Fast, solvent-free and hydrogen bonding mediated asymmetric Michael addition in a ball mill

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1. General methods

Flash chromatography (FC) was carried out using silica gel (200-300 mesh). Monitoring of reactions was performed by TLC on silica gel precoated on glass plates, and spots were visualized with UV light at 254nm. ^{1}H and ^{13}C NMR were recorded in $CDCl_3$ on Bruker AVANCE III (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR). TMS served as internal standard (δ = 0 ppm) for ^{1}H NMR and $CDCl_3$ was used as internal standard (δ = 77.0 ppm) for ^{13}C NMR; ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. HPLC experiments were carried out using a JASCO LC-2000 Plus system with MD-2010 HPLC diode array detector.

All experiments were carried out under air. Reactions in the ball mill were conducted using a Fritsch Planetary Micro Mill model “Pulverisette 7”. The milling instrument consists of a main disk which can rotate at a speed of 100-800 rpm and accommodates two grinding bowls (45 mL). Both bowls and balls (2 mm diameter) are made of stainless steel.

Catalysts **I-III**[1], compounds **2**[2] were synthesized according to the reported procedures. Commercially available compound **1** and solvents were used without further purification or drying. All reactions were carried out in oven-dried glassware.

1. J. P. Malerich, K. Hagihara and V. H. Rawal, *J. Am. Chem. Soc.*, 2008, **130**, 14416-14417.
2. J. T. Liu and C. F. Yao, *Tetrahedron Lett.*, 2001, **42**, 6147-6150.

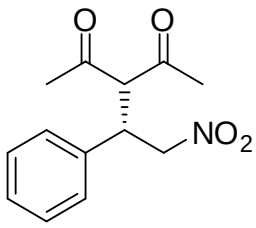
2. General procedure:

A clean, dry ball milling vessel was charged with 80 stainless steel grinding balls (2 mm diameter), the catalyst **IIIg** (0.04 mmol, 0.5 mol %), nitroolefins **2** (8.00 mmol), 1,3-dicarbonyl compounds **1** (2.0 equiv.) sequentially. The vessel was closed, and the milling was started (milling cycle: 5 min milling at 400 rpm, followed by a 2 min pause). As the reactions were proceeding, the yellowish nitroolefins disappeared, and the reaction mixture turned colorless. During the pause, the mixture was sampled and dissolved in CH_2Cl_2, followed by the TLC analysis immediately. Upon consumption of nitroolefin substrate (monitored by TLC), the mixture was obtained by washing the vessel and the balls with 3 × 35 mL EtOAc. The EtOAc solution was concentrated and purified by Flash chromatography to afford the conjugate addition product. The enantiomeric excess was determined by chiral-phase HPLC analyses.

The two equivalents of the 1,3-dicarbonyl compound is necessary for the completion of the reaction. If 1:1 reagent ratios are used (other conditions was same with Table 3, entry 1), the yield was low and couldn't consume the nitroolefin entirely even with longer milling time (58% yield, 30min), but the high enantioselectivity was maintained (93% ee). The excess of 1,3-dicarbonyl compound was removed by Flash chromatography.

3. Characterization results

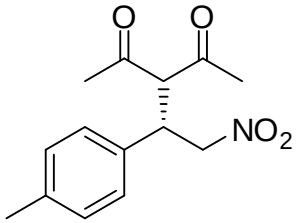
3a



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36-7.26 (m, 3H), 7.21-7.15 (m, 2H), 4.69-4.57 (m, 2H), 4.37 (d, *J* = 10.8 Hz, 1H), 4.24 (ddd, *J* = 10.8, 7.9, 4.8 Hz, 1H), 2.29 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 201.75, 200.97, 136.08, 129.34, 128.55, 127.96, 78.19, 70.76, 42.83, 30.40, 29.54; HPLC (AS-H, 15% *i*PrOH in hexane, flow rate 1.0 ml/min): t_R major

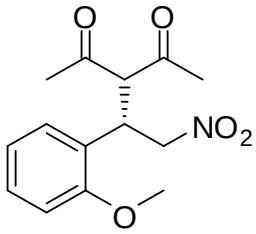
isomer = 17.4 min, t_R minor isomer = 27.8 min.

3b



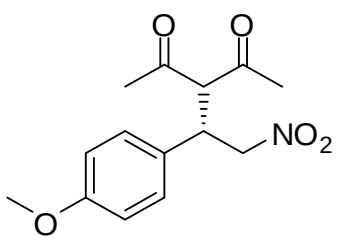
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.12 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 4.66-4.55 (m, 2H), 4.35 (d, *J* = 10.8 Hz, 1H), 4.20 (ddd, *J* = 10.9, 7.7, 5.0 Hz, 1H), 2.30 (s, 3H), 2.29 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 201.86, 201.09, 138.34, 132.89, 129.98, 127.79, 78.35, 70.84, 42.48, 30.36, 29.45, 21.02; HPLC (AD-H, 10% *i*PrOH in hexane, flow rate 1.0 ml/min): t_R major isomer = 13.0 min, t_R minor isomer = 20.3 min.

3c



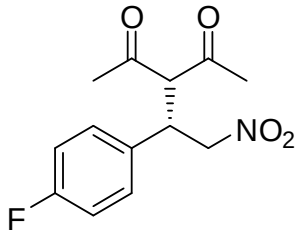
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.28-7.08 (m, 1H), 7.08 (d, *J* = 7.7 Hz, 1H), 6.95-6.79 (m, 2H), 4.78 (dd, *J* = 12.1, 7.9 Hz, 1H), 4.67-4.54 (m, 2H), 4.49 (ddd, *J* = 10.9, 7.9, 4.4 Hz, 1H), 3.88 (s, 3H), 2.28 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 202.22, 201.52, 157.03, 130.22, 129.70, 123.58, 121.12, 111.25, 76.52, 68.95, 55.40, 38.97, 30.36, 28.76; HPLC (AD-H, 1% *i*PrOH in hexane, flow rate 1.0 ml/min): t_R major isomer = 47.2 min, t_R minor isomer =55.3 min.

3d



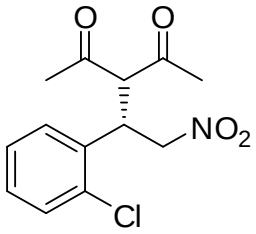
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.10 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 4.66-4.49 (m, 2H), 4.33 (d, *J* = 10.9 Hz, 1H), 4.20-4.19 (m, 1H), 3.77 (s, 3H), 2.29 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 201.84, 201.14, 159.53, 129.07, 127.70, 114.68, 78.43, 70.91, 55.21, 42.13, 30.32, 29.45; HPLC (AD-H, 10% *i*PrOH in hexane, flow rate 1.0 ml/min): t_R major isomer = 20.4 min, t_R minor isomer = 30.9 min.

3e



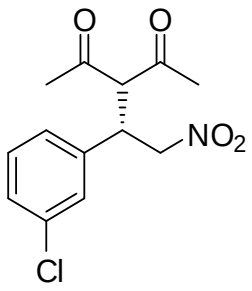
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.21-7.14 (m, 2H), 7.07-6.99 (m, 2H), 4.61 (d, *J* = 6.3 Hz, 2H), 4.33 (d, *J* = 10.8 Hz, 1H), 4.25 (dt, *J* = 10.8, 6.3 Hz, 1H), 2.29 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 201.47, 200.75, 163.46, 161.49, 131.87, 131.84, 129.75, 129.68, 116.40, 116.23, 78.11, 70.66, 42.06, 30.37, 29.63; HPLC (OD-H, 5% *i*PrOH in hexane, flow rate 1.0 ml/min): t_R major isomer = 44.7 min, t_R minor isomer = 52.2 min.

3f



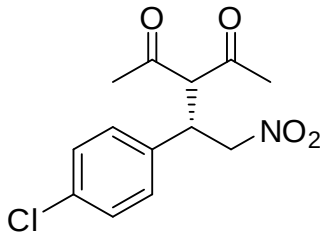
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.47-7.39 (m, 1H), 7.30-7.21 (m, 2H), 7.19-7.12 (m, 1H), 4.84 (dd, *J* = 12.4, 6.8 Hz, 1H), 4.78-4.72 (m, 1H), 4.67 (dd, *J* = 12.4, 4.0 Hz, 1H), 4.60 (d, *J* = 9.9 Hz, 1H), 2.29 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 201.84, 200.83, 133.77, 133.52, 130.64, 129.68, 129.03, 127.63, 76.19, 68.90, 38.88, 30.85, 28.60; HPLC (AD-H, 1% *i*PrOH in hexane, flow rate 1.0 ml/min): t_R major isomer = 36.3 min, t_R minor isomer = 42.5 min.

3g



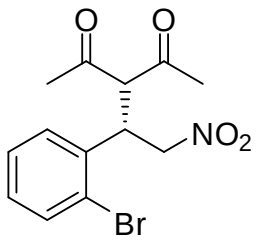
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39-7.24 (m, 2H), 7.20 (s, 1H), 7.12-7.04 (m, 1H), 4.73-4.54 (m, 2H), 4.34 (d, *J* = 10.6 Hz, 1H), 4.22 (ddd, *J* = 10.6, 7.8, 4.8 Hz, 1H), 2.30 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 201.32, 200.45, 138.28, 135.20, 130.58, 128.85, 128.19, 126.15, 77.74, 70.37, 42.37, 30.46, 29.76; HPLC (AS-H, 15% *i*PrOH in hexane, flow rate 1.0 ml/min): t_R major isomer = 19.4 min, t_R minor isomer =40.5min.

3h



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31 (d, *J* = 5.4 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 4.68-4.51 (m, 2H), 4.33 (d, *J* = 10.7 Hz, 1H), 4.23 (ddd, *J* = 10.7, 7.5, 5.1 Hz, 1H), 2.30 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 201.38, 200.56, 134.61, 134.58, 129.57, 129.34, 77.92, 70.55, 42.16, 30.42, 29.66; HPLC (AS-H, 15% *i*PrOH in hexane, flow rate 1.0 ml/min): t_R major isomer = 17.0 min, t_R minor isomer = 33.9 min.

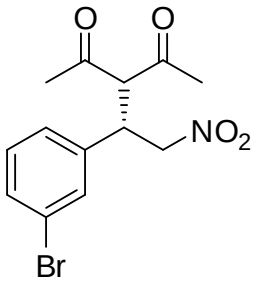
3i



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.63 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.29 (td, *J* = 7.6, 1.0 Hz, 1H), 7.21-7.04 (m, 2H), 4.84 (dd, *J* = 12.4, 6.4 Hz, 1H), 4.77-4.71 (m, 1H), 4.67 (dd, *J* = 12.4, 4.1 Hz, 1H), 4.60 (d, *J* = 9.7 Hz, 1H), 2.29 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 201.91,

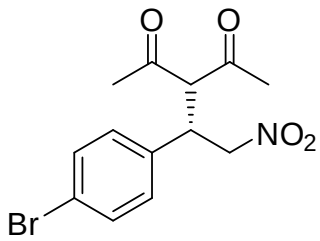
200.83, 135.11, 134.00, 129.94, 128.82, 128.24, 124.55, 76.25, 69.08, 41.08, 30.95, 28.43; HPLC (OD-H, 5% *i*PrOH in hexane, flow rate 0.8 ml/min): t_R major isomer = 40.9 min, t_R minor isomer = 52.6 min.

3j



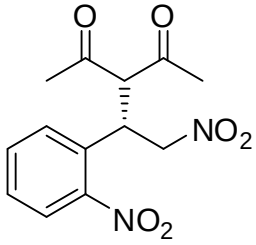
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 7.9 Hz, 1H), 7.36 (t, *J* = 1.5 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 4.66-4.59 (m, 2H), 4.35 (d, *J* = 10.6 Hz, 1H), 4.22 (ddd, *J* = 10.6, 7.7, 5.0 Hz, 1H), 2.30 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 201.32, 200.52, 138.57, 131.73, 131.06, 130.82, 126.65, 123.24, 77.72, 70.25, 42.30, 30.50, 29.84; HPLC (AS-H, 15% *i*PrOH in hexane, flow rate 1.0 ml/min): t_R major isomer = 19.5 min, t_R minor isomer = 40.5 min.

3k



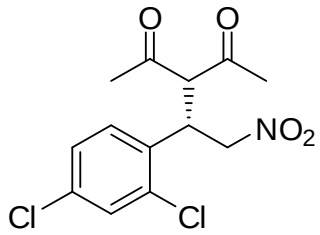
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 4.62 (d, *J* = 6.4 Hz, 2H), 4.33 (d, *J* = 10.7 Hz, 1H), 4.22 (dt, *J* = 10.7, 6.4 Hz, 1H), 2.29 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 201.35, 200.60, 135.21, 132.46, 129.67, 122.58, 77.82, 70.35, 42.21, 30.44, 29.77; HPLC (OD-H, 10% *i*PrOH in hexane, flow rate 0.8 ml/min): t_R major isomer = 40.5 min, t_R minor isomer = 44.5 min.

3l



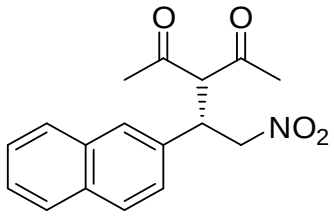
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.93 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.62-7.55 (m, 1H), 7.53-7.43 (m, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 4.98 (dd, *J* = 13.3, 7.1 Hz, 1H), 4.84 (dd, *J* = 13.3, 3.7 Hz, 1H), 4.78-4.70 (m, 1H), 4.67 (d, *J* = 8.8 Hz, 1H), 2.31 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 201.55, 200.50, 149.82, 138.63, 133.45, 131.25, 129.34, 129.23, 125.51, 76.54, 69.06, 37.14, 31.21, 29.31; HPLC (OD-H, 10% *i*PrOH in hexane, flow rate 1.0 ml/min): t_R major isomer = 42.6 min, t_R minor isomer = 77.9 min.

3m



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 2.1 Hz, 1H), 7.23 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 4.83 (dd, *J* = 12.4, 6.7 Hz, 1H), 4.72-4.67 (m, 1H), 4.64 (dd, *J* = 12.4, 4.1 Hz, 1H), 4.55 (d, *J* = 9.8 Hz, 1H), 2.30 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 201.54, 200.50, 135.06, 134.52, 132.17, 130.46, 127.97, 75.96, 68.80, 38.46, 30.84, 28.63; HPLC (AD-H, 10% *i*PrOH in hexane, flow rate 1.0 ml/min): t_R major isomer = 11.7 min, t_R minor isomer = 14.7 min.

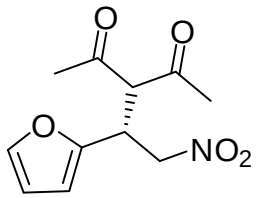
3n



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84-7.77 (m, 3H), 7.65 (s, 1H), 7.52-7.45 (m, 2H), 7.30 (dd, *J* =

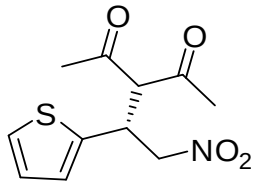
8.5, 1.6 Hz, 1H), 4.72 (qd, *J* = 12.5, 6.2 Hz, 2H), 4.49 (d, *J* = 10.7 Hz, 1H), 4.45-4.36 (m, 1H), 2.31 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 201.76, 200.92, 133.40, 133.30, 133.01, 129.36, 127.94, 127.71, 127.51, 126.74, 126.66, 125.04, 78.14, 70.71, 42.92, 30.46, 29.61; HPLC (AD-H, 10% *i*PrOH in hexane, flow rate 1.0 ml/min): t_R major isomer = 21.0 min, t_R minor isomer = 26.9 min.

3o



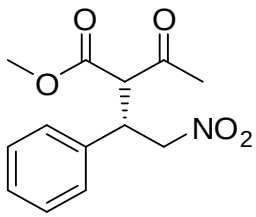
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 1.2 Hz, 1H), 6.30 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.18 (d, *J* = 3.3 Hz, 1H), 4.67 (d, *J* = 5.7 Hz, 2H), 4.39 (d, *J* = 9.8 Hz, 1H), 4.36-4.32 (m, 1H), 2.28 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 201.47, 200.82, 149.50, 142.86, 110.79, 108.79, 75.81, 67.82, 36.56, 30.59, 29.32; HPLC (AD-H, 10% *i*PrOH in hexane, flow rate 1.0 ml/min): t_R major isomer = 13.8 min, t_R minor isomer = 16.3 min.

3p



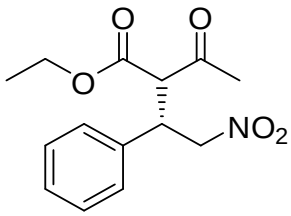
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.24 (s, 1H), 6.91 (d, *J* = 18.1 Hz, 2H), 4.66 (d, *J* = 3.9 Hz, 2H), 4.54 (d, *J* = 4.0 Hz, 1H), 4.41 (d, *J* = 9.6 Hz, 1H), 2.29 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 201.44, 200.64, 138.52, 127.35, 126.98, 125.70, 78.49, 71.00, 38.23, 30.51, 29.64; HPLC (AD-H, 10% *i*PrOH in hexane, flow rate 1.0 ml/min): t_R major isomer = 16.4 min, t_R minor isomer = 22.1 min.

4a



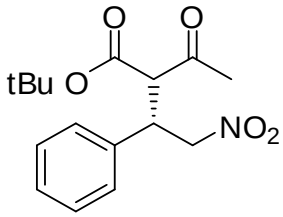
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34-7.25 (m, 3H), 7.22-7.18 (m, 2H), 4.87-4.80 (m, 0.32H), 4.79-4.75 (m, 1.73H), 4.26-4.18 (m, 1H), 4.14 (d, *J* = 9.6 Hz, 0.8H), 4.05 (d, *J* = 9.8 Hz, 0.15H), 3.77 (s, 0.44H), 3.52 (s, 2.58H), 2.29 (s, 2.58H), 2.05 (s, 0.45H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 201.05, 200.24, 167.95, 167.33, 136.40, 136.27, 129.09, 128.90, 128.30, 128.20, 127.82, 127.79, 77.71, 77.59, 61.76, 61.34, 52.85, 52.65, 42.55, 42.25, 30.26, 30.12; HPLC (AD-H, 5% *i*PrOH in hexane, flow rate 1.0 ml/min): dr=1.6:1, major diastereomer: t_R major isomer = 20.3 min, t_R minor isomer = 38.6 min, minor diastereomer: t_R major isomer = 36.4 min, t_R minor isomer = 31.1 min.

4b



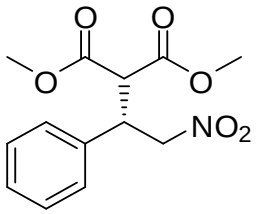
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33-7.25 (m, 3.48H), 7.23-7.18 (m, 2.24H), 4.88-4.79 (m, 0.93H), 4.75 (d, *J* = 6.5 Hz, 1.32H), 4.26-4.17 (m, 2H), 4.15-4.01 (m, 1.47H), 3.97 (q, *J* = 7.2 Hz, 1.32H), 2.30 (s, 2H), 2.04 (d, *J* = 10.0 Hz, 1.83H), 1.27 (dt, *J* = 10.5, 7.1 Hz, 1.89H), 1.0 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 201.12, 200.43, 167.53, 166.87, 136.50, 136.48, 129.08, 128.86, 128.28, 128.20, 128.03, 127.92, 77.89, 77.80, 62.15, 62.00, 61.88, 61.60, 42.57, 42.32, 30.24, 29.95, 13.91, 13.60; HPLC (AD-H, 1% *i*PrOH in hexane, flow rate 0.8 ml/min): dr=1.5:1, major diastereomer: t_R major isomer = 48.2 min, t_R minor isomer = 82.1 min, minor diastereomer: t_R major isomer = 145.1 min, t_R minor isomer = 99.7 min.

4c



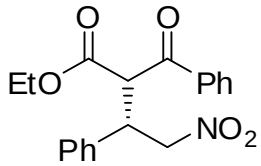
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.27-7.31 (m, 3H), 7.21-7.22 (m, 2H), 4.77-4.65 (m, 2H), 4.14 (m, 1H), 4.02 (d, *J* = 10.3 Hz, 1H), 2.30 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 201.34, 165.86, 136.65, 128.82, 128.25, 128.18, 82.91, 78.35, 63.05, 42.35, 29.66, 27.34; HPLC (AD-H, 5% *i*PrOH in hexane, flow rate 1.0 ml/min): dr=1.4:1, major diastereomer: t_R major isomer = 25.4 min, t_R minor isomer = 18.9 min, minor diastereomer: t_R major isomer = 10.5 min, t_R minor isomer = 15.9 min.

4d



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34-7.26 (m, 3H), 7.23 (dd, *J* = 5.3, 3.1 Hz, 2H), 4.90 (qd, *J* = 13.2, 7.0 Hz, 2H), 4.25 (td, *J* = 9.0, 5.1 Hz, 1H), 3.87 (d, *J* = 9.1 Hz, 1H), 3.76 (s, 3H), 3.56 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.83, 167.23, 136.18, 129.00, 128.40, 127.86, 77.39, 54.76, 52.96, 52.77, 42.94; HPLC (OD-H, 10% *i*PrOH in hexane, flow rate 1.0 ml/min): t_R major isomer = 24.0 min, t_R minor isomer = 26.5 min.

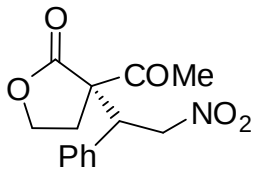
4e



^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 7.1 Hz, 2H), 7.61 (d, *J* = 6.7 Hz, 1H), 7.49 (t, *J* = 6.8 Hz, 2H), 7.30 (s, 5H), 4.93 (d, *J* = 9.7 Hz, 1H), 4.77 (q, *J* = 12.4 Hz, 2H), 4.49 (s, 1H), 3.86 (d, *J* = 3.8 Hz, 2H), 0.89 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 192.77, 166.98, 136.28,

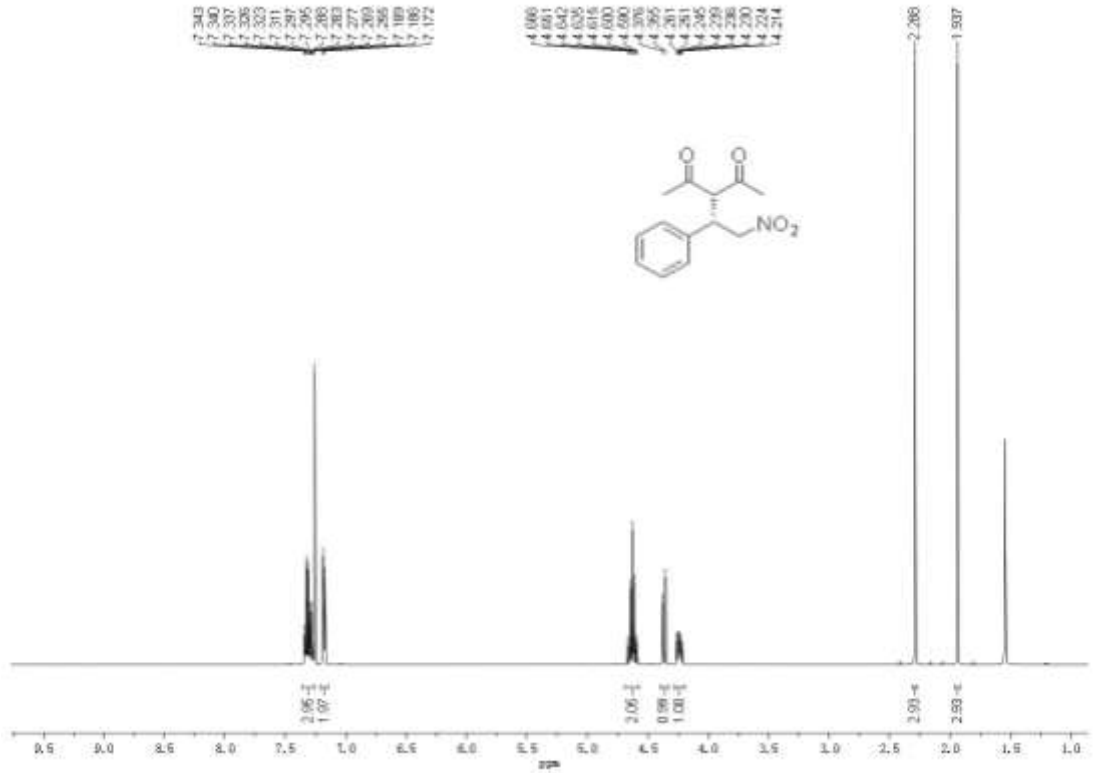
135.85, 134.23, 128.89, 128.30, 77.98, 61.93, 57.04, 43.13, 13.57; HPLC (OD-H, 10% *i*PrOH in hexane, flow rate 1.0 ml/min): dr=1.7:1, major diastereomer: t_R major isomer = 19.6 min, t_R minor isomer = 17.0 min, minor diastereomer: t_R major isomer = 21.9 min, t_R minor isomer = 38.1 min.

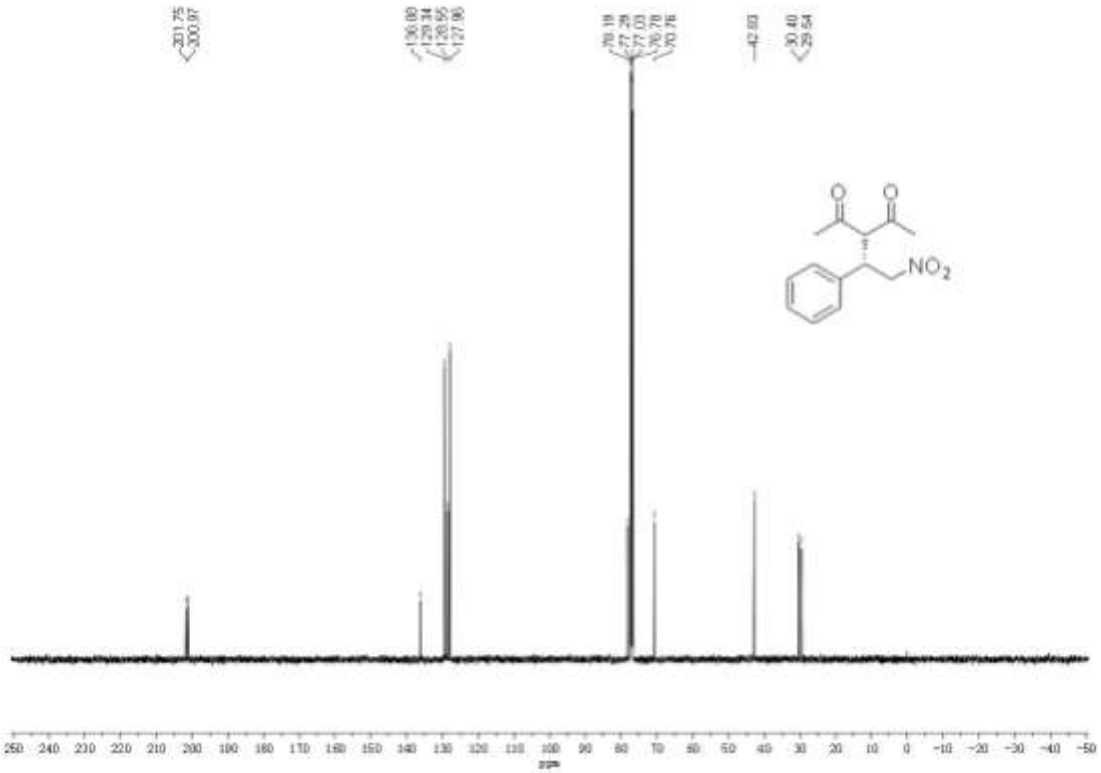
4f



^{1}H NMR (500 MHz, DMSO): δ = 7.47 (d, *J* = 7.0 Hz, 1H), 7.35 (dd, *J* = 14.2, 6.7 Hz, 4H), 5.22 (t, *J* = 12.4 Hz, 1H), 5.00-4.89 (m, 1H), 4.41-4.31 (m, 1H), 4.10 (dd, *J* = 15.9, 8.2 Hz, 0.5H), 4.01 (dd, *J* = 16.5, 8.1 Hz, 0.5H), 3.73 (dt, *J* = 8.6, 5.0 Hz, 1H), 2.80 (ddd, *J* = 13.5, 8.1, 5.1 Hz, 0.5H), 2.64-2.57 (m, 0.5H), 2.56-2.46 (m, 1H), 2.38 (s, 2H), 2.34 (s, 2H); ^{13}C NMR (126 MHz, DMSO): δ = 201.64, 201.55, 174.52, 173.33, 134.85, 134.64, 129.26, 128.86, 128.74, 128.57, 128.47, 128.32, 76.63, 75.13, 66.15, 66.07, 64.01, 63.71, 45.44, 45.14, 28.08, 26.08, 26.01, 25.45; HPLC (OD-H, 20% EtOH in hexane, flow rate 1.0 ml/min): dr=5.3:1, major diastereomer: t_R major isomer = 13.2 min, t_R minor isomer = 19.9 min, minor diastereomer: t_R major isomer = 17.6 min, t_R minor isomer = 44.7 min.

3a





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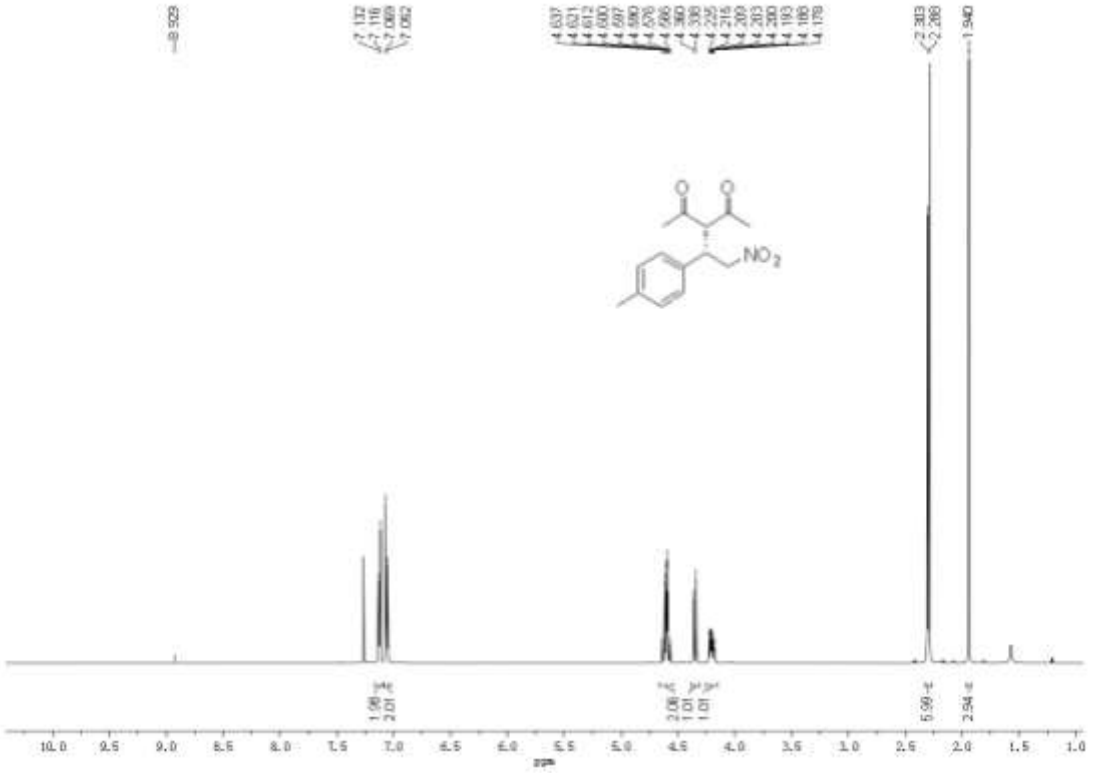

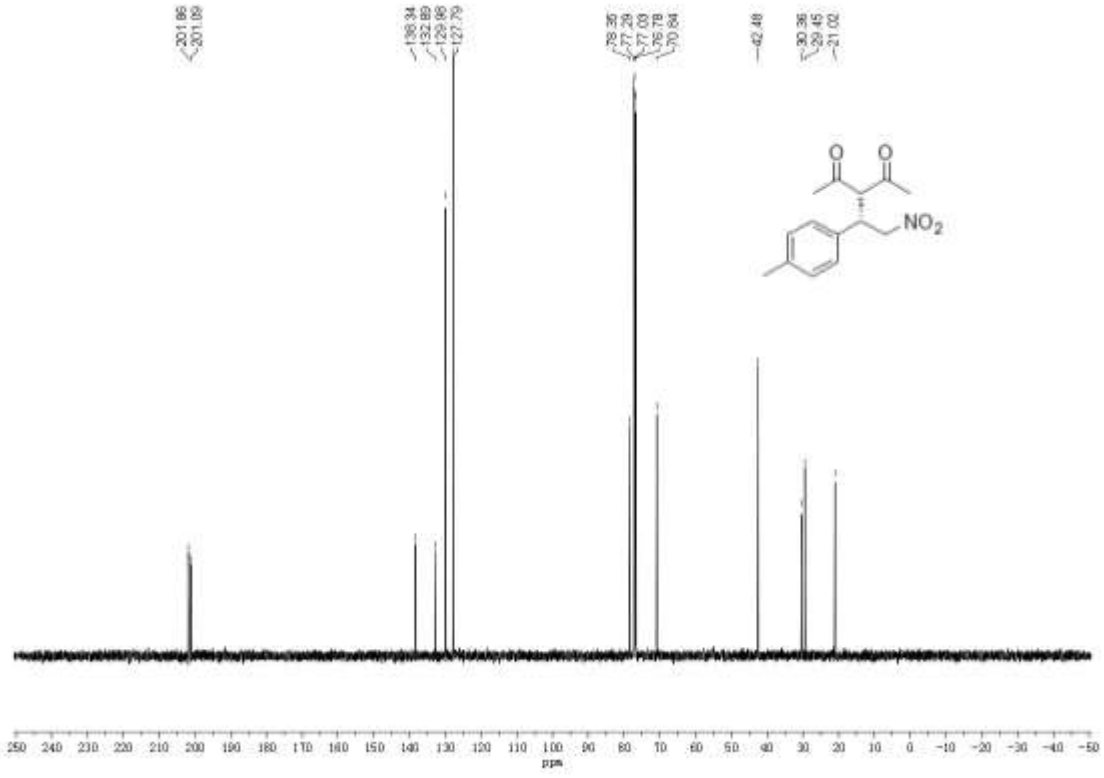

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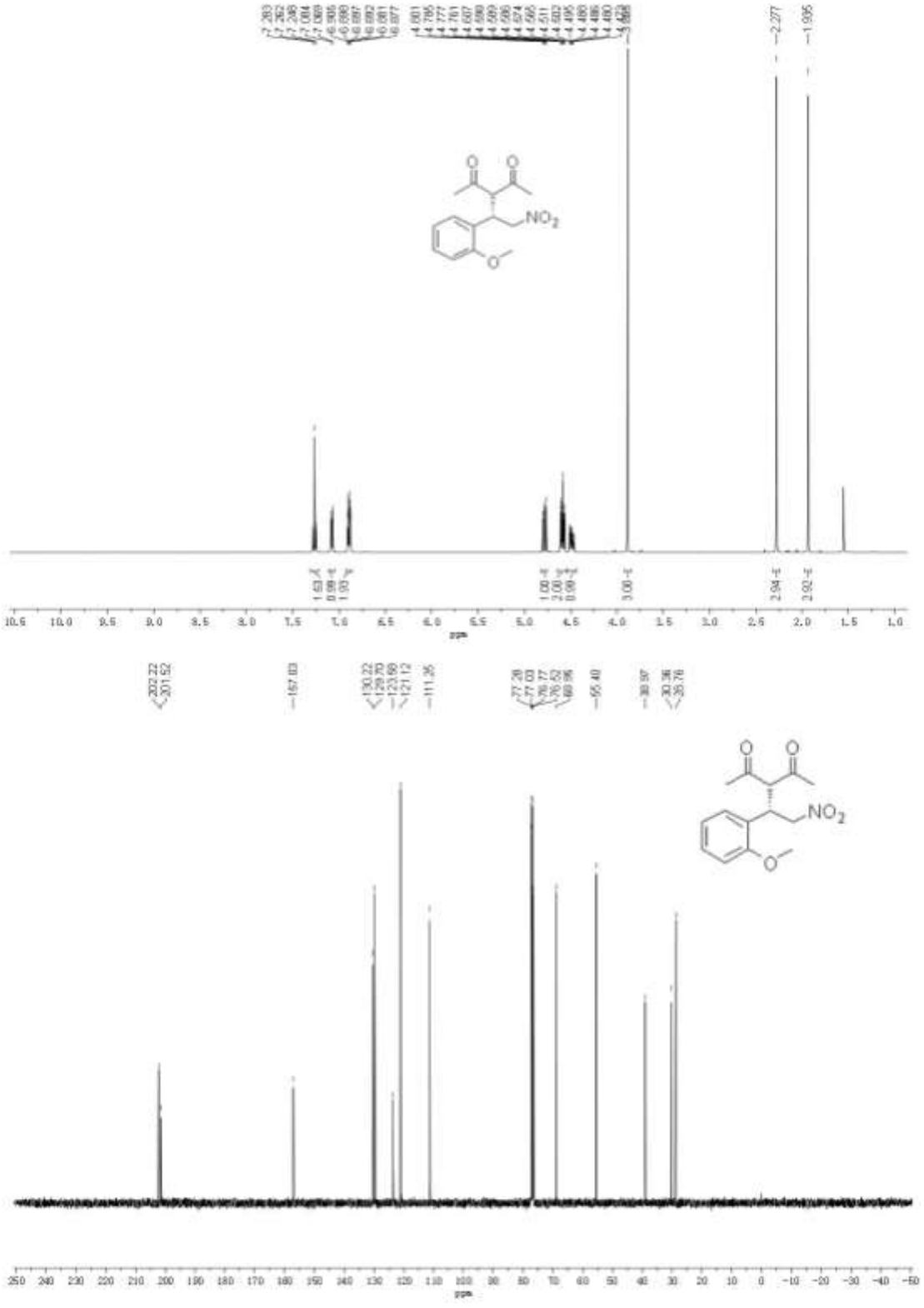

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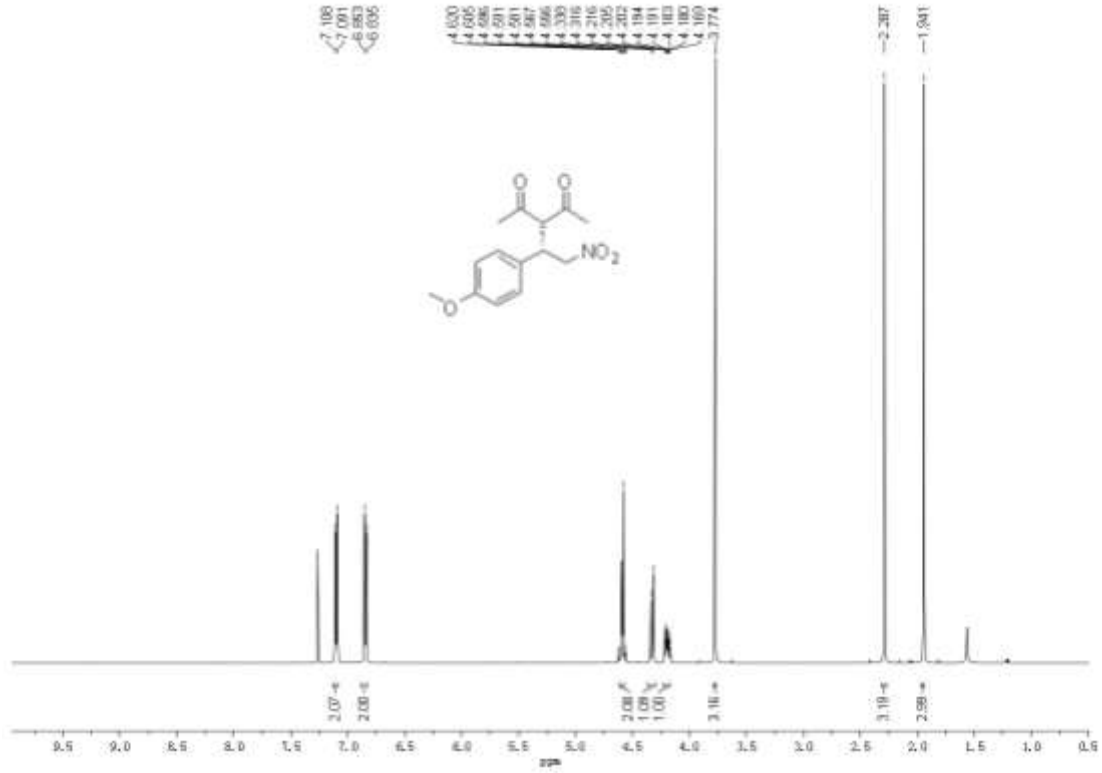

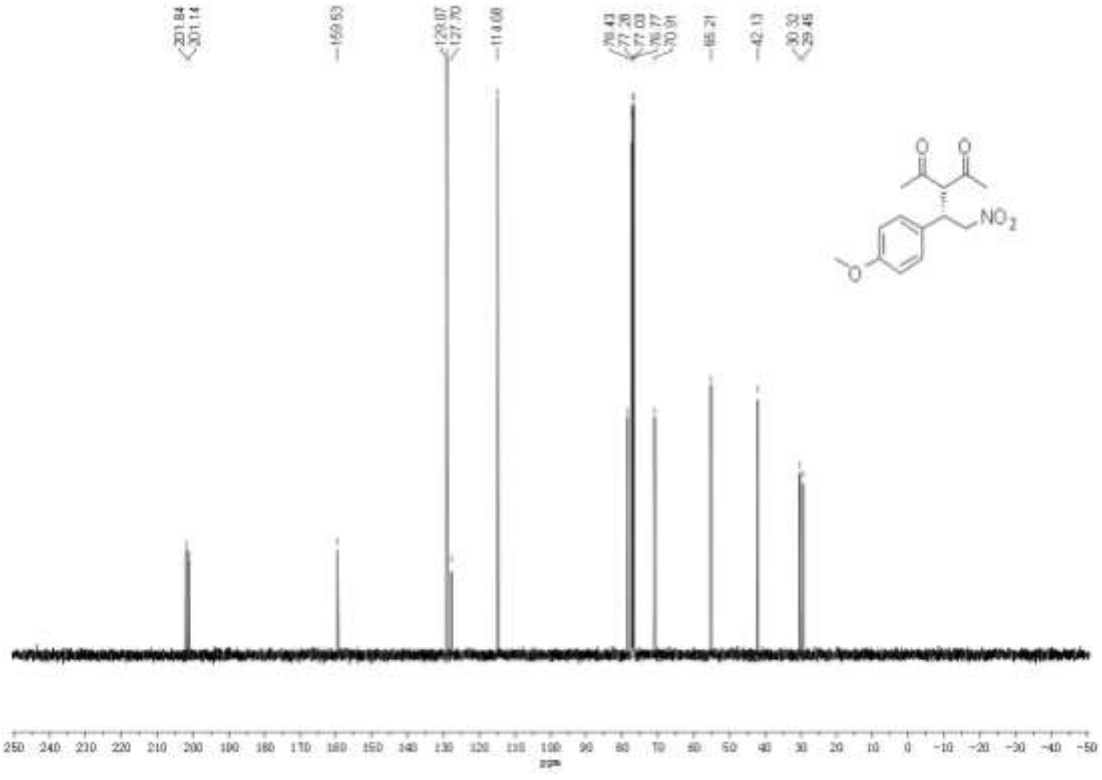

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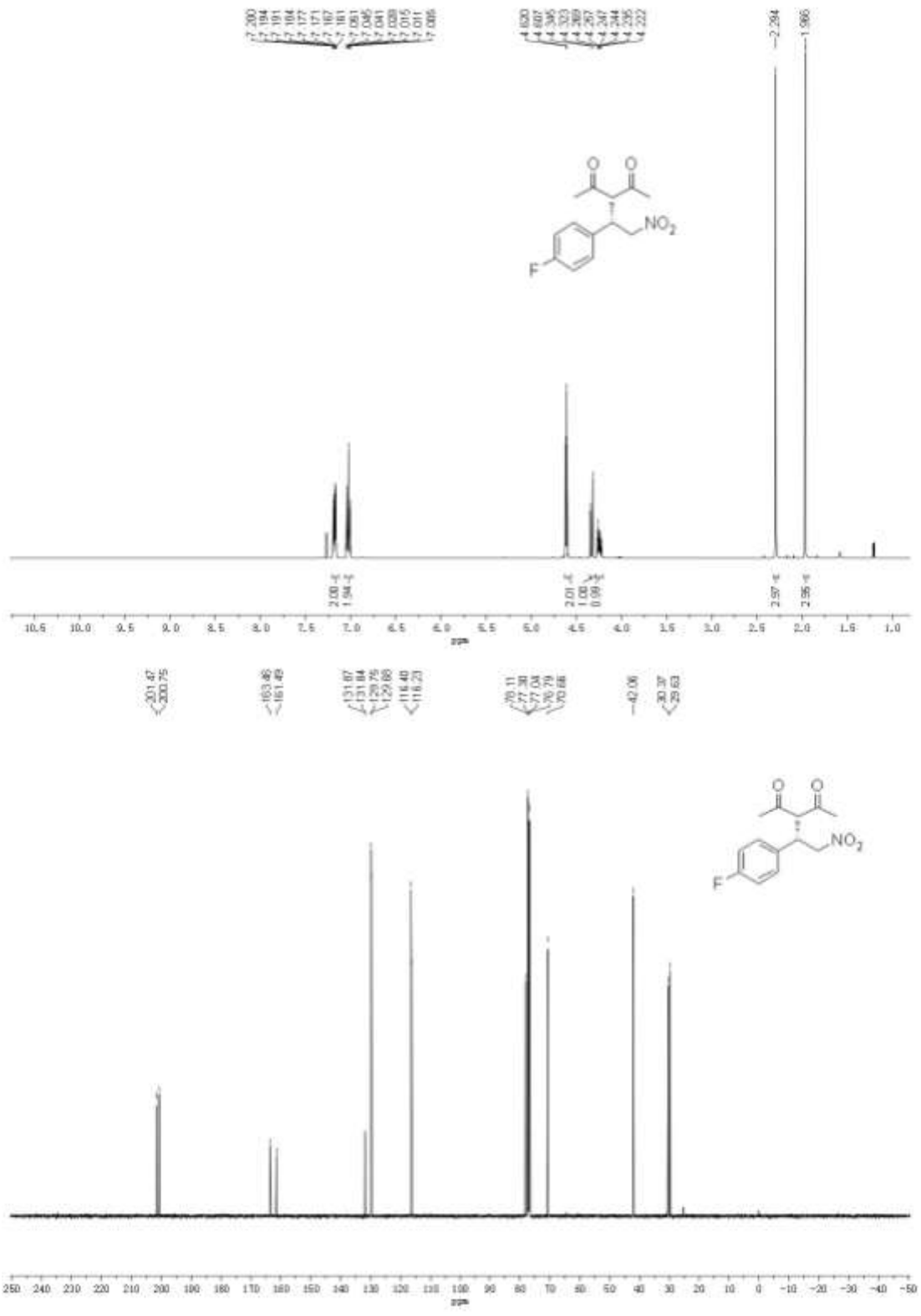

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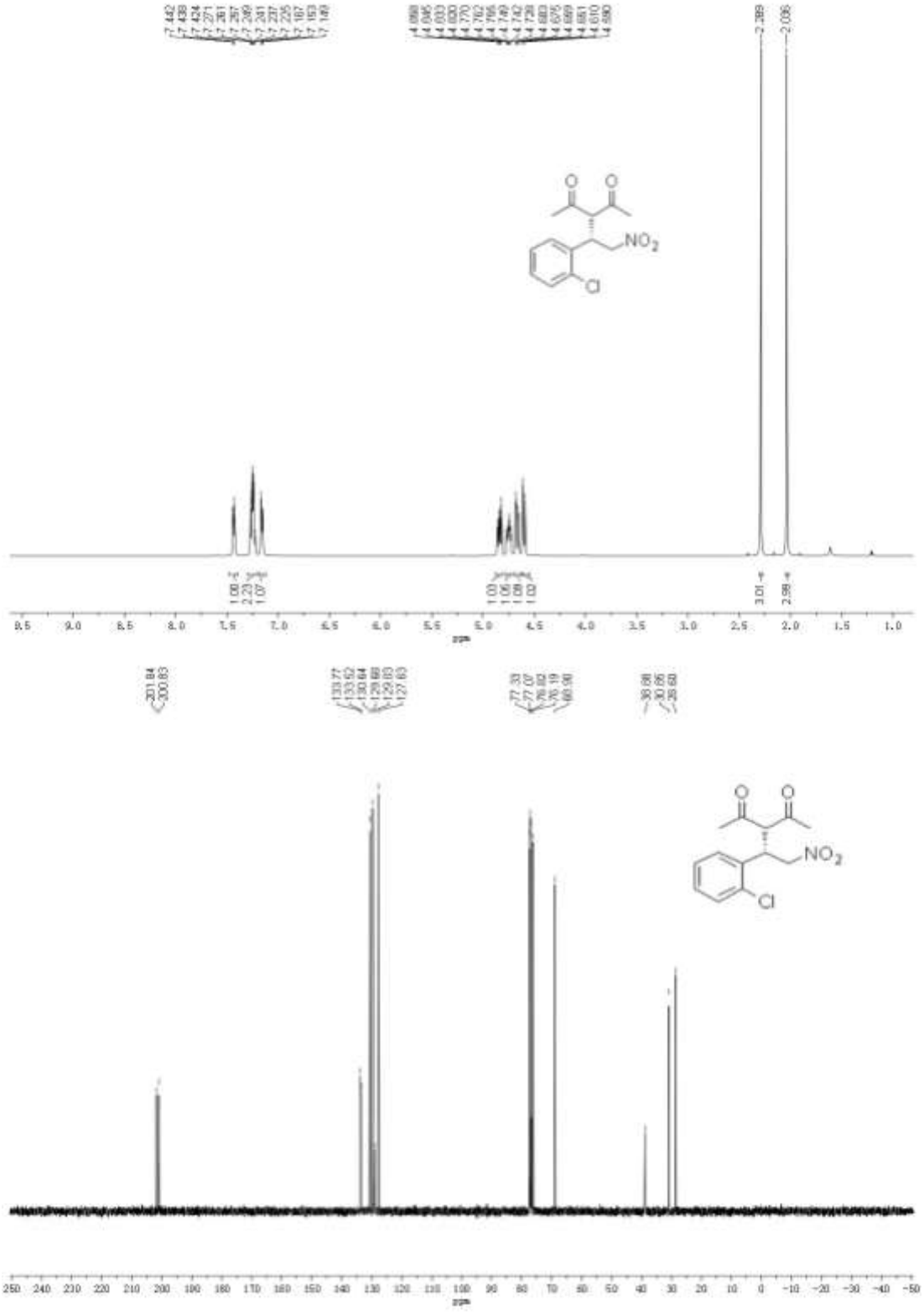

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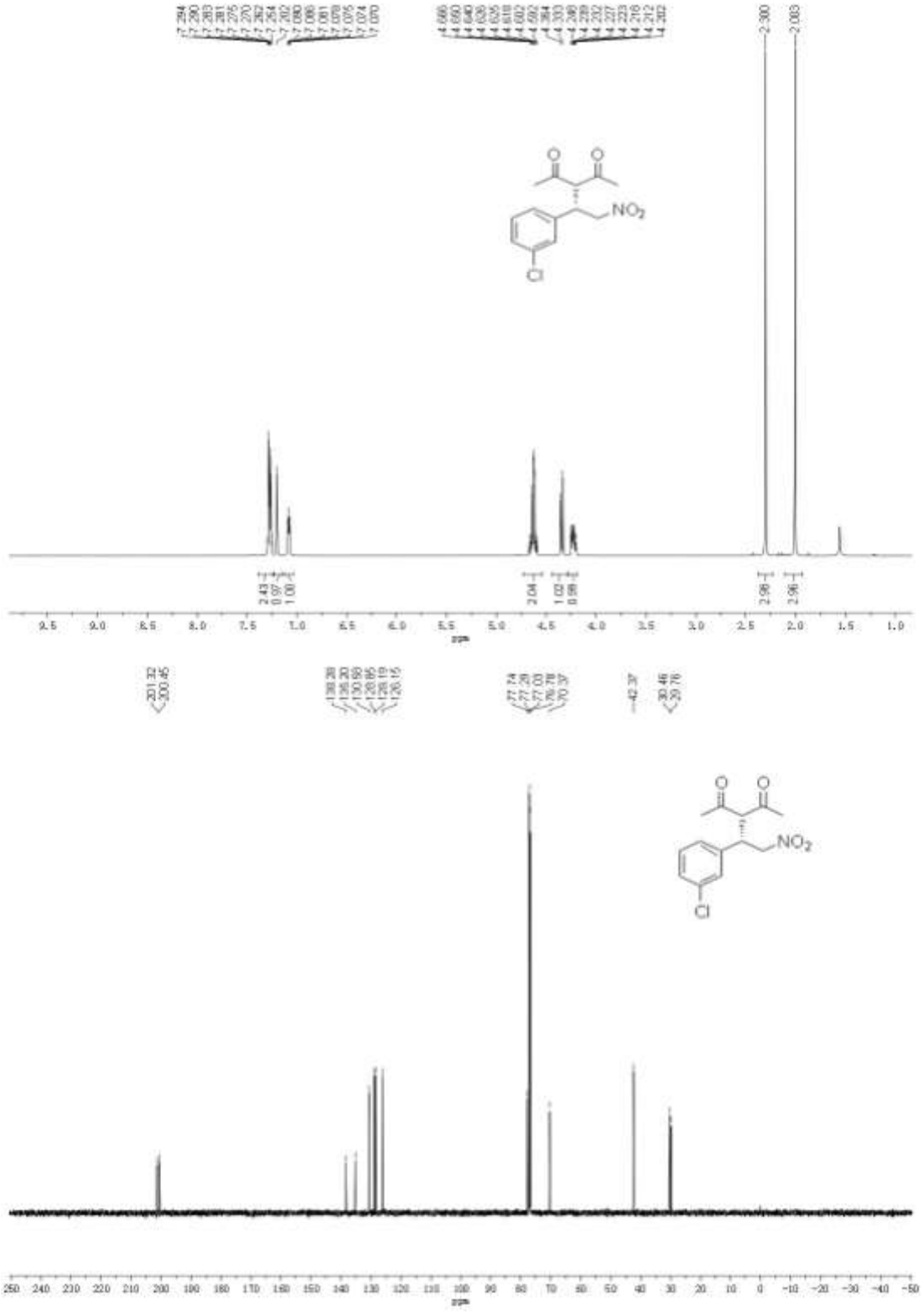

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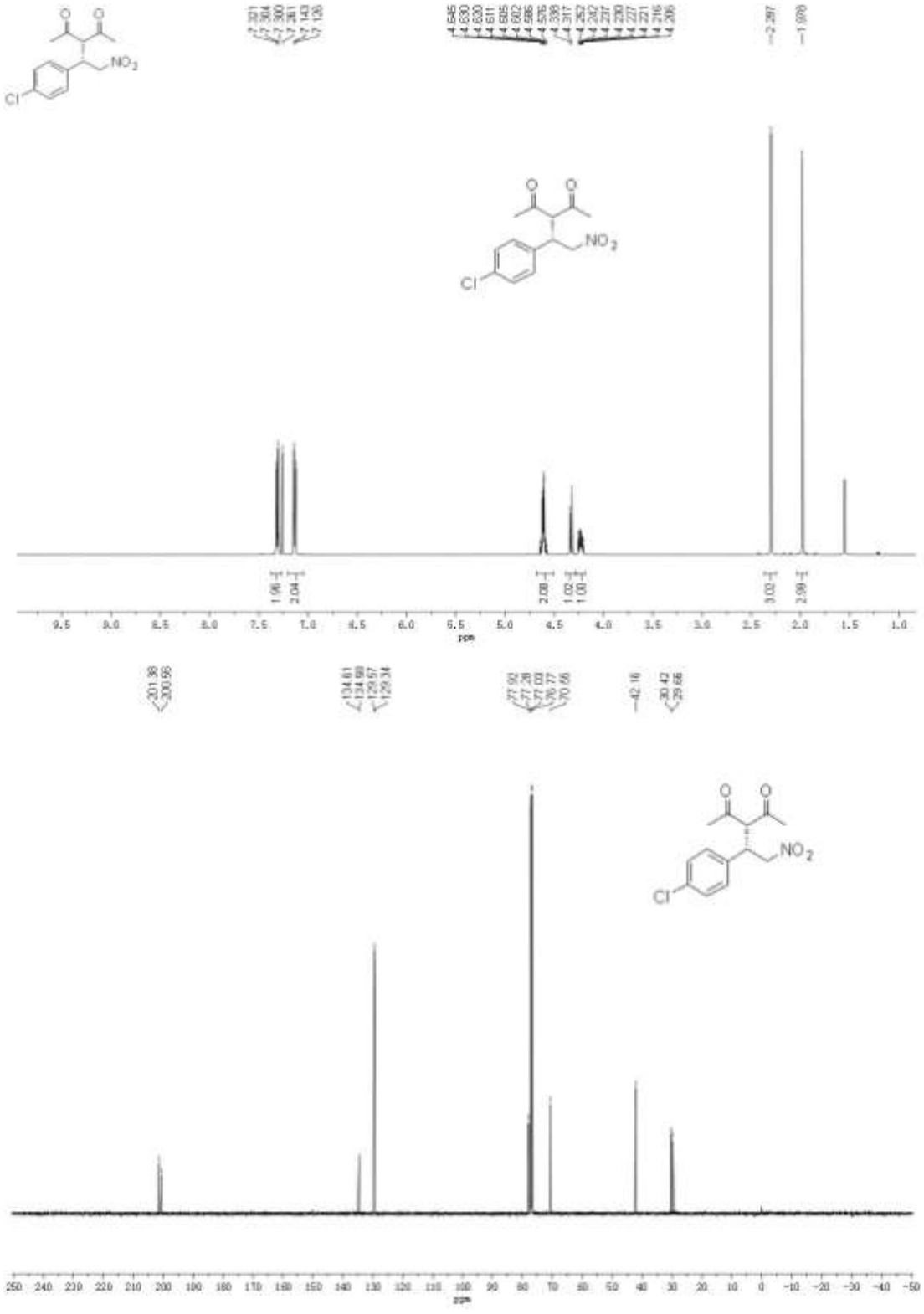

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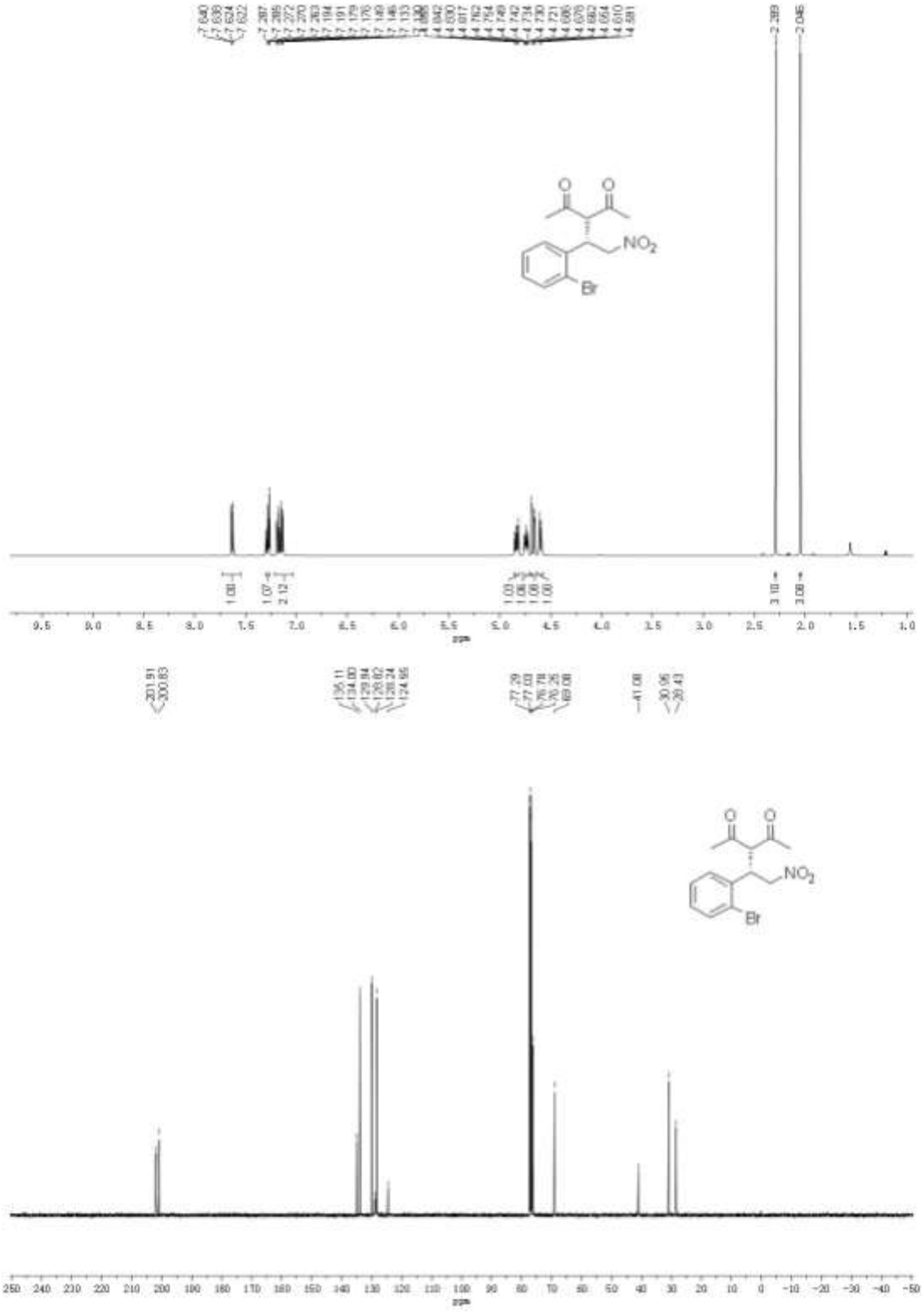

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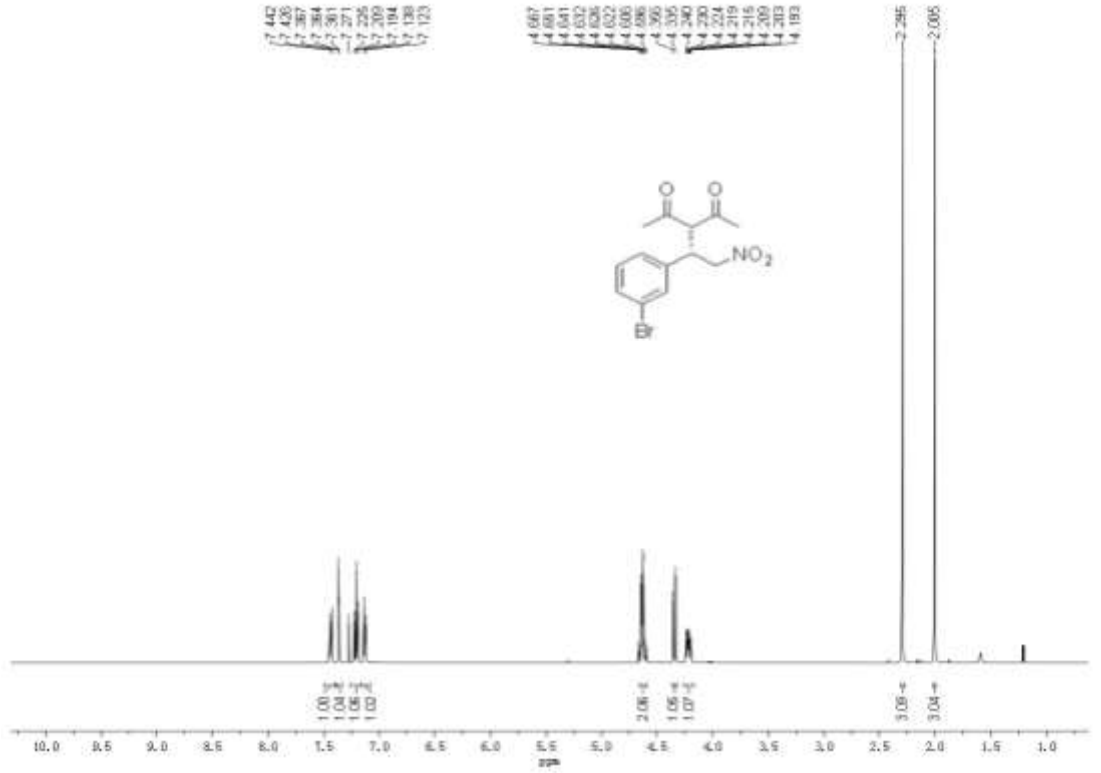

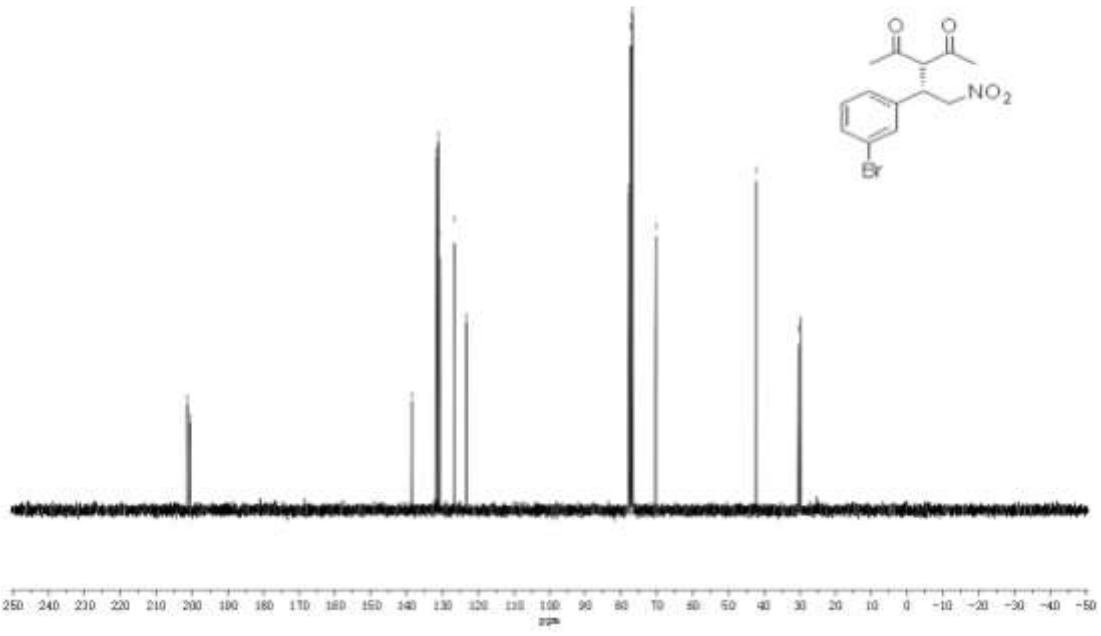

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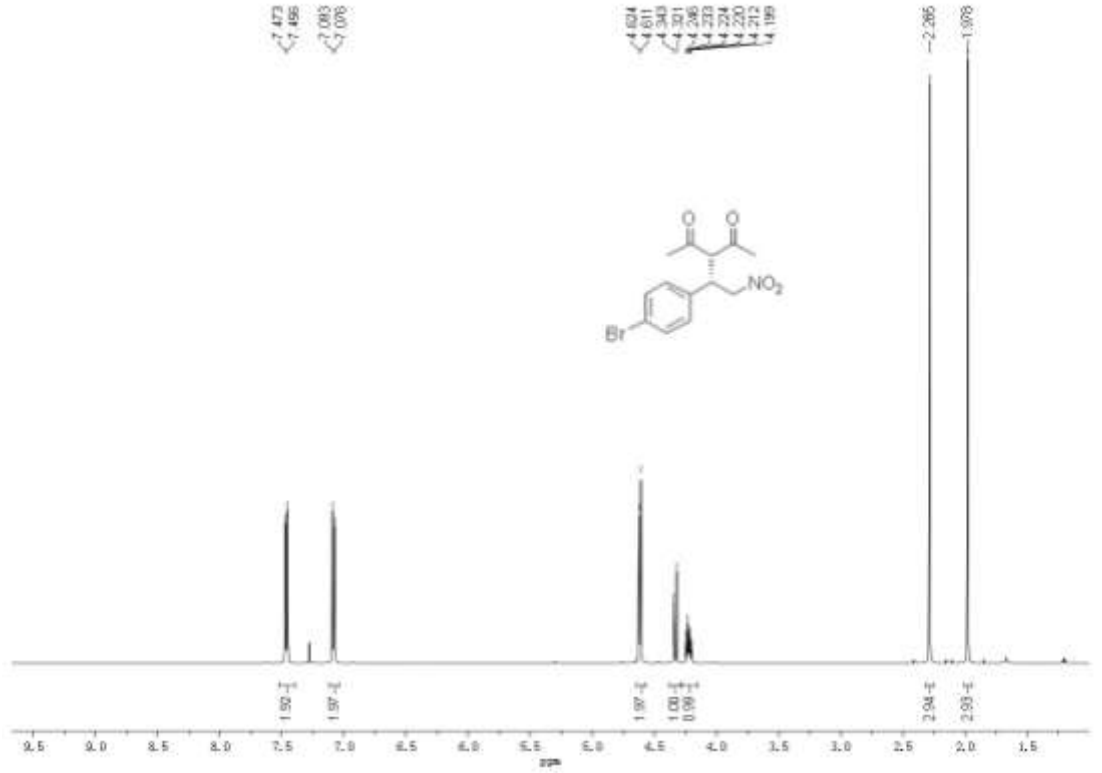

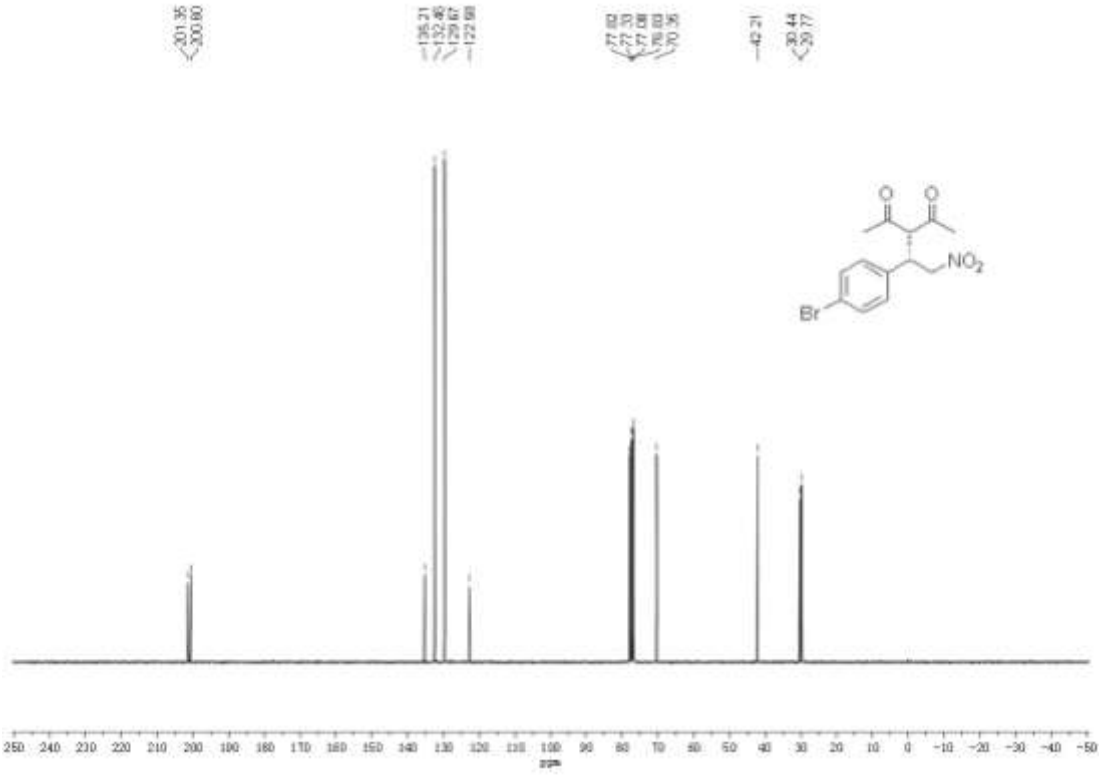

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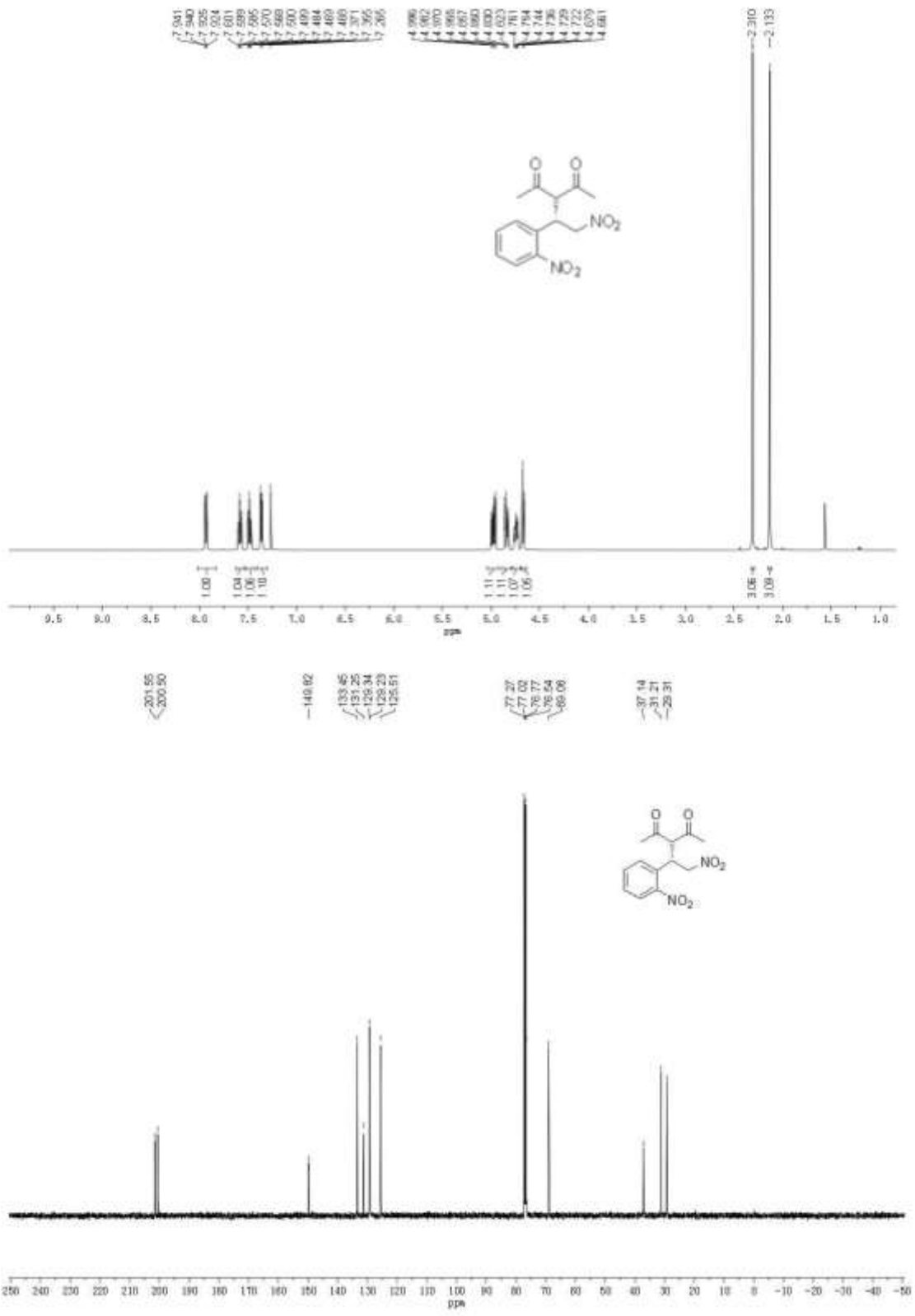

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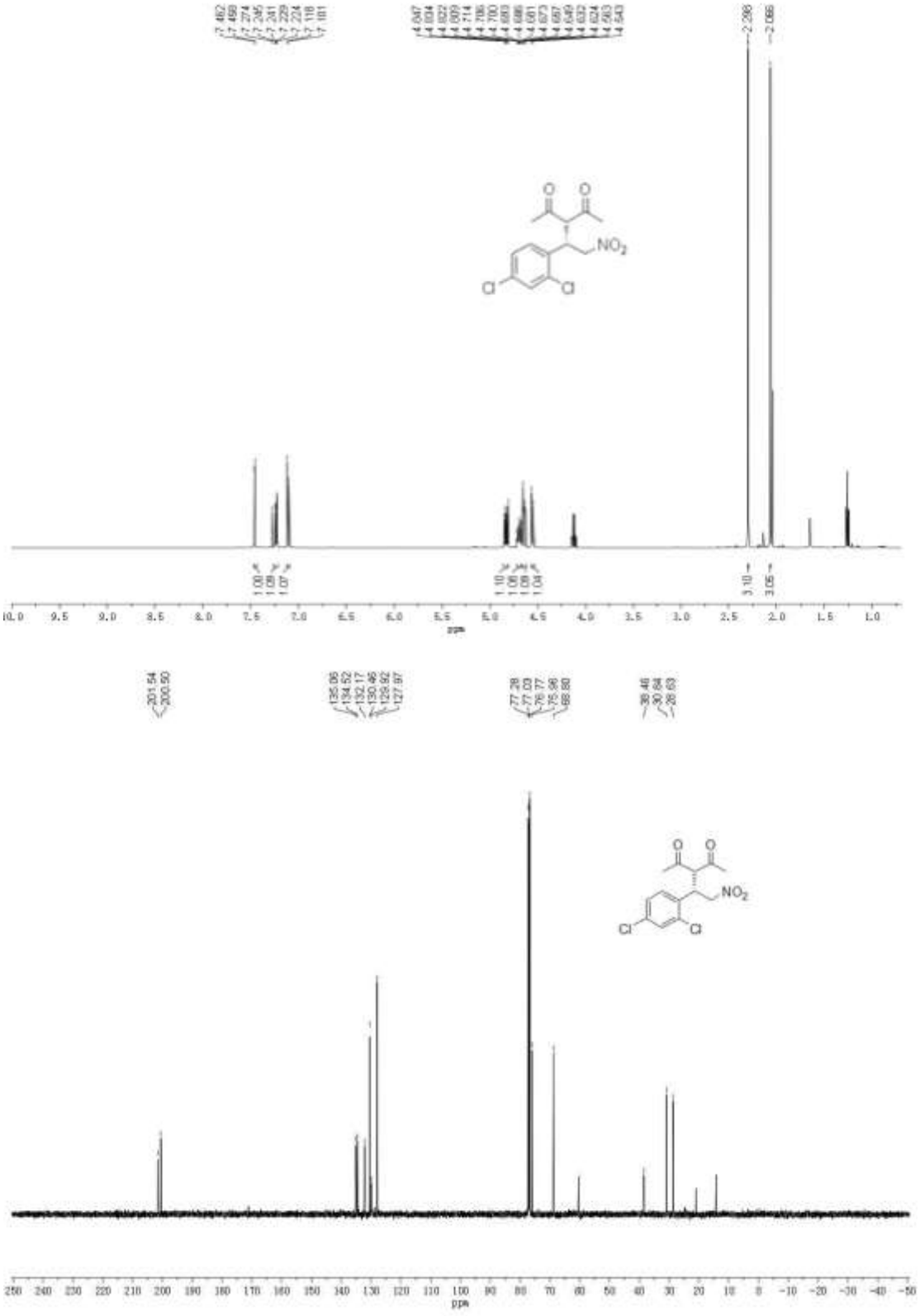

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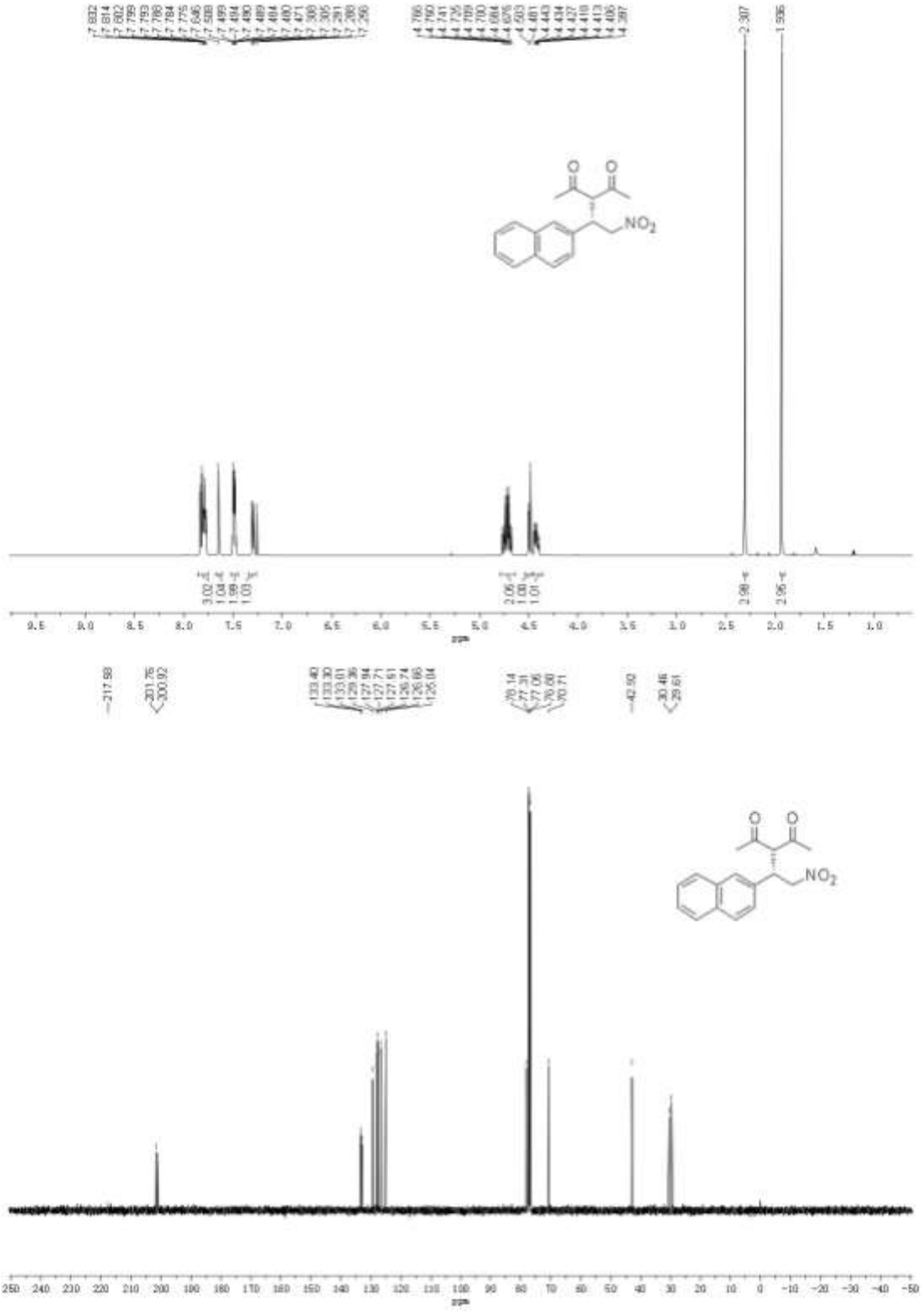

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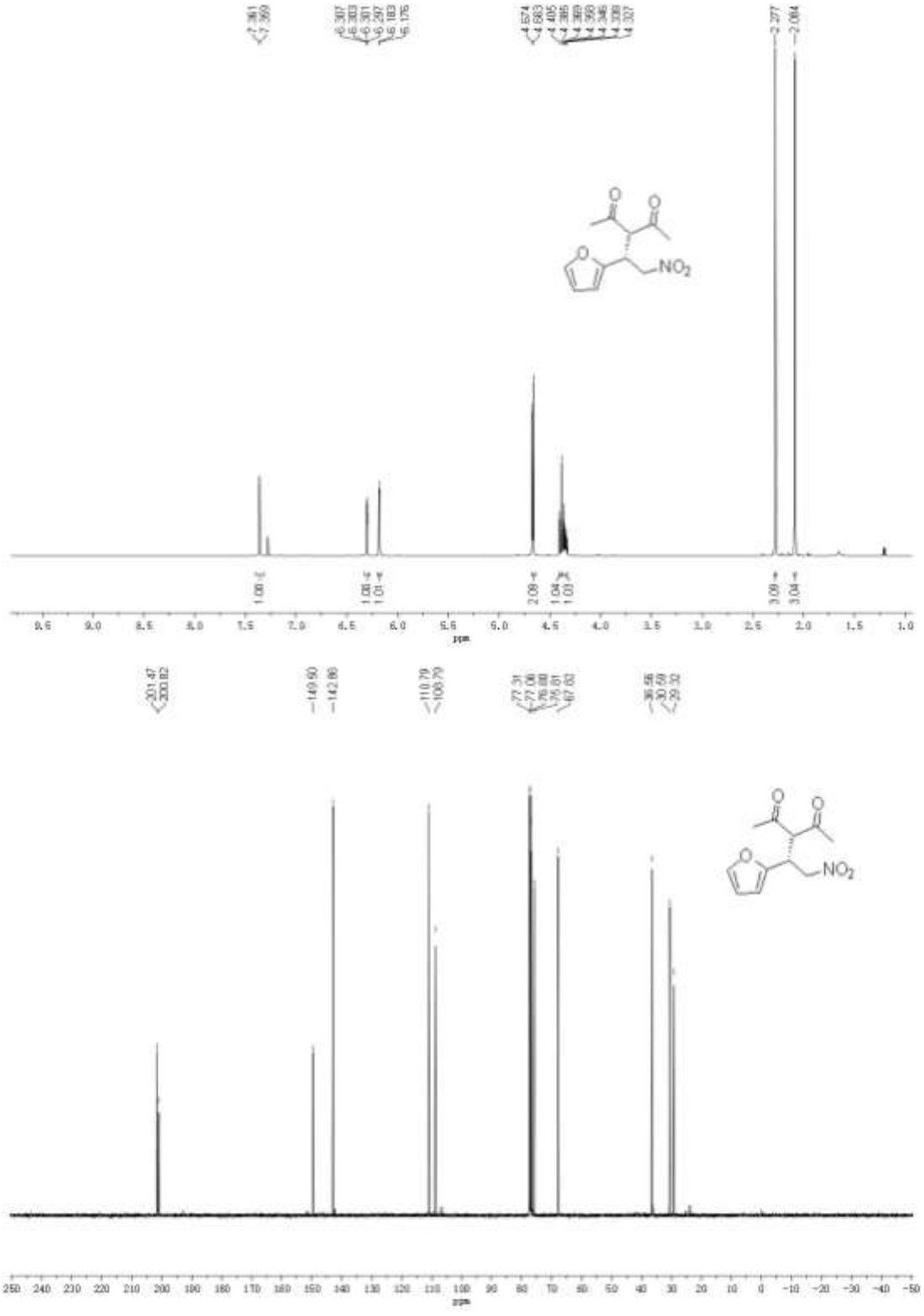

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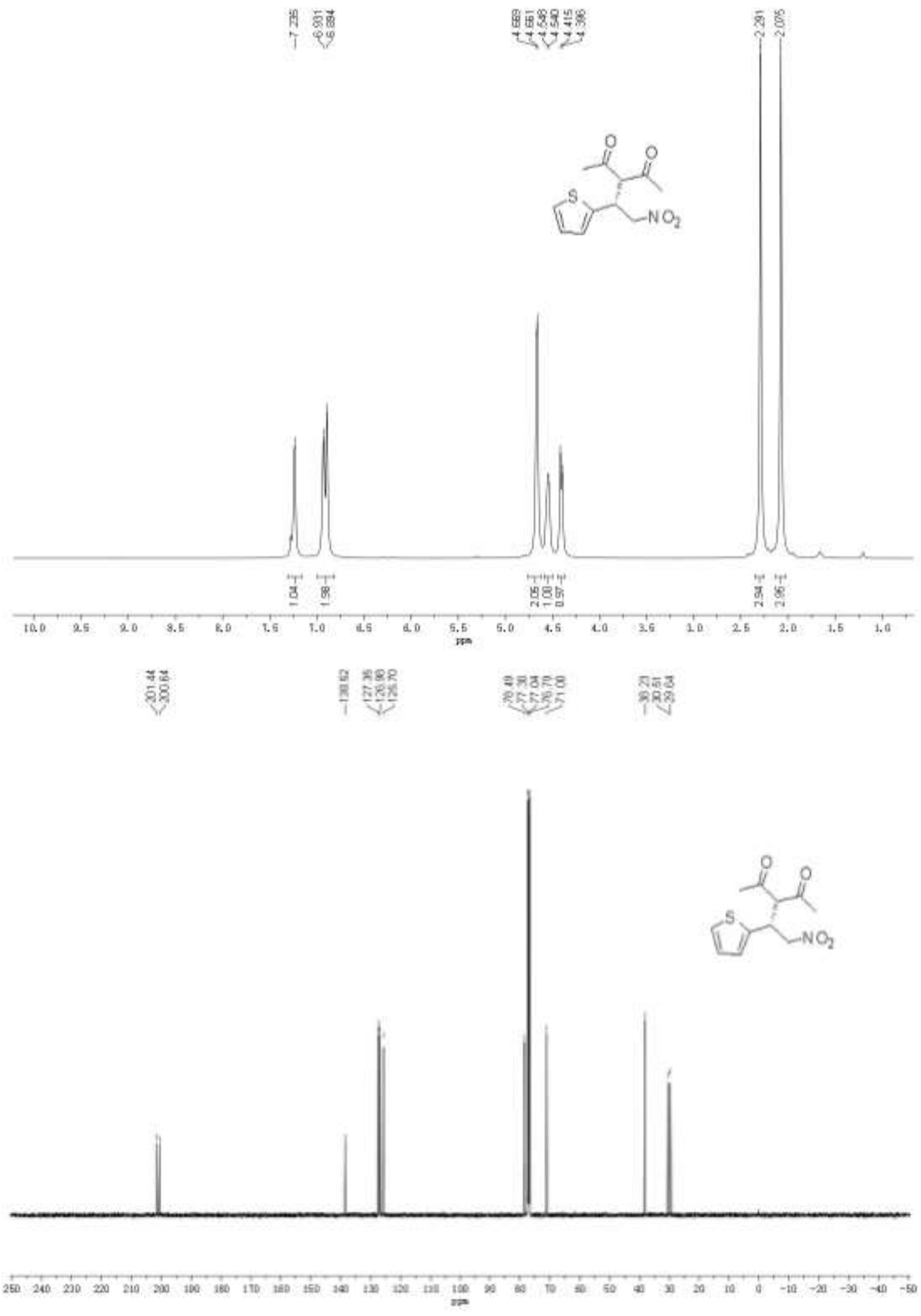
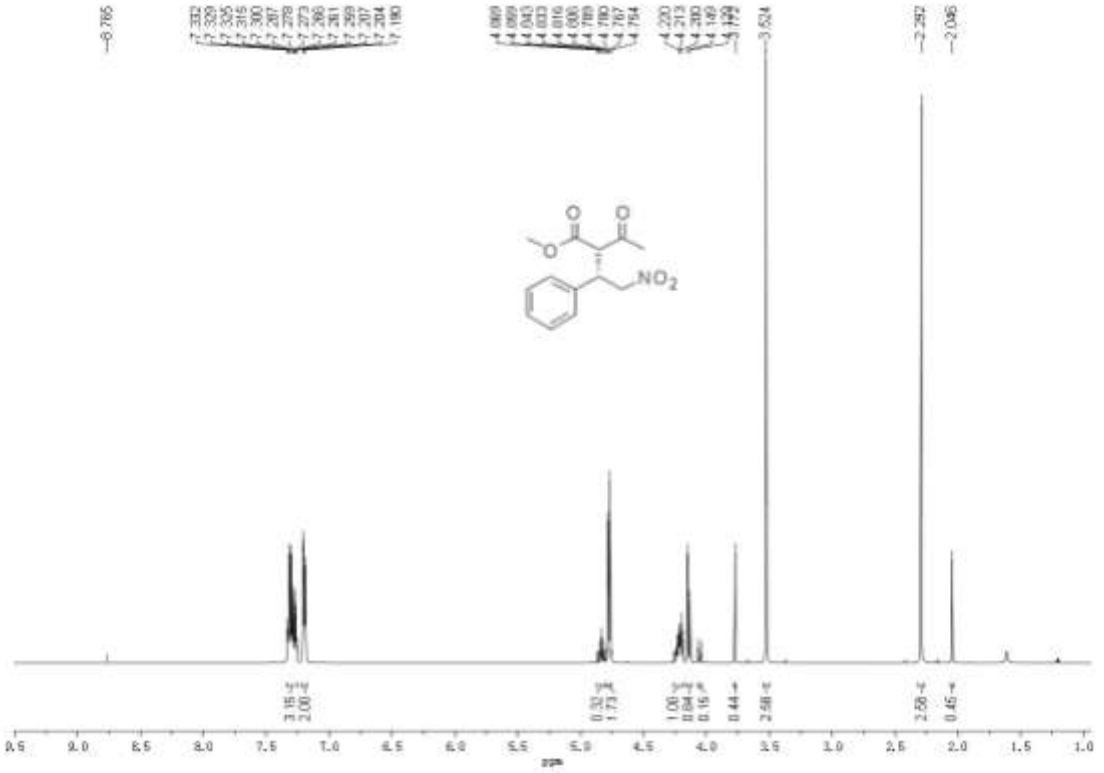
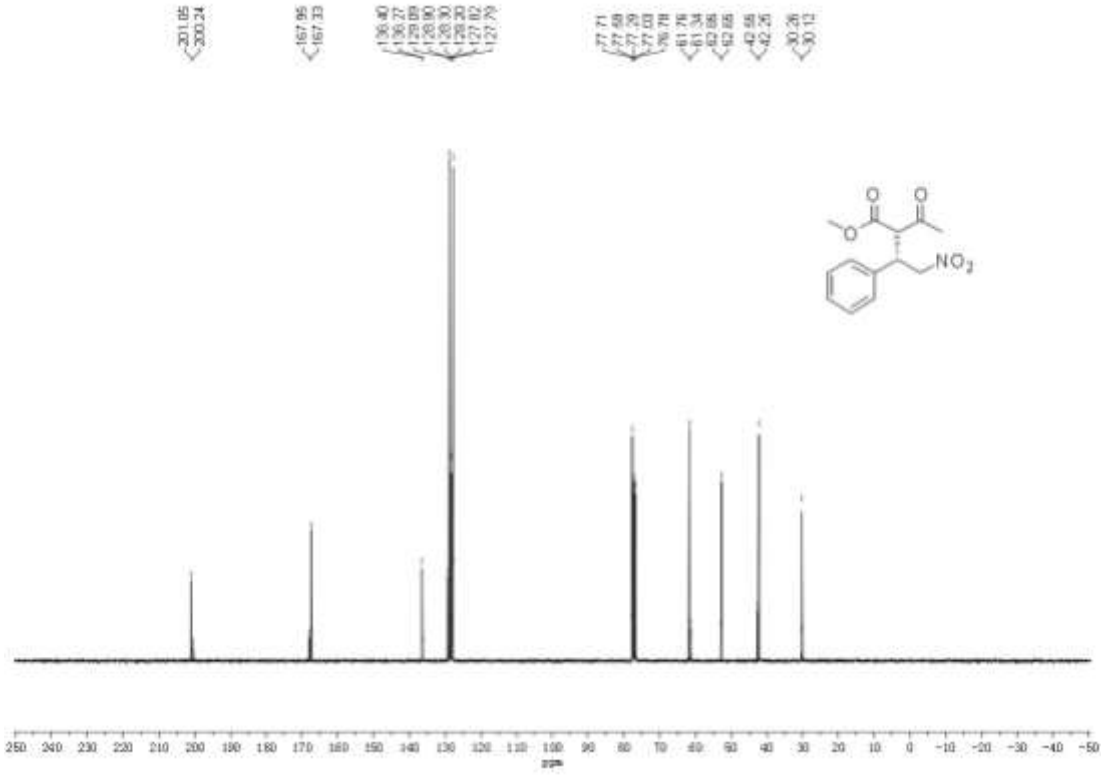


4a





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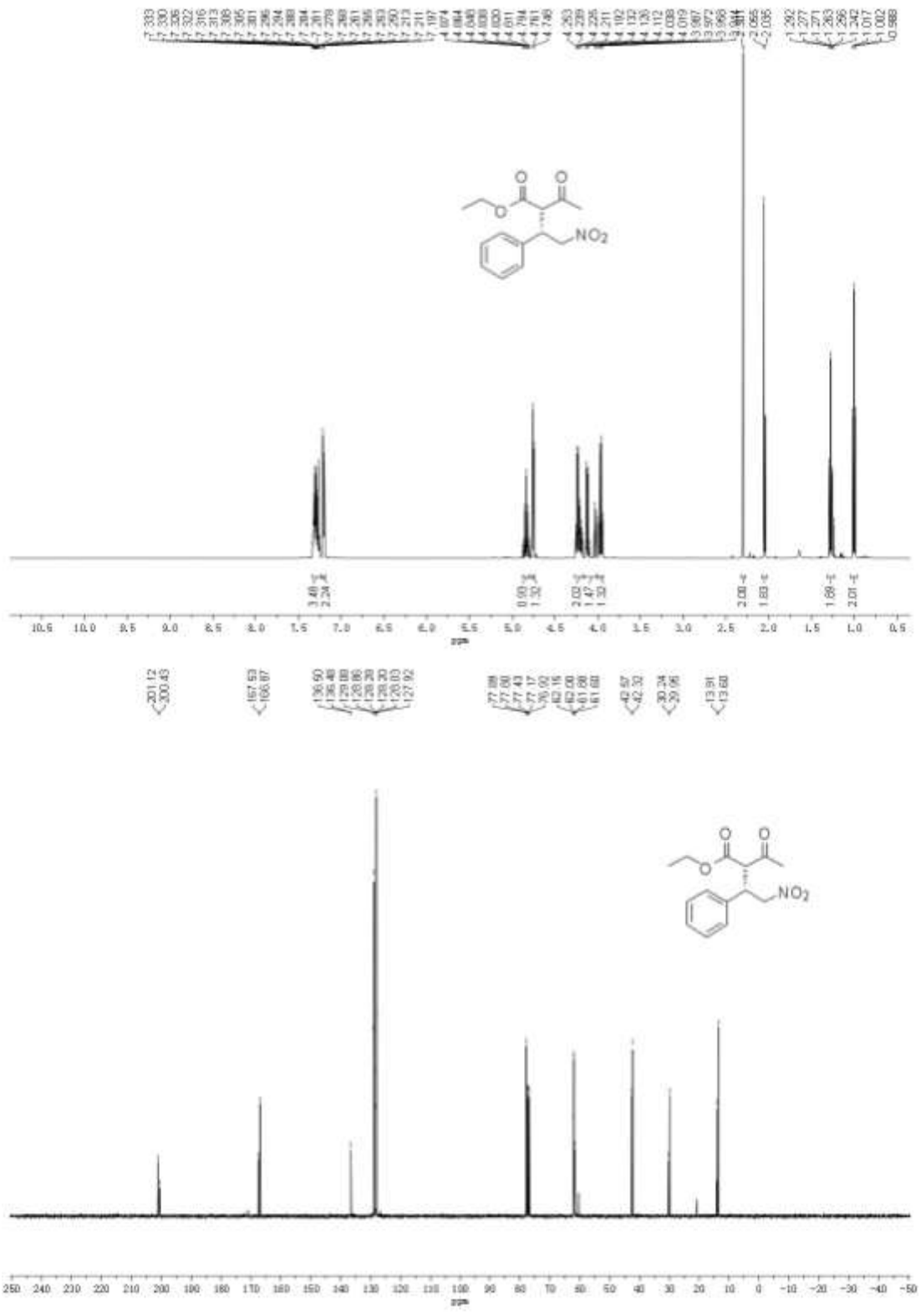

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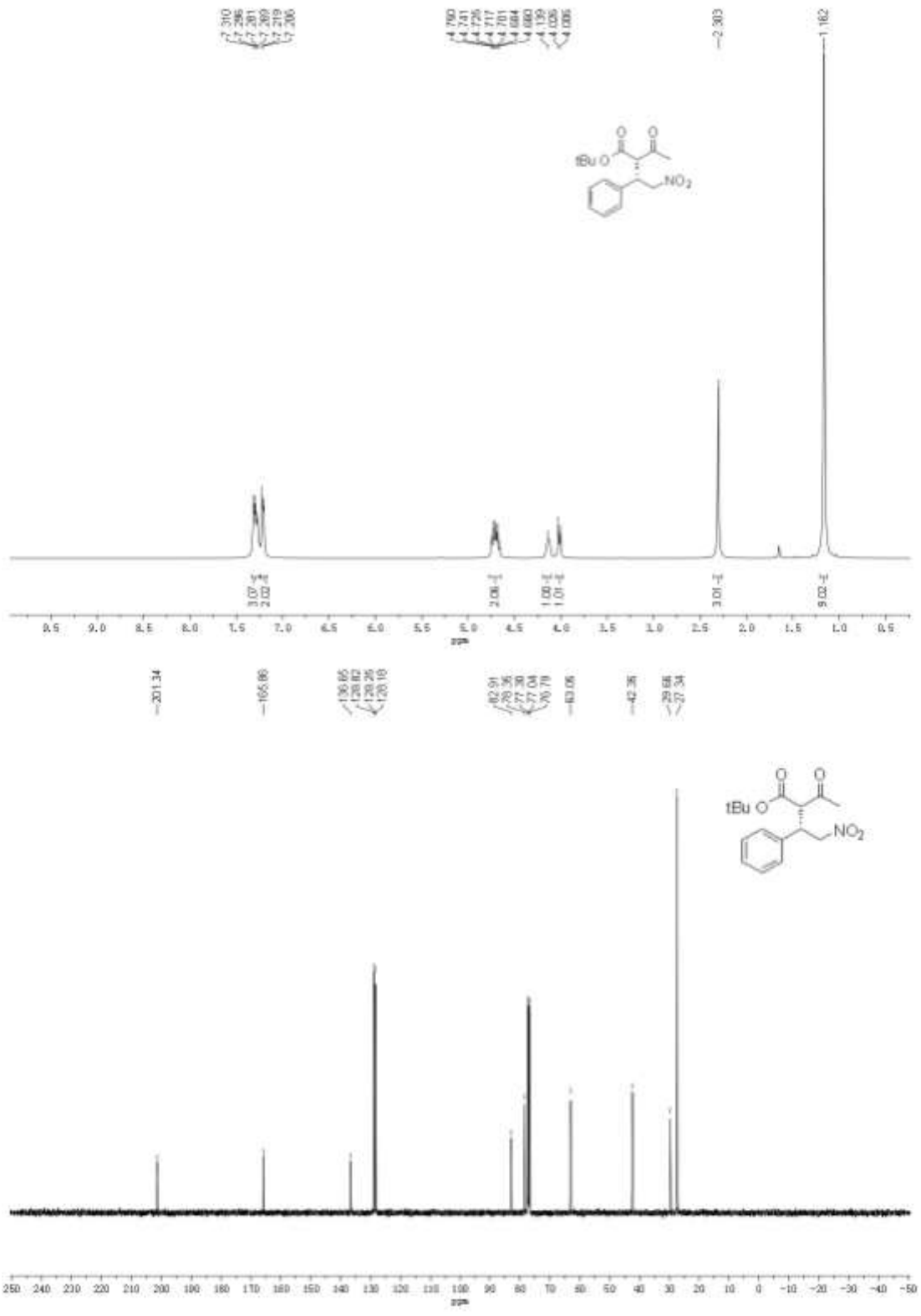
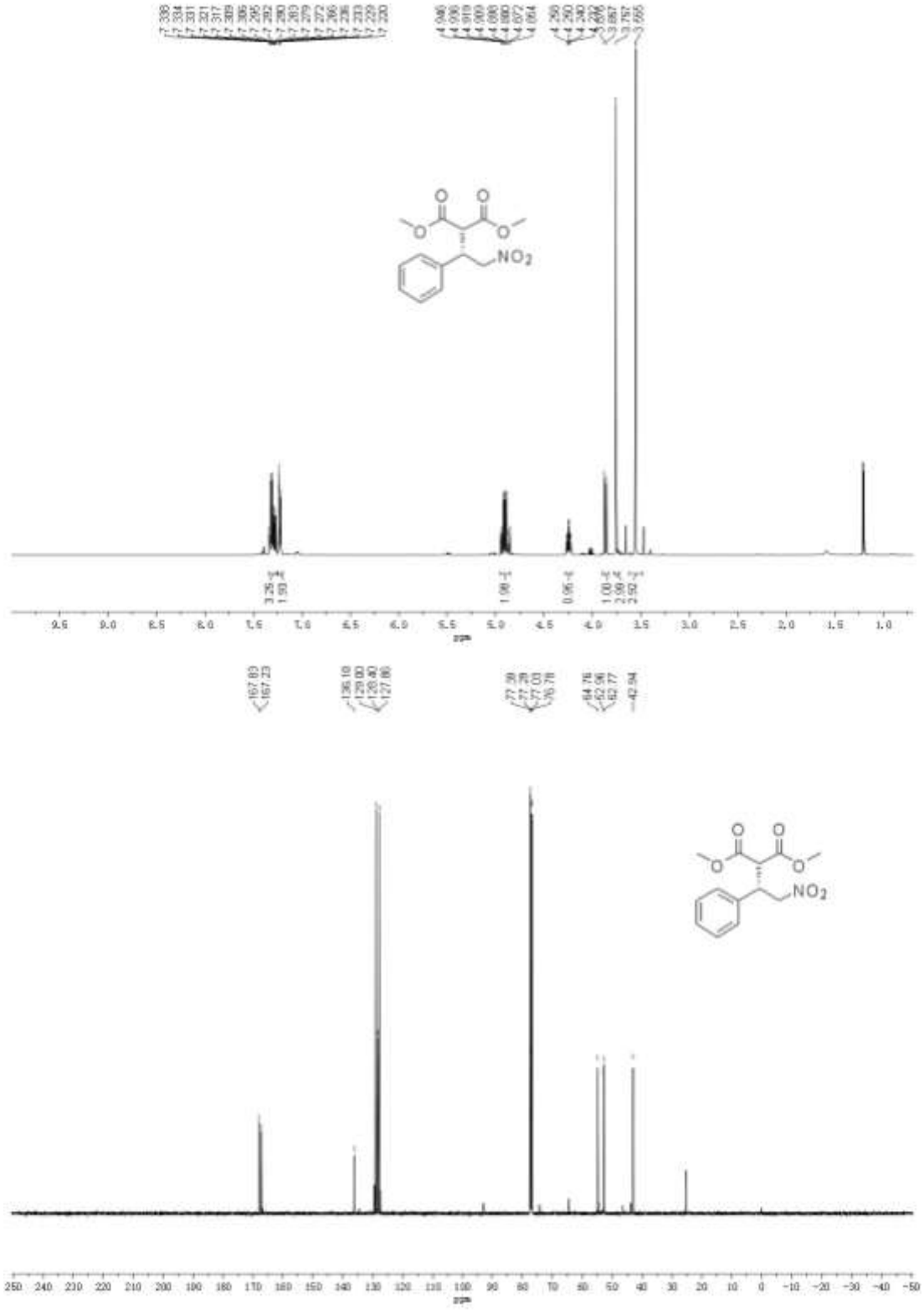


4d



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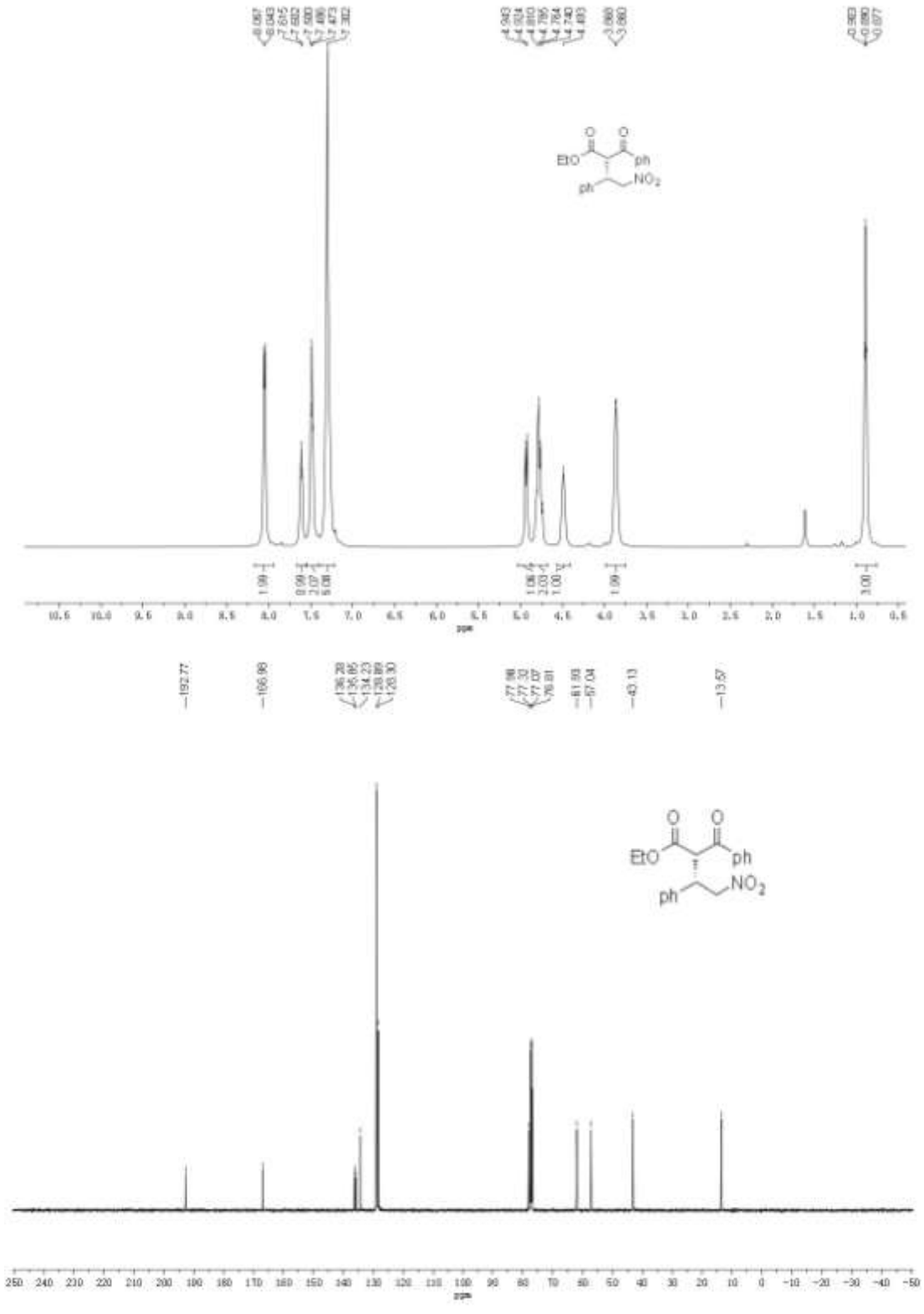

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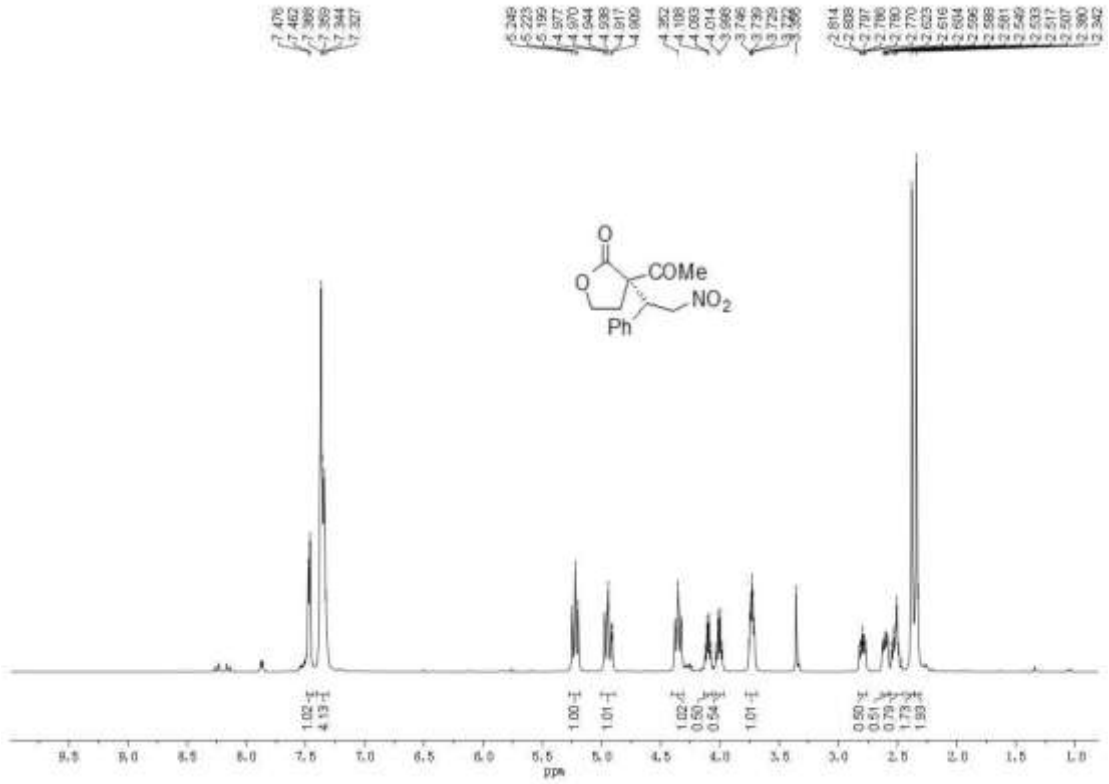
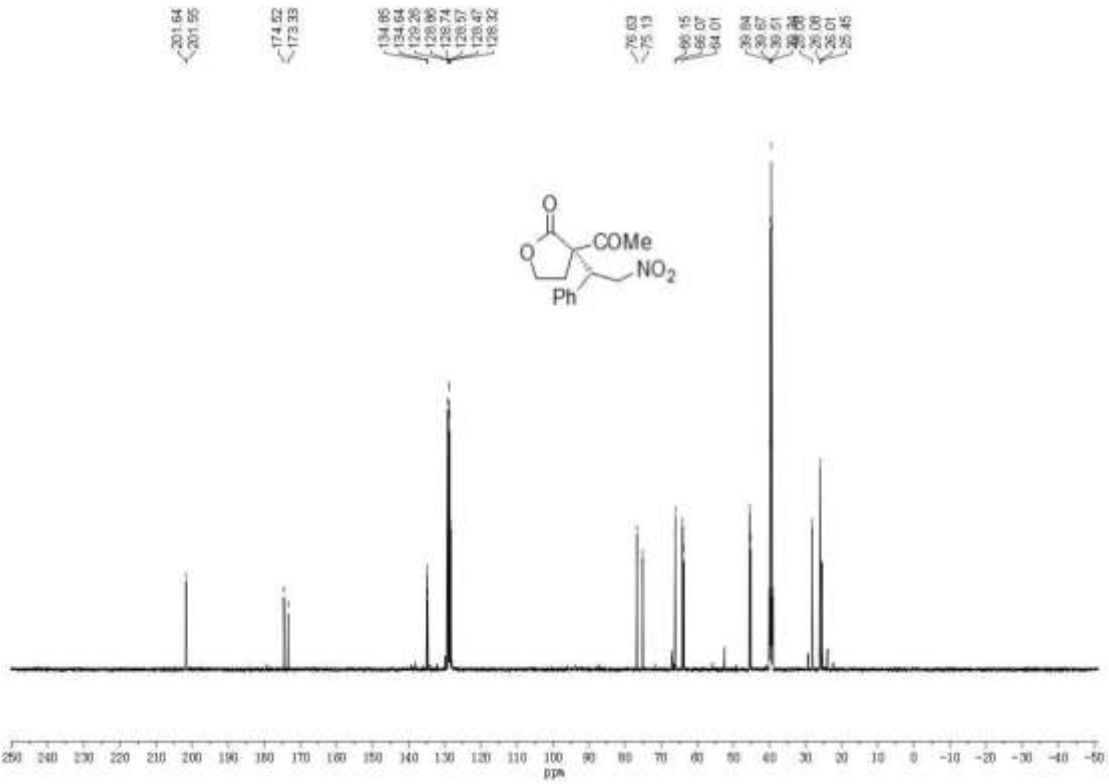
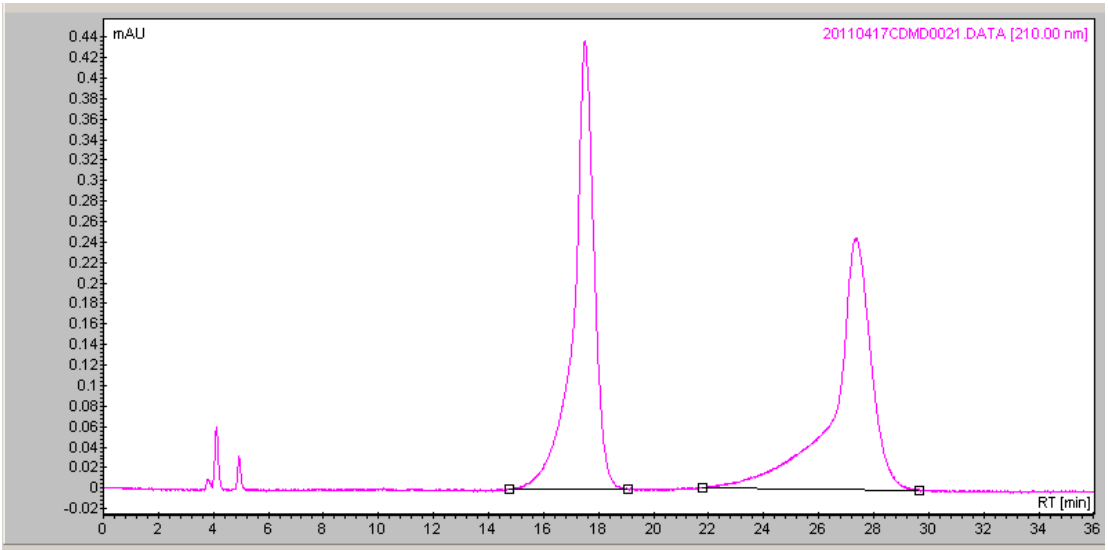




3a



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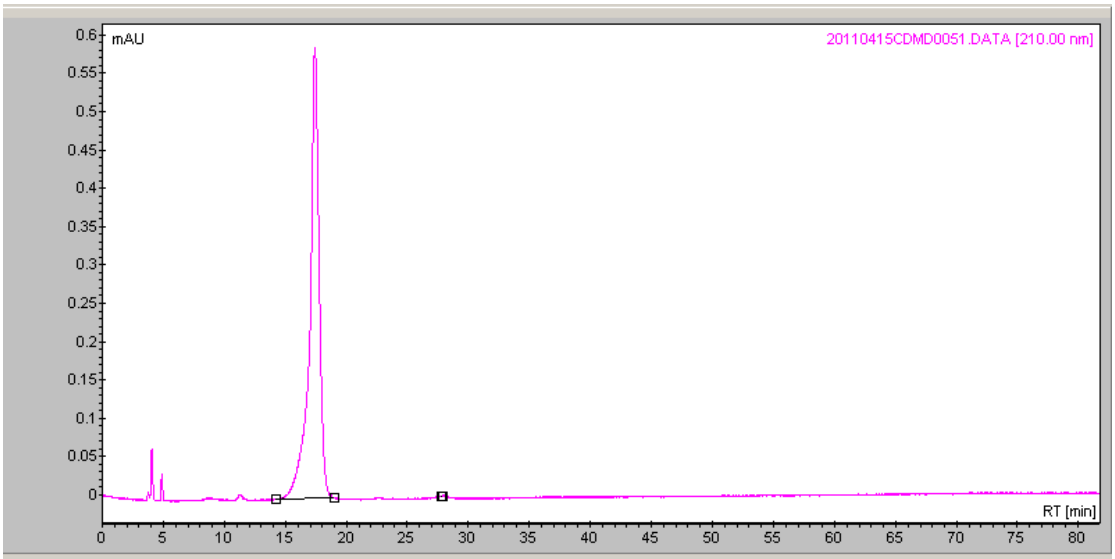

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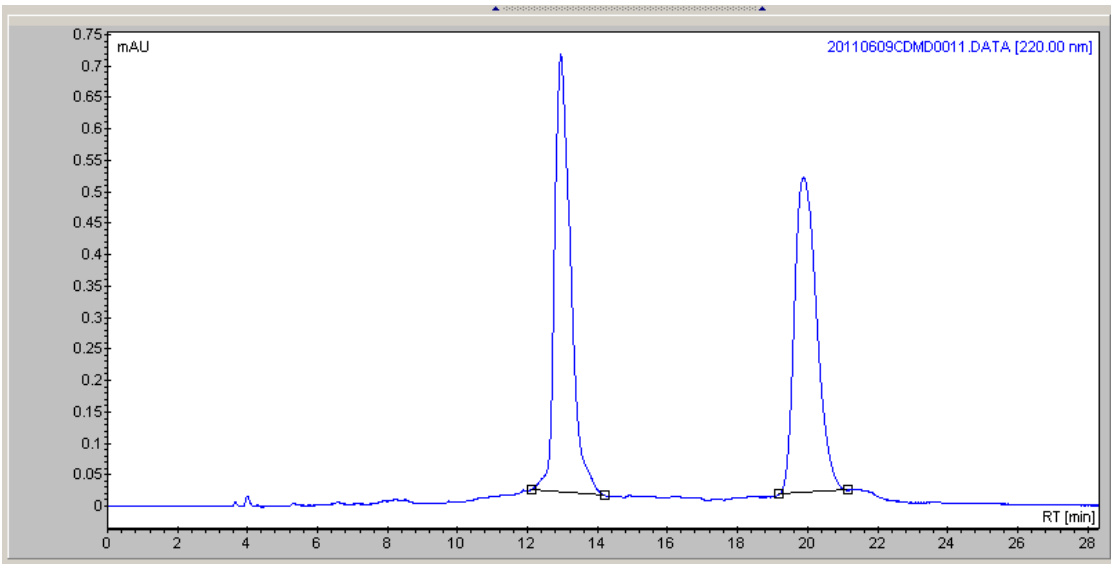
Total			100.000

3b



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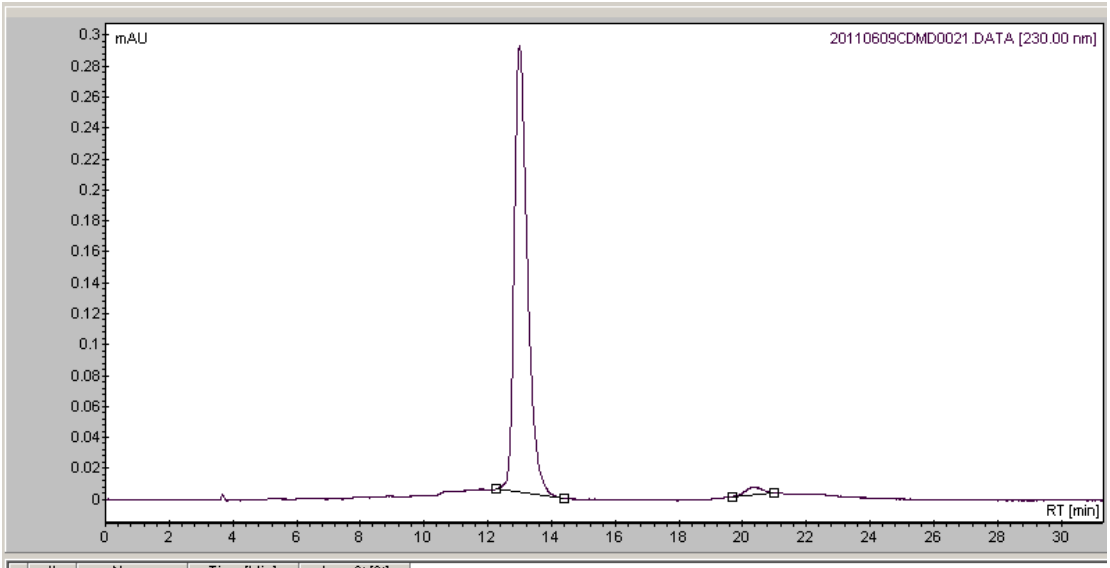

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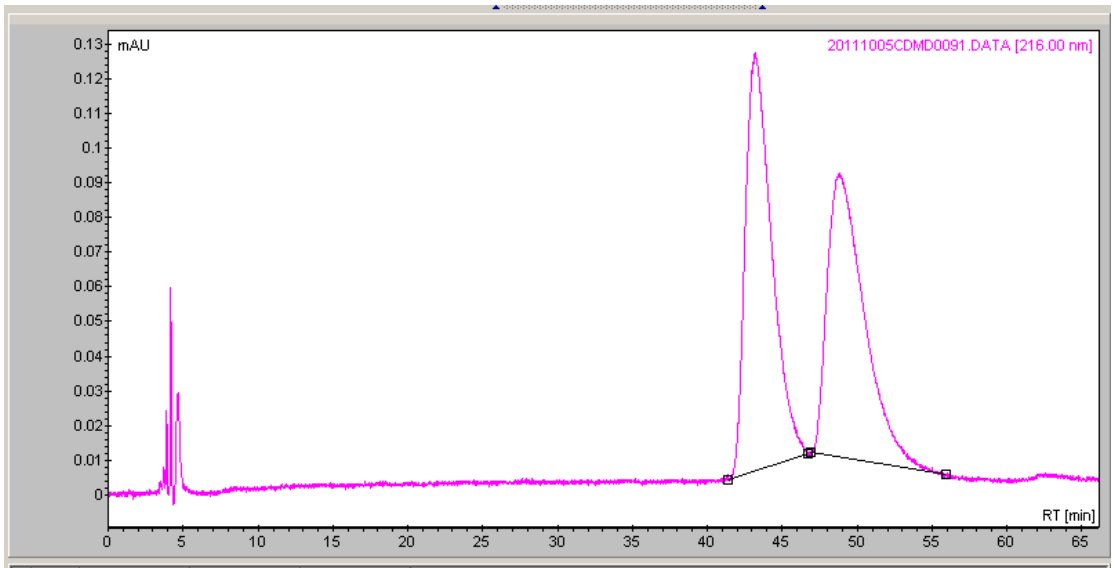
Total			100.000

3c



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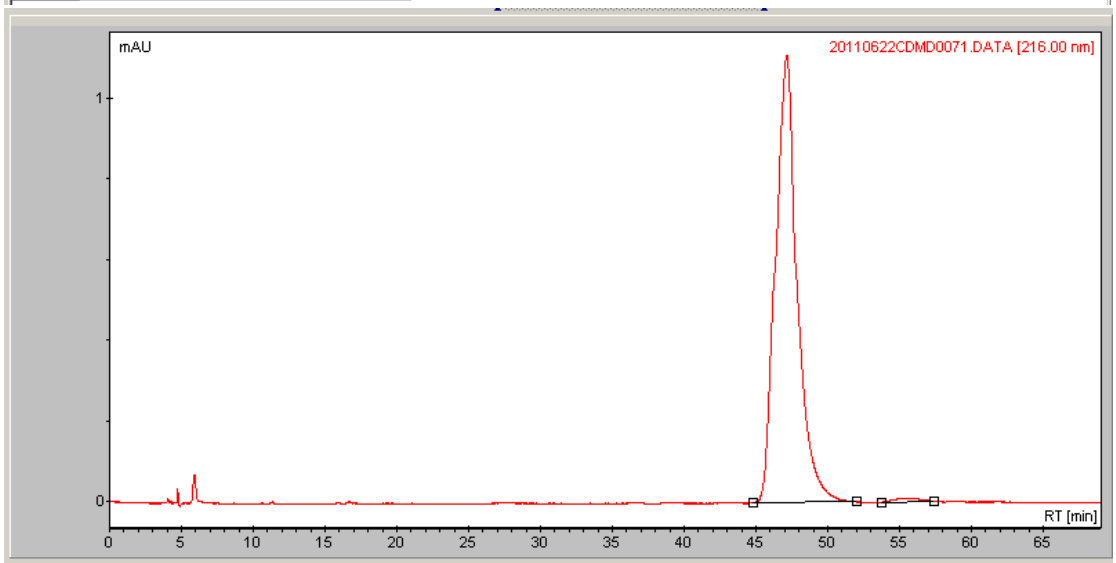

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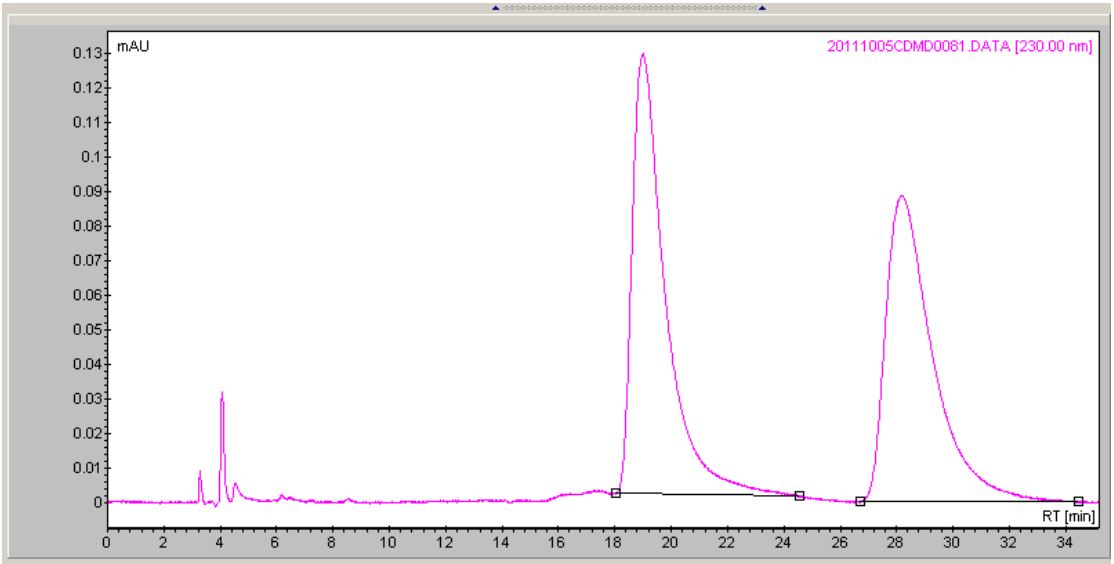
Total			100.000

3d



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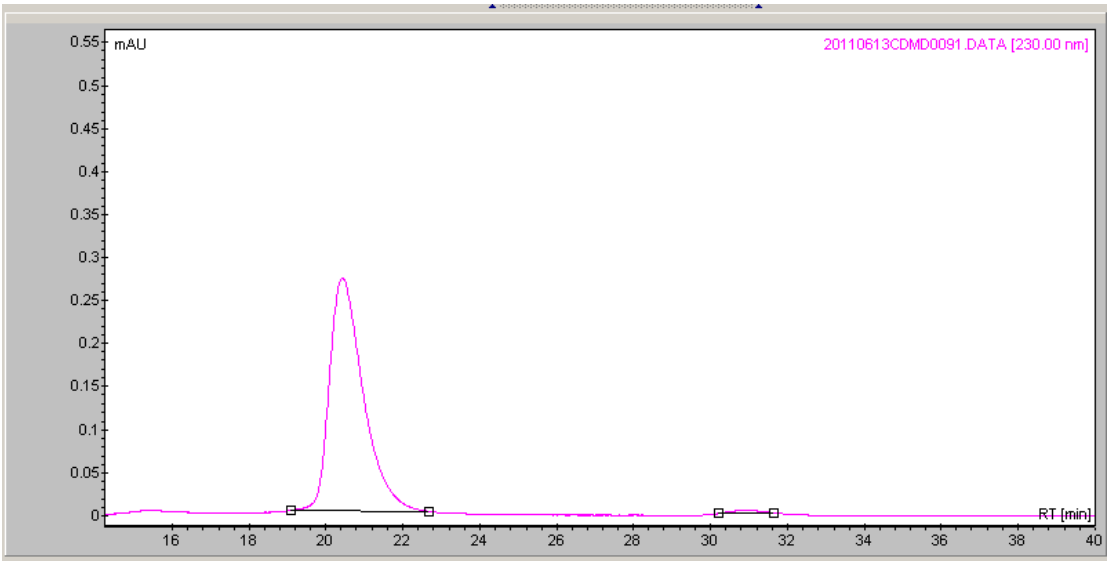

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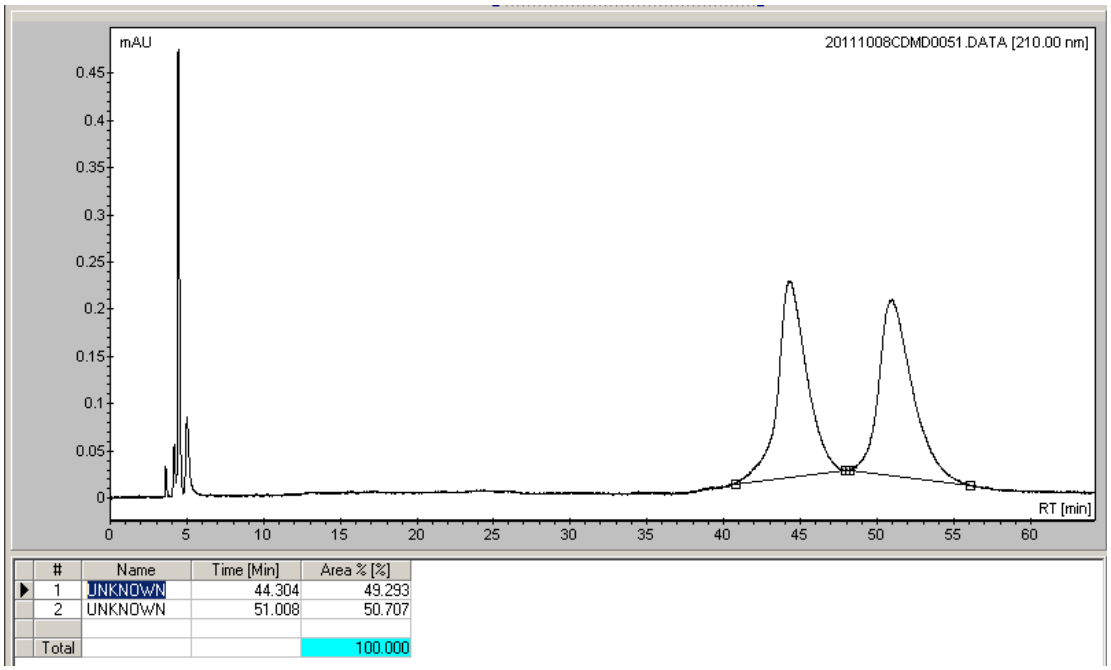
Total			100.000

3e



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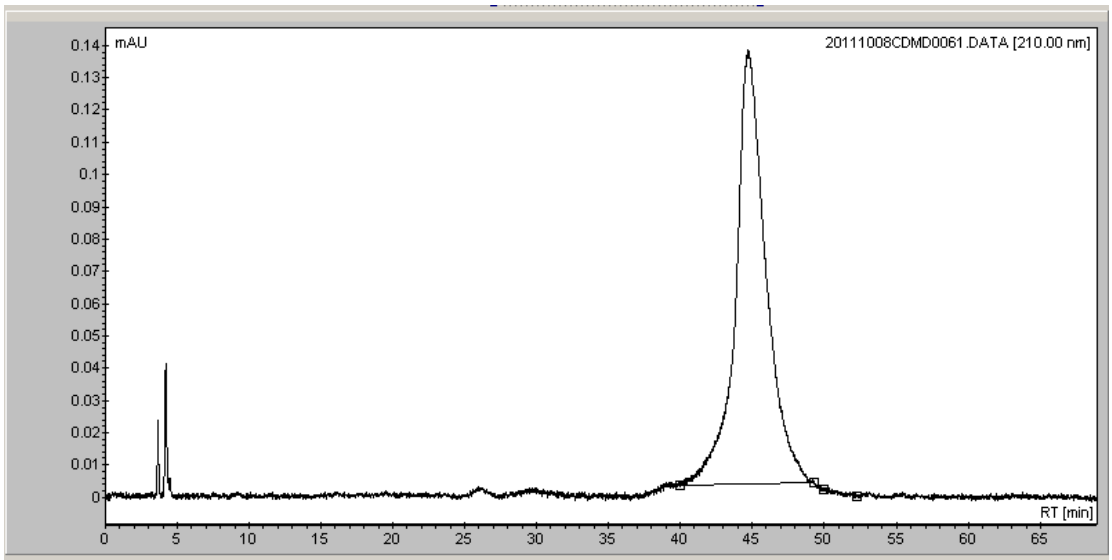

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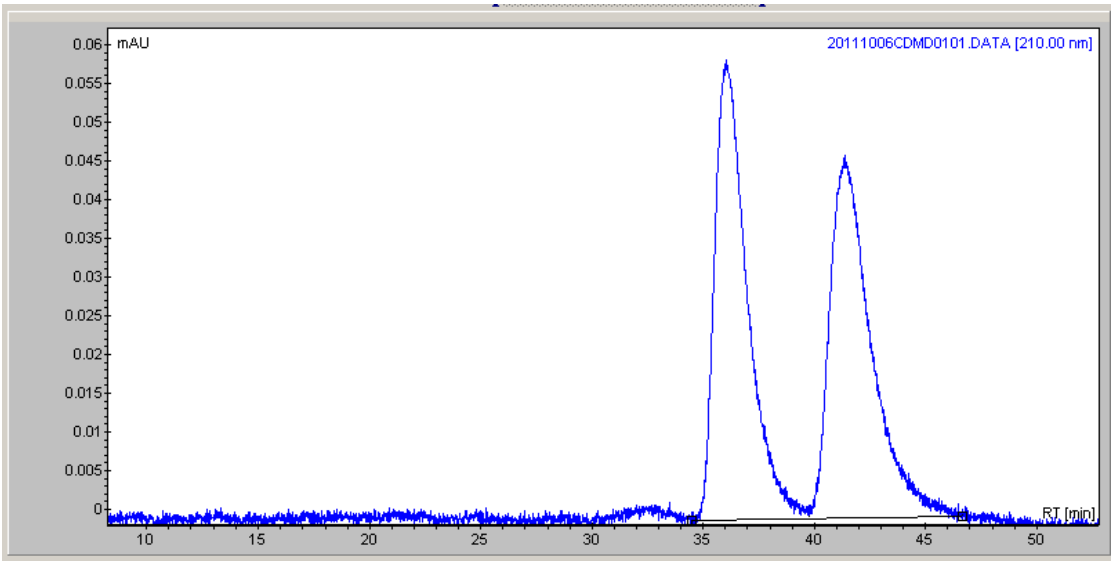
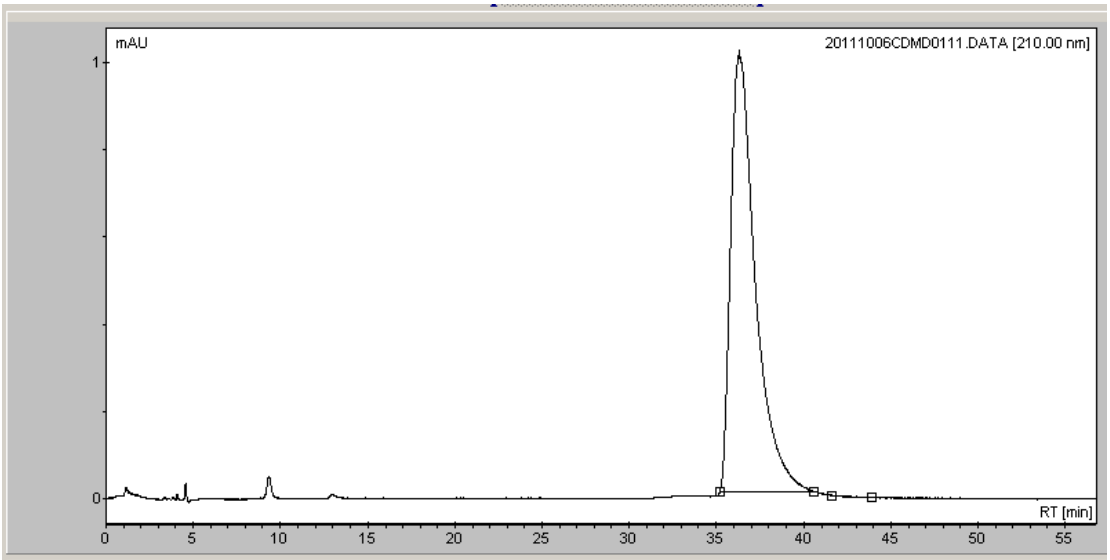
Total			100.000

3f

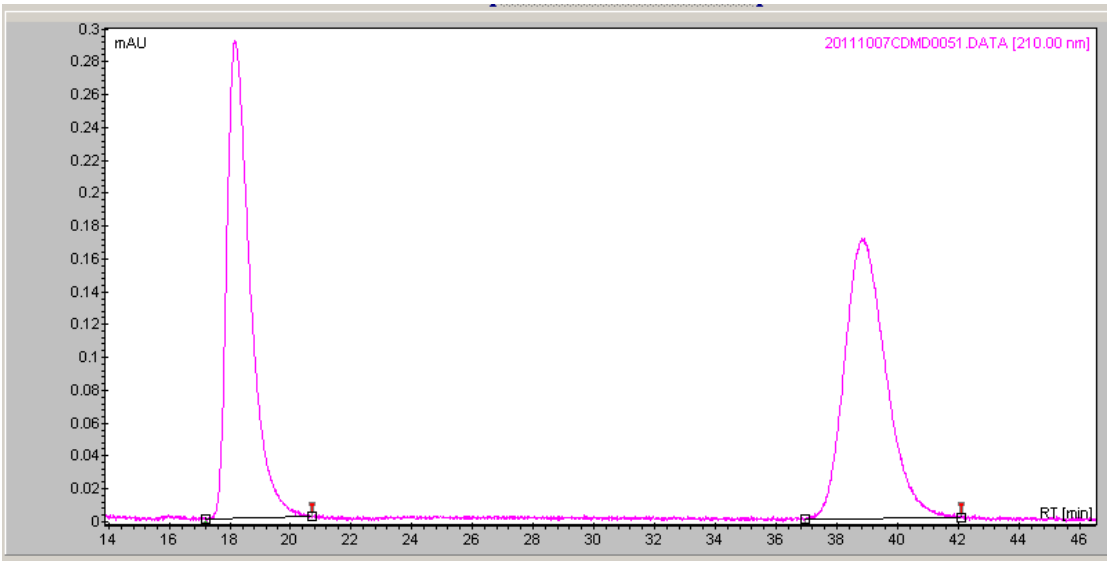


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	36.037	50.093
2	UNKNOWN	41.370	49.907
Total			100.000

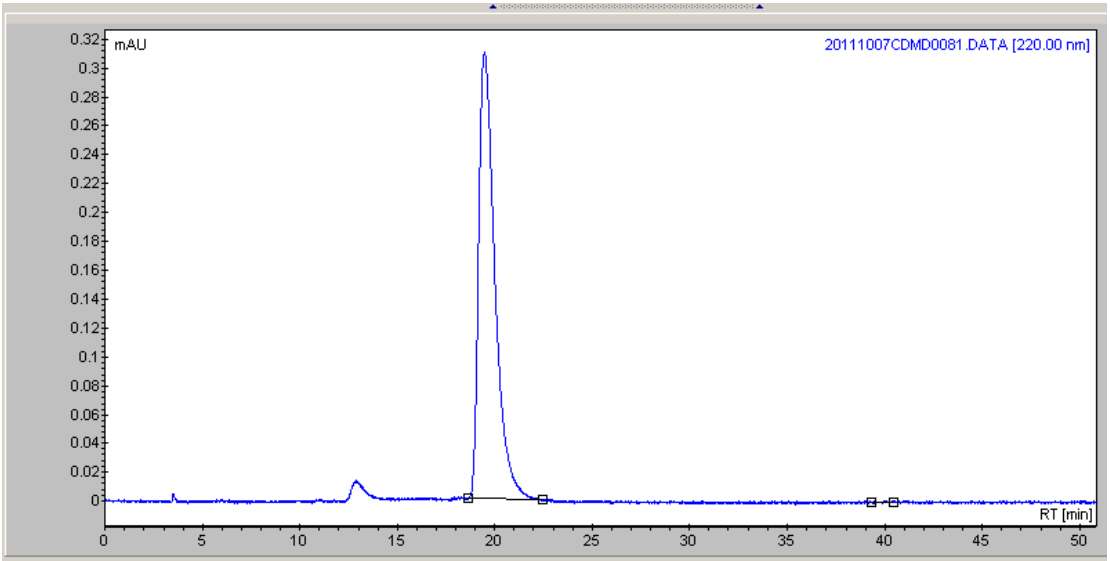


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	36.304	99.867
2	UNKNOWN	42.544	0.133
Total			100.000

3g

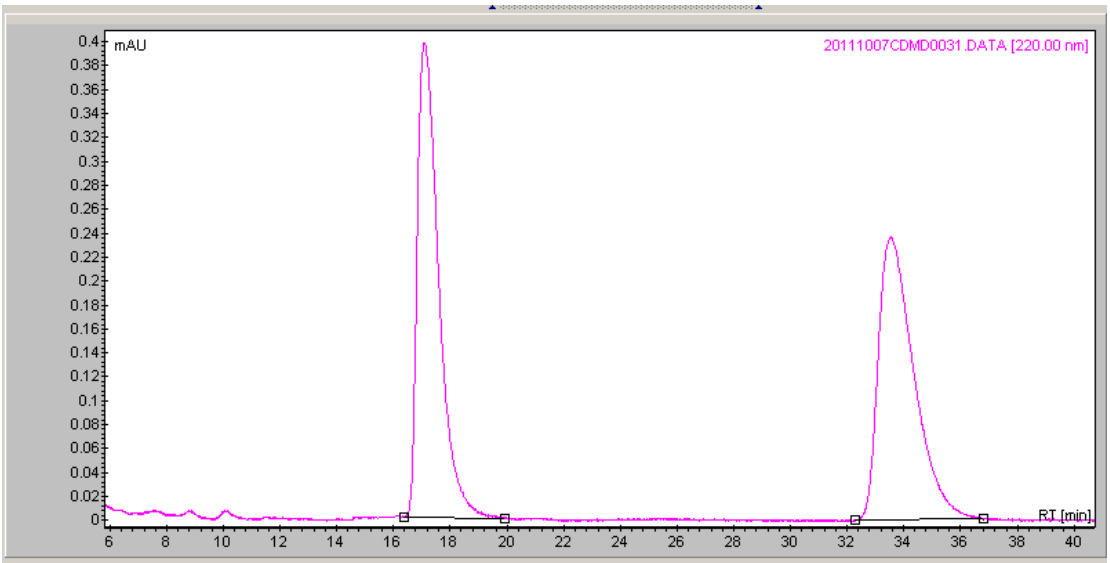


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	18.172	49.059
2	UNKNOWN	38.837	50.941
Total			100.000

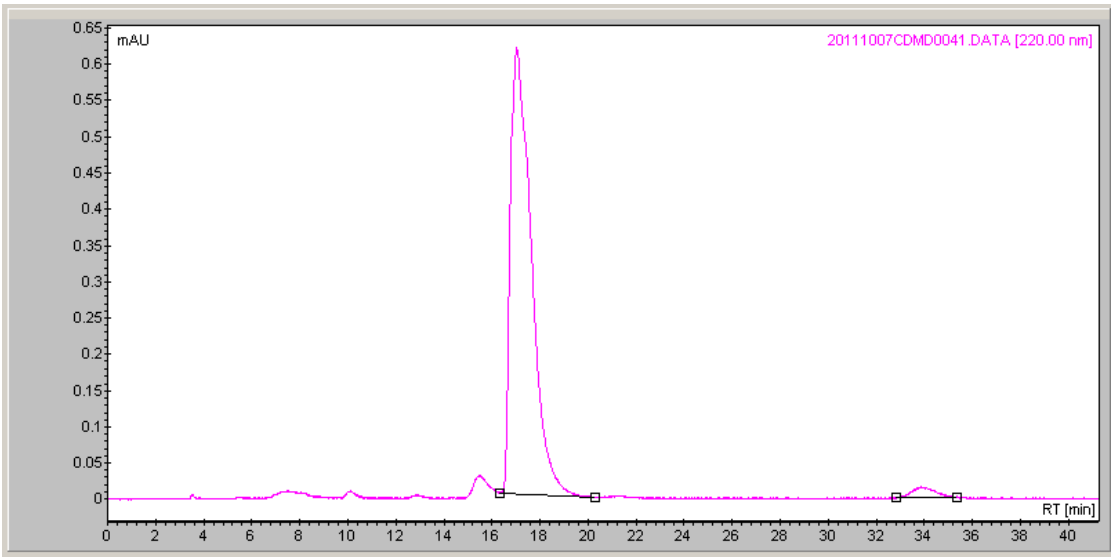


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	19.465	99.950
2	UNKNOWN	40.450	0.050
Total			100.000

3h

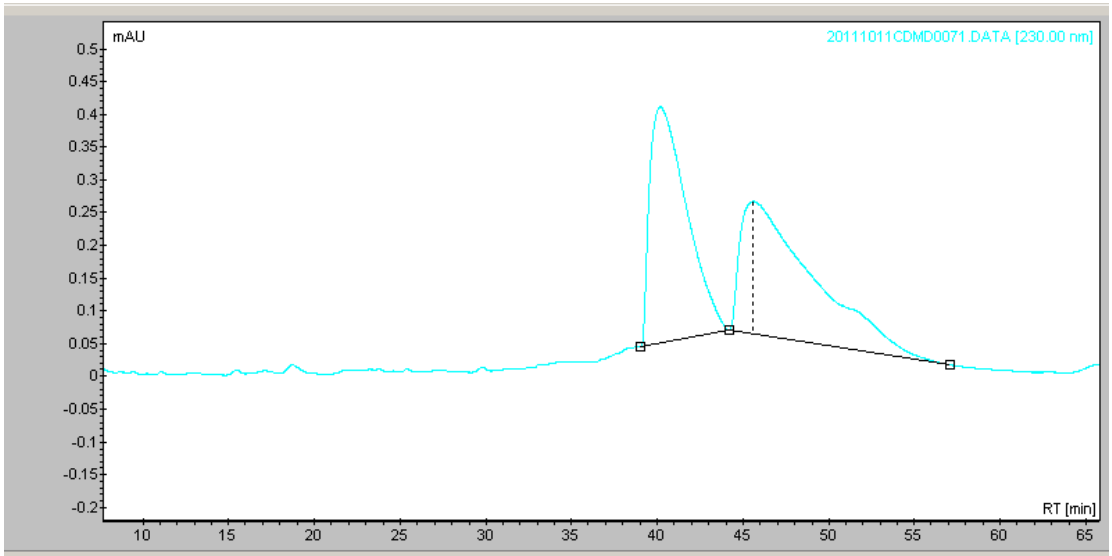


#	Name	Time [Min]	Area % [%]
2	UNKNOWN	17.092	50.390
1	UNKNOWN	33.531	49.610
Total			100.000

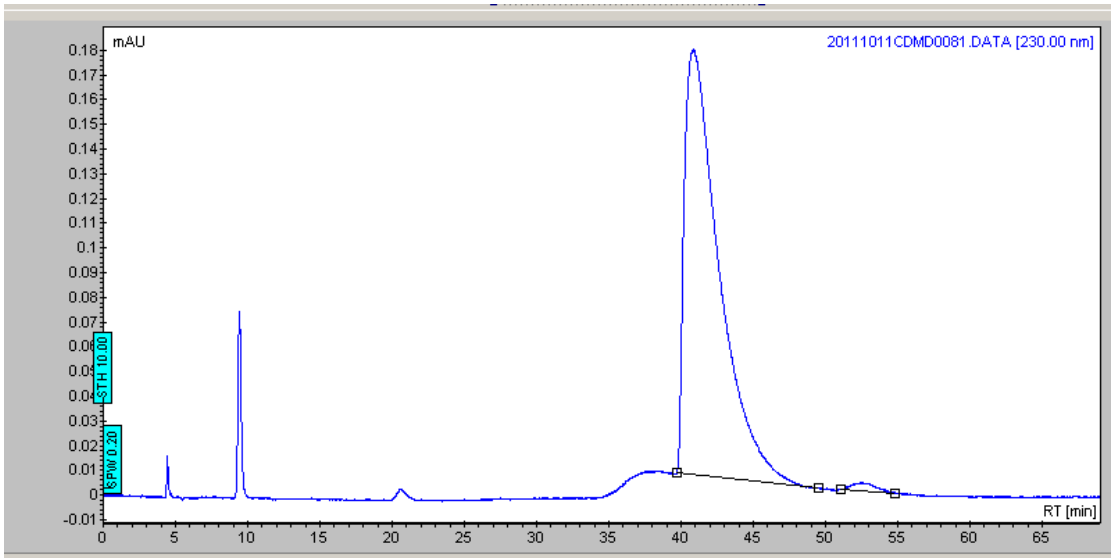


#	Name	Time [Min]	Area % [%]
2	UNKNOWN	17.025	97.396
1	UNKNOWN	33.904	2.604
Total			100.000

3i

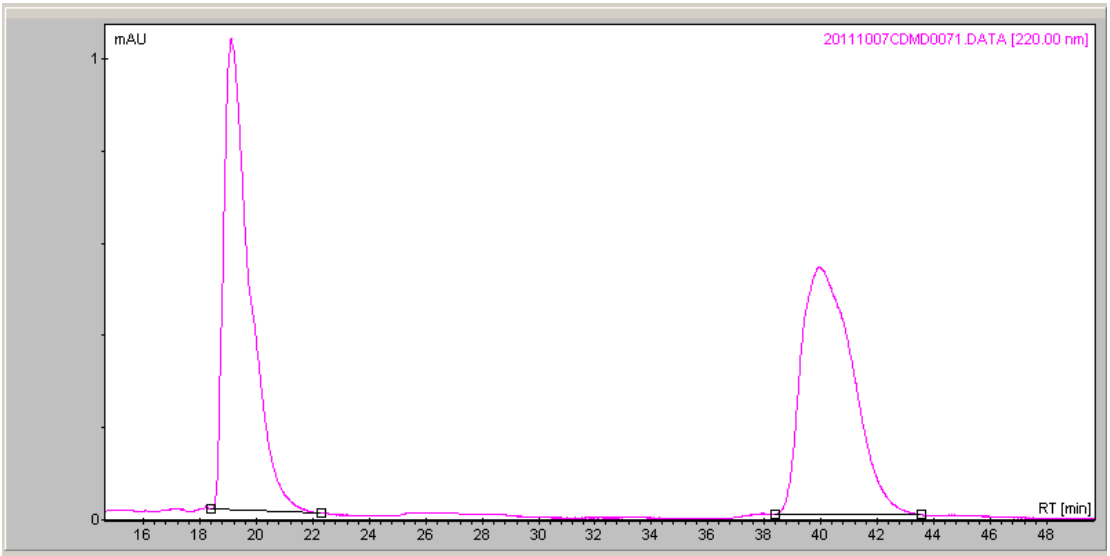


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	40.226	51.686
2	UNKNOWN	45.664	48.314
Total			100.000

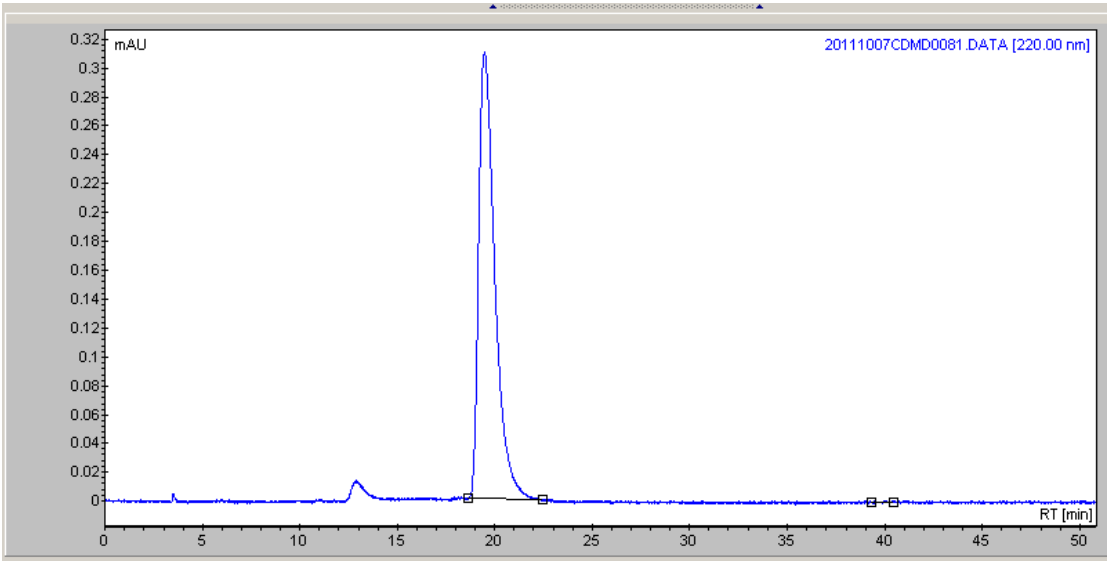


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	40.865	98.810
2	UNKNOWN	52.554	1.190
Total			100.000

3j

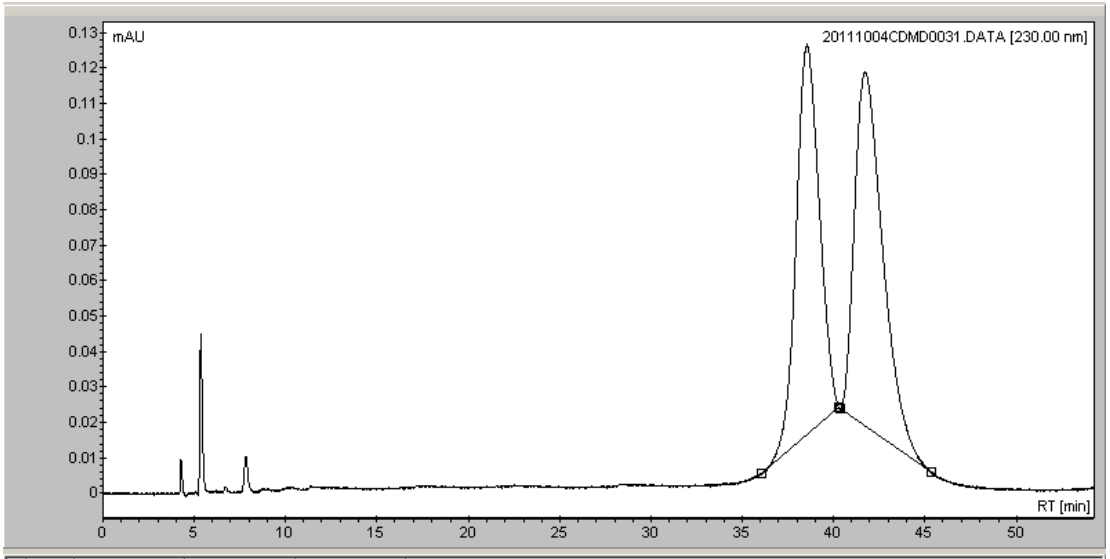


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	19.105	49.081
2	UNKNOWN	39.944	50.919
Total			100.000

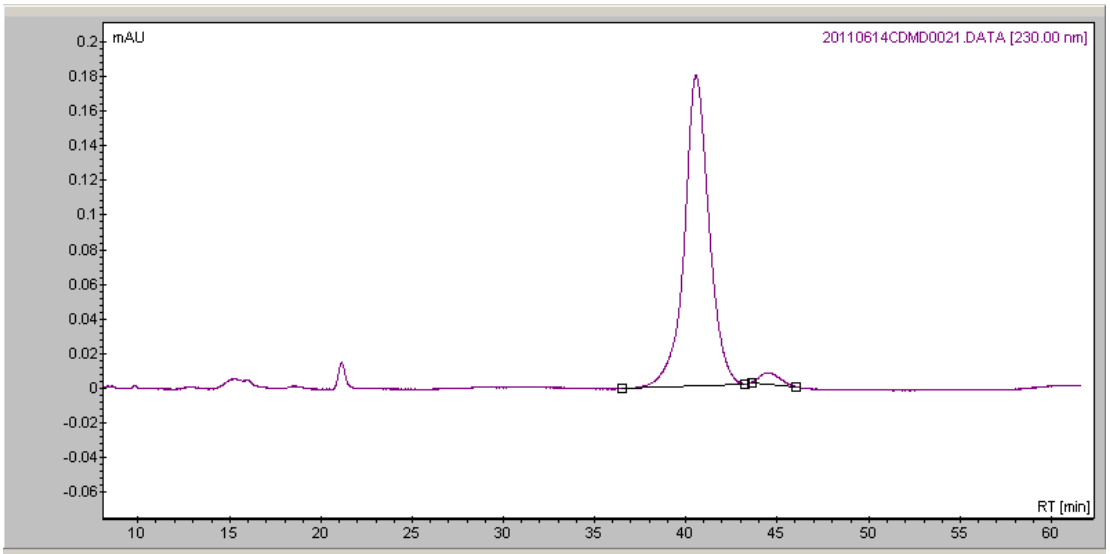


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	19.465	99.950
2	UNKNOWN	40.450	0.050
Total			100.000

3k

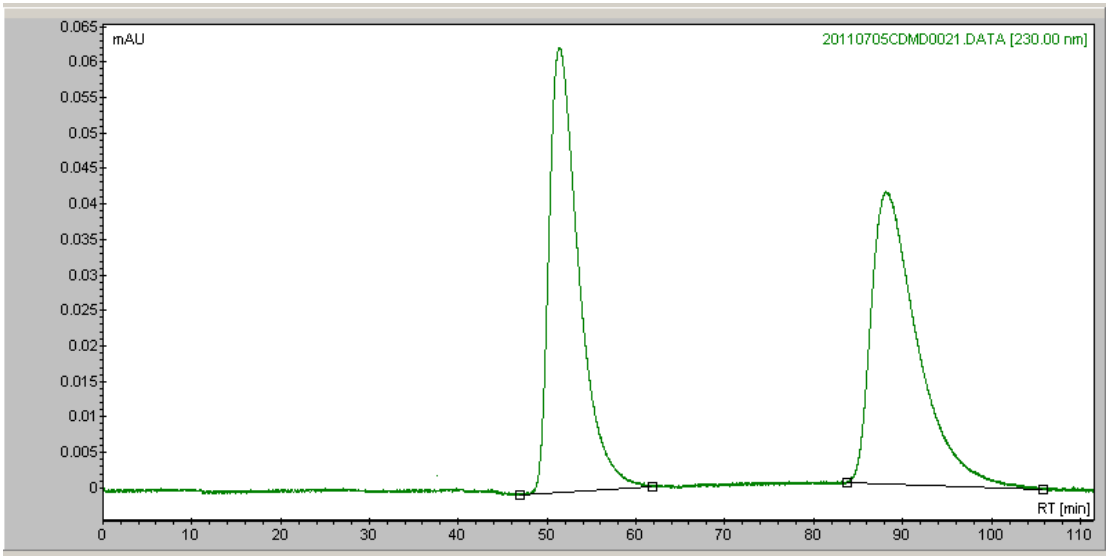


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	38.531	47.384
2	UNKNOWN	41.730	52.616
Total			100.000

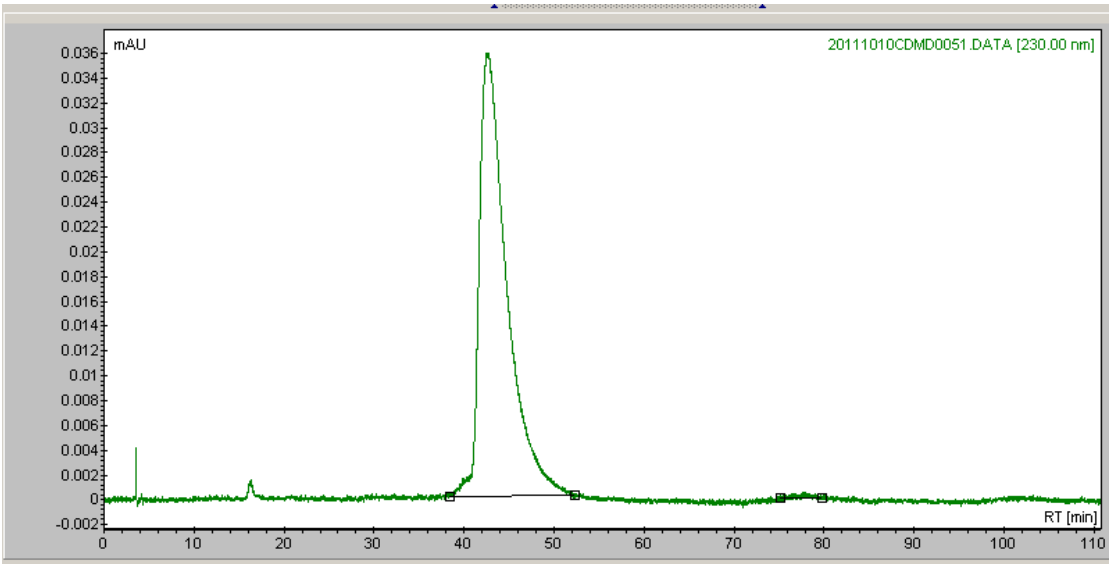


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	40.544	97.086
2	UNKNOWN	44.530	2.914
Total			100.000

3l

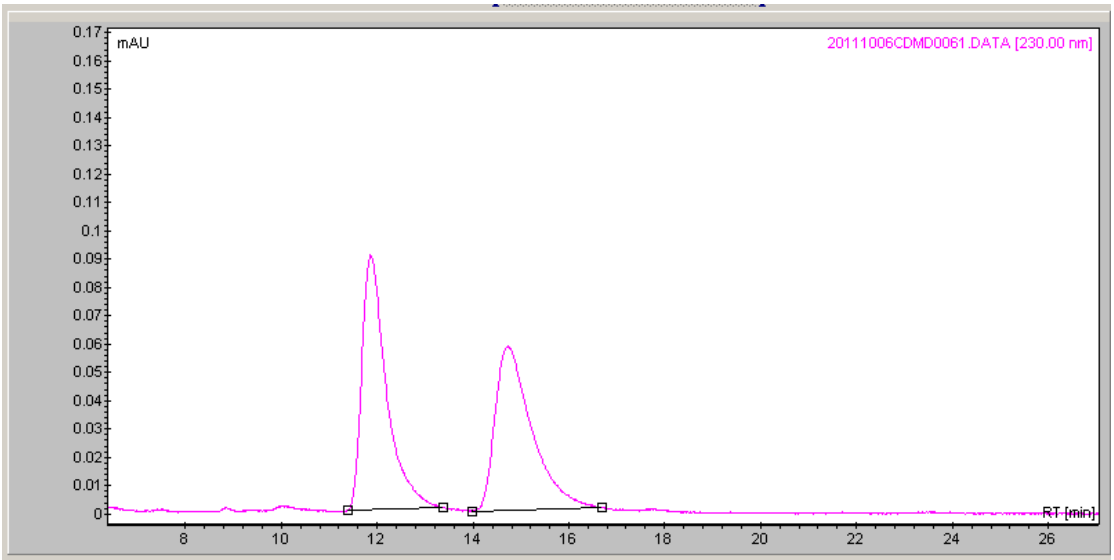


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	51.382	49.486
2	UNKNOWN	88.142	50.514
Total			100.000

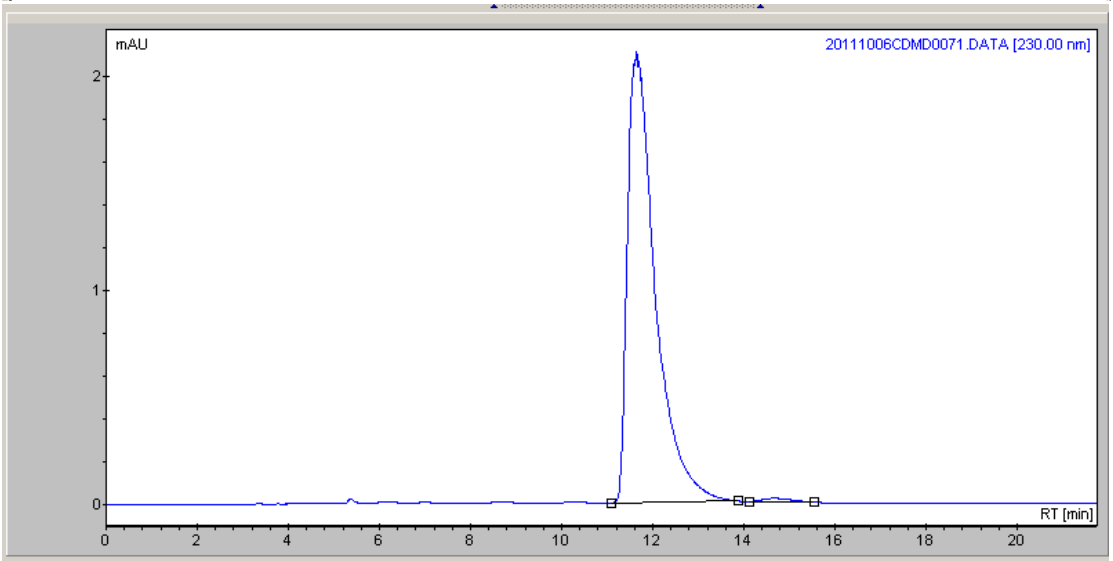


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	42.611	99.542
2	UNKNOWN	77.945	0.458
Total			100.000

3m

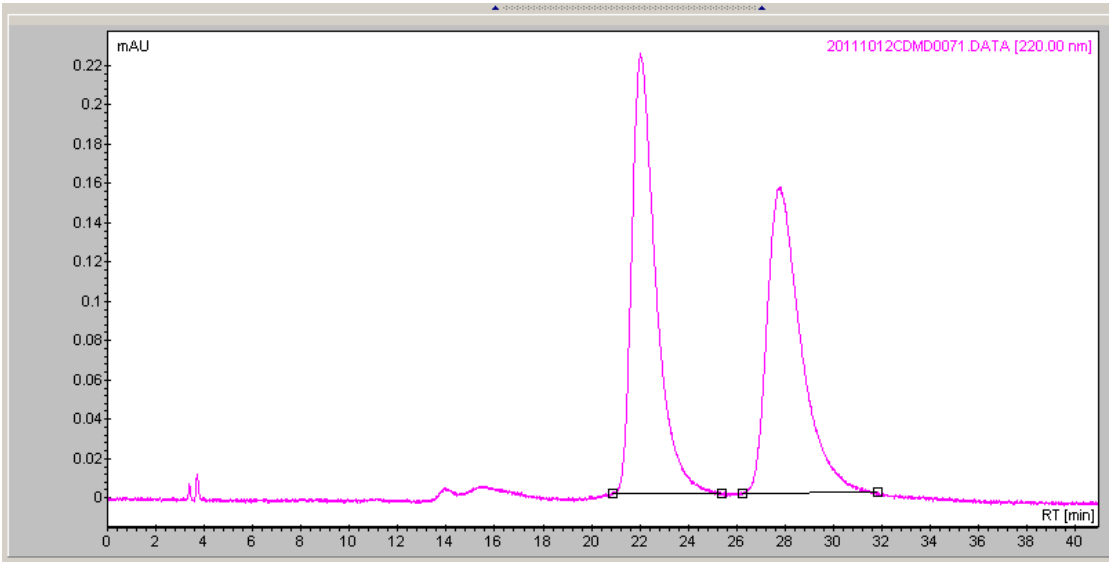


#	Name	Time [Min]	Area % [%]
2	UNKNOWN	11.866	50.969
1	UNKNOWN	14.732	49.031
Total			100.000

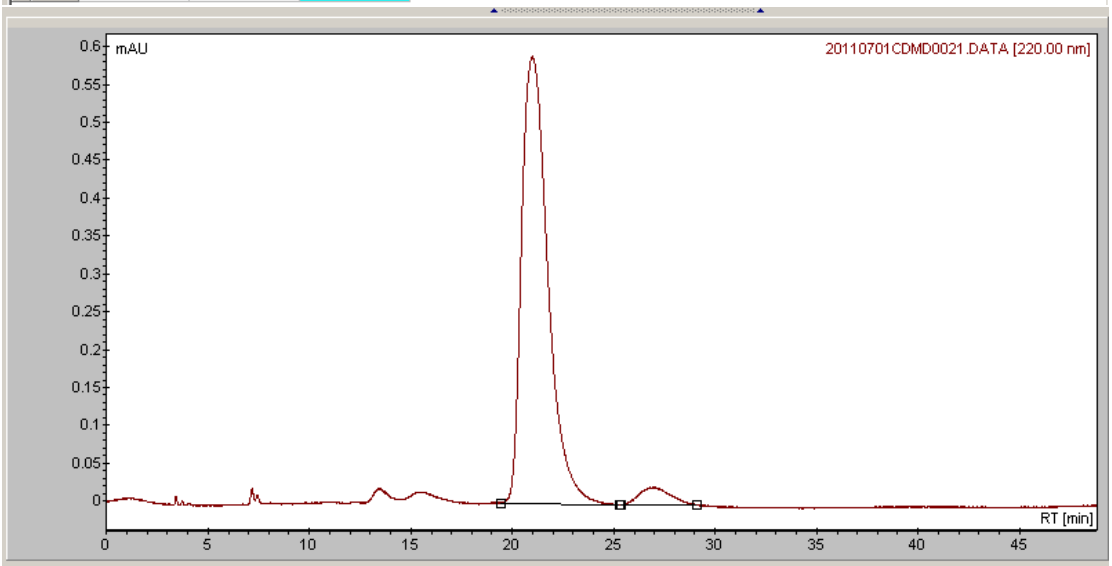


#	Name	Time [Min]	Area % [%]
2	UNKNOWN	11.652	99.226
1	UNKNOWN	14.706	0.774
Total			100.000

3n

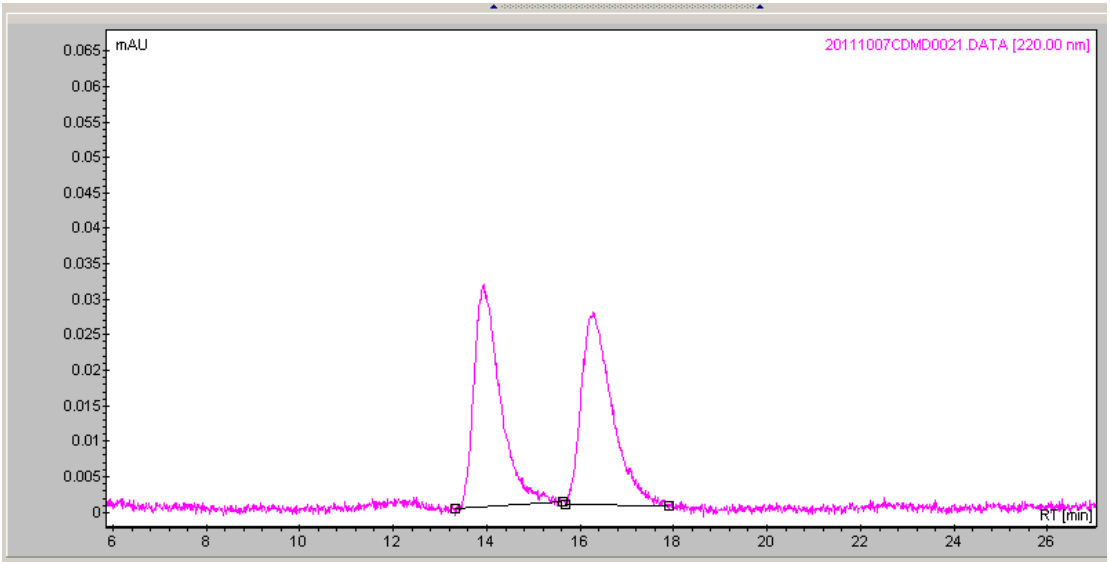


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	22.038	50.431
2	UNKNOWN	27.811	49.569
Total			100.000

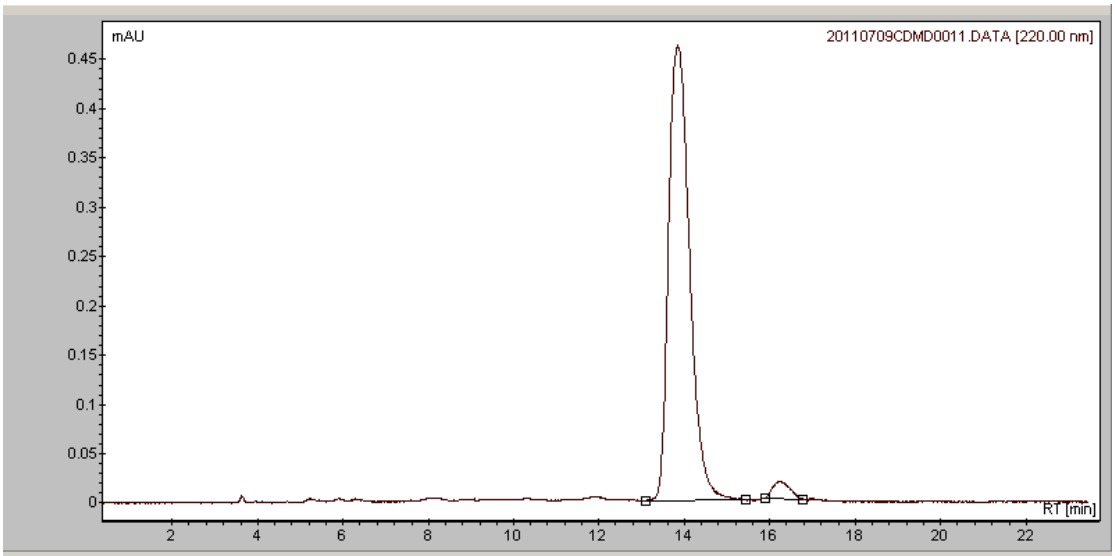


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	21.012	95.604
2	UNKNOWN	26.931	4.396
Total			100.000

3o

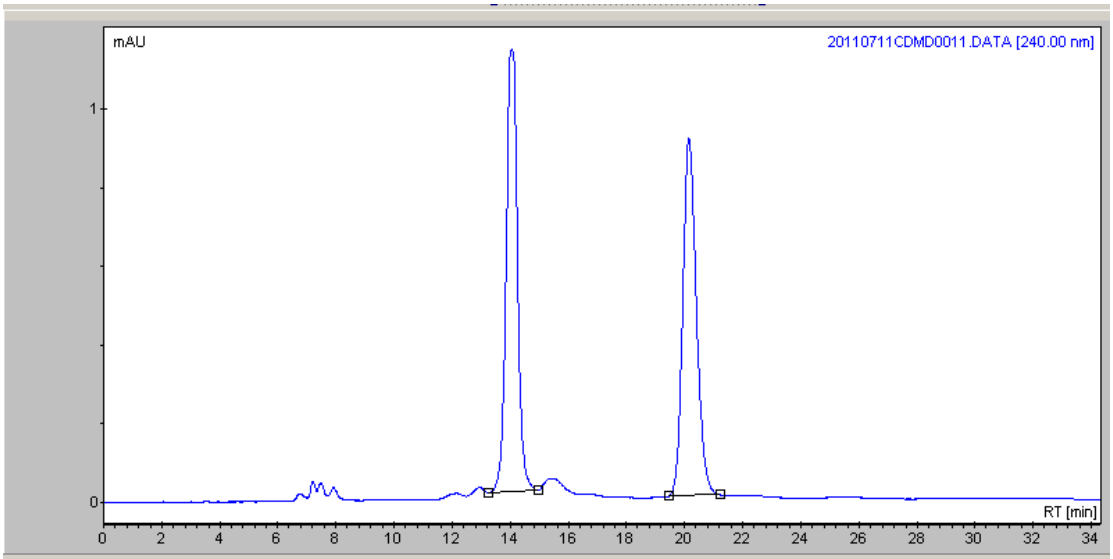


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	13.932	49.861
2	UNKNOWN	16.265	50.139
Total			100.000

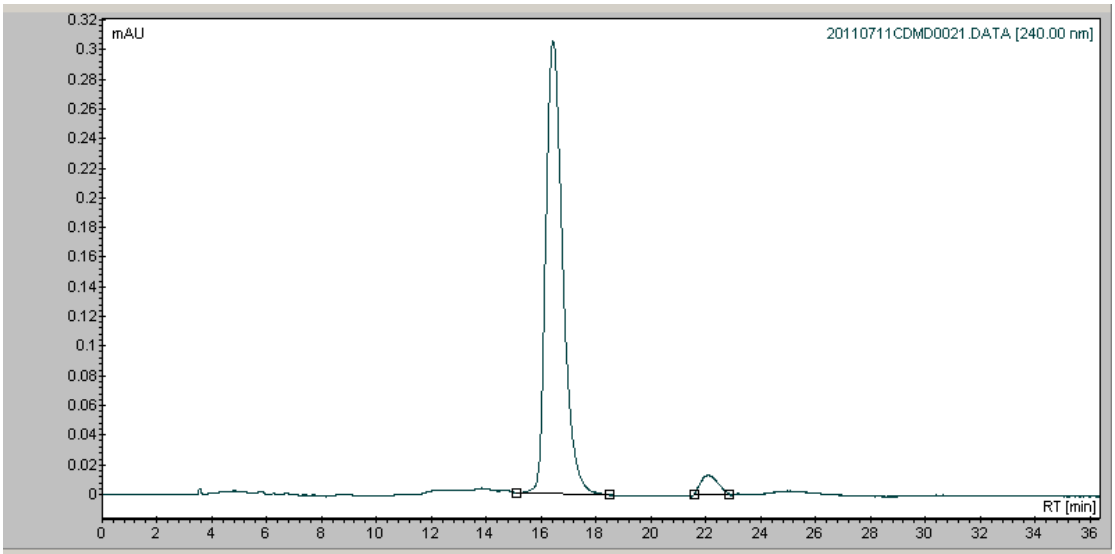


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	13.839	96.834
2	UNKNOWN	16.252	3.166
Total			100.000

3p

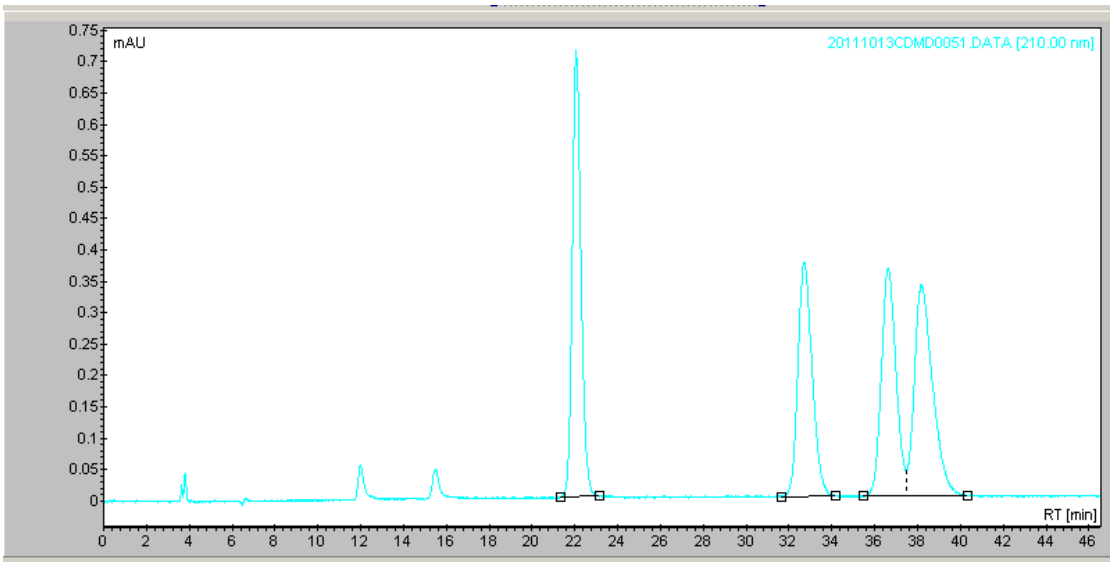


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	14.052	50.830
2	UNKNOWN	20.145	49.170
Total			100.000

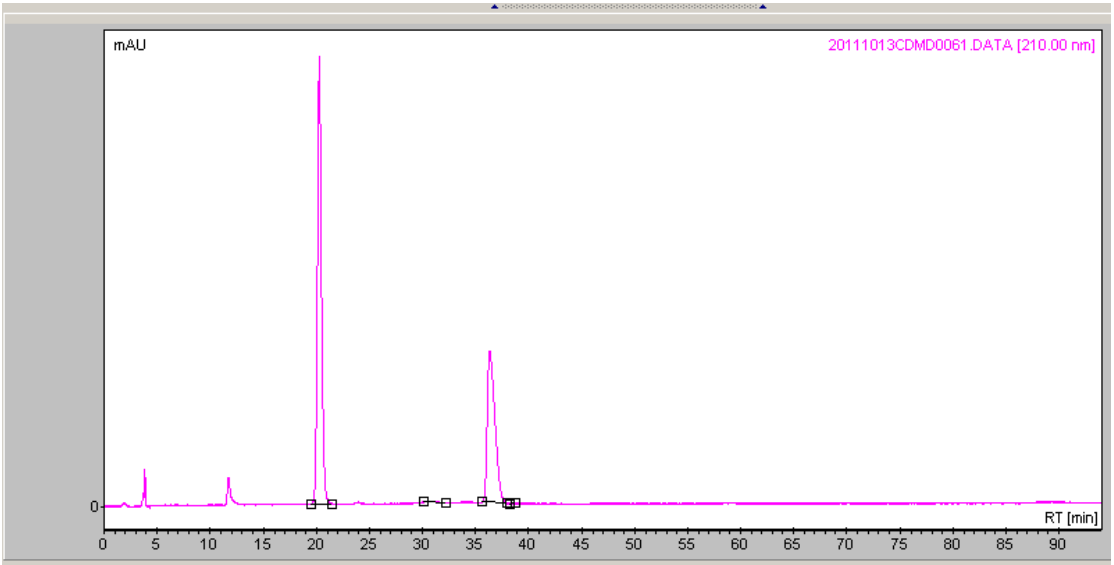


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	16.439	96.041
2	UNKNOWN	22.092	3.959
Total			100.000

4a

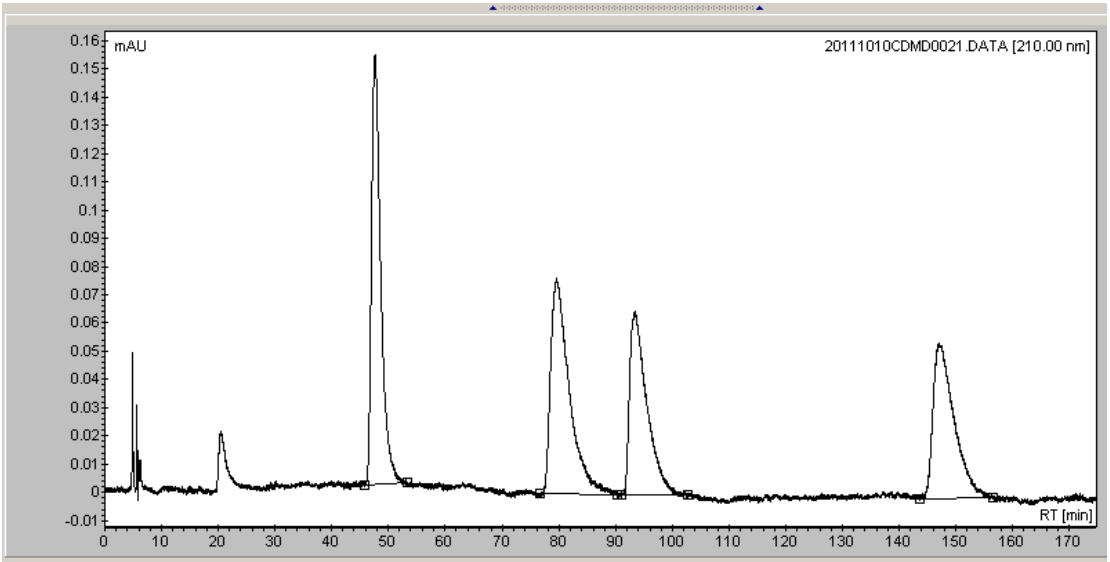


#	Name	Time [Min]	Area % [%]
4	UNKNOWN	22.052	26.946
1	UNKNOWN	32.718	23.043
2	UNKNOWN	36.624	23.074
3	UNKNOWN	38.184	26.936
Total			100.000

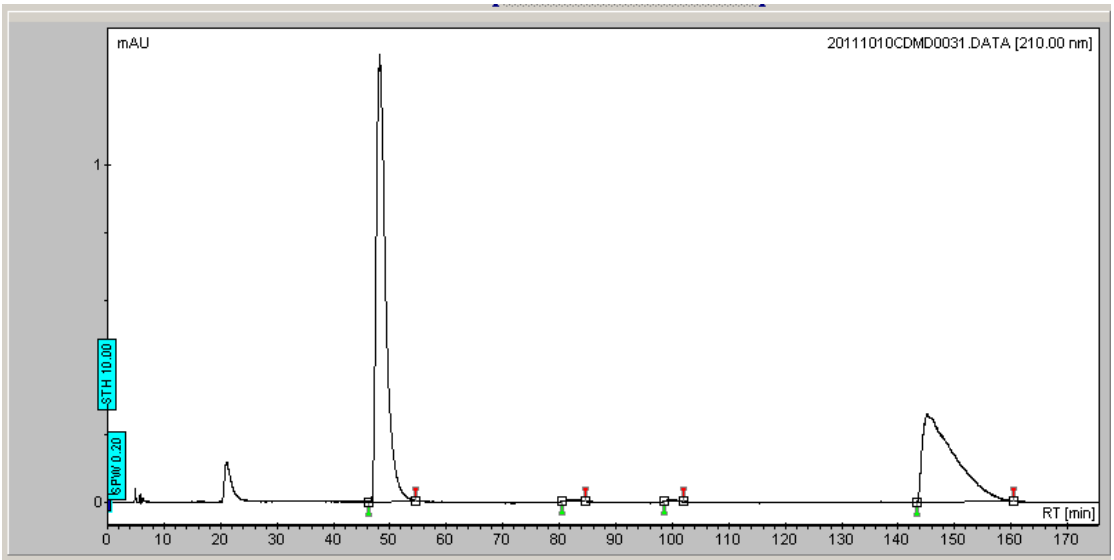


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	20.286	60.818
2	UNKNOWN	31.149	0.277
3	UNKNOWN	36.360	38.890
4	UNKNOWN	38.560	0.015
Total			100.000

4b

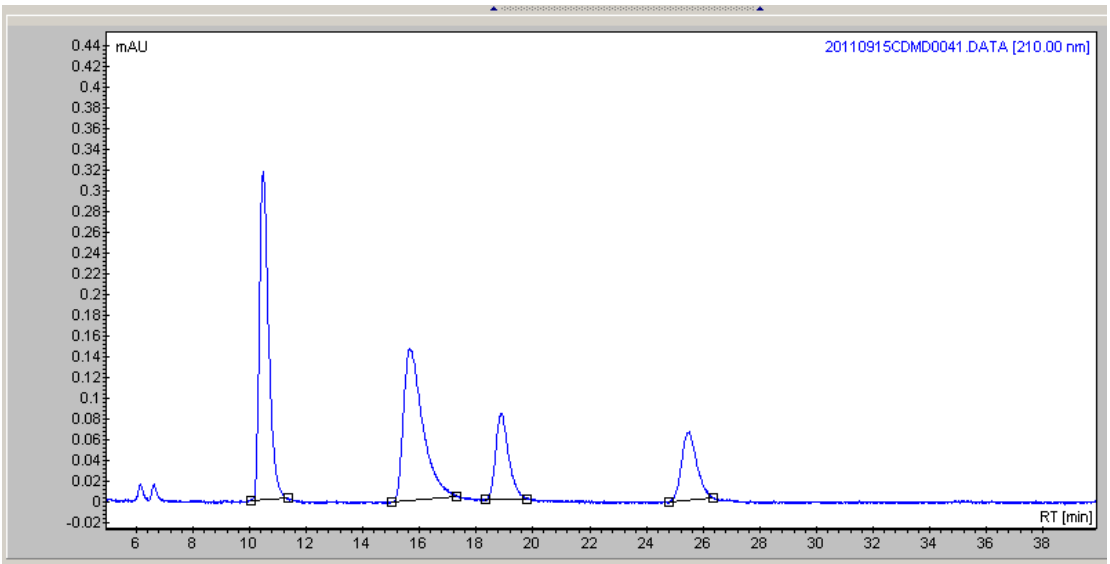


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	47.622	27.621
2	UNKNOWN	79.606	27.920
3	UNKNOWN	93.380	21.667
4	UNKNOWN	146.916	22.792
Total			100.000

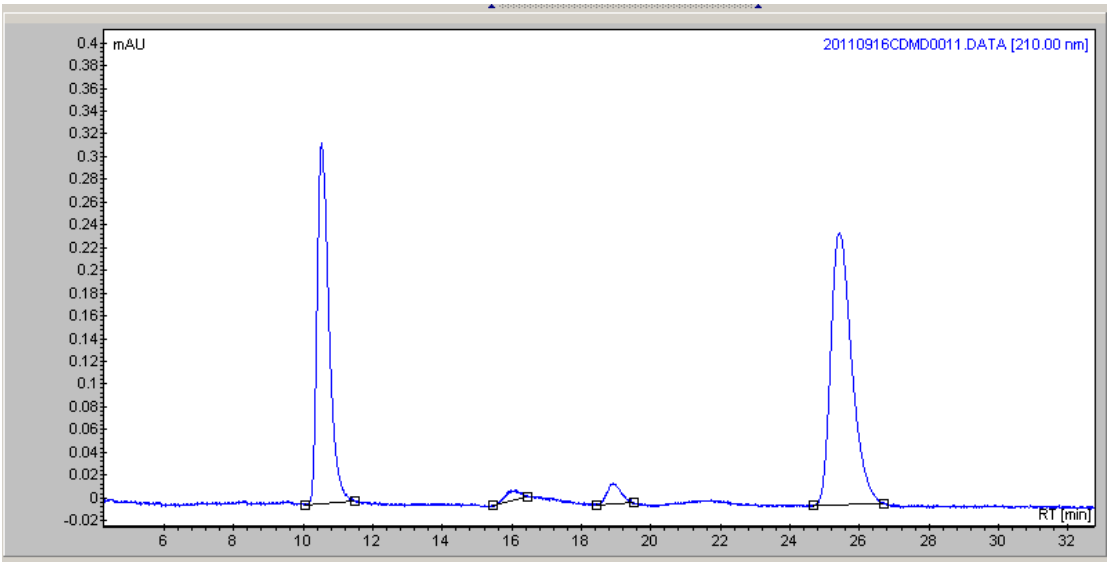


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	48.222	59.627
2	UNKNOWN	82.070	0.260
3	UNKNOWN	99.680	0.249
4	UNKNOWN	145.145	39.864
Total			100.000

4c

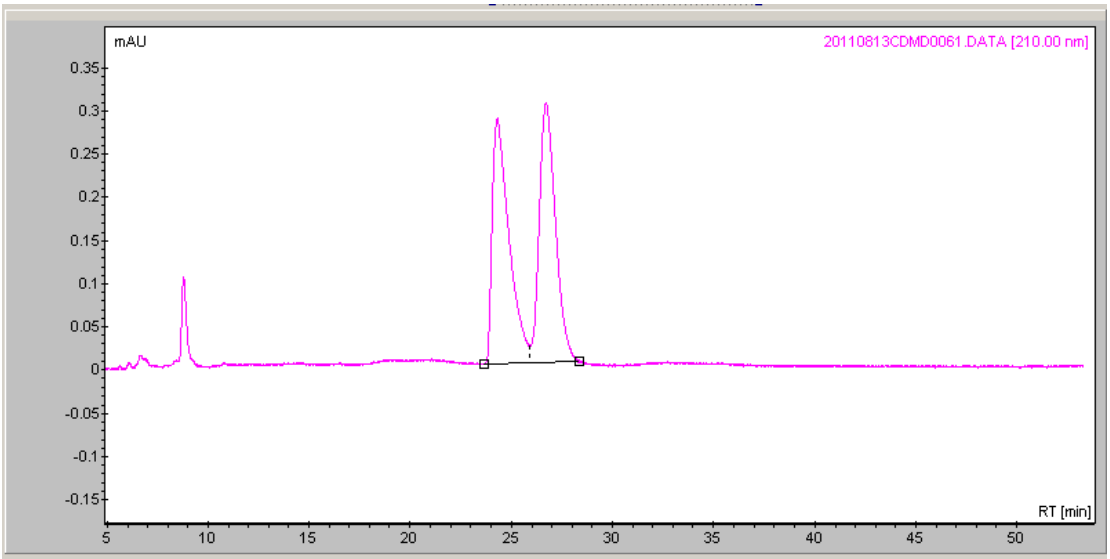


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	10.466	37.121
2	UNKNOWN	15.652	36.351
3	UNKNOWN	18.879	13.650
4	UNKNOWN	25.478	12.878
Total			100.000

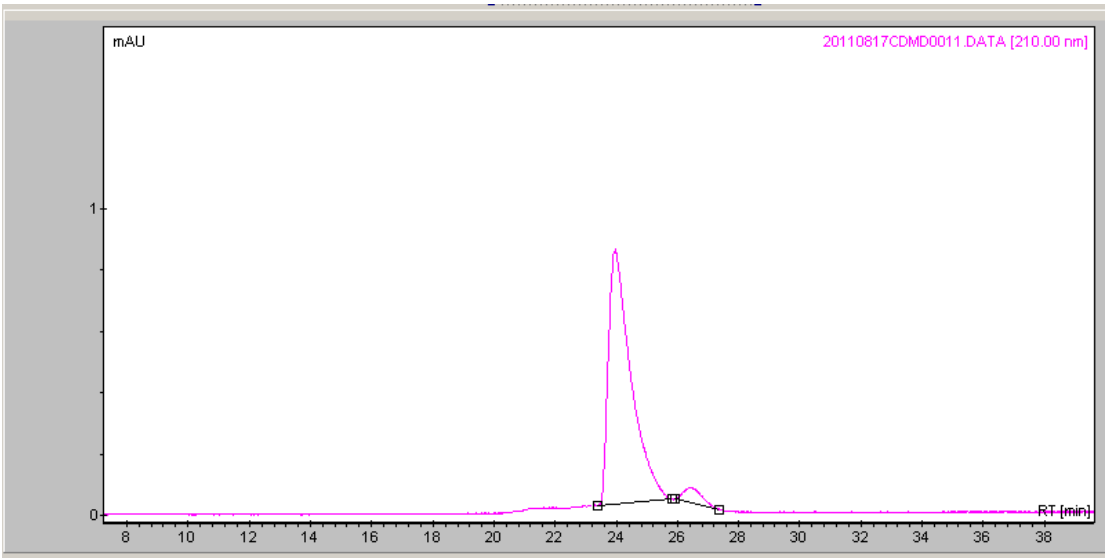


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	10.519	40.582
2	UNKNOWN	15.946	1.443
3	UNKNOWN	18.919	2.754
4	UNKNOWN	25.425	55.221
Total			100.000

4d

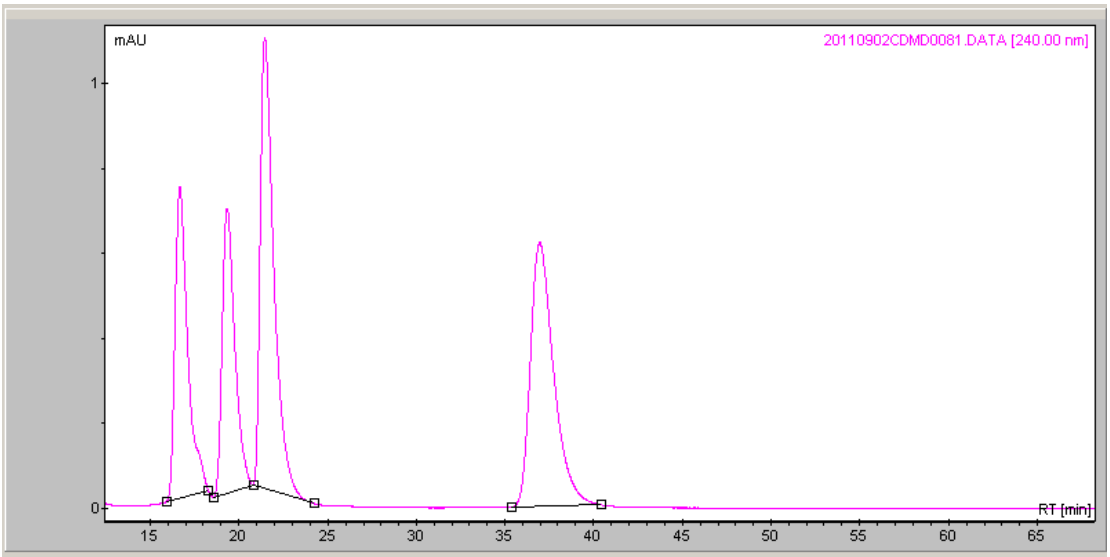


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	24.305	49.529
2	UNKNOWN	26.718	50.471
Total			100.000

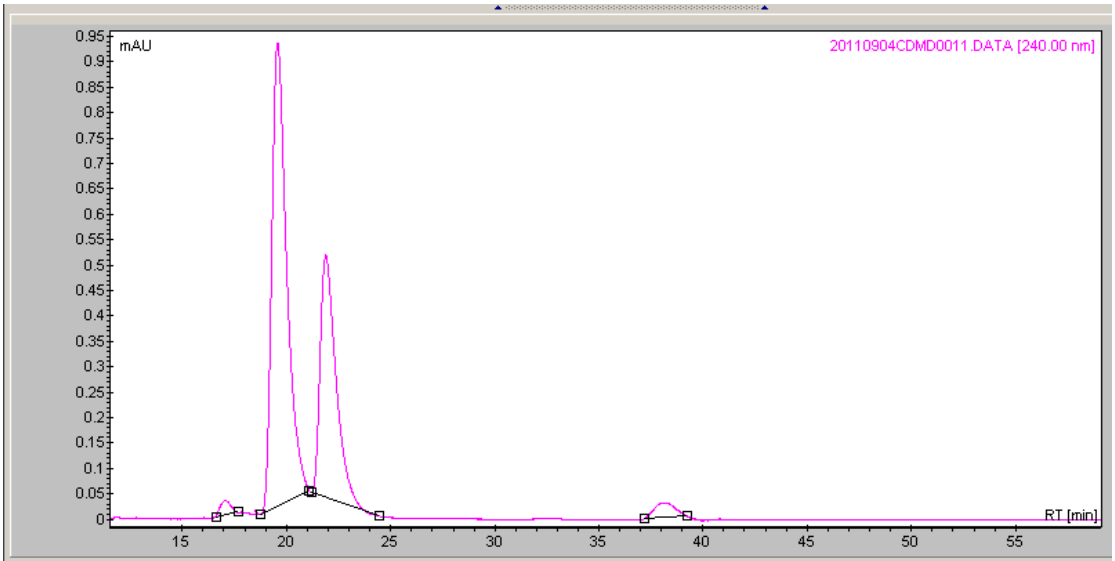


#	Name	Time [Min]	Area % [%]
1	UNKNOWN	23.958	95.379
2	UNKNOWN	26.465	4.621
Total			100.000

4e

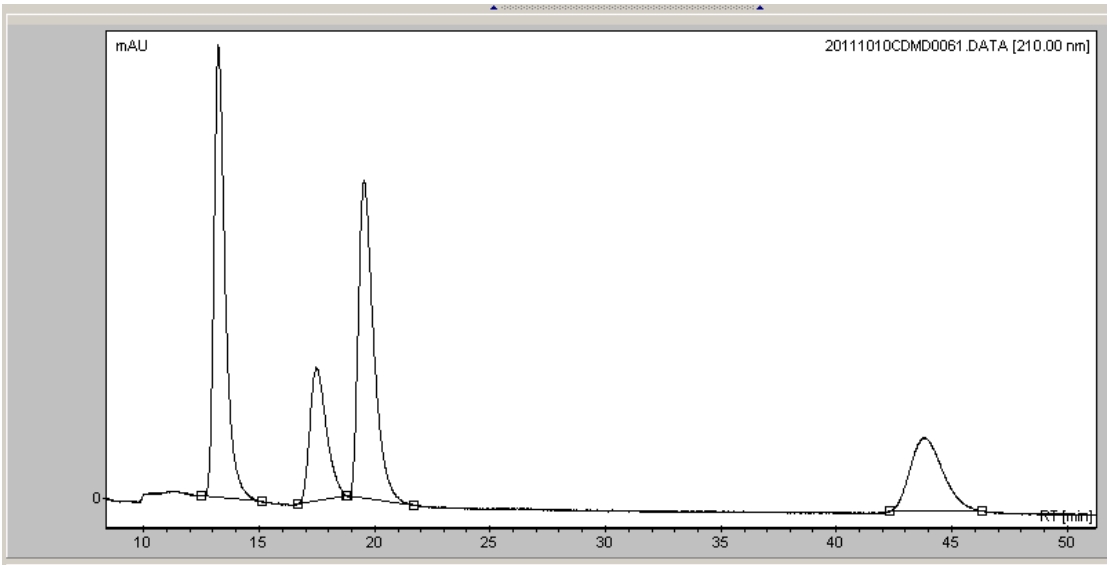


#	Name	Time [Min]	Area % [%]
4	UNKNOWN	16.661	19.943
3	UNKNOWN	19.326	18.154
2	UNKNOWN	21.459	30.898
1	UNKNOWN	36.973	31.005
Total			100.000

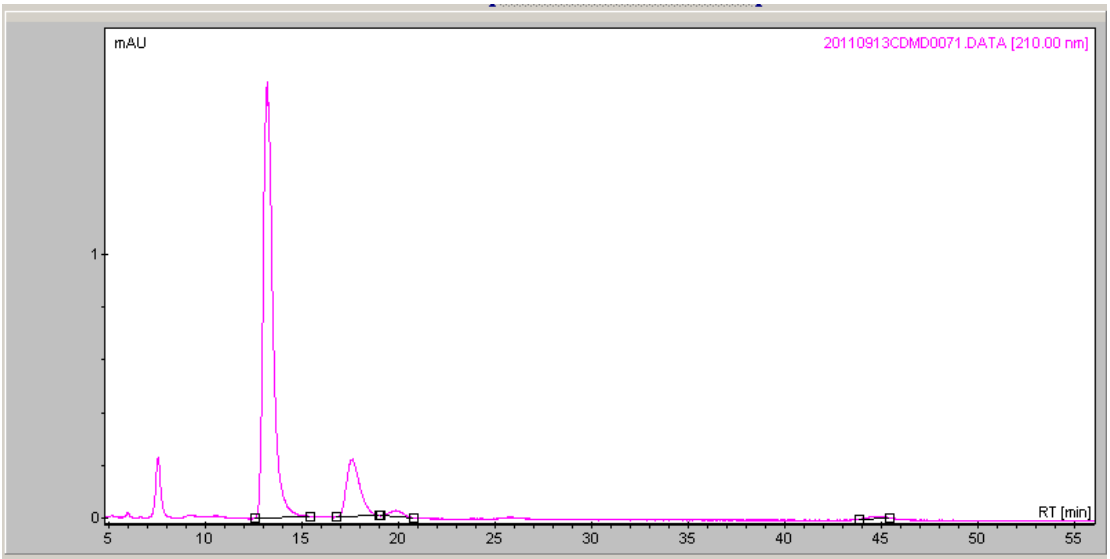


#	Name	Time [Min]	Area % [%]
4	UNKNOWN	17.039	1.297
1	UNKNOWN	19.572	61.773
2	UNKNOWN	21.878	34.195
3	UNKNOWN	38.104	2.736
Total			100.000

4f



#	Name	Time [Min]	Area % [%]
4	UNKNOWN	13.226	35.028
1	UNKNOWN	17.492	15.079
2	UNKNOWN	19.532	33.448
3	UNKNOWN	43.810	16.445
Total			100.000



#	Name	Time [Min]	Area % [%]
1	UNKNOWN	13.172	82.375
2	UNKNOWN	17.559	15.312
3	UNKNOWN	19.865	1.659
4	UNKNOWN	44.690	0.654
Total			100.000