Supporting Information

The Reaction of Acyl Cyanides with Huisgen Zwitterion: an Interesting Rearrangement involving Ester Group Migration between Oxygen and Nitrogen Atoms

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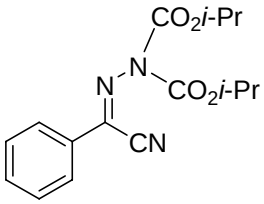
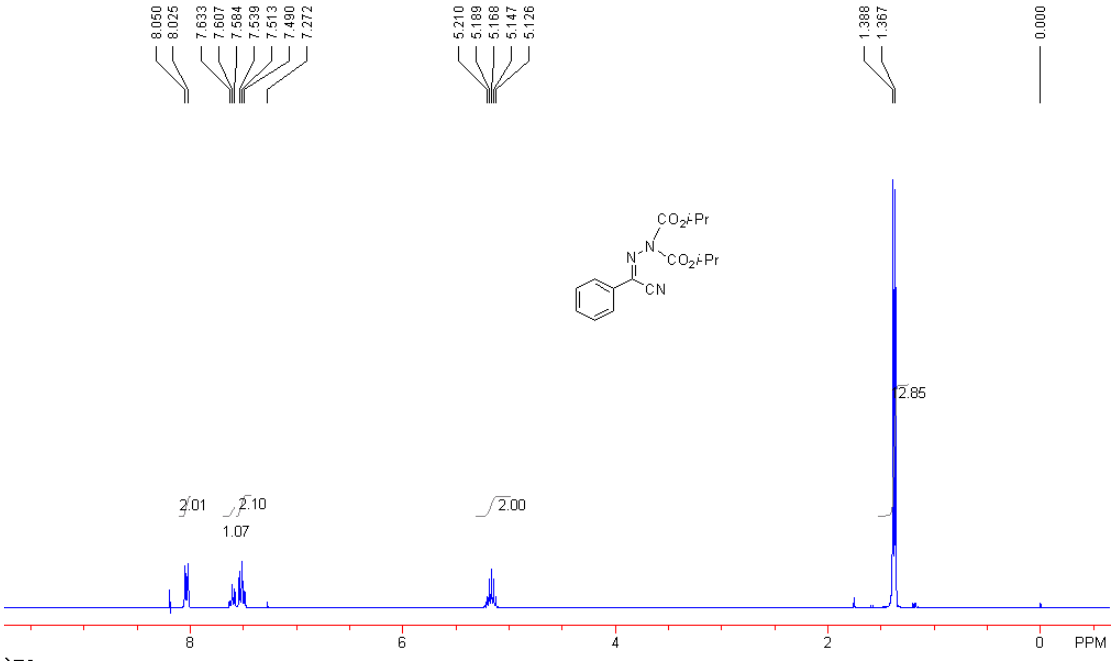
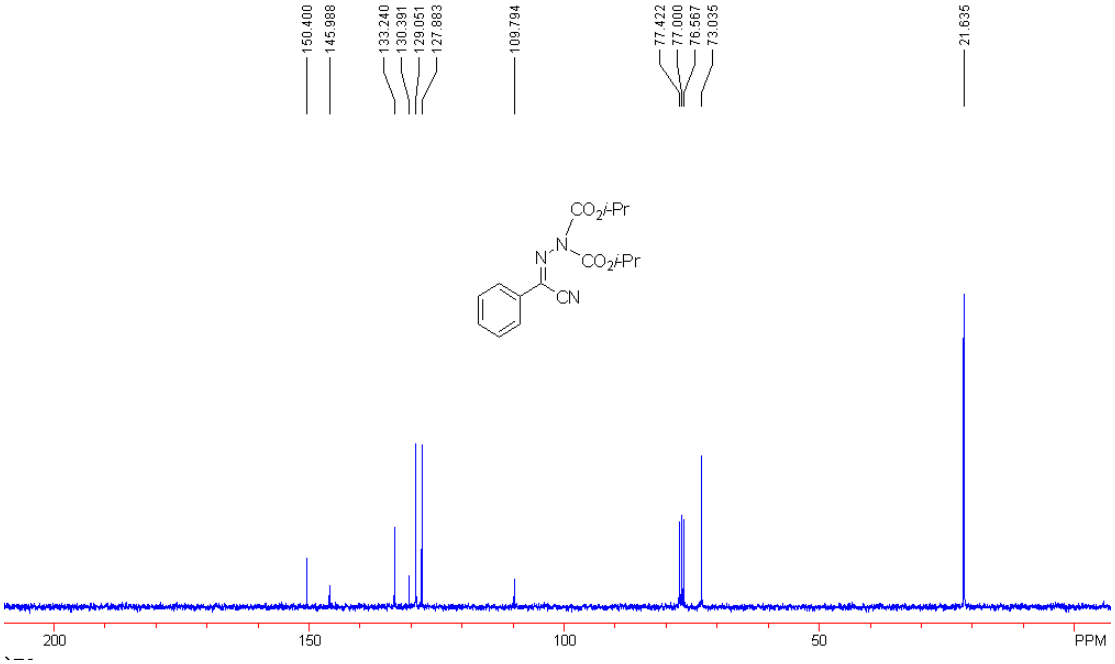
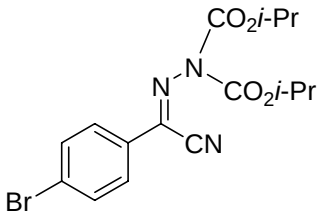


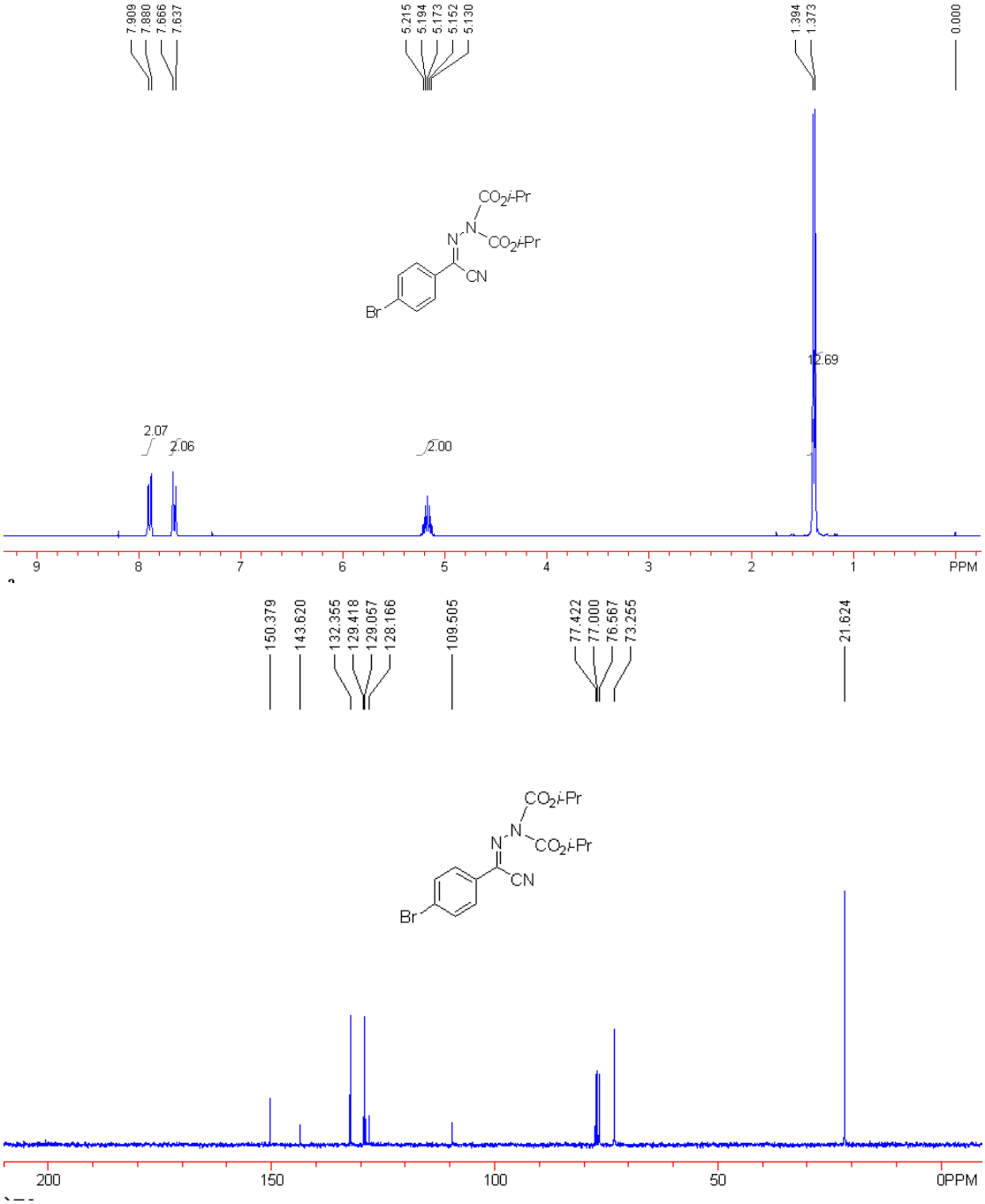
(Z)-diisopropyl 2-(cyano(phenyl)methylene)hydrazine-1,1-dicarboxylate (3a). Oil. IR (CH_2Cl_2) ν 2985, 2940, 2228, 1791, 1763, 1358, 1304, 1231, 1094, 910 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 1.38 (12H, d, *J* = 6.3 Hz, CH_3), 5.12-5.21 (2H, m, CH), 7.51 (2H, t, *J* = 6.9 Hz, Ar), 7.61 (1H, t, *J* = 7.8 Hz, Ar), 8.04 (2H, d, *J* = 7.5 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.6, 73.0, 109.8, 127.9, 129.1, 130.4, 133.2, 146.0, 150.4. MS (ESI) *m/z* 318.2 (M^++1). HRMS (ESI) Calcd. for $C_{16}H_{19}N_3O_4$ requires (M^++1) 318.1376, Found 318.14538.

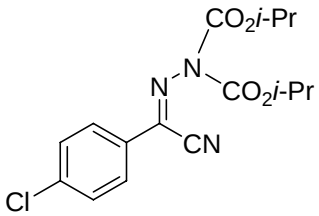






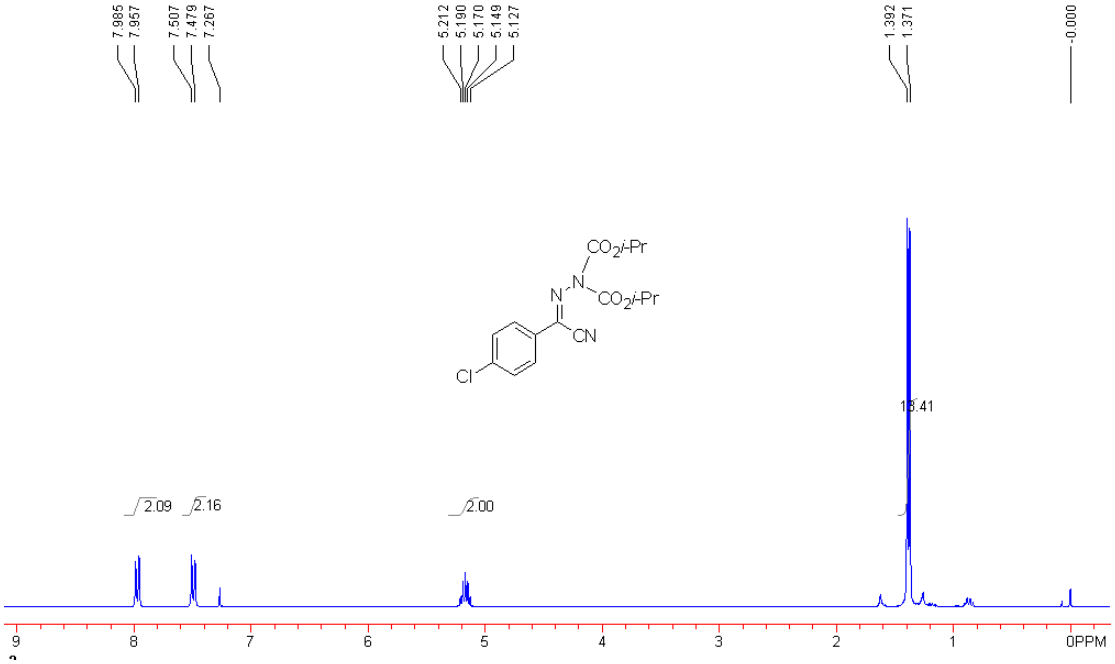
(Z)-diisopropyl 2-((4-bromophenyl)(cyano)methylene)hydrazine-1,1-dicarboxylate (3b). mp. 94-96 ^{o}C; IR (CH_2Cl_2) ν 2985, 2938, 2228, 1798, 1764, 1376, 1300,1094, 910 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 1.38 (12H, d, *J* = 6.3 Hz, CH_3), 5.13-5.22 (2H, m, CH), 7.65 (2H, d, *J* = 8.7 Hz, Ar), 7.89 (2H, d, *J* = 8.7 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.6, 73.3, 109.5, 128.2, 129.1, 129.4, 132.3, 143.6, 150.4. MS (EI) *m/z* 309 (M^{+}-86, 2.43), 269 (6.13), 267 (7.11), 223 (5.91), 195 (7.81), 114 (10.90), 44 (5.86), 43 (100.00), 41 (17.73). Anal. Calcd for $C_{16}H_{18}BrN_3O_4$ (%) (395.05): C, 48.50; H, 4.58; Br, 20.17; N, 10.60; O, 16.15 Found: C, 48.39; H, 4.57; N, 10.58.

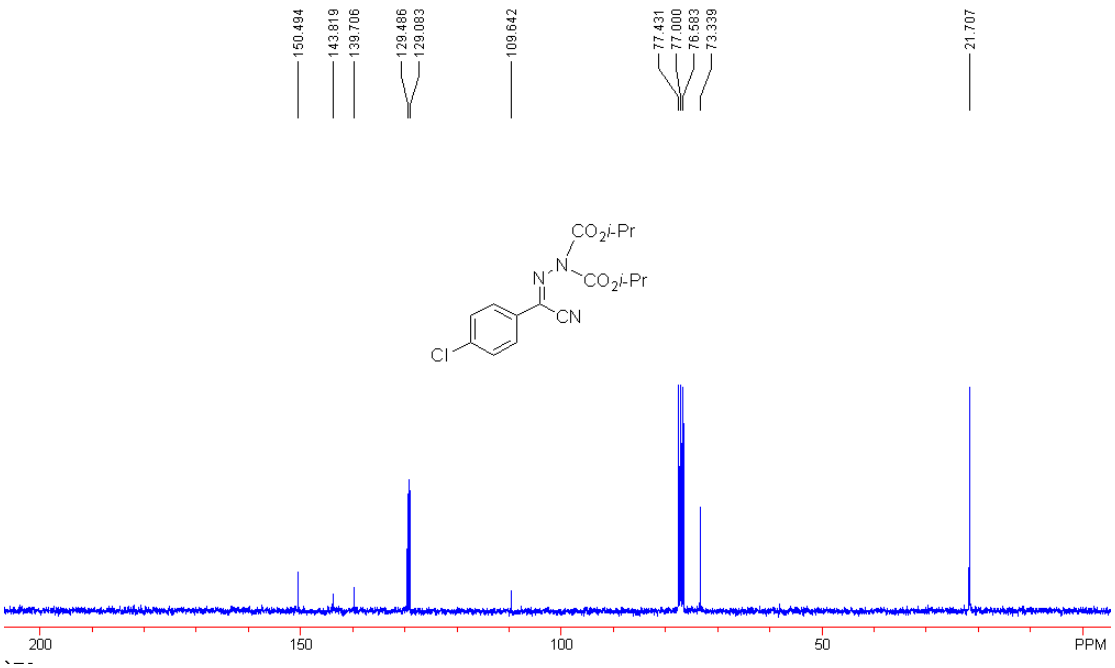


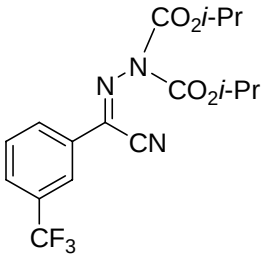


(Z)-diisopropyl 2-((4-chlorophenyl)(cyano)methylene)hydrazine-1,1-dicarboxylate (3c). mp. 81-83 ^{o}C; IR (CH_2Cl_2) ν 2985, 2939, 2228, 1798, 1764, 1300, 1094, 837 cm^{-1}; ^{1}H NMR

($CDCl_3$, 300 MHz, TMS): δ 1.38 (12H, d, *J* = 6.3 Hz, CH_3), 5.12-5.22 (2H, m, CH), 7.49 (2H, d, *J* = 8.4 Hz, Ar), 7.97 (2H, d, *J* = 8.4 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.6, 73.3, 109.6, 129.0, 129.4, 139.6, 143.7, 150.4. MS (EI) *m/z* 265 (M^+-86, 3.49), 223 (9.16), 179 (7.16), 151 (8.82), 43 (100.00), 42 (4.60). Anal. Calcd for $C_{16}H_{18}ClN_3O_4$ (%) (351.09): C, 54.63; H, 5.16; Cl, 10.08; N, 11.94; O, 18.19 Found: C, 54.73; H, 5.28; N, 12.01.

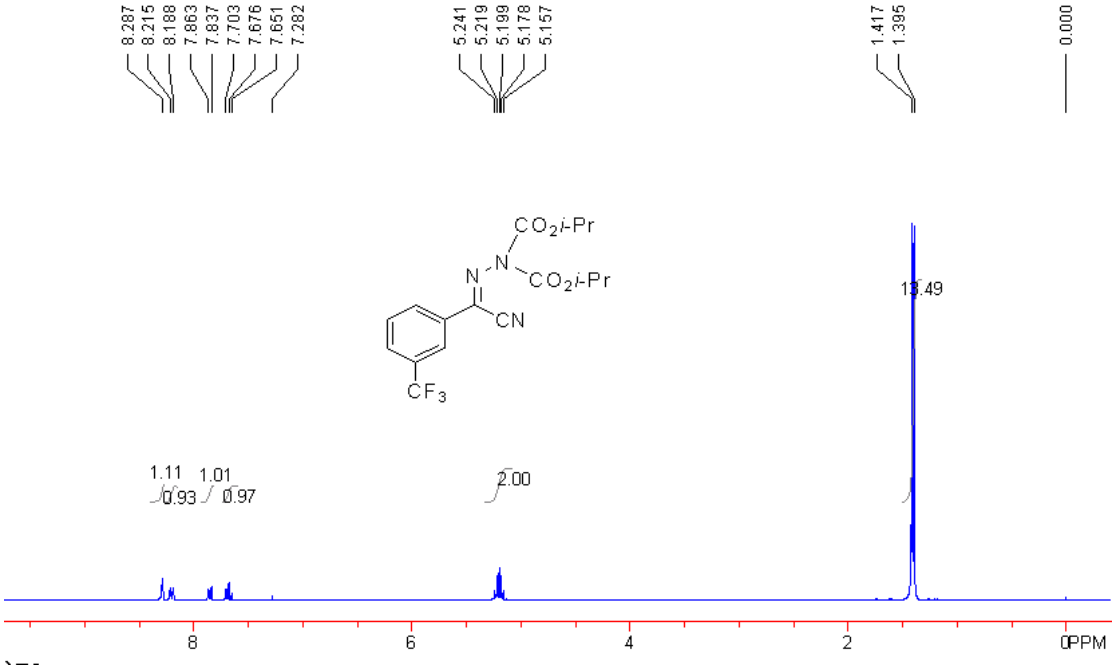


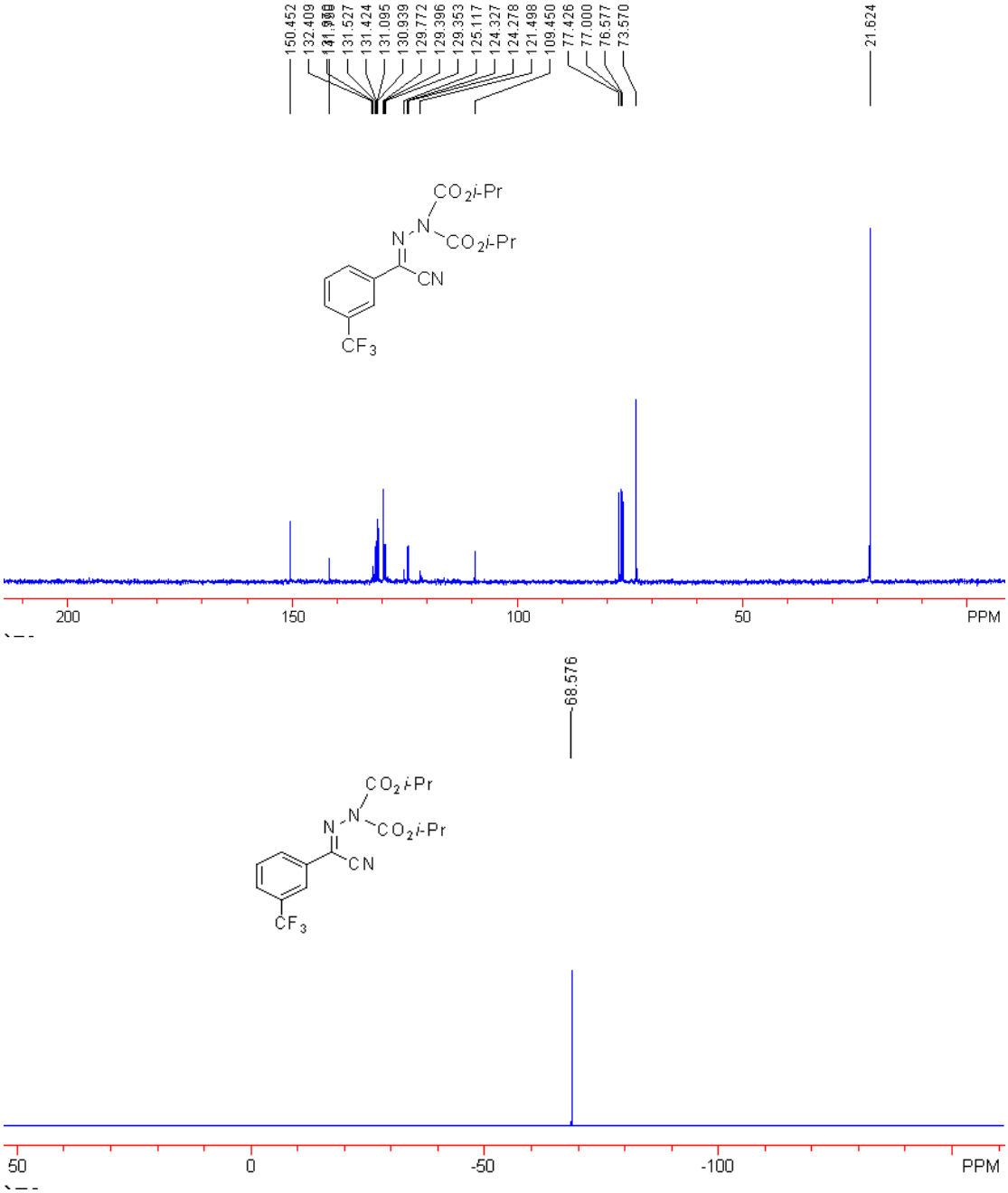


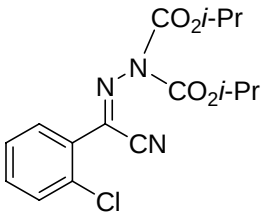


(Z)-diisopropyl

2-(cyano(3-(trifluoromethyl)phenyl)methylene)hydrazine-1,1-dicarboxylate (3d). Oil. IR (CH_2Cl_2) ν 2987, 2941, 2228, 1799, 1767, 1377, 1232, 1097 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 1.41 (12H, d, *J* = 6.6 Hz, CH_3), 5.15-5.24 (2H, m, CH), 7.68 (1H, dd, J_1 = 7.8 Hz, J_2 = 8.1 Hz, Ar), 7.85 (1H, d, *J* = 7.8 Hz, Ar), 8.20 (1H, d, *J* = 8.1 Hz, Ar), 8.29 (1H, s, Ar). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -68.6. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.6, 73.6, 109.4, 123.3 (q, *J* = 271.4 Hz), 124.2 (q, *J* = 3.7 Hz), 129.6 (q, *J* = 3.2 Hz), 129.8, 130.9, 131.4, 131.7 (q, *J* = 33.2 Hz), 141.8, 150.4. MS (ESI) *m/z* 386.2 (M^++1). HRMS (ESI) Calcd. for $C_{17}H_{18}F_3N_3O_4$ requires (M^++1) 386.1249 Found 386.13197.



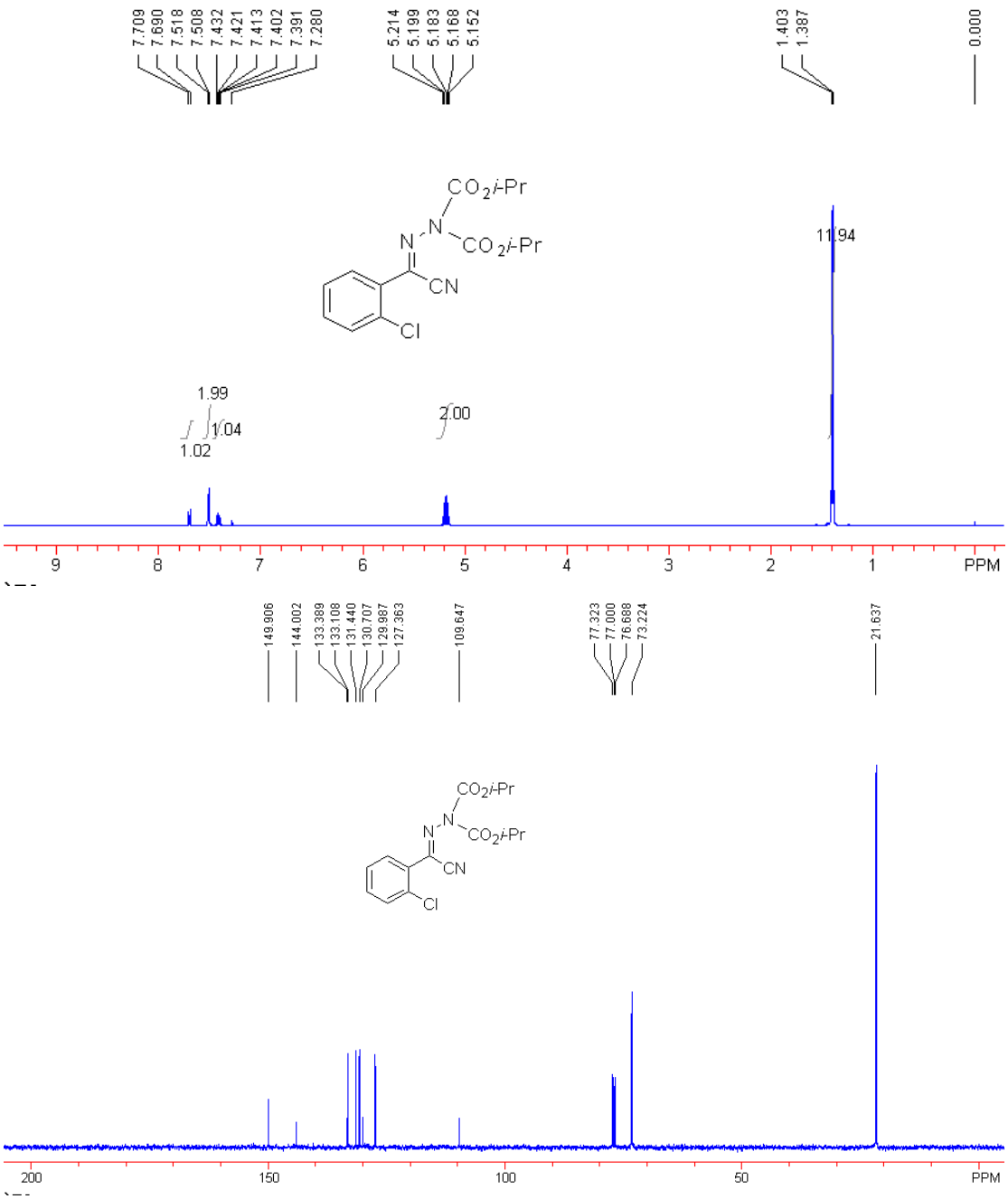


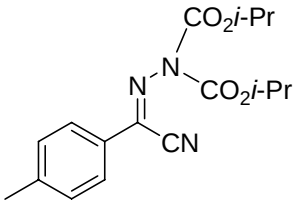


(Z)-diisopropyl 2-((2-chlorophenyl)(cyano)methylene)hydrazine-1,1-dicarboxylate (3e).

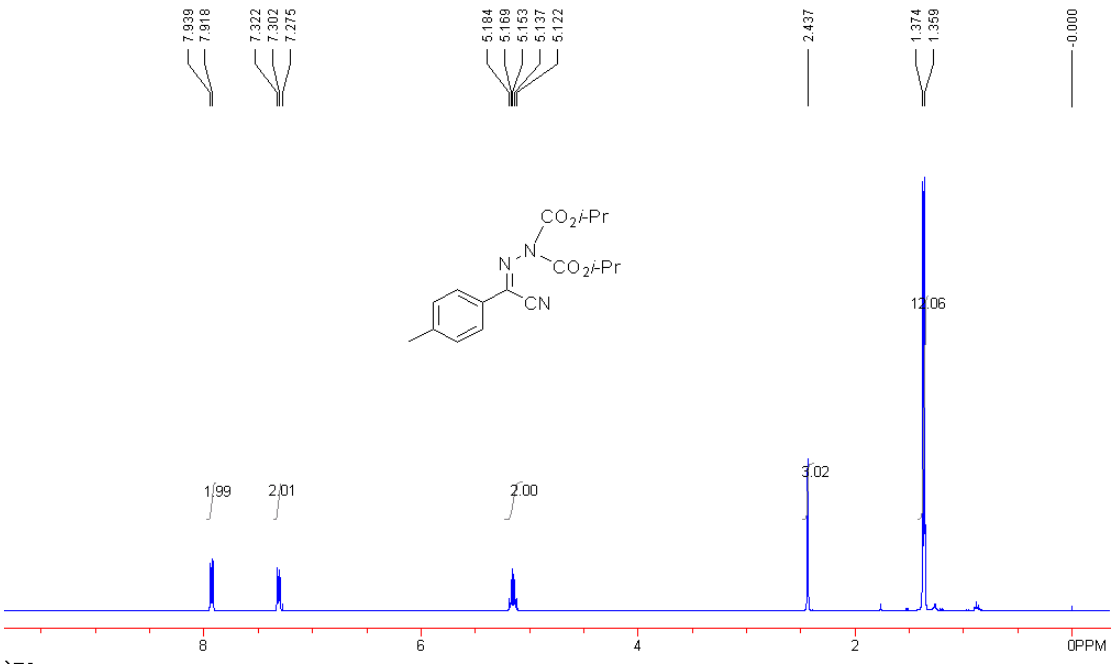
Oil. IR (CH_2Cl_2) ν 2986, 2939, 2225, 1799, 1766, 1590, 1377, 1311, 1093 cm^{-1}; ^1H NMR

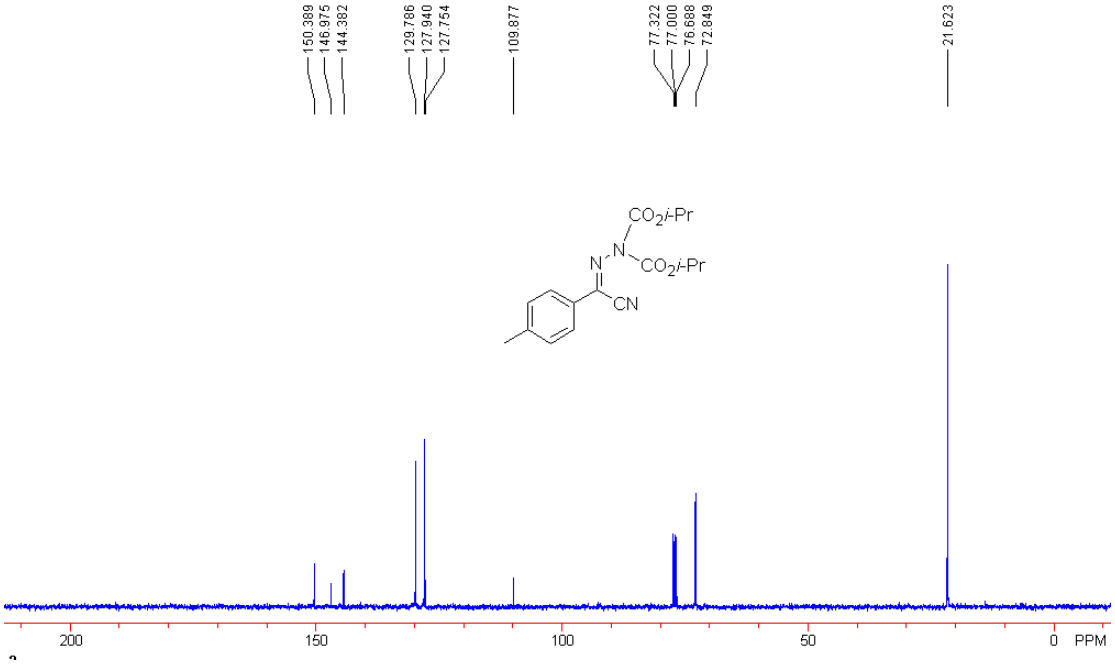
($CDCl_3$, 400 MHz, TMS): δ 1.40 (12H, d, *J* = 6.4 Hz, CH_3), 5.15-5.22 (2H, m, CH), 7.39-7.43 (1H, m, Ar), 7.50-7.52 (2H, m, Ar), 7.70 (1H, d, *J* = 7.6 Hz, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.6, 73.2, 109.6, 127.4, 129.9, 130.7, 131.4, 133.1, 133.4, 144.0, 149.9. MS (ESI) *m/z* 352.2 (M^++1). HRMS (ESI) Calcd. for $C_{16}H_{18}ClN_3O_4$ requires (M^++1) 352.0986 Found 352.10558.

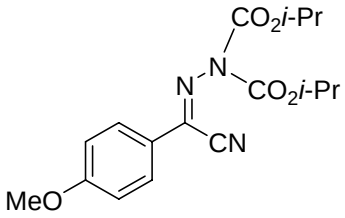




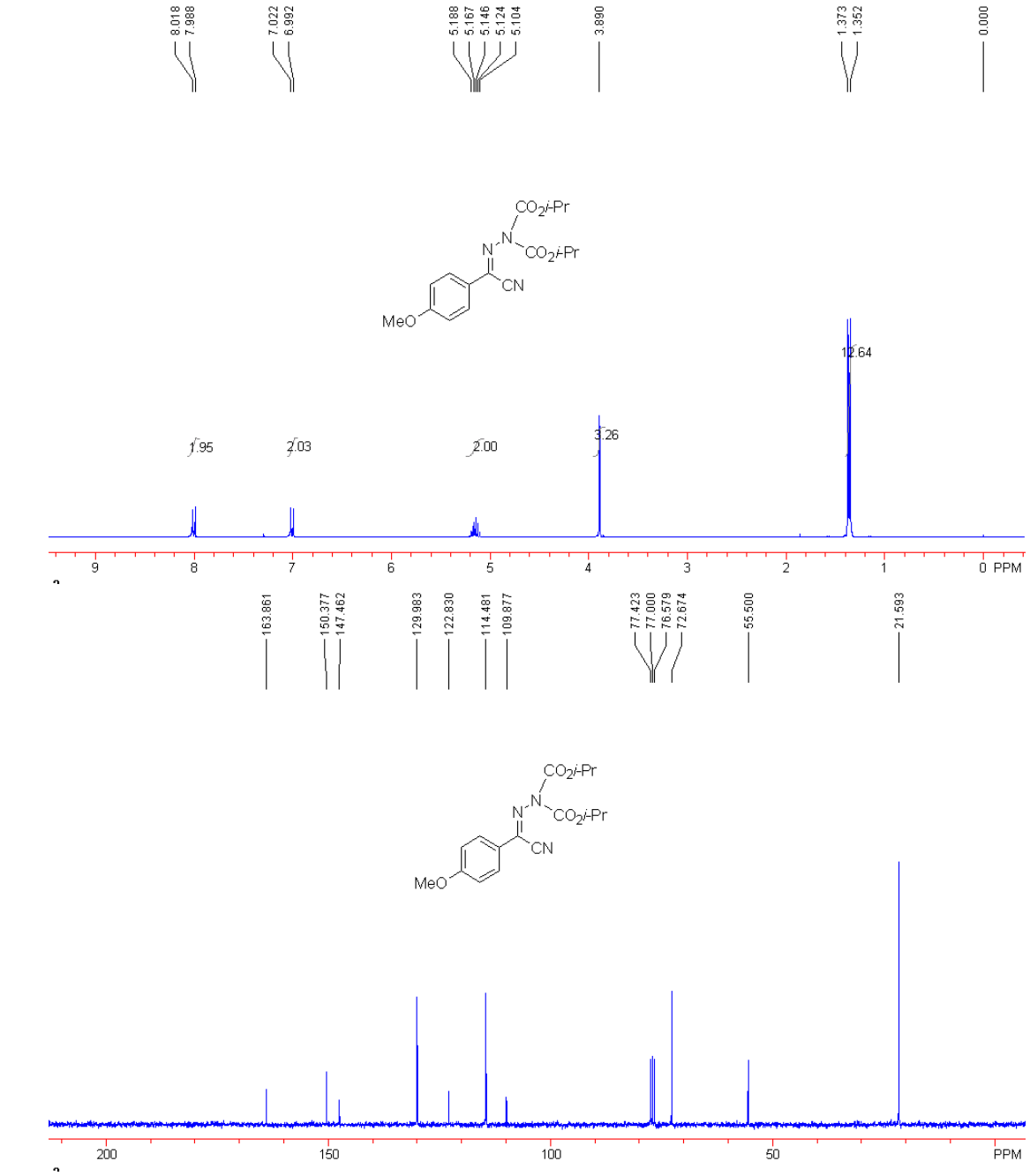
(Z)-diisopropyl 2-(cyano(p-tolyl)methylene)hydrazine-1,1-dicarboxylate (3f). Oil. IR (CH_2Cl_2) ν 2985, 2939, 2229, 1797, 1762, 1305, 1094, 910 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.37 (12H, d, *J* = 6.0 Hz, CH_3), 2.44 (3H, s, CH_3), 5.12-5.19 (2H, m, CH), 7.31 (2H, d, *J* = 8.0 Hz, Ar), 7.93 (2H, d, *J* = 8.0 Hz, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.6, 72.8, 109.9, 127.8, 127.9, 144.4, 147.0, 150.4. MS (ESI) *m/z* 332.0 (M^++1), 354.0 (M^++Na). HRMS (ESI) Calcd. for $C_{17}H_{21}N_3O_4$ requires (M^++Na) 354.1430, Found 354.14226.

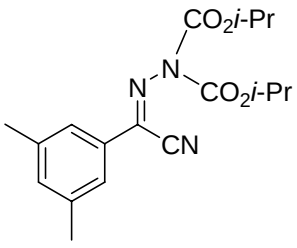






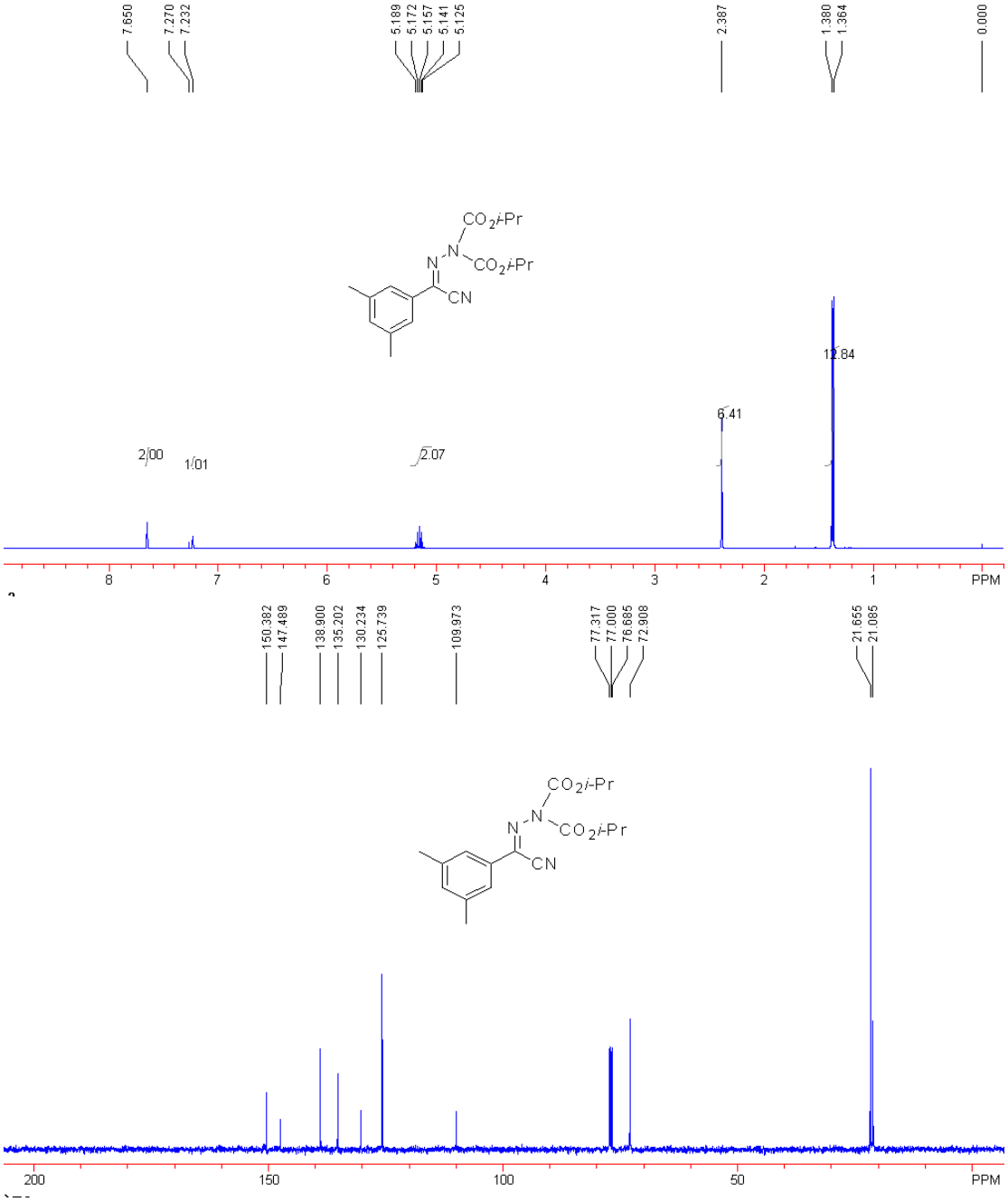
(Z)-diisopropyl 2-(cyano(4-methoxyphenyl)methylene)hydrazine-1,1-dicarboxylate (3g). Oil. IR (CH_2Cl_2) ν 2985, 2939, 2228, 1795, 1764, 1606, 1308, 1095 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 1.36 (12H, d, *J* = 6.3 Hz, CH_3), 3.89 (3H, s, OCH_3), 5.10-5.19 (2H, m, CH), 7.01 (2H, d, *J* = 9.0 Hz, Ar), 8.00 (2H, d, *J* = 9.0 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.6, 55.5, 72.7, 109.9, 114.5, 122.8, 130.0, 147.5, 150.4, 163.9. MS (ESI) *m/z* 348.2 (M^++1). HRMS (ESI) Calcd. for $C_{17}H_{21}N_3O_5$ requires (M^++1) 348.1481, Found 348.15603.

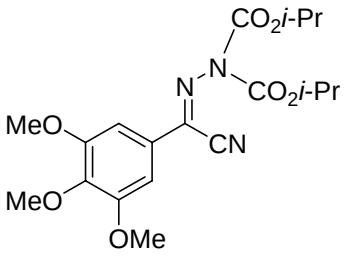




(Z)-diisopropyl 2-(cyano(3,5-dimethylphenyl)methylene)hydrazine-1,1-dicarboxylate (3h). Oil. IR (CH_2Cl_2) ν 2985, 2939, 2229, 1789, 1763, 1609, 1233, 1095 cm^{-1}; ^1H NMR

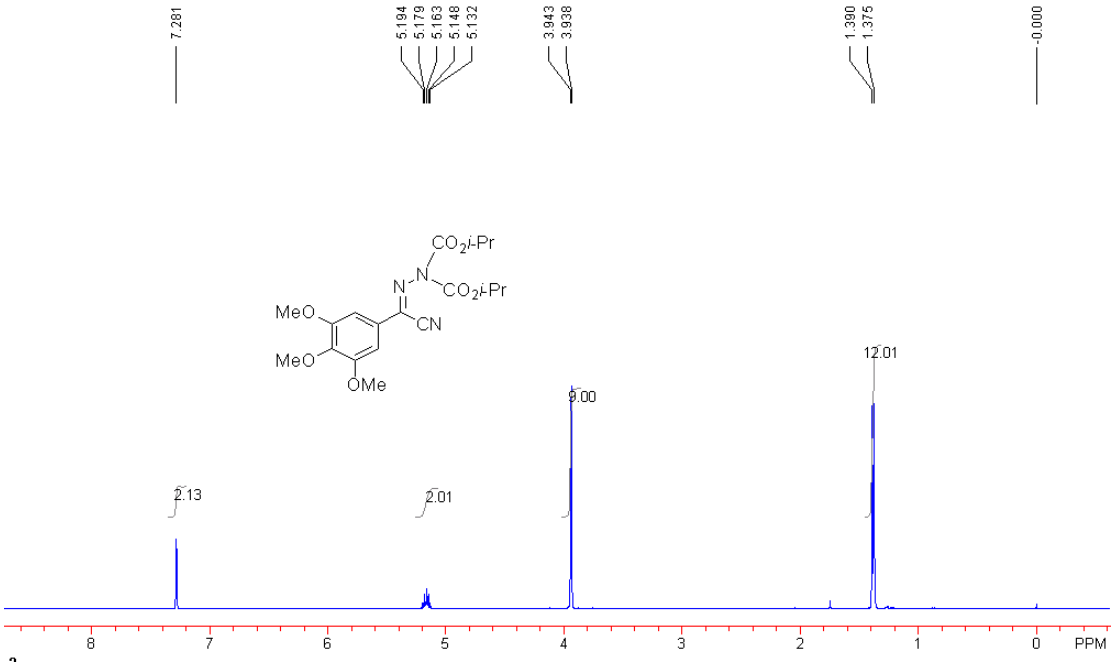
($CDCl_3$, 400 MHz, TMS): δ 1.37 (12H, d, *J* = 6.4 Hz, CH_3), 2.39 (6H, s, CH_3), 5.12-5.19 (2H, m, CH), 7.23 (1H, s, Ar), 7.65 (2H, s, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.1, 21.7, 72.9, 110.0, 125.7, 130.2, 135.2, 138.9, 147.5, 150.4. MS (ESI) *m/z* 346.2 (M^++1). HRMS (MALDI) Calcd. for $C_{18}H_{23}N_3O_4$ requires (M^++Na) 368.1588, Found 368.15808.

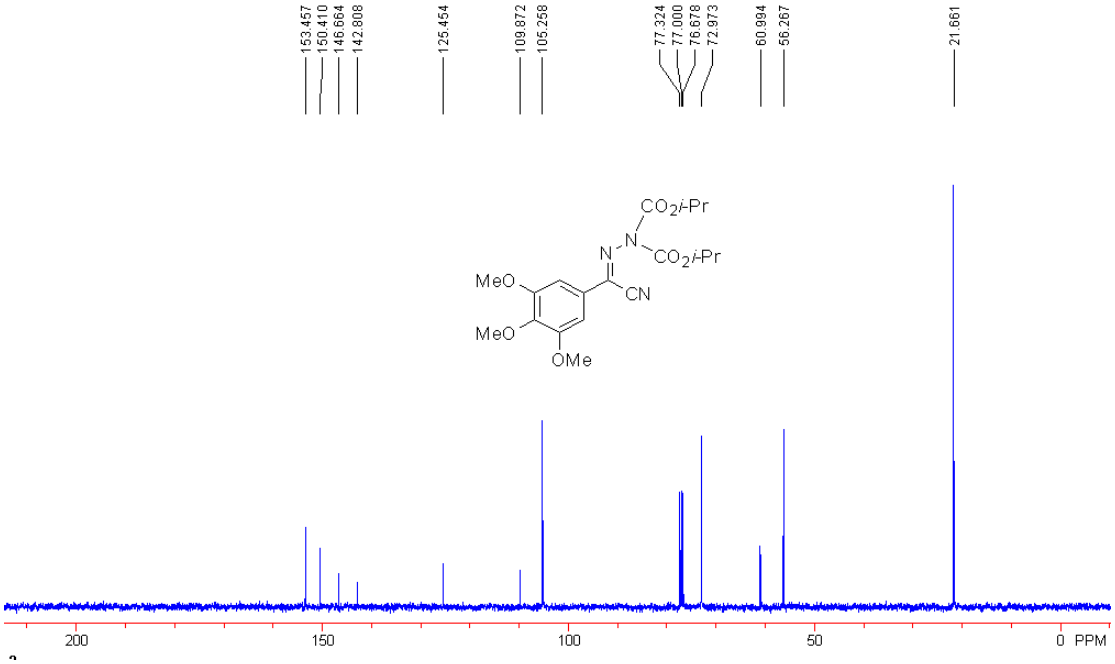


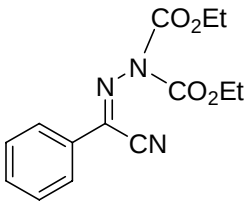


(Z)-diisopropyl

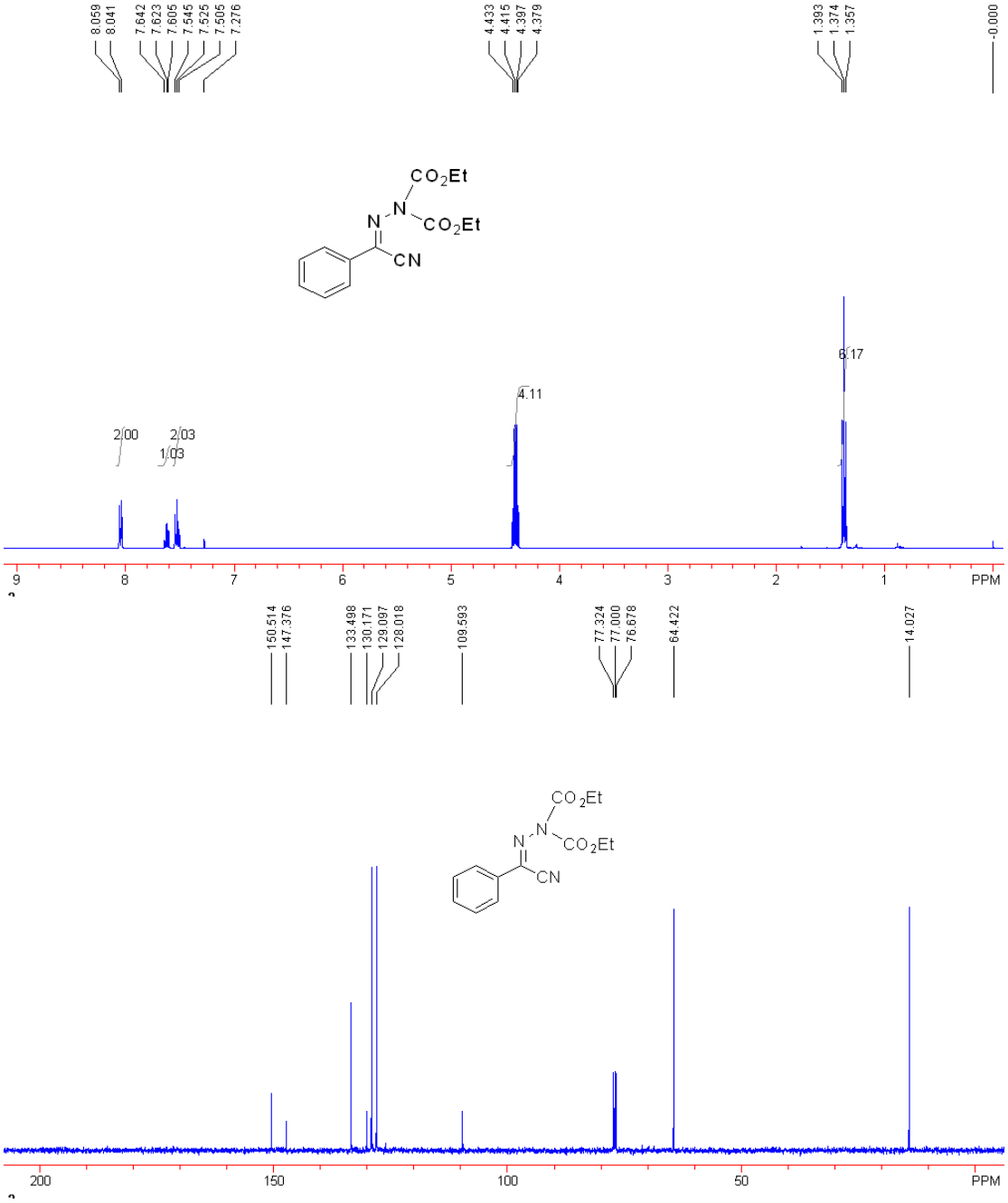
2-(cyano(3,4,5-trimethoxyphenyl)methylene)hydrazine-1,1-dicarboxylate (3i). Oil. IR (CH_2Cl_2) ν 2985, 2941, 1842, 2229, 1798, 1762, 1504, 1351, 1130 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.38 (12H, d, *J* = 6.0 Hz, CH_3), 3.93 (6H, s, OCH_3), 3.94 (3H, s, OCH_3), 5.13-5.20 (2H, m, CH), 7.28 (2H, s, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.7, 56.3, 61.0, 73.0, 105.3, 110.0, 125.5, 142.8, 146.7, 150.4, 153.5. MS (ESI) *m/z* 408.0 (M^++1). HRMS (ESI) Calcd. for $C_{19}H_{25}N_3O_7$ requires (M^++Na) 430.1585 Found 430.15769.

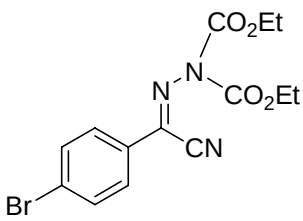






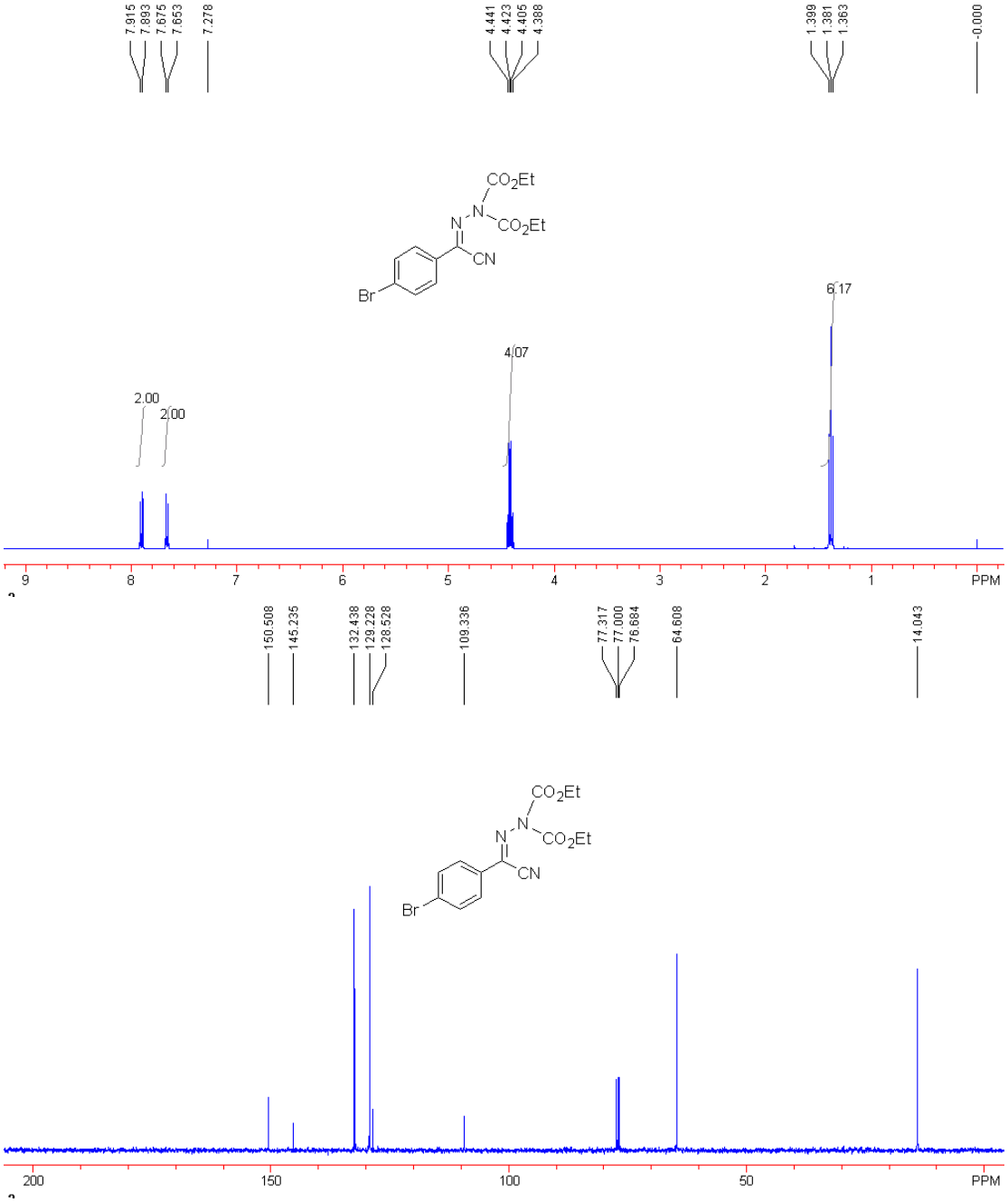
(Z)-diethyl 2-(cyano(phenyl)methylene)hydrazine-1,1-dicarboxylate (3j). Oil. IR (CH_2Cl_2) ν 2985, 2938, 2228, 1802, 1768, 1102 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.37 (6H, t, *J* = 7.6 Hz, CH_3), 4.40 (4H, q, *J* = 7.6 Hz, CH_2), 7.52 (2H, t, *J* = 8.0 Hz, Ar), 7.62 (1H, t, *J* = 7.6 Hz, Ar), 8.05 (2H, d, *J* = 7.2 Hz, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.0, 64.4, 109.6, 128.0, 129.1, 130.2, 133.5, 147.4, 150.5. MS (ESI) *m/z* 290.2 (M^++1), 312.2 (M^++Na). HRMS (ESI) Calcd. for $C_{14}H_{15}N_3O_4$ requires (M^++1) 290.1063 Found 290.11353.

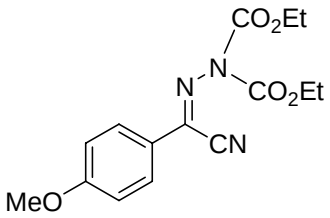




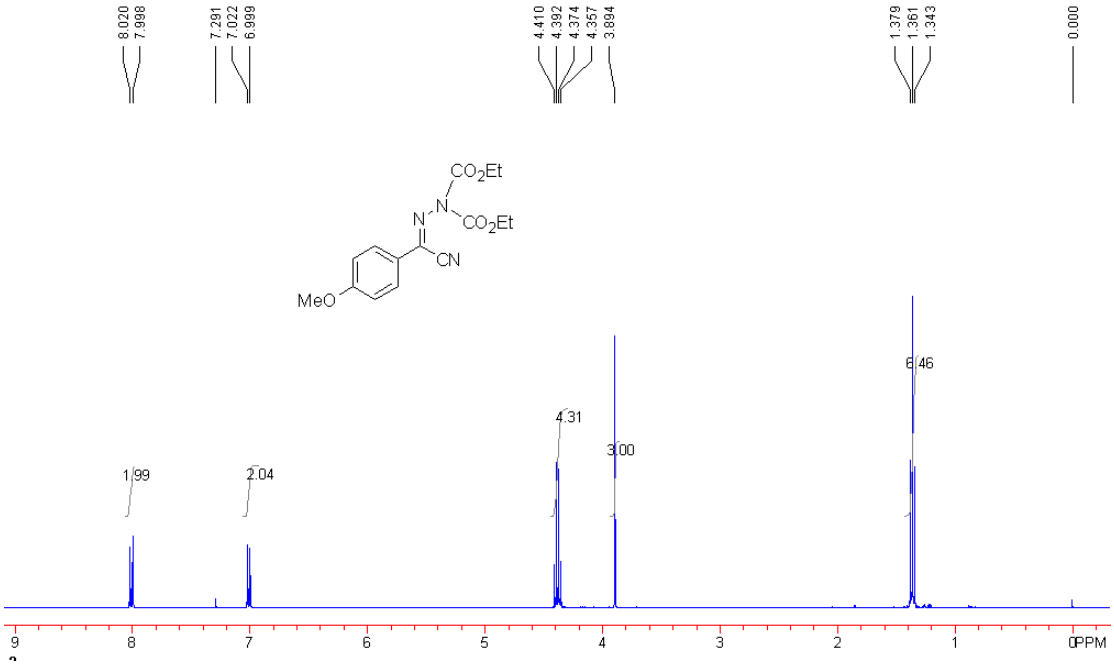
(Z)-diethyl 2-((4-bromophenyl)(cyano)methylene)hydrazine-1,1-dicarboxylate (3k). mp. 82-84 ^{o}C; IR (CH_2Cl_2) ν 2984, 1937, 2228, 1802, 1767, 1588, 1310,1006 cm^{-1}; ^{1}H NMR

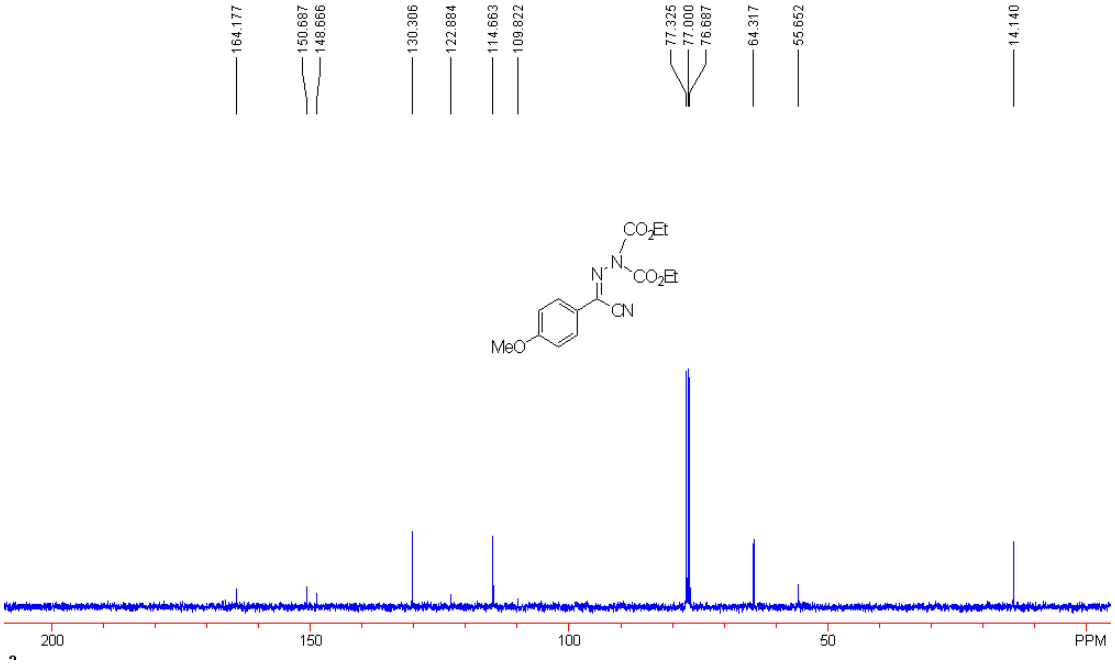
($CDCl_3$, 400 MHz, TMS): δ 1.38 (6H, t, *J* = 7.2 Hz, CH_3), 4.41 (4H, q, *J* = 7.2 Hz, CH_2), 7.66 (2H, d, *J* = 8.8 Hz, Ar), 7.90 (2H, d, *J* = 8.8 Hz, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.0, 64.6, 109.3, 128.5, 129.2, 132.4, 145.2, 150.5. MS (ESI) *m/z* 368.0 (M^++1). HRMS (ESI) Calcd. for $C_{14}H_{14}BrN_3O_4$ requires (M^++1) 368.0168 Found 368.02421.

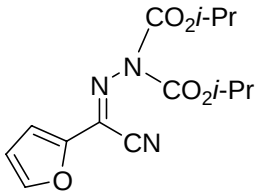




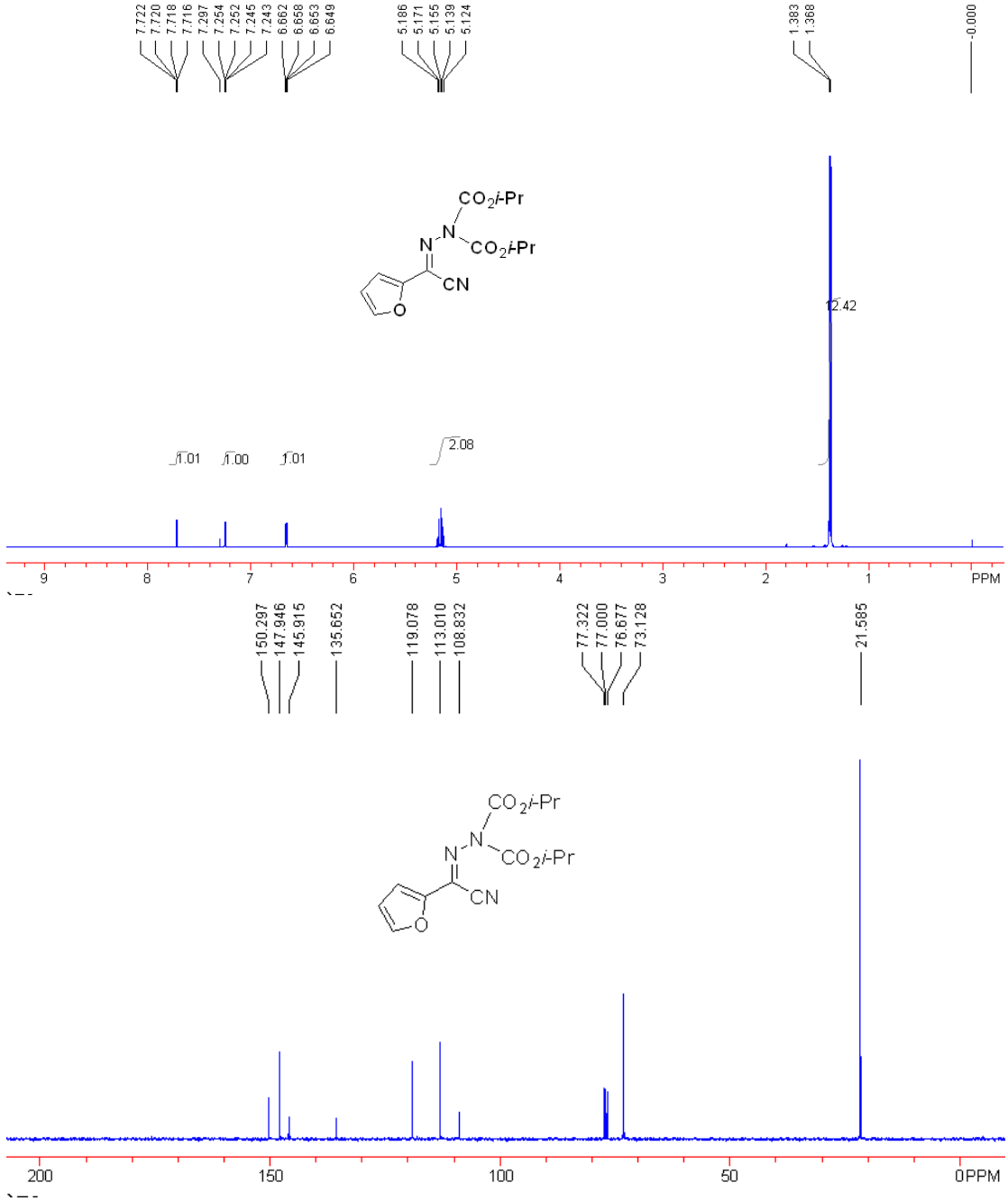
(Z)-diethyl 2-(cyano(4-methoxyphenyl)methylene)hydrazine-1,1-dicarboxylate (3l). Oil. IR (CH_2Cl_2) ν 2984, 2939, 2229, 1799, 1761, 1605, 1176, 1103 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.36 (6H, t, *J* = 7.2 Hz, CH_3), 3.89 (3H, s, OCH_3), 4.38 (4H, q, *J* = 7.2 Hz, CH_2), 7.01 (2H, d, *J* = 9.2 Hz, Ar), 8.01 (2H, d, *J* = 9.2 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1, 55.6, 64.3, 109.8, 114.7, 122.9, 130.3, 148.7, 150.7, 164.2. MS (ESI) *m/z* 320.2 (M^++1). HRMS (ESI) Calcd. for $C_{15}H_{17}N_3O_5$ requires (M^++1) 320.1168 Found 320.12407.

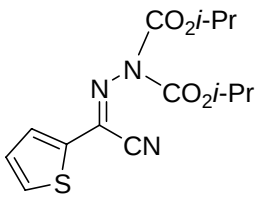






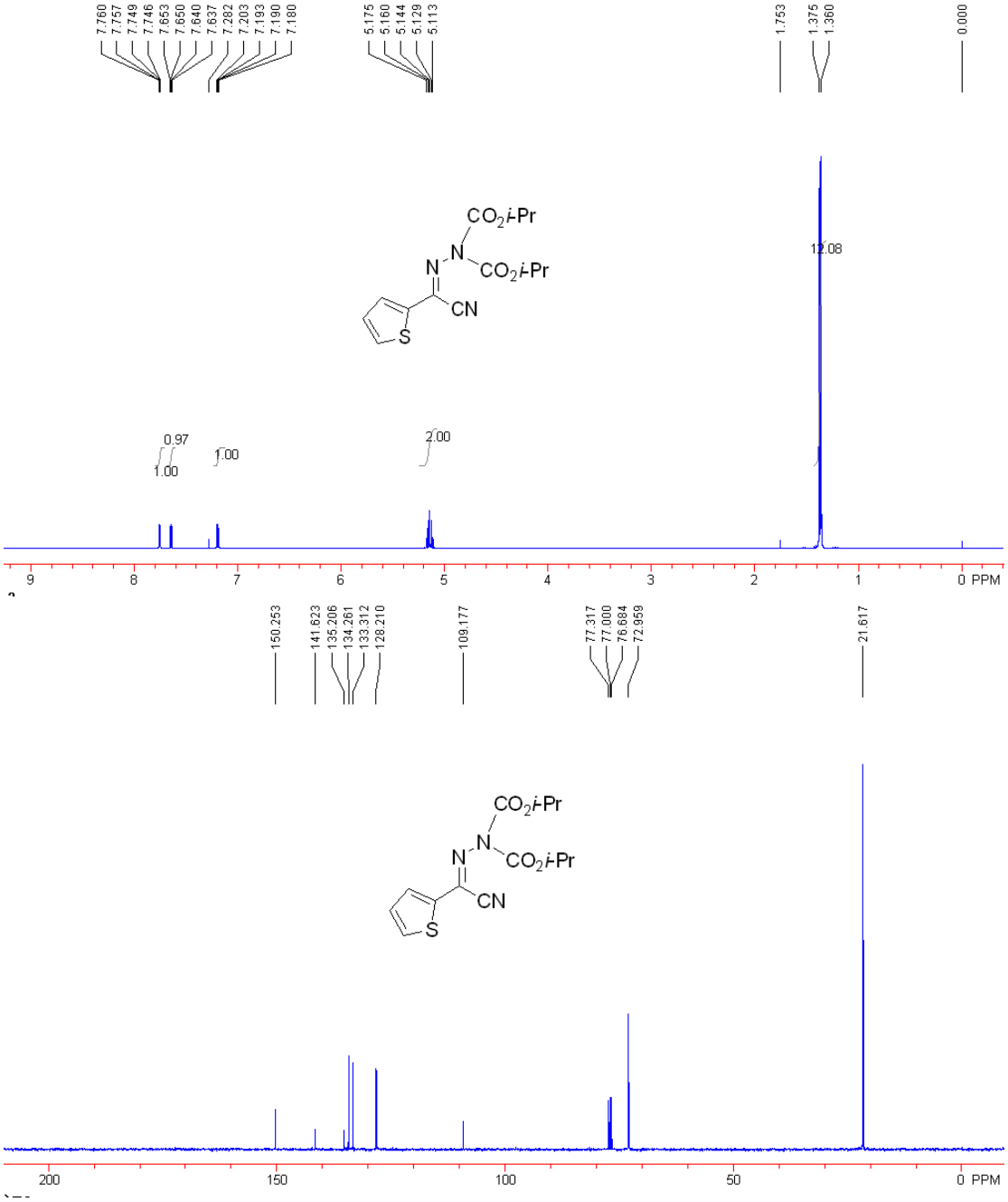
(E)-diisopropyl 2-(cyano(furan-2-yl)methylene)hydrazine-1,1-dicarboxylate (3m). Oil. IR (CH_2Cl_2) ν 3131, 2986, 2940, 2234, 1791, 1794, 1095 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.37 (12H, d, J = 6.0 Hz, CH_3), 5.12-5.19 (2H, m, CH), 6.65 (1H, dd, J_1 = 1.6 Hz, J_2 = 3.6 Hz, Ar), 7.25 (1H, dd, J_1 = 0.8 Hz, J_2 = 3.6 Hz, Ar), 7.72 (1H, dd, J_1 = 0.8 Hz, J_2 = 1.6 Hz, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.6, 73.1, 108.8, 113.0, 119.1, 135.6, 145.9, 147.9, 150.3. MS (ESI) *m/z* 308.2 (M^++1). HRMS (ESI) Calcd. for $C_{14}H_{17}N_3O_5$ requires (M^++1) 308.1168 Found 308.12402.

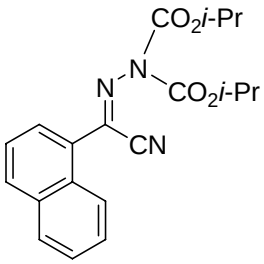




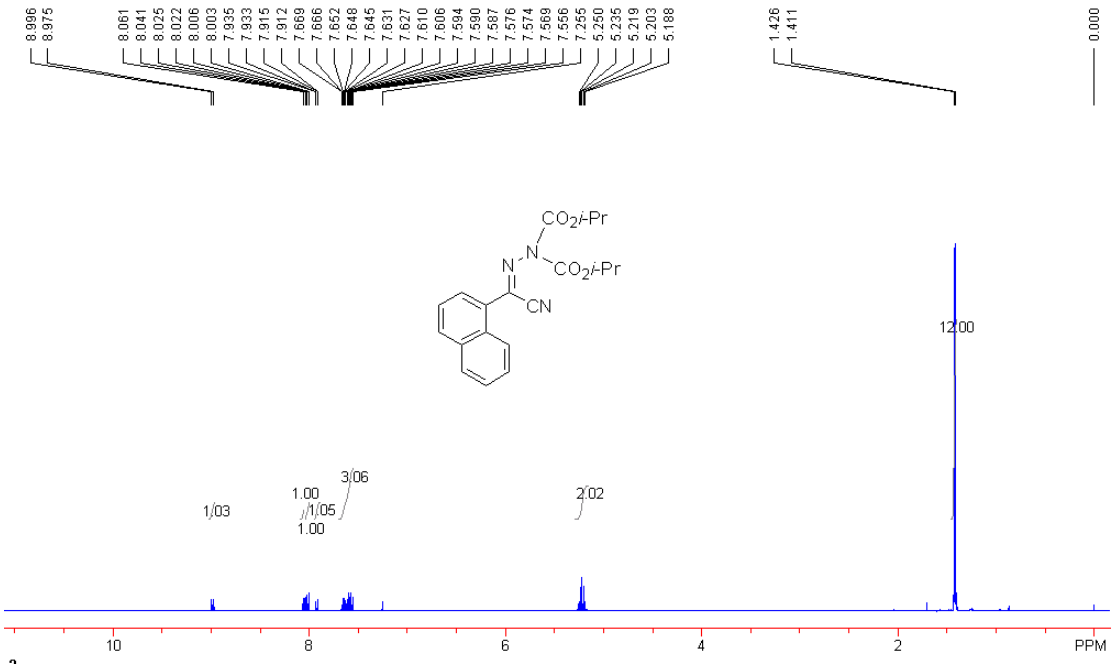
(E)-diisopropyl 2-(cyano(thiophen-2-yl)methylene)hydrazine-1,1-dicarboxylate (3n). Oil. IR (CH_2Cl_2) ν 3107, 2984, 2938, 2230, 1795, 1763, 1309,1093 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.37 (12H, d, J = 6.0 Hz, CH_3), 5.11-5.18 (2H, m, CH), 7.20 (1H, dd, J_1 = 4.4

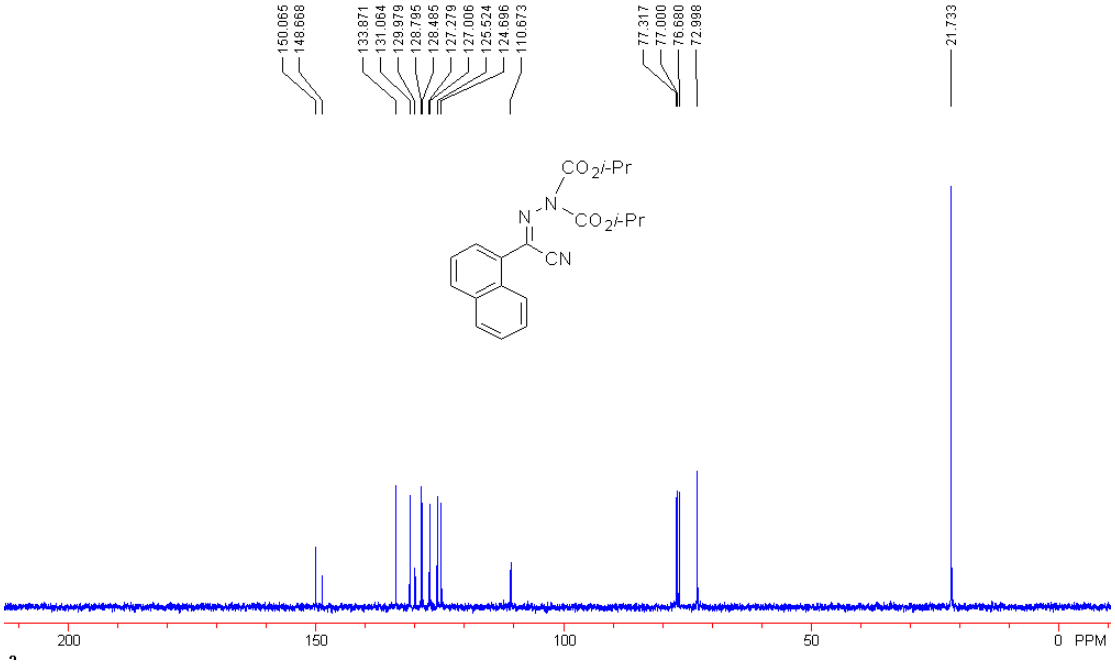
Hz, J_2 = 5.2 Hz, Ar), 7.64 (1H, dd, J_1 = 1.2 Hz, J_2 = 5.2 Hz, Ar), 7.75 (1H, dd, J_1 = 1.2 Hz, J_2 = 4.4 Hz, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.6, 72.9, 109.2, 128.2, 133.3, 134.3, 135.2, 141.6, 150.3. MS (ESI) *m/z* 324.2 (M^++1). HRMS (ESI) Calcd. for $C_{14}H_{17}N_3O_4S$ requires (M^++1) 324.0940 Found 324.10089.

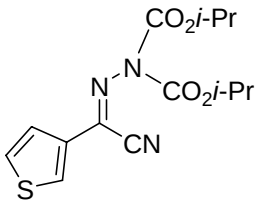




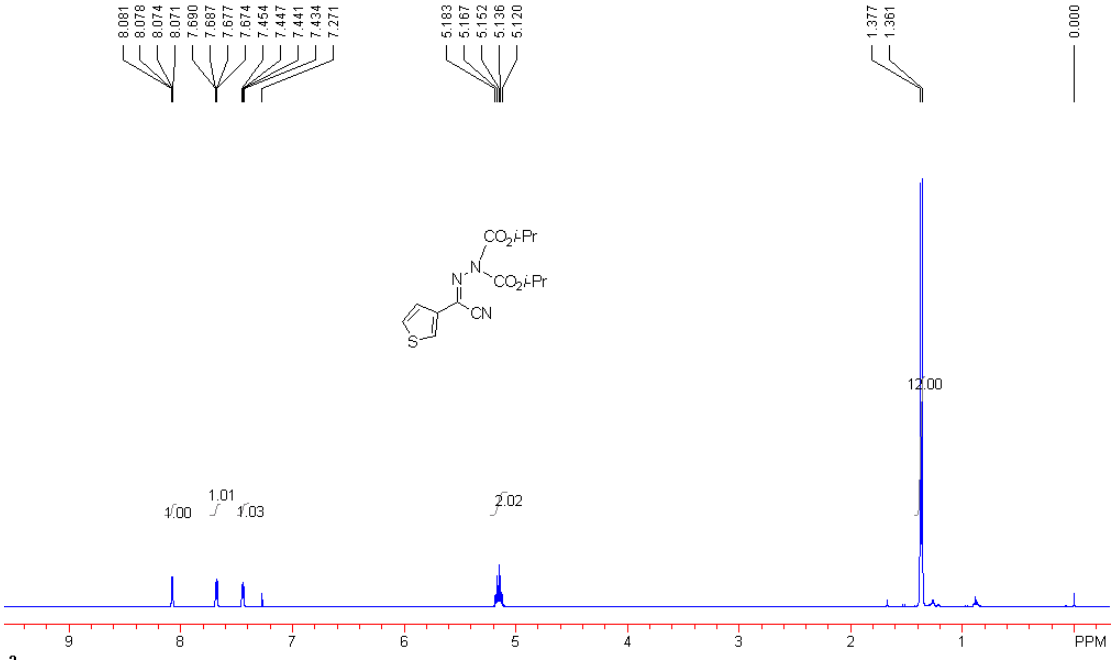
(Z)-diisopropyl 2-(cyano(naphthalen-1-yl)methylene)hydrazine-1,1-dicarboxylate (3o). Oil. IR (CH_2Cl_2) ν 2985, 2939, 2226, 1798, 1761, 1511, 1093 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.42 (12H, d, *J* = 6.0 Hz, CH_3), 5.18-5.25 (2H, m, CH), 7.55-7.67 (3H, m, Ar), 7.91-7.93 (1H, m, Ar), 8.00-8.03 (1H, m, Ar), 8.05 (1H, d, *J* = 8.0 Hz, Ar), 8.99 (1H, d, *J* = 8.4 Hz, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.7, 73.0, 110.7, 124.7, 125.5, 127.0, 127.3, 128.5, 128.8, 130.0, 131.1, 133.9, 148.7, 150.1. MS (ESI) *m/z* 368.0 (M^++1), 389.9 (M^++Na). HRMS (ESI) Calcd. for $C_{20}H_{21}N_3O_4$ requires (M^++Na) 390.1424 Found 390.14222.







(Z)-diisopropyl 2-(cyano(thiophen-3-yl)methylene)hydrazine-1,1-dicarboxylate (3p). Oil. IR (CH_2Cl_2) ν 3107, 2984, 1938, 2230, 1795, 1763, 1561, 1093 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.37 (12H, d, J = 6.4 Hz, CH_3), 5.12-5.19 (2H, m, CH), 7.44 (1H, dd, J_1 = 2.8 Hz, J_2 = 5.2 Hz, Ar), 7.68 (1H, dd, J_1 = 1.2 Hz, J_2 = 5.2 Hz, Ar), 8.08 (1H, dd, J_1 = 1.2 Hz, J_2 = 2.8 Hz, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.7, 73.0, 110.1, 125.3, 128.0, 132.1, 133.9, 141.8, 150.4. MS (ESI) *m/z* 323.9 (M^++1). HRMS (ESI) Calcd. for $C_{14}H_{17}N_3O_4S$ requires (M^++Na) 346.0832 Found 346.08304.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8.078
8.074
8.071
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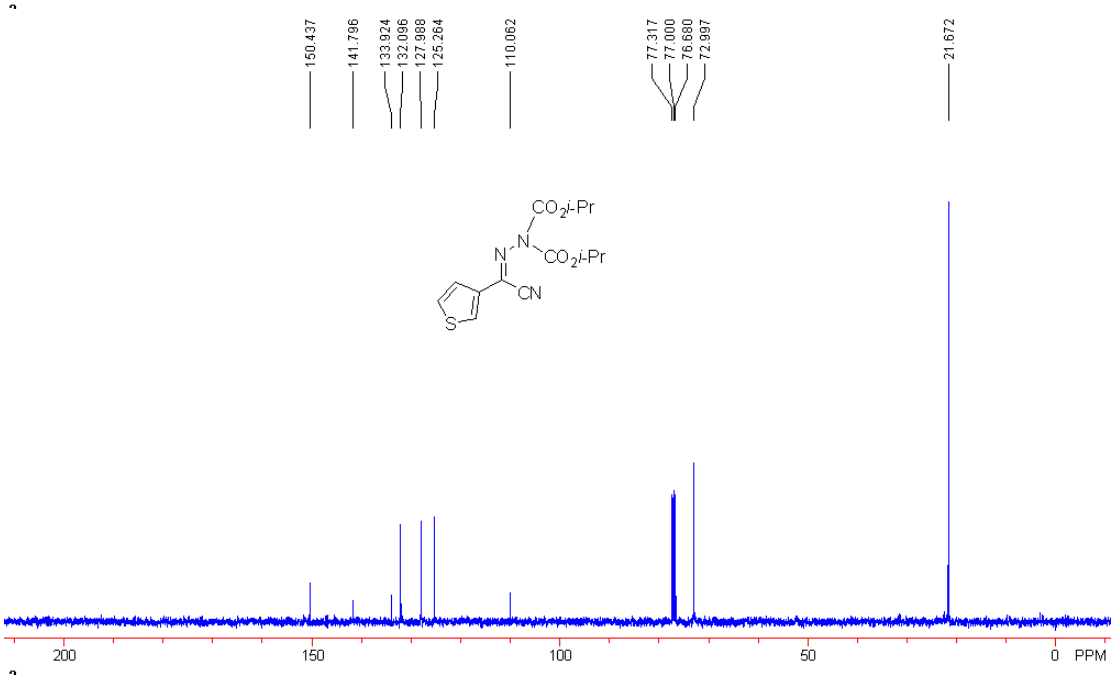
7.687
7.677
7.674
7.454
7.447
7.441
7.434
7.271
5.183
5.167
5.152
5.136
5.120
1.377
1.361
0.000
CO2i-Pr
N
N
CO2i-Pr
CN
S
12.00
1.00
1.01
1.03
2.02
9
8
7
6
5
4
3
2
1
PPM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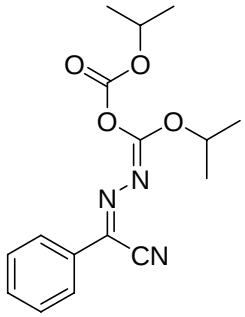
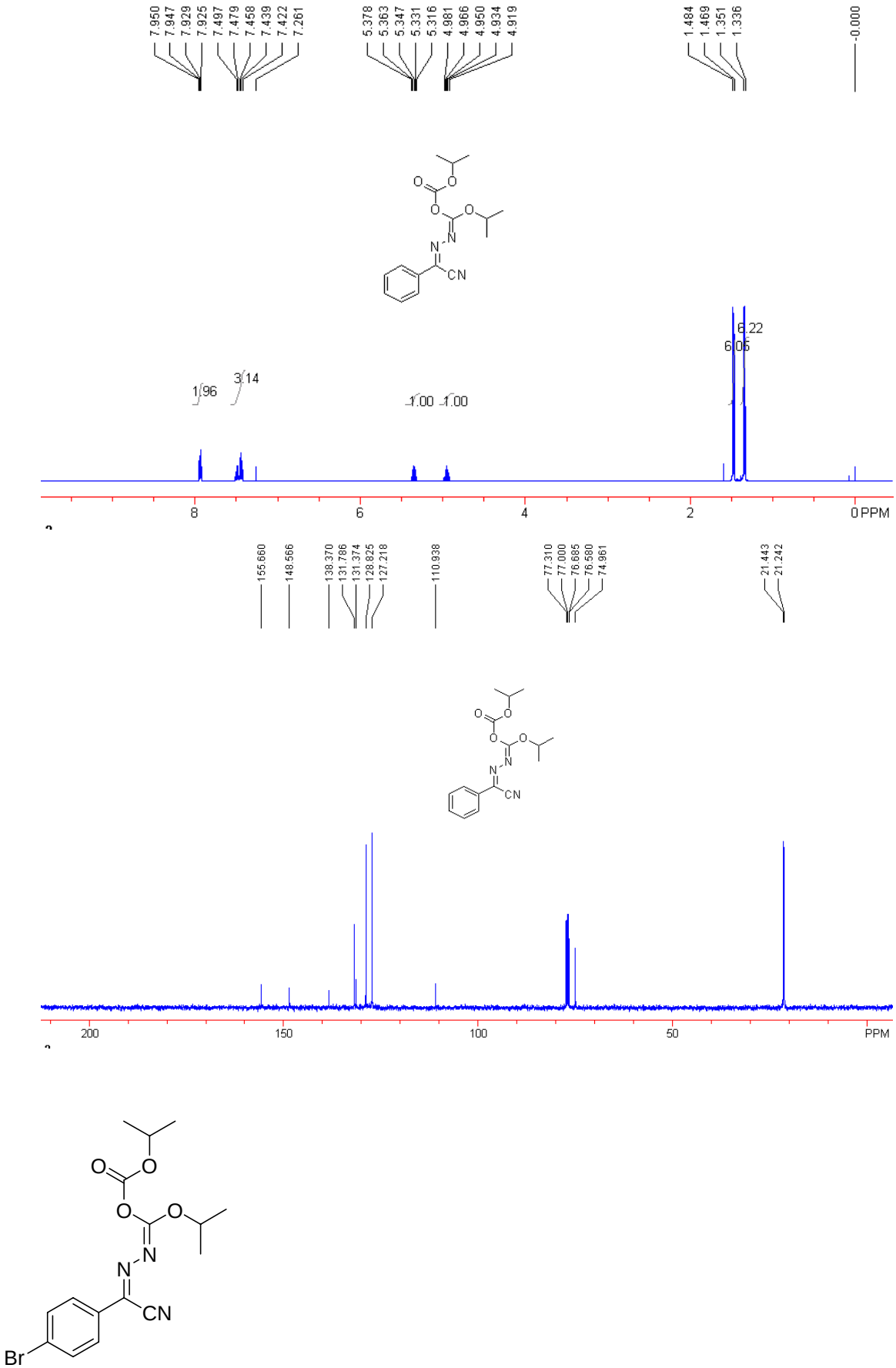
132.096
127.988
125.264
110.062
77.317
77.000
76.680
72.997
21.672
CO2i-Pr
N
N
CO2i-Pr
CN
S
200
150
100
50
0
PPM

Typical reaction procedure for the preparation of 4.

To a stirred solution of acyl cyanide **1** (0.3 mmol) and Ph_3P (0.3 mmol) in anhydrous toluene (2.0 mL) under argon was added diisopropyl azodicarboxylate/diethyl azodicarboxylate **2** (0.3 mmol) at 20 degree, the mixture was maintained at 20 degree to stir for the time needed. The solvent was removed under reduced pressure on a rotary evaporator. The residue was subjected to column chromatography on silica gel (300-400 mesh) to afford the products **4**.

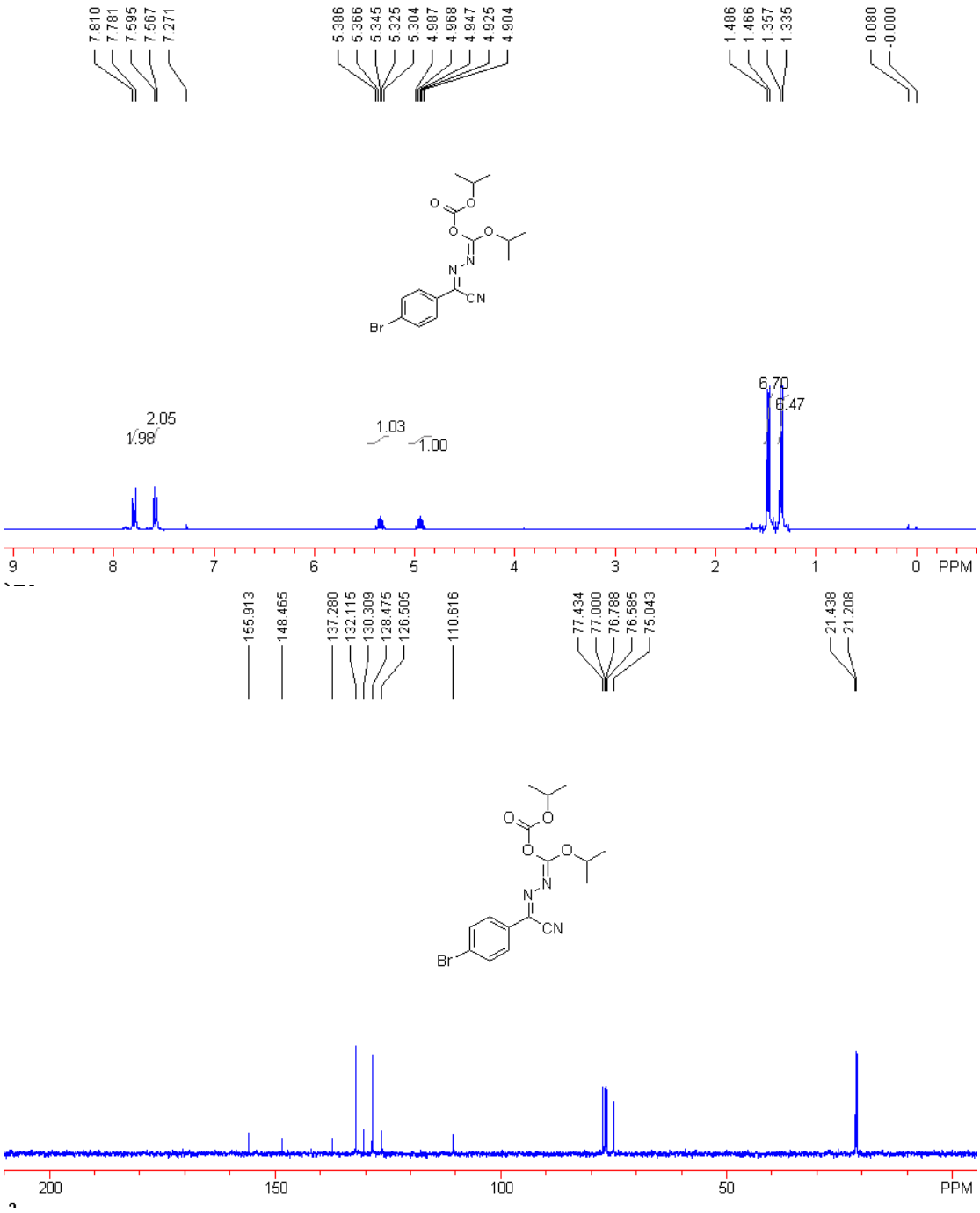


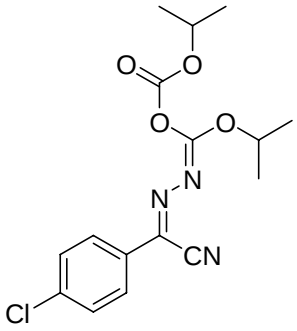
(4a) Oil. IR (CH_2Cl_2) ν 2986, 2940, 1783, 1626, 1214, 1095 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.34 (6H, d, *J* = 6.0 Hz, CH_3), 1.48 (6H, d, *J* = 6.0 Hz, CH_3), 4.91-4.99 (1H, m, CH), 5.31-5.38 (1H, m, CH), 7.42-7.52 (3H, m, Ar), 7.92-7.95 (2H, m, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.2, 21.4, 74.9, 76.6, 110.9, 127.2, 128.8, 131.4, 131.8, 138.4, 148.6, 155.7. MS (ESI) *m/z* 318.0 (M^++1), 340.1 (M^++Na). HRMS (ESI) Calcd. for $C_{16}H_{19}N_3O_4$ requires (M^++Na) 340.1268 Found 340.12676.



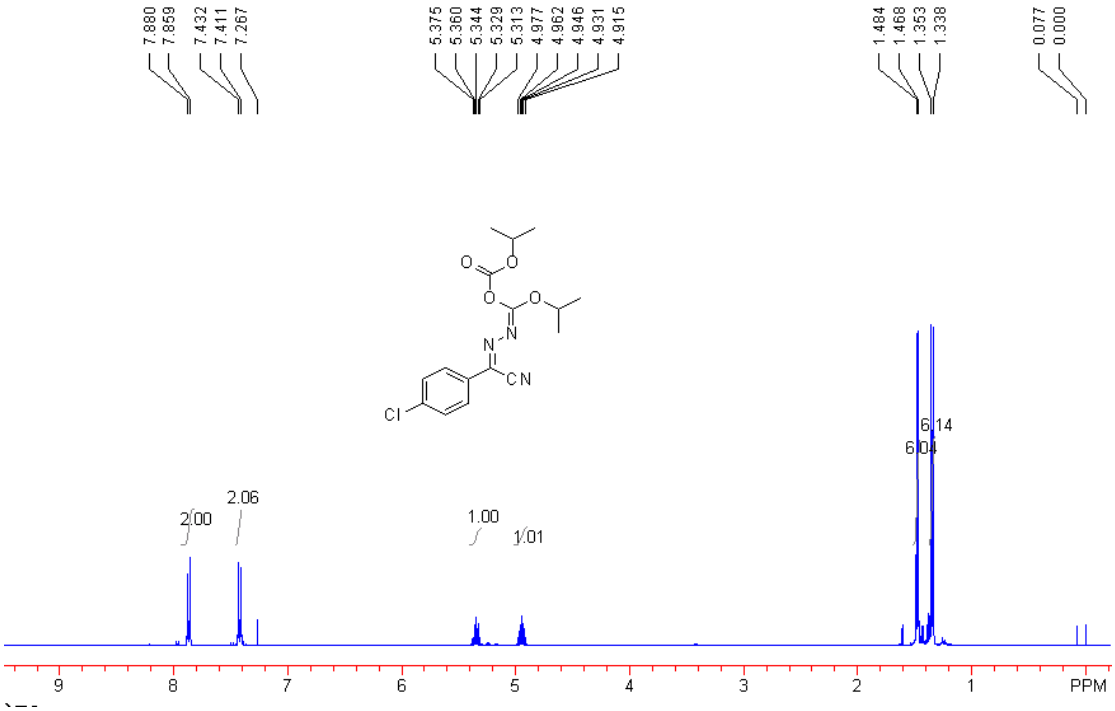
(4b) Oil. IR (CH_2Cl_2) ν 2986, 1939, 2225, 1783, 1622, 1213, 1095 cm^{-1}; ^1H NMR ($CDCl_3$,

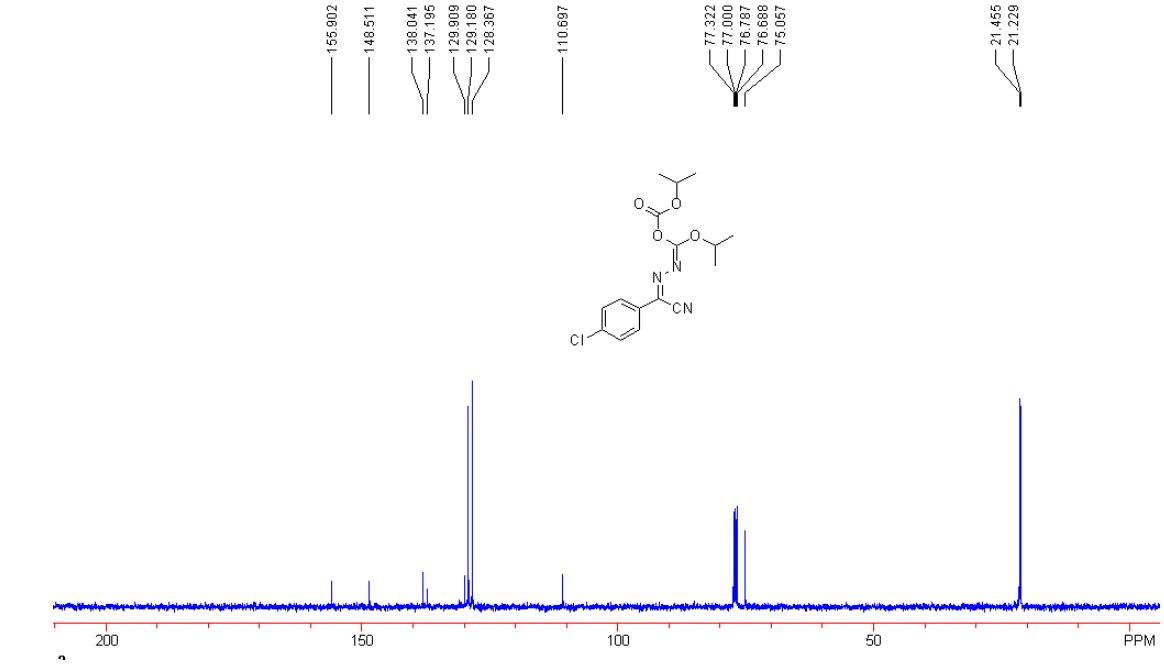
300 MHz, TMS): δ 1.35 (6H, d, *J* = 6.3 Hz, CH_3), 1.48 (6H, d, *J* = 6.3 Hz, CH_3), 4.90-4.99 (1H, m, CH), 5.30-5.39 (1H, m, CH), 7.58 (2H, d, *J* = 8.7 Hz, Ar), 7.80 (2H, d, *J* = 8.7 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.2, 21.4, 75.0, 76.8, 110.6, 126.5, 128.5, 130.3, 132.1, 137.3, 148.5, 155.9. MS (ESI) *m/z* 395.9 (M^++1), 418.9 (M^++Na). HRMS (ESI) Calcd. for $C_{16}H_{18}BrN_3O_4$ requires (M^++Na) 418.0373 Found 418.03621.

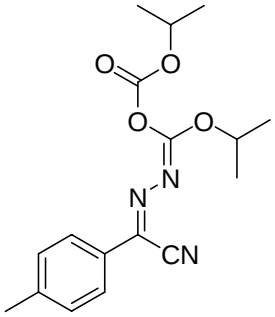




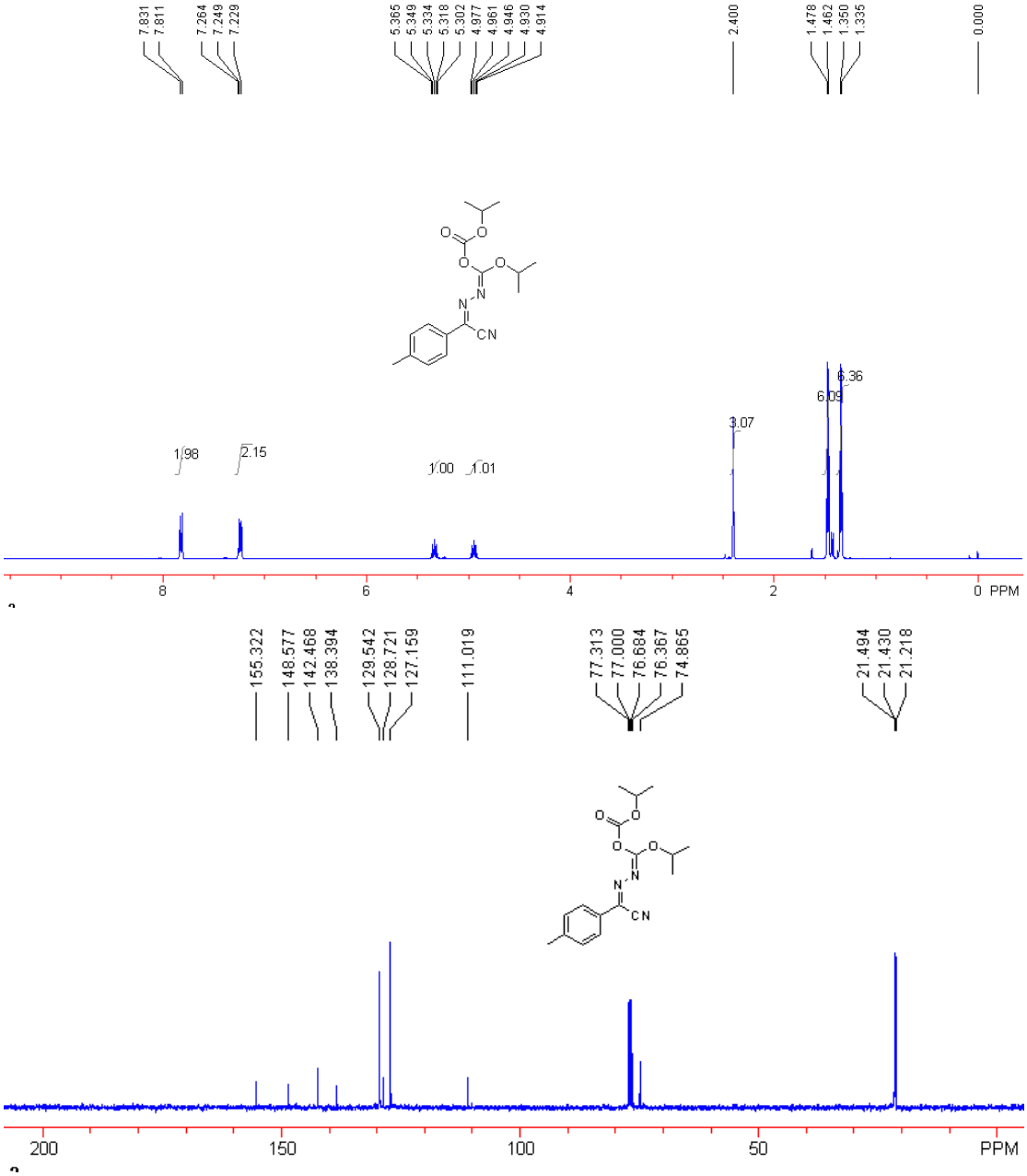
(4c) Oil. IR (CH_2Cl_2) ν 2987, 2940, 2225, 1783, 1622, 1214, 1094 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.35 (6H, d, *J* = 6.0 Hz, CH_3), 1.48 (6H, d, *J* = 6.0 Hz, CH_3), 4.91-4.98 (1H, m, CH), 5.31-5.38 (1H, m, CH), 7.42 (2H, d, *J* = 8.4 Hz, Ar), 7.87 (2H, d, *J* = 8.4 Hz, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.2, 21.5, 75.1, 76.8, 110.7, 128.4, 129.2, 129.9, 137.2, 138.0, 148.5, 155.9. MS (ESI) *m/z* 352.0 (M^++1), 373.9 (M^++Na). HRMS (ESI) Calcd. for $C_{16}H_{18}ClN_3O_4$ requires (M^++Na) 374.0878 Found 374.08694.

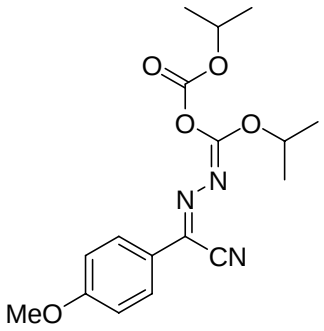






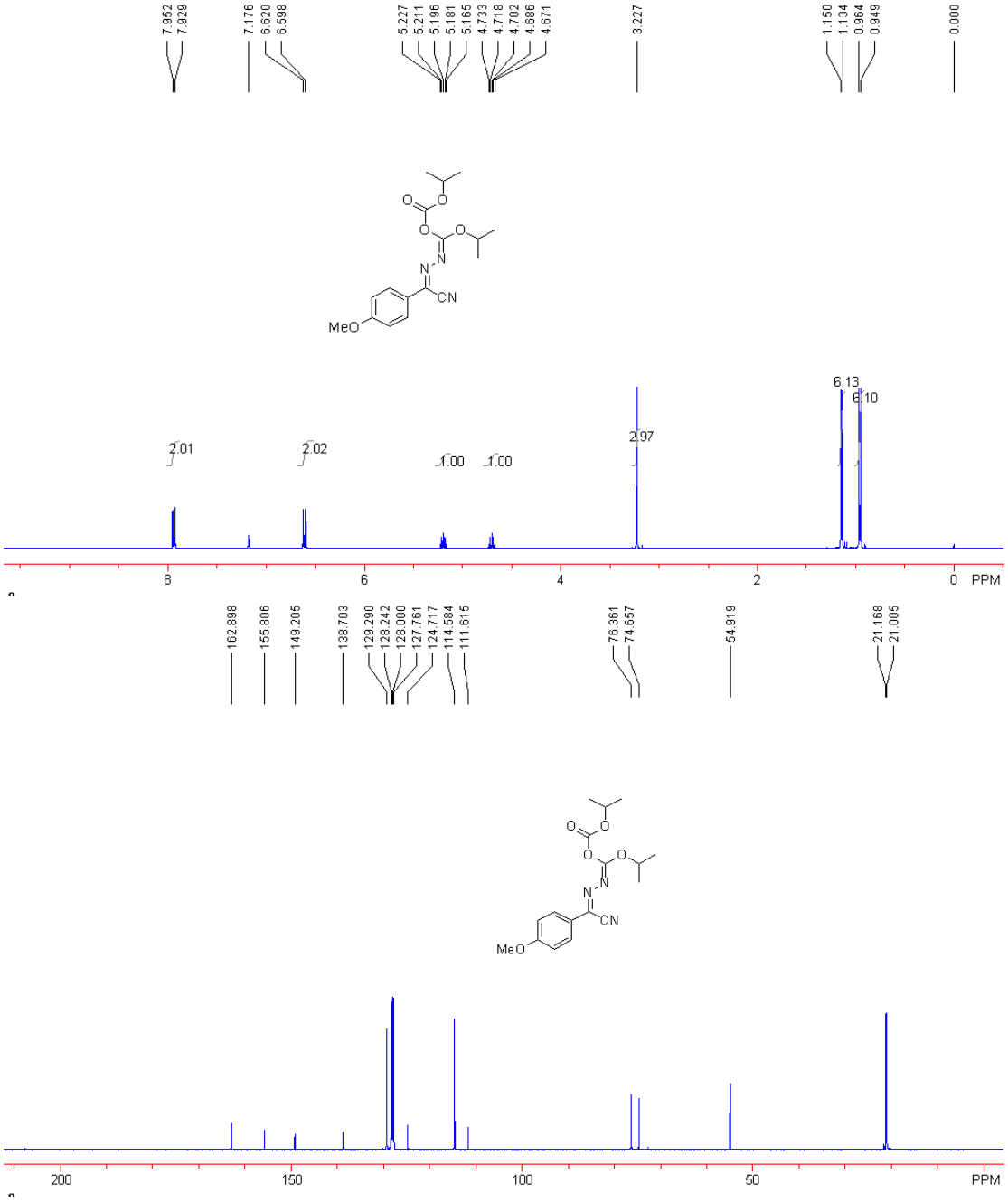
(4d) Oil. IR (CH_2Cl_2) ν 2986, 2940, 2879, 2225, 1782, 1627, 1377, 1095 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.34 (6H, d, *J* = 6.4 Hz, CH_3), 1.47 (6H, d, *J* = 6.4 Hz, CH_3), 2.40 (3H, s, CH_3), 4.91-4.98 (1H, m, CH), 5.30-5.37 (1H, m, CH), 7.24 (2H, d, *J* = 8.0 Hz, Ar), 7.82 (2H, d, *J* = 8.0 Hz, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 21.2, 21.4, 21.5, 74.9, 76.4, 111.0, 127.2, 128.7, 129.5, 138.4, 142.5, 148.6, 155.3. MS (ESI) *m/z* 332.0 (M^++1), 354.0 (M^++Na). HRMS (ESI) Calcd. for $C_{17}H_{21}N_3O_4$ requires (M^++Na) 354.1424 Found 354.14211.

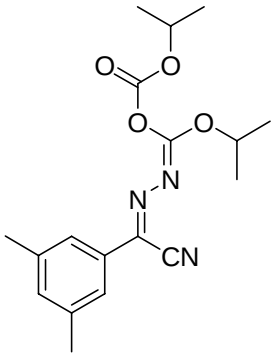




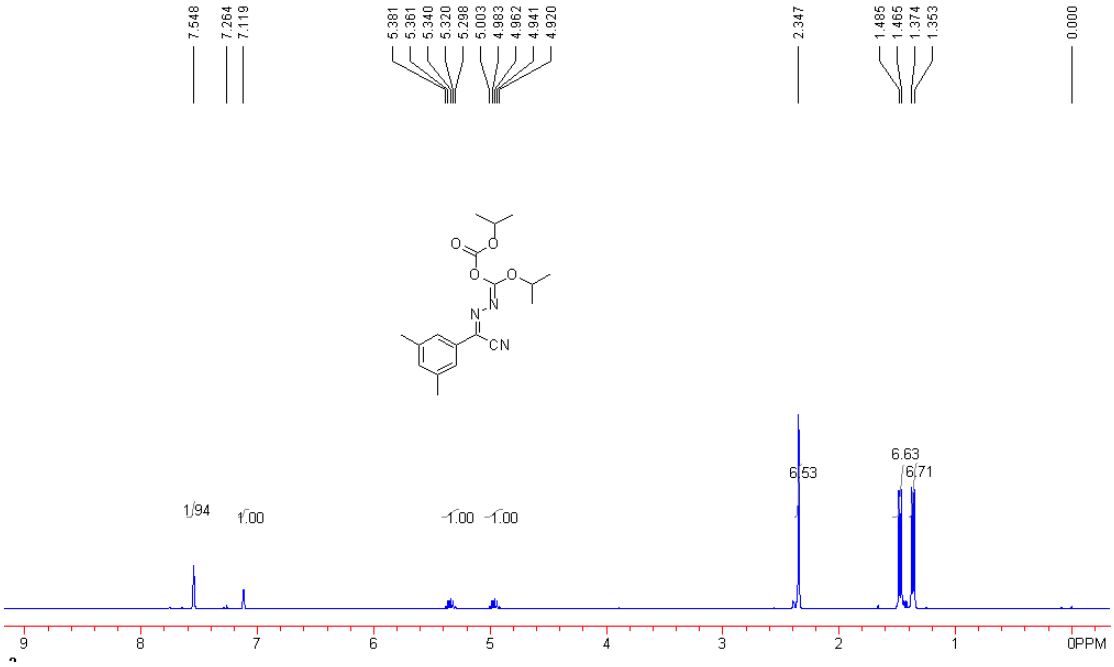
(4e) mp. 75-77 ^{o}C; IR (CH_2Cl_2) ν 2986, 1939, 2225, 1783, 1627, 1214, 1095 cm^{-1}; ^{1}H NMR (benzene-d_6, 400 MHz, TMS): δ 0.96 (6H, d, J = 6.0 Hz, CH_3), 1.14 (6H, d, J = 6.0 Hz, CH_3),

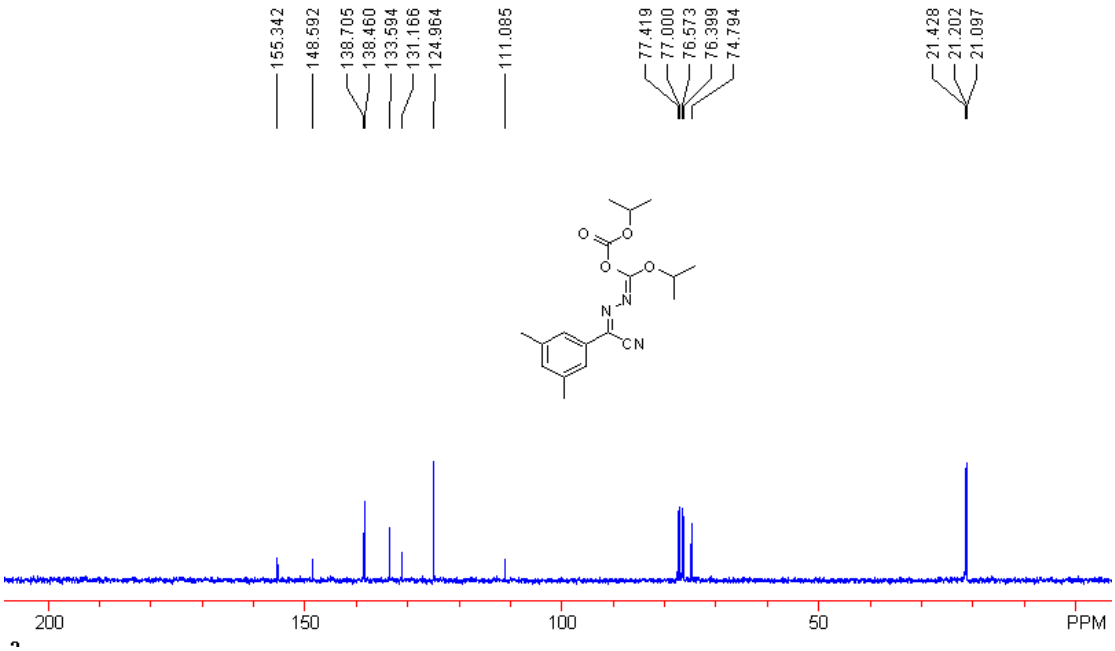
3.23 (3H, s, OCH_3), 4.67-4.74 (1H, m, CH), 5.16-5.23 (1H, m, CH), 6.61 (2H, d, *J* = 8.8 Hz, Ar), 7.94 (2H, d, *J* = 8.8 Hz, Ar). ^{13}C NMR (benzene-d_6, 100 MHz): δ 21.0, 21.2, 54.9, 74.6, 76.4, 111.6, 114.6, 124.7, 129.3, 138.7, 149.2, 155.8, 162.9. MS (ESI) *m/z* 348.1 (M^++1). HRMS (ESI) Calcd. for $C_{17}H_21N_3O_5$ requires (M^++Na) 370.1373 Found 370.13749.

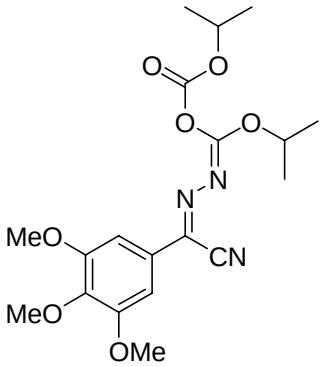




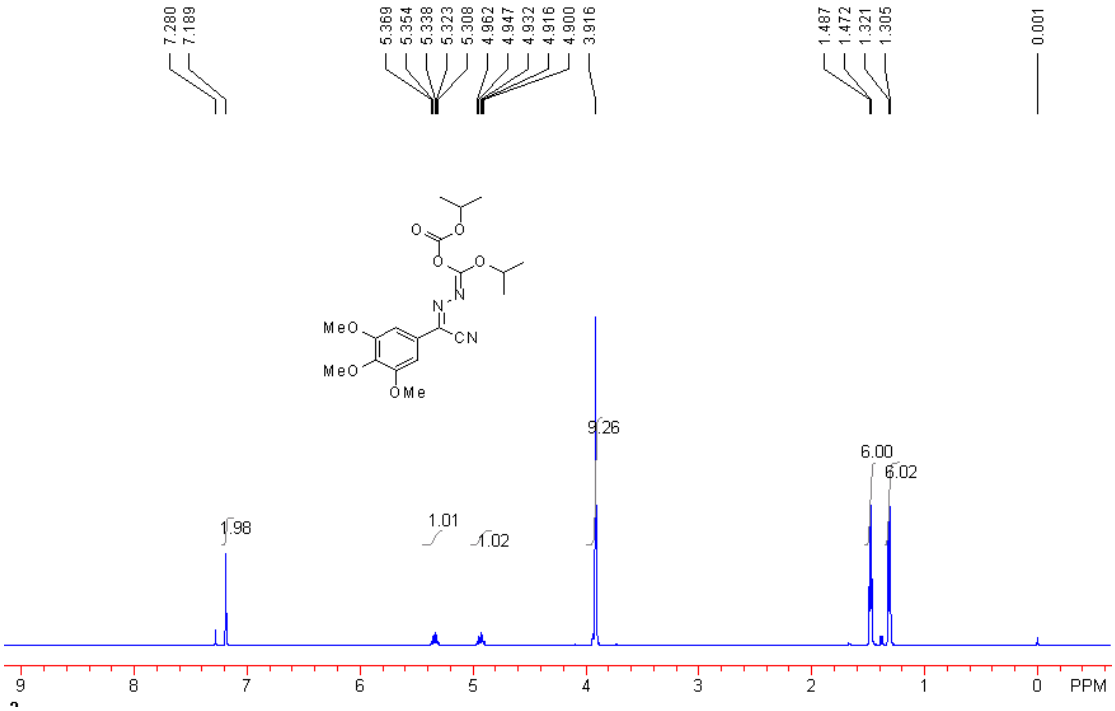
(4f) Oil. IR (CH_2Cl_2) ν 2986, 2939, 2225, 1782, 1627, 1207, 1086 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 1.36 (6H, d, *J* = 6.0 Hz, CH_3), 1.48 (6H, d, *J* = 6.0 Hz, CH_3), 2.35 (6H, s, CH_3), 4.92-5.01 (1H, m, CH), 5.29-5.39 (1H, m, CH), 7.12 (1H, s, Ar), 7.55 (2H, s, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.1, 21.2, 21.4, 74.8, 76.4, 111.1, 125.0, 131.2, 133.6, 138.5, 138.7, 148.6, 155.3. MS (ESI) *m/z* 346.0 (M^++1), 368.0 (M^++Na). HRMS (ESI) Calcd. for $C_{18}H_{23}N_3O_4$ requires (M^++Na) 368.1581 Found 368.15692.







(4g) Oil. IR (CH_2Cl_2) ν 2986, 2942, 2842, 2226, 1784, 1628, 1590, 1212, 1096 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.31 (6H, d, *J* = 6.4 Hz, CH_3), 1.48 (6H, d, *J* = 6.0 Hz, CH_3), 3.92 (9H, s, OCH_3), 4.90-4.97 (1H, m, CH), 5.30-5.37 (1H, m, CH), 7.19 (2H, s, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.2, 21.4, 56.2, 61.0, 74.9, 76.5, 104.4, 110.9, 126.6, 138.0, 141.4, 148.4, 153.4, 155.2. MS (ESI) *m/z* 407.9 (M^++1), 429.9 (M^++Na). HRMS (ESI) Calcd. for $C_{19}H_{25}N_3O_7$ requires (M^++Na) 430.1585 Found 430.15792.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1.321
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MeO
OMe
CN
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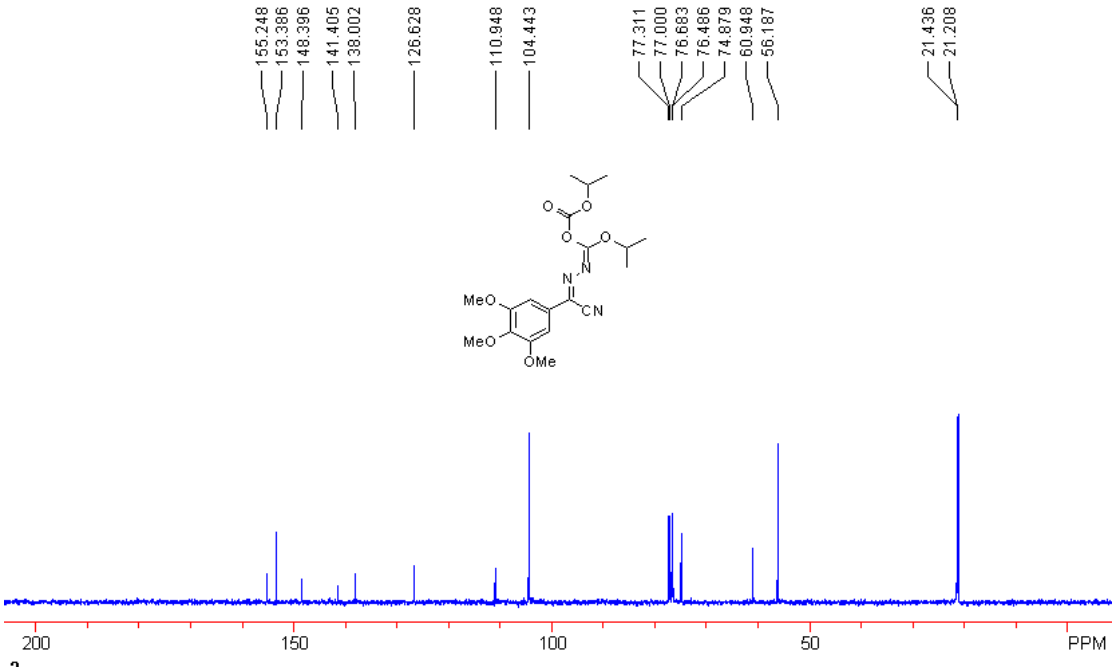
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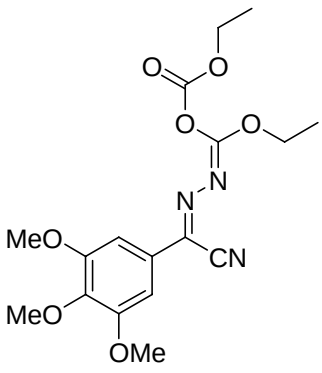
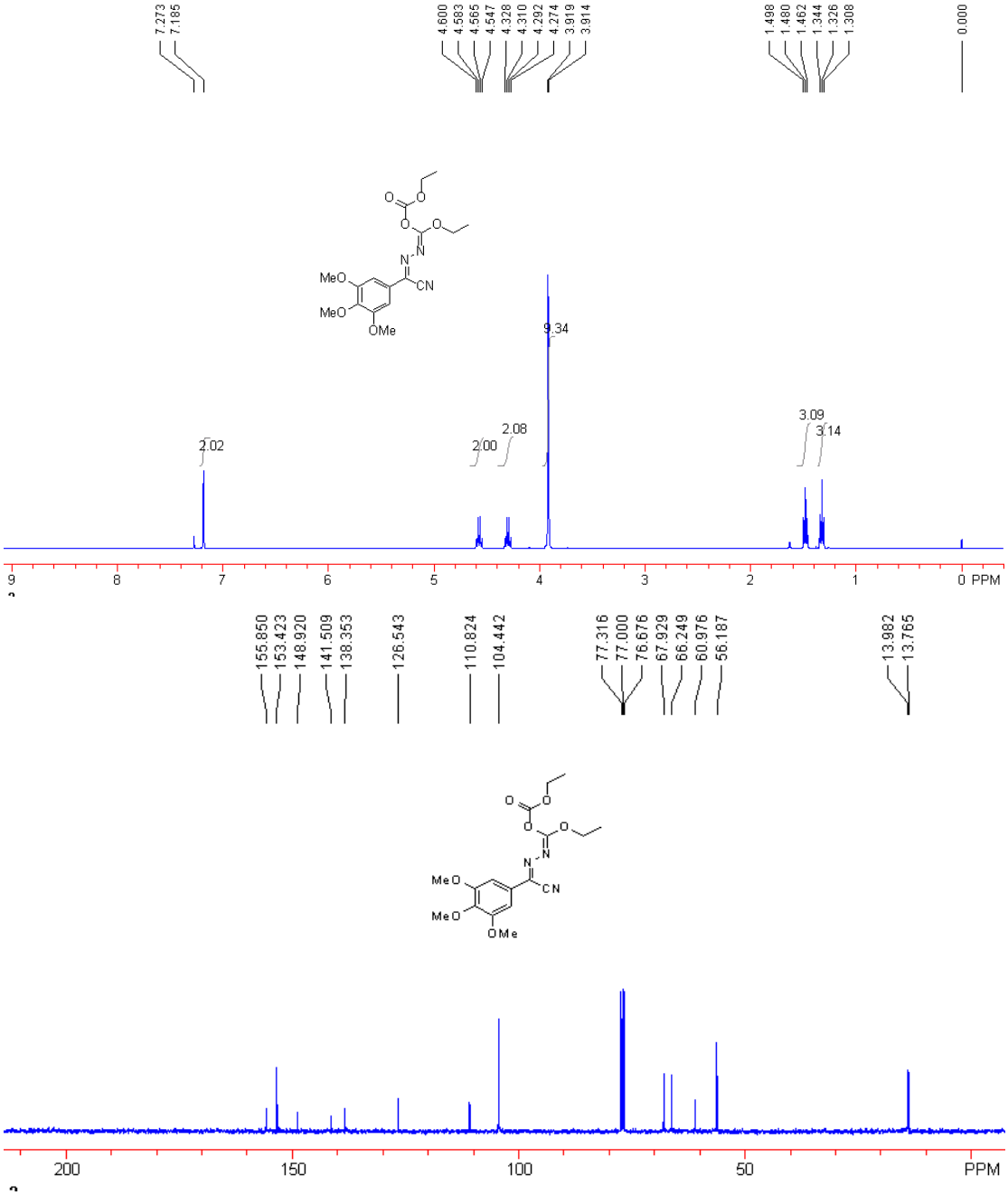
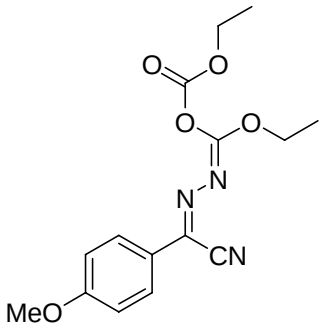
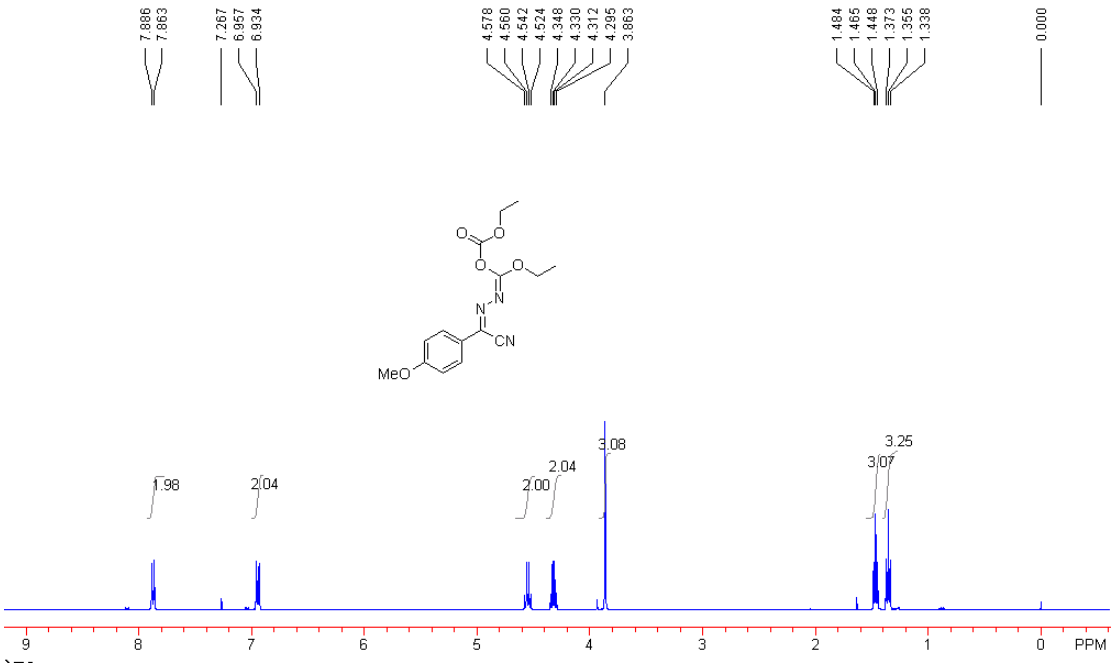

MeO
MeO
OMe
CN

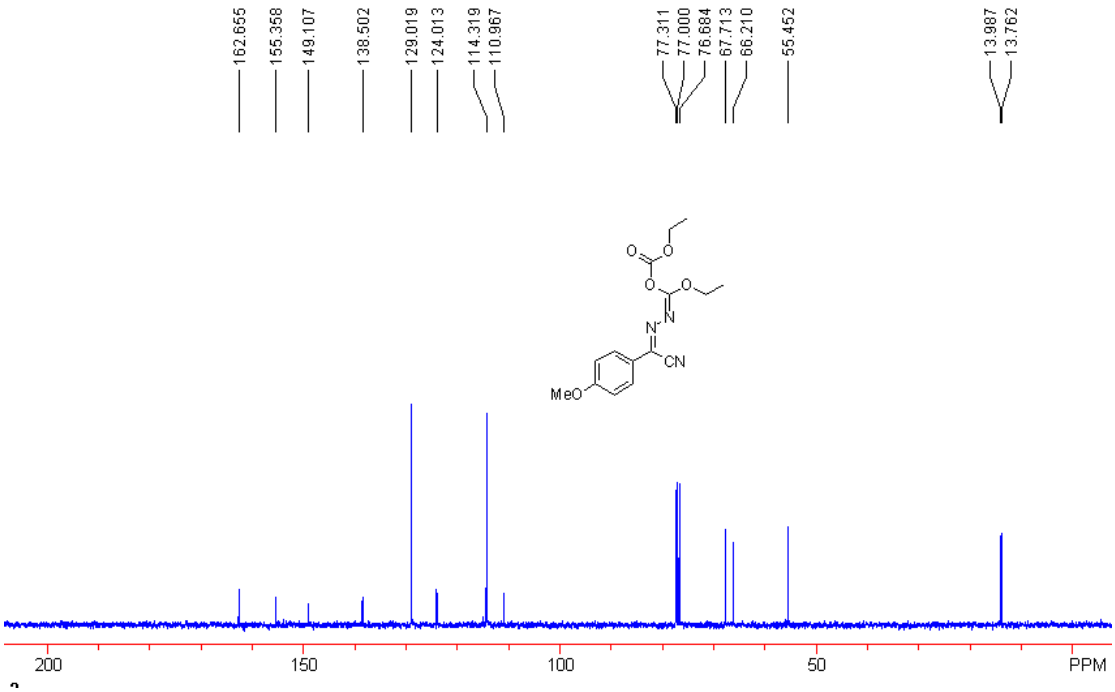
(4h) Oil. IR (CH_2Cl_2) ν 2985, 2942, 2842, 2227, 1789, 1633, 1590, 1206 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.33 (3H, t, *J* = 7.2 Hz, CH_3), 1.48 (3H, t, *J* = 7.2 Hz, CH_3), 3.91 (3H, s, OCH_3), 3.92 (6H, s, OCH_3), 4.31 (2H, q, *J* = 7.2 Hz, CH_2), 4.57 (2H, q, *J* = 7.2 Hz, CH), 7.19 (2H, s, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 13.8, 14.0, 56.2, 61.0, 66.2, 68.0, 104.4, 110.8, 126.5, 138.4, 141.5, 148.9, 153.4, 155.9. MS (ESI) *m/z* 380.0 (M^++1). HRMS (ESI) Calcd. for $C_{17}H_{21}N_3O_7$ requires (M^++Na) 402.1272 Found 402.12674.

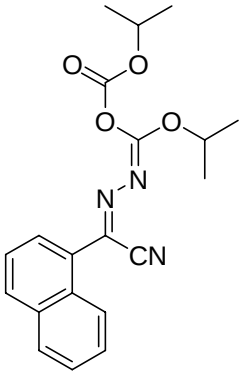




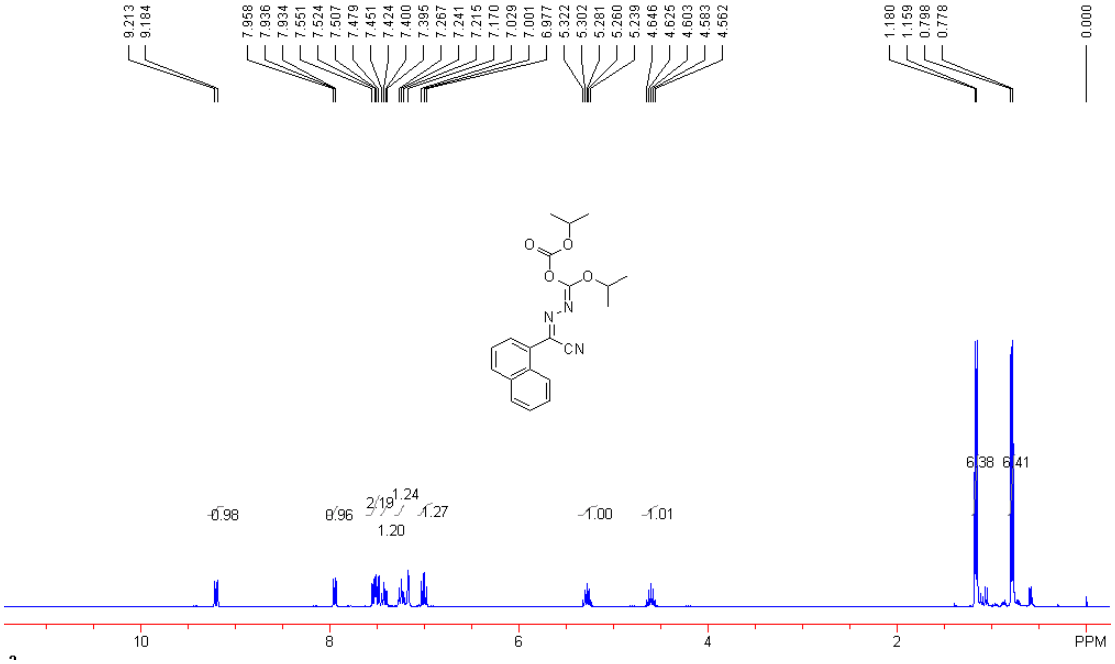
(4i) Oil. IR (CH_2Cl_2) ν 2985, 2940, 2842, 2225, 1785, 1630, 1604, 1261, 1205 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.35 (3H, t, *J* = 7.2 Hz, CH_3), 1.46 (3H, t, *J* = 7.2 Hz, CH_3), 3.86 (3H, s, OCH_3), 4.32 (2H, q, *J* = 7.2 Hz, CH_2), 4.55 (2H, q, *J* = 7.2 Hz, CH), 6.95 (2H, d, *J* = 9.2 Hz, Ar), 7.87 (2H, d, *J* = 9.2 Hz, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 13.7, 14.0, 55.5, 66.2, 67.7, 111.0, 114.3, 124.0, 129.0, 138.5, 149.1, 155.4, 162.7. MS (ESI) *m/z* 320.0 (M^++1), 341.9 (M^++Na). HRMS (ESI) Calcd. for $C_{15}H_{17}N_3O_5$ requires (M^++Na) 342.1060 Found 342.10585.

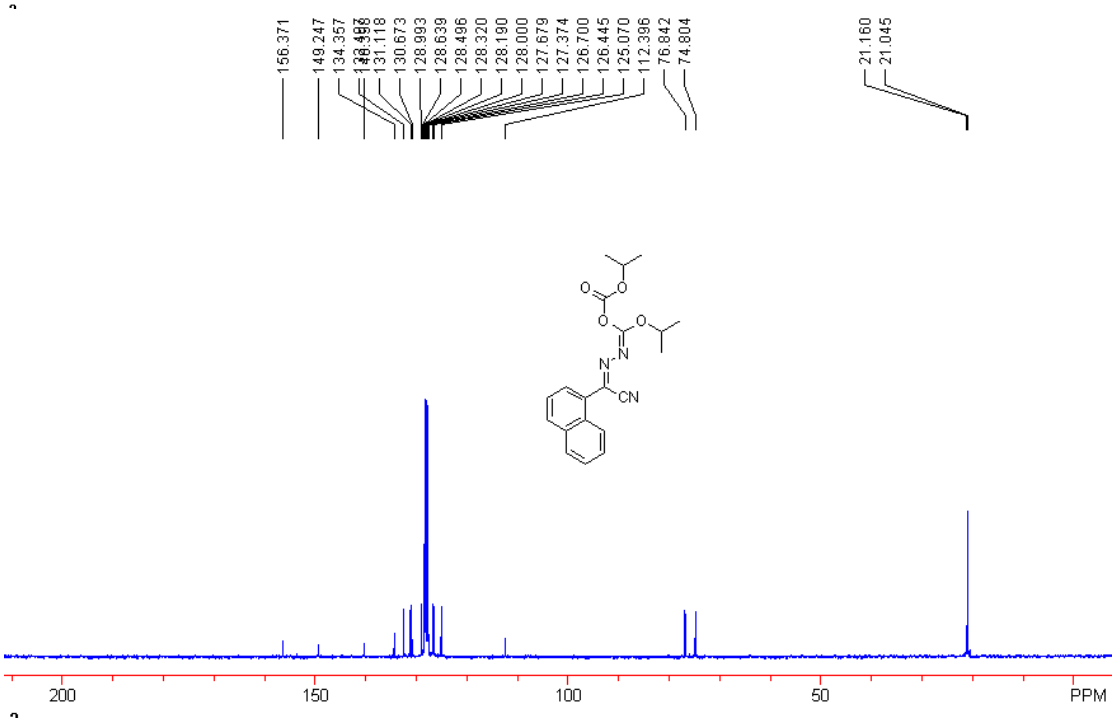


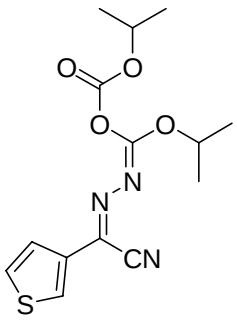




(4j) Oil. IR (CH_2Cl_2) ν 3051, 2985, 2939, 2223, 1778, 1628, 1217, 1093 cm^{-1}; ^1H NMR (benzene-d_6, 300 MHz, TMS): δ 0.79 (6H, d, *J* = 6.3 Hz, CH_3), 1.17 (6H, d, *J* = 6.3 Hz, CH_3), 4.56-4.65 (1H, m, CH), 5.24-5.33 (1H, m, CH), 7.00 (1H, t, *J* = 7.8 Hz, Ar), 7.24 (1H, t, *J* = 7.8 Hz, Ar), 7.42 (1H, t, *J* = 8.4 Hz, Ar), 7.49 (1H, d, *J* = 8.1 Hz, Ar), 7.54 (1H, d, *J* = 8.1 Hz, Ar), 7.95 (1H, d, *J* = 8.1 Hz, Ar), 9.20 (1H, d, *J* = 8.4 Hz, Ar). ^{13}C NMR (benzene-d_6, 75 MHz, TMS): δ 21.0, 21.2, 74.8, 76.8, 112.4, 125.1, 126.4, 126.7, 128.2, 128.5, 129.0, 130.7, 131.1, 132.5, 134.4, 140.4, 149.2, 156.4. MS (ESI) *m/z* 368.0 (M^++1). HRMS (ESI) Calcd. for $C_{20}H_{21}N_3O_4$ requires (M^++Na) 390.1424 Found 390.14189.

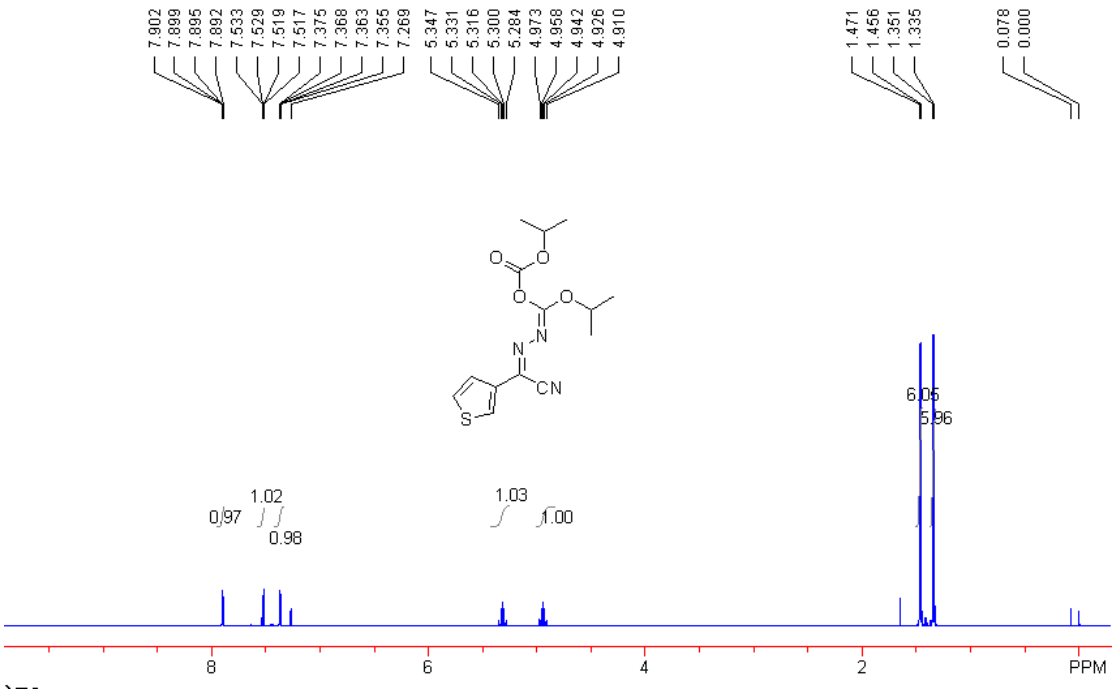


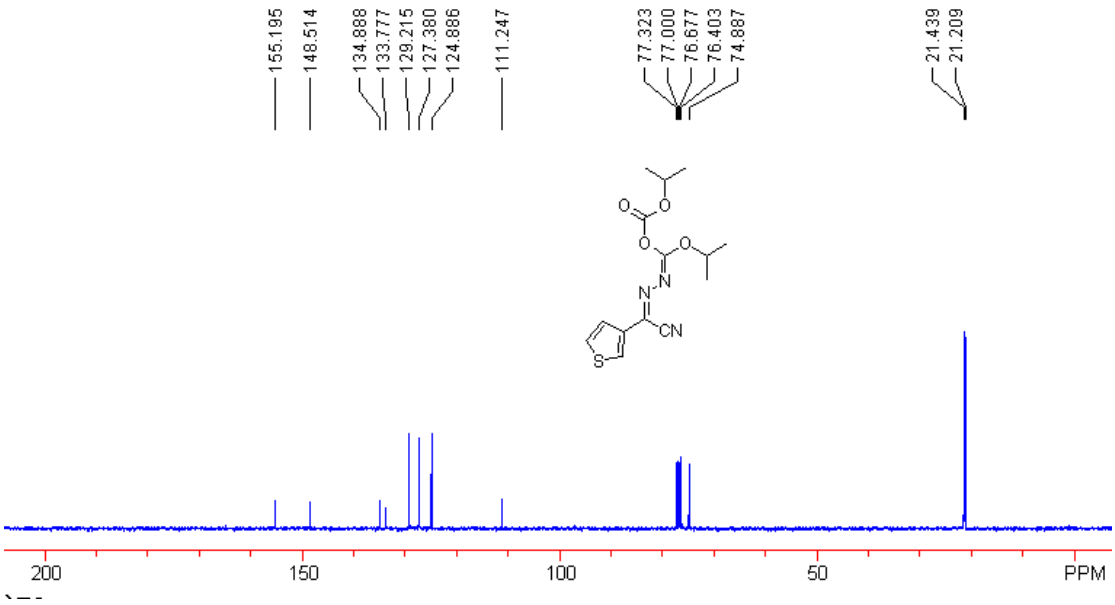


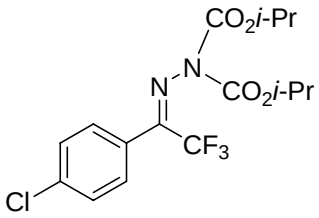


(4k) Oil. IR (CH_2Cl_2) ν 3105, 2986, 2940, 2227, 1783, 1626, 1218, 1095 cm^{-1}; ^1H NMR

($CDCl_3$, 400 MHz, TMS): δ 1.34 (6H, d, J = 6.4 Hz, CH_3), 1.46 (6H, d, J = 6.0 Hz, CH_3), 4.91-4.98 (1H, m, CH), 5.28-5.35 (1H, m, CH), 7.36 (1H, dd, J_1 = 2.8 Hz, J_2 = 4.8 Hz, Ar), 7.52 (1H, dd, J_1 = 1.2 Hz, J_2 = 4.8 Hz, Ar), 7.90 (1H, dd, J_1 = 1.2 Hz, J_2 = 2.8 Hz, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 21.2, 21.4, 74.9, 76.4, 111.2, 124.9, 127.4, 129.2, 133.8, 134.9, 148.5, 155.2. MS (ESI) *m/z* 323.9 (M^++1), 345.9 (M^++Na). HRMS (ESI) Calcd. for $C_{14}H_{17}N_3O_4S$ requires (M^++Na) 346.0832 Found 346.08309.

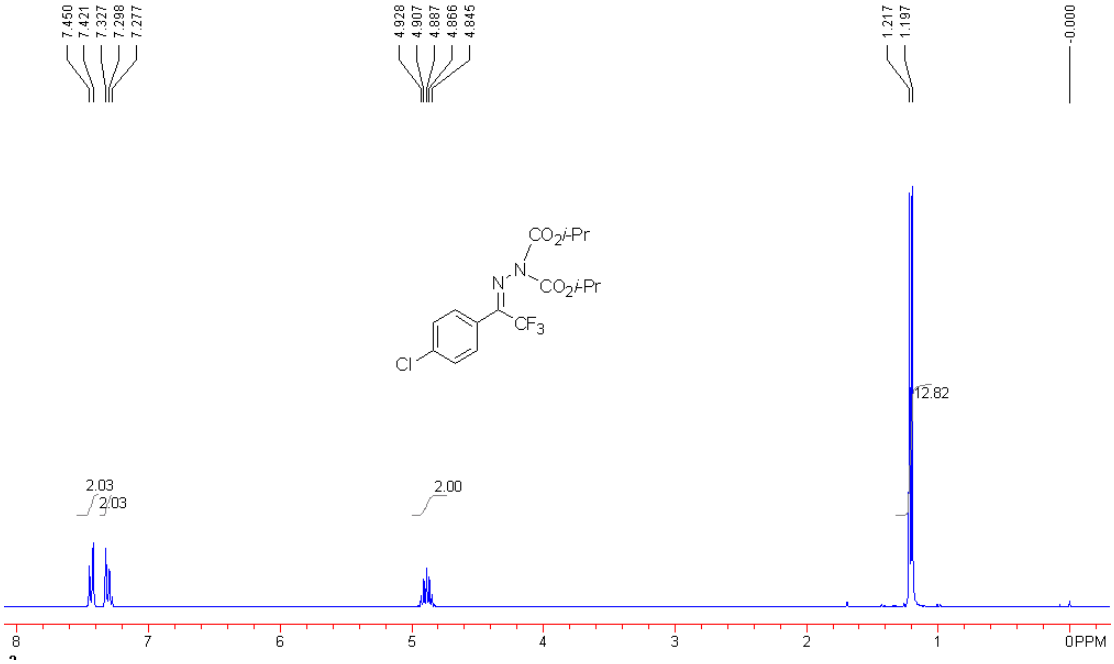


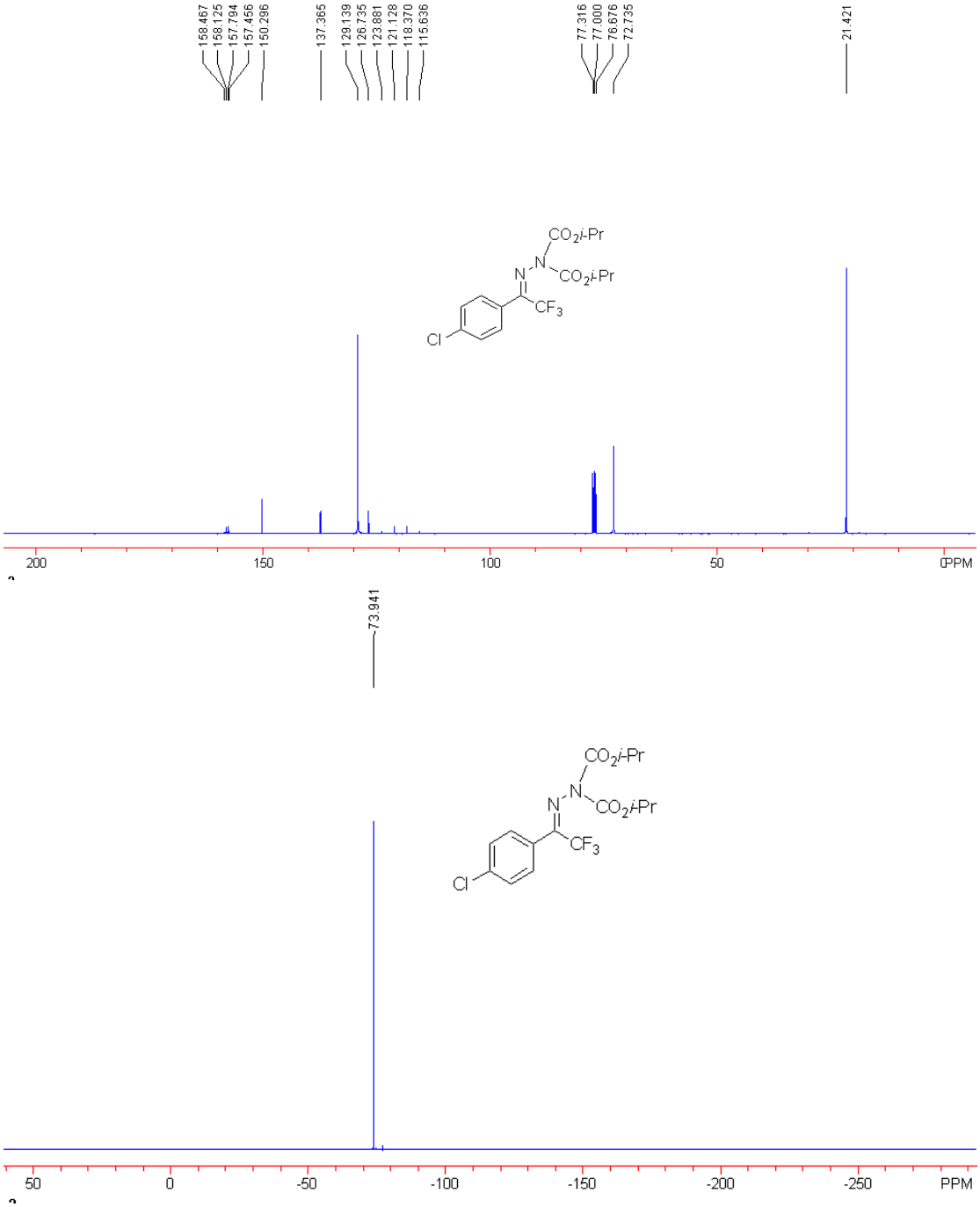


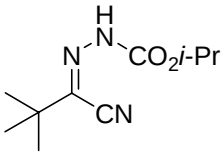


(Z)-diisopropyl

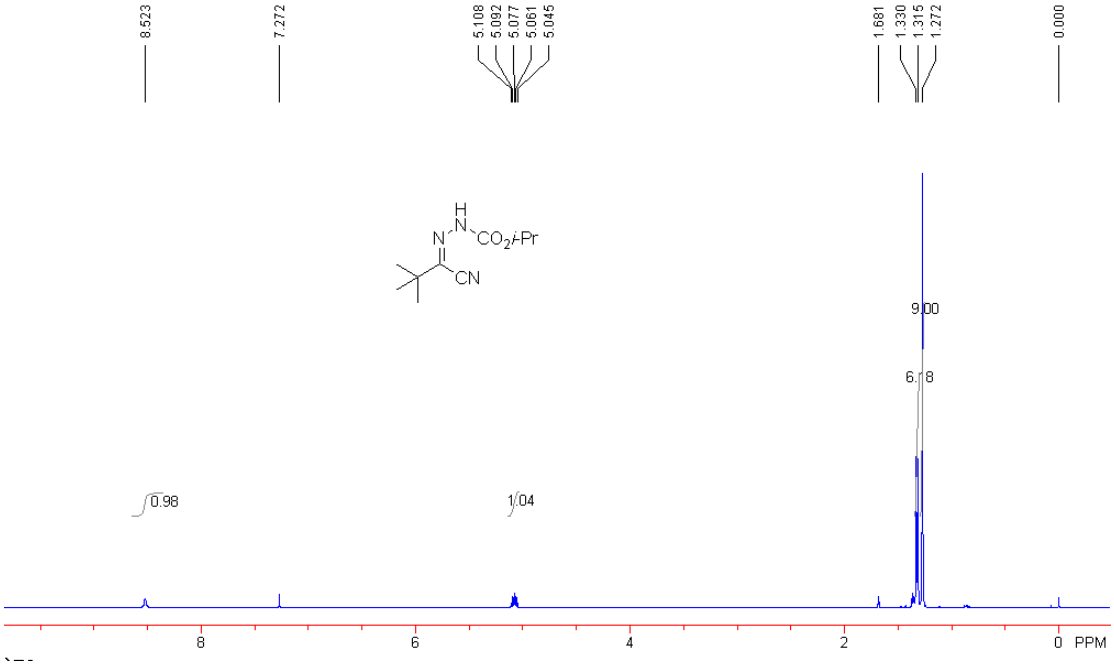
2-(1-(4-chlorophenyl)-2,2,2-trifluoroethylidene)hydrazine-1,1-dicarboxylate (6). Oil. IR (CH_2Cl_2) ν 2986, 2941, 1752, 1594, 1281, 1147 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 1.21 (12H, d, *J* = 6.0 Hz, CH_3), 4.84-4.93 (2H, m, CH), 7.31 (2H, d, *J* = 8.7 Hz, Ar), 7.44 (2H, d, *J* = 8.7 Hz, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.4, 72.7, 119.7 (q, *J* = 275.8 Hz), 126.7, 129.1, 137.4, 150.3, 158.0 (q, *J* = 33.5 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -73.94. MS (ESI) *m/z* 395.2 (M^++1). HRMS (MALDI) Calcd. for $C_{16}H_{18}ClF_3N_2O_4$ requires (M^++Na) 417.0811 Found 417.07994.

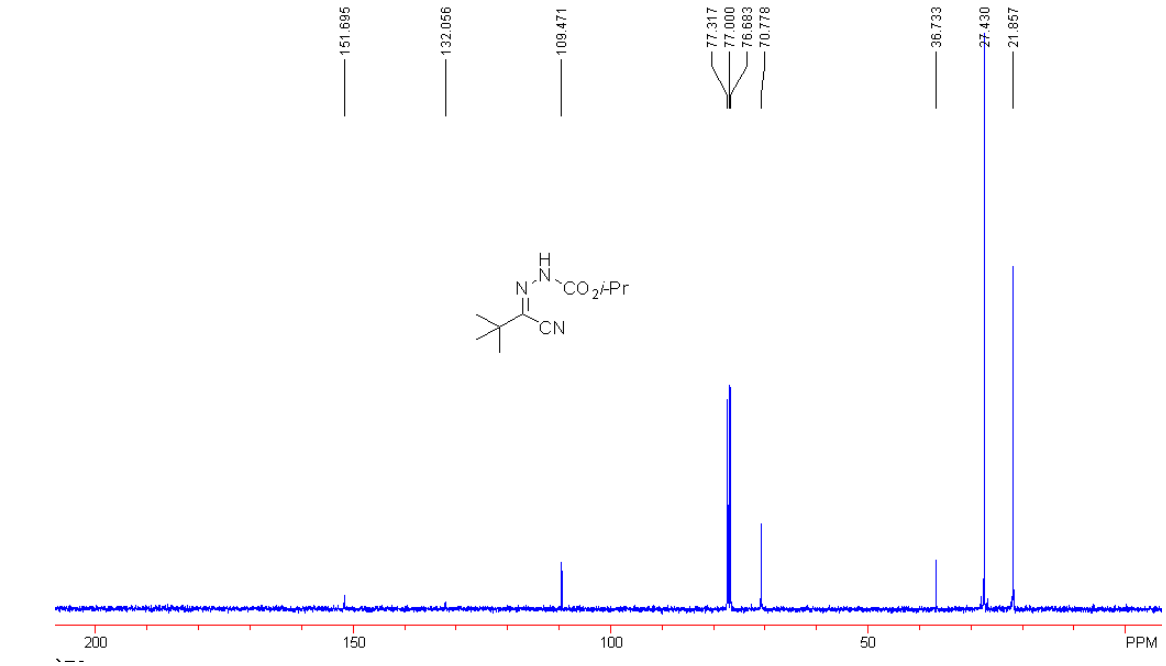


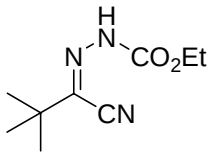

158.467
158.125
157.794
157.456
150.296
137.365
129.139
126.735
123.881
121.128
118.370
115.636
77.316
77.000
76.676
72.735
21.421
CO2i-Pr
N
N
CO2i-Pr
CF3
Cl
200
150
100
50
0PPM
-73.941
CO2i-Pr
N
N
CO2i-Pr
CF3
Cl
50
0
-50
-100
-150
-200
-250
PPM



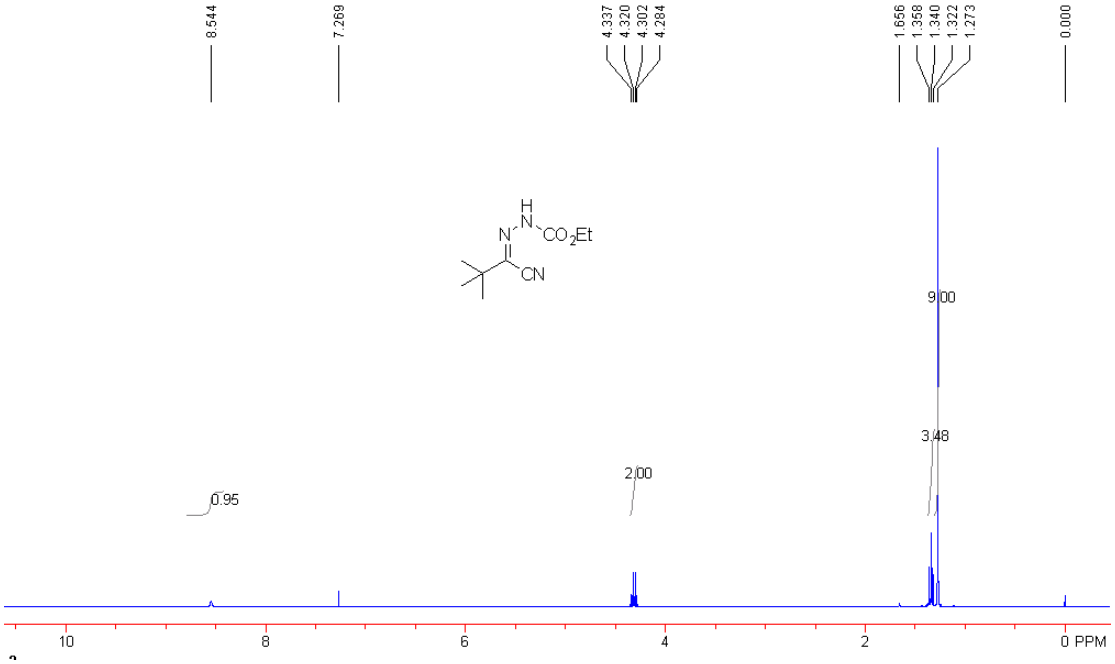
(Z)-isopropyl 2-(1-cyano-2,2-dimethylpropylidene)hydrazinecarboxylate (7). Oil. IR (CH_2Cl_2) ν 3226, 2979, 2211, 1760, 1513, 1222, 1108 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.27 (9H, s, CH_3), 1.32 (6H, d, J = 6.0 Hz, CH_3), 5.04-5.11 (1H, m, CH), 8.52 (1H, s, NH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.9, 27.4, 36.7, 70.8, 109.5, 132.1, 151.7. MS (ESI) *m/z* 212.1 (M^++1). HRMS (EI) Calcd. for $C_{10}H_{17}N_3O_2$ requires (M^+) 211.1321, Found 211.1321.

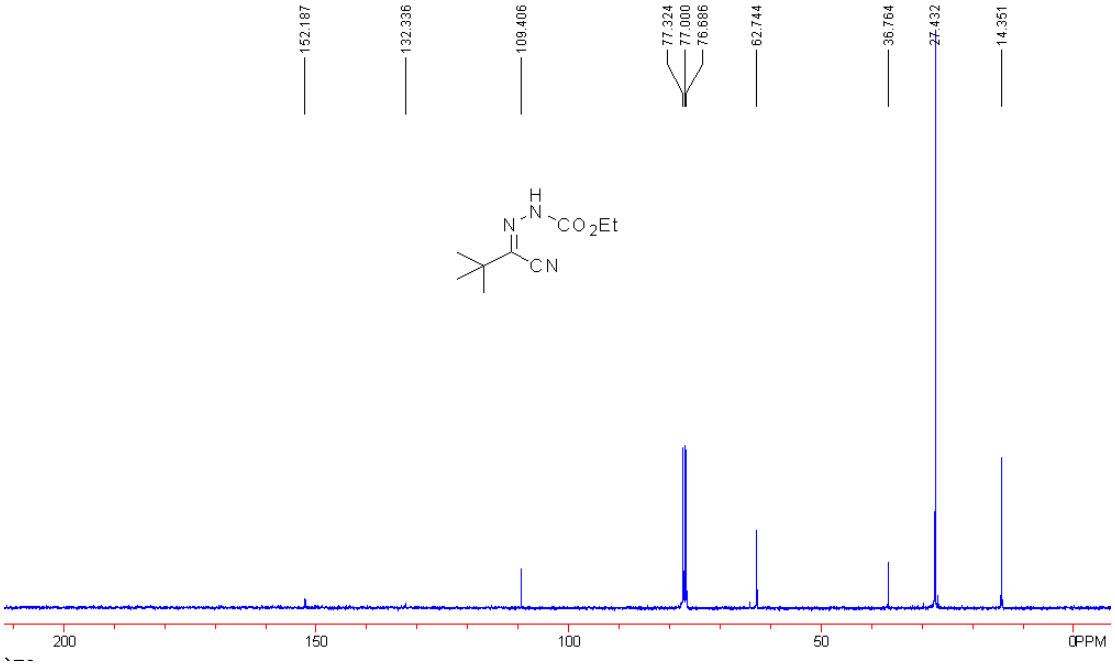




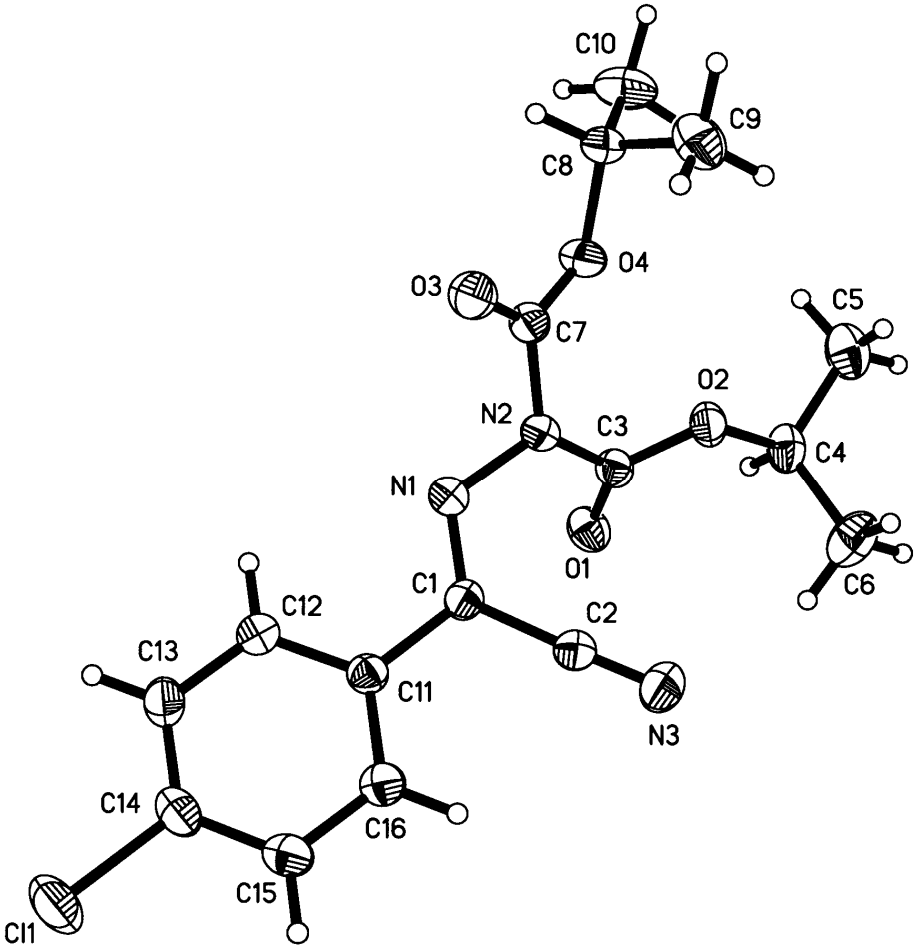


(Z)-Ethyl 2-(1-cyano-2,2-dimethylpropylidene)hydrazinecarboxylate (8). Oil. IR (CH_2Cl_2) ν 3239, 2971, 2211, 1766, 1514, 1216, 1031 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.27 (9H, s, CH_3), 1.34 (3H, t, *J* = 7.2 Hz, CH_3), 4.31 (2H, q, *J* = 7.2 Hz, CH), 8.54 (1H, s, NH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.4, 27.4, 36.8, 62.7, 109.4, 132.3, 152.2. MS (ESI) *m/z* 198.1 (M^++1). HRMS (EI) Calcd. for $C_9H_{15}N_3O_2$ requires (M^+) 197.1164, Found 197.1168.


8.544
7.269
4.337
4.320
4.302
4.284
1.656
1.358
1.340
1.322
1.273
0.000
H
N
N
CO2Et
CN
9.00
3.48
2.00
0.95
10
8
6
4
2
0 PPM


152.187
132.336
109.406
77.324
77.000
76.686
62.744
36.764
27.432
14.351
H
N
N
CO2Et
CN
200
150
100
50
0PPM

X-ray crystal structure compound **3c**



The crystal data of **3c** have been deposited in CCDC with number 713523. Empirical Formula: $C_{16}H_{18}ClN_3O_4$; Formula Weight: 351.78; Crystal Color, Habit: colorless, prismatic; Crystal System: Monoclinic; Lattice Type: Primitive; Unit cell dimension: 0.378 x 0.346 x 0.267 mm; Lattice Parameters: a = 10.8230(18)Å, b = 6.4408(11)Å, c = 25.686(4)Å, $\alpha = 90^o$, $\beta = 100.893(3)^o$, $\gamma = 90^o$, V = 1758.3(5)Å^3; Space group: P2(1)/c; Z = 4; D_{calc} = 1.329 g/cm^3; F_{000} = 736; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0457, 0.1049.

Table 1. Crystal data and structure refinement for cd28573.

Identification code	cd28573
Empirical formula	C16 H18 Cl N3 O4
Formula weight	351.78
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 10.8230(18) A alpha = 90 deg. b = 6.4408(11) A beta = 100.893(3) deg. c = 25.686(4) A gamma = 90 deg.
Volume	1758.3(5) A^3
Z, Calculated density	4, 1.329 Mg/m^3
Absorption coefficient	0.242 mm^-1
F(000)	736
Crystal size	0.378 x 0.346 x 0.267 mm
Theta range for data collection	1.61 to 25.99 deg.
Limiting indices	-13<=h<=13, -7<=k<=7, -31<=l<=23
Reflections collected / unique	9077 / 3434 [R(int) = 0.0647]
Completeness to theta = 25.99	99.7 %
Absorption correction	Empirical
Max. and min. transmission	1.0000 and 0.7534
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3434 / 0 / 222
Goodness-of-fit on F^2	0.950
Final R indices [I>2sigma(I)]	R1 = 0.0457, wR2 = 0.1049
R indices (all data)	R1 = 0.0695, wR2 = 0.1144
Extinction coefficient	0.0010(10)
Largest diff. peak and hole	0.247 and -0.295 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cd28573.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cl(1)	655(1)	11587(1)	11076(1)	85(1)
N(1)	2231(1)	4853(3)	9333(1)	47(1)
N(2)	2719(1)	3757(3)	8948(1)	44(1)
N(3)	4617(2)	8114(3)	9134(1)	68(1)
O(1)	4673(1)	3234(2)	9459(1)	53(1)
O(2)	4378(1)	3014(2)	8571(1)	50(1)
O(3)	720(1)	3413(2)	8482(1)	59(1)
O(4)	2208(1)	1072(2)	8389(1)	49(1)
C(1)	2786(2)	6520(3)	9516(1)	40(1)
C(2)	3842(2)	7399(3)	9315(1)	46(1)
C(3)	4037(2)	3278(3)	9028(1)	42(1)
C(4)	5692(2)	2420(3)	8581(1)	54(1)
C(5)	5668(2)	966(5)	8125(1)	88(1)
C(6)	6425(2)	4358(4)	8542(1)	83(1)
C(7)	1774(2)	2759(3)	8582(1)	44(1)
C(8)	1437(2)	182(3)	7912(1)	51(1)
C(9)	1594(2)	1480(4)	7445(1)	75(1)
C(10)	1880(2)	-2004(4)	7887(1)	79(1)
C(11)	2298(2)	7743(3)	9916(1)	40(1)
C(12)	1376(2)	6912(3)	10167(1)	51(1)
C(13)	871(2)	8080(4)	10524(1)	57(1)
C(14)	1287(2)	10069(4)	10630(1)	53(1)
C(15)	2204(2)	10915(3)	10392(1)	54(1)
C(16)	2713(2)	9742(3)	10038(1)	48(1)

Table 3. Bond lengths [A] and angles [deg] for cd28573.

Cl(1)-C(14)	1.741(2)
N(1)-C(1)	1.276(2)
N(1)-N(2)	1.396(2)
N(2)-C(7)	1.407(2)
N(2)-C(3)	1.436(2)
N(3)-C(2)	1.131(2)
O(1)-C(3)	1.188(2)
O(2)-C(3)	1.307(2)
O(2)-C(4)	1.468(2)
O(3)-C(7)	1.197(2)
O(4)-C(7)	1.318(2)
O(4)-C(8)	1.463(2)
C(1)-C(2)	1.455(3)
C(1)-C(11)	1.468(2)
C(4)-C(6)	1.493(3)
C(4)-C(5)	1.496(3)
C(4)-H(4)	0.9800
C(5)-H(5A)	0.9600
C(5)-H(5B)	0.9600
C(5)-H(5C)	0.9600
C(6)-H(6A)	0.9600
C(6)-H(6B)	0.9600
C(6)-H(6C)	0.9600
C(8)-C(10)	1.493(3)
C(8)-C(9)	1.496(3)
C(8)-H(8)	0.9800
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-C(16)	1.381(3)
C(11)-C(12)	1.394(3)
C(12)-C(13)	1.376(3)
C(12)-H(12)	0.9300
C(13)-C(14)	1.368(3)
C(13)-H(13)	0.9300
C(14)-C(15)	1.373(3)
C(15)-C(16)	1.374(3)
C(15)-H(15)	0.9300
C(16)-H(16)	0.9300

C(1)-N(1)-N(2)	118.15(15)
N(1)-N(2)-C(7)	112.27(14)
N(1)-N(2)-C(3)	120.46(15)
C(7)-N(2)-C(3)	125.02(16)
C(3)-O(2)-C(4)	117.08(16)
C(7)-O(4)-C(8)	116.81(15)
N(1)-C(1)-C(2)	122.88(17)
N(1)-C(1)-C(11)	120.18(16)
C(2)-C(1)-C(11)	116.72(16)
N(3)-C(2)-C(1)	176.2(2)
O(1)-C(3)-O(2)	128.42(19)
O(1)-C(3)-N(2)	121.52(18)
O(2)-C(3)-N(2)	110.01(17)
O(2)-C(4)-C(6)	107.82(17)
O(2)-C(4)-C(5)	106.03(18)
C(6)-C(4)-C(5)	113.7(2)
O(2)-C(4)-H(4)	109.7
C(6)-C(4)-H(4)	109.7
C(5)-C(4)-H(4)	109.7
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5

C(4)-C(6)-H(6A)	109.5
C(4)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(4)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
O(3)-C(7)-O(4)	127.04(18)
O(3)-C(7)-N(2)	121.69(18)
O(4)-C(7)-N(2)	111.25(17)
O(4)-C(8)-C(10)	105.55(18)
O(4)-C(8)-C(9)	108.60(18)
C(10)-C(8)-C(9)	114.0(2)
O(4)-C(8)-H(8)	109.5
C(10)-C(8)-H(8)	109.5
C(9)-C(8)-H(8)	109.5
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(8)-C(10)-H(10A)	109.5
C(8)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(16)-C(11)-C(12)	118.86(18)
C(16)-C(11)-C(1)	121.01(17)
C(12)-C(11)-C(1)	120.10(17)
C(13)-C(12)-C(11)	120.53(19)
C(13)-C(12)-H(12)	119.7
C(11)-C(12)-H(12)	119.7
C(14)-C(13)-C(12)	119.18(19)
C(14)-C(13)-H(13)	120.4
C(12)-C(13)-H(13)	120.4
C(13)-C(14)-C(15)	121.41(19)
C(13)-C(14)-Cl(1)	120.10(17)
C(15)-C(14)-Cl(1)	118.49(18)
C(14)-C(15)-C(16)	119.3(2)
C(14)-C(15)-H(15)	120.3
C(16)-C(15)-H(15)	120.3
C(15)-C(16)-C(11)	120.67(18)
C(15)-C(16)-H(16)	119.7
C(11)-C(16)-H(16)	119.7

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cd28573.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Cl(1)	87(1)	101(1)	71(1)	-34(1)	26(1)	10(1)
N(1)	48(1)	47(1)	48(1)	-10(1)	15(1)	-6(1)
N(2)	42(1)	48(1)	45(1)	-12(1)	12(1)	-6(1)
N(3)	69(1)	60(1)	82(2)	-4(1)	33(1)	-14(1)
O(1)	54(1)	63(1)	41(1)	1(1)	6(1)	8(1)
O(2)	42(1)	69(1)	40(1)	-1(1)	13(1)	-2(1)
O(3)	44(1)	69(1)	63(1)	-12(1)	8(1)	5(1)
O(4)	47(1)	48(1)	47(1)	-10(1)	1(1)	2(1)
C(1)	39(1)	42(1)	41(1)	1(1)	8(1)	-2(1)
C(2)	49(1)	42(1)	49(1)	-5(1)	12(1)	-3(1)
C(3)	49(1)	39(1)	39(1)	1(1)	11(1)	-2(1)
C(4)	45(1)	69(2)	52(1)	6(1)	16(1)	6(1)
C(5)	84(2)	100(2)	92(2)	-22(2)	47(2)	-1(2)
C(6)	55(1)	91(2)	106(2)	3(2)	22(1)	-14(1)
C(7)	48(1)	43(1)	41(1)	-1(1)	11(1)	-2(1)
C(8)	48(1)	59(1)	45(1)	-13(1)	5(1)	-9(1)
C(9)	86(2)	88(2)	50(2)	1(1)	11(1)	3(1)
C(10)	91(2)	58(2)	82(2)	-24(1)	-2(2)	-3(1)
C(11)	38(1)	42(1)	39(1)	-2(1)	5(1)	0(1)
C(12)	49(1)	52(1)	55(1)	-9(1)	14(1)	-10(1)
C(13)	50(1)	73(2)	52(1)	-7(1)	19(1)	-4(1)
C(14)	48(1)	67(2)	43(1)	-11(1)	6(1)	11(1)
C(15)	57(1)	48(1)	55(1)	-10(1)	7(1)	-1(1)
C(16)	50(1)	46(1)	48(1)	-2(1)	10(1)	-4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cd28573.

	x	y	z	U(eq)
H(4)	6028	1703	8914	65
H(5A)	5184	-242	8174	132
H(5B)	6512	560	8107	132
H(5C)	5293	1649	7801	132
H(6A)	6073	5083	8222	125
H(6B)	7285	4008	8538	125
H(6C)	6389	5230	8842	125
H(8)	551	187	7947	61
H(9A)	1303	2864	7490	112
H(9B)	1113	888	7128	112
H(9C)	2467	1519	7419	112
H(10A)	2772	-2014	7902	119
H(10B)	1464	-2633	7562	119
H(10C)	1687	-2772	8182	119
H(12)	1100	5557	10094	62
H(13)	254	7525	10690	68
H(15)	2478	12269	10469	64
H(16)	3344	10300	9880	58

Table 6. Torsion angles [deg] for cd28573.

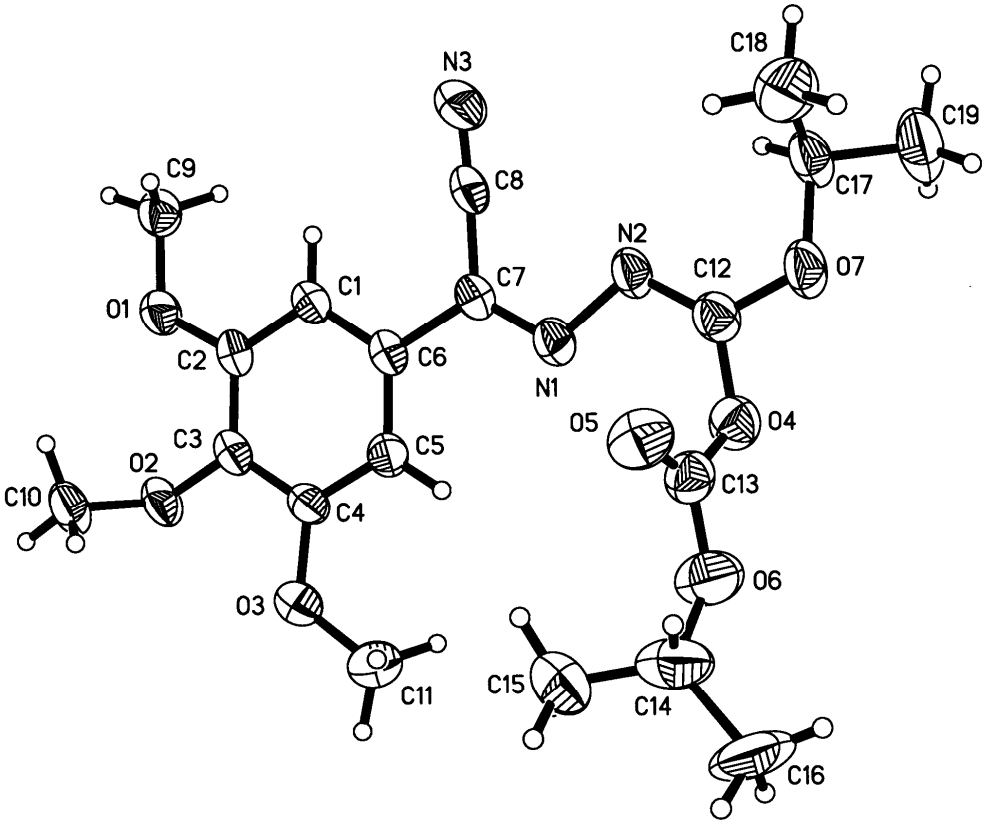
C(1)-N(1)-N(2)-C(7)	-147.01(18)
C(1)-N(1)-N(2)-C(3)	49.2(3)
N(2)-N(1)-C(1)-C(2)	4.6(3)
N(2)-N(1)-C(1)-C(11)	179.14(16)
N(1)-C(1)-C(2)-N(3)	72(3)
C(11)-C(1)-C(2)-N(3)	-102(3)
C(4)-O(2)-C(3)-O(1)	5.5(3)
C(4)-O(2)-C(3)-N(2)	-177.35(15)
N(1)-N(2)-C(3)-O(1)	22.0(3)
C(7)-N(2)-C(3)-O(1)	-139.6(2)
N(1)-N(2)-C(3)-O(2)	-155.42(16)
C(7)-N(2)-C(3)-O(2)	43.0(2)
C(3)-O(2)-C(4)-C(6)	-93.7(2)
C(3)-O(2)-C(4)-C(5)	144.11(19)
C(8)-O(4)-C(7)-O(3)	16.5(3)
C(8)-O(4)-C(7)-N(2)	-164.79(15)
N(1)-N(2)-C(7)-O(3)	27.6(3)
C(3)-N(2)-C(7)-O(3)	-169.49(18)
N(1)-N(2)-C(7)-O(4)	-151.18(16)
C(3)-N(2)-C(7)-O(4)	11.7(3)
C(7)-O(4)-C(8)-C(10)	-161.01(18)
C(7)-O(4)-C(8)-C(9)	76.3(2)
N(1)-C(1)-C(11)-C(16)	-166.44(18)
C(2)-C(1)-C(11)-C(16)	8.4(3)
N(1)-C(1)-C(11)-C(12)	11.8(3)
C(2)-C(1)-C(11)-C(12)	-173.34(18)
C(16)-C(11)-C(12)-C(13)	1.3(3)
C(1)-C(11)-C(12)-C(13)	-176.95(19)
C(11)-C(12)-C(13)-C(14)	-0.2(3)
C(12)-C(13)-C(14)-C(15)	-0.6(3)
C(12)-C(13)-C(14)-Cl(1)	179.55(17)
C(13)-C(14)-C(15)-C(16)	0.2(3)
Cl(1)-C(14)-C(15)-C(16)	-179.95(16)
C(14)-C(15)-C(16)-C(11)	1.0(3)
C(12)-C(11)-C(16)-C(15)	-1.8(3)
C(1)-C(11)-C(16)-C(15)	176.52(18)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd28573 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

X-ray crystal structure compound **4g**



The crystal data of **4g** have been deposited in CCDC with number 724590. Empirical Formula: $C_{19}H_{25}N_3O_7$; Formula Weight: 407.42; Crystal Color, Habit: colorless, prismatic; Crystal System: Triclinic; Lattice Type: Primitive; Unit cell dimension: 0.450 x 0.423 x 0.351 mm; Lattice Parameters: a = 7.5749(13)Å, b = 12.355(2)Å, c = 12.896(2)Å, α = 99.071(3)^o, β = 102.604(3)^o, γ = 106.451(3)^o, V = 1098.1(3)Å^3; Space group: P-1; Z = 2; D_{calc} = 1.232 g/cm^3; F_{000} = 432; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0579, 0.1325.

Table 1. Crystal data and structure refinement for cd29130.

Identification code	cd29130
Empirical formula	C19 H25 N3 O7
Formula weight	407.42
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 7.5749(13) A alpha = 99.071(3) deg. b = 12.355(2) A beta = 102.604(3) deg. c = 12.896(2) A gamma = 106.451(3) deg.
Volume	1098.1(3) A^3
Z, Calculated density	2, 1.232 Mg/m^3
Absorption coefficient	0.095 mm^-1
F(000)	432
Crystal size	0.450 x 0.423 x 0.351 mm
Theta range for data collection	1.66 to 26.00 deg.
Limiting indices	-8<=h<=9, -14<=k<=15, -15<=l<=15
Reflections collected / unique	6074 / 4247 [R(int) = 0.1019]
Completeness to theta = 26.00	98.2 %
Absorption correction	Empirical
Max. and min. transmission	1.0000 and 0.7488
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4247 / 2 / 291
Goodness-of-fit on F^2	0.850
Final R indices [I>2sigma(I)]	R1 = 0.0579, wR2 = 0.1325
R indices (all data)	R1 = 0.1196, wR2 = 0.1559
Extinction coefficient	0.011(2)
Largest diff. peak and hole	0.250 and -0.163 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cd29130.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	125(3)	4270(2)	1764(1)	72(1)
O(2)	-2989(2)	4914(2)	1216(1)	74(1)
O(3)	-3744(3)	6398(2)	2599(2)	78(1)
O(4)	900(3)	8620(2)	7862(2)	80(1)
O(5)	2172(3)	9946(2)	6997(2)	96(1)
O(6)	-775(3)	9607(2)	7222(2)	111(1)
O(7)	3436(3)	8554(2)	9005(2)	84(1)
N(1)	1529(3)	7340(2)	6215(2)	65(1)
N(2)	2875(3)	7622(2)	7229(2)	66(1)
N(3)	4993(4)	6139(3)	5893(2)	119(1)
C(1)	1074(3)	5474(2)	3610(2)	57(1)
C(2)	-122(4)	5045(2)	2553(2)	57(1)
C(3)	-1734(4)	5370(2)	2243(2)	59(1)
C(4)	-2142(3)	6136(2)	2997(2)	58(1)
C(5)	-961(3)	6562(2)	4053(2)	59(1)
C(6)	657(3)	6242(2)	4353(2)	53(1)
C(7)	1922(3)	6689(2)	5483(2)	55(1)
C(8)	3633(5)	6381(3)	5738(2)	72(1)
C(9)	1745(4)	3901(2)	2045(2)	76(1)
C(10)	-2379(4)	5406(3)	378(2)	92(1)
C(11)	-4244(4)	7181(3)	3321(3)	89(1)
C(12)	2484(4)	8251(3)	7973(3)	71(1)
C(13)	895(5)	9460(3)	7315(3)	73(1)
C(14)	-1151(6)	10518(4)	6726(5)	120(1)
C(15)	-1690(40)	10119(14)	5555(10)	129(8)
C(16)	-2090(50)	11250(30)	7250(30)	230(20)
C(15')	-3140(20)	9982(10)	5938(13)	218(7)
C(16')	-1210(20)	11341(8)	7643(13)	160(5)
C(17)	4924(5)	8049(3)	9368(2)	85(1)
C(18)	6785(6)	8799(3)	9303(3)	120(1)
C(19)	4868(6)	7963(3)	10513(3)	128(1)

Table 3. Bond lengths [A] and angles [deg] for cd29130.

O(1)-C(2)	1.365(3)
O(1)-C(9)	1.421(3)
O(2)-C(3)	1.373(3)
O(2)-C(10)	1.420(3)
O(3)-C(4)	1.357(3)
O(3)-C(11)	1.422(3)
O(4)-C(13)	1.344(4)
O(4)-C(12)	1.387(3)
O(5)-C(13)	1.177(3)
O(6)-C(13)	1.311(3)
O(6)-C(14)	1.445(4)
O(7)-C(12)	1.305(3)
O(7)-C(17)	1.463(3)
N(1)-C(7)	1.282(3)
N(1)-N(2)	1.395(3)
N(2)-C(12)	1.277(3)
N(3)-C(8)	1.137(3)
C(1)-C(2)	1.386(3)
C(1)-C(6)	1.390(3)
C(1)-H(1)	0.9300
C(2)-C(3)	1.389(3)
C(3)-C(4)	1.393(4)
C(4)-C(5)	1.382(3)
C(5)-C(6)	1.387(3)
C(5)-H(5)	0.9300
C(6)-C(7)	1.478(3)
C(7)-C(8)	1.438(4)
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(14)-C(15)	1.439(12)
C(14)-C(16')	1.450(13)
C(14)-C(16)	1.47(3)
C(14)-C(15')	1.515(11)
C(14)-H(14)	0.9800
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
C(16)-H(16A)	0.9600
C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600
C(15')-H(15D)	0.9600
C(15')-H(15E)	0.9600
C(15')-H(15F)	0.9600
C(16')-H(16D)	0.9600
C(16')-H(16E)	0.9600
C(16')-H(16F)	0.9600
C(17)-C(18)	1.479(4)
C(17)-C(19)	1.506(4)
C(17)-H(17)	0.9800
C(18)-H(18A)	0.9600
C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600
C(19)-H(19A)	0.9600
C(19)-H(19B)	0.9600
C(19)-H(19C)	0.9600
C(2)-O(1)-C(9)	117.4(2)
C(3)-O(2)-C(10)	115.1(2)
C(4)-O(3)-C(11)	117.7(2)
C(13)-O(4)-C(12)	116.2(2)
C(13)-O(6)-C(14)	118.9(3)

C(12)-O(7)-C(17)	118.5(2)
C(7)-N(1)-N(2)	111.8(2)
C(12)-N(2)-N(1)	112.7(2)
C(2)-C(1)-C(6)	119.4(2)
C(2)-C(1)-H(1)	120.3
C(6)-C(1)-H(1)	120.3
O(1)-C(2)-C(1)	124.5(2)
O(1)-C(2)-C(3)	115.3(2)
C(1)-C(2)-C(3)	120.2(3)
O(2)-C(3)-C(2)	121.2(3)
O(2)-C(3)-C(4)	118.9(2)
C(2)-C(3)-C(4)	119.8(2)
O(3)-C(4)-C(5)	125.2(3)
O(3)-C(4)-C(3)	114.6(2)
C(5)-C(4)-C(3)	120.2(2)
C(4)-C(5)-C(6)	119.6(3)
C(4)-C(5)-H(5)	120.2
C(6)-C(5)-H(5)	120.2
C(5)-C(6)-C(1)	120.7(2)
C(5)-C(6)-C(7)	119.9(2)
C(1)-C(6)-C(7)	119.4(2)
N(1)-C(7)-C(8)	120.7(2)
N(1)-C(7)-C(6)	121.6(2)
C(8)-C(7)-C(6)	117.8(2)
N(3)-C(8)-C(7)	176.8(3)
O(1)-C(9)-H(9A)	109.5
O(1)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
O(1)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
O(2)-C(10)-H(10A)	109.5
O(2)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
O(2)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
O(3)-C(11)-H(11A)	109.5
O(3)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
O(3)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
N(2)-C(12)-O(7)	124.5(3)
N(2)-C(12)-O(4)	127.0(3)
O(7)-C(12)-O(4)	108.2(3)
O(5)-C(13)-O(6)	128.7(3)
O(5)-C(13)-O(4)	125.0(3)
O(6)-C(13)-O(4)	106.3(3)
C(15)-C(14)-O(6)	109.2(7)
C(15)-C(14)-C(16')	146.2(8)
O(6)-C(14)-C(16')	102.6(6)
C(15)-C(14)-C(16)	120.6(13)
O(6)-C(14)-C(16)	118.3(12)
C(16')-C(14)-C(16)	28.3(14)
C(15)-C(14)-C(15')	51.4(7)
O(6)-C(14)-C(15')	105.9(6)
C(16')-C(14)-C(15')	109.1(7)
C(16)-C(14)-C(15')	81.8(13)
C(15)-C(14)-H(14)	101.6
O(6)-C(14)-H(14)	101.6
C(16')-C(14)-H(14)	82.7
C(16)-C(14)-H(14)	101.6
C(15')-C(14)-H(14)	146.6
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
C(14)-C(16)-H(16A)	109.5
C(14)-C(16)-H(16B)	109.5
C(14)-C(16)-H(16C)	109.5
C(14)-C(15')-H(15D)	109.5
C(14)-C(15')-H(15E)	109.5

H(15D)-C(15')-H(15E)	109.5
C(14)-C(15')-H(15F)	109.5
H(15D)-C(15')-H(15F)	109.5
H(15E)-C(15')-H(15F)	109.5
C(14)-C(16')-H(16D)	109.5
C(14)-C(16')-H(16E)	109.5
H(16D)-C(16')-H(16E)	109.5
C(14)-C(16')-H(16F)	109.5
H(16D)-C(16')-H(16F)	109.5
H(16E)-C(16')-H(16F)	109.5
O(7)-C(17)-C(18)	109.6(3)
O(7)-C(17)-C(19)	103.9(3)
C(18)-C(17)-C(19)	113.8(3)
O(7)-C(17)-H(17)	109.8
C(18)-C(17)-H(17)	109.8
C(19)-C(17)-H(17)	109.8
C(17)-C(18)-H(18A)	109.5
C(17)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(17)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(17)-C(19)-H(19A)	109.5
C(17)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(17)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cd29130.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	79(1)	81(1)	48(1)	4(1)	7(1)	32(1)
O(2)	70(1)	90(1)	44(1)	11(1)	-2(1)	14(1)
O(3)	69(1)	95(2)	67(1)	18(1)	7(1)	34(1)
O(4)	93(2)	81(1)	76(1)	28(1)	29(1)	33(1)
O(5)	84(2)	89(2)	119(2)	33(1)	42(1)	21(1)
O(6)	104(2)	130(2)	138(2)	61(2)	56(2)	64(2)
O(7)	120(2)	77(1)	49(1)	-3(1)	8(1)	44(1)
N(1)	69(1)	66(2)	49(1)	6(1)	7(1)	18(1)
N(2)	82(2)	66(2)	42(1)	3(1)	6(1)	25(1)
N(3)	109(2)	177(3)	64(2)	-7(2)	-8(2)	82(2)
C(1)	57(2)	62(2)	46(2)	17(1)	8(1)	16(1)
C(2)	68(2)	56(2)	40(1)	10(1)	10(1)	14(1)
C(3)	59(2)	65(2)	44(2)	16(1)	6(1)	10(1)
C(4)	53(2)	67(2)	53(2)	20(1)	8(1)	19(1)
C(5)	59(2)	65(2)	51(2)	14(1)	15(1)	18(1)
C(6)	56(2)	53(2)	42(1)	12(1)	8(1)	7(1)
C(7)	63(2)	51(2)	46(2)	14(1)	10(1)	14(1)
C(8)	78(2)	91(2)	37(2)	2(1)	1(1)	30(2)
C(9)	89(2)	79(2)	61(2)	11(2)	20(2)	35(2)
C(10)	97(2)	125(3)	50(2)	30(2)	9(2)	37(2)
C(11)	72(2)	106(3)	95(2)	24(2)	26(2)	39(2)
C(12)	84(2)	63(2)	61(2)	9(2)	10(2)	28(2)
C(13)	75(2)	71(2)	69(2)	6(2)	19(2)	24(2)
C(14)	106(3)	130(4)	160(5)	66(4)	43(3)	71(3)
C(15)	164(17)	163(13)	88(10)	49(9)	26(9)	90(12)
C(16)	300(30)	380(50)	230(30)	180(30)	170(30)	310(40)
C(15')	222(14)	270(12)	158(10)	8(9)	-18(10)	149(11)
C(16')	225(12)	78(6)	197(11)	44(6)	58(10)	72(6)
C(17)	127(3)	71(2)	50(2)	2(2)	-1(2)	50(2)
C(18)	128(3)	112(3)	116(3)	0(3)	25(3)	57(3)
C(19)	202(4)	127(3)	60(2)	18(2)	21(2)	75(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cd29130.

	x	y	z	U(eq)
H(1)	2146	5250	3821	68
H(5)	-1249	7061	4560	71
H(9A)	2895	4551	2200	114
H(9B)	1704	3316	1446	114
H(9C)	1728	3586	2679	114
H(10A)	-2236	6217	531	138
H(10B)	-3315	5019	-312	138
H(10C)	-1173	5314	350	138
H(11A)	-4310	6910	3973	133
H(11B)	-5467	7226	2969	133
H(11C)	-3291	7937	3506	133
H(14)	146	11065	6871	144
H(15A)	-2856	9472	5322	194
H(15B)	-690	9884	5341	194
H(15C)	-1871	10736	5223	194
H(16A)	-2169	11851	6864	329
H(16B)	-1357	11600	7994	329
H(16C)	-3356	10786	7223	329
H(15D)	-3116	9424	5336	327
H(15E)	-3549	10578	5670	327
H(15F)	-4015	9602	6309	327
H(16D)	-2049	10940	8022	240
H(16E)	-1676	11922	7381	240
H(16F)	55	11704	8133	240
H(17)	4594	7271	8905	101
H(18A)	6709	8835	8557	179
H(18B)	7769	8484	9570	179
H(18C)	7083	9566	9741	179
H(19A)	5100	8720	10950	192
H(19B)	5836	7655	10824	192
H(19C)	3631	7458	10494	192

Table 6. Torsion angles [deg] for cd29130.

C(7)-N(1)-N(2)-C(12)	-178.6(2)
C(9)-O(1)-C(2)-C(1)	-1.4(4)
C(9)-O(1)-C(2)-C(3)	-179.3(2)
C(6)-C(1)-C(2)-O(1)	-178.6(2)
C(6)-C(1)-C(2)-C(3)	-0.8(4)
C(10)-O(2)-C(3)-C(2)	-78.5(3)
C(10)-O(2)-C(3)-C(4)	104.2(3)
O(1)-C(2)-C(3)-O(2)	1.2(3)
C(1)-C(2)-C(3)-O(2)	-176.8(2)
O(1)-C(2)-C(3)-C(4)	178.5(2)
C(1)-C(2)-C(3)-C(4)	0.4(4)
C(11)-O(3)-C(4)-C(5)	0.7(4)
C(11)-O(3)-C(4)-C(3)	-179.6(2)
O(2)-C(3)-C(4)-O(3)	-3.2(3)
C(2)-C(3)-C(4)-O(3)	179.5(2)
O(2)-C(3)-C(4)-C(5)	176.6(2)
C(2)-C(3)-C(4)-C(5)	-0.7(4)
O(3)-C(4)-C(5)-C(6)	-178.9(2)
C(3)-C(4)-C(5)-C(6)	1.4(4)
C(4)-C(5)-C(6)-C(1)	-1.7(4)
C(4)-C(5)-C(6)-C(7)	-179.6(2)
C(2)-C(1)-C(6)-C(5)	1.4(4)
C(2)-C(1)-C(6)-C(7)	179.3(2)
N(2)-N(1)-C(7)-C(8)	-3.0(4)
N(2)-N(1)-C(7)-C(6)	177.7(2)
C(5)-C(6)-C(7)-N(1)	2.4(4)
C(1)-C(6)-C(7)-N(1)	-175.5(2)
C(5)-C(6)-C(7)-C(8)	-176.8(2)
C(1)-C(6)-C(7)-C(8)	5.2(3)
N(1)-C(7)-C(8)-N(3)	-145(6)
C(6)-C(7)-C(8)-N(3)	35(6)
N(1)-N(2)-C(12)-O(7)	174.4(2)
N(1)-N(2)-C(12)-O(4)	1.9(4)
C(17)-O(7)-C(12)-N(2)	-6.8(5)
C(17)-O(7)-C(12)-O(4)	166.9(2)
C(13)-O(4)-C(12)-N(2)	-73.4(4)
C(13)-O(4)-C(12)-O(7)	113.1(3)
C(14)-O(6)-C(13)-O(5)	-3.9(5)
C(14)-O(6)-C(13)-O(4)	176.0(3)
C(12)-O(4)-C(13)-O(5)	-5.4(4)
C(12)-O(4)-C(13)-O(6)	174.7(2)
C(13)-O(6)-C(14)-C(15)	81.0(12)
C(13)-O(6)-C(14)-C(16')	-110.8(7)
C(13)-O(6)-C(14)-C(16)	-135.9(18)
C(13)-O(6)-C(14)-C(15')	134.9(9)
C(12)-O(7)-C(17)-C(18)	90.7(3)
C(12)-O(7)-C(17)-C(19)	-147.3(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd29130 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)