Supplementary Information

Distinct Reactivity of Morita-Baylis-Hillman Acetates as A Novel C_2 Component in Amine-Catalyzed [2 + 2 + 2] and [2 + 4] Annulations

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1. General Remarks

Unless otherwise noted, all reactions were carried out in a nitrogen atmosphere. Allylic acetates **1** were prepared according to previously reported procedures[1] by treating the corresponding Morita-Baylis–Hillman alcohols[2] with AcCl/pyridine. Substrates **3** and **5** were prepared according to literature methods.[3,4] All other reagents were purchased from commercial sources and used without further purification. NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 with tetramethylsilane (TMS) as the internal standard. Column chromatography was performed on silica gel (200-300 mesh) using a mixture of petroleum ether/ethyl acetate as eluant.

1. S. Nag, G. P. Yadav, P. R. Maulik, S. Batra, *Synthesis* 2007, **6**, 911.

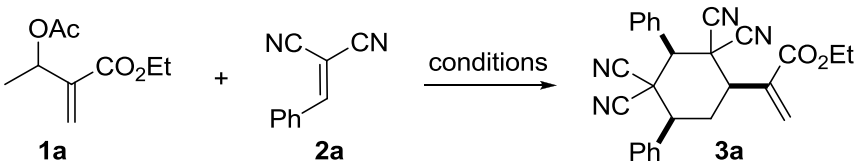
2. (*a*) C. Z. Yu, B. Liu, L. Q. Hu, *J. Org. Chem.* 2001, **66**, 5413; (*b*) V. K. Aggarwal, A. Mereu, *Chem. Commun*.. 1999, 2311.

3. D. Prajapati, K. C. Lekhok, J. S. Sandhu, A. C. Ghosh, *J. Chem. Soc., Perkin Trans. 1.* 1996, 959.

4. H. Dückert, V. Khedkar, H. Waldmann, K. Kumar, *Chem.–Eur. J.* 2011, **17**, 5130.

2. Optimization on Conditions for the [2 + 2 + 2] and [2 + 4] Annulations

Table S1. Survey on Conditions for the [2 + 2 + 2] Annulation Reaction.[a]

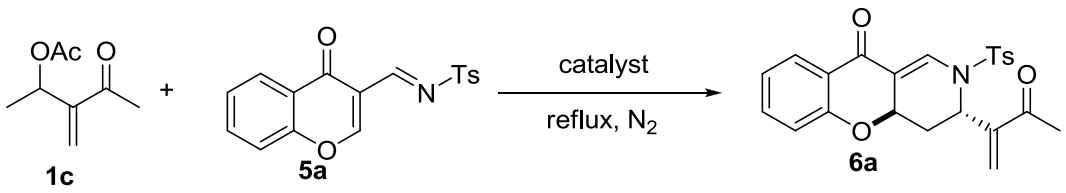


1a **2a** **3a**

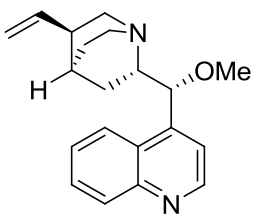
Entry	Catalyst	Solvent	Time (h)	Yield[b](%)
1	DABCO	THF	24	54
2	DMAP	THF	24	43
3	DBU	THF	24	37
4	quinine	THF	24	trace
5	imidazole	THF	24	trace
6	NEt_3	THF	24	trace
7	DABCO	DMSO	12	85
8	***DABCO***	***DMF***	***12***	***93***
9	DABCO	ethanol	48	/
10	DABCO	CH_3CN	12	64
11	DABCO	1,4-dioxane	12	39
12	DABCO	CH_2Cl_2	48	43
13	DABCO	toluene	48	21
14[c]	DABCO	DMF	48	81
15[d]	DABCO	DMF	72	54

[a] Typical conditions: under N_2 and at r.t.**,** to a stirred solution of **1a** (0.5 mmol) and **2a** (0.5 mmol) in solvent (3.0 mL) was added the amine catalyst (0.05 mmol). [b] Isolated yield based on **2a**. [c] catalyst loading 5 mol %. [d] catalyst loading 1 mol %.

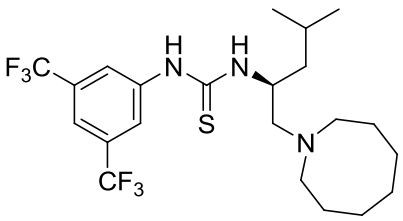
Table S2. Survey on Conditions for the [2+ 4] Annulation Reaction.[a]



Entry	Catalyst	Solvent	Time (h)	Yield[b](%)
1	DABCO	THF	5	46
2	DMAP	THF	5	66
3	DBU	THF	24	0
4	pyridine	THF	24	0
5	NEt_3	THF	24	0
6	imidazole	THF	24	36
7	Catalyst **1**	THF	24	0
8	Catalyst **2**	THF	24	0
9	DMAP	xylene	12	50
10	DMAP	toluene	24	73
11	DMAP	1,4-dioxane	24	26
12	DMAP	DMF	48	0
13	DMAP	CH_2Cl_2	24	76
14	DMAP	CH_3CN	24	45
15	***DMAP***	***$CHCl_3$***	***6***	***79***
16[c]	DMAP	$CHCl_3$	24	53
17[d]	DMAP	$CHCl_3$	12	77
18[e]	DMAP	$CHCl_3$	12	72
19[f]	DMAP	$CHCl_3$	12	69



Catalyst **1**



Catalyst **2**

[a] Typical procedure : a mixture of allylic acetate **1c** (0.3 mmol), **5** (0.2 mmol) and the catalyst (0.04 mmol) in solvent (2.0 mL) was refluxed. [b] Isolated yield based on **5a**. [c] run at r.t. [d] 0.4 mmol of **1c** was used. [e] a solution of **1c** (0.3 mmol) in $CHCl_3$ (1.0 mL) was dropwise added over15 min. [f] catalyst loading 10 mol %.

3. General Reaction Procedures

a. General Procedure for DABCO-Catalyzed [2 + 2 + 2] Annulation (Table 1)

Under a N_2 atmosphere and at room temperature, to a stirred solution of **1** (0.3 mmol; for entries 11, 12, 16, 17, 21, 0.5 mmol) and **2** (0.5 mmol) in DMF (3.0 mL) was added DABCO (0.05 mmol), and the resulting mixture was continuously stirred at r.t. for the specified hours (monitored by TLC). Water (10 mL) was added into it and the mixture was extracted twice with CH_2Cl_2 (20 mL × 2). The combined organic layer was dried over anhydrous sodium sulfate. After filtration and concentrated on a rotary evaporator under reduced pressure, the residue was subjected to column chromatography on silica gel (gradient eluant: petroleum ether/ethyl acetate 5:1–2:1) to give the [2 + 2 + 2] annulation products **3**.

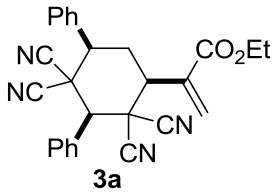
b. General Procedure for DMAP-Catalyzed [2 + 4] Annulation (Table 2)

Under a N_2 atmosphere, a mixture of MBH acetates **1** (for entries 1–6, 0.3 mmol; for entries 7–10, 0.4 mmol), azadienes **5** (0.2 mmol), and DMAP (0.04 mmol) in chloroform or THF (2.0 mL) was refluxed for 24 h. After evaporation of the solvent and volatile components on a rotary evaporator, the residue was isolated by column chromatography on silica gel (gradient eluant: petroleum ether/ethyl acetate 20:1–5:1) to afford the [2 + 4] annulation products **6**.

c. Procedure for PPh_3-Catalyzed [3 + 2] Annulation of 1a and 2a (Scheme 2)

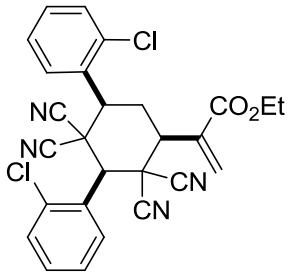
Under a N_2 atmosphere, a mixture of MBH acetate **1a** (85 mg, 0.5 mmol), **2a** (77 mg, 0.5 mmol) and K_2CO_3 (104 mg, 0.75 mmol) with PPh_3 (13 mg, 0.05 mmol) in toluene (3.0 mL) was refluxed with stirring for 24 h. After work-up and chromatographic isolation on silica gel (eluant: petroleum ether/ethyl acetate 20:1), product **4a** (101 mg, yield 72%) was obtained as slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (s, 5H), 6.58 (d, *J* = 1.7 Hz, 1H), 4.31 (m, 2H), 3.60 (m, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.32 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5, 147.8, 133.0, 130.5, 129.6, 129.3, 128.5, 114.2, 111.6, 63.3, 61.7, 45.0, 43.0, 16.9, 14.1; HRMS-ESI: calcd for $C_{17}H_{16}N_2O_2$ $[M + NH_4]^+$ 298.1550, found 298.1549.

4. Analytical Data for Compounds 3 and 6



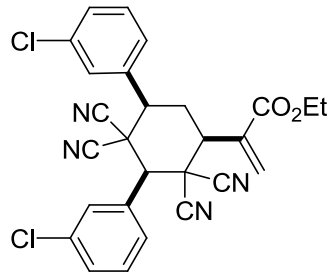
3a

3a, 101 mg, 93% yield; as a white solid, mp 233–236 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (m, 2H), 7.56-7.45 (m, 8H), 6.80 (s, 1H), 6.36 (s, 1H), 4.30 (m, 2H), 4.03 (d, *J* = 16.0 Hz, 1H), 3.77 (s, 1H), 3.54 (d, *J* = 12.0 Hz, 1H), 2.85 (dt, *J* = 12.0, 16.0 Hz, 1H), 2.26 (d, *J* = 12.0 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 136.4, 134.5, 131.3, 131.1, 130.7, 130.0, 129.9, 129.5, 129.2, 128.7, 112.7, 112.1, 111.2, 111.0, 62.4, 54.0, 51.2, 45.3, 43.7, 43.5, 30.1, 14.1; HRMS-ESI calcd for $C_{27}H_{22}N_4O_2$ $[M + Na]^+$ 457.1635, found 457.1629.



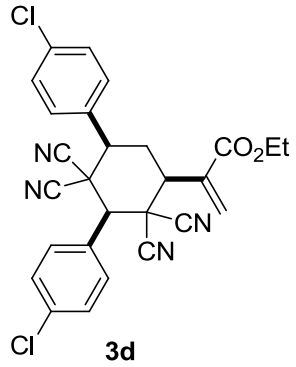
3b

3b, 96 mg, 77% yield; as a white solid, mp 200–202 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, J = 7.5 Hz, 1H), 7.75 (d, *J* = 7.4 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.51 (m, 3H), 7.40 (m, 2H), 6.79 (s, 1H), 6.31 (s, 1H), 4.84 (s, 1H), 4.43 (d, *J* = 12.0 Hz, 1H), 4.31 (m, 2H), 4.12 (d, *J* = 12.0 Hz, 1H), 2.77 (dt, *J* = 12.0, 16.0 Hz, 1H), 2.17 (d, *J* = 16.0 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 136.0(2C), 134.7, 132.1(2C), 130.9, 130.8(2C), 130.6, 128.8, 128.6, 128.5, 128.4, 127.7, 111.3, 111.2, 111.1(2C), 62.3, 47.4, 45.8, 44.1, 43.1, 42.8, 30.6, 14.0; HRMS-ESI calcd for $C_{27}H_{20}Cl_2N_4O_2$ $[M + Na]^+$ 525.0856, found 525.0864.



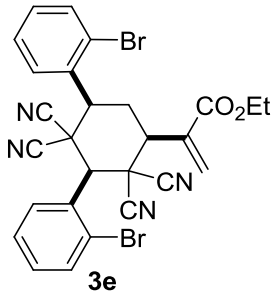
3c

3c, 109 mg, 87% yield; as a white solid, mp 177–179 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.5 Hz, 1H), 7.77 (s, 1H), 7.47 (m, 6H), 6.84 (s, 1H), 6.40 (s, 1H), 4.31 (m, 2H), 4.06 (dd, *J* = 12.0, 2.1 Hz, 1H), 3.84 (s, 1H), 3.54 (dd, *J* = 12.0, 2.4 Hz, 1H), 2.80 (dt, *J* = 12.0, 16.0 Hz, 1H), 2.26 (d, *J* = 16.0 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 136.2, 136.0, 135.8, 135.2, 132.7, 131.7, 131.3, 131.2, 130.5, 130.2, 129.9, 128.8, 127.1, 127.0, 112.3, 111.9, 110.8, 110.5, 62.5, 52.8, 50.4, 44.7, 43.4, 43.3, 29.8, 14.0; HRMS-ESI calcd for $C_{27}H_{20}Cl_2N_4O_2$ $[M + Na]^+$ 525.0856, found 525.0860.



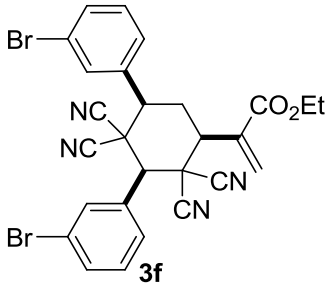
3d

3d, 110 mg, 88% yield; as a white solid, mp 221–223 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.4 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.44 (s, 4H), 6.82 (s, 1H), 6.36 (s, 1H), 4.29 (m, 2H), 4.03 (d, *J* = 12.0 Hz, 1H), 3.81 (s, 1H), 3.54 (d, *J* = 12.0 Hz, 1H), 2.79 (dt, *J* = 12.0, 16.0 Hz, 1H), 2.24 (d, *J* = 16.0 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 137.8, 136.2, 136.1, 132.7, 131.0, 130.7, 130.3, 130.0, 129.5, 129.3, 112.4, 111.9, 110.9, 110.7, 62.5, 53.0, 50.4, 45.0, 43.4, 43.3, 29.9, 14.0; HRMS-ESI calcd for $C_{27}H_{20}Cl_2N_4O_2$ $[M + Na]^+$ 525.0856, found 525.0853.



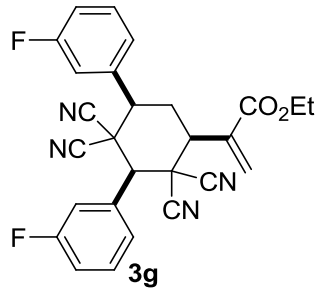
3e

3e, 80 mg, 54% yield; as a white solid, mp 198–201 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.73 (m, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.44 (m, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 6.80 (s, 1H), 6.31 (s, 1H), 4.87 (s, 1H), 4.42 (d, *J* = 12.0 Hz, 1H), 4.32 (m, 2H), 4.10 (d, *J* = 12.0 Hz, 1H), 2.75 (dt, *J* = 12.0, 16.0 Hz, 1H), 2.18 (d, *J* = 16.0 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 136.0, 134.4, 134.0, 133.8, 132.4, 131.1, 130.9, 130.2, 129.2, 128.9, 128.5, 128.4, 127.5, 125.8, 111.3, 111.2, 111.0(2C), 62.4, 50.3, 48.6, 44.3, 43.1, 42.8, 30.8, 14.0; HRMS-ESI calcd for $C_{27}H_{20}Br_2N_4O_2$ $[M + Na]^+$ 612.9845, found 612.9840.



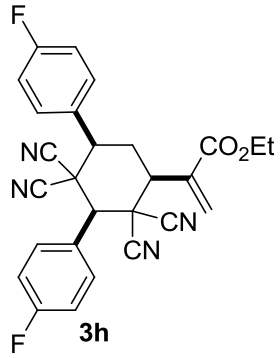
3f

3f, 130 mg, 88% yield; as a white solid, mp 191–193 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (m, 2H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.64 (s, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 1H), 6.83 (s, 1H), 6.37 (s, 1H), 4.31 (m, 2H), 4.00 (d, *J* = 12.0 Hz, 1H), 3.71 (s, 1H), 3.49 (d, *J* = 12.0 Hz, 1H), 2.78 (dt, *J* = 12.0, 16.0 Hz, 1H), 2.26 (d, *J* = 16.0 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 136.3, 136.0, 134.7, 133.3, 132.9, 132.8, 131.7, 131.6, 131.0, 130.8, 127.5(2C), 123.9, 123.3, 112.3, 111.8, 110.8, 110.5, 62.5, 53.2, 50.7, 44.7, 43.6, 43.2, 29.9, 14.1; HRMS-ESI calcd for $C_{27}H_{20}Br_2N_4O_2$ $[M + Na]^+$ 612.9845, found 612.9841.



3g

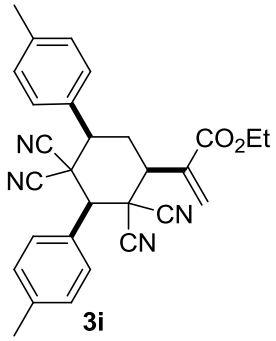
3g, 90 mg, 77% yield; as a white solid, mp 223–226 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 7.7 Hz, 1H), 7.56 (m, 2H), 7.44 (m, 1H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 9.4 Hz, 1H), 7.17 (t, *J* = 8.2 Hz, 1H), 6.84 (s, 1H), 6.39 (s, 1H), 4.30 (m, 2H), 4.07 (d, *J* = 12.0 Hz, 1H), 3.86 (s, 1H), 3.57 (d, *J* = 12.0 Hz, 1H), 2.80 (dt, *J* = 12.0, 16.0 Hz, 1H), 2.28 (d, *J* = 16.0 Hz, 1H), 1.33 (q, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 164.1 (d, J_{CF} = 14.6 Hz), 161.6 (d, J_{CF} = 13.3 Hz), 136.5 (d, J_{CF} = 7.1 Hz), 136.1, 132.9 (d, J_{CF}= 7.1 Hz), 131.8 (d, J_{CF}= 8.2 Hz), 131.1, 130.9 (d, J_{CF} = 8.2 Hz), 125.2 (d, J_{CF} = 2.5 Hz), 124.5 (d, J_{CF} = 2.8 Hz), 118.6 (d, J_{CF} = 20.7 Hz), 117.1 (d, J_{CF} = 20.9 Hz), 116.8 (d, J_{CF} = 23.3 Hz), 115.8 (d, J_{CF} = 22.7 Hz), 112.3, 111.9, 110.9, 110.6, 62.5, 52.9, 50.4, 44.7, 43.3(2C), 29.9, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ 141.1, 139.5; HRMS-ESI calcd for $C_{27}H_{20}F_2N_4O_2$ $[M + Na]^+$ 493.1447, found 493.1449.



3h

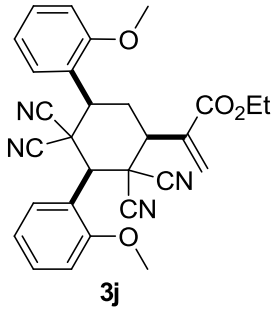
3h, 99 mg, 84% yield; as a white solid, mp 214–215 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (dd, *J* = 8.3, 4.9 Hz, 2H), 7.50 (dd, *J* = 8.4, 5.1 Hz, 2H), 7.25 (d, *J* = 6.7 Hz, 2H), 7.16 (t, *J* = 8.4 Hz, 2H), 6.82 (s, 1H), 6.36 (s, 1H), 4.29 (m, 2H), 4.03 (d, *J* = 12.0 Hz, 1H), 3.80 (m, 1H), 3.55 (d, *J* = 12.0 Hz, 1H), 2.79 (dt, *J* = 12.0, 16.0 Hz, 1H), 2.25 (d, *J* = 16.0 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6 (d, J_{CF} = 4.8 Hz), 165.1 (d, J_{CF} = 79.4 Hz), 162.6 (d, J_{CF} = 77.2 Hz), 136.2,

131.5 (d, J_{CF} = 8.7 Hz), 130.9, 130.5 (d, J_{CF} = 8.4 Hz), 130.2, 126.9, 117.3 (d, J_{CF} = 22.0 Hz), 116.4 (d, J_{CF} = 21.8 Hz), 112.6, 112.0, 111.0, 110.8, 62.4, 52.9 (d, J_{CF} = 9.1 Hz), 50.3 (d, J_{CF} = 5.5 Hz), 45.4, 43.5(2C), 30.1, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ 141.8, 139.4; HRMS-ESI calcd for $C_{27}H_{20}F_2N_4O_2$ $[M + Na]^+$ 493.1447, found 493.1448.



3i

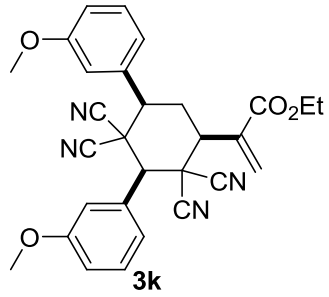
3i, 90 mg, 78% yield; as a white solid, mp 212–213 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.79 (s, 1H), 6.36 (s, 1H), 4.29 (m, 2H), 4.03 (d, *J* = 12.0 Hz, 1H), 3.77 (s, 1H), 3.51 (d, *J* = 12.0 Hz, 1H), 2.81 (dt, *J* = 12.0, 16.0 Hz, 1H), 2.40 (s, 3H), 2.37 (s, 3H), 2.22 (d, *J* = 16.0 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 141.4, 139.8, 136.5, 131.6, 130.7, 130.5, 129.8, 129.2, 128.5, 128.2, 112.9, 112.3, 111.3, 111.2, 62.3, 53.5, 50.7, 45.6, 43.64, 43.59, 30.1, 21.3, 21.2, 14.0; HRMS-ESI calcd for $C_{29}H_{26}N_4O_2$ $[M + Na]^+$ 485.1948, found 485.1948.



3j

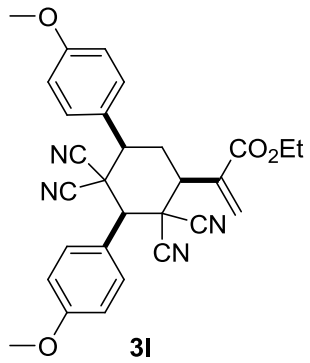
3j, 85 mg, 69% yield; as a white solid, mp 217–219 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.05 (dd, *J* = 14.3, 7.7 Hz, 2H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.75 (s, 1H), 6.31 (s, 1H), 4.80 (s, 1H), 4.32 (m, 3H), 4.02 (d, *J* = 12.0 Hz, 1H), 3.95 (s, 3H), 3.89 (s, 3H), 2.75 (dt, *J* = 12.0, 16.0 Hz, 1H), 2.07 (d, *J* =

16.0 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 157.5, 156.8, 136.6, 131.9, 130.5, 130.3, 128.2, 127.8, 123.4, 121.7, 121.0, 120.0, 112.4, 112.2, 112.0, 111.6(2C), 111.1, 62.2, 56.2, 55.6, 44.1, 43.9, 43.3, 43.0, 42.0, 30.4, 14.1; HRMS-ESI calcd for $C_{29}H_{26}N_4O_4$ $[M + Na]^+$ 517.1846, found 517.1847.



3k

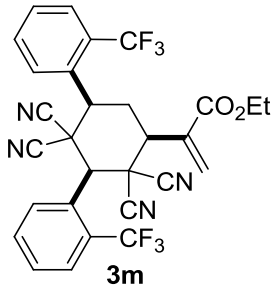
3k, 103 mg, 84% yield; as a white solid, mp 158–162 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (m, 4H), 7.06 (m, 3H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.81 (s, 1H), 6.37 (s, 1H), 4.31 (m, 2H), 4.06 (d, *J* = 12.0 Hz, 1H), 3.82 (s, 7H), 3.52 (d, *J* = 12.0 Hz, 1H), 2.80 (dt, *J* = 12.0, 16.0 Hz, 1H), 2.26 (d, *J* = 16.0 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 160.2, 159.9, 136.3, 136.0, 132.4, 130.9(2C), 130.2, 121.6, 120.9, 116.8, 115.0, 114.7, 114.6, 112.7, 112.2, 111.3, 111.2, 62.4, 55.4, 55.3, 53.4, 50.9, 45.0, 43.48(2C), 30.1, 14.0; HRMS-ESI calcd for $C_{29}H_{26}N_4O_4$ $[M + Na]^+$ 517.1846, found 517.1846.



3l

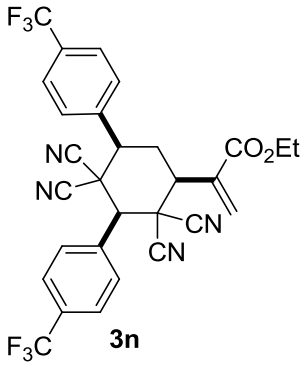
3l, 50 mg, 40% yield; as a white solid, mp 127–129 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.79 (s, 1H), 6.35 (s, 1H), 4.29 (m, 2H), 4.01 (d, *J* = 12.0 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 3.76 (s, 1H), 3.49 (d, *J* = 12.0 Hz, 1H), 2.78 (dt, *J* = 12.0, 16.0 Hz, 1H), 2.21 (d, *J* = 16.0 Hz, 1H), 1.33 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 161.4, 160.5, 136.5, 130.7, 130.6, 129.8, 126.6, 123.0, 115.2,

114.4, 113.0, 112.3, 111.3(2C), 62.3, 55.3(2C), 53.1, 50.4, 46.0, 43.8, 43.6, 30.2, 14.0; HRMS-ESI calcd for $C_{29}H_{26}N_4O_4$ $[M + Na]^+$ 517.1846, found 517.1852.



3m

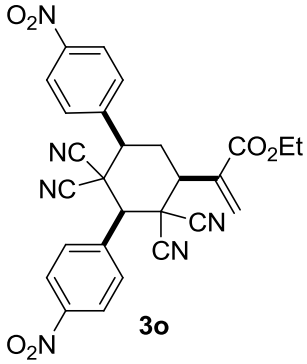
3m, 104 mg, 73% yield; as a white solid, mp 194–195 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 7.9 Hz, 1H), 7.86 (m, 3H), 7.72 (m, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 6.82 (s, 1H), 6.30 (s, 1H), 4.32 (m, 2H), 4.16 (s, 1H), 3.95 (m, 2H), 2.83 (dt, *J* = 12.0, 16.0 Hz, 1H), 2.26 (d, *J* = 16.0 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 135.7, 133.7, 133.3, 132.9, 131.3, 131.1, 130.6 (q, J_{CF} = 29.7 Hz), 129.9, 129.5, 129.4 (q, J_{CF} = 29.4 Hz), 128.5, 128.4, 127.9 (q, J_{CF} = 5.7 Hz), 127.2 (q, J_{CF} = 5.8 Hz), 123.8 (q, J_{CF} = 274.3 Hz), 123.6 (q, J_{CF} = 274.6 Hz), 112.0, 111.3, 111.0, 110.7, 62.4, 47.9, 46.5, 45.0, 43.8, 43.2, 31.9, 14.0; HRMS-ESI calcd for $C_{29}H_{20}F_6N_4O_2$ $[M + Na]^+$ 593.1383, found 593.1378.



3n

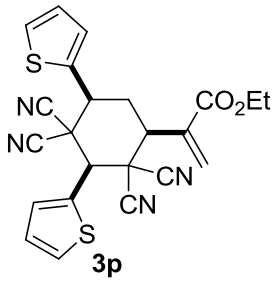
3n, 135 mg, 95% yield; as a white solid, mp 157–159 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 6.85 (s, 1H), 6.40 (s, 1H), 4.30 (m, 2H), 4.11 (d, *J* = 12.0 Hz, 1H), 3.96 (d, *J* = 3.3 Hz, 1H), 3.67 (d, *J* = 12.0 Hz, 1H), 2.87 (dt, *J* = 12.0, 16.0 Hz, 1H), 2.30 (d, *J* = 16.0 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 138.0, 136.0, 134.6, 133.5 (q, J_{CF} = 33.3 Hz), 132.3 (q, J_{CF} = 32.9 Hz), 131.3, 130.1, 129.3, 127.0 (q, J_{CF} = 3.5 Hz), 126.3 (q, J_{CF} = 4.0 Hz), 123.4 (q, J_{CF} = 272.5

Hz), 123.3 (q, J_{CF} = 272.7 Hz), 112.2, 112.0, 110.8, 110.5, 62.6, 52.7, 50.3, 44.4, 43.22, 43.18, 29.8, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ 186.9, 186.8; HRMS-ESI calcd for $C_{29}H_{20}F_6N_4O_2$ $[M + Na]^+$ 593.1383, found 593.1387.



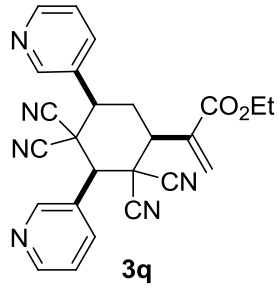
3o

3o, 110 mg, 84% yield; as a white solid, mp 132–134 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, *J* = 8.6 Hz, 2H), 8.35 (d, *J* = 8.6 Hz, 2H), 8.12 (d, *J* = 8.6 Hz, 2H), 7.74 (d, *J* = 8.6 Hz, 2H), 6.88 (s, 1H), 6.42 (s, 1H), 4.31 (m, 2H), 4.15 (d, *J* = 12.0 Hz, 1H), 4.11 (s, 1H), 3.79 (d, *J* = 12.0 Hz, 1H), 2.90 (dt, *J* = 12.0, 16.0 Hz, 1H), 2.35 (d, *J* = 16.0 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 149.7, 148.9, 140.6, 137.0, 135.7, 131.4, 130.8, 129.9, 125.1, 124.5, 111.9, 111.5, 110.6, 110.2, 62.7, 52.7, 50.3, 44.0, 43.2, 42.9, 29.6, 14.0; HRMS-ESI calcd for $C_{27}H_{20}N_6O_6$ $[M + Na]^+$ 547.1337, found 547.1335.



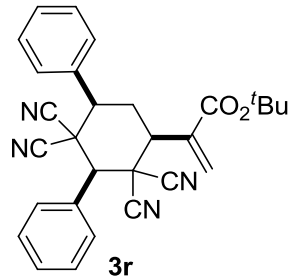
3p

3p, 45 mg, 40% yield; as a white solid, mp 235–237 ºC; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.84 (d, *J* = 4.2 Hz, 1H), 7.66 (s, 2H), 7.43 (s, 1H), 7.28 (s, 1H), 7.16 (s, 1H), 6.68 (s, 1H), 6.44 (s, 1H), 5.54 (s, 1H), 4.30 (d, *J* = 12.0 Hz, 1H), 4.22 (m, 2H), 4.10 (d, *J* = 12.0 Hz, 1H), 2.71 (dt, *J* = 12.0, 16.0 Hz, 1H), 2.39 (d, *J* = 16.0 Hz, 1H), 1.27 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.7, 137.3, 136.2, 132.5, 131.2, 129.9, 129.1, 127.7, 127.6, 127.0, 126.7, 113.1, 112.4, 111.4, 111.1, 61.1, 46.5, 44.5, 44.2, 43.0, 41.2, 29.9, 13.5; HRMS-ESI calcd for $C_{23}H_{18}N_4O_2S_2$ $[M + Na]^+$ 469.0763, found 469.0765.



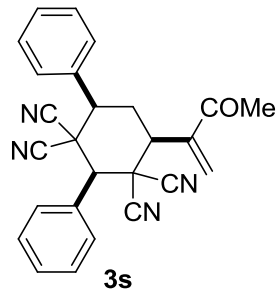
3q

3q, 61 mg, 56% yield; as a white solid, mp 205–207 ºC; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.97 (s, 1H), 8.84 (d, J = 3.6 Hz, 1H), 8.79 (s, 1H), 8.67 (d, J = 3.2 Hz, 1H), 8.38 (d, J = 7.8 Hz, 1H), 8.13 (d, J = 7.6 Hz, 1H), 7.74 (m, 1H), 7.57 (m, 1H), 6.73 (s, 1H), 6.61 (s, 1H), 5.34 (s, 1H), 4.18 (m, 4H), 3.05 (dt, J = 12.0, 16.0 Hz, 1H), 2.31 (d, J = 16.0 Hz, 1H), 1.27 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.6, 151.7, 149.9(2C), 149.6, 136.12, 136.08, 135.3, 131.5, 131.0, 128.0, 124.3, 123.3, 112.4, 112.1, 111.0(2C), 61.0, 45.8, 45.2, 44.3, 42.7, 41.3, 27.5, 13.4; HRMS-ESI calcd for $C_{25}H_{20}N_6O_2$ $[M + Na]^+$ 437.1720, found 437.1717.



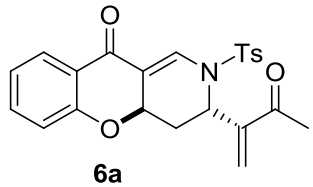
3r

3r, 115 mg, 99% yield; as a white solid, mp 235–237 ºC; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.87 (d, J = 7.0 Hz, 2H), 7.62 (dd, J = 15.2, 7.2 Hz, 5H), 7.47 (m, 3H), 6.61 (s, 1H), 6.45 (s, 1H), 5.05 (s, 1H), 4.11 (d, J = 11.1 Hz, 1H), 4.04 (d, J = 10.8 Hz, 1H), 2.89 (q, J = 13.0 Hz, 1H), 2.20 (d, J = 15.0 Hz, 1H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.7, 137.5, 135.4, 132.2, 130.2(2C), 129.2, 128.7(2C), 128.5, 128.2, 112.9, 112.4, 111.5, 111.4, 81.2, 48.4, 47.4, 44.7, 43.0, 41.2, 28.3, 27.0; HRMS-ESI calcd for $C_{29}H_{26}N_4O_2$ $[M + Na]^+$ 485.1948, found 485.1950.



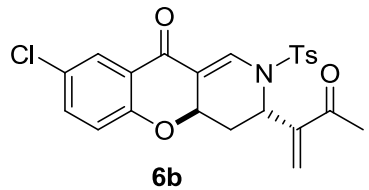
3s

3s, 101 mg, 99% yield; as a white solid, mp 222–225 ºC; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.87 (d, J = 6.7 Hz, 2H), 7.60 (t, J = 7.3 Hz, 5H), 7.46 (m, 3H), 6.84 (s, 1H), 6.76 (s, 1H), 5.05 (s, 1H), 4.26 (d, J = 12.0 Hz, 1H), 4.02 (d, J = 12.0 Hz, 1H), 2.88 (dt, J = 12.0, 16.0 Hz, 1H), 2.43 (s, 3H), 2.10 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 197.0, 143.6, 135.4, 132.27, 131.9, 130.2, 129.1, 128.7, 128.6, 128.5, 128.2, 112.8, 112.5, 111.6, 111.5, 48.4, 47.4, 44.6, 42.8, 28.3, 25.0 (one carbon was overlapped by signals of DMSO-d_6); HRMS-ESI calcd for $C_{26}H_{20}N_4O$ [M + Na]$^+$ 427.1529, found 427.1532.



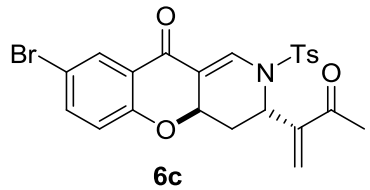
6a

6a, 67 mg, 79% yield; as a light yellow solid, mp 186-187 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.93 (dd, J = 7.8, 1.7 Hz, 1H), 7.74 (d, J = 8.3 Hz, 2H), 7.44–7.38 (m, 1H), 7.36 (d, J = 8.1 Hz, 2H), 7.06 – 7.00 (m, 1H), 6.87 – 6.83 (m, 1H), 6.24 (s, 1H), 5.84 (s, 1H), 5.19 (d, J = 4.2 Hz, 1H), 4.72 (ddd, J = 10.8, 5.8, 1.0 Hz, 1H), 2.45 (s, 4H), 2.39 (s, 3H), 1.71 (ddd, J = 13.2, 11.0, 5.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 179.8, 160.5, 145.4, 144.8, 135.3, 134.5, 133.6, 130.4, 127.4, 127.2, 122.5, 122.1, 117.6, 112.2, 69.6, 52.3, 29.4, 26.3, 21.7; HRMS-ESI calcd for $C_{23}H_{21}NO_5S$ [M + Na]$^+$ 446.1033, found 446.1029.



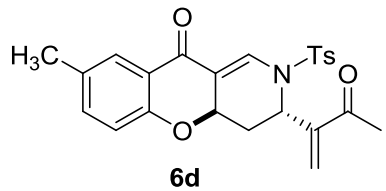
6b

6b, 70 mg, 77% yield; as a light yellow solid, mp 234-236 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (s, 1H), 7.88 (d, J = 2.6 Hz, 1H), 7.74 (d, J = 8.3 Hz, 2H), 7.39–7.31 (m, 3H), 6.81 (d, J = 8.8 Hz, 1H), 6.24 (s, 1H), 5.83 (s, 1H), 5.19 (d, J = 4.2 Hz, 1H), 4.71 (dd, J = 10.9, 5.8 Hz, 1H), 2.48–2.42 (m, 5H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5, 178.7, 158.9, 145.5, 144.7, 135.0, 134.4, 130.4, 127.4, 127.2, 126.7, 123.3, 119.3, 111.2, 69.8, 52.3, 29.3, 26.3, 21.6; HRMS-ESI calcd for $C_{23}H_{20}ClNO_5S$ [M + Na]$^+$ 480.0643, found 480.0643.



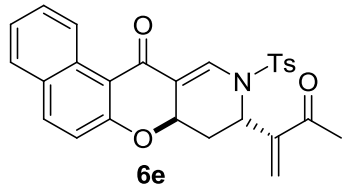
6c

6c, 71 mg, 71% yield; as a light yellow solid, mp 225-227 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (s, 1H), 8.03 (d, *J* = 2.2 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.47 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 1H), 6.24 (s, 1H), 5.82 (s, 1H), 5.19 (d, *J* = 4.3 Hz, 1H), 4.71 (dd, *J* = 10.6, 5.6 Hz, 1H), 2.49–2.41 (m, 4H), 2.39 (s, *J* = 10.3 Hz, 3H), 1.71 (ddd, *J* = 13.2, 11.0, 5.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5, 178.6, 159.3, 145.5, 144.7, 137.8, 134.4, 130.4, 129.8, 127.4, 127.2, 123.8, 119.6, 114.6, 111.1, 69.8, 52.3, 29.3, 26.3, 21.6; HRMS-ESI calcd for $C_{23}H_{20}BrNO_5S$ $[M + Na]^+$ 524.0138, found 524.0134.



6d

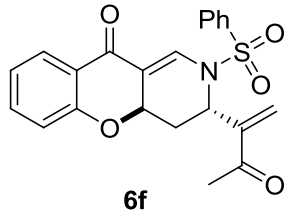
6d, 66 mg, 76% yield; as a light yellow solid, mp 218-220 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.75 (s, 1H), 7.73 (s, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.22 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.23 (s, 1H), 5.84 (s, 1H), 5.18 (d, *J* = 4.3 Hz, 1H), 4.70–4.63 (m, 1H), 2.46–2.40 (m, 4H), 2.38 (s, 3H), 2.30 (s, 3H), 1.69 (ddd, *J* = 13.2, 11.0, 5.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5, 180.0, 158.5, 145.3, 144.8, 136.3, 134.6, 133.4, 131.5, 130.3, 127.3, 127.2, 127.0, 122.1, 117.3, 112.4, 69.4, 52.3, 29.4, 26.3, 21.6, 20.4; HRMS-ESI calcd for $C_{24}H_{23}NO_5S$ $[M + Na]^+$ 524.0138, found 524.0134.



6e

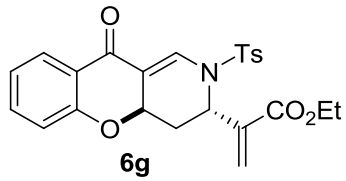
6e, 92 mg, 97% yield; as a light yellow solid, mp 147-149 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.39 (d, *J* = 8.7 Hz, 1H), 8.26 (s, 1H), 7.85 (d, *J* = 9.0 Hz, 1H), 7.77 (s, 1H), 7.75–7.71 (m, 2H), 7.66–7.60 (m, 1H), 7.42 (t, *J* = 7.1 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 8.9 Hz, 1H), 6.25 (s, 1H), 5.91 (s, 1H), 5.21 (d, *J* = 4.3 Hz,

1H), 4.76 (dd, *J* = 10.5, 5.6 Hz, 1H), 2.50 (ddd, *J* = 13.1, 5.9, 2.2 Hz, 1H), 2.44 (s, 3H), 2.38 (s, 3H), 1.75 (ddd, *J* = 13.1, 11.0, 5.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 180.6, 162.5, 145.2, 144.8, 136.7, 134.7, 132.9, 131.7, 130.3, 129.6, 129.3, 128.3, 127.5, 127.2, 126.3, 125.0, 118.5, 114.7, 113.6, 69.5, 52.2, 29.2, 26.3, 21.6; HRMS-ESI calcd for $C_{27}H_{23}NO_5S$ $[M + Na]^+$ 496.1189, found 496.1197.



6f

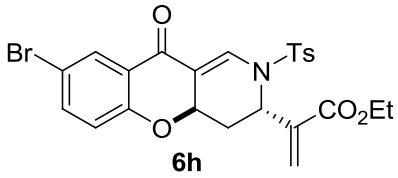
6f, 61 mg, 75% yield; as a light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 1H), 7.94 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.88–7.83 (m, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 7.44–7.38 (m, 1H), 7.06–7.00 (m, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 6.23 (s, 1H), 5.83 (d, *J* = 9.5 Hz, 1H), 5.21 (d, *J* = 4.3 Hz, 1H), 4.73 (ddd, *J* = 10.8, 5.8, 1.0 Hz, 1H), 2.46 (ddd, *J* = 13.2, 5.9, 2.3 Hz, 1H), 2.40–2.37 (m, 3H), 1.72 (ddd, *J* = 13.2, 10.9, 5.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5, 179.8, 160.5, 144.7, 137.5, 135.3, 134.1, 133.4, 129.7, 127. 3, 127.3, 127.1, 122.4, 122.0, 117.6, 112.4, 69.5, 52.3, 29.3, 26.3; HRMS-ESI calcd for $C_{22}H_{19}NO_5S$ $[M + Na]^+$ 432.0876, found 436.0871.



6g

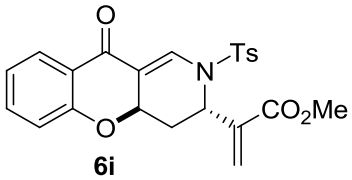
6g, 42 mg, 46% yield; as a light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.94 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.45–7.38 (m, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.08–6.99 (m, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 6.34 (s, 1H), 5.59 (d, *J* = 1.3 Hz, 1H), 5.15 (d, *J* = 4.0 Hz, 1H), 4.79 (dd, *J* = 10.4, 5.4 Hz, 1H), 4.32–4.19 (m, 2H), 2.59 (ddd, *J* = 13.2, 5.9, 2.3 Hz, 1H), 2.45 (s, 3H), 1.75 (ddd, *J* = 13.2, 11.0, 5.3 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.8, 164.6, 160.5, 145.3, 136.7, 135.3, 134.6, 133.3, 130.3, 127.4, 127.2, 126.7, 122.4, 122.0, 117.5, 112.4, 69.4, 61.4, 53.2, 29.3, 21.6, 14.1; HRMS-ESI calcd for

$C_{24}H_{23}NO_6S$ [M + Na]$^+$ 476.1138, found 476.1137.



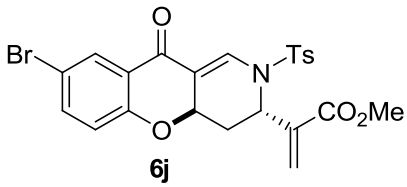
6h

6h, 42 mg, 46% yield; as a light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 8.03 (d, *J* = 2.5 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.48 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 1H), 6.33 (s, 1H), 5.56 (d, *J* = 1.3 Hz, 1H), 5.15 (d, *J* = 4.0 Hz, 1H), 4.81–4.73 (m, 1H), 4.31–4.20 (m, 2H), 2.59 (ddd, *J* = 13.2, 5.9, 2.3 Hz, 1H), 2.45 (s, *J* = 8.8 Hz, 3H), 1.76 (ddd, *J* = 13.2, 11.0, 5.3 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.6, 164.6, 159.4, 145.5, 137.8, 136.7, 134.5, 134.1, 130.4, 129.8, 127.3, 126.7, 123.8, 119.6, 114.6, 111.4, 69.7, 61.5, 53.2, 29.3, 21.7, 14.1; HRMS-ESI calcd for $C_{24}H_{22}BrNO_6S$ [M + Na]$^+$ 554.0243, found 554.0247.



6i

6i, 41 mg, 47% yield; as a light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.34 (s, 1H), 5.60 (s, 1H), 5.15 (s, 1H), 4.78 (dd, *J* = 10.6, 5.7 Hz, 1H), 3.82 (s, 3H), 2.59 (dd, *J* = 13.1, 4.0 Hz, 1H), 2.45 (s, 3H), 1.76 (td, *J* = 12.9, 5.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.7, 165.1, 160.5, 145.3, 136.5, 135.3, 134.6, 133.3, 130.3, 127.4, 127.2, 127.0, 122.4, 122.0, 117.5, 112.4, 69.4, 53.2, 52. 3, 29.3, 21.1; HRMS-ESI calcd for $C_{23}H_{21}NO_6S$ [M + Na]$^+$ 462.0982, found 462.0981.



6j

6j, 47 mg, 46% yield; as a light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 8.03 (d, *J* = 2.5 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.48 (dd, *J* = 8.8, 2.5 Hz,

1H), 7.37 (d, *J* = 8.1 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 1H), 6.34 (s, 1H), 5.58 (d, *J* = 1.2 Hz, 1H), 5.15 (d, *J* = 4.0 Hz, 1H), 4.82–4.72 (m, 1H), 3.82 (s, 3H), 2.59 (ddd, *J* = 13.2, 5.9, 2.3 Hz, 1H), 2.45 (s, 3H), 1.76 (ddd, *J* = 13.2, 11.0, 5.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.5, 165.0, 159.4, 145.5, 137.8, 136.4, 134.5, 134.1, 130.4, 129.8, 127.3, 127.1, 123.8, 119.6, 114.6, 111.4, 69.7, 53.2, 52.4, 29.3, 21.7; HRMS-ESI calcd for $C_{23}H_{20}BrNO_6S$ $[M + Na]^+$ 540.0087, found 540.0082.

5. ORTEP Drawings for 3a and 6a

Table S3. Crystal data and structure refinement for **3a**

Identification code	**3a**
Empirical formula	$C_{27}H_{23}N_4O_2$
Formula weight	435.49
Temperature	113(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 11.699(5) Å, α = 90°.
	b = 15.495(7 Å, β =95.201(8)°.
	c = 12.654(6) Å, γ = 90°.
Volume	2284.5(17) $Å^3$
Z, Calculated density	4, 1.266 Mg/m^3
Absorption coefficient	0.082 mm^{-1}
F(000)	916
Crystal size	0.20 x 0.18 x 0.12 mm^3
Theta range for data collection	1.75 to 25.02°.
Limiting indices	-13<=h<=13, -18<=k<=18, -14<=l<=14
Reflections collected / unique	20084 / 4030 [R(int) = 0.0657]
Completeness to the θ = 25.02°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9902 and 0.9838
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4030 / 32 / 308
Goodness-of-fit on F^2	1.169
Final R indices[I>2σ(I)]	R1 = 0.0792, wR2 = 0.1929
R indices (all data)	R1 = 0.0920, wR2 = 0.2026
Largest diff. peak and hole	0.516 and -0.588 e. $Å^{-3}$

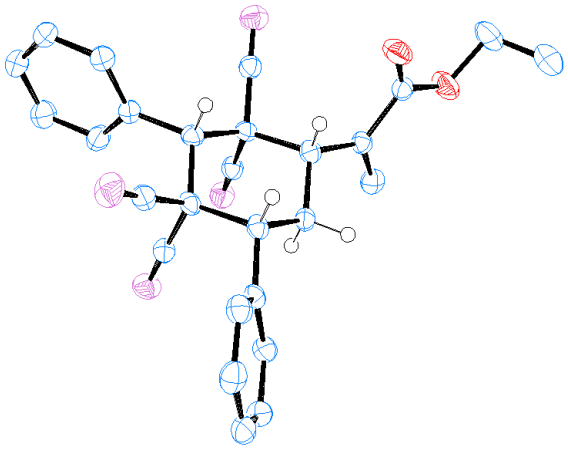


Figure S1. ORTEP Drawing for **3a**

Table S4. Crystal data and structure refinement for **6a**

Identification code	**6a**
Empirical formula	$C_{23}H_{21}NO_5S$
Formula weight	423.47
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 7.8575(16) Å, α = 100.47(3)°.
	b = 8.2529(17) Å, β = 92.60(3)°.
	c = 17.024(3) Å, γ = 108.88(3)°.
Volume	1020.7(4) $Å^3$
Z, Calculated density	2, 1.378 Mg/m^3
Absorption coefficient	0.194 mm^{-1}
F(000)	444
Crystal size	0.20 x 0.18 x 0.14 mm^3
Theta range for data collection	2.45 to 27.91°.
Limiting indices	-10<=h<=10, -10<=k<=10, -22<=l<=22
Reflections collected / unique	10574 / 4800 [R(int) = 0.0550]
Completeness to the θ = 27.91°	98.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9733 and 0.9622
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4800 / 0 / 273
Goodness-of-fit on F^2	0.964
Final R indices[I>2σ(I)]	R1 = 0.0442, wR2 = 0.0951
R indices (all data)	R1 = 0.0865, wR2 = 0.1081
Largest diff. peak and hole	0.245 and -0.358 e. $Å^{-3}$

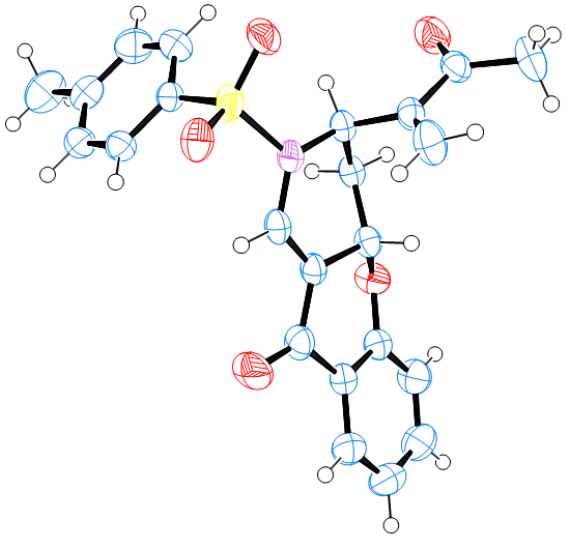
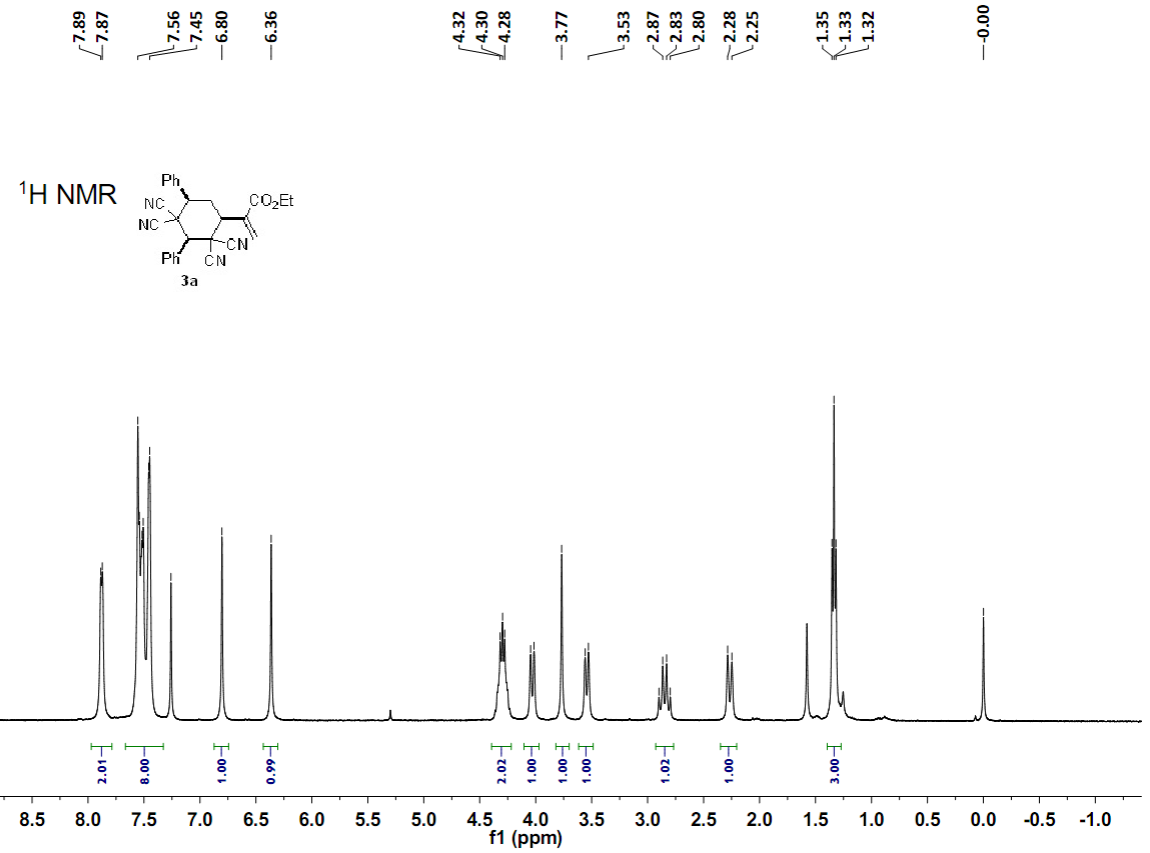
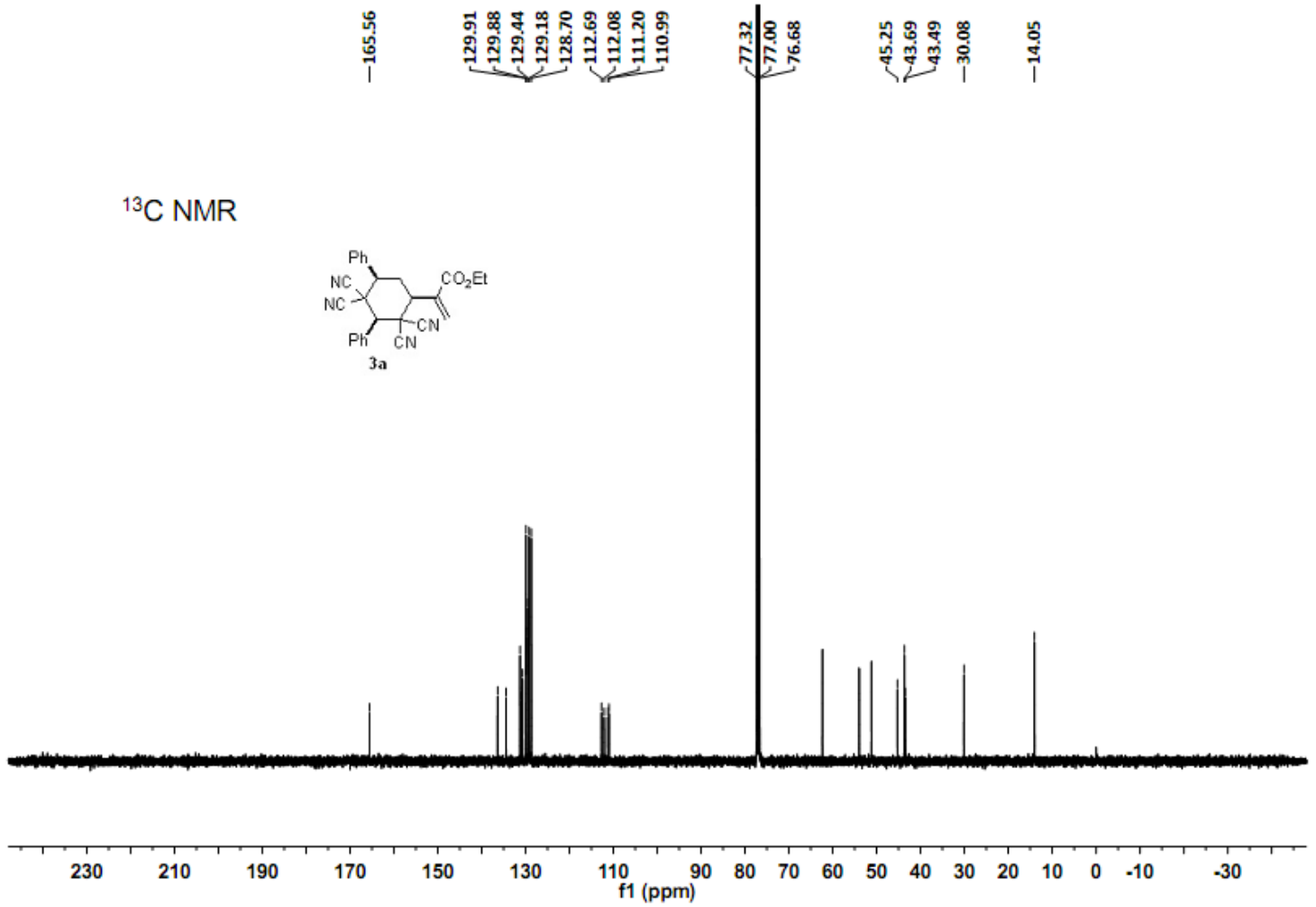
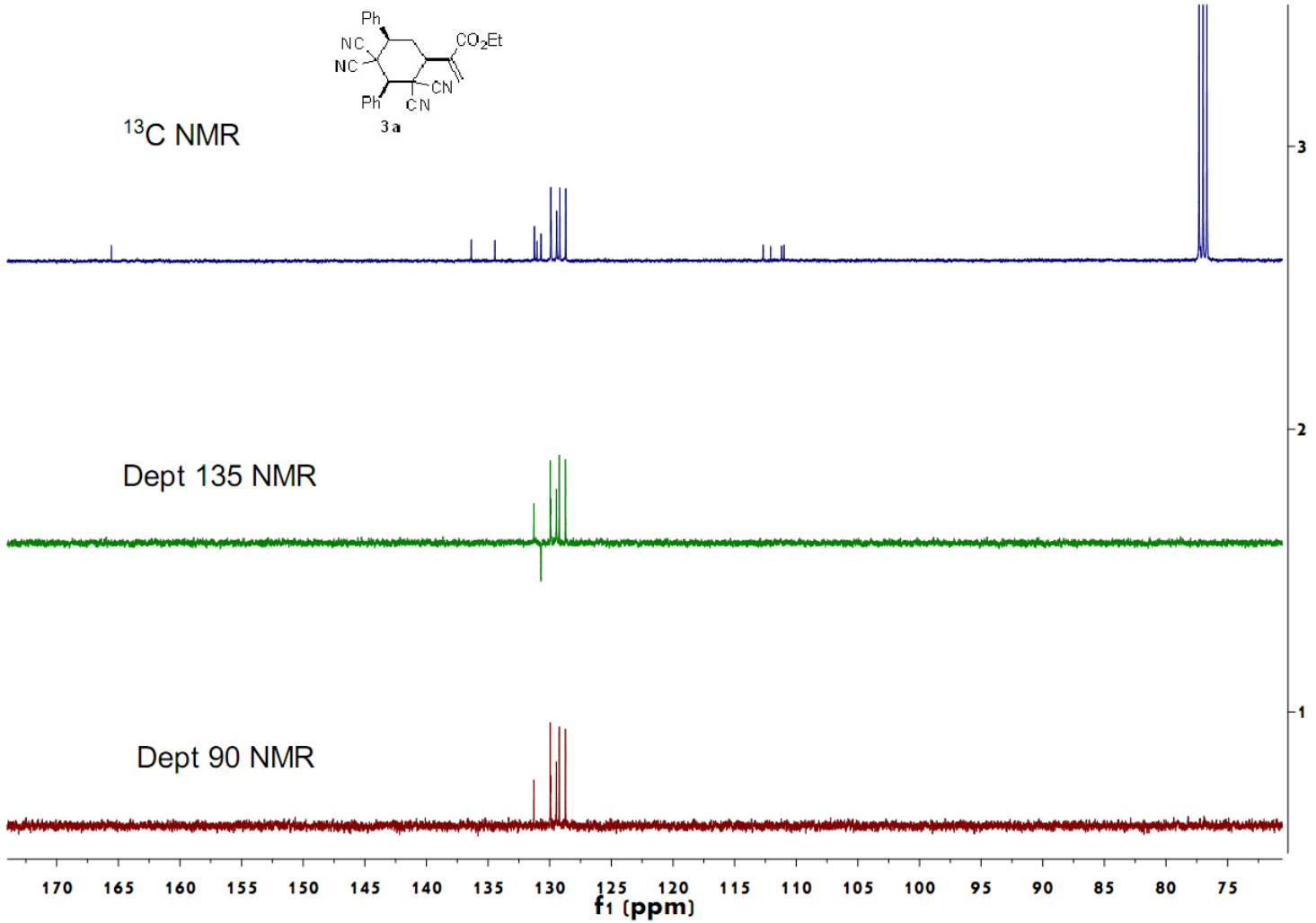


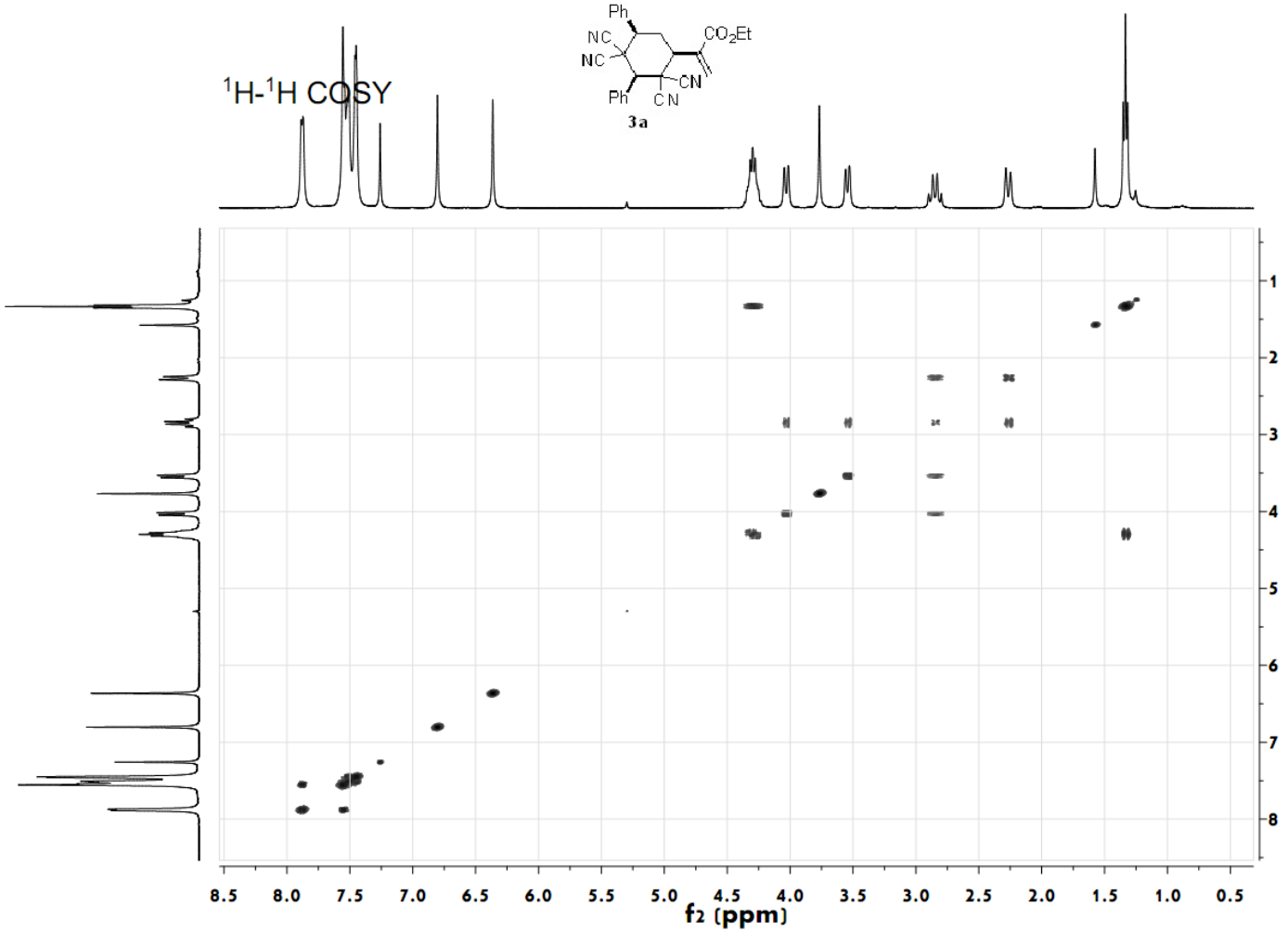
Figure S2. ORTEP Drawing for **6a**

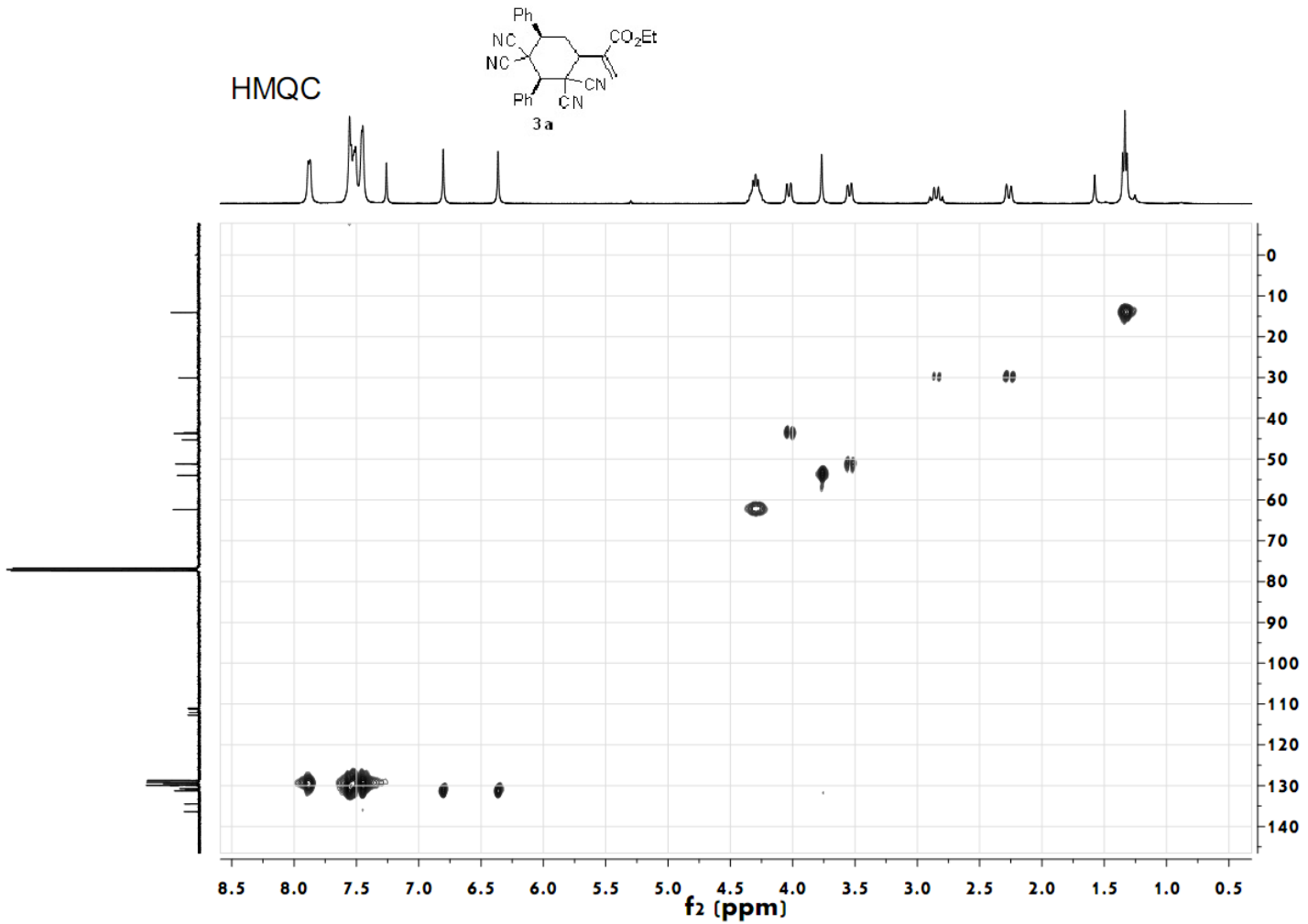
6. NMR Spectra for Compounds 3, 4a, and 6

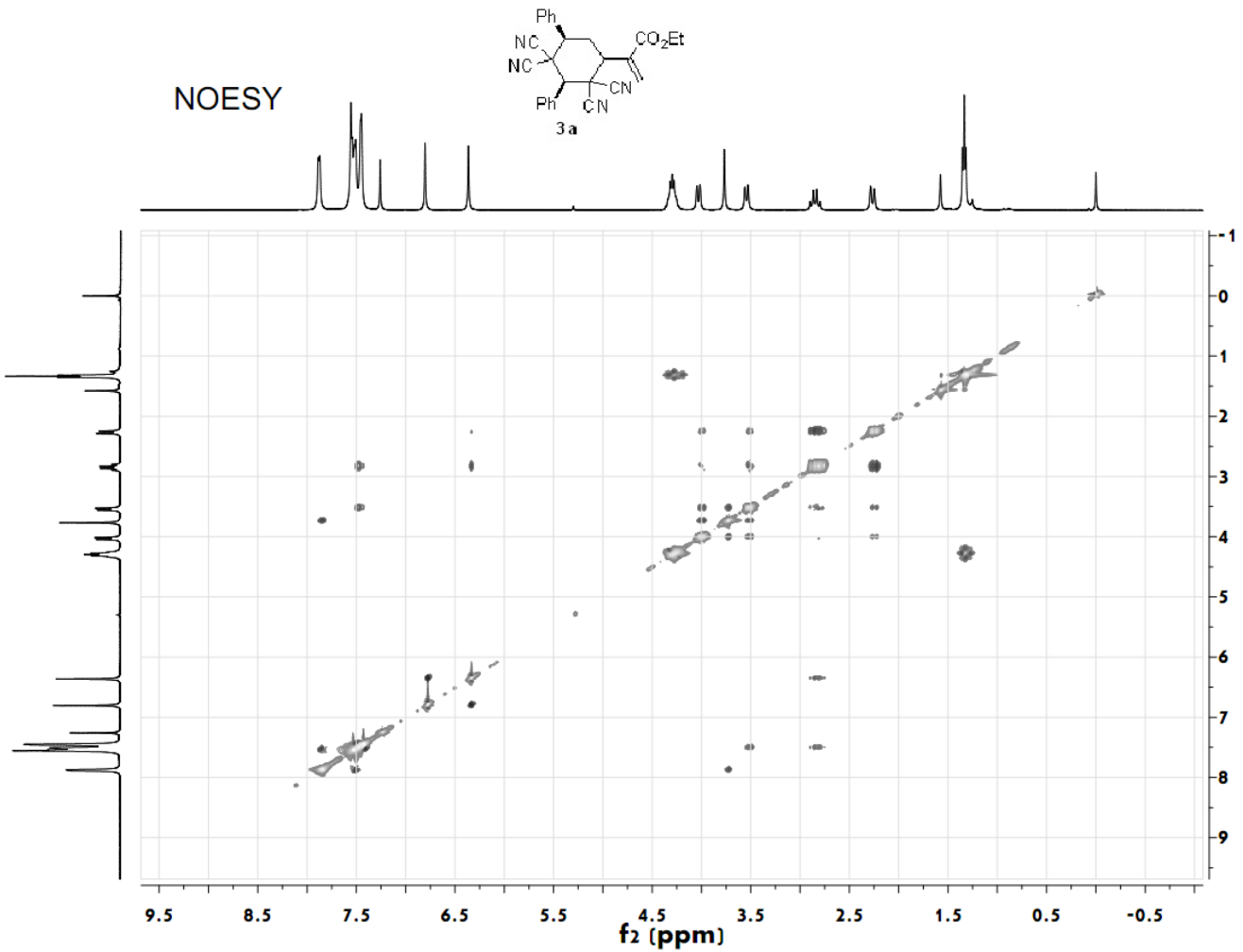


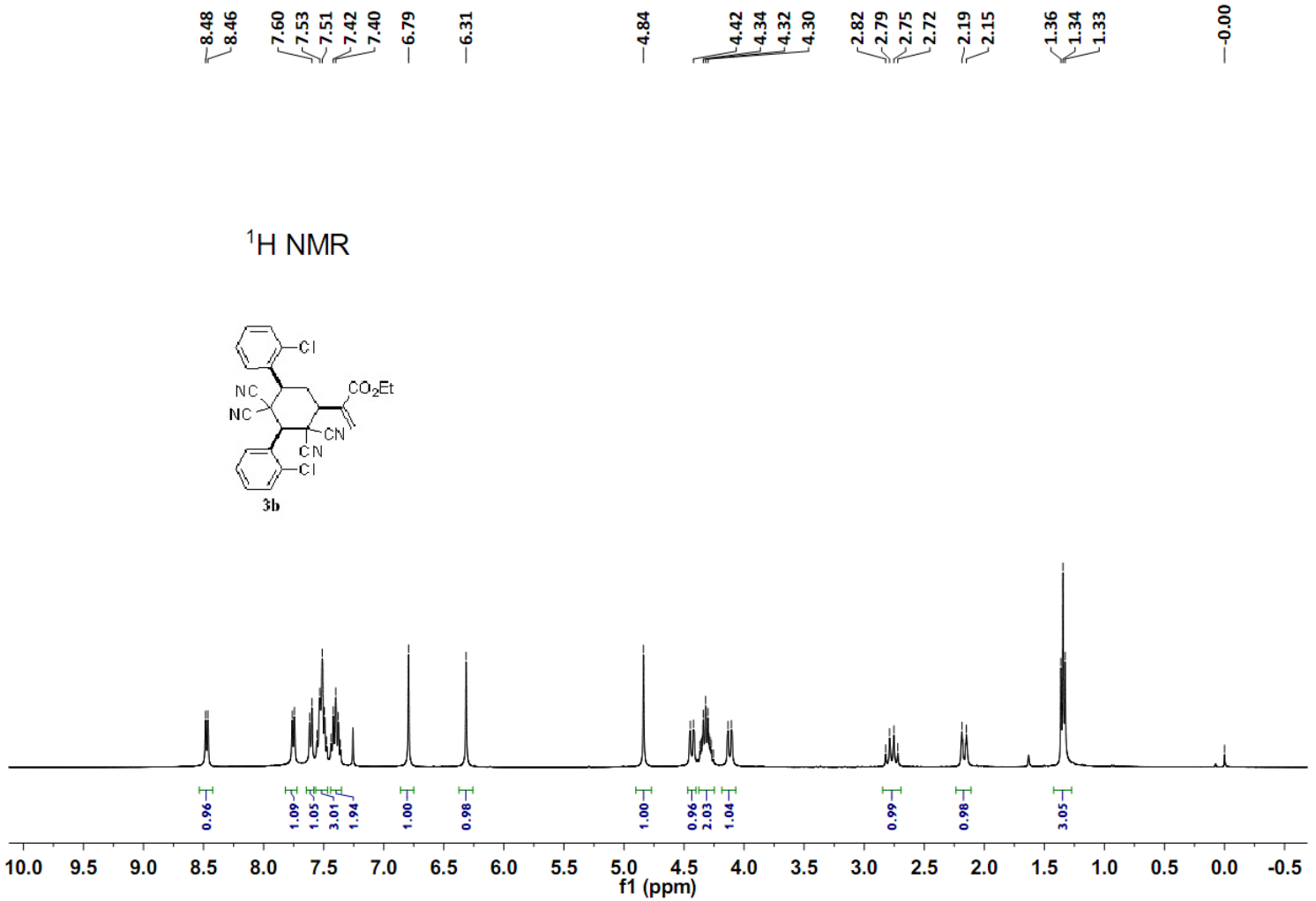









NOESY
Ph
NC
NC
CO2Et
CN
Ph
CN
3a
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f2 (ppm)
-1
0
1
2
3
4
5
6
7
8
9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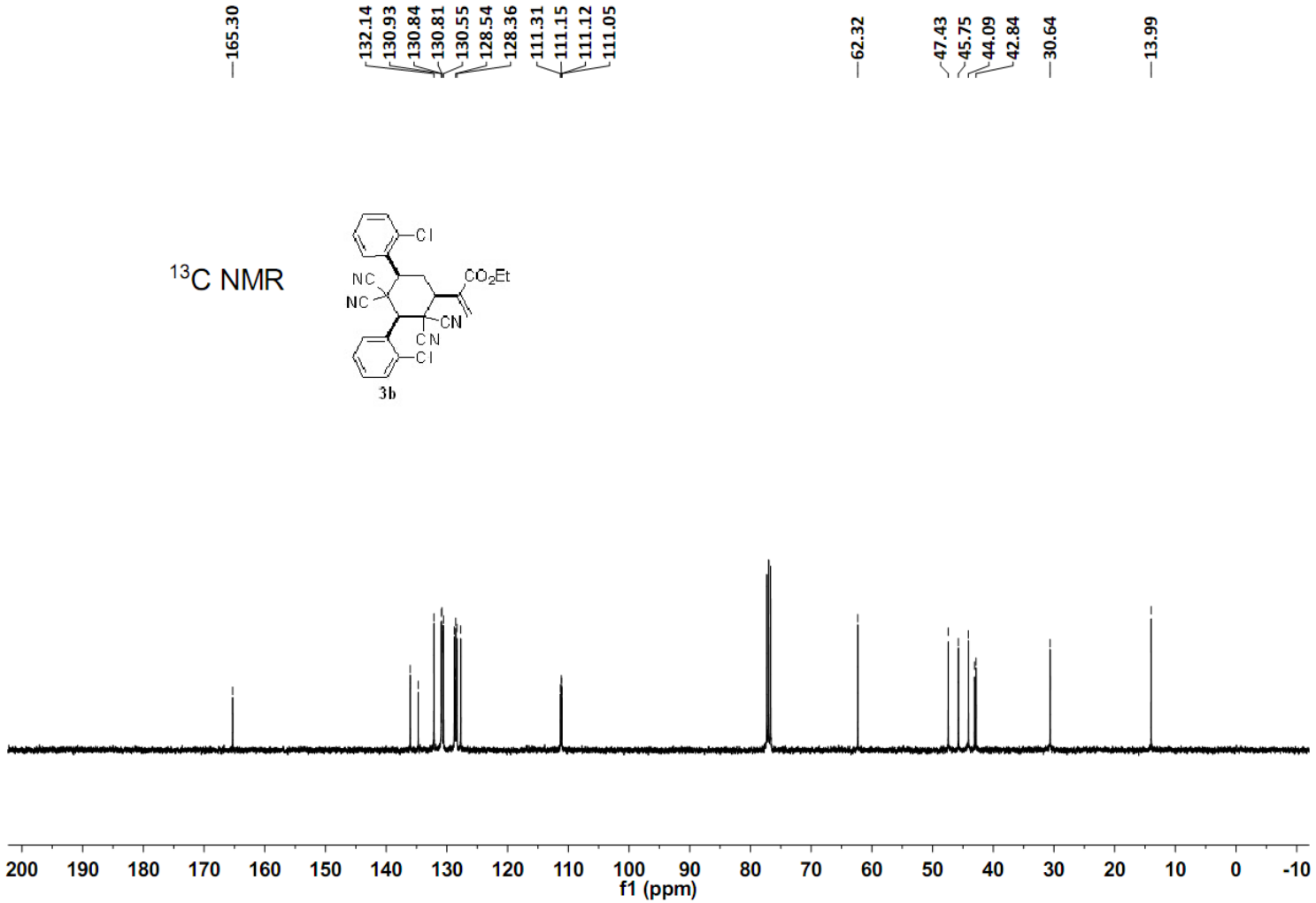
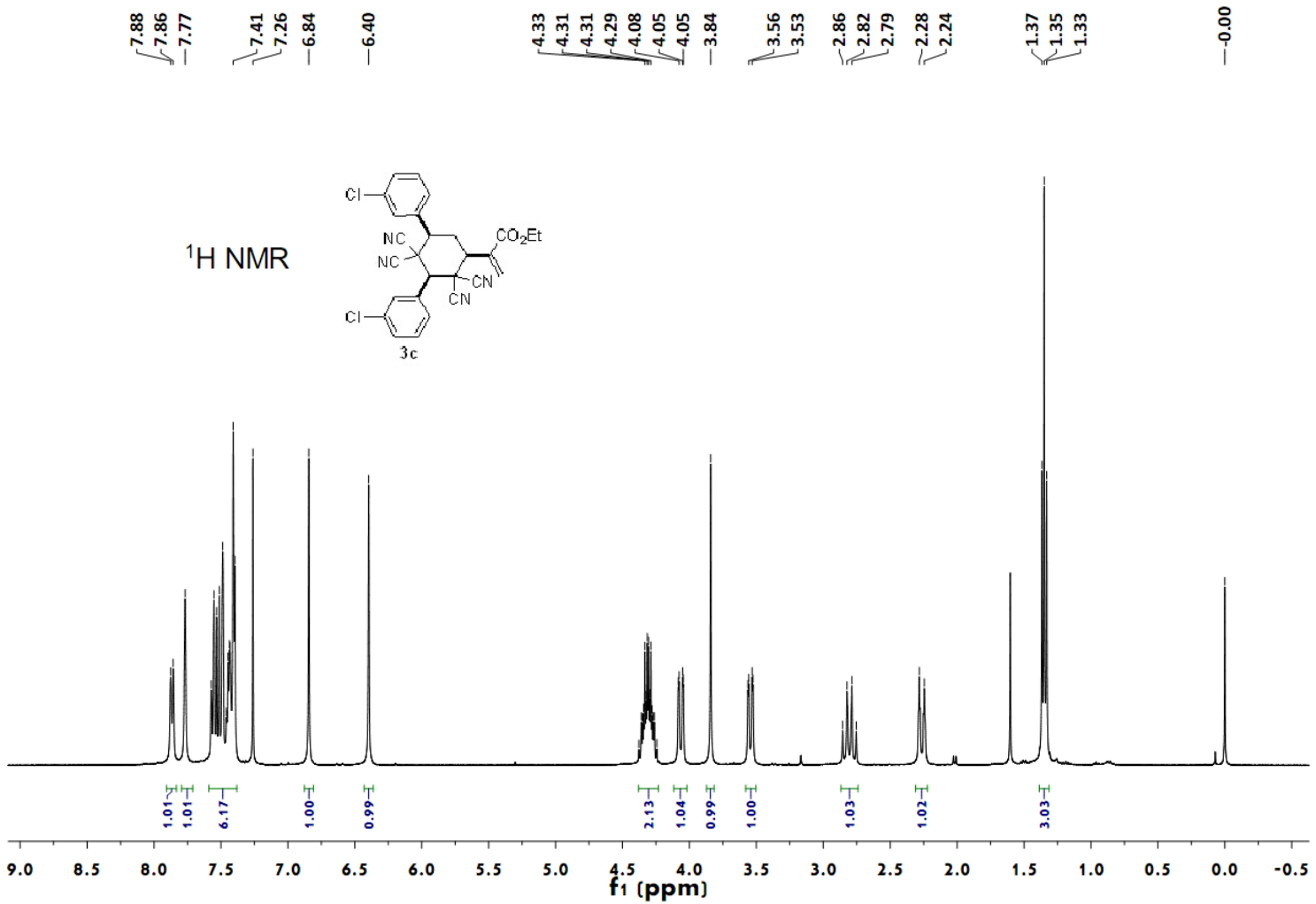
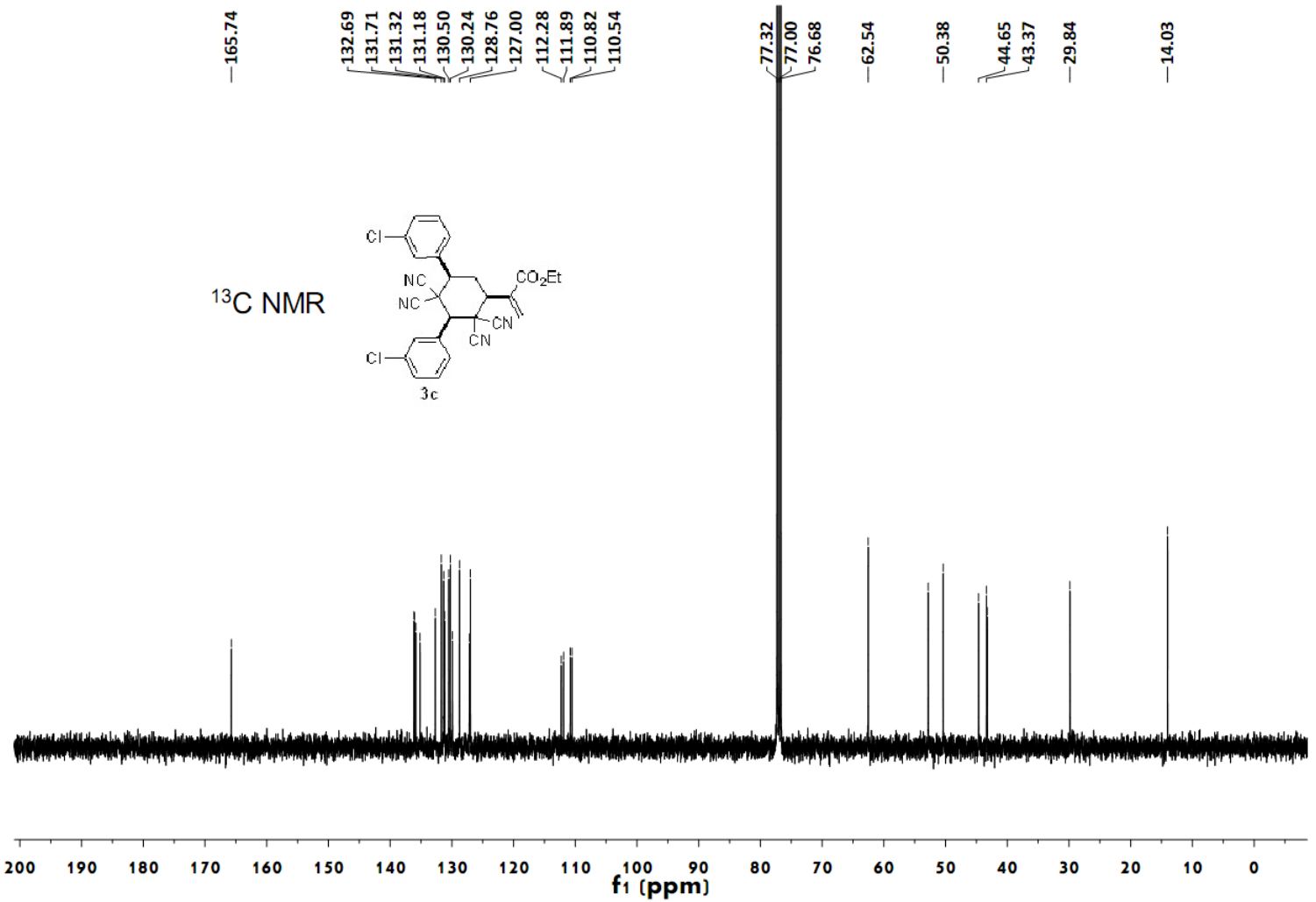
8.46
7.60
7.53
7.51
7.42
7.40
6.79
6.31
4.84
4.42
4.34
4.32
4.30
2.82
2.79
2.75
2.72
2.19
2.15
1.36
1.34
1.33
0.00
^{1}H NMR
Cl
NC
NC
CO$_2$Et
CN
CN
Cl
3b
0.96
1.09
1.05
3.01
1.94
1.00
0.98
1.00
0.96
2.03
1.04
0.99
0.98
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


165.30
132.14
130.93
130.84
130.81
130.55
128.54
128.36
111.31
111.15
111.12
111.05
62.32
47.43
45.75
44.09
42.84
30.64
13.99
13C NMR
Cl
NC
NC
CO2Et
CN
CN
Cl
3b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

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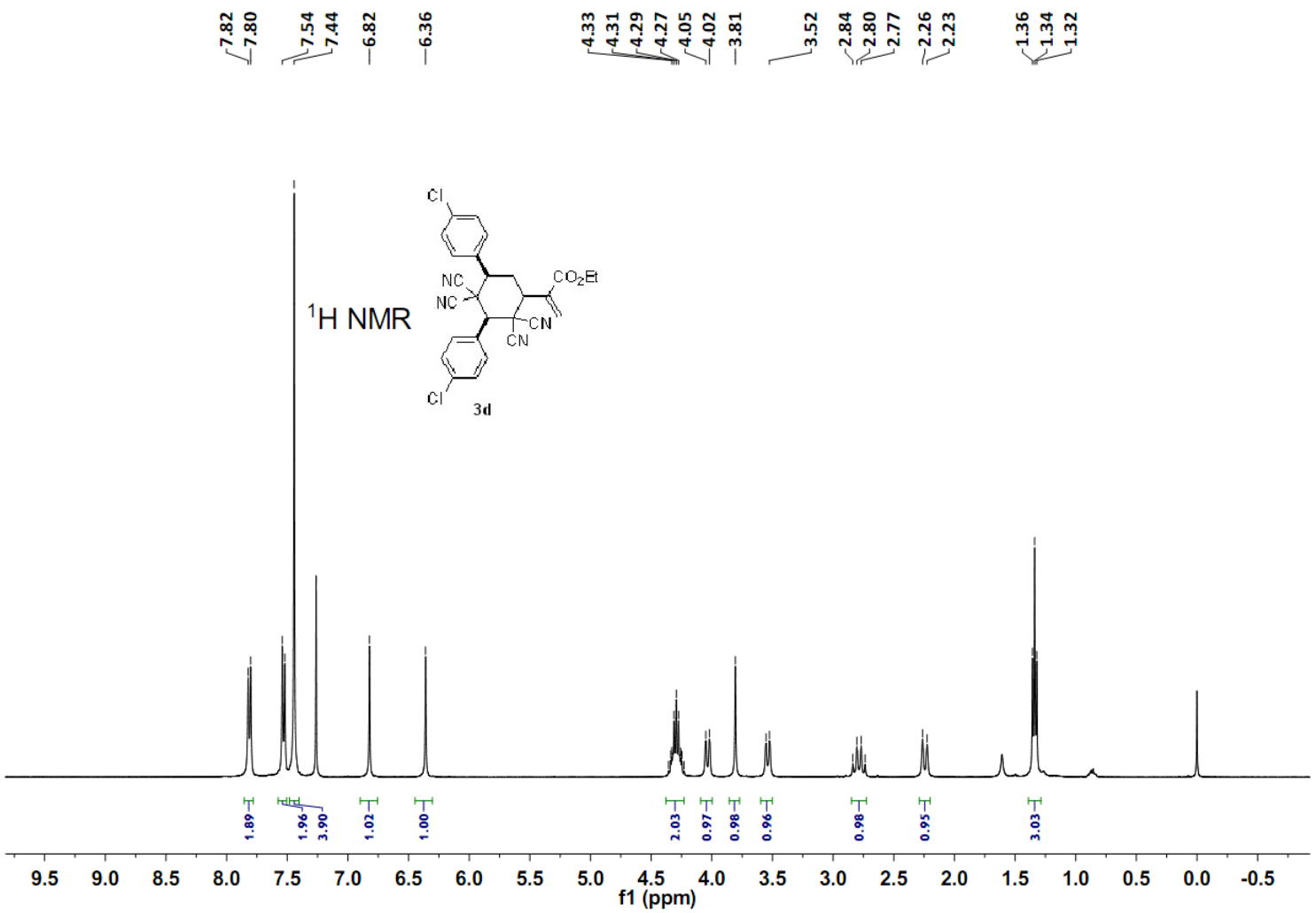
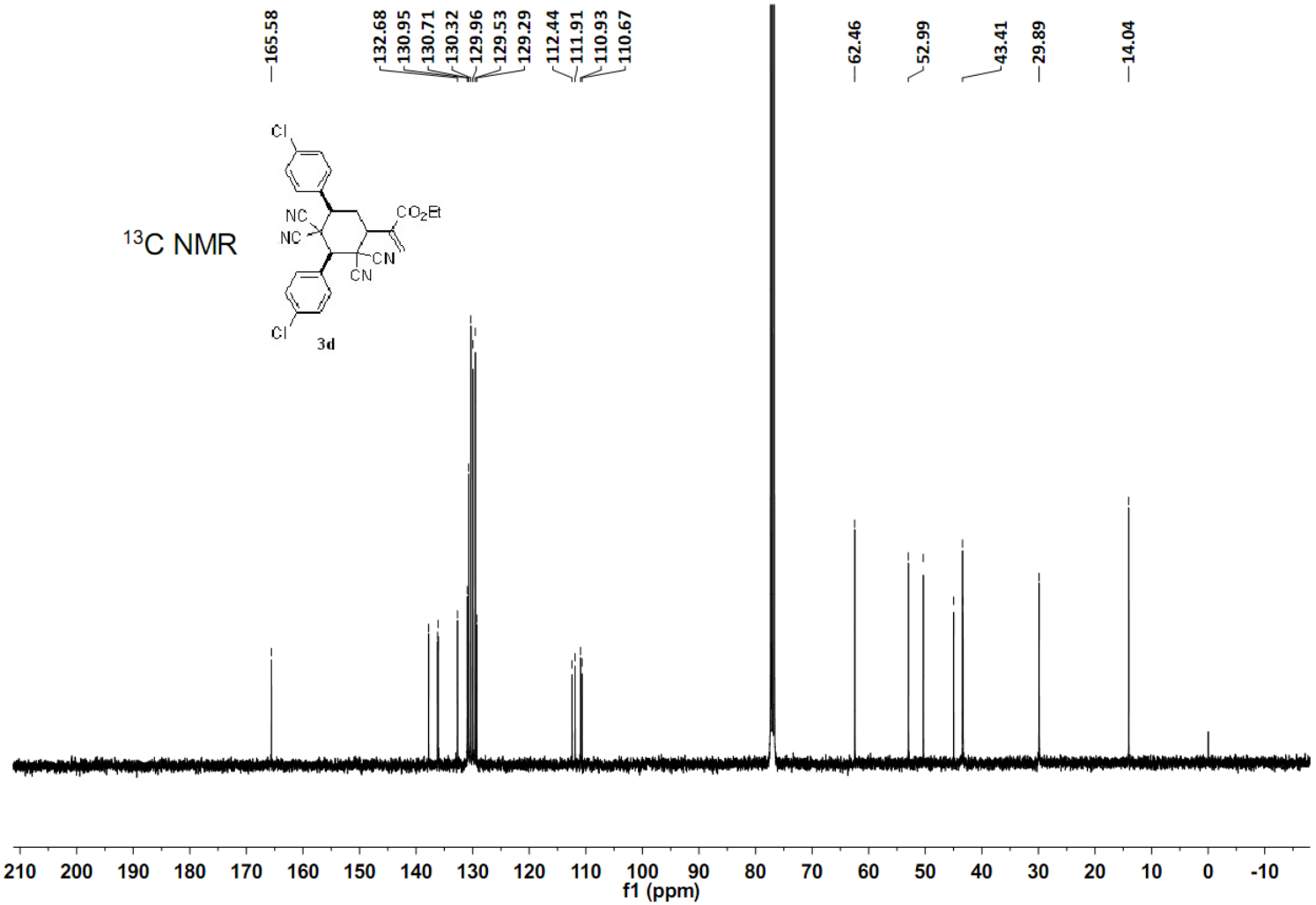
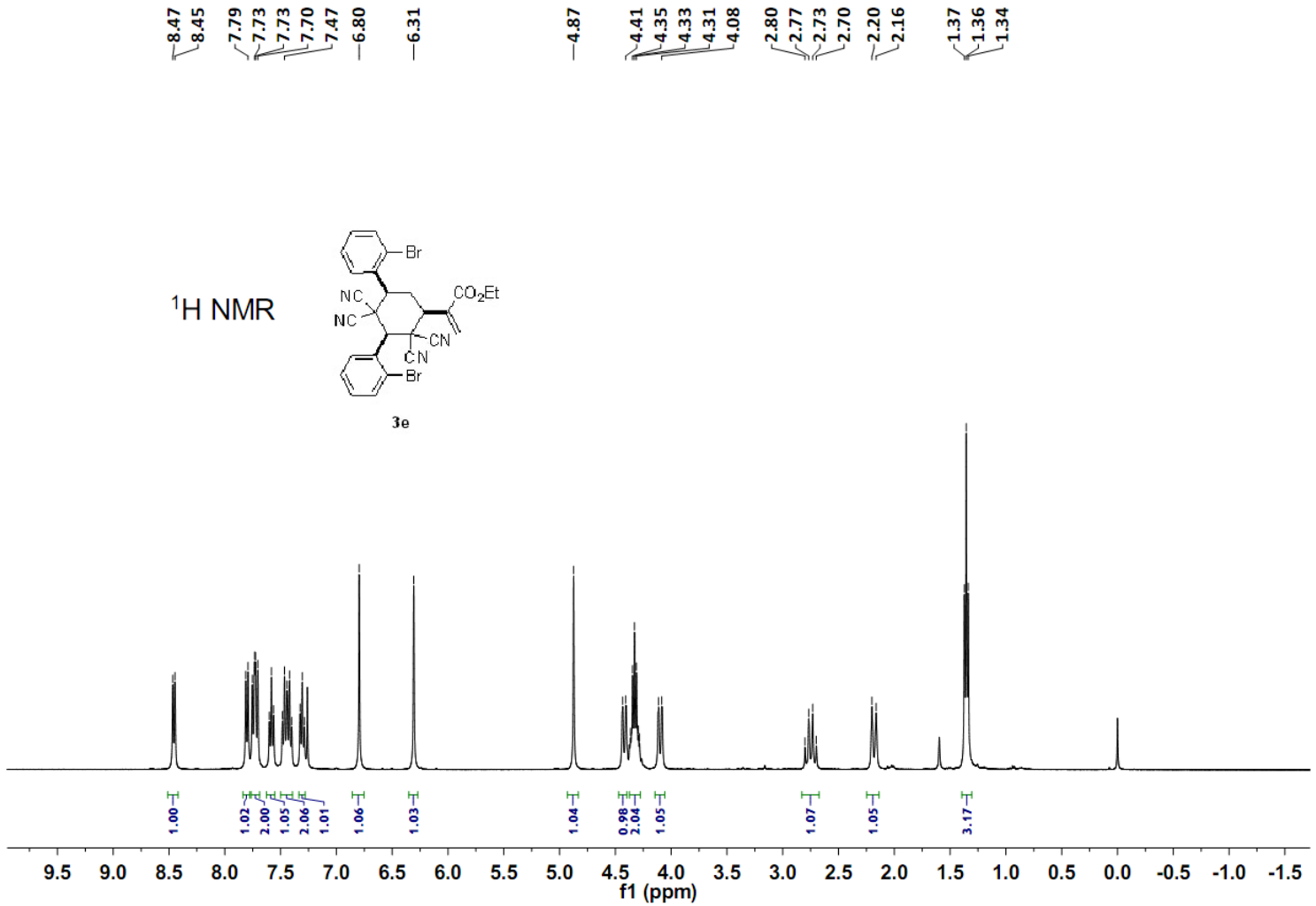
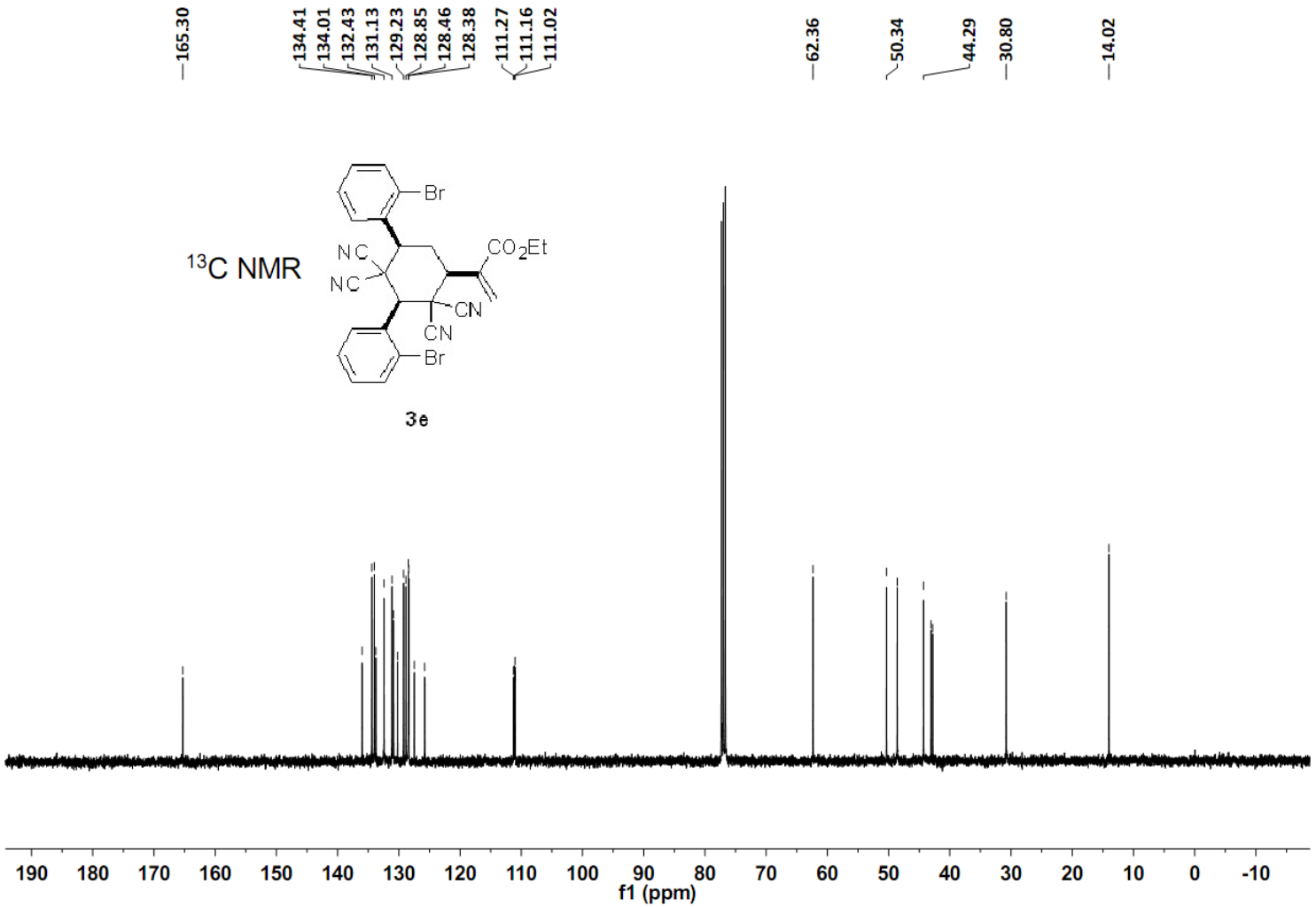
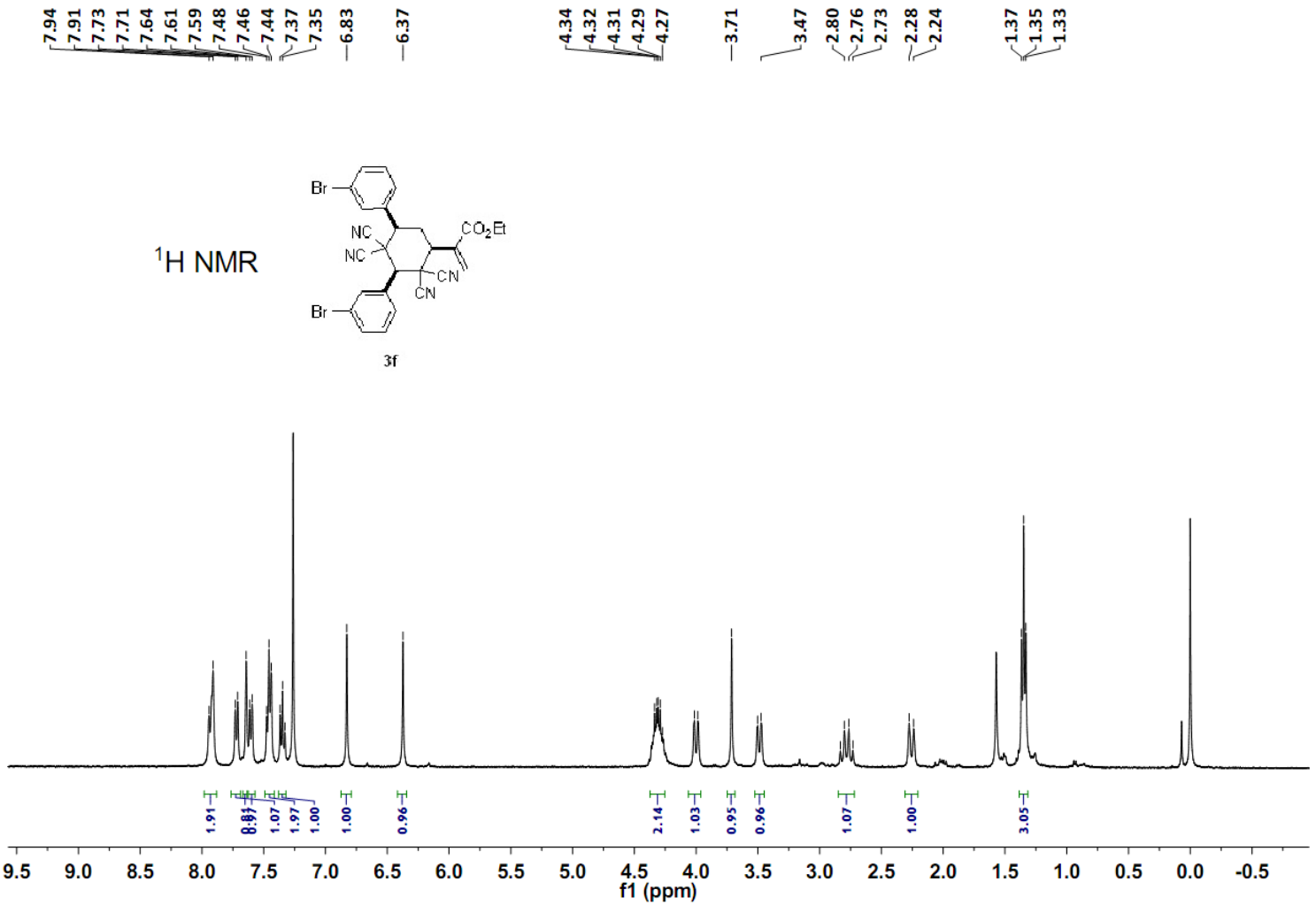
132.69
131.71
131.32
131.18
130.50
130.24
128.76
127.00
112.28
111.89
110.82
110.54
77.32
77.00
76.68
62.54
50.38
44.65
43.37
29.84
14.03
13C NMR
Cl
NC
NC
CO2Et
CN
CN
Cl
3c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)







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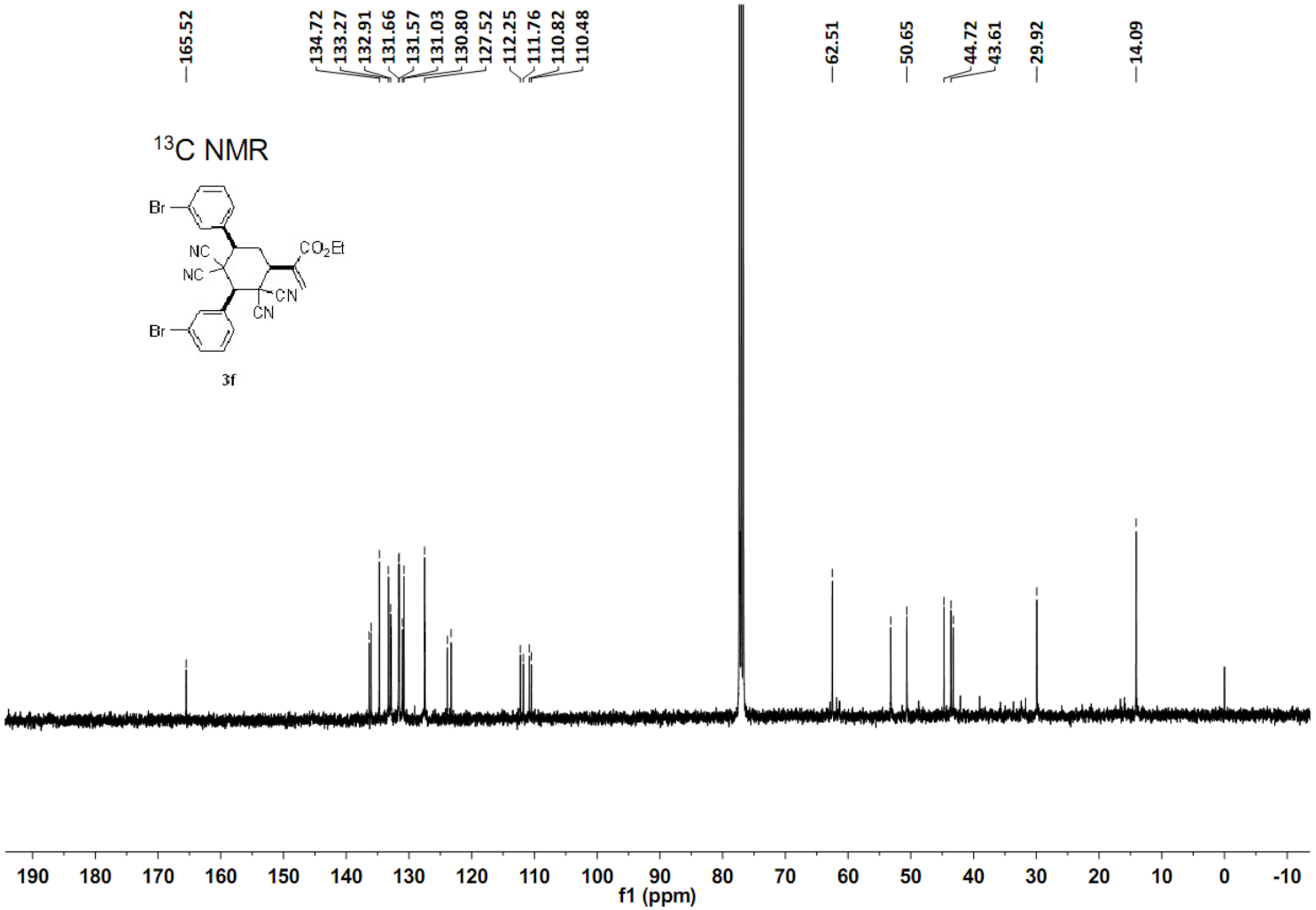
7.91
7.73
7.71
7.64
7.61
7.59
7.48
7.46
7.44
7.37
7.35
6.83
6.37
4.34
4.32
4.31
4.29
4.27
3.71
3.47
2.80
2.76
2.73
2.28
2.24
1.37
1.35
1.33
^{1}H NMR
Br
NC
NC
CO$_2$Et
CN
CN
Br
3f
1.91
1.07
1.97
1.00
1.00
0.96
2.14
1.03
0.95
0.96
1.07
1.00
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


165.52
134.72
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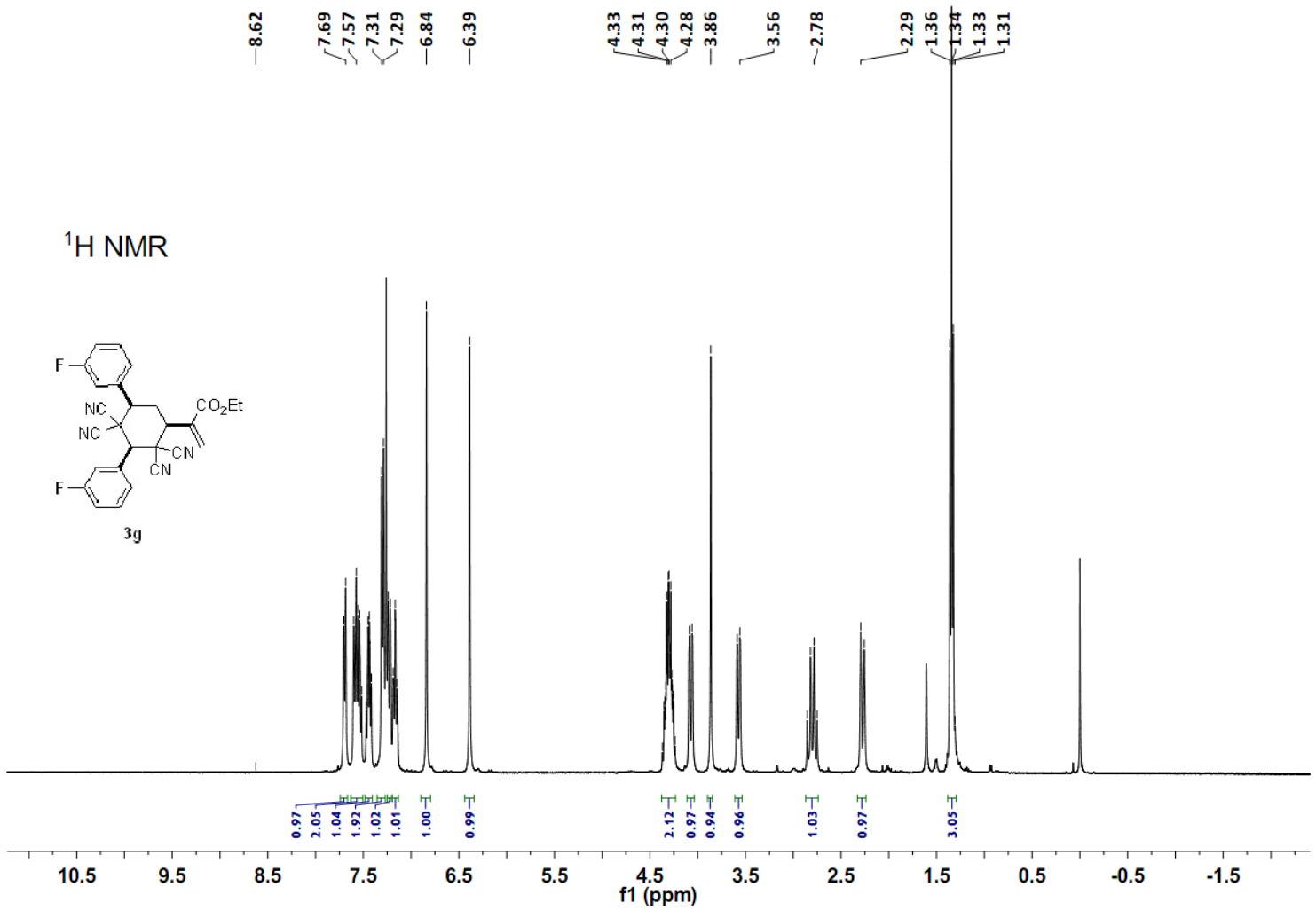
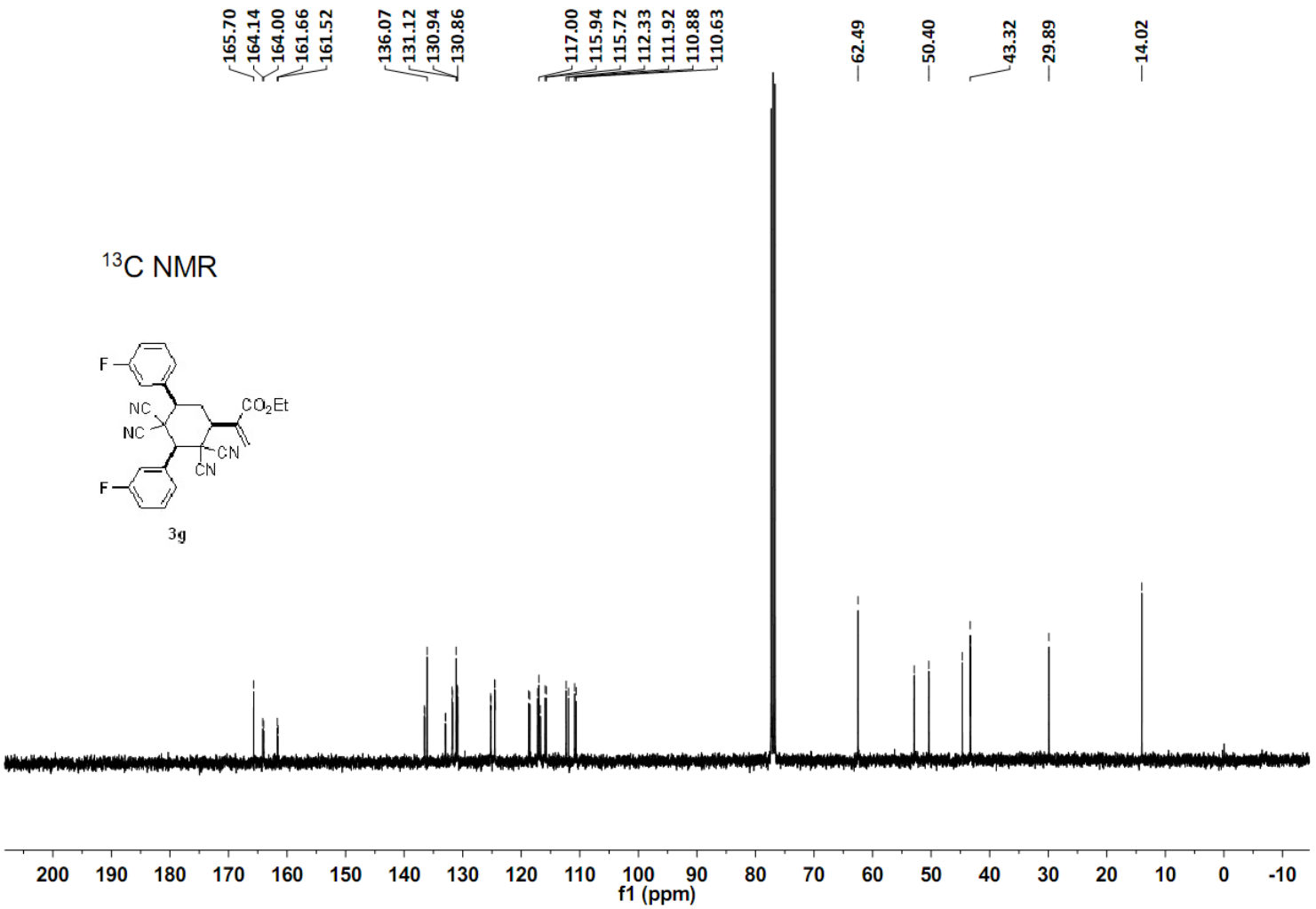
132.91
131.66
131.57
131.03
130.80
127.52
112.25
111.76
110.82
110.48
62.51
50.65
44.72
43.61
29.92
14.09
13C NMR
Br
NC
NC
CO2Et
CN
CN
Br
3f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

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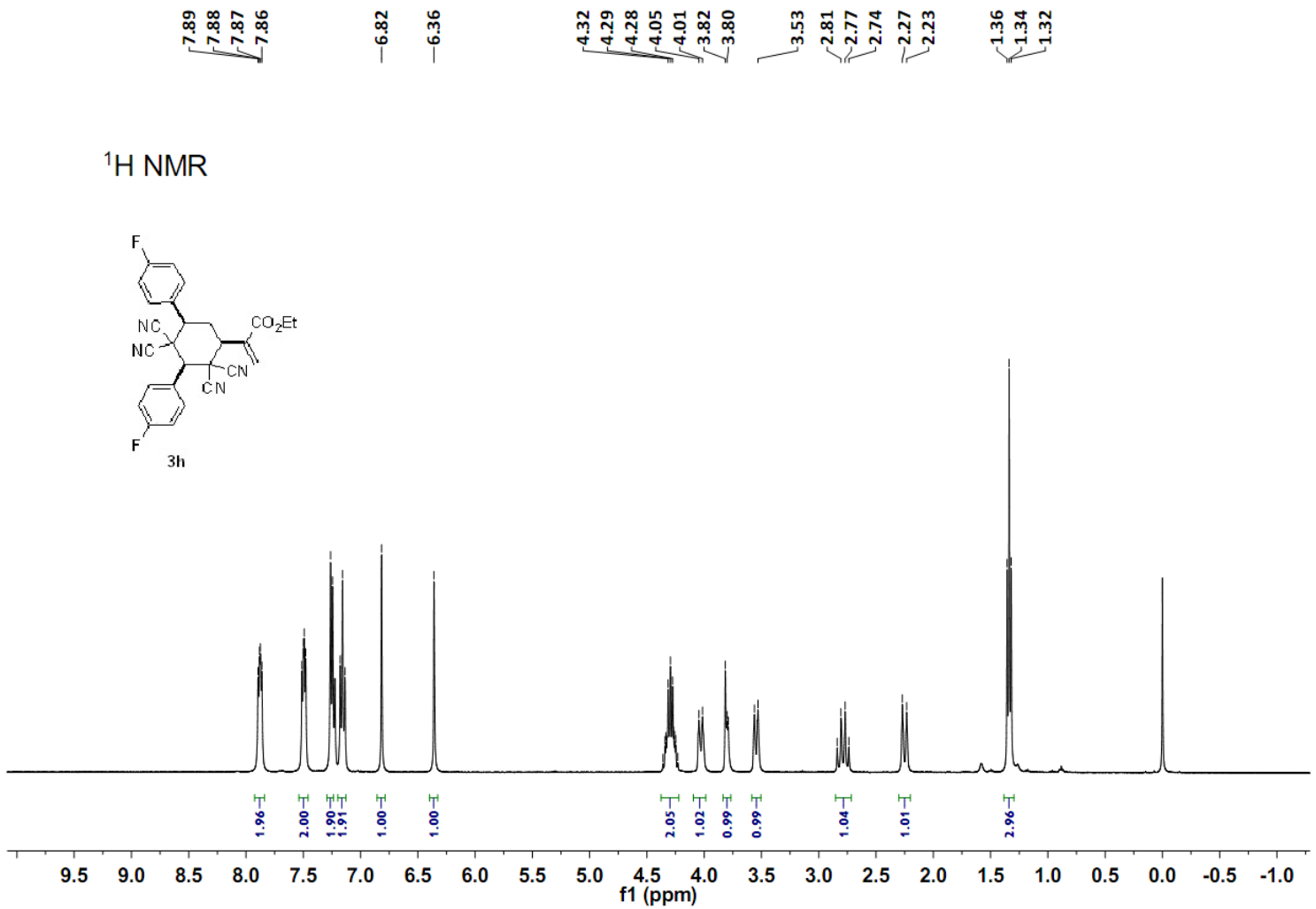
164.00
161.66
161.52
136.07
131.12
130.94
130.86
117.00
115.94
115.72
112.33
111.92
110.88
110.63
62.49
50.40
43.32
29.89
14.02
13C NMR
F
NC
NC
CO2Et
CN
CN
F
3g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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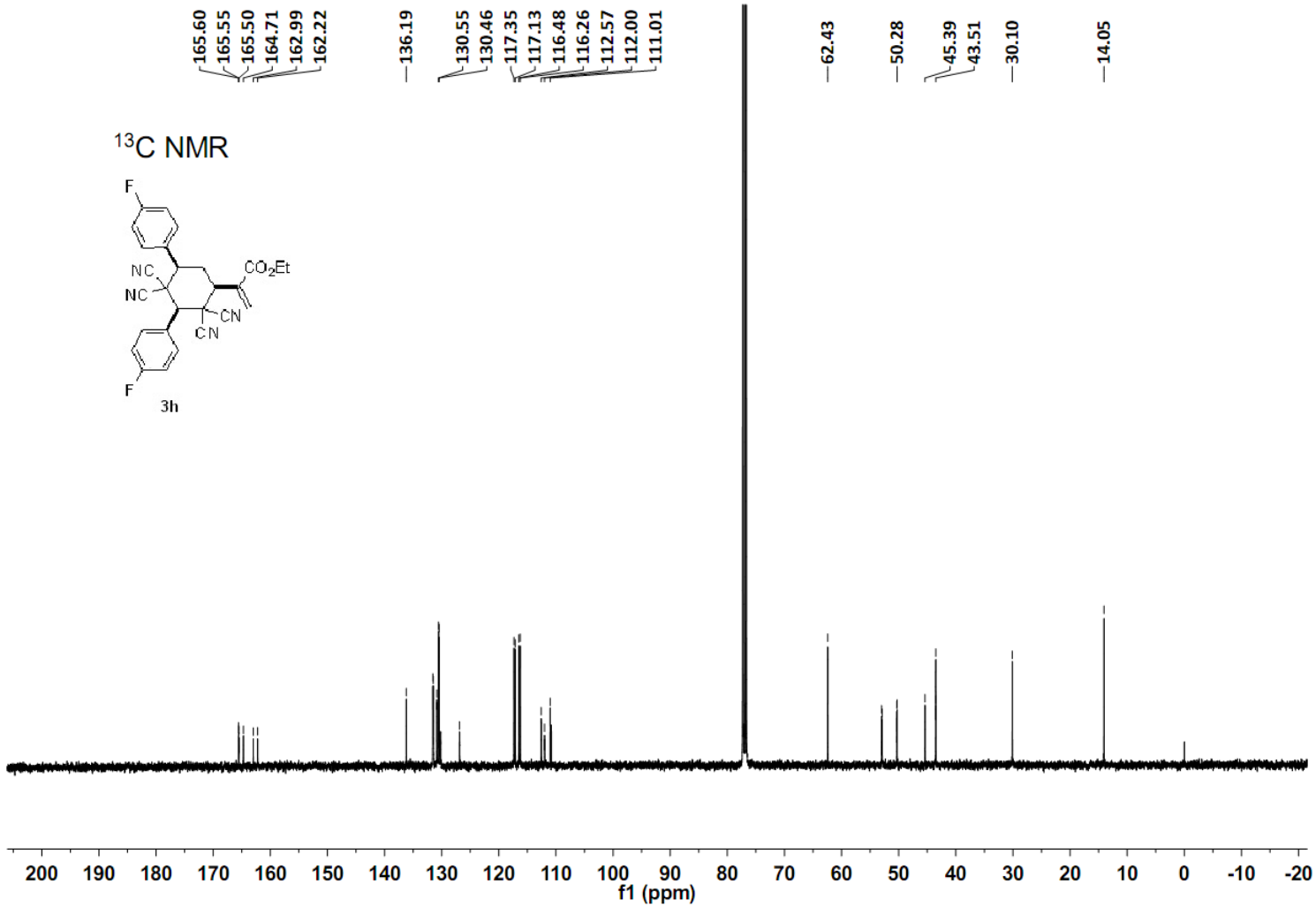
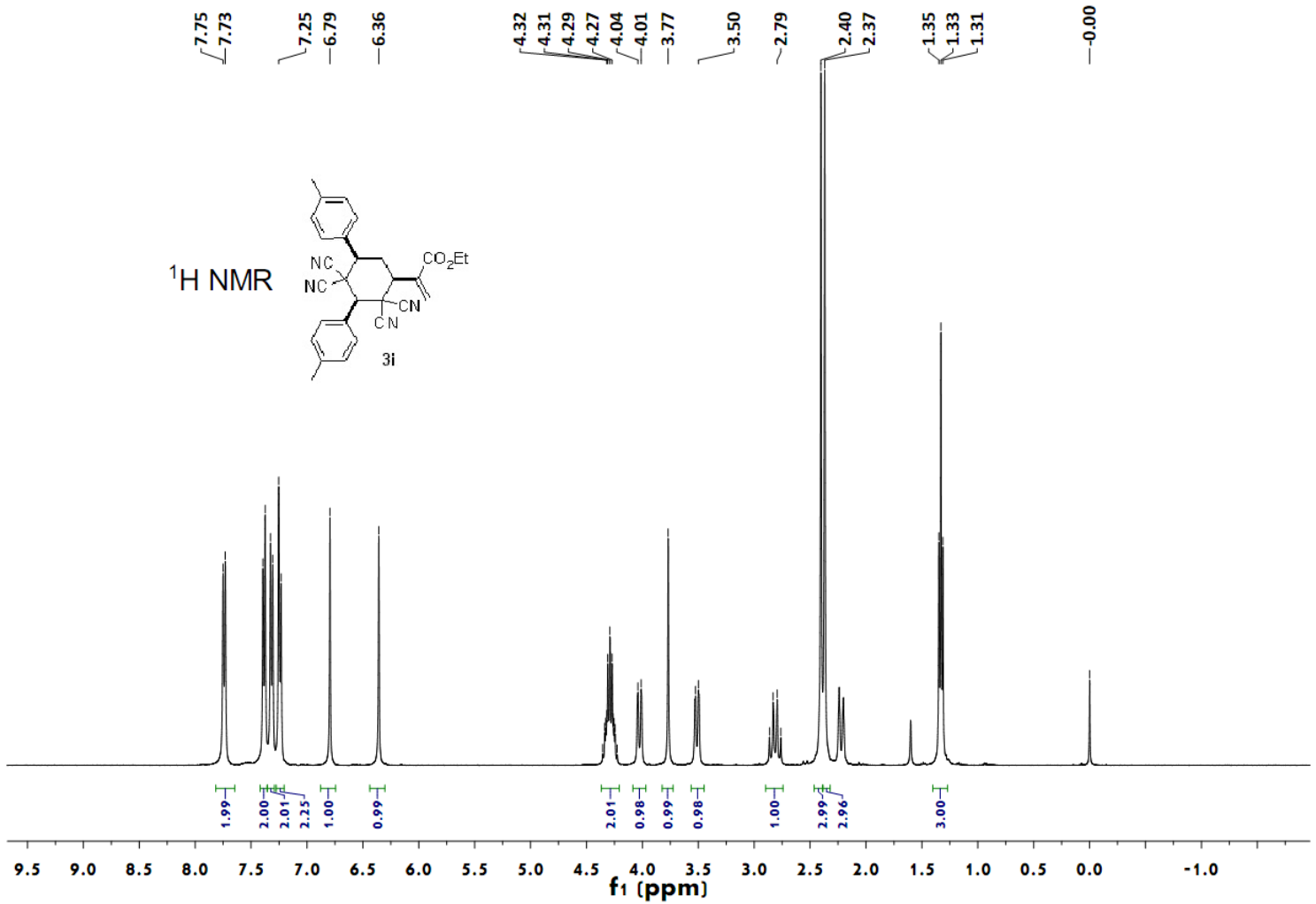
7.86
6.82
6.36
4.32
4.29
4.28
4.05
4.01
3.82
3.80
3.53
2.81
2.77
2.74
2.27
2.23
1.36
1.34
1.32
^{1}H NMR
F
NC
NC
CO$_2$Et
CN
CN
F
3h
1.96
2.00
1.90
1.91
1.00
1.00
2.05
1.02
0.99
0.99
1.04
1.01
2.96
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

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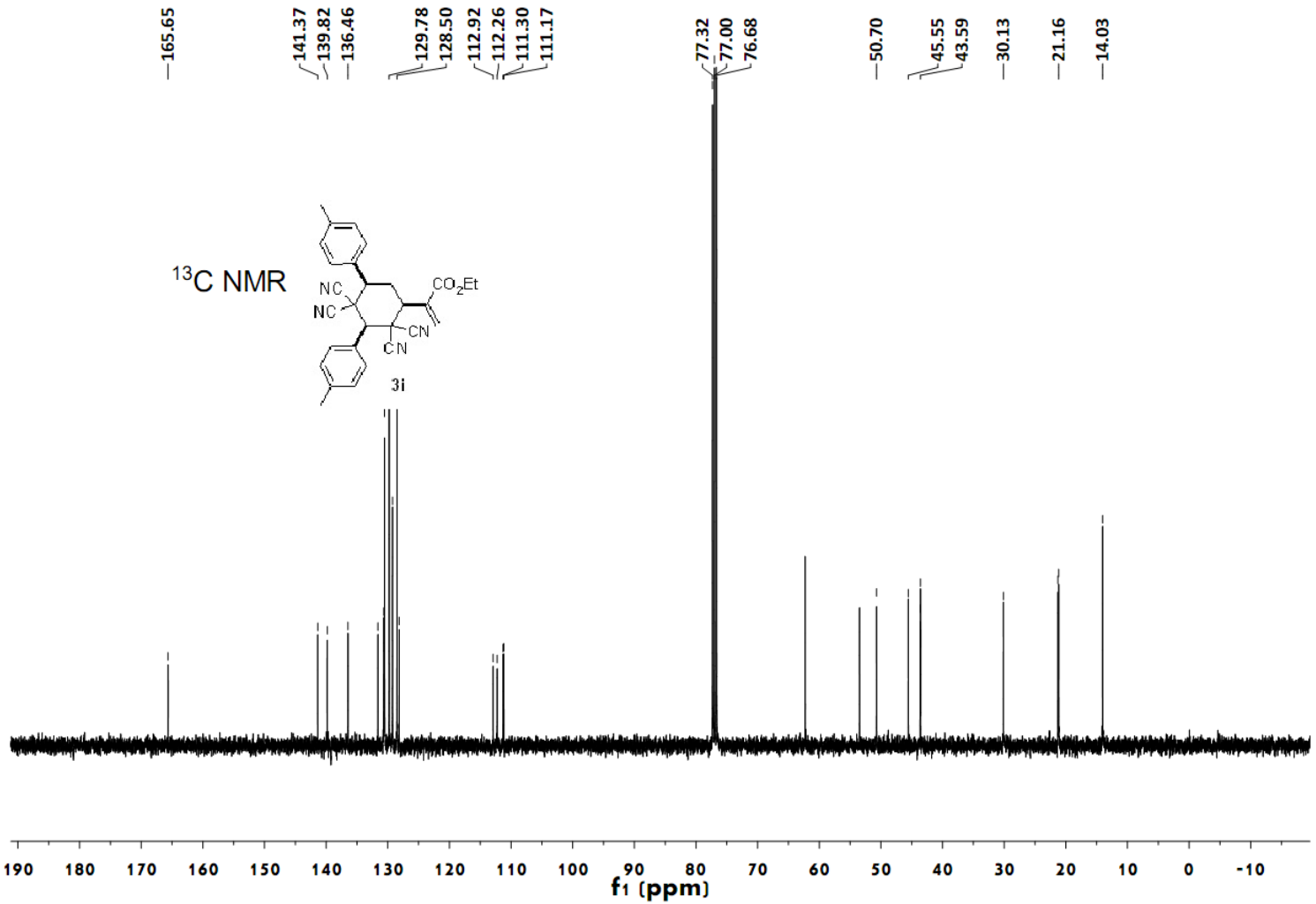
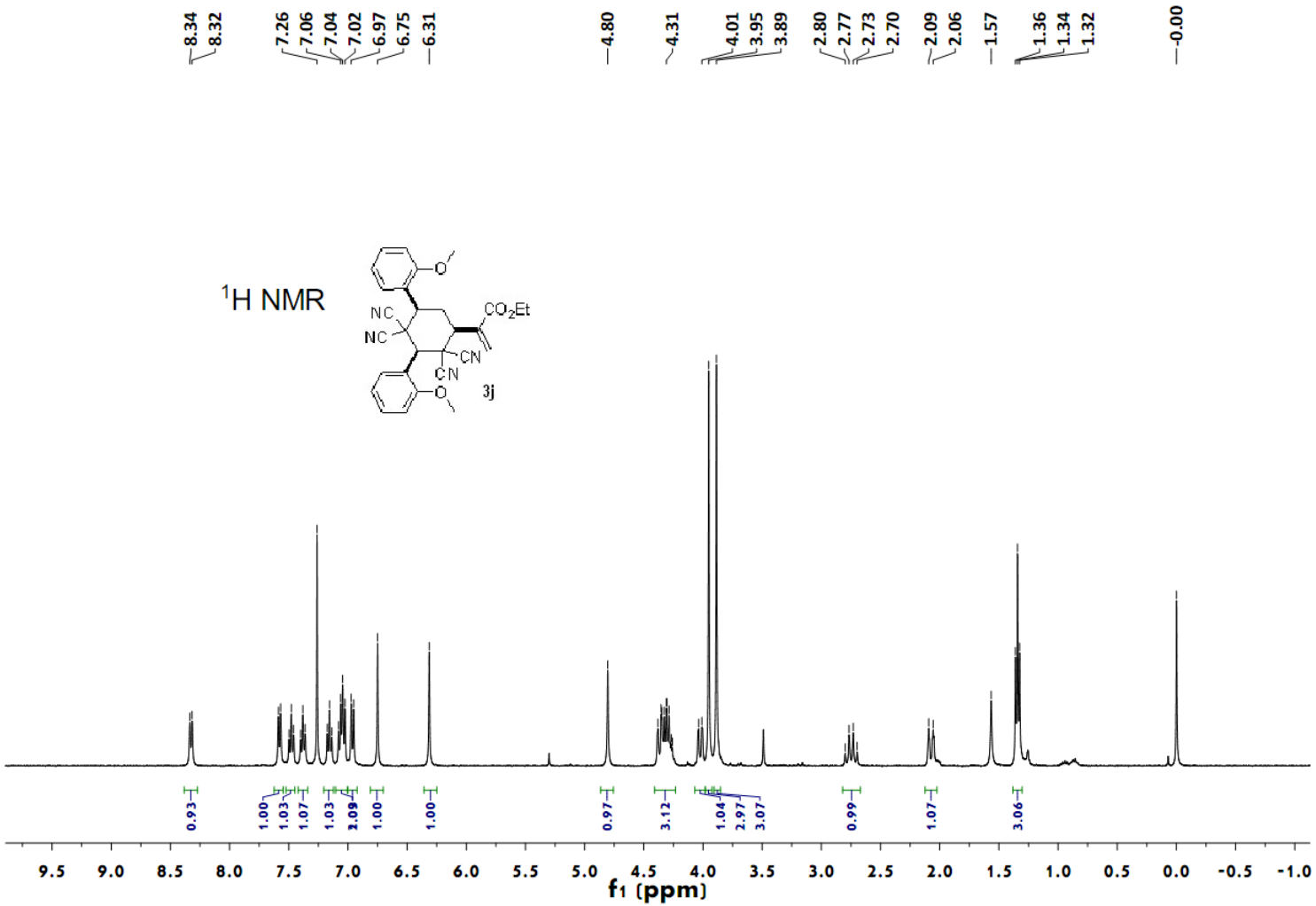
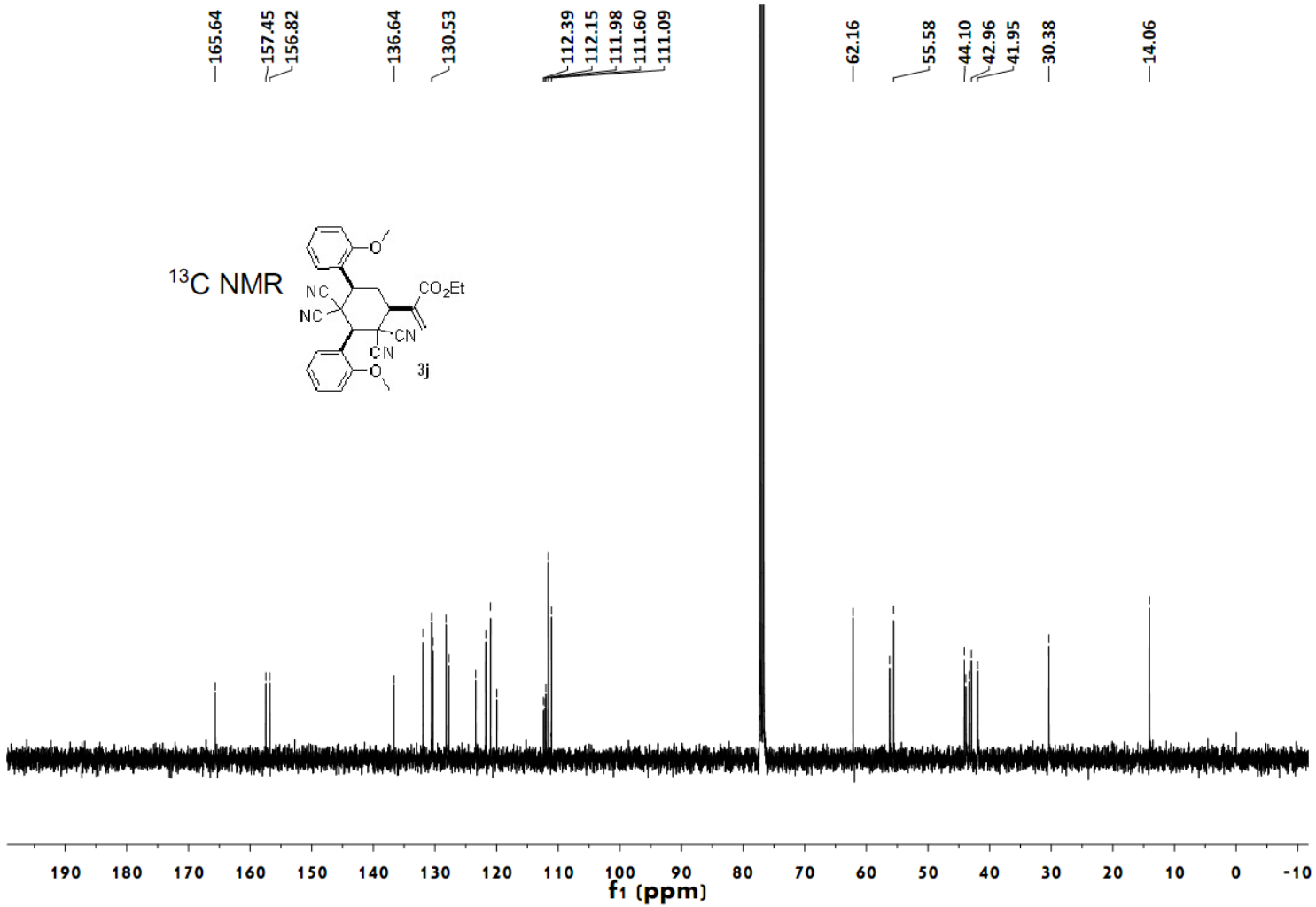
7.73
7.25
6.79
6.36
4.32
4.31
4.29
4.27
4.04
4.01
3.77
3.50
2.79
2.40
2.37
1.35
1.33
1.31
0.00
^{1}H NMR
NC
NC
CN
CN
CO_2Et
3i
1.99
2.00
2.01
2.25
1.00
0.99
2.01
0.98
0.99
0.98
1.00
2.99
2.96
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0
f1 (ppm)



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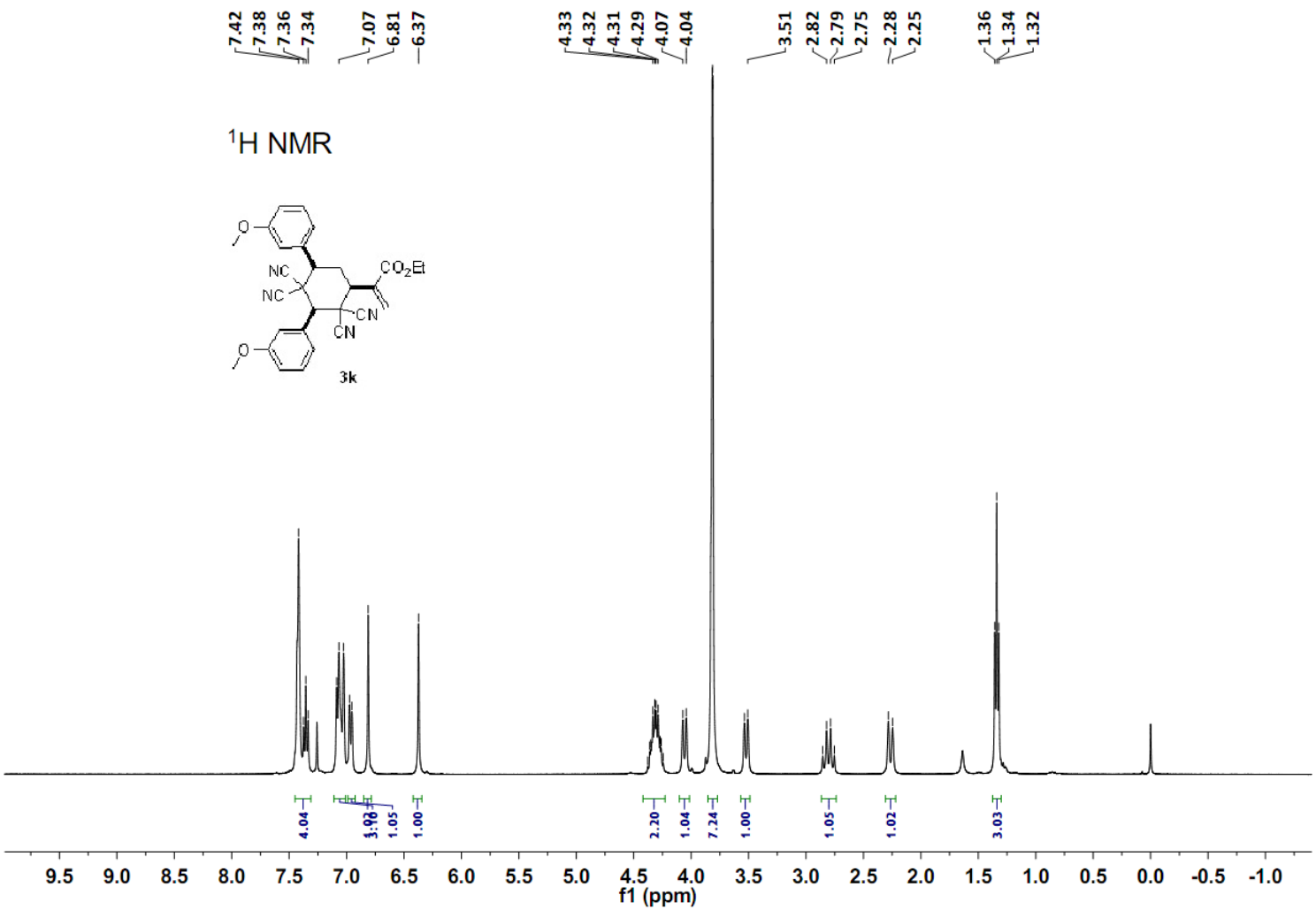
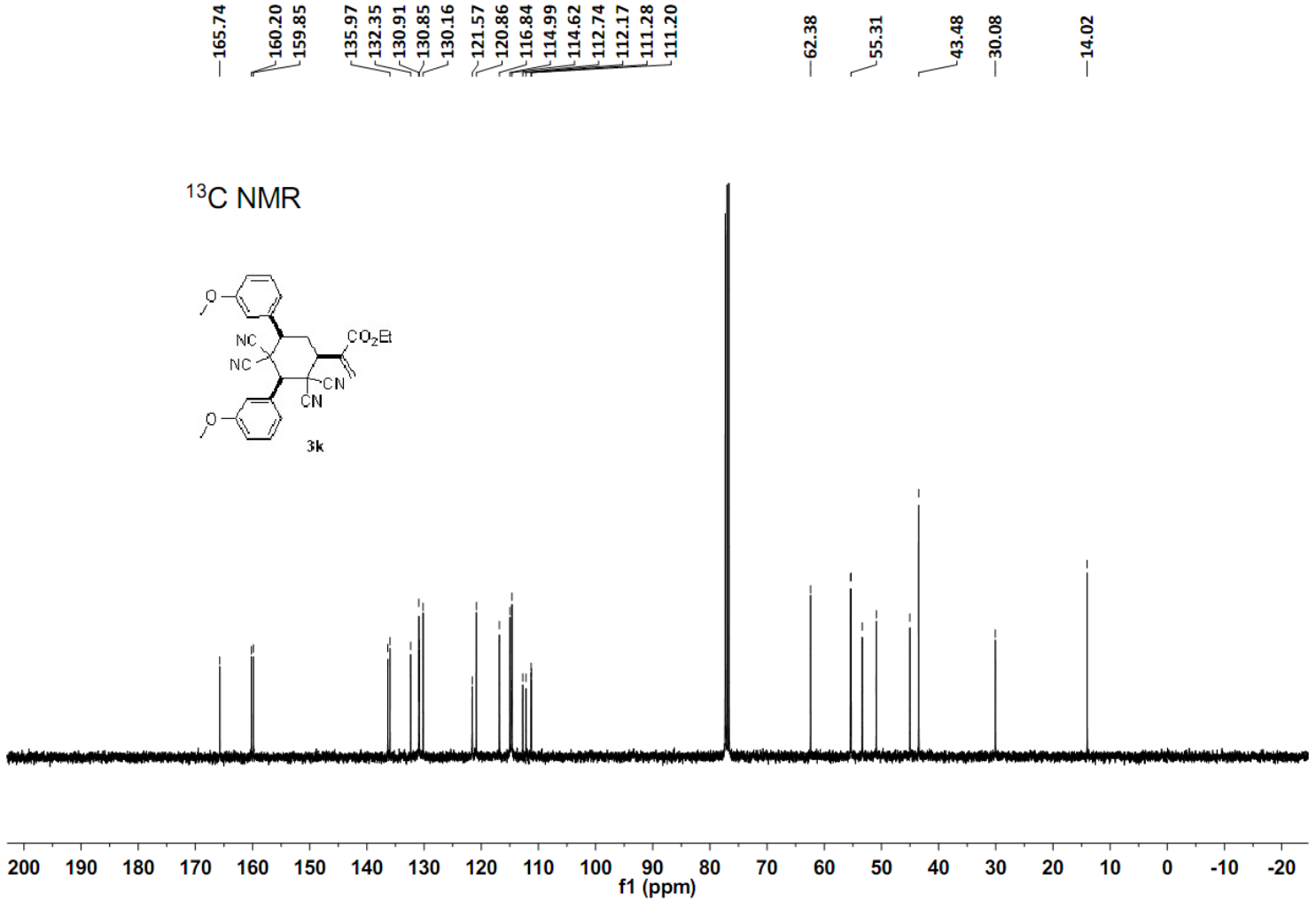
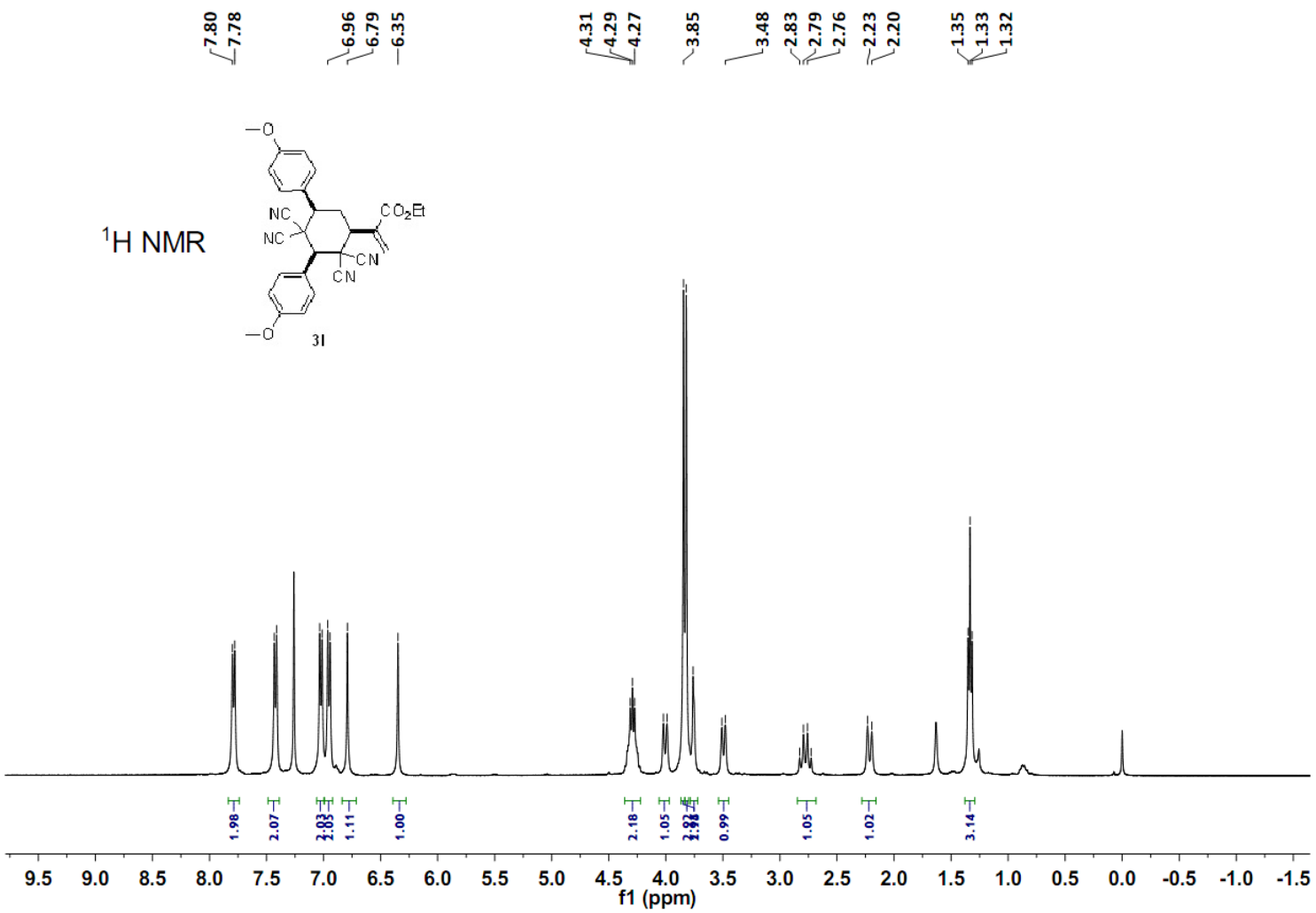
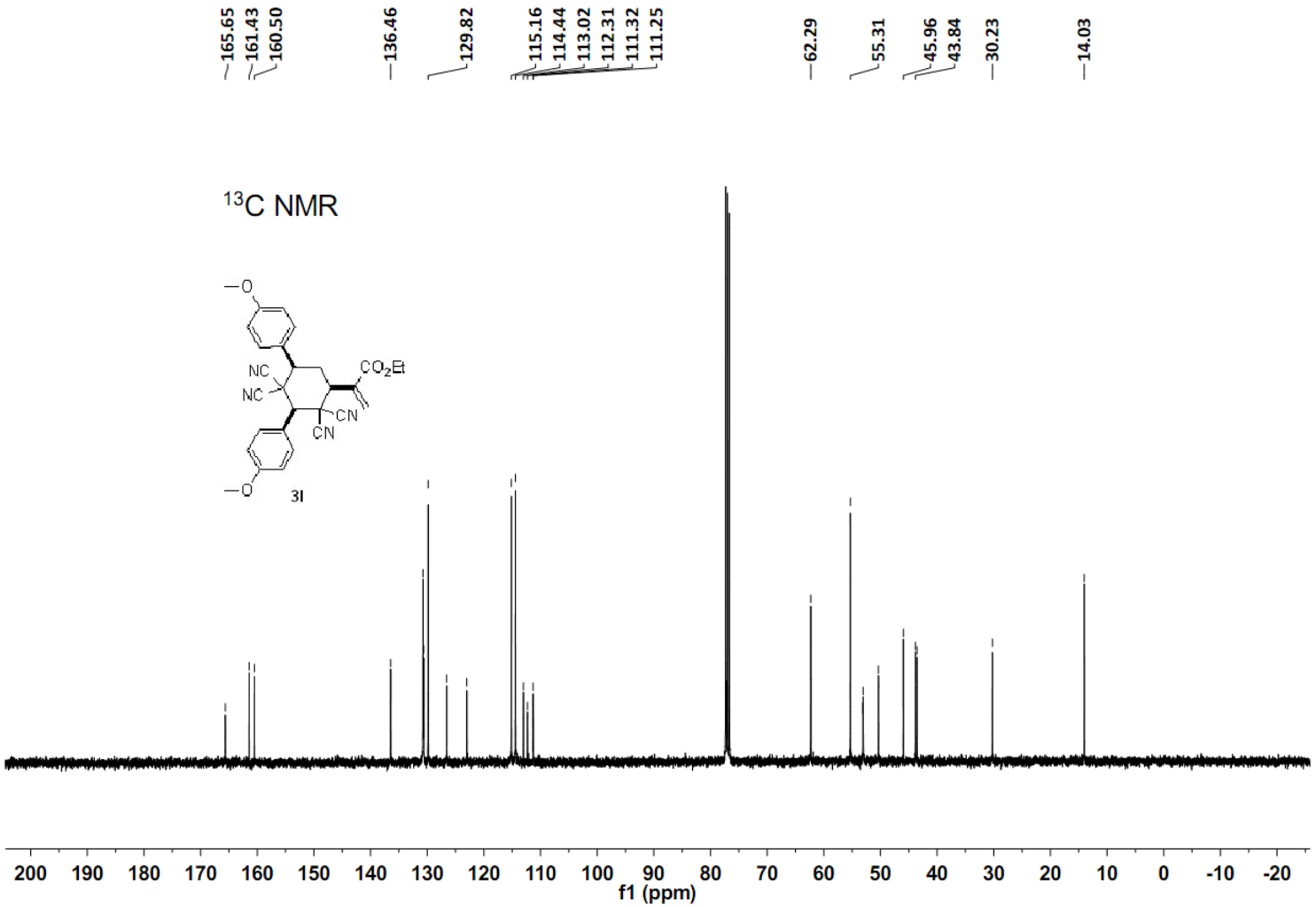
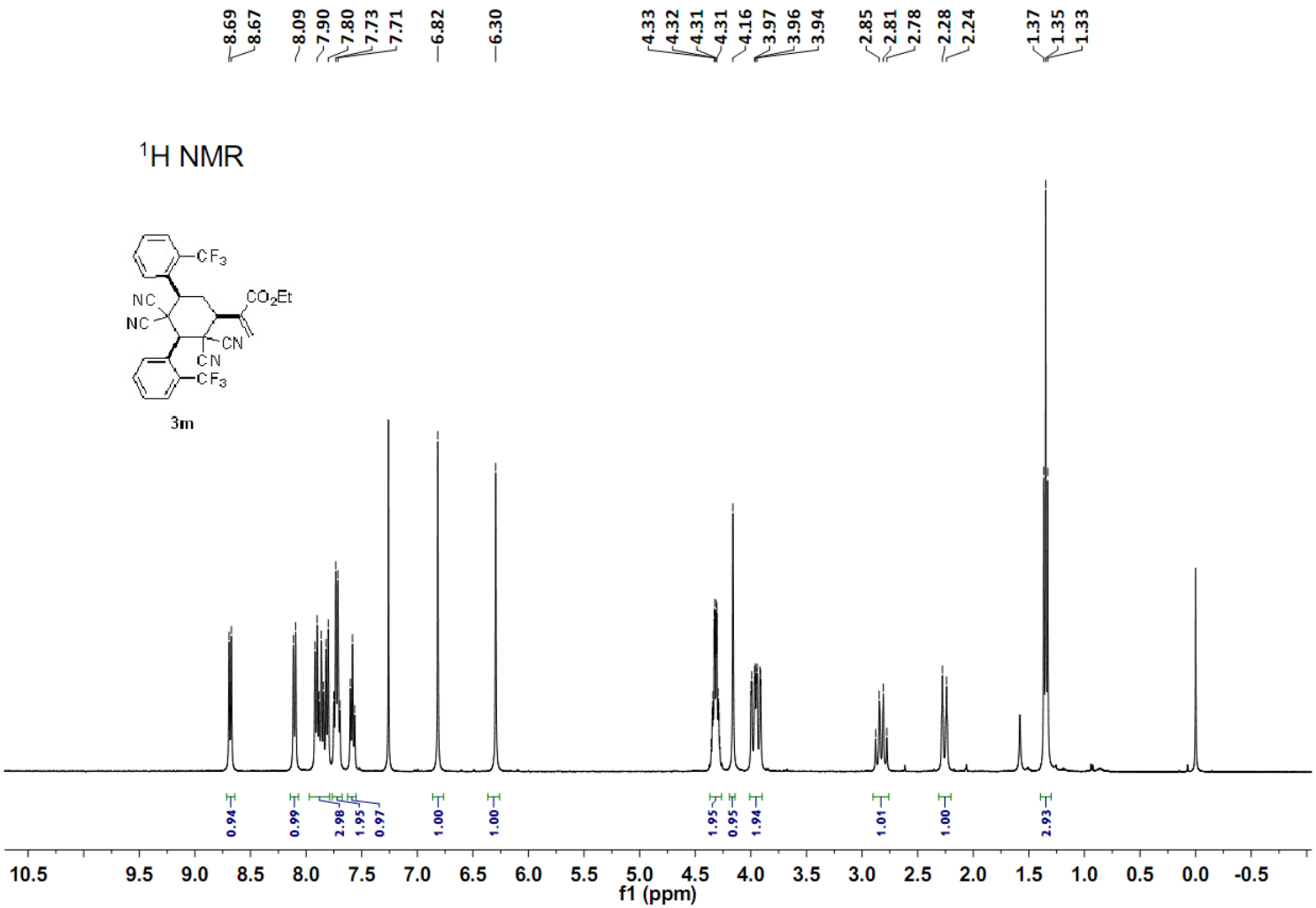
157.45
156.82
136.64
130.53
112.39
112.15
111.98
111.60
111.09
62.16
55.58
44.10
42.96
41.95
30.38
14.06
13C NMR
NC
NC
CN
CN
CO2Et
O
O
3j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

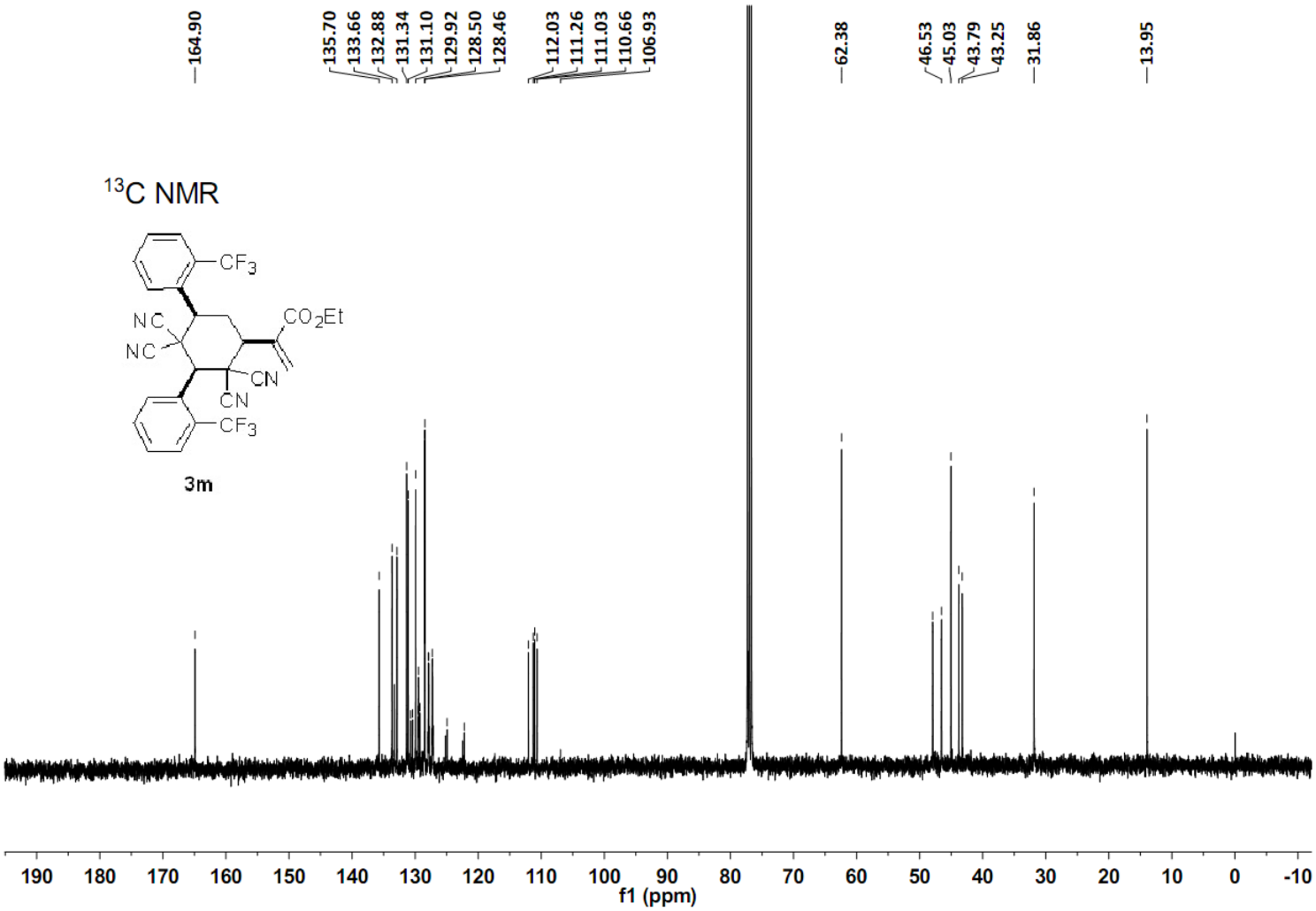

7.42
7.38
7.36
7.34
7.07
6.81
6.37
4.33
4.32
4.31
4.29
4.07
4.04
3.51
2.82
2.79
2.75
2.28
2.25
1.36
1.34
1.32
^{1}H NMR
O
NC
NC
CO$_2$Et
CN
CN
O
3k
4.04
1.05
1.00
2.20
1.04
7.24
1.00
1.05
1.02
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

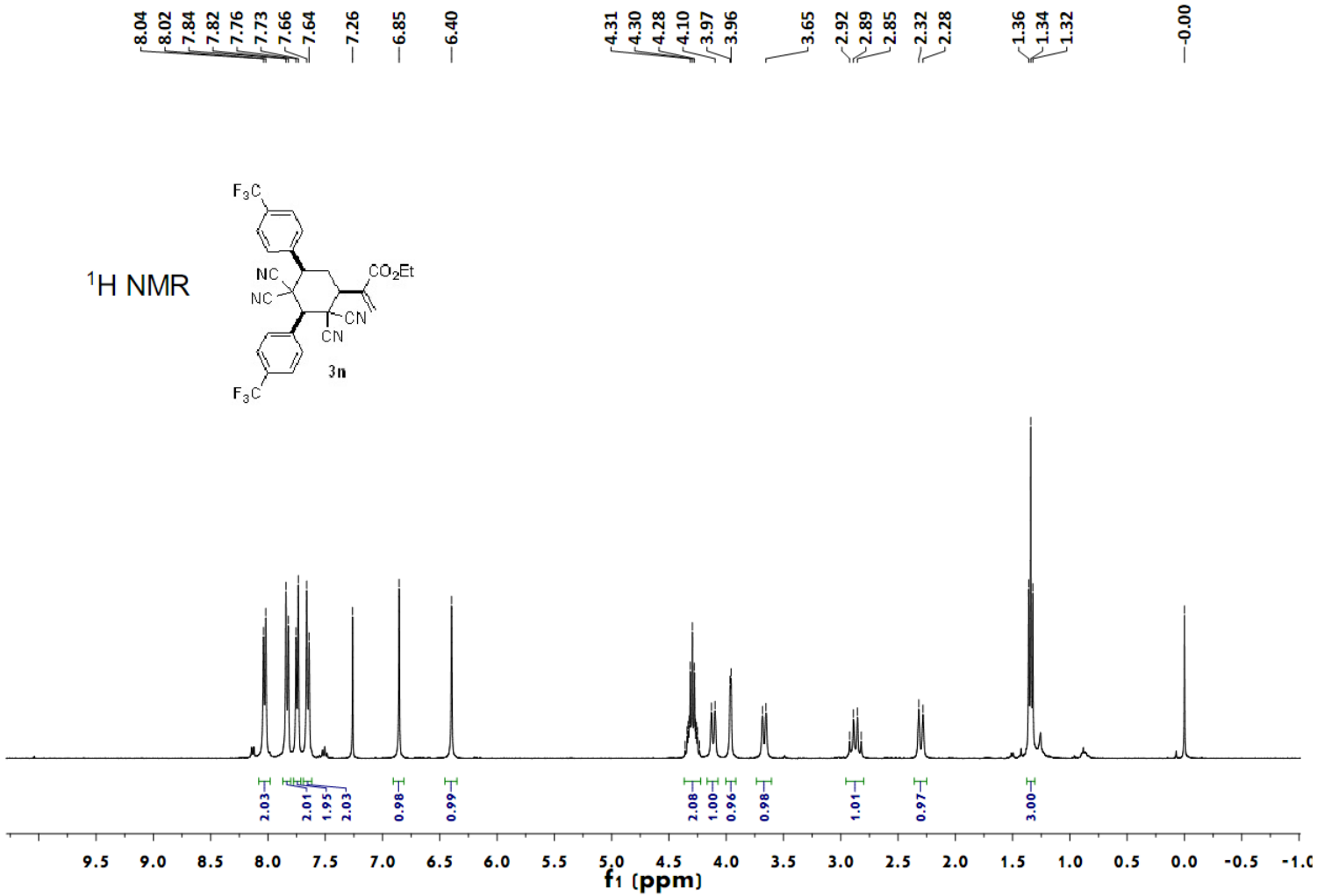

165.74
160.20
159.85
135.97
132.35
130.91
130.85
130.16
121.57
120.86
116.84
114.99
114.62
112.74
112.17
111.28
111.20
62.38
55.31
43.48
30.08
14.02
13C NMR
O
NC
NC
CO2Et
CN
CN
O
3k
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

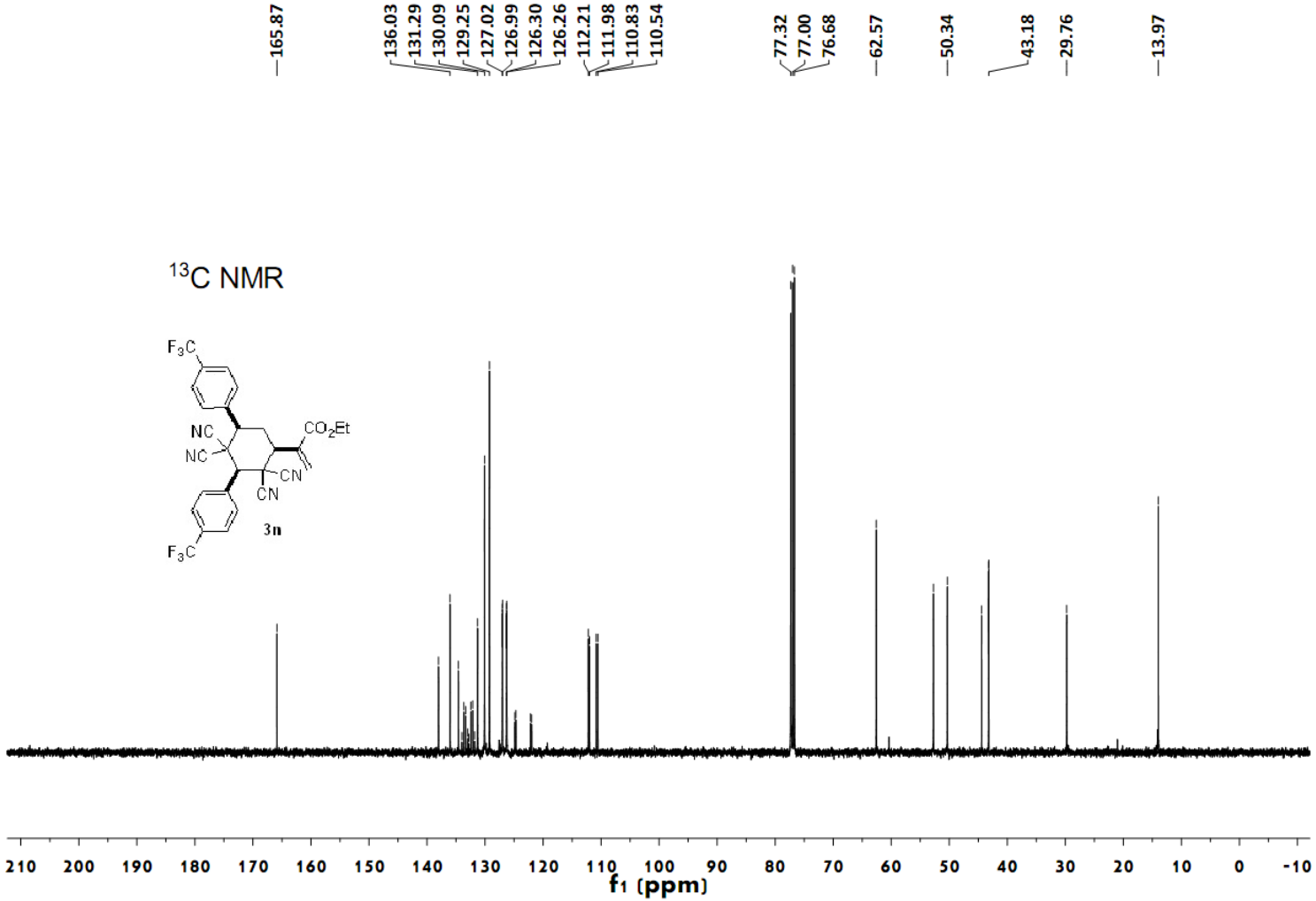


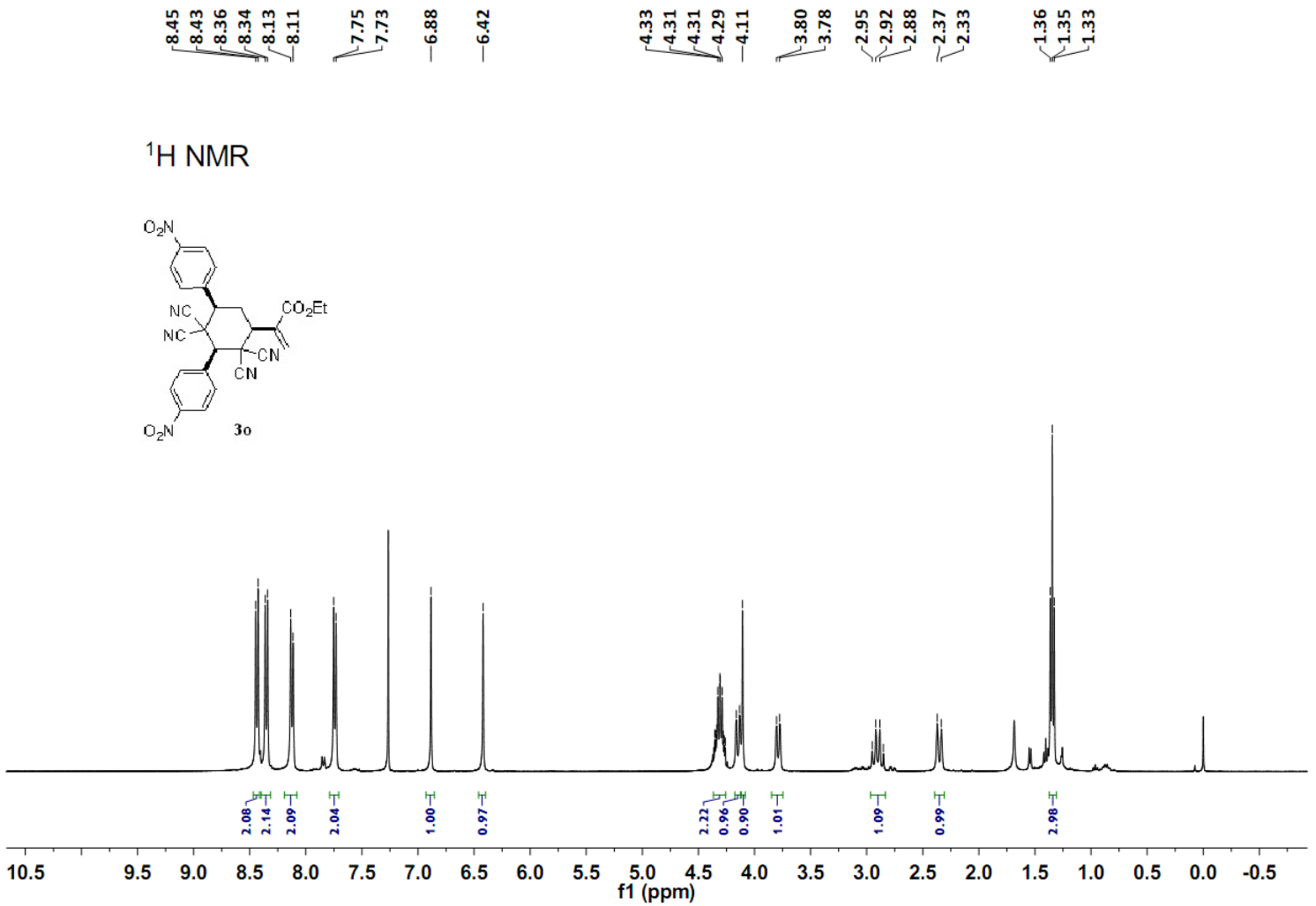

165.65
161.43
160.50
136.46
129.82
115.16
114.44
113.02
112.31
111.32
111.25
62.29
55.31
45.96
43.84
30.23
14.03
13C NMR
NC
NC
CO2Et
CN
CN
3l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

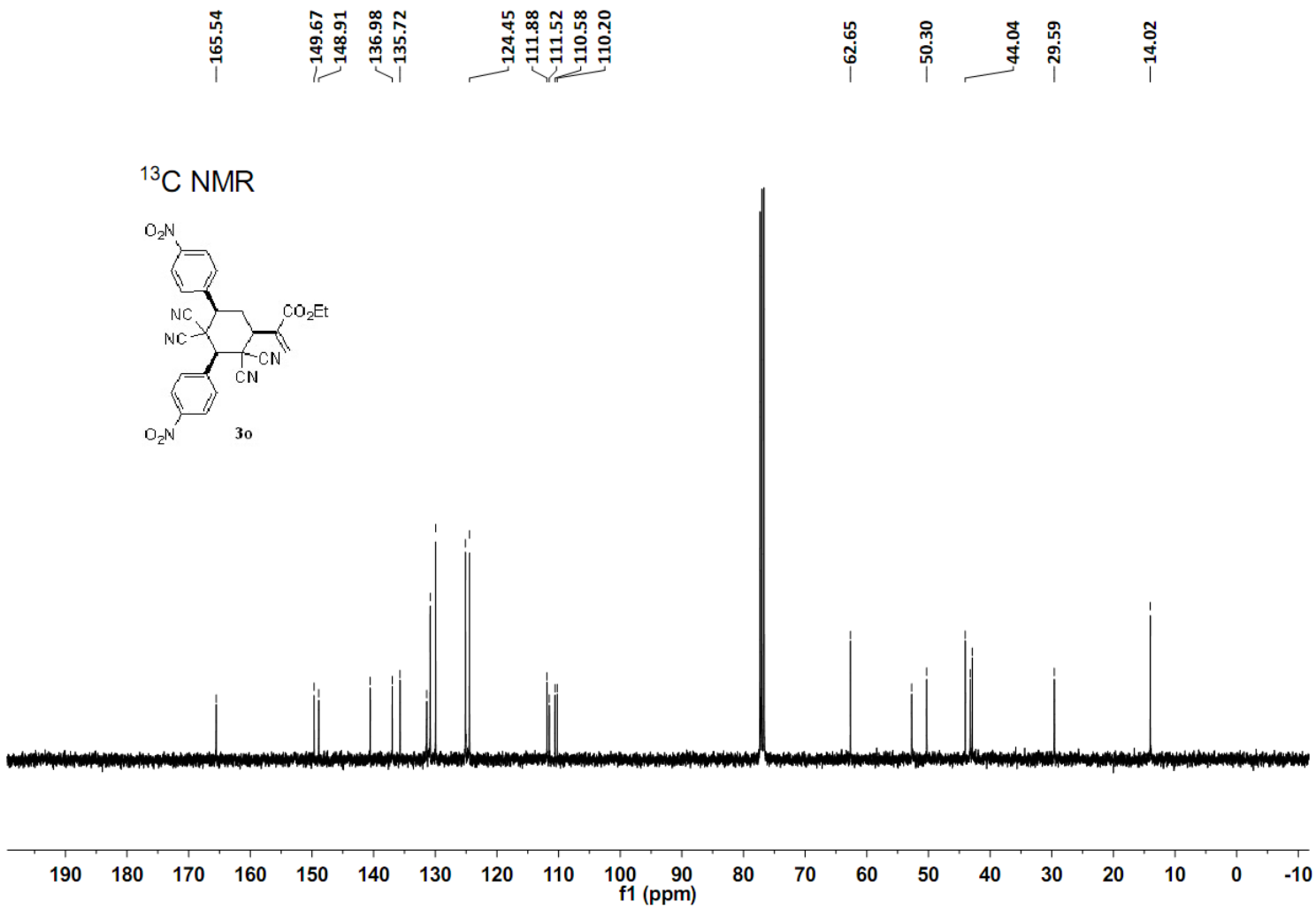


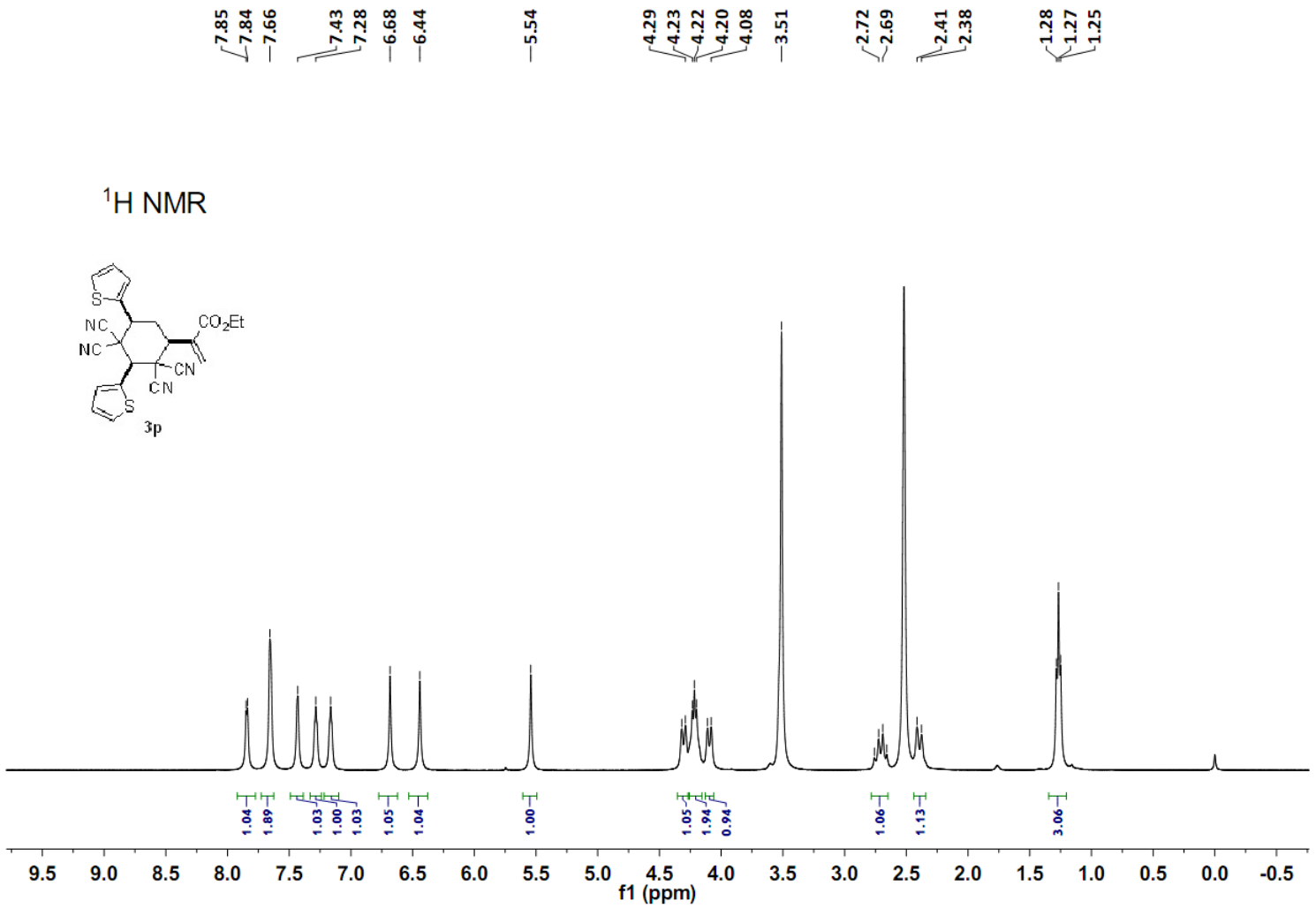


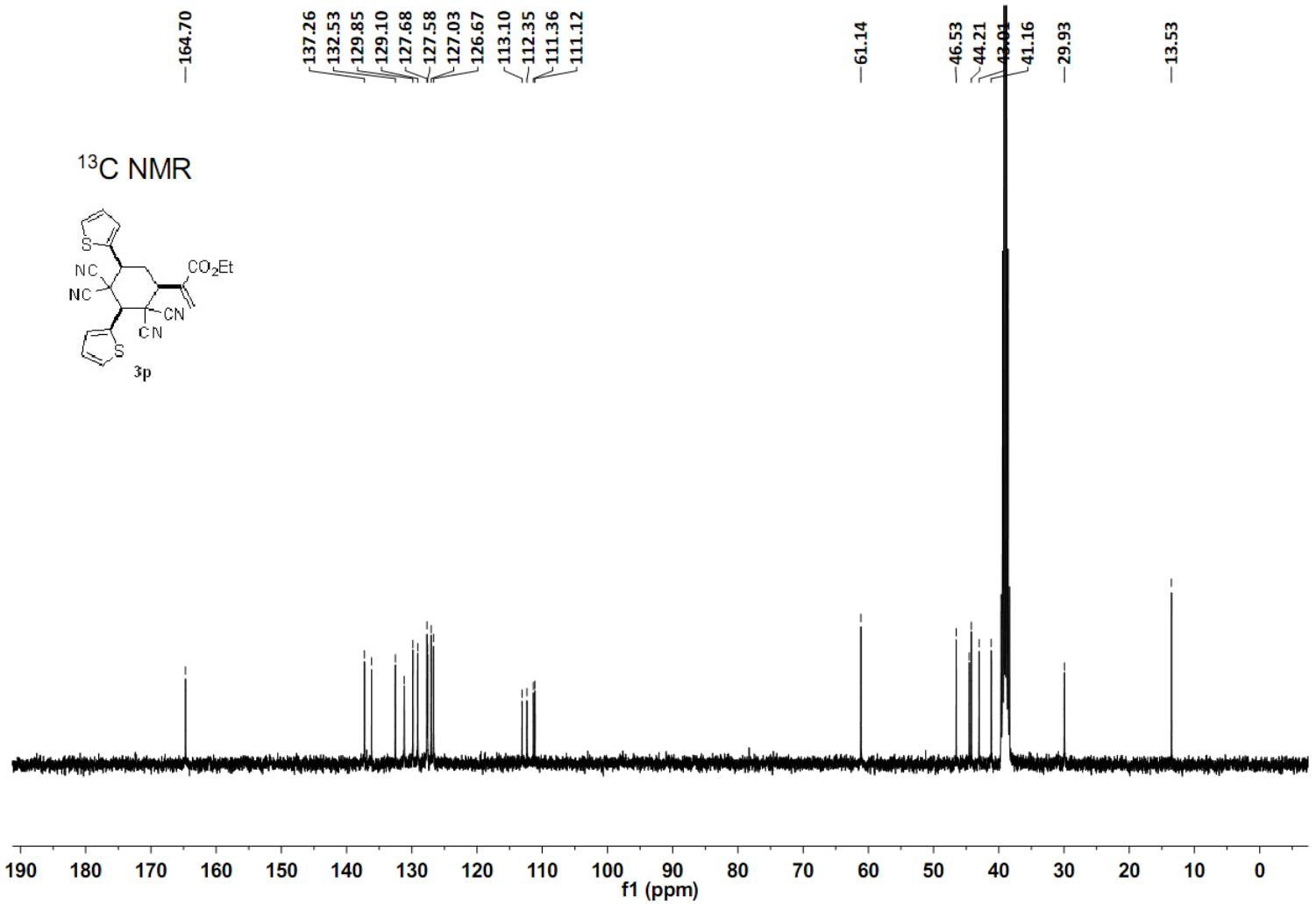

8.04
8.02
7.84
7.82
7.76
7.73
7.66
7.64
7.26
6.85
6.40
4.31
4.30
4.28
4.10
3.97
3.96
3.65
2.92
2.89
2.85
2.32
2.28
1.36
1.34
1.32
0.00
1H NMR
F3C
NC
NC
CO2Et
CN
CN
3n
F3C
2.03
2.01
1.95
2.03
0.98
0.99
2.08
1.00
0.96
0.98
1.01
0.97
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

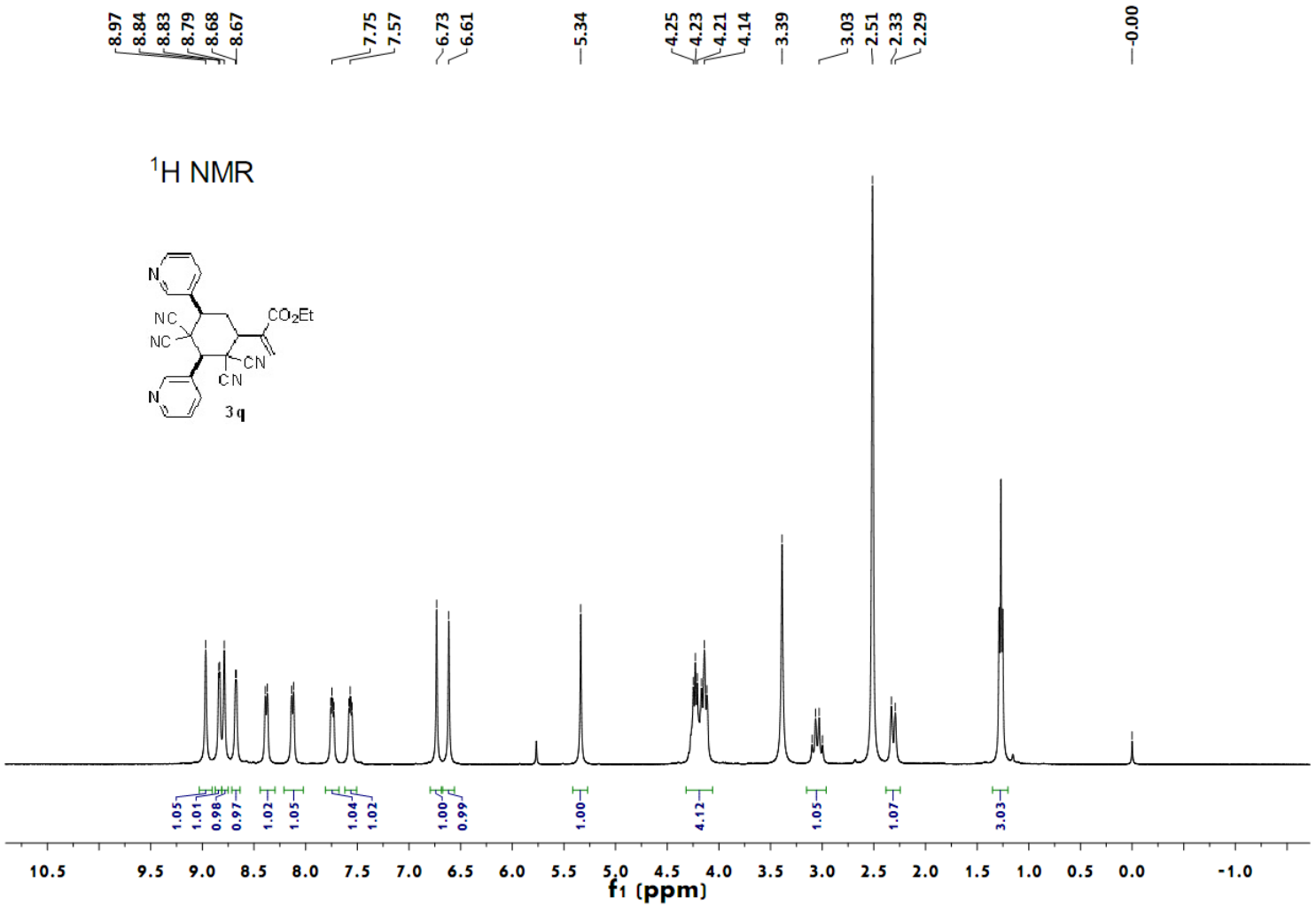


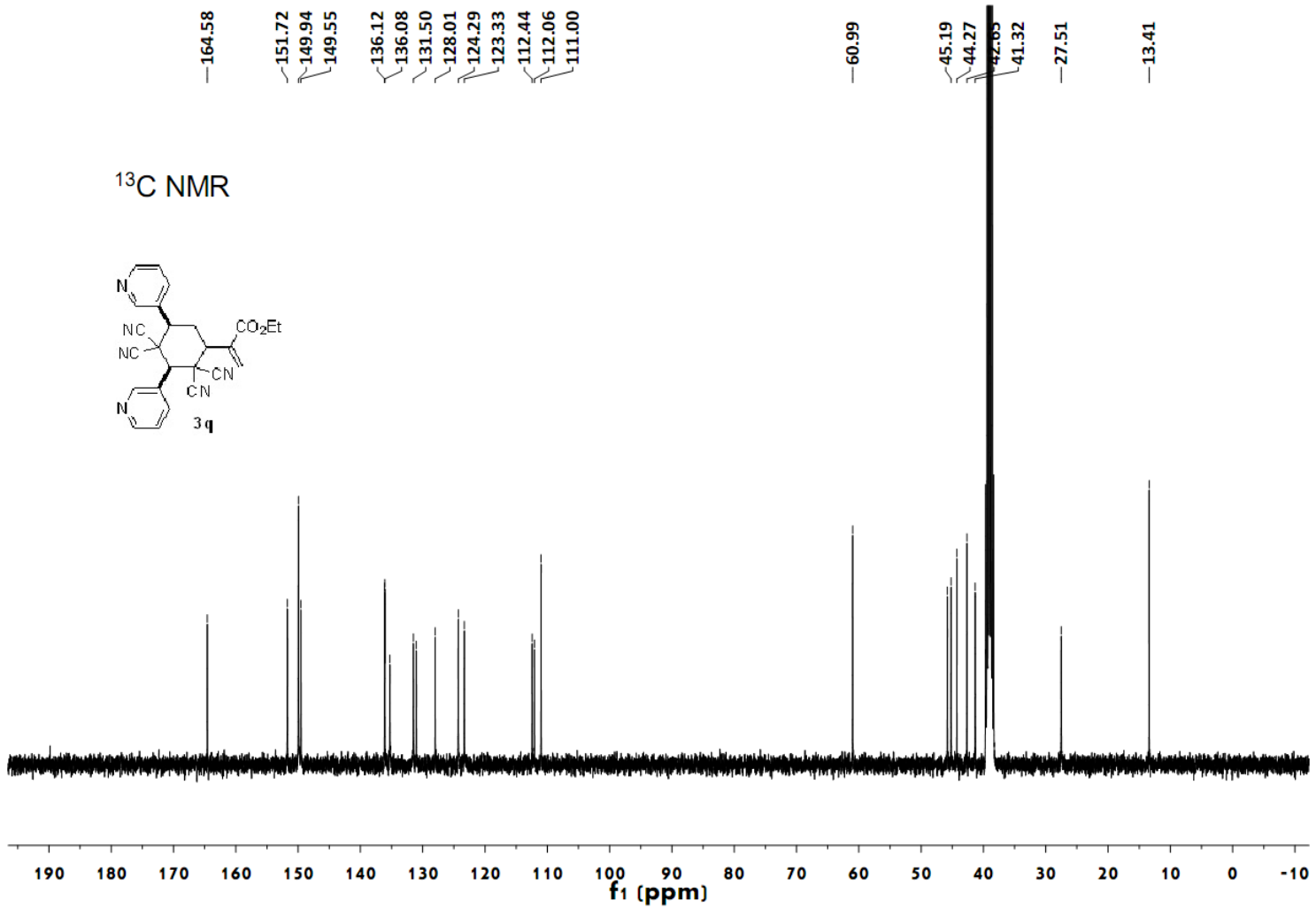

8.45
8.43
8.36
8.34
8.13
8.11
7.75
7.73
6.88
6.42
4.33
4.31
4.31
4.29
4.11
3.80
3.78
2.95
2.92
2.88
2.37
2.33
1.36
1.35
1.33
^{1}H NMR
O_2N
NC
NC
CO_2Et
CN
CN
O_2N
3o
2.08
2.14
2.09
2.04
1.00
0.97
2.22
0.96
0.90
1.01
1.09
0.99
2.98
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

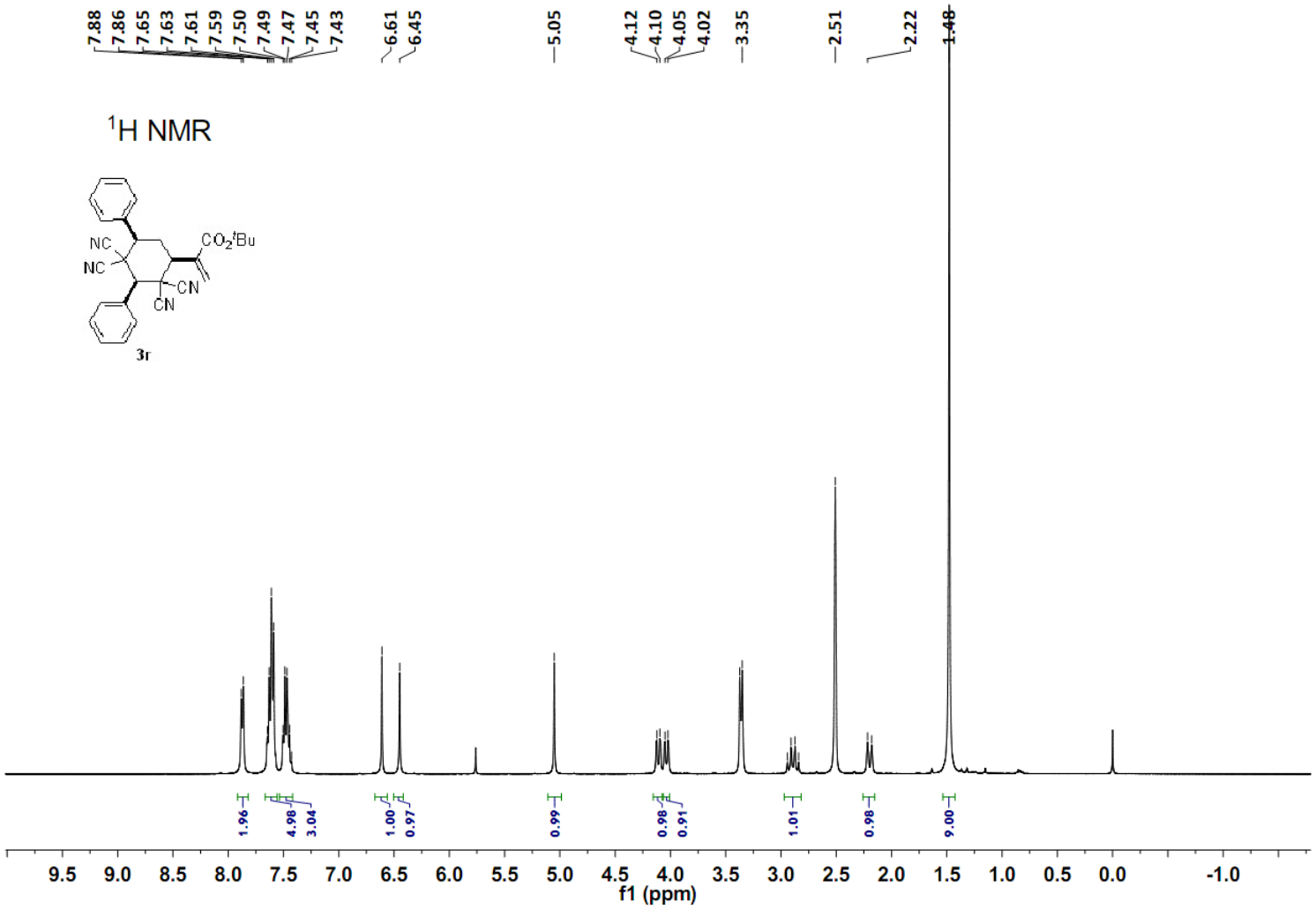


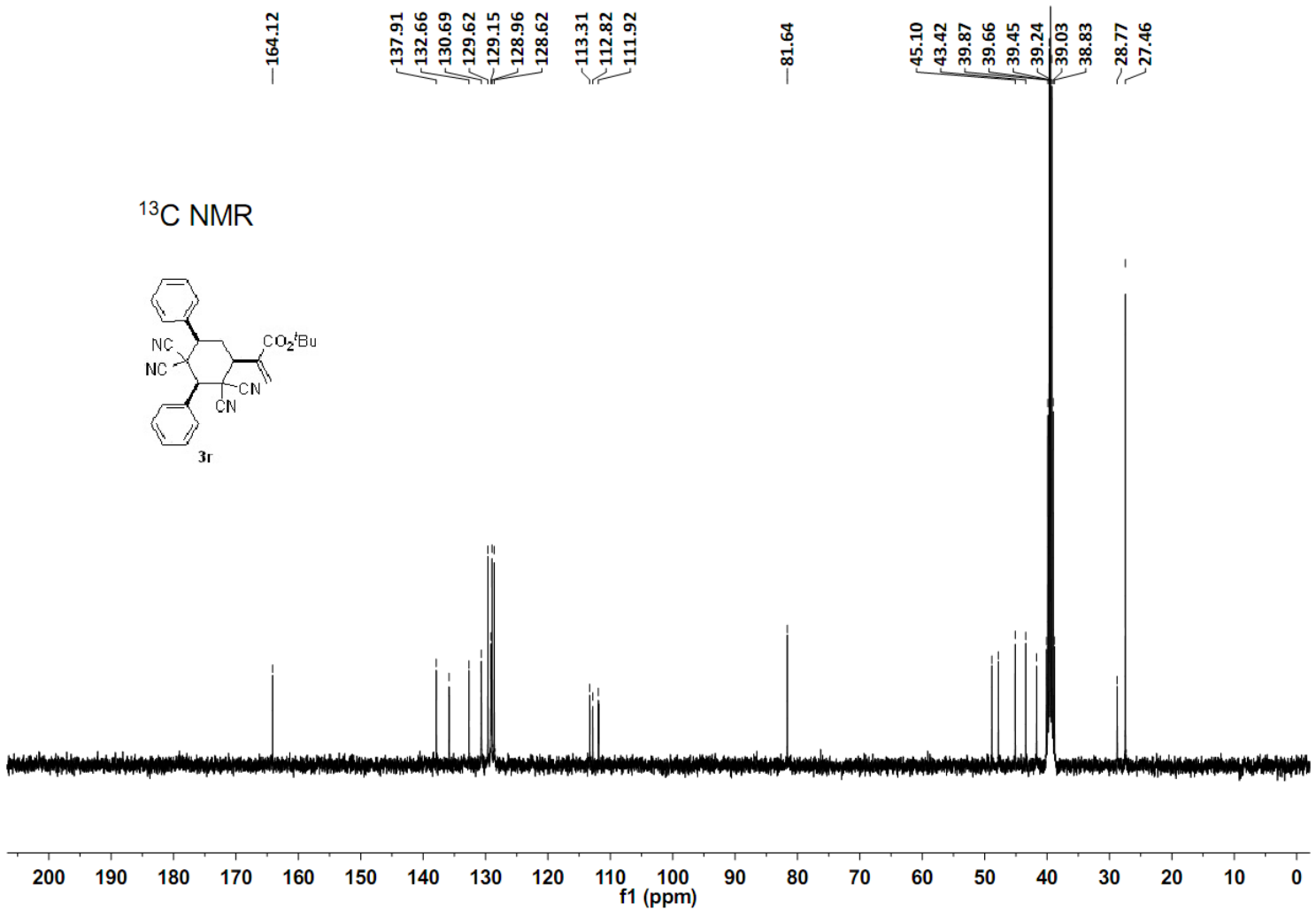


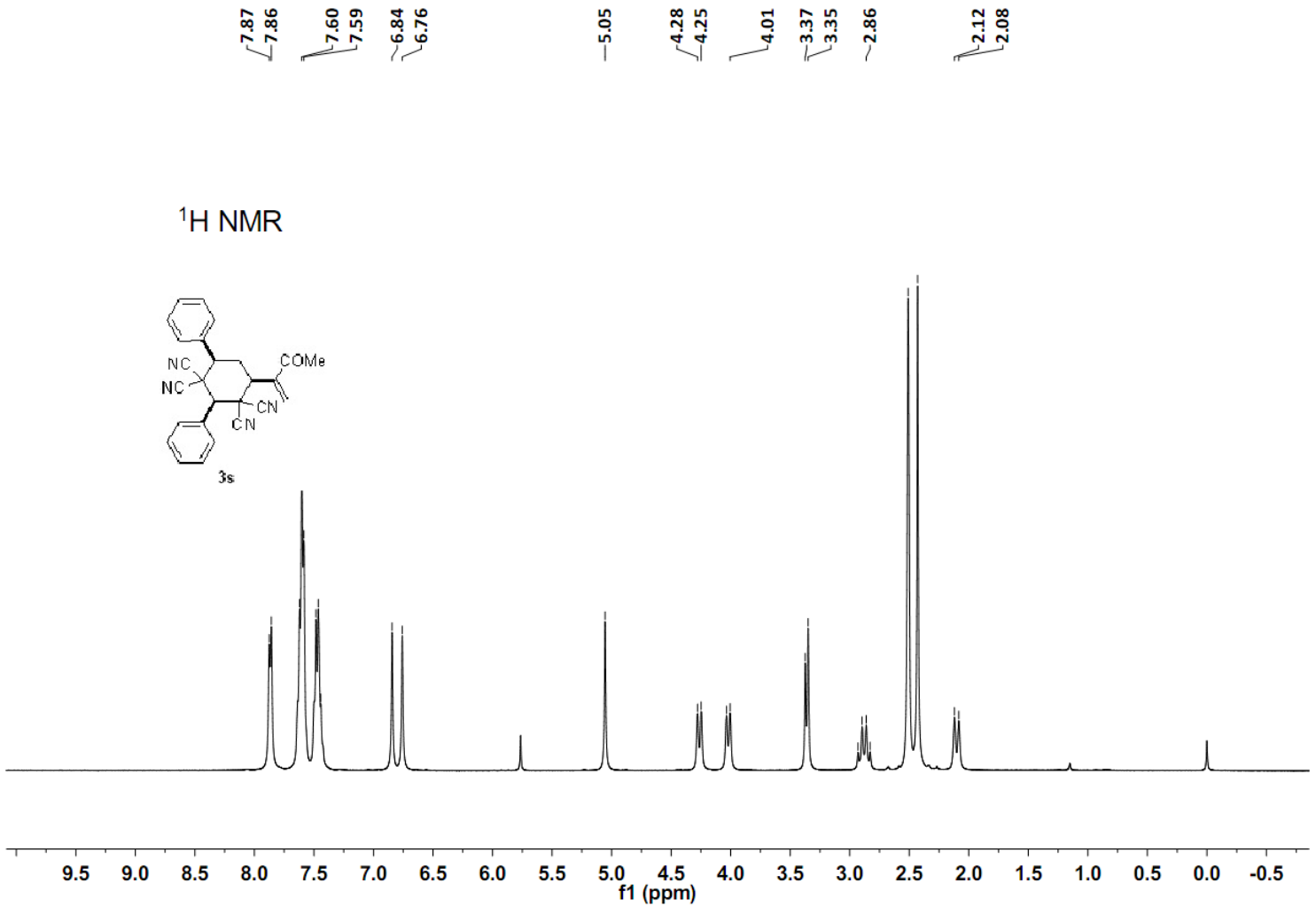


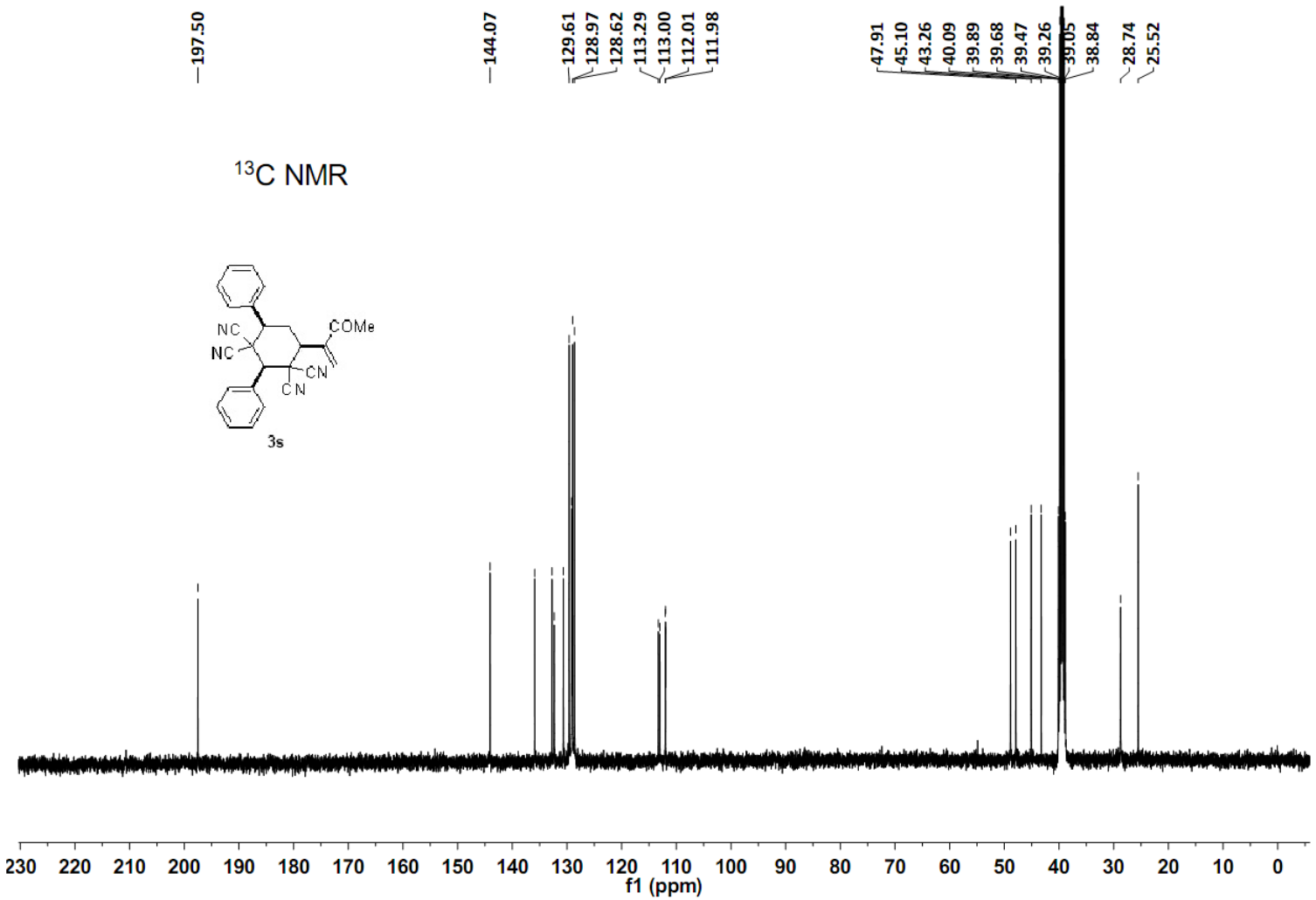

8.97
8.84
8.83
8.79
8.68
8.67
7.75
7.57
6.73
6.61
5.34
4.25
4.23
4.21
4.14
3.39
3.03
2.51
2.33
2.29
0.00
1H NMR
N
NC
NC
CO2Et
CN
CN
N
3q
1.05
1.01
0.98
0.97
1.02
1.05
1.04
1.02
1.00
0.99
1.00
4.12
1.05
1.07
3.03
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

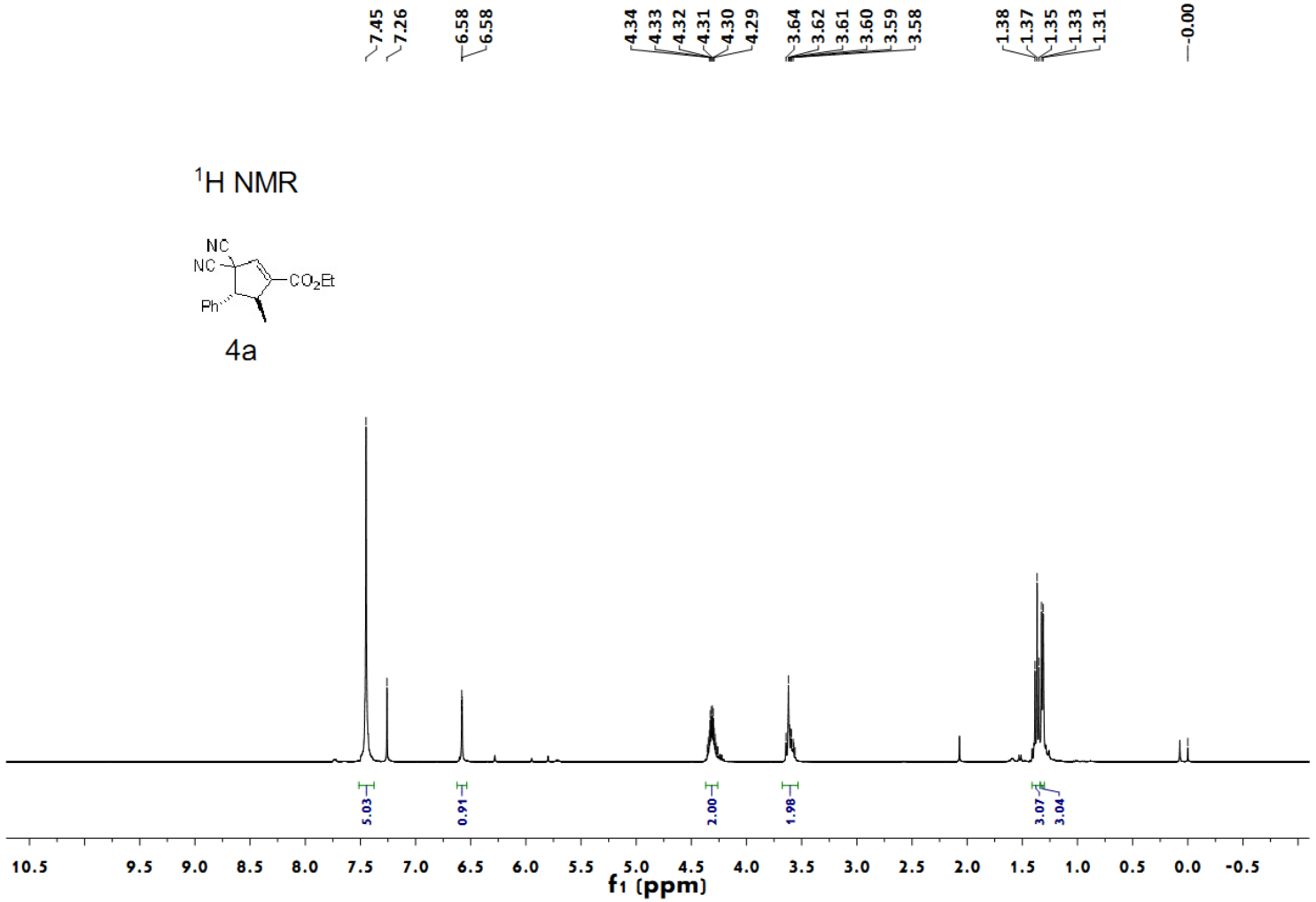


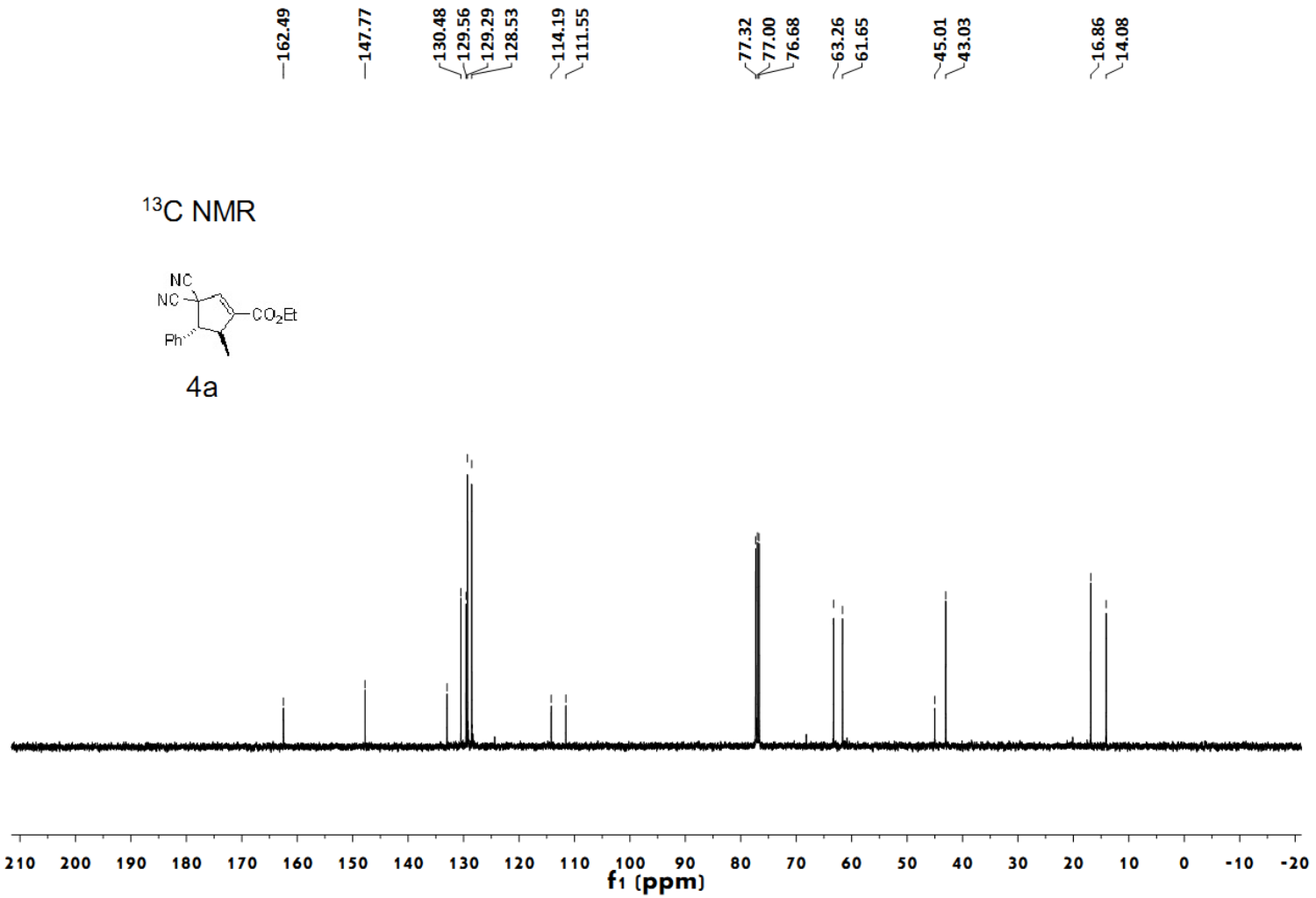

7.88
7.86
7.65
7.63
7.61
7.59
7.50
7.49
7.47
7.45
7.43
6.61
6.45
5.05
4.12
4.10
4.05
4.02
3.35
2.51
2.22
1.48
1H NMR
NC
NC
CO2tBu
CN
CN
3r
1.96
4.98
3.04
1.00
0.97
0.99
0.98
0.91
1.01
0.98
9.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0
f1 (ppm)

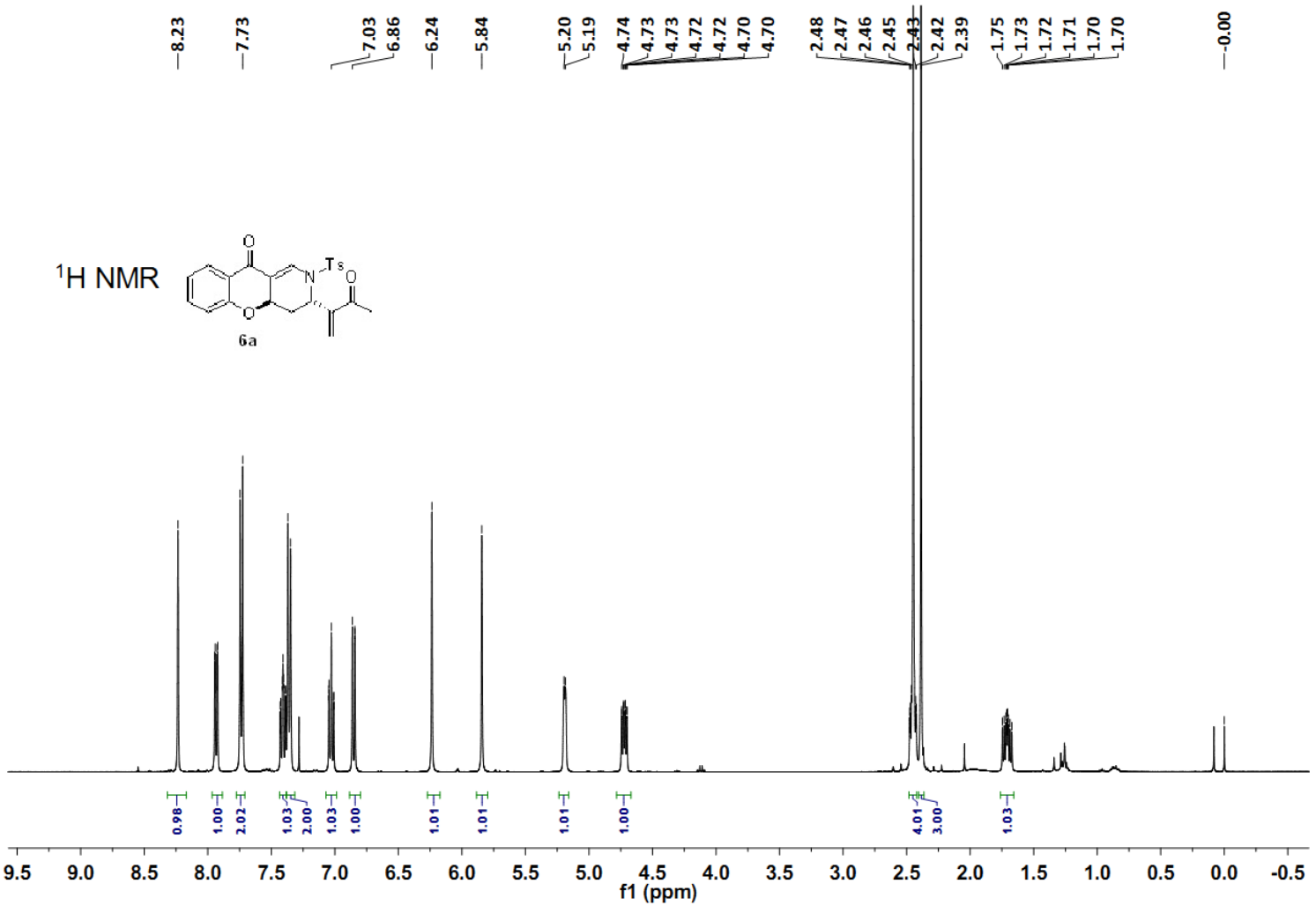


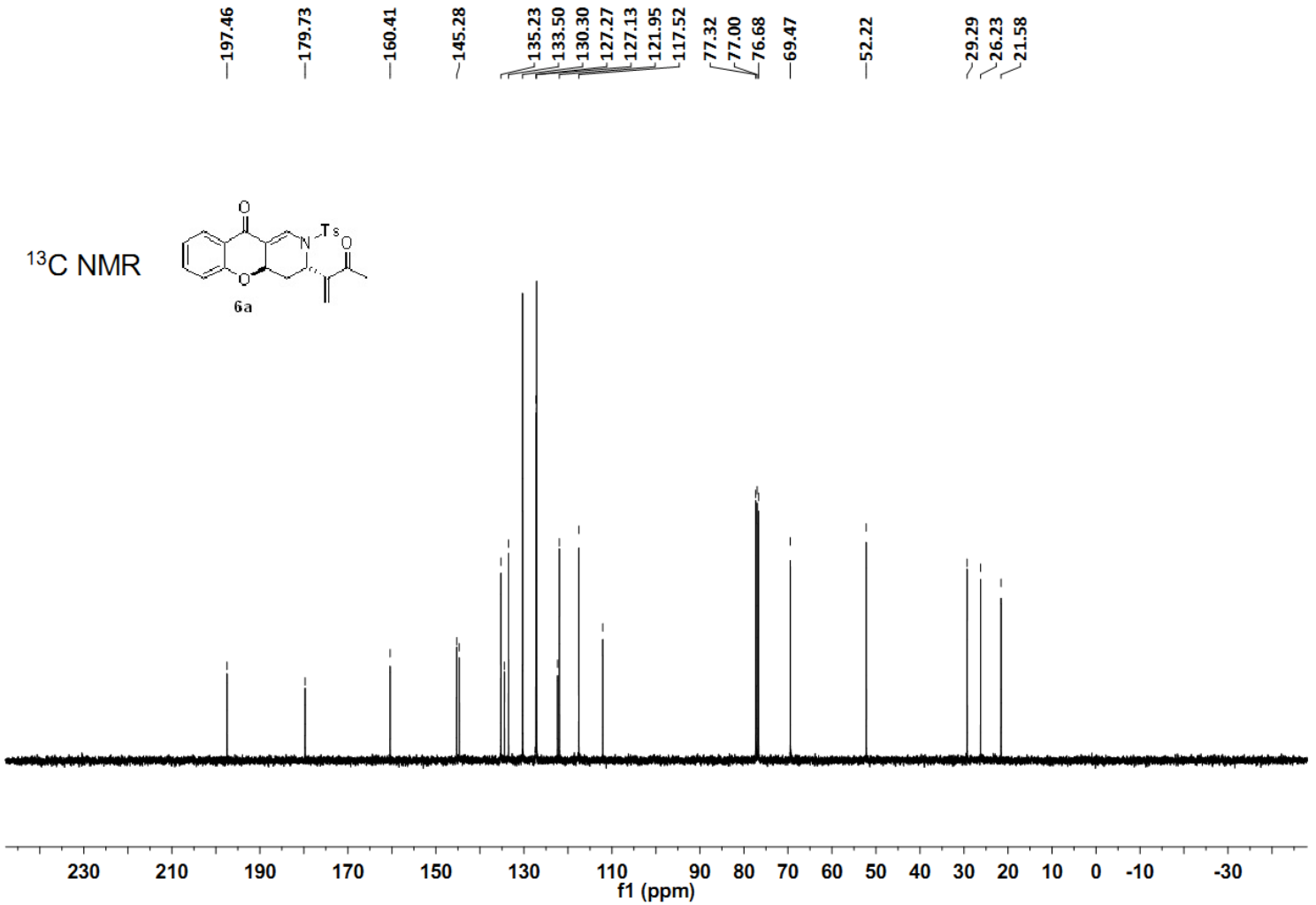




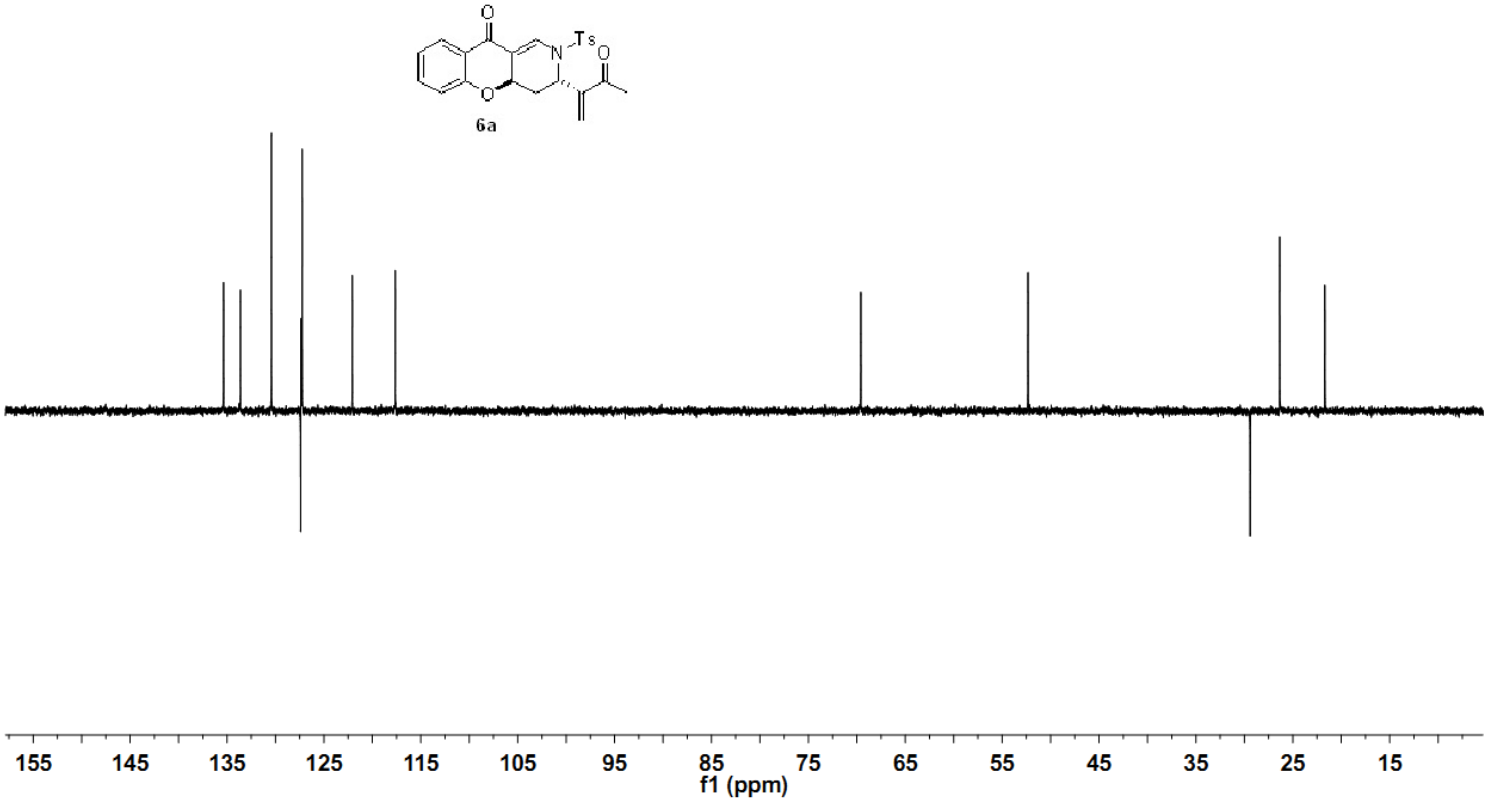

7.45
7.26
6.58
6.58
4.34
4.33
4.32
4.31
4.30
4.29
3.64
3.62
3.61
3.60
3.59
3.58
1.38
1.37
1.35
1.33
1.31
0.00
1H NMR
NC
NC
CO2Et
Ph
4a
5.03
0.91
2.00
1.98
3.07
3.04
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

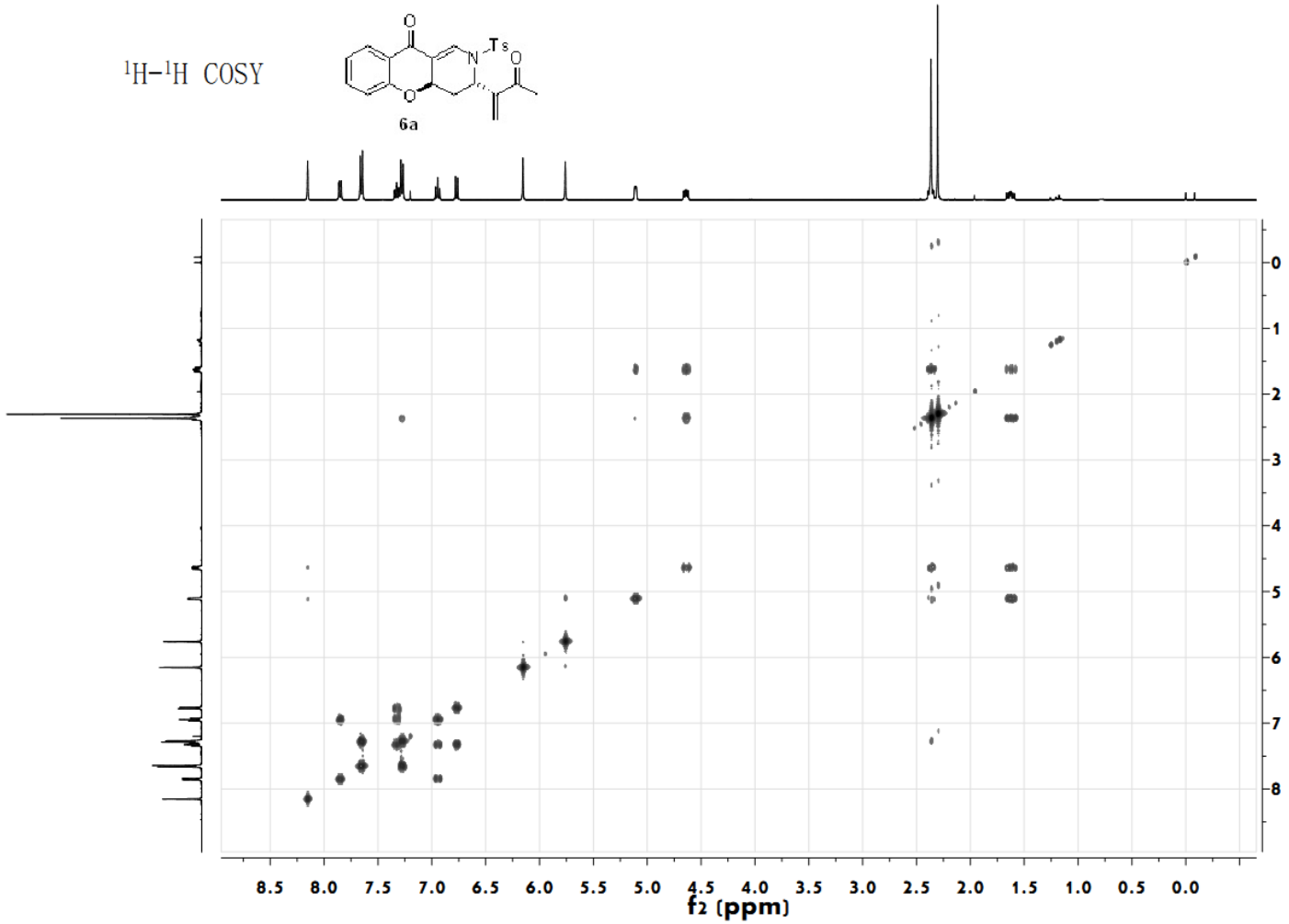


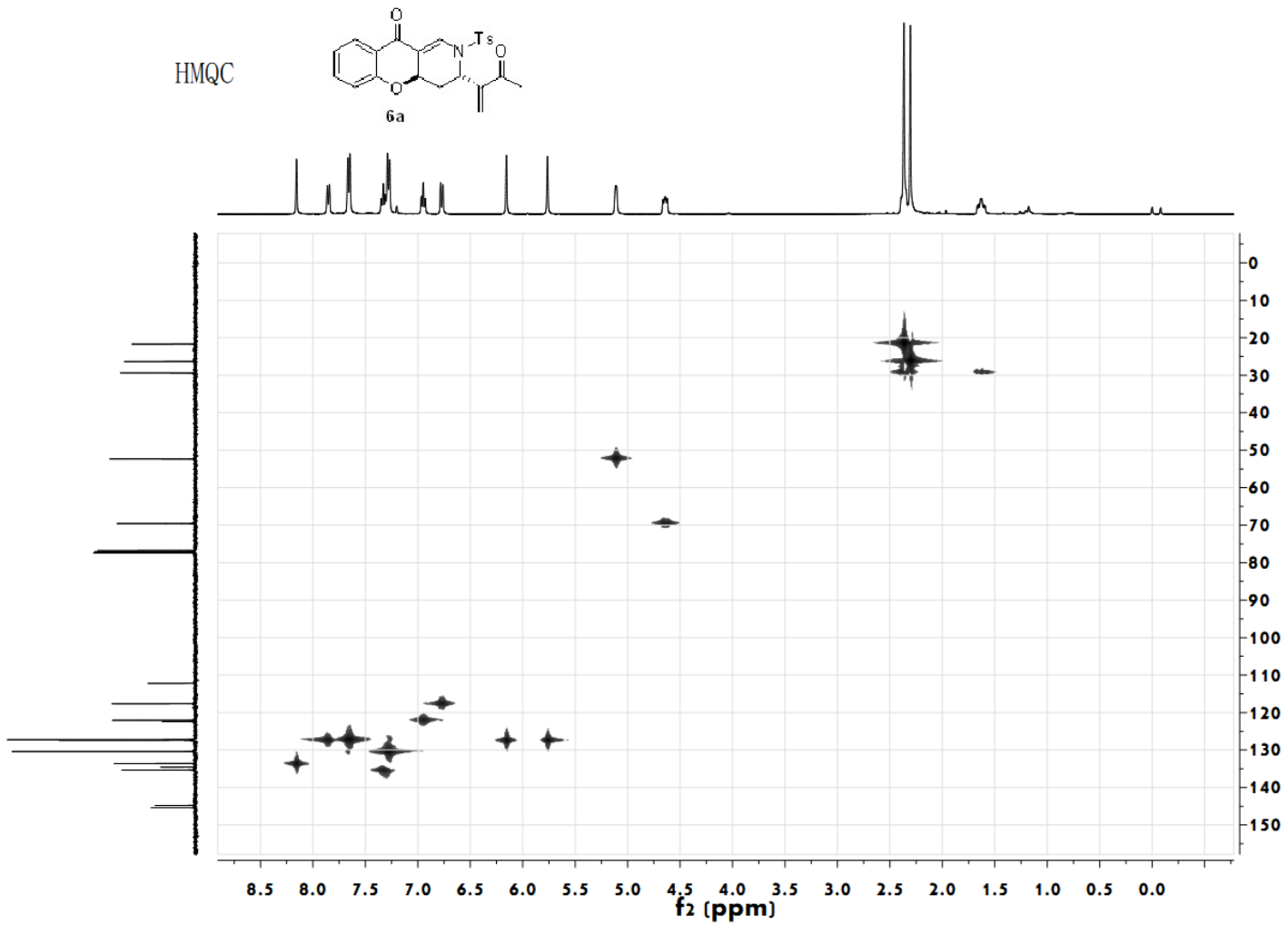


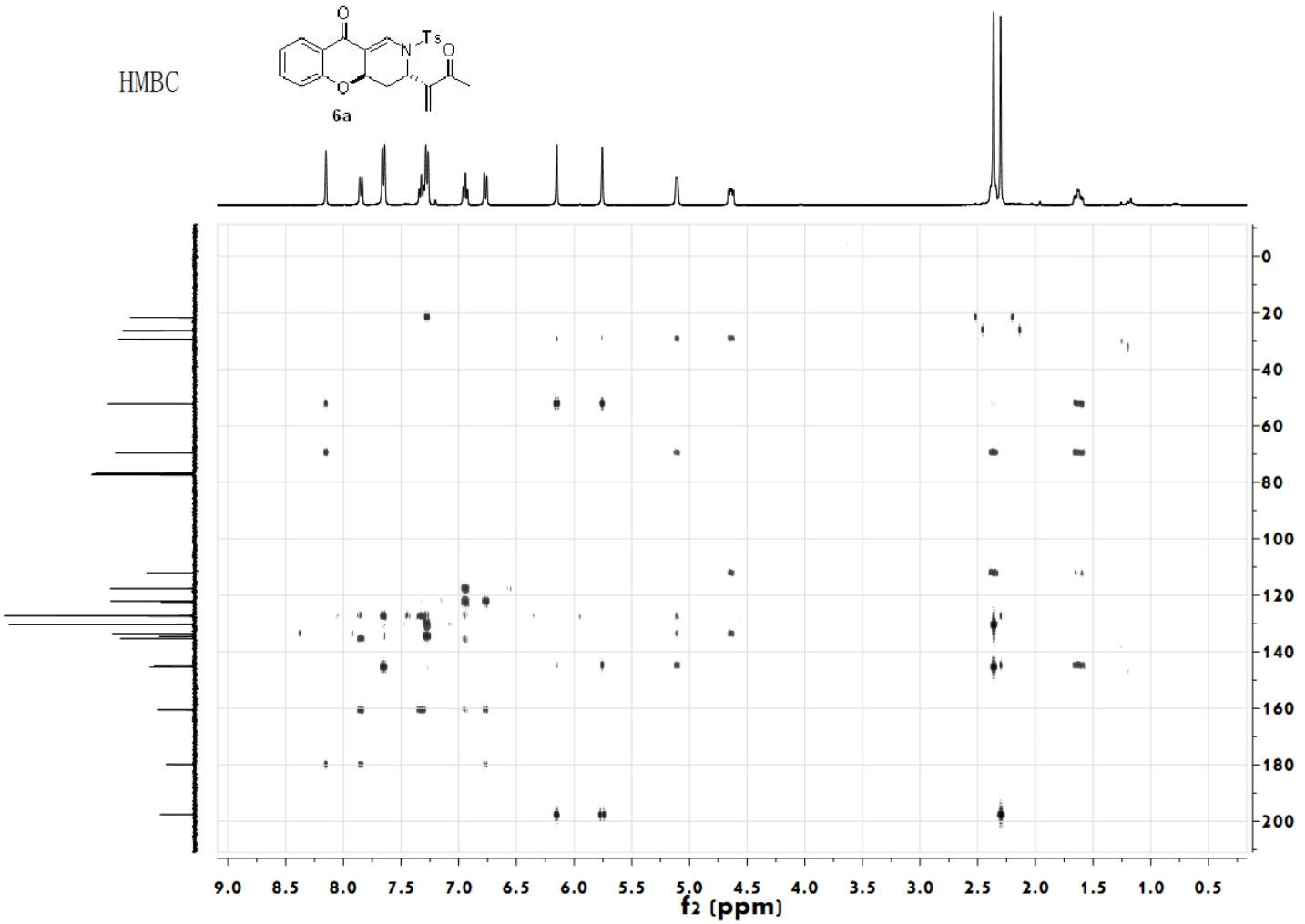


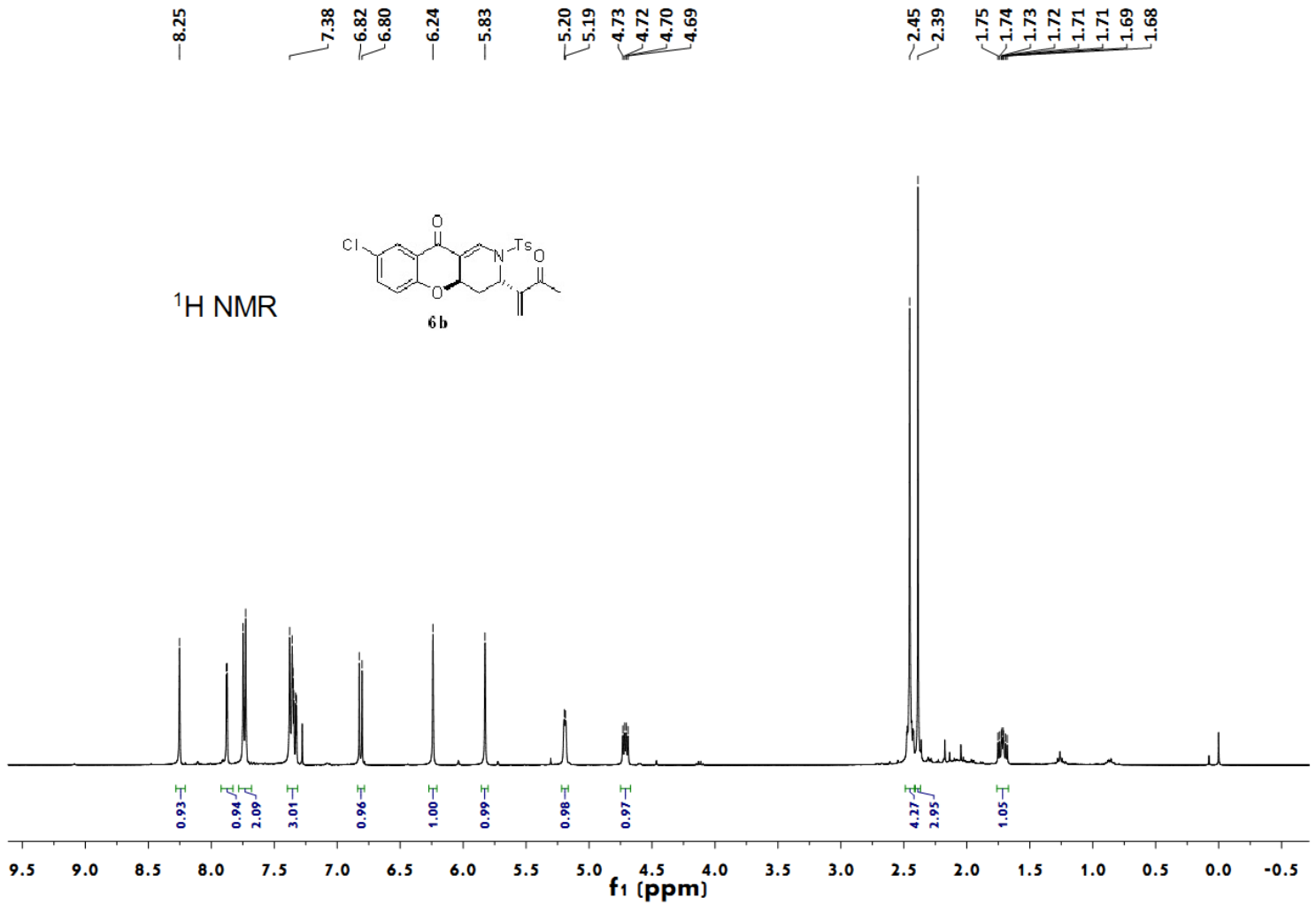
Dept 135 NMR

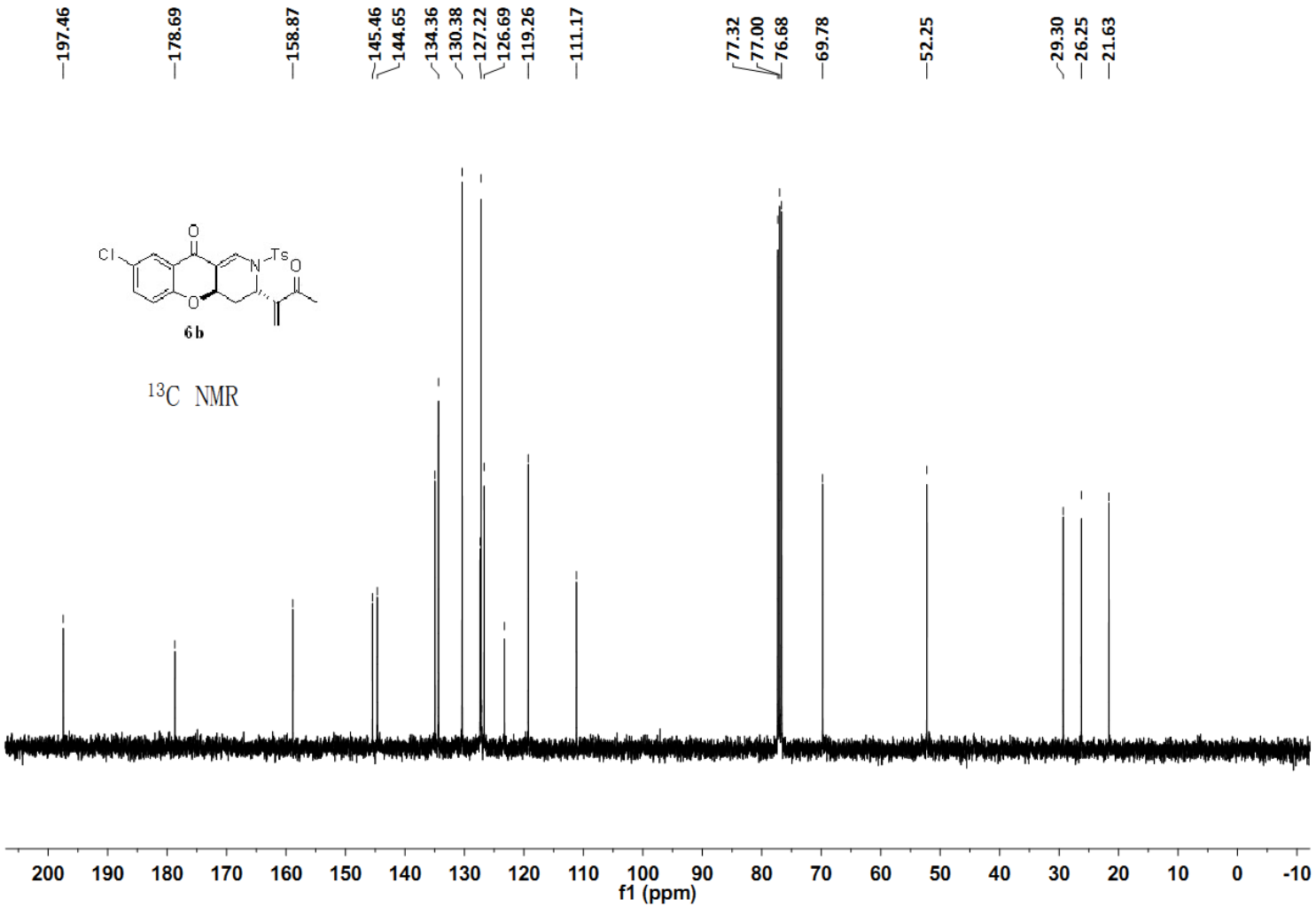


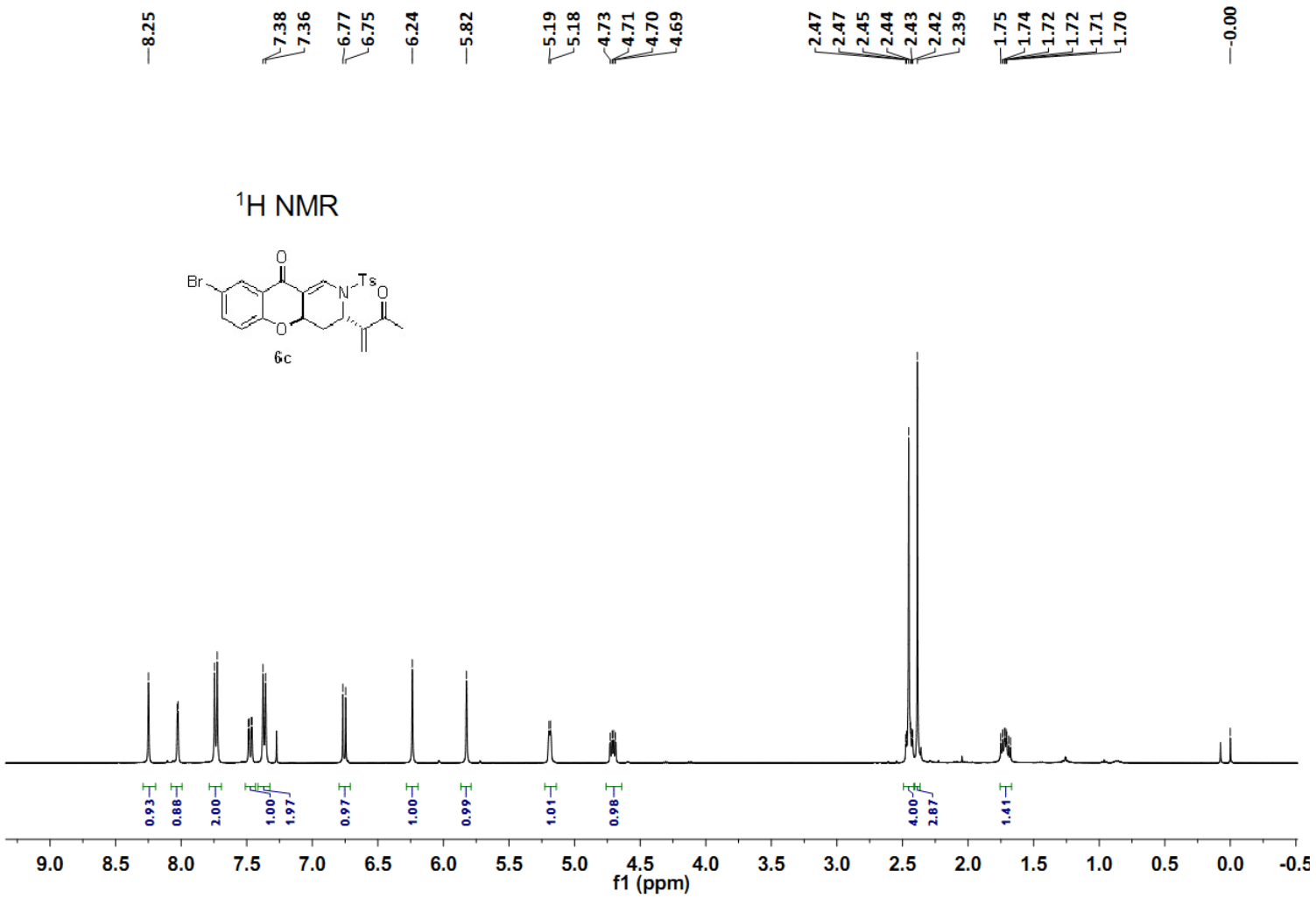


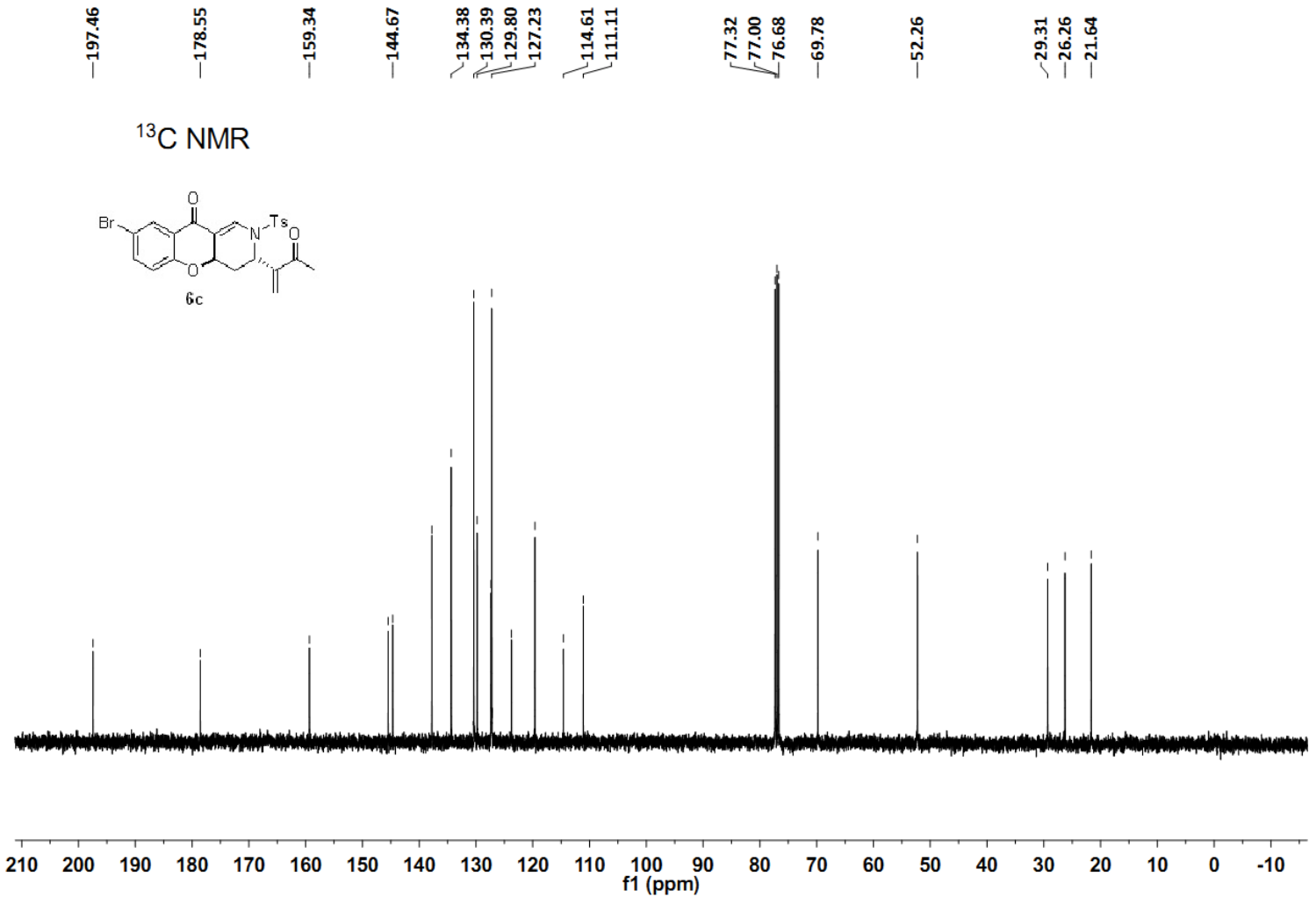


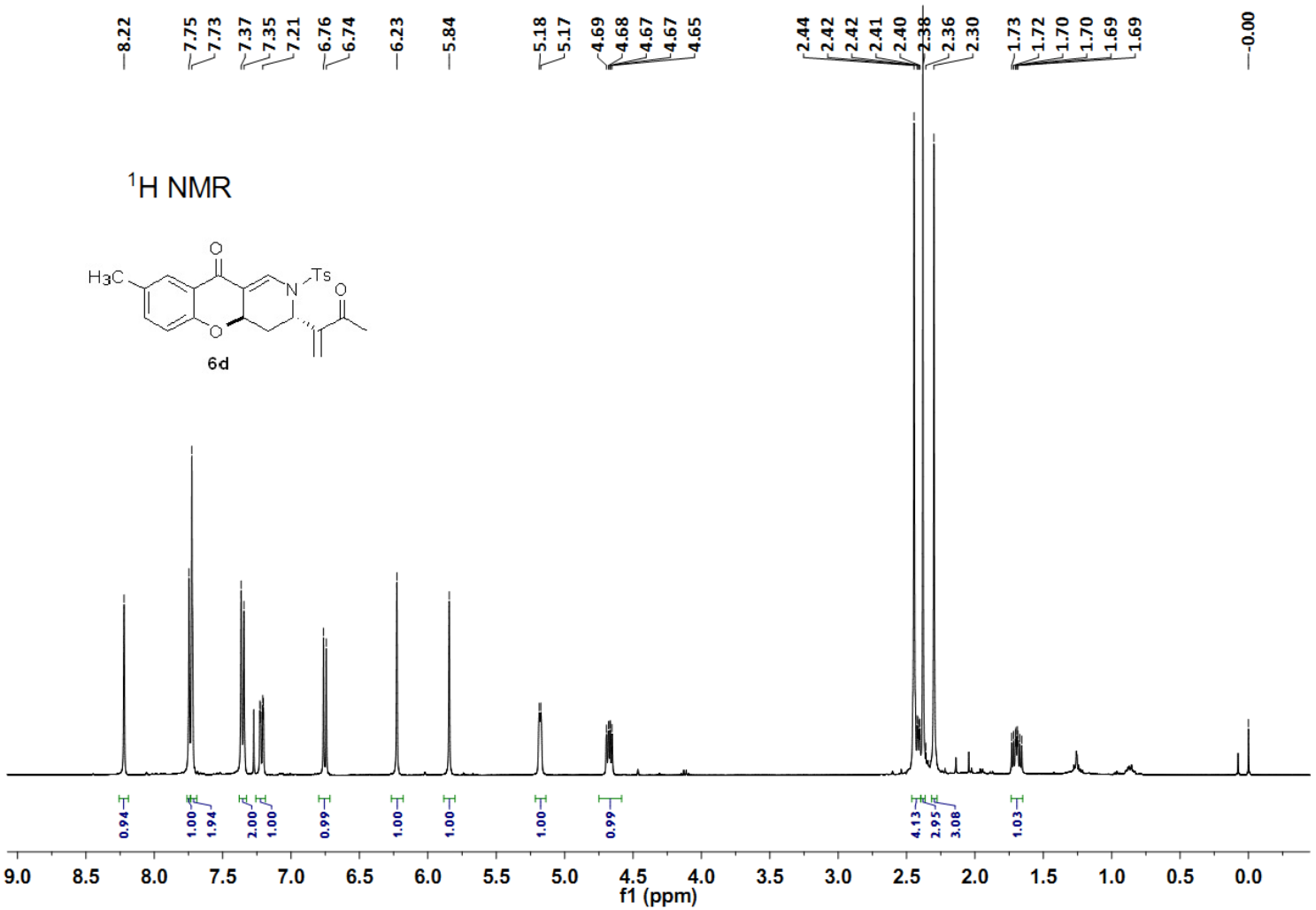

HMBC
6a
Ts
N
O
O
O
0
20
40
60
80
100
120
140
160
180
200
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)

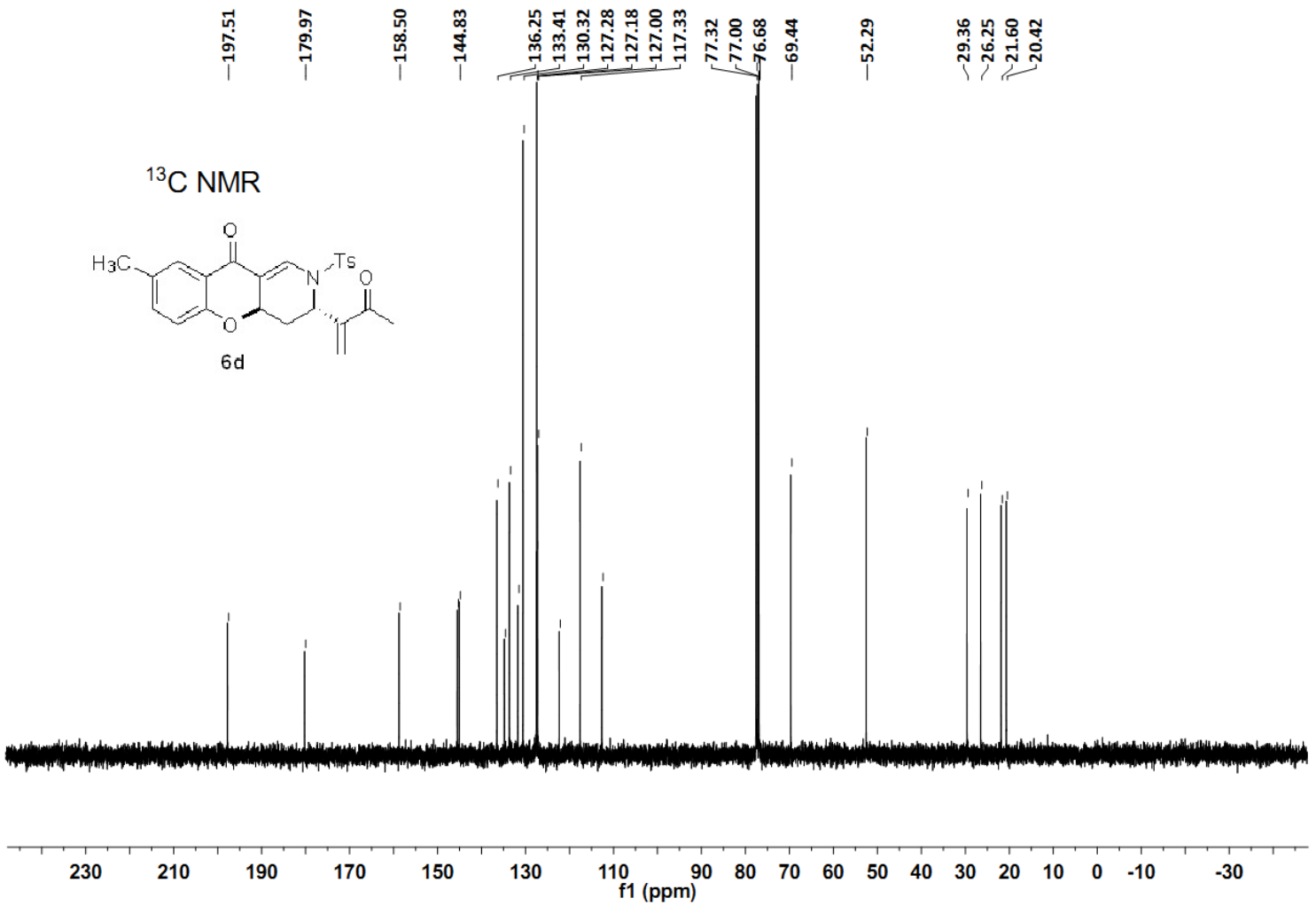

8.25
7.38
6.82
6.80
6.24
5.83
5.20
5.19
4.73
4.72
4.70
4.69
2.45
2.39
1.75
1.74
1.73
1.72
1.71
1.71
1.69
1.68
1H NMR
Cl
O
N
Ts
O
O
6b
0.93
0.94
2.09
3.01
0.96
1.00
0.99
0.98
0.97
4.27
2.95
1.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

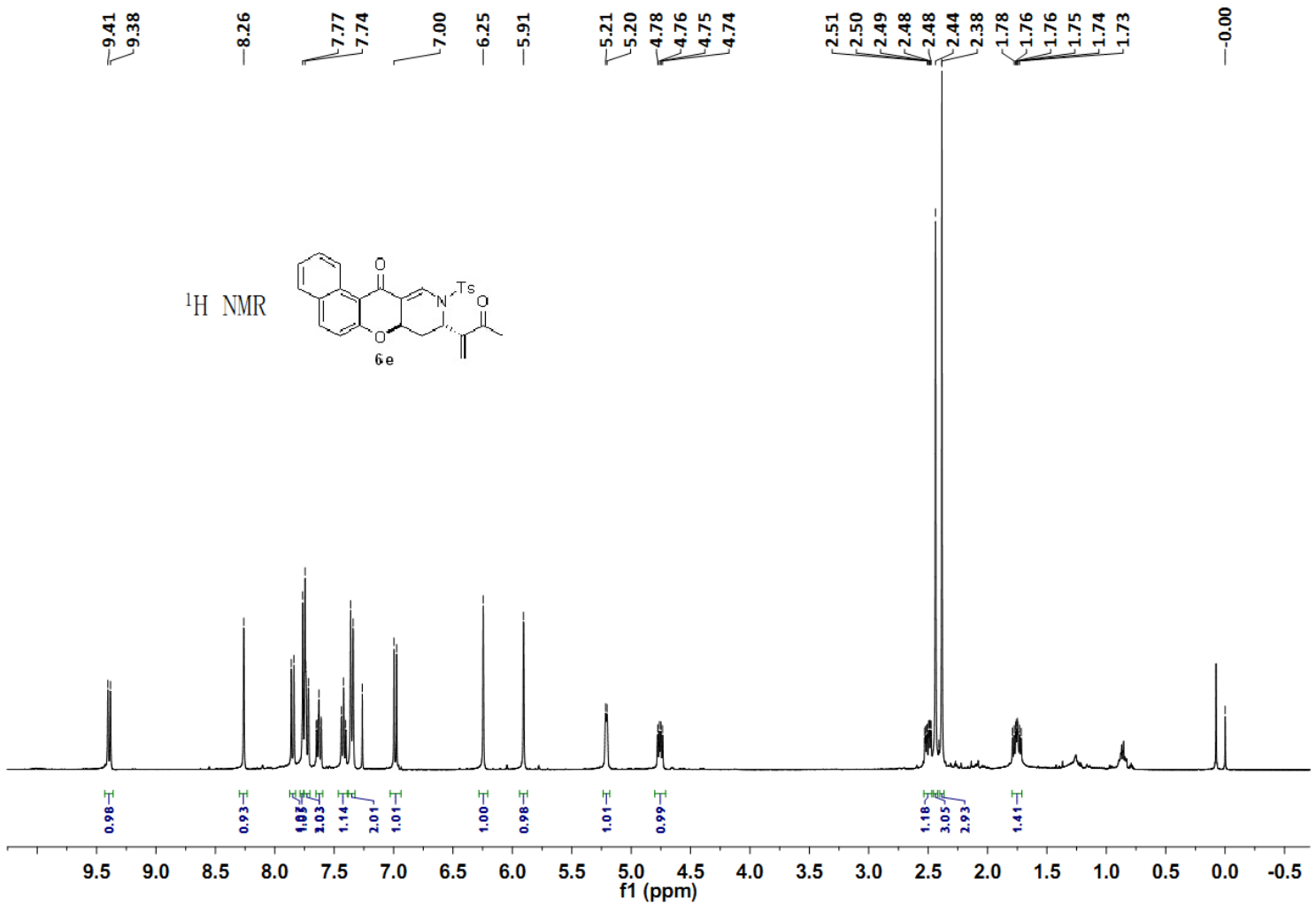


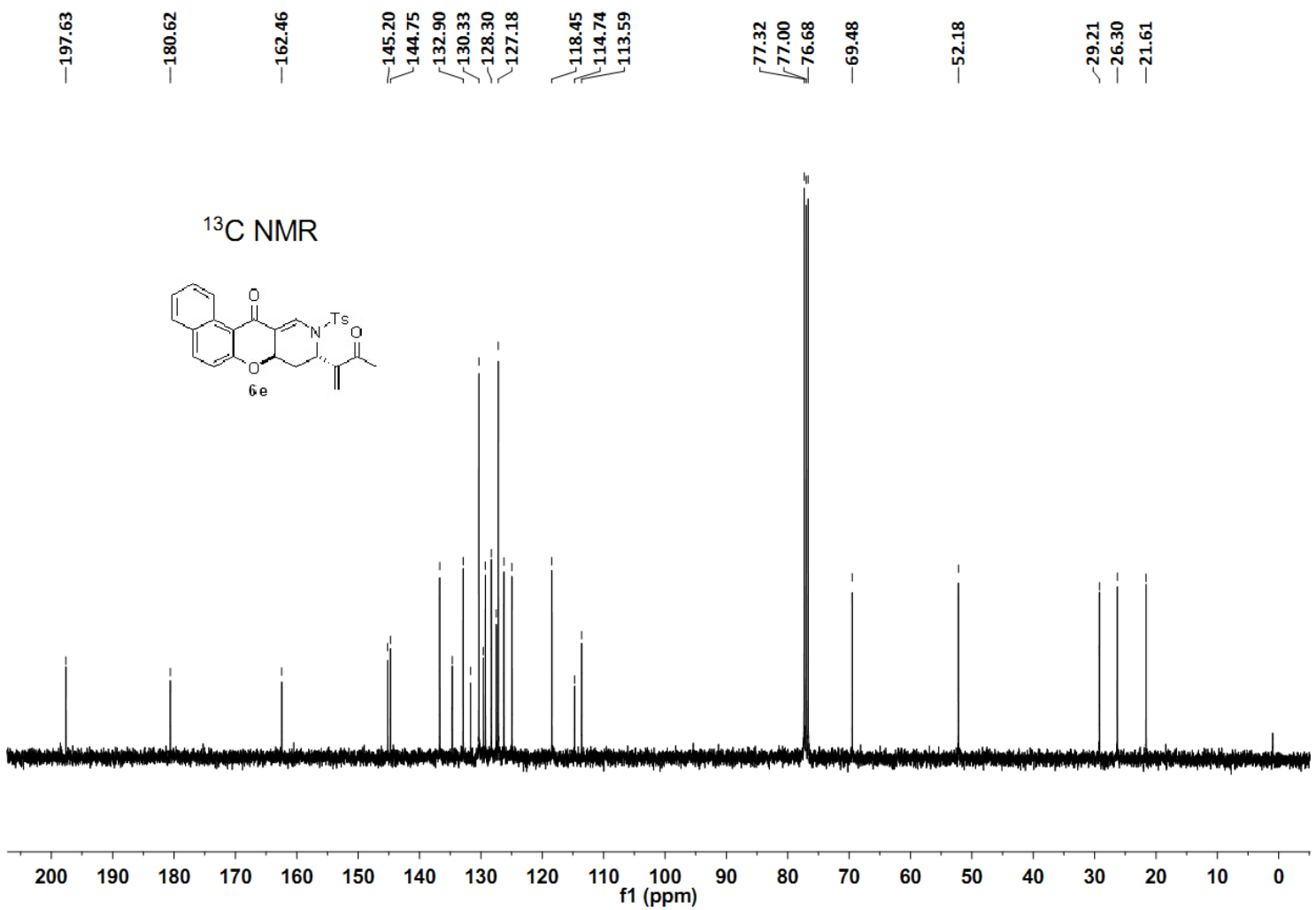


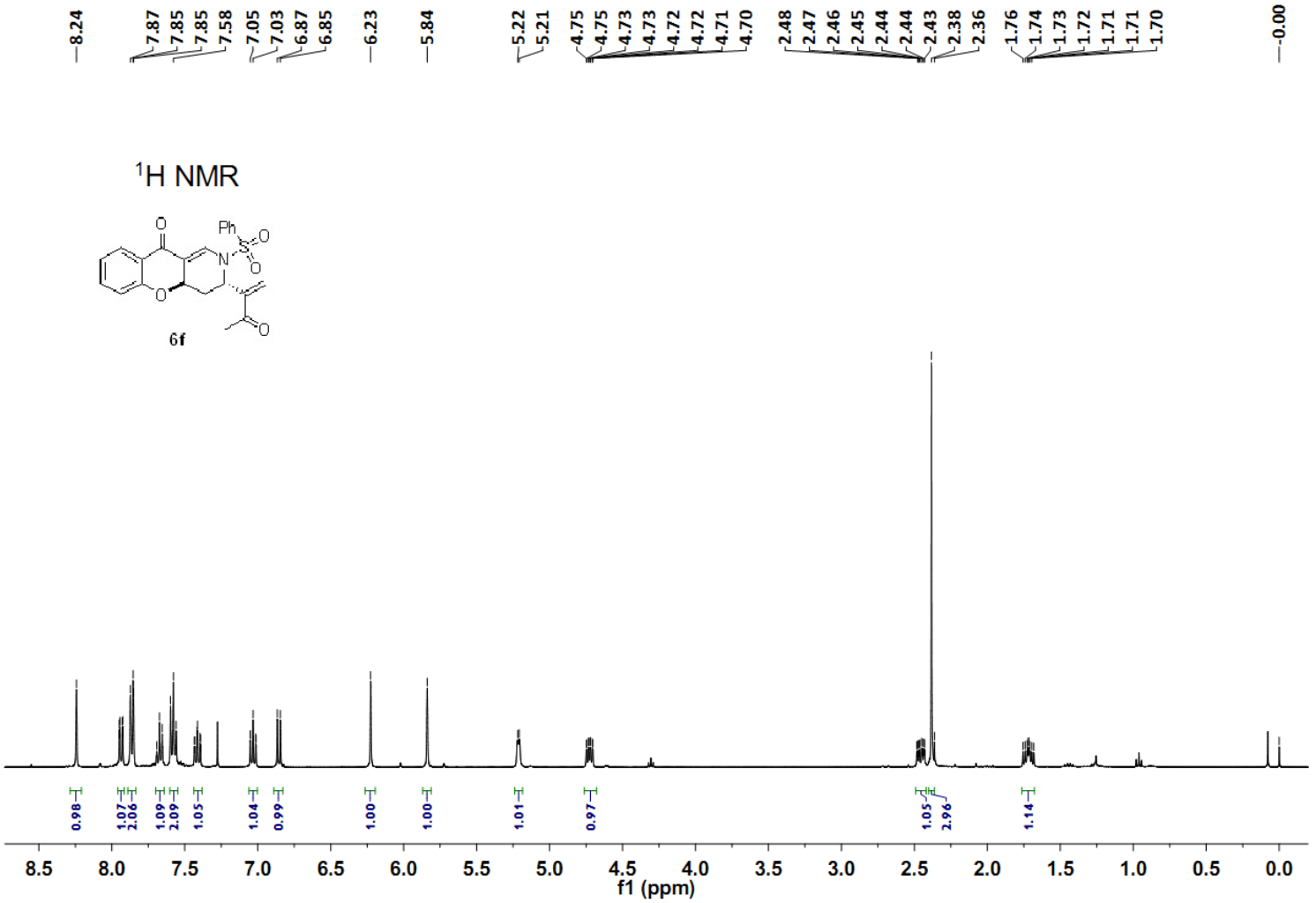


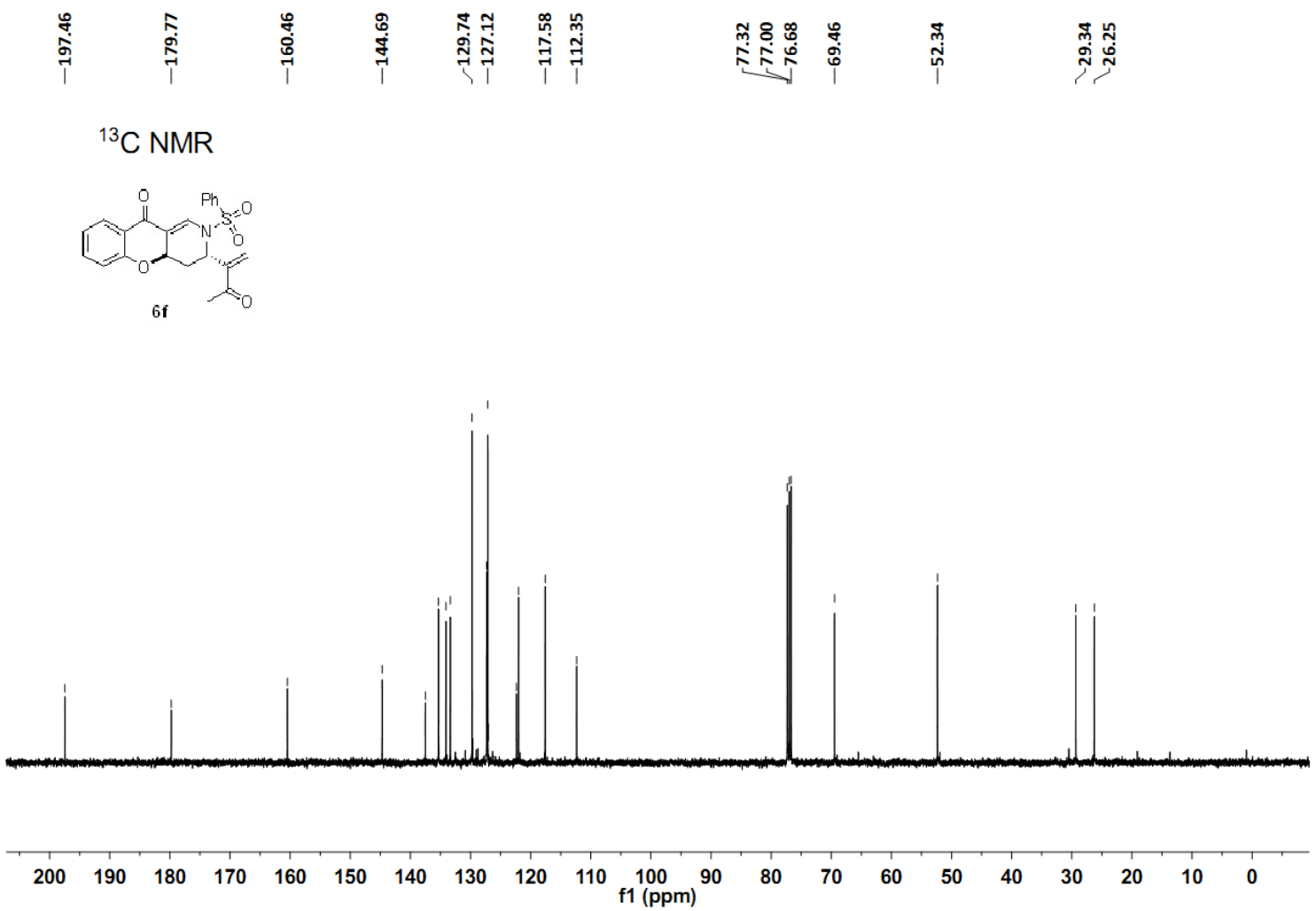


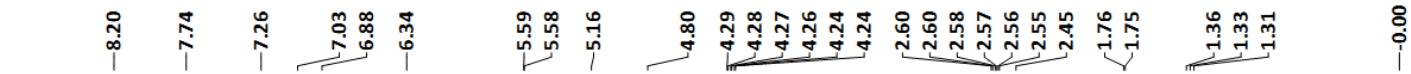




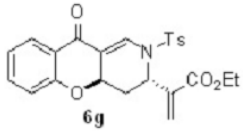

197.63
180.62
162.46
145.20
144.75
132.90
130.33
128.30
127.18
118.45
114.74
113.59
77.32
77.00
76.68
69.48
52.18
29.21
26.30
21.61
13C NMR
Ts
6e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



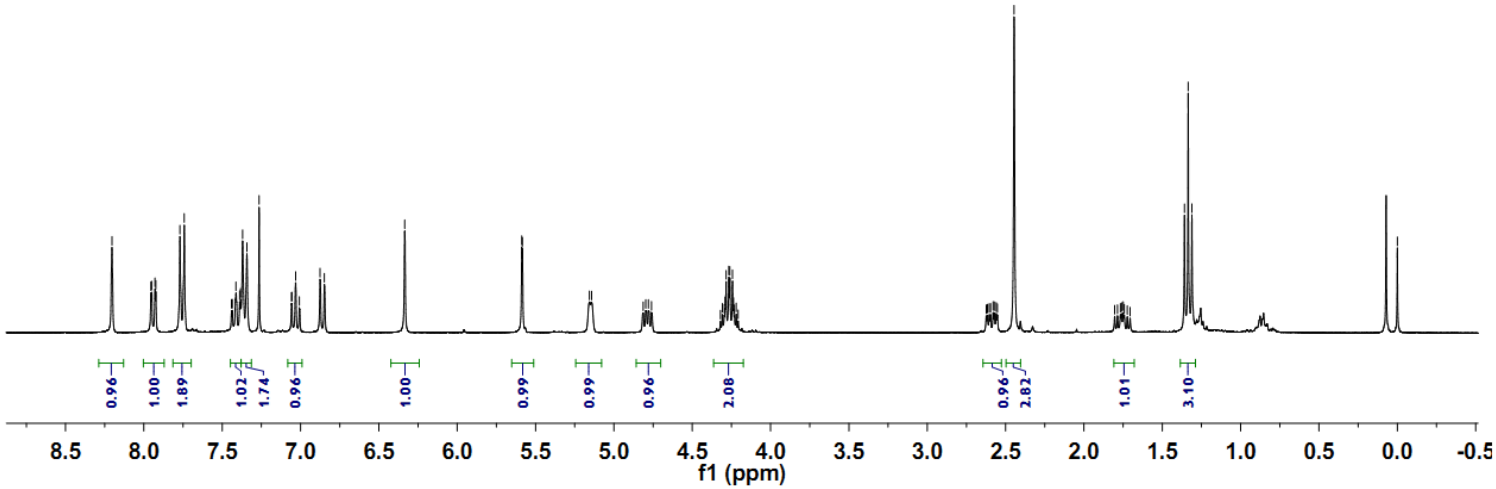


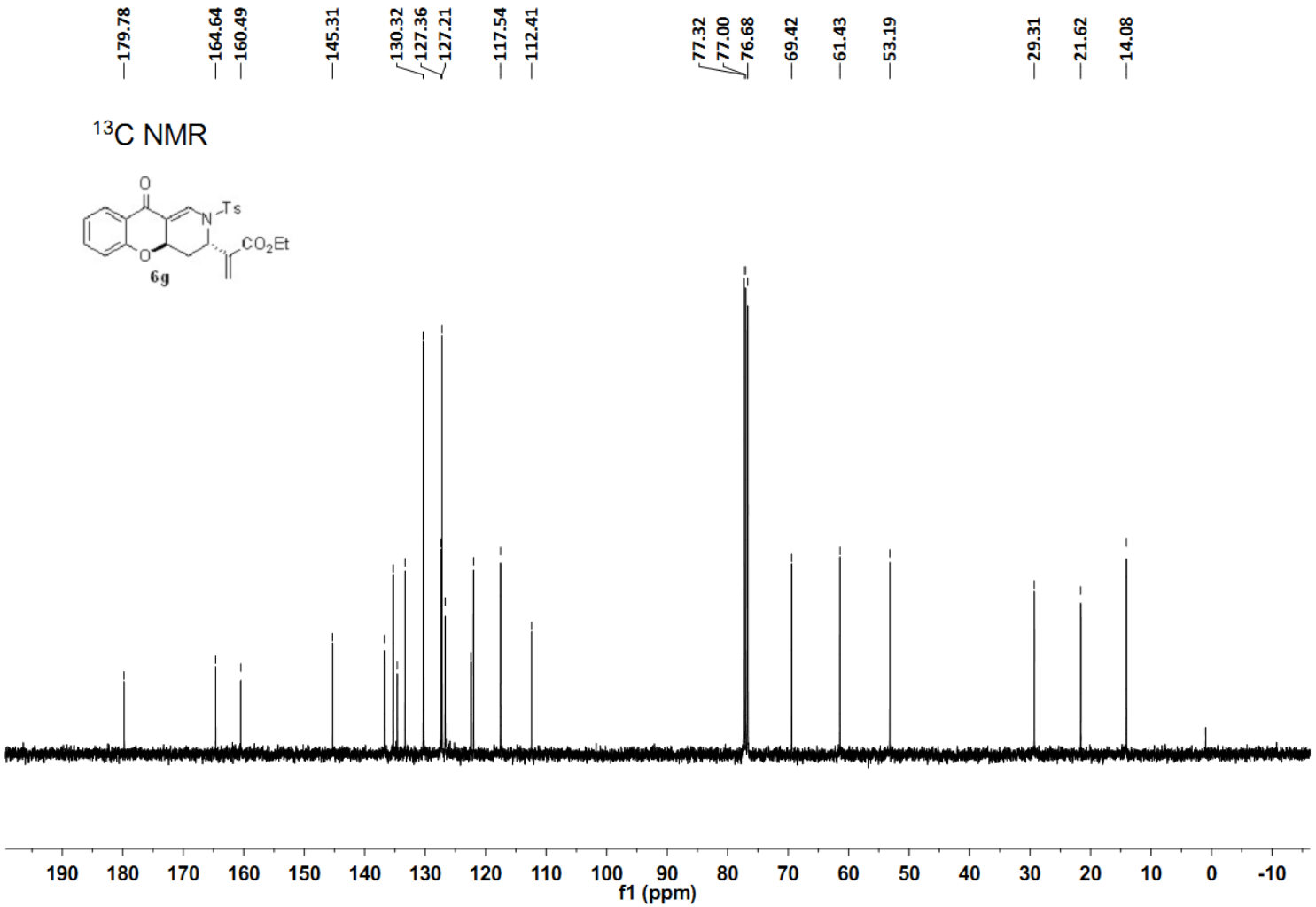

8.20
7.74
7.26
7.03
6.88
6.34
5.59
5.58
5.16
4.80
4.29
4.28
4.27
4.26
4.24
4.24
2.60
2.60
2.58
2.57
2.56
2.55
2.45
1.76
1.75
1.36
1.33
1.31
0.00

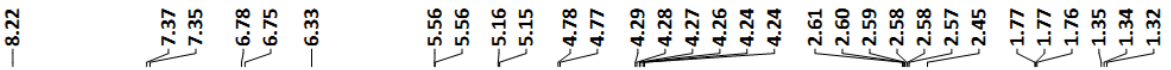
^{1}H NMR


O
Ts
N
O
CO2Et

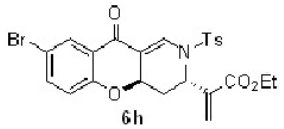
6g

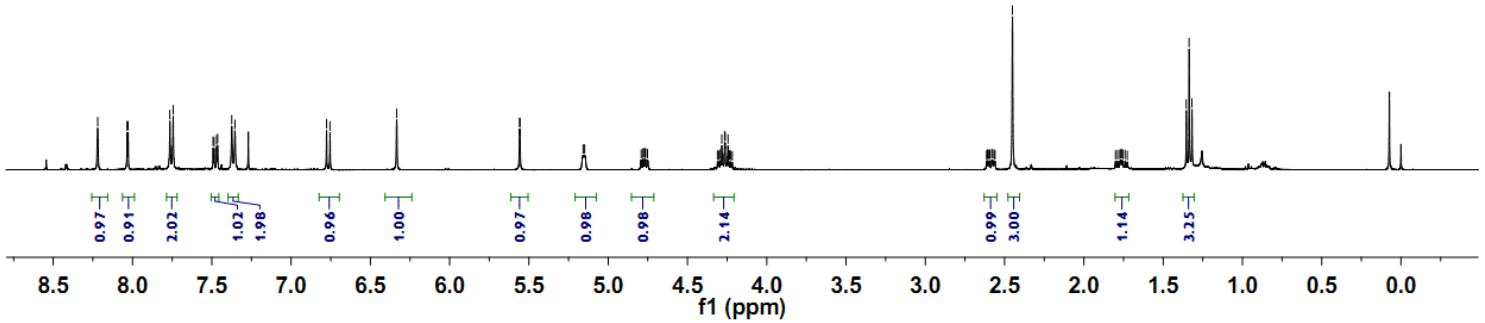

0.96
1.00
1.89
1.02
1.74
0.96
1.00
0.99
0.99
0.96
2.08
0.96
2.82
1.01
3.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

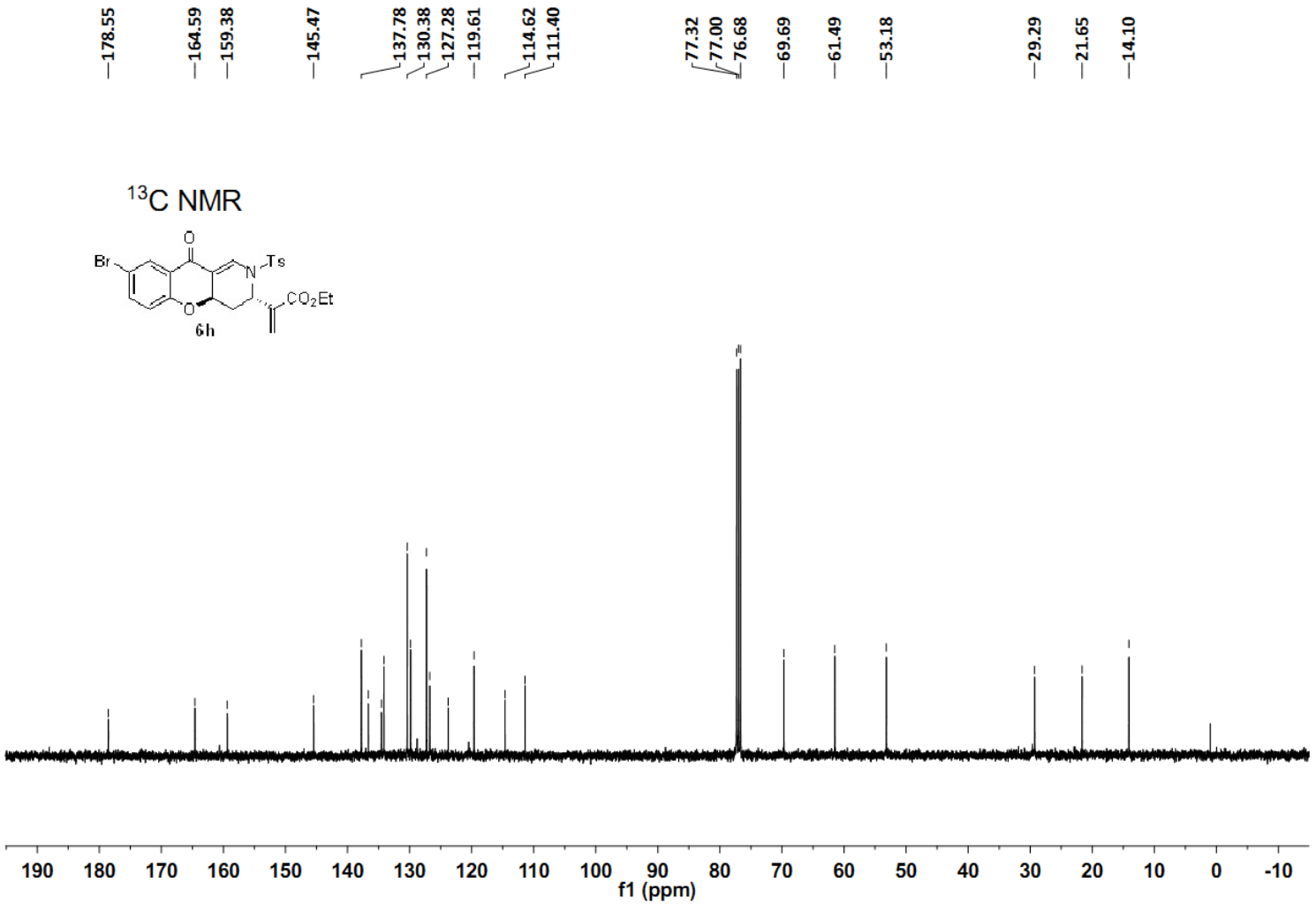


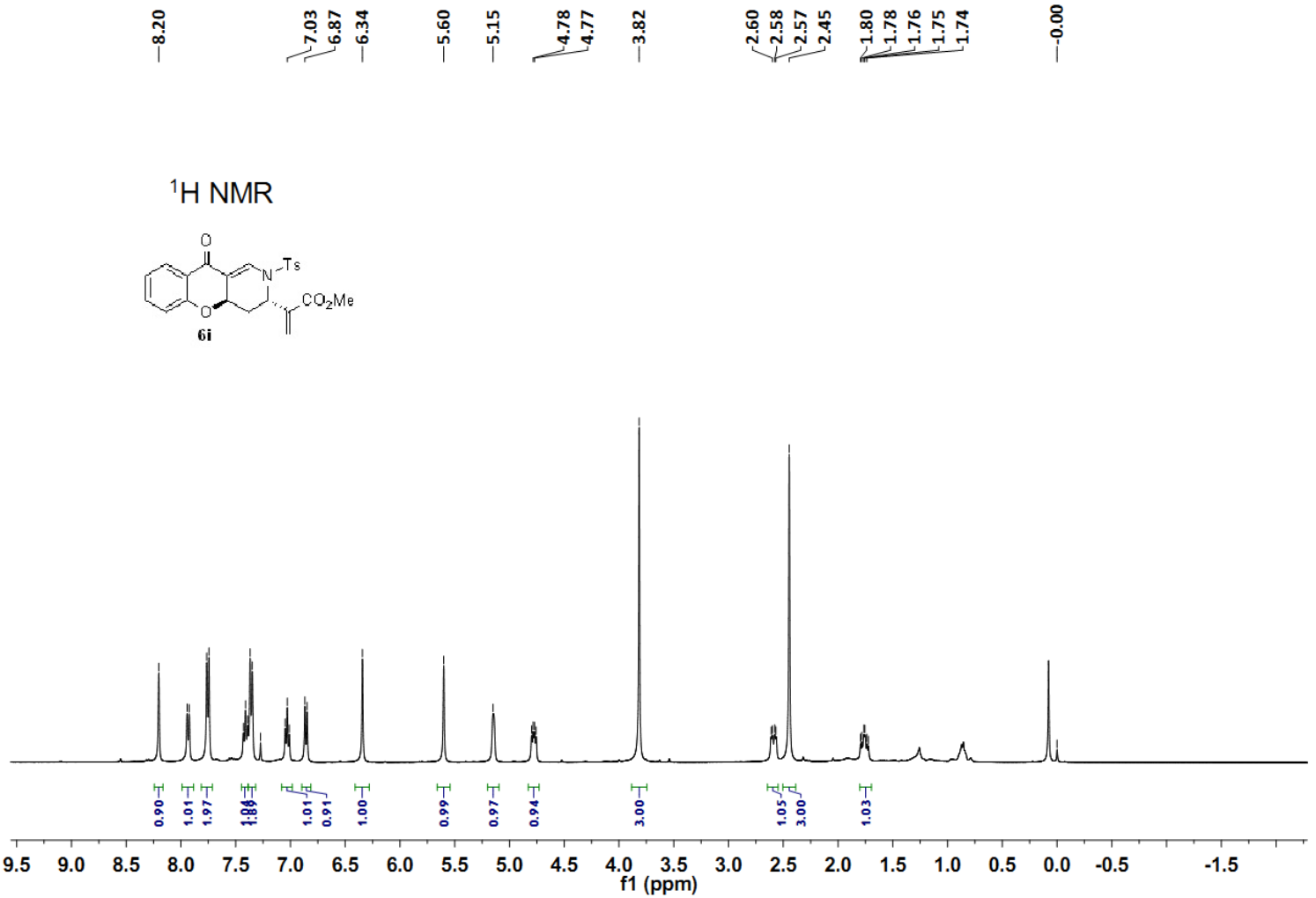


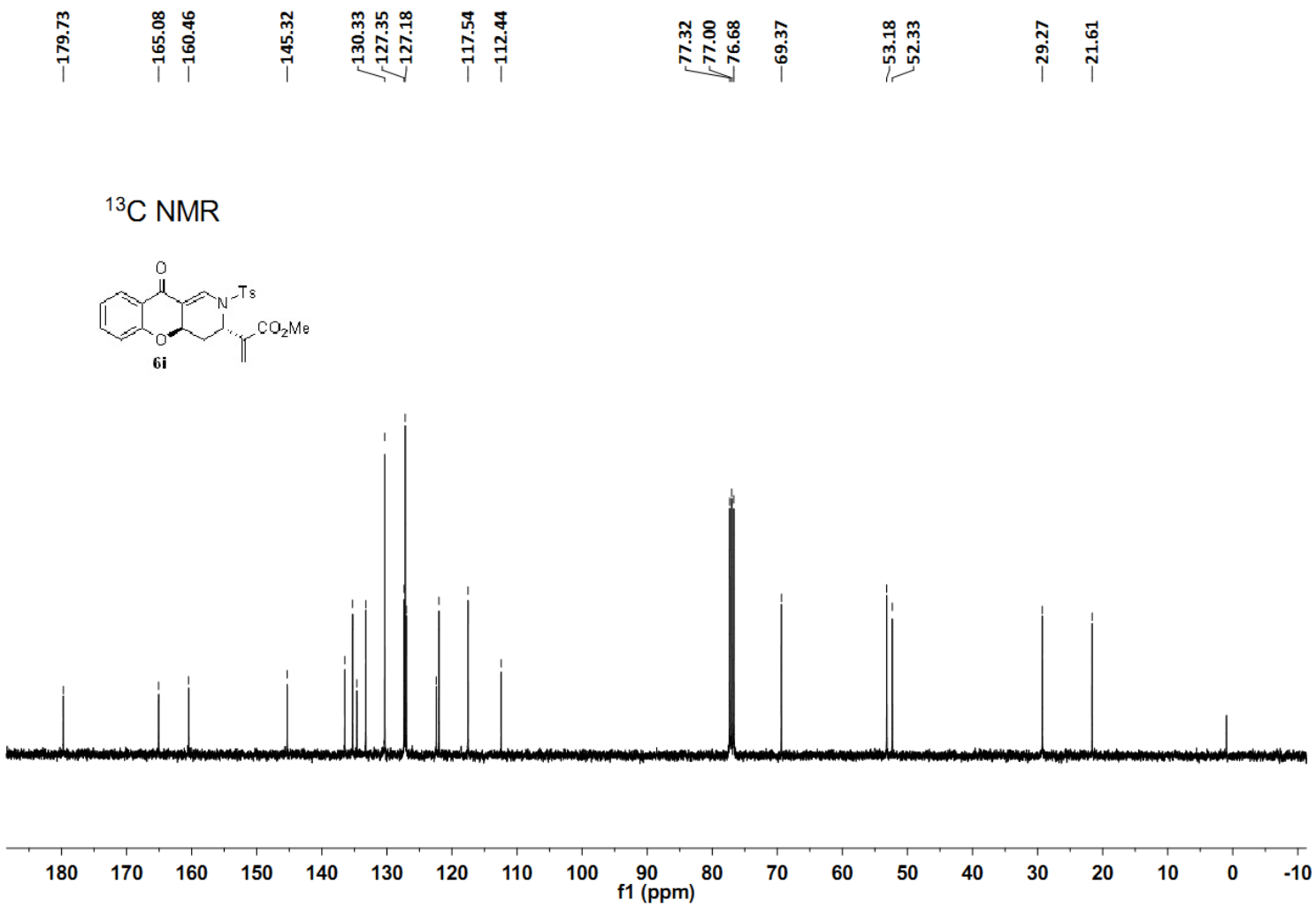
^{1}H NMR

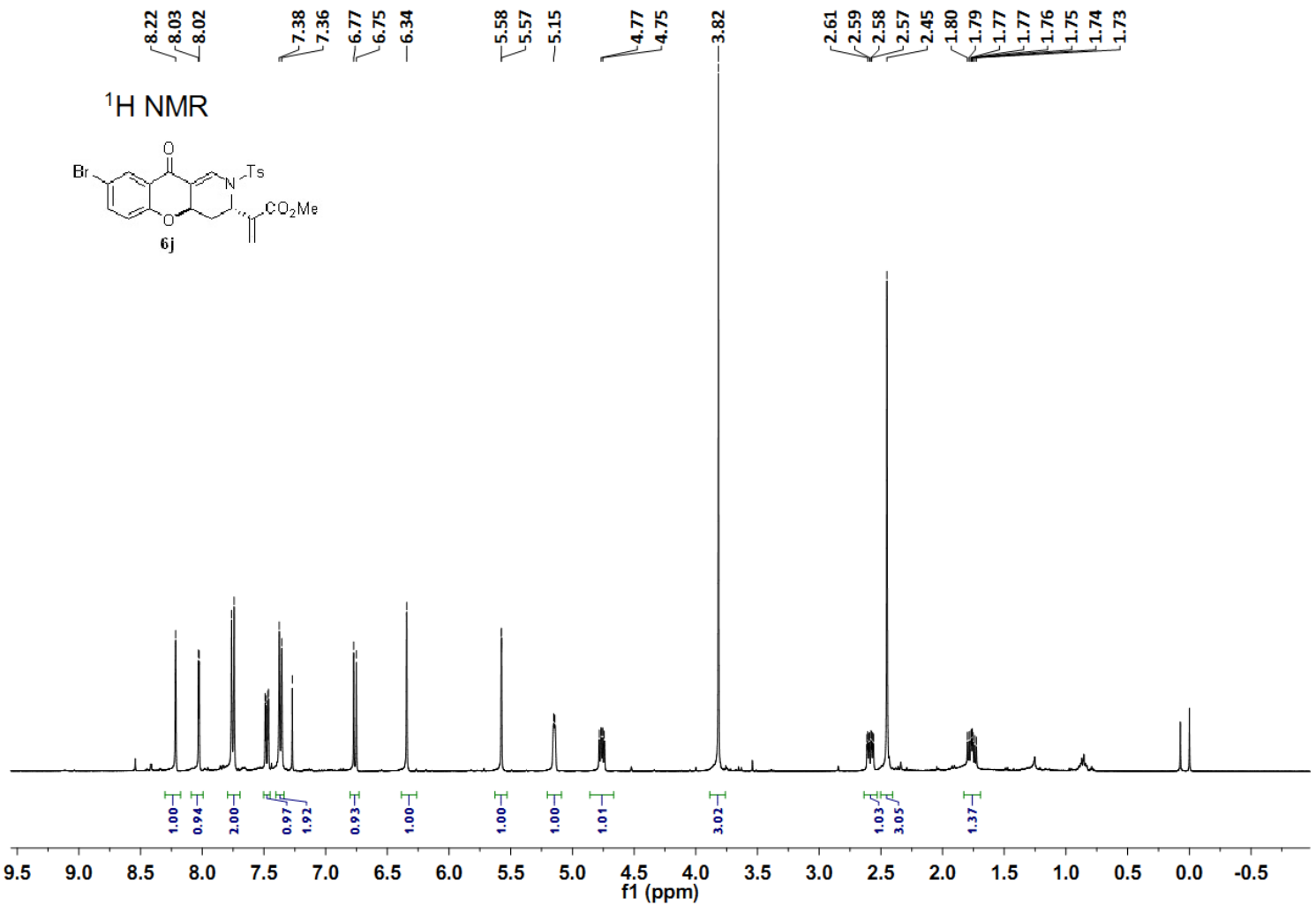


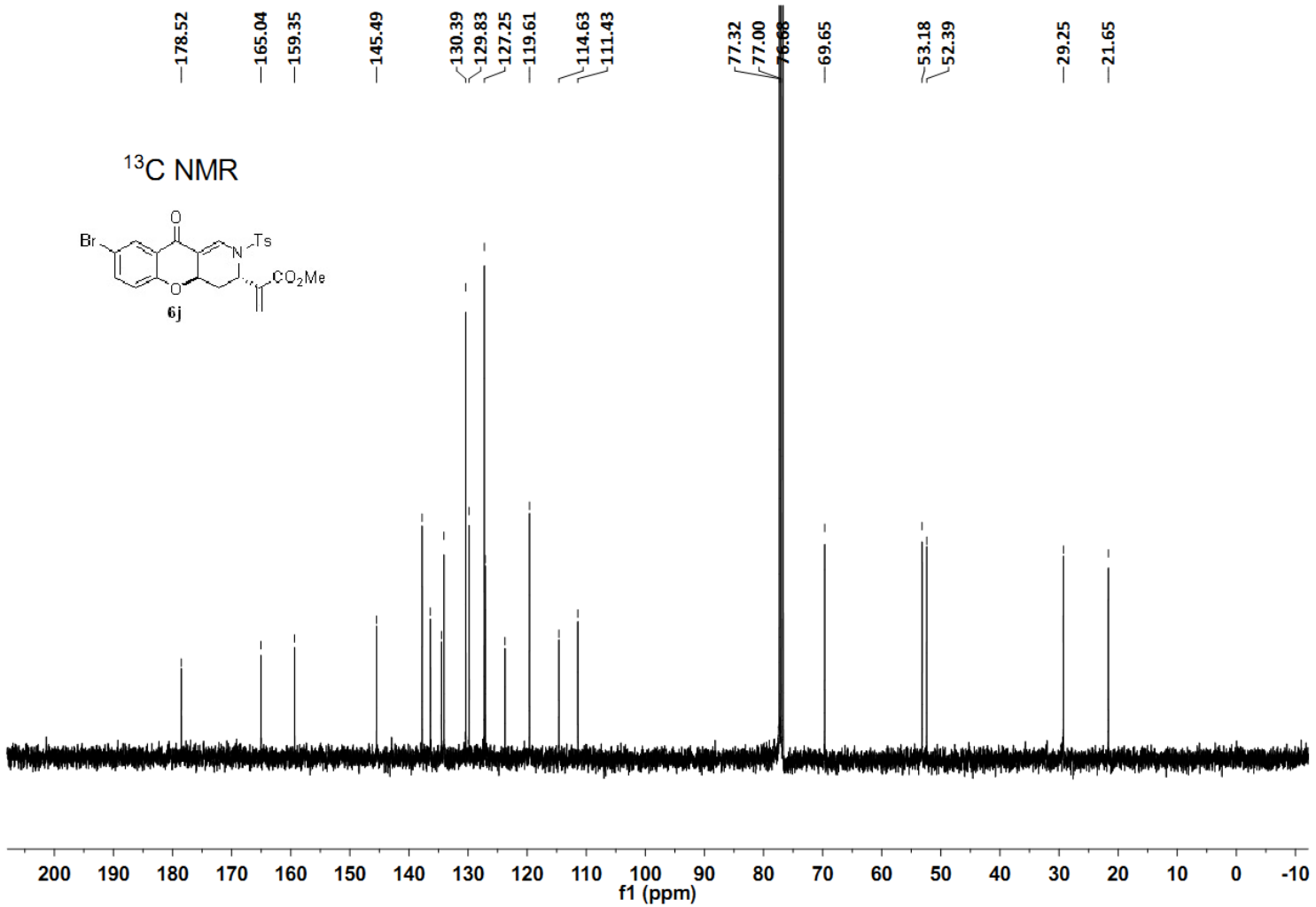











178.52
165.04
159.35
145.49
130.39
129.83
127.25
119.61
114.63
111.43
77.32
77.00
76.68
69.65
53.18
52.39
29.25
21.65
13C NMR
Br
O
N
Ts
CO2Me
O
6j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)