0, 123.7, 40.4, 38.4, 36.1, 27.6.

The NMR data are identical to those reported in the literature.[5]

1,3-Dioxoisoindolin-2-yl tridecanoate (B4): Following the general procedure **A** using



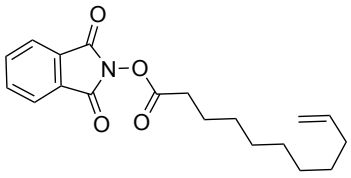
tridecanoic acid (2.56 g, 12 mmol), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 95-5) to afford the desired compound **B4** (2.58 g, 72%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.84 (m, 2H), 7.78 – 7.75 (m, 2H), 2.65 (t, *J* = 7.4 Hz, 2H), 1.77 (quint., *J* = 7.1 Hz, 2H), 1.42 (q, *J* = 6.5 Hz, 2H), 1.30 – 1.25 (m, 16H), 0.87 (t, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 161.9, 134.6, 128.9, 123.8, 31.9, 30.9, 29.6, 29.5, 29.3, 29.3, 29.1, 28.8, 24.6, 22.6, 14.0.

The NMR data are identical to those reported in the literature.[6]

1,3-Dioxoisoindolin-2-yl undec-10-enoate (B5): Following the general **A** procedure using undec-10-enoic acid (2.11 g, 12 mmol), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 95-5) to afford the desired compound **B5** (2.57g, 79%) as a white oil.

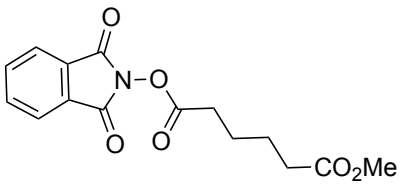


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.83 (m, 2H), 7.78 – 7.74 (m, 2H), 5.85 – 5.72 (m, 1H), 5.07 – 4.84 (m, 2H), 2.65 (t, *J* = 7.4 Hz, 2H), 2.03 (q, *J* = 6.6 Hz, 2H), 1.77 (quint., *J* = 7.3 Hz, 2H), 1.50 – 1.20 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 161.9, 139.0, 134.7, 128.9, 123.8, 114.1, 33.7, 30.9, 29.1, 29.0, 28.9, 28.8, 28.7, 24.6.

The NMR data are identical to those reported in the literature.[7]

1,3-Dioxoisoindolin-2-yl methyl adipate (B6): Following the general **A** procedure using mono-methyl adipate (1.92 g, 12 mmol), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 95-5) to afford the desired compound **B6** (2.16g, 71%) as a white oil.

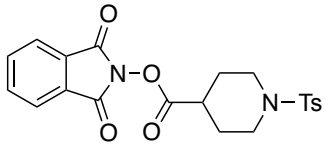


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.70 (m, 2H), 7.67 – 7.64 (m, 2H), 3.53 (s, 3H), 2.57 (t, *J* = 7.0 Hz, 2H), 2.25 (t, *J* = 6.9 Hz, 2H), 1.77 – 1.51 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 169.1, 161.7, 134.7, 128.6, 123.7, 51.3, 33.2, 30.4, 23.9, 23.8.

HRMS (ESI) Calcd for: $C_{15}H_{16}NO_6$: 306.0972; Found: 306.0974 $[M+H]^+$.

1,3-Dioxoisoindolin-2-yl 1-tosylpiperidine-4-carboxylate (B7): To a solution of piperidine-4- carboxylic acid (2.6 g, 20.0 mmol) in diethyl ether (20 mL) and water (20 mL) in a 100-mL round-bottom flask was added NaOH (1.6 g, 40.0 mmol). To the vigorously stirring solution was added TsCl (3.82 g, 20.0 mmol) portionwise over 15 min. The reaction



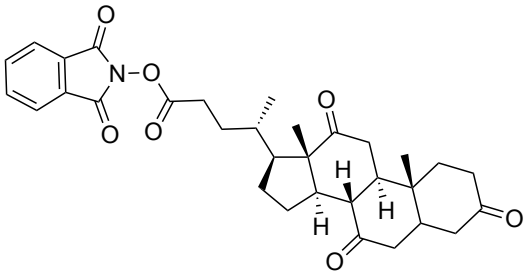
was stirred at ambient temperature for 6 h, and then was diluted with equal portions of diethyl ether and water until all precipitates were redissolved. The aqueous layer was collected and acidified to pH = 2–3 with dropwise addition of 6N HCl. The precipitate was collected by filtration and used without further purification in the next step. Following the general **A** procedure using 1-tosylpiperidine-4-carboxylic acid (3.4 g, 12 mmol), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 80-2) to afford the desired compound **B7** (3.28 g, 64%) as a white oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.83 – 7.75 (m, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 3.73 – 3.56 (m, 2H), 2.80 – 2.71 (m, 1H), 2.67 (ddd, *J* = 12.4, 10.2, 3.1 Hz, 2H), 2.45 (s, 3H), 2.23 – 2.13 (m, 2H), 2.11 – 1.98 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 161.8, 143.8, 134.9, 133.2, 129.8, 128.8, 127.6, 124.0, 123.9, 44.9, 37.5, 27.3, 21.5.

The NMR data are identical to those reported in the literature.[3c]

1,3-Dioxoisoindolin-2-yl dehydrocholoate (B8): Following the general procedure using dehydrocholic acid (4.83 g, 12 mmol), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 40-60) to afford the desired compound **B8** (3.17 g, 58%) as a white solid.

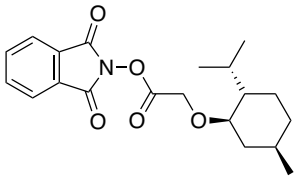


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.81 (dd, *J* = 5.5, 3.1 Hz, 2H), 3.00 – 2.84 (m, 3H), 2.82 – 2.74 (m, 1H), 2.70 – 2.62 (m, 1H), 2.44 – 2.14 (m, 8H), 2.05 – 1.82 (m, 4H), 1.78 – 1.51 (m, 4H), 1.42 (s, 3H), 1.36 – 1.21 (m, 3H), 1.14 (s, 3H), 0.94 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 211.8, 209.0, 208.6, 169.8, 161.9, 134.7, 128.9, 123.9, 56.9, 51.7, 49.0, 46.8, 45.6, 45.5, 44.9, 42.8, 38.6, 36.5, 36.0, 35.2, 33.9, 30.3, 28.5, 27.6, 25.6, 25.1, 24.9, 21.9, 18.5, 11.8.

The NMR data are identical to those reported in the literature.[8]

(-) 1,3-Dioxoisoindolin-2-yl menthyloxyacetoate ((-)B9): Following the general procedure using (-)-menthyloxyacetic acid (2.57 g, 12 mmol), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 40-60) to afford the desired compound **(-)B8** (3.19 g, 89%) as a white solid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.53 (s, 2H), 3.30 (td, *J* = 10.6, 4.2 Hz, 1H), 2.38 – 2.23 (m, 1H), 2.15 (dtd, *J* = 12.1, 3.8, 1.8 Hz, 1H), 1.71 –

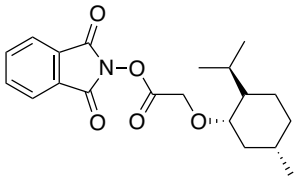
1.61 (m, 2H), 1.46 – 1.26 (m, 2H), 1.07 – 0.98 (m, 1H), 0.95 (d, *J* = 7.4 Hz, 3H), 0.91 (d, *J* = 7.1 Hz, 3H), 0.90 – 0.84 (m, 2H), 0.80 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 161.7, 134.8, 128.9, 124.0, 80.8, 63.5, 48.2, 39.8, 34.3, 31.4, 25.4, 23.2, 22.2, 21.0, 16.2.

HRMS (ESI) Calcd for: $C_{20}H_{26}NO_5$: 360.1805; Found: 360.1806 $[M+H]^+$.

$[\alpha]_D^{25}$ = -75.2 (c = 0.002 in CH_2Cl_2)

(+) 1,3-Dioxoisoindolin-2-yl menthyloxyacetoate ((+)B9): Following the general procedure using (+)-menthyloxyacetic acid (2.57 g, 12 mmol), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 40-60) to afford the desired compound **(+)B8** (3.05 g, 85%) as a white solid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.53 (s, 2H), 3.30 (td, *J* = 10.6, 4.2 Hz, 1H), 2.38 – 2.23 (m, 1H), 2.15 (dtd, *J* = 12.1, 3.8, 1.8 Hz, 1H), 1.71 – 1.61 (m, 2H), 1.46 – 1.26 (m, 2H), 1.07 – 0.98 (m, 1H), 0.95 (d, *J* = 7.4 Hz, 3H), 0.91 (d, *J* = 7.1 Hz, 3H), 0.90 – 0.84 (m, 2H), 0.80 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 161.7, 134.8, 128.9, 124.0, 80.8, 63.5, 48.2, 39.8, 34.3, 31.4, 25.4, 23.2, 22.2, 21.0, 16.2.

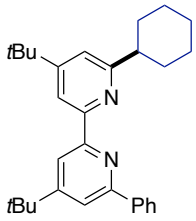
HRMS (ESI) Calcd for: $C_{20}H_{26}NO_5$: 360.1805; Found: 360.1806 $[M+H]^+$.

$[\alpha]_D^{25}$ = 75.2 (c = 0.02 in CH_2Cl_2)

3. Procedure for Photo Photoredox-catalyzed Minisci-type alkylation of 6-aryl-2,2'-bipyridines & product characterizations

General Procedure B: To a 15 mL oven-dried Schlenk tube, *fac*-[Ir(ppy)$_3$] (4.08 mg, 0.0125 mmol, 2.5 mol%), bipyridine (0.5 mmol), NHPI redox-active esters (2 equiv., 1 mmol), DMS) (1.6 mL), and TFA (0.4 mL) were successfully added under an argon atmosphere. The Schlenk was positioned on a stir plate approximately 2−3 cm from two ABI PAR38 (24 W) LED lamps supplying blue light (λ = 440−460 nm). Fans were used for cooling. After irradiation for 72 h, the reaction mixture was poured into a saturated aqueous solution of K_2CO_3 (10 mL) and extracted several times with AcOEt (4 × 15 mL). The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (petroleum ether/ethyl acetate) to produce the desired product.

4,4'-Di-*tert*-butyl-6-cyclohexyl-6'-phenyl-2,2'-bipyridine (C1): Following the general procedure **B** using 4,4'-di-tert-butyl-6-phenyl-2,2'-bipyridine (172 mg, 0.5 mmol) and 1,3-dioxoisoindolin-2-yl cyclohexanecarboxylate (**B1**) (273 mg, 1 mmol, 2 equiv.), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 90-10) to afford the desired compound **C1** (143 mg, 67%) as a white solid.

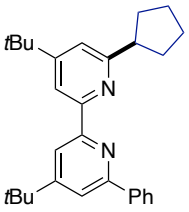


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.53 (s, 1H), 8.26 (d, *J* = 7.5 Hz, 2H), 7.85 (s, 1H), 7.60 (t, *J* = 7.5 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.27 (s, 1H), 2.91 (tt, *J* = 11.8, 3.4 Hz, 1H), 2.23 – 2.10 (m, 2H), 2.03 – 1.98 (m, 2H), 1.90 – 1.86 (m, 1H), 1.82 – 1.70 (m, 2H), 1.66 – 1.56 (m, 2H), 1.55 (s, 9H), 1.50 (s, 9H), 1.50 – 1.43 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 161.3, 160.8, 157.0, 156.3, 155.8, 140.3, 128.7, 127.1, 117.8, 117.2, 117.0, 115.9, 46.7, 35.2, 35.0, 33.2, 30.8, 30.8, 26.8, 26.3.

HRMS (ESI) Calcd for: $C_{30}H_{38}N_2Na$: 449.2927; Found: 449.2927 $[M+Na]^+$.

4,4'-Di-*tert*-butyl-6-cyclopentyl-6'-phenyl-2,2'-bipyridine (C2): Following the general procedure **B** using 4,4'-di-tert-butyl-6-phenyl-2,2'-bipyridine (172 mg, 0.5 mmol) and 1,3-dioxoisoindolin-2-yl cyclopentanecarboxylate (**B2**) (259 mg, 1 mmol, 2 equiv.), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 90-10) to afford the desired compound **C2** (128 mg, 62%) as a white solid.

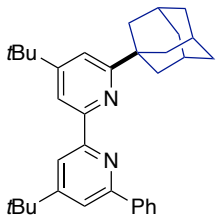


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.57 (s, 1H), 8.29 (d, *J* = 7.3 Hz, 2H), 7.87 (s, 1H), 7.62 (t, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 2H), 7.30 (s, 1H), 3.42 (quint., *J* = 7.7 Hz, 2H), 2.37 – 2.18 (m, 2H), 2.15 – 1.94 (m, 4H), 1.93 – 1.78 (m, 2H), 1.56 (s, 9H), 1.52 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 161.3, 160.7, 156.9, 156.4, 155.8, 140.3, 128.7, 127.1, 118.6, 117.2, 117.0, 115.6, 48.0, 35.2, 34.9, 33.8, 30.8, 30.8, 26.1.

HRMS (ESI) Calcd for: $C_{29}H_{36}N_2Na$: 435.2770; Found: 435.2772 $[M+Na]^+$.

4,4'-Di-*tert*-butyl-6-adamantyl-6'-phenyl-2,2'-bipyridine (B3): Following the general procedure **B** using 4,4'-di-tert-butyl-6-phenyl-2,2'-bipyridine (172 mg, 0.5 mmol) and 1,3-dioxoisoindolin-2-yl adamantane-1-carboxylate (**B3**) (325 mg, 1 mmol, 2 equiv.), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 90-10) to afford the desired compound **B3** (206 mg, 86%) as a white solid.

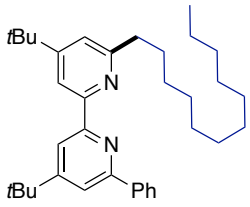


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.57 (s, 1H), 8.28 (d, *J* = 7.5 Hz, 2H), 7.86 (s, 1H), 7.62 (t, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.0 Hz, 1H), 7.42 (s, 1H), 2.28 – 2.22 (m, 10H), 1.96 – 1.95 (m, 5H), 1.57 (s, 9H), 1.53 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 161.2, 160.6, 157.2, 156.3, 155.1, 140.4, 128.7, 128.7, 127.1, 117.1, 117.0, 115.5, 115.3, 42.3, 39.4, 37.1, 35.2, 30.9, 30.8, 29.1.

HRMS (ESI) Calcd for: $C_{34}H_{42}N_2Na$: 501.3240; Found: 501.3240 $[M+Na]^+$.

4,4'-di-*tert*-butyl-6-dodecyl-6'-phenyl-2,2'-bipyridine (**C4**): Following the general procedure **B** using 4,4'-di-tert-butyl-6-phenyl-2,2'-bipyridine (172 mg, 0.5 mmol) and 1,3-dioxoisoindolin-2-yl tridecanoate (**B4**) (359 mg, 1 mmol, 2 equiv.), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 90-10) to afford the desired compound **C4** (241 mg, 47%) as a white solid.

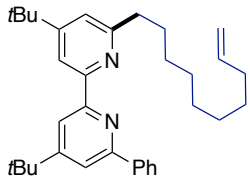


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.49 (s, 1H), 8.23 (d, *J* = 7.2 Hz, 2H), 7.82 (s, 1H), 7.57 (t, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.22 (s, 1H), 2.95 (t, *J* = 7.6 Hz, 2H), 1.92 (p, *J* = 7.6 Hz, 2H), 1.52 (s, 9H), 1.47 (s, 9H), 1.37 – 1.34 (m, 17H), 1.05 – 0.84 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 161.3, 160.7, 156.8, 156.3, 156.0, 140.2, 128.6, 128.6, 127.1, 119.5, 117.2, 116.9, 115.7, 38.5, 35.1, 34.9, 31.9, 30.7, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 22.7, 14.1.

HRMS (ESI) Calcd for: $C_{36}H_{52}N_2Na$: 535.4023; Found: 535.4022 $[M+Na]^+$.

4,4'-Di-*tert*-butyl-6-(dec-9-en-1-yl)-6'-phenyl-2,2'-bipyridine (C5) : Following the general procedure **B** using 4,4'-di-tert-butyl-6-phenyl-2,2'-bipyridine (172 mg, 0.5 mmol) and 1,3-dioxoisoindolin-2-yl undec-10-enoate (**B5**) (329 mg, 1 mmol, 2 equiv.), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 90-10) to afford the desired compound **C5** (94 mg, 39%) as a white solid.

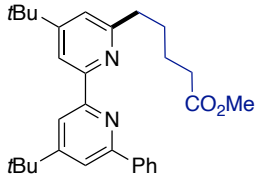


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.48 (s, 1H), 8.22 (d, *J* = 7.2 Hz, 2H), 7.81 (s, 1H), 7.57 (t, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.21 (s, 1H), 5.92 – 5.82 (m, 1H), 5.11 – 4.93 (m, 2H), 2.94 (t, *J* = 6.8 Hz, 2H), 2.10 (q, *J* = 6.8 Hz, 2H), 1.91 (quint., *J* = 7.6 Hz, 2H), 1.51 (s, 9H), 1.46 (s, 9H), 1.44 – 1.33 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 161.3, 160.7, 156.8, 156.3, 156.0, 140.2, 139.2, 128.6, 128.6, 127.1, 119.5, 117.2, 116.9, 115.7, 114.1, 38.5, 35.1, 34.9, 33.8, 30.7, 29.7, 29.5, 29.5, 29.5, 29.2, 29.0.

HRMS (ESI) Calcd for: $C_{34}H_{46}N_2Na$: 505.3553; Found: 505.3550 $[M+Na]^+$.

Methyl 5-(4,4'-di-*tert*-butyl-6'-phenyl-[2,2'-bipyridin]-6-yl)pentanoate (C6): Following the general procedure **B** using 4,4'-di-tert-butyl-6-phenyl-2,2'-bipyridine (172 mg, 0.5 mmol) and 1,3-dioxoisoindolin-2-yl methyl adipate (**B6**) (305 mg, 1 mmol, 2 equiv.), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 80-20) to afford the desired compound **C6** (133 mg, 58%) as a white solid.

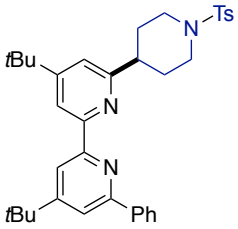


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 2H), 8.18 (d, *J* = 7.2 Hz, 2H), 7.78 (s, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.18 (s, 1H), 3.70 (s, 3H), 2.93 (t, *J* = 7.5 Hz, 2H), 2.45 (t, *J* = 7.4 Hz, 2H), 1.98 – 1.88 (m, 2H), 1.88 – 1.77 (m, 2H), 1.48 (s, 9H), 1.43 (s, 9H).

13C NMR (101 MHz, $CDCl_3$) δ 174.1, 161.4, 160.9, 160.8, 156.6, 156.3, 156.1, 140.1, 128.6, 128.6, 127.0, 119.5, 117.3, 116.8, 115.9, 51.4, 37.9, 35.1, 34.9, 34.0, 30.7, 30.7, 29.1, 24.7.

HRMS (ESI) Calcd for: $C_{30}H_{38}N_2O_2Na$: 481.2825; Found: 481.2827 $[M+Na]^+$.

4,4'-Di-*tert*-butyl-6-phenyl-6'-(1-tosylpiperidin-4-yl)-2,2'-bipyridine (C7): Following the general procedure **B** using 4,4'-di-tert-butyl-6-phenyl-2,2'-bipyridine (172 mg, 0.5 mmol) and 1,3-dioxoisoindolin-2-yl 1-tosylpiperidine-4-carboxylate (**B7**) (428 mg, 1 mmol, 2 equiv.), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 80-20) to afford the desired compound **C7** (212 mg, 73%) as a white solid.

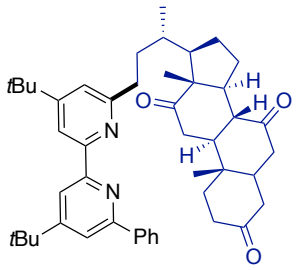


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 1.8 Hz, 1H), 8.44 (d, *J* = 1.7 Hz, 1H), 8.27 – 8.08 (m, 2H), 7.78 (d, *J* = 1.7 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.49 – 7.43 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 1.8 Hz, 1H), 4.01 (dd, *J* = 9.9, 5.1 Hz, 2H), 2.74 (d, *J* = 7.8 Hz, 1H), 2.46 (d, *J* = 10.8 Hz, 5H), 2.11 (dt, *J* = 7.9, 4.7 Hz, 4H), 1.47 (s, 9H), 1.41 (s, 9H).

13C NMR (101 MHz, $CDCl_3$) δ 162.7, 161.5, 161.3, 156.4, 156.0, 143.5, 140.1, 133.2, 129.6, 128.7, 128.7, 127.8, 127.7, 127.1, 117.8, 117.4, 116.8, 116.4, 46.7, 43.7, 35.2, 35.0, 31.3, 30.8, 30.7, 21.6.

HRMS (ESI) Calcd for: $C_{36}H_{43}N_3O_2SNa$ 627.2866; Found: 627.2865 $[M+Na]^+$.

(8*S*,9*R*,10*R*,13*S*,14*R*,17*S*)-17-((*R*)-4-(4,4'-Di-*tert*-butyl-6'-phenyl-[2,2'-bipyridin]-6-yl)butan-2-yl)-10,13-dimethyldodecahydro-3*H*-cyclopenta[*a*]phenanthrene-3,7,12(2*H*,4*H*)-trione (C8) : Following the general procedure **B** using 4'-di-tert-butyl-6-phenyl-2,2'-bipyridine (172 mg, 0.5 mmol) and 1,3-dioxoisoindolin-2-yl dehydrocholoate (**B8**) (547 mg, 1 mmol, 2 equiv.), the residue was purified by flash



chromatography on silica gel (heptane-EtOAc, 40-60) to afford the desired compound **C8** (165 mg, 47%) as a white solid.

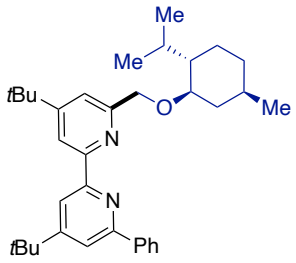
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.42 (s, 1H), 8.16 (d, *J* = 7.2 Hz, 2H), 7.76 (s, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.16 (s, 1H), 3.05 – 2.75 (m, 5H), 2.41 – 2.09 (m, 6H), 2.06 – 1.81 (m, 9H), 1.63 (tdd, *J* = 13.8, 10.1, 4.1 Hz, 2H), 1.45 (s, 9H), 1.43 – 1.36 (m, 10H), 1.09 – 1.05 (m, 4H), 1.03 – 1.00 (m, 3H), 0.91 – 0.82 (m, 3H).

13C NMR (101 MHz, $CDCl_3$) δ 212.1, 209.1, 208.8, 161.6, 161.4, 160.8, 156.7, 156.3, 155.9, 140.1, 128.7, 128.6, 127.0, 119.6, 117.3, 116.9, 115.6, 57.0, 51.8, 49.0, 46.8, 46.0, 45.6, 45.0, 42.8, 38.7, 37.4, 36.5, 36.0, 35.7, 35.3, 34.9, 33.9, 30.7, 27.9, 25.6, 25.2, 25.0, 21.9, 19.0, 18.5, 11.9, 10.9.

HRMS (ESI) Calcd for: $C_{47}H_{60}N_2O_3Na$: 723.4496; Found: 723.4495 $[M+Na]^+$.

$[\alpha]_D^{25}$ = -134.4 (c = 0.02 in CH_2Cl_2)

4,4'-Di-*tert*-butyl-6-((((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)-6'-phenyl-2,2'-bipyridine ((-)C9): Following the general procedure **B** using 4'-di-tert-butyl-6-phenyl-2,2'-bipyridine (172 mg, 0.5 mmol) and (-) 1,3-dioxoisoindolin-2-yl menthyloxyacetoate (**(-)B9**) (359 mg, 1 mmol, 2 equiv.), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 40-60) to afford the desired compound **(-)C9** (171 mg, 67%) as a white solid.



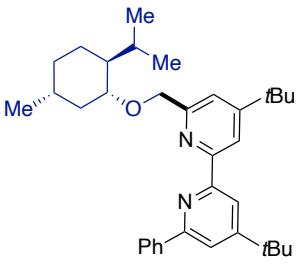
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 1.8 Hz, 1H), 8.47 (d, *J* = 1.7 Hz, 1H), 8.20 (dt, *J* = 6.5, 1.3 Hz, 2H), 7.80 (d, *J* = 1.7 Hz, 1H), 7.58 (d, *J* = 1.8 Hz, 1H), 7.55 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.49 – 7.42 (m, 1H), 4.94 (d, *J* = 12.9 Hz, 1H), 4.71 (d, *J* = 12.9 Hz, 1H), 3.40 – 3.25 (m, 2H), 2.50 – 2.38 (m, 1H), 2.37 – 2.26 (m, 1H), 2.27 – 2.12 (m, 1H), 1.81 – 1.59 (m, 5H), 1.49 (s, 3H), 1.46 (s, 3H), 1.34 – 1.22 (m, 4H), 1.11 – 1.03 (m, 4H), 1.02 – 0.98 (m, 5H), 0.98 – 0.88 (m, 8H).

13C NMR (101 MHz, $CDCl_3$) δ 161.5, 161.2, 158.7, 156.4, 155.8, 140.1, 128.7, 128.7, 127.1, 118.7, 117.4, 117.0, 116.9, 111.9, 95.3, 79.8, 72.0, 64.6, 48.3, 40.6, 35.2, 35.1, 34.7, 31.6, 30.8, 30.7, 26.0, 23.5, 22.4, 21.0, 16.4.

HRMS (ESI) Calcd for: $C_{35}H_{48}N_2ONa$: 535.3659; Found: 535.3658 $[M+Na]^+$.

$[\alpha]_D^{25}$ = -146.9 (c = 0.02 in CH_2Cl_2)

4,4'-Di-*tert*-butyl-6-((((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)-6'-phenyl-2,2'-bipyridine ((+)C9): Following the general procedure **B** using 4'-di-tert-butyl-6-phenyl-2,2'-bipyridine (172 mg, 0.5 mmol) and (-) 1,3-dioxoisoindolin-2-yl menthyloxyacetoate (**(+)B9**) (359 mg, 1 mmol, 2 equiv.), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 40-60) to afford the desired compound **(-)C9** (184 mg, 72%) as a white solid.



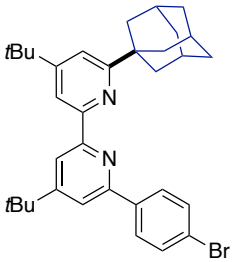
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 1.8 Hz, 1H), 8.47 (d, *J* = 1.7 Hz, 1H), 8.20 (dt, *J* = 6.5, 1.3 Hz, 2H), 7.80 (d, *J* = 1.7 Hz, 1H), 7.58 (d, *J* = 1.8 Hz, 1H), 7.55 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.49 – 7.42 (m, 1H), 4.94 (d, *J* = 12.9 Hz, 1H), 4.71 (d, *J* = 12.9 Hz, 1H), 3.40 – 3.25 (m, 2H), 2.50 – 2.38 (m, 1H), 2.37 – 2.26 (m, 1H), 2.27 – 2.12 (m, 1H), 1.81 – 1.59 (m, 5H), 1.49 (s, 3H), 1.46 (s, 3H), 1.34 – 1.22 (m, 4H), 1.11 – 1.03 (m, 4H), 1.02 – 0.98 (m, 5H), 0.98 – 0.88 (m, 8H).

13C NMR (101 MHz, $CDCl_3$) δ 161.5, 161.2, 158.7, 156.4, 155.8, 140.1, 128.7, 128.7, 127.1, 118.7, 117.4, 117.0, 116.9, 111.9, 95.3, 79.8, 72.0, 64.6, 48.3, 40.6, 35.2, 35.1, 34.7, 31.6, 30.8, 30.7, 26.0, 23.5, 22.4, 21.0, 16.4.

HRMS (ESI) Calcd for: $C_{35}H_{48}N_2ONa$: 535.3659; Found: 535.3658 $[M+Na]^+$.

$[\alpha]_D^{25}$ = 146.9 (c = 0.002 in CH_2Cl_2)

4,4'-Di-*tert*-butyl-6-adamantyl-6'-(4-bromophenyl)-2,2'-bipyridine (C10): Following the general procedure **B** using 6-(4-bromophenyl)-4,4'-di-*tert*-butyl-2,2'-bipyridine (211 mg, 0.5 mmol) and 1,3-dioxoisoindolin-2-yl adamantane-1-carboxylate (**B3**) (325 mg, 1 mmol, 2 equiv.), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 90-10) to afford the desired compound **B10** (201 mg, 71%) as a white solid.

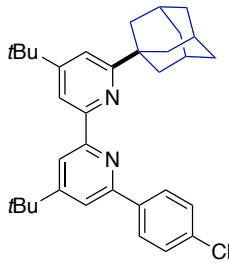


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 1.7 Hz, 1H), 8.40 (d, *J* = 1.7 Hz, 1H), 8.10 – 7.99 (m, 2H), 7.72 (d, *J* = 1.7 Hz, 1H), 7.69 – 7.61 (m, 2H), 7.32 (d, *J* = 1.7 Hz, 1H), 2.22 – 2.16 (m, 3H), 2.17 – 2.11 (m, 6H), 1.90 – 1.82 (m, 6H), 1.47 (s, 9H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 161.4, 160.7, 157.3, 155.1, 154.8, 139.2, 131.7, 128.7, 123.0, 117.3, 116.8, 115.7, 115.2, 42.2, 39.3, 37.0, 35.1, 35.1, 30.9, 30.7, 29.0.

HRMS (ESI) Calcd for: $C_{34}H_{41}BrN_2Na$: 579.2345; Found: 579.2342 $[M+Na]^+$.

4,4'-Di-*tert*-butyl-6-adamantyl-6'-(4-chlorophenyl)-2,2'-bipyridine (C11): Following the general procedure **B** using 6-(4-chlorophenyl)-4,4'-di-*tert*-butyl-2,2'-bipyridine (189 mg, 0.5 mmol) and 1,3-dioxoisoindolin-2-yl adamantane-1-carboxylate (**B3**) (325 mg, 1 mmol, 2 equiv.), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 90-10) to afford the desired compound **C11** (189 mg, 74%) as a white solid.

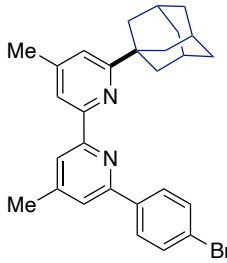


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 1.7 Hz, 1H), 8.40 (d, *J* = 1.7 Hz, 1H), 8.16 – 8.06 (m, 2H), 7.71 (d, *J* = 1.7 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 1.7 Hz, 1H), 2.27 – 2.17 (m, 3H), 2.15 – 2.10 (m, 6H), 1.93 – 1.83 (m, 6H), 1.47 (s, 9H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 161.4, 160.7, 157.2, 155.1, 154.9, 138.7, 134.7, 128.8, 128.3, 117.2, 116.8, 115.6, 115.2, 42.2, 39.3, 37.0, 35.1, 35.1, 30.9, 30.7, 29.0.

HRMS (ESI) Calcd for: $C_{34}H_{41}ClN_2Na$: 535.2850; Found: 535.2850 $[M+Na]^+$.

4,4'-Dimethyl-6-adamantyl-6'-(4-bromophenyl)-2,2'-bipyridine (C12): Following the general procedure **B** using 6-(4-bromophenyl)-4,4'-dimethyl-2,2'-bipyridine (169 mg, 0.5 mmol) and 1,3-dioxoisoindolin-2-yl adamantane-1-carboxylate (**B3**) (325 mg, 1 mmol, 2 equiv.), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 90-10) to afford the desired compound **C12** (158 mg, 67%) as a white solid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.21 (s, 1H), 8.04 (d, *J* = 8.6 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.55 (s, 1H), 7.14 (s, 1H), 2.54 (s, 3H), 2.47 (s, 3H), 2.21 – 2.15 (m, 3H), 2.13 – 2.09 (m, 6H), 1.89 – 1.80 (m, 6H).

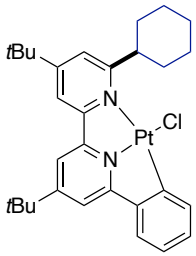
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 156.8, 155.1, 154.6, 148.6, 147.7, 138.7, 131.7, 128.6, 123.1, 120.8, 120.7, 119.9, 119.0, 42.1, 39.0, 37.0, 29.7, 28.9, 21.6, 21.5.

HRMS (ESI) Calcd for: $C_{28}H_{29}BrN_2Na$: 495.1406; Found: 495.1403 $[M+Na]^+$.

4. Procedure for the preparation of cyclometalated Pt(II) chloride complexes & product characterizations

General Procedure C: A mixture of 6'-alkyl-4,4'-di-tert-butyl-6-phenyl-2,2'-bipyridine pro-ligands (0.25 mmol) and K_2PtCl_4 (62 mg, 0.15 mmol) in CH_3CO_2H (15 mL) was refluxed for 48 h. The red solution was evaporated to dryness and was purified by flash chromatography on silica gel (heptane-EtOAc) to afford the desired compound.

Chloro(*N*,*N*,*6C''*)-4,4'-di-tert-butyl-6-cyclohexyl-6'-phenyl-2,2'-bipyridine platinum (D1):



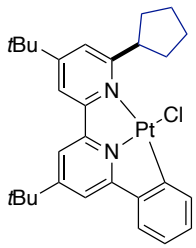
Following the general procedure **C** using 4,4'-di-*tert*-butyl-6-cyclohexyl-6'-phenyl-2,2'-bipyridine (**C1**) (64.0 mg, 0.15 mmol), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 80-20) to afford the desired compound **D1** (83.6 mg, 85%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.6 Hz, 1H), 7.75 (s, 1H), 7.59 (s, 1H), 7.56 (s, 1H), 7.54 (s, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 4.66 (tt, *J* = 11.9, 3.2 Hz, 1H), 2.23 – 2.05 (m, 2H), 1.83 (dt, *J* = 15.3, 10.7 Hz, 5H), 1.47 (s, 9H), 1.45 (s, 9H), 1.39 – 1.26 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 165.4, 163.2, 162.6, 156.6, 155.3, 145.7, 136.4, 133.8, 130.3, 123.9, 123.4, 121.7, 116.6, 115.1, 114.7, 43.5, 35.8, 35.4, 34.1, 30.3, 26.2, 25.5.

Elemental Analysis: calcd for: $C_{30}H_{37}ClN_2Pt$: C, 54.91. H, 5.68, N, 4.27. Found: C, 54.86. H, 5.67. N, 4.12.

Chloro(*N*,*N*,*6C''*)-4,4'-di-tert-butyl-6-cyclopentyl-6'-phenyl-2,2'-bipyridine platinum (D2):



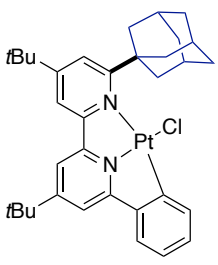
Following the general procedure **C** using 4,4'-di-*tert*-butyl-6-cyclopentyl-6'-phenyl-2,2'-bipyridine (**C2**) (61.9 mg, 0.15 mmol), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 80-20) to afford the desired compound **D2** (81.9 mg, 85%) as a yellow solid.

^{1}H NMR (400 MHz, Acetone-d_6) δ 8.32 (s, 1H), 8.16 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.86 (s, 1H), 7.78 (s, 1H), 7.55 (d, *J* = 8.7 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 5.10 – 4.98 (m, 1H), 2.40 – 2.24 (m, 2H), 1.90 – 1.76 (m, 4H), 1.73 – 1.63 (m, 2H), 1.50 (s, 9H), 1.47 (s, 9H).

^{13}C NMR (101 MHz, Acetone-d_6) δ 171.5, 164.9, 164.0, 163.4, 156.5, 155.3, 146.4, 137.2, 133.5, 129.2, 123.8, 123.4, 121.7, 118.2, 116.5, 115.6, 46.6, 35.9, 35.3, 34.5, 29.5, 29.5, 25.4.

Elemental Analysis: calcd for: $C_{29}H_{35}ClN_2Pt$: C, 54.24. H, 5.49, N, 4.36. Found: C, 54.08. H, 5.31. N, 4.49.

Chloro(*N*,*N*,*6C''*)-4,4'-di-tert-butyl-6-adamantyl-6'-phenyl-2,2'-bipyridine platinum (D3):



Following the general procedure **C** using 4,4'-di-*tert*-butyl-6-adamantyl-6'-phenyl-2,2'-bipyridine (**C3**) (71.8 mg, 0.15 mmol), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 80-20) to afford the desired compound **D3** (37.2 mg, 35%) as a yellow solid.

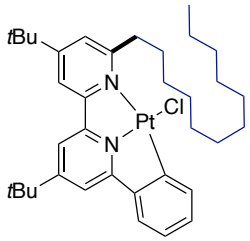
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 1H), 7.84 (s, 1H), 7.69 (s, 1H), 7.52 (s, 1H), 7.50 (s, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.15 (t, *J* = 6.9 Hz,

1H), 7.06 (t, *J* = 7.4 Hz, 1H), 2.17 – 2.16 (m, 7H), 2.06 – 2.03 (m, 4H), 1.74 – 1.71 (m, 4H), 1.45 (s, 9H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 164.3, 163.2, 162.9, 156.5, 155.4, 144.8, 134.4, 131.5, 129.9, 123.9, 123.4, 122.0, 116.1, 115.8, 115.0, 41.4, 40.6, 36.3, 35.8, 35.3, 30.9, 30.4, 29.0.

Elemental Analysis: calcd for: $C_{34}H_{41}ClN_2Pt$: C, 57.66. H, 5.84, N, 3.96. Found: C, 57.89. H, 5.98. N, 4.09.

Chloro(*N,N,6C''*)-4,4'-Di-tert-butyl-6-dodecyl-6'-phenyl-2,2'-bipyridine platinum (D4):



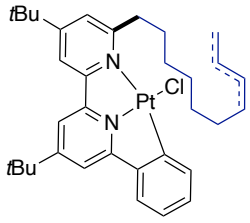
Following the general procedure **C** using 4,4'-di-*tert*-butyl-6-dodecyl-6'-phenyl-2,2'-bipyridine (**C4**) (76.9 mg, 0.15 mmol), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 80-20) to afford the desired compound **D4** (63.5 mg, 57%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 1H), 7.72 (s, 1H), 7.53 (s, 1H), 7.50 (s, 1H), 7.41 (s, 1H), 7.32 (d, *J* = 7.0 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 3.53 (t, *J* = 7.8 Hz, 3H), 1.78 (quint., *J* = 7.8 Hz, 2H), 1.46 (s, 9H), 1.44 (s, 9H), 1.26 (m, 18H), 0.89 (t, *J* = 6.8 Hz, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 165.4, 162.9, 162.6, 157.1, 155.1, 145.8, 136.9, 133.8, 130.2, 125.3, 123.7, 123.4, 116.5, 115.1, 114.8, 38.5, 35.8, 35.2, 31.9, 31.7, 30.4, 30.3, 29.7, 29.6, 29.3, 29.1, 22.6, 14.1.

Elemental Analysis: calcd for: $C_{36}H_{51}ClN_2Pt$: C, 58.25. H, 6.93, N, 4.78. Found: C, 58.44. H, 7.12. N, 4.53.

Mixture of isomers chloro(*N,N,6C''*)-4,4'-Di-tert-butyl-6-decenyl-6'-phenyl-2,2'-bipyridine platinum (D5):



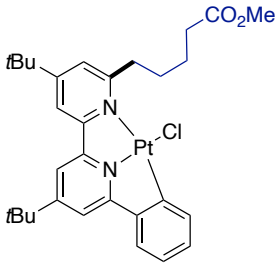
Following the general procedure **C** using 4,4'-di-*tert*-butyl-6-(dec-9-en-1-yl)-6'-phenyl-2,2'-bipyridine (**C5**) (72.4 mg, 0.15 mmol), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 80-20) to afford the desired compound **D5** (50.1 mg, 47%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.74 (d, *J* = 2.0 Hz, 1H), 7.54 (dd, *J* = 10.1, 1.7 Hz, 2H), 7.43 (d, *J* = 2.0 Hz, 1H), 7.35 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.22 (td, *J* = 7.5, 1.5 Hz, 1H), 7.07 (td, *J* = 7.5, 1.3 Hz, 1H), 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 0.2H), 5.48 – 5.32 (m, 1.4H), 4.99 (dq, *J* = 17.2, 1.7 Hz, 0.2H), 4.93 (ddt, *J* = 10.2, 2.4, 1.3 Hz, 0.2H), 3.62 – 3.51 (m, 2H), 2.08 – 1.91 (m, 2H), 1.85 – 1.73 (m, 2H), 1.68 – 1.57 (m, 3H), 1.46 (s, 9H), 1.44 (s, 9H), 1.40 – 1.24 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 165.5, 163.1, 162.7, 157.2, 155.2, 145.9, 139.3, 136.9, 133.9, 131.8, 131.8, 131.0, 130.4, 129.4, 125.4, 124.5, 123.9, 123.5, 123.5, 116.5, 115.2, 114.9, 114.8, 114.0, 38.5, 35.8, 35.2, 33.8, 32.6, 30.4, 30.3, 29.6, 29.6, 29.6, 29.5, 29.5, 29.5, 29.2, 29.2, 29.1, 29.1, 28.9.

Elemental Analysis: calcd for: $C_{34}H_{45}ClN_2Pt$: C, 57.33. H, 6.37, N, 3.93. Found: C, 57.21. H, 6.24. N, 3.87.

Methyl chloro(*N,N,6C''*)-5-(4,4'-di-*tert*-butyl-6'-phenyl-[2,2'-bipyridin]-6-yl)pentanoate platinum (D6): Following the general procedure **C** using methyl 5-(4,4'-di-*tert*-butyl-6'-phenyl-[2,2'-bipyridin]-6-yl)pentanoate (**C6**) (68.8 mg, 0.15 mmol), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 70-30) to afford the desired compound **D6** (63.9 mg, 62%) as a yellow solid.

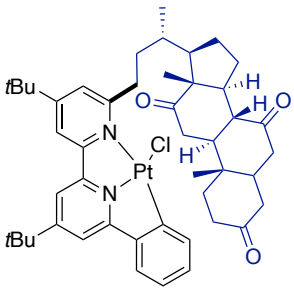


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 1H), 7.73 (s, 1H), 7.53 (s, 1H), 7.49 (s, 1H), 7.41 (s, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 3.65 (s, 3H), 3.54 – 3.50 (m, 2H), 2.41 – 2.37 (m, 2H), 1.84 – 1.81 (m, 4H), 1.45 (s, 9H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 167.9, 165.3, 163.2, 162.7, 157.2, 155.0, 145.8, 136.8, 133.7, 130.2, 125.3, 123.8, 123.5, 116.7, 115.2, 114.9, 51.4, 38.1, 35.8, 35.2, 33.9, 31.0, 30.4, 30.3, 24.3.

Elemental Analysis: calcd for: $C_{30}H_{37}ClN_2O_2Pt$: C, 52.36. H, 5.42, N, 4.07. Found: C, 52.41. H, 5.37. N, 4.31.

Chloro(*N,N,6C''*)-(8*S*,9*R*,10*R*,13*S*,14*R*,17*S*)-17-((*R*)-4-(4,4'-Di-*tert*-butyl-6'-phenyl-[2,2'-bipyridin]-6-yl)butan-2-yl)-10,13-dimethyldodecahydro-3*H*-cyclopenta[*a*]phenanthrene-3,7,12(2*H*,4*H*)-trione platinum (D8) : Following the general procedure **C** using *8S*,9*R*,10*R*,13*S*,14*R*,17*S*)-17-((*R*)-4-(4,4'-di-*tert*-butyl-6'-phenyl-[2,2'-bipyridin]-6-yl)butan-2-yl)-10,13-dimethyldodecahydro-3*H*-cyclopenta[*a*]phenanthrene-3,7,12(2*H*,4*H*)-trione (**C8**) (105.0 mg, 0.15 mmol), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 70-30) to afford the desired compound **D8** (67.0 mg, 48%) as a yellow solid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.7 Hz, 1H), 7.75 (s, 1H), 7.55 (s, 1H), 7.51 (s, 1H), 7.43 (s, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.19 (t, *J* = 8.1 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 3.96 (td, *J* = 12.4, 4.8 Hz, 1H), 3.22 (td, *J* = 12.4, 4.8 Hz, 1H), 2.98 – 2.76 (m, 3H), 2.38 – 2.27 (m,

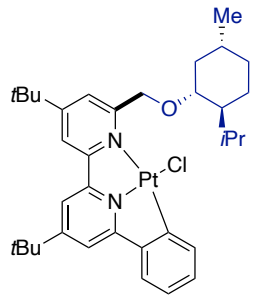
2H), 2.27 – 2.08 (m, 6H), 2.07 – 1.88 (m, 5H), 1.84 – 1.77 (m, 1H), 1.74 – 1.55 (m, 3H), 1.45 (s, 9H), 1.43 (s, 9H), 1.40 (s, 3H), 1.11 (s, 3H), 0.98 (d, *J* = 6.6 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 212.5, 209.2, 208.9, 169.3, 165.3, 163.2, 162.7, 157.0, 155.1, 145.9, 136.9, 133.8, 130.2, 125.2, 123.9, 123.5, 116.6, 115.1, 114.8, 57.1, 51.9, 49.0, 46.8, 46.6, 45.7, 45.0, 42.7, 38.7, 38.0, 36.5, 36.3, 36.0, 35.8, 35.5, 35.2, 30.4, 27.5, 25.2, 22.6, 21.9, 19.0, 14.1, 11.9.

$[\alpha]_D^{25}$ = -366 (c = 1.4.10^{-4} M in CH_2Cl_2)

Elemental Analysis: calcd for: $C_{47}H_{59}ClN_2O_3Pt$: C, 60.67. H, 6.39, N, 3.01. Found: C, 60.89. H, 6.41. N, 2.87.

Chloro(*N*,*N*,*6C''*)-4,4'-Di-*tert*-butyl-6-((((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)-6'-phenyl-2,2'-bipyridine platinum ((-)D9):



Following the general procedure **C** using 4,4'-di-*tert*-butyl-6-((((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)-6'-phenyl-2,2'-bipyridine (**(-)C9**) (76.9 mg, 0.15 mmol), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 70-30) to afford the desired compound **(-)-D9** (86.9 mg, 78%) as a yellow solid.

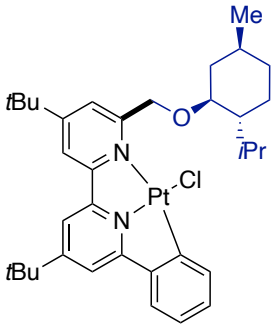
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 2.0 Hz, 1H), 7.81 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.72 (d, *J* = 2.1 Hz, 1H), 7.52 (d, *J* = 1.6 Hz, 1H), 7.48 (d, *J* = 1.7 Hz, 1H), 7.26 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.13 (td, *J* = 7.5, 1.4 Hz, 1H), 6.98 (td, *J* = 7.4, 1.3 Hz, 1H), 5.41 (d, *J* = 17.2 Hz, 1H), 5.04 (d, *J* = 17.1 Hz, 1H), 3.43 (td, *J* = 10.5, 4.0 Hz, 1H), 2.49 – 2.42 (m, 1H), 2.40 – 2.29 (m, 1H), 1.76 – 1.62 (m, 3H), 1.46 (s, 9H), 1.45 (s, 9H), 1.09 – 1.01 (m, 2H), 1.01 – 0.95 (m, 6H), 0.94 – 0.88 (m, 2H), 0.85 (d, *J* = 7.0 Hz, 3H).

13C NMR (101 MHz, $CDCl_3$) δ 165.9, 165.4, 163.3, 162.7, 156.6, 154.8, 146.1, 137.5, 133.5, 130.0, 123.8, 123.4, 122.0, 117.0, 115.3, 114.9, 80.6, 71.7, 48.2, 40.8, 35.8, 35.5, 34.6, 31.5, 30.4, 30.3, 26.5, 23.6, 22.4, 21.0, 16.6.

$[\alpha]_D^{25}$ = -248 (c = 1.2.10^{-4} M in CH_2Cl_2)

Elemental Analysis: calcd for: $C_{35}H_{47}ClN_2OPt$: C, 56.63. H, 6.38, N, 3.77. Found: C, 56.45. H, 6.20. N, 3.91.

Chloro(*N*,*N*,*6C''*)-4,4'-Di-*tert*-butyl-6-((((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)-6'-phenyl-2,2'-bipyridine platinum ((+)D9): Following the general procedure **C** using 4,4'-di-*tert*-butyl-6-((((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)-6'-phenyl-2,2'-bipyridine (**(+)C9**) (76.9 mg, 0.15 mmol), the residue was purified by flash chromatography on silica gel (heptane-EtOAc, 70-30) to afford the desired compound **(+)-D9** (86.9 mg, 78%) as a yellow solid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 2.0 Hz, 1H), 7.81 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.72 (d, *J* = 2.1 Hz, 1H), 7.52 (d, *J* = 1.6 Hz, 1H), 7.48 (d, *J* = 1.7 Hz, 1H), 7.26 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.13 (td, *J* = 7.5, 1.4 Hz, 1H), 6.98 (td, *J* = 7.4, 1.3 Hz, 1H), 5.41 (d, *J* = 17.2 Hz, 1H), 5.04 (d, *J* = 17.1 Hz, 1H), 3.43 (td, *J* = 10.5, 4.0 Hz, 1H), 2.49 – 2.42 (m, 1H), 2.40 – 2.29 (m, 1H), 1.76 – 1.62 (m, 3H), 1.46 (s, 9H), 1.45 (s, 9H), 1.09 – 1.01 (m, 2H), 1.01 – 0.95 (m, 6H), 0.94 – 0.88 (m, 2H), 0.85 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 165.4, 163.3, 162.7, 156.6, 154.8, 146.1, 137.5, 133.5, 130.0, 123.8, 123.4, 122.0, 117.0, 115.3, 114.9, 80.6, 71.7, 48.2, 40.8, 35.8, 35.5, 34.6, 31.5, 30.4, 30.3, 26.5, 23.6, 22.4, 21.0, 16.6.

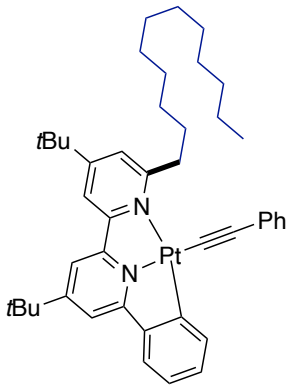
$[\alpha]_D^{25}$ = +258 (c = $1.8.10^{-4}$ M in CH_2Cl_2)

Elemental Analysis: calcd for: $C_{35}H_{47}ClN_2OPt$: C, 56.63. H, 6.38, N, 3.77. Found: C, 56.71. H, 6.21. N, 3.86.

5. Procedure for the preparation of alkynyl cyclometalated Pt(II) complexes & Product Characterizations

General Procedure D: A mixture of Chloro(*N*,*N*,*6C''*)-4,4'-Di-tert-butyl-6-alkyl-6'-phenyl-2,2'-bipyridine platinum (0.03 mmol), phenyl acetylene (0.04 mmol) and copper iodide (3.10^{-6} mol) in CH_2Cl_2/Et_3N (2/1 v/v mL) or DMF/Et_3N (2/1 v/v mL) was stirred at room temperature for 12 h. The resultant solution was evaporated to dryness and was purified over preparative chromatography plate on silica gel (CH_2Cl_2/Pentane 1/1 v/v) to afford the desired compound.

Phenyl acetylene (*N,N,6C''*)-4,4'-Di-tert-butyl-6-dodecyl-6'-phenyl-2,2'-bipyridine platinum (E4): Following the general procedure **D** using Chloro(*N,N,6C''*)-4,4'-Di-tert-butyl-6-dodecyl-6'-phenyl-2,2'-bipyridine platinum **(D4)** (1000 mg, 0.136 mmol) the desired complex **E4** was isolated (87.2 mg, 80%).

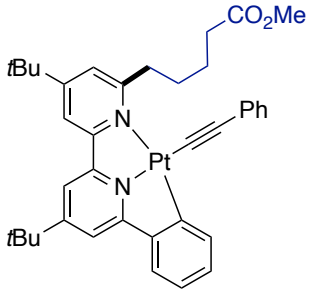


^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.16 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.83 (d, *J* = 2.0 Hz, 1H), 7.74 – 7.67 (m, 2H), 7.52 (dd, *J* = 4.3, 1.8 Hz, 2H), 7.49 – 7.40 (m, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.08 (m, 3H), 3.72 (t, *J* = 7.7 Hz, 2H), 1.89 (t, *J* = 7.6 Hz, 2H), 1.50 (s, 9H), 1.46 (s, 9H), 1.30 (m, 18H), 0.92 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 167.8, 163.9, 163.6, 163.4, 158.3, 155.5, 146.5, 137.9, 137.2, 131.2, 130.5, 129.5, 127.8, 127.8, 124.6, 124.3, 123.8, 123.4, 117.1, 115.3, 115.2, 107.5, 106.8, 41.3, 35.9, 35.2, 31.9, 31.7, 30.2, 30.0, 29.8, 29.7, 29.6, 29.4, 29.2, 22.7, 13.9.

Elemental Analysis: calcd for: $C_{44}H_{56}N_2Pt$: C, 65.40. H, 6.99, N, 24.14. Found: C, 65.44. H, 7.19. N, 23.98.

Phenyl acetylene (*N,N,6C''*)-5-(4,4'-di-*tert*-butyl-6'-phenyl-[2,2'-bipyridin]-6-yl)methylpentanoate platinum (E6): Following the general procedure **D** using chloro(*N,N,6C''*)-5-(4,4'-di-*tert*-butyl-6'-phenyl-[2,2'-bipyridin]-6-yl) methyl pentanoate platinum **(D6)** (100 mg, 0.141 mmol) the desired complex **E6** was isolated (65.8 mg, 67%).

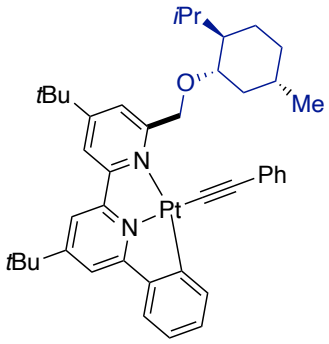


^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.11 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.81 (d, *J* = 2.0 Hz, 1H), 7.73 – 7.59 (m, 2H), 7.50 (d, *J* = 2.0 Hz, 1H), 7.48 (d, *J* = 1.4 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.20 – 7.03 (m, 3H), 3.70 (t, *J* = 7.5 Hz, 2H), 3.56 (s, 3H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.98 – 1.84 (m, 2H), 1.75 (m, 2H), 1.46 (s, 9H), 1.43 (s, 9H).

^{13}C NMR (125 MHz, CD_2Cl_2) δ 173.7, 167.0, 163.9, 163.6, 163.6, 158.4, 155.4, 146.4, 137.7, 137.1, 131.1, 130.5, 129.3, 127.8, 124.6, 124.2, 123.7, 123.4, 117.2, 115.3, 115.2, 107.4, 106.7, 51.1, 40.8, 35.8, 33.8, 30.9, 30.1, 29.9, 24.3.

Elemental Analysis: calcd for: $C_{38}H_{42}N_2O_2Pt$: C, 60.54, H, 5.62, N, 3.72. Found: C, 60.31. H, 5.78. N, 3.54.

Phenyl acetylene (*N*,*N*,*6C''*)-4,4'-Di-*tert*-butyl-6-((((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)-6'-phenyl-2,2'-bipyridine platinum ((-)-E9): Following the general procedure **D** using Chloro(*N*,*N*,*6C''*)-4,4'-Di-*tert*-butyl-6-((((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)-6'-phenyl-2,2'-bipyridine platinum **((-)-D9)** (35.1 mg, 0.047 mmol) the desired complex **(-)-E9** was isolated (29.2 mg, 83%).



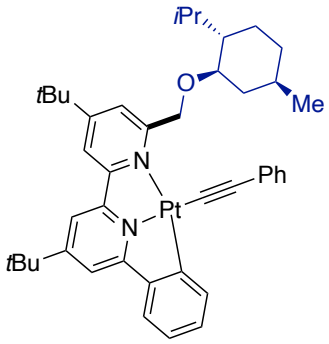
^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.05 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.99 (d, *J* = 1.8 Hz, 1H), 7.82 (d, *J* = 1.8 Hz, 1H), 7.67 (dd, *J* = 15.0, 1.3 Hz, 2H), 7.48 (d, *J* = 1.3 Hz, 1H), 7.48 – 7.37 (m, 2H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.17 – 7.04 (m, 3H), 5.50 (d, *J* = 17.0 Hz, 1H), 5.11 (d, *J* = 17.0 Hz, 1H), 3.33 (td, *J* = 10.5, 4.1 Hz, 1H), 2.33 – 2.27 (m, 2H), 1.46 (s, 9H), 1.43 (s, 9H), 1.04 (m, 1H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.79 (d, *J* = 7.0 Hz, 3H), 0.60 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 165.1, 164.7, 164.4, 158.6, 155.6, 147.2, 139.0, 137.7, 131.7, 131.2, 129.9, 128.5, 125.3, 124.5, 124.1, 122.3, 122.3, 118.2, 116.0, 115.7, 109.7, 80.9, 74.6, 48.8, 41.0, 36.5, 36.1, 35.1, 31.8, 30.8, 30.6, 27.1, 24.2, 22.3, 21.2, 17.0.

$[\alpha]_D^{25}$ = -167 (c = 1.8.10^{-4} M in CH_2Cl_2).

Elemental Analysis: calcd for: $C_{43}H_{52}N_2OPt$, ¼ CH_2Cl_2: C, 62.65. H, 6.38, N, 3.38. Found: C, 62.45. H, 6.45. N, 3.31.

Phenyl acetylene (*N*,*N*,*6C''*)-4,4'-Di-*tert*-butyl-6-((((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)-6'-phenyl-2,2'-bipyridine platinum ((+)-E9): Following the general procedure **D** using Chloro(*N*,*N*,*6C''*)-4,4'-Di-*tert*-butyl-6-((((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)-6'-phenyl-2,2'-bipyridine platinum **((+)-D9)** (36.4 mg, 0.049 mmol) the desired complex **(+)-E9** was isolated (28.7 mg, 79%).



^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.06 (d, *J* = 7.5 Hz, 1H), 8.00 (s, 1H), 7.83 (s, 1H), 7.68 (d, *J* = 15.0 Hz, 2H), 7.56 – 7.37 (m, 3H), 7.26 (t, *J* = 7.6 Hz, 3H), 7.18 – 7.07(m, 3H), 5.51 (d, *J* = 17.0 Hz, 1H), 5.12 (d, *J* = 17.0 Hz, 1H), 3.34 (td, *J* = 10.5, 4.1 Hz, 1H), 2.33 – 2.27 (m, 2H), 1.47 (s, 9H), 1.44 (s, 9H), 1.04 (m, 1H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.79 (d, *J* = 7.0 Hz, 4H), 0.61 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 165.1, 164.7, 164.4, 158.6, 155.6, 147.2, 139.0, 137.7, 131.7, 131.2, 129.9, 128.5, 125.3, 124.5, 124.1, 122.3, 122.3, 118.2, 116.0, 115.7, 109.7, 80.9, 74.6, 48.8, 41.0, 36.5, 36.1, 35.1, 31.8, 30.8, 30.6, 27.1, 24.2, 22.3, 21.2, 17.0.

$[\alpha]_D^{25}$ = +181 (c = 2.5.10^{-4} M in CH_2Cl_2)

Elemental Analysis: calcd for: $C_{43}H_{52}N_2OPt$, ¼ CH_2Cl_2: C, 62.65. H, 6.38, N, 3.38. Found: C, 62.45. H, 6.45. N, 3.31

6. X-ray crystallographic data

The numbering of the .cif files have been adapted to obtained the labelling presented below:

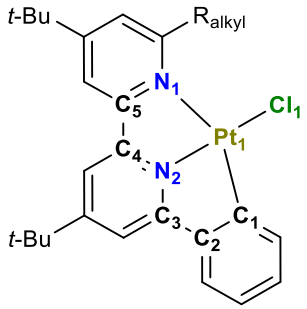


Table S1. Selected Bond Lengths [Å], Angles [deg], and Torsion Angle [deg] for **D1**, **D2**, **D3**, **D5**, **D6**, **(+)-D9** and **(+)-D9**.

		D1	**D2**	**D3**	**D5**	**D6**	**(+)-D9**	**(-)-D9**
Bond length [Å]	Pt1-N2	1.963(4)	1.966(3)	1.961(3)	1.968(3)	1.961(3)	1.989(9)	1.924(8)
	Pt1-C1	1.986(5)	1.989(4)	1.979(4)	1.987(5)	1.993(4)	2.012(11)	2.024(9)
	Pt1-N1	2.206(4)	2.194(3)	2.312(3)	2.204(4)	2.204(4)	2.182(9)	2.193(8)
Angles [deg]	N2-Pt1-C1	82.04(18)	82.26(15)	81.83(15)	82.07(17)	82.16(16)	81.9(5)	81.4(5)
	N2-Pt1-N1	78.31(16)	78.20(13)	77.28(12)	78.37(14)	78.25(13)	78.9(4)	78.2(4)
	C1-Pt1-N1	160.34(18)	160.27(15)	159.05(14)	160.27(16)	160.41(16)	160.4(5)	159.1(4)
	N2-Pt1-Cl1	175.14(12)	171.01(10)	174.51(10)	174.87(11)	174.52(10)	175.2(3)	174.8(4)
	C1-Pt1-Cl1	93.16(14)	93.02(12)	93.78(12)	93.47(13)	92.97(13)	94.2(4)	95.1(4)
	N1-Pt1-Cl1	106.49(11)	106.71(9)	107.17(8)	106.18(10)	106.59(9)	105.2(3)	105.6(3)
Torsion angle [deg]	Pt1-N1-C5-C4	-2.30(5)	-6.80(4)	-28.50(4)	-3.00(4)	-1.00(4)	0.6(11)	0.8(10)
	Pt1-N2-C4-C5	-0.50(5)	5.90(5)	-1.00(5)	-6.00(5)	-0.80(5)	5.9(13)	-2.2(10)
	Pt1-N2-C3-C2	0.80(5)	-4.20(4)	4.40(4)	2.10(4)	-0.20(4)	-1.4(13)	-1.8(10)
	C3-C2-C1-Pt1	-0.70(5)	-0.60(5)	-6.10(4)	-0.70 (5)	0.80(4)	1.1(13)	-4.2(10)

7. Additional photophysical data

Table S2. Absorption and emission data for platinum chloro complexes **D1**, **D2**, **D3**, **D4**, **D6**, **D8**, **(-)-D9**, **(+)-D9**.

	λ_{abs}[a] / nm (ε 10^{-3} / $M^{-1}cm^{-1}$)	λ_{em}[b] / nm (τ/μs ; Φ)[c]
D1	284 (25.6), 329 (13.8), 360 (6.9), 412 (2.2)	544 (0.021)
D2	283 (25.5), 329 (13.4), 359 (7.2), 410 (2.1)	544 (0.020)
D3	266 (23.0), 284 (24.3), 324 (1.35), 366 (5.2), 404 (2.5)	-
D4	285 (26.5), 329 (13.4), 360 (6.9), 410 (2.2)	593 (< 0.01)
D6	284 (27.1), 328 (13.8), 360 (6.9), 410 (2.3)	566 (0.038)
D7	285 (26.5), 329 (13.3), 360 (7.0), 410 (2.2)	570 (0.062)
(-)-D8	282 (22.3), 328 (11.9), 360 (6.9), 411 (2.2)	567 (0.029)
(+)-D8	282 (22.3), 328 (11.9), 360 (6.9), 411 (2.2)	567 (0.029)

[a] Measured in CH_2Cl_2 solution at 298 K (C ≈ 10^{-5} M). [b] In degassed CH_2Cl_2 solution at 298 K (C ≈ 10^{-5} M). [c] With $Ru(bpy)_3Cl_2$ as reference.

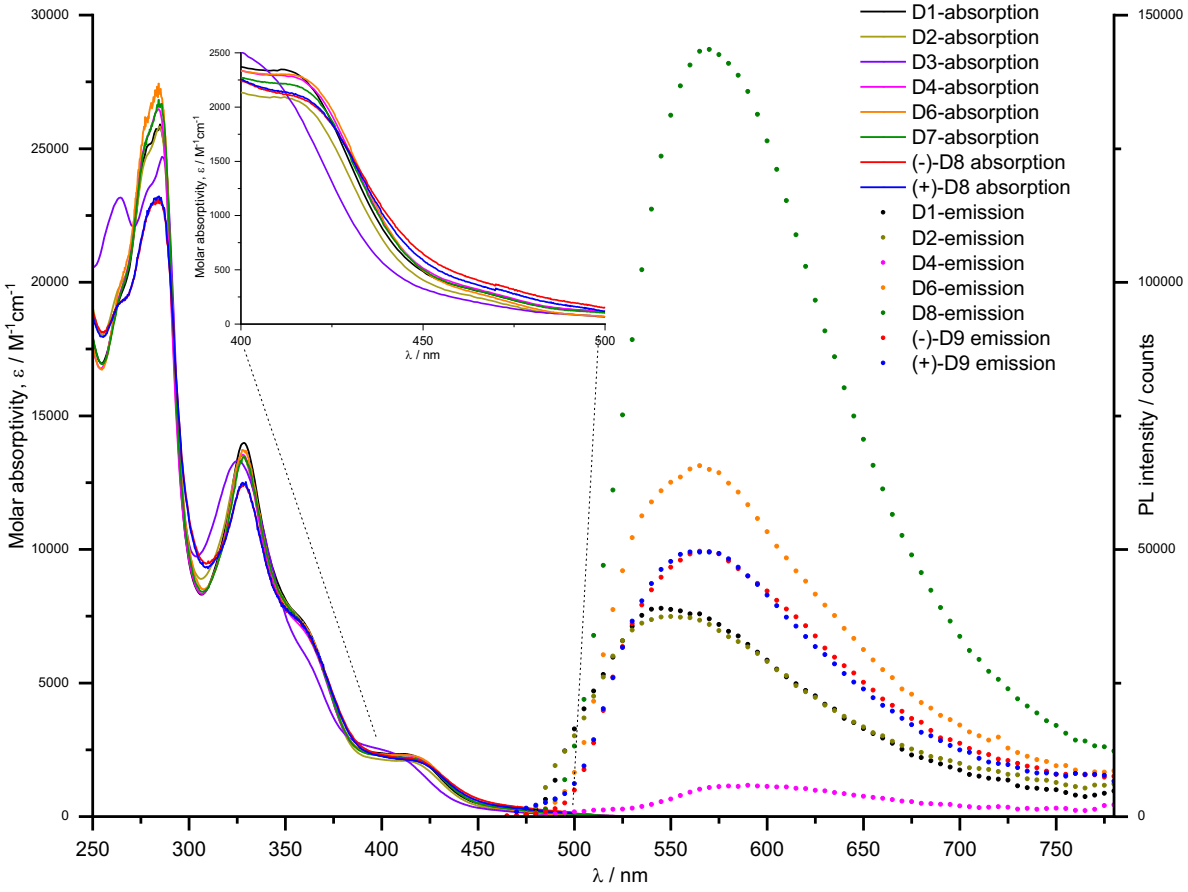


Figure S1. Absorption and emission spectra in CH_2Cl_2 at 298 K (C ≈ 10^{-5} M) of the **D** series of complexes (λ_{ex} = 400 nm).

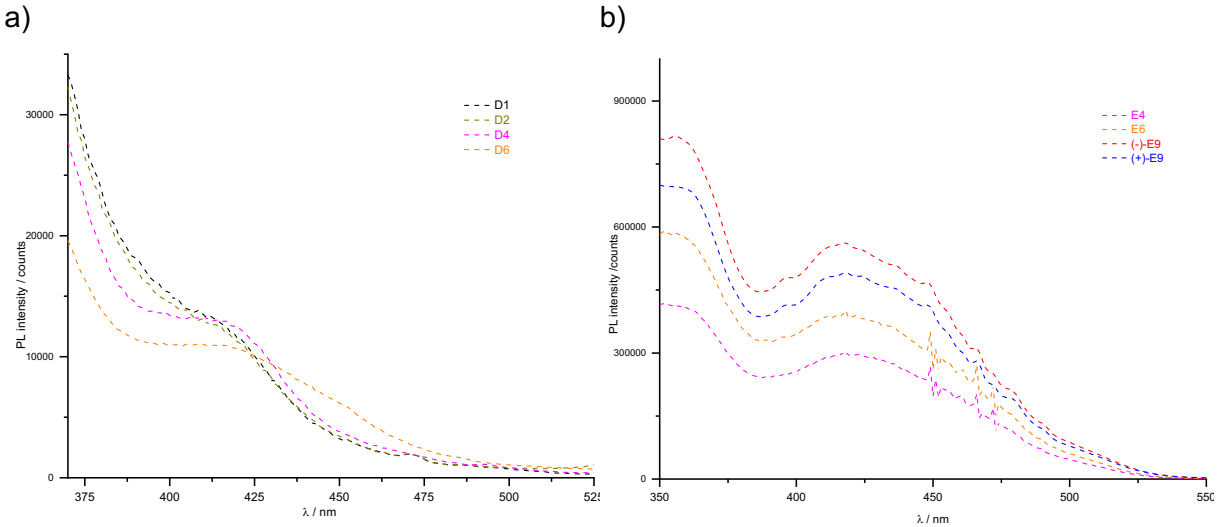


Figure S2. Excitation spectra in degassed CH_2Cl_2 at 298 K of a) **D1**, **D2**, **D4** and **D6** (λ_{em} = 550 nm) and b) **E4**, **E6**, **(-)-E9** and **(+)-E9** (λ_{em} = 584 nm).

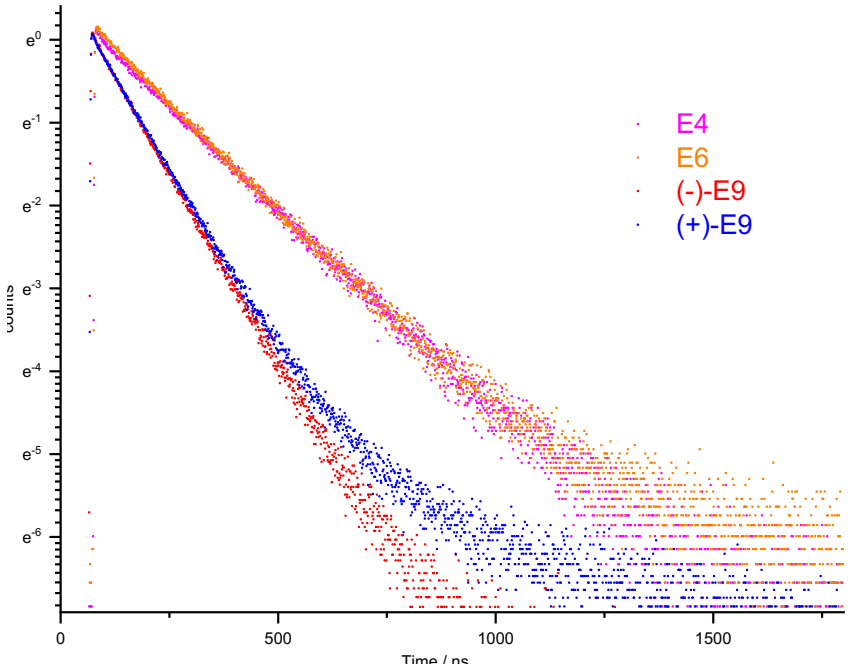
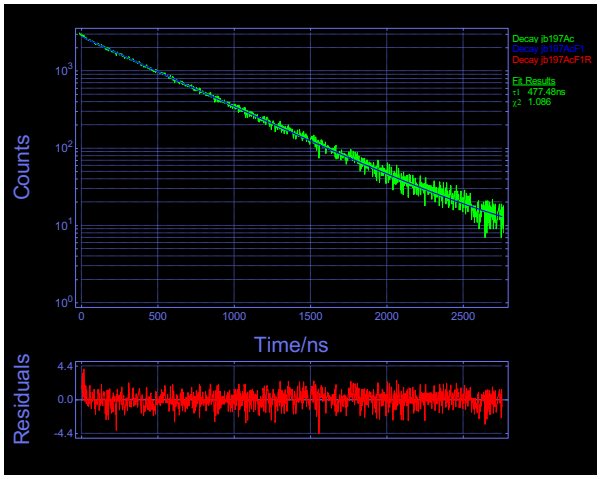


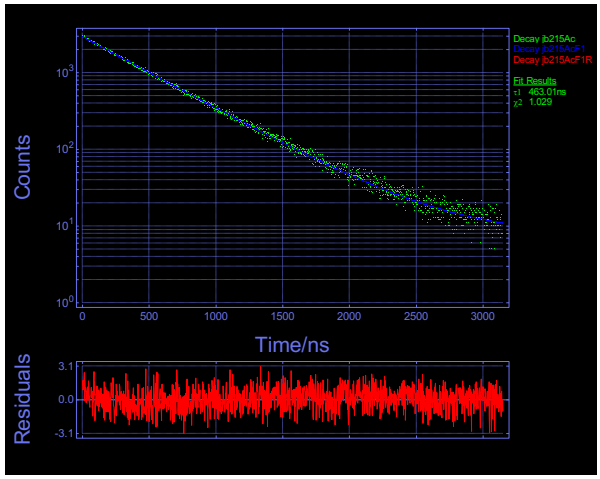
Figure S3. Emission decay curves of **E4**, **E6**, **(-)-E9** and **(+)-E9** in degassed CH_2Cl_2 at 298 K, λ_{ex} = 375 nm.

Table S2. Fitting of luminescence decays in degassed dichloromethane at 298 K for complexes **E4**, **E6**, **(-)-E9** and **(+)-E9** ($C \approx 10^{-5}$ M, λ_{ex} = 375 nm). Experimental decays in green, monoexponential fits in blue and residual traces in red.

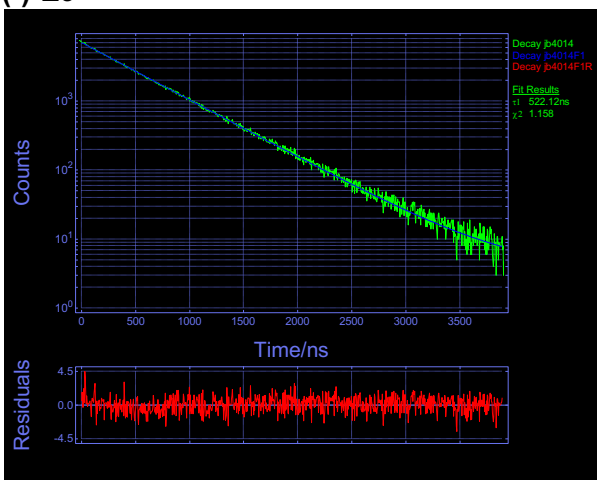
E4



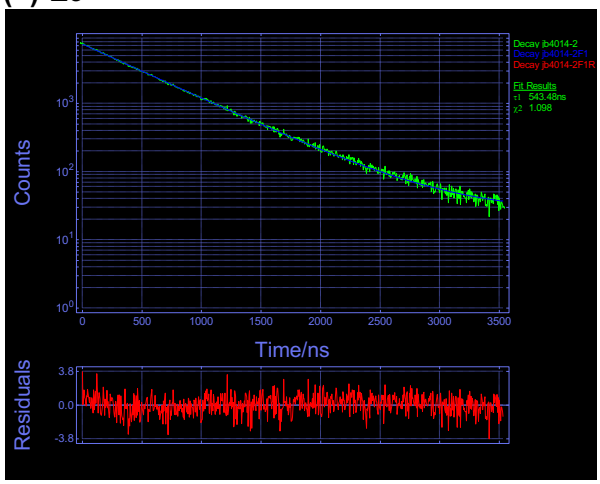
E6



(-)-E9



(+)-E9



8. References

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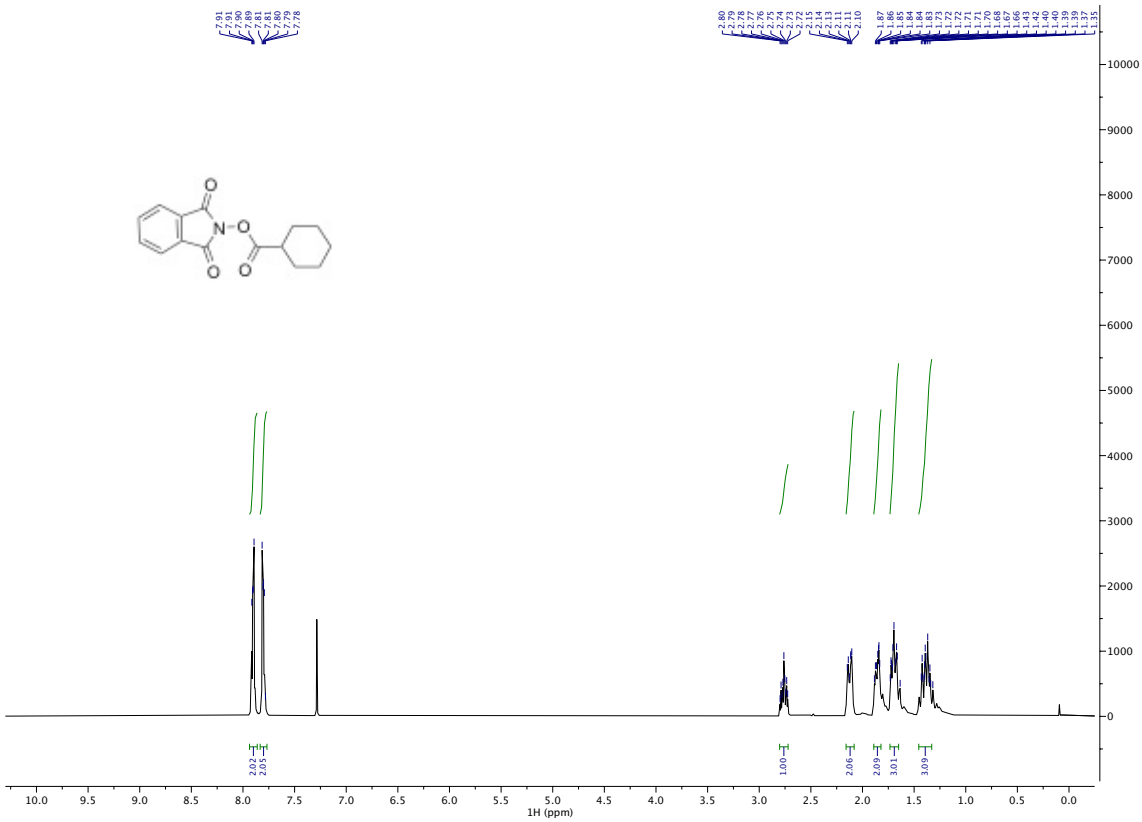
9. Copy of the NMR spectrum

B1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7.78
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2.79
2.78
2.77
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1.86
1.85
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1.71
1.71
1.70
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1.66
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1.42
1.40
1.40
1.39
1.39
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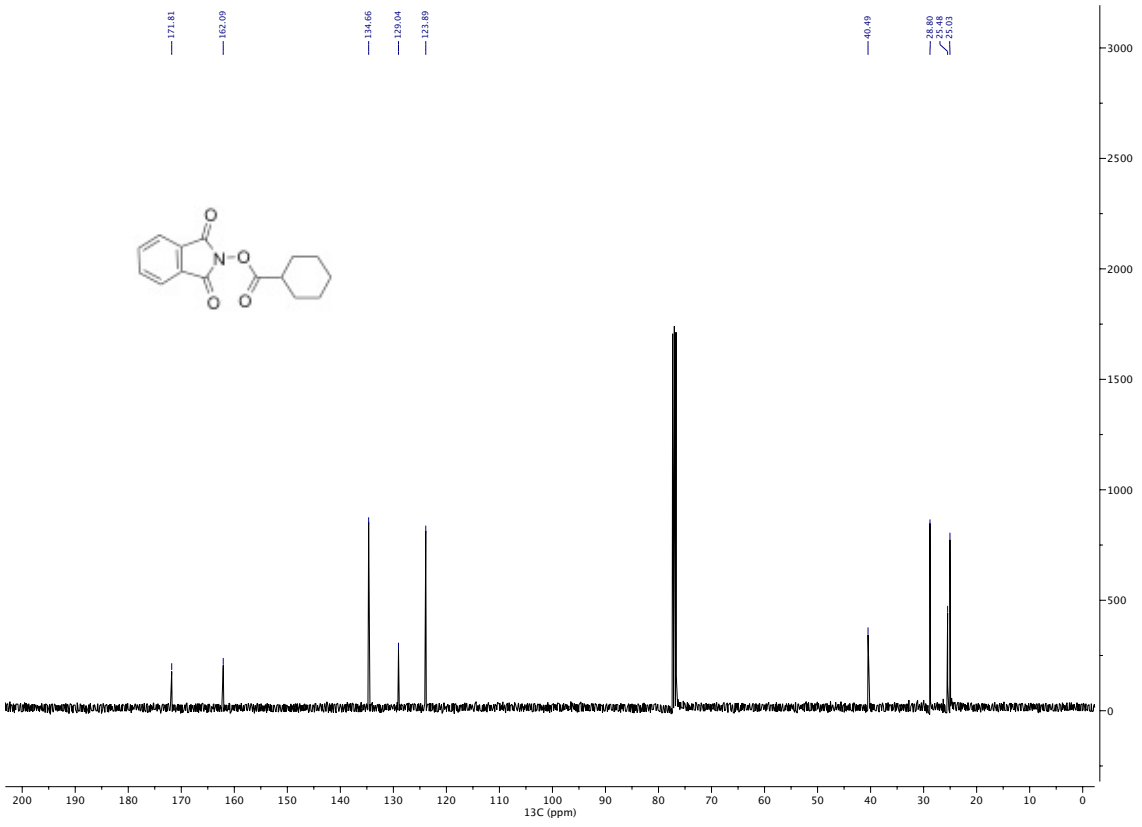
2.05
1.00
2.06
2.09
3.01
3.09
1H (ppm)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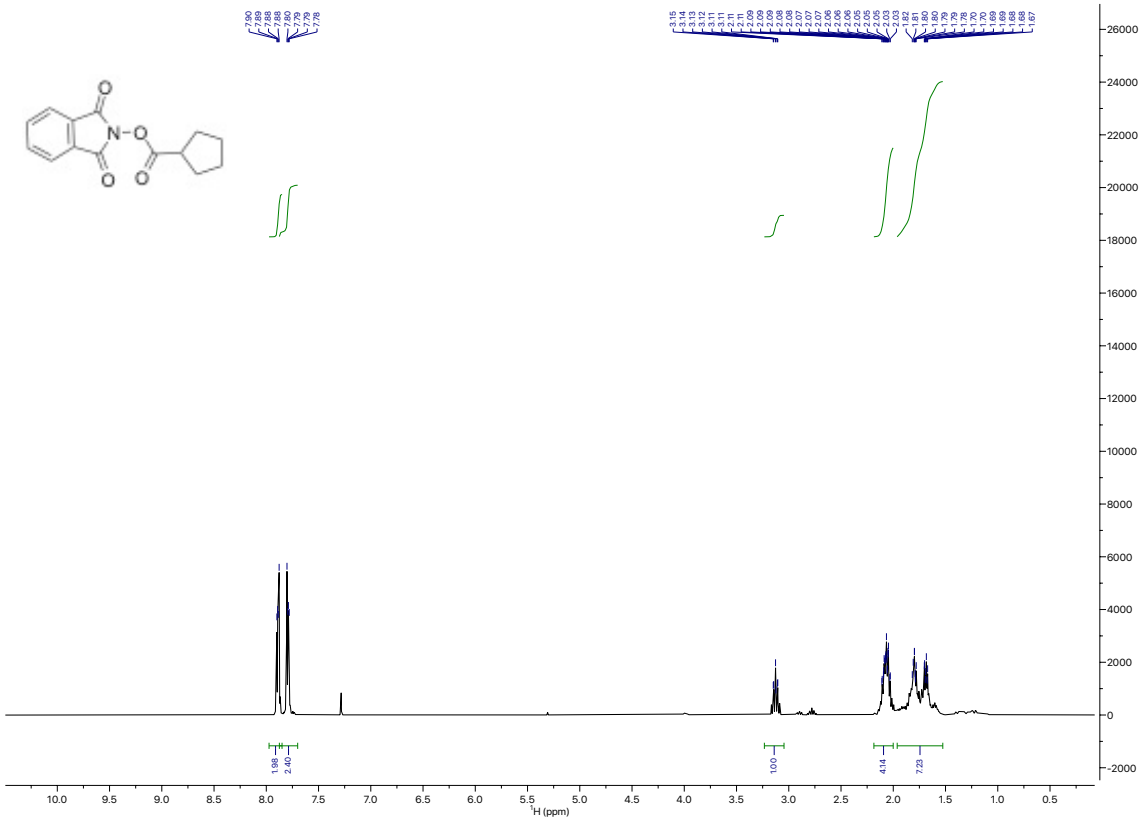
25.03
13C (ppm)

B2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3.12
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2.06
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1.69
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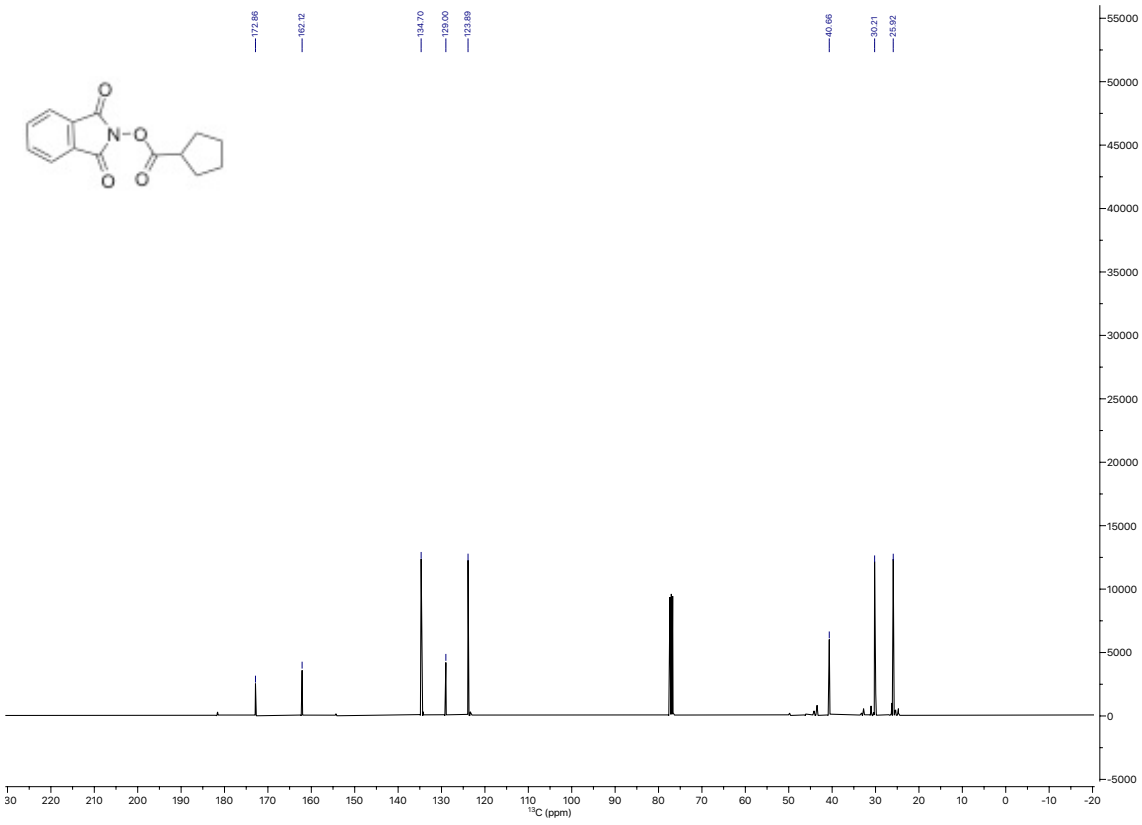
1.00
4.14
7.23
^{1}H (ppm)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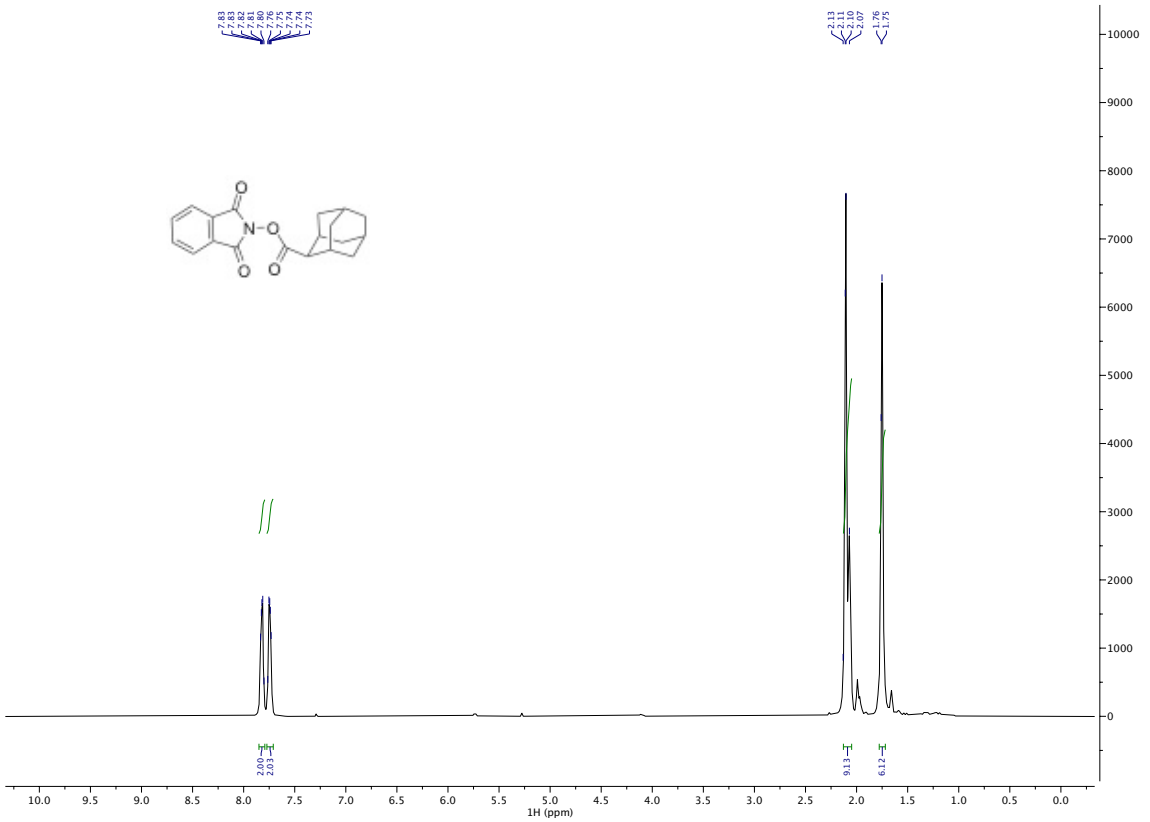
N
O
O
O
^{13}C (ppm)

B3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2.00
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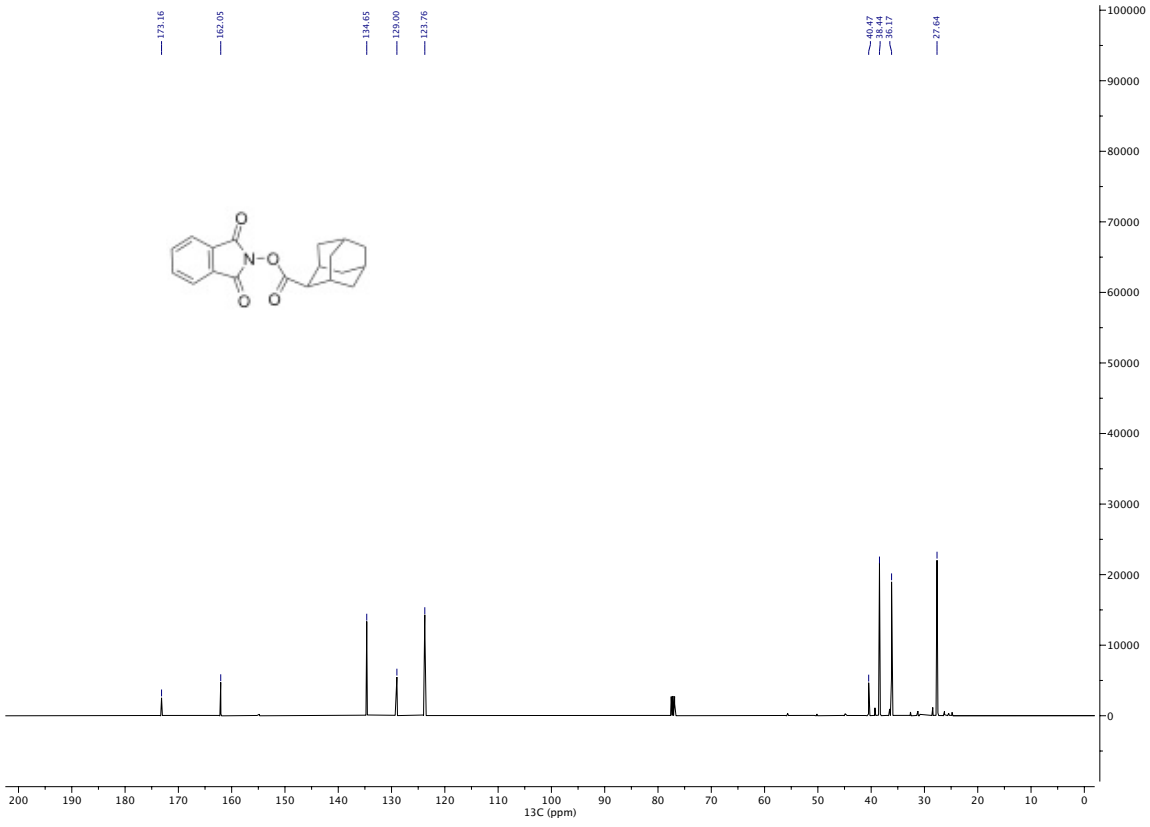
9.13
6.12
1H (ppm)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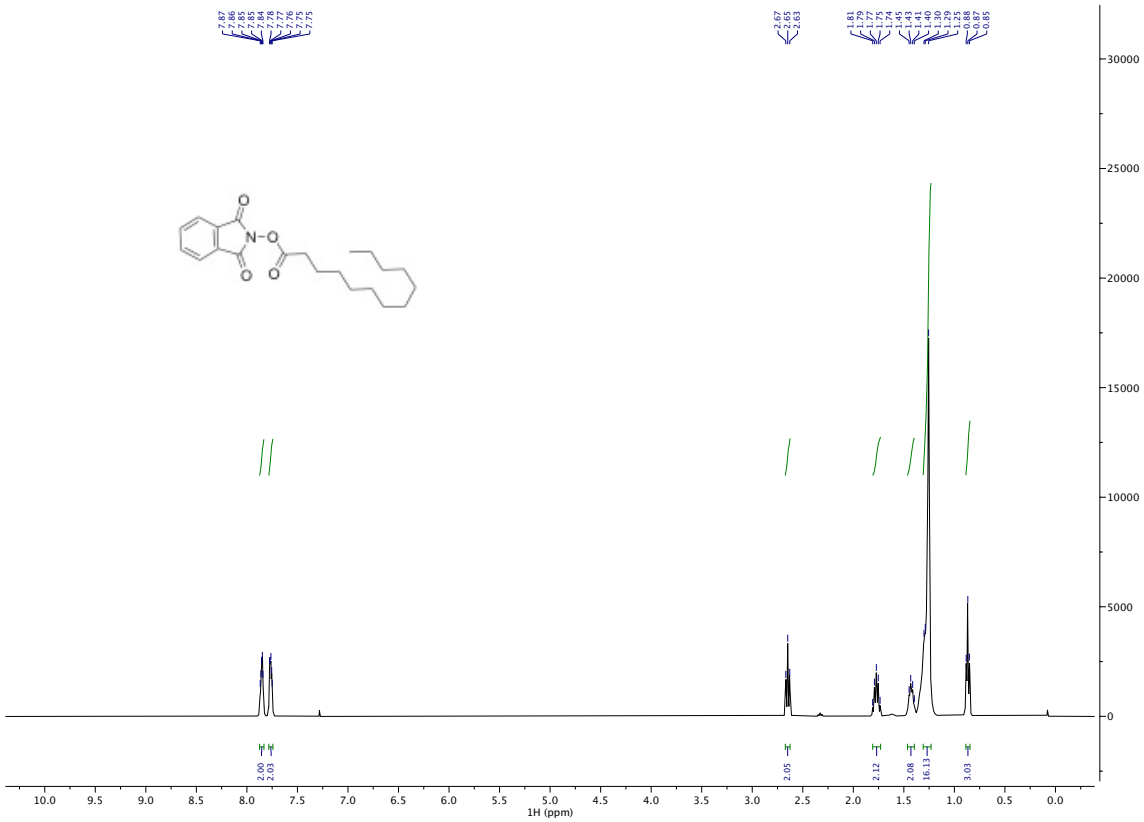
B4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1.79
1.77
1.75
1.74
1.45
1.43
1.41
1.40
1.30
1.29
1.25
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0.87
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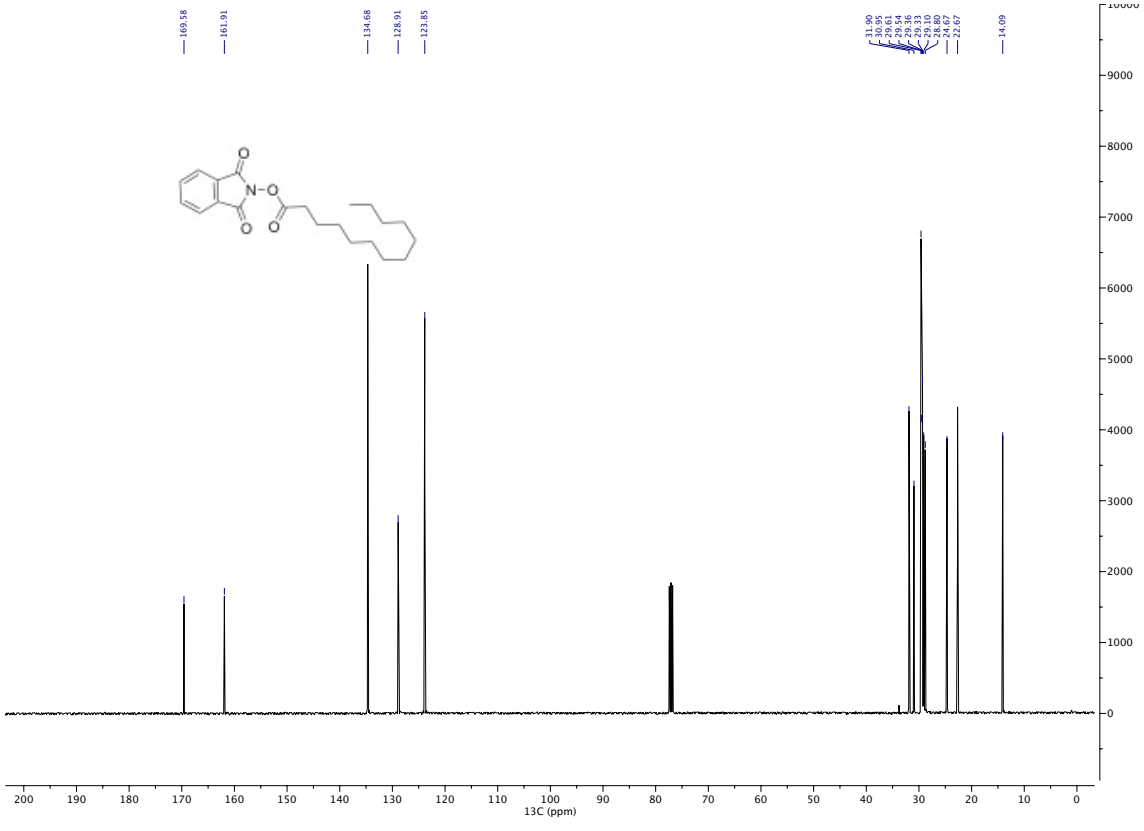
2.05
2.12
2.08
16.13
3.03
1H (ppm)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29.10
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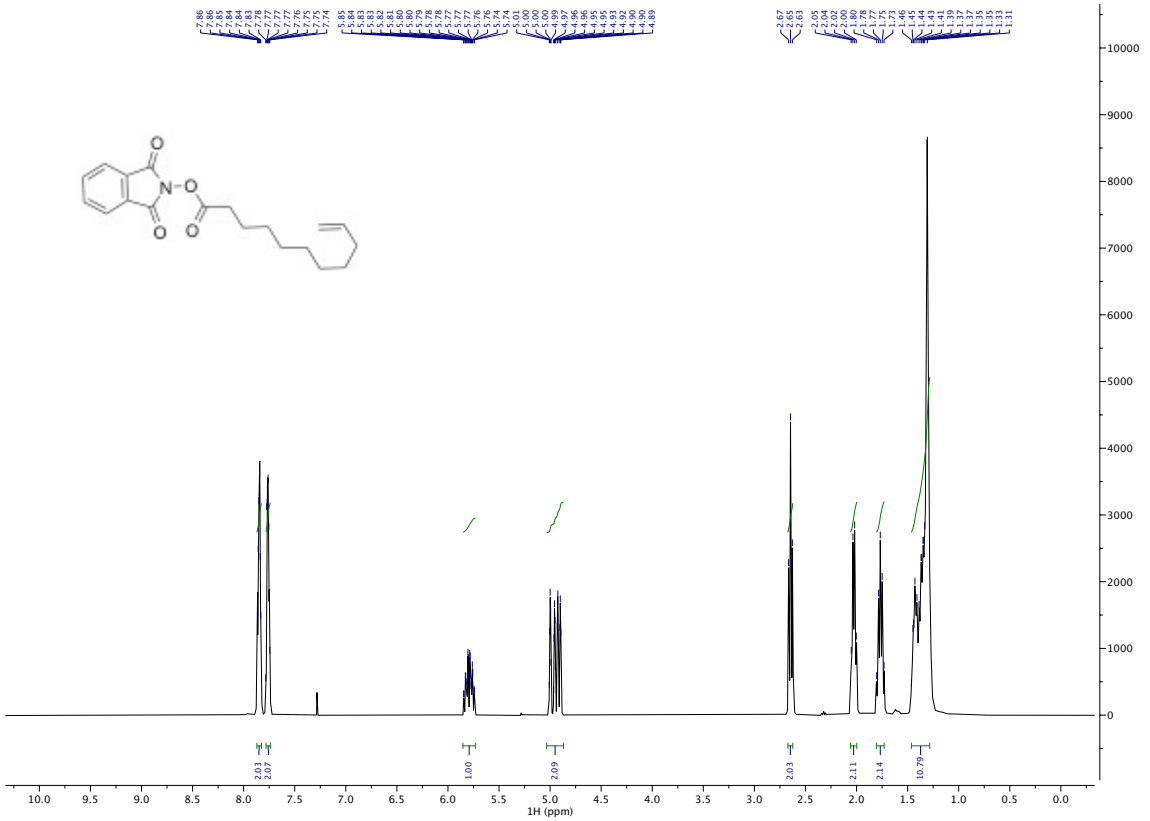
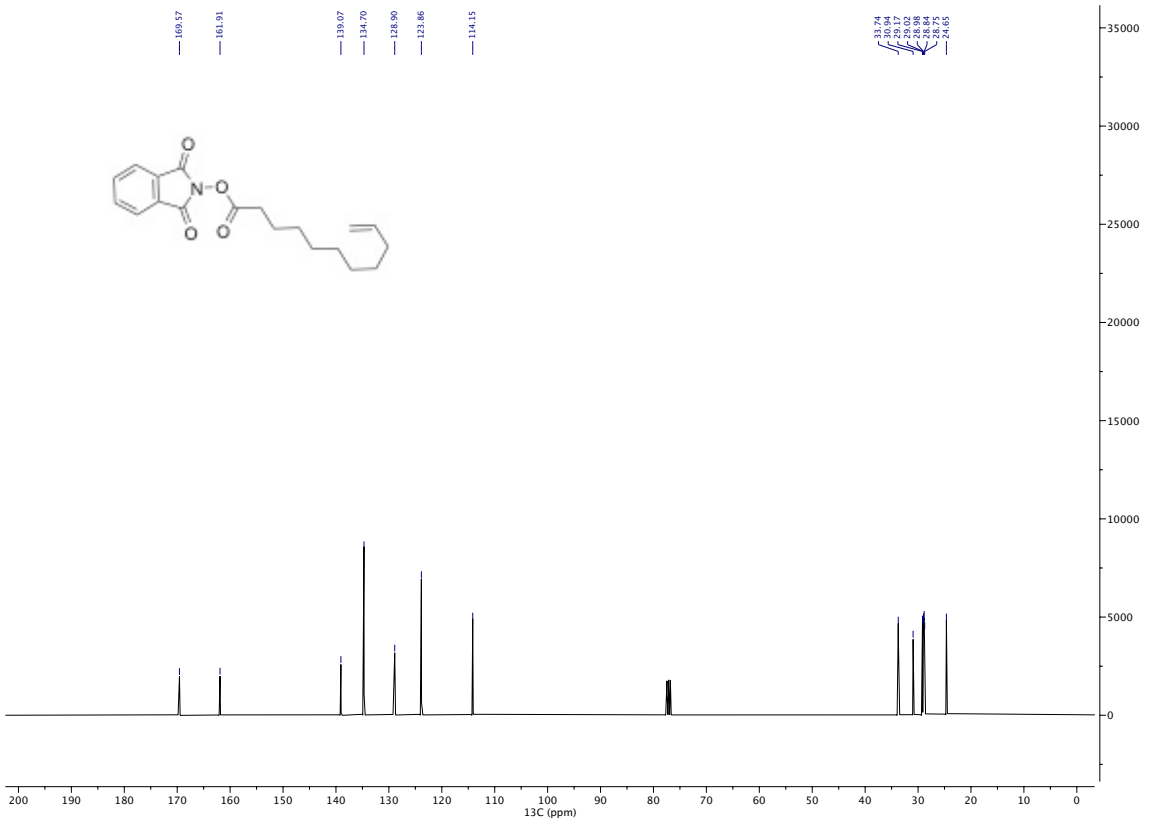
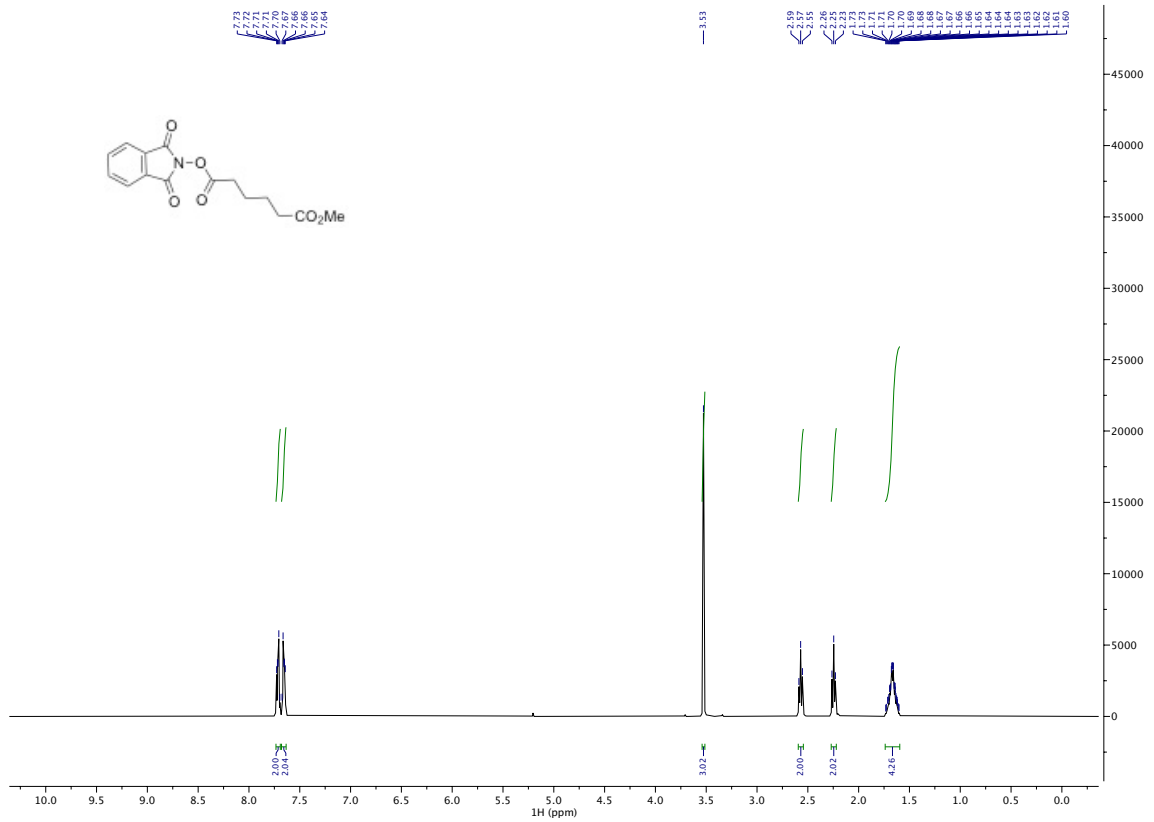
24.67
22.67
14.09
13C (ppm)

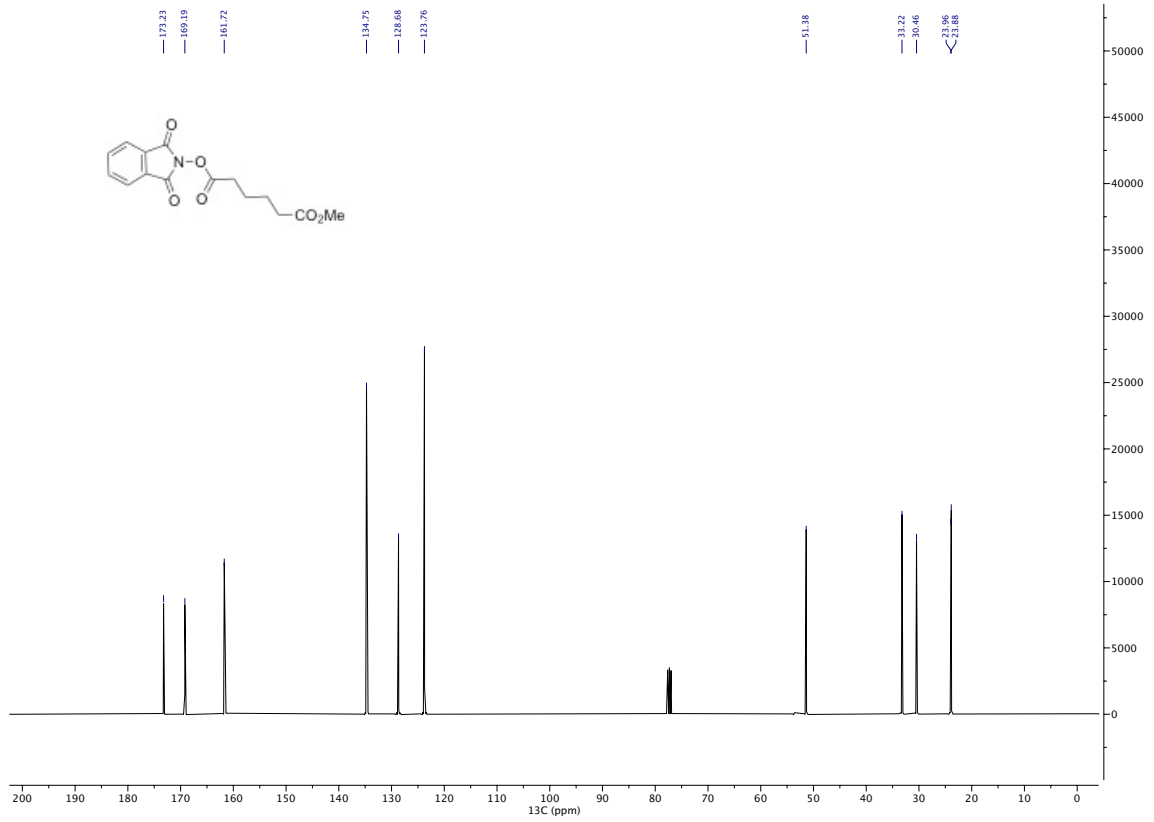
B5



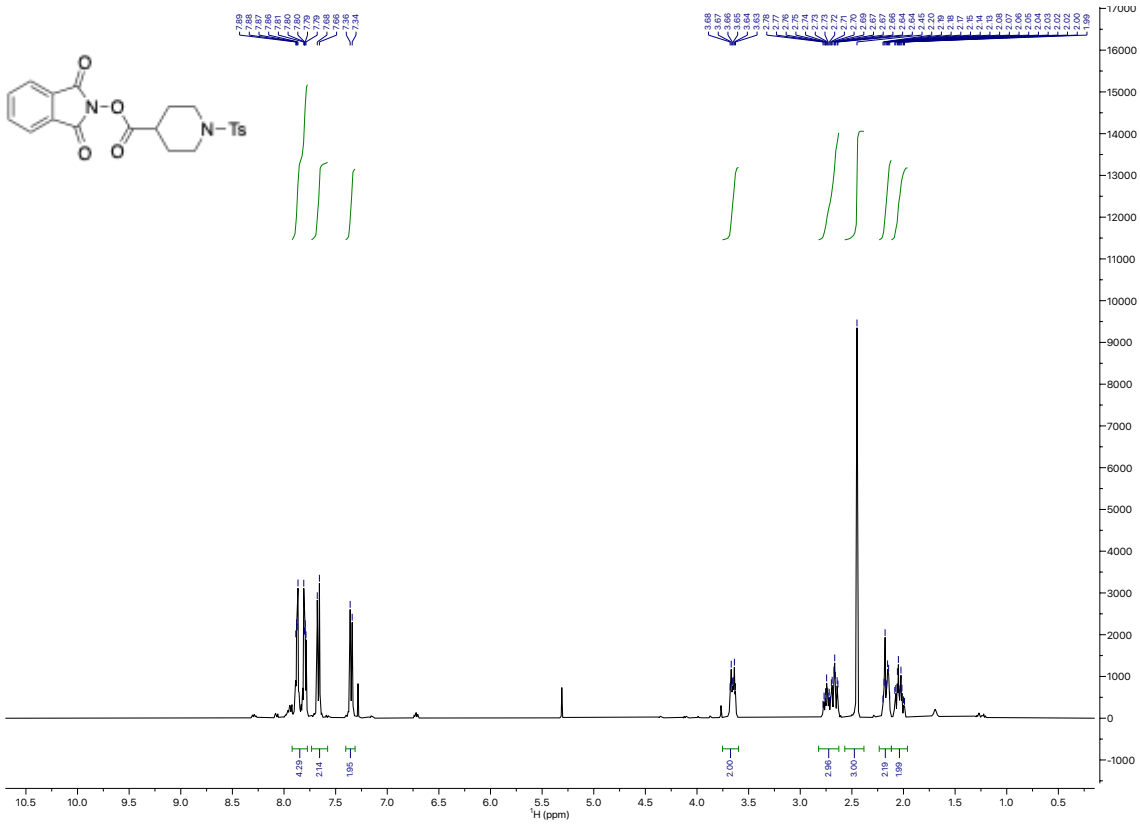


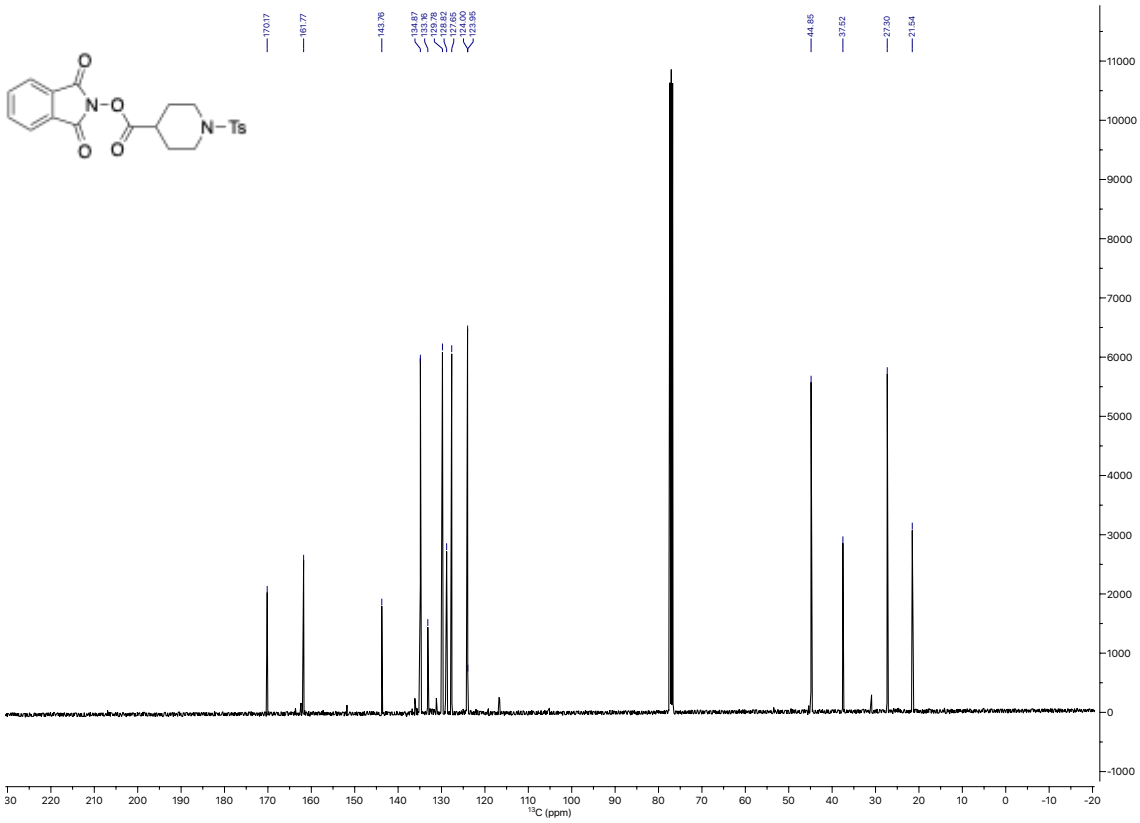
B6


7.73
7.72
7.72
7.71
7.70
7.67
7.66
7.66
7.65
7.64
3.53
2.59
2.57
2.55
2.26
2.25
2.23
1.73
1.73
1.71
1.71
1.70
1.70
1.69
1.68
1.68
1.67
1.67
1.66
1.66
1.65
1.64
1.64
1.63
1.63
1.62
1.62
1.61
1.60
O
N-O
O
O
CO2Me
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
2.00
2.04
3.02
2.00
2.02
4.26
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H (ppm)

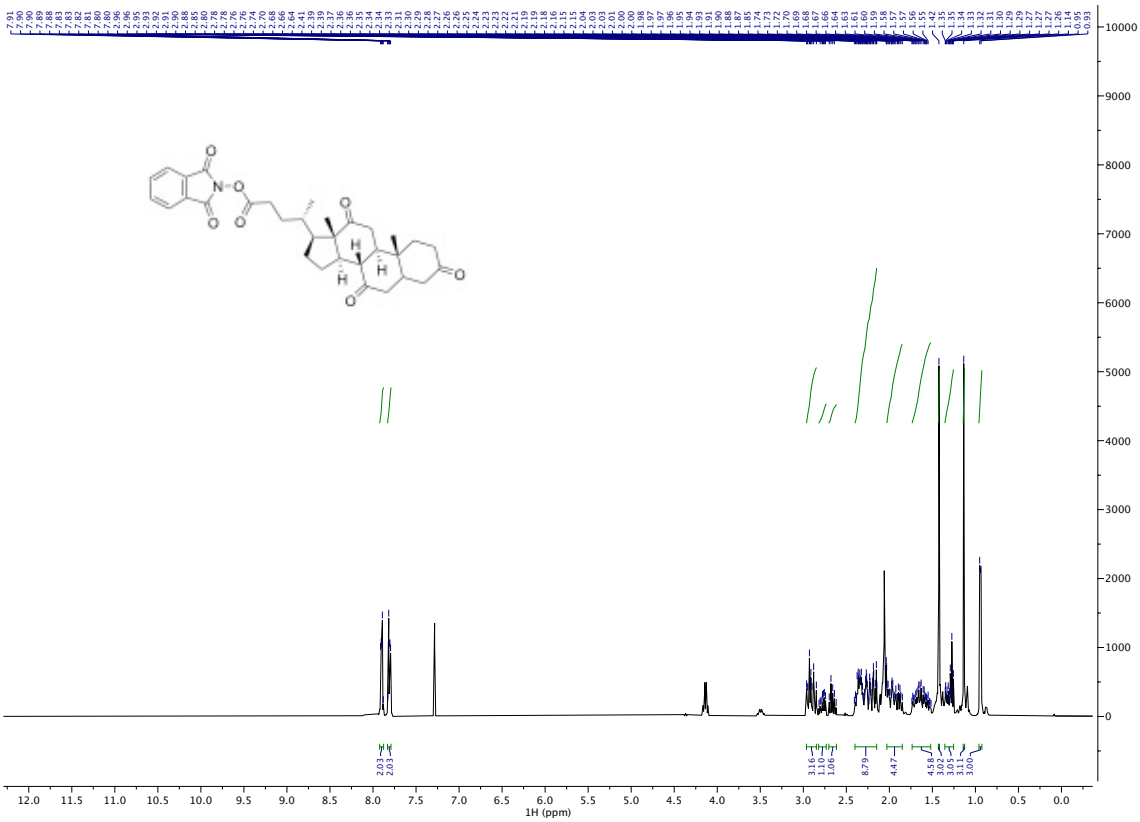

173.23
169.19
161.72
134.75
128.68
123.76
51.38
33.22
30.46
23.96
23.88
O
N-O
O
O
CO2Me
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C (ppm)

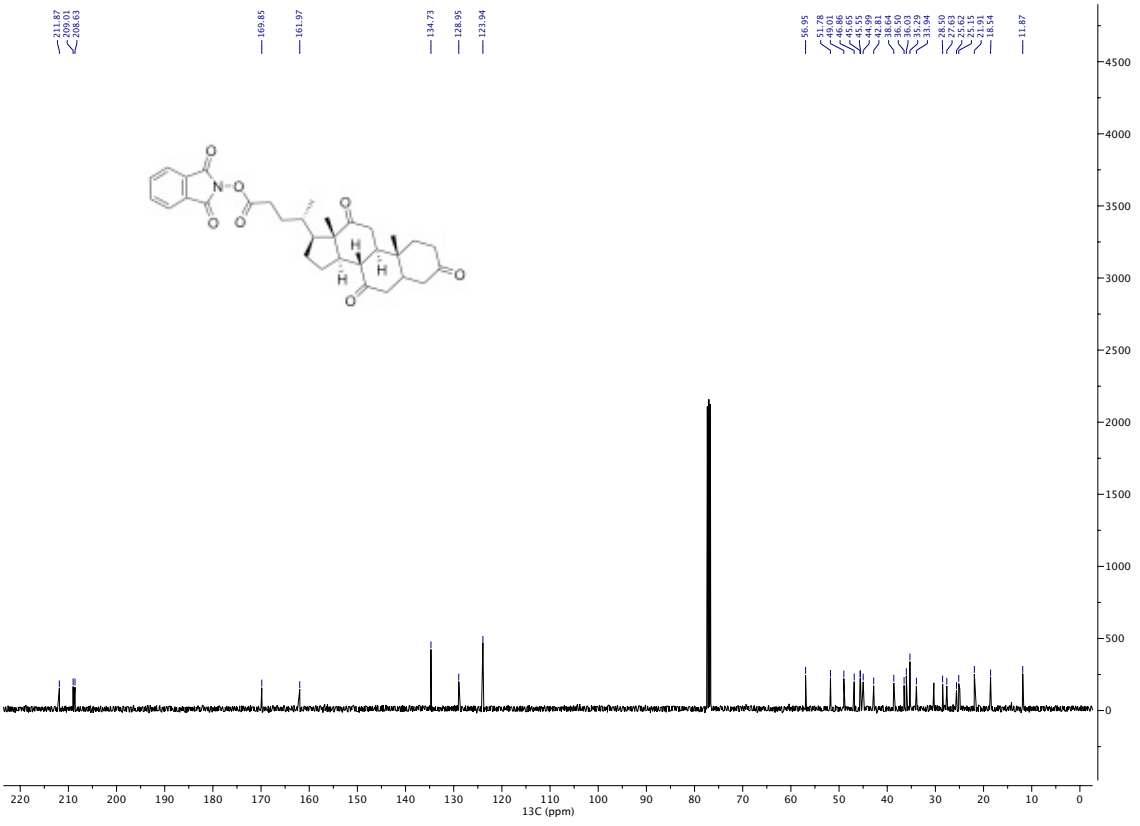
B7


N-Ts
4.29
2.14
1.95
2.00
2.96
3.00
2.19
1.99
^{1}H (ppm)

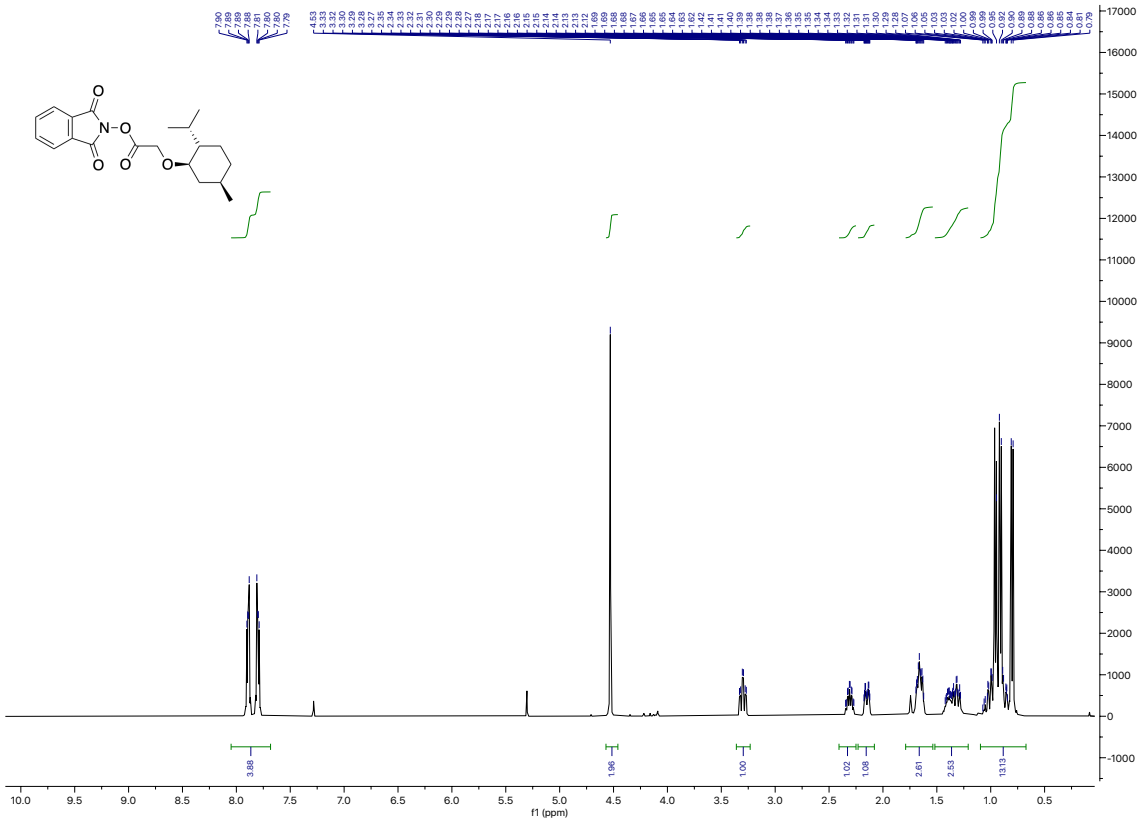

N-Ts
170.17
161.77
143.76
134.87
133.95
133.78
128.82
127.65
124.00
123.95
44.85
37.52
27.30
21.54
^{13}C (ppm)

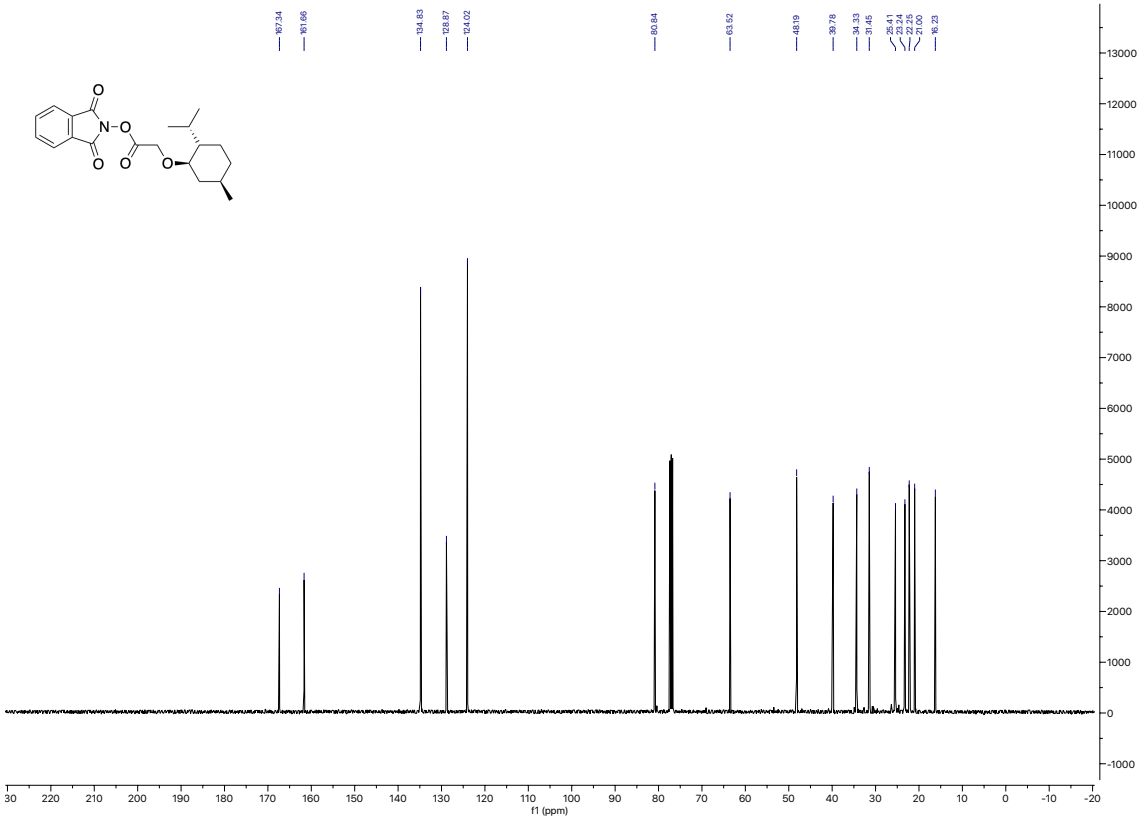
B8



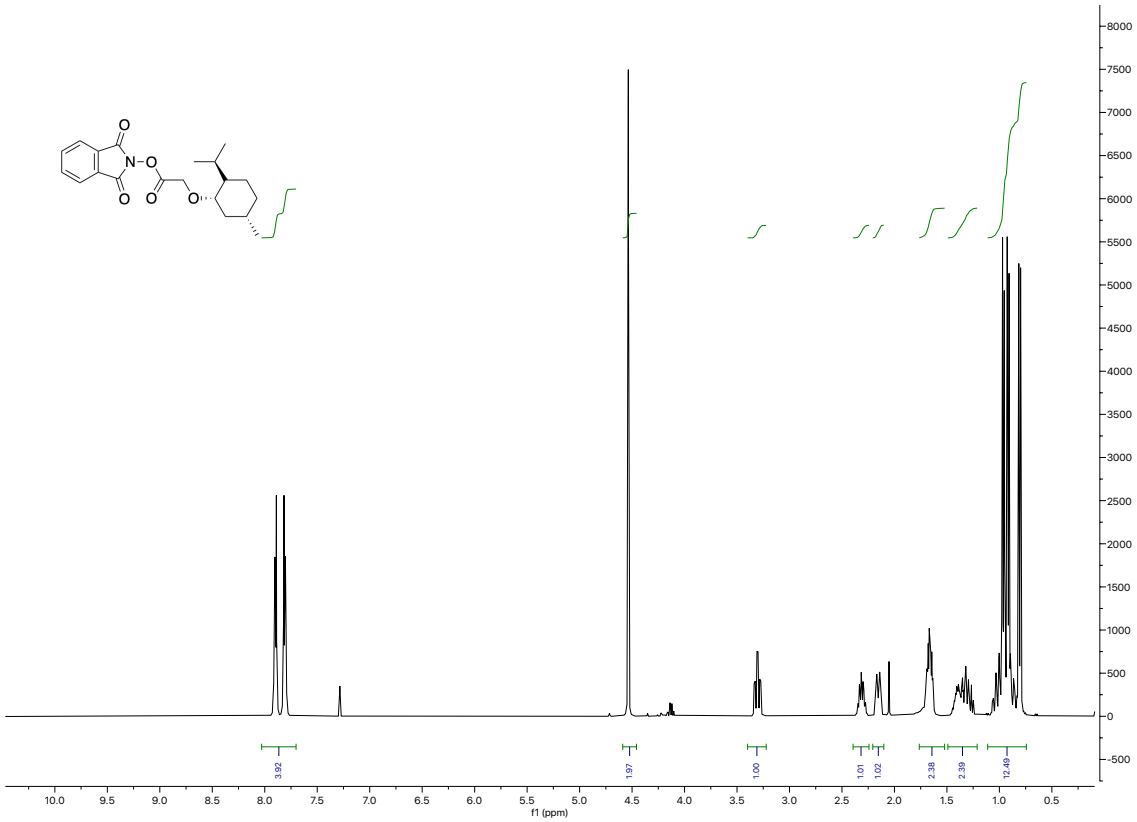


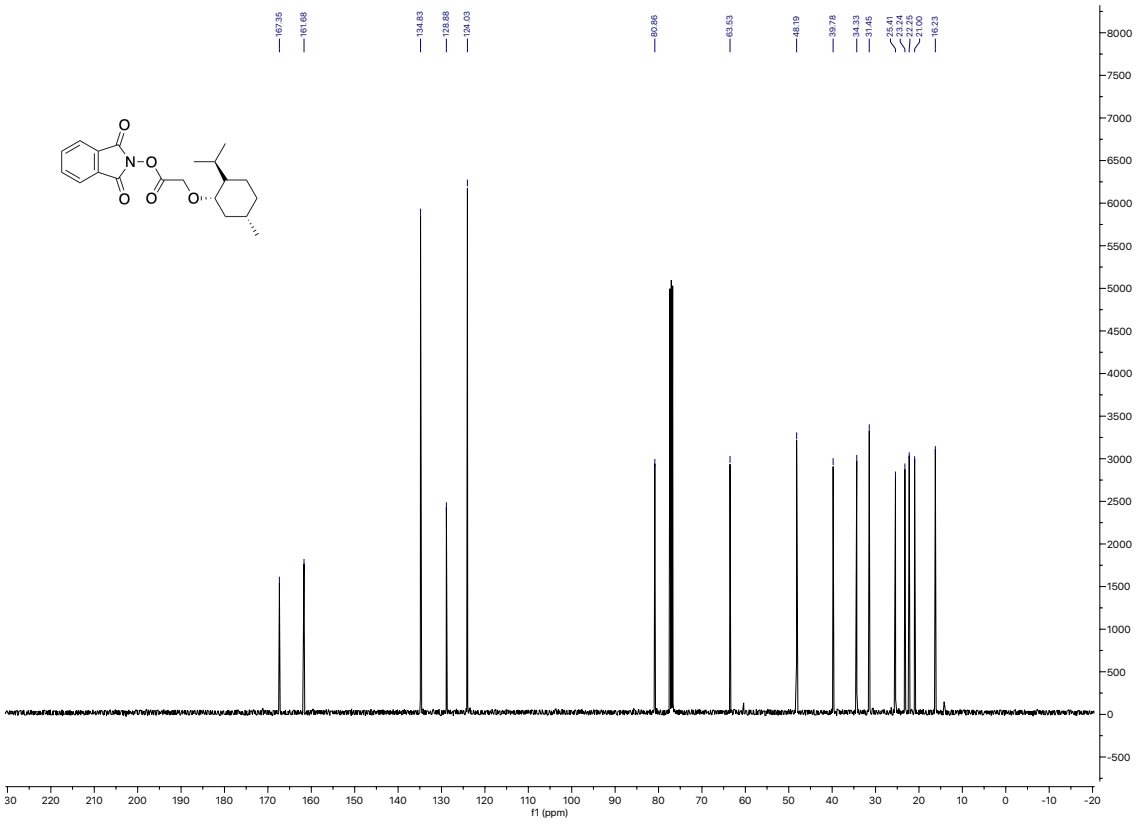
(-)-B9



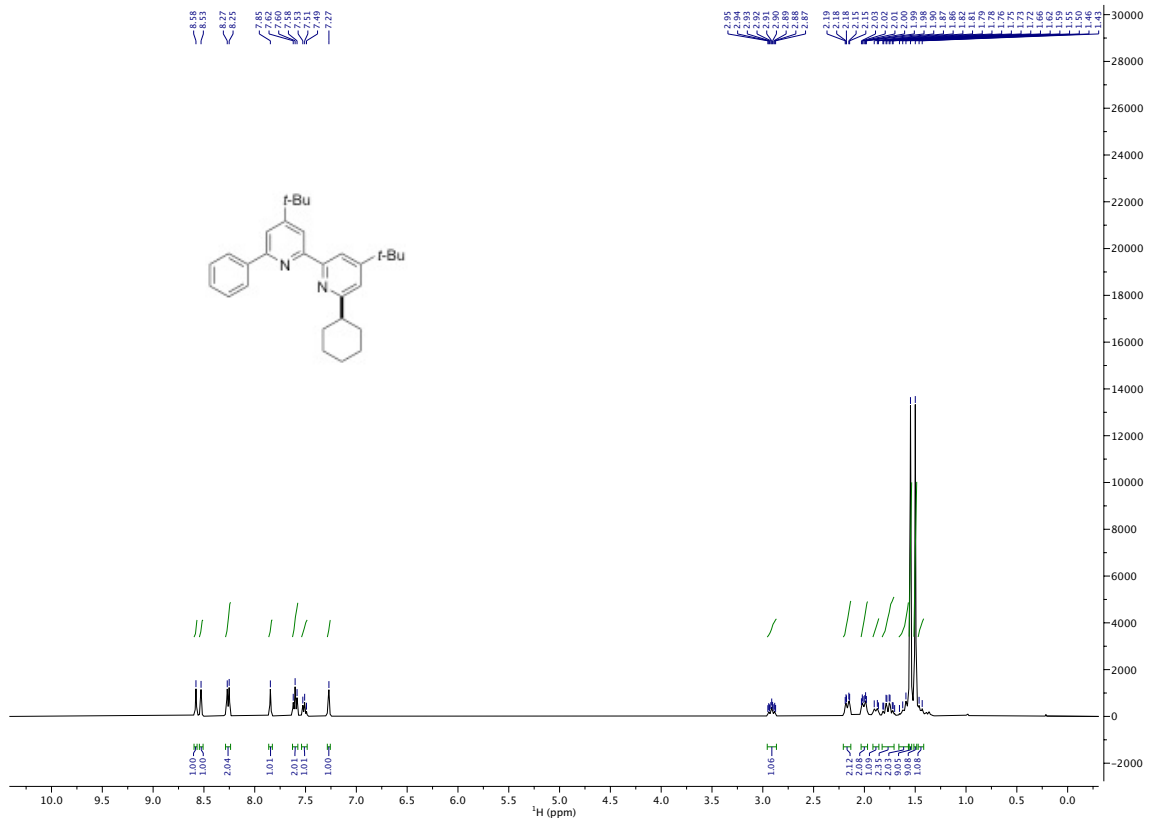


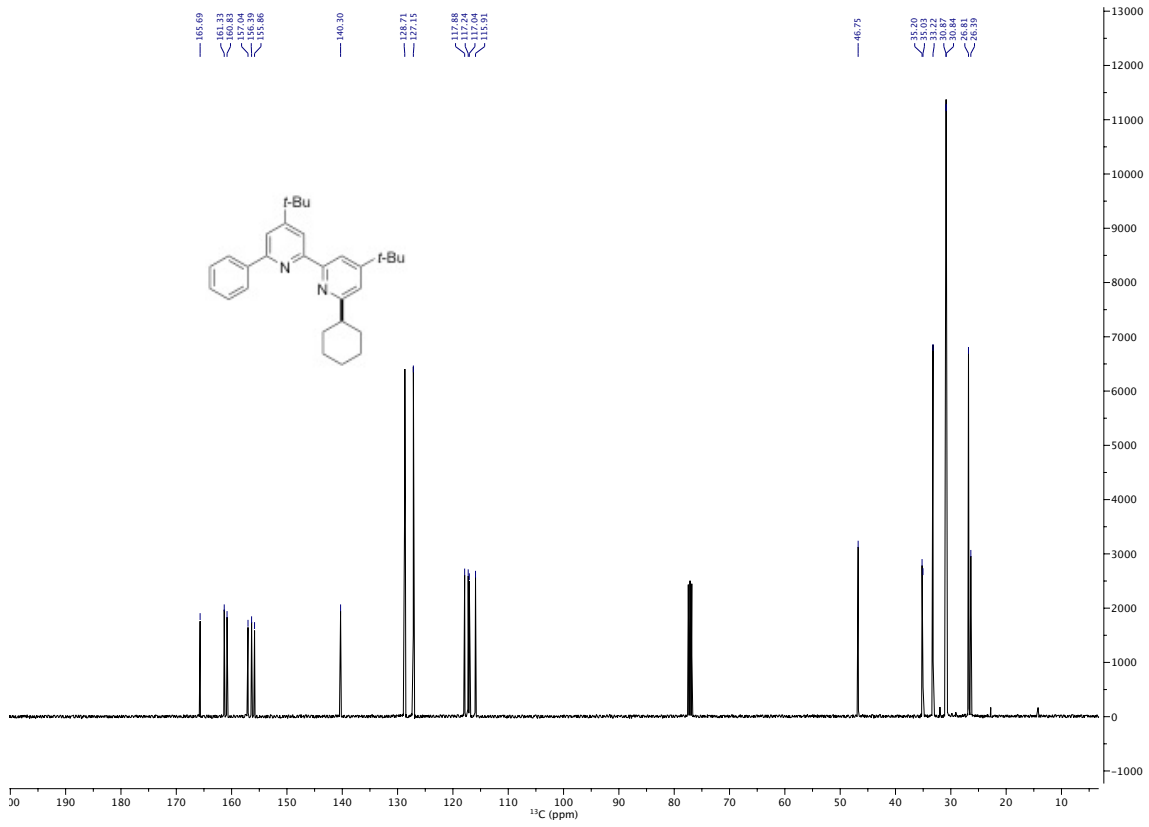
(+)-B9


3.92
1.97
1.00
1.01
1.02
2.38
2.39
12.49
f1 (ppm)

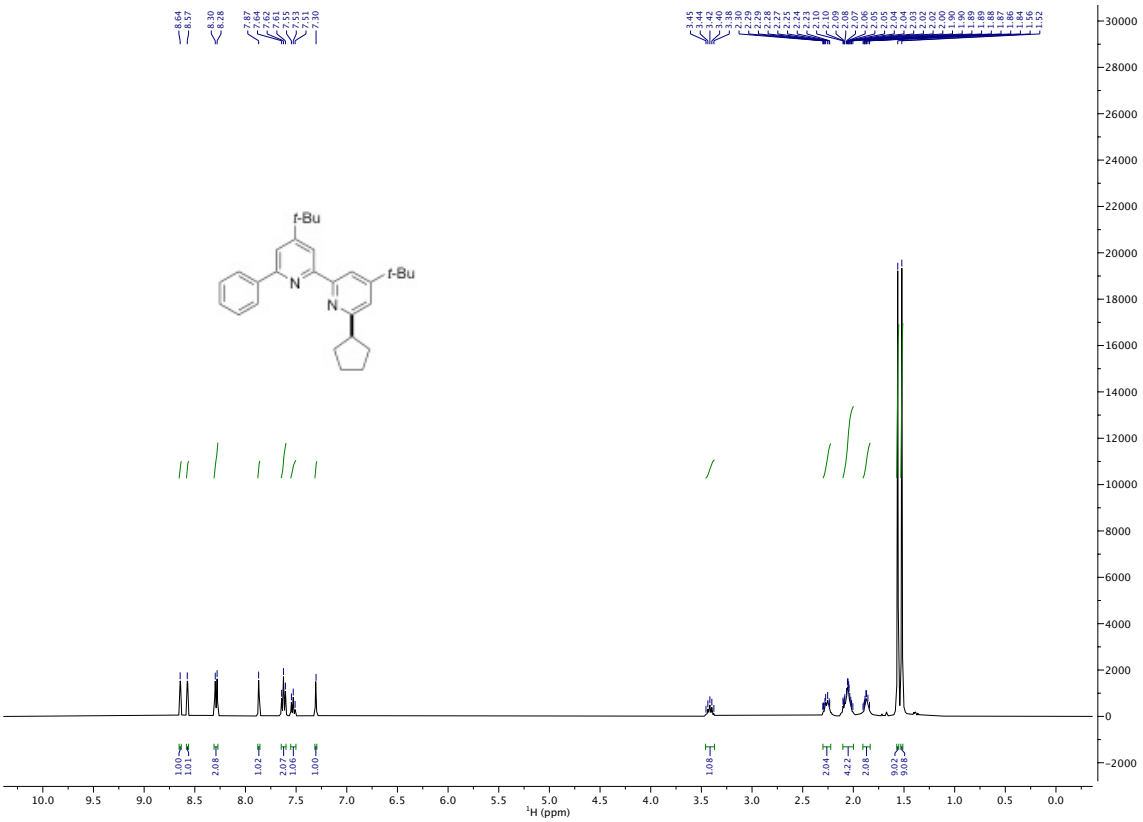

167.35
161.68
134.83
128.88
124.03
80.86
63.53
48.19
39.78
34.33
31.45
25.41
23.14
22.25
21.00
16.23
f1 (ppm)

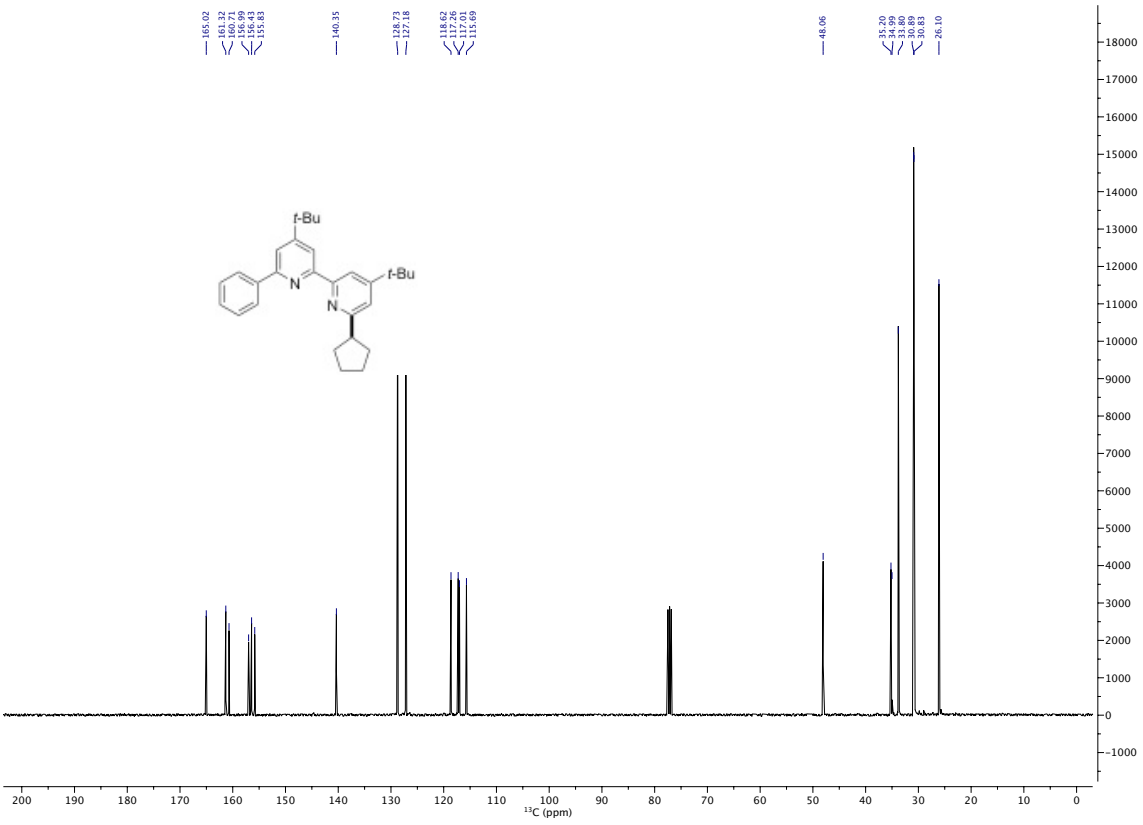
C1


8.58
8.53
8.27
8.25
7.85
7.62
7.60
7.58
7.53
7.51
7.49
7.27
2.95
2.94
2.93
2.92
2.91
2.90
2.89
2.88
2.87
2.19
2.18
2.18
2.15
2.15
2.03
2.02
2.01
2.00
1.99
1.98
1.90
1.87
1.86
1.82
1.81
1.79
1.78
1.76
1.75
1.73
1.72
1.66
1.62
1.59
1.55
1.50
1.46
1.45
t-Bu
t-Bu
N
N
1.00
1.00
2.04
1.01
2.01
1.01
1.00
1.06
2.12
2.06
1.09
2.15
2.03
9.01
9.08
1.08
^{1}H (ppm)

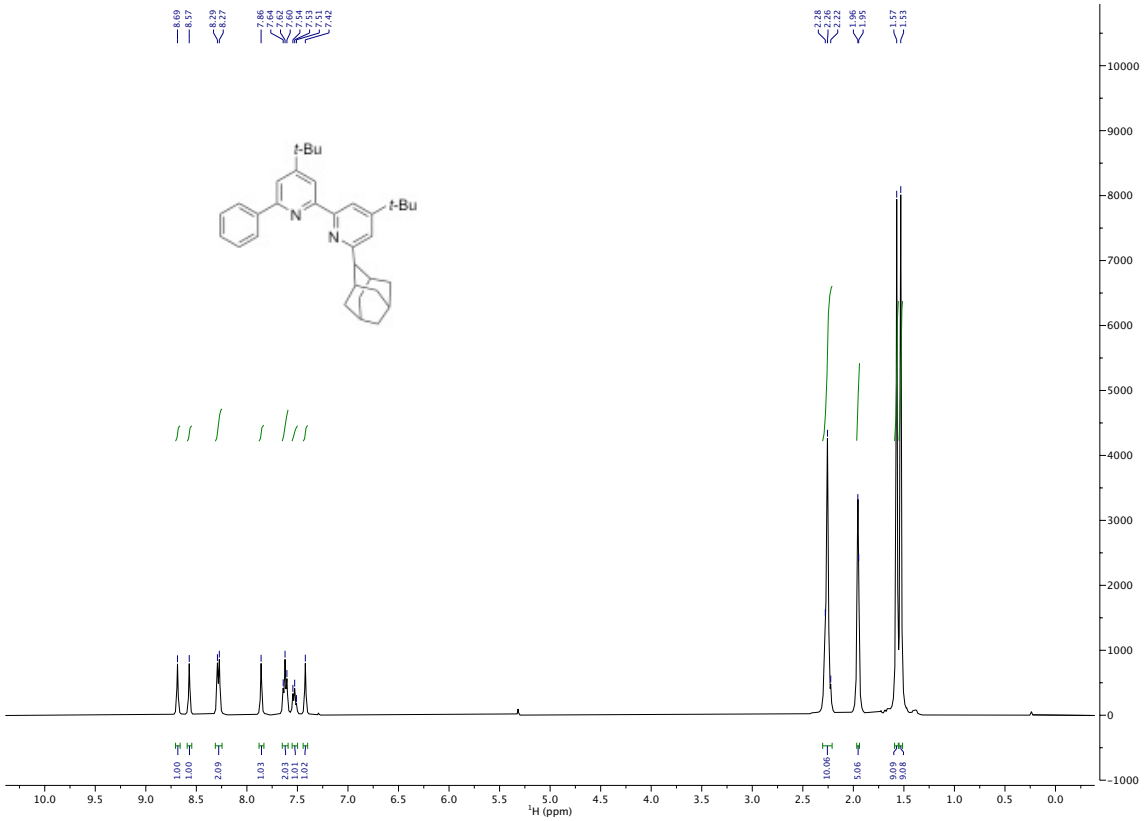

165.69
161.33
160.68
157.04
156.39
155.86
140.30
128.71
127.15
117.88
117.24
117.04
115.91
46.75
35.20
35.03
33.22
30.87
30.84
26.81
26.39
t-Bu
t-Bu
N
N
^{13}C (ppm)

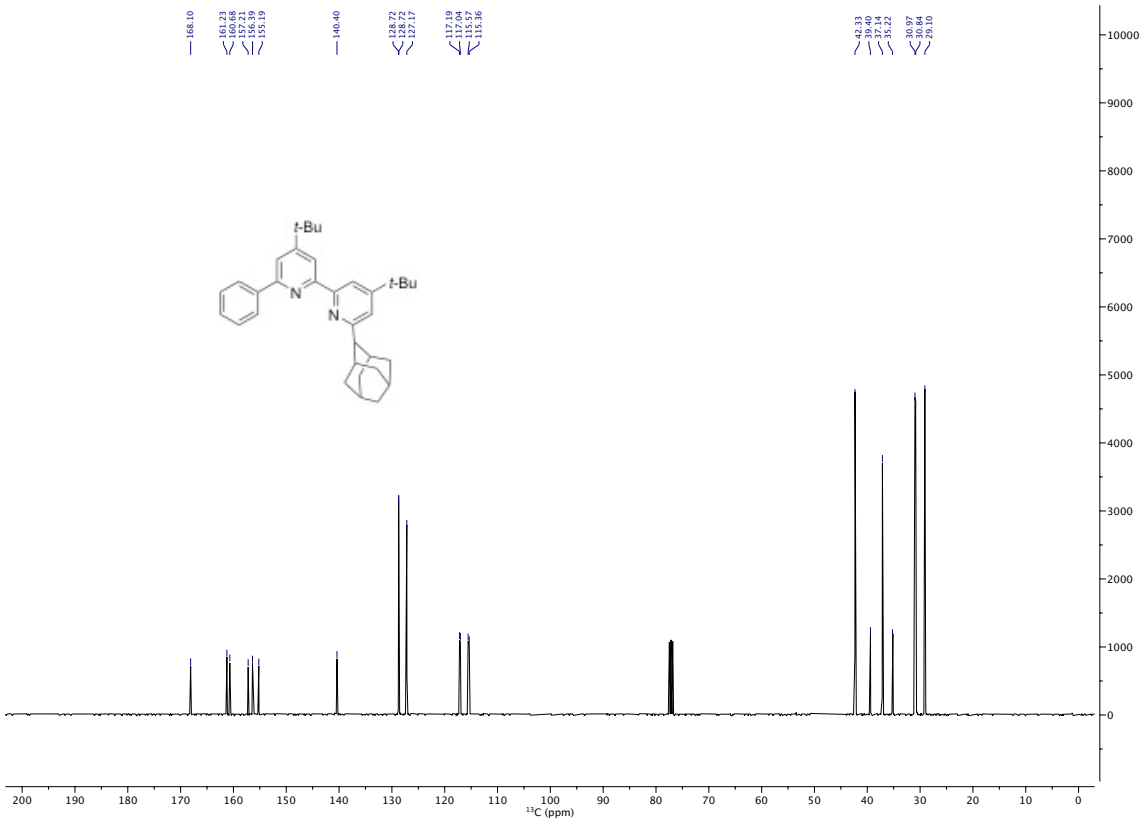
C2


8.64
8.57
8.30
8.28
7.87
7.64
7.62
7.61
7.55
7.53
7.51
7.30
3.45
3.44
3.42
3.40
3.38
2.30
2.29
2.28
2.27
2.25
2.24
2.23
2.10
2.10
2.09
2.08
2.07
2.06
2.05
2.05
2.04
2.03
2.02
2.02
2.00
1.99
1.90
1.89
1.89
1.88
1.87
1.86
1.84
1.56
1.52
t-Bu
t-Bu
N
N
1.00
1.01
2.08
1.02
2.07
1.06
1.00
1.08
2.04
4.22
2.08
9.02
9.08
^{1}H (ppm)

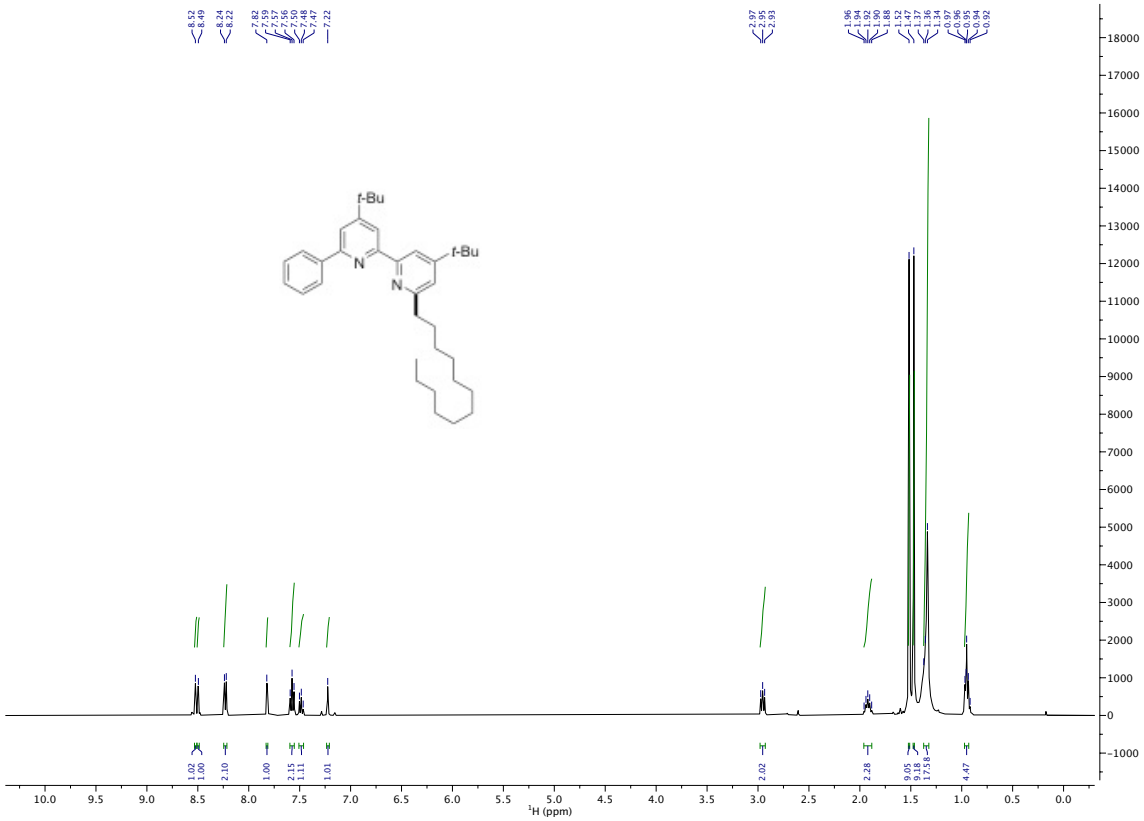

165.02
161.32
160.71
156.99
156.43
155.83
140.35
128.73
127.18
118.62
117.26
117.01
115.69
48.06
35.20
34.99
33.80
30.83
30.83
26.10
t-Bu
t-Bu
N
N
^{13}C (ppm)

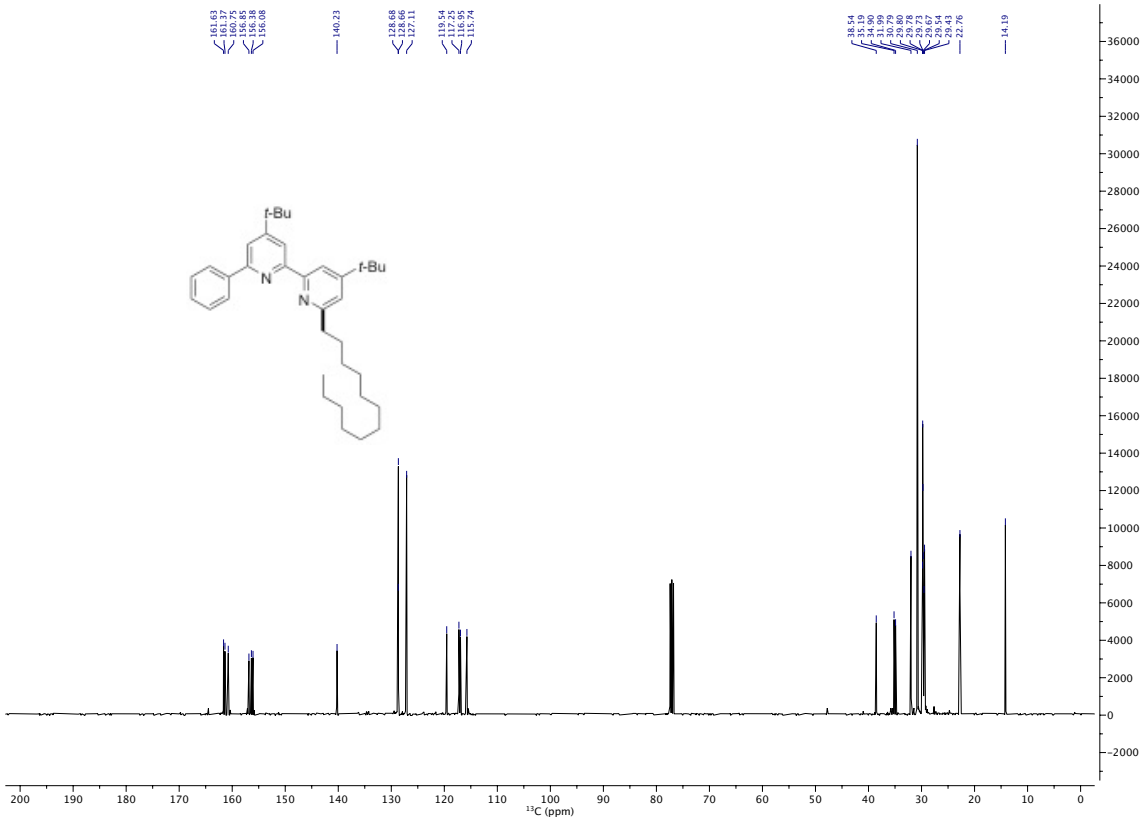
C3


8.69
8.57
8.29
8.27
7.86
7.64
7.62
7.60
7.54
7.53
7.51
7.42
2.28
2.26
2.22
1.96
1.95
1.57
1.53
t-Bu
t-Bu
N
N
1.00
1.00
2.09
1.03
2.01
2.01
1.02
10.06
5.06
9.09
9.08
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
¹H (ppm)

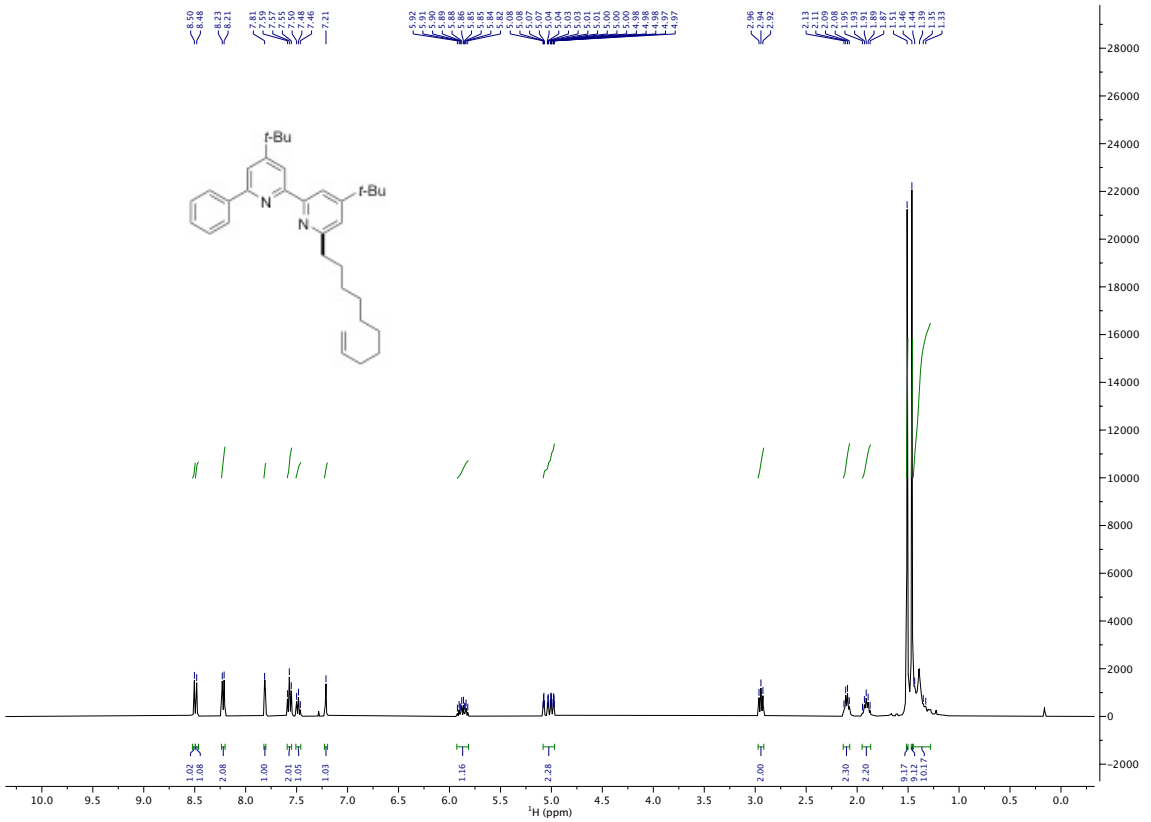

168.10
161.23
160.68
157.71
156.39
155.19
140.40
128.72
128.72
127.17
117.19
117.04
115.57
115.36
49.33
39.40
37.14
35.22
30.97
30.84
29.10
t-Bu
t-Bu
N
N
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
¹³C (ppm)

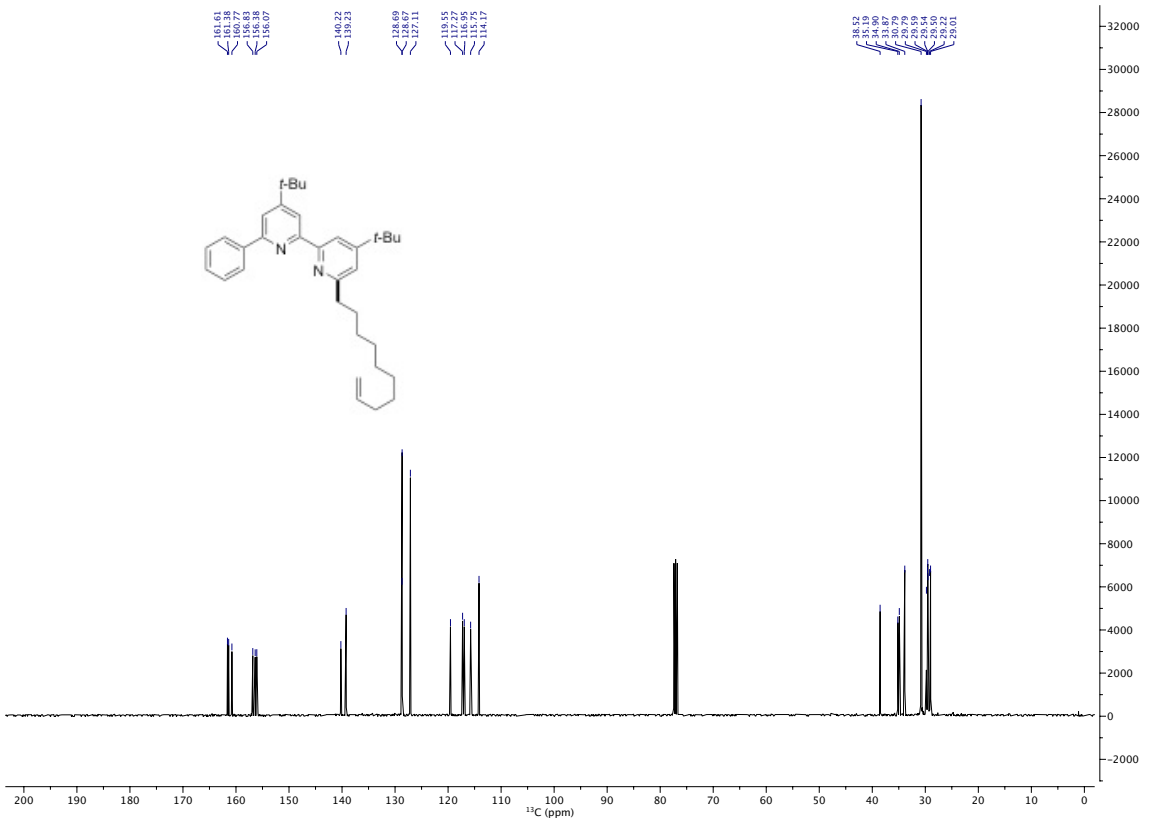
C4


8.52
8.49
8.24
8.22
7.82
7.59
7.57
7.56
7.50
7.48
7.47
7.22
2.97
2.95
2.93
1.96
1.94
1.92
1.90
1.88
1.52
1.47
1.37
1.36
1.34
0.97
0.96
0.95
0.94
0.92
t-Bu
t-Bu
N
N
1.02
1.00
2.10
1.00
2.15
1.11
1.01
2.02
2.28
9.05
9.18
1.75
8.4
4.47
^{1}H (ppm)

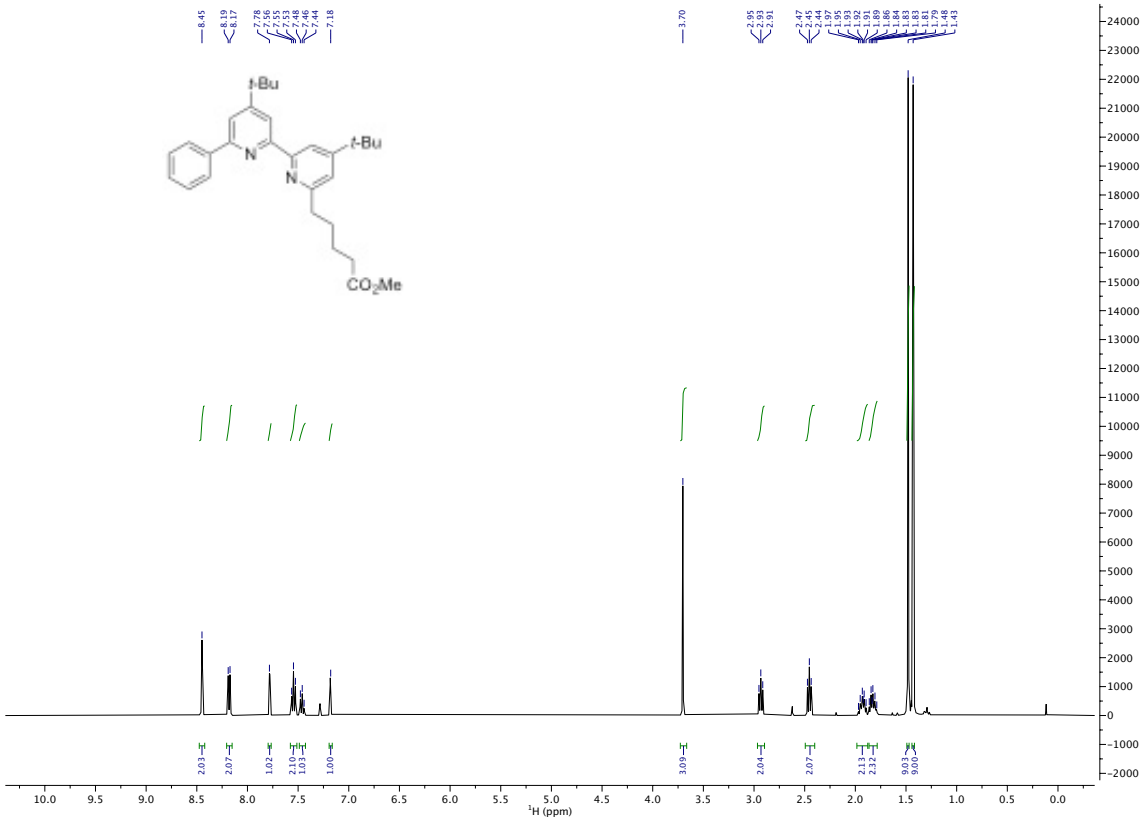

161.63
161.37
160.75
156.85
156.38
156.08
140.23
128.68
128.66
127.11
119.54
117.35
116.95
115.74
38.54
35.19
34.90
31.99
30.79
30.60
29.78
29.73
29.67
29.54
29.43
22.76
14.19
t-Bu
t-Bu
N
N
^{13}C (ppm)

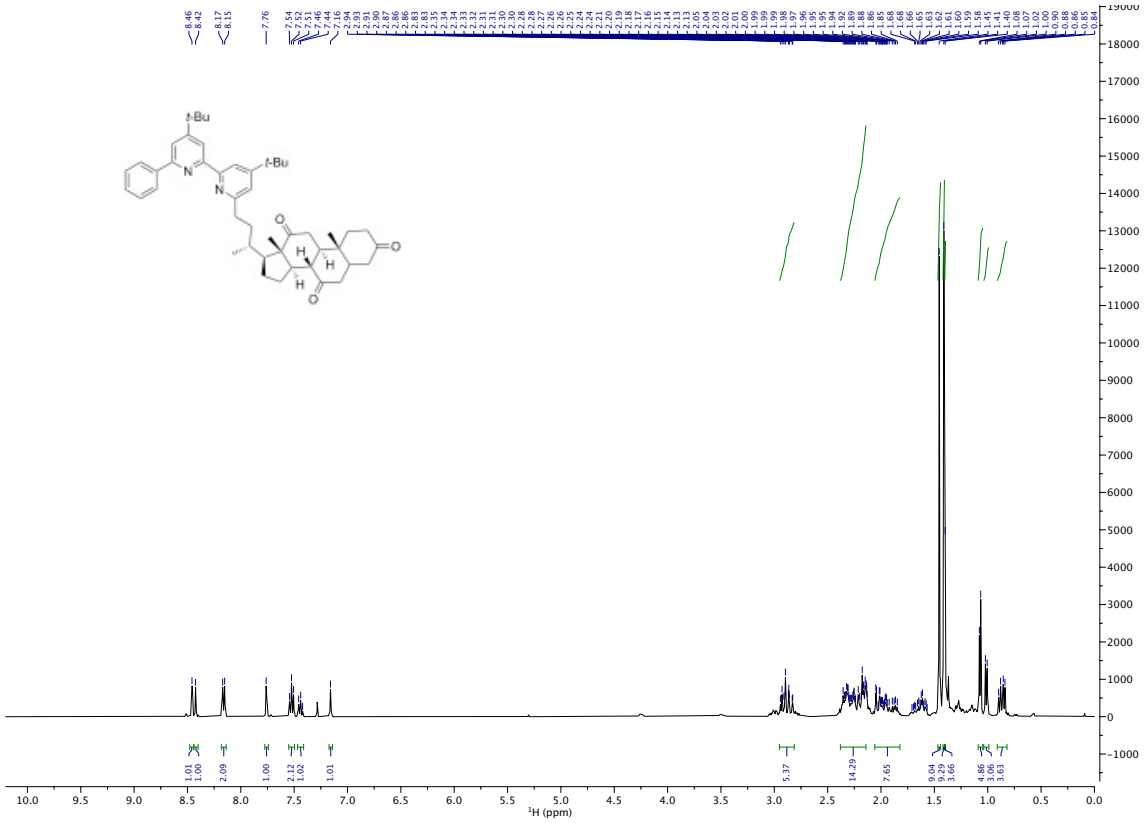
C5


8.50
8.48
8.23
8.21
7.81
7.59
7.57
7.55
7.50
7.48
7.46
7.21
5.92
5.91
5.90
5.89
5.88
5.86
5.85
5.85
5.84
5.82
5.08
5.08
5.07
5.07
5.04
5.04
5.03
5.03
5.01
5.01
5.00
5.00
5.00
4.98
4.98
4.98
4.97
4.97
2.96
2.94
2.92
2.13
2.11
2.09
2.08
1.95
1.93
1.91
1.89
1.87
1.51
1.46
1.44
1.39
1.35
1.33
t-Bu
t-Bu
N
N
1.02
1.08
2.08
1.00
2.01
1.05
1.03
1.16
2.28
2.00
2.30
2.20
9.17
12.17
10.17
^{1}H (ppm)

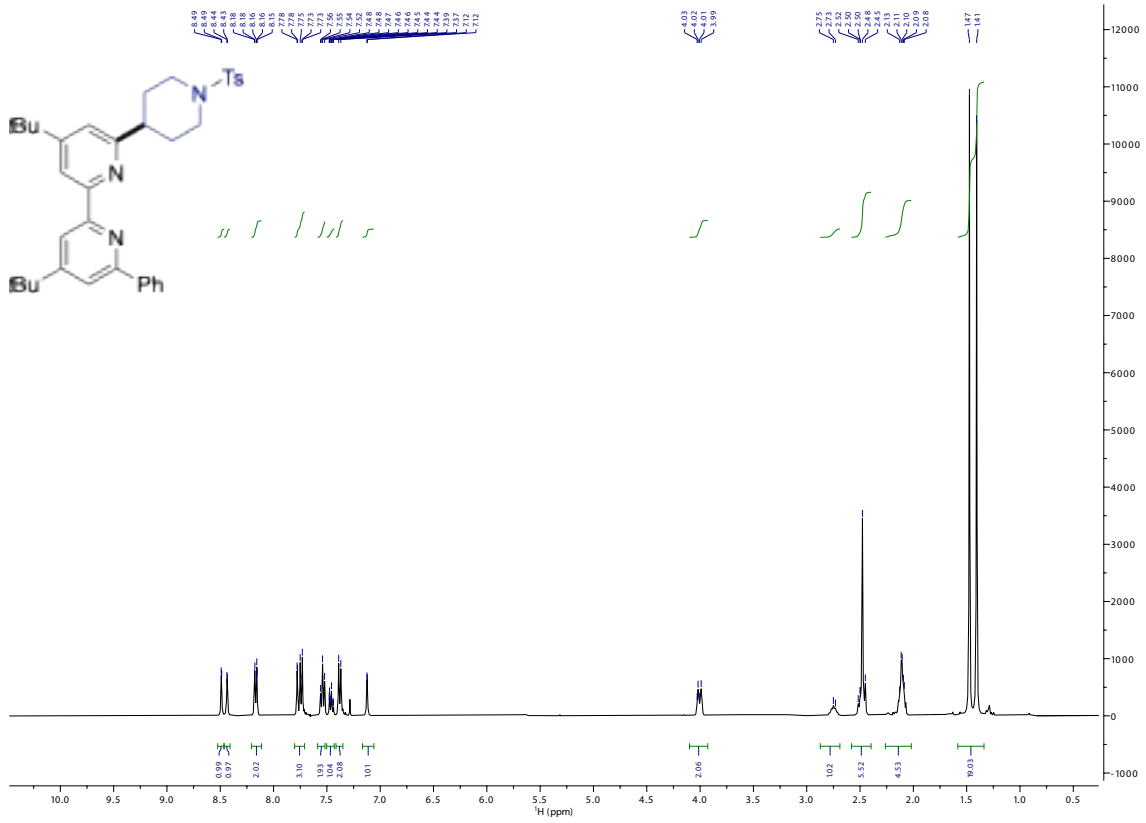

161.61
161.38
160.77
156.83
156.38
156.07
140.22
139.23
128.69
128.67
127.11
119.55
117.27
116.95
115.75
114.17
38.52
35.19
34.90
31.87
30.79
29.79
29.59
29.54
29.50
29.22
29.01
t-Bu
t-Bu
N
N
^{13}C (ppm)

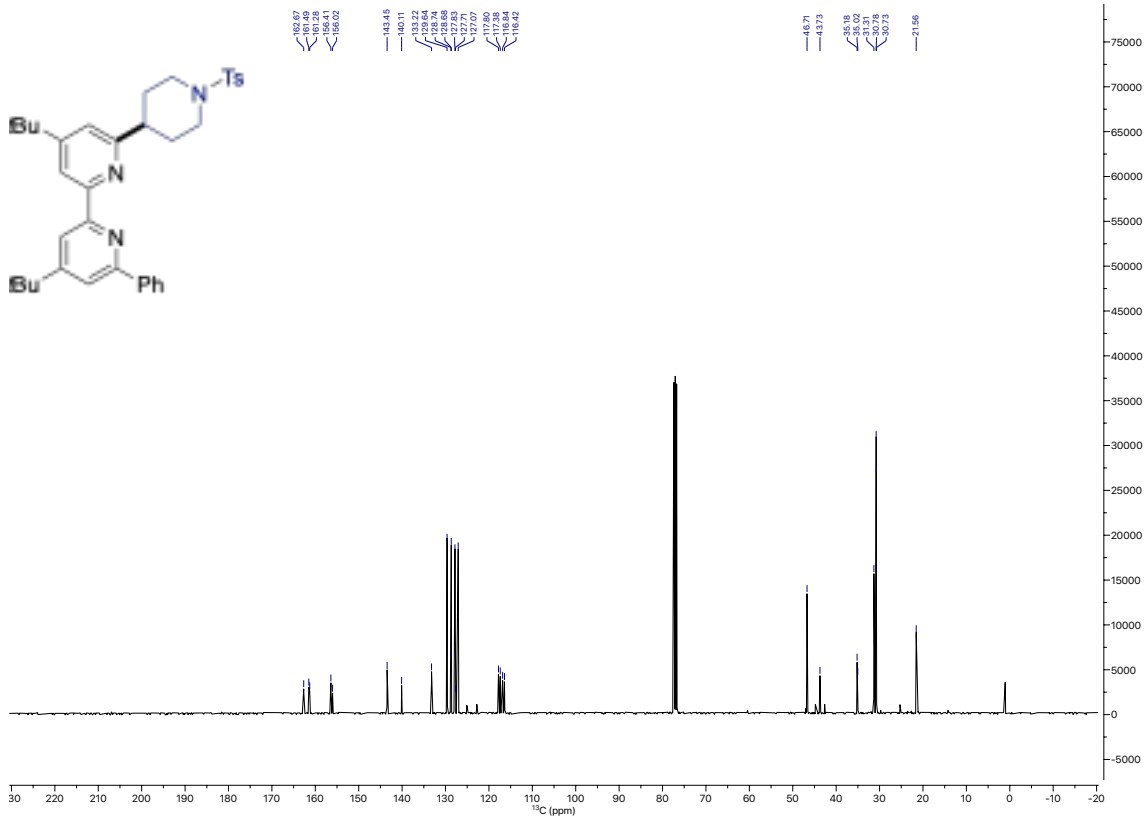
C6


t-Bu
t-Bu
N
N
CO2Me
8.45
8.19
8.17
7.78
7.56
7.55
7.53
7.48
7.46
7.44
7.18
3.70
2.95
2.93
2.91
2.47
2.45
2.44
2.37
1.95
1.93
1.92
1.91
1.89
1.86
1.84
1.83
1.81
1.79
1.48
1.43
2.03
2.07
1.02
2.10
1.03
1.00
3.09
2.04
2.07
2.13
2.32
9.03
9.00
1H (ppm)

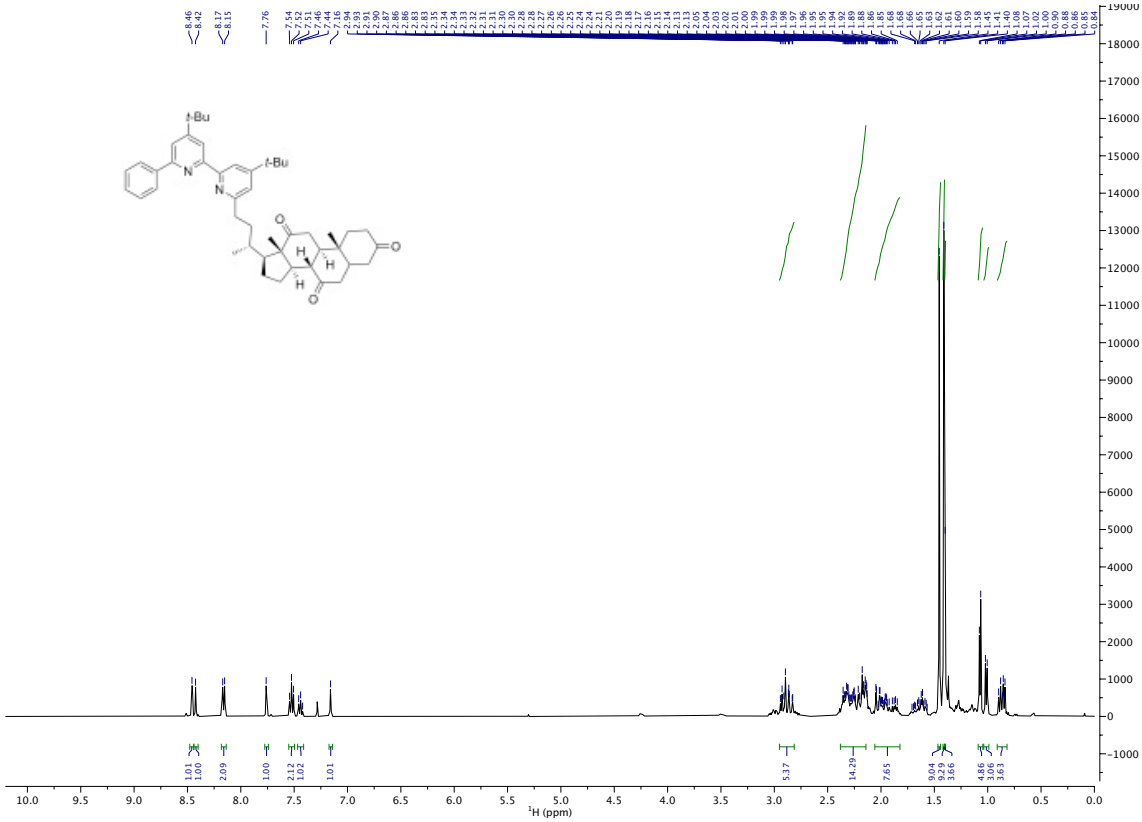

t-Bu
t-Bu
N
N
O
O
O
H
H
H
8.46
8.42
8.17
8.15
7.76
1.01
1.00
2.09
1.00
2.12
1.02
1.01
5.37
14.29
7.65
9.04
9.00
3.68
4.86
3.06
3.63
1H (ppm)

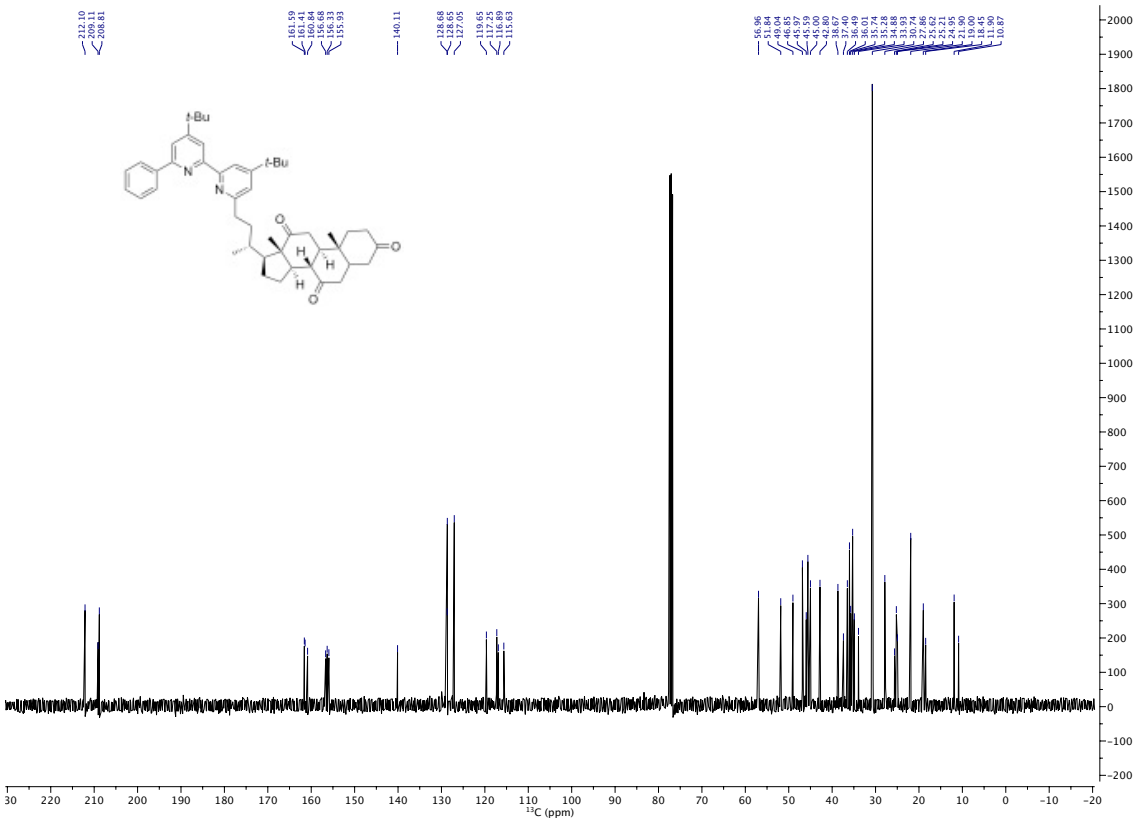
C7



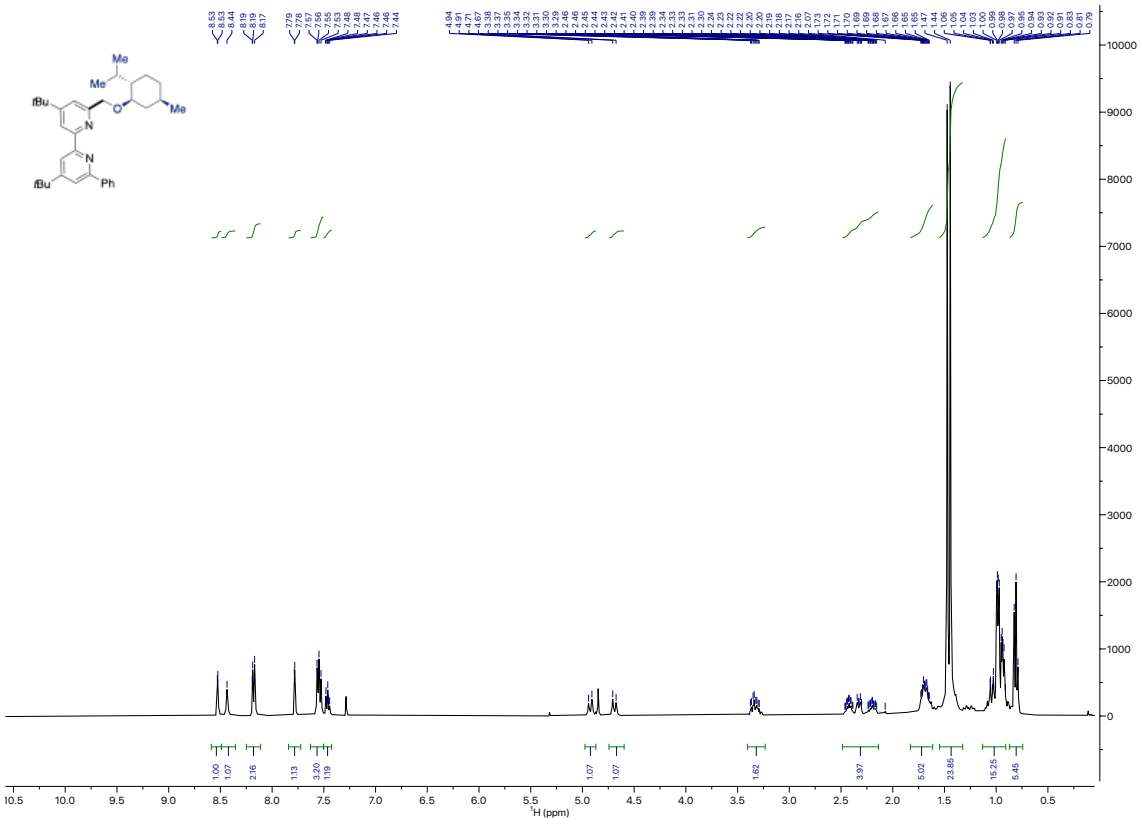


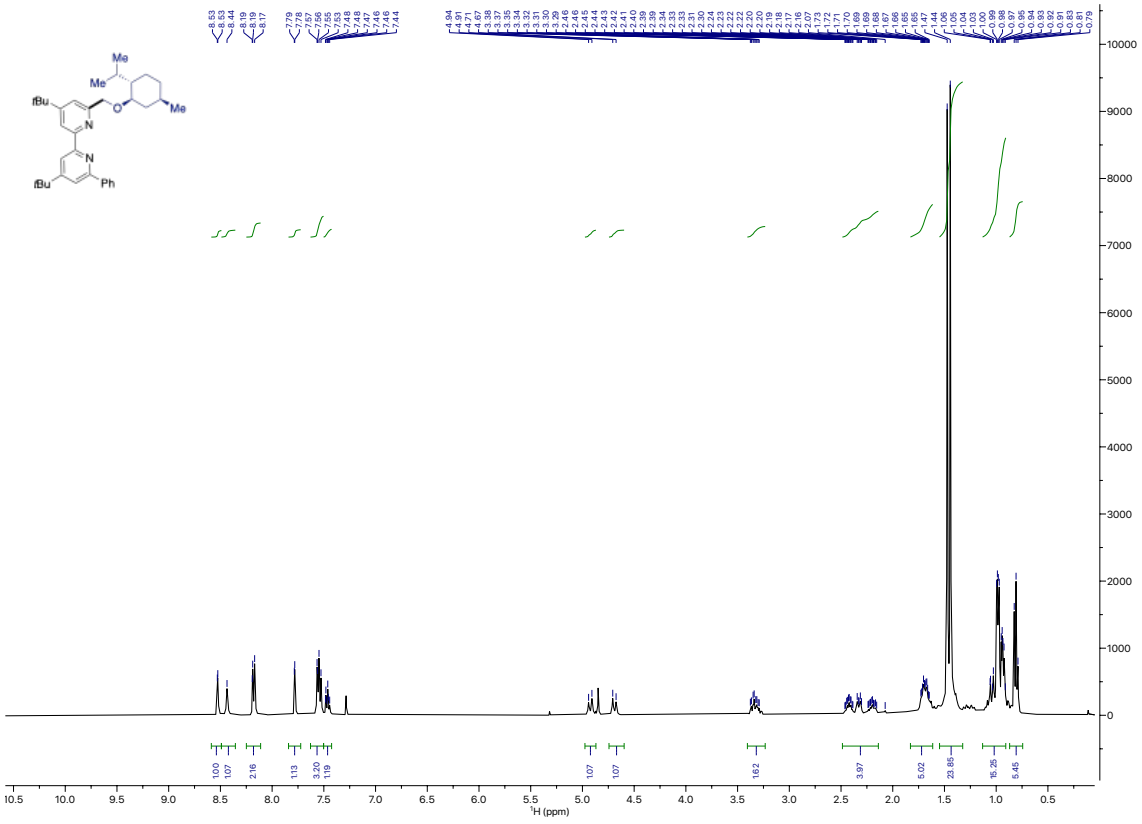
C8


t-Bu
t-Bu
N
N
O
O
H
H
H
O
8.46
8.42
8.17
8.15
7.76
1.01
1.00
2.09
1.00
2.12
1.02
1.01
5.37
14.29
7.65
9.04
9.00
3.66
4.86
3.06
3.63
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
^{1}H (ppm)

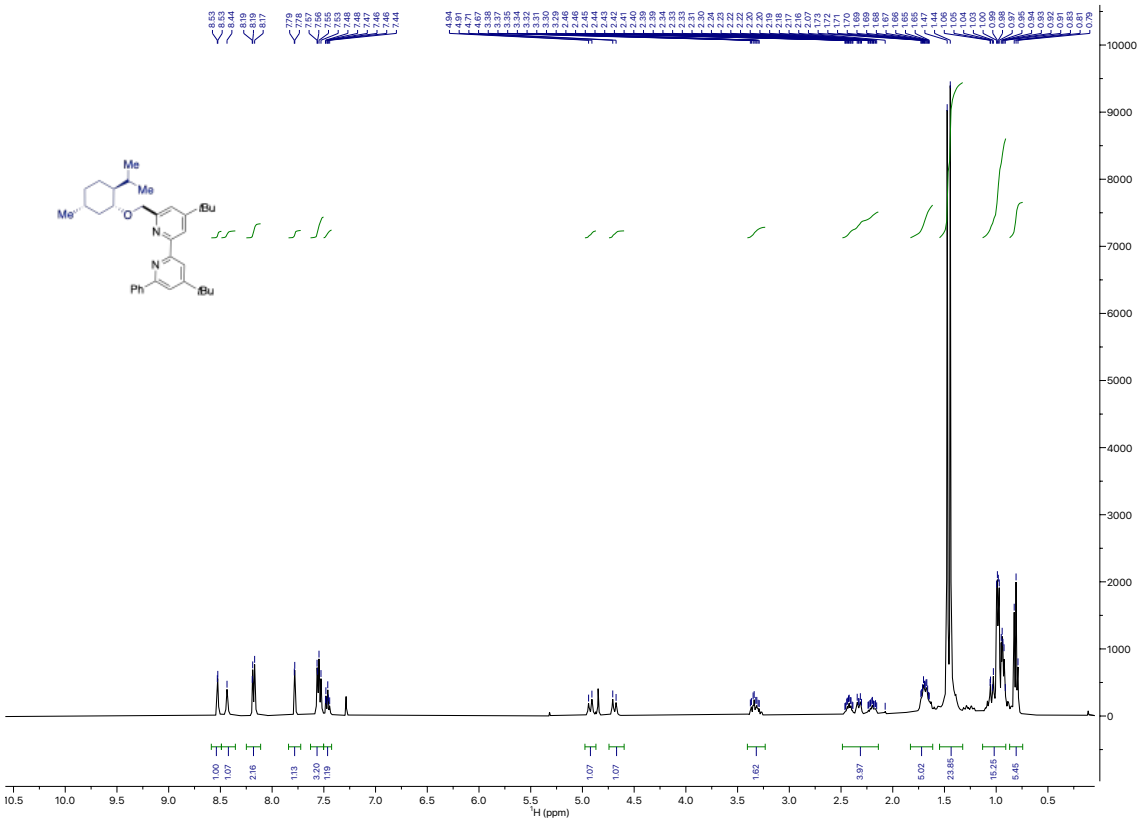

t-Bu
t-Bu
N
N
O
O
H
H
H
O
212.10
209.11
208.61
161.59
161.41
160.84
156.68
156.33
155.93
140.11
128.68
128.55
127.05
119.65
117.25
116.89
115.63
56.96
51.84
49.04
47.85
45.97
45.59
42.00
41.60
38.67
37.40
36.49
36.01
35.74
35.28
34.88
33.93
33.74
27.86
25.62
24.51
24.05
21.90
18.00
14.45
11.90
10.87
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
^{13}C (ppm)

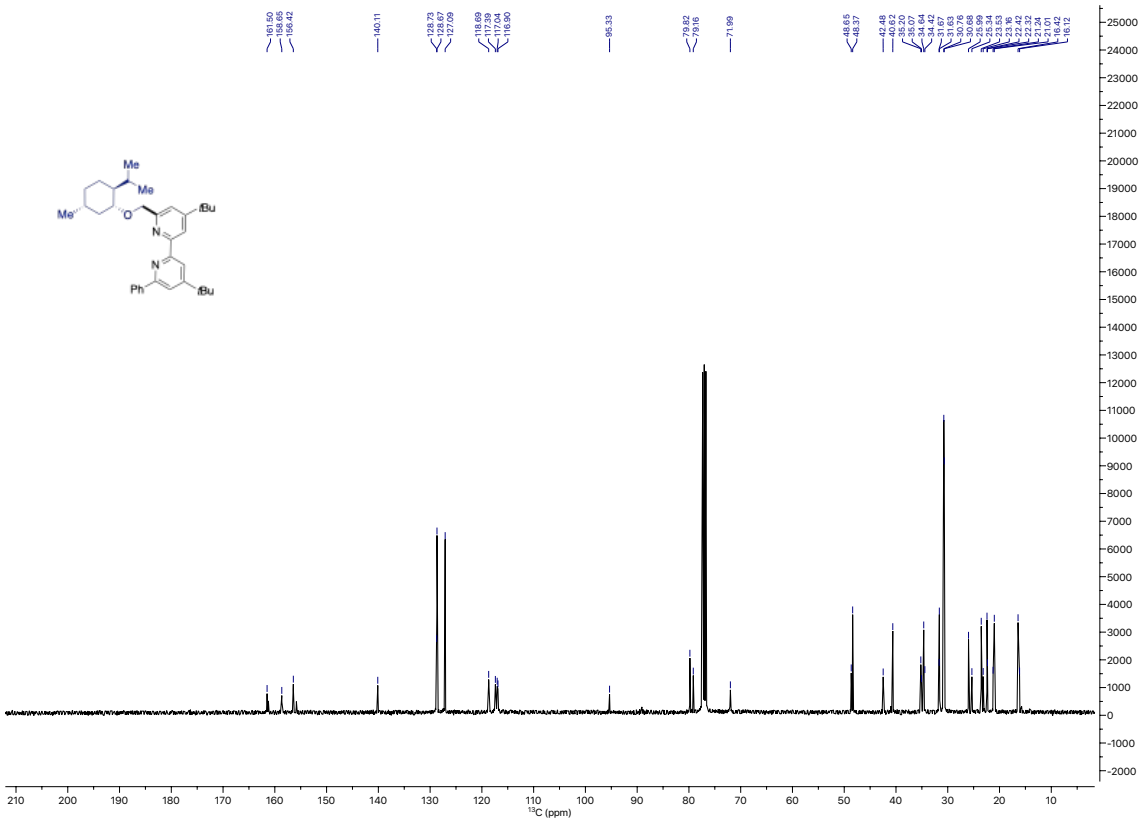
(-)-C9


Me
Me
Me
tBu
N
O
N
tBu
Ph
8.53
8.44
8.19
8.17
7.79
7.56
7.46
7.44
4.94
4.91
4.67
3.38
3.37
3.35
3.34
3.32
3.31
3.30
3.29
2.46
2.45
2.44
2.43
2.42
2.41
2.40
2.39
2.34
2.33
2.31
2.30
2.24
2.23
2.22
2.20
2.19
2.18
2.17
2.16
2.07
1.73
1.72
1.71
1.70
1.69
1.68
1.67
1.66
1.65
1.47
1.44
1.06
1.05
1.04
1.03
1.00
0.99
0.98
0.97
0.96
0.95
0.94
0.93
0.92
0.91
0.83
0.81
0.79
1.00
1.07
2.16
1.13
3.20
1.19
1.07
1.07
1.62
3.97
5.02
23.85
15.25
5.45
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
¹H (ppm)

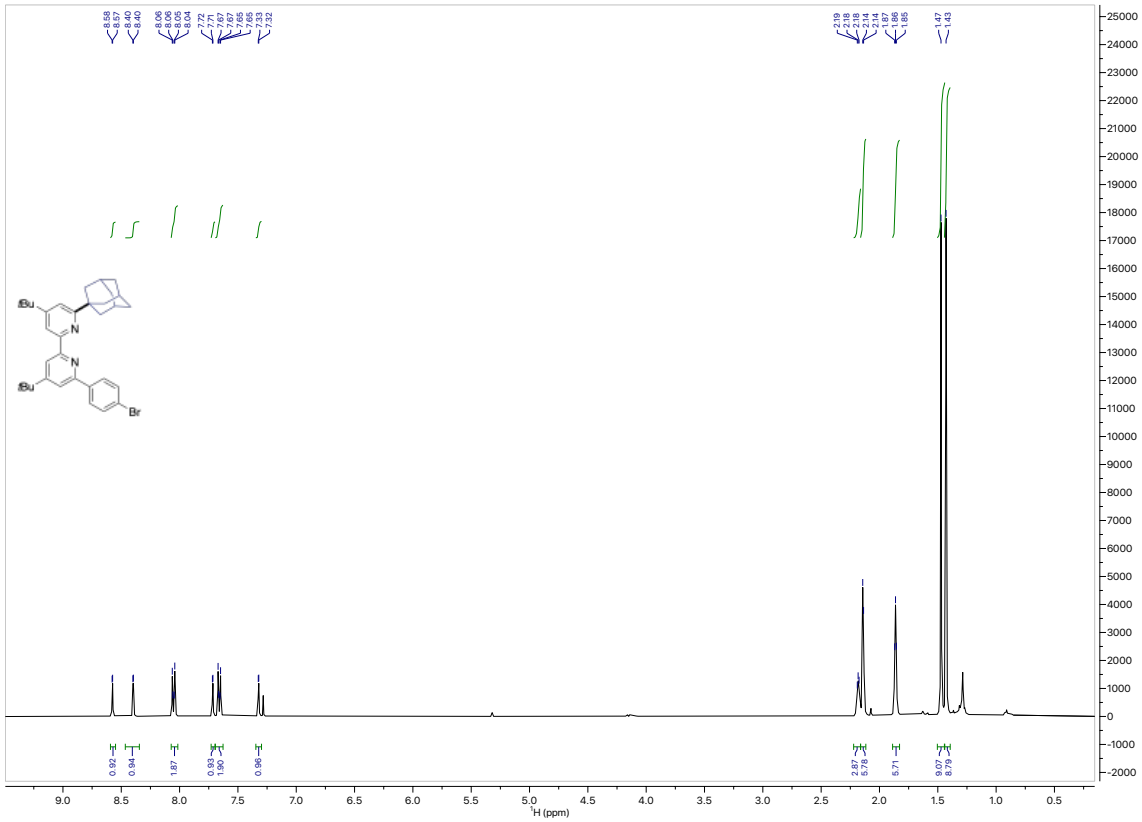

Me
Me
Me
tBu
N
O
N
tBu
Ph
8.53
8.44
8.19
8.17
7.79
7.56
7.46
7.44
4.94
4.91
4.67
3.38
3.37
3.35
3.34
3.32
3.31
3.30
3.29
2.46
2.45
2.44
2.43
2.42
2.41
2.40
2.39
2.34
2.33
2.31
2.30
2.24
2.23
2.22
2.20
2.19
2.18
2.17
2.16
2.07
1.73
1.72
1.71
1.70
1.69
1.68
1.67
1.66
1.65
1.47
1.44
1.06
1.05
1.04
1.03
1.00
0.99
0.98
0.97
0.96
0.95
0.94
0.93
0.92
0.91
0.83
0.81
0.79
1.00
1.07
2.16
1.13
3.20
1.19
1.07
1.07
1.62
3.97
5.02
23.85
15.25
5.45
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
¹H (ppm)

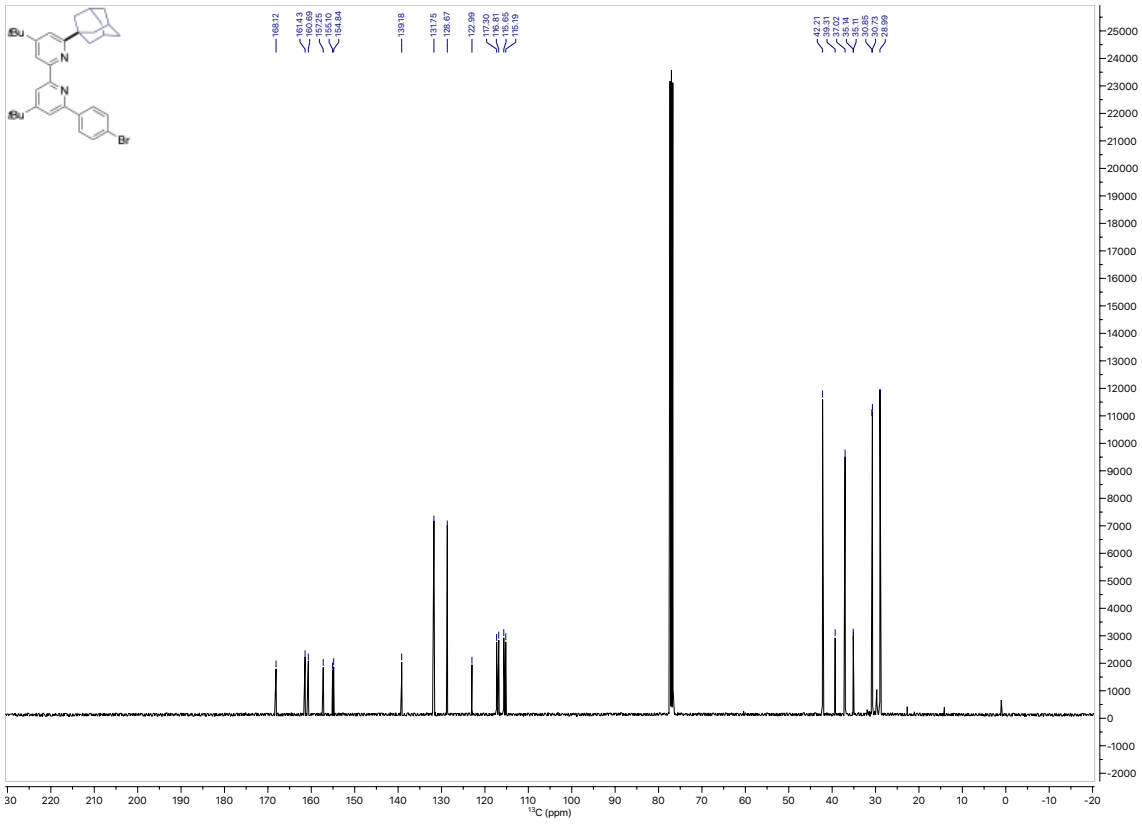
(+)-C9



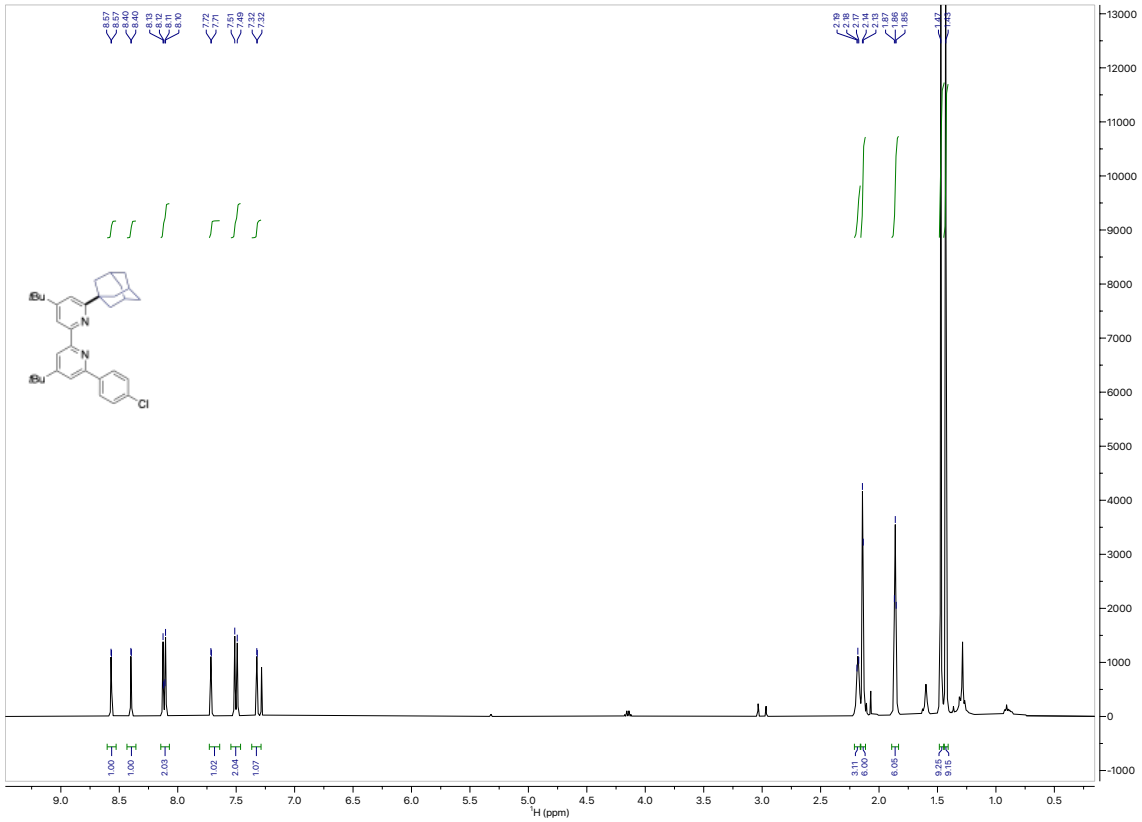


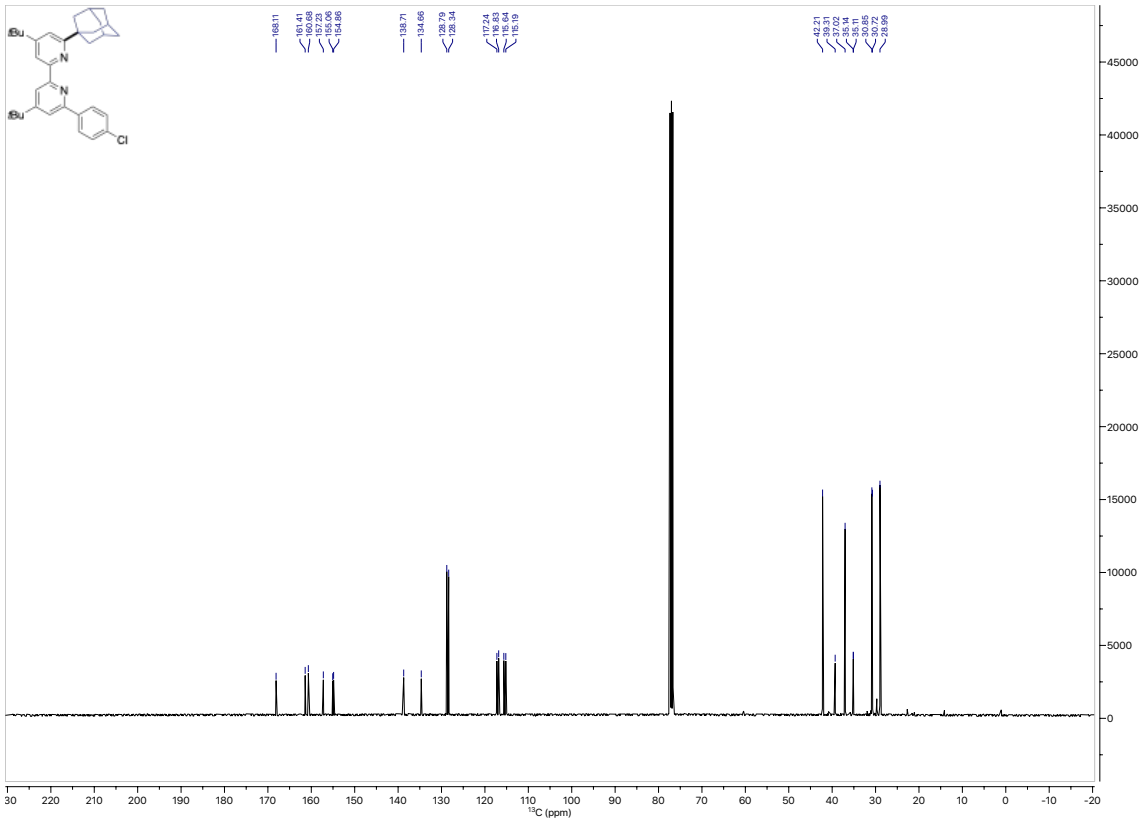
C10


8.58
8.57
8.40
8.40
8.06
8.06
8.05
8.04
7.72
7.71
7.67
7.67
7.65
7.65
7.33
7.32
2.19
2.18
2.18
2.14
2.14
1.87
1.86
1.85
1.47
1.43
tBu
tBu
Br
0.92
0.94
1.87
0.93
1.90
0.96
2.87
5.78
5.71
9.07
8.79
^{1}H (ppm)

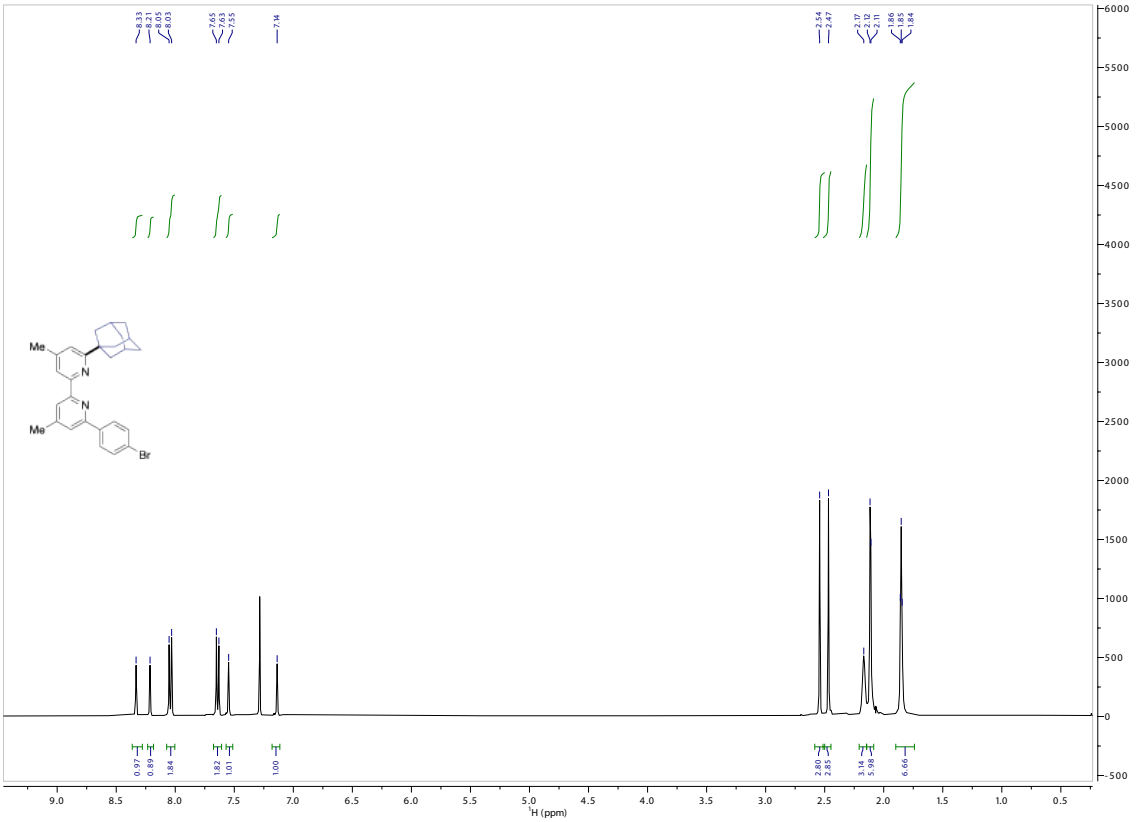

tBu
tBu
Br
168.12
161.43
160.69
157.25
155.10
154.84
139.18
131.75
128.67
122.99
117.30
116.81
116.65
115.19
45.21
43.31
37.02
35.14
31.71
30.85
30.73
28.99
^{13}C (ppm)

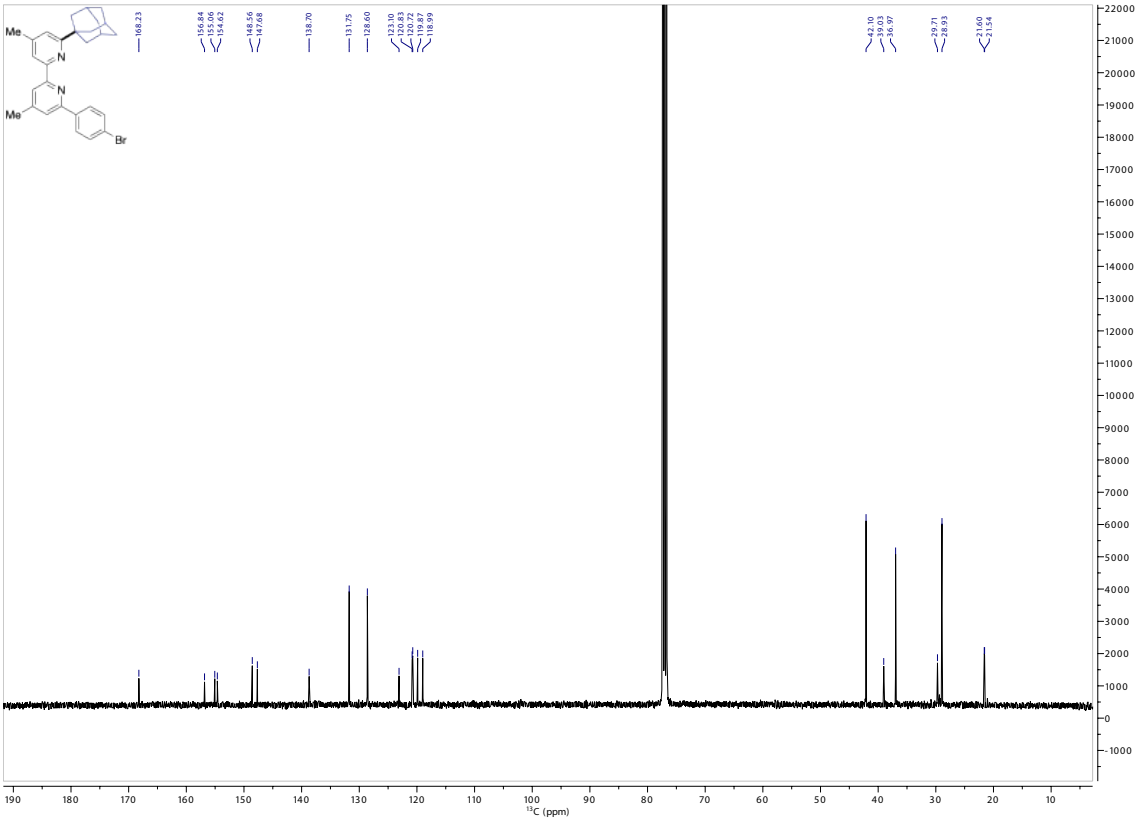
C11


8.57
8.57
8.40
8.40
8.13
8.12
8.11
8.10
7.72
7.71
7.51
7.49
7.32
7.32
2.19
2.18
2.17
2.14
2.13
1.87
1.86
1.85
1.47
1.43
tBu
N
N
tBu
Cl
1.00
1.00
2.03
1.02
2.04
1.07
3.11
6.00
6.05
9.25
9.15
^{1}H (ppm)

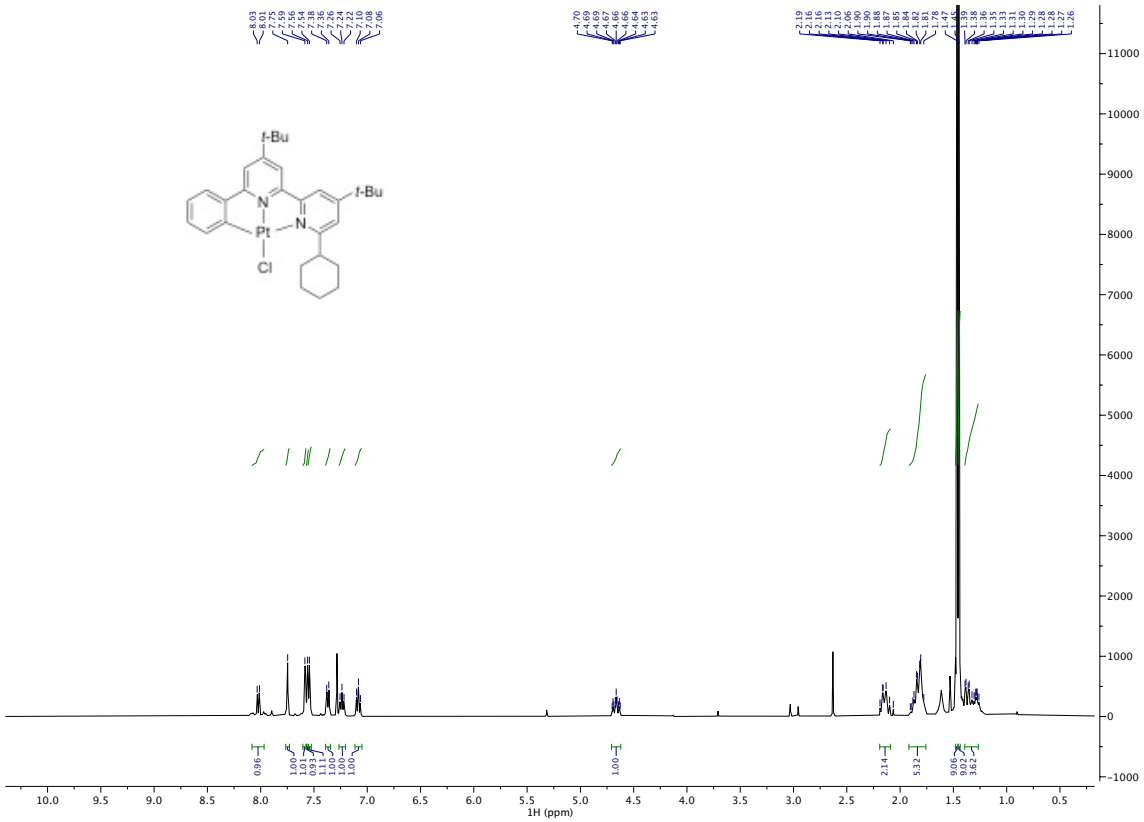

tBu
N
N
tBu
Cl
168.11
161.41
160.68
157.23
155.06
154.66
138.71
134.66
128.79
128.34
117.24
116.83
116.44
115.19
45.21
43.31
37.02
35.14
31.71
30.85
30.72
28.99
^{13}C (ppm)

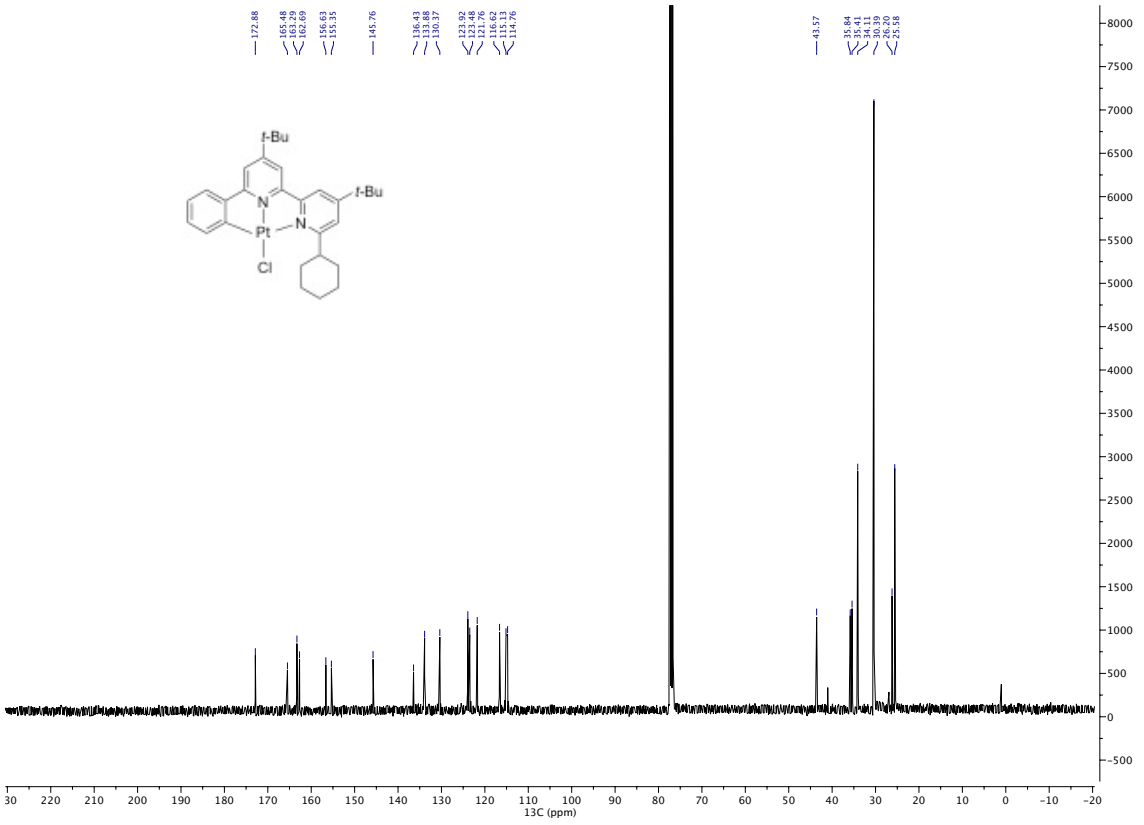
C12


8.33
8.21
8.05
8.03
7.65
7.63
7.55
7.14
2.54
2.47
2.17
2.13
2.11
1.86
1.85
1.84
Me
N
N
Me
Br
0.97
0.89
1.84
1.82
1.01
1.00
2.80
2.85
3.14
5.98
6.66
^{1}H (ppm)

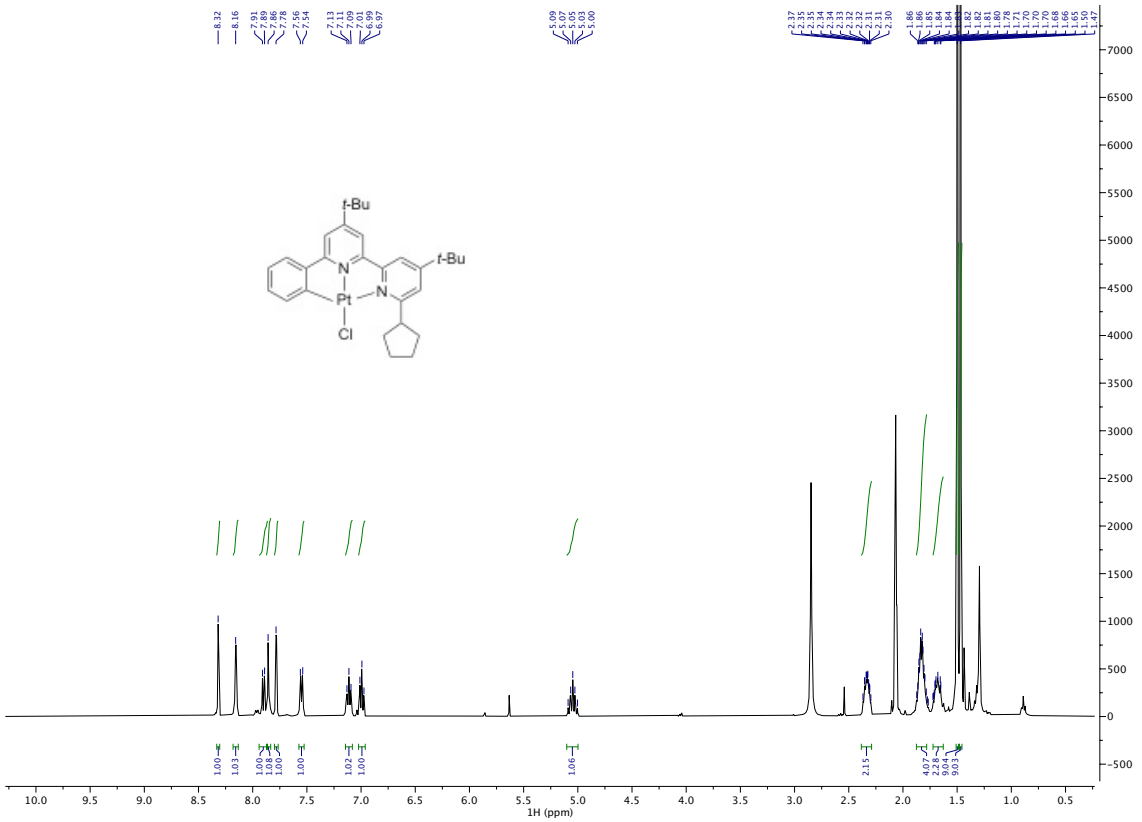

168.23
156.84
155.66
154.62
148.56
147.68
138.70
131.75
128.60
123.10
120.83
120.72
119.87
118.99
42.10
39.03
36.97
29.71
28.93
21.60
21.54
Me
N
N
Me
Br
^{13}C (ppm)

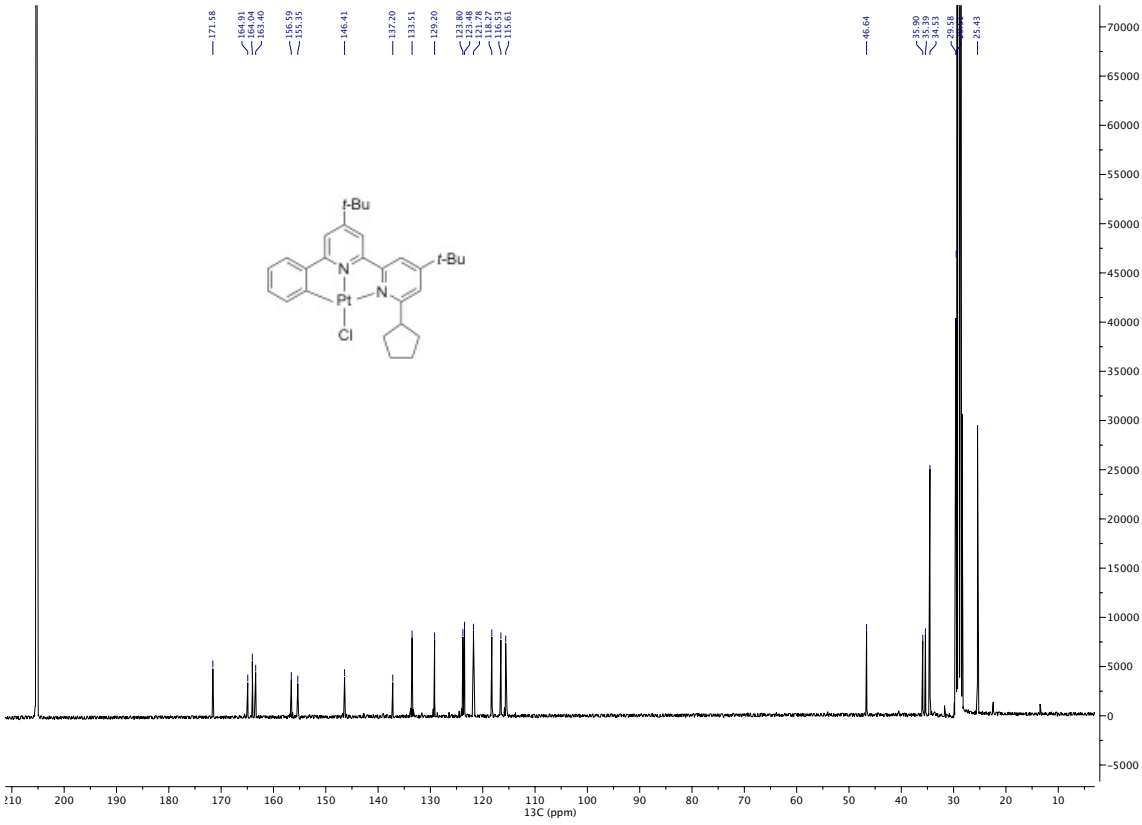
D1



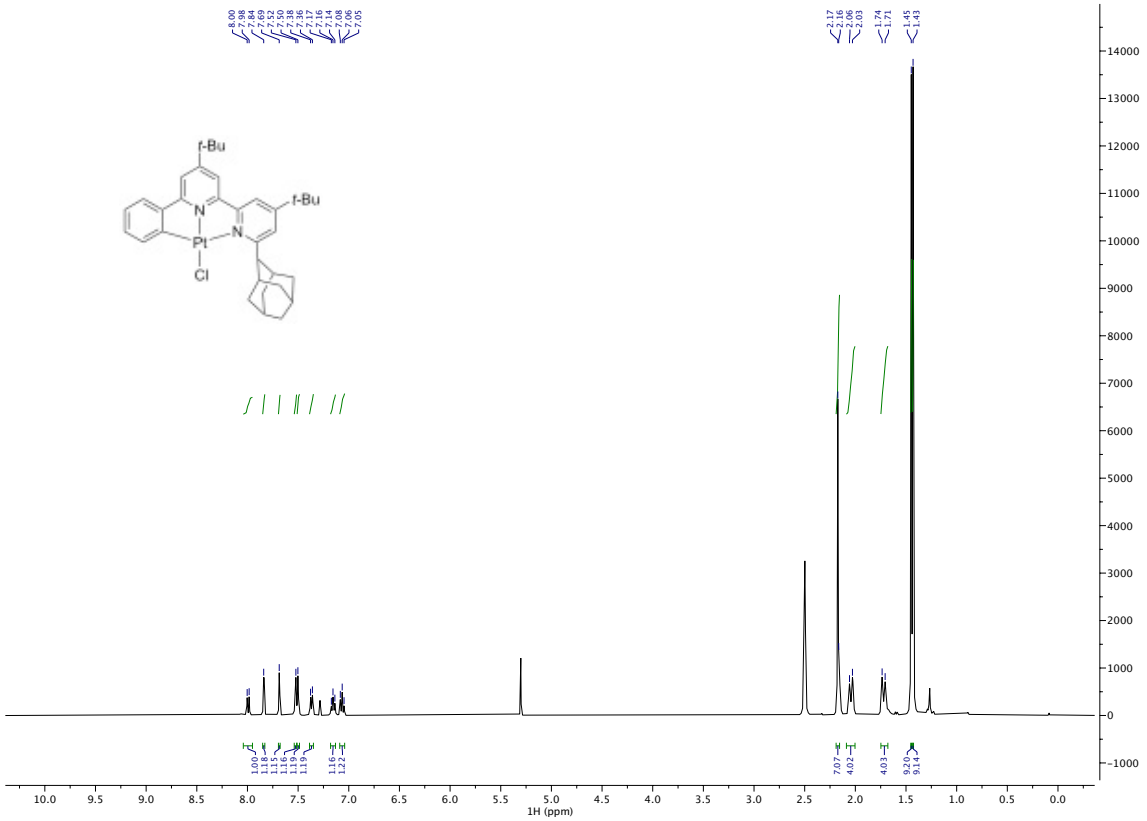


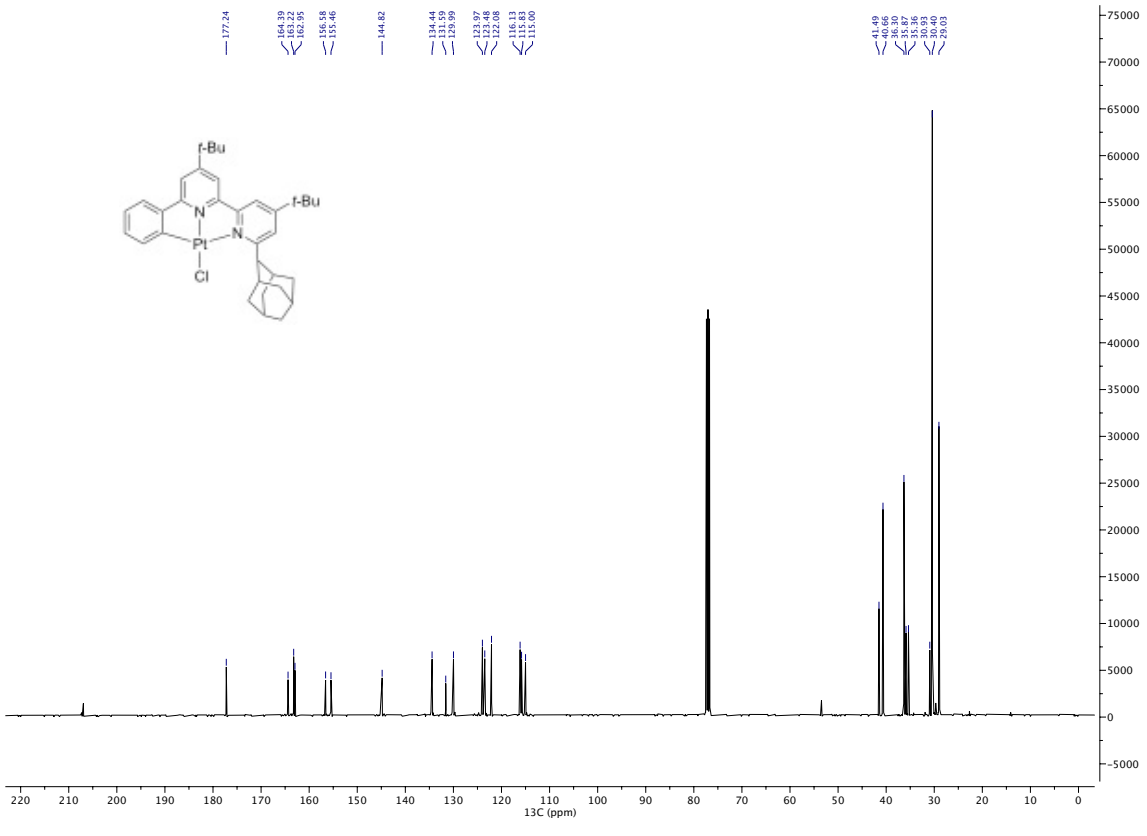
D2



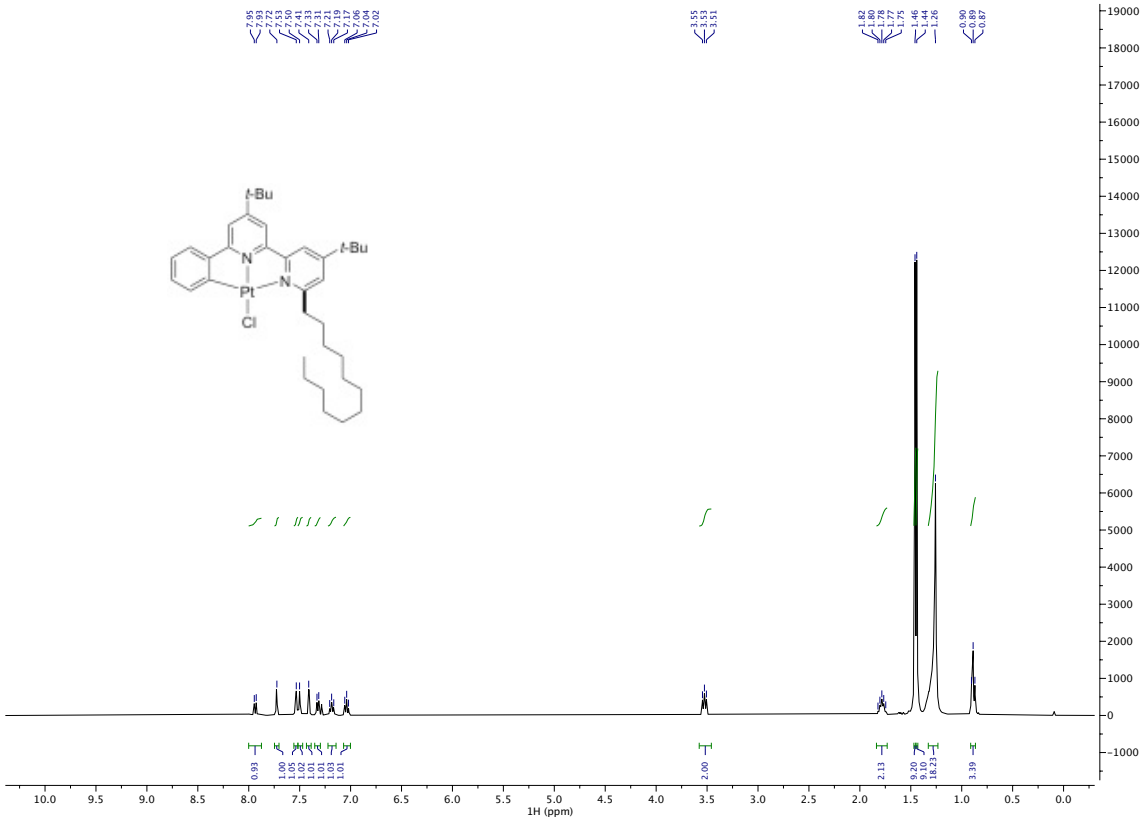


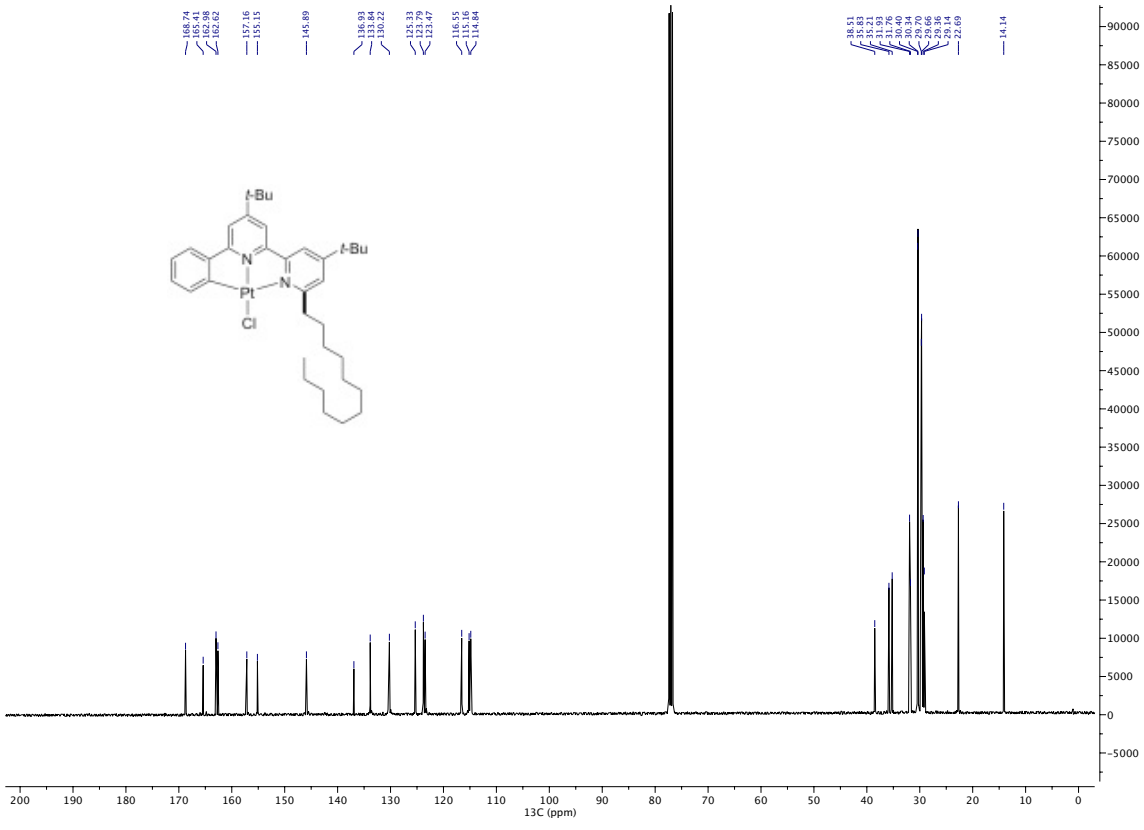
D3


8.00
7.98
7.84
7.69
7.52
7.50
7.38
7.36
7.17
7.16
7.14
7.08
7.06
7.05
2.17
2.16
2.06
2.03
1.74
1.71
1.45
1.43
f-Bu
f-Bu
N
N
Pt
Cl
1.00
1.18
1.15
1.15
1.19
1.19
1.16
1.22
7.07
4.02
4.03
9.20
9.14
1H (ppm)

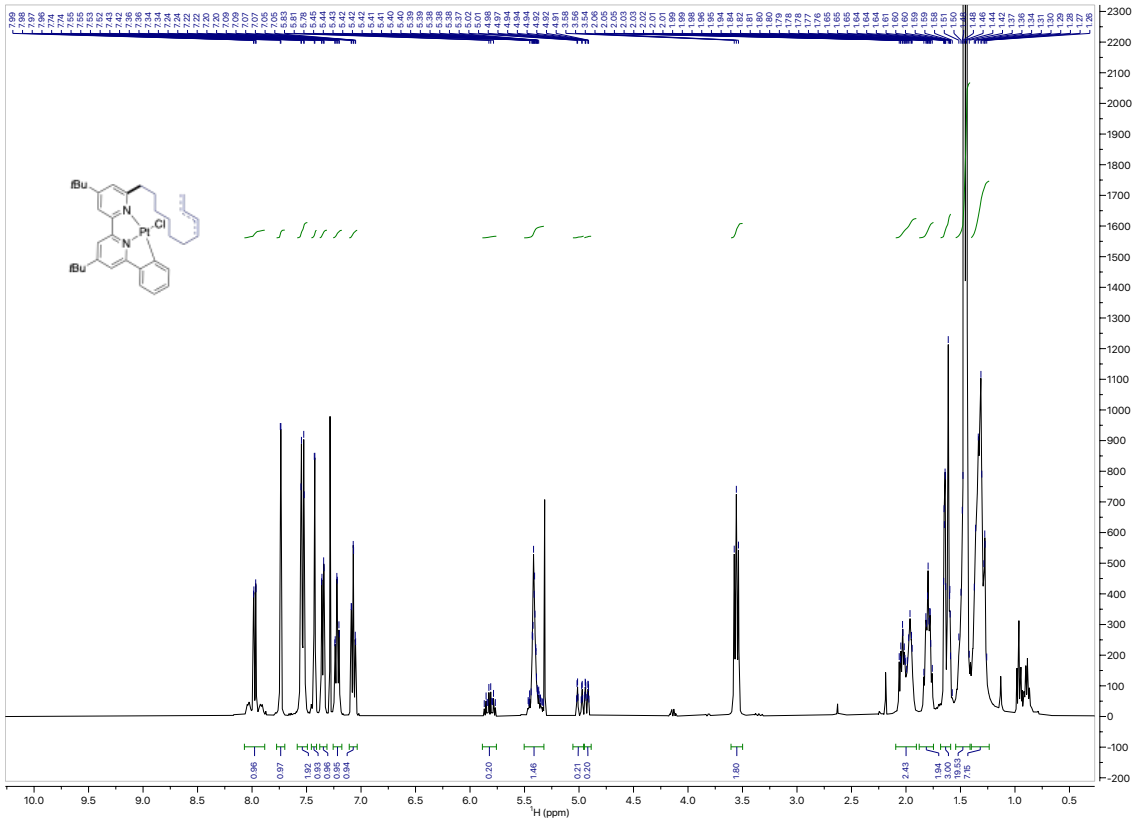

177.24
164.39
163.22
162.95
156.58
155.46
144.82
134.44
131.59
129.99
123.97
123.48
122.08
116.13
115.93
115.00
41.49
40.66
36.30
35.87
35.36
30.39
30.40
29.03
f-Bu
f-Bu
N
N
Pt
Cl
13C (ppm)

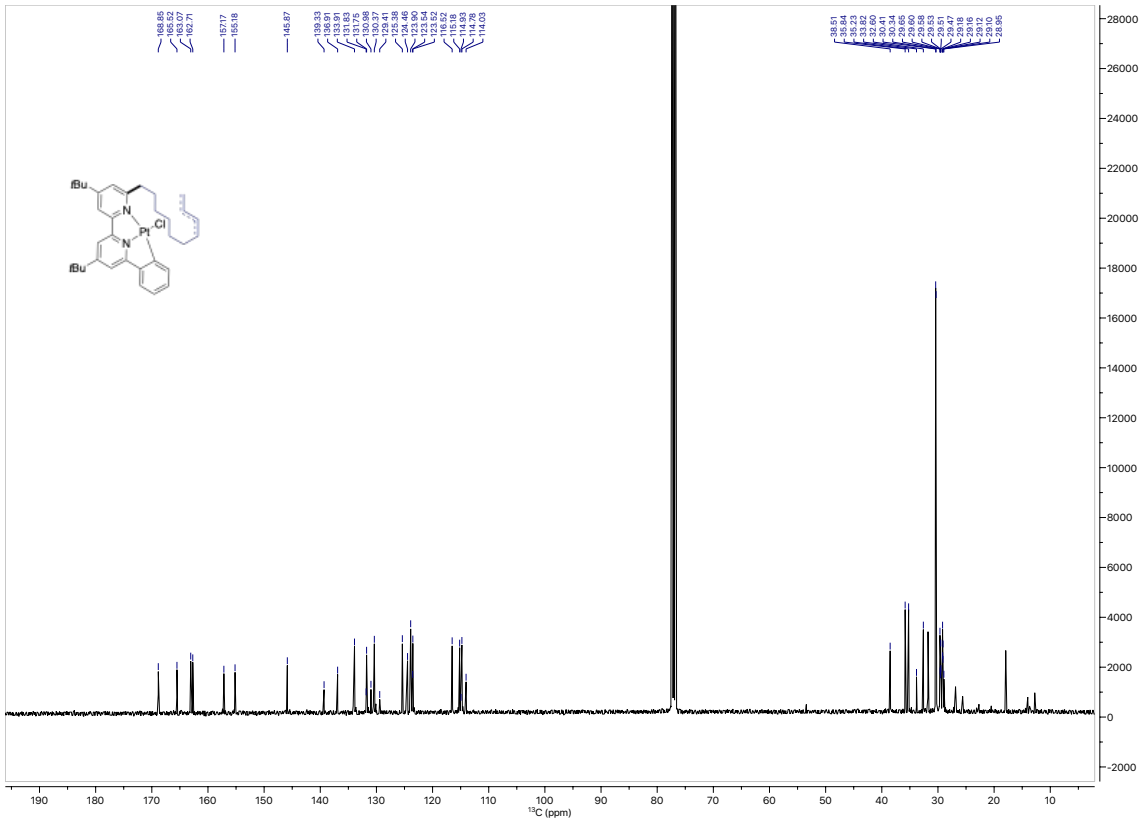
D4


7.95
7.93
7.72
7.53
7.50
7.41
7.33
7.31
7.21
7.19
7.17
7.06
7.04
7.02
3.55
3.53
3.51
1.82
1.80
1.78
1.77
1.75
1.46
1.44
1.26
0.90
0.89
0.87
t-Bu
t-Bu
N
N
Pt
Cl
0.93
1.00
1.05
1.02
1.01
1.01
1.03
1.01
2.00
2.13
9.20
9.10
18.23
3.39
1H (ppm)

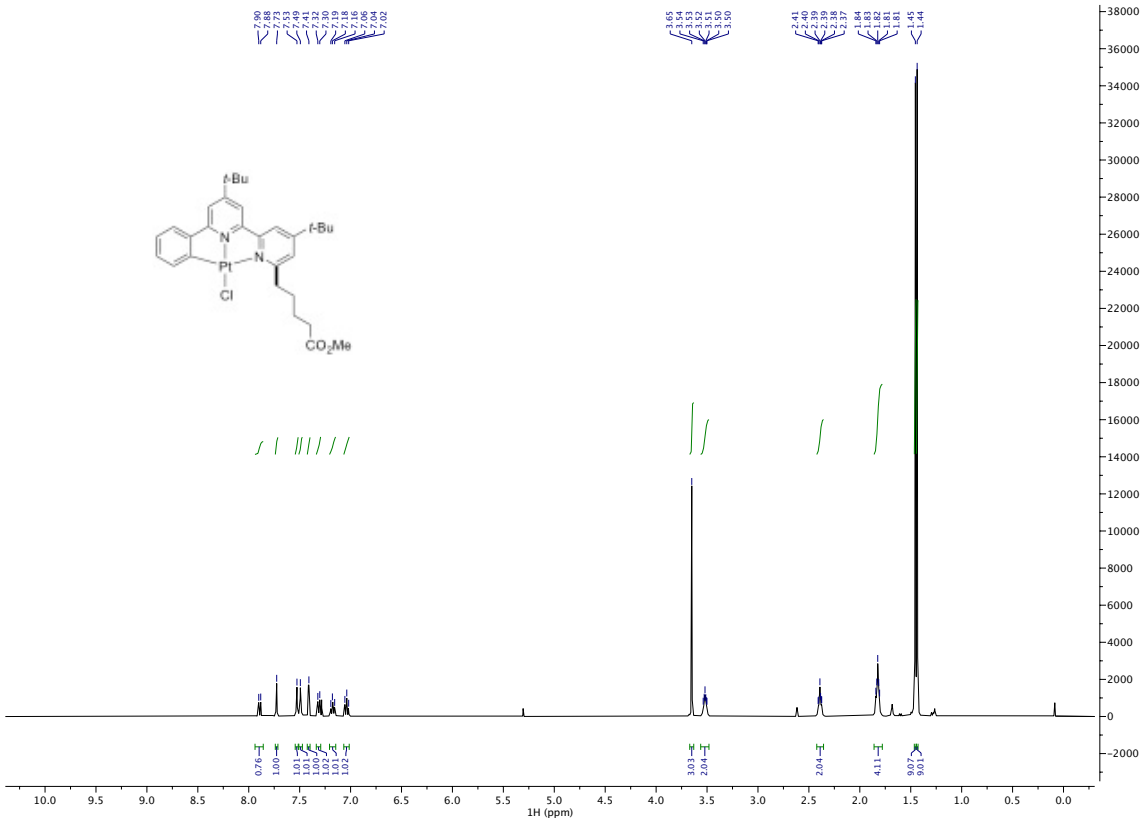

168.74
165.41
162.98
162.62
157.16
155.15
145.89
136.93
133.84
130.22
125.33
123.79
123.47
116.55
115.16
114.84
38.51
35.83
32.21
31.93
31.76
30.40
30.34
29.70
29.66
29.58
29.14
22.69
14.14
t-Bu
t-Bu
N
N
Pt
Cl
13C (ppm)

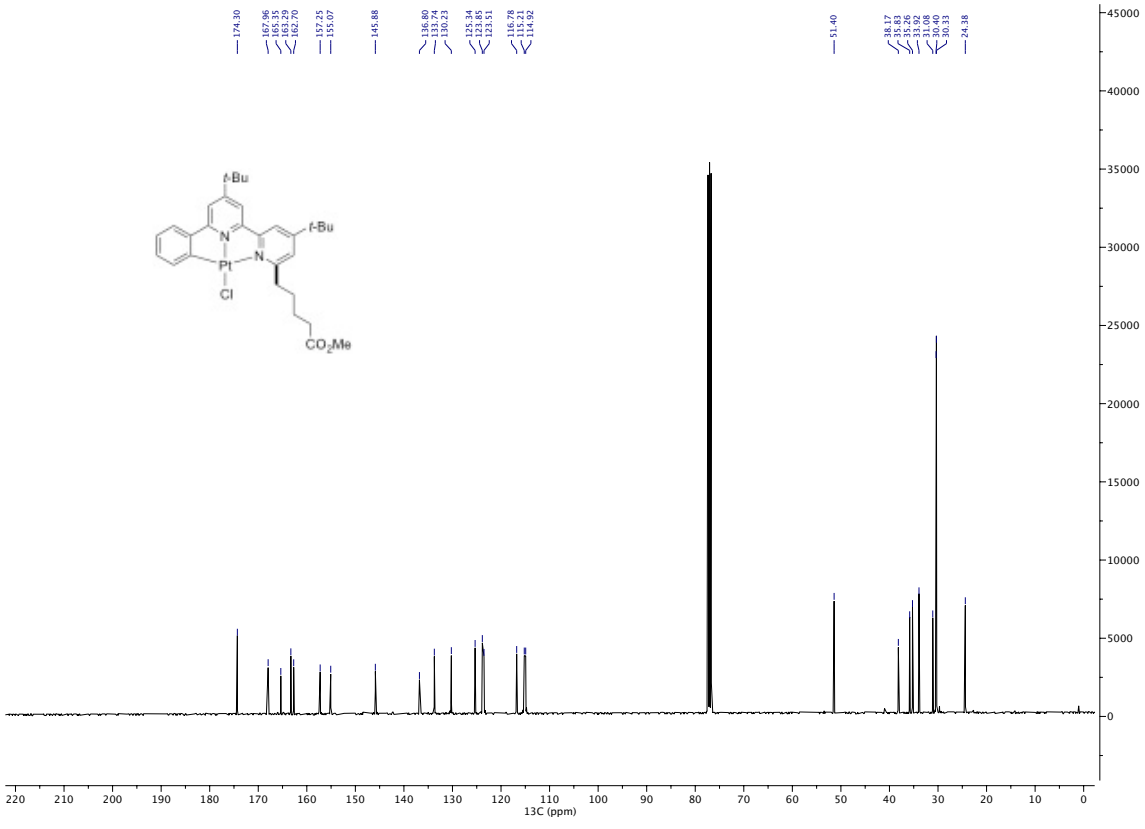
D5


tBu
N
Pt
Cl
N
tBu
0.96
0.97
1.92
0.93
0.96
0.96
0.94
0.20
1.46
0.21
0.20
1.80
2.43
1.94
3.00
19.53
7.75
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
^{1}H (ppm)

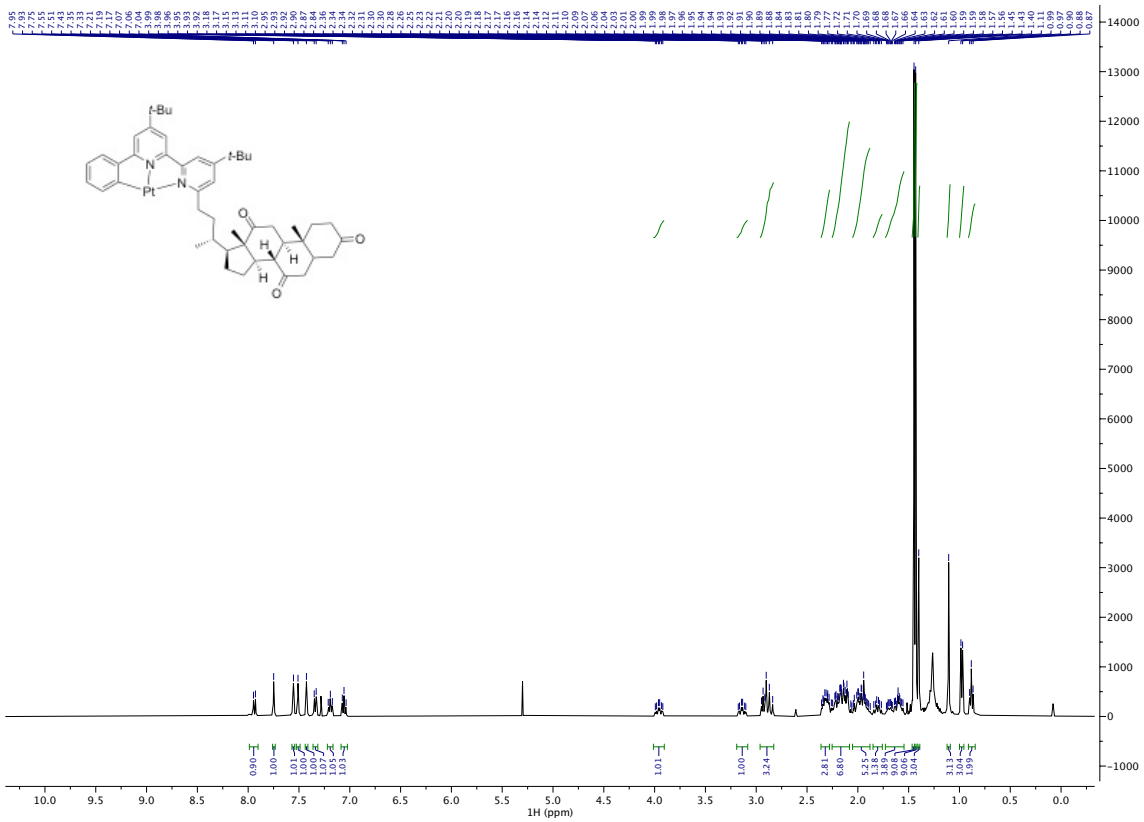

tBu
N
Pt
Cl
N
tBu
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
^{13}C (ppm)

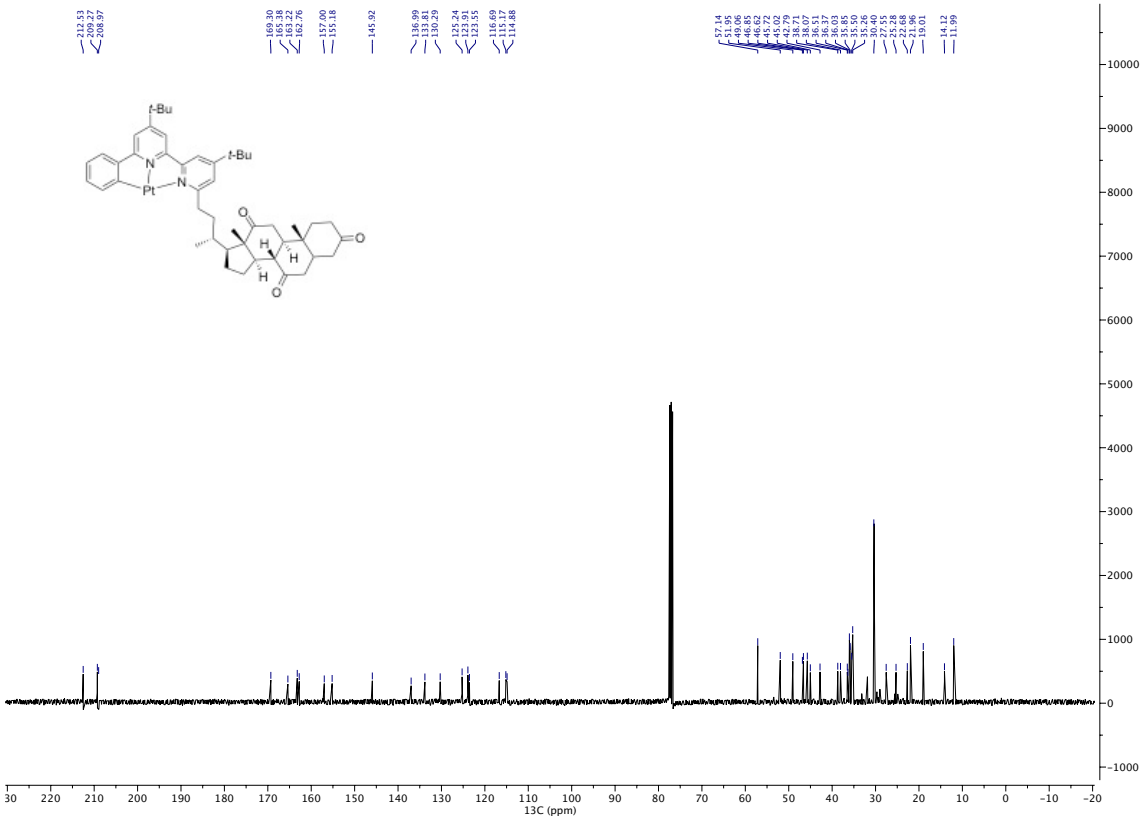
D6



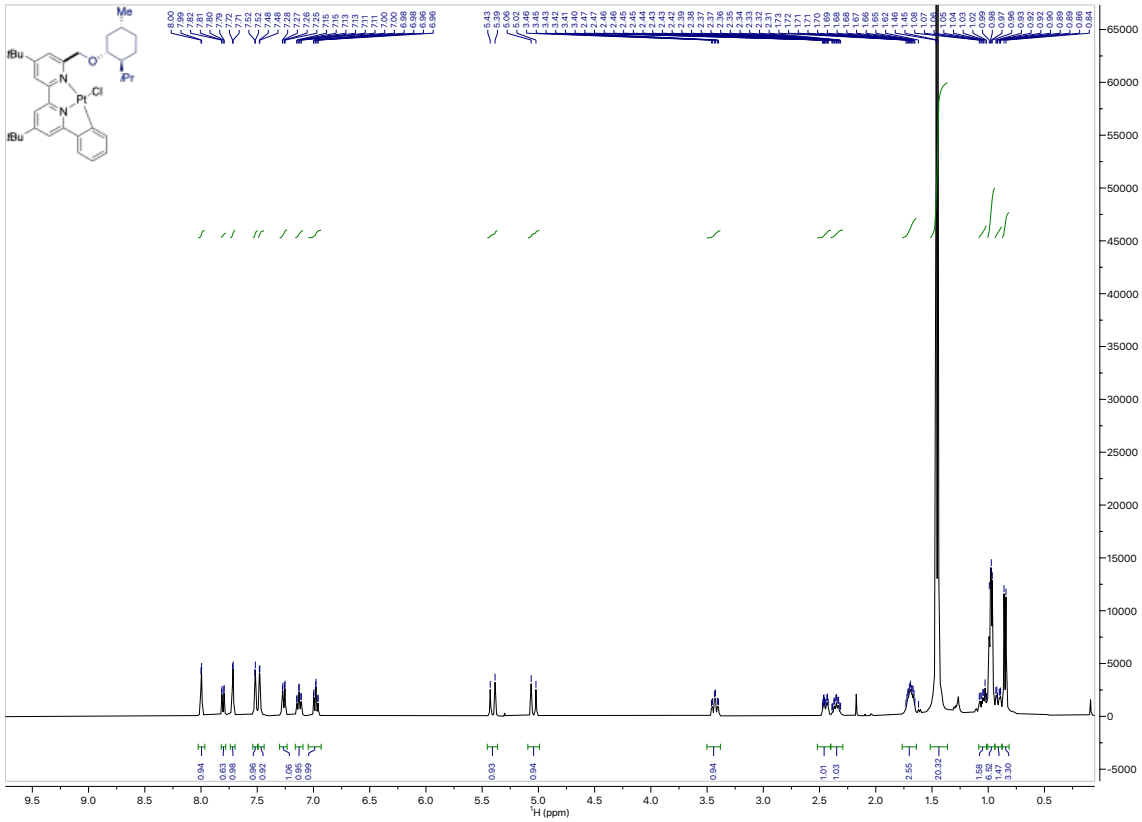


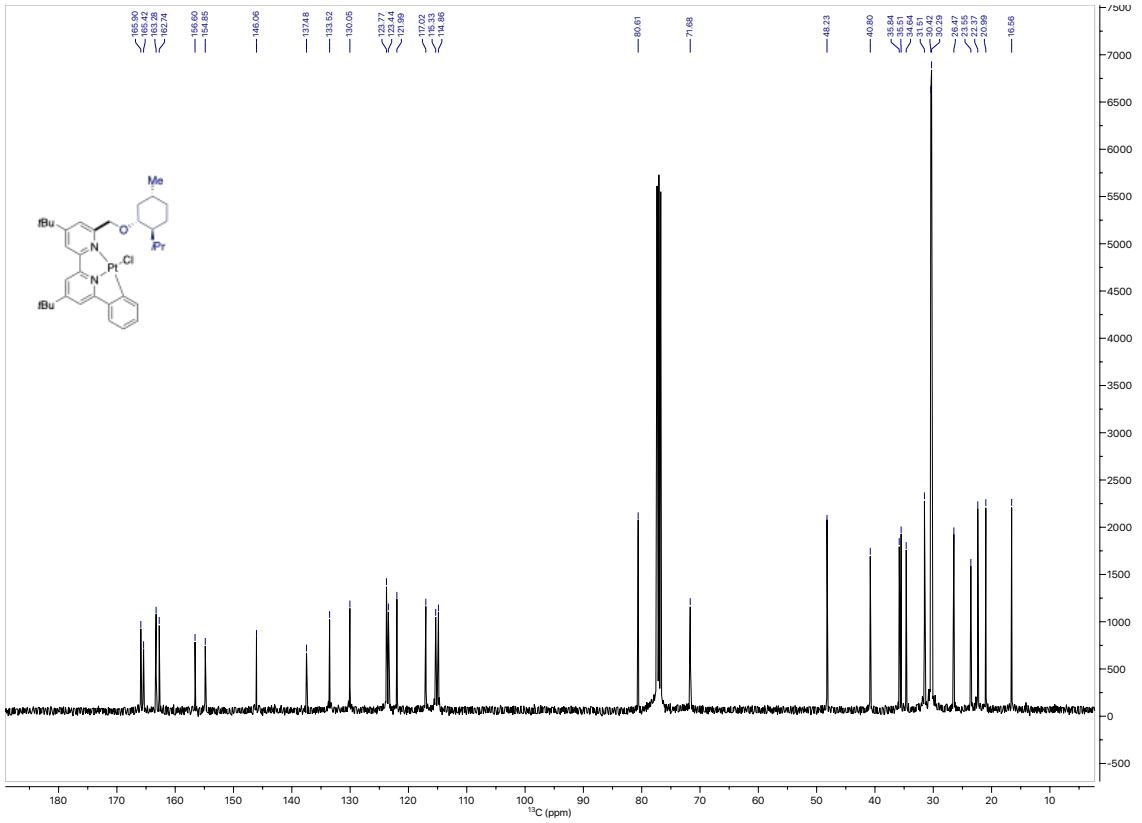
D8



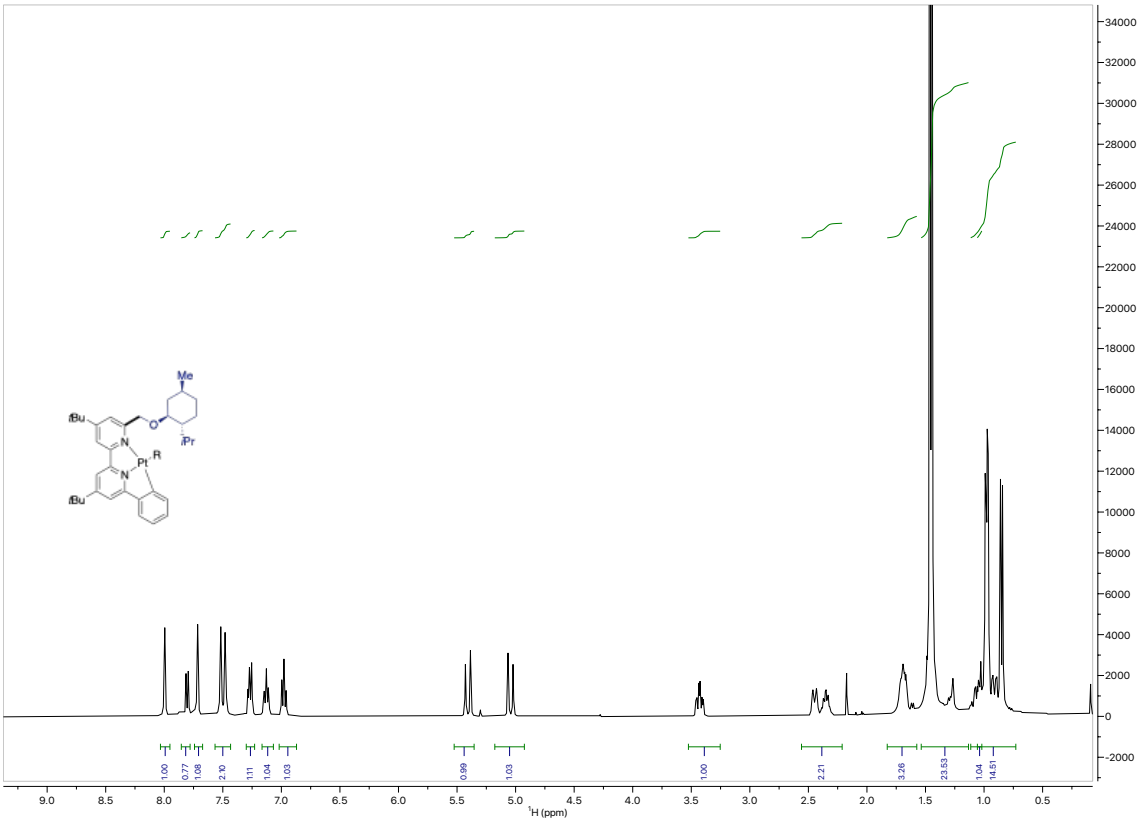


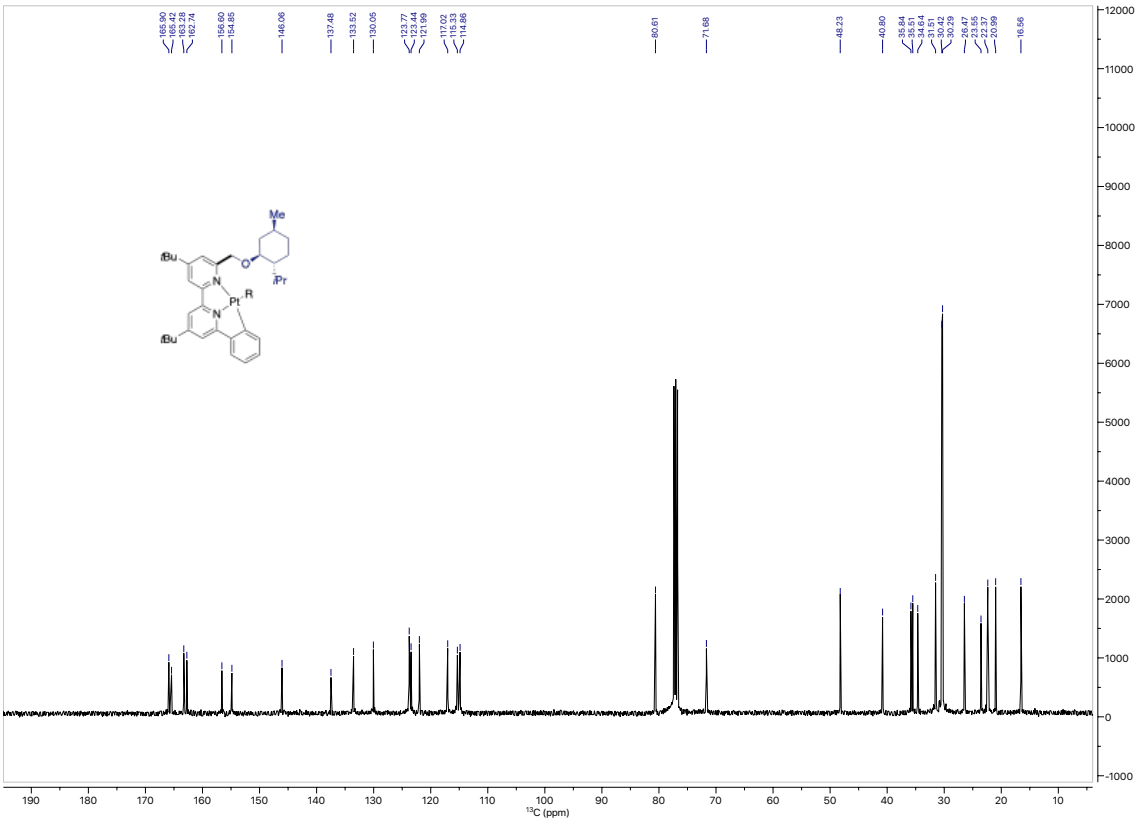
(-)-D9


Me
fBu
O
iPr
N
Pt
Cl
N
fBu
0.94
0.63
0.98
0.96
0.92
1.06
0.98
0.99
0.93
0.94
0.94
1.01
1.03
2.55
20.32
1.58
6.52
1.47
3.00
^{1}H (ppm)

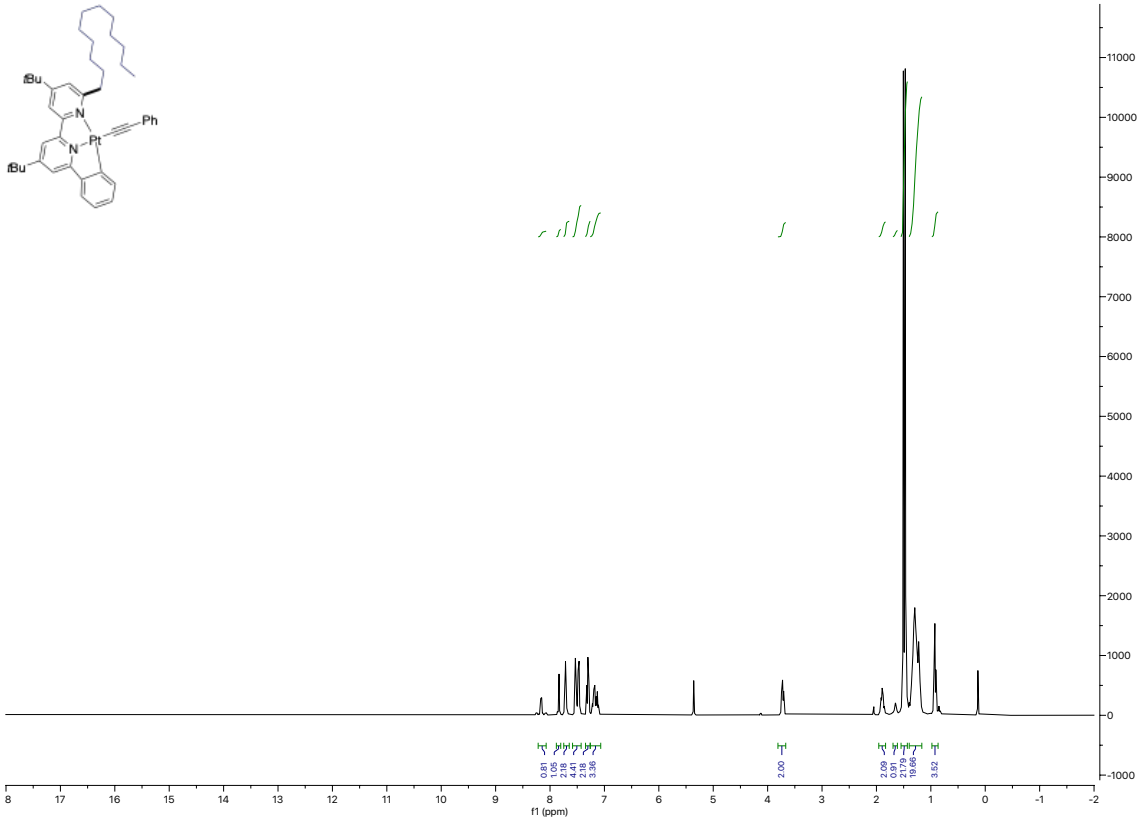

165.90
165.42
163.38
162.74
156.60
154.85
146.06
137.48
133.52
130.05
123.77
123.44
121.99
117.02
116.33
114.86
80.61
71.68
48.23
40.80
35.84
34.61
34.51
31.51
30.42
30.20
26.47
23.85
22.37
20.99
16.56
^{13}C (ppm)

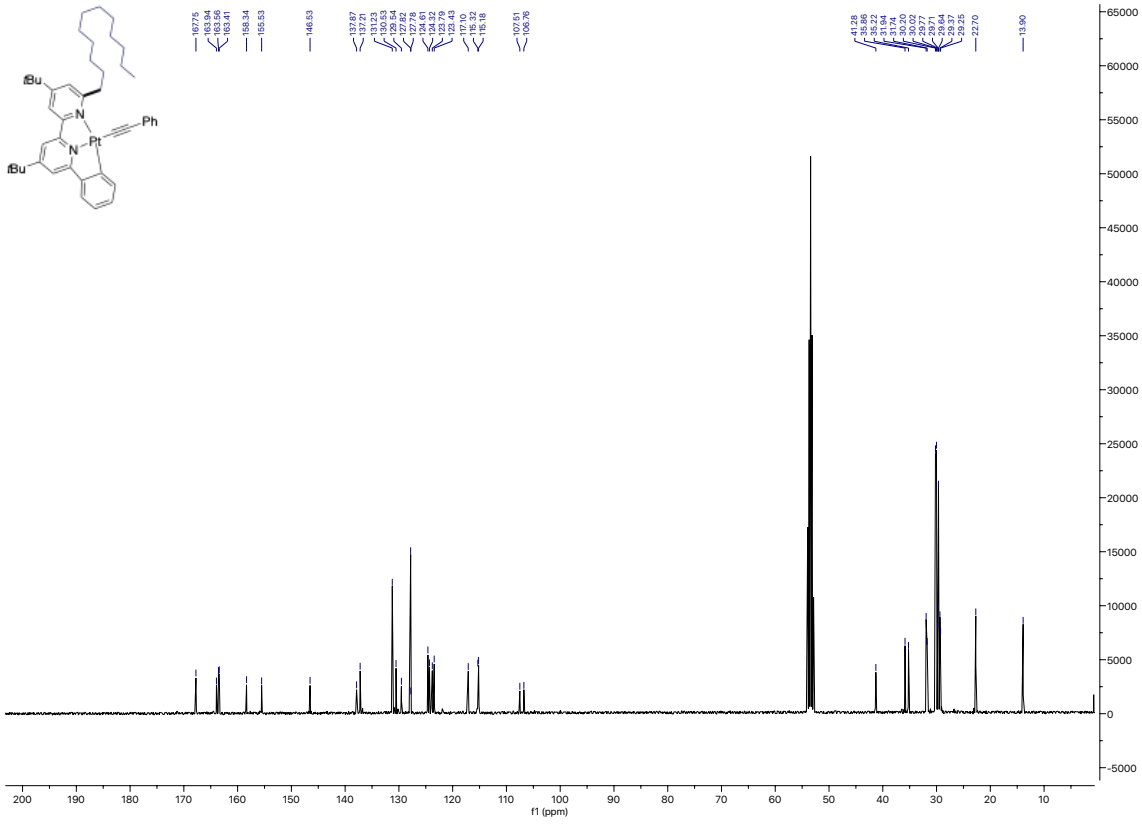
(+)-D9


Me
tBu
O
iPr
N
Pt
R
N
tBu
1.00
0.77
1.08
2.10
1.11
1.04
1.03
0.99
1.03
1.00
2.21
3.26
23.53
1.04
14.51
^{1}H (ppm)

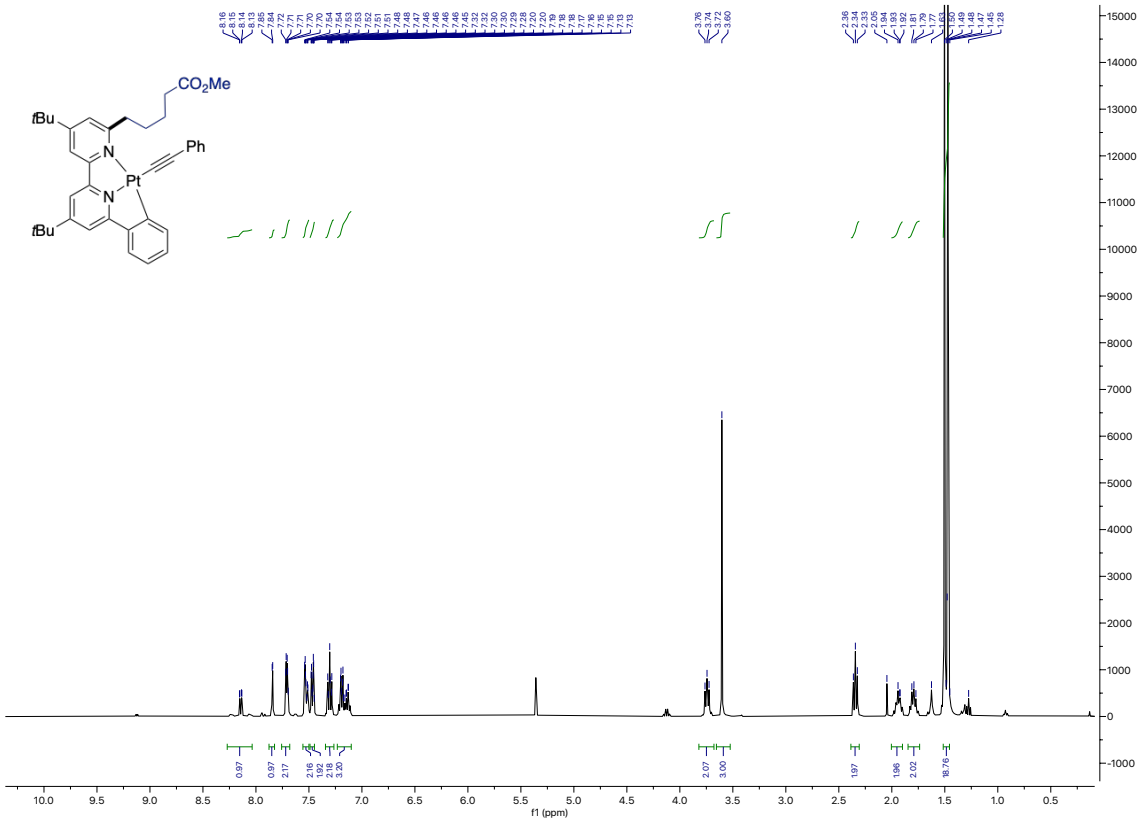

165.90
165.42
163.39
162.74
156.60
154.85
146.06
137.48
133.52
130.05
123.77
123.44
121.99
117.02
115.33
114.86
80.61
71.68
48.23
40.80
35.84
35.51
34.64
31.51
30.42
30.29
26.47
23.55
22.37
20.99
16.56
Me
tBu
O
iPr
N
Pt
R
N
tBu
^{13}C (ppm)

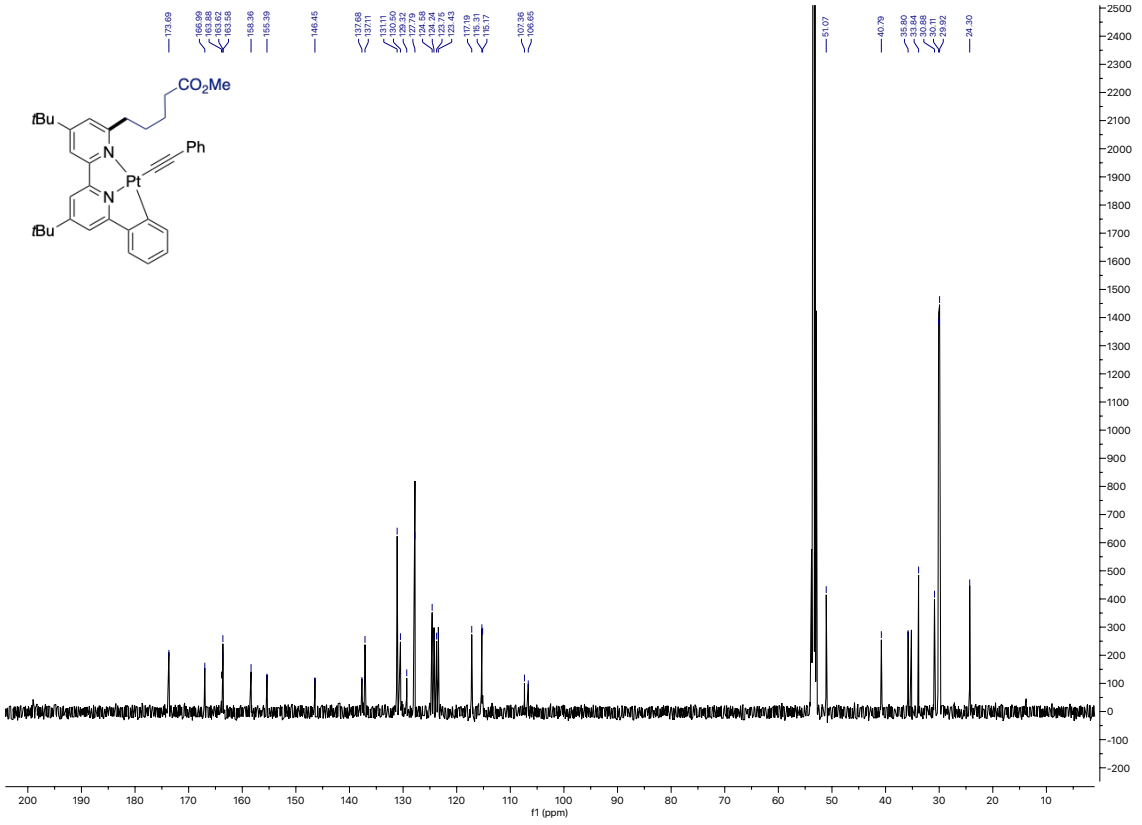
E4



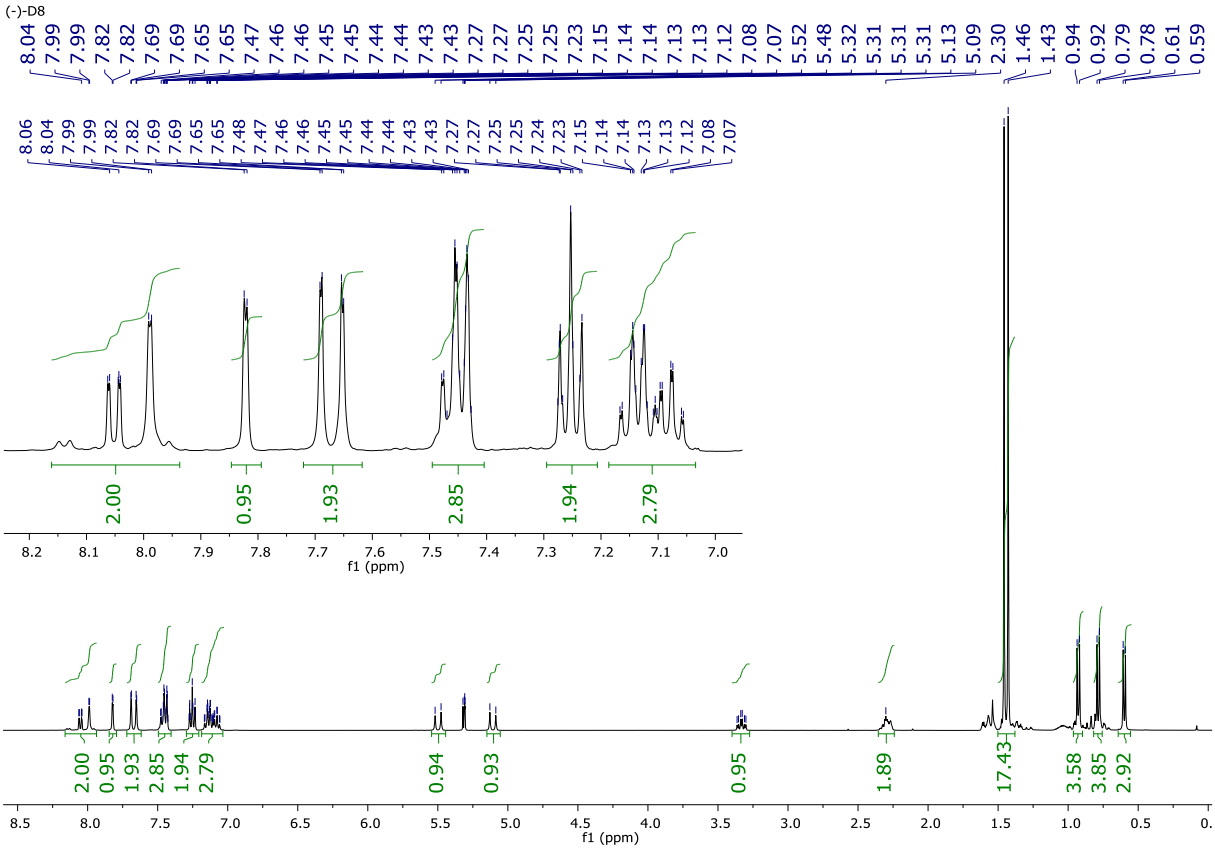


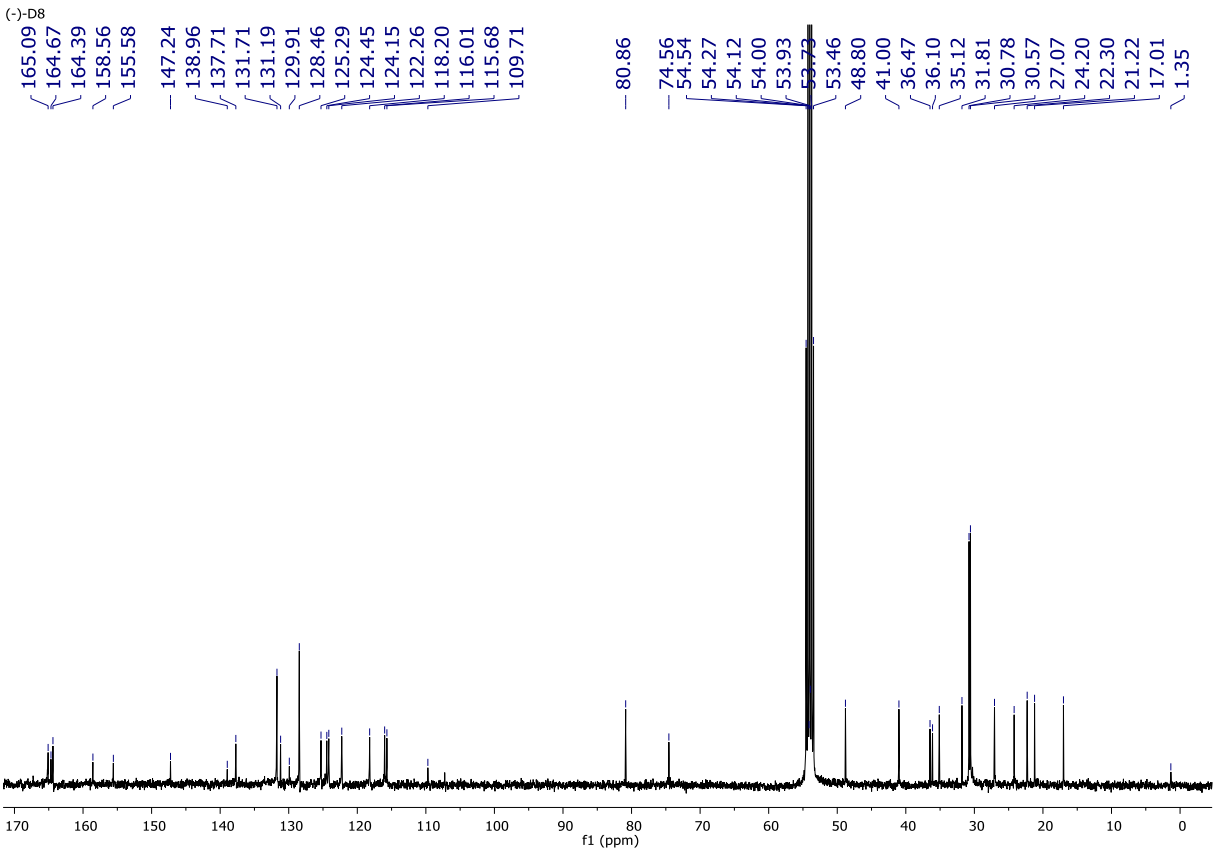
E6





(-)-E9





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