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Supporting Information

Concise synthesis of pyrrolo[3,4-*c*]quinolines via a $P(NMe_2)_3$-catalyzed [4 + 2] annulation followed by a Zn/AcOH-mediated reduction-hydroamination-isomerization

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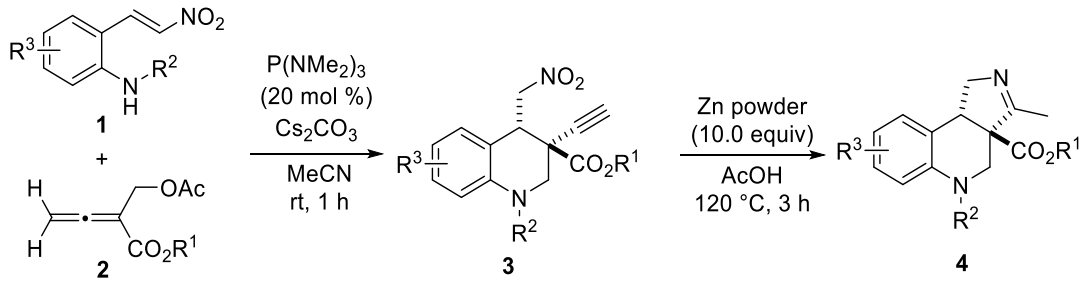
I. General Information

Unless otherwise specified, **all reactions** were carried out under a nitrogen atmosphere at room temperature. **All solvents** were purified according to the standard procedures. **All chemicals** which are commercially available were employed without further purification. **Thin-layer chromatography (TLC)** was performed on silica gel plates (GF254) using UV-light (254 and 365 nm). **Flash chromatography** was conducted on silica gel (200–300 mesh). **^{1}H and ^{13}C{^{1}H} NMR spectra** were recorded at ambient temperature in $CDCl_3$ on a Bruker 400 MHz spectrometer. Chemical shifts were reported in parts per million (ppm). The ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$ or DMSO-d6 as the internal reference ($CDCl_3$: δ = 7.260 ppm, DMSO-d6: δ = 2.500 ppm). The ^{13}C{^{1}H} NMR (100 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d6 as the internal standard ($CDCl_3$: δ = 77.00 ppm, DMSO-d6: 40.00 ppm). **All high-resolution mass spectra (HR-MS)** were obtained on a Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer solariX (Bruker Daltonik GmbH, Bremen, Germany). **Crystal measurement** was performed by Bruker D8 Venture X-ray diffractionmeter.

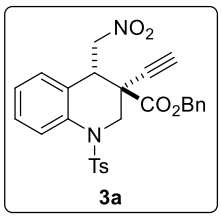
II. Representative Procedure of the Reaction



To a stirred solution of 2-amino-*β*-nitrostyrenes **1** (0.1 mmol) and *β*'-acetoxy allenoates **2** (0.15 mmol, 1.5 equiv) in MeCN (1.0 mL) was added $P(NMe_2)_3$ (3.3 mg, 20 mol %) and Cs_2CO_3 (39.1 mg, 120 mol %) at room temperature for 1 h. The reaction mixture was concentrated under reduced pressure and purified via flash chromatography on silica gel (PE:EtOAc = 10:1) to afford compounds **3**. To a stirred solution of compounds **3** (0.1 mmol) and zinc powder (65.4 mg, 1.0 mmol, 10 equiv) in AcOH (2 mL) at 120 ℃ for 3 h. After cooling to room temperature, the reaction was quenched with saturated aq. $NaHCO_3$ (5 mL) and the mixture was stirred for 30 mins. Then it was extracted with EtOAc (3 x 10 mL). The combined organic extracts were dried over dry Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE:EtOAc = 3:1) to afford compounds **4**.

III. Analytical Data

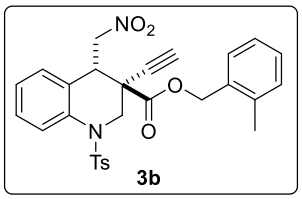
Benzyl 3-ethynyl-4-(nitromethyl)-1-tosyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3a)



3a

The **3a** was prepared according to the general procedure described above using **1a** (31.8 mg, 0.1 mmol), **2a** (36.9 mg, 0.15 mmol), $P(NMe_2)_3$ (3.3 mg, 20 mol %) and Cs_2CO_3 (39.1 mg, 120 mol %) and isolated as a yellow liquid (37.8 mg, 75% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 8:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (d, J = 8.3 Hz, 1H), 7.57 (d, J = 8.0 Hz, 2H), 7.32 – 7.26 (m, 5H), 7.25 – 7.20 (m, 1H), 7.18 – 7.08 (m, 2H), 7.01 – 6.89 (m, 2H), 5.08 – 4.97 (m, 2H), 4.61 (dd, J = 13.4, 3.9 Hz, 1H), 4.57 (d, J = 12.8, 1H), 4.06 (dd, J = 10.0, 3.9 Hz, 1H), 3.69 – 3.57 (m, 2H), 2.49 (s, 1H), 2.41 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 167.3, 144.8, 135.1, 134.4, 130.1, 129.3, 129.2, 128.6, 128.3, 126.8, 125.3, 125.1, 123.2, 78.2, 76.0, 68.5, 49.9, 46.3, 42.0, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{27}H_{24}N_2NaO_6S^+$ $(M + Na)^+$ 527.1247, found 527.1250.

2-Methylbenzyl 3-ethynyl-4-(nitromethyl)-1-tosyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3b)

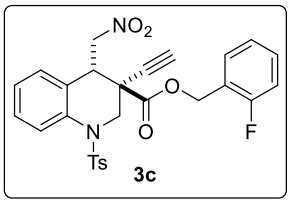


3b

The **3b** was prepared according to the general procedure described above using **1a** (31.8 mg, 0.1 mmol), **2b** (39.6 mg, 0.15 mmol), $P(NMe_2)_3$ (3.3 mg, 20 mol %) and Cs_2CO_3 (39.1 mg, 120 mol %) and isolated as a yellow liquid (39.0 mg, 70% yield, 13:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 8:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (d, J = 8.3 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.28 (s, 1H), 7.26 – 7.06 (m, 6H), 6.97 (td, J = 7.5, 1.1 Hz, 1H), 6.91 (dd, J = 7.7, 1.6 Hz, 1H), 5.05 (d, J = 12.1 Hz, 1H), 5.01 (d, J = 12.2 Hz, 1H), 4.60 (dd, J = 13.4, 3.9 Hz, 1H), 4.55 (dd, J = 12.8, 1.5 Hz, 1H), 4.04 (dd, J = 9.9, 3.5 Hz, 1H), 3.64 (d, J = 12.8 Hz, 1H), 3.56 (dd, J = 13.4, 9.9 Hz, 1H), 2.49 (s, 1H), 2.41 (s, 3H), 2.25 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 167.3, 144.8, 137.2, 135.0, 134.9, 132.3, 130.4, 130.1, 129.5, 129.3, 129.2, 129.0, 126.8, 126.0, 125.3, 125.1, 123.2, 78.2, 76.03,

75.97, 67.0, 49.8, 46.3, 42.0, 21.6, 18.8. **HRMS (ESI)** m/z: calcd. for $C_{28}H_{26}N_2NaO_6S^+$ $(M + Na)^+$541.1404, found 541.1413.

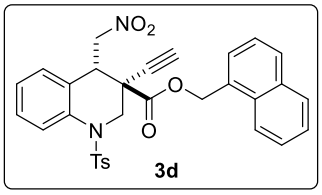
2-Fluorobenzyl 3-ethynyl-4-(nitromethyl)-1-tosyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3c)



3c

The **3c** was prepared according to the general procedure described above using **1a** (31.8 mg, 0.1 mmol), **2c** (39.6 mg, 0.15 mmol), $P(NMe_2)_3$ (3.3 mg, 20 mol %) and Cs_2CO_3 (39.1 mg, 120 mol %) and isolated as a yellow liquid (38.1 mg, 73% yield, 17:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 8:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.70 (dd, J = 8.3, 1.0 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.35 – 7.26 (m, 3H), 7.21 (m, 1H), 7.14 – 7.01 (m, 3H), 6.99 – 6.90 (m, 2H), 5.09 (t, J = 12.4 Hz, 2H), 4.61 (dd, J = 13.4, 3.8 Hz, 1H), 4.55 (dd, J = 12.8, 1.4 Hz, 1H), 4.05 (ddd, J = 10.0, 3.9, 1.4 Hz, 1H), 3.64 (d, J = 12.8 Hz, 1H), 3.58 (dd, J = 13.4, 10.0 Hz, 1H), 2.50 (s, 1H), 2.41 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 167.2, 160.9 (J = 247.5 Hz), 144.8, 135.0 (J = 3.5 Hz), 130.70, 130.66, 130.6, 130.1, 129.3 (J = 14.1 Hz), 126.7, 125.2, 125.1, 124.2 (J = 3.7 Hz), 123.2, 121.5 (J = 14.5 Hz), 115.5 (J = 20.8 Hz), 78.0, 76.1, 75.9, 62.3, 49.8, 46.2, 41.9, 21.6. **^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$)** δ -117.6. **HRMS (ESI)** m/z: calcd. for $C_{27}H_{23}FN_2NaO_6S^+$ $(M + Na)^+$545.1153, found 545.1147.

Naphthalen-1-ylmethyl-3-ethynyl-4-(nitromethyl)-1-tosyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3d)

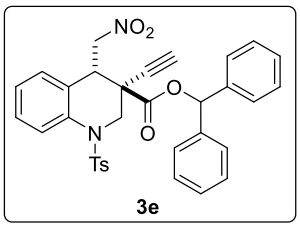


3d

The **3d** was prepared according to the general procedure described above using **1a** (31.8 mg, 0.1 mmol), **2d** (44.4 mg, 0.15 mmol), $P(NMe_2)_3$ (3.3 mg, 20 mol %) and Cs_2CO_3 (39.1 mg, 120 mol %) and isolated as a yellow liquid (40.1 mg, 72% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 8:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85 – 7.75 (m, 3H), 7.67 – 7.60 (m, 2H), 7.58 – 7.53 (m, 2H), 7.53 – 7.46 (m, 2H), 7.22 (m, 3H), 7.10 – 7.04 (m,

1H), 6.83 (dd, *J* = 7.7, 1.7 Hz, 1H), 6.76 (td, *J* = 7.5, 1.1 Hz, 1H), 5.23 (d, *J* = 12.1 Hz, 1H), 5.14 (d, *J* = 12.1 Hz, 1H), 4.64 – 4.60 (dd, *J* = 13.2, 4.0 Hz, 1H), 4.60 – 4.56 (dd, *J* = 12.8, 1.6 Hz, 1H), 4.07 (ddd, *J* = 10.0, 4.0, 1.6 Hz, 1H), 3.64 (d, *J* = 12.8 Hz, 1H), 3.56 (dd, *J* = 13.2, 10.0 Hz, 1H), 2.51 (s, 1H), 2.38 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 167.3, 144.8, 134.98, 134.95, 133.2, 133.1, 131.7, 130.1, 129.24, 129.22, 128.5, 128.1, 127.9, 127.7, 126.7, 126.5, 126.3, 125.8, 125.1, 124.9, 123.1, 78.2, 76.1, 76.0, 68.6, 49.8, 46.2, 42.0, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{31}H_{26}N_2NaO_6S^+$ $(M + Na)^+$ 577.1404, found 577.1398.

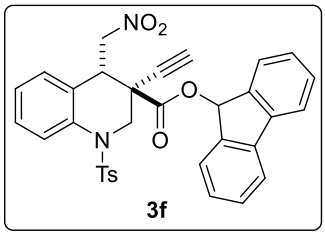
Benzhydryl 3-ethynyl-4-(nitromethyl)-1-tosyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3e)



3e

The **3e** was prepared according to the general procedure described above using **1a** (31.8 mg, 0.1 mmol), **2e** (48.3 mg, 0.15 mmol), $P(NMe_2)_3$ (3.3 mg, 20 mol %) and Cs_2CO_3 (39.1 mg, 120 mol %) and isolated as a yellow liquid (36.5 mg, 63% yield, 5:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 8:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.70 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.27 (m, 7H), 7.25 – 7.18 (m, 4H), 7.12 – 7.03 (m, 2H), 6.91 (td, *J* = 7.5, 1.2 Hz, 1H), 6.79 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.66 (s, 1H), 4.59 (dd, *J* = 13.3, 3.6 Hz, 2H), 4.05 (dd, *J* = 10.3, 2.9 Hz, 1H), 3.66 (d, *J* = 12.8 Hz, 1H), 3.57 (dd, *J* = 13.3, 10.3 Hz, 1H), 2.53 (s, 1H), 2.40 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 166.4, 144.8, 138.54, 138.51, 135.0, 134.8, 130.1, 129.3, 129.2, 128.5, 128.3, 128.1, 127.3, 126.74, 126.71, 125.2, 125.1, 123.4, 79.4, 78.1, 76.1, 75.8, 49.7, 46.4, 42.0, 21.6. **HRMS (ESI)** m/z: calcd. for $C_{33}H_{28}N_2NaO_6S^+$ $(M + Na)^+$ 603.1560, found 603.1556.

9H-fluoren-9-yl 3-ethynyl-4-(nitromethyl)-1-tosyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3f)

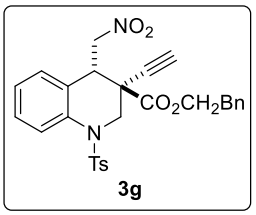


3f

The **3f** was prepared according to the general procedure described above using **1a** (31.8 mg, 0.1 mmol), **2f** (48.0 mg, 0.15 mmol), $P(NMe_2)_3$ (3.3 mg, 20 mol %) and

Cs_2CO_3 (39.1 mg, 120 mol %) and isolated as a white solid (35.2 mg, 61% yield, 8:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 8:1). m.p.: 149.7 – 151.3 ^{o}C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.67 – 7.60 (m, 2H), 7.59 – 7.54 (m, 2H), 7.41 – 7.29 (m, 3H), 7.25 – 7.19 (m, 4H), 7.11 (td, *J* = 7.5, 1.1 Hz, 1H), 6.99 (td, *J* = 7.5, 1.1 Hz, 1H), 6.88 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.80 (dd, *J* = 7.6, 0.9 Hz, 1H), 6.60 (s, 1H), 4.63 (dd, *J* = 12.8, 1.6 Hz, 1H), 4.62 – 4.56 (dd, *J* = 13.2, 3.6 Hz, 1H), 4.07 (ddd, *J* = 10.4, 3.6, 1.5 Hz, 1H), 3.63 (d, *J* = 12.8 Hz, 1H), 3.47 (dd, *J* = 13.2, 10.4 Hz, 1H), 2.54 (s, 1H), 2.39 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 168.2, 144.9, 141.0, 140.9, 140.6, 140.4, 135.0, 134.8, 130.1, 129.82, 129.77, 129.7, 129.6, 127.92, 127.87, 126.7, 125.7, 125.5, 125.14, 125.10, 123.4, 120.1, 120.0, 78.0, 76.1, 75.8, 49.5, 46.3, 42.0, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{33}H_{26}N_2NaO_6S^+$ $(M + Na)^+$601.1404, found 601.1407.

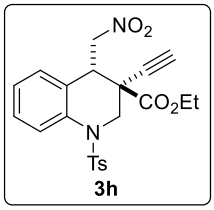
Phenethyl 3-ethynyl-4-(nitromethyl)-1-tosyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3g)



3g

The **3g** was prepared according to the general procedure described above using **1a** (31.8 mg, 0.1 mmol), **2g** (39.0 mg, 0.15 mmol), $P(NMe_2)_3$ (3.3 mg, 20 mol %) and Cs_2CO_3 (39.1 mg, 120 mol %) and isolated as a yellow liquid (26.4 mg, 51% yield, 8:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 8:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.70 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.36 – 7.27 (m, 5H), 7.24 – 7.21 (m, 1H), 7.19 – 7.13 (m, 2H), 6.98 (t, *J* = 7.6, 1H), 6.80 (dd, *J* = 7.7, 1.5 Hz, 1H), 4.58 (dd, *J* = 13.4, 3.9 Hz, 1H), 4.48 (dd, *J* = 12.8, 1.5 Hz, 1H), 4.23 (dt, *J* = 10.8, 6.7 Hz, 1H), 4.12 (dt, *J* = 10.8, 7.2 Hz, 1H), 4.03 (dd, *J* = 9.8, 3.9 Hz, 1H), 3.64 (d, *J* = 12.8 Hz, 1H), 3.58 (dd, *J* = 13.4, 9.8 Hz, 1H), 2.77 (t, *J* = 7.0 Hz, 2H), 2.48 (s, 1H), 2.42 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 167.4, 144.8, 137.0, 135.1, 130.1, 129.3, 129.2, 128.9, 128.6, 126.78, 126.76, 125.4, 125.0, 123.1, 78.2, 76.0, 75.9, 67.3, 49.8, 46.2, 42.0, 34.5, 21.6. **HRMS (ESI)** m/z: calcd. for $C_{28}H_{26}N_2NaO_6S^+$ $(M + Na)^+$541.1404, found 541.1414.

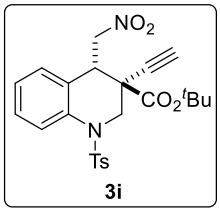
Ethyl 3-ethynyl-4-(nitromethyl)-1-tosyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3h)



3h

The **3h** was prepared according to the general procedure described above using **1a** (31.8 mg, 0.1 mmol), **2h** (27.6 mg, 0.15 mmol), $P(NMe_2)_3$ (3.3 mg, 20 mol %) and Cs_2CO_3 (39.1 mg, 120 mol %) and isolated as a yellow liquid (29.6 mg, 67% yield, 8:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 8:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 – 7.71 (m, 1H), 7.64 – 7.57 (m, 2H), 7.33 – 7.26 (m, 2H), 7.09 – 7.01 (m, 2H), 4.65 (dd, *J* = 13.4, 3.9 Hz, 1H), 4.53 (dd, *J* = 12.7, 1.5 Hz, 1H), 4.14 – 4.02 (m, 3H), 3.66 – 3.63 (d, *J* = 12.7 Hz, 1H) 3.62 (dd, *J* = 13.4, 9.8 Hz, 1H), 2.49 (s, 1H), 2.42 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 167.4, 144.8, 135.2, 135.1, 130.1, 129.4, 129.3, 126.8, 125.4, 125.0, 123.1, 78.3, 76.1, 75.9, 63.0, 49.8, 46.1, 42.0, 21.6, 13.6. **HRMS (ESI)** m/z: calcd. for $C_{22}H_{22}N_2NaO_6S^+$ $(M + Na)^+$465.1091, found 465.1091.

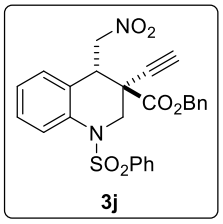
Tert-butyl 3-ethynyl-4-(nitromethyl)-1-tosyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3i)



3i

The **3i** was prepared according to the general procedure described above using **1a** (31.8 mg, 0.1 mmol), **2i** (31.8 mg, 0.15 mmol), $P(NMe_2)_3$ (3.3 mg, 20 mol %) and Cs_2CO_3 (39.1 mg, 120 mol %) and isolated as a yellow liquid (14.5 mg, 31% yield, 1.2 :1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 8:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.29 (m, 1H), 7.23 (s, 2H), 7.16 (td, *J* = 7.6, 1.2 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 4.83 (dd, *J* = 14.5, 3.0 Hz, 1H), 4.74 (dd, *J* = 14.5, 9.8 Hz, 1H), 4.33 (d, *J* = 12.7 Hz, 1H), 4.02 (d, *J* = 12.7 Hz, 1H), 2.98 (dd, *J* = 9.8, 3.0 Hz, 1H), 2.47 (s, 1H), 2.41 (s, 3H), 1.20 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 166.2, 144.7, 135.9, 134.6, 130.0, 128.8, 128.4, 126.7, 125.9, 125.8, 125.2, 84.2, 79.4, 75.4, 74.8, 53.1, 48.7, 42.3, 27.3, 21.6. **HRMS (ESI)** m/z: calcd. for $C_{24}H_{26}N_2NaO_6S^+$ $(M + Na)^+$493.1404, found 493.1395.

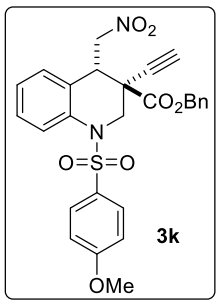
Benzyl 3-ethynyl-4-(nitromethyl)-1-(phenylsulfonyl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (3j)



3j

The **3j** was prepared according to the general procedure described above using **1b** (30.4 mg, 0.1 mmol), **2a** (36.9 mg, 0.15 mmol), $P(NMe_2)_3$ (3.3 mg, 20 mol %) and Cs_2CO_3 (39.1 mg, 120 mol %) and isolated as a white solid (33.8 mg, 69% yield, 10:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 8:1). m.p.: 84.5 - 86.2 ^oC, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 – 7.66 (m, 3H), 7.65 – 7.58 (m, 1H), 7.53 – 7.47 (m, 2H), 7.35 – 7.27 (m, 3H), 7.23 (ddd, *J* = 8.6, 7.4, 1.7 Hz, 1H), 7.18 – 7.10 (m, 2H), 6.98 (td, *J* = 7.5, 1.1 Hz, 1H), 6.91 (dd, *J* = 7.7, 1.7 Hz, 1H), 5.06 (d, *J* = 12.1 Hz, 1H), 5.00 (d, *J* = 12.1 Hz, 1H), 4.64 (dd, *J* = 13.3, 4.0 Hz, 1H), 4.58 (dd, *J* = 12.8, 1.4 Hz, 1H), 4.11 – 4.03 (m, 1H), 3.74 (dd, *J* = 13.3, 9.8 Hz, 1H), 3.71 (d, *J* = 12.8 Hz, 1H), 2.50 (s, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 167.3, 138.3, 135.1, 134.4, 133.6, 129.5, 129.3, 129.2, 128.60, 128.59, 128.3, 126.8, 125.3, 125.2, 123.0, 78.1, 76.11, 76.08, 68.5, 50.0, 46.3, 42.0. **HRMS (ESI)** m/z: calcd. for $C_{26}H_{23}N_2O_6S^+$ $(M + H)^+$ 491.1271, found 491.1271.

Benzyl 3-ethynyl-1-((4-methoxyphenyl)sulfonyl)-4-(nitromethyl)-1,2,3,4-tetrahydro-quinoline-3-carboxylate (3k)

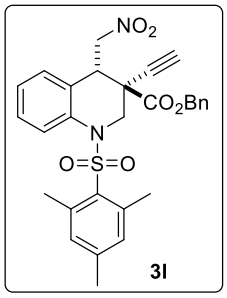


3k

The **3k** was prepared according to the general procedure described above using **1c** (34.9 mg, 0.1 mmol), **2a** (36.9 mg, 0.15 mmol), $P(NMe_2)_3$ (3.3 mg, 20 mol %) and Cs_2CO_3 (39.1 mg, 120 mol %) and isolated as a yellow liquid (27.0 mg, 52% yield, 10:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 8:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74 – 7.70 (m, 1H), 7.66 – 7.59 (m, 2H), 7.30 (m, 3H), 7.26 – 7.20 (m, 1H), 7.16 – 7.09 (m, 2H), 7.01 – 6.88 (m, 4H), 5.05 (d, *J* = 12.1 Hz, 1H), 4.99 (d, *J* = 12.1 Hz, 1H), 4.63 (dd, *J* = 13.3, 3.9 Hz, 1H), 4.57 (dd, *J* = 12.8, 1.5 Hz, 1H), 4.06 (dt, *J* = 10.0, 2.4 Hz, 1H), 3.84 (s, 3H), 3.68 (dd, *J* =13.3, 10.0 Hz, 1H), 3.64 (d, *J* = 12.8 Hz, 1H), 2.50 (s, 1H).**^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 167.3, 163.6, 135.1, 134.4, 129.5, 129.3, 129.2, 128.9, 128.6, 128.2, 125.2, 125.0, 123.2,

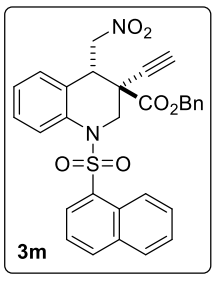
114.7, 78.1, 76.1, 76.0, 68.5, 55.7, 49.8, 46.2, 42.0. **HRMS (ESI)** m/z: calcd. for $C_{27}H_{25}N_2O_7S^+$ $(M + H)^+$ 521.1377, found 521.1382.

Benzyl 3-ethynyl-1-(mesitylsulfonyl)-4-(nitromethyl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (3l)



The **3l** was prepared according to the general procedure described above using **1d** (34.6 mg, 0.1 mmol), **2a** (36.9 mg, 0.15 mmol), $P(NMe_2)_3$ (3.3 mg, 20 mol %) and Cs_2CO_3 (39.1 mg, 120 mol %) and isolated as a yellow liquid (44.2 mg, 83% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 8:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 – 7.29 (m, 3H), 7.21 (dt, *J* = 4.6, 3.5 Hz, 2H), 7.09 (m, 1H), 7.06 – 7.01 (m, 3H), 7.00 – 6.95 (m, 2H), 5.11 (d, *J* = 12.1 Hz, 1H), 5.03 (d, *J* = 12.1 Hz, 1H), 4.94 (dd, *J* = 13.7, 4.4 Hz, 1H), 4.52 (dd, *J* = 13.7, 8.8 Hz, 1H), 4.38 (dd, *J* = 12.8, 1.2 Hz, 1H), 4.34 (dd, *J* = 8.8, 4.4 Hz, 1H), 3.89 (d, *J* = 12.8 Hz, 1H), 2.55 (s, 6H), 2.53 (s, 1H), 2.34 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 167.8, 143.4, 139.6, 136.1, 134.6, 134.5, 132.5, 129.3, 128.9, 128.5, 128.4, 125.8, 124.9, 122.0, 78.0, 76.4, 68.5, 49.1, 46.2, 41.9, 22.9, 21.0. **HRMS (ESI)** m/z: calcd. for $C_{29}H_{28}N_2NaO_6S^+$ $(M + Na)^+$ 555.1560, found 555.1550.

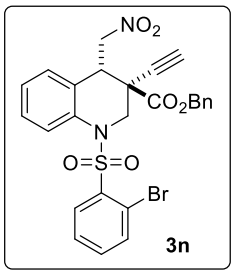
Benzyl 3-ethynyl-1-(naphthalen-2-ylsulfonyl)-4-(nitromethyl)-1,2,3,4-tetrahydro-quinoline-3-carboxylate (3m)



The **3m** was prepared according to the general procedure described above using **1e** (35.4 mg, 0.1 mmol), **2a** (36.9 mg, 0.15 mmol), $P(NMe_2)_3$ (3.3 mg, 20 mol %) and Cs_2CO_3 (39.1 mg, 120 mol %) and isolated as a yellow liquid (33.8 mg, 53% yield, 3:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 8:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.39 (d, *J* = 8.7 Hz, 1H), 8.21 – 8.16 (m, 1H), 8.10 (d, *J* = 8.3 Hz, 1H), 7.96 – 7.91 (m, 1H), 7.60 – 7.46 (m, 4H), 7.35 – 7.29 (m, 3H), 7.24 – 7.15 (m, 3H), 7.03 – 6.91 (m, 2H), 5.06 (d, *J* = 12.1 Hz, 1H), 5.02 (d, *J* = 12.1 Hz, 1H), 4.63 (dd, *J* = 13.5, 3.9 Hz, 1H) , 4.61 (dd, *J* = 12.7, 1.1 Hz, 1H), 4.11 (dd, *J* = 9.4,

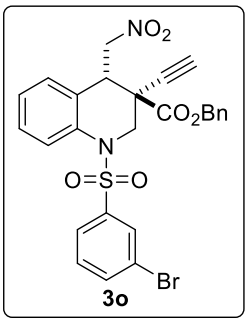
3.9 Hz, 1H), 3.99 (dd, *J* = 13.5, 9.4 Hz, 1H), 3.93 (d, *J* = 12.7 Hz, 1H), 2.49 (s, 1H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 167.6, 135.6, 134.7, 134.6, 134.5, 134.4, 129.1, 129.02, 129.00, 128.61, 128.59, 128.5, 128.3, 128.2, 127.3, 125.4, 125.0, 124.4, 124.1, 123.2, 77.9, 76.1, 75.5, 68.5, 50.0, 46.6, 42.1. **HRMS (ESI)** m/z: calcd. for $C_{30}H_{24}N_2NaO_6S^+$ $(M + Na)^+$ 563.1247, found 563.1256.

Benzyl 1-((2-bromophenyl)sulfonyl)-3-ethynyl-4-(nitromethyl)-1,2,3,4-tetrahydro-quinoline-3-carboxylate (3n)



The **3n** was prepared according to the general procedure described above using **1f** (38.19 mg, 0.1 mmol), **2a** (36.9 mg, 0.15 mmol), $P(NMe_2)_3$ (3.3 mg, 20 mol %) and Cs_2CO_3 (39.1 mg, 120 mol %) and isolated as a yellow liquid (31.2 mg, 55% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 8:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.17 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.79 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.48 (m, 2H), 7.34 (m, 4H), 7.25 – 7.22 (m, 1H), 7.15 – 7.03 (m, 3H), 6.99 (m, 1H), 5.16 (d, *J* = 12.2 Hz, 1H), 5.09 (d, *J* = 12.2 Hz, 1H), 5.00 (dd, *J* = 13.9, 4.5 Hz, 1H), 4.59 (dd, J = 13.9, 8.4 Hz, 1H), 4.53 (d, J = 13.0 Hz, 1H), 4.37 (dd, *J* = 8.4, 4.5 Hz, 1H), 4.20 (d, *J* = 13.0 Hz, 1H), 2.55 (s, 1H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 167.9, 140.1, 136.1, 135.7, 134.5, 134.2, 131.4, 129.1, 128.8, 128.6, 128.4, 128.1, 125.1, 124.9, 121.3, 120.2, 77.7, 77.1, 68.6, 50.9, 46.2, 41.9. **HRMS (ESI)** m/z: calcd. for $C_{26}H_{21}BrN_2NaO_6S^+$ $(M + Na)^+$ 591.0196, found 591.0187.

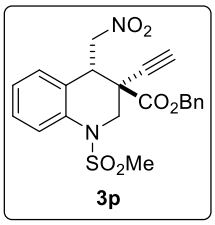
Benzyl 1-((3-bromophenyl)sulfonyl)-3-ethynyl-4-(nitromethyl)-1,2,3,4-tetrahydro-quinoline-3-carboxylate (3o)



The **3o** was prepared according to the general procedure described above using **1g** (34.6 mg, 0.1 mmol), **2a** (36.9 mg, 0.15 mmol), $P(NMe_2)_3$ (3.3 mg, 20 mol %) and Cs_2CO_3 (39.1 mg, 120 mol %) and isolated as a yellow liquid (44.2 mg, 57% yield, >20:1 *d.r.*) after flash column chromatography on silica

gel (PE:EtOAc = 8:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (t, *J* = 1.9 Hz, 1H), 7.74 (m, 1H), 7.68 – 7.55 (m, 2H), 7.39 – 7.29 (m, 4H), 7.25 – 7.19 (m, 1H), 7.19 – 7.12 (m, 2H), 7.05 – 6.90 (m, 2H), 5.09 (d, *J* = 12.1 Hz, 1H), 5.04 (d, *J* = 12.1 Hz, 1H), 4.72 (dd, *J* = 13.2, 3.9 Hz, 1H), 4.56 (dd, *J* = 12.8 1.3 Hz, 1H), 4.07 (dd, *J* = 9.7, 3.8 Hz, 1H), 3.96 (dd, *J* = 13.2, 9.7 Hz, 1H), 3.79 (d, *J* = 12.8 Hz, 1H), 2.51 (s, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 167.4, 140.3, 136.6, 134.8, 134.3, 131.0, 129.7, 129.4, 129.1, 128.7, 128.6, 128.4, 125.4, 125.24, 125.23, 123.5, 122.6, 77.9, 76.4, 76.2, 68.6, 50.3, 46.3, 41.9. **HRMS (ESI)** m/z: calcd. for $C_{26}H_{21}BrN_2NaO_6S^+$ $(M + Na)^+$ 591.0196, found 591.0197.

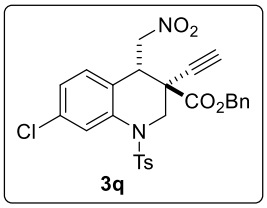
Benzyl 3-ethynyl-1-(methylsulfonyl)-4-(nitromethyl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (3p)



3p

The **3p** was prepared according to the general procedure described above using **1h** (24.1 mg, 0.1 mmol), **2a** (36.9 mg, 0.15 mmol), $P(NMe_2)_3$ (3.3 mg, 20 mol %) and Cs_2CO_3 (39.1 mg, 120 mol %) and isolated as a yellow liquid (27.0 mg, 54% yield, 10:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 8:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.29 (m, 4H), 7.16 – 7.09 (m, 2H), 7.07 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.00 (td, *J* = 7.5, 1.0 Hz, 1H), 5.12 (d, J = 12.0 Hz, 1H), 5.05 (d, J = 12.2 Hz, 1H), 5.01 (dd, *J* = 13.4, 4.5 Hz, 1H), 4.56 (dd, *J* = 13.4, 8.6 Hz, 1H), 4.48 (dd, *J* = 13.2, 1.3 Hz, 1H), 4.40 (dd, *J* = 8.6, 4.6 Hz, 1H), 3.84 (d, *J* = 13.2 Hz, 1H), 2.98 (s, 3H), 2.55 (s, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 167.6, 135.3, 134.4, 129.8, 129.6, 128.7, 128.6, 128.3, 123.9, 122.5, 118.7, 77.8, 77.6, 68.6, 48.8, 44.3, 41.9, 38.3. **HRMS (ESI)** m/z: calcd. for $C_{21}H_{20}N_2NaO_6S^+$ $(M + Na)^+$ 451.0934, found 451.0926.

Benzyl 7-chloro-3-ethynyl-4-(nitromethyl)-1-tosyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3q)

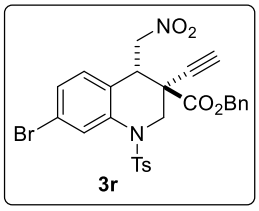


3q

The **3q** was prepared according to the general procedure described above using **1i** (35.2 mg, 0.1 mmol), **2a** (36.9 mg, 0.15 mmol), $P(NMe_2)_3$ (3.3 mg, 20 mol %) and Cs_2CO_3 (39.1

mg, 120 mol %) and isolated as a yellow liquid (30.6 mg, 57% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 8:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 2.0 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.27 (m, 5H), 7.13 – 7.07 (m, 2H), 6.86 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 5.09 (d, *J* = 12.0 Hz, 1H), 4.98 (d, *J* = 12.0 Hz, 1H), 4.60 (dd, *J* = 13.3, 3.7 Hz, 1H), 4.55 (dd, *J* = 12.7, 1.6 Hz, 1H), 4.04 (dd, *J* = 10.3, 3.1 Hz, 1H), 3.56 (d, *J* = 12.7 Hz, 1H), 3.44 (dd, *J* = 13.3, 10.3 Hz, 1H), 2.53 (s, 1H), 2.42 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 166.9, 145.2, 135.9, 135.0, 134.4, 134.2, 130.3, 130.2, 128.7, 128.6, 128.5, 126.8, 125.0, 123.2, 123.0, 77.8, 76.3, 75.8, 68.6, 49.3, 45.7, 41.6, 21.6. **HRMS (ESI)** m/z: calcd. for $C_{27}H_{23}ClN_2NaO_6S^+$ $(M + Na)^+$ 561.0858, found 561.0869.

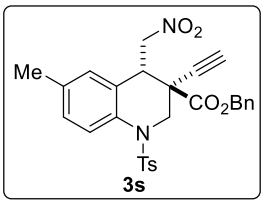
Benzyl 7-bromo-3-ethynyl-4-(nitromethyl)-1-tosyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3r)



3r

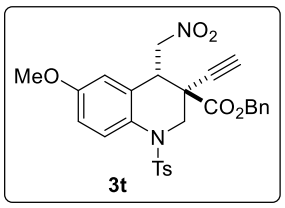
The **3r** was prepared according to the general procedure described above using **1j** (39.6 mg, 0.1 mmol), **2a** (36.9 mg, 0.15 mmol), $P(NMe_2)_3$ (3.3 mg, 20 mol %) and Cs_2CO_3 (39.1 mg, 120 mol %) and isolated as a yellow liquid (36.1 mg, 62% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE : EtOAc = 8:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 (d, *J* = 1.9 Hz, 1H), 7.63 – 7.53 (m, 2H), 7.35 – 7.27 (m, 5H), 7.10 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.00 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.70 (d, *J* = 8.2 Hz, 1H), 5.10 (d, *J* = 11.9 Hz, 1H), 4.98 (d, *J* = 11.9 Hz, 1H), 4.64 – 4.58 (dd, *J* = 13.3, 3.7 Hz, 1H), 4.57 – 4.52 (dd, *J* = 12.7, 1.6 Hz, 1H), 4.02 (ddd, *J* = 10.3, 3.8, 1.5 Hz, 1H), 3.55 (d, *J* = 12.7 Hz, 1H), 3.43 (dd, *J* = 13.3, 10.3 Hz, 1H), 2.52 (s, 1H), 2.42 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 166.9, 145.3, 136.0, 134.4, 134.2, 130.5, 130.2, 128.8, 128.6, 128.5, 128.0, 126.8, 125.8, 123.7, 123.0, 77.7, 76.3, 75.7, 68.6, 49.3, 45.7, 41.7, 21.6. **HRMS (ESI)** m/z: calcd. for $C_{27}H_{23}BrN_2NaO_6S^+$ $(M + Na)^+$ 605.0352, found 605.0357.

Benzyl 3-ethynyl-6-methyl-4-(nitromethyl)-1-tosyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3s)



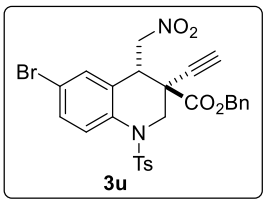
The **3s** was prepared according to the general procedure described above using **1k** (30.1 mg, 0.1 mmol), **2a** (36.9 mg, 0.15 mmol), $P(NMe_2)_3$ (3.3 mg, 20 mol %) and Cs_2CO_3 (39.1 mg, 120 mol %) and isolated as a yellow liquid (36.1 mg, 58% yield, 16:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 8:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.61 (d, *J* = 8.5 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.40 – 7.27 (m, 5H), 7.15 – 7.08 (m, 2H), 7.03 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.72 – 6.66 (m, 1H), 5.07 (d, *J* = 12.1 Hz, 1H), 4.97 (d, *J* = 12.1 Hz, 1H), 4.56 (dd, *J* = 13.2, 3.8 Hz, 2H), 4.00 (dd, *J* = 10.0, 3.8 Hz, 1H), 3.59 (d, *J* = 12.8 Hz, 1H), 3.49 (dd, *J* = 13.2, 10.0 Hz, 1H), 2.49 (s, 1H), 2.41 (s, 3H), 2.19 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 167.3, 144.7, 135.0, 134.8, 134.4, 132.3, 130.12. 130.07, 129.6, 128.53, 128.49, 128.2, 126.7, 125.2, 123.3, 78.2, 75.97, 75.95, 68.4, 49.7, 46.2, 41.8, 21.5, 20.7. **HRMS (ESI)** m/z: calcd. for $C_{28}H_{26}N_2NaO_6S^+$ $(M + Na)^+$541.1404, found 541.1404.

Benzyl 3-ethynyl-6-methoxy-4-(nitromethyl)-1-tosyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3t)



The **3t** was prepared according to the general procedure described above using **1l** (34.8 mg, 0.1 mmol), **2a** (36.9 mg, 0.15 mmol), $P(NMe_2)_3$ (3.3 mg, 20 mol %) and Cs_2CO_3 (39.1 mg, 120 mol %) and isolated as a yellow liquid (35.4 mg, 66% yield, 8:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 8:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.67 (d, *J* = 9.0 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.25 (m, 5H), 7.18 – 7.09 (m, 2H), 6.78 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.41 (d, *J* = 2.9 Hz, 1H), 5.10 (d, *J* = 12.0 Hz, 1H), 4.98 (d, *J* = 12.0 Hz, 1H), 4.57 (dd, *J* = 12.9, 1.5 Hz, 1H), 4.47 (dd, *J* = 13.5, 3.6 Hz, 1H), 3.90 (dd, *J* = 10.2, 3.0 Hz, 1H), 3.67 (s, 3H), 3.53 (d, *J* = 12.9 Hz, 1H), 3.38 (dd, *J* = 13.5, 10.2 Hz, 1H), 2.47 (s, 1H), 2.41 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 167.3, 156.9, 144.8, 134.42, 134.38, 130.1, 128.60, 128.55, 128.3, 127.7, 127.5, 126.8, 125.7, 115.0, 113.7, 78.3, 75.9, 75.5, 68.5, 55.3, 50.1, 46.7, 41.9, 21.6. **HRMS (ESI)** m/z: calcd. for $C_{28}H_{26}N_2NaO_7S^+$ $(M + Na)^+$557.1353, found 557.1360.

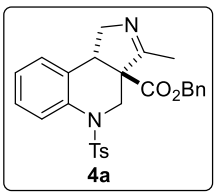
Benzyl 6-bromo-3-ethynyl-4-(nitromethyl)-1-tosyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3u)



3u

The **3u** was prepared according to the general procedure described above using **1m** (39.6 mg, 0.1 mmol), **2a** (36.9 mg, 0.15 mmol), $P(NMe_2)_3$ (3.3 mg, 20 mol %) and Cs_2CO_3 (39.1 mg, 120 mol %) and isolated as a yellow liquid (32.0 mg, 55% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 8:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 (m, 3H), 7.32 (m, 6H), 7.16 – 7.09 (m, 2H), 7.06 (d, *J* = 2.3 Hz, 1H), 5.08 (d, *J* = 11.9 Hz, 1H), 4.99 (d, *J* = 11.9 Hz, 1H), 4.60 – 4.56 (m, 1H), 4.56 – 4.52 (m, 1H), 4.02 (dd, *J* = 10.0, 3.2 Hz, 1H), 3.55 (d, *J* = 12.8 Hz, 1H), 3.42 (dd, *J* = 13.7, 10.0 Hz, 1H), 2.52 (s, 1H), 2.42 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 166.9, 145.2, 134.4, 134.08, 134.06, 132.5, 132.0, 130.3, 128.8, 128.7,128.4, 127.2, 126.7, 124.8, 118.1, 77.7, 76.4, 75.5, 68.8, 49.5, 45.9, 41.6, 21.6. **HRMS (ESI)** m/z: calcd. for $C_{27}H_{23}BrN_2NaO_6S^+$ $(M + Na)^+$ 605.0352, found 605.0332.

Benzyl 3-methyl-5-tosyl-1,4,5,9b-tetrahydro-3aH-pyrrolo[3,4-c]quinoline-3a-carboxylate (4a)

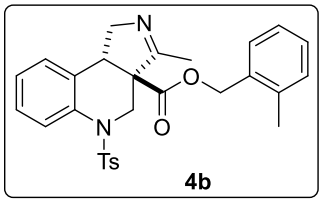


4a

The **3a** (37.8 mg, 75% yield, >20:1 *d.r.*) was obtained according to the general procedure. The **4a** was prepared according to the general procedure described above using **3a** (25.2 mg, 0.05 mmol), zinc powder (32.7 mg, 0.5 mmol) and AcOH (2 mL) and isolated as a white solid (19.6 mg, 83% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 3:1). m.p.: 107.6 – 108.9 ^{o}C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72 – 7.67 (m, 2H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.41 – 7.31 (m, 5H), 7.27 – 7.25 (m, 2H), 7.13 – 7.02 (m, 3H), 5.20 (d, *J* = 12.0 Hz, 1H), 5.16 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 13.7 Hz, 1H), 4.41 (m, 1H), 3.94 (dd, *J* = 9.3, 5.4 Hz, 1H), 3.77 (d, *J* = 13.7 Hz, 1H), 3.40 – 3.32 (m, 1H), 2.39 (s, 3H), 2.10 (t, *J* = 2.4 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.5, 170.0, 144.0, 137.4, 137.1, 134.9, 132.5, 129.7, 129.2, 128.71, 128.67, 128.4, 127.3, 127.1, 125.1, 120.8, 70.0, 68.8, 67.7, 48.1, 44.0, 21.5, 16.6.

HRMS (ESI) m/z: calcd. for $C_{27}H_{27}N_2O_4S^+$ $(M + H)^+$ 475.1686, found 475.1672.

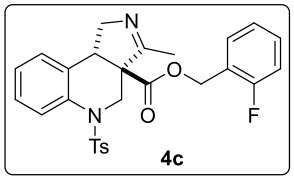
2-Methylbenzyl 3-methyl-5-tosyl-1,4,5,9b-tetrahydro-3aH-pyrrolo[3,4-c]quinoline-3a-carboxylate (4b)



4b

The **3b** (39.0 mg, 70% yield, 13:1 *d.r.*) was obtained according to the general procedure. The **4b** was prepared according to the general procedure described above using **3b** (29.0 mg, 0.056 mmol), zinc powder (36.6 mg, 0.56 mmol) and AcOH (2 mL) and isolated as a yellow liquid (22.1 mg, 81% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 3:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 2.6 Hz, 2H), 7.20 (d, *J* = 7.4 Hz, 2H), 7.13 – 7.01 (m, 3H), 5.23 (d, *J* = 12.3 Hz, 14H), 5.18 (d, *J* = 12.3 Hz, 1H), 4.59 (d, *J* = 13.7 Hz, 1H), 4.44 – 4.34 (m, 1H), 3.93 (dd, *J* = 9.4, 5.4 Hz, 1H), 3.74 (d, *J* = 13.7 Hz, 1H), 3.34 (m, 1H), 2.39 (s, 3H), 2.34 (s, 3H), 2.10 (t, *J* = 2.0 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.6, 170.1, 144.0, 137.4, 137.04, 137.02, 132.9, 132.5, 130.5, 129.7, 129.5, 129.1, 129.0, 127.3, 127.1, 126.1, 125.1, 120.8, 70.0, 68.9, 66.1, 48.1, 44.0, 21.5, 18.9, 16.5. **HRMS (ESI)** m/z: calcd. for $C_{28}H_{29}N_2O_4S^+$ $(M + H)^+$ 489.1843, found 489.1849.

2-Fluorobenzyl 3-methyl-5-tosyl-1,4,5,9b-tetrahydro-3aH-pyrrolo[3,4-c]quinoline-3a-carboxylate (4c)

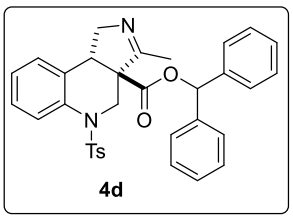


4c

The **3c** (38.1 mg, 73% yield, 17:1 *d.r.*) was obtained according to the general procedure. The **4c** was prepared according to the general procedure described above using **3c** (26.1 mg, 0.05 mmol), zinc powder (32.9 mg, 0.5 mmol) and AcOH (2 mL) and isolated as a white solid (19.1 mg, 78% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 3:1). m.p.: 82.6 – 84.7 ^{o}C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74 – 7.66 (m, 2H), 7.49 – 7.41 (m, 1H), 7.40 – 7.30 (m, 2H), 7.27 (m, 2H), 7.18 – 7.02 (m, 5H), 5.25 (t, *J* = 13.2 Hz, 2H), 4.57 (d, *J* = 13.7 Hz, 1H), 4.45 – 4.34 (m, 1H), 3.95 (dd, *J* = 9.4, 5.4 Hz, 1H), 3.76 (d, *J* = 13.7 Hz, 1H), 3.42 –

3.30 (m, 1H), 2.39 (s, 3H), 2.13 (t, *J* = 2.0 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.4, 170.1, 161.1 (*J* = 247.6 Hz), 144.0, 137.4, 137.1, 132.4, 130.9 (*J* = 2.8 Hz), 130.8 (*J* = 1.8 Hz), 129.7, 129.2, 127.3, 127.1, 125.1, 124.3 (*J* = 3.7 Hz), 122.1 (*J* = 14.3 Hz), 120.8, 115.7 (*J* = 20.8 Hz), 69.9, 68.8, 61.8, 48.1, 43.9, 21.5, 16.5. **^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$)** δ -117.5. **HRMS (ESI)** m/z: calcd. for $C_{27}H_{26}FN_2O_4S^+$ $(M + H)^+$ 493.1592, found 493.1602.

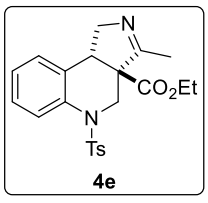
Benzhydryl 3-methyl-5-tosyl-1,4,5,9b-tetrahydro-3aH-pyrrolo[3,4-c]quinoline-3a-carboxylate (4d)



4d

The **3e** (36.5 mg, 63% yield, 5:1 *d.r.*) was obtained according to the general procedure. The **4d** was prepared according to the general procedure described above using **3e** (29.1 mg, 0.05 mmol), zinc powder (32.9 mg, 0.5 mmol) and AcOH (2 mL) and isolated as a yellow solid (23.1 mg, 84% yield, 10:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 3:1). m.p.: 100.1- 101.6 ^{o}C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73 – 7.66 (m, 2H), 7.51 – 7.47 (m, 1H), 7.38 – 7.27 (m, 10H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.10 (m, 1H), 7.08 – 7.01 (m, 2H), 6.90 (s, 1H), 4.71 (d, *J* = 13.7 Hz, 1H), 4.52 – 4.42 (m, 1H), 3.91 (dd, *J* = 9.3, 5.0 Hz, 1H), 3.72 (d, *J* = 13.7 Hz, 1H), 3.40 (m, 1H), 2.38 (s, 3H), 2.05 (t, *J* = 2.4 Hz, 3H).**^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.2, 169.7, 144.0, 139.19, 139.16, 137.5, 137.0, 132.6, 129.7, 129.2, 128.71, 128.67, 128.33, 128.28, 127.3, 127.12, 127.05, 126.9, 125.1, 120.9, 78.4, 70.2, 69.1, 48.0, 44.2, 21.5, 16.6. **HRMS (ESI)** m/z: calcd. for $C_{33}H_{31}N_2O_4S^+$ $(M + H)^+$ 551.1999, found 551.1993.

Ethyl 3-methyl-5-tosyl-1,4,5,9b-tetrahydro-3aH-pyrrolo[3,4-c]quinoline-3a-carboxylate (4e)

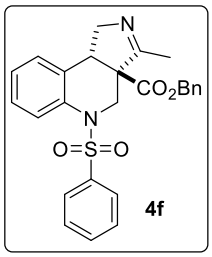


4e

The **3h** (29.6 mg, 67% yield, 8:1 *d.r.*) was obtained according to the general procedure. The **4e** was prepared according to the general procedure described above using **3h** (18 mg, 0.04 mmol), zinc powder (26.6 mg, 0.4 mmol) and AcOH (2 mL) and isolated as a yellow liquid (13.4 mg, 81% yield, 10:1 *d.r.*) after flash column chromatography on

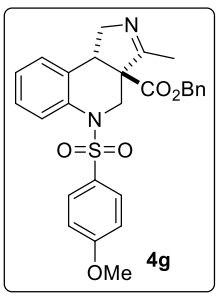
silica gel (PE:EtOAc = 3:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 – 7.66 (m, 2H), 7.51 – 7.42 (m, 1H), 7.27 (d, *J* = 7.7 Hz, 2H), 7.15 – 7.00 (m, 3H), 4.55 (d, *J* = 13.6 Hz, 1H), 4.42 (m, 1H), 4.27 – 4.19 (m, 2H), 3.95 (dd, *J* = 9.4, 5.5 Hz, 1H), 3.77 (d, *J* = 13.6 Hz, 1H), 3.42 – 3.33 (m, 1H), 2.39 (s, 3H), 2.20 (t, *J* = 2.0 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.6, 170.5, 144.0, 137.4, 137.1, 132.4, 129.8, 129.2, 127.3, 127.0, 125.0, 120.7, 69.8, 68.7, 62.1, 48.1, 43.9, 21.5, 16.6, 14.1. **HRMS (ESI)** m/z: calcd. for $C_{22}H_{24}N_2NaO_6S^+$ $(M + Na)^+$ 435.1349, found 435.1349.

Benzyl 3-methyl-5-(phenylsulfonyl)-1,4,5,9b-tetrahydro-3aH-pyrrolo[3,4-c]-quinoline-3a-carboxylate (4f)



The **3j** (33.8 mg, 69% yield, 10:1 *d.r.*) was obtained according to the general procedure. The **4f** was prepared according to the general procedure described above using **3j** (33.1 mg, 0.067 mmol), zinc powder (44 mg, 0.67 mmol) and AcOH (2 mL) and isolated as a yellow liquid (25.1 mg, 81% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 3:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85 – 7.78 (m, 2H), 7.58 – 7.53 (m, 1H), 7.47 (m, 3H), 7.41 – 7.29 (m, 5H), 7.15 – 7.04 (m, 3H), 5.23 – 5.14 (m, 2H), 4.58 (d, *J* = 13.8 Hz, 1H), 4.46 – 4.36 (m, 1H), 3.95 (dd, *J* = 9.4, 5.4 Hz, 1H), 3.79 (d, *J* = 13.8 Hz, 1H), 3.34 (m, 1H), 2.09 (t, *J* = 2.0 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.5, 169.9, 140.2, 137.3, 134.9, 133.1, 132.6, 129.2, 129.1, 128.72, 128.68, 128.4, 127.2, 127.1, 125.3, 121.0, 70.0, 68.8, 67.7, 48.2, 44.0, 16.6. **HRMS (ESI)** m/z: calcd. for $C_{26}H_{25}N_2O_4S^+$ $(M + H)^+$ 461.1530, found 461.1526.

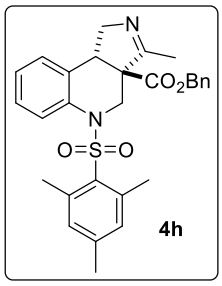
Benzyl 5-((4-methoxyphenyl)sulfonyl)-3-methyl-1,4,5,9b-tetrahydro-3aH-pyrrolo-[3,4-c]quinoline-3a-carboxylate (4g)



The **3k** (27.0 mg, 52% yield, 10:1 *d.r.*) was obtained according to the general procedure. The **4g** was prepared according to the general procedure described above using **3k** (28.5 mg, 0.055 mmol), zinc powder (36.5 mg, 0.55 mmol) and AcOH (2 mL) and

isolated as a yellow liquid (22.8 mg, 85% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 3:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 – 7.71 (m, 2H), 7.49 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.43 – 7.28 (m, 5H), 7.07 (m, 3H), 6.95 – 6.88 (m, 2H), 5.19 (d, *J* = 12.1 Hz, 1H), 5.17 (d, *J* = 12.1 Hz, 1H), 4.58 (d, *J* = 13.7 Hz, 1H), 4.41 (m, 1H), 3.94 (dd, *J* = 9.4, 5.4 Hz, 1H), 3.83 (s, 3H), 3.75 (d, *J* = 13.7 Hz, 1H), 3.39 – 3.31 (m, 1H), 2.11 (t, *J* = 2.0 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.5, 170.2, 163.2, 137.5, 134.9, 132.5, 131.3, 129.6, 129.1, 128.71, 128.66, 128.3, 127.0, 125.0, 120.8, 114.2, 70.0, 68.9, 67.7, 55.6, 47.9, 43.9, 16.6. **HRMS (ESI)** m/z: calcd. for $C_{27}H_{26}N_2NaO_5S^+$ $(M + Na)^+$ 513.1455, found 513.1459.

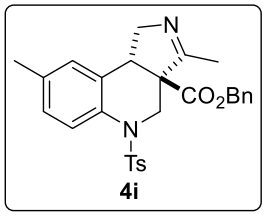
Benzyl 5-(mesitylsulfonyl)-3-methyl-1,4,5,9b-tetrahydro-3aH-pyrrolo-[3,4-c]quinoline-3a-carboxylate (4h)



The **3l** (44.2 mg, 83% yield, >20:1 *d.r.*) was obtained according to the general procedure. The **4h** was prepared according to the general procedure described above using **3l** (69.0 mg, 0.13 mmol), zinc powder (84.8 mg, 1.3 mmol) and AcOH (2 mL) and isolated as a white solid (52.1 mg, 80% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 3:1). m.p.: 110.7 – 112.9 ^{o}C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 (d, *J* = 3.6 Hz, 5H), 7.17 – 7.13 (m, 1H), 7.08 (td, *J* = 7.4, 1.2 Hz, 1H), 7.03 – 6.96 (m, 3H), 6.62 (dd, *J* = 8.1, 1.2 Hz, 1H), 5.20 (d, *J* = 12.1 Hz, 1H), 5.17 (d, *J* = 12.1 Hz, 1H), 4.52 (m, 1H), 4.38 (d, *J* = 14.3 Hz, 1H), 4.03 (dd, *J* = 9.7, 6.0 Hz, 1H), 3.90 – 3.79 (m, 2H), 2.53 (s, 6H), 2.34 (s, 3H), 1.96 (d, *J* = 2.0 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.9, 169.9, 143.0, 139.8, 137.7, 135.4, 135.0, 133.8, 132.3, 129.3, 128.7, 128.6, 128.4, 127.1, 125.8, 121.9, 69.8, 68.9, 67.6, 48.3, 43.9, 22.8, 21.0, 16.4. **HRMS (ESI)** m/z: calcd. for $C_{29}H_{30}N_2NaO_4S^+$ $(M + Na)^+$ 525.1818, found 525.1809.

Benzyl 3,8-dimethyl-5-tosyl-1,4,5,9b-tetrahydro-3aH-pyrrolo-[3,4-c]quinoline-3a-carboxylate (4i)

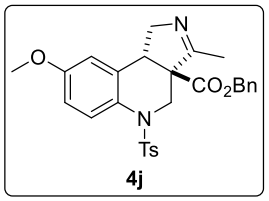
The **3s** (36.1 mg, 58% yield, 16:1 *d.r.*) was obtained according to the general



4i

procedure. The **4i** was prepared according to the general procedure described above using **3s** (32.0 mg, 0.06 mmol), zinc powder (41.7 mg, 0.6 mmol) and AcOH (2 mL) and isolated as a white solid (25.7 mg, 88% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 3:1). m.p.: 152.7-155.3 ^{o}C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.42 – 7.28 (m, 6H), 7.24 (d, *J* = 8.5 Hz, 2H), 6.95 – 6.86 (m, 2H), 5.20 (d, *J* = 12.2 Hz, 1H), 5.18 (d, *J* = 12.2 Hz, 1H), 4.55 (d, *J* = 13.7 Hz, 1H), 4.43 – 4.34 (m, 1H), 3.89 (dd, *J* = 9.4, 5.5 Hz, 1H), 3.75 (d, *J* = 13.7 Hz, 1H), 3.38 – 3.28 (m, 1H), 2.38 (s, 3H), 2.25 (s, 3H), 2.10 (t, *J* = 2.0 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 170.6, 170.1, 143.9, 137.2, 134.9, 134.81, 134.75, 132.3, 129.7, 129.6, 128.7, 128.6, 128.3, 127.7, 127.3, 120.8, 69.9, 68.7, 67.6, 48.1, 43.9, 21.5, 20.7, 16.6. **HRMS (ESI)** m/z: calcd. for $C_{28}H_{28}N_2NaO_4S^+$ $(M + Na)^+$ 511.1662, found 511.1671.

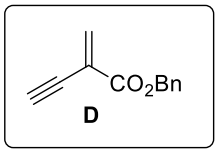
Benzyl 8-methoxy-3-methyl-5-tosyl-1,4,5,9b-tetrahydro-3aH-pyrrolo-[3,4-c]quinoline-3a-carboxylate (4j)



4j

The **3t** (35.4 mg, 66% yield, 8:1 *d.r.*) was obtained according to the general procedure. The **4j** was prepared according to the general procedure described above using **3t** (45.9 mg, 0.086 mmol), zinc powder (56.3 mg, 0.86 mmol) and AcOH (2 mL) and isolated as a white solid (33.5 mg, 77% yield, 10:1 *d.r.*) after flash column chromatography on silica gel (PE:EtOAc = 3:1). m.p.: 127.8 - 130.2 ^{o}C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.28 (m, 6H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.71 – 6.56 (m, 2H), 5.19 (d, *J* = 12.1 Hz, 1H), 5.15 (d, *J* = 12.1 Hz, 1H), 4.57 (d, *J* = 14.0 Hz, 1H), 4.42 – 4.32 (m, 1H), 3.89 (dd, *J* = 9.5, 5.6 Hz, 1H), 3.73 (m, 4H), 3.34 – 3.22 (m, 1H), 2.38 (s, 3H), 2.09 (t, *J* = 2.0 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 170.6, 170.1, 156.9, 143.9, 137.2, 134.9, 134.3, 130.2, 129.6, 128.71, 128.67, 128.3, 127.3, 122.7, 114.1, 112.4, 69.7, 68.9, 67.7, 55.4, 48.4, 44.2, 21.5, 16.5. **HRMS (ESI)** m/z: calcd. for $C_{28}H_{29}N_2O_5S^+$ $(M + H)^+$ 505.1792, found 505.1791.

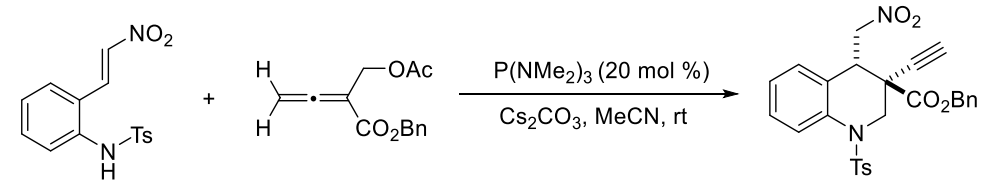
Benzyl 2-methylenebut-3-ynoate (D)



To a stirred solution of *β*'-acetoxy allenoate **2a** (49.3 mg, 0.2 mmol) in MeCN (2.0 mL) was added $P(NMe_2)_3$ (6.5 mg , 20 mol %) and Cs_2CO_3 (78.2 mg, 120 mol %) at room temperature for 1 h. The reaction mixture was concentrated under reduced pressure and purified via flash column chromatography on silica gel (PE:EtOAc = 100:1) to afford the intermediate **D** (33.9 mg, 91% yield) as a pale yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 – 7.31 (m, 5H), 6.69 (s, 1H), 6.22 (s, 1H), 5.26 (s, 2H), 3.12 (s, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 163.6, 136.2, 135.4, 128.6, 128.3, 128.1, 123.3, 80.6, 78.6, 67.3.

IV. Gram-Scale and Synthetic Manipulations

(a) Synthesis of 3a on gram-scale.

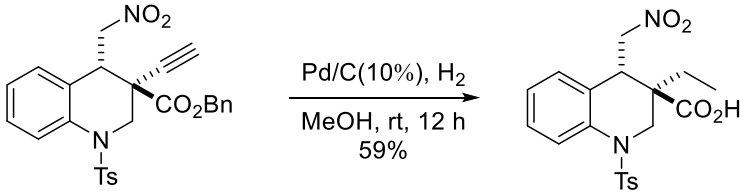


1a (1.45 g, 4.5 mmol) **2a** (1.67 g, 6.8 mmol) **3a** (1.12 g, 50% yield)

To a stirred solution of 2-amino-*β*-nitrostyrenes **1a** (1.45 g, 4.5 mmol, 1.0 equiv) and *β*'-acetoxy allenoate **2a** (1.67 g, 6.8 mmol, 1.5 equiv) in MeCN (30.0 mL) was added $P(NMe_2)_3$ (146.7 mg , 20 mol %) and Cs_2CO_3 (1.76 g, 120 mol %) at room temperature for 1.5 h. The reaction mixture was concentrated under reduced pressure and purified via flash column chromatography on silica gel (PE:EtOAc = 8:1) to afford product **3a** (1.12 g) in 50% yield with >20:1 *d.r.*.

(b) Synthetic manipulations of 3a.

4-(Aminomethyl)-3-ethyl-1-tosyl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid (5)

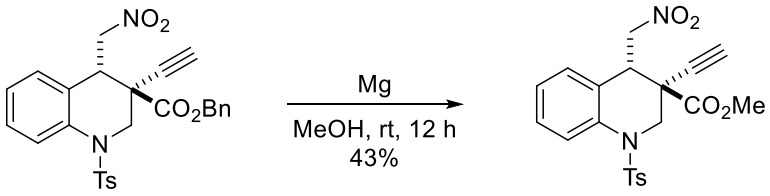


3a **5**

The According to the known procedure.[1] A round-bottomed flask with magnetic stir bar was charged with the **3a** (25.2 mg, 0.05 mmol) and MeOH (1 mL), then was added Pd/C (10%, 2.5 mg). The flask was evacuated and back-filled with H_2. After stirring for 12 h under a H_2 atmosphere (balloon), the reaction mixture was filtered through a short pad of Celite that was carefully rinsed with EtOAc (3 x 5 mL). The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE/EtOAc 1:1 as the eluent) to afford a yellow liquid **5** (12.3 mg, 59% yield). **^{1}H NMR (400 MHz, DMSO-d6)** δ 7.75 – 7.69 (m, 2H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.19 (m, 1H), 6.98 – 6.86 (m, 2H), 4.84 (dd, *J* = 12.4, 4.0 Hz, 1H), 4.27 (dd, *J* = 12.0, 1.8 Hz, 1H), 3.82 – 3.75 (m,

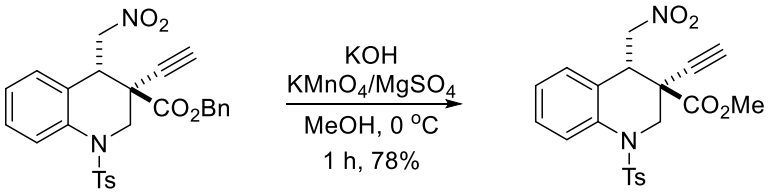
1H), 3.66 (dd, *J* = 12.4, 10.8 Hz, 1H), 3.43 (d, *J* = 12.0 Hz, 1H), 2.37 (s, 3H), 1.76 – 1.64 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d6)** δ 173.7, 144.8, 135.7, 135.5, 130.6, 130.2, 128.9, 127.4, 127.3, 124.0, 121.1, 77.1, 49.7, 49.6, 41.7, 27.7, 21.5, 9.2. **HRMS (ESI)** m/z: calcd. for $C_{20}H_{22}N_2NaO_6S^+$ $(M + Na)^+$ 441.1091, found 441.1086.

Methyl-3-ethynyl-4-(nitromethyl)-1-tosyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (6)



3a **6**

According to the known procedure.[2] Mg powder (2.43 mg, 0.1 mmol) were added to a solution of **3a** (25.2 mg, 0.05 mmol) in MeOH (2 mL) at room temperature. After stirring at room temperature for 12 h. The reaction mixture was filtered through a short pad of Celite that was carefully rinsed with EtOAc (3 x 5 mL). The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE/EtOAc 8:1 as the eluent) to afford a yellow liquid **6** (9.1 mg, 43% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 7.9 Hz, 1H), 7.65 – 7.59 (m, 2H), 7.36 – 7.27 (m, 3H), 7.09 – 7.03 (m, 2H), 4.69 – 4.63 (dd, *J* = 13.6, 4.0 Hz,1H), 4.52 (dd, *J* = 12.8, 1.6 Hz, 1H), 4.10 (ddd, *J* = 9.5, 4.1, 1.3 Hz, 1H), 3.75 – 3.71 (d, *J* = 13.6 Hz, 1H),3.72 – 3.69(d, *J* = 12.8 Hz, 1H), 3.63 (s, 3H), 2.50 (s, 1H), 2.42 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 168.1, 144.8, 135.3, 135.2, 130.1, 129.3, 129.1, 126.78, 126.75, 125.1, 123.0, 78.1, 76.2, 76.0, 53.7, 50.0, 46.2, 41.9, 21.6. **HRMS (ESI)** m/z: calcd. for $C_{21}H_{20}N_2NaO_6S^+$ $(M + Na)^+$ 451.0934, found 451.0936.



3a **6**

According to the known procedure.[3] To a solution of **3a** (50.5 mg, 0.1 mmol) in MeOH (1.0 mL) was added 1.6 M KOH in MeOH (0.1 mL, 1.6 M, 0.16 mmol, 1.6 eq). The mixture was stirred at room temperature for 30 min, cooled to 0 ^{o}C, and a freshly prepared aq. solution of $KMnO_4$ (0.05 M, 1.05 eq)/$MgSO_4$ (0.043 M, 0.9 eq) was added slowly keeping internal temperature below 10 ^{o}C. The resulting mixture was stirred at 0 ^{o}C. After 25 min, saturated $Na_2S_2O_3$ (1.0 mL) was added at 0 ^{o}C followed by 1 M H_2SO_4 (0.5 mL). The reaction mixture was extracted with MTBE (3 x 5 mL) and the organic phase was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE/EtOAc 8:1 as the eluent) to afford a yellow liquid **6** (33.4 mg, 78% yield).

V. References

1. Aspin, S.; López-Suárez, L.; Larini, P.; Goutierre, A.-S.; Jazzar, R.; Baudoin, O., Palladium-Catalyzed *β*-Arylation of Silyl Ketene Acetals and Application to the Synthesis of Benzo-Fused *δ*-Lactones. *Org. Lett.* **2013,** *15*, 5056-5059.

2. Fan, T.; Zhang, Z.-J.; Zhang, Y.-C.; Song, J., Construction of All-Carbon Quaternary Stereocenters via Sequential Photoactivation/Isothiourea Catalysis. *Org Lett.* **2019**, *21*, 7897-7901.

3. Zeng, X.; Gao,J. J.; Song, J. J.; Ma, S.; Desrosiers, J.-N.; Mulder, J. A.; Rodriguez, S.; Herbage, M. A.; Haddad, N.; Qu, B.; Fandrick, K. R.; Grinberg, N.; Lee, H.; Wei, X.; Yee, N. K.; Senanayake, C. H., Remarkable Enhancement of Enantioselectivity in the Asymmetric Conjugate Addition of Dimethylzinc to (Z)-Nitroalkenes with a Catalytic [(MeCN)4Cu]PF6–Hoveyda Ligand Complex. *Angew. Chem. Int. Ed*. **2014**, *53*, 12153-12157.

VI. X-Ray Crystallographic Analysis

Crystal Growth Method: 15 mg of **3j** was added in a HPLC vial and dissolved by 1.0 mL EtOAc, closed the lid. Then put it in a large bottle, added petroleum ether to the same level of the liquid in the HPLC vial, tighten the lid, put it in a fumehood and waited for growth.

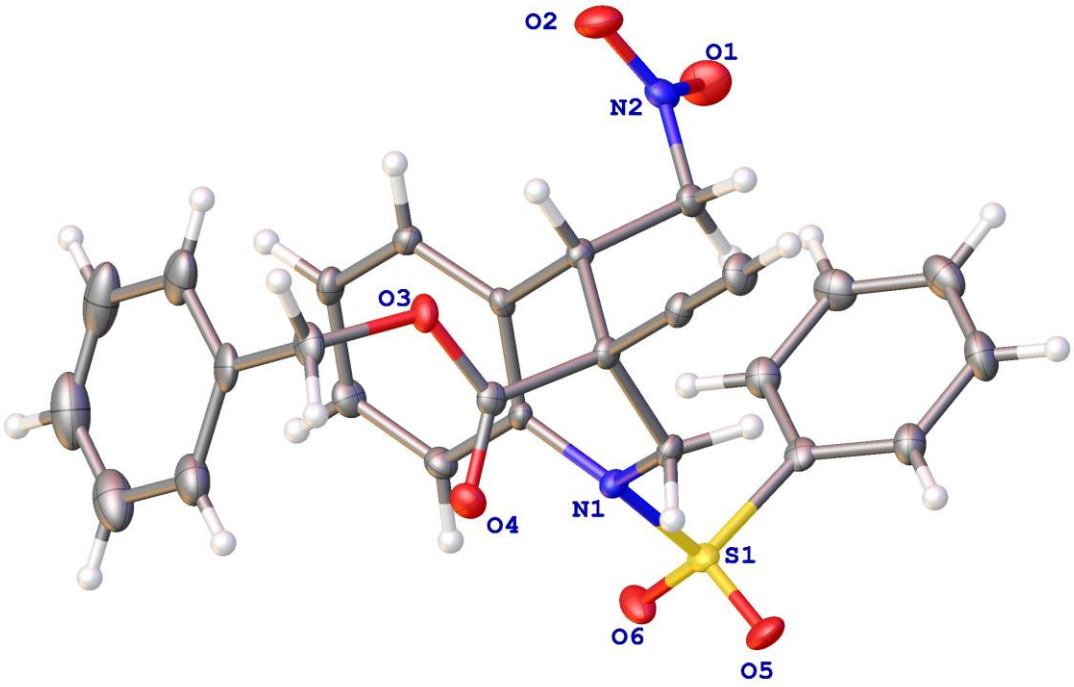


Figure S1. X-ray structure of **3j** (ellipsoid contour at 50% probability CCDC 2287287)

Crystal Growth Method: 15 mg of **4d** was added in a HPLC vial and dissolved by EtOAc 1.0 mL , closed the lid. Then put it in a large bottle, added petroleum ether to the same level of the liquid in the HPLC vial, tighten the lid, put it in a fumehood and waited for growth.

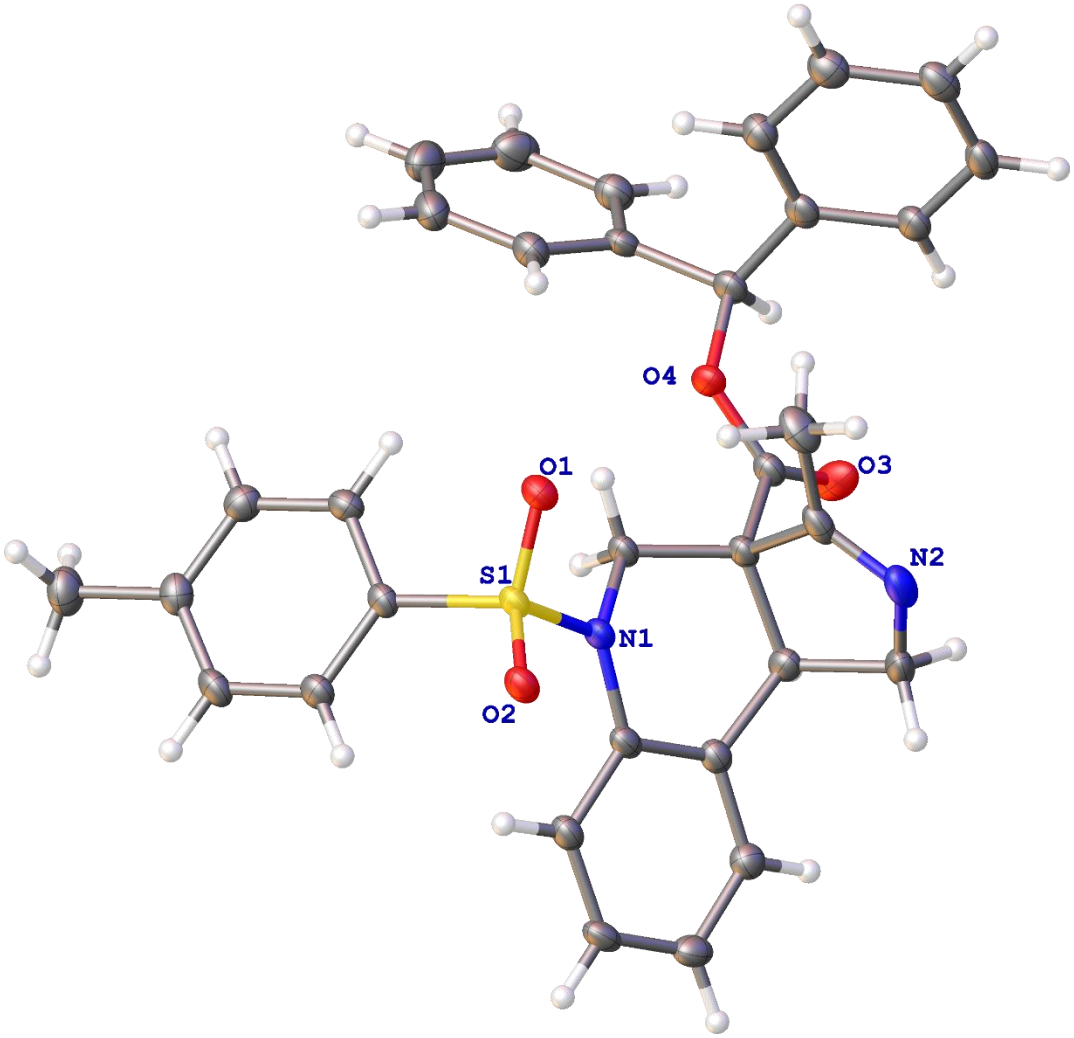
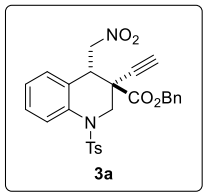


Figure S1. X-ray structure of **4d** (ellipsoid contour at 50% probability CCDC 2303256)

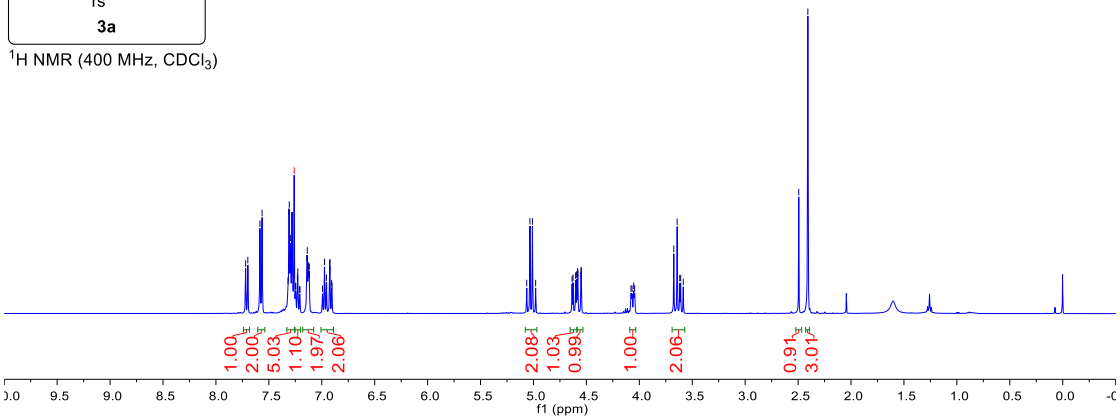
Table 1 Crystal data and structure refinement for 3j and 4d.

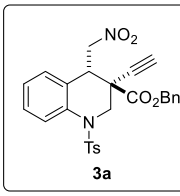
Identification code	**3j**	**4d**
Empirical formula	$C_{26}H_{22}N_2O_6S$	$C_{33}H_{30}N_2O_4S$
Formula weight	490.51	550.65
Temperature/K	119.99(14)	158(14)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	9.3636(5)	10.0509(5)
b/Å	14.6831(6)	11.7269(5)
c/Å	18.2931(7)	12.5630(5)
α/°	103.066(3)	100.660(4)
β/°	102.730(4)	98.042(4)
γ/°	91.504(4)	109.309(5)
Volume/Å^3	2382.05(19)	1340.68(11)
Z	4	2
ρ_{calc} (g/cm^3)	1.368	1.364
μ/mm^{-1}	0.181	1.420
F(000)	1024.0	580.0
Crystal size/mm^3	0.15 × 0.12 × 0.1	0.14 × 0.13 × 0.1
Radiation	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.108 to 50	7.334 to 147.714
Index ranges	-10 ≤ h ≤ 11, -17 ≤ k ≤ 17, -21 ≤ l ≤ 21	-12 ≤ h ≤ 11, -14 ≤ k ≤ 9, -15 ≤ l ≤ 15
Reflections collected	22002	9131
Independent reflections	8386 [R_{int} = 0.0439, R_{sigma} = 0.0540]	5230 [R_{int} = 0.1152, R_{sigma} = 0.0879]
Data/restraints/parameters	8386/0/631	5230/0/363
Goodness-of-fit on F^2	1.081	0.989
Final R indexes [I>=2σ (I)]	R_1 = 0.0542, wR_2 = 0.1555	R_1 = 0.0792, wR_2 = 0.2000
Final R indexes [all data]	R_1 = 0.0679, wR_2 = 0.1682	R_1 = 0.0878, wR_2 = 0.2061
Largest diff. peak/hole / e Å^{-3}	0.41/-0.45	1.01/-0.71

VII. Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra

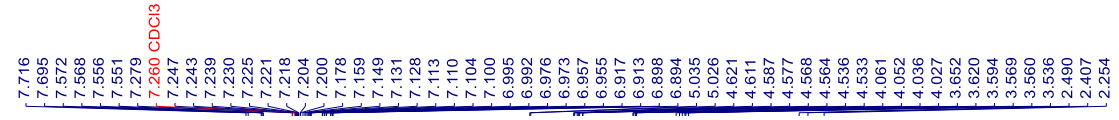


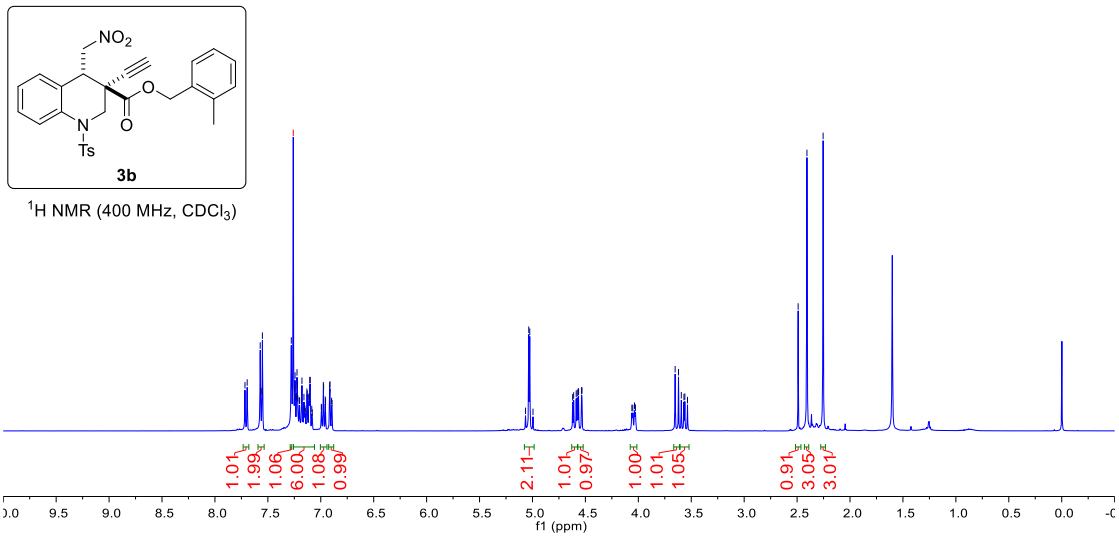
^{1}H NMR (400 MHz, $CDCl_3$)



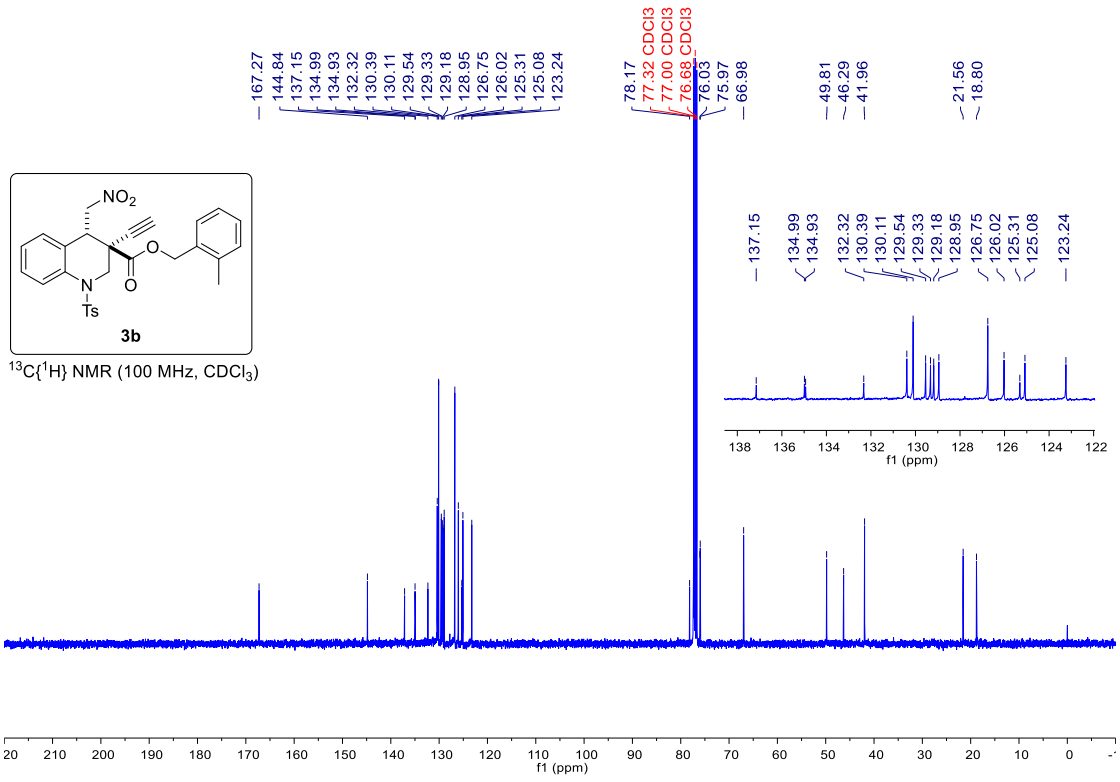


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

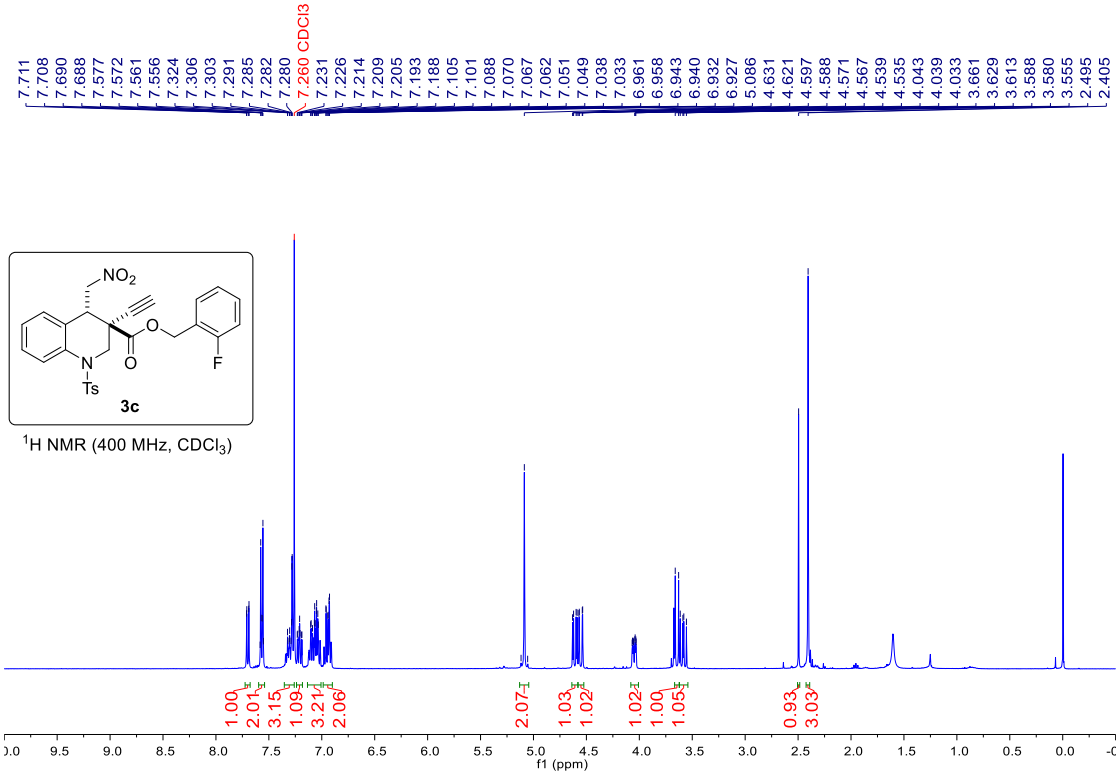




^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)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7.688
7.577
7.572
7.561
7.556
7.324
7.306
7.303
7.291
7.285
7.282
7.280
7.260 CDCl3
7.231
7.226
7.214
7.209
7.205
7.193
7.188
7.105
7.101
7.088
7.070
7.067
7.062
7.051
7.049
7.038
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6.927
5.086
4.631
4.621
4.597
4.588
4.571
4.567
4.539
4.535
4.043
4.039
4.033
3.661
3.629
3.613
3.588
3.580
3.555
2.495
2.405
NO2
O
O
N
Ts
F
3c
1H NMR (400 MHz, CDCl3)
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2.01
3.15
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2.07
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1.02
1.02
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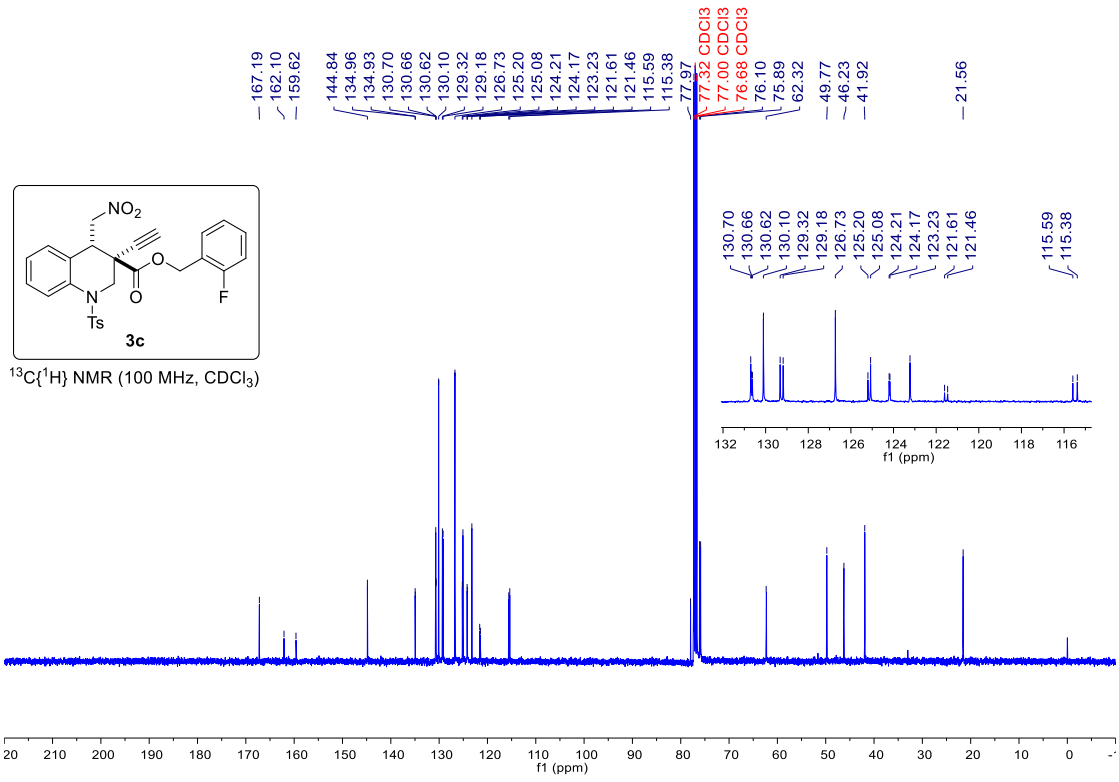
3.03
f1 (ppm)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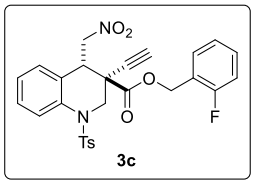
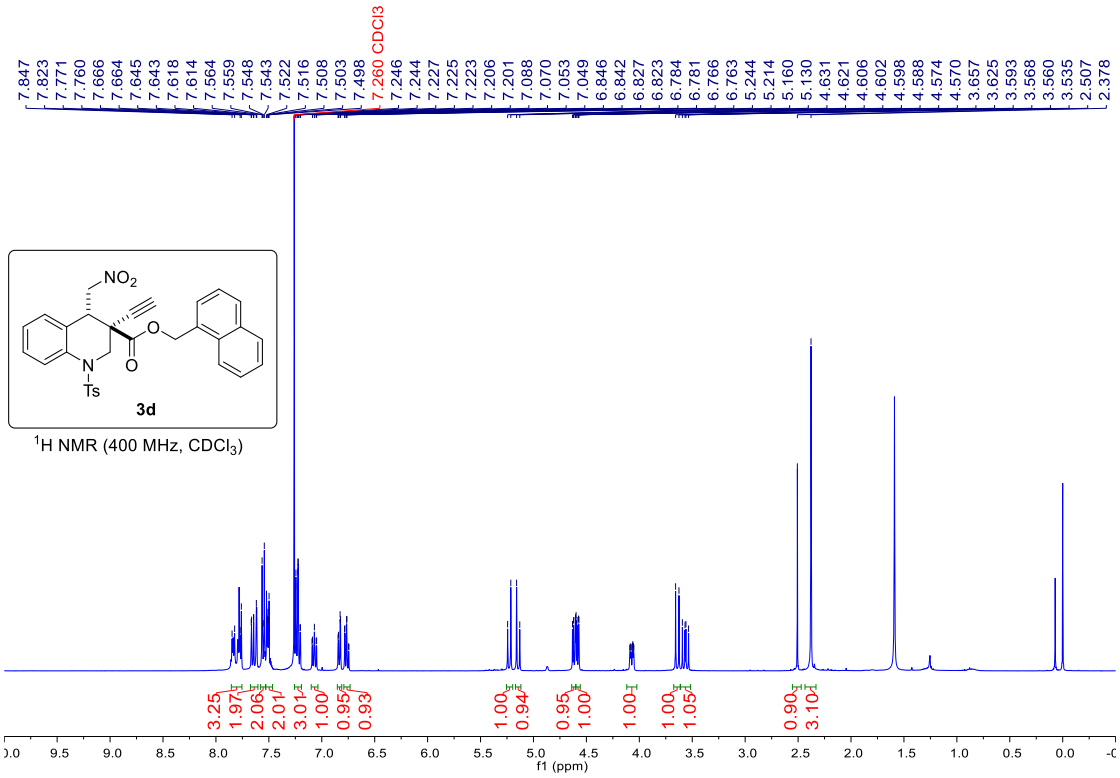
126.73
125.20
125.08
124.21
124.17
123.23
121.61
121.46
115.59
115.38
77.97
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
76.10
75.89
62.32
49.77
46.23
41.92
21.56
NO2
O
O
N
Ts
F
3c
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)



3c

$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)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7.503
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7.244
7.227
7.225
7.223
7.206
7.201
7.088
7.070
7.053
7.049
6.846
6.842
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6.781
6.766
6.763
5.244
5.214
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Ts
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3d
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2.01
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1.00
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1.00
1.00
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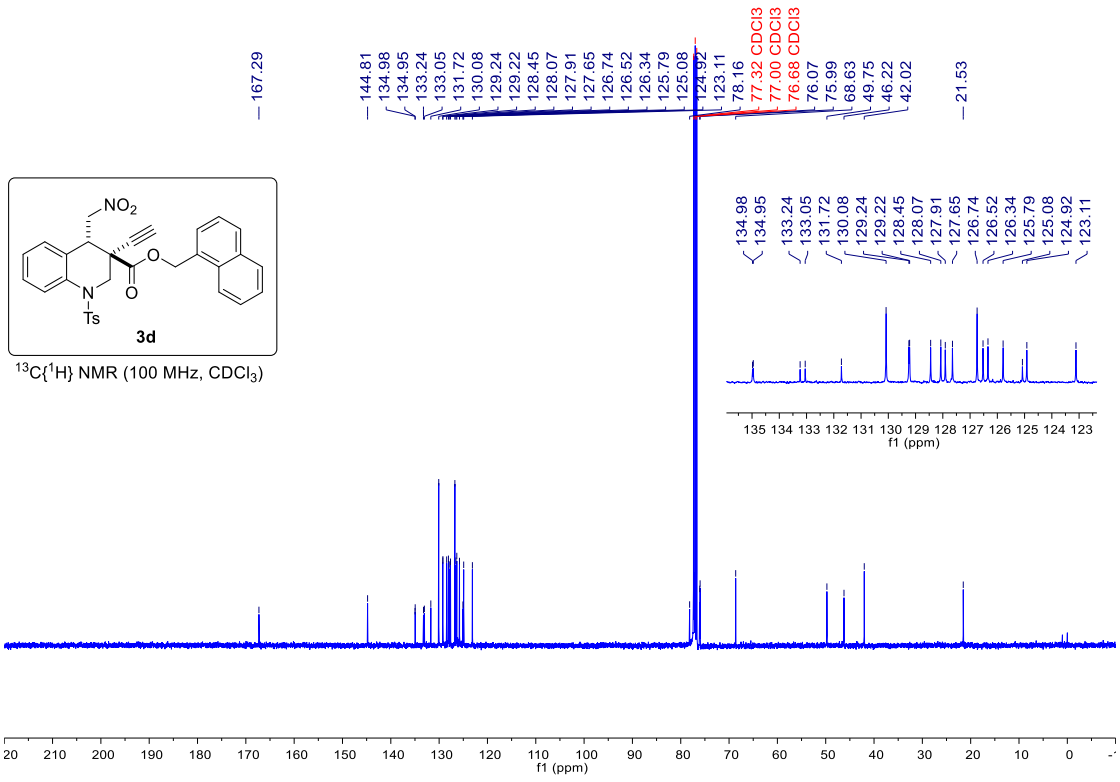
f1 (ppm)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127.65
126.74
126.52
126.34
125.79
125.08
124.92
123.11
78.16
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77.00 CDCl3
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76.07
75.99
68.63
49.75
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N
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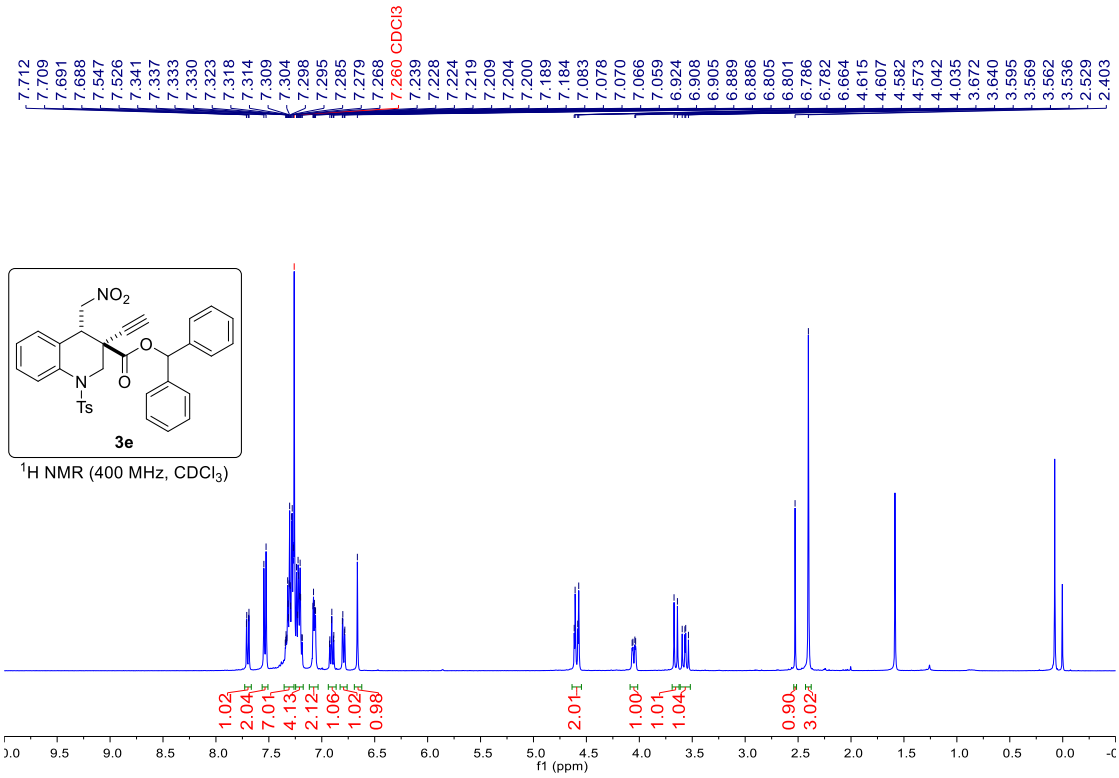
f1 (ppm)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7.078
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3.595
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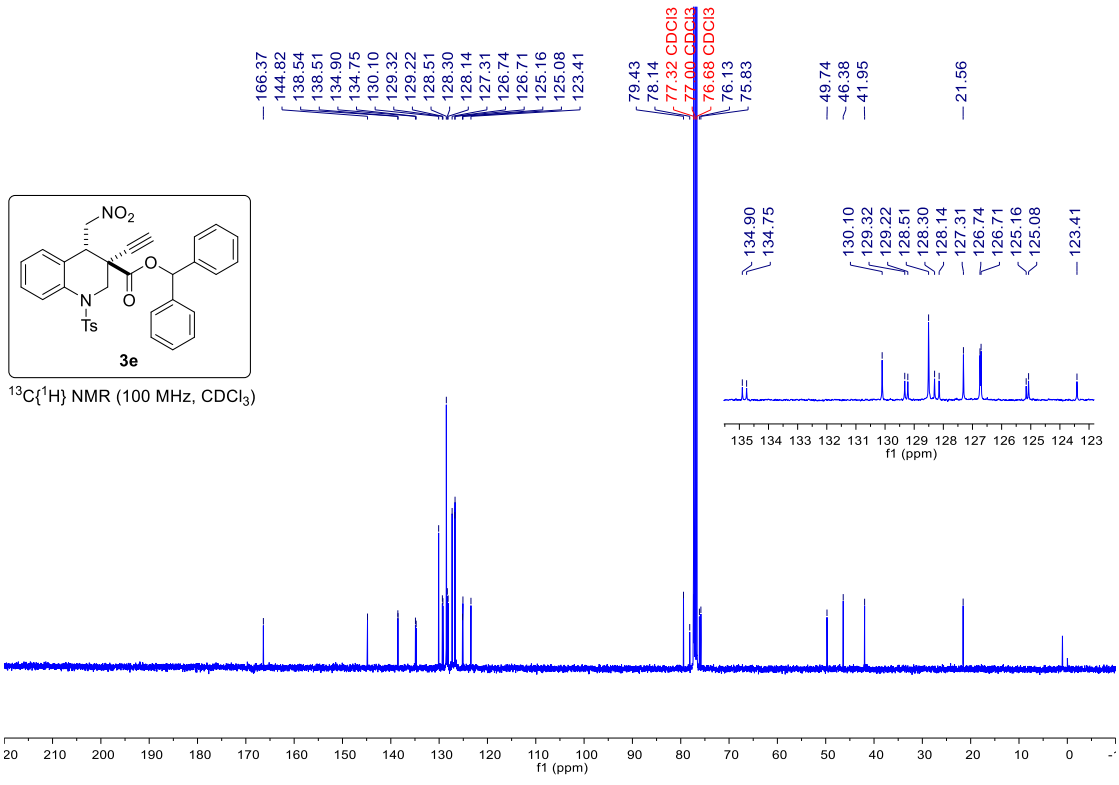
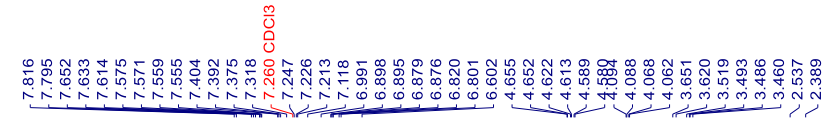
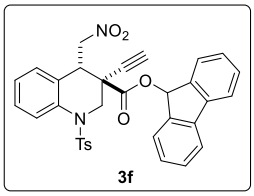
3.536
2.529
2.403
NO2
O
O
N
Ts
3e
1H NMR (400 MHz, CDCl3)
1.02
2.04
7.01
4.13
2.12
1.06
1.02
0.98
2.01
1.00
1.01
1.04
0.90
3.02
f1 (ppm)

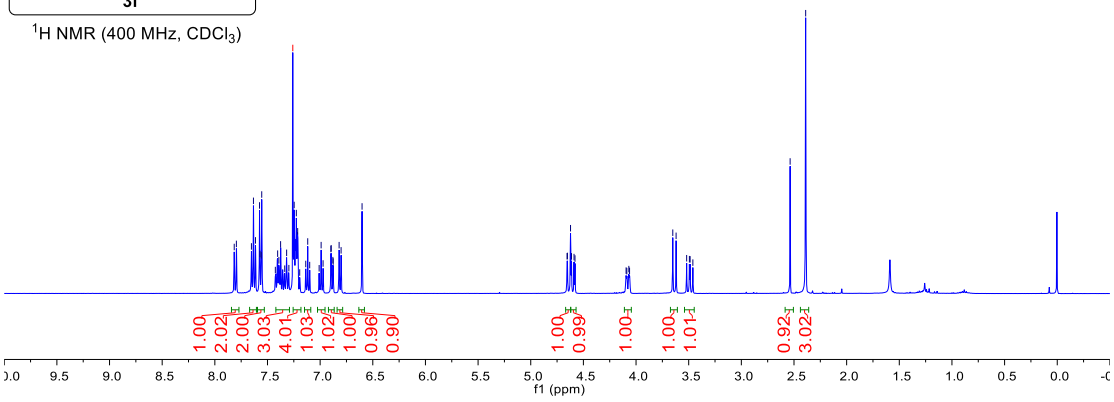

166.37
144.82
138.54
138.51
134.90
134.75
130.10
129.32
129.22
128.51
128.30
128.14
127.31
126.74
126.71
125.16
125.08
123.41
79.43
78.14
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
76.13
75.83
49.74
46.38
41.95
21.56
NO2
O
O
N
Ts
3e
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)

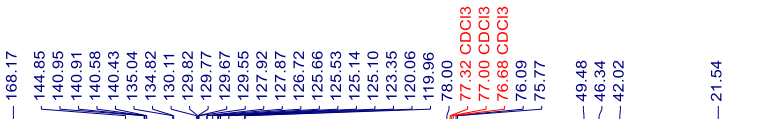


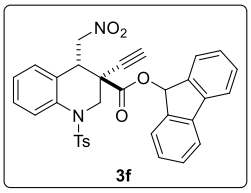


3f

^{1}H NMR (400 MHz, $CDCl_3$)

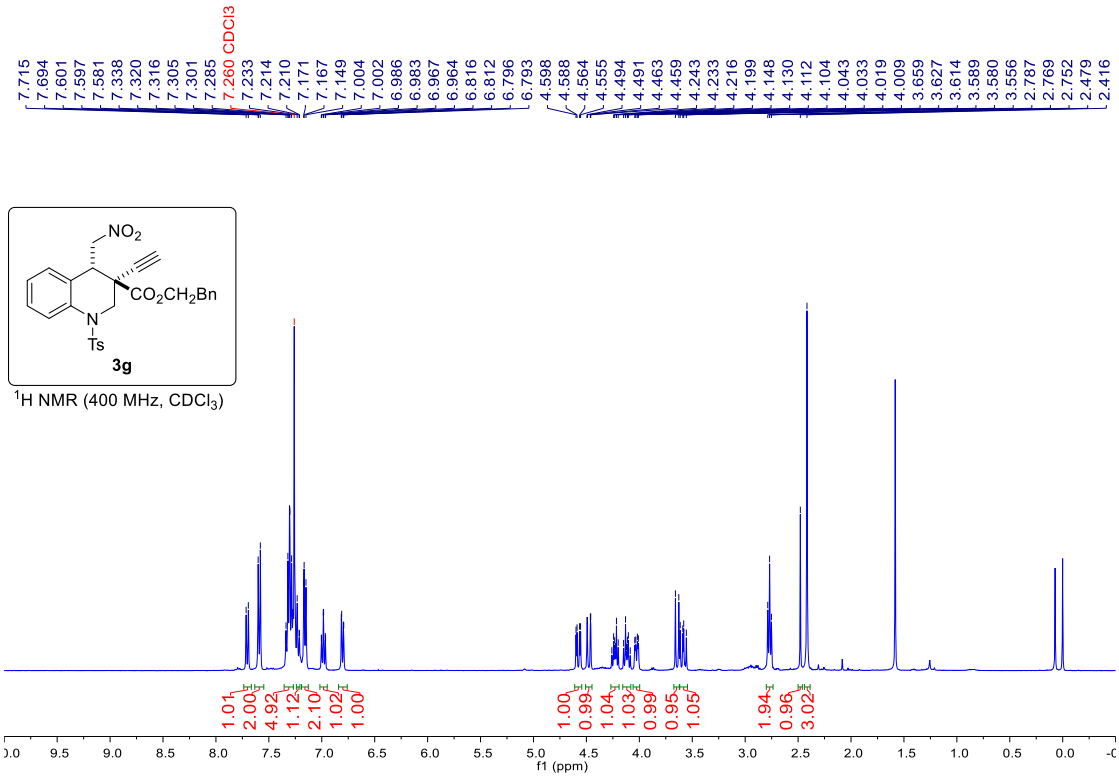


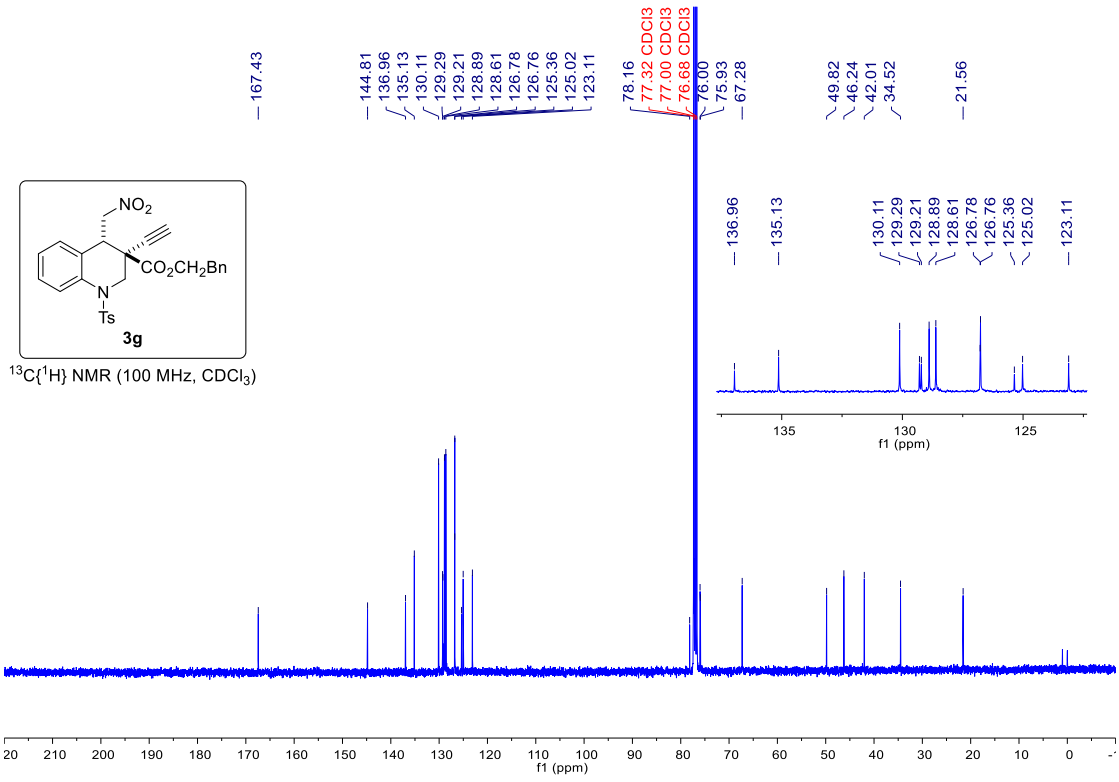


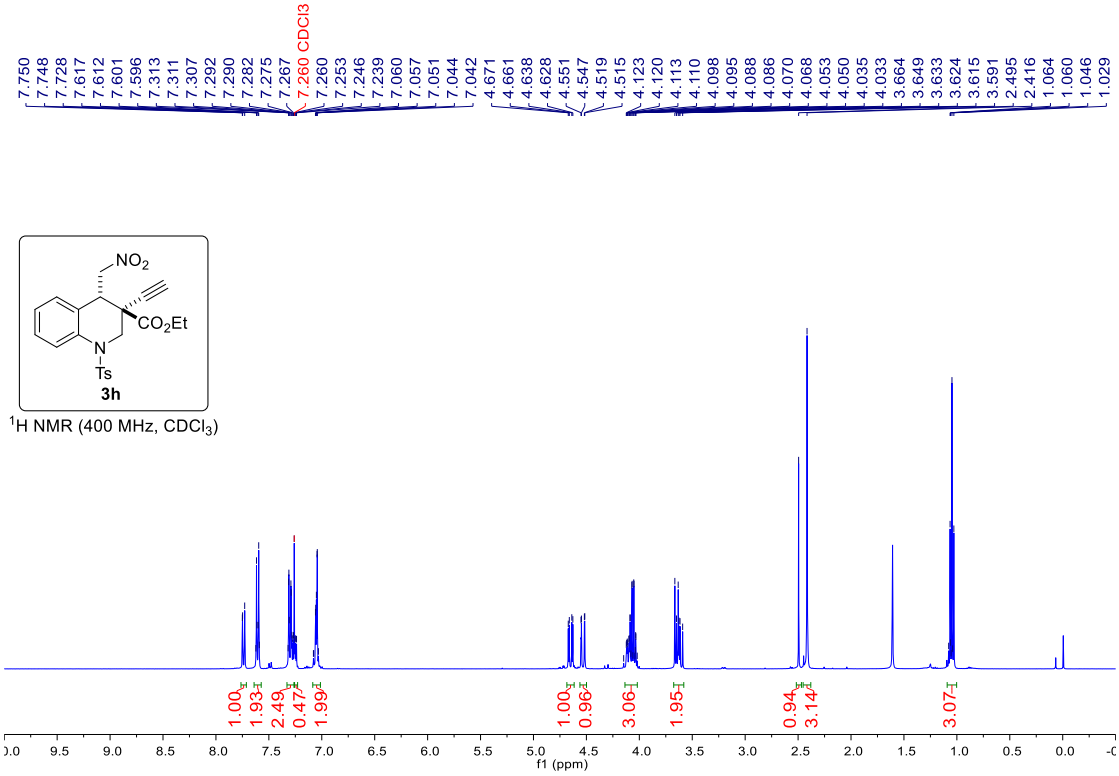


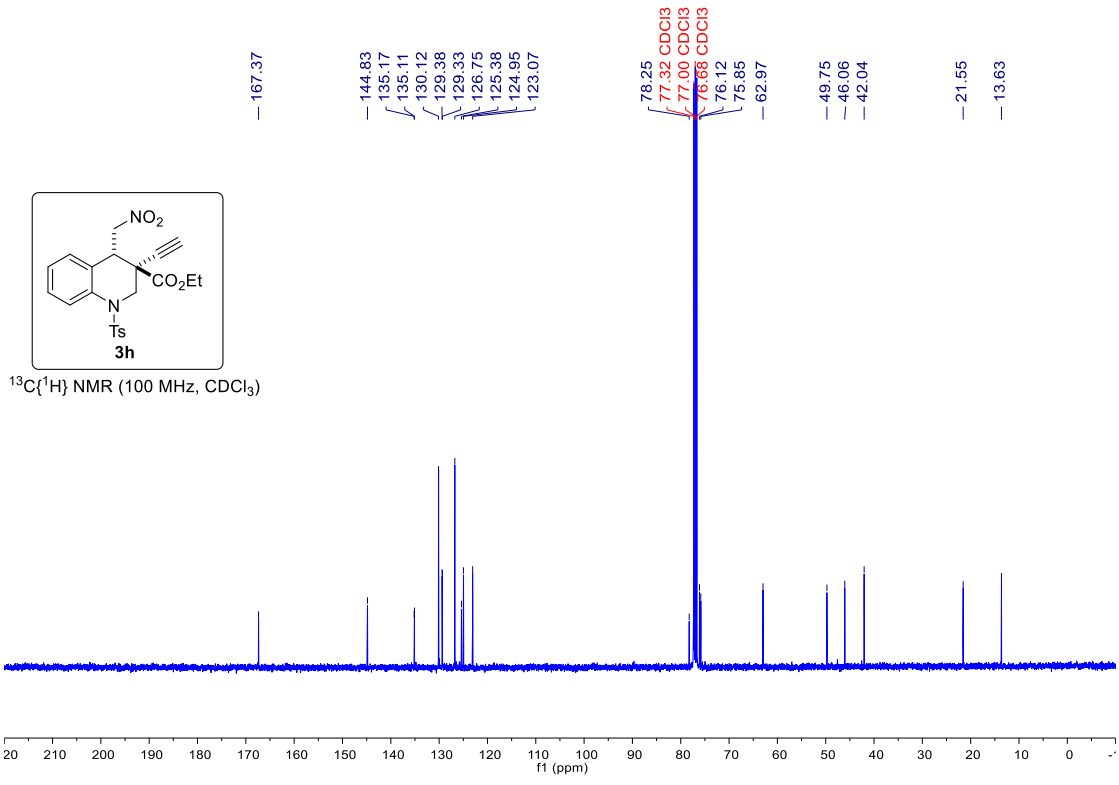
3f

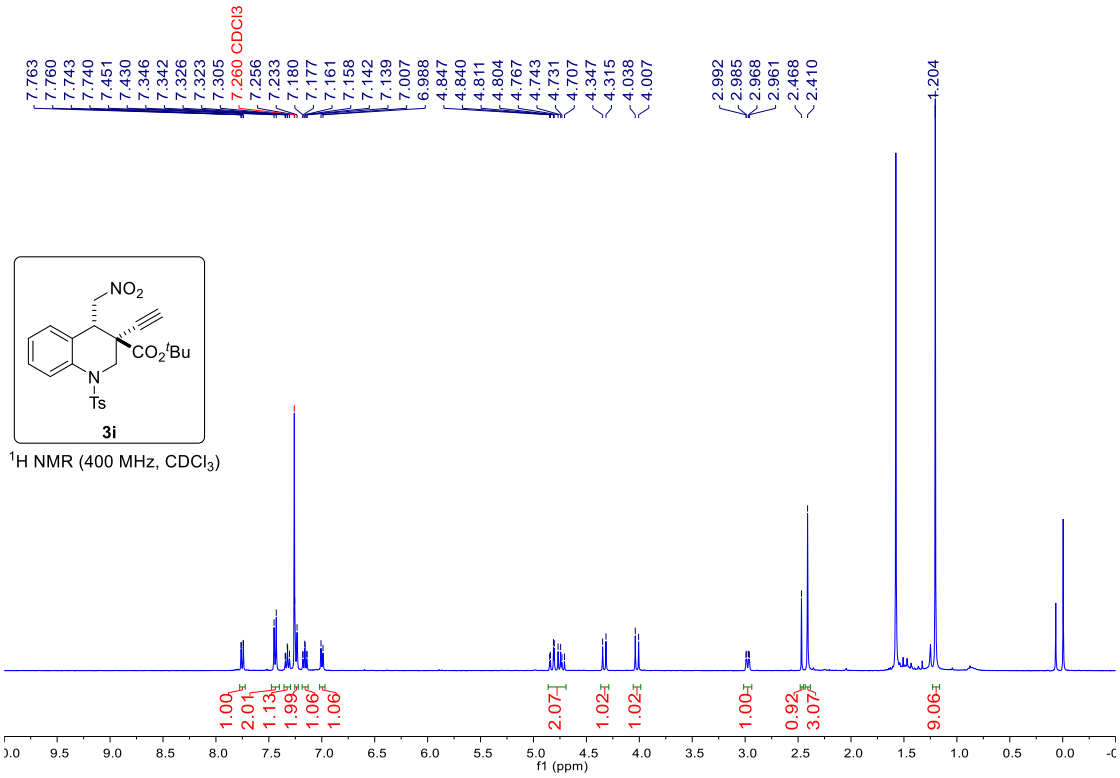
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

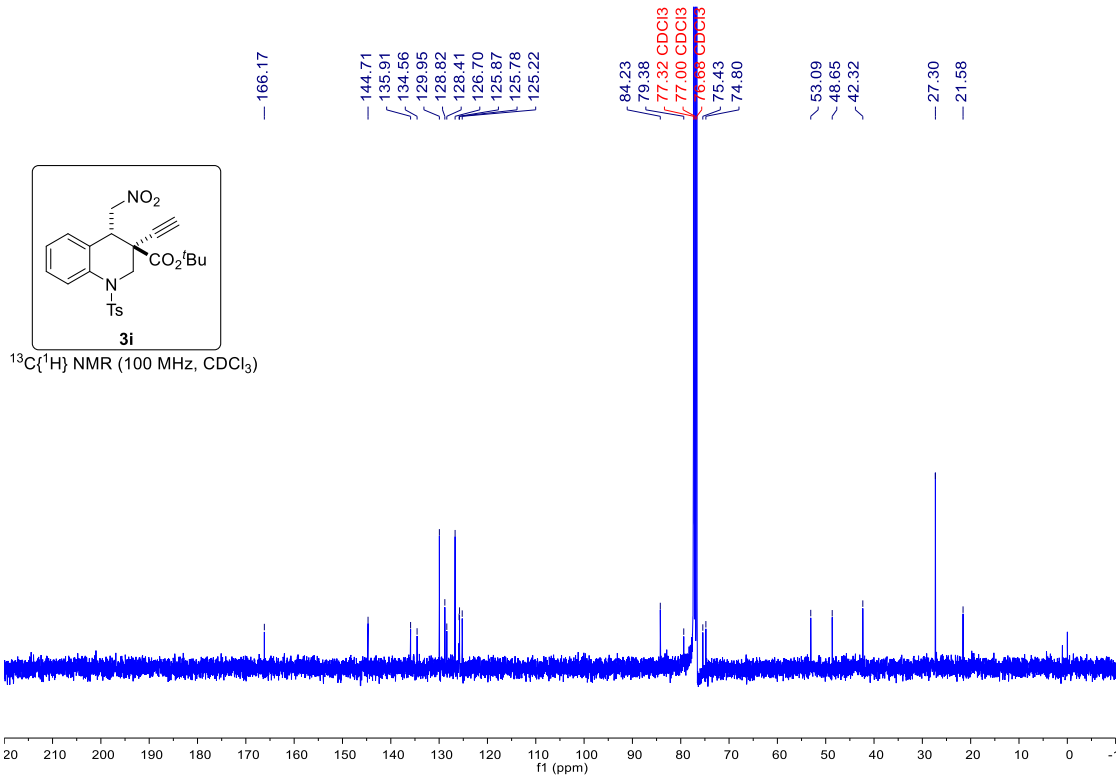

7.715
7.694
7.601
7.597
7.581
7.338
7.320
7.316
7.305
7.301
7.285
7.260 CDCl3
7.233
7.214
7.210
7.171
7.167
7.149
7.004
7.002
6.986
6.983
6.967
6.964
6.816
6.812
6.796
6.793
4.598
4.588
4.564
4.555
4.494
4.491
4.463
4.459
4.243
4.233
4.216
4.199
4.148
4.130
4.112
4.104
4.043
4.033
4.019
4.009
3.659
3.627
3.614
3.589
3.580
3.556
2.787
2.769
2.752
2.479
2.416
NO2
CO2CH2Bn
N
Ts
3g
1H NMR (400 MHz, CDCl3)
1.01
2.00
4.92
1.12
2.10
1.02
1.00
1.00
0.99
1.04
1.03
0.99
0.95
1.05
1.94
0.96
3.02
f1 (ppm)

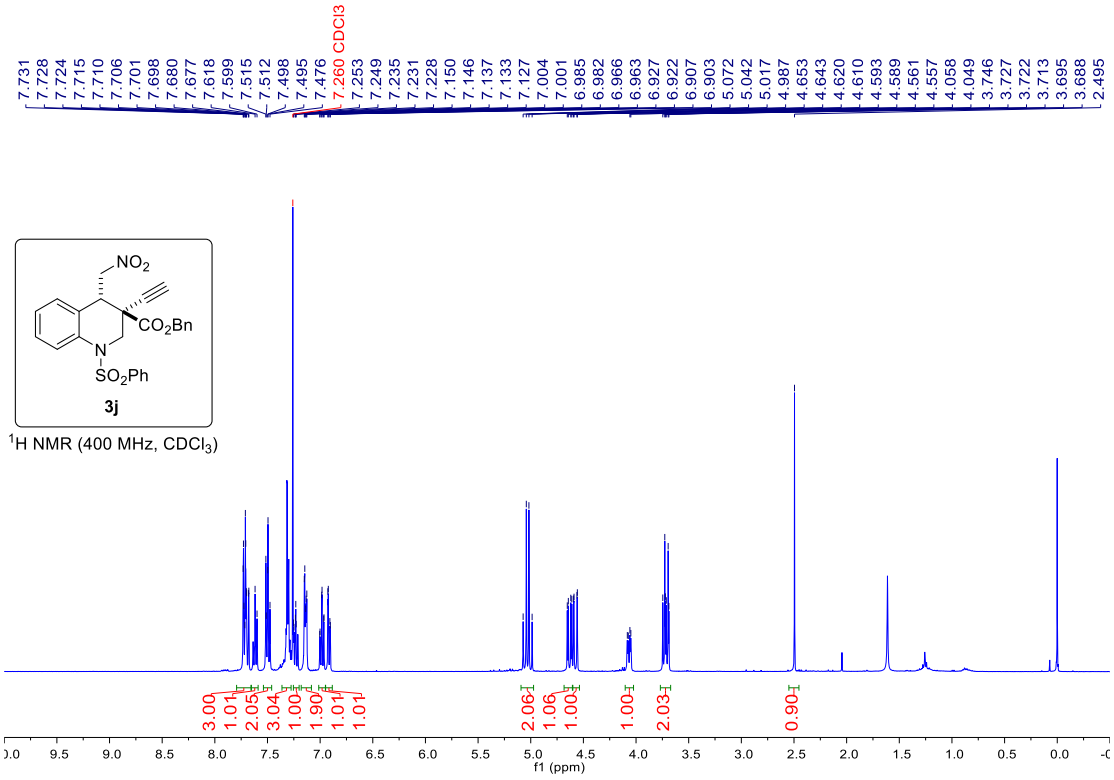

167.43
144.81
136.96
135.13
130.11
129.29
129.21
128.89
128.61
126.78
126.76
125.36
125.02
123.11
78.16
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
76.00
75.93
67.28
49.82
46.24
42.01
34.52
21.56
NO2
CO2CH2Bn
N
Ts
3g
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)

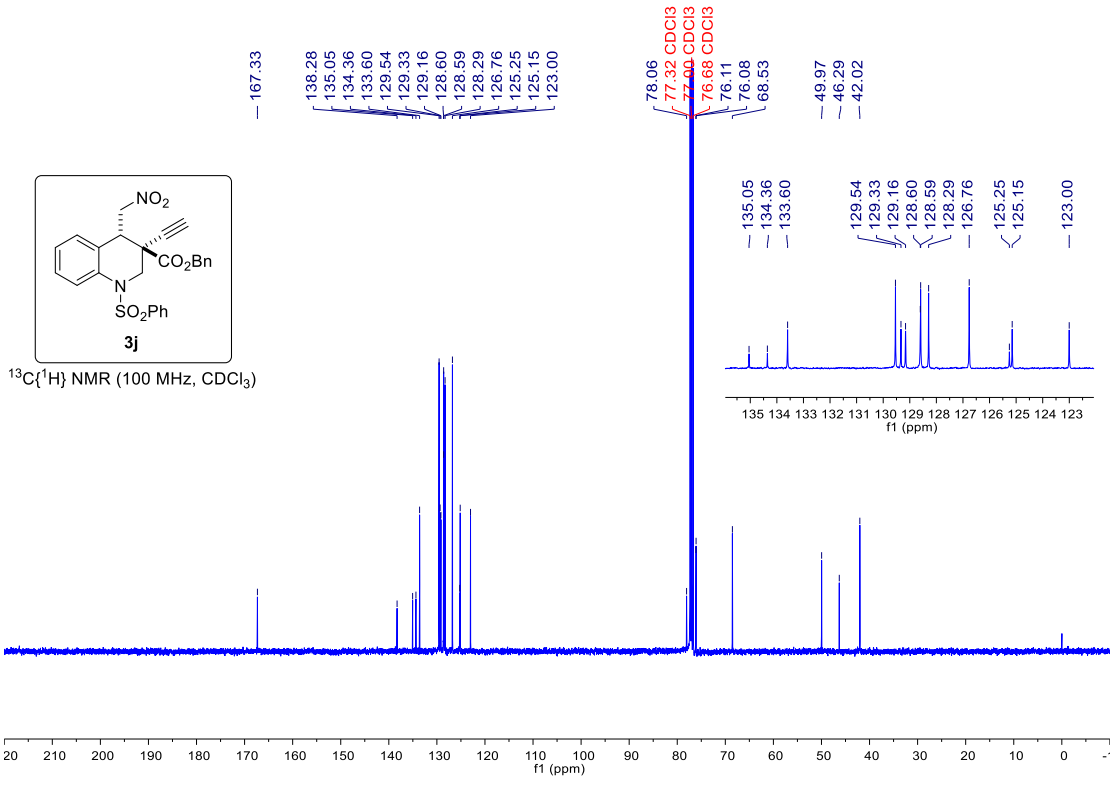

7.750
7.748
7.728
7.617
7.612
7.601
7.596
7.313
7.311
7.307
7.292
7.290
7.282
7.275
7.267
7.260 CDCl3
7.260
7.253
7.246
7.239
7.060
7.057
7.051
7.044
7.042
4.671
4.661
4.638
4.628
4.551
4.547
4.519
4.515
4.123
4.120
4.113
4.110
4.098
4.095
4.088
4.086
4.070
4.068
4.053
4.050
4.035
4.033
3.664
3.649
3.633
3.624
3.615
3.591
2.495
2.416
1.064
1.060
1.046
1.029
NO2
CO2Et
N
Ts
3h
1H NMR (400 MHz, CDCl3)
1.00
1.93
2.49
0.47
1.99
1.00
0.96
3.06
1.95
0.94
3.14
3.07
f1 (ppm)

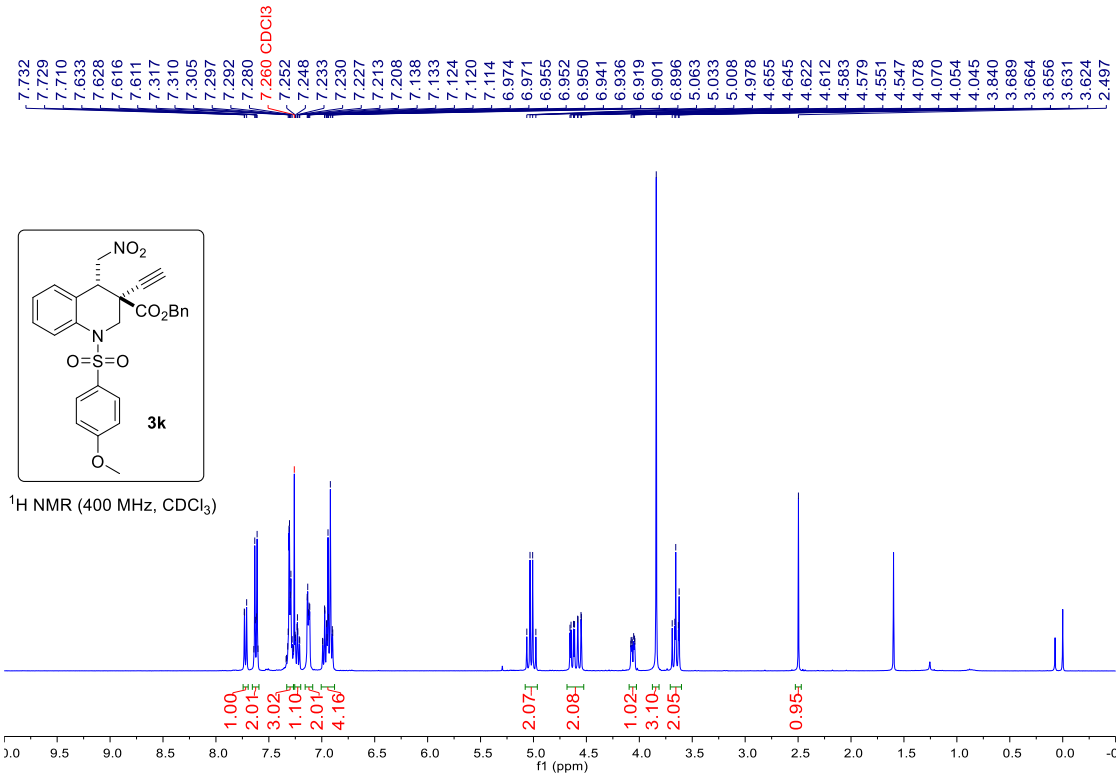

167.37
144.83
135.17
135.11
130.12
129.38
129.33
126.75
125.38
124.95
123.07
78.25
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
76.12
75.85
62.97
49.75
46.06
42.04
21.55
13.63
NO2
CO2Et
N
Ts
3h
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)

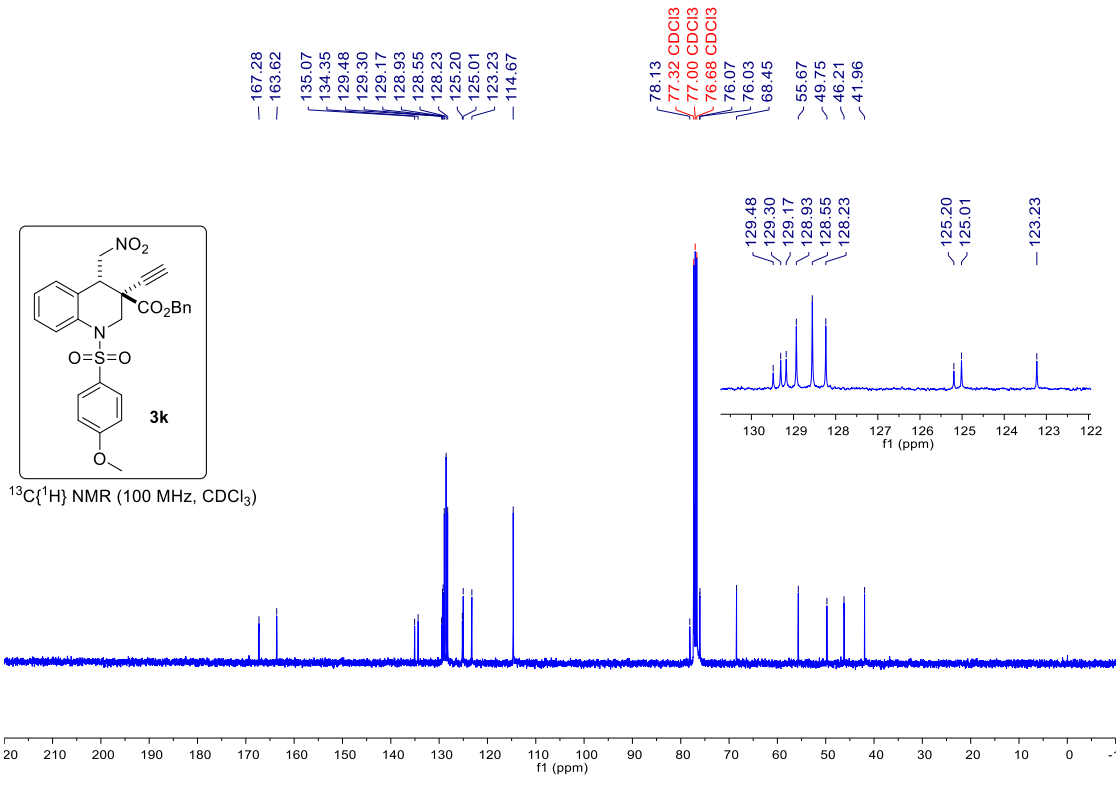

7.763
7.760
7.743
7.740
7.451
7.430
7.346
7.342
7.326
7.323
7.305
7.260 CDCl3
7.256
7.233
7.180
7.177
7.161
7.158
7.142
7.139
7.007
6.988
4.847
4.840
4.811
4.804
4.767
4.743
4.731
4.707
4.347
4.315
4.038
4.007
2.992
2.985
2.968
2.961
2.468
2.410
1.204
NO2
CO2tBu
N
Ts
3i
1H NMR (400 MHz, CDCl3)
1.00
2.01
1.13
1.99
1.06
1.06
2.07
1.02
1.02
1.00
0.92
3.07
9.06
f1 (ppm)

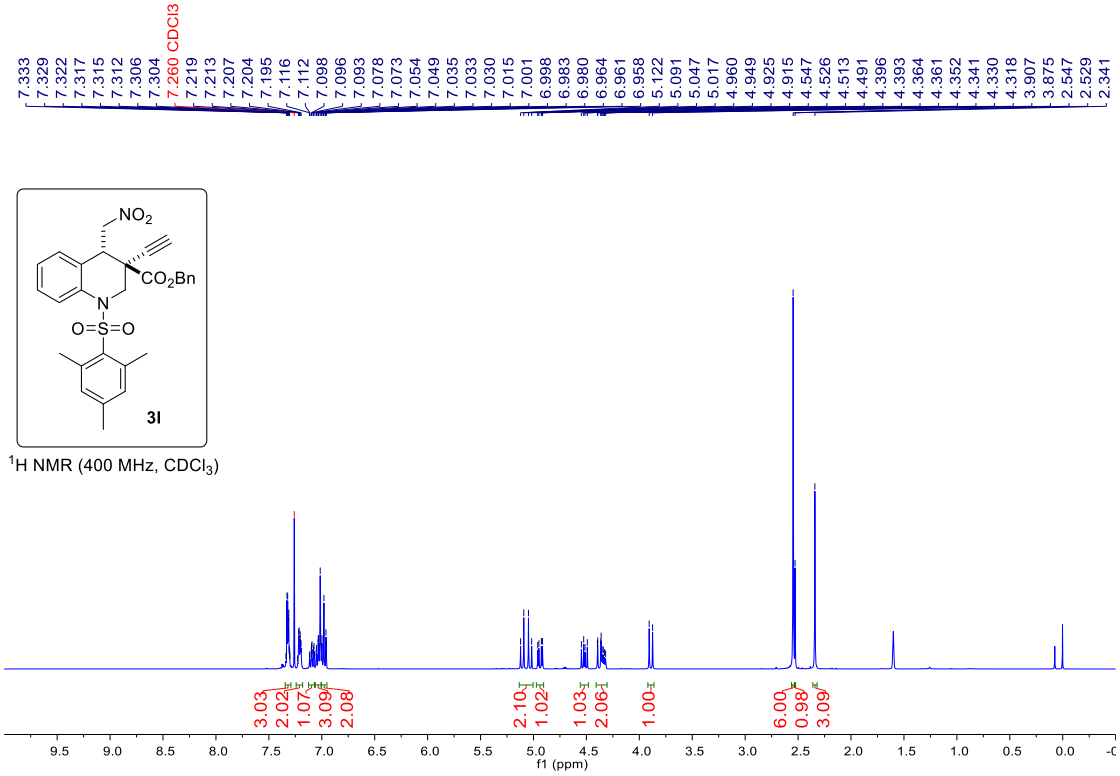

166.17
144.71
135.91
134.56
129.95
128.82
128.41
126.70
125.87
125.78
125.22
84.23
79.38
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
75.43
74.80
53.09
48.65
42.32
27.30
21.58
NO2
CO2tBu
N
Ts
3i
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)


7.731
7.728
7.724
7.715
7.710
7.706
7.701
7.698
7.680
7.677
7.618
7.599
7.515
7.512
7.498
7.495
7.476
7.260 CDCl3
7.253
7.249
7.235
7.231
7.228
7.150
7.146
7.137
7.133
7.127
7.004
7.001
6.985
6.982
6.966
6.963
6.927
6.922
6.907
6.903
5.072
5.042
5.017
4.987
4.653
4.643
4.620
4.610
4.593
4.589
4.561
4.557
4.058
4.049
3.746
3.727
3.722
3.713
3.695
3.688
2.495
NO2
CO2Bn
N
SO2Ph
3j
1H NMR (400 MHz, CDCl3)
3.00
1.01
2.05
3.04
1.00
1.90
1.01
1.01
2.06
1.06
1.00
1.00
2.03
0.90
f1 (ppm)

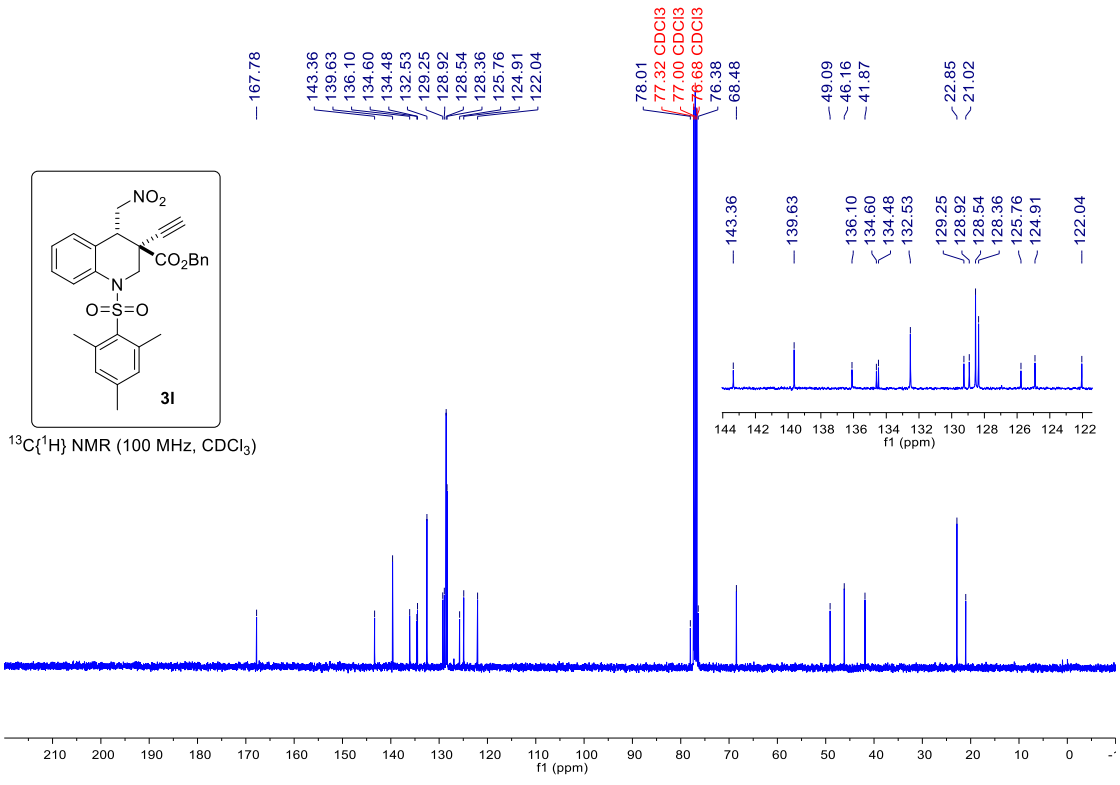

167.33
138.28
135.05
134.36
133.60
129.54
129.33
129.16
128.60
128.59
128.29
126.76
125.25
125.15
123.00
78.06
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
76.11
76.08
68.53
49.97
46.29
42.02
NO2
CO2Bn
N
SO2Ph
3j
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)


7.732
7.729
7.710
7.633
7.628
7.616
7.611
7.317
7.310
7.305
7.297
7.292
7.280
7.260 CDCl3
7.252
7.248
7.233
7.230
7.227
7.213
7.208
7.138
7.133
7.124
7.120
7.114
6.974
6.971
6.955
6.952
6.950
6.941
6.936
6.919
6.901
6.896
5.063
5.033
5.008
4.978
4.655
4.645
4.622
4.612
4.583
4.579
4.551
4.547
4.078
4.070
4.054
4.045
3.840
3.689
3.664
3.656
3.631
3.624
2.497
NO2
CO2Bn
N
O=S=O
3k
O
1H NMR (400 MHz, CDCl3)
1.00
2.01
3.02
1.10
2.01
4.16
2.07
2.08
1.02
3.10
2.05
0.95
f1 (ppm)

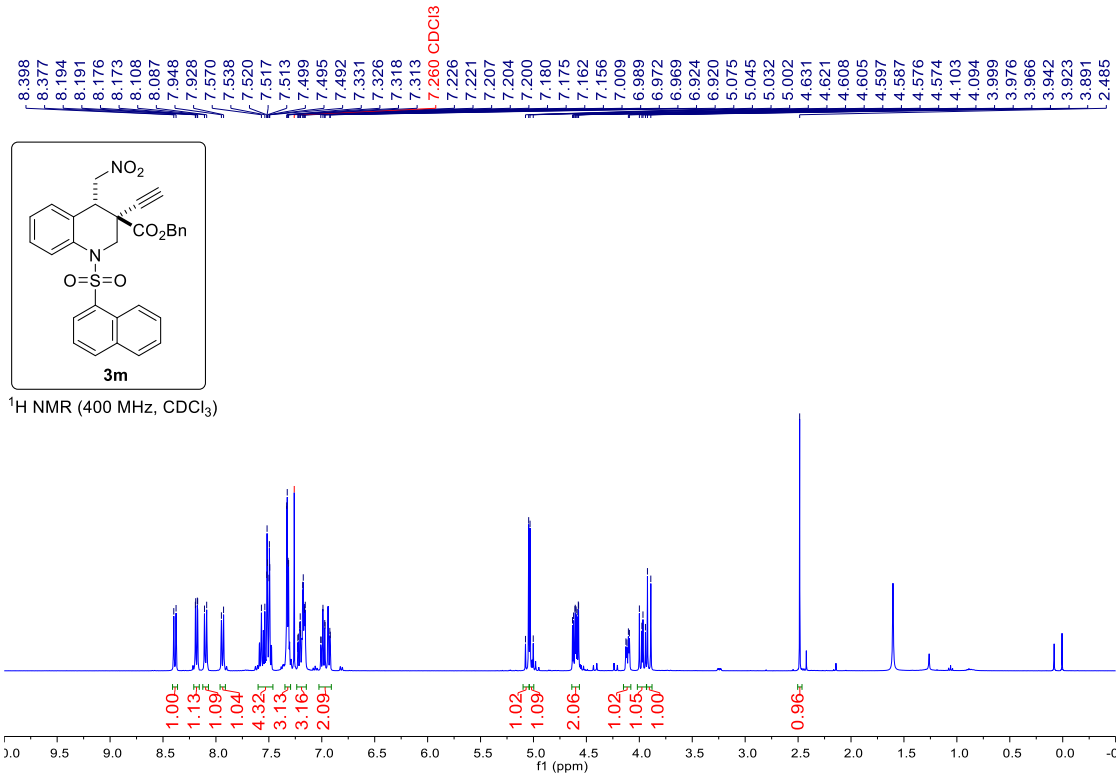

167.28
163.62
135.07
134.35
129.48
129.30
129.17
128.93
128.55
128.23
125.20
125.01
123.23
114.67
78.13
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
76.07
76.03
68.45
55.67
49.75
46.21
41.96
NO2
CO2Bn
N
O=S=O
3k
O
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)

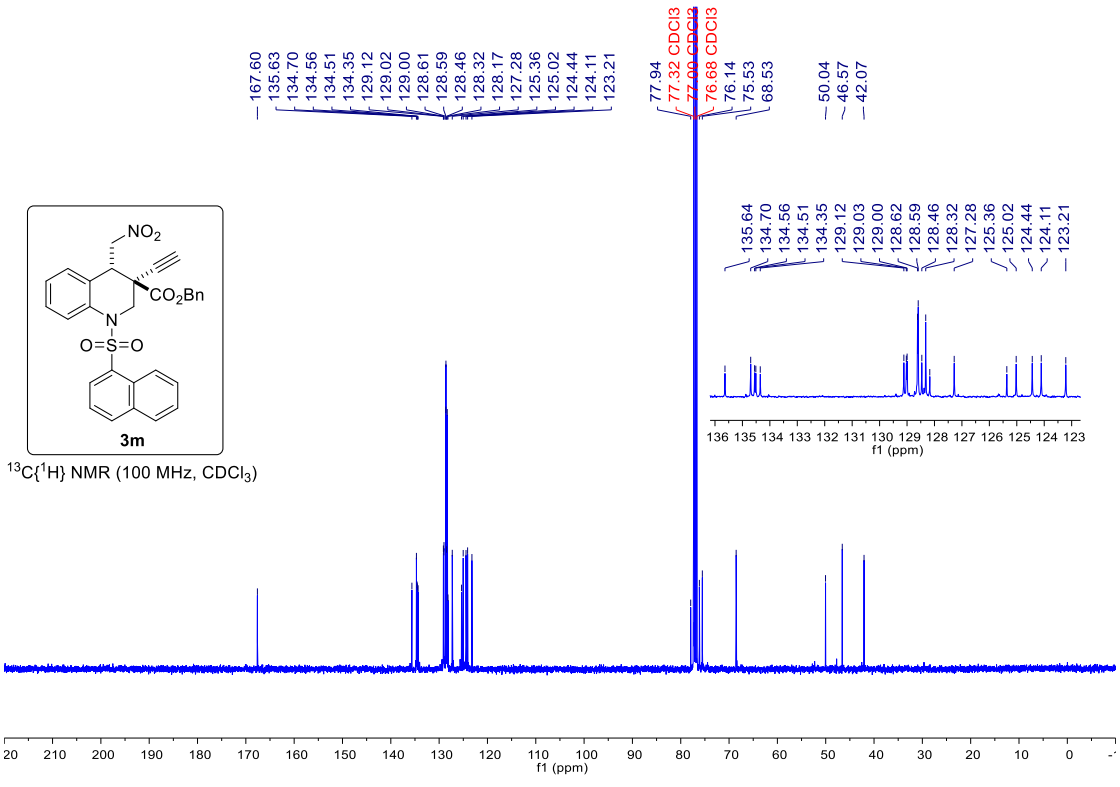


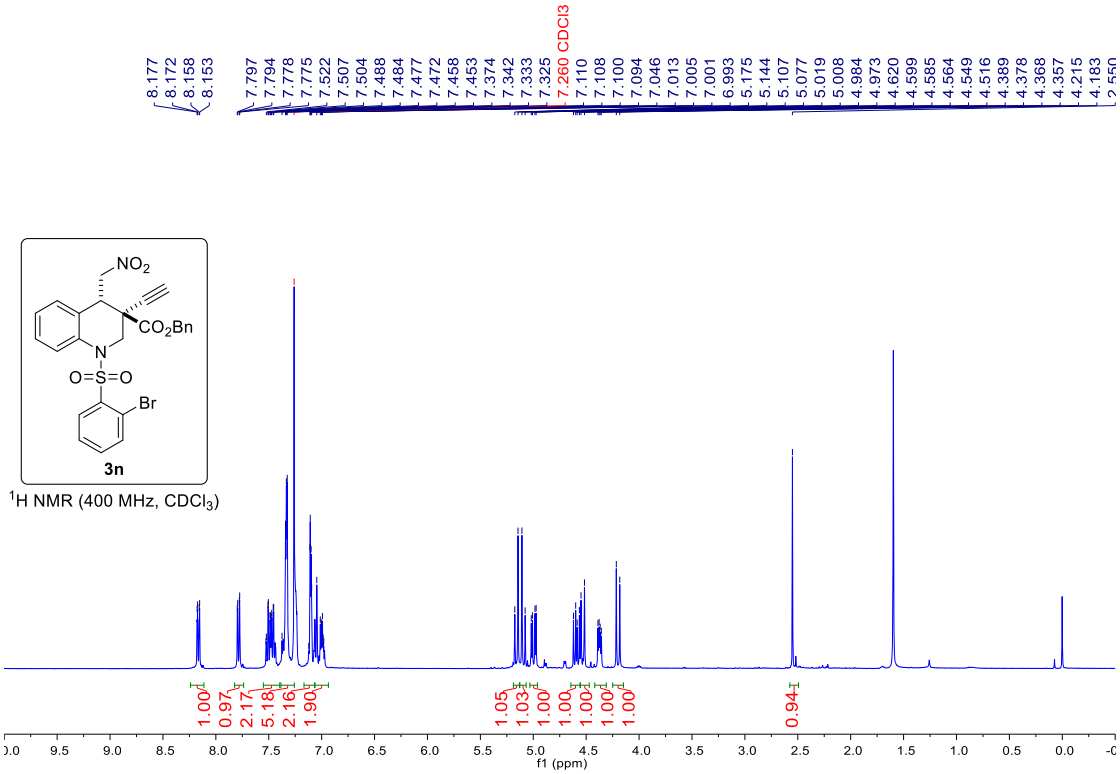
^{1}H NMR (400 MHz, $CDCl_3$)

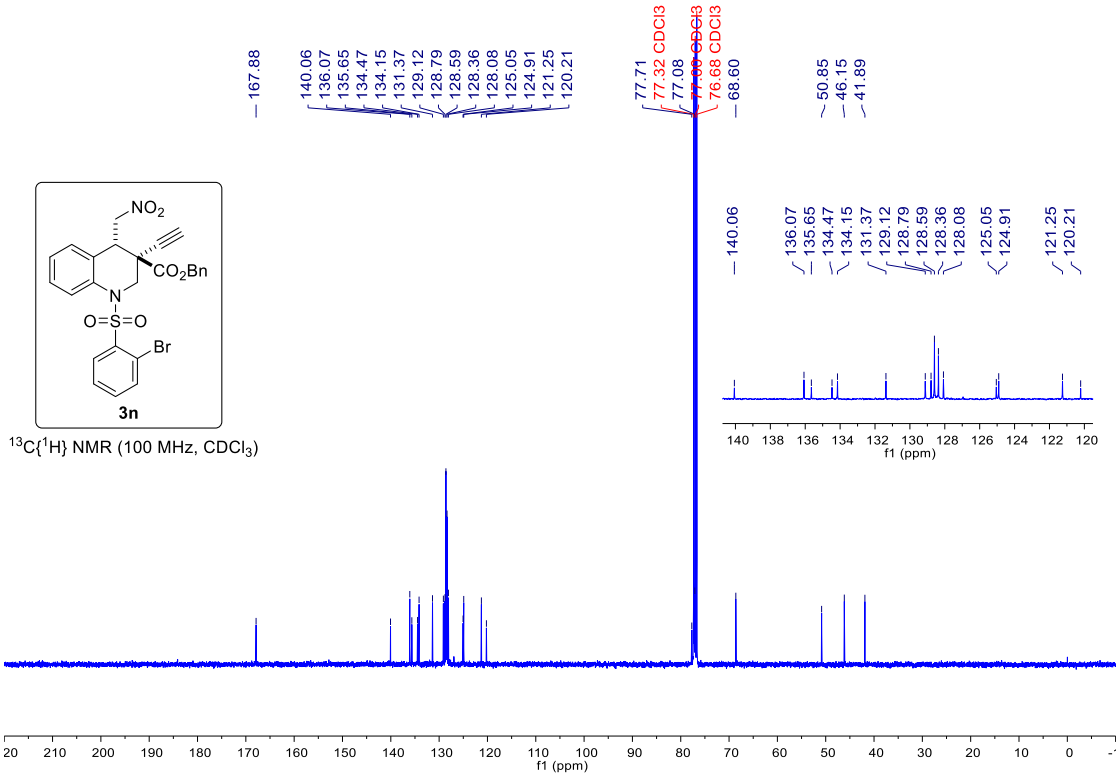


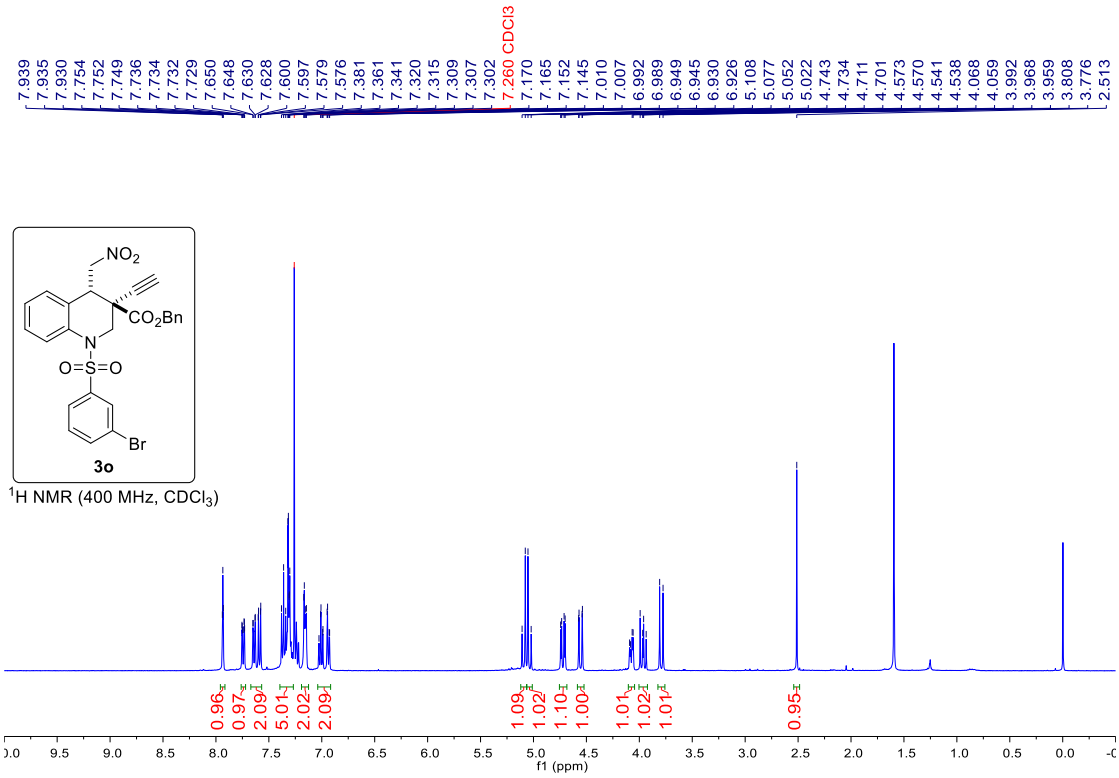
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

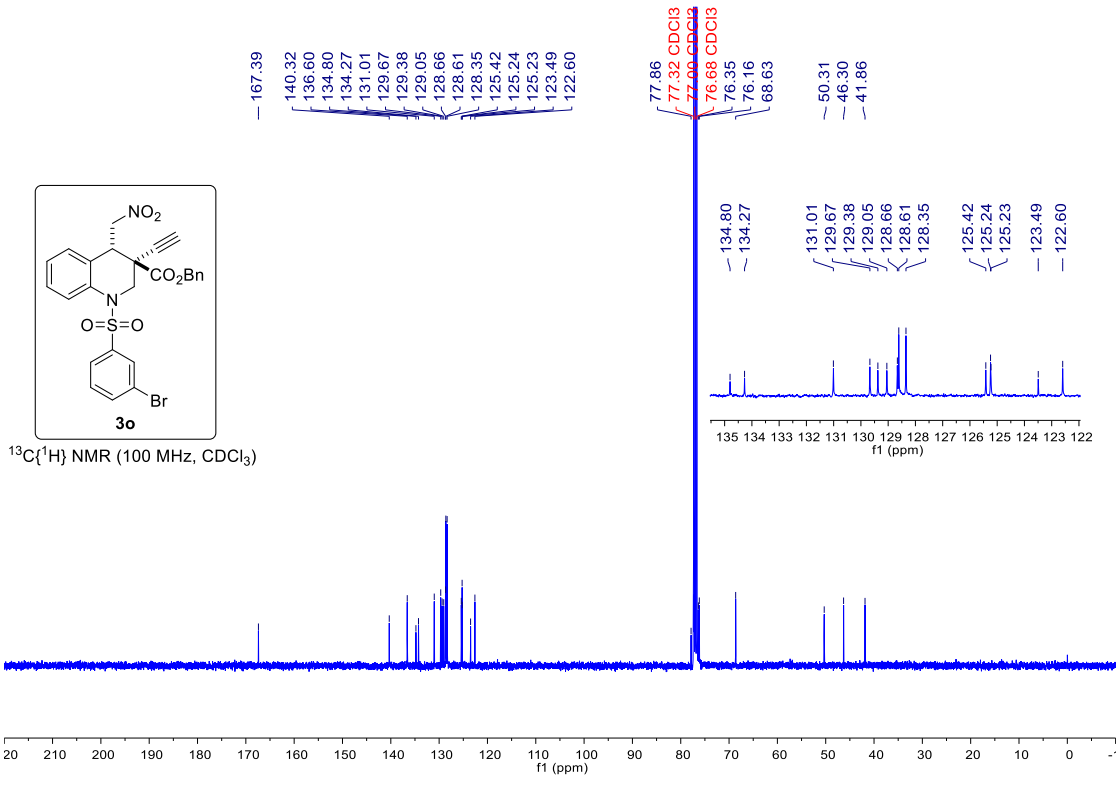

8.398
8.377
8.194
8.191
8.176
8.173
8.108
8.087
7.948
7.928
7.570
7.538
7.520
7.517
7.513
7.499
7.495
7.492
7.331
7.326
7.318
7.313
7.260 CDCl3
7.226
7.221
7.207
7.204
7.200
7.180
7.175
7.162
7.156
7.009
6.989
6.972
6.969
6.924
6.920
5.075
5.045
5.032
5.002
4.631
4.621
4.608
4.605
4.597
4.587
4.576
4.574
4.103
4.094
3.999
3.976
3.966
3.942
3.923
3.891
2.485
NO2
CO2Bn
N
O=S=O
3m
1H NMR (400 MHz, CDCl3)
1.00
1.13
1.09
1.04
4.32
3.13
3.16
2.09
1.02
1.09
2.06
1.02
1.05
1.00
0.96
f1 (ppm)

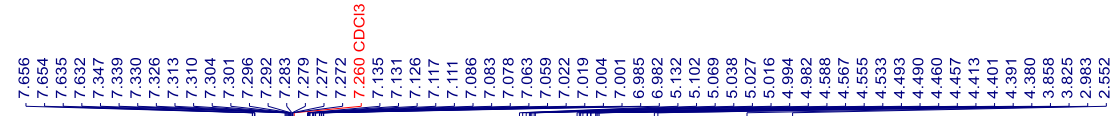

167.60
135.63
134.70
134.56
134.51
134.35
129.12
129.02
129.00
128.61
128.59
128.46
128.32
128.17
127.28
125.36
125.02
124.44
124.11
123.21
77.94
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
76.14
75.53
68.53
50.04
46.57
42.07
NO2
CO2Bn
N
O=S=O
3m
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)

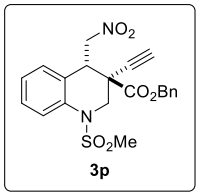

8.177
8.172
8.158
8.153
7.797
7.794
7.778
7.775
7.522
7.507
7.504
7.488
7.484
7.477
7.472
7.458
7.453
7.374
7.342
7.333
7.325
7.260 CDCl3
7.110
7.108
7.100
7.094
7.046
7.013
7.005
7.001
6.993
5.175
5.144
5.107
5.077
5.019
5.008
4.984
4.973
4.620
4.599
4.585
4.564
4.549
4.516
4.389
4.378
4.368
4.357
4.215
4.183
NO2
CO2Bn
N
O=S=O
Br
3n
1H NMR (400 MHz, CDCl3)
1.00
0.97
2.17
5.18
2.16
1.90
1.05
1.03
1.00
1.00
1.00
1.00
1.00
0.94
f1 (ppm)


167.88
140.06
136.07
135.65
134.47
134.15
131.37
129.12
128.79
128.59
128.36
128.08
125.05
124.91
121.25
120.21
77.71
77.32 CDCl3
77.08
76.68 CDCl3
68.60
50.85
46.15
41.89
NO2
CO2Bn
N
O=S=O
Br
3n
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)


7.939
7.935
7.930
7.754
7.752
7.749
7.736
7.734
7.732
7.729
7.650
7.648
7.630
7.628
7.600
7.597
7.579
7.576
7.381
7.361
7.341
7.320
7.315
7.309
7.307
7.302
7.260 CDCl3
7.170
7.165
7.152
7.145
7.010
7.007
6.992
6.989
6.949
6.945
6.930
6.926
5.108
5.077
5.052
5.022
4.743
4.734
4.711
4.701
4.573
4.570
4.541
4.538
4.068
4.059
3.992
3.968
3.959
3.808
3.776
2.513
NO2
CO2Bn
N
O=S=O
Br
3o
1H NMR (400 MHz, CDCl3)
0.96
0.97
2.09
5.01
2.02
2.09
1.09
1.02
1.10
1.00
1.01
1.02
1.01
0.95
f1 (ppm)

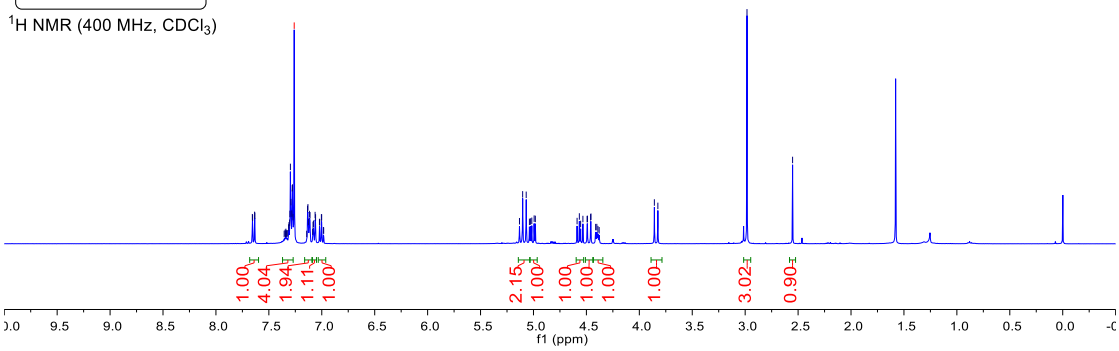

167.39
140.32
136.60
134.80
134.27
131.01
129.67
129.38
129.05
128.66
128.61
128.35
125.42
125.24
125.23
123.49
122.60
77.86
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
76.35
76.16
68.63
50.31
46.30
41.86
NO2
CO2Bn
N
O=S=O
Br
3o
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)

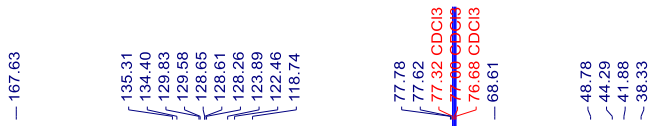


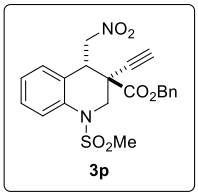


3p

^{1}H NMR (400 MHz, $CDCl_3$)

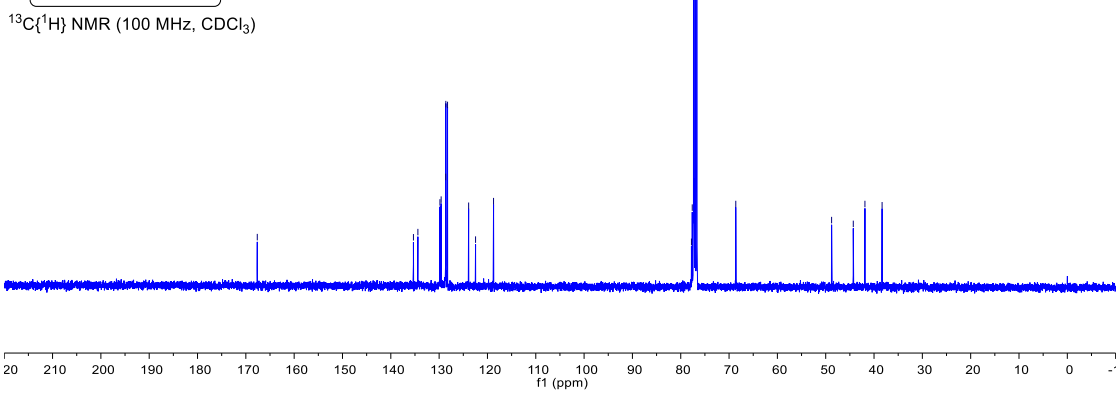


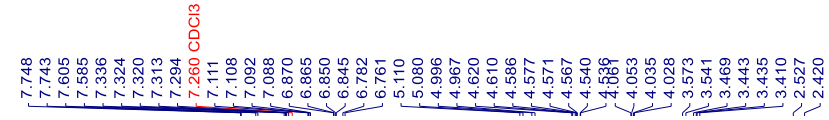


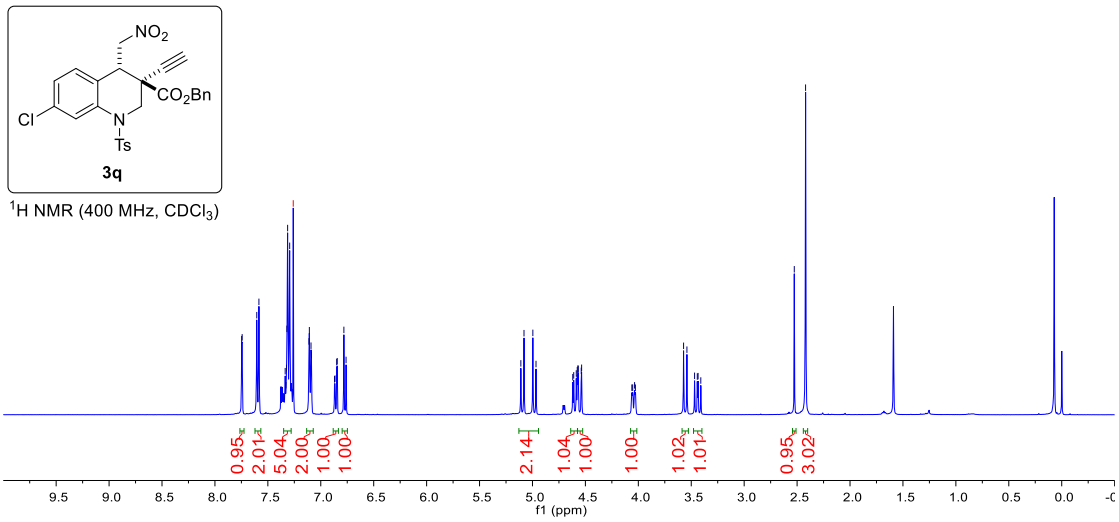


3p

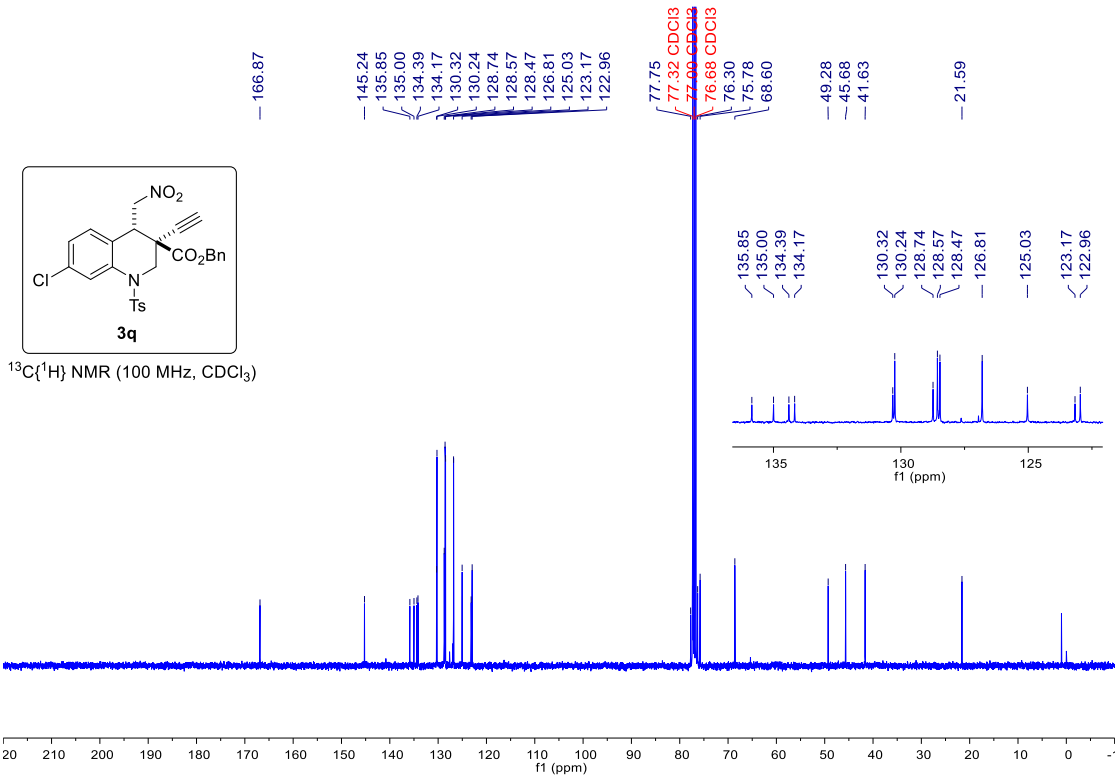
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



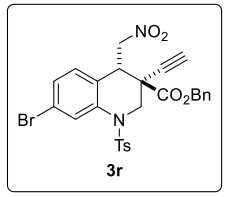




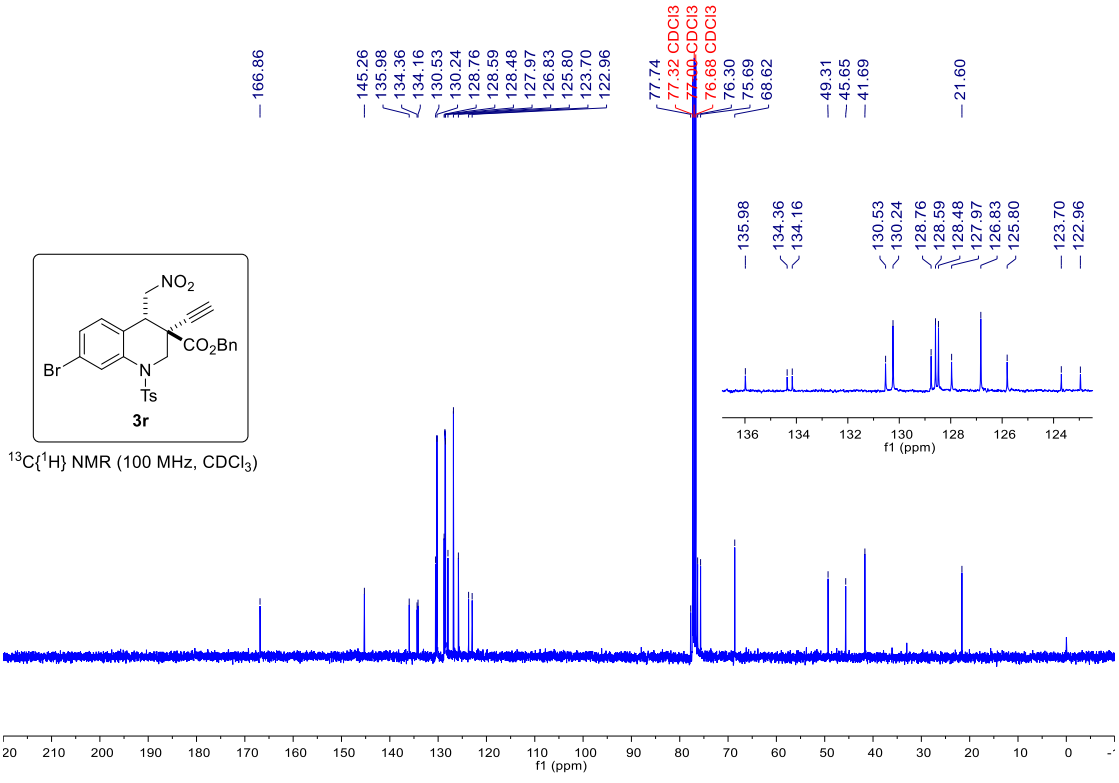
^{1}H NMR (400 MHz, $CDCl_3$)



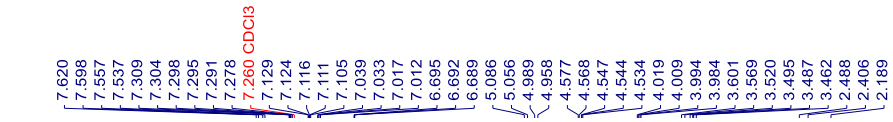
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

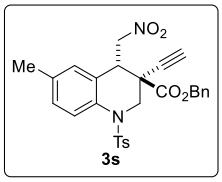


^{1}H NMR (400 MHz, $CDCl_3$)

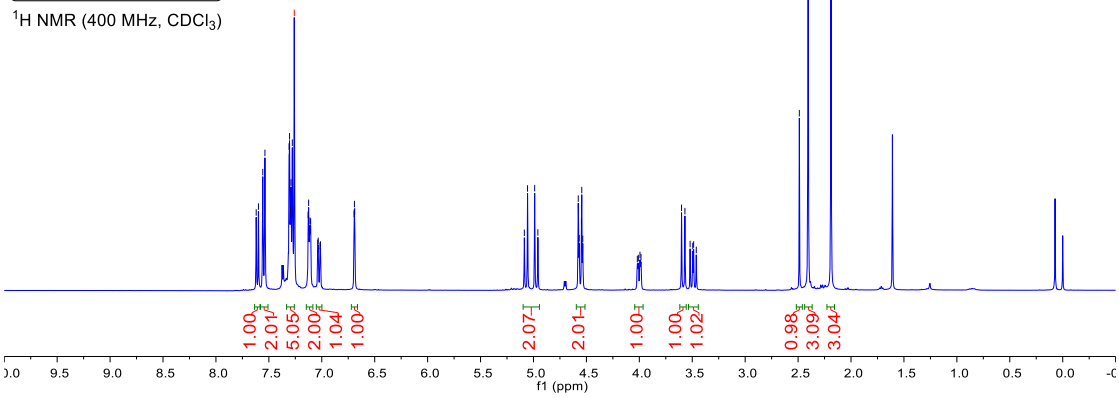


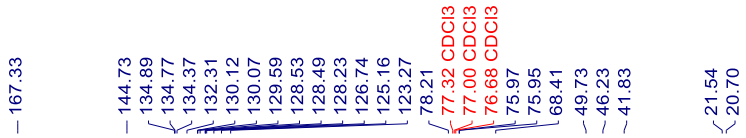
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

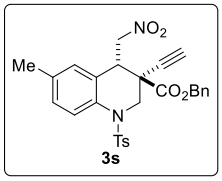




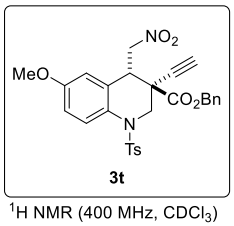
^{1}H NMR (400 MHz, $CDCl_3$)





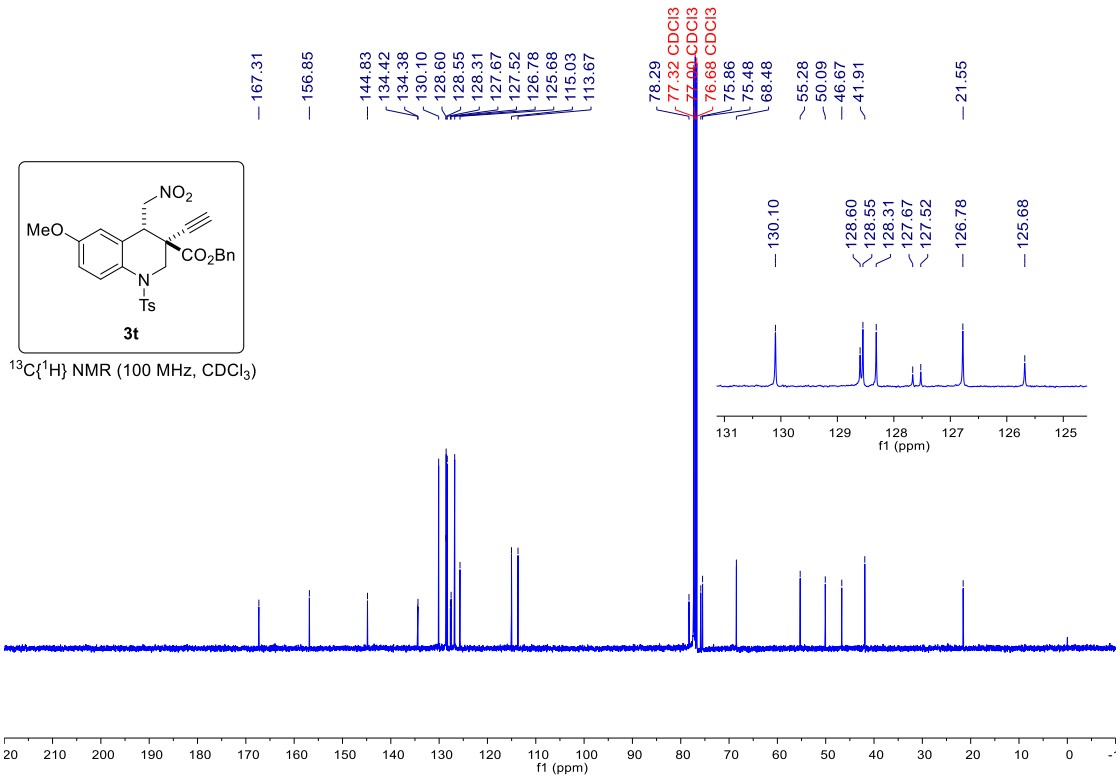


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



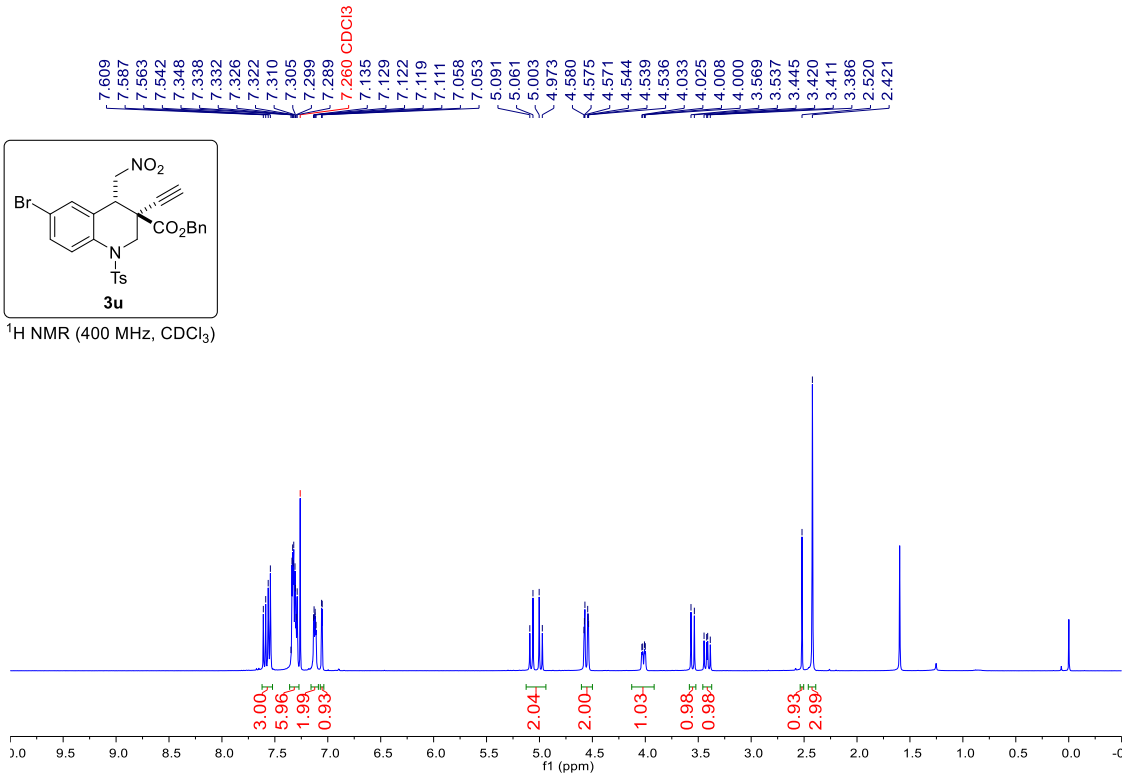
3t

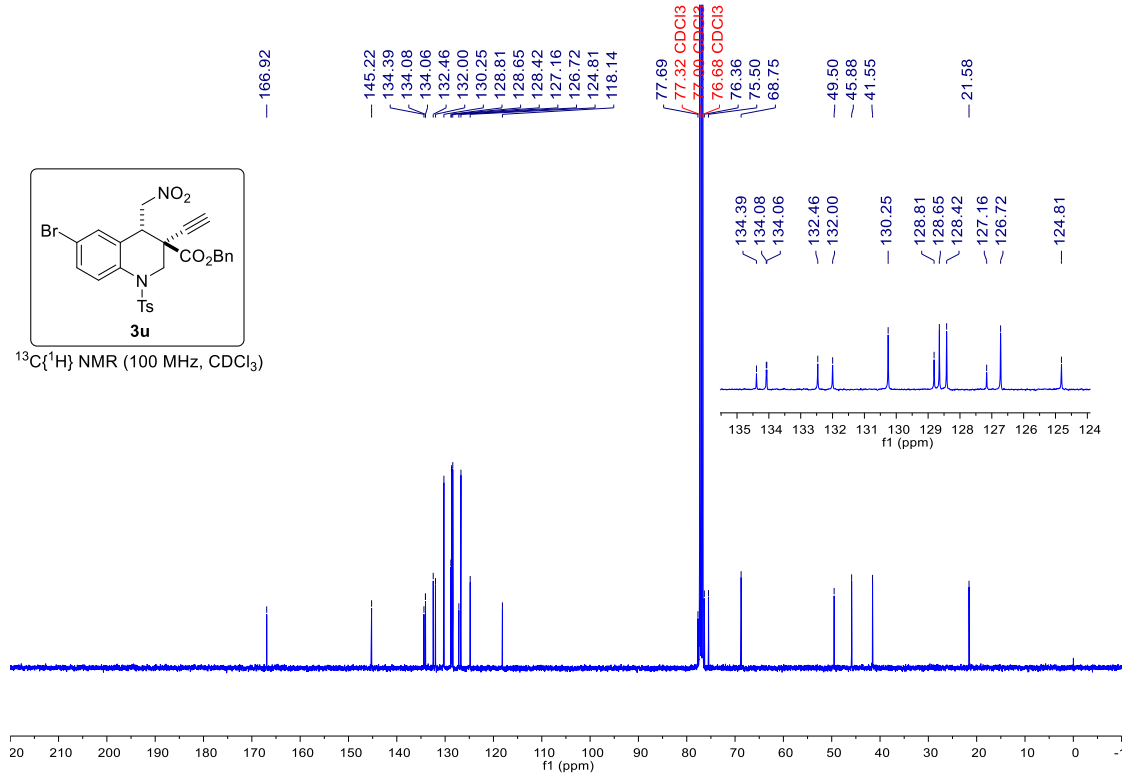
^{1}H NMR (400 MHz, $CDCl_3$)

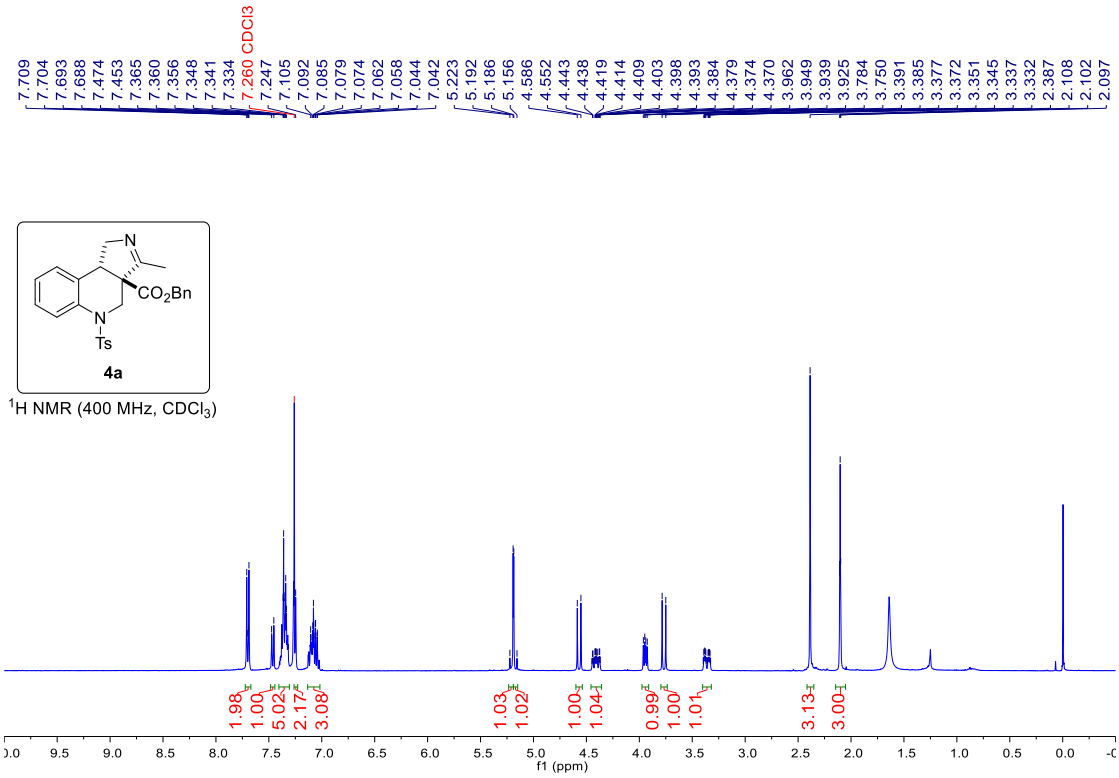


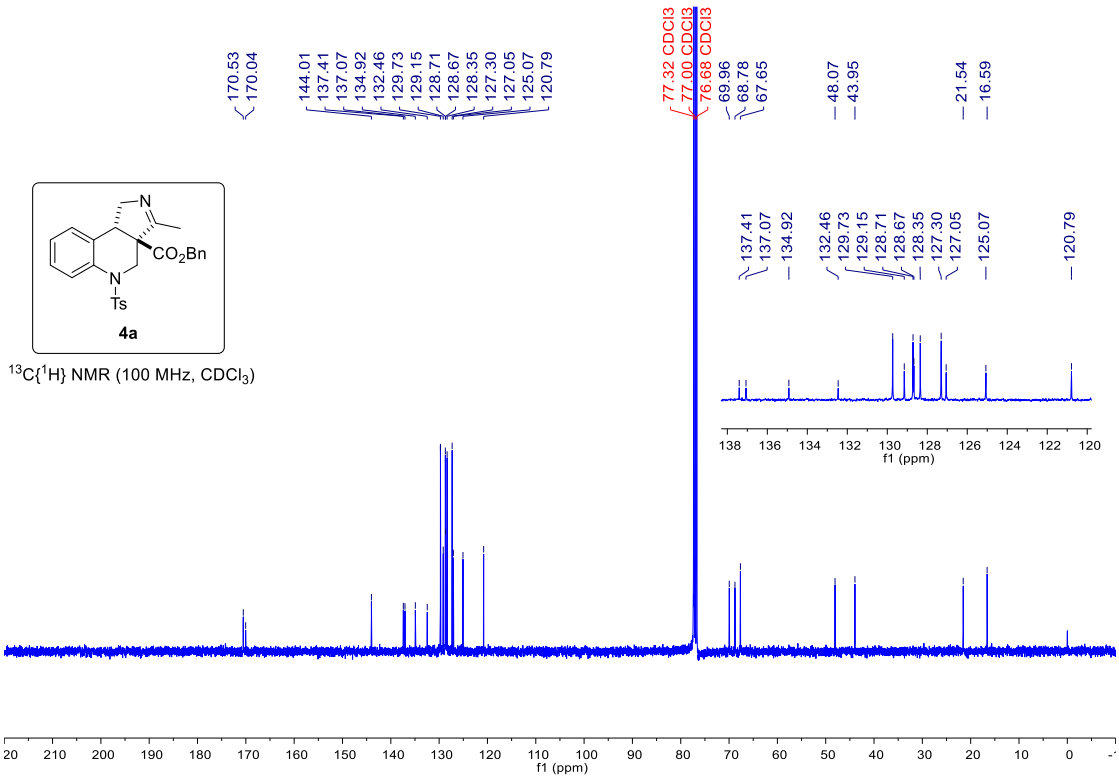
3t

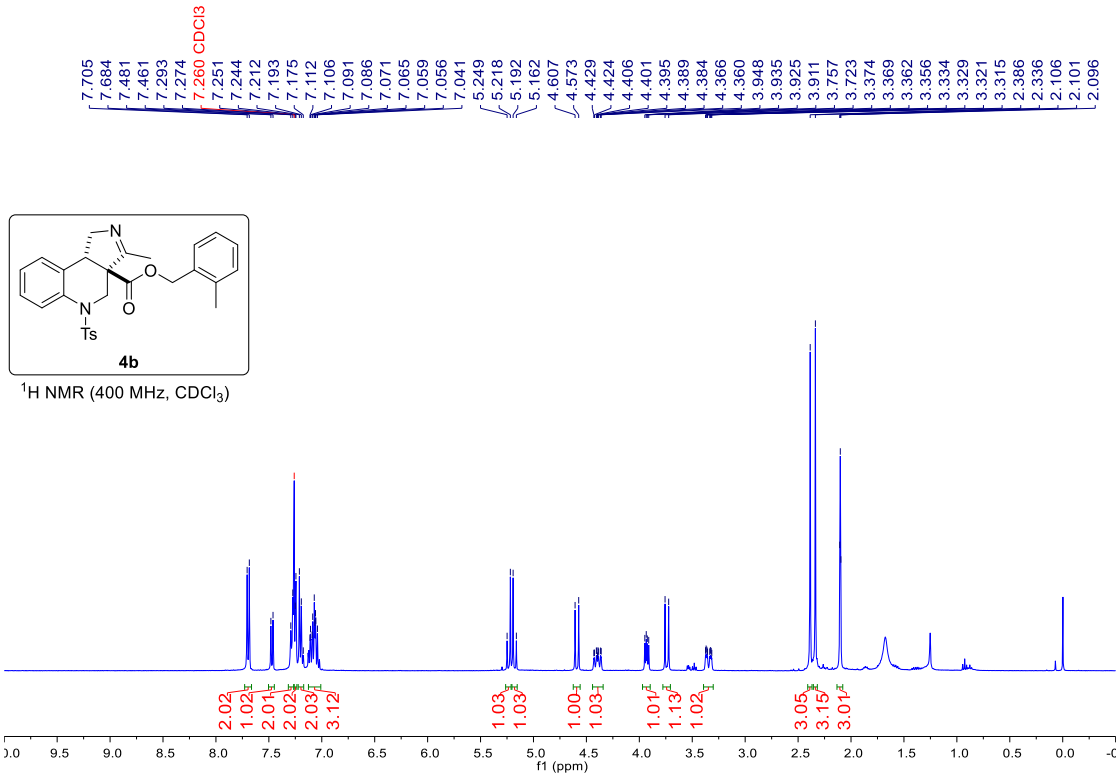
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

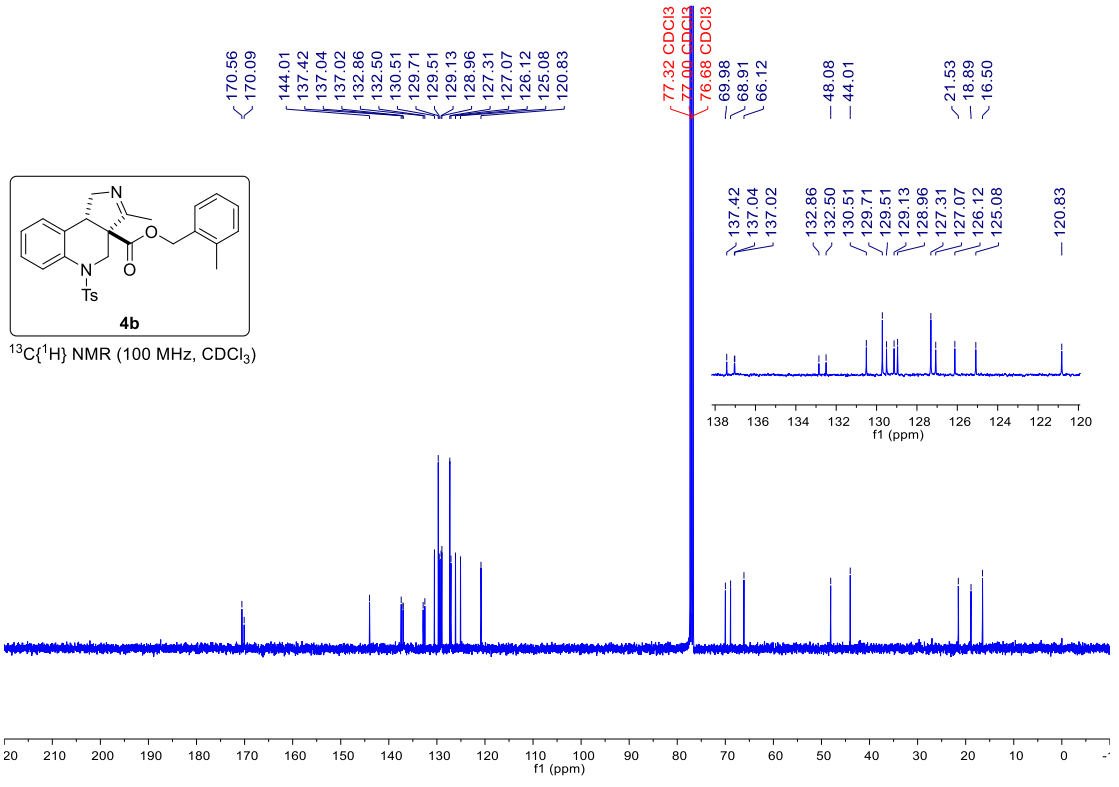

7.609
7.587
7.563
7.542
7.348
7.338
7.332
7.326
7.322
7.310
7.305
7.299
7.289
7.260 CDCl3
7.135
7.129
7.122
7.119
7.111
7.058
7.053
5.091
5.061
5.003
4.973
4.580
4.575
4.571
4.544
4.539
4.536
4.033
4.025
4.008
4.000
3.569
3.537
3.445
3.420
3.411
3.386
2.520
2.421
NO2
Br
CO2Bn
N
Ts
3u
1H NMR (400 MHz, CDCl3)
3.00
5.96
1.99
0.93
2.04
2.00
1.03
0.98
0.98
0.93
2.99
f1 (ppm)

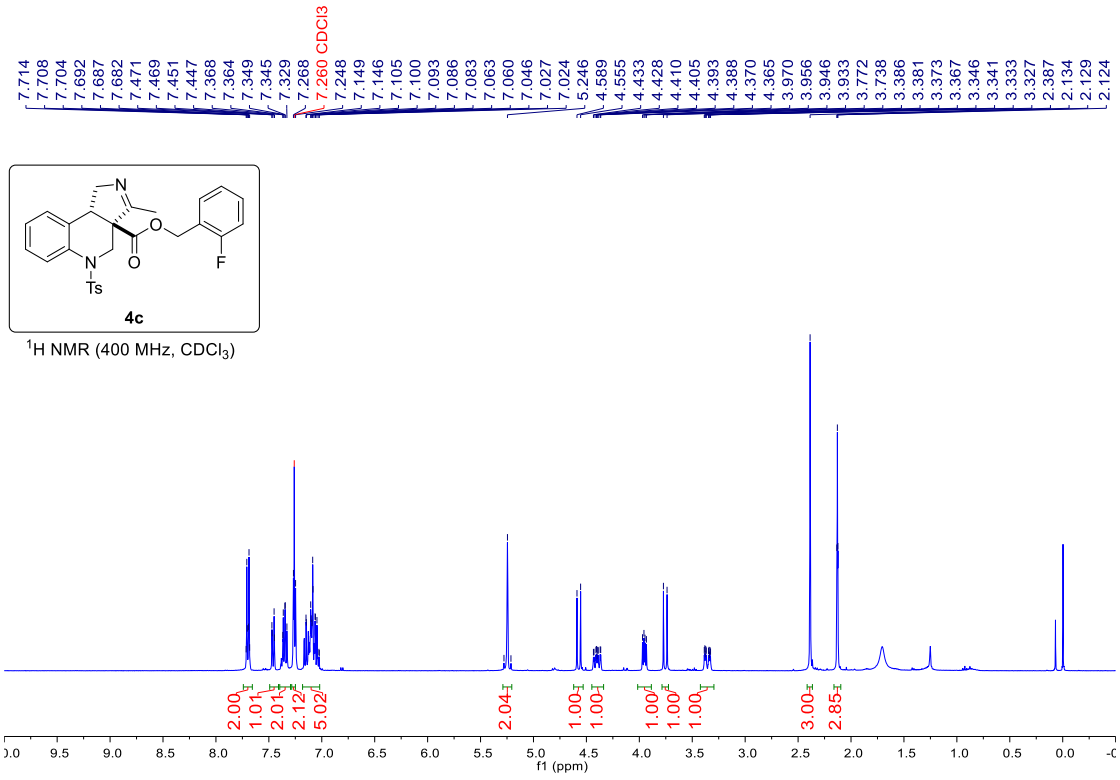

166.92
145.22
134.39
134.08
134.06
132.46
132.00
130.25
128.81
128.65
128.42
127.16
126.72
124.81
118.14
77.69
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
76.36
75.50
68.75
49.50
45.88
41.55
21.58
NO2
Br
CO2Bn
N
Ts
3u
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)

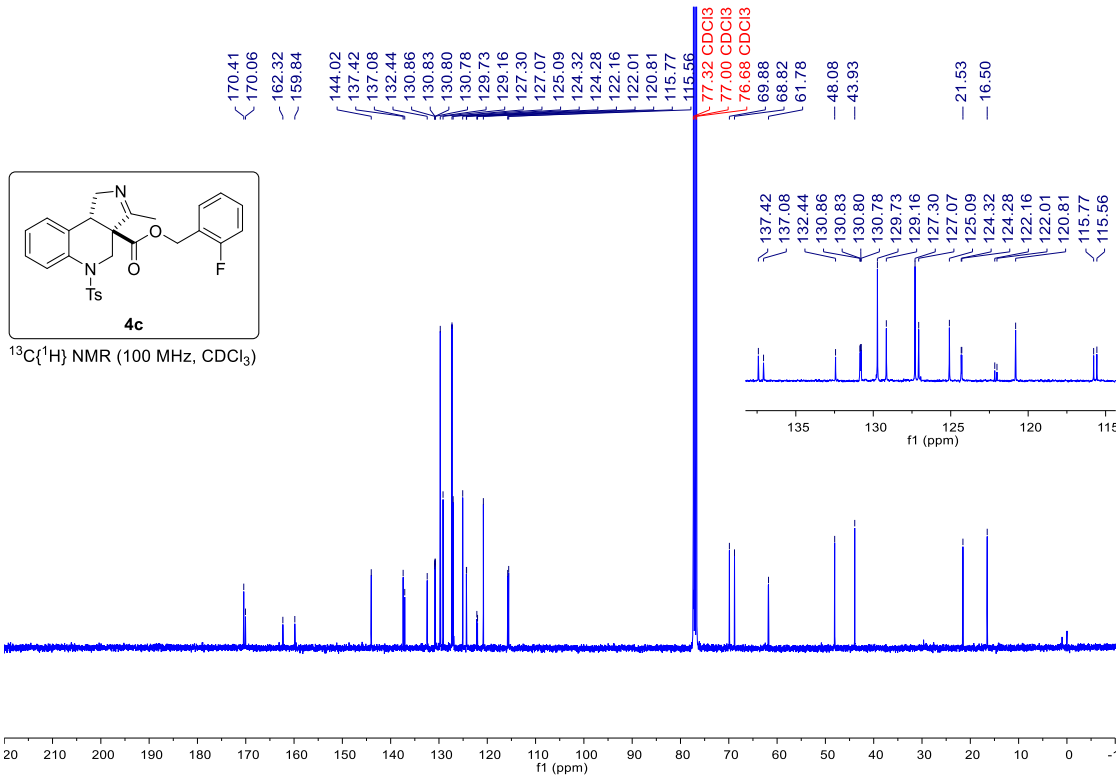

7.709
7.704
7.693
7.688
7.474
7.453
7.365
7.360
7.356
7.348
7.341
7.334
7.260 CDCl3
7.247
7.105
7.092
7.085
7.079
7.074
7.062
7.058
7.044
7.042
5.223
5.192
5.186
5.156
4.586
4.552
4.443
4.438
4.419
4.414
4.409
4.403
4.398
4.393
4.384
4.379
4.374
4.370
3.962
3.949
3.939
3.925
3.784
3.750
3.391
3.385
3.377
3.372
3.351
3.345
3.337
3.332
2.387
2.108
2.102
2.097
N
CO2Bn
N
Ts
4a
1H NMR (400 MHz, CDCl3)
1.98
1.00
5.02
2.17
3.08
1.03
1.02
1.00
1.04
0.99
1.00
1.01
3.13
3.00
f1 (ppm)

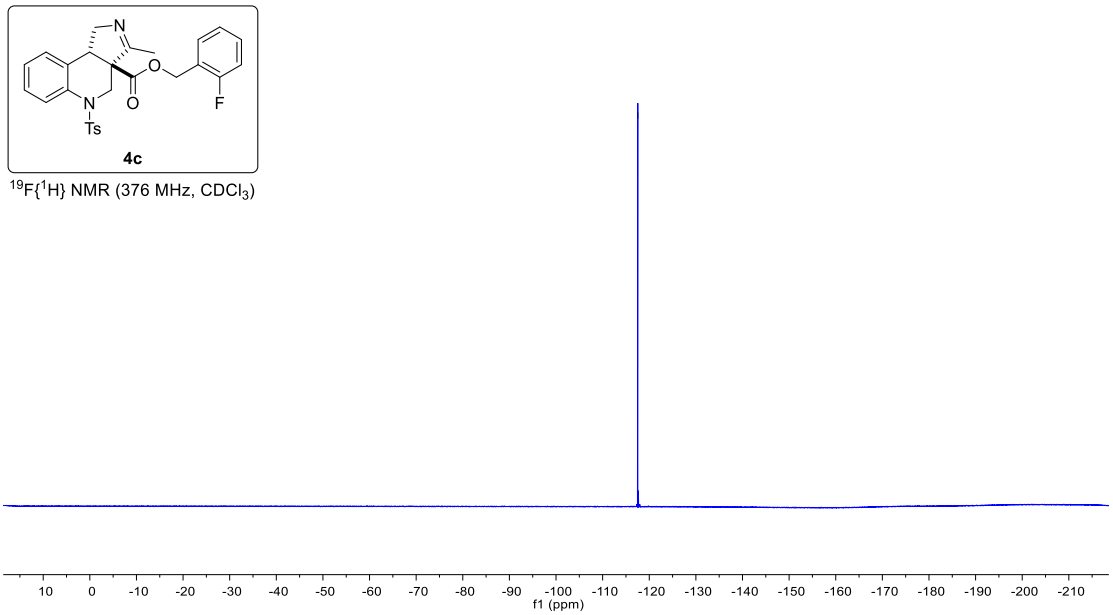

170.53
170.04
144.01
137.41
137.07
134.92
132.46
129.73
129.15
128.71
128.67
128.35
127.30
127.05
125.07
120.79
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
69.96
68.78
67.65
48.07
43.95
21.54
16.59
N
CO2Bn
N
Ts
4a
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)


7.705
7.684
7.481
7.461
7.293
7.274
7.260 CDCl3
7.251
7.244
7.212
7.193
7.175
7.112
7.106
7.091
7.086
7.071
7.065
7.059
7.056
7.041
5.249
5.218
5.192
5.162
4.607
4.573
4.429
4.424
4.406
4.401
4.395
4.389
4.384
4.366
4.360
3.948
3.935
3.925
3.911
3.757
3.723
3.374
3.369
3.362
3.356
3.334
3.329
3.321
3.315
2.386
2.336
2.106
2.101
2.096
N
O
O
N
Ts
4b
1H NMR (400 MHz, CDCl3)
2.02
1.02
2.01
2.02
2.03
3.12
1.03
1.03
1.00
1.03
1.01
1.13
1.02
3.05
3.15
3.01
f1 (ppm)


170.56
170.09
144.01
137.42
137.04
137.02
132.86
132.50
130.51
129.71
129.51
129.13
128.96
127.31
127.07
126.12
125.08
120.83
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
69.98
68.91
66.12
48.08
44.01
21.53
18.89
16.50
N
O
O
N
Ts
4b
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)

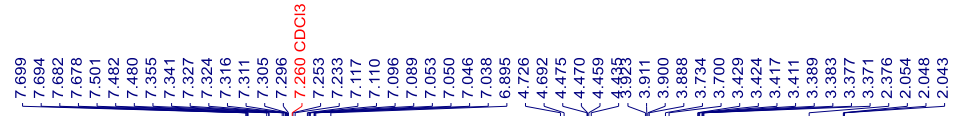

7.714
7.708
7.704
7.692
7.687
7.682
7.471
7.469
7.451
7.447
7.368
7.364
7.349
7.345
7.329
7.268
7.260 CDCl3
7.248
7.149
7.146
7.105
7.100
7.093
7.086
7.083
7.063
7.060
7.046
7.027
7.024
5.246
4.589
4.555
4.433
4.428
4.410
4.405
4.393
4.388
4.370
4.365
3.970
3.956
3.946
3.933
3.772
3.738
3.386
3.381
3.373
3.367
3.346
3.341
3.333
3.327
2.387
2.134
2.129
2.124
N
O
O
F
N
Ts
4c
1H NMR (400 MHz, CDCl3)
2.00
1.01
2.01
2.12
5.02
2.04
1.00
1.00
1.00
1.00
1.00
3.00
2.85
f1 (ppm)

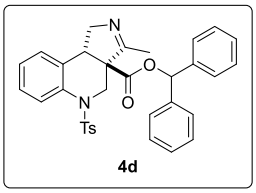

170.41
170.06
162.32
159.84
144.02
137.42
137.08
132.44
130.86
130.83
130.80
130.78
129.73
129.16
127.30
127.07
125.09
124.32
124.28
122.16
122.01
120.81
115.77
115.56
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
69.88
68.82
61.78
48.08
43.93
21.53
16.50
N
O
O
F
N
Ts
4c
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)



4c

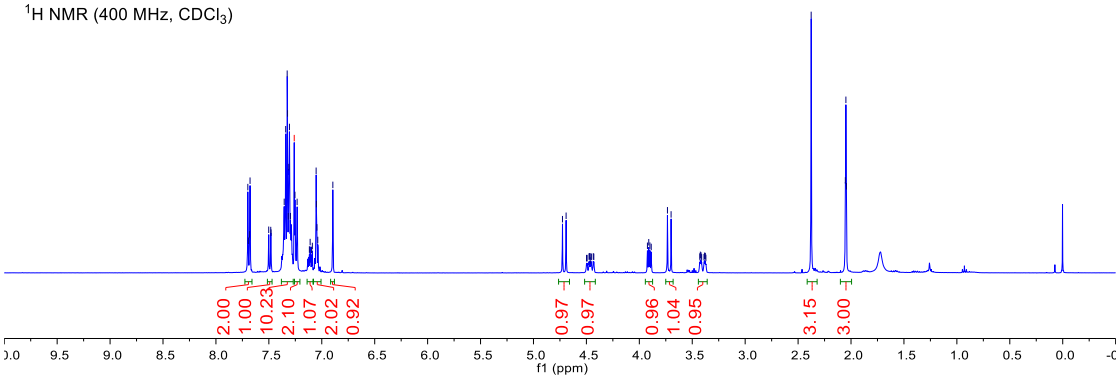
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)

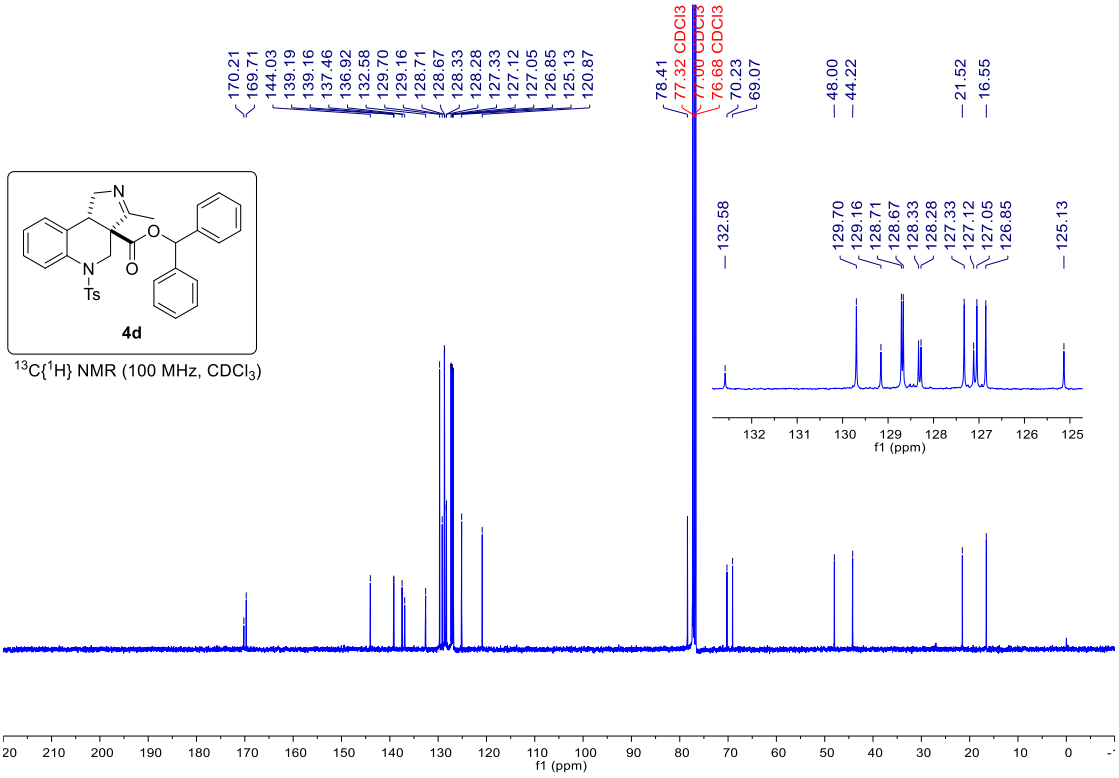




4d

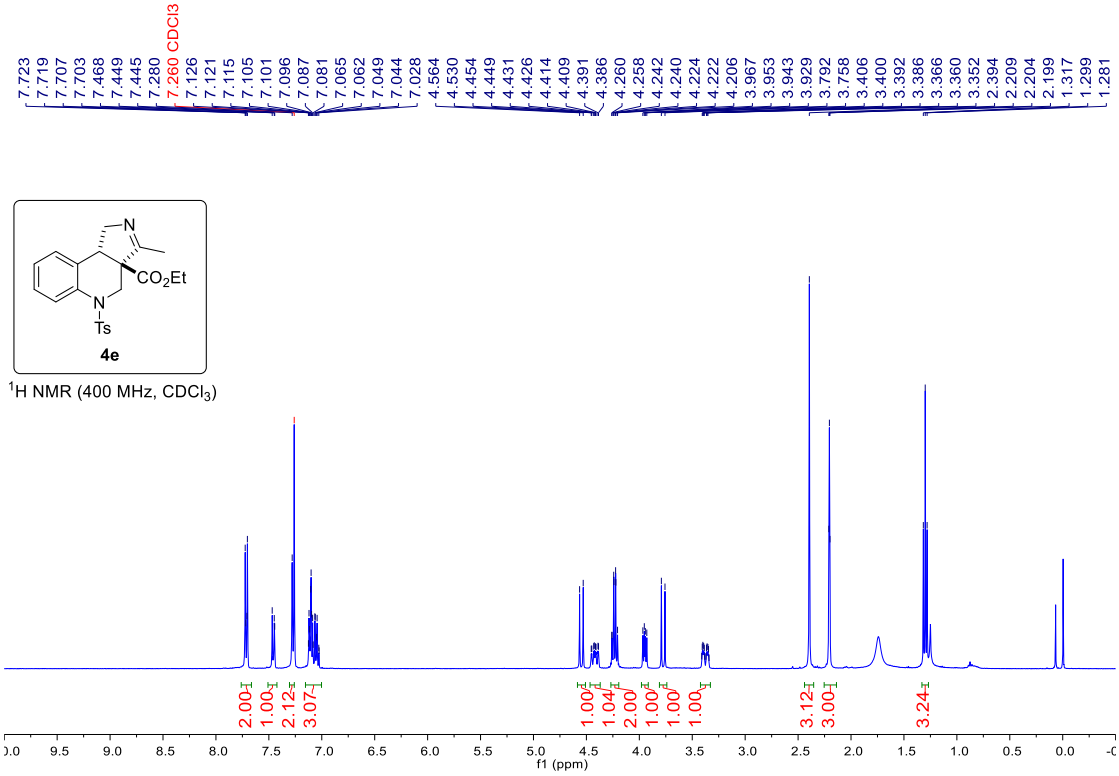
^{1}H NMR (400 MHz, $CDCl_3$)

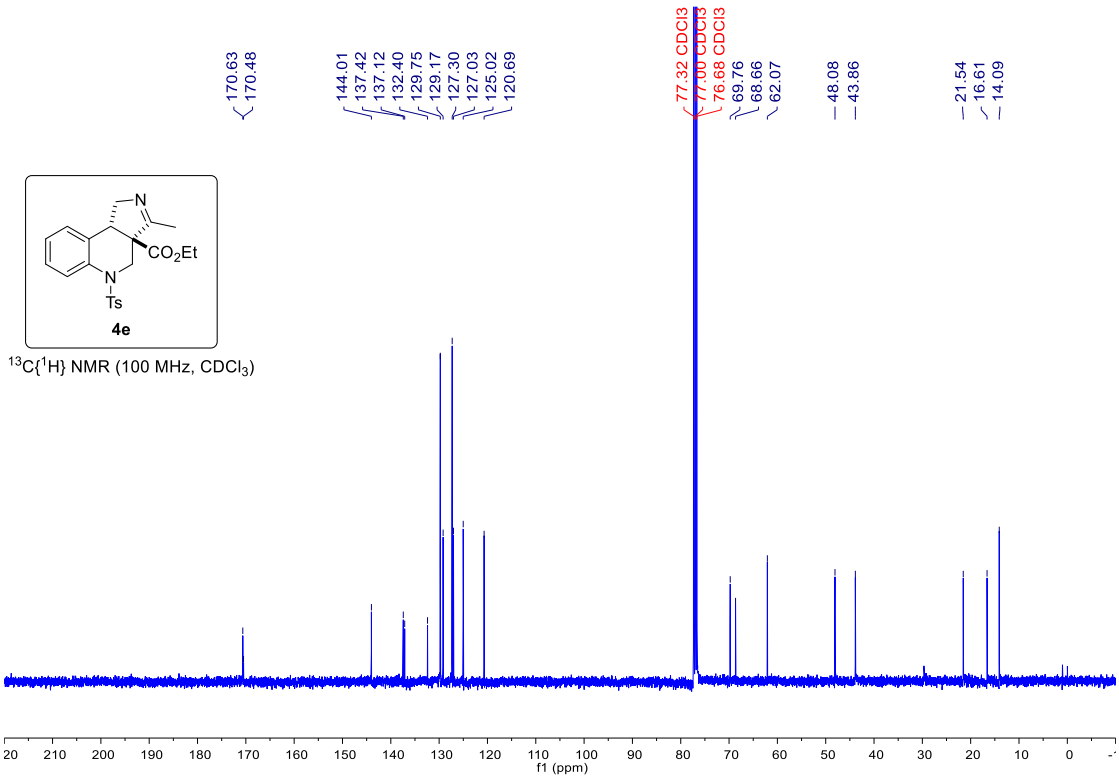


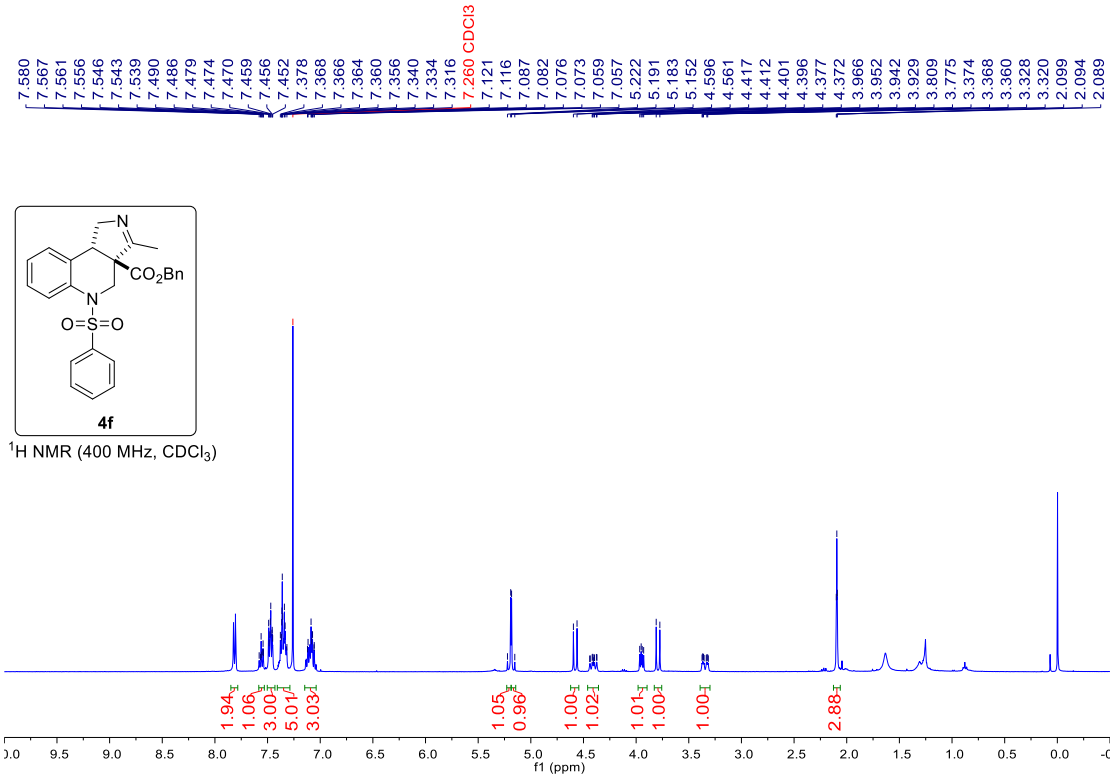


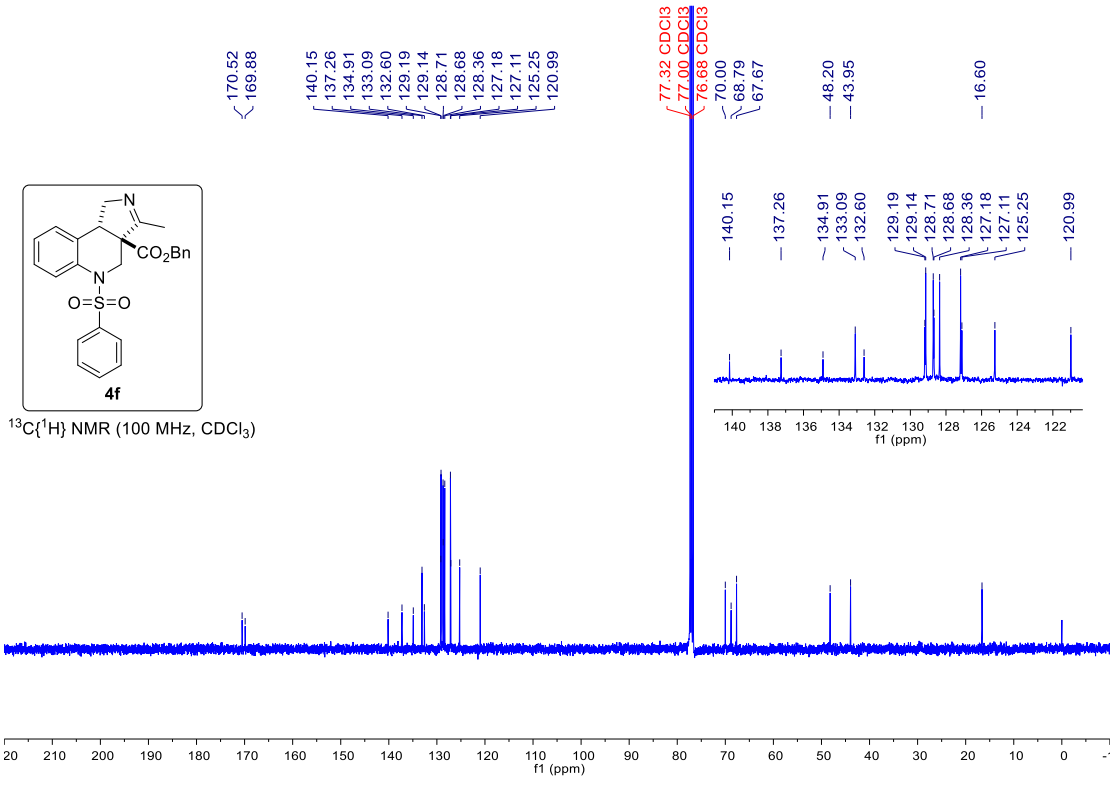
4d

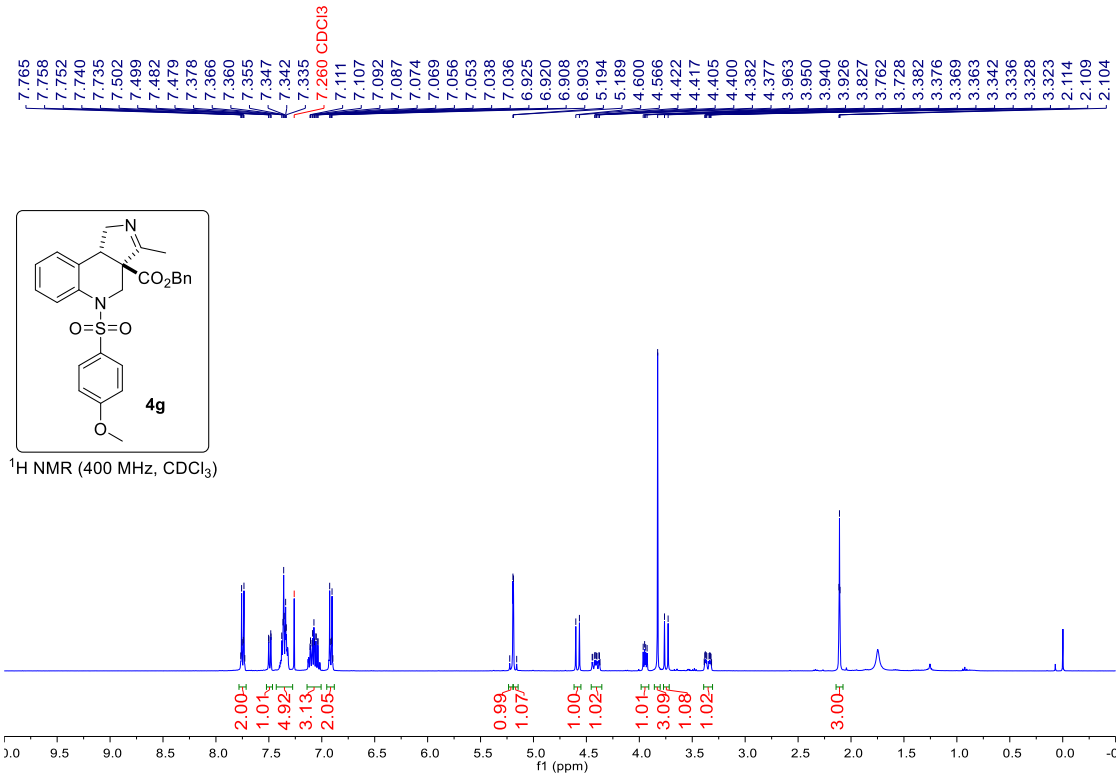
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

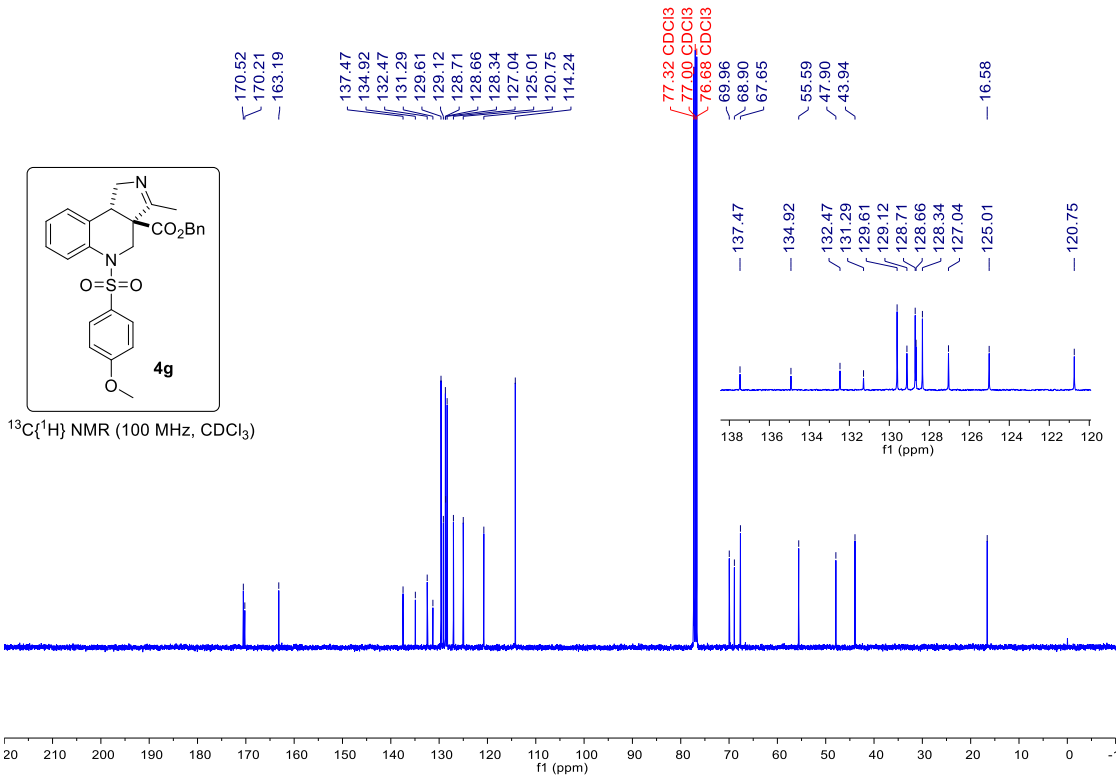

7.723
7.719
7.707
7.703
7.468
7.449
7.445
7.280
7.260 CDCl3
7.126
7.121
7.115
7.105
7.101
7.096
7.087
7.081
7.065
7.062
7.049
7.044
7.028
4.564
4.530
4.454
4.449
4.431
4.426
4.414
4.409
4.391
4.386
4.260
4.258
4.242
4.240
4.224
4.222
4.206
3.967
3.953
3.943
3.929
3.792
3.758
3.406
3.400
3.392
3.386
3.366
3.360
3.352
2.394
2.209
2.204
2.199
1.317
1.299
1.281
CO2Et
N
Ts
4e
1H NMR (400 MHz, CDCl3)
2.00
1.00
2.12
3.07
1.00
1.04
2.00
1.00
1.00
1.00
3.12
3.00
3.24
f1 (ppm)

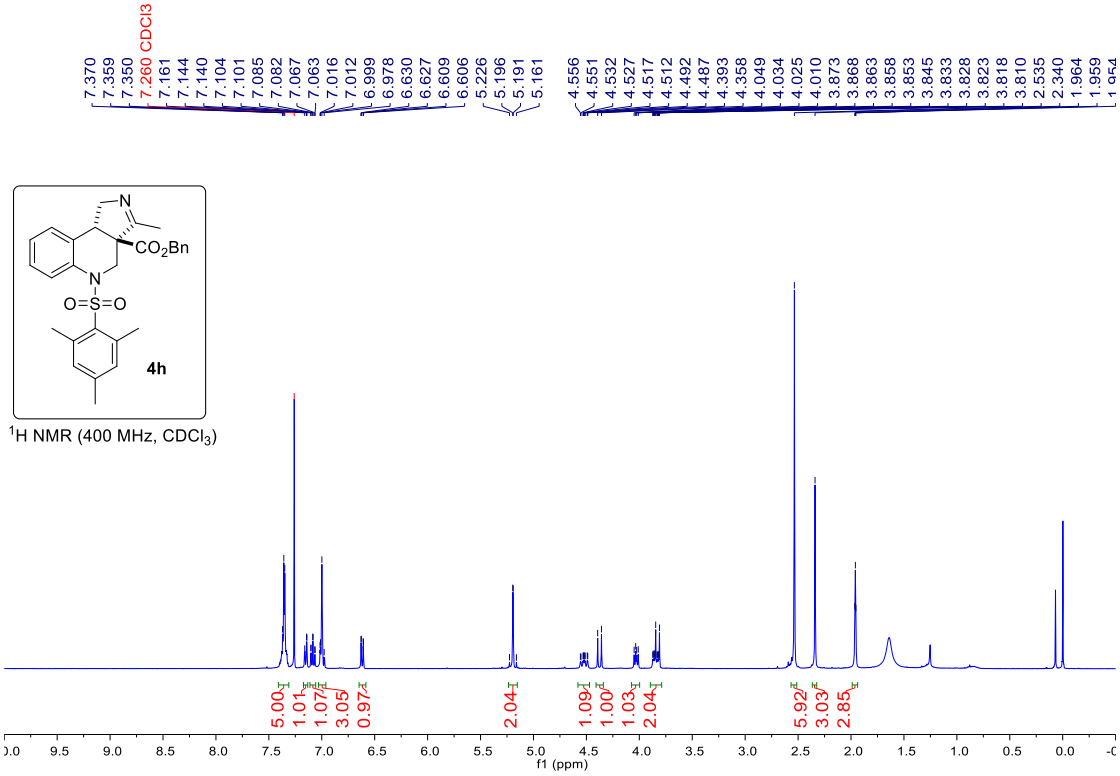

170.63
170.48
144.01
137.42
137.12
132.40
129.75
129.17
127.30
127.03
125.02
120.69
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
69.76
68.66
62.07
48.08
43.86
21.54
16.61
14.09
CO2Et
N
Ts
4e
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)

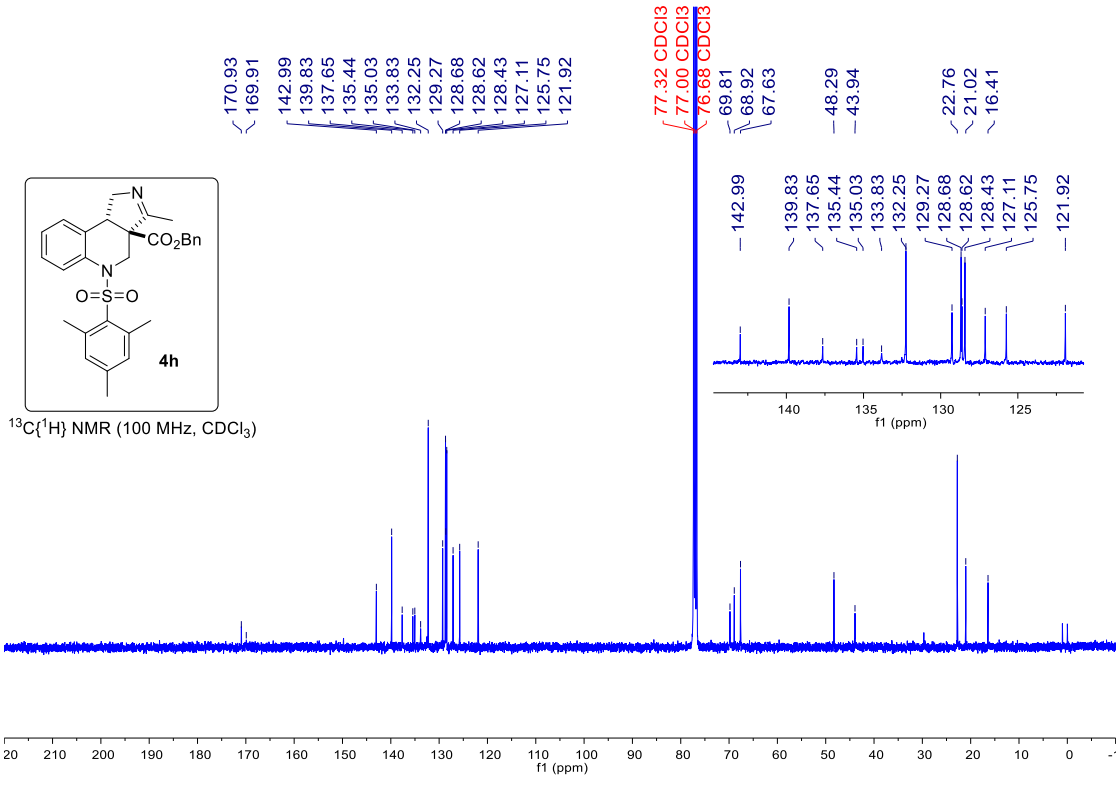

7.580
7.567
7.561
7.556
7.546
7.543
7.539
7.490
7.486
7.479
7.474
7.470
7.459
7.456
7.452
7.378
7.368
7.366
7.364
7.360
7.356
7.340
7.334
7.316
7.260 CDCl3
7.121
7.116
7.087
7.082
7.076
7.073
7.059
7.057
5.222
5.191
5.183
5.152
4.596
4.561
4.417
4.412
4.401
4.396
4.377
4.372
3.966
3.952
3.942
3.929
3.809
3.775
3.374
3.368
3.360
3.328
3.320
2.099
2.094
2.089
CO2Bn
O=S=O
4f
1H NMR (400 MHz, CDCl3)
1.94
1.06
3.00
5.01
3.03
1.05
0.96
1.00
1.02
1.01
1.00
1.00
2.88
f1 (ppm)

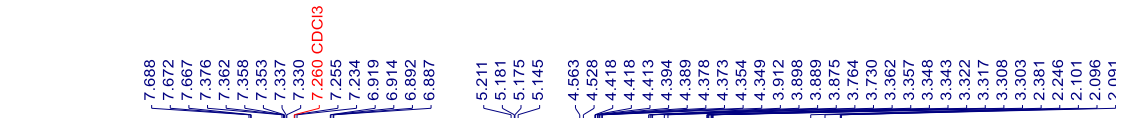

170.52
169.88
140.15
137.26
134.91
133.09
132.60
129.19
129.14
128.71
128.68
128.36
127.18
127.11
125.25
120.99
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
70.00
68.79
67.67
48.20
43.95
16.60
CO2Bn
O=S=O
4f
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)

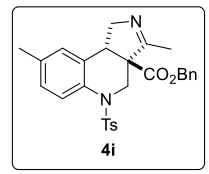

7.765
7.758
7.752
7.740
7.735
7.502
7.499
7.482
7.479
7.378
7.366
7.360
7.355
7.347
7.342
7.335
7.260 CDCl3
7.111
7.107
7.092
7.087
7.074
7.069
7.056
7.053
7.038
7.036
6.925
6.920
6.908
6.903
5.194
5.189
4.600
4.566
4.422
4.417
4.405
4.400
4.382
4.377
3.963
3.950
3.940
3.926
3.827
3.762
3.728
3.382
3.376
3.369
3.363
3.342
3.336
3.328
3.323
2.114
2.109
2.104
CO2Bn
N
O=S=O
4g
1H NMR (400 MHz, CDCl3)
2.00
1.01
4.92
3.13
2.05
0.99
1.07
1.00
1.02
1.01
3.09
1.08
1.02
3.00
f1 (ppm)


170.52
170.21
163.19
137.47
134.92
132.47
131.29
129.61
129.12
128.71
128.66
128.34
127.04
125.01
120.75
114.24
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
69.96
68.90
67.65
55.59
47.90
43.94
16.58
CO2Bn
N
O=S=O
4g
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)


7.370
7.359
7.350
7.260 CDCl3
7.161
7.144
7.140
7.104
7.101
7.085
7.082
7.067
7.063
7.016
7.012
6.999
6.978
6.630
6.627
6.609
6.606
5.226
5.196
5.191
5.161
4.556
4.551
4.532
4.527
4.517
4.512
4.492
4.487
4.393
4.358
4.049
4.034
4.025
4.010
3.873
3.868
3.863
3.858
3.853
3.845
3.833
3.828
3.823
3.818
3.810
2.535
2.340
1.964
1.959
CO2Bn
N
O=S=O
4h
1H NMR (400 MHz, CDCl3)
5.00
1.01
1.07
3.05
0.97
2.04
1.09
1.00
1.03
2.04
5.92
3.03
2.85
f1 (ppm)

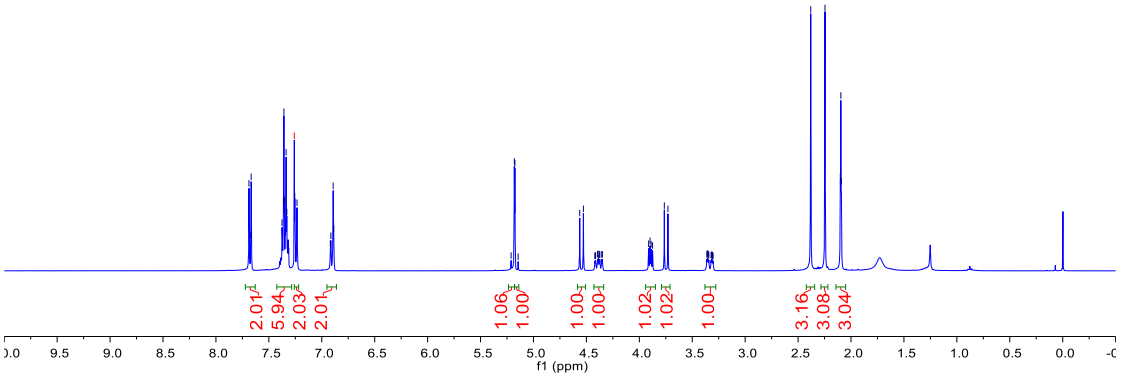

170.93
169.91
142.99
139.83
137.65
135.44
135.03
133.83
132.25
129.27
128.68
128.62
128.43
127.11
125.75
121.92
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
69.81
68.92
67.63
48.29
43.94
22.76
21.02
16.41
CO2Bn
N
O=S=O
4h
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)

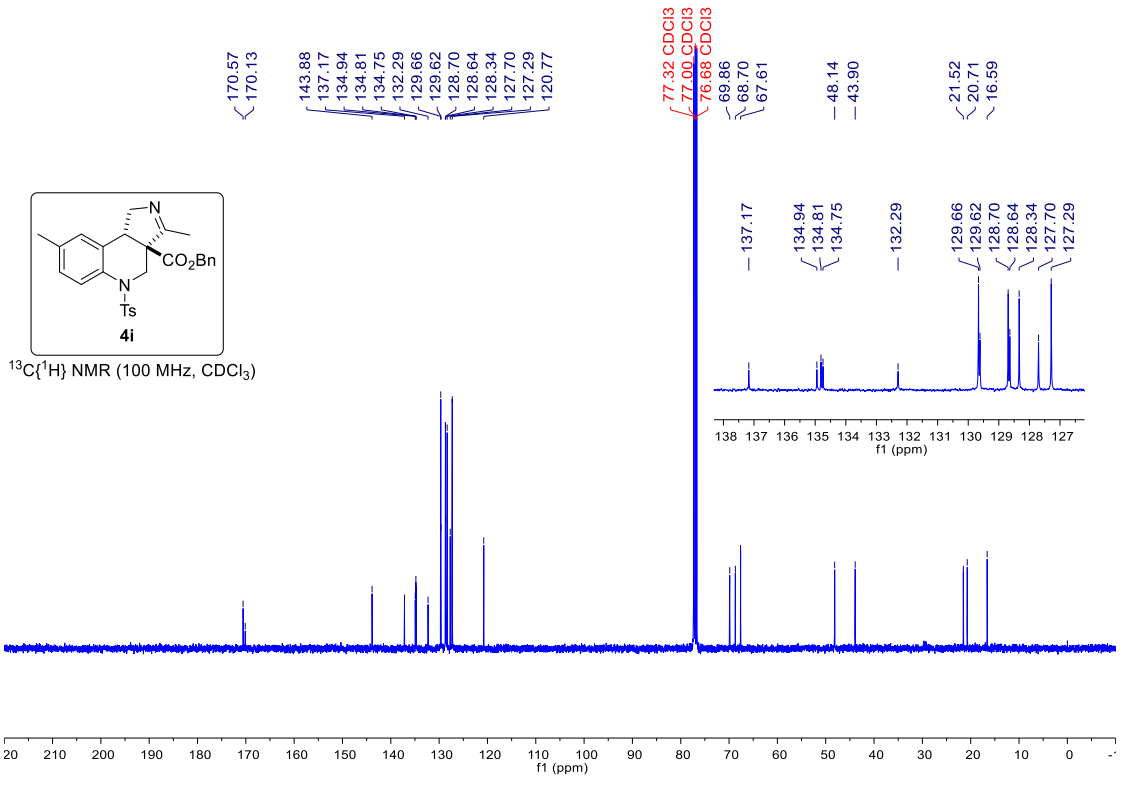




4i

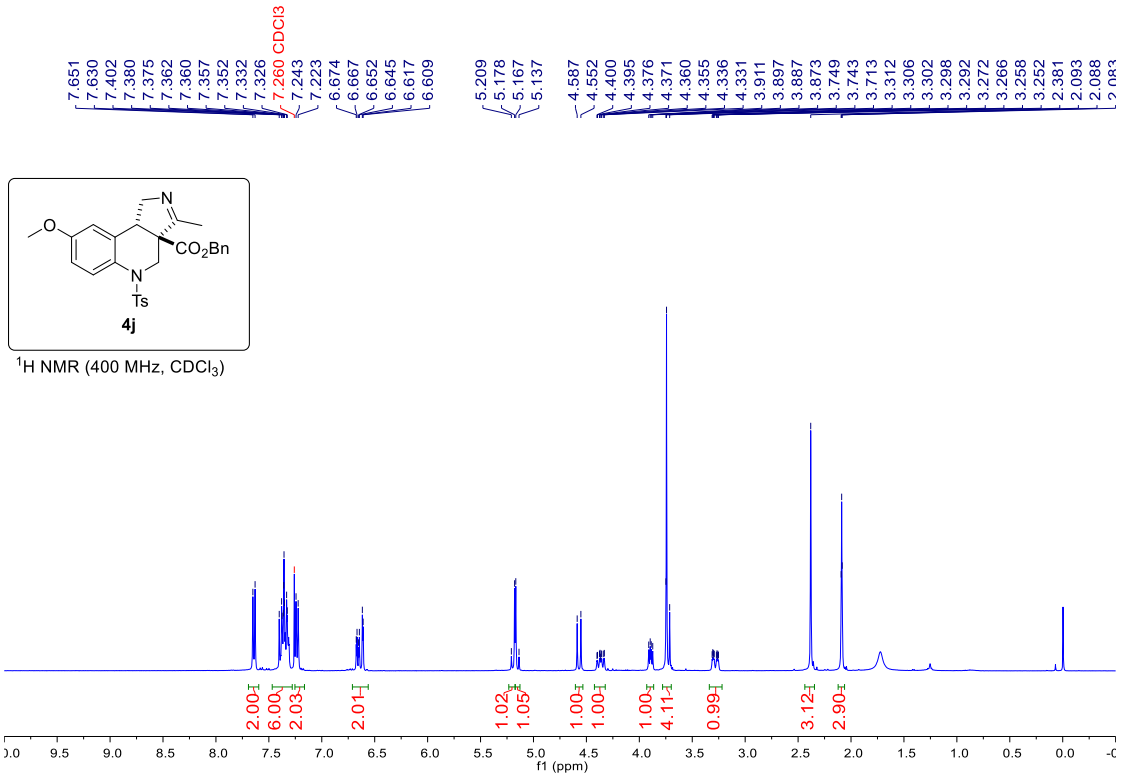
^{1}H NMR (400 MHz, $CDCl_3$)

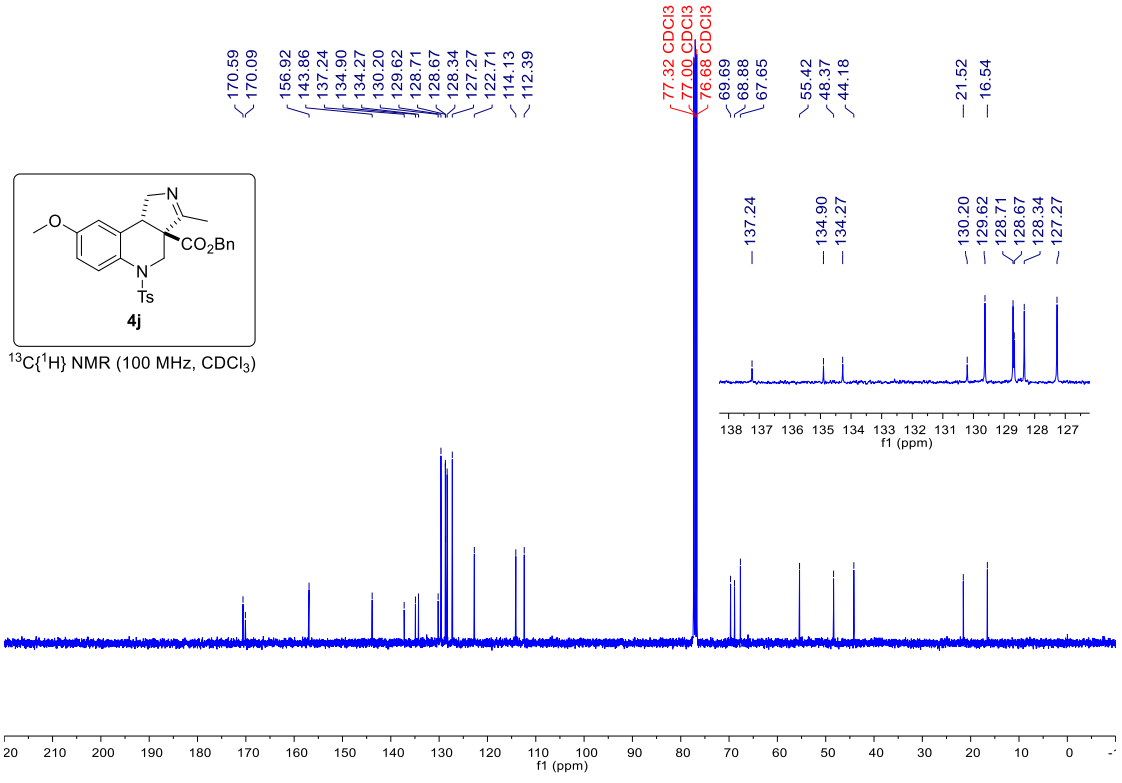


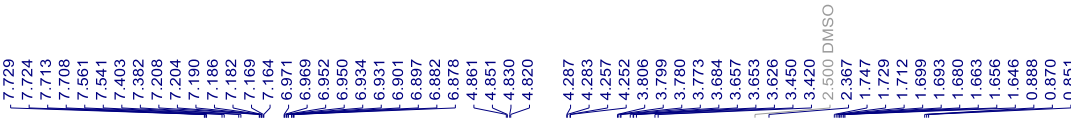


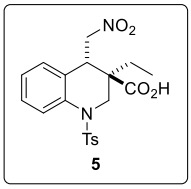
4i

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

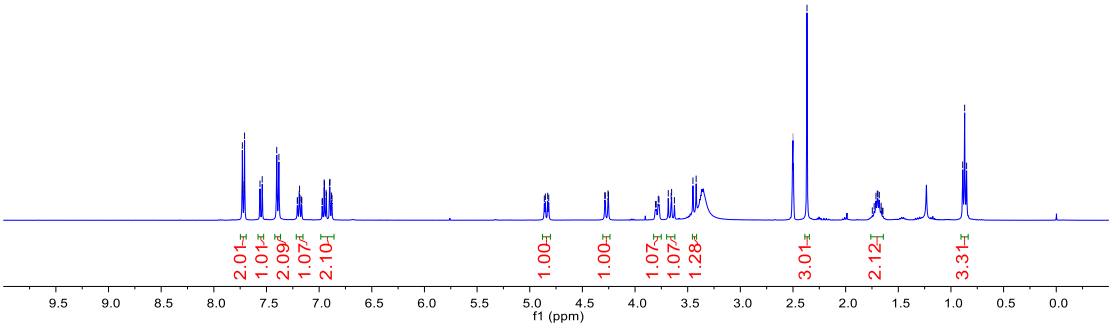

7.651
7.630
7.402
7.380
7.375
7.362
7.360
7.357
7.352
7.332
7.326
7.260 CDCl3
7.243
7.223
6.674
6.667
6.652
6.645
6.617
6.609
5.209
5.178
5.167
5.137
4.587
4.552
4.400
4.395
4.376
4.371
4.360
4.355
4.336
4.331
3.911
3.897
3.887
3.873
3.749
3.743
3.713
3.312
3.306
3.302
3.298
3.292
3.272
3.266
3.258
3.252
2.381
2.093
2.088
N
O
CO2Bn
N
Ts
4j
1H NMR (400 MHz, CDCl3)
2.00
6.00
2.03
2.01
1.02
1.05
1.00
1.00
1.00
4.11
0.99
3.12
2.90
f1 (ppm)

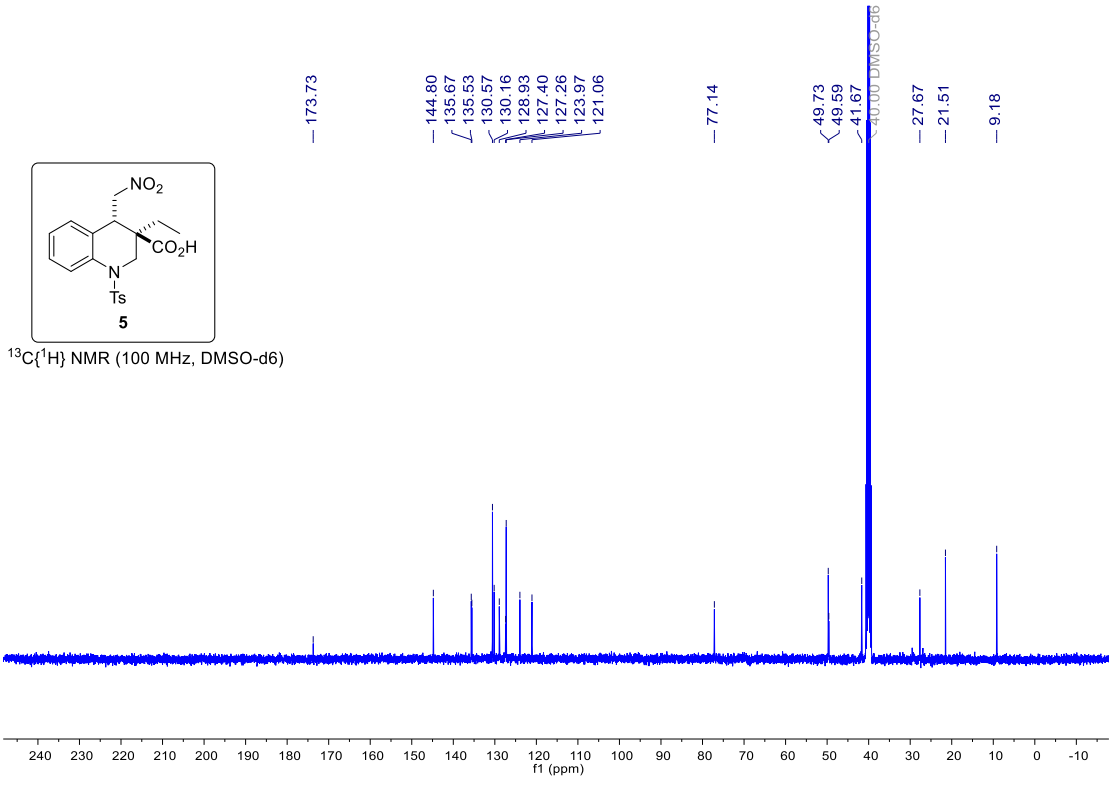

170.59
170.09
156.92
143.86
137.24
134.90
134.27
130.20
129.62
128.71
128.67
128.34
127.27
122.71
114.13
112.39
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
69.69
68.88
67.65
55.42
48.37
44.18
21.52
16.54
137.24
134.90
134.27
130.20
129.62
128.71
128.67
128.34
127.27
N
O
CO2Bn
N
Ts
4j
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)
f1 (ppm)



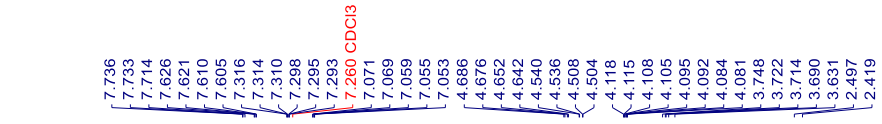


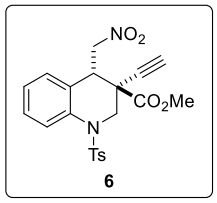
^{1}H NMR (400 MHz, DMSO-d6)





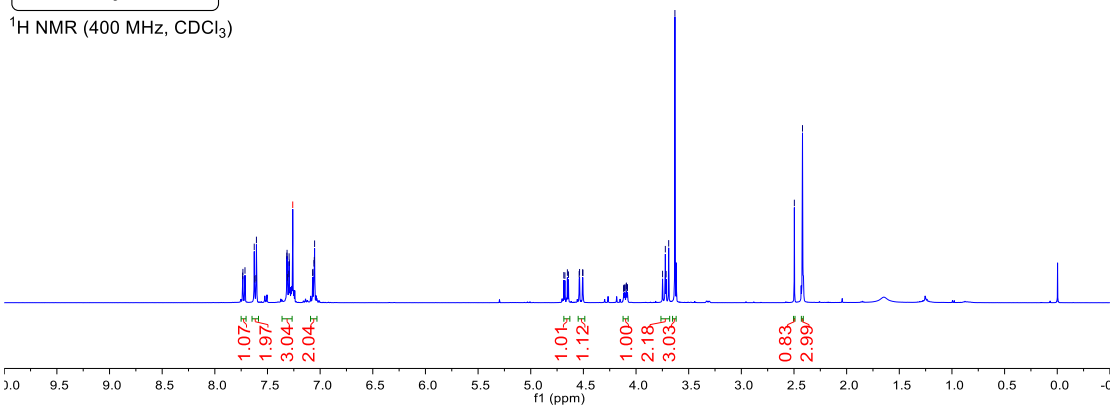
^{13}C{^{1}H} NMR (100 MHz, DMSO-d6)

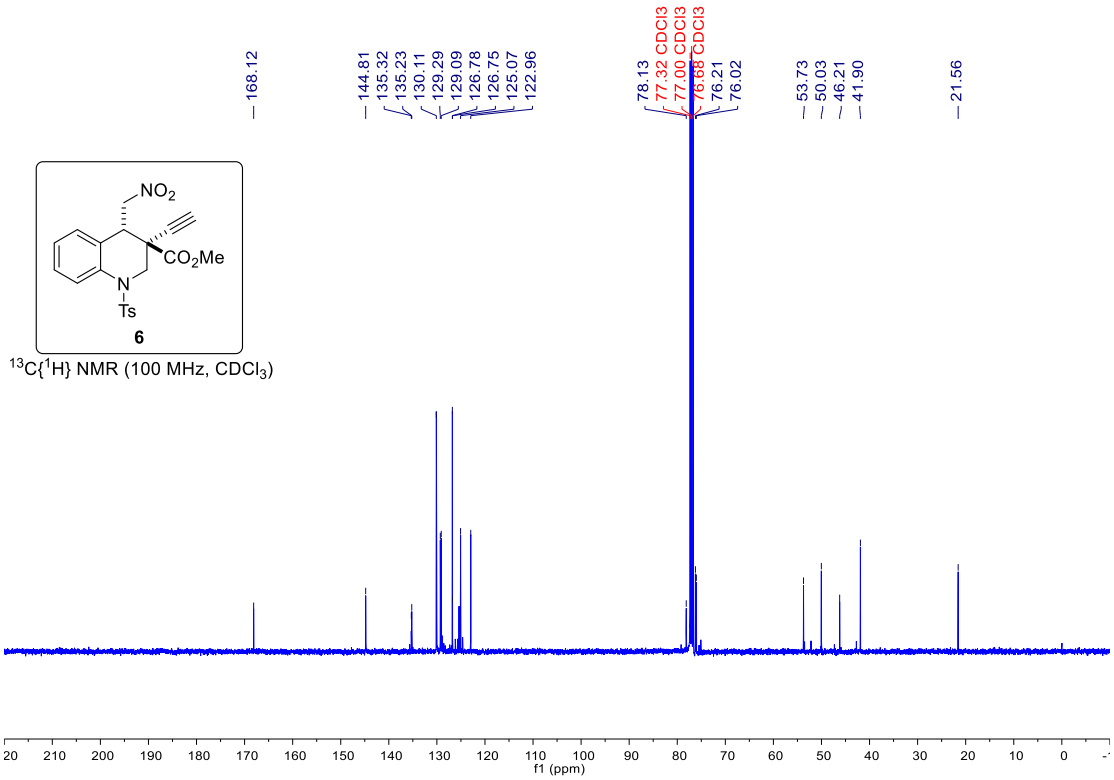




6

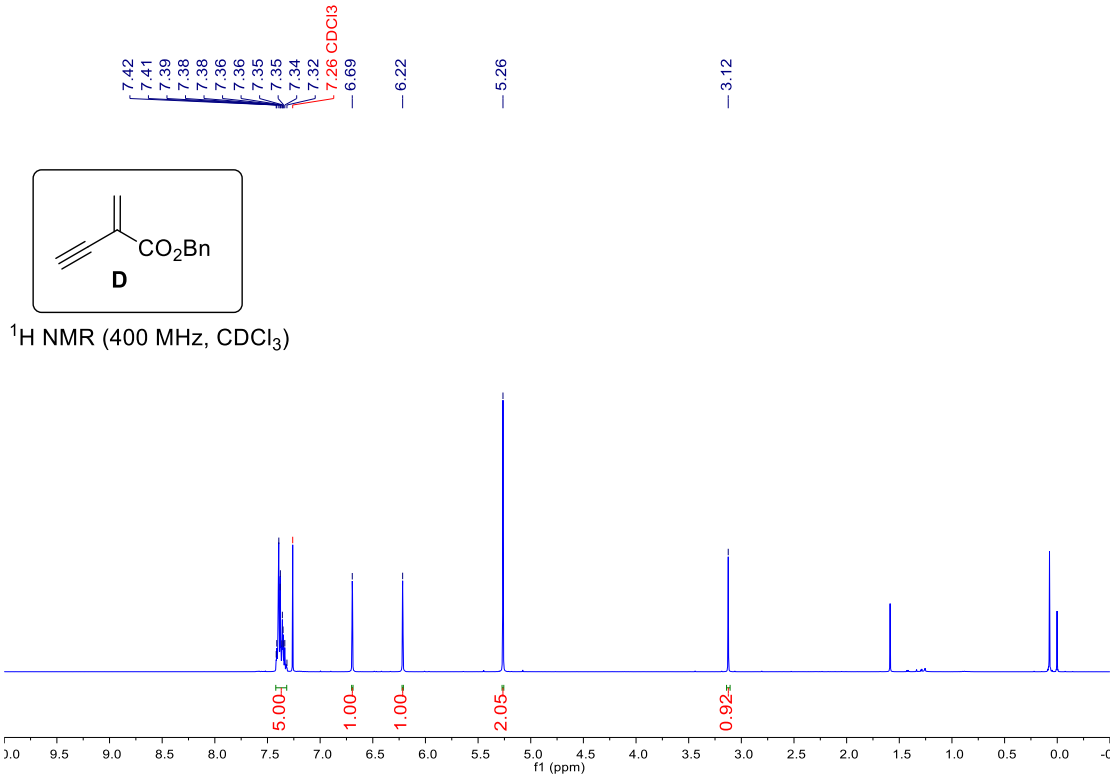
^{1}H NMR (400 MHz, $CDCl_3$)



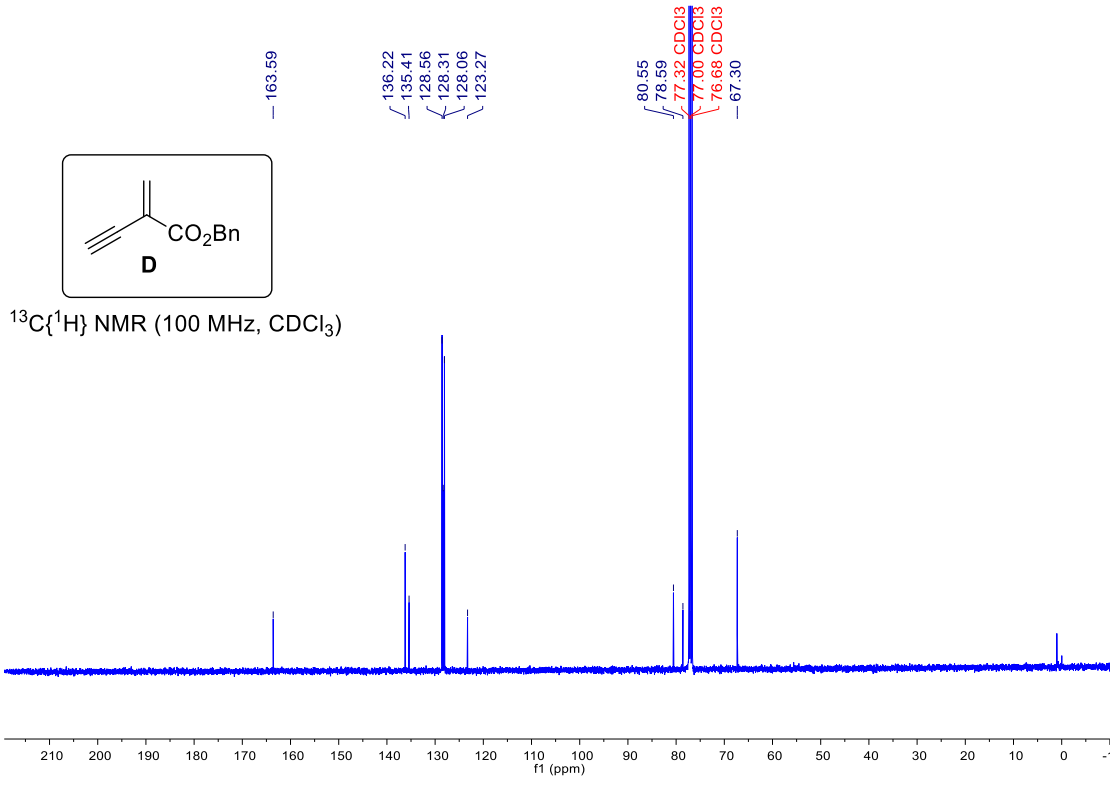


6

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)