Novel Thiourea-Amine Bifunctional Catalysts for Asymmetric Conjugate Addition of Ketones/Aldehydes to Nitroalkenes: Rational Structural Combination for High Catalytic Efficiency

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Supporting Information

Table of Contents

Experimental Section

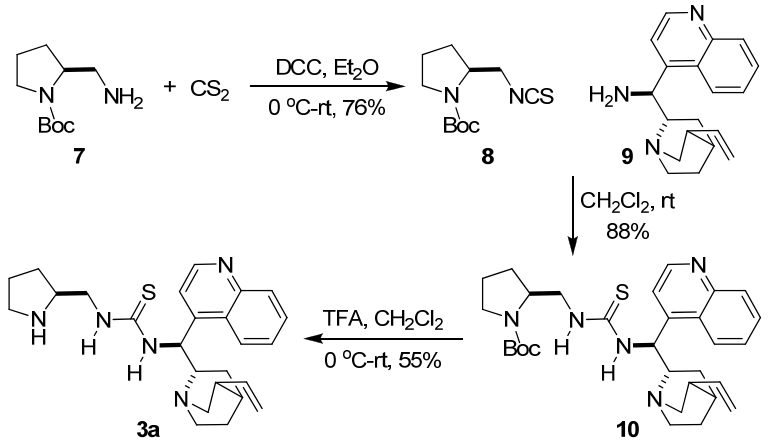
1.0 General Information

Unless otherwise noted, material were purchased from commercial suppliers and used without further purification. Cyclohexanone and dichloromethane were freshly distilled from calcium hydride. n-Hexane, ethyl ether and tetrahydrofuran (THF) were distilled from sodium / benzophenone. Reactions were monitored by thin layer chromatography (TLC), and column chromatography purifications were performed using 200-300 mesh silica gel.

^{1}HNMR spectra were recorded on 400 MHz or 600 MHz spectrophotometers. Solvent for NMR is $CDCl_3$, unless the otherwise noted. Chemical shifts are reported in delta (δ) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = single, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. ^{13}CNMR spectra were recorded on 100 MHz or 150 MHz. Chemical shifts are reported in ppm relative to the central line of the heptalet at 77.0 ppm for $CDCl_3$. The ee values determination was carried out using chiral high-performance liquid chromatography (HPLC) with Daicel Chiracel AD-H, OD-H and AS-H column and the dr values were determined by 400 MHz or 600 MHz ^{1}H NMR. Organocatalys **3-6** were prepared according to the previous procedure[1-2] from proline-derived amine and cinchona alkaloid-derived amines.[3-4]

2.0 Characterization data of catalysts 3-6

General Procedure for Preparing Bifunctional Organocatalysts 3-6. Preparation of 3a is typical.



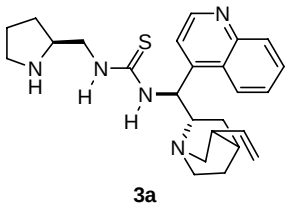
The pure (*s*)-2-amino-1-*N*-Boc-pyrrolidine **7** was obtained as a colorless oil according to the reported procedures.[3a] Carbon bisulfide (6.23 mL, 103.09 mmol) and N,N'-dicyclohexylcarbodiimide (DCC) (3.22 g, 10 mmol) were added to a solution of (*s*)-2-amino-1-*N*-Boc-pyrrolidine **7** (3.13 g, 15.62 mmol) in dry ether (50 mL) at 0 °C. The reaction mixture was allowed to warm slowly to room temperature over a period of 3 h and then was stirred for a further 12 h at room temperature. After separation of the precipitated thiourea by filtration, the solvent was removed under reduced pressure. The residue was purified through flash column chromatography on silica gel (eluent, petroleum ether / ethyl acetate = 20:1 to 5:1) to give the corresponding isothiocyanate **8** in 76% yield (2.89 g).[3b] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.46 (s, 9H), 1.84-1.99 (m, 3H), 2.03-2.14 (m, 1H), 3.37-3.47 (m, 2H), 3.61-3.89 (m, 2H), 3.96-3.97 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.8, 23.6, 28.3, 28.6, 29.3, 46.6, 47.0, 47.1, 47.8, 56.3, 79.7, 80.0, 131.0, 153.9, 154.4.

To a solution of the above isothiocyanate **8** (2.23 g, 9.2 mmol) in dry dichloromethane (50 mL) was added cinchonidine-derived amine **9** (2.70 g, 9.2 mmol).[4] The reaction mixture was stirred for 9 h at room temperature

and was concentrated in vacuo. After column chromatography on silica gel (eluent: ethyl acetate / methanol = 10:1 to 5:1 (0.5% v/v Et_3N)), the Boc-protected thiourea-amine **10** as a white solid was isolated in 88 % yield (4.32 g), which was used directly in the next step. The above Boc-protected thiourea-amine **10** was dissolved in a mixture of TFA/CH_2Cl_2 (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 first purified through flash column chromatography on silica gel (eluent: methanol / TEA = 10:1), then second purification through a short pad of Na_2SO_4 (eluent: CH_2Cl_2) gave **3a** as a white solid in 55% yield (1.93 g).

Other thiourea-amine catalysts (**3b**-**6**) were synthesized according to the above procedures.

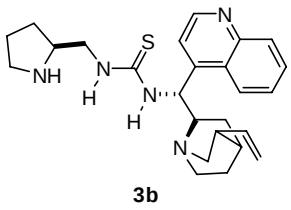
Catalyst 3a



3a

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.81 (s, 1H), 1.14-1.32 (m, 2H), 1.56-1.71 (m, 5H), 2.05 (s, 2H), 2.31 (s, 1H), 2.69-2.91 (m, 4H), 3.15 (s, 1H), 3.25-3.59 (m, 5H), 4.97 (t, J = 14.4 Hz, 2H), 5.69-5.75 (m, 1H), 6.08 (br s, 3H), 7.65 (t, J = 7.8 Hz, 2H), 7.72 (t, J = 7.2 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 8.65 (s, 1H), 8.89 (d, J = 4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.7, 25.4, 27.1, 27.3, 27.9, 39.0, 41.4, 45.1, 45.8, 55.4, 58.9, 114.4, 124.4, 126.6, 127.1, 129.0, 129.8, 140.8, 148.2, 150.0, 182.7; MS (EI) *m/z* 435 (rel intensity) (M^+); Analysis calculated for $C_{25}H_{33}N_5S$: C, 68.93, H, 7.64, N, 16.08. Found: C, 68.89; H, 7.61; N, 16.14.

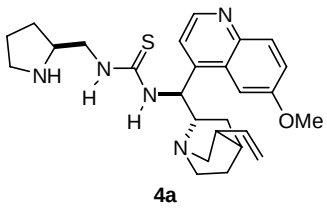
Catalyst 3b



3b

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.75 (s, 1H), 1.09-1.51 (m, 5H), 1.65-1.69 (m, 2H), 1.68-1.89 (m, 1H), 2.22 (q, J = 6.8, 14.8 Hz, 1H), 2.76-2.97 (m, 5H), 3.21-3.79 (m, 4H), 5.15 (t, J = 6.8 Hz, 1H), 5.46 (br s, 2H), 5.80-5.89 (m, 1H), 7.63-7.82 (m, 3H), 8.08 (d, J = 9.6 Hz, 1H), 8.60 (d, J = 8.4 Hz, 1H), 8.90 (d, J = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.4, 24.7, 25.6, 26.9, 28.3, 39.0, 45.3, 45.9, 46.5, 47.3, 48.8, 59.5, 60.5, 114.9, 119.6, 124.3, 126.5, 127.2, 129.1, 129.7, 147.7, 148.1, 150.0, 183.0; MS (EI) *m/z* 436 (rel intensity) (M^++1); Analysis calculated for $C_{25}H_{33}N_5S$: C, 68.93, H, 7.64, N, 16.08. Found: C, 68.97; H, 7.69; N, 16.04.

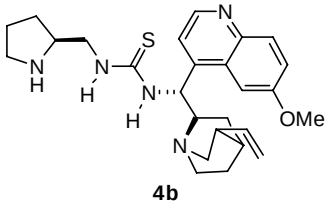
Catalyst 4a



4a

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.74-0.79 (m, 1H), 1.27-1.41 (m, 1H), 1.65-1.78 (m, 7H), 2.33 (s, 1H), 2.80-3.06 (m, 4H), 3.23-3.32 (m, 2H), 3.55-3.87 (m, 4H), 4.03 (s, 3H), 4.90 (d, J = 10.4 Hz, 1H), 4.97 (d, J = 17.2 Hz, 1H), 5.61-5.70 (m, 1H), 6.57 (br s, 3H), 7.37 (dd, J = 2.4, 9.2 Hz, 1H), 7.60 (s, 1H), 7.95 (d, J = 9.2 Hz, 1H), 8.10 (s, 1H), 8.67 (d, J = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.0, 25.2, 26.9, 27.7, 38.6, 41.8, 45.0, 45.8, 53.7, 55.2, 55.7, 59.1,60.1, 102.5, 114.8, 119.7, 122.0, 128.1, 131.0, 140.0, 144.4, 145.2, 147.5, 157.7, 182.5; MS (EI) *m/z* 465 (rel intensity) (M^+); Analysis calculated for $C_{26}H_{35}N_5OS$: C, 67.06, H, 7.58, N, 15.04. Found: C, 67.09; H, 7.54; N, 15.09.

Catalyst 4b

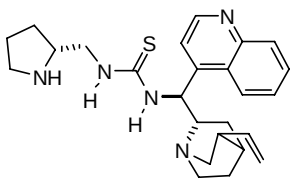


4b

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.81-0.87 (m, 1H), 1.12-1.50 (m, 4H), 1.62-1.79 (m, 2H), 1.86-1.96 (m, 1H), 2.21-2.26 (m, 1H), 2.72-2.95 (m, 5H), 3.33-3.82 (m, 4H), 4.03 (s, 3H), 5.11 (d, J = 10.4 Hz, 1H), 5.19 (d, J = 17.2

Hz, 1H), 5.80-5.89 (m, 1H), 6.57 (br s, 1H), 7.34 (dd, J = 2.4, 9.2 Hz, 1H), 7.80 (s, 1H), 7.93 (d, J = 9.2 Hz, 1H), 8.03 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.8, 24.7, 25.2, 26.5, 27.8, 38.4, 44.8, 45.5, 47.0, 48.6, 52.9, 55.4, 59.9, 102.1, 114.6, 119.6, 122.1, 128.0, 130.6, 139.5, 144.2, 145.5, 147.3, 157.5, 182.7; MS (EI) *m/z* 465 (rel intensity) (M^+); Analysis calculated for $C_{26}H_{35}N_5OS$: C, 67.06, H, 7.58, N, 15.04. Found: C, 67.10; H, 7.53; N, 15.08.

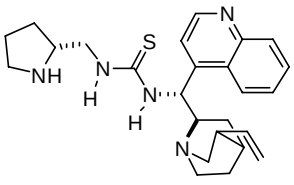
Catalyst 5



5

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.85-.89 (m, 1H), 1.31-1.47 (m, 2H), 1.63-1.76 (m, 5H), 1.90-1.92 (m, 1H), 2.34 (s, 1H), 2.84-2.93 (m, 4H), 3.23-3.27 (m, 1H), 3.54-3.75 (m, 5H), 4.93 (d, J = 6.8 Hz, 1H), 4.98 (d, J = 11.2 Hz, 1H), 5.60-5.65 (m, 1H), 6.35 (br s, 3H), 7.65 (t, J = 5.2 Hz, 1H), 7.72 (t, J = 4.8 Hz, 2H), 8.10 (d, J = 5.6 Hz, 1H), 8.64 (d, J = 5.2 Hz, 1H), 8.90 (d, J = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.9, 24.5, 24.9, 26.8, 27.8, 38.6, 41.3, 44.8, 45.4, 45.9, 55.0, 59.2, 60.3, 114.5, 119.6, 124.2, 126.4, 127.0, 128.9, 129.6, 140.0, 147.2, 147.9, 149.9, 182.6; MS (EI) *m/z* 435 (rel intensity) (M^+); Analysis calculated for $C_{25}H_{33}N_5S$: C, 68.93, H, 7.64, N, 16.08. Found: C, 68.96; H, 7.62; N, 16.03.

Catalyst 6

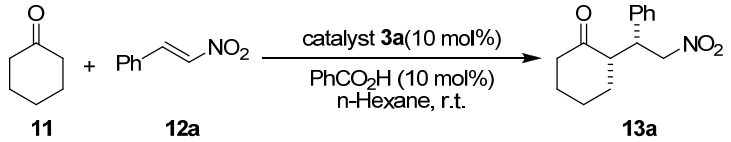


6

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.78-0.82 (m, 1H), 1.09-1.20 (m, 2H), 1.42-1.58 (m, 7H), 2.24-2.30 (m, 1H), 2.57-3.15 (m, 10H), 3.91 (br s, 1H), 5.16 (dd, J = 6.0, 7.2 Hz, 2H), 5.84-5.93 (m, 1H), 7.48 (s, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.72 (t, J = 8.0 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 8.53 (s, 1H), 8.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.6, 25.8, 26.8, 28.1, 38.7, 45.4, 46.8, 48.5, 57.7, 60.2, 114.4, 123.9, 126.1, 126.8, 128.7, 129.4, 139.6, 147.7, 149.6, 182.2; MS (EI) *m/z* 435 (rel intensity) (M^+); Analysis calculated for $C_{25}H_{33}N_5S$: C, 68.93, H, 7.64, N, 16.08. Found: C, 68.99; H, 7.67; N, 16.04.

3.0 Characterization data of Michael products 13a-o

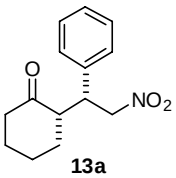
Representative procedure for the Asymmetric Michael Reaction of Nitroolefin 12a with Cyclohexanone 11 (Table 3, entry 1).



11 **12a** **13a**

The organocatalyst **3a** (22.0 mg, 0.05 mmol), $PhCO_2H$ (6.1 mg, 0.05 mmol) and cyclohexanone **11** (0.53 mL, 5.0 mmol) were stirred in 1 mL of n-hexane for 10 min at room temperature. *trans-β*-Styrene **12a** (75.0 mg, 0.5 mmol) was then added and the reaction mixture was stirred for 5 h. After the complete consumption of **12a** (as monitored by TLC). The reaction mixture was concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (petroleum ether / ethyl acetate (4:1 to 2:1)) to give the corresponding pure Michael product **13a** (110.0 mg, 89%) as a white solid. 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 **13a-o** and **15** are known.[1-2,5]

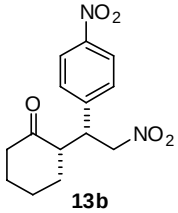
2-(2-nitro-1-phenylethyl)cyclohexanone (13a), (Table 3, entry 1).



13a

The ee was determined by HPLC (Chiralpak AS column, hexane/*i*-PrOH 75:25, flow rate 1.0 mL/min, λ = 210 nm, 20 ^{o}C). t_R (minor) = 9.3 min; t_R (major) = 13.3 min. *syn*/*anti* = 97/3, *syn*: ee = 96%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.18-1.28 (m, 1H), 1.51-1.61 (m, 1H), 1.66-1.81 (m, 3H), 2.05-2.11 (m, 1H), 2.35-2.43 (m, 1H), 2.45-2.50 (m, 1H), 2.65-2.72 (m, 1H), 3.73-3.79 (m, 1H), 4.62 (dd, J = 10.0, 12.4 Hz, 1H), 4.95 (dd, J = 4.4, 12.4 Hz, 1H), 7.16-7.18 (m, 2H), 7.24-7.34 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.8, 28.3, 33.0, 42.5, 43.7, 52.2, 78.7, 127.5, 127.9, 128.7, 137.5, 211.9.

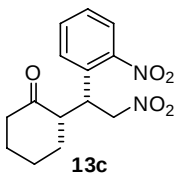
2-(2-nitro-1-(4-nitrophenyl)ethyl)cyclohexanone (13b), (Table 3, entry 2).



13b

The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 75:25, flow rate 1.0 mL/min, λ = 254 nm, 20 ^{o}C). t_R (minor) = 13.1 min; t_R (major) = 28.9 min, *syn*/*anti* = 93/7, *syn*: ee = 94%. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 1.24-1.30 (m, 1H), 1.57-1.71 (m, 4H), 1.81-1.84 (m, 1H), 2.11-2.13 (m, 1H), 2.36-2.42 (m, 1H), 2.48-2.50 (m, 1H), 2.70-2.75 (m, 1H), 3.91-3.95 (m, 1H), 4.70 (dd, J = 10.8, 12.6 Hz, 1H), 5.00 (dd, J = 4.2, 13.2 Hz, 1H), 7.40 (d, J = 8.4 Hz, 2H), 8.20 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.9, 28.1, 33.0, 42.5, 43.6, 52.0, 77.9, 123.9, 129.2, 145.5, 147.2, 210.8.

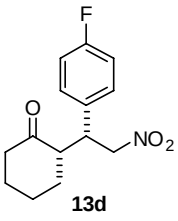
2-(2-nitro-1-(2-nitrophenyl)ethyl)cyclohexanone (13c) , (Table 3, entry 3).



13c

The ee was determined by HPLC (Chiralpak AS column, hexane/*i*-PrOH 80:20, flow rate 1.0 mL/min, λ = 254 nm, 20 ^{o}C). t_R (minor) = 23.2 min; t_R (major) = 29.8 min, *syn*/*anti* = 98/2, *syn*: ee = 95%. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 1.45-1.51 (m, 1H), 1.60-1.73 (m, 2H), 1.80-1.85 (m, 2H), 2.10-2.13 (m, 1H), 2.34-2.41 (m, 1H), 2.46-2.49 (m, 1H), 2.92-2.96 (m, 1H), 4.31-3.35 (m, 1H), 4.92 (d, J = 6.6 Hz, 2H), 7.42-7.47 (m, 2H), 7.59 (t, J = 7.8 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.2, 28.2, 33.0, 41.8, 42.7, 52.1, 77.6, 124.7, 128.4, 129.0, 132.7, 133.0, 150.7, 211.0.

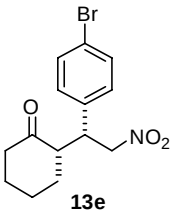
2-(1-(4-fluorophenyl)-2-nitroethyl)cyclohexanone (13d) , (Table 3, entry 4).



13d

The ee was determined by HPLC (Chiralpak OD column, hexane/*i*-PrOH 95:5, flow rate 1.0 mL/min, λ = 210 nm, 20 ^{o}C). t_R (minor) = 18.8 min; t_R (major) = 20.8 min, *syn*/*anti* = 97/3, *syn*: ee = 94%. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 1.20-1.26 (m, 1H), 1.55-1.73 (m, 2H), 1.79-1.87 (m, 1H), 2.07-2.10 (m, 1H), 2.33-2.41 (m, 1H), 2.46-2.48 (m, 1H), 2.63-2.67 (m, 1H), 3.75-3.79 (m, 1H), 4.60 (t, *J* = 10.8 Hz, 1H), 4.93 (dd, *J* = 4.2, 12.0 Hz, 1H), 7.01 (t, *J* = 8.4 Hz, 2H), 7.14-7.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.9, 28.3, 33.0, 42.6, 43.1, 52.4, 78.7, 115.6, 115.8, 129.6, 129.7, 133.4, 133.5, 160.7, 163.2, 211.6.

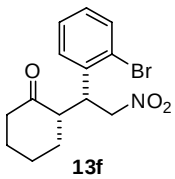
2-(1-(4-bromophenyl)-2-nitroethyl)cyclohexanone (13e) , (Table 3, entry 5).



13e

The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 90:10, flow rate 1.0 mL/min, λ = 210 nm, 20 ^{o}C). t_R (minor) = 14.0 min; t_R (major) = 22.9 min, *syn*/*anti* = 94/6, *syn*: ee = 94%. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 1.19-1.26 (m, 1H), 1.56-1.73 (m, 3H), 1.78-1.81 (m, 1H), 2.07-2.10 (m, 1H), 2.34-2.40 (m, 1H), 2.46-2.48 (m, 1H), 2.62-2.67 (m, 1H), 3.72-3.76 (m, 1H), 4.60 (dd, *J* = 10.2, 12.6 Hz, 1H), 4.93 (dd, *J* = 4.2, 12.6 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.9, 28.3, 33.0, 42.6, 43.3, 52.2, 78.4, 121.6, 129.8, 131.9, 136.7, 211.4.

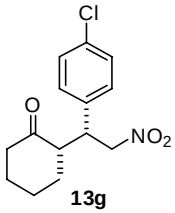
2-(1-(2-bromophenyl)-2-nitroethyl)cyclohexanone (13f) , (Table 3, entry 6).



13f

The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 85:15, flow rate 1.0 mL/min, λ = 210 nm, 20 ^{o}C). t_R (minor) = 8.9 min; t_R (major) = 14.3 min, *syn*/*anti* = 98/2, *syn*: ee = 90%. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 1.37-1.39 (m, 1H), 1.61-1.76 (m, 3H), 1.81-1.87 (m, 1H), 2.09-2.12 (m, 1H), 2.35-2.41 (m, 1H), 2.46-2.48 (m, 1H), 2.90 (s, 1H), 4.30 (s, 1H), 4.86-4.94 (m, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.0, 28.3, 32.7, 41.7, 42.5, 52.0, 77.2, 127.8, 128.8, 133.3, 137.1, 211.3.

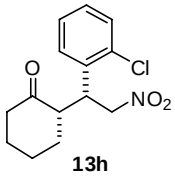
2-(1-(4-chlorophenyl)-2-nitroethyl)cyclohexanone (13g) , (Table 3, entry 7).



13g

The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 90:10, flow rate 1.0 mL/min, λ = 210 nm, 20 ^{o}C). t_R (minor) = 13.2 min; t_R (major) = 20.0 min, *syn*/*anti* = 93/7, *syn*: ee = 94%. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 1.19-1.26 (m, 1H), 1.53-1.59 (m, 1H), 1.63-1.73 (m, 2H), 1.78-1.81 (m, 1H), 2.07-2.11 (m, 1H), 2.32-2.40 (m, 1H), 2.45-2.48 (m, 1H), 2.62-2.67 (m, 1H), 3.74-3.78 (m, 1H), 4.60 (dd, *J* = 9.6, 12.0 Hz, 1H), 4.93 (dd, *J* = 4.2, 12.6 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.9, 28.3, 33.0, 42.6, 43.2, 52.2, 78.5, 129.0, 129.4, 133.4, 136.2, 211.4.

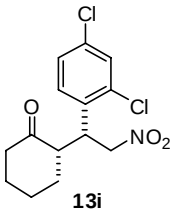
2-(1-(2-chlorophenyl)-2-nitroethyl)cyclohexanone (13h) , (Table 3, entry 8).



13h

The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 95:5, flow rate 1.0 mL/min, λ = 210 nm, 20 ^{o}C). t_R (minor) = 13.8 min; t_R (major) = 24.3 min, *syn*/*anti* = 97/3, *syn*: ee = 94%. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 1.30-1.36 (m, 1H), 1.57-1.73 (m, 3H), 1.80-1.87 (m, 1H), 2.08-2.11 (m, 1H), 2.32-2.41 (m, 1H), 2.46-2.48 (m, 1H), 2.91 (s, 1H), 4.29 (d, *J* = 7.8 Hz, 1H), 4.89 (d, *J* = 6.6 Hz, 2H), 7.19-7.25 (m, 3H), 7.37 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.0, 28.3, 32.7, 40.7, 42.5, 51.5, 77.1, 127.2, 128.6, 129.2, 130.0, 134.3, 135.3, 211.5.

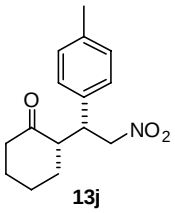
2-(1-(2,4-dichlorophenyl)-2-nitroethyl)cyclohexanone (13i) , (Table 3, entry 9).



13i

The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 90:10, flow rate 1.0 mL/min, λ = 210 nm, 20 °C). t_R (minor) = 10.1 min; t_R (major) = 14.6 min, *syn*/*anti* = 95/5, *syn*: ee = 95%. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 1.30-1.36 (m, 1H), 1.59-1.75 (m, 3H), 1.82-1.87 (m, 1H), 2.09-2.12 (m, 1H), 2.37-2.40 (m, 1H), 2.46-2.48 (m, 1H), 2.87 (s, 1H), 4.24 (dd, *J* = 7.2, 15.6 Hz, 1H), 4.88 (d, *J* = 6.6 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.40 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.2, 27.0, 28.4, 32.9, 40.5, 42.7, 51.6, 77.4, 127.7, 130.0, 133.9, 134.2, 135.2, 211.3.

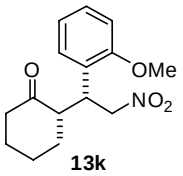
2-(2-nitro-1-*p*-tolylethyl)cyclohexanone (13j) , (Table 3, entry 10).



13j

The ee was determined by HPLC (Chiralpak AS column, hexane/*i*-PrOH 90:10, flow rate 0.8 mL/min; λ = 210 nm, 20 °C). t_R (minor) = 15.9 min; t_R (major) = 28.1 min, *syn*/*anti* = 94/6, *syn*: ee = 92%. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 1.19-1.26 (m, 1H), 1.53-1.59 (m, 1H), 1.64-1.79 (m, 3H), 2.05-2.09 (m, 1H), 2.31 (s, 3H), 2.35-2.40 (m, 1H), 2.45-2.48 (m, 1H), 2.64-2.68 (m, 1H), 3.69-3.73 (m, 1H), 4.60 (dd, *J* = 10.2, 12.0 Hz, 1H), 4.92 (dd, *J* = 4.8, 12.6 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.9, 24.9, 28.4, 33.0, 42.6, 43.4, 52.4, 78.9, 127.9, 129.4, 134.5, 137.2, 211.9.

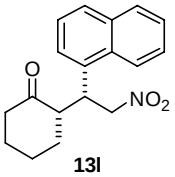
2-(1-(2-methoxyphenyl)-2-nitroethyl)cyclohexanone (13k) , (Table 3, entry 11).



13k

The ee was determined by HPLC (Chiralpak AS column, hexane/*i*-PrOH 90:10, flow rate 1.0 mL/min, λ = 210 nm, 20 °C). t_R (minor) = 15.3 min; t_R (major) = 17.7 min, *syn*/*anti* = 95/5, *syn*: ee = 92%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.15-1.25 (m, 1H), 1.51-1.52 (m, 1H), 1.66-1.87 (m, 3H), 2.03-2.09 (m, 1H), 2.31-2.42 (m, 1H), 2.44-2.48 (m, 1H), 2.94-3.01 (m, 1H), 3.84 (s, 3H), 3.93-3.99 (m, 1H), 4.82 (dd, *J* = 2.4, 5.2 Hz, 2H), 6.88 (t, *J* = 7.6 Hz, 2H), 7.08 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.22-7.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.9, 28.3, 33.1, 41.1, 42.5, 50.3, 55.1, 110.8, 120.6, 125.1, 128.7, 130.7, 157.4, 212.3.

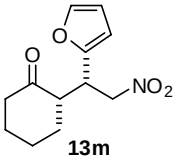
2-(1-(naphthalen-1-yl)-2-nitroethyl)cyclohexanone (13l) , (Table 3, entry 12).



13l

The ee was determined by HPLC (Chiralpak AS column, hexane/*i*-PrOH 50:50, flow rate 0.7 mL/min, λ = 254 nm, 20 °C). t_R (minor) = 12.0 min; t_R (major) = 17.2 min, *syn*/*anti* = 93/7, *syn*: ee = 92%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.20-1.30 (m, 1H), 1.47-1.56 (m, 1H), 1.62-1.71 (m, 3H), 2.06-2.11 (m, 1H), 2.38-2.53 (m, 1H), 2.85 (s, 1H), 4.77 (s, 1H), 4.91 (t, *J* = 10.0 Hz, 1H), 5.08 (dd, *J* = 4.4, 12.8 Hz, 1H), 7.37-7.58 (m, 4H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 8.18 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.0, 28.5, 33.1, 36.6, 42.7, 53.6, 78.6, 122.6, 123.4, 125.2, 125.7, 126.4, 127.9, 128.8, 132.3, 133.8, 134.5, 212.1.

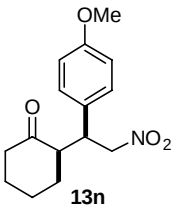
2-(1-(furan-2-yl)-2-nitroethyl)cyclohexanone (13m) , (Table 3, entry 13).



13m

The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 90:10, flow rate 1.0 mL/min, λ = 210 nm, 20 °C). t_R (major) = 11.1 min; t_R (minor) = 13.5 min, *syn*/*anti* = 92/8, *syn*: ee = 85%. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 1.25-1.32 (m, 1H), 1.62-1.66 (m, 2H), 1.74-1.77 (m, 1H), 1.83-1.85 (m, 1H), 2.09-2.11 (m, 1H), 2.34-2.39 (m, 1H), 2.45-2.47 (m, 1H), 2.73-2.77 (m, 1H), 3.95-3.99 (m, 1H), 4.67 (dd, *J* = 9.6, 12.6 Hz, 1H), 4.79 (dd, *J* = 4.8, 12.6 Hz, 1H), 6.18 (d, *J* = 3.0 Hz, 1H), 6.28 (dd, *J* = 1.8, 3.0 Hz, 1H), 7.34 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.9, 28.0, 32.3, 37.4, 42.3, 50.9, 76.5, 108.7, 110.1, 142.1, 150.8, 210.8.

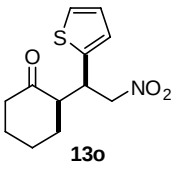
2-(1-(4-methoxyphenyl)-2-nitroethyl)cyclohexanone (13n) , (Table 3, entry 25).



13n

The ee was determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 75:25, flow rate 0.7 mL/min, λ = 210 nm, 20 ^{o}C). t_R (major) = 11.8 min; t_R (minor) = 14.3 min, *syn*/*anti* = 89/11, *syn*: ee = -85%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.17-1.18 (m, 1H), 1.51-1.58 (m, 1H), 1.65-1.81 (m, 3H), 2.04-2.11 (m, 1H), 2.33-2.41 (m, 1H), 2.44-2.49 (m, 1H), 2.61-2.67 (m, 1H), 3.68-3.74 (m, 1H), 3.77 (s, 3H), 4.58 (dd, J = 10.0, 12.4 Hz, 1H), 4.90 (dd, J = 4.4, 12.0 Hz, 1H), 6.84 (d, J = 8.8 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.8, 28.4, 33.0, 42.5, 43.0, 52.5, 55.0, 78.9, 114.1, 129.0, 129.4, 158.8, 211.9.

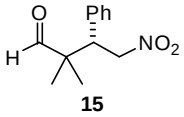
2-(2-nitro-1-(thiophen-2-yl)ethyl)cyclohexanone (13o) , (Table 3, entry 26).



13o

The ee was determined by HPLC (Chiralpak AS column, hexane/*i*-PrOH 90:10, flow rate 1.0 mL/min, λ = 210 nm, 20 ^{o}C). t_R (major) = 21.0 min; t_R (minor) = 29.2 min, *syn*/*anti* = 85/15, *syn*: ee = -82%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.27-1.43 (m, 1H), 1.60-1.73 (m, 2H), 1.83-1.93 (m, 2H), 2.04-2.12 (m, 1H), 2.32-2.39 (m, 1H), 2.42-2.48 (m, 1H), 2.64-2.71 (m, 1H), 4.10-4.16 (m, 1H), 4.65 (dd, J = 9.2, 12.4 Hz, 1H), 4.89 (dd, J = 4.8, 12.8 Hz, 1H), 6.87 (d, J = 2.8 Hz, 1H), 6.93 (dd, J = 3.6, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.9, 28.1, 32.6, 39.2, 42.4, 53.1, 79.1, 124.8, 126.4, 126.7, 140.3, 211.1.

(S)-2,2-dimethyl-4-nitro-3-phenylbutanal (15) , (Eq 1).



15

The ee was determined by HPLC (Chiralpak OD column, hexane/*i*-PrOH 80:20, flow rate 0.8 mL/min, λ = 210 nm, 20 ^{o}C). t_R (major) = 17.6 min; t_R (minor) = 25.8 min, ee = 85%. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 1.01 (s, 3H), 1.14 (s, 3H), 3.78 (dd, J = 3.0, 10.8 Hz, 1H), 4.69 (dd, J = 3.6, 13.2 Hz, 1H), 4.85 (t, J = 12.6 Hz, 1H), 7.20 (d, J = 7.2 Hz, 2H), 7.29-7.34 (m, 3H), 9.53 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.5, 21.4, 48.1, 76.1, 127.9, 128.5, 128.9, 135.1, 204.2.

4.0 References

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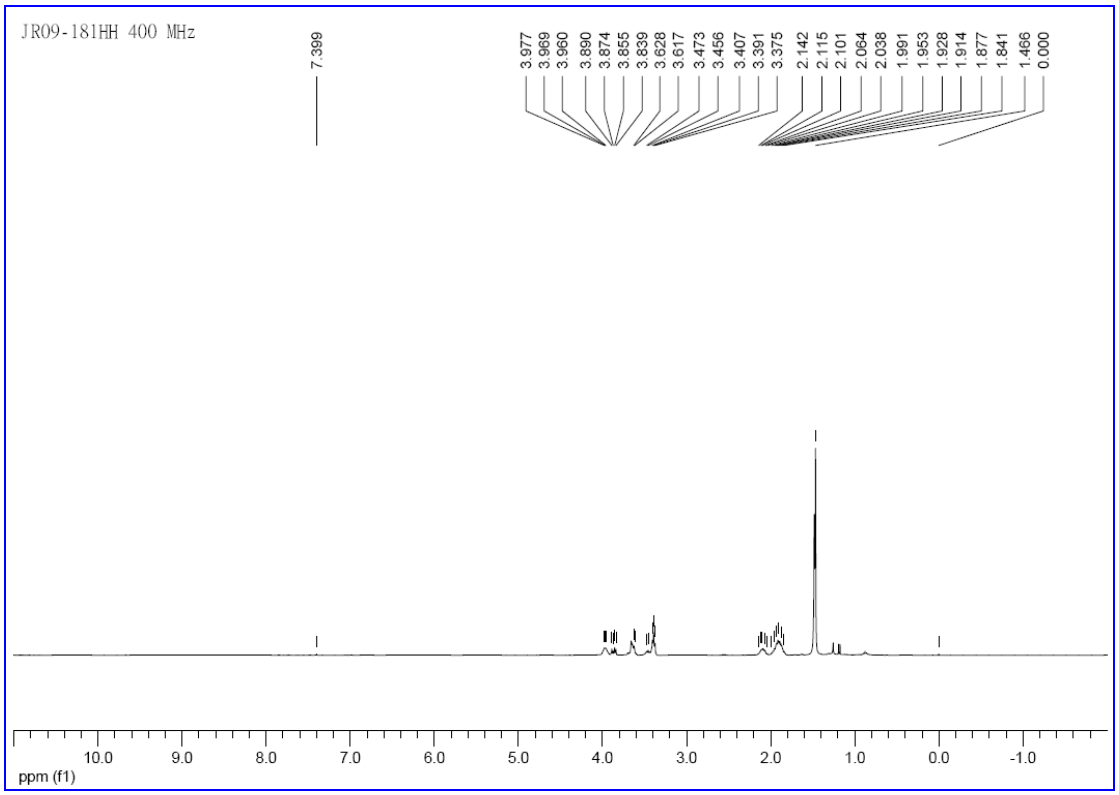
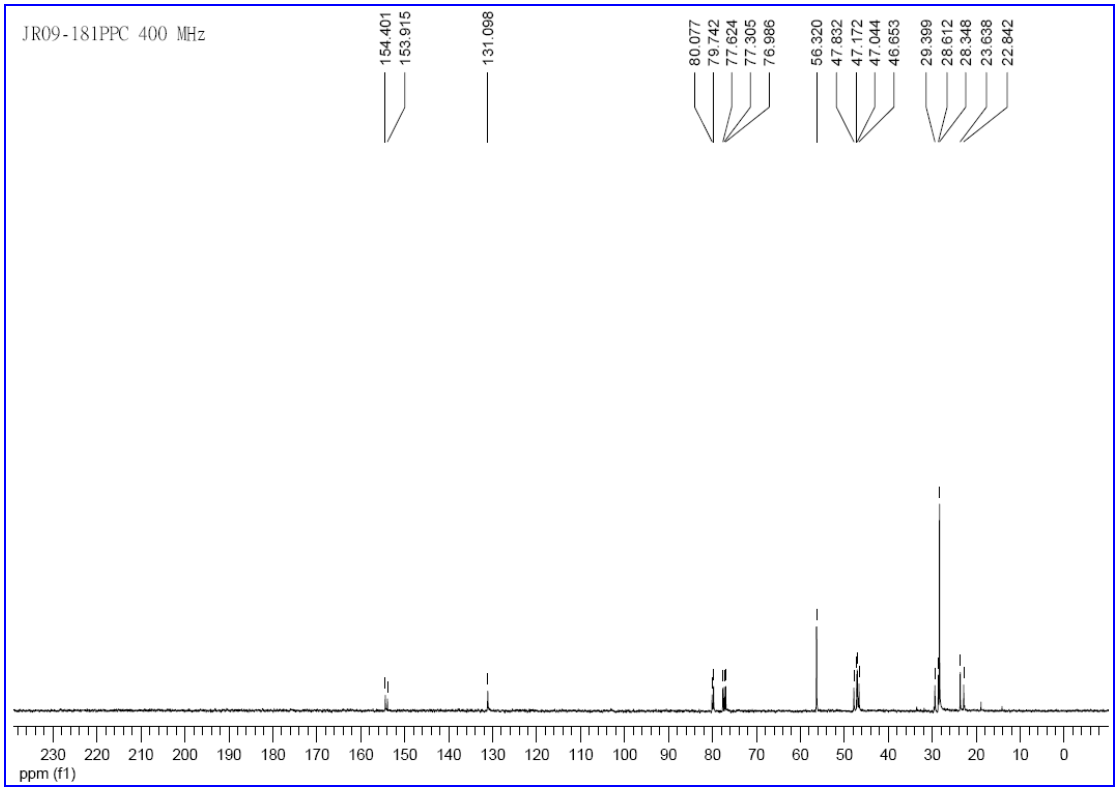
5.0 NMR Spectra

Catalyst NMR Spectra

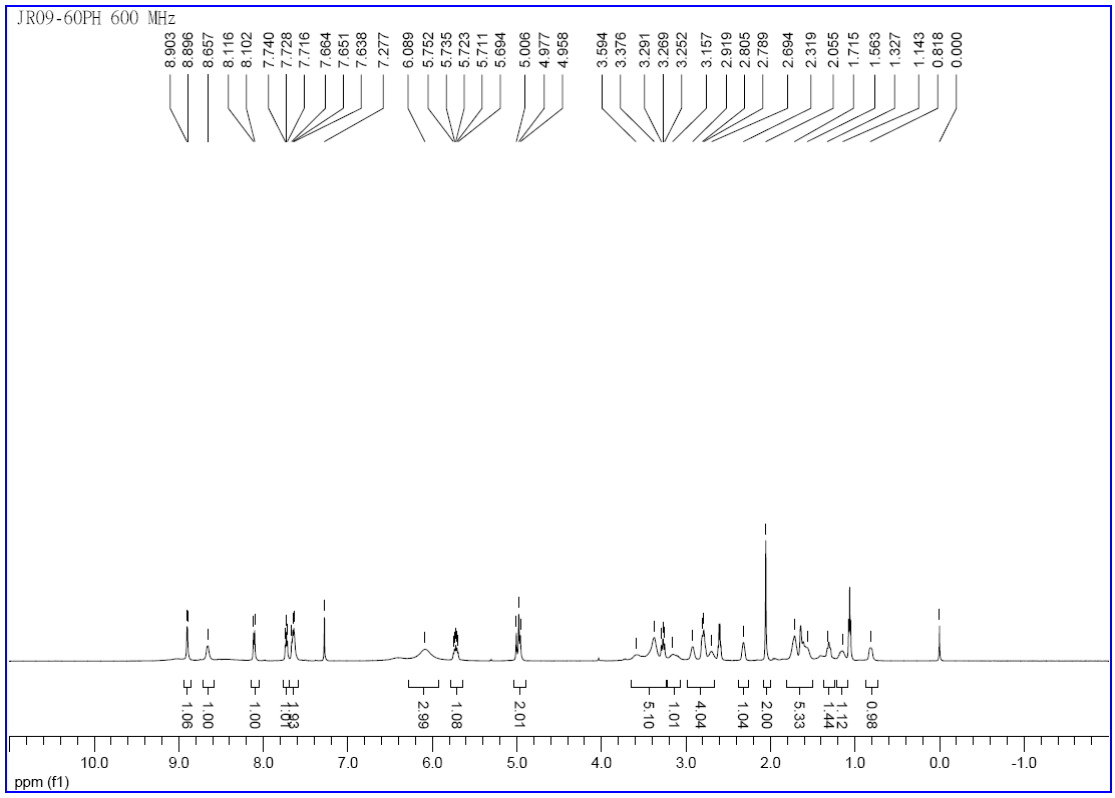
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of isothiocyanate 8



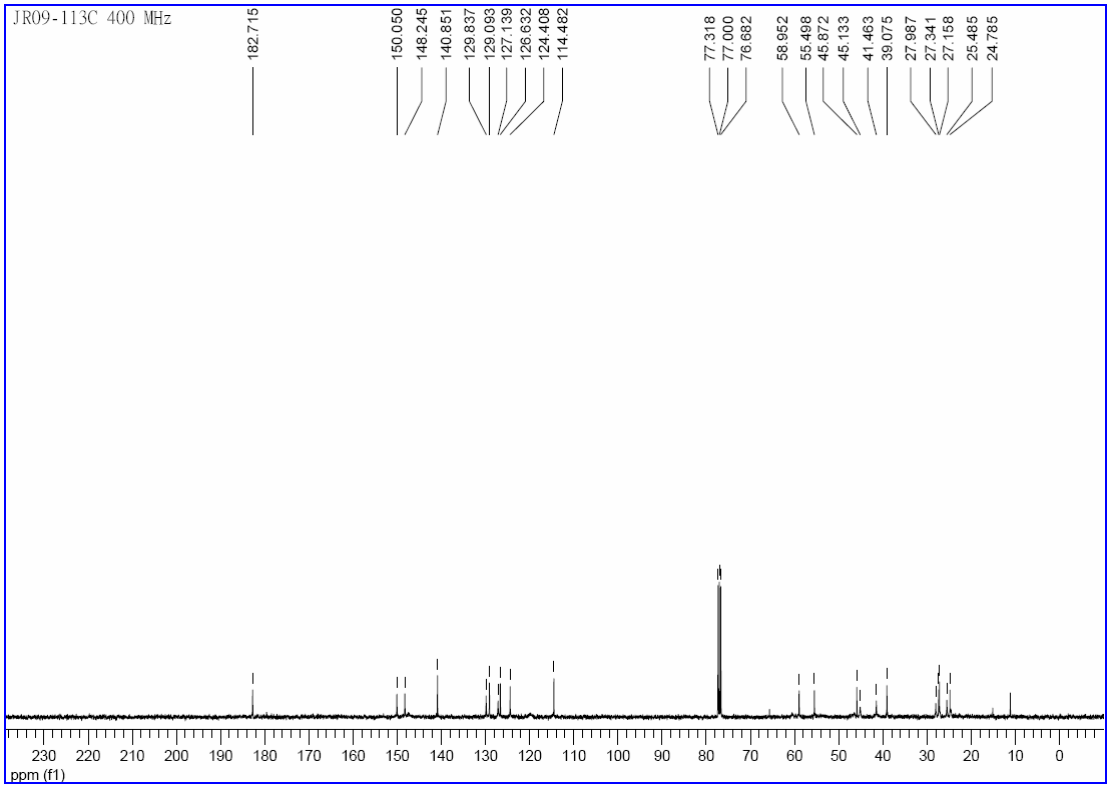
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of isothiocyanate 8



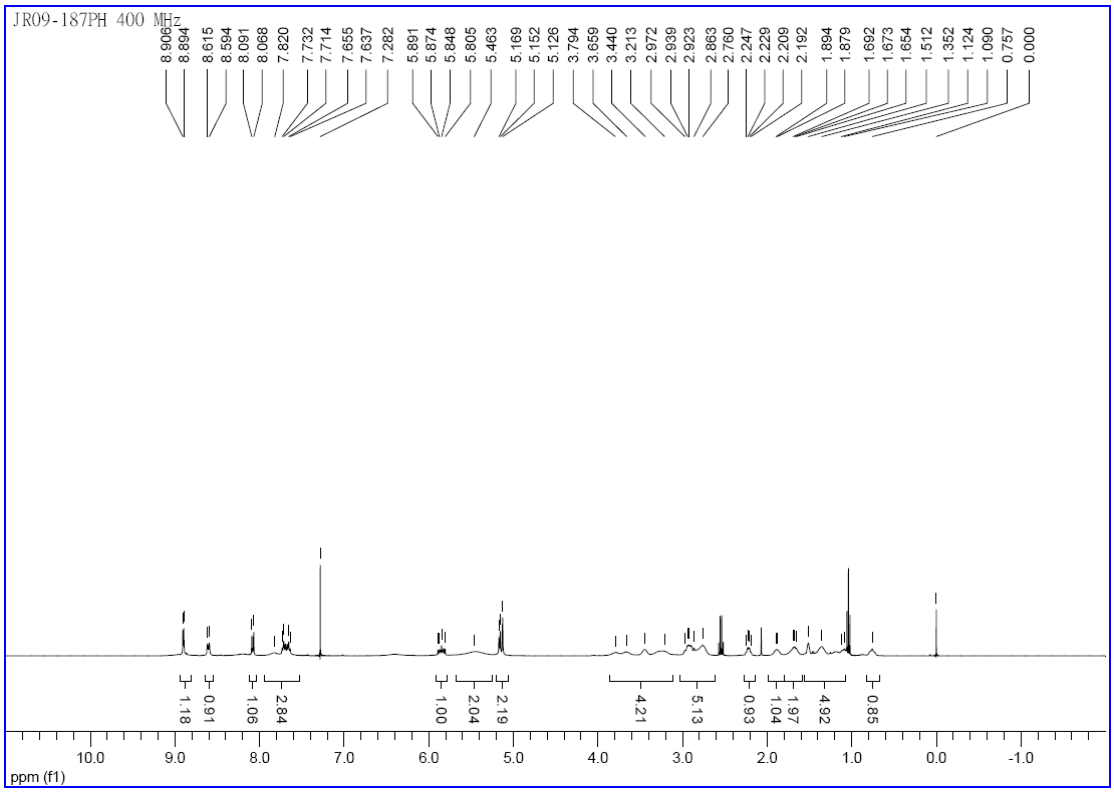
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of catalyst 3a



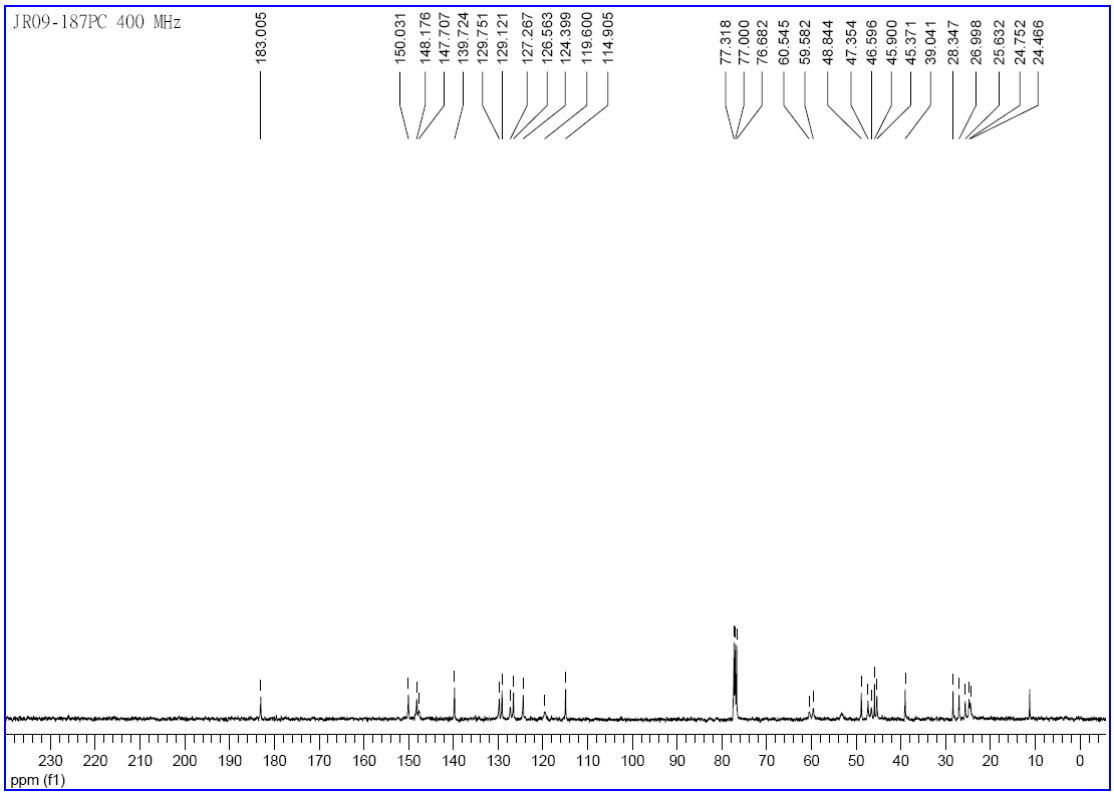
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of catalyst 3a



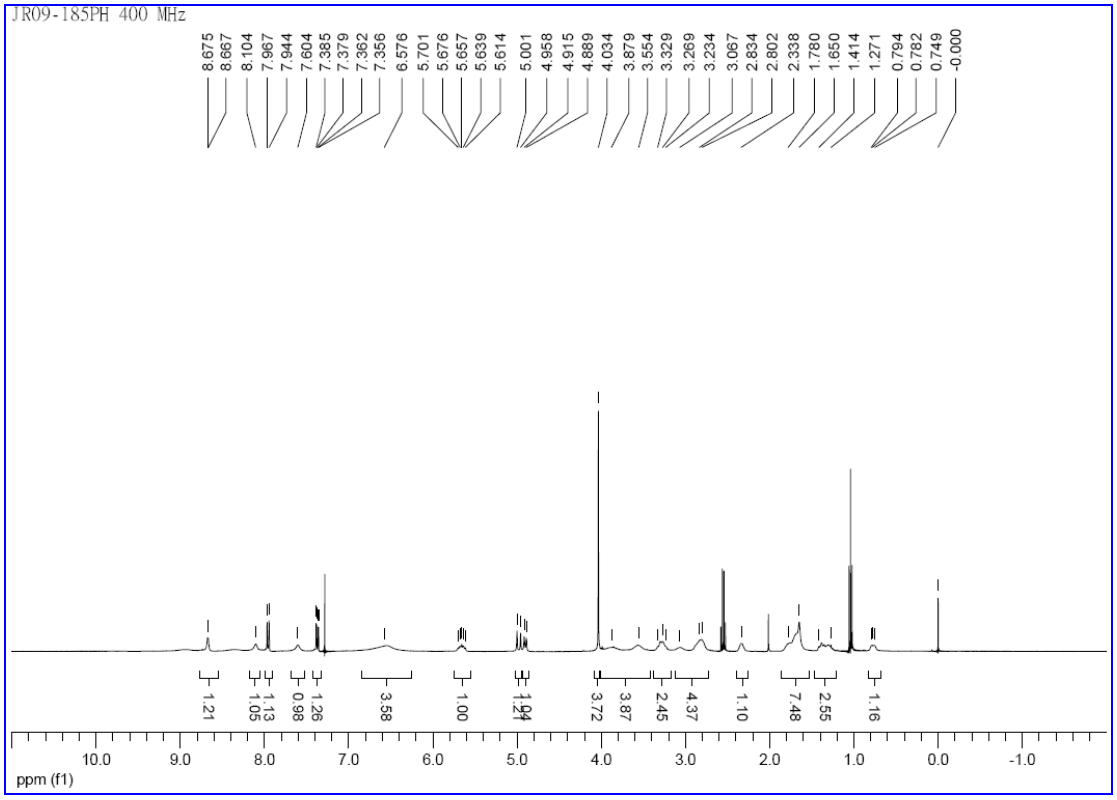
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of catalyst 3b



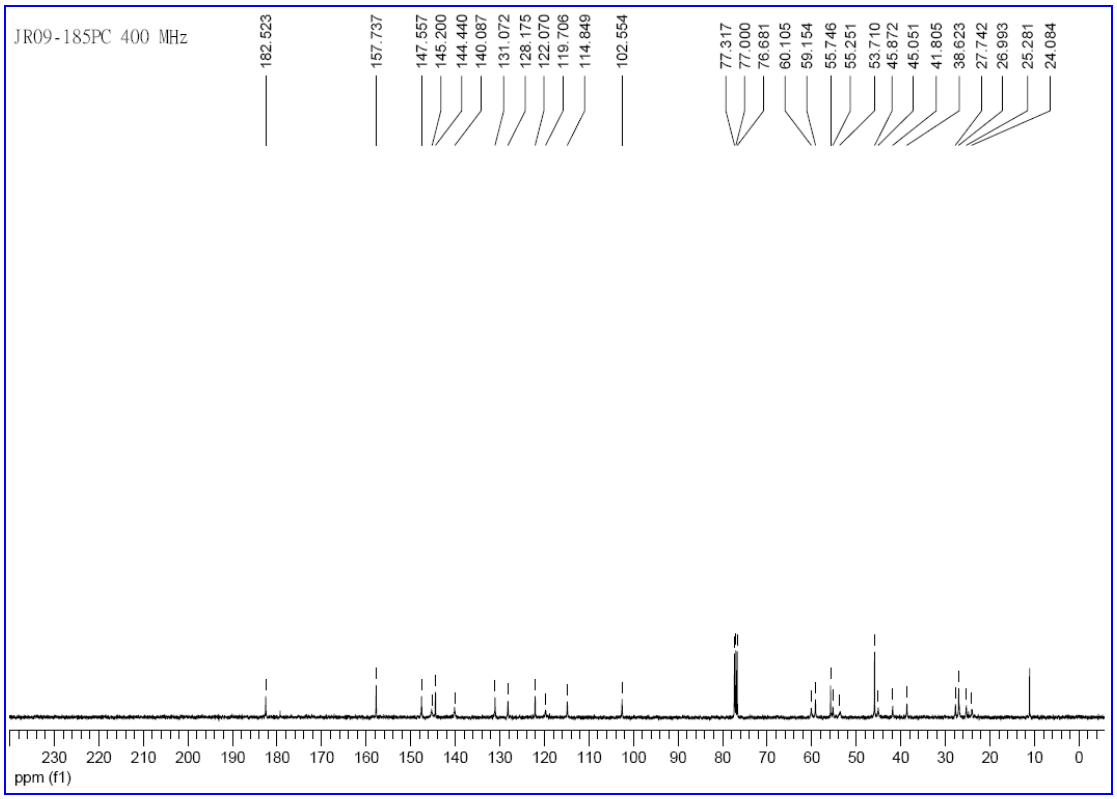
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of catalyst 3b



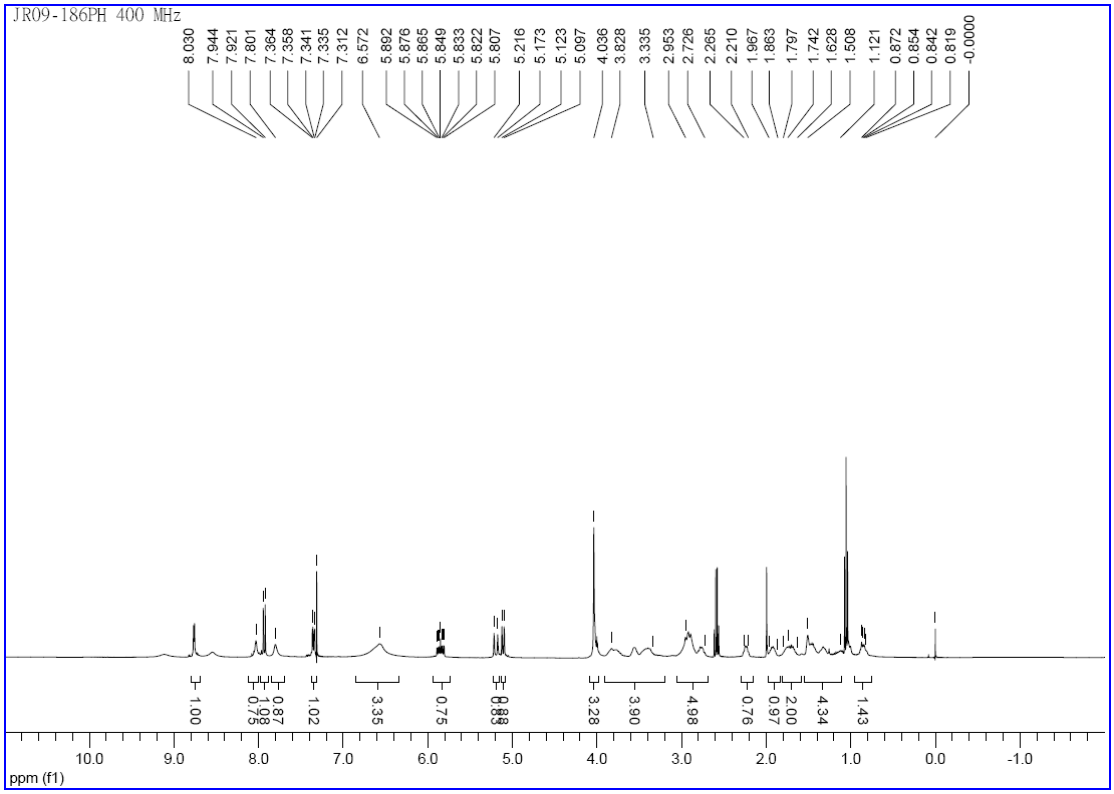
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of catalyst 4a



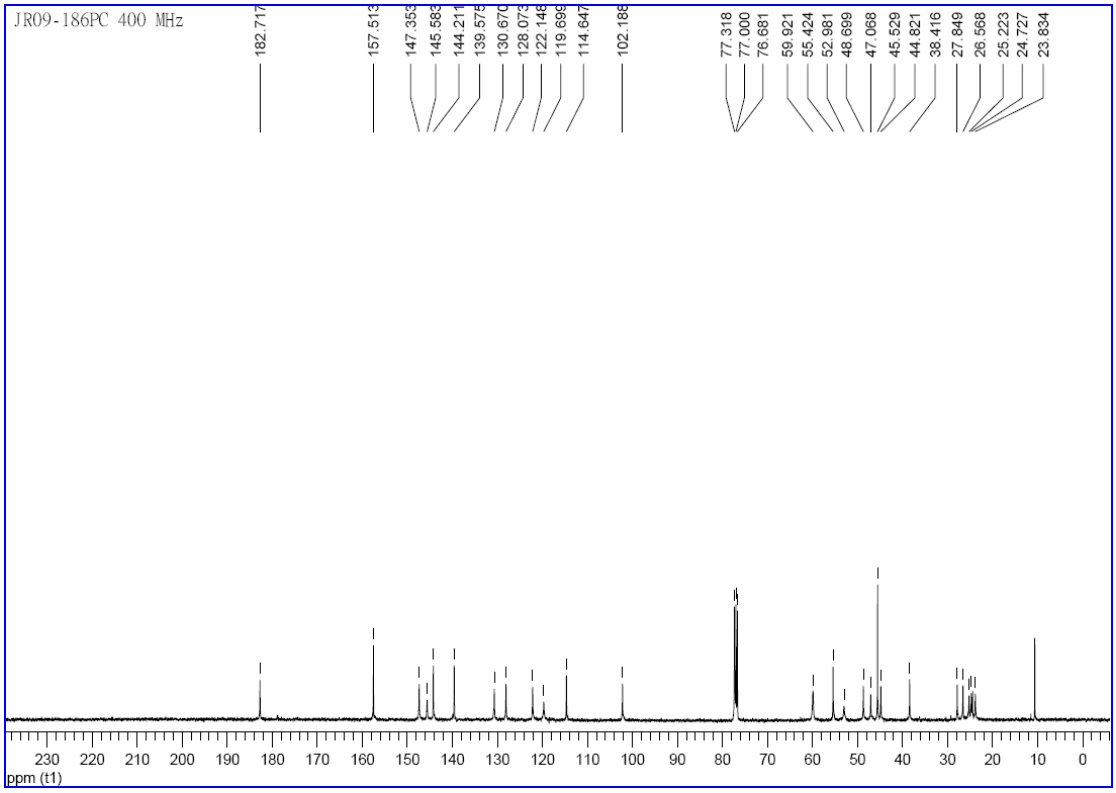
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of catalyst 4a



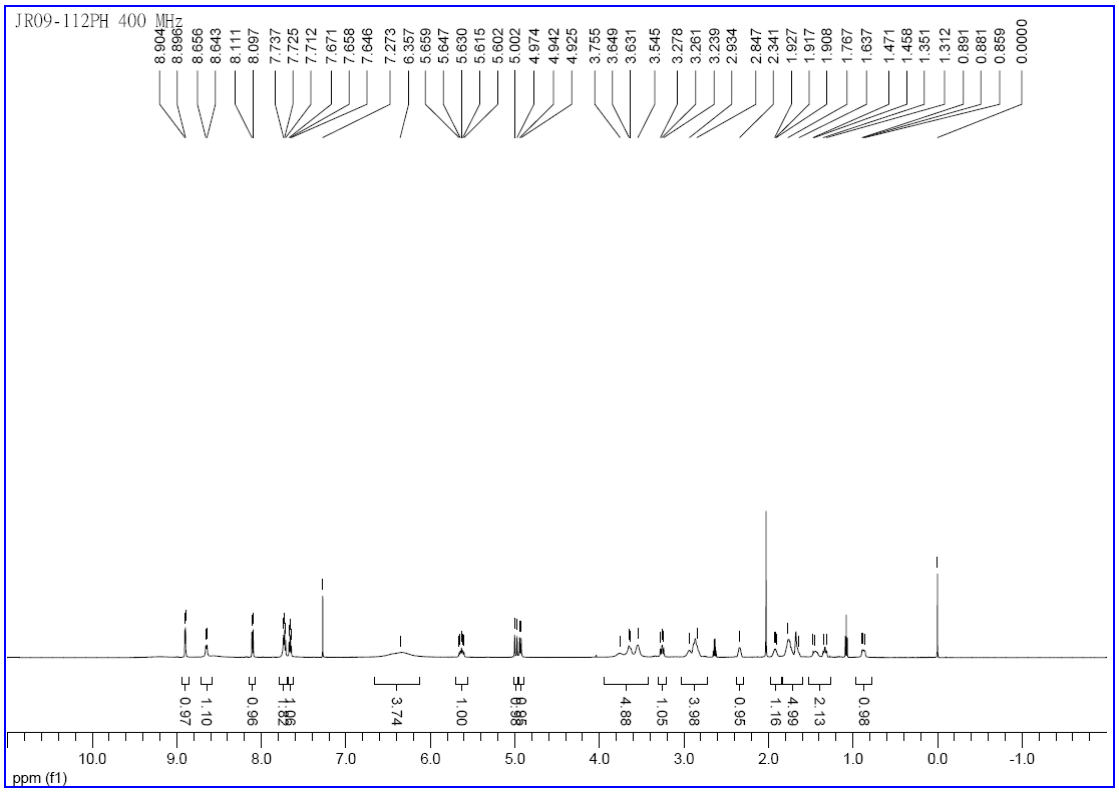
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of catalyst 4b



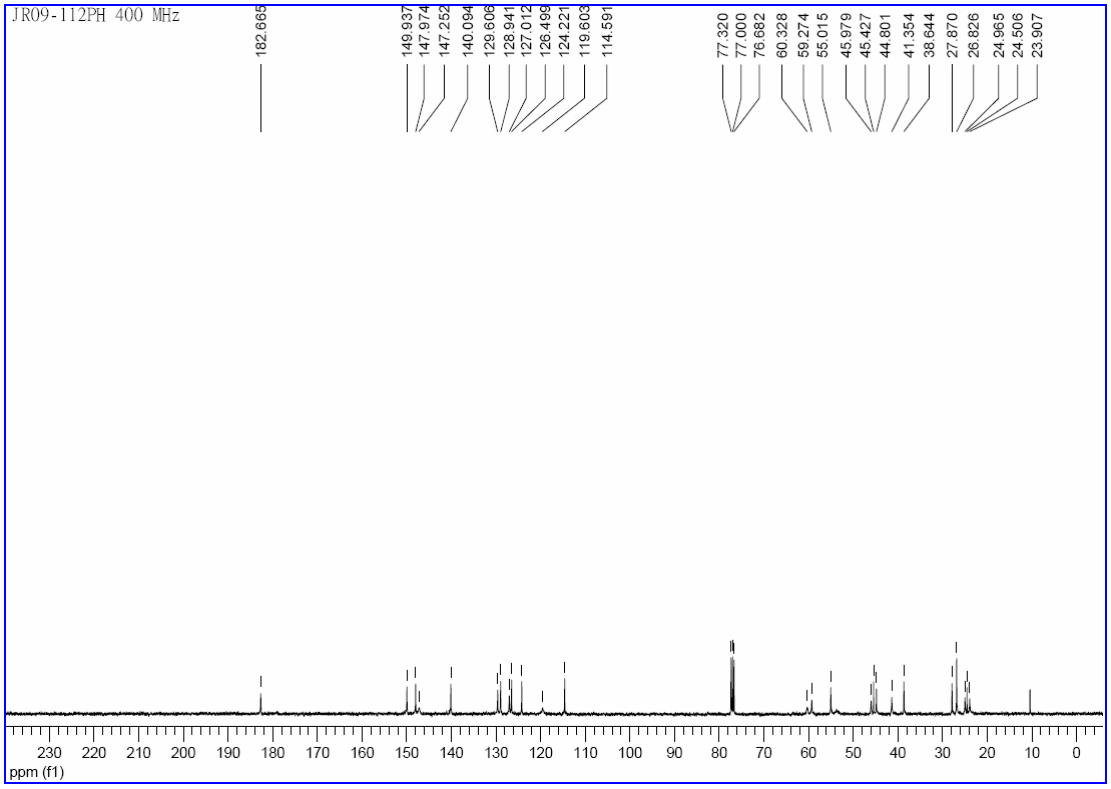
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of catalyst 4b



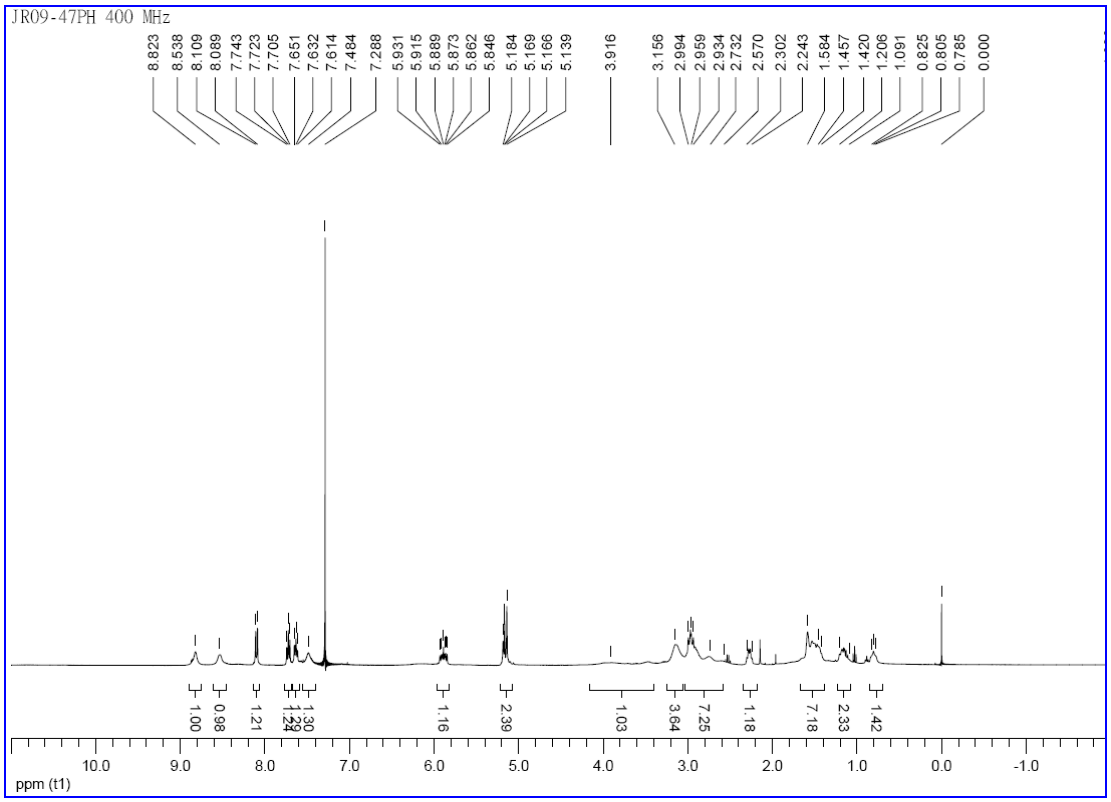
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of catalyst 5



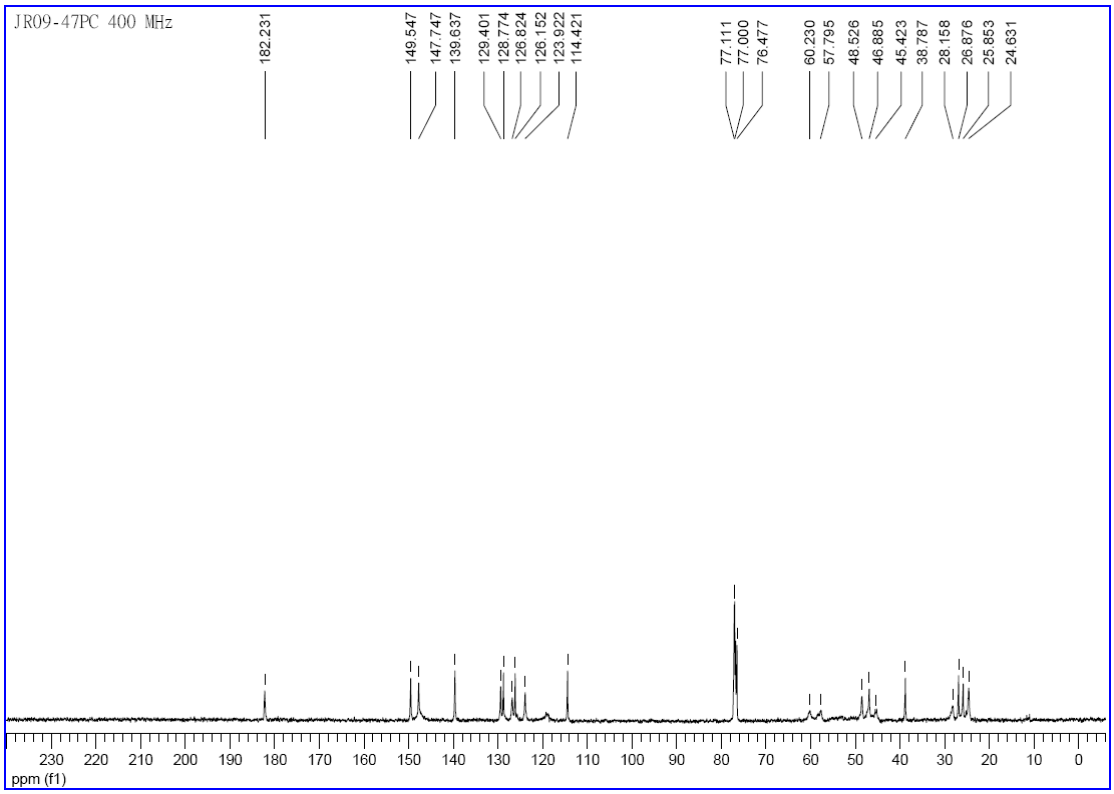
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of catalyst 5



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of catalyst 6

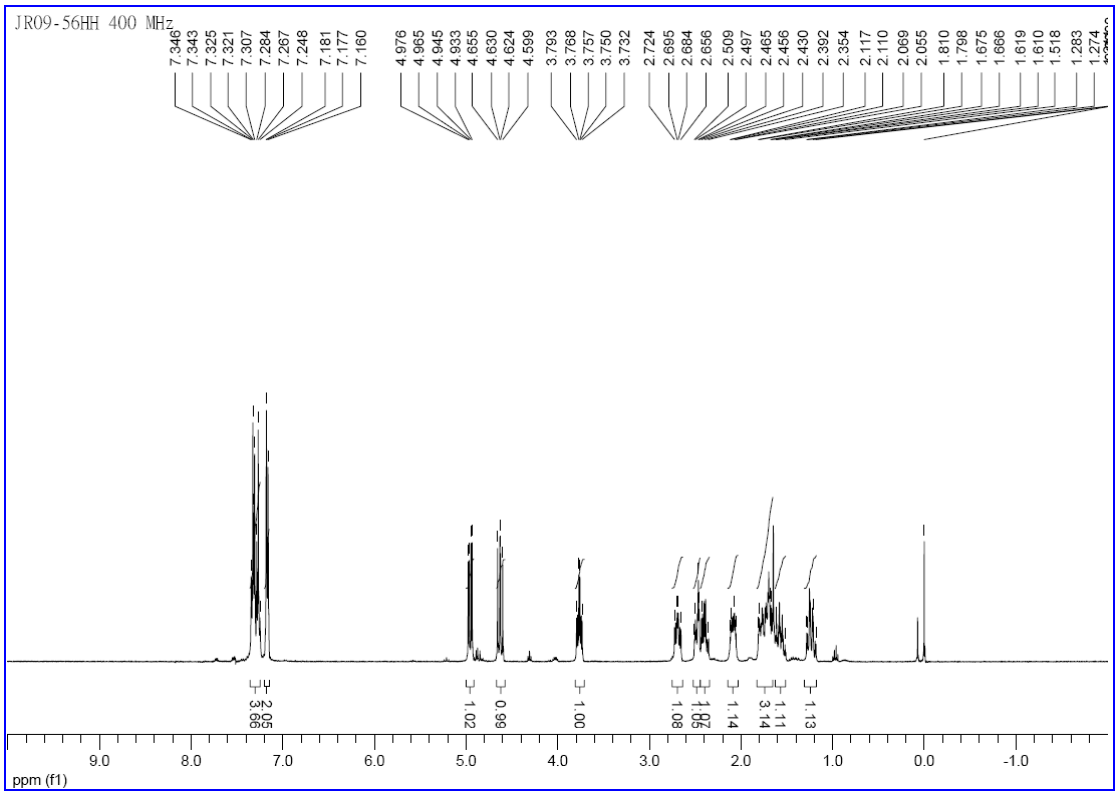


^{13}C NMR spectrum (100 MHz, $CDCl_3$) of catalyst 6

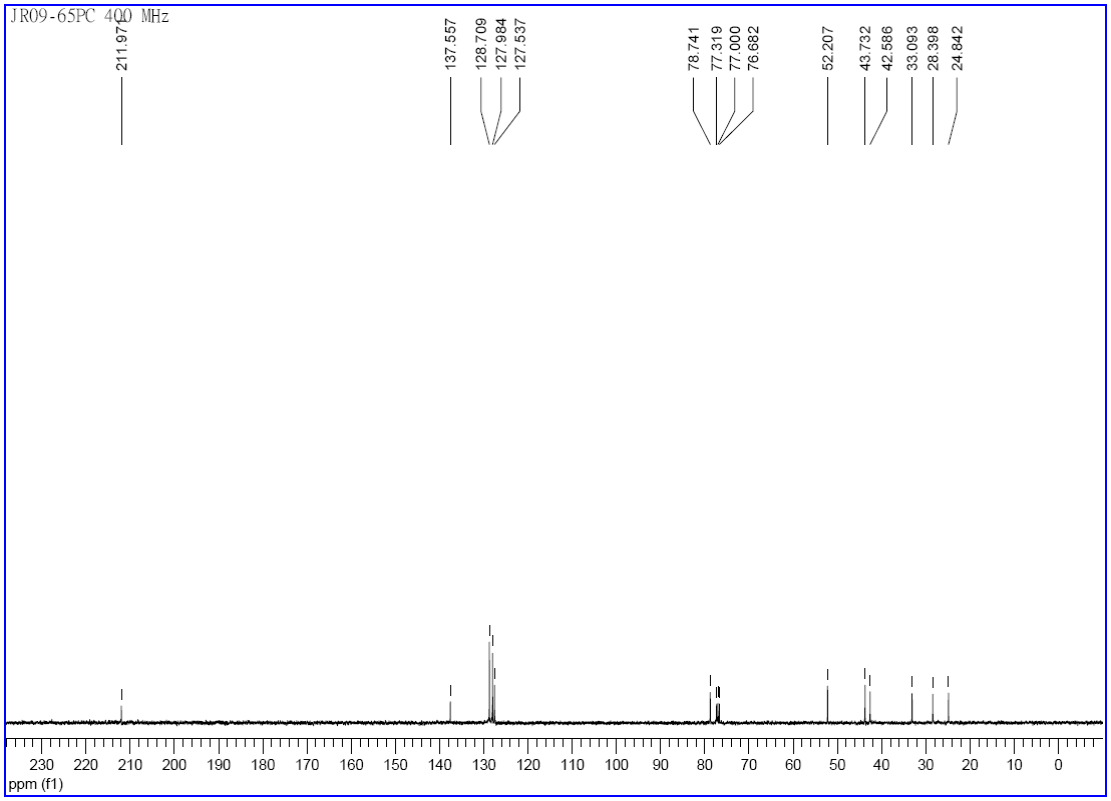


Michael product NMR Spectra

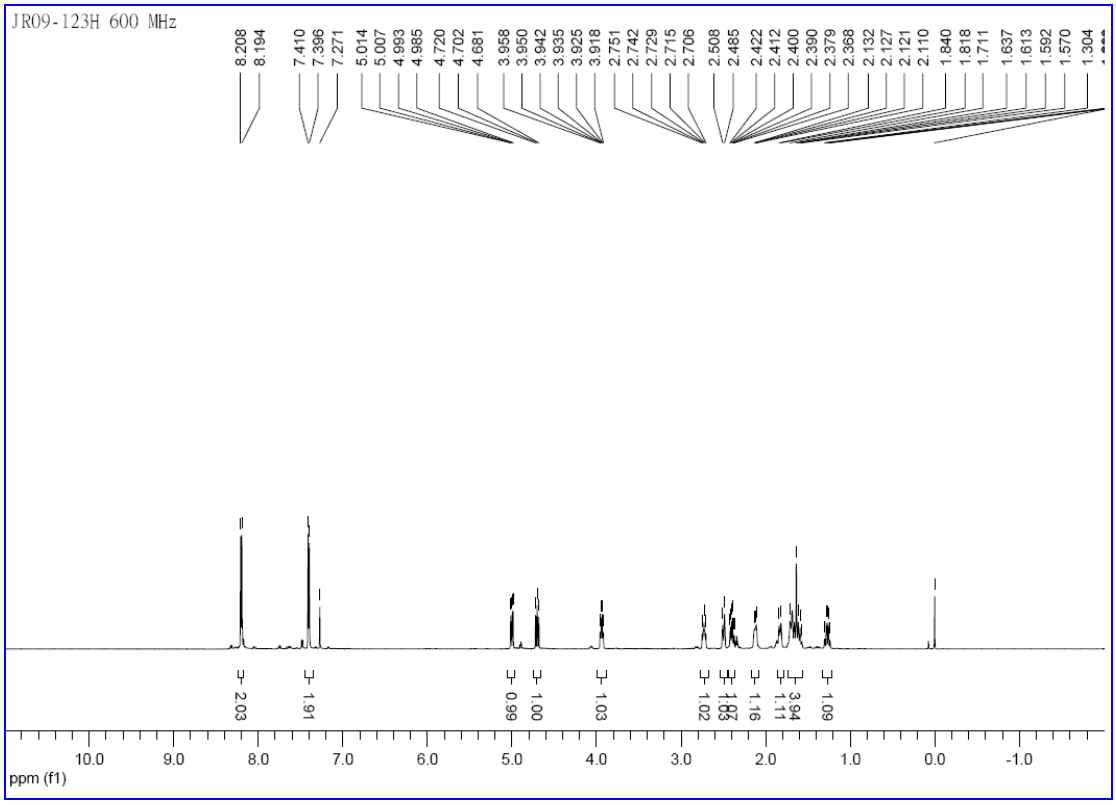
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of Michael product 13a



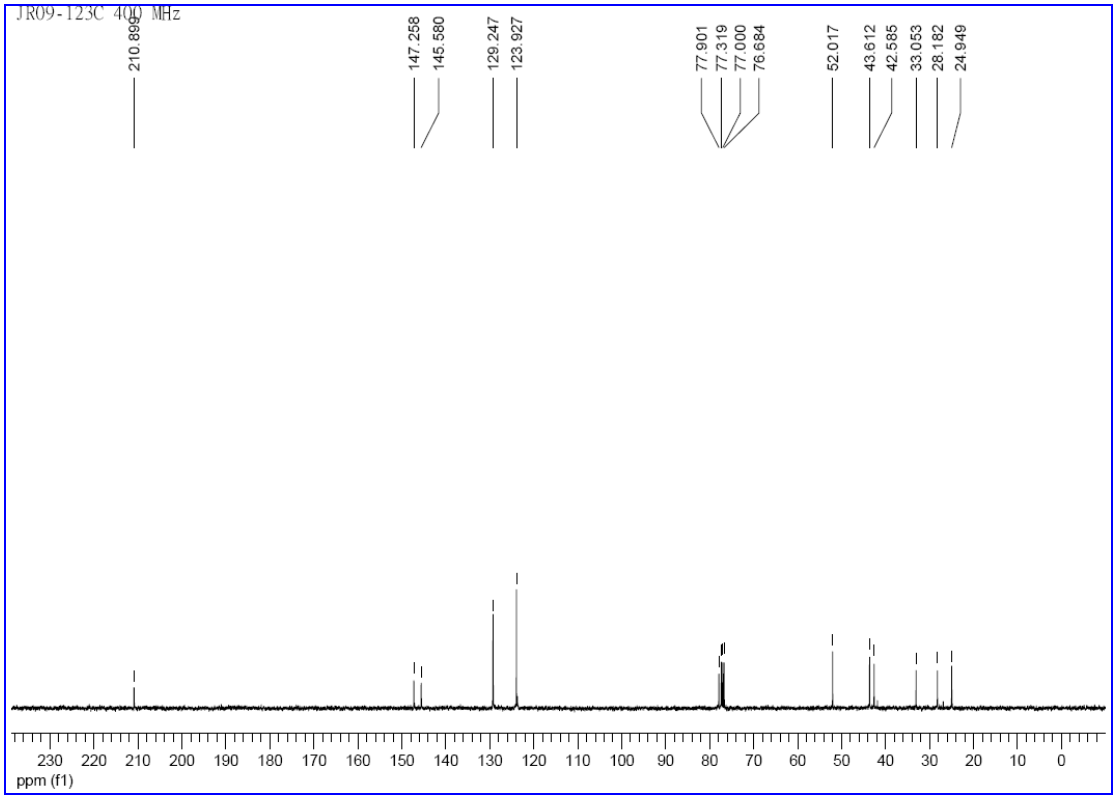
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of Michael product 13a



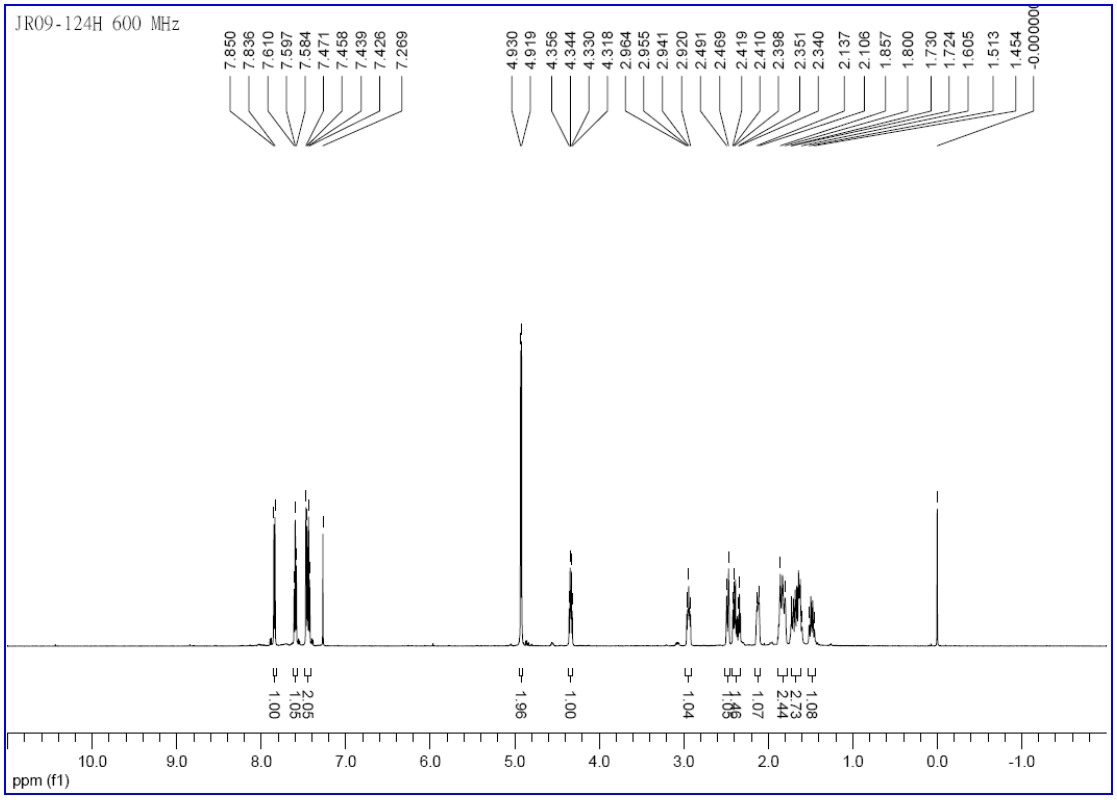
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of Michael product 13b



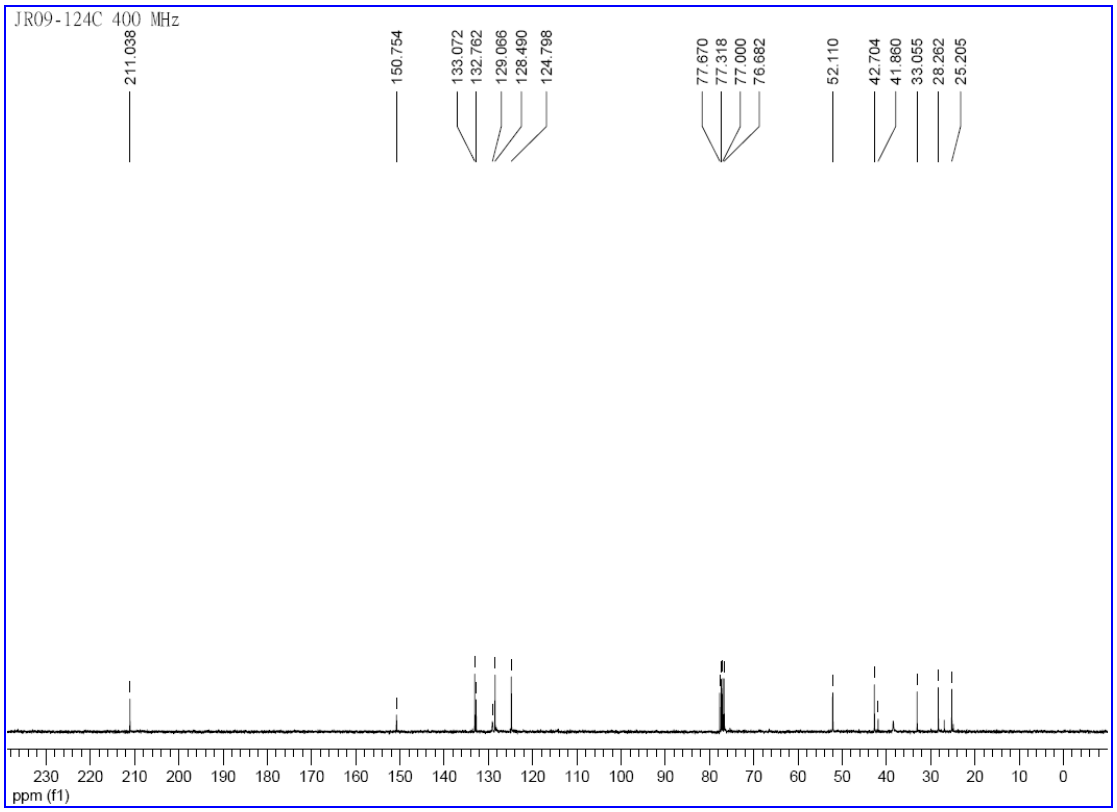
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of Michael product 13b



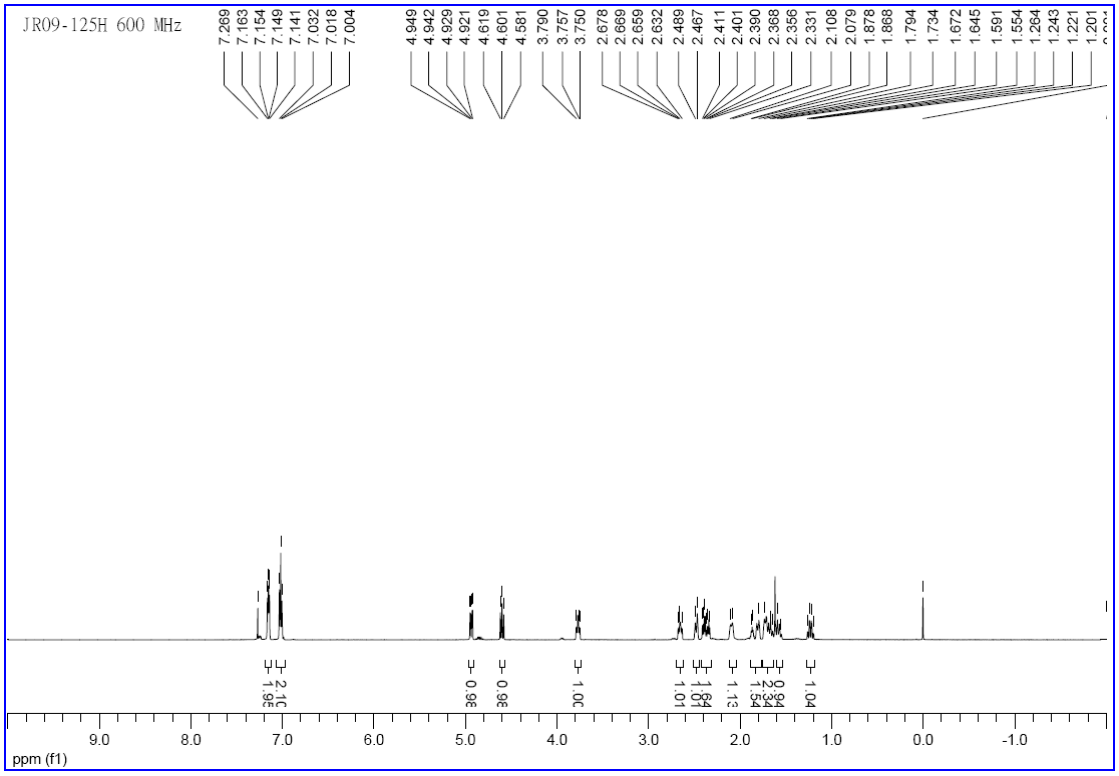
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of Michael product 13c



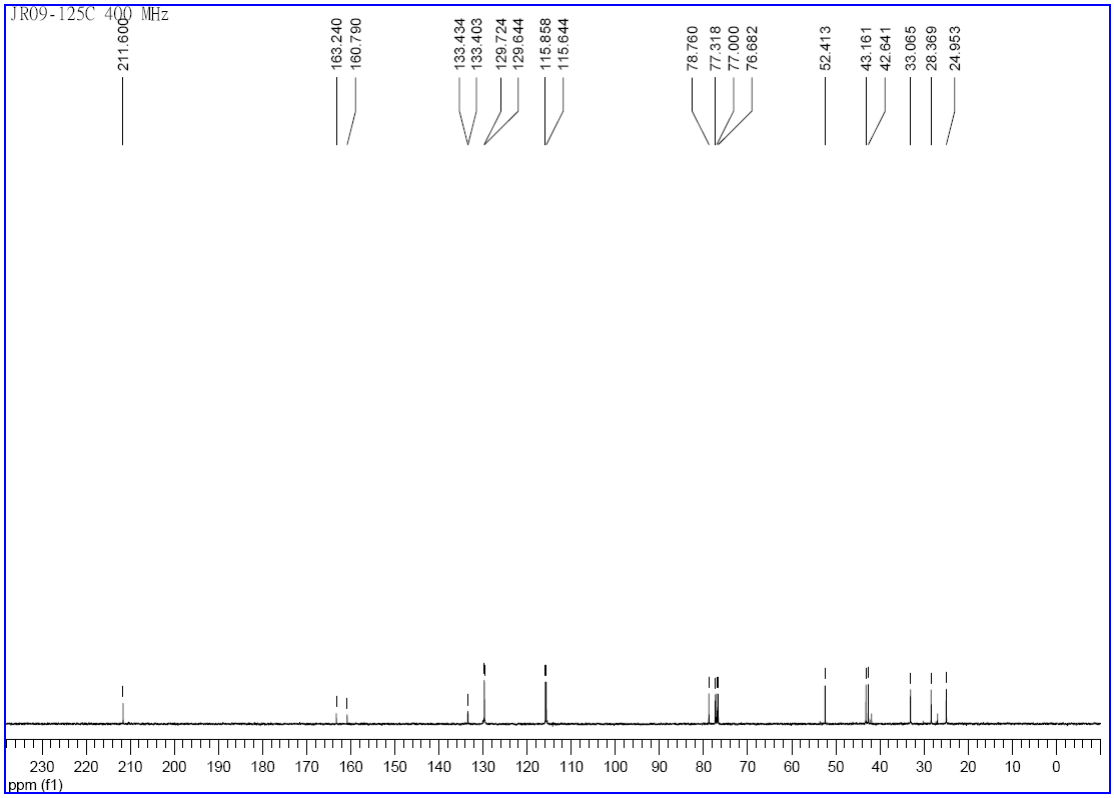
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of Michael product 13c



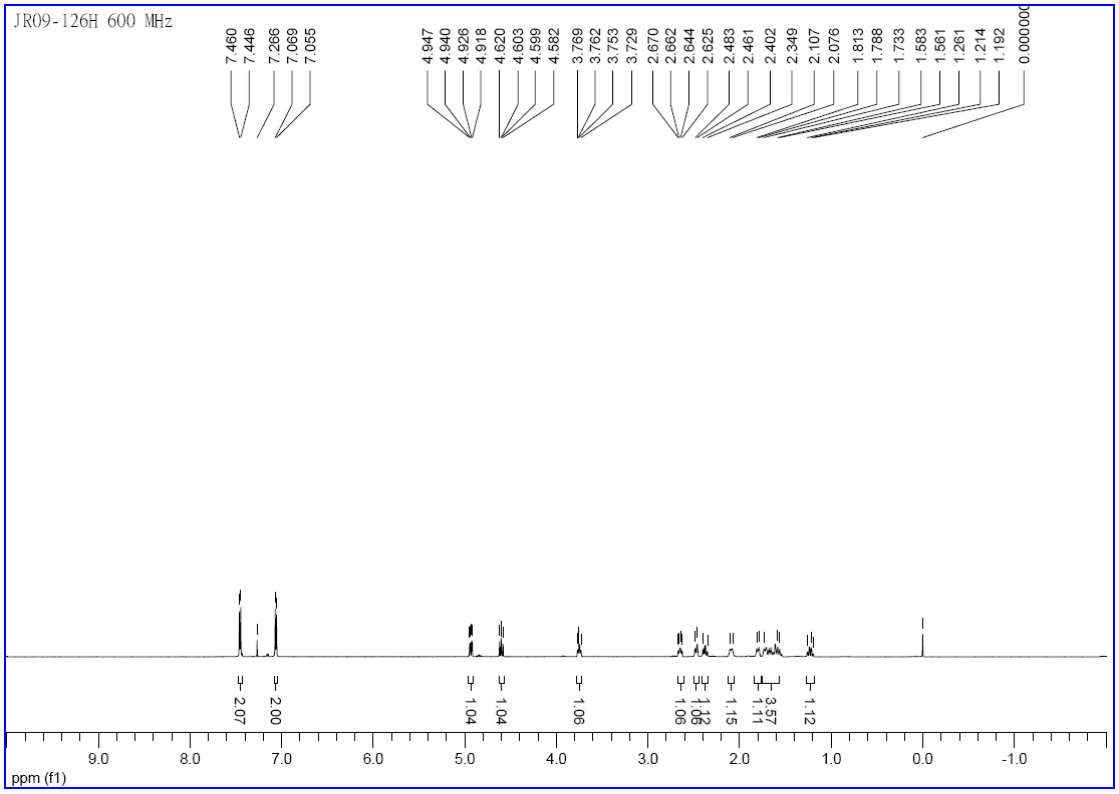
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of Michael product 13d



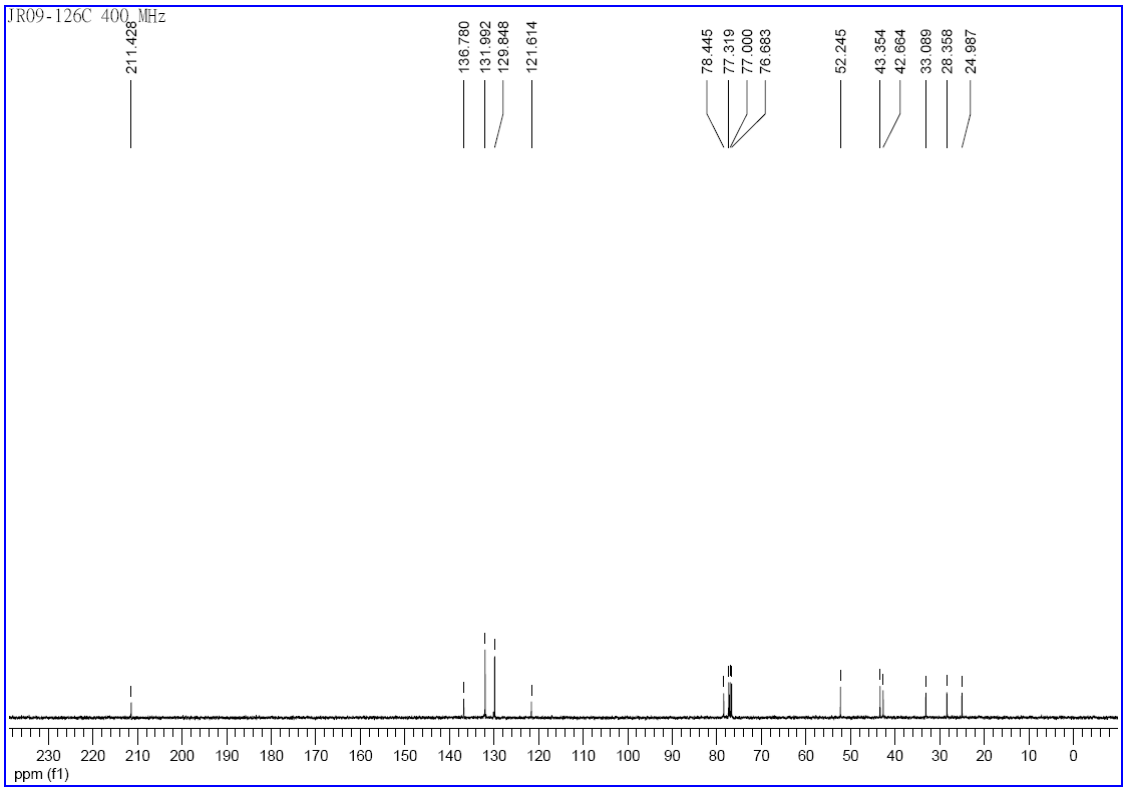
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of Michael product 13d



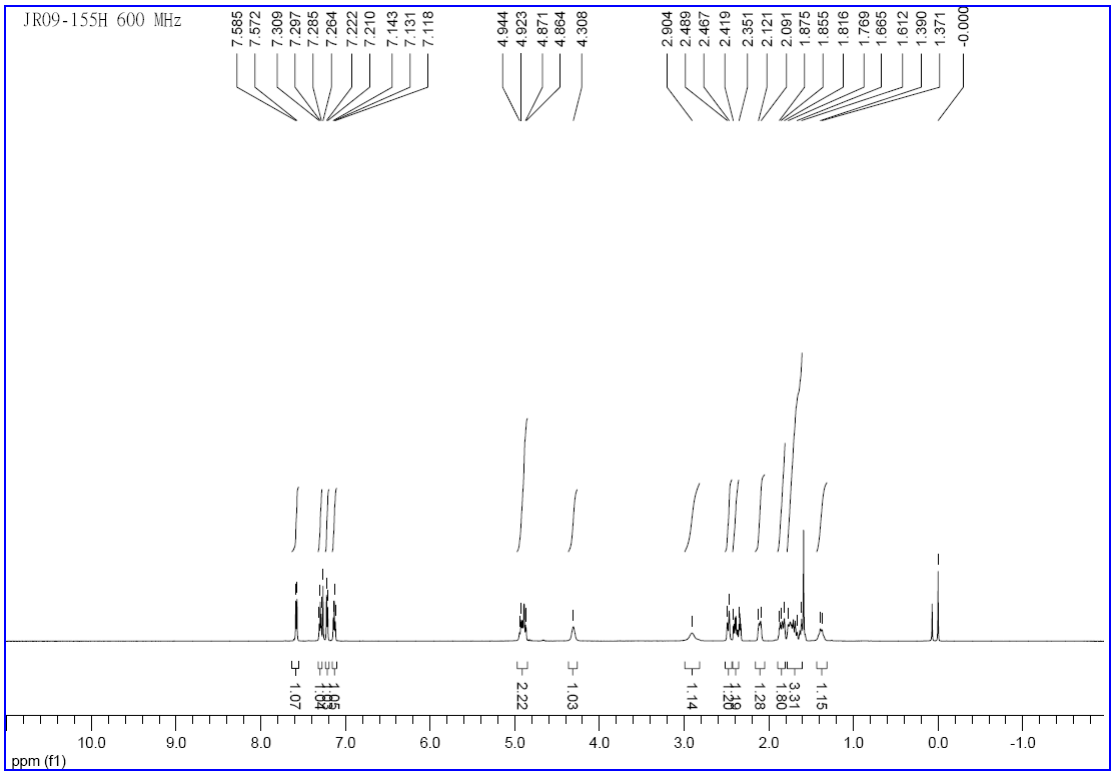
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of Michael product 13e



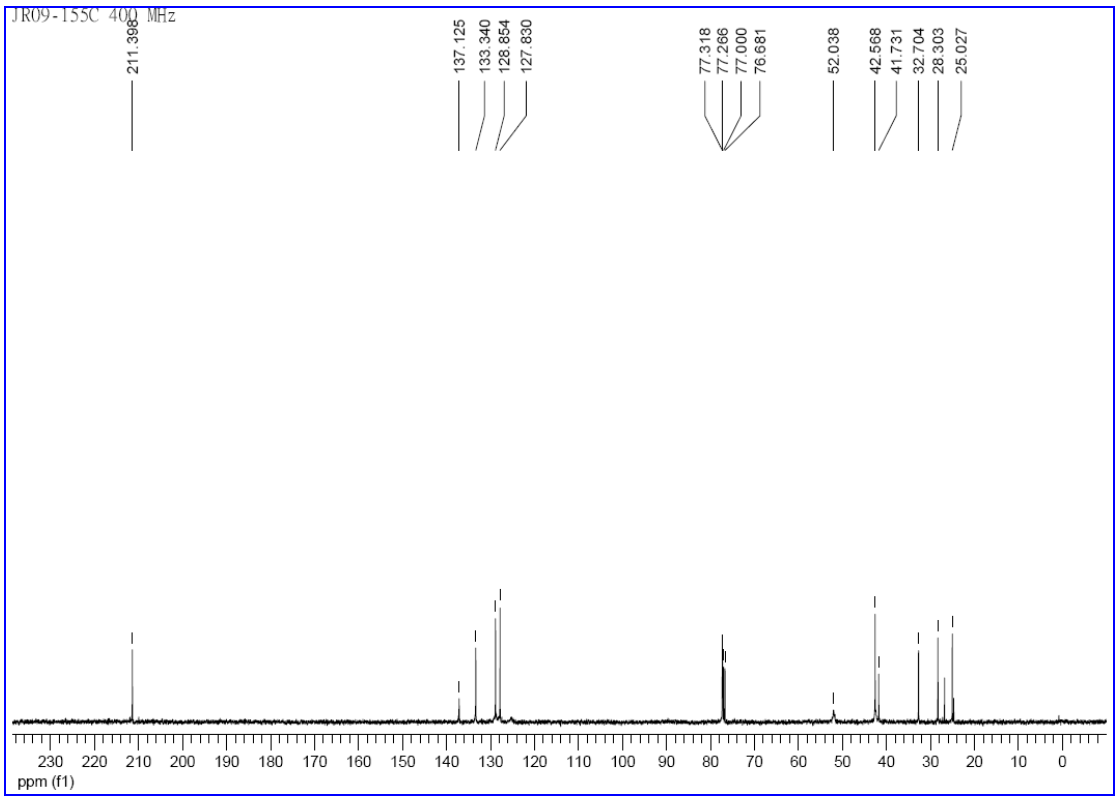
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of Michael product 13e



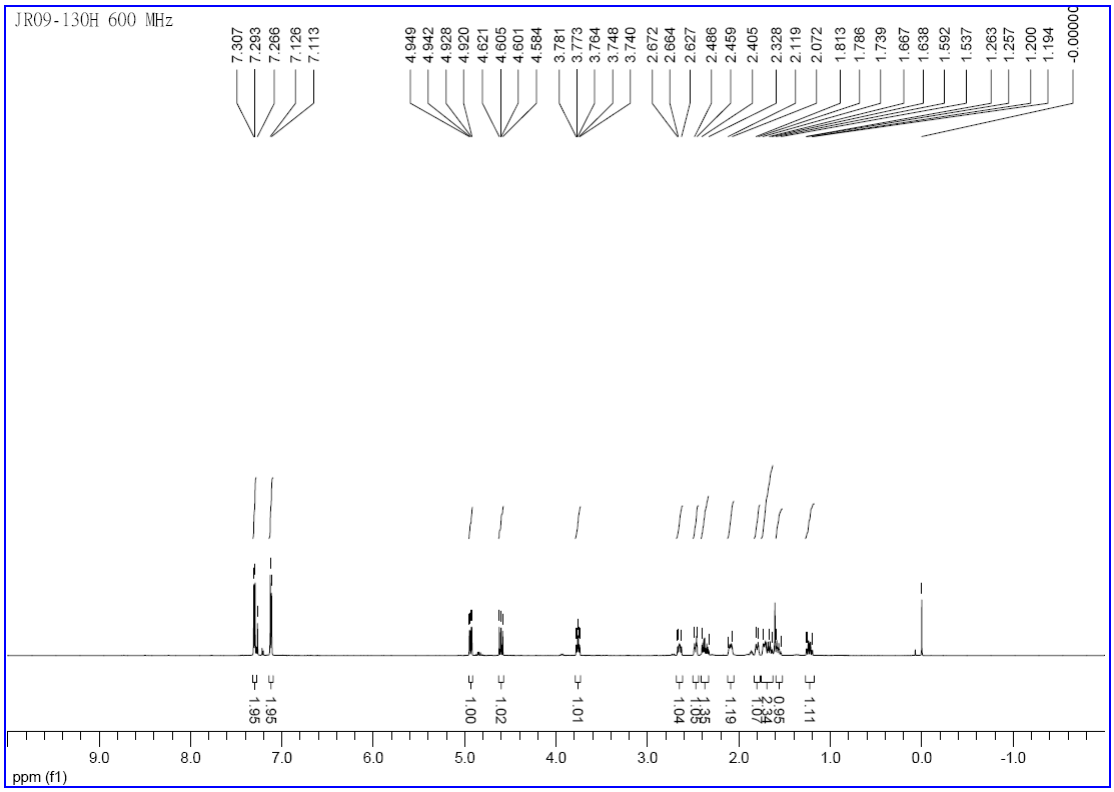
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of Michael product 13f



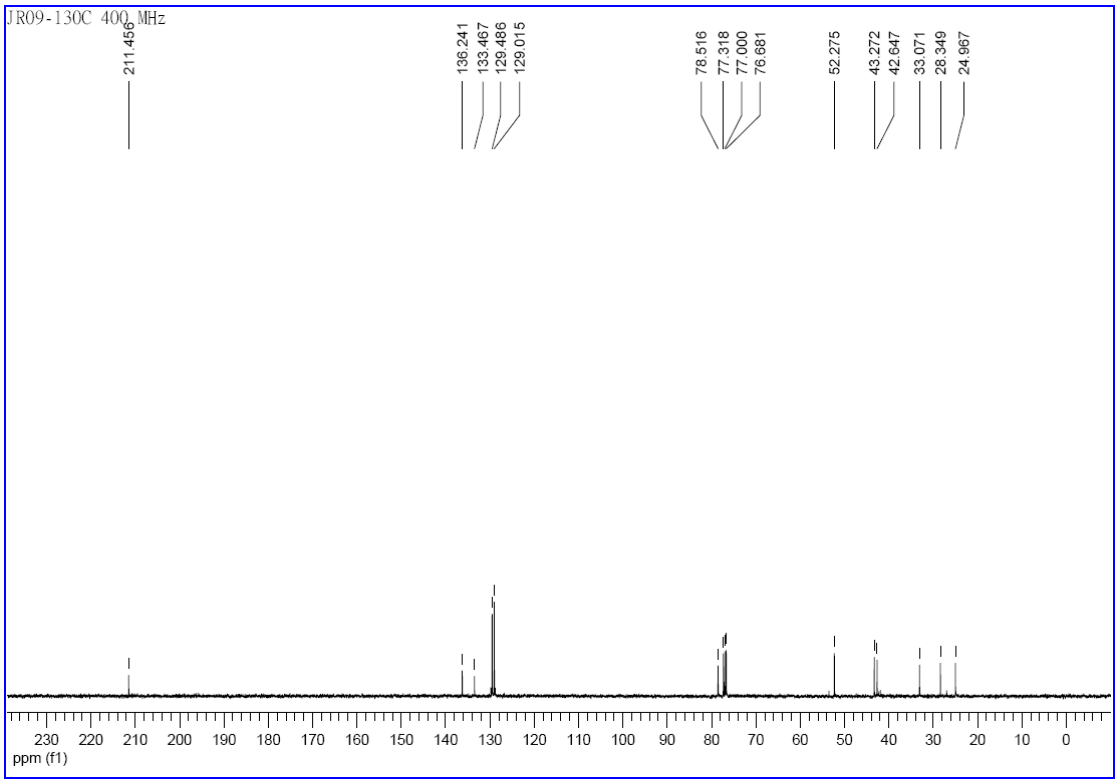
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of Michael product 13f



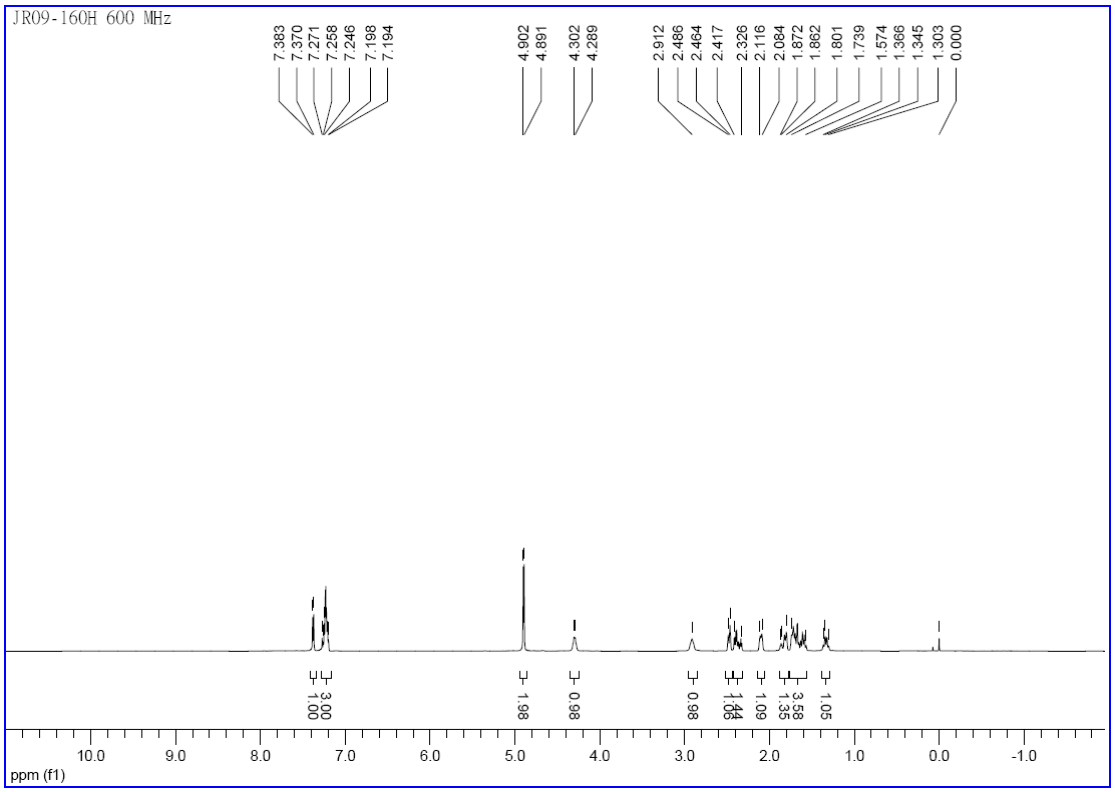
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of Michael product 13g



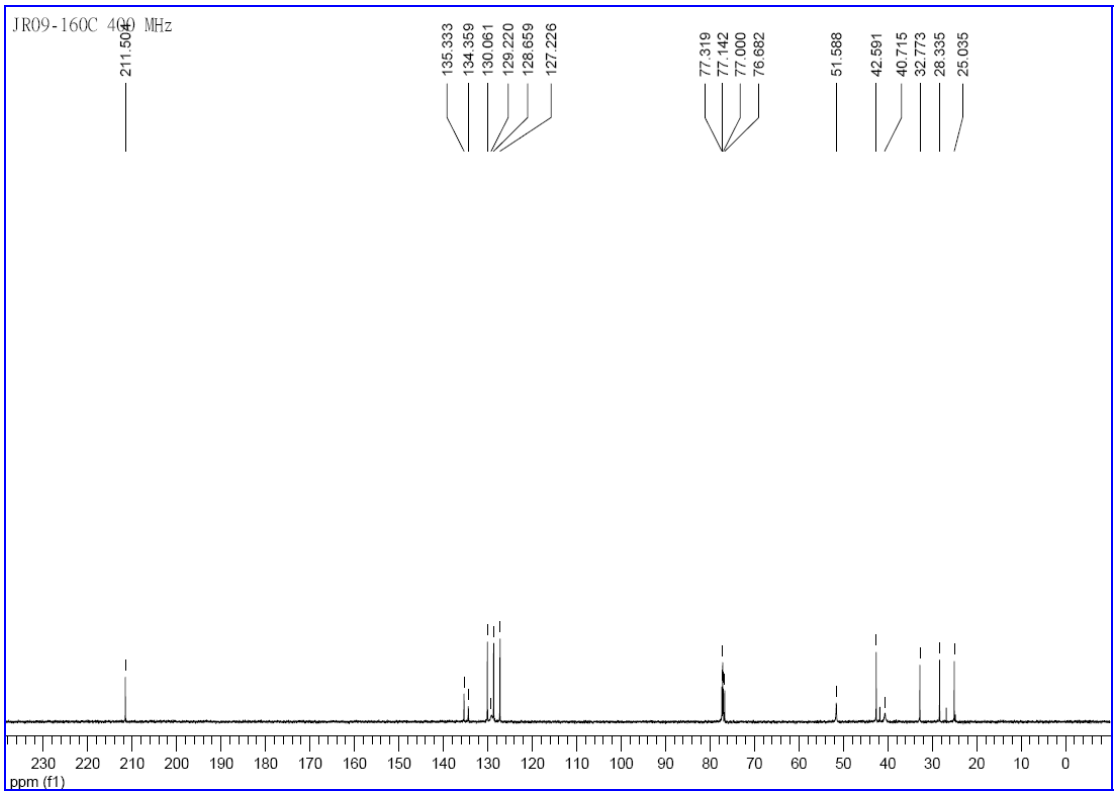
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of Michael product 13g



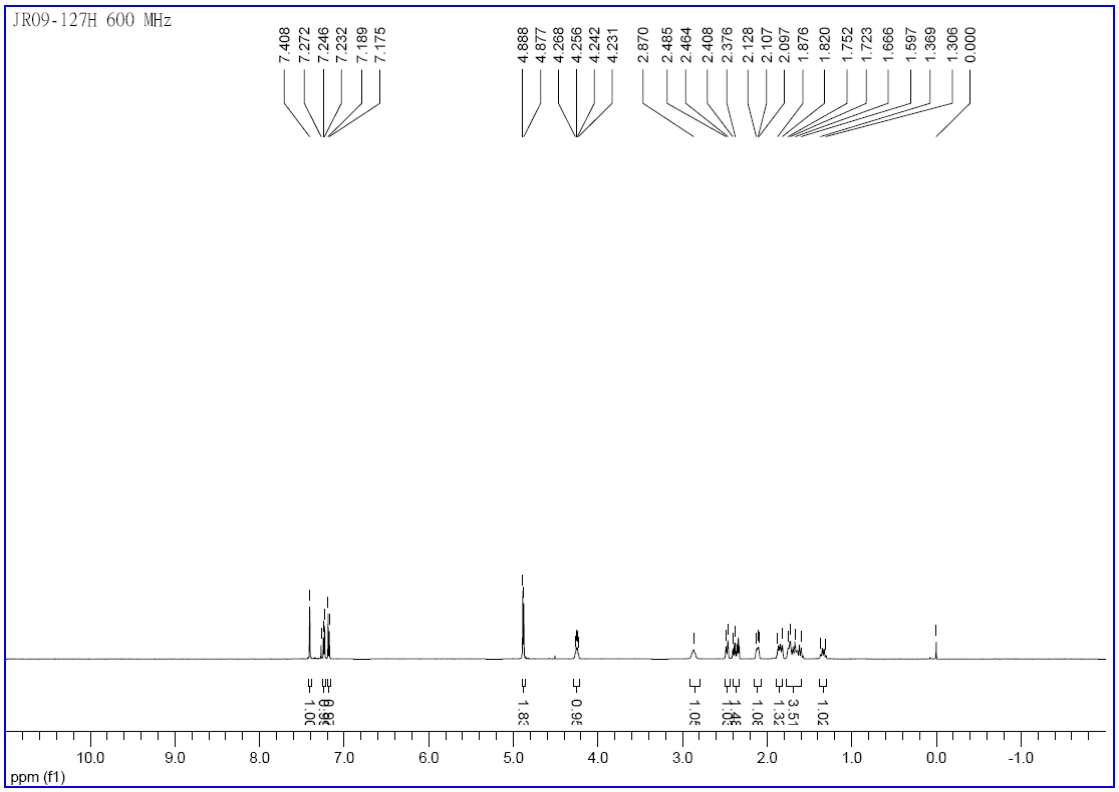
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of Michael product 13h



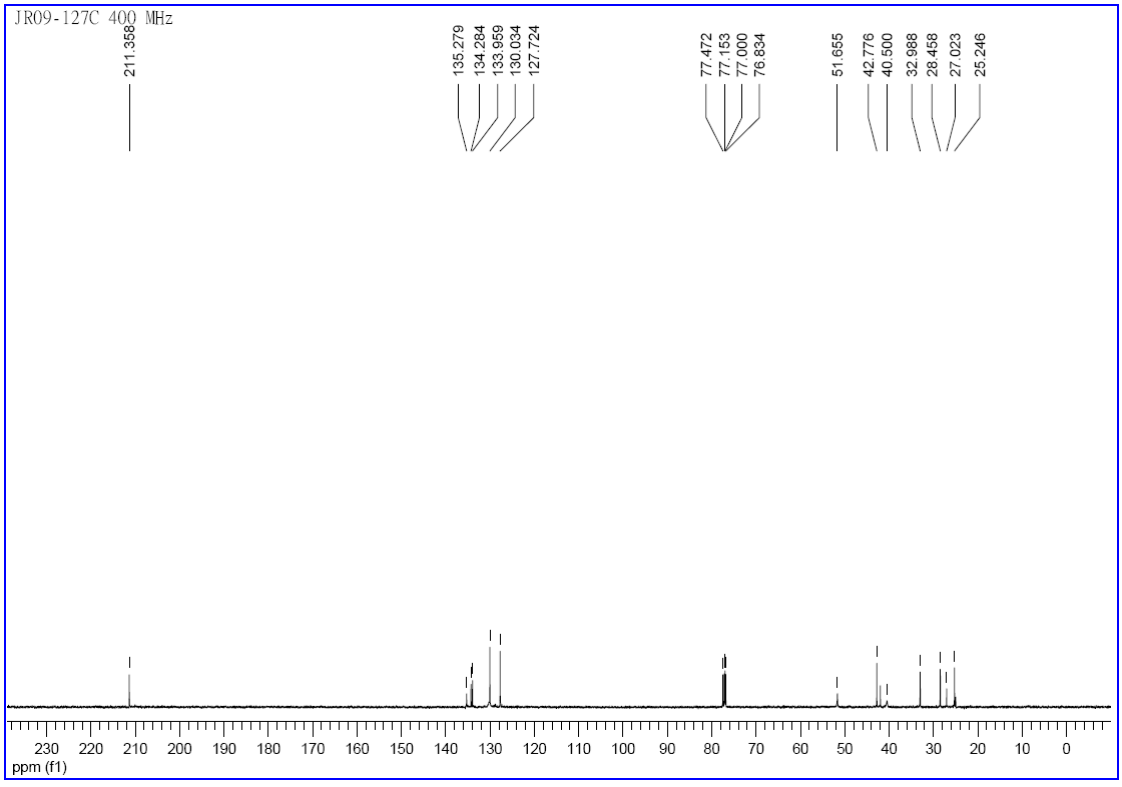
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of Michael product 13h



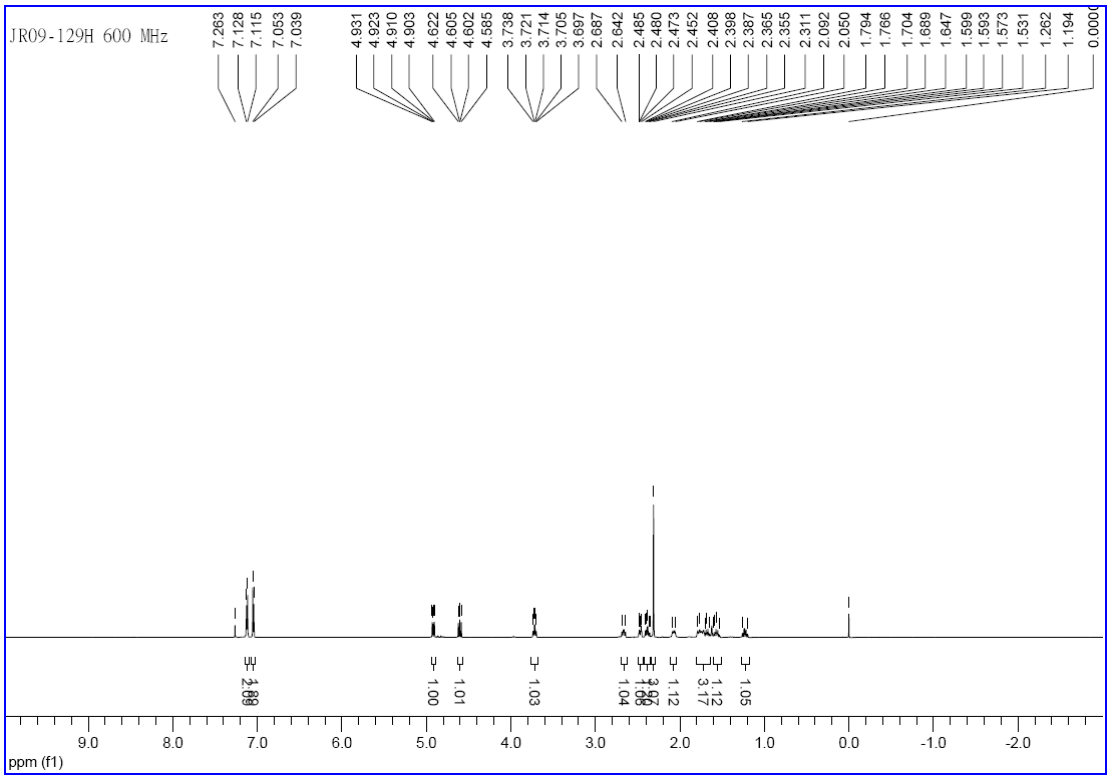
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of Michael product 13i



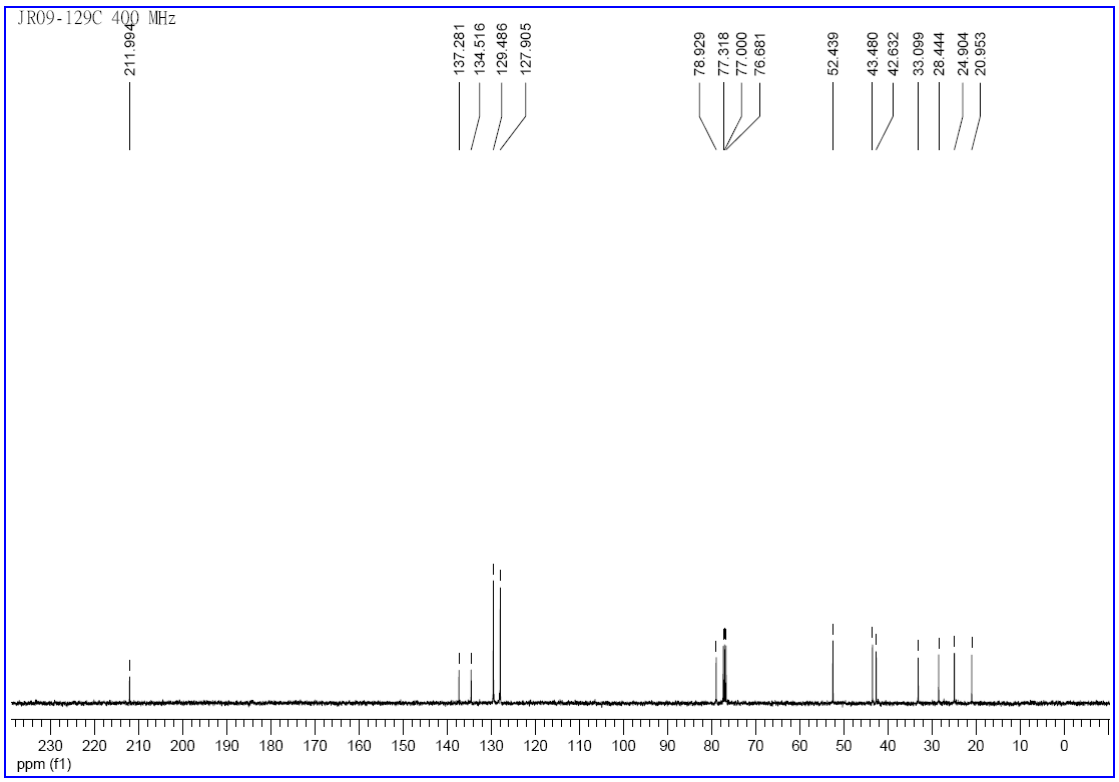
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of Michael product 13i



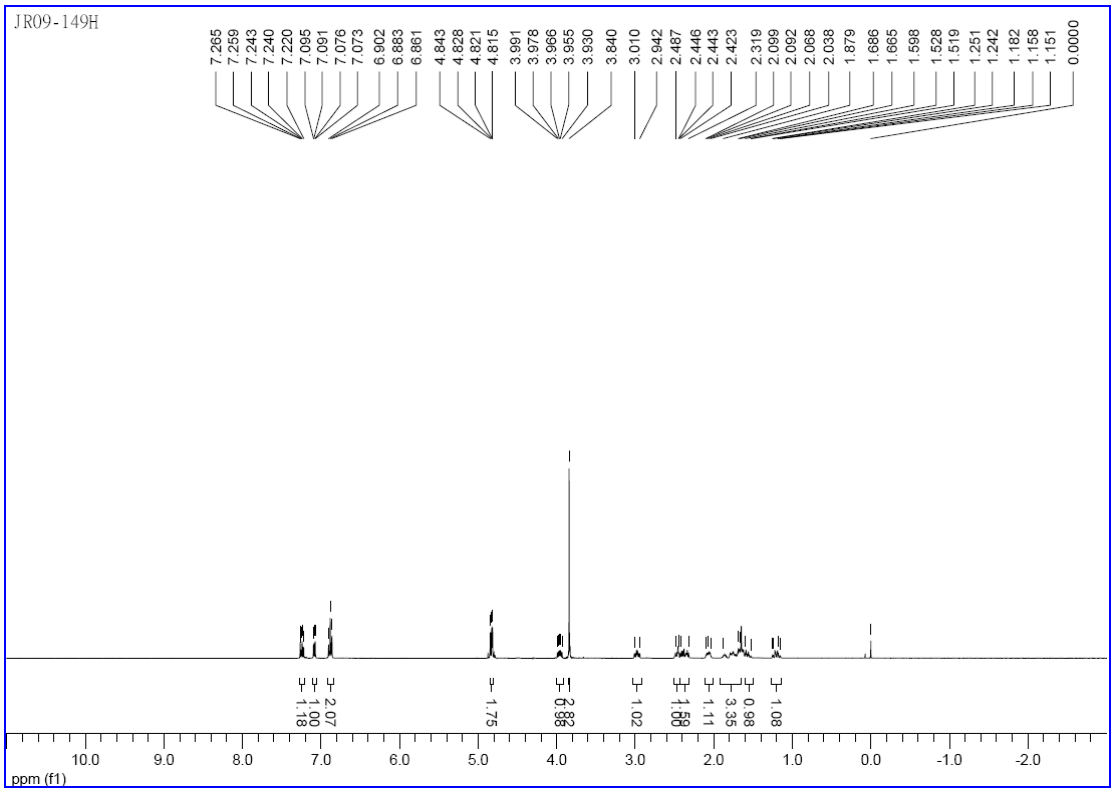
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of Michael product 13j



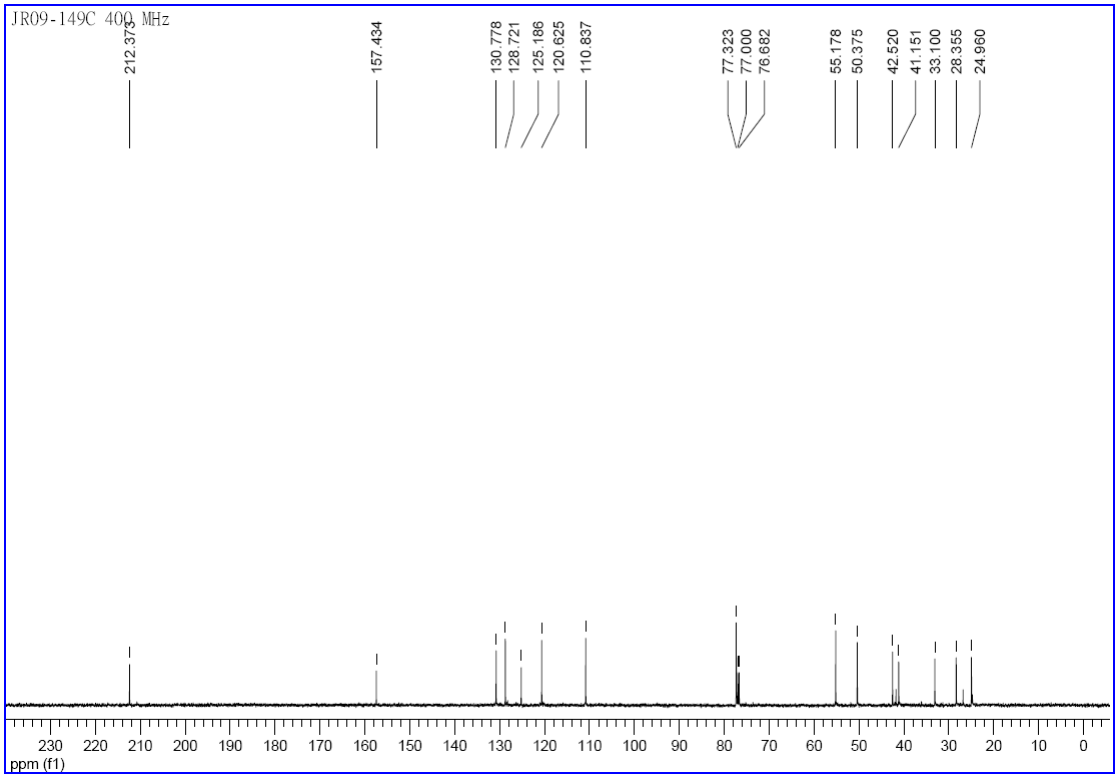
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of Michael product 13j



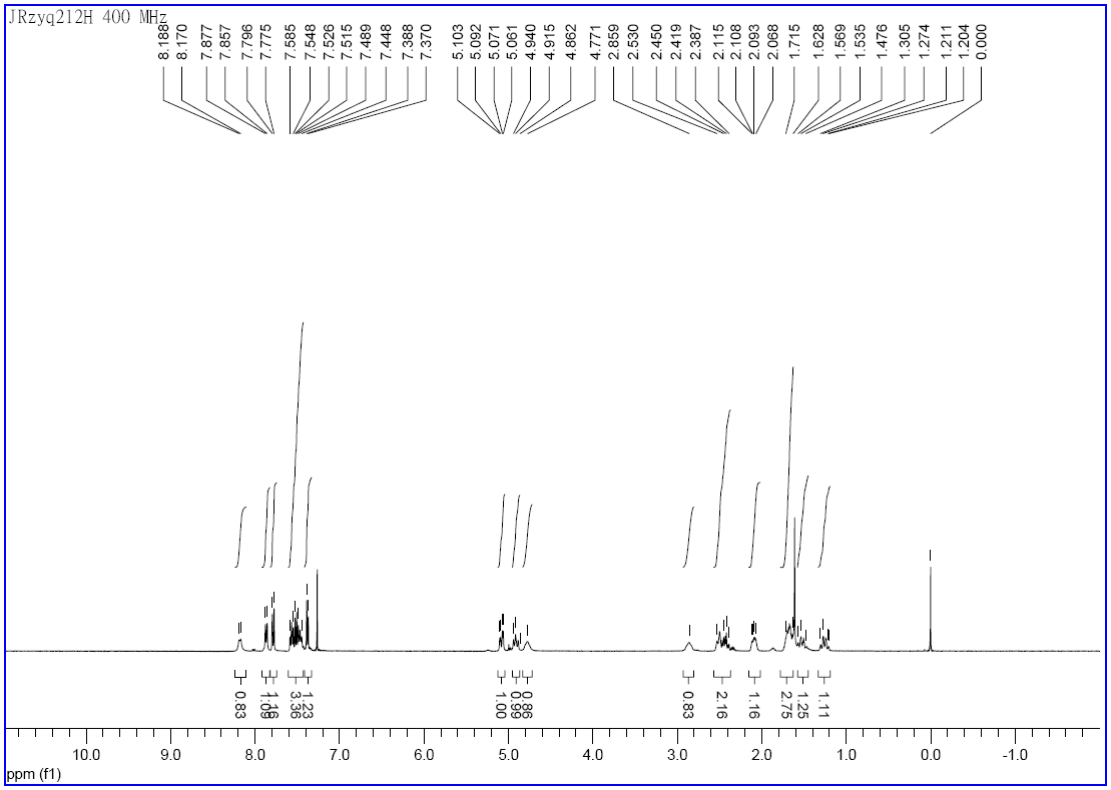
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of Michael product 13k



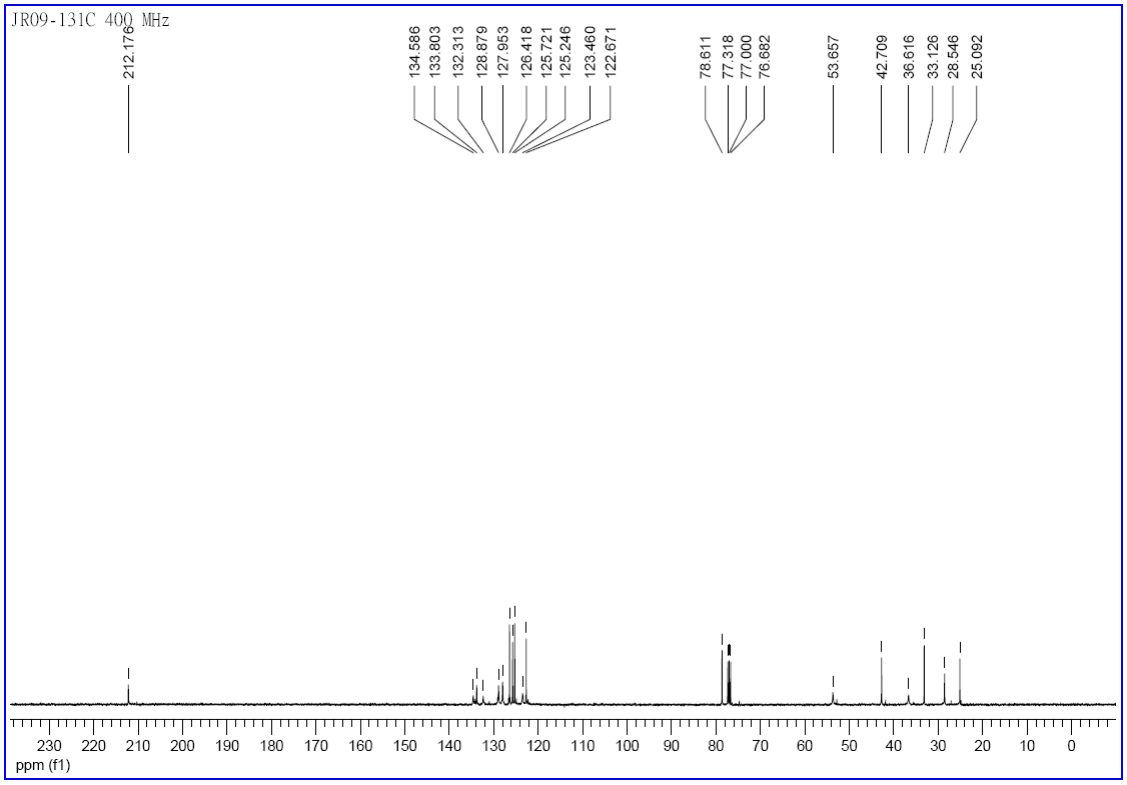
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of Michael product 13k



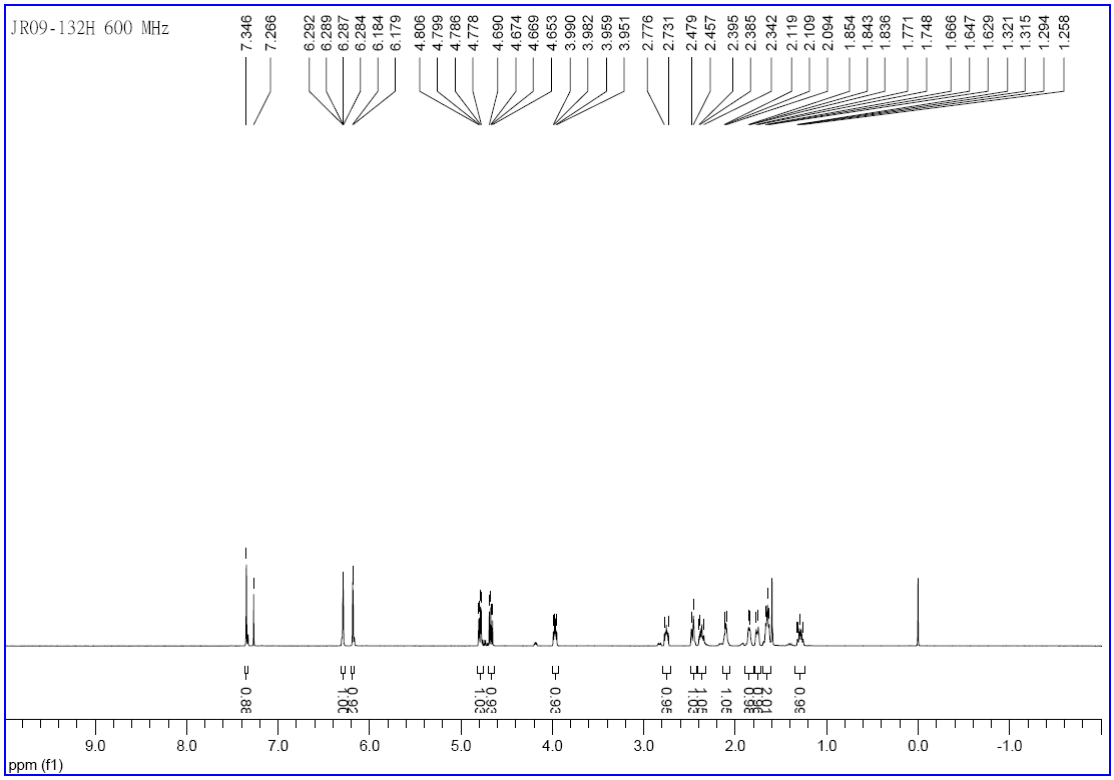
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of Michael product 13l



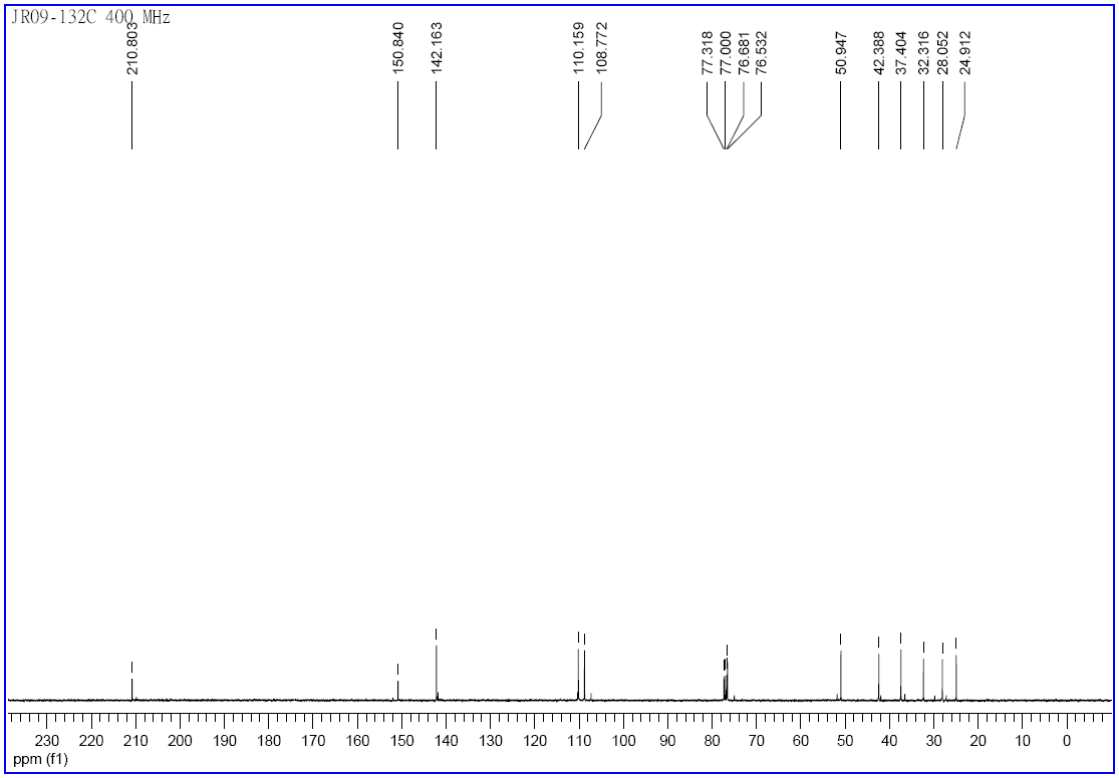
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of Michael product 13l



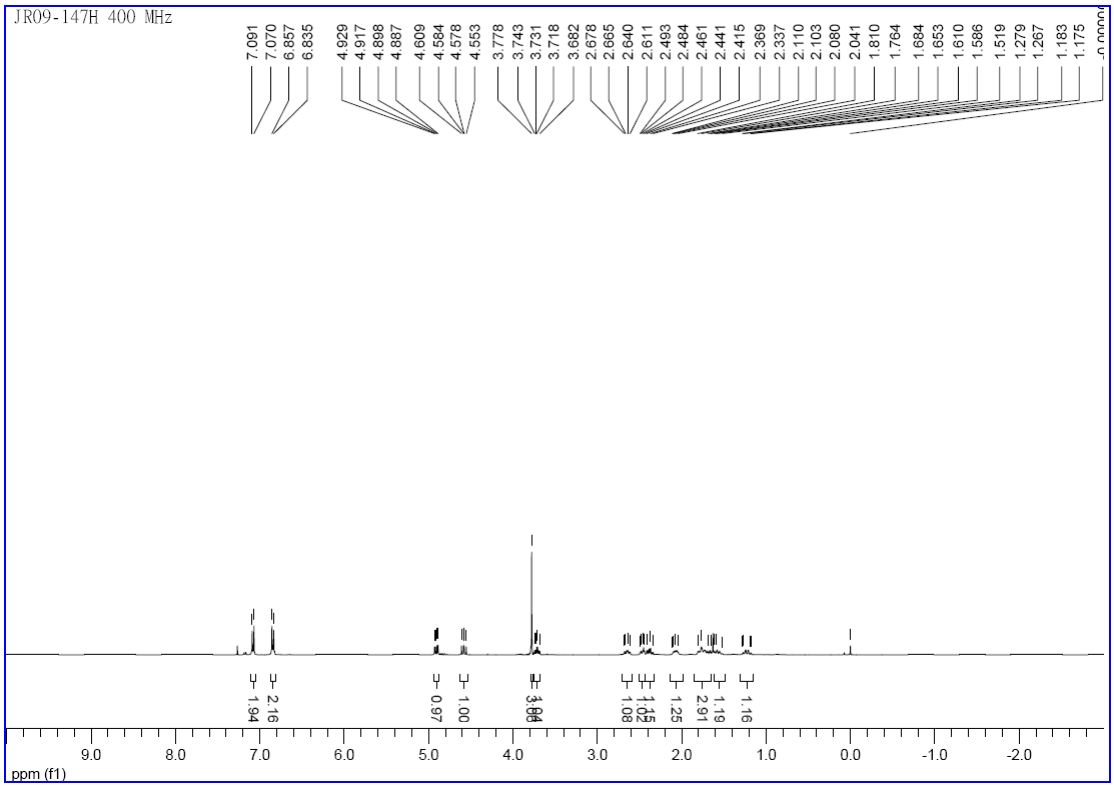
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of Michael product 13m



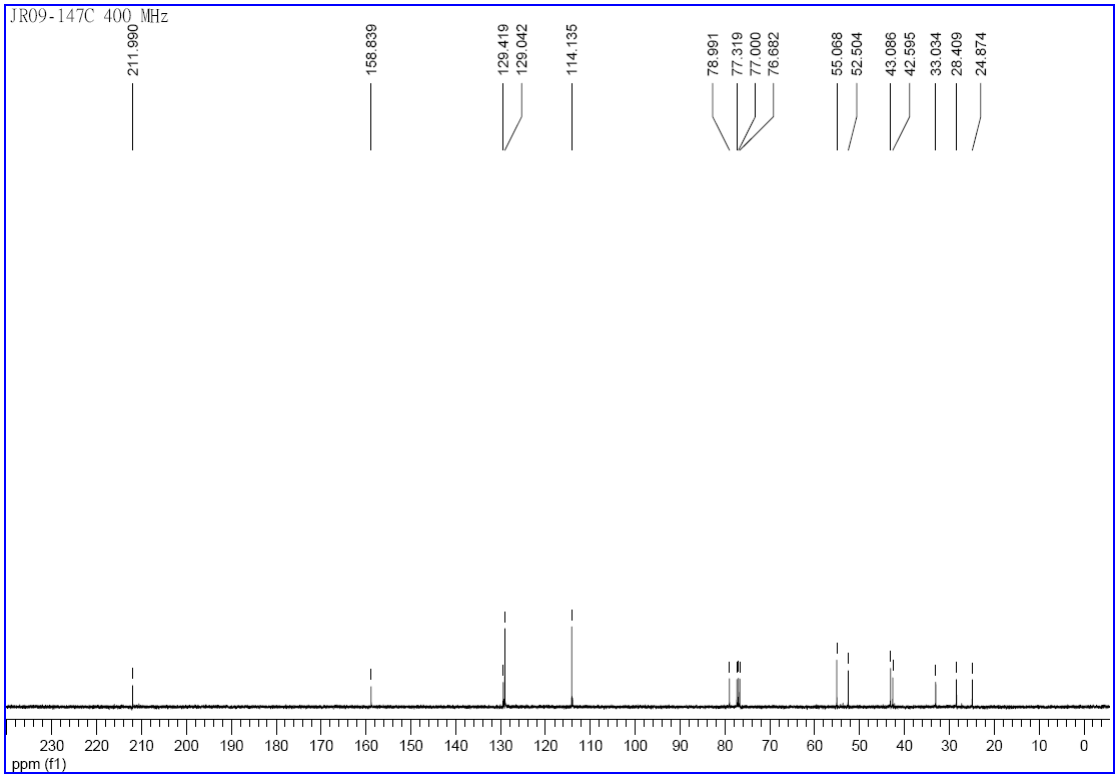
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of Michael product 13m



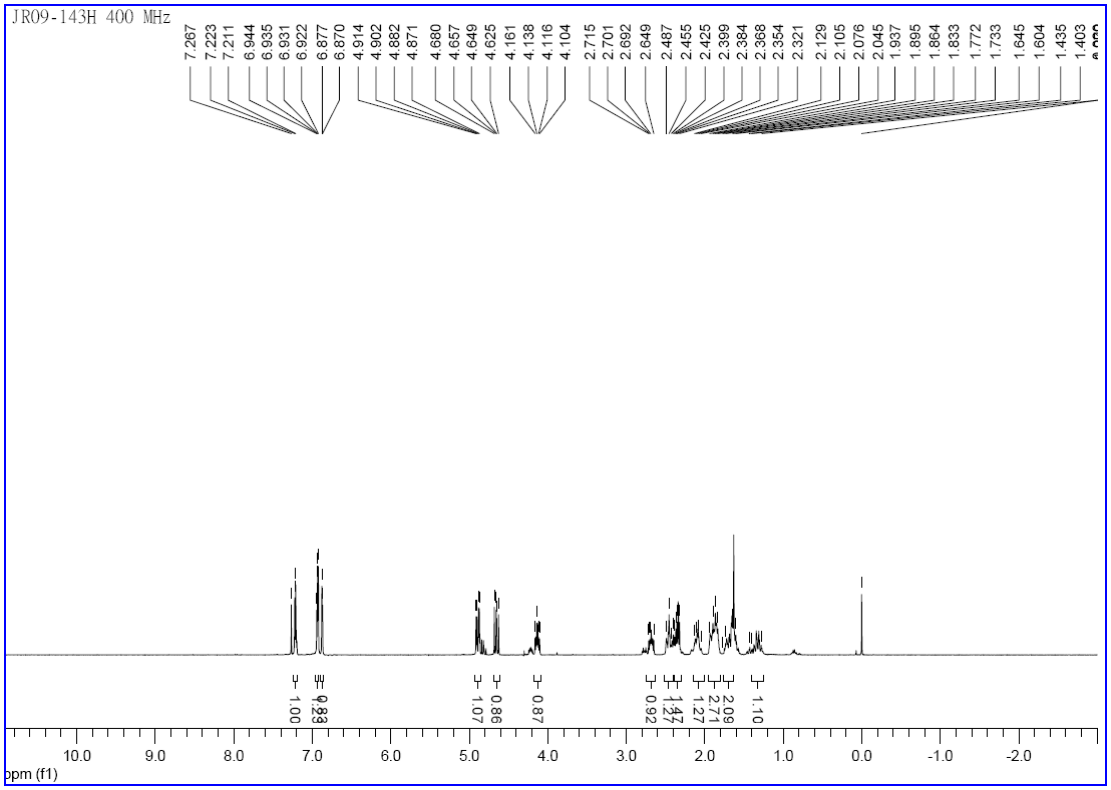
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of Michael product 13n



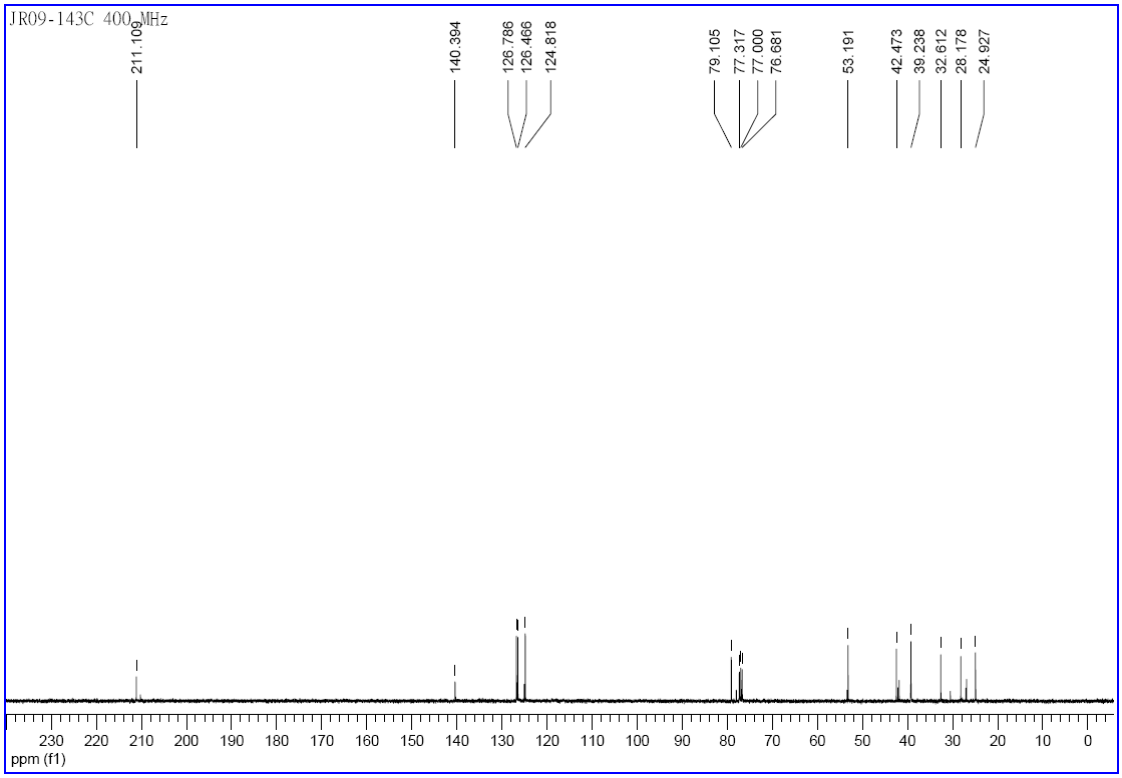
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of Michael product 13n



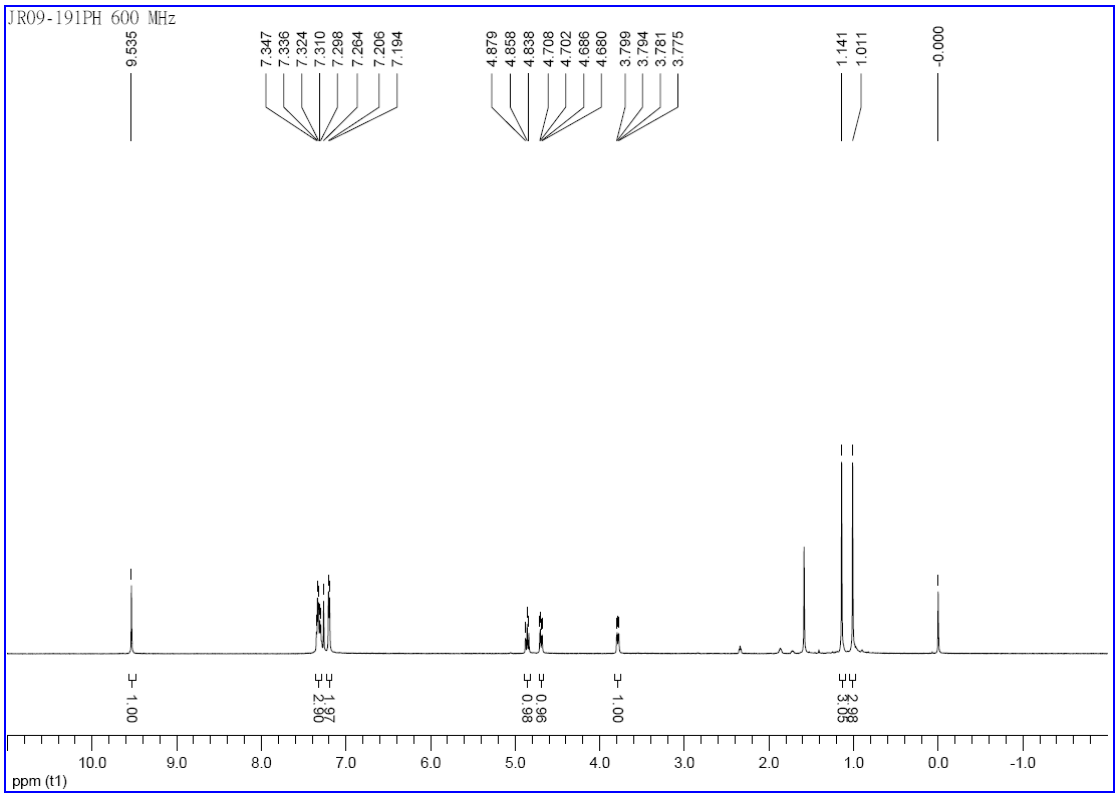
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of Michael product 13o



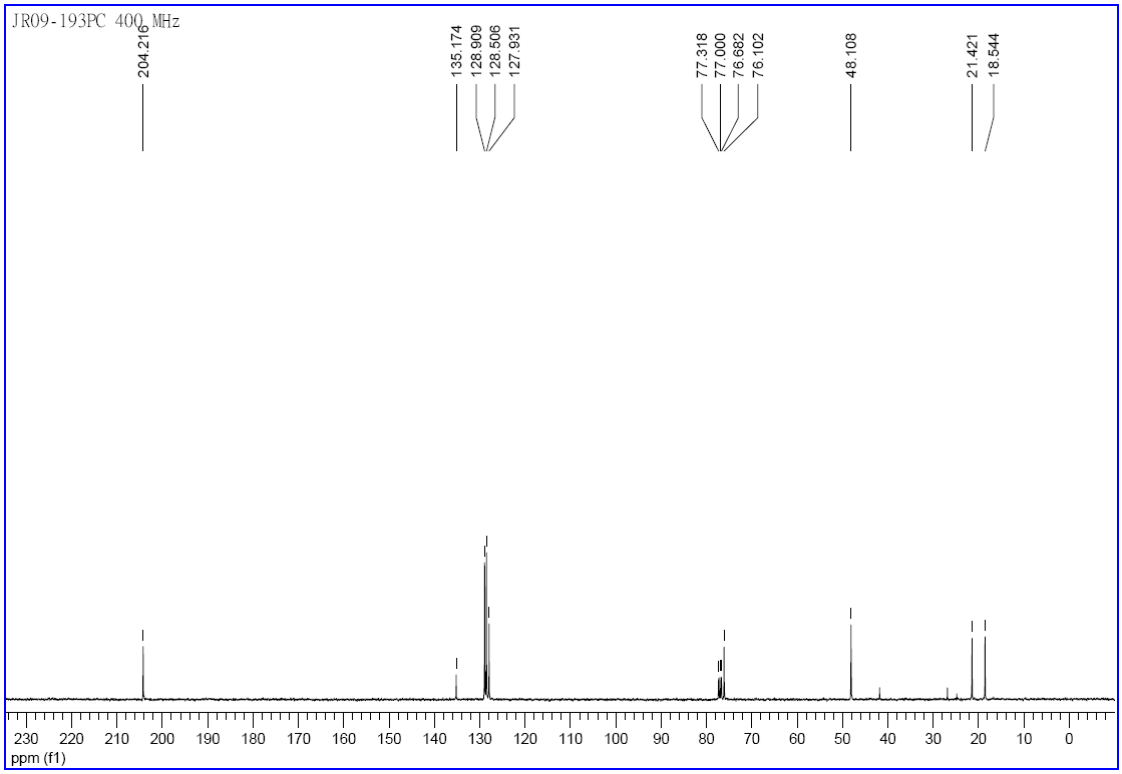
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of Michael product 13o



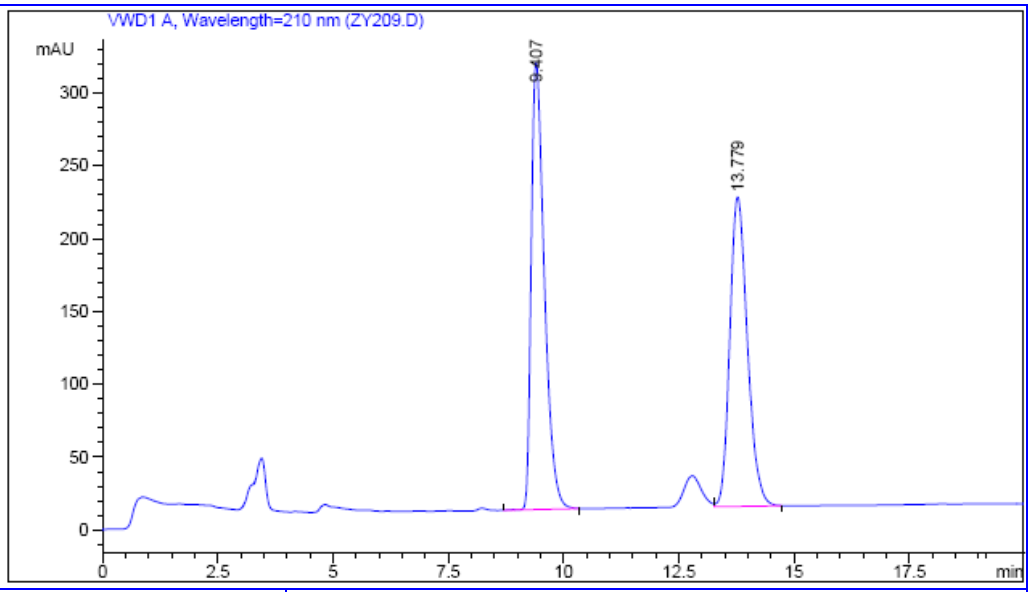
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of Michael product 15

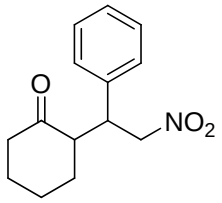


^{13}C NMR spectrum (100 MHz, $CDCl_3$) of Michael product 15



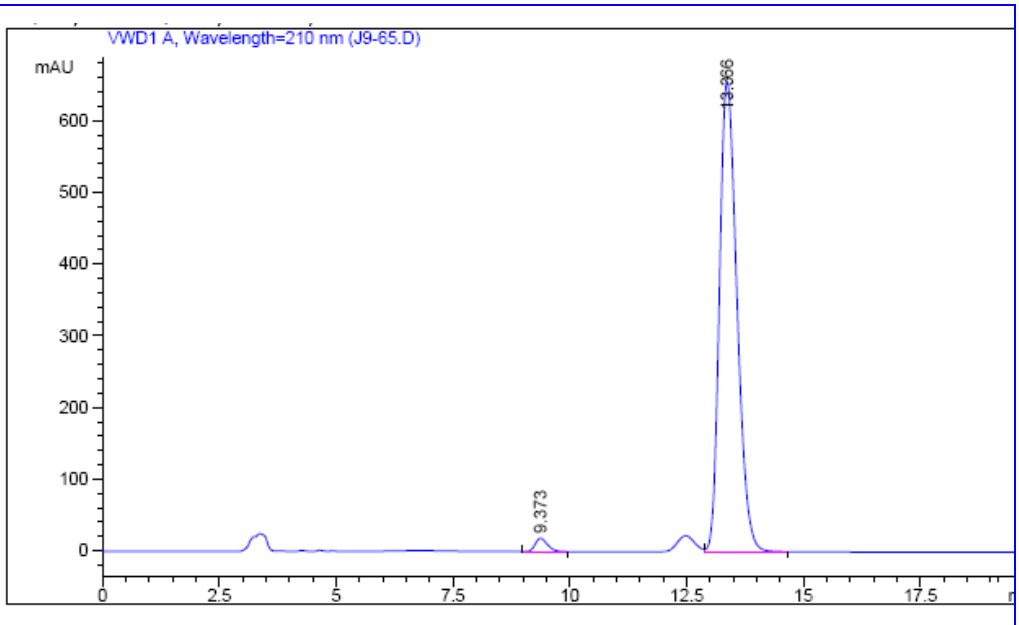
6.0 HPLC Chromatograms

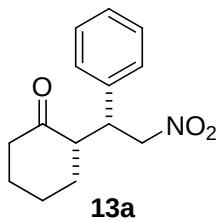




rac-syn-**13a**

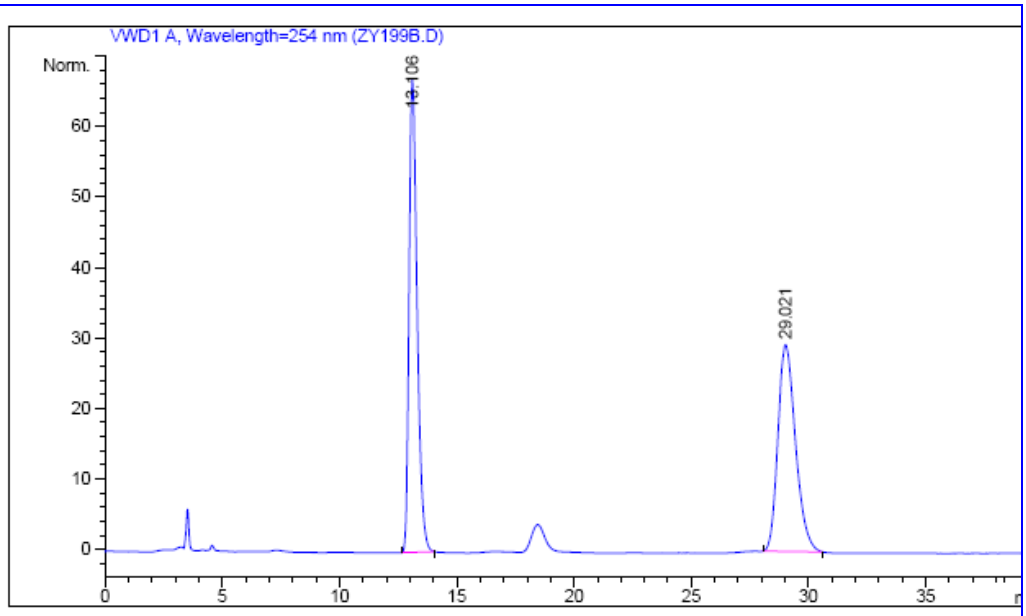
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.407	BB	0.3021	6070.53369	306.95505	51.8591
2	13.779	VB	0.4085	5635.29688	212.43985	48.1409
Totals :				1.17058e4	519.39490	

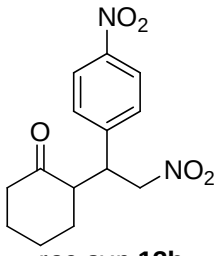




13a

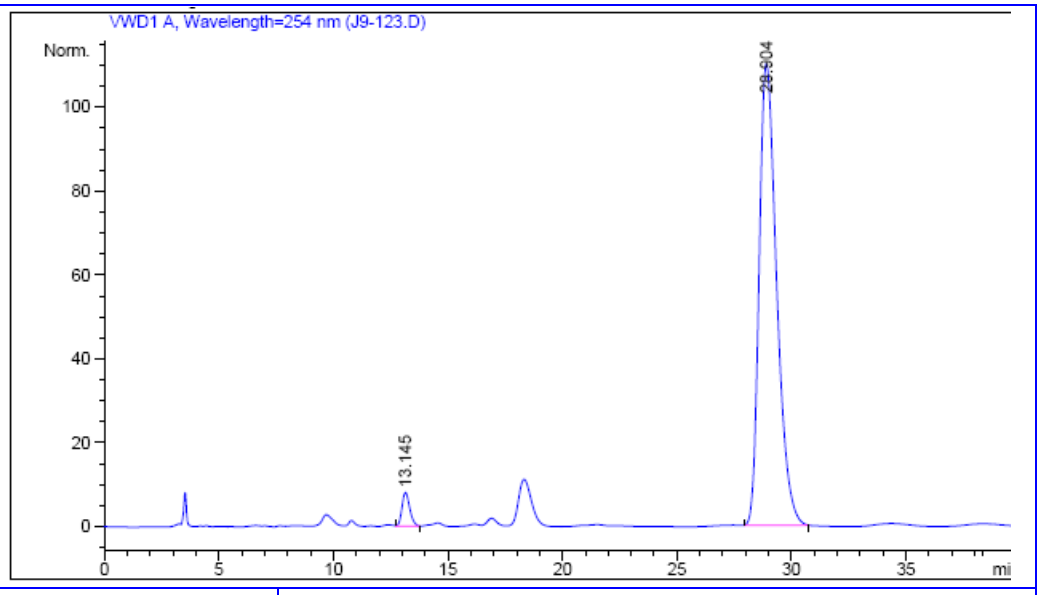
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.373	VB	0.2758	333.25992	18.62162	1.9214
2	13.366	VB	0.4048	1.70117e4	655.29358	98.0786
Totals :				1.73450e4	673.91520	

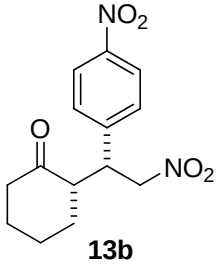




rac-syn-**13b**

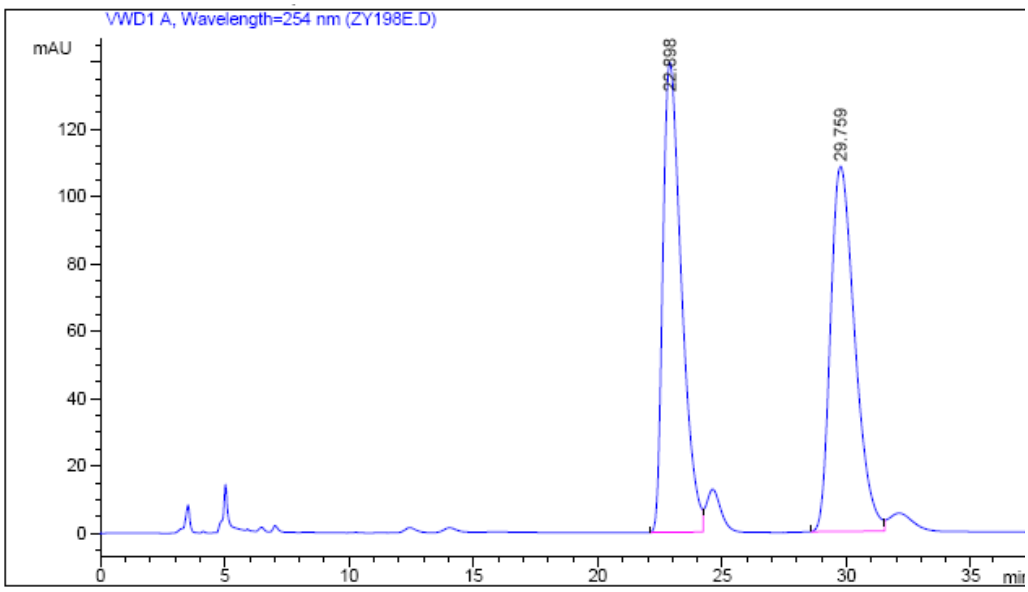
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.106	BB	0.3648	1604.75476	67.12949	51.1726
2	29.021	BB	0.8008	1531.21082	29.35373	48.8274
Totals :				3135.96558	96.48322	

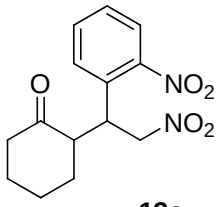




13b

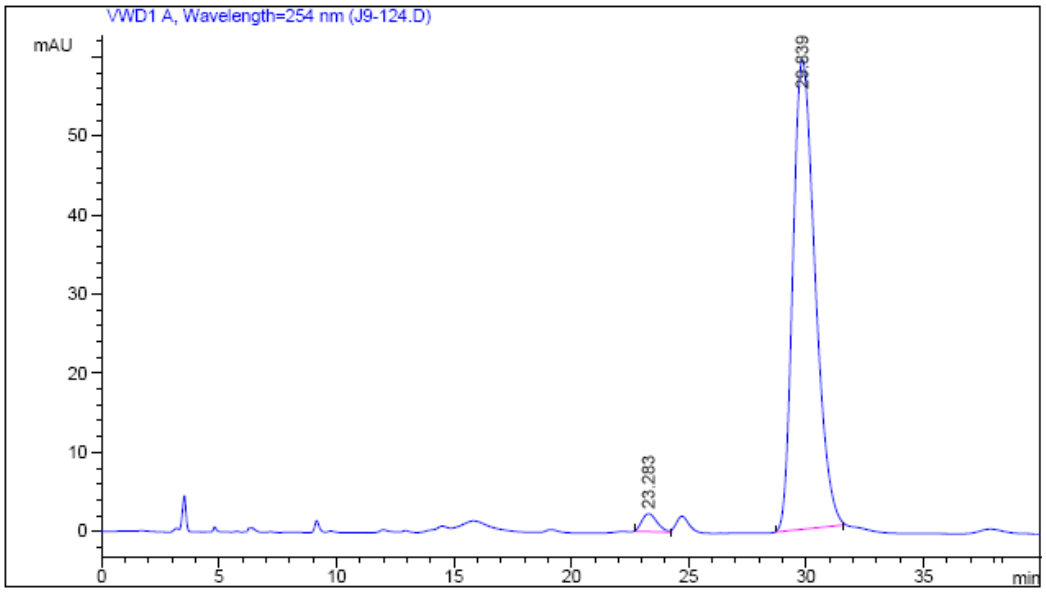
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.145	BB	0.3604	188.72328	8.06292	3.1306
2	28.904	BB	0.8123	5839.62695	110.13315	96.8694
Totals :				6028.35023	118.19607	

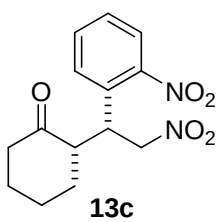




rac-syn-**13c**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.898	BV	0.7987	7279.53418	139.68964	49.6941
2	29.759	BB	1.0468	7369.14160	108.55841	50.3059
Totals :				1.46487e4	248.24805	





13c

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
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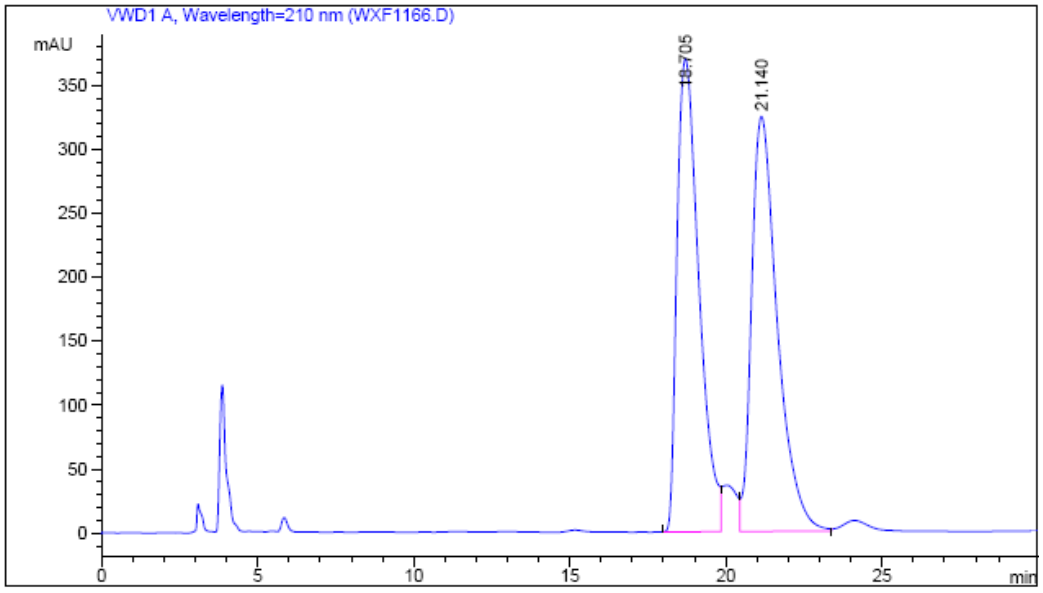
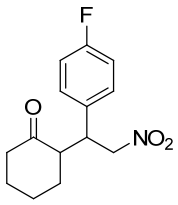
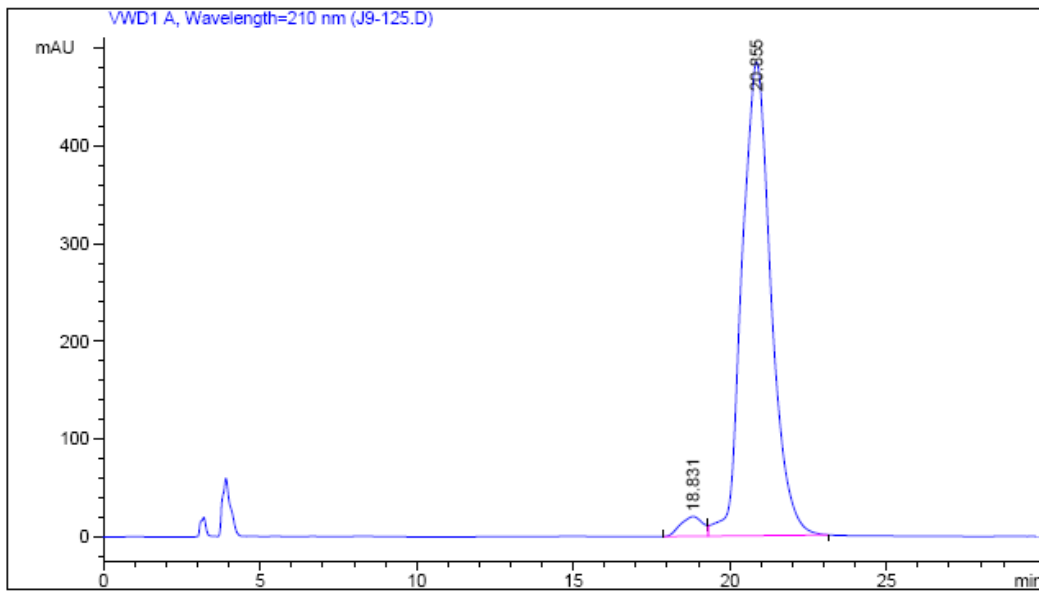
2	29.839	BB	1.0070	3898.47290	59.43320	97.4312
Totals :				4001.25774	61.71144	

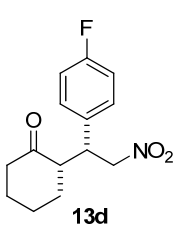




rac-syn-**13d**

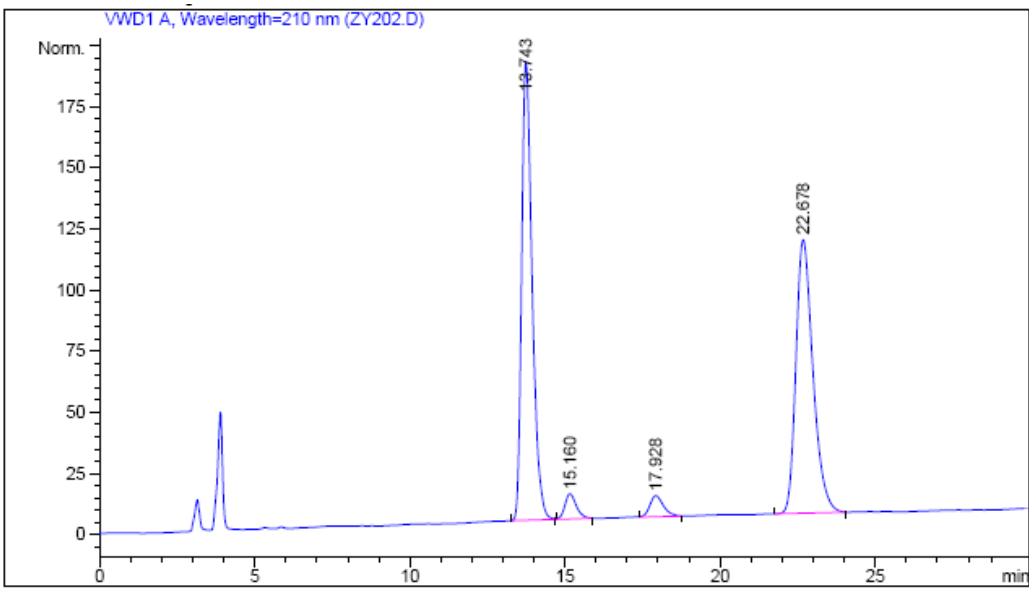
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.705	BV	0.7531	1.80739e4	370.13577	49.1837
2	21.140	VB	0.8739	1.86739e4	324.43109	50.8163
Totals :				3.67478e4	694.56686	

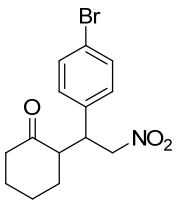




13d

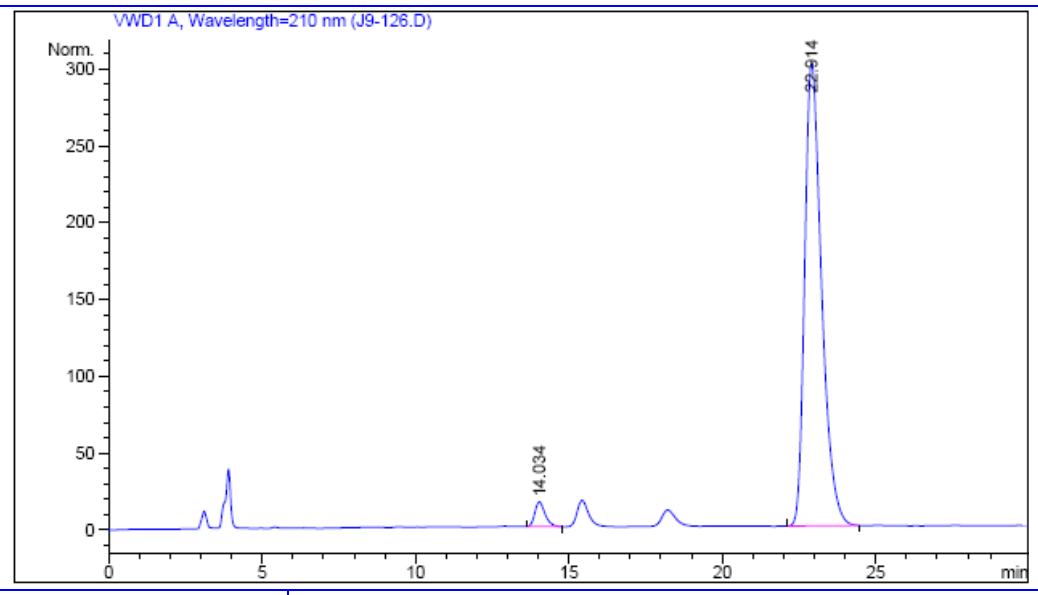
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.831	BV	0.7069	997.02838	20.19934	3.1038
2	20.855	VB	0.9159	3.11256e4	484.21994	96.8962
Totals :				3.21226e4	504.41928	

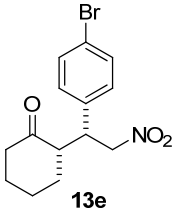




rac-syn-**13e**

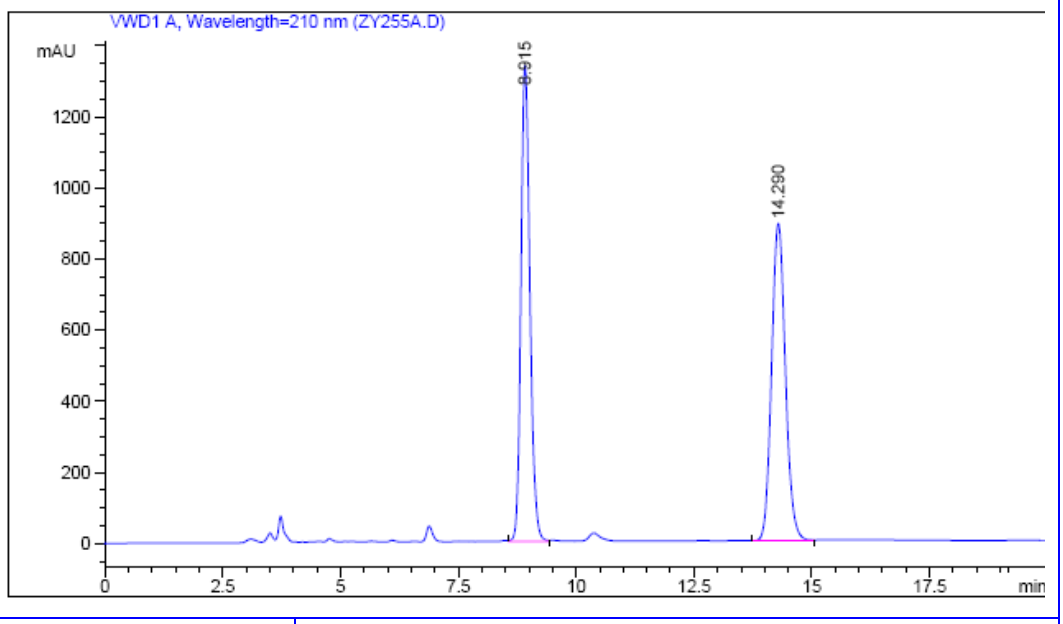
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.743	BB	0.3566	4399.88379	187.63319	47.8409
2	15.160	BB	0.3894	265.05792	10.28758	2.8820
3	17.928	BB	0.4558	264.36295	8.64444	2.8745
4	22.678	BB	0.5820	4267.60156	111.84785	46.4026
Totals :				9196.90622	318.41306	

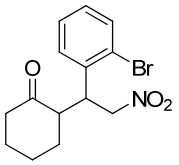




13e

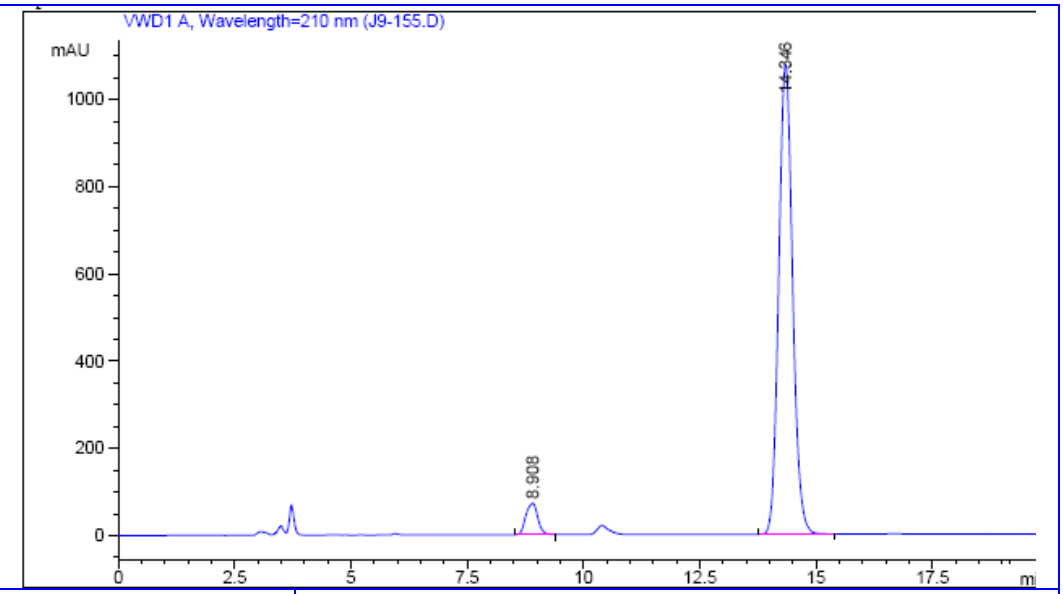
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.034	PP	0.3552	371.19769	16.07867	3.1187
2	22.914	BB	0.5850	1.15313e4	301.17044	96.8813
Totals :				1.19025e4	317.24911	

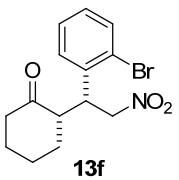




rac-syn-**13f**

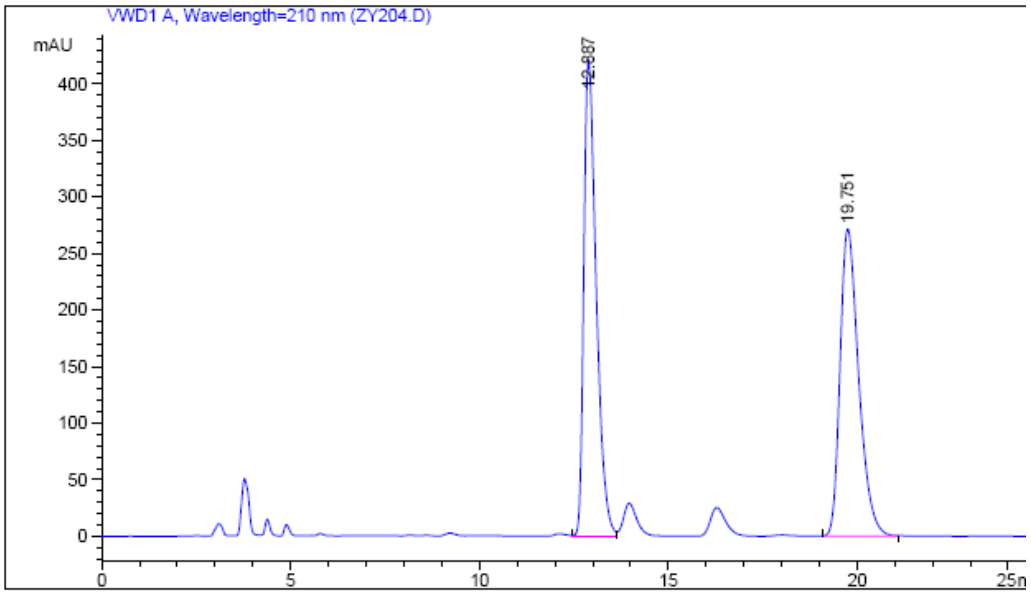
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.915	VV	0.2051	1.76988e4	1339.44299	49.3313
2	14.290	BV	0.3163	1.81786e4	892.22156	50.6687
Totals :				3.58773e4	2231.66455	

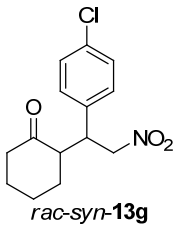




13f

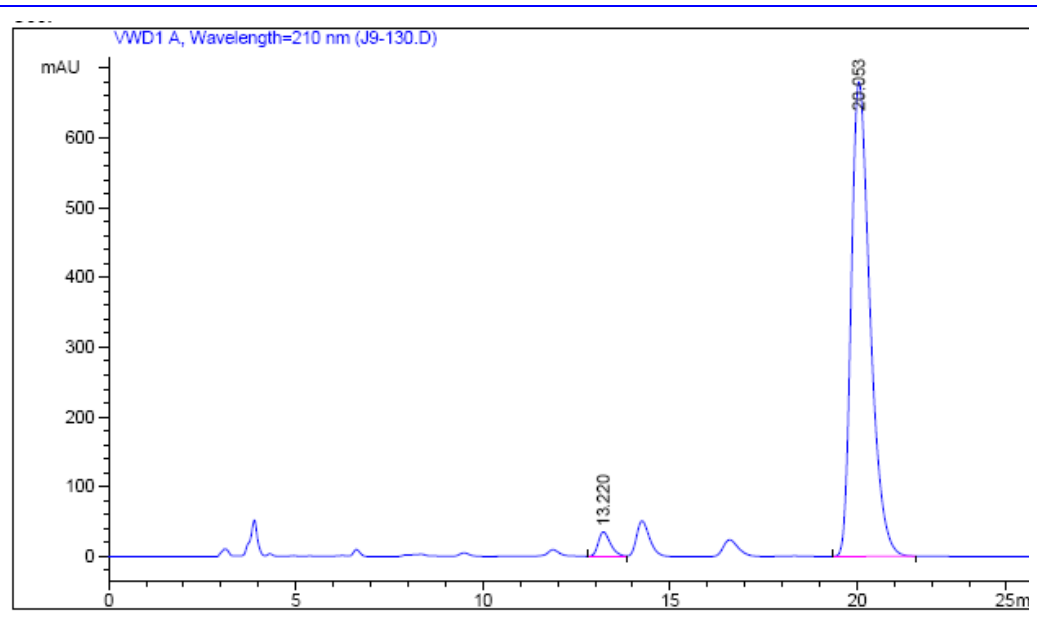
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.908	PV	0.2865	1275.00562	72.06560	5.4040
2	14.346	PB	0.3220	2.23187e4	1076.41309	94.5960
Totals :				2.35937e4	1148.47868	

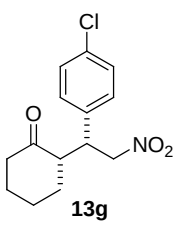




rac-syn-**13g**

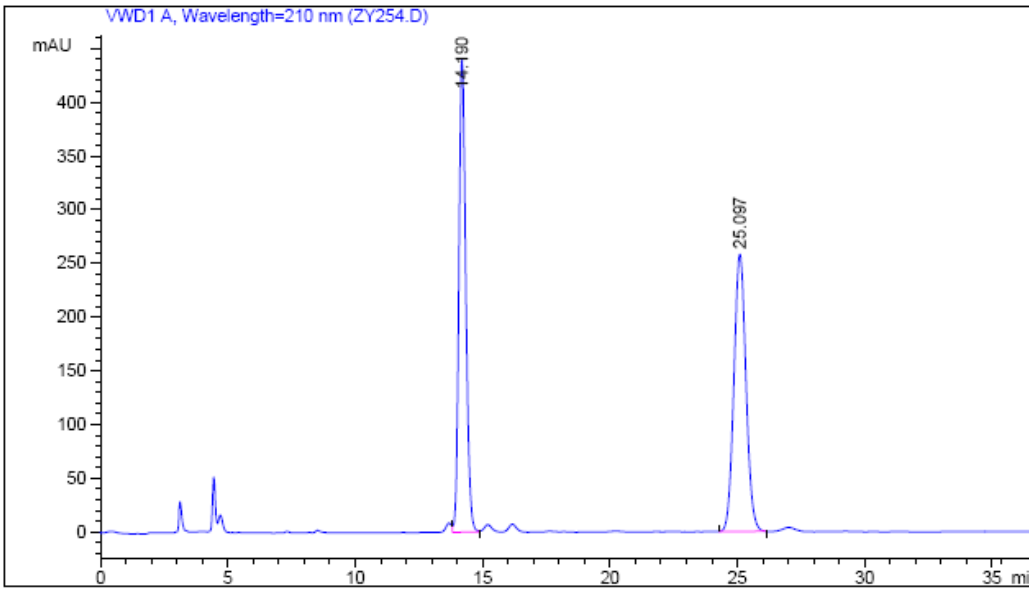
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.887	VV	0.3474	9601.69727	421.28802	50.8179
2	19.751	BB	0.5215	9292.63574	271.55841	49.1821
Totals :				1.88943e4	692.84644	





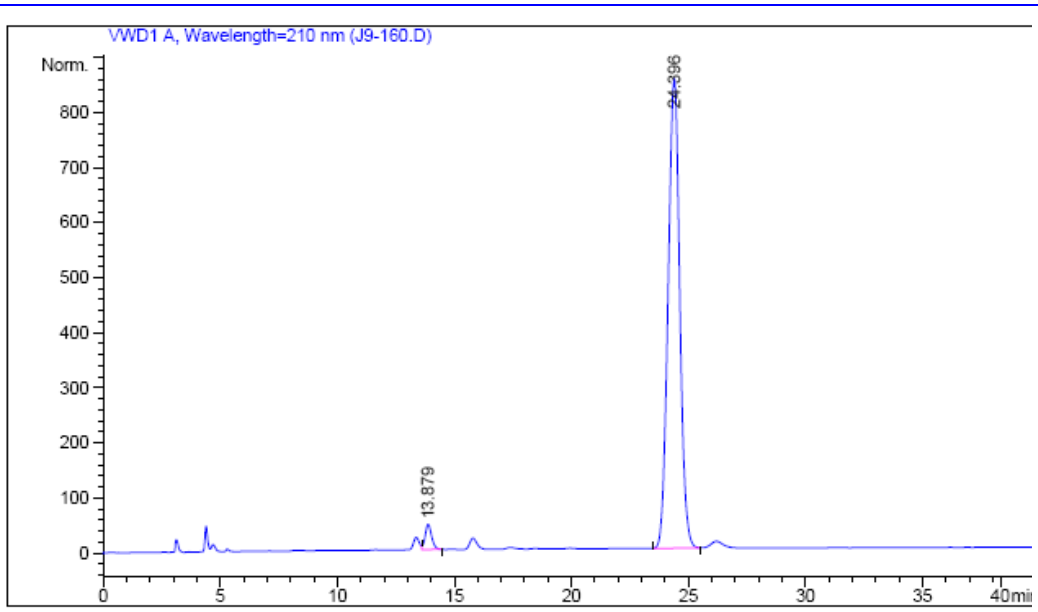
13g

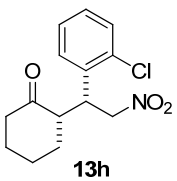
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.220	BV	0.3488	805.84784	35.17484	3.2808
2	20.053	BB	0.5355	2.37569e4	680.41827	96.7192
Totals :				2.45627e4	715.59311	



rac-syn-**13h**

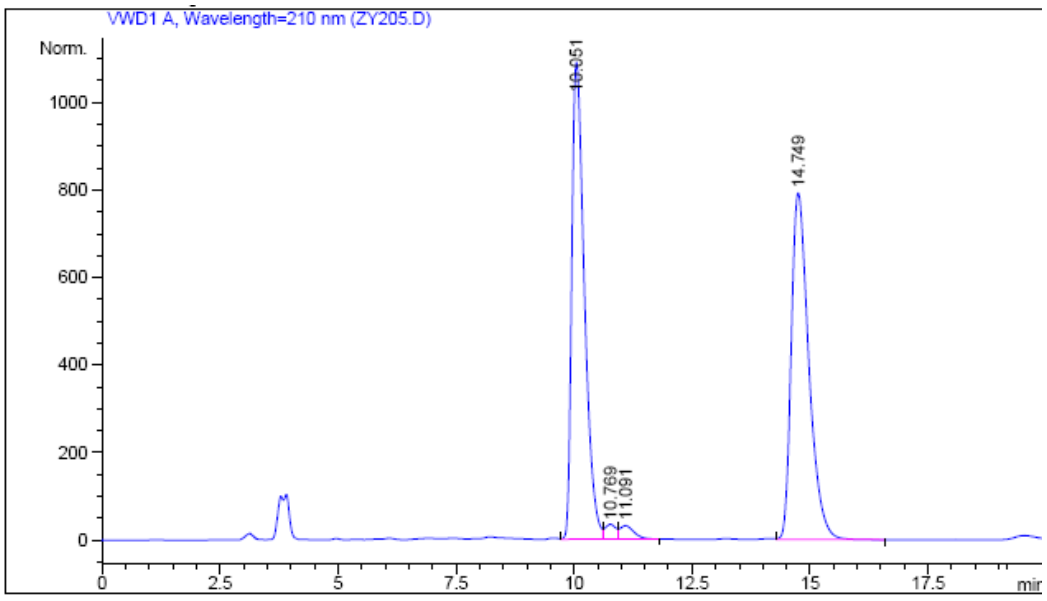
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.190	VB	0.2916	8301.11816	439.61340	49.3708
2	25.097	BB	0.5116	8512.69629	257.97824	50.6292
Totals :				1.68138e4	697.59164	

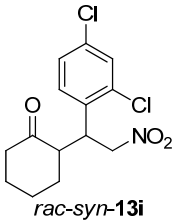




13h

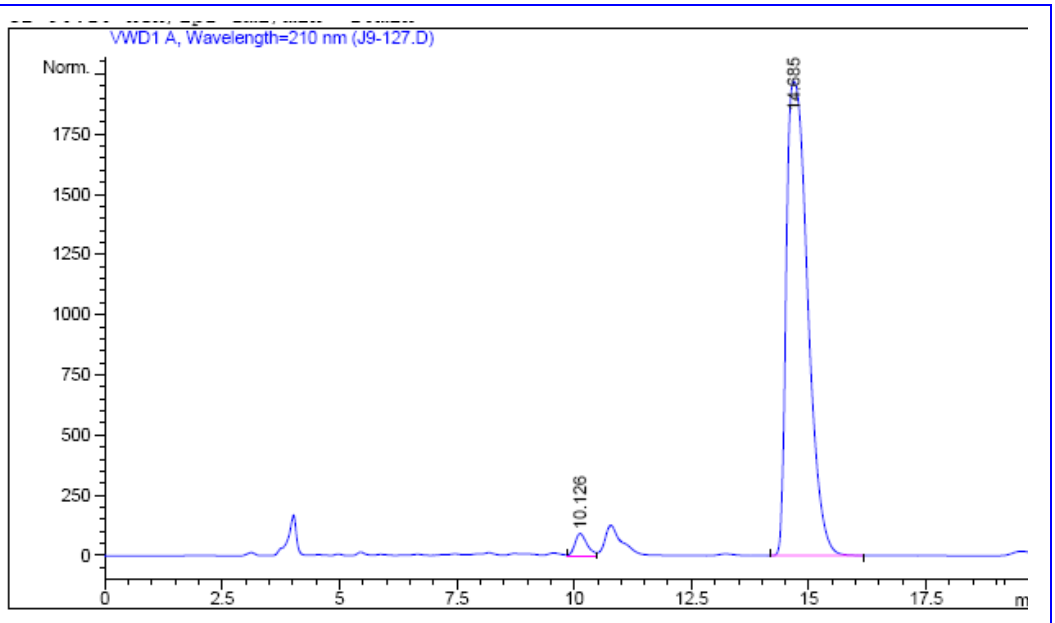
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.879	VB	0.2945	891.68451	46.01762	2.9340
2	24.396	BB	0.5343	2.94997e4	853.37006	97.0660
Totals :				3.03914e4	899.38767	

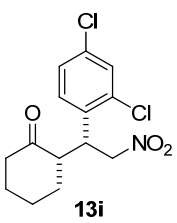




rac-syn-**13i**

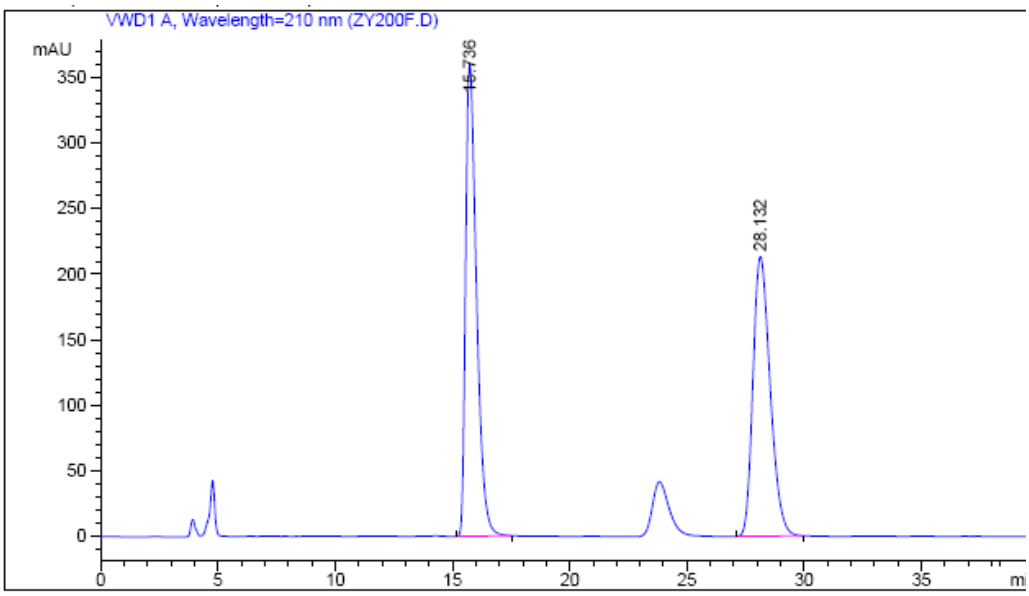
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.051	VV	0.2858	2.03116e4	1090.00305	48.4357
2	10.769	VV	0.2382	551.88666	34.12330	1.3160
3	11.091	VB	0.3073	642.03308	30.98374	1.5310
4	14.749	VB	0.3941	2.04296e4	792.04572	48.7172
Totals :				4.19352e4	1947.15580	

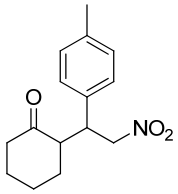




13i

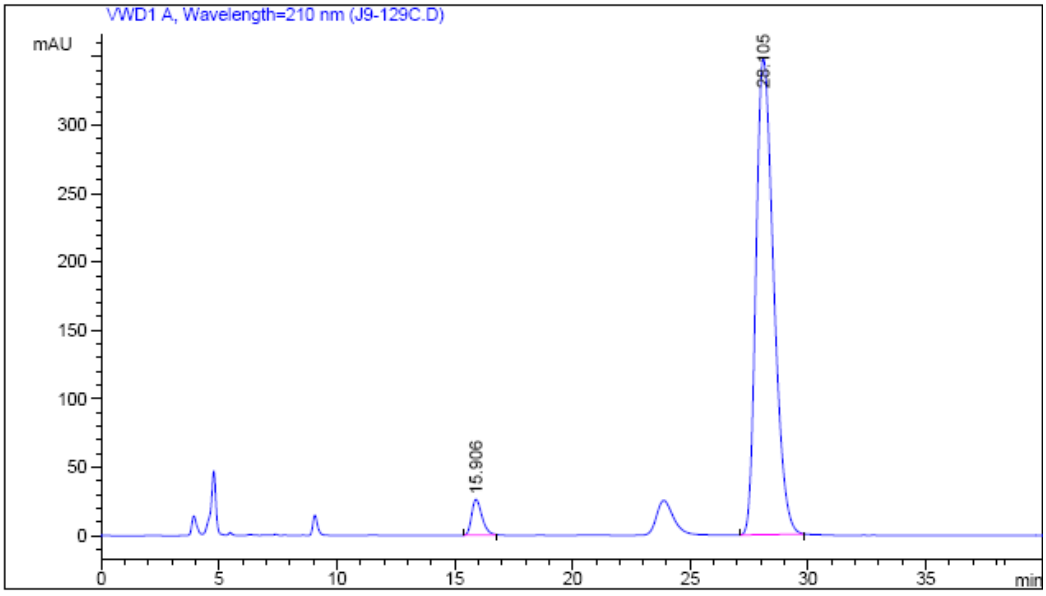
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.126	VV	0.2706	1616.82764	91.34882	2.5399
2	14.685	BB	0.4955	6.20395e4	1969.97559	97.4601
Totals :				6.36563e4	2061.32441	

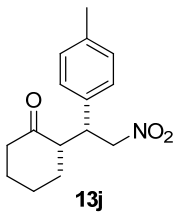




rac-syn-**13j**

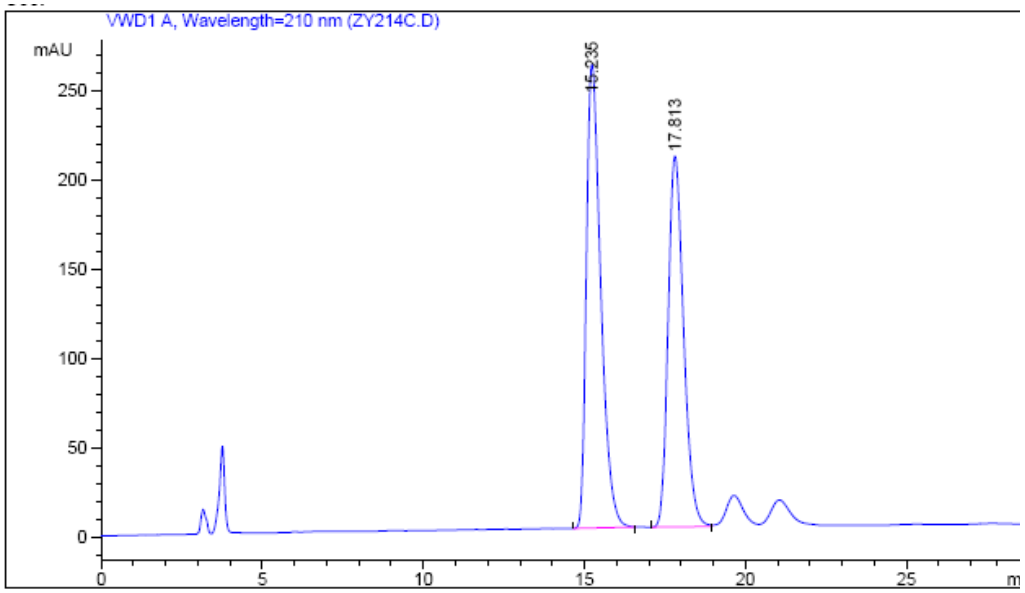
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.736	BB	0.4924	1.16181e4	360.54147	51.7356
2	28.132	BB	0.7887	1.08386e4	213.04189	48.2644
Totals :				2.24567e4	573.58336	

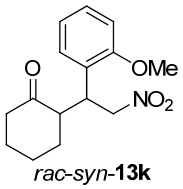




13j

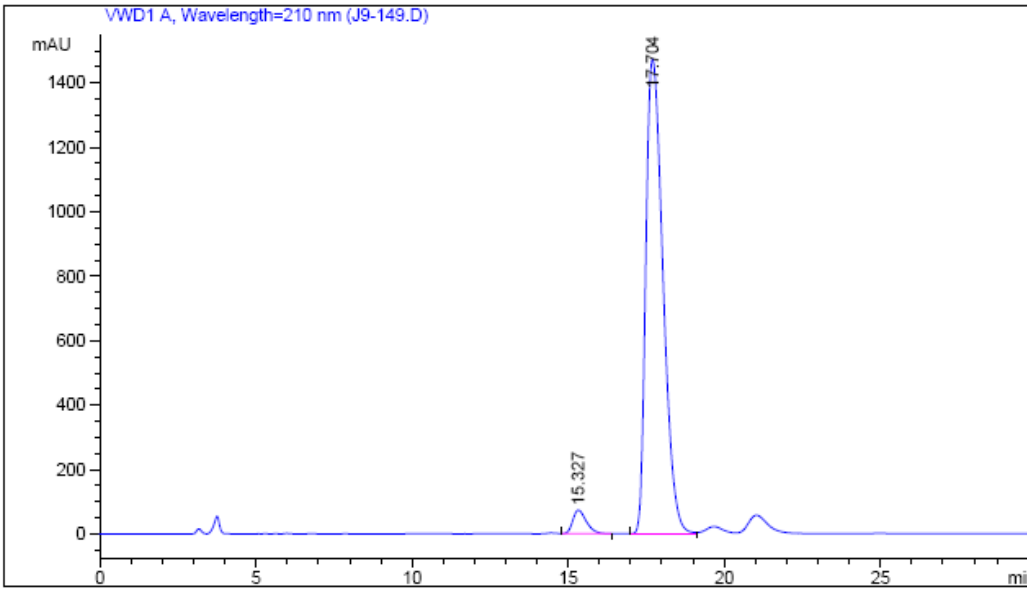
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.906	BB	0.4634	797.02655	26.14407	4.2182
2	28.105	BB	0.8133	1.80981e4	348.09836	95.7818
Totals :				1.88951e4	374.24243	

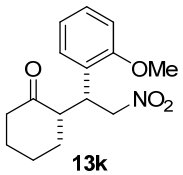




rac-syn-**13k**

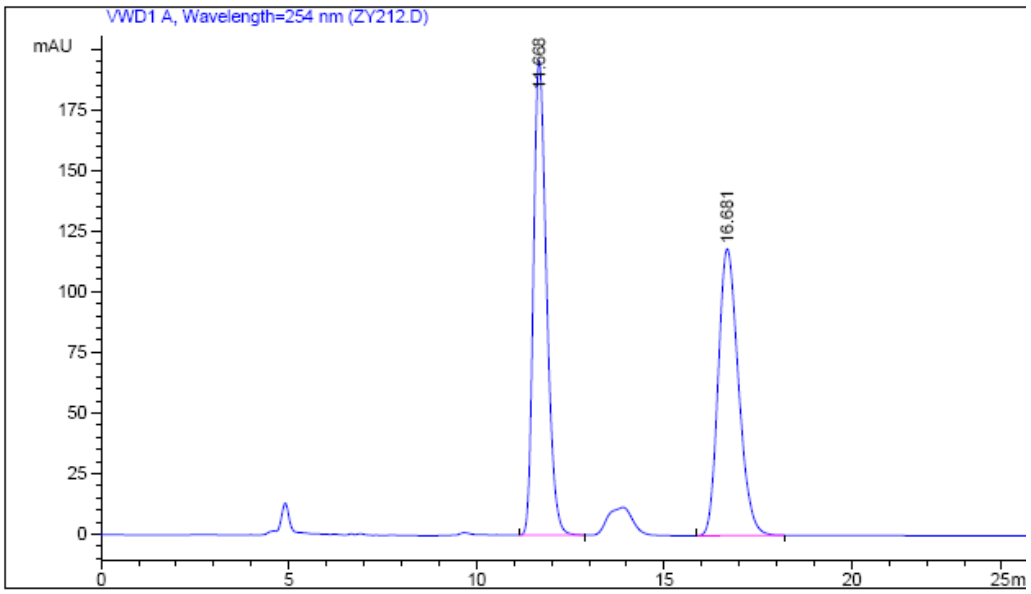
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.235	PB	0.4731	8054.07275	260.28098	53.6494
2	17.813	PB	0.5152	6958.35693	208.18619	46.3506
Totals :				1.50124e4	468.46716	

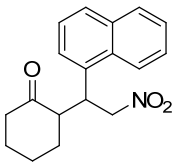




13k

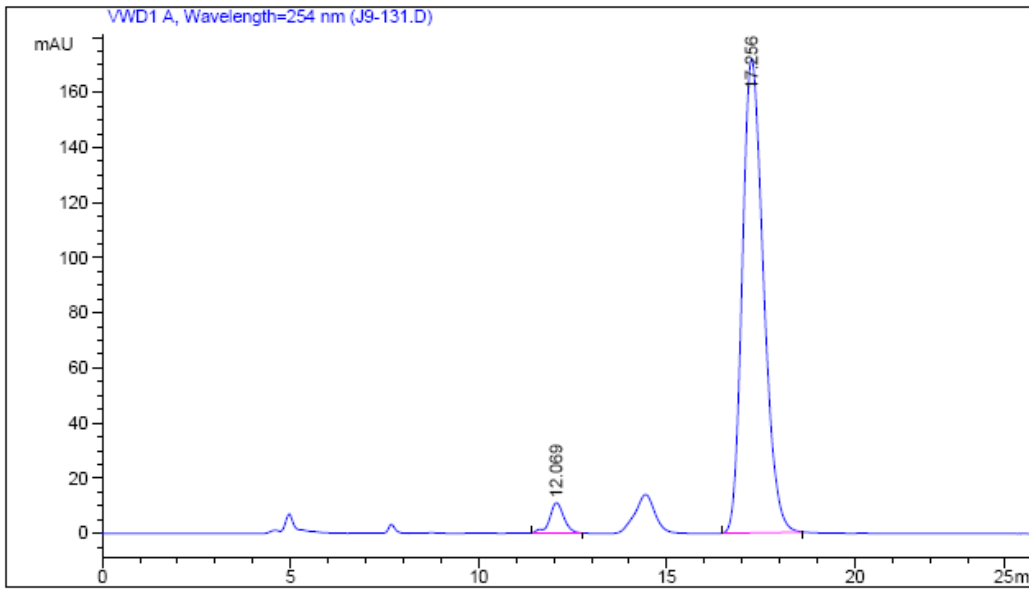
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.327	VB	0.4640	2228.57446	73.58053	3.8156
2	17.704	BV	0.6007	5.61778e4	1473.24707	96.1844
Totals :				5.84064e4	1546.82760	

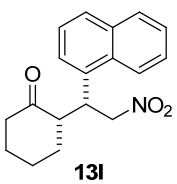




rac-syn-**13l**

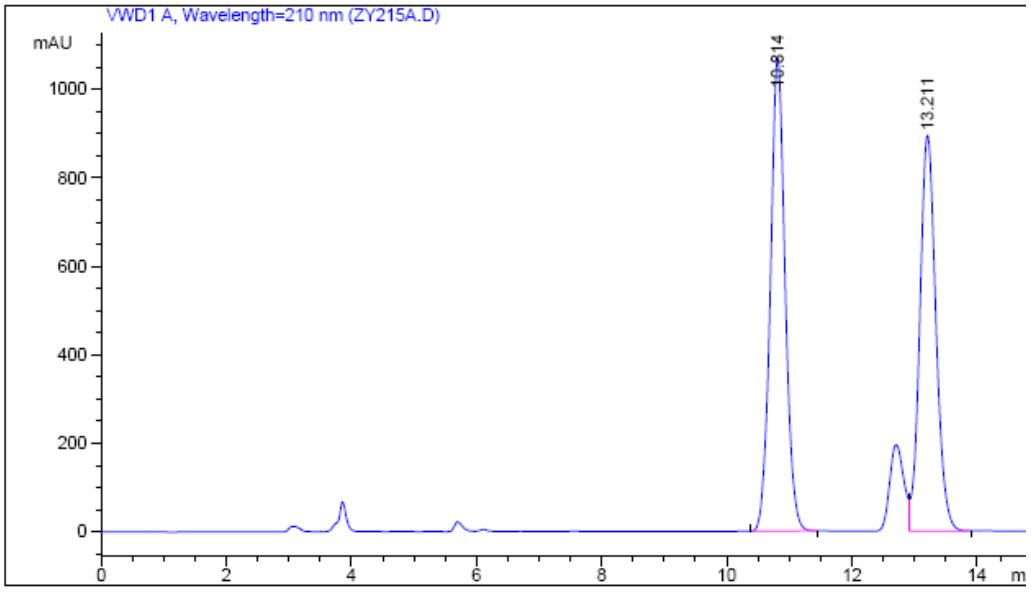
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.668	BB	0.3742	4756.83350	195.47298	51.7687
2	16.681	BB	0.5817	4431.78662	118.15968	48.2313
Totals :				9188.62012	313.63265	

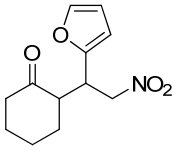




13l

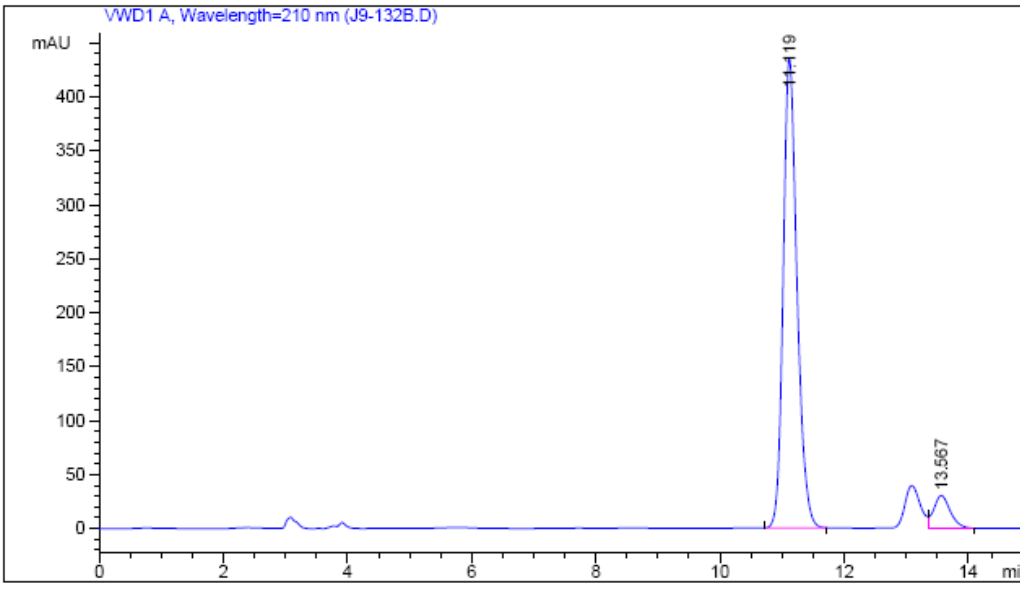
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.069	BB	0.4053	294.62332	11.06538	4.1998
2	17.256	BB	0.6076	6720.60400	171.87505	95.8002
Totals :				7015.22733	182.94042	

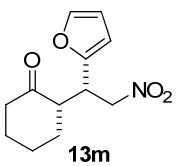




rac-syn-**13m**

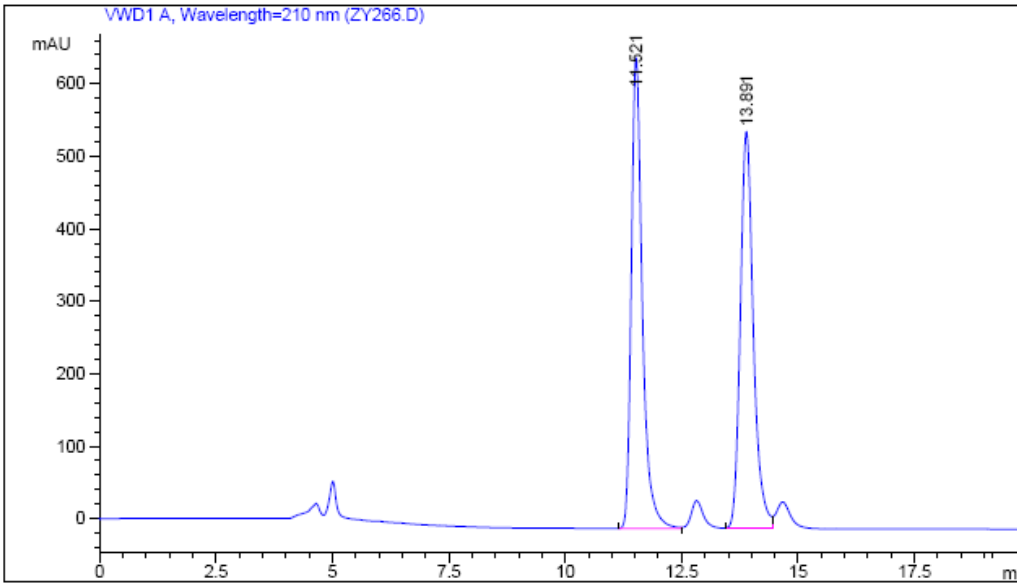
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.814	BB	0.2463	1.74992e4	1069.08752	52.2673
2	13.211	VB	0.2754	1.59810e4	894.35168	47.7327
Totals :				3.34803e4	1963.43921	

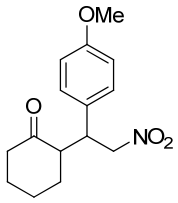




13m

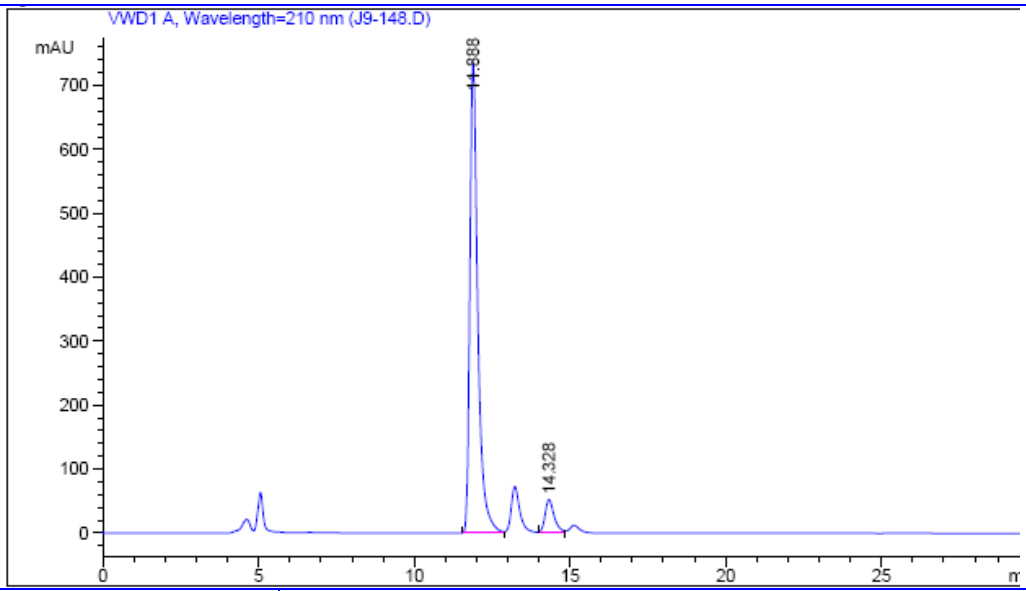
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.119	BB	0.2341	6730.83398	435.72806	92.2417
2	13.567	VB	0.2807	566.11761	30.28307	7.7583
Totals :				7296.95160	466.01113	

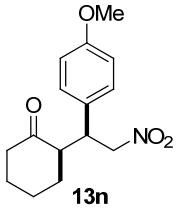




rac-syn-**13n**

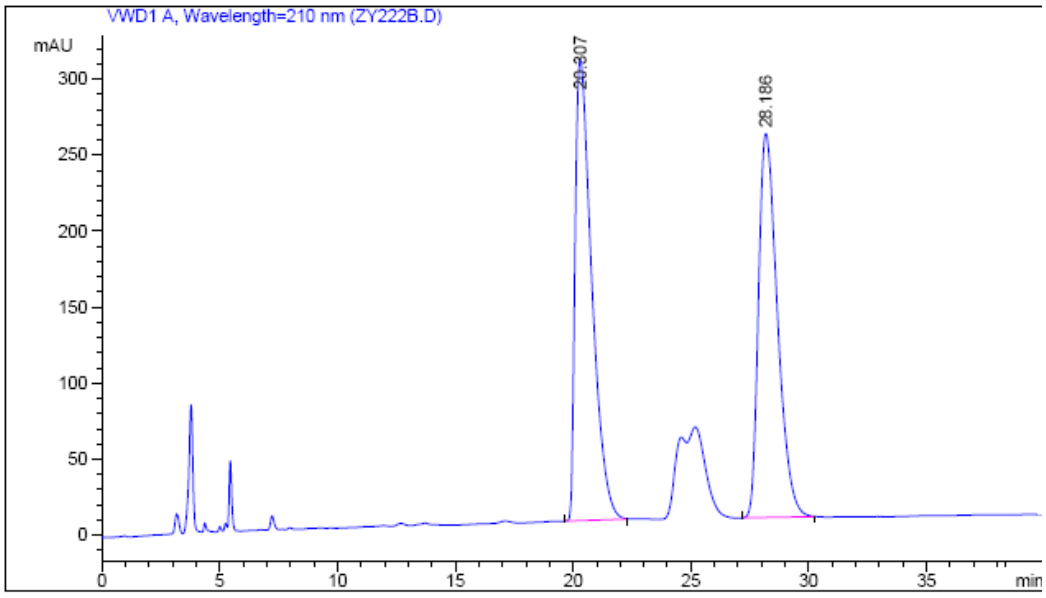
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.521	BB	0.2476	1.07024e4	649.37018	50.0478
2	13.891	BV	0.2959	1.06820e4	547.88300	49.9522
Totals :				2.13844e4	1197.25317	

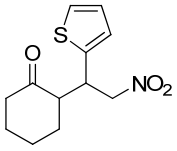




13n

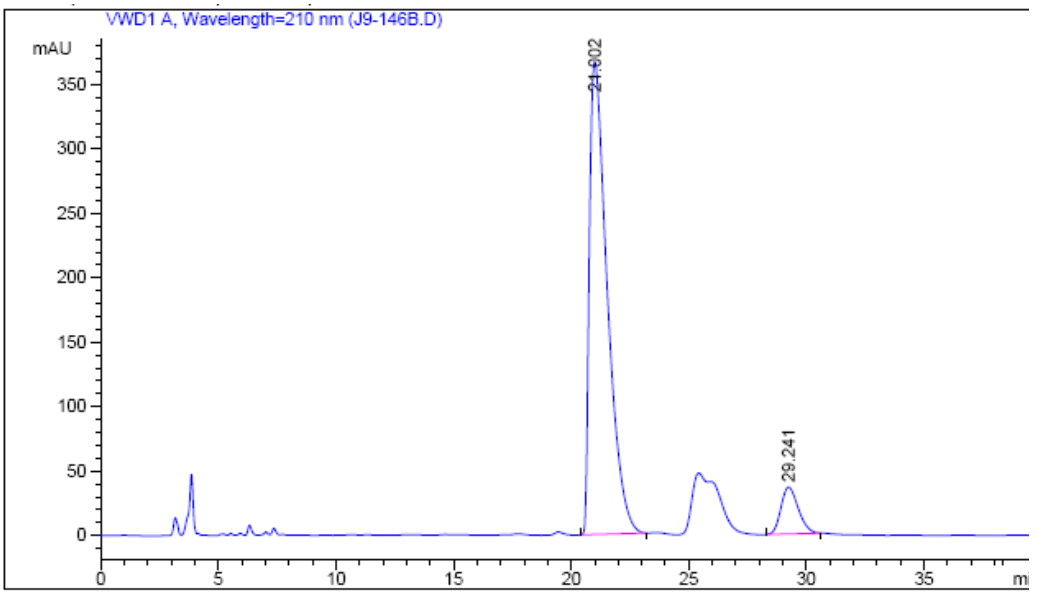
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.888	BV	0.2651	1.30814e4	737.81830	92.3359
2	14.328	BV	0.3102	1085.79321	52.39791	7.6641
Totals :				1.41672e4	790.21621	

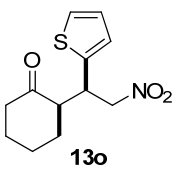




rac-syn-**13o**

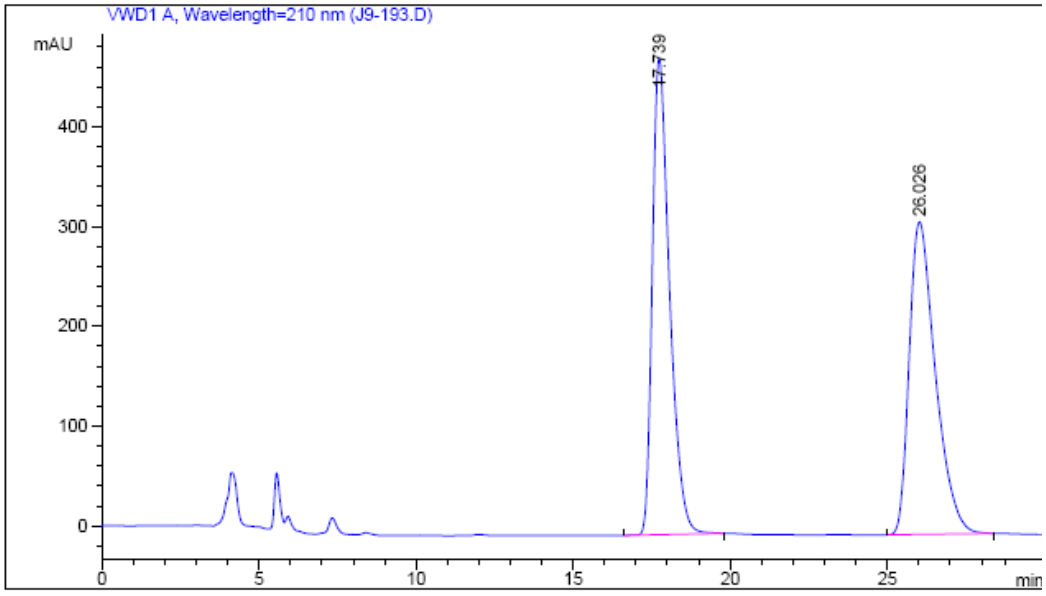
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.307	PB	0.7513	1.48770e4	303.33551	51.4211
2	28.186	BB	0.8602	1.40547e4	252.61896	48.5789
Totals :				2.89317e4	555.95447	

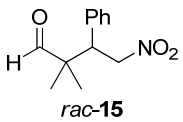




13o

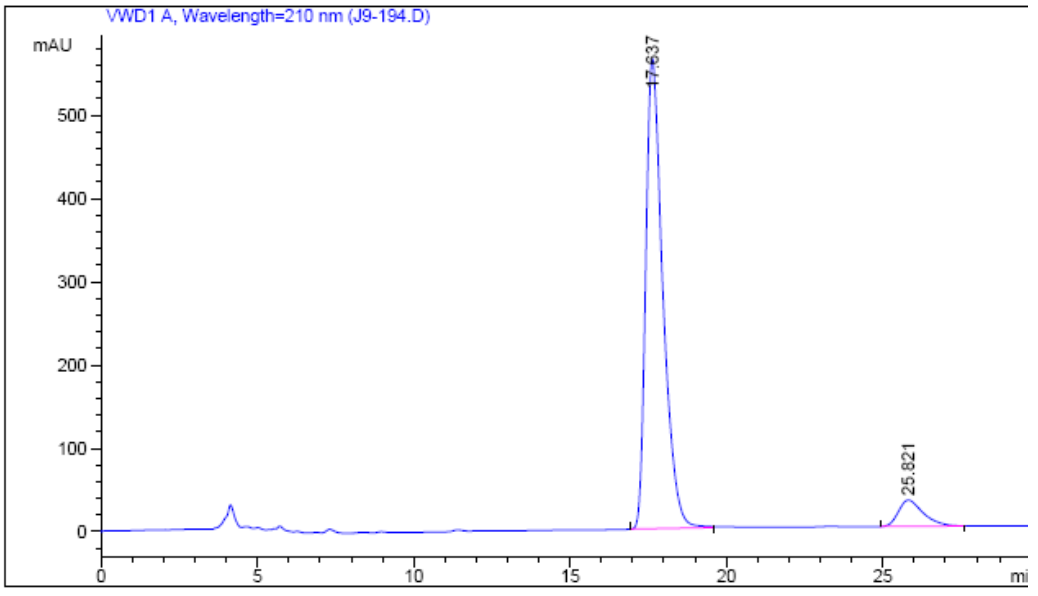
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.002	BP	0.7973	1.93005e4	366.81381	91.1598
2	29.241	PB	0.7905	1871.64771	36.40496	8.8402
Totals :				2.11721e4	403.21877	

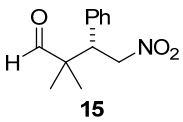




rac-**15**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.739	PB	0.5758	1.81896e4	477.16873	50.1249
2	26.026	PB	0.8756	1.80989e4	312.95905	49.8751
Totals :				3.62885e4	790.12778	





15

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.637	BB	0.5721	2.14428e4	563.48169	92.4643
2	25.821	PB	0.8327	1747.54810	31.54666	7.5357
Totals :				2.31903e4	595.02835	