An Atom Economical Method for Quinoline Derivatives Directly from Substituted *o*-Nitrotoluenes

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Supplementary Information

Contents

1. General Information:

^{1}H NMR spectra were obtained on 400 or 600 MHz spectrometers and ^{13}C NMR spectra were obtained on 100 or 150 MHz spectrometers with $CDCl_3$ as the solvent. The chemical shifts are reported in ppm relative to $CDCl_3$ ($\delta = 7.26$) for ^{1}H NMR and relative to the central $CDCl_3$ resonance ($\delta = 77.0$) for ^{13}C NMR. Coupling constants (*J*) are quoted in Hz. Infrared spectra were recorded on a Perkin-Elmer Model 1600 FT-IR spectrophotometer or Nicolet Magna 550 FT-IR spectrophotometer. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m).

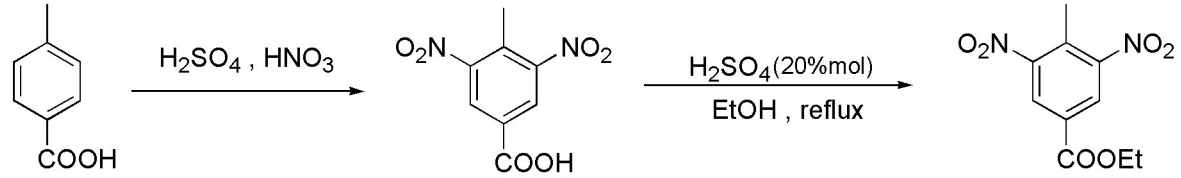
Materials and Methods: Unless otherwise noted, all reactions were performed under an atmosphere of dry N_2 with oven-dried glassware and anhydrous solvents. THF was dried using sodium/benzophenone under a N_2 atmosphere and distilled prior to use. Reactions were monitored by analytical thin layer chromatography on 0.20 mm Anhui Liangchen silica gel plates. Silica gel (200-

300 mesh) (from Anhui Liangchen Chem. Company, Ltd.) was used for flash chromatography. The substrates were prepared according to the literature procedures.[1] Other chemicals or reagents were obtained from commercial sources and used directly.

2. Supporting Data of Extra Experiments

2.1. Preparation of substituted *o*-nitrotoluenes

2.1.1 Preparation of ethyl 4-methyl-3,5-dinitrobenzoate (1f):

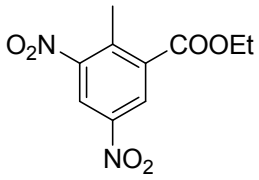


4-Methyl-3,5-dinitro-benzoic acid (S1): Para-toluic acid (2.0 g, 14.7 mmol) was added to a 100-mL 3-neck round bottom flask equipped with a condenser, dropping funnel and magnetic stirrer. The flask was put in a water bath maintained at 20 °C and sulfuric acid (20 mL, 98%) and then nitric acid (8 mL, 70%) were each slowly added over 10 min. The resulting mixture was stirred for 2 h at ambient temperature and then poured into ice water (40 mL) to quench the reaction. A yellow solid was formed. The solid was filtered, washed with cold water and dried in an oven over night (3.18 g, 96%).

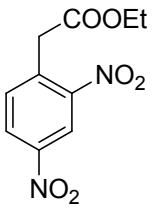
Ethyl 4-methyl-3,5-dinitrobenzoate (1f): A mixture of 4-methyl-3,5-dinitro-benzoic acid (14.1 mmol), sulfuric acid (2.82 mmol, 98%) and ethanol (20 mL) was refluxed overnight. After cooling to room temperate, a yellow solid was formed. The solid was filtered, washed with cold water and dried in an oven over night. (3.5 g, 98%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.43 (t, J = 7.2 Hz, 3H), 2.63 (s, 3H), 4.46 (q, J = 7.2 Hz, 2H), 8.59 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 162.52, 151.62, 131.34, 130.67, 127.82, 62.66, 15.18, 14.18; HRMS (ESI) m/z: 255.0937 $[M + H]^+$ (calcd. 255.0939); IR

(KBr): *v* 3075, 2993, 1721, 1543, 1344, 1284 cm^{-1}; Analytical Data. Found (calcd) for: $C_{10}H_{10}N_2O_6$ C, 47.24 (47.25); H, 3.95 (3.97); N, 11.07 (11.02).

The other substituted o-nitrotoluenes were prepared as above using the corresponding acid.

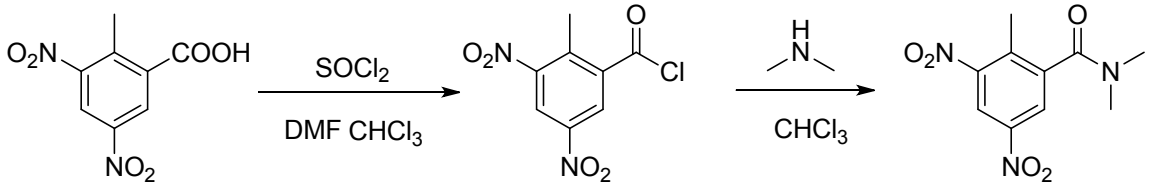


Ethyl 2-methyl-3,5-dinitrobenzoate (1i): Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 1.44 (t, J = 7.2 Hz, 3H), 2.73 (s, 3H), 4.46 (q, J = 6.8 Hz, 2H), 8.66 (d, J = 2 Hz, 1H), 8.80 (d, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.30, 151.81, 145.43, 140.01, 135.13, 127.57, 121.28, 62.68, 16.65,14.12; HRMS (ESI) m/z: 255.0934 $[M + H]^+$ (calcd. 255.0939); IR (KBr): *v* 3103, 2990, 1729, 1614, 1538, 1400, 1152 cm^{-1}; Analytical Data. Found (calcd) for: $C_{10}H_{10}N_2O_6$ C, 47.26 (47.25); H, 3.95 (3.97); N, 11.05 (11.02).



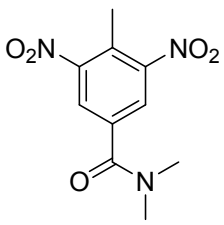
Ethyl 2-(2,4-dinitrophenyl)acetate (1m): Yellow solid. ^1H NMR (400 MHz, $CDCl_3$): δ 1.28 (t, J = 6.8 Hz, 3H), 4.16 (s, 2H), 4.21 (q, J = 7.2 Hz, 2H), 7.63 (d, J = 8.4 Hz, 1H), 8.46 (dd, J = 2, 8.4 Hz, 1H), 8.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.55, 148.99, 147.43, 136.48, 127.44, 120.73, 61.86, 39.70, 14.07; HRMS (ESI) m/z: 255.0935 $[M + H]^+$ (calcd. 255.0939); IR (KBr): *v* 3111, 2987, 1734, 1609, 1536, 1348, 1026 cm^{-1}; Analytical Data. Found (calcd) for: $C_{10}H_{10}N_2O_6$ C, 47.21 (47.25); H, 3.92 (3.97); N, 11.00 (11.02).

2.1.2 Preparation of N,N,2-trimethyl-3,5-dinitrobenzamide (1h):



2-Methyl-3,5-dinitro-benzoyl chloride (S2): First 2-methyl-3,5-dinitro-benzoic acid (2.0 g, 8.8 mmol) was added to a 100-mL 3-neck round bottom flask equipped with a condenser, dropping funnel and magnetic stirrer. Then chloroform (20 mL) and DMF (5 mol %) were added. The mixture was heated to 80 °C, and thionyl chloride (2.6 g, 22 mmol) was slowly added over 10 min. The mixture was refluxed overnight and then, the solvent and the excess sulfoxide chloride was removed under reduced pressure to give a brown oil (2.1 g, 98%).

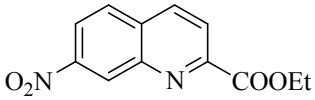
N,N,2-trimethyl-3,5-dinitrobenzamide (1h): A mixture of 2-methyl-3,5-dinitro-benzoyl chloride (2.1 g, 8.6 mmol) and chloroform (20 mL) was stirred in an ice-bath while dimethylamine (7.7 g, 17.2 mmol) was slowly added, The reaction mixture was warmed to room temperature and stirred 2-3 h. Then a brown solid was formed. The solid was filtered, washed with benzene and dried in an oven over night (2.1 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.58 (s, 3H), 2.91 (s, 3H), 3.21 (s, 3H), 8.29 (d, J = 2 Hz, 1H), 8.72 (d, J = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.66, 150.33, 146.05, 141.50, 136.61, 124.48, 119.74; HRMS (ESI) m/z: 254.0495 $[M + H]^+$ (calcd. 254.0499); IR (KBr): v 3097, 2934, 1647, 1537, 1349 cm^{-1}; Analytical Data. Found (calcd) for: $C_{10}H_{11}N_3O_5$ C, 47.40 (47.43); H, 4.37 (4.38); N, 16.61 (16.59).



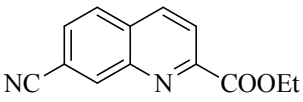
N,N,4-trimethyl-3,5-dinitrobenzamide (1g): Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.60 (s, 3H), 3.07 (s, 3H), 3.14 (s, 3H), 8.08 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.41, 151.37, 136.06, 128.47, 126.30, 39.52, 35.71, 14.99; HRMS (ESI) m/z: 254.0496 $[M + H]^+$ (calcd. 254.0499); IR (KBr): ν 3042, 2932, 1731, 1538, 1352, 1123 cm^{-1}; Analytical Data. Found (calcd) for: $C_{10}H_{11}N_3O_5$ C, 47.46 (47.43); H, 4.39 (4.38); N, 16.58 (16.59).

2.2. General Experimental Procedure for Synthesis of Quinoline Derivates

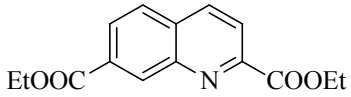
An oven-dried 10-mL round-bottom flask equipped with a condenser and a Teflon-coated stir bar was charged with a solution of 1.0 mmol **1(a - r)** in 5.0 mL THF. Next, Cs_2CO_3 (2.0 mmol, 2 equiv.) and olefin (3.0 mmol, 3 equiv.) were added and the mixture was stirred and heated to 65 ^{o}C for 6-12 h under N_2. Then, the solvent and the excess olefins were removed and recycled under reduced pressure, and the products were extracted with dichloromethane, and purified by column chromatography on silica gel (using dichloromethane as the eluting solvent) to give the desired quinoline derivatives **3** and **4**.



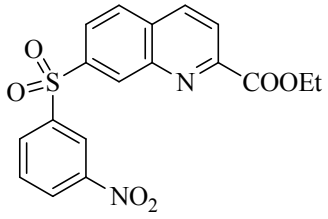
Ethyl 7-nitroquinoline-2-carboxylate (3a): Yellow solid. Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.16 (s, 1H), 8.43 (d, J = 8.6 Hz, 1H), 8.37 (d, J = 9.0 Hz, 1H), 8.32 (d, J = 8.6 Hz, 1H), 8.05 (d, J = 8.9 Hz, 1H), 4.56 (q, J = 7.1 Hz, 2H), 1.49 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.56, 150.60, 148.63, 146.50, 137.32, 132.03, 129.28, 126.88, 123.80, 121.86, 62.71, 14.32; HRMS (ESI) m/z: 269.0531 $[M + Na]^+$ (calcd. 269.0538); IR (KBr): ν 3102, 1713, 1606, 1534, 1447, 1348 cm^{-1}; Analytical Data. Found (calcd) for: $C_{12}H_{10}N_2O_4$ C, 58.59 (58.54); H, 4.04 (4.09); N, 11.36 (11.38).



Ethyl 7-cyanoquinoline-2-carboxylate (3b): Yellow solid. Yield: 74%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (s, 1H), 8.40 (d, J = 8.6 Hz, 1H), 8.34 (d, J = 8.6 Hz, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 4.60 (q, J = 7.1 Hz, 2H), 1.53 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.66, 150.24, 143.34, 137.30, 136.54, 129.56, 129.07, 128.96, 123.41, 117.96, 113.97, 60.63, 14.10; HRMS (ESI) m/z: 249.0633 $[M + Na]^+$ (calcd. 249.0640); IR (KBr): ν 3085, 2981, 2938, 2235, 1731, 1615, 1537, 1448, 1357 cm^{-1}; Analytical Data. Found (calcd) for: $C_{13}H_{10}N_2O_2$ C, 69.06 (69.02); H, 4.46 (4.46); N, 12.39 (12.38).

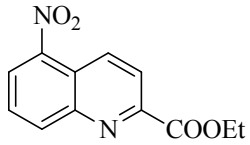


Diethyl quinoline-2,7-dicarboxylate (3c): Yellow solid. Yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.35 (s, 1H), 9.21 (d, J = 9.0 Hz, 1H), 9.06 (d, J = 1.4 Hz, 1H), 8.60 (d, J = 10.8 Hz, 1H), 8.49 (d, J = 9.1 Hz, 1H), 4.63 (q, J = 7.1 Hz, 2H), 4.53 (dd, J = 14.2, 7.1 Hz, 2H), 1.52 (dt, J = 17.7, 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.13, 163.83, 150.36, 147.37, 139.00, 133.55, 130.87, 128.06, 125.77, 125.10, 124.06, 62.78, 62.37, 14.28, 14.21; HRMS (ESI) m/z: 296.0896 $[M + Na]^+$ (calcd. 296.0899); IR (KBr): ν 3092, 2983, 2937, 1726, 1625, 1455 cm^{-1}; Analytical Data. Found (calcd) for: $C_{15}H_{15}NO_4$ C, 65.93 (65,92); H, 5.63 (5.53); N, 5.11 (5.13).

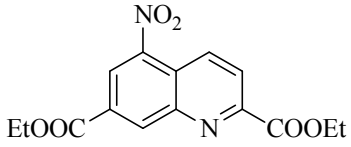


Ethyl 7-((3-nitrophenyl)sulfonyl)quinoline-2-carboxylate (3d): Colorless liquid. Yield: 81%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.94 (s, 1H), 8.79 (s, 1H), 8.45-8.35 (m, 2H), 8.31 (t, J = 9.6 Hz, 2H),

8.11-8.03 (m, 2H), 7.77 (q, J = 8.0 Hz, 1H), 4.54 (q, J = 7.1Hz, 2H), 1.47 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.48, 150.34, 148.44, 146.43, 143.08, 141.66, 137.53, 133.51, 132.06, 131.52, 131.08, 130.05, 128.12, 124.92, 123.87, 123.15, 62.68, 14.30; HRMS (ESI) m/z: 409.0465 $[M + Na]^+$ (calcd. 409.0470); IR (KBr): ν 3085, 2981, 2938, 1731, 1605, 1531, 1448, 1352 cm^{-1}; Analytical Data. Found (calcd) for: $C_{18}H_{14}N_2O_6S$ C, 55.96 (55.95); H, 3.67 (3.65); N, 7.26 (7.25).

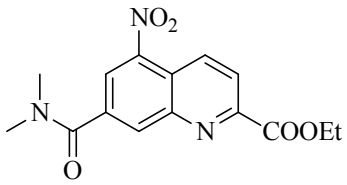


Ethyl 5-nitroquinoline-2-carboxylate (3e): Yellow solid. Yield: 66%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.20 (d, J = 9.0 Hz, 1H), 8.66 (d, J = 8.4 Hz, 1H), 8.52 (d, J = 7.7 Hz, 1H), 8.42 (d, J = 9.0 Hz, 1H), 7.91 (t, J = 8.1 Hz, 1H), 4.61 (q, J = 7.1 Hz, 2H), 1.53 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.48, 149.58, 147.69, 145.41, 137.71, 133.53, 128.21, 126.38, 123.74, 122.16, 62.64, 14.30; HRMS (ESI) m/z: 269.0535 $[M + Na]^+$ (calcd. 269.0538); IR (KBr): ν 3096, 2982, 2886, 1732, 1613, 1534, 1462, 1352 cm^{-1}; Analytical Data. Found (calcd) for: $C_{12}H_{10}N_2O_4$ C, 58.57 (58.54); H, 4.08 (4.09); N, 11.36 (11.38).

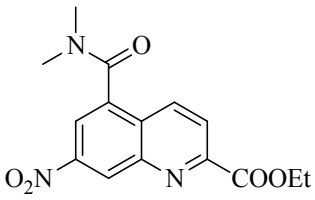


Diethyl 5-nitroquinoline-2,7-dicarboxylate (3f): Yellow solid. Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.32 (s, 1H), 9.18 (d, J = 9.2 Hz, 1H), 9.03 (s, 1H), 8.46 (d, J = 8.8 Hz, 1H), 4.60 (q, J = 6.8 Hz, 2H), 4.51 (q, J = 6.8 Hz, 2H), 1.51 (t, J = 7.2 Hz, 3H), 1.47 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.15, 163.85, 150.33, 147.37, 145.56, 139.08, 133.60, 130.85, 125.85, 125.14, 124.09, 62.83, 62.39, 14.30, 14.23; HRMS (ESI) m/z: 319.0927 $[M + H]^+$ (calcd. 319.0924);

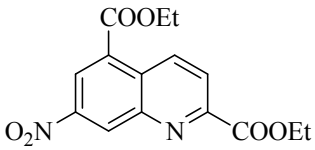
IR (KBr): *v* 3111, 2986, 1723, 1534, 1294, 1109 cm^{-1}; Analytical Data. Found (calcd) for: $C_{15}H_{14}N_2O_6$ C, 56.61 (56.60); H, 4.41 (4.43); N, 8.81 (8.80).



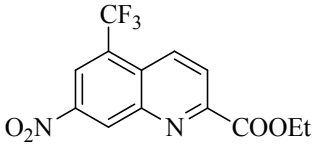
Ethyl 7-(dimethylcarbamoyl)-5-nitroquinoline-2-carboxylate (3g): Yellow solid. Yield: 73%. ^1H NMR (400 MHz, $CDCl_3$): δ 9.41 (d, J = 8.8 Hz, 1H), 8.61 (d, J = 4.8 Hz, 2H), 8.43 (d, J = 8.8 Hz, 1H), 4,59 (q, J = 7.2 Hz, 2H), 3.21 (s, 3H), 3.12 (s, 3H), 1.51 (t, J = 7.2, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.75, 164.21, 150.21, 147.14, 145.66, 135.25, 135.12, 133.60, 125.93, 124.48, 122.34, 62.81, 39.67, 35.73, 14.29; HRMS (ESI) m/z: 318.1088 $[M + H]^+$ (calcd. 318.1084); IR (KBr): *v* 3321, 3157, 2906, 1701, 1516, 1326, 1162 cm^{-1}; Analytical Data. Found (calcd) for: $C_{15}H_{15}N_3O_5$ C, 56.81 (56.78); H, 4.75 (4.76); N, 13.26 (13.24).



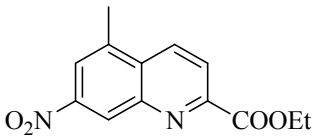
Ethyl 5-(dimethylcarbamoyl)-7-nitroquinoline-2-carboxylate (3h): Yellow solid. Yield: 80%. ^1H NMR (400 MHz, $CDCl_3$): δ 9.29 (s, 1H), 8.44 (d, J = 8.8 Hz, 1H), 8.38-8.36 (m, 2H), 4.59 (q, J = 7.2 Hz, 2H), 3.30 (s, 3H), 2.91 (s, 3H), 1.51 (t, J = 7.2, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.97, 164.29, 150.93, 147.66, 146.78, 136.59, 135.18, 129.11, 127.49, 124.43, 119.69, 62.85, 39.06, 35.24, 14.30; HRMS (ESI) m/z: 318.1087 $[M + H]^+$ (calcd. 318.1084); IR (KBr): *v* 3426, 3092, 2927, 1725, 1643, 1533, 1399, 1276, 1118 cm^{-1}; Analytical Data. Found (calcd) for: $C_{15}H_{15}N_3O_5$ C,56.84 (56.78); H, 4.74 (4.76); N, 13.26 (13.24).



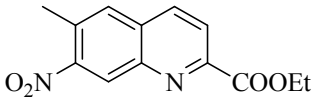
Diethyl 7-nitroquinoline-2,5-dicarboxylate (3i): Yellow solid. Yield: 81%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.65 (d, J = 8.8 Hz, 1H), 9.41 (d, J = 1.6 Hz, 1H), 9.13 (d, J = 2.4 Hz, 1H), 8.45 (d, J = 9.2 H, 1H), 4.62 (q, J = 7.2 Hz, 2H), 4.57 (q, J = 7.2 Hz, 2H), 1.56-1.52 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.52, 164.33, 150.63, 147.27, 147.08, 136.18, 131.00, 129.07, 125.34, 124.82, 62.79, 62.39, 14.31, 14.28; HRMS (ESI) m/z: 319.0924 $[M + H]^+$ (calcd. 319.0924); IR (KBr): ν 3094, 2957, 2923, 1723, 1536, 1293, 1087 cm^{-1}; Analytical Data. Found (calcd) for: $C_{15}H_{14}N_2O_6$ C, 56.62 (56.60); H, 4.47 (4.43); N, 8.85 (8.80).



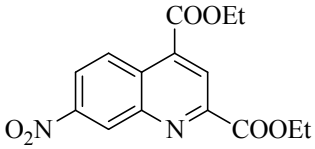
Ethyl 7-nitro-5-(trifluoromethyl)quinoline-2-carboxylate (3j): Yellow liquid. Yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.46 (s, 1H), 8.84 (s, 1H), 8.77 (d, J = 8.9 Hz, 1H), 8.50 (d, J = 9.0 Hz, 1H), 4.63 (q, J = 7.1 Hz, 2H), 1.55 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDC_{l3}): δ 164.21, 151.37, 147.42, 147.23, 134.42, 134.41, 131.14, 128.51, 125.19, 123.51, 120.93, 63.24, 14.53; HRMS (ESI) m/z: 337.0410 $[M + Na]^+$ (calcd. 337.0412); IR (KBr): ν 3072, 2984, 2949, 1731, 1532, 1345, 1132cm^{-1}; Analytical Data. Found (calcd) for: $C_{13}H_9F_3N_2O_4$ C, 46.51 (46.69); H, 2.81 (2.89); F, 18.16 (18.14); N, 8.87 (8.92).



Ethyl 5-methyl-7-nitroquinoline-2-carboxylate (3k): Yellow solid. Yield: 79%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.10 (s, 1H), 8.57 (d, J = 8.8 Hz, 1H), 8.38 (d, J = 8.8 Hz, 1H), 8.28 (s, 1H), 4.61 (q, J = 7.1 Hz, 2H), 2.85 (s, 3H), 1.54 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.90, 150.31, 148.36, 147.15, 137.56, 134.20, 131.83, 125.24, 123.63, 122.01, 62.91, 19.23, 14.57; HRMS (ESI) m/z: 283.0690 $[M + Na]^+$ (calcd. 283.0694); IR (KBr): v 3105, 2978, 2923, 1733, 1600, 1533, 1459, 1357cm^{-1}; Analytical Data. Found (calcd) for: $C_{13}H_{12}N_2O_4$ C, 60.04 (60.00); H, 4.69 (4.65); N, 10.79 (10.76).

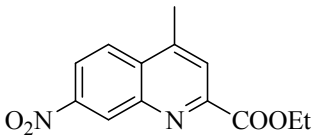


Ethyl 6-methyl-7-nitroquinoline-2-carboxylate (3l): Yellow solid. Yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.93 (s, 1H), 8.32 (d, J = 1.8 Hz, 2H), 7.85 (s, 1H), 4.60 (dd, J = 14.0, 7.0 Hz, 2H), 2.78 (s, 3H), 1.52 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.94, 150.08, 145.50, 136.63, 132.99, 132.33, 130.95, 127.29, 123.79, 121.22, 62.84, 20.54, 14.56; HRMS (ESI) m/z: 283.0683 $[M + Na]^+$ (calcd. 283.0694); IR (KBr): v 3120, 2980, 2936, 1732, 1614, 1531, 1456, 1346 cm^{-1}; Analytical Data. Found (calcd) for: $C_{13}H_{12}N_2O_4$ C, 60.02 (60.00); H, 4.69 (4.65); N, 10.71 (10.76).

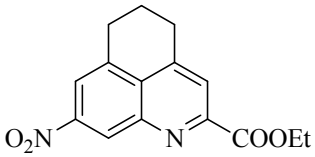


Diethyl 7-nitroquinoline-2,4-dicarboxylate (3m): Yellow solid. Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.23 (d, J = 2 Hz, 1H), 9.08 (d, J = 9.6 Hz, 1H), 8,79 (s, 1H), 8.47 (dd, J = 2.4, 9.6 Hz, 1H), 4.63-4.53 (m, 4H), 1.53-1.48 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.64, 163.04, 149.34, 147.40, 146.76, 135.58, 128.19, 126.76, 125.92, 123.73, 121.97, 61.93, 61.67, 13.29, 13.19; HRMS (ESI) m/z: 319.0920 $[M + H]^+$ (calcd. 319.0924); IR (KBr): v 3103, 2924, 1719, 1534, 1341, 1245,

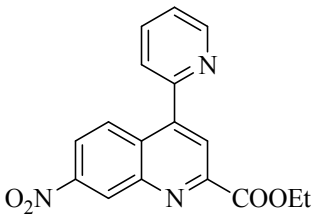
1142 cm^{-1}; Analytical Data. Found (calcd) for: $C_{15}H_{14}N_2O_6$ C, 56.57 (56.60); H, 4.44 (4.43); N, 8.85 (8.80).



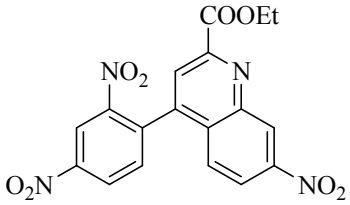
Ethyl 4-methyl-7-nitroquinoline-2-carboxylate (3n): Yellow solid. Yield: 79%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.23 (d, J = 1.7 Hz, 1H), 8.43 (dd, J = 9.1, 1.7 Hz, 1H), 8.22 (d, J = 12.3 Hz, 2H), 4.60 (q, J = 7.1 Hz, 2H), 2.87 (s, 3H), 1.52 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.81, 150.25, 148.36, 146.44, 132.25, 127.30, 125.59, 124.19, 121.45, 62.61, 18.98, 14.32; HRMS (ESI) m/z: 283.0686 $[M + Na]^+$ (calcd. 283.0695); IR (KBr): v 3100, 2980, 2936, 1731, 1604, 1536, 1455 , 1348 cm^{-1}; Analytical Data. Found (calcd) for: $C_{13}H_{12}N_2O_4$ C, 60.01 (60.00); H, 4.68 (4.65); N, 10.77 (10.76).



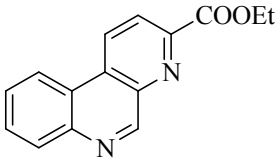
Ethyl 8-nitro-5,6-dihydro-4H-benzo[de]quinoline-2-carboxylate (3o): Yellow solid. Yield: 63%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.06 (s, 1H), 8.17 (s, 1H), 8.11 (s, 1H), 4.60 (q, J = 7.1 Hz, 2H), 3.26 (dt, J = 11.9, 6.0 Hz, 4H), 2.20 (dt, J = 12.3, 6.2 Hz, 2H), 1.53 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.02, 149.95, 148.15, 146.98, 139.09, 129.72, 124.52, 121.50, 120.48, 119.05 , 62.51, 30.60, 29.67, 22.25, 14.31; HRMS (ESI) m/z: 309.0845 $[M + Na]^+$ (calcd. 309.0851); IR (KBr): v 3105, 2924, 2835, 1723, 1614, 1599, 1537, 1460, 1440, 1345 cm^{-1}; Analytical Data. Found (calcd) for: $C_{15}H_{14}N_2O_4$ C,62.96 (62.93); H, 4.92 (4.93); N, 9.71 (9.79).



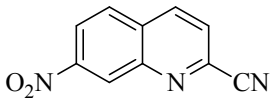
Ethyl 7-nitro-4-(pyridin-2-yl)quinoline-2-carboxylate (3p): Yellow solid. Yield: 67%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.30 (s, 1H), 8.88 (d, J = 4.4 Hz, 1H), 8.51 (d, J = 9.2 Hz, 1H), 8.45 (s, 1H), 8.41-8.38 (m, 1H), 7.98 (t, J = 7.6 Hz, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.53-7.50 (m, 1H), 4.61 (q, J = 7.2 Hz, 2H), 1.52 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.55, 155.20, 150.21, 150.08, 148.36, 147.69, 147.62, 137.44, 130.12, 128.02, 127.06, 124.93, 123.96, 123.77, 121.94, 62.79, 14.35; HRMS (ESI) m/z: 324.0978 $[M + H]^+$ (calcd. 324.0978); IR (KBr): ν 3137, 2923, 2316, 1714, 1532, 1397, 1347, 1250, 1124 cm^{-1}; Analytical Data. Found (calcd) for: $C_{17}H_{13}N_3O_4$ C, 63.13 (63.16); H, 4.06 (4.05); N, 13.02 (13.00).



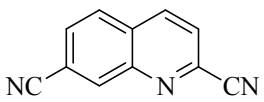
Ethyl 4-(2,4-dinitrophenyl)-7-nitroquinoline-2-carboxylate (3q): Yellow solid. Yield: 68%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.37 (d, J = 1.9 Hz, 1H), 9.18 (d, J = 2.0 Hz, 1H), 8.72 (dd, J = 8.3, 2.1 Hz, 1H), 8.39 (dd, J = 9.2, 2.1 Hz, 1H), 8.23 (s, 1H), 7.77 (d, J = 8.3 Hz, 1H), 7.57 (d, J = 9.1 Hz, 1H), 4.63 (dd, J = 7.1, 2.8 Hz, 2H), 1.54 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO): δ 164.33, 150.42, 149.11, 148.81, 148.47, 146.28, 145.88, 136.92, 134.76, 130.25, 128.90, 127.81, 126.48 , 123.06, 123.02, 121.04, 62.62, 14.57; HRMS (ESI) m/z: 435.0554 $[M + Na]^+$ (calcd. 435.0553); IR (KBr): ν 3105, 2924, 2853, 1723, 1614, 1599, 1537, 1460, 1440, 1345 cm^{-1}; Analytical Data. Found (calcd) for: $C_{18}H_{12}N_4O_8$ C,52.46 (52.43); H, 2.92 (2.93); N, 13.63(13.59).



Ethyl benzo[f][1,7]naphthyridine-3-carboxylate (3r): White solid. Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.73 (s, 1H), 9.05 (t, J = 13.7 Hz, 1H), 8.59 (dd, J = 11.8, 8.5 Hz, 2H), 8.33 (dd, J = 25.8, 8.7 Hz, 1H), 7.90 (t, J = 7.5 Hz, 1H), 7.80 (t, J = 7.5 Hz, 1H), 4.63 (q, J = 7.1 Hz, 2H), 1.55 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.77, 155.20, 148.89, 144.89, 141.43, 131.40, 130.80, 130.43, 129.62, 128.04, 125.57, 122.84, 122.56, 62.53, 14.36; HRMS (ESI) m/z: 275.0796 $[M + Na]^+$ (calcd. 275.0796); IR (KBr): ν 3064, 1739, 1609, 1471 cm^{-1}; Analytical Data. Found (calcd) for: $C_{15}H_{12}N_2O_2$ C, 71.47 (71.42); H, 4.75 (4.79); N, 11.14 (11.10).

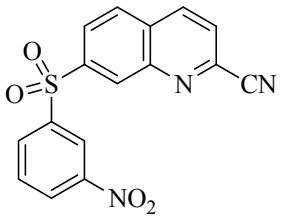


7-Nitroquinoline-2-carbonitrile (4a): Yellow solid. Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.06 (s, 1H), 8.50 (dd, J = 8.3, 4.1 Hz, 2H), 8.14 (d, J = 9.0 Hz, 1H), 7.92 (d, J = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.15, 147.14, 137.79, 136.13, 131.31, 129.74, 126.09, 125.96, 122.76, 116.66; HRMS (ESI) m/z: 222.0277 $[M + Na]^+$ (calcd. 222.0279); IR (KBr): ν 3080, 2251, 1623, 1530, 1425, 1349 cm^{-1}; Analytical Data. Found (calcd) for: $C_{10}H_5N_3O_2$ C, 60.35 (60.31); H, 2.51 (2.53); N, 21.08 (21.10).

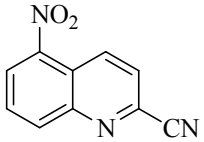


Quinoline-2,7-dicarbonitrile (4b): Yellow solid. Yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (s, 1H), 8.43 (d, J = 8.4 Hz, 1H), 8.06 (d, J = 8.5 Hz, 1H), 7.87 (d, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, DMSO): δ 146.57, 139.35, 135.67, 135.44, 131.00, 130.62, 130.38, 126.69, 118.37, 114.43;

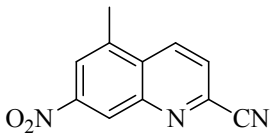
HRMS (ESI) m/z: 202.0385 $[M + Na]^+$ (calcd. 202.0381); IR (KBr): *v* 3086, 2232, 1620, 1426 cm^{-1}; Analytical Data. Found (calcd) for: $C_{11}H_5N_3$ C, 73.71 (73.74); H, 2.82 (2.81); N, 23.47 (23.45).



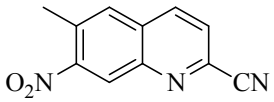
7-((3-Nitrophenyl)sulfonyl)quinoline-2-carbonitrile (4d): White solid. Yield: 84%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.88 (d, J = 7.4 Hz, 2H), 8.49 (d, J = 8.1 Hz, 1H), 8.41 (dd, J = 13.1, 8.3 Hz, 2H), 8.19 (d, J = 8.7 Hz, 1H), 8.12 (d, J = 8.7 Hz, 1H), 7.89 (d, J = 8.5 Hz, 1H), 7.81 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO): δ 148.79, 146.67, 142.56, 142.03, 139.45, 135.73, 134.44, 132.49, 131.69, 131.49, 130.51, 129.31, 127.10, 126.25, 123.17, 117.53; HRMS (ESI) m/z: 362.0208 $[M + Na]^+$ (calcd. 362.0211); IR (KBr): *v* 3084, 2252, 1603, 1534, 1426, 1354 cm^{-1}; Analytical Data. Found (calcd) for: $C_{16}H_9N_3O_4S$ C, 56.61 (56.63); H, 2.64 (2.67); N, 12.39 (12.38).



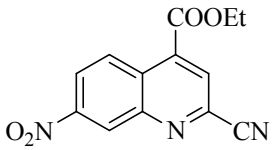
5-Nitroquinoline-2-carbonitrile (4e): Yellow solid. Yield: 74%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.23 (d, J = 8.9 Hz, 1H), 8.56 (d, J = 7.6 Hz, 1H), 8.51 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 8.9 Hz, 1H) ,7.60 (t J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.28, 148.03, 136.96, 134.10, 129.33, 129.02, 128.68, 127.28, 125.94, 118.44; HRMS (ESI) m/z: 222.0276 $[M + Na]^+$ (calcd. 222.0279); IR (KBr): *v* 3094, 2251, 1611, 1532, 1424, 1356 cm^{-1}; Analytical Data. Found (calcd) for: $C_{10}H_5N_3O_2$ C, 60.37 (60.31); H, 2.50 (2.53); N, 21.16 (21.10).



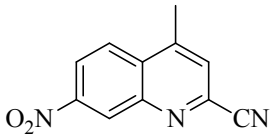
5-Methyl-7-nitroquinoline-2-carbonitrile (4k): Yellow solid. Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.93 (s, 1H), 8.60 (d, J = 8.7 Hz, 1H), 8.33 (s, 1H), 7.92 (d, J = 8.7 Hz, 1H), 2.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.91, 147.87, 138.07, 135.92, 134.62, 131.14, 125.78, 124.44, 122.87, 116.92, 19.18; HRMS (ESI) m/z: 236.0428 $[M + Na]^+$ (calcd. 236.0436); IR (KBr): v 3100, 2966, 2251, 1624, 1529, 1398, 1348 cm^{-1}; Analytical Data. Found (calcd) for: $C_{11}H_7N_3O_2$ C,61.92 (61.97); H, 3.27 (3.31); N, 19.68 (19.71).



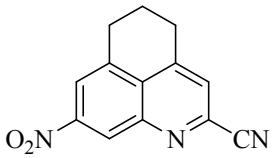
6-Methyl-7-nitroquinoline-2-carbonitrile (4l): Yellow solid. Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (s, 1H), 8.34 (d, J = 8.3 Hz, 1H), 7.88 (s, 1H), 7.83 (d, J = 8.5 Hz, 1H), 2.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.72, 146.01, 136.68, 135.35, 133.12, 130.92, 126.09, 125.63, 122.22, 118.61, 20.12; HRMS (ESI) m/z: 236.0433 $[M + Na]^+$ (calcd. 236.0436); IR (KBr): v 3121, 2980, 2251, 1626, 1527, 1423, 1345 cm^{-1}; Analytical Data. Found (calcd) for: $C_{11}H_7N_3O_2$ C,61.92 (61.97); H, 3.34 (3.31); N, 19.74 (19.71).



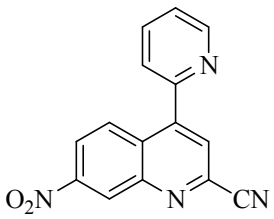
Ethyl 2-cyano-7-nitroquinoline-4-carboxylate (4m): Yellow solid. Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.17 (d, J = 9.6 Hz, 1H), 9.10 (d, J = 1.6 Hz, 1H), 8.55 (dd, J = 2.4, 9.6 Hz, 1H), 8.39 (s, 1H), 4.58 (q, J = 7.2 Hz, 2H), 1.52 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 163.55, 148.94, 148.49, 136.89, 135.93, 128.709, 128.17, 126.93, 126.26, 123.95, 116.14, 63.17, 14.17; HRMS (ESI) m/z: 272.0673 $[M + H]^+$ (calcd. 272.0665); IR (KBr): v 3059, 2925, 1726, 1529, 1348, 1250, 1193 cm^{-1}; Analytical Data. Found (calcd) for: $C_{13}H_9N_3O_4$ C, 57.58 (57.57); H, 3.31 (3.34); N, 15.44 (15.49).



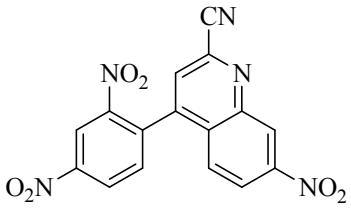
4-Methyl-7-nitroquinoline-2-carbonitrile (4n): Yellow solid. Yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.01 (d, J = 2.1 Hz, 1H), 8.62 (d, J = 2.2 Hz, 1H), 8.46 (d, J = 2.1 Hz, 1H), 8.44 (d, J = 2.2 Hz, 1H), 2.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.98, 145.95, 129.46, 127.06, 126.53, 126.29, 126.00, 122.30, 119.83, 118.49, 21.21; HRMS (ESI) m/z: 236.0428 $[M + Na]^+$ (calcd. 236.0436); IR (KBr): v 3101, 2977, 2251, 1620, 1533, 1422, 1351 cm^{-1}; Analytical Data. Found (calcd) for: $C_{11}H_7N_3O_2$ C, 61.95 (61.97); H, 3.32 (3.31); N, 19.73 (19.71).



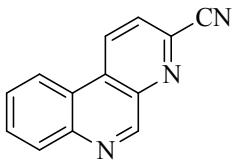
8-Nitro-5,6-dihydro-4*H*-benzo[de]quinoline-2-carbonitrile (4o): Yellow solid. Yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.37 (d, J = 1.9 Hz, 1H), 8.30 (s, 1H), 7.47 (s, 1H), 3.26 (t, J = 6.1 Hz, 2H), 3.13 (t, J = 5.9 Hz, 2H), 2.26-2.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.56, 141.47, 141.13, 134.51, 130.87, 130.33, 123.79, 122.26, 114.64, 112.22, 30.06, 29.27, 22.00; HRMS (ESI) m/z: 262.0589 $[M + Na]^+$ (calcd. 262.0592); IR (KBr): v 3100, 2942, 2251, 1599, 1530, 1427, 1345 cm^{-1}; Analytical Data. Found (calcd) for: $C_{13}H_9N_3O_2$ C, 65.29 (65.27); H, 3.81 (3.79); N, 17.52 (17.56).



7-Nitro-4-(pyridin-2-yl)quinoline-2-carbonitrile (4p): Yellow solid. Yield: 71%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.11 (s, 1H), 8.89 (d, J = 4.4 Hz, 1H), 8.53 (d, J = 9.2 Hz, 1H), 8.43 (d, J = 9.2 Hz,1H), 8.02-7.98 (m, 2H), 7.71 (d, J = 7.6 Hz, 1H), 7.57-7.54 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.82, 150.43, 148.79, 148.22, 148.16, 137.60, 135.82, 129.49, 128.37, 126.26, 125.84, 124.93, 124.46, 122.71, 116.60; HRMS (ESI) m/z: 277.0725 $[M + H]^+$ (calcd. 277.0720); IR (KBr): v 3107, 2923, 1529, 1404, 1351 cm^{-1}; Analytical Data. Found (calcd) for: $C_{15}H_8N_4O_2$ C, 65.24 (65.22); H, 2.87 (2.92); N, 20.24 (20.28).



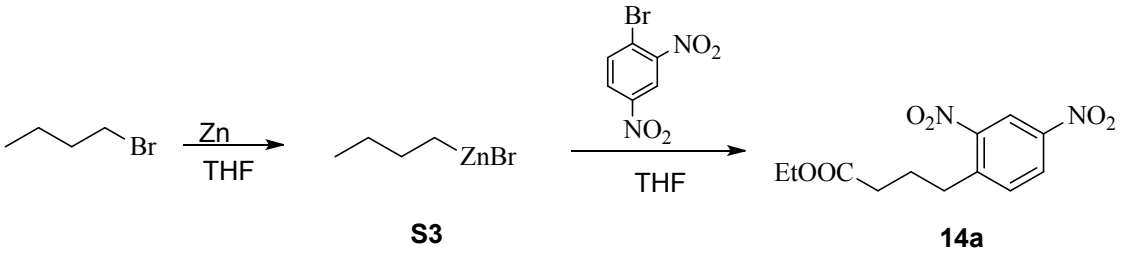
4-(2,4-Dinitrophenyl)-7-nitroquinoline-2-carbonitrile (4q): Yellow solid. Yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.19 (d, J = 2.1 Hz, 2H), 8.74 (dd, J = 8.3, 1.9 Hz, 1H), 8.42 (dd, J = 9.2, 1.9 Hz, 1H), 7.77 (s, 1H), 7.74 (d, J = 8.3 Hz, 1H), 7.58 (d, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 149.24, 148.96, 148.32, 147.17, 146.02, 136.69, 133.77, 131.07, 128.16, 128.30, 126.22, 122.36, 121.15, 120.79, 118.81; HRMS (ESI) m/z: 388.0282 $[M + Na]^+$ (calcd. 388.0294); IR (KBr): v 3105, 2250, 1599, 1531, 1434, 1346 cm^{-1}; Analytical Data. Found (calcd) for: $C_{16}H_7N_5O_6$ C, 52.65 (52.61); H, 1.90 (1.93); N, 19.14 (19.17).



Benzo[*f*][1,7]naphthyridin-2-amine (4r): White solid. Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.55 (s, 1H), 9.06 (d, J = 8.5 Hz, 1H), 8.57 (d, J = 8.0 Hz, 1H), 8.30 (d, J = 8.1 Hz, 1H), 8.09 (d, J = 8.5 Hz, 1H), 8.00-7.88 (m, 1H), 7.84 (t, J = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.99, 145.02, 142.03, 134.05, 131.73, 131.17, 130.80, 129.25, 128.55, 128.01, 122.91, 121.92, 116.95;

HRMS (ESI) m/z: 228.0533 $[M + Na]^+$ (calcd. 228.0538); IR (KBr): *v* 3017, 2240, 1580, 1455 cm^{-1}; Analytical Data. Found (calcd) for: $C_{13}H_7N_3$ C, 79.11 (76.09); H, 3.42 (3.44); N, 20.41 (20.47).

2.3. Preparation of 14a



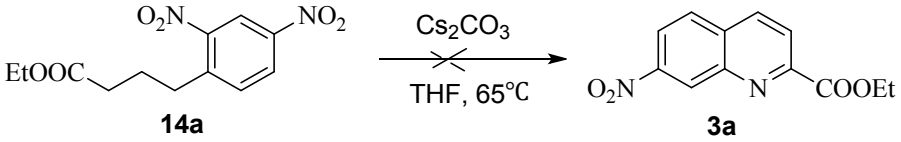
S3 **14a**

Ethyl 4-(2,4-dinitrophenyl)butanoate (S3) [1]: Two 50-mL two-necked flasks, A and B, were equipped with rubber septa, condensers topped with argon inlets, and Teflon-coated magnetic stir bars. Flask A was charged with freshly cut lithium (0.21 g, 30.63 mmol) and naphthalene (3.98 g, 31.15 mmol). Flask B was charged with anhydrous $ZnCl_2$ (2.09 g, 15.37 mmol). The flasks were then transferred to a manifold system and connected to nitrogen. Freshly distilled THF (15 mL) was added to both flasks via a syringe, and the mixtures were stirred at room temperature. The solution in flask A changed from colorless to dark green almost immediately. The lithium was consumed in about 2 h, and the $ZnCl_2$ solution was then transferred drop wise to flask A by a cannula over 15 min. The activated zinc was typically used at this point. Neat ethyl-4-bromobutanoate (0.70 g, 3.62 mmol) was added via syringe to the active zinc (4.00 mmol) at room temperature. The reaction mixture was stirred at room temperature for 18 h, giving a dark solution of the alkylzinc bromide species (**S3**).

Ethyl 4-(2,4-dinitrophenyl)butanoate (14a): S3 (2.16 mmol, in 10 mL THF) was transferred via a cannula to a THF solution of 5 mol % $Pd(PPh_3)_4$ (0.127 g**,** 0.11 mmol) and 1-bromo-2,4-dinitro-benzene (0.54 g, 2.19 mmol) at room temperature under an argon atmosphere. The solution was then stirred for 3 h. The mixture was worked up by pouring it into a saturated NH_4Cl aqueous solution (20 mL) and extracting with diethyl ether (3×20 mL).The combined organic layers were dried over

anhydrous $CaC1_2$. The resultant crude product was purified by flash chromatography using **s**ilica gel with gradient elution (hexanes to remove naphthalene first, then hexanes/ethyl acetate) to give a yellow oil (**14a**) (0.49 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, J = 2.4 Hz, 1H), 8.31 (dd, J = 2.4, 8.8 Hz, 1H), 8.02 (d, J = 8.8 Hz, 1H), 4.15 (q, J = 7.2 Hz, 2H), 3.48 (t, J = 2.4 Hz, 2H), 2.50 (t, J = 7.2 Hz, 2H), 2.22-2.15 (m, 2H), 1.27 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.47, 149.80, 146.99, 136.51, 127.16, 121.87, 120.91, 60.54, 32.87, 32.46, 27.76, 14.21; HRMS (ESI) m/z: 305.0856 $[M + Na]^+$ (calcd. 305.0852); IR (KBr): v 3099, 2870, 1730, 1597, 1534, 1348, 1035 cm^{-1}; Analytical Data. Found (calcd) for: $C_{12}H_{14}N_2O_6$ C, 51.09 (51.06); H, 5.01 (5.00); N, 9.91 (9.93).

2.4. Preparation of 3a from 14a



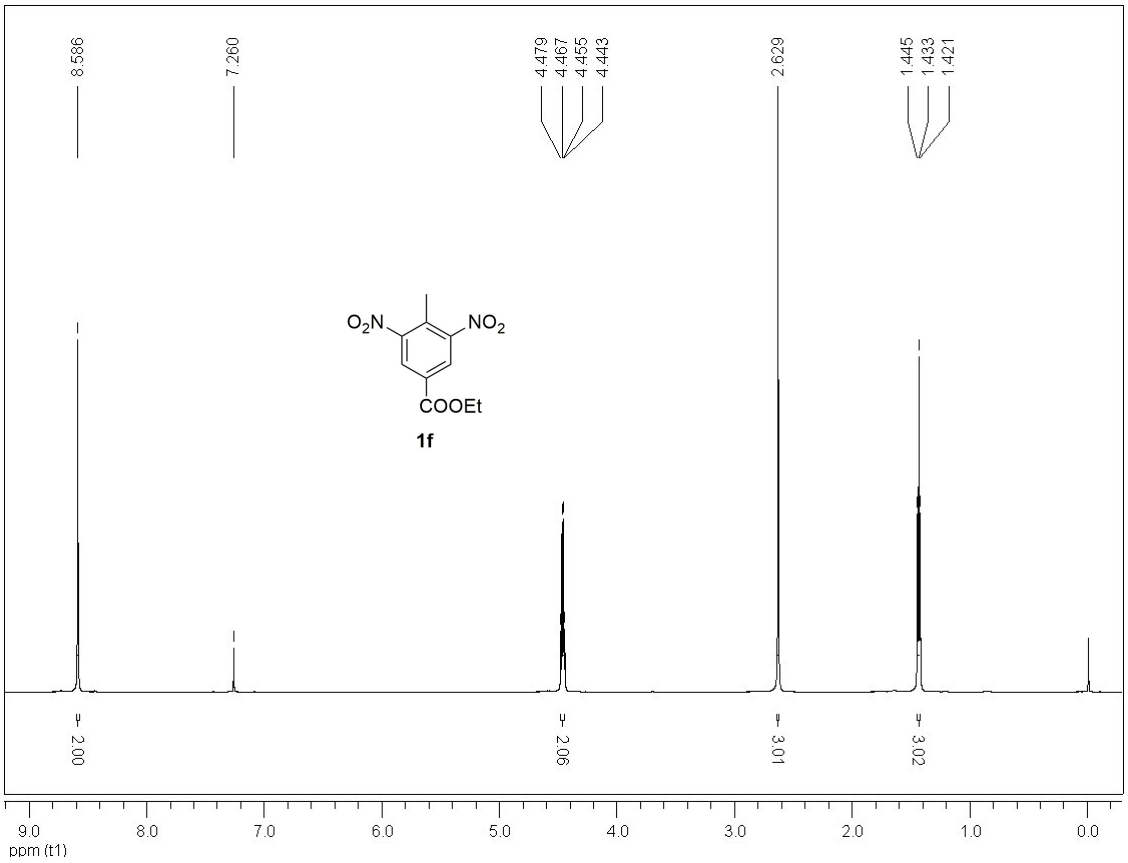
14a **3a**

An oven-dried 10-mL round-bottom flask equipped with a condenser and a Teflon-coated stir bar was charged with a solution of 1.0 mmol **14a** in 0.5 mL THF. Then, Cs_2CO_3 (0.2 mmol, 2 equiv.) was added and the mixture was stirred and heated under N_2 at 65 ^{o}C for 12 h. After a similar work up procedure, no **3a** could be isolated.

Reference:

(1) Zhu, L.; Wehmeyer, R. M.; Rieke, R. D. *J. Org. Chem.* **1991,** *56***,** 1445.

3. NMR spectra and for products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4.467
4.455
4.443
2.629
1.445
1.433
1.421
2.00
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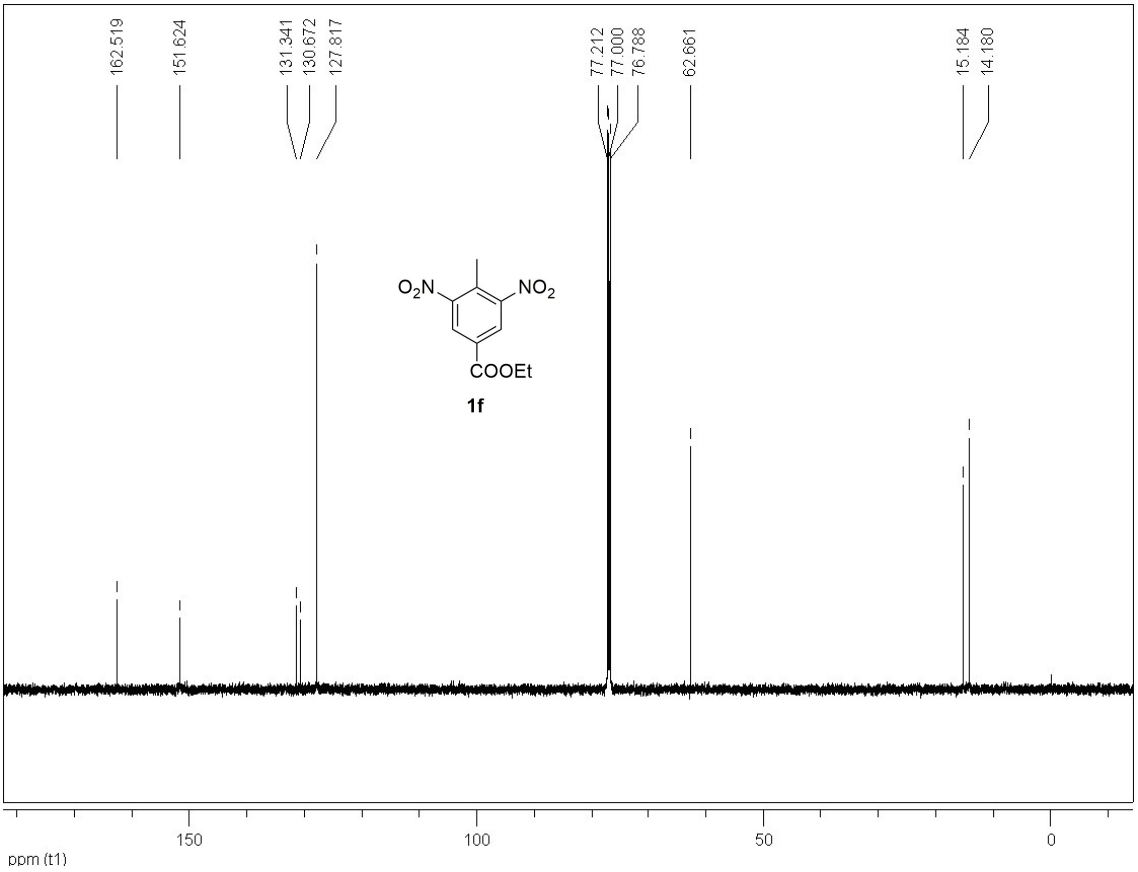
3.01
3.02
O2N
NO2
COOEt
1f
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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151.624
131.341
130.672
127.817
77.212
77.000
76.788
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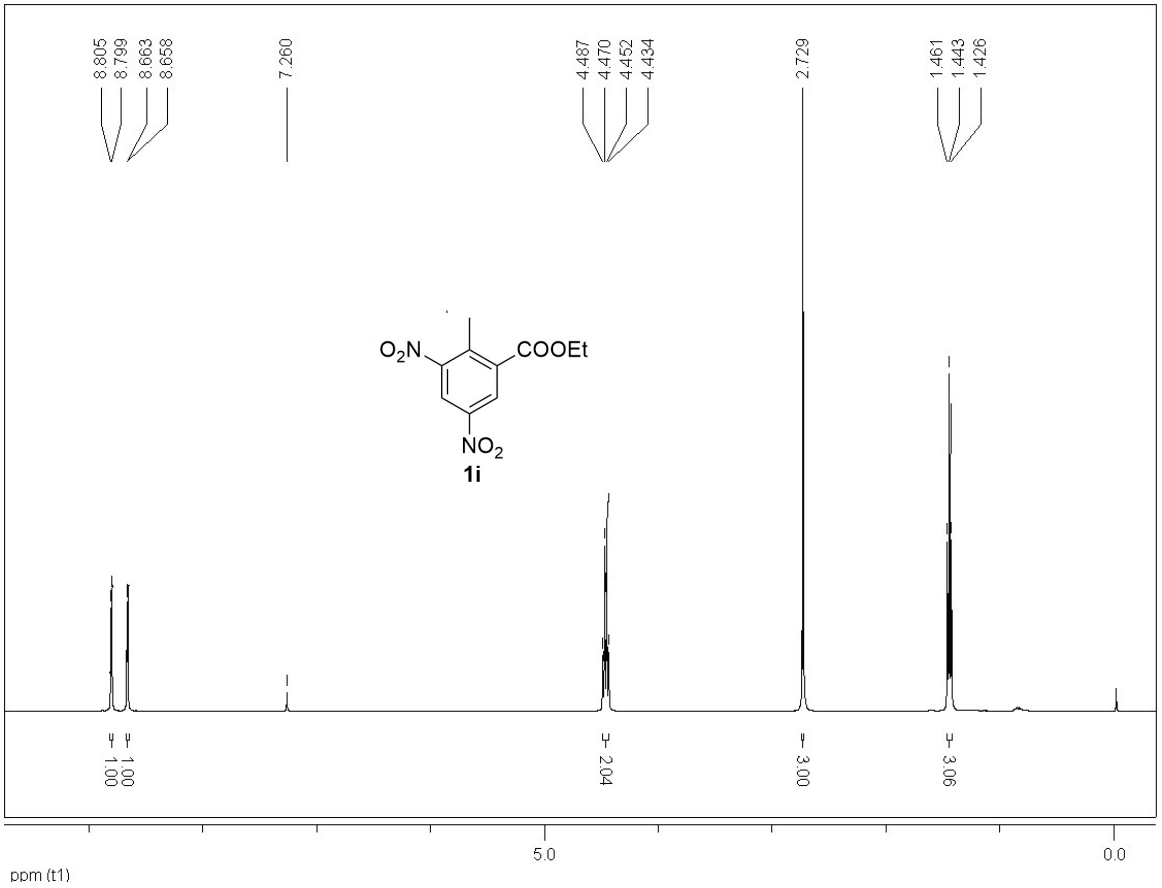
14.180
O2N
NO2
COOEt
1f
150
100
50
0
ppm (t1)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1.443
1.426
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COOEt
NO2
1i
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1.00
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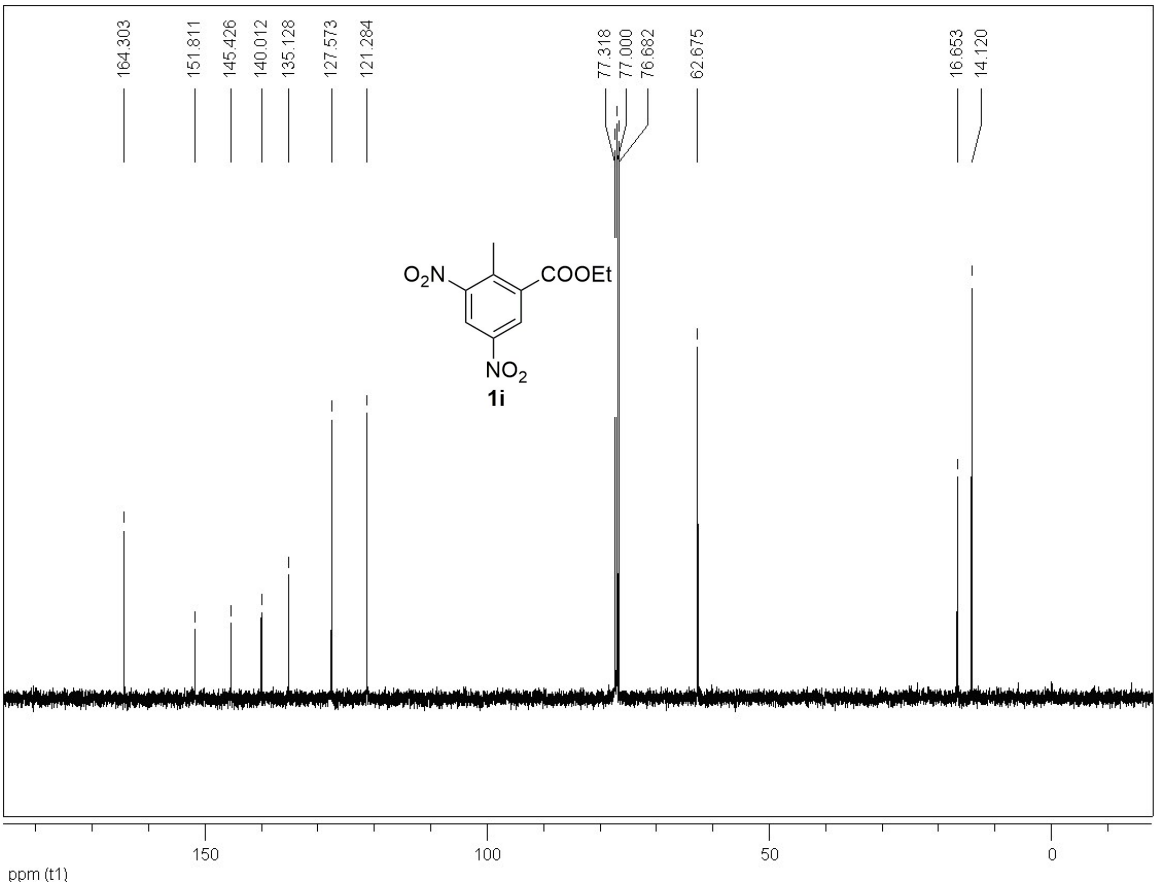
3.00
3.06
5.0
0.0
ppm (t1)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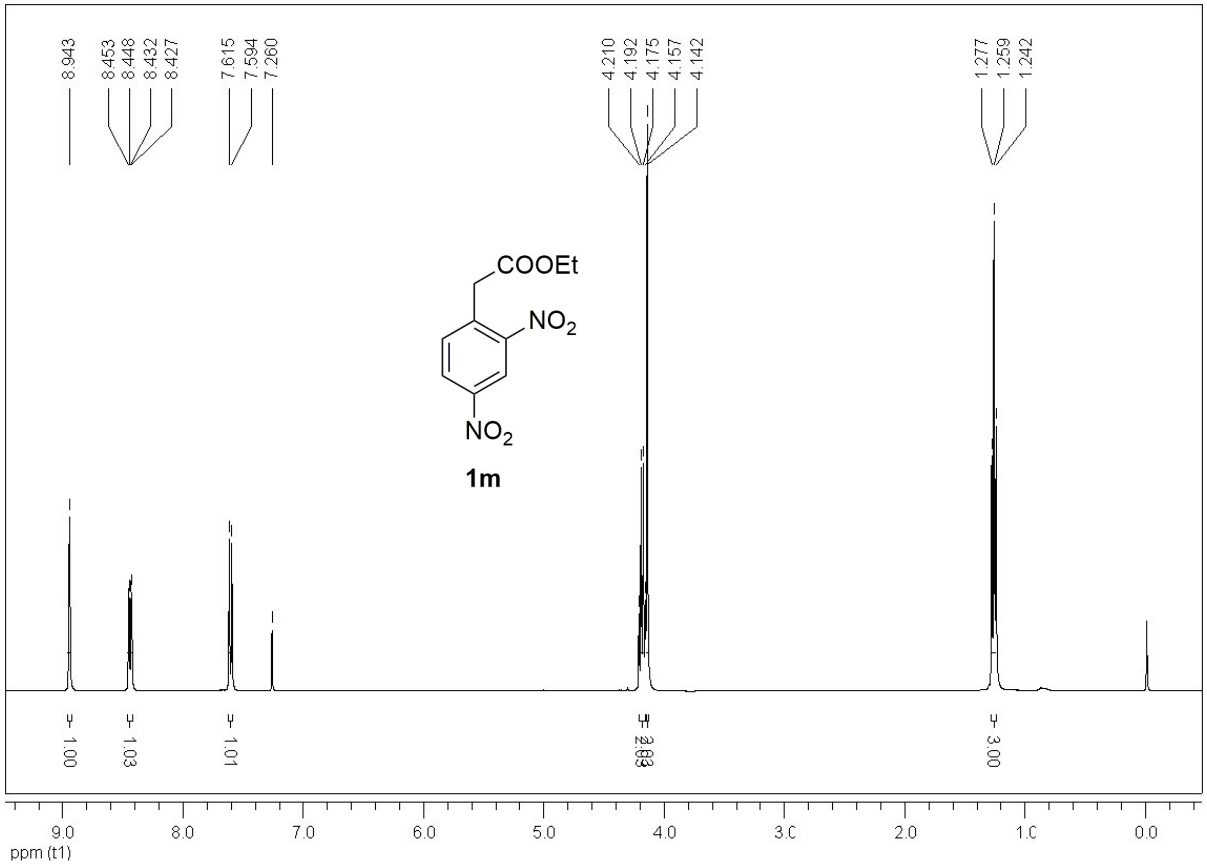
145.426
140.012
135.128
127.573
121.284
77.318
77.000
76.682
62.675
16.653
14.120
O2N
COOEt
NO2
1i
150
100
50
0
ppm (t1)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8.432
8.427
7.615
7.594
7.260
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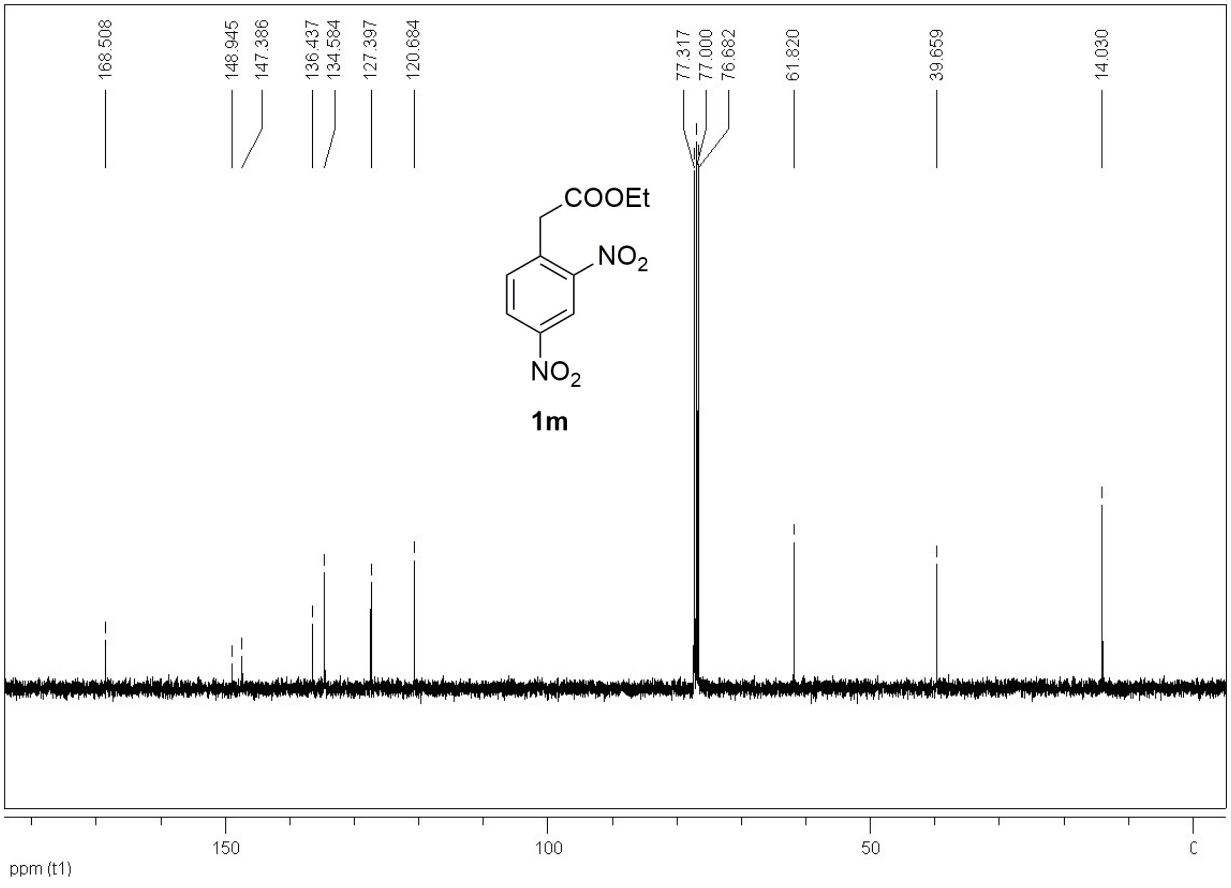
4.192
4.175
4.157
4.142
1.277
1.259
1.242
COOEt
NO2
NO2
1m
1.00
1.03
1.01
2.03
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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136.437
134.584
127.397
120.684
77.317
77.000
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61.820
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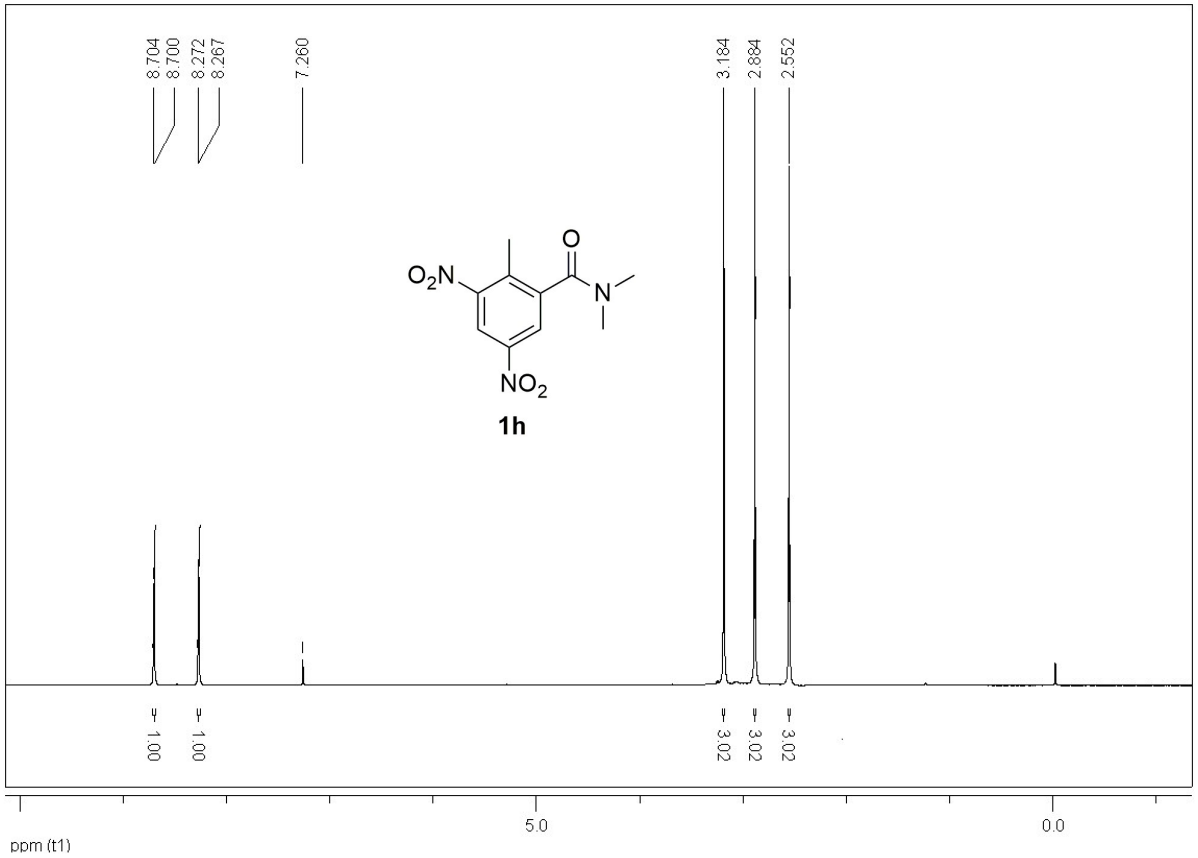
14.030
COOEt
NO2
NO2
1m
150
100
50
0
ppm (t1)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8.272
8.267
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2.884
2.552
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1.00
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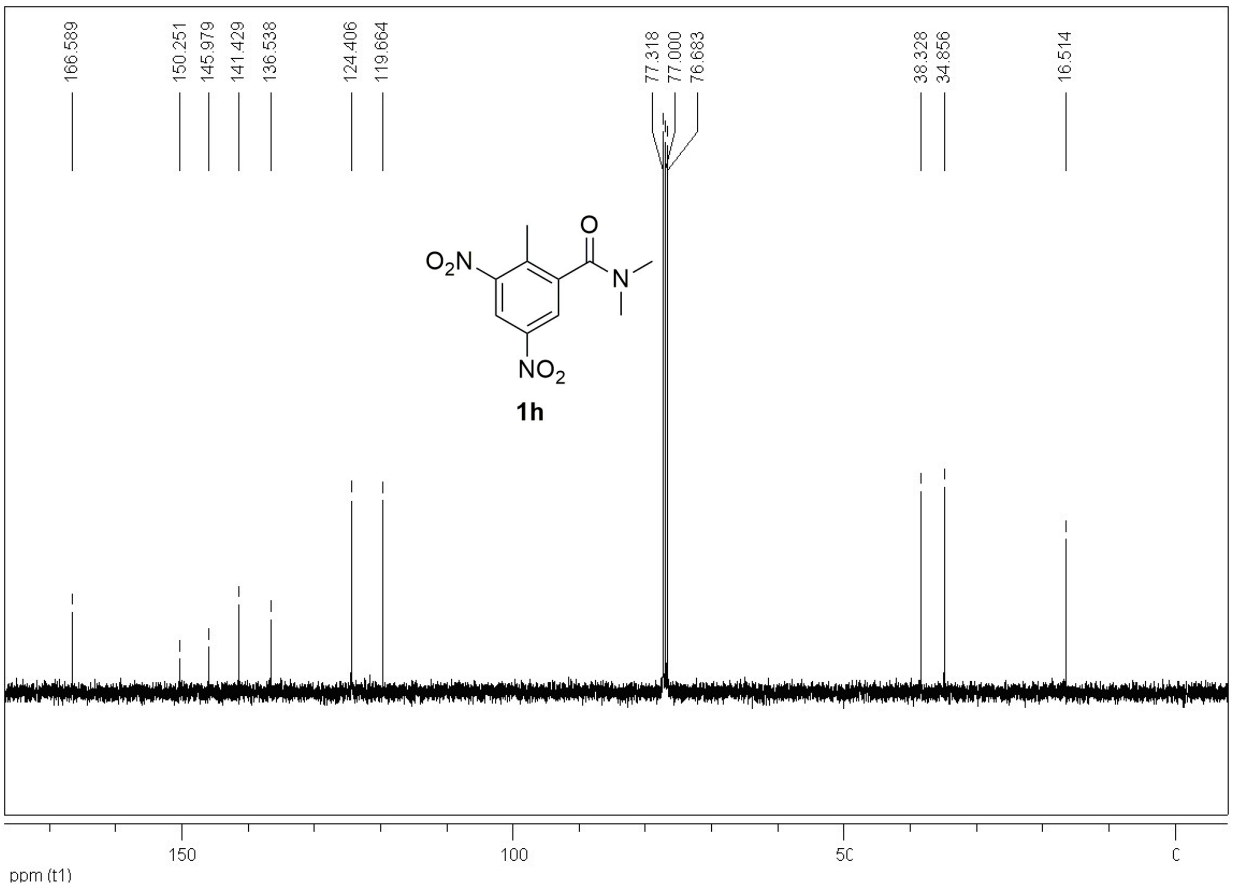
2.02
3.02
O2N
O
N
NO2
1h
5.0
0.0
ppm (t1)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141.429
136.538
124.406
119.664
77.318
77.000
76.683
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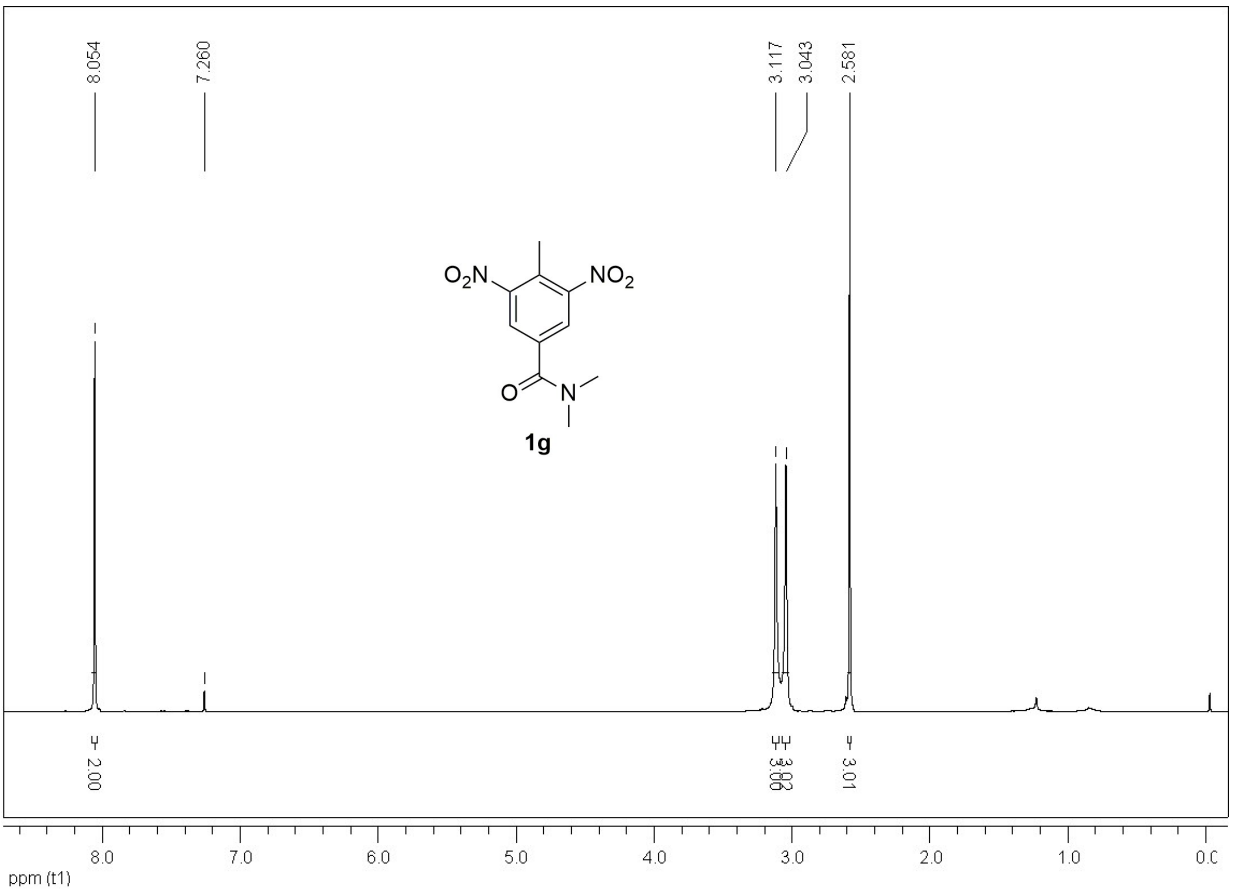
34.856
16.514
O2N
O
N
NO2
1h
150
100
50
0
ppm (t1)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O
N
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2.0
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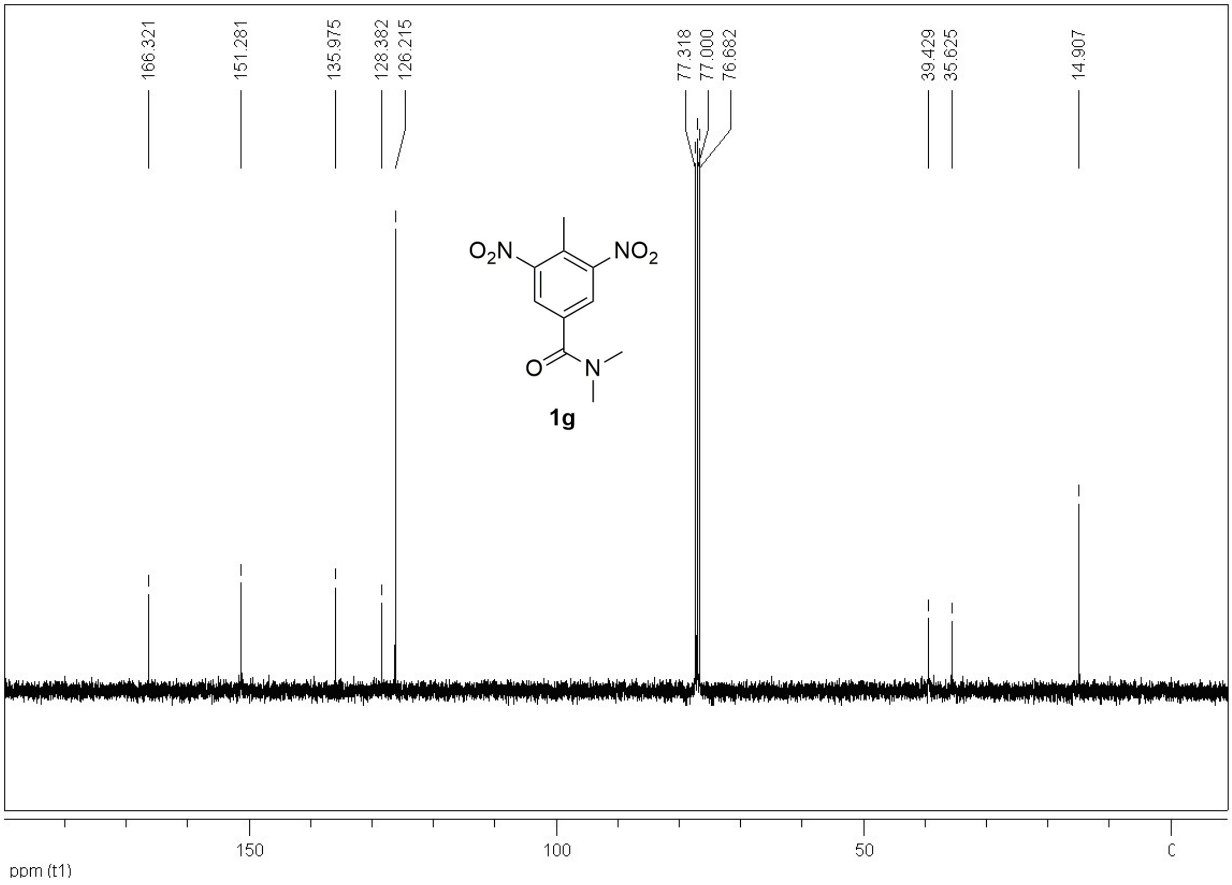
0.0
ppm (t1)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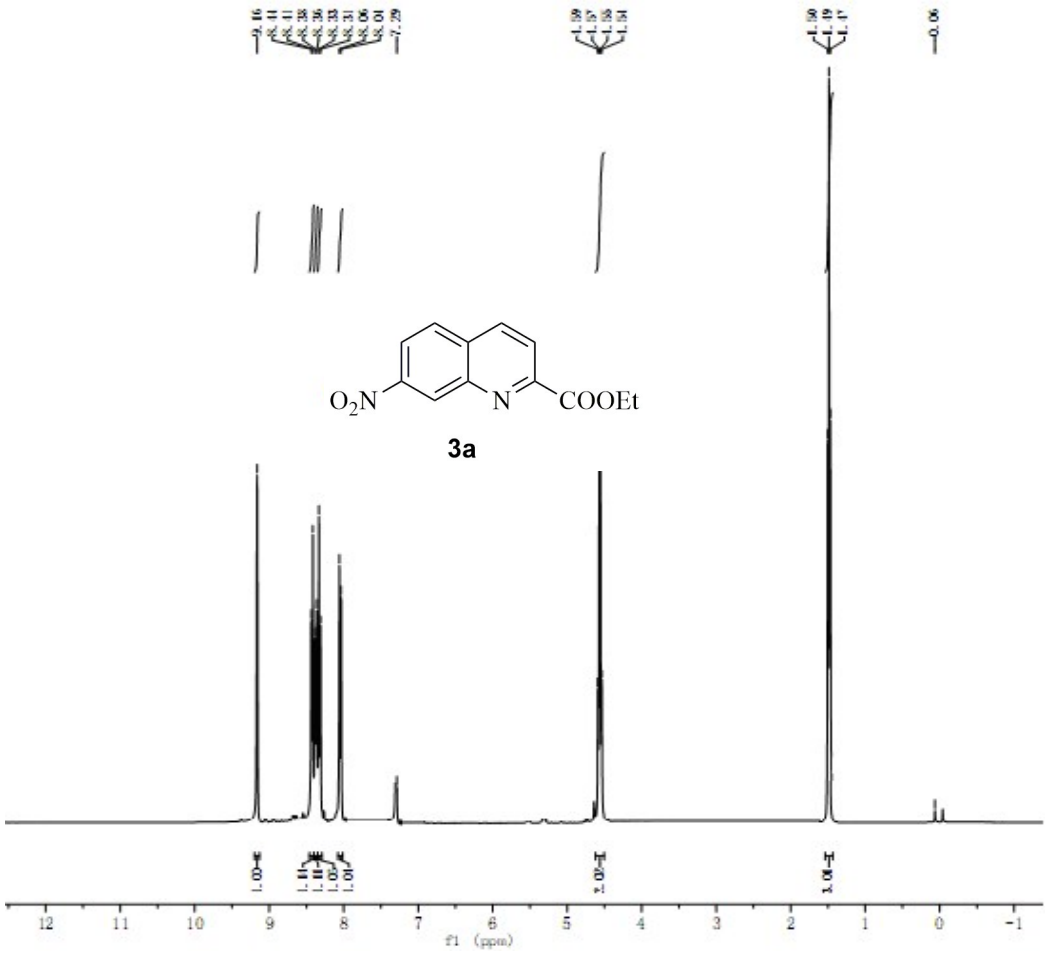
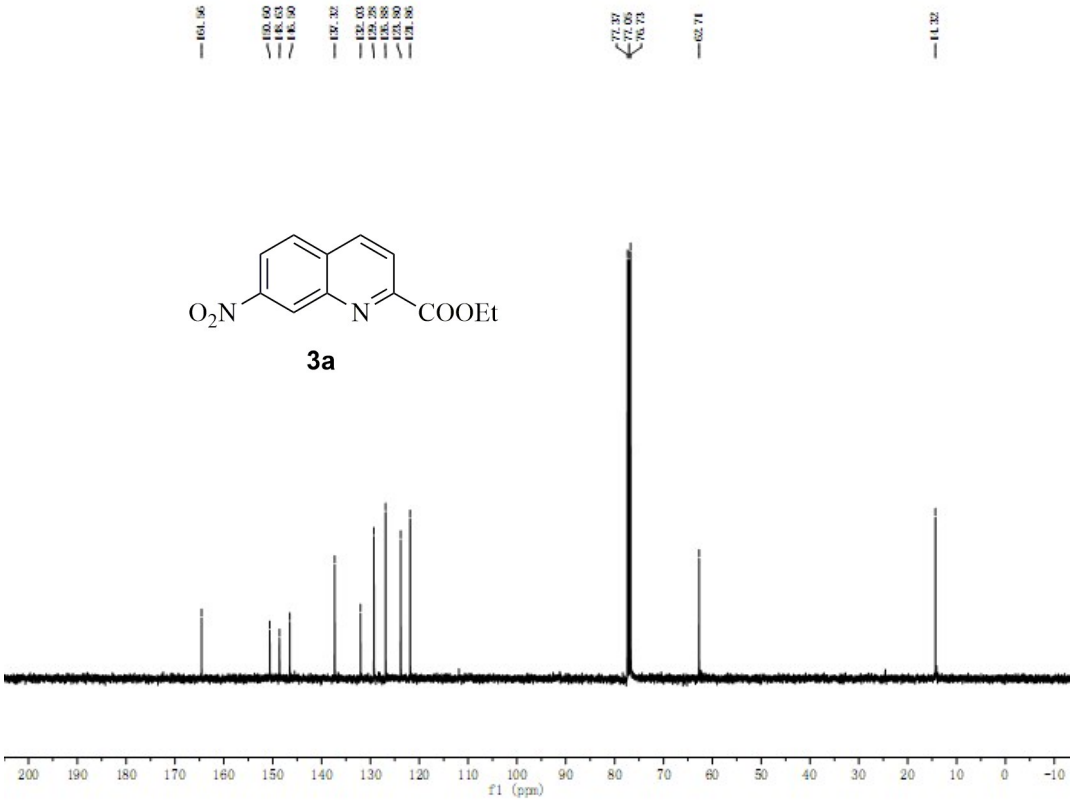
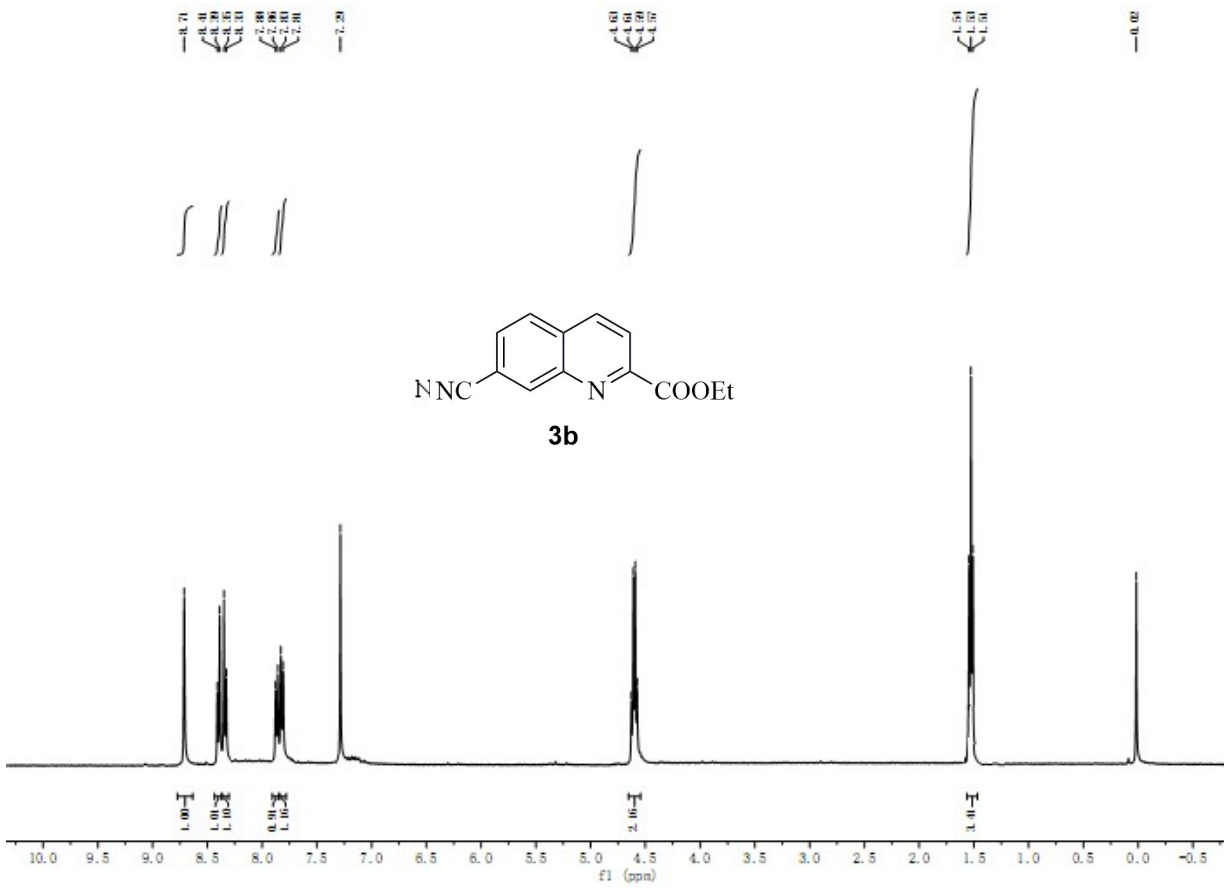
ppm (t1)



3a



3a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8.33
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7.80
7.80
7.29
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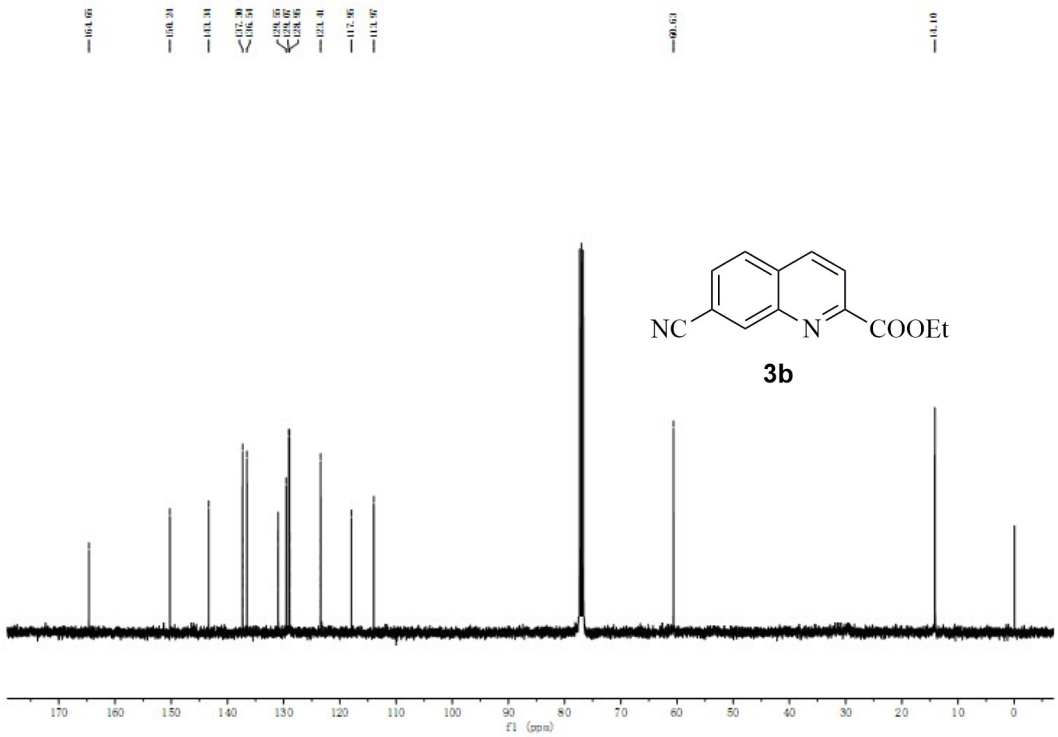
4.61
4.59
4.57
1.54
1.53
1.51
0.02
NC
N
COOEt
1.00
1.01
1.10
0.91
1.16
2.16
3.47
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

3b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136.54
129.65
129.62
128.96
123.48
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14.10
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COOEt
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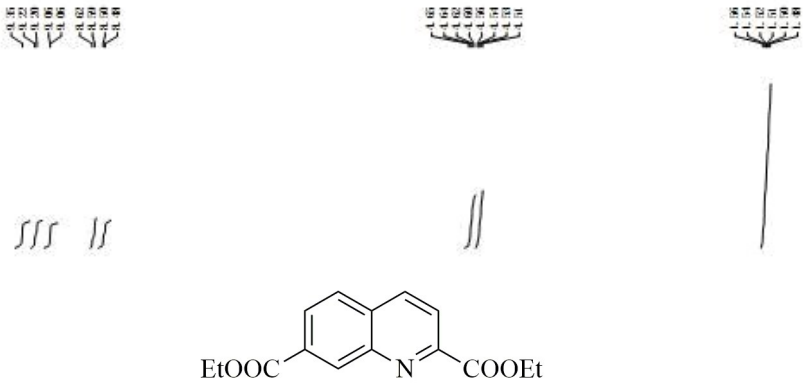
f1 (ppm)

3b



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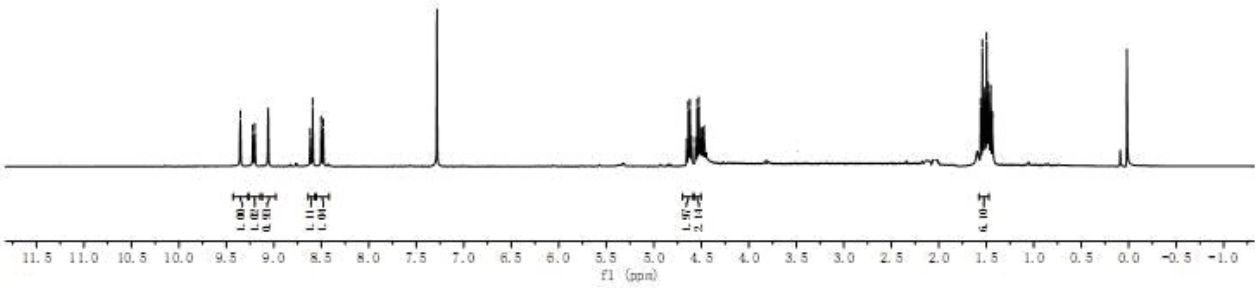

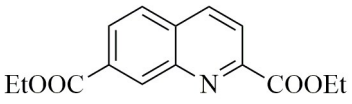

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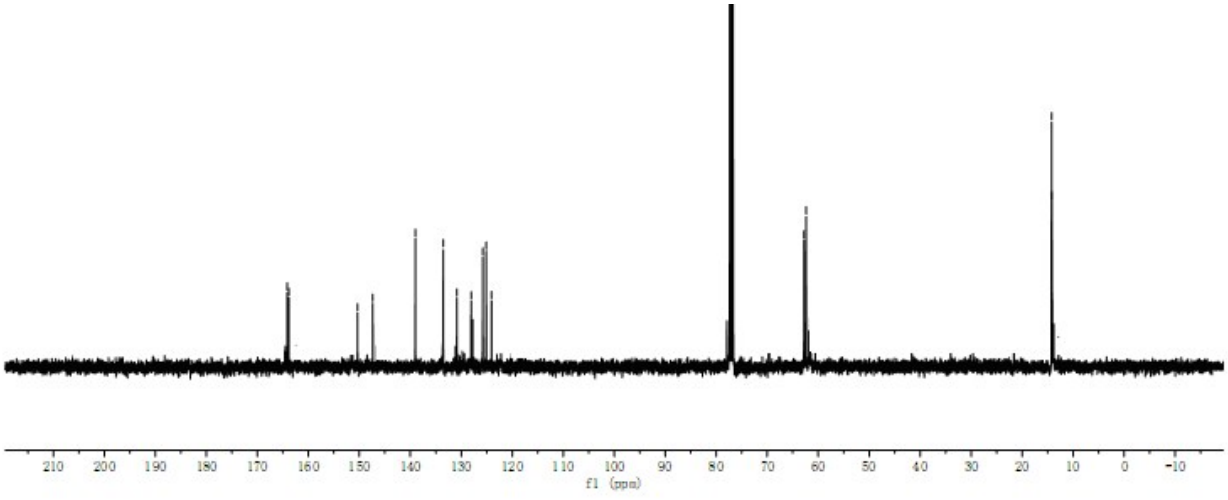

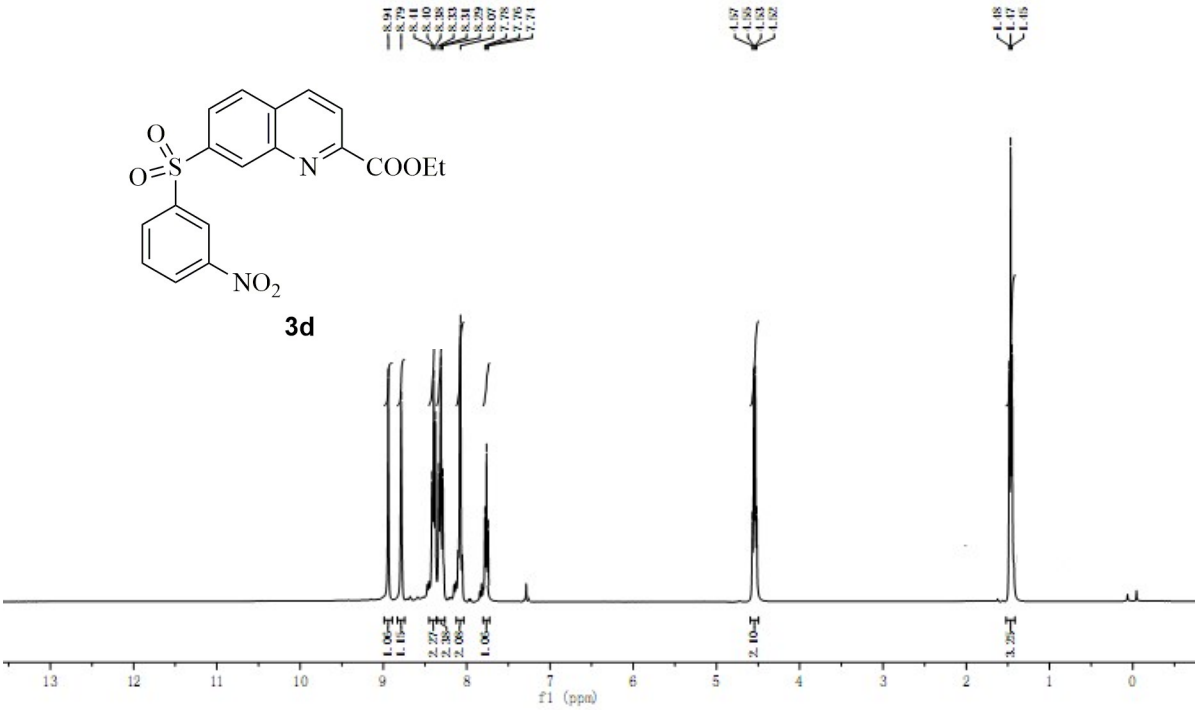
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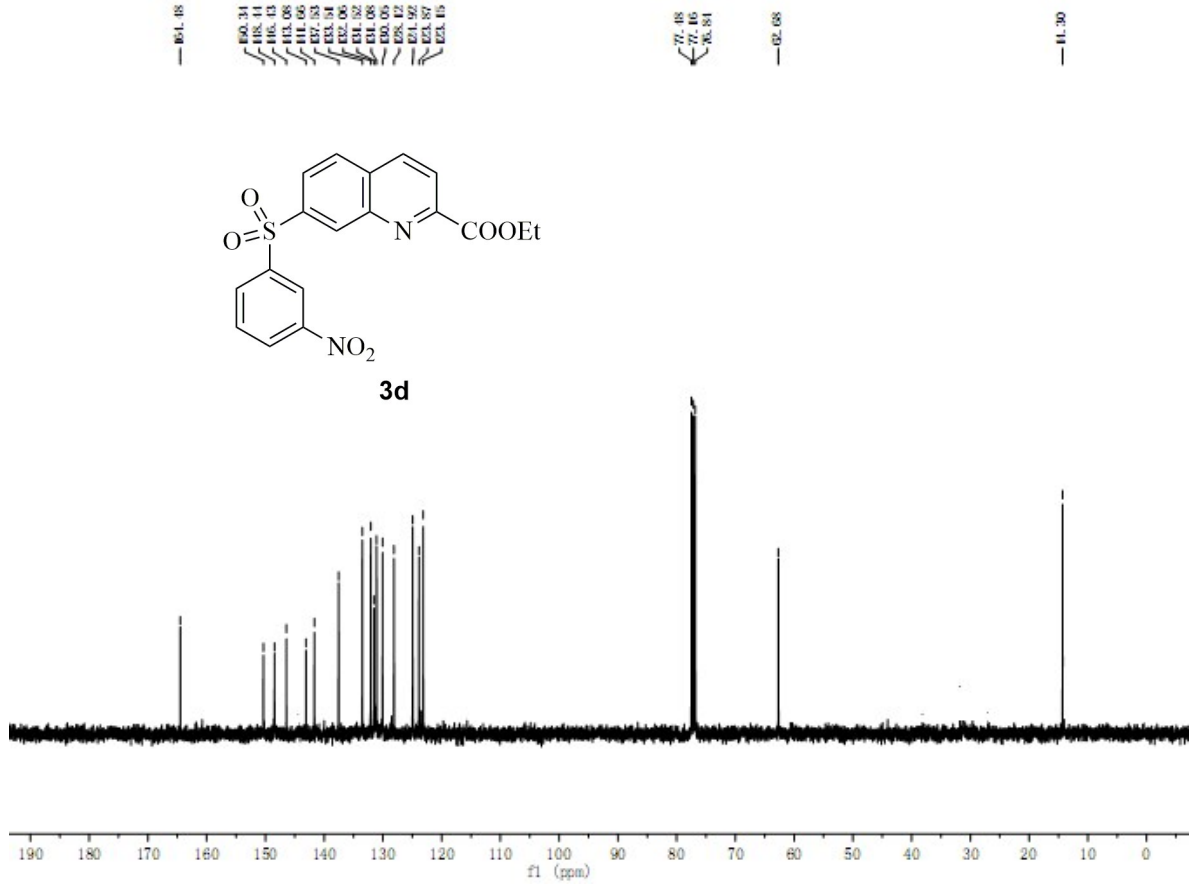
1.55
1.53
1.52
1.18
1.17
1.15
O
O=S
N
COOEt
NO2
1.06
1.10
2.27
2.39
2.08
1.06
2.10
3.25
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

3d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121.52
121.08
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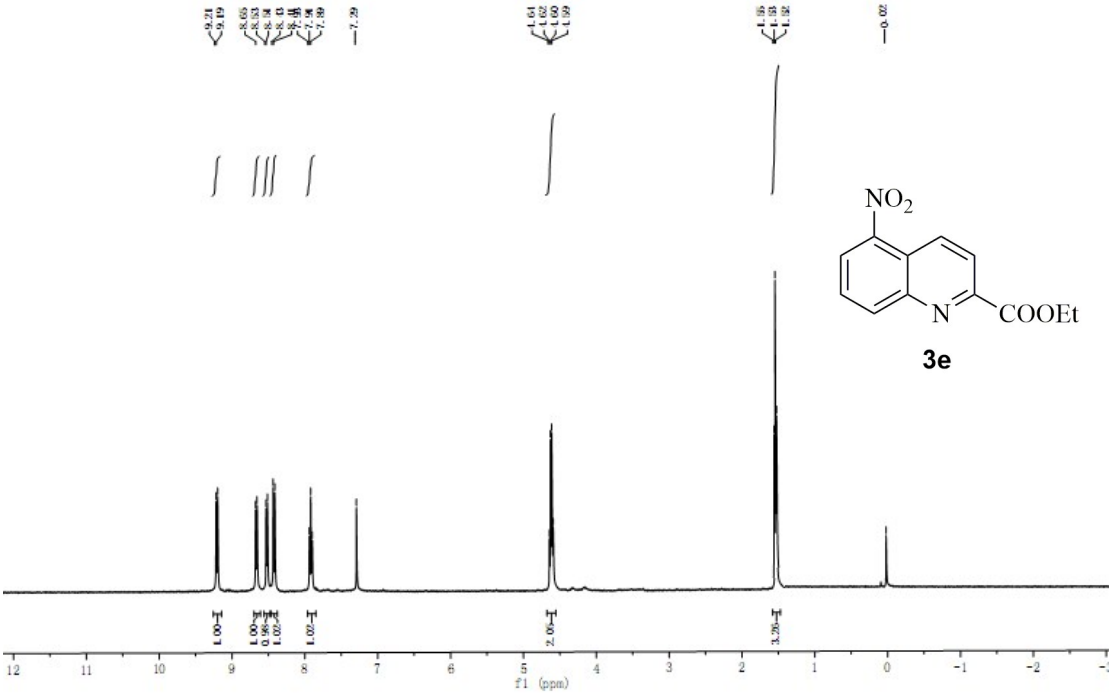
118.12
121.92
123.87
123.15
77.48
77.16
76.84
62.08
11.39
O
O=S
N
COOEt
NO2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3d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7.39
7.29
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1.60
1.59
1.35
1.33
1.32
0.02
1.00
1.00
0.96
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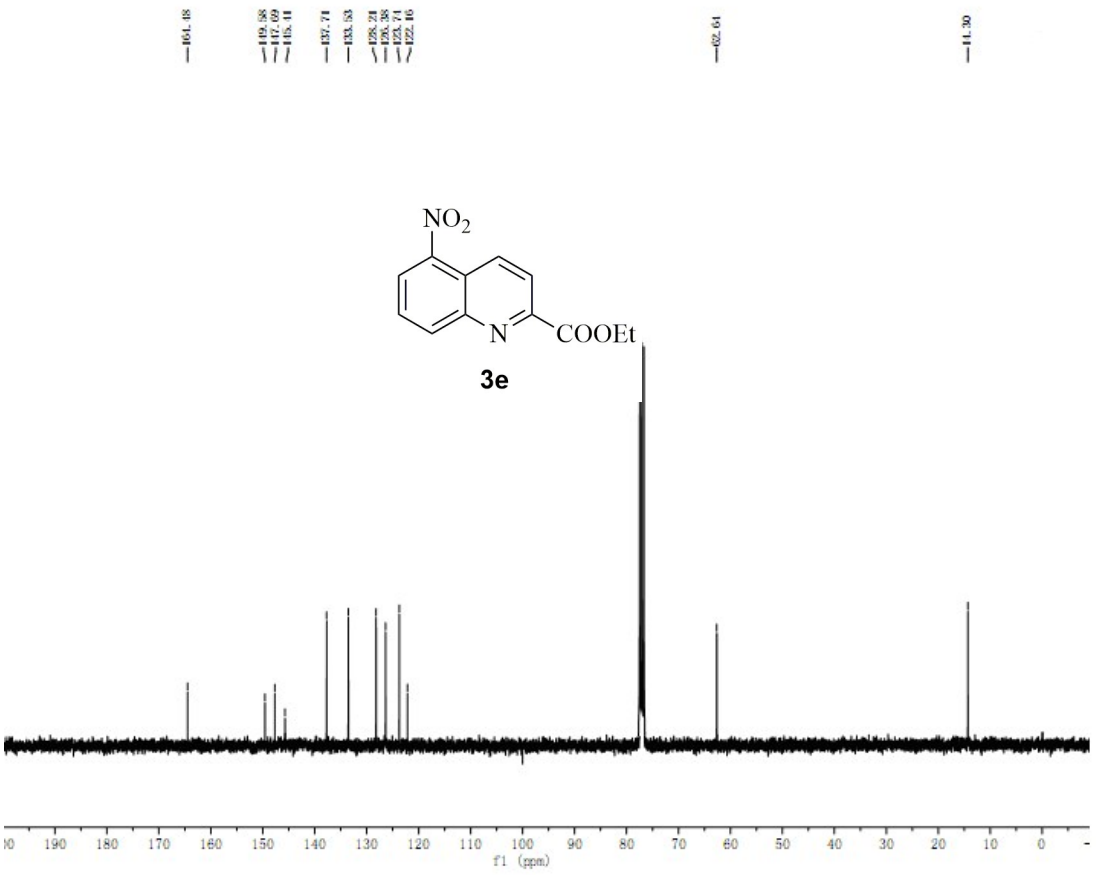
2.05
3.26
f1 (ppm)

NO2
N
COOEt

3e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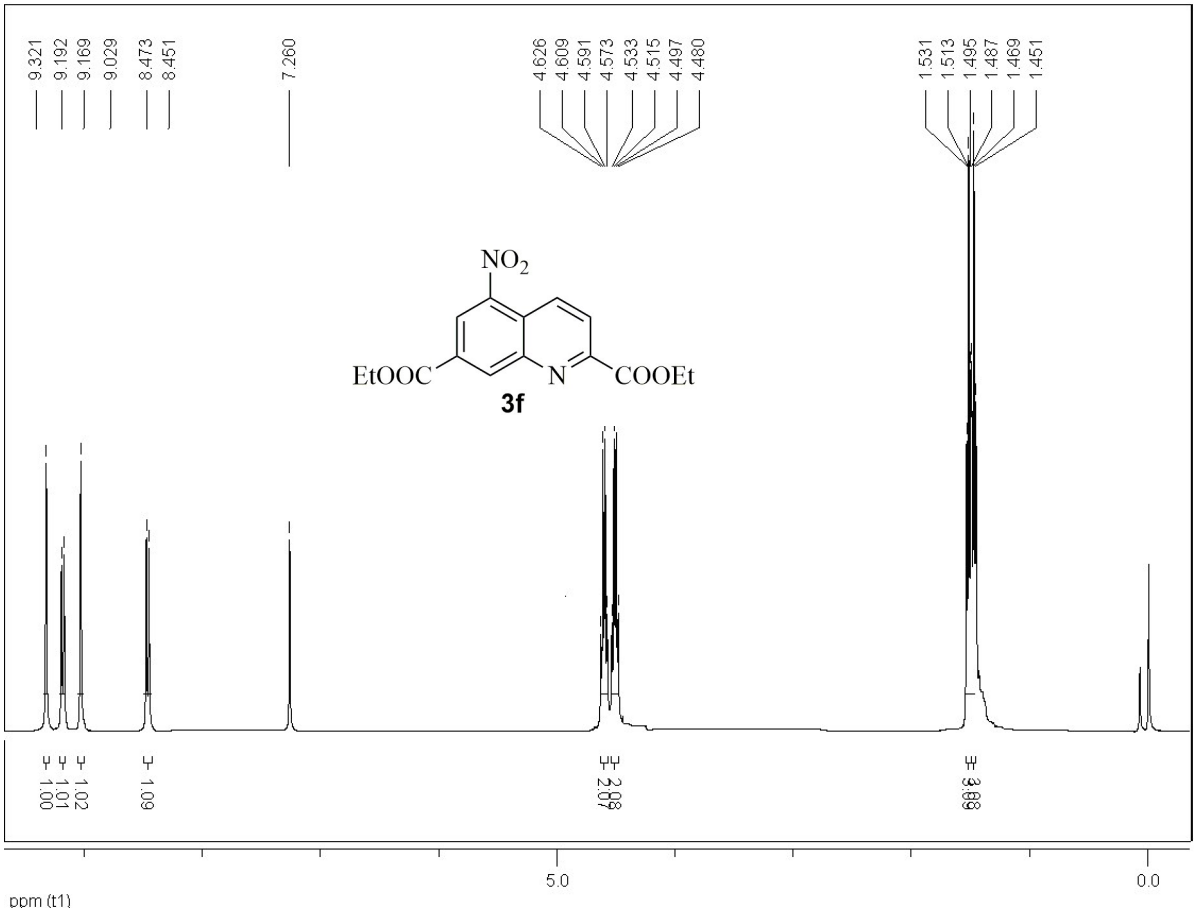
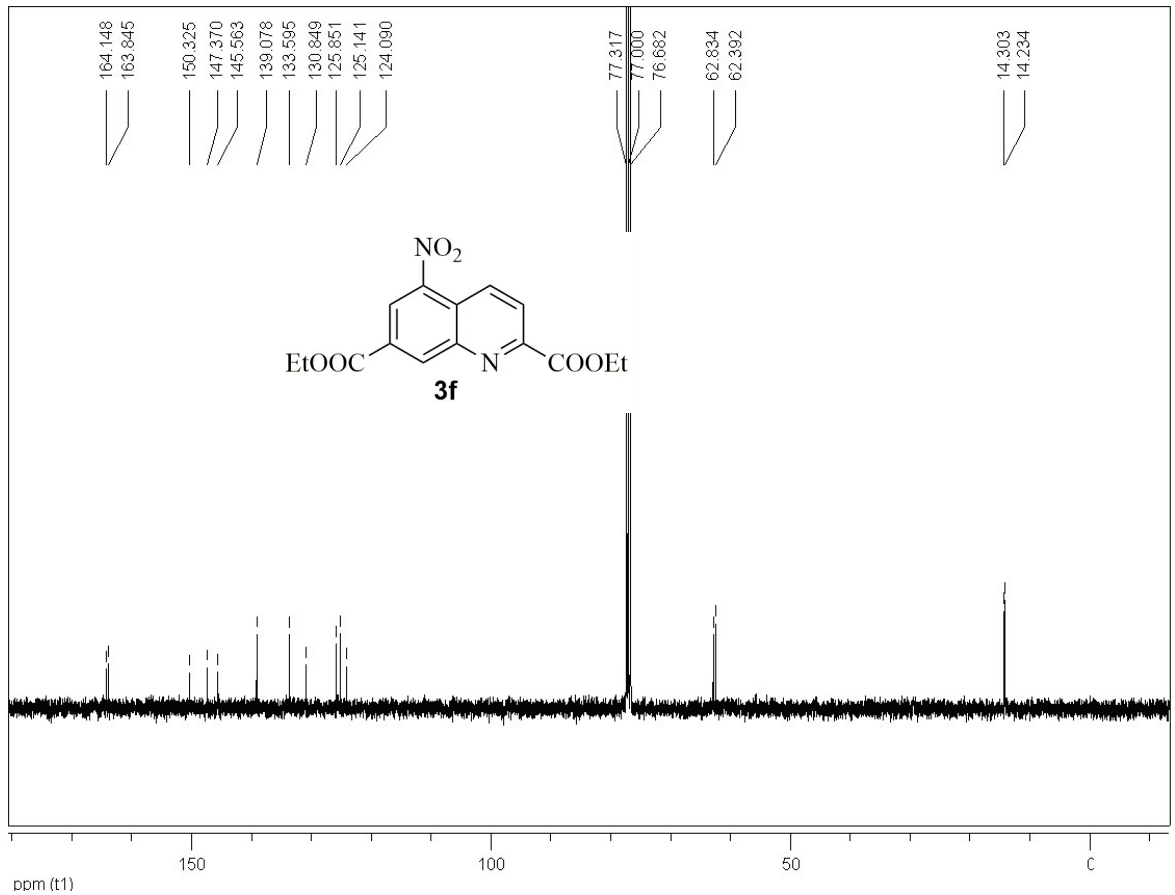
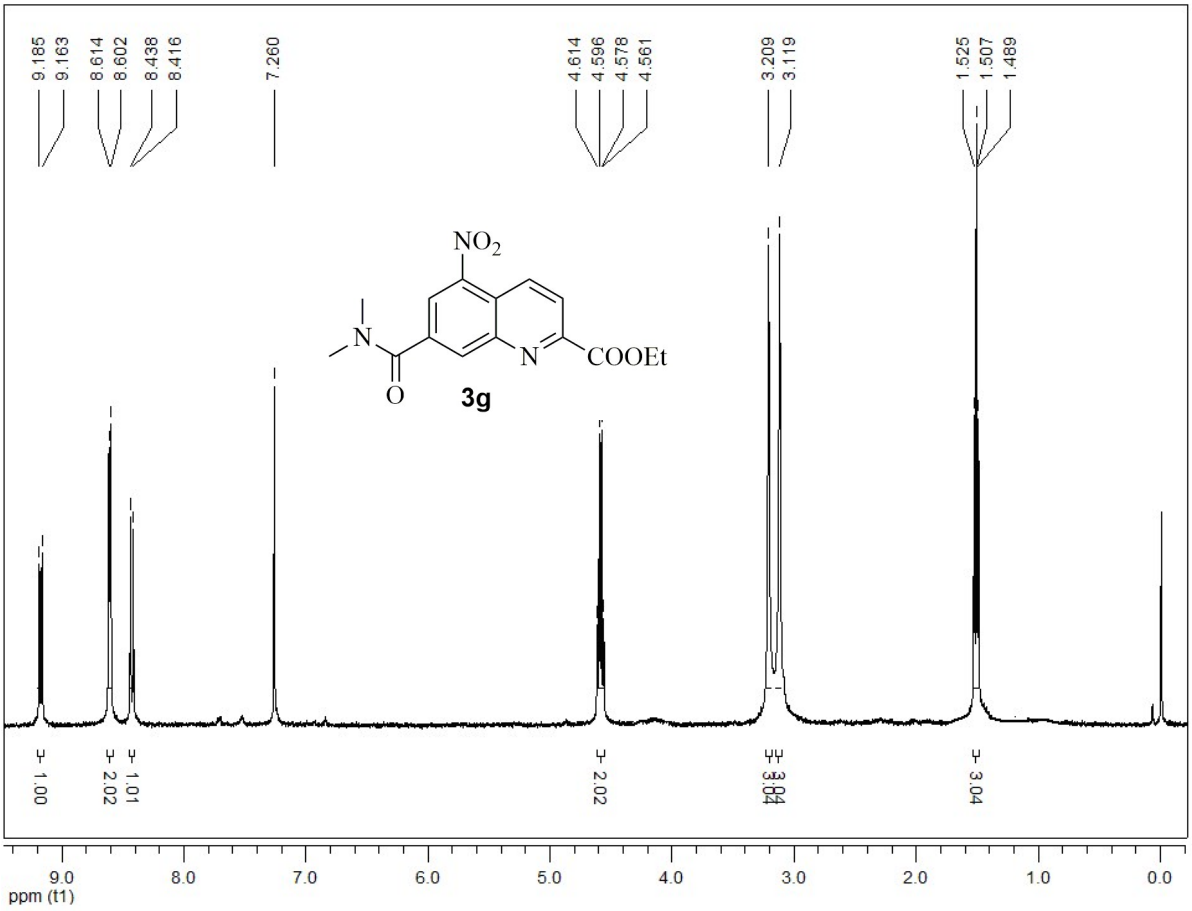
123.71
122.16
62.61
11.30
f1 (ppm)

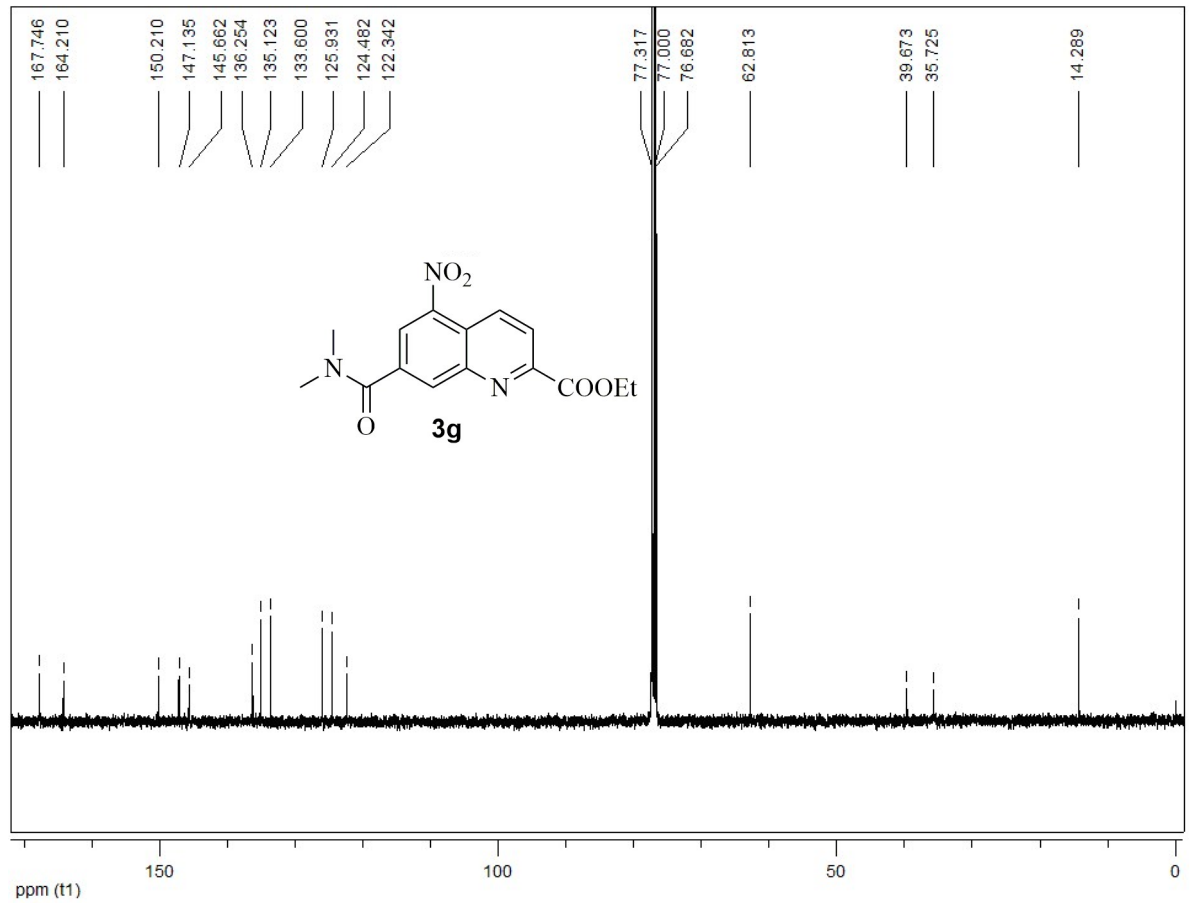
NO2
N
COOEt

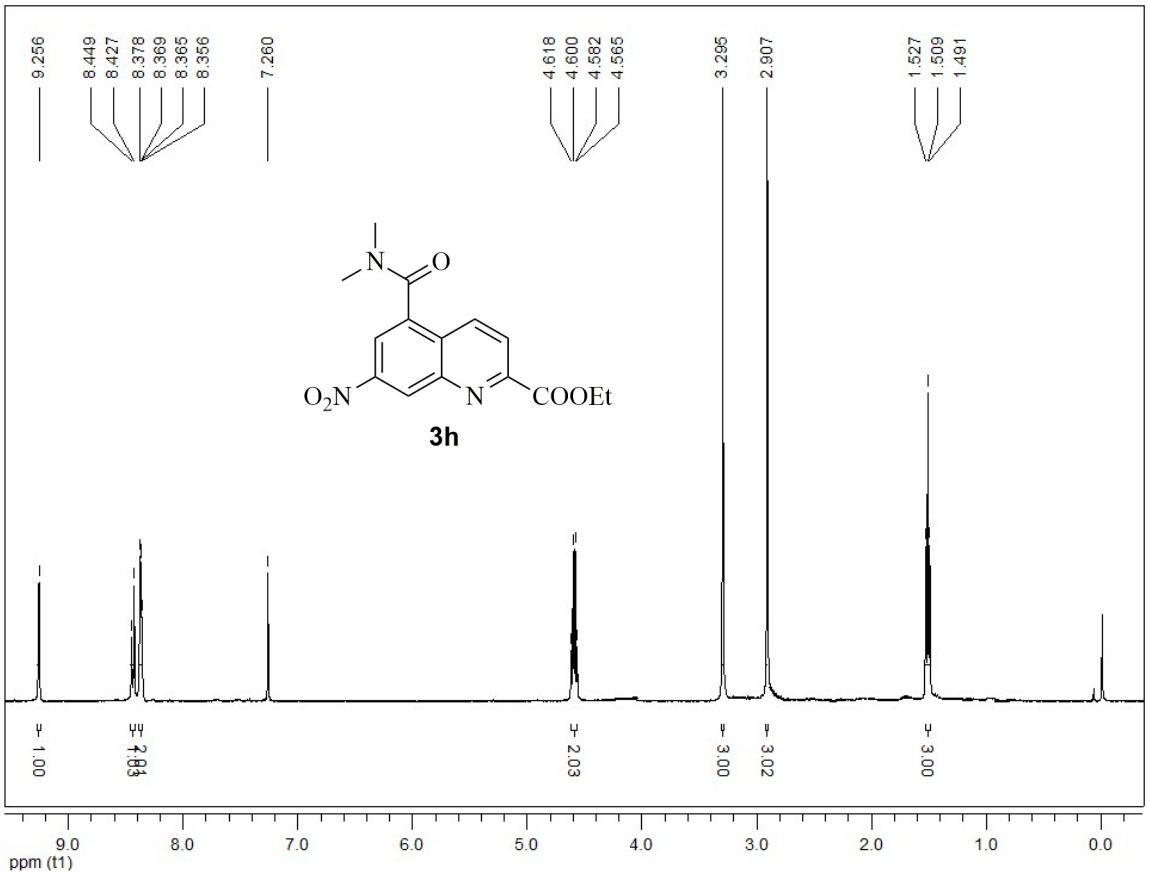
3e

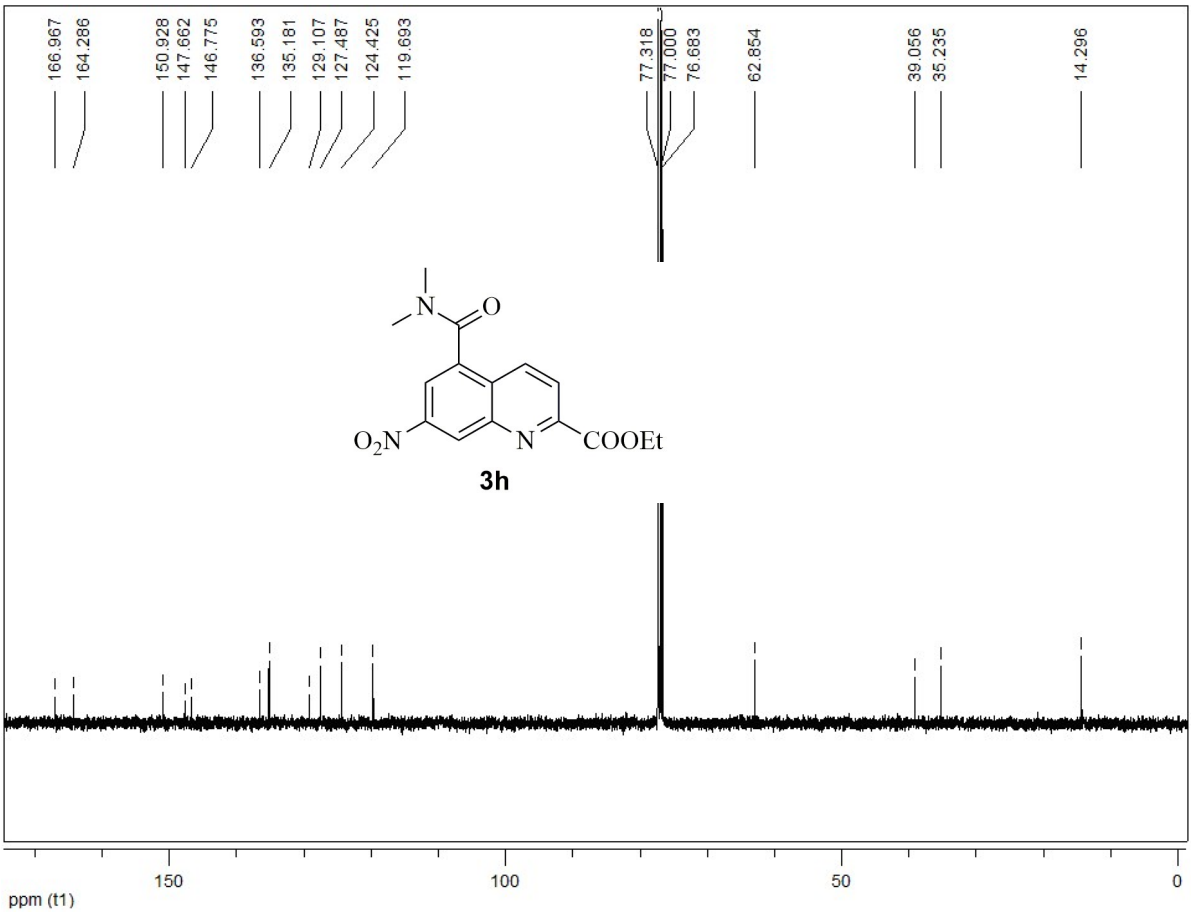

9.321
9.192
9.169
9.029
8.473
8.451
7.260
4.626
4.609
4.591
4.573
4.533
4.515
4.497
4.480
1.531
1.513
1.495
1.487
1.469
1.451
NO2
EtOOC
N
COOEt
3f
1.00
1.01
1.02
1.09
2.08
2.08
3.08
3.08
5.0
0.0
ppm (t1)


164.148
163.845
150.325
147.370
145.563
139.078
133.595
130.849
125.851
125.141
124.090
77.317
77.000
76.682
62.834
62.392
14.303
14.234
NO2
EtOOC
N
COOEt
3f
150
100
50
0
ppm (t1)

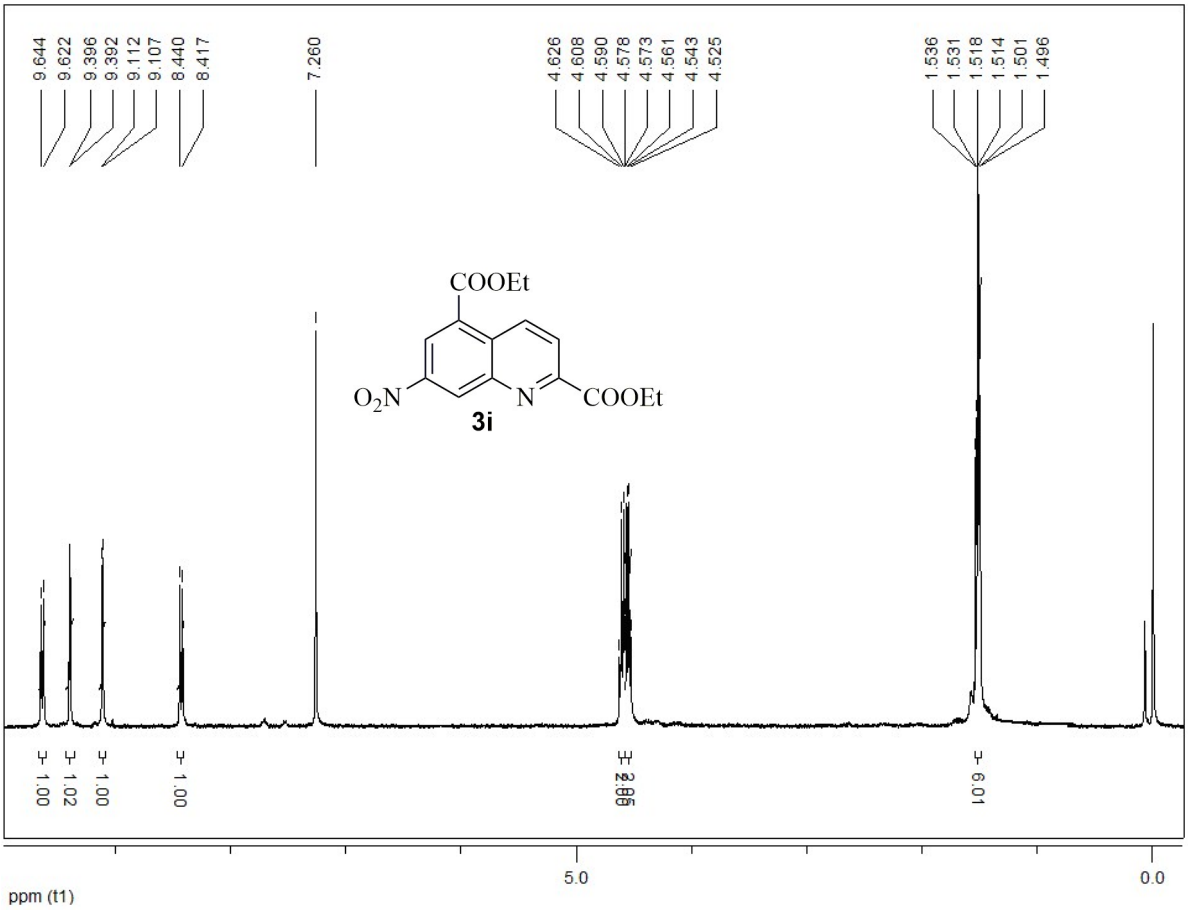

9.185
9.163
8.614
8.602
8.438
8.416
7.260
4.614
4.596
4.578
4.561
3.209
3.119
1.525
1.507
1.489
NO2
N
O
N
COOEt
3g
1.00
2.02
1.01
2.02
3.04
3.04
3.04
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

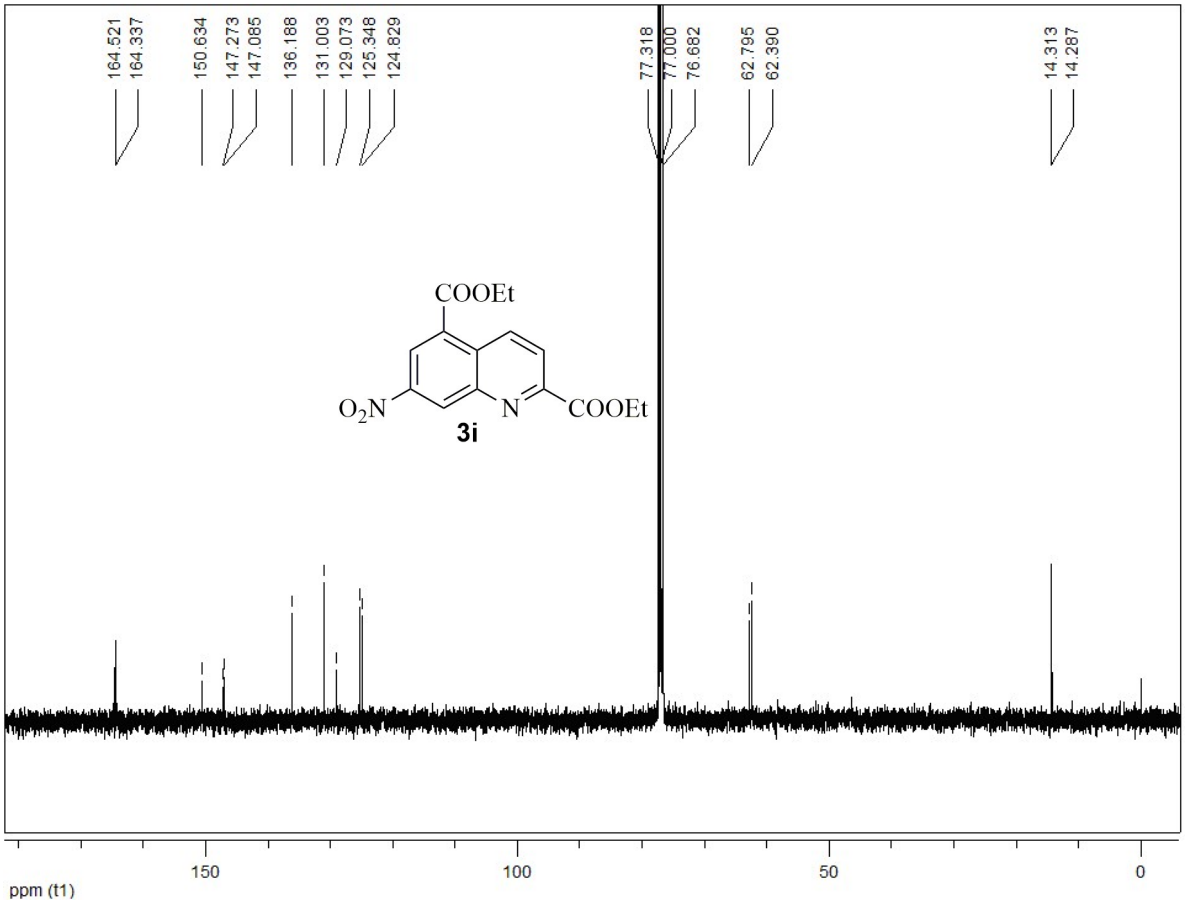

167.746
164.210
150.210
147.135
145.662
136.254
135.123
133.600
125.931
124.482
122.342
77.317
77.000
76.682
62.813
39.673
35.725
14.289
NO2
N
O
N
COOEt
3g
150
100
50
0
ppm (t1)

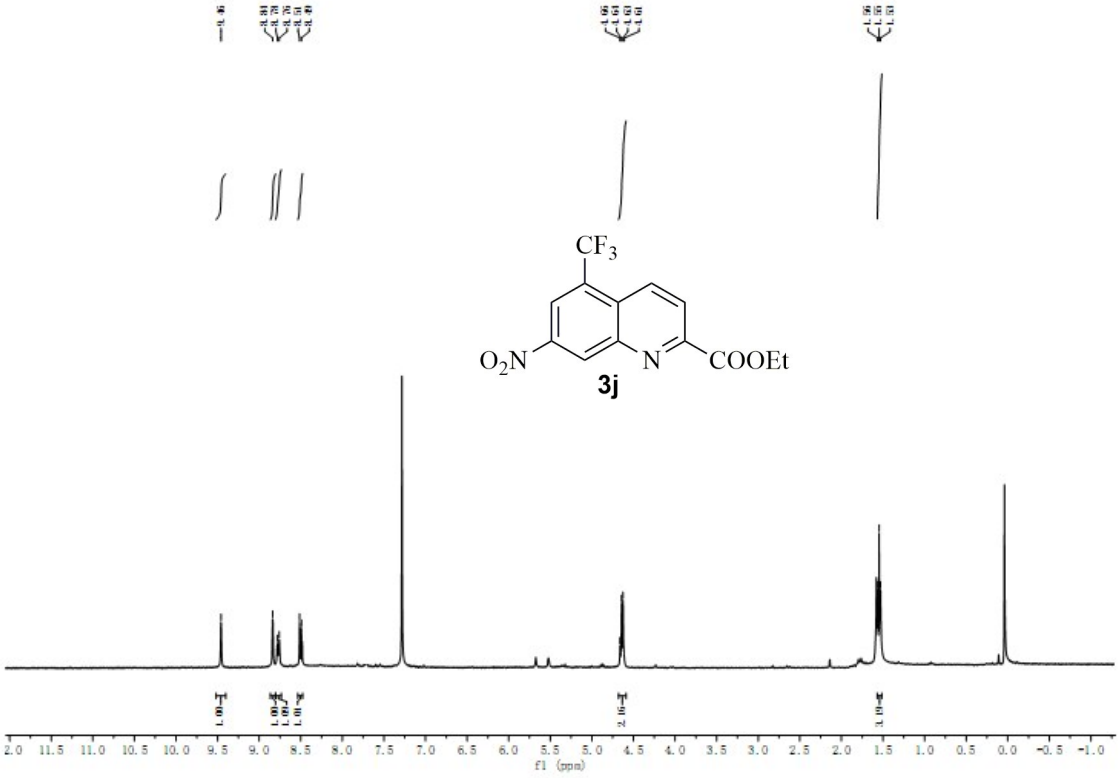

9.256
8.449
8.427
8.378
8.369
8.365
8.356
7.260
4.618
4.600
4.582
4.565
3.295
2.907
1.527
1.509
1.491
1.00
2.03
2.03
2.03
3.00
3.02
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

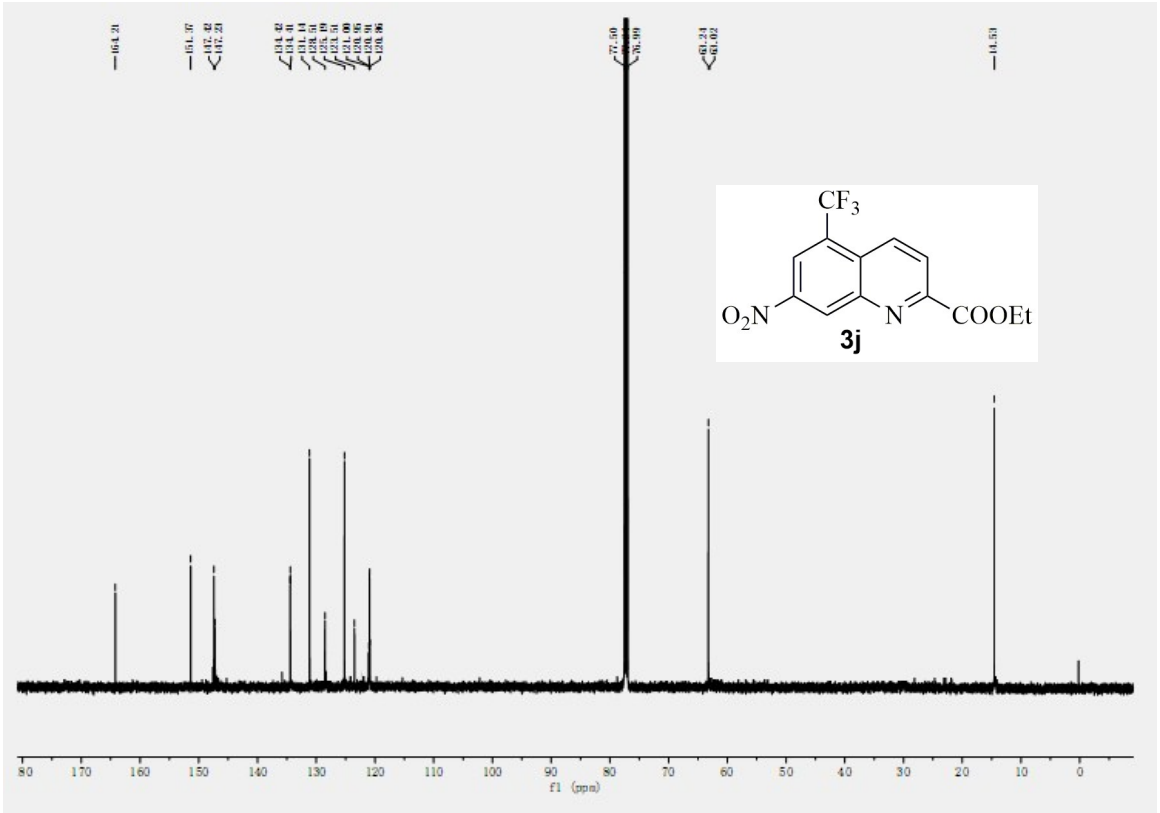

166.967
164.286
150.928
147.662
146.775
136.593
135.181
129.107
127.487
124.425
119.693
77.318
77.000
76.683
62.854
39.056
35.235
14.296
150
100
50
0
ppm (t1)

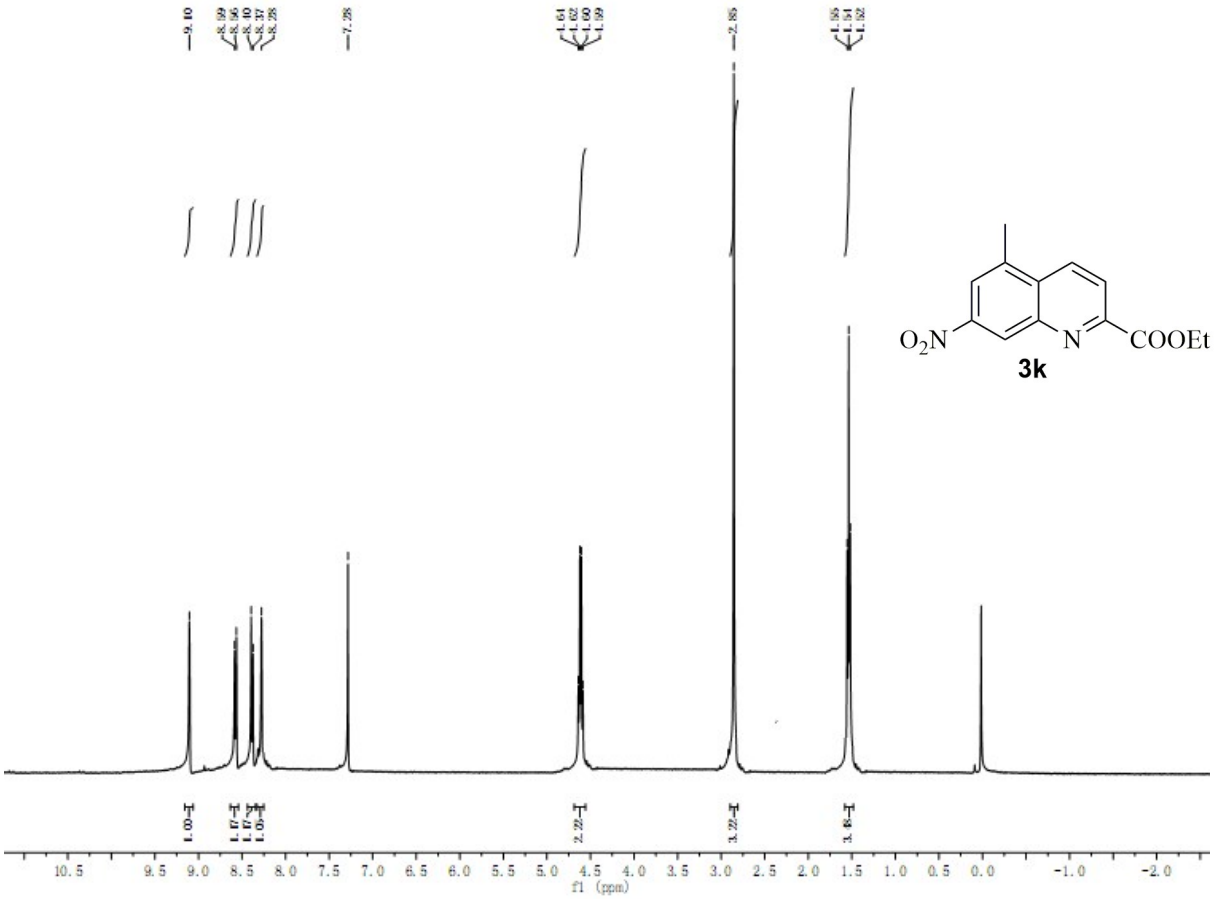
3h

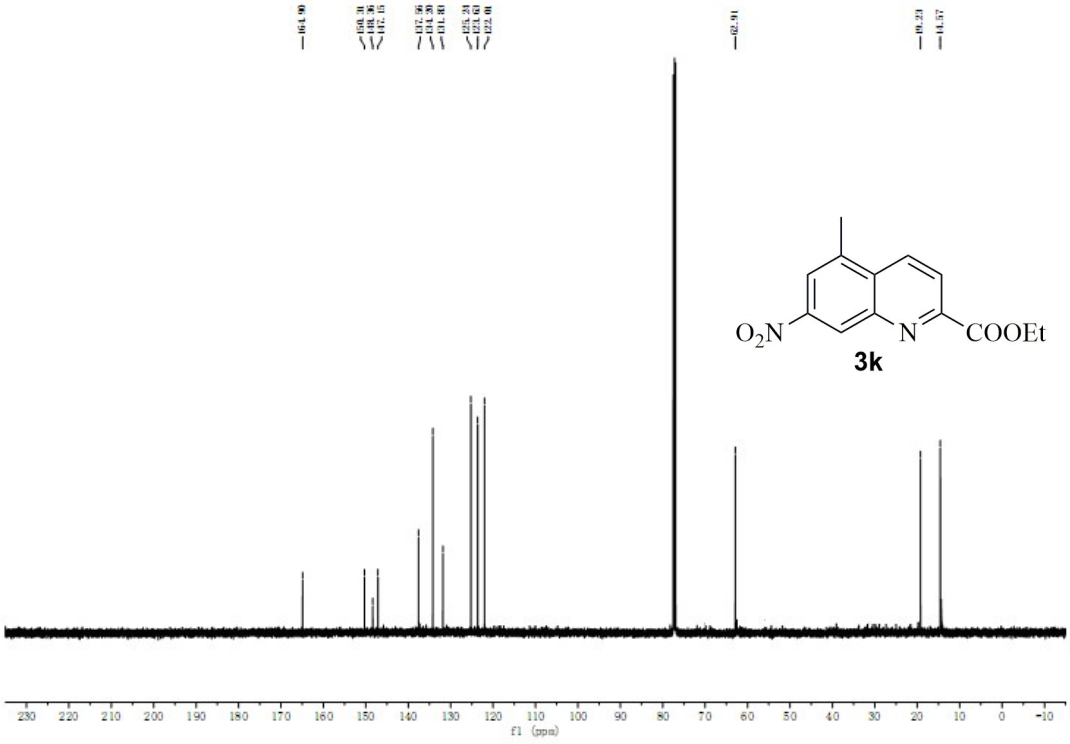

9.644
9.622
9.396
9.392
9.112
9.107
8.440
8.417
7.260
4.626
4.608
4.590
4.578
4.573
4.561
4.543
4.525
1.536
1.531
1.518
1.514
1.501
1.496
COOEt
O_2N
N
COOEt
3i
1.00
1.02
1.00
1.00
2.06
6.01
5.0
0.0
ppm (t1)

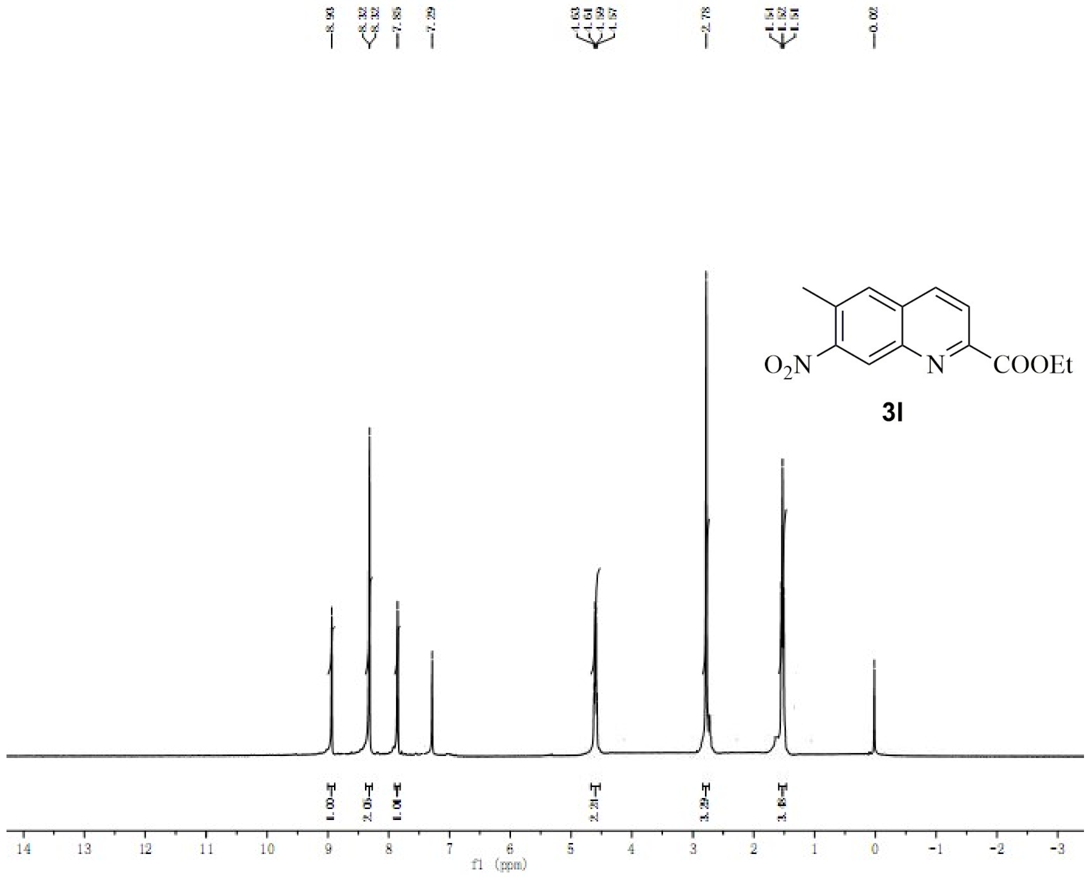

164.521
164.337
150.634
147.273
147.085
136.188
131.003
129.073
125.348
124.829
77.318
77.000
76.682
62.795
62.390
14.313
14.287
COOEt
O_2N
N
COOEt
3i
150
100
50
0
ppm (t1)

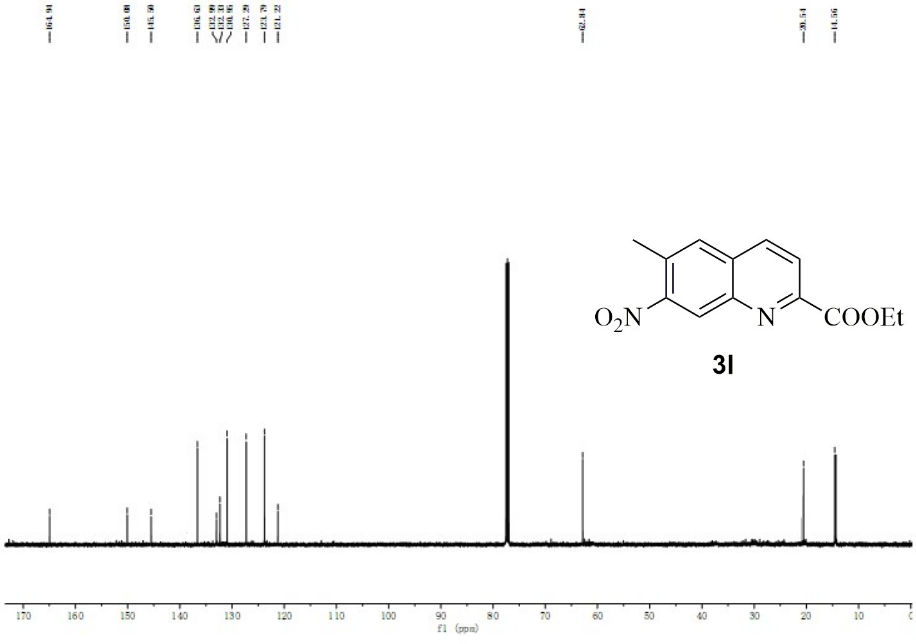

CF3
O2N
N
COOEt
3j
f1 (ppm)

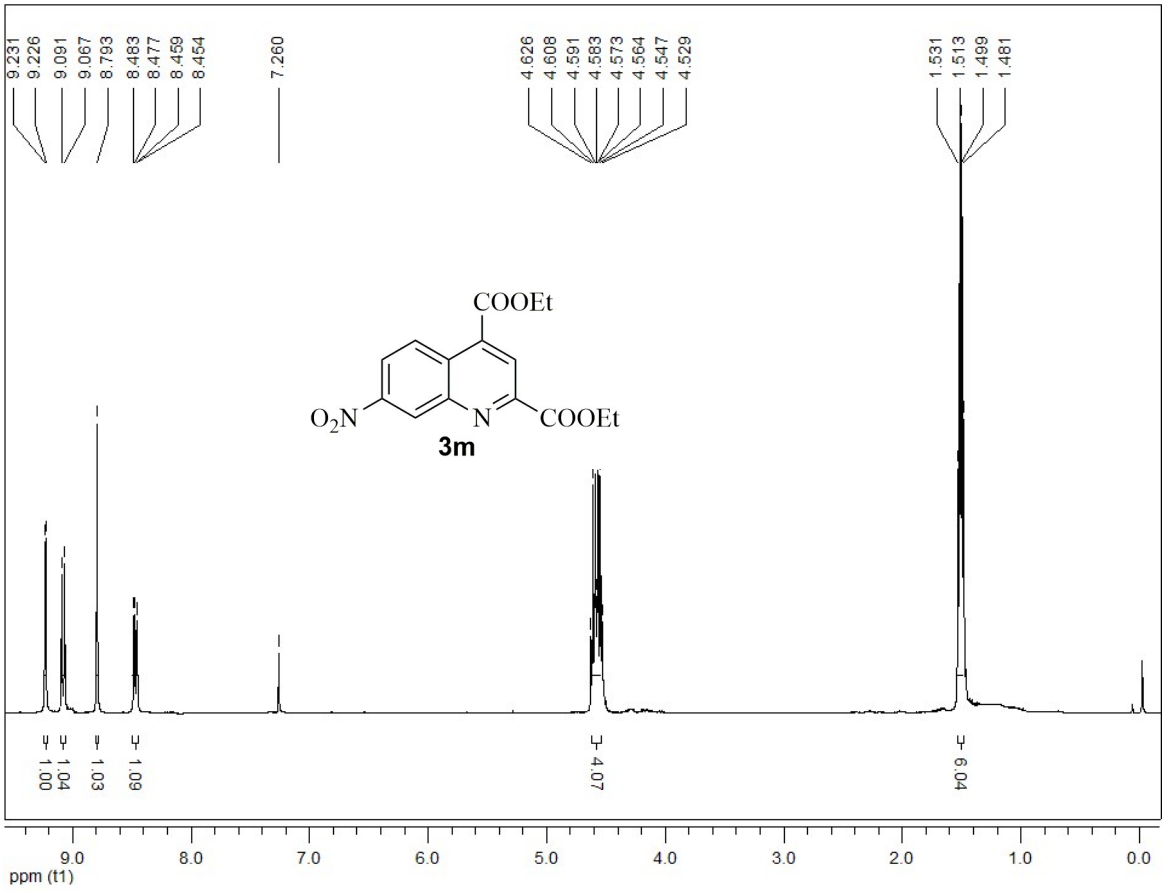

CF3
O2N
N
COOEt
3j
f1 (ppm)

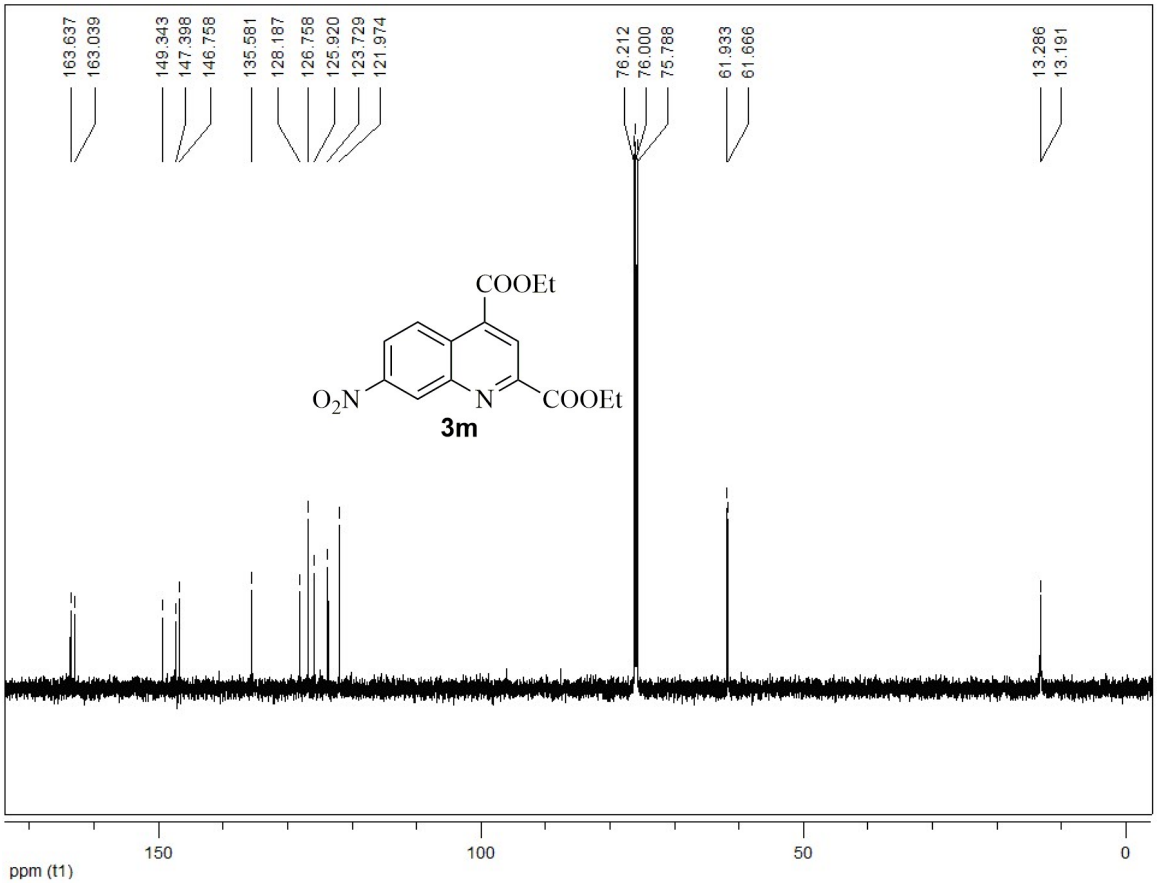

9.10
8.99
8.96
8.39
8.37
8.35
7.28
1.64
1.62
1.60
1.59
2.89
1.56
1.54
1.52
1.00
1.97
1.97
1.95
2.22
3.22
3.64
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0 -2.0
f1 (ppm)
O2N
N
COOEt
3k

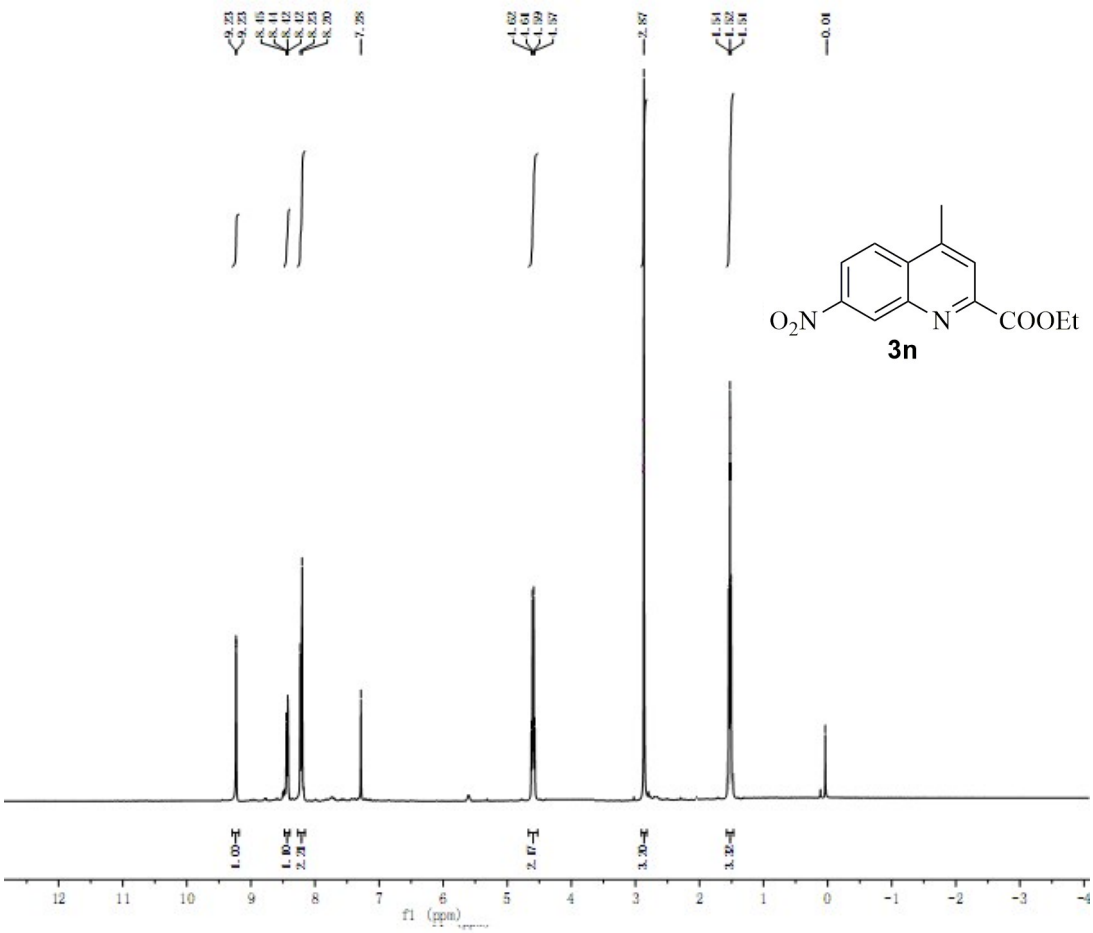

164.99
158.31
148.38
142.15
137.56
134.39
131.46
125.31
123.63
122.86
62.91
19.23
14.57
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
O2N
N
COOEt
3k

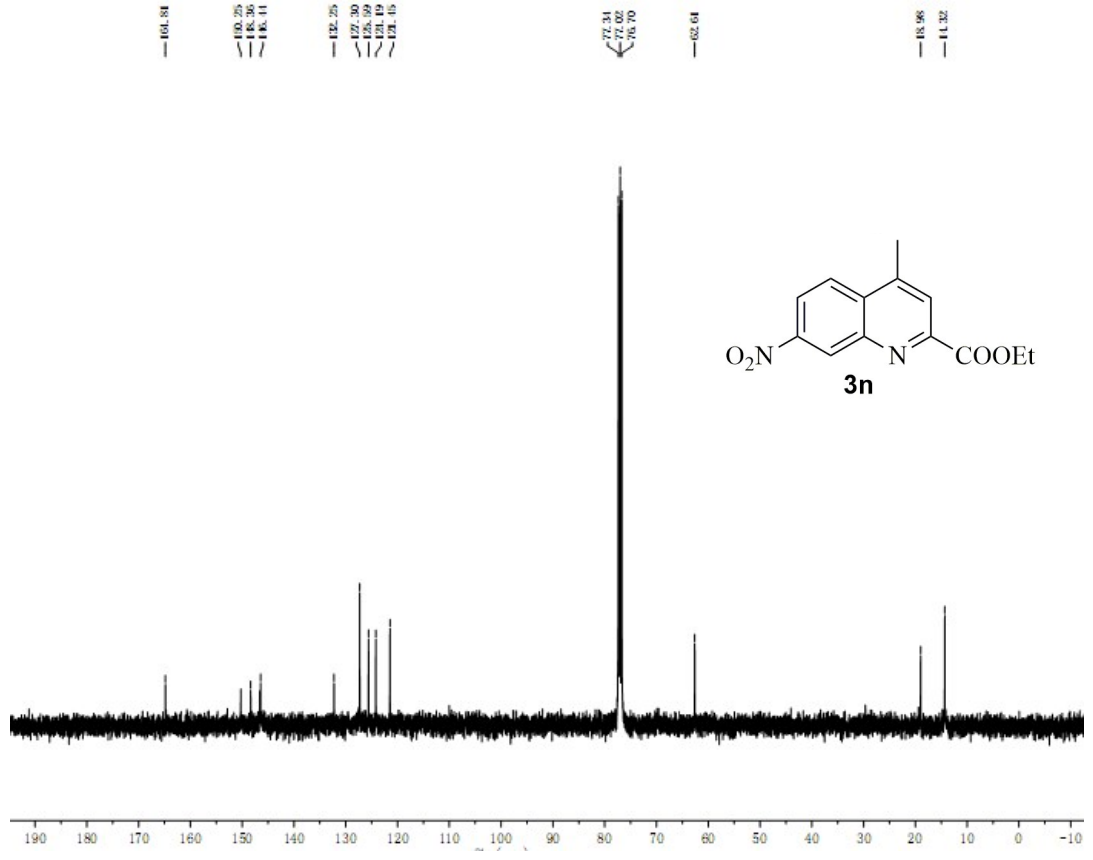

8.93
8.32
8.32
7.85
7.29
4.63
4.61
4.59
4.57
2.78
1.54
1.52
1.50
0.02
O2N
N
COOEt
3l
f1 (ppm)

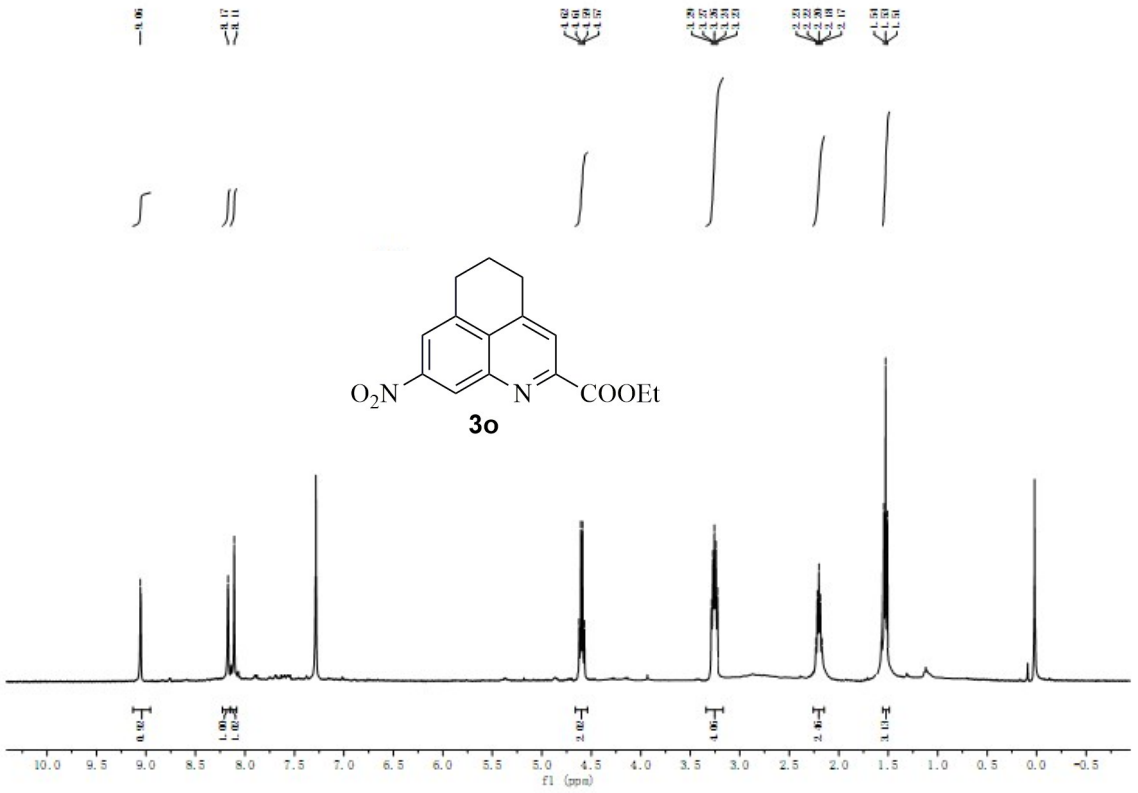

164.91
62.84
O2N
N
COOEt
3l
f1 (ppm)

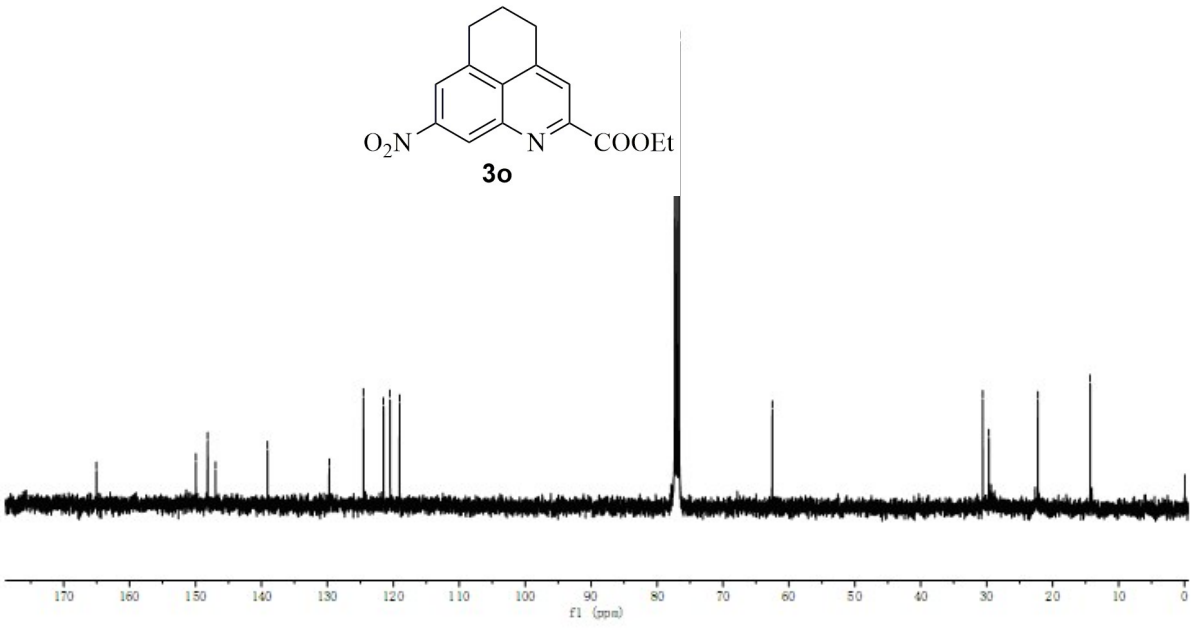

9.231
9.226
9.091
9.067
8.793
8.483
8.477
8.459
8.454
7.260
4.626
4.608
4.591
4.583
4.573
4.564
4.547
4.529
1.531
1.513
1.499
1.481
COOEt
O2N
N
COOEt
3m
1.00
1.04
1.03
1.09
4.07
6.04
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

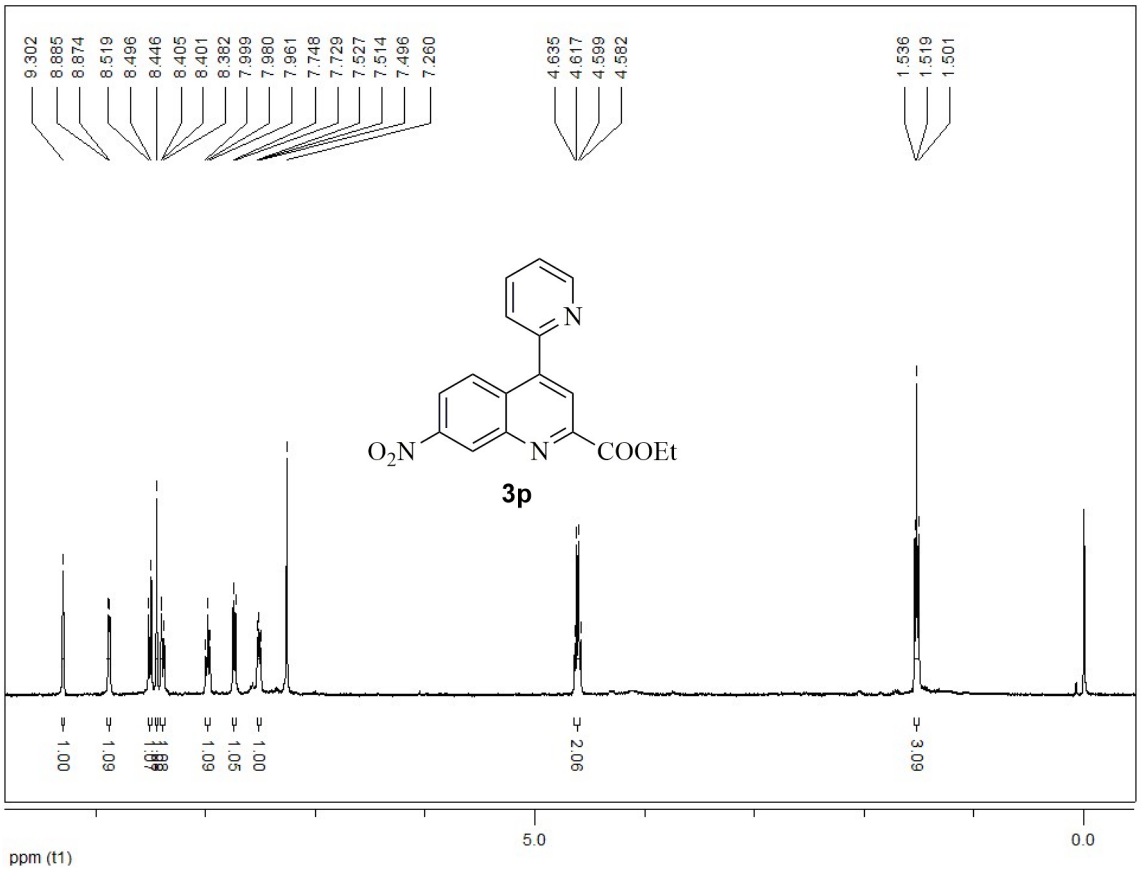

163.637
163.039
149.343
147.398
146.758
135.581
128.187
126.758
125.920
123.729
121.974
76.212
76.000
75.788
61.933
61.666
13.286
13.191
COOEt
O2N
N
COOEt
3m
150
100
50
0
ppm (t1)


9.23
9.23
8.15
8.11
8.12
8.12
8.25
8.25
8.20
7.28
1.62
1.64
1.59
1.57
2.87
1.54
1.52
1.50
0.01
1.00
1.10
2.23
2.17
3.30
3.32
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)
O2N
N
COOEt
3n


164.84
150.25
148.36
146.11
132.25
127.39
125.39
121.19
121.15
77.34
77.02
76.70
62.64
18.98
14.32
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
O2N
N
COOEt
3n


O2N
N
COOEt
3o
f1 (ppm)


O2N
N
COOEt
3o
f1 (ppm)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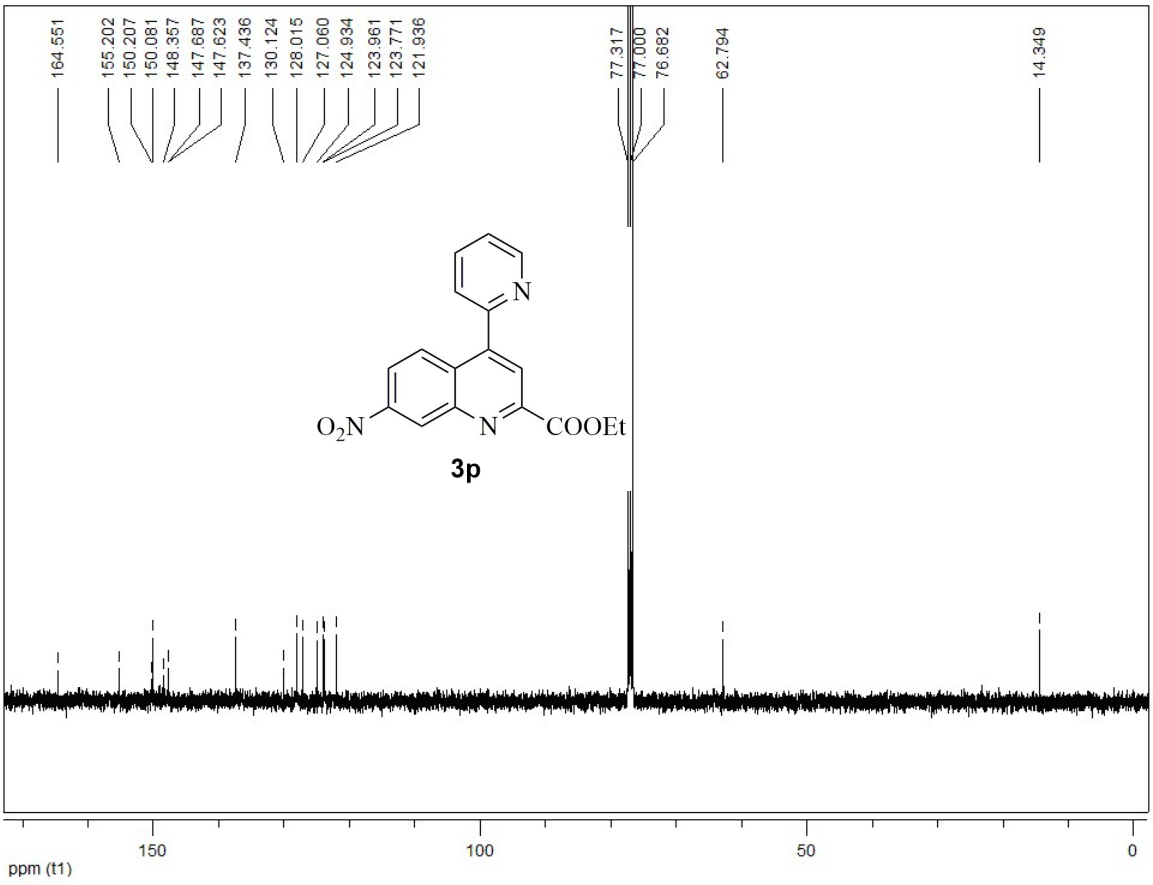
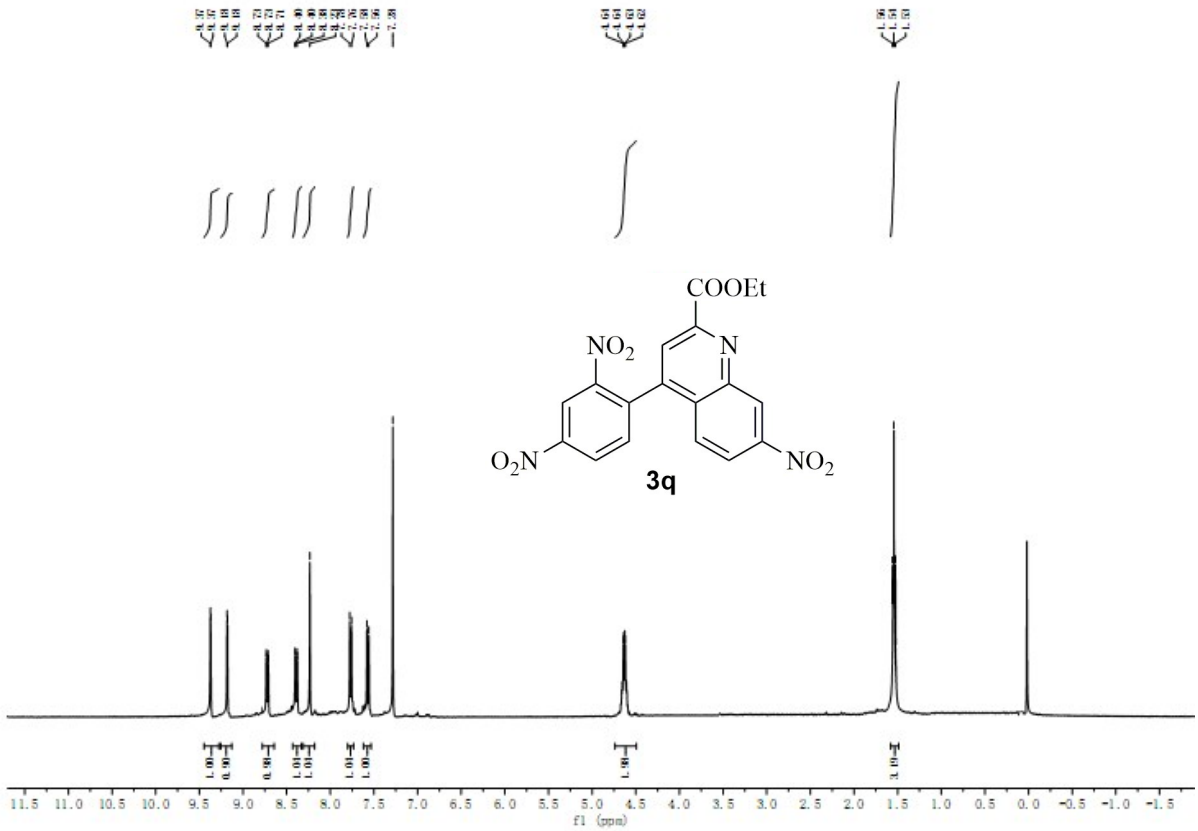
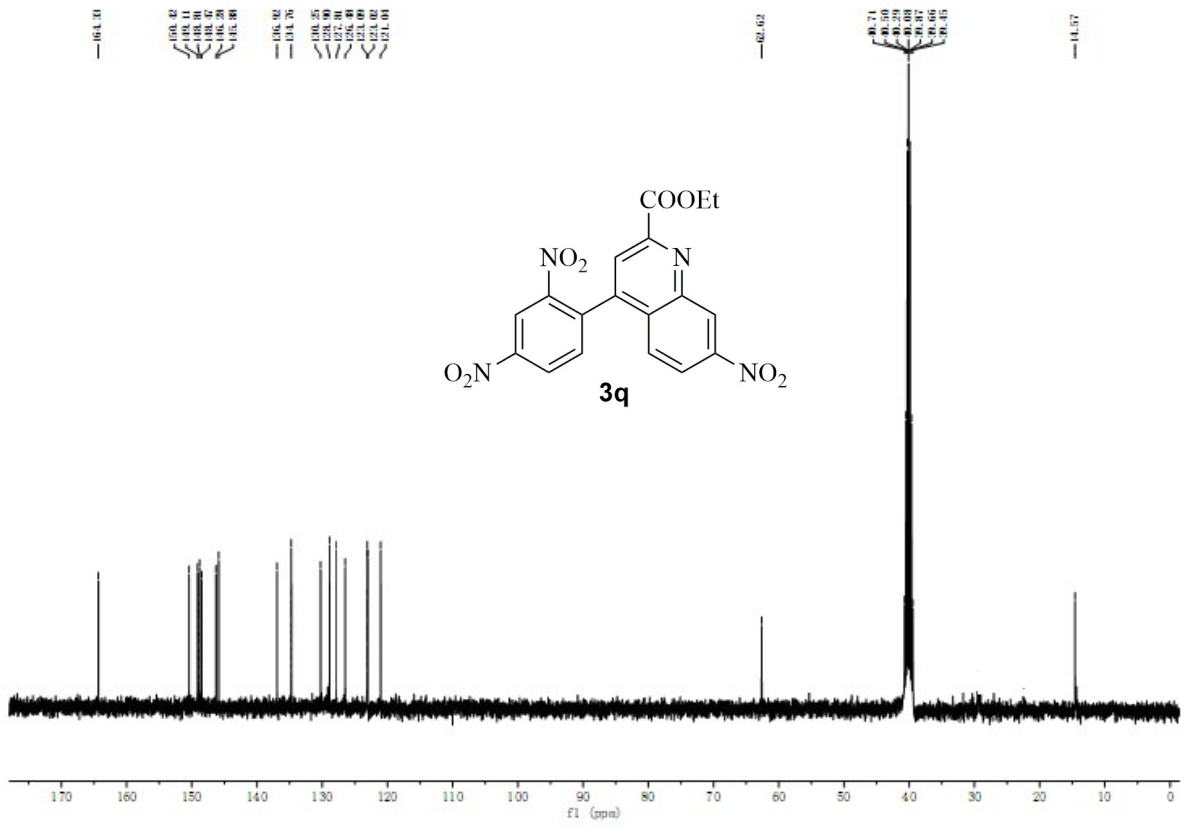
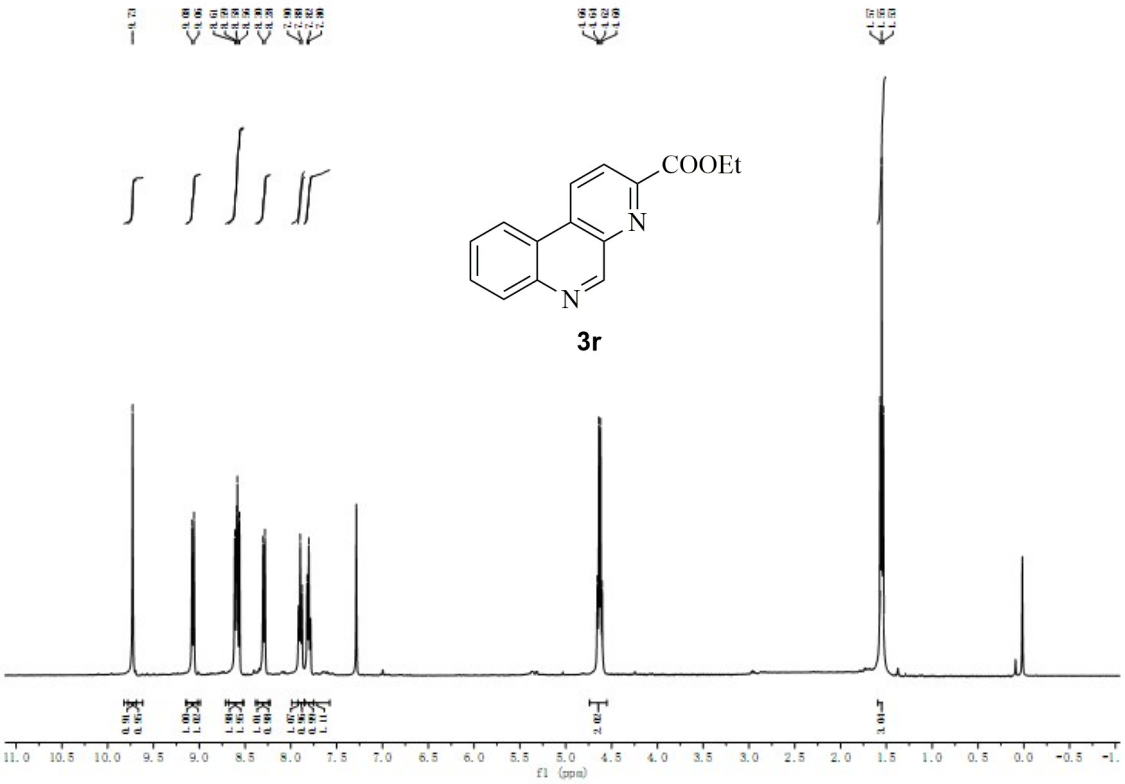
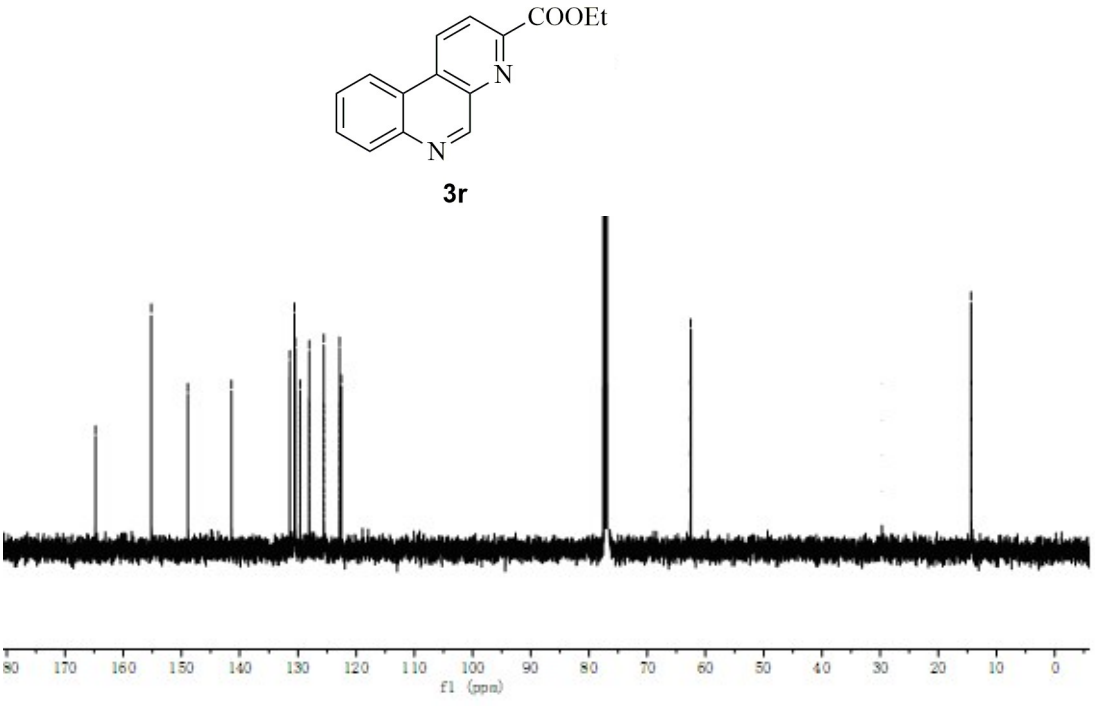
8.874
8.519
8.496
8.446
8.405
8.401
8.382
7.999
7.980
7.961
7.748
7.729
7.527
7.514
7.496
7.260
4.635
4.617
4.599
4.582
1.536
1.519
1.501
N
O2N
N
COOEt
3p
1.00
1.09
1.09
1.05
1.00
2.06
3.09
5.0
0.0
ppm (t1)

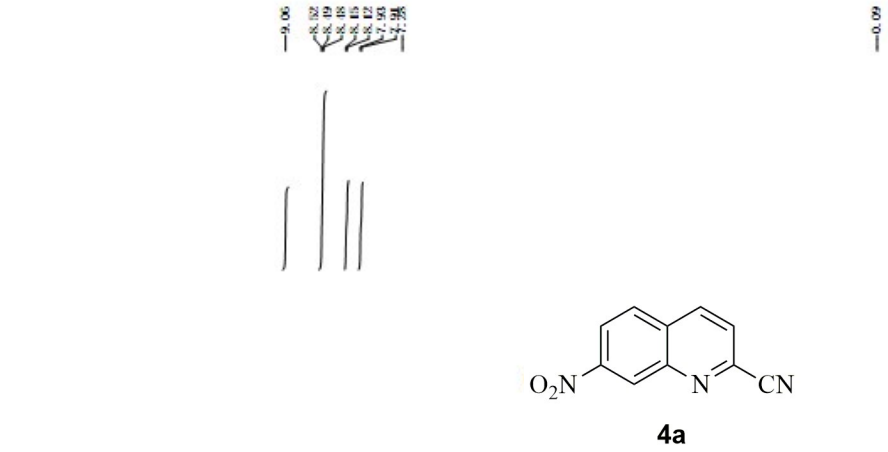

164.551
155.202
150.207
150.081
148.357
147.687
147.623
137.436
130.124
128.015
127.060
124.934
123.961
123.771
121.936
77.317
77.000
76.682
62.794
14.349
N
O2N
N
COOEt
3p
150
100
50
0
ppm (t1)


COOEt
NO2
N
O2N
NO2
3q
f1 (ppm)

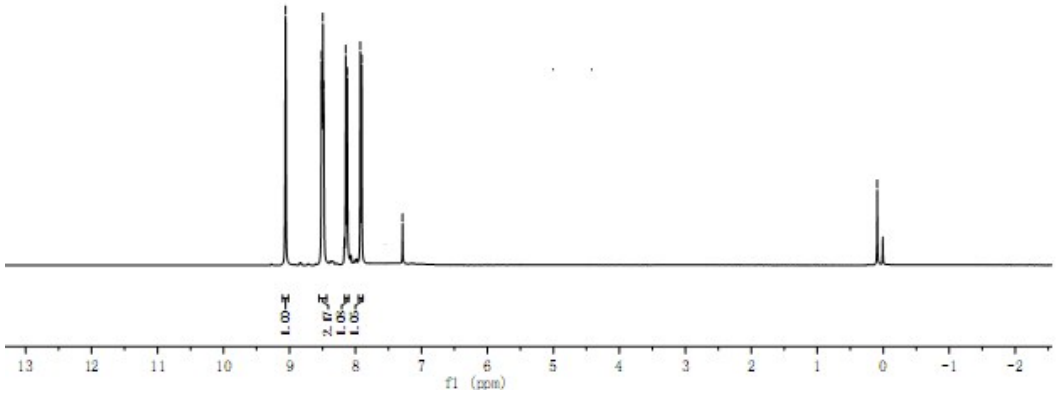

COOEt
NO2
N
O2N
NO2
3q
f1 (ppm)

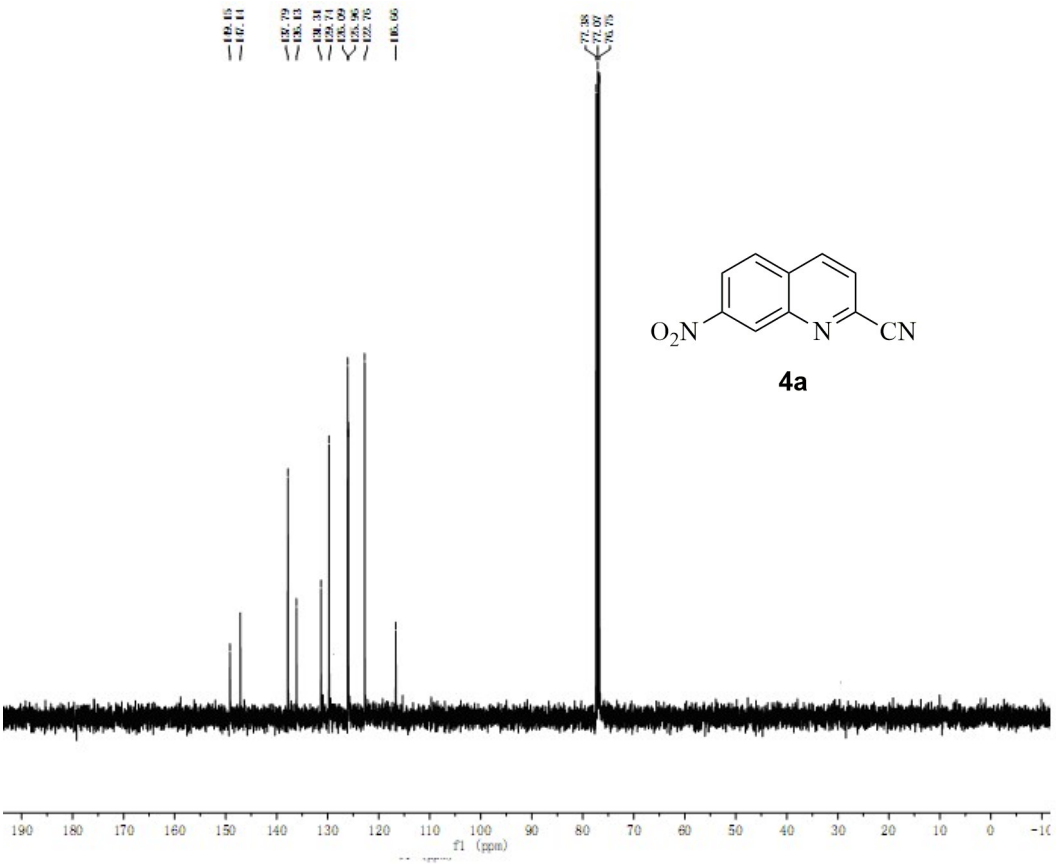

COOEt
N
N
3r
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)


COOEt
N
N
3r
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

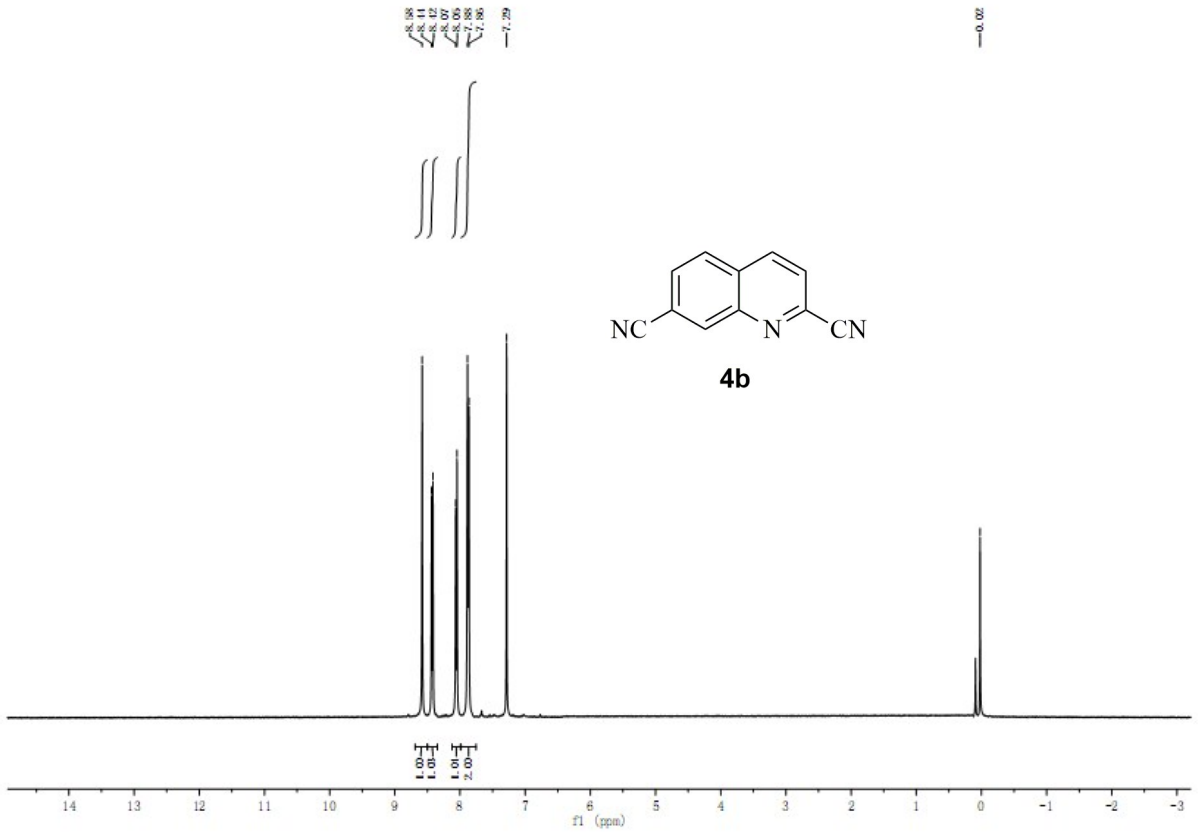


4a

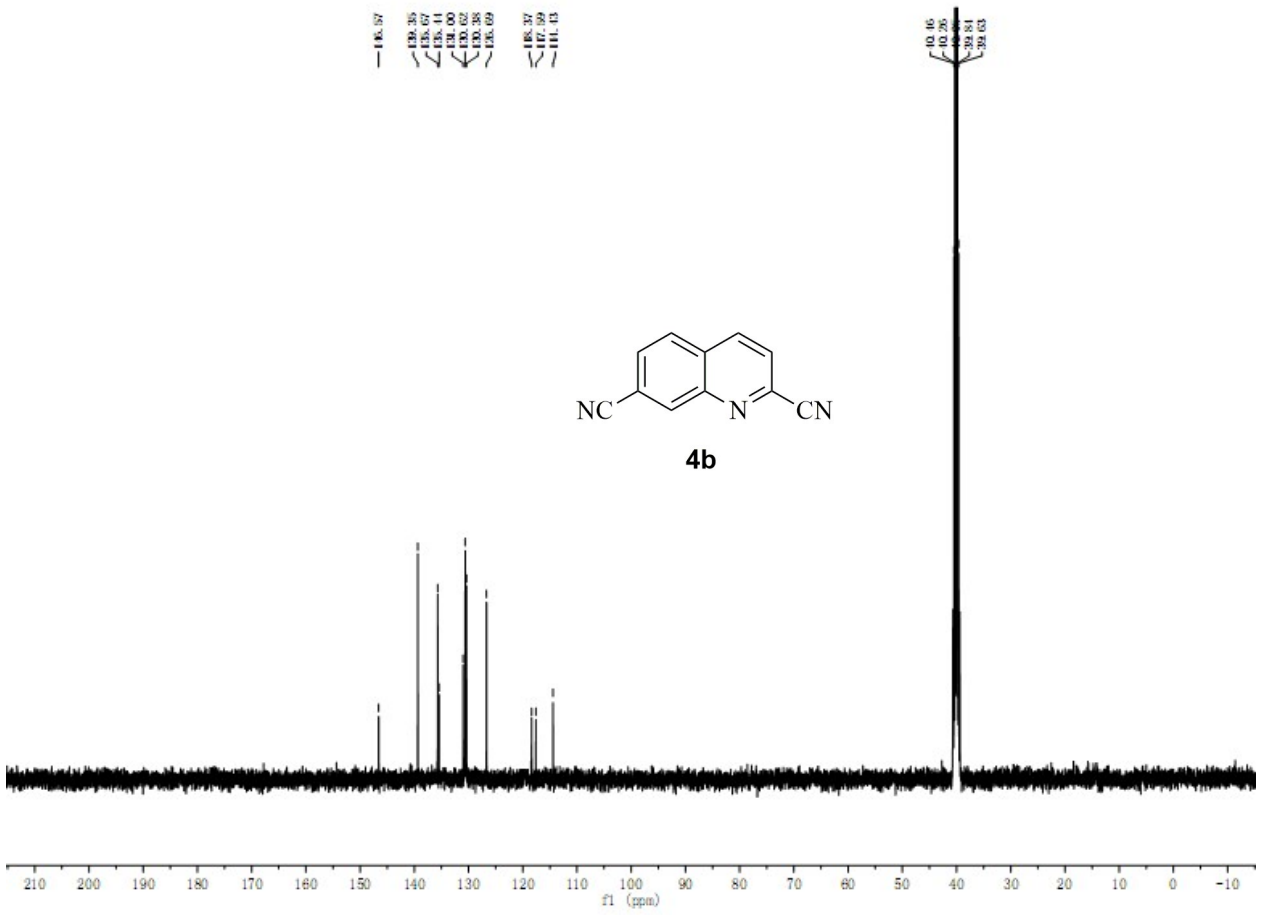




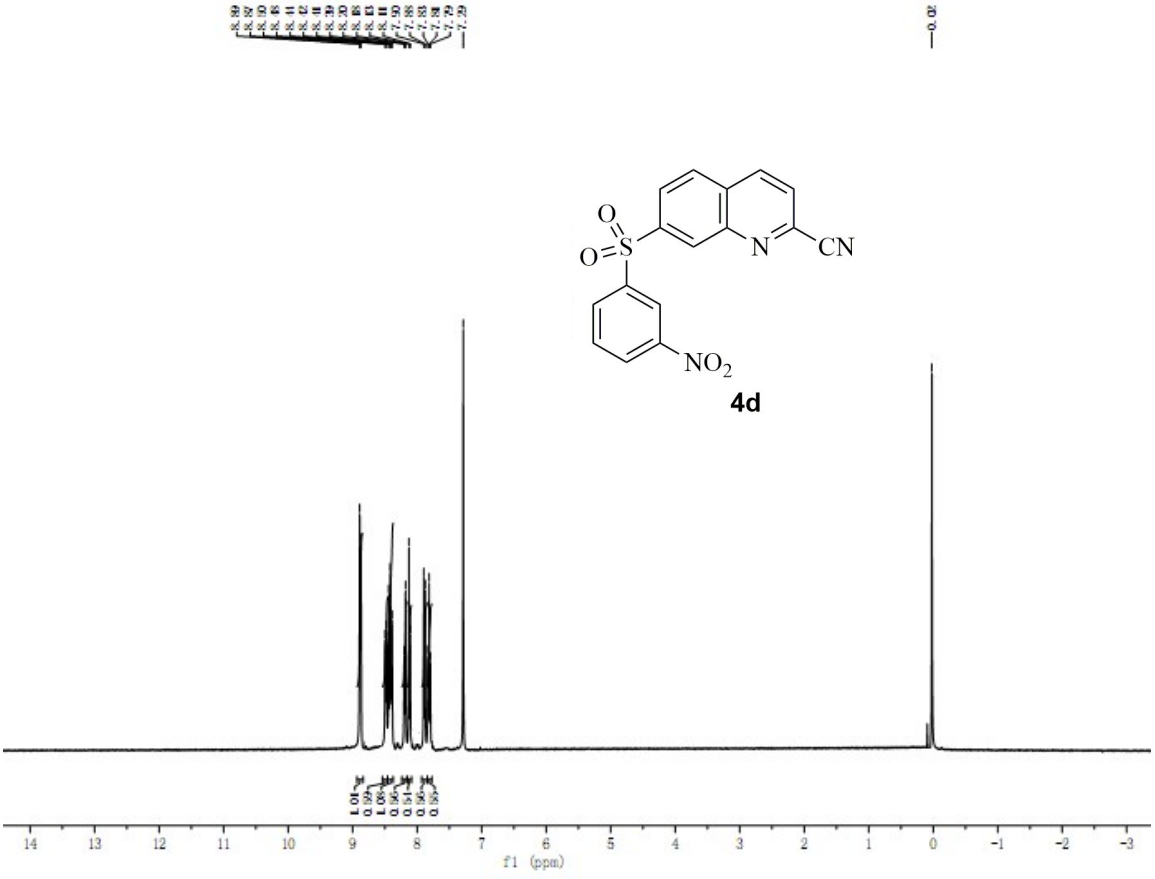
4a

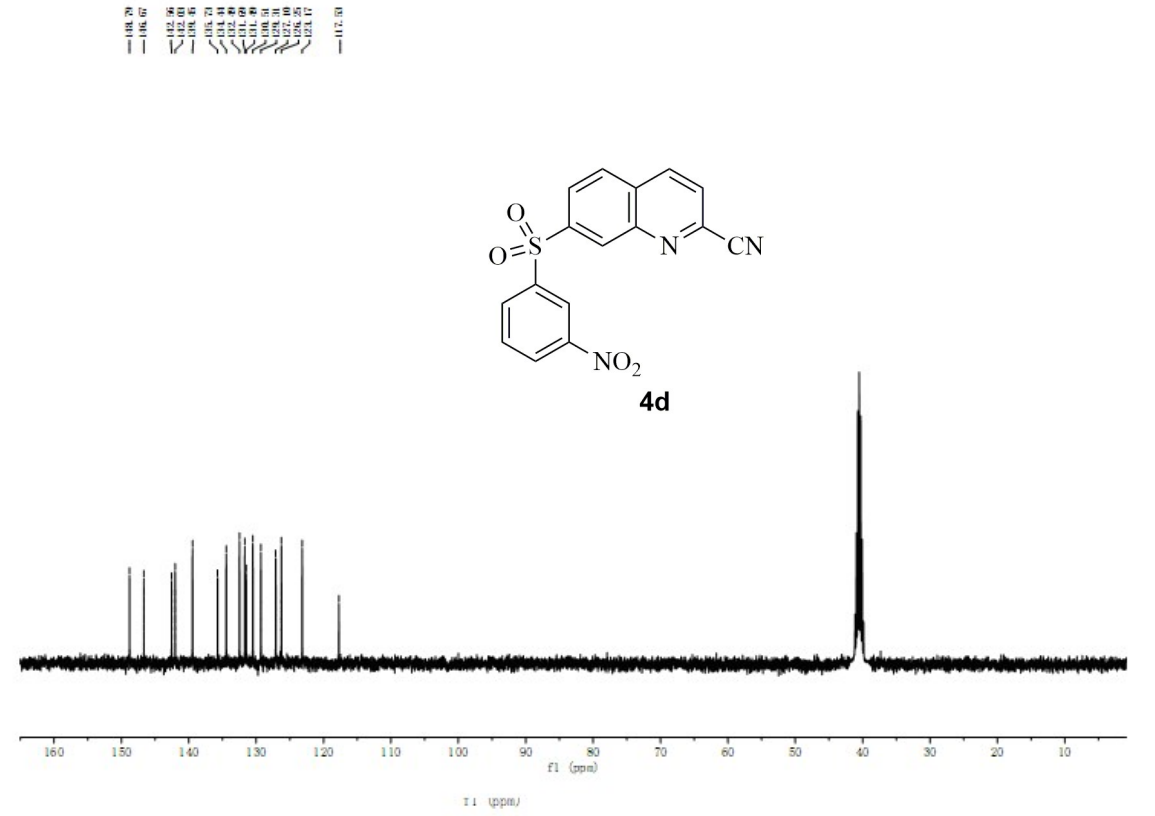

8.08
8.11
8.12
8.07
8.06
7.88
7.86
7.29
0.00
NC
N
CN
1.03
1.05
1.01
2.03
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

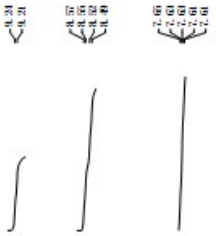
4b

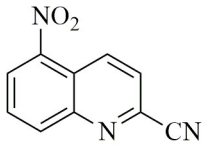

146.57
139.35
135.67
135.11
131.00
130.62
130.38
125.09
118.37
117.99
111.13
40.16
40.05
39.84
39.63
NC
N
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

4b

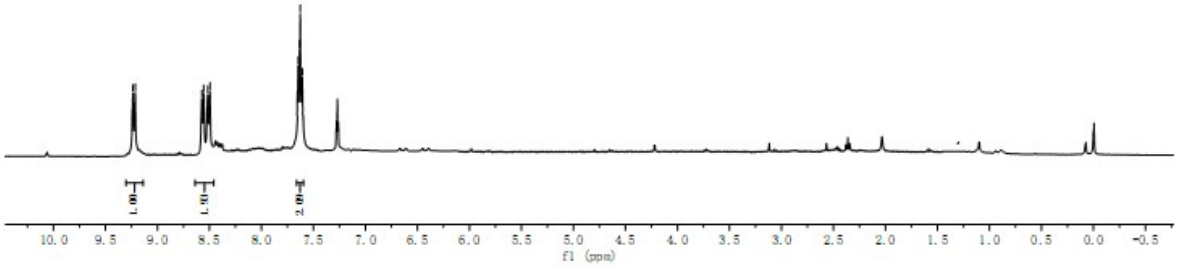

O
O
S
N
CN
NO2
4d
f1 (ppm)

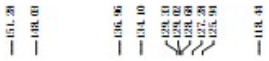

O
O
S
N
CN
NO2
4d
f1 (ppm)

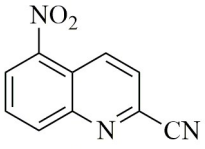




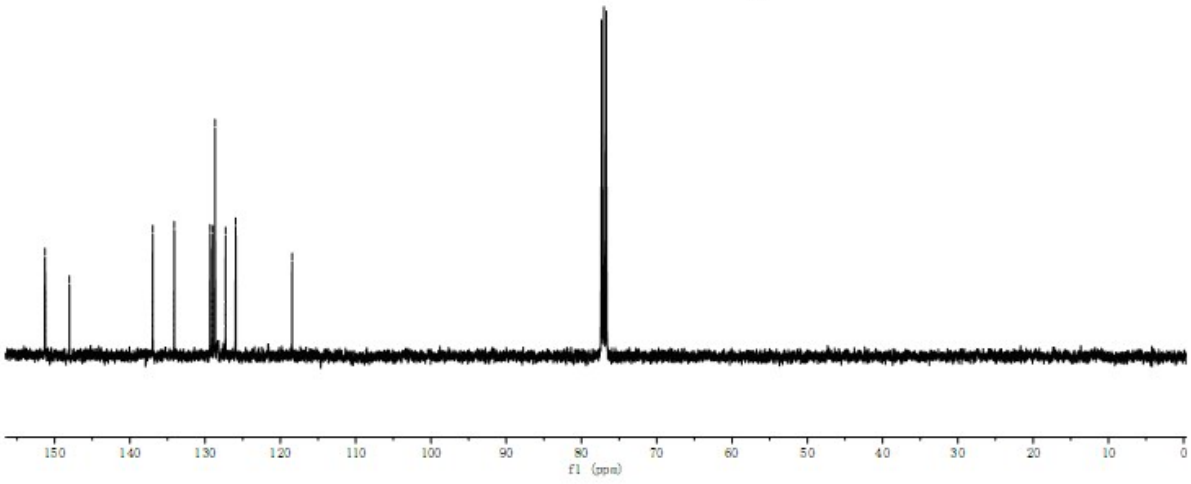
4e

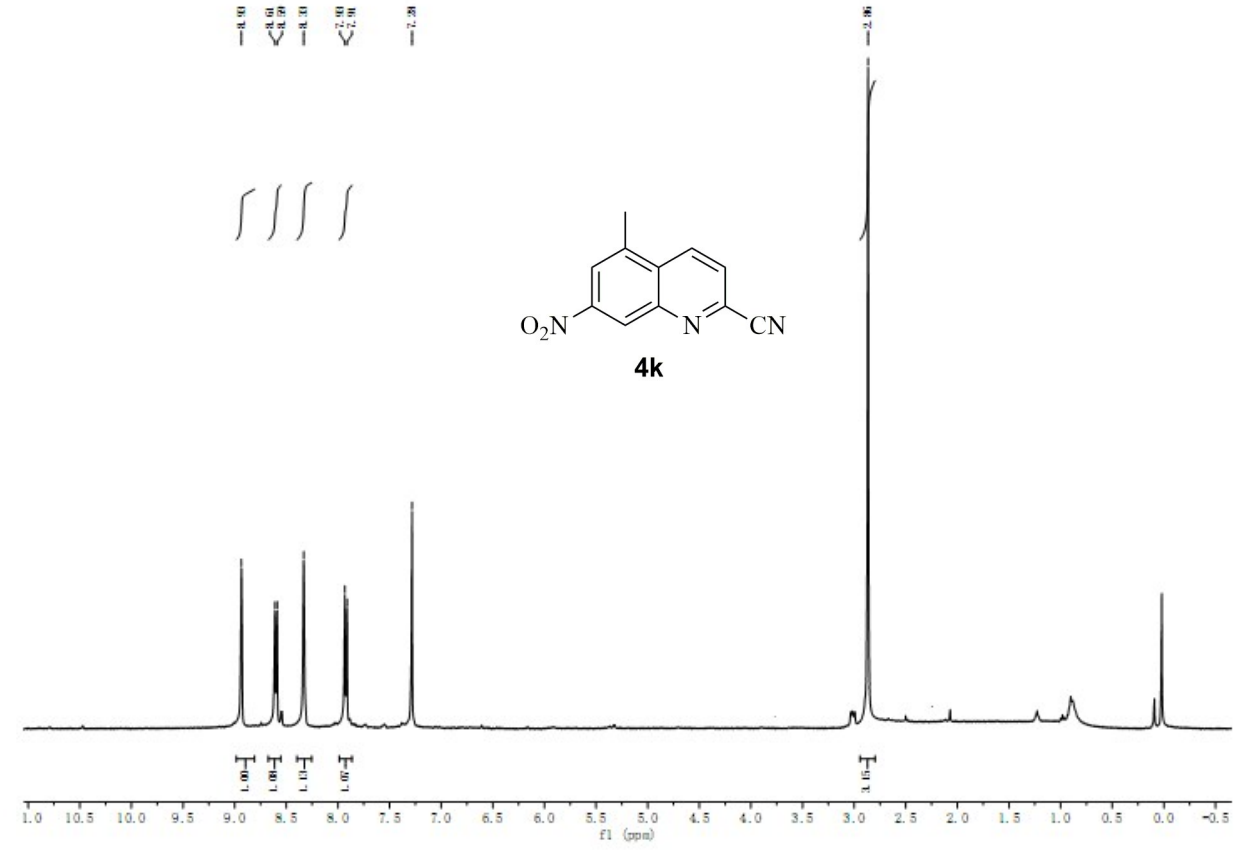






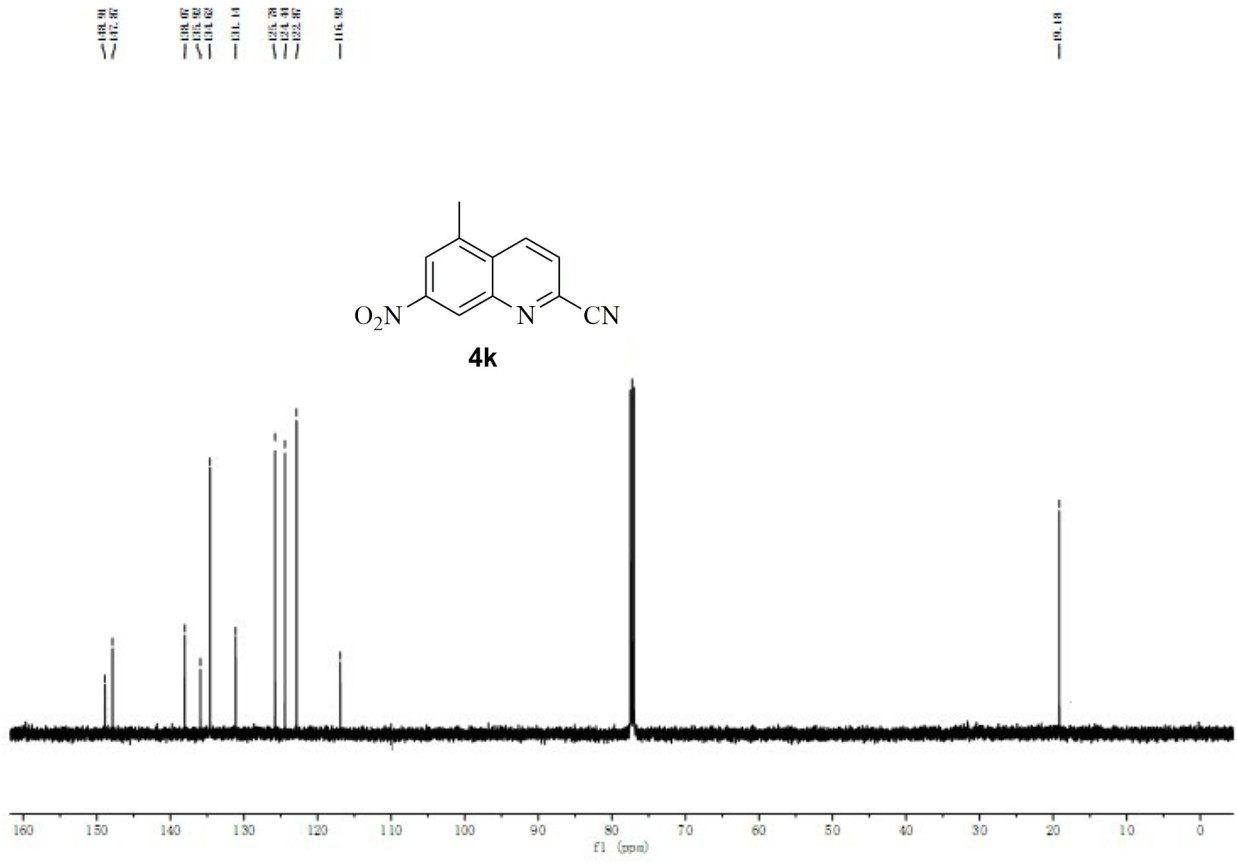
4e




8.99
8.61
8.59
8.30
7.93
7.91
7.28
2.96
1.00
1.08
1.03
1.07
3.15
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

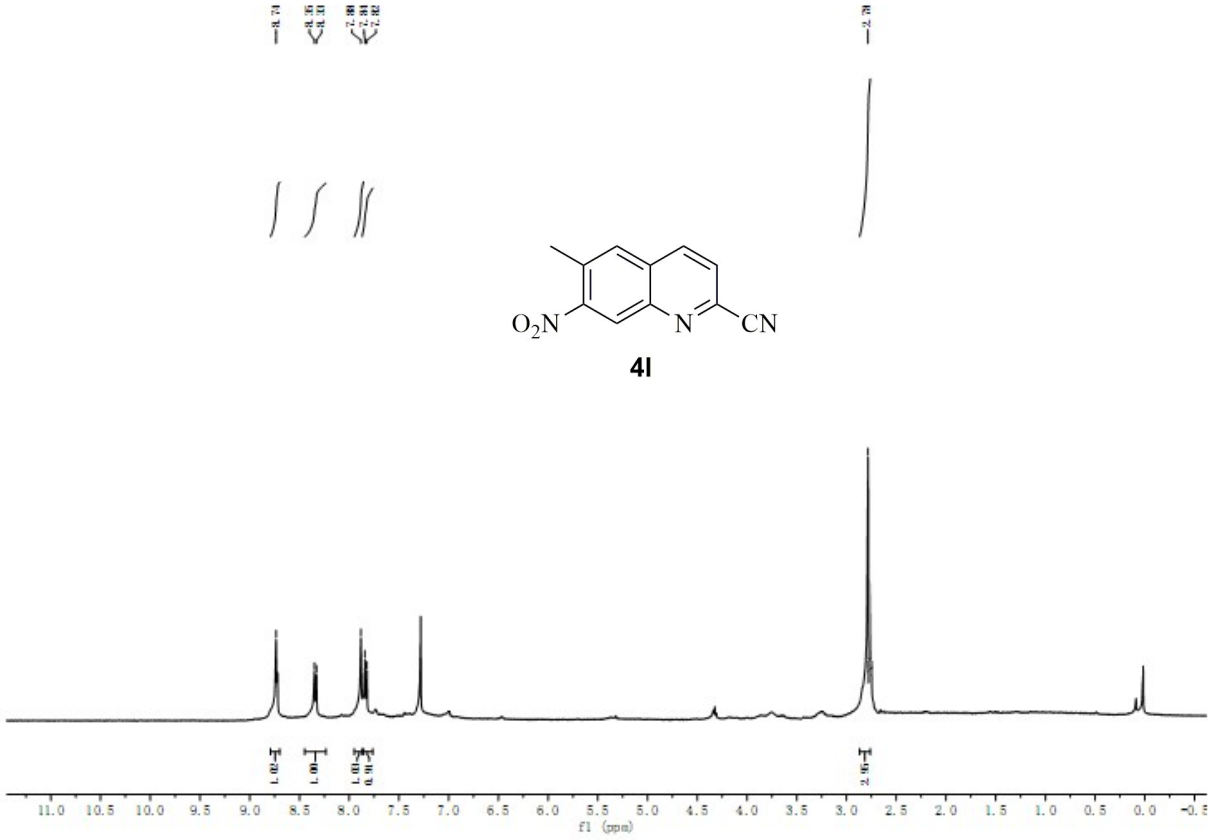
O2N
N
CN

4k

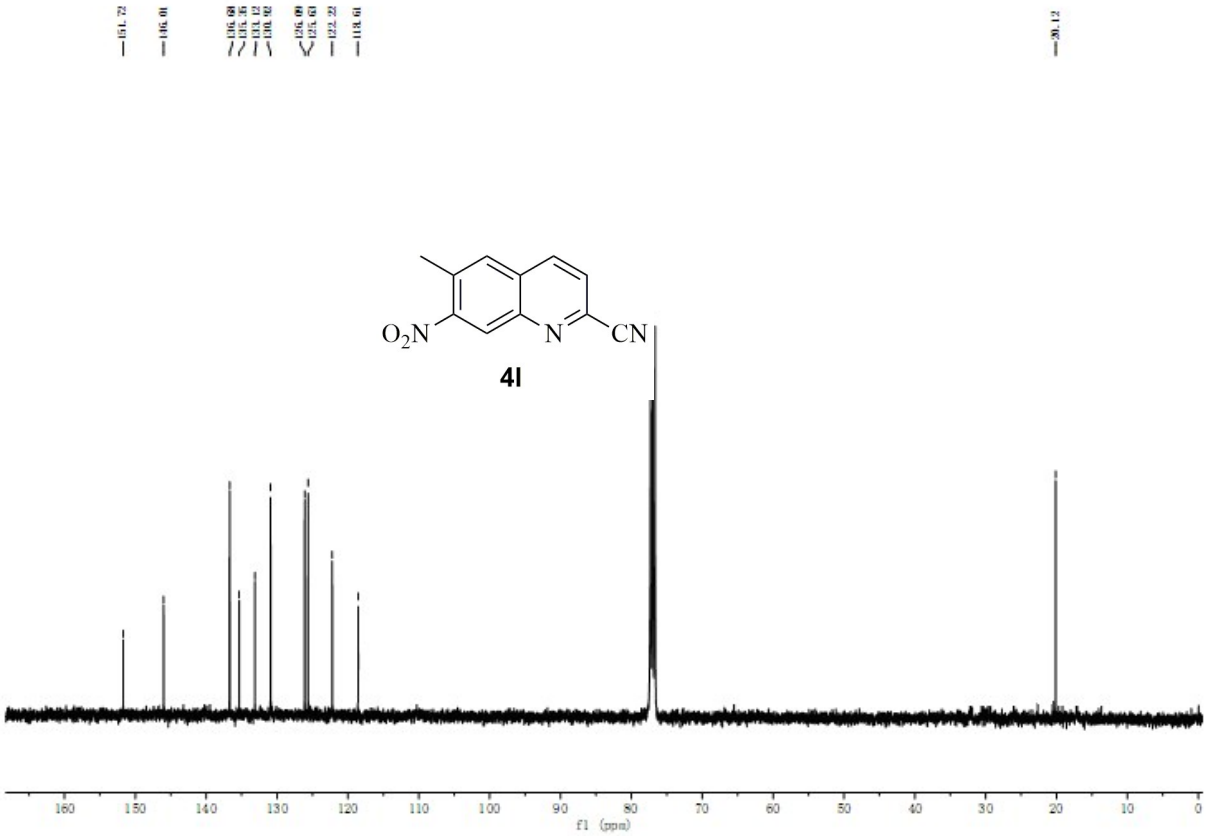

148.91
147.87
138.67
135.92
134.62
131.14
125.78
124.44
122.87
116.92
19.18
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

O2N
N
CN

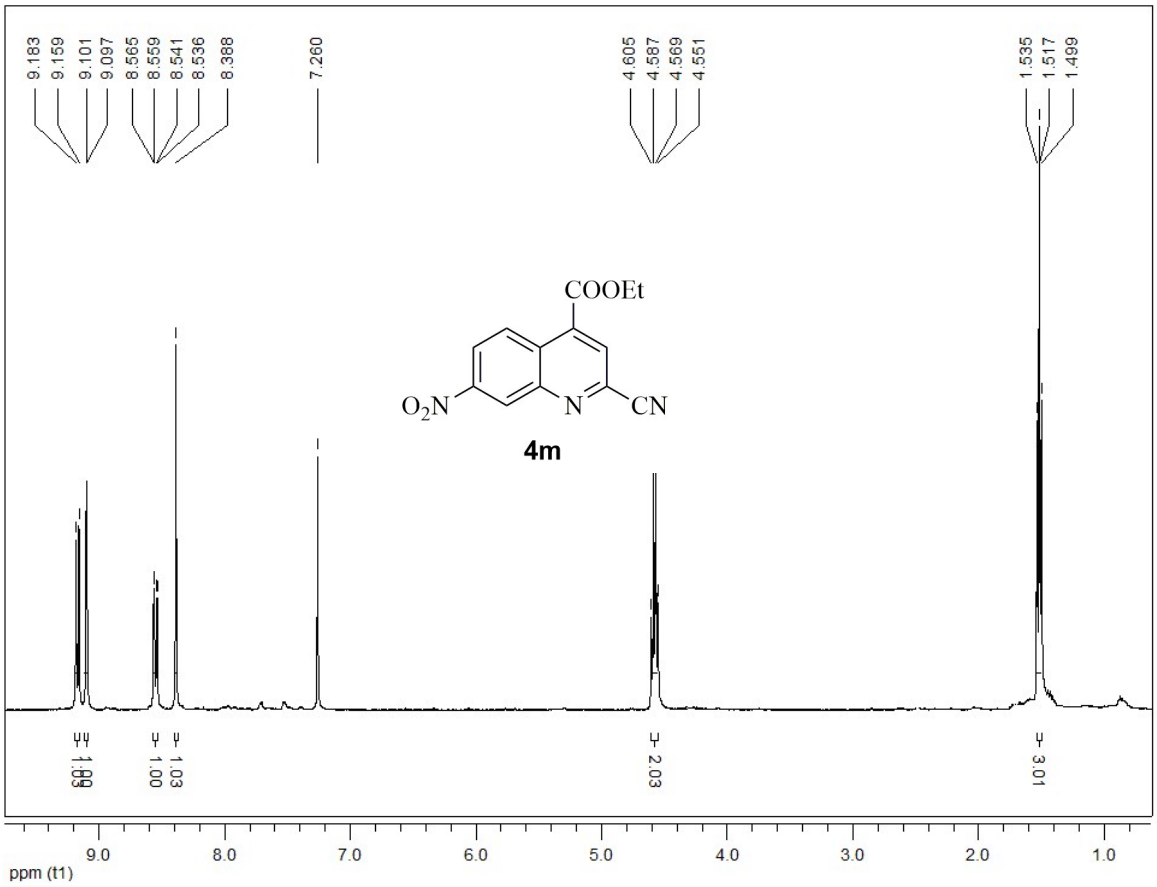
4k

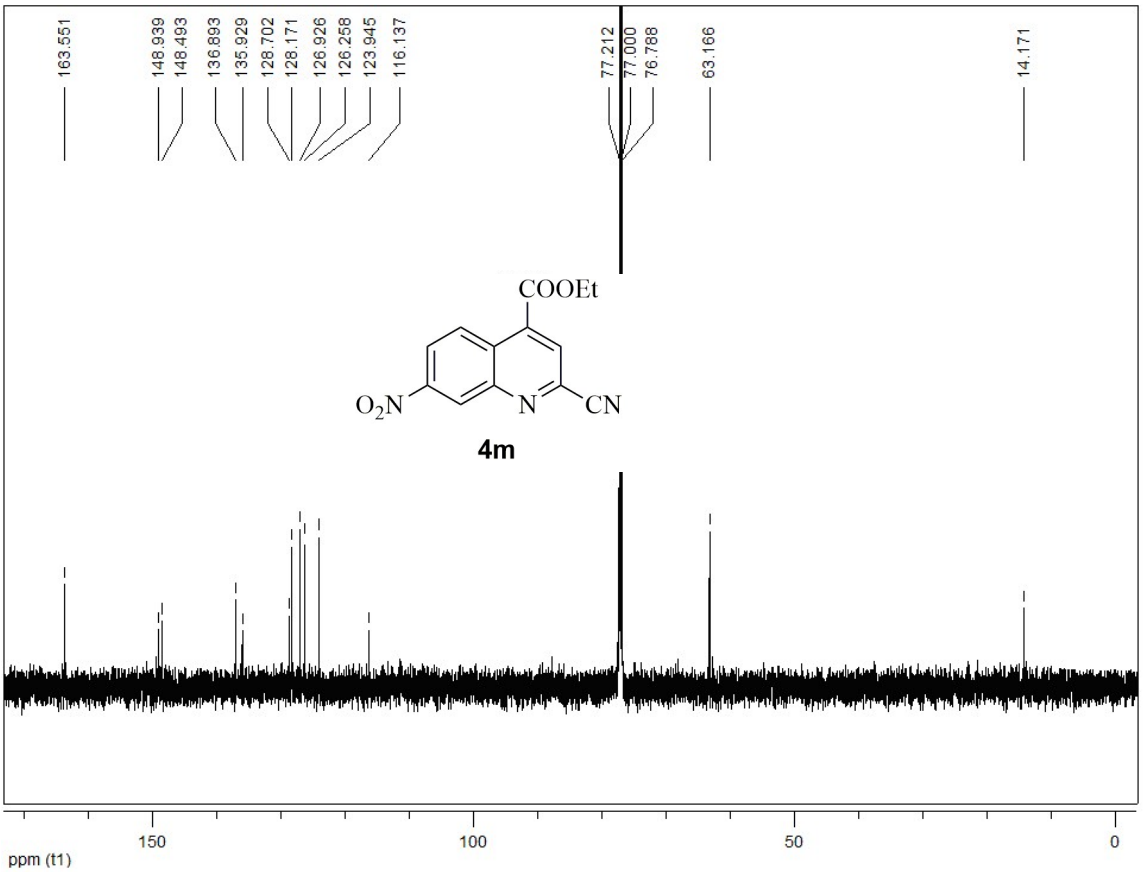

8.74
8.45
8.43
7.88
7.86
7.82
2.78
O2N
N
CN
1.02
1.00
1.03
0.91
2.96
f1 (ppm)

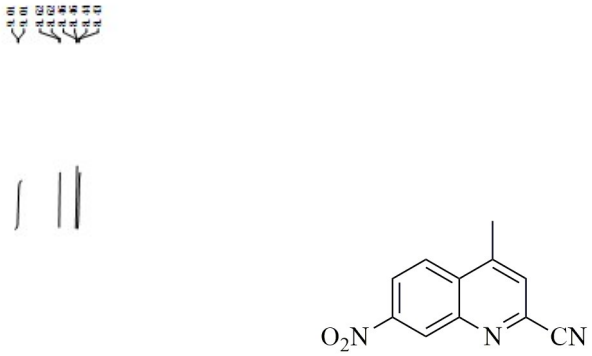
4l


151.72
146.01
136.68
135.36
133.12
130.92
126.09
125.63
122.22
118.61
20.12
O2N
N
CN
f1 (ppm)

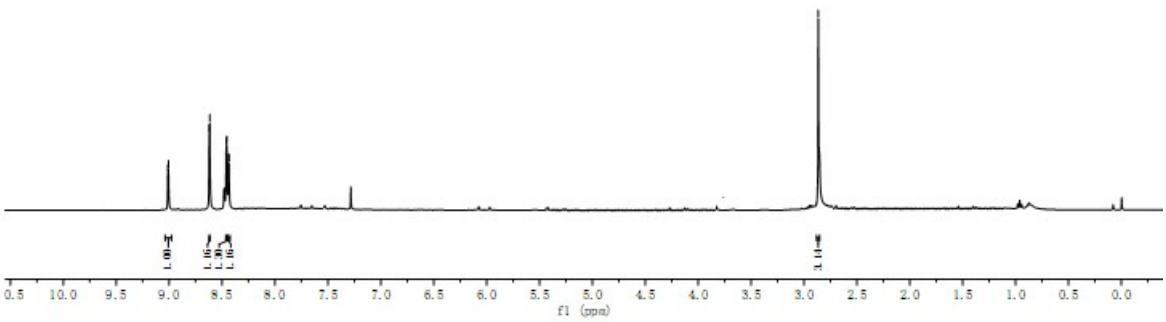
4l

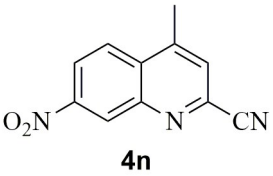

9.183
9.159
9.101
9.097
8.565
8.559
8.541
8.536
8.388
7.260
4.605
4.587
4.569
4.551
1.535
1.517
1.499
COOEt
O2N
N
CN
4m
1.00
1.03
2.03
3.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


163.551
148.939
148.493
136.893
135.929
128.702
128.171
126.926
126.258
123.945
116.137
77.212
77.000
76.788
63.166
14.171
COOEt
O2N
N
CN
4m
150
100
50
0
ppm (t1)

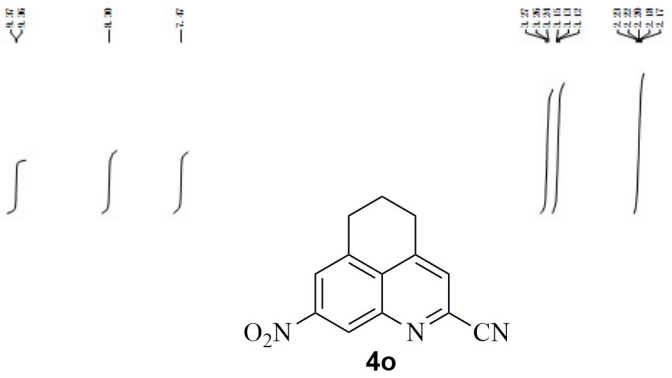


4n

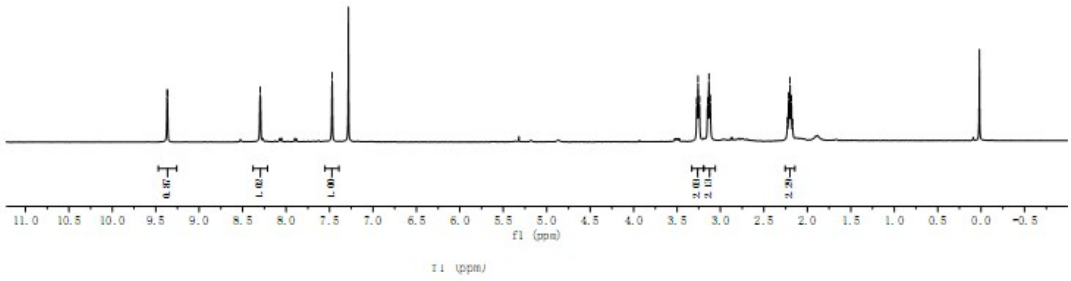




4n

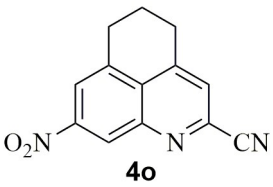

9.37
9.36
8.00
7.47
4.37
4.36
4.35
4.15
4.13
4.12
2.23
2.22
2.20
2.18
2.17
O_2N
N
CN

4o

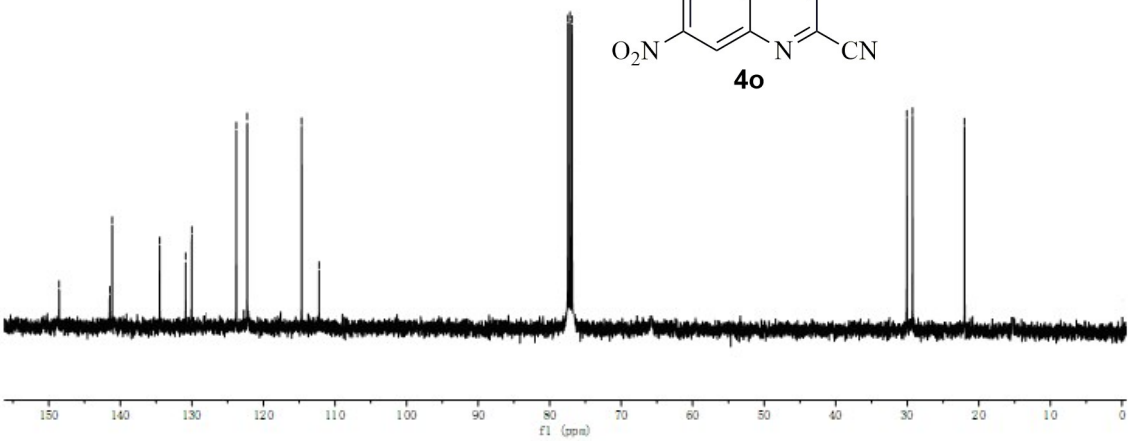

0.87
1.00
1.00
2.03
2.13
2.29
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

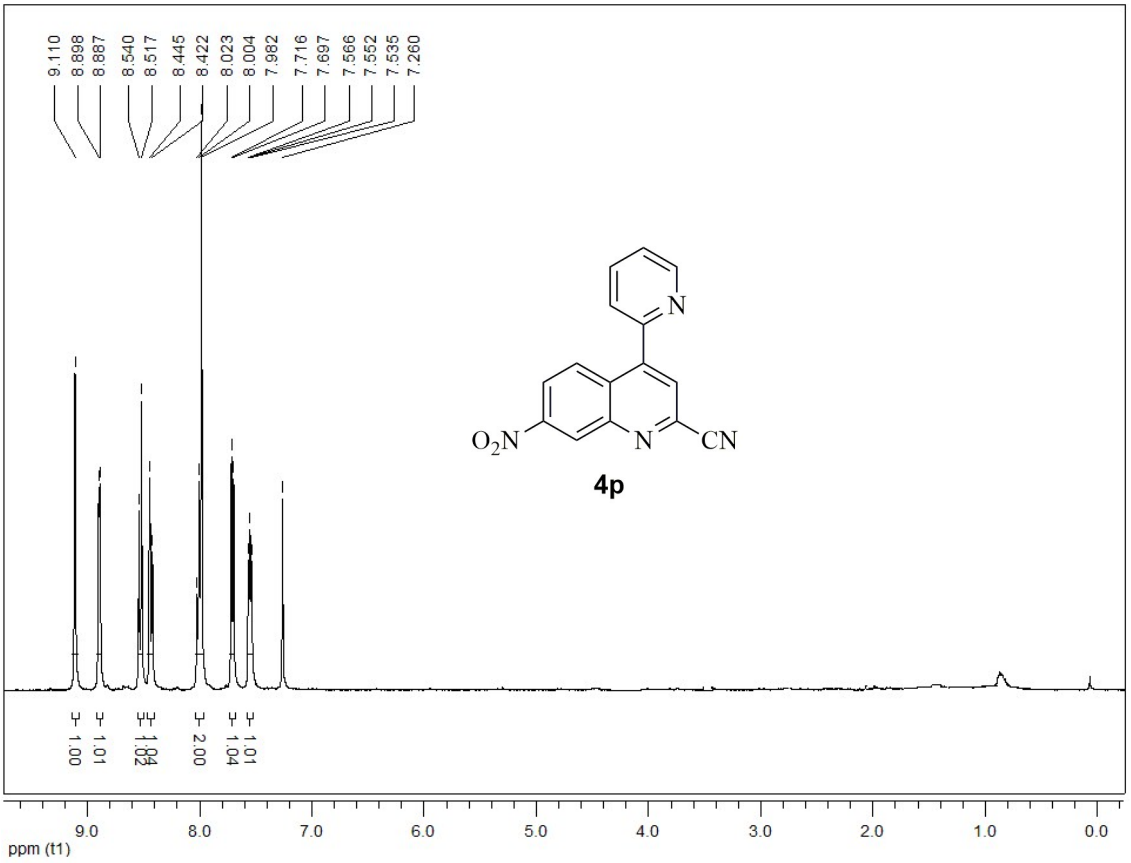

f1 (ppm)

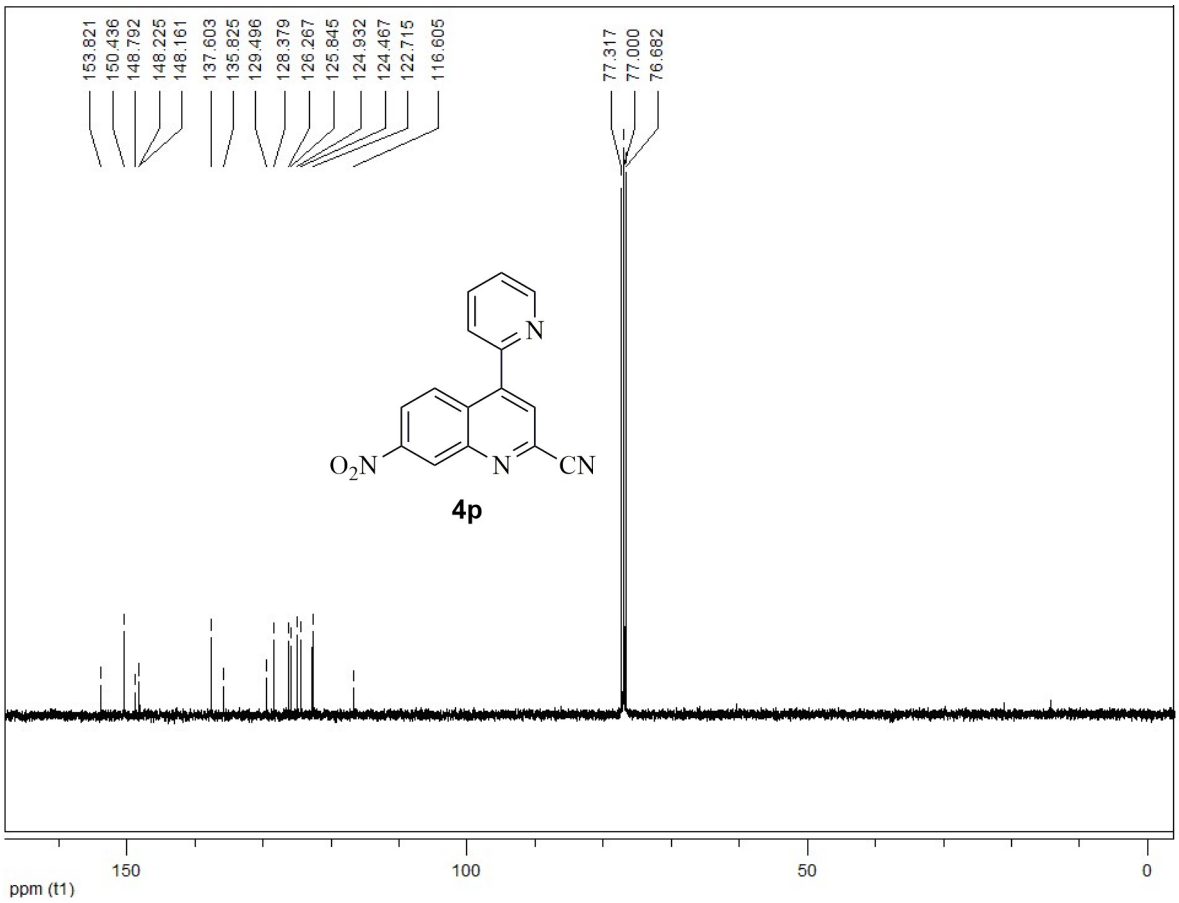
148.96
141.47
141.13
134.54
130.87
130.30
123.79
122.36
114.64
112.22
77.30
76.98
76.67
30.06
29.27
22.00

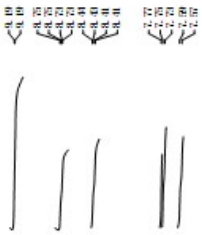

O_2N
N
CN

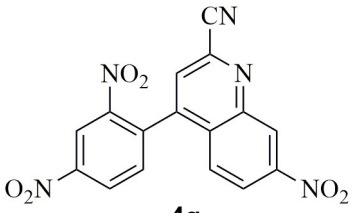
4o


150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

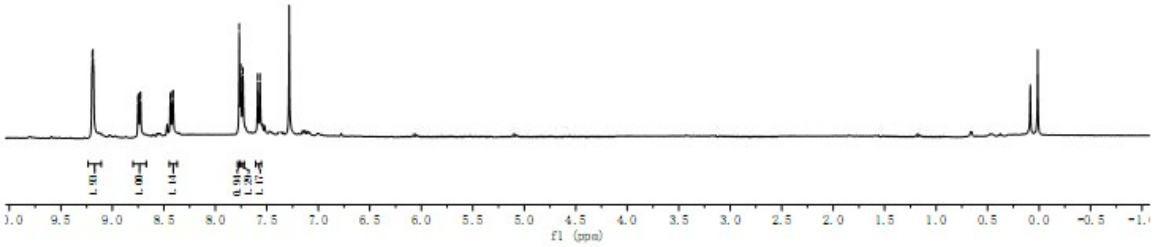

9.110
8.898
8.887
8.540
8.517
8.445
8.422
8.023
8.004
7.982
7.716
7.697
7.566
7.552
7.535
7.260
1.00
1.01
1.02
2.00
1.04
1.01
N
O2N
N
CN
4p
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

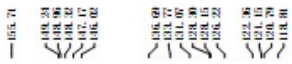

153.821
150.436
148.792
148.225
148.161
137.603
135.825
129.496
128.379
126.267
125.845
124.932
124.467
122.715
116.605
77.317
77.000
76.682
N
O2N
N
CN
4p
150
100
50
0
ppm (t1)

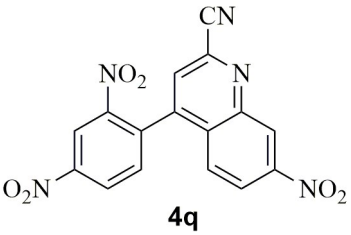




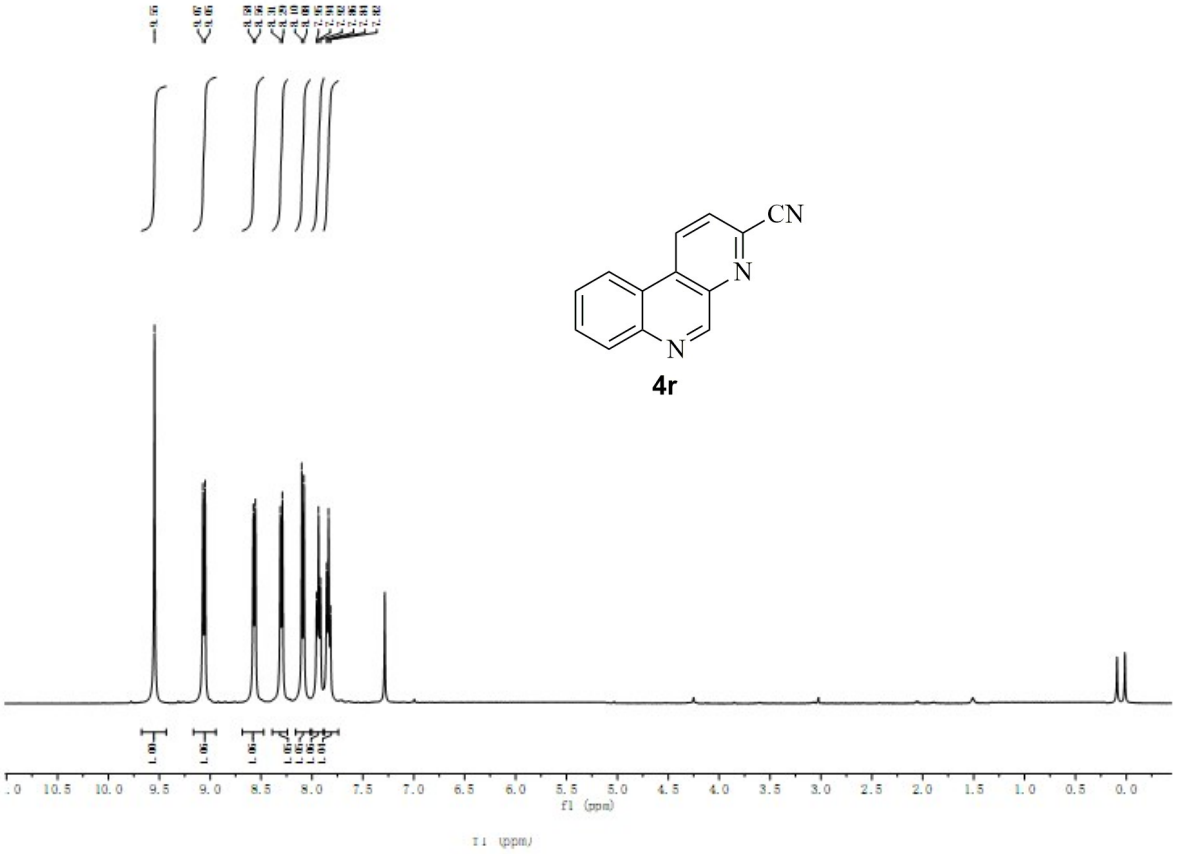
4q

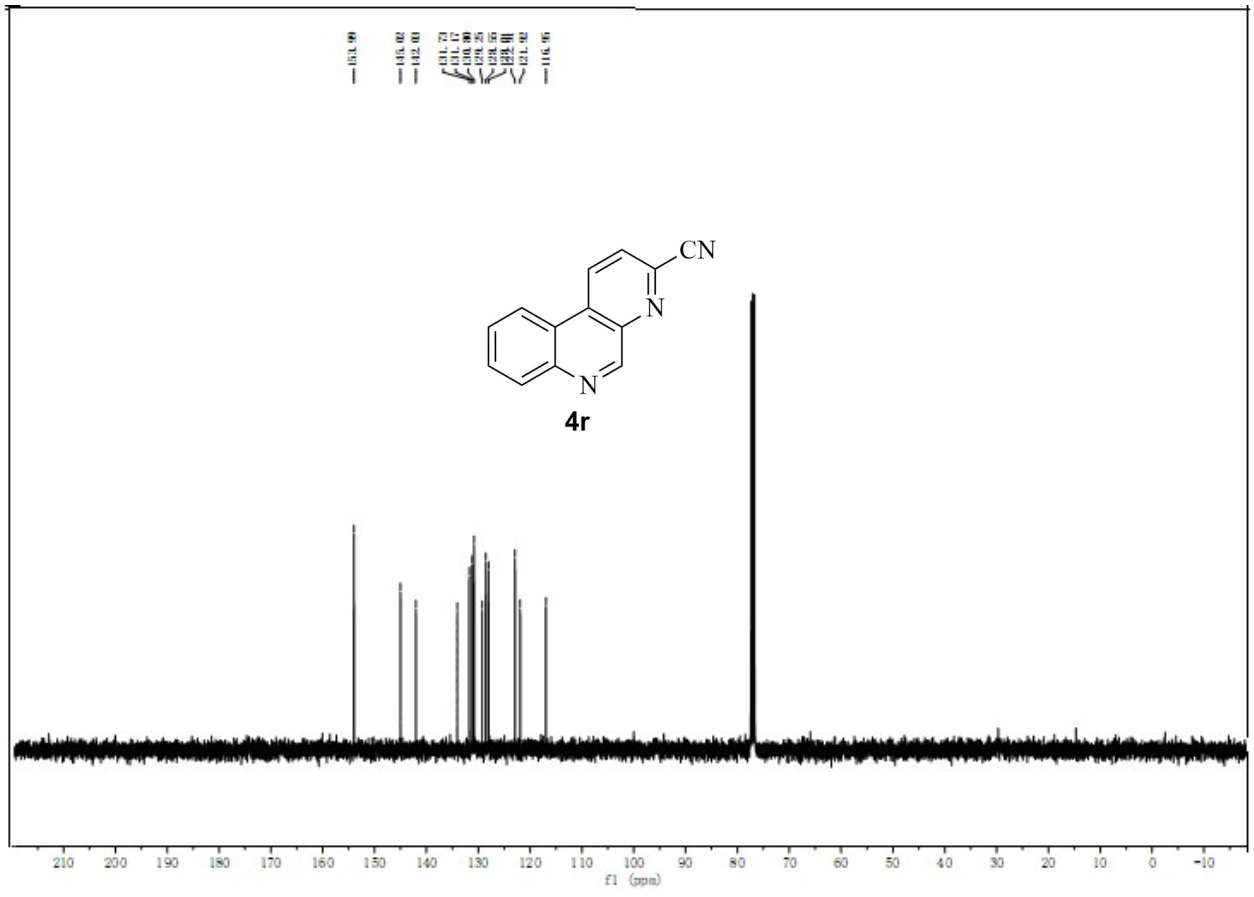


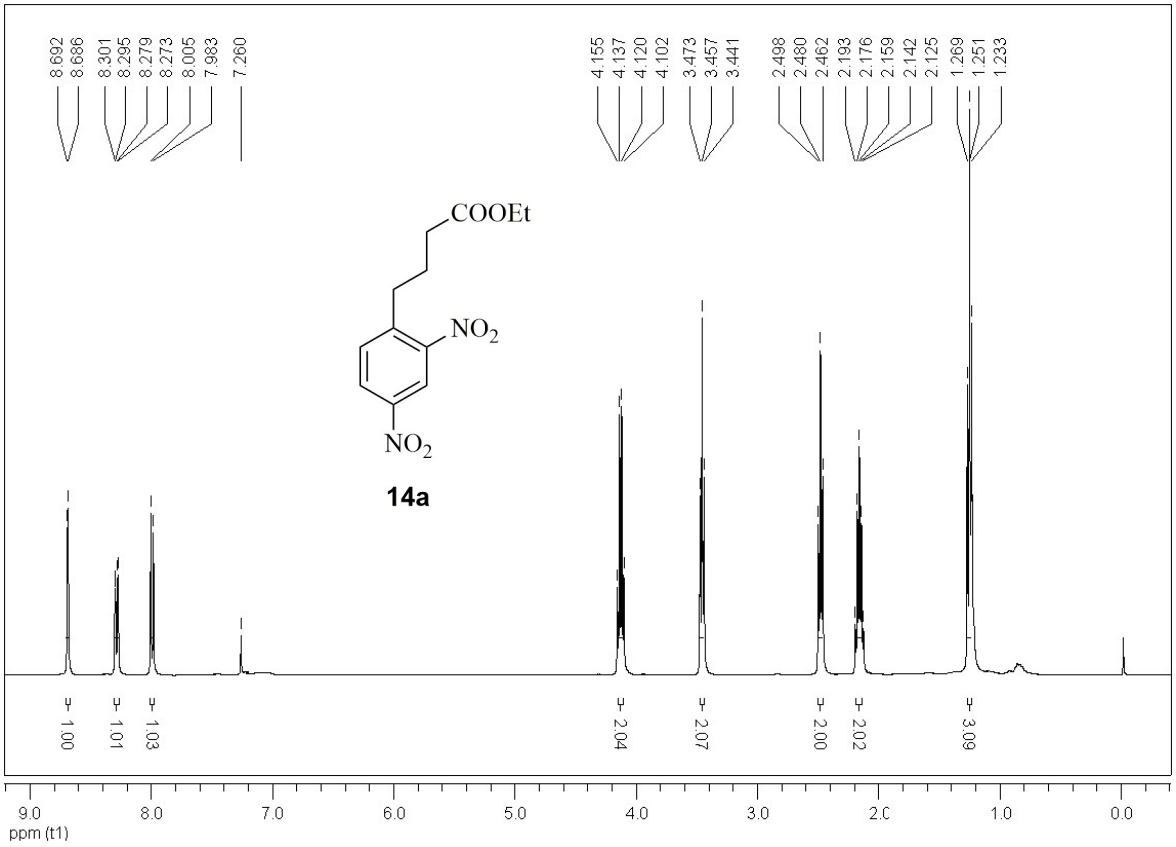


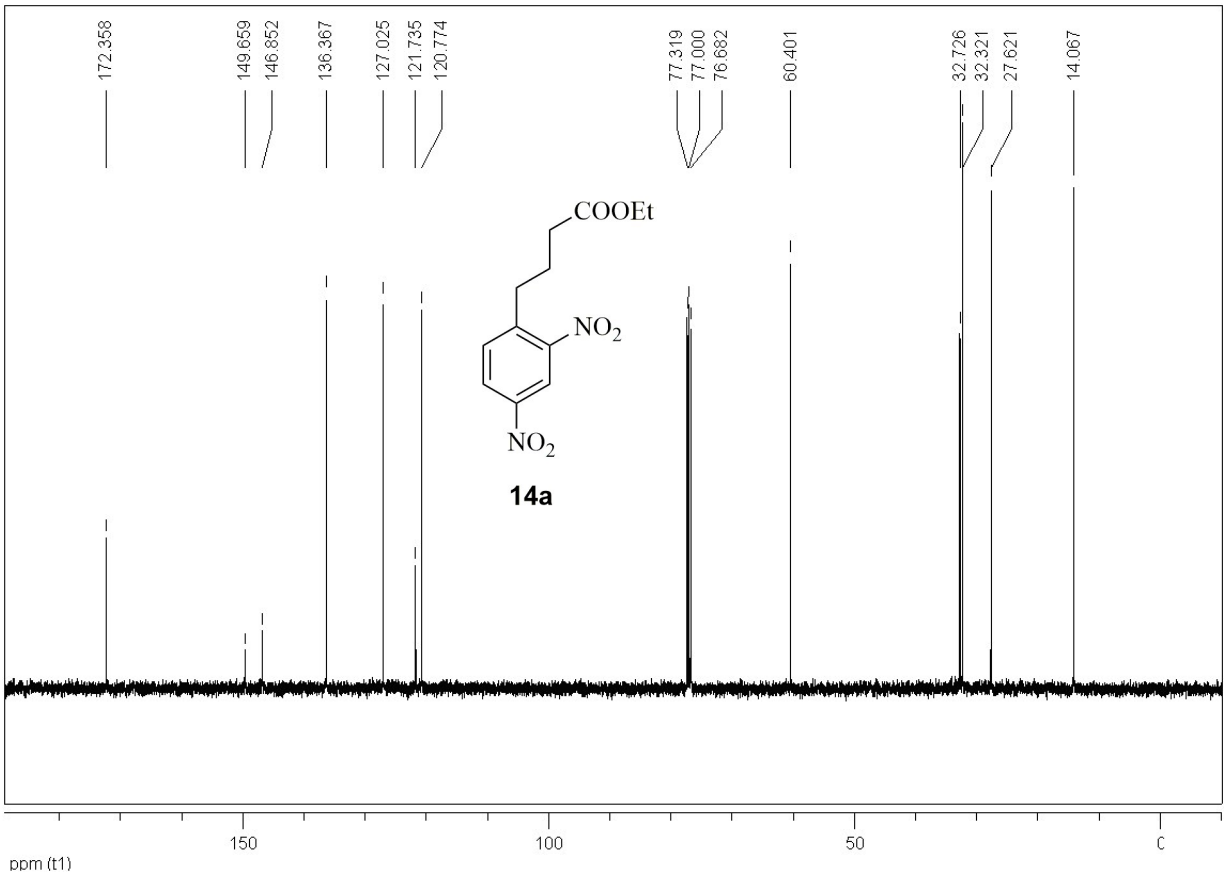


4q


CN
N
N
4r
1.00
1.00
1.00
1.67
1.67
1.67
f1 (ppm)


153.99
145.02
142.03
131.71
131.17
130.90
129.25
128.55
122.88
121.92
116.95
CN
N
N
4r
f1 (ppm)


8.692
8.686
8.301
8.295
8.279
8.273
8.005
7.983
7.260
4.155
4.137
4.120
4.102
3.473
3.457
3.441
2.498
2.480
2.462
2.193
2.176
2.159
2.142
2.125
1.269
1.251
1.233
COOEt
NO2
NO2
14a
1.00
1.01
1.03
2.04
2.07
2.00
2.02
3.09
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


172.358
149.659
146.852
136.367
127.025
121.735
120.774
77.319
77.000
76.682
60.401
32.726
32.321
27.621
14.067
COOEt
NO2
NO2
14a
150
100
50
0
ppm (t1)