Supporting Information for

The first electrocatalytic stereoselective multicomponent synthesis of cyclopropanecarboxylic acid derivatives

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1. Chemicals and equipment.

All starting materials were obtained from commercial sources and used without further purification.

GLC analyses were carried out on an Agilent 7820A chromatograph with a flame-ionisation detector (column HP-5). All melting points were measured with a Gallenkamp melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded with Bruker AM300 spectrometer at ambient temperature. Chemical shifts values are relative to Me_4Si for $CDCl_3$ and DMSO-d_6. IR spectra were registered with a SPECORD M82 spectrometer in KBr pellets. Massspectra (EI = 70 eV) were obtained directly with a Finningan MAT INCOS 50 spectrometer. High-resolution mass spectrometry (HRMS) (electrospray ionization, ESI) was measured on a BrukermicroTOF II instrument; external or internal calibration was done with an Electrospray Calibrant Solution (Fluka).

2. Typical electrolysis procedure

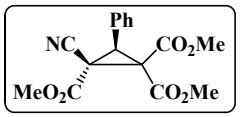
A solution of aromatic aldehyde **1** (15 mmol), alkyl cyanoacetate **2** (15 mmol), dialkyl malonate **3** (15 mmol), sodium acetate (5 mmol, 0.41 g) and sodium bromide (5 mmol, 0.51 g) in alcohol (35 mL) was stirred in a 50 ml baker at rt for 30 min. Then the mixture was cooled to 0 °C and electrolyzed (graphite anode and an iron cathode, electrode squares 5 cm^2) under a constant current density of 100 mA/cm^2 (I = 500 mA) until requared quantity of electricity was passed (Table 2). After the electrolysis reaction mixture was concentrated to 20 ml and cooled to –10 °C for 2 h, filtered out and dried under reduced pressure to give pure **4**. Cyclopropane **4b** was isolated as follows: the reaction mixture was concentrated, extracted with chloroform, washed with water, and dried over Na_2SO_4. After evaporation of the chloroform, cyclopropane **4b** was isolated by flash chromatography (eluent chloroform-hexane 1:1).

3. Large-scale electrolysis

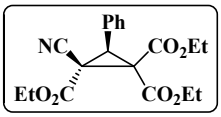
A solution of benzaldehyde **1a** (50 mmol, 5.30 g), methyl cyanoacetate **2a** (50 mmol, 4.95 g), dimethyl malonate **3a** (50 mmol, 6.60 g), sodium acetate (5 mmol, 0.41 g) and sodium bromide (5 mmol, 0.51 g) in methanol (70 mL) was stirred in a 100 ml baker at rt for 30 min. Then the mixture was cooled to 0 °C and electrolyzed until the quantity of electricity 3.5 F/mol was passed. After the electrolysis reaction mixture was concentrated to 30 ml and cooled to –10 °C for 2 h, filtered out and dried under reduced pressure to give 13.8 g (87%) of pure **4a**.

4. Analytical data

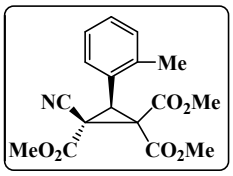
Trimethyl (2*R,3*R**)-2-cyanocyclopropane-3-phenyl-1,1,2-tricarboxylate (2a)**; yield 3.80 g (80%); white solid; m.p. 142 °C (lit.[1] m.p. 140-142 ºC); ^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.70 (s, 3H, CH_3O), 3.76 (s, 3H, CH_3O), 3.86 (s, 3H, CH_3O), 3.93 (s, 1H, CH), 7.30-7.44 (m, 5H, Ph).



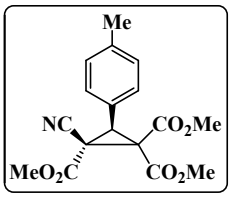
Triethyl (2*R,3*R**)-2-cyanocyclopropane-3-phenyl-1,1,2-tricarboxylate (4b)**; yield 3.98 g (74%); colourless oil; n_D^{20} 1.5034 (lit.[2] n_D^{20} 1.5040); ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.12 (t, CH_3, J = 7.1 Hz), 1.29 (t, CH_3, J = 7.1 Hz), 1.38 (t, CH_3, J = 7.1 Hz), 3.93 (s, 1H, CH), 4.12 (q, 2H, CH_2O, J = 7.1 Hz), 4.20-4.45 (m, 4H, CH_2O), 7.25-7.51 (m, 5H, Ph).



Trimethyl (2*R,3*R**)-2-cyanocyclopropane-3-(2-methylphenyl)-1,1,2-tricarboxylate (4c)**; yield 3.57 g (72%); white solid; m.p. 92-93 °C; ^{1}H NMR (300 MHz, $CDCl_3$), δ: 2.37 (s, 3H, CH_3), 3.70 (s, 3H, CH_3O), 3.83 (s, 3H, CH_3O), 3.89 (s, 1H, CH), 3.91 (s, 3H, CH_3O), 7.15-7.32 (m, 3H, Ar), 7.32-7.40 (m, 1H, Ar); ^{13}C NMR (75.47 MHz, $CDCl_3$), δ: 19.3, 30.9, 39.5, 47.6, 53.5, 53.6, 54.7, 112.7, 126.0, 127.7, 128.1, 128.8, 130.7, 137.8, 163.0, 164.5, 165.1; IR (cm^{-1}), ν: 2250, 1747, 1441, 1272, 1239; MS, m/*z* (*%*): 313 (M^+, 14), 300 (3), 272 (83), 240 (21), 212 (100), 196 (13), 184 (27), 153 (31), 127 (48), 59 (94); HRMS m/z (ESI) calcd for $C_{17}H_{17}NNaO_6$ $(M+Na)^+$ 354.0948, found 354.0943.

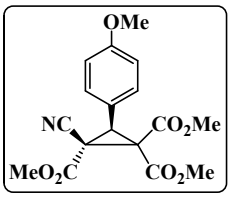


Trimethyl (2*R,3*R**)-2-cyanocyclopropane-3-(3-methylphenyl)-1,1,2-tricarboxylate (4d)**; yield 3.72 g (75%); white solid; m.p. 102-103 °C; ^{1}H NMR (300 MHz, $CDCl_3$), δ: 2.34 (s, 3H, CH_3), 3.72 (s, 3H, CH_3O), 3.83 (s, 3H, CH_3O), 3.90 (s, 1H, CH), 3.93 (s, 3H, CH_3O), 7.10-7.35 (m, 4H, Ar); ^{13}C NMR (75.47 MHz, $CDCl_3$), δ: 20.9, 30.3, 39.3, 47.5, 53.5, 53.6, 54.6, 112.6, 126.0, 127.7, 128.1, 128.7, 130.7, 137.8, 163.0, 164.5, 165.1; IR (cm^{-1}), ν: 2255, 1752, 1432, 1266, 1240; MS, m/*z* (*%*): 331 (M^+, 18), 300 (3), 272 (86), 240 (14), 212 (100), 184 (17), 154 (25), 135 (32), 91 (19), 59 (71); HRMS m/z (ESI) calcd for $C_{17}H_{17}NNaO_6$ $(M+Na)^+$ 354.0948, found 354.0943.



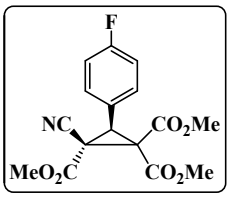
Trimethyl (2*R,3*R**)-2-cyanocyclopropane-3-(4-methylphenyl)-1,1,2-tricarboxylate (4e)**; yield 3.87 g (78%); white solid; m.p. 73-74 °C (lit.[1] m.p. 72-74 ºC); ^{1}H NMR (300 MHz, $CDCl_3$), δ: 2.34 (s, 3H, CH_3), 3.72 (s, 3H, CH_3O), 3.83 (s, 3H, CH_3O), 3.89 (s, 1H, CH), 3.91 (s, 3H, OCH_3), 7.18 (d, 2H, J = 8.3 Hz), 7.25 (d, 2H, J = 8.3 Hz).

Trimethyl (2*R,3*R**)-2-cyanocyclopropane-3-(4-methoxyphenyl)-1,1,2-tricarboxylate (4f)**;



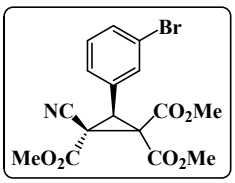
yield 4.42 g (85%); white solid; m.p. 112 °C (lit.[1] m.p. 110-112 ºC); ^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.72 (s, 3H, CH_3O), 3.80 (s, 3H, CH_3O), 3.82 (s, 3H, CH_3O), 3.87 (s, 1H, CH), 3.91 (s, 3H, CH_3O), 6.88 (d, 2H, Ar, J = 8.2 Hz), 7.29 (d, 2H, Ar, J = 8.2 Hz).

Trimethyl (2*R,3*R**)-2-cyanocyclopropane-3-(4-fluorophenyl)-1,1,2-tricarboxylate (4g)**;



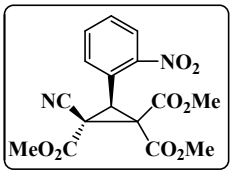
yield 4.12 g (82%); white solid; m.p. 116-117 °C; ^{1}H NMR (300 MHz, DMSO-d_6), δ: 3.72 (s, 3H, CH_3O), 3.75 (s, 3H, CH_3O), 3.83 (s, 3H, CH_3O), 3.90 (s, 1H, CH), 7.27 (t, J = 8.4 Hz, 2H, Ar), 7.35-7.45 (m, 2H, Ar); ^{13}C NMR (75.47 MHz, DMSO-d_6), δ: 30.8, 38.0, 47.1, 53.7, 53.9, 54.5, 112.3, 115.6 (2C, d, $^2J_{CF}$ = 21.9 Hz), 125.8 (2C, d, $^4J_{CF}$ = 3.3 Hz), 130.9 (2C, d, $^3J_{CF}$ = 8.3 Hz), 162.0 (2C, d, $^1J_{CF}$ = 244 Hz), 162.5, 163.7, 164.0; IR (cm^{-1}), ν: 2252, 1750, 1438, 1272, 1240, 1220; MS, m/*z* (%): 335 (M^+, 3), 304 (2), 276 (35), 244 (6), 216 (16), 188 (8), 158 (21), 139 (21), 59 (100), 15 (72); HRMS m/z (ESI) calcd for $C_{16}H_{14}FNNaO_6$ $(M+Na)^+$ 358.0691, found 358.0697.

Trimethyl (2*R,3*R**)-3-(3-bromophenyl)-2-cyanocyclopropane-1,1,2-tricarboxylate (4h)**;



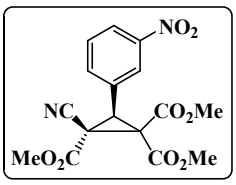
yield 5.17 g (87%); yellowish solid; m.p. 89-90 °C (lit.[1] m.p. 89-91 ºC); ^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.73 (s, 3H, CH_3O), 3.80 (s, 3H, CH_3O), 3.87 (s, 1H, CH), 3.89 (s, 3H, CH_3O), 7.20-7.33 (m, 2H, Ar), 7.40-7.50 (m, 2H, Ar).

Trimethyl (2*R,3*R**)-2-cyanocyclopropane-3-(2-nitrophenyl)-1,1,2-tricarboxylate (4i)**; yield



3.53 g (65%); white solid; m.p. 168-170 °C; ^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.74 (s, 3H, CH_3O), 3.85 (s, 3H, CH_3O), 3.95 (s, 3H, CH_3O), 4.28 (s, 1H, CH), 7.48 (d, J = 7.6 Hz, 1H, Ar), 7.52-7.74 (m, 2H, Ar), 8.19 (d, J = 8.1 Hz, 1H, Ar); ^{13}C NMR (75.47 MHz, $CDCl_3$), δ: 31.6, 38.1, 47.2, 53.8, 54.2, 54.6, 112.0, 124.8, 125.3, 130.4, 132.0, 134.2, 148.4, 162.7, 163.4, 163.8; IR (cm^{-1}), ν: 2252, 1744, 1525, 1297, 1244; MS, m/*z* (%): 362 (M^+, 2), 331 (2), 316 (9), 271 (7), 196 (24), 166 (4), 135 (100), 91 (68), 79 (46), 59 (63); HRMS m/z (ESI) calcd for $C_{16}H_{14}N_2NaO_8$ $(M+Na)^+$ 385.0642, found 385.0641.

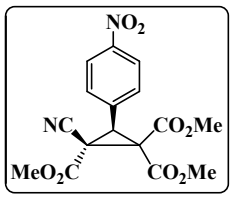
Trimethyl (2*R,3*R**)-2-cyanocyclopropane-3-(3-nitrophenyl)-1,1,2-tricarboxylate (4j)**; yield



3.64 g (67%); white solid; m.p. 120-122 °C; ^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.78 (s, 3H, CH_3O), 3.86 (s, 3H, CH_3O), 3.95 (s, 3H, CH_3O), 3.99 (s, 1H, CH), 7.55-7.65 (m, 1H, Ar), 7.70-7.80 (m, 1H, Ar), 8.18-8.30 (m, 2H, Ar); ^{13}C NMR (75.47 MHz, $CDCl_3$), δ: 30.7, 38.2, 47.3, 53.9 (2C), 54.8, 111.8,

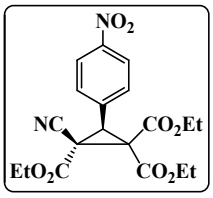
123.7, 123.9, 130.0, 131.5, 134.9, 148.3, 162.4, 163.7, 164.2; IR (cm^{-1}), ν: 2259, 1748, 1524, 1266, 1232; MS, m/*z* (%): 362 (M^+, 1), 331 (8), 303 (100), 259 (5), 244 (6), 218 (5), 166 (17), 139 (8), 113 (7), 59 (54); HRMS m/z (ESI) calcd for $C_{16}H_{14}N_2NaO_8$ $(M+Na)^+$ 385.0642, found 385.0639.

Trimethyl (2*R,3*R**)-2-cyanocyclopropane-3-(4-nitrophenyl)-1,1,2-tricarboxylate (4k)**; yield



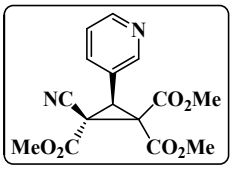
3.48 g (64%); white solid; m.p. 152-154 °C; ^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.73 (s, 3H, CH_3O), 3.83 (s, 3H, CH_3O), 3.94 (s, 3H, CH_3O), 3.96 (s, 1H, CH), 7.56 (d, *J* = 8.6 Hz, 2H, Ar), 8.24 (d, *J* = 8.6 Hz, 2H, Ar); ^{13}C NMR (75.47 MHz, $CDCl_3$), δ: 30.7, 38.5, 47.4, 53.9 (2C), 54.9, 111.9, 123.9 (2C), 129.9, 136.7 (2C), 136.7, 162.4, 163.7, 164.3; IR (cm^{-1}), ν: 2255, 1748, 1524, 1269, 1240, 1237; MS, m/*z* (%): 362 (M^+, 2), 331 (7), 303 (100), 270 (3), 243 (11), 218 (5), 166 (12), 127 (9), 101 (5), 59 (52); HRMS m/z (ESI) calcd for $C_{16}H_{14}N_2NaO_8$ $(M+Na)^+$ 385.0642, found 385.0636.

Trimethyl (2*R,3*R**)-2-cyanocyclopropane-3-(4-nitrophenyl)-1,1,2-tricarboxylate (4l)**; yield



4.00 g (66%); yellowish solid; m.p. 122-123 °C (lit.[2] m.p. 123-124 ºC); ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.18 (t, *J* = 7.1 Hz, 3H, CH_3), 1.32 (t, *J* = 7.1 Hz, 3H, CH_3), 1.40 (t, *J* = 7.1 Hz, 3H, CH_3), 3.97 (s, 1H, CH), 4.20 (q, *J* = 7.1 Hz, 2H, CH_2O), 4.29 (q, *J* = 7.1 Hz, 2H, CH_2O), 4.37 (q, *J* = 7.1 Hz, 2H, CH_2O), 7.58 (d, *J* = 8.6 Hz, 2H, Ar), 8.26 (d, *J* = 8.6 Hz, 2H, Ar).

Trimethyl (2*R*,3*R*)-2-cyano-3-pyridin-3-ylcyclopropane-1,1,2-tricarboxylate (4m); yield



2.48 g (52%); yellow solid; m.p. 123-124 °C; ^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.74 (s, 3H, CH_3O), 3.86 (s, 3H, CH_3O), 3.90 (s, 1H, CH), 3.95 (s, 3H, CH_3O), 7.26-7.38 (m, 1H, Ar), 7.70-7.80 (m, 1H, Ar), 8.54-8.64 (m, 2H, Ar); ^{13}C NMR (75.47 MHz, $CDCl_3$), δ: 30.7, 38.4, 46.7, 53.8, 54.0, 54.6, 112.2, 123.5, 126.0, 136.4, 149.5, 149.7, 162.5, 163.5, 163.9; IR (cm^{-1}), ν: 2247, 1754, 1435, 1260, 1236; MS, m/*z* (%): 318 (M^+, 4), 287 (8), 259 (100), 215 (6), 200 (15), 183 (13), 156 (10), 141 (12), 122 (26), 59 (90); HRMS m/z (ESI) calcd for $C_{15}H_{14}N_2NaO_6$ $(M+Na)^+$ 341.0744, found 341.0746.

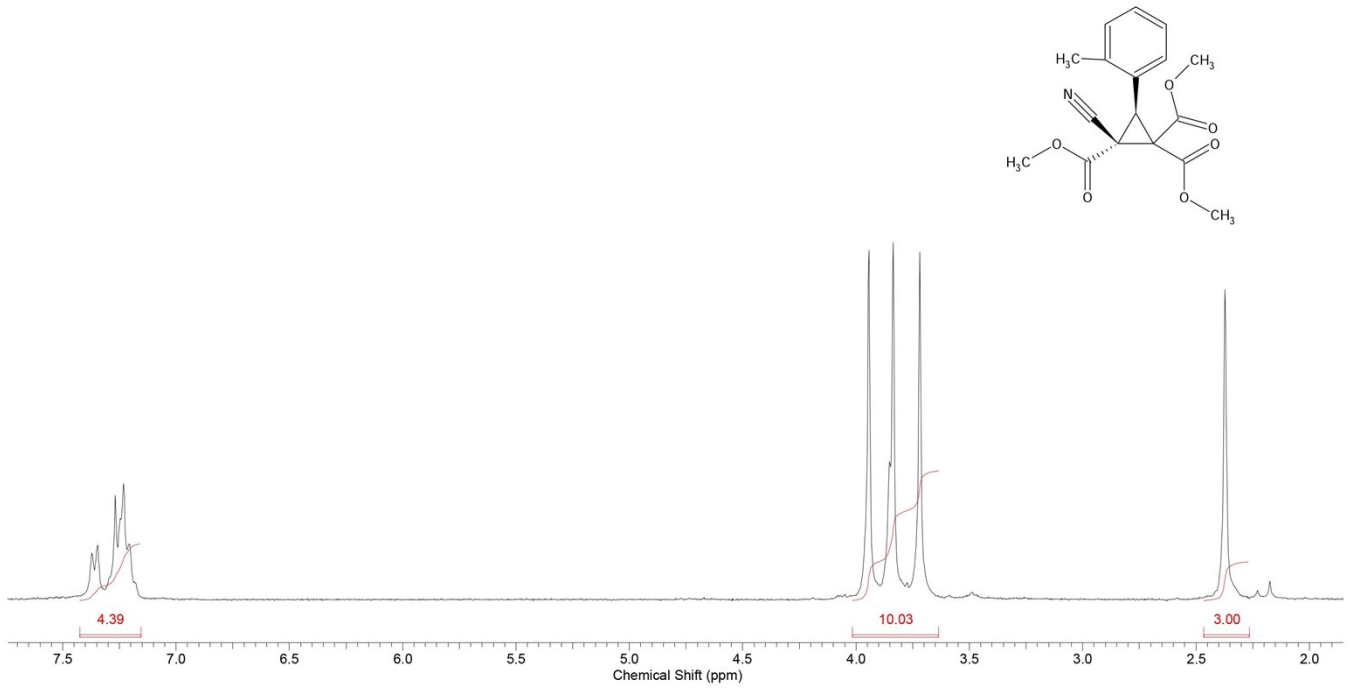
5. References

1 M. N. Elinson, S. K. Feducovich, Z. A. Starikova, A. N. Vereshchagin, P. A. Belyakov, G. I. Nikishin, *Tetrahedron*, 2006, **62**, 3989.

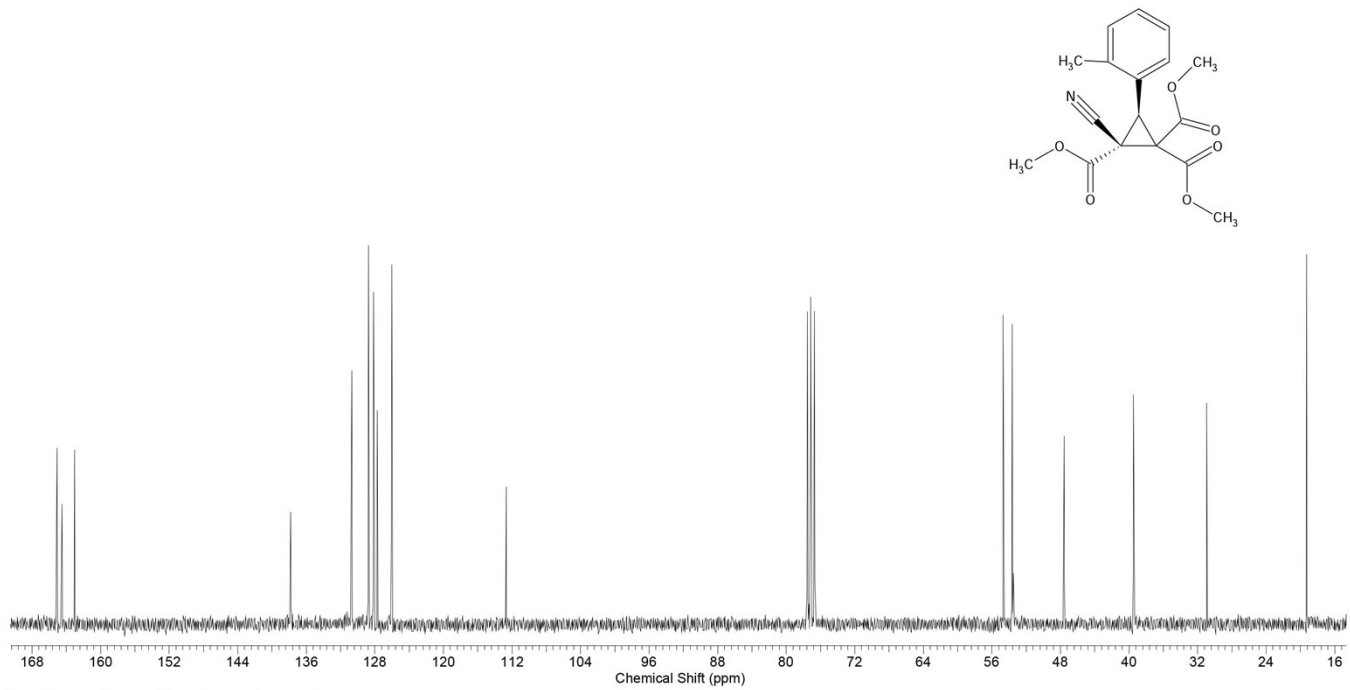
2 G. V. Kryshtal, G. M. Zhdankina, S. G. Zlotin, *Russ. Chem. Bull.*, 2011, **60**, 2286.

6. Spectra of the new compounds

^{1}H NMR for **4c**

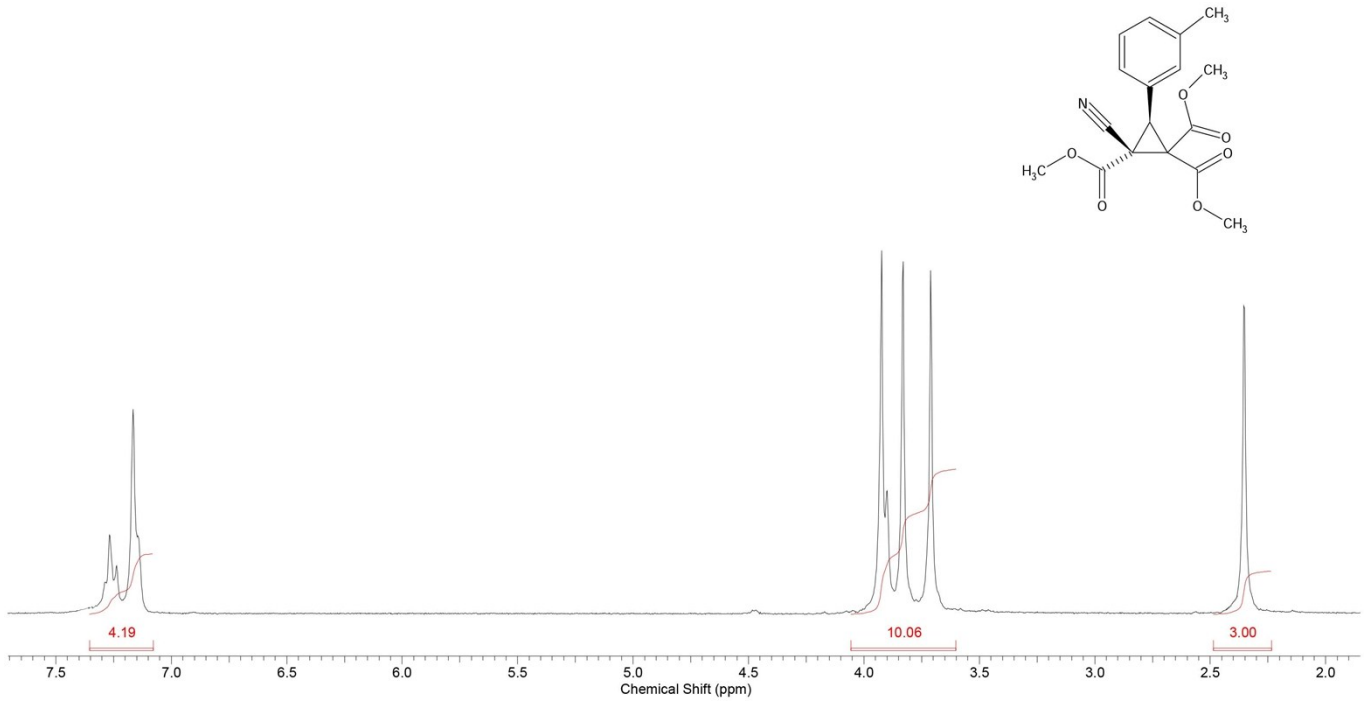


^{13}C NMR for **4c**

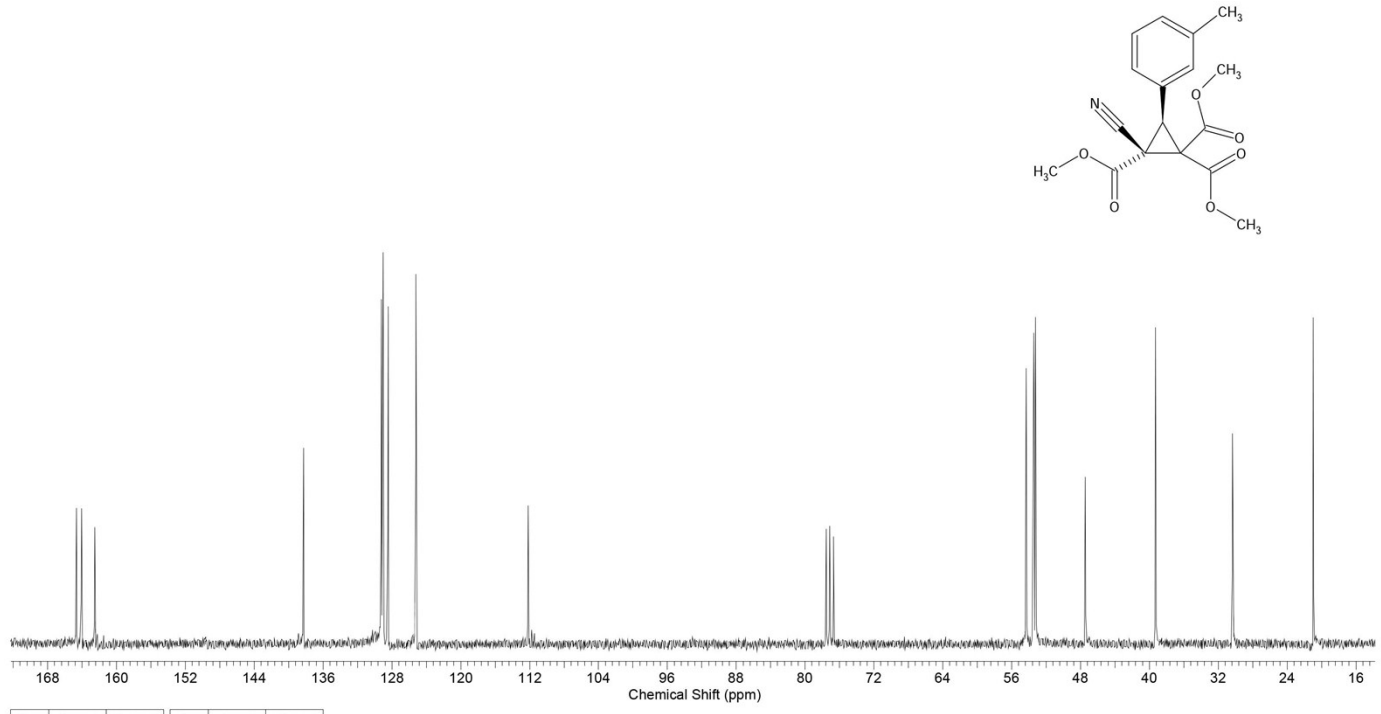


No.	(ppm)	Height	No.	(ppm)	Height
1	19.28	0.9764	10	127.70	0.5661
2	30.93	0.5862	11	128.14	0.8772
3	39.49	0.6076	12	128.75	1.0000
4	47.57	0.4978	13	130.67	0.6713
5	53.54	0.5754	14	137.81	0.2991
6	53.64	0.7935	15	163.03	0.4619
7	54.68	0.8158	16	164.50	0.3207
8	112.67	0.3651	17	165.07	0.4675
9	126.04	0.9488			

^{1}H NMR for **4d**

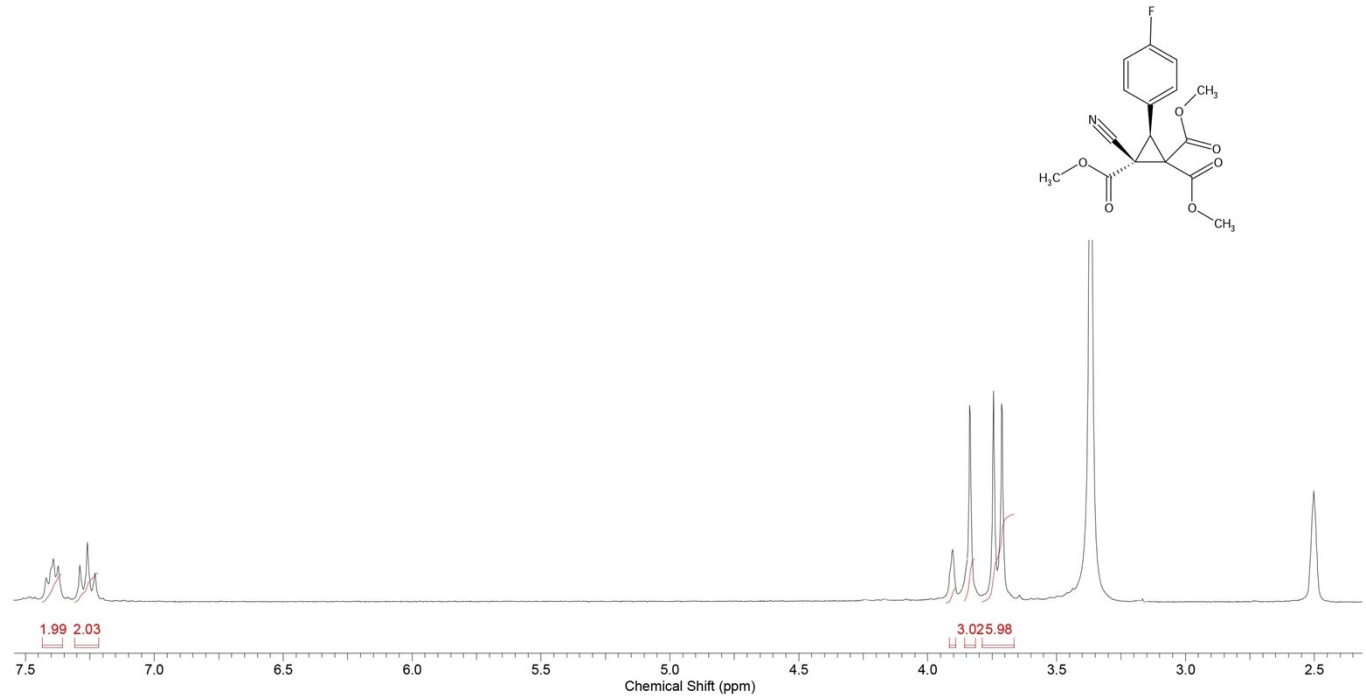


^{13}C NMR for **4d**

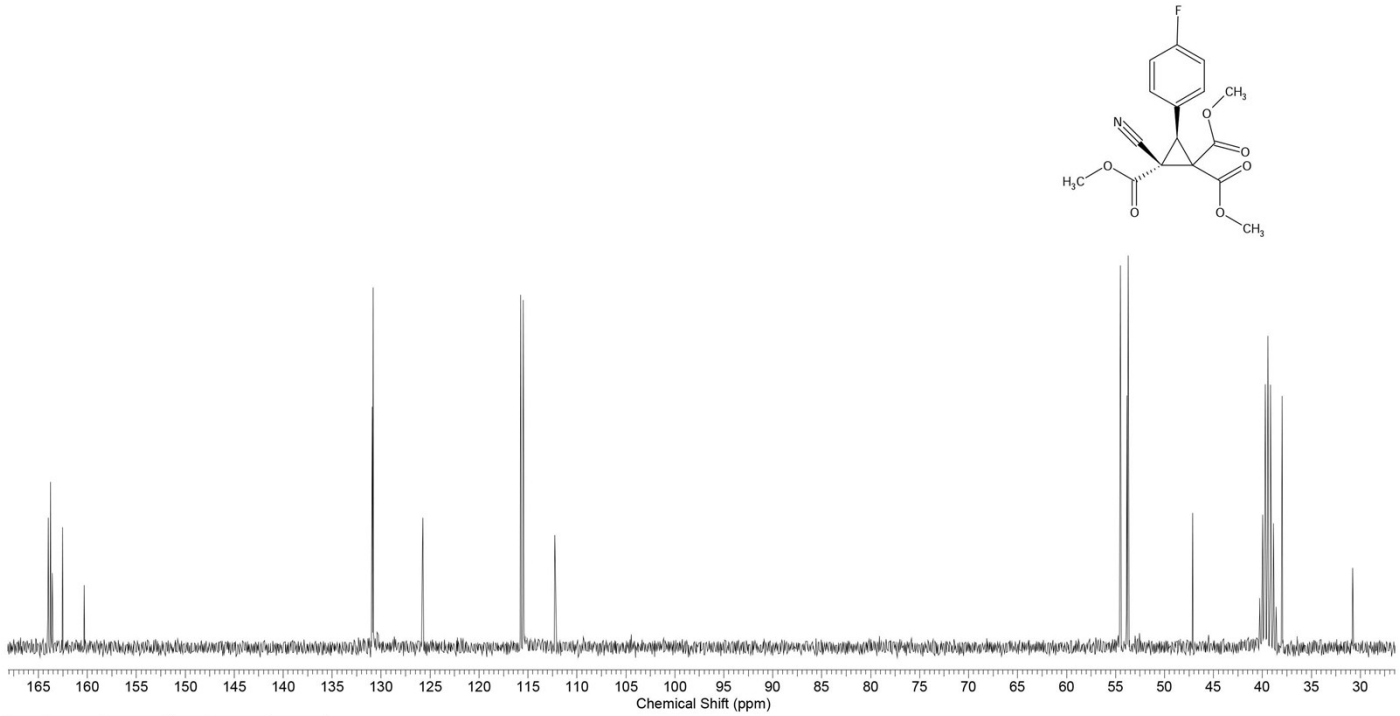


No.	(ppm)	Height	No.	(ppm)	Height
1	20.96	0.8329	10	128.45	0.8608
2	30.36	0.5337	11	129.01	1.0000
3	39.30	0.8078	12	129.05	0.7207
4	47.45	0.4217	13	129.23	0.8795
5	53.22	0.8340	14	138.28	0.4967
6	53.42	0.7926	15	162.53	0.2923
7	54.32	0.7016	16	164.07	0.3410
8	112.16	0.3481	17	164.62	0.3413
9	125.21	0.9440			

^{1}H NMR for **4g**

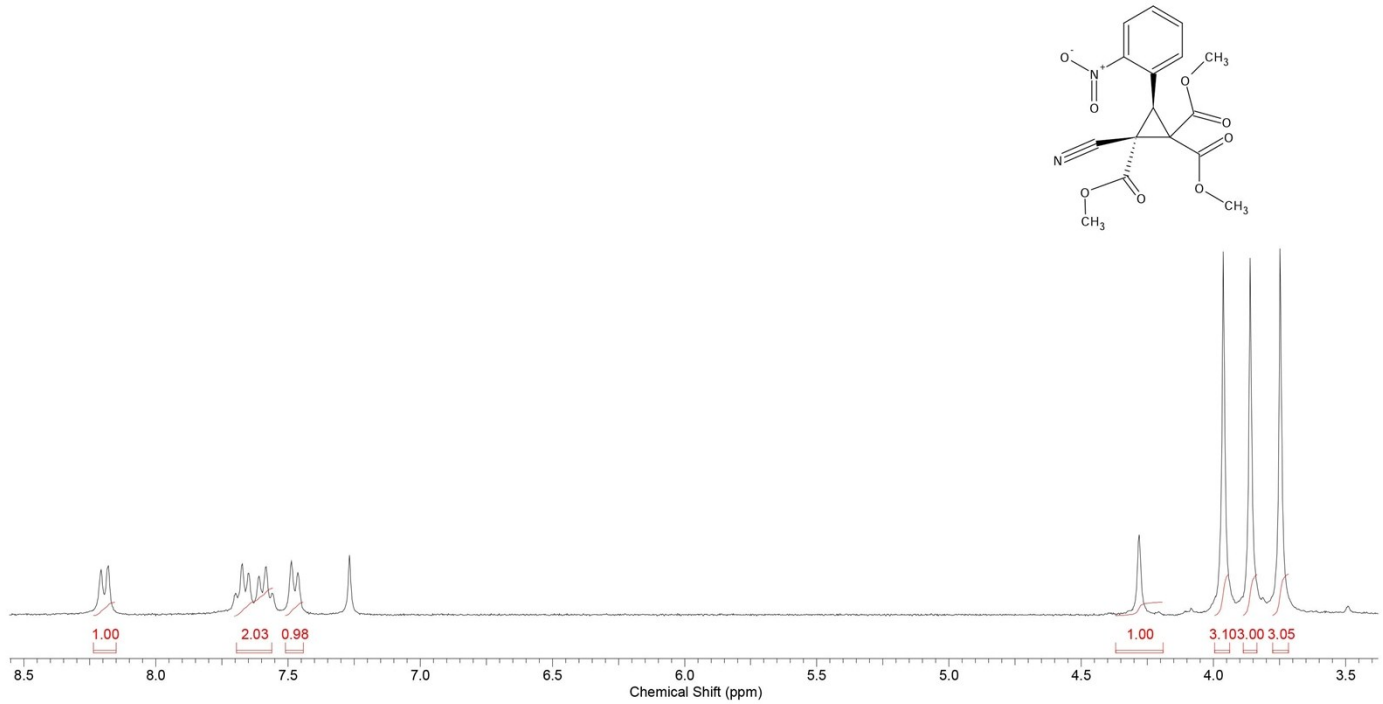


^{13}C NMR for **4g**

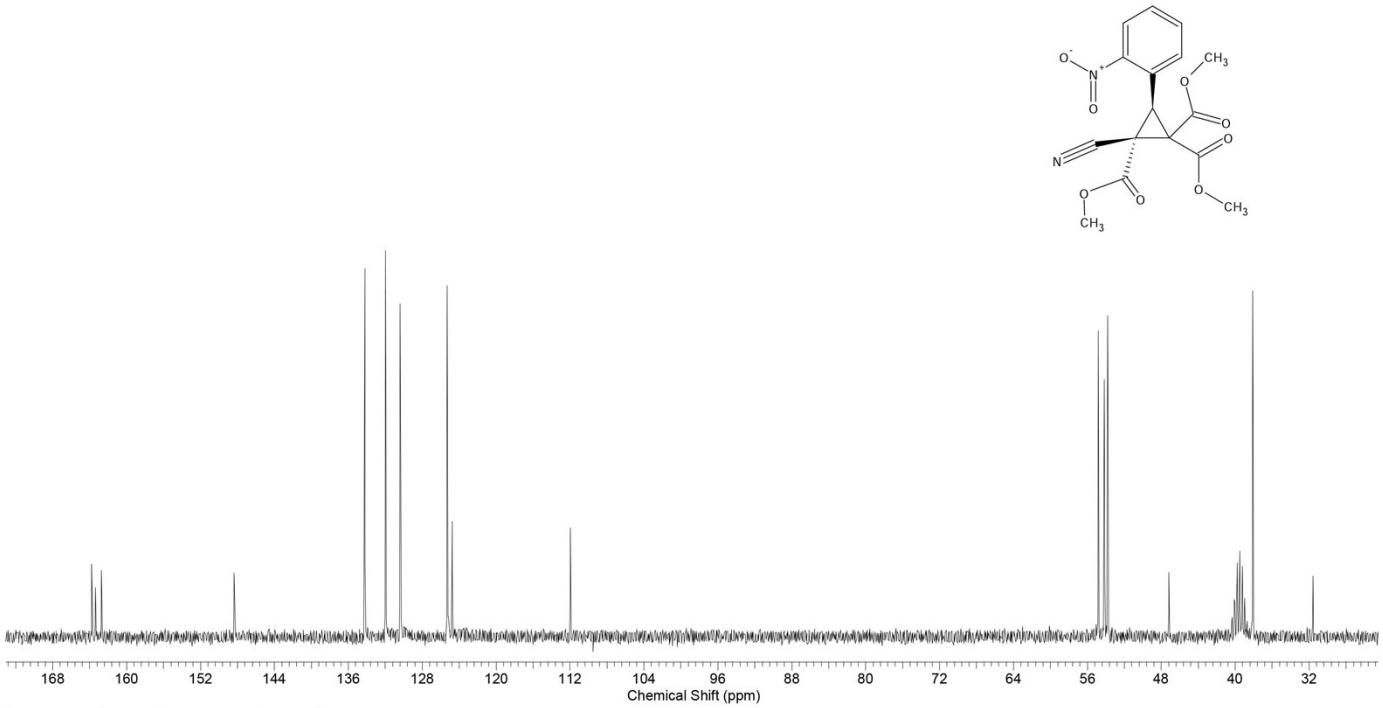


No.	(ppm)	Height	No.	(ppm)	Height
1	30.80	0.2032	10	125.73	0.3320
2	38.01	0.6423	11	125.78	0.2404
3	47.12	0.3439	12	130.81	0.9192
4	53.69	1.0000	13	130.92	0.6150
5	53.85	0.6437	14	160.34	0.1600
6	54.50	0.9752	15	162.50	0.3074
7	112.26	0.2872	16	163.59	0.1902
8	115.48	0.8865	17	163.74	0.4232
9	115.77	0.8998	18	164.00	0.3319

^{1}H NMR for **4i**

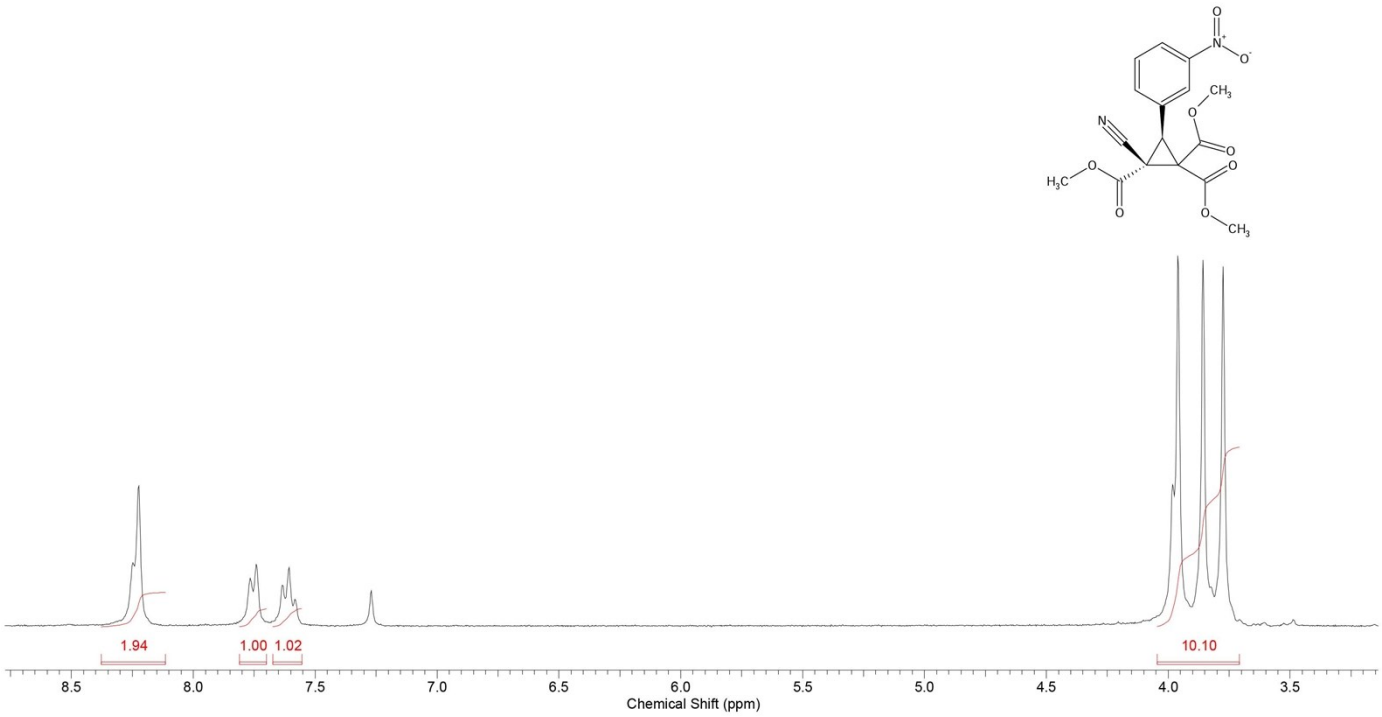


^{13}C NMR for **4i**

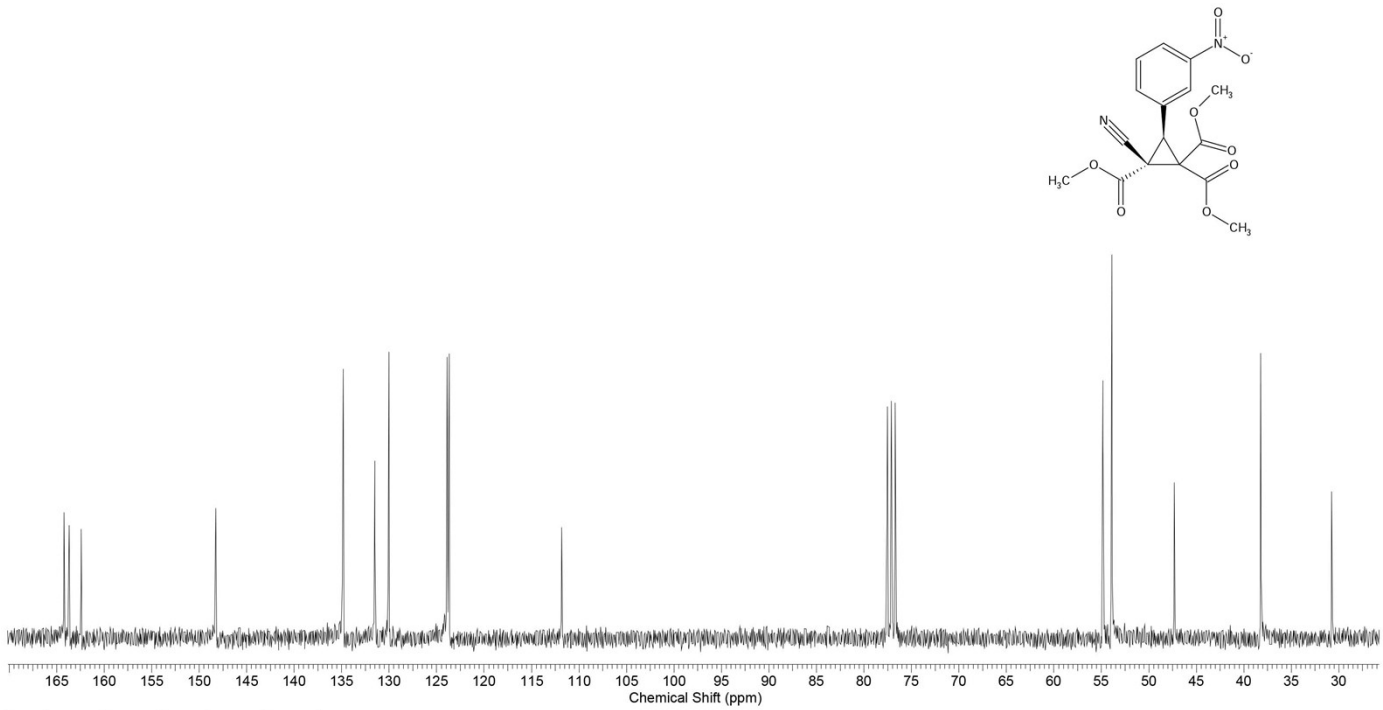


No.	(ppm)	Height	No.	(ppm)	Height
1	31.59	0.1579	9	125.29	0.9088
2	38.08	0.8955	10	130.38	0.8629
3	47.17	0.1670	11	131.98	1.0000
4	53.79	0.8312	12	134.22	0.9534
5	54.17	0.6666	13	148.37	0.1658
6	54.83	0.7930	14	162.73	0.1722
7	111.97	0.2820	15	163.36	0.1282
8	124.76	0.2993	16	163.77	0.1890

^{1}H NMR for **4j**



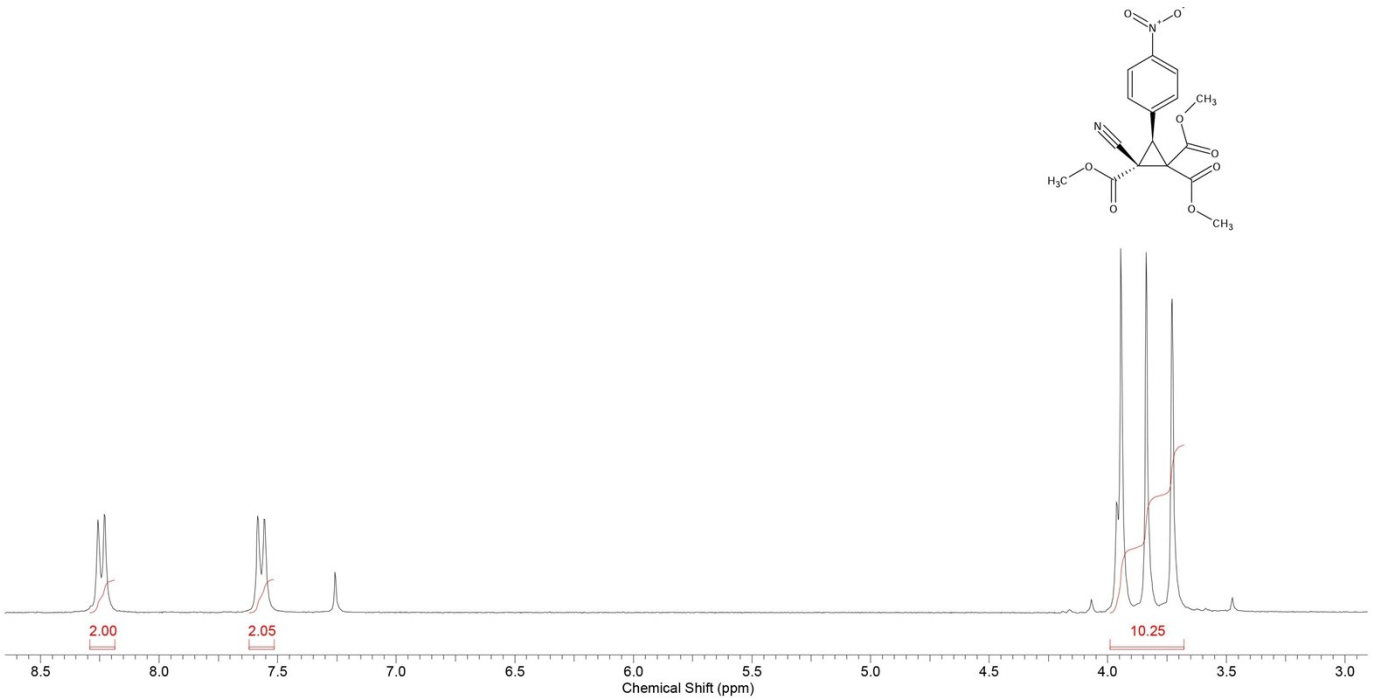
^{13}C NMR for **4j**



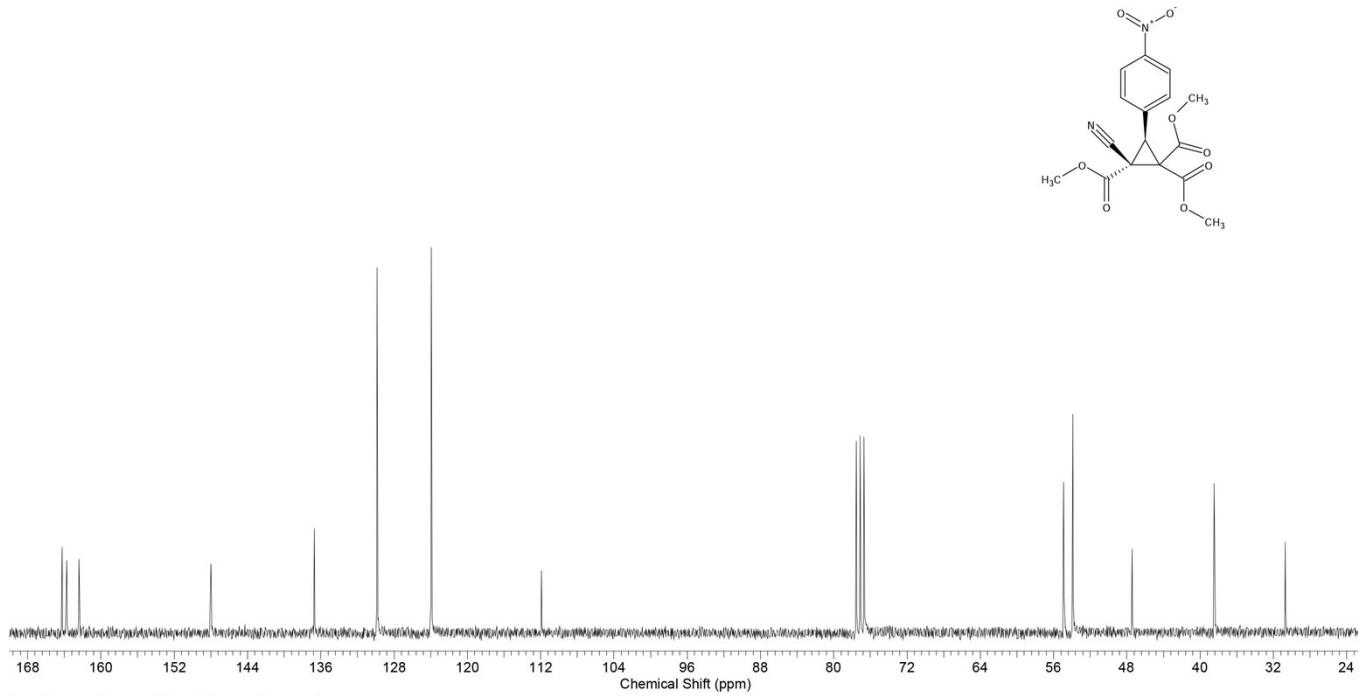
No.	(ppm)	Height
1	30.74	0.3824
2	38.22	0.7428
3	47.31	0.4065
4	53.92	1.0000
5	54.84	0.6723
6	111.82	0.2893
7	123.68	0.7426
8	123.87	0.7333

No.	(ppm)	Height
9	130.03	0.7471
10	131.52	0.4626
11	134.85	0.7026
12	148.27	0.3394
13	162.40	0.2850
14	163.69	0.2943
15	164.21	0.3277

^{1}H NMR for **4k**

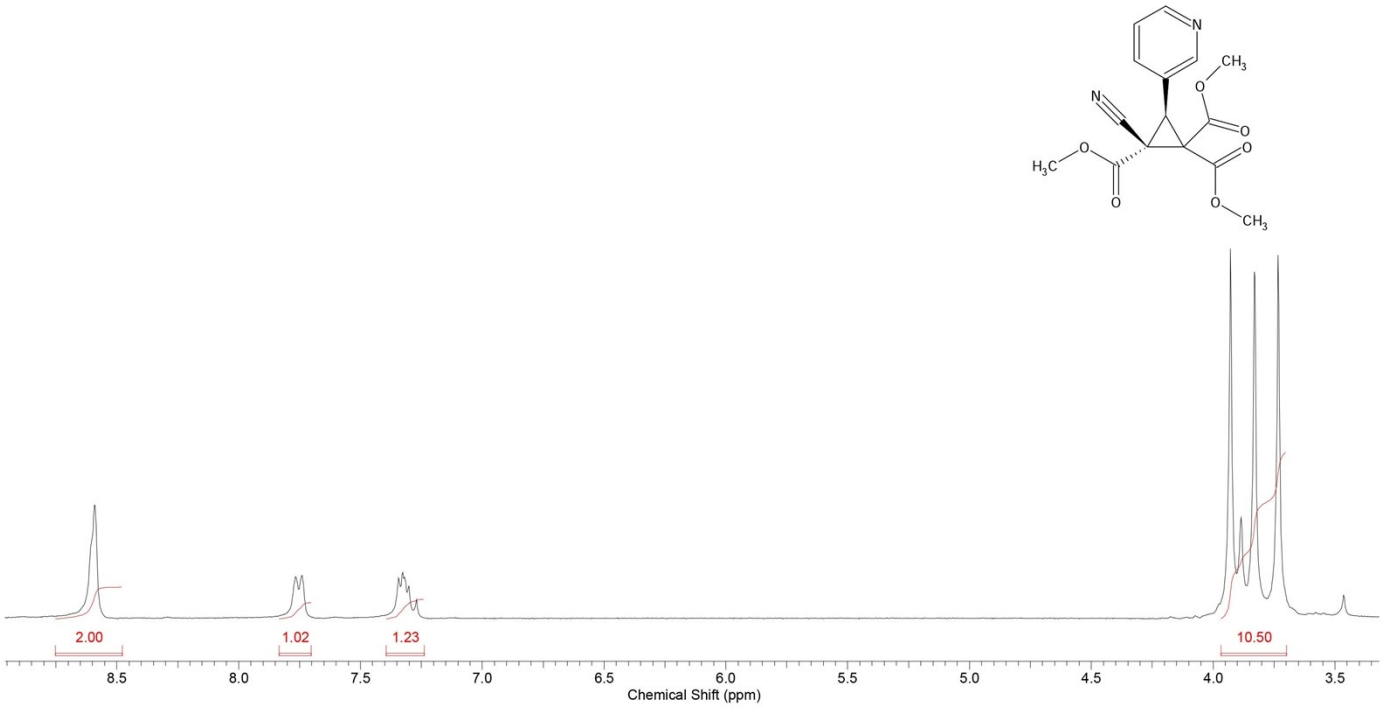


^{13}C NMR for **4k**

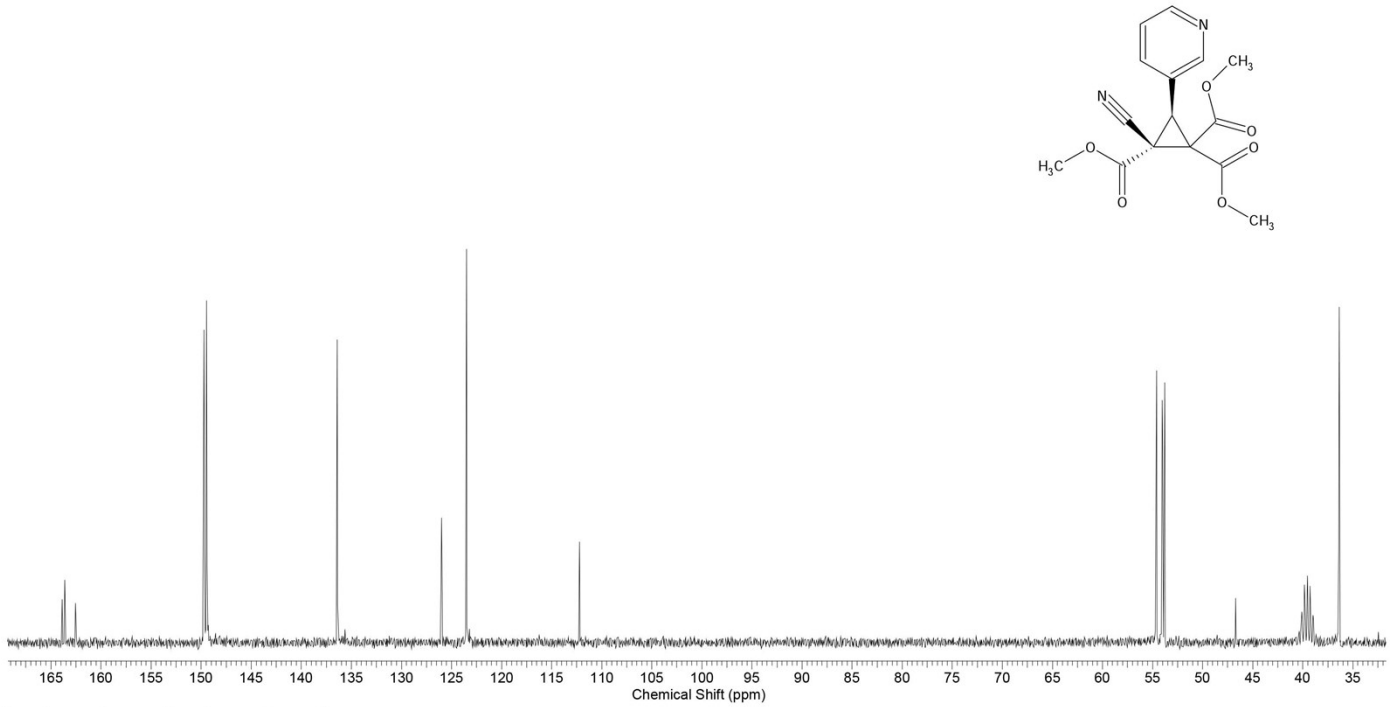


No.	(ppm)	Height	No.	(ppm)	Height
1	30.71	0.2347	8	129.85	0.9478
2	38.46	0.3883	9	136.69	0.2703
3	47.44	0.2171	10	147.97	0.1797
4	53.91	0.5684	11	162.40	0.1914
5	54.90	0.3909	12	163.74	0.1881
6	111.92	0.1607	13	164.25	0.2224
7	123.94	1.0000			

^{1}H NMR for **4m**



^{13}C NMR for **4m**



No.	(ppm)	Height	No.	(ppm)	Height
1	30.67	0.0918	9	125.97	0.3172
2	36.37	0.8528	10	136.40	0.7700
3	46.71	0.1129	11	149.46	0.8692
4	53.80	0.6615	12	149.72	0.7948
5	54.02	0.6164	13	162.53	0.1005
6	54.61	0.6913	14	163.62	0.1585
7	112.23	0.2559	15	163.87	0.1096
8	123.51	1.0000			