Supplementary Material

Novel Bifunctional Chiral Squaramide-Amine Catalysts for Highly Enantioselective Addition of Mono and Diketones to Nitroalkenes

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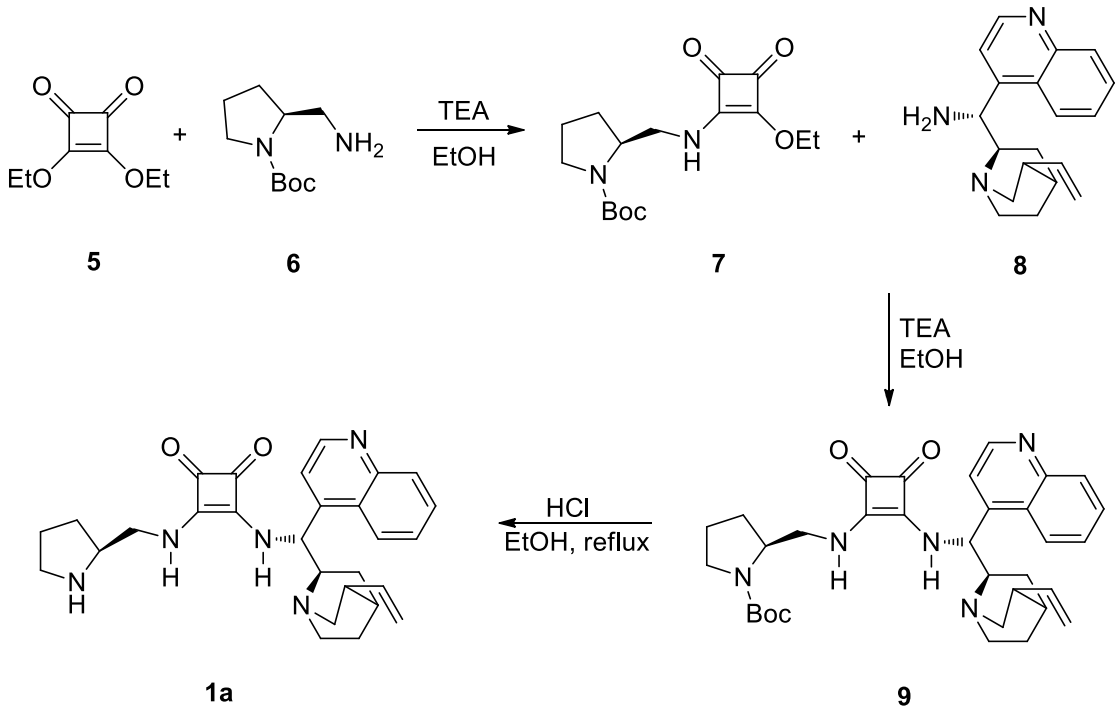
1. General information

Tetrahydrofuran, diethyl ether and toluene were dried over Na/benzophenone, dichloromethane was dried over CaH_2 and distilled prior to use. Reaction progress was monitored using analytical thin-layer chromatography (TLC) on 0.25mm Merck F-254 silica gel glass plates. Visualization was achieved by UV light (254 nm). Flash chromatography was performed with silica gel (Merck, 230-400 mesh). Unless otherwise noted, all NMR spectra were recorded using $CDCl_3$ as the solvent with reference to residual $CHCl_3$ (^1H at 7.24 ppm and ^{13}C at 77.0 ppm). Optical rotations were measured at room temperature on a Perkin–Elmer 241MC automatic polarimeter (concentration in g/100 mL). Melting points were obtained on a micro-melting apparatus and the data were uncorrected. Determination of % ee was achieved using a chiral HPLC equipped with a chiralpak AD column with 99:1 *n*-hexanes: 2-propanol as the mobile phase at a flow rate of 1 mL/min. Catalyst **4** was synthesized according to the literature.[1a]

2. Characterization of catalysts (1-3)

General procedure for preparation of bifunctional organocatalysts (1-3). Preparation of 1a is typical

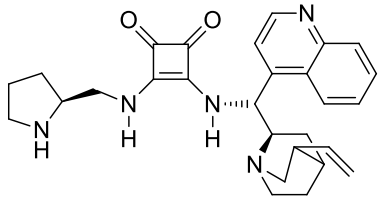


The pure (*S*)-2-amino-1-*N*-Boc-pyrrolidine **6** was obtained as a colorless oil according to the reported procedures.[2] To a solution of diethylsquarate **5** (0.1 mmol) in EtOH (5 mL) with TEA was

added (*S*)-2-amino-1-*N*-Boc-pyrrolidine **6** (0.11 mmol) EtOH (5 mL) at rt. The reaction mixture was stirred overnight and subjected to column chromatography to afford **7** (87%). To a solution of **7** (0.1 mmol) and amine **8** (0.12 mmol) in EtOH (10 mL) was added TEA (0.1 mmol). After 36 h, the reaction mixture was concentrated and subjected to column chromatography to afford squaramide **9** (72%) as a yellow solid: ^{1}H NMR（400 MHz $CDCl_3$）δ 1.03-1.18 (m, 9H), 1.53 (s, 9H), 3.0-3.73 (m, 11H), 5.05 (m, 1H), 5.7 (m, 1H), 7.5-8.7 (m, 4H). ^{13}C NMR (100Hz $CDCl_3$) 183.6, 181.7, 171.2, 168.2, 167.7, 155.5, 150.0, 148.6, 139.9, 139.0, 130.1, 129.5, 127.1, 124.1, 115.0, 114.6, 80.6, 59.2, 49.4, 46.9, 46.5, 45.8, 42.0, 39.2, 28.6, 27.9, 25.1, 24.2, 23.0, 21.0, 14.1.

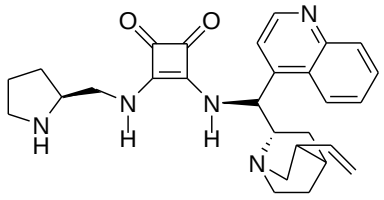
The above Boc-protected squaramide **9** was dissolved in a mixture of HCl/EtOH (12 mL/60 mL) and stirred for 12 h at room temperature. The mixture was basified with concentrated ammonia solution and extracted with CH_2Cl_2 (2×40 mL). After the removal of the solvent in vacuo, the residue was purified through flash column chromatography on silica gel (eluent: methanol / TEA = 10:1), gave **1a** as a white solid in 55% yield.

Catalyst (1a)



^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.80-1.87 (m, 9H), 2.10-3.95 (m, 13H), 5.01-5.11 (m, 2H), 5.72-5.80 (m, 1H), 6.25 (s, br, 1H), 7.57-8.79 (m, 6H) ppm; ^{13}C NMR (100Hz, $CDCl_3$) □δ: 183.7, 182.5, 167.9, 150.4, 150.2, 148.8, 147.2, 140.0, 130.4, 129.9, 127.6, 127.1, 124.0, 119.5, 115.4, 60.5, 49.7, 46.6, 45.5, 44.8, 39.3, 29.8, 28.5, 27.9, 26.7, 25.7, 24.2. HRMS (ESI) calcd for $C_{28}H_{33}N_5O_2H$ $[M + H]^+$ 472.2713; found 472.2703; m.p. 159-161 ^{o}C.

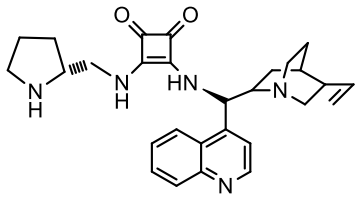
Catalyst (1b)



^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.78-1.93 (m, 9H), 2.0-4.05 (m, 13H), 5.11-5.19 (m, 2H),

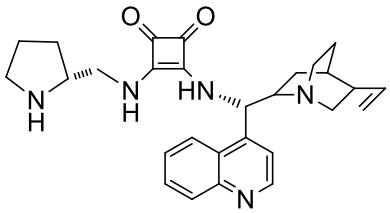
5.65-5.83 (m, 1H), 6.25 (s, br, 1H), 7.50-8.73 (m, 6H) ppm; ^{13}C NMR (100Hz, $CDCl_3$) δ: 183.9, 180.7, 168.2, 166.7, 155.4, 149.9, 139.9, 138.8, 130.1, 129.5, 126.8, 124.1, 115.0, 114.6, 59.2, 49.4, 46.9, 46.5, 45.8, 42.0, 39.2, 28.6, 27.9, 25.1, 24.2, 23.3. HRMS (ESI) calcd for $C_{28}H_{33}N_5O_2H$ $[M + H]^+$ 472.2713; found 472.2707; m.p. 177-180 ºC.

Catalyst (1c)



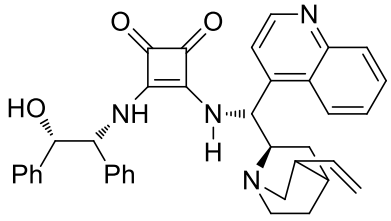
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.91 (d, 1H), 8.53 (d, 1H), 8.13 (d, 1H), 7.85 – 7.52 (m, 3H), 6.22 (s, 3H), 5.78 (s, 1H), 5.19 – 4.91 (m, 2H), 3.64 (d, 4H), 3.19 (d, 2H), 2.75 (t, 3H), 2.36 (s, 1H), 1.99 (s, 5H), 1.65 (d, 3H), 1.44 (s, 1H), 1.25 (s, 1H), 1.11 (t, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.85, 182.09, 178.96, 168.09, 167.82, 150.28, 148.36, 145.38, 140.63, 130.34, 129.66, 127.49, 126.69, 123.30, 115.21, 60.13, 55.42, 45.58, 44.99, 40.59, 38.88, 27.62, 27.26, 27.07, 25.73, 24.44, 23.72, 9.63;. HRMS (ESI) calcd for $C_{28}H_{33}N_5O_2H$ $[M + H]^+$ 472.26343; found 472.27070; m.p. 188-193 ºC

Catalyst (1d)



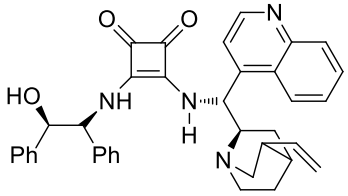
^{1}H NMR (400 MHz, $CDCl_3$) δ = 11.81 (s, 4H), 10.15 – 9.27 (m, 2H), 9.05 (s, 1H), 8.56 (s, 1H), 8.28 (s, 1H), 7.81 (d, 1H), 5.80 (s, 1H), 5.58 (s, 1H), 5.35 (d, 1H), 3.91 (d, 3H), 3.60 (s, 4H), 3.27 (s, 2H), 2.78 (s, 1H), 1.98 (s, 5H), 1.48 (s, 3H), 1.40 (s, 4H), 1.26 (s, 1H), 1.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.79, 182.35, 168.25, 167.61, 150.25, 148.29, 139.78, 139.69, 130.02, 129.60, 127.33, 126.72, 115.13, 115.02, 60.35, 57.68, 49.11, 48.60, 46.50, 46.19, 45.47, 38.84, 27.42, 26.09, 25.10, 24.00, 23.94, 18.34. HRMS (ESI) calcd for $C_{28}H_{33}N_5O_2H$ $[M + H]^+$ 472.26343; found 472.27070; m.p. 151-154 °C

Catalyst (2a)



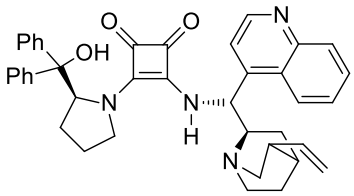
^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.78–0.91 (m, 2H), 0.99-1.04 (m, 1H), 1.48-1.54 (m, 3H), 2.18-2.23 (m, 1H), 2.63 – 2.93 (m, 4H), 3.06-3.09 (m, 1H), 4.96 (d, *J* = 4.5 Hz, 1H), 5.05 (d, *J* = 10.5 Hz, 1H), 5.14 (d, *J* = 17.4 Hz, 1H), 5.20-5.23 (m, 1H), 5.76-5.84 (m, 1H), 6.01 (d, *J* = 11.0 Hz, 1H), 7.03-7.22 (m, 9H), 7.62 (d, *J* = 4.5 Hz, 1H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.81 (t, *J* = 7.5 Hz, 1H), 7.97 (t, *J* = 7.7 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 8.40 (d, *J* = 8.4 Hz, 1H), 8.98 (d, *J* = 4.5 Hz, 1H). ^{13}C NMR (100MHz, DMSO-d_6) δ 182.8, 182.6, 167.6, 163.5, 151.1, 148.6, 145.7, 143.3, 141.5, 139.5, 136.5, 135.4, 131.6, 131.1, 130.6, 129.5, 128.6, 128.0, 127.0, 126.7, 124.0, 115.3, 75.6, 73.2, 63.1, 59.9, 49.6, 49.4, 27.9, 26.8, 25.9. HRMS (ESI) calcd for $C_{37}H_{36}N_4O_3H$ $[M + H]^+$ 585.2866; found 585.2876; m.p. 286-189 °C.

Catalyst (2b)



^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.80–0.90 (m, 2H), 0.98-1.04 (m, 1H), 1.51-1.52 (m, 3H), 2.2 (s, br, 1H), 2.60 – 3.23 (m, 4H), 5.12 (d, *J* = 4.5 Hz, 1H), 5.16 (d, *J* = 10.5 Hz, 1H), 5.19 (d, *J* = 17.4 Hz, 1H), 5.20-5.23 (m, 1H), 5.81-5.84 (m, 1H), 5.95-5.97 (m, 1H), 6.07, (s, br, 1H), 7.00-7.18 (m, 9H), 7.64-7.76 (m, 2H), 7.78 (t, *J* = 7.5 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 8.10-8.13 (m, 1H), 8.40 (d, *J* = 8.5 Hz, 1H), 8.96 (d, *J* = 5.0 Hz, 1H). ^{13}C NMR (100MHz, DMSO-d_6) δ 182.9, 182.4, 167.3, 163.3, 150.9, 148.5, 142.3, 141.3, 139.5, 139.0, 133.4, 132.6, 131.1, 130.6, 129.9, 128.6, 128.0, 127.6, 126.8, 123.6, 115.1, 81.3, 75.4, 73.5, 62.7, 59.5, 49.4, 27.7, 26.0, 25.5. HRMS (ESI) calcd for $C_{37}H_{36}N_4O_3H$ $[M + H]^+$ 585.2866; found 585.2876; m.p. 279-283 ºC.

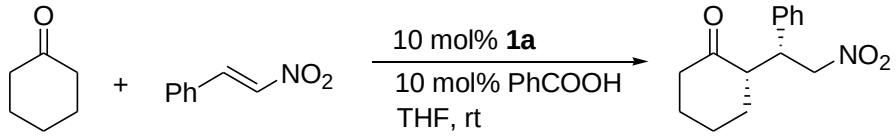
Catalyst (3)



^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.45 (s, 1H), 8.11 (s, 1H), 7.81 – 7.43 (m, 3H), 7.43 – 6.97 (m, 11H), 5.54 – 5.12 (m, 3H), 3.65 (s, 1H), 3.33 (s, 4H), 2.63 (s, 1H), 2.17 (s, 1H), 2.07 (s, 2H), 1.85 (s, 5H), 1.54 (s, 2H), 1.36–1.08 (m, 3H), 1.03 – 0.81 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$) δ: 183.9, 178.9, 169.5, 132.4, 130.0, 129.8, 128.2, 128.1, 127.9, 127.6, 123.2, 49.9, 49.1, 45.4, 29.7, 26.9, 24.9, 23.7. HRMS (ESI) calcd for $C_{40}H_{40}N_4O_3H$ $[M + H]^+$ 625.3179; found 625.3176; m.p. 192-195 ^{o}C.

3. Characterization data of Michael products (12a-m)

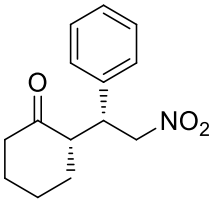
Representative procedure for the Asymmetric Michael Reaction of Nitroolefin 11a with Cyclohexanone (10)



10 **11a** **12a**

The organocatalyst **1a** (23.5 mg, 0.05 mmol), $PhCO_2H$ (6.0 mg, 0.05 mmol) and cyclohexanone **10** (490.7 mg, 5.0 mmol) were stirred in 2 mL of THF for 10 min at room temperature. *trans-β*-Nitrostyrene **11a** (75.0 mg, 0.5 mmol) was then added and the reaction mixture was stirred for 48 h. The reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether / ethyl acetate (6:1)) to give the corresponding pure Michael product **12a** (29.5 mg, 60%) as a white solid. Compounds **12a-l** are known [3].

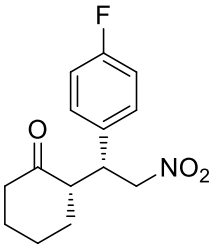
2-(2-nitro-1-phenylethyl) cyclohexanone (12a)



The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 90:10, flow rate 1.0 mL/min, λ = 220 nm, 25 ^{o}C). t_R (minor) = 20.0 min; t_R (major) = 24.8 min, *syn*/*anti* = 88/12, *syn*: ee = 93%.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 – 7.23 (m, 3H), 7.18 – 7.15 (m, 2H), 4.94 (dd, *J* = 12.5, 4.5 Hz, 1H), 4.64 (dd, *J* = 12.5, 9.9 Hz, 1H), 3.76 (td, *J* = 9.9, 4.5 Hz, 1H), 2.74 – 2.64 (m, 1H), 2.54 – 2.33 (m, 2H), 2.13 – 2.02 (m, 1H), 1.83 – 1.63 (m, 3H), 1.58 – 1.48 (m, 1H), 1.33 – 1.13 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) 212.0, 137.9, 129.2, 128.4, 128.1, 79.1, 52.8, 44.2, 43.0, 33.5, 28.6, 25.2; m.p. 125-127 ^{o}C.

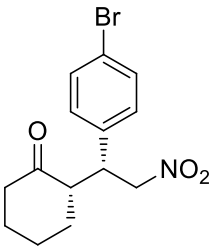
2-(1-(4-fluorophenyl)-2-nitroethyl) cyclohexanone (12b)



The ee was determined by HPLC (Chiralpak OD column, hexane/*i*-PrOH 98:2, flow rate 1.0 mL/min, λ = 220 nm, 25 ^{o}C). t_R (minor) = 25.4 min; t_R (major) = 27.0 min, *syn*/*anti* = 86/14, *syn*: ee = 82%.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.15 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.01 (t, *J* = 8.6 Hz, 2H), 4.93 (dd, *J* = 12.5, 4.5 Hz, 1H), 4.59 (dd, *J* = 12.5, 10.1 Hz, 1H), 3.77 (td, *J* = 9.9, 4.5 Hz, 1H), 2.65 (ddd, *J* = 12.0, 10.2, 5.1 Hz, 1H), 2.51 – 2.43 (m, 1H), 2.42 – 2.33 (m, 1H), 2.14 – 2.03 (m, 1H), 1.84 – 1.53 (m, 3H), 1.25 – 1.15 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.7, 163.4, 160.9, 133.5, 133.4, 129.8, 129.7, 116.0, 115.8, 78.8, 52.5, 43.3, 42.7, 33.2, 28.5, 25.0; m.p. 72-74 ^{o}C.

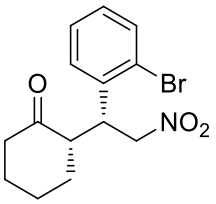
2-(1-(4-bromophenyl)-2-nitroethyl) cyclohexanone (12c)



The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 90:10, flow rate 1.0 mL/min, λ = 220 nm, 20 ^{o}C). t_R (minor) = 12.8 min; t_R (major) = 20.4 min, *syn*/*anti* = 87/13, *syn*: ee = 83%.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 4.93 (dd, *J* = 12.6, 4.5 Hz, 1H), 4.60 (dd, *J* = 12.6, 10.0 Hz, 1H), 3.75 (td, *J* = 9.9, 4.5 Hz, 1H), 2.65 (ddd, *J* = 11.6, 9.9, 5.1 Hz, 1H), 2.50 – 2.43 (m, 1H), 2.42 – 2.32 (m, 1H), 2.13 – 2.03 (m, 1H), 1.84 – 1.53 (m, 4H), 1.26 – 1.16 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): □221.5, 136.8, 131.7, 129.9, 121.7, 78.5, 52.4, 43.4, 42.8, 33.2, 28.4, 25.1; m.p. 120-122 ^{o}C.

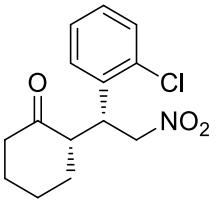
2-(1-(2-bromophenyl)-2-nitroethyl) cyclohexanone (12d)



The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 85:15, flow rate 0.8 mL/min, λ = 220 nm, 20^{o}C). t_R (minor) = 10.4 min; t_R (major) = 16.1 min, *syn*/*anti* = 97/3, *syn*: ee = 84%.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.30 (t, *J* = 7.9 Hz, 1H), 7.22 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.12 (td, *J* = 7.9, 1.7 Hz, 1H), 4.94 – 4.85 (m, 2H), 4.32 (dd, *J* = 15.3, 7.1 Hz, 1H), 2.90 (s, 1H), 2.50 – 2.43 (m, 1H), 2.43 – 2.33 (m, 1H), 2.14 – 2.05 (m, 1H), 1.86 – 1.53 (m, 4H), 1.44 – 1.30 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 211.7, 137.3, 133.7, 129.1, 128.0, 42.8, 33.0, 28.5, 25.3; m.p. 80-81 ^{o}C.

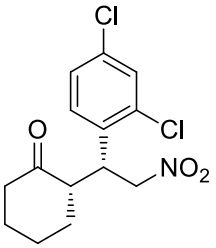
2-(1-(2-chlorophenyl)-2-nitroethyl) cyclohexanone (12e)



The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 95:5, flow rate 1.0 mL/min, λ = 220 nm, 20 ^{o}C). t_R (minor) = 11.7 min; t_R (major) = 20.5 min, *syn*/*anti* = 98/2, *syn*: ee = 93%.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 – 7.35 (m, 1H), 7.28 – 7.18 (m, 3H), 4.92 – 4.88 (m, 2H), 4.29 (dd, *J* = 16.6, 7.0 Hz, 1H), 2.92 (td, *J* = 12.1, 4.9 Hz, 1H), 2.52 – 2.45 (m, 1H), 2.44 – 2.35 (m, 1H), 2.14 – 2.07 (m, 1H), 1.85 – 1.54 (m, 4H), 1.33 (ddd, *J* = 24.9, 12.5, 3.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 211.7, 138.8, 135.4, 133.6, 130.4, 128.9, 127.4, 77.1, 51.7, 42.8, 33.1, 30.9, 28.5, 25.3.

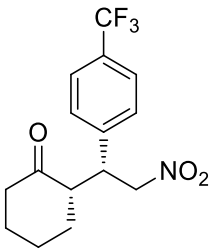
2-(1-(2,4-dichlorophenyl)-2-nitroethyl)cyclohexanone (12f)



The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 90:10, flow rate 1.0 mL/min, λ = 220 nm, 20^{o}C). t_R (minor) = 9.3 min; t_R (major) = 13.1 min, *syn*/*anti* = 80/20, *syn*: ee = 85%.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 (d, *J* = 2.1 Hz, 1H), 7.23 (d, *J* = 2.1 Hz, 1H), 7.19 (s, 1H), 4.89 (d, *J* = 2.1 Hz, 1H), 4.87 (s, 1H), 4.24 (dd, *J* = 15.7, 7.9 Hz, 1H), 2.92 – 2.82 (m, 1H), 2.52 – 2.44 (m, 1H), 2.43 – 2.33 (m, 1H), 2.16 – 2.07 (m, 1H), 1.87 – 1.61 (m, 4H), 1.39 – 1.29 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 211.3, 135.1, 134.1, 133.5, 130.2, 127.7, 51.6, 42.8, 40.3, 33.1, 28.5, 27.2, 25.3, m.p. 105-107 ^{o}C.

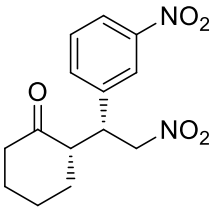
2-(1-(4-trifluorophenyl)-2-nitroethyl) cyclohexanone (12g)



The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 95:5, flow rate 0.8 mL/min, λ = 220 nm, 20°C). t_R (minor) = 18.4 min; t_R (major) = 39.7 min, *syn*/*anti* = 88/12, *syn*: ee = 80%.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.98 (dd, *J* = 12.8, 4.5 Hz, 1H), 4.67 (dd, *J* = 12.8, 10.1 Hz, 1H), 3.86 (td, *J* = 9.8, 4.5 Hz, 1H), 2.70 (ddd, *J* = 12.9, 9.9, 5.1 Hz, 1H), 2.52 – 2.44 (m, 1H), 2.43 – 2.33 (m, 1H), 2.14 – 2.05 (m, 1H), 1.84 – 1.77 (m, 1H), 1.74 – 1.57 (m, 3H), 1.30 – 1.19 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): □211.2, 142.1, 132.3 (q, *J* = 38.5 Hz), 128.6, 125.7, 109.3 (q, *J* = 275.5 Hz), 78.3, 52.3, 43.7, 42.7, 33.2, 28.4, 25.1; m.p. 85-86 °C.

2-(1-(3-nitrophenyl)-2-nitroethyl) cyclohexanone (12h)

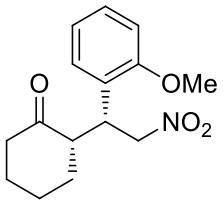


The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 95:5, flow rate 0.8 mL/min, λ = 220 nm, 20°C). t_R (minor) = 12.0 min; t_R (major) = 16.1 min, *syn*/*anti* = 86/14, *syn*: ee = 86%.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.17 – 8.13 (m, 1H), 8.09 (t, *J* = 1.9 Hz, 1H), 7.56 – 7.52 (m, 2H), 5.01 (dd, *J* = 13.0, 4.4 Hz, 1H), 4.71 (dd, *J* = 13.0, 10.2 Hz, 1H), 3.95 (td, *J* = 9.8, 4.4 Hz, 1H), 2.75 (ddd, *J* = 14.1, 9.4, 5.1 Hz, 1H), 2.53 – 2.47 (m, 1H), 2.44 – 2.38 (m, 1H), 2.13 – 2.09 (m, 1H), 1.84 – 1.79 (m, 1H), 1.65 – 1.54 (m, 3H), 1.34 – 1.27 (m, *J* = 12.6, 4.0 Hz, 1H). ^{13}C NMR

(100 MHz, $CDCl_3$): □211.0, 148.6, 143.9, 140.2, 134.9, 130.0, 122.9, 78.1, 52.2, 43.7, 42.8, 33.2, 30.9, 28.3, 25.1; m.p. 77-79 °C.

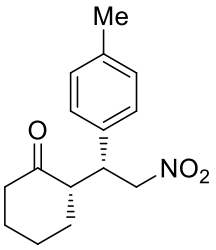
2-(1-(2-methoxyphenyl)-2-nitroethyl) cyclohexanone (12i)



The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 99:1, flow rate 1.0 mL/min, λ = 220 nm, 20°C). t_R (minor) = 22.5 min; t_R (major) = 23.5 min, *syn*/*anti* = 97/3, *syn*: ee = 81%.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 – 7.22 (m, 1H), 7.08 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.88 (t, *J* = 8.4 Hz, 2H), 4.83 (dd, *J* = 7.0, 4.7 Hz, 1H), 4.00 – 3.92 (m, 1H), 3.84 (s, 3H), 2.98 (td, *J* = 11.6, 5.2 Hz, 1H), 2.51 – 2.44 (m, 1H), 2.43 – 2.34 (m, 1H), 2.11 – 2.03 (m, 1H), 1.80 – 1.54 (m, 4H), 1.20 (dd, *J* = 13.0, 3.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): □212.6, 157.6, 131.0, 129.0, 125.4, 120.9, 111.0, 55.4, 50.6, 41.3, 40.2, 33.3, 28.6, 25.2; m.p. 98-100 °C.

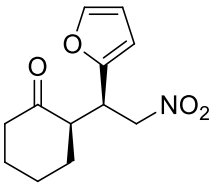
2-(2-nitro-1-p-tolylethyl) cyclohexanone (12j)



The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 95:5, flow rate 1.0 mL/min, λ = 220 nm, 20°C). t_R (minor) = 21.1 min; t_R (major) = 32.2 min, *syn*/*anti* = 83/7, *syn*: ee = 80%.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.12 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 8.1 Hz, 2H), 4.91 (dd, *J* = 12.4, 4.6 Hz, 1H), 4.61 (dd, *J* = 12.3, 9.9 Hz, 1H), 3.72 (td, *J* = 9.9, 4.5 Hz, 1H), 2.71 – 2.62 (m, 1H), 2.50 – 2.44 (m, 1H), 2.43 – 2.33 (m, 1H), 2.11 – 2.03 (m, 1H), 1.81 – 1.64 (m, 3H), 1.62 – 1.51 (m, 1H), 1.25 – 1.19 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): □212.1, 137.5, 134.6, 129.6, 128.0, 79.0, 52.6, 43.6, 42.7, 33.2, 28.5, 25.0, 21.1; m.p. 123-127 °C.

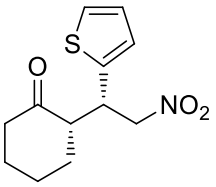
2-(1-(furan-2-yl)-2-nitroethyl) cyclohexanone (12k)



The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 90:10, flow rate 1.0 mL/min, λ = 220 nm, 20°C). t_R (minor) = 26.9 min; t_R (major) = 20.9 min, *syn*/*anti* = 80/20, *syn*: ee = 81%.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 (d, *J* = 1.5 Hz, 1H), 6.29 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.18 (d, *J* = 3.2 Hz, 1H), 4.79 (dd, *J* = 12.5, 4.8 Hz, 1H), 4.67 (dd, *J* = 12.5, 9.4 Hz, 1H), 3.97 (td, *J* = 9.2, 4.8 Hz, 1H), 2.79 – 2.71 (m, 1H), 2.49 – 2.42 (m, 1H), 2.41 – 2.31 (m, 1H), 2.13 – 2.06 (m, 1H), 1.87 – 1.80 (m, 1H), 1.79 – 1.72 (m, 1H), 1.69 – 1.59 (m, 2H), 1.31 – 1.26 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) □211.0, 151.0, 142.3, 110.3, 109.0, 76.7, 51.1, 42.6, 37.6, 32.5, 28.2, 25.1.

2-(1-(thiophen-2-yl)-2-nitroethyl) cyclohexanone (12l)

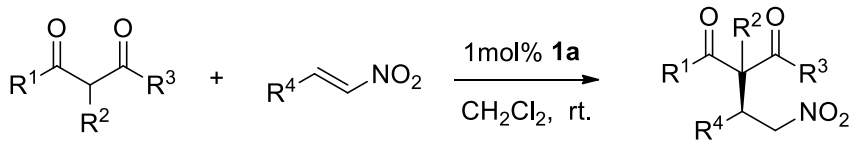


The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 95:5, flow rate 1.0 mL/min, λ = 220 nm, 20°C). t_R (minor) = 20.1 min; t_R (major) = 23.6 min, *syn*/*anti* = 83/7, *syn*: ee = 75%.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.21 (dd, *J* = 7.1, 4.1 Hz, 1H), 6.93 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.87 (dd, *J* = 3.5, 0.7 Hz, 1H), 4.89 (dd, *J* = 12.6, 4.7 Hz, 1H), 4.65 (dd, *J* = 12.6, 9.4 Hz, 1H), 4.13 (td, *J* = 9.1, 4.7 Hz, 1H), 2.72 – 2.64 (m, 1H), 2.50 – 2.43 (m, 1H), 2.41 – 2.31 (m, 1H), 2.14 – 2.04 (m, 1H), 1.95 – 1.87 (m, 1H), 1.87 – 1.80 (m, 1H), 1.67 – 1.60 (m, 2H), 1.32 (dd, *J* = 12.8, 3.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): □211.3, 140.5, 126.9, 126.6, 125.0, 79.2, 53.4, 42.6, 39.4, 32.8, 28.3, 25.1; m.p. 84-86 °C.

4. Characterization data of Michael products (14a-l)

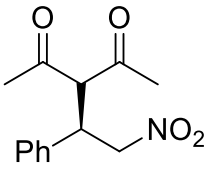
General procedure for the Asymmetric Michael Reaction of Nitroolefin 11 with diketones (13)



13 **11** **14**

To a solution of nitroolefin **11** (0.5 mmol) in CH_2Cl_2 (1.5 mL) was added catalyst **1a** (0.005 mmol) and 1,3-dicarbonyl compound **13** (5.0 mmol). Upon consumption of nitroolefin substrate (monitored by TLC), the reaction mixture was concentrated and purified by column chromatography to afford the conjugate addition product **14**. Relative and absolute configurations of the products were determined by comparison of ^{1}H NMR, ^{13}C NMR spectra and HPLC data with the known literature. Compounds **14a-l** are known.[1]

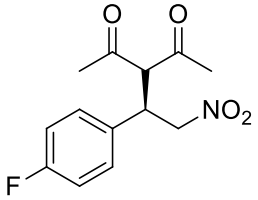
3-(2-nitro-1-phenylethyl)pentane-2,4-dione (14a)



The ee was determined by HPLC (Chiralpak AD column, hexane/EtOH 90:10, flow rate 1.0 mL/min, λ = 220 nm, 25^{o}C). t_R (minor) = 28.3 min; t_R (major) = 30.4 min, ee = 93%.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 – 7.26 (m, 3H), 7.19 (dd, *J* = 7.9, 1.5 Hz, 2H), 4.69 – 4.59 (m, 2H), 4.37 (d, *J* = 10.8 Hz, 1H), 4.24 (ddd, *J* = 10.8, 7.6, 5.1 Hz, 1H), 2.29 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 201.8, 201.0, 136.0, 129.3, 128.6, 128.0, 78.2, 70.7, 42.8, 30.4, 29.6; m.p. 115-118 ^{o}C.

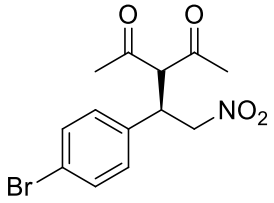
3-(1-(4-fluorophenyl)-2-nitroethyl)pentane-2,4-dione (14b)



The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 90:10, flow rate 1.0 mL/min, λ = 220 nm, 25ºC). t_R (minor) = 10.8 min; t_R (major) = 22.9 min, ee = 88%.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.18 (dd, *J* = 8.7, 5.1 Hz, 2H), 7.03 (t, *J* = 8.6 Hz, 2H), 4.63 – 4.59 (m, 2H), 4.34 (d, *J* = 10.8 Hz, 1H), 4.24 (ddd, *J* = 10.9, 7.0, 5.5 Hz, 1H), 2.30 (s, 3H), 1.97 (s, 3H). ^{13}CNMR (100 MHz, $CDCl_3$): 221.4, 169.4, 137.6, 128.7, 126.8, 126.1, 77.62, 62.4, 62.3, 42.2, 38.0, 31.6, 19.4, 14.0.

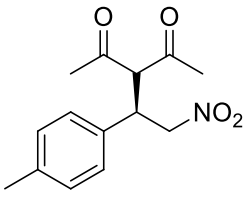
3-(1-(4-bromophenyl)-2-nitroethyl)pentane-2,4-dione (14c)



The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 90:10, flow rate 1.0 mL/min, λ = 220 nm, 25ºC). t_R (minor) = 32.5 min; t_R (major) = 35.1 min, ee = 81%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 4.56 – 4.52 (m, 2H), 4.26 (d, *J* = 10.7 Hz, 1H), 4.18 – 4.11 (m, 1H), 2.23 (s, 3H), 1.91 (s, 3H). ^{13}CNMR (100 MHz, $CDCl_3$): 200.4, 199.5, 134.1, 131.5, 128.6, 121.7, 76.8, 69.4, 41.2, 29.4, 28.6.

3-(2-nitro-1-(p-tolyl)ethyl)pentane-2,4-dione (14d)

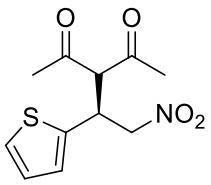


The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 90:10, flow rate 1.0 mL/min, λ = 220 nm, 25 ºC). t_R (minor) = 10.6 min; t_R (major) = 18.0 min, ee = 88%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 4.63 – 4.58 (m, 2H), 4.35 (d, *J* = 10.8 Hz, 1H), 4.25 – 4.17 (m, 1H), 2.30 (s, 3H), 2.28 (s, 3H), 1.94 (s, 3H). ^{13}C

NMR (100 MHz, $CDCl_3$): 201.9, 201.2, 138.3, 132.9, 130.0, 127.8, 78.4, 70.7, 42.5, 30.4, 29.6, 21.0; m.p. 101-103 ^oC.

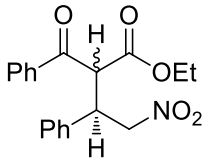
3-(2-nitro-1-(thiophen-2-yl) ethyl)pentane-2,4-dione (14e)



The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 90:10, flow rate 1.0 mL/min, λ = 220 nm, 25^{o}C). t_R (minor) = 16.3 min; t_R (major) = 21.9 min, ee = 83%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17 (dd, *J* = 5.1, 0.9 Hz, 1H), 6.87 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.82 (d, *J* = 3.3 Hz, 1H), 4.61 – 4.58 (m, 2H), 4.51 – 4.44 (m, 1H), 4.33 (d, *J* = 10.1 Hz, 1H), 2.23 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 200.5, 199.6, 137.4, 126.4, 126.0, 124.7, 77.5, 70.0, 37.2, 29.5, 28.6.

2-benzoyl-4-nitro-3-phenylbutyric acid ethyl ester (14f)

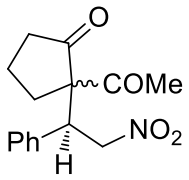


The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 90:10, flow rate 1.0 mL/min, λ = 220 nm, 25^{o}C) (1:1 mixture of diastereomers). Major diastereomer: t_R (minor) = 14.3 min; t_R (major) = 17.5 min, ee = 85%; minor diastereomer: t_R (minor) = 16.8 min; t_R (major) = 34.6 min, ee = 84%.

major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 7.2 Hz, 2H), 7.58 – 7.53 (m, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.34 – 7.28 (m, 3H), 7.23 – 7.17 (m, 3H), 4.96 (d, *J* = 1.7 Hz, 1H), 4.95 – 4.90 (m, 2H), 4.46 – 4.40 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H).

minor diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (d, *J* = 7.2 Hz, 2H), 7.62 (t, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.24 – 7.16 (m, 3H), 4.95 – 4.90 (m, 1H), 4.79 (t, *J* = 6.4 Hz, 2H), 4.49 (ddd, *J* = 8.4, 7.4, 4.2 Hz, 1H), 3.87 (qd, *J* = 7.1, 2.0 Hz, 2H), 0.90 (t, *J* = 7.1 Hz, 3H); m.p. 94-96 ^{o}C.

2-acetyl-2-(2-nitro-1-phenylethyl)cyclopentanone (14g)

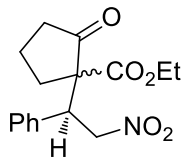


The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 90:10, flow rate 1.0 mL/min, λ = 220 nm, 25ºC) (1:1 mixture of diastereomers). Major diastereomer: t_R (minor) = 14.5 min; t_R (major) = 24.0 min, ee = 88%; minor diastereomer: t_R (minor) = 12.6 min; t_R (major) = 18.5 min, ee = 86%.

major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 – 7.17 (m, 4H), 7.11 (dd, *J* = 7.2, 2.2 Hz, 1H), 4.95 (dd, *J* = 13.1, 11.0 Hz, 1H), 4.53 (dd, *J* = 13.1, 3.8 Hz, 1H), 4.21 (dd, *J* = 11.0, 3.8 Hz, 1H), 2.43 – 2.27 (m, 2H), 2.11 (s, 3H), 1.96 – 1.86 (m, 2H), 1.71 – 1.60 (m, 1H), 1.37 – 1.28 (m, 1H).

minor diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 – 7.17 (m, 4H), 7.11 (dd, *J* = 7.2, 2.2 Hz, 1H), 4.79 (dd, *J* = 13.5, 11.6 Hz, 1H), 4.44 (dd, *J* = 13.5, 3.9 Hz, 1H), 4.32 (dd, *J* = 11.6, 3.8 Hz, 1H), 2.54 – 2.45 (m, 1H), 2.26 (s, 3H), 2.17 – 1.96 (m, 2H), 1.71 – 1.61 (m, 3H).

1-(2-nitro-1-phenylethyl)-2-oxocyclopentanecarboxylic acid ethyl ester (14h)

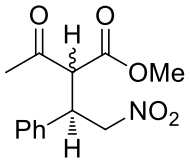


The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 90:10, flow rate 1.0 mL/min, λ = 220 nm, 25ºC) (24:1 mixture of diastereomers). Major diastereomer: t_R (minor) = 15.6 min; t_R (major) = 26.3 min, ee = 83%; minor diastereomer: t_R (minor) = 13.6 min; t_R (major) = 20.6 min, ee = 87%.

major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 – 7.23 (m, 5H), 5.17 (dd, *J* = 13.6, 3.9 Hz, 1H), 5.01 (dd, *J* = 13.6, 11.0 Hz, 1H), 4.25 – 4.18 (m, 2H), 4.08 (dd, *J* = 11.0, 3.9 Hz, 1H), 2.42 – 2.26 (m, 2H), 2.08 – 1.77 (m, 4H), 1.27 (t, *J* = 7.1 Hz, 3H).

minor diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 – 7.23 (m, 5H), 5.29 (dd, *J* = 13.4, 11.1 Hz, 1H), 4.84 (dd, *J* = 13.5, 3.5 Hz, 1H), 4.33 – 4.26 (m, 2H), 4.14 (dd, *J* = 12.5, 5.4 Hz, 1H), 2.54 – 2.43 (m, 2H), 2.19 – 2.08 (m, 6H), 1.29 (t, *J* = 7.1 Hz, 3H).

2-acetyl-4-nitro-3-phenylbutyric acid methyl ester (14i)

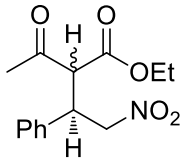


The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 90:10, flow rate 1.0 mL/min, λ = 220 nm, 25^{o}C) (1.1:1 mixture of diastereomers). Major diastereomer: t_R (minor) = 27.6 min; t_R (major) = 23.9 min, ee = 86%; minor diastereomer: t_R (minor) = 33.6 min; t_R (major) = 42.8 min, ee = 80%.

major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 – 7.27 (m, 3H), 7.22 – 7.18 (m, 2H), 4.82 (d, *J* = 4.7 Hz, 1H), 4.78 (d, *J* = 1.5 Hz, 1H), 4.27 – 4.17 (m, 1H), 4.14 (d, *J* = 9.6 Hz, 1H), 3.53 (s, 3H), 2.30 (s, 3H).

minor diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 – 7.27 (m, 3H), 7.22 – 7.18 (m, 2H), 4.84 (d, *J* = 2.0 Hz, 1H), 4.77 (s, 1H), 4.27 – 4.17 (m, 1H), 4.05 (d, *J* = 9.8 Hz, 1H), 3.78 (s, 3H), 2.05 (s, 3H); m.p. 100-102 ^{o}C.

2-acetyl-4-nitro-3-phenylbutyric acid ethyl ester (14j)

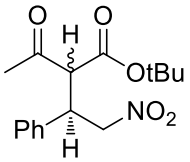


The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 90:10, flow rate 1.0 mL/min, λ = 220 nm, 25^{o}C) (1.1:1 mixture of diastereomers). Major diastereomer: t_R (minor) = 32.4 min; t_R (major) = 29.6 min, ee = 87%; minor diastereomer: t_R (minor) = 35.3 min; t_R (major) = 39.8 min, ee = 86%.

major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 – 7.26 (m, 3H), 7.20 (d, *J* = 7.5 Hz, 2H), 4.84 (dd, *J* = 6.9, 4.6 Hz, 1H), 4.75 (d, *J* = 6.2 Hz, 1H), 4.27 – 4.16 (m, 2H), 4.12 (d, *J* = 10.0 Hz, 1H), 3.97 (q, *J* = 7.1 Hz, 1H), 2.30 (s, 3H), 1.00 (t, *J* = 7.1 Hz, 3H).

minor diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 – 7.26 (m, 3H), 7.20 (d, *J* = 7.5 Hz, 2H), 4.84 (dd, *J* = 6.9, 4.6 Hz, 1H), 4.75 (d, *J* = 6.2 Hz, 1H), 4.27 – 4.16 (m, 2H), 4.03 (d, *J* = 9.7 Hz, 1H), 3.97 (q, *J* = 7.1 Hz, 1H), 2.06 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

2-acetyl-4-nitro-3-phenylbutyric acid *tert*-butyl ester (14k)

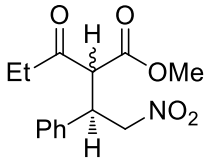


The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 90:10, flow rate 1.0 mL/min, λ = 220 nm, 25ºC) (12:1 mixture of diastereomers). Major diastereomer: t_R (minor) = 9.4 min; t_R (major) = 12.6 min, ee = 86%; minor diastereomer: t_R (minor) = 18.2 min; t_R (major) = 15.3 min, ee = 86%.

major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 – 7.27 (m, 3H), 7.21 (dd, *J* = 7.9, 1.5 Hz, 2H), 4.71 (dd, *J* = 8.3, 6.3 Hz, 2H), 4.17 – 4.07 (m, 1H), 4.02 (d, *J* = 10.4 Hz, 1H), 2.31 (s, 3H), 1.16 (s, 9H); m.p. 128-132 ºC.

minor diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 – 7.27 (m, 3H), 7.21 (dd, *J* = 7.9, 1.5 Hz, 2H), 4.86 – 4.81 (m, 2H), 4.19 (dd, *J* = 9.2, 4.1 Hz, 1H), 3.92 (d, *J* = 9.6 Hz, 1H), 2.06 (s, 3H), 1.47 (s, 9H).

2-(-2-nitro-1-phenylethyl)-3-oxopentanoic methyl ester (14l)



The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 90:10, flow rate 1.0 mL/min, λ = 220 nm, 25ºC) (1:1 mixture of diastereomers). Major diastereomer: t_R (minor) = 19.7 min; t_R (major) = 31.5 min, ee = 86%; minor diastereomer: t_R (minor) = 28.9 min; t_R (major) = 36.5 min, ee = 80%.

major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 – 7.26 (m, 3H), 7.19 (d, *J* = 7.0 Hz, 2H), 4.85 (dd, *J* = 8.2, 7.0 Hz, 1H), 4.79 (d, *J* = 6.4 Hz, 1H), 4.28 – 4.20 (m, 1H), 4.03 (d, *J* = 9.9 Hz, 1H), 3.75 (s, 3H), 2.67 (dq, *J* = 18.5, 7.2 Hz, 1H), 2.53 – 2.42 (m, 1H), 0.83 (t, *J* = 7.2 Hz, 3H).

minor diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 – 7.26 (m, 3H), 7.19 (d, *J* = 7.0 Hz, 2H), 4.85 (dd, *J* = 8.2, 7.0 Hz, 1H), 4.79 (d, *J* = 6.4 Hz, 1H), 4.28 – 4.20 (m, 1H), 4.14 (d, *J* = 9.3 Hz, 1H), 3.52 (s, 3H), 2.52 – 2.42 (m, 1H), 2.13 (dq, *J* = 18.5, 7.2 Hz, 1H), 1.06 (t, *J* = 7.2 Hz, 3H).

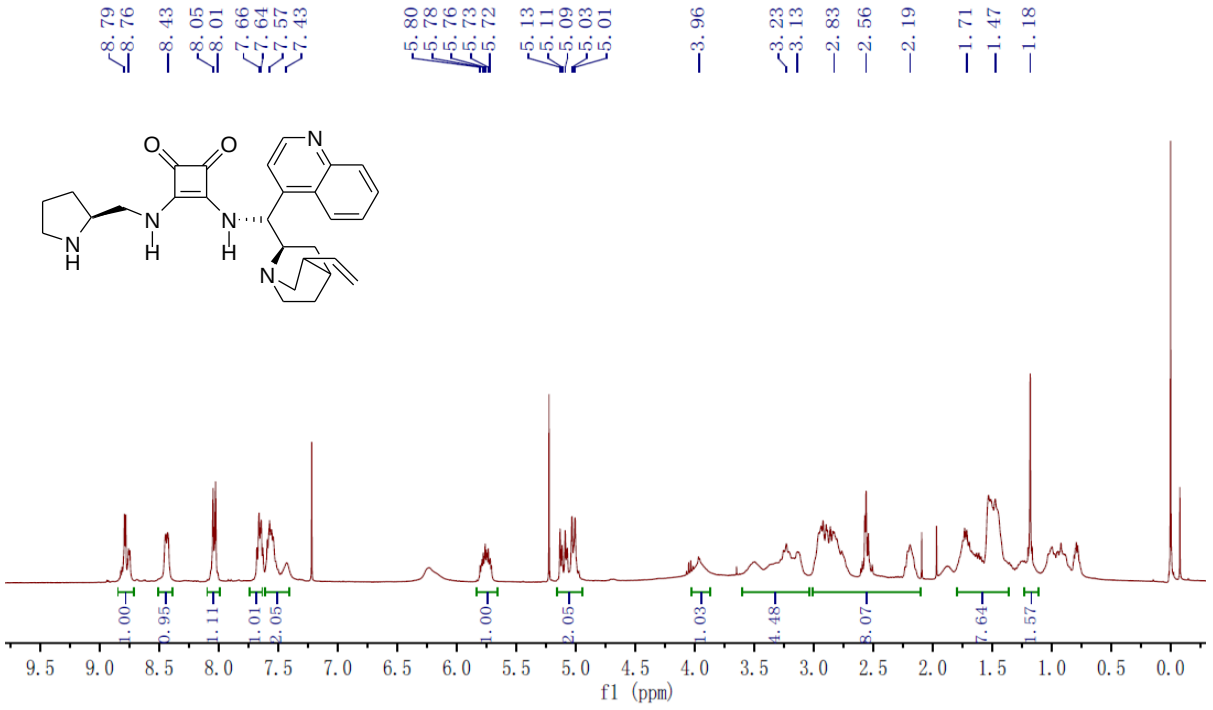
5. Synthesis and Characterization data of (15)

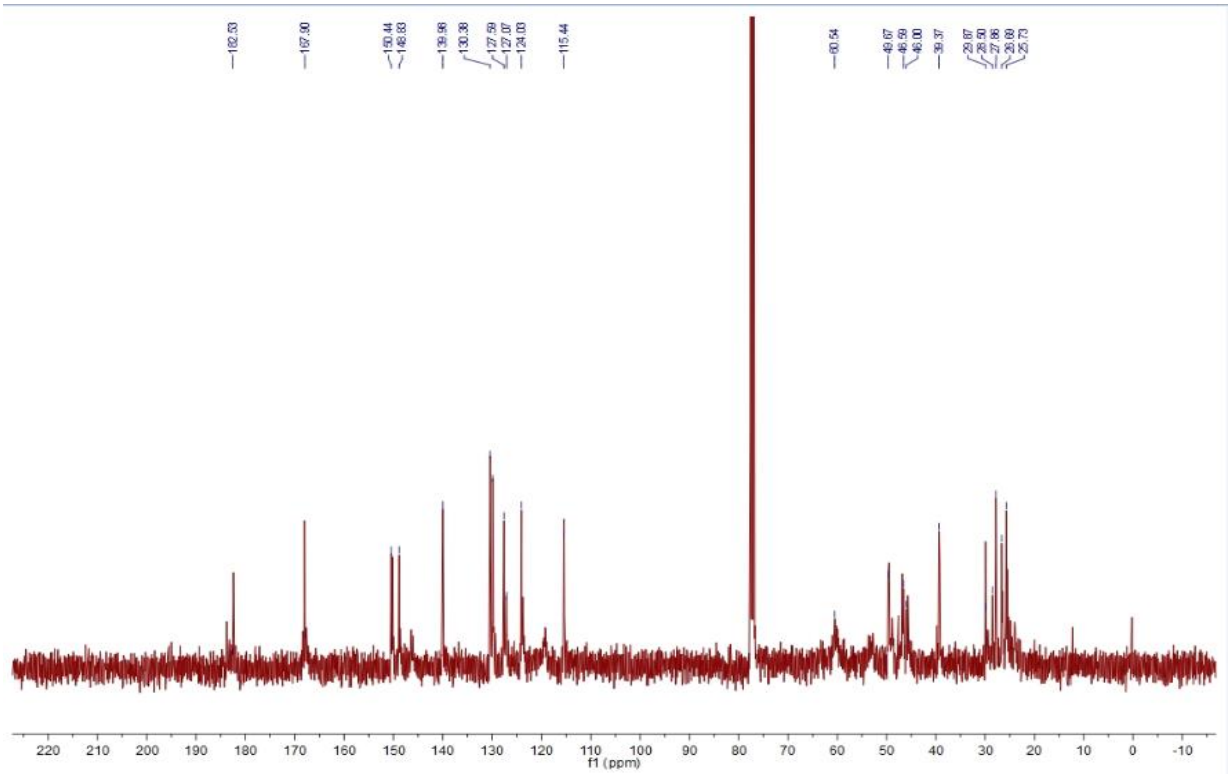
A suspension of **14j** (0.2 mmol) and zinc powder (5.0 mmol, 25 eq.) in 5 mL of ethanol was heated at 70 °C with stirring, and 2 mL of acetate acid was added dropwise and the resulting mixture was then refluxed for 30 min. Upon completion as shown by TLC, the reaction mixture was cooled to room temperature. Saturated aqueous ammonia was added dropwise to the reaction mixture till the pH>8, which was then extracted with CH_2Cl_2 (3 × 25 mL). The CH_2Cl_2 extracts were washed with water, dried ($MgSO_4$), filtered, and were removed by rotary evaporation. The remaining material was purified by flash chromatography on silica gel using a 10-30% EtOAc/hexane to give **15** as a yellow viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (m, 3H), 7.15 (m, 2H), 4.46 (m, 1H), 4.22 (m, 1H), 3.70 (m, 1H), 2.31 (m, 2H), 1.98 (s, 3H), 1.86 (m, 3H), 1.36 (m, 1H). MS *m/z*: 245 (M^+).

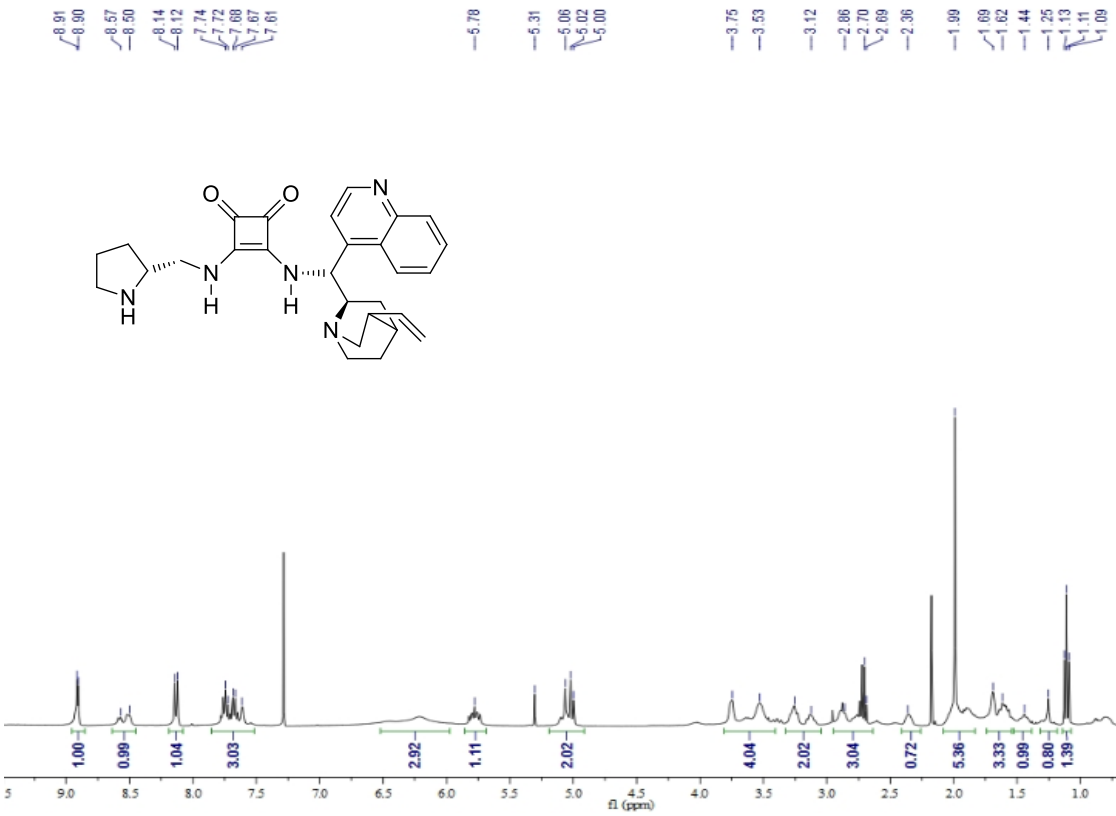
6. References

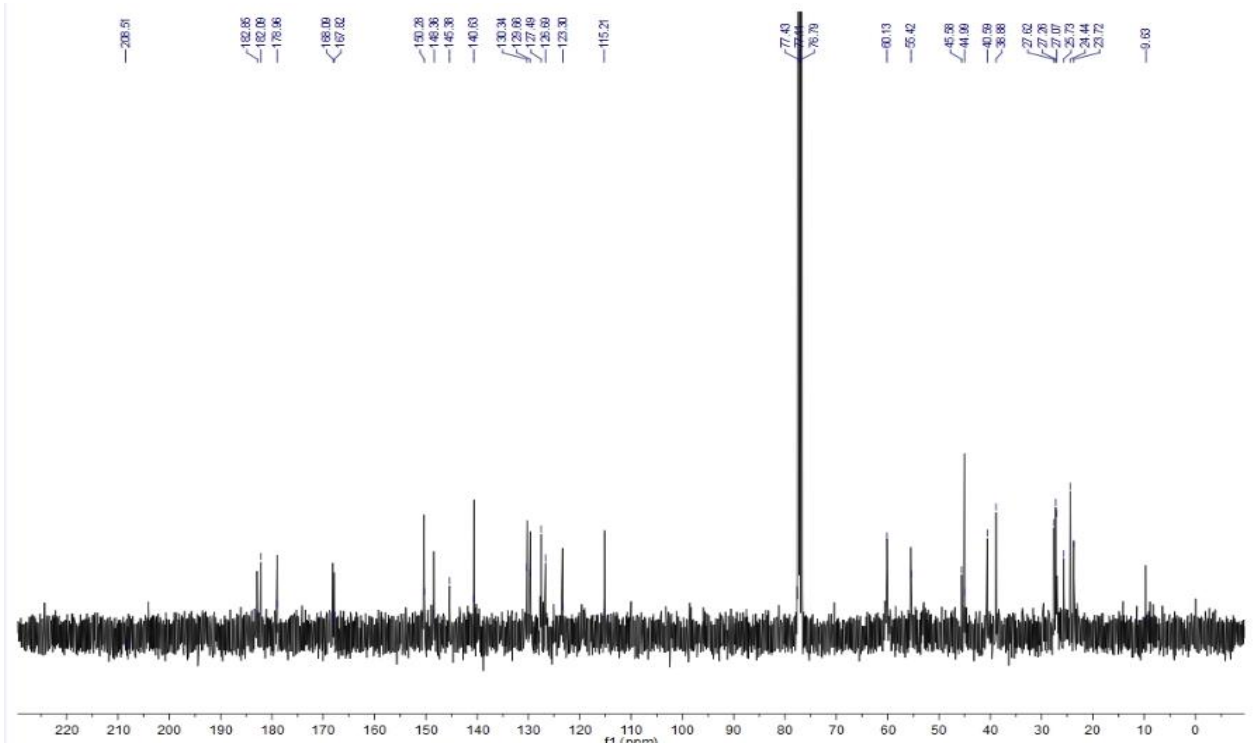
1. (a) J. P. Malerich, K. Hagihara, V. H. Rawal, *J. Am. Chem. Soc.* **2008**, *130* (*44*), 14416. (b) X. X. Jiang, Y. F. Zhang, X. Liu, G. Zhang, L. H. Lai, L. P. Wu, J. N. Zhang, R. Wang, *J. Org. Chem.* **2009**, *74* (*15*), 5562.
2. N. Dahlin,A. Bogevig, H. Adolfsson, *Adv. Synth. Catal.* **2004**, *346* (*9-10*), 1101.
3. (a) C. L. Cao, M. C. Ye, X. L. Sun, Y.Tang, *Org. Lett.* **2006**, *8* (*14*), 2901. (b) Y. J. Cao, H. H. Lu, Y. Y. Lai, L. Q. Lu, W. J. Xiao, *Synthesis* **2006**, *22*, 3795.

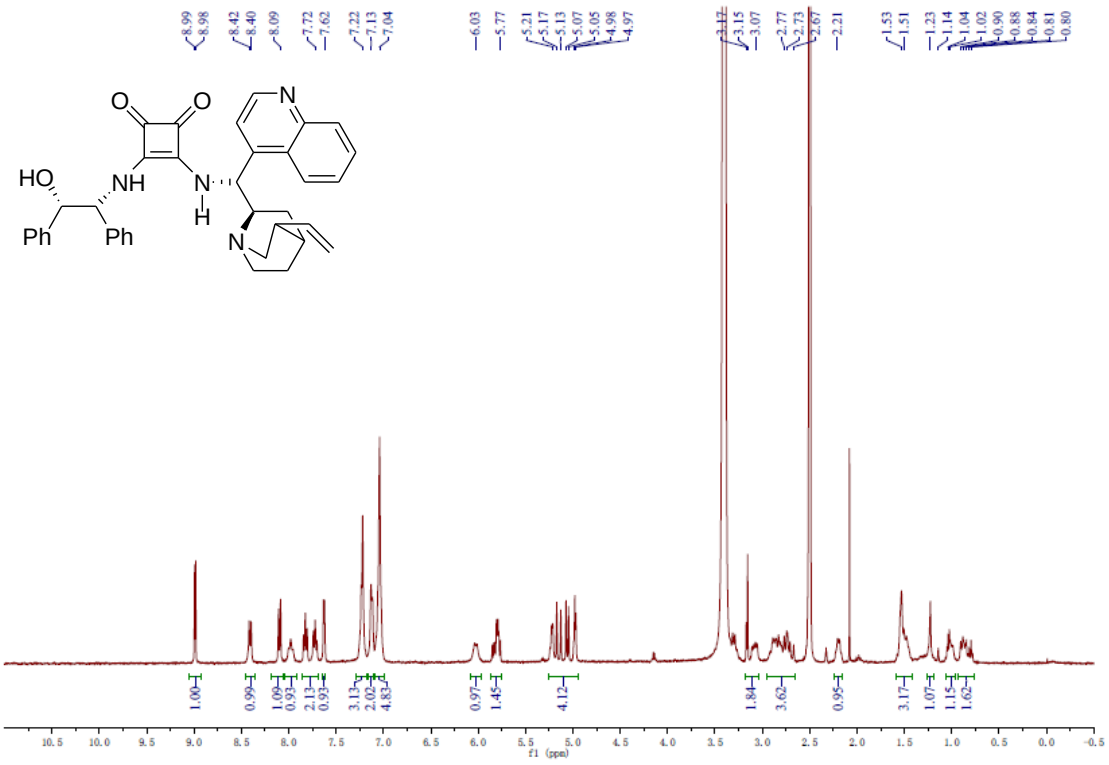
7. Representative NMR spectra

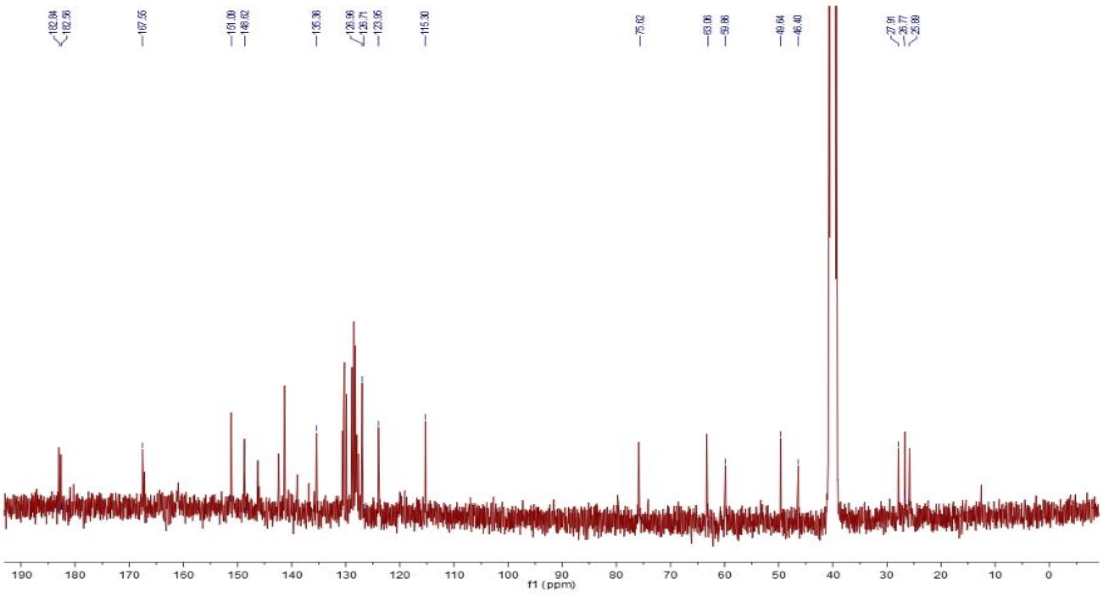


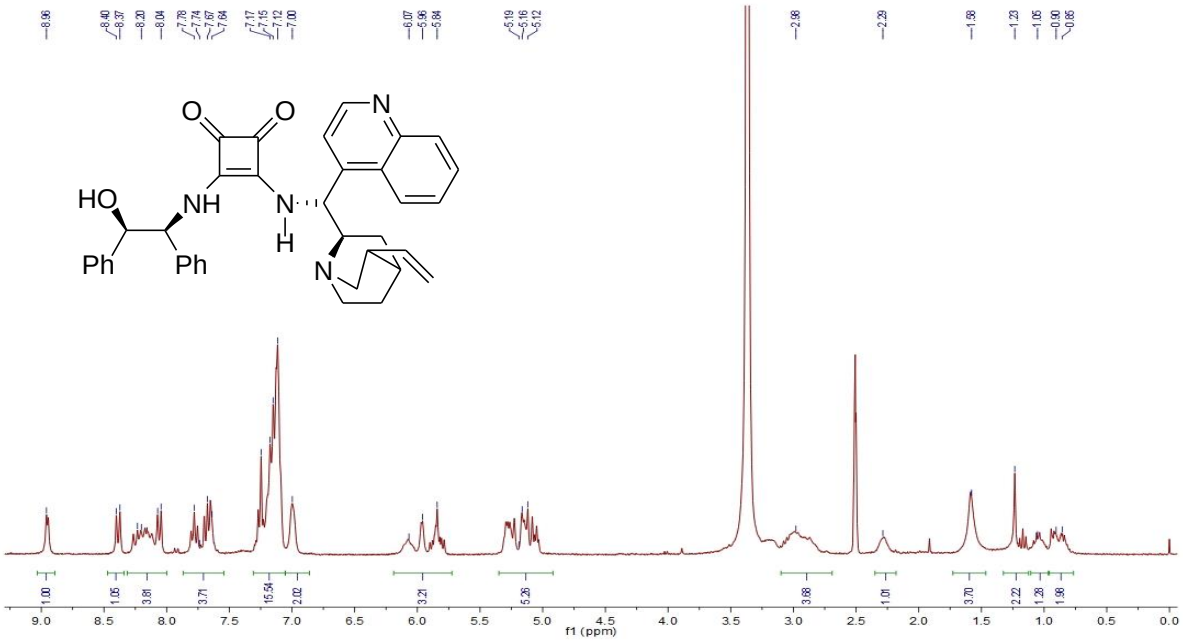


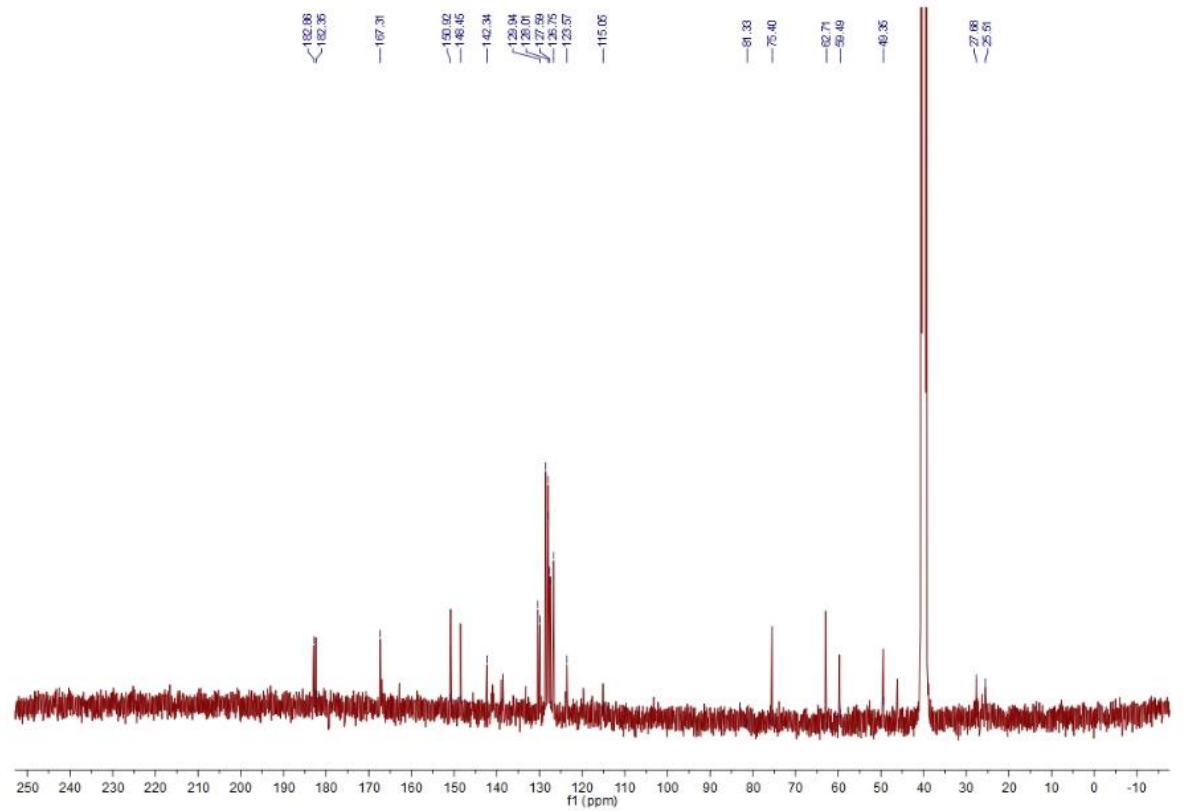


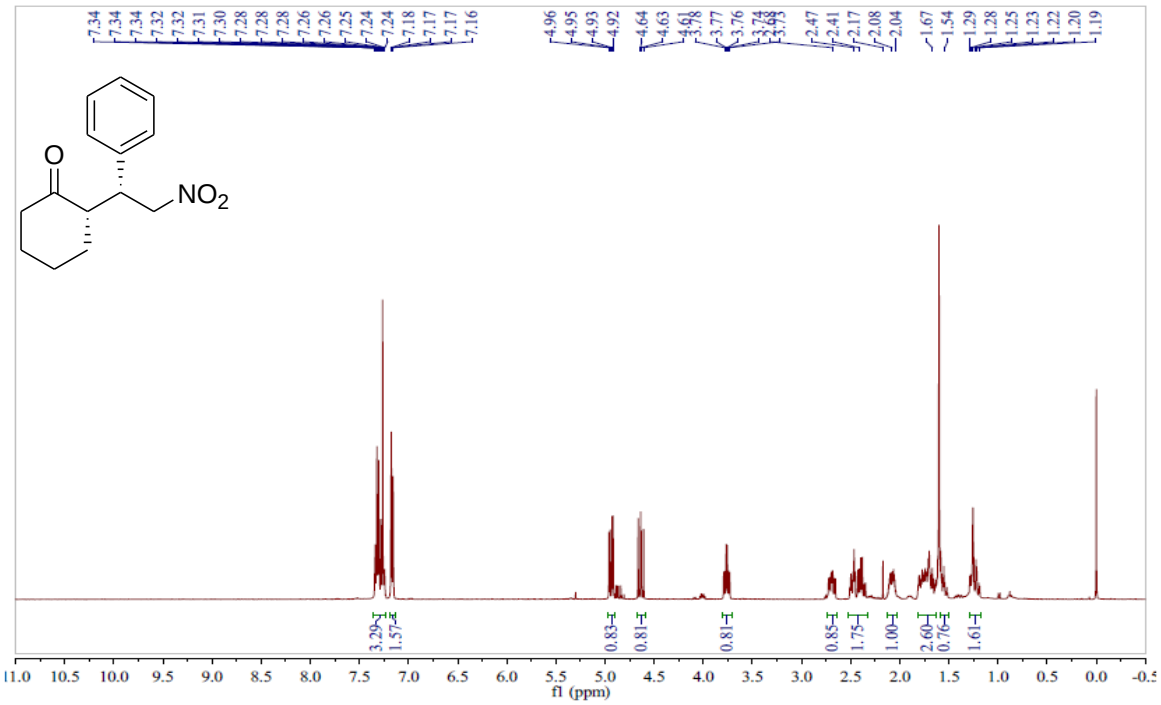


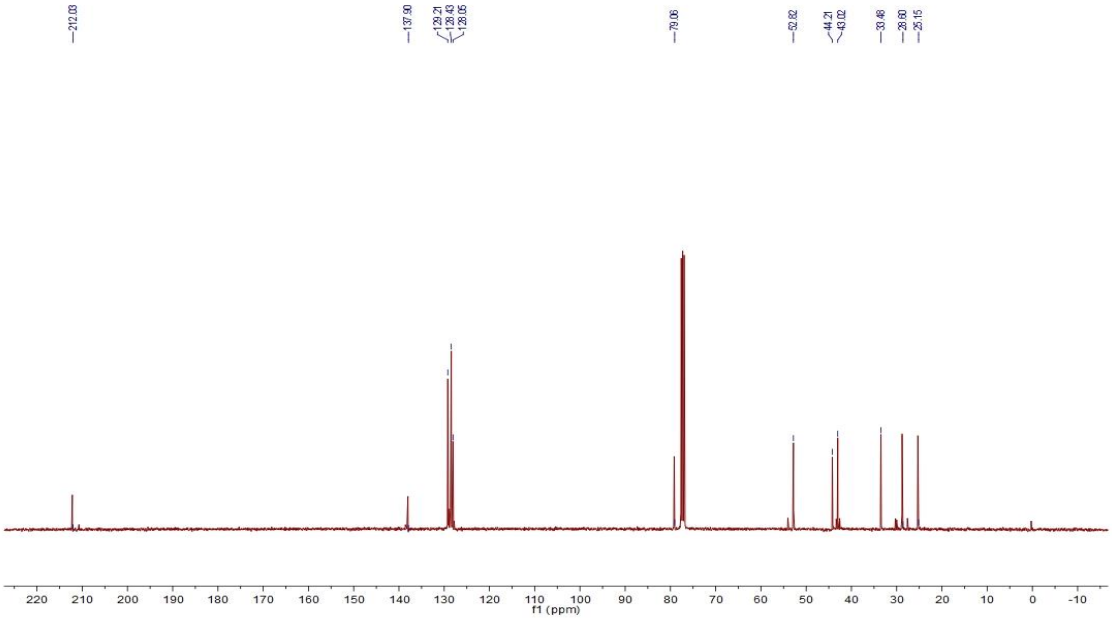


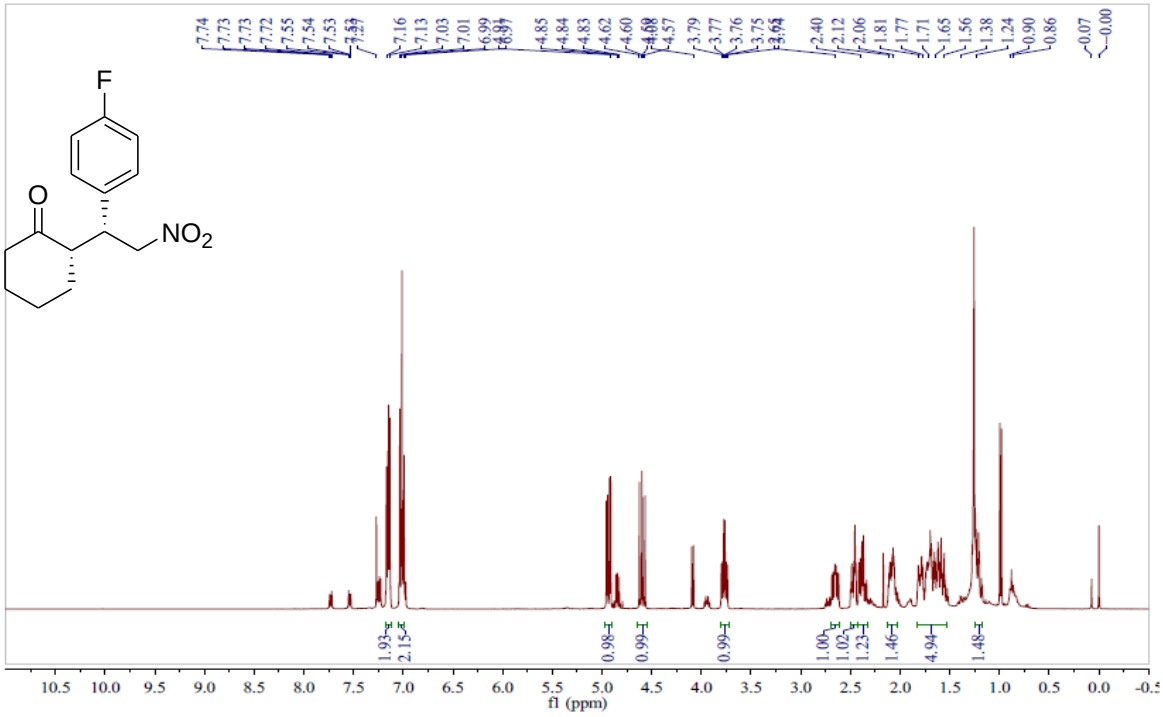


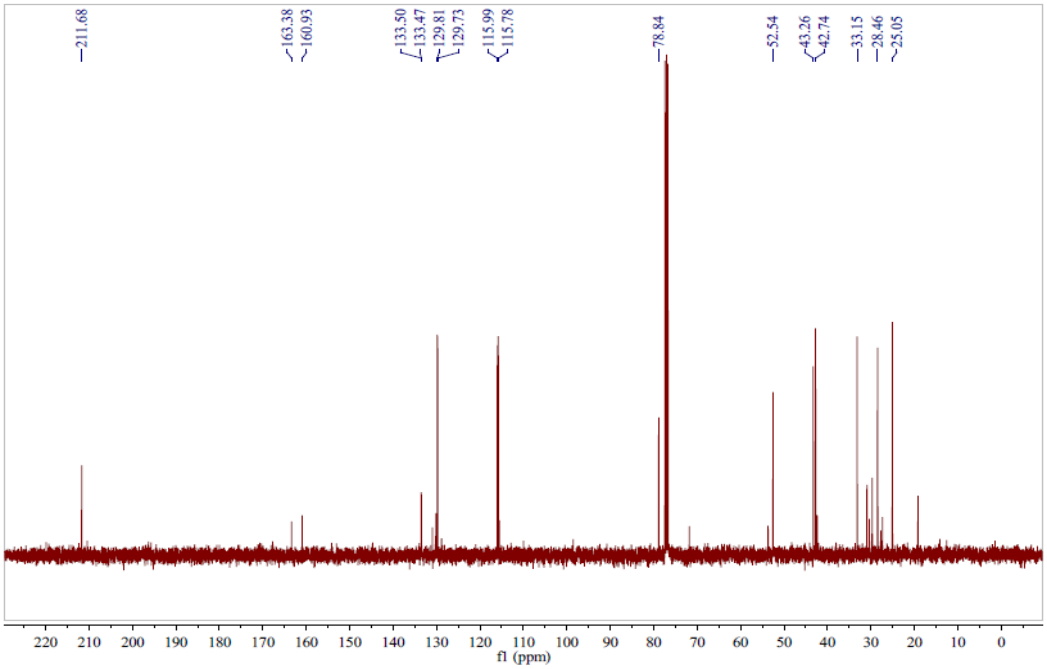


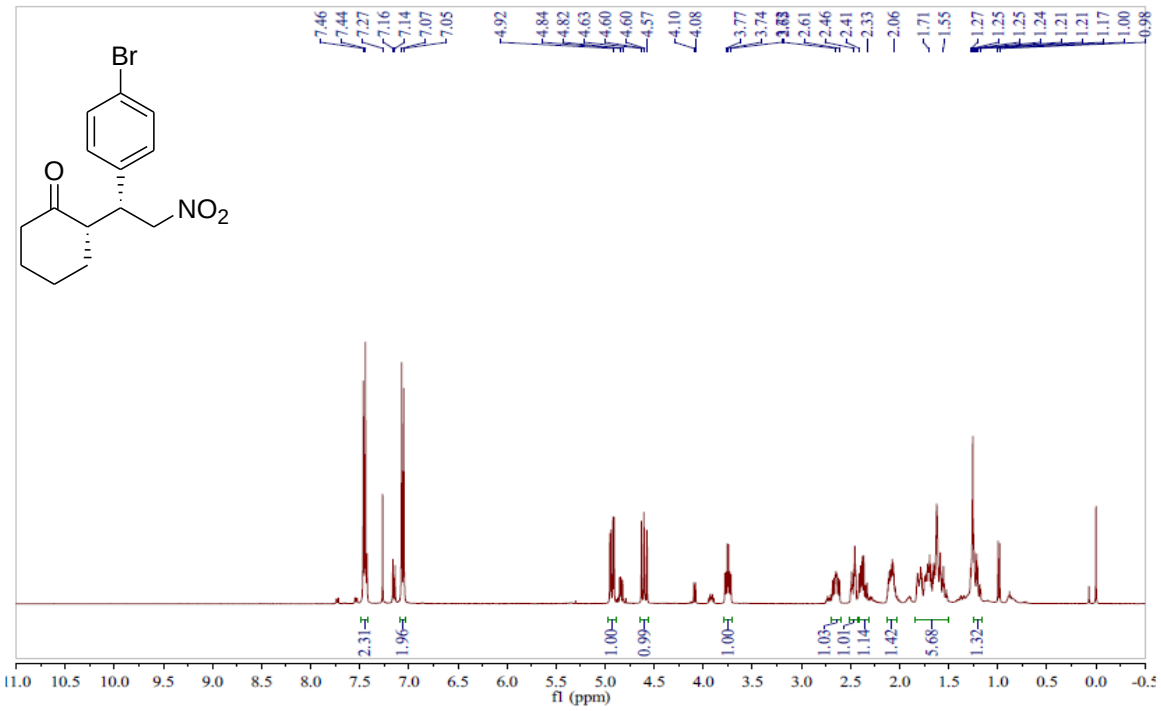


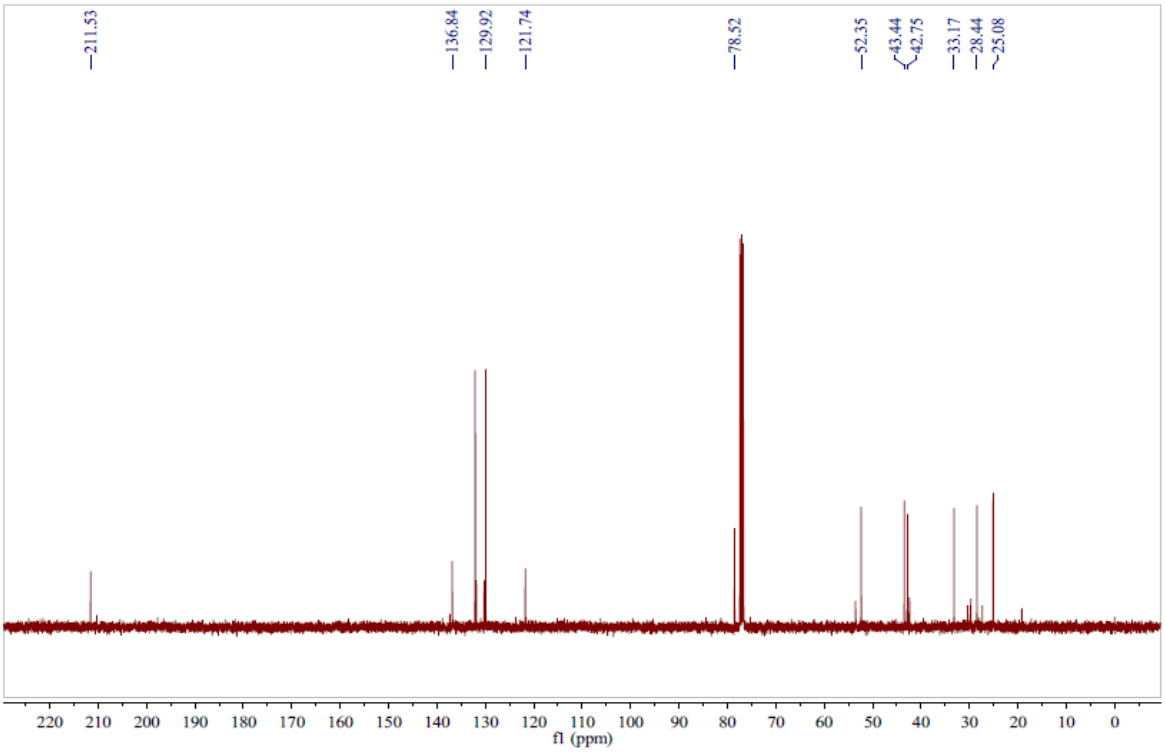


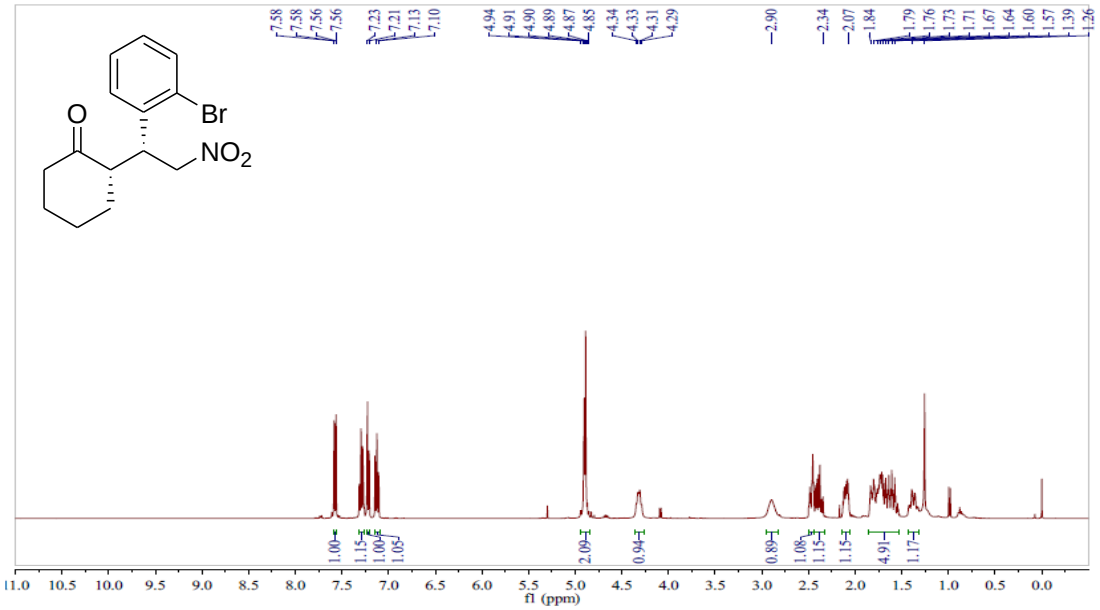


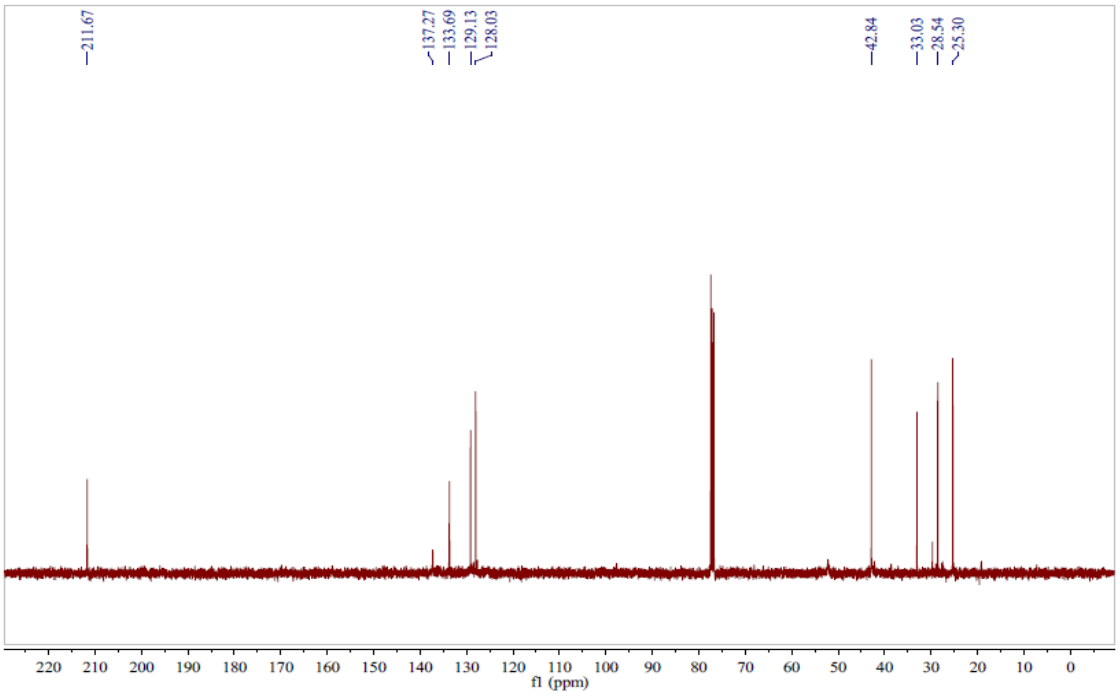


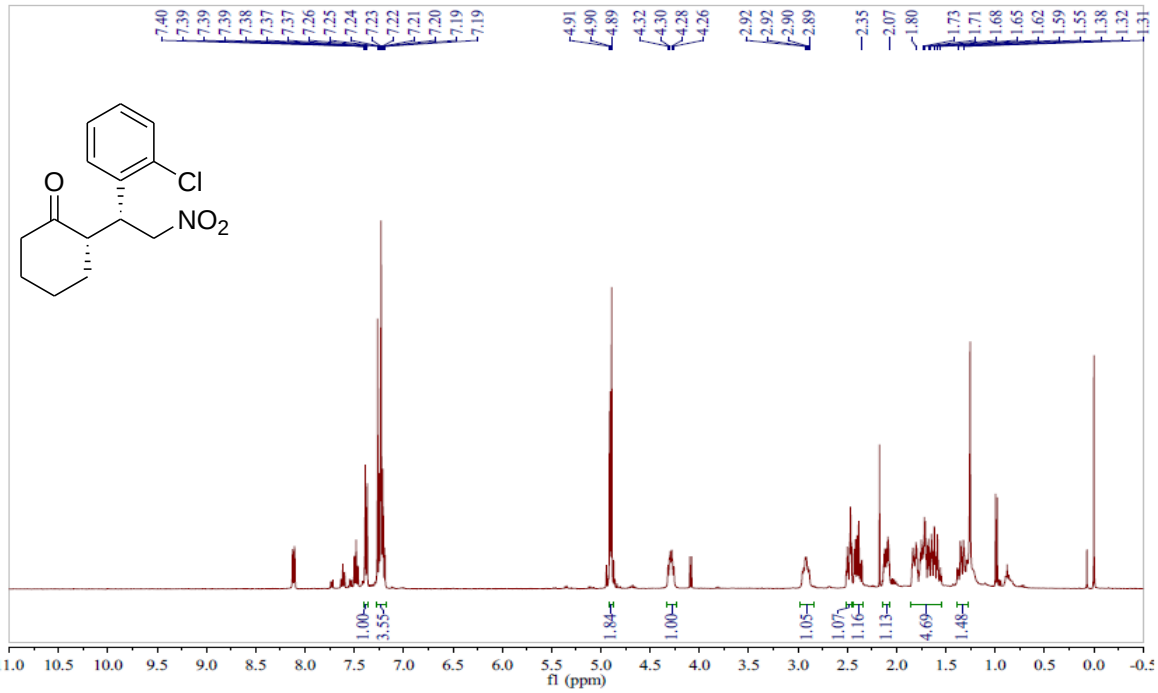


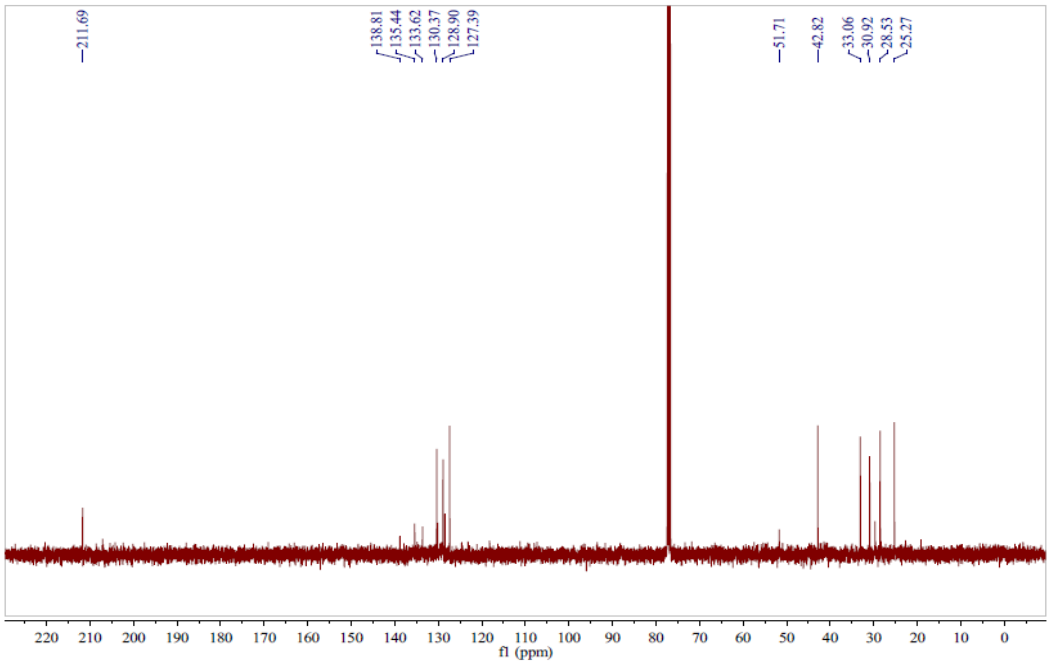


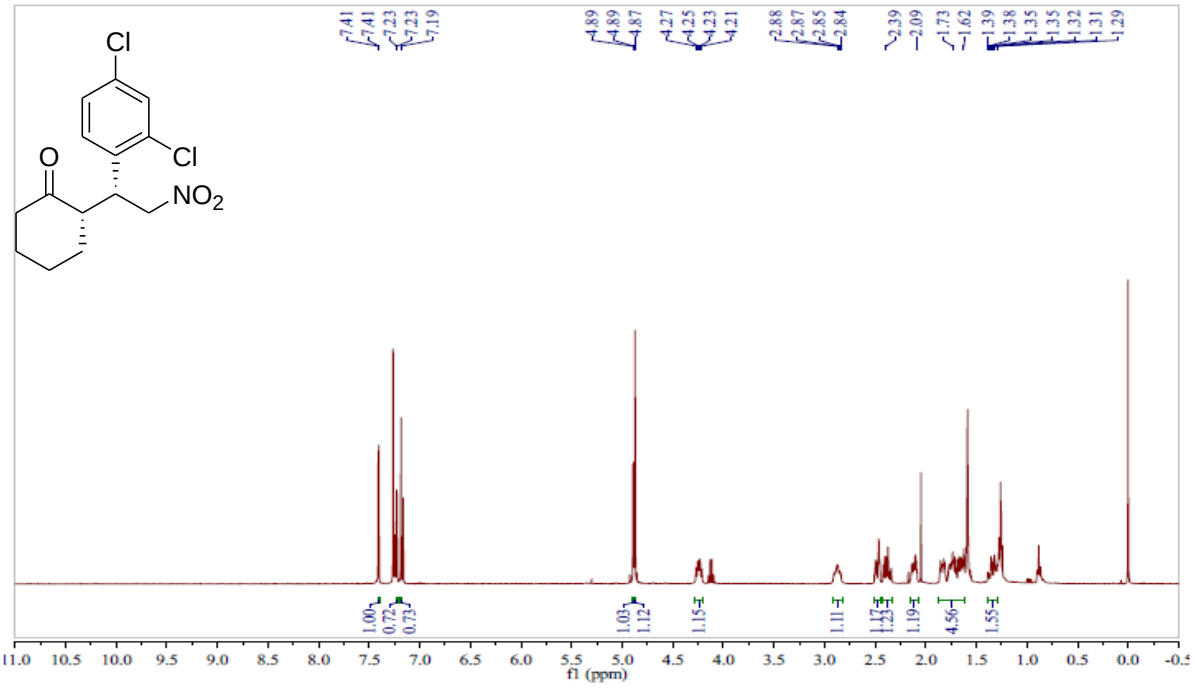


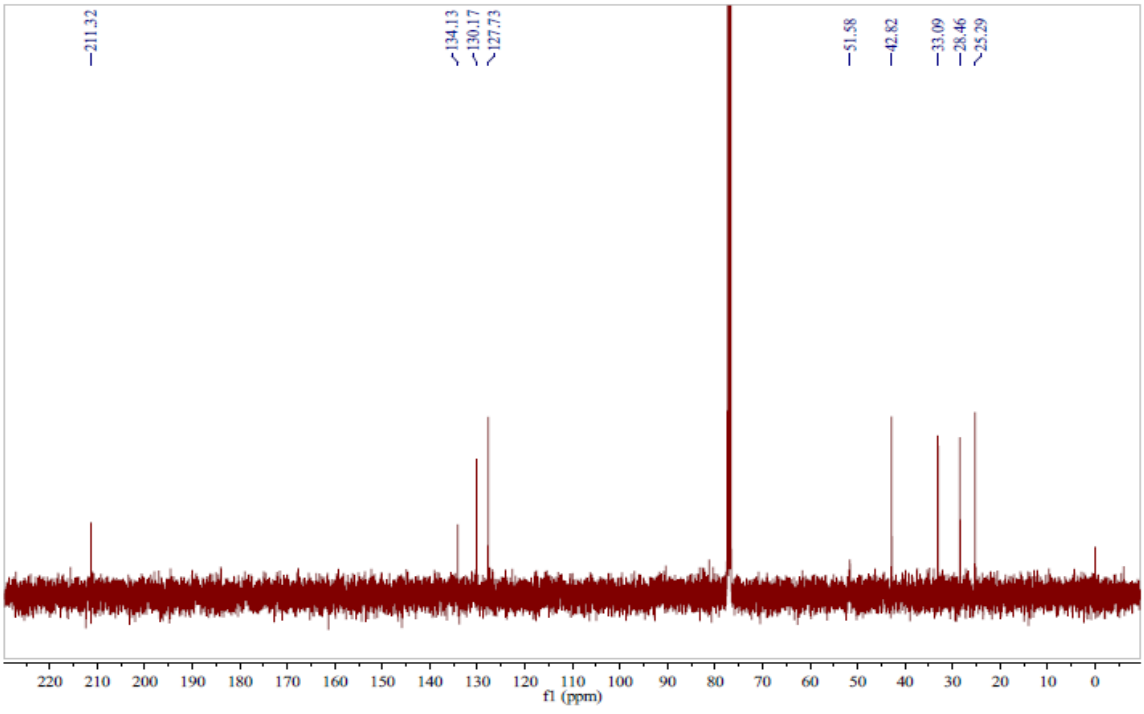


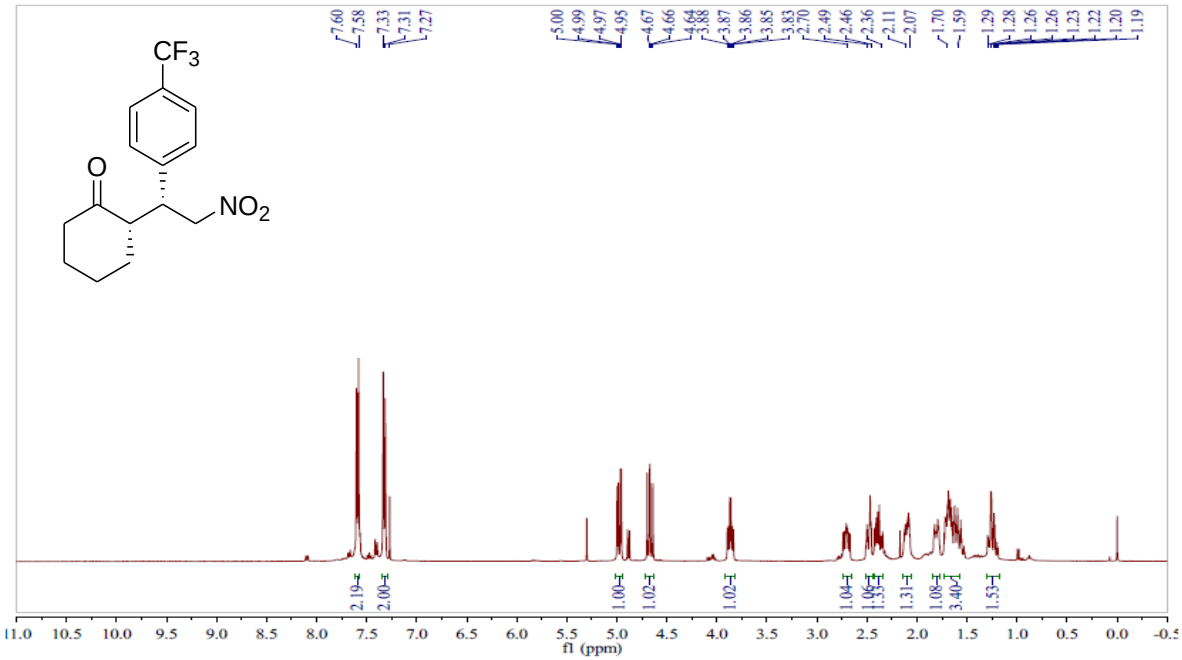


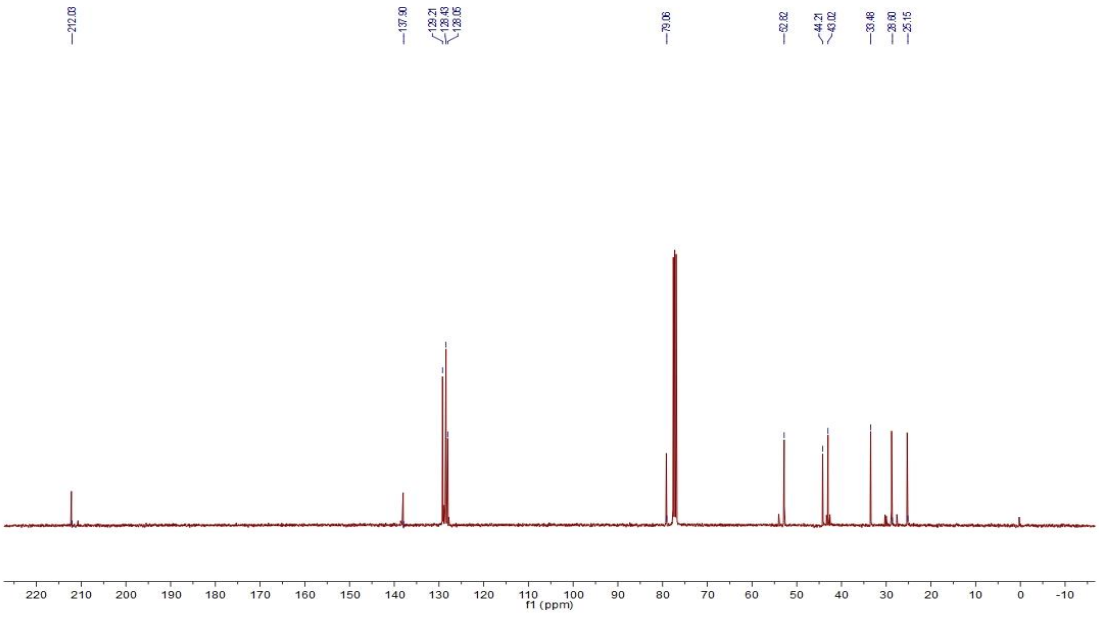


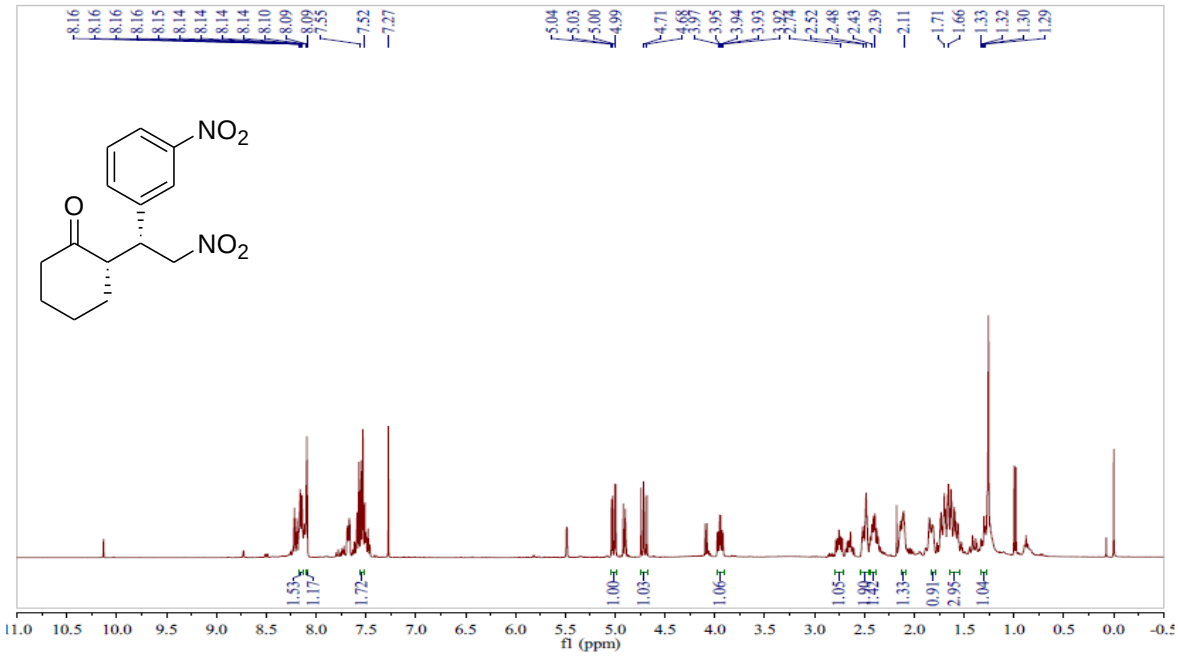


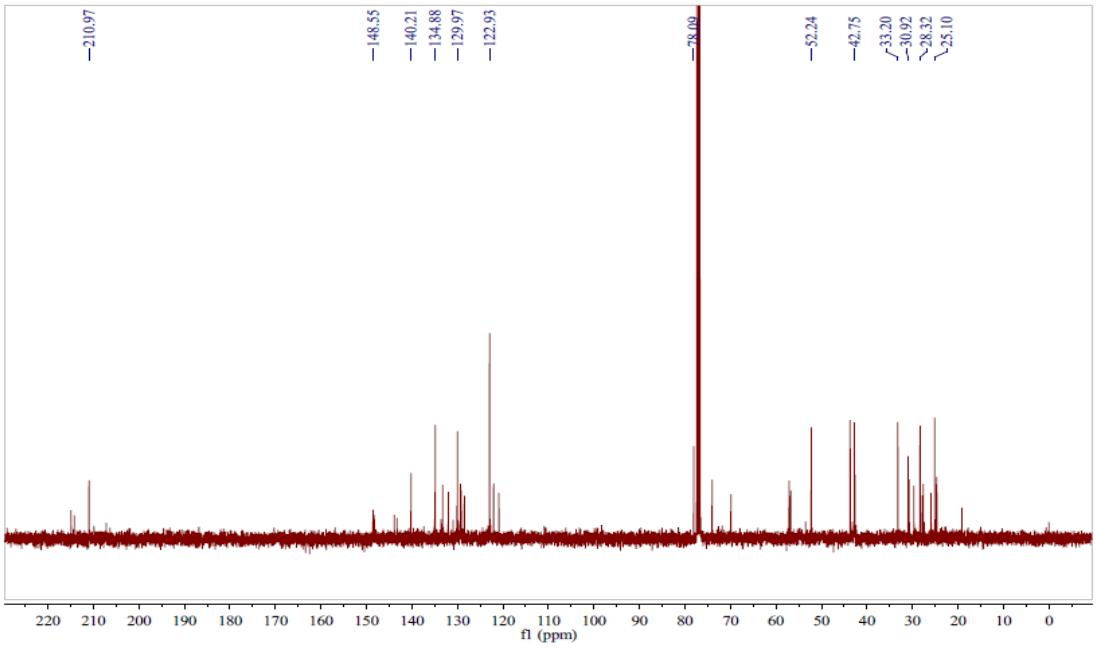


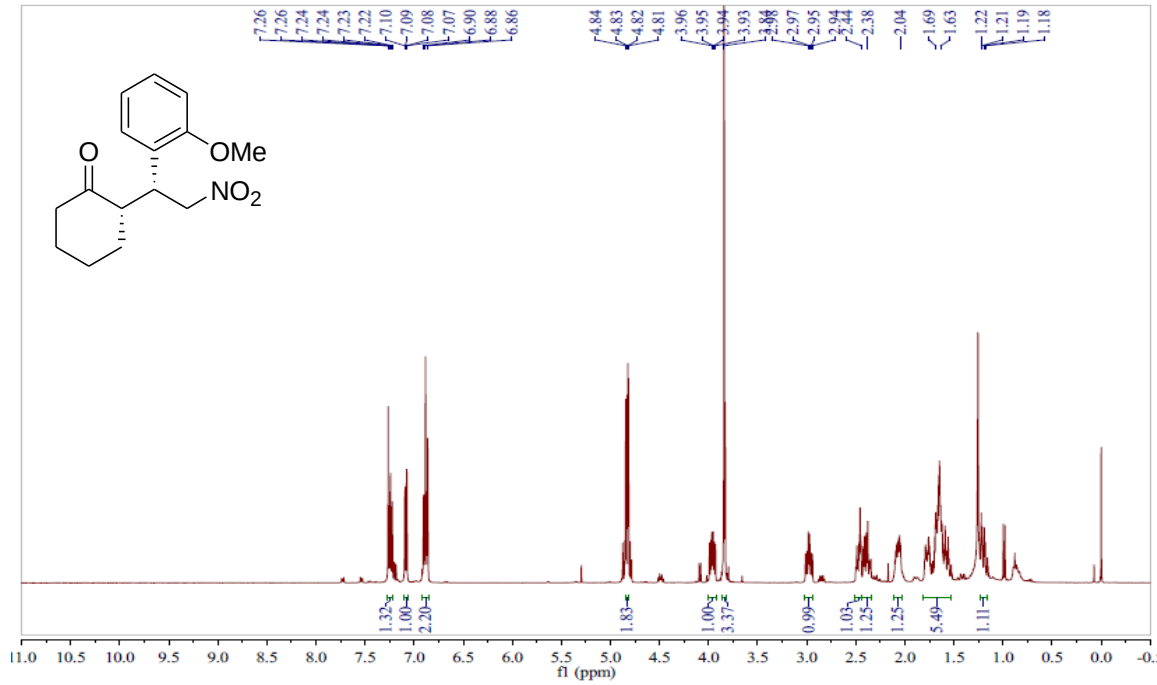


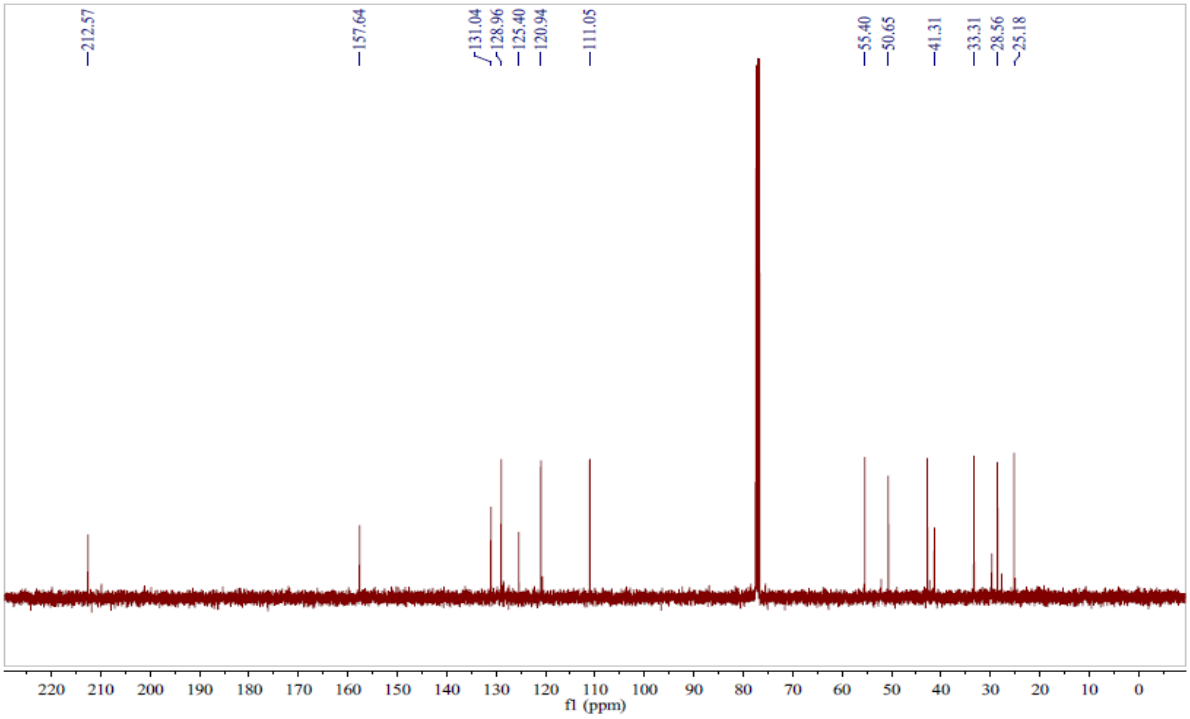


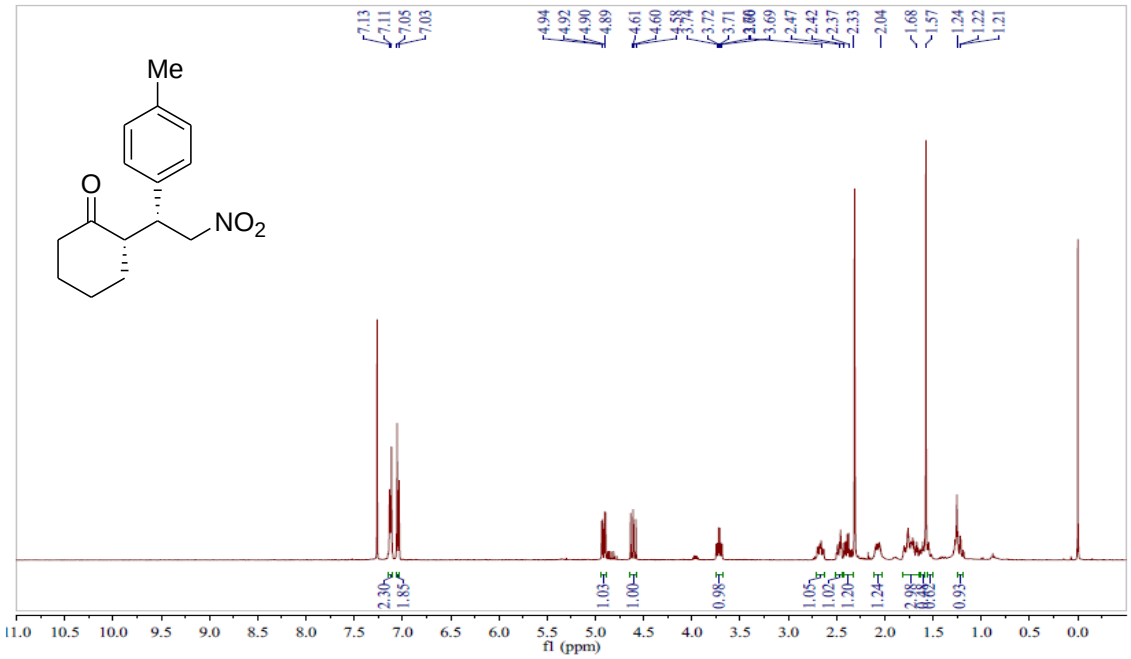


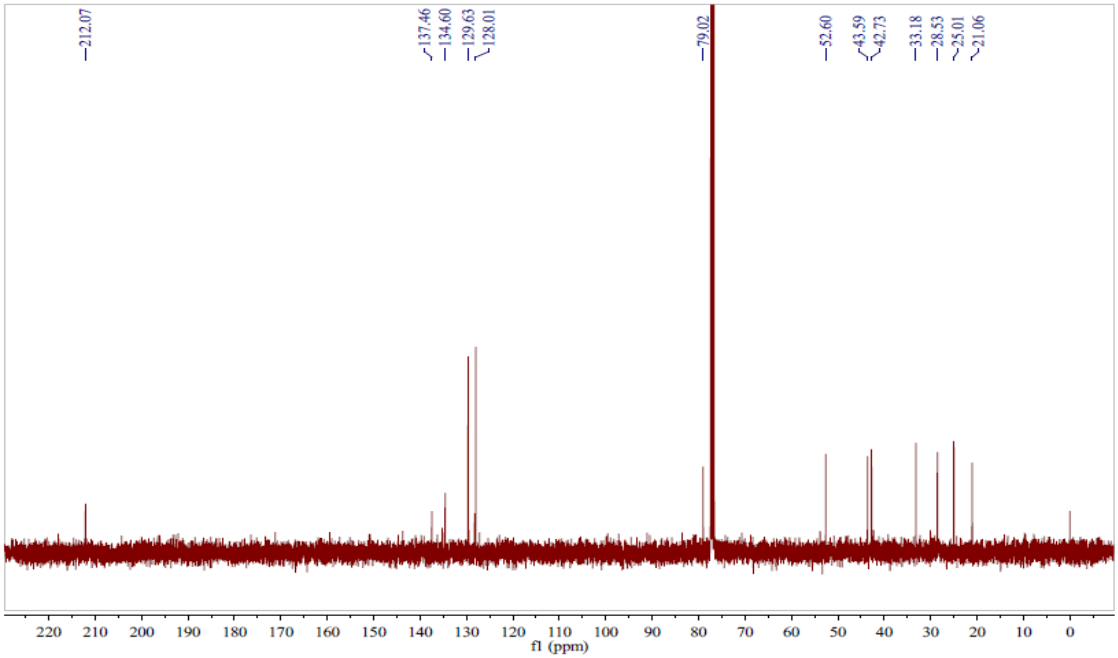


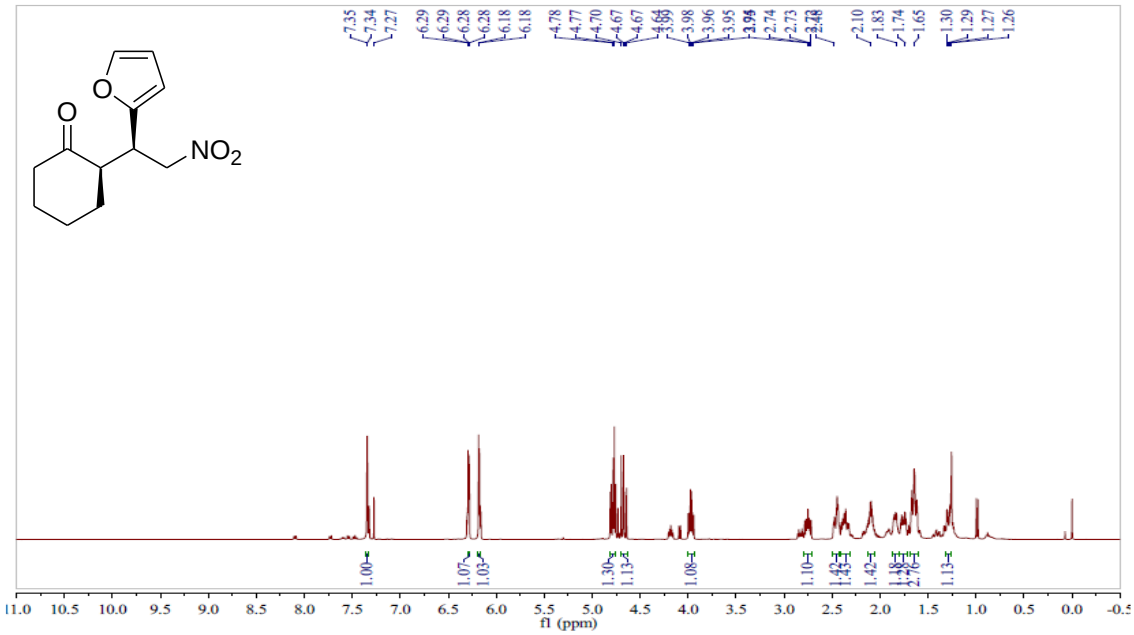


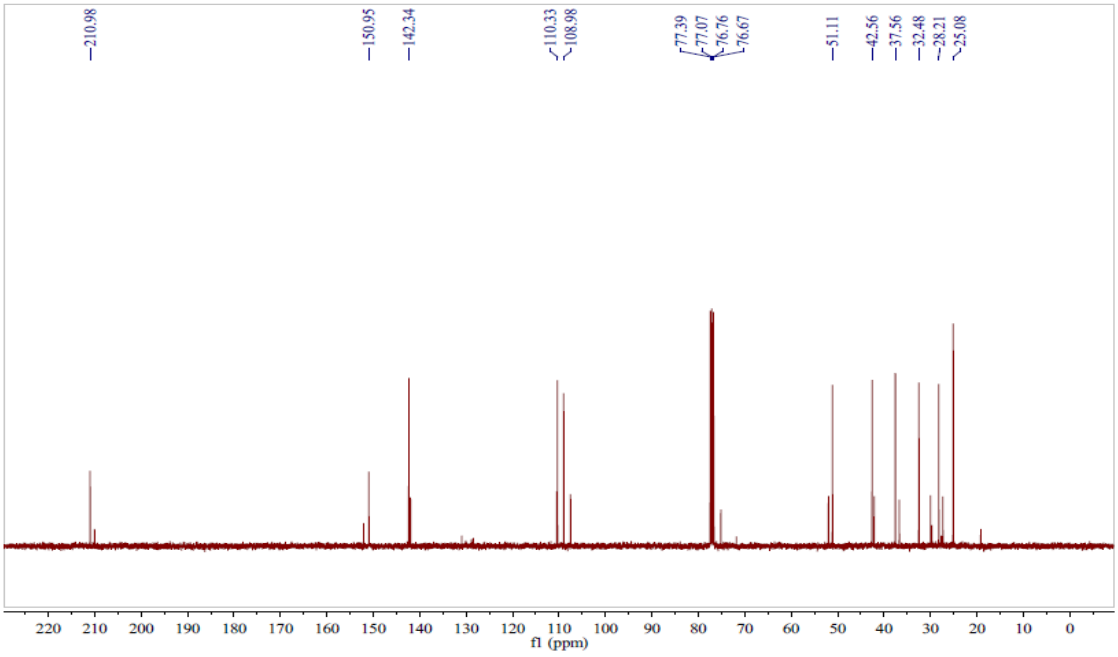


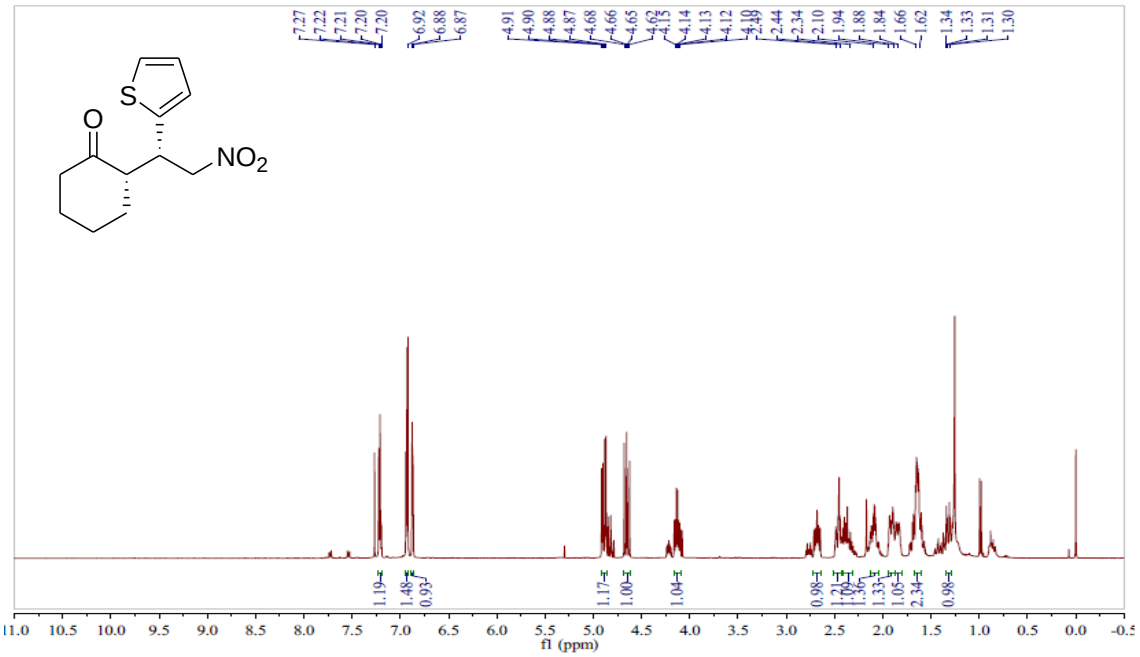


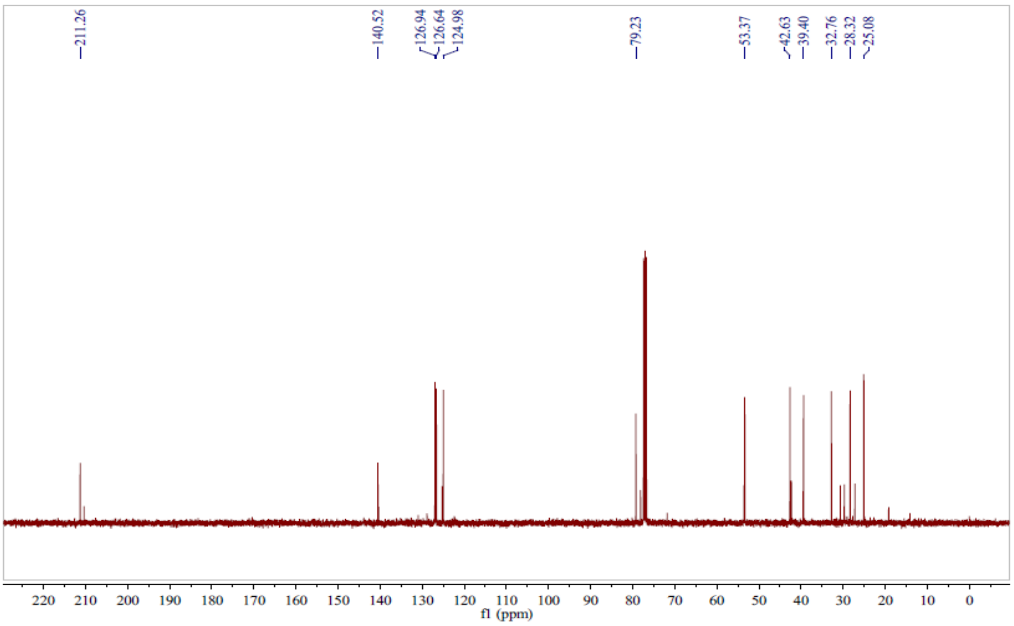


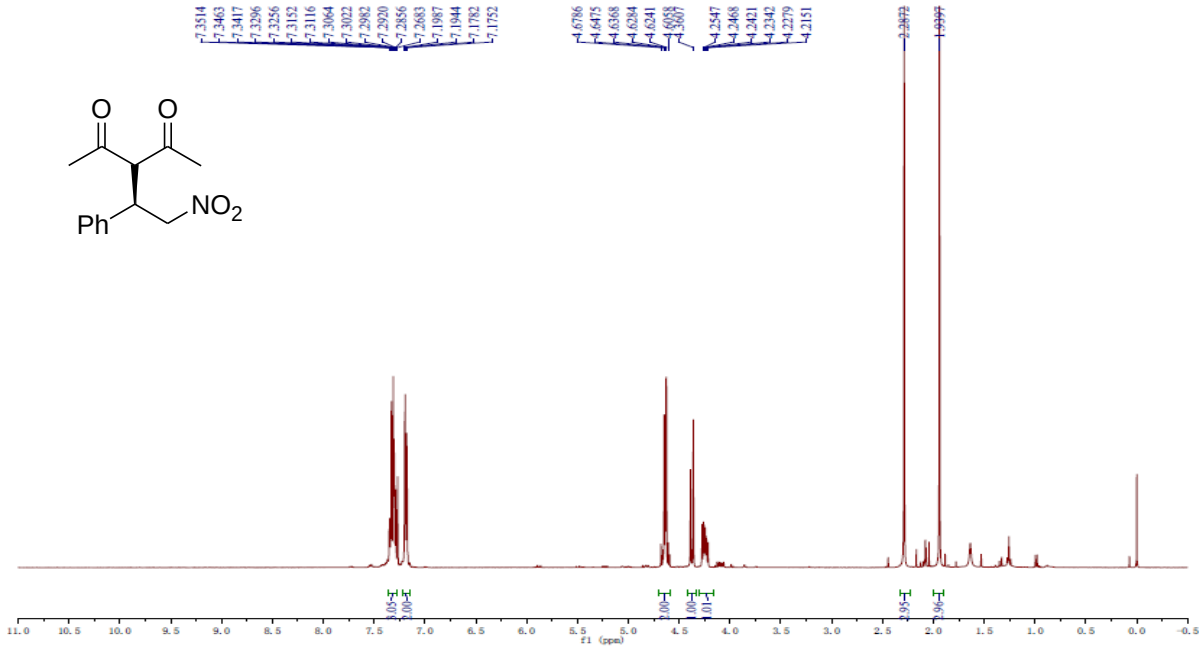


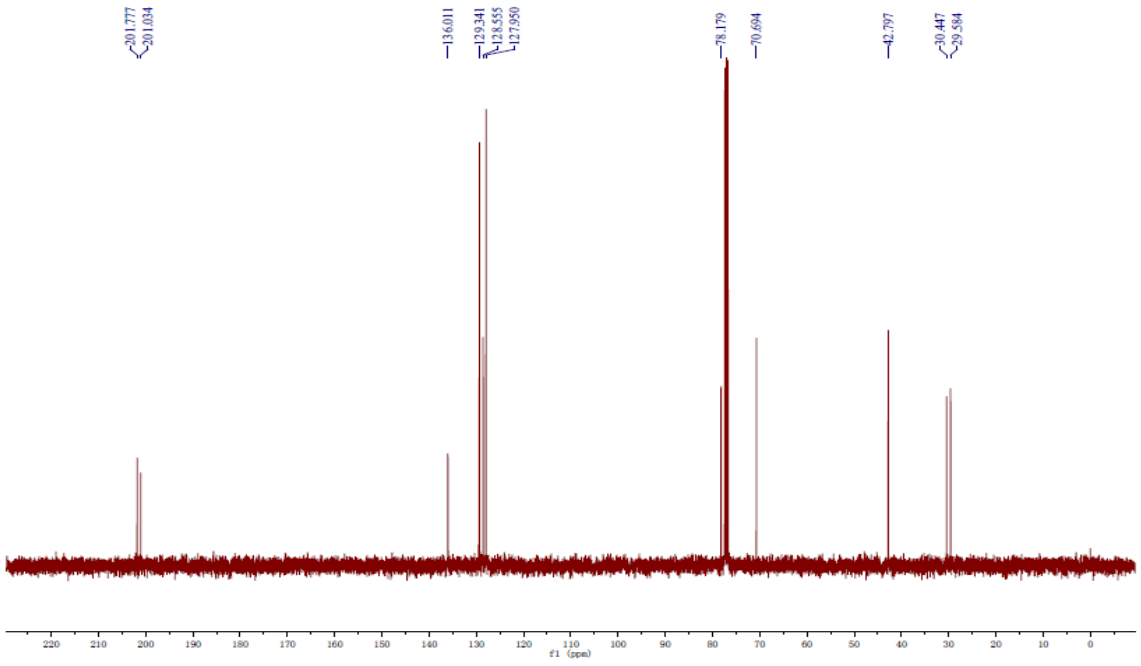


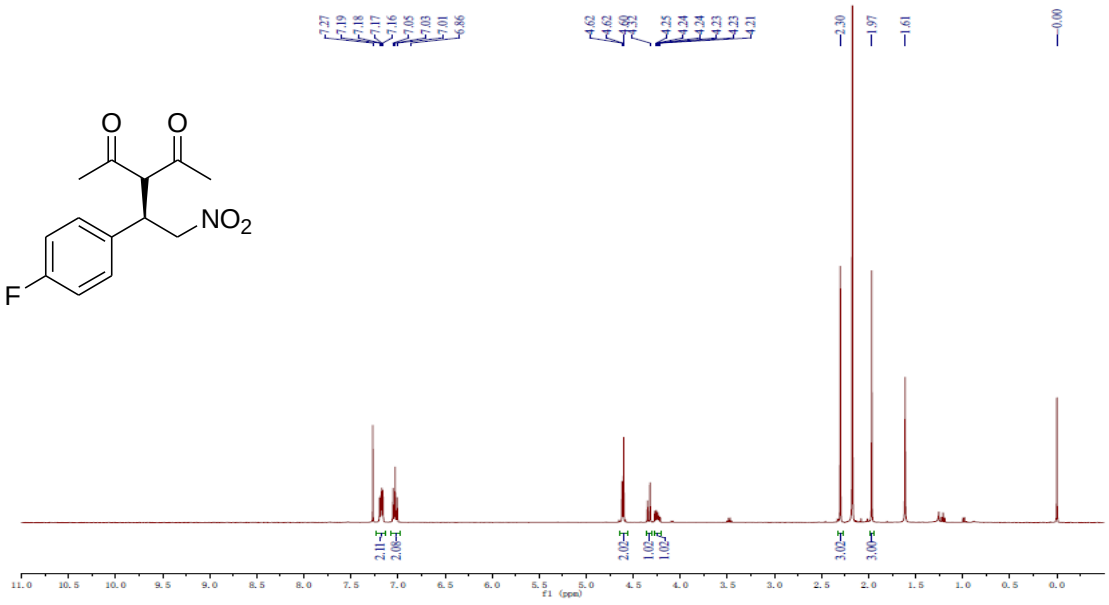


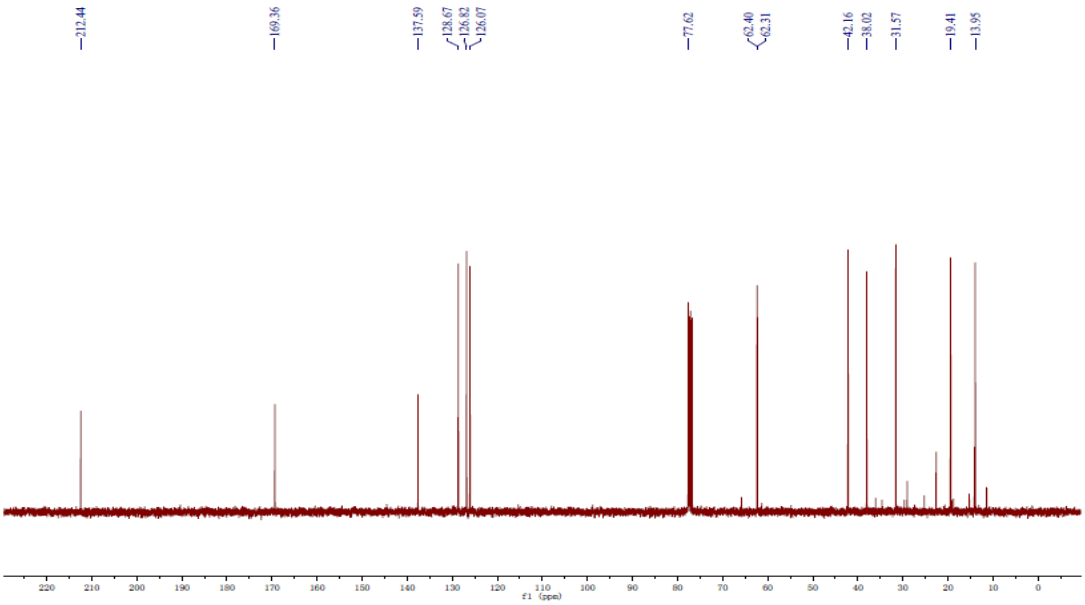


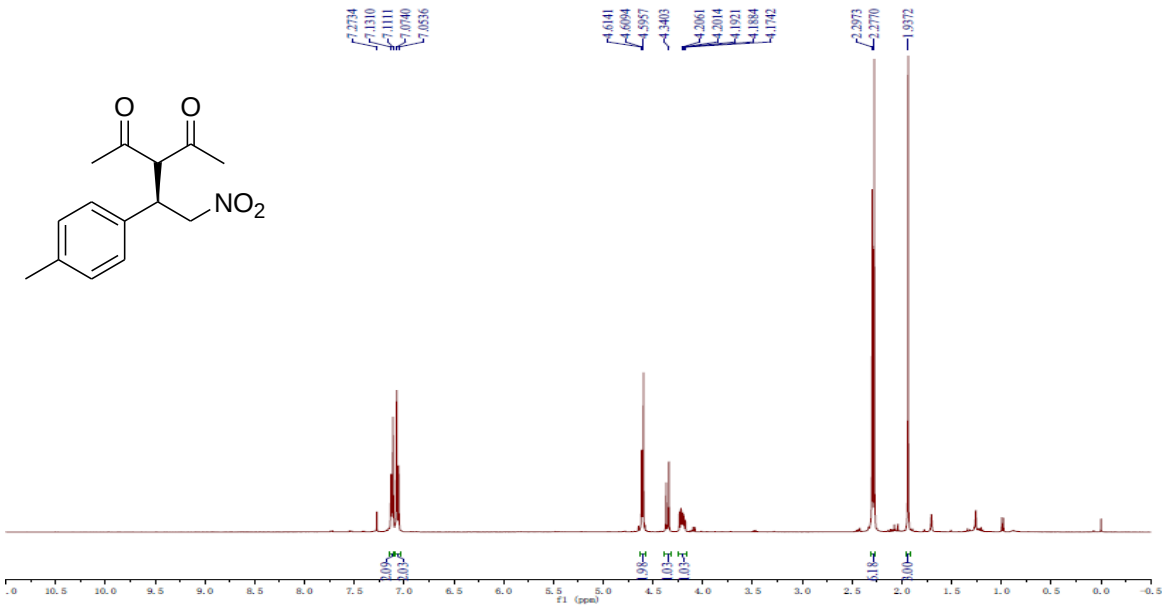


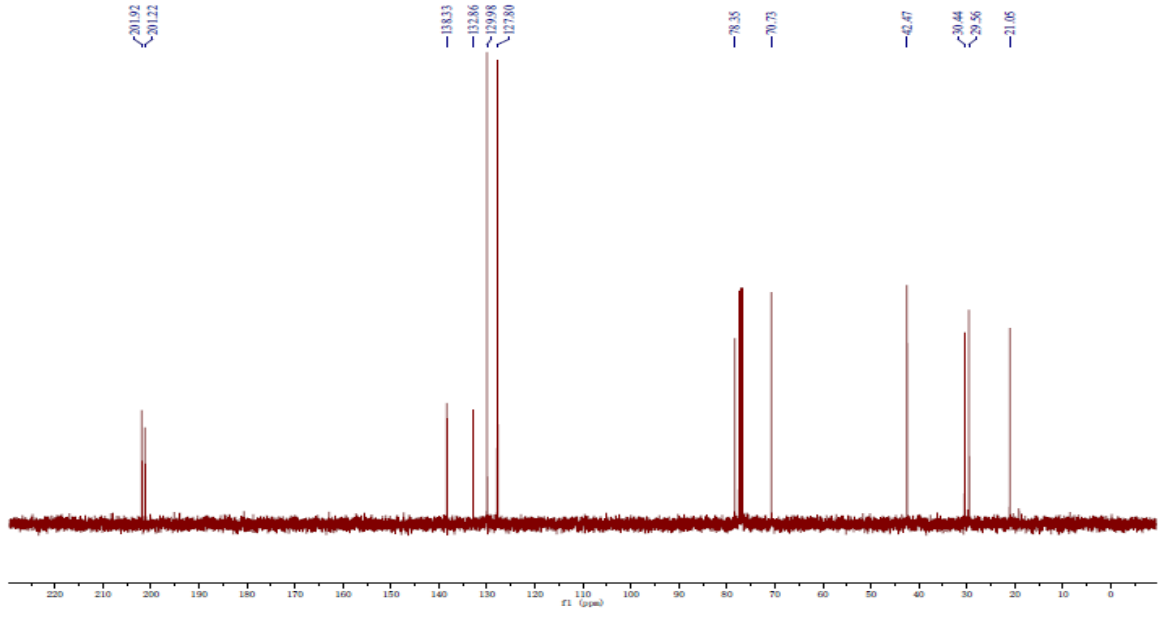


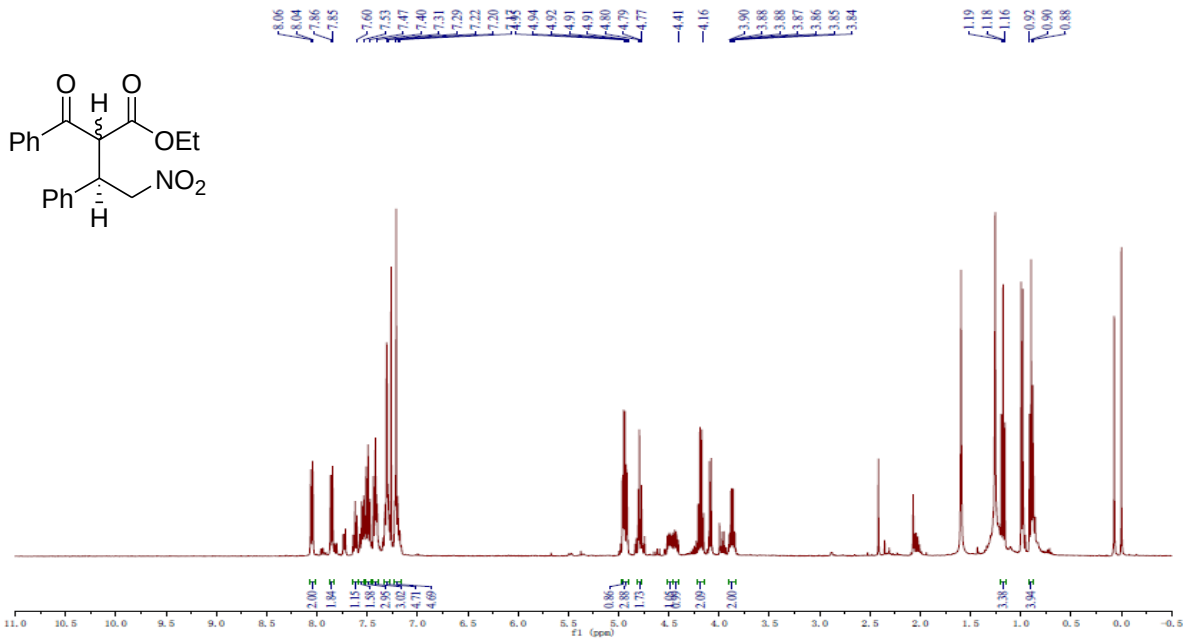


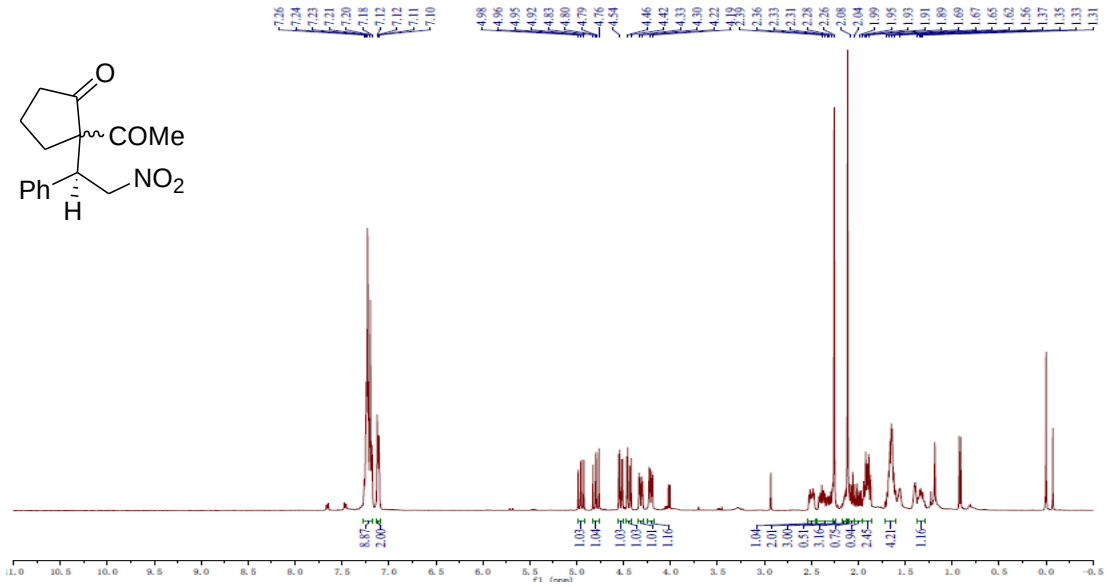


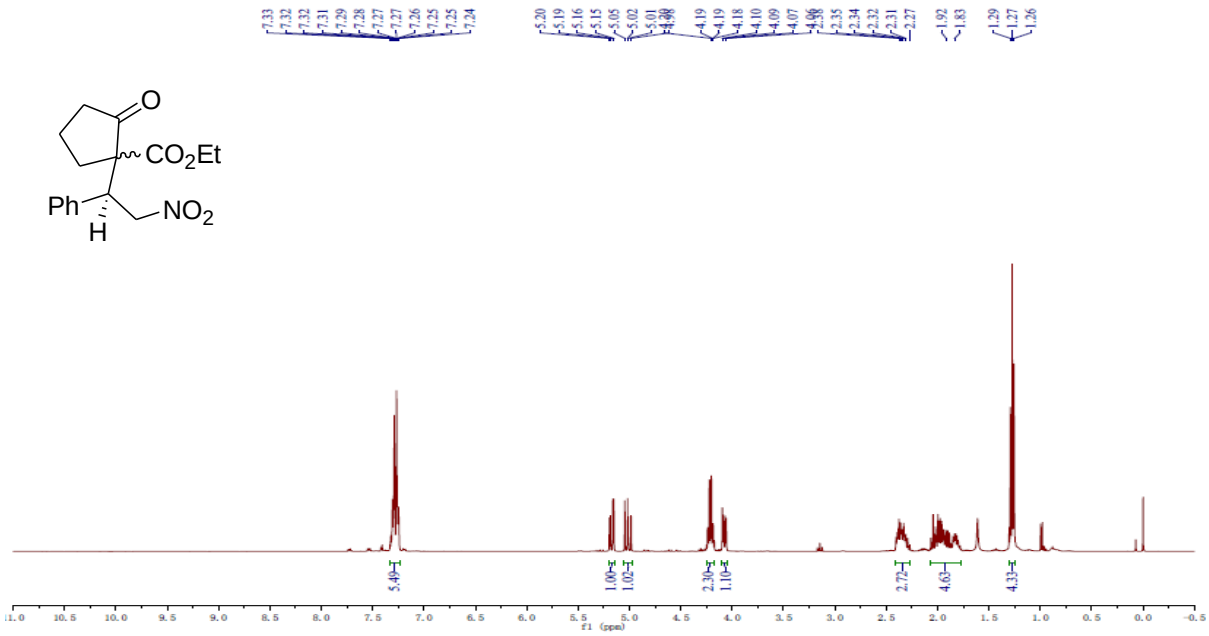


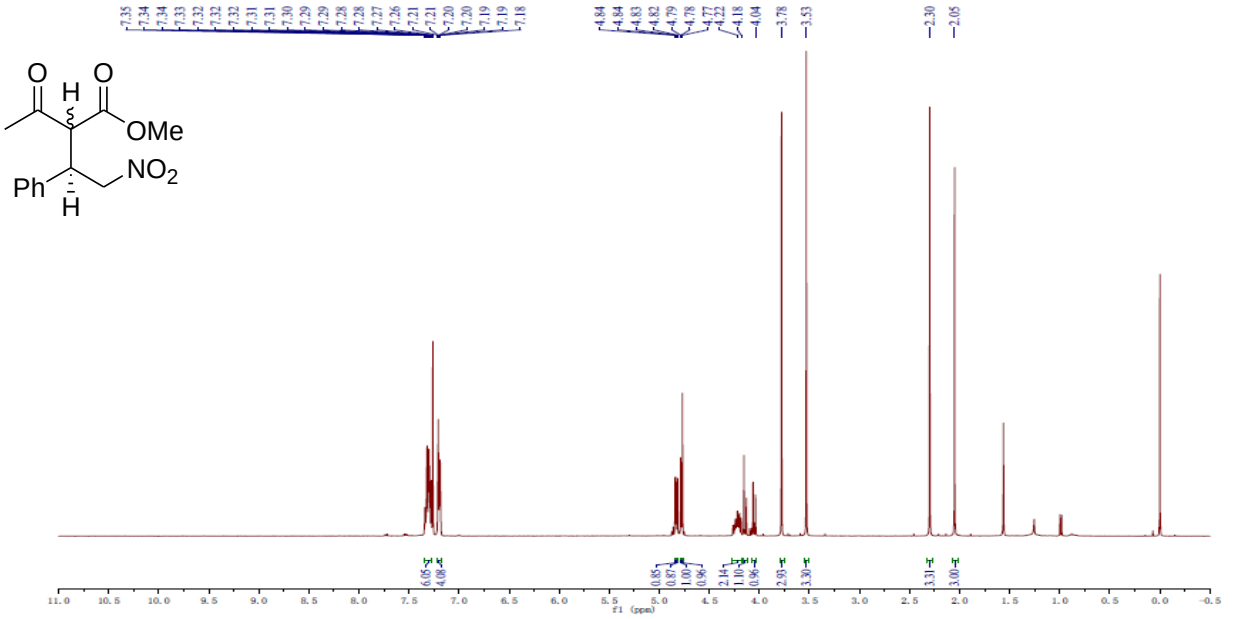


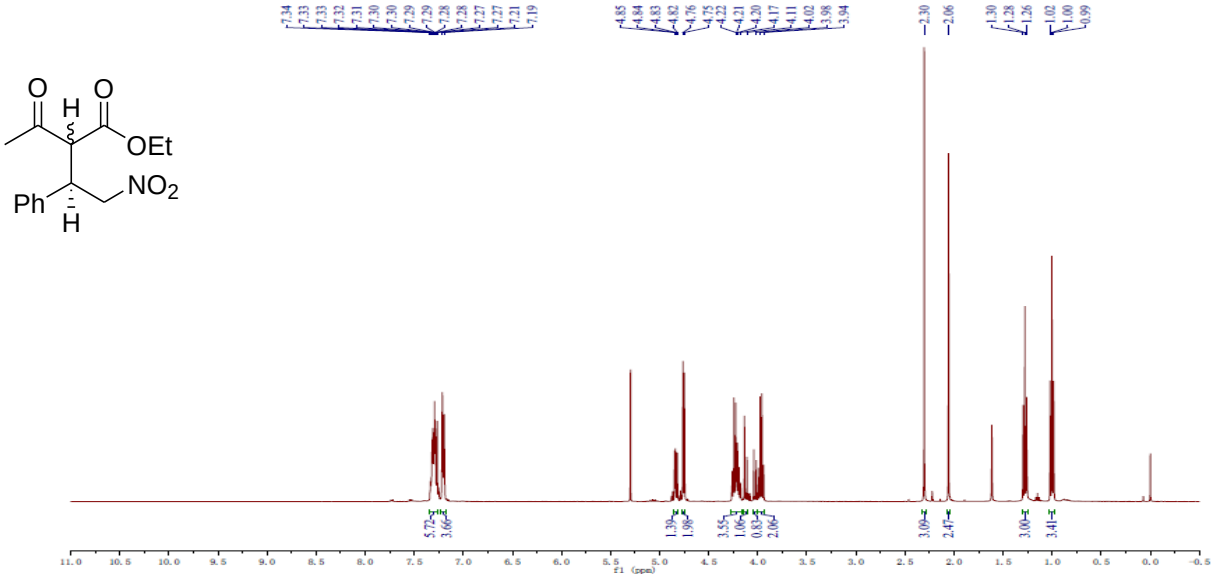


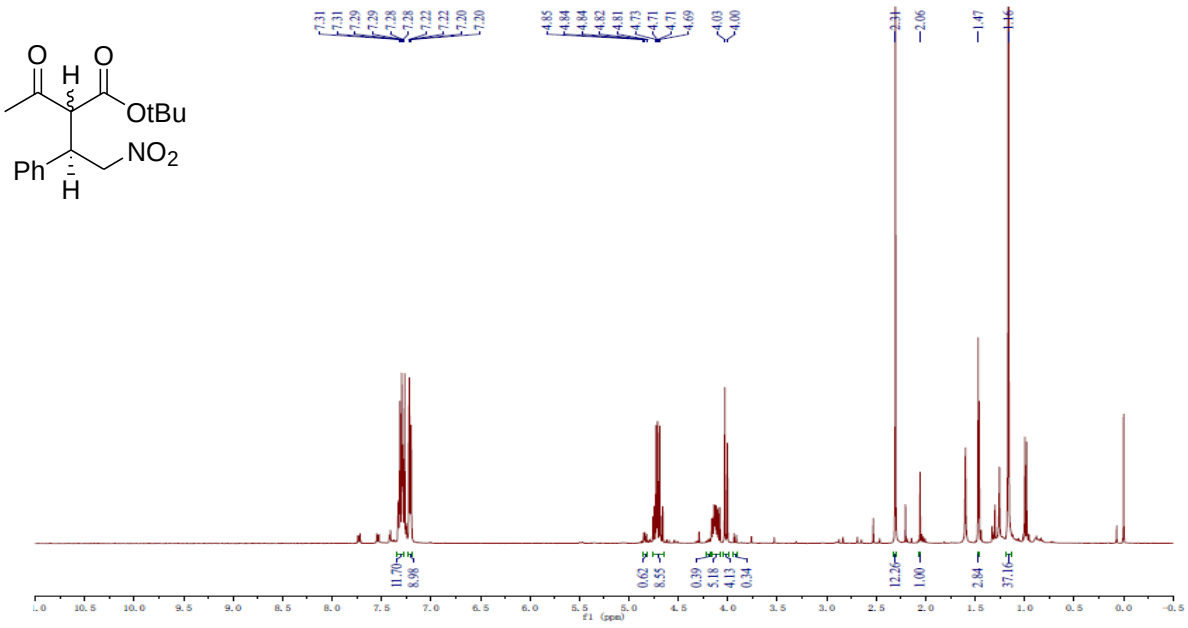


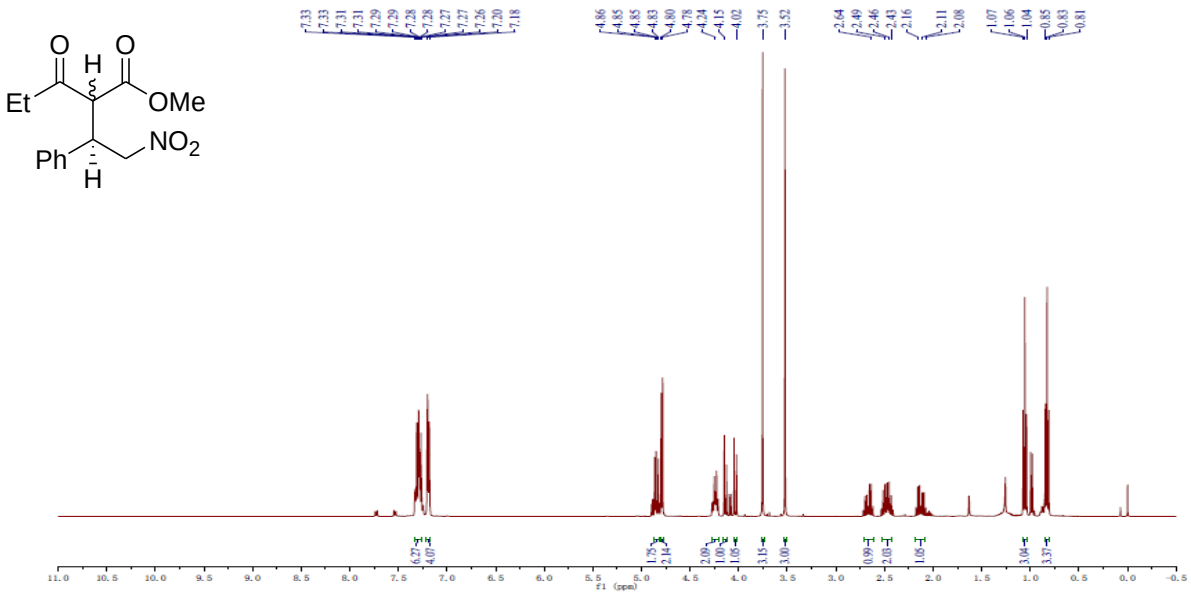




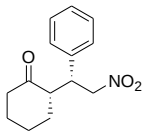


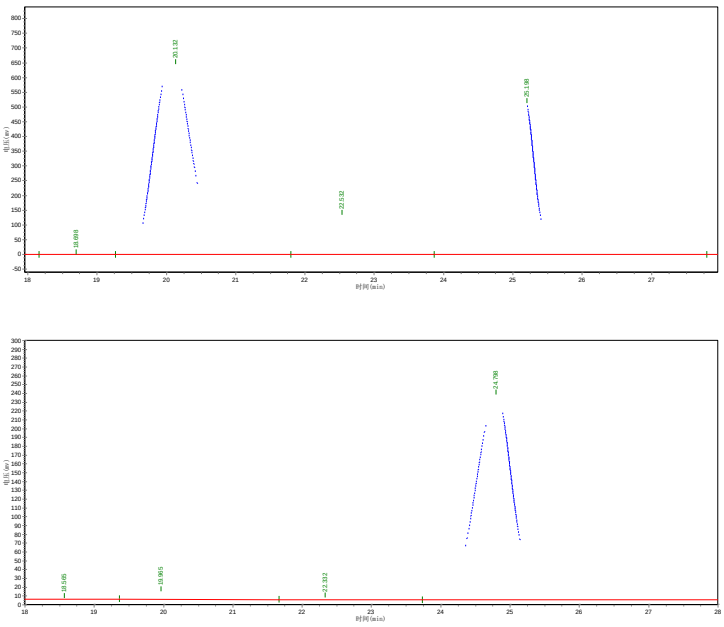




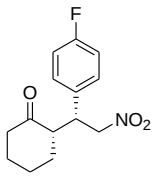


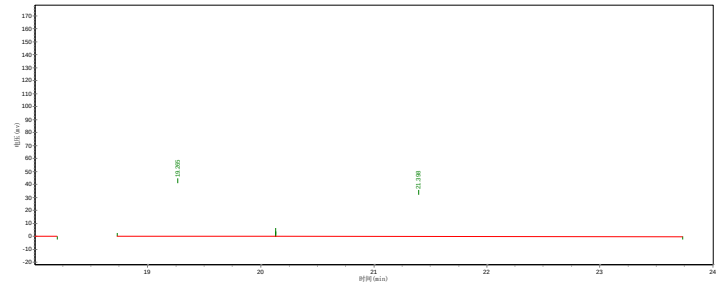
8. Representative HPLC spectra

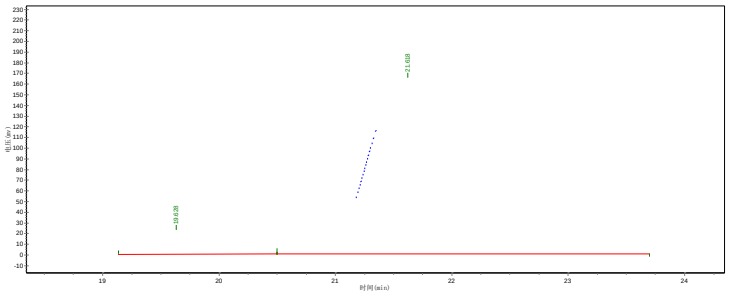




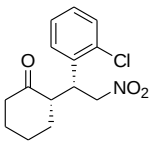
Peak	Ret. Time (min)	Height (mV)	Area (mV*min)	Area (%)
1	19.965	8874.243	305330.188	3.39
2	24.798	230911.078	8699720.000	96.61
Totals				93

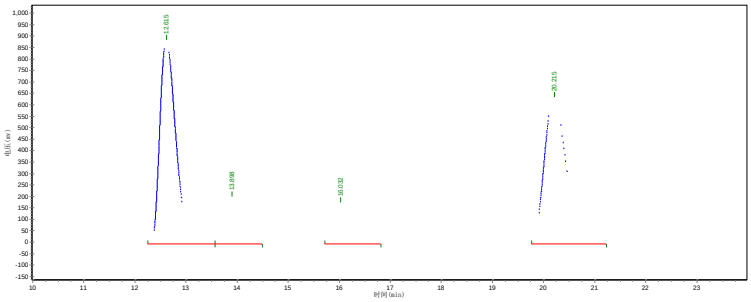


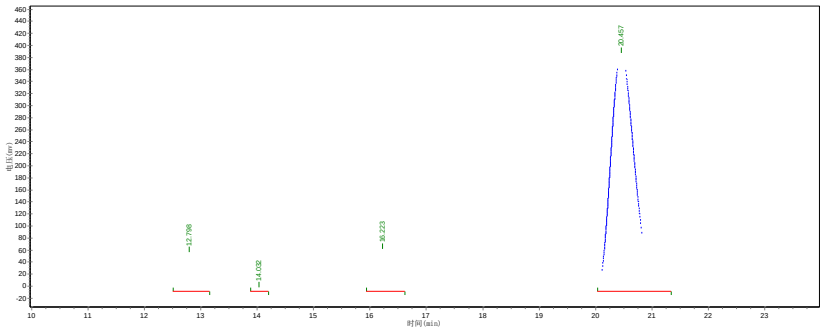




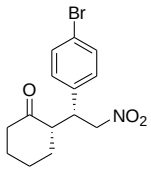
Peak	Ret. Time (min)	Height (mV)	Area (mV*min)	Area (%)
1	19.628	22368.396	846535.813	9.24
2	21.618	165169.391	8320523.000	90.76
Totals				82

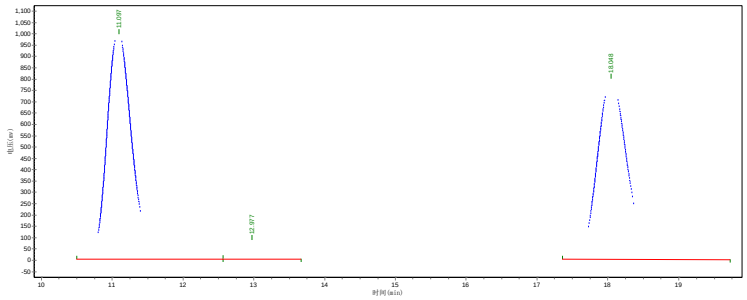


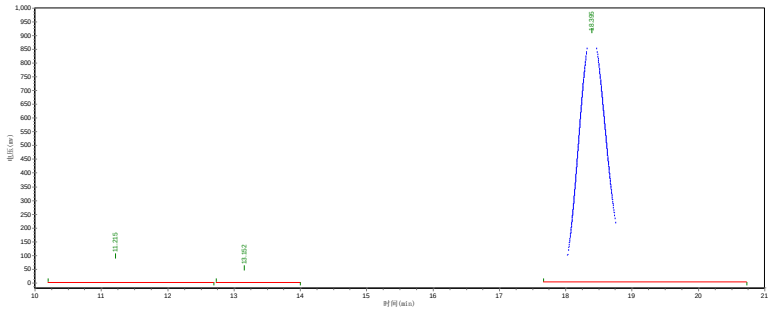




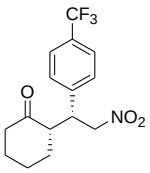
Peak	Ret. Time (min)	Height (mV)	Area (mV*min)	Area (%)
1	12.798	65527.676	1060722.500	8.63
2	20.457	395572.406	11234555.000	91.37
Totals				83

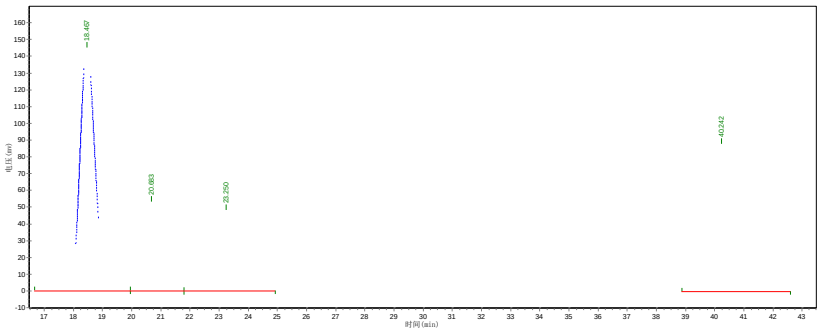


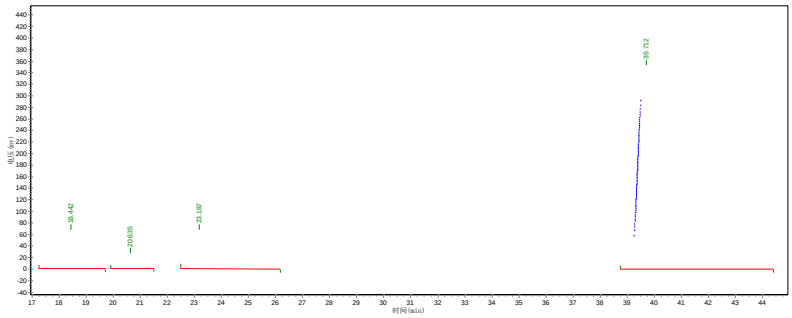




Peak	Ret. Time (min)	Height (mV)	Area (mV*min)	Area (%)
1	11.215	85210.547	2285664.250	7.80
2	18.395	905982.563	27020646.000	92.20
Totals				84

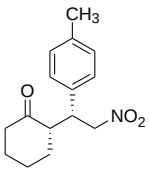


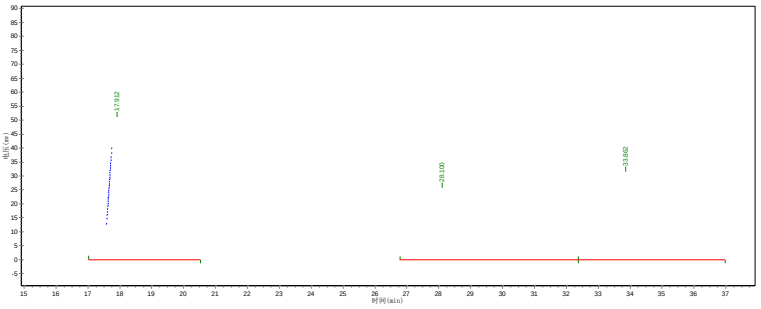


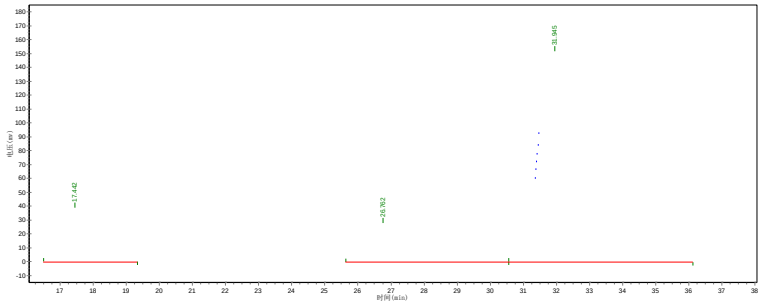


Peak	Ret. Time (min)	Height (mV)	Area (mV*min)	Area (%)
1	18.442	67089.438	2720848.250	10.18

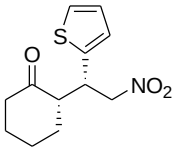
2	39.712	353623.469	24020984.000	89.82
Totals				80

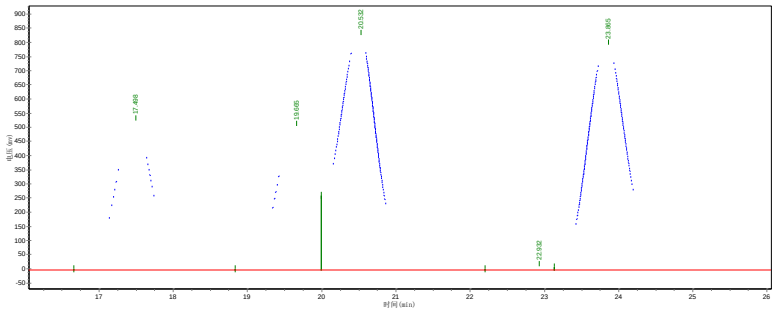


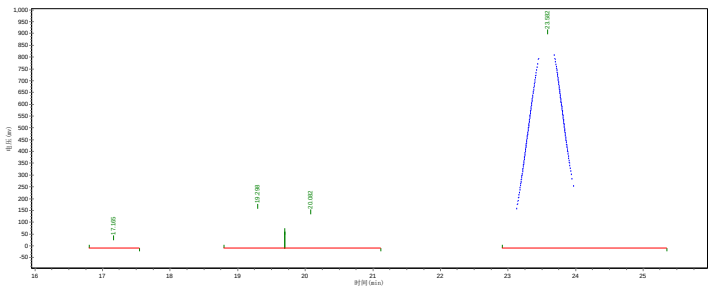




Peak	Ret. Time (min)	Height (mV)	Area (mV*min)	Area (%)
1	17.442	39133.758	1508271.000	10.31
2	31.945	151902.250	13115318.000	89.69
Totals				80

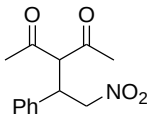


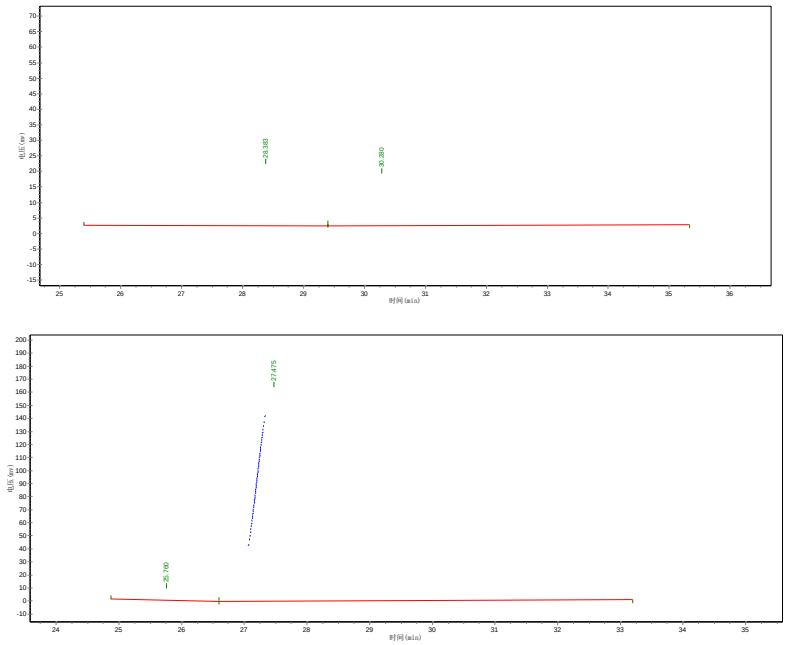




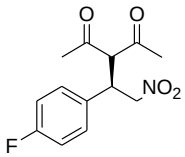
Peak	Ret. Time (min)	Height (mV)	Area (mV*min)	Area (%)
1	20.082	140803.891	4744161.000	12.38

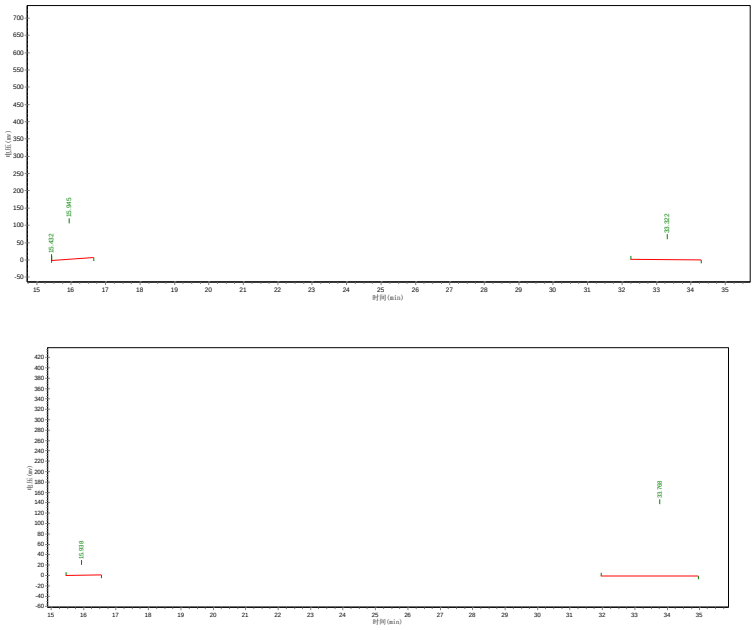
2	23.582	904975.438	33584012.000	87.62
Totals				75





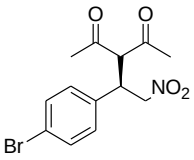
Peak	Ret. Time (min)	Height (mV)	Area (mV*min)	Area (%)
1	25.760	9084.296	375649.031	3.42
2	27.475	164236.344	10620019.000	96.58
Totals				93

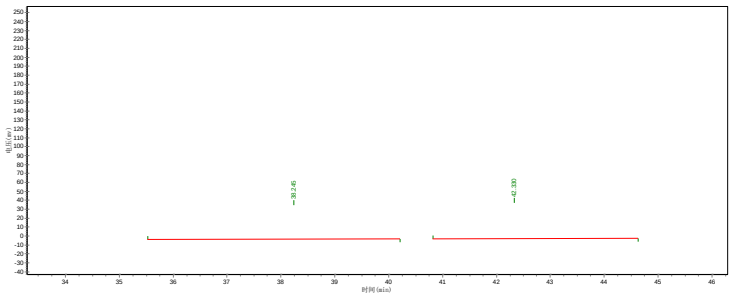


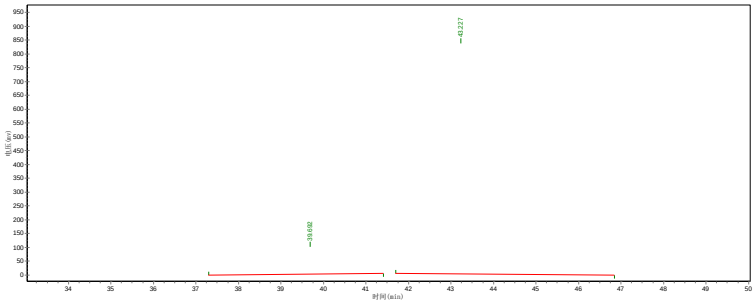


Peak	Ret. Time (min)	Height (mV)	Area (mV*min)	Area (%)
1	15.938	20368.398	588482.000	6.33

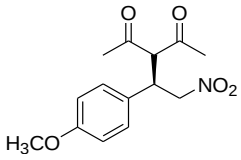
2	33.768	138336.703	8705237.000	93.67
Totals				88

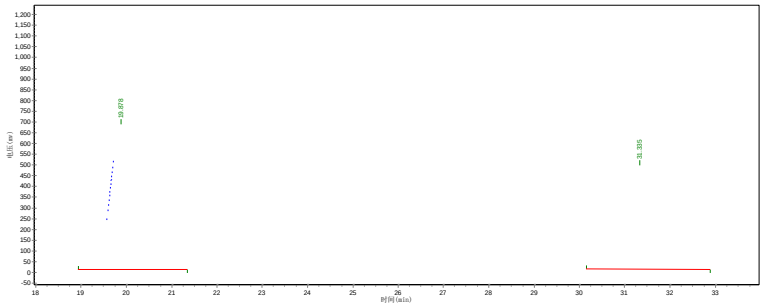


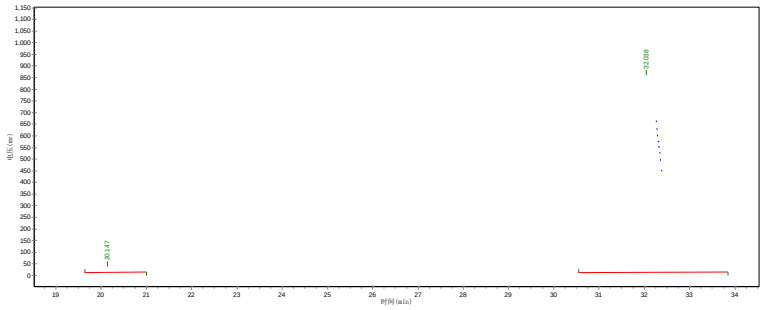




Peak	Ret. Time (min)	Height (mV)	Area (mV*min)	Area (%)
1	39.692	98558.008	8353256.000	9.72
2	43.227	833338.500	77555608.000	90.28
totals				81







Peak	Ret. Time (min)	Height (mV)	Area (mV*min)	Area (%)
1	20.147	24718.764	869847.375	1.89
2	32.038	847358.875	45104788.000	98.11
Totals				96