ESI

Selective α–arylation of α,β-unsaturated imides mediated by a visible light photoredox catalyst

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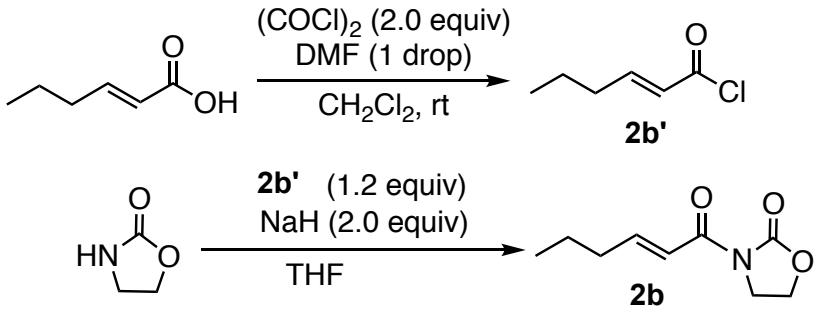
Instrumentation and Materials

^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were recorded on a Bruker AVANCE III HD spectrometer, and chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ (δ = 7.260 ppm) for ^{1}H NMR and $CHCl_3$ (δ = 77.16 ppm) for ^{13}C NMR. UV/vis absorption spectra were recorded on a Shimadzu UV-2550. Mass spectra were recorded on a Bruker microTOF using positive mode ESI-TOF method for acetonitrile solutions. X-ray data were taken on a Bruker D8 QUEST X-ray diffractometer equipped with PHOTON 100 CMOS active pixel sensor detector and IμS micro focus source using Mo-Kα radiation (λ = 0.71073 Å). Photoirradiation was carried out by a Xenon light source ASAHI SPECTRA MAX-303 (300 W) with an UV cut-off filter (>385 nm, light intensity: 10%). Fluorescence lifetime was recorded on a Hamamatsu Photonics Quantaurus-tau (C11367-25). Melting points were measured by a SRS MPA100 OptiMelt Automated Melting Point System. All reactions were carried out under dry argon or nitrogen atmosphere. Solvents were dried by the general methods, and degassed before use. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. 5-Substituted-pent-2-enoic acids,[S1] and photocatalysts[S2] were prepared according to the literature procedures.

Synthesis of alkenes 2.

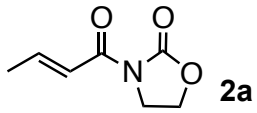


A typical experimental procedure for the synthesis of **2b** is described below. In a 100 mL round-bottomed flask were placed pent-2-enoic acid (16.1 mmol), oxalyl chloride (2.8 mL, 2 equiv), DMF (1 drop), and CH_2Cl_2 (50 mL) under air. The reaction mixture was stirred at rt until no further gas evolution took place (ca. 30 min). The resulting mixture was concentrated *in vacuo* to give **2b'** (814 mg, 6.14 mmol, 89% yield), which was used in the following reaction without further purification.

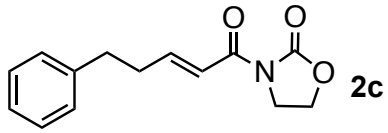
In a 50 mL Schlenk flask was placed 60% NaH (1.07 g, 2.0 equiv) under argon and washed with hexane (5 mL × 3). After drying NaH *in vacuo*, THF (15 mL) was added and then 2-oxazolidone (1.17 g, 13.4 mmol) was added to the suspension at 0 °C. The suspension was stirred for 30 min at 0 °C. After a solution of **2b'** (1.2 equiv) in THF (17 mL) was added dropwise, the suspension was stirred overnight at rt. Sat. NH_4Cl aq. was added to the suspension and the resulting mixture was extracted with EtOAc (15 mL × 3). The combined organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2) with CH_2Cl_2 to give **2b** (1.74g, 9.52 mmol, 59% yield).

2b[S3]: A white solid, m.p. 35.4–36.1 °C. ^{1}H NMR: δ 7.24 (dt, *J* = 15.5 and 1.0 Hz, 1H), 7.17 (dt, *J* = 15.5 and 6.5 Hz, 1H), 4.42 (t, *J* = 8.0 Hz, 2H), 4.07 (t, *J* = 8.0 Hz, 2H), 2.26 (ddd, *J* = 7.5, 6.5 and 1.0 Hz, 2H), 1.52 (sext, *J* = 7.5 Hz, 2H), 0.95 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR: δ 165.5, 153.7, 151.8, 120.2, 62.2, 42.9, 34.8, 21.5, 13.8.

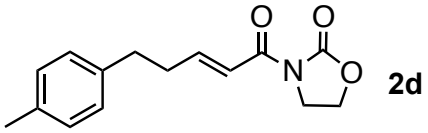
Isolated yields and spectroscopic data of **2** are as follows:



2a [S4]: 79% yield. A white solid, m.p. 40.7–41.9 °C. ^{1}H NMR: δ 7.26 (dq, *J* = 15.5 and 1.5 Hz, 1H), 7.18 (dq, *J* = 15.5 and 6.5 Hz, 1H), 4.42 (t, *J* = 8.0 Hz, 2H), 4.07 (t, *J* = 8.0 Hz, 2H), 1.96 (dd, *J* = 6.5 and 1.5 Hz, 3H). ^{13}C NMR: δ = 165.3, 153.7, 147.0, 121.6, 62.2, 42.8, 18.6.

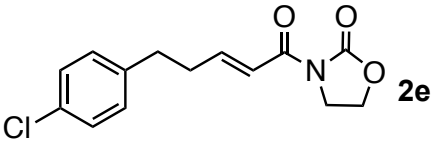


2c[S5]: 70% yield. A pale yellow solid, m.p. 73.2–74.6 °C. ^{1}H NMR: δ 7.31–7.28 (m, 2H), 7.28 (dt, *J* = 15.5 and 1.5 Hz, 1H), 7.22–7.18 (m, 3H), 7.20 (dt, *J* = 15.5 and 6.5 Hz, 1H), 4.42 (t, *J* = 8.0 Hz, 2H), 4.06 (t, *J* = 8.0 Hz, 2H), 2.81 (t, *J* = 7.5 Hz, 2H), 2.61 (ddd, *J* = 7.5, 6.5 and 1.5 Hz, 2H). ^{13}C NMR: δ 165.3, 153.6, 150.5, 140.9, 128.6, 128.5, 126.3, 120.6, 62.2, 42.8, 34.44, 34.41.



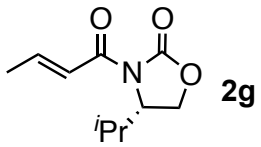
2d

2d: 44% yield. A pale yellow solid, m.p. 75.6–76.6 °C. ^{1}H NMR: δ 7.28 (dt, *J* = 15.5 and 1.5 Hz, 1H), 7.19 (dt, *J* = 15.5 and 6.5 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 4.42 (t, *J* = 8.0 Hz, 2H), 4.06 (t, *J* = 8.0 Hz, 2H), 2.77 (t, *J* = 7.5 Hz, 2H), 2.59 (ddd, *J* = 7.5, 6.5 and 1.5 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR: δ 165.3, 153.6, 150.7, 137.8, 135.7, 129.3, 128.3, 120.5, 62.2, 42.8, 34.6, 34.0, 21.1. HRMS (ESI) Calcd. for $C_{15}H_{17}NO_3K$ [M + K]: 298.0840. Found: 298.0839.



2e

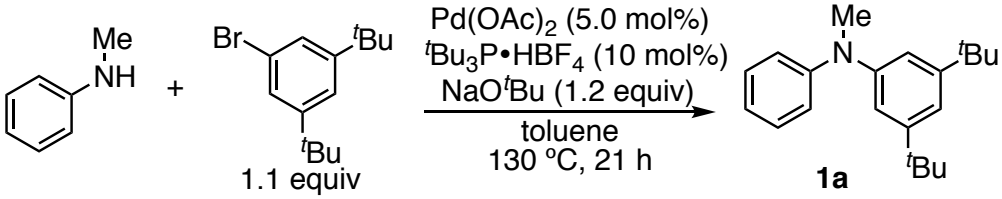
2e: 35% yield. A pale yellow solid, m.p. 71.2–72.4 °C. ^{1}H NMR: δ 7.27 (dt, *J* = 15.5 and 1.5 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.15 (dt, *J* = 15.5 and 7.0 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.42 (t, *J* = 8.0 Hz, 2H), 4.06, (t, *J* = 8.0 Hz, 2H), 2.79 (t, *J* = 8.0 Hz, 2H), 2.58 (qd, *J* = 8.0 and 1.5 Hz, 2H). ^{13}C NMR: δ 165.2, 153.6, 149.9, 139.2, 132.0, 129.9, 128.7, 120.8, 62.2, 42.8, 34.2, 33.8. HRMS (ESI) Calcd. for $C_{14}H_{14}ClNO_3K$ [M + K]: 318.0294. Found: 318.0300.



2g

2g [S6]: 80% yield. A white solid, m.p. 58.2–58.9 °C. ^{1}H NMR: δ = 7.29 (dq, *J* = 15.0 and 1.5 Hz, 1H), 7.16 (dq, *J* = 15.0 and 7.0 Hz, 1H), 4.49 (ddd, *J* = 8.5, 4.0 and 3.5 Hz, 1H), 4.28 (t, *J* = 8.5 Hz, 1H), 4.21 (dd, *J* = 8.5 and 3.5 Hz, 1H), 2.41 (sepd, *J* = 7.0 and 4.0 Hz, 1H), 1.96 (dd, *J* = 7.0 and 1.5 Hz, 3H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.88 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR: δ = 165.2, 154.2, 146.7, 122.1, 63.5, 58.7, 28.7, 18.6, 18.1, 14.9.

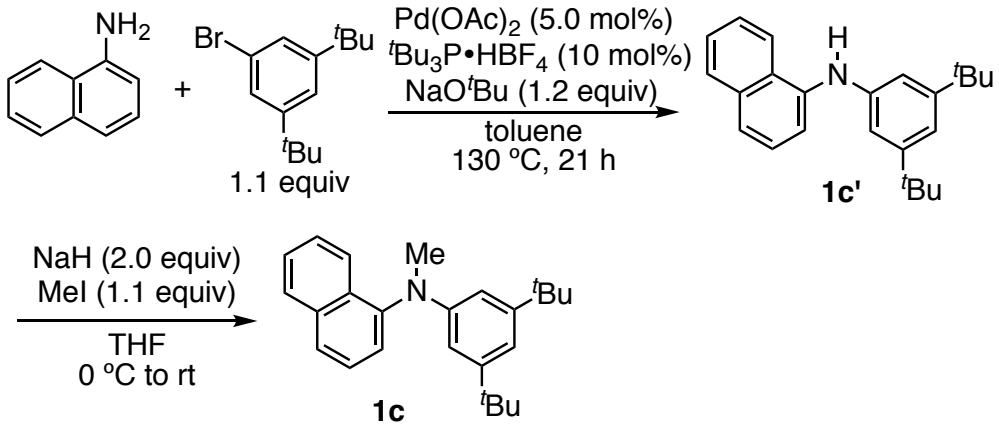
Synthesis of 1a.



In a 50 mL sealed vessel were placed *N*-methylaniline (0.44 mL, 4.0 mmol), 1-bromo-3,5-di-*tert*-butylbenzene (1.18 g, 1.1 equiv), $Pd(OAc)_2$ (45.0 mg, 5.0 mol%), $^tBu_3P{\bullet}HBF_4$ (116 mg, 10 mol%), NaO^tBu (465 mg, 1.2 equiv), and toluene (12 mL) under argon. The reaction mixture was stirred for 21 h at 130 °C. After cooling, the mixture was filtered through a pad of Celite and concentrated. The crude residue was purified by column chromatography (SiO_2) with hexane to give **1a** (quant.) as pale yellow oil.

1a: A pale yellow oil. ^{1}H NMR: δ 7.23 (t, *J* = 7.5 Hz, 2H), 7.12 (t, *J* = 1.5 Hz, 1H), 6.97 (d, *J* = 1.5 Hz, 2H), 6.91 (d, *J* = 7.5 Hz, 2H), 6.84 (t, *J* = 7.5 Hz, 1H), 3.33 (s, 3H), 1.30 (s, 18H). ^{13}C NMR: δ 152.0, 149.5, 148.2, 129.1, 119.3, 117.7, 117.5, 117.2, 40.5, 35.1, 31.6. HRMS (ESI) Calcd. for $C_{21}H_{30}N$ [M + H]: 296.2373. Found: 296.2369.

Synthesis of amines 1.



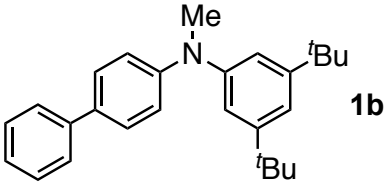
A typical experimental procedure for the synthesis of **1c** is described below. In a 50 mL sealed vessel were placed 1-naphthylamine (715.7 mg, 5.0 mmol), 1-bromo-3,5-di-*tert*-butylbenzene (1.4815 g, 1.1 equiv), $Pd(OAc)_2$ (56.2 mg, 5.0 mol%), $^tBu_3P{\bullet}HBF_4$ (145.1 mg, 10 mol%), NaO^tBu (576.9 mg, 1.2 equiv), and toluene (15 mL) under argon. The reaction mixture was stirred for 21 h at 130 °C. After cooling, the mixture was filtered through a pad of Celite and concentrated. The crude residue was purified by column chromatography (SiO_2 supported by amino group) with hexane/EtOAc to give **1c'** (1.3797 g, 4.16 mmol) as a white solid.

In a 20 mL Schlenk flask was placed 60% NaH (160 mg, 2.0 equiv) under argon and washed with hexane (5 mL × 3). After drying NaH *in vacuo*, THF (4 mL) was added and then **1c'** (663 mg, 2.00 mmol) was added dropwise to the suspension at 0 °C. The suspension was stirred for 30 min at 0 °C. After MeI (0.14 mL, 1.1 equiv) was added dropwise, the suspension was stirred overnight at rt. Sat. NH_4Cl aq. was added to the suspension and the resulting mixture was extracted with EtOAc (15 mL × 3). The combined organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2 supported by amino group) with hexane to give **1c** (533 mg, 1.54 mmol, 77% yield).

1c: A pale yellow solid, m.p. 120.9–122.9 °C. ^{1}H NMR: δ 7.96 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.0 Hz, 1H), 7.48 (t, *J* = 7.0 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.38 (d, *J*

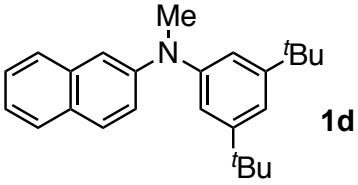
= 7.5 Hz, 1H), 6.85 (t, *J* = 1.5 Hz, 1H), 6.54 (d, *J* = 1.5 Hz, 2H), 3.40 (s, 3H), 1.22 (s, 18H). ^{13}C NMR: δ 151.2, 149.6, 146.3, 135.2, 131.5, 128.4, 126.4, 126.2, 126.2, 126.2, 124.9, 124.3, 112.2, 108.9, 40.6, 35.0, 31.6 ppm. HR-MS (ESI) Calcd. for $C_{25}H_{32}N$ [M + H]: 346.2529. Found: 346.2513.

Isolated yields and spectroscopic data of other products are as follows:



1b

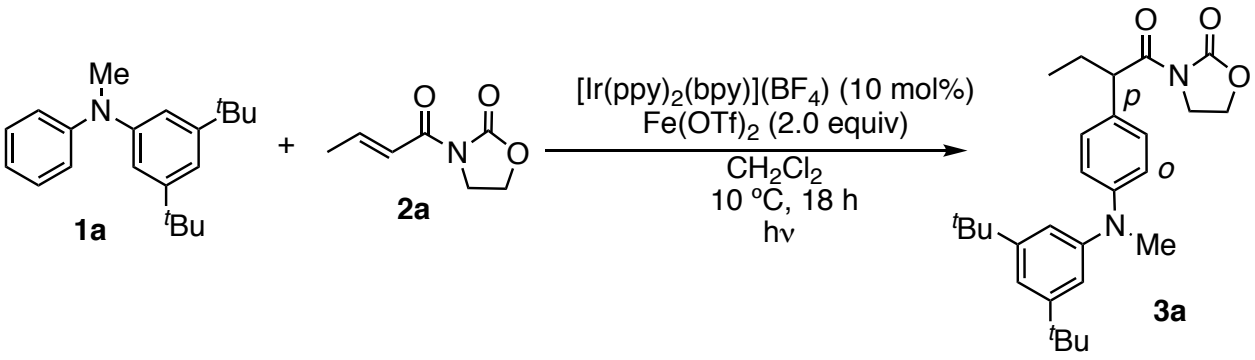
1b: 38% yield. A pale yellow solid, m.p. 121.6–123.5 °C. ^{1}H NMR: δ 7.57 (d, *J* = 7.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 1.5 Hz, 1H), 7.04 (d, *J* = 1.5 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 3.38 (s, 3H), 1.32 (s, 18H). ^{13}C NMR: δ 152.1, 148.8, 148.0, 141.2, 131.5, 128.8, 127.7, 126.6, 126.4, 118.5, 117.7, 116.8, 40.5, 35.1, 31.6. HRMS (ESI) Calcd. for $C_{27}H_{34}N$ [M + H]: 372.2686. Found: 372.2676.



1d

1d: 51% yield. A pale yellow solid, m.p. 141.4–143.1 °C. ^{1}H NMR: δ 7.72 (d, *J* =8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.62 (d, 9.0 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 2.5 Hz, 1H), 7.18 (t, *J* = 1.5 Hz, 1H), 7.16 (dd, *J* = 9.0 and 2.5 Hz, 1H), 7.04 (d, *J* = 1.5 Hz, 2H), 3.45 (s, 3H), 1.32 (s, 18H). ^{13}C NMR: δ 152.1, 148.4, 147.2, 135.1, 128.5, 128.3, 127.6, 126.7, 126.3, 123.1, 120.7, 118.1, 117.5, 111.4, 40.9, 35.1, 31.6. HRMS (ESI) Calcd. for $C_{25}H_{32}N$ [M + H]: 346.2529. Found: 346.2513.

Photocatalytic reaction of amines 1 with α,β-unsaturated imides 2.

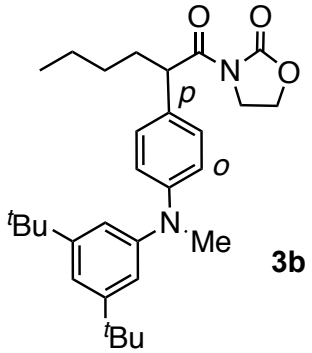


A typical experimental procedure for photocatalytic reaction of **1a** with **2a** is described below. In a 20 mL Schlenk flask (diameter: 2.5 cm) were placed $[Ir(ppy)_2(bpy)](BF_4)$ as a photocatalyst (7.7 mg, 10 mol%), amine **1a** (29.5 mg, 0.10 mmol), alkene **2a** (31.0 mg, 0.20 mmol), $Fe(OTf)_2$ (70.8 mg, 0.20 mmol), and CH_2Cl_2 (1 mL) under argon. The reaction flask was placed in a water bath and irradiated from the side at 10 °C for 18 h. Aftre the reaction, water was added to the suspension and the resulting mixture was extracted

with $CHCl_3$ (15 mL × 3). The combined organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The resulting mixture was purified by column chromatography (SiO_2) with hexane/ethyl acetate (5/1) to give **3a** (23.3 mg, 0.0517 mmol, 52% yield).

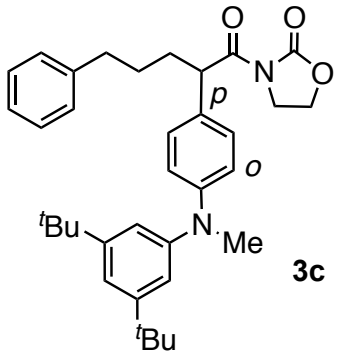
3a: (para/ortho: 5/1). (para-isomer) ^{1}H NMR: δ 7.22 (d, *J* = 9.0 Hz, 2H), 7.15 (t, *J* = 1.0 Hz, 1H), 6.98 (d, *J* = 1.0 Hz, 2H), 6.81 (d, *J* = 9.0 Hz, 2H), 4.84 (t, *J* = 7.5 Hz, 1H), 4.39–4.34 (m, 1H), 4.32–4.27, (m, 1H), 4.09–4.03 (m, 1H), 3.96–3.90 (m, 1H), 3.32 (s, 3H), 2.13–2.05 (m, 1H), 1.85–1.76 (m, 1H), 1.31 (s, 18H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR: δ 174.8, 153.3, 152.0, 148.5, 147.9, 129.4, 128.7, 118.4, 117.7, 116.3, 61.8, 49.3, 43.0, 40.4, 35.1, 31.6, 27.3, 12.2. (ortho-isomer) ^{1}H NMR: δ 7.58 (dd, *J* = 7.5 and 1.0 Hz, 1H), 7.37 (td, *J* = 7.5 and 1.0 Hz, 1H), 7.32 (td, *J* = 7.5 and 1.5 Hz, 1H), 7.16 (dd, *J* = 7.5 and 1.5 Hz, 1H), 6.79 (s, 1H), 6.26 (s, 2H), 5.24 (t, *J* = 6.5 Hz, 1H), 4.06–4.01 (m, 1H), 3.68–3.62 (m, 1H), 3.50–3.45 (m, 1H), 3.24–3.19 (m, 1H), 3.19 (s, 3H), 2.13–2.05 (m, 1H), 1.98–1.91 (m, 1H), 1.23 (s, 18H), 0.99 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR: δ 174.1, 153.0, 151.1, 149.3, 147.5, 138.6, 129.8, 129.2, 128.6, 127.3, 111.6, 107.8, 61.5, 42.8, 40.2, 35.0, 29.8, 25.5, 22.8, 14.3. HRMS (ESI) Calcd. for $C_{28}H_{39}N_2O_3$ [M + H]: 451.2955. Found: 451.2976.

Isolated yields and spectroscopic data of other products are as follows:



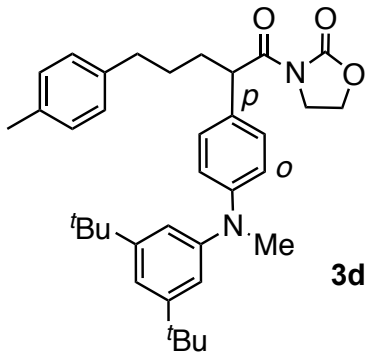
3b

3b: 49% yield (para/ortho = 6/1). (para-isomer) ^{1}H NMR: δ 7.23 (d, *J* = 9.0 Hz, 2H), 7.15 (t, *J* = 1.5 Hz, 1H), 6.98 (d, *J* = 1.5 Hz, 2H), 6.81 (d, *J* = 9.0 Hz, 2H), 4.94 (t, *J* = 7.5 Hz, 1H), 4.39–4.34 (m, 1H), 4.32–4.27 (m, 1H), 4.08–4.03 (m, 1H), 3.95–3.90 (m, 1H), 3.32 (s, 1H), 2.10–2.03 (m, 1H), 1.81–1.74 (m, 1H), 1.39–1.17 (m, 4H), 1.30 (s, 18H), 0.86 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR: δ 174.9, 153.2, 152.0, 148.5, 147.9, 129.3, 128.9, 118.4, 117.6, 116.4, 61.7, 47.5, 43.0, 40.4, 35.1, 33.9, 31.6, 29.8, 22.7, 14.1. (ortho-isomer) ^{1}H NMR: δ 7.58 (dd, *J* = 7.5 and 1.5 Hz, 1H), 7.37 (td, *J* = 7.5 and 1.5 Hz, 1H), 7.32 (td, *J* = 7.5 and 1.5 Hz, 1H), 7.16 (dd, *J* = 7.5 and 1.5 Hz, 1H), 6.78 (t, *J* = 1.5 Hz, 1H), 6.25 (br, 2H), 5.32 (t, *J* = 7.5 Hz, 1H), 4.06–4.01 (m, 1H), 3.68–3.62 (m, 1H), 3.52–3.44 (m, 1H), 3.27–3.18 (m, 1H), 3.19 (s, 3H), 2.08–2.00 (m, 1H), 1.94–1.84 (m, 1H), 1.39–1.17 (m, 4H), 1.22 (s, 18H), 0.86 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR: δ 174.2, 153.0, 151.1, 149.3, 147.5, 138.7, 129.8, 129.2, 128.6, 127.3, 111.6, 107.8, 61.5, 42.8, 40.2, 35.0, 31.6, 29.8, 22.8, 14.0. HRMS (ESI) Calcd. for $C_{30}H_{45}N_2O_3$ [M + H]: 479.3268. Found: 479.3274.



3c

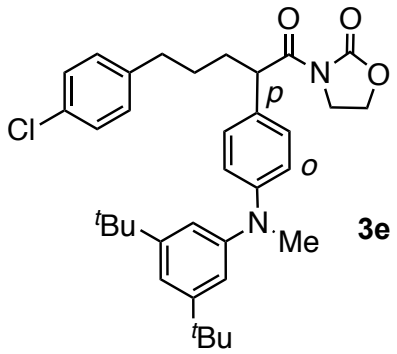
3c: 46% yield (para/ortho = 8/1). (para-isomer) ^{1}H NMR: δ 7.26 (t, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.16 (t, *J* = 1.5 Hz, 1H), 7.16 (td, *J* = 7.5 and 1.0 Hz, 1H), 7.15 (dd, *J* = 7.5 and 1.0 Hz, 2H), 6.99 (d, *J* = 1.5 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 4.98 (t, *J* = 7.5 Hz, 1H), 4.38–4.33 (m, 1H), 4.31–4.26 (m, 1H), 4.06–4.01 (m, 1H), 3.94–3.87 (m, 1H), 3.22 (s, 3H), 2.68–2.57 (m, 2H), 2.15–2.07 (m, 1H), 1.88–1.81 (m, 1H), 1.63–1.55 (m, 2H), 1.31 (s, 18H). ^{13}C NMR: δ 174.7, 153.2, 152.0, 148.5, 147.8, 142.3, 129.3, 128.5, 128.4, 125.8, 118.5, 117.7, 116.3, 61.7, 47.4, 43.0, 40.4, 35.8, 35.1, 33.7, 31.6, 29.4. (ortho-isomer) ^{1}H NMR: δ 7.52 (dd, *J* = 7.5 and 1.5 Hz, 1H), 7.35 (td, *J* = 7.0 and 1.0 Hz, 1H), 7.32 (td, *J* = 7.0 and 1.5 Hz, 1H), 6.25 (br, 2H), 5.37 (br, 1H), 4.15–4.11 (m, 1H), 3.66–3.60 (m, 1H), 3.50–3.42 (m, 1H), 3.25–3.17 (m, 1H), 3.20 (s, 3H), 2.68–2.57 (m, 2H), 2.15–2.07 (m, 1H), 1.99–1.90 (m, 1H), 1.77–1.65 (m, 2H), 1.23 (s, 18H). ^{13}C NMR: δ 174.0, 153.0, 151.1, 149.3, 147.5, 142.1, 138.5, 129.7, 129.2, 128.7, 128.5, 127.4, 125.9, 111.6, 107.9, 61.5, 42.7, 40.2, 36.0, 35.0, 29.3. HRMS (ESI) Calcd. for $C_{35}H_{54}N_2O_3$ [M + H]: 541.3425. Found: 541.3426.



3d

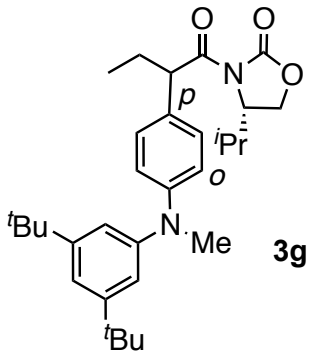
3d: 47% yield (para/ortho = 8/1). (para-isomer) ^{1}H NMR: δ 7.22 (d, *J* = 8.5 Hz, 2H), 7.16 (t, *J* = 1.0 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 2H), 7.04 (d, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 1.0 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 4.97 (t, *J* = 7.5 Hz, 1H), 4.37–4.32 (m, 1H), 4.31–4.25 (m, 1H), 4.06–4.00 (m, 1H), 3.94–3.88 (m, 1H), 3.31 (s, 3H), 2.63–2.53 (m, 2H), 2.30 (s, 3H), 2.14–2.06 (m, 1H), 1.86–1.79 (m, 1H), 1.61–1.51 (m, 2H), 1.31 (s, 18H). ^{13}C NMR: δ 174.8, 153.2, 152.0, 148.0, 147.5, 139.3, 135.2, 129.3, 129.1, 128.7, 128.4, 118.4, 117.7, 116.4, 61.7, 47.4, 43.0, 40.4, 35.4, 35.1, 33.7, 31.6, 29.5, 21.1. (ortho-isomer) ^{1}H NMR: δ 7.52 (dd, *J* = 7.5 and 1.5 Hz, 1H), 7.35 (td, *J* = 7.5 and 1.5 Hz, 1H), 7.31 (td, *J* = 7.5 and 1.5 Hz, 1H), 7.14 (dd, *J* = 7.5 and 1.5 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.78 (t, *J* = 1.5 Hz, 1H), 6.25 (d, *J* = 1.5 Hz, 2H), 5.37 (br, 1H), 4.03–3.99 (m, 1H), 3.64–3.59 (m, 1H), 3.47–3.40 (m, 1H), 3.23–3.16 (m, 1H), 3.19 (s, 3H), 2.64–2.54 (m, 2H), 2.30 (s, 3H), 2.12–2.05 (m, 1H), 1.97–1.88 (m, 1H), 1.74–1.58 (m, 2H), 1.21 (s, 18H). ^{13}C NMR: δ 174.0, 153.0, 151.2, 149.4, 148.6, 139.1, 138.6, 135.3, 129.8, 129.2, 128.4, 127.3, 111.6, 107.9,

61.5, 42.8, 40.2, 35.5, 35.0, 31.6, 29.4. HRMS (ESI) Calcd. for $C_{36}H_{47}N_2O_3$ [M + H]: 555.3581. Found: 555.3608.



3e

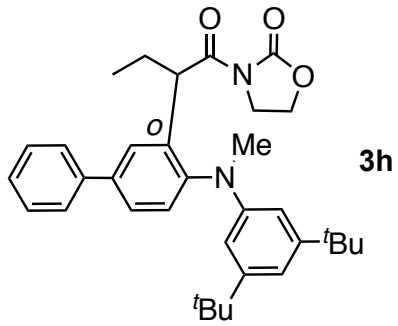
3e: 53% yield (para/ortho = 8/1). (para-isomer) ^{1}H NMR: δ 7.21 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.16 (t, *J* = 1.5 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 1.5 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 4.96 (t, *J* = 7.5 Hz, 1H), 4.38–4.33 (m, 1H), 4.31–4.26 (m, 1H), 4.06–4.01 (m, 1H), 3.94–3.88 (m, 1H), 3.31 (s, 3H), 2.63–2.53 (m, 2H), 2.11–2.03 (m, 1H), 1.85–1.77 (m, 1H), 1.61–1.50 (m, 2H), 1.31 (s, 18H). ^{13}C NMR: δ 174.6, 153.2, 152.0, 148.6, 147.8, 140.7, 131.5, 129.9, 129.3, 128.5, 128.2, 118.6, 117.8, 116.1, 61.8, 47.3, 43.0, 40.4, 35.1, 33.4, 31.6, 29.2. (ortho-isomer) ^{1}H NMR: δ 7.51 (d, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.78 (s, 1H), 6.24 (s, 2H), 5.36 (s, 1H), 4.05–4.00 (m, 1H), 3.66–3.60 (m, 1H), 3.49–3.43 (m, 1H), 3.25–3.19 (m, 1H), 3.19 (s, 3H), 2.60–2.57 (m, 2H), 2.10–2.02 (m, 1H), 1.92–1.85 (m, 1H), 1.70–1.49 (m, 2H), 1.22 (s, 18H). ^{13}C NMR: δ 173.9, 153.0, 151.2, 149.3, 147.5, 140.5, 138.4, 131.6, 129.9, 129.7, 129.3, 128.8, 128.5, 127.4, 111.7, 107.9, 61.5, 42.8, 40.3, 35.2, 35.0, 31.6, 29.8, 29.2. HRMS (ESI) Calcd. for $C_{35}H_{44}ClN_2O_3$ [M+H]: 575.3035. Found: 575.3019.



3g

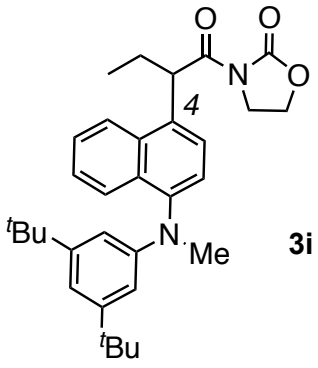
3g: 23% yield (para/ortho: 10/1, diastereomeric excess of para isomer: 3% de). (para-isomer-major) ^{1}H NMR: δ 7.21 (d, *J* = 8.0 Hz, 2H), 7.10 (s, 1H), 6.92 (s, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 4.87 (t, *J* = 7.5 Hz, 1H), 4.51–4.48 (m, 1H), 4.24 (t, *J* = 8.5 Hz, 1H), 4.15–4.10 (m, 1H), 3.30 (s, 3H), 2.20–2.14 (m, 1H), 2.13–2.03 (m, 1H), 1.83–1.74 (m, 1H), 1.28 (s, 18H), 0.91 (d, *J* = 7.0 Hz, 3H), 0.88 (t, *J* = 7.5 Hz, 3H), 0.79 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR: δ 174.6, 153.7, 151.8, 148.5, 148.3, 129.7, 129.2, 118.3, 117.8, 117.3, 63.0, 58.2, 50.0, 40.5, 40.5, 35.1, 31.6, 28.0, 26.4, 17.9, 14.3, 12.2. (para-isomer-minor) ^{1}H NMR: δ 7.21 (d, *J* = 8.5 Hz, 2H), 7.14 (s, 1H), 6.97 (s, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 4.90 (t, *J* = 7.5 Hz, 1H), 4.39–4.36 (m, 1H), 4.31 (t, *J* =

8.0 Hz, 1H), 4.15–4.10 (m, 1H), 3.31 (s, 3H), 2.47–2.41 (m, 1H), 2.13–2.03 (m, 1H), 1.83–1.74 (m, 1H), 1.30 (s, 18H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.90 (t, *J* = 7.5 Hz, 3H), 0.49 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR: δ 174.8, 153.9, 152.0, 148.5, 147.9, 129.4, 128.8, 117.6, 117.0, 116.4, 63.0, 59.1, 49.3, 40.4, 35.1, 31.6, 28.7, 27.9, 18.2, 14.8, 12.3. (ortho-isomer) ^{1}H NMR: δ 7.50 (d, *J* = 7.0 Hz, 1H), 7.29 (t, *J* = 7.0 Hz, 1H), 7.27 (t, *J* = 7.0 Hz, 1H), 7.04 (d, *J* = 7.0 Hz, 1H), 6.87 (s, 1H), 6.41 (s, 2H), 5.36 (t, *J* = 7.5 Hz, 1H), 4.36–4.33 (m, 1H), 4.17 (t, *J* = 7.5 Hz, 1H), 4.11–4.09 (m, 1H), 3.17 (s, 3H), 2.20–2.14 (m, 1H), 2.01–1.95 (m, 1H), 1.94–1.89 (m, 1H), 1.22 (s, 18H), 0.91 (t, *J* = 7.5 Hz, 3H), 0.74 (d, *J* = 7.0 Hz, 3H), 0.41 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR: δ 174.6, 153.7, 151.3 150.7, 149.7, 137.0, 129.1, 128.8, 128.5, 126.4, 112.5, 109.6, 62.6, 58.8, 44.9, 35.0, 31.5, 29.8, 28.2, 18.2, 13.7, 12.7. HRMS (ESI) Calcd. for $C_{31}H_{45}N_2O_3$ [M+H]: 493.3425. Found: 493.3401.



3h

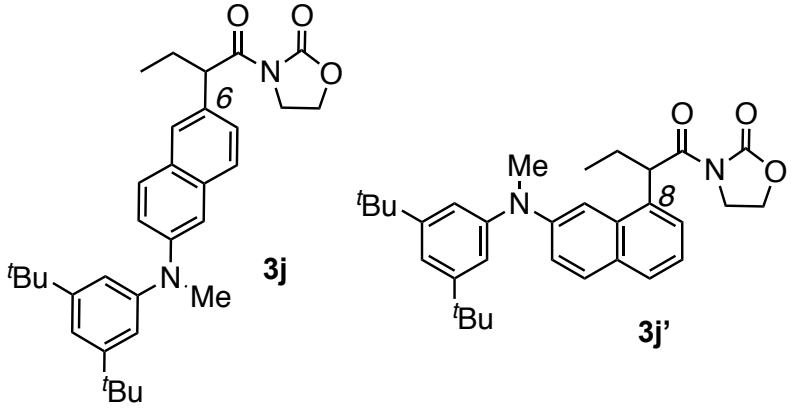
3h: 57% yield. ^{1}H NMR: δ 7.79 (d, *J* = 3.5 Hz, 1H), 7.68 (dd, *J* = 12.0 and 3.0 Hz, 2H), 7.56 (dd, *J* = 13.5 and 3.5 Hz, 1H), 7.49 (t, *J* = 12.0 Hz, 2H), 7.36 (tt, *J* = 12.0 and 3.0, 1H), 7.23 (d, *J* = 13.5 Hz, 1H), 6.81 (t, *J* = 2.0 Hz, 1H), 6.32 (d, *J* = 2.0 Hz, 2H), 5.29 (t, *J* = 12.0 Hz, 1H), 4.10–4.02 (m, 1H), 3.73–3.64 (m, 1H), 3.56–3.47 (m, 1H), 3.30–3.24 (m, 1H), 3.22 (s, 3H), 2.23–2.09 (m, 1H), 2.05–1.93 (m, 1H), 1.24 (s, 18H), 1.02 (t, *J* = 12.0 Hz, 3H). ^{13}C NMR: δ 174.0, 153.1, 151.2, 149.3, 146.9, 140.9, 139.9, 138.8, 129.4, 128.9, 128.6, 127.4, 127.4, 127.3, 111.8, 108.0, 61.5, 44.5, 42.8, 40.3, 35.1, 31.6, 25.7, 12.3. HRMS (ESI) Calcd. for $C_{34}H_{43}N_2O_3$ [M + H]: 527.3268. Found: 527.3245.



3i

3i: 21% yield. ^{1}H NMR: δ 8.31 (dd, *J* = 8.5 and 1.0 Hz, 1H), 8.00 (dd, *J* = 8.5 and 1.0 Hz, 1H), 7.56 (ddd, *J* = 8.5, 7.5 and 1.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.43 (ddd, *J* =8.5, 7.5 and 1.0 Hz, 1H), 7.31 (d, 8.0 Hz, 1H), 6.83 (t, *J* = 1.5 Hz, 1H), 6.49 (d, *J* = 1.5 Hz, 2H), 5.78 (dd, *J* = 8.0 and 6.5, 1H), 4.43–4.38 (m, 1H), 4.32–4.27 (m, 1H), 4.17–4.12 (m, 1H), 4.03–3.99 (1H, m), 3.36 (s, 3H), 2.29–2.20 (m, 1H), 2.02–1.93 (m,

1H), 1.20 (s, 18H), 0.99 (t, J = 7.0 Hz, 3H). ^{13}C NMR: δ 174.7, 153.3, 151.2, 149.6, 145.7, 133.5, 133.5, 131.9, 126.6, 126.0, 125.2, 124.9, 124.5, 124.2, 112.2, 108.8, 61.9, 45.9, 43.2, 40.5, 35.0, 31.5, 27.8, 12.7. HRMS (ESI) Calcd. for $C_{32}H_{41}N_2O_3$ [M + H]: 501.3112. Found: 501.3107.



3j+3j': 22% yield (**3j/3j'** = 5/2). (**3j**) ^{1}H NMR: δ 7.70 (d, J = 1.5 Hz, 1H), 7.63 (d, J = 8.5 Hz, 1H), 7.58 (d, J = 9.0 Hz, 1H), 7.44 (dd, J = 8.5 and 1.5 Hz, 1H), 7.16 (t, J = 1.5 Hz, 1H), 7.16 (d, J = 1.5 Hz, 1H), 7.15 (dd, J = 8.0 and 2.0 Hz, 1H), 7.12 (d, J = 1.5 Hz, 2H), 5.02 (t, J = 7.5 Hz, 1H), 4.39–4.34 (m, 1H), 4.30–4.23 (m, 1H), 4.11–4.05 (m, 1H), 3.95–3.90 (m, 1H), 3.43 (s, 3H), 2.21–2.14 (m, 1H), 1.95–1.88 (m, 1H), 1.30 (s, 18H), 0.91 (t, J = 7.5 Hz, 3H). ^{13}C NMR: δ 174.6, 153.3, 152.0, 148.3, 147.2, 134.3, 133.2, 128.3, 127.5, 127.1, 126.9, 120.8, 119.8, 118.1, 117.9, 110.9, 61.8, 50.2, 43.0, 41.0, 35.1, 31.6, 27.1, 12.3. (**3j'**) ^{1}H NMR: δ 7.61 (d, J = 9.0 Hz, 1H), 7.58 (d, J = 9.0 Hz, 1H), 7.54 (d, J = 2.0 Hz, 1H), 7.43 (dd, J = 7.5 and 1.5 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.19 (t, J = 1.5 Hz, 1H), 7.12 (dd, J = 10 and 2.5 Hz, 1H), 7.05 (d, J = 1.5 Hz, 2H), 5.71 (dd, J = 8.0 and 6.0 Hz, 1H), 4.43–4.38 (m, 1H), 4.30–4.23 (m, 1H), 4.16–4.10 (m, 1H), 4.01–3.96 (m, 1H), 3.49 (s, 3H), 2.29–2.21 (m, 1H), 2.01–1.94 (m, 1H), 1.32 (s, 18H), 1.00 (t, J = 7.5 Hz, 3H). ^{13}C NMR: δ 175.0, 153.3, 152.1, 148.2, 147.4, 146.8, 133.7, 133.5, 129.0, 128.6, 125.4, 122.4, 119.8, 118.6, 117.6, 106.6, 61.8, 46.0, 43.2, 42.6, 41.0, 31.6, 27.4, 12.9. HRMS (ESI) Calcd. for $C_{32}H_{41}N_2O_3$ [M + H]: 501.3112. Found: 501.3117.

Stern-Volmer plot for 1a.

Stern-Volmer plot for emission quenching of [**4a**][BF_4] by **1a** in CH_2Cl_2 solution was shown in Figure S1a. The slope (94.0) and excited-state lifetime of **4a** (143 ns; Figure S1b) was converted to kinetic constant (5.43×10^9 M^{-1} s^{-1}). On the other hand, no fluorescence quenching of **4a** was observed at all in the presence of **2a** with or without $Fe(OTf)_2$. These results indicate that single-electron reduction of **2a** scarcely occur.

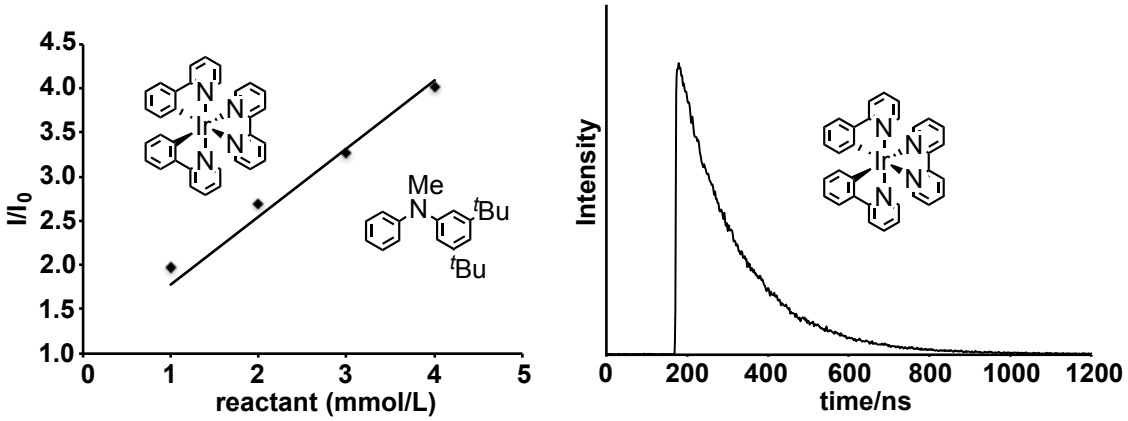


Figure S1. (a) Stern-Volmer plot and (b) lifetime of $Ir(ppy)_2(bpy)(BF_4)$ in CH_2Cl_2

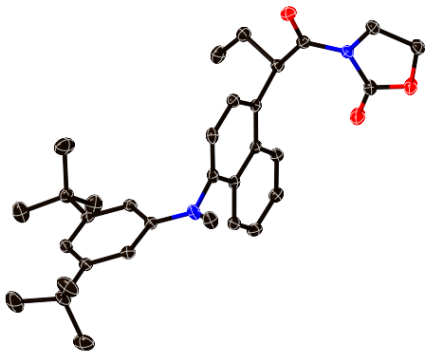


Figure S2. X-ray crystal structure of **3i**. Hydrogen atoms are omitted for clarity. The ellipsoids are scaled at 50% probability level.

Table S1. Crystallographic data of **3i.**

Formula	$C_{32}H_{40}N_2O_3$
Formula weight	500.66
Crystal system	Monoclinic
Space group	$P2_1/c$
Crystal color	Colorless
Crystal description	Prism
a [Å]	24.5341(10)
b [Å]	10.0047(4)
c [Å]	11.5533(5)
α [°]	90
β [°]	97.721(1)
γ [°]	90
V [Å^3]	2810.1(2)
Z	4
d_{calcd} [g cm^{-3}]	1.183
$R1$ ($F^2 < 2\sigma < (F^2)$)	0.0433
Rw (all data)	0.1115
GOF	1.070
Temperature [K]	93
Structure solution	SHELXL
Structure refinement	SHELXL

(S1) Xu, D.; Yang, X.; Jiang, B.; Lei, P.; Liu, X.; Wang, Q.; Zhang, X.; Ling, Y. *Bioorg. Med. Chem. Lett.* **2016**, *26*, 1849-1853.

(S2) Miyake, Y.; Nakajima, K.; Nishibayashi, Y. *J. Am. Chem. Soc.* **2012**, *134*, 3338-3341.

(S3) Davies, P. W.; Cremonesi, A.; Martin, N. *Chem. Commun.*, **2011**, *47*, 379-381.

(S4) Nakamura, T.; Oshida, M.; Nomura, T.; Nakazaki, A.; Kobayashi, S. *Org. Lett*. **2007**, *9*, 5533-5536.

(S5) Sudo, Y.; Shirasaki, D.; Harada, S.; Nishida, A. *J. Am. Chem. Soc.* **2008**, *130*, 12588–12589.

(S6) Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc*. **1988**, *110*, 1988.

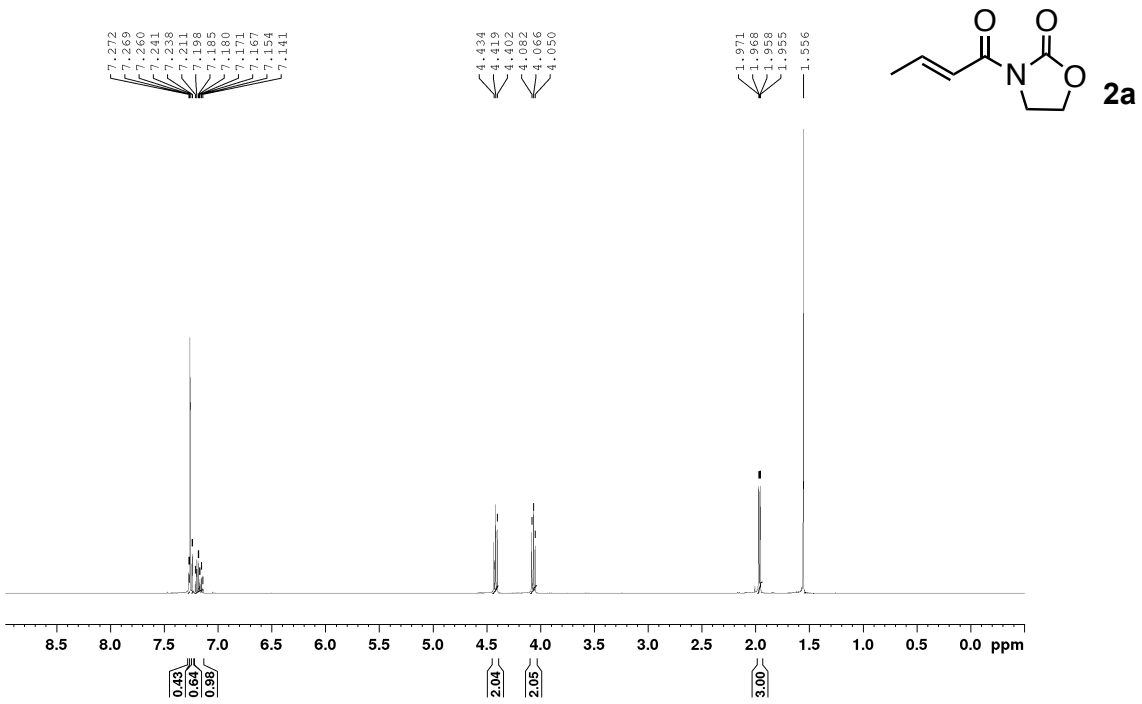


Figure S3. ^{1}H NMR spectrum of **2a** in $CDCl_3$.

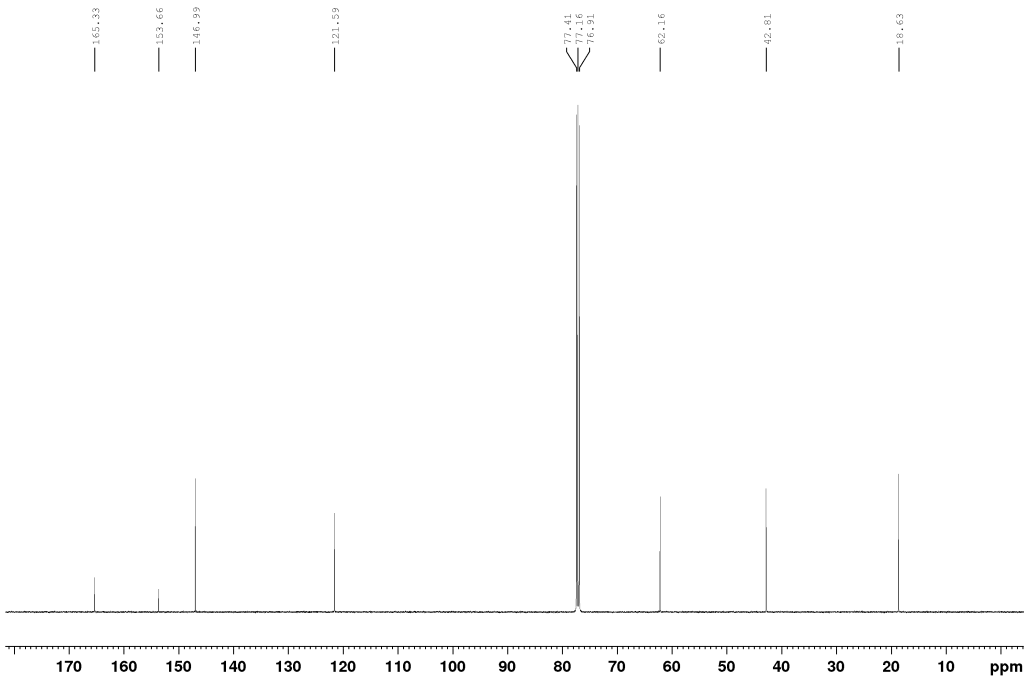


Figure S4. ^{13}C NMR spectrum of **2a** in $CDCl_3$.

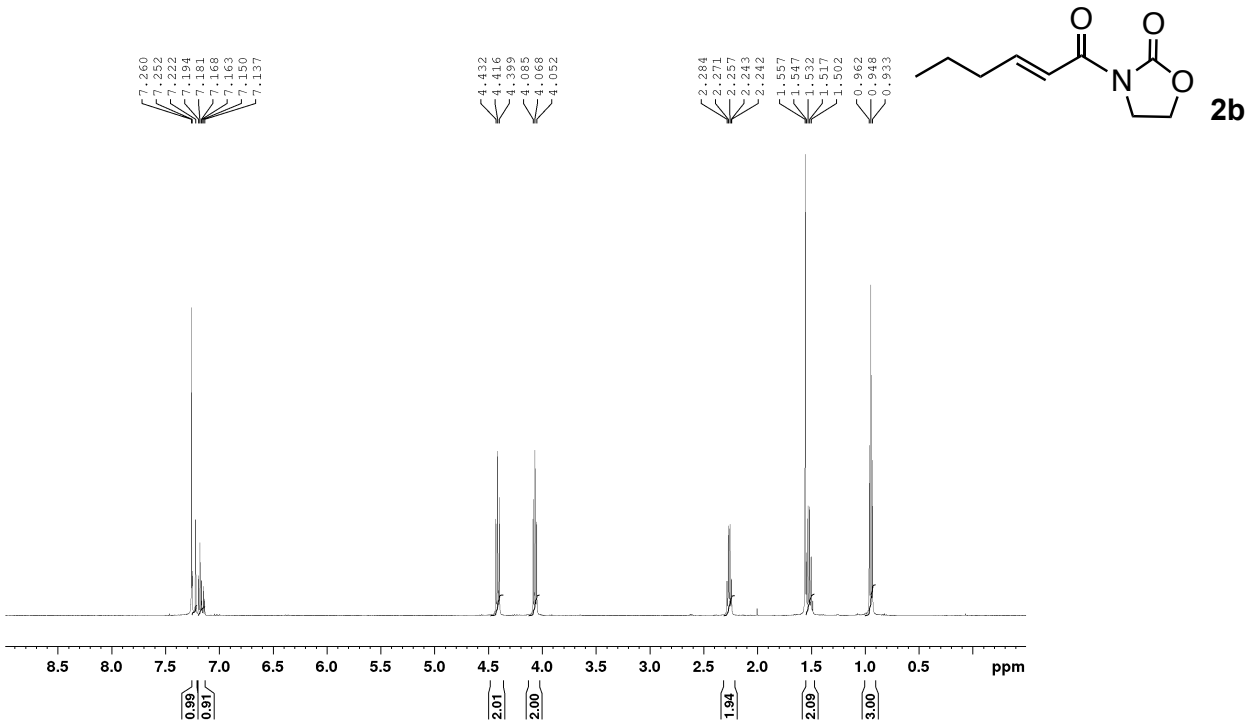


Figure S5. ^{1}H NMR spectrum of **2b** in $CDCl_3$.

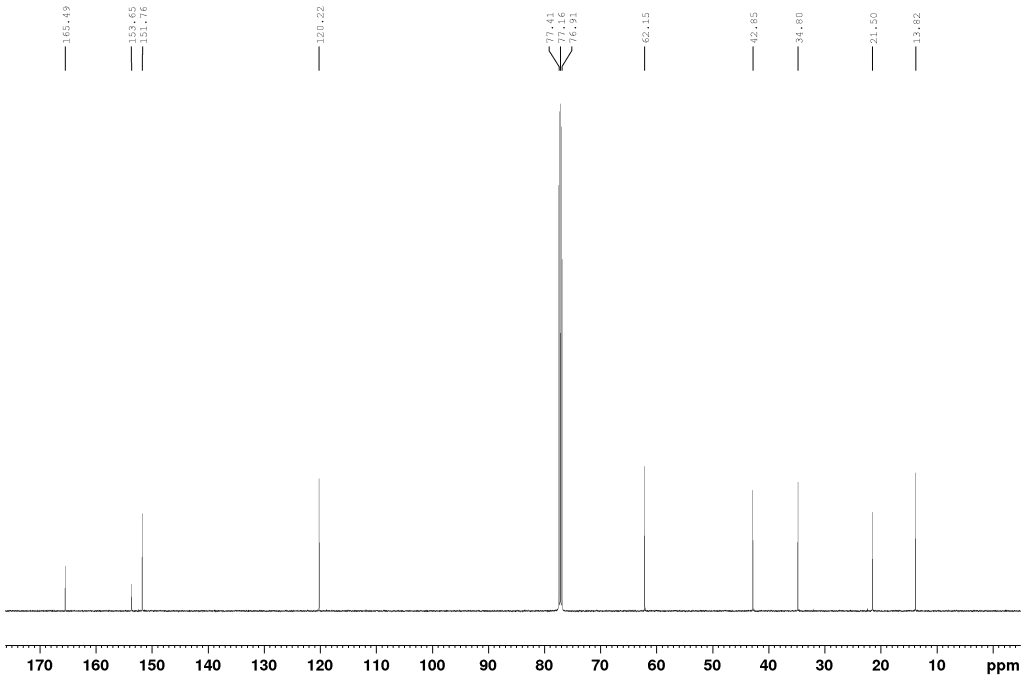


Figure S6. ^{13}C NMR spectrum of **2b** in $CDCl_3$.

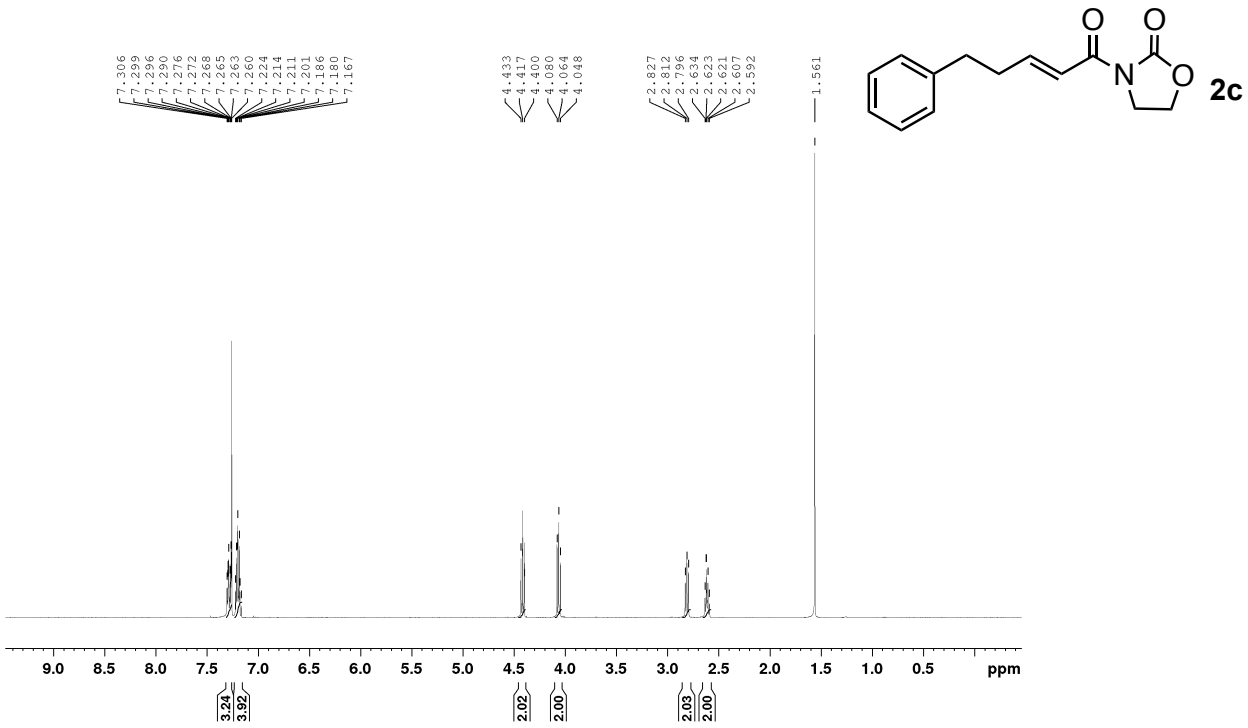


Figure S7. ^{1}H NMR spectrum of **2c** in $CDCl_3$.

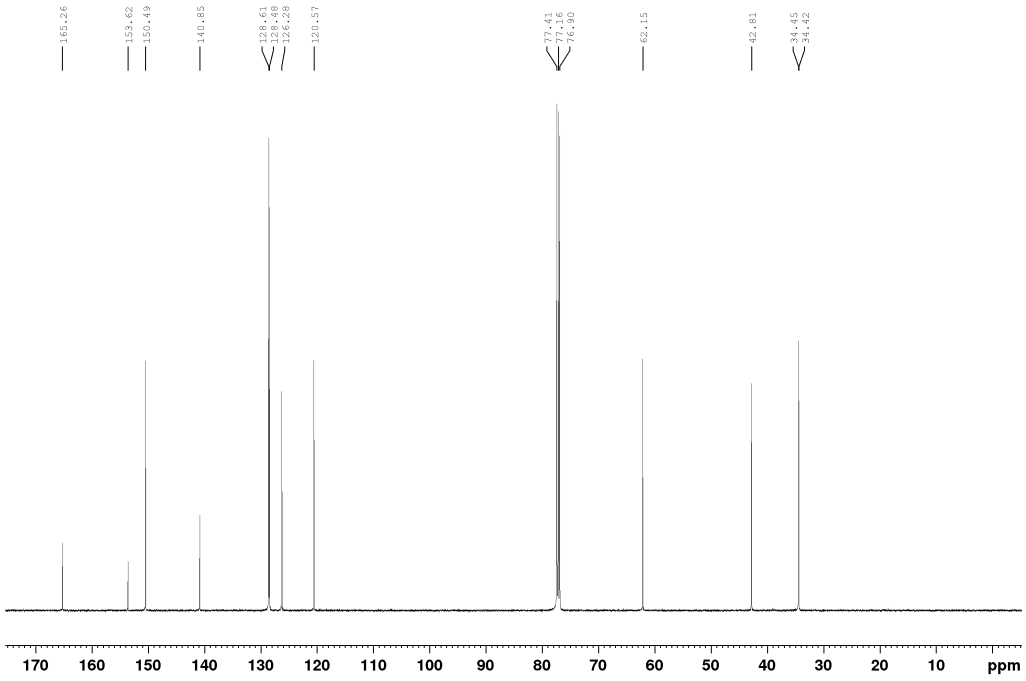


Figure S8. ^{13}C NMR spectrum of **2c** in $CDCl_3$.

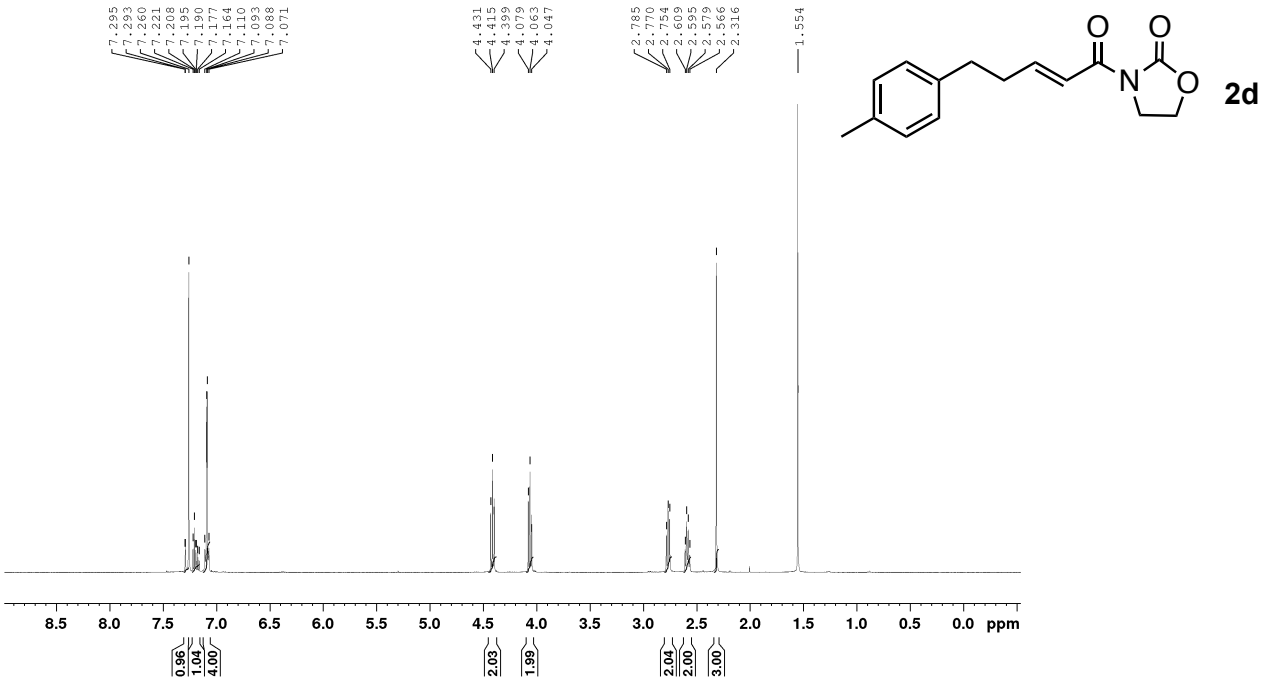


Figure S9. ^{1}H NMR spectrum of **2d** in $CDCl_3$.

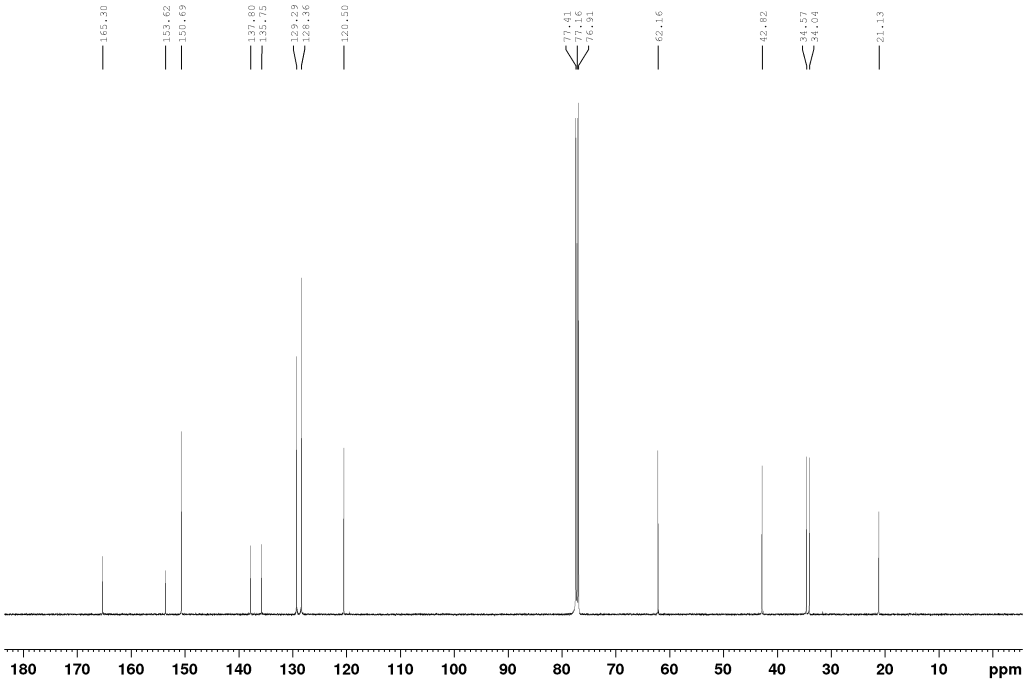


Figure S10. ^{13}C NMR spectrum of **2d** in $CDCl_3$.

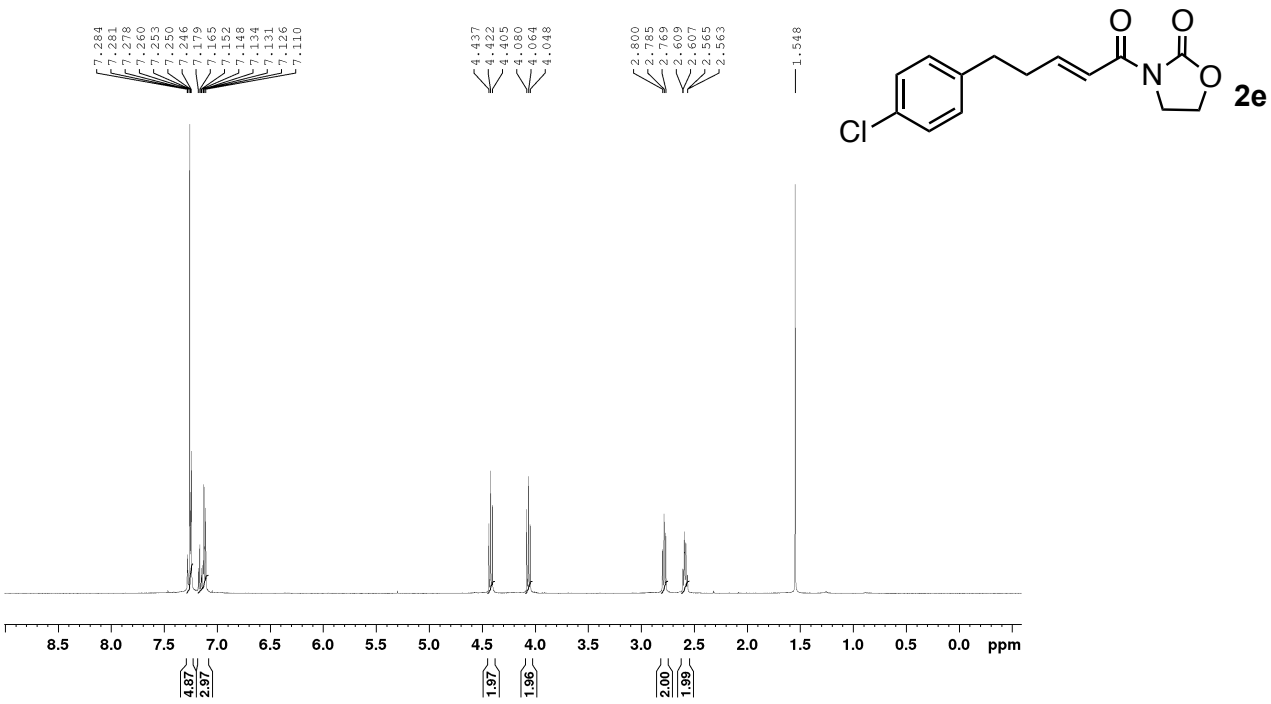


Figure S11. ^{1}H NMR spectrum of **2e** in $CDCl_3$.

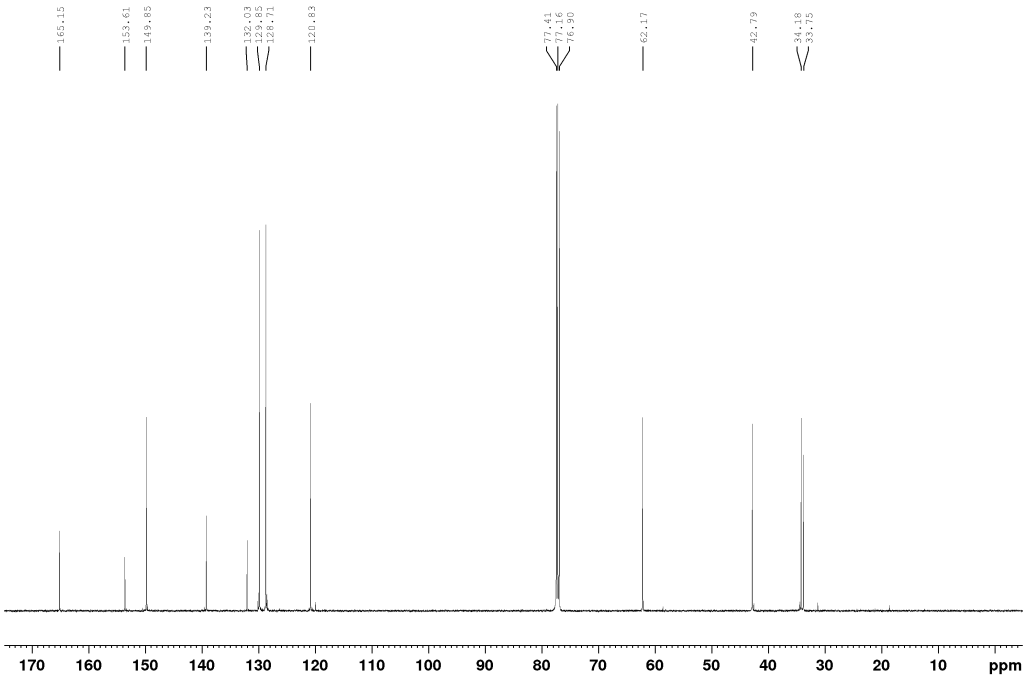


Figure S12. ^{13}C NMR spectrum of **2e** in $CDCl_3$.

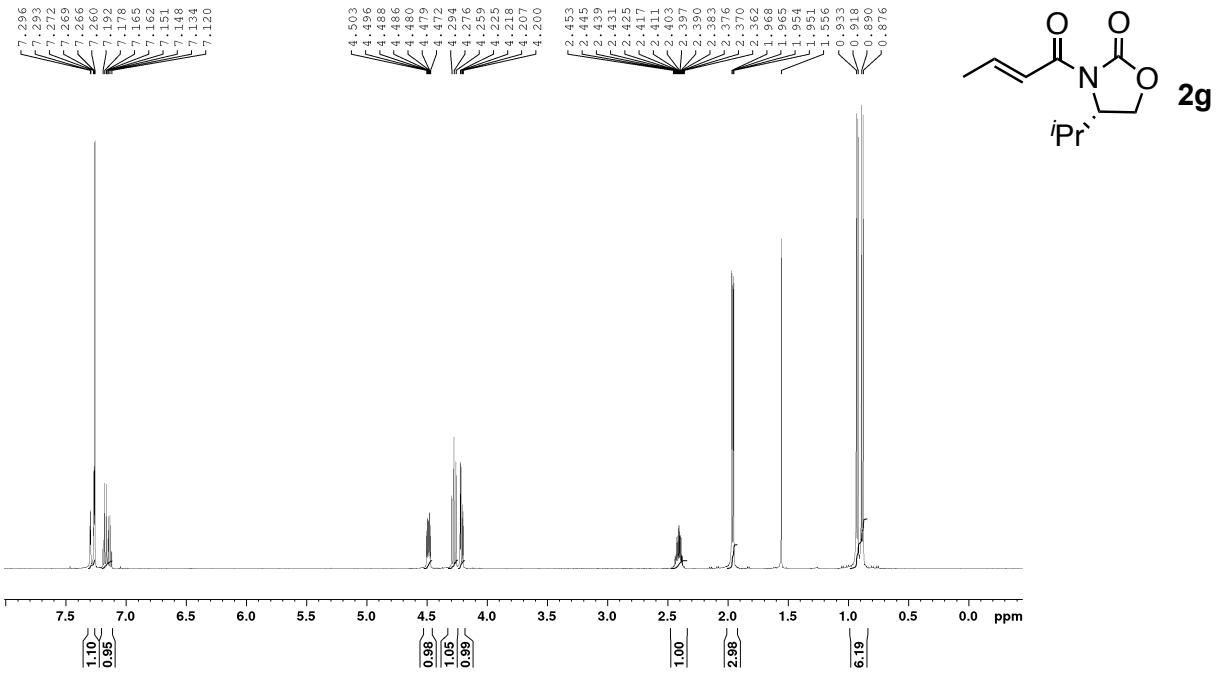


Figure S13. ^{1}H NMR spectrum of **2g** in $CDCl_3$.

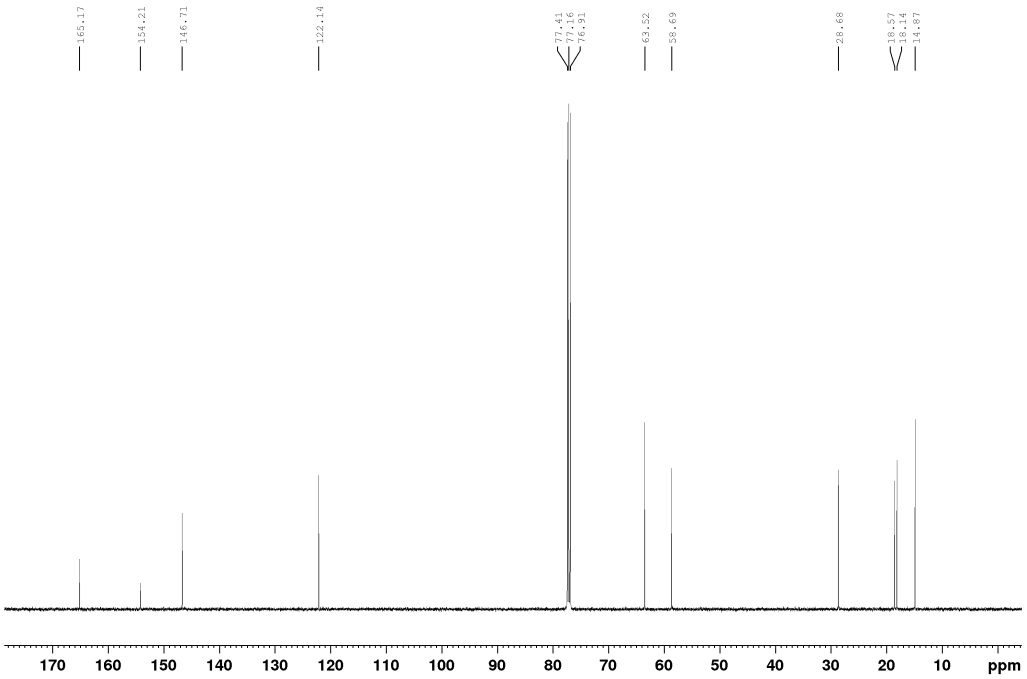


Figure S14. ^{13}C NMR spectrum of **2g** in $CDCl_3$.

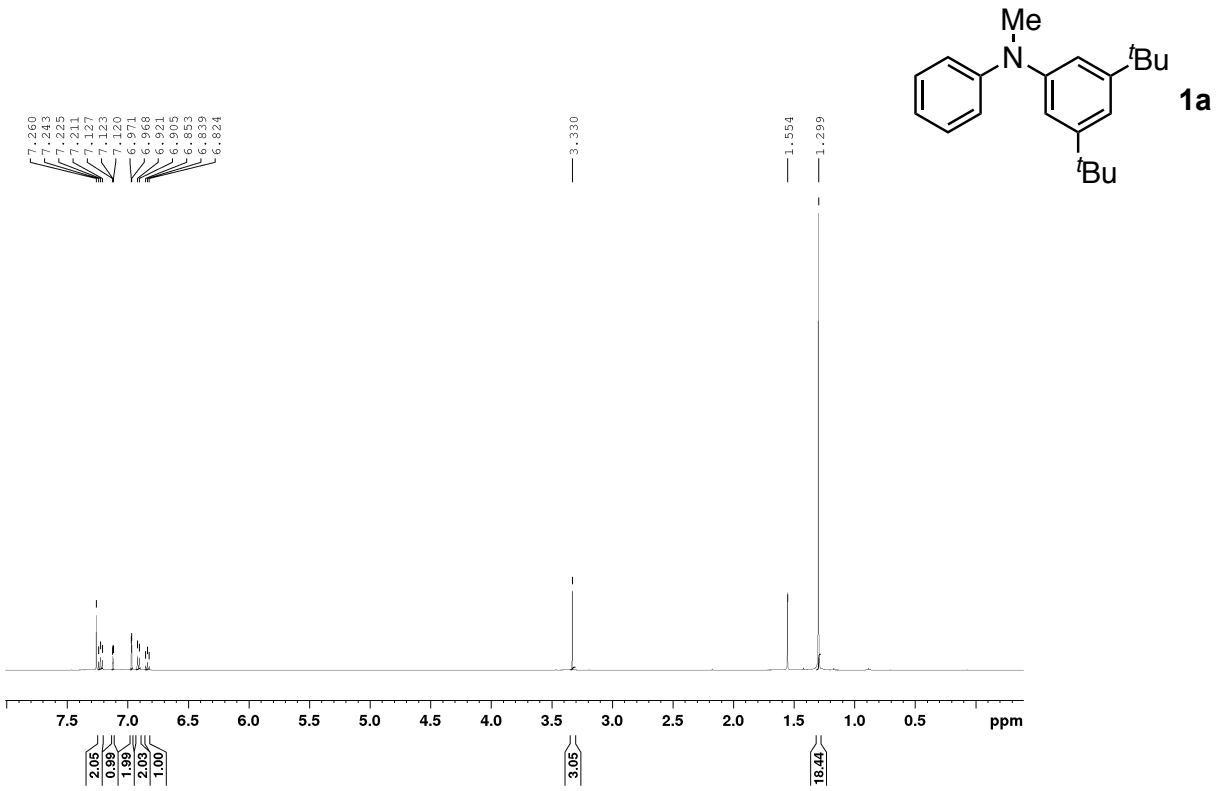


Figure S15. ^{1}H NMR spectrum of **1a** in $CDCl_3$.

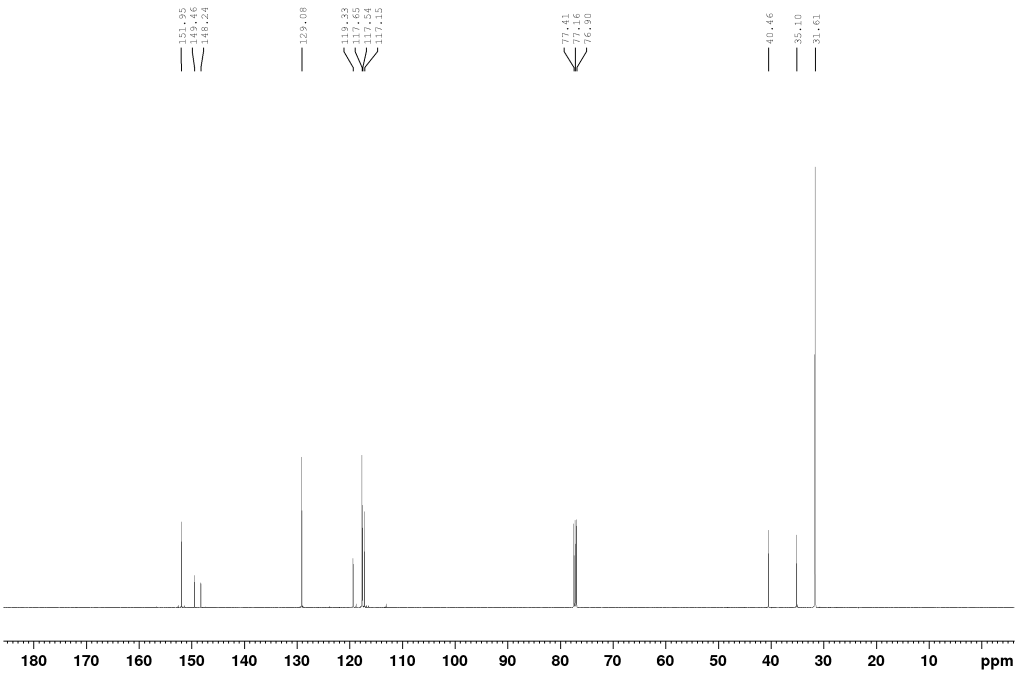


Figure S16. ^{13}C NMR spectrum of **1a** in $CDCl_3$.

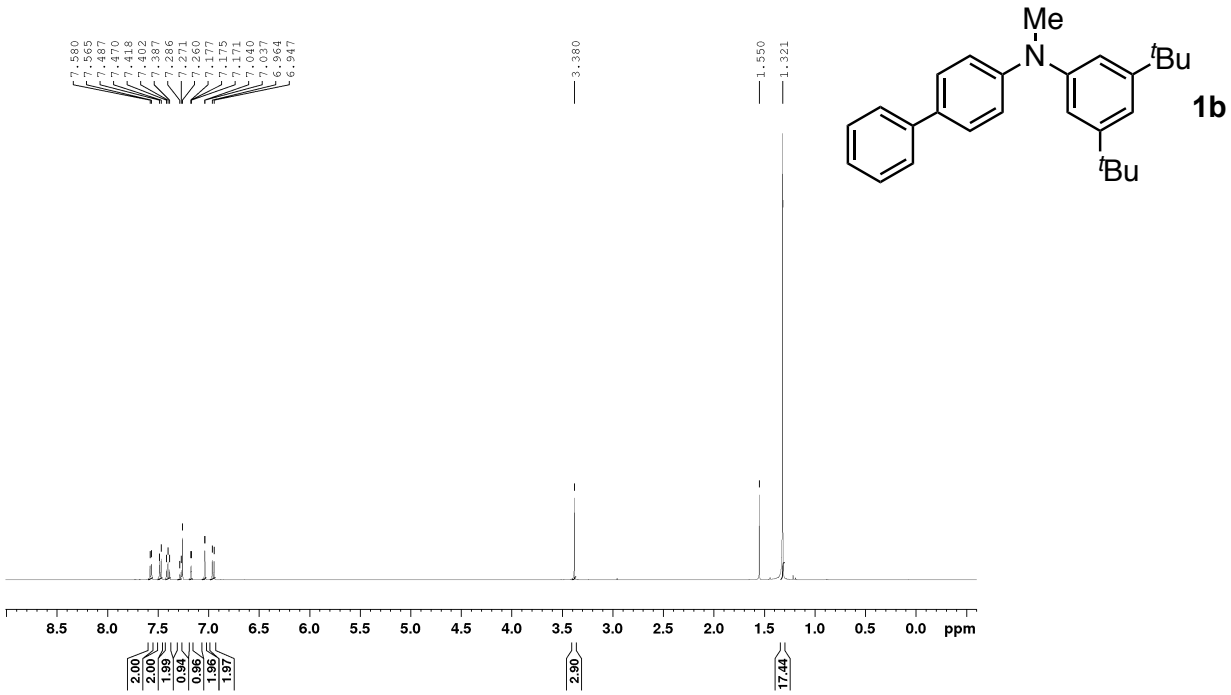


Figure S17. ^{1}H NMR spectrum of **1b** in $CDCl_3$.

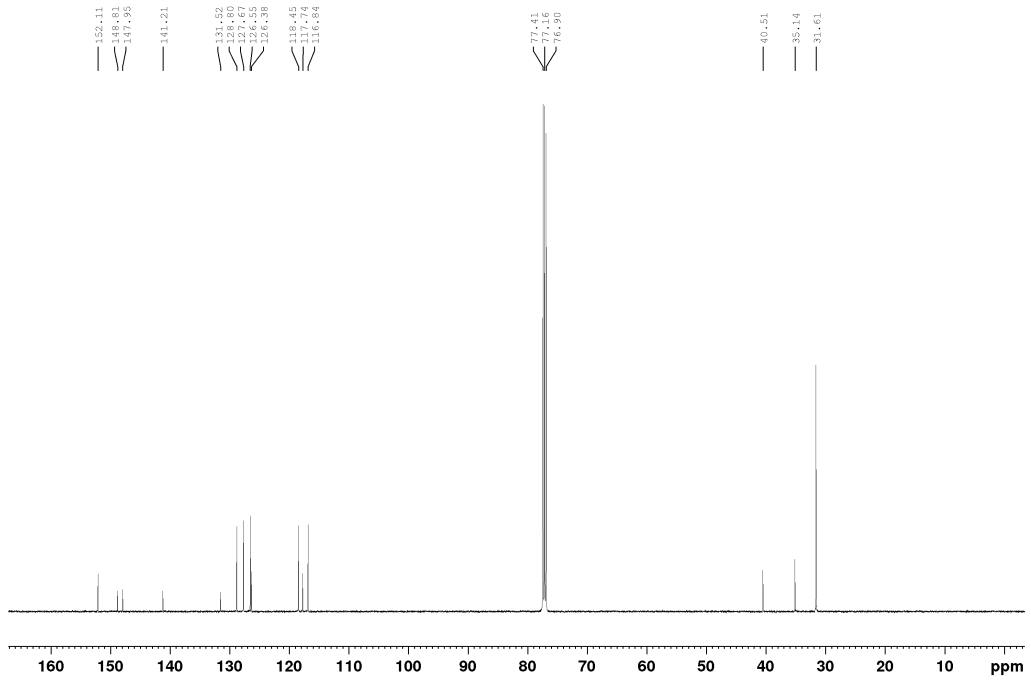


Figure S18. ^{13}C NMR spectrum of **1b** in $CDCl_3$.

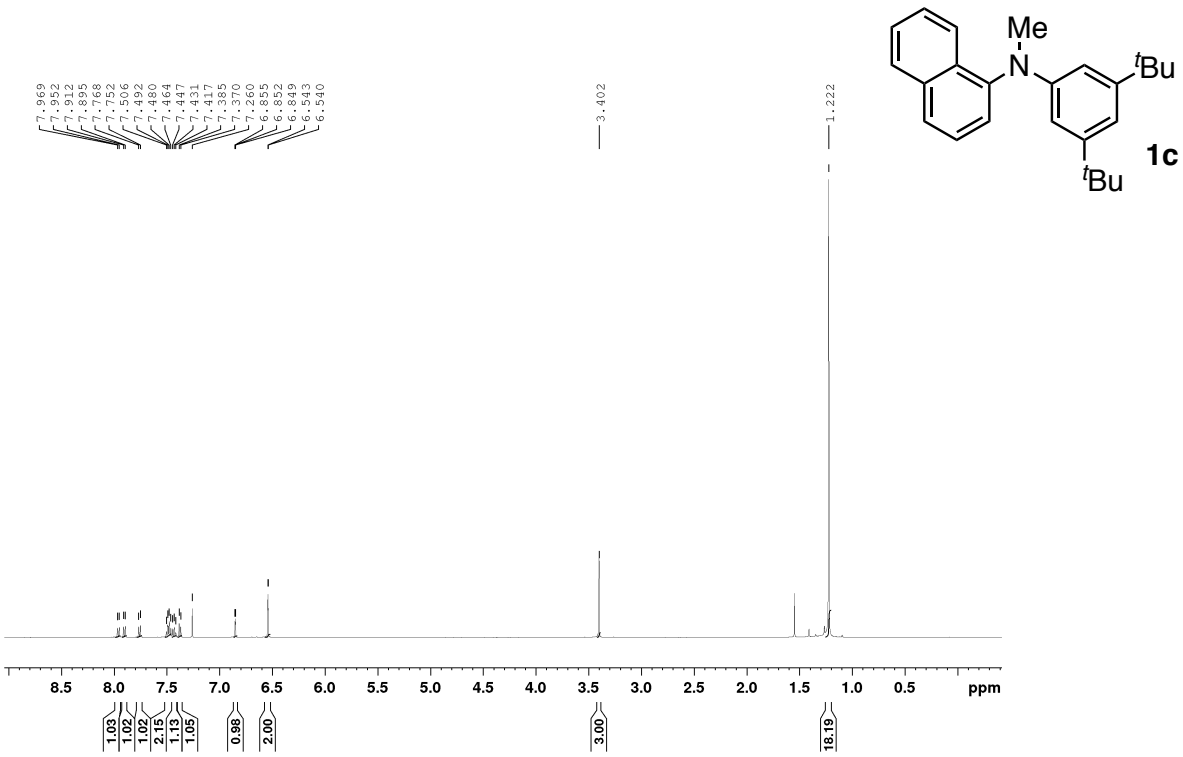


Figure S19. ^{1}H NMR spectrum of **1c** in $CDCl_3$.

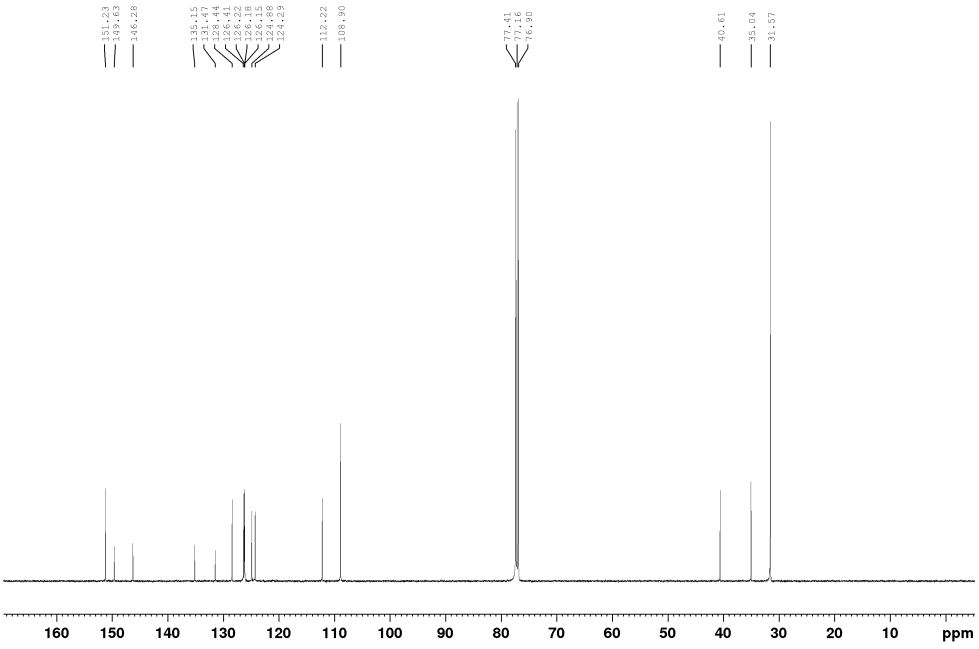


Figure S20. ^{13}C NMR spectrum of **1c** in $CDCl_3$.

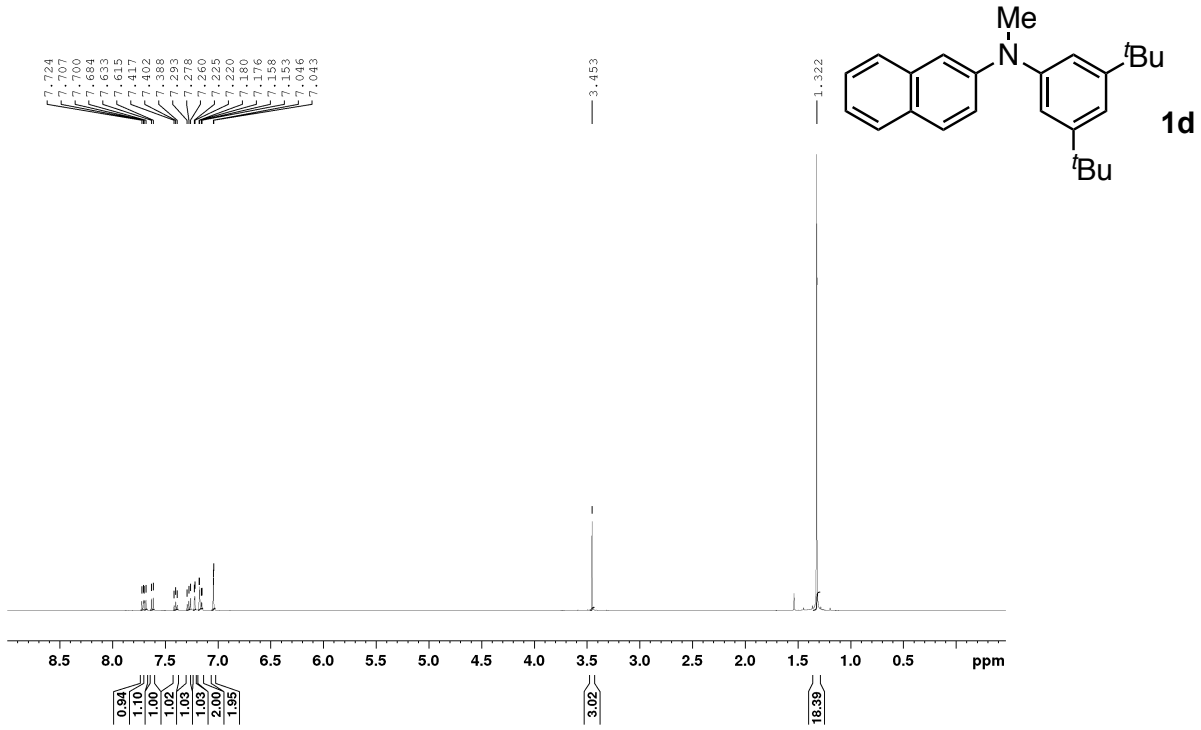


Figure S21. ^{1}H NMR spectrum of **1d** in $CDCl_3$.

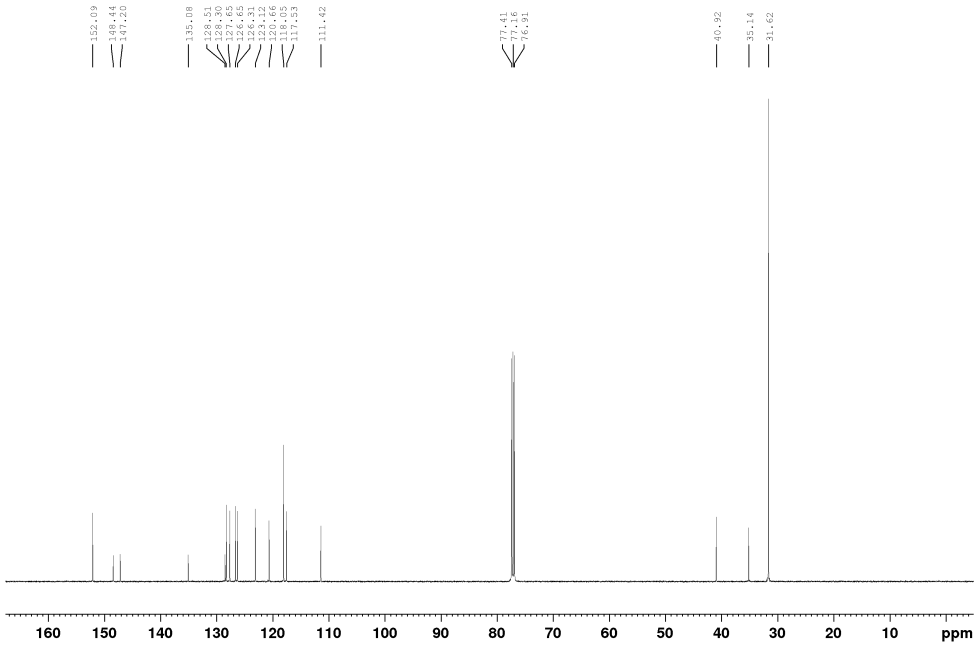


Figure S22. ^{13}C NMR spectrum of **1d** in $CDCl_3$.

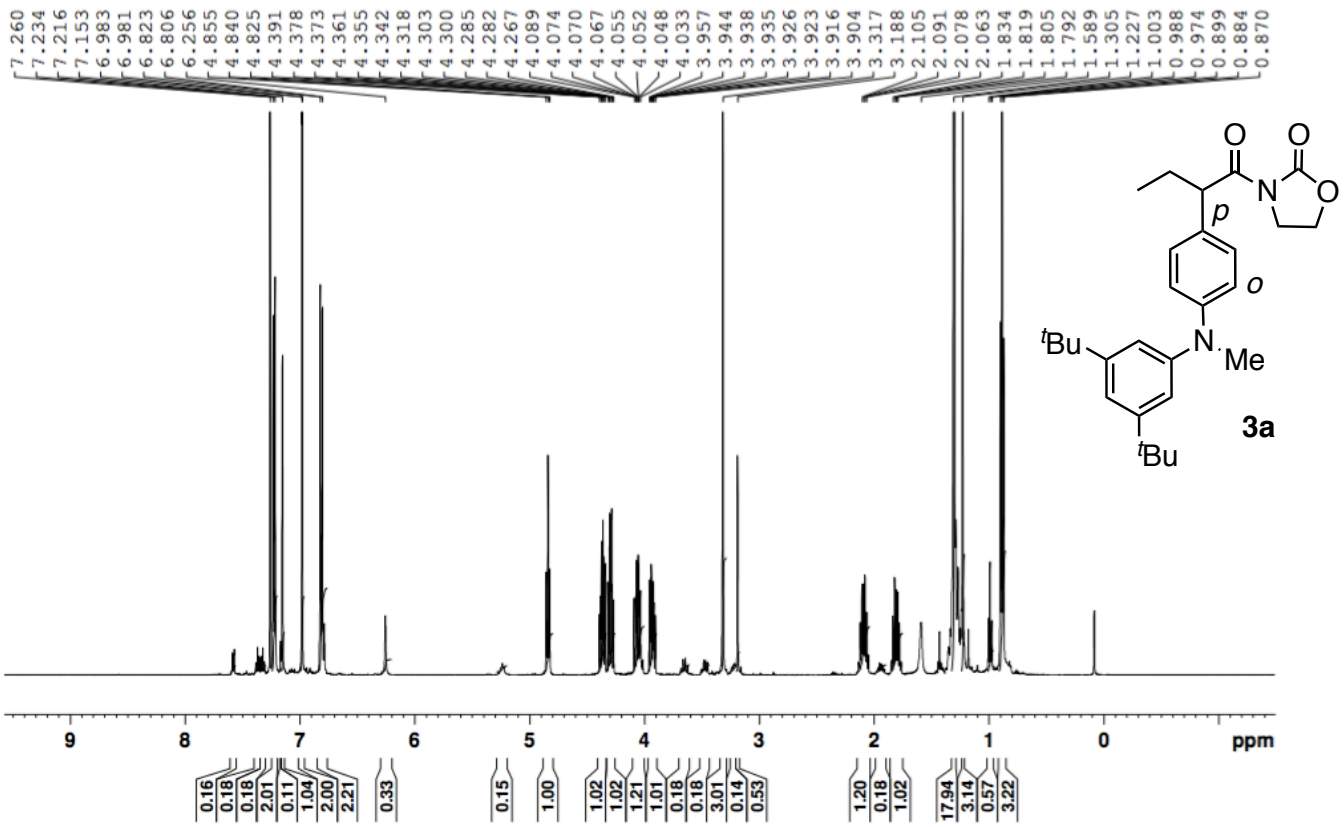


Figure S23. ^{1}H NMR spectrum of **3a** in $CDCl_3$.

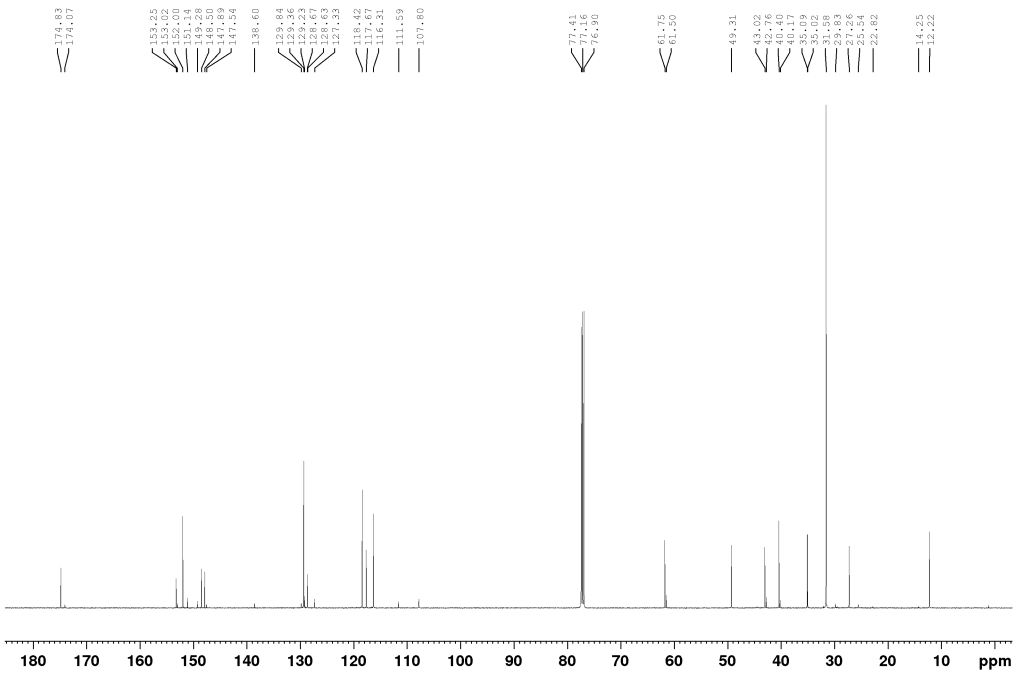


Figure S24. ^{13}C NMR spectrum of **3a** in $CDCl_3$.

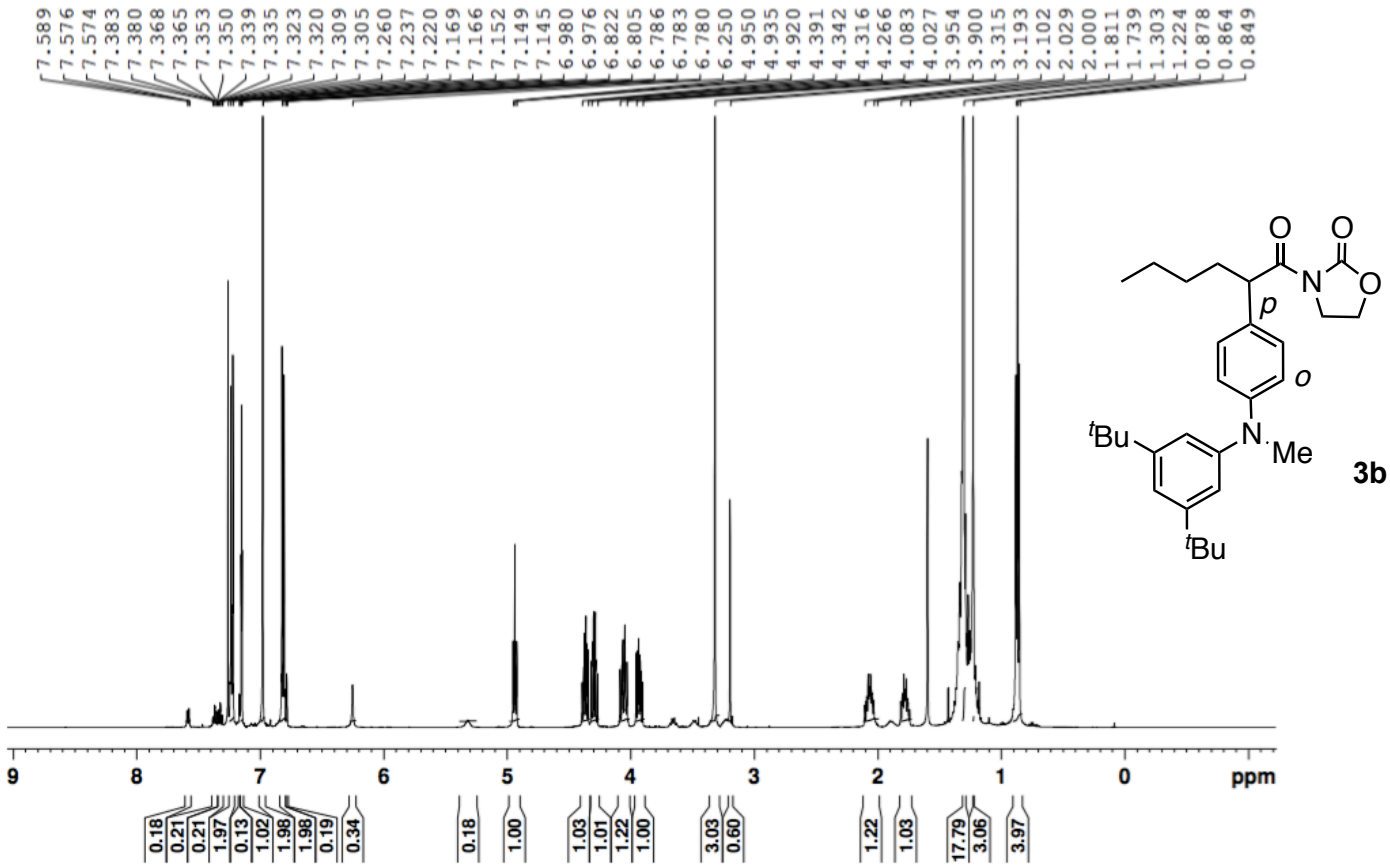


Figure S25. ^{1}H NMR spectrum of **3b** in $CDCl_3$.

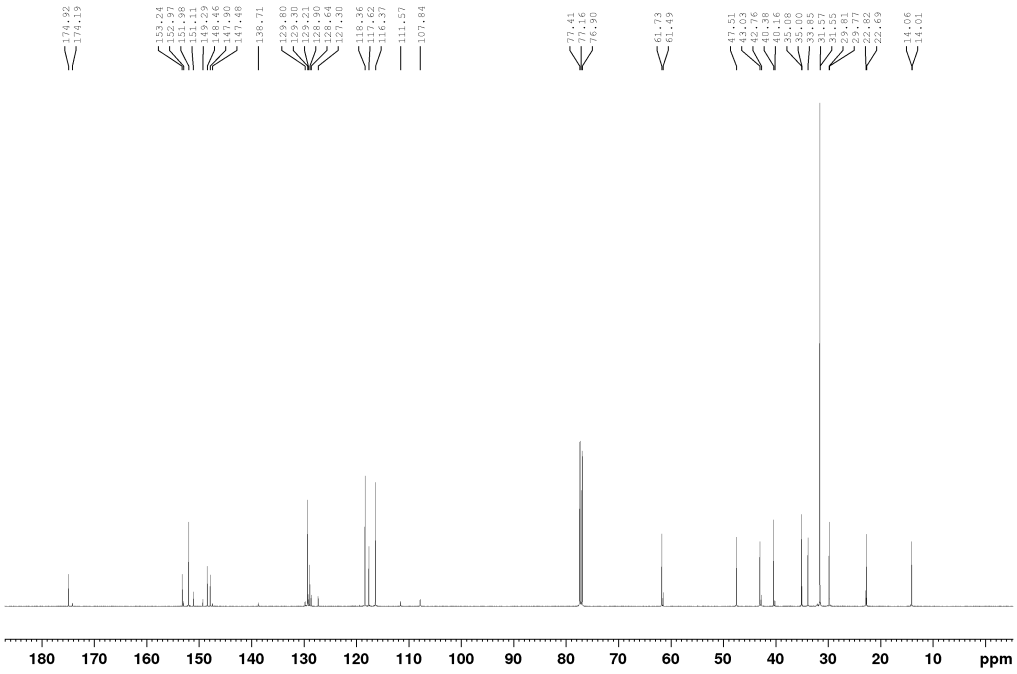


Figure S26. ^{13}C NMR spectrum of **3b** in $CDCl_3$.

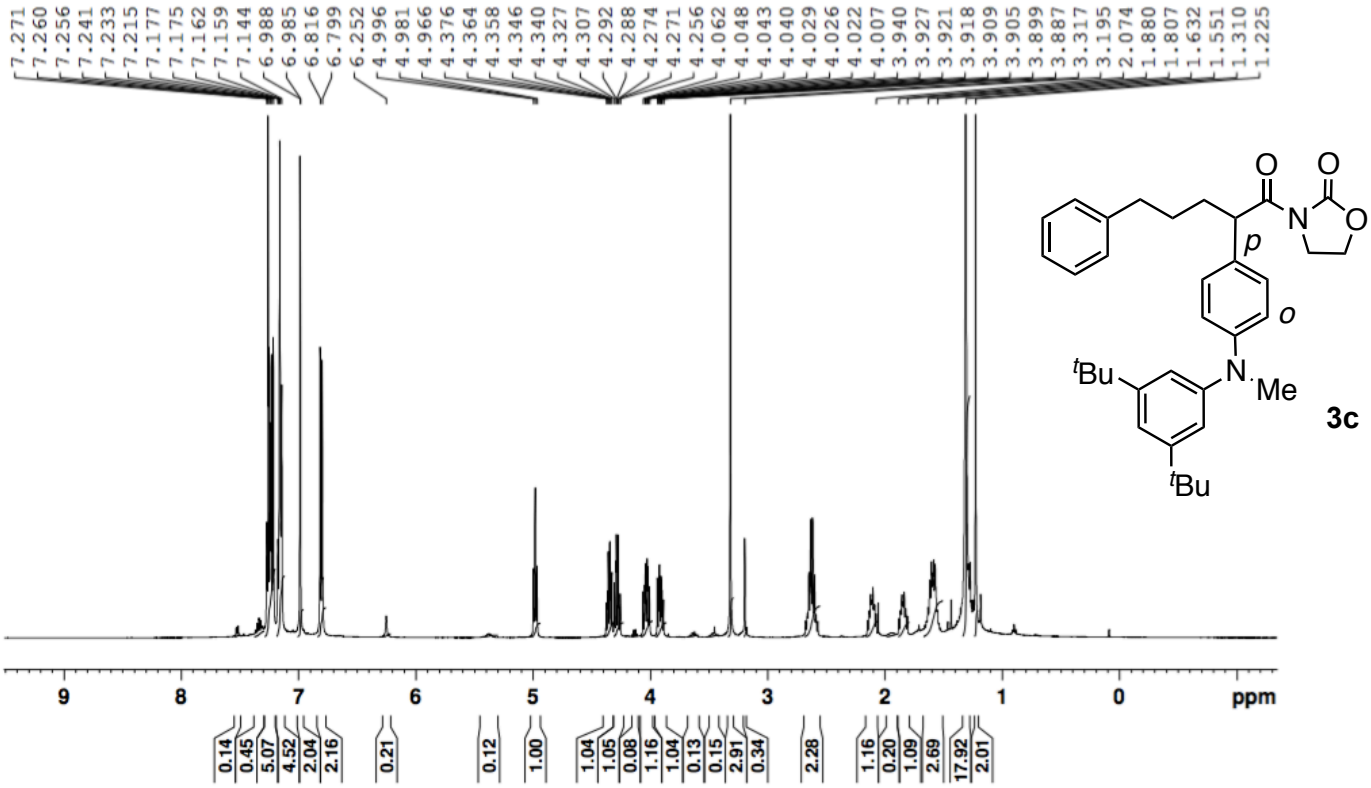


Figure S27. ^{1}H NMR spectrum of **3c** in $CDCl_3$.

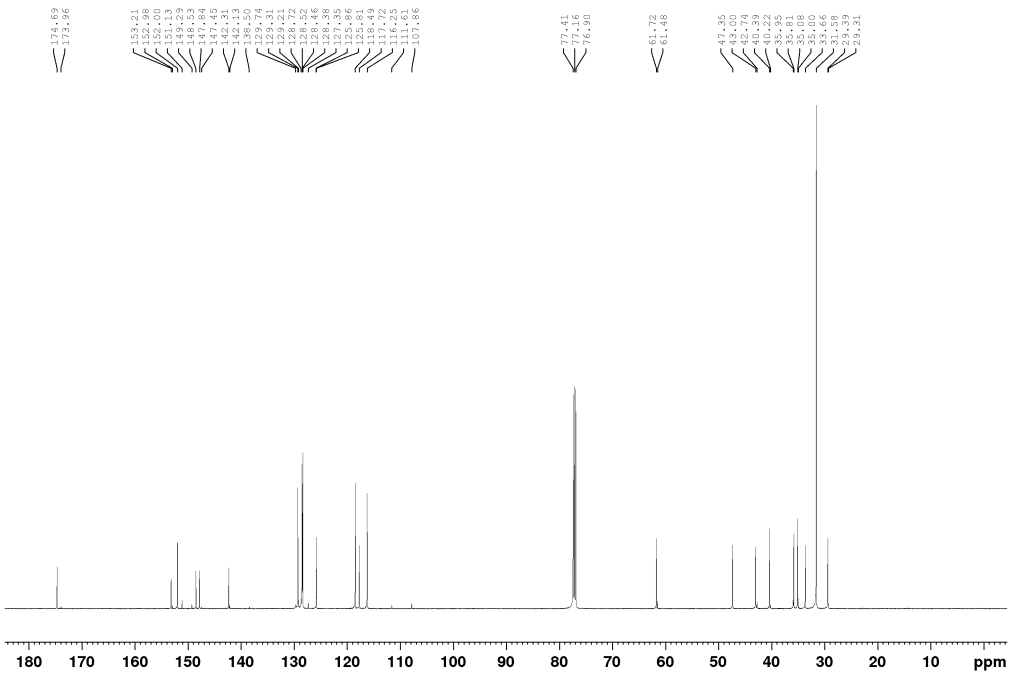


Figure S28. ^{13}C NMR spectrum of **3c** in $CDCl_3$.

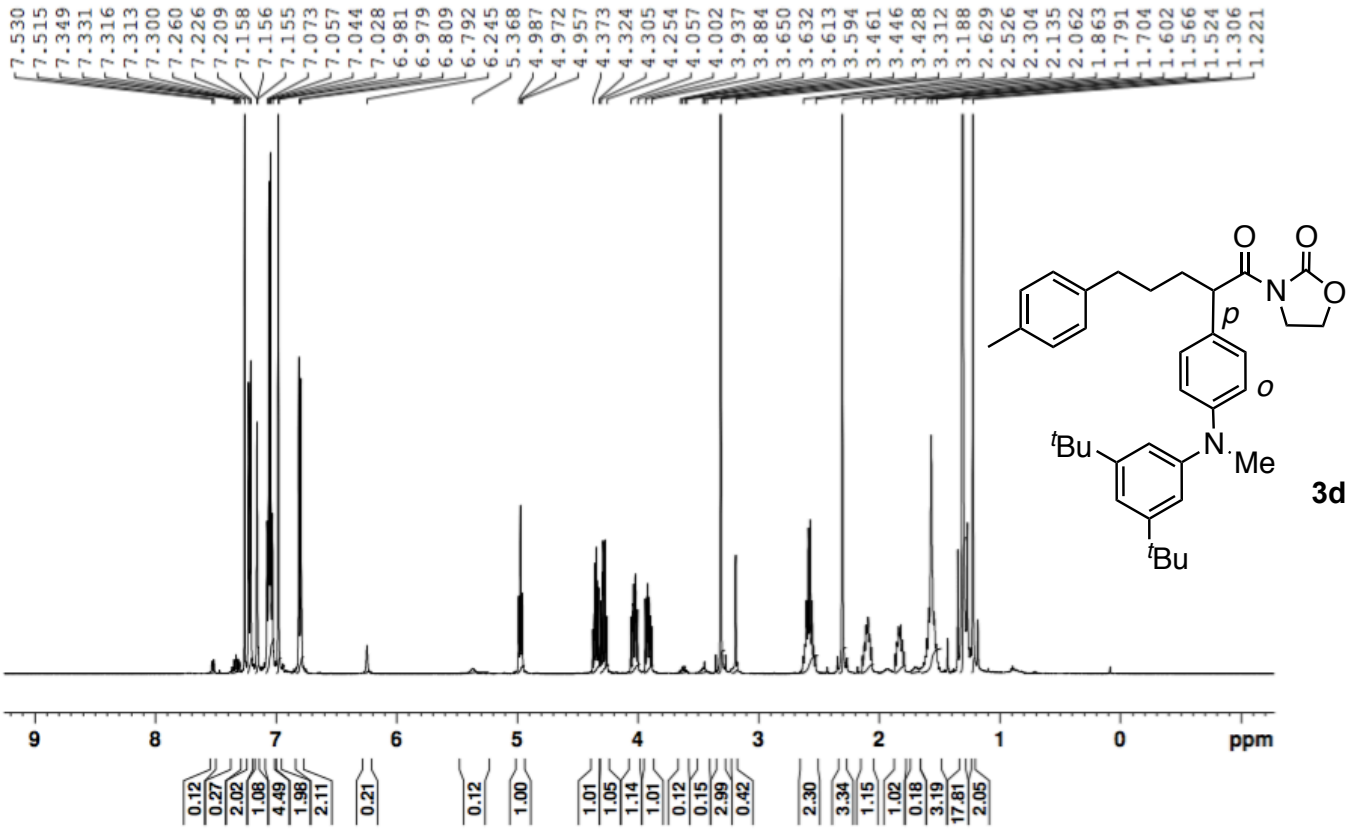


Figure S29. ^{1}H NMR spectrum of **3d** in $CDCl_3$.

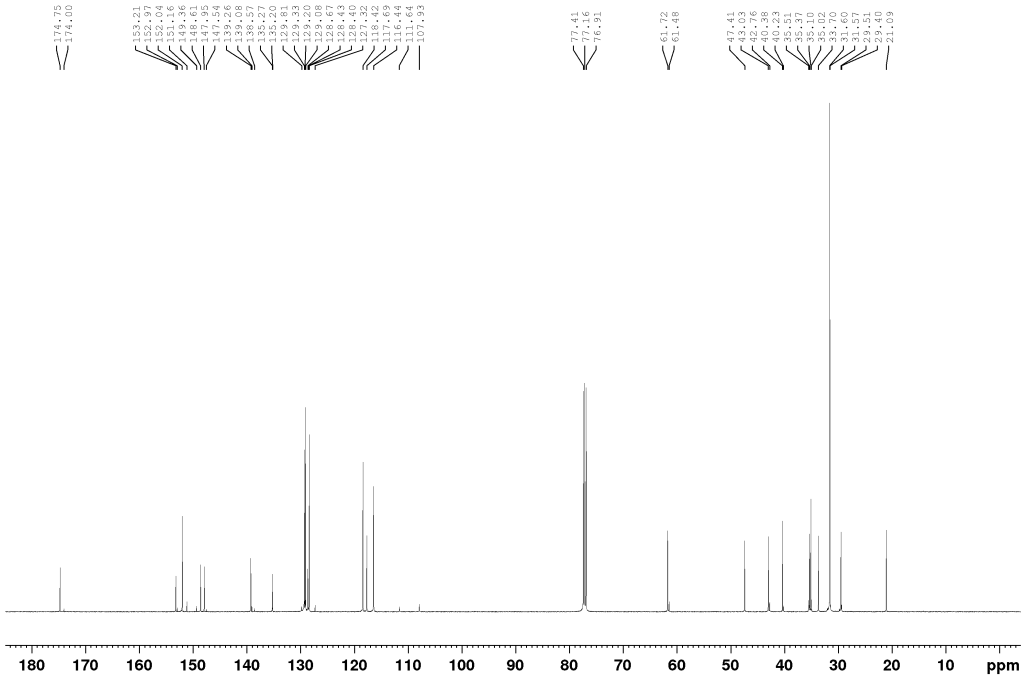


Figure S30. ^{13}C NMR spectrum of **3d** in $CDCl_3$.

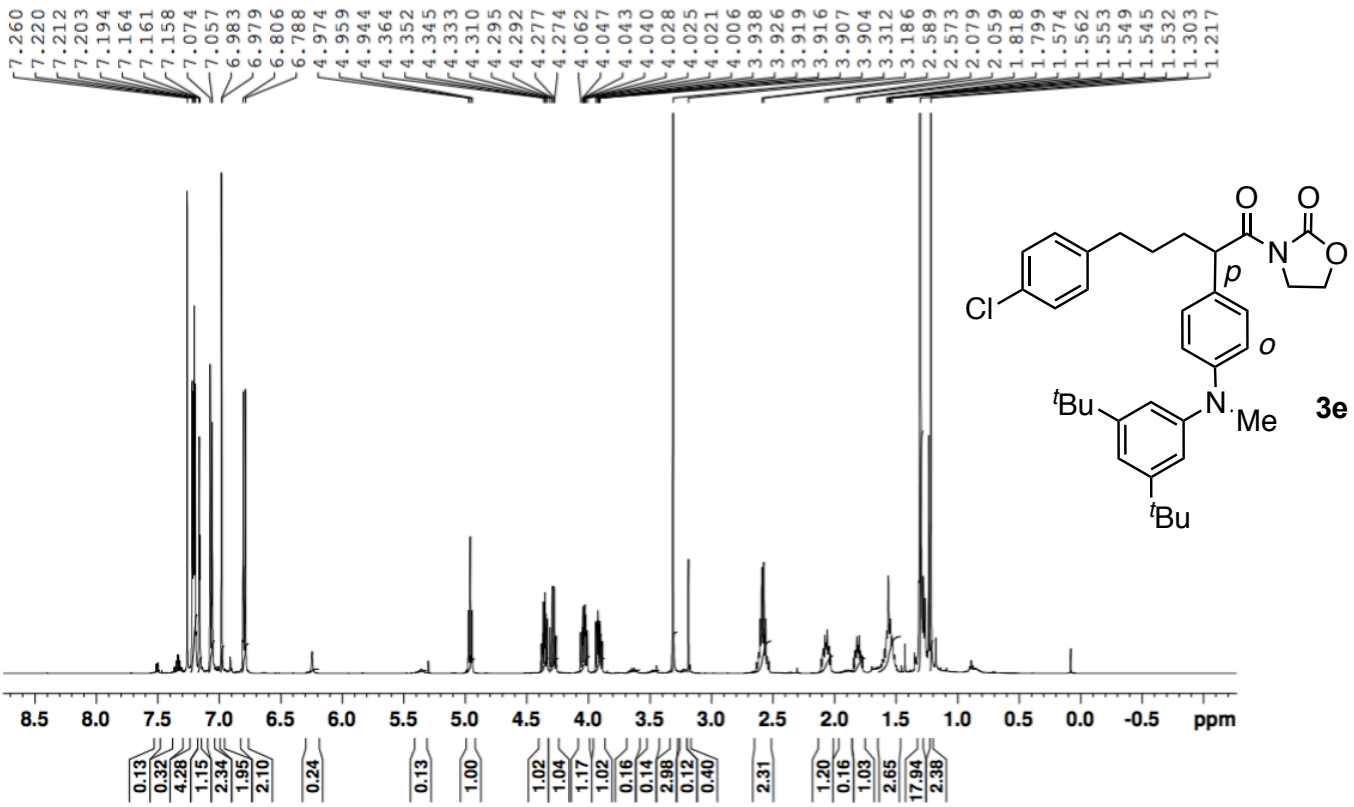


Figure S31. ^{1}H NMR spectrum of **3e** in $CDCl_3$.

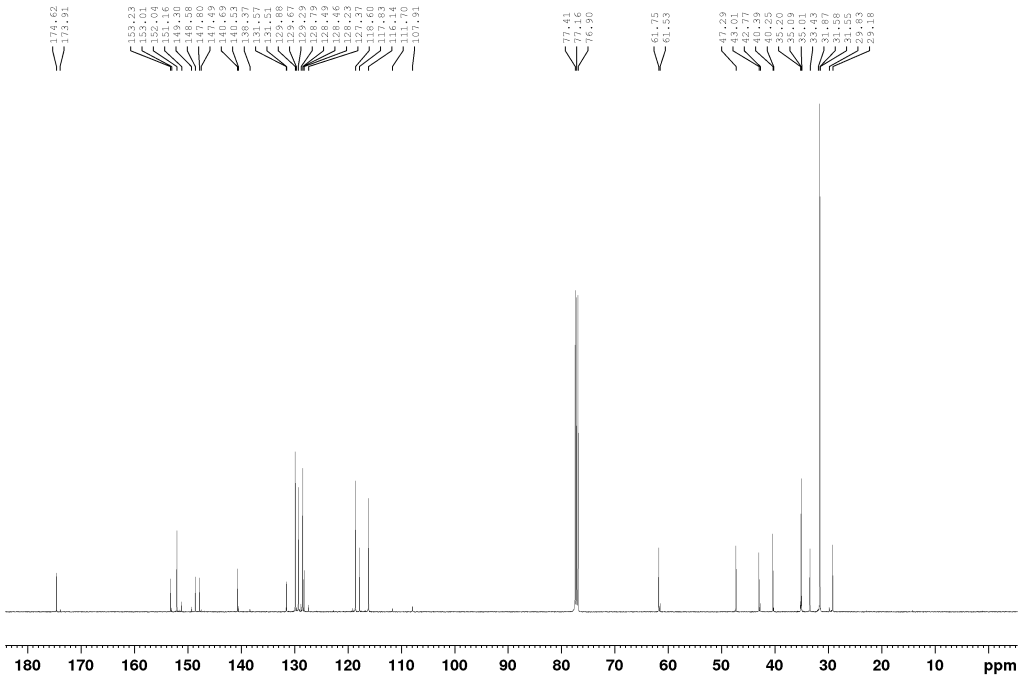


Figure S32. ^{13}C NMR spectrum of **3e** in $CDCl_3$.

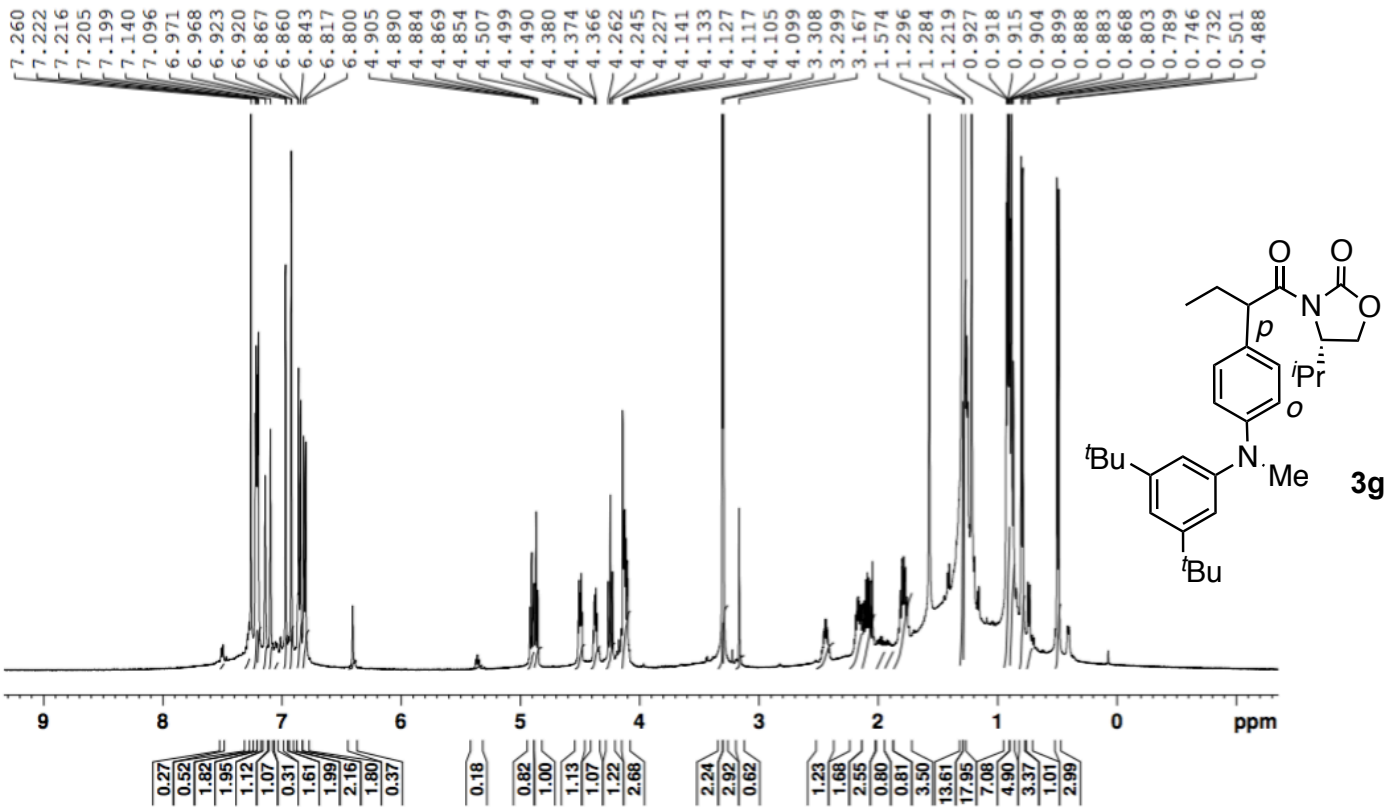


Figure S33. ^{1}H NMR spectrum of **3g** in $CDCl_3$.

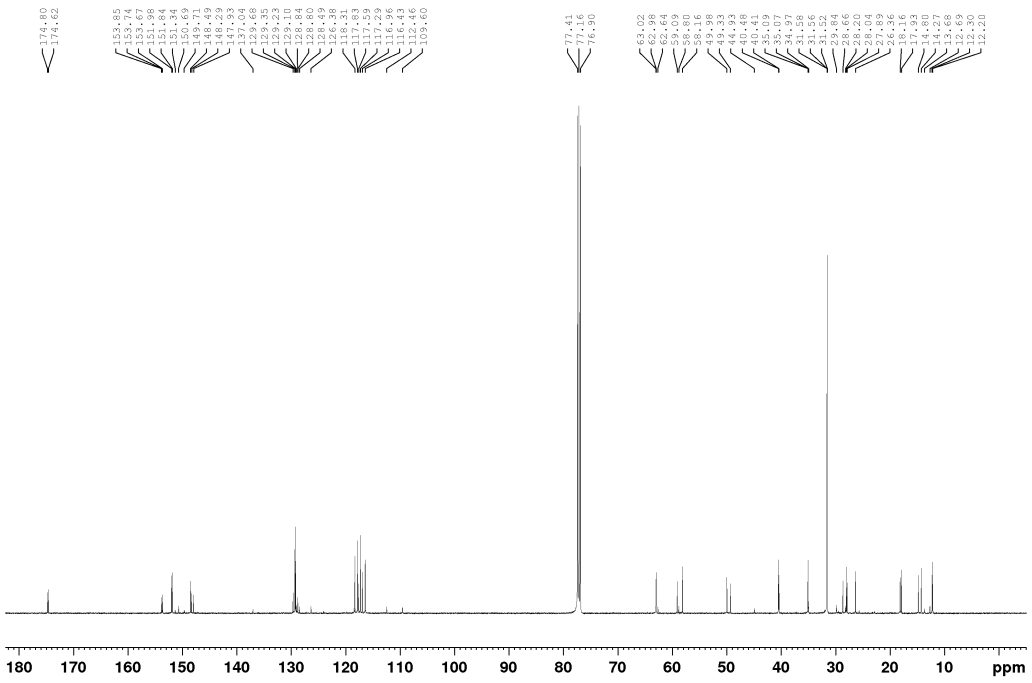


Figure S34. ^{13}C NMR spectrum of **3g** in $CDCl_3$.

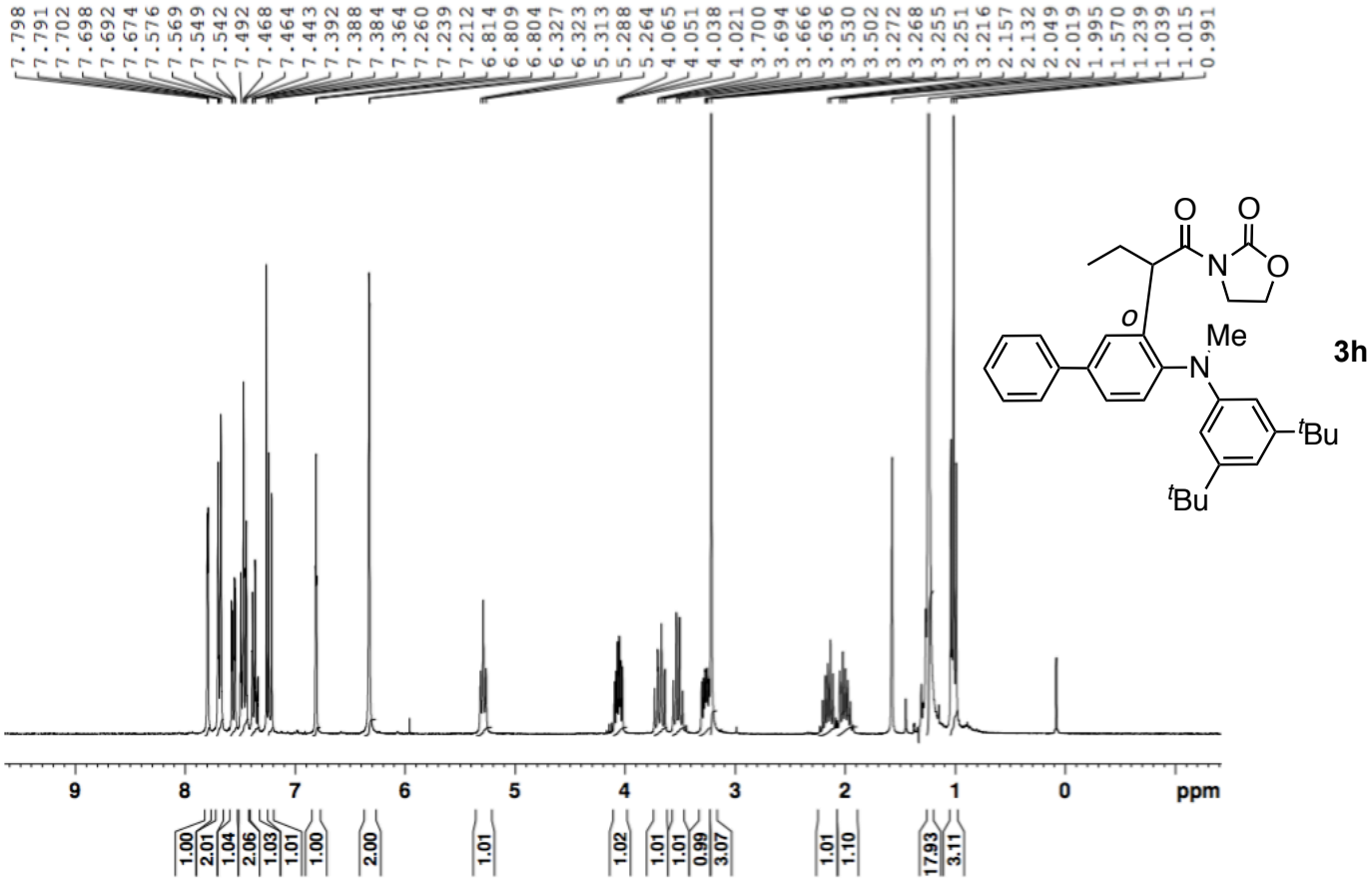


Figure S35. ^{1}H NMR spectrum of **3h** in $CDCl_3$.

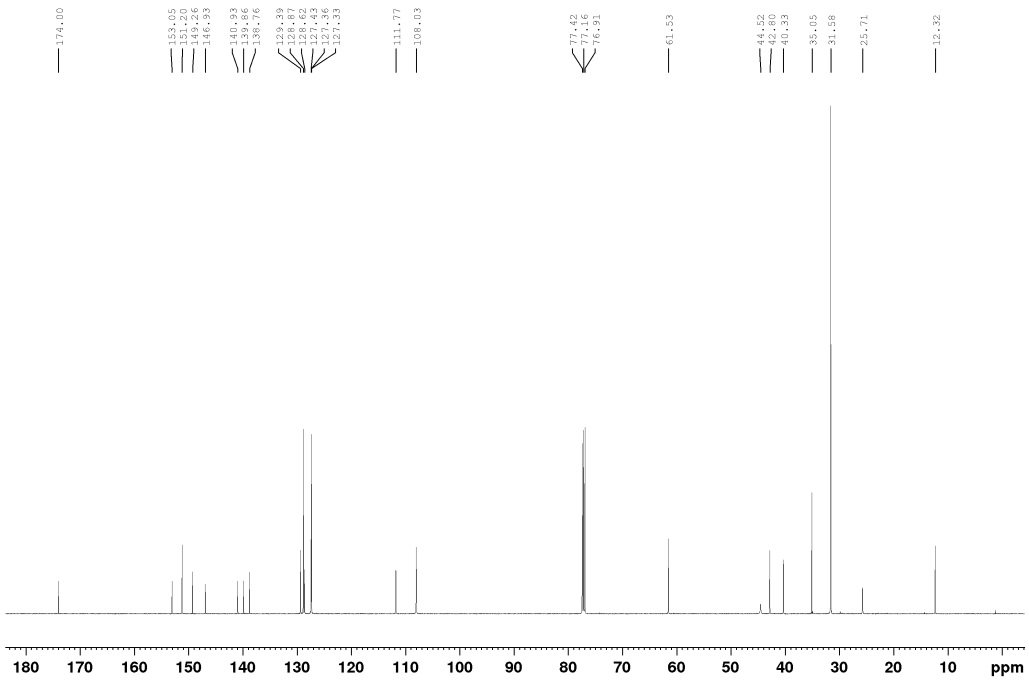


Figure S36. ^{13}C NMR spectrum of **3h** in $CDCl_3$.

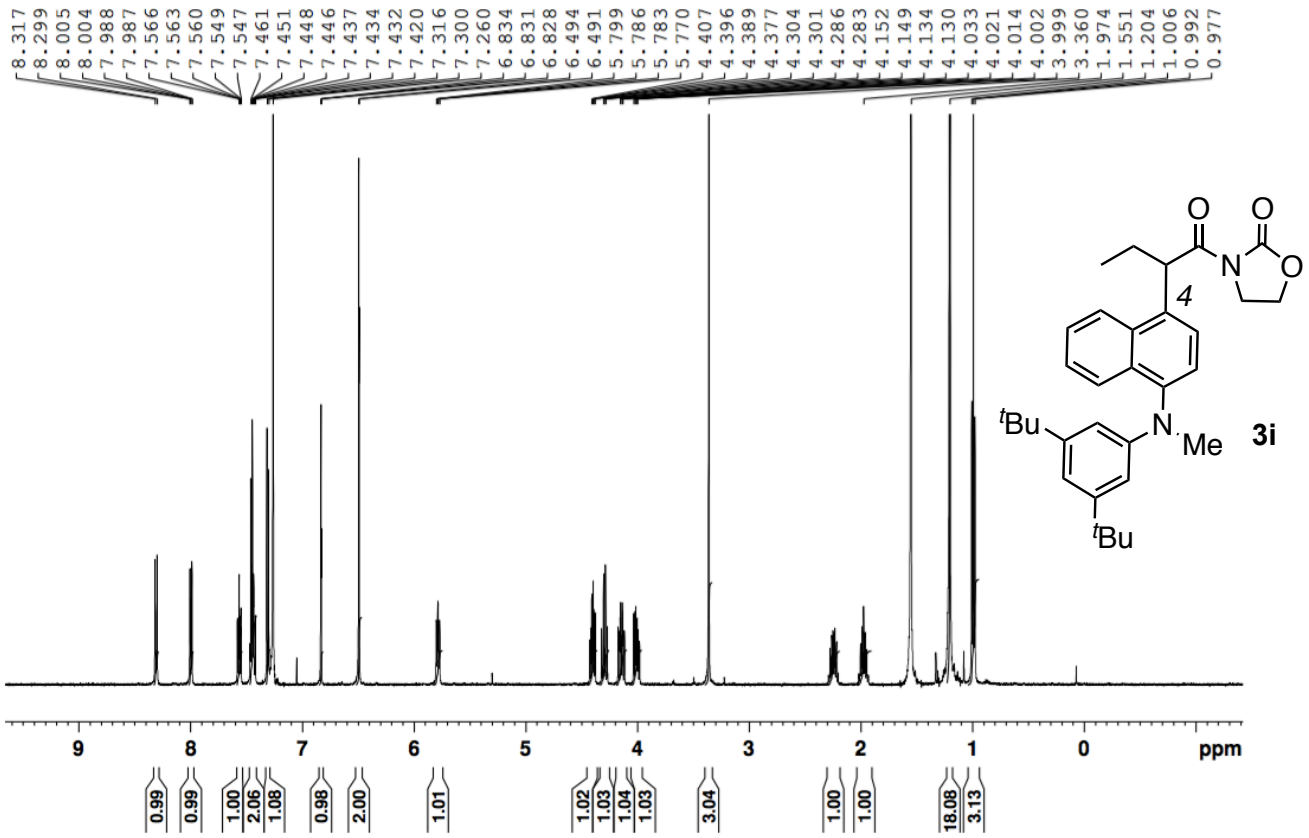


Figure S37. ^{1}H NMR spectrum of **3i** in $CDCl_3$.

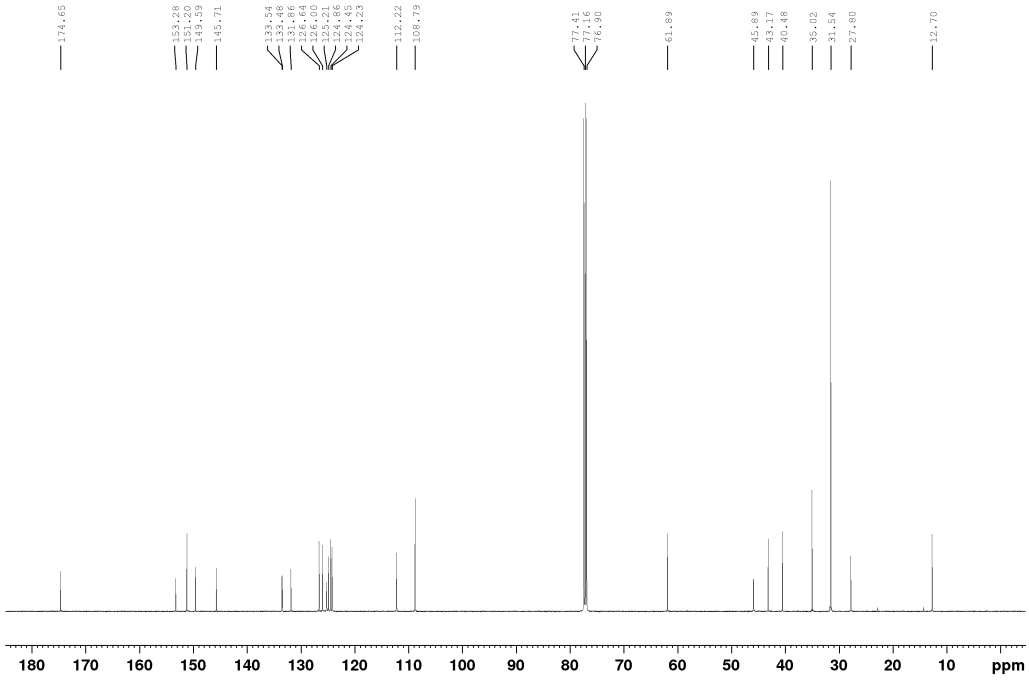


Figure S38. ^{13}C NMR spectrum of **3i** in $CDCl_3$.

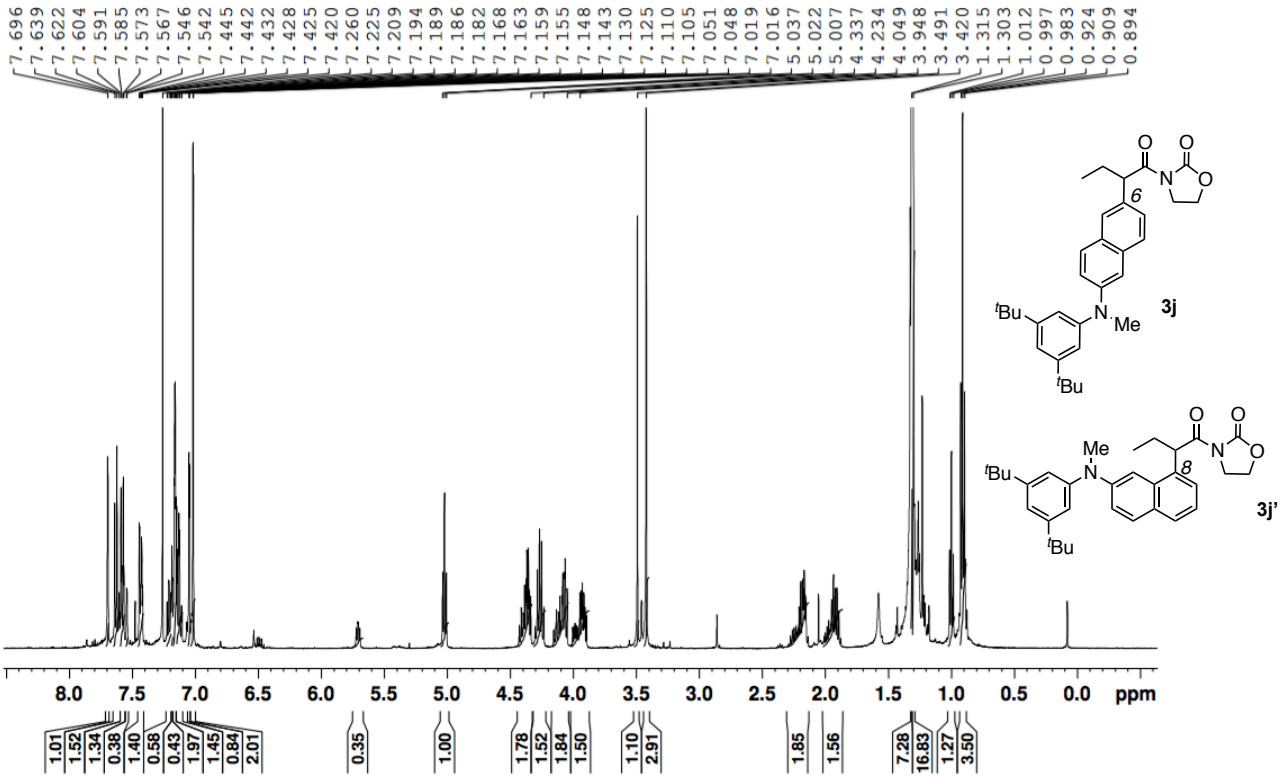


Figure S39. ^{1}H NMR spectrum of **3j+3j'** in $CDCl_3$.

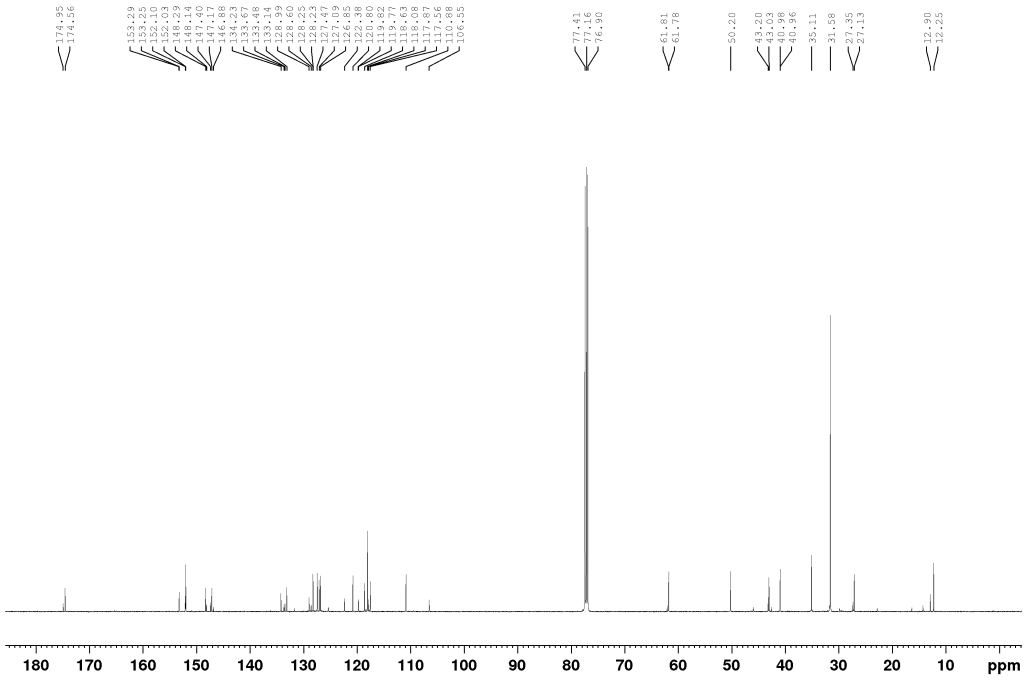


Figure S40. ^{13}C NMR spectrum of **3j+3j'** in $CDCl_3$.