*Supplementary Information*

# Phosphine-Catalyzed [4 + 1] Annulations of 1,3-(Aza)dienes with Maleimides: Highly Efficient Construction of Azaspiro[4.4]nonenes

Mei Yang, Tianyi Wang, Shixuan Cao and Zhengjie He*

*The State Key Laboratory of Elemento-Organic Chemistry and Department of Chemistry, Nankai University, and Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300071, P.R. China. E-mail: zhengjiehe@nankai.edu.cn*

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# 1. General Remarks

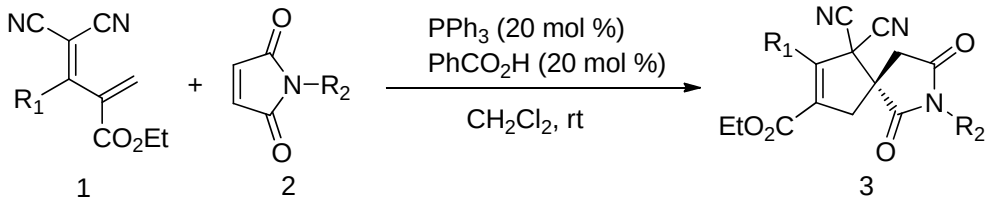
Unless otherwise noted, all reactions were carried out in a nitrogen atmosphere. All the solvents were purified according to the standard procedures. $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker AV 400 in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard. Melting points were measured on a RY-I apparatus and uncorrected. High resolution ESI mass spectra were acquired with Varian 7.0 T FTMS instrument. X-ray crystal diffraction data were collected on a Nonius Kappa CCD diffractometer with Mo Kα radiation (λ = 0.7107 Å) at room temperature. Column chromatography was performed on silica gel (200-300 mesh) using a mixture of petroleum ether/ethyl acetate as eluent. Substrates **1** and **4** were prepared according to literature methods.[1,2] Maleimides **2** were prepared through the reported method from maleic anhydride and the corresponding amines.[3]

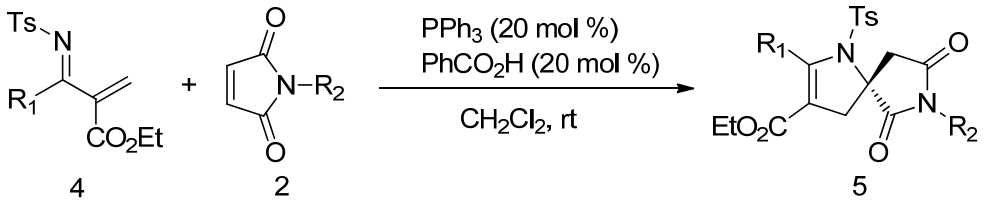
1. X. Jiang, D. Fu, X. Shi, S. Wang and R. Wang, *Chem. Commun*., 2011, **47**, 8289-8291.

2. H. Liu, Q. Zhang, L. Wang and X. Tong, *Chem. Eur. J.*, 2010,**16**,1968-1972.

3. M. Sortino, F. Garibotto, V. C. Filho, M. Gupta, R. Enriz and S, Zacchino, *Bioorg. Med. Chem.*, 2011, **19**, 2823-2834.

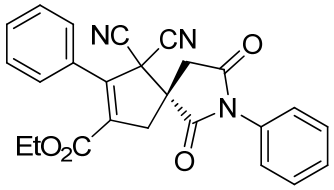
## 2. General Procedure



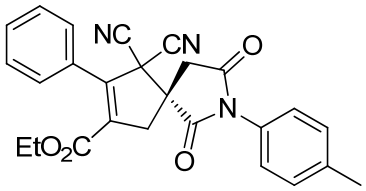

Under a $N_2$ atmosphere, a mixture of **1** or **4** (0.2 mmol), **2** (0.24 mmol), benzoic acid (0.04 mmol), and $PPh_3$(0.04 mmol) in $CH_2Cl_2$ (2.0 mL) was stirred at room temperature for the specified hours (monitored by TLC). After the reaction was completed, the mixture was concentrated on a rotary evaporator under reduced pressure. The residue was isolated by column chromatography on silica gel eluted with a mixture of petroleum ether / ethyl acetate (8:1–5:1) to afford the [4 + 1] annulation products **3** or **5**.

## 3. Analytical Data for Compounds 3 and 5



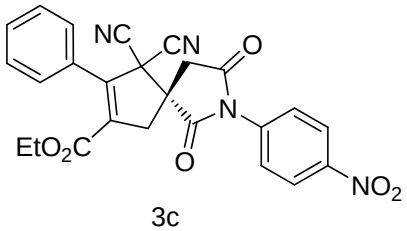

3a

**3a**, 94% yield; as a white solid, mp 127-128℃; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.59 - 7.39 (m, 8H), 7.33 (d, *J* = 7.3 Hz, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.60 (d, *J* = 17.2 Hz, 1H), 3.53 (d, *J* = 18.8 Hz, 1H), 3.31 (d, *J* = 17.2 Hz, 1H), 3.23 (d, *J* = 18.8 Hz, 1H), 1.03 (t, *J* = 7.1 Hz, 3H)；$^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.7, 170.7, 162.1, 143.3, 135.0, 130.7, 130.4, 130.3, 129.4, 128.7, 128.2, 126.4, 111.4, 110.7, 61.6, 56.1, 53.3, 42.3, 37.9, 13.6；HRMS-ESI calcd for $C_{25}H_{23}N_4O_4$ $[M + NH_4]^+$ 443.1714, found 443.1717.



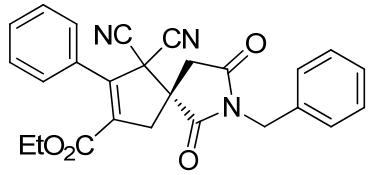

3b

**3b**, 99% yield; as a white solid, mp 186-187℃; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 5H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.60 (d, *J* = 17.2 Hz, 1H), 3.51 (d, *J* = 18.8 Hz, 1H), 3.31 (d, *J* = 17.2 Hz, 1H), 3.21 (d, *J* = 18.8 Hz, 1H), 2.40 (s, 3H), 1.03 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.8, 170.9, 162.1, 143.3, 139.6, 135.1, 130.4, 130.3, 130.1, 128.7, 128.2 (2C), 126.2, 111.4, 110.7, 61.6, 56.1, 53.3, 42.3, 37.9, 21.3, 13.6; HRMS-ESI calcd for $C_{26}H_{25}N_4O_4$ $[M + NH_4]^+$ 457.1870, found 457.1874.



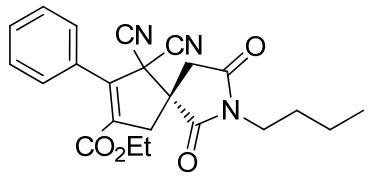

3c

**3c**, 88% yield; as a white solid, mp 173-175℃; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 9.0 Hz, 2H), 7.62 (d, *J* = 9.0 Hz, 2H), 7.53 – 7.44 (m, 5H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.64 (d, *J* = 16.8 Hz, 1H), 3.59 (d, *J* = 18.1 Hz, 1H), 3.35 (d, *J* = 16.8 Hz, 1H), 3.30 (d, *J* = 18.1 Hz, 1H), 1.03 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.1, 169.8, 162.0, 147.6, 143.1, 136.1, 135.0, 130.5, 130.1, 128.7, 128.1, 127.1, 124.6, 111.2, 110.7, 61.8, 56.2, 53.4, 42.2, 38.0, 13.6; HRMS-ESI calcd for $C_{25}H_{22}N_5O_6$ $[M + NH_4]^+$ 488.1564, found 488.1574.




3d

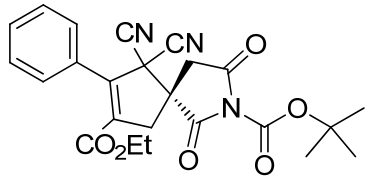
**3d**, 89% yield; as a colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 5H), 7.38 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.35 – 7.28 (m, 3H), 4.77 (d, *J* = 14.1 Hz, 1H), 4.68 (d, *J* = 14.1 Hz, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.39 (d, *J* = 17.2 Hz, 1H), 3.35 (d, *J* = 18.7 Hz, 1H), 3.18 (d, *J* = 17.2 Hz, 1H), 3.03 (d, *J* = 18.7 Hz, 1H), 1.01 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100MHz, $CDCl_3$) δ 174.2, 171.4, 162.2, 143.4, 134.9, 134.6, 130.4, 130.3, 128.9, 128.8, 128.6, 128.5, 128.2, 111.4, 110.6, 61.6, 56.0, 52.9, 43.4, 42.5, 38.1, 13.6; HRMS-ESI calcd for $C_{26}H_{25}N_4O_4$ $[M + NH_4]^+$ 457.1870, found 457.1878.




3e

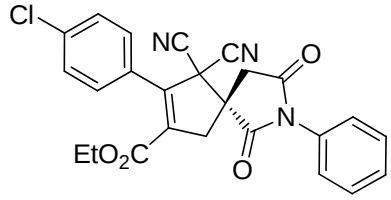
**3e**, 81% yield; as a colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.40 (m, 5H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.59 (td, *J* = 7.1, 2.7 Hz, 2H), 3.45 (d, *J* = 17.2 Hz, 1H), 3.35 (d, *J* = 18.7 Hz, 1H), 3.22 (d, *J* = 17.2 Hz, 1H), 3.04 (d, *J* = 18.7 Hz, 1H), 1.65 – 1.56 (m, 2H), 1.34 (dd, *J* = 15.1, 7.5 Hz, 2H), 1.03 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.3

Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 174.5, 171.7, 162.2, 143.3, 135.0, 130.4, 130.3, 128.6, 128.2, 111.5, 110.65, 61.6, 56.0, 53.0, 42.4, 39.5, 37.9, 29.5, 20.0, 13.6, 13.5; HRMS-ESI calcd for $C_{23}H_{27}N_4O_4$ $[M + NH_4]^+$ 423.2027, found 423.2033.



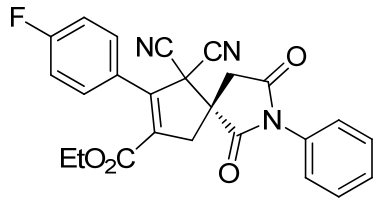

3f

**3f**, 59% yield; as a semisolid; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 5H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.58 (d, *J* = 17.3 Hz, 1H), 3.41 (d, *J* = 18.6 Hz, 1H), 3.25 (d, *J* = 17.3 Hz, 1H), 3.12 (d, *J* = 18.6 Hz, 1H), 1.59 (s, 9H), 1.03 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.4, 167.3, 162.0, 145.0, 143.4, 134.5, 130.4, 130.2, 128.6, 128.2, 111.2, 110.3, 87.7, 61.7, 56.4, 52.6, 42.6, 38.3, 27.7, 13.6; HRMS-ESI calcd for $C_{24}H_{27}N_4O_6$ $[M + NH_4]^+$ 467.1925, found 467.1929.



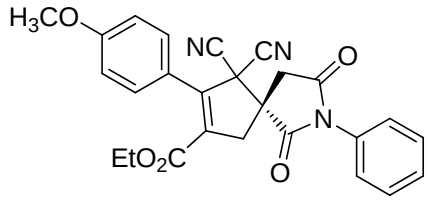

3g

**3g**, 80% yield; as a white solid, mp 193-194℃; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.43 (m, 5H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.5 Hz, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.60 (d, *J* = 17.3 Hz, 1H), 3.53 (d, *J* = 18.8 Hz, 1H), 3.33 (d, *J* = 17.3 Hz, 1H), 3.25 (d, *J* = 18.8 Hz, 1H), 1.09 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.7, 170.5, 161.8, 142.2, 136.7, 135.7, 130.6, 129.6, 129.5 (2C), 129.1, 128.7, 126.3, 111.2, 110.5, 61.9, 56.1, 53.1, 42.2, 37.7, 13.7; HRMS-ESI calcd for $C_{25}H_{22}ClN_4O_4$ $[M + NH_4]^+$ 477.1324, found 477.1330.



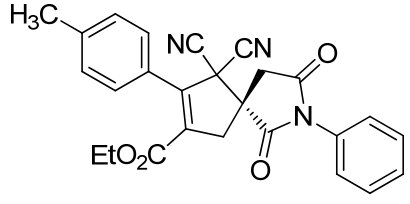

3h

**3h**, 88% yield; as a white solid, mp 180-181℃; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.46 (m, 5H), 7.35 (d, *J* = 7.4 Hz, 2H), 7.20 (t, *J* = 8.6 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.62 (d, *J* = 17.3 Hz, 1H), 3.55 (d, *J* = 18.8 Hz, 1H), 3.34 (d, *J* = 17.3 Hz, 1H), 3.26 (d, *J* = 18.8 Hz, 1H), 1.10 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.7, 170.6, 163.8 (d, $J_{CF}$ = 251.3Hz), 161.9, 142.4, 135.5, 130.7, 130.4 (d, $J_{CF}$ = 8.7 Hz), 129.5 (2C), 126.4, 126.3 (d, $J_{CF}$ = 3.7 Hz), 116.0 (d, $J_{CF}$ = 22.1 Hz), 111.3, 110.6, 61.8, 56.1, 53.2, 42.2, 37.8, 13.7; HRMS-ESI calcd for $C_{25}H_{22}FN_4O_4$ [M + $NH_4$]$^{+}$ 461.1619, found 461.1624.



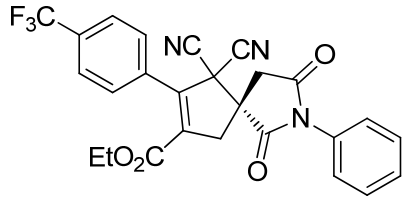

3i

**3i**, 76% yield; as a white solid, mp 187-189℃; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.41 (m, 5H), 7.33 (d, *J* = 7.3 Hz, 2H), 6.98 (d, *J* = 7.7 Hz, 2H), 4.11 (q, *J* = 6.6 Hz, 2H), 3.85 (s, 3H), 3.59 (d, *J* = 17.2 Hz, 1H), 3.52 (d, *J* = 18.8 Hz, 1H), 3.30 (d, *J* = 17.2 Hz, 1H), 3.22 (d, *J* = 18.8 Hz, 1H), 1.11 (t, *J* = 6.9 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.7, 170.7, 162.3, 161.3, 143.4, 133.6, 130.8, 130.0, 129.4, 126.4, 122.3, 114.1, 111.6, 110.9, 61.6, 56.0, 55.4, 53.2, 42.4, 38.0, 13.8; HRMS-ESI calcd for $C_{26}H_{25}N_4O_5$ [M + $NH_4$]$^{+}$ 473.1819, found 473.1826.



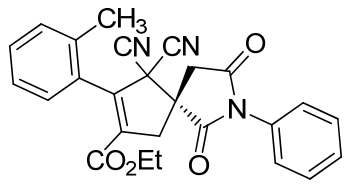

3j

**3j**, 99% yield; as a white solid, mp 162-163℃; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 3H), 7.38 – 7.31 (m, 4H), 7.27 (d, *J* = 9.4 Hz, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.59 (d, *J* = 17.2 Hz, 1H), 3.51 (d, *J* = 18.8 Hz, 1H), 3.29 (d, *J* = 17.2 Hz, 1H), 3.21 (d, *J* = 18.8 Hz, 1H), 2.40 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.7, 170.8, 162.2, 143.6, 140.6, 134.3, 130.8, 129.4, 129.3, 128.1, 127.3, 126.4, 111.5, 110.8, 61.6, 56.1, 53.2, 42.3, 38.0, 21.5, 13.7; HRMS-ESI calcd for $C_{26}H_{25}N_4O_4$ $[M + NH_4]^+$ 457.1870, found 457.1878.




3k

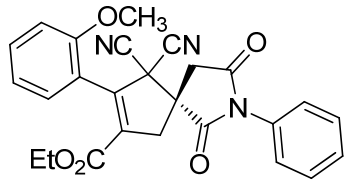
**3k**, 73% yield; as a white solid, mp 204-206℃; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 2H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.51 (dq, *J* = 13.9, 7.0 Hz, 3H), 7.36 (d, *J* = 7.4 Hz, 2H), 4.11 (q, *J* = 6.9 Hz, 2H), 3.65 (d, *J* = 17.4 Hz, 1H), 3.56 (d, *J* = 18.8 Hz, 1H), 3.37 (d, *J* = 17.4 Hz, 1H), 3.28 (d, *J* = 18.8 Hz, 1H), 1.06 (t, *J* = 7.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.7, 170.4, 161.6, 141.8, 136.6, 134.0, 132.3 (q, $J_{CF}$ = 32.9 Hz), 130.6, 129.6, 129.5, 128.8, 126.3, 125.7 (q, $J_{CF}$ = 3.7 Hz), 123.6 (q, $J_{CF}$ = 272.6 Hz), 111.1, 110.4, 61.9, 56.3, 53.1, 42.2, 37.7, 13.6; HRMS-ESI calcd for $C_{26}H_{22}F_3N_4O_4$ $[M + NH_4]^+$ 511.1587, found 511.1589.




3l

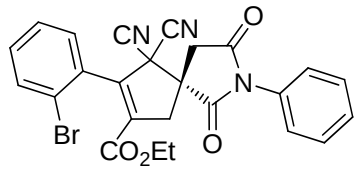
**3l**, 99% yield; as a colorless oil, diastereomeric mixture (dr = 2:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.41 (m, 3H), 7.39 – 7.25 (m, 6H), 4.03 (m, 2H), 3.65 – 3.50 (m, 2H), 3.37 – 3.18 (m, 2H), 2.42 (s, 3H), 0.96 (t, *J* = 7.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 174.1, 170.8, 161.9, 143.0, 138.1, 137.0, 130.8, 130.7, 130.3, 129.9, 129.5, 129.4, 126.9, 126.5, 125.8, 111.5, 110.6, 61.6, 55.6, 53.9, 42.2, 38.3, 19.7, 13.5;

Selected NMR data for the minor isomer: $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.7, 170.7, 162.0, 142.4, 136.5, 136.0, 130.1, 129.9, 128.5, 126.4, 126.0, 111.2, 110.6, 61.6, 56.3, 53.6, 41.9, 38.2, 19.6; HRMS-ESI calcd for $C_{26}H_{25}N_4O_4$ $[M + NH_4]^+$ 457.1870, found 457.1880.



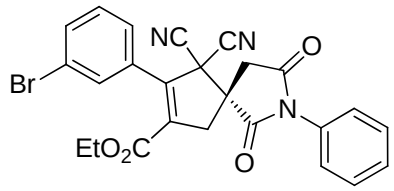

3m

**3m**, 58% yield; as a colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 4H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 2H), 7.00 (t, *J* = 9.4 Hz, 2H), 4.16 – 4.03 (m, 2H), 3.91 (s, 3H), 3.60 (d, *J* = 17.2 Hz, 1H), 3.54 (d, *J* = 18.8 Hz, 1H), 3.30 (d, *J* = 17.2 Hz, 1H), 3.22 (d, *J* = 18.8 Hz, 1H), 1.07 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.5, 171.0, 162.5, 156.7, 142.7, 134.9, 132.2, 131.9, 130.8, 129.4, 129.3, 126.4, 120.7, 119.3, 111.9, 111.1, 110.8, 61.5, 57.3, 55.0, 52.2, 41.5, 38.0, 13.7; HRMS-ESI calcd for $C_{25}H_{25}N_4O_5$ $[M + NH_4]^+$ 473.1819, found 473.1825.



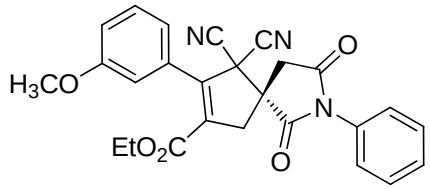

3n

**3n**, 62% yield; as a semisolid, diastereomeric mixture (dr = 3:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.71 (t, *J* = 6.8 Hz, 1H), 7.54 – 7.43 (m, 5H), 7.36 (d, *J* = 7.3 Hz, 3H), 4.15 – 3.98 (m, 2H), 3.74 – 3.59 (m, 2H), 3.40 – 3.20 (m, 2H), 0.99 (t, *J* = 6.9 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.2, 170.6, 161.6, 140.6, 138.3, 133.6, 132.9, 131.6, 131.4, 130.8, 130.0, 129.4, 127.7, 126.3, 123.0, 110.5, 110.4, 61.8, 56.5, 52.9, 41.9, 39.0, 13.5; Selected NMR data for the minor isomer: $^{13}$C NMR (100 MHz, $CDCl_3$) δ 140.4, 138.9, 133.6, 131.3, 130.8, 127.5, 126.4, 55.4, 42.1, 39.0; HRMS-ESI calcd for $C_{25}H_{22}BrN_4O_4$ $[M + NH_4]^+$ 521.0819, found 521.0823.



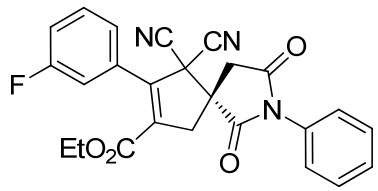

3o

**3o**, 48% yield; as a yellow oil, $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 2H), 7.53 – 7.33 (m, 7H), 4.10 (q, *J* = 7.0 Hz, 2H), 3.60 (d, *J* = 17.3 Hz, 1H), 3.53 (d, *J* = 18.8 Hz, 1H), 3.33 (d, *J* = 17.3 Hz, 1H), 3.25 (d, *J* = 18.8 Hz, 1H), 1.07 (t, *J* = 7.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.7, 170.5, 161.7, 141.5, 136.2, 133.4, 132.2, 131.4, 130.6, 130.2, 129.5 (2C), 126.6, 126.3, 122.6, 111.1, 110.5, 61.9, 56.2, 53.1, 42.2, 37.7, 13.6; HRMS-ESI calcd for $C_{25}H_{22}BrN_4O_4$ $[M + NH_4]^+$ 521.0819, found 521.0827.



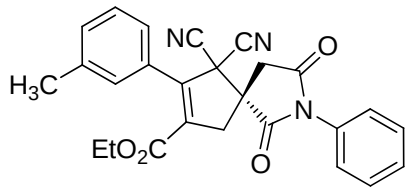

3p

**3p**, 99% yield; as a white solid, mp 50-52℃; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 3H), 7.40 – 7.33 (m, 3H), 7.02 (dd, *J* = 14.8, 8.0 Hz, 3H), 4.09 (q, *J* = 7.0 Hz, 2H), 3.83 (s, 3H), 3.60 (d, *J* = 17.2 Hz, 1H), 3.53 (d, *J* = 18.8 Hz, 1H), 3.31 (d, *J* = 17.2 Hz, 1H), 3.23 (d, *J* = 18.8 Hz, 1H), 1.06 (t, *J* = 7.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.7, 170.7, 162.1, 159.6, 143.0, 135.0, 131.5, 130.7, 129.9, 129.4, 126.4, 120.4, 116.1, 113.6, 111.4, 110.7, 61.7, 56.1, 55.4, 53.3, 42.3, 37.9, 13.7; HRMS-ESI calcd for $C_{26}H_{25}N_4O_5$ $[M + NH_4]^+$ 473.1819, found 473.1825.



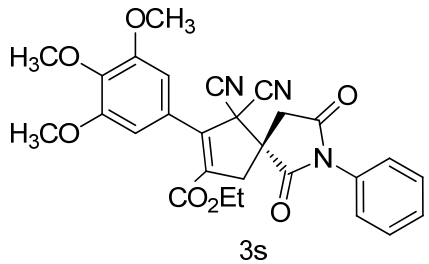

3q

**3q**, 87% yield; as a white solid, mp 162-163℃; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.43 (m, 4H), 7.33 (d, *J* = 7.7 Hz, 2H), 7.24 – 7.18 (m, 3H), 4.09 (q, *J* = 7.0 Hz, 2H), 3.60 (d, *J* = 17.3 Hz, 1H), 3.52 (d, *J* = 18.8 Hz, 1H), 3.32 (d, *J* = 17.3 Hz, 1H), 3.24 (d, *J* = 18.8 Hz, 1H), 1.06 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.7, 170.6, 162.4 (d, $J_{CF}$ = 247.1 Hz), 161.8, 141.7 (d, $J_{CF}$ = 2.0 Hz), 136.0, 132.2 (d, $J_{CF}$ = 8.3 Hz), 130.7, 130.6 (d, $J_{CF}$ = 8.3 Hz), 129.5 (2C), 126.3, 123.9 (d, $J_{CF}$ = 3.2 Hz), 117.5 (d, $J_{CF}$ = 20.9 Hz), 115.7 (d, $J_{CF}$ = 23.2 Hz), 111.2, 110.5, 61.8, 56.2, 53.1, 42.2, 37.7, 13.6; HRMS-ESI calcd for $C_{25}H_{22}FN_4O_4$ $[M + NH_4]^+$ 461.1619, found 461.1628.




3r

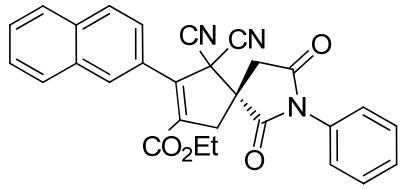
**3r**, 99% yield; as a white solid, mp 168-169℃; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.47 (dq, *J* = 14.6, 7.2 Hz, 3H), 7.37 - 7.28 (m, 6H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.59 (d, *J* = 17.2 Hz, 1H), 3.52 (d, *J* = 18.8 Hz, 1H), 3.30 (d, *J* = 17.2 Hz, 1H), 3.22 (d, *J* = 18.8 Hz, 1H), 2.40 (s, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.7, 170.7, 162.2, 143.5, 138.4, 134.7, 131.1, 130.8, 130.3, 129.4, 128.6, 128.5, 126.4, 125.1, 111.4, 110.8, 61.6, 56.2, 53.3, 42.2, 37.9, 21.4, 13.6; HRMS-ESI calcd for $C_{26}H_{25}N_4O_4$ $[M + NH_4]^+$ 457.1870, found 457.1877.




3s

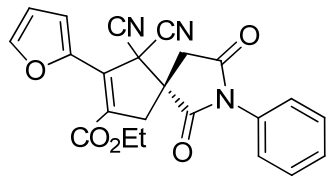
**3s**, 99% yield; as a white solid, mp 72-74℃; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.44 (m, 3H), 7.34 (d, *J* = 7.5 Hz, 2H), 6.67 (s, 2H), 4.12 (q, *J* = 6.9 Hz, 2H), 3.90 (s, 3H), 3.88 (s, 6H), 3.59 (d, *J* = 17.2 Hz, 1H), 3.54 (d, *J* = 18.8 Hz, 1H), 3.31 (d, *J* =

17.2 Hz, 1H), 3.24 (d, *J* = 18.8 Hz, 1H), 1.11 (t, *J* = 7.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.8, 170.7, 162.1, 153.3, 142.9, 139.6, 134.8, 130.7, 129.5, 126.4, 125.4, 111.5, 110.9, 105.5, 61.7, 61.0, 56.3, 55.9, 53.3, 42.4, 37.9, 13.8; HRMS-ESI calcd for $C_{28}H_{29}N_4O_7$ $[M + NH_4]^+$ 533.2031, found 533.2038.



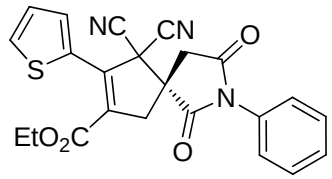

3t

**3t**, 99% yield; as a white solid, mp 181-183℃; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.94 – 7.88 (m, 3H), 7.59 – 7.43 (m, 6H), 7.35 (d, *J* = 7.5 Hz, 2H), 4.05 (q, *J* = 6.7 Hz, 2H), 3.66 (d, *J* = 17.3 Hz, 1H), 3.56 (d, *J* = 18.8 Hz, 1H), 3.37 (d, *J* = 17.3 Hz, 1H), 3.27 (d, *J* = 18.8 Hz, 1H), 0.96 (t, *J* = 7.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.8, 170.7, 162.1, 143.4, 135.1, 133.8, 132.7, 130.7, 129.4, 128.6, 128.5, 128.2, 127.9, 127.7, 127.5, 126.9, 126.4, 125.1, 111.5, 110.8, 61.7, 56.3, 53.3, 42.3, 37.9, 13.6; HRMS-ESI calcd for $C_{29}H_{25}N_4O_4$ $[M + NH_4]^+$ 493.1870, found 493.1880.



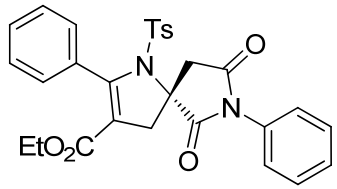

3u

**3u**, 99% yield; as a colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 3.5 Hz, 1H), 7.66 (s, 1H), 7.44 (dq, *J* = 14.4, 7.2 Hz, 3H), 7.32 (d, *J* = 7.3 Hz, 2H), 6.61 (dd, *J* = 3.5, 1.6 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.58 (d, *J* = 17.6 Hz, 1H), 3.55 (d, *J* = 18.9 Hz, 1H), 3.29 (d, *J* = 17.6 Hz, 1H), 3.18 (d, *J* = 18.9 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.7, 170.9, 162.1, 145.3, 144.5, 131.5, 130.8, 129.3, 128.2, 126.4, 119.6, 113.2, 111.7, 111.5, 61.8, 55.5, 49.9, 42.7, 37.9, 14.1; HRMS-ESI calcd for $C_{23}H_{21}N_4O_5$ $[M + NH_4]^+$ 433.1506, found 433.1513.



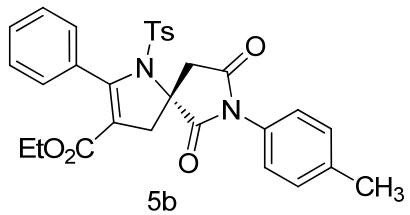

3v

**3v**, 94% yield; as a white solid, mp 58-60℃; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.8 Hz, 2H), 7.50 – 7.41 (m, 3H), 7.33 (d, *J* = 7.5 Hz, 2H), 7.16 (t, *J* = 3.9 Hz, 1H), 4.23 (q, *J* = 7.0 Hz, 2H), 3.60 (d, *J* = 17.4 Hz, 1H), 3.54 (d, *J* = 18.8 Hz, 1H), 3.32 (d, *J* = 17.4 Hz, 1H), 3.20 (d, *J* = 18.8 Hz, 1H), 1.25 (t, *J* = 7.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.4, 170.6, 162.2, 135.6, 132.8, 131.0, 130.8, 130.6, 129.9, 129.4, 127.3, 126.3, 111.6, 111.1, 62.0, 55.8, 53.0, 42.7, 38.1, 13.9; HRMS-ESI calcd for $C_{23}H_{21}N_4O_4S$ $[M + NH_4]^+$ 449.1278, found 449.1285.




5a

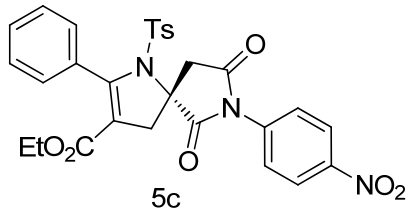
**5a**, 82% yield; as a white solid, mp 182-184℃; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.54 - 7.39 (m, 7H), 7.29 – 7.26 (m, 3H), 7.01 (d, *J* = 8.1 Hz, 2H), 6.84 (br s, 1H), 6.41 (br s, 1H), 3.95 – 3.86 (m, 2H), 3.82 (d, *J* = 18.5 Hz, 1H), 3.65 (d, *J* = 15.7 Hz, 1H), 3.30 (d, *J* = 18.5 Hz, 1H), 3.10 (d, *J* = 15.7 Hz, 1H), 2.35 (s, 3H), 0.89 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.8, 172.2, 163.7, 151.0, 144.6, 135.9, 131.9, 129.3, 129.2, 129.1, 129.0, 128.4 (2C), 126.8, 108.0, 69.6, 60.0, 46.0, 42.6, 21.6, 13.7; HRMS-ESI calcd for $C_{29}H_{27}N_2O_6S$ $[M + H]^+$ 531.1585, found 531.1589.




5b

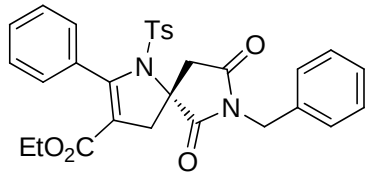
**5b**, 69% yield; as a white solid, mp 91- 93℃; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.26 (m, 9H), 7.00 (d, *J* = 7.7 Hz, 2H), 6.84 (br s, 1H), 6.39 (br s, 1H), 3.88 (m,

2H), 3.81 (d, *J* = 18.4 Hz, 1H), 3.64 (d, *J* = 15.7 Hz, 1H), 3.28 (d, *J* = 18.4 Hz, 1H), 3.09 (d, *J* = 15.7 Hz, 1H), 2.40 (s, 3H), 2.35 (s, 3H), 0.89 (t, *J* = 6.9 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.9, 172.4, 163.7, 151.0, 144.5, 139.2, 136.0, 130.0, 129.2 (2C), 129.0, 128.4 (2C), 126.6, 108.0, 69.6, 60.0, 46.1, 42.6, 21.6, 21.3, 13.7; HRMS-ESI calcd for $C_{30}H_{29}N_2O_6S$ $[M + H]^+$ 545.1741, found 545.1744.



5c

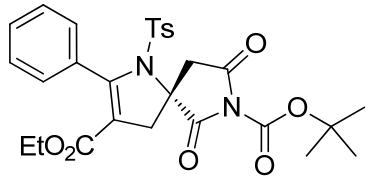
**5c**, 87% yield; as a white solid, mp 106-108℃; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.23 (m, 5H), 7.03 (d, *J* = 7.8 Hz, 2H), 6.86 (br s, 1H), 6.42 (br s, 1H), 3.88 (m, 2H), 3.85 (d, *J* = 18.7 Hz, 1H), 3.66 (d, *J* = 15.7 Hz, 1H), 3.34 (d, *J* = 18.7 Hz, 1H), 3.12 (d, *J* = 15.7 Hz, 1H), 2.37 (s, 3H), 0.89 (t, *J* = 7.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.2, 171.4, 163.6, 150.9, 147.4, 144.8, 137.3, 135.6, 129.4, 129.1, 128.3, 128.2, 127.5, 124.6, 108.1, 69.5, 60.1, 45.9, 42.6, 21.6, 13.7; HRMS-ESI calcd for $C_{29}H_{26}N_3O_8S$ $[M + H]^+$ 576.1435, found 576.1446.



5d

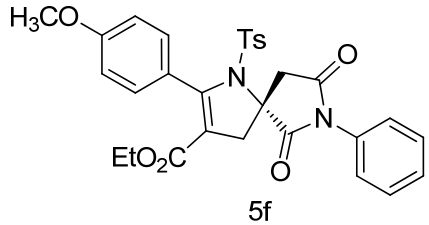
**5d**, 49% yield; as a white solid, mp 182-183℃; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.3 Hz, 2H), 7.35 – 7.21 (m, 8H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.85 (br s, 1H), 6.41 (br s, 1H), 4.87 (d, *J* = 14.4 Hz, 1H), 4.79 (d, *J* = 14.4 Hz, 1H), 3.90 – 3.81 (m, 2H), 3.68 (d, *J* = 18.1 Hz, 1H), 3.44 (d, *J* = 15.7 Hz, 1H), 3.12 (d, *J* = 18.1 Hz, 1H), 2.92 (d, *J* = 15.7 Hz, 1H), 2.36 (s, 3H), 0.86 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 177.1, 172.6, 163.7, 151.2, 144.5, 136.0, 135.2, 129.2, 129.0, 128.7, 128.5,

128.4 (2C), 128.0, 107.9, 69.5, 60.0, 45.8, 43.0, 42.5, 21.6, 13.7; HRMS-ESI calcd for $C_{30}H_{29}N_2O_6S$ $[M + H]^+$ 545.1741, found 545.1752.



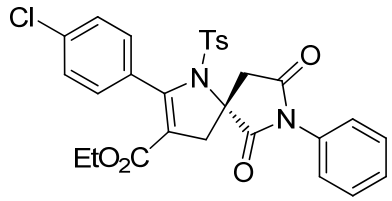

5e

**5e**, 32% yield; as a white solid, mp 68-70℃; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 5H), 7.04 (d, *J* = 7.7 Hz, 2H), 6.88 (br s, 1H), 6.44 (br s, 1H), 3.89 (m, 2H), 3.76 (d, *J* = 18.4 Hz, 1H), 3.57 (d, *J* = 15.8 Hz, 1H), 3.17 (d, *J* = 18.4 Hz, 1H), 3.01 (d, *J* = 15.8 Hz, 1H), 2.38 (s, 3H), 1.64 (s, 9H), 0.90 (t, *J* = 6.9 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.6, 168.7, 163.6, 151.1, 145.9, 144.7, 135.7, 129.2, 129.1, 128.5, 128.3, 107.8, 86.6, 69.4, 60.0, 45.7, 42.7, 27.8, 21.6, 13.7; HRMS-ESI calcd for $C_{28}H_{34}N_3O_8S$ $[M + NH_4]^+$ 572.2061, found 572.2061.




5f

**5f**, 76% yield; as a colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.26 (m, 9H), 7.03 (d, *J* = 7.8 Hz, 2H), 6.90 (br s, 1H), 6.36 (br s, 1H), 3.92 (m, 2H), 3.80 (d, *J* = 18.5 Hz, 1H) 3.79 (s, 3H), 3.64 (d, *J* = 15.8 Hz, 1H), 3.29 (d, *J* = 18.5 Hz, 1H), 3.09 (d, *J* = 15.8 Hz, 1H), 2.35 (s, 3H), 0.96 (t, *J* = 6.9 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.9, 172.3, 163.8, 160.2, 151.2, 144.5, 136.1, 129.4, 129.2, 129.1, 128.4, 126.8, 120.3, 112.7, 107.8, 69.4, 60.0, 55.3, 46.2, 42.6, 21.6, 13.9; HRMS-ESI calcd for $C_{30}H_{29}N_2O_7S$ $[M + H]^+$ 561.1690, found 561.1698.




5g

**5g**, 45% yield; as a white solid; mp 194-196 ℃; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.31 (m, 9H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.83 (br s, 1H), 6.35 (br s, 1H), 3.92 (m, 2H), 3.81 (d, *J* = 18.5 Hz, 1H), 3.64 (d, *J* = 15.8 Hz, 1H), 3.28 (d, *J* = 18.5 Hz, 1H), 3.10 (d, *J* = 15.8 Hz, 1H), 2.38 (s, 3H), 0.96 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.7, 172.0, 163.5, 149.8, 145.0, 135.9, 135.5, 131.8, 129.4, 129.3, 129.1, 128.4, 126.9, 126.7, 108.5, 69.6, 60.2, 46.0, 42.6, 21.7, 13.8; HRMS-ESI calcd for $C_{29}H_{26}ClN_2O_6S$ $[M + H]^+$ 565.1195, found 565.1199.

# 4. ORTEP Drawings for 3a and 5a

**Table S2.** Crystal data and structure refinement for **3a**

| | |
|---|---|
| Identification code | **3a** |
| Empirical formula | $C_{25}H_{19}N_3O_4$ |
| Formula weight | 425.43 |
| Temperature | 173(2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Monoclinic, Pc |
| Unit cell dimensions | a = 11.697(2) Å, α = 90°. |
| | b = 14.397(3) Å, β = 104.09(3)°. |
| | c = 26.731(7) Å, γ = 90°. |
| Volume | 4366.1 (16) $Å^3$ |
| Z, Calculated density | 8, 1.294 $Mg/m^3$ |
| Absorption coefficient | 0.089 $mm^{-1}$ |
| F(000) | 1776 |
| Crystal size | 0.20 x 0.18 x 0.12 $mm^3$ |
| Theta range for data collection | 1.57 to 27.91°. |
| Limiting indices | -15<=h<=15, -17<=k<=18, -35<=l<=35 |
| Reflections collected / unique | 43094 / 19506 [R(int) = 0.0790] |
| Completeness to the θ = 25.02° | 99.7 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9893 and 0.9823 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 19506 / 60 / 1173 |
| Goodness-of-fit on $F^2$ | 0.994 |
| Final R indices[I>2σ(I)] | R1 = 0.0579, wR2 = 0.1229 |
| R indices (all data) | R1 = 0.0842, wR2 = 0.1372 |
| Absolute structure parameter | 0.1(8) |
| Extinction coefficient | 0.0203(6) |
| Largest diff. peak and hole | 0.485 and -0.319 e. $Å^{-3}$ |

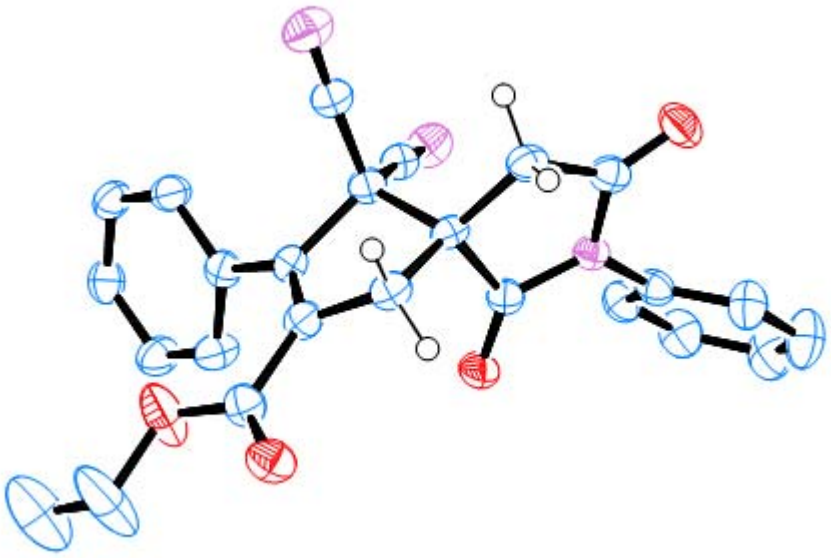


**Figure S1**. ORTEP Drawing for **3a**

**Table S3.** Crystal data and structure refinement for **5a**

| | |
|---|---|
| Identification code | **5a** |
| Empirical formula | $C_{29}H_{26}N_2O_6S$ |
| Formula weight | 530.58 |
| Temperature | 113(2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Monoclinic, P2(1)/n |
| Unit cell dimensions | a = 18.614(4) Å, α = 90°. |
| | b = 8.3550(17) Å, β = 116.82(3)°. |
| | c = 18.861(4) Å, γ = 90°. |
| Volume | 2617.6(9) $Å^3$ |
| Z, Calculated density | 4, 1.346 $Mg/m^3$ |
| Absorption coefficient | 0.171 $mm^{-1}$ |
| F(000) | 1112 |
| Crystal size | 0.20 x 0.18 x 0.12 $mm^3$ |
| Theta range for data collection | 1.28 to 27.91°. |
| Limiting indices | -24<=h<=24, -9<=k<=10, -24<=l<=24 |
| Reflections collected / unique | 21094 / 6179 [R(int) = 0.0547] |
| Completeness to the θ = 27.91° | 98.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9798 and 0.9667 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 6179 / 0 /345 |
| Goodness-of-fit on $F^2$ | 1.025 |
| Final R indices[I>2σ(I)] | R1 = 0.0468, wR2 = 0.1142 |
| R indices (all data) | R1 = 0.0587, wR2 = 0.1255 |
| Largest diff. peak and hole | 0.319 and -0.481 e. $Å^{-3}$ |

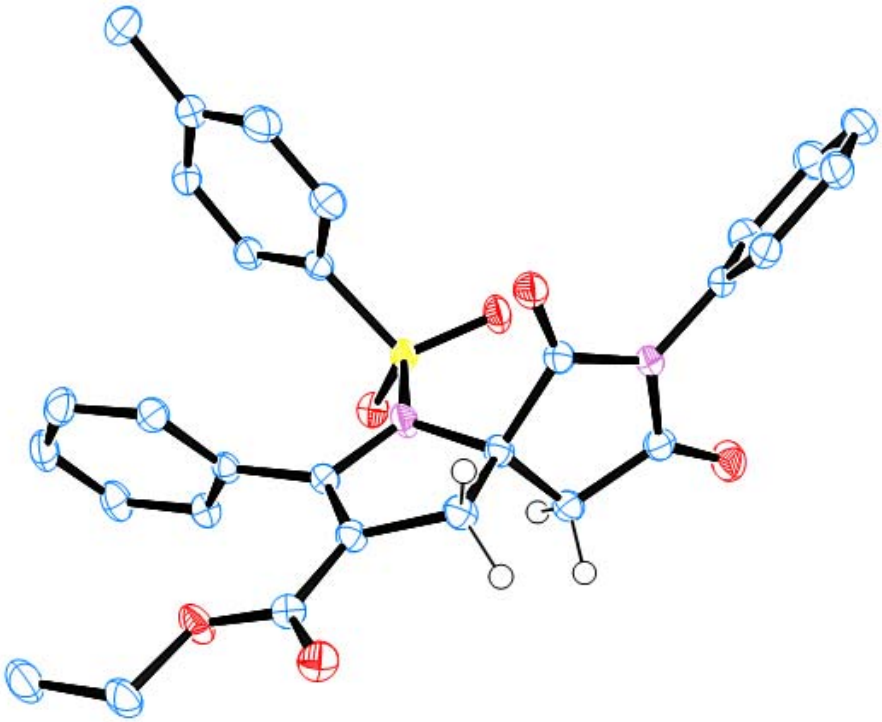
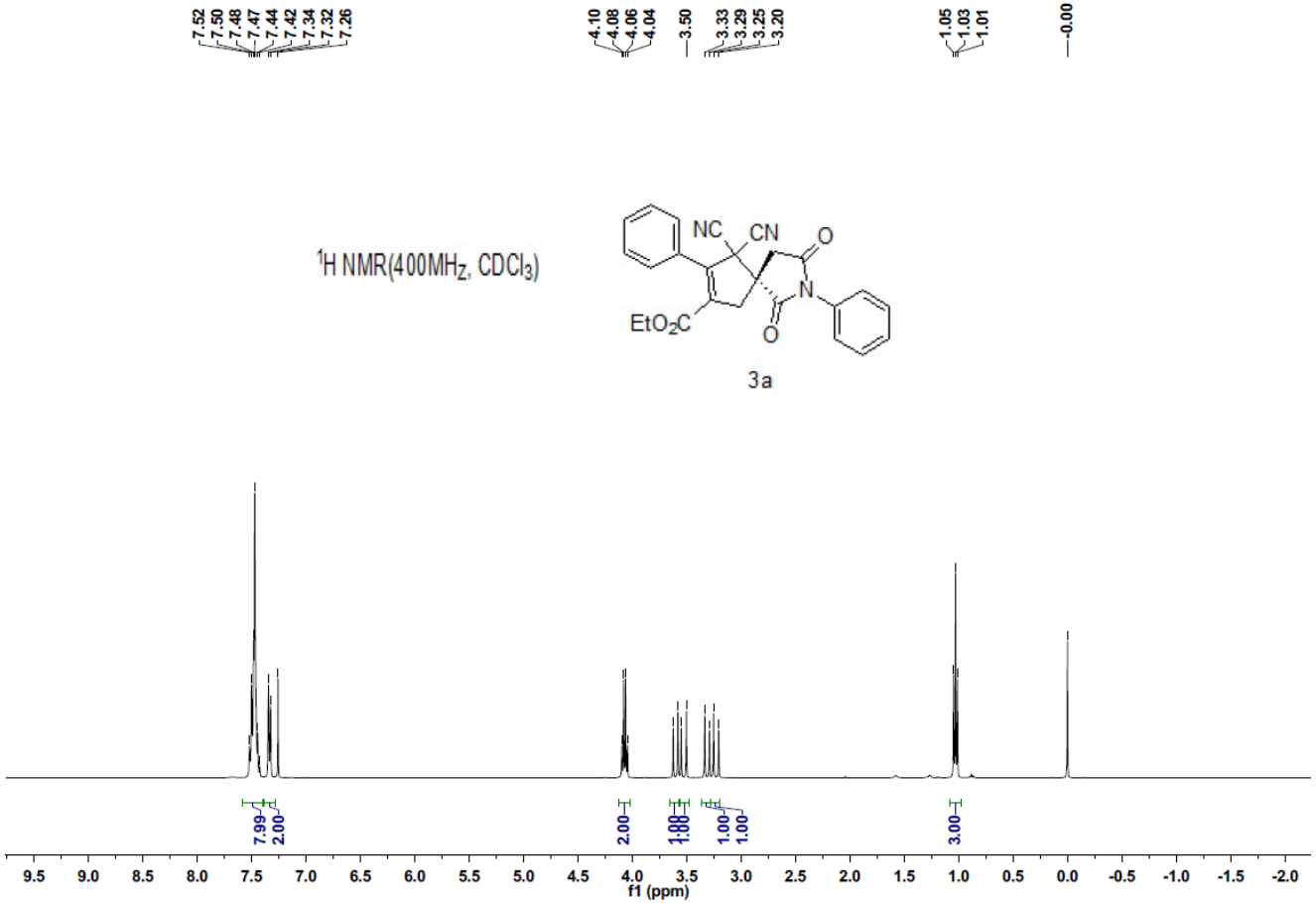
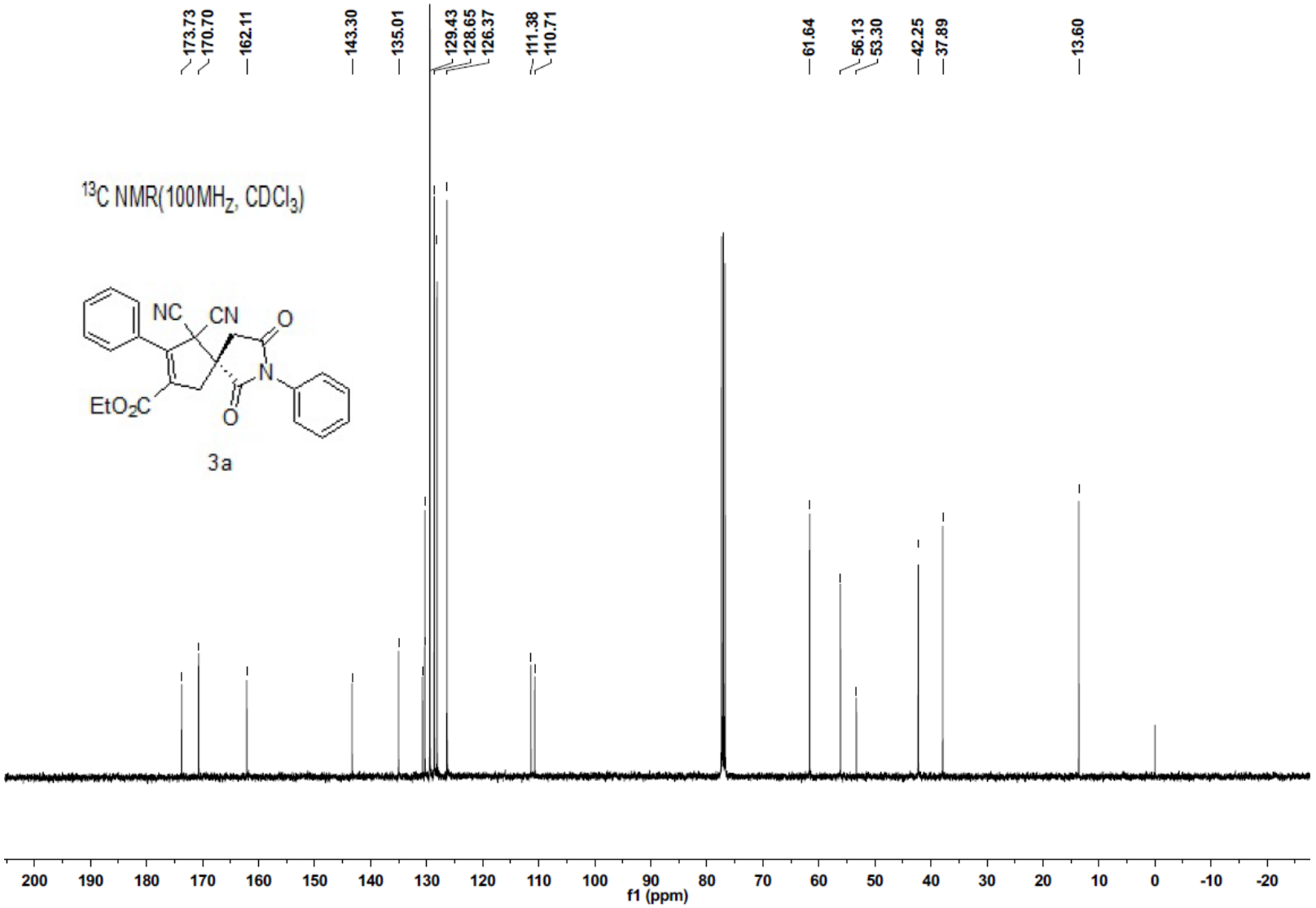
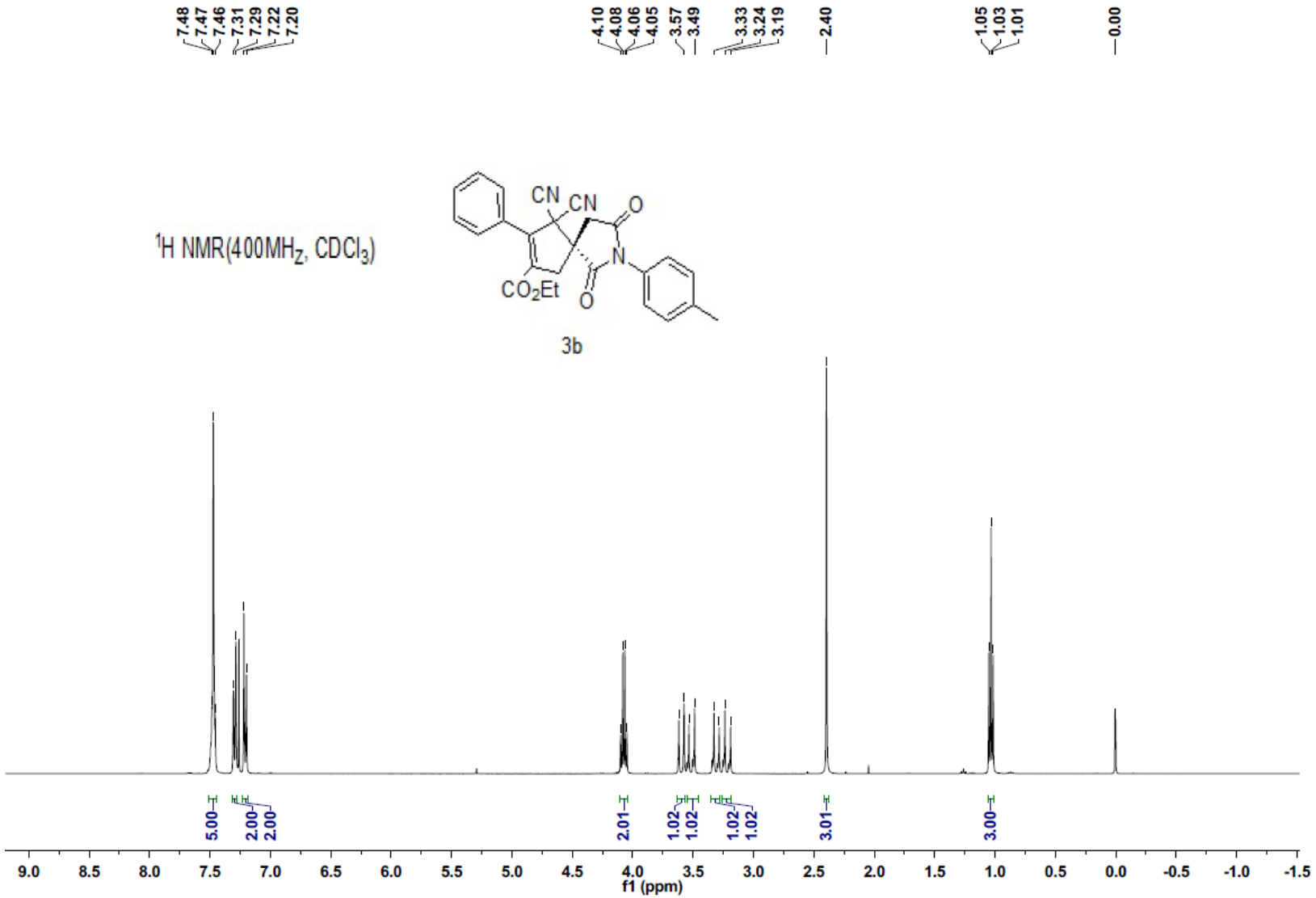


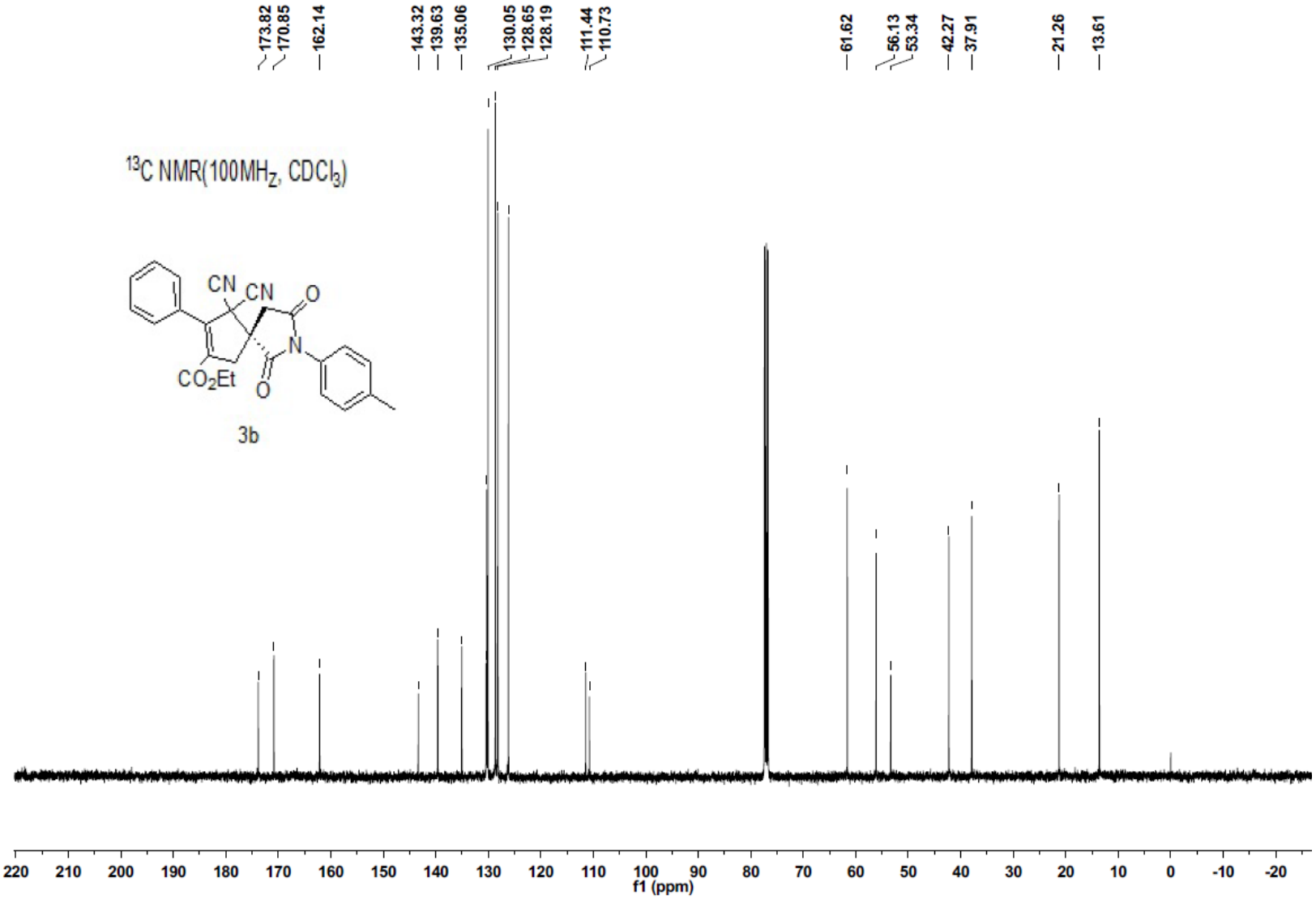
**Figure S2**. ORTEP Drawing for **5a**

## 5. NMR Spectra for Compounds 3 and 5




173.73
170.70
162.11
143.30
135.01
129.43
128.65
126.37
111.38
110.71
61.64
56.13
53.30
42.25
37.89
13.60
13C NMR(100MHz, CDCl3)
NC
CN
O
N
O
EtO2C
3a
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)


7.48
7.47
7.46
7.31
7.29
7.22
7.20
4.10
4.08
4.06
4.05
3.57
3.49
3.33
3.24
3.19
2.40
1.05
1.03
1.01
0.00
1H NMR(400MHz, CDCl3)
CN
CN
O
N
CO2Et
O
3b
5.00
2.00
2.00
2.01
1.02
1.02
1.02
1.02
3.01
3.00
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
-1.5
f1 (ppm)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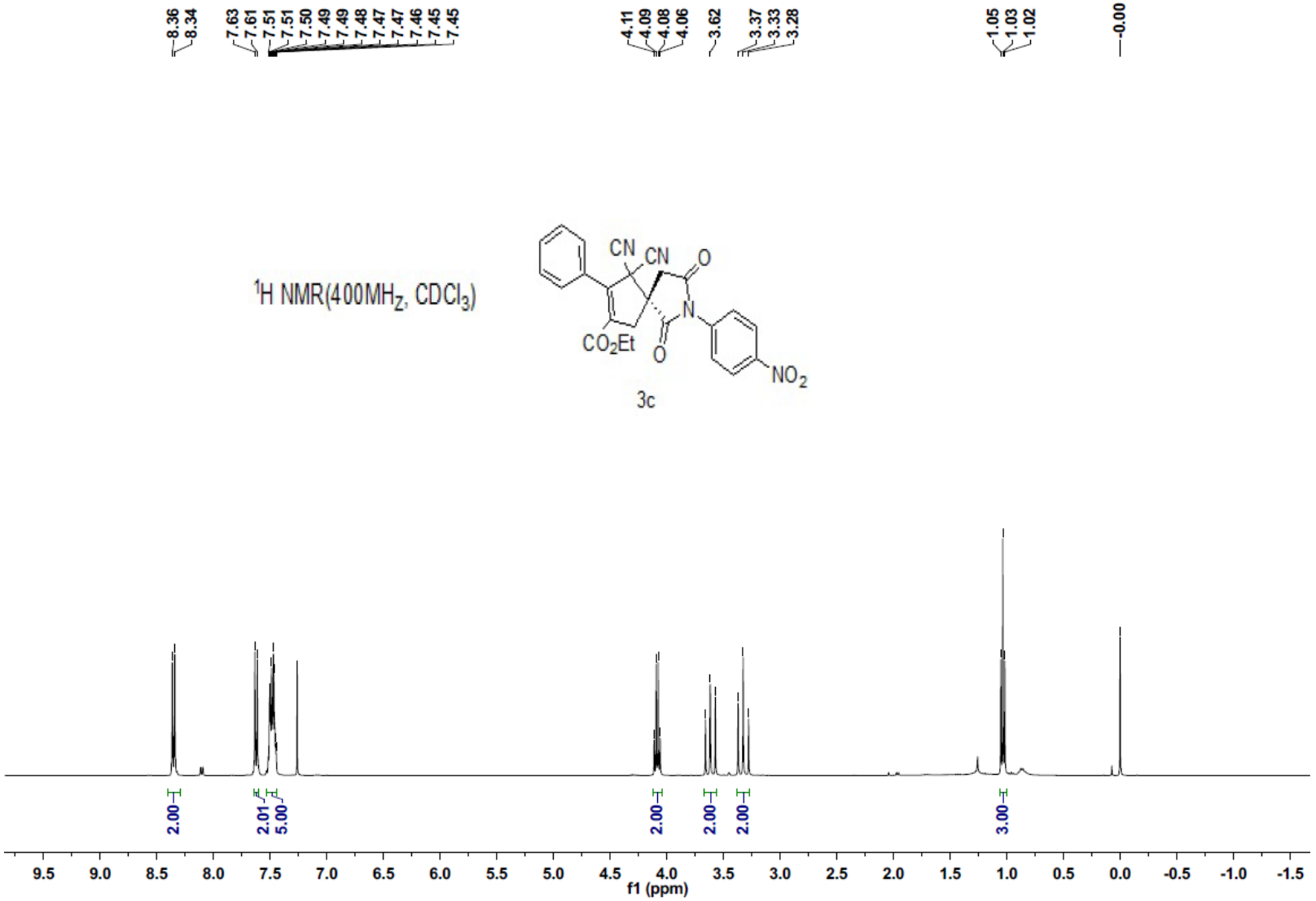
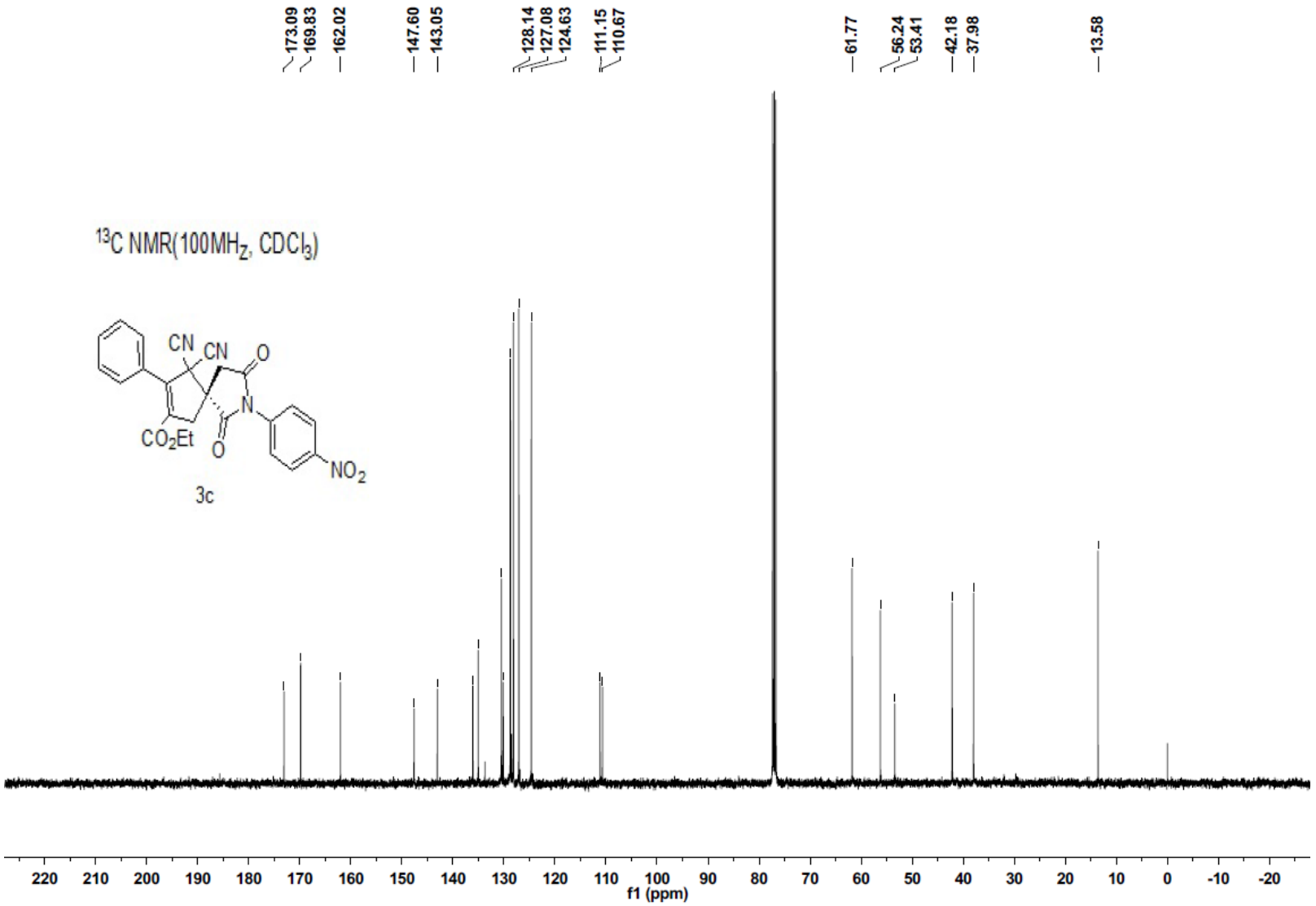
170.85
162.14
143.32
139.63
135.06
130.05
128.65
128.19
111.44
110.73
61.62
56.13
53.34
42.27
37.91
21.26
13.61
13C NMR(100MHz, CDCl3)
CN
CN
O
N
O
CO2Et
3b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


8.36
8.34
7.63
7.61
7.51
7.51
7.50
7.49
7.49
7.48
7.47
7.47
7.46
7.45
7.45
4.11
4.09
4.08
4.06
3.62
3.37
3.33
3.28
1.05
1.03
1.02
0.00
$^1$H NMR(400MH$_Z$, CDCl$_3$)
CN
CN
O
N
O
CO$_2$Et
NO$_2$
3c
2.00
2.01
5.00
2.00
2.00
2.00
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
-1.5
f1 (ppm)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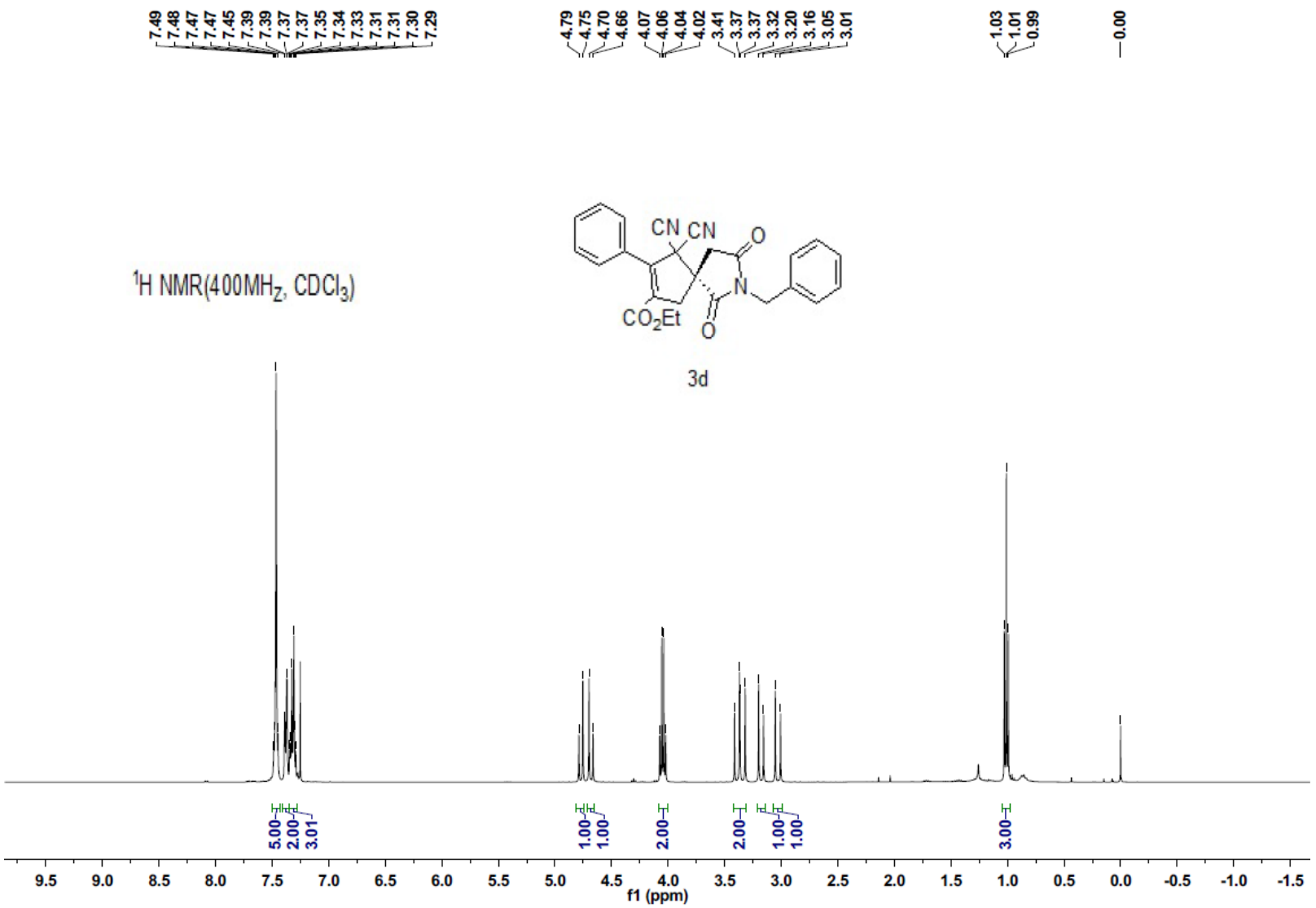
169.83
162.02
147.60
143.05
128.14
127.08
124.63
111.15
110.67
61.77
56.24
53.41
42.18
37.98
13.58
13C NMR(100MHz, CDCl3)
CN
CN
O
N
O
CO2Et
NO2
3c
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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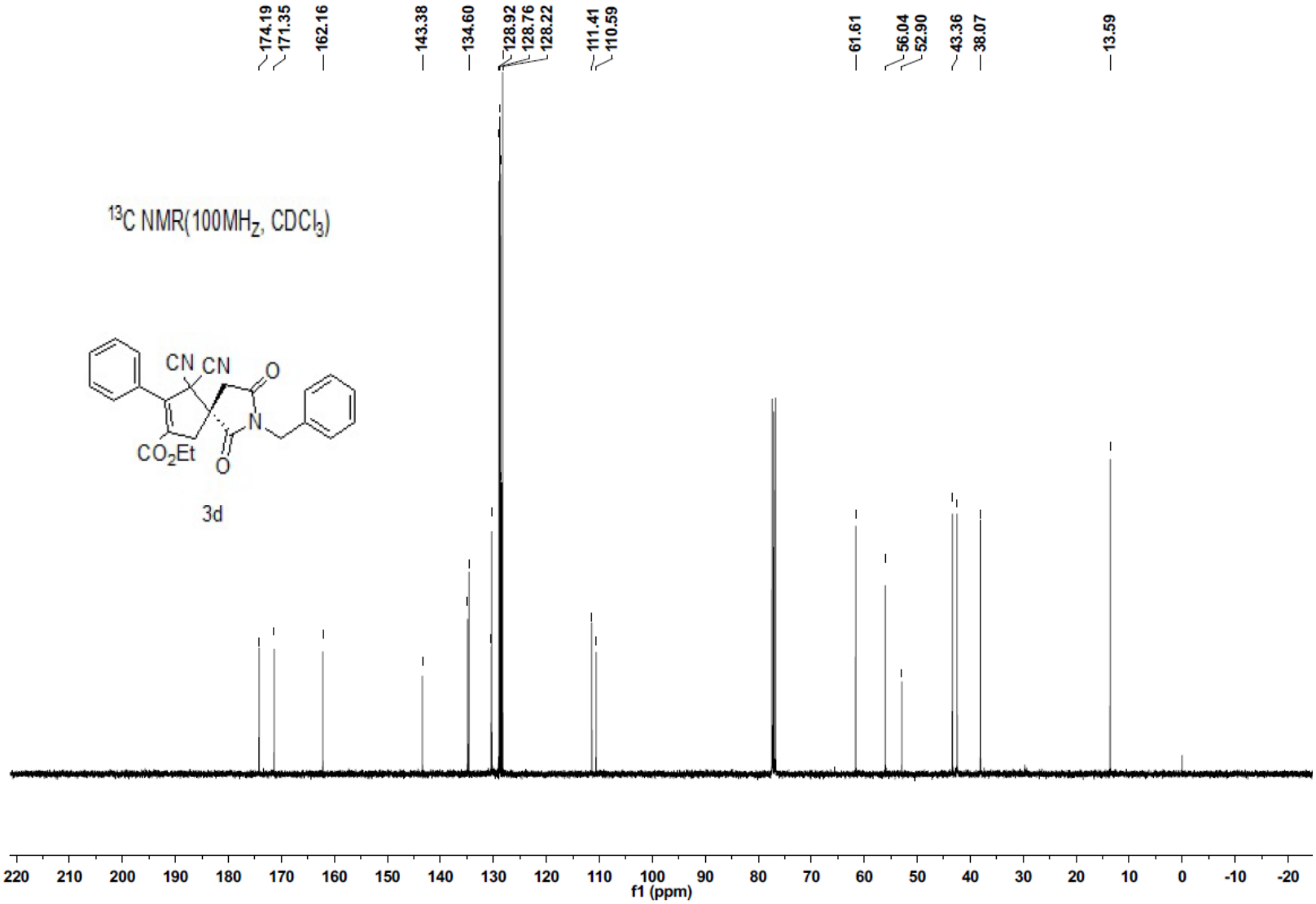
7.48
7.47
7.47
7.45
7.39
7.39
7.37
7.37
7.35
7.34
7.33
7.31
7.31
7.30
7.29
4.79
4.75
4.70
4.66
4.07
4.06
4.04
4.02
3.41
3.37
3.37
3.32
3.20
3.16
3.05
3.01
1.03
1.01
0.99
0.00
CN CN
O
N
CO2Et
O
1H NMR(400MHz, CDCl3)
3d
5.00
2.00
3.01
1.00
1.00
2.00
2.00
1.00
1.00
3.00
f1 (ppm)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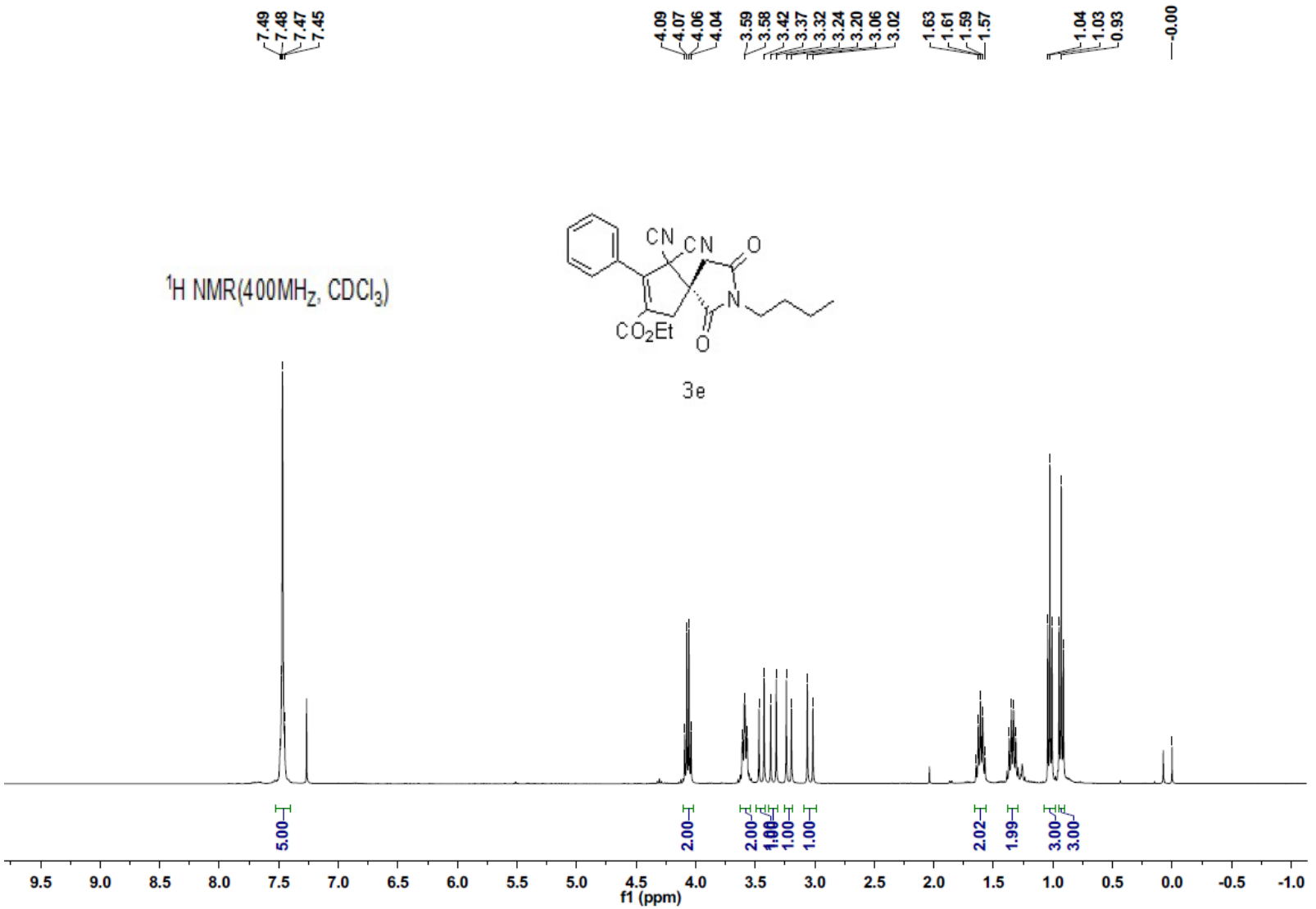
171.35
162.16
143.38
134.60
128.92
128.76
128.22
111.41
110.59
61.61
56.04
52.90
43.36
38.07
13.59
13C NMR(100MHz, CDCl3)
CN CN
O
N
CO2Et
O
3d
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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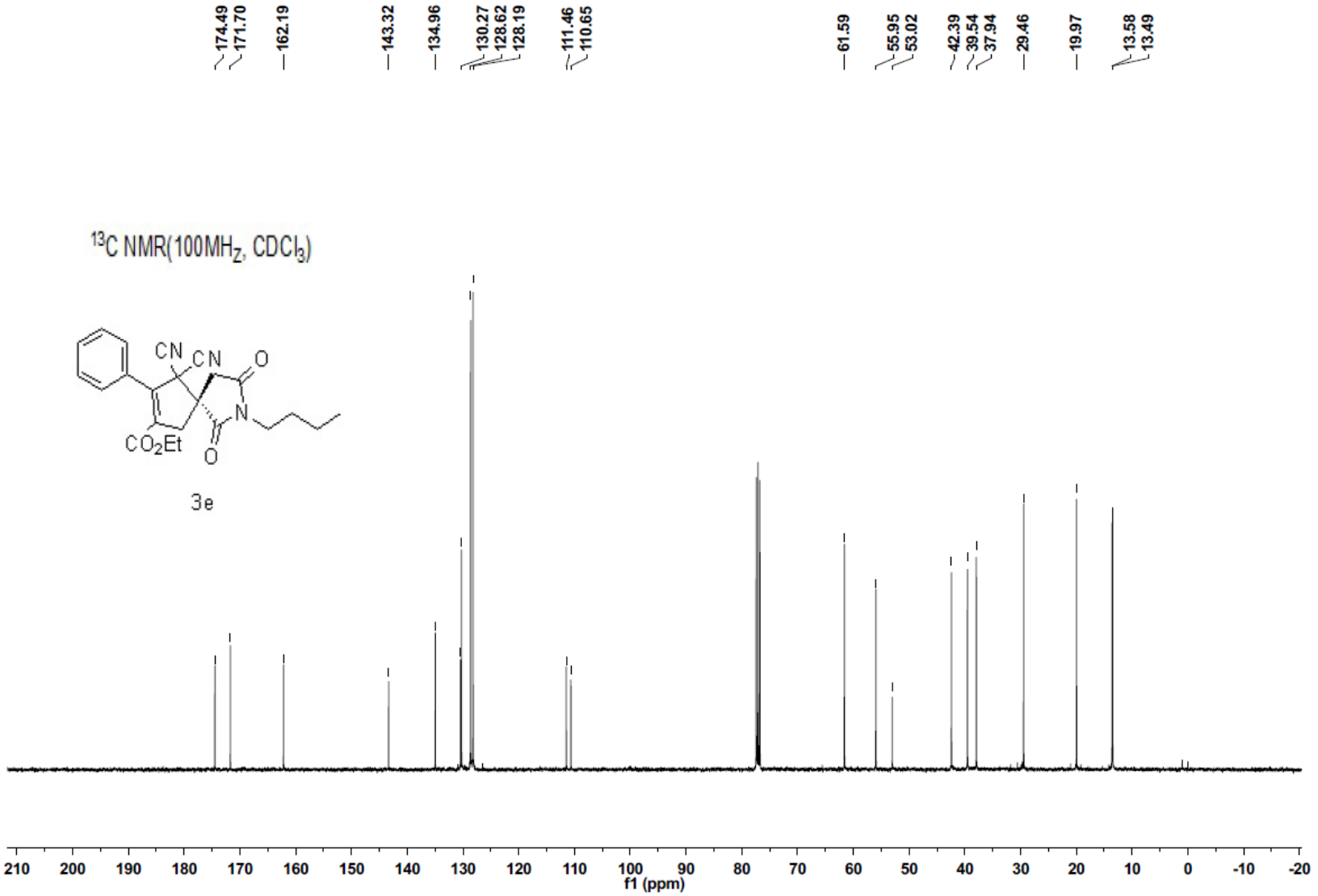
7.48
7.47
7.45
4.09
4.07
4.06
4.04
3.59
3.58
3.42
3.37
3.32
3.24
3.20
3.06
3.02
1.63
1.61
1.59
1.57
1.04
1.03
0.93
0.00
$^1$H NMR(400MH$_Z$, CDCl$_3$)
CN
CN
O
N
CO$_2$Et
O
3e
5.00
2.00
2.00
1.00
1.00
2.02
1.99
3.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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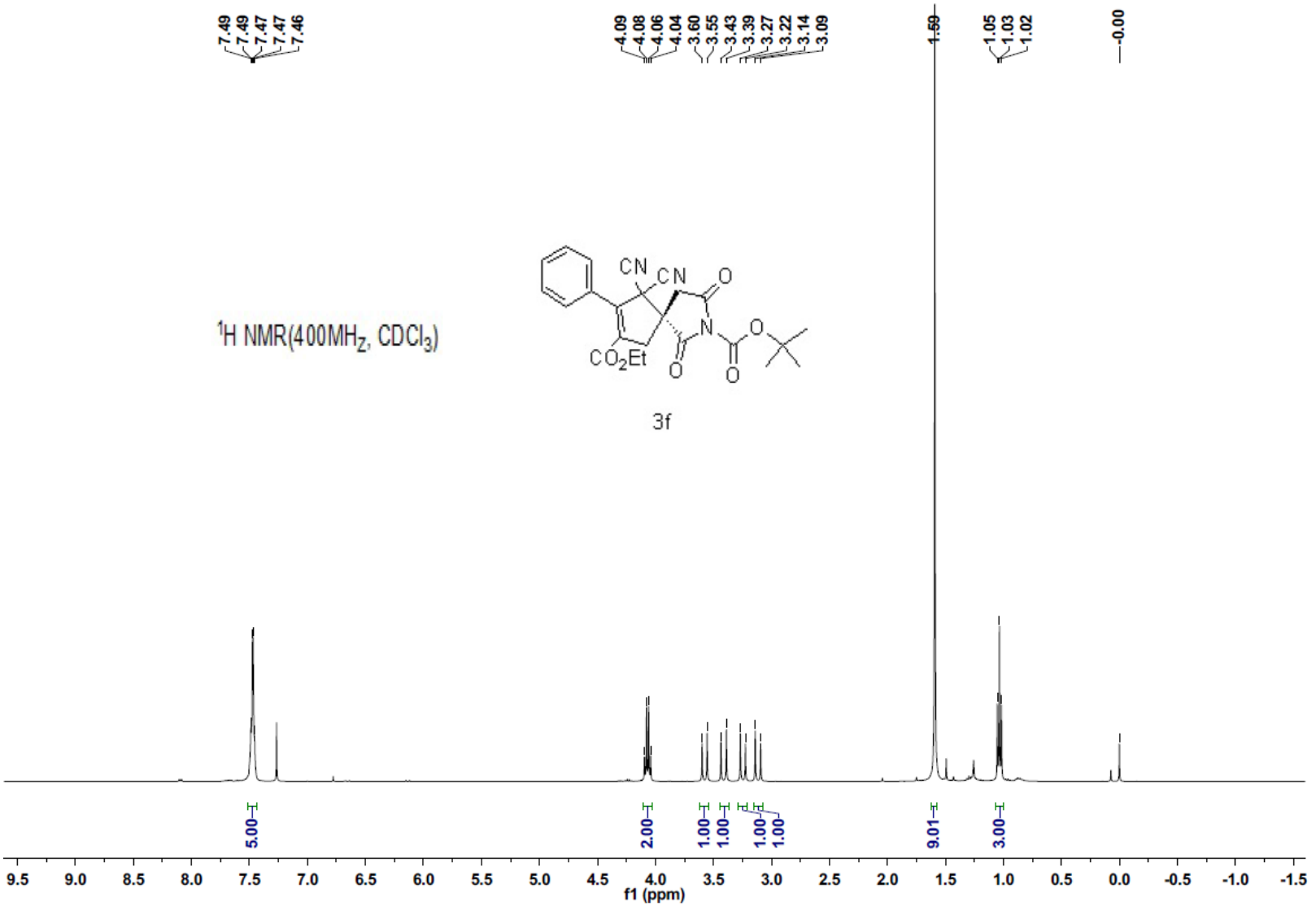
171.70
162.19
143.32
134.96
130.27
128.62
128.19
111.46
110.65
61.59
55.95
53.02
42.39
39.54
37.94
29.46
19.97
13.58
13.49
13C NMR(100MHz, CDCl3)
CN
CN
O
N
O
CO2Et
O
3e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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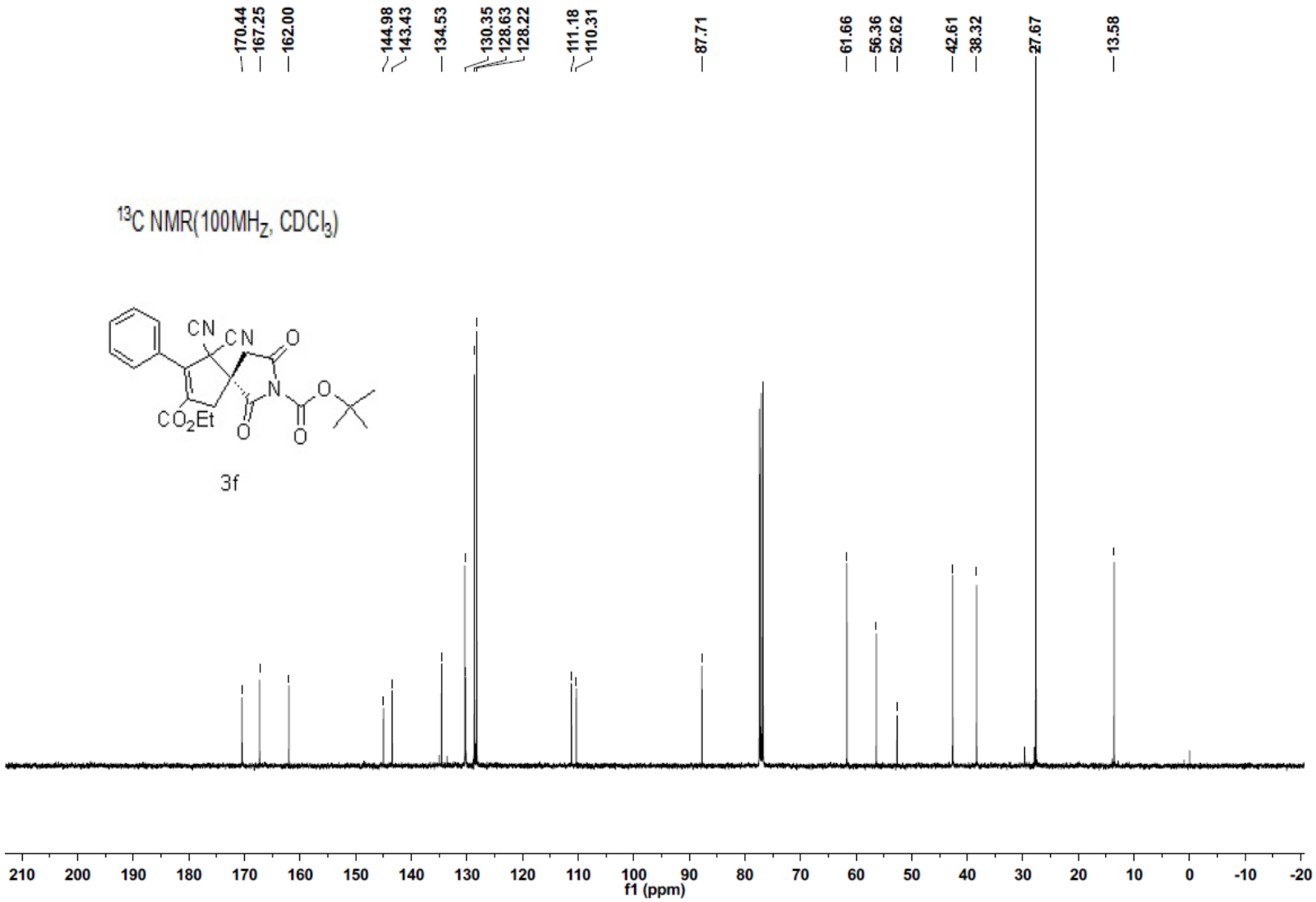
7.49
7.47
7.47
7.46
4.09
4.08
4.06
4.04
3.60
3.55
3.43
3.39
3.27
3.22
3.14
3.09
1.59
1.05
1.03
1.02
-0.00
$^1$H NMR(400MHz, CDCl$_3$)
CN
CN
O
N
O
O
CO$_2$Et
O
O
3f
5.00
2.00
1.00
1.00
1.00
1.00
9.01
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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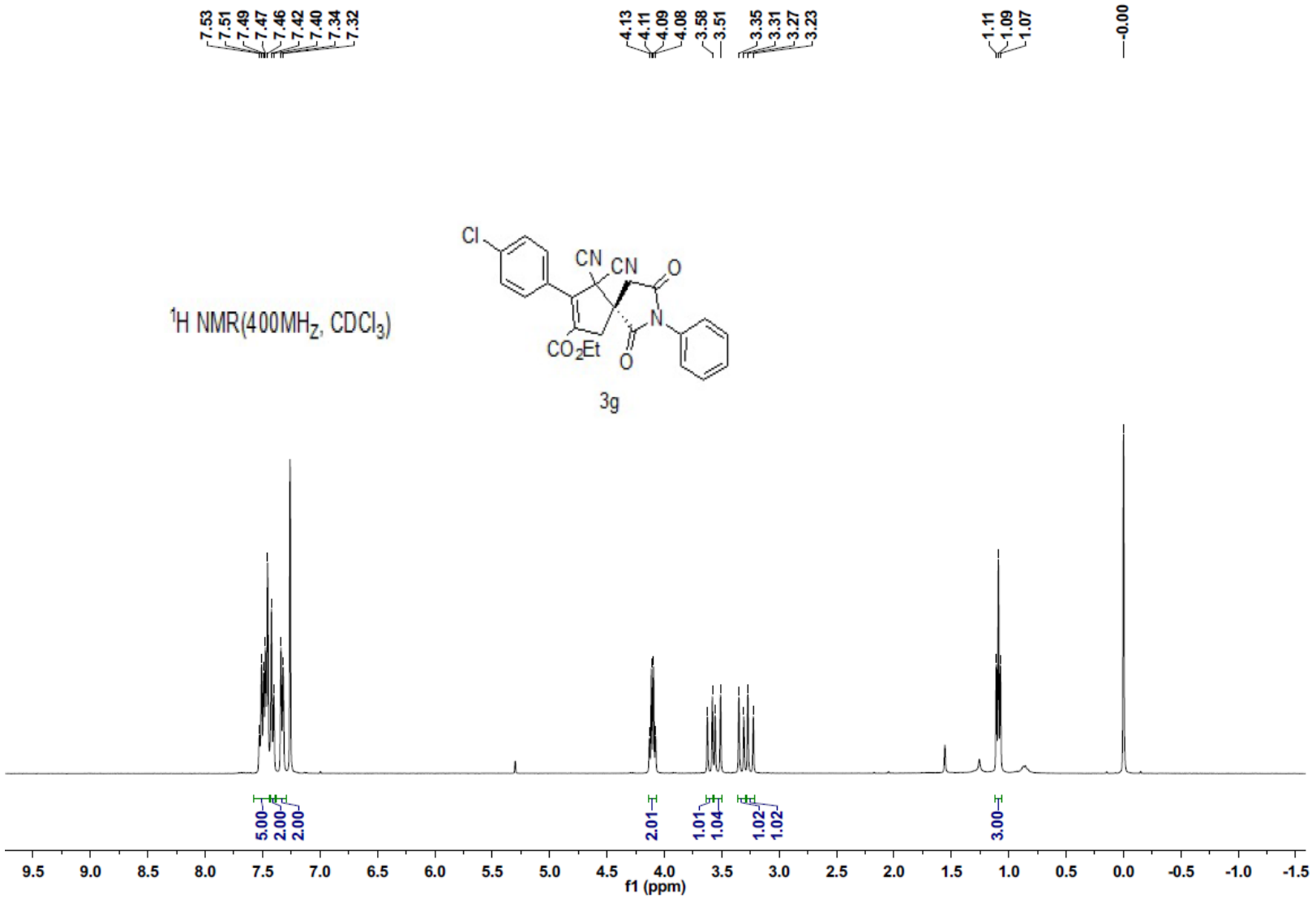
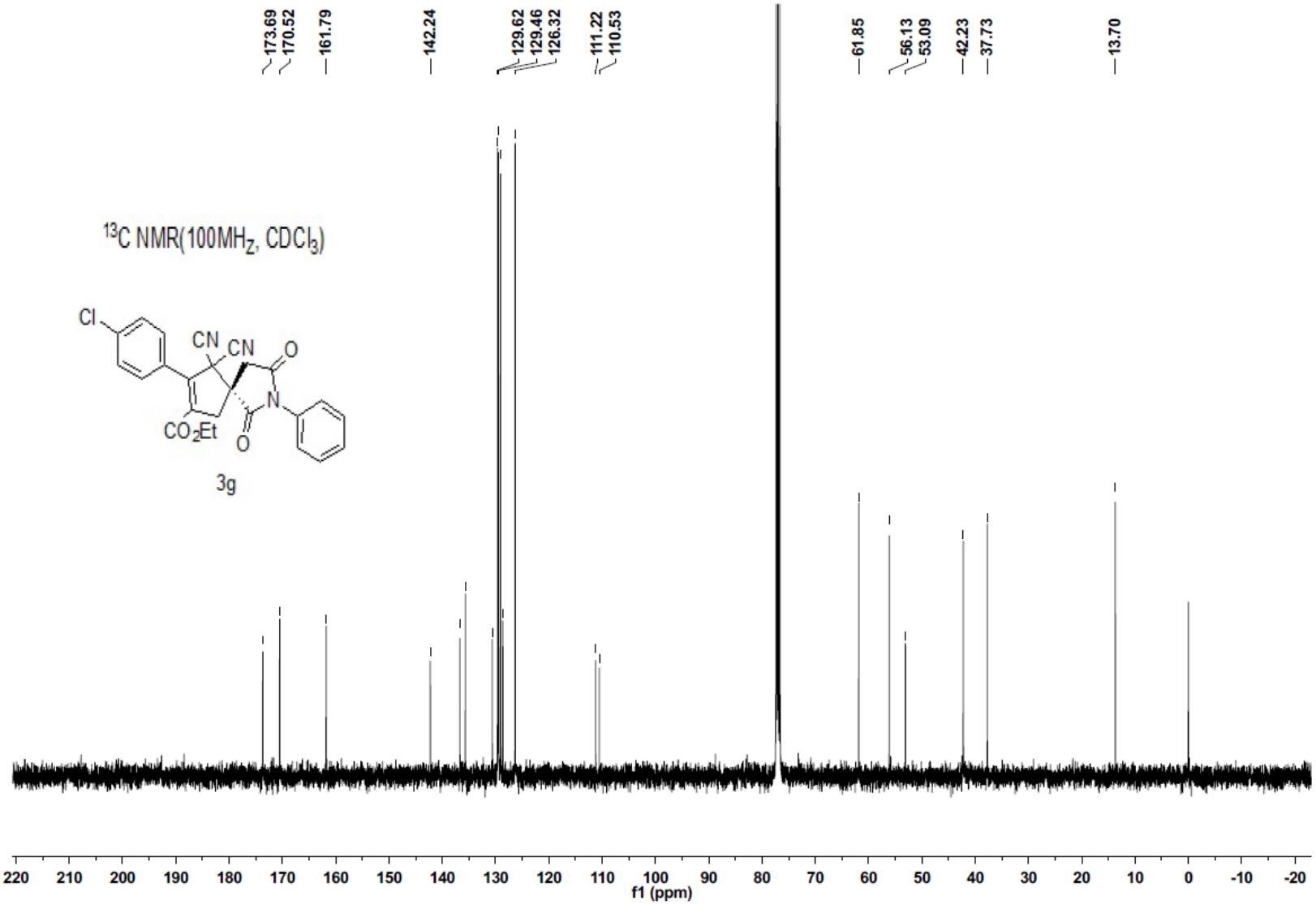
167.25
162.00
144.98
143.43
134.53
130.35
128.63
128.22
111.18
110.31
87.71
61.66
56.36
52.62
42.61
38.32
27.67
13.58
13C NMR(100MHz, CDCl3)
CN
CN
O
N
O
O
CO2Et
O
O
3f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


7.53
7.51
7.49
7.47
7.46
7.42
7.40
7.34
7.32
4.13
4.11
4.09
4.08
3.58
3.51
3.35
3.31
3.27
3.23
1.11
1.09
1.07
0.00
$^1$H NMR(400MH$_Z$, CDCl$_3$)
Cl
CN
CN
O
N
O
CO$_2$Et
O
3g
5.00
2.00
2.00
2.01
1.01
1.04
1.02
1.02
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
-1.5
f1 (ppm)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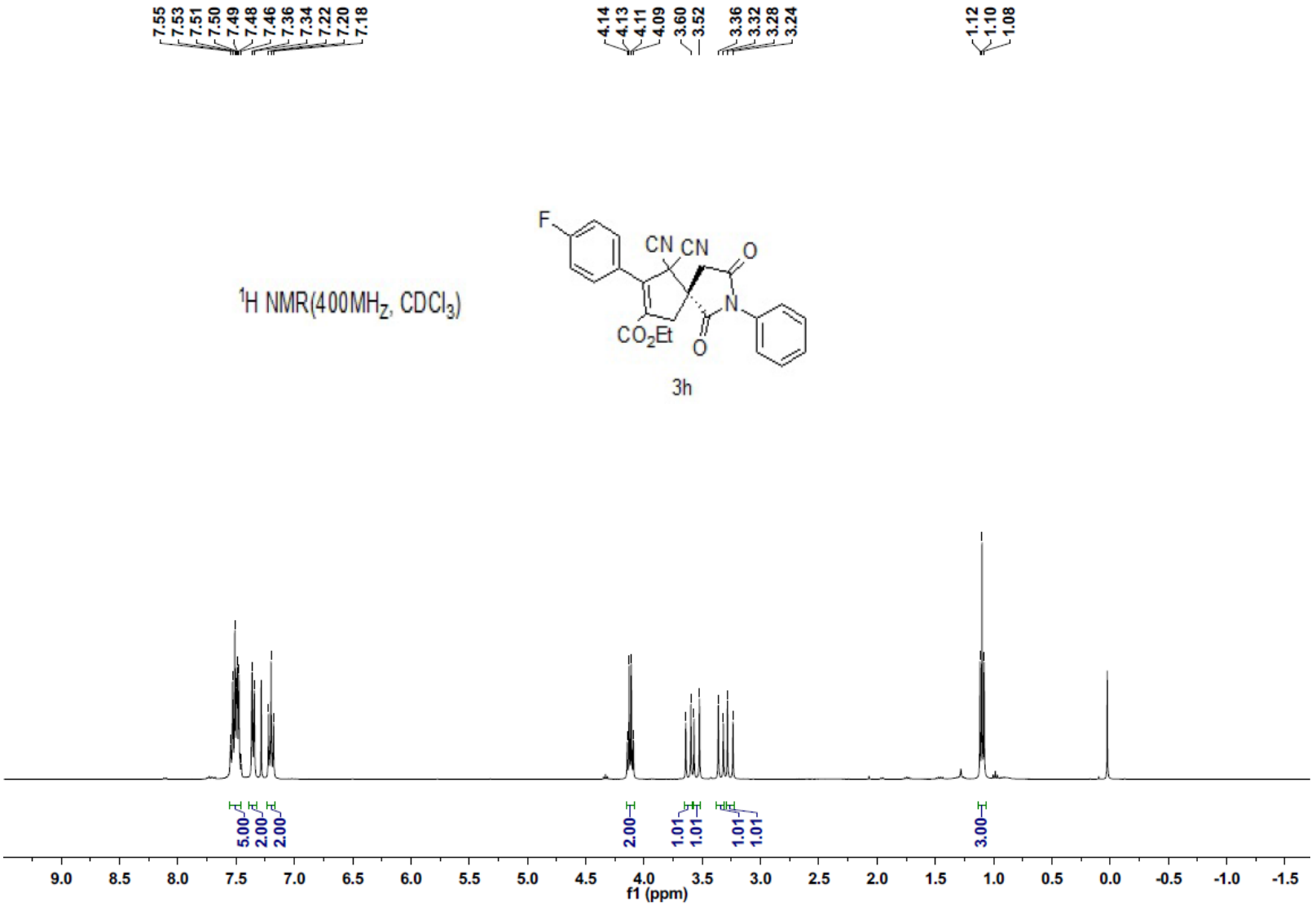
161.79
142.24
129.62
129.46
126.32
111.22
110.53
61.85
56.13
53.09
42.23
37.73
13.70
13C NMR(100MHz, CDCl3)
Cl
CN
CN
O
N
O
CO2Et
O
3g
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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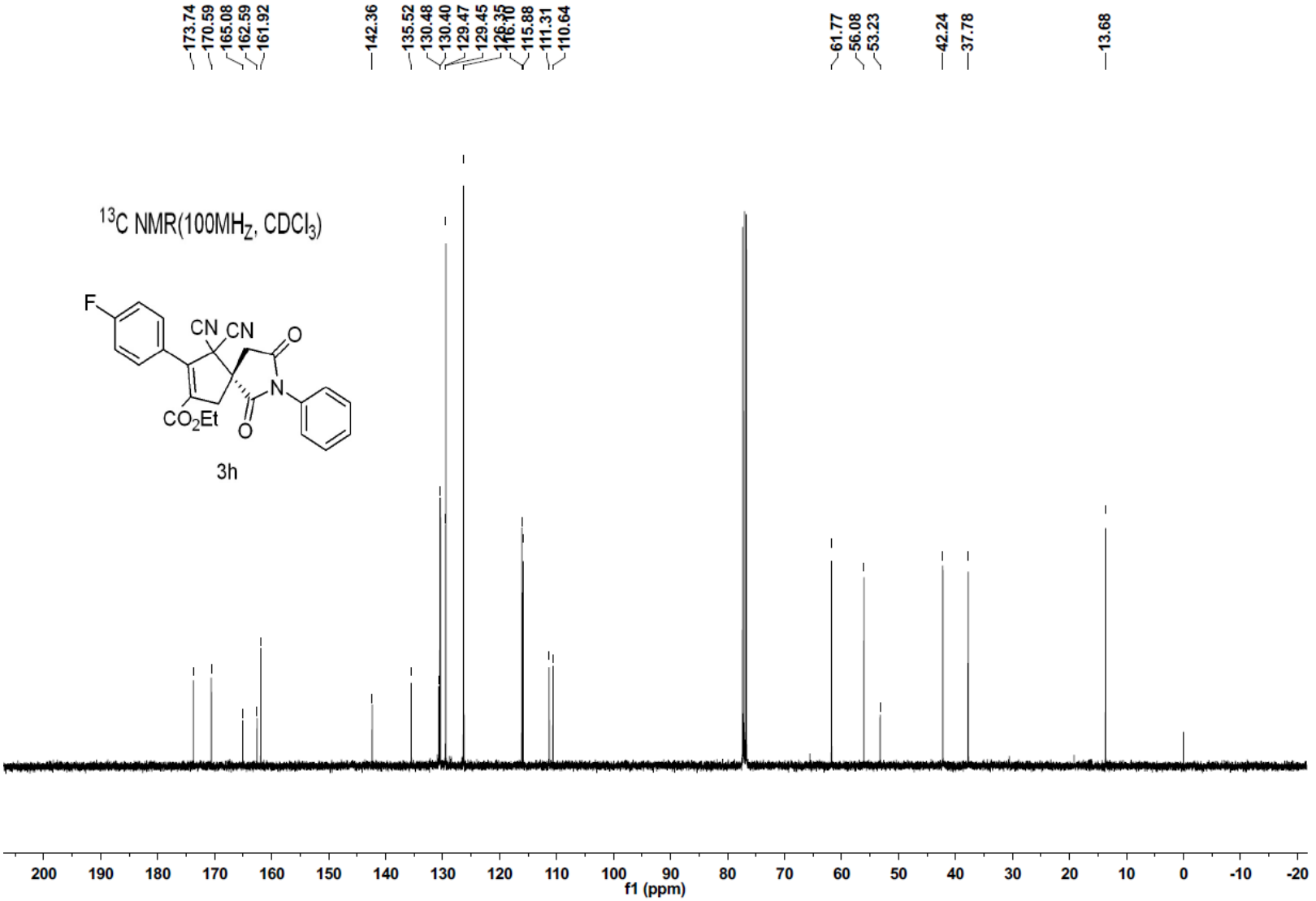
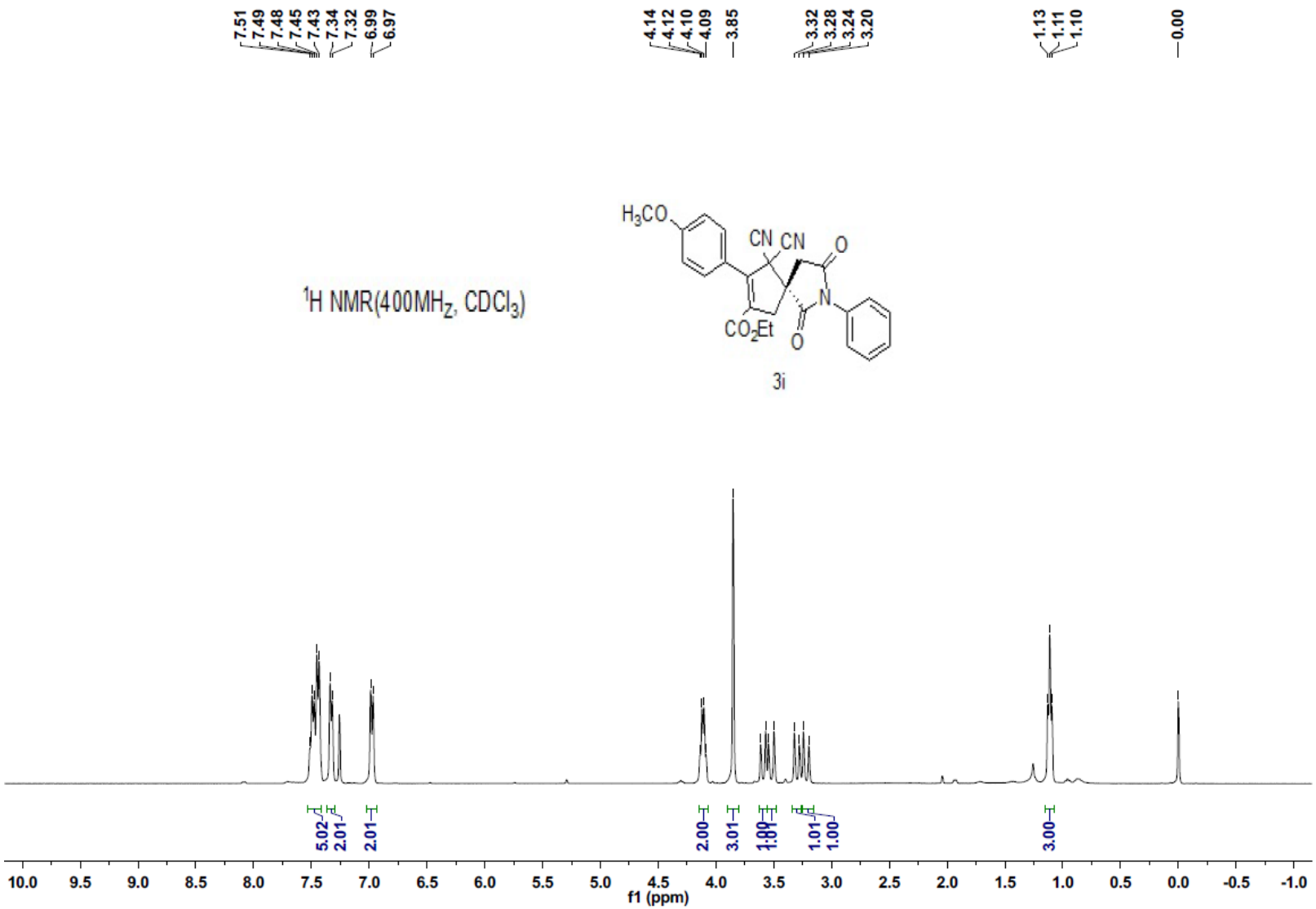
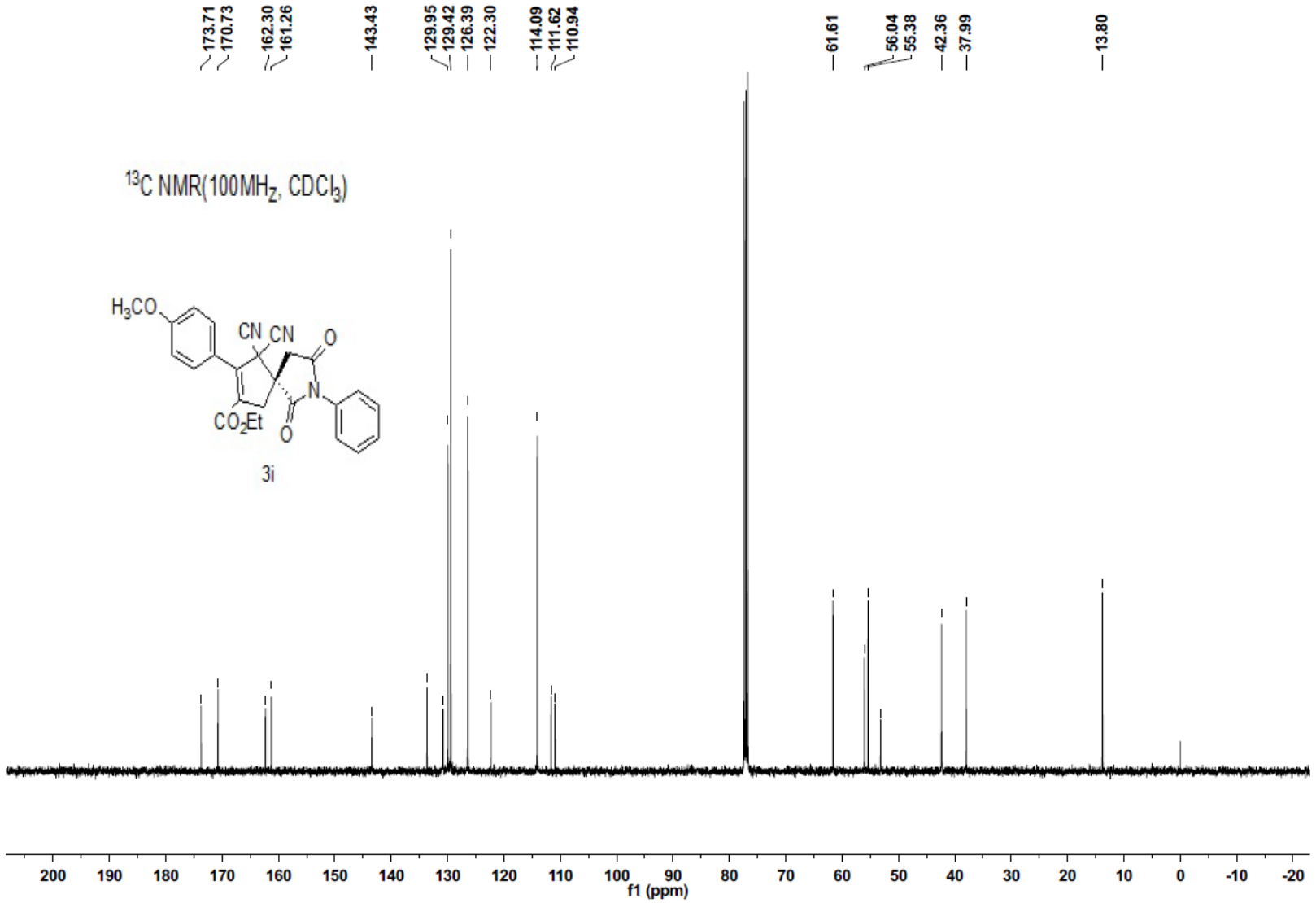
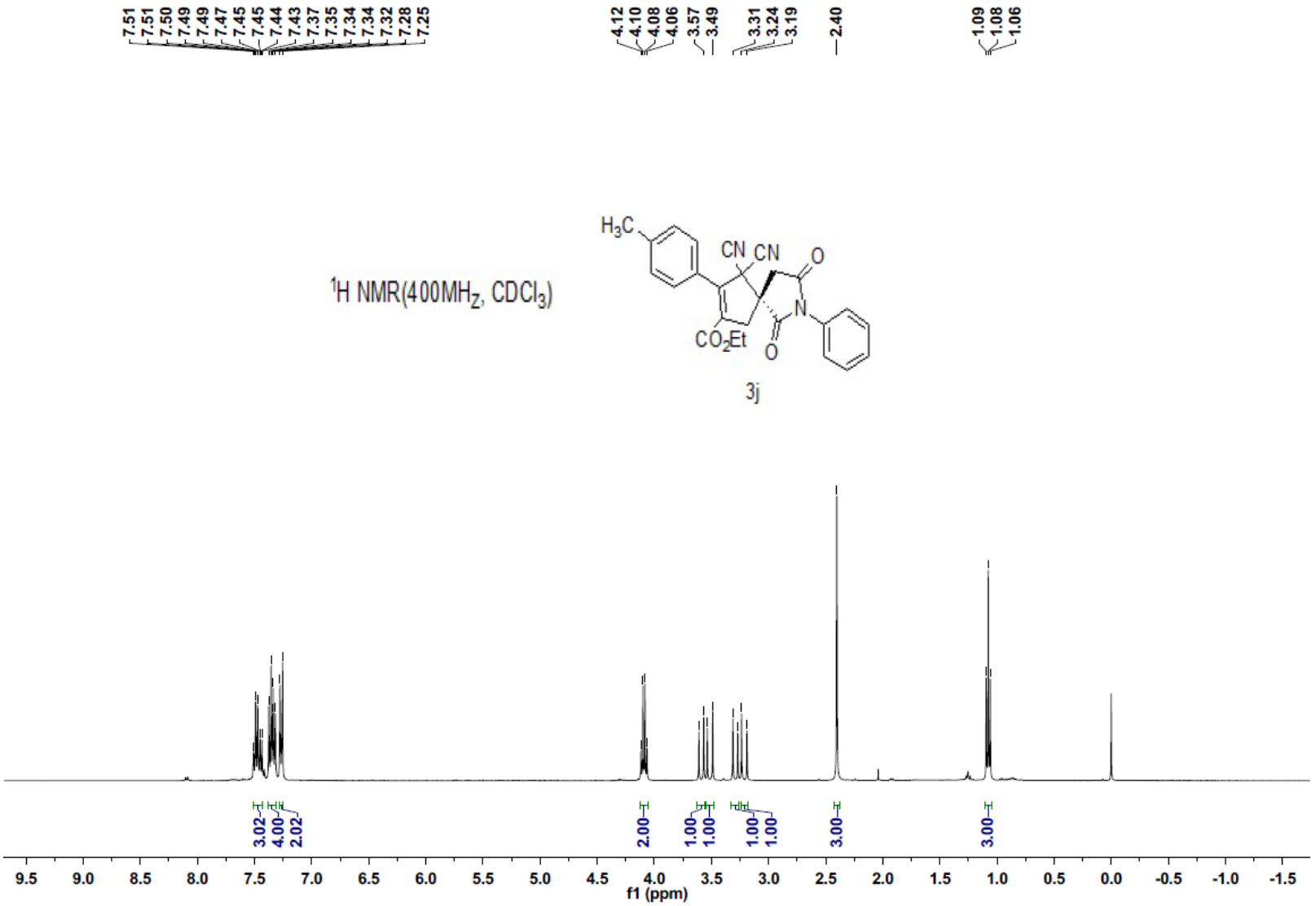
7.53
7.51
7.50
7.49
7.48
7.46
7.36
7.34
7.22
7.20
7.18
4.14
4.13
4.11
4.09
3.60
3.52
3.36
3.32
3.28
3.24
1.12
1.10
1.08
$^1$H NMR(400MH$_Z$, CDCl$_3$)
F
CN CN
O
N
CO$_2$Et
O
3h
5.00
2.00
2.00
2.00
1.01
1.01
1.01
1.01
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


173.74
170.59
165.08
162.59
161.92
142.36
135.52
130.48
130.40
129.47
129.45
115.88
111.31
110.64
61.77
56.08
53.23
42.24
37.78
13.68
13C NMR(100MHZ, CDCl3)
F
CN CN
O
N
O
CO2Et
O
3h
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)


7.51
7.49
7.48
7.45
7.43
7.34
7.32
6.99
6.97
4.14
4.12
4.10
4.09
3.85
3.32
3.28
3.24
3.20
1.13
1.11
1.10
0.00
$^1$H NMR(400MH$_Z$, CDCl$_3$)
H$_3$CO
CN
CN
O
N
CO$_2$Et
O
3i
5.02
2.01
2.01
2.00
3.01
1.00
1.00
1.01
1.00
3.00
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
-1.0
f1 (ppm)


173.71
170.73
162.30
161.26
143.43
129.95
129.42
126.39
122.30
114.09
111.62
110.94
61.61
56.04
55.38
42.36
37.99
13.80
13C NMR(100MHz, CDCl3)
H3CO
CN CN
O
N
CO2Et
O
3i
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)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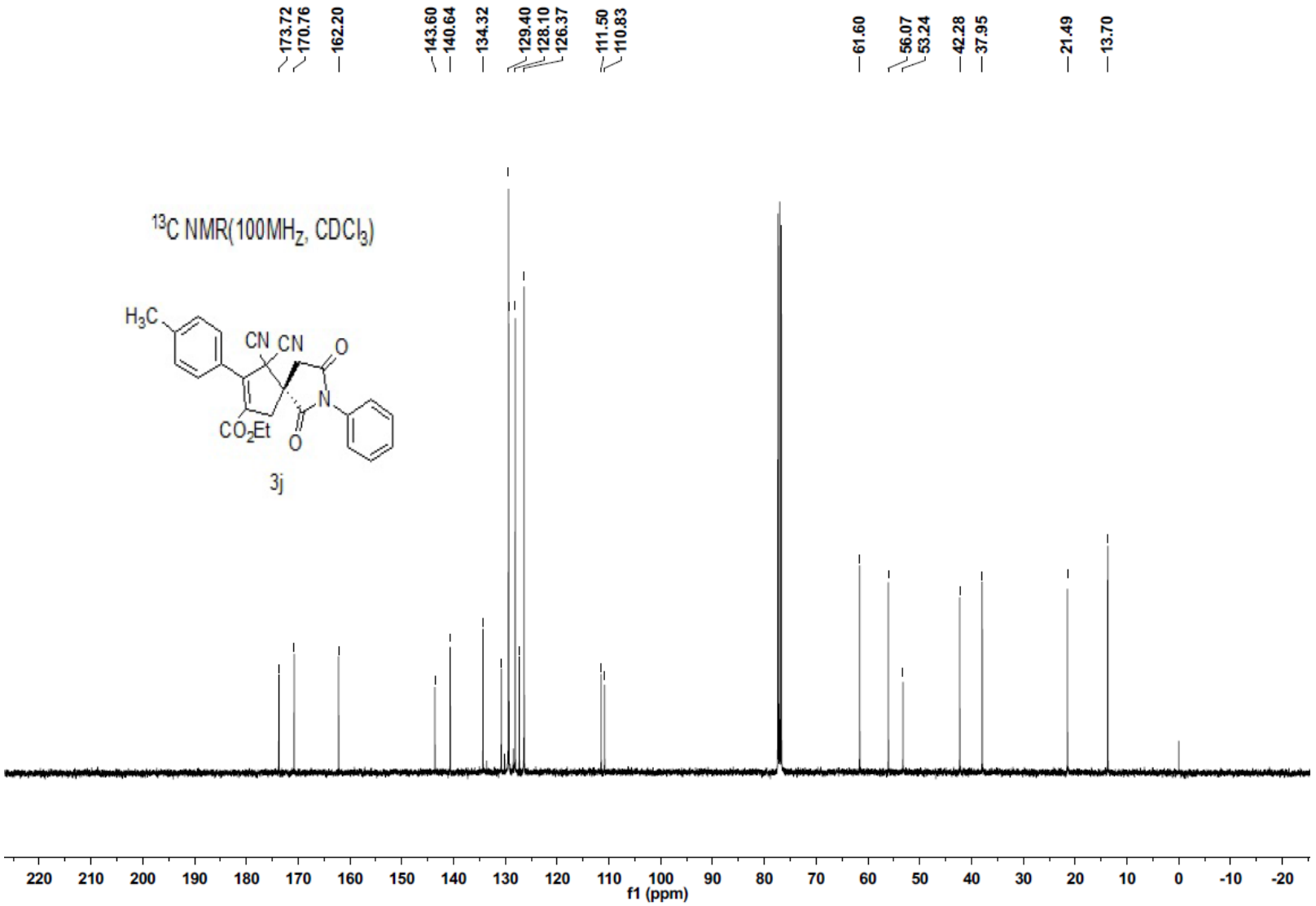
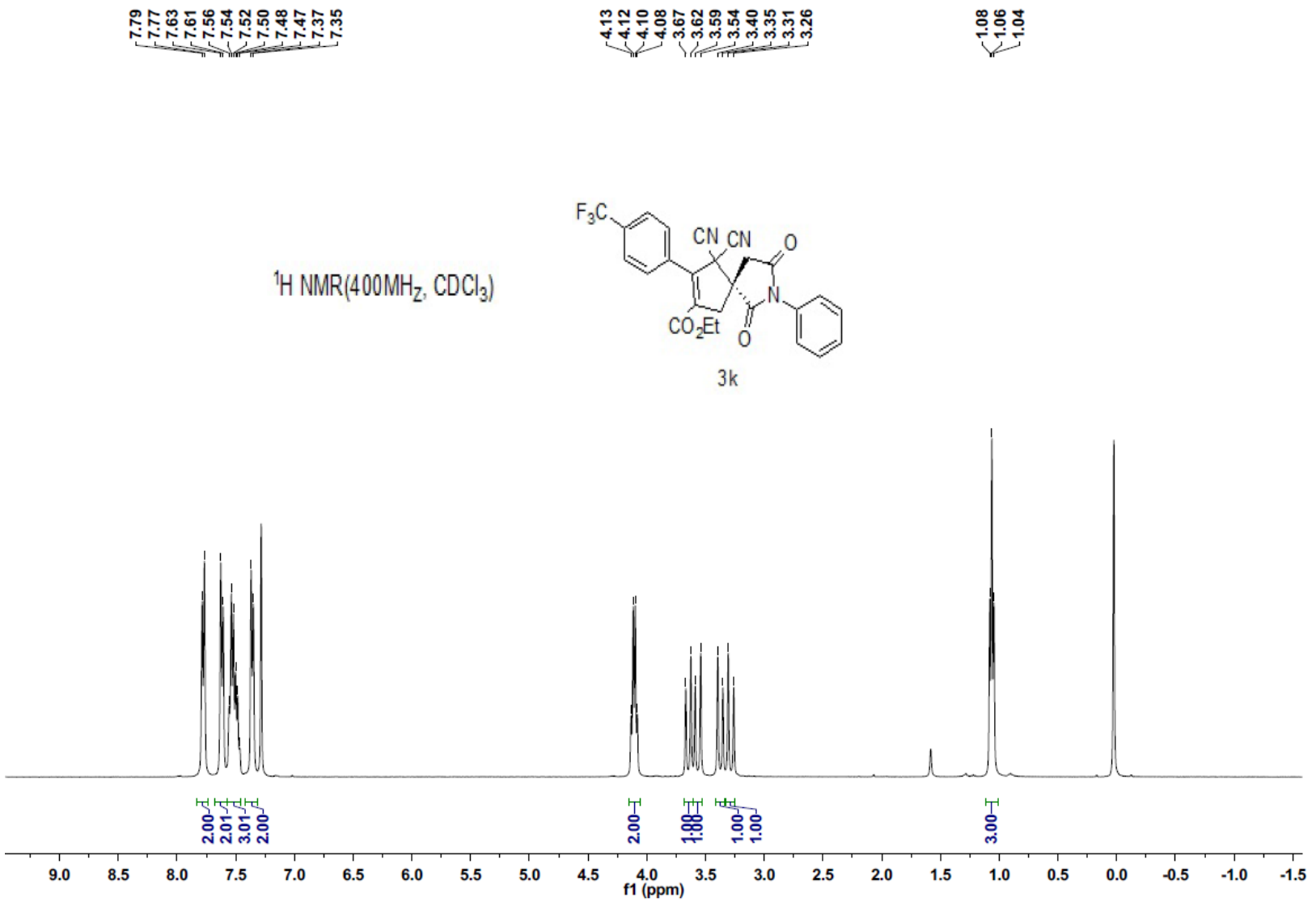
7.51
7.50
7.49
7.49
7.47
7.45
7.45
7.44
7.43
7.37
7.35
7.34
7.34
7.32
7.28
7.25
4.12
4.10
4.08
4.06
3.57
3.49
3.31
3.24
3.19
2.40
1.09
1.08
1.06
$^1$H NMR(400MH$_Z$, CDCl$_3$)
H$_3$C
CN CN
O
N
CO$_2$Et
O
3j
3.02
4.00
2.02
2.00
1.00
1.00
1.00
1.00
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


173.72
170.76
162.20
143.60
140.64
134.32
129.40
128.10
126.37
111.50
110.83
61.60
56.07
53.24
42.28
37.95
21.49
13.70
13C NMR(100MHz, CDCl3)
H3C
CN CN
O
N
CO2Et
O
3j
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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7.50
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7.47
7.37
7.35
4.13
4.12
4.10
4.08
3.67
3.62
3.59
3.54
3.40
3.35
3.31
3.26
1.08
1.06
1.04
$^1$H NMR(400MH$_Z$, CDCl$_3$)
F$_3$C
CN
CN
O
N
CO$_2$Et
O
3k
2.00
2.01
3.01
2.00
2.00
1.00
1.00
1.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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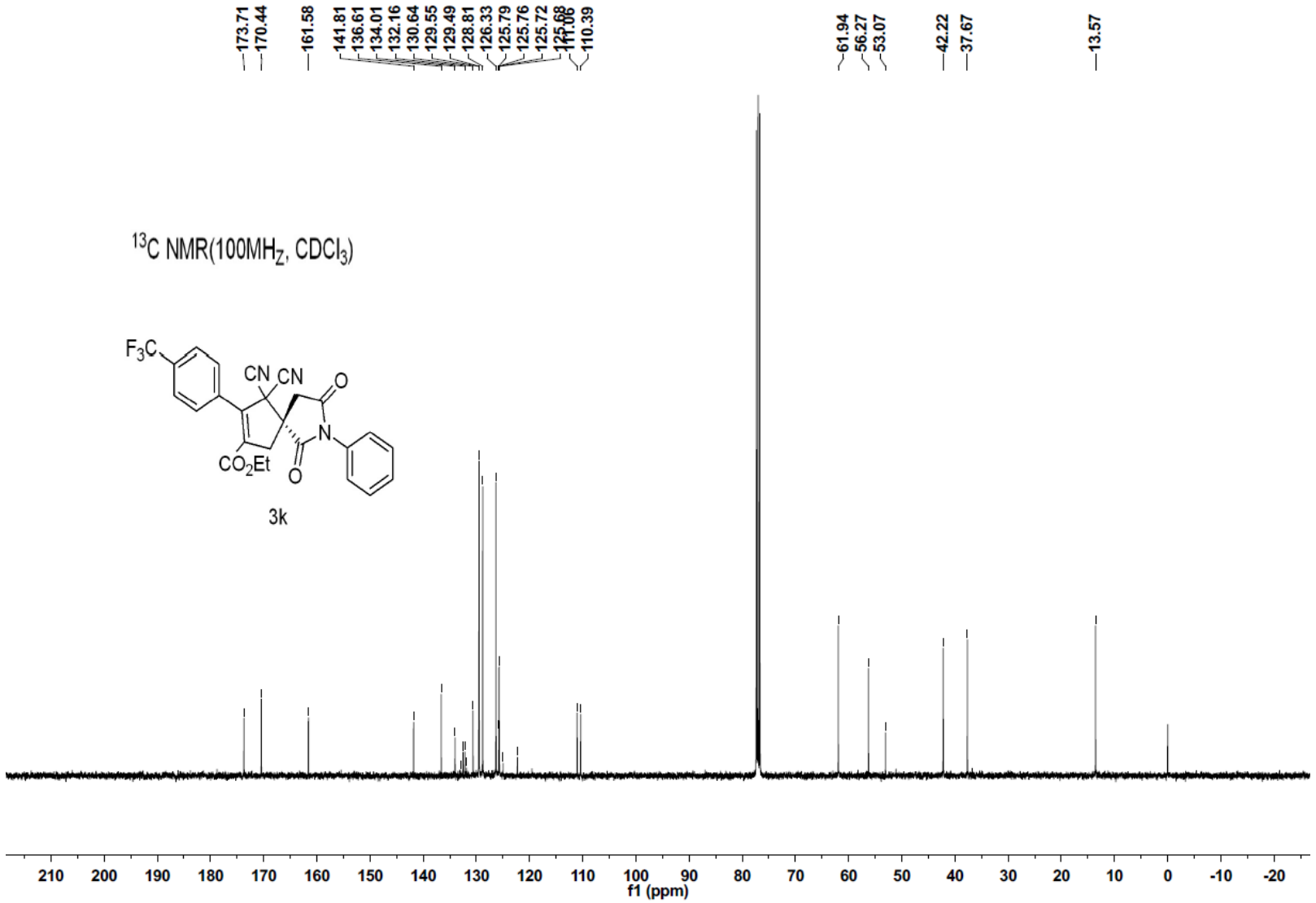
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)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130.64
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129.49
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126.33
125.79
125.76
125.72
125.68
111.06
110.39
61.94
56.27
53.07
42.22
37.67
13.57
13C NMR(100MHz, CDCl3)
F3C
CN CN
O
N
CO2Et
O
3k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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40
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10
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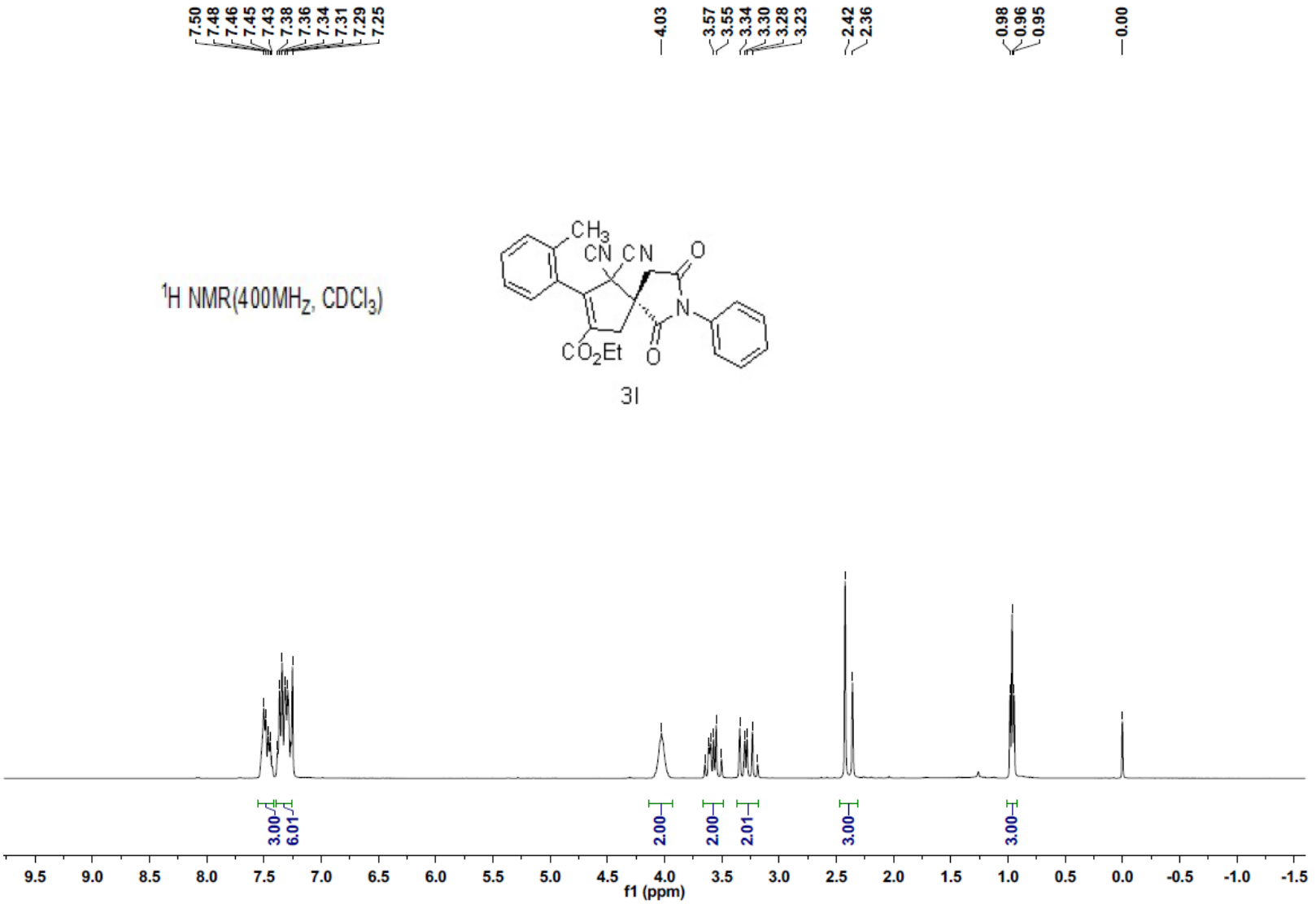
-20
f1 (ppm)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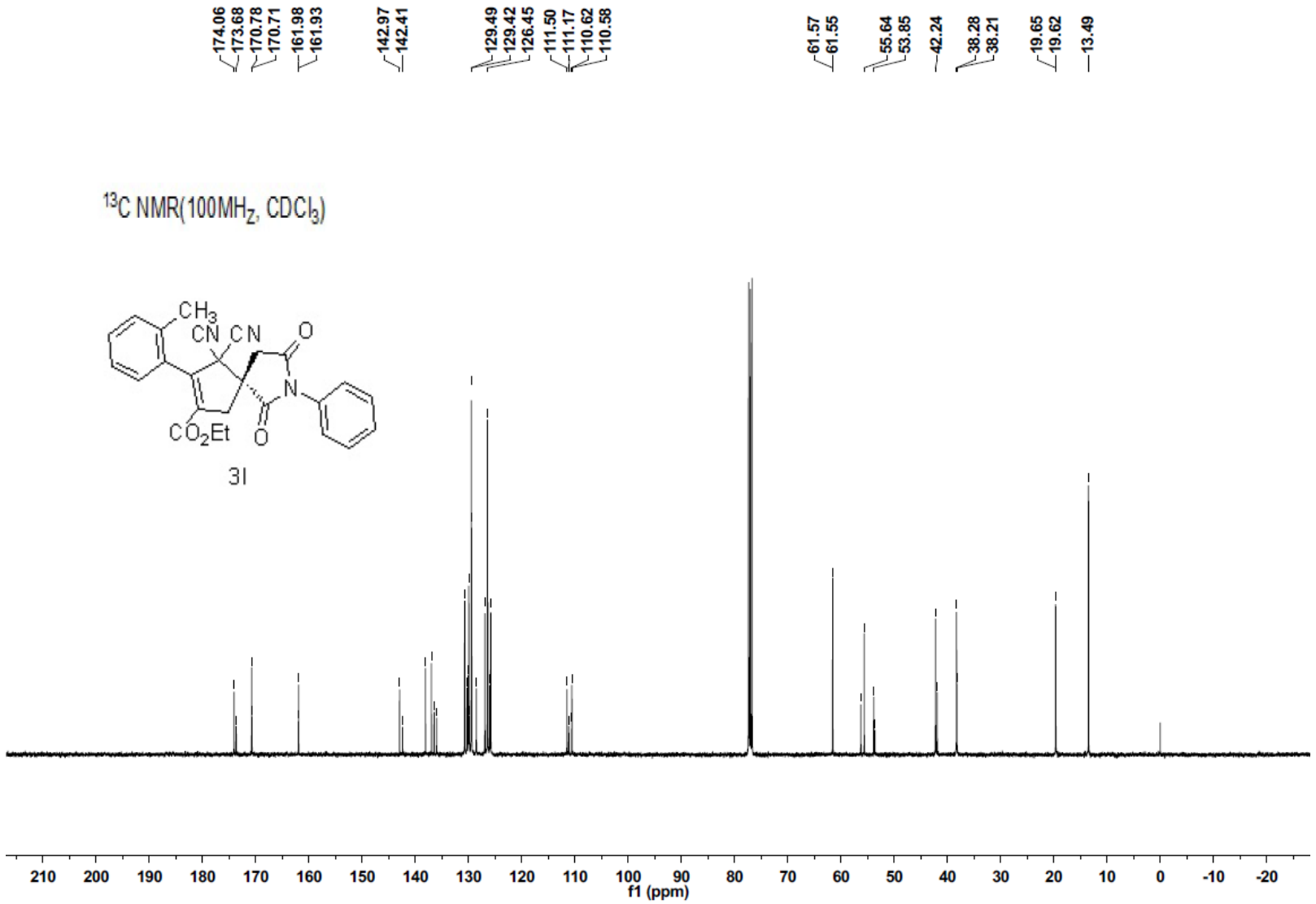
3.57
3.55
3.34
3.30
3.28
3.23
2.42
2.36
0.98
0.96
0.95
0.00
$^1$H NMR(400MH$_Z$, CDCl$_3$)
CH$_3$
CN
CN
O
N
O
CO$_2$Et
O
3l
3.00
6.01
2.00
2.00
2.01
3.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)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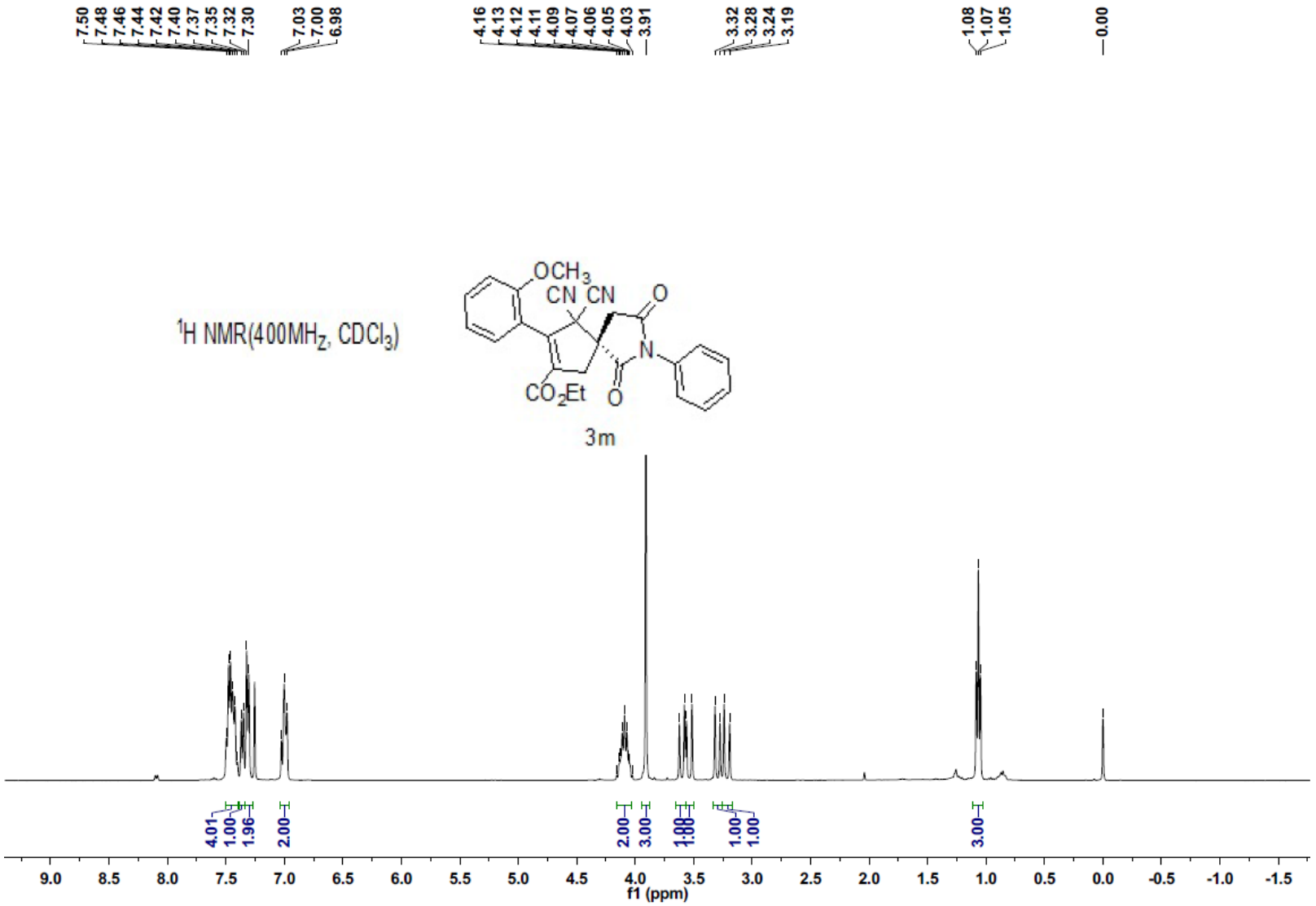
111.50
111.17
110.62
110.58
61.57
61.55
55.64
53.85
42.24
38.28
38.21
19.65
19.62
13.49
13C NMR(100MHz, CDCl3)
CH3
CN CN
O
N
CO2Et
O
3l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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7.48
7.46
7.44
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7.37
7.35
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7.30
7.03
7.00
6.98
4.16
4.13
4.12
4.11
4.09
4.07
4.06
4.05
4.03
3.91
3.32
3.28
3.24
3.19
1.08
1.07
1.05
0.00
$^1$H NMR(400MH$_Z$, CDCl$_3$)
OCH$_3$
CN CN
O
N
CO$_2$Et
O
3m
4.01
1.00
1.96
2.00
2.00
3.00
1.00
1.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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1.5
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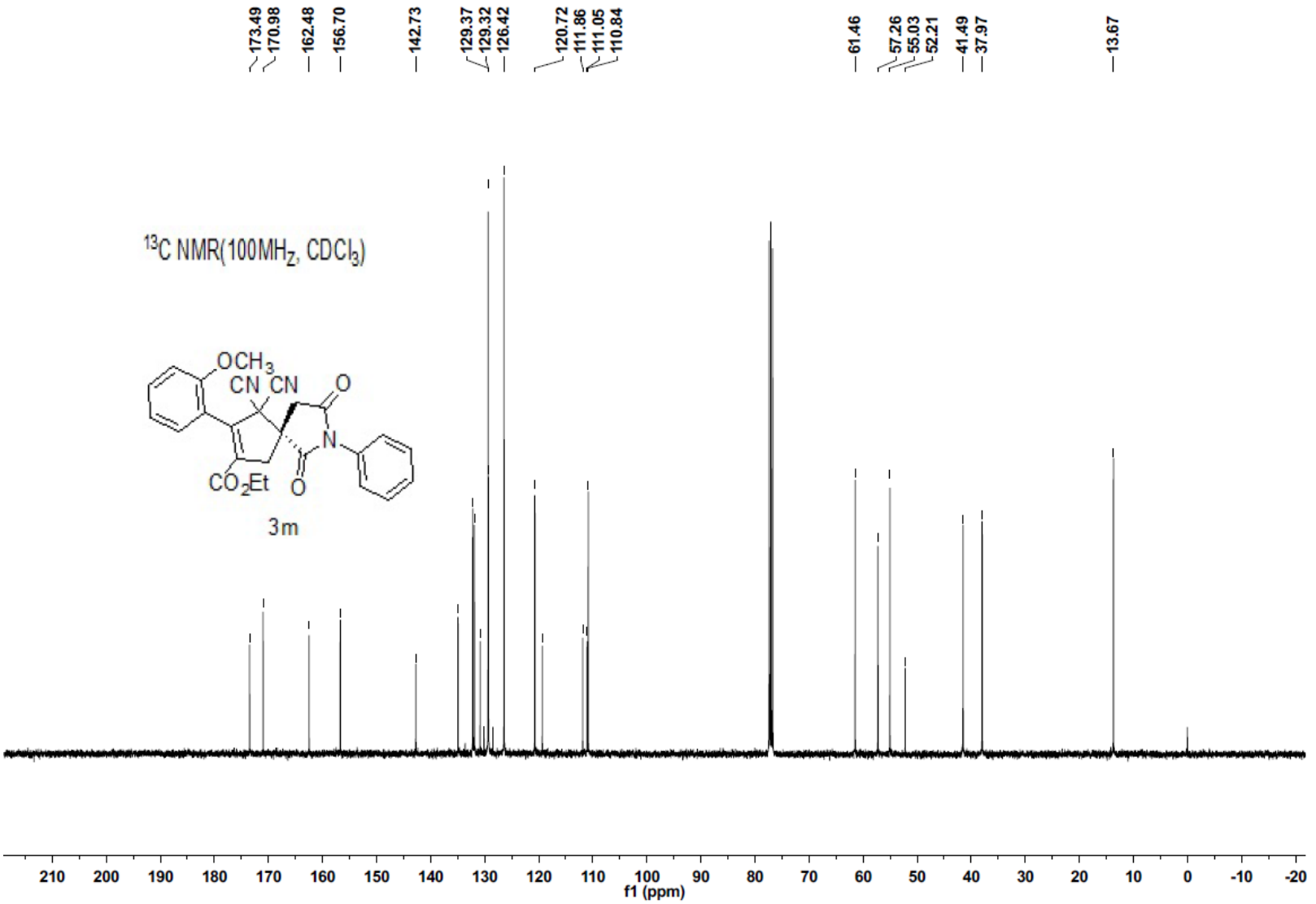
0.0
-0.5
-1.0
-1.5
f1 (ppm)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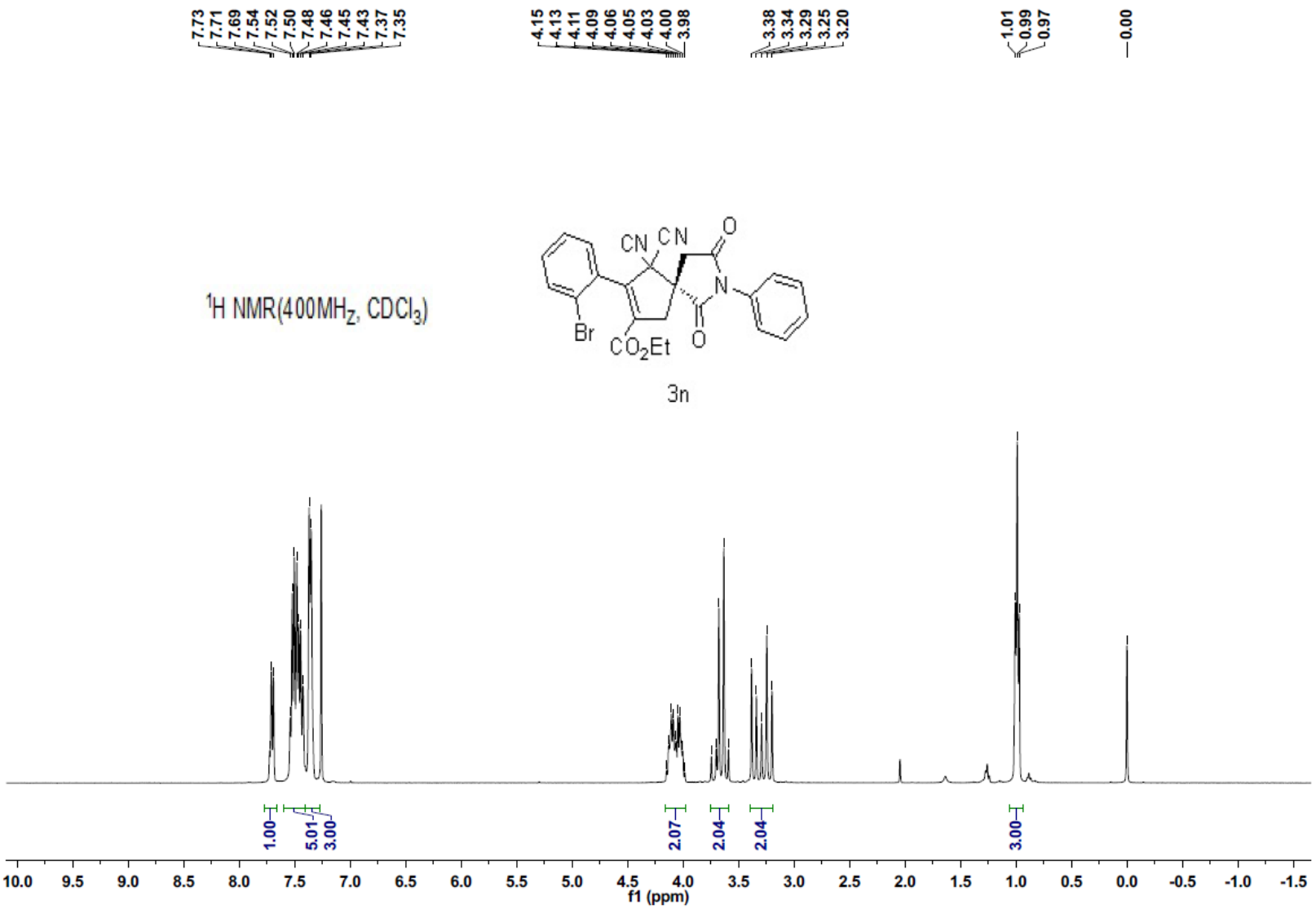
129.32
126.42
120.72
111.86
111.05
110.84
61.46
57.26
55.03
52.21
41.49
37.97
13.67
13C NMR(100MHz, CDCl3)
OCH3
CN CN
O
N
O
CO2Et
O
3m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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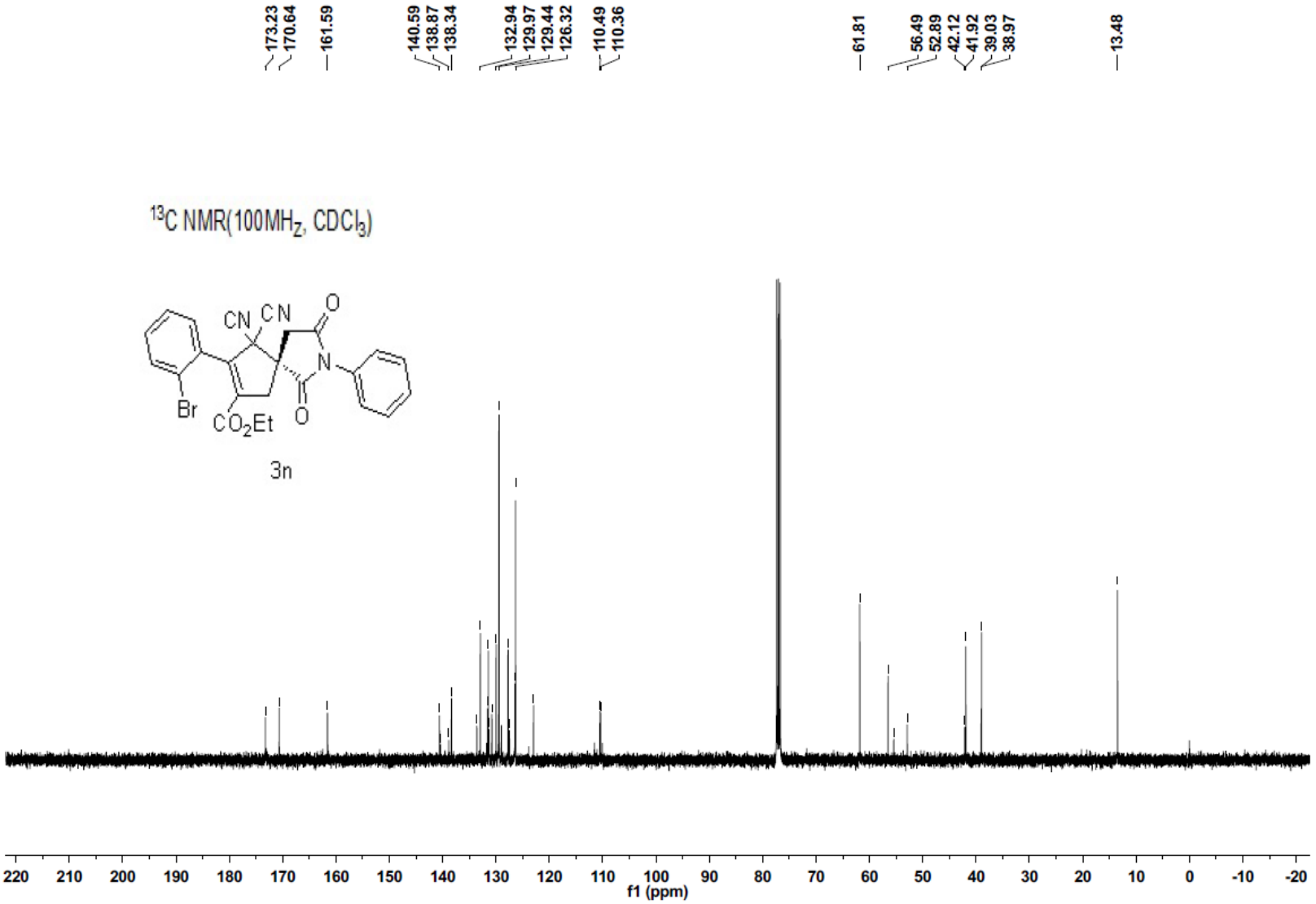
7.46
7.45
7.43
7.37
7.35
4.15
4.13
4.11
4.09
4.06
4.05
4.03
4.00
3.98
3.38
3.34
3.29
3.25
3.20
1.01
0.99
0.97
0.00
1H NMR(400MHz, CDCl3)
CN
CN
O
N
Br
CO2Et
O
3n
1.00
5.01
3.00
2.07
2.04
2.04
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)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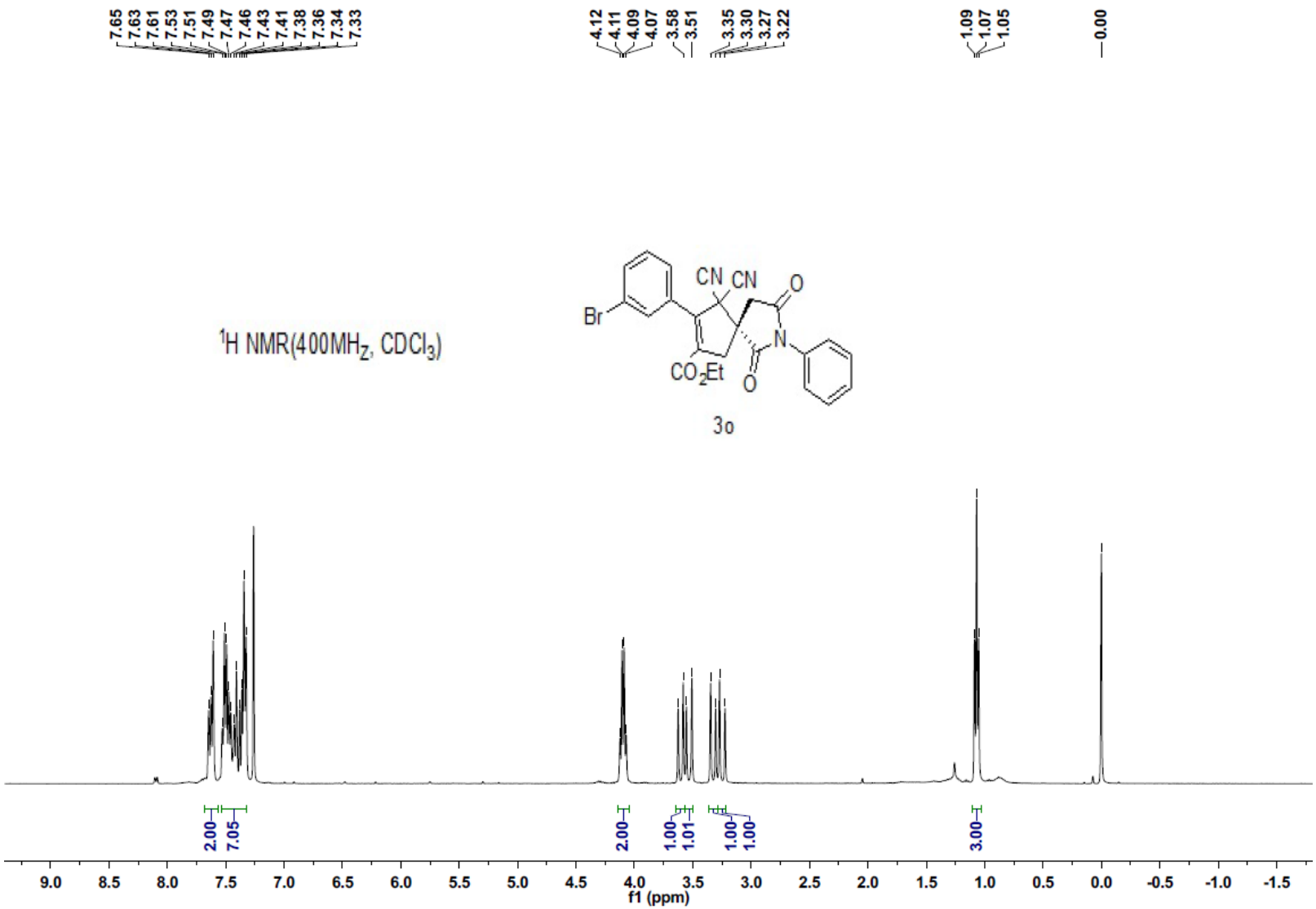
129.97
129.44
126.32
110.49
110.36
61.81
56.49
52.89
42.12
41.92
39.03
38.97
13.48
13C NMR(100MHz, CDCl3)
CN
CN
O
N
O
Br
CO2Et
3n
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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7.61
7.53
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7.46
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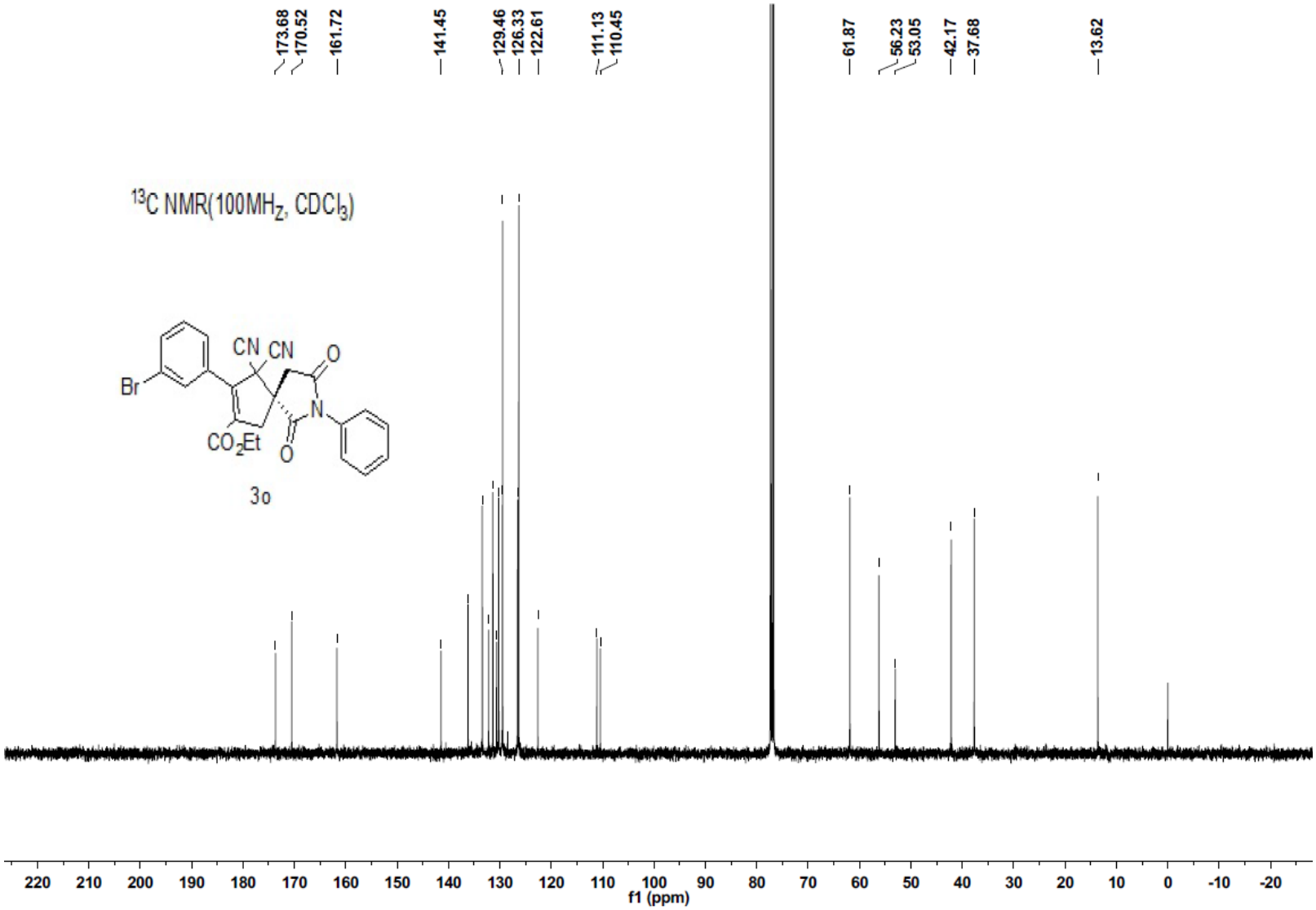
7.38
7.36
7.34
7.33
4.12
4.11
4.09
4.07
3.58
3.51
3.35
3.30
3.27
3.22
1.09
1.07
1.05
0.00
$^1$H NMR(400MH$_Z$, CDCl$_3$)
Br
CN CN
O
N
CO$_2$Et
O
3o
2.00
7.05
2.00
1.00
1.01
1.00
1.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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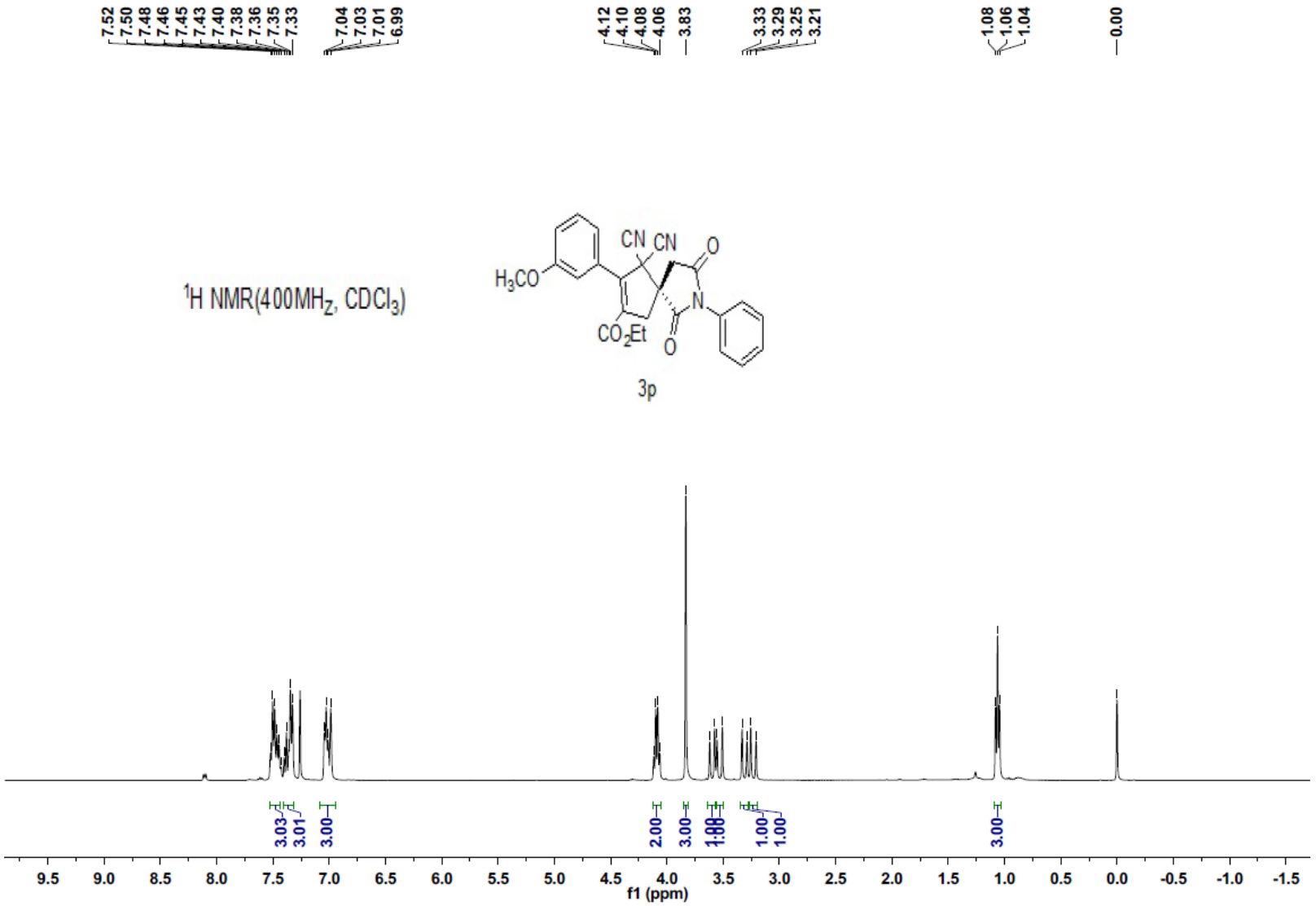
161.72
141.45
129.46
126.33
122.61
111.13
110.45
61.87
56.23
53.05
42.17
37.68
13.62
13C NMR(100MHz, CDCl3)
CN CN
O
Br
N
CO2Et
O
3o
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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7.50
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7.46
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7.43
7.40
7.38
7.36
7.35
7.33
7.04
7.03
7.01
6.99
4.12
4.10
4.08
4.06
3.83
3.33
3.29
3.25
3.21
1.08
1.06
1.04
0.00
$^1$H NMR(400MH$_Z$, CDCl$_3$)
H$_3$CO
CN
CN
O
N
O
CO$_2$Et
O
3p
3.03
3.01
3.00
2.00
3.00
1.00
1.00
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
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1.5
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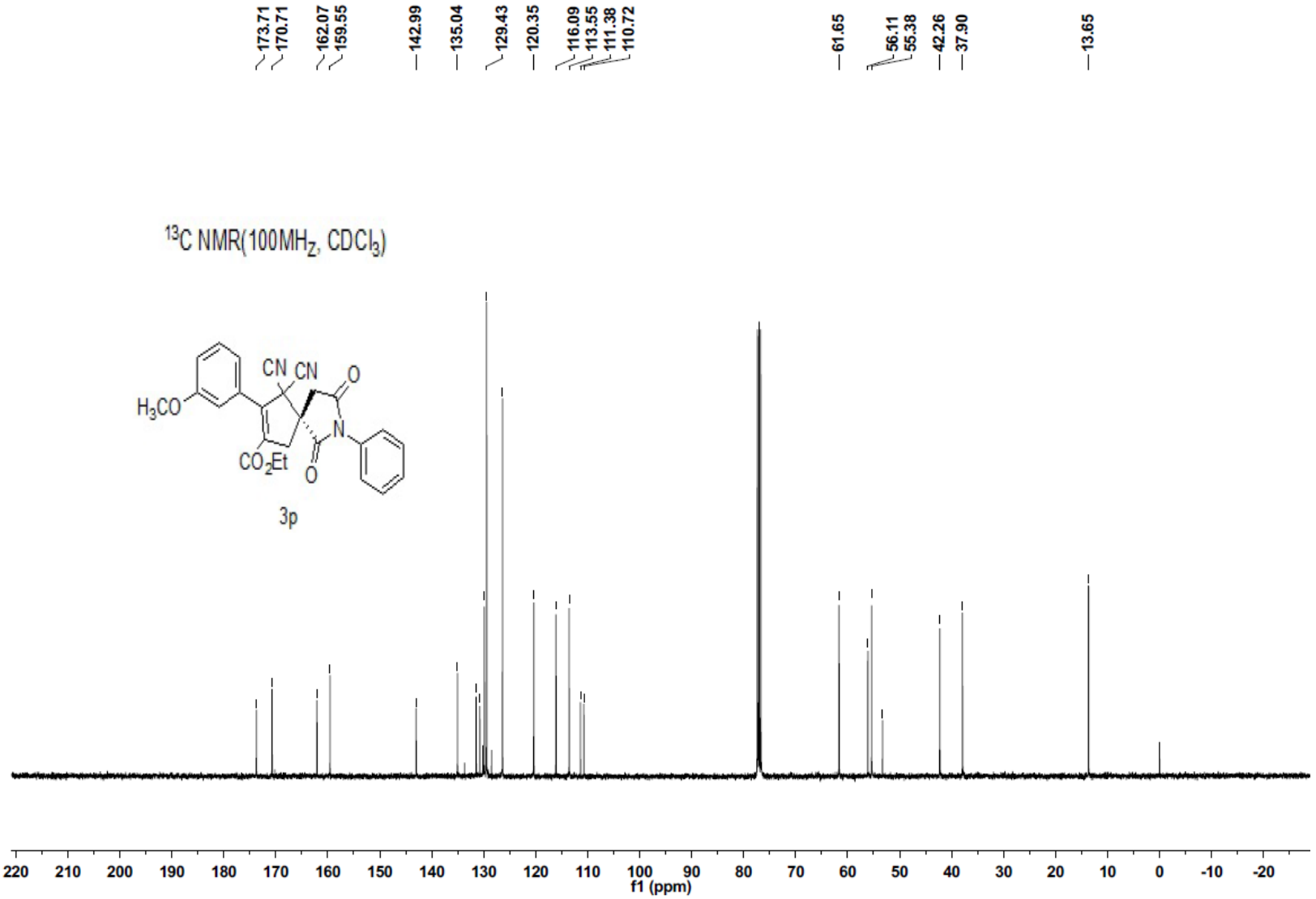
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)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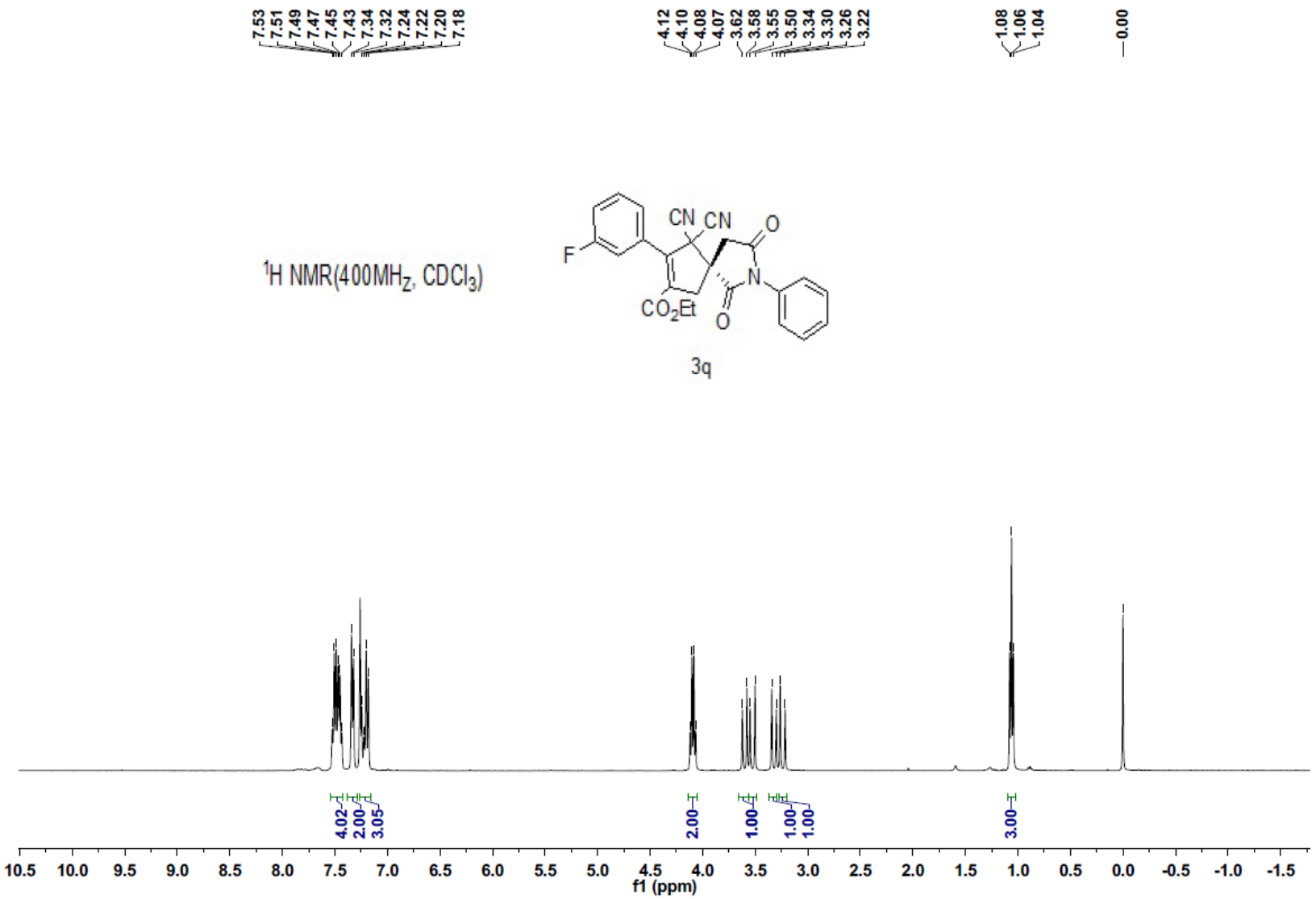
170.71
162.07
159.55
142.99
135.04
129.43
120.35
116.09
113.55
111.38
110.72
61.65
56.11
55.38
42.26
37.90
13.65
13C NMR(100MHz, CDCl3)
CN CN
O
H3CO
N
CO2Et
O
3p
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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7.43
7.34
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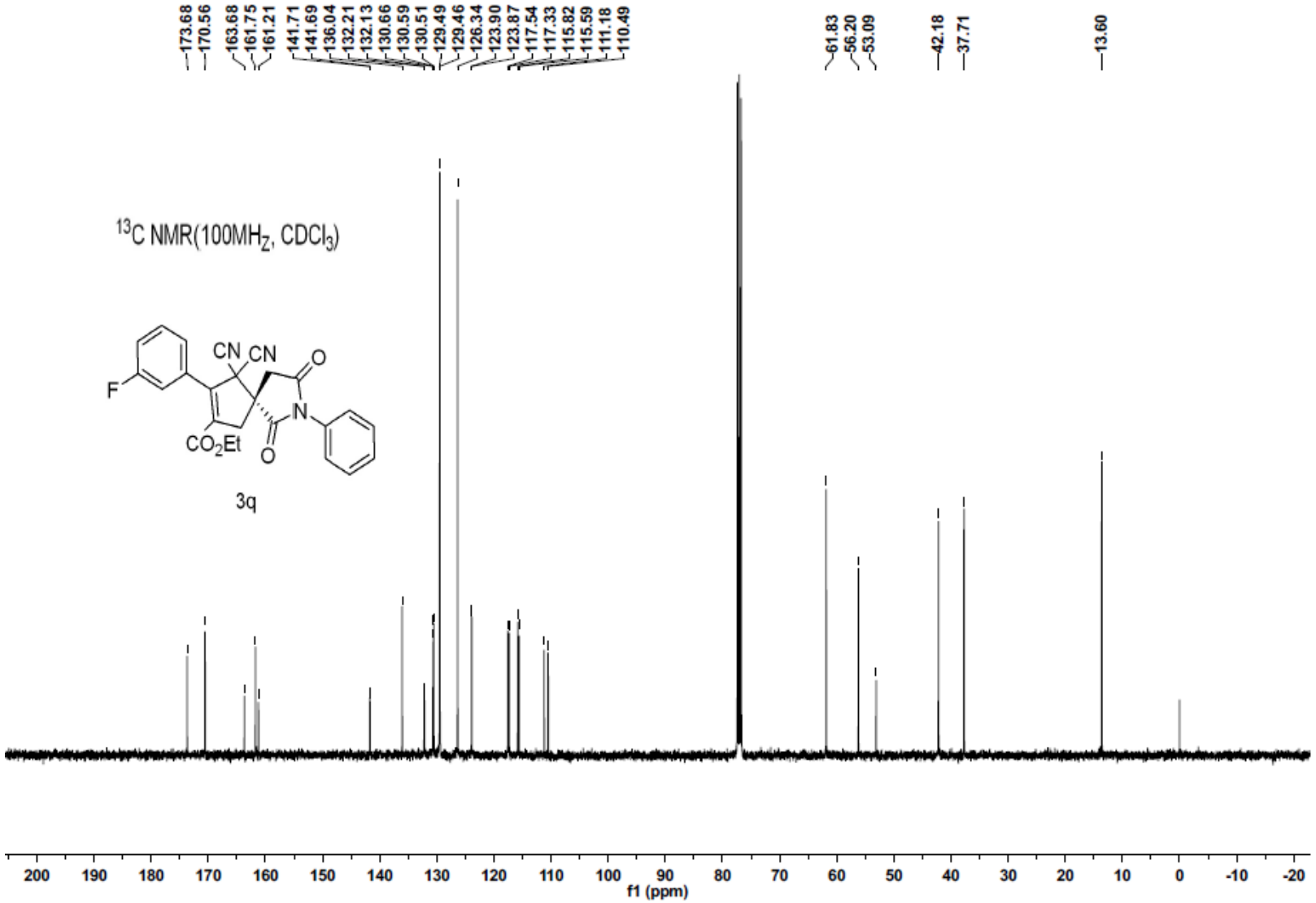
7.24
7.22
7.20
7.18
4.12
4.10
4.08
4.07
3.62
3.58
3.55
3.50
3.34
3.30
3.26
3.22
1.08
1.06
1.04
0.00
$^1$H NMR(400MH$_Z$, CDCl$_3$)
CN CN
O
F
N
CO$_2$Et
O
3q
4.02
2.00
3.05
2.00
1.00
1.00
1.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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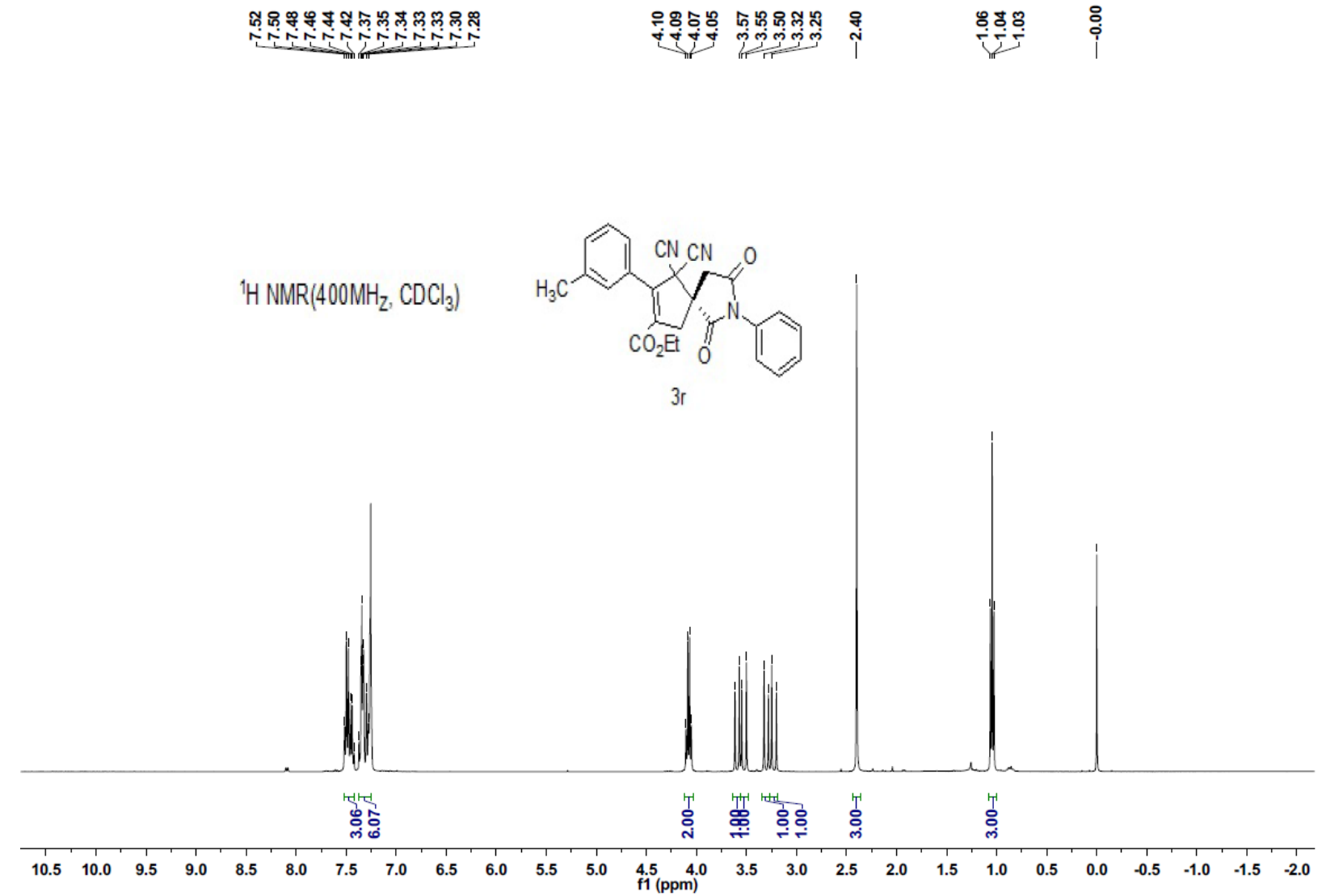
130.51
129.49
129.46
126.34
123.90
123.87
117.54
117.33
115.82
115.59
111.18
110.49
61.83
56.20
53.09
42.18
37.71
13.60
13C NMR(100MHz, CDCl3)
CN CN
O
F
N
CO2Et
O
3q
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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7.50
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7.46
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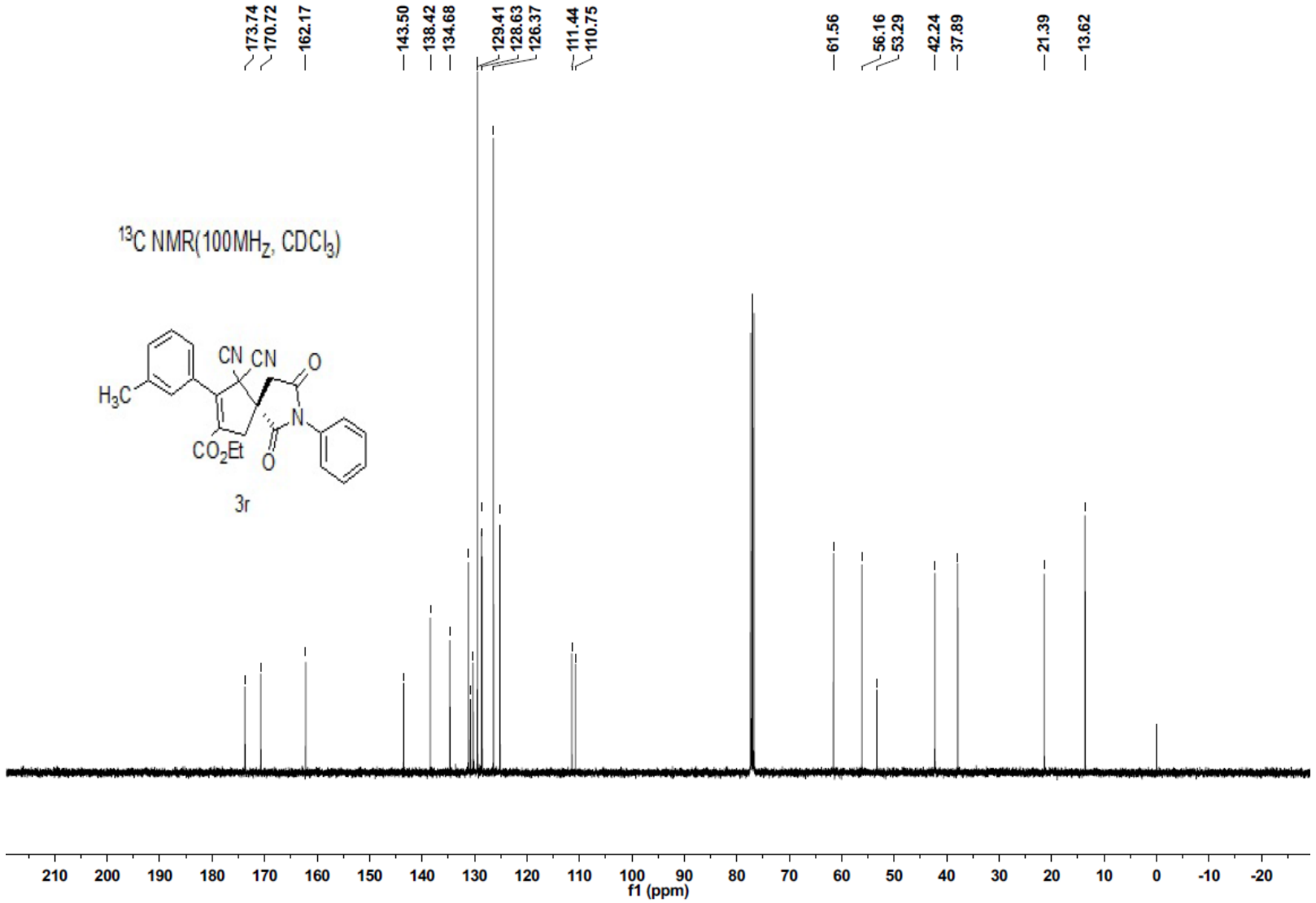
7.42
7.37
7.35
7.34
7.33
7.33
7.30
7.28
4.10
4.09
4.07
4.05
3.57
3.55
3.50
3.32
3.25
2.40
1.06
1.04
1.03
0.00
$^1$H NMR(400MH$_Z$, CDCl$_3$)
CN CN
O
H$_3$C
N
CO$_2$Et
O
3r
3.06
6.07
2.00
1.00
1.00
1.00
3.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)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134.68
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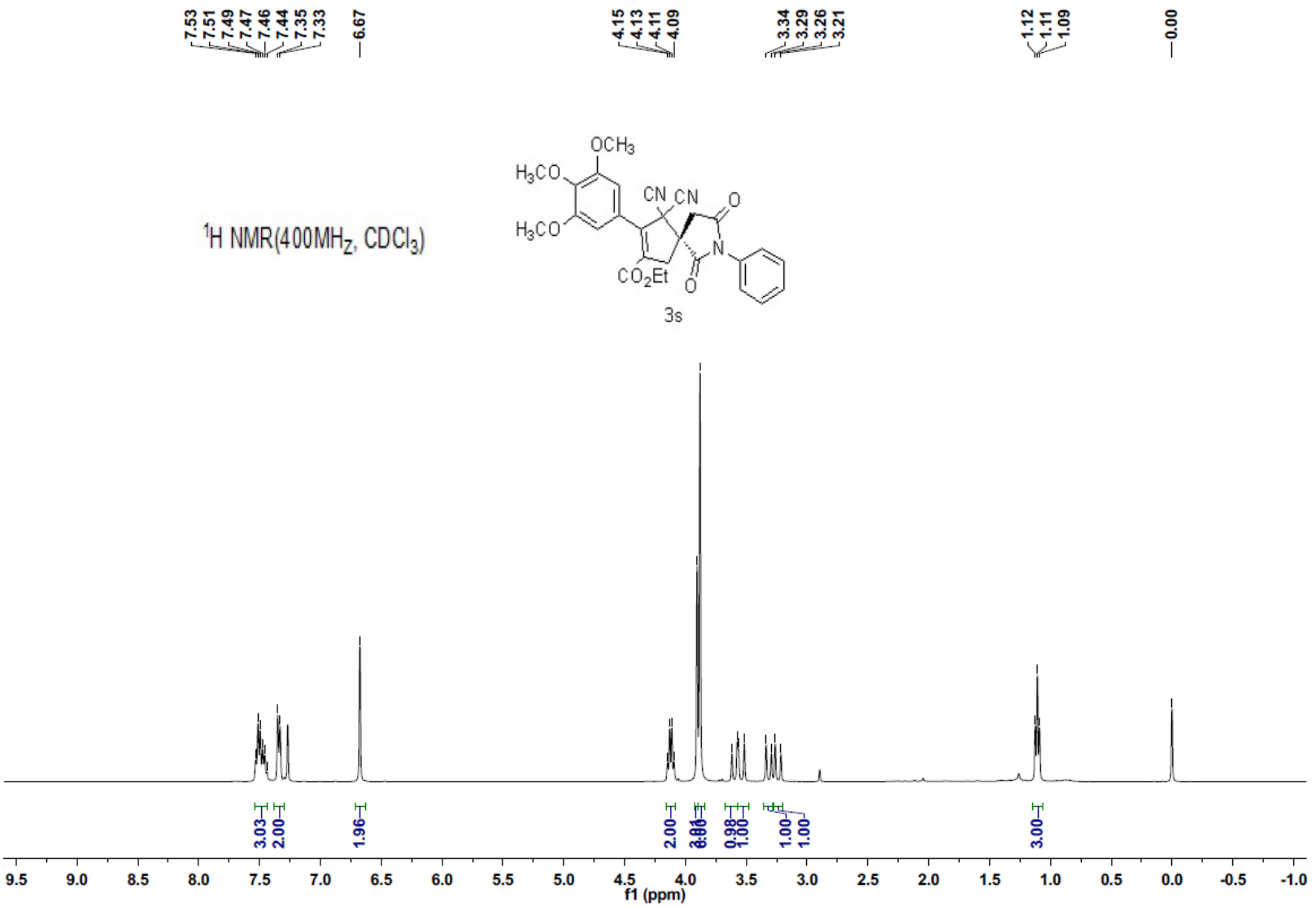
128.63
126.37
111.44
110.75
61.56
56.16
53.29
42.24
37.89
21.39
13.62
13C NMR(100MHz, CDCl3)
CN CN
O
H3C
N
CO2Et
O
3r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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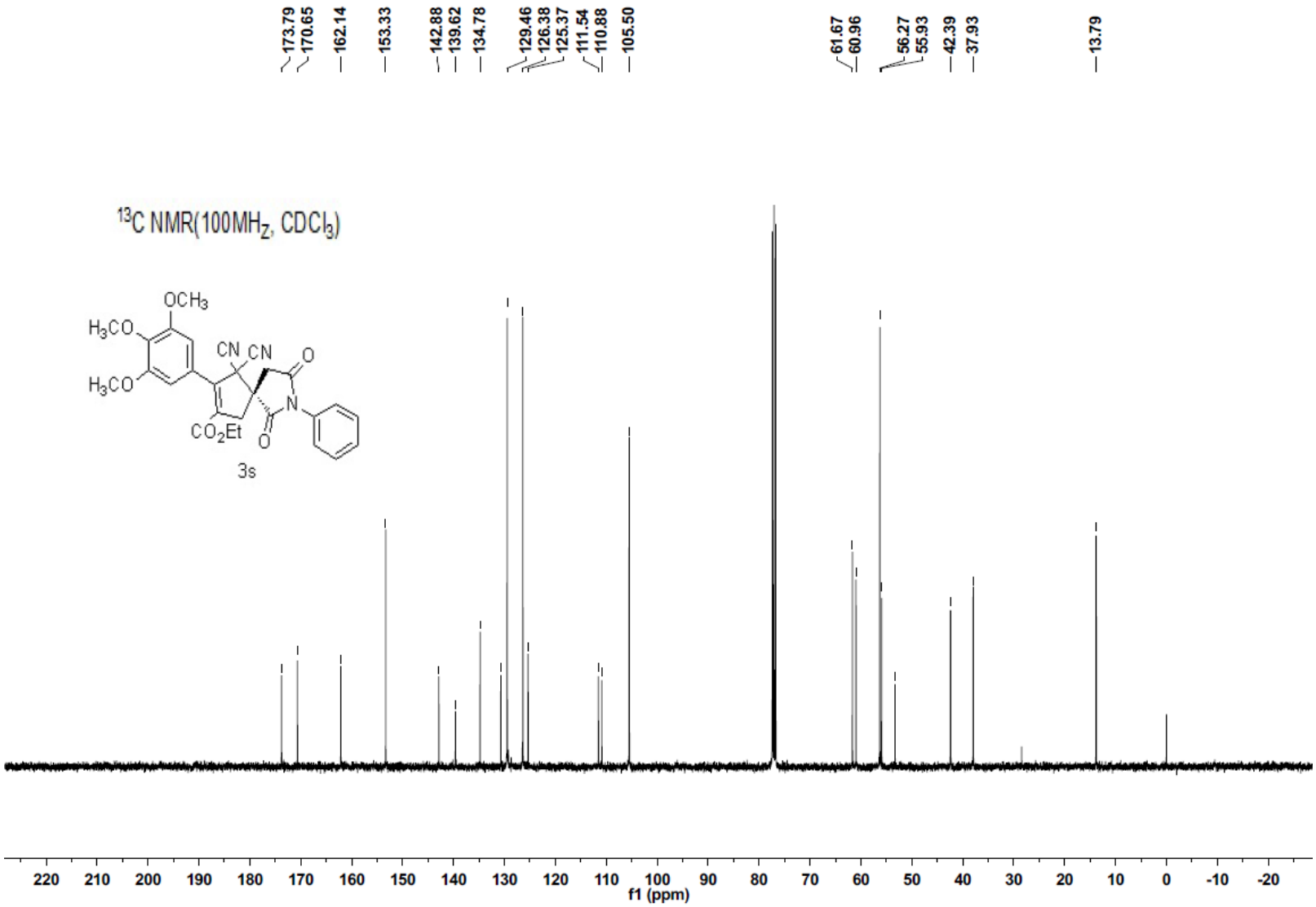
7.35
7.33
6.67
4.15
4.13
4.11
4.09
3.34
3.29
3.26
3.21
1.12
1.11
1.09
0.00
$^1$H NMR(400MHz, CDCl$_3$)
OCH$_3$
H$_3$CO
H$_3$CO
CN CN
O
N
O
CO$_2$Et
3s
3.03
2.00
1.96
2.00
0.98
1.00
1.00
1.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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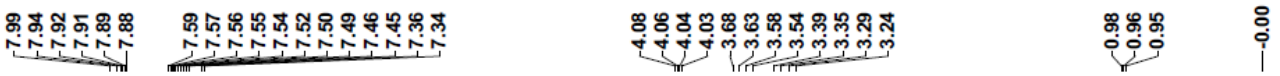
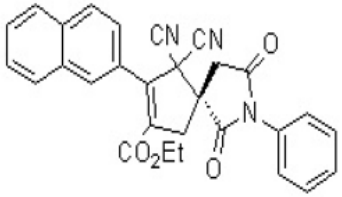
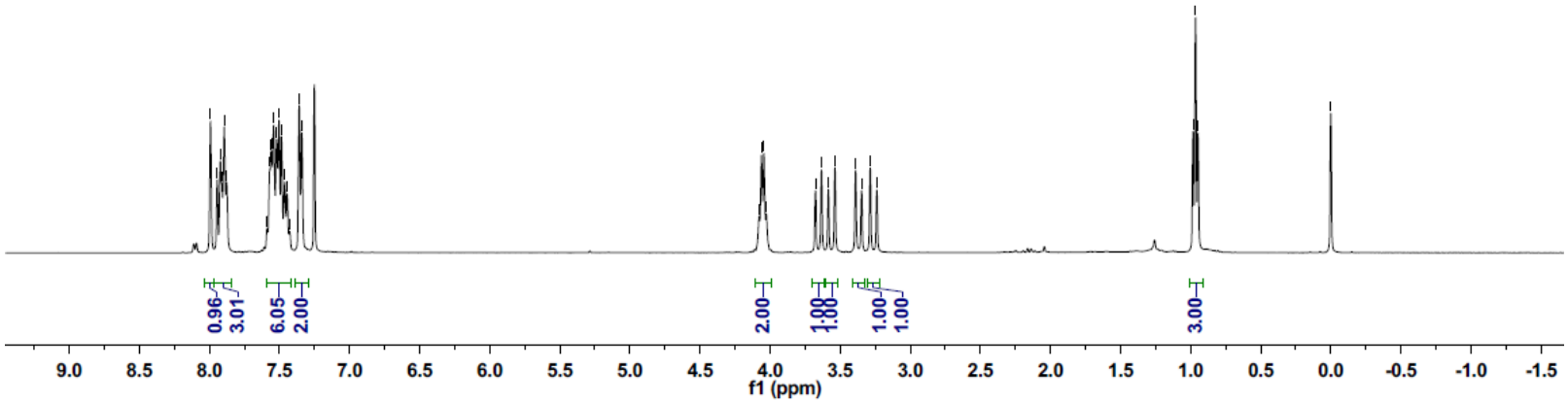
170.65
162.14
153.33
142.88
139.62
134.78
129.46
126.38
125.37
111.54
110.88
105.50
61.67
60.96
56.27
55.93
42.39
37.93
13.79
13C NMR(100MHz, CDCl3)
OCH3
H3CO
H3CO
CN CN
O
N
O
CO2Et
O
3s
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

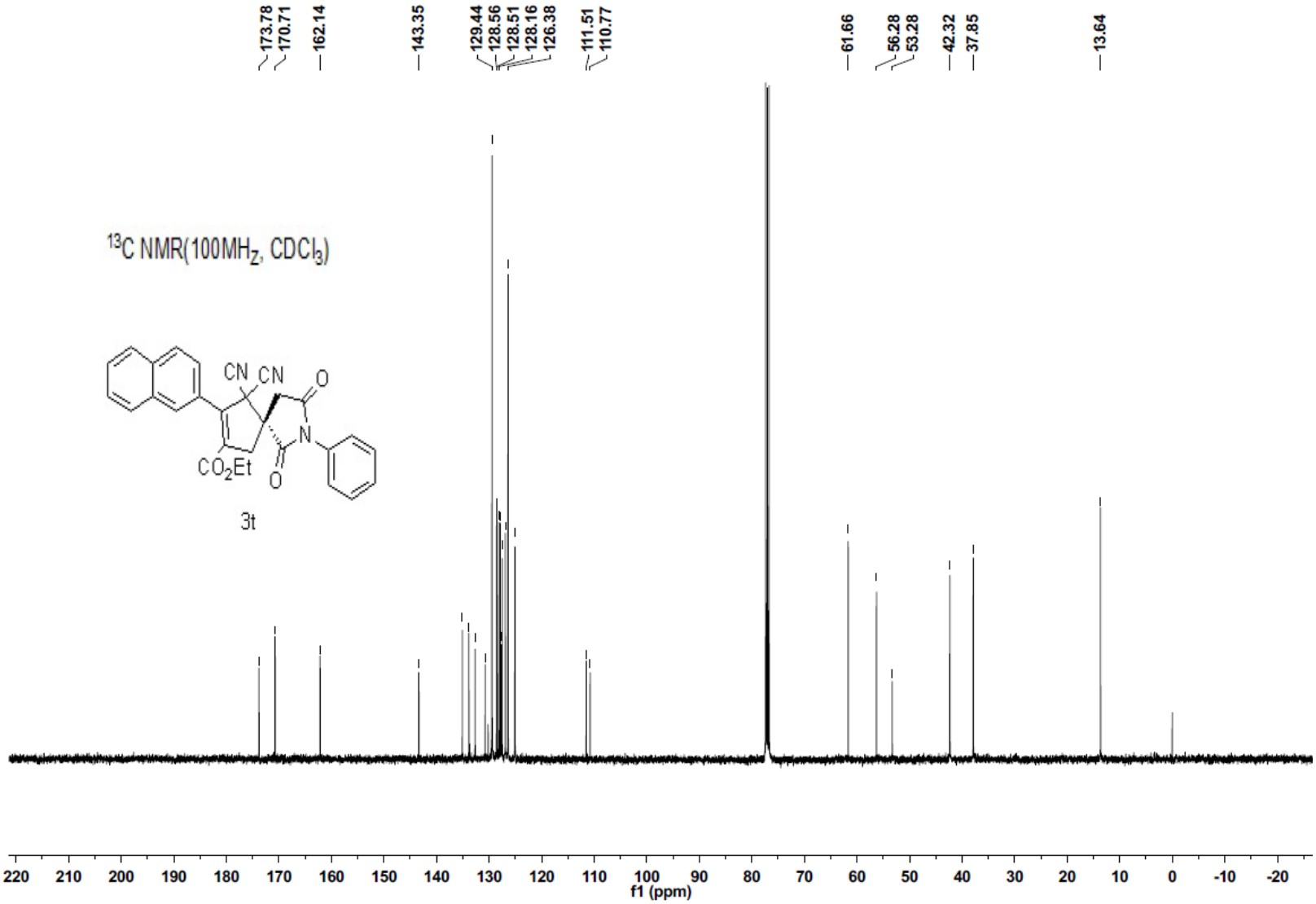



$^1$H NMR(400MH$_Z$, CDCl$_3$)




3t

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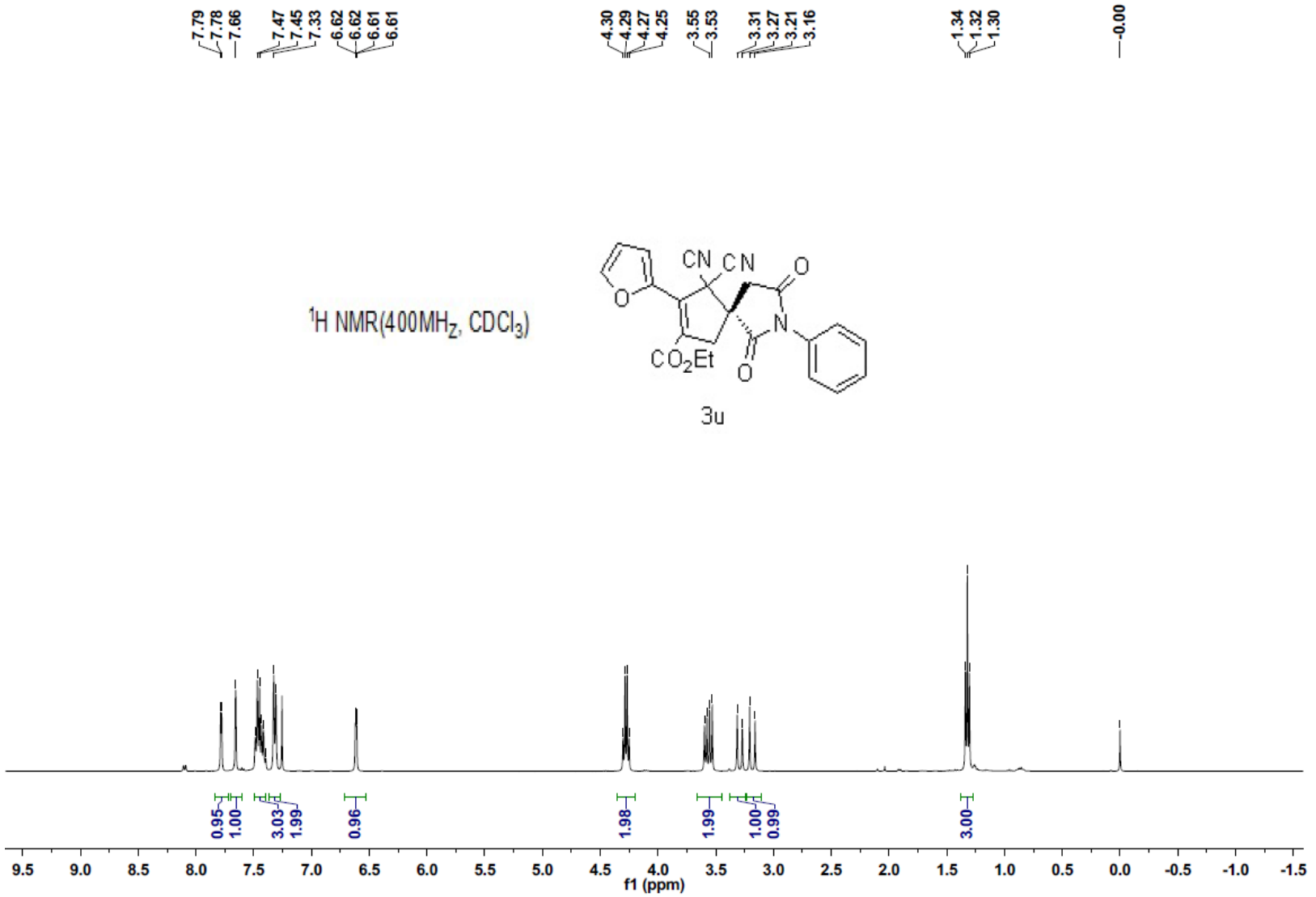
162.14
143.35
129.44
128.56
128.51
128.16
126.38
111.51
110.77
61.66
56.28
53.28
42.32
37.85
13.64
13C NMR(100MHz, CDCl3)
CN
CN
O
N
O
CO2Et
3t
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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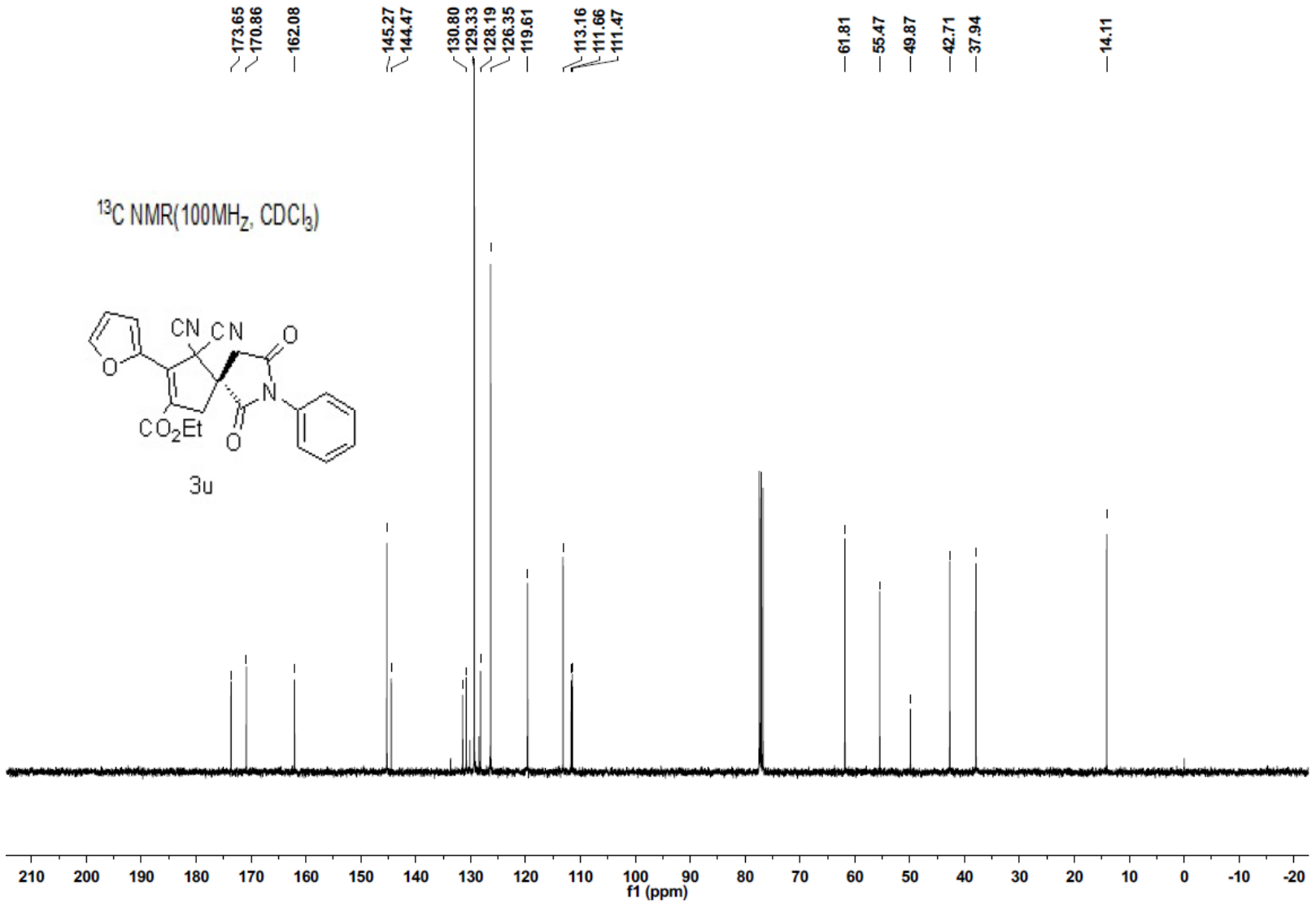
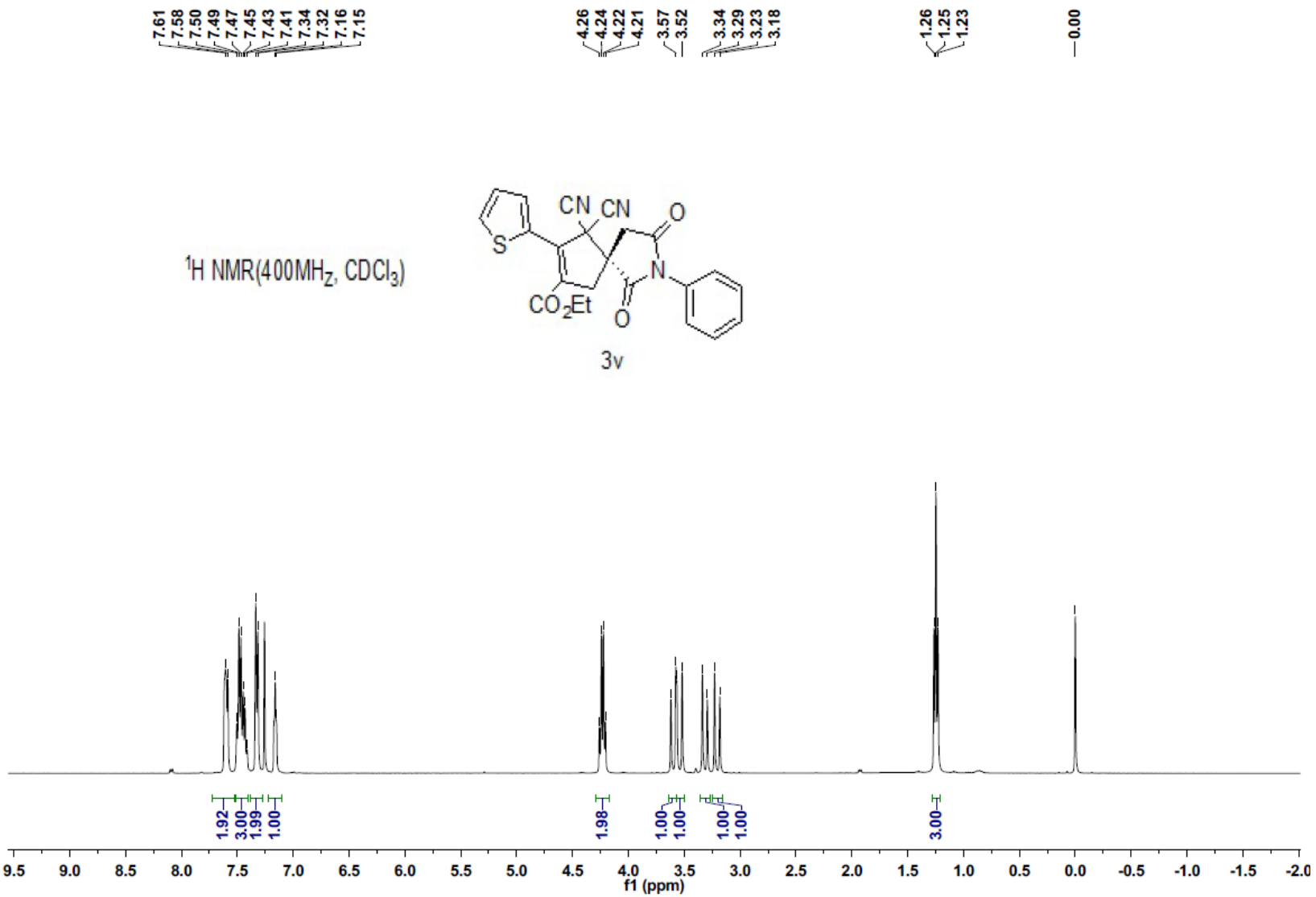
7.78
7.66
7.47
7.45
7.33
6.62
6.62
6.61
6.61
4.30
4.29
4.27
4.25
3.55
3.53
3.31
3.27
3.21
3.16
1.34
1.32
1.30
0.00
$^1$H NMR(400MHz, CDCl$_3$)
CN
CN
O
O
N
O
CO$_2$Et
3u
0.95
1.00
3.03
1.99
0.96
1.98
1.99
1.00
0.99
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)


173.65
170.86
162.08
145.27
144.47
130.80
129.33
128.19
126.35
119.61
113.16
111.66
111.47
61.81
55.47
49.87
42.71
37.94
14.11
13C NMR(100MHz, CDCl3)
CN
CN
O
O
N
O
CO2Et
O
3u
210
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)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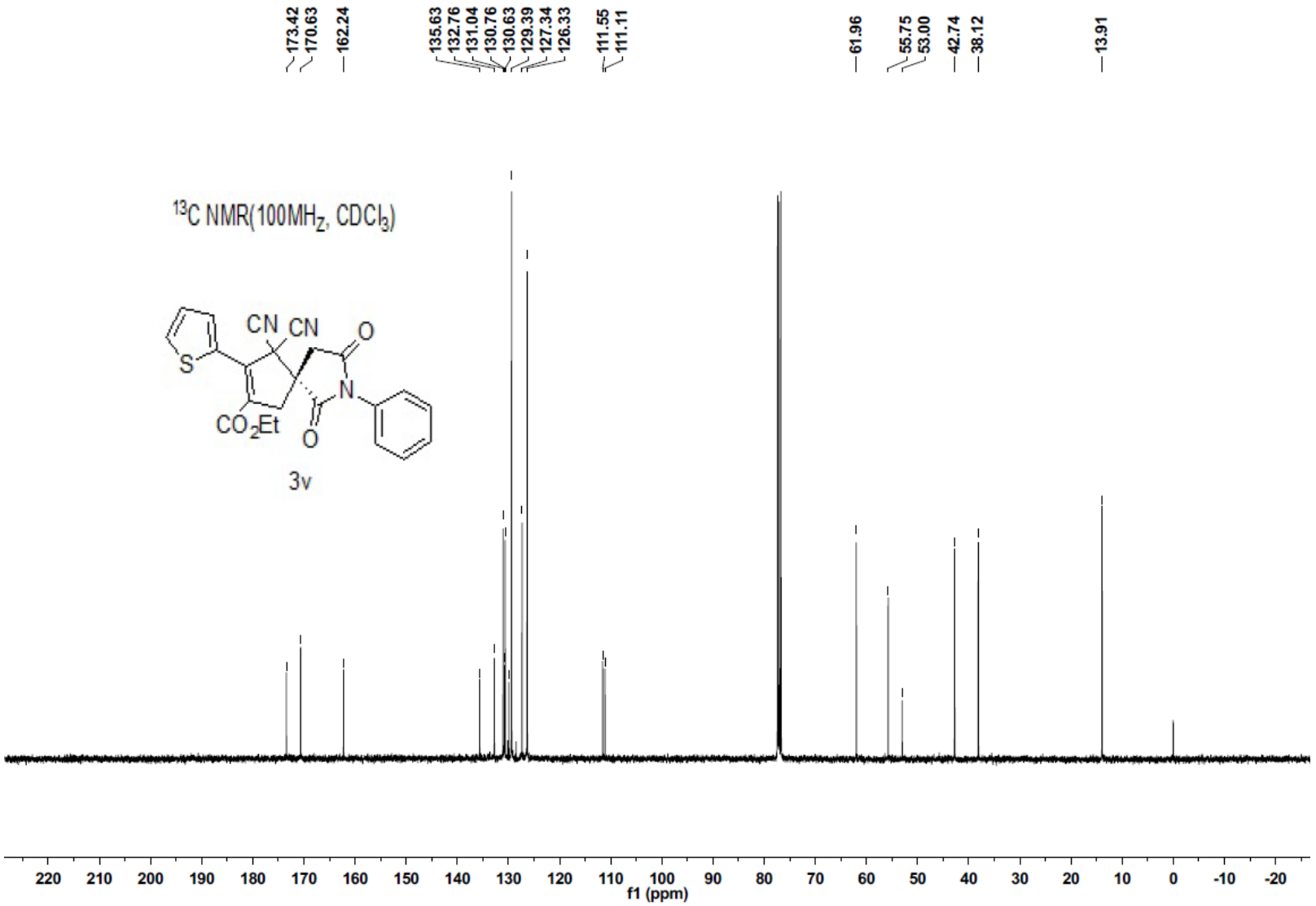
7.58
7.50
7.49
7.47
7.45
7.43
7.41
7.34
7.32
7.16
7.15
4.26
4.24
4.22
4.21
3.57
3.52
3.34
3.29
3.23
3.18
1.26
1.25
1.23
0.00
$^1$H NMR(400MH$_Z$, CDCl$_3$)
CN
CN
O
S
N
CO$_2$Et
O
3v
1.92
3.00
1.99
1.00
1.98
1.00
1.00
1.00
1.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
f1 (ppm)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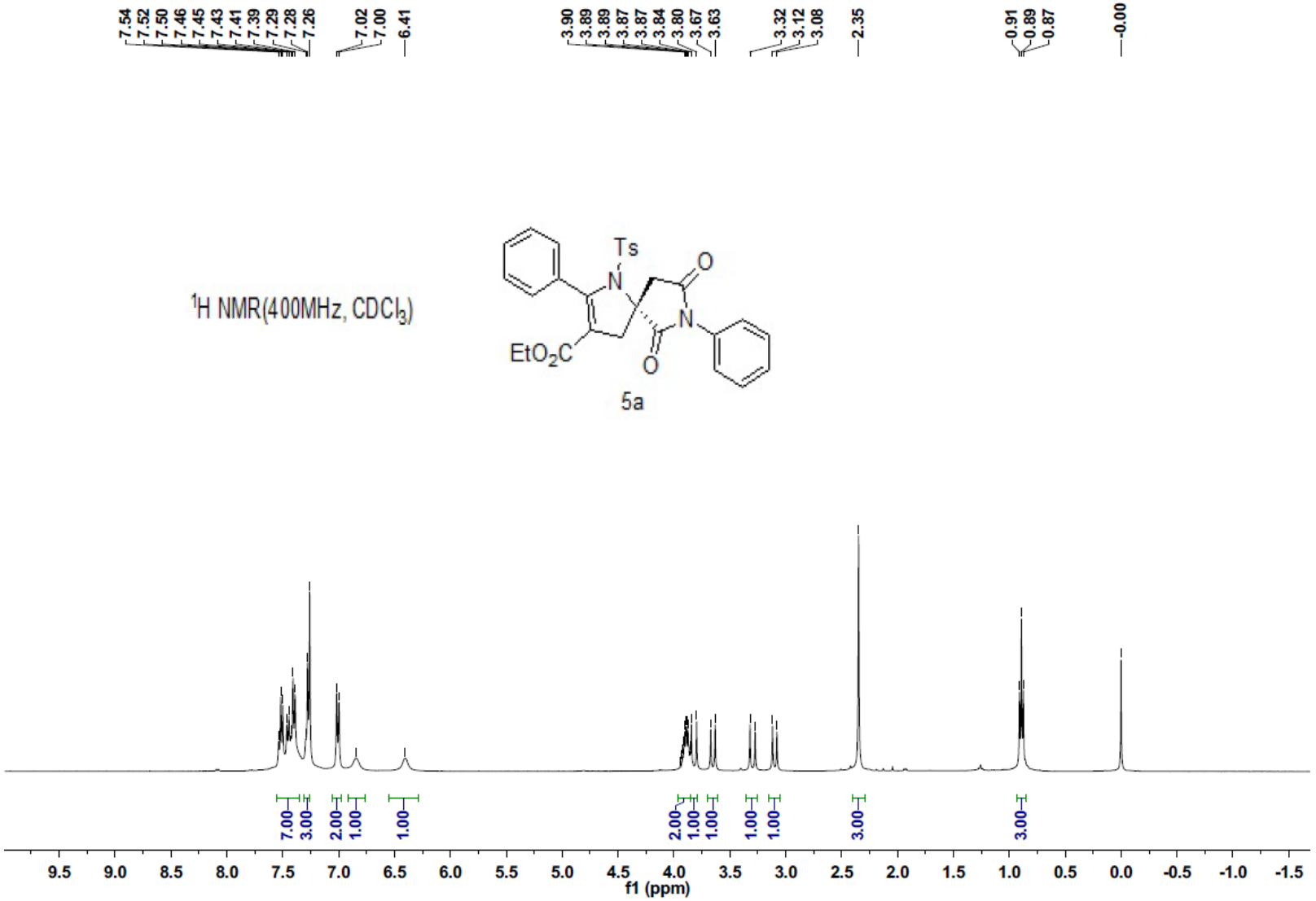
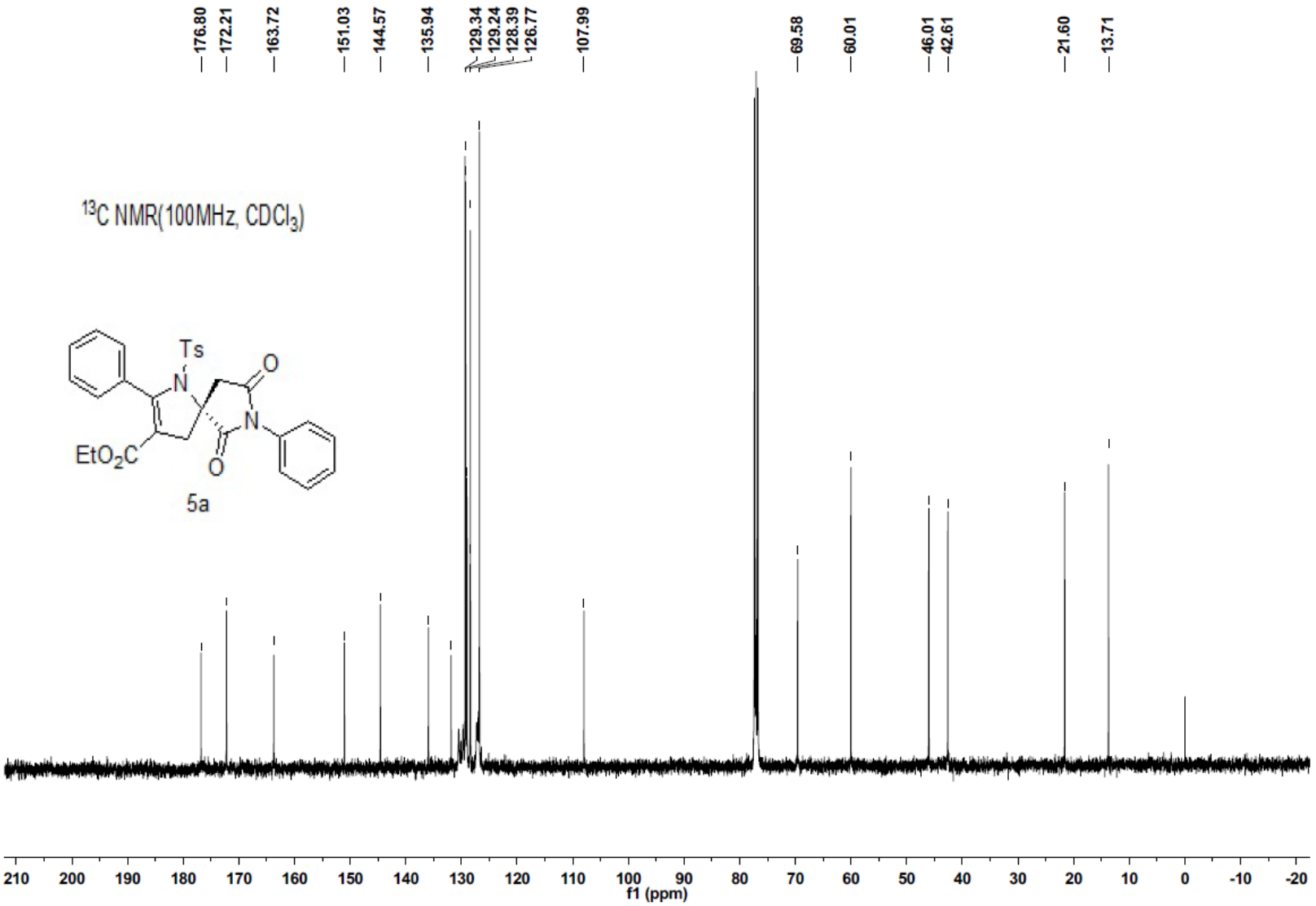
170.63
162.24
135.63
132.76
131.04
130.76
130.63
129.39
127.34
126.33
111.55
111.11
61.96
55.75
53.00
42.74
38.12
13.91
13C NMR(100MHz, CDCl3)
CN CN
O
S
N
CO2Et
O
3v
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.54
7.52
7.50
7.46
7.45
7.43
7.41
7.39
7.29
7.28
7.26
7.02
7.00
6.41
3.90
3.89
3.89
3.87
3.87
3.84
3.80
3.67
3.63
3.32
3.12
3.08
2.35
0.91
0.89
0.87
0.00
1H NMR(400MHz, CDCl3)
Ts
N
O
N
O
EtO2C
O
5a
7.00
3.00
2.00
1.00
1.00
2.00
1.00
1.00
1.00
1.00
3.00
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
-1.5
f1 (ppm)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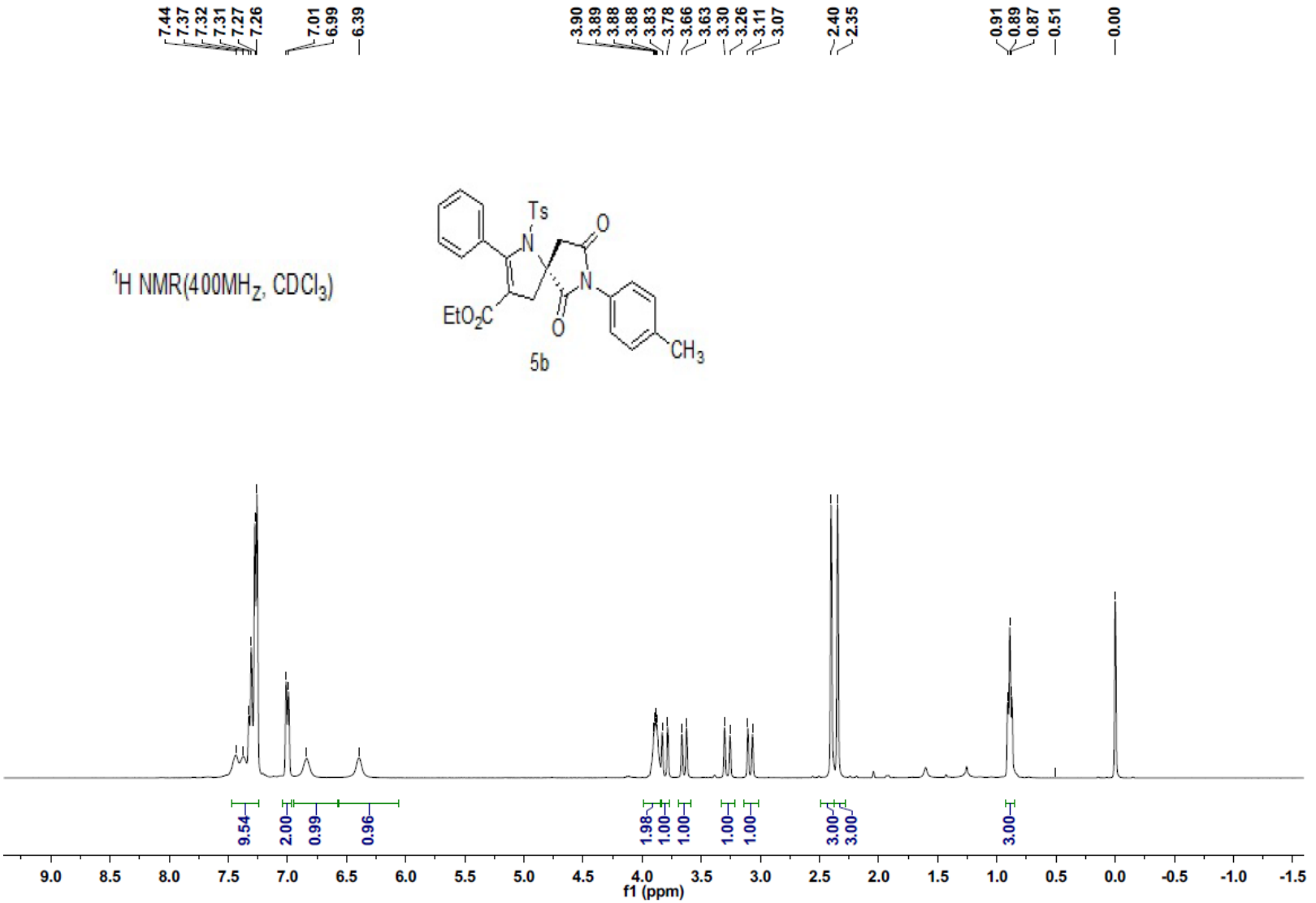
172.21
163.72
151.03
144.57
135.94
129.34
129.24
128.39
126.77
107.99
69.58
60.01
46.01
42.61
21.60
13.71
13C NMR(100MHz, CDCl3)
Ts
N
O
N
O
EtO2C
O
5a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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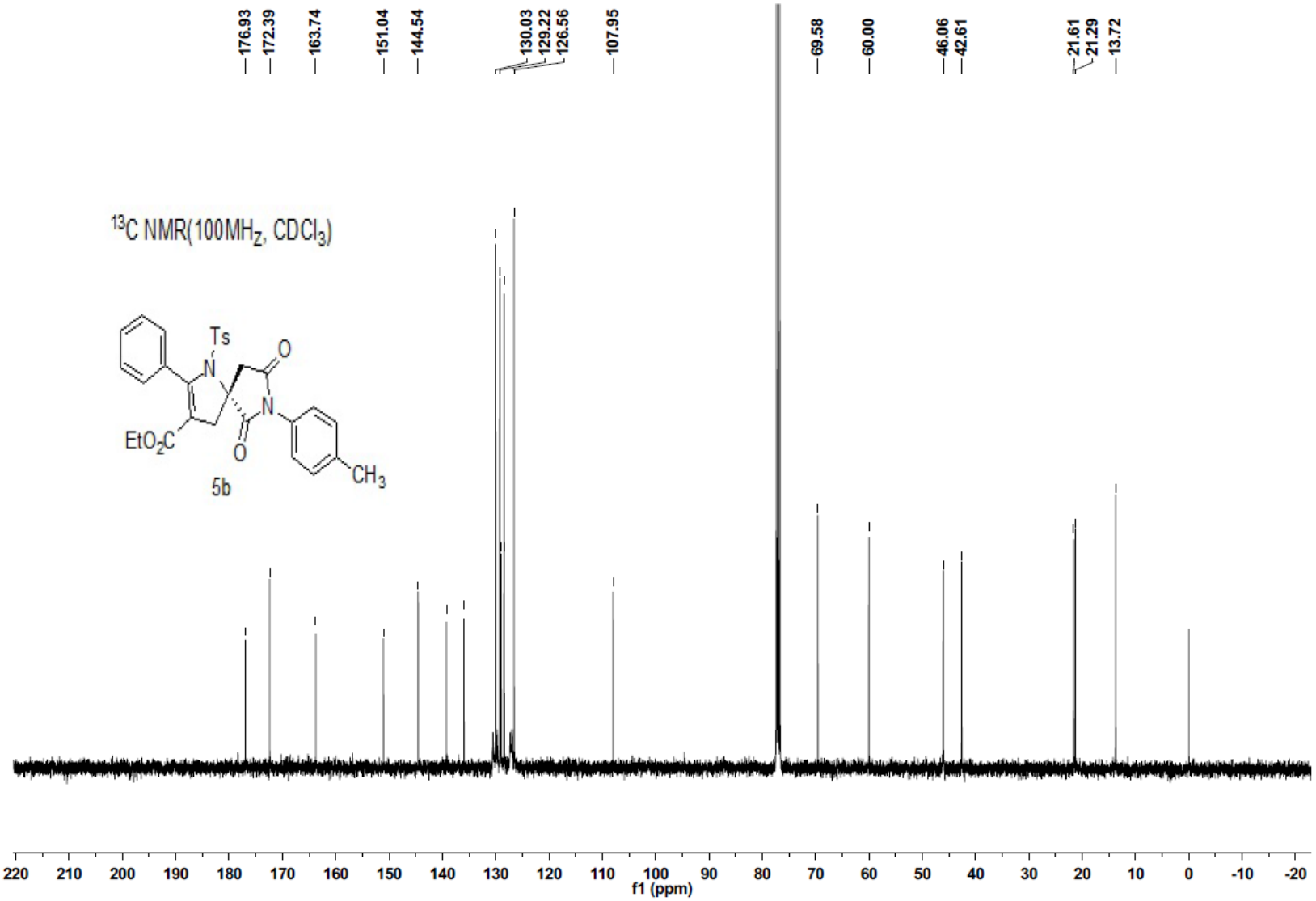
7.37
7.32
7.31
7.27
7.26
7.01
6.99
6.39
3.90
3.89
3.88
3.88
3.83
3.78
3.66
3.63
3.30
3.26
3.11
3.07
2.40
2.35
0.91
0.89
0.87
0.51
0.00
1H NMR(400MHZ, CDCl3)
Ts
N
O
N
O
EtO2C
O
CH3
5b
9.54
2.00
0.99
0.96
1.98
1.00
1.00
1.00
1.00
3.00
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)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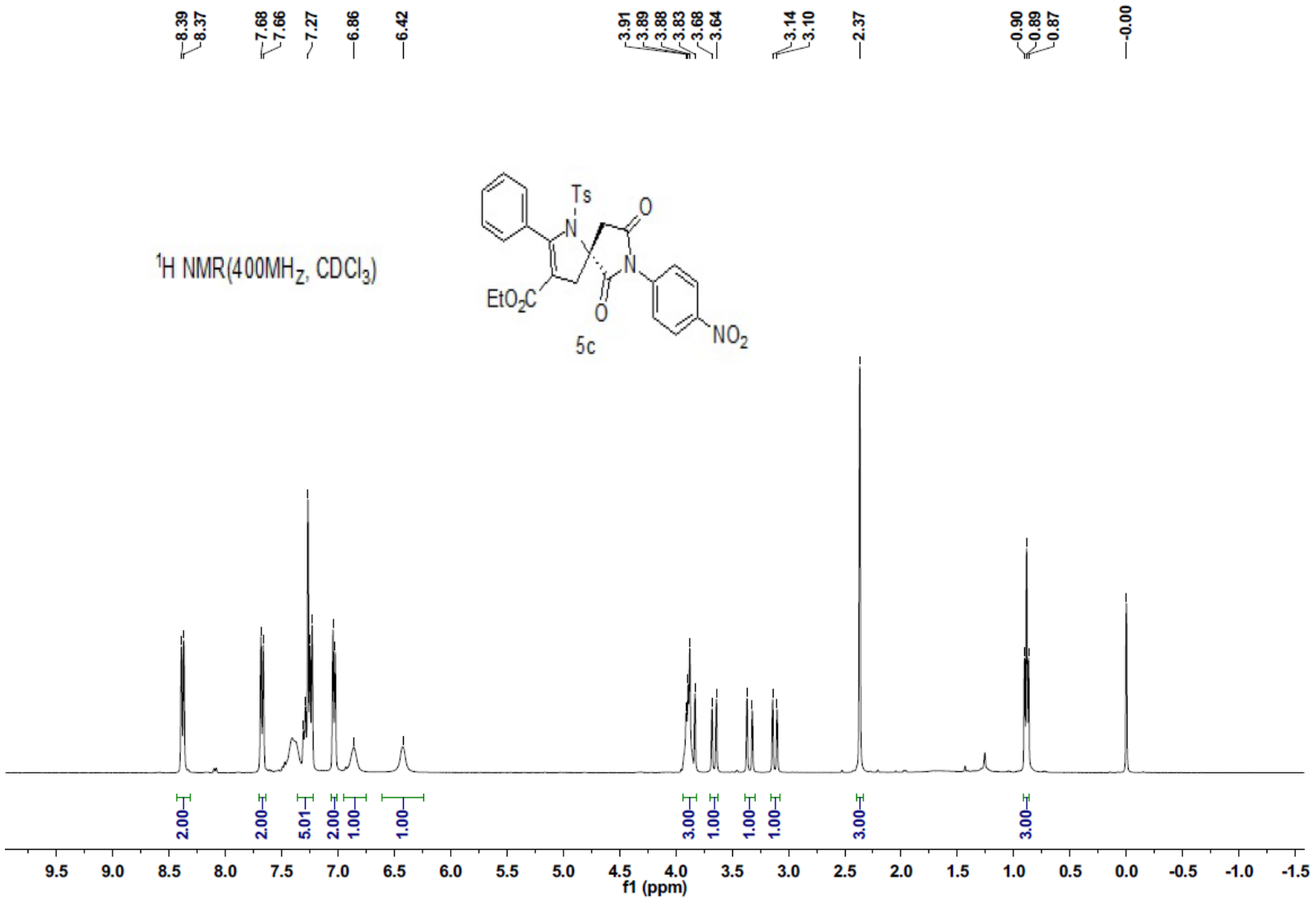
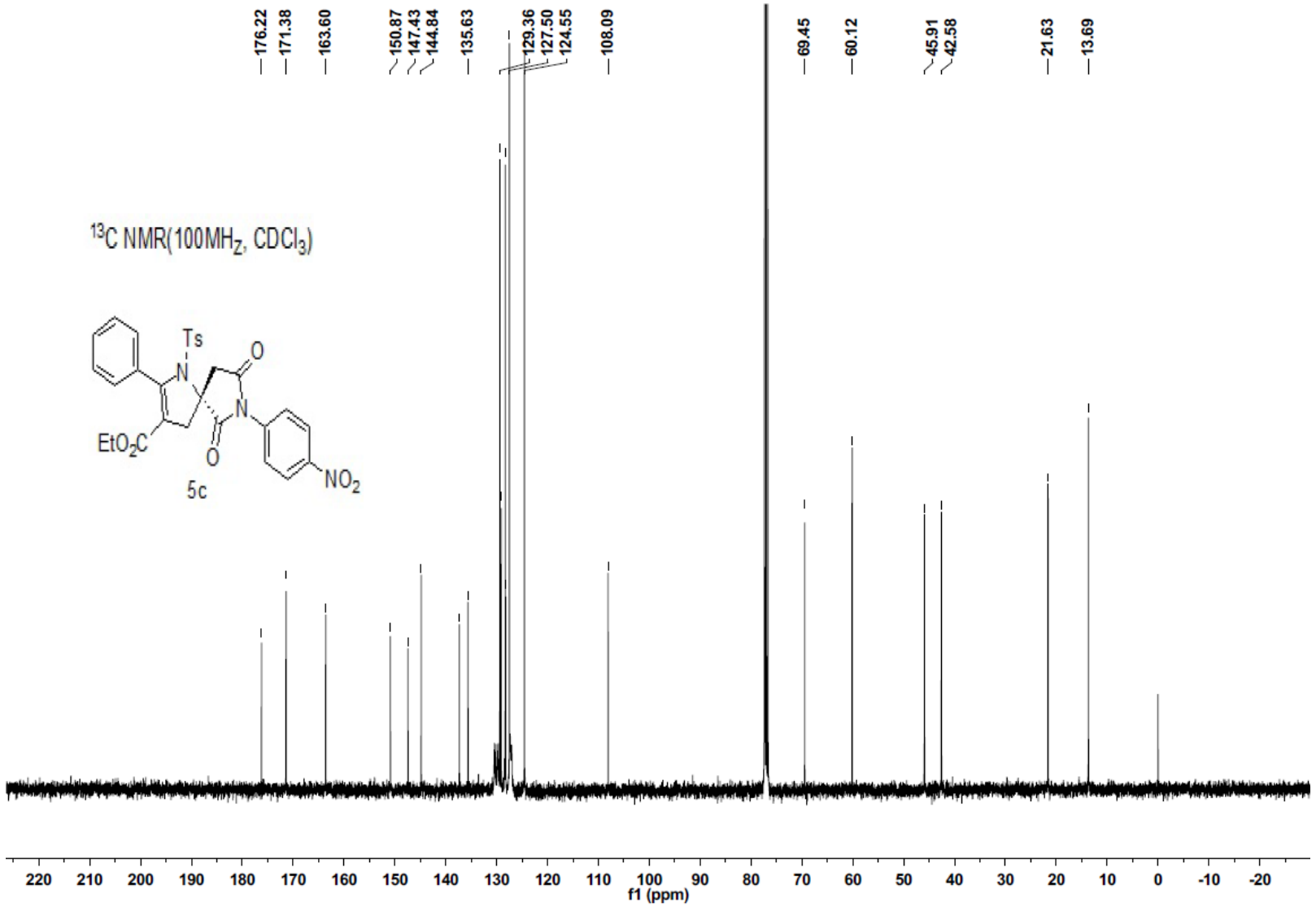
172.39
163.74
151.04
144.54
130.03
129.22
126.56
107.95
69.58
60.00
46.06
42.61
21.61
21.29
13.72
13C NMR(100MHz, CDCl3)
Ts
N
O
N
O
EtO2C
CH3
5b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


8.39
8.37
7.68
7.66
7.27
6.86
6.42
3.91
3.89
3.88
3.83
3.68
3.64
3.14
3.10
2.37
0.90
0.89
0.87
0.00
$^1$H NMR(400MH$_Z$, CDCl$_3$)
Ts
N
O
N
EtO$_2$C
O
NO$_2$
5c
2.00
2.00
5.01
2.00
1.00
1.00
3.00
1.00
1.00
1.00
3.00
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 -1.5
f1 (ppm)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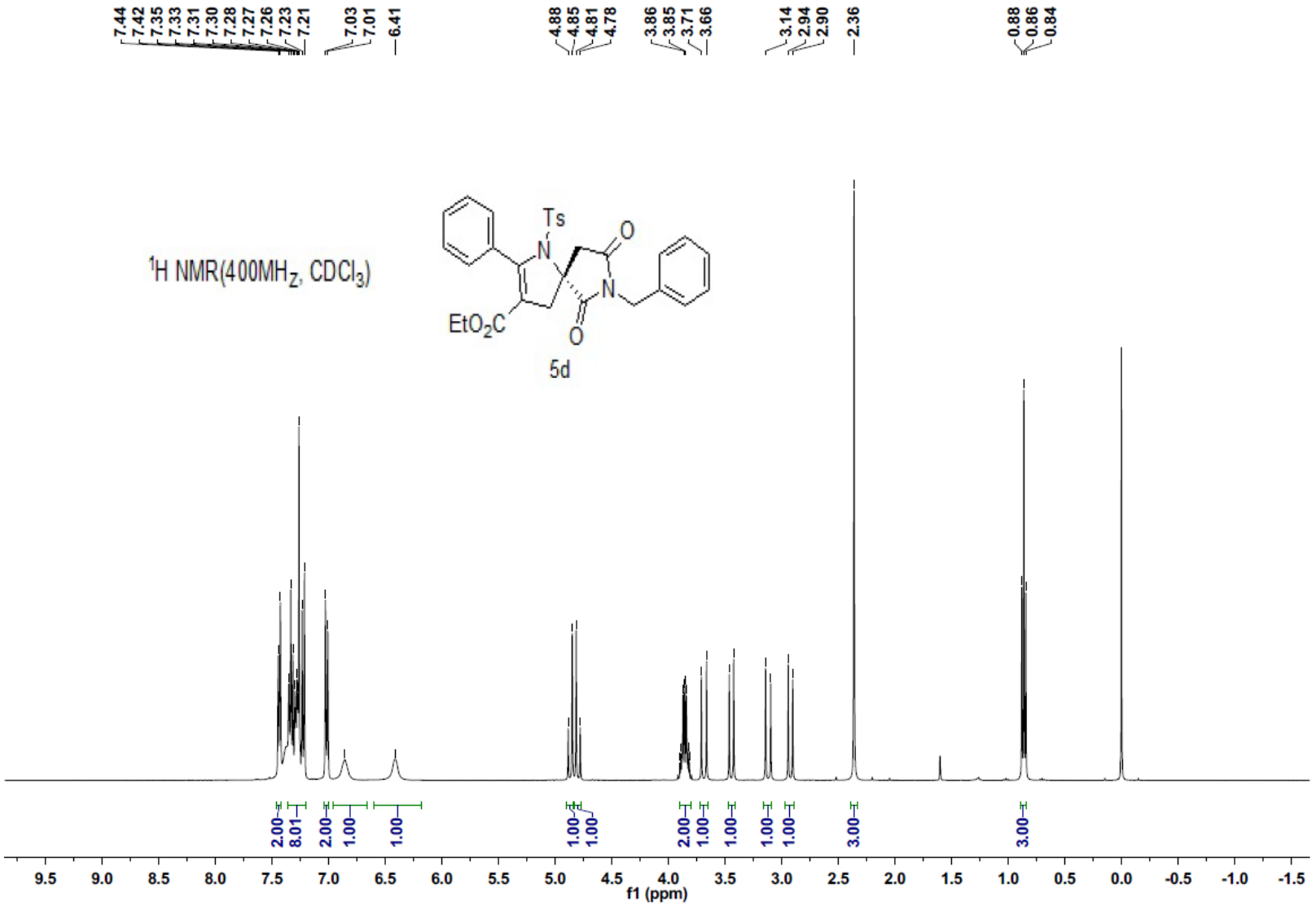
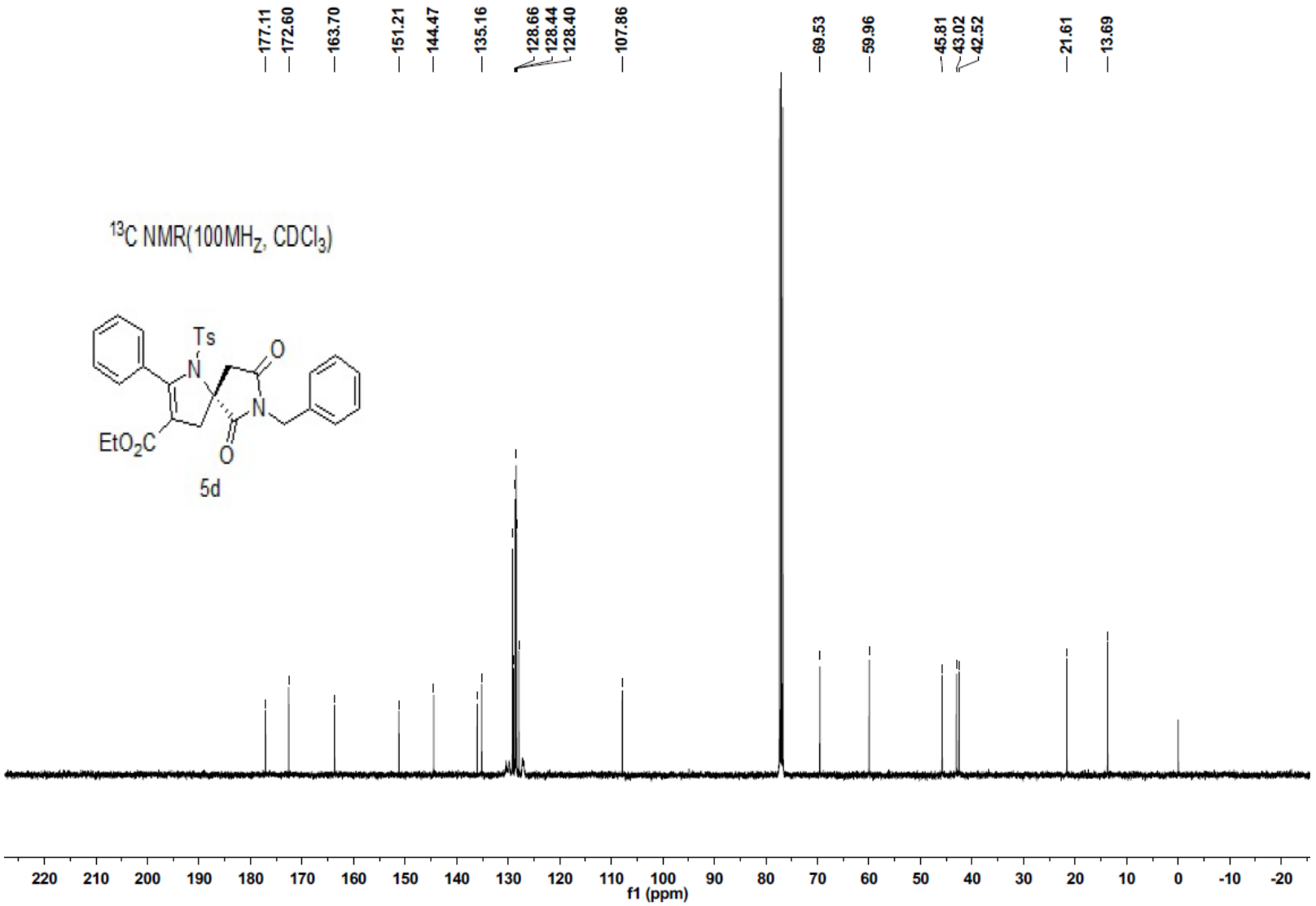
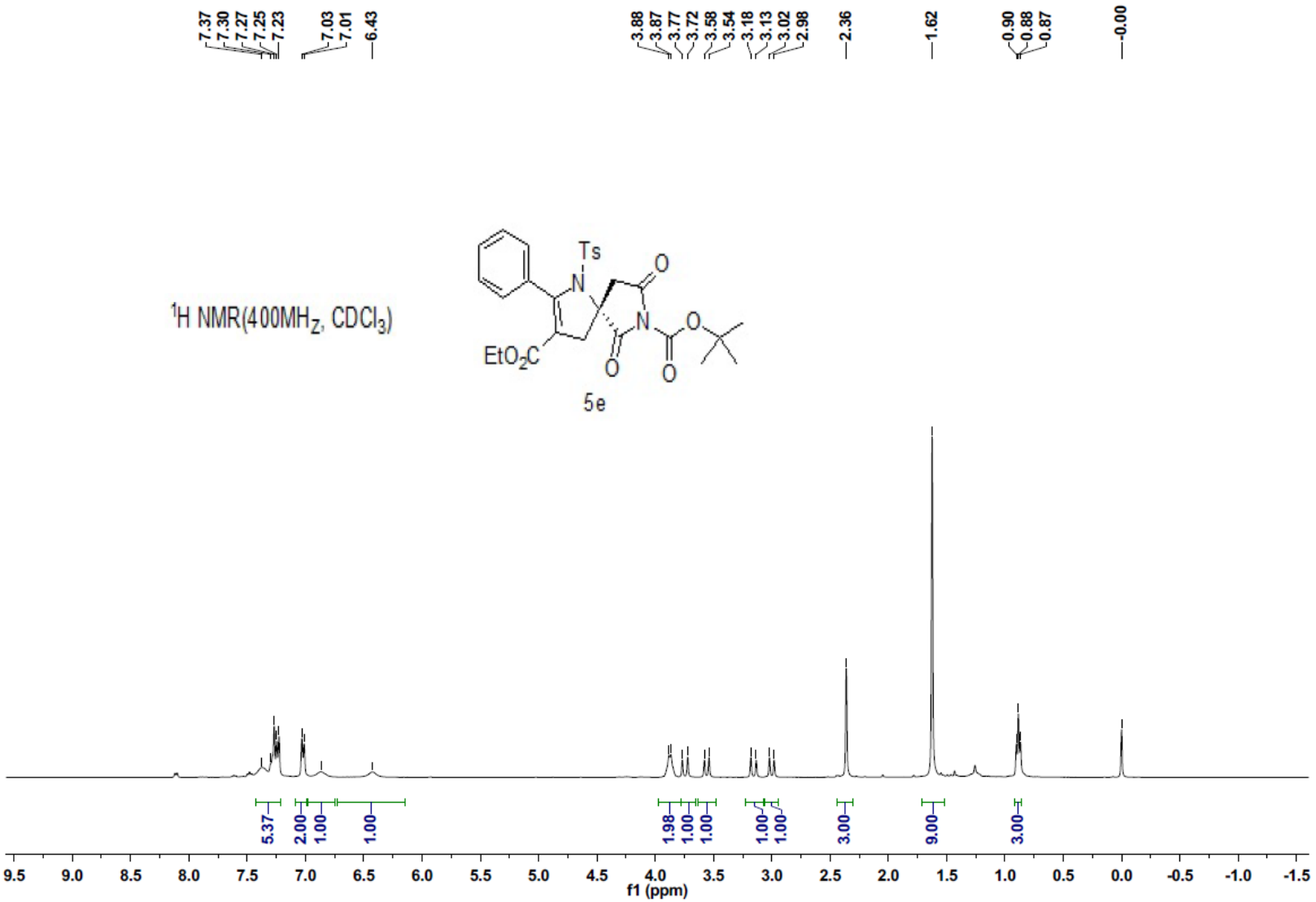
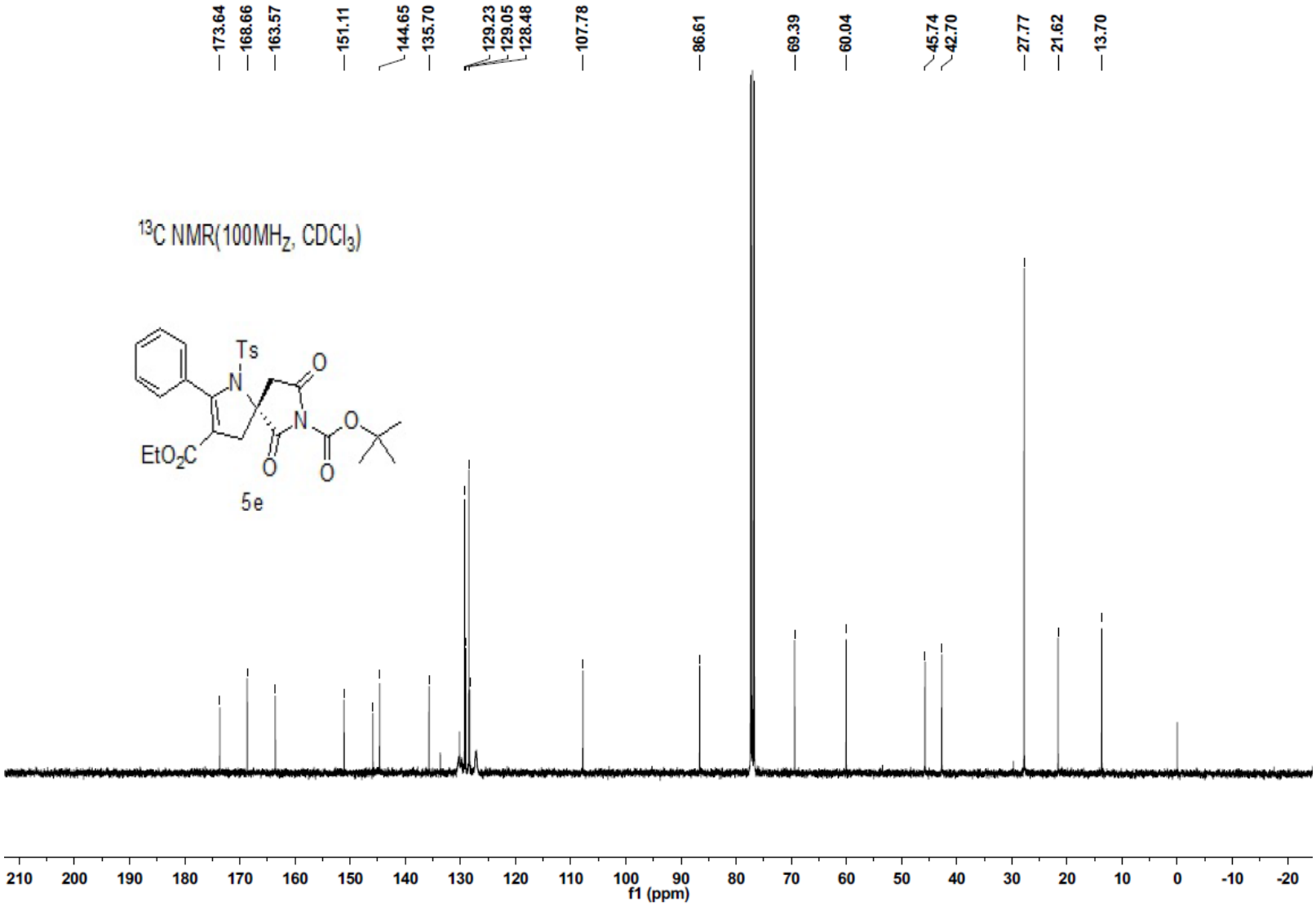
171.38
163.60
150.87
147.43
144.84
135.63
129.36
127.50
124.55
108.09
69.45
60.12
45.91
42.58
21.63
13.69
13C NMR(100MHz, CDCl3)
Ts
N
O
N
O
EtO2C
NO2
5c
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.44
7.42
7.35
7.33
7.31
7.30
7.28
7.27
7.26
7.23
7.21
7.03
7.01
6.41
4.88
4.85
4.81
4.78
3.86
3.85
3.71
3.66
3.14
2.94
2.90
2.36
0.88
0.86
0.84
$^1$H NMR(400MH$_Z$, CDCl$_3$)
Ts
N
O
N
O
EtO$_2$C
O
5d
2.00
8.01
2.00
1.00
1.00
1.00
1.00
2.00
1.00
1.00
1.00
3.00
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 -1.5
f1 (ppm)


177.11
172.60
163.70
151.21
144.47
135.16
128.66
128.44
128.40
107.86
69.53
59.96
45.81
43.02
42.52
21.61
13.69
13C NMR(100MHz, CDCl3)
Ts
N
O
N
O
EtO2C
O
5d
220
210
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)


7.37
7.30
7.27
7.25
7.23
7.03
7.01
6.43
3.88
3.87
3.77
3.72
3.58
3.54
3.18
3.13
3.02
2.98
2.36
1.62
0.90
0.88
0.87
0.00
$^1$H NMR(400MH$_Z$, CDCl$_3$)
Ts
N
O
N
O
O
O
EtO$_2$C
O
5e
5.37
2.00
1.00
1.00
1.98
1.00
1.00
1.00
1.00
3.00
9.00
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
-1.5
f1 (ppm)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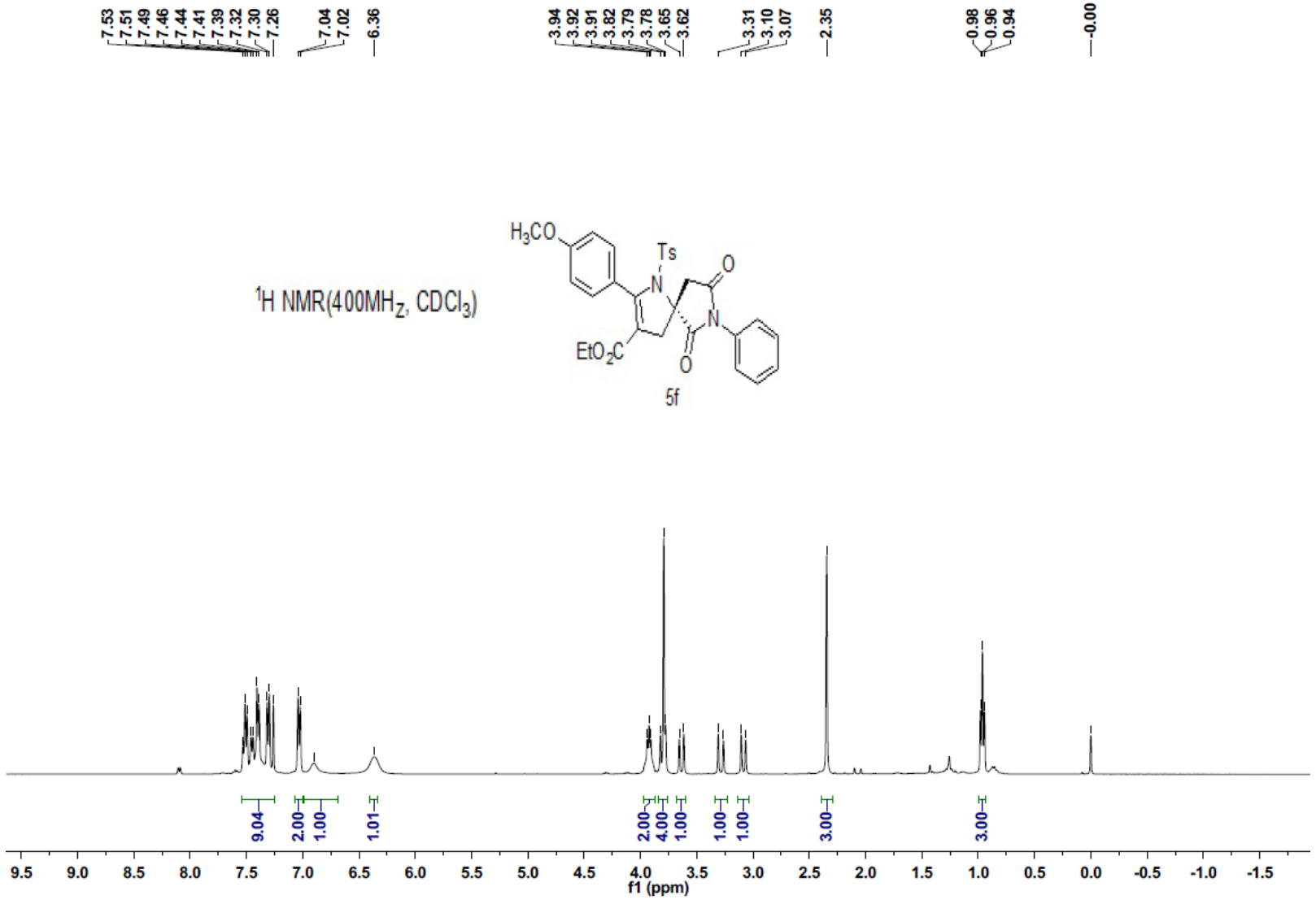
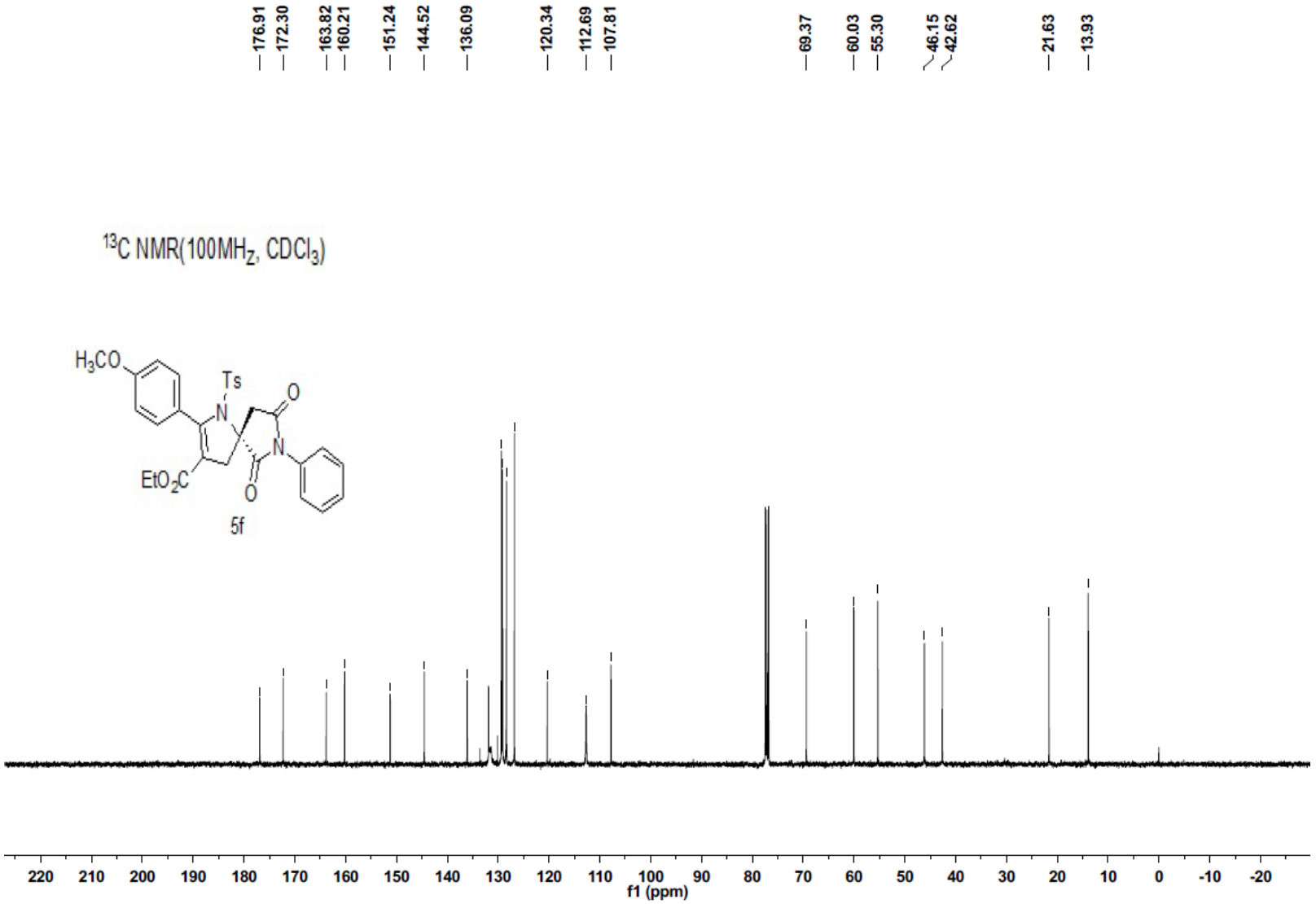
168.66
163.57
151.11
144.65
135.70
129.23
129.05
128.48
107.78
86.61
69.39
60.04
45.74
42.70
27.77
21.62
13.70
13C NMR(100MHz, CDCl3)
Ts
N
O
N
O
O
O
O
EtO2C
5e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


7.53
7.51
7.49
7.46
7.44
7.41
7.39
7.32
7.30
7.26
7.04
7.02
6.36
3.94
3.92
3.91
3.82
3.79
3.78
3.65
3.62
3.31
3.10
3.07
2.35
0.98
0.96
0.94
0.00
1H NMR(400MHZ, CDCl3)
H3CO
Ts
N
O
N
O
EtO2C
O
5f
9.04
2.00
1.00
1.01
2.00
4.00
1.00
1.00
1.00
3.00
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 -1.5
f1 (ppm)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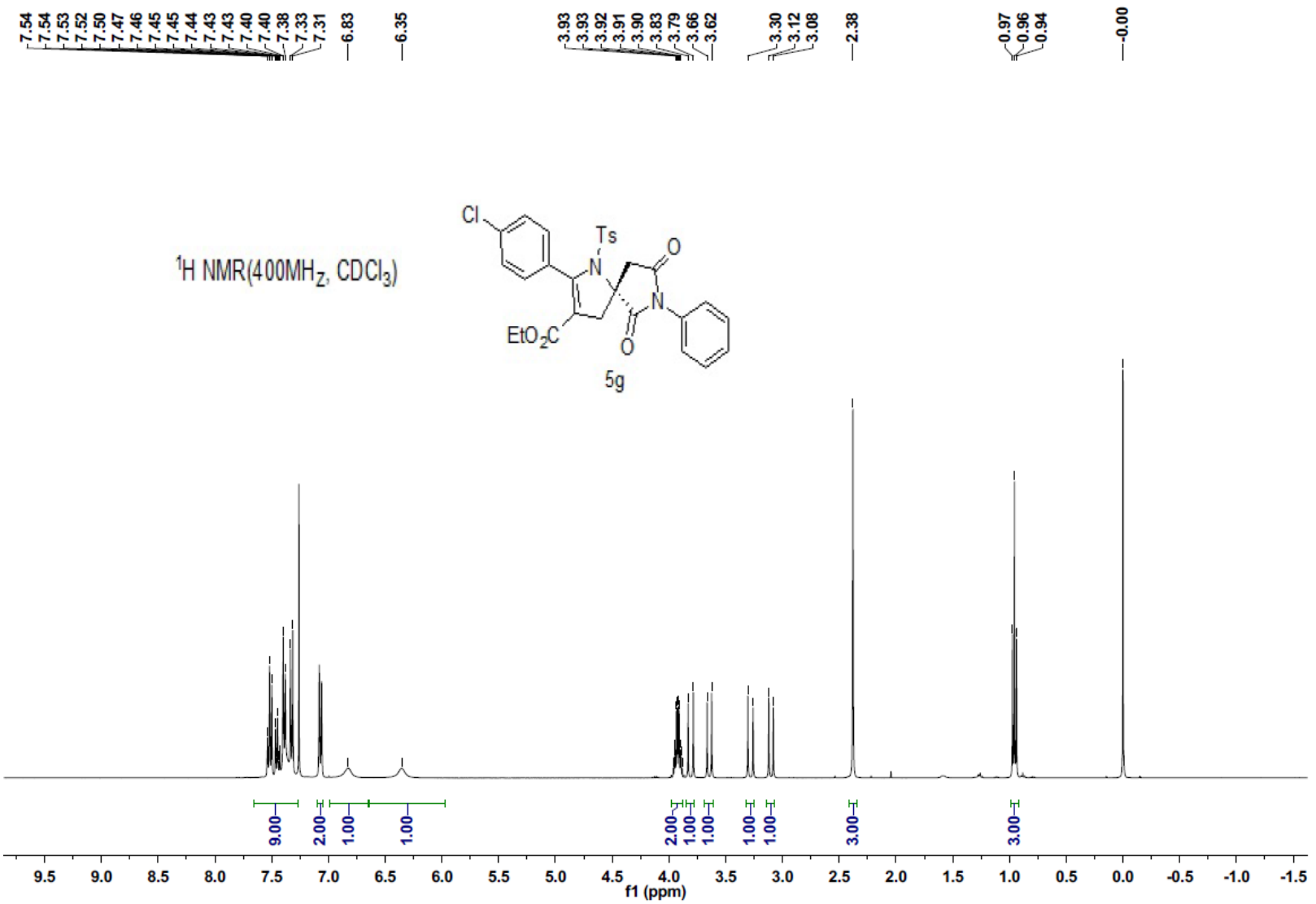
160.21
151.24
144.52
136.09
120.34
112.69
107.81
69.37
60.03
55.30
46.15
42.62
21.63
13.93
13C NMR(100MHz, CDCl3)
H3CO
Ts
N
O
N
EtO2C
O
5f
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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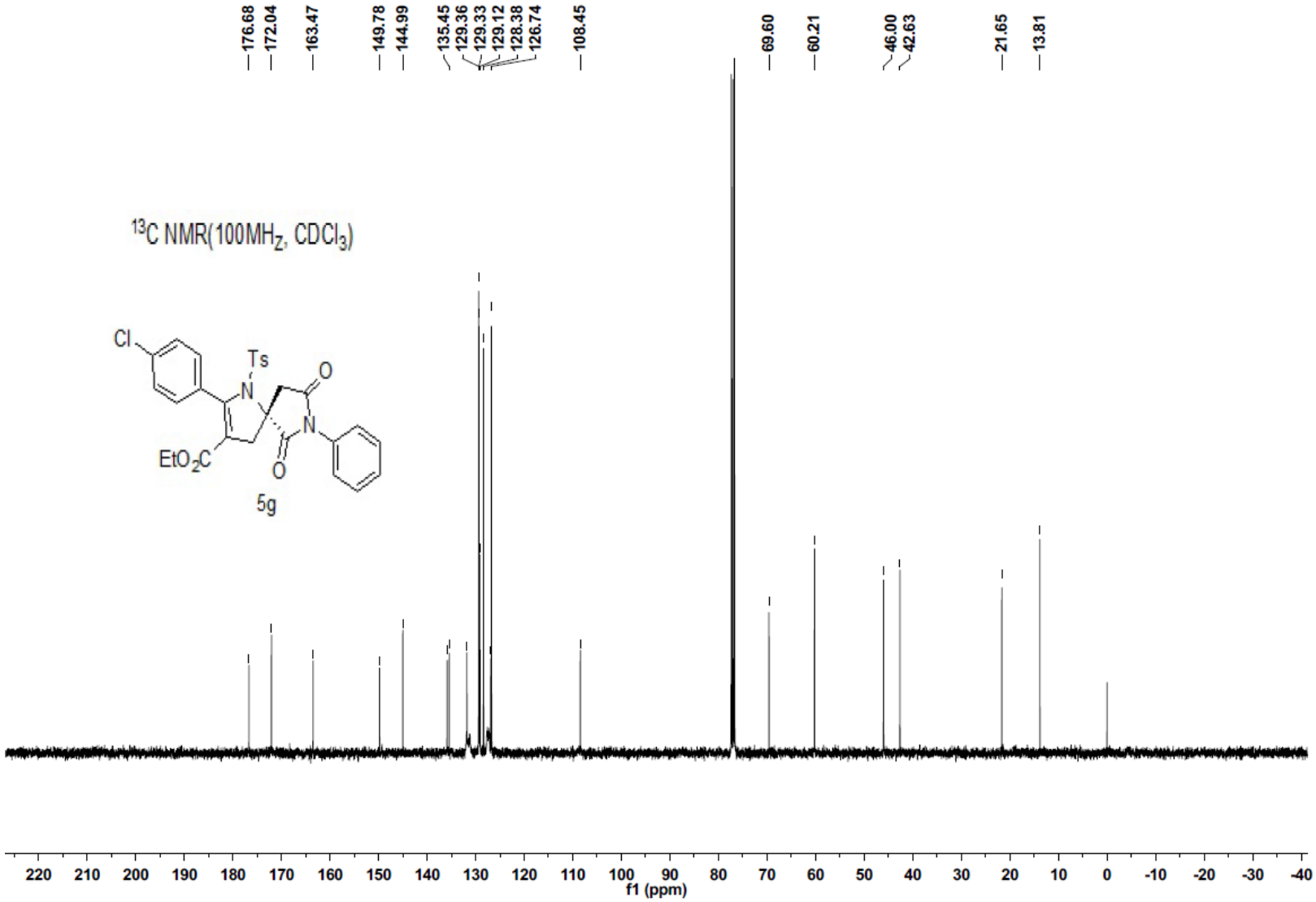
7.54
7.53
7.52
7.50
7.47
7.46
7.45
7.45
7.44
7.43
7.43
7.40
7.40
7.38
7.33
7.31
6.83
6.35
3.93
3.93
3.92
3.91
3.90
3.83
3.79
3.66
3.62
3.30
3.12
3.08
2.38
0.97
0.96
0.94
0.00
1H NMR(400MHz, CDCl3)
Cl
Ts
N
O
N
O
EtO2C
O
5g
9.00
2.00
1.00
1.00
2.00
1.00
1.00
1.00
1.00
3.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
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
-1.5
f1 (ppm)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163.47
149.78
144.99
135.45
129.36
129.33
129.12
128.38
126.74
108.45
69.60
60.21
46.00
42.63
21.65
13.81
13C NMR(100MHz, CDCl3)
Cl
Ts
N
O
N
O
EtO2C
O
5g
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)