Highly Enantioselective and Regioselective Organocatalytic Direct Mannich Reaction of Methyl Alkyl Ketones with Cyclic Imines Benzo[*e*][1,2,3]oxathiazine 2,2-dioxides

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Supporting Information

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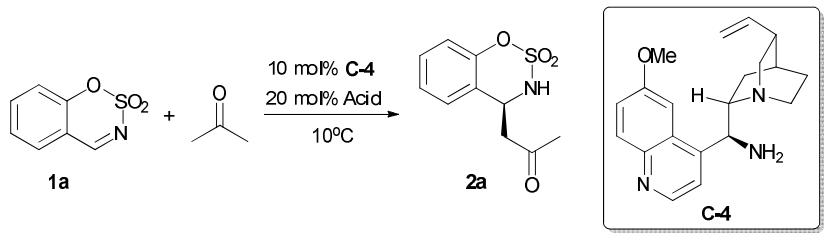
1. General methods.

General: ^{1}H NMR, and ^{13}C NMR spectra were recorded on Bruker DRX-400 spectrometers. The chemical shifts for ^{1}H NMR were recorded in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$, d 7.26 ppm). The chemical shifts for ^{13}C NMR were recorded in ppm downfield using the central peak of deuterochloroform (77.0 ppm) as the internal standard. Flash column chromatography was performed on silica gel (200-300 mesh). TLC analysis was performed using glass-backed plates coated with 0.2 mm silica. After elution, plate was visualized under at 254 nm UV illumination. All commercially available compounds were used as provided without further purification. The solvents were distilled from appropriate drying agents prior to use, unless otherwise noted. Cyclic imines **1** were prepared according to the procedures reported in the literature.[1]

2. More results on the condition optimization of asymmetric Mannich reaction



Entry[a]	Acid	Solvent	Temp. (°C)	Time (h)	Yield (%)	*ee* (%)
1	TFA	THF	10	22	51	90
2	(+)-CSA	THF	10	72	35	96

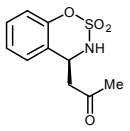
[1] (a) S. R. Hanson, L. J. Whalen and C.-H. Wong, *Bioorg. Med. Chem.,* 2006, **14**, 8386; (b) Y. Wang, H. Dong, Y. Zhang and J. Li *Journal of Henan University(Natural Science)* 2013, **43**, 253; (c) Y.-Q. Wang, Y. Zhang, H. Dong, J. Zhang and J. Zhao, *Eur. J. Org. Chem.*, 2013, 3764.

3	TsOH	THF	10	72	50	95
4	AcOH	THF	10	96	0	-
5	TFA	Toluene	10	12	99	96
6	(+)-CSA	Toluene	10	84	71	94
7	(-)-CSA	Toluene	10	96	75	84
8	TFA	Toluene	0	24	99	91

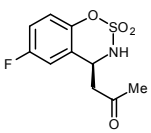
The effects of acid were investigated in THF (entries 1-4). In spite of the best *ee*, the reaction was slower with (+)-CSA than TFA (entries 1*vs* 2). However, in optimized solvent (Toluene) TFA afforded the better reactivities and enantioselectivities than CSA (entries 5-7). While temperature was decreased to 0°C, a slightly lower ee values was obtained (entry 8).

3. Procedure and data of asymmetric Mannich reaction

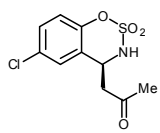
Typical procedure: To the mixture of quinine-NH_2 **C-4** (0.015 mmol, 10 mol%) and cyclic imine **1** (0.15 mmol) in toluene (1.45 mL) was added the solution of TFA (0.03 mmol, 20 mol%) in toluene (0.05 mL). After the reaction mixture was cooled to 10°C, acetone (0.75 mmol) was added. This reaction mixture was stirred in showed reaction time. Direct purification reaction mixture by column chromatography on a silica gel (petroleum ether/DCM) gave the desired Mannich products. The enantiomeric excess was determined by HPLC. Racemic Mannich products were obtained with the combination of 10 mol% benzyl amine and 20 mol% TFA.



2a: Known compound[2]; R_f = 0.18 (CH_2Cl_2); 96% *ee*, $[\alpha]^{32}_D$ = -21.3 (*c* 0.97, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (t, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.11-7.10 (m, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 5.82 (s, 1H), 5.17 (dd, *J* = 7.2, 3.8 Hz, 1H), 3.62 (dd, *J* = 18.1, 7.5 Hz, 1H), 2.97 (dd, *J* = 18.1, 3.8 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.7, 151.1, 129.6, 125.8, 125.4, 121.3, 119.1, 53.3, 46.4, 31.0; HPLC (Chiralcel IC column, hexane/iPrOH = 70/30, 0.8 mL/min, 220 nm): t_1 = 10.1 min (major, *S*), t_2 = 15.0 min.



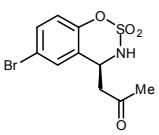
2b: White solid; mp 114.4-115.3°C; R_f = 0.30 (CH_2Cl_2); 96% *ee*, $[\alpha]^{32}_D$ = -18.4 (*c* 1.03, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03-6.96 (m, 2H), 6.84-6.81 (m, 1H), 5.89 (s, 1H), 5.14 (dd, *J* = 6.7, 3.9 Hz, 1H), 3.57 (dd, *J* = 18.3, 7.4 Hz, 1H), 2.98 (dd, *J* = 18.3, 4.1 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.6, 159.3 (d, $^1J_{F\text{-}C}$ = 244.3 Hz), 147.0 (d, $^4J_{F\text{-}C}$ = 2.7 Hz), 123.1 (d, $^3J_{F\text{-}C}$ = 7.1 Hz), 120.6 (d, $^3J_{F\text{-}C}$ = 8.3 Hz), 116.6 (d, $^2J_{F\text{-}C}$ = 23.5 Hz), 112.7 (d, $^2J_{F\text{-}C}$ = 24.8 Hz), 53.0, 46.4, 30.8; HRMS (ESI): m/z calculated for $C_{10}H_{10}FNNaO_4S$ $[M+Na]^+$ 282.0207, found: 282.0210; HPLC (Chiralcel IC column, hexane/iPrOH = 70/30, 0.8 mL/min, 220 nm): t_1 = 8.5 min (major, *S*), t_2 = 10.7 min.



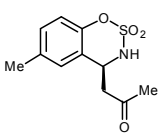
2c: White solid; mp 123.2-124.1°C; R_f = 0.34 (CH_2Cl_2); 97% *ee*, $[\alpha]^{30}_D$ = -52.3 (*c* 1.17, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (ddd, *J* = 8.8, 2.4, 0.5 Hz, 1H), 7.10 – 7.09 (m, 1H), 6.98 (d, *J* = 8.8 Hz, 1H), 5.78 (d, *J* = 5.2 Hz, 1H), 5.14 (d, *J* = 3.6 Hz, 1H), 3.61 (dd, *J* = 18.4, 7.2 Hz, 1H), 2.99 (dd, *J* = 18.4, 4.0 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ206.3, 149.7, 130.7, 129.7, 125.7, 122.9, 120.5, 53.1, 46.1, 30.9; HRMS (ESI): m/z calculated for $C_{10}H_{10}ClNNaO_4S$ $[M+Na]^+$ 297.9911, found: 297.9914; HPLC (Chiralcel IC column, hexane/iPrOH = 70/30, 0.8 mL/min, 220 nm): t_1 = 7.2 min

[2] H.-X. Zhang, J. Nie, H. Cai and J.-A. Ma *Org. Lett.*, 2014, **16**, 2542.

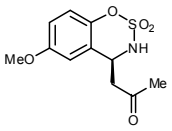
(major, *S*), t_2 = 8.5 min.



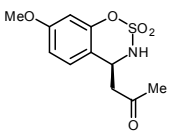
2d: White solid; mp 125.3-126.6°C; R_f = 0.34 (CH_2Cl_2); 91% *ee*, $[\alpha]^{30}_D$ = -42.3 (*c* 0.93, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.2 Hz, 1H), 7.25 (s, 1H), 6.92 (d, *J* = 8.6 Hz, 1H), 5.82 (s, 1H), 5.15 (s, 1H), 3.61 (dd, *J* = 18.3, 7.0 Hz, 1H), 2.98 (dd, *J* = 167.6, 1.2 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.4, 150.1, 132.6, 128.7, 123.3, 120.8, 118.1, 52.9, 46.3, 30.9; HRMS (ESI): m/z calculated for $C_{10}H_{1O}BrNNaO_4S$ $[M+Na]^+$ 341.9406, found: 341.9408; HPLC (Chiralcel IC column, hexane/iPrOH = 70/30, 0.8 mL/min, 220 nm): t_1 = 7.4 min (major, *S*), t_2 = 8.7 min.



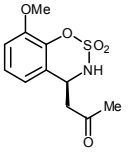
2e: White solid; mp 111.9-112.6°C; R_f = 0.29 (CH_2Cl_2); 95% *ee*, $[\alpha]^{30}_D$ = -46.8 (*c* 1.06, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (d, *J* = 8.4 Hz, 1H), δ 6.89-6.88 (m, 2H), 5.78 (s, 1H), 5.12 (s, 1H), 3.59 (dd, *J* = 18.1, 7.9 Hz, 1H), 2.94 (dd, *J* = 18.1, 3.8 Hz, 1H), 2.30 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.7, 149.00, 135.2, 130.2, 126.1, 120.9, 118.8, 53.3, 46.6, 31.0, 20.8; HRMS (ESI): m/z calculated for $C_{11}H_{13}NNaO_4S$ $[M+Na]^+$ 278.0458, found: 278.0464; HPLC (Chiralcel IC column, hexane/iPrOH = 70/30, 0.8 mL/min, 220 nm): t_1 = 10.1 min (major, *S*), t_2 = 12.1 min.



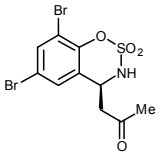
2f: White solid; mp 89.3-89.7°C; R_f = 0.27 (CH_2Cl_2); 95% *ee*, $[\alpha]^{30}_D$ = -35.1 (*c* 1.30, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.94 (d, *J* = 9.0 Hz, 1H), 6.82 (dd, *J* = 9.0, 2.8 Hz, 1H), 6.60 (d, *J* = 2.8 Hz, 1H), 5.76 (d, *J* = 7.5 Hz, 1H), 5.12 (d, *J* = 3.8 Hz, 1H), 3.76 (s, 3H), 3.58 (dd, *J* = 18.1, 7.7 Hz, 1H), 2.95 (dd, *J* = 18.1, 3.9 Hz, 1H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.9, 160.3, 151.8, 126.4, 113.0, 112.4, 103.8, 55.6, 53.0, 46.3, 31.1; HRMS (ESI): m/z calculated for $C_{11}H_{13}NNaO_5S$ $[M+Na]^+$294.0407, found: 294.0409; HPLC (Chiralcel IC column, hexane/iPrOH = 70/30, 0.8 mL/min, 220 nm): t_1 = 10.3 min (major, *S*), t_2 = 12.3 min.



2g: Colorless oil; R_f = 0.23 (CH_2Cl_2); 96% *ee*, $[\alpha]^{30}_D$ = -27.3 (*c* 1.17, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.94 (d, *J* = 8.6 Hz, 1H), 6.66 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.45 (s, 1H), 5.06 (dd, *J* = 7.7, 3.8 Hz, 1H), 4.83 (s, 1H), 3.75 (s, 3H), 3.47 (dd, *J* = 17.7, 8.0 Hz, 1H), 2.88 (dd, *J* = 17.8, 3.7 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.9, 160.3, 151.8, 126.4, 113.0, 112.4, 103.8, 55.6, 53.0, 46.3, 31.1; HRMS (ESI): m/z calculated for $C_{11}H_{13}NNaO_5S$ $[M+Na]^+$ 294.0407, found: 294.0410; HPLC (Chiralcel IC column, hexane/iPrOH = 70/30, 0.8 mL/min, 220 nm): t_1 = 15.2 min (major, *S*), t_2 = 21.7 min.

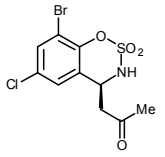


2h: White solid; mp 116.2-117.0°C; R_f = 0.21 (CH_2Cl_2); 95% *ee*, $[\alpha]^{31}_D$ = -24.3 (*c* 1.44, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (t, *J* = 8.1 Hz, 1H), 6.87 (d, *J* = 7.9 Hz, 1H), 6.66 (d, *J* = 7.9 Hz, 1H), 5.84 (s, 1H), 5.16 (s, 1H), 3.84 (s, 3H), 3.59 (dd, *J* = 18.1, 7.6 Hz, 1H), 2.94 (dd, *J* = 18.1, 3.9 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.7, 156.7, 144.8, 122.2, 119.9, 114.5, 111.1, 55.7, 53.4, 46.5, 31.0; HRMS (ESI): m/z calculated for $C_{11}H_{13}NNaO_5S$ $[M+Na]^+$ 294.0407, found: 294.0411; HPLC (Chiralcel IC column, hexane/iPrOH = 70/30, 0.8 mL/min, 220 nm): t_1 = 15.0 min (major, *S*), t_2 = 26.6 min.

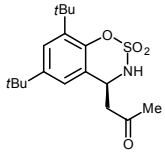


2i: White solid; mp 133.9-135.1°C; R_f = 0.28 (CH_2Cl_2); 97% *ee*, $[\alpha]^{31}_D$ = -12.6 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69-7.67 (m, 1H), 7.19 (s, 1H), 5.98 (s, 1H), 5.15 (s, 1H), 3.64-3.56 (m, 1H), 2.99 (d, *J* = 18.4 Hz, 1H), 2.26-2.25 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.2, 147.3, 135.8, 127.7, 124.8, 117.9,

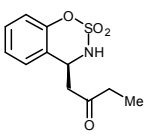
113.9, 53.1, 46.2, 30.9; HRMS (ESI): m/z calculated for $C_{10}H_9Br_2NNaO_4S$ $[M+Na]^+$ 419.8511, found: 419.8514; HPLC (Chiralcel IC column, hexane/iPrOH = 70/30, 0.8 mL/min, 220 nm): t_1 = 6.3 min (major, *S*), t_2 = 7.9 min.



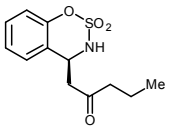
2j: White solid; mp 121,7-122.2°C; R_f = 0.26 (CH_2Cl_2); 96% *ee*, $[\alpha]^{32}_D$ = -6.1 (*c* 1.12, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 2.1 Hz, 1H), 7.05 (d, *J* = 1.8 Hz, 1H), 5.95 (s, 1H), 5.15 (s, 1H), 3.60 (dd, *J* = 18.4, 7.2 Hz, 1H), 3.00 (dd, *J* = 18.4, 4.0 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.2, 146.8, 133.1, 130.8, 124.9, 124.4, 113.5, 53.1, 46.3, 30.8; HRMS (ESI): m/z calculated for $C_{10}H_9BrClNNaO_4S$ $[M+Na]^+$ 375.9016, found: 375.9015; HPLC (Chiralcel IC column, hexane/iPrOH = 70/30, 0.8 mL/min, 220 nm): t_1 = 6.1 min (major, *S*), t_2 = 7.8 min.



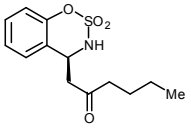
2k: White solid; mp 143.3-144.5°C; R_f = 0.29 (CH_2Cl_2); 93% *ee*, $[\alpha]^{31}_D$ = -37.3 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, *J* = 2.2 Hz, 1H), 6.94 (d, *J* = 2.0 Hz, 1H), 5.74 (s, 1H), 5.15 (dd, *J* = 8.4, 3.8 Hz, 1H), 3.61 (dd, *J* = 17.9, 8.5 Hz, 1H), 2.92 (dd, *J* = 17.9, 3.9 Hz, 1H), 2.24 (s, 3H), 1.40 (s, 9H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.8, 148.0, 147.6, 139.4, 124.3, 121.8, 120.7, 53.6, 47.4, 35.1, 34.6, 31.3, 30.9, 30.0; HRMS (ESI): m/z calculated for $C_{18}H_{27}NNaO_4S$ $[M+Na]^+$ 376.1553, found: 376.1557; HPLC (Chiralcel IC column, hexane/iPrOH = 70/30, 0.8 mL/min, 220 nm): t_1 = 5.8 min (major, *S*), t_2 = 6.4 min.



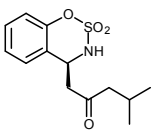
4a: Known compound[2]; R_f = 0.34 (CH_2Cl_2); 96% *ee*, $[\alpha]^{31}_D$ = -26.7 (*c* 0.97, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.29 (m, 1H), 7.17 (td, *J* = 7.6, 1.0 Hz, 1H), 7.11-7.09 (m, 1H), 7.03 (dd, *J* = 8.2, 0.8 Hz, 1H), 5.78 (d, *J* = 4.3 Hz, 1H), 5.19 (d, *J* = 3.4 Hz, 1H), 3.61 (dd, *J* = 17.9, 7.5 Hz, 1H), 2.93 (dd, *J* = 17.9, 3.9 Hz, 1H), 2.58-2.46 (m, 2H), 1.06 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.5, 151.2, 129.6, 125.7, 125.4, 121.4, 119.2, 53.6, 45.0, 37.2, 7.4; HPLC (Chiralcel IC column, hexane/iPrOH = 70/30, 0.8 mL/min, 220 nm): t_1 = 9.5 min (major, *S*), t_2 = 15.9 min.



4b: Known compound[2]; R_f = 0.18 (CH_2Cl_2); 95% *ee*, $[\alpha]^{31}_D$ = -21.3 (*c* 0.97, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.27 (m, 1H), 7.16 (td, *J* = 7.5, 0.8 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 5.93 (d, *J* = 8.0 Hz, 1H), 5.18 (td, *J* = 7.8, 3.9 Hz, 1H), 3.58 (dd, *J* = 17.9, 7.7Hz, 1H), 2.91 (dd, *J* = 17.9, 3.9 Hz, 1H), 2.48-2.43 (m, 2H), 1.59 (dd, *J* = 14.7, 7.4 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.3, 151.1, 129.5, 125.8, 125.4, 121.4, 119.0, 53.4, 45.7, 45.5, 16.8, 13.5; HPLC (Chiralcel IC column, hexane/iPrOH = 70/30, 0.8 mL/min, 220 nm): t_1 = 8.3 min (major, *S*), t_2 = 13.3 min.

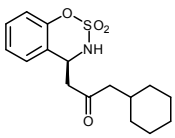


4c: White solid; mp 43.1-44.3°C; R_f = 0.56 (CH_2Cl_2); 97% *ee*, $[\alpha]^{31}_D$ = -31.4 (*c* 0.92, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.29 (m, 1H), 7.16 (t, *J* = 7.1 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 5.90 (s, 1H), 5.18 (s, 1H), 3.59 (dd, *J* = 17.9, 7.6 Hz, 1H), 2.91 (dd, *J* = 17.9, 3.9 Hz, 1H), 2.54-2.41 (m, 2H), 1.58-1.50 (m, 2H), 1.33-1.24 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.4, 151.1, 129.5, 125.8, 125.4, 121.4, 119.0, 53.4, 45.5, 43.6, 25.4, 22.1, 13.7; HRMS (ESI): m/z calculated for $C_{13}H_{17}NNaO_4S$ $[M+Na]^+$ 306.0771, found: 306.0773; HPLC (Chiralcel IC column, hexane/iPrOH = 70/30, 0.8 mL/min, 220 nm): t_1 = 7.3 min (major, *S*), t_2 = 12.4 min.

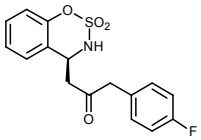


4d: Yellow solid; mp 36.3-37.5°C; R_f = 0.47 (CH_2Cl_2); 96% *ee*, $[\alpha]^{32}_D$ = -31.4 (*c*

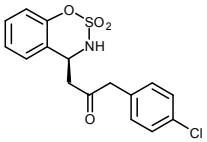
0.97, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.29 (t, *J* = 7.7 Hz, 1H), 7.18-7.14 (m, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 5.96 (s, 1H), 5.18 (td, *J* = 7.8, 4.0 Hz, 1H), 3.58 (dd, *J* = 18.0, 7.6 Hz, 1H), 2.88 (dd, *J* = 18.0, 3.9 Hz, 1H), 2.35 (d, *J* = 7.0 Hz, 2H), 2.17-2.07 (m, 1H), 0.89 (dd, *J* = 6.6, 2.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.1, 151.1, 129.5, 1265.9, 125.3, 121.5, 119.0, 53.3, 52.7, 46.0, 24.4, 22.4, 22.3; HRMS (ESI): m/z calculated for $C_{13}H_{17}NNaO_4S$ $[M+Na]^+$ 306.0771, found: 306.0774; HPLC (Chiralcel IC column, hexane/iPrOH = 70/30, 0.8 mL/min, 220 nm): t_1 = 6.4 min (major, *S*), t_2 = 8.8 min.



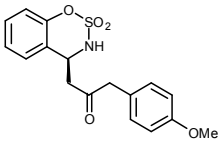
4e: White solid; mp 76.5-77.8°C; R_f = 0.32 (PE/EtOAc, 5:1); 87% *ee*, $[\alpha]^{32}_D$ = -38.1 (*c* 1.25, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ7.33-7.28 (m, 1H), 7.16 (td, *J* = 7.5, 1.0 Hz, 1H), 7.10-7.08 (m, 1H), 7.02 (dd, *J* = 8.3 Hz, 1.0 Hz, 1H), 5.87 (d, *J* = 8.0 Hz, 1H), 5.20-5.15 (m, 1H), 3.59 (dd, *J* = 18.0, 7.3 Hz, 1H), 2.89 (dd, *J* = 18.0, 3.9 Hz, 1H), 2.34 (d, *J* = 6.9 Hz, 2H), 1.87-1.76 (m, 1H), 1.68-1.60 (m, 4H), 1.30-1.06 (m, 4H), 0.96-0.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.1, 151.2, 129.6, 125.8, 125.3, 121.4, 119.2, 53.5, 51.6, 45.8, 33.8, 33.2, 33.1, 26.1, 26.02, 25.98; HRMS (ESI): m/z calculated for $C_{16}H_{21}NNaO_4S$ $[M+Na]^+$ 346.1089, found: 346.1088; HPLC (Chiralcel IC column, hexane/iPrOH = 70/30, 0.8 mL/min, 220 nm): t_1 = 7.2 min (major, *S*), t_2 = 9.3 min.



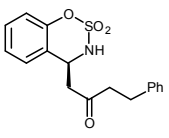
4f: White solid; mp 121.7-122.2°C; R_f = 0.29 (PE/EtOAc, 3:1); 92% *ee*, $[\alpha]^{32}_D$ = -13.8 (*c* 1.73, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.32-7.28 (m, 1H), 7.15-7.11 (m, 2H), 7.09-7.07 (m, 1H), 7.06-7.00 (m, 3H), 6.90 (d, *J* = 8.0 Hz, 7.7H), 5.66 (d, *J* = 8.1 Hz, 1H), 5.14 (td, *J* = 7.8, 3.9 Hz, 1H), 3.74 (s, 2H), 3.66 (dd, *J* = 18.0, 7.5 Hz, 1H), 2.92 (dd, *J* = 18.0, 3.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.1, 162.2 (d, $^1J_{F\text{-}C}$ = 245.0 Hz), 151.1, 131.1 (d, $^3J_{F\text{-}C}$ = 8.0 Hz), 129.7, 128.38 (d, $^4J_{F\text{-}C}$ = 3.3 Hz), 125.6, 125.4, 121.0, 119.1, 115.9 (d, $^2J_{F\text{-}C}$ = 21.4 Hz), 53.5, 50.0, 44.6; HRMS (ESI): m/z calculated for $C_{16}H_{14}FNNaO_4S$ $[M+Na]^+$ 358.0525, found: 358.0510; HPLC (Chiralcel IC column, hexane/iPrOH = 70/30, 0.8 mL/min, 220 nm): t_1 = 8.8 min (major, *S*), t_2 = 12.0 min.



4g: White solid; mp 121.7-122.2°C; R_f = 0.29 (PE/EtOAc, 3:1); 94% *ee*, $[\alpha]^{32}_D$ = -6.8 (*c* 1.66, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.31-7.28 (m, 3H), 7.12-7.08 (m, 3H), 7.01- 6.99 (m, 1H), 6.91 (d, *J* = 7.7 Hz, 1H), 5.69 (s, 1H), 5.14 (d, *J* = 3.5 Hz, 1H), 3.73 (s, 2H), 3.66 (dd, *J* = 18.0, 7.7 Hz, 1H), 2.92 (dd, *J* = 18.0, 3.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.9, 151.1, 133.5, 131.1, 130.8, 129.7, 129.1, 125.7, 125.4, 121.0, 119.1, 53.5, 50.1, 44.9; HRMS (ESI): m/z calculated for $C_{16}H_{14}ClNNaO_4S$ $[M+Na]^+$ 374.0230, found: 374.0198; HPLC (Chiralcel IC column, hexane/iPrOH = 70/30, 0.8 mL/min, 220 nm): t_1 = 9.3 min (major, *S*), t_2 = 12.3 min.

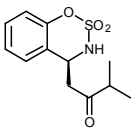


4h: White solid; mp 121.7-122.2°C; Yellow solid; mp 102.7-103.8°C; R_f = 0.43 (CH_2Cl_2); 94% *ee*, $[\alpha]^{31}_D$ = 6.1 (*c* 1.73, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.30-7.25 (m, 1H), 7.09-7.04 (m, 3H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.88-6.84 (m, 3H), 5.79 (s, 1H), 5.10 (d, *J* = 3.4 Hz, 1H), 3.80 (s, 3H), 3.68 (s, 2H), 3.63 (dd, *J* = 18.1, 7.2 Hz, 1H), 2.90 (dd, *J* = 18.1, 3.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.0, 158.9, 151.1, 130.5, 129.5, 125.7, 125.3, 124.7, 121.1, 118.9, 55.2, 53.4, 50.0, 44.1; HRMS (ESI): m/z calculated for $C_{17}H_{17}NNaO_5S$ $[M+Na]^+$ 370.0720, found: 370.0719; HPLC (Chiralcel IC column, hexane/iPrOH = 70/30, 0.8 mL/min, 220 nm): t_1 = 16.3 min (major, *S*), t_2 = 37.5 min.

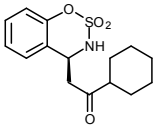


4i: White solid; mp 36.3-37.5°C; R_f = 0.57 (CH_2Cl_2); 96% *ee*, $[\alpha]^{31}_D$ = -23.4 (*c* 0.98, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.31-7.25 (m, 3H), 7.19 (t, *J* = 7.3

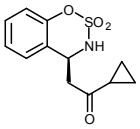
Hz, 1H), 7.15-7.11 (m, 3H), 7.00 (d, *J* = 8.4 Hz, 1H), 5.78 (s, 1H), 5.16 (d, *J* = 3.6 Hz, 1H), 3.56 (dd, *J* = 18.0, 7.7 Hz, 1H), 2.90-2.79 (5, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.1, 151.1, 140.2, 129.6, 128.6, 128.2, 126.3, 125.8, 125.4, 121.2, 119.1, 53.3, 45.9, 45.1, 29.3; HRMS (ESI): m/z calculated for $C_{17}H_{17}NNaO_4S$ $[M+Na]^+$ 354.0771, found: 354.0771; HPLC (Chiralcel IC column, hexane/iPrOH = 70/30, 0.8 mL/min, 220 nm): t_1 = 9.9 min (major, *S*), t_2 = 15.9 min.



4j: Known compound[2]; R_f = 0.49 (CH_2Cl_2); 96% ee, $[\alpha]^{20}_D$ = -51.2 (*c* 1.44 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.8 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.09 (m, 1H), 7.02 (dd, *J* = 8.2, 1.9 Hz, 1H), 5.84 (d, *J* = 10.9 Hz, 1H), 5.20 (s, 1H), 3.69 (dd, *J* = 18.1, 7.6 Hz, 1H), 2.93 (dd, *J* = 18.1, 3.8 Hz, 1H), 2.64 (m, *J* = 6.9 Hz, 1H), 1.11 (t, *J* = 6.8 Hz, 6H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ212.8, 151.1 129.6, 125.8, 125.4, 121.4, 119.1, 53.5, 43.5, 41.6, 17.8, 17.7; HPLC (Chiralcel IC column, hexane/iPrOH = 70/30, 0.8 mL/min 220 nm): t_1 = 6.6 min (major), t_2 = 10.7 min (minor).



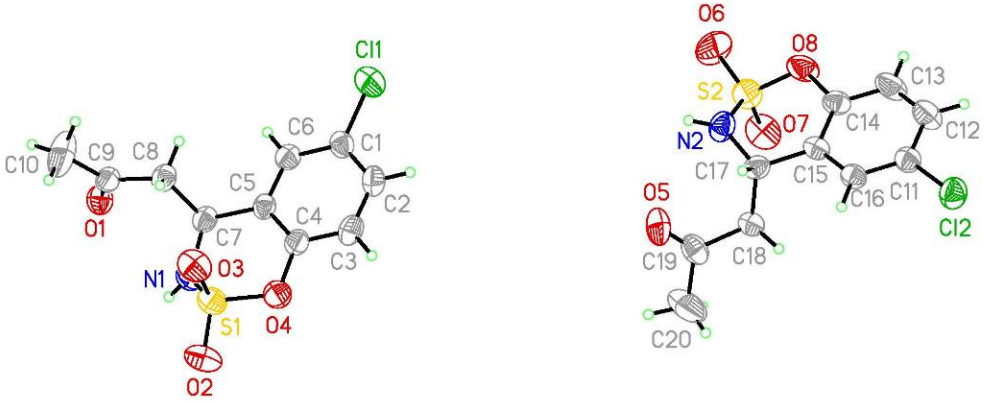
4k: Known compound[2]; R_f = 0.51 (CH_2Cl_2); 97% *ee*, $[\alpha]^{32}_D$ = -19.4 (*c* 0.97, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.27 (m, 1H), 7.16 (td, *J* = 7.5, 1.0 Hz, 1H), 7.08 (m, 1H), 7.00 (d, *J* = 8.3 Hz, 1H), 5.92 (s, 1H), 5.19 (d, *J* = 3.7 Hz, 1H), 3.67 (dd, *J* = 18.2, 7.6 Hz, 1H), 2.91 (dd, *J* = 18.2, 3.9 Hz, 1H), 2.38-2.34 (m, 1H), 1.87-1.81 (m, 2H), 1.79-1.76 (m, 2H), 1.68-1.65 (m, 1H), 1.39-1.29 (m, 2H), 1.25-1.15 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.1, 151.2, 129.5, 125.8, 125.3, 121.5, 119.1, 53.4, 51.3, 43.6, 28.1, 28.0, 25.6, 25.4; HPLC (Chiralcel IC column, hexane/iPrOH = 70/30, 0.8 mL/min, 220 nm): t_1 = 6.9 min (major, *S*), t_2 = 12.5 min.



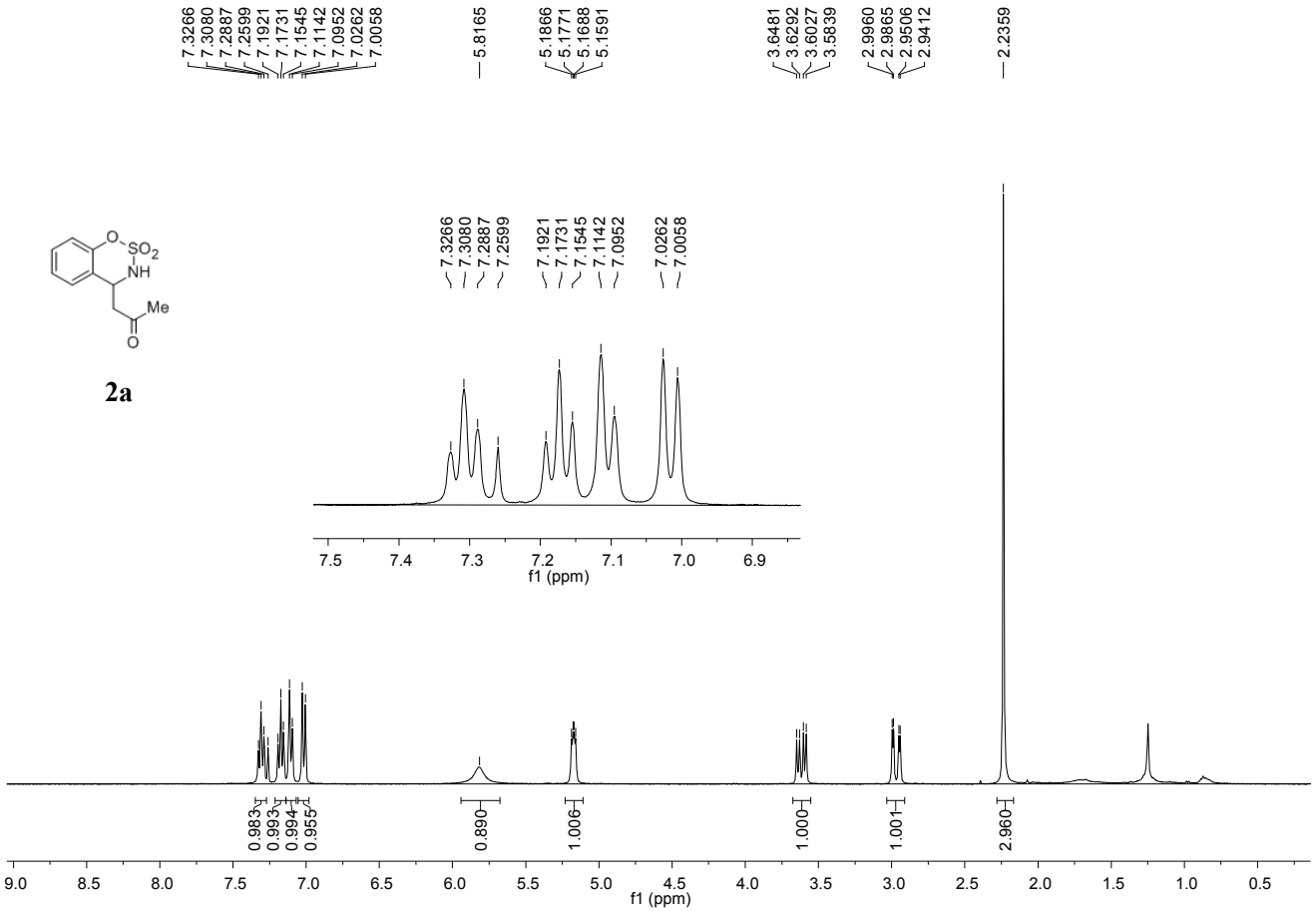
4l: Known compound[2]; R_f = 0.41 (CH_2CL_2); 95% ee, $[\alpha]^{30}_D$ = -43.92 (*c* 1.11 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 1H), 7.19 – 7.12 (m, 2H), 7.01 (d, *J* = 8.2 Hz, 1H), 5.96 (s, 1H), 5.17 (dd, *J* = 7.0, 3.8 Hz, 1H), 3.72 (dd, *J* = 18.0, 7.2 Hz, 1H), 3.11 (dd, *J* = 18.0, 3.9 Hz, 1H), 2.02 – 1.96 (m, 1H), 1.13 – 1.07 (m, 1H), 1.04 – 0.93 (m, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.0, 151.2, 129.5, 125.8, 125.3, 121.5, 119.0, 53.4, 45.7, 21.7, 11.7.5, 11.71; HPLC (Chiralcel IC column, hexane/iPrOH = 70/30, 0.8 mL/min 220 nm): t_1 = 9.7 min (major), t_2 = 13.7 min (minor).

4. X-ray structure for compound 2c

The needle-like crystals of the compound **2c** were grown from its solution in dichloromethane and hexane, and one of them is suitable for X-ray diffraction analysis. The correctness of the X-ray data and the structure had been checked by using the CheckCIF utility on the submission Web site: http://checkcif.iucr.org.



Copy of NMR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2.9412
2.2359
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SO2
NH
Me
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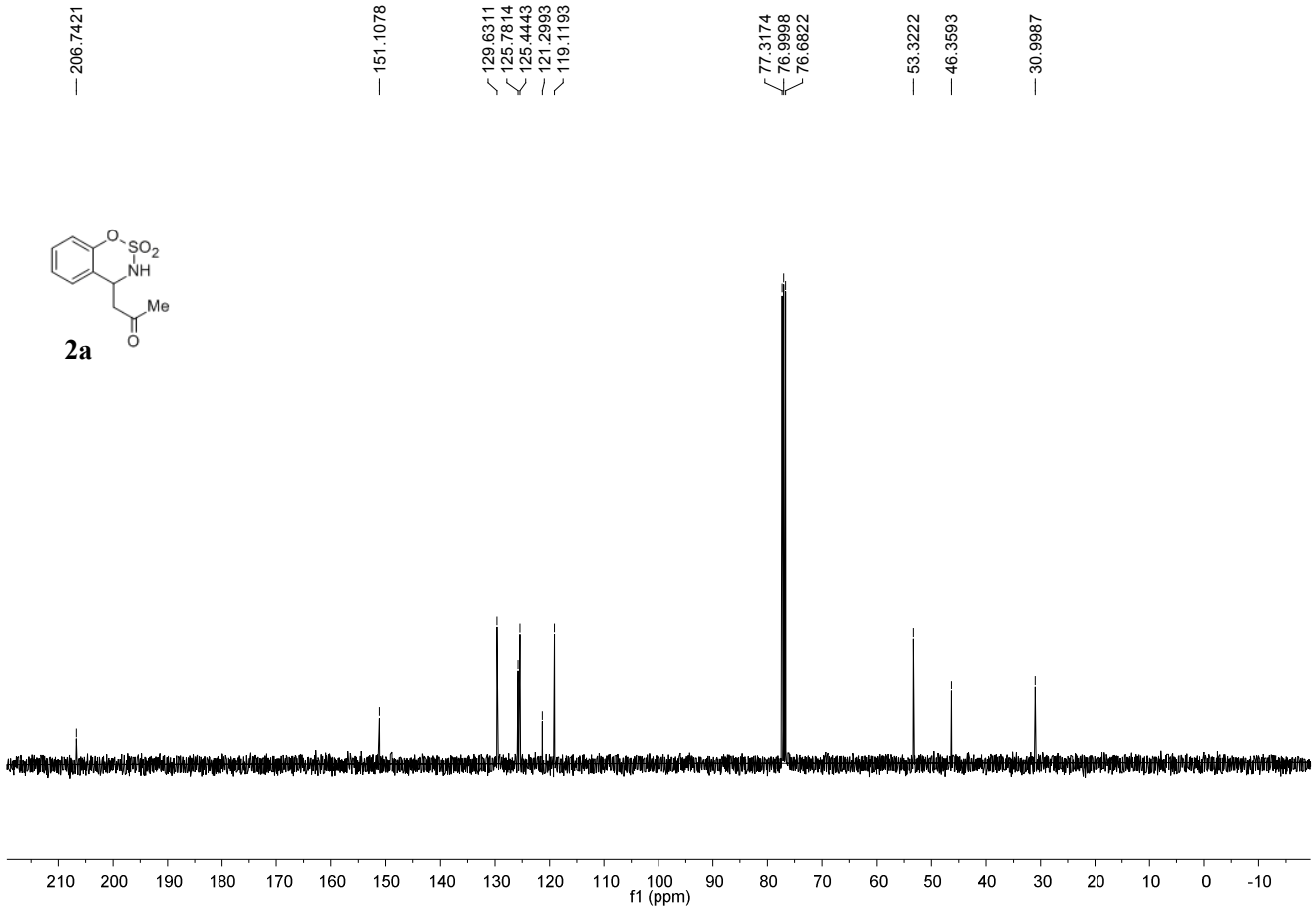
1.001
2.960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SO2
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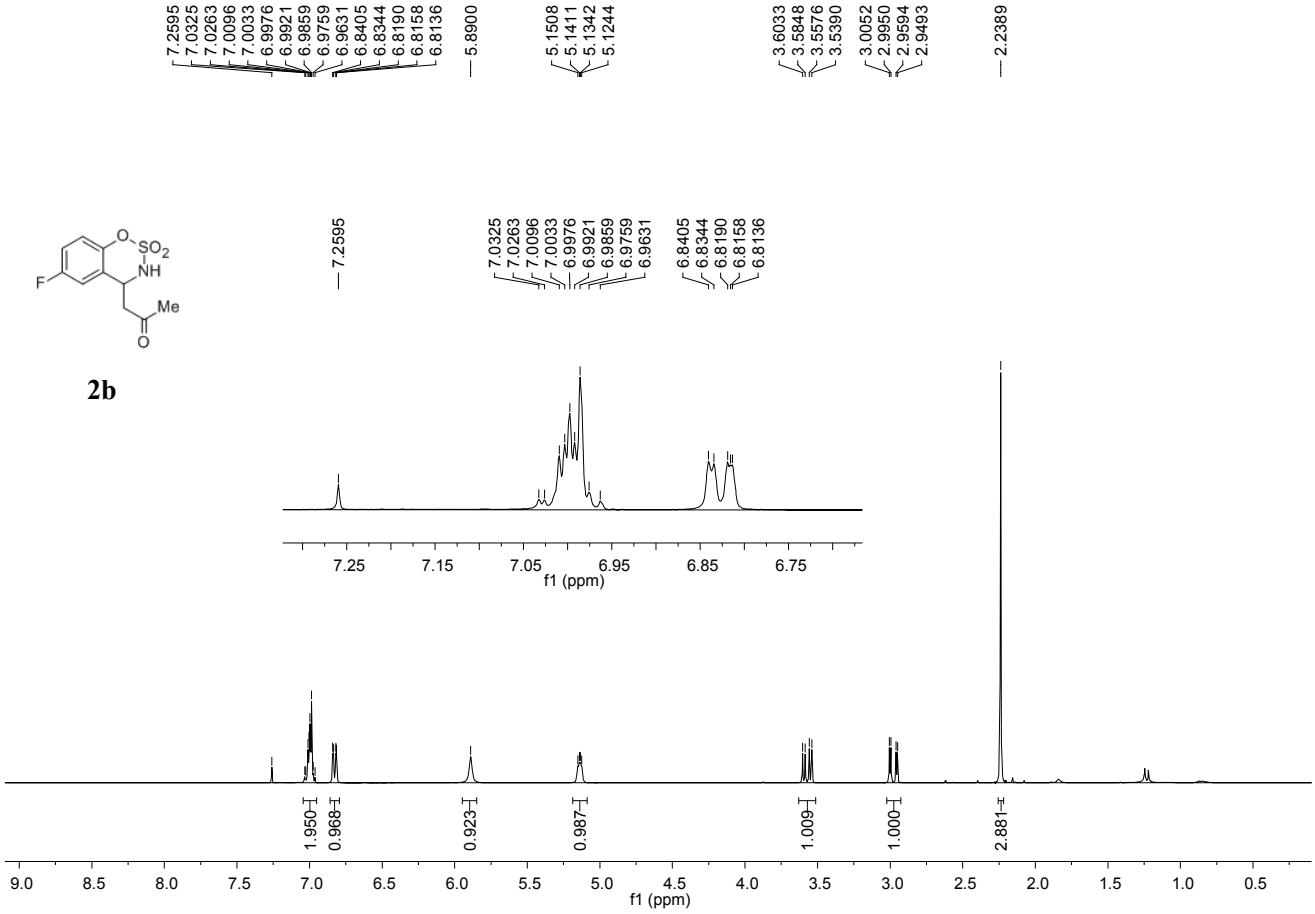
2a
f1 (ppm)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2.9950
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2b
f1 (ppm)
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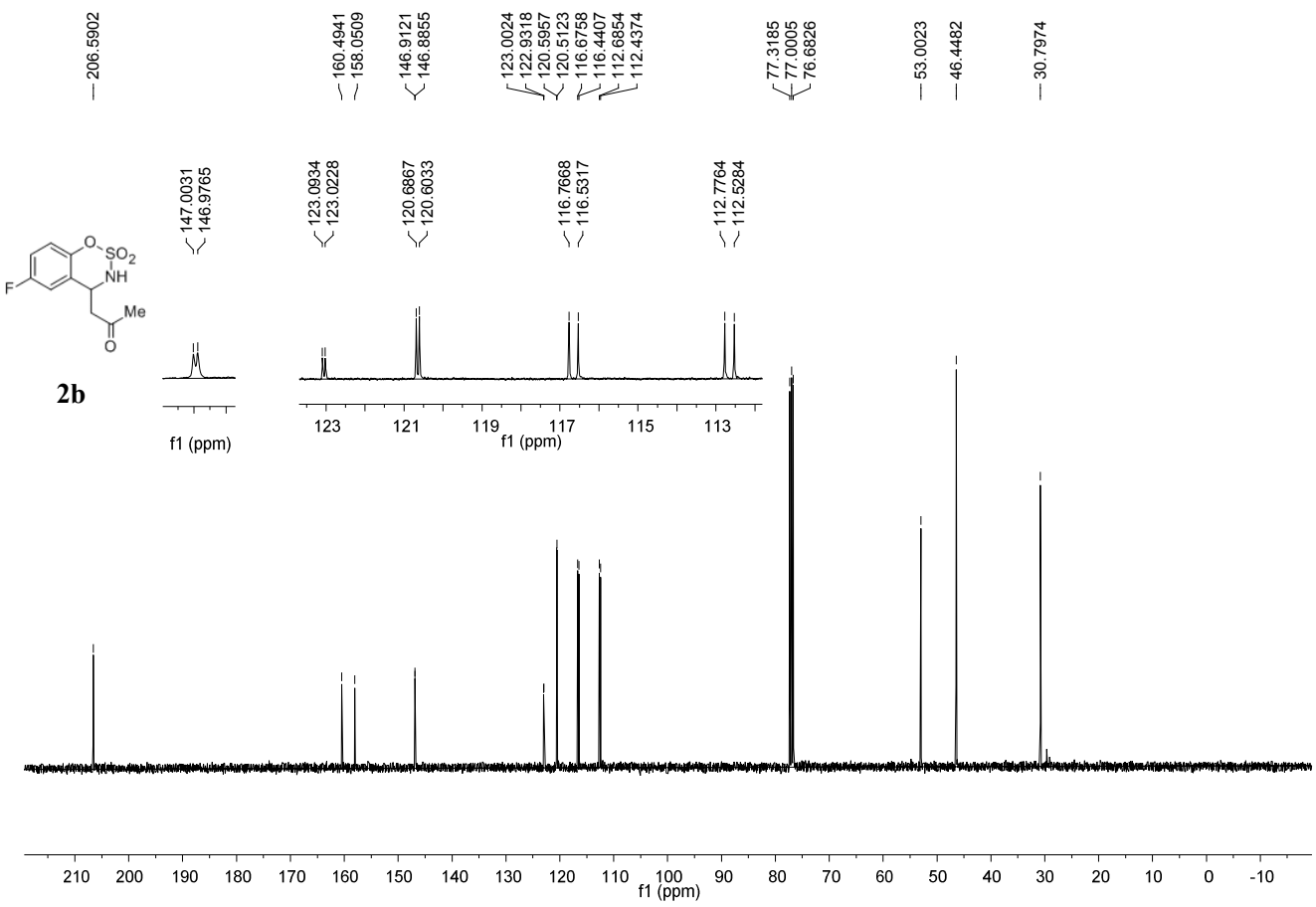
1.000
2.881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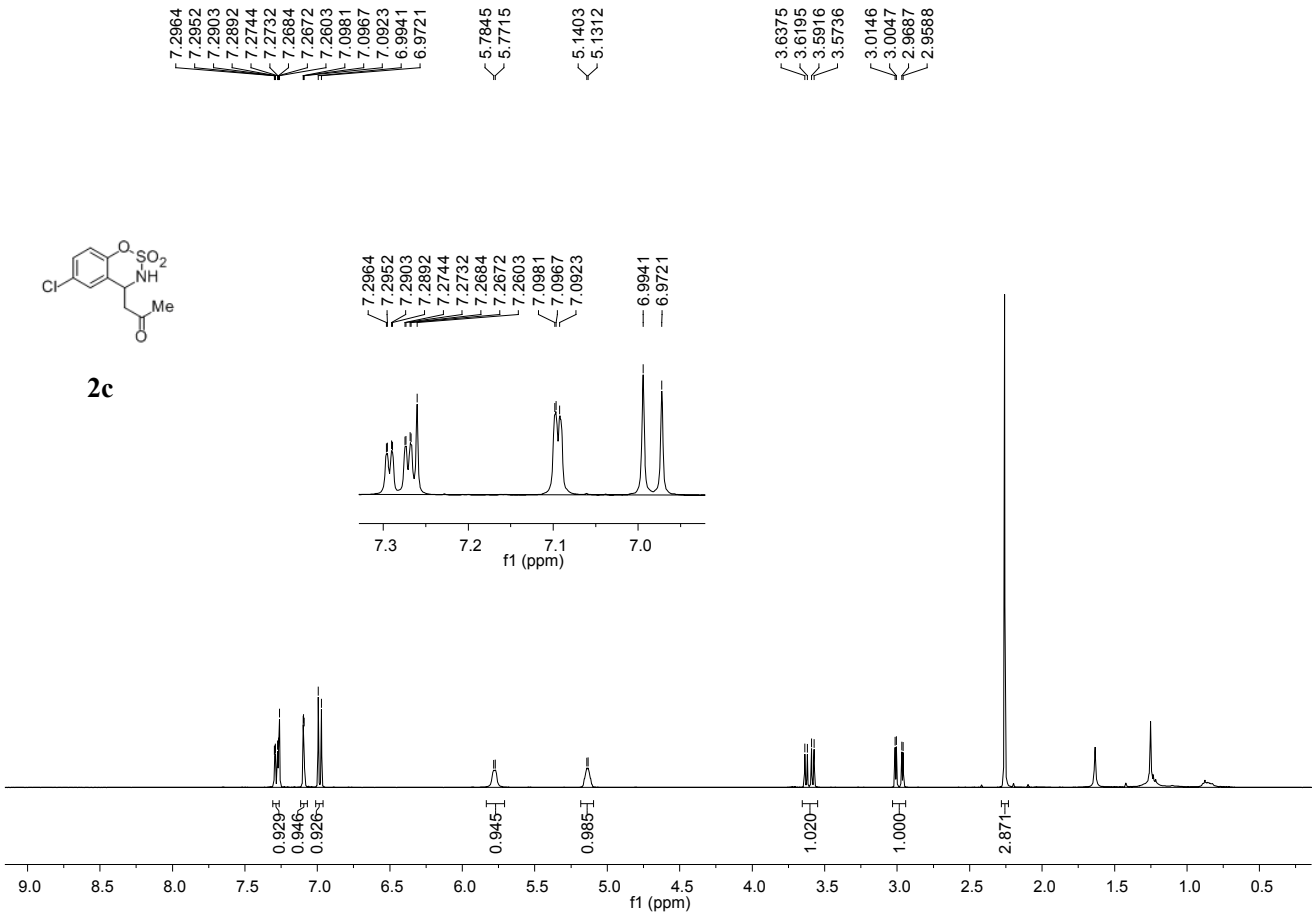
2b
f1 (ppm)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2.9588
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Me
O
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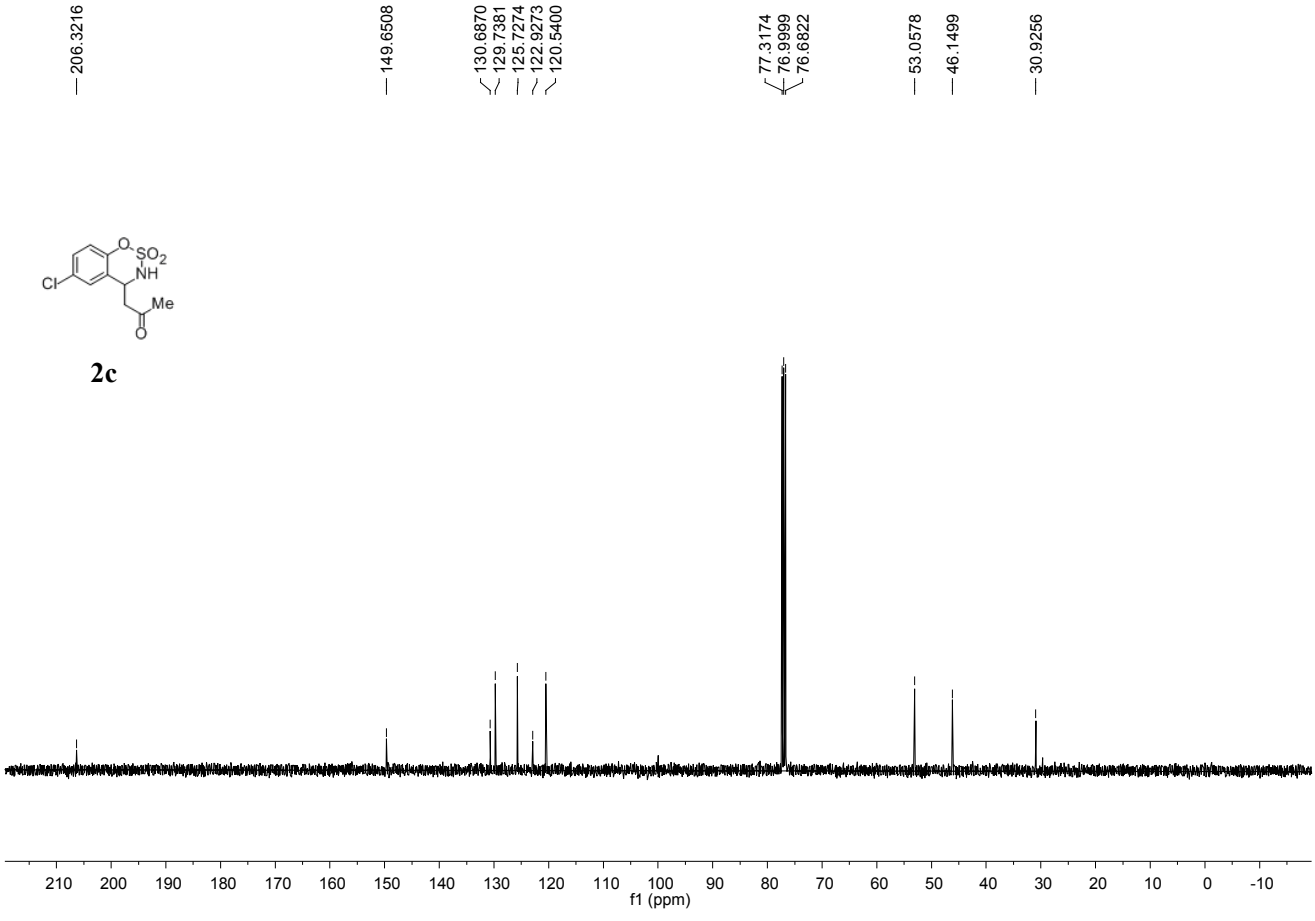
f1 (ppm)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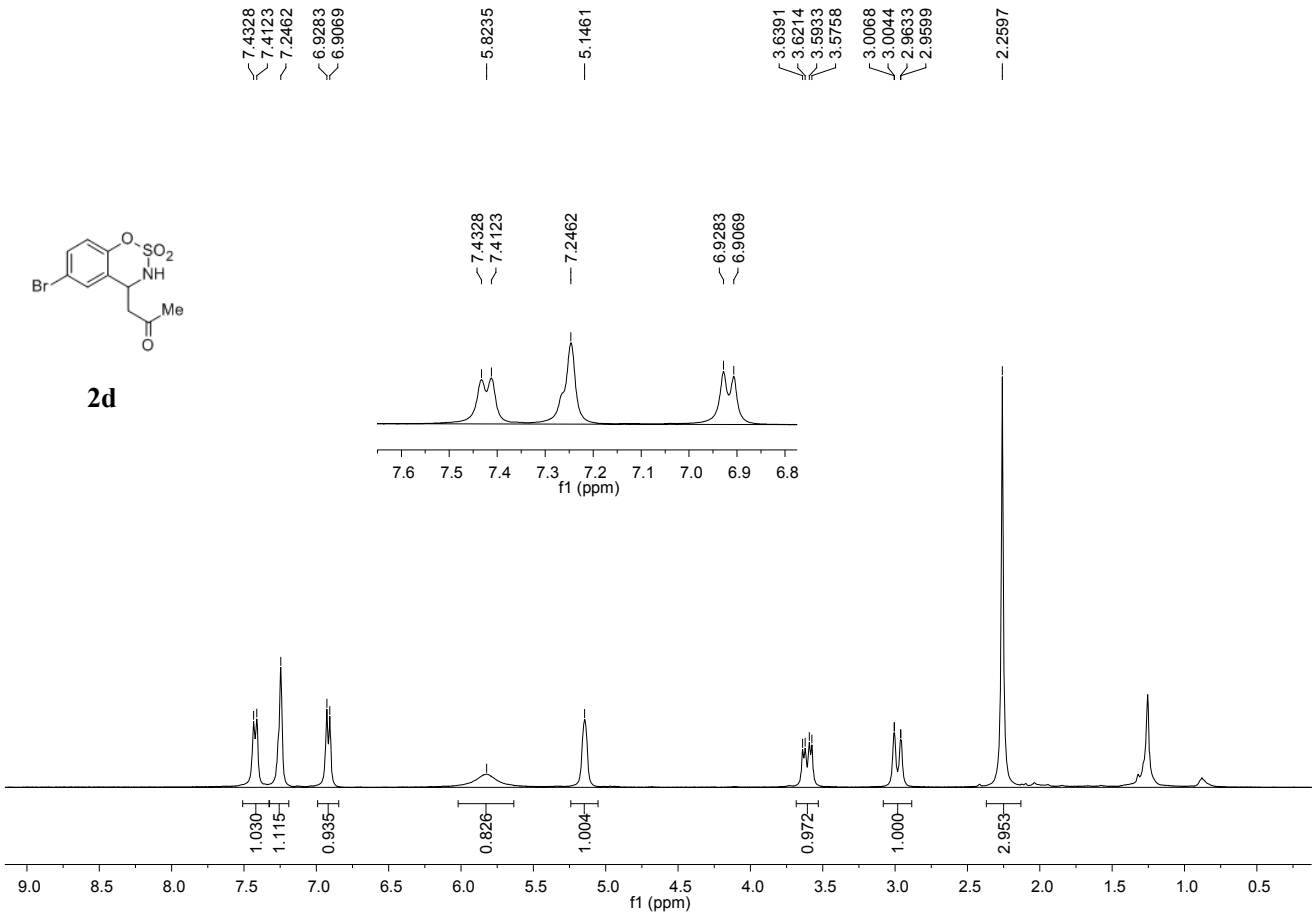
SO2
NH
O
Me
O
2c
f1 (ppm)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2d
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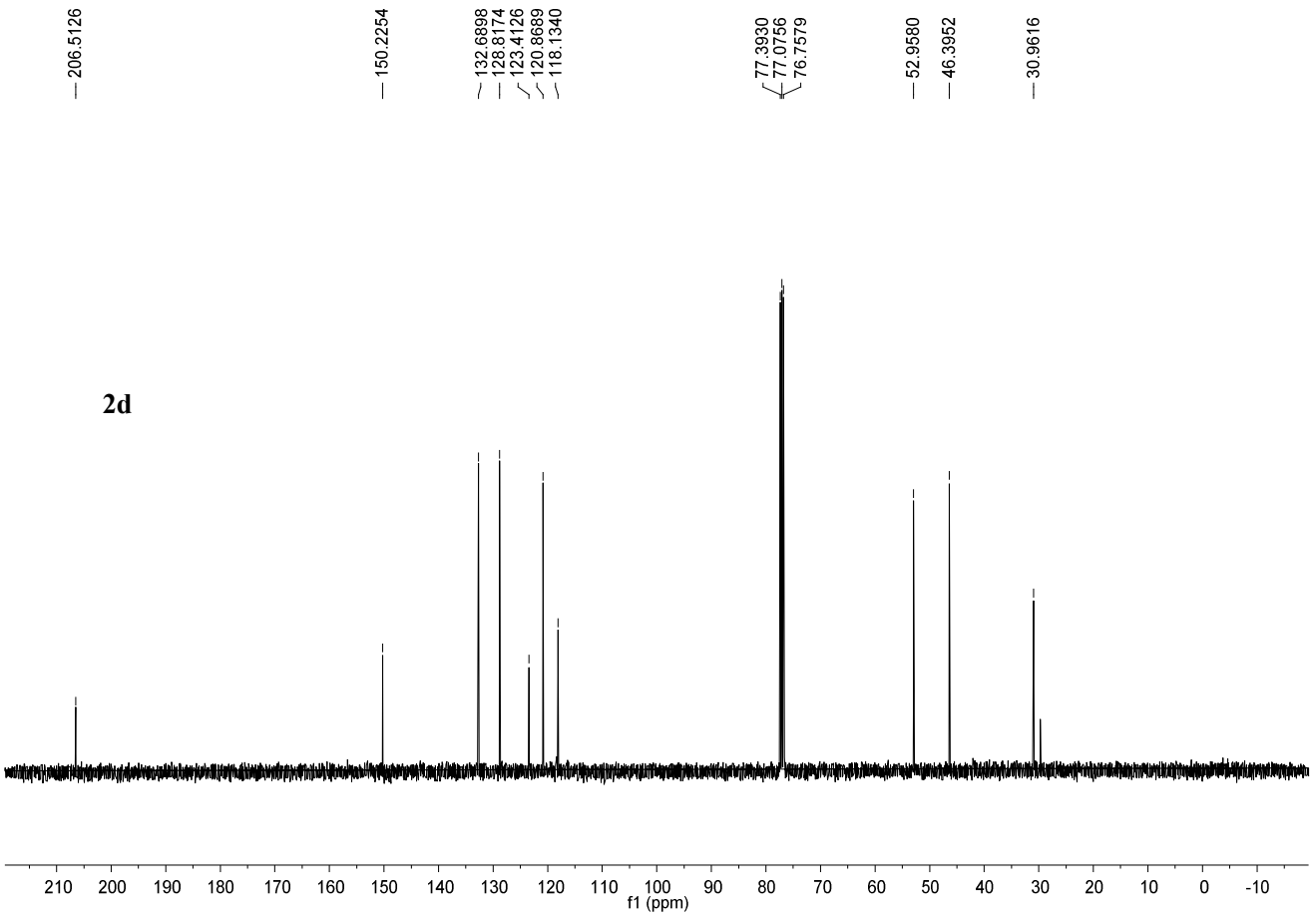
0.972
1.000
2.953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128.8174
123.4126
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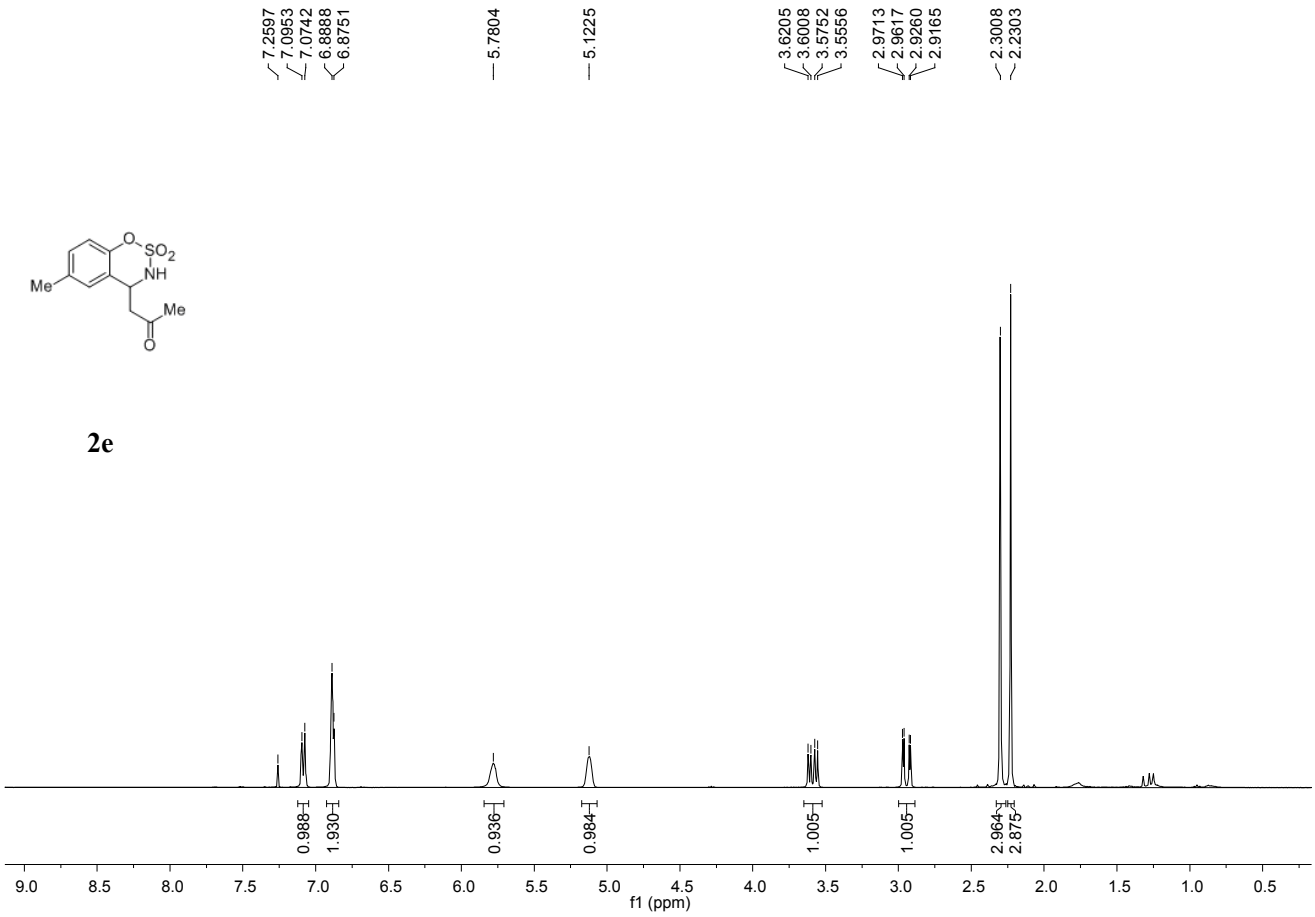
77.3930
77.0756
76.7579
52.9580
46.3952
30.9616
2d
f1 (ppm)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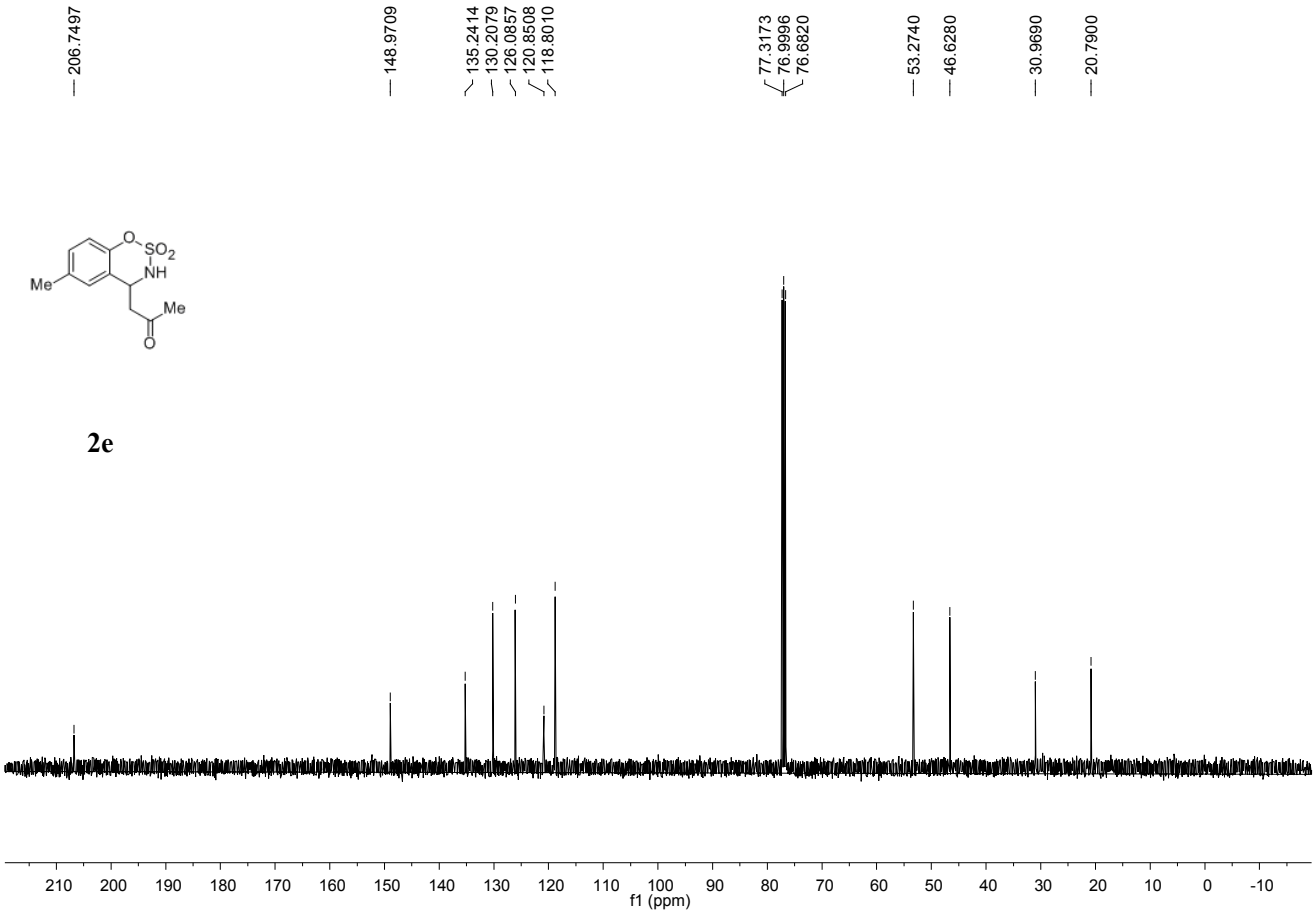
7.0953
7.0742
6.8888
6.8751
5.7804
5.1225
3.6205
3.6008
3.5752
3.5556
2.9713
2.9617
2.9260
2.9165
2.3008
2.2303
O
SO2
NH
Me
Me
O
0.988
1.930
0.936
0.984
1.005
1.005
2.964
2.875
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

2e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135.2414
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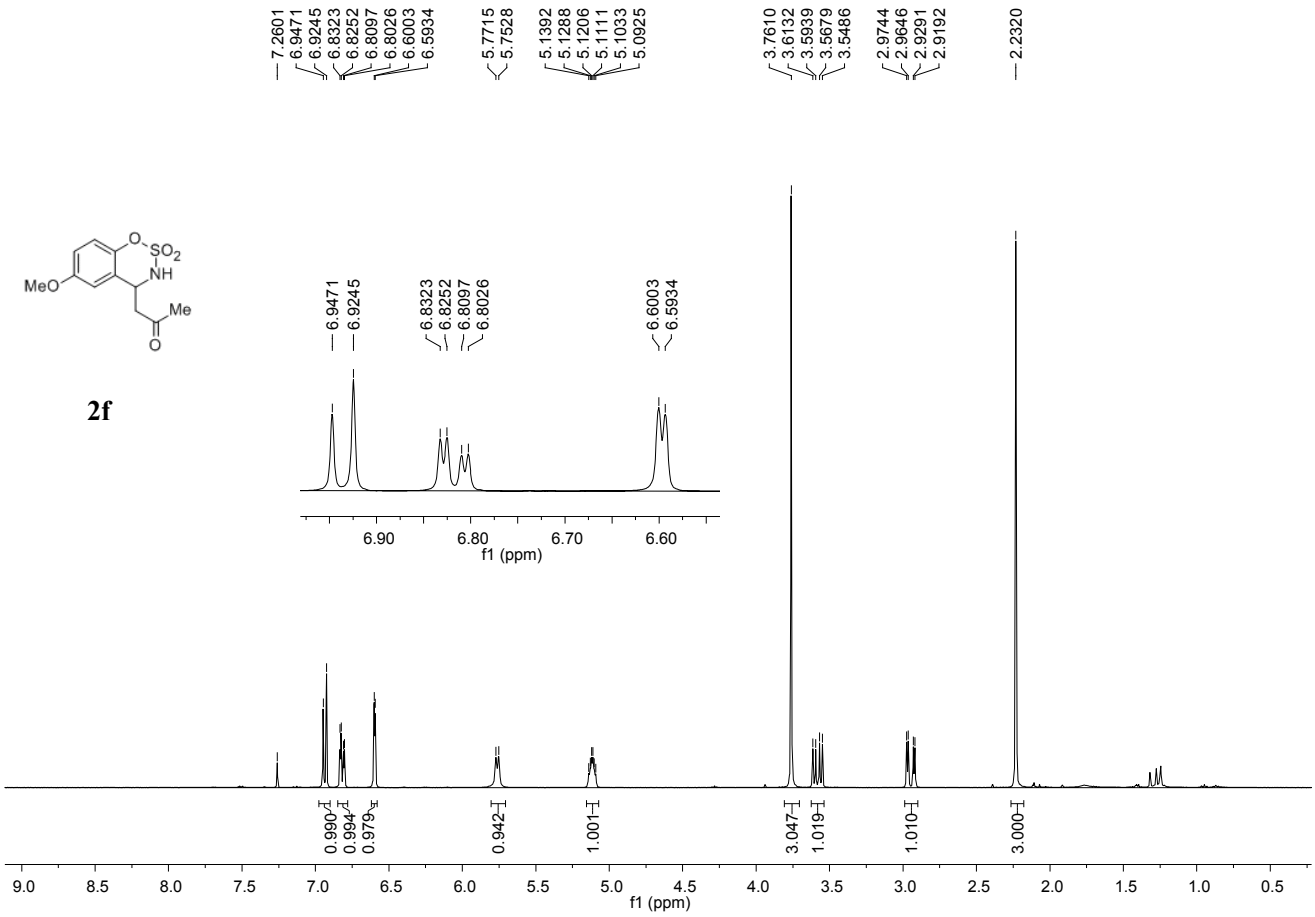
118.8010
77.3173
76.9996
76.6820
53.2740
46.6280
30.9690
20.7900
O
SO2
NH
Me
Me
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

2e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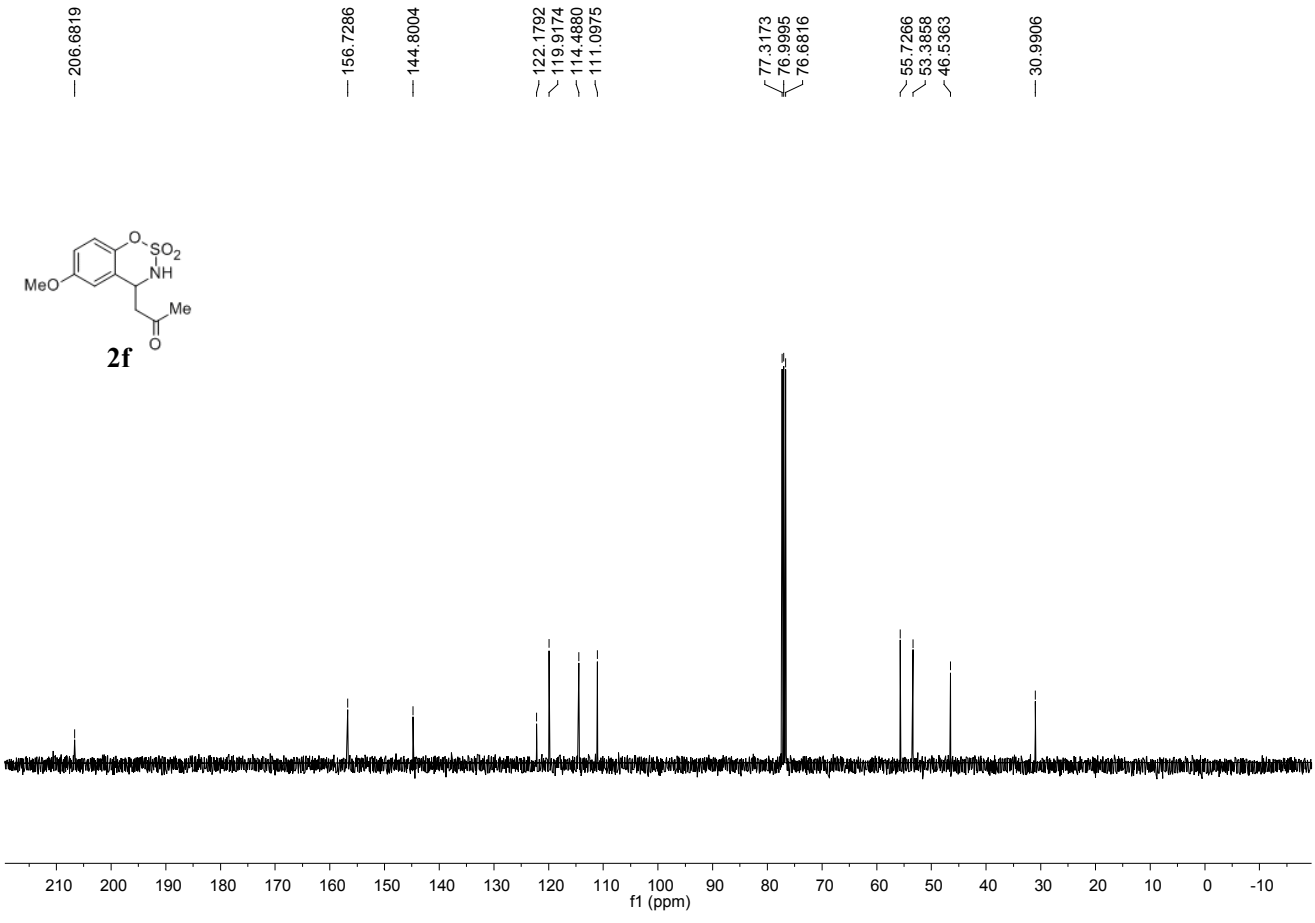
6.8252
6.8097
6.8026
6.6003
6.5934
5.7715
5.7528
5.1392
5.1288
5.1206
5.1111
5.1033
5.0925
3.7610
3.6132
3.5939
3.5679
3.5486
2.9744
2.9646
2.9291
2.9192
2.2320
MeO
SO2
NH
Me
O
2f
6.90
6.80
6.70
6.60
f1 (ppm)
0.990
0.994
0.979
0.942
1.001
3.047
1.019
1.010
3.000
f1 (ppm)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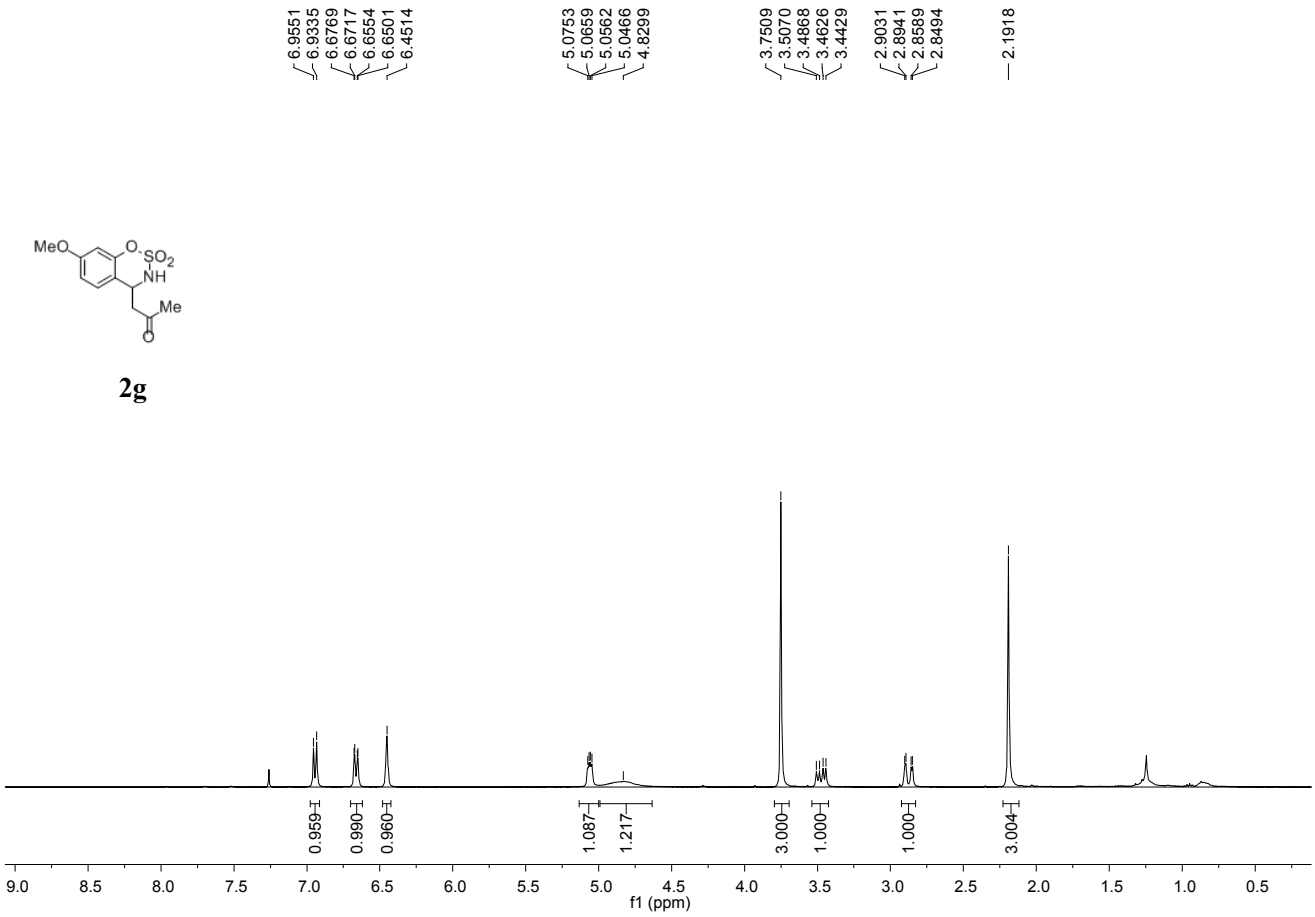
144.8004
122.1792
119.9174
114.4880
111.0975
77.3173
76.9995
76.6816
55.7266
53.3858
46.5363
30.9906
MeO
SO2
NH
Me
O
2f
f1 (ppm)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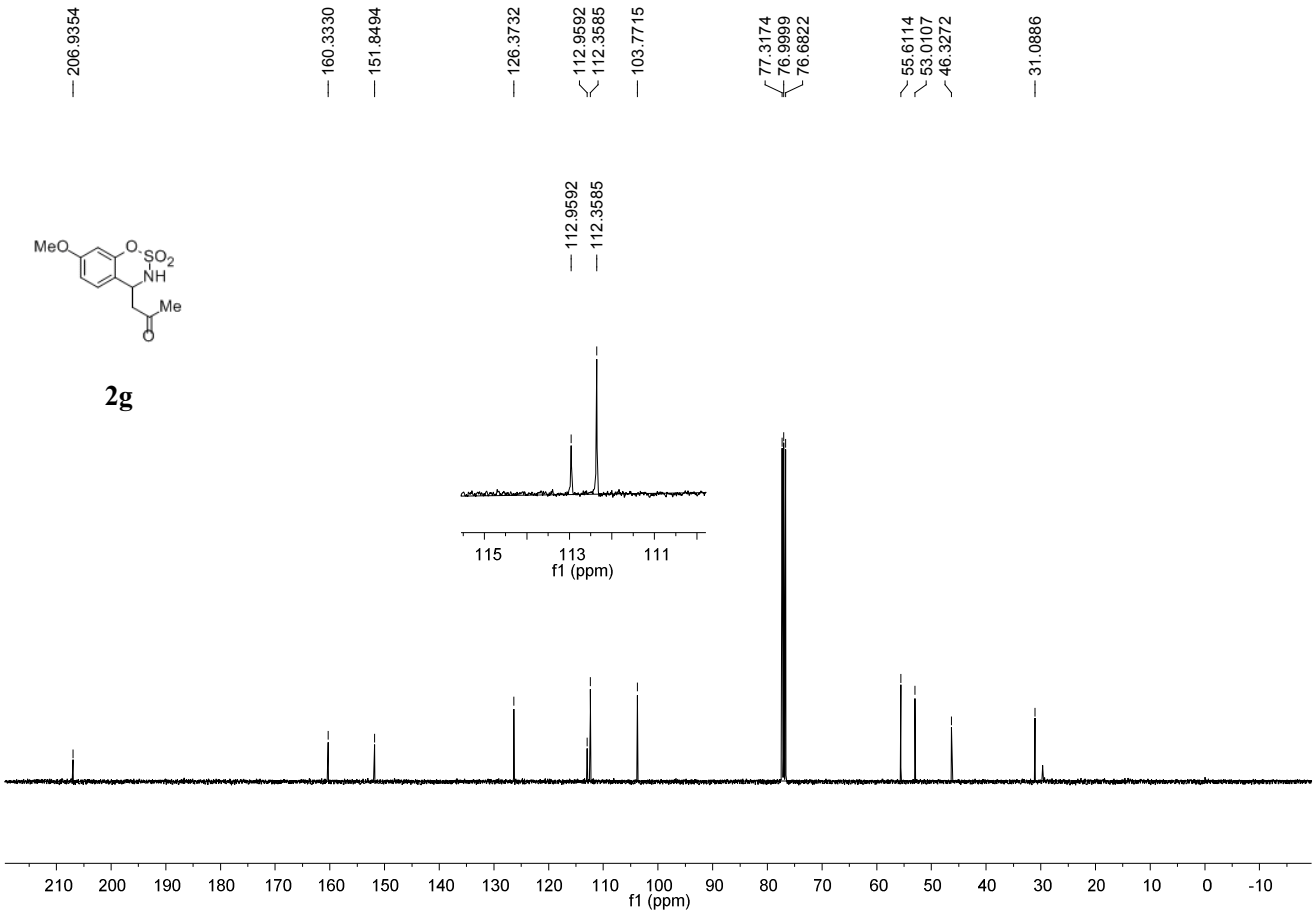
6.9335
6.6769
6.6717
6.6554
6.6501
6.4514
5.0753
5.0659
5.0562
5.0466
4.8299
3.7509
3.5070
3.4868
3.4626
3.4429
2.9031
2.8941
2.8589
2.8494
2.1918
MeO
O
SO2
NH
Me
O
0.959
0.990
0.960
1.087
1.217
3.000
1.000
1.000
3.004
f1 (ppm)

2g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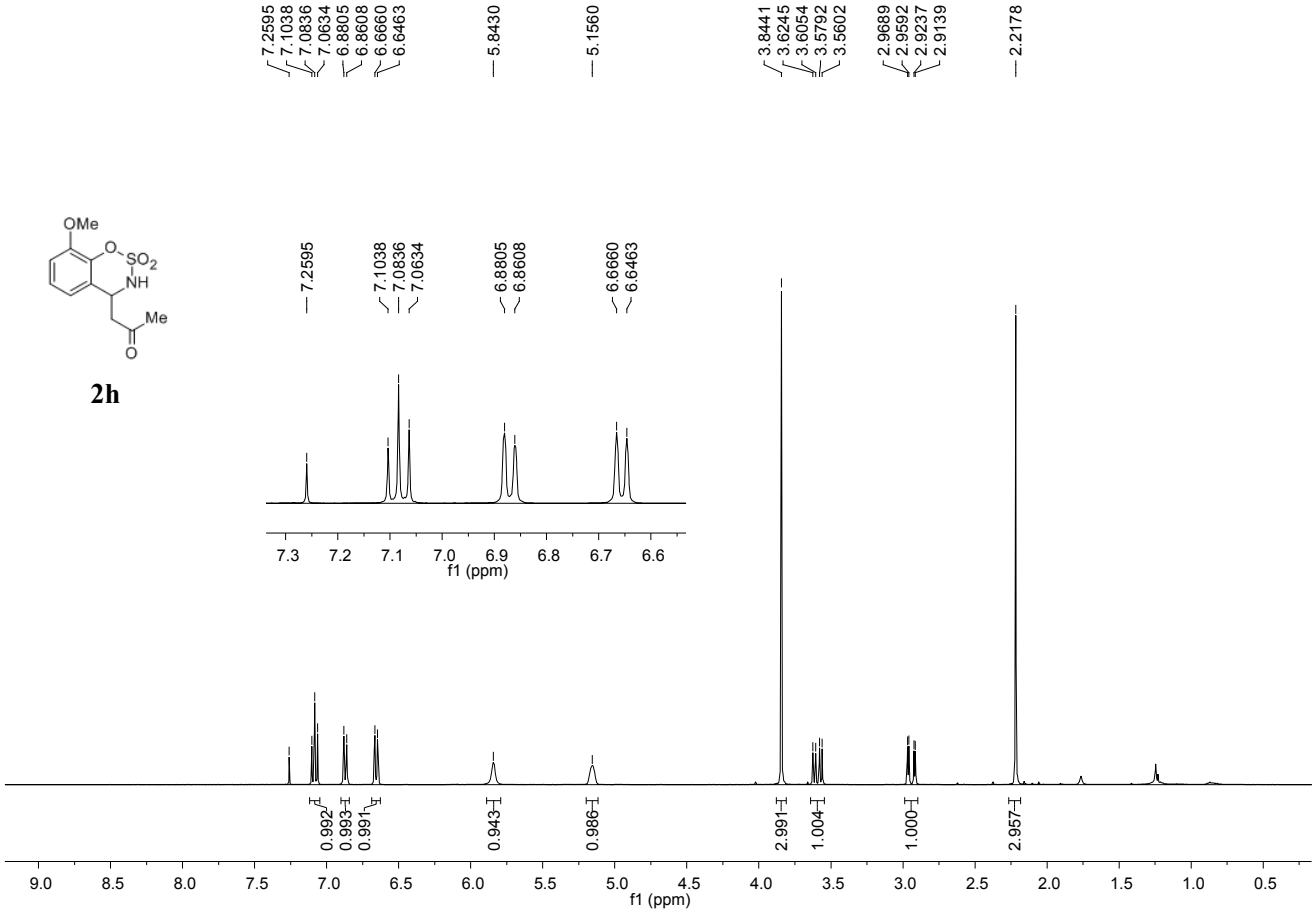
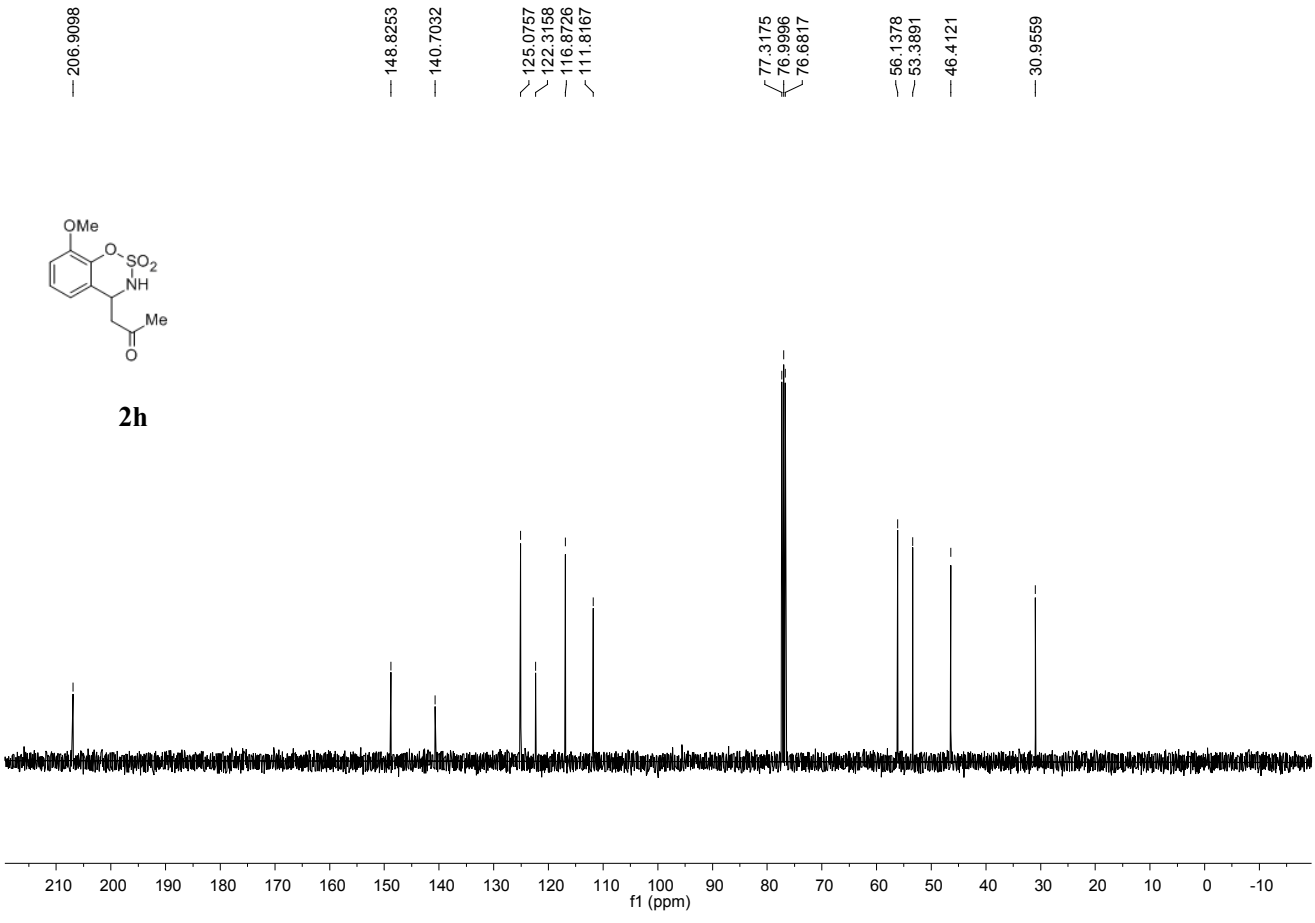
160.3330
151.8494
126.3732
112.9592
112.3585
103.7715
77.3174
76.9999
76.6822
55.6114
53.0107
46.3272
31.0886
MeO
O
SO2
NH
Me
O
112.9592
112.3585
115
113
111
f1 (ppm)
f1 (ppm)

2g


7.2595
7.1038
7.0836
7.0634
6.8805
6.8608
6.6660
6.6463
5.8430
5.1560
3.8441
3.6245
3.6054
3.5792
3.5602
2.9689
2.9592
2.9237
2.9139
2.2178
OMe
SO2
NH
Me
O
2h
f1 (ppm)
0.992
0.993
0.991
0.943
0.986
2.991
1.004
1.000
2.957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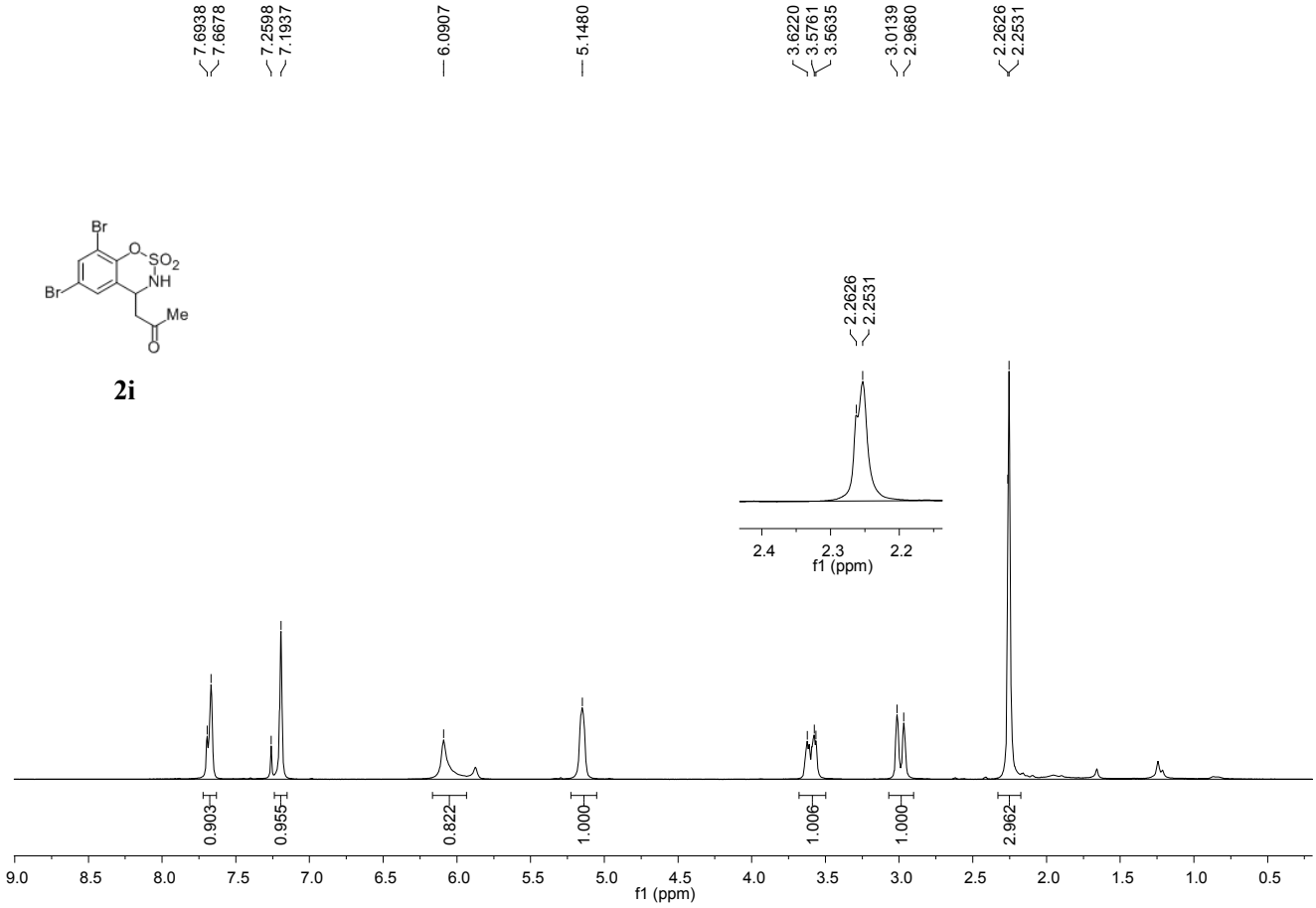
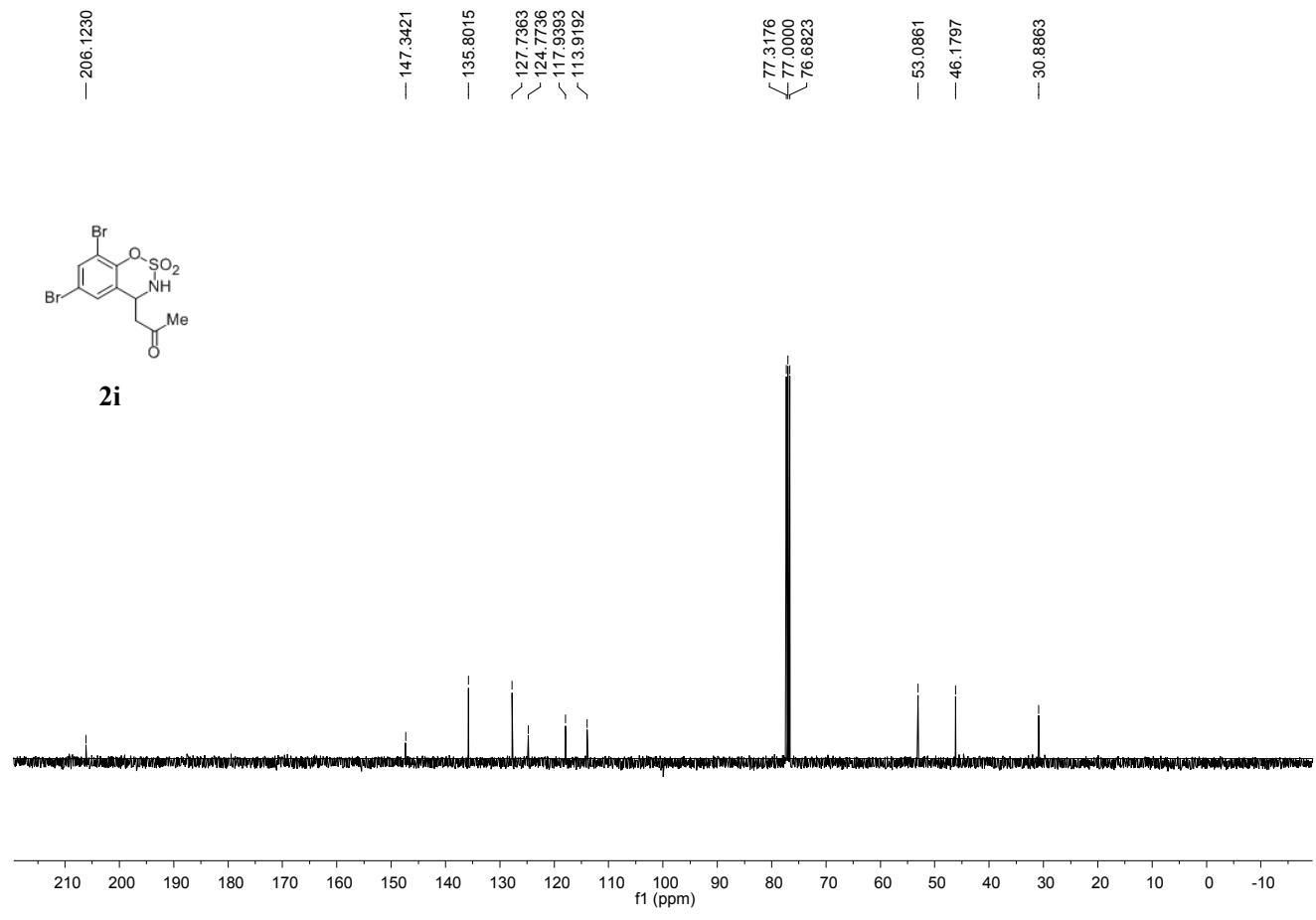
148.8253
140.7032
125.0757
122.3158
116.8726
111.8167
77.3175
76.9996
76.6817
56.1378
53.3891
46.4121
30.9559
OMe
SO2
NH
Me
O
2h
f1 (ppm)


7.6938
7.6678
7.2598
7.1937
6.0907
5.1480
3.6220
3.5761
3.5635
3.0139
2.9680
2.2626
2.2531
Br
O
SO2
NH
Br
Me
O
2.2626
2.2531
2.4
2.3
2.2
f1 (ppm)
0.903
0.955
0.822
1.000
1.006
1.000
2.962
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

2i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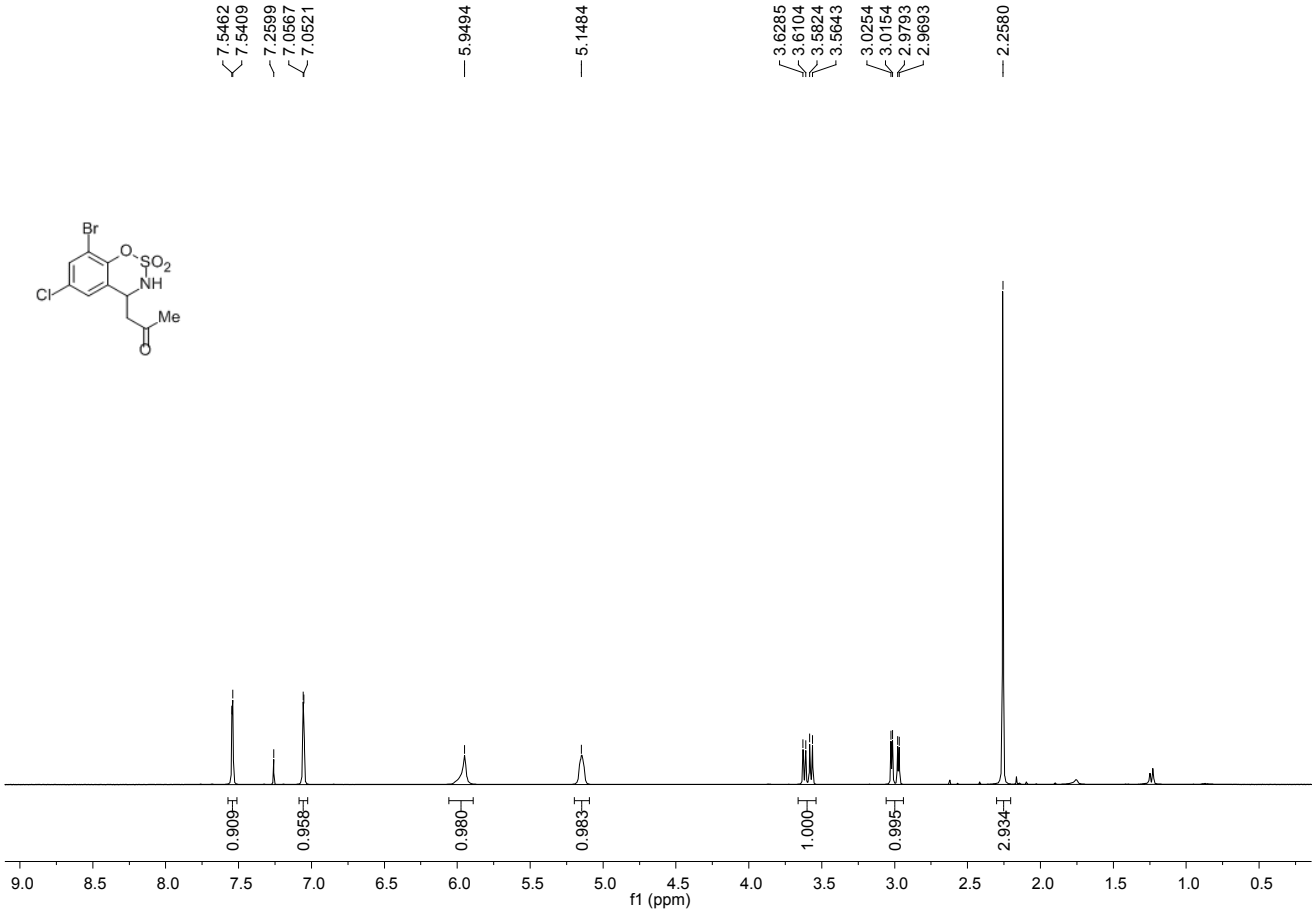
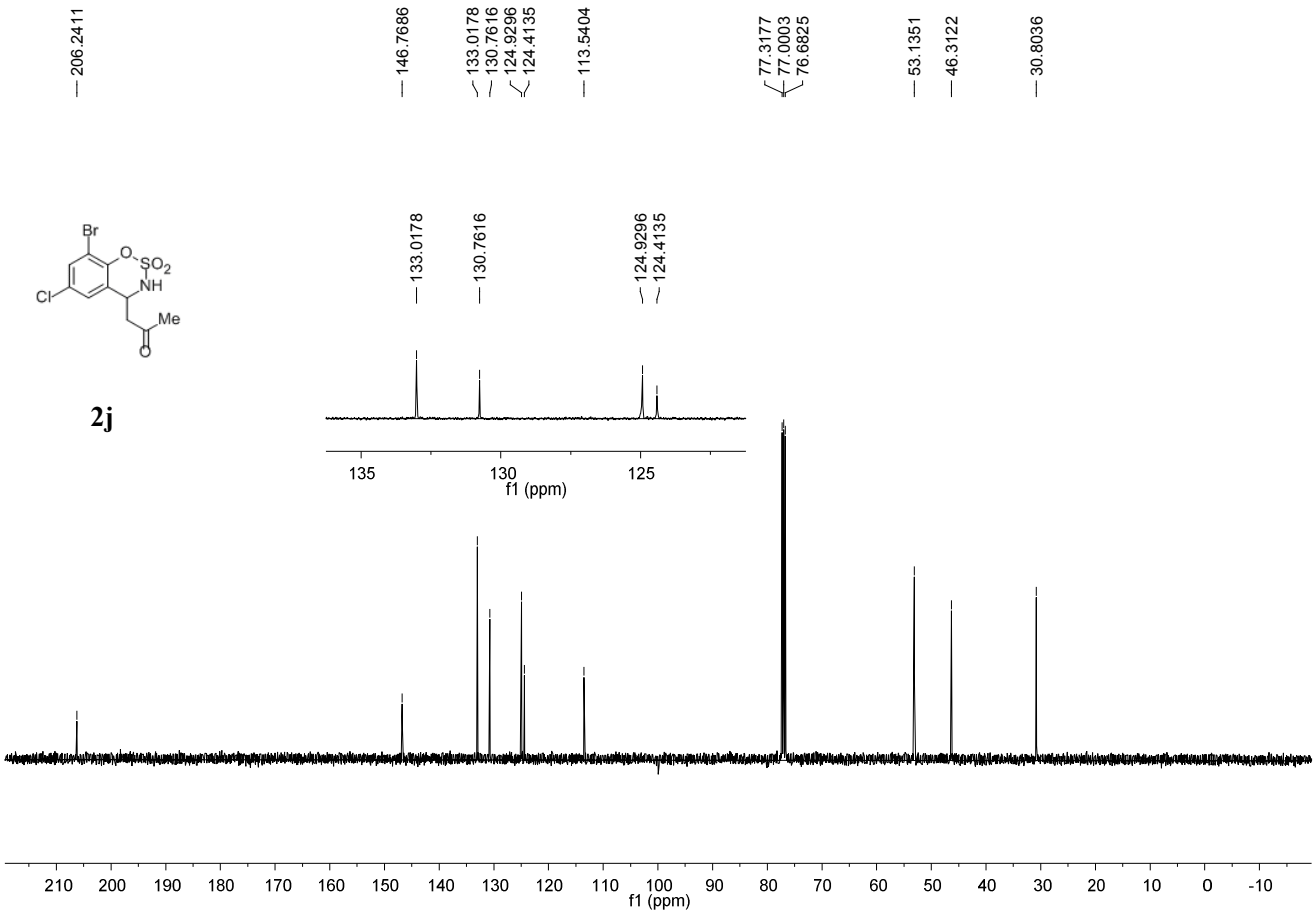
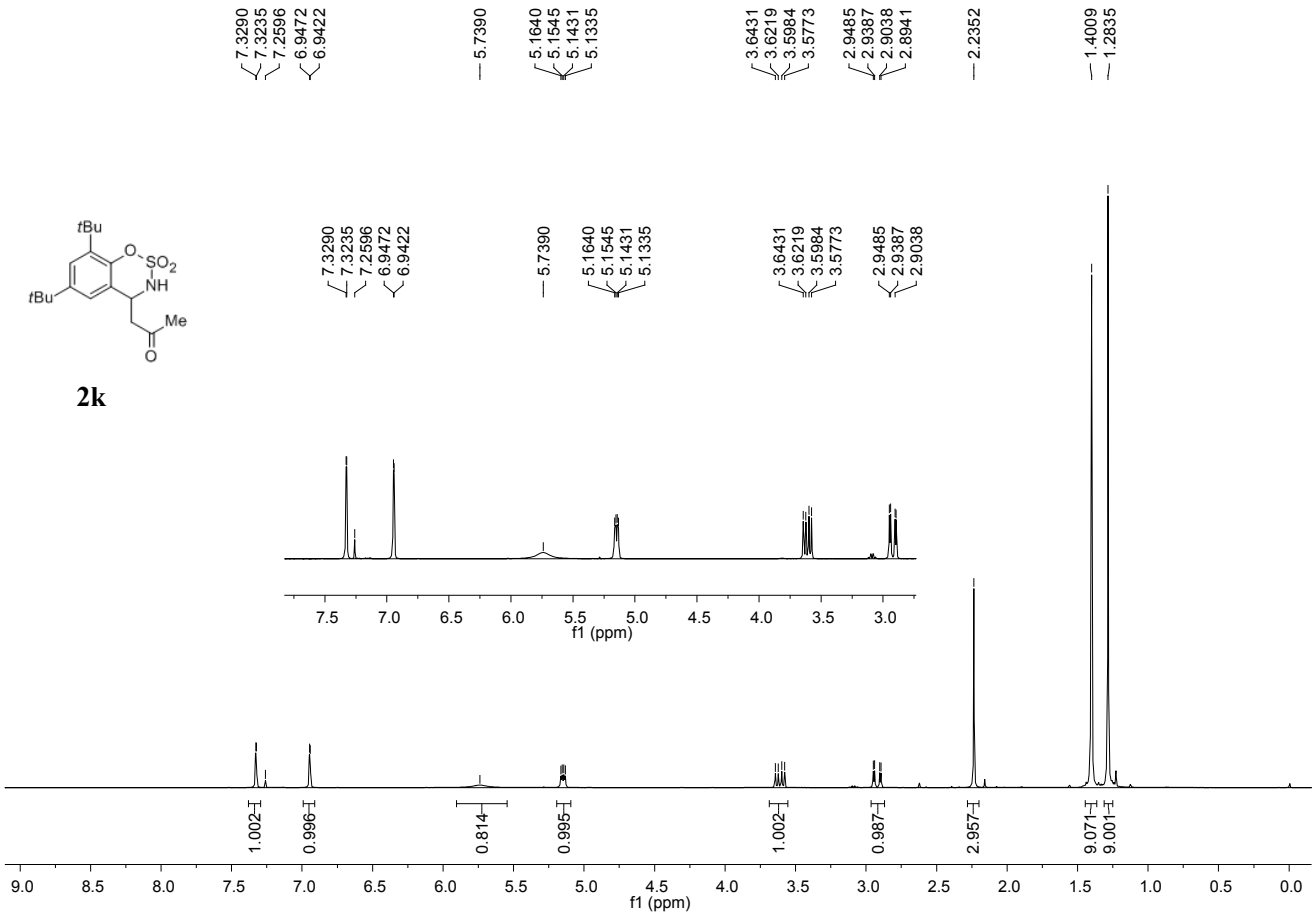
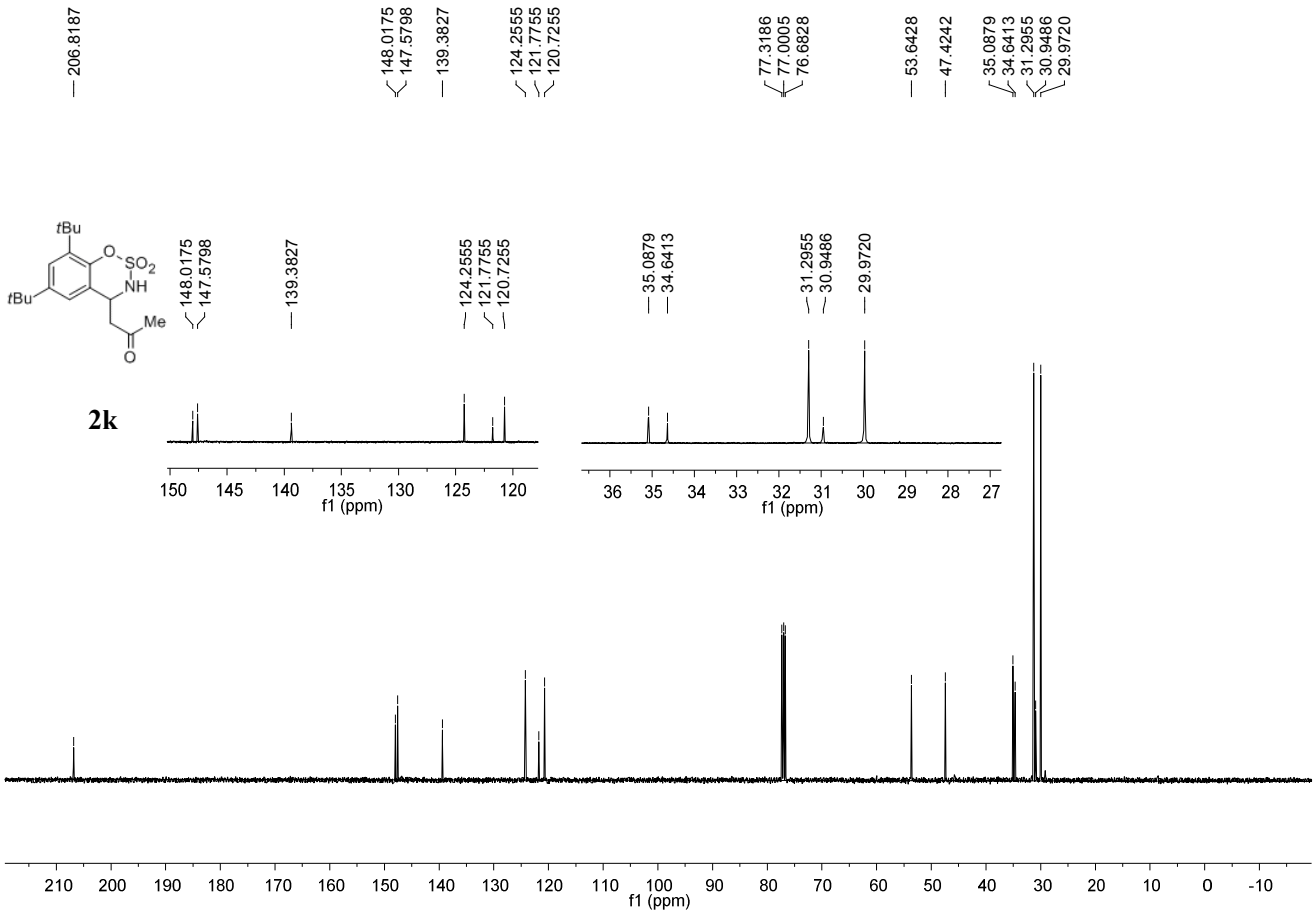
147.3421
135.8015
127.7363
124.7736
117.9393
113.9192
77.3176
77.0000
76.6823
53.0861
46.1797
30.8863
Br
O
SO2
NH
Br
Me
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

2i


7.5462
7.5409
7.2599
7.0567
7.0521
5.9494
5.1484
3.6285
3.6104
3.5824
3.5643
3.0254
3.0154
2.9793
2.9693
2.2580
Br
O
SO2
NH
Cl
Me
O
0.909
0.958
0.980
0.983
1.000
0.995
2.934
f1 (ppm)


206.2411
146.7686
133.0178
130.7616
124.9296
124.4135
113.5404
77.3177
77.0003
76.6825
53.1351
46.3122
30.8036
Br
O
SO2
NH
Cl
Me
O
2j
133.0178
130.7616
124.9296
124.4135
135
130
125
f1 (ppm)
f1 (ppm)


7.3290
7.3235
7.2596
6.9472
6.9422
5.7390
5.1640
5.1545
5.1431
5.1335
3.6431
3.6219
3.5984
3.5773
2.9485
2.9387
2.9038
2.8941
2.2352
1.4009
1.2835
tBu
tBu
O
SO2
NH
Me
O
2k
1.002
0.996
0.814
0.995
1.002
0.987
2.957
9.071
9.001
f1 (ppm)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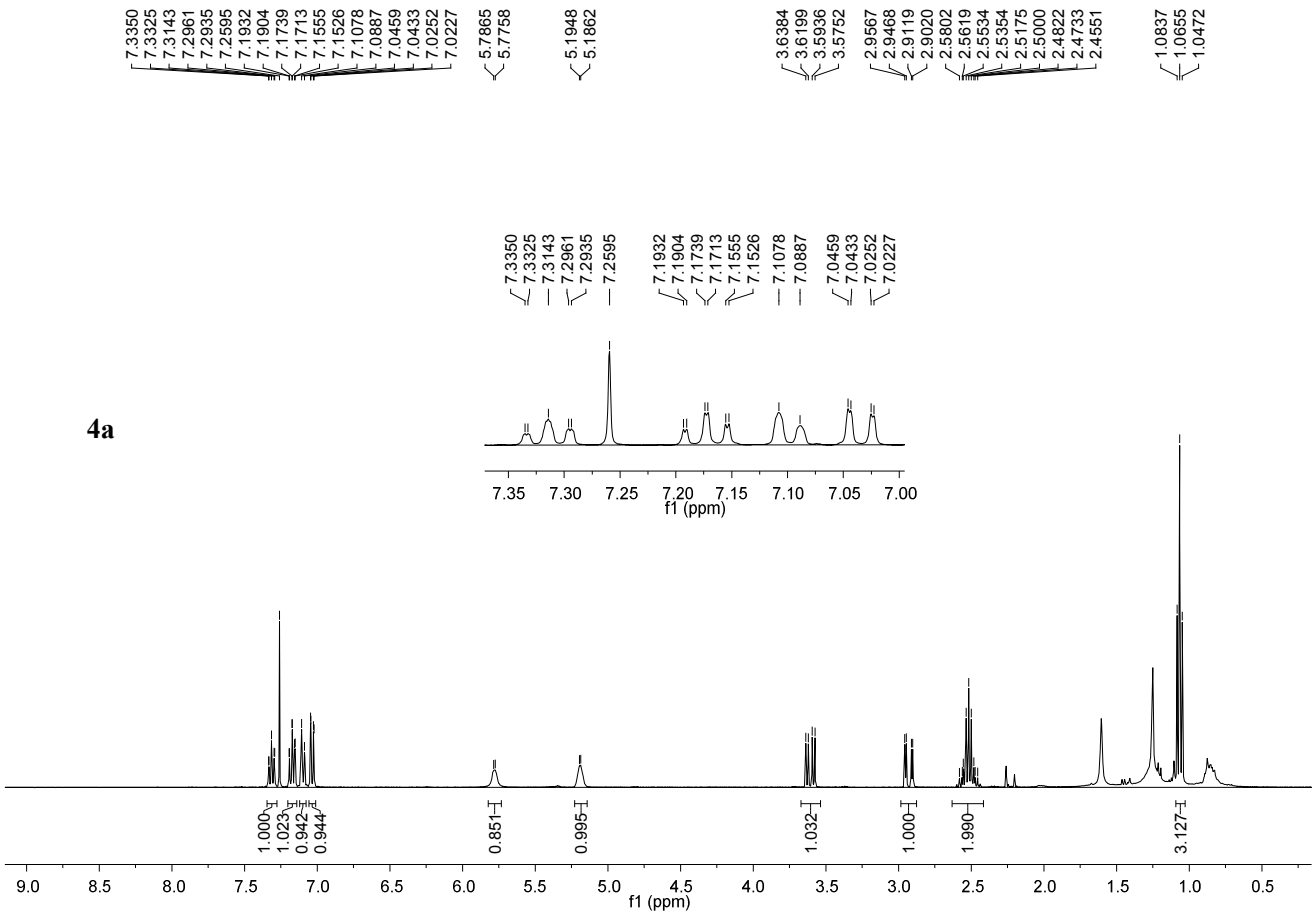
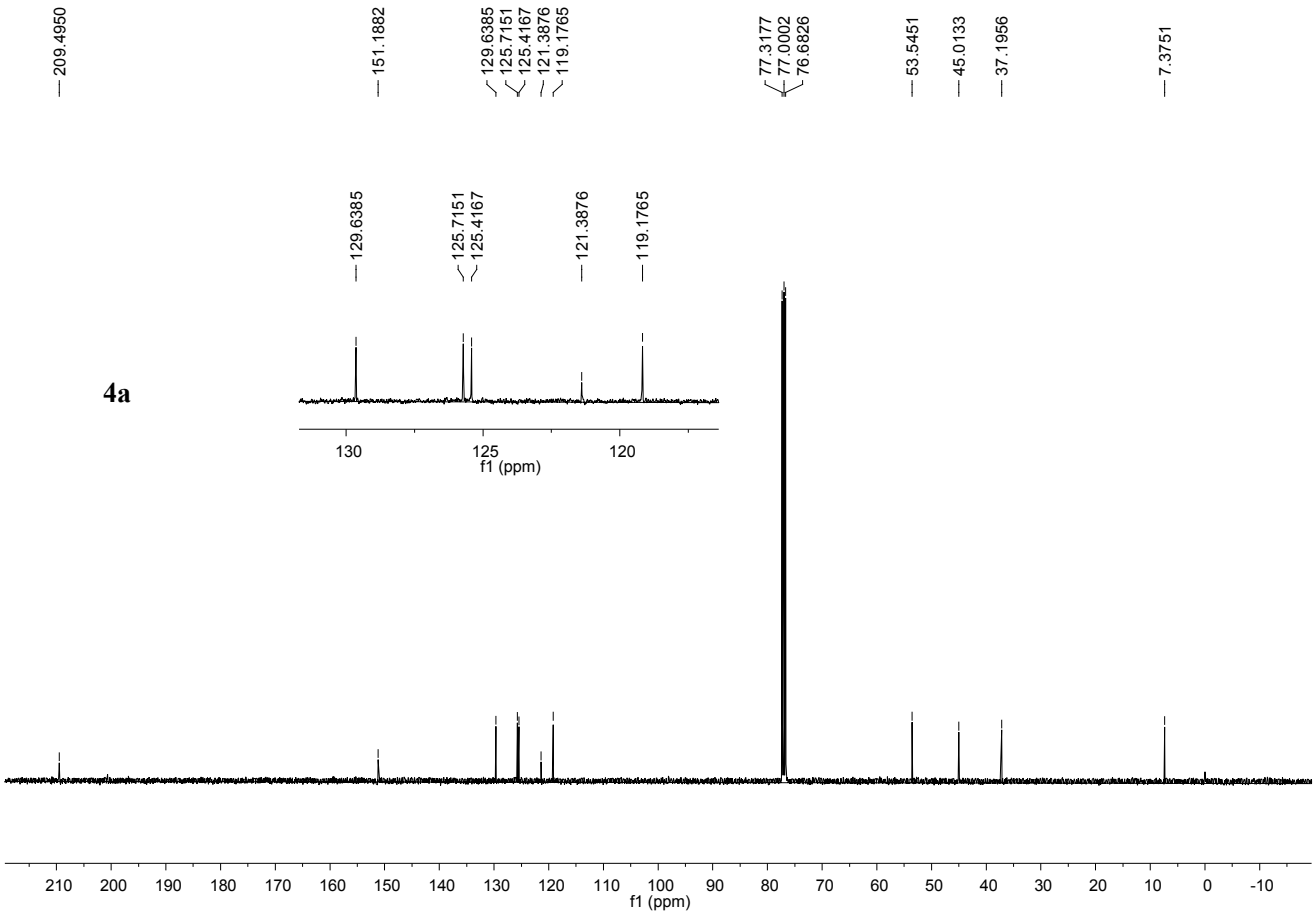
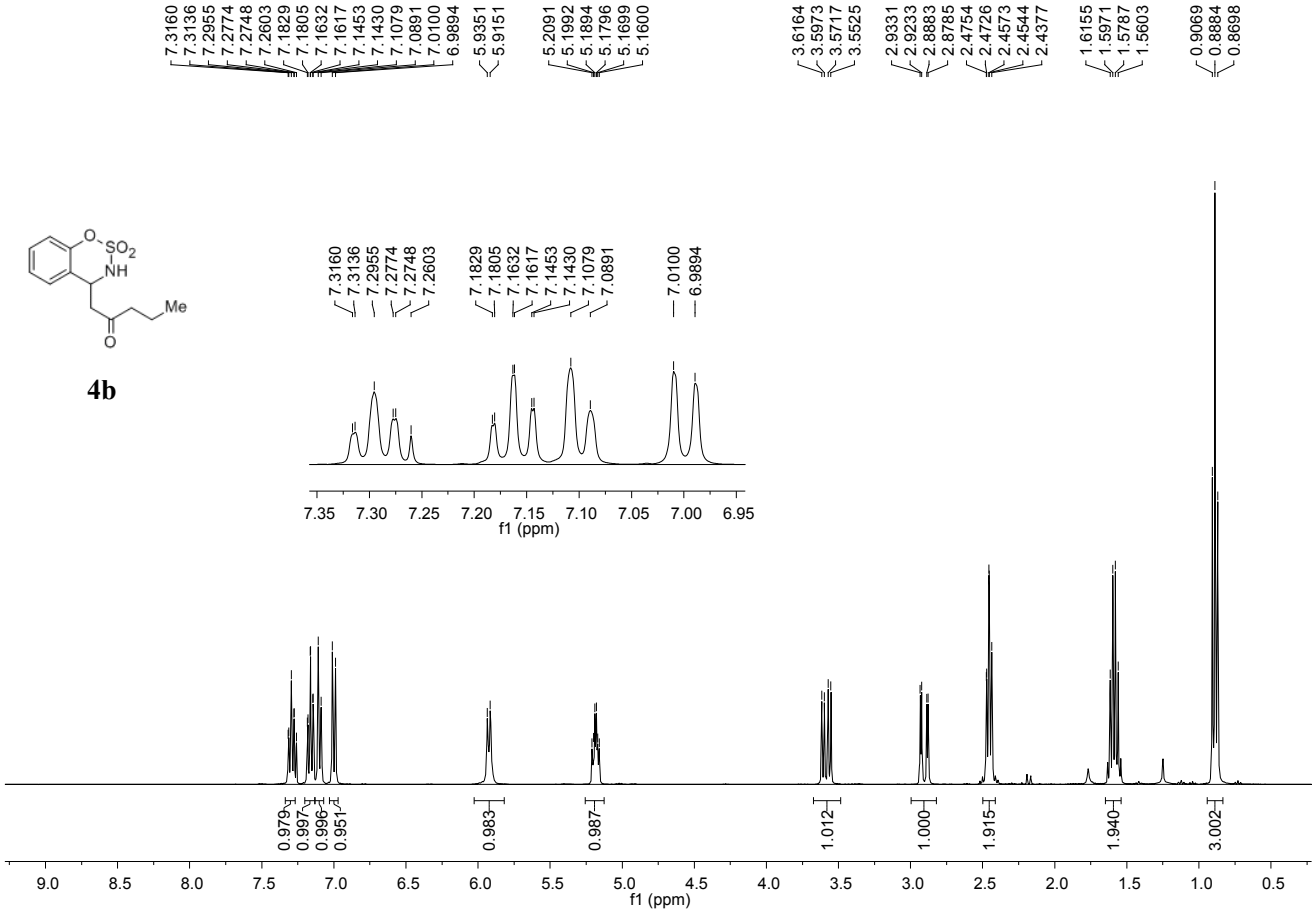
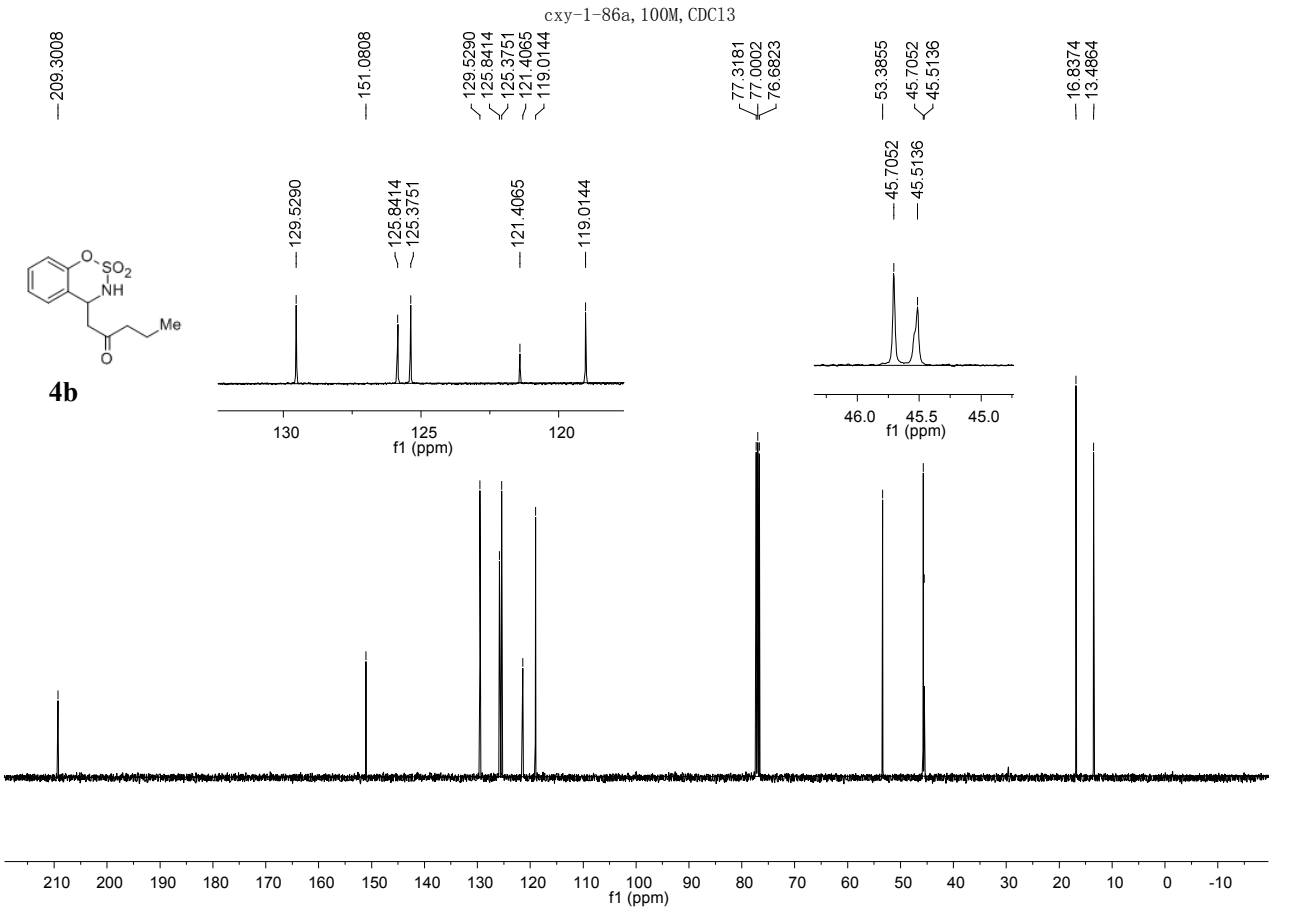
148.0175
147.5798
139.3827
124.2555
121.7755
120.7255
77.3186
77.0005
76.6828
53.6428
47.4242
35.0879
34.6413
31.2955
30.9486
29.9720
tBu
tBu
O
SO2
NH
Me
O
2k
f1 (ppm)


7.3350
7.3325
7.3143
7.2961
7.2935
7.2595
7.1932
7.1904
7.1739
7.1713
7.1555
7.1526
7.1078
7.0887
7.0459
7.0433
7.0252
7.0227
5.7865
5.7758
5.1948
5.1862
3.6384
3.6199
3.5936
3.5752
2.9567
2.9468
2.9119
2.9020
2.5802
2.5619
2.5534
2.5354
2.5175
2.5000
2.4822
2.4733
2.4551
1.0837
1.0655
1.0472
4a
f1 (ppm)
1.000
1.023
0.942
0.944
0.851
0.995
1.032
1.000
1.990
3.127


209.4950
151.1882
129.6385
125.7151
125.4167
121.3876
119.1765
77.3177
77.0002
76.6826
53.5451
45.0133
37.1956
7.3751
4a
f1 (ppm)


7.3160
7.3136
7.2955
7.2774
7.2748
7.2603
7.1829
7.1805
7.1632
7.1617
7.1453
7.1430
7.1079
7.0891
7.0100
6.9894
5.9351
5.9151
5.2091
5.1992
5.1894
5.1796
5.1699
5.1600
3.6164
3.5973
3.5717
3.5525
2.9331
2.9233
2.8883
2.8785
2.4754
2.4726
2.4573
2.4544
2.4377
1.6155
1.5971
1.5787
1.5603
0.9069
0.8884
0.8698
4b
f1 (ppm)
0.979
0.997
0.996
0.951
0.983
0.987
1.012
1.000
1.915
1.940
3.002


cxy-1-86a, 100M, CDC13
209.3008
151.0808
129.5290
125.8414
125.3751
121.4065
119.0144
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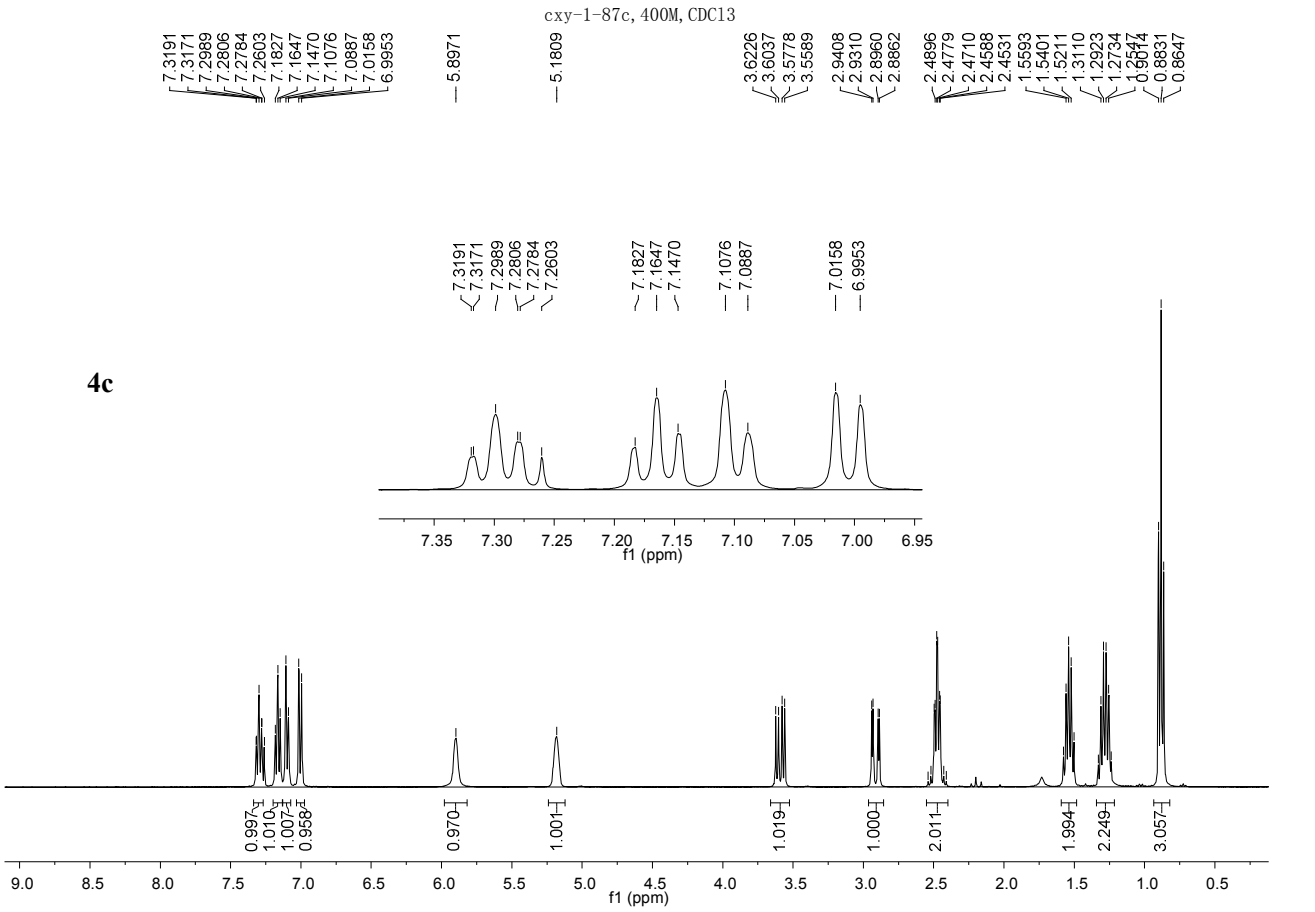
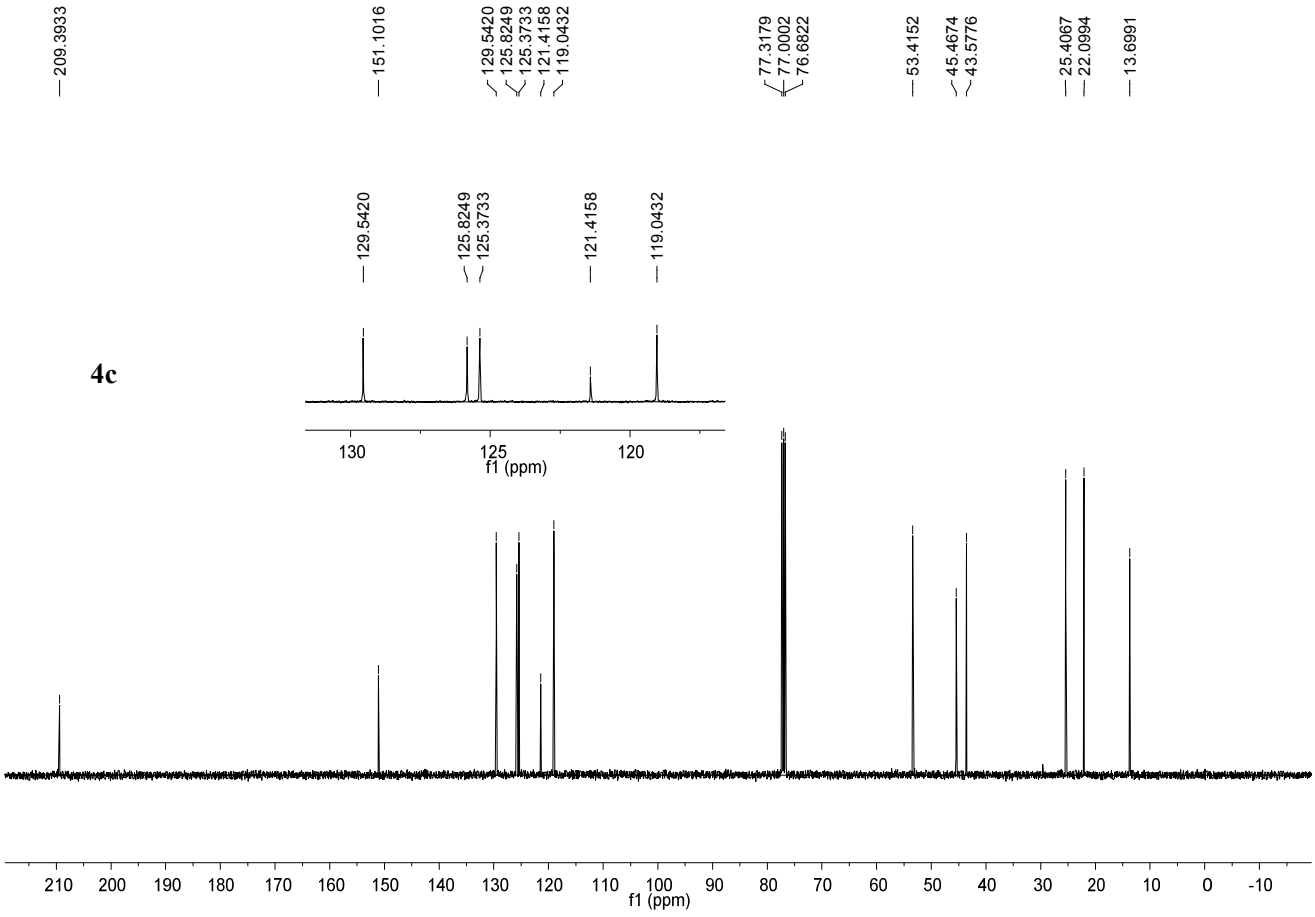
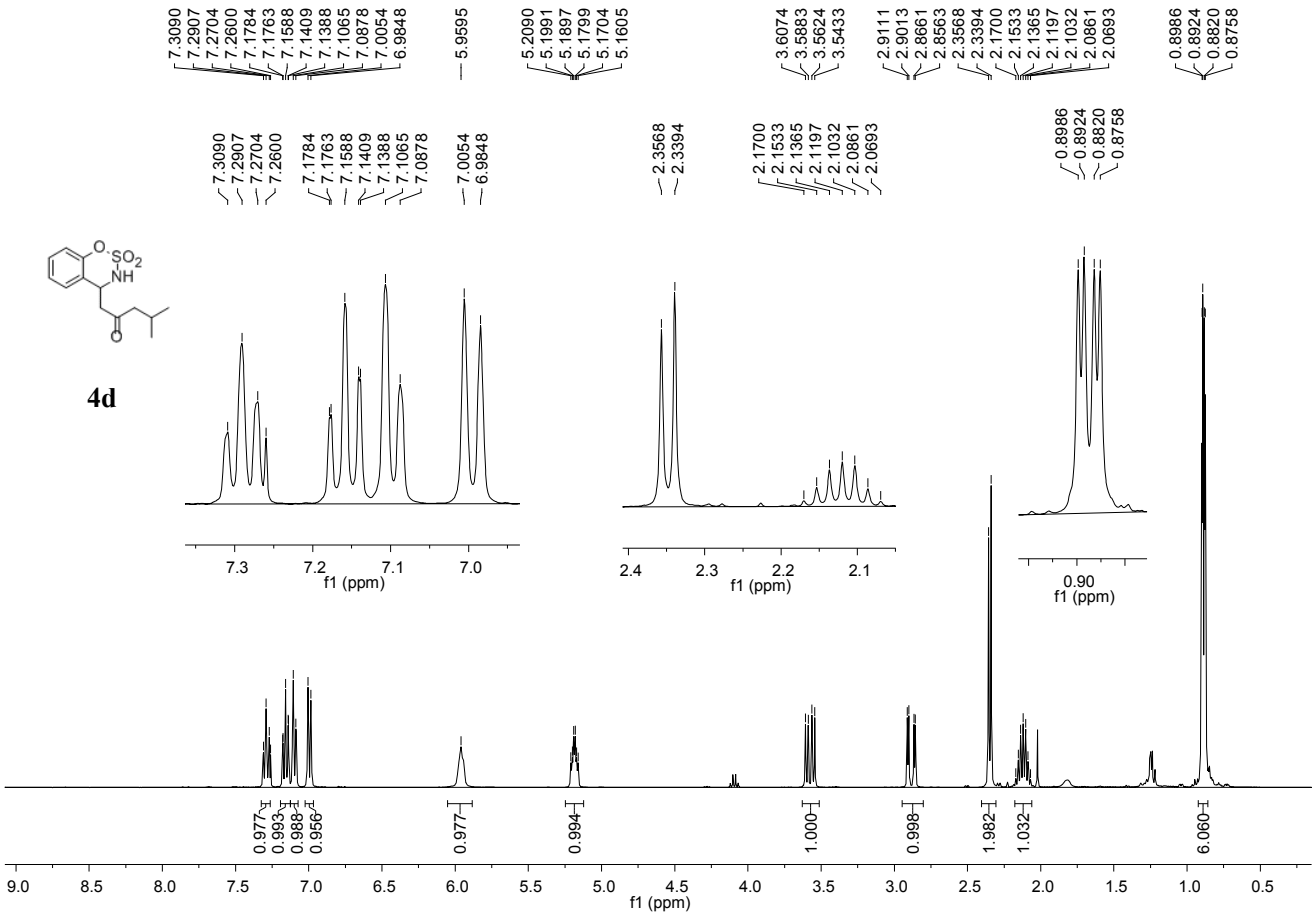
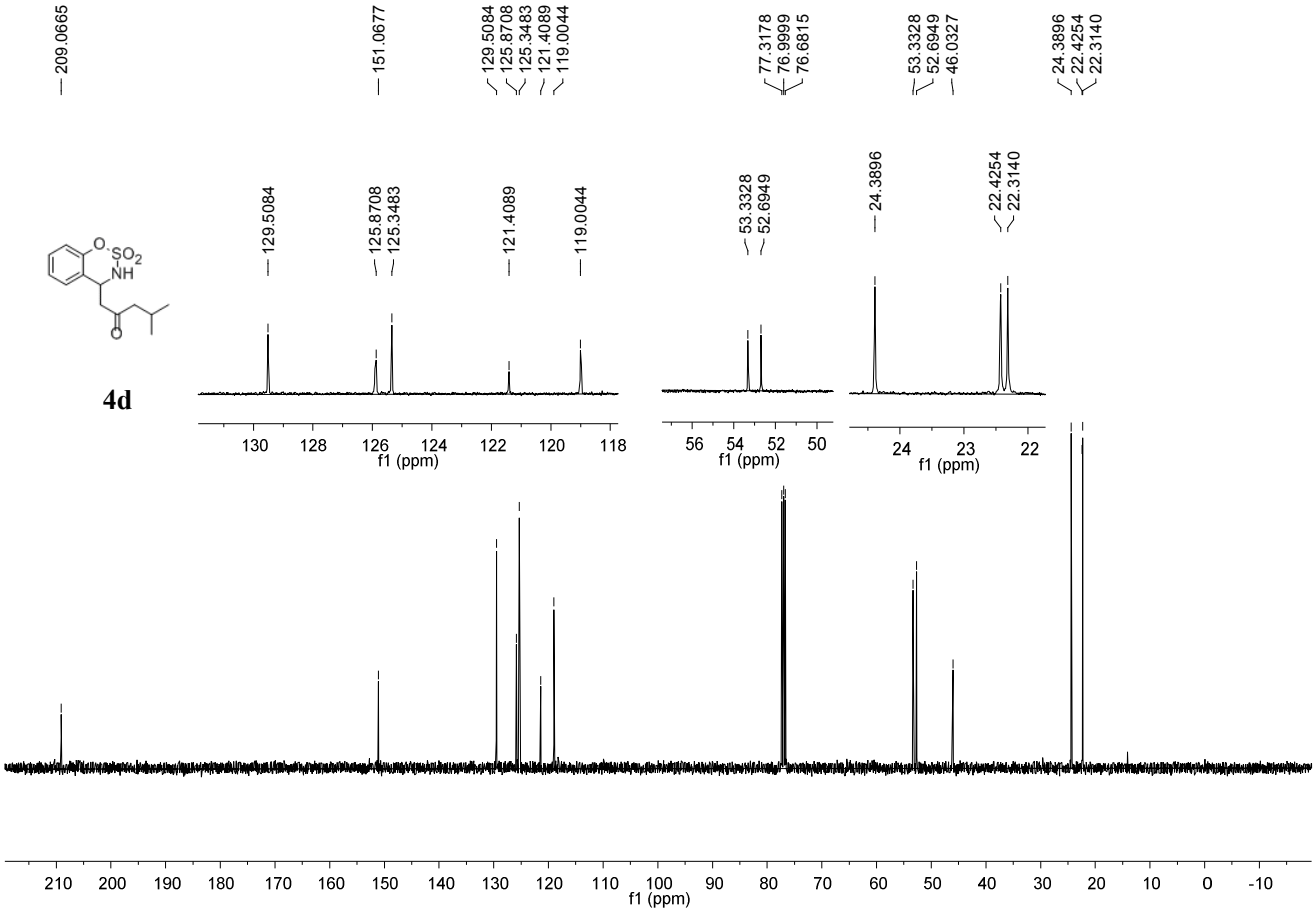
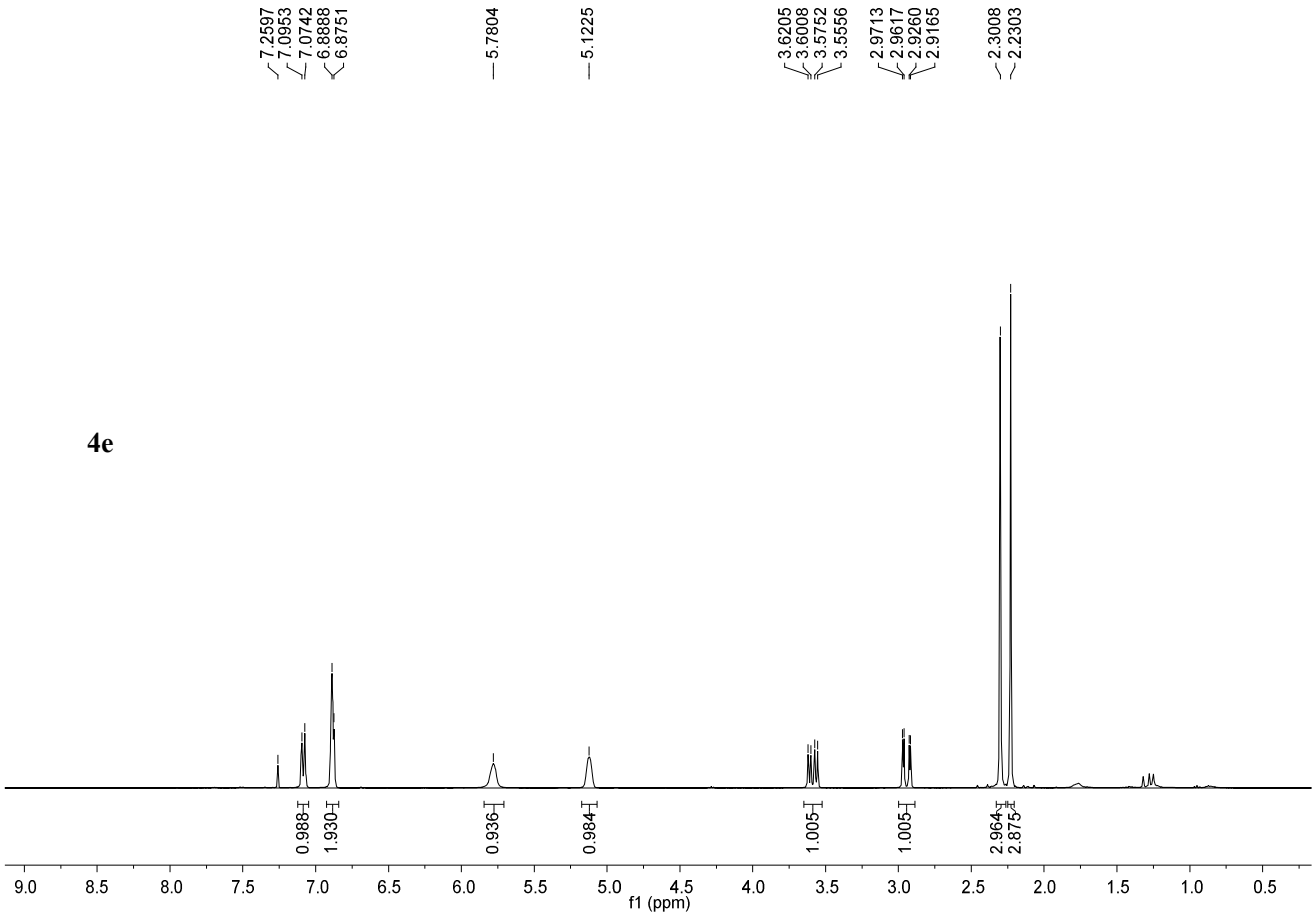
77.0002
76.6823
53.3855
45.7052
45.5136
16.8374
13.4864
4b
f1 (ppm)

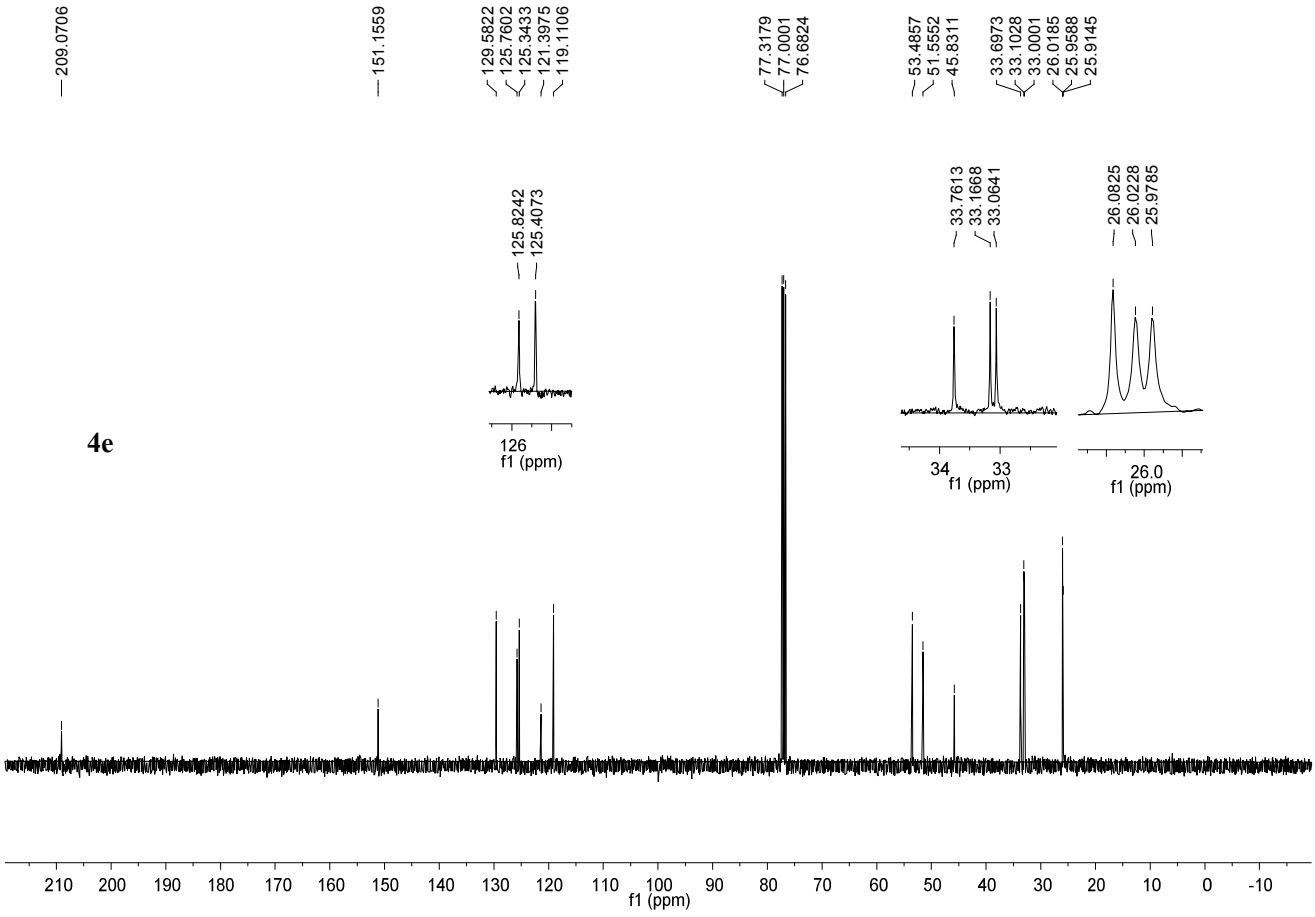

cxy-1-87c, 400M, CDCl3
4c
f1 (ppm)


4c
f1 (ppm)


4d
f1 (ppm)


4d
f1 (ppm)


4e
7.2597
7.0953
7.0742
6.8888
6.8751
5.7804
5.1225
3.6205
3.6008
3.5752
3.5556
2.9713
2.9617
2.9260
2.9165
2.3008
2.2303
0.988
1.930
0.936
0.984
1.005
1.005
2.964
2.875
f1 (ppm)


4e
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129.5822
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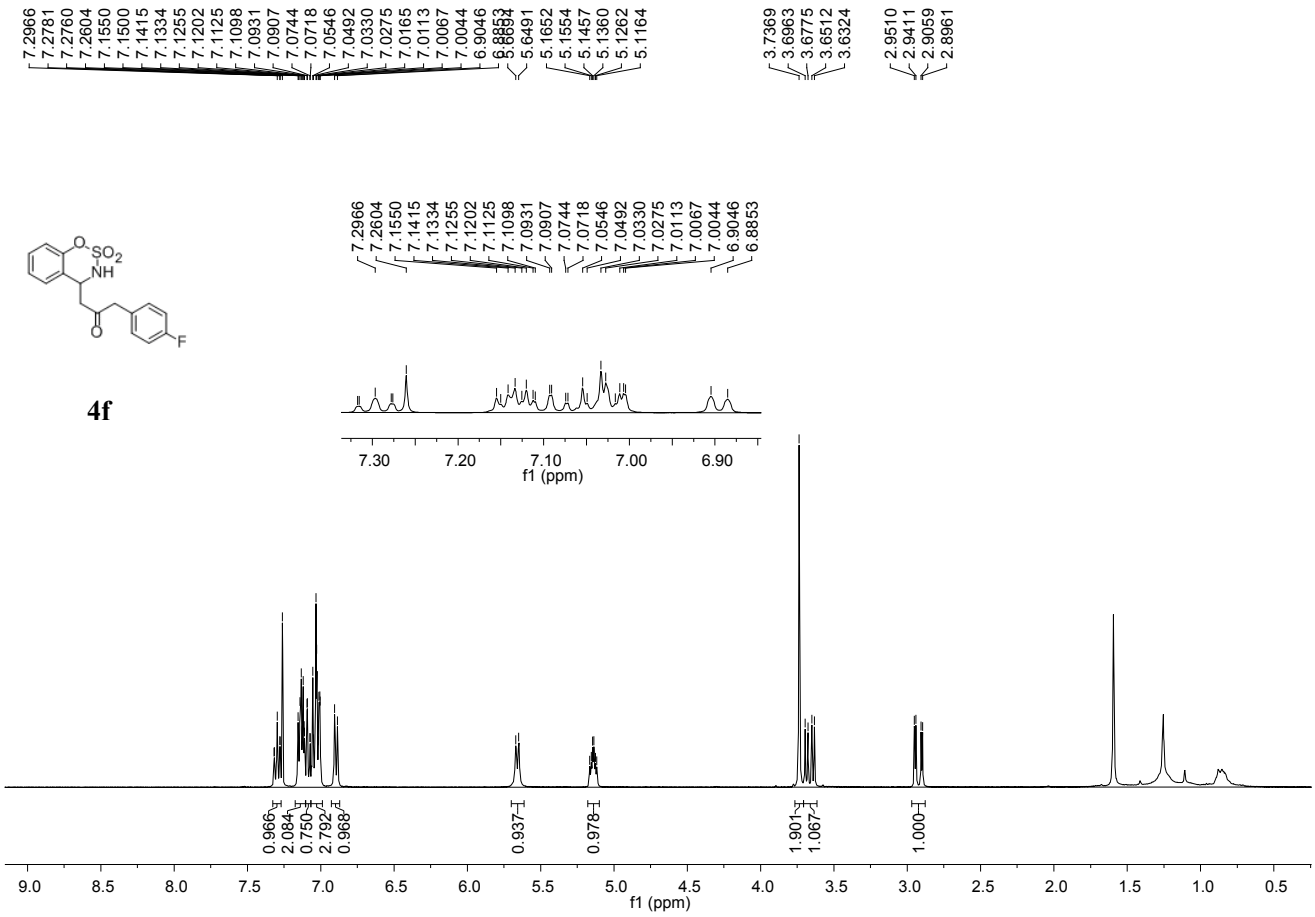
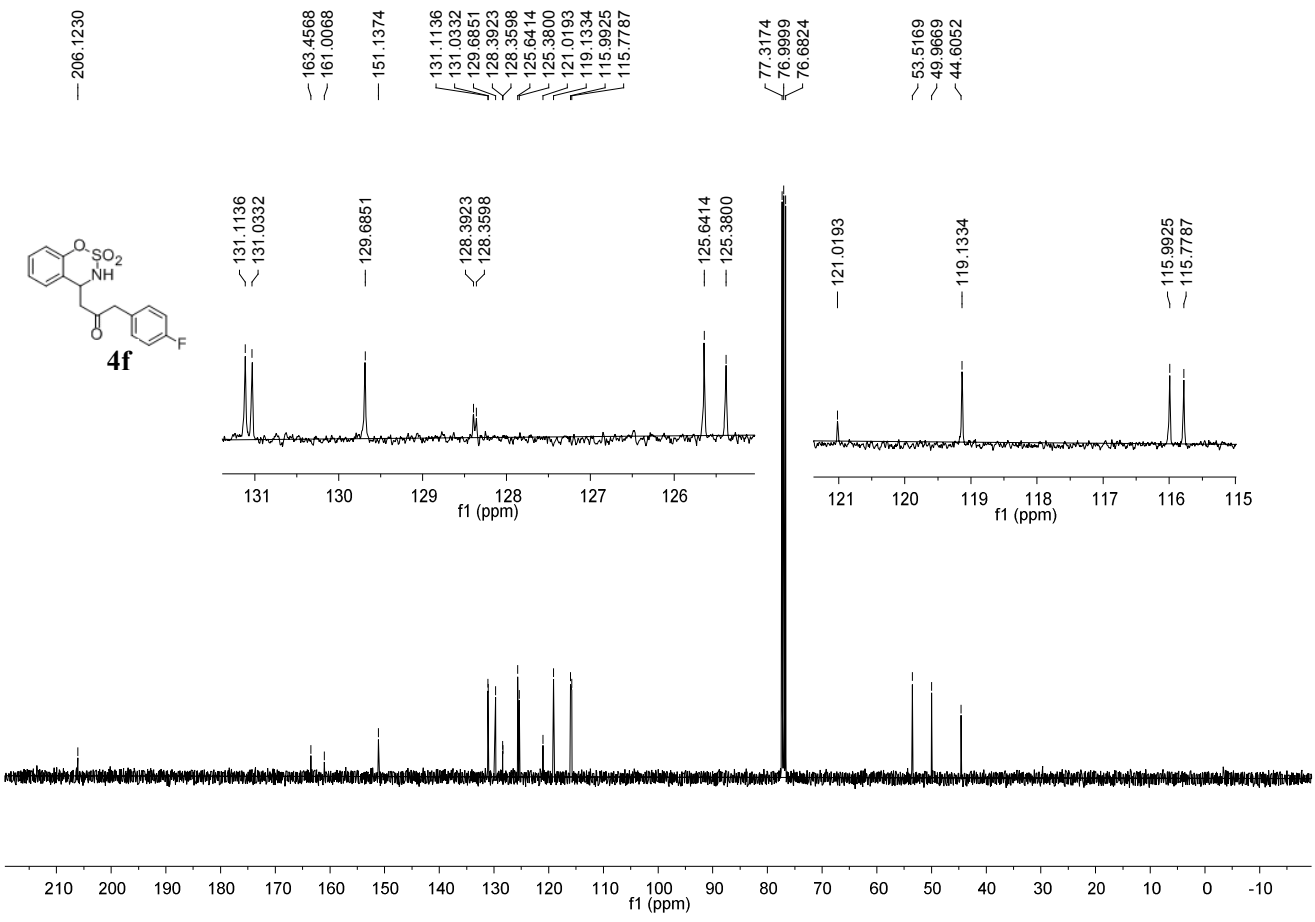
125.3433
121.3975
119.1106
77.3179
77.0001
76.6824
53.4857
51.5552
45.8311
33.6973
33.1028
33.0001
26.0185
25.9588
25.9145
125.8242
125.4073
33.7613
33.1668
33.0641
26.0825
26.0228
25.9785
f1 (ppm)


7.2966
7.2781
7.2760
7.2604
7.1550
7.1500
7.1415
7.1334
7.1255
7.1202
7.1125
7.1098
7.0931
7.0907
7.0744
7.0718
7.0546
7.0492
7.0330
7.0275
7.0165
7.0113
7.0067
7.0044
6.9046
6.8853
5.6491
5.1652
5.1554
5.1457
5.1360
5.1262
5.1164
3.7369
3.6963
3.6775
3.6512
3.6324
2.9510
2.9411
2.9059
2.8961
4f
f1 (ppm)
0.966
2.084
0.750
2.792
0.968
0.937
0.978
1.901
1.067
1.000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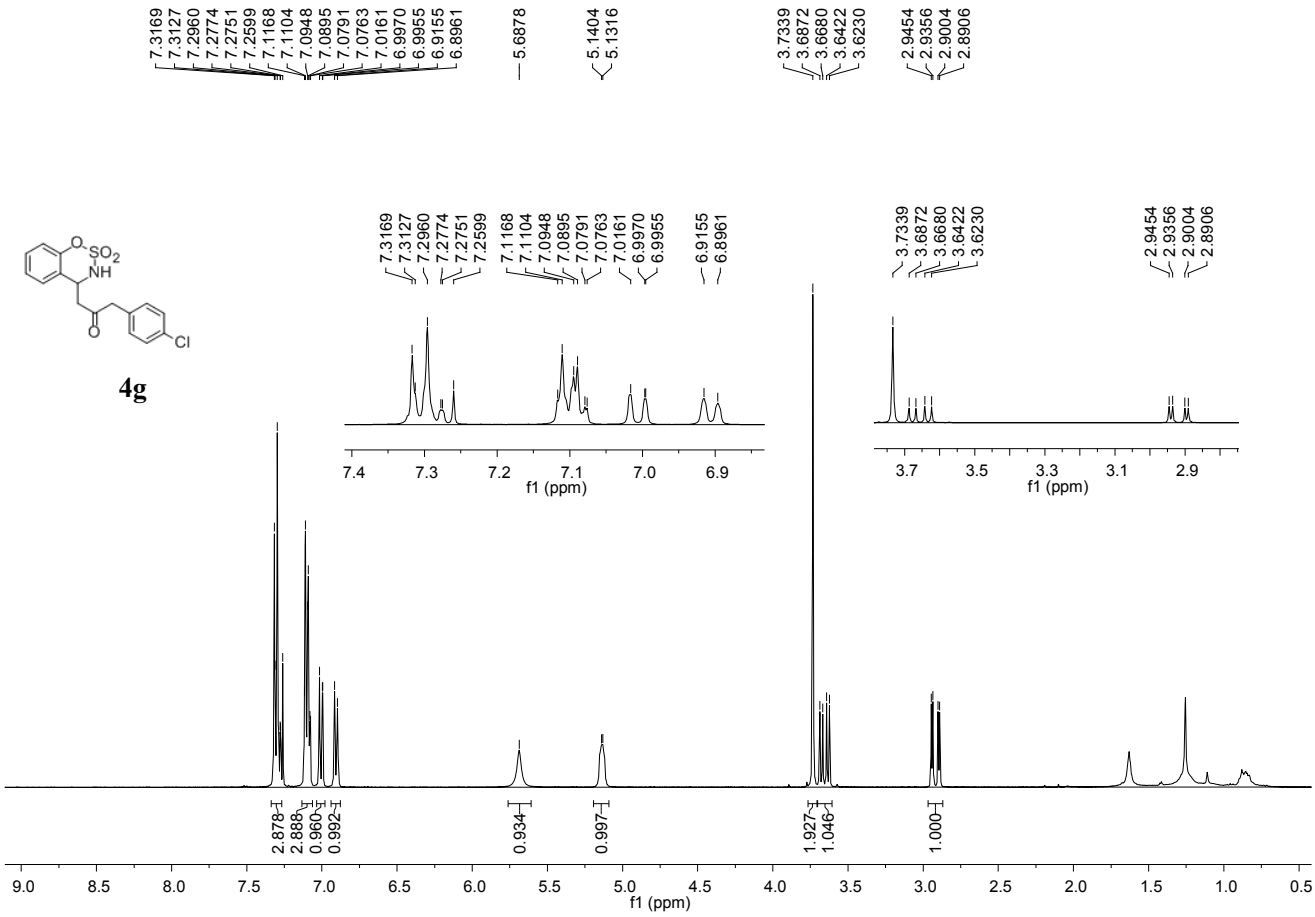
163.4568
161.0068
151.1374
131.1136
131.0332
129.6851
128.3923
128.3598
125.6414
125.3800
121.0193
119.1334
115.9925
115.7787
77.3174
76.9999
76.6824
53.5169
49.9669
44.6052
4f
f1 (ppm)


7.3169
7.3127
7.2960
7.2774
7.2751
7.2599
7.1168
7.1104
7.0948
7.0895
7.0791
7.0763
7.0161
6.9970
6.9955
6.9155
6.8961
5.6878
5.1404
5.1316
3.7339
3.6872
3.6680
3.6422
3.6230
2.9454
2.9356
2.9004
2.8906
O
SO2
NH
O
Cl
4g
f1 (ppm)
2.878
2.888
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0.992
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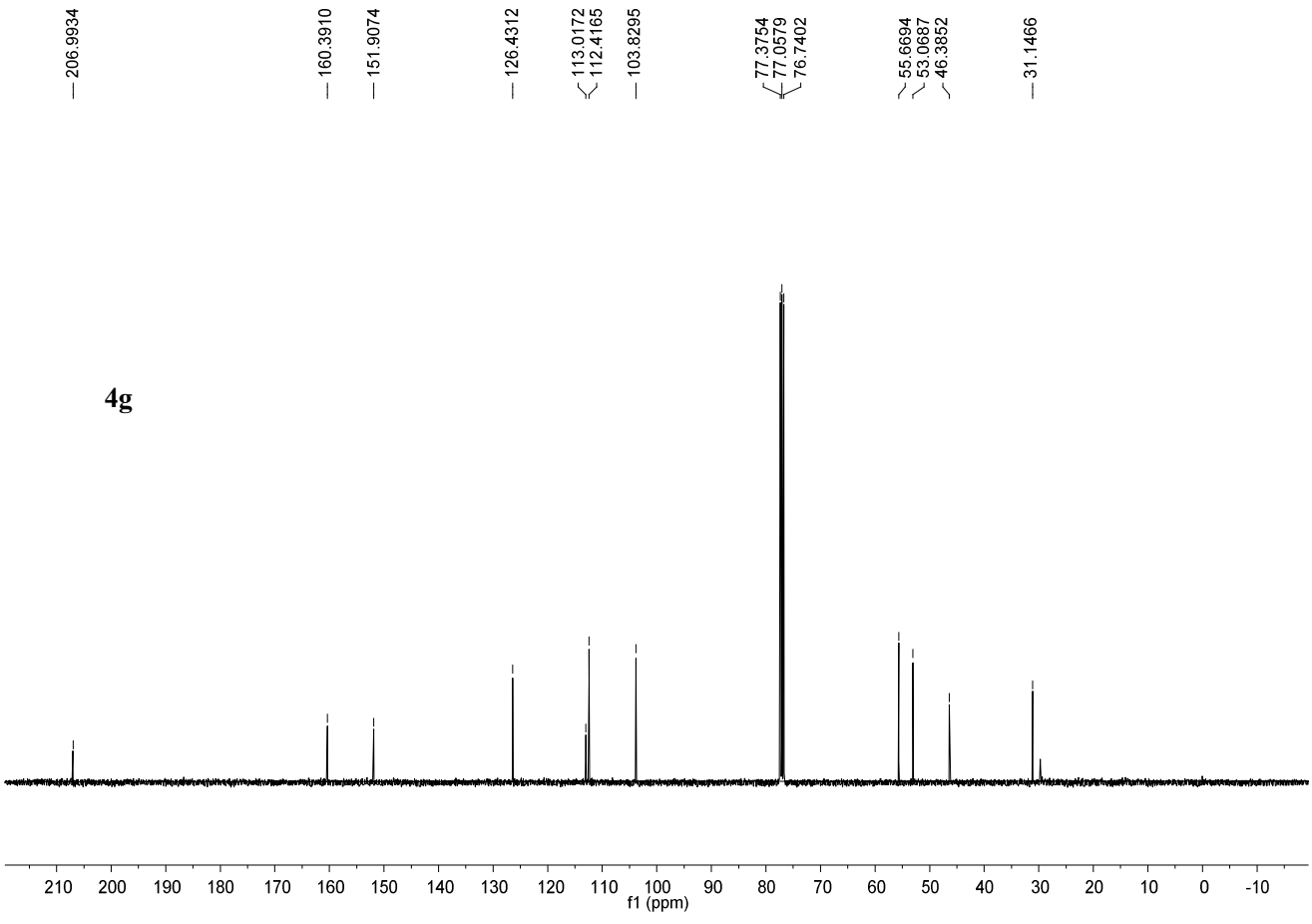
1.046
1.000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55.6694
53.0687
46.3852
31.1466
4g
f1 (ppm)


7.2753
7.2736
7.2598
7.2548
7.0925
7.0877
7.0762
7.0709
7.0601
7.0576
7.0412
7.0385
7.0038
6.9831
6.8892
6.8819
6.8768
6.8653
6.8601
5.1032
5.0946
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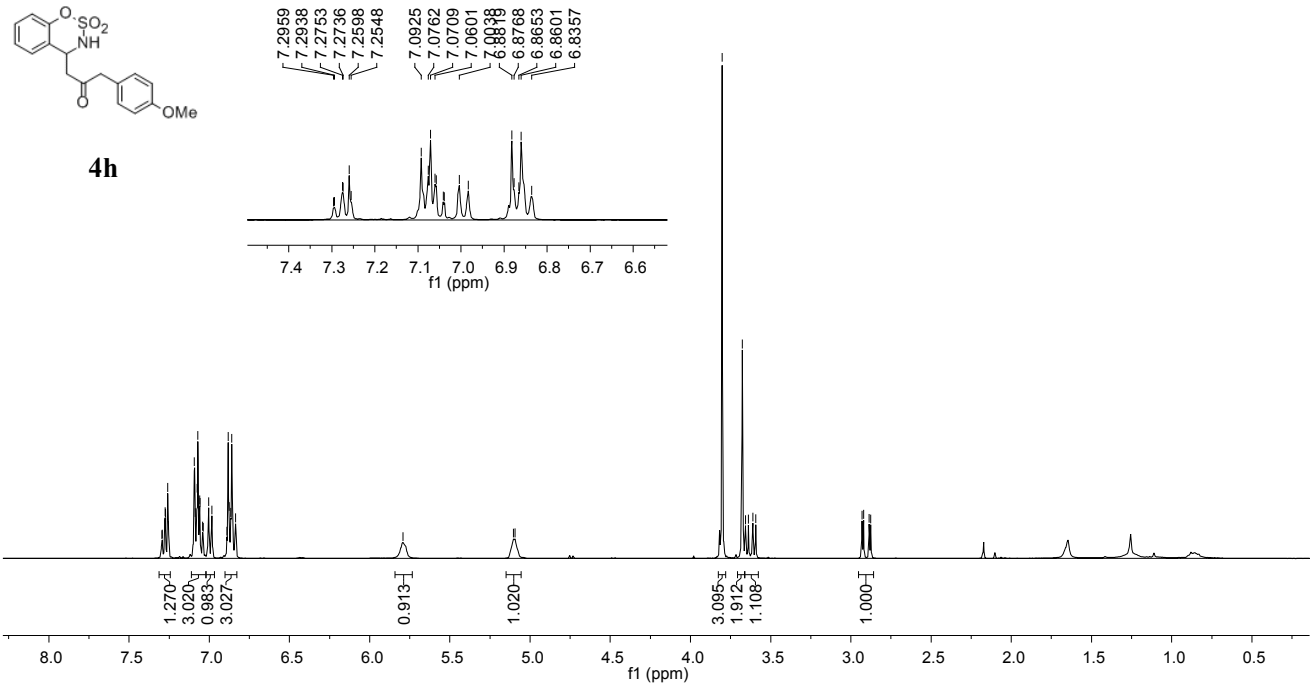
3.5938
2.9310
2.9212
2.8858
2.8760


4h
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7.0601
6.8768
6.8653
6.8601
6.8357
f1 (ppm)
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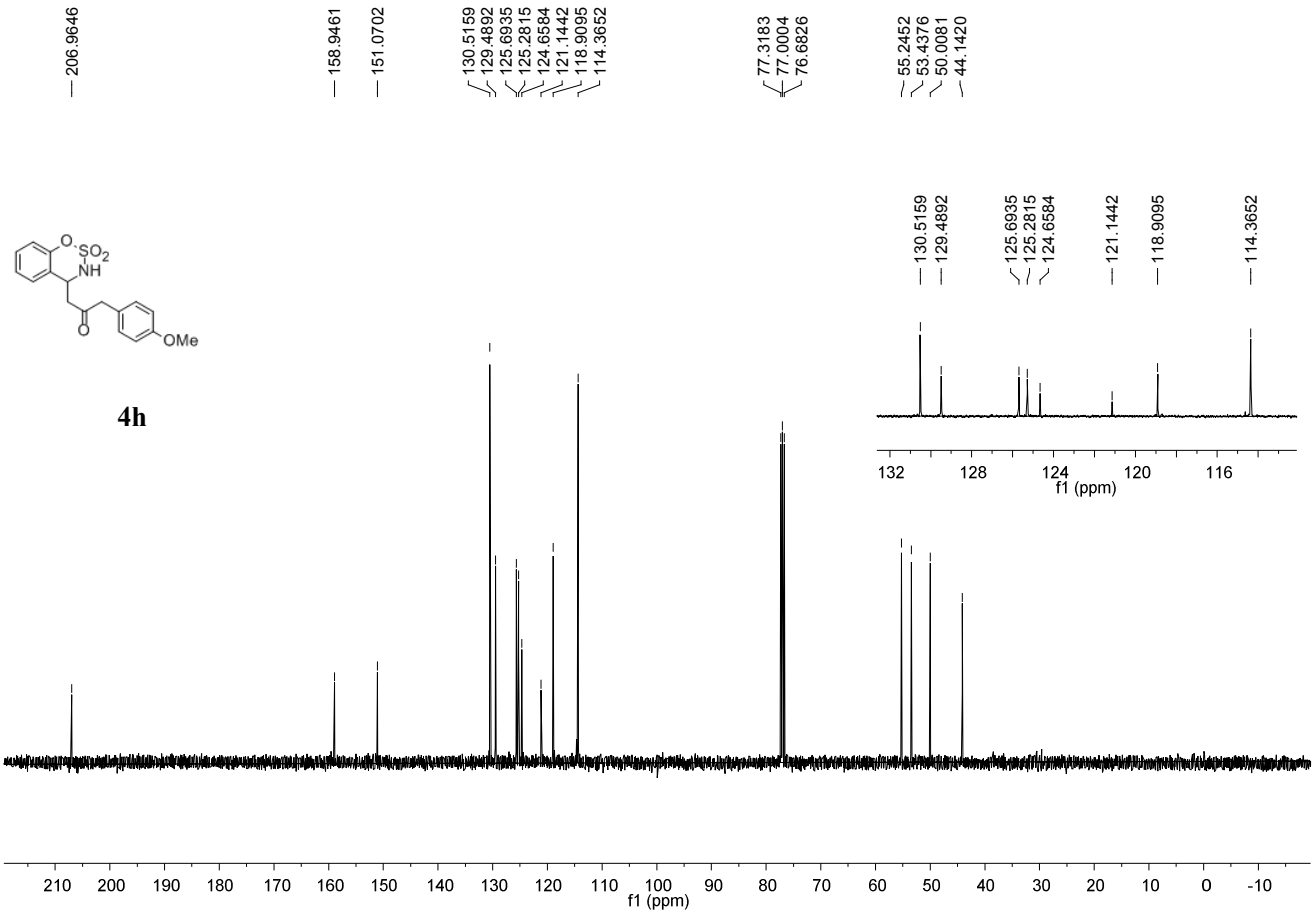
0.983
3.027
0.913
1.020
3.095
1.912
1.108
1.000
f1 (ppm)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50.0081
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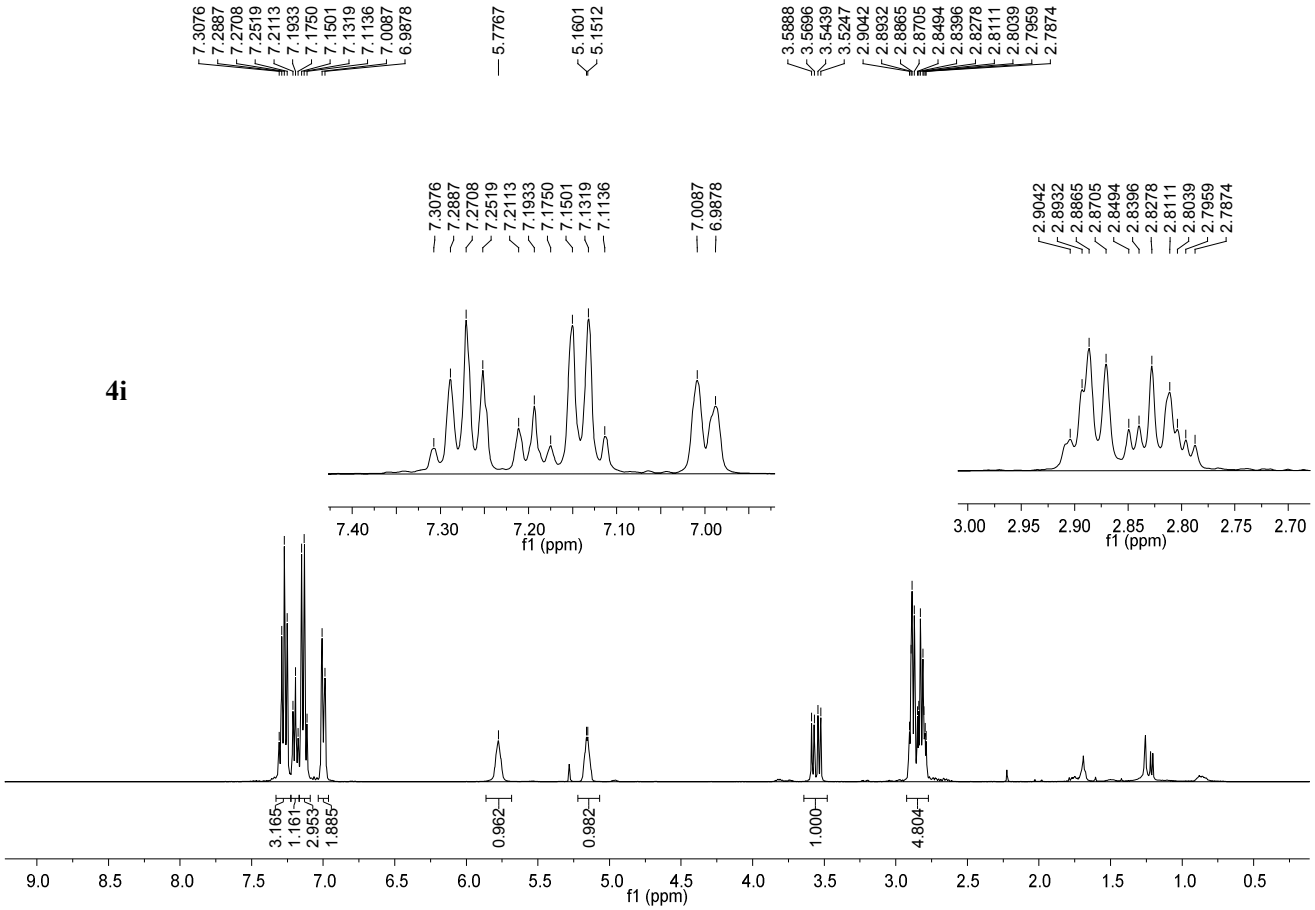
4h
f1 (ppm)
f1 (ppm)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7.1319
7.1136
7.0087
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5.1601
5.1512
3.5888
3.5696
3.5439
3.5247
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2.8865
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2.8396
2.8278
2.8111
2.8039
2.7959
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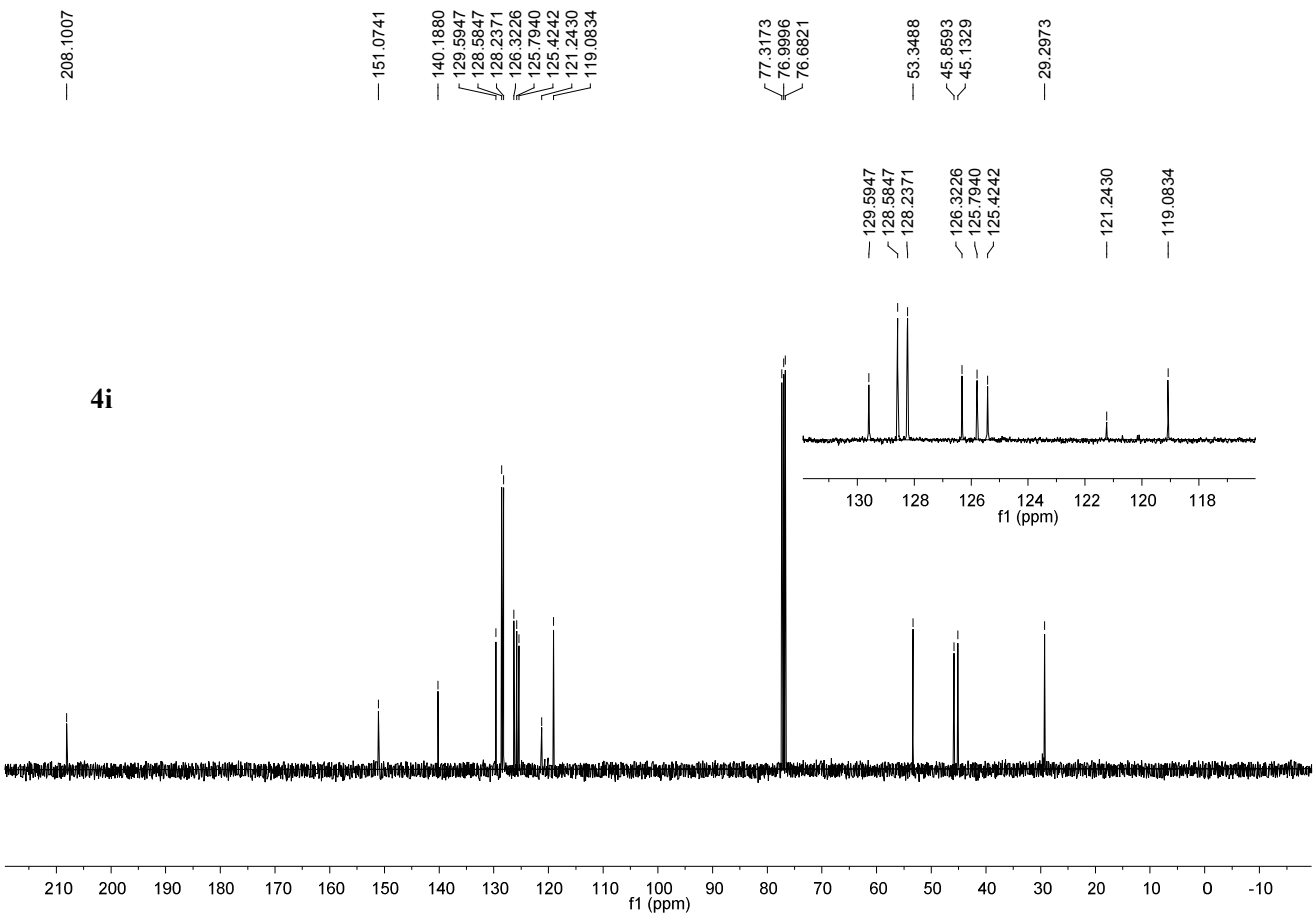
4i
3.165
1.161
2.953
1.885
0.962
0.982
1.000
4.804
f1 (ppm)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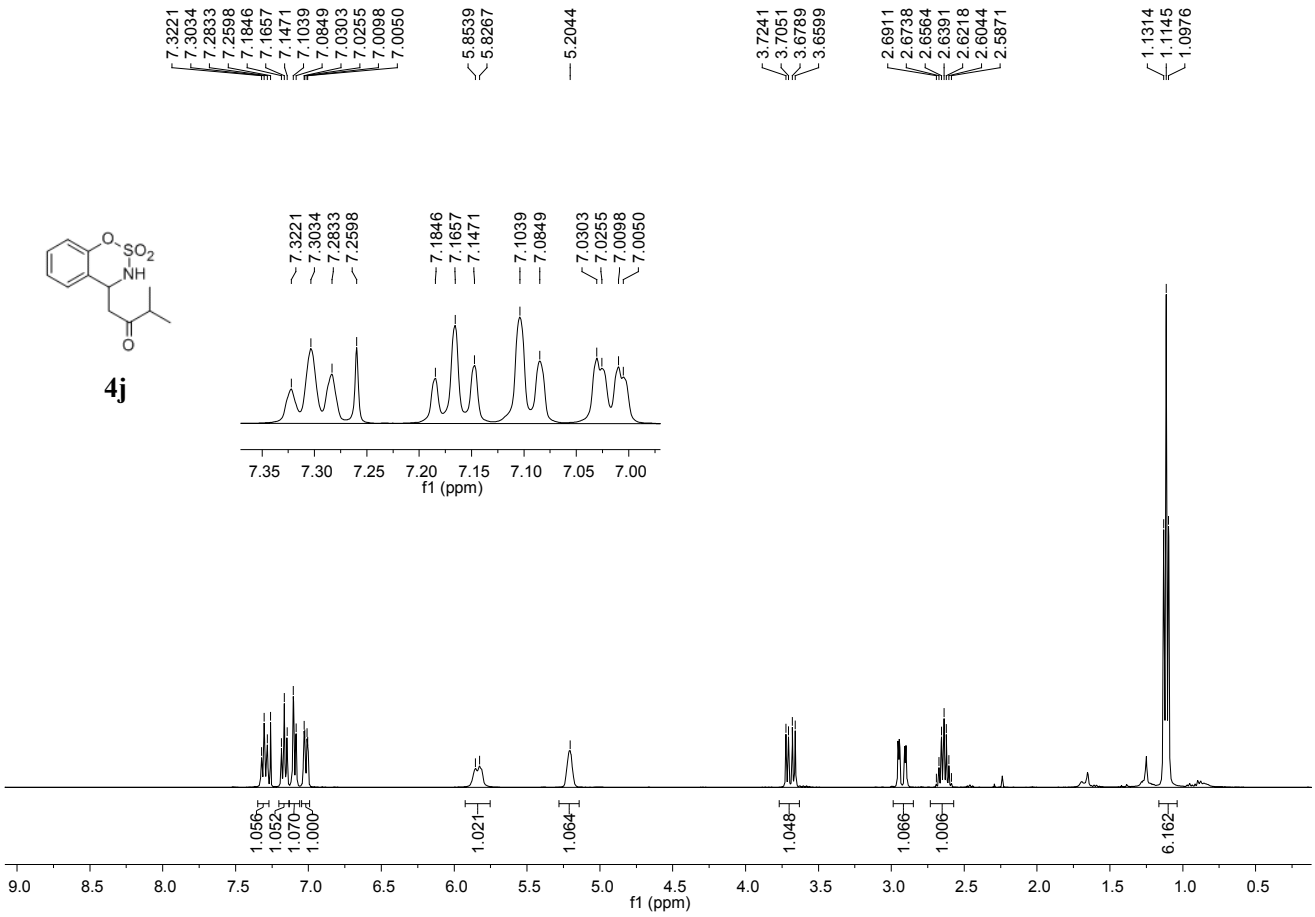
45.1329
29.2973
4i
f1 (ppm)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7.0098
7.0050
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5.8267
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3.6789
3.6599
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2.6044
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1.1145
1.0976
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f1 (ppm)
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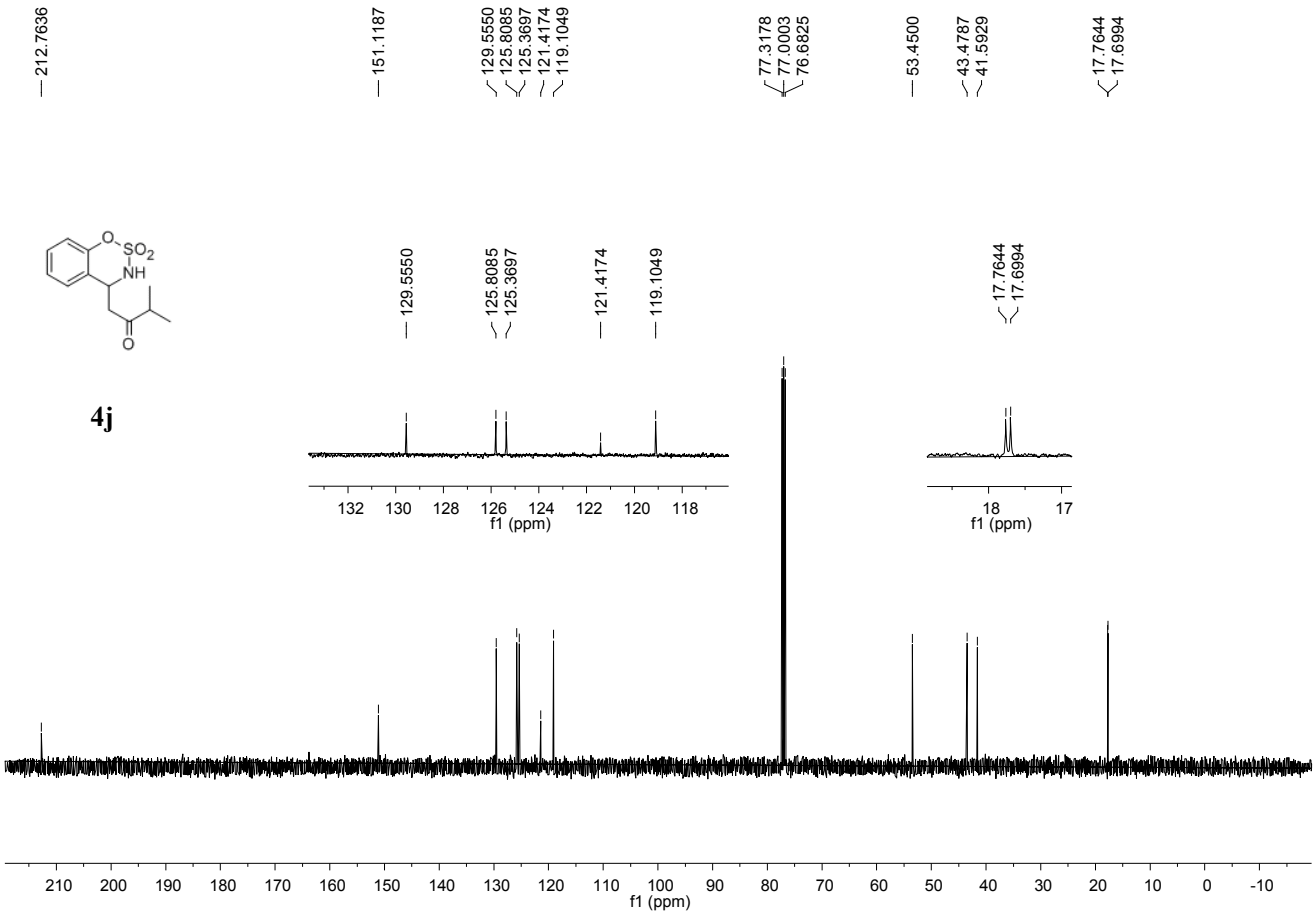
1.066
1.006
6.162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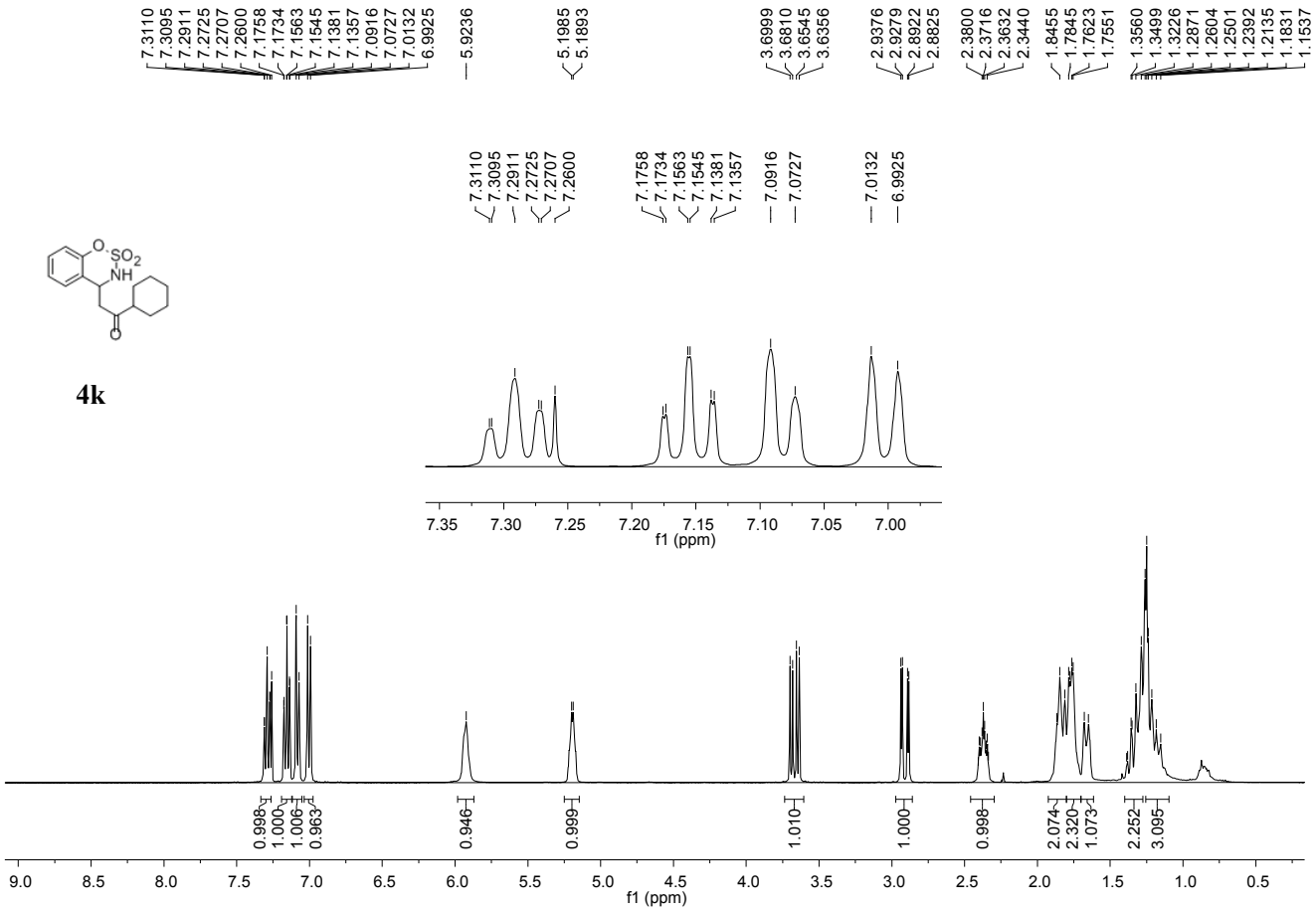
17.6994
4j
f1 (ppm)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7.2911
7.2725
7.2707
7.2600
7.1758
7.1734
7.1563
7.1545
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7.1357
7.0916
7.0727
7.0132
6.9925
5.9236
5.1985
5.1893
3.6999
3.6810
3.6545
3.6356
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2.9279
2.8922
2.8825
2.3800
2.3716
2.3632
2.3440
1.8455
1.7845
1.7623
1.7551
1.3560
1.3499
1.3226
1.2871
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1.2501
1.2392
1.2135
1.1831
1.1537
4k
f1 (ppm)
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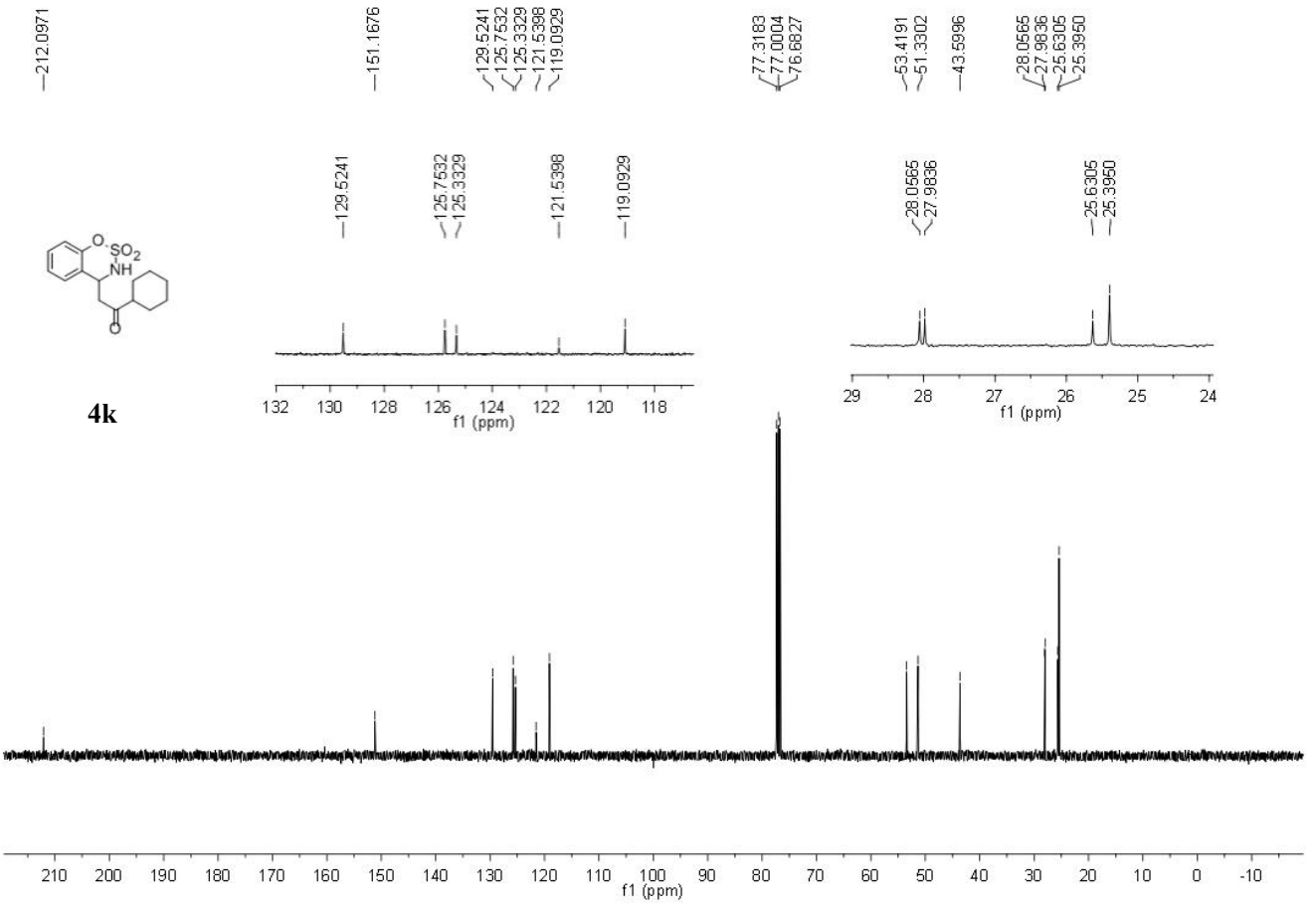
1.000
1.006
0.963
0.946
0.999
1.010
1.000
0.998
2.074
2.320
1.073
2.252
3.095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76.6827
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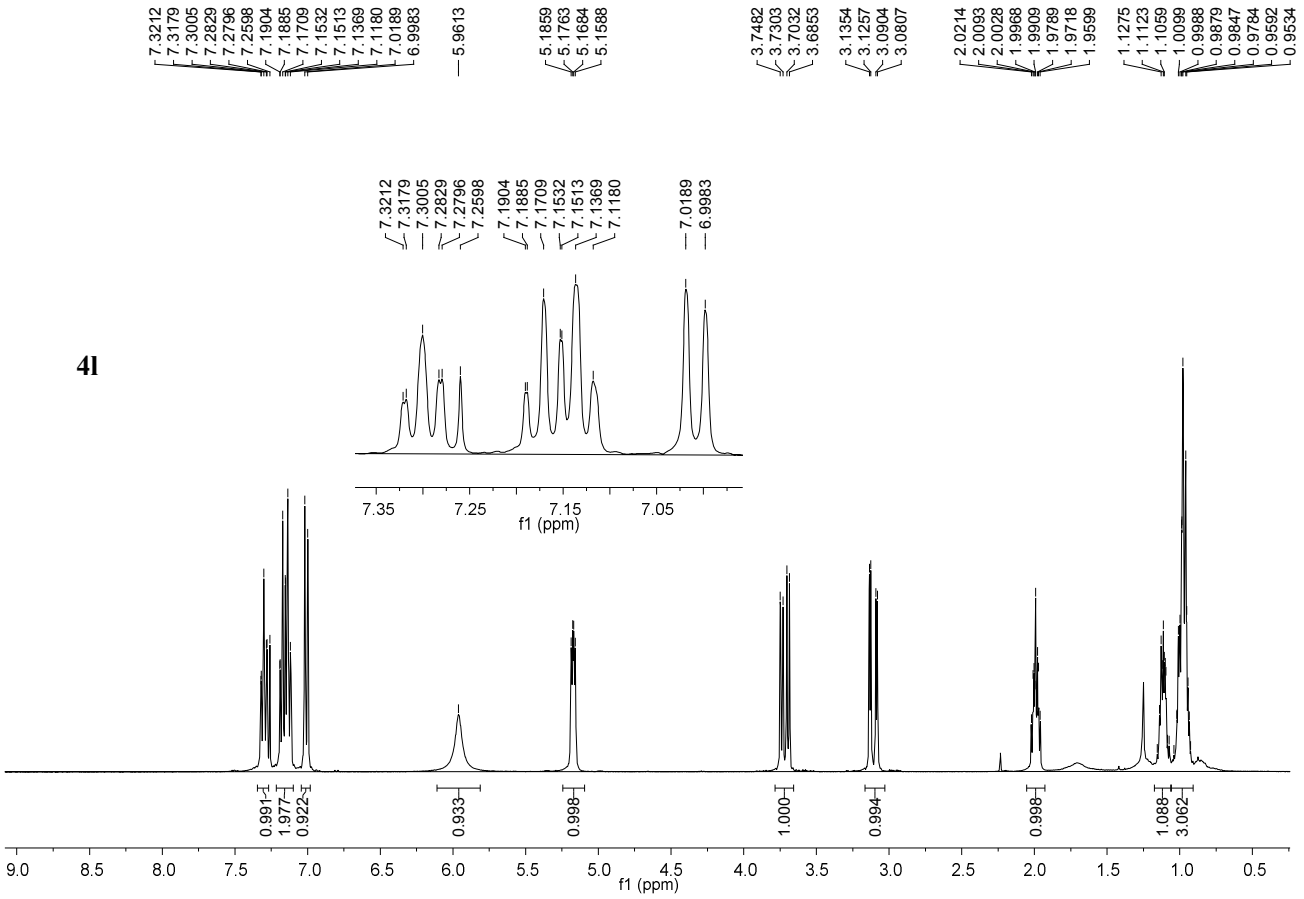
28.0565
27.9836
25.6305
25.3950
4k
f1 (ppm)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7.3005
7.2829
7.2796
7.2598
7.1904
7.1885
7.1709
7.1532
7.1513
7.1369
7.1180
7.0189
6.9983
5.9613
5.1859
5.1763
5.1684
5.1588
3.7482
3.7303
3.7032
3.6853
3.1354
3.1257
3.0904
3.0807
2.0214
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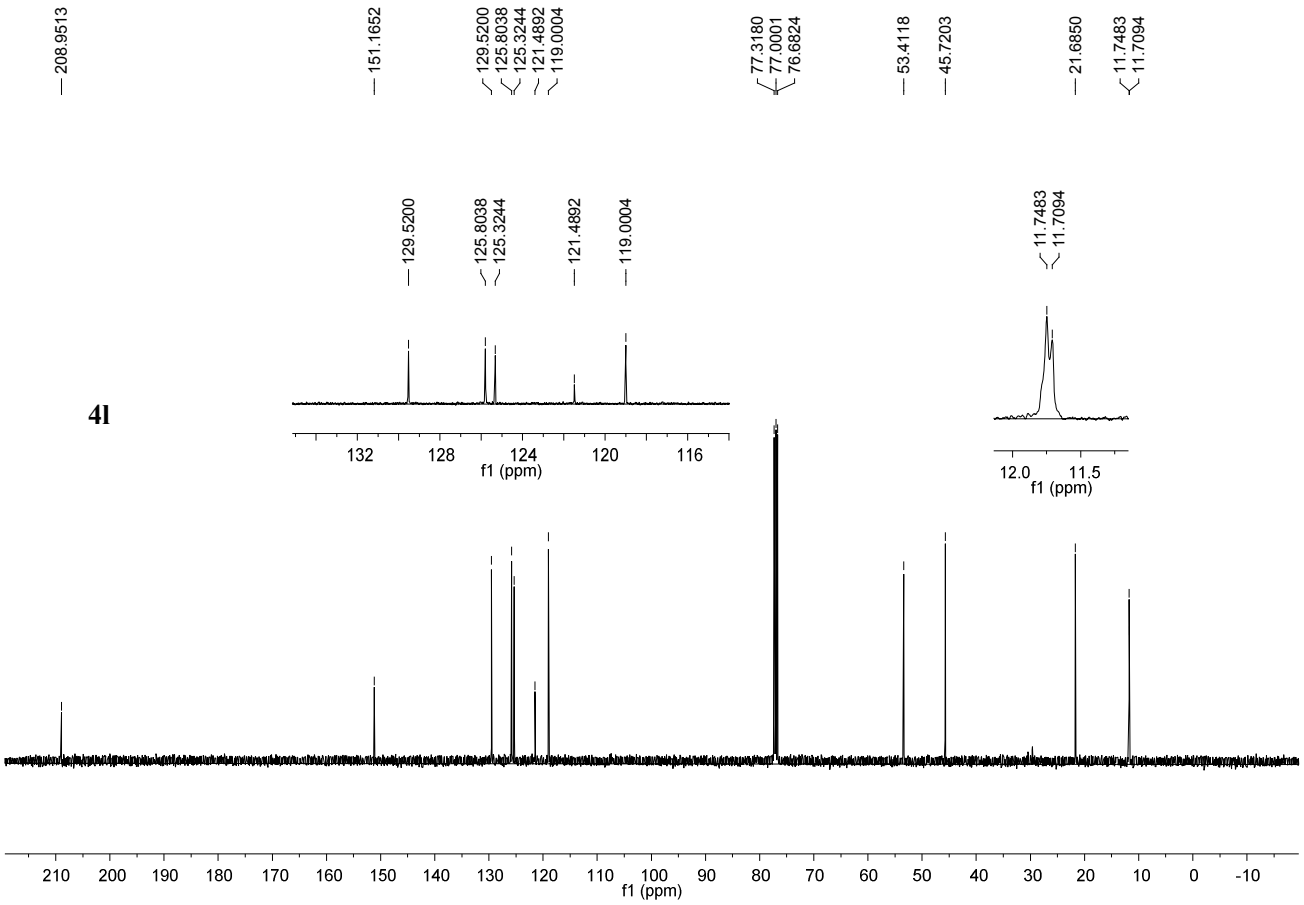
2.0028
1.9968
1.9909
1.9789
1.9718
1.9599
1.1275
1.1123
1.1059
1.0099
0.9988
0.9879
0.9847
0.9784
0.9592
0.9534
0.991
1.977
0.922
0.933
0.998
1.000
0.994
0.998
1.088
3.062
f1 (ppm)


4l
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151.1652
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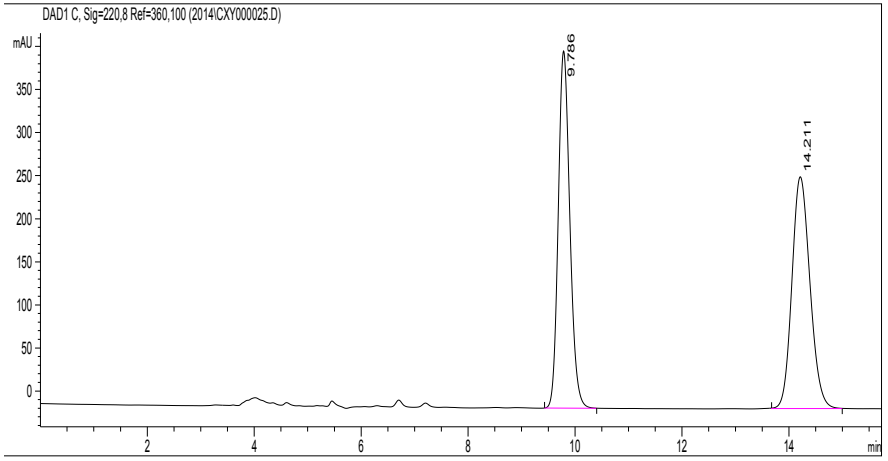
125.8038
125.3244
121.4892
119.0004
77.3180
77.0001
76.6824
53.4118
45.7203
21.6850
11.7483
11.7094
f1 (ppm)

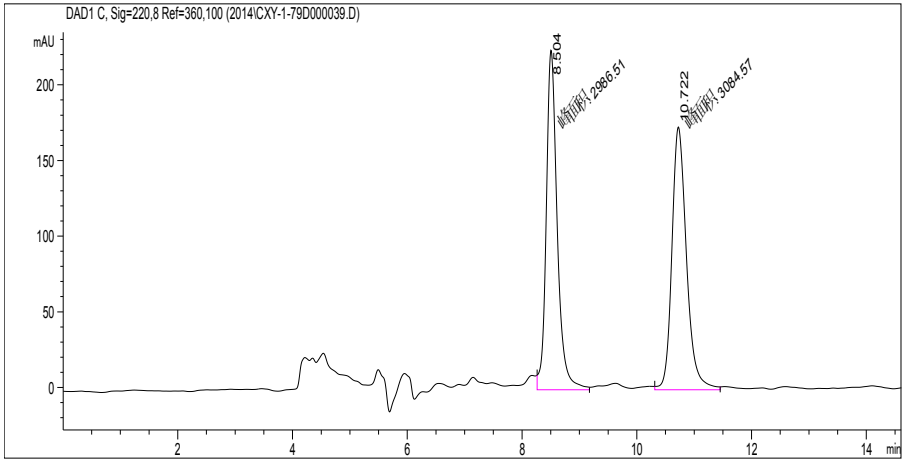
HPLC for racemic and pure enantioenriched sample **2a**



信号 2: DAD1 C, Sig=220,8 Ref=360,100

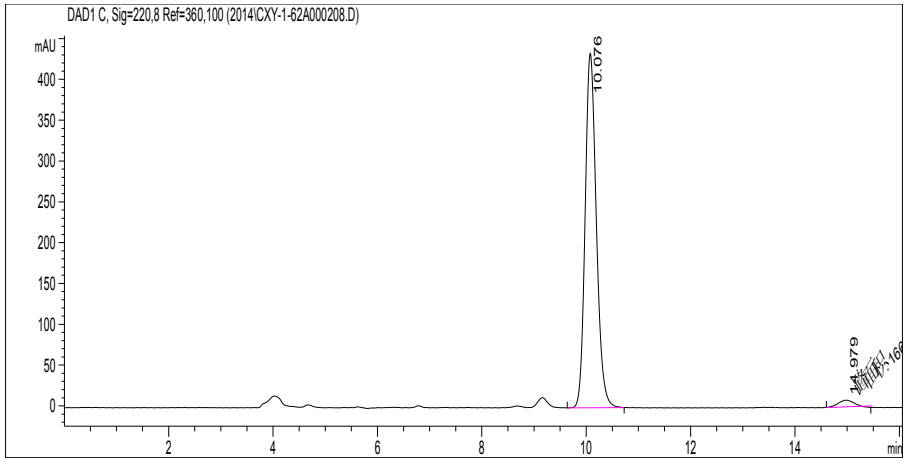
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.786	BB	0.2314	6234.88721	414.71365	49.7203
2	14.211	BB	0.3633	6305.02637	269.11935	50.2797
总量：				1.25399e4	683.83301	

HPLC for racemic and pure enantioenriched sample **2b**



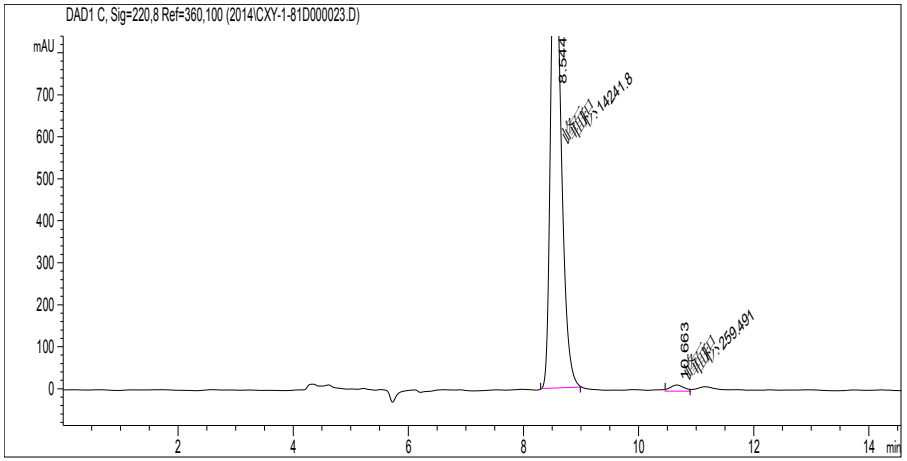
信号 2: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.504	MM	0.2216	2986.50659	224.65845	49.1924
2	10.722	MM	0.2957	3084.57227	173.87868	50.8076
总量：				6071.07886	398.53712	



信号 2: DAD1 C, Sig=220,8 Ref=360,100

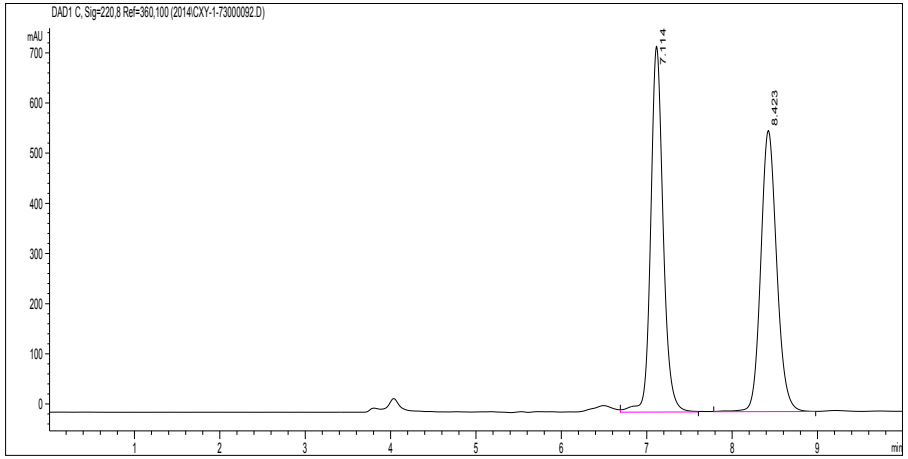
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.076	VB	0.2298	6467.71094	434.06915	97.9809
2	14.979	MM	0.3062	133.28027	7.25523	2.0191
总量：				6600.99121	441.32438	



信号 2: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.544	MM	0.2199	1.42418e4	1079.23364	98.2106
2	10.663	MM	0.2863	259.49130	15.10346	1.7894
总量：				1.45013e4	1094.33711	

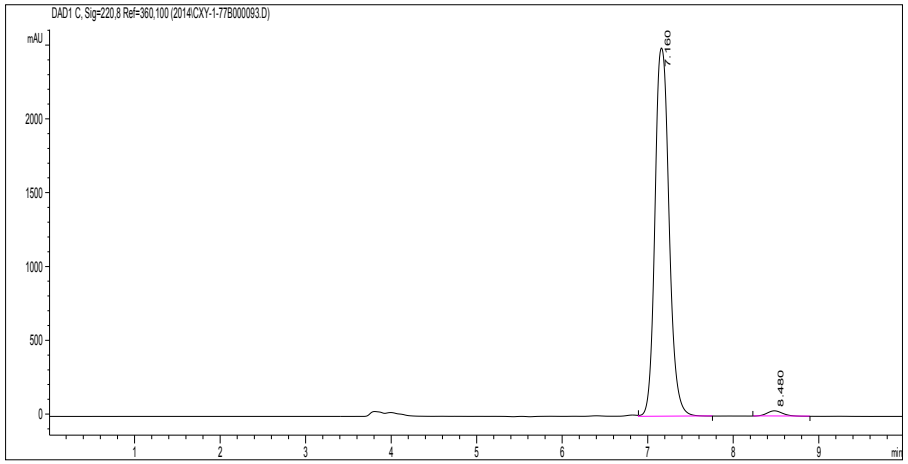
HPLC for racemic and pure enantioenriched sample **2c**



信号 2: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.114	VB	0.1544	7400.45898	729.31238	50.3926
2	8.423	BB	0.1996	7285.16162	560.66992	49.6074

总量 : 1.46856e4 1289.98230

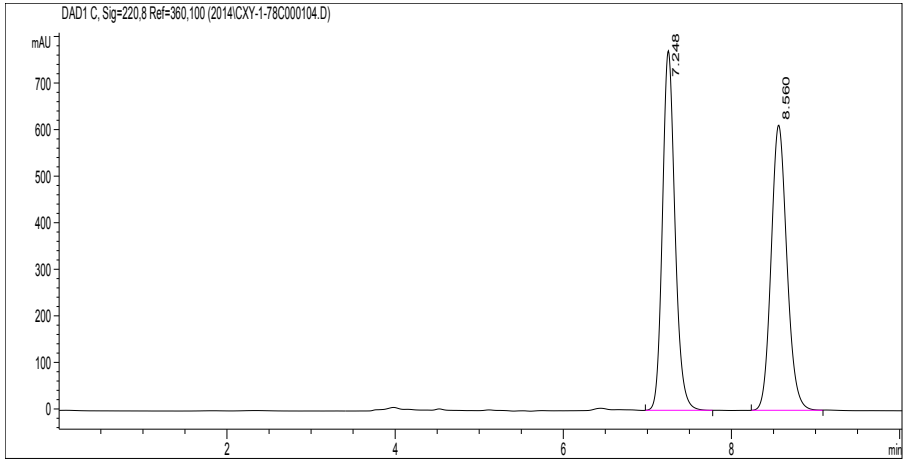


信号 2: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.160	VB	0.1798	2.86179e4	2495.20410	98.3903
2	8.480	BB	0.1989	468.20709	36.20536	1.6097

总量 : 2.90861e4 2531.40947

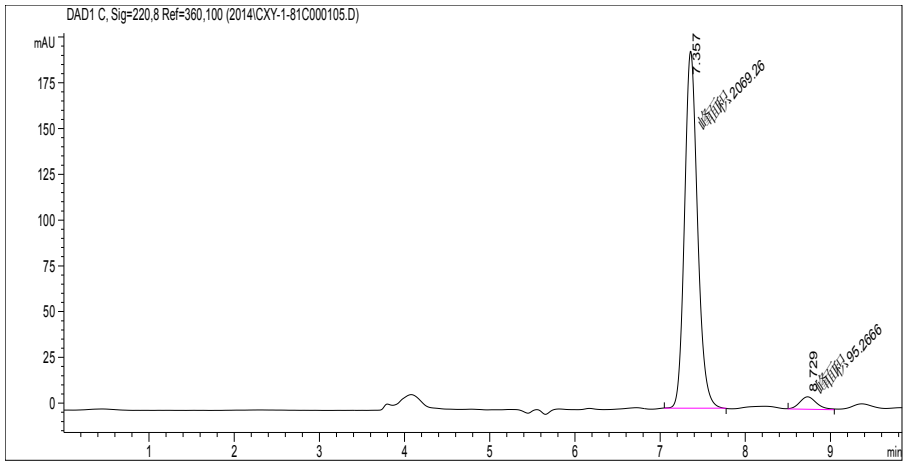
HPLC for racemic and pure enantioenriched sample **2d**



信号 2: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.248	BB	0.1590	8012.18311	772.50812	50.0890
2	8.560	BB	0.2000	7983.71680	612.90918	49.9110

总量 : 1.59959e4 1385.41730

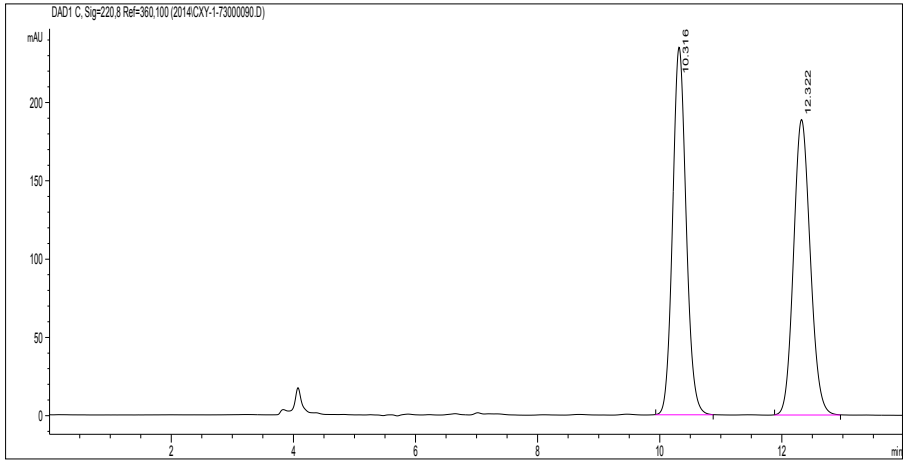


信号 2: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.357	VB	0.1735	2256.32910	197.16563	95.4992
2	8.729	VB	0.2222	106.33968	7.20407	4.5008

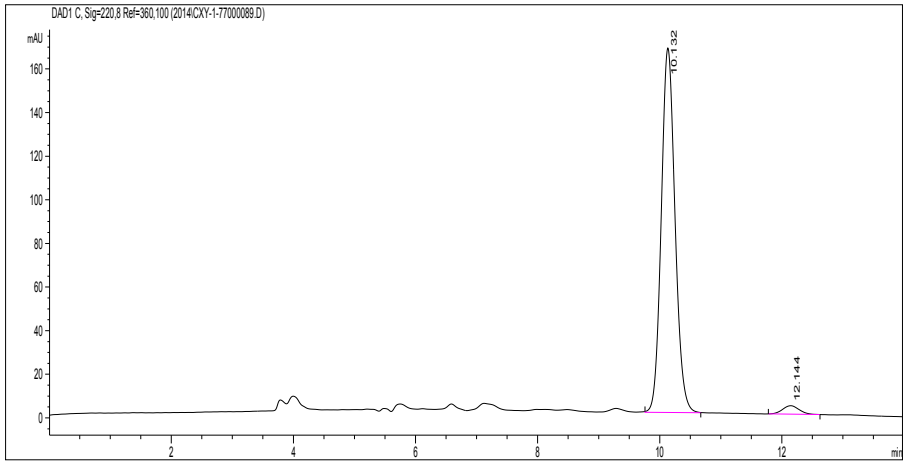
总量 : 2362.66878 204.36970

HPLC for racemic and pure enantioenriched sample **2e**



信号 2: DAD1 C, Sig=220,8 Ref=360,100

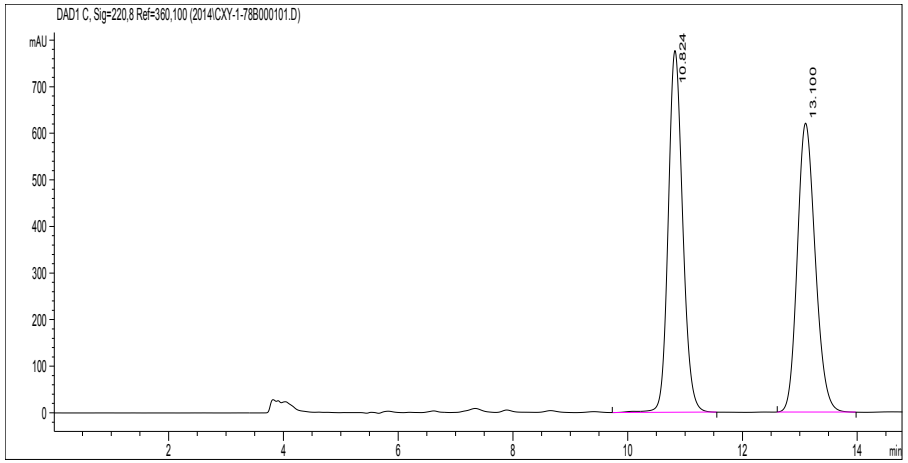
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.316	BB	0.2360	3624.50977	234.90344	50.2459
2	12.322	BB	0.2958	3589.02783	188.74948	49.7541
总量：				7213.53760	423.65292	



信号 2: DAD1 C, Sig=220,8 Ref=360,100

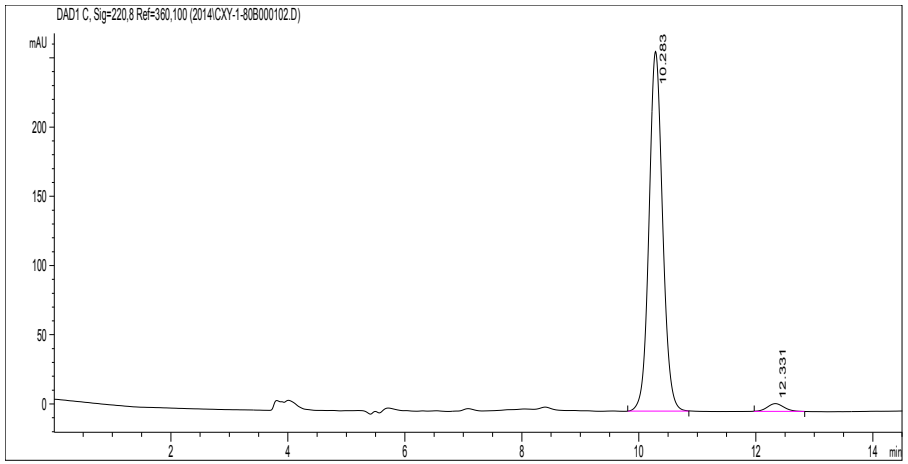
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.132	BB	0.2408	2618.16797	167.10361	97.2569
2	12.144	BB	0.2915	73.84595	3.89032	2.7431
总量：				2692.01392	170.99393	

HPLC for racemic and pure enantioenriched sample **2f**



信号 2: DAD1 C, Sig=220,8 Ref=360,100

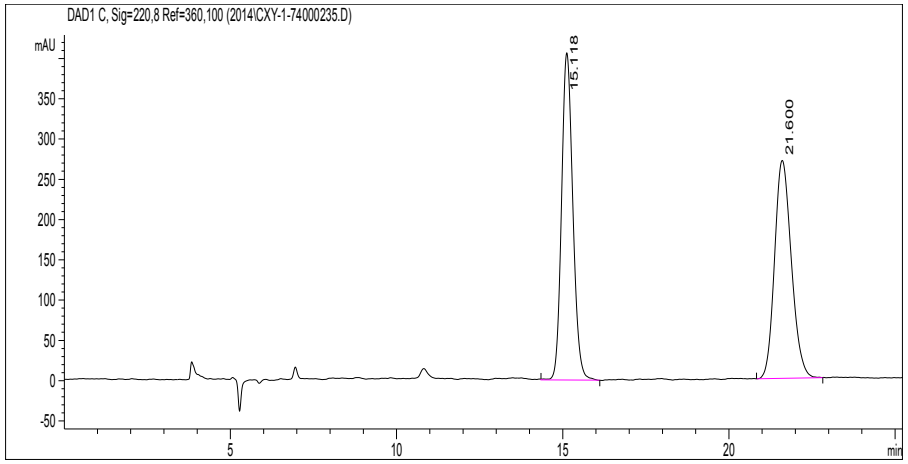
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.824	VB	0.2686	1.36193e4	776.67523	50.2752
2	13.100	BB	0.3354	1.34702e4	620.27850	49.7248
总量：				2.70895e4	1396.95374	



信号 2: DAD1 C, Sig=220,8 Ref=360,100

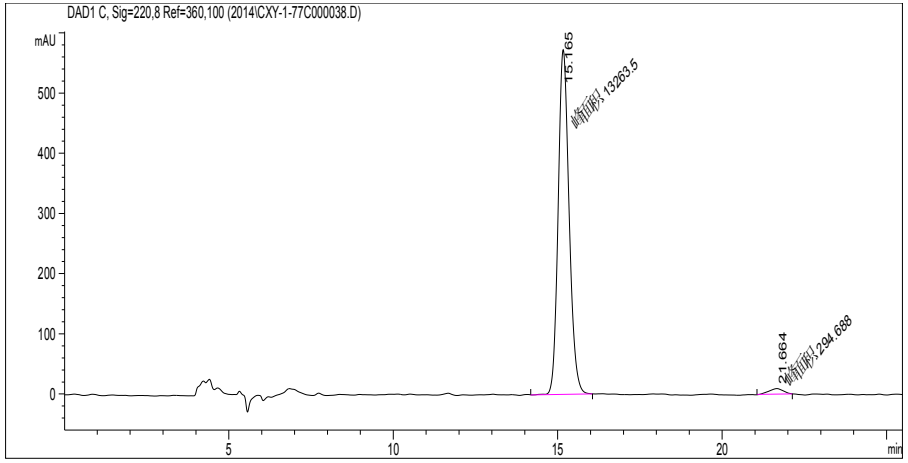
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.283	BB	0.2483	4193.51563	259.80078	97.3584
2	12.331	BB	0.3043	113.78202	5.66606	2.6416
总量：				4307.29765	265.46684	

HPLC for racemic and pure enantioenriched sample **2g**



信号 2: DAD1 C, Sig=220,8 Ref=360,100

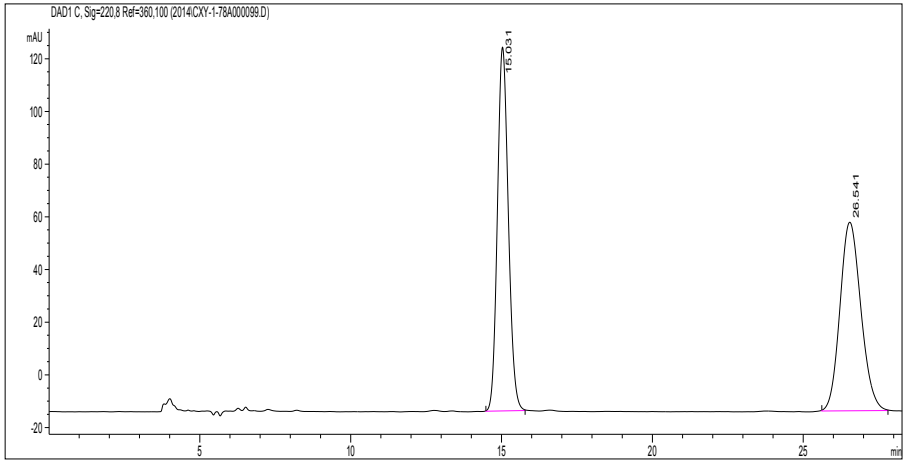
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.118	VB	0.3643	9625.43945	406.41882	50.2909
2	21.600	VB	0.5441	9514.09473	270.69171	49.7091
总量：				1.91395e4	677.11053	



信号 2: DAD1 C, Sig=220,8 Ref=360,100

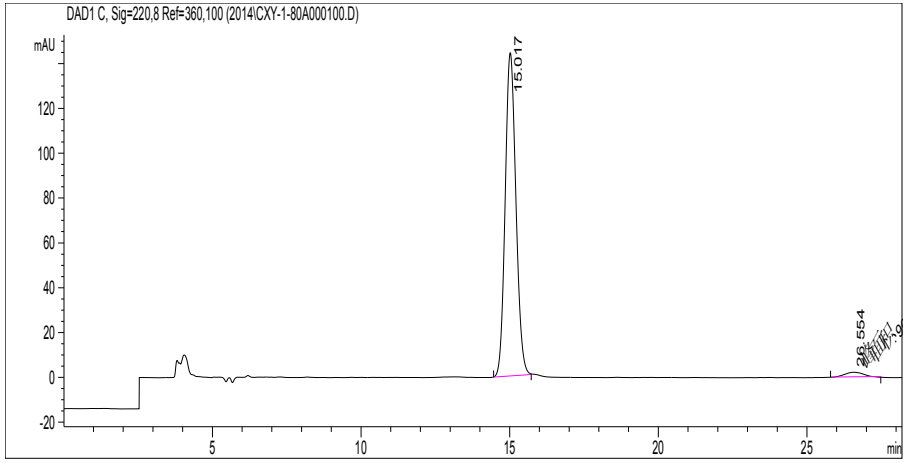
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.165	MM	0.3857	1.32635e4	573.10760	97.8265
2	21.664	MM	0.5167	294.68802	9.50520	2.1735
总量：				1.35582e4	582.61280	

HPLC for racemic and pure enantioenriched sample **2h**



信号 2: DAD1 C, Sig=220,8 Ref=360,100

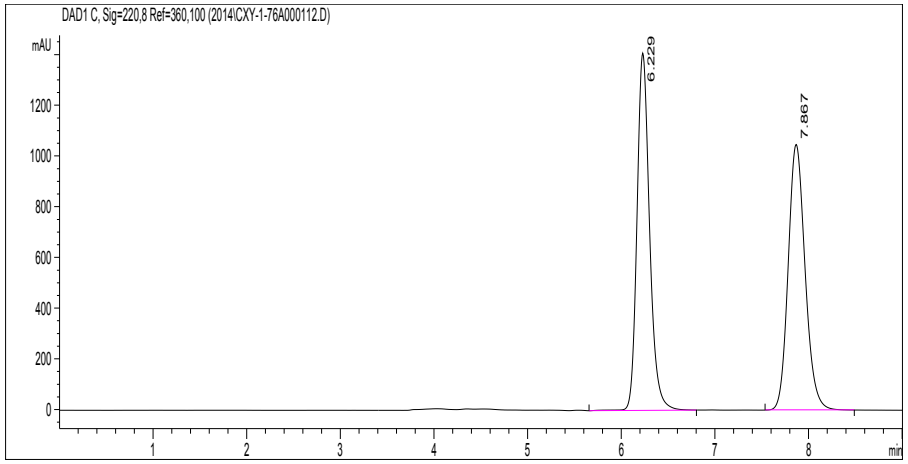
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.031	BB	0.3899	3479.35278	138.09999	50.1868
2	26.541	BB	0.7484	3453.45459	71.63691	49.8132
总量：				6932.80737	209.73690	



信号 2: DAD1 C, Sig=220,8 Ref=360,100

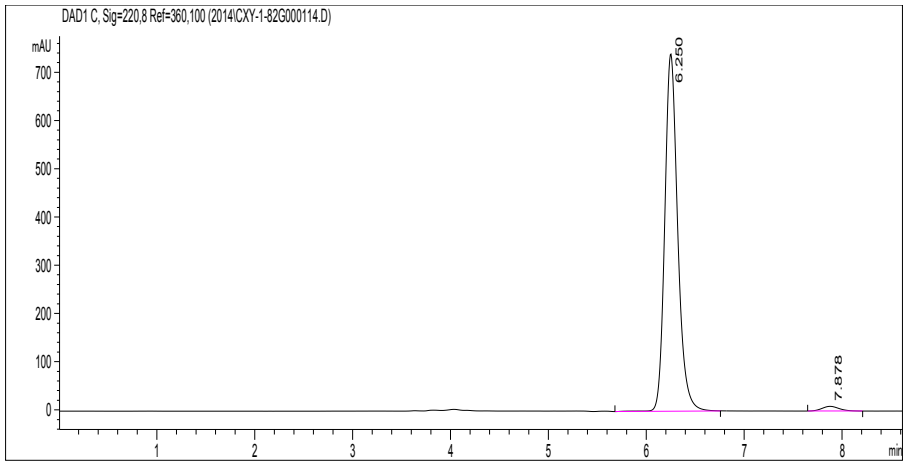
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.017	BB	0.3904	3613.97607	144.21667	97.5697
2	26.554	MM	0.7112	90.01949	2.10960	2.4303
总量：				3703.99556	146.32627	

HPLC for racemic and pure enantioenriched sample **2i**



信号 2: DAD1 C, Sig=220,8 Ref=360,100

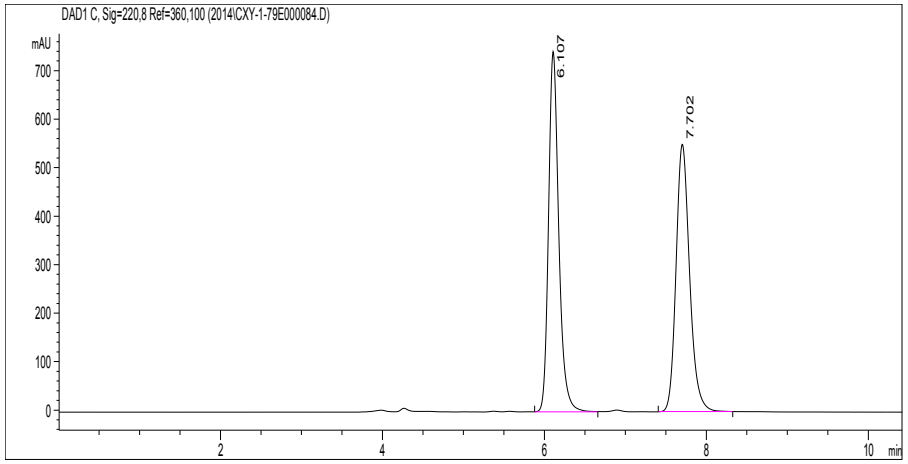
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.229	VB	0.1432	1.31888e4	1408.87585	50.0834
2	7.867	BB	0.1944	1.31448e4	1047.55847	49.9166
总量：				2.63336e4	2456.43433	



信号 2: DAD1 C, Sig=220,8 Ref=360,100

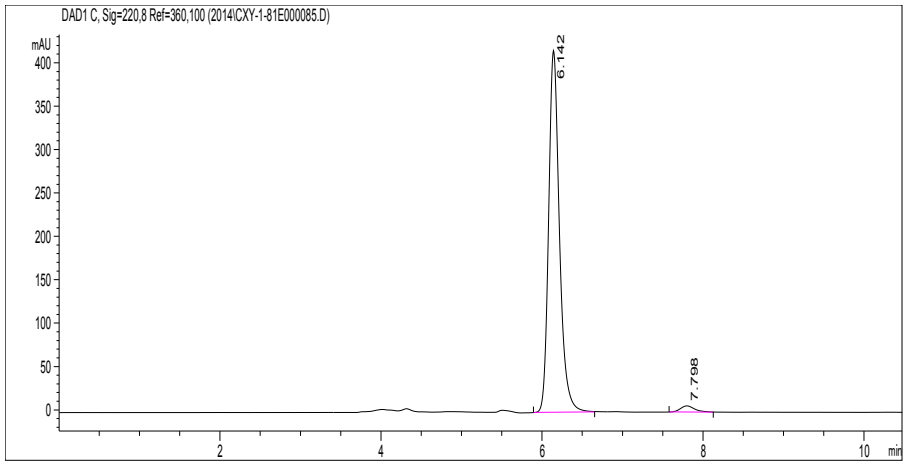
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.250	VB	0.1391	6802.08105	741.24585	98.2709
2	7.878	BB	0.1891	119.68291	9.76028	1.7291
总量：				6921.76397	751.00613	

HPLC for racemic and pure enantioenriched sample **2j**



信号 2: DAD1 C, Sig=220,8 Ref=360,100

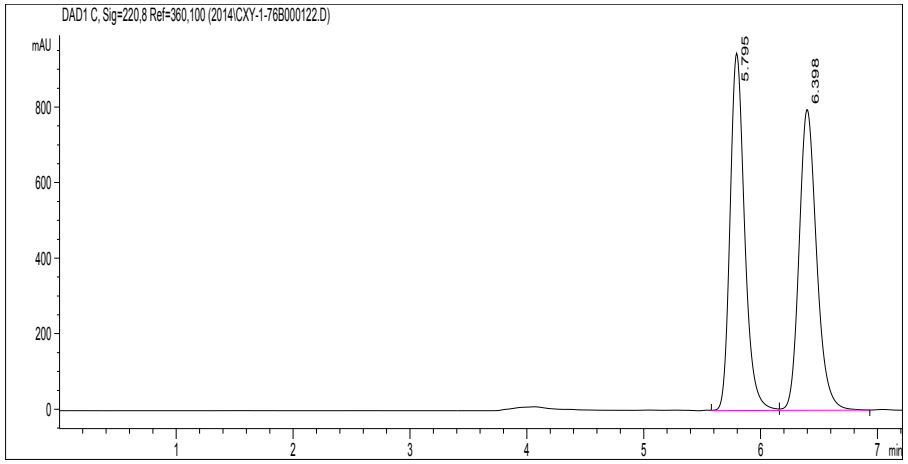
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.107	BB	0.1325	6528.36963	742.84656	50.3988
2	7.702	BB	0.1778	6425.06152	551.78943	49.6012
总量：				1.29534e4	1294.63599	



信号 2: DAD1 C, Sig=220,8 Ref=360,100

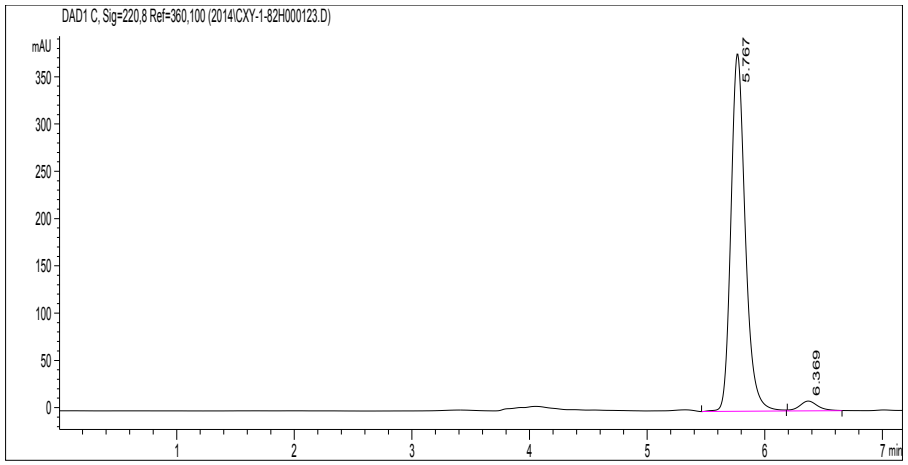
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.142	BB	0.1428	3888.69312	416.97598	97.7505
2	7.798	BB	0.1896	89.49083	7.17051	2.2495
总量：				3978.18394	424.14649	

HPLC for racemic and pure enantioenriched sample **2k**



信号 2: DAD1 C, Sig=220,8 Ref=360,100

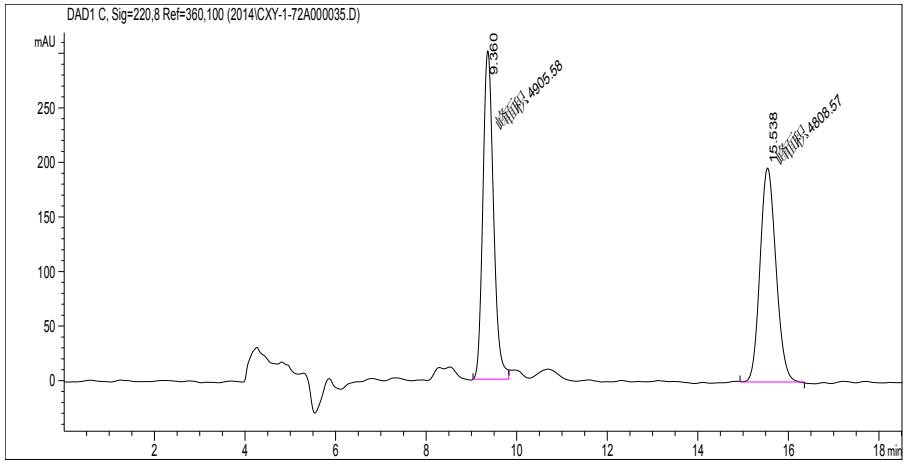
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.795	VV	0.1311	8201.44531	946.36481	49.6127
2	6.398	VV	0.1619	8329.48047	797.23413	50.3873
总量：				1.65309e4	1743.59894	



信号 2: DAD1 C, Sig=220,8 Ref=360,100

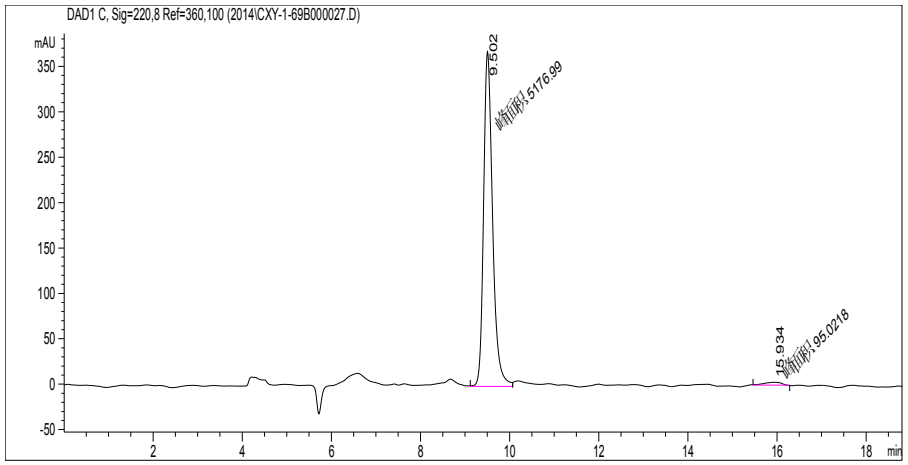
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.767	VB	0.1289	3209.33057	378.65247	96.5736
2	6.369	BB	0.1634	113.86711	10.42829	3.4264
总量：				3323.19768	389.08075	

HPLC for racemic and pure enantioenriched sample **4a**



信号 2: DAD1 C, Sig=220,8 Ref=360,100

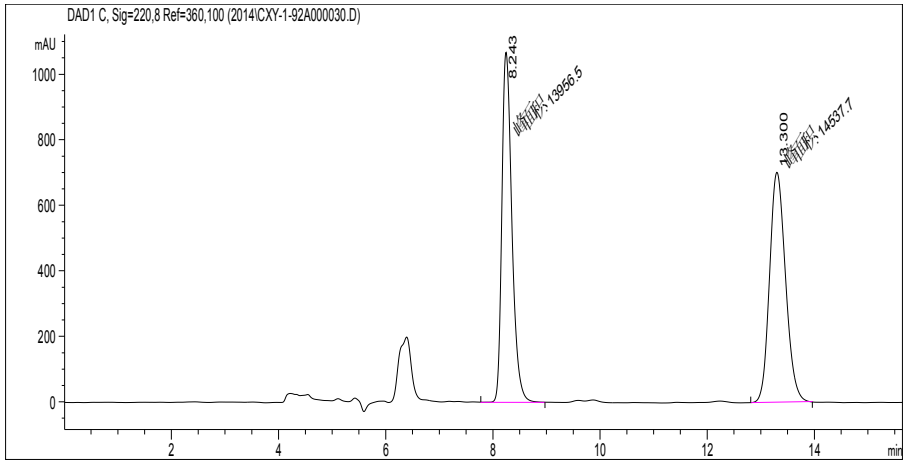
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.360	MM	0.2715	4905.58496	301.10931	50.4993
2	15.538	MM	0.4082	4808.57031	196.32689	49.5007
总量：				9714.15527	497.43620	



信号 2: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.502	MM	0.2340	5176.98926	368.71222	98.1976
2	15.934	MM	0.4683	95.02184	3.38194	1.8024
总量：				5272.01109	372.09416	

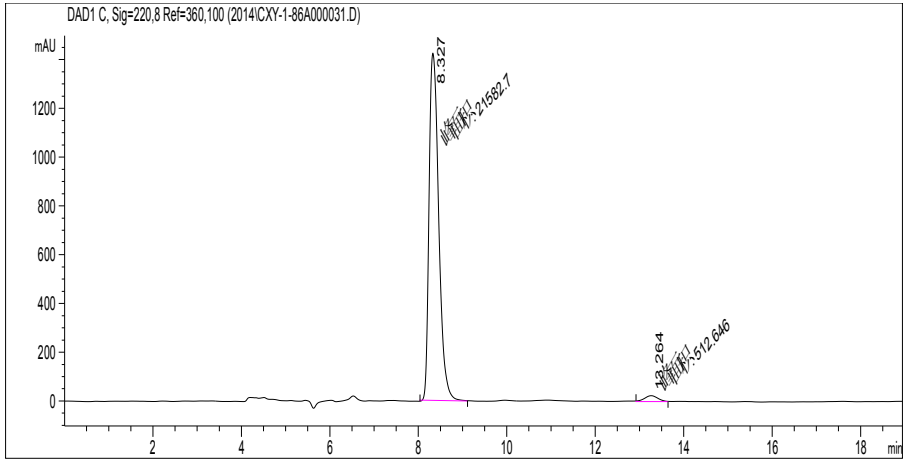
HPLC for racemic and pure enantioenriched sample **4b**



信号 2: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.243	MM	0.2175	1.39565e4	1069.31714	48.9801
2	13.300	MM	0.3452	1.45377e4	701.88049	51.0199

总量 : 2.84942e4 1771.19763

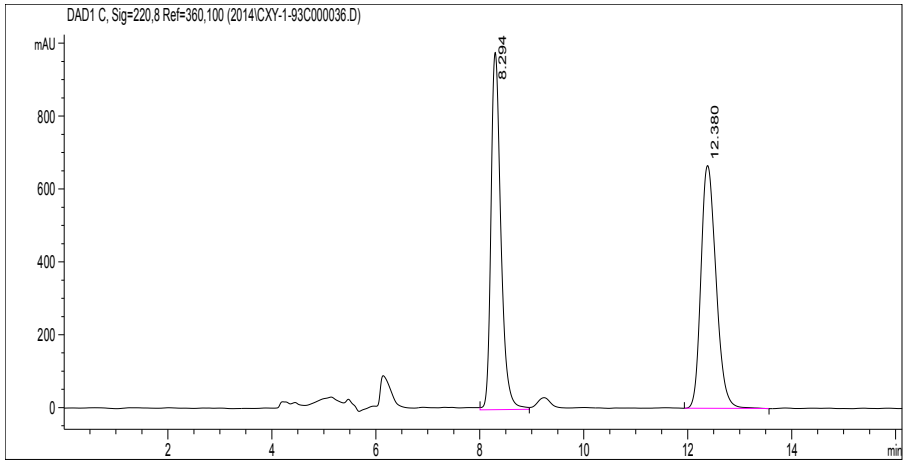


信号 2: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.327	MM	0.2527	2.15827e4	1423.50037	97.6798
2	13.264	MM	0.3532	512.64600	24.18923	2.3202

总量 : 2.20954e4 1447.68959

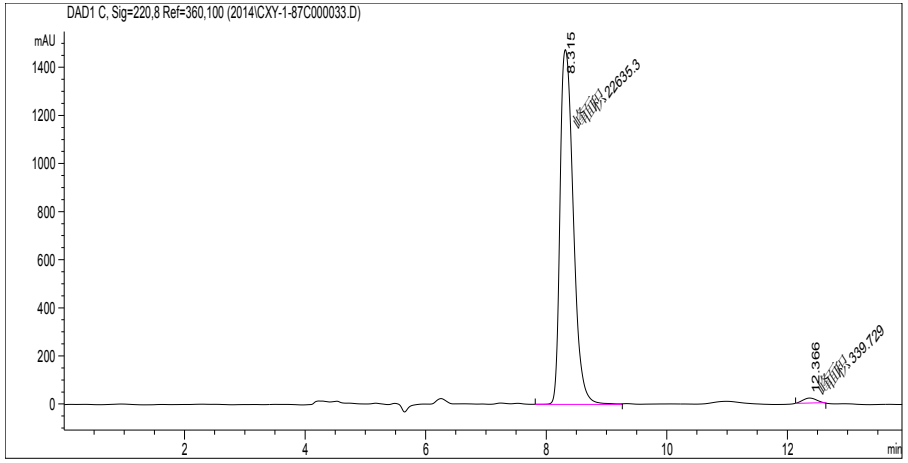
HPLC for racemic and pure enantioenriched sample **4c**



信号 2: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.294	BV	0.2025	1.29819e4	980.54248	49.1016
2	12.380	VB	0.3216	1.34569e4	666.39166	50.8984

总量 : 2.64388e4 1646.93414

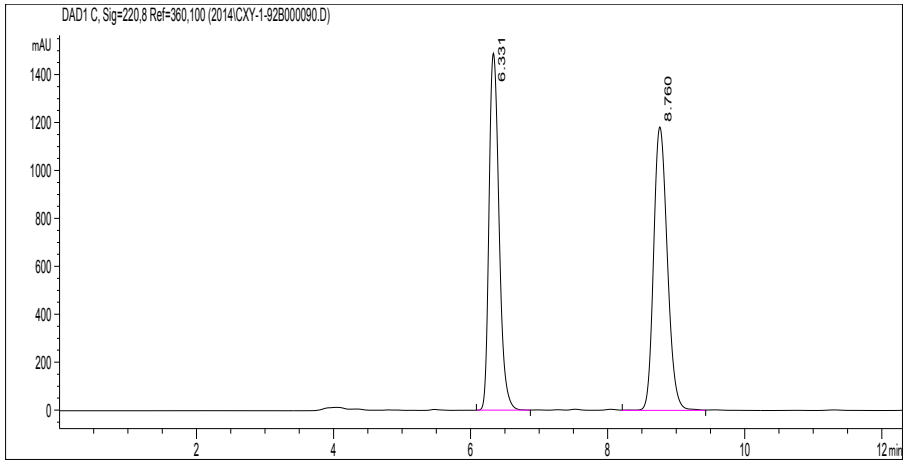


信号 2: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.315	MM	0.2556	2.26353e4	1476.19519	98.5213
2	12.366	MM	0.2645	339.72885	21.40765	1.4787

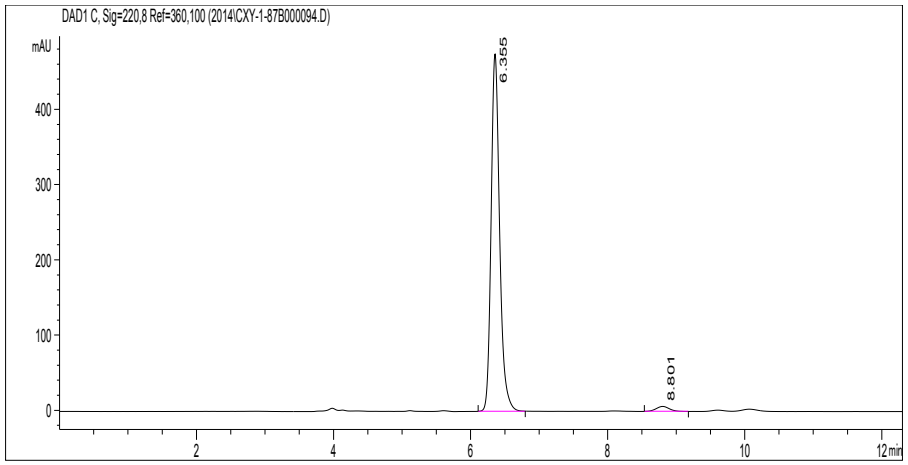
总量 : 2.29750e4 1497.60284

HPLC for racemic and pure enantioenriched sample **4d**



信号 2: DAD1 C, Sig=220,8 Ref=360,100

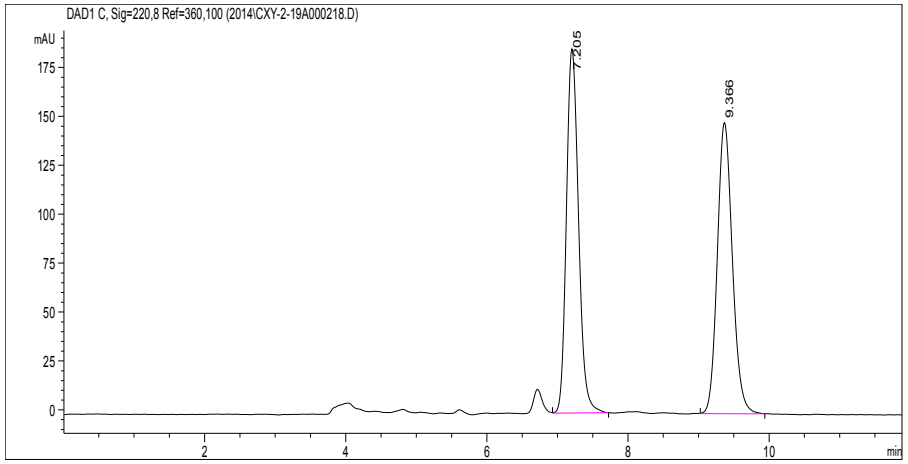
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.331	BB	0.1589	1.51879e4	1490.37976	47.9665
2	8.760	VV	0.2185	1.64757e4	1182.84839	52.0335
总量：				3.16636e4	2673.22815	



信号 2: DAD1 C, Sig=220,8 Ref=360,100

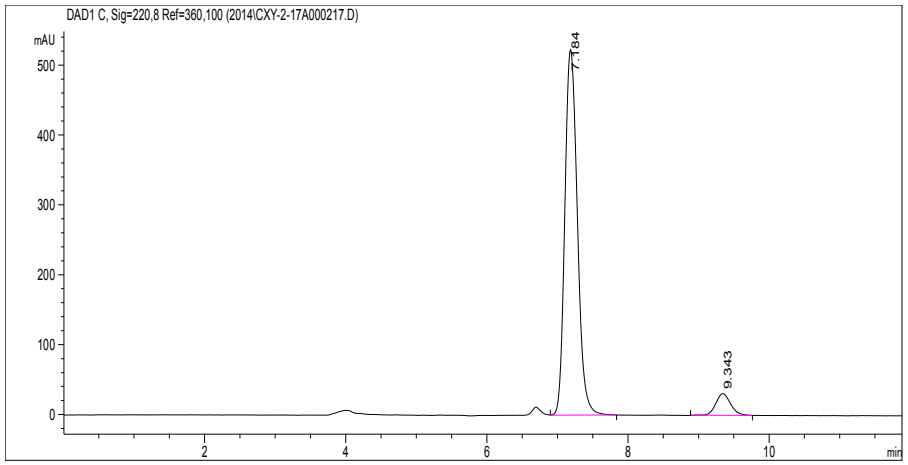
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.355	BB	0.1327	4102.70215	475.52829	97.8840
2	8.801	BB	0.2056	88.69110	6.64887	2.1160
总量：				4191.39325	482.17716	

HPLC for racemic and pure enantioenriched sample **4e**



信号 2: DAD1 C, Sig=220,8 Ref=360,100

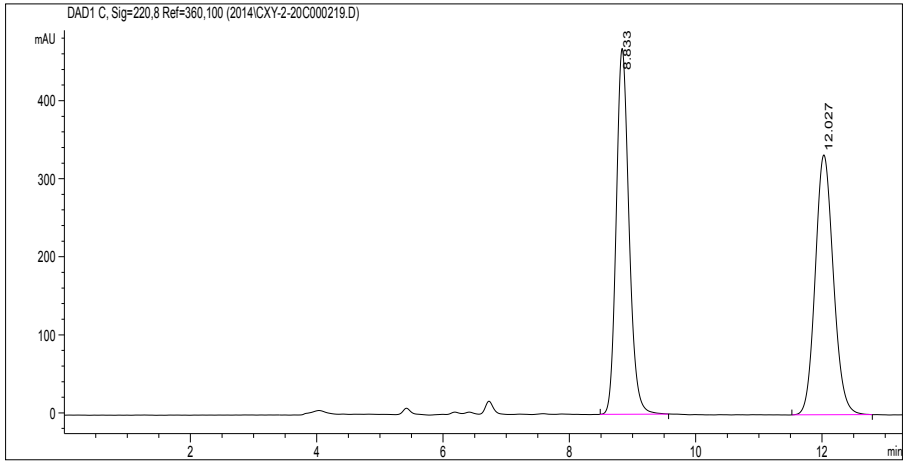
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.205	VB	0.1874	2224.38403	186.17825	50.1371
2	9.366	BB	0.2294	2212.22192	148.81844	49.8629
总量：				4436.60596	334.99669	



信号 2: DAD1 C, Sig=220,8 Ref=360,100

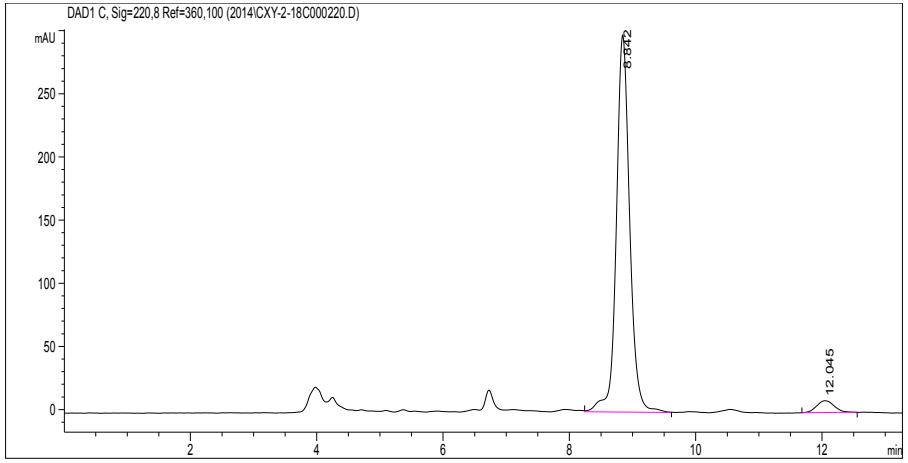
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.184	VB	0.1961	6459.75684	522.95007	93.3360
2	9.343	BB	0.2267	461.21164	31.14886	6.6640
总量：				6920.96848	554.09893	

HPLC for racemic and pure enantioenriched sample **4f**



信号 2: DAD1 C, Sig=220,8 Ref=360,100

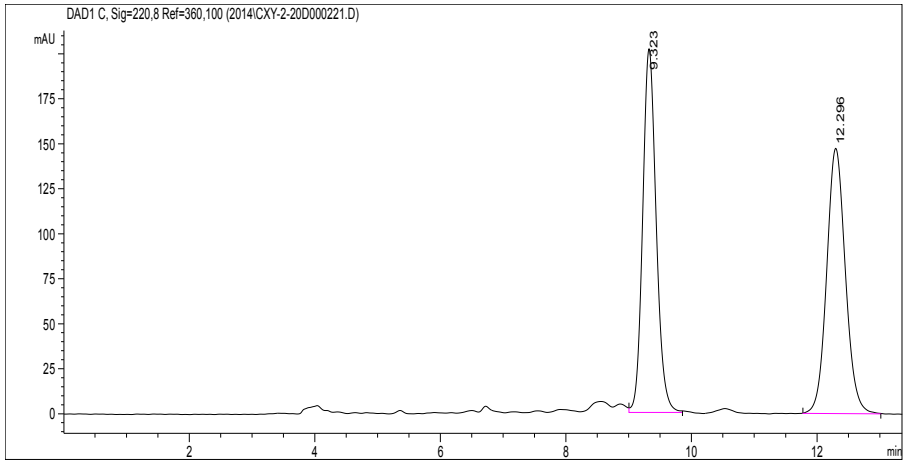
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.833	BB	0.2164	6607.58252	468.86636	49.8497
2	12.027	BB	0.3089	6647.43701	333.02460	50.1503
总量：				1.32550e4	801.89096	



信号 2: DAD1 C, Sig=220,8 Ref=360,100

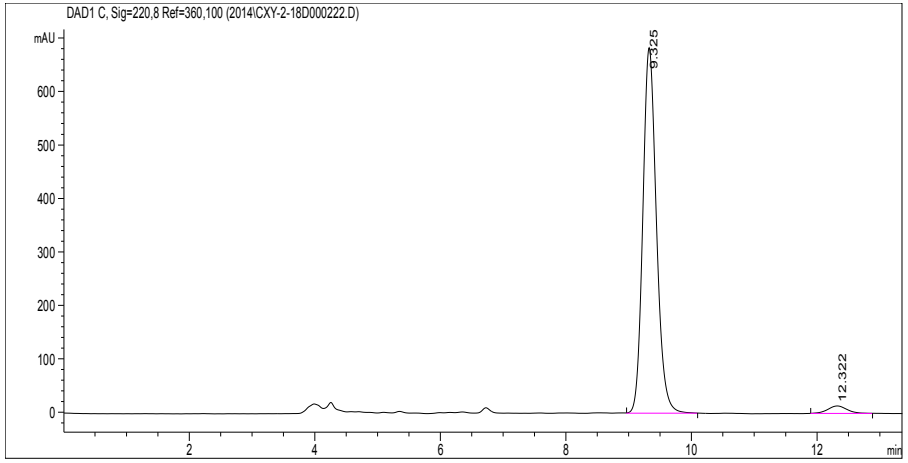
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.842	VB	0.2218	4395.56738	298.44586	95.9480
2	12.045	BB	0.3010	185.63002	9.45831	4.0520
总量：				4581.19740	307.90417	

HPLC for racemic and pure enantioenriched sample **4g**



信号 2: DAD1 C, Sig=220,8 Ref=360,100

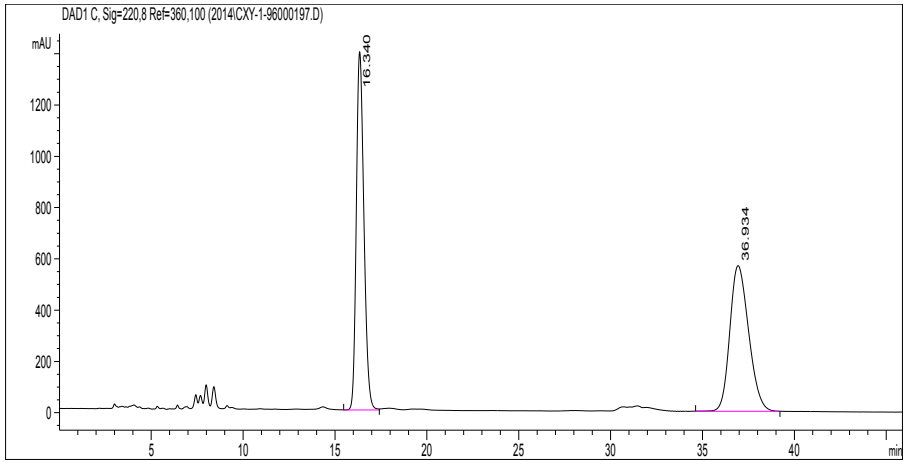
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.323	VB	0.2288	3027.01074	202.04700	49.7277
2	12.296	BB	0.3202	3060.16162	147.43176	50.2723
总量：				6087.17236	349.47876	



信号 2: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.325	BB	0.2298	1.03054e4	683.76392	97.1335
2	12.322	BB	0.3260	304.12646	14.07875	2.8665
总量：				1.06095e4	697.84266	

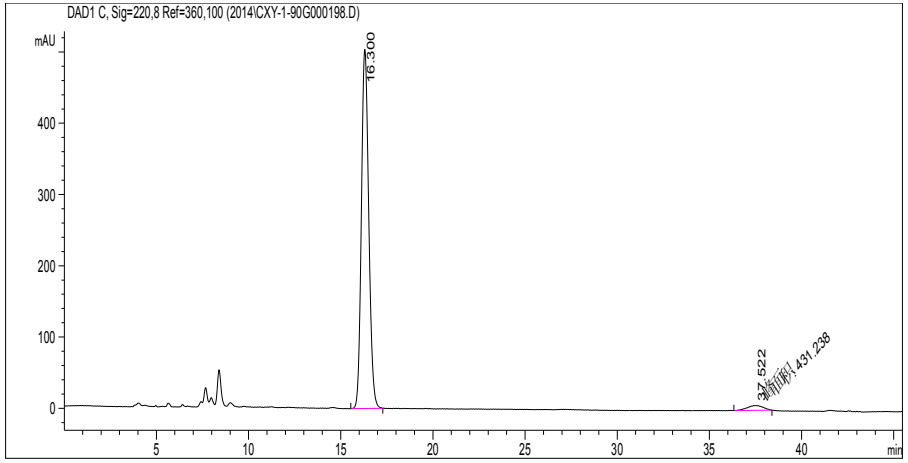
HPLC for racemic and pure enantioenriched sample **4h**



信号 2: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.340	VB	0.4452	4.01542e4	1397.59692	49.7229
2	36.934	BB	1.1236	4.06018e4	568.26166	50.2771

总量 : 8.07560e4 1965.85858

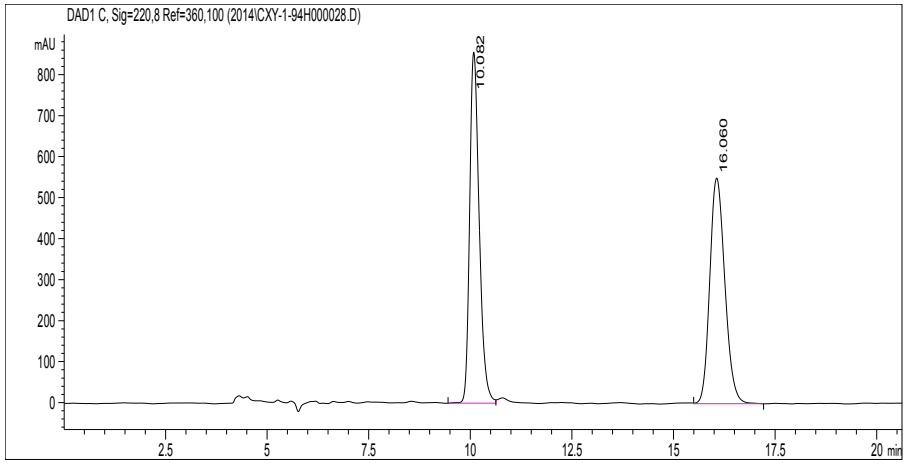


信号 2: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.300	VB	0.4276	1.39786e4	503.98010	97.0073
2	37.522	MM	1.0318	431.23782	6.96586	2.9927

总量 : 1.44099e4 510.94597

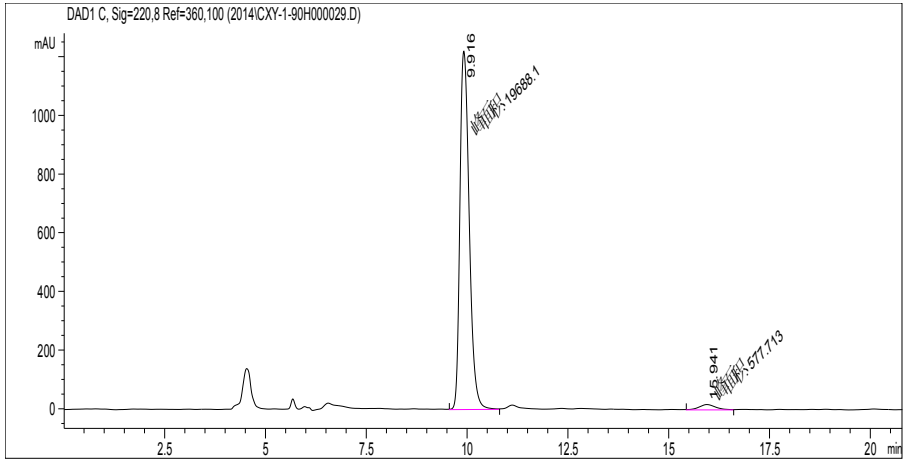
HPLC for racemic and pure enantioenriched sample **4i**



信号 2: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.082	BV	0.2470	1.40130e4	856.15204	49.5989
2	16.060	VB	0.3956	1.42396e4	550.74084	50.4011

总量 : 2.82526e4 1406.89288

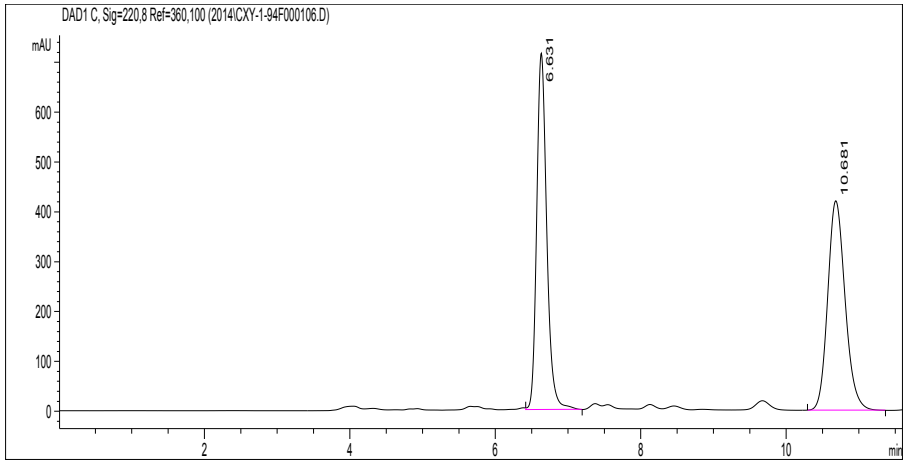


信号 2: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.916	MM	0.2686	1.96881e4	1221.48560	97.1493
2	15.941	MM	0.5090	577.71265	18.91502	2.8507

总量 : 2.02658e4 1240.40062

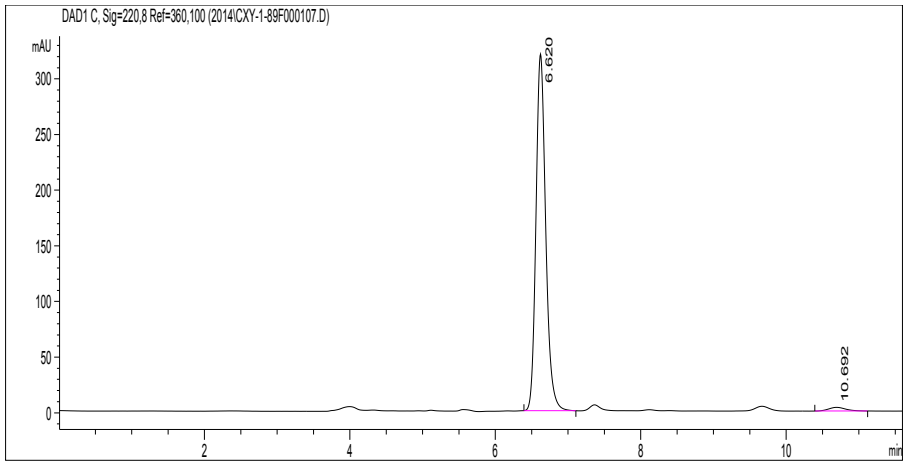
HPLC for racemic and pure enantioenriched sample **4j**



信号 2: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.631	VV	0.1480	6866.25977	715.41711	49.5523
2	10.681	BB	0.2561	6990.33545	420.25735	50.4477

总量 : 1.38566e4 1135.67447

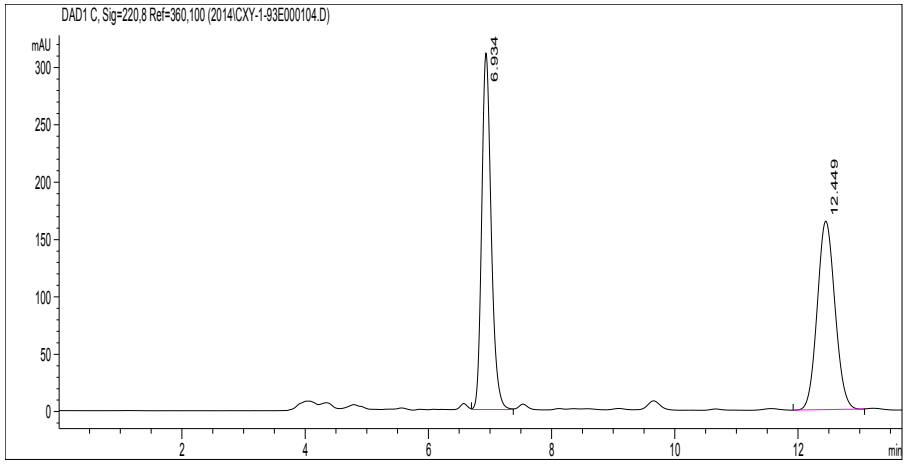


信号 2: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.620	BB	0.1428	2990.46167	320.57642	98.1537
2	10.692	BB	0.2566	56.25220	3.33892	1.8463

总量 : 3046.71387 323.91534

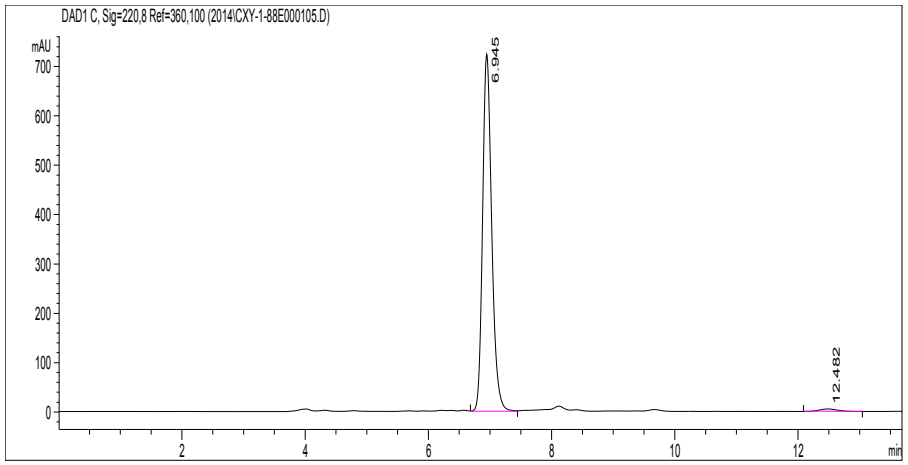
HPLC for racemic and pure enantioenriched sample **4k**



信号 2: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.934	VV	0.1651	3334.88257	310.93454	50.3115
2	12.449	VB	0.3097	3293.59229	164.39861	49.6885

总量 : 6628.47485 475.33315

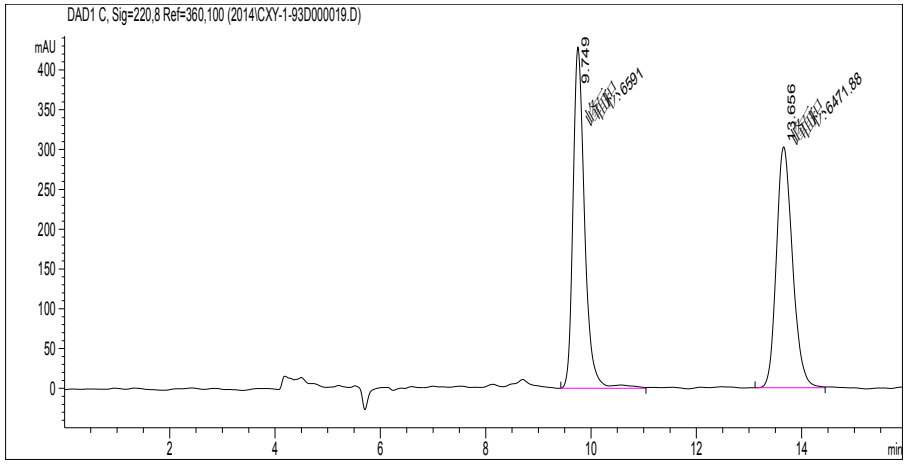


信号 2: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.945	VV	0.1581	7450.79297	723.85913	98.6527
2	12.482	BB	0.3210	101.75320	5.00923	1.3473

总量 : 7552.54617 728.86836

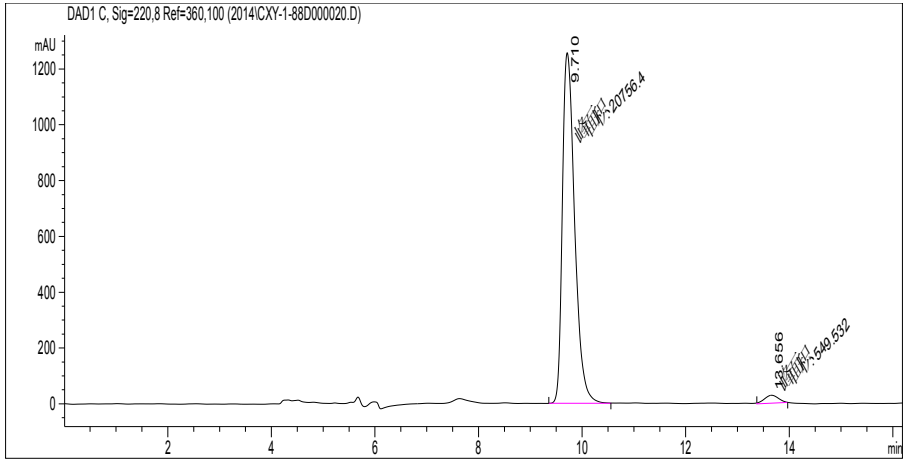
HPLC for racemic and pure enantioenriched sample **4l**



信号 2: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.749	MM	0.2562	6590.99561	428.69244	50.4559
2	13.656	MM	0.3562	6471.88281	302.83783	49.5441

总量 : 1.30629e4 731.53027



信号 2: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.710	MM	0.2752	2.07564e4	1257.24915	97.4208
2	13.656	MM	0.3172	549.53210	28.87473	2.5792

总量 : 2.13060e4 1286.12388