Supporting Information

Synthesis of Cyclic *gem*-Dinitro Compounds via Radical Nitration of 1,6-Diynes with $Fe(NO_3)_3.9H_2O$

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Contents

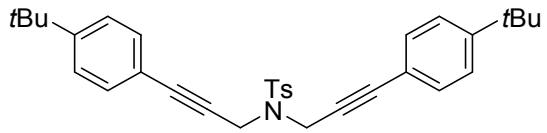
I. General Information

Starting materials **1** was synthesized according to the previous literature.[1] $Fe(NO_3)_3 \cdot 9H_2O$ (a purity of 98.5%) and HNO_3 (65~68%) are available from Sinopharm Chemical Reagent Co. Other reagents (chemicals) were purchased from commercial sources (J&K, Sigma Aldrich, Alfa Aesar, etc.), and used without further purification. Solvents were dried and distilled prior to use. ^{1}H NMR spectra were recorded in deuterated solvents on a Bruker 400 (400 MHz) spectrometer and calibrated to the residual solvent peak or tetramethylsilane (δ = 0 ppm). Splitting patterns are designated as singlet (s), doublet (d), triplet (t), broad (br), multiplet (m). *J*-values are in Hz. High-resolution mass spectra (HRMS) data were obtained by using EI or ESI ionization. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 200-300 mesh silica gel at increased pressure. Unless otherwise noted, all reactions were carried out under nitrogen atmosphere with magnetic stirring.

1. (a) Sinclair, G. S.; Yang, T.; Wang, S.; Chen, W. H.; Schipper, D. J., *Org. Lett.* **2017,** *19*, 802-805; (b) Lian, J.-J.; Chen, P.-C.; Lin, Y.-P.; Ting, H.-C.; Liu, R.-S., *J. Am. Chem. Soc.* **2006,** *128*, 11372-11373; (c) Xu, T.; Yang, Q.; Ye, W.; Jiang, Q.; Xu, Z.; Chen, J.; Yu, Z., *Chem. Eur. J.* **2011,** *17*, 10547-10551.

1. Characterization data of starting materials 1

***N,N*-bis(3-(4-(*tert*-butyl)phenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1d)**

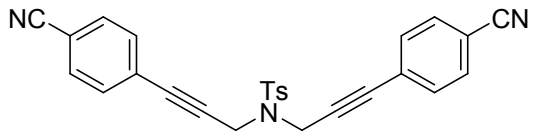


Yellow solid (m. p. 111 - 112 °C); yield: (76%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 4H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 4H), 4.34 (s, 4H), 2.21 (s, 3H), 1.20 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.80, 143.79, 135.42, 131.50, 129.63, 128.01, 125.19, 119.27, 85.92, 80.99, 37.54, 34.78, 31.17, 21.46; HRMS (GC-TOF) calculated for

$C_{33}H_{37}NO_2S$: 511.2545; found: 511.2547.

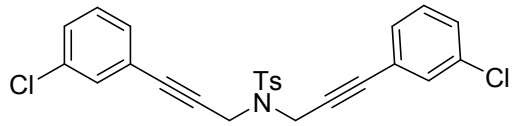
***N,N*-bis(3-(4-cyanophenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1f)**



Yellow solid (m. p. 162 - 163 °C); yield: (15%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 4H), 7.29 (d, *J* = 8.Hz, 4H), 7.27 (d, *J* = 8.0 Hz, 2H), 4.45 (s, 4H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.14, 135.26, 132.17, 131.95, 129.71, 128.02, 126.85, 118.17, 112.15, 86.09, 84.30, 37.52, 21.50; HRMS (ESI-TOF) calculated for $C_{27}H_{19}N_3O_2S$ ($[M+Na]^+$): 472.1096; found: 472.1088.

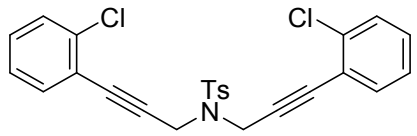
***N,N*-bis(3-(3-chlorophenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1h)**



White solid (m. p. 87 - 88 °C); yield: (77%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.23 - 7.17 (m, 4H), 7.10 (t, *J* = 8.0 Hz, 2H), 7.06 - 7.00 (m, 4H), 4.35 (s, 4H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.17, 135.36, 134.01, 131.56, 129.76, 129.68, 129.49, 128.88, 128.09, 123.80, 84.52, 82.94, 37.65, 21.50; HRMS (ESI-TOF) calculated for $C_{25}H_{19}Cl_2NO_2S$ ($[M+Na]^+$) : 490.0412; found: 490.0404.

***N,N*-bis(3-(2-chlorophenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1i)**

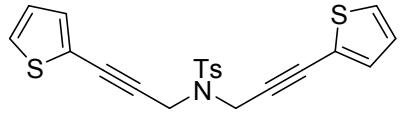


Brown solid (m. p. 122 - 123 °C); yield: (73%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.19 -

7.11 (m, 6H), 7.07 (t, J = 7.6 Hz, 2H), 4.46 (s, 4H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.98, 135.94, 135.07, 133.36, 129.62, 129.56, 129.17, 127.93, 126.31, 122.23, 86.91, 82.73, 37.54, 21.36; HRMS (ESI-TOF) calculated for $C_{25}H_{19}Cl_2NO_2S$ ($[M+Na]^+$): 490.0412; found: 490.0404.

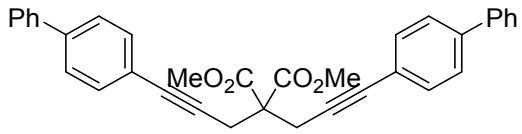
4-methyl-*N*,*N*-bis(3-(thiophen-2-yl)prop-2-yn-1-yl)benzenesulfonamide (1k)



Brown solid (m. p. 73 - 74 °C); yield: (52%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.21 (dd, J = 5.2 and 1.2 Hz, 2H), 7.03 (dd, J = 3.6 and 1.2 Hz, 2H), 6.90 (dd, J_1 = 5.2 and 3.6 Hz, 2H), 4.42 (s, 4H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.10, 135.14, 132.61, 129.78, 127.90, 127.54, 126.91, 122.06, 85.64, 79.23, 37.78, 21.61; HRMS (ESI-TOF) calculated for $C_{21}H_{17}NO_2S_3$ ($[M+Na]^+$): 434.0319; found: 434.0339.

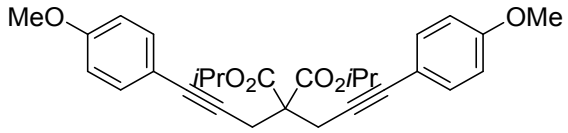
dimethyl 2,2-bis(3-([1,1'-biphenyl]-4-yl)prop-2-yn-1-yl)malonate (1p)



White solid (m. p. 129 - 130 °C); yield: (51%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.2 Hz, 4H), 7.54 (d, J = 8.4 Hz, 4H), 7.48 (d, J = 8.0 Hz, 4H), 7.45 (d, J = 8.0 Hz, 4H), 7.37 (t, J = 7.2 Hz, 2H), 3.85 (s, 6H), 3.34 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.46, 140.90, 140.40, 132.18, 128.88, 127.64, 127.05, 126.96, 121.99, 84.64, 83.77, 57.36, 53.02, 24.01; HRMS (ESI-TOF) calculated for $C_{35}H_{28}O_4$ ($[M+Na]^+$): 535.1886; found: 535.1863.

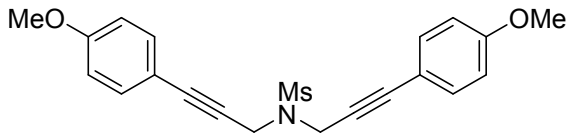
diisopropyl 2,2-bis(3-(4-methoxyphenyl)prop-2-yn-1-yl)malonate (1r)



White solid (m. p. 66 - 67 °C); yield: (41%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.8 Hz, 4H), 6.80 (d, *J* = 8.8 Hz, 4H), 5.11 (hept, *J* = 6.4 Hz, 2H), 3.78 (s, 6H), 3.20 (s, 4H), 1.26 (d, *J* = 6.4 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.57, 159.32, 133.04, 115.43, 113.81, 83.25, 82.78, 69.34, 57.13, 55.25, 23.56, 21.57; HRMS (ESI-TOF) calculated for $C_{29}H_{32}O_6$ ($[M+Na]^+$): 499.2097; found: 499.2077.

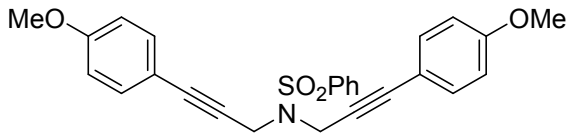
_N,N_-bis(3-(4-methoxyphenyl)prop-2-yn-1-yl)methanesulfonamide (1u)



Red oil; yield: (72%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.8 Hz, 4H), 6.81 (d, *J* = 8.8 Hz, 4H), 4.43 (s, 4H), 3.81 (s, 6H), 3.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.97, 133.28, 114.13, 114.01, 86.10, 80.84, 55.33, 38.78, 37.90; HRMS (ESI-TOF) calculated for $C_{21}H_{21}NO_4S$ ($[M+Na]^+$): 406.1089; found: 406.1091.

_N,N_-bis(3-(4-methoxyphenyl)prop-2-yn-1-yl)benzenesulfonamide (1v)



White solid (m. p. 97 - 98 °C); yield: (31%);

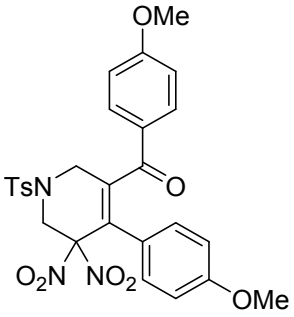
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 4H), 6.78 (d, *J* = 8.8 Hz, 4H), 4.44 (s, 4H), 3.80 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.76, 138.64, 133.19, 132.81, 128.91, 127.98, 114.28, 113.82, 85.71, 80.22, 55.29, 37.53; HRMS (ESI-TOF) calculated for $C_{26}H_{23}NO_4S$ ($[M+K]^+$): 484.2331; found: 484.2321.

2. General procedure for products 2 and 3

To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added 1,6-diyne **1** (0.20 mmol), $Fe(NO_3)_3 \cdot 9H_2O$ (81 mg, 0.20 mmol, 1.0 eq.), MeCN (0.5mL), and HNO_3 (65~68 %, 2.5 μL) under N_2 atmosphere. The reaction was carried out at room temperature. The reaction mixture was filtered through Celite, and the filtrate was evaporated in vacuum. The residue was purified by silica gel column chromatography to give the products **2** or **3**.

3. Characterization data of products 2 and 3

(4-methoxyphenyl)(4-(4-methoxyphenyl)-5,5-dinitro-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanone (2a)



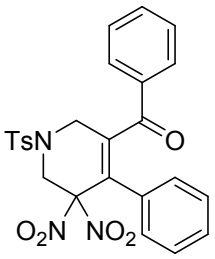
Yellow solid (m. p. 171 - 172 °C); yield: 97 mg (85%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 4.42 (s, 2H), 4.12 (s, 2H), 3.83 (s, 3H), 3.63 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.15, 164.75, 160.35, 145.44, 144.79, 132.08, 131.90, 131.27, 130.48, 127.79, 127.40, 126.66, 122.60, 116.84, 114.20, 113.82, 55.60, 55.06, 50.64, 47.28, 21.68;

IR (cm^{-1}): 2939, 2842, 1662, 1599, 1560, 1512, 1456, 1357, 1308, 1294, 1256, 1181, 1165, 1032, 1006, 846, 810, 784, 771, 755, 664, 565, 549; HRMS (ESI-TOF) calculated for $C_{27}H_{25}N_3O_9S$ ($[M+Na]^+$) calcd. 590.1210; found: 590.1184.

(5,5-dinitro-4-phenyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)(phenyl)methanone

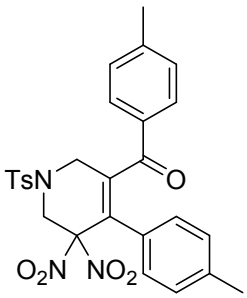
(2b)



Yellow solid (m. p. 82 - 83 °C); yield: 60 mg (59%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.09 - 7.05 (m, 5H), 4.46 (s, 2H), 4.18 (s, 2H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.76, 145.51, 145.11, 134.63, 133.89, 131.97, 130.51, 130.40, 129.96, 129.89, 129.39, 128.80, 128.49, 128.40, 127.80, 116.52, 50.58, 47.19, 21.70; IR (cm^{-1}): 2925, 1654, 1589, 1566, 1450, 1384, 1359, 1318, 1163, 1124, 1035, 1009, 816, 770, 749, 699, 684, 669, 571, 549; HRMS (ESI-TOF) calculated for $C_{25}H_{21}N_3O_7S$ ($[M+Na]^+$) calcd. 530.0998; found: 530.0967.

(5,5-dinitro-4-(*p*-tolyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)(*p*-tolyl)methanone (2c)

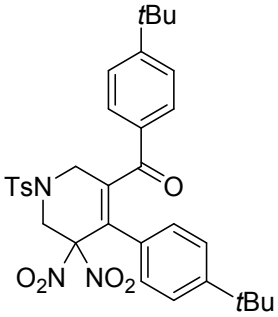


Yellow solid (m. p. 77 - 78 °C); yield: 44 mg (42%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 4.43 (s, 2H), 4.13 (s, 2H), 2.49 (s, 3H), 2.35 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.30, 145.98, 145.44, 144.87, 139.89, 131.95, 131.30, 130.47, 129.73, 129.66, 129.60, 129.12, 127.92, 127.79, 127.45, 116.68, 50.61, 47.20, 21.87, 21.68, 21.14;

IR (cm^{-1}): 2924, 1664, 1604, 1589, 1568, 1540, 1451, 1359, 1316, 1289, 1260, 1185, 1164, 1090, 1005, 817, 779, 771, 664, 560, 549; HRMS (ESI-TOF) calculated for $C_{27}H_{25}N_3O_7S$ ($[M+Na]^+$) calcd. 558.1311; found: 558.1263.

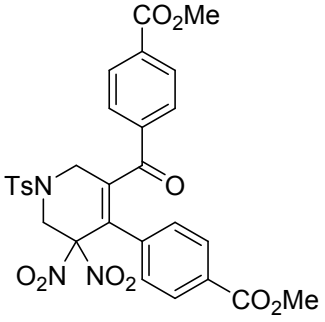
(4-(*tert*-butyl)phenyl)(4-(4-(*tert*-butyl)phenyl)-5,5-dinitro-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanone (2d)



White solid (m. p. 107 - 108 °C); yield: 80 mg (65%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 4.45 (s, 2H), 4.17 (s, 2H), 2.48 (s, 3H), 1.25 (s, 9H), 1.08 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.75, 158.23, 152.83, 145.43, 144.91, 131.95, 131.74, 130.49, 129.73, 129.31, 128.75, 127.81, 127.62, 125.50, 125.12, 116.67, 50.61, 47.27, 35.23, 34.46, 30.91, 30.87, 21.68; IR (cm^{-1}): 2965, 2870, 1664, 1603, 1589, 1569, 1384, 1365, 1264, 1164, 1091, 1004, 767, 662, 585, 549; HRMS (ESI-TOF) calculated for $C_{33}H_{37}N_3O_7S$ ($[M+Na]^+$) calcd. 642.2250; found: 642.2240.

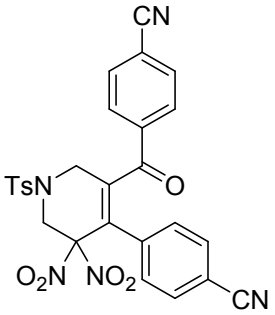
methyl 4-(5-(4-(methoxycarbonyl)benzoyl)-3,3-dinitro-1-tosyl-1,2,3,6-tetrahydropyridin-4-yl)benzoate (2e)



Yellow solid (m. p. 83 - 84 °C); yield: 40 mg (32%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 4.46 (s, 2H), 4.21 (s, 2H), 3.93 (s, 3H), 3.81 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.45, 165.27, 165.13, 145.18, 144.93, 136.27, 134.80, 134.11, 131.40, 131.06, 130.07, 129.60, 129.53, 129.15, 128.67, 127.88, 127.29, 115.55, 52.15, 51.83, 49.98, 46.64, 21.22; IR (cm^{-1}): 2955, 2926, 2853, 1726, 1664, 1588, 1570, 1437, 1406, 1360, 1282, 1162, 1111, 1018, 966, 853, 787, 774, 732, 706, 660, 577, 549; HRMS (ESI-TOF) calculated for $C_{29}H_{25}N_3O_{11}S$ ($[M+Na]^+$) calcd. 646.1108; found: 646.1099.

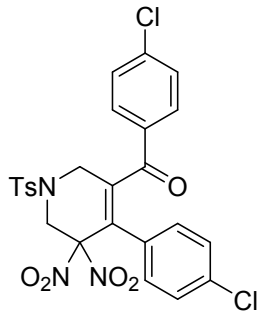
4-(5-(4-cyanobenzoyl)-3,3-dinitro-1-tosyl-1,2,3,6-tetrahydropyridin-4-yl)benzonitrile (2f)



Yellow solid (m. p. 84 - 85 °C); yield: 47 mg (42%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 2H), 4.46 (s, 2H), 4.21 (s, 2H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.88, 145.89, 136.37, 134.55, 132.91, 132.36, 131.76, 130.76, 130.65, 129.49, 128.05, 127.77, 118.33, 117.23, 117.12, 115.68, 114.55, 50.36, 47.02, 21.74; IR (cm^{-1}): 2925, 2854, 2232, 1676, 1589, 1571, 1405, 1359, 1314, 1289, 1254, 1163, 1090, 1005, 855, 814, 773, 664, 576, 548; HRMS (ESI-TOF) calculated for $C_{27}H_{19}N_5O_7S$ ($[M+Na]^+$) calcd. 580.0903; found: 580.0902.

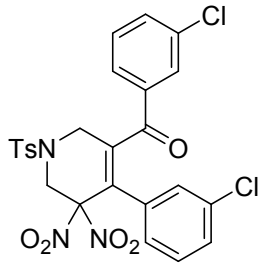
(4-chlorophenyl)(4-(4-chlorophenyl)-5,5-dinitro-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanone (2g)



Yellow solid (m. p. 73 - 74 °C); yield: 52 mg (45%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 4.43 (s, 2H), 4.15 (s, 2H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.27, 145.66, 145.31, 141.75, 136.56, 131.95, 131.83, 131.23, 130.68, 130.56, 129.48, 128.96, 128.59, 127.78, 127.61, 116.20, 50.48, 47.09, 21.72; IR (cm^{-1}): 2924, 1665, 1588, 1570, 1488, 1401, 1359, 1256, 1164, 1091, 1017, 788, 757, 662, 578, 549; HRMS (ESI-TOF) calculated for $C_{25}H_{19}Cl_2N_3O_7S$ ($[M+Na]^+$) calcd. 598.0219; found: 598.0187.

(3-chlorophenyl)(4-(3-chlorophenyl)-5,5-dinitro-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanone (2h)

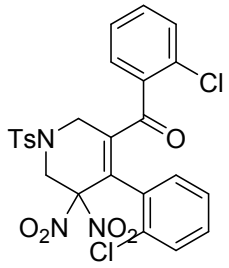


Yellow oil; yield: 42 mg (37%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.69 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.07 (s, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 4.44 (s, 2H), 4.18 (s, 2H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.23, 145.68, 145.34, 135.32, 135.25, 134.68, 134.61, 131.88, 130.58, 130.41, 130.25, 130.03, 129.83, 128.94, 128.14, 128.05, 127.78, 127.53, 116.03, 50.45, 47.10, 29.71, 21.72; IR (cm^{-1}): 2925, 2854, 1664, 1588, 1570, 1448, 1356, 1290, 1251, 1174, 1089, 1008, 770, 758, 722, 667,

550; HRMS (ESI-TOF) calculated for $C_{25}H_{19}Cl_2N_3O_7S$ ([M+Na]$^+$) calcd. 598.0219; found: 598.0203.

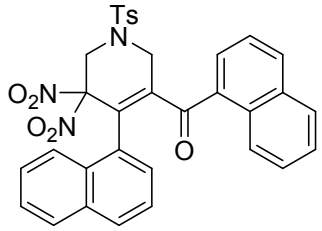
(2-chlorophenyl)(4-(2-chlorophenyl)-5,5-dinitro-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanone (2i)



Yellow solid (m. p. 78 - 79 °C); yield: 50 mg (44%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.25 - 7.18 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.01 - 6.92 (m, 3H), 6.79 (t, *J* = 8.0 Hz, 1H), 5.00, 3.87 (both d, *J* = 12.8 Hz, each 1H), 4.65, 4.14 (both d, *J* = 18.4 Hz, each 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.70, 148.14, 145.39, 136.98, 134.45, 132.89, 132.42, 131.44, 131.32, 131.16, 130.49, 129.78, 129.44, 129.26, 127.79, 126.92, 126.60, 126.05, 115.49, 49.78, 47.13, 21.72; IR (cm^{-1}): 2925, 1664, 1587, 1572, 1534, 1470, 1450, 1436, 1356, 1295, 1245, 1162, 1090, 1061, 1003, 852, 766, 753, 732, 719, 663, 573, 548; HRMS (ESI-TOF) calculated for $C_{25}H_{19}Cl_2N_3O_7S$ ([M+Na]$^+$) calcd. 598.0219; found: 598.0211.

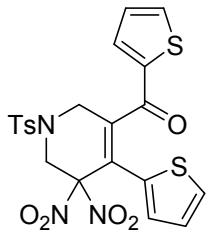
naphthalen-1-yl(4-(naphthalen-1-yl)-5,5-dinitro-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanone (2j)



Yellow solid (m. p. 182 - 183 °C); yield: 28 mg (23%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 7.2 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.41 - 7.29 (m, 5H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.11 - 7.08 (m, 2H), 6.76 (t, *J* = 8.0 Hz, 1H), 5.09,4.11 (both d, *J* = 12.6 Hz, each 1H), 4.73, 4.36 (both d, *J* = 18.4 Hz, each 1H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.16, 148.91, 145.52, 134.07, 133.35, 133.23, 132.80, 132.25, 131.61, 130.62, 130.25, 129.74, 129.41, 128.78, 128.45, 127.98, 127.88, 127.37, 127.01, 126.87, 126.29, 126.01, 124.29, 124.20, 123.97, 116.37, 50.49, 47.72, 21.78; IR (cm^{-1}): 3048, 2923, 2853, 1660, 1587, 1566, 1508, 1450, 1365, 1231, 1175, 1090, 979, 814, 804, 781, 663, 573, 549; HRMS (ESI-TOF) calculated for $C_{37}H_{25}N_3O_7S$ ($[M+Na]^+$) calcd. 630.1311; found: 630.1323.

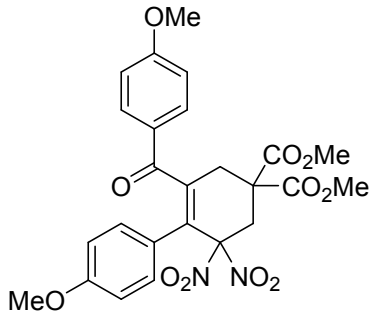
(5,5-dinitro-4-(thiophen-2-yl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)(thiophen -2-yl)methanone (2k)



White solid (m. p. 124 - 125 °C); yield: 28 mg (27%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 - 7.69 (m, 4H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.23 (dd, *J* = 5.2 and1.2 Hz, 1H), 7.07 (t, *J* = 4.4 Hz, 1H), 6.91 (dd, *J* = 3.6 and 1.2 Hz, 1H), 6.77 (dd, *J* = 5.2 and 3.6 Hz, 1H), 4.44 (s, 2H), 4.16 (s, 2H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.40, 145.63, 145.45, 140.24, 137.13, 136.47, 132.43, 131.68, 130.54, 130.24, 130.04, 128.69, 127.81, 127.04, 122.86, 115.84, 50.38, 47.23, 21.69; IR (cm^{-1}): 3092, 2924, 1649, 1584, 1568, 1410, 1352, 1330, 1317, 1173, 1153, 1053, 833, 770, 745, 714, 663, 548; HRMS (ESI-TOF) calculated for $C_{21}H_{17}N_3O_7S_3$ ($[M+Na]^+$) calcd. 542.0127; found: 542.0102.

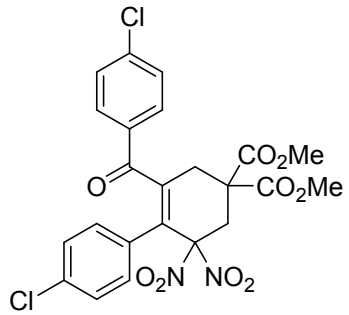
dimethyl 4'-methoxy-6-(4-methoxybenzoyl)-2,2-dinitro-2,5-dihydro-[1,1'-biphenyl]-4,4(3*H*)-dicarboxylate (2l)



Yellow solid (m. p. 110 - 111 °C); yield: 27 mg (26%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.80 (s, 6H), 3.74 (s, 2H), 3.65 (s, 3H), 3.21 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.89, 168.71, 164.39, 159.95, 149.63, 132.08, 131.81, 127.25, 125.99, 123.34, 120.35, 113.96, 113.51, 55.53, 55.02, 53.70, 50.47, 35.45, 32.66; IR (cm^{-1}): 3024, 2958, 2842, 1761, 1655, 1597, 1560, 1513, 1459, 1441, 1321, 1262, 1210, 1180, 1169, 1029, 1019, 953, 846, 830, 809, 754, 620, 566; HRMS (ESI-TOF) calculated for $C_{25}H_{24}N_2O_{11}$ ($[M+Na]^+$) calcd. 551.1278; found: 551.1239.

dimethyl 4'-chloro-6-(4-chlorobenzoyl)-2,2-dinitro-2,5-dihydro-[1,1'-biphenyl]-4,4(3*H*)-dicarboxylate (2m)

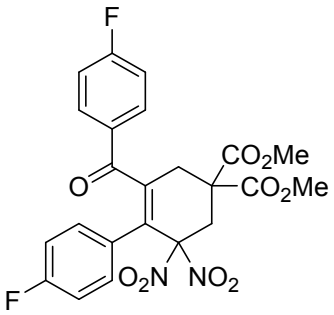


Orange solid (m. p. 72 - 73 °C); yield: 36 mg (34%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 6H), 3.74 (s, 2H), 3.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.94, 168.48, 150.04, 141.14, 135.93, 132.58, 131.85, 130.77, 129.43, 129.24, 128.58, 126.00, 119.75, 53.84, 50.39, 35.32, 32.58; IR (cm^{-1}): 2955, 2923, 1740, 1671, 1589, 1570, 1437, 1314, 1272, 1215, 1093, 1016, 952, 847, 827,

789, 550; HRMS (ESI-TOF) calculated for $C_{23}H_{18}Cl_2N_2O_9$ ([M+Na]$^+$) calcd. 559.0287; found: 559.0285.

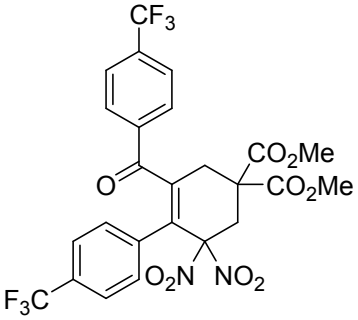
dimethyl 4'-fluoro-6-(4-fluorobenzoyl)-2,2-dinitro-2,5-dihydro-[1,1'-biphenyl]-4,4(3*H*)-dicarboxylate (2n)



Yellow solid (m. p. 140 - 141 °C); yield: 30 mg (30%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 8.8 and 5.6 Hz, 2H), 7.08 (t, J = 8.8 Hz, 2H), 7.01 (dd, J = 8.8 and 5.6 Hz, 2H), 6.75 (t, J = 8.8 Hz, 2H), 3.81 (s, 6H), 3.74 (s, 2H), 3.23 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.74, 168.54, 167.65 (d, $^1J_{CF}$ = 256 Hz), 164.29 (d, $^1J_{CF}$ = 249 Hz), 150.14, 132.63 (d, $^3J_{CF}$ = 8 Hz), 132.25 (d, $^3J_{CF}$ = 10 Hz), 130.81, 127.02, 126.04, 119.91, 116.21 (d, $^2J_{CF}$ = 22 Hz), 115.52 (d, $^2J_{CF}$ = 22 Hz), 53.83, 50.40, 35.35, 32.60; ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.96, -110.57; IR (cm^{-1}): 2961, 2921, 1752, 1670, 1592, 1562, 1507, 1437, 1316, 1230, 1158, 1099, 1067, 964, 848, 749, 687, 612, 565; HRMS (ESI-TOF) calculated for $C_{23}H_{18}F_2N_2O_9$ ([M+Na]$^+$) calcd. 527.0878; found: 527.0868.

dimethyl 2,2-dinitro-4'-(trifluoromethyl)-6-(4-(trifluoromethyl)benzoyl)-2,5-dihydro-[1,1'-biphenyl]-4,4(3*H*)-dicarboxylate (2o)

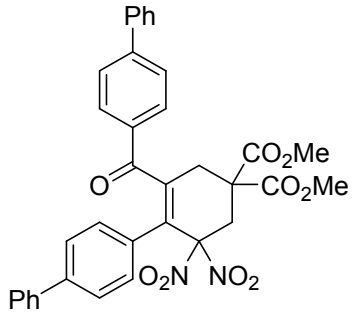


Yellow oil; yield: 21 mg (17%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 3.83 (s, 6H), 3.77 (s, 2H), 3.26 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.17, 168.39, 150.43, 137.09, 135.64 (q, $^2J_{CF}$ = 33 Hz), 131.50 (q, $^2J_{CF}$ = 33 Hz), 131.11, 129.55, 128.74, 128.19, 126.47, 125.93 (q, $^3J_{CF}$ = 4 Hz), 125.23(q, $^3J_{CF}$ = 4 Hz), 124.68 (q, $^1J_{CF}$ = 271 Hz), 121.97 (q, $^1J_{CF}$ = 271 Hz), 119.48, 53.93, 50.41, 35.28, 32.58; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.31, -63.41;

IR (cm^{-1}): 2961, 2921, 1742, 1680, 1591, 1570, 1327, 1268, 1173, 1130, 1068, 1020, 849, 756, 665, 612; HRMS (ESI-TOF) calculated for $C_{25}H_{18}F_6N_2O_9$ ([M+Na]$^+$) calcd. 627.0814; found: 627.0819.

dimethyl 6-([1,1'-biphenyl]-4-carbonyl)-2,2-dinitro-2,5-dihydro-[1,1':4',1''-terphenyl]-4,4(3*H*)-dicarboxylate (2p)

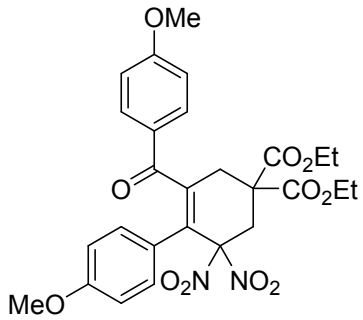


White solid (m. p. 88 - 89 °C); yield: 101 mg (81%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.44 (t, J = 7.2 Hz, 2H), 7.44 - 7.36 (m, 3H), 7.31 (t, J = 7.2 Hz, 2H), 7.29 - 7.25 (m, 3H), 7.12 (d, J = 8.4 Hz, 2H), 3.83 (s, 6H), 3.80 (s, 2H), 3.30 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.03, 168.67, 149.86, 146.75, 141.88, 139.77, 139.51, 133.18, 131.01, 130.16, 130.11, 128.98, 128.72, 128.50, 127.69, 127.28, 127.23, 126.96, 126.69, 126.67, 120.12, 53.79, 50.55, 35.51, 32.71; IR (cm^{-1}): 3036, 2957, 1742, 1662, 1597, 1563, 1445, 1316, 1260 1213, 1187, 845, 766, 733, 696; HRMS (ESI-TOF) calculated for $C_{35}H_{28}N_2O_9$ ([M+Na]$^+$) calcd. 643.1693; found: 643.1672.

diethyl 4'-methoxy-6-(4-methoxybenzoyl)-2,2-dinitro-2,5-dihydro-[1,1'-biphenyl]-

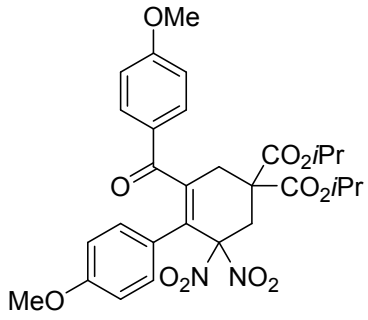
4,4(3*H*)-dicarboxylate (2q)



Yellow solid (m. p. 97 - 98 °C); yield: 42 mg (38%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 8.8 Hz, 2H), 4.29 - 4.20 (m, 4H), 3.84 (s, 3H), 3.73 (s, 2H), 3.64 (s, 3H), 3.19 (s, 2H), 1.28 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.03, 168.34, 164.39, 159.92, 149.76, 132.11, 131.82, 127.29, 125.93, 123.42, 120.43, 113.95, 113.49, 71.09, 63.04, 55.52, 55.01, 50.50, 35.28, 32.57, 13.81; IR (cm^{-1}): 2986, 2842, 1737, 1647, 1596, 1562, 1509, 1254, 1181, 1032, 841, 752; HRMS (ESI-TOF) calculated for $C_{27}H_{28}N_2O_{11}$ ($[M+Na]^+$) calcd.579.1591; found:579.1612.

diisopropyl 4'-methoxy-6-(4-methoxybenzoyl)-2,2-dinitro-2,5-dihydro-[1,1'-biphenyl]-4,4(3*H*)-dicarboxylate (2r)

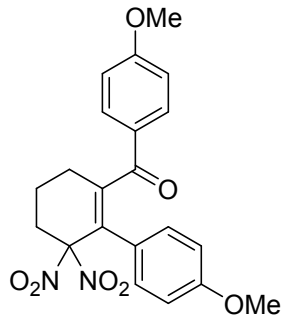


White solid (m. p. 102 - 103 °C); yield: 36 mg (31%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 8.8 Hz, 2H), 5.08 (hept, *J* = 6.4 Hz, 2H), 3.84 (s, 3H), 3.70 (s, 2H), 3.64 (s, 3H), 3.15 (s, 2H), 1.27 (d, *J* = 6.4 Hz, 6H), 1.24 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.18, 167.93, 164.39, 159.89, 149.80, 132.15, 131.83, 127.29, 125.85, 123.49, 120.48, 113.95, 113.47, 71.09, 55.52, 55.01, 50.46, 35.06, 32.51,

21.47, 21.20; IR (cm^{-1}): 2983, 2937, 2841, 1728, 1647, 1599, 1556, 1512, 1454, 1421, 1375, 1260, 1212, 1177, 1106, 1030, 963, 905, 849, 835, 756, 693, 615, 577, 515; HRMS (ESI-TOF) calculated for $C_{29}H_{32}N_2O_{11}$ ($[M+Na]^+$) calcd. 607.1904; found: 607.1888.

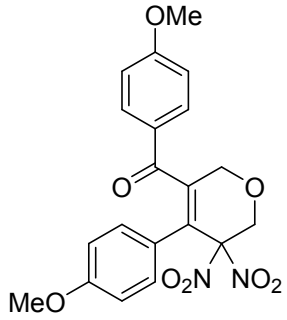
(4'-methoxy-6,6-dinitro-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)(4-methoxyphenyl)methanone (2s)



Colorless oil; yield: 54 mg (66%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 3.65 (s, 3H), 3.11 (t, *J* = 6.8 Hz, 2H), 2.69 (t, *J* = 6.8 Hz, 2H), 2.01 - 1.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.03, 164.21, 159.82, 150.47, 131.78, 131.56, 127.23, 127.11, 124.26, 122.00, 113.94, 113.48, 55.51, 55.01, 33.15, 27.59, 17.45; IR (cm^{-1}): 2923, 2840, 1662, 1598, 1556, 1512, 1459, 1317, 1253, 1172, 1030, 839, 794, 747, 581; HRMS (ESI-TOF) calculated for $C_{21}H_{20}N_2O_7$ ($[M+Na]^+$) calcd. 435.1169; found: 435.1179.

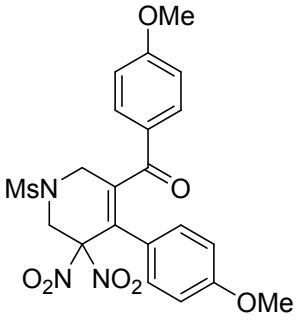
(4-methoxyphenyl)(4-(4-methoxyphenyl)-5,5-dinitro-5,6-dihydro-2*H*-pyran-3-yl)methanone (2t)



Yellow oil; yield: 42 mg (51%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.8 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.62 (d, *J* = 8.8 Hz, 2H), 4.87 (s, 2H), 4.71 (s, 2H), 3.82 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.31, 164.56, 160.30, 146.21, 131.94, 131.16, 127.21, 126.95, 122.87, 115.10, 114.10, 113.85, 70.26, 68.06, 55.55, 55.08; IR (cm^{-1}): 2935, 2841, 1731, 1659, 1598, 1512, 1460, 1259, 1168, 1029, 841, 607; HRMS (ESI-TOF) calculated for $C_{20}H_{18}N_2O_8$ ($[M+Na]^+$) calcd. 437.0961; found: 437.0970.

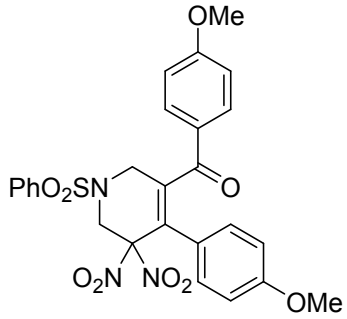
(4-methoxyphenyl)(4-(4-methoxyphenyl)-1-(methylsulfonyl)-5,5-dinitro-1,2,5,6-tetrahydropyridin-3-yl)methanone (2u)



Yellow oil; yield: 63 mg (64%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 9.2 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.62 (d, *J* = 9.2 Hz, 2H), 4.66 (s, 2H), 4.36 (s, 2H), 3.83 (s, 3H), 3.66 (s, 3H), 2.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.98, 164.73, 160.43, 144.90, 132.02, 131.29, 127.66, 126.73, 122.55, 116.66, 114.21, 113.90, 55.60, 55.10, 50.39, 46.94, 38.00; IR (cm^{-1}): 2930, 2838, 1660, 1598, 1513, 1458, 1301, 1262, 1168, 1027, 840, 773, 551; HRMS (ESI-TOF) calculated for $C_{21}H_{21}N_3O_9S$ ($[M+Na]^+$) calcd. 514.0896; found: 514.0884.

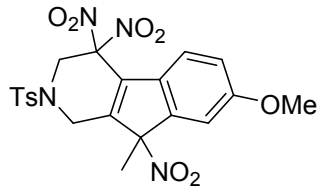
(4-methoxyphenyl)(4-(4-methoxyphenyl)-5,5-dinitro-1-(phenylsulfonyl)-1,2,5,6-tetrahydropyridin-3-yl)methanone (2v)



White solid (m. p. 73 - 74 °C); yield: 97 mg (85%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.8 Hz, 2H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 8.8 Hz, 2H), 4.45 (s, 2H), 4.15 (s, 2H), 3.84 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.12, 164.77, 160.37, 144.67, 135.14, 134.23, 132.09, 131.26, 129.88, 127.72, 127.46, 126.64, 122.55, 116.73, 114.22, 113.83, 55.61, 55.07, 50.58, 47.21; IR (cm^{-1}): 2931, 2837, 1657, 1598, 1566, 1513, 1447, 1361, 1317, 1293, 1262, 1174, 1029, 844, 811, 771, 751, 692, 612, 577; HRMS (ESI-TOF) calculated for $C_{26}H_{23}N_3O_9S$ ($[M+Na]^+$) calcd. 576.1053; found: 576.1023.

7-methoxy-9-methyl-4,4,9-trinitro-2-tosyl-2,3,4,9-tetrahydro-1*H*-indeno[2,1-*c*]pyridine (3a)

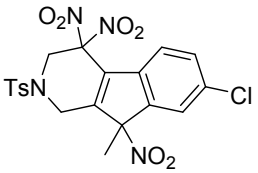


White solid (m. p. 160 - 161 °C); yield: 14 mg (14%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 2.4 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.90 (dd, J_1 = 8.4 and 2.4 Hz, 1H), 4.78, 4.07 (both d, *J* = 13.2 Hz, each 1H), 4.30, 4.02 (both d, *J* = 18.0 Hz, each 1H), 3.84 (s, 3H), 2.47 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.38, 145.73, 145.44, 142.65, 132.50, 130.47, 130.36, 128.33, 127.74, 122.32, 115.31, 112.12, 110.60, 94.05, 55.82, 50.06, 43.29, 22.60, 21.68; IR (cm^{-1}): 2922, 1584, 1546, 1493, 1443, 1357, 109, 1168, 1119, 1090, 1029, 954, 823, 664, 550; HRMS (ESI-TOF) calculated for $C_{21}H_{20}N_4O_9S$

([M+Na]$^+$) calcd. 527.0849; found: 527.0858.

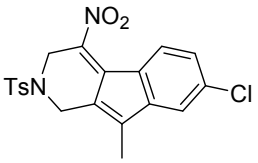
7-chloro-9-methyl-4,4,9-trinitro-2-tosyl-2,3,4,9-tetrahydro-1*H*-indeno[2,1-*c*]pyridine (3b)



White solid (m. p. 170 -171 °C); yield: 20 mg (20%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 1.6 Hz, 1H), 7.48 - 7.39 (m, 3H), 7.10 (d, *J* = 8.4 Hz, 1H), 4.79, 4.07 (both d, *J* = 13.6 Hz, each 1H), 4.32, 4.05 (both d, *J* = 18.4 Hz, each 1H), 2.47 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.36, 145.59, 142.15, 135.08, 134.50, 132.38, 131.15, 130.53, 130.07, 127.75, 124.26, 122.51, 111.78, 94.03, 50.00, 43.36, 22.42, 21.70; IR (cm^{-1}): 2923, 1584, 1577, 1546, 1493, 1357, 1309, 1168, 1119, 1090, 1029, 954, 823, 664, 550; HRMS (ESI-TOF) calculated for $C_{20}H_{17}ClN_4O_8S$ ([M+Na]$^+$) calcd. 531.0354; found: 531.0361.

7-chloro-9-methyl-4-nitro-2-tosyl-2,3-dihydro-1*H*-indeno[2,1-*c*]pyridine (4b)



Orange solid (m. p. 173 -174 °C); yield: 10 mg (12%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.12 (dd, *J* = 8.4 and 2.0 Hz, 1H), 7.06 (d, *J* = 2.0 Hz, 1H), 4.49 (s, 2H), 4.24 (s, 2H), 2.26 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.96, 144.50, 140.40, 139.32, 137.63, 137.23, 133.52, 131.95, 129.71, 128.83, 128.08, 127.97, 127.49, 126.99, 119.98, 45.37, 42.88, 21.38, 11.01; IR (cm^{-1}): 3068, 2988, 2918, 2836, 1593, 1516, 1452, 1356, 1164, 1103, 950, 814, 658, 546; HRMS (ESI-TOF) calculated for $C_{20}H_{17}ClN_2O_4S$ ([M+Na]$^+$) calcd. 439.0496; found: 439.0505.

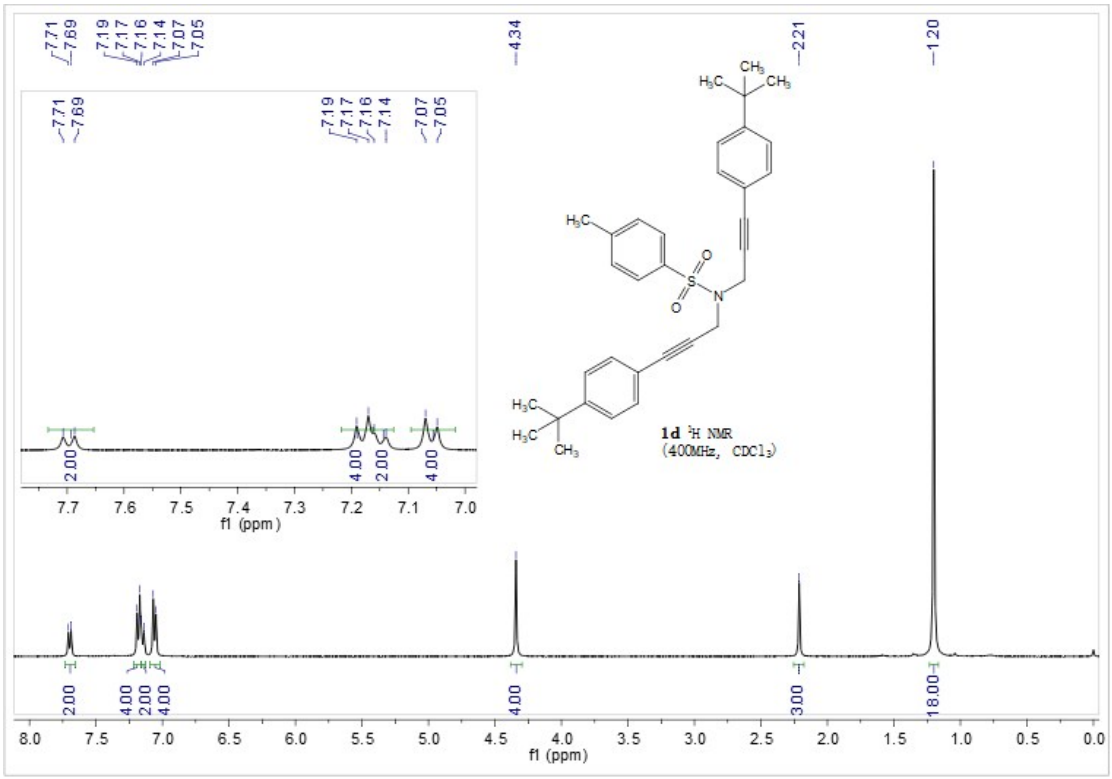
II. X-Ray crystallographic Data for 2a, 2j and 3a

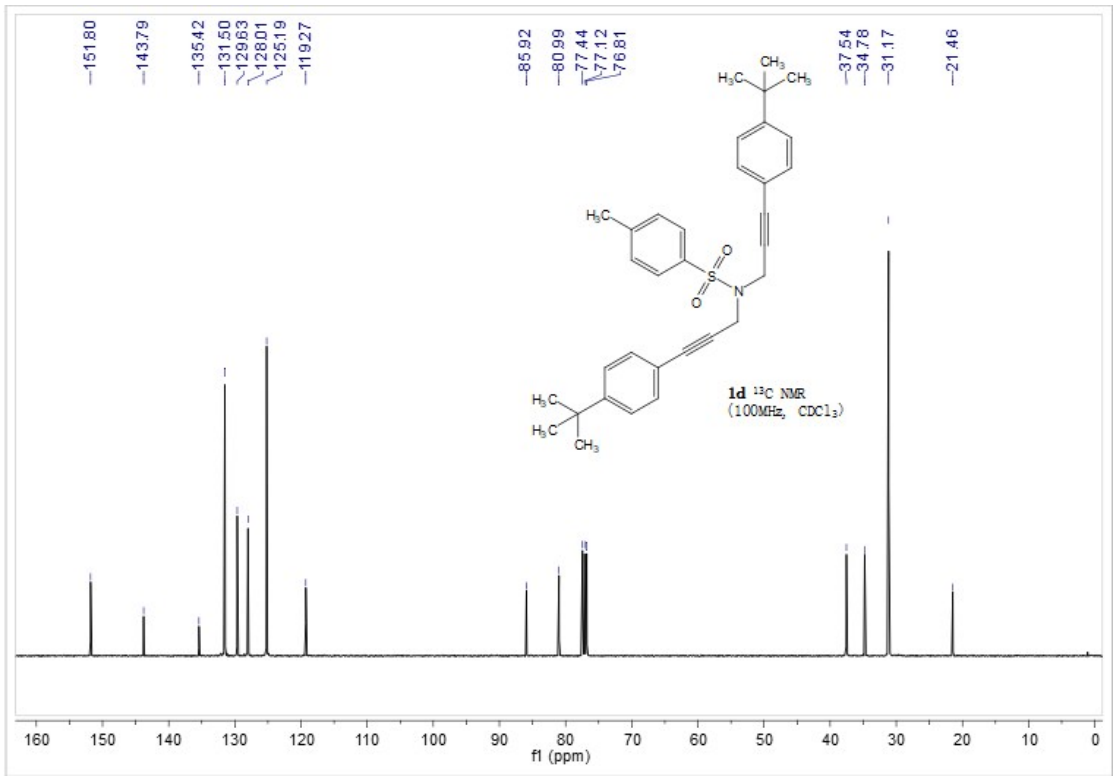
Single-crystal X-ray diffraction data were collected at 298(2) K on a Siemens Smart/CCD area-detector diffractometer with a Mo Kα radiation (λ = 0.71073 Å) by using the ω-2θ scan mode. Unit-cell dimensions were obtained with least-squares refinement. Data collection and reduction were performed using the SMART and SAINT software. The structures were solved by direct methods, and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 using the SHELXTXL package. Hydrogen atom positions for all of the structures were calculated and allowed to ride on their respective C atoms with C-H distances of 0.93-0.97 Å and U_{iso}(H) = -1.2 - 1.5U_{eq}(C).

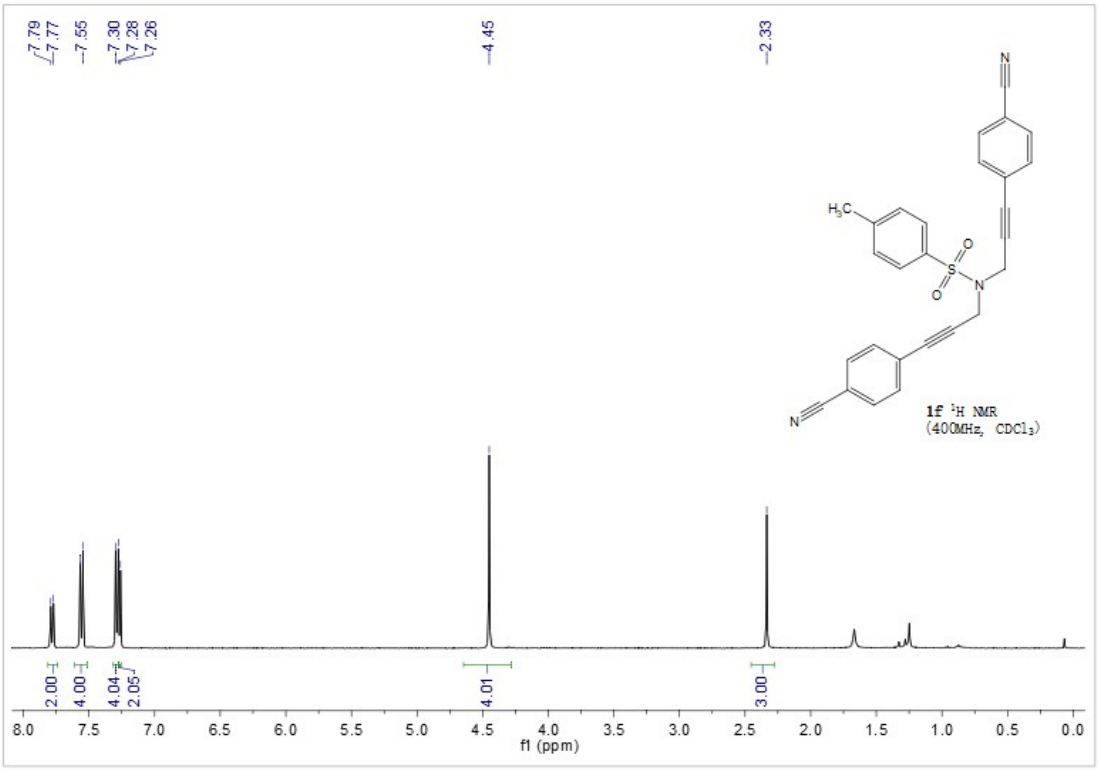
Table S1. Crystallographic data

complex	**2a**	**2j**	**3a**
Formula	$C_{27}H_{25}N_3O_9S$	$C_{33}H_{25}N_3O_7S$	$C_{21}H_{20}N_4O_9S$
Formula weight	567.56	607.62	504.47
Crystal system	Monoclinic	Orthorhombic	Monoclinic
space group	$P2_1/c$	$Pbca$	$P2_1/c$
a (Å)	10.9913(8)	16.5068(7)	16.1433(7)
b (Å)	20.6489(12)	12.2903(6)	9.7950(4)
c (Å)	12.3839(8)	29.5223(10)	16.3549(7)
α(º)	90.00	90.00	90.00
β (º)	99.075(6)	90.00	114.957(2)
γ (º)	90.00	90.00	90.00
Volume (Å^3)	2775.4(3)	5989.3(4)	2344.62(17)
Z	4	8	4
T (K)	293(2)	300(2)	293(2)
D_{calcd} (g/m^3)	1.358	1.348	1.429
F(000)	1184	2528	1048
Reflections	10619	17515	14081
Unique	4885	3762	4094
Goof	1.015	1.041	1.101
$R_1[I > 2\sigma(I)]$	0.0587	0.0382	0.0805
$wR_2[I > 2\sigma(I)]$	0.1498	0.0973	0.2554
CCDC NO.	**1894188**	**1894189**	**1894190**

III. NMR Spectra



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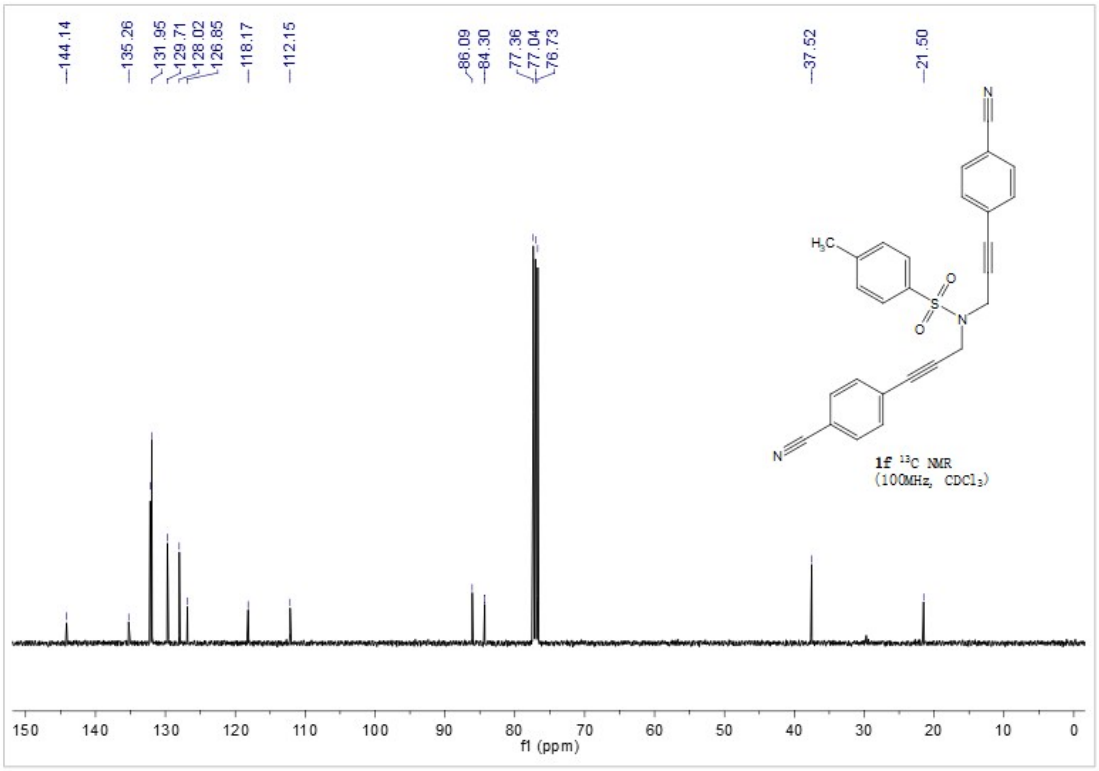
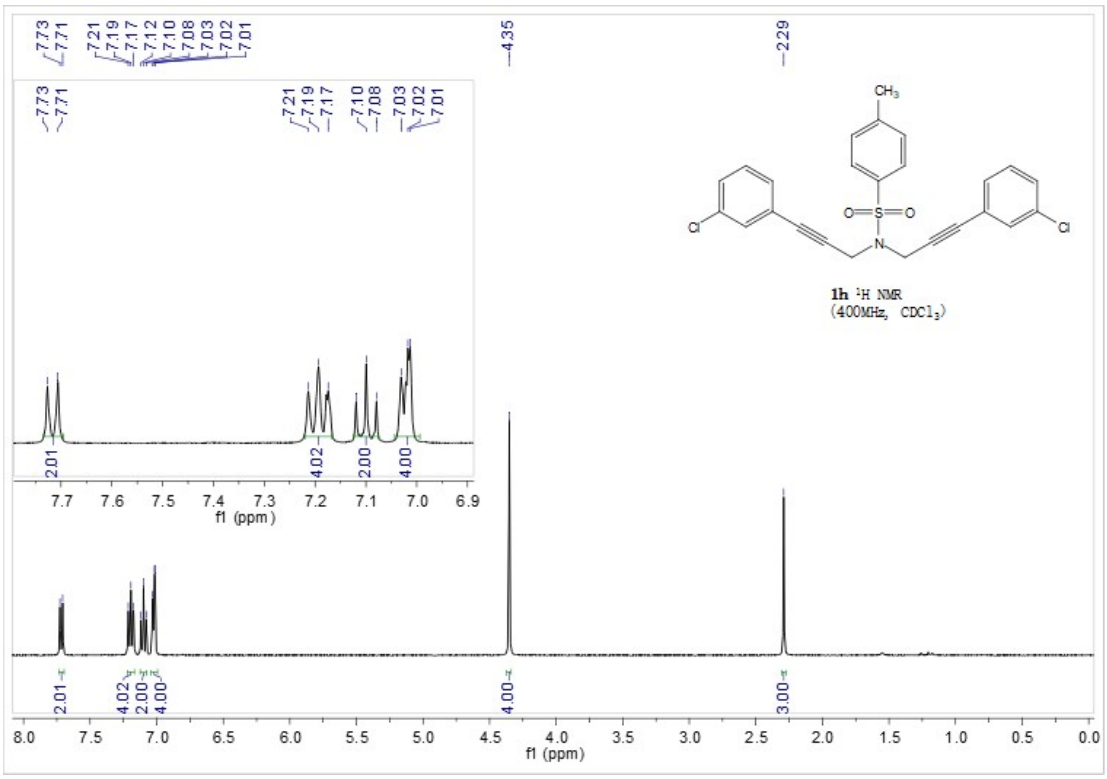
7.77
7.55
7.30
7.28
7.26
4.45
2.33
1f ^{1}H NMR
(400MHz, $CDCl_3$)
2.00
4.00
4.04
2.05
4.01
3.00
f1 (ppm)


144.14
135.26
131.95
129.71
128.02
126.85
118.17
112.15
86.09
84.30
77.36
77.04
76.73
37.52
21.50
1f ^{13}C NMR
(100MHz, $CDCl_3$)
f1 (ppm)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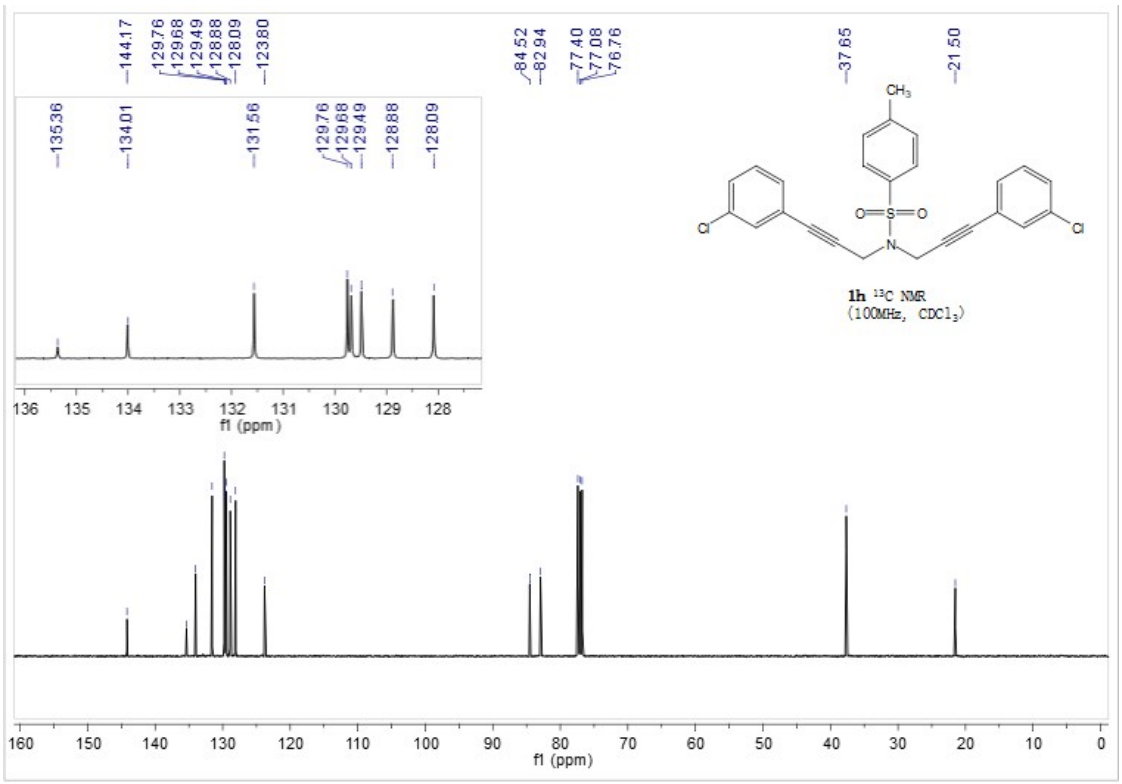
7.71
7.21
7.19
7.17
7.12
7.10
7.08
7.03
7.02
7.01
4.35
2.29
CH3
O=S=O
N
Cl
Cl
1h 1H NMR
(400MHz, CDCl3)
2.01
4.02
2.00
4.00
4.00
3.00
f1 (ppm)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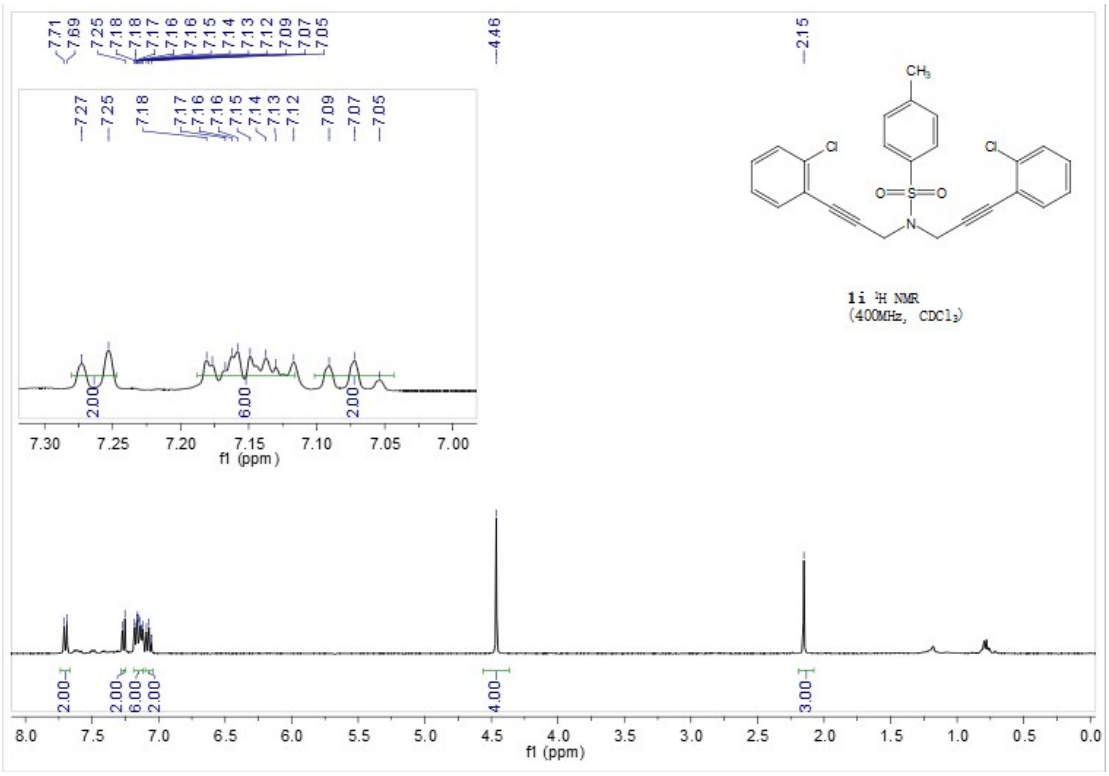
84.52
82.94
77.40
77.08
76.76
37.65
21.50
135.36
134.01
131.56
129.76
129.68
129.49
128.88
128.09
CH3
O=S=O
N
Cl
Cl
1h 13C NMR
(100MHz, CDCl3)
f1 (ppm)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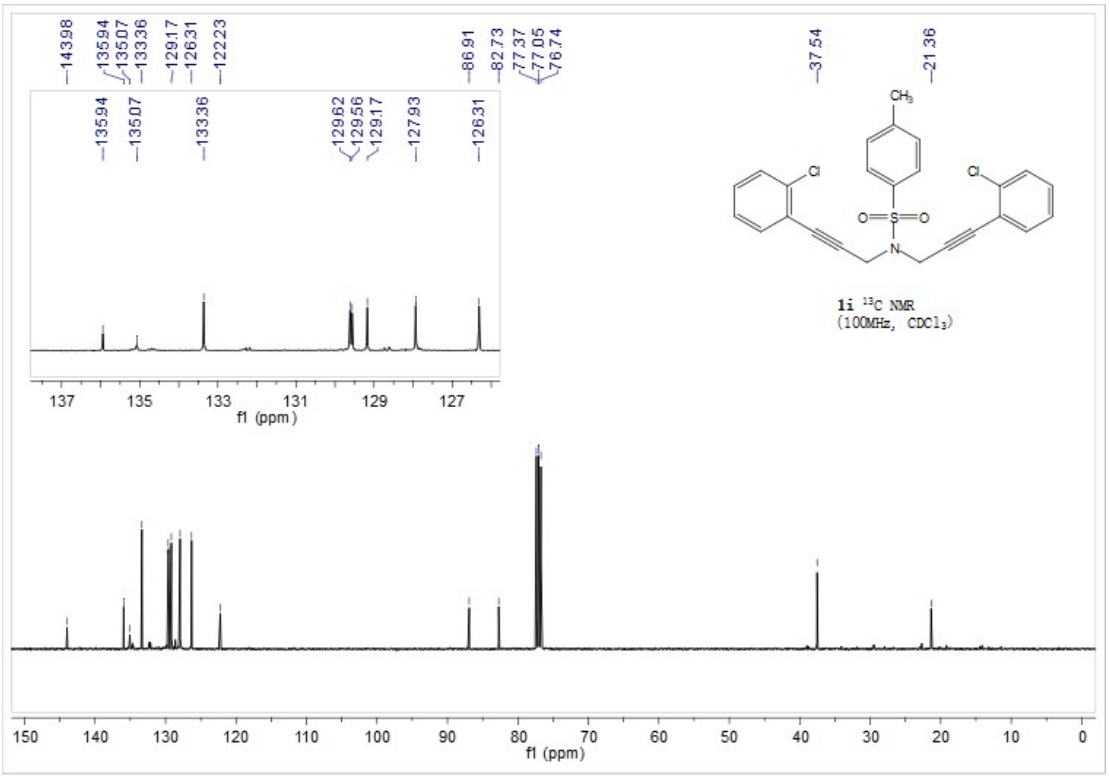
7.69
7.25
7.18
7.17
7.16
7.16
7.15
7.14
7.13
7.12
7.09
7.07
7.05
4.46
2.15
CH3
Cl
Cl
O=S=O
N
1i ¹H NMR
(400MHz, CDCl3)
2.00
6.00
2.00
f1 (ppm)
2.00
2.00
6.00
2.00
4.00
3.00
f1 (ppm)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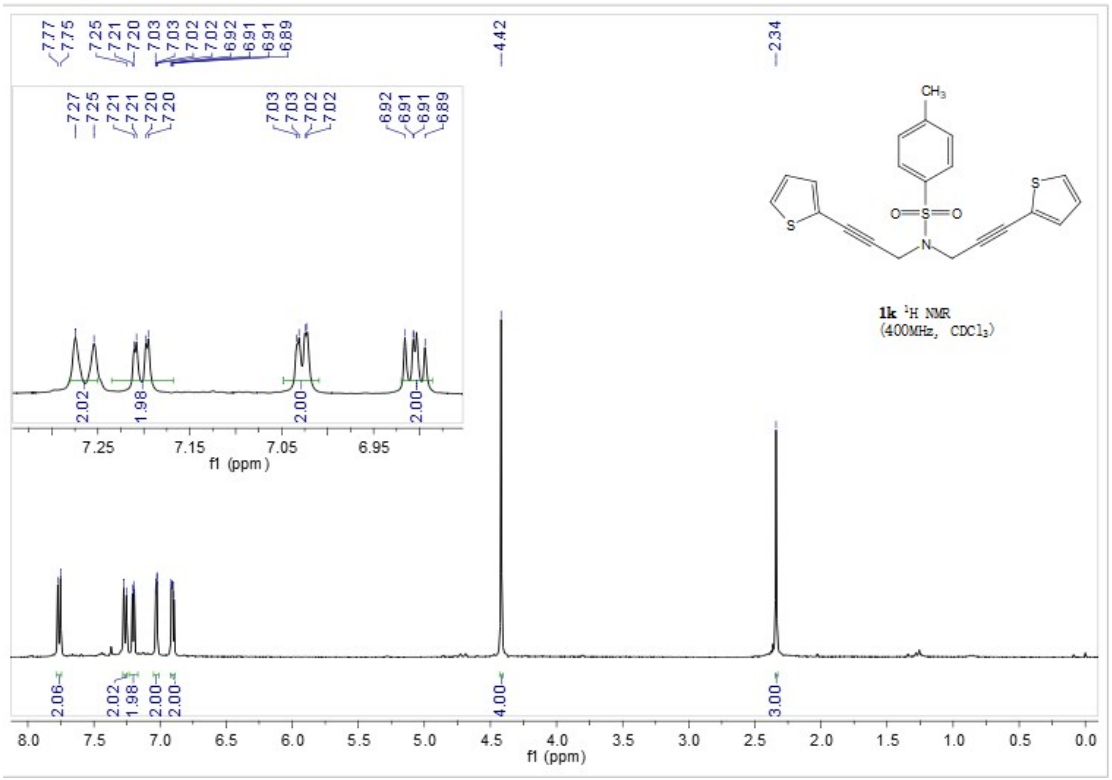
122.23
86.91
82.73
77.37
77.05
76.74
37.54
21.36
CH3
Cl
Cl
O=S=O
N
1i ¹³C NMR
(100MHz, CDCl3)
f1 (ppm)
f1 (ppm)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7.03
7.02
7.02
6.92
6.91
6.91
6.89
4.42
2.34
2.02
1.98
2.00
2.00
7.25
7.15
7.05
6.95
f1 (ppm)
2.06
2.02
1.98
2.00
2.00
4.00
3.00
8.0
7.5
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
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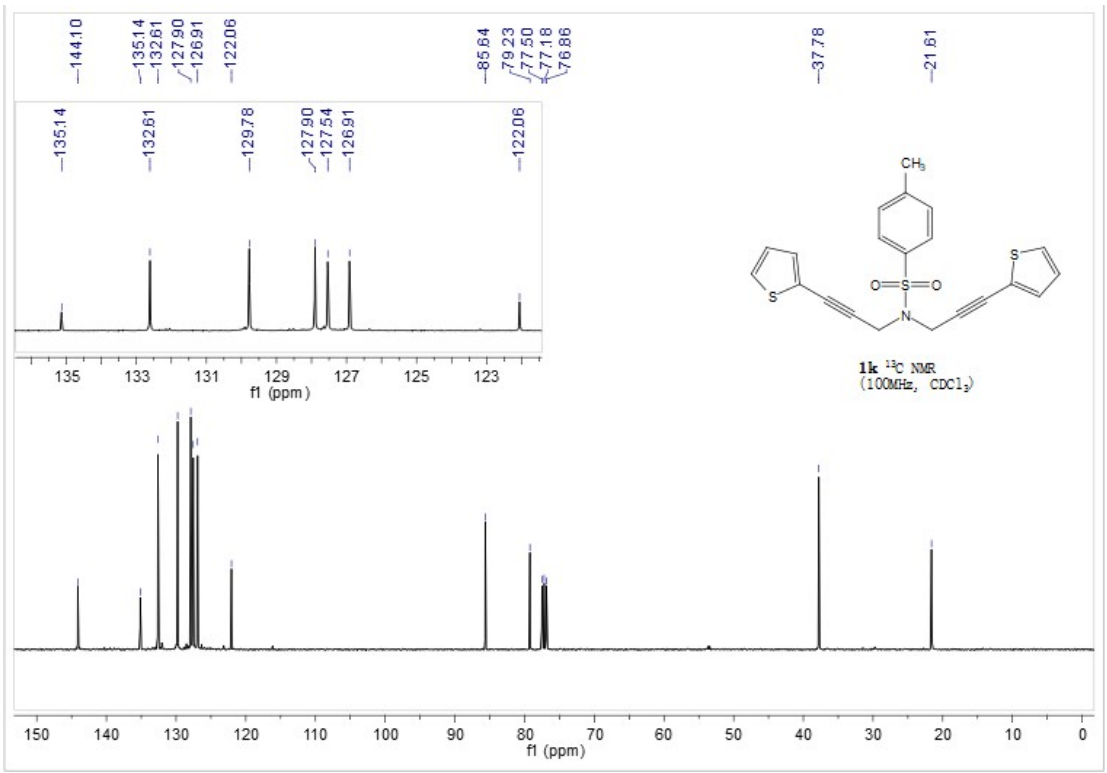
0.0
f1 (ppm)
CH3
S
O=S=O
N
S
1k 1H NMR
(400MHz, CDCl3)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122.06
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79.23
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77.18
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122.06
135
133
131
129
127
125
123
f1 (ppm)
150
140
130
120
110
100
90
80
70
60
50
40
30
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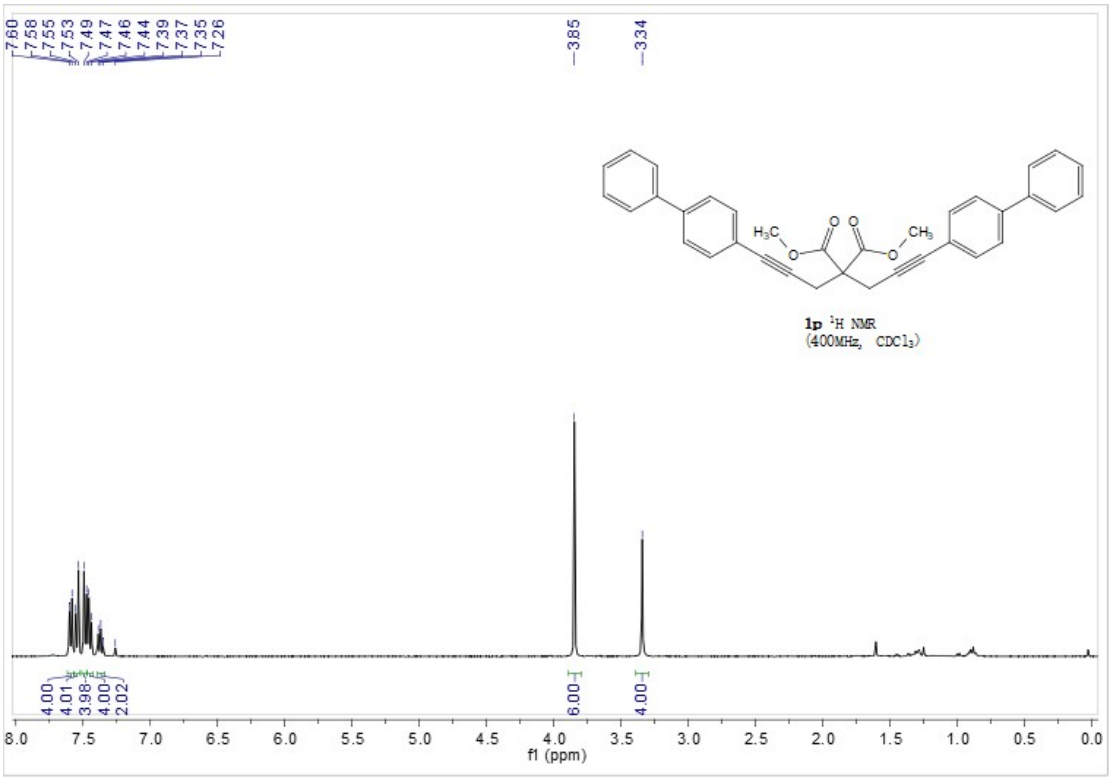
10
0
f1 (ppm)
CH3
S
O=S=O
N
S
1k 13C NMR
(100MHz, CDCl3)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7.37
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7.26
3.85
3.34
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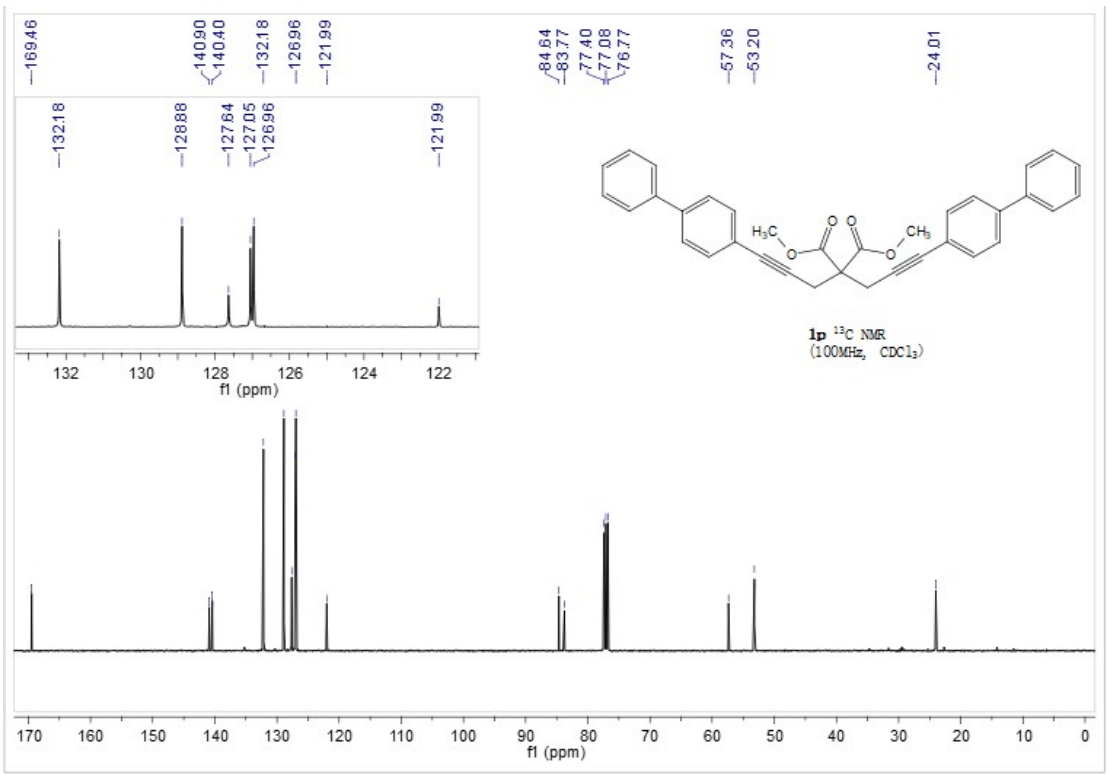
3.98
4.00
2.02
6.00
4.00
f1 (ppm)
1p 1H NMR
(400MHz, CDCl3)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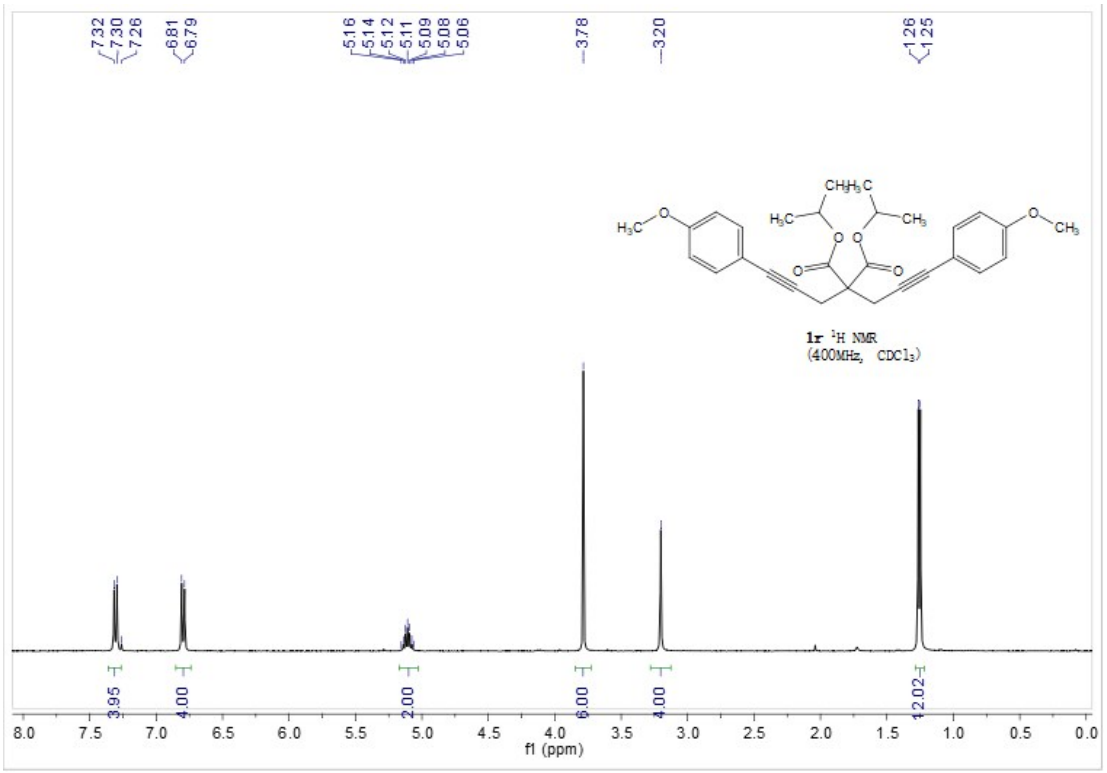
121.99
84.64
83.77
77.40
77.08
76.77
57.36
53.20
24.01
132.18
128.88
127.64
127.05
126.96
121.99
f1 (ppm)
1p 13C NMR
(100MHz, CDCl3)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7.26
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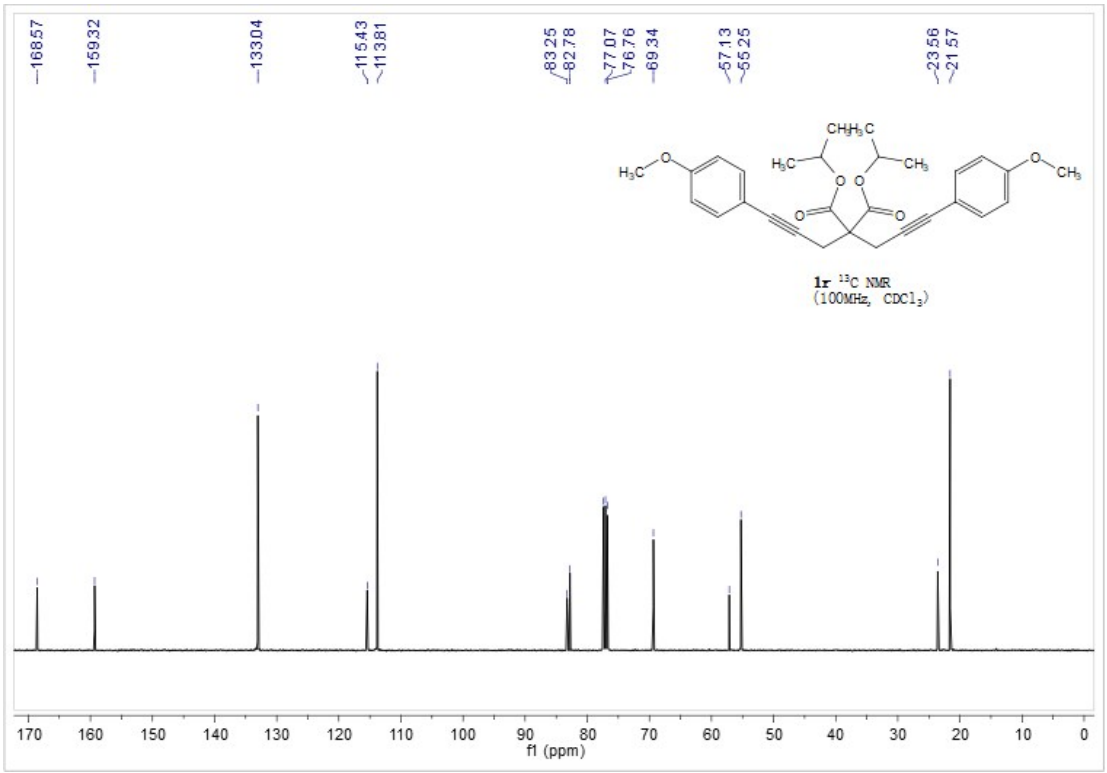
6.79
5.16
5.14
5.12
5.11
5.09
5.08
5.06
3.78
3.20
1.26
1.25
1r ¹H NMR
(400MHz, CDCl₃)
3.95
4.00
2.00
6.00
4.00
12.02
f1 (ppm)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113.81
83.25
82.78
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57.13
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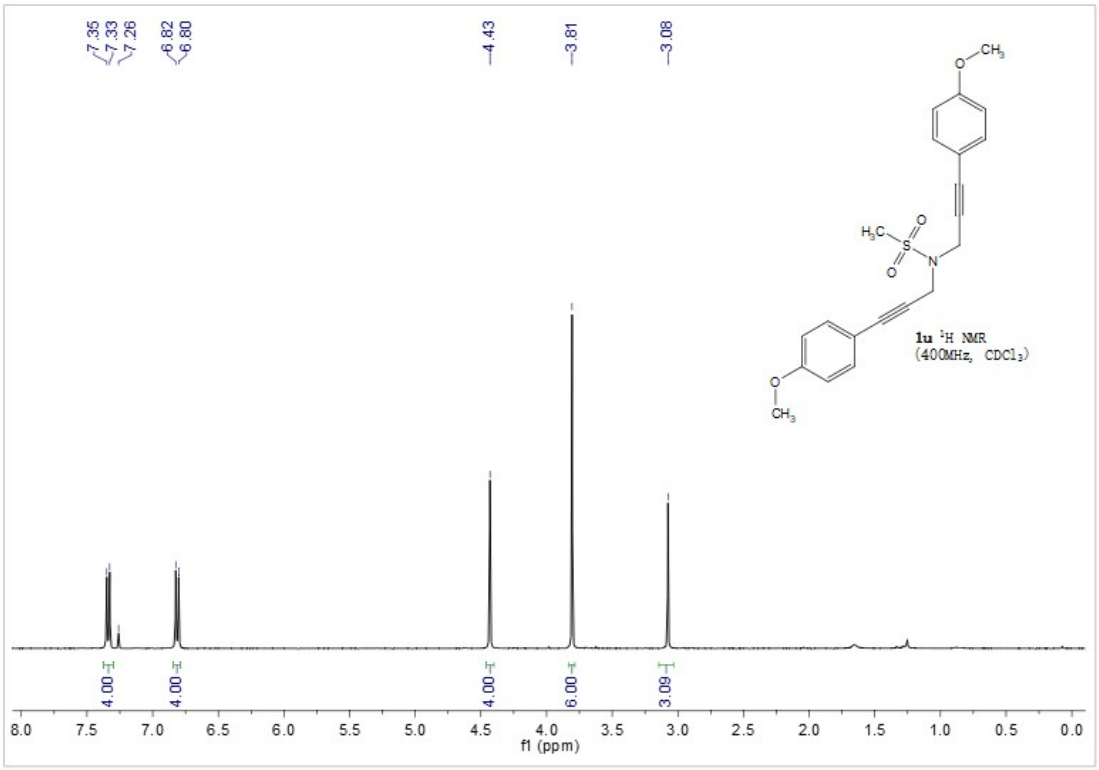
1r ¹³C NMR
(100MHz, CDCl₃)
f1 (ppm)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7.33
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6.82
6.80
4.43
3.81
3.08
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4.00
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6.00
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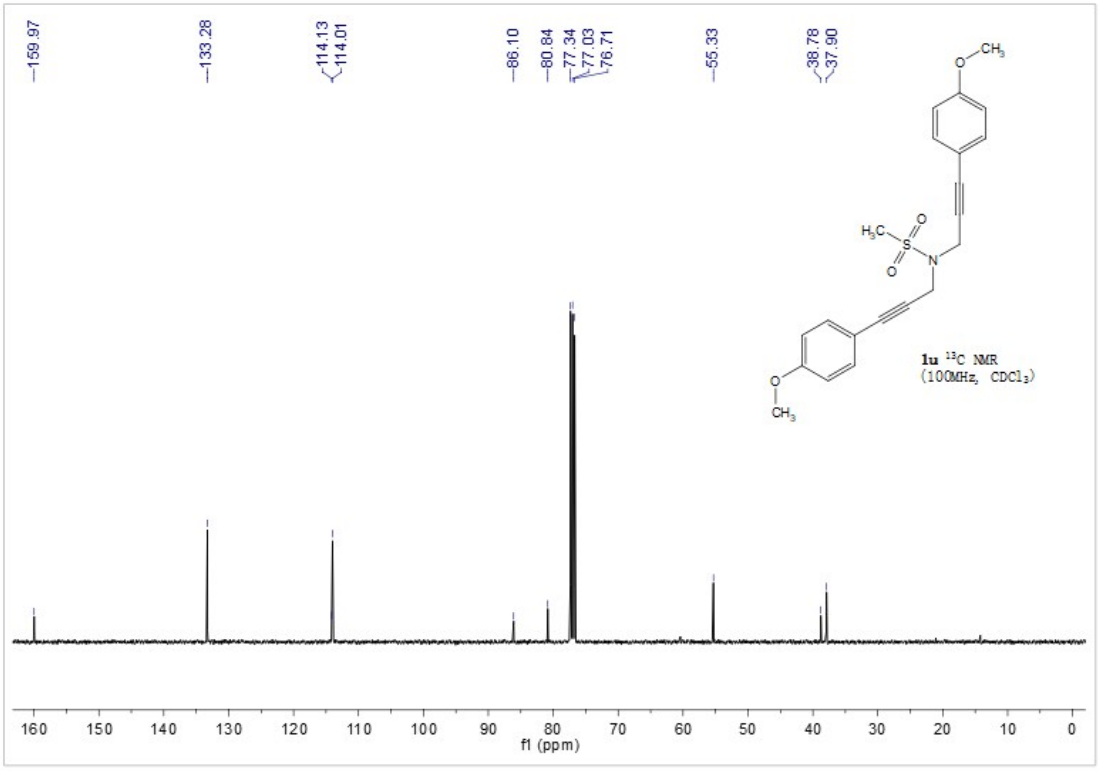
f1 (ppm)
1u ^{1}H NMR
(400MHz, CDCl$_3$)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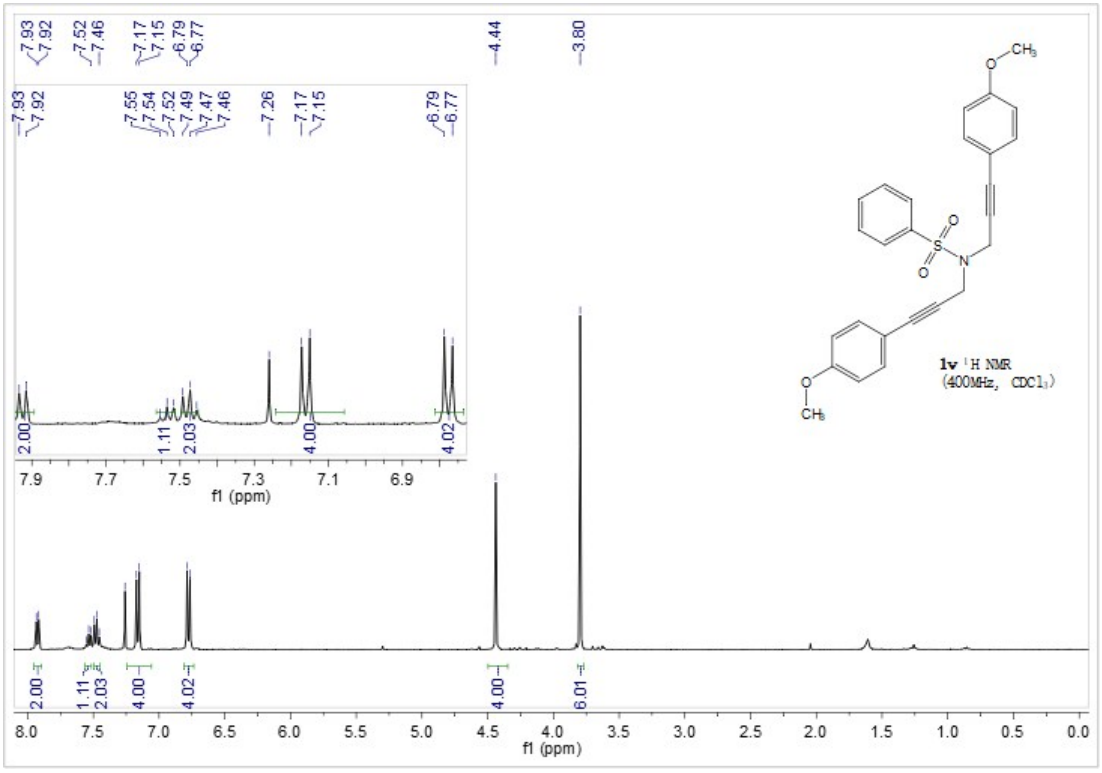
114.01
86.10
80.84
77.34
77.03
76.71
55.33
38.78
37.90
f1 (ppm)
1u ^{13}C NMR
(100MHz, CDCl$_3$)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7.92
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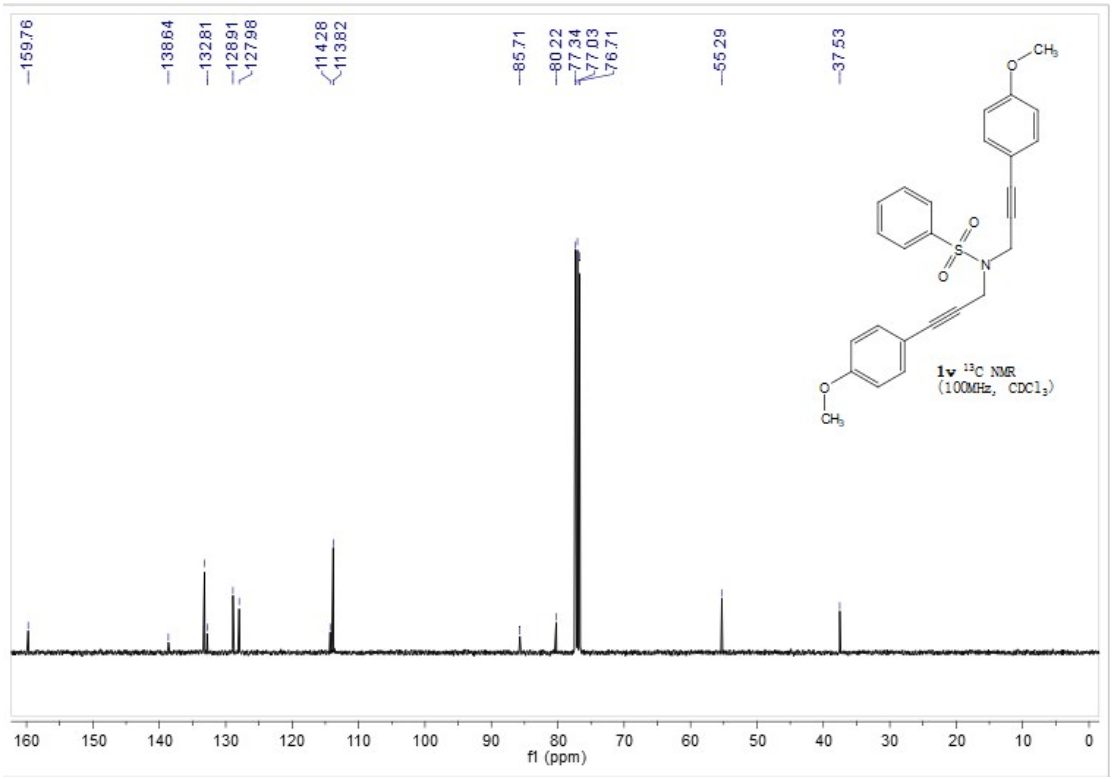
6.79
6.77
4.44
3.80
7.55
7.54
7.52
7.49
7.47
7.46
7.26
7.17
7.15
6.79
6.77
2.00
1.11
2.03
4.00
4.02
f1 (ppm)
4.00
6.01
1v ¹H NMR
(400MHz, CDCl₃)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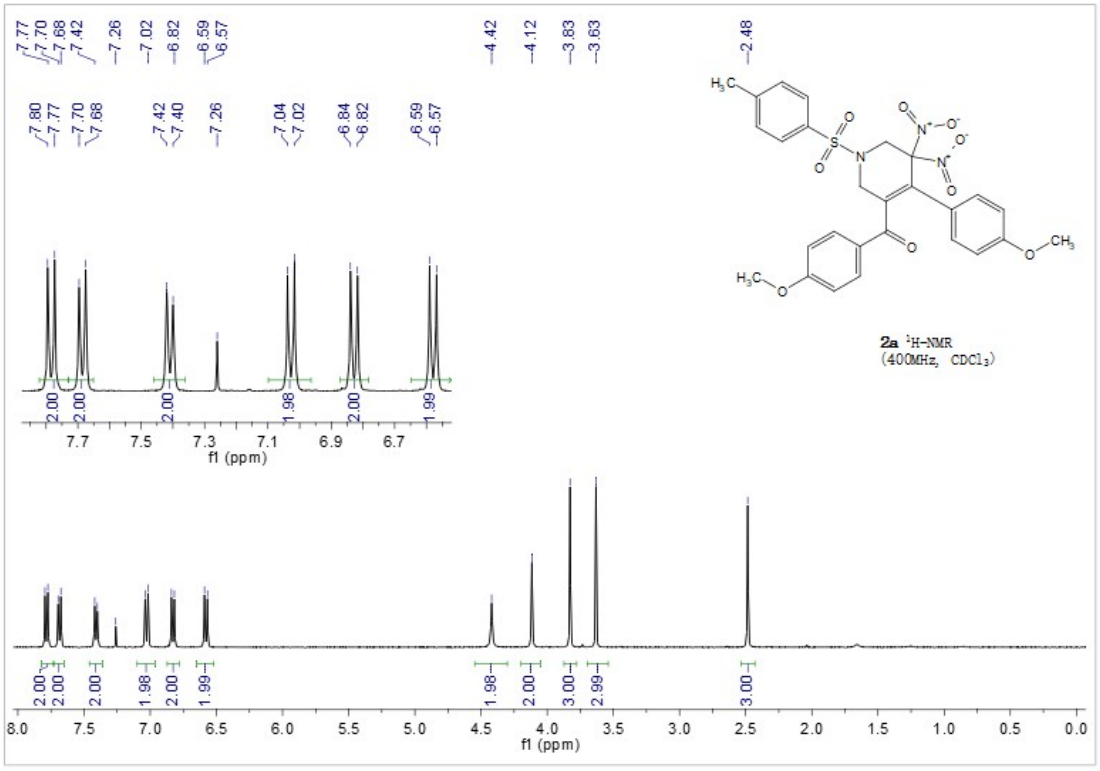
138.64
132.81
128.91
127.98
114.28
113.82
85.71
80.22
77.34
77.03
76.71
55.29
37.53
f1 (ppm)
1v ¹³C NMR
(100MHz, CDCl₃)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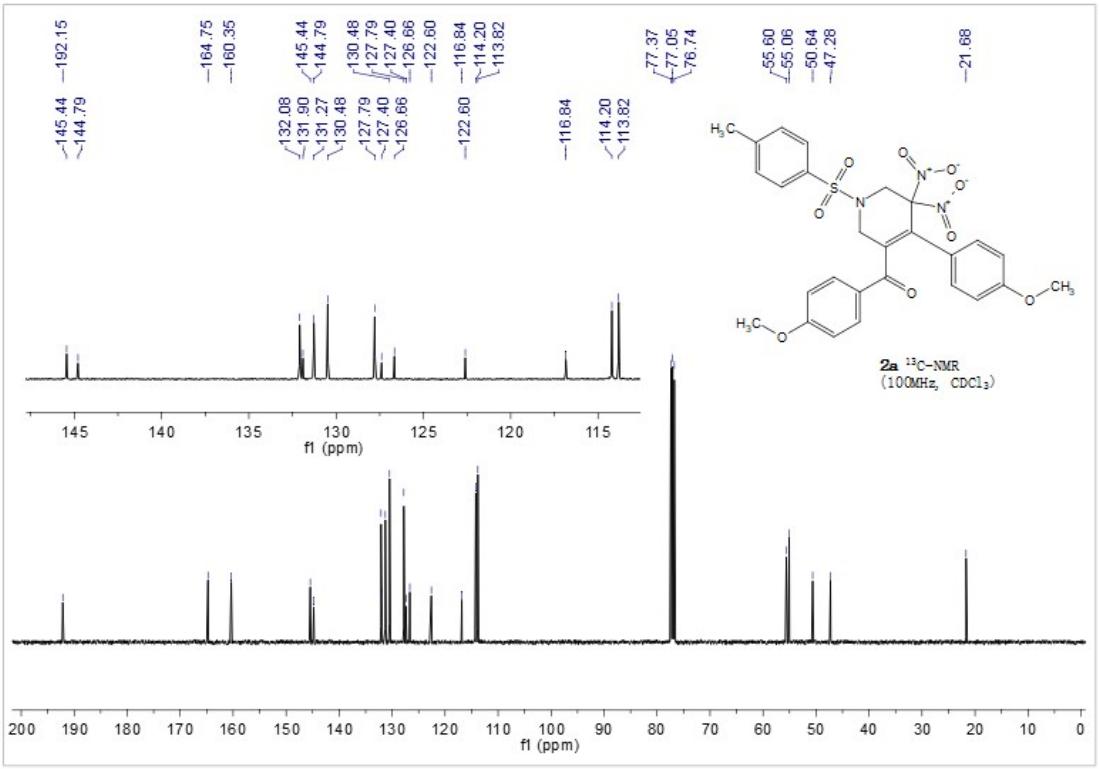
7.68
7.42
7.26
7.02
6.82
6.59
6.57
4.42
4.12
3.83
3.63
2.48
7.80
7.77
7.70
7.68
7.42
7.40
7.26
7.04
7.02
6.84
6.82
6.59
6.57
2.00
2.00
2.00
1.98
2.00
1.99
f1 (ppm)
2a ¹H-NMR
(400MHz, CDCl3)
2.00
2.00
2.00
1.98
2.00
1.99
1.98
2.00
3.00
2.99
3.00
f1 (ppm)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127.40
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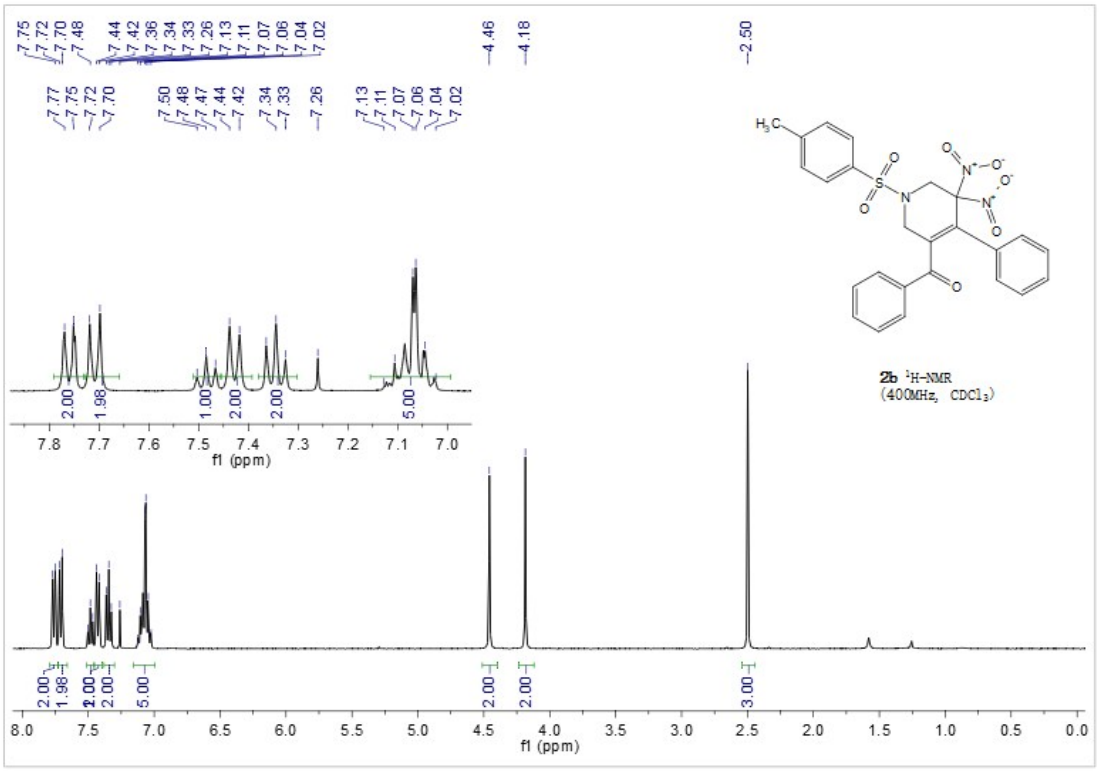
113.82
77.37
77.05
76.74
55.60
55.06
50.64
47.28
21.68
145.44
144.79
132.08
131.90
131.27
130.48
127.79
127.40
126.66
122.60
116.84
114.20
113.82
f1 (ppm)
2a ¹³C-NMR
(100MHz, CDCl3)
f1 (ppm)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7.72
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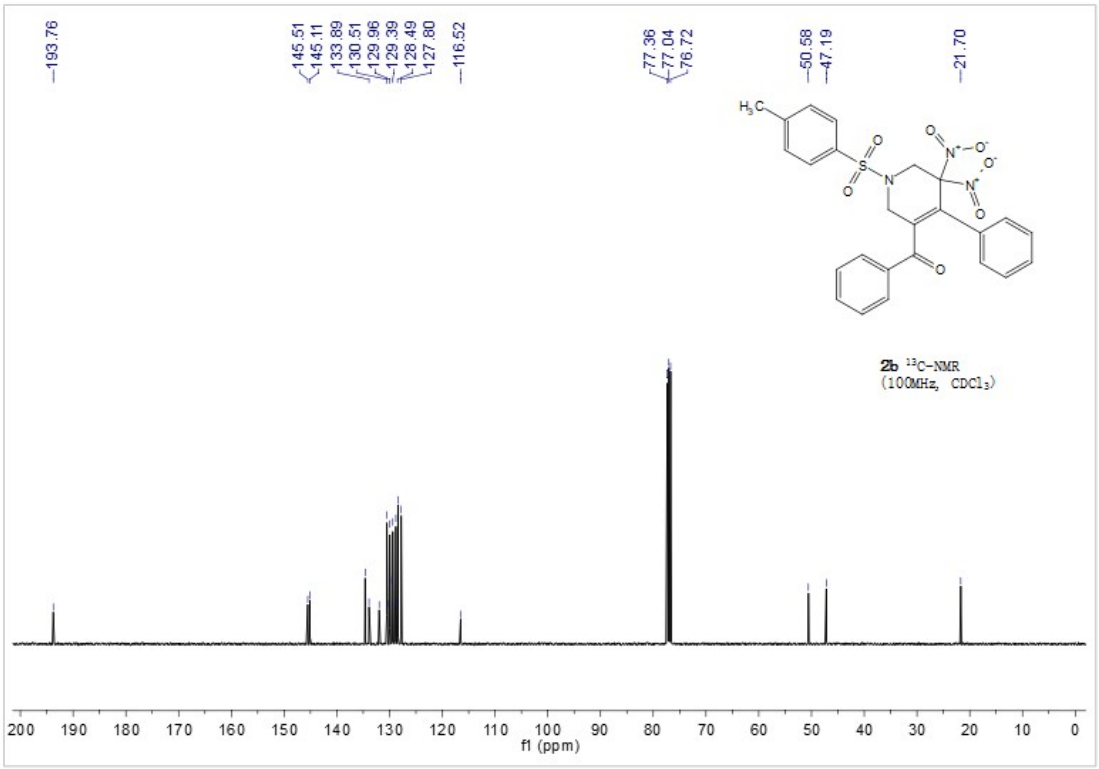
7.48
7.44
7.42
7.36
7.34
7.33
7.26
7.13
7.11
7.07
7.06
7.04
7.02
4.46
4.18
2.50
2b ¹H-NMR
(400MHz, CDCl3)
f1 (ppm)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129.96
129.39
128.49
127.80
116.52
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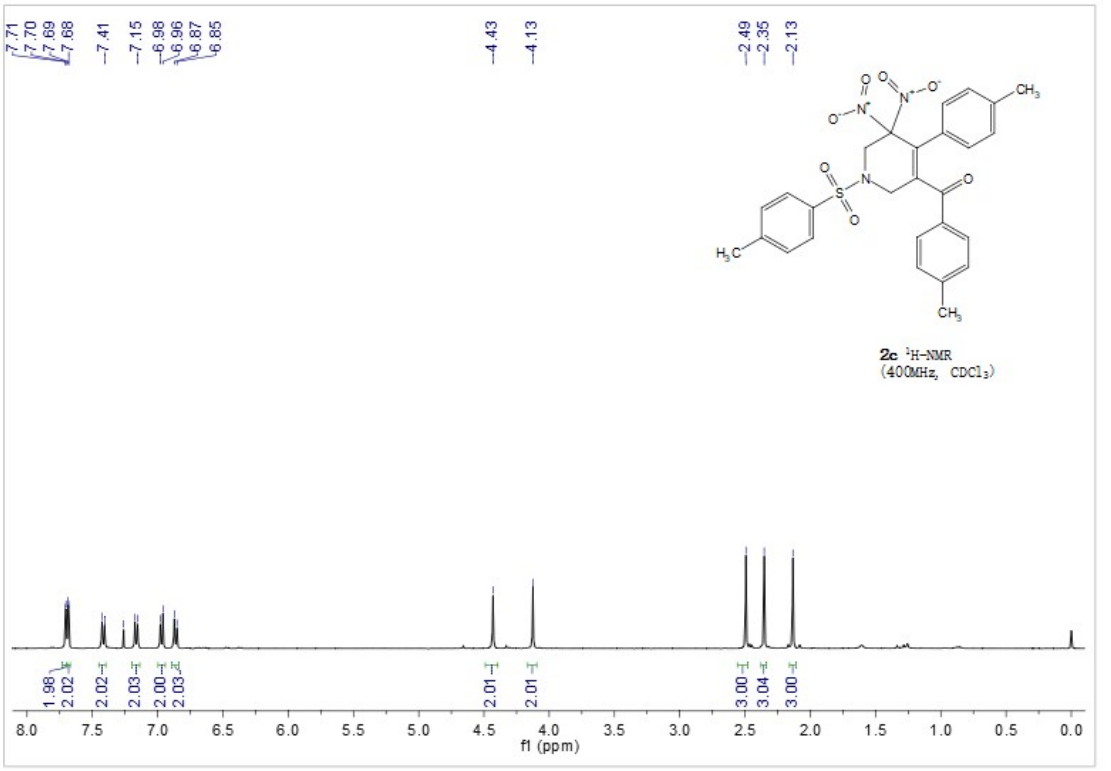
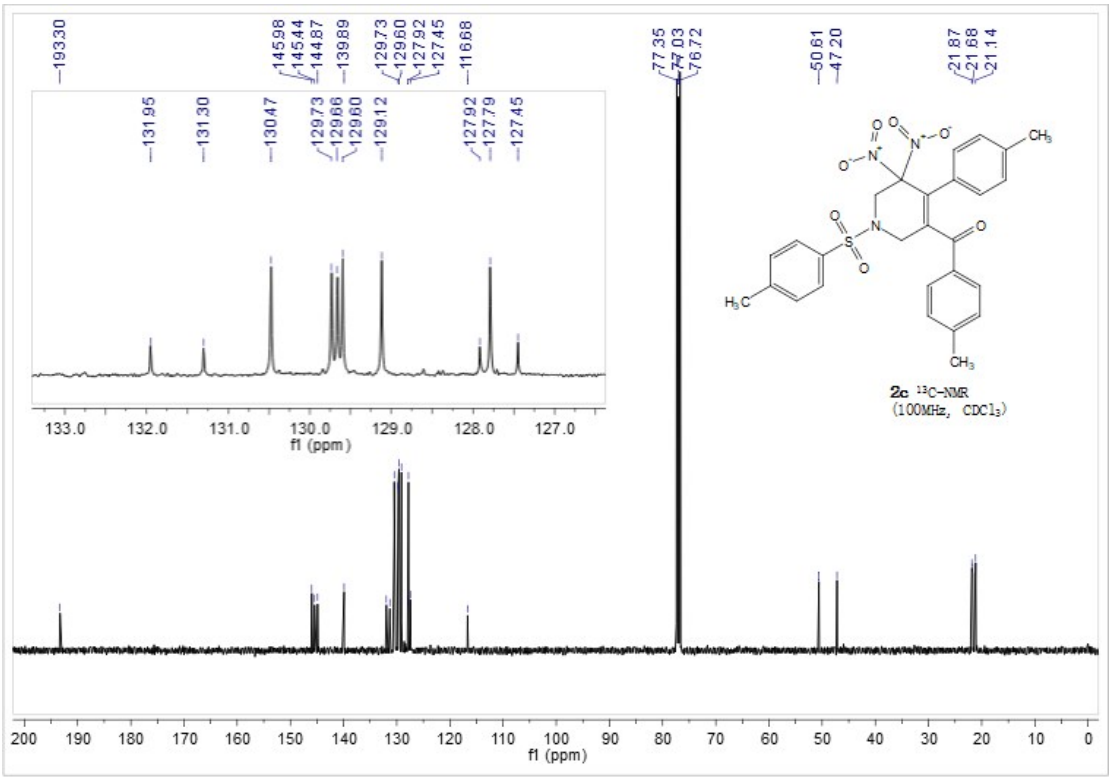
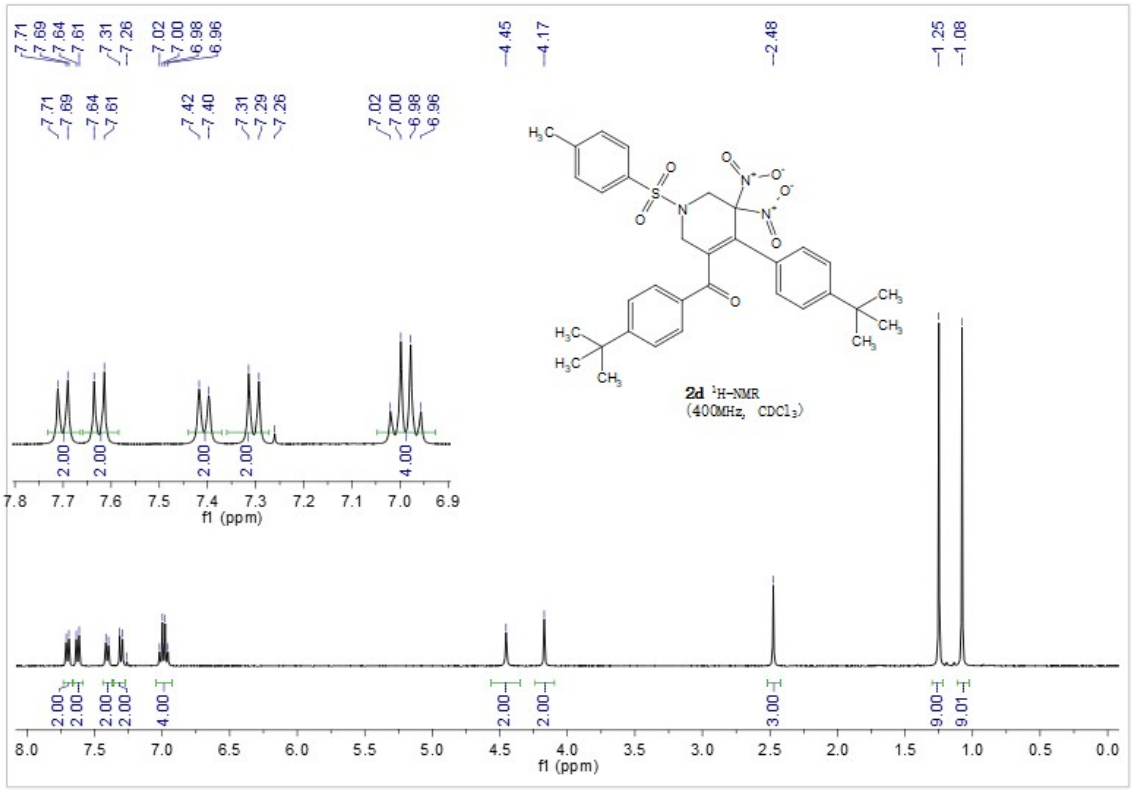
77.04
76.72
50.58
47.19
21.70
2b ¹³C-NMR
(100MHz, CDCl3)
f1 (ppm)



2c ^{1}H-NMR
(400MHz, $CDCl_3$)



2c ^{13}C-NMR
(100MHz, $CDCl_3$)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7.69
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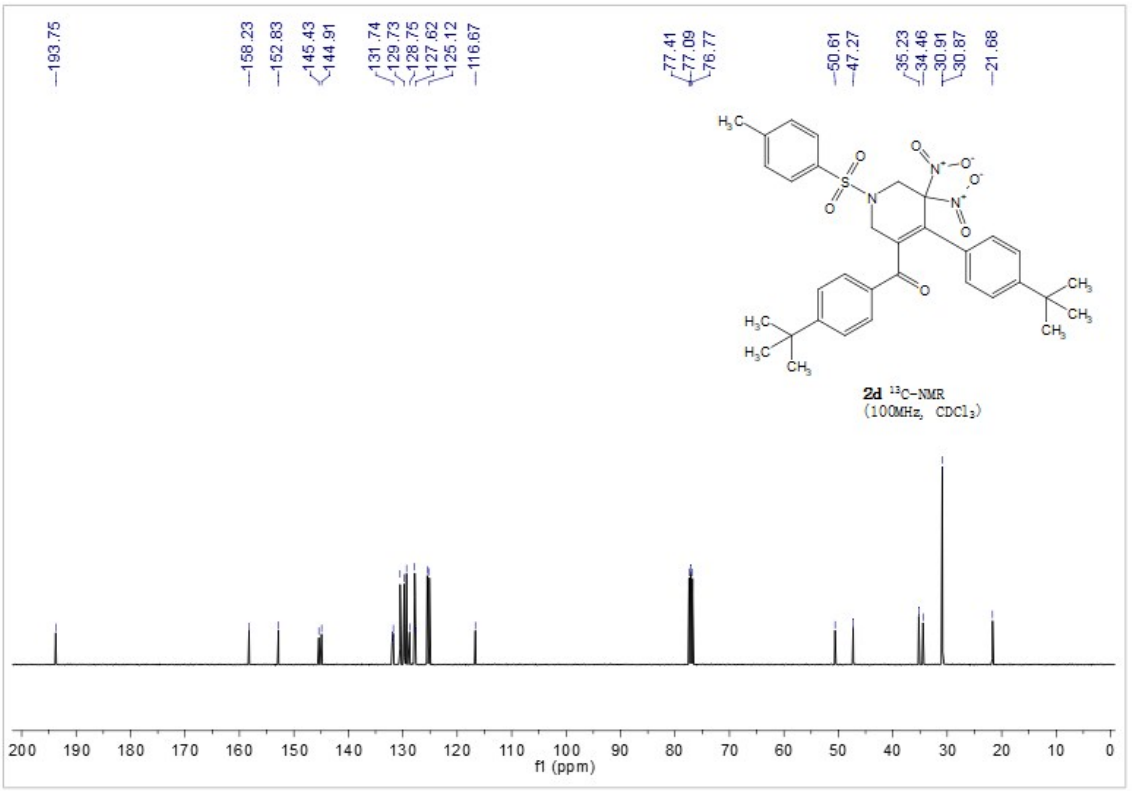
7.61
7.31
7.26
7.02
7.00
6.98
6.96
4.45
4.17
2.48
1.25
1.08
2d ¹H-NMR
(400MHz, CDCl₃)
f1 (ppm)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158.23
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144.91
131.74
129.73
128.75
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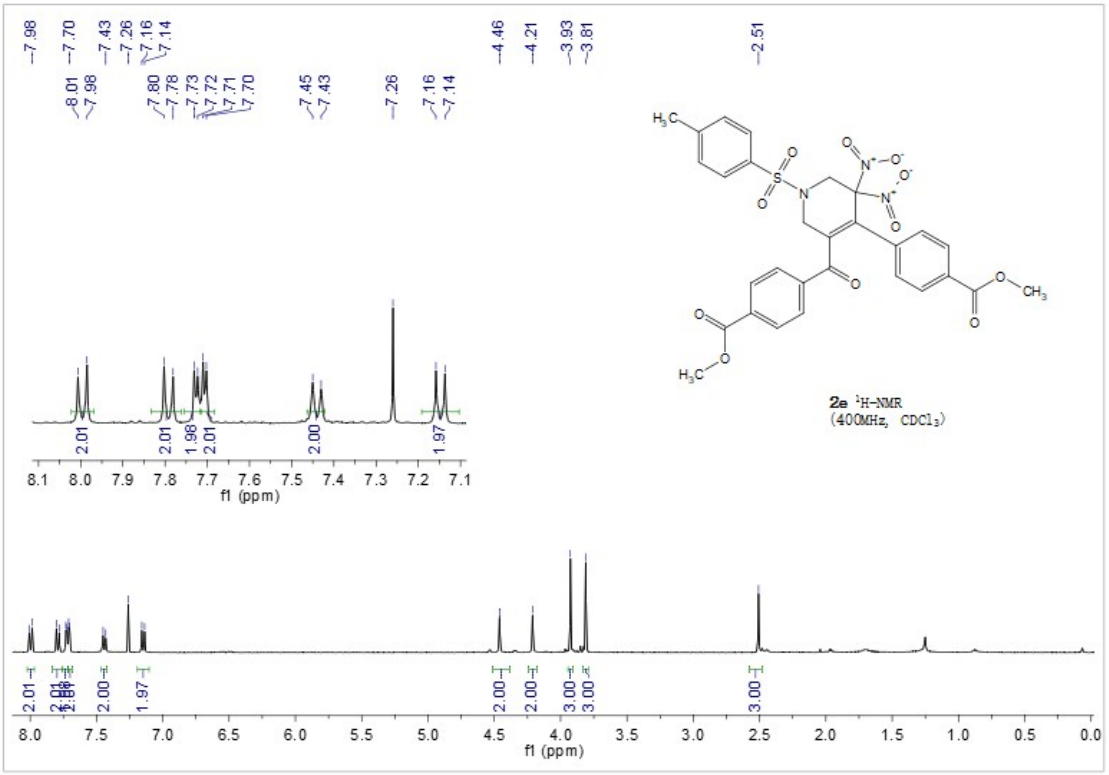
125.12
116.67
77.41
77.09
76.77
50.61
47.27
35.23
34.46
30.91
30.87
21.68
2d ¹³C-NMR
(100MHz, CDCl₃)
f1 (ppm)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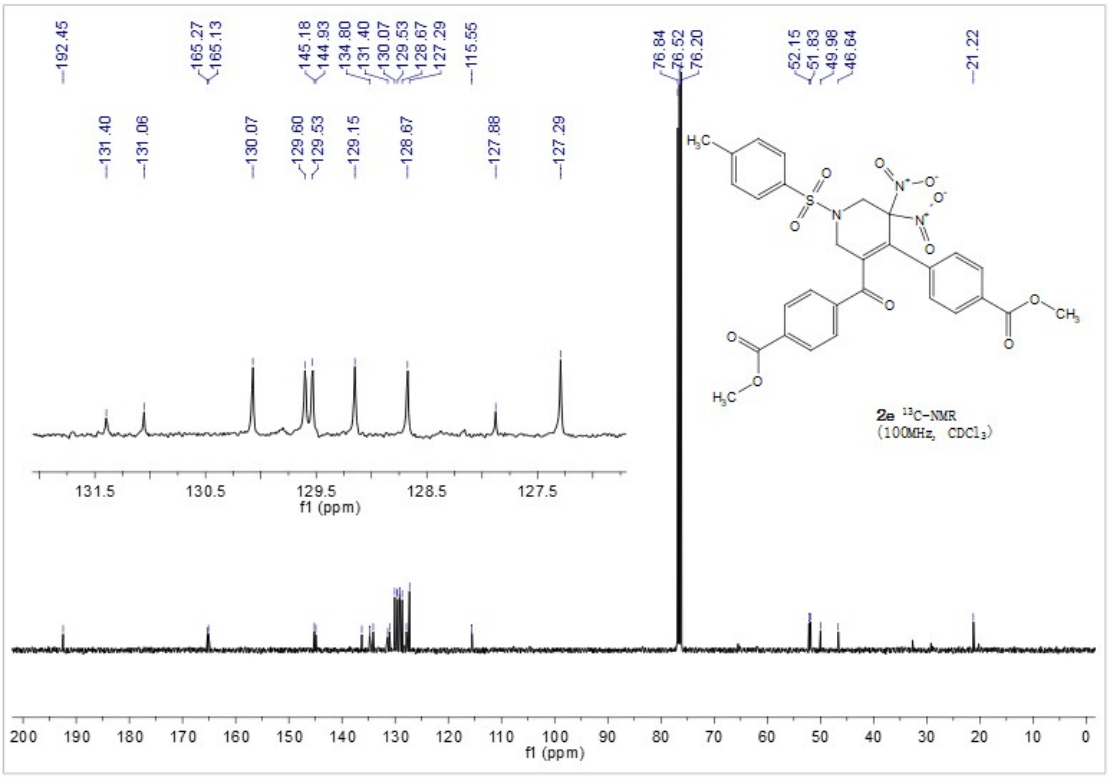
4.21
3.93
3.81
2.51
2e ^{1}H-NMR
(400MHz, $CDCl_3$)
f1 (ppm)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134.80
131.40
130.07
129.53
128.67
127.29
115.55
76.84
76.52
76.20
52.15
51.83
49.98
46.64
21.22
131.40
131.06
130.07
129.60
129.53
129.15
128.67
127.88
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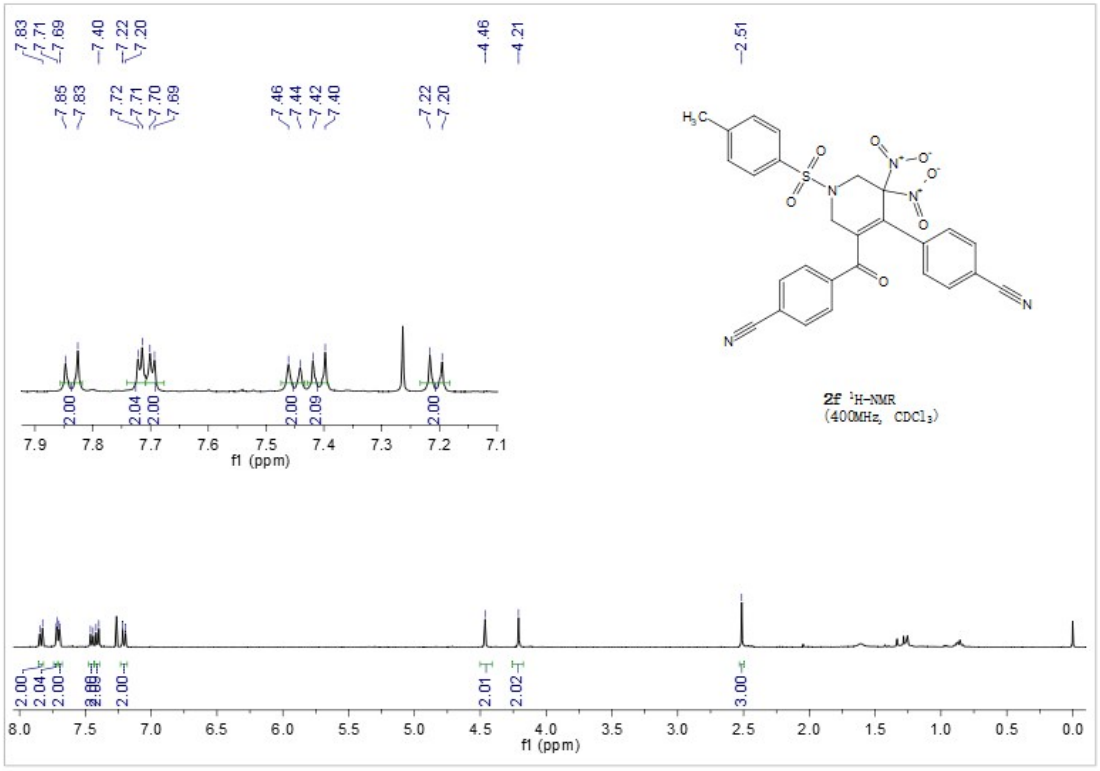
2e ^{13}C-NMR
(100MHz, $CDCl_3$)
f1 (ppm)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4.21
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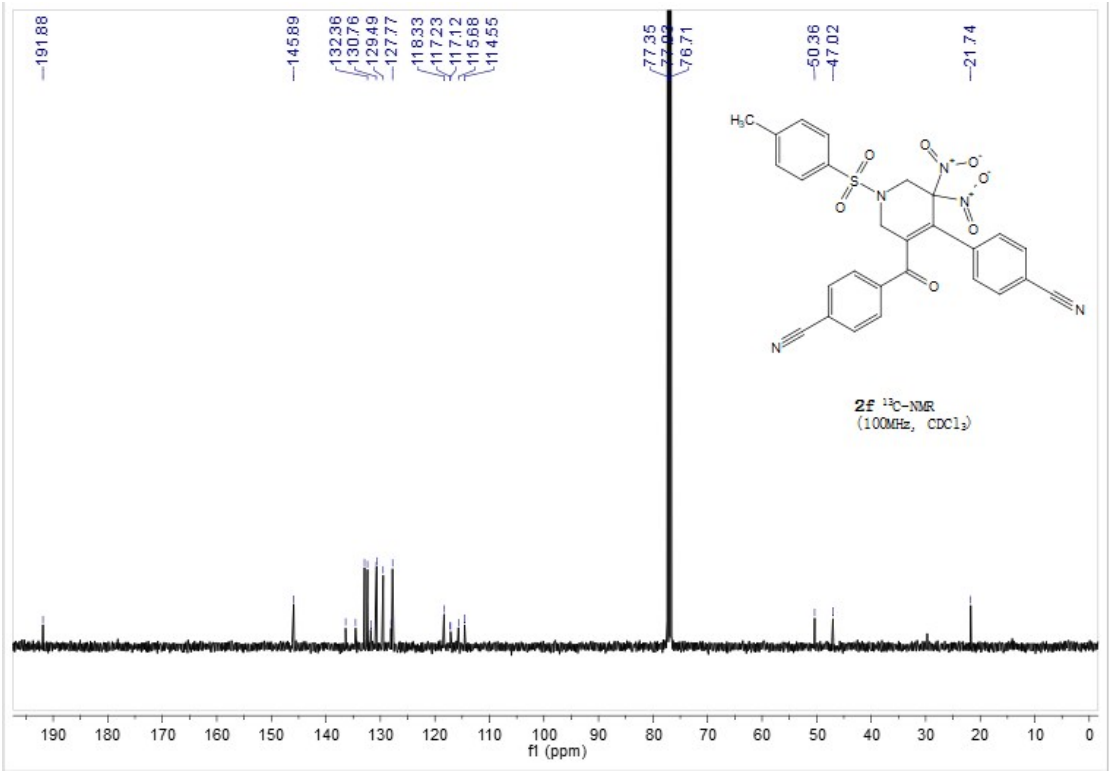
7.85
7.83
7.72
7.71
7.70
7.69
7.46
7.44
7.42
7.40
7.22
7.20
2.00
2.04
2.00
2.00
2.09
2.00
f1 (ppm)
2f ¹H-NMR
(400MHz, CDCl3)
2.00
2.04
2.00
2.00
2.01
2.02
3.00
f1 (ppm)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127.77
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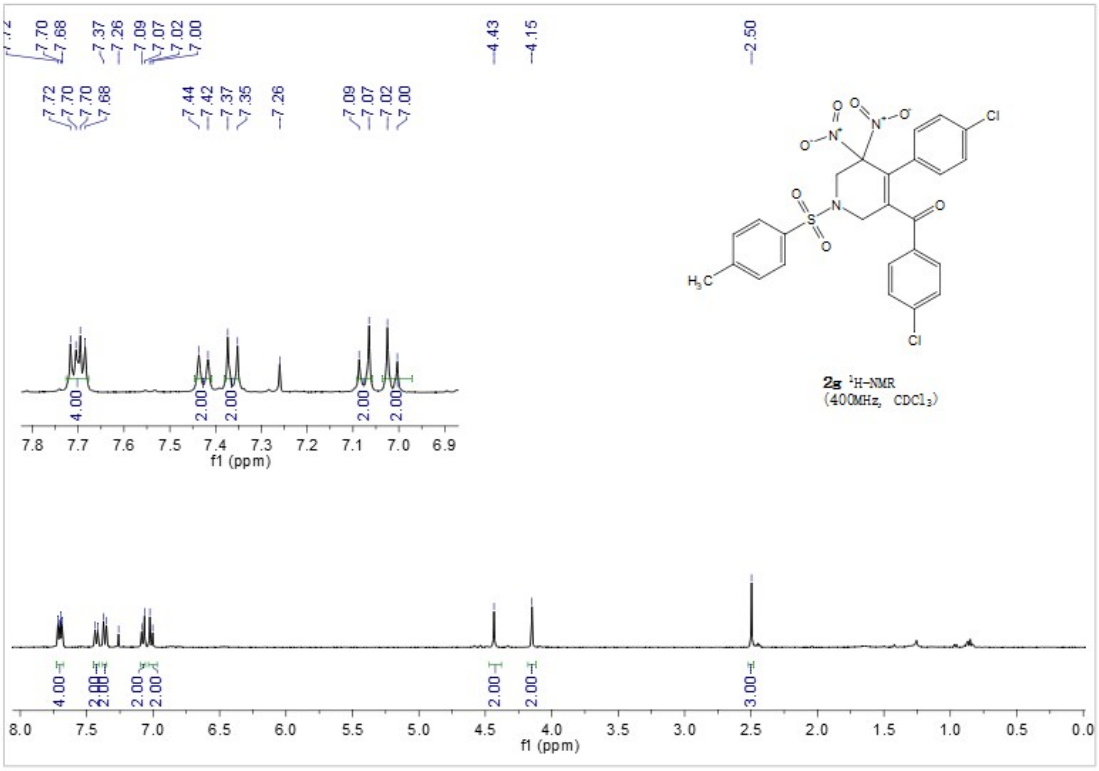
117.23
117.12
115.68
114.55
77.35
77.02
76.71
50.36
47.02
21.74
2f ¹³C-NMR
(100MHz, CDCl3)
f1 (ppm)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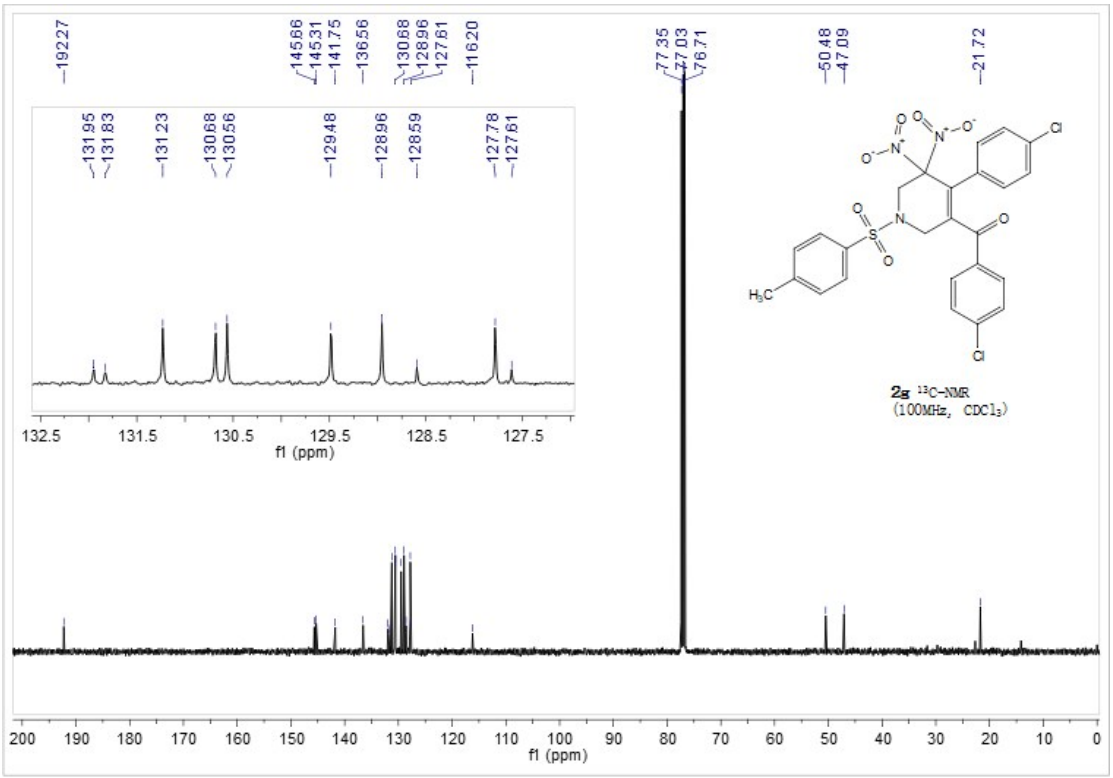
7.07
7.02
7.00
4.43
4.15
2.50
7.72
7.70
7.70
7.68
7.44
7.42
7.37
7.35
7.26
7.09
7.07
7.02
7.00
4.00
2.00
2.00
2.00
2.00
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
4.00
2.00
2.00
2.00
2.00
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
2g ¹H-NMR
(400MHz, CDCl₃)


19227
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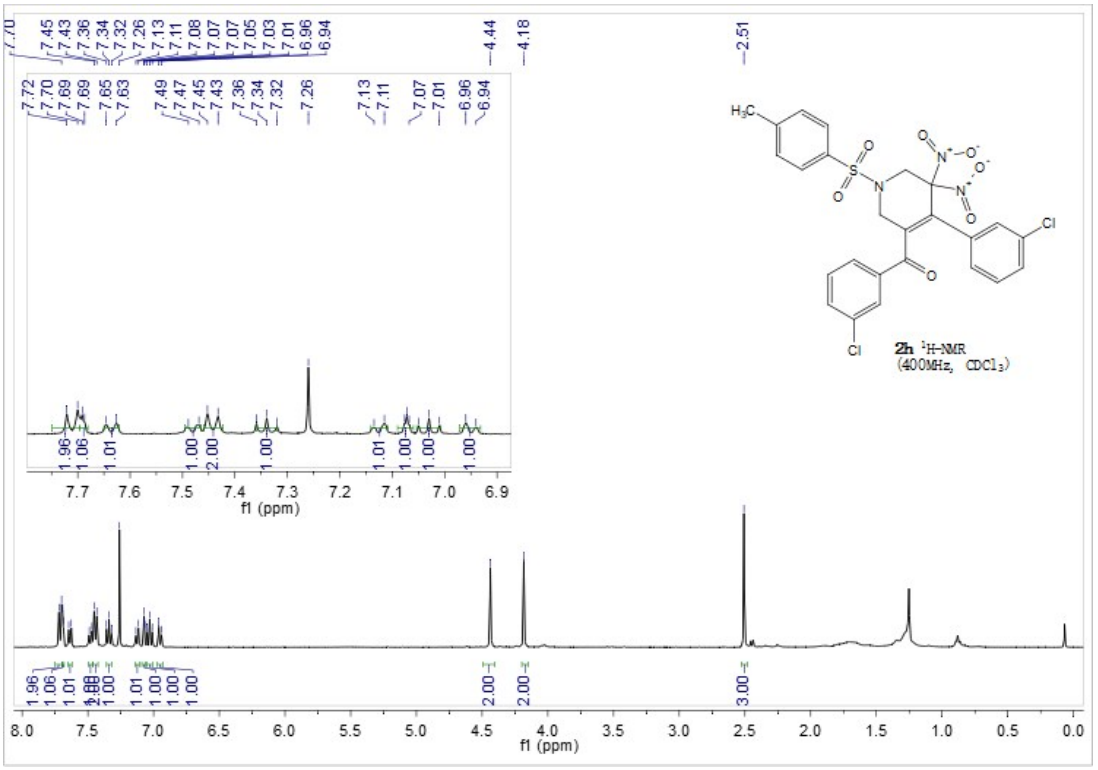
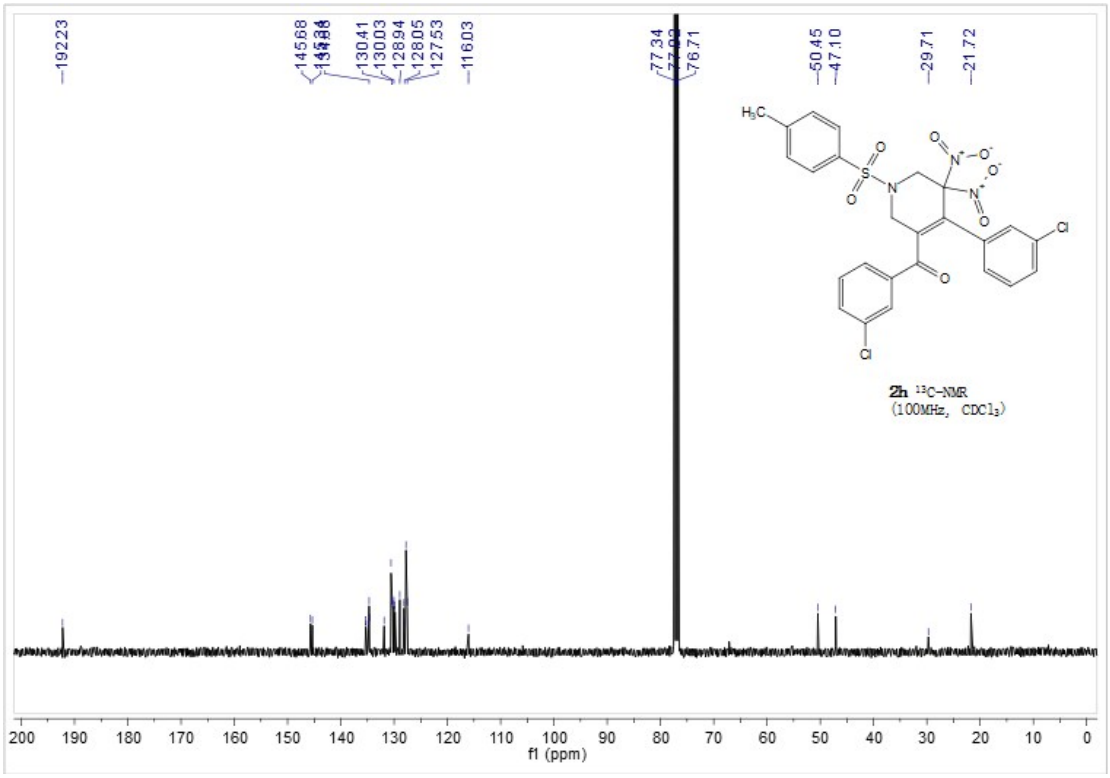
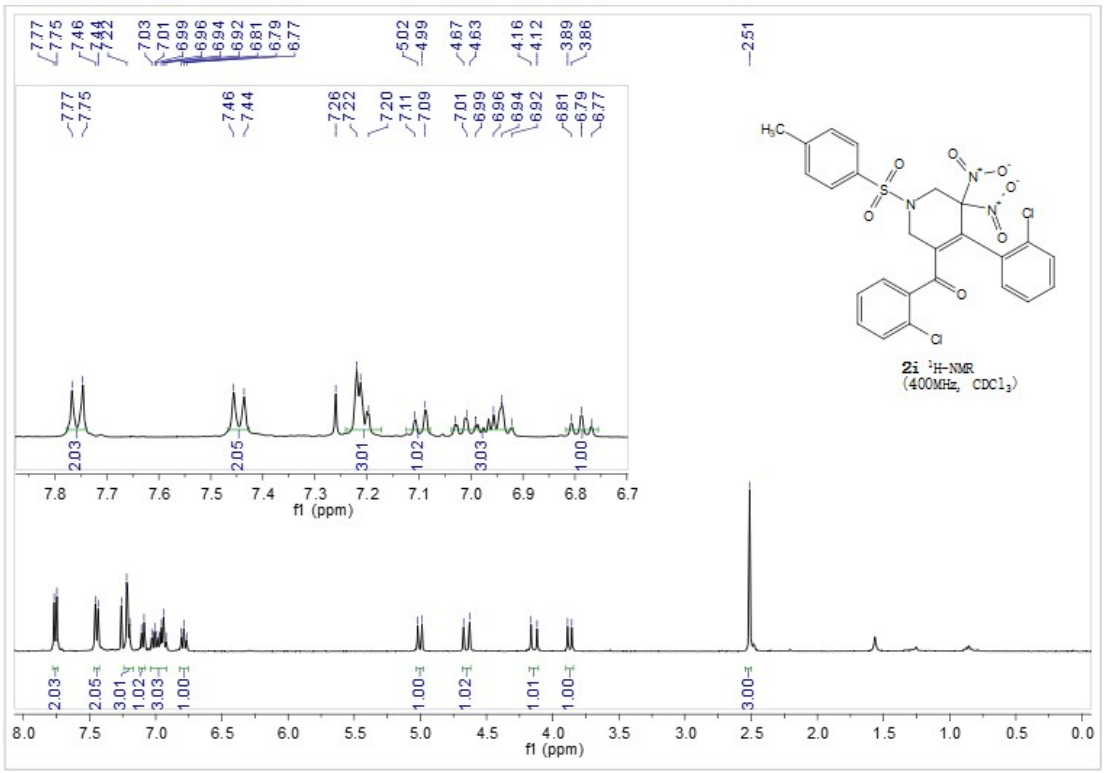
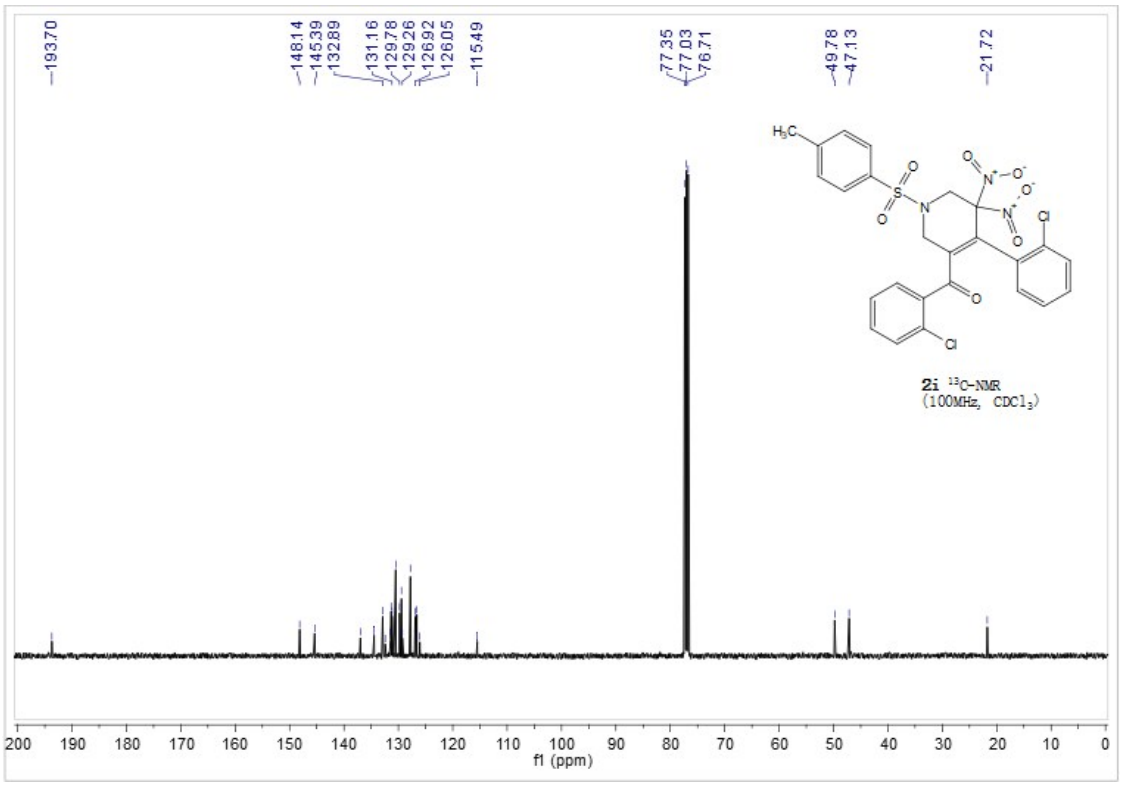
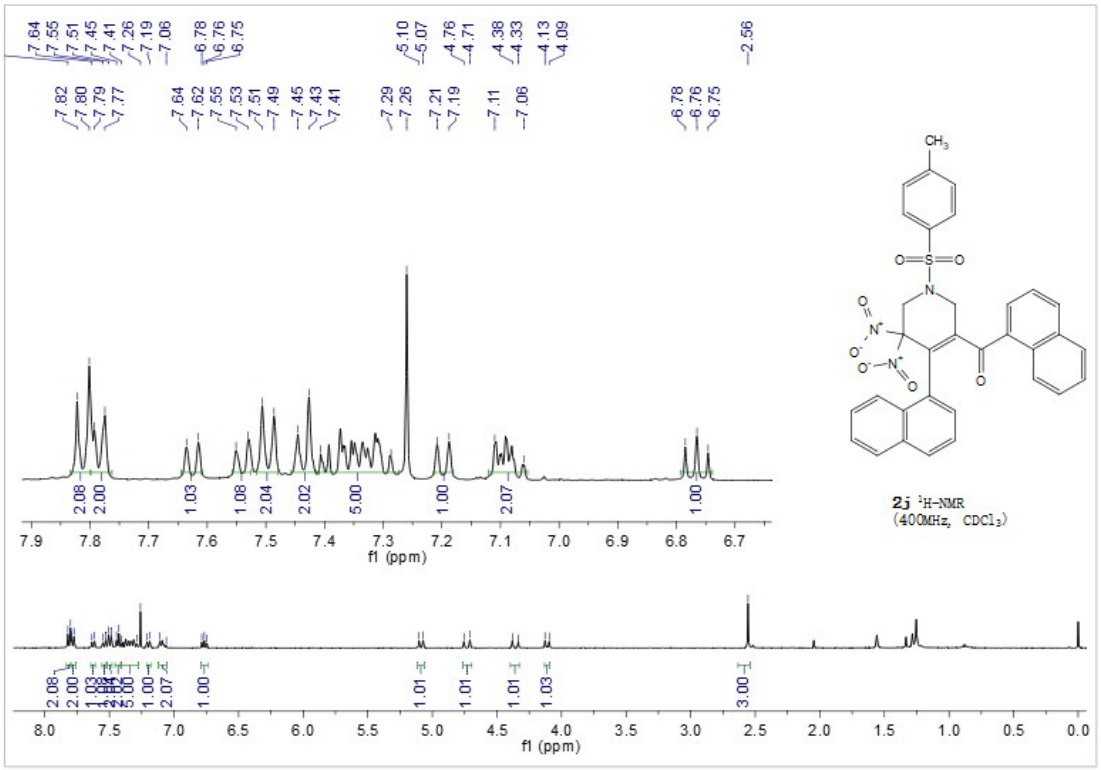
127.61
116.20
77.35
77.03
76.71
50.48
47.09
21.72
131.95
131.83
131.23
130.68
130.56
129.48
128.96
128.59
127.78
127.61
132.5 131.5 130.5 129.5 128.5 127.5
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
2g ¹³C-NMR
(100MHz, CDCl₃)


2h ^{1}H-NMR
(400MHz, $CDCl_3$)
f1 (ppm)


2h ^{13}C-NMR
(100MHz, $CDCl_3$)
f1 (ppm)


2i ^{1}H-NMR
(400MHz, $CDCl_3$)
f1 (ppm)


2i ^{13}C-NMR
(100MHz, $CDCl_3$)
f1 (ppm)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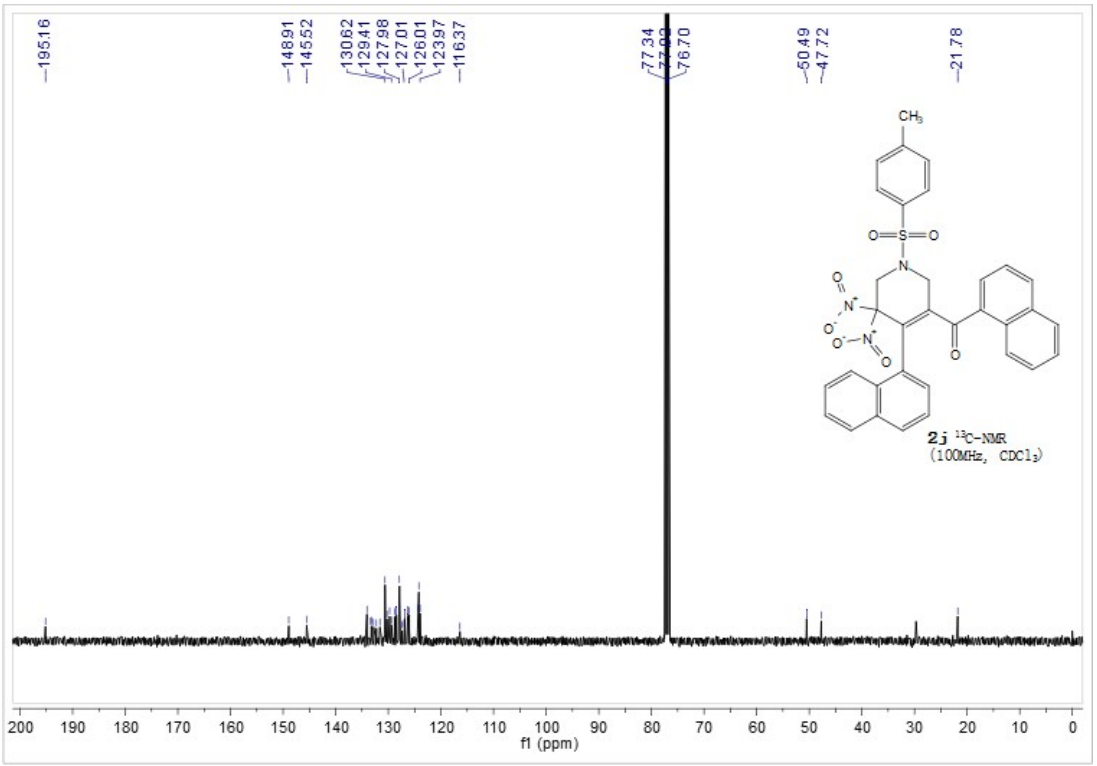
5.07
4.76
4.71
4.38
4.33
4.13
4.09
2.56
7.82
7.80
7.79
7.77
7.64
7.62
7.55
7.53
7.51
7.49
7.45
7.43
7.41
7.29
7.26
7.21
7.19
7.11
7.06
6.78
6.76
6.75
2.08
2.00
1.03
1.08
2.04
2.02
5.00
1.00
2.07
1.00
f1 (ppm)
2.08
2.00
1.00
1.07
1.00
2.07
1.00
1.01
1.01
1.01
1.03
3.00
f1 (ppm)
2j ¹H-NMR
(400MHz, CDCl₃)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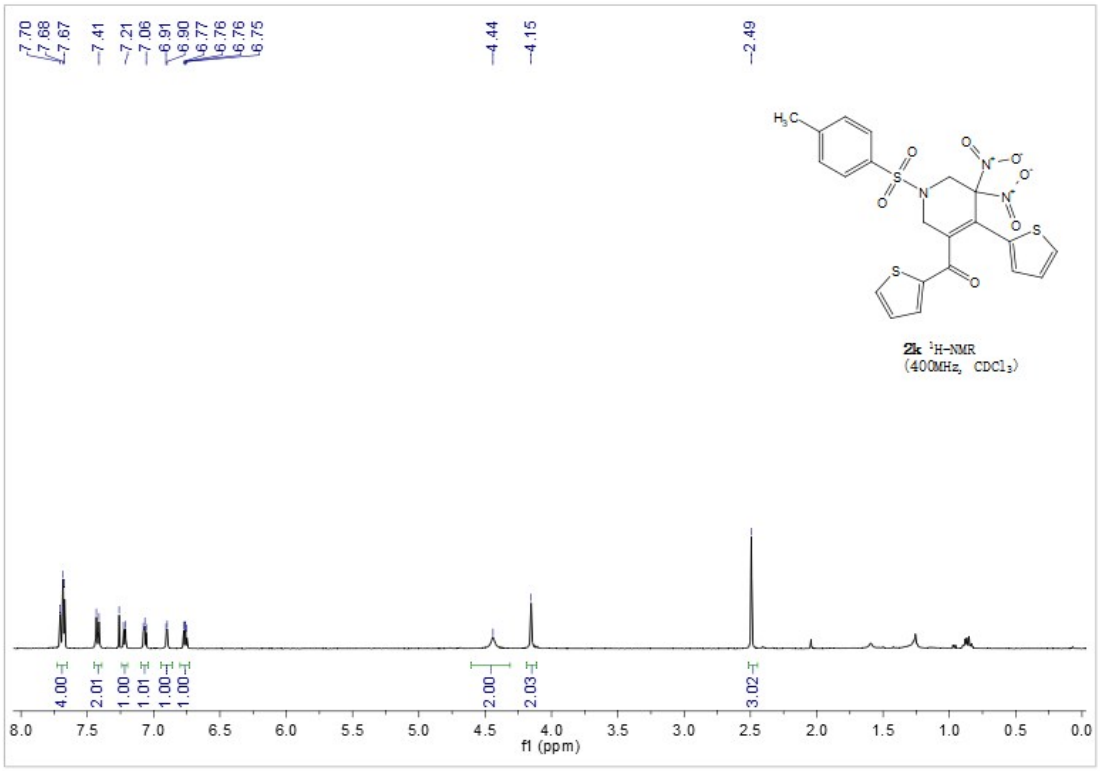
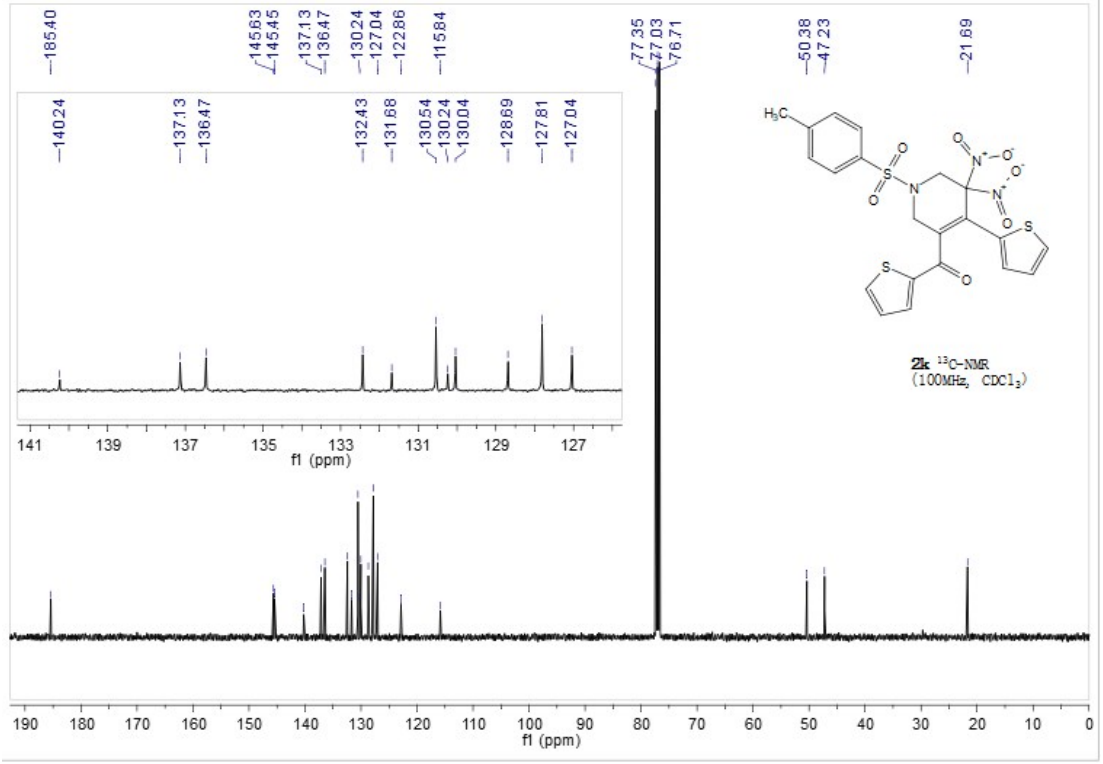
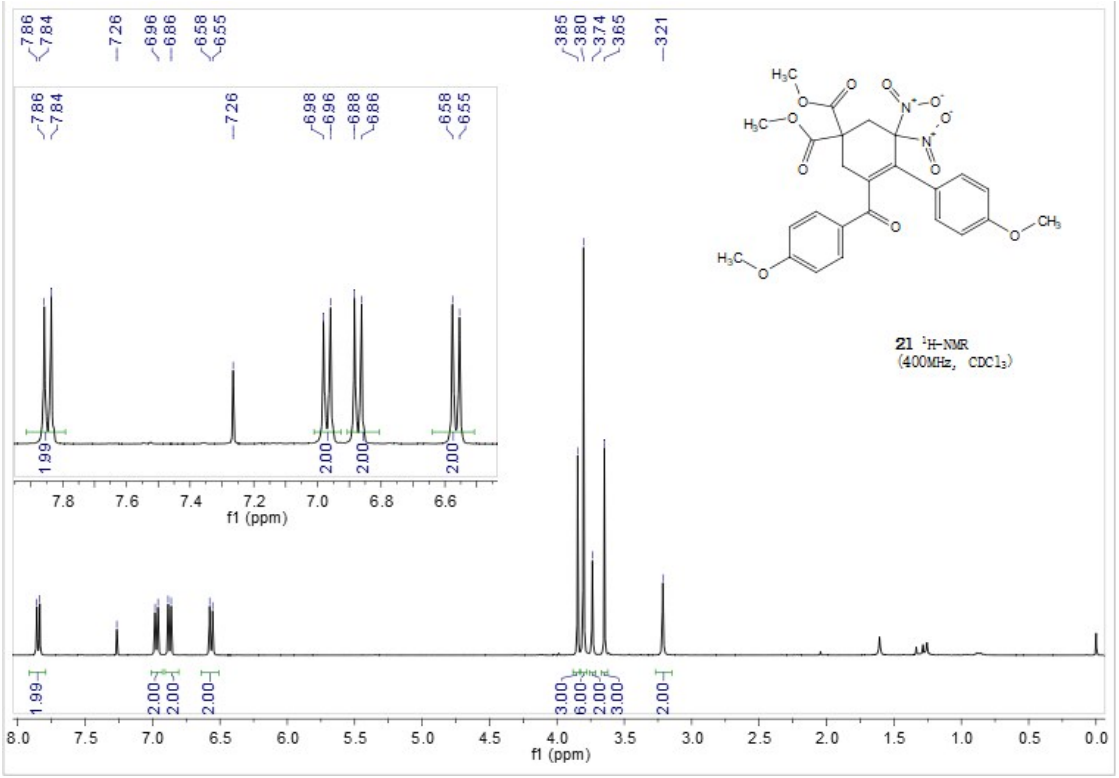
127.98
127.01
126.01
123.97
116.37
77.34
77.00
76.70
50.49
47.72
21.78
f1 (ppm)
2j ¹³C-NMR
(100MHz, CDCl₃)



2k ^{1}H-NMR
(400MHz, $CDCl_3$)



2k ^{13}C-NMR
(100MHz, $CDCl_3$)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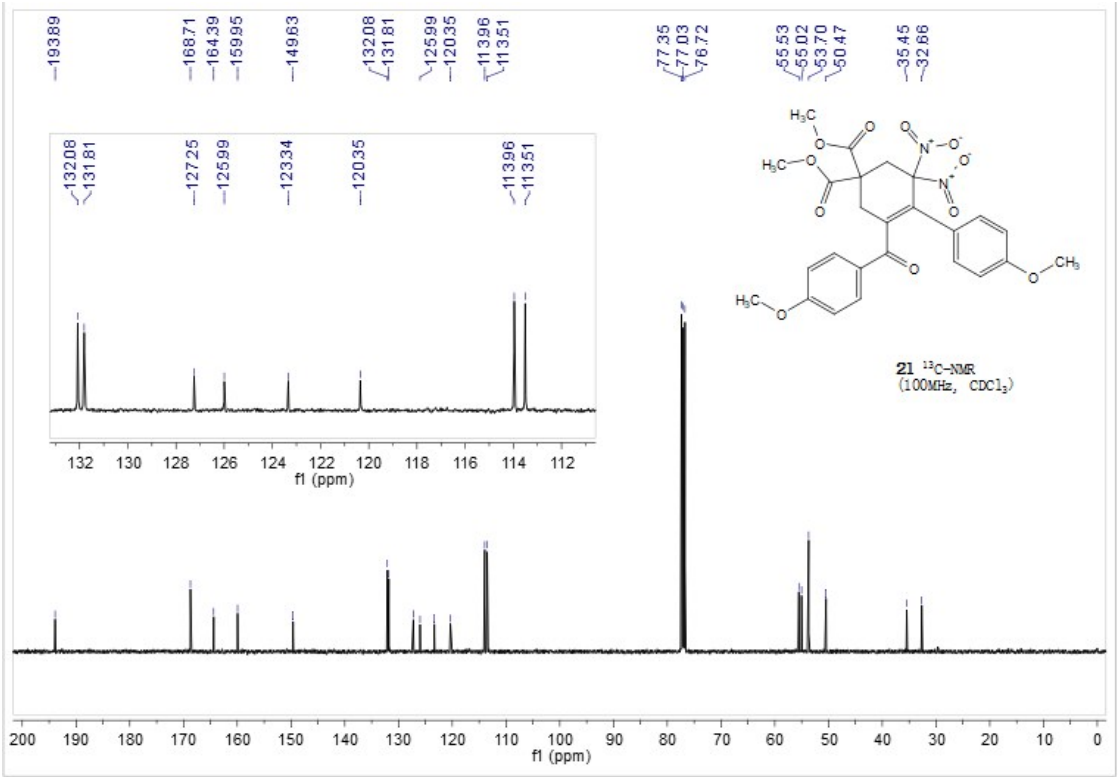
6.58
6.55
3.85
3.80
3.74
3.65
3.21
1.99
2.00
2.00
2.00
3.00
6.00
2.00
3.00
2.00
f1 (ppm)
21 ¹H-NMR
(400MHz, CDCl₃)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164.39
159.95
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132.08
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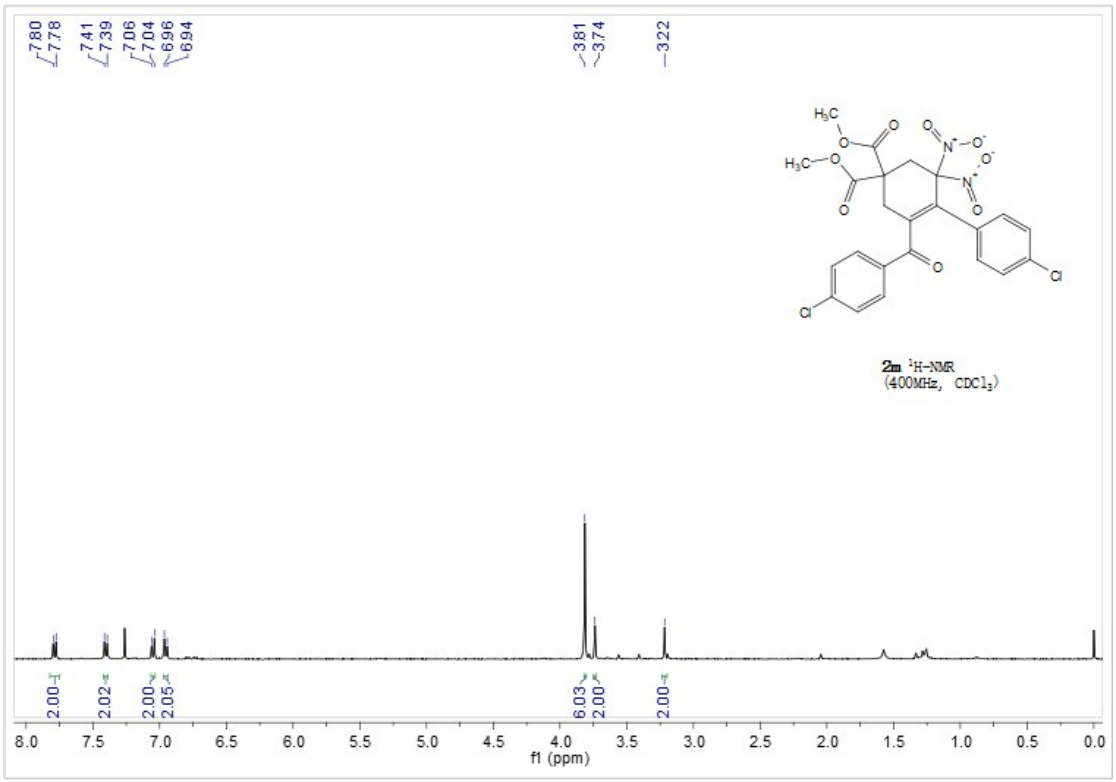
120.35
113.96
113.51
77.35
77.03
76.72
55.53
55.02
53.70
50.47
35.45
32.66
f1 (ppm)
21 ¹³C-NMR
(100MHz, CDCl₃)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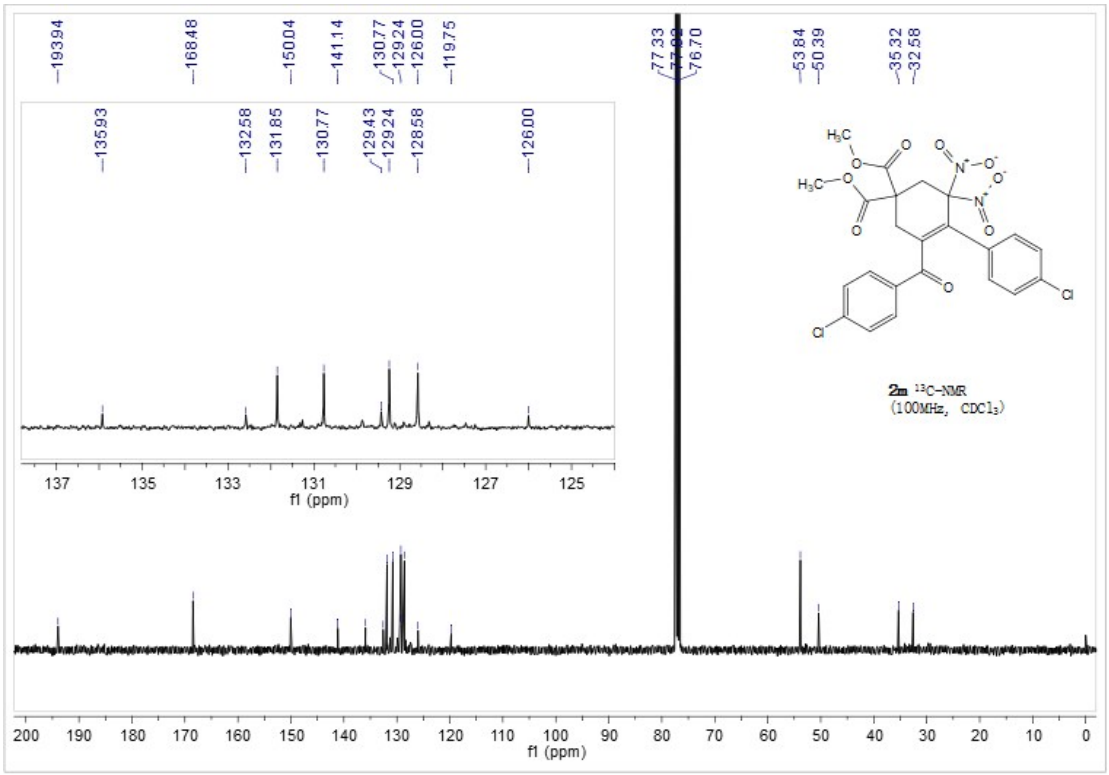
7.04
6.96
6.94
3.81
3.74
3.22
2.00
2.02
2.00
2.05
6.03
2.00
2.00
f1 (ppm)
2m ^{1}H-NMR
(400MHz, $CDCl_3$)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126.00
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135.93
132.58
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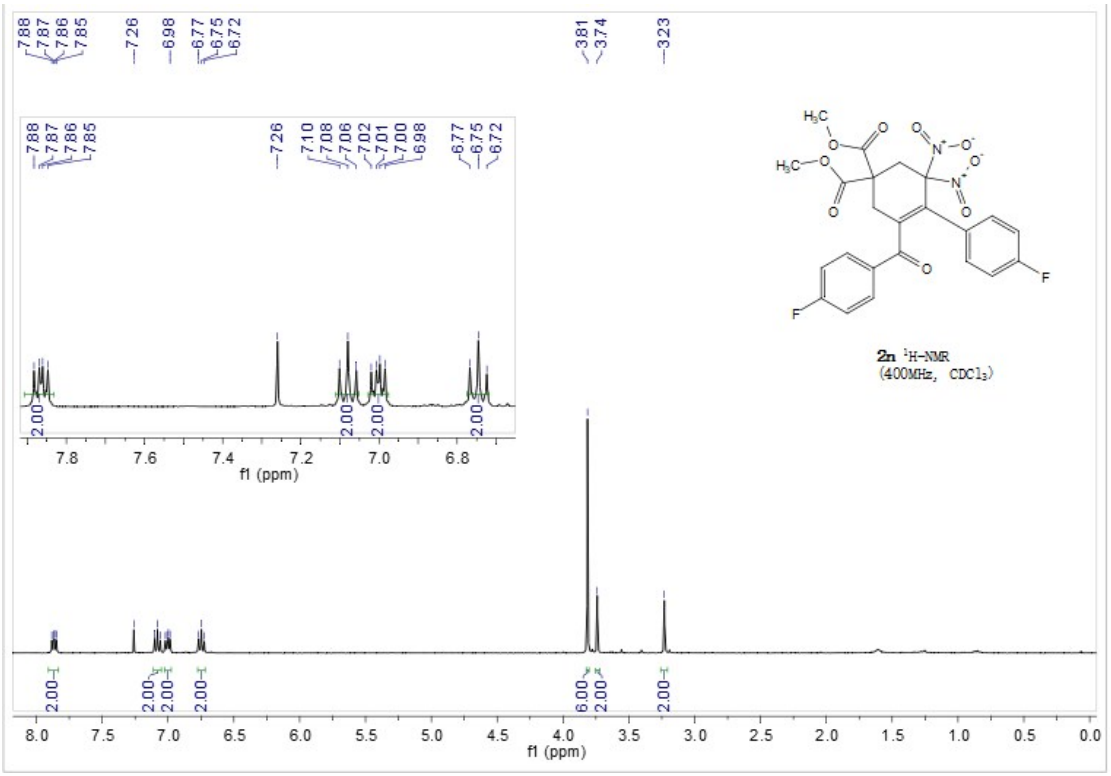
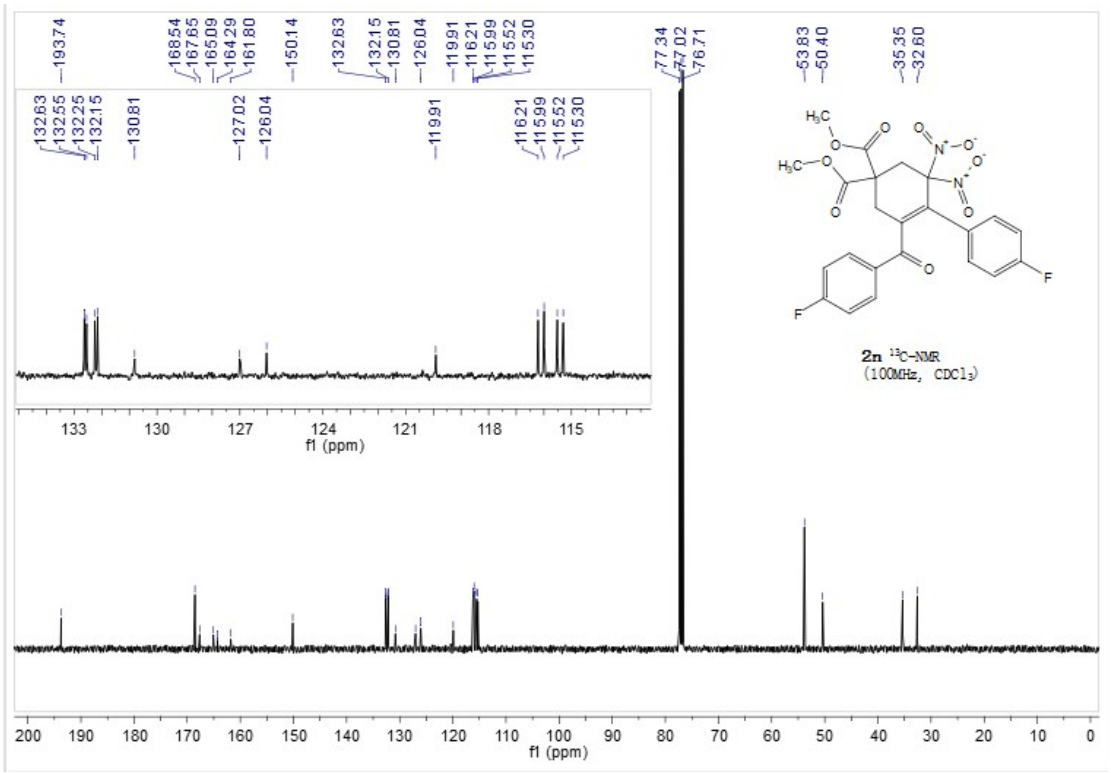
130.77
129.43
129.24
128.58
126.00
77.33
76.70
53.84
50.39
35.32
32.58
f1 (ppm)
2m ^{13}C-NMR
(100MHz, $CDCl_3$)


7.88
7.87
7.86
7.85
7.26
6.98
6.77
6.75
6.72
3.81
3.74
3.23
f1 (ppm)
2n ^{1}H-NMR
(400MHz, CDCl$_3$)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168.54
167.65
165.09
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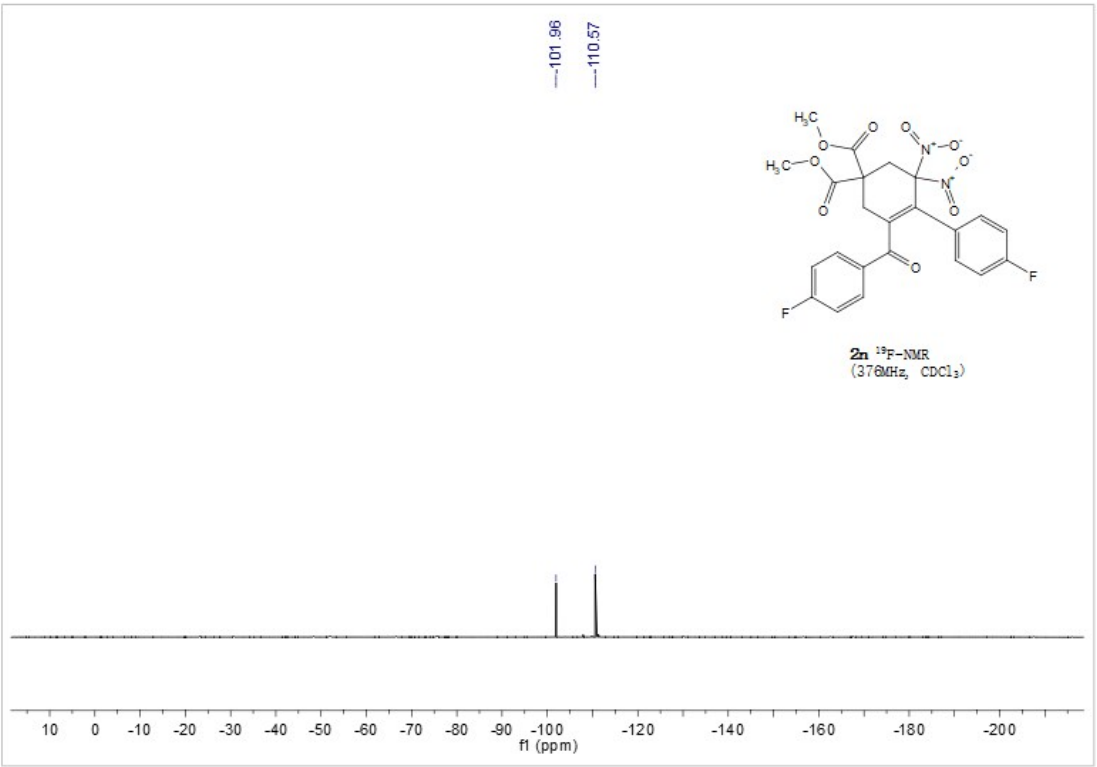
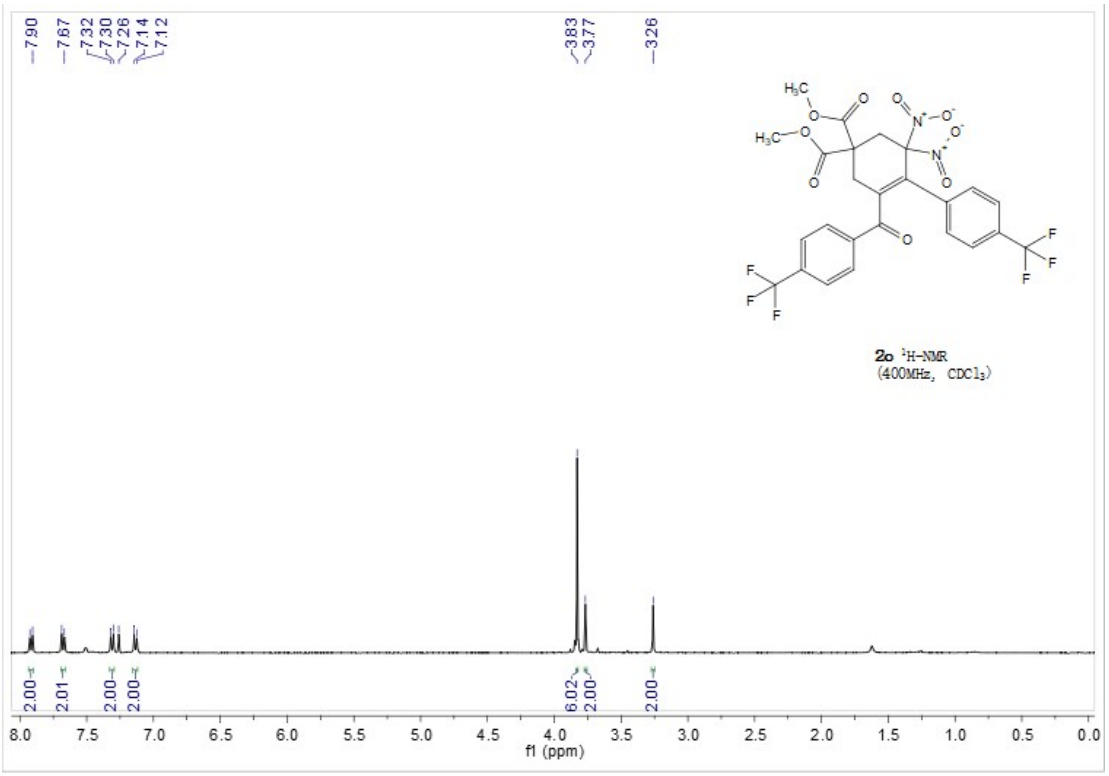
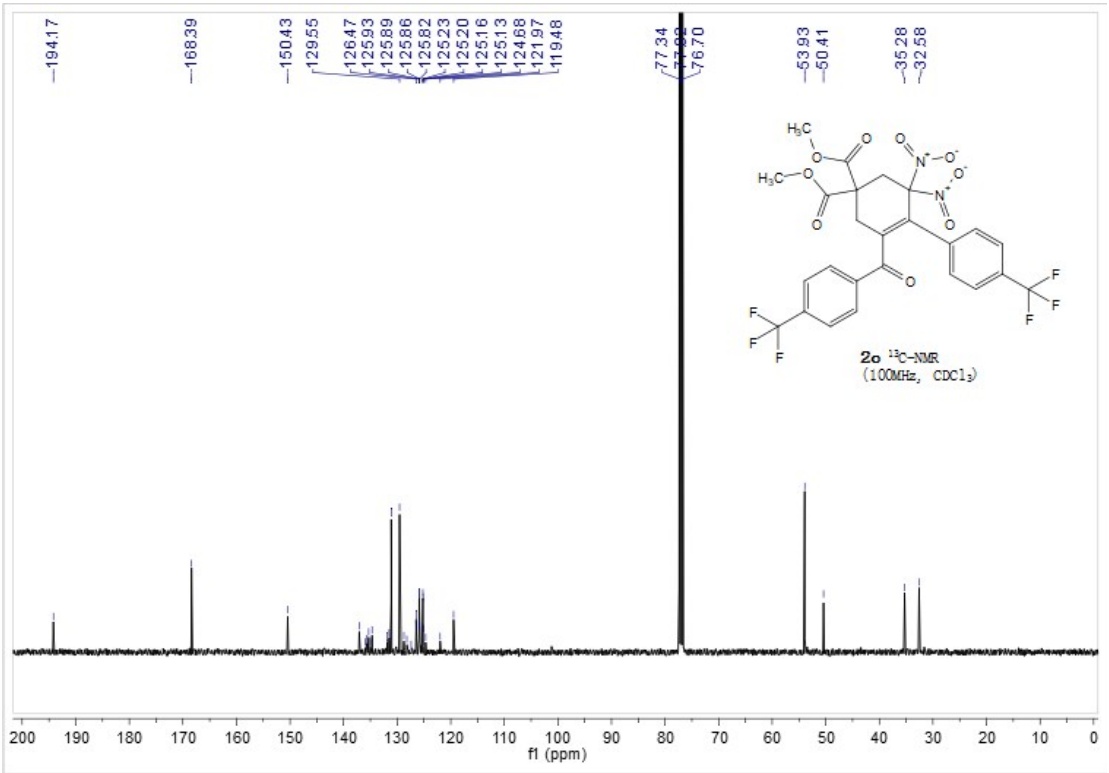
161.80
150.14
132.63
132.15
130.81
126.04
119.91
116.21
115.99
115.52
115.30
77.34
77.02
76.71
53.83
50.40
35.35
32.60
f1 (ppm)
2n ^{13}C-NMR
(100MHz, CDCl$_3$)

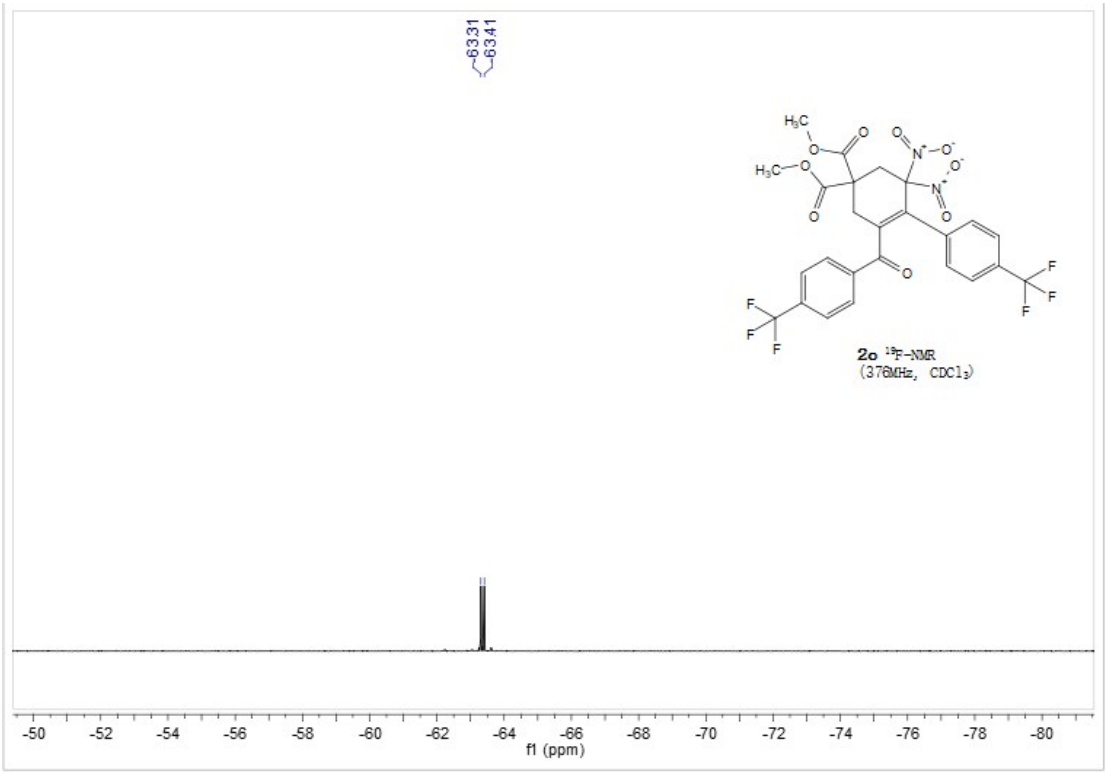

-101.96
-110.57
2n ^{19}F-NMR
(376MHz, $CDCl_3$)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

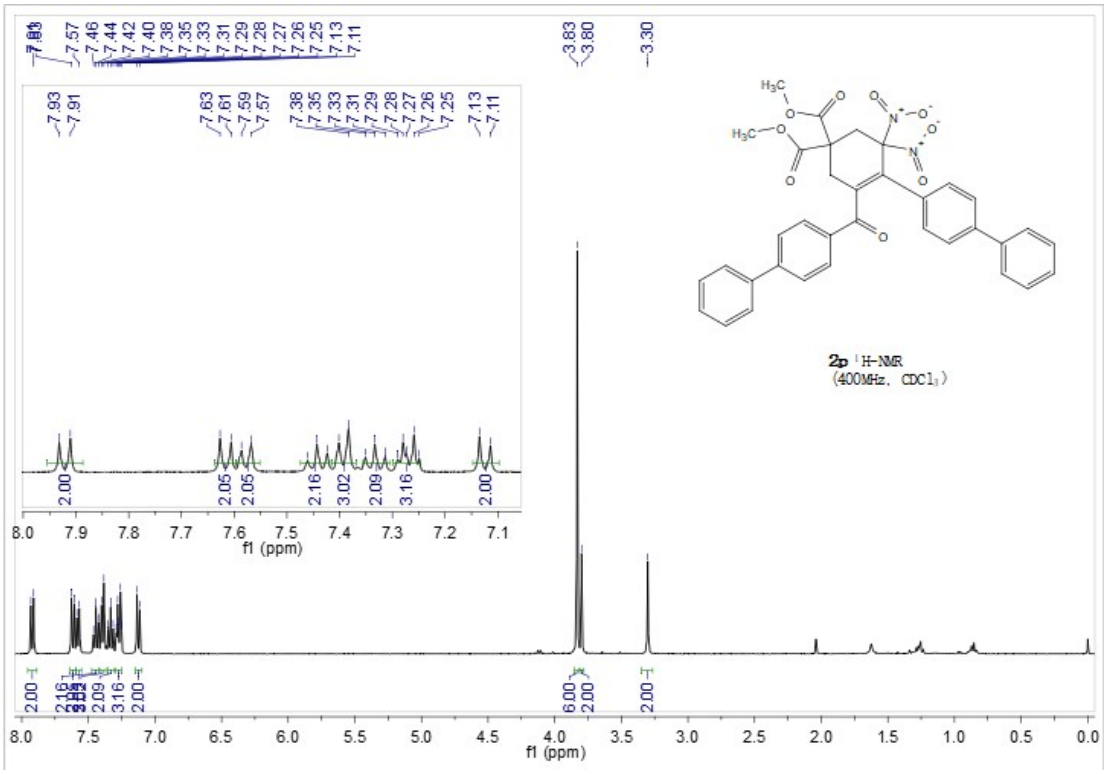


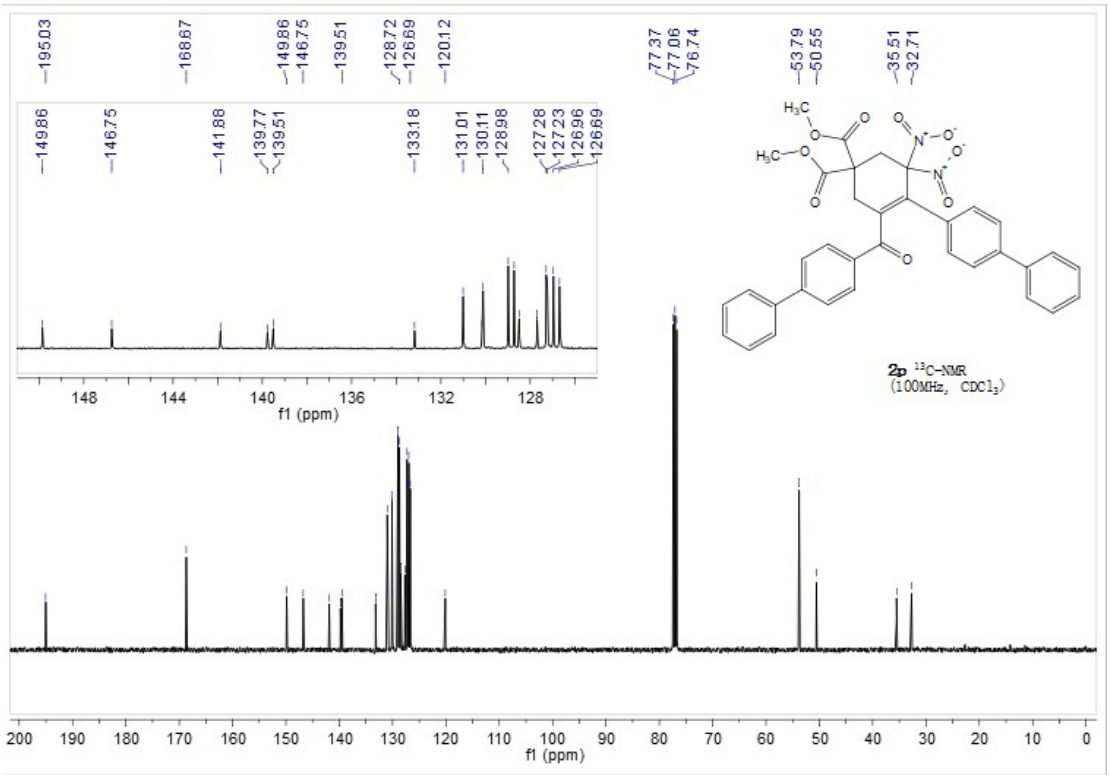
2o ^{1}H-NMR
(400MHz, $CDCl_3$)

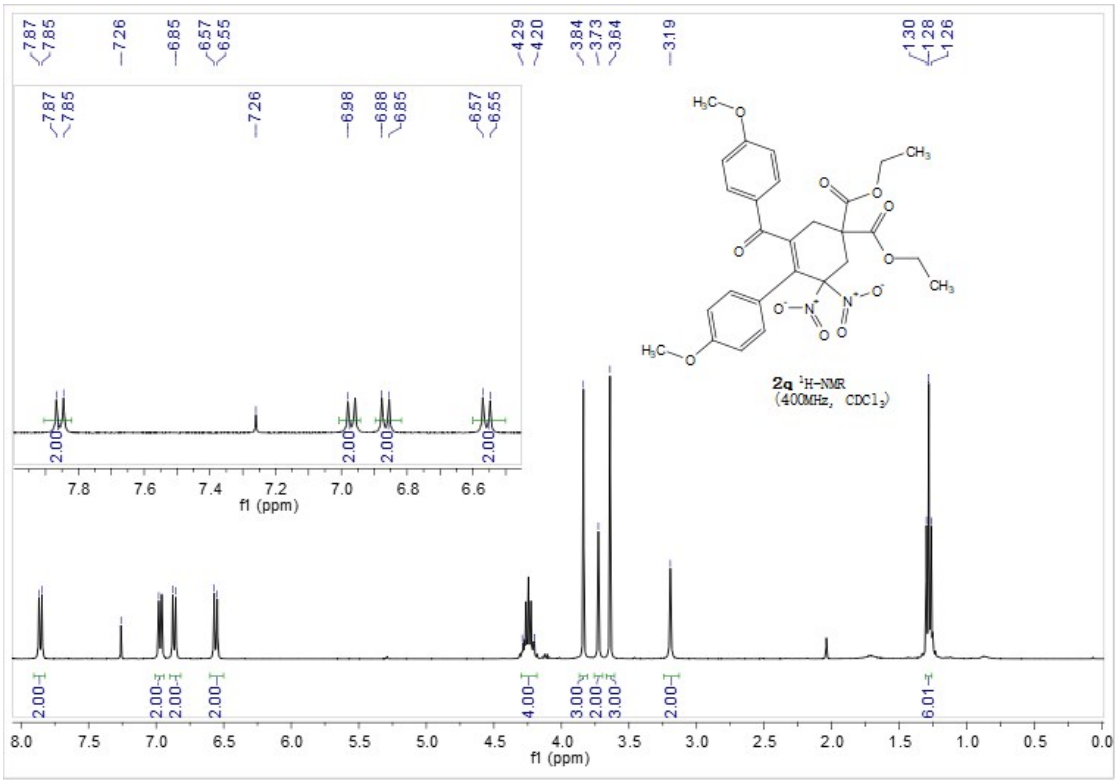


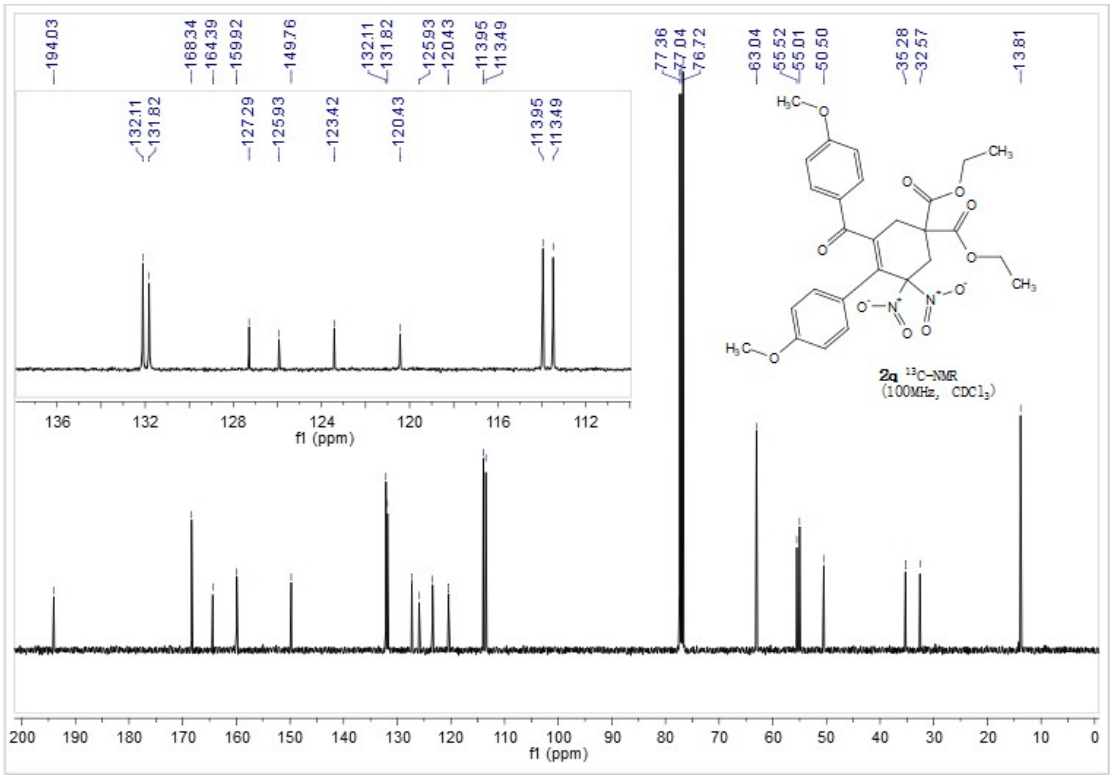
2o ^{13}C-NMR
(100MHz, $CDCl_3$)

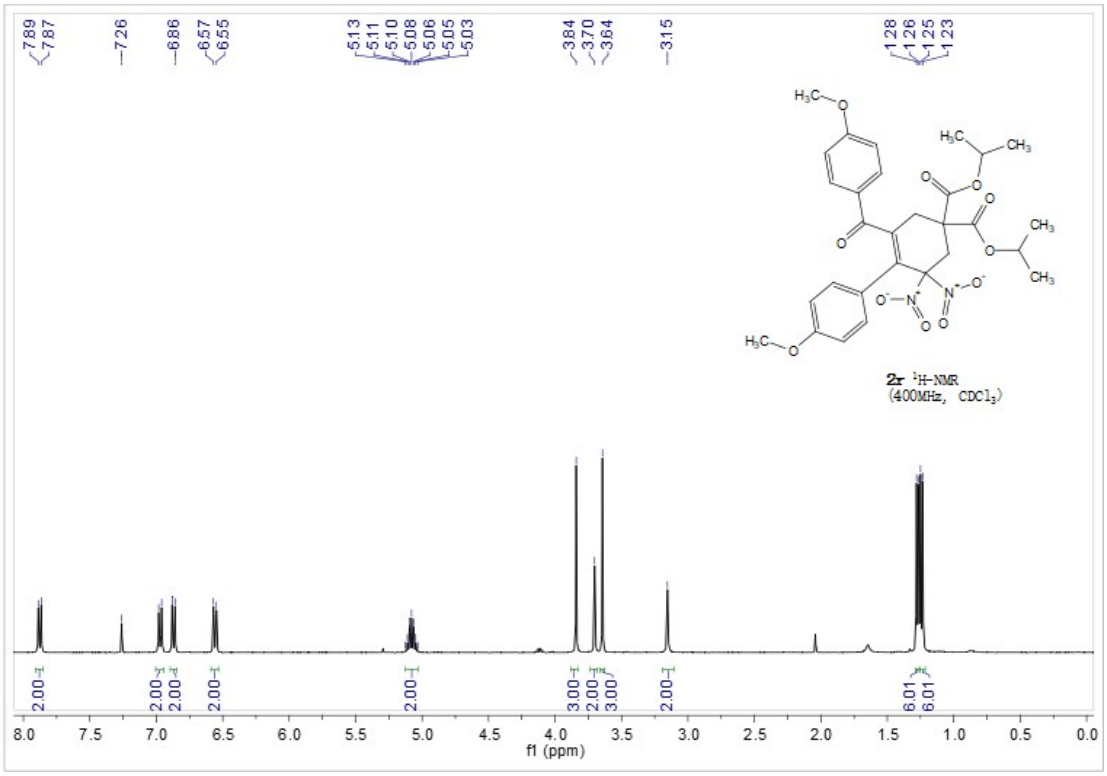

-63.31
-63.41
2o ^{19}F-NMR
(376MHz, CDCl$_3$)
-50
-52
-54
-56
-58
-60
-62
-64
-66
-68
-70
-72
-74
-76
-78
-80
f1 (ppm)

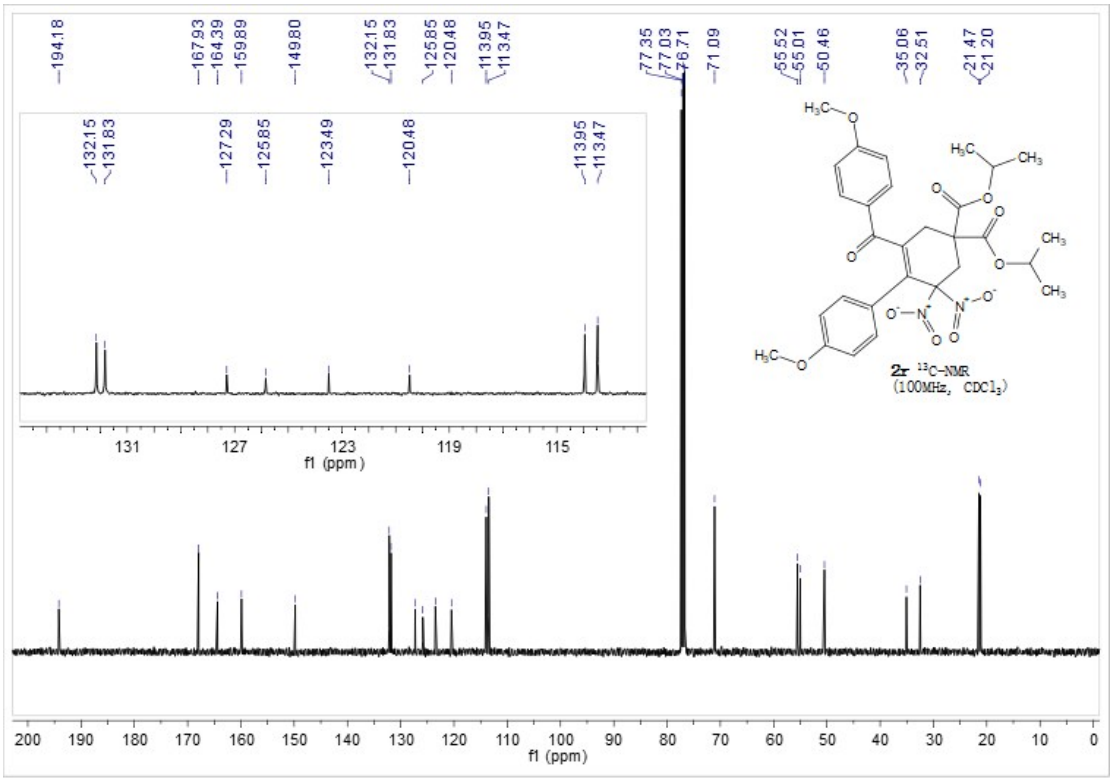

2p ¹H-NMR
(400MHz, CDCl₃)
f1 (ppm)

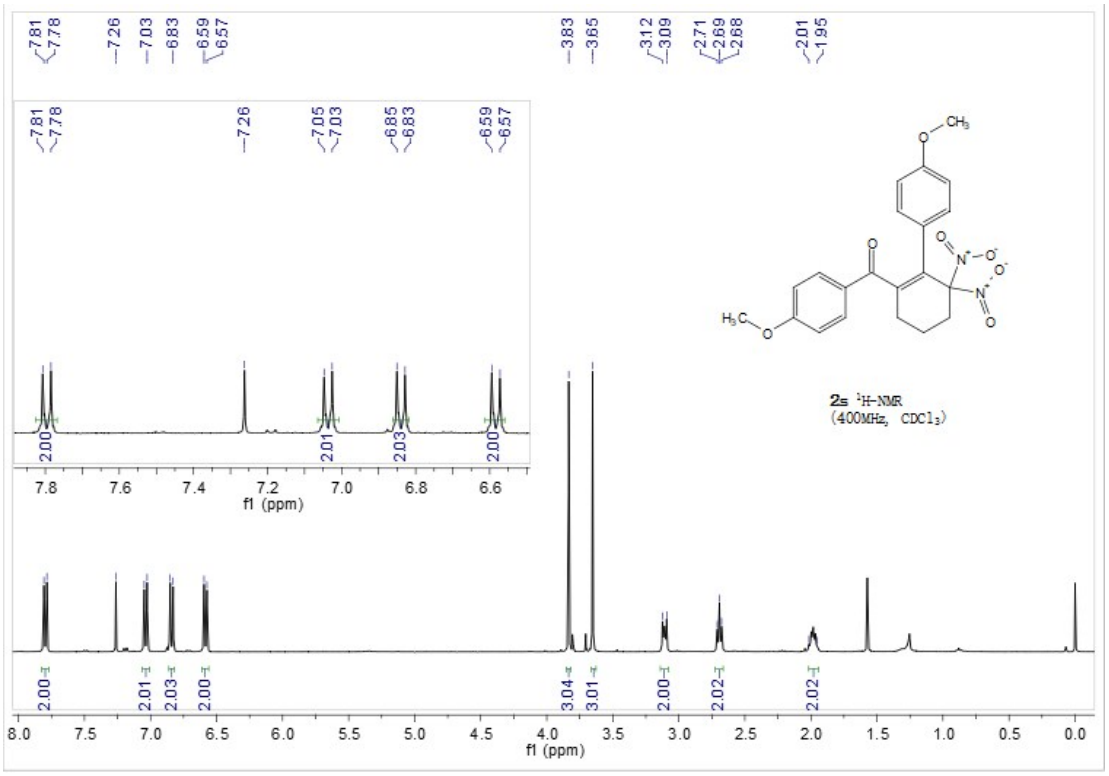

2p ¹³C-NMR
(100MHz, CDCl₃)
f1 (ppm)

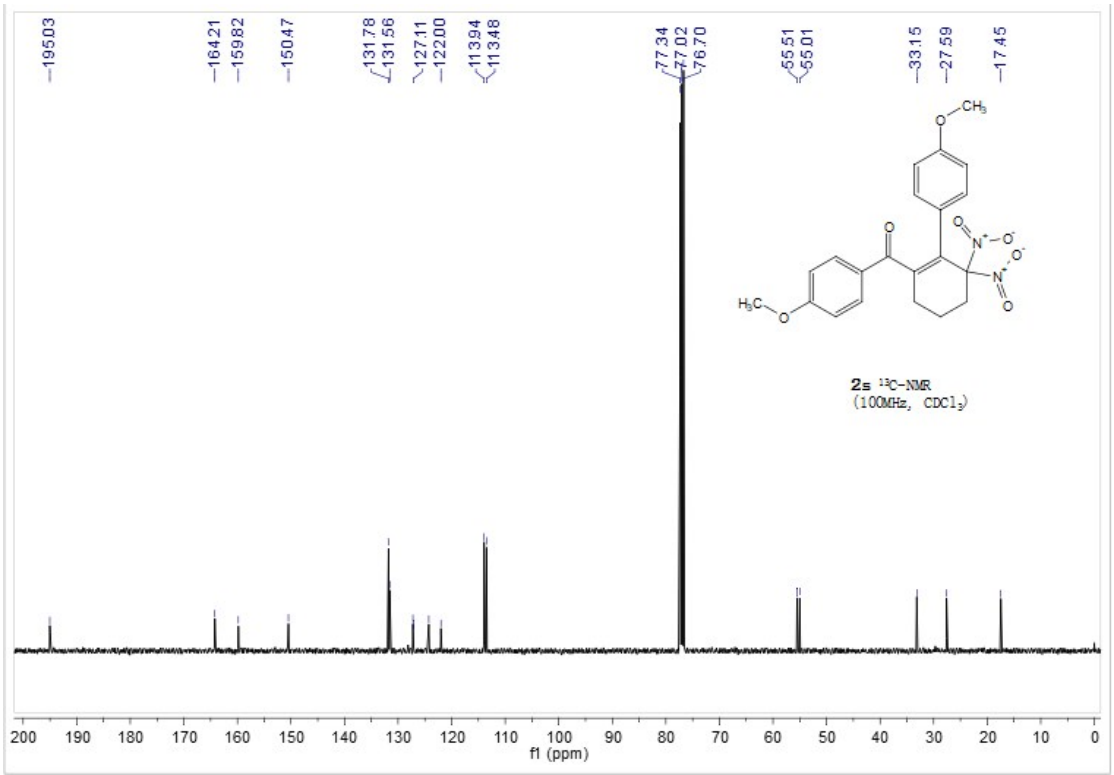

7.87
7.85
7.26
6.85
6.57
6.55
4.29
4.20
3.84
3.73
3.64
3.19
1.30
1.28
1.26
6.98
6.88
6.85
2.00
4.00
3.00
2.00
3.00
2.00
6.01
f1 (ppm)
2q ^{1}H-NMR
(400MHz, CDCl$_3$)

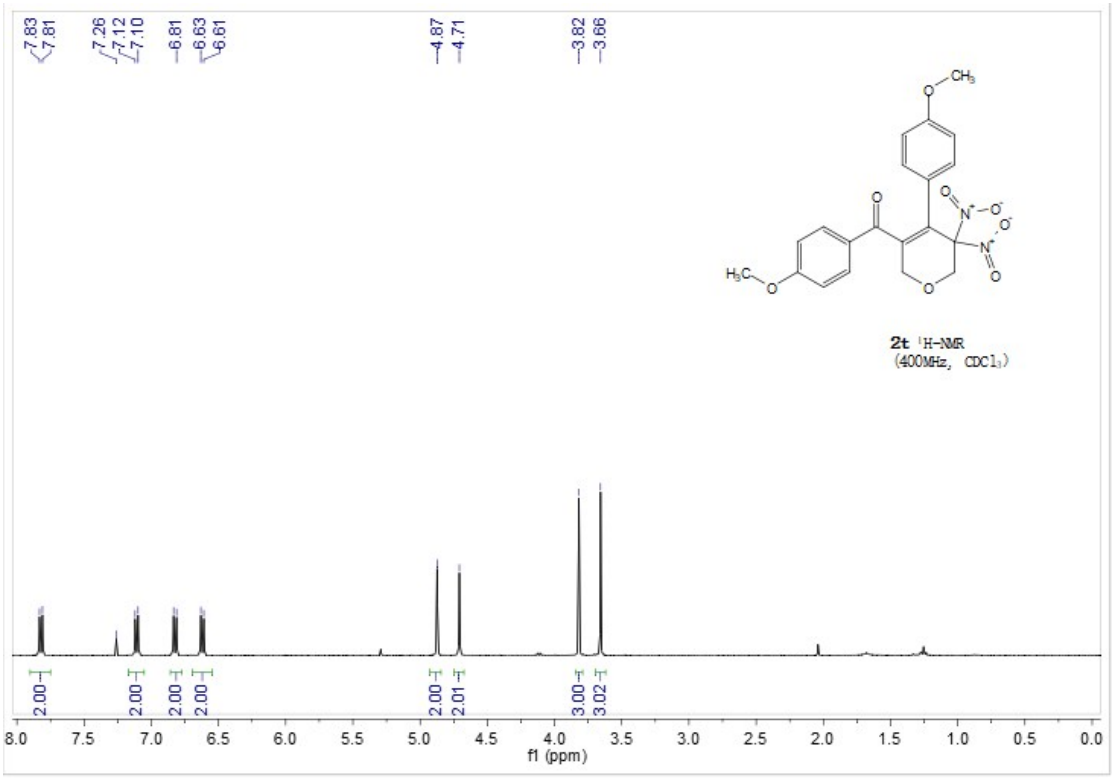

194.03
168.34
164.39
159.92
149.76
132.11
131.82
125.93
120.43
113.95
113.49
77.36
77.04
76.72
63.04
55.52
55.01
50.50
35.28
32.57
13.81
127.29
123.42
f1 (ppm)
2q ^{13}C-NMR
(100MHz, CDCl$_3$)

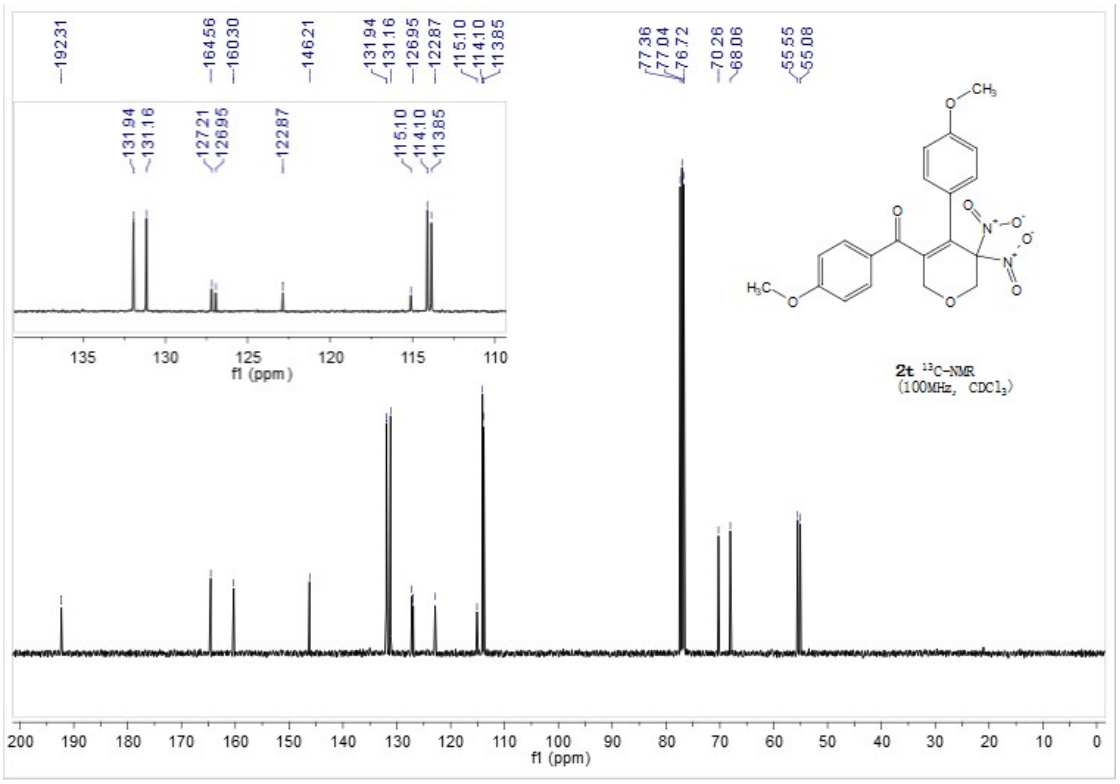

7.89
7.87
7.26
6.86
6.57
6.55
5.13
5.11
5.10
5.08
5.06
5.05
5.03
3.84
3.70
3.64
3.15
1.28
1.26
1.25
1.23
2r ¹H-NMR
(400MHz, CDCl₃)
2.00
2.00
2.00
2.00
3.00
2.00
3.00
2.00
6.01
6.01
f1 (ppm)

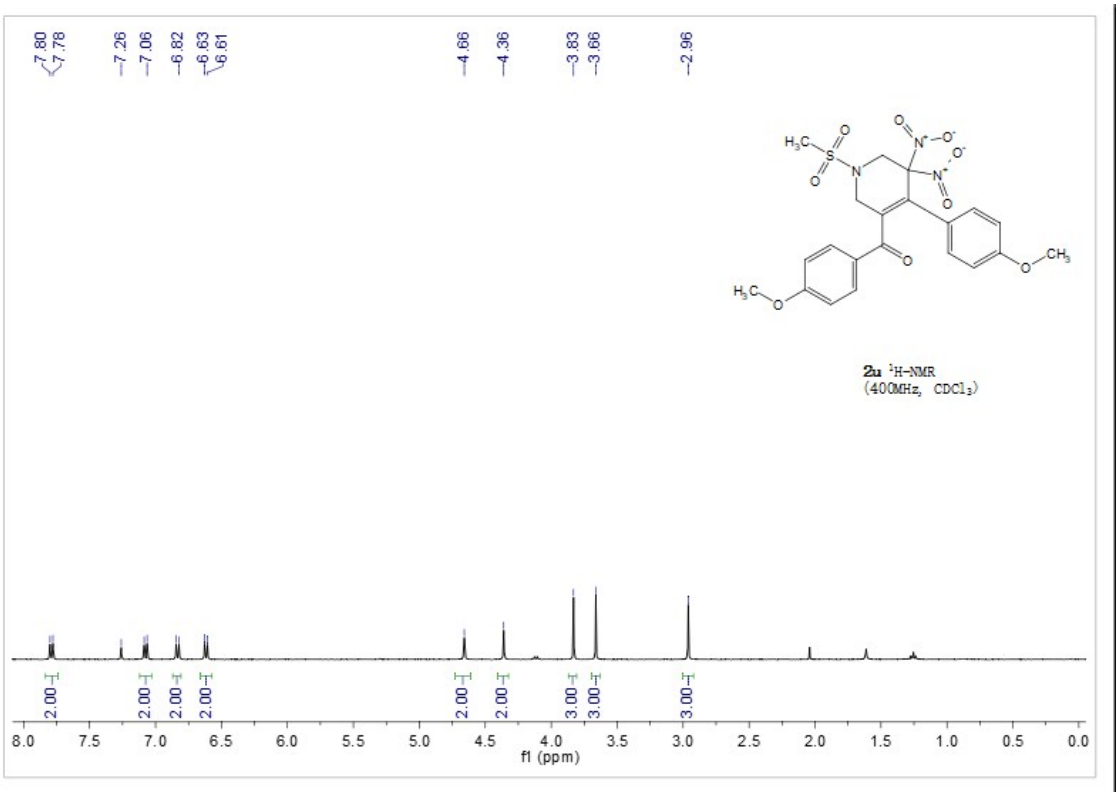

194.18
167.93
164.39
159.89
149.80
132.15
131.83
125.85
120.48
113.95
113.47
77.35
77.03
76.71
71.09
55.52
55.01
50.46
35.06
32.51
21.47
21.20
2r ¹³C-NMR
(100MHz, CDCl₃)
f1 (ppm)


7.81
7.78
7.26
7.03
6.83
6.59
6.57
3.83
3.65
3.12
3.09
2.71
2.69
2.68
2.01
1.95
2.00
2.01
2.03
2.00
f1 (ppm)
2.00
2.01
2.03
2.00
3.04
3.01
2.00
2.02
2.02
f1 (ppm)
2s ^{1}H-NMR
(400MHz, $CDCl_3$)

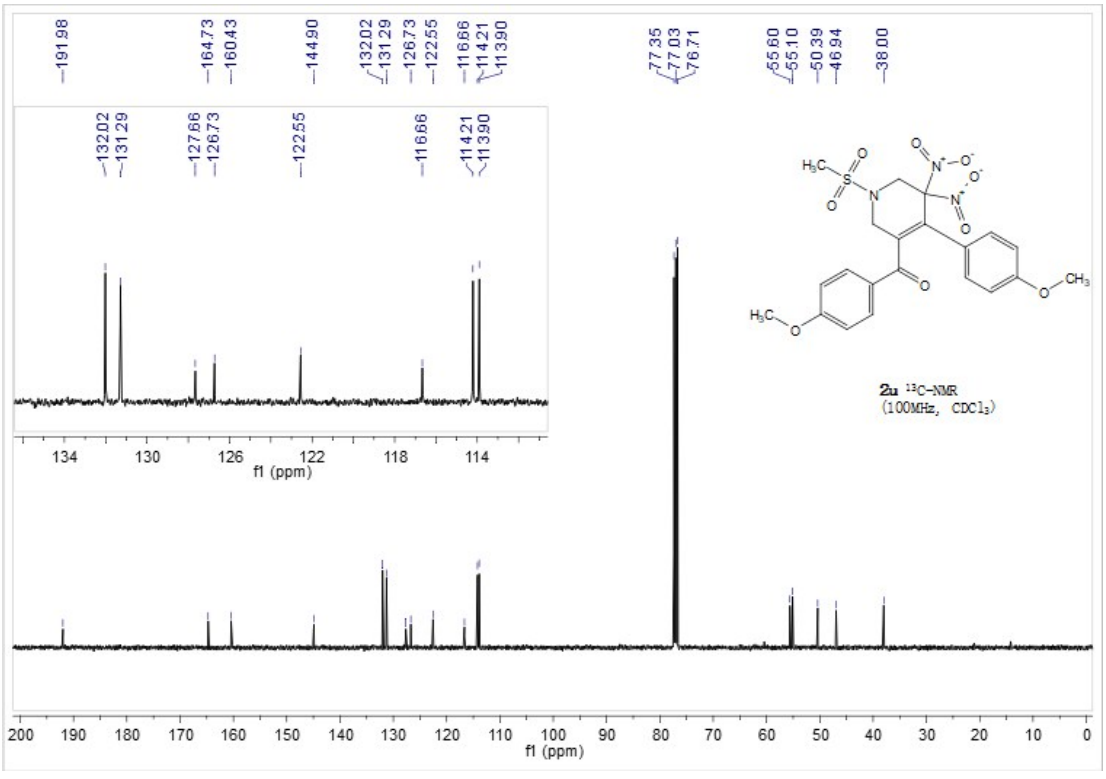

195.03
164.21
159.82
150.47
131.78
131.56
127.11
122.00
113.94
113.48
77.34
77.02
76.70
55.51
55.01
33.15
27.59
17.45
f1 (ppm)
2s ^{13}C-NMR
(100MHz, $CDCl_3$)


7.83
7.81
7.26
7.12
7.10
6.81
6.63
6.61
4.87
4.71
3.82
3.66
2.00
2.00
2.00
2.00
2.00
2.01
3.00
3.02
f1 (ppm)
2t ¹H-NMR
(400MHz, CDCl₃)

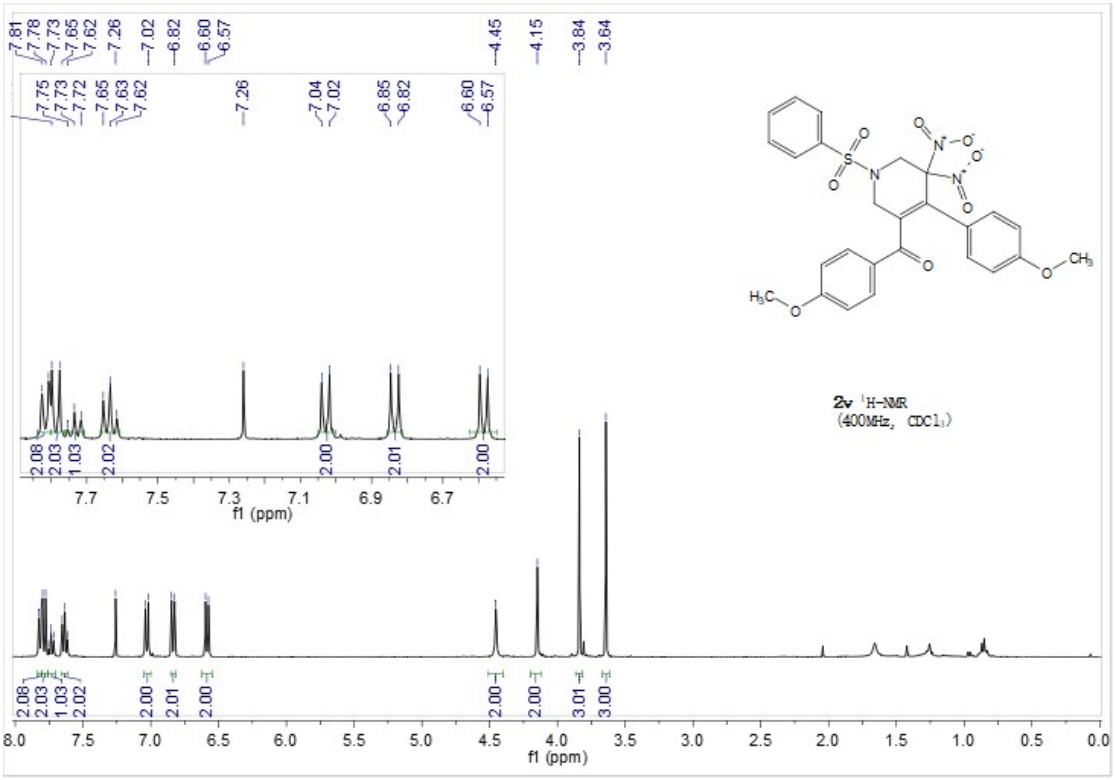

19231
16456
16030
14621
13194
13116
12695
12287
11510
11410
11385
77.36
77.04
76.72
70.26
68.06
55.55
55.08
f1 (ppm)
2t ¹³C-NMR
(100MHz, CDCl₃)

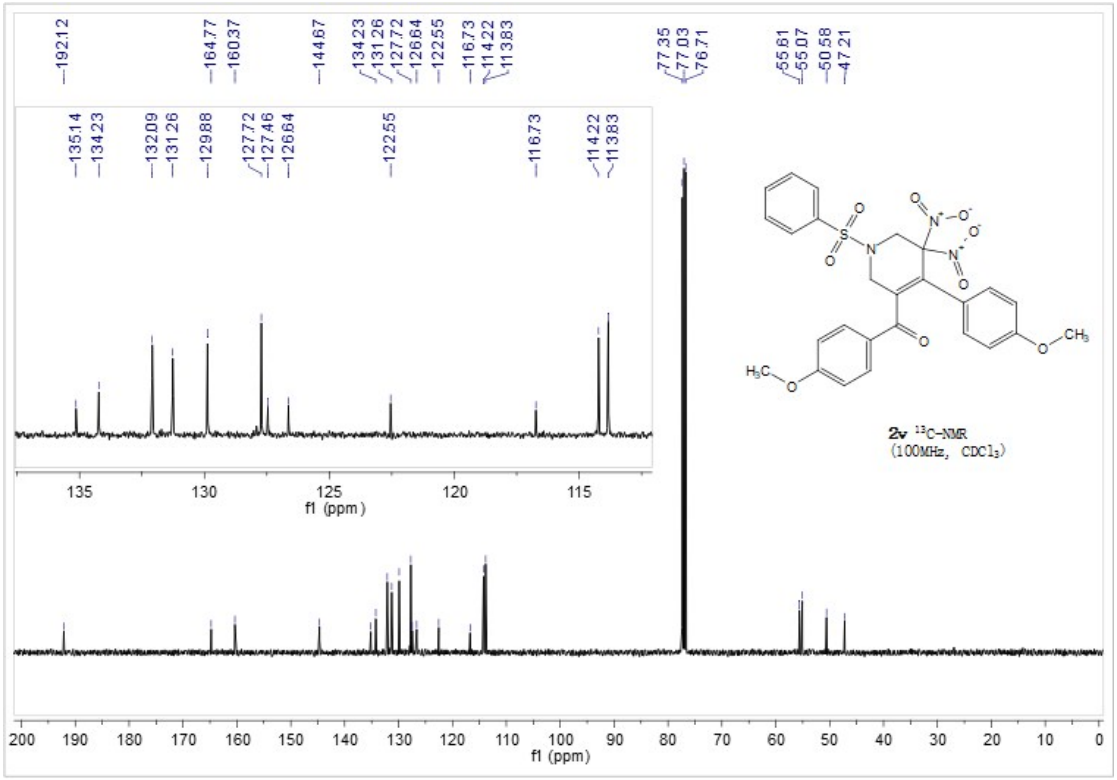


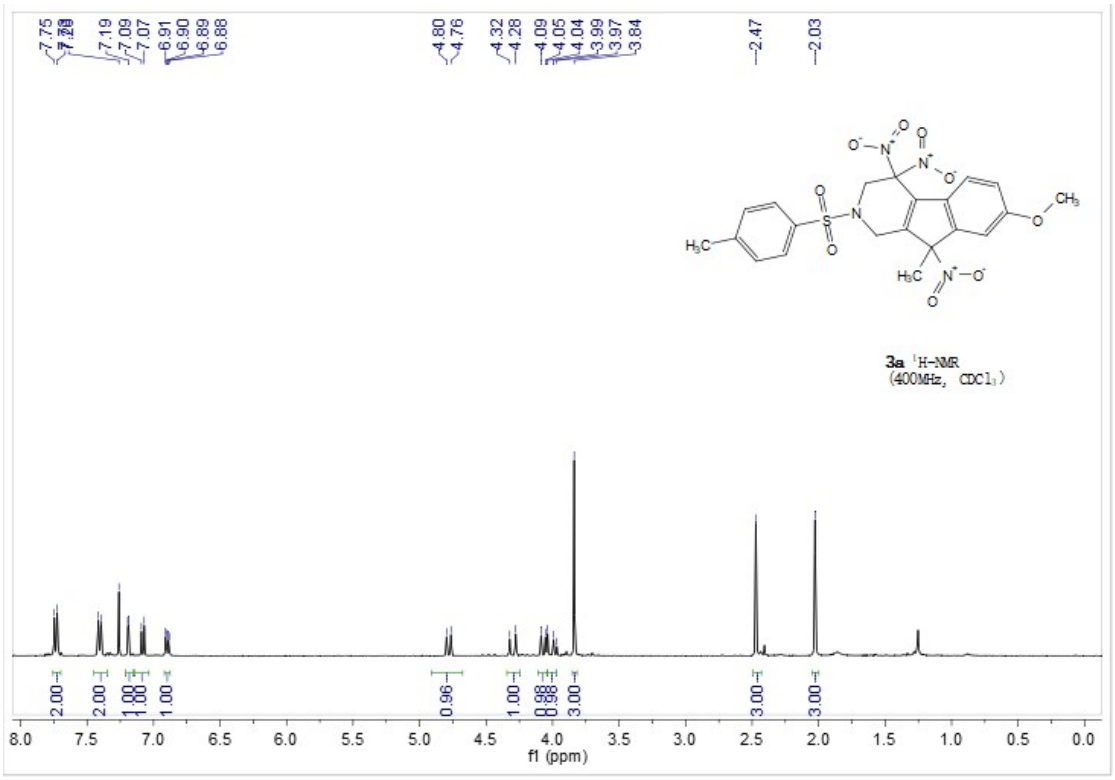
2u ^{1}H-NMR
(400MHz, $CDCl_3$)



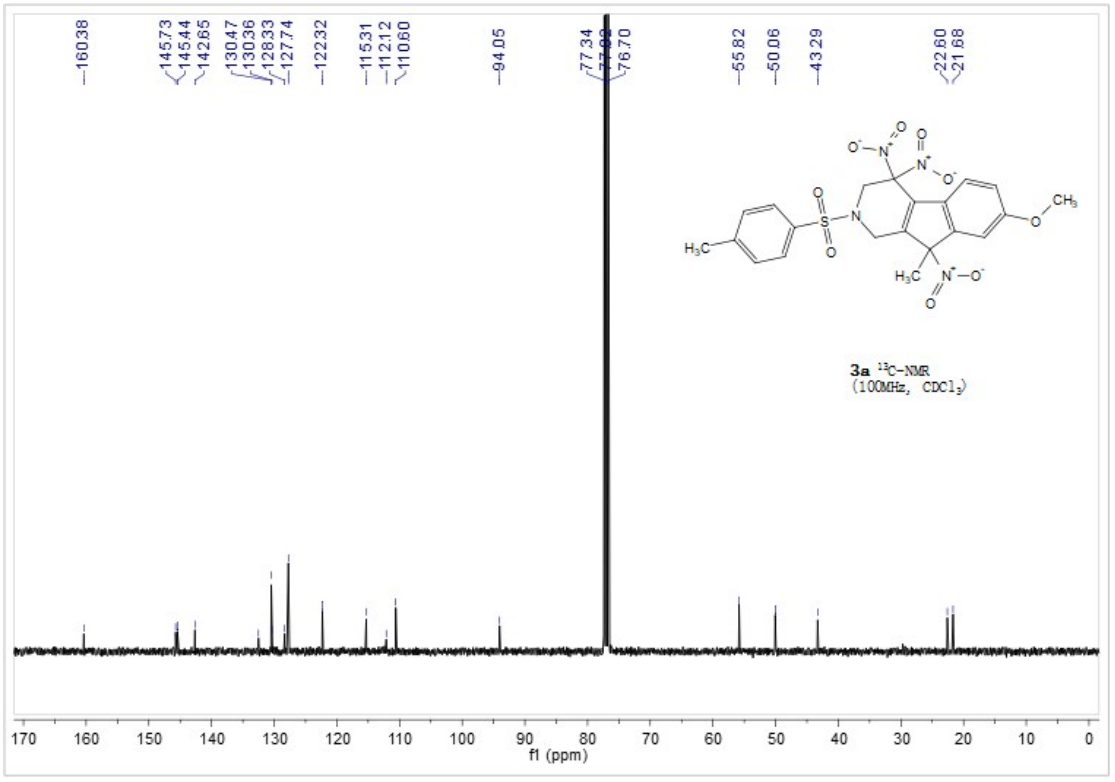
2u ^{13}C-NMR
(100MHz, $CDCl_3$)


2v ^{1}H-NMR
(400MHz, CDCl$_3$)
f1 (ppm)

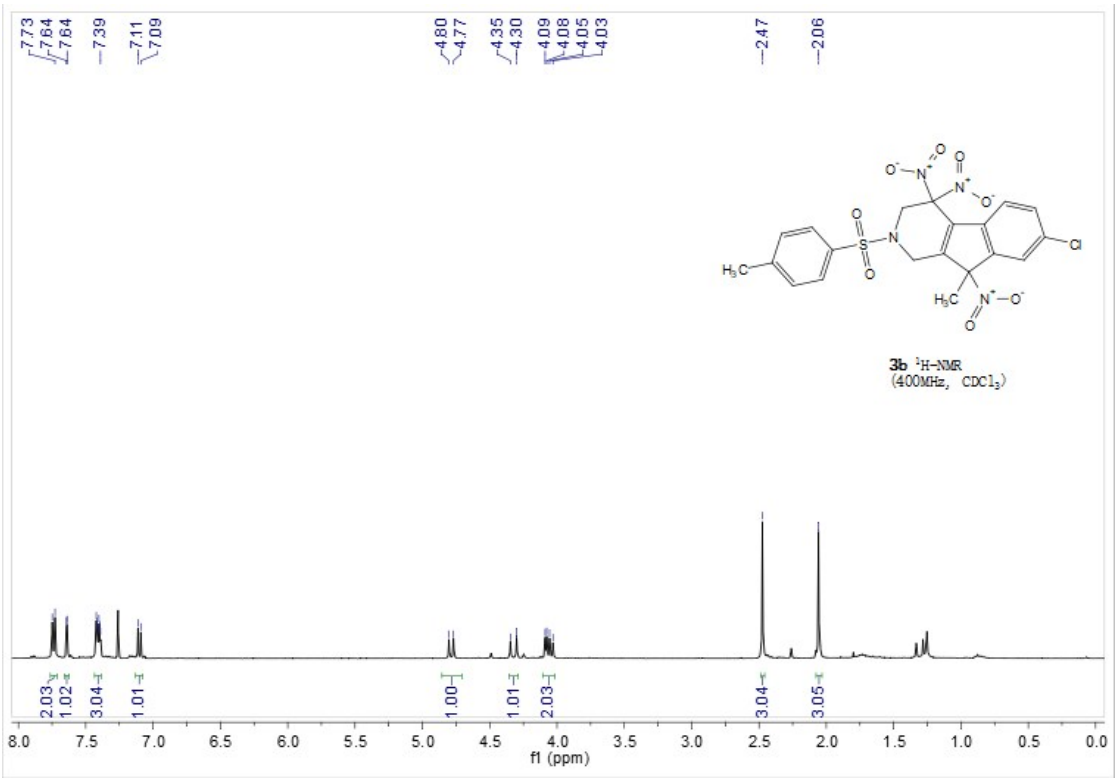

2v ^{13}C-NMR
(100MHz, CDCl$_3$)
f1 (ppm)

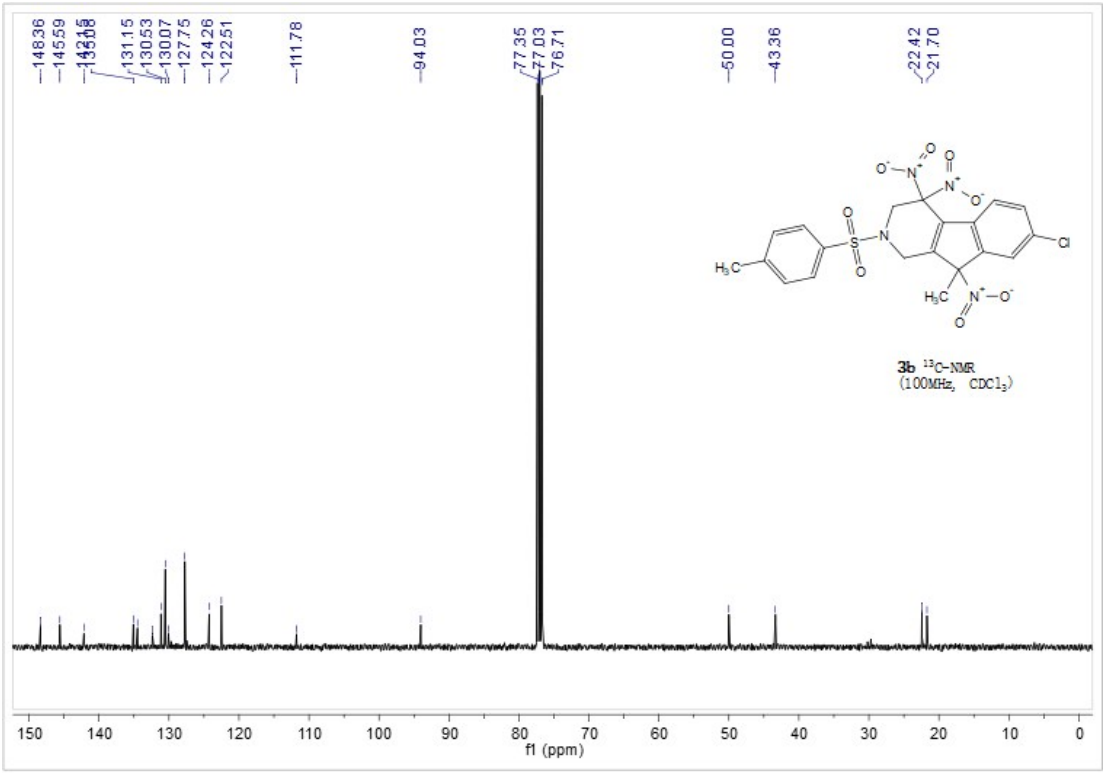


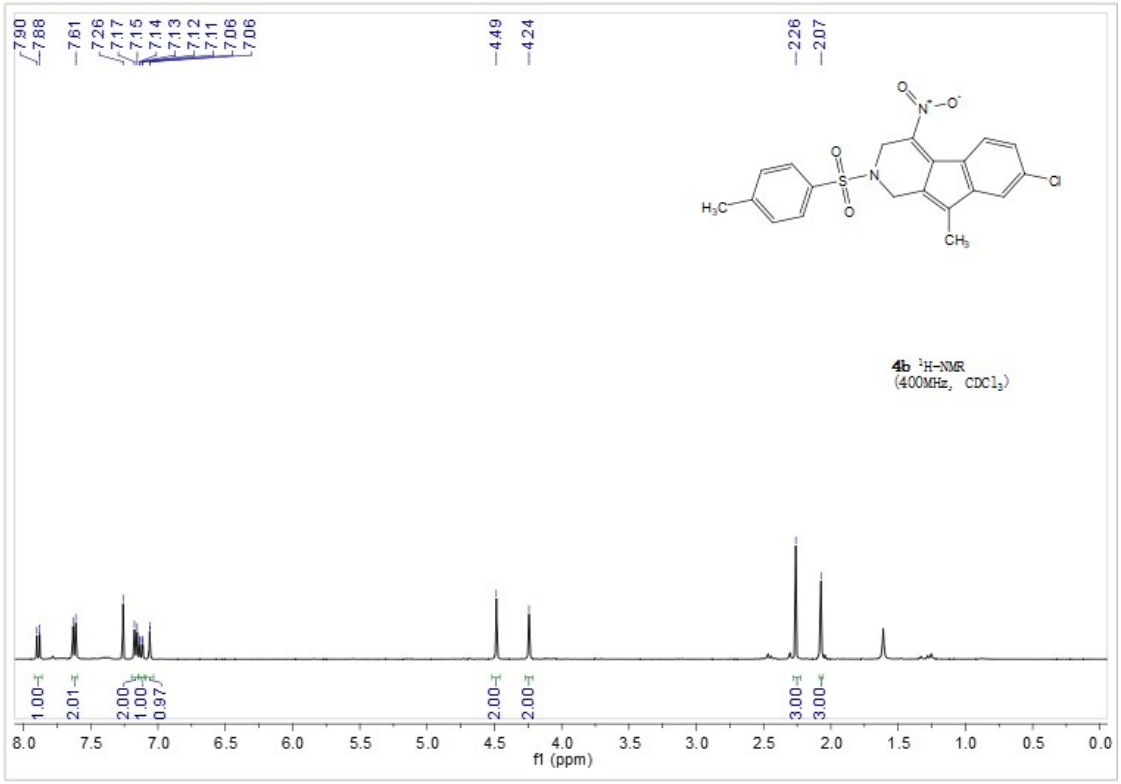
3a ^{1}H-NMR
(400MHz, $CDCl_3$)

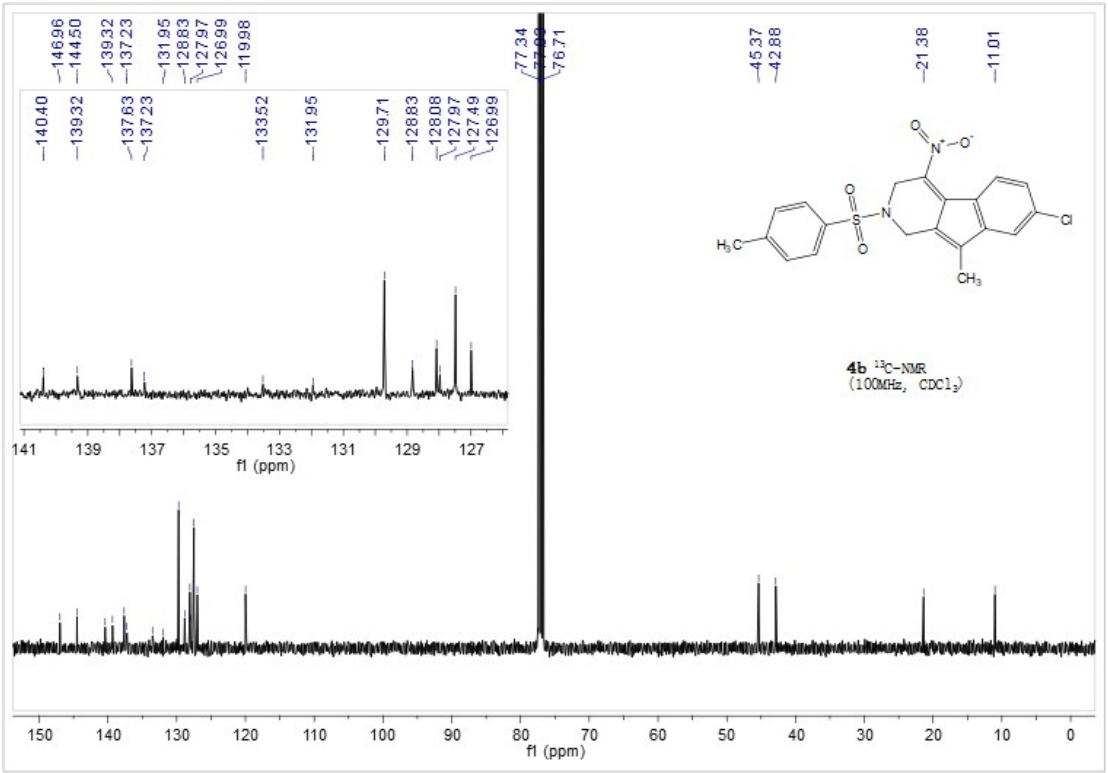


3a ^{13}C-NMR
(100MHz, $CDCl_3$)


7.73
7.64
7.64
7.39
7.11
7.09
4.80
4.77
4.35
4.30
4.09
4.08
4.05
4.03
2.47
2.06
2.03
1.02
3.04
1.01
1.00
1.01
2.03
3.04
3.05
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
f1 (ppm)
3b ^{1}H-NMR
(400MHz, $CDCl_3$)


148.36
145.59
131.15
130.53
130.07
127.75
124.26
122.51
111.78
94.03
77.35
77.03
76.71
50.00
43.36
22.42
21.70
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
3b ^{13}C-NMR
(100MHz, $CDCl_3$)


7.90
7.88
7.61
7.26
7.17
7.15
7.14
7.13
7.12
7.11
7.06
7.06
4.49
4.24
2.26
2.07
1.00
2.01
2.00
1.00
0.97
2.00
2.00
3.00
3.00
f1 (ppm)
4b ^{1}H-NMR
(400MHz, $CDCl_3$)


146.96
144.50
139.32
137.23
131.95
128.83
127.97
126.99
119.98
140.40
139.32
137.63
137.23
133.52
131.95
129.71
128.83
128.08
127.97
127.49
126.99
77.34
77.09
76.71
45.37
42.88
21.38
11.01
f1 (ppm)
4b ^{13}C-NMR
(100MHz, $CDCl_3$)