

Electronic Supporting Information

Base-mediated isocyanide-based three-component reactions: divergent synthesis of spiro-substituted furans and pyrroles

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Experimental Section

General information:

All reagents and solvents were acquired from commercially available suppliers and used without further purification, unless specified. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer in CDCl_3 using TMS as the internal standard. IR spectra were recorded on a Nicolet 740 FT-IR spectrometer. HRMS were measured on an Agilent Technologies 6510, Q-TOFLC/MS ESI Technique. Melting points were determined in capillaries and are uncorrected. UV-vis spectra were recorded on a Shimadzu UV-2501PC spectrometer; fluorescence spectra were obtained on an Hitachi FL-4500 spectrofluorimeter. All reactions were monitored using thin layer chromatography (TLC) on pre-coated silica gel 60 F_{254} (mesh); spots were observed under UV light.

X-ray single crystal structure determination

X-ray diffraction single-crystal data were measured on a Bruker Apex II CCD diffractometer at 150 K using graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Data reduction was made with the Bruker SAINT program. The structure was solved by direct methods and refined with full-matrix least squares technique using the SHELXTL package¹. Displacement parameters were refined anisotropically, and the positions of the hydrogen atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement.

CCDC 1439402, 1439403 contains the supplementary crystallographic data for **4a** and **5a**. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK.

General procedure for the preparation of spiro-substituted furans 4.

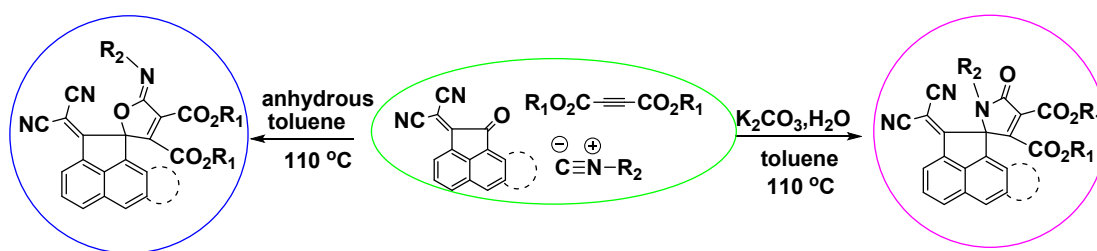
To a magnetically stirred solution of 2-(2-oxoacenaphthylen-1(2*H*)-ylidene)malononitrile (**1a**, 1 mmol) or 2-(2-oxoaceanthrylen-1(2*H*)-ylidene)malononitrile (**1b**, 1 mmol), the corresponding dialkyl acetylenedicarboxylate (**2**, 1 mmol) in anhydrous toluene (2 mL) was added dropwise a solution of corresponding isocyanide (**3**, 1 mmol) in anhydrous toluene (1 mL) at 25 °C for 5 min. The reaction mixture was then stirred at 110 °C for 24 h. The solvent was removed and the residue was purified by column chromatography using n-hexane–EtOAc (1:4) as eluent. The solvent was removed and the product **4** was obtained.

General procedure for the synthesis of compound 5.

To a magnetically stirred solution of To a magnetically stirred solution of 2-(2-oxoacenaphthylen-1(2*H*)-ylidene)malononitrile (**1a**, 1 mmol) or 2-(2-oxoaceanthrylen-1(2*H*)-ylidene)malononitrile (**1b**, 1 mmol), the corresponding dialkyl acetylenedicarboxylate (**2**, 1 mmol) and K₂CO₃ (0.5 mmol) in toluene and water (V_t/V_w = 100:1, 2.0 mL) was added dropwise a solution of corresponding isocyanide (**3**, 1 mmol) in toluene and water (V_t/V_w = 100:1, 1.0 mL) at 25 °C for 10 min. The reaction mixture was then stirred at 110 °C for 24 h. The solvent was removed and the residue was purified by column chromatography using n-hexane–EtOAc (1:4) as eluent. The solvent was removed and the product **5** was obtained.

General procedure for the synthesis of compound 5m-5o.

To a magnetically stirred solution of 2-(10-oxophenanthren-9(10H)-ylidene)malononitrile (**1c**, 1 mmol), the corresponding dimethyl acetylenedicarboxylate (**2a**, 1 mmol) and K_2CO_3 (0.5 mmol) in toluene and water ($V_t/V_w = 100:1$, 2.0 mL) was added dropwise a solution of corresponding isocyanide (**3**, 1 mmol) in toluene and water ($V_t/V_w = 100:1$, 1.0 mL) at 25 °C for 10 min. The reaction mixture was then stirred at 110 °C for 24 h. The solvent was removed and the residue was purified by column chromatography using n-hexane–EtOAc (1:4) as eluent. The solvent was removed and the product **6** was obtained.



Scheme 1 Reagents and conditions.

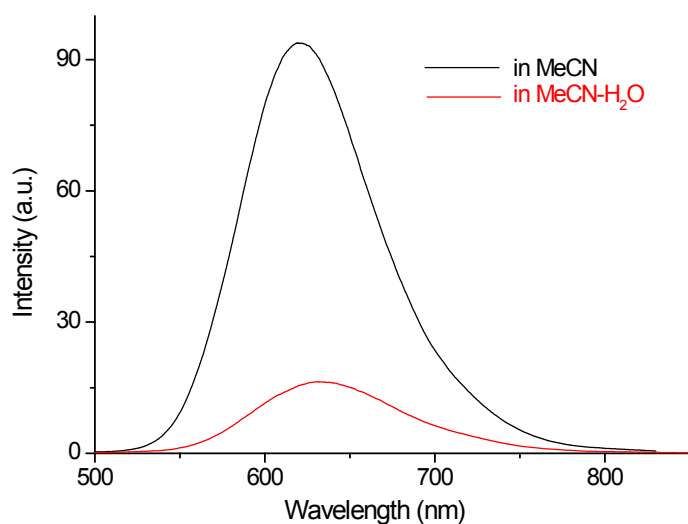


Fig. S1 Emission spectra of **4g** (excited at 490 nm) in MeCN and MeCN–H₂O (MeCN/water, 8:2, v/v, 1.0×10^{-5} mol/L).

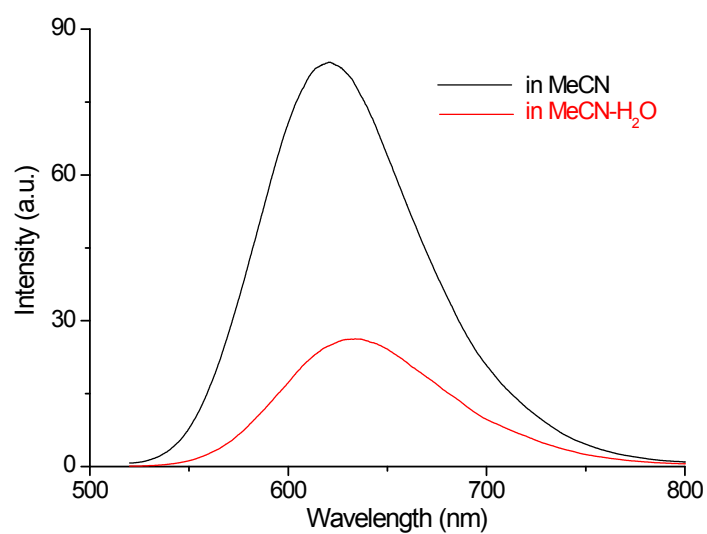


Fig. S2 Emission spectra of **5g** (excited at 490 nm) in MeCN and MeCN-H₂O (MeCN/water, 8:2, v/v, 1.0×10^{-5} mol/L).

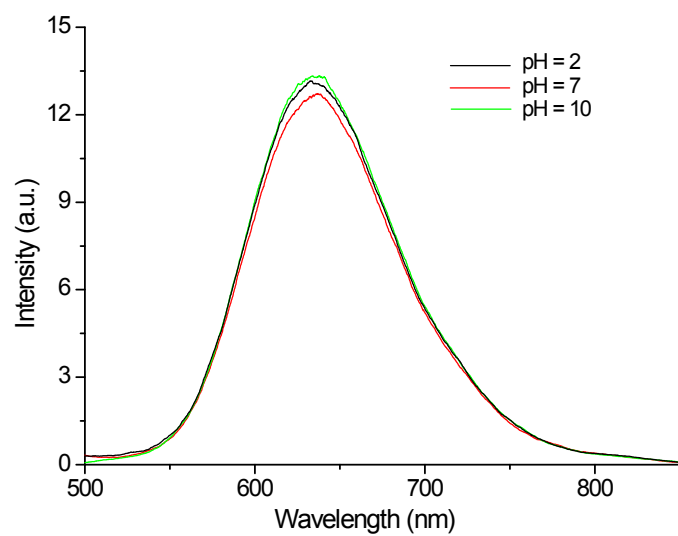


Fig. S3 pH-dependence of the emission spectra of **4g** (1.0×10^{-5} mol/L).

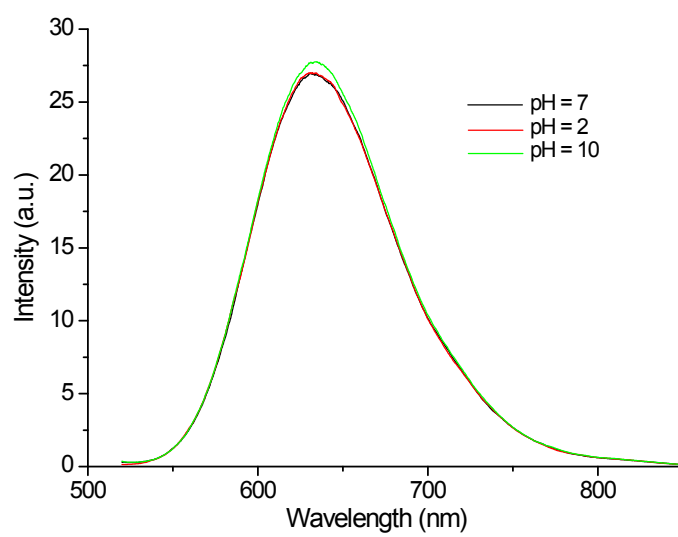


Fig. S4 pH-dependence of the emission spectra of **5g** (1.0×10^{-5} mol/L).

Reference

- [1] G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112.

(Z)-dimethyl 5'-(*tert*-butylimino)-2-(dicyanomethylene)-2*H*,5'*H*-spiro[acenaphthylene-1,2'-furan]-3',4'-dicarboxylate (**4a**): Mp 190-192 °C; pale yellow powder; IR(KBr): 2970, 2902, 2230, 1758, 1577, 1299, 779 cm⁻¹ ¹H NMR (400 MHz, CDCl₃) δ 8.61 (d, *J* = 8.0 Hz, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.86-7.80 (m, 1H), 7.69 (m, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 3.99 (s, 3H), 3.52 (s, 3H), 1.33 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 170.5, 161.8, 159.8, 151.3, 140.0, 139.2, 138.3, 135.6, 132.7, 132.5, 130.8, 129.2, 127.2, 125.1, 120.2, 112.5, 110.4, 94.4, 79.7, 55.9, 53.5, 53.1, 29.4; HRMS (ESI) calcd for C₂₆H₂₁N₃O₅ [M-H]⁻ 454.1403, found 454.1397.

(Z)-dimethyl 5'-(cyclohexylimino)-2-(dicyanomethylene)-2*H*,5'*H*-spiro[acenaphthylene-1,2'-furan]-3',4'-dicarboxylate (**4b**): Mp 202-204 °C; pale yellow powder; IR (KBr): 2932, 2854, 2229, 1754, 1582, 1302, 780 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.60 (d, *J* = 8.0 Hz, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.89-7.78 (m, 1H), 7.71 (m, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 3.99 (s, 3H), 3.71-3.60 (m, 1H), 3.52 (s, 3H), 1.88 (d, *J* = 16.0 Hz, 1H), 1.79-1.68 (m, 3H), 1.60-1.41 (m, 3H), 1.32-1.17 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.4, 161.5, 159.7, 153.5, 139.2, 139.2, 138.6, 135.5, 132.6, 132.4, 130.8, 129.2, 129.2, 127.2, 125.1, 120.5, 112.5, 110.5, 93.9, 79.9, 57.4, 53.5, 53.1, 33.3, 32.8, 25.6, 24.6; HRMS (ESI) calcd for C₂₈H₂₃N₃O₅ [M-H]⁻ 480.1559, found 480.1567.

(Z)-dimethyl 5'-(benzylimino)-2-(dicyanomethylene)-2*H*,5'*H*-spiro[acenaphthylene-1,2'-furan]-3',4'-dicarboxylate (**4c**): Mp 183-186 °C; pale yellow powder; IR (KBr): 2954, 2227, 1731, 1686, 1574, 1439, 1364, 1299, 1052, 776 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.62 (d, *J* = 7.4 Hz, 1H), 8.18 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.84 (t, *J* = 7.8 Hz, 1H), 7.70 (t, *J* = 7.7 Hz, 1H), 7.48 (m, 1H), 7.34 (m, *J* = 15.0, 4.7 Hz, 4H), 7.23 (t, *J* = 7.1 Hz, 1H), 4.73 (d, *J* = 7.3 Hz, 2H), 4.01 (s, 3H), 3.54 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.7, 161.2, 159.6, 155.9, 140.1, 139.2, 138.9, 138.0, 135.1, 132.5, 130.8, 129.3, 129.2, 128.3, 127.8, 127.4, 126.8, 125.2, 120.6, 112.4, 110.3, 94.5, 80.0, 62.9, 53.6, 53.2, 52.1, 14.2; HRMS (APCI) calcd for C₂₉H₁₉N₃O₅ [M+H]⁺ 490.1403, found 490.1403.

(Z)-diethyl 5'-(*tert*-butylimino)-2-(dicyanomethylene)-2*H*,5'*H*-spiro[acenaphthylene-1,2'-furan]-3',4'-dicarboxylate (**4d**): Mp 204-206 °C; pale yellow powder; IR (KBr): 2988, 2968, 2229, 1747, 1685, 1580, 1335, 1276, 1030 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.60 (d, *J* = 7.4 Hz, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.82 (t, *J* = 7.8 Hz, 1H), 7.73-7.65 (m, 1H), 7.48 (d, *J*

= 7.0 Hz, 1H), 4.46 (m, 2H), 3.88 (m, 2H), 1.41 (t, $J = 7.1$ Hz, 3H), 1.34 (s, 9H), 0.80 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.5, 161.2, 159.2, 151.6, 140.1, 139.2, 138.4, 135.8, 132.8, 132.3, 130.8, 129.3, 129.1, 127.0, 124.9, 120.3, 112.6, 110.3, 94.3, 79.8, 62.6, 62.0, 55.9, 30.2, 29.5, 14.1, 13.2; HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{25}\text{N}_3\text{O}_5$ $[\text{M}+\text{Na}]^+$ 506.1692, found 506.1691.

(Z)-diethyl 5'-(cyclohexylimino)-2-(dicyanomethylene)-2*H*,5'*H*-spiro[acenaphthylene-1,2'-furan]-3',4'-dicarboxylate (**4e**): Mp 213-215 °C; pale yellow powder; IR (KBr): 2982, 2927, 2230, 1749, 1689, 1578, 1335, 1260, 1023, 784 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.59 (d, $J = 7.4$ Hz, 1H), 8.16 (d, $J = 8.2$ Hz, 1H), 7.96 (d, $J = 8.2$ Hz, 1H), 7.82 (t, $J = 7.8$ Hz, 1H), 7.70 (t, $J = 7.6$ Hz, 1H), 7.50 (d, $J = 6.9$ Hz, 1H), 4.47 (m, 2H), 3.88 (m, 2H), 3.73-3.61 (m, 1H), 1.88 (d, $J = 12.8$ Hz, 1H), 1.73 (s, 3H), 1.52 (m, 3H), 1.40 (t, $J = 7.1$ Hz, 3H), 1.26 (d, $J = 21.1$ Hz, 3H), 0.79 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.5, 161.0, 159.2, 153.5, 139.3, 139.2, 138.9, 135.7, 132.8, 132.3, 130.7, 129.2, 129.2, 127.1, 124.9, 120.5, 112.6, 110.4, 93.9, 79.9, 62.7, 62.0, 57.2, 33.3, 32.8, 25.7, 24.6, 14.1, 13.2; HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{27}\text{N}_3\text{O}_5$ $[\text{M}+\text{Na}]^+$ 532.1848, found 532.1848.

(Z)-diethyl 5'-(benzylimino)-2-(dicyanomethylene)-2*H*,5'*H*-spiro[acenaphthylene-1,2'-furan]-3',4'-dicarboxylate (**4f**): Mp 191-194 °C; yellow powder; IR (KBr): 2987, 2950, 2223, 1735, 1686, 1570, 1440, 1367, 1230, 1045, 778 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.61 (d, $J = 8.0$ Hz, 1H), 8.18 (d, $J = 8.0$ Hz, 1H), 7.98 (d, $J = 8.0$ Hz, 1H), 7.87-7.80 (m, 1H), 7.71 (m, 1H), 7.49 (d, $J = 8.0$ Hz, 1H), 7.38 (d, $J = 8.0$ Hz, 2H), 7.31 (m, 2H), 7.26-7.21 (m, 1H), 4.80-4.68 (m, 2H), 4.48 (m, 2H), 3.91 (m, 2H), 1.42 (t, $J = 8.0$ Hz, 3H), 0.82 (t, $J = 8.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.9, 160.8, 159.0, 156.0, 140.1, 139.3, 139.0, 138.3, 135.2, 132.7, 132.4, 130.8, 129.3, 129.2, 128.3, 127.7, 127.3, 126.7, 125.0, 120.7, 112.5, 110.3, 94.4, 80.0, 62.9, 62.2, 52.0, 14.1, 13.2; HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{23}\text{N}_3\text{O}_5$ $[\text{M}+\text{H}]^+$ 518.1716, found 518.1713.

(Z)-dimethyl 5'-(*tert*-butylimino)-1-(dicyanomethylene)-1*H*,5'*H*-spiro[aceanthrylene-2,2'-furan]-3',4'-dicarboxylate (**4g**): Mp 190-193 °C; red powder; IR (KBr): 2961, 2904, 2228, 1758, 1732, 1571, 1429, 1279, 1029, 970 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.63 (d, $J = 7.1$ Hz, 1H), 8.58 (s, 1H), 8.29 (d, $J = 8.5$ Hz, 1H), 8.16 (d, $J = 8.5$ Hz, 1H), 7.80 (m, 2H), 7.72-7.64 (m, 1H), 7.61 – 7.55 (m, 1H), 4.02 (s, 3H), 3.43 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.0, 161.8, 159.7, 151.7, 140.4, 138.5, 137.4, 134.4, 132.9, 132.6, 130.3, 128.6, 128.4, 128.0, 128.0, 127.8, 126.9, 126.3, 125.3, 122.0, 112.7, 110.5, 96.3, 79.3, 56.2, 53.4, 53.0, 29.4; HRMS (ESI) calcd for

$C_{30}H_{23}N_3O_5$ [M+Na]⁺ 528.1535, found 528.1535.

(Z)-dimethyl 5'-(cyclohexylimino)-1-(dicyanomethylene)-1*H*,5'*H*-spiro[aceanthrylene-2,2'-furan]-3',4'-dicarboxylate (**4h**): Mp 210-213 °C; red powder; IR (KBr): 2936, 2852, 2228, 1729, 1693, 1431, 1298, 1029, 979 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.66-8.55 (m, 2H), 8.27 (d, *J* = 8.5 Hz, 1H), 8.17 (d, *J* = 8.6 Hz, 1H), 7.79 (m, 2H), 7.69-7.64 (m, 1H), 7.62-7.56 (m, 1H), 4.02 (s, 3H), 3.76-3.68 (m, 1H), 3.43 (s, 3H), 2.00-1.88 (m, 1H), 1.81-1.65 (m, 3H), 1.53 (d, *J* = 14.3 Hz, 3H), 1.29-1.15 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.9, 161.5, 159.7, 153.9, 139.5, 139.0, 137.4, 134.4, 132.9, 132.5, 130.4, 128.7, 128.2, 128.0, 127.9, 127.9, 127.0, 126.3, 125.3, 121.8, 112.7, 110.6, 95.8, 79.5, 57.6, 53.5, 53.0, 33.3, 33.0, 25.6, 24.6, 24.6; HRMS (ESI) calcd for C₃₂H₂₅N₃O₅ [M+Na]⁺ 554.1692, found 554.1689.

(Z)-dimethyl 5'-(benzylimino)-1-(dicyanomethylene)-1*H*,5'*H*-spiro[aceanthrylene-2,2'-furan]-3',4'-dicarboxylate (**4i**): Mp 211-214 °C; red powder; IR (KBr): 3031, 2954, 2229, 1720, 1686, 1570, 1440, 1300, 1048, 985, 734 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 8.86 (s, 1H), 8.55 (d, *J* = 8.4 Hz, 1H), 8.42 (d, *J* = 7.3 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 7.97 (t, *J* = 7.8 Hz, 1H), 7.62 (m, *J* = 15.2, 6.7 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 1H), 6.96 (t, *J* = 7.8 Hz, 1H), 6.80 (t, *J* = 7.4 Hz, 2H), 6.45 (d, *J* = 7.7 Hz, 2H), 4.70-4.64 (m, 1H), 3.96 (s, 3H), 3.85 (d, *J* = 14.8 Hz, 1H), 3.33 (s, 3H); ¹³C NMR (100 MHz, DMSO) δ 167.8, 165.6, 161.9, 159.6, 142.9, 138.9, 137.9, 134.3, 134.1, 133.9, 133.7, 131.1, 129.3, 128.8, 128.8, 128.3, 128.2, 128.1, 126.7, 126.7, 125.8, 125.7, 120.0, 113.0, 110.6, 79.0, 78.2, 53.9, 51.9, 44.8; HRMS (APCI) calcd for C₃₃H₂₁N₃O₅ [M+H]⁺ 540.1559, found 540.1557.

(Z)-diethyl 5'-(*tert*-butylimino)-1-(dicyanomethylene)-1*H*,5'*H*-spiro[aceanthrylene-2,2'-furan]-3',4'-dicarboxylate (**4j**): Mp 182-185 °C; red powder; IR (KBr): 2974, 2935, 2227, 1748, 1730, 1686, 1574, 1428, 1335, 1275, 1030, 973 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.62 (d, *J* = 7.1 Hz, 1H), 8.58 (s, 1H), 8.28 (d, *J* = 8.5 Hz, 1H), 8.16 (d, *J* = 8.6 Hz, 1H), 7.88-7.81 (m, 1H), 7.77 (m, 1H), 7.71-7.64 (m, 1H), 7.62-7.54 (m, 1H), 4.55-4.43 (m, 2H), 3.85-3.72 (m, 2H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.35 (s, 9H), 0.72 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.1, 161.3, 159.1, 151.7, 140.7, 138.5, 137.4, 134.4, 133.1, 132.4, 130.2, 128.7, 128.5, 127.9, 127.7, 126.9, 126.3, 125.1, 122.1, 112.8, 110.5, 96.2, 79.4, 62.6, 62.0, 56.0, 29.5, 14.1, 13.1; HRMS (ESI) calcd for C₃₂H₂₇N₃O₅ [M+Na]⁺ 556.1848, found 556.1843.

(Z)-diethyl 5'-(cyclohexylimino)-1-(dicyanomethylene)-1*H*,5'*H*-spiro[aceanthrylene-2,2'-furan]-

3',4'-dicarboxylate (4k): Mp 208-211 °C; red powder; IR (KBr): 2932, 2856, 2230, 1720, 1696, 1575, 1429, 1335, 1276, 1020, 748 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.63-8.56 (m, 2H), 8.27 (d, *J* = 8.5 Hz, 1H), 8.17 (d, *J* = 8.6 Hz, 1H), 7.83 (m, 1H), 7.76 (m, 1H), 7.70-7.63 (m, 1H), 7.62-7.56 (m, 1H), 4.53-4.44 (m, 2H), 3.84-3.69 (m, 3H), 1.97-1.90 (m, 1H), 1.71 (t, *J* = 19.0 Hz, 3H), 1.58-1.49 (m, 3H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.30-1.15 (m, 3H), 0.71 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.0, 161.0, 159.1, 153.9, 139.5, 139.3, 137.4, 134.4, 133.1, 132.4, 130.3, 128.7, 128.5, 127.9, 127.7, 126.9, 126.3, 125.1, 121.9, 112.8, 110.5, 95.7, 79.6, 62.7, 62.0, 57.4, 33.3, 33.0, 25.7, 24.6, 24.5, 14.1, 13.1; HRMS (APCI) calcd for C₃₄H₂₉N₃O₅ [M+H]⁺ 560.2185, found 560.2187.

(Z)-diethyl 5'-(benzylimino)-1-(dicyanomethylene)-1H,5'H-spiro[aceanthrylene-2,2'-furan]-3',4'-dicarboxylate (4l): Mp 200-203 °C; red powder; IR (KBr): 3030, 2954, 2220, 1731, 1686, 1575, 1435, 1364, 1299, 1052, 986, 735 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.65-8.57 (m, 2H), 8.29 (d, *J* = 8.0 Hz, 1H), 8.21-8.14 (m, 1H), 7.78 (t, *J* = 8.0 Hz, 2H), 7.60 (m, 2H), 7.39 (d, *J* = 4.0 Hz, 2H), 7.30 – 7.25 (m, 2H), 7.21 (t, *J* = 8.0 Hz, 1H), 4.85-4.72 (m, 2H), 4.55-4.43 (m, 2H), 3.88-3.74 (m, 2H), 1.43 (t, *J* = 8.0 Hz, 3H), 0.73 (t, *J* = 8.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.4, 160.8, 159.0, 156.3, 140.4, 139.0, 138.9, 137.5, 134.4, 133.0, 132.5, 130.3, 128.9, 128.3, 128.0, 127.9, 127.9, 127.8, 127.0, 126.7, 126.4, 125.2, 121.8, 112.6, 110.3, 96.3, 79.7, 62.9, 62.2, 52.2, 14.1, 13.1; HRMS (ESI) calcd for C₃₅H₂₅N₃O₅ [M+Na]⁺ 590.1692, found 590.1717.

Dimethyl 1'-tert-butyl-2-(dicyanomethylene)-5'-oxo-1',5'-dihydro-2H-spiro[acenaphthylene-1,2'-pyrrole]-3',4'-dicarboxylate (5a): Mp 219-222 °C; yellow powder; IR (KBr): 2930, 2849, 2225, 1745, 1690, 1570, 1438, 1346, 1274, 1089, 786 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.68 (d, *J* = 7.4 Hz, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.84 (t, *J* = 7.8 Hz, 1H), 7.69 (m, 1H), 7.42 (d, *J* = 7.0 Hz, 1H), 3.95 (d, *J* = 5.3 Hz, 3H), 3.41 (d, *J* = 1.9 Hz, 3H), 1.23 (d, *J* = 7.1 Hz, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 171.2, 166.4, 161.7, 159.5, 142.1, 139.3, 138.1, 135.4, 134.0, 132.8, 131.2, 129.3, 129.0, 127.0, 125.5, 120.6, 112.6, 110.1, 78.6, 77.9, 59.2, 53.3, 53.0, 27.7; HRMS (APCI) calcd for C₂₆H₂₁N₃O₅ [M+H]⁺ 456.1559, found 456.1552.

Dimethyl 1'-cyclohexyl-2-(dicyanomethylene)-5'-oxo-1',5'-dihydro-2H-spiro[acenaphthylene-1,2'-pyrrole]-3',4'-dicarboxylate (5b): Mp 247-250 °C; yellow powder; IR (KBr): 2948, 2226, 1780, 1708, 1576, 1436, 1303, 1285, 1116, 784 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.69 (d, *J* = 7.4 Hz,

1H), 8.22 (d, $J = 8.2$ Hz, 1H), 7.99 (d, $J = 8.2$ Hz, 1H), 7.87 (t, $J = 7.8$ Hz, 1H), 7.73-7.65 (m, 1H), 7.40 (d, $J = 7.0$ Hz, 1H), 3.98 (s, 3H), 3.48 (s, 3H), 2.59 (m, $J = 15.8, 8.0, 3.8$ Hz, 1H), 2.22-2.02 (m, 2H), 1.70 (t, $J = 10.5$ Hz, 2H), 1.58-1.49 (m, 1H), 1.46-1.33 (m, 2H), 0.98 (m, $J = 18.8, 12.8, 3.2$ Hz, 2H), 0.81-0.67 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.5, 165.1, 161.7, 159.7, 141.3, 140.0, 139.8, 133.9, 133.7, 133.0, 131.2, 129.3, 128.9, 127.2, 125.5, 120.9, 112.5, 109.9, 79.1, 56.2, 53.3, 53.1, 29.7, 29.7, 25.9, 25.7, 24.7; HRMS (APCI) calcd for $\text{C}_{28}\text{H}_{23}\text{N}_3\text{O}_5$ $[\text{M}+\text{H}]^+$ 482.1716, found 482.1714.

Dimethyl 1'-benzyl-2-(dicyanomethylene)-5'-oxo-1',5'-dihydro-2H-spiro[acenaphthylene-1,2'-pyrrole]-3',4'-dicarboxylate (5c): Mp 173-175 °C; yellow powder; IR (KBr): 2957, 2231, 1708, 1576, 1445, 1383, 1270, 1109, 780 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.41 (d, $J = 7.4$ Hz, 1H), 8.20 (d, $J = 8.2$ Hz, 1H), 7.98 (d, $J = 8.3$ Hz, 1H), 7.87-7.78 (t, 1H), 7.65 (m, 1H), 7.25-7.16 (m, 2H), 7.05 (t, $J = 7.6$ Hz, 2H), 6.66 (d, $J = 7.3$ Hz, 2H), 4.97 (d, $J = 14.7$ Hz, 1H), 4.01 (d, $J = 1.7$ Hz, 3H), 3.56 (d, $J = 14.7$ Hz, 1H), 3.49 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.1, 165.5, 161.6, 159.7, 142.5, 139.7, 138.5, 134.3, 133.7, 133.5, 132.5, 131.0, 129.3, 129.1, 128.8, 128.4, 127.1, 125.1, 120.5, 111.9, 109.8, 79.5, 53.4, 53.1, 44.9; HRMS (APCI) calcd for $\text{C}_{29}\text{H}_{19}\text{N}_3\text{O}_5$ $[\text{M}+\text{H}]^+$ 490.1403, found 490.1422.

Diethyl 1'-tert-butyl-2-(dicyanomethylene)-5'-oxo-1',5'-dihydro-2H-spiro[acenaphthylene-1,2'-pyrrole]-3',4'-dicarboxylate (5d): Mp 214-217 °C; yellow powder; IR (KBr): 2935, 2850, 2227, 1740, 1686, 1574, 1439, 1340, 1280, 1070, 776 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.67 (d, $J = 8.0$ Hz, 1H), 8.18 (d, $J = 8.0$ Hz, 1H), 7.96 (d, $J = 8.0$ Hz, 1H), 7.83 (t, $J = 8.0$ Hz, 1H), 7.74-7.66 (m, 1H), 7.44 (d, $J = 8.0$ Hz, 1H), 4.41 (q, $J = 8.0$ Hz, 2H), 3.85-3.73 (m, 2H), 1.38 (t, $J = 8.0$ Hz, 3H), 1.23 (s, 9H), 0.74 (t, $J = 8.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.4, 166.5, 161.3, 159.0, 142.0, 139.4, 138.5, 135.7, 134.2, 132.7, 131.2, 129.2, 129.0, 126.9, 125.4, 120.6, 112.6, 110.1, 78.6, 77.8, 62.5, 62.1, 59.1, 27.8, 14.1, 13.2; HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{25}\text{N}_3\text{O}_5$ $[\text{M}+\text{Na}]^+$ 506.1692, found 506.1659.

Diethyl 1'-cyclohexyl-2-(dicyanomethylene)-5'-oxo-1',5'-dihydro-2H-spiro[acenaphthylene-1,2'-pyrrole]-3',4'-dicarboxylate (5e): Mp:164-167 °C; yellow powder; IR (KBr): 2950, 2222, 1750, 1700, 1574, 1439, 1364, 1283, 1110, 780 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.69 (d, $J = 8.0$ Hz, 1H), 8.22 (d, $J = 8.0$ Hz, 1H), 7.98 (d, $J = 8.0$ Hz, 1H), 7.86 (t, $J = 8.0$ Hz, 1H), 7.69 (m, 1H), 7.42 (d, $J = 8.0$ Hz, 1H), 4.45 (m, 2H), 3.93-3.77 (m, 2H), 2.60 (m, 1H), 2.12 (m, 2H), 1.83-1.65 (m,

3H), 1.58-1.48 (m, 2H), 1.40 (m, 3H), 0.90 (m, 3H), 0.78 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.7, 165.3, 161.3, 159.1, 141.2, 140.3, 140.1, 134.1, 133.9, 132.9, 131.1, 129.2, 129.0, 127.1, 126.6, 125.4, 120.9, 112.6, 109.9, 62.6, 62.1, 56.2, 25.9, 25.8, 24.7, 14.1, 13.2; HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{27}\text{N}_3\text{O}_5$ $[\text{M}+\text{Na}]^+$ 532.1848, found 532.1829.

Diethyl 1'-benzyl-2-(dicyanomethylene)-5'-oxo-1',5'-dihydro-2H-spiro[acenaphthylene-1,2'-pyrrole]-3',4'-dicarboxylate (5f): Mp 207-210 °C; yellow powder; IR (KBr): 2960, 2229, 1710, 1686, 1574, 1440, 1375, 1285, 1111, 776 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.40 (d, $J = 8.0$ Hz, 1H), 8.20 (d, $J = 8.0$ Hz, 1H), 7.97 (d, $J = 8.0$ Hz, 1H), 7.84 – 7.78 (m, 1H), 7.65 (m, 1H), 7.25 (d, $J = 8.0$ Hz, 1H), 7.19 (t, $J = 8.0$ Hz, 1H), 7.05 (t, $J = 8.0$ Hz, 2H), 6.67 (d, $J = 8.0$ Hz, 2H), 4.98 (d, $J = 16.0$ Hz, 1H), 4.51 – 4.44 (m, 2H), 3.92 – 3.81 (m, 2H), 3.58 (d, $J = 16.0$ Hz, 1H), 1.42 (t, $J = 8.0$ Hz, 3H), 0.78 (t, $J = 8.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.3, 165.6, 161.2, 159.1, 142.4, 139.7, 138.9, 134.3, 133.8, 133.7, 132.4, 131.0, 129.3, 129.2, 129.1, 128.8, 128.3, 127.0, 124.9, 120.6, 112.0, 109.7, 79.5, 62.7, 62.2, 44.9, 31.9, 22.7, 14.1, 13.2; HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{23}\text{N}_3\text{O}_5$ $[\text{M}+\text{Na}]^+$ 540.1535, found 540.1561.

Dimethyl 1'-tert-butyl-1-(dicyanomethylene)-5'-oxo-1',5'-dihydro-1H-spiro[aceanthrylene-2,2'-pyrrole]-3',4'-dicarboxylate (5g): Mp 264-267 °C; red powder; IR (KBr): 2951, 2222, 1700, 1561, 1425, 1274, 1197, 1092, 745 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.75 (d, $J = 7.2$ Hz, 1H), 8.59 (s, 1H), 8.31 (d, $J = 8.5$ Hz, 1H), 8.20-8.13 (m, 1H), 7.83-7.73 (m, 2H), 7.65-7.56 (m, 2H), 3.98 (s, 3H), 3.32 (s, 3H), 1.17 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.2, 166.6, 161.6, 159.5, 142.2, 138.6, 137.3, 134.3, 134.2, 133.1, 130.4, 128.6, 128.3, 128.2, 128.0, 127.8, 126.7, 126.5, 126.1, 121.8, 112.8, 110.3, 79.1, 78.2, 59.5, 53.3, 53.0, 27.7; HRMS (APCI) calcd for $\text{C}_{30}\text{H}_{23}\text{N}_3\text{O}_5$ $[\text{M}+\text{H}]^+$ 506.1716, found 506.1726.

Dimethyl 1'-cyclohexyl-1-(dicyanomethylene)-5'-oxo-1',5'-dihydro-1H-spiro[aceanthrylene-2,2'-pyrrole]-3',4'-dicarboxylate (5h): Mp 256-259 °C; red powder; IR (KBr): 2933, 2220, 1706, 1550, 1429, 1339, 1276, 1156, 1031, 746 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.75 (d, $J = 7.2$ Hz, 1H), 8.62 (s, 1H), 8.35 (d, $J = 8.5$ Hz, 1H), 8.21-8.13 (m, 1H), 7.83 (m, 1H), 7.78-7.71 (m, 1H), 7.65-7.55 (m, 2H), 4.01 (s, 3H), 3.39 (s, 3H), 2.71 (m, 1H), 2.17-1.91 (m, 2H), 1.68 (m, 2H), 1.41-1.31 (m, 2H), 1.09 (d, $J = 12.4$ Hz, 1H), 0.99-0.85 (m, 2H), 0.56 (m, $J = 13.2, 6.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.7, 165.3, 161.7, 159.7, 141.7, 140.3, 138.1, 134.2, 133.9, 133.3, 130.4, 128.8, 128.3, 128.0, 127.1, 126.5, 126.0, 121.6, 112.7, 110.1, 79.0, 78.7, 56.3, 53.3, 53.0, 29.4,

29.0, 25.9, 25.7, 24.7; HRMS (APCI) calcd for C₃₂H₂₅N₃O₅ [M+H]⁺ 532.1872, found 532.1876.

Dimethyl 1'-benzyl-1-(dicyanomethylene)-5'-oxo-1',5'-dihydro-1H-spiro[aceanthrylene-2,2'-pyrrole]-3',4'-dicarboxylate (5i): Mp 203-206 °C; red powder; IR (KBr): 3025, 2960, 2222, 1703, 1655, 1565, 1427, 1278, 1110, 745 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.61 (s, 1H), 8.45 (d, *J* = 7.2 Hz, 1H), 8.32 (d, *J* = 8.5 Hz, 1H), 8.20-8.12 (m, 1H), 7.77 (m, 1H), 7.64-7.54 (m, 3H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.92 (t, *J* = 7.7 Hz, 2H), 6.60-6.51 (m, 2H), 4.99 (d, *J* = 14.6 Hz, 1H), 4.04 (s, 3H), 3.56 (d, *J* = 14.6 Hz, 1H), 3.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.5, 165.7, 161.6, 159.7, 143.0, 138.9, 138.0, 134.2, 133.8, 133.7, 132.7, 130.4, 129.4, 129.1, 128.6, 128.2, 128.0, 127.1, 126.5, 125.8, 125.5, 120.6, 112.2, 109.9, 78.9, 78.3, 53.4, 53.1, 45.2; HRMS (APCI) calcd for C₃₃H₂₁N₃O₅ [M+H]⁺ 540.1559, found 540.1580.

Diethyl 1'-tert-butyl-1-(dicyanomethylene)-5'-oxo-1',5'-dihydro-1H-spiro[aceanthrylene-2,2'-pyrrole]-3',4'-dicarboxylate (5j): Mp 239-242 °C; red powder; IR (KBr): 2954, 2222, 1705, 1574, 1420, 1275, 1120, 1087, 750 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.74 (d, *J* = 8.0 Hz, 1H), 8.59 (s, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.84-7.75 (m, 2H), 7.65-7.56 (m, 2H), 4.49-4.40 (m, 2H), 3.75-3.63 (m, 2H), 1.40 (t, *J* = 8.0 Hz, 3H), 1.17 (s, 9H), 0.64 (t, *J* = 8.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.3, 166.8, 161.2, 159.1, 142.0, 138.9, 137.3, 134.4, 134.3, 133.0, 130.3, 128.6, 128.5, 128.3, 128.0, 127.6, 126.7, 126.6, 126.0, 121.9, 112.9, 110.2, 79.1, 78.3, 62.6, 62.0, 59.4, 27.7, 14.1, 13.0; HRMS (ESI) calcd for C₃₂H₂₇N₃O₅ [M+Na]⁺ 556.1848, found 556.1858.

Diethyl 1'-cyclohexyl-1-(dicyanomethylene)-5'-oxo-1',5'-dihydro-1H-spiro[aceanthrylene-2,2'-pyrrole]-3',4'-dicarboxylate (5k): Mp 182-185 °C; red powder; IR (KBr): 2930, 2220, 1712, 1550, 1435, 1345, 1276, 1155, 1031, 746 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.74 (d, *J* = 8.0 Hz, 1H), 8.61 (s, 1H), 8.35 (d, *J* = 8.0 Hz, 1H), 8.19-8.14 (m, 1H), 7.83 (m, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.65-7.56 (m, 2H), 4.53-4.44 (m, 2H), 3.83-3.67 (m, 2H), 2.72 (m, 1H), 2.19-1.92 (m, 2H), 1.78-1.60 (m, 2H), 1.42 (t, *J* = 8.0 Hz, 3H), 1.39-1.32 (m, 2H), 1.10 (d, *J* = 8.0 Hz, 1H), 1.00-0.91 (m, 2H), 0.68 (t, *J* = 8.0 Hz, 3H), 0.57 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 169.8, 165.5, 161.3, 159.1, 141.5, 140.7, 138.1, 134.2, 134.1, 133.2, 130.3, 128.7, 128.2, 128.0, 127.9, 127.2, 126.8, 126.5, 125.8, 121.7, 112.8, 110.0, 78.9, 62.6, 62.1, 56.3, 29.4, 29.1, 25.9, 25.7, 24.7, 14.2, 13.1; HRMS (ESI) calcd for C₃₄H₂₉N₃O₅ [M+Na]⁺ 582.2005, found 582.2025.

Dimethyl 1'-benzyl-1-(dicyanomethylene)-5'-oxo-1',5'-dihydro-1H-spiro[aceanthrylene-2,2'-

pyrrole]-3',4'-dicarboxylate (**5l**): Mp 158-161 °C; red powder; IR (KBr): 3032, 2960, 2227, 1700, 1660, 1574, 1420, 1299, 1111, 746 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.61 (s, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 8.20-8.13 (m, 1H), 7.80-7.73 (m, 1H), 7.62-7.56 (m, 3H), 7.08 (t, *J* = 8.0 Hz, 1H), 6.92 (t, *J* = 8.0 Hz, 2H), 6.56 (d, *J* = 8.0 Hz, 2H), 5.01 (d, *J* = 16.0 Hz, 1H), 4.51 (m, 2H), 3.83-3.71 (m, 2H), 3.57 (d, *J* = 16.0 Hz, 1H), 1.44 (t, *J* = 8.0 Hz, 3H), 0.69 (t, *J* = 8.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.7, 165.9, 161.2, 159.2, 142.8, 139.3, 138.0, 134.1, 134.0, 133.8, 132.6, 130.3, 129.4, 129.1, 128.6, 128.1, 127.9, 127.8, 127.1, 126.5, 126.1, 125.3, 120.7, 112.3, 109.8, 79.0, 78.3, 62.8, 62.2, 45.2, 14.1, 13.1; HRMS (ESI) calcd for C₃₅H₂₅N₃O₅ [M+Na]⁺ 590.1692, found 590.1681.

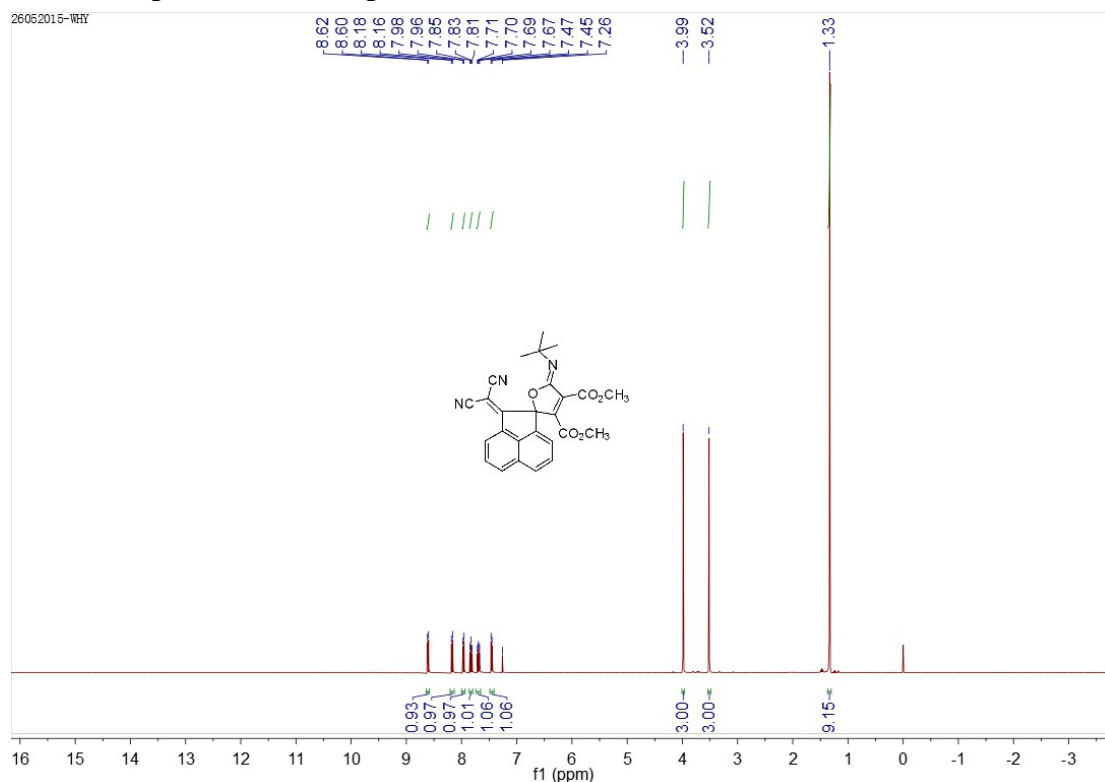
Dimethyl 1'-t-Butyl-10-(dicyanomethylene)-5'-oxo-1',5'-dihydro-10H-spiro[phenanthrene-9,2'-pyrrole]-3',4'-dicarboxylate (**5m**): Mp 231-234 °C; yellow powder; IR (KBr): 2980, 2953, 2220, 1702, 1670, 1531, 1445, 1286, 1197, 1093, 764 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.74 (d, *J* = 8.3 Hz, 1H), 8.17 (d, *J* = 8.1 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.79-7.73 (m, 1H), 7.49 (m, *J* = 9.3, 8.2, 4.3 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 4.00-3.92 (m, 3H), 3.46 (d, *J* = 1.7 Hz, 3H), 1.30 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 167.5, 166.4, 161.7, 159.4, 144.1, 137.7, 135.9, 133.8, 130.7, 130.0, 129.8, 129.6, 128.7, 127.0, 126.6, 124.6, 124.0, 115.4, 113.0, 82.4, 69.7, 59.2, 53.3, 53.1, 27.9; HRMS (APCI) calcd for C₂₈H₂₃N₃O₅ [M+H]⁺ 482.1716, found 482.1730.

Dimethyl 1'-cyclohexyl-10-(dicyanomethylene)-5'-oxo-1',5'-dihydro-10H-spiro[phenanthrene-9,2'-pyrrole]-3',4'-dicarboxylate (**5n**): Mp 196-199 °C; yellow powder; IR (KBr): 2926, 2855, 2220, 1700, 1661, 1525, 1447, 1278, 1091, 762 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.45 (d, *J* = 8.1, 1H), 8.07 (t, *J* = 7.9 Hz, 2H), 7.83-7.73 (m, 1H), 7.55-7.45 (m, 2H), 7.40-7.32 (m, 1H), 7.14 (d, *J* = 8.0, 1H), 3.99 (s, 3H), 3.57 (s, 3H), 2.81 (m, *J* = 12.0, 3.6 Hz, 1H), 1.91-1.92 (m, 2H), 1.63 (d, *J* = 10.1 Hz, 2H), 1.51 (dd, *J* = 13.4, 1.6 Hz, 1H), 1.40 (d, *J* = 11.2, 1H), 1.16 (d, *J* = 12.3 Hz, 1H), 1.03-0.91 (m, 1H), 0.89-0.71 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 165.4, 165.2, 161.7, 159.8, 143.9, 139.7, 135.9, 134.2, 131.3, 130.4, 130.0, 129.9, 128.7, 128.6, 127.0, 126.9, 124.7, 124.1, 114.9, 112.5, 83.9, 69.3, 56.8, 53.3, 53.2, 29.8, 29.0, 26.0, 25.9, 24.8; HRMS (APCI) calcd for C₃₀H₂₅N₃O₅ [M+H]⁺ 508.1872, found 508.1872.

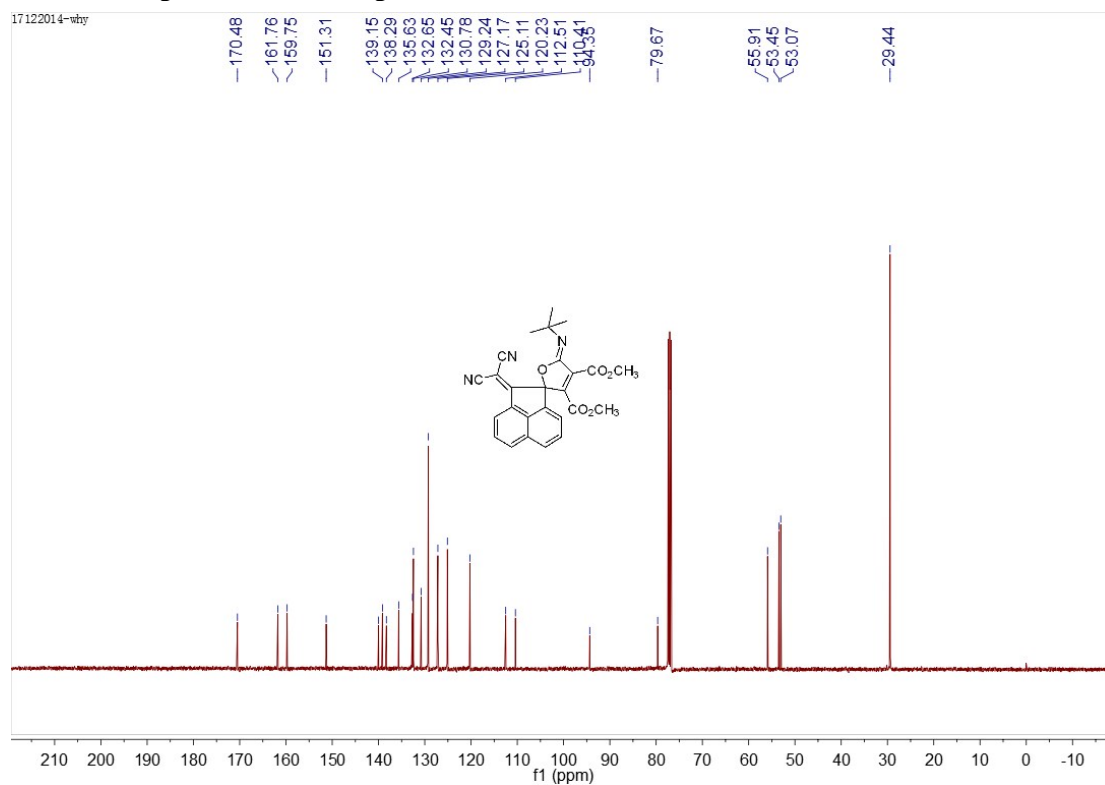
Dimethyl 1'-benzyl-10-(dicyanomethylene)-5'-oxo-1',5'-dihydro-10H-spiro[phenanthrene-9,2'-pyrrole]-3',4'-dicarboxylate (**5o**): Mp 233-236 °C; yellow powde; IR (KBr): 2951, 2219, 1707,

1661, 1538, 1448, 1363, 1270, 1099, 759 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.08-7.99 (m, 3H), 7.75-7.67 (m, 1H), 7.49-7.40 (m, 1H), 7.38-7.32 (m, 1H), 7.24-7.14 (m, 2H), 7.09 (t, $J = 7.3$ Hz, 2H), 6.91 (d, $J = 7.1$ Hz, 2H), 6.83 (d, $J = 8.0$, 1H), 4.73 (d, $J = 14.8$ Hz, 1H), 3.99 (s, 3H), 3.92 (d, $J = 14.8$ Hz, 1H), 3.44 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 166.5, 164.0, 161.5, 159.8, 146.0, 136.5, 135.6, 133.8, 133.7, 131.8, 130.4, 130.3, 130.1, 129.4, 128.7, 128.4, 128.4, 127.6, 126.8, 126.5, 124.4, 123.9, 114.5, 112.4, 84.0, 69.8, 53.4, 53.1, 45.8; HRMS (APCI) calcd for $\text{C}_{31}\text{H}_{21}\text{N}_3\text{O}_5$ $[\text{M}+\text{H}]^+$ 516.1559, found 516.1558.

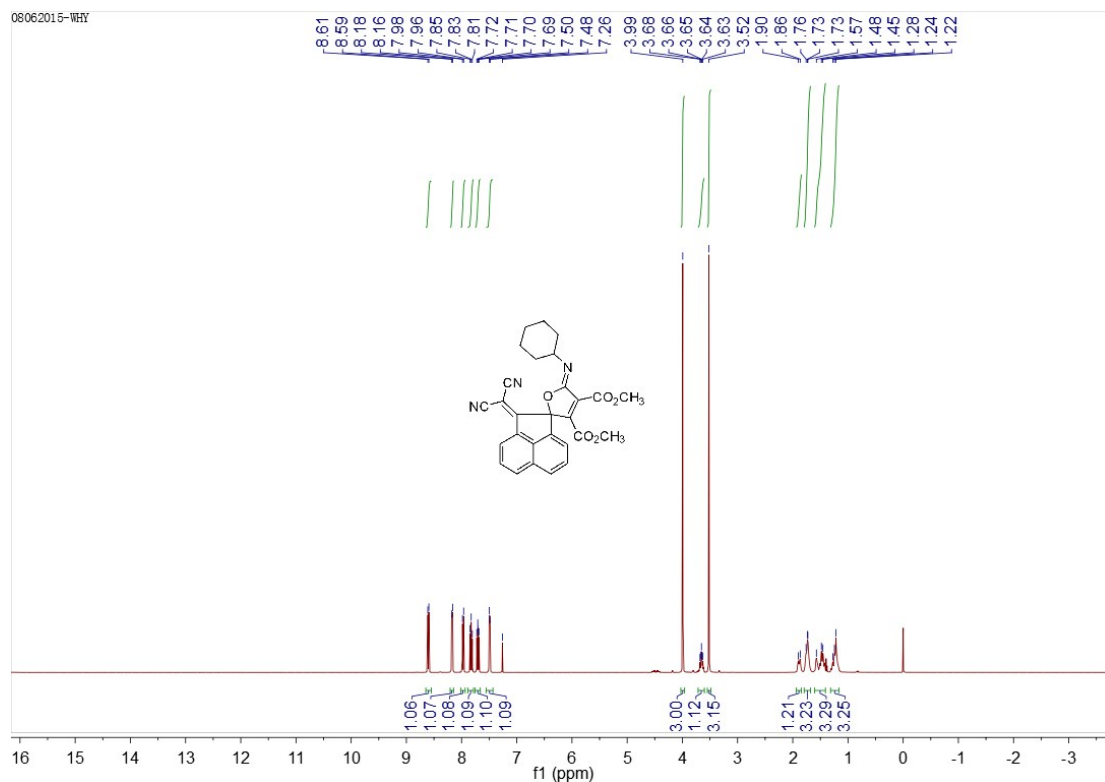
¹H NMR spectrum of compound 4a in CDCl₃, 400 MHz



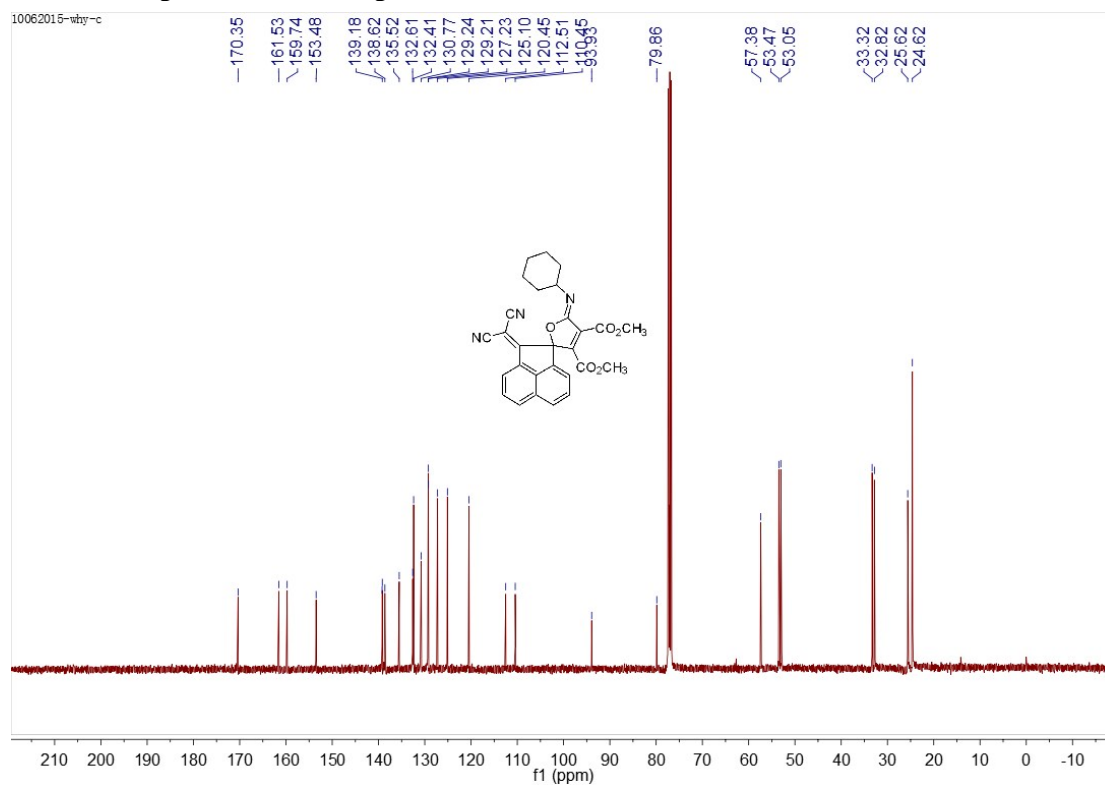
¹³C NMR spectrum of compound 4a in CDCl₃, 100 MHz



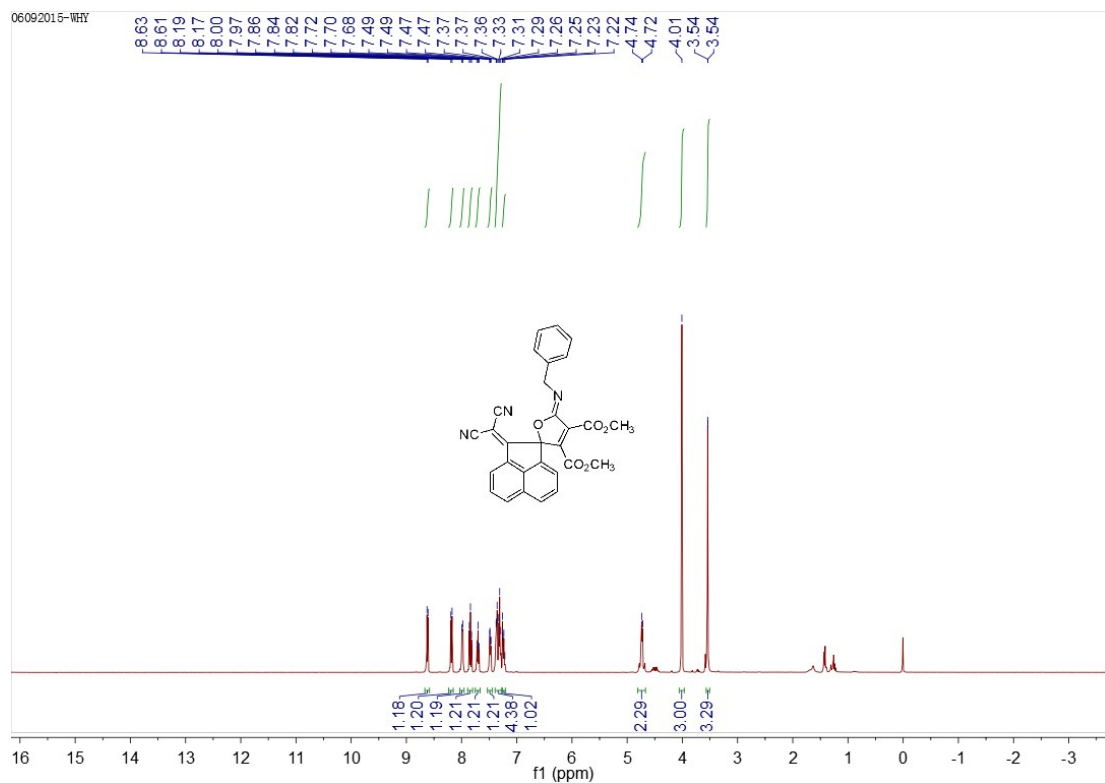
¹H NMR spectrum of compound 4b in CDCl₃, 400 MHz



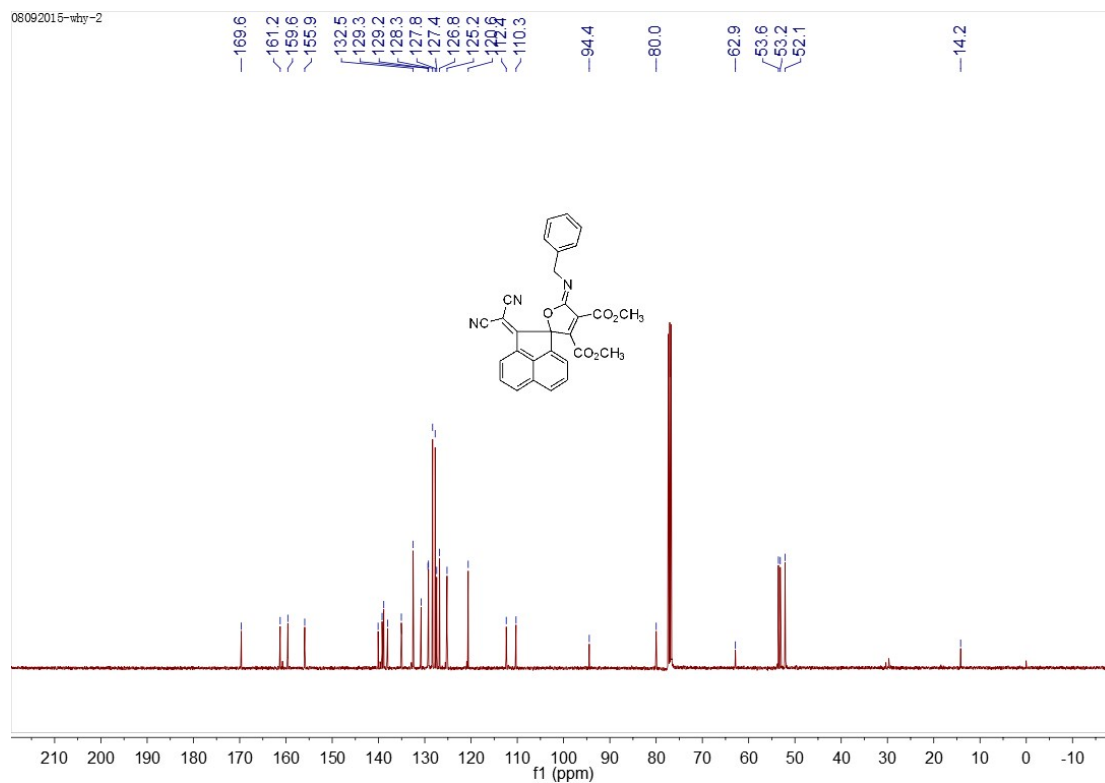
¹³C NMR spectrum of compound 4b in CDCl₃, 100 MHz



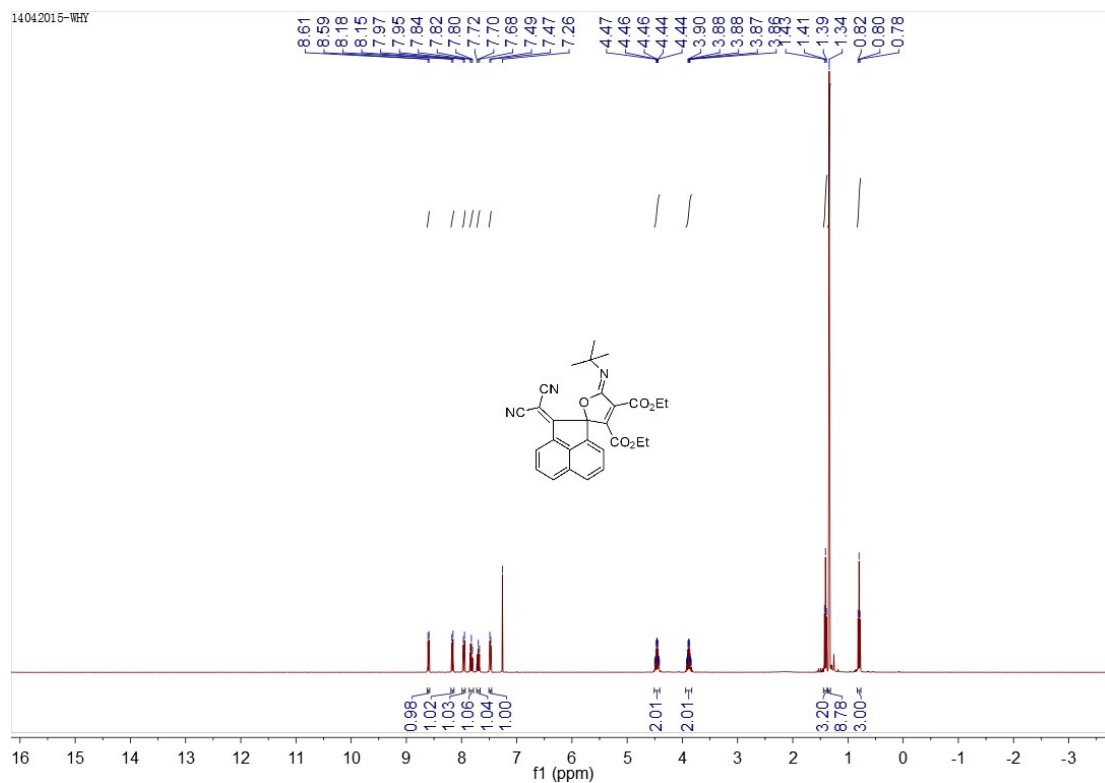
¹H NMR spectrum of compound 4c in CDCl₃, 400 MHz



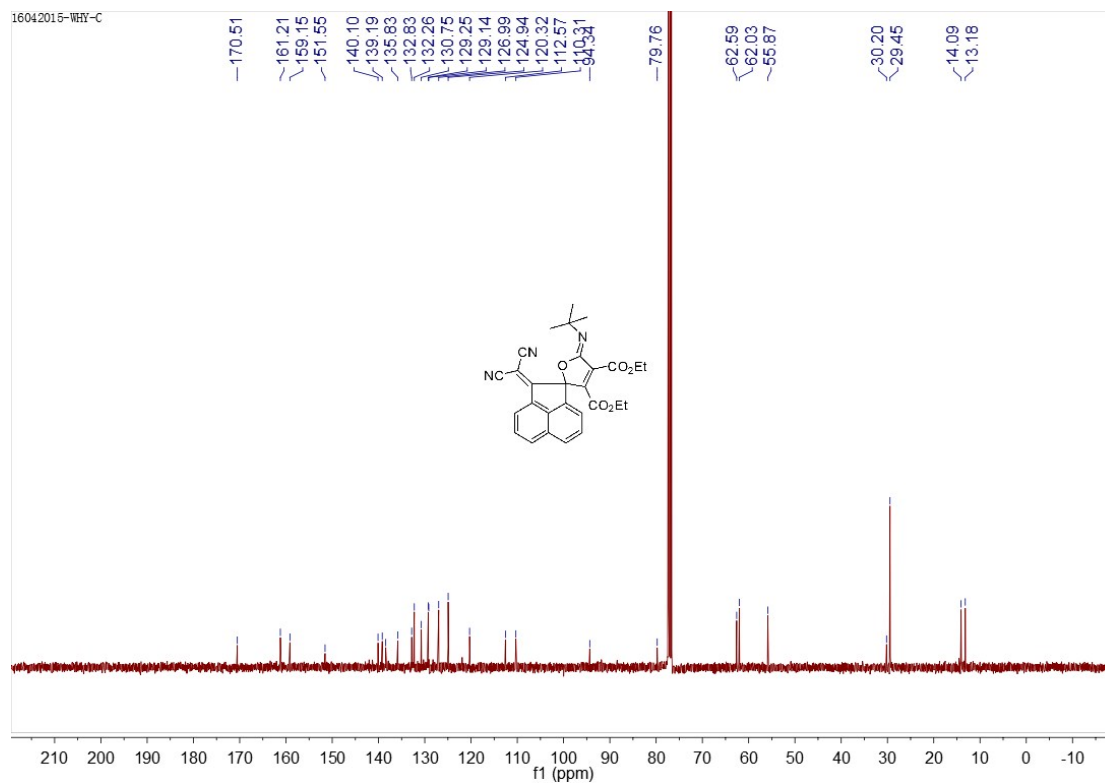
¹³C NMR spectrum of compound 4c in CDCl₃, 100 MHz



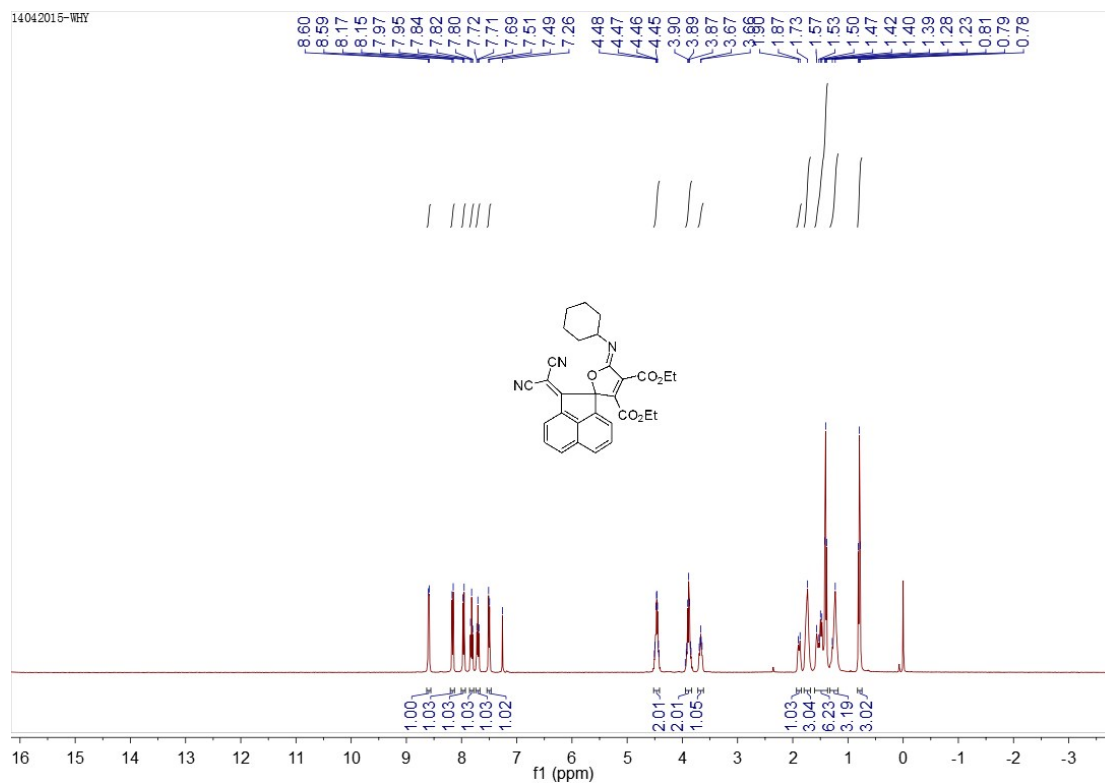
¹H NMR spectrum of compound 4d in CDCl₃, 400 MHz



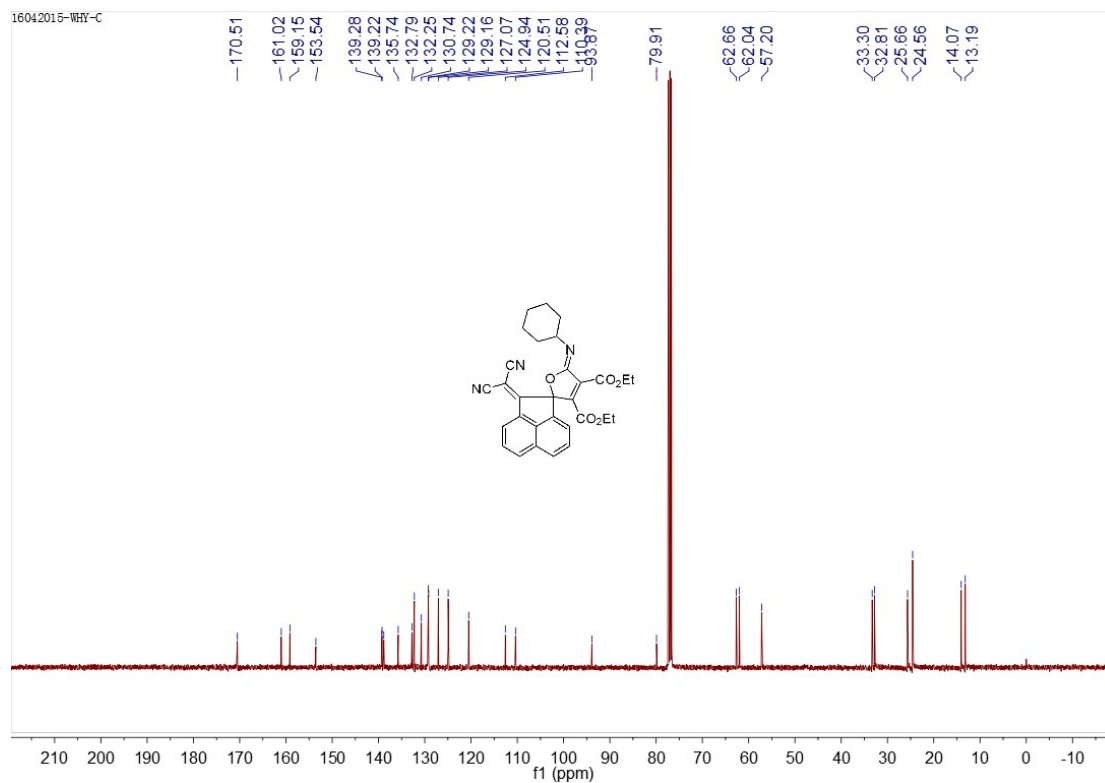
¹³C NMR spectrum of compound 4d in CDCl₃, 100 MHz



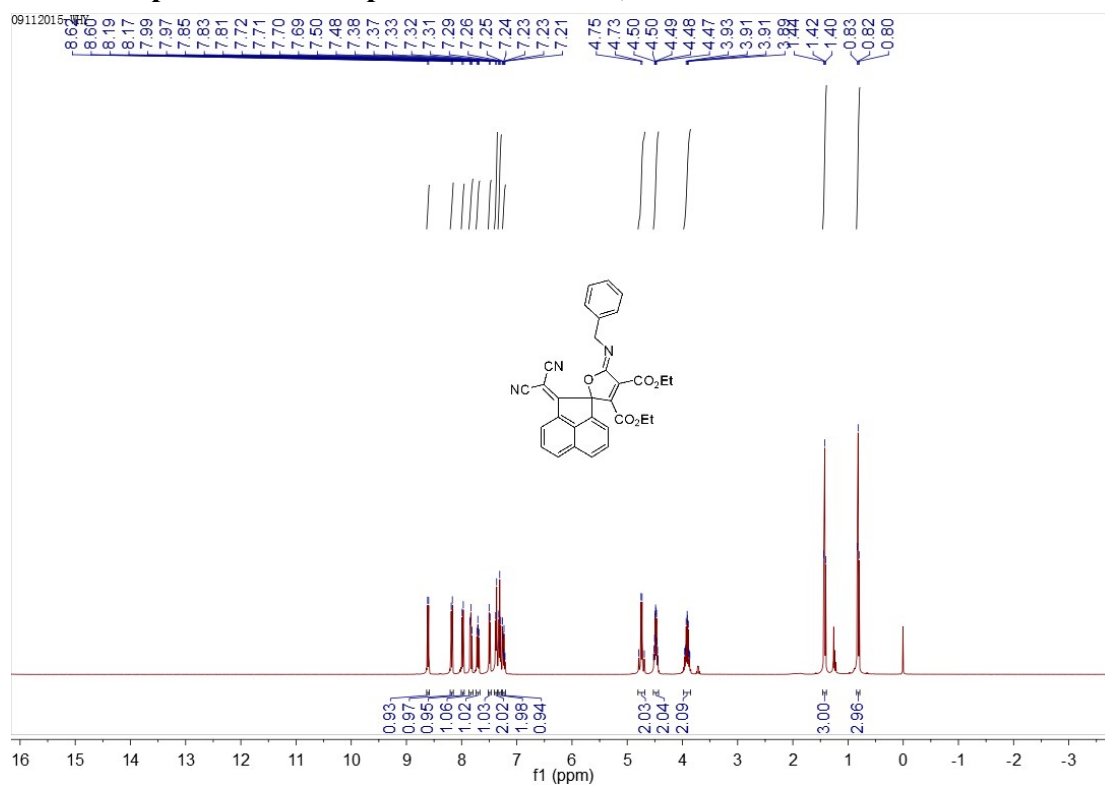
¹H NMR spectrum of compound 4e in CDCl₃, 400 MHz



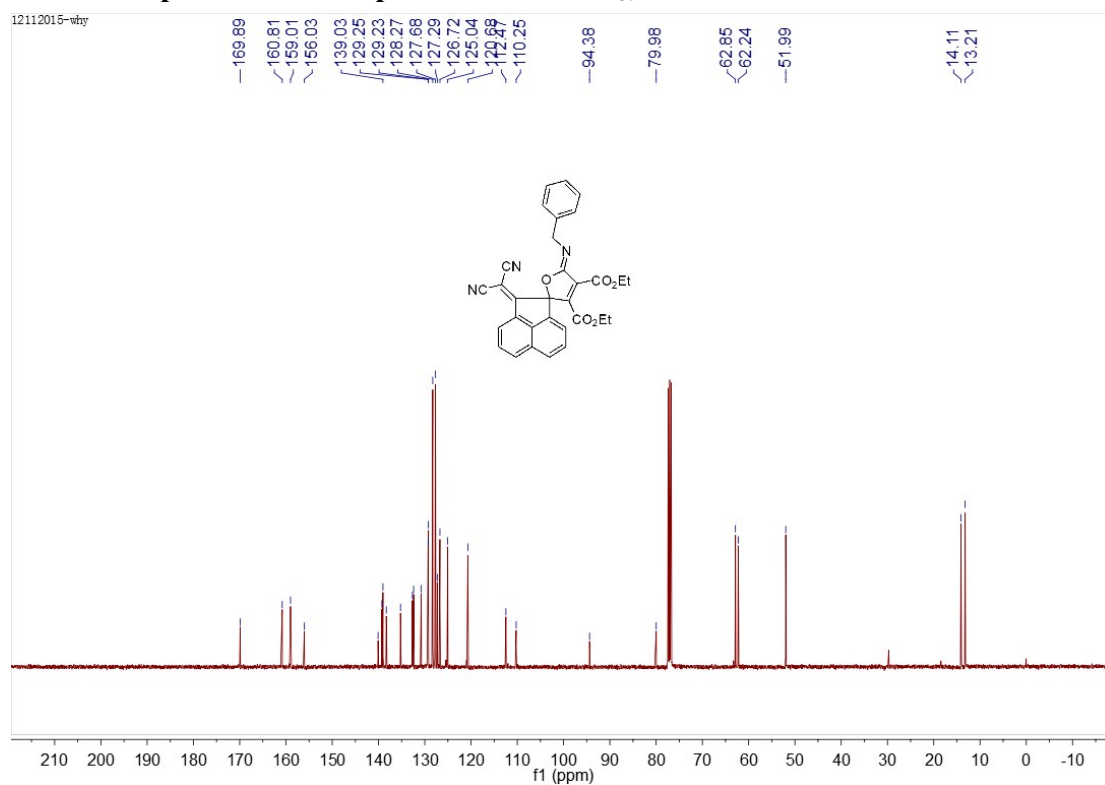
¹³C NMR spectrum of compound 4e in CDCl₃, 100 MHz



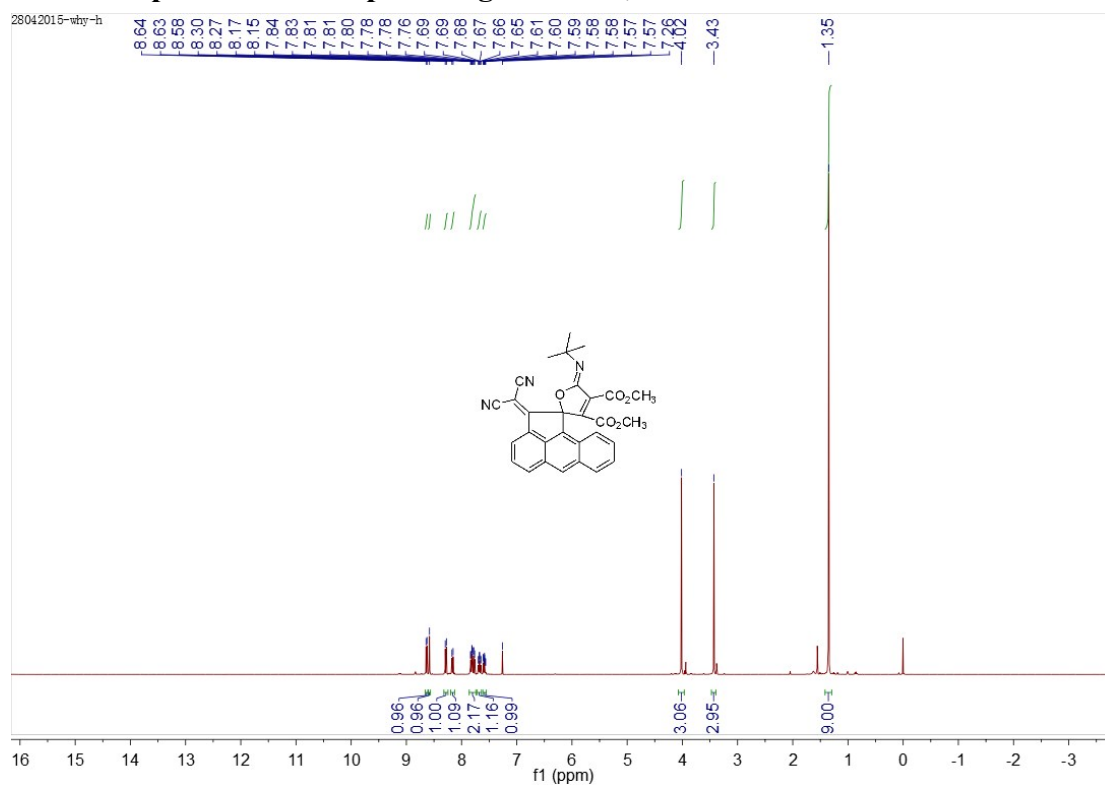
¹H NMR spectrum of compound 4f in CDCl₃, 400 MHz



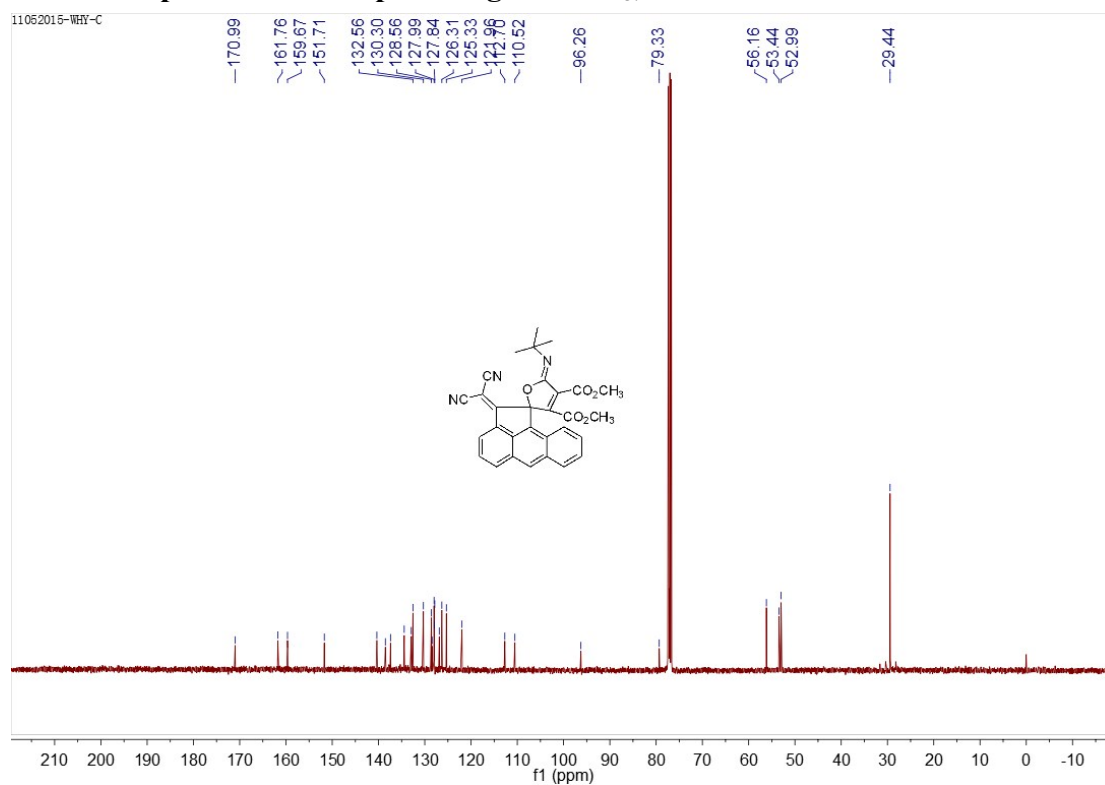
¹³C NMR spectrum of compound 4f in CDCl₃, 100 MHz



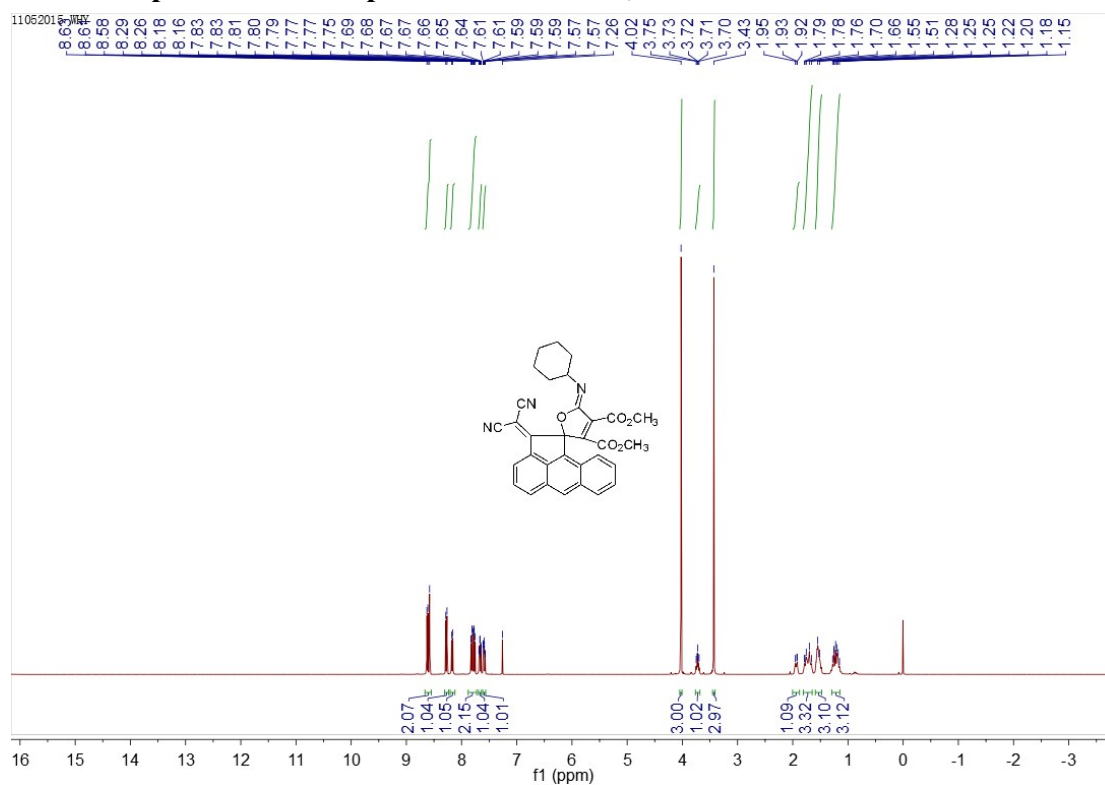
¹H NMR spectrum of compound 4g in CDCl₃, 400 MHz



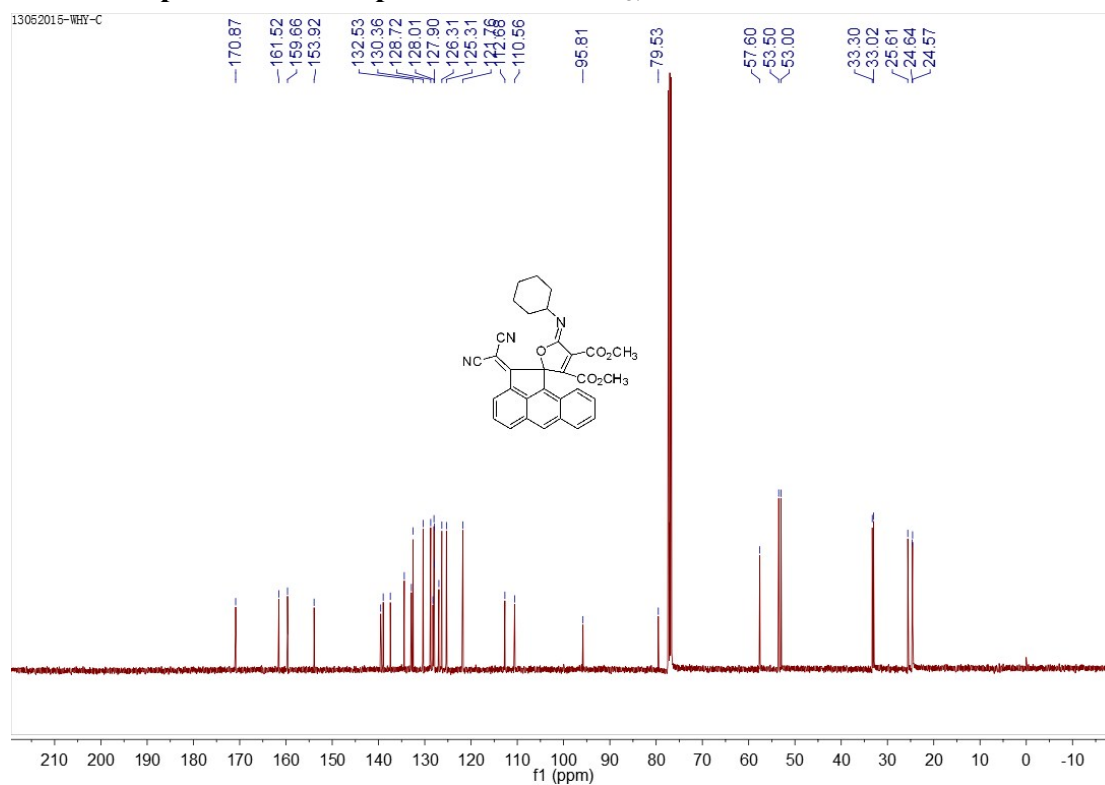
¹³C NMR spectrum of compound 4g in CDCl₃, 100 MHz



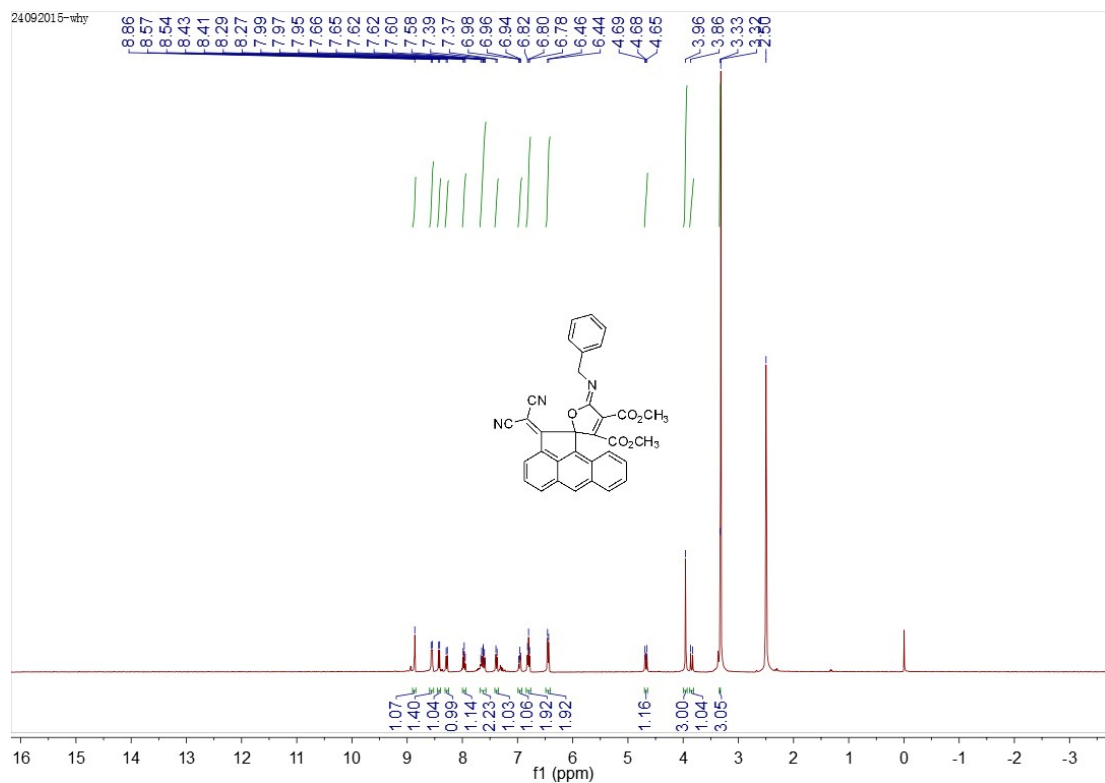
¹H NMR spectrum of compound 4h in CDCl₃, 400 MHz



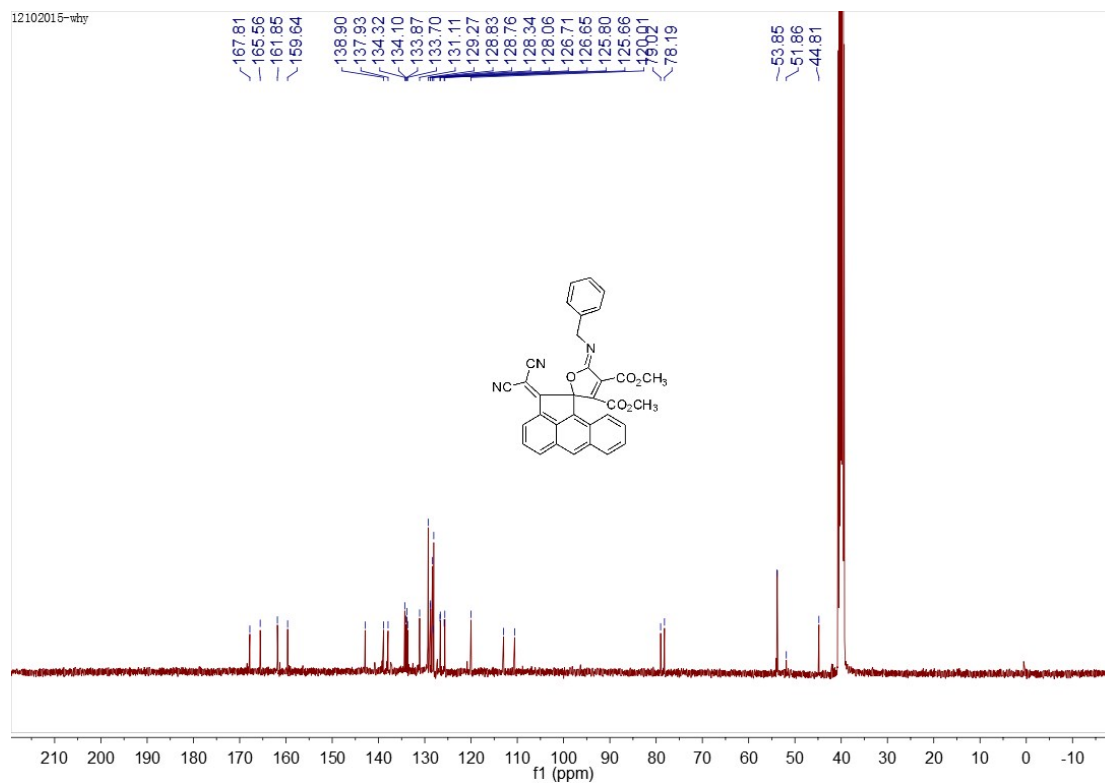
¹³C NMR spectrum of compound 4h in CDCl₃, 100 MHz



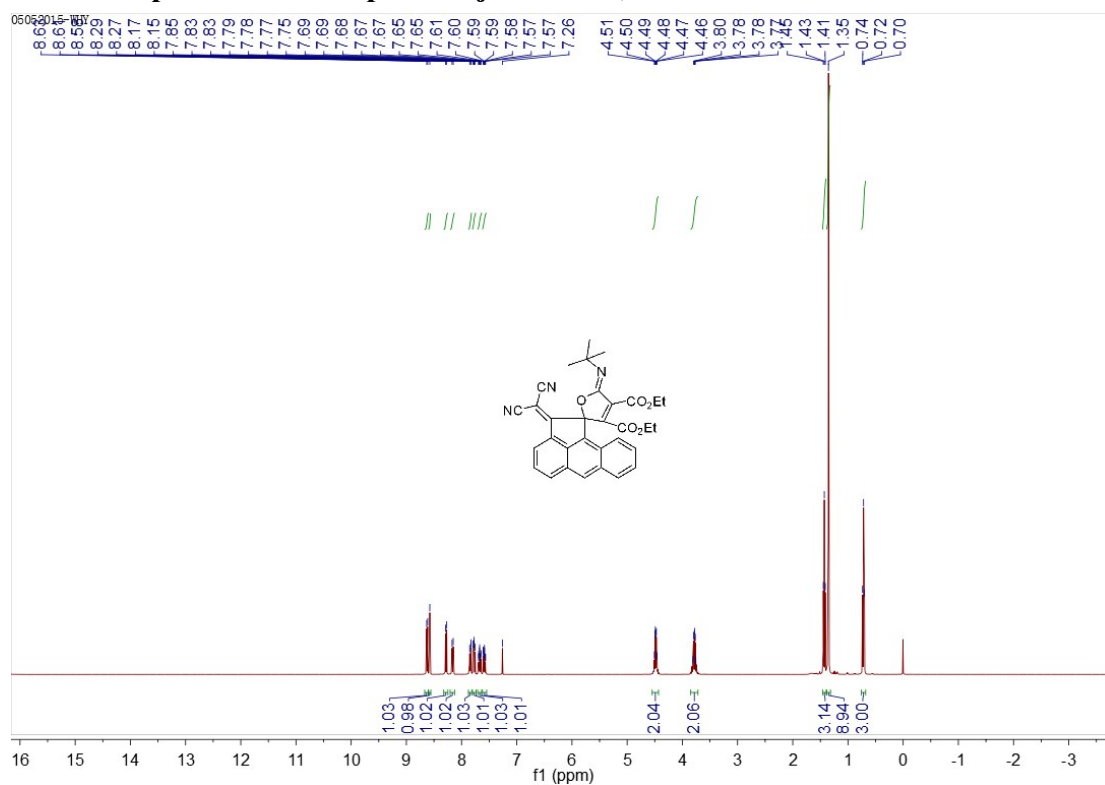
¹H NMR spectrum of compound 4i in DMSO, 400 MHz



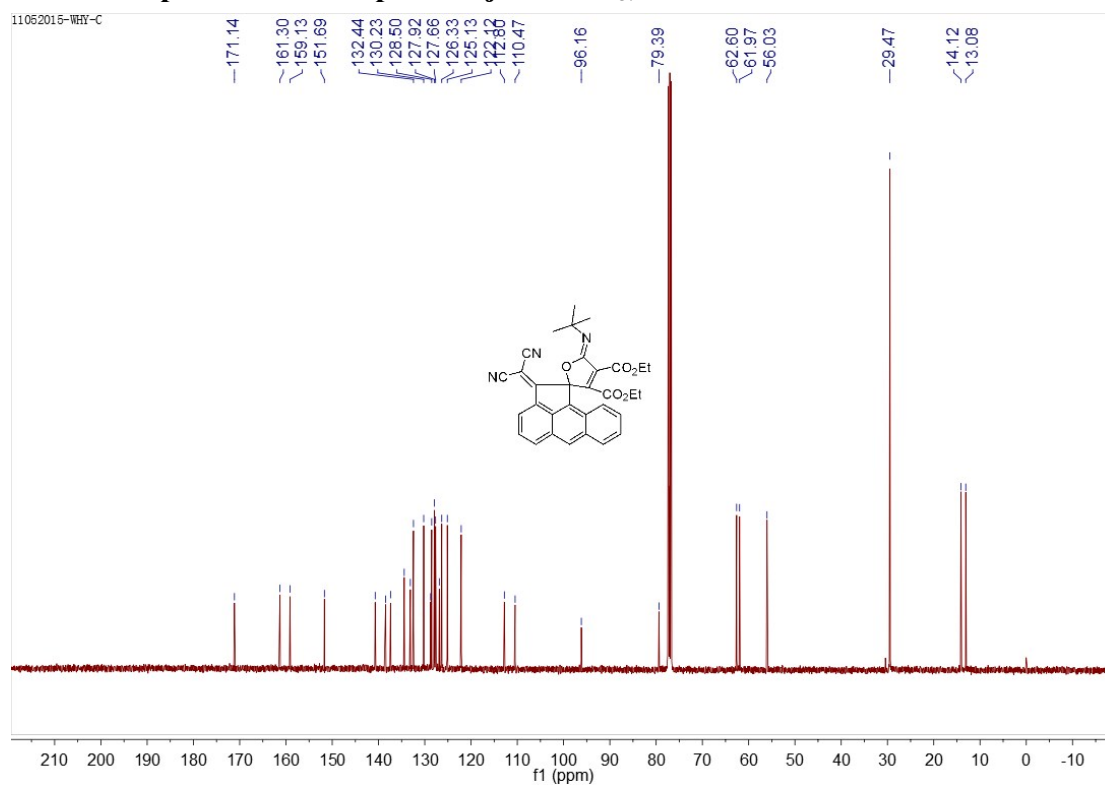
¹³C NMR spectrum of compound 4i in DMSO, 100 MHz



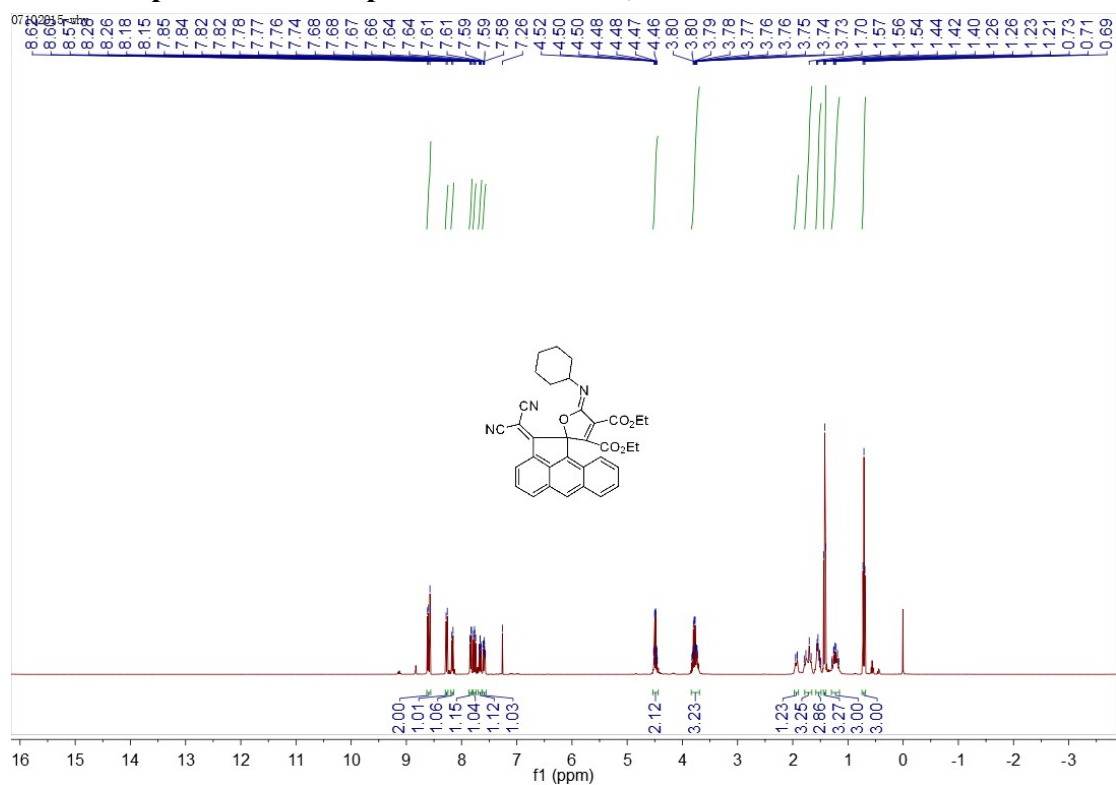
¹H NMR spectrum of compound 4j in CDCl₃, 400 MHz



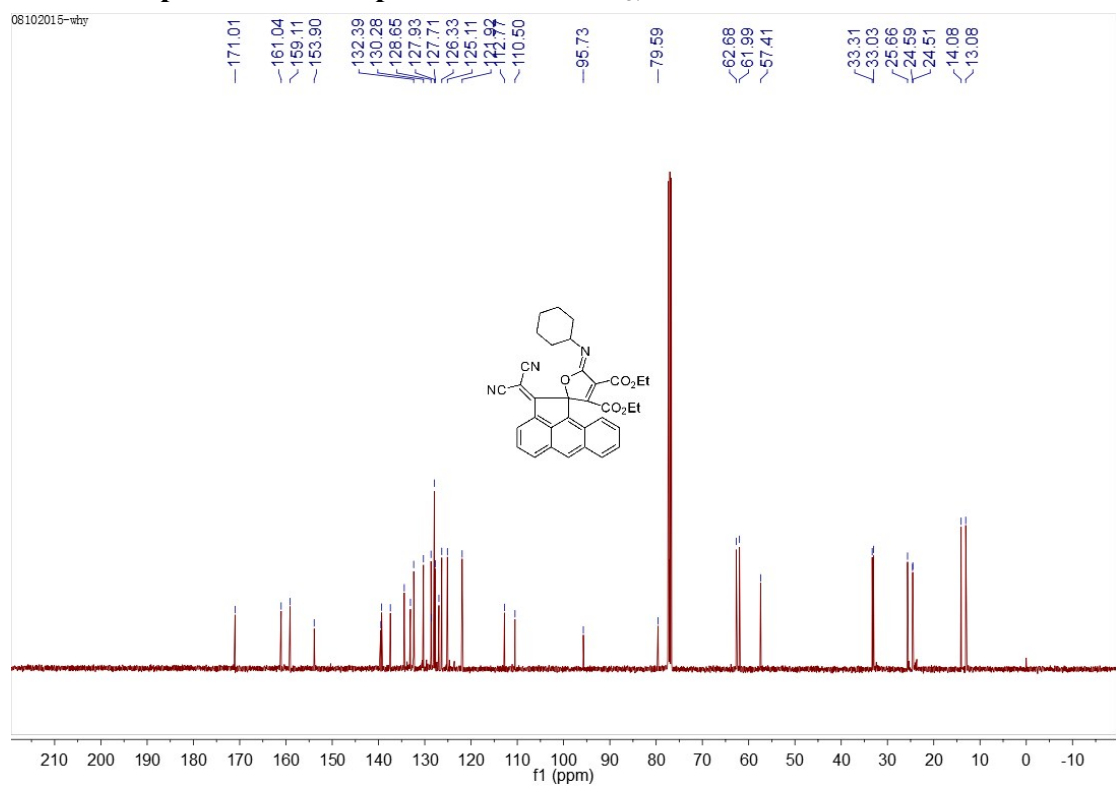
¹³C NMR spectrum of compound 4j in CDCl₃, 100 MHz



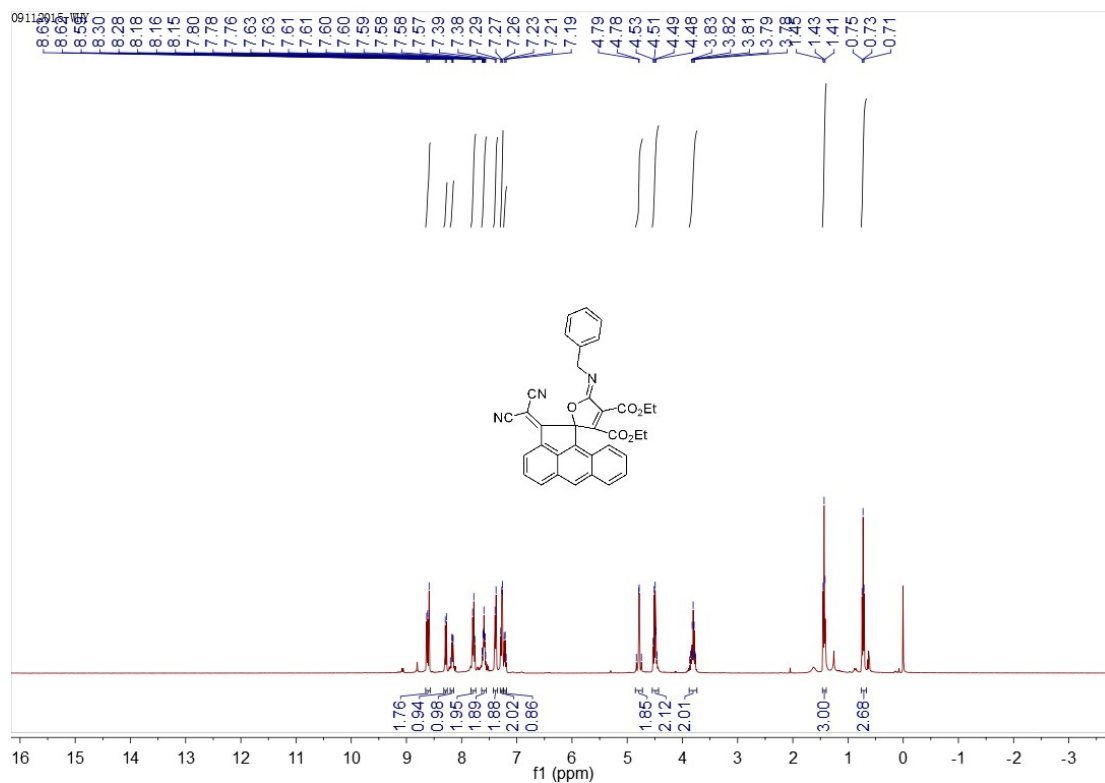
¹H NMR spectrum of compound 4k in CDCl₃, 400 MHz



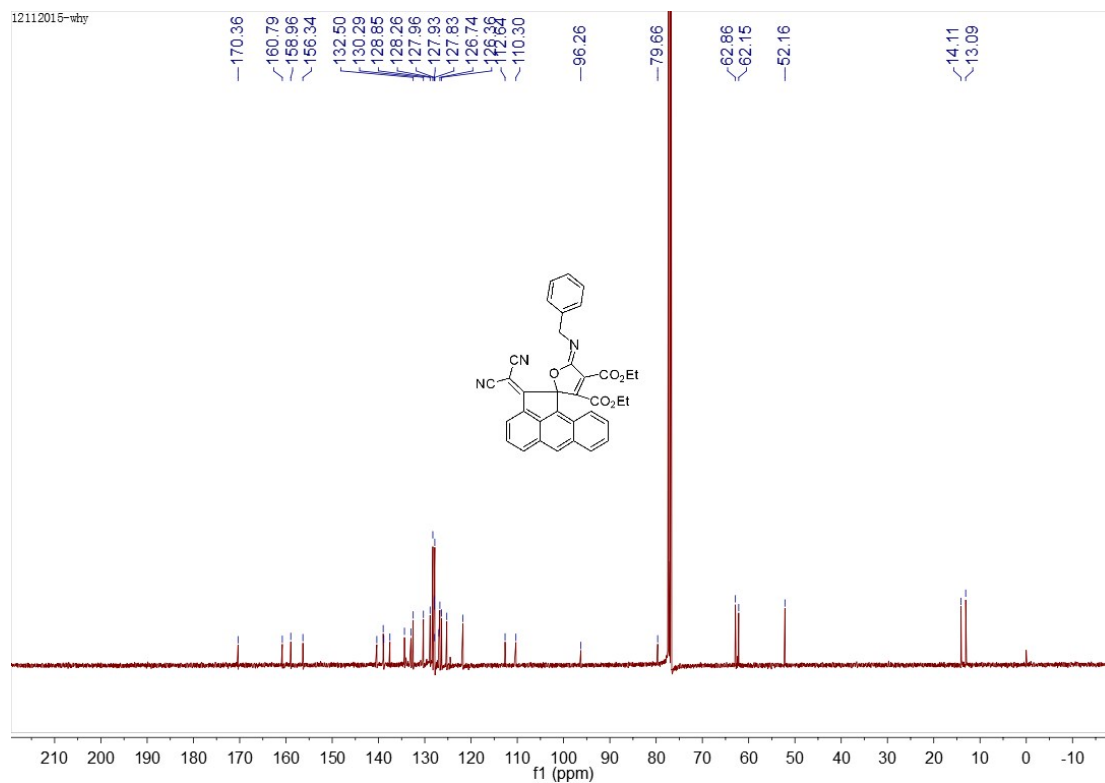
¹³C NMR spectrum of compound 4k in CDCl₃, 100 MHz



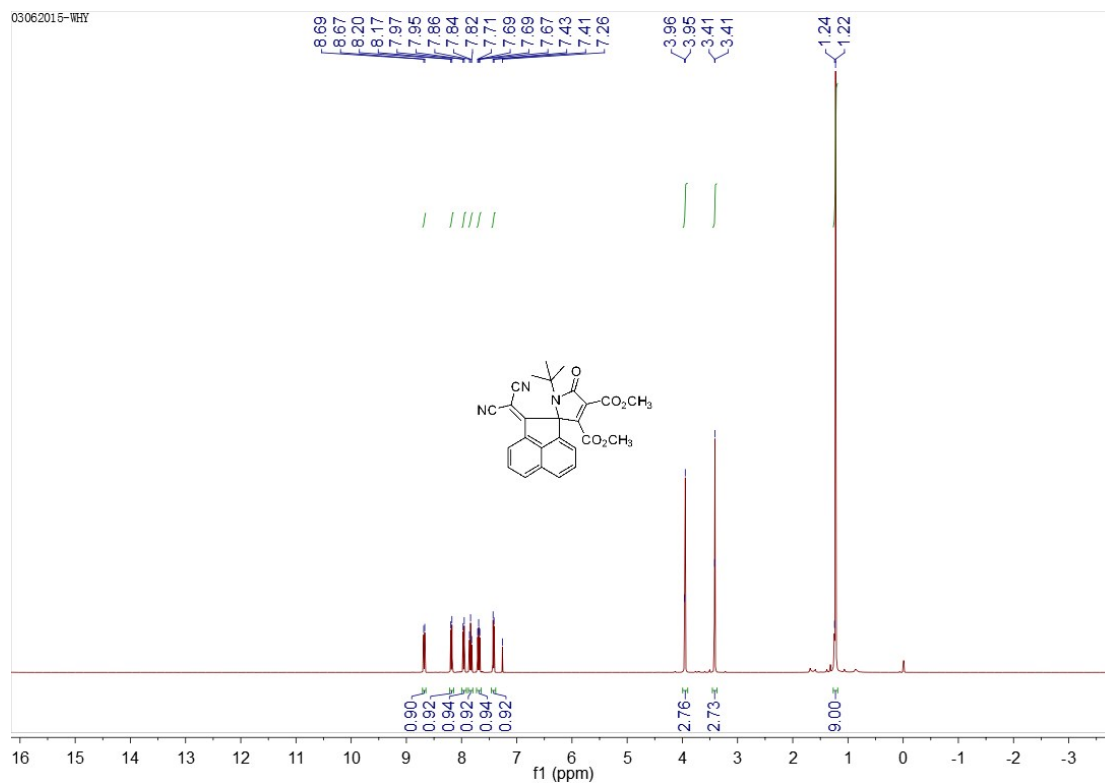
¹H NMR spectrum of compound 4l in CDCl₃, 400 MHz



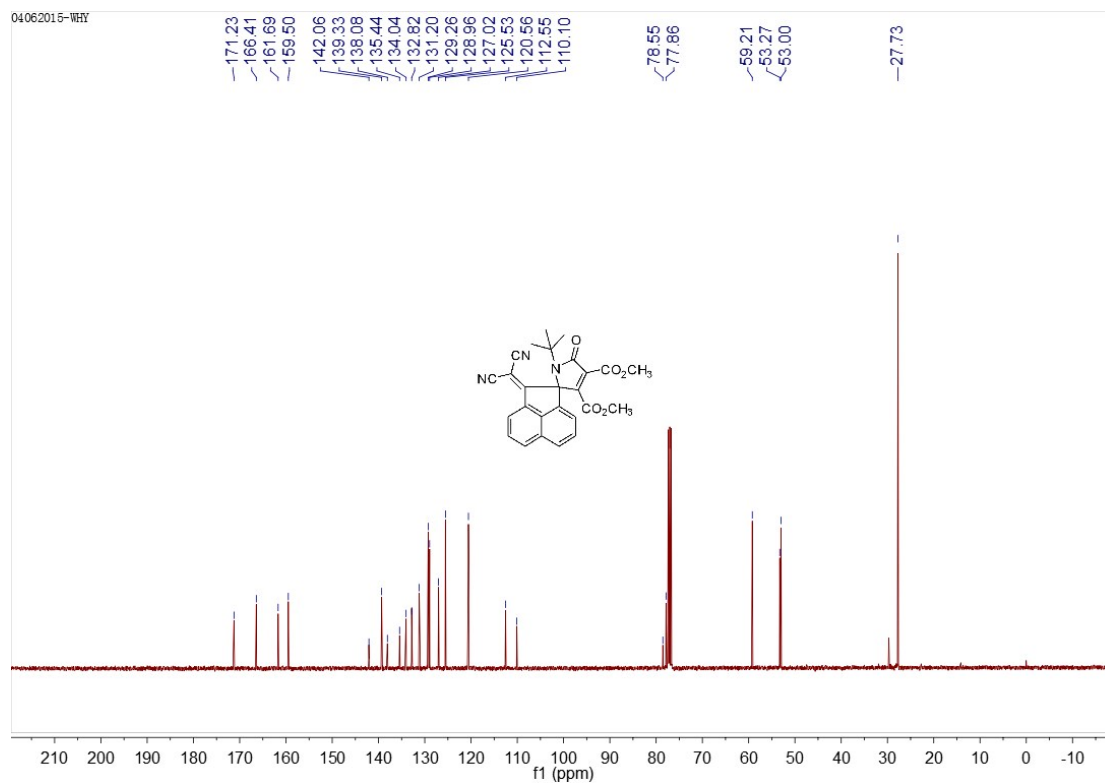
¹³C NMR spectrum of compound 4l in CDCl₃, 100 MHz



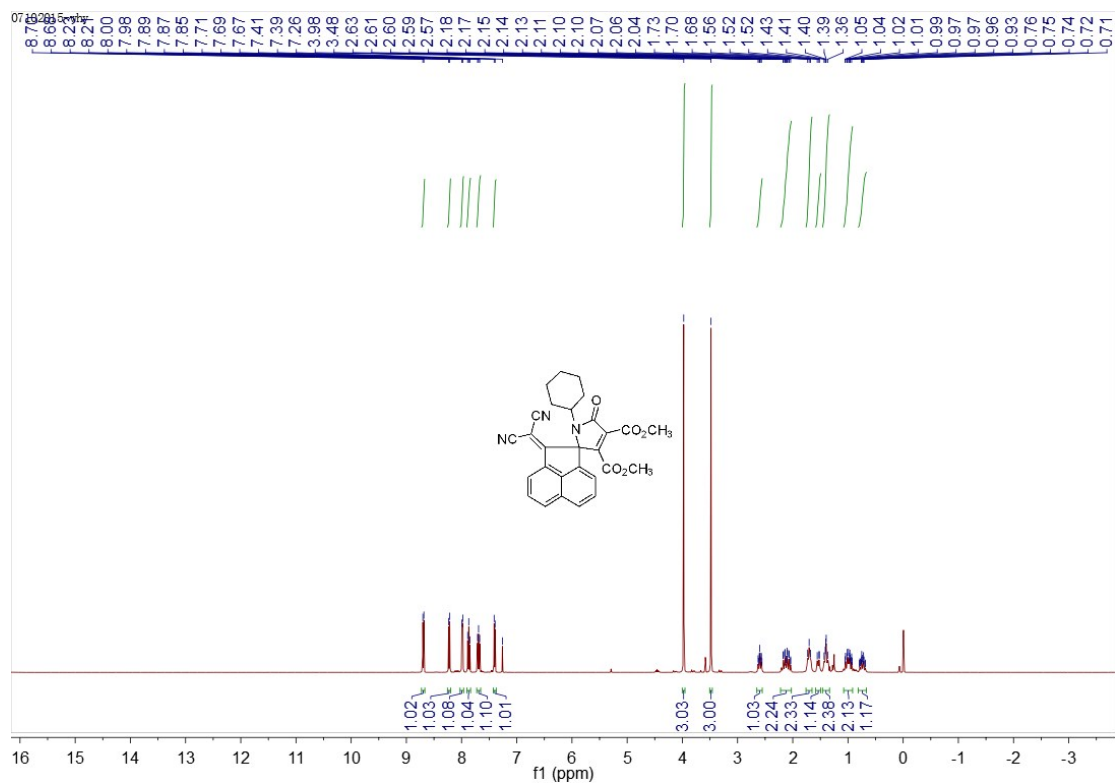
¹H NMR spectrum of compound 5a in CDCl₃, 400 MHz



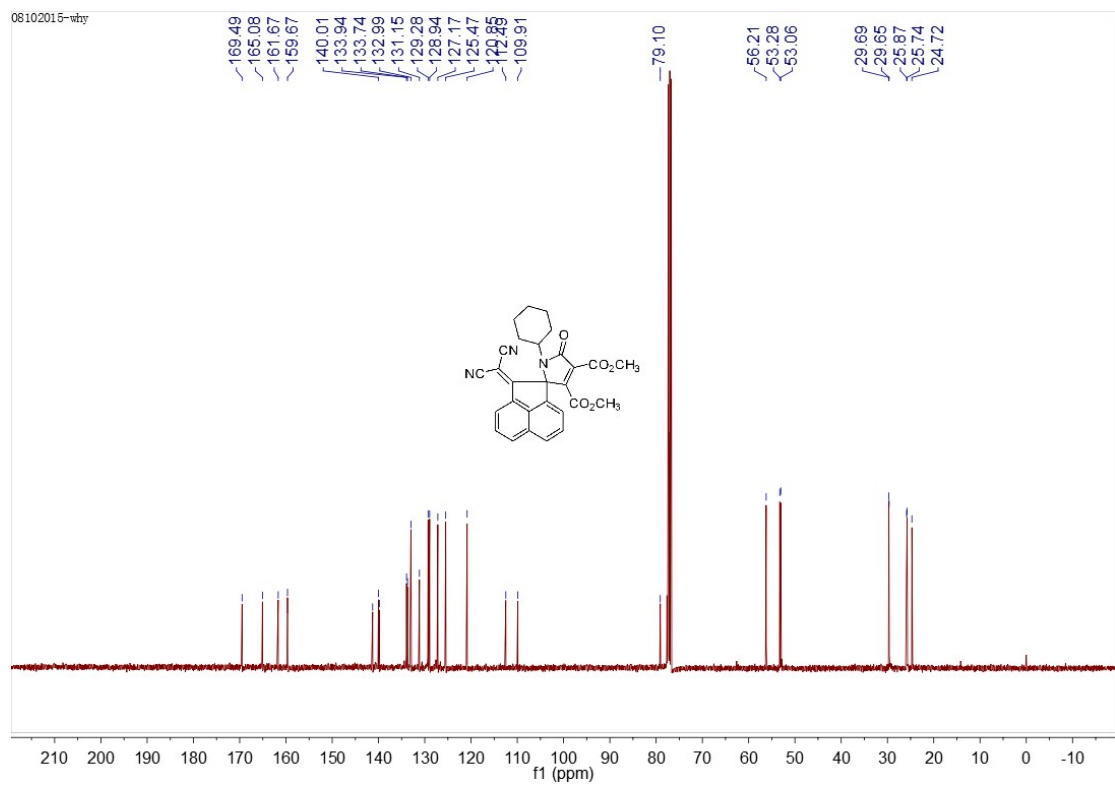
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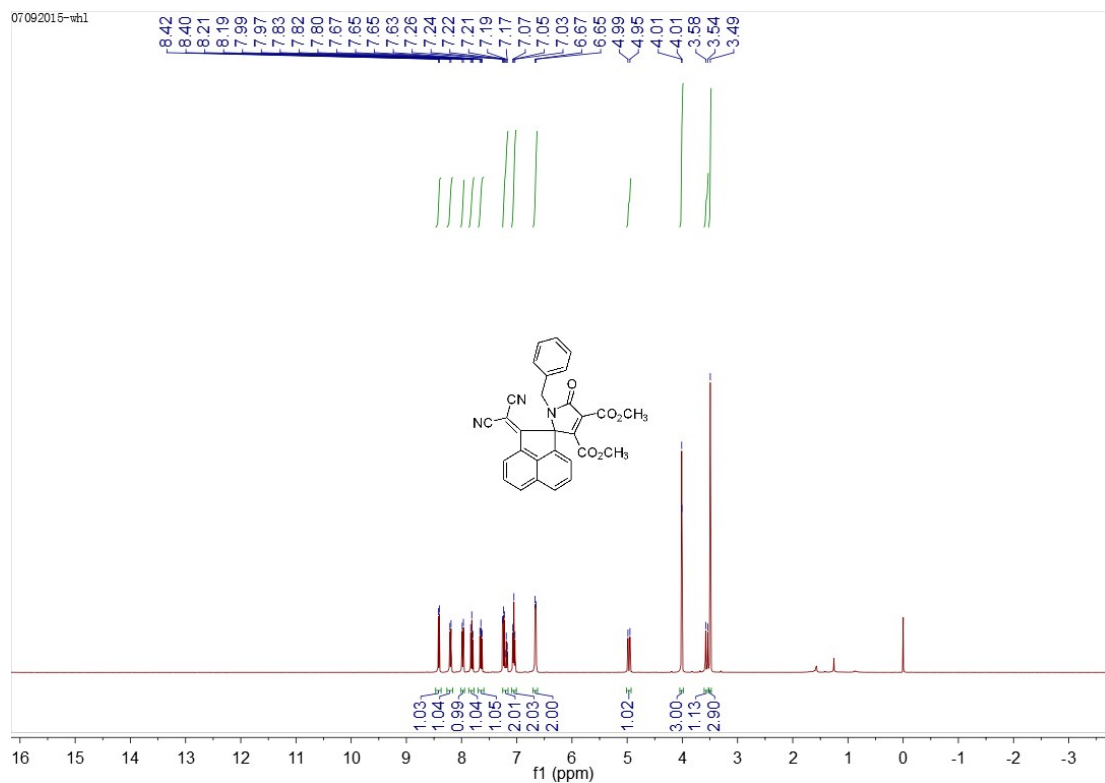
¹H NMR spectrum of compound 5b in CDCl₃, 400 MHz



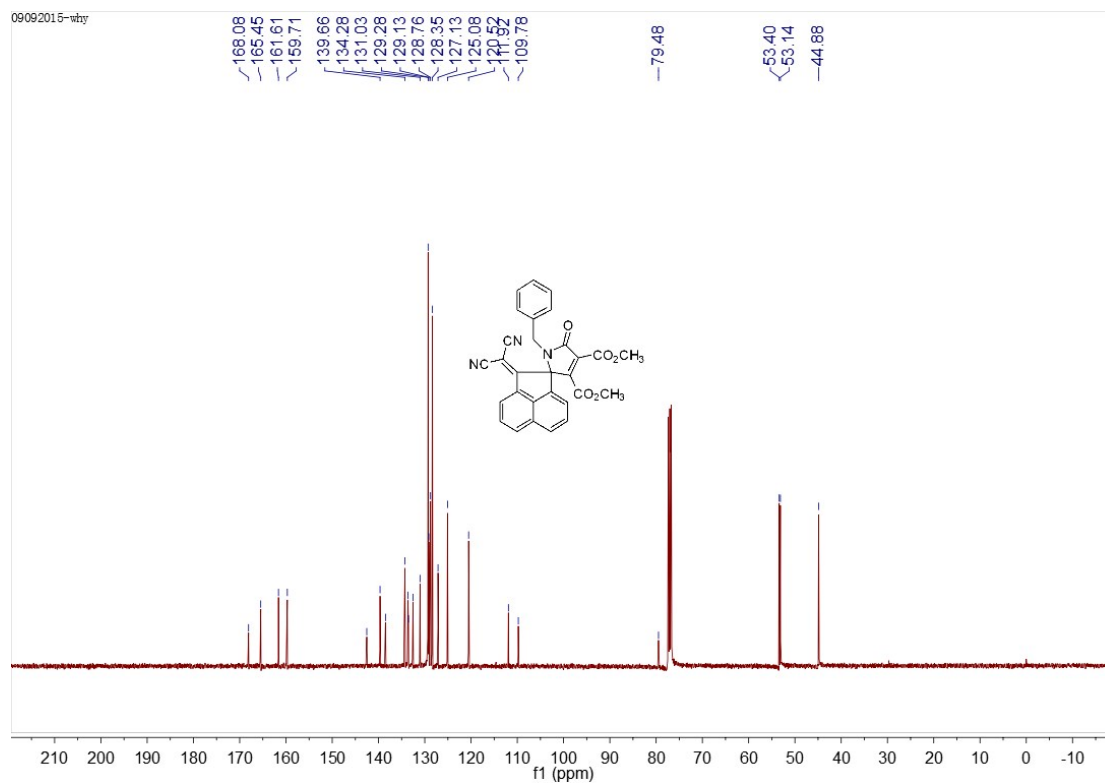
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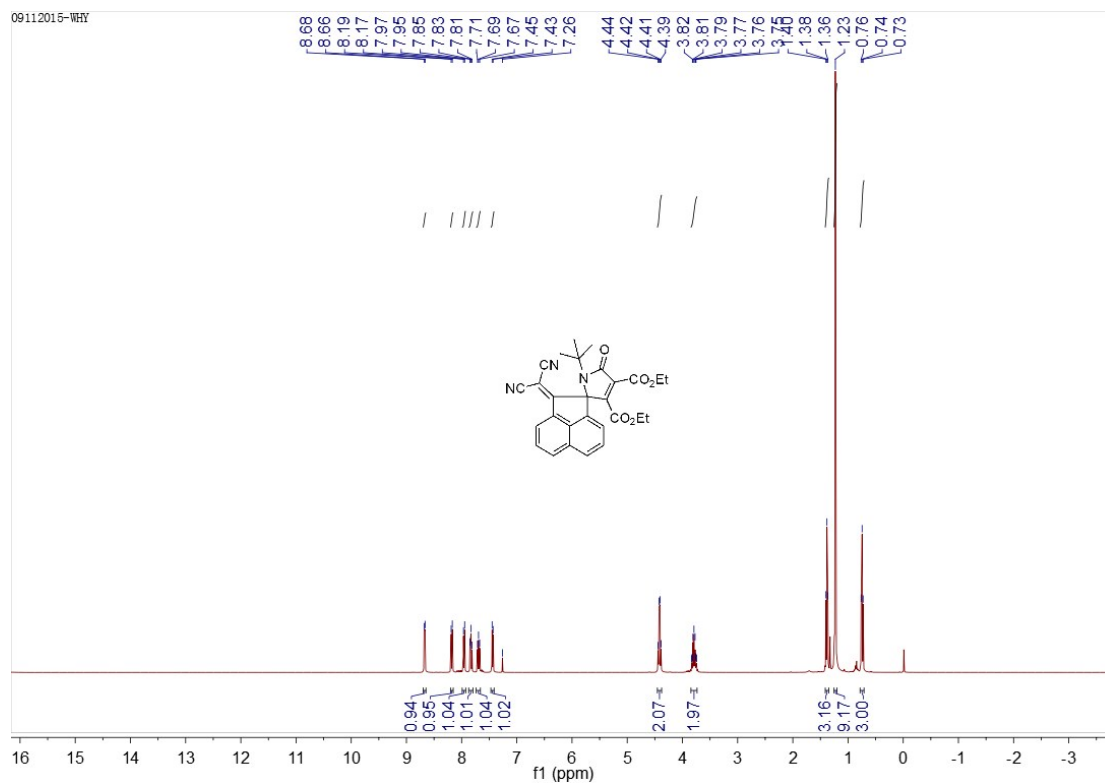
¹H NMR spectrum of compound 5c in CDCl₃, 400 MHz



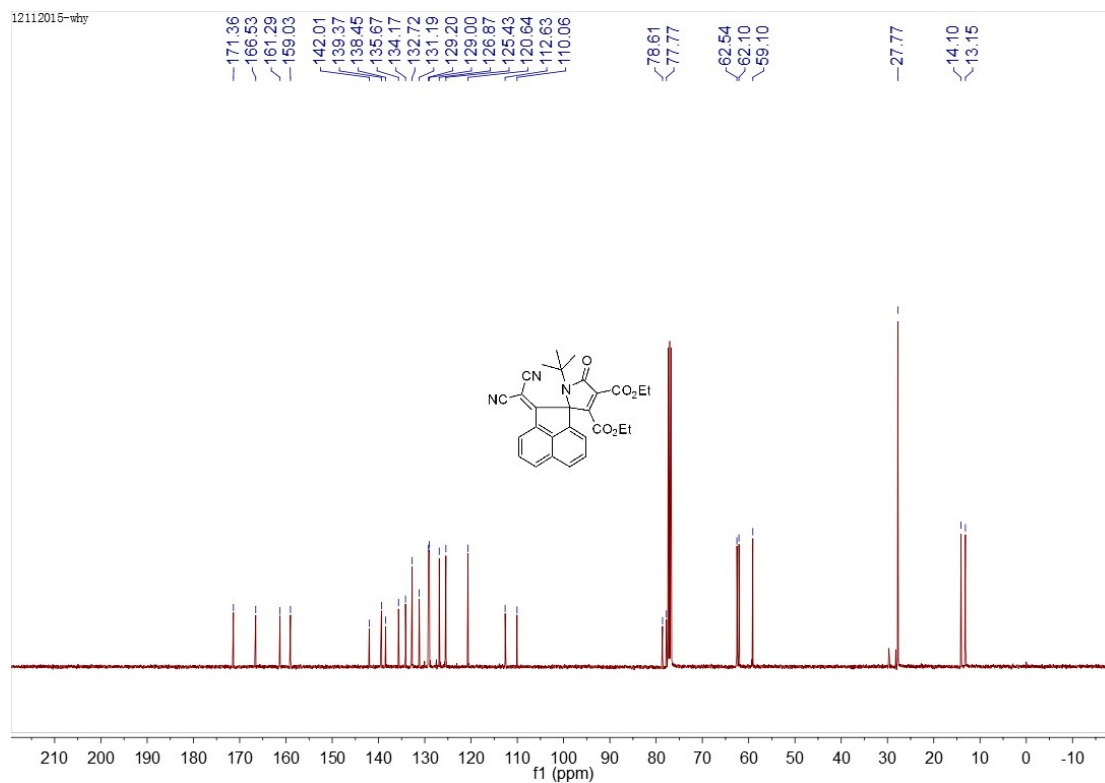
¹³C NMR spectrum of compound 5c in CDCl₃, 100 MHz



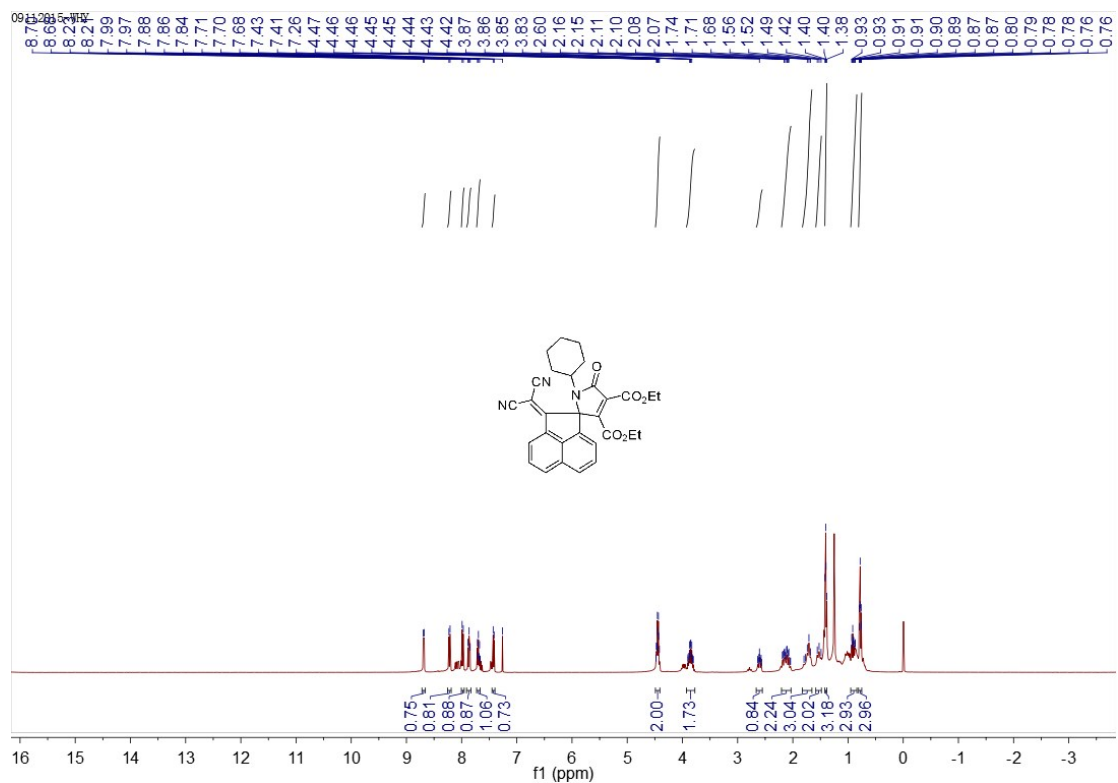
¹H NMR spectrum of compound 5d in CDCl₃, 400 MHz



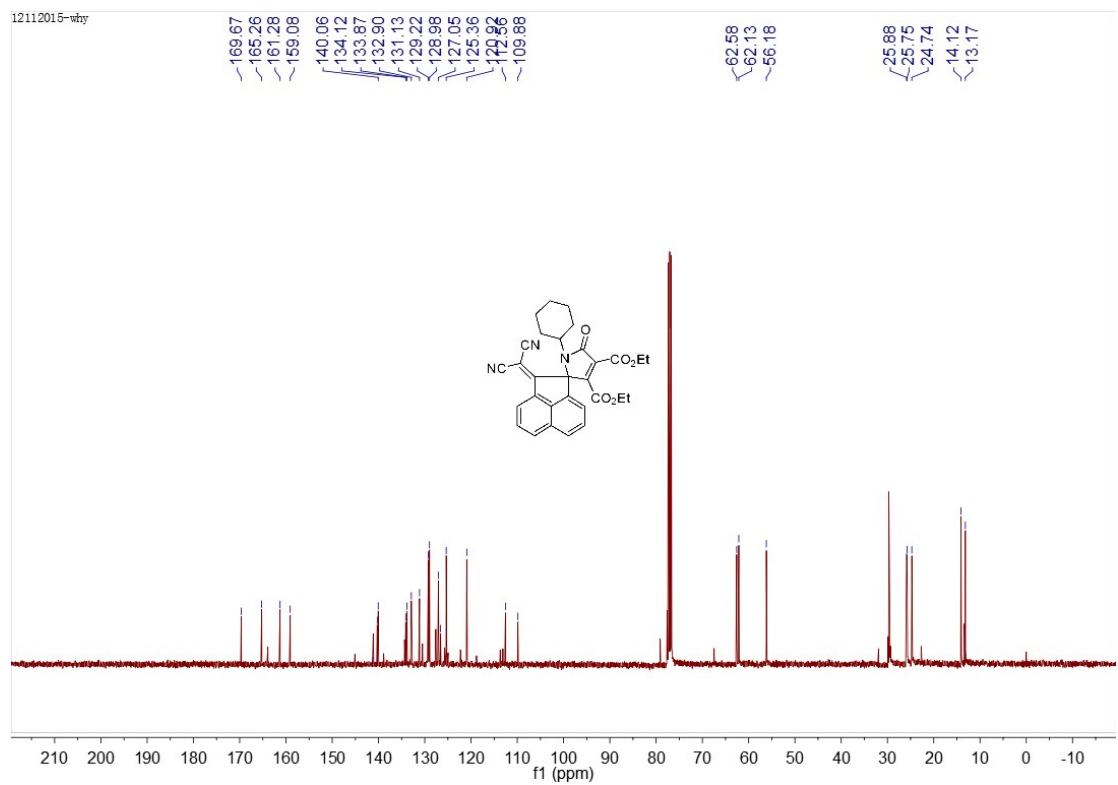
¹³C NMR spectrum of compound 5d in CDCl₃, 100 MHz



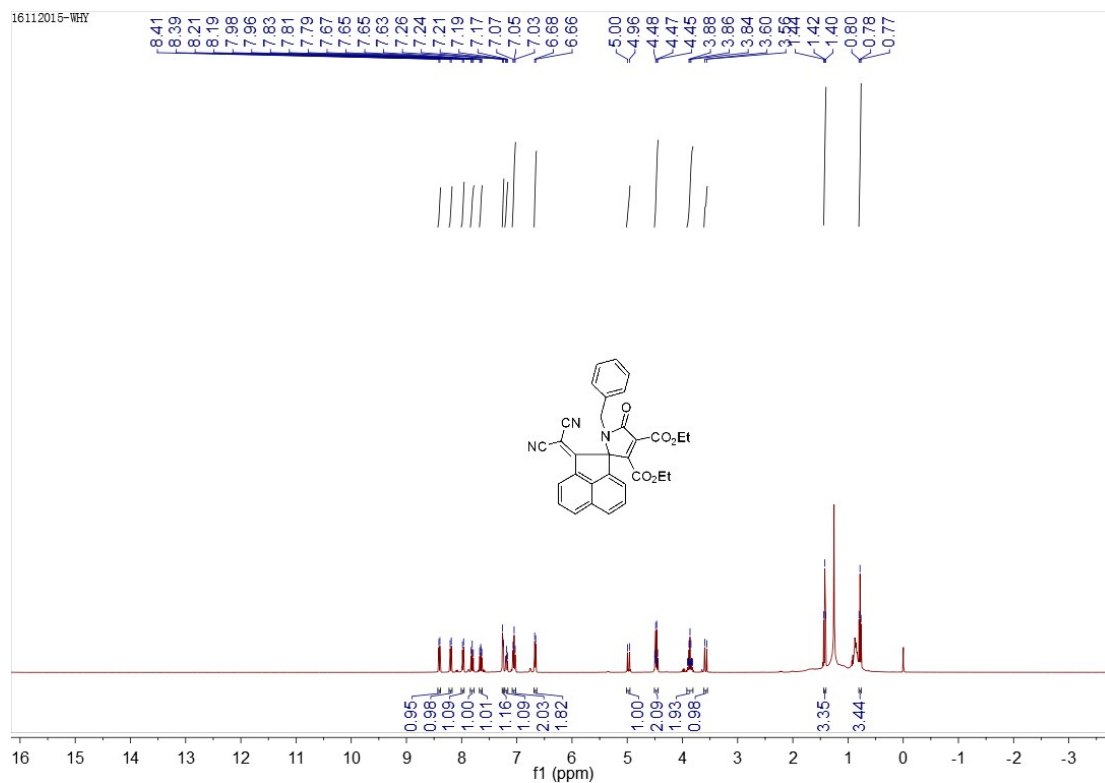
¹H NMR spectrum of compound 5e in CDCl₃, 400 MHz



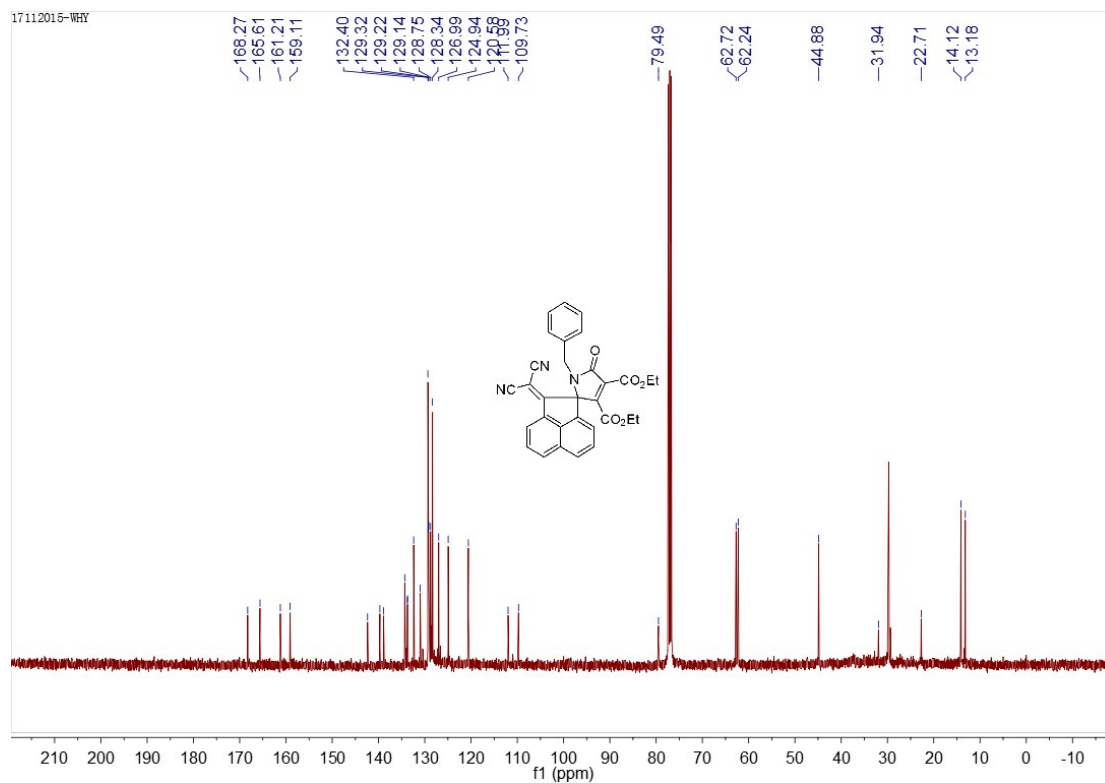
¹³C NMR spectrum of compound 5e in CDCl₃, 100 MHz



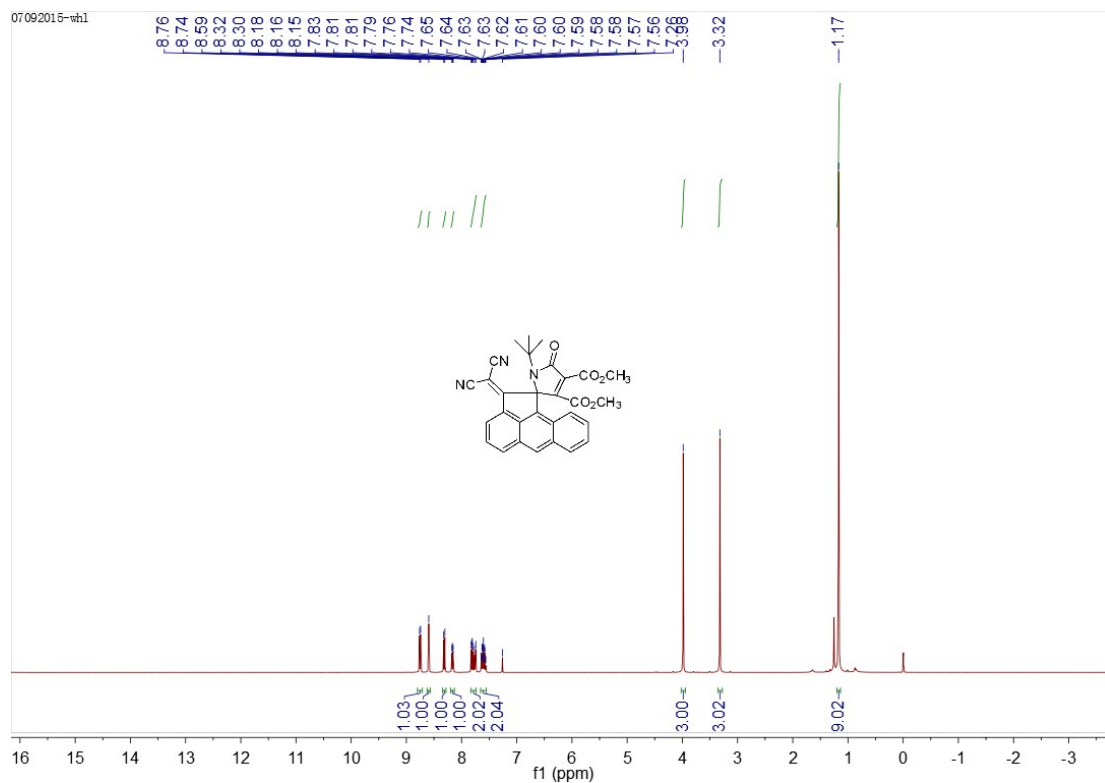
¹H NMR spectrum of compound 5f in CDCl₃, 400 MHz



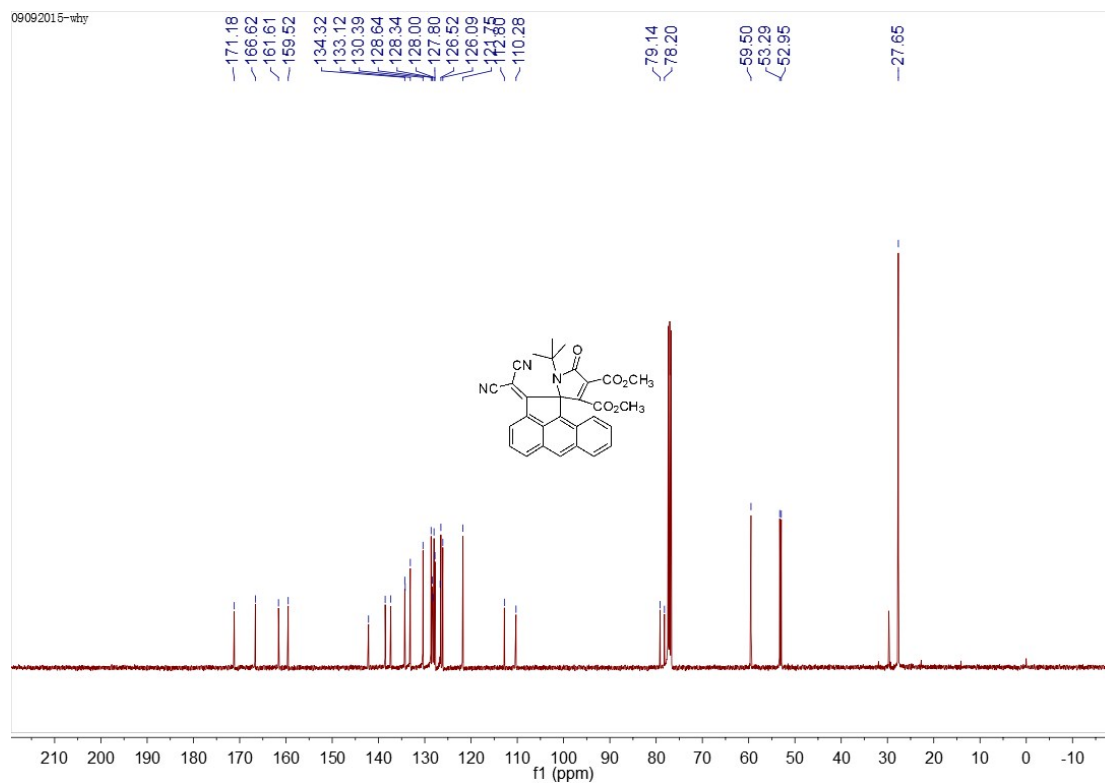
¹³C NMR spectrum of compound 5f in CDCl₃, 100 MHz



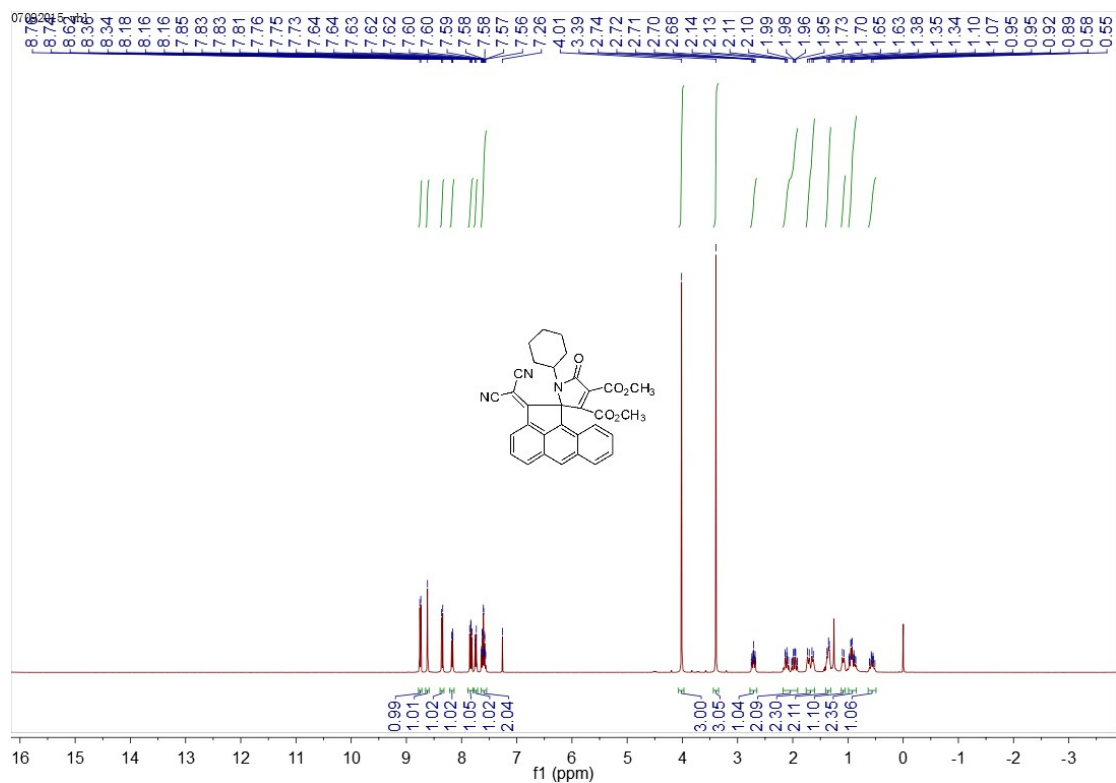
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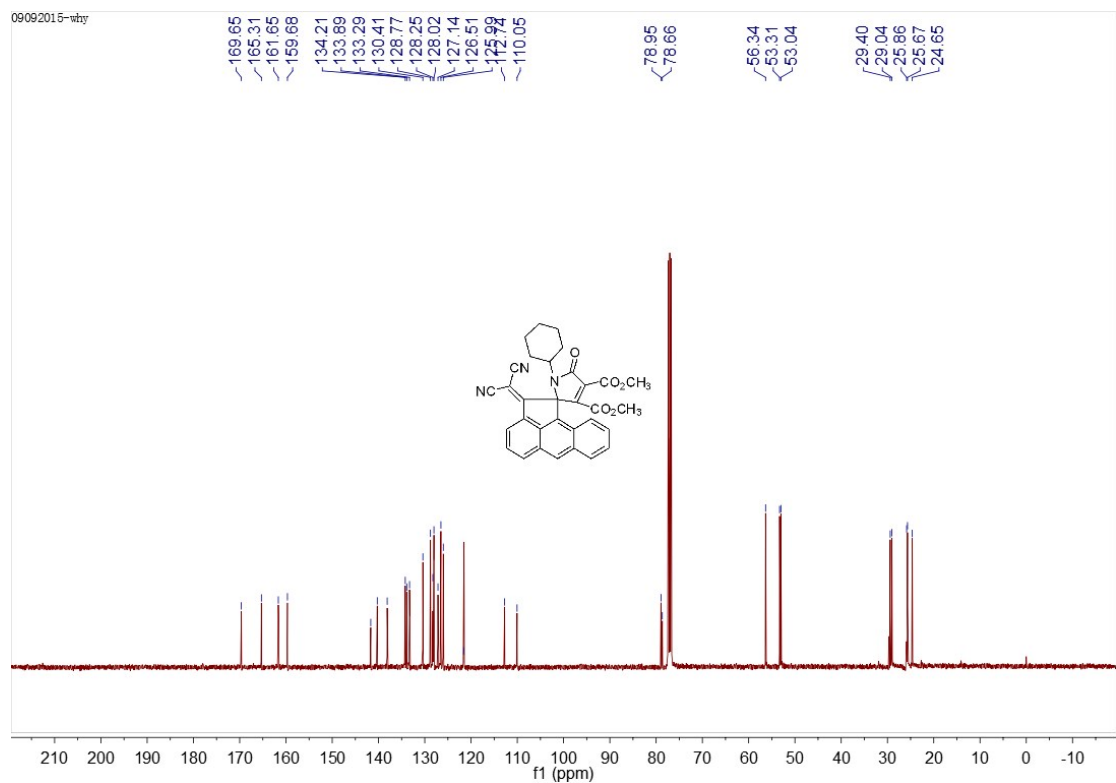
¹³C NMR spectrum of compound 5g in CDCl₃, 100 MHz



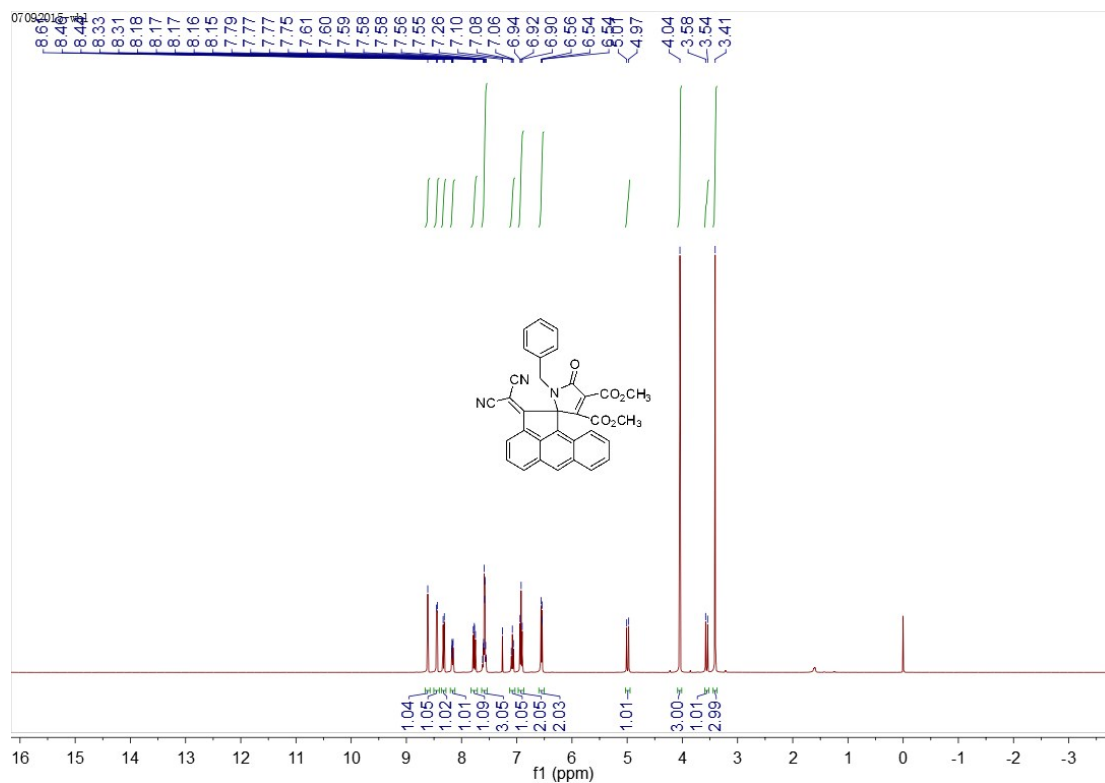
¹H NMR spectrum of compound 5h in CDCl₃, 400 MHz



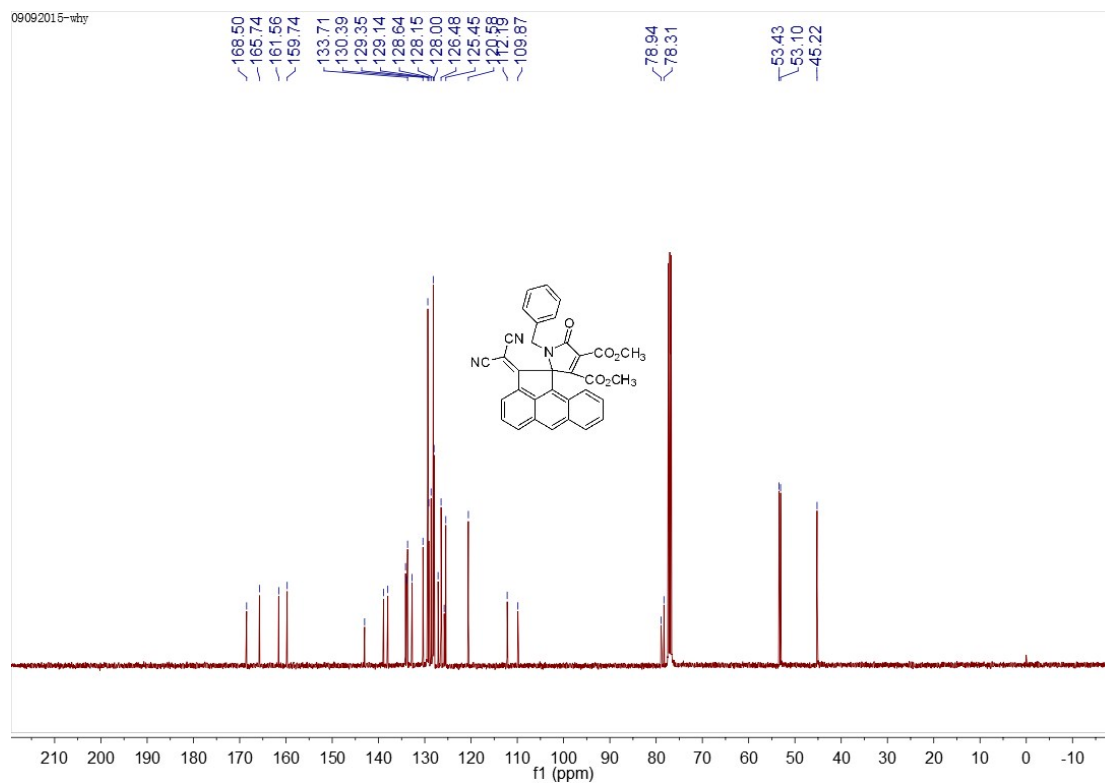
¹³C NMR spectrum of compound 5h in CDCl₃, 100 MHz



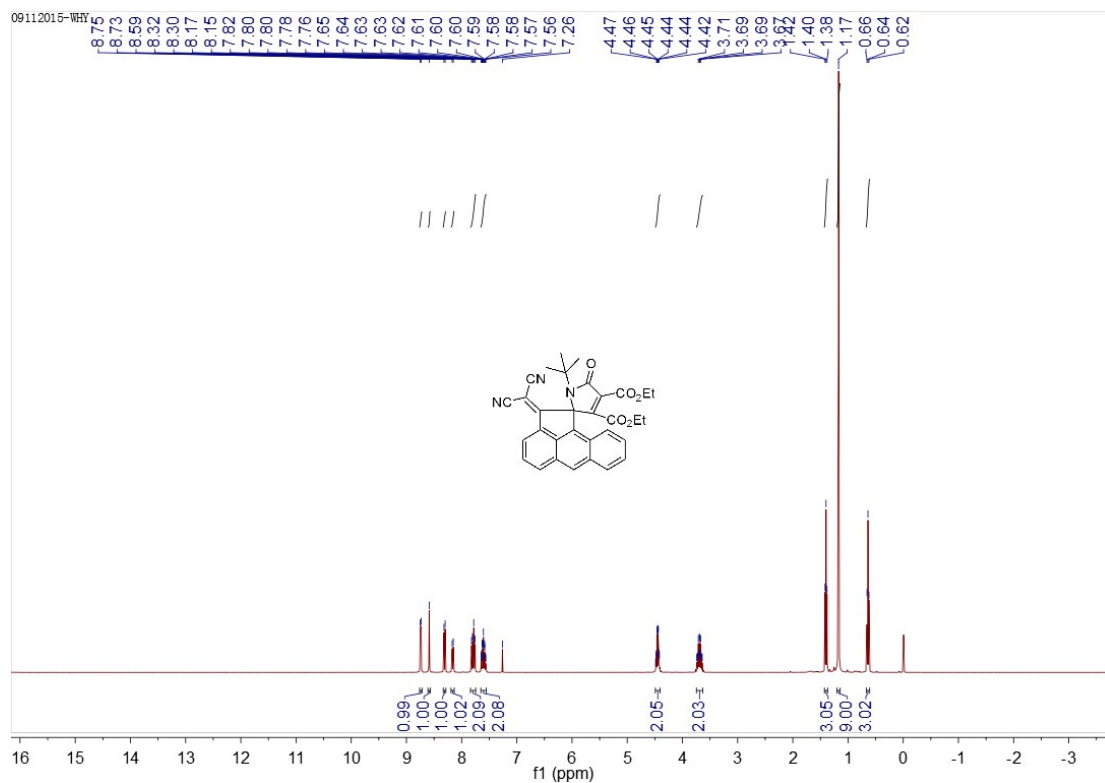
¹H NMR spectrum of compound 5i in CDCl₃, 400 MHz



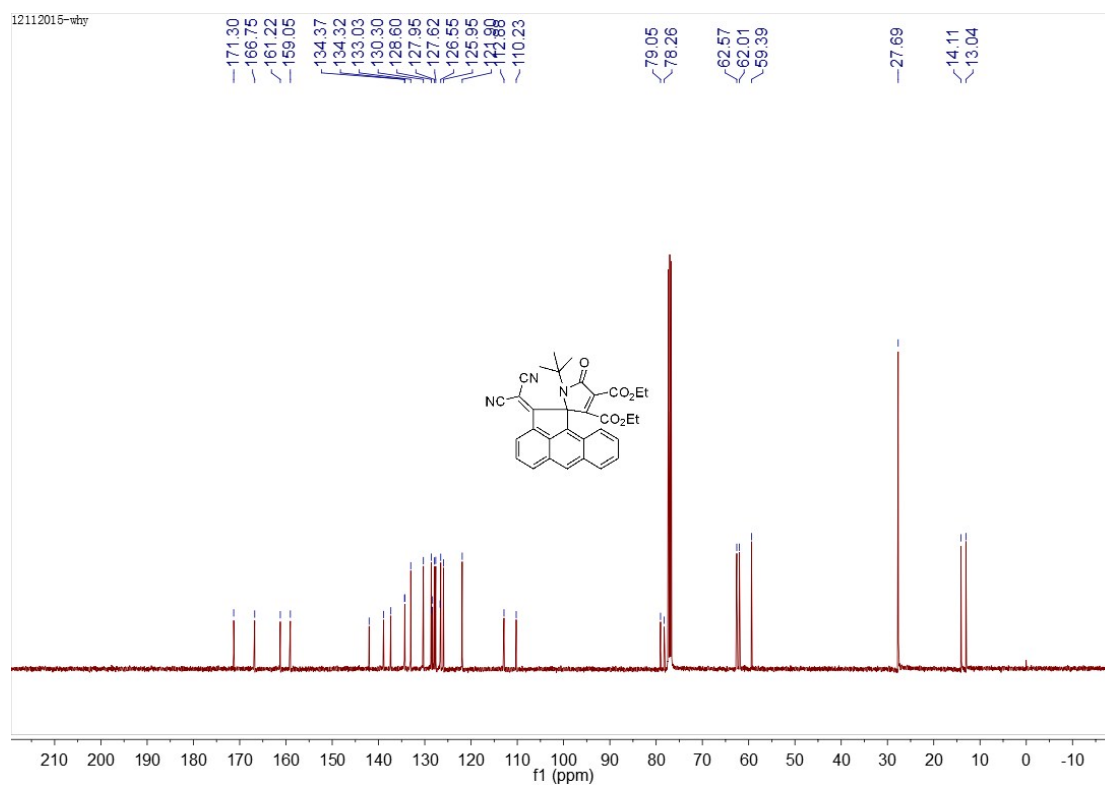
¹³C NMR spectrum of compound 5i in CDCl₃, 100 MHz



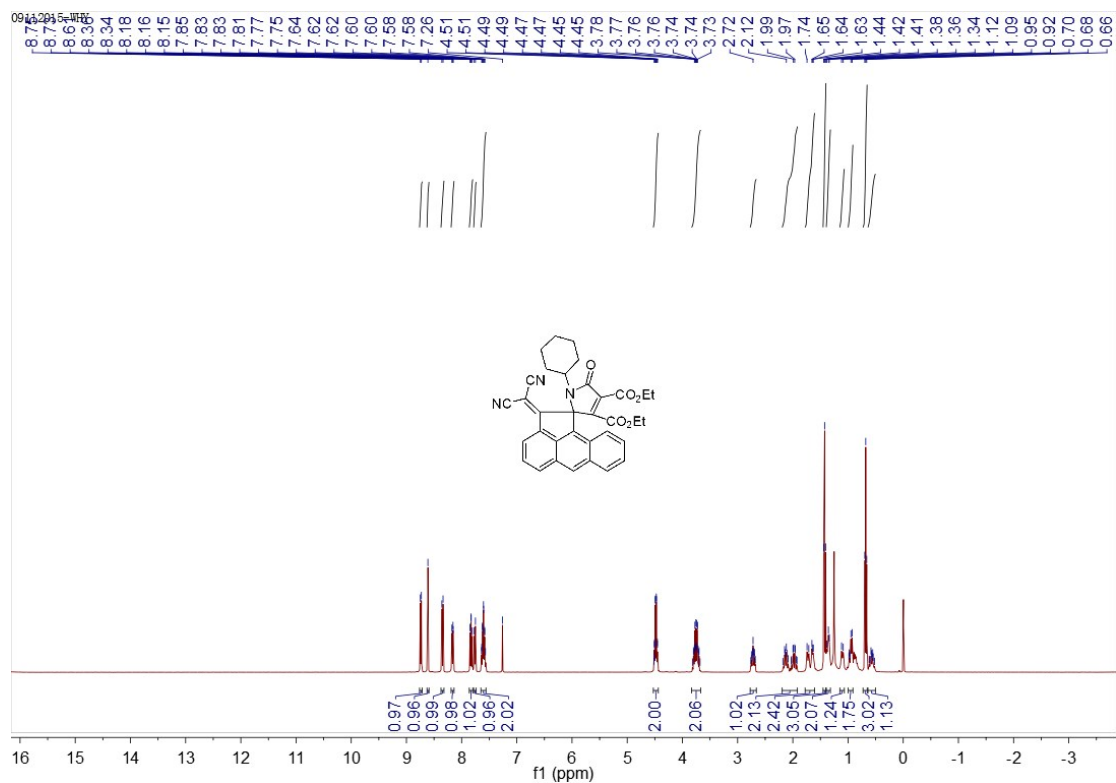
¹H NMR spectrum of compound 5j in CDCl₃, 400 MHz



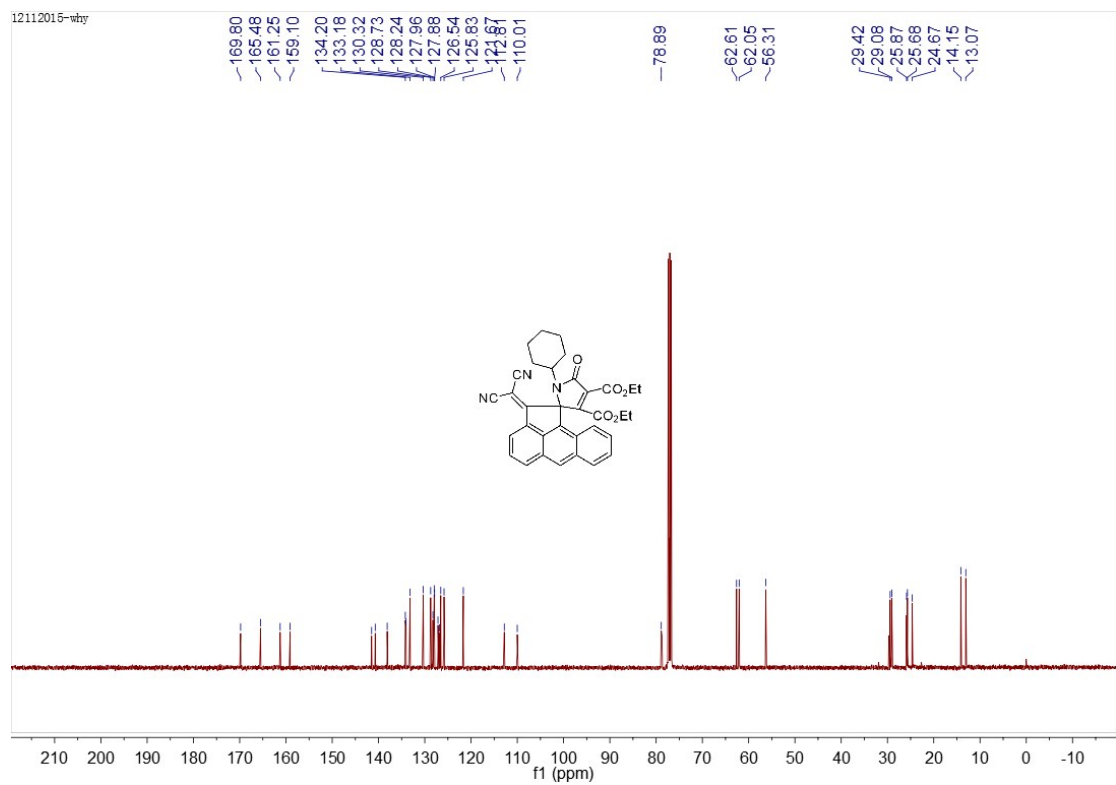
¹³C NMR spectrum of compound 5j in CDCl₃, 100 MHz



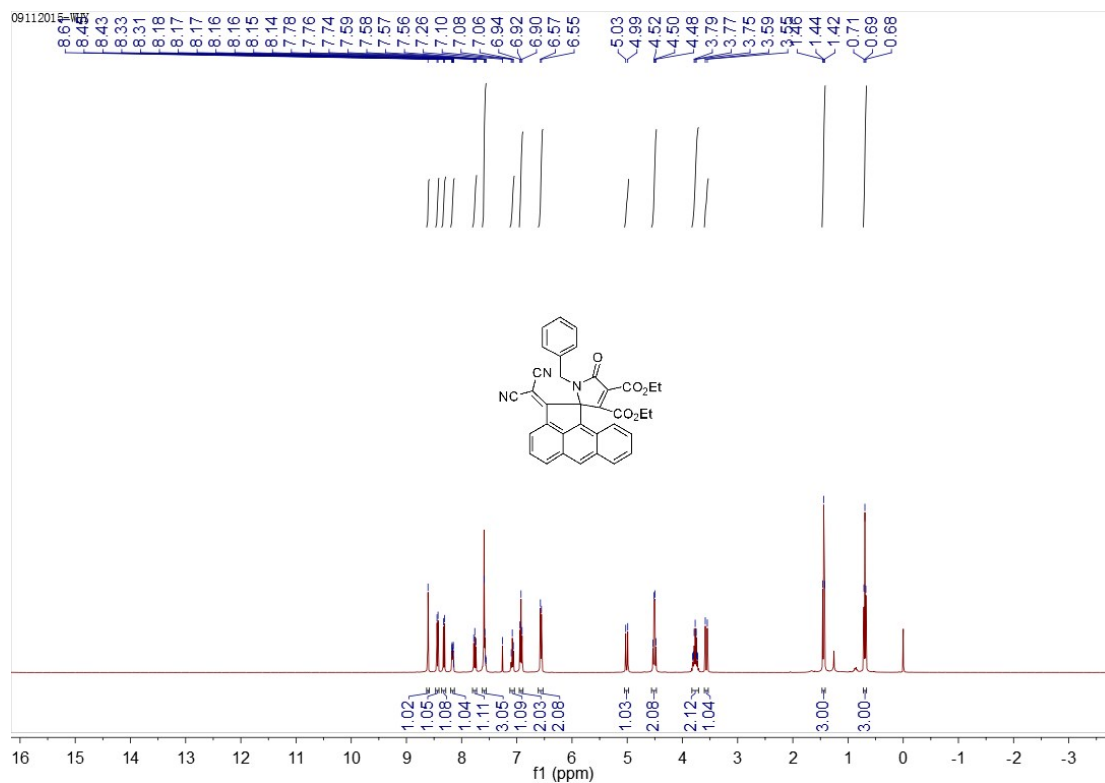
¹H NMR spectrum of compound 5k in CDCl₃, 400 MHz



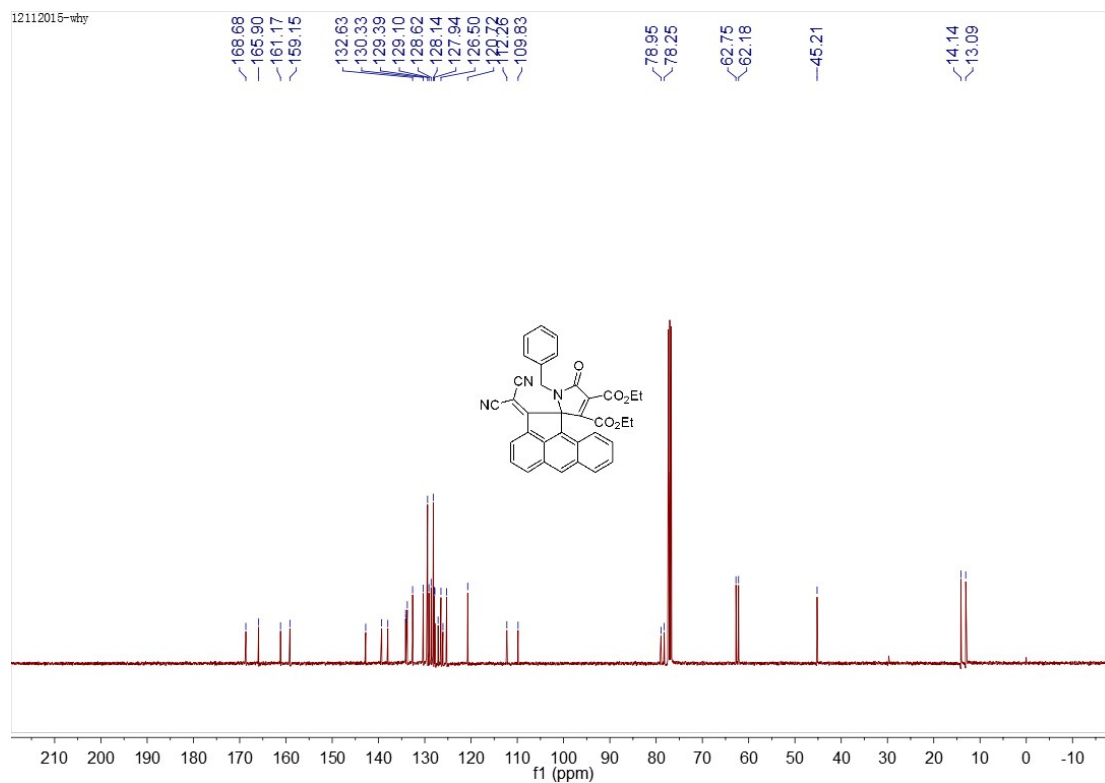
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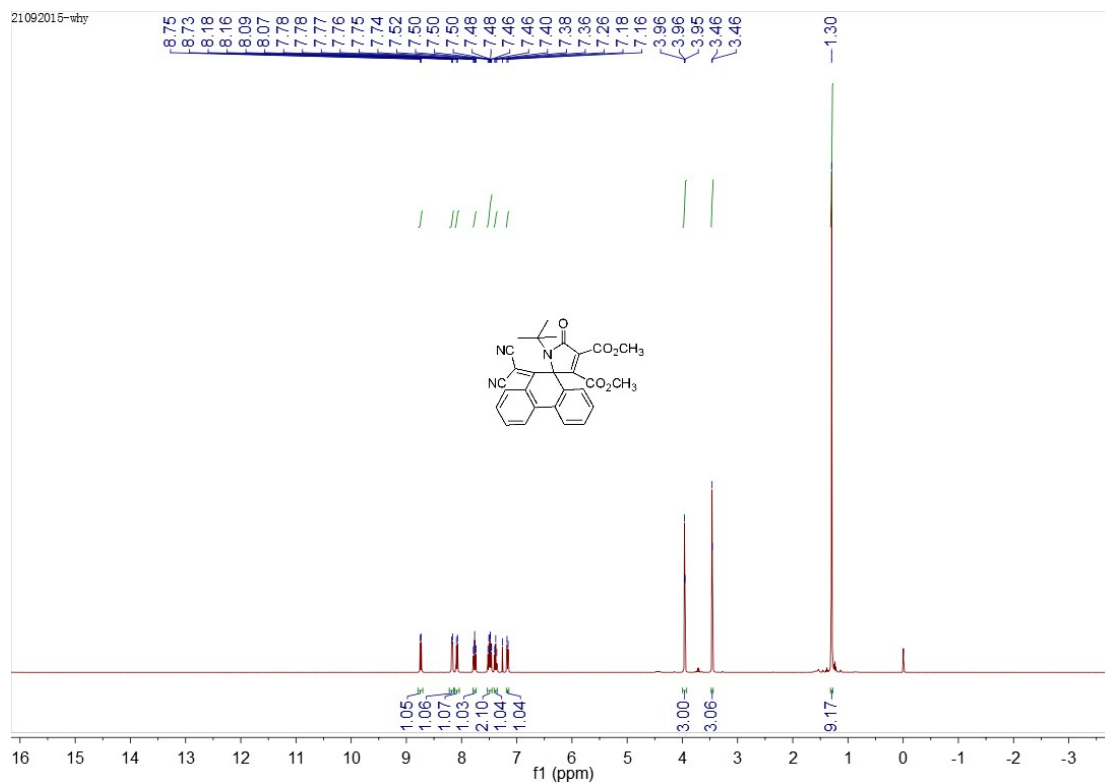
¹H NMR spectrum of compound 5l in CDCl₃, 400 MHz



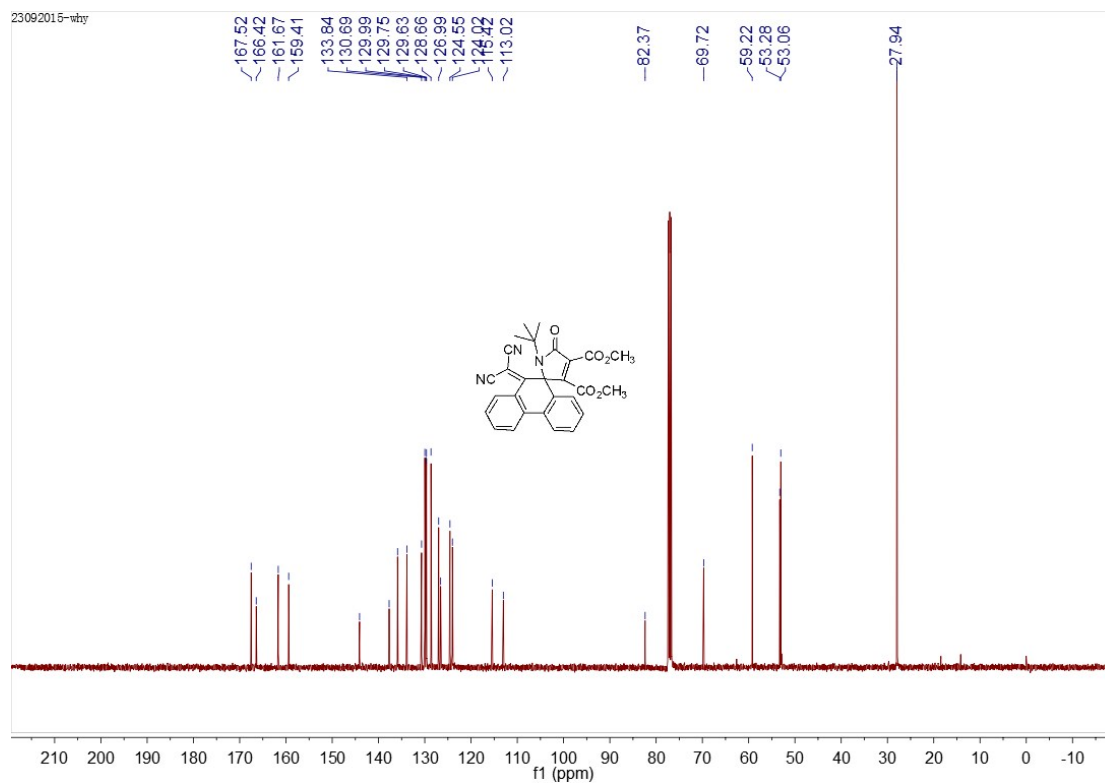
¹³C NMR spectrum of compound 5l in CDCl₃, 100 MHz



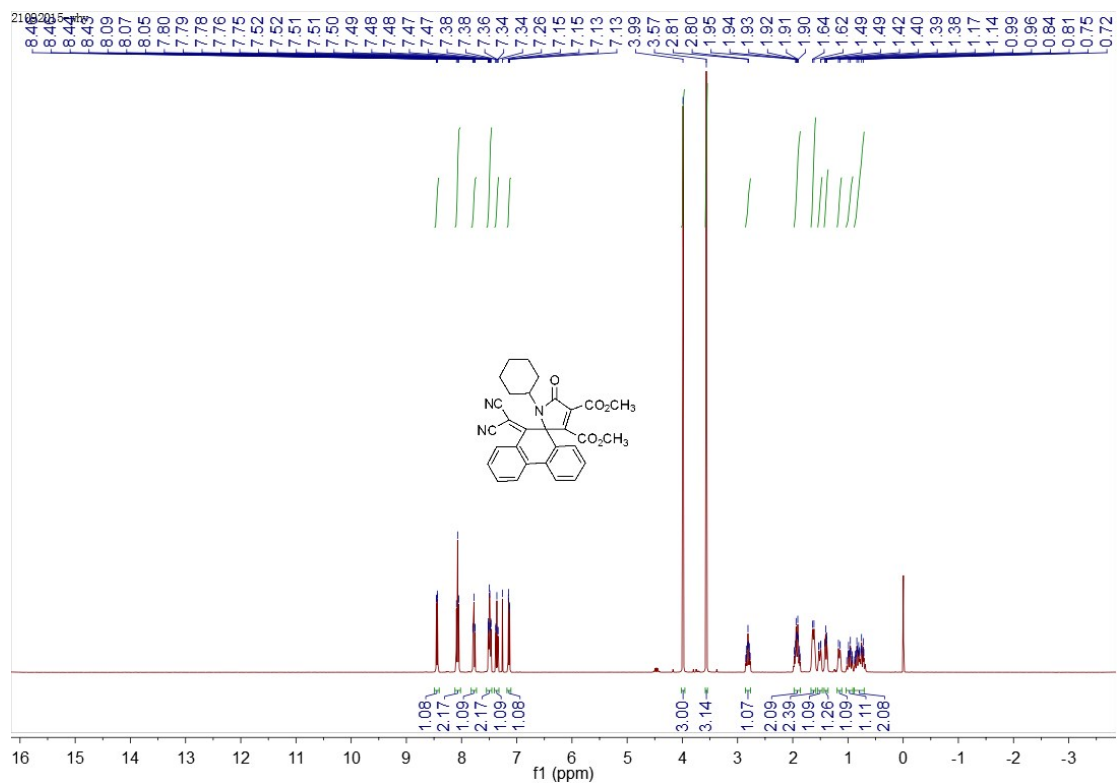
¹H NMR spectrum of compound 5m in CDCl₃, 400 MHz



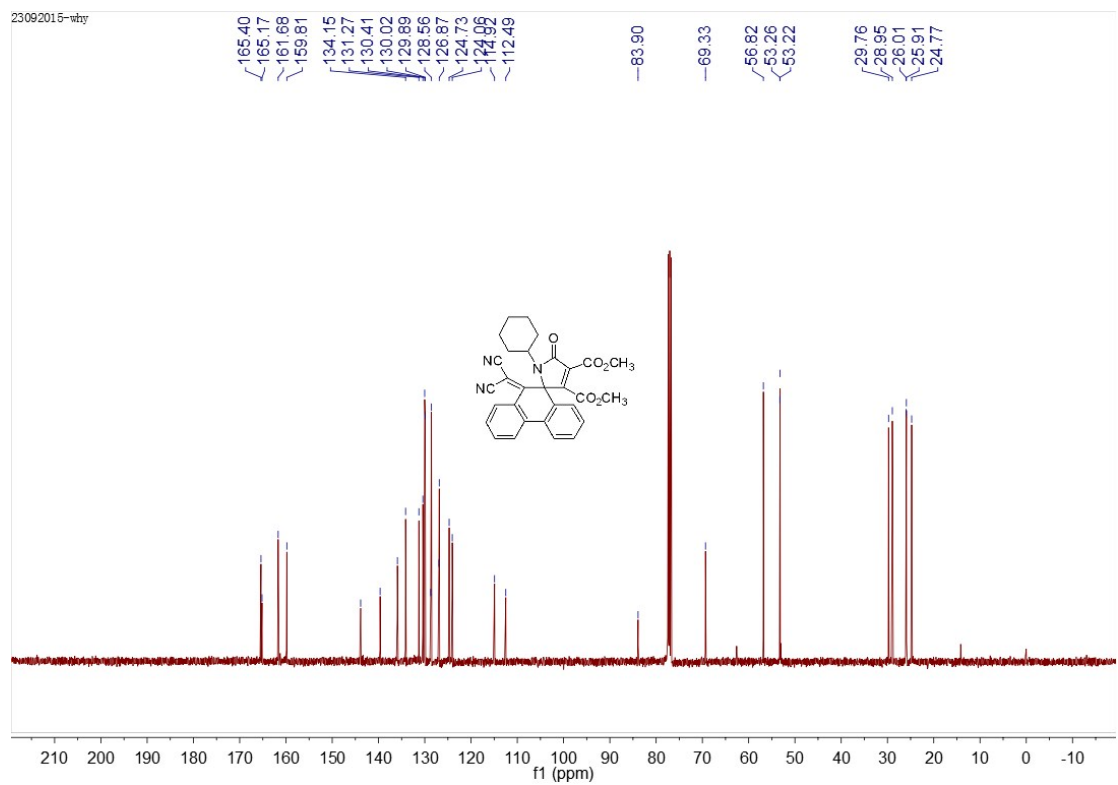
¹³C NMR spectrum of compound 5m in CDCl₃, 100 MHz



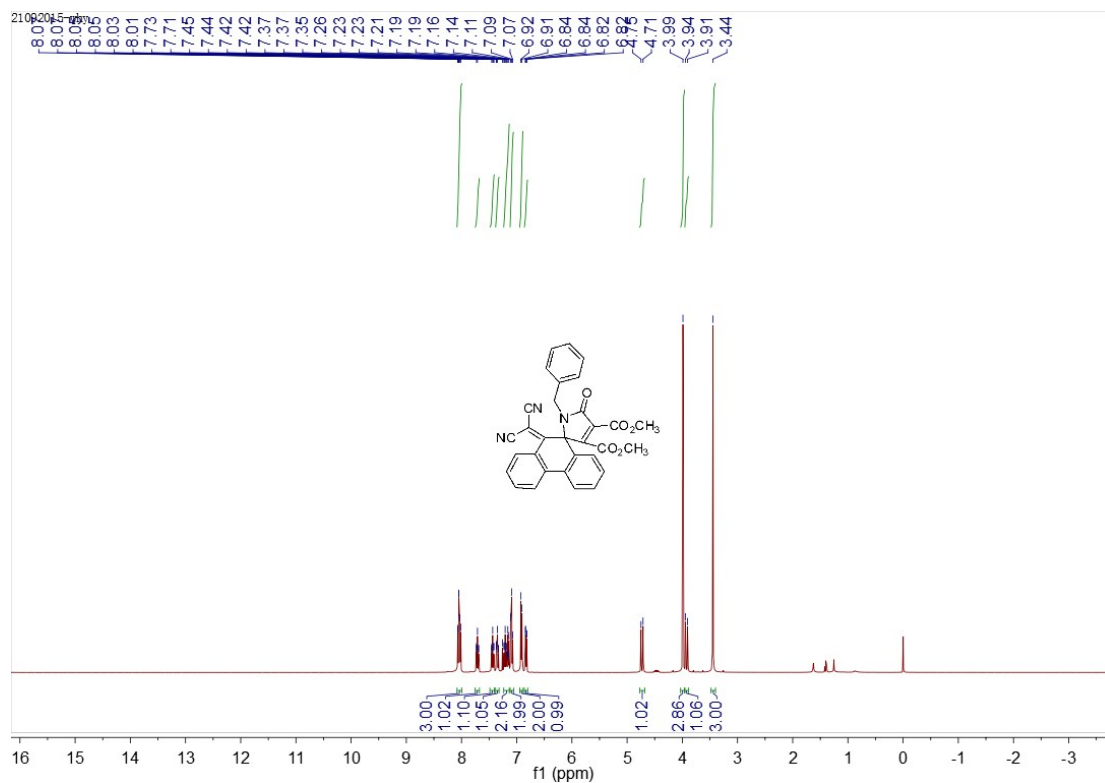
¹H NMR spectrum of compound 5n in CDCl₃, 400 MHz



¹³C NMR spectrum of compound 5n in CDCl₃, 100 MHz



¹H NMR spectrum of compound 5o in CDCl₃, 400 MHz



¹³C NMR spectrum of compound 5o in CDCl₃, 100 MHz

