Supporting Information

Functionalized Heterocyclic Scaffolds Derived from Morita-Baylis-Hillman Acetates

*Huajian Zhu, Nana Shao, Tong Chen, Hongbin Zou**
Institute of Materia Medica, College of Pharmaceutical Sciences, Zhejiang University, Hangzhou 310058 (China)
zouhb@zju.edu.cn

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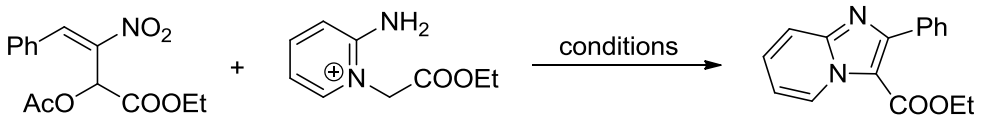
I. General Remarks

DMF was distilled from calcium hydride. Purifications of reaction products were carried out by chromatography using silica gel (200–300 mesh). Melting points were measured on a Perkin-Taike X-4 apparatus and have been corrected. High resolution MS data were recorded on a Agilent 6200 Series TOF spectrometer. NMR spectra were recorded on Bruker AVIII for ^{1}H NMR at 500 MHz and for ^{13}C NMR at 125 MHz. For ^{1}H NMR, tetramethylsilane (TMS) served as internal standard (δ). The spectra data presented here are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant(s) in Hertz. For ^{13}C NMR TMS (δ = 0) or $CDCl_3$ (δ = 77.26) was used as internal standard and spectra were obtained with complete proton decoupling. The starting materials MBHAs were prepared according to literature methods.[1] Compounds **6**–**10** are commercially available.

II. Optimization of Reaction Conditions

Intitially we optimized the reaction of MBHAs with bifunctional nucleophilies. Ethyl-2-acetoxy-3-nitro-4-phenylbut-3(E)-enoate (**M1**) was used as the model reactant of MBHAs. Different solvents, bases and temperature were examined and the results were shown in Table 1–5. The most successful entry is highlighted in bold and used as the reaction system to form the heterocycles.

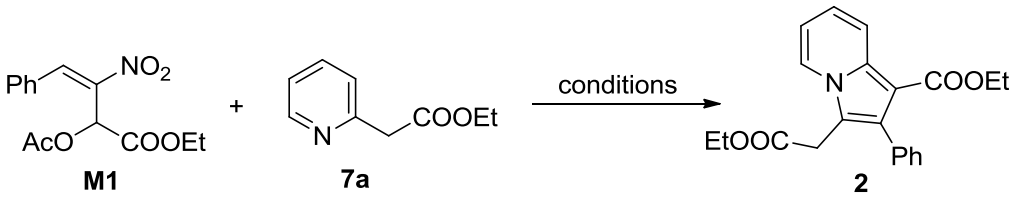
Table 1: Optimization of reaction conditions for imidazo[1,2-a]pyridines.[a]



Entry	Solvent	Base	T (°C)	Yield (%)[b]
1	DMF	K_2CO_3	25	0
2	DMF	K_2CO_3	80	30
3	**DMF**	**K_2CO_3**	**115**	**81**
4	MeCN	K_2CO_3	80	18
5	MeOH	K_2CO_3	65	0
6	toluene	K_2CO_3	110	trace
7	DMF	DABCO	115	24
8	DMF	Na_2CO_3	115	72
9	DMF	DBU	115	42
10	DMF	Et_3N	115	15

[a] Reaction conditions: **M1** (0.2 mmol), **6** (0.2 mmol), K_2CO_3 (0.2 mmol), solvent (2 mL) were stirred at rt for 30 min, then heated to corresponding temperature. [b] Determined by high-performance liquid chromatography based on the disappearance of the starting **M1**.

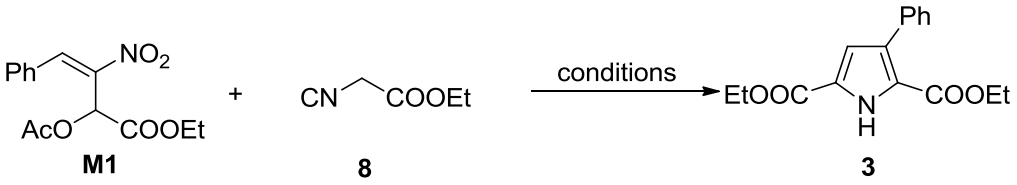
Table 2: Optimization of reaction conditions for indolizines.[a]



Entry	Solvent	Base	T (°C)	Yield (%)[b]
1	DMF	K_2CO_3	25	62
2	DMF	K_2CO_3	80	21
3	MeCN	K_2CO_3	25	70
4	MeOH	K_2CO_3	25	0
5	toluene	K_2CO_3	25	56
6	MeCN	DABCO	25	66
7	MeCN	Na_2CO_3	25	60
8	MeCN	DBU	25	34
9	**MeCN**	**Et_3N**	**25**	**88**

[a] Reaction conditions: **M1** (0.2 mmol), **7a** (0.2 mmol), base (0.3 mmol), solvent (2 mL) were stirred overnight. [b] Determined by high-performance liquid chromatography based on the disappearance of the starting **M1**.

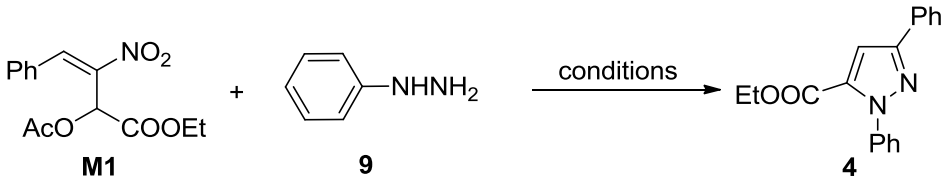
Table 3: Optimization of reaction conditions for pyrroles.[a]



Entry	Solvent	Base	T (°C)	Yield (%)[b]
1	MeCN	DBU	25	44
2	MeCN	DBU	80	<10
3	DMF	DBU	25	0
4	MeOH	DBU	25	0
5	**toluene**	**DBU**	**25**	**70**
6	toluene	Na_2CO_3	25	0
7	toluene	K_2CO_3	25	0
8	toluene	DABCO	25	0
9	toluene	Et_3N	25	0

[a] Reaction conditions: **M1** (0.2 mmol), **8** (0.2 mmol), base (0.2 mmol), solvent (2 mL) were stirred for 2h. [b] Determined by high-performance liquid chromatography based on the disappearance of the starting **M1**.

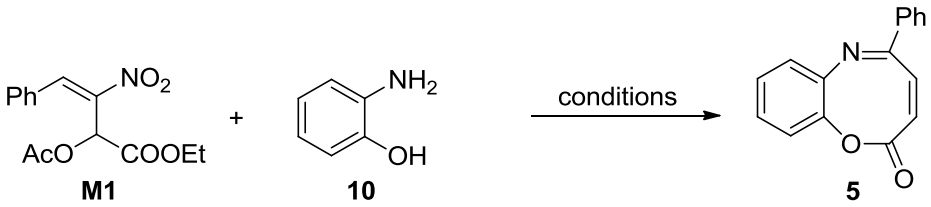
Table 4: Optimization of reaction conditions for pyrazoles.[a]



Entry	Solvent	Base	T (°C)	Yield (%)[b]
1	MeOH	-	25	39
2	MeOH	-	50	85
3	**MeOH**	-	**65**	**90**
4	MeOH	Na_2CO_3	65	80
5	MeOH	K_2CO_3	65	79
6	MeOH	DABCO	65	83
7	MeOH	DBU	65	41
8	MeOH	Et_3N	65	76
9	MeCN	-	65	25
10	DMF	-	65	<15
11	toluene	-	65	trace

[a] Reaction conditions: **M1** (0.2 mmol), **9** (0.2 mmol), base (0.2 mmol) or absence, solvent (2 mL) were stirred overnight. [b] Determined by high-performance liquid chromatography based on the disappearance of the starting **M1**.

Table 5: Optimization of reaction conditions for benzo[b][1,6]oxazocin-2-ones.[a]



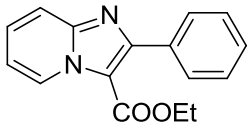
Entry	Solvent	Base	T (°C)	Yield (%)[b]
1	MeOH	-	40	0
2	**MeOH**	**Na_2CO_3**	**40**	**78**
3	MeOH	K_2CO_3	40	31
4	MeOH	DABCO	40	29
5	MeOH	DBU	40	trace
6	MeOH	Et_3N	40	33
7	MeOH	Na_2CO_3	25	0
8	MeCN	Na_2CO_3	40	<15
9	DMF	Na_2CO_3	40	0
10	toluene	Na_2CO_3	40	trace

[a] Reaction conditions: **M1** (0.2 mmol), **10** (0.2 mmol), solvent (2 mL) were stirred at rt for 15 min. Then base (0.2 mmol) was added and the mixture was heated to corresponding temperature for 2h. [b] Determined by high-performance liquid chromatography based on the disappearance of the starting **M1**.

III. General Procedure for the Synthesis of Imidazo[1,2-a]pyridines

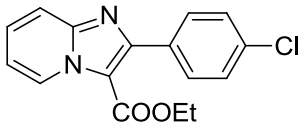
A mixture of MBHAs (0.3 mmol, 1.0 equiv), 2-amino-1-ethoxycarbonylmithyl-pyridium (**6**, 0.3 mmol, 1.0 equiv) and K_2CO_3 (0.3 mmol, 1.0 equiv) was stirred in DMF (2.0 mL) at room temperature for 30 min, then the mixture was heated to 115 ºC for 1h. Water (5 mL) was added to it and the mixture was extracted three times with EtOAc (10 mL × 3). The combined organic layers were washed with water (10 mL × 3) and brine (10 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuum. Purification of the residue by chromatography (silica gel) affords the product.

Ethyl 2-phenylimidazo[1,2-a]pyridine-3-carboxylate (1a):



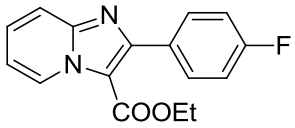
Yellow solid. m.p.: 70 – 72 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.41 (1H, d, J = 7.0 Hz), 7.75 (3H, m), 7.43 (4H, m), 7.03 (1H, td, J = 7.0, 1.5 Hz), 4.30 (2H, q, J = 7.0 Hz), 1.22 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.2, 153.6, 147.1, 134.5, 130.2, 128.7, 128.3, 127.9, 127.5, 117.5, 114.1, 111.9, 60.5, 13.9. HRMS Calcd. For $C_{16}H_{14}N_2O_2 + H^+$: 267.1134, found: 267.1146.

Ethyl 2-(4-chlorophenyl)imidazo[1,2-a]pyridine-3-carboxylate (1b):



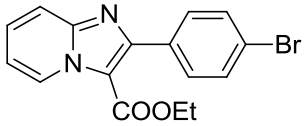
Yellow solid. m.p.: 110 – 112 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.41 (1H, d, J = 7.0 Hz), 7.73 (3H, m), 7.45 (1H, t, J = 7.5 Hz), 7.41 (2H, d, J = 8.5 Hz), 7.05 (1H, t, J = 7.0 Hz), 4.32 (2H, q, J = 7.0 Hz), 1.25 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.9, 152.3, 147.1, 134.8, 132.9, 131.6, 128.4, 128.2, 127.8, 117.5, 114.3, 112.0, 60.6, 14.1. HRMS Calcd. For $C_{16}H_{13}ClN_2O_2 + H^+$: 301.0744, found: 301.0738.

Ethyl 2-(4-fluorophenyl)imidazo[1,2-a]pyridine-3-carboxylate (1c):



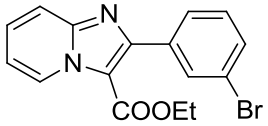
Yellow solid. m.p.: 95 – 97 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.41(1H, d, J = 7.0 Hz), 7.74 (3H, m), 7.44(1H, m), 7.12 (2H, t, J = 9.0 Hz), 7.05 (1H, td, J = 7.0, 1.0 Hz), 4.32 (2H, q, J = 7.0 Hz), 1.24 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.2 (d, J = 247 Hz), 161.0, 152.6, 147.1, 132.1 (d, J = 8 Hz), 130.5 (d, J = 4 Hz), 128.4, 128.1, 117.5, 114.6 (d, J = 21 Hz), 114.2, 111.9, 60.6, 14.1. HRMS Calcd. For $C_{16}H_{13}FN_2O_2 + H^+$: 285.1039, found: 285.1035.

Ethyl 2-(4-bromophenyl)imidazo[1,2-a]pyridine-3-carboxylate (1d):



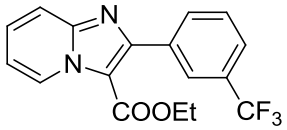
Yellow solid. m.p.: 120 – 122 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.40 (1H, dt, J = 7.0, 1.0 Hz), 7.30 (1H, dt, J = 9.0, 1.0 Hz), 7.66 (2H, dt, J = 7.5, 2.0 Hz), 7.56 (1H, dt, J = 8.5, 2.0 Hz), 7.45 (1H, m), 7.05 (1H, td, J = 7.0, 1.5 Hz), 4.32 (2H, q, J = 7.0 Hz), 1.25 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.9, 152.3, 147.1, 133.4, 131.9, 130.8, 128.4, 128.2, 123.1, 117.5, 114.3, 112.0, 60.6, 14.1. HRMS Calcd. For $C_{16}H_{13}BrN_2O_2 + H^+$: 345.0239, found: 345.0229.

Ethyl 2-(3-bromophenyl)imidazo[1,2-a]pyridine-3-carboxylate (1e):



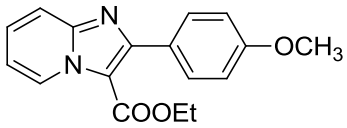
Yellow solid. m.p.: 107 – 109 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.43 (1H, dt, J = 7.0, 2.0 Hz), 7.93 (1H, t, J = 7.0), 7.74 (1H, d, J = 9.0), 7.71 (1H, dt, J = 7.0, 2.0 Hz), 7.55 (1H, ddd, J = 8.0, 2.0, 1.0 Hz), 7.46 (1H, ddd, J = 9.0, 7.0, 1.5 Hz), 7.31 (1H, d, J = 7.5 Hz), 7.06 (1H, td, J = 7.0, 1.0 Hz), 4.33 (2H, q, J = 7.0 Hz), 1.27 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.9, 151.7, 147.1, 136.5, 133.3, 129.2, 128.8, 128.4, 128.2, 121.5, 117.6, 114.4, 112.1, 60.7, 14.0. HRMS Calcd. For $C_{16}H_{13}BrN_2O_2 + H^+$: 345.0239, found: 345.0229.

Ethyl 2-(3-(trifluoromethyl)phenyl)imidazo[1,2-a]pyridine-3-carboxylate (1f):



Yellow solid. m.p.: 108 – 110 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.45 (1H, d, J = 7.0 Hz), 8.05 (1H, s), 7.97 (1H, d, J = 7.5 Hz), 7.76 (1H, d, J = 9.0 Hz), 7.68 (1H, d, J = 7.5 Hz), 7.57 (1H, t, J = 8.0 Hz), 7.47 (1H, t, J = 7.5 Hz), 7.07 (1H, t, J = 7.0 Hz), 4.31 (2H, q, J = 7.0 Hz), 1.21 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.8, 151.8, 147.2, 135.3, 133.5, 129.9 (d, J = 33 Hz), 128.4, 128.3, 128.2, 127.3 (q, J = 4 Hz), 125.4 (q, J = 4 Hz), 125.3 (q, J = 271 Hz), 117.6, 114.5, 112.2, 60.7, 13.8. HRMS Calcd. For $C_{17}H_{13}F_3N_2O_2 + H^+$: 335.1007, found: 335.1004.

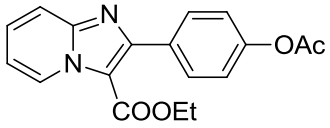
Ethyl 2-(4-methoxyphenyl)imidazo[1,2-a]pyridine-3-carboxylate (1g):



Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.39 (1H, d, J = 7.0 Hz), 7.75 (2H, d, J = 8.5 Hz), 7.71 (1H, d, J = 9.5 Hz), 7.39 (1H, t, J = 7.5 Hz), 7.00 (1H, t, J = 6.5 Hz), 6.96 (2H, d, J = 8.5 Hz), 4.32 (2H, q, J = 7.0 Hz), 3.85 (3H, s), 1.26 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.2, 160.1, 153.4, 147.1, 131.6, 128.4, 127.9, 126.7, 117.3, 113.9, 113.0, 111.6, 60.4, 55.3, 14.1.

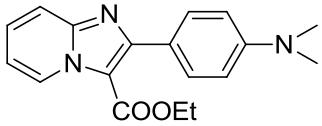
HRMS Calcd. For $C_{17}H_{16}N_2O_3 + H^+$: 297.1239, found: 297.1230.

Ethyl 2-(4-acetoxyphenyl)imidazo[1,2-a]pyridine-3-carboxylate (1h):



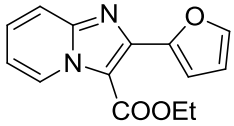
Yellow solid. m.p.: 112 – 114 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.42 (1H, d, J = 7.0 Hz), 7.80 (2H, d, J = 8.5 Hz), 7.74 (1H, d, J = 9.0 Hz), 7.45 (1H, m), 7.18 (2H, d, J = 8.5 Hz), 7.05 (1H, td, J = 7.0, 1.0 Hz), 4.32 (2H, q, J = 7.0 Hz), 2.33 (3H, s), 1.24 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.3, 161.1, 152.6, 151.1, 147.1, 132.0, 131.4, 128.4, 128.1, 120.7, 117.5, 114.2, 95.9, 60.6, 21.3, 14.0. HRMS Calcd. For $C_{18}H_{16}N_2O_4 + H^+$: 325.1188, found: 325.1182.

Ethyl 2-(4-(dimethylamino)phenyl)imidazo[1,2-a]pyridine-3-carboxylate (1i):



Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.39 (1H, d, J = 7.0 Hz), 7.75 (2H, d, J = 8.5 Hz), 7.71 (1H, d, J = 8.5 Hz), 7.39 (1H, m), 6.98 (1H, t, J = 7.0 Hz), 6.76 (1H, d, J = 8.5 Hz), 4.35 (2H, q, J = 7.0 Hz), 1.32 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.5, 154.1, 150.8, 147.1, 131.3, 128.4, 127.7, 121.7, 117.1, 113.6, 111.2, 111.1, 60.4, 40.4, 14.3. HRMS Calcd. For $C_{18}H_{19}N_3O_2 + H^+$: 310.1556, found: 310.1555.

Ethyl 2-(furan-2-yl)imidazo[1,2-a]pyridine-3-carboxylate (1j):

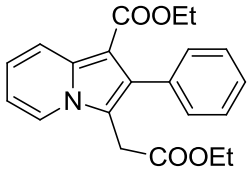


Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.36 (1H, d, J = 7.0 Hz), 7.74 (1H, d, J = 9.0 Hz), 7.62 (1H, d, J = 1.5 Hz), 7.41 (2H, m), 7.01 (1H, td, J = 7.0, 1.0 Hz), 6.56 (1H, dd, J = 3.5, 2.0 Hz), 4.50 (2H, q, J = 7.0 Hz), 1.47 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.6, 147.6, 147.2, 143.7, 143.1, 128.5, 128.3, 117.6, 114.2, 113.9, 111.6, 110.9, 60.9, 14.5. HRMS Calcd. For $C_{14}H_{12}N_2O_3 + H^+$: 257.0926, found: 257.0917.

IV. General Procedure for the Synthesis of Indolizines

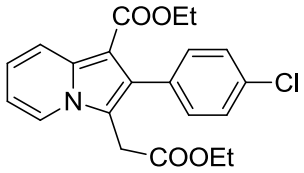
A mixture of MBHAs (0.3 mmol, 1.0 equiv), ethyl 2-pyridylacetate (**7a**, 0.3 mmol, 1.0 equiv) and Et_3N (0.45 mmol, 1.5 equiv) was stirred in MeCN (2 mL) at room temperature overnight. Once starting material was consumed (monitored by TLC), the organic solvent was removed and the residue was purified by column chromatography (silica gel) to give the product. The same method can also be used to prepare indolizines with cyano group from 2-pyridylacetonitrile (**7b**).

Ethyl 3-(2-ethoxy-2-oxoethyl)-2-phenylindolizine-1-carboxylate (2a):



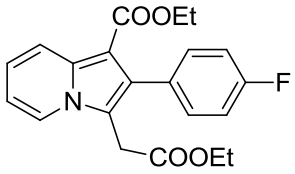
Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.32 (1H, d, J = 8.5 Hz), 7.97 (1H, d, J = 7.0 Hz), 7.38 (5H, m), 7.12 (1H, ddd, J = 9.5, 7.0, 1.0 Hz), 6.82 (1H, td, J = 7.0, 1.0 Hz), 4.1 (4H, m), 3.75 (2H, s), 1.23 (3H, t, J = 7.5 Hz), 1.10 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.7, 164.9, 136.2, 134.8, 131.8, 130.5, 127.5, 127.1, 123.1, 122.3, 120.2, 116.5, 112.8, 102.2, 61.4, 59.2, 30.9, 14.1. HRMS Calcd. For $C_{21}H_{21}NO_4 + H^+$: 352.1549, found: 352.1537.

Ethyl 2-(4-chlorophenyl)-3-(2-ethoxy-2-oxoethyl)indolizine-1-carboxylate (2b):



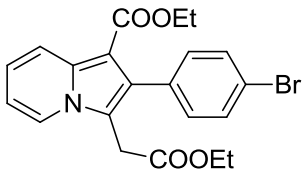
Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31 (1H, d, J = 9.0 Hz), 7.98 (1H, d, d, J = 7.0 Hz), 7.38 (2H, m), 7.32 (2H, m), 7.13 (1H, ddd, d, J = 9.5, 7.0, 1.0 Hz), 6.83 (1H, td, d, J = 7.0, 1.0 Hz), 4.17 (4H, m), 3.73 (2H, s), 1.24 (3H, t, d, J = 7.0 Hz), 1.16 (3H, t, d, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.6, 164.8, 136.3, 133.4, 133.3, 132.0, 130.4, 127.9, 123.3, 122.6, 120.4, 116.7, 113.1, 102.2, 61.6, 59.4, 30.9, 14.3, 14.2. HRMS Calcd. For $C_{21}H_{20}ClNO_4 + H^+$: 386.1159, found: 386.1155.

Ethyl 3-(2-ethoxy-2-oxoethyl)-2-(4-fluorophenyl)indolizine-1-carboxylate (2c):



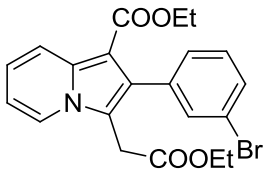
Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31 (1H, d, J = 9.0 Hz), 7.98 (1H, d, J = 7.0 Hz), 7.35 (2H, m), 7.12 (3H, m), 6.82 (1 H, td, J = 6.5, 1.0 Hz), 4.17 (4H, m), 3.73 (2H, s), 1.23 (3H, t, J = 7.0 Hz), 1.15 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.5, 164.8, 162.3 (d, J = 244 Hz), 136.2, 132.1 (d, J = 8 Hz), 130.7, 130.6 (d, J = 4 Hz), 123.1, 122.5, 120.2, 116.6, 114.4 (d, J = 21 Hz), 112.9, 102.2, 61.4, 59.2, 30.8, 14.2, 14.1. HRMS Calcd. For $C_{21}H_{20}FNO_4 + H^+$: 370.1455, found: 370.1449.

Ethyl 2-(4-bromophenyl)-3-(2-ethoxy-2-oxoethyl)indolizine-1-carboxylate (2d):



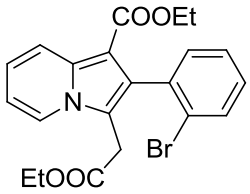
Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31 (1H, d, J = 9.0 Hz), 7.98 (1H, d, J = 7.0 Hz), 7.53 (2H, d, J = 8.0 Hz), 7.27 (2H, d, J = 8.0 Hz), 7.13 (1H, ddd, J = 8.0, 7.0, 1.0 Hz), 6.83 (1H, td, J = 7.0, 1.0 Hz), 4.19 (2H, q, J = 7.0 Hz), 4.15 (2H, q, J = 7.0 Hz), 1.24 (3H, t, J = 7.0 Hz), 1.16 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.6, 164.8, 136.3, 133.8, 132.4, 130.8, 130.6, 123.3, 122.7, 121.6, 120.4, 116.6, 113.1, 102.2, 61.6, 59.4, 30.9, 14.3, 14.2. HRMS Calcd. For $C_{21}H_{20}BrNO_4 + H^+$: 430.0654, found: 430.0652.

Ethyl 2-(3-bromophenyl)-3-(2-ethoxy-2-oxoethyl)indolizine-1-carboxylate (2e):



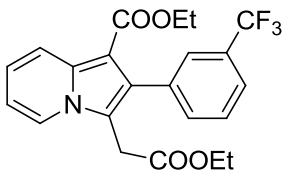
Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.32 (1H, d, J = 9.5 Hz), 8.00 (1H, d, J = 7.0 Hz), 7.56 (1H, t, J = 1.5 Hz), 7.49 (1H, dt, J = 8.0, 1.0 Hz), 7.33 (1H, d, J = 7.5 Hz), 7.27 (1H, t, J = 7.5 Hz), 7.13 (1H, dd, J = 8.0, 7.0 Hz), 6.83 (1H, td, J = 7.0, 1.0 Hz), 4.16 (4H, m), 3.74 (2H, s), 1.25 (3H, t, J = 7.0 Hz), 1.13 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.5, 164.8, 137.1, 136.4, 133.7, 130.3, 130.1, 129.4, 129.1, 123.3, 122.7, 121.6, 120.3, 116.7, 113.2, 102.2, 61.6, 59.4, 31.0, 14.3, 14.2. HRMS Calcd. For $C_{21}H_{20}BrNO_4 + H^+$: 430.0654, found: 430.0652.

Ethyl 2-(2-bromophenyl)-3-(2-ethoxy-2-oxoethyl)indolizine-1-carboxylate (2f):



Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.32 (1H, d, J = 9.0 Hz), 8.00 (1H, d, J = 7.0 Hz), 7.65 (1H, dd, J = 8.0, 1.0 Hz), 7.33 (2H, m), 7.23 (1H, td, J = 8.0, 2.0 Hz), 7.12 (1H, ddd, J = 8.0, 7.0, 1.0 Hz), 6.82 (1H, td, J = 7.0, 1.0 Hz), 4.11 (4H, m), 3.70 (1H, d, J = 16.5 Hz), 3.66 (1H, d, J = 16.5 Hz), 1.19 (3H, t, J = 7.0 Hz), 1.03 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.3, 164.7, 136.5, 136.1, 132.2, 131.9, 130.3, 129.0, 126.8, 125.2, 123.4, 122.5, 120.3, 116.5, 112.9, 102.8, 61.4, 59.2, 30.8, 14.2, 14.0. HRMS Calcd. For $C_{21}H_{20}BrNO_4 + H^+$: 430.0654, found: 430.0652.

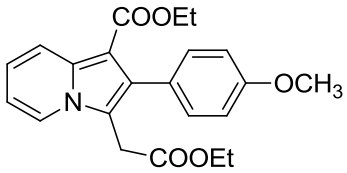
Ethyl 3-(2-ethoxy-2-oxoethyl)-2-(3-(trifluoromethyl)phenyl)indolizine-1-carboxy late (2g):



Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.38 (1H, d, J = 9.0 Hz), 8.03 (1H, d, J = 7.0 Hz), 7.69 (1H, s), 7.63 (1H, d, J = 7.5 Hz), 7.60 (1H, d, J = 7.5 Hz), 7.53 (1H, t, J = 7.5 Hz), 7.16 (1H, m), 6.86 (1H, td, J = 7.0, 1.0 Hz), 4.16 (4H, m), 3.72 (2H, s), 1.24 (3H, t, J = 7.0 Hz), 1.06 (3H, t, J =

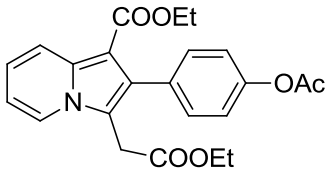
7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.3, 164.6, 136.4, 135.7, 134.0, 130.0, 129.9 (d, J = 32 Hz), 127.9, 127.5 (q, J = 4 Hz), 125.4, 123.9 (q, J = 4 Hz), 123.2, 122.7, 120.3, 116.6, 113.2, 102.2, 61.5, 59.3, 30.9, 14.0, 13.9. HRMS Calcd. For $C_{22}H_{20}F_3NO_4$ + H^+: 420.1423, found: 420.1416.

Ethyl 3-(2-ethoxy-2-oxoethyl)-2-(4-methoxyphenyl)indolizine-1-carboxylate (2h):



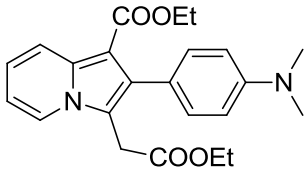
Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (1H, d, J = 9.0 Hz), 7.96 (1H, d, J = 7.0 Hz), 7.32 (2H, dt, J = 8.5, 2.0 Hz), 7.11 (1H, dd, J = 9.0, 6.5 Hz), 6.95 (2H, dt, J = 8.5, 2.0 Hz), 6.81 (1H, td, J = 8.5, 2.0 Hz), 4.20 (2H, q, J = 7.5 Hz), 4.15 (2H, q, J = 7.5 Hz), 3.86 (3H, s), 3.76 (2H, s), 1.23 (3H, t, J = 7.0 Hz), 1.18 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.7, 164.9, 158.8, 136.1, 131.7, 131.5, 126.9, 122.2, 120.2, 116.6, 113.0, 112.7, 102.2, 61.3, 59.2, 55.3, 30.9, 14.3, 14.2. HRMS Calcd. For $C_{22}H_{23}NO_5$ + H^+: 382.1654, found: 382.1645.

Ethyl 2-(4-acetoxyphenyl)-3-(2-ethoxy-2-oxoethyl)indolizine-1-carboxylate (2i):



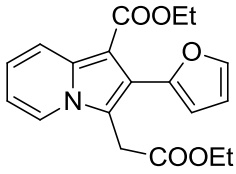
Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.32 (1H, d, J = 9.0 Hz), 7.96 (1H, d, J = 7.0 Hz), 7.40 (2H, d, J = 8.5 Hz), 7.13 (3H, m), 6.82 (1H, t, J = 7.0 Hz), 4.16 (4H, m), 3.76 (2H, s), 2.33 (3H, s), 1.24 (3H, t, J = 7.0 Hz), 1.12 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.7, 169.6, 165.0, 150.1, 136.4, 132.4, 131.7, 130.8, 123.2, 122.6, 120.7, 120.3, 116.7, 113.1, 102.3, 61.5, 59.4, 30.9, 21.4, 14.2, 14.2. HRMS Calcd. For $C_{23}H_{23}NO_6$ + H^+: 410.1604, found: 410.1600.

Ethyl 2-(4-(dimethylamino)phenyl)-3-(2-ethoxy-2-oxoethyl)indolizine-1-carboxy Late (2j):



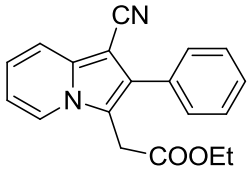
Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (1H, d, J = 9.0 Hz), 7.95 (1H, d, J = 7.0 Hz), 7.28 (2H, dt, J = 8.5, 3.0 Hz), 7.09 (1H, m), 6.79 (3H, m), 4.23 (2H, q, J = 7.0 Hz), 4.16 (2H, q, J = 7.0 Hz), 3.80 (2H, s), 2.99 (6H, s), 1.23 (6H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.1, 165.2, 149.9, 136.3, 132.4, 131.5, 123.2, 122.5, 122.0, 120.3, 116.6, 112.7, 111.9, 102.3, 61.4, 59.2, 10.8, 31.2, 14.5, 14.3. HRMS Calcd. For $C_{23}H_{26}N_2O_4$ + H^+: 395.1971, found: 395.1970.

Ethyl 3-(2-ethoxy-2-oxoethyl)-2-(furan-2-yl)indolizine-1-carboxylate (2k):



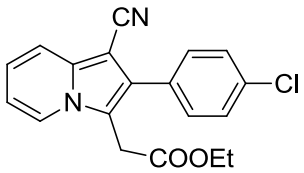
Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.28 (1H, d, J = 9.0 Hz), 7.98 (1H, d, J = 7.0 Hz), 7.56 (1H, m), 7.10 (1H, ddd, J = 9.0, 7.0, 1.0 Hz), 6.80 (1H, td, J = 7.0, 1.0 Hz), 6.68 (1H, d, J = 8.0 Hz), 6.52 (1H, m), 4.29 (2H, q, J = 7.0 Hz), 4.15 (2H, q, J = 7.0 Hz), 3.96 (2H, s), 1.28 (3H, t, J = 7.0 Hz), 1.23 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.4, 164.5, 147.4,142.4, 136.4, 123.2, 122.5, 120.4, 120.3, 117.7, 113.0, 110.8, 110.8, 102.1, 61.4, 59.4, 31.2, 14.4, 14.1. HRMS Calcd. For $C_{19}H_{19}NO_5 + H^+$: 342.1341, found: 342.1333.

Ethyl 2-(1-cyano-2-phenylindolizin-3-yl)acetate (2l):



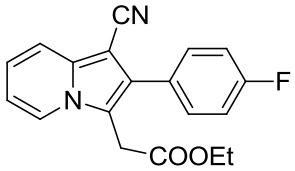
Brown solid. m.p.: 134 – 136 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (1H, d, J = 7.0 Hz), 7.70 (1H, d, J = 9.0 Hz), 7.58 (2H, d, J = 8.0 Hz), 7.50 (2H, t, J = 7.0 Hz), 7.42 (1H, t, J = 7.0 Hz), 7.14 (1H, t, J = 7.5 Hz), 6.86 (1H, t, J = 7.0 Hz), 4.22 (2H, q, J = 7.0 Hz), 3.92 (2H, s), 1.28 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.3, 138.1, 132.0, 131.8, 129.6, 128.9, 128.2, 123.8, 122.5, 117.9, 116.7, 115.3, 113.4, 81.9, 61.7, 31.1, 14.2. HRMS Calcd. For $C_{19}H_{16}N_2O_2 + H^+$: 305.1290, found: 305.1278.

Ethyl 2-(2-(4-chlorophenyl)-1-cyanoindolizin-3-yl)acetate (2m):



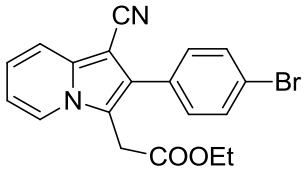
Brown solid. m.p.: 139 – 141 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (1H, d, J = 7.0 Hz), 7.69 (1H, d, J = 8.5 Hz), 7.53 (2H, d, J = 8.5 Hz), 7.47 (2H, d, J = 8.5 Hz), 7.15 (1H, dd, J = 8.5, 7.0 Hz), 6.87 (1H, td, J = 7.0, 1.0 Hz), 4.23 (2H, q, J = 7.0 Hz), 3.88 (2H, s), 1.28 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.1, 138.2, 134.4, 130.9, 130.6, 130.5, 129.1, 123.8, 122.8, 117.9, 116.5, 115.4, 113.5, 81.9, 61.8, 31.0, 14.2. HRMS Calcd. For $C_{19}H_{15}ClN_2O_2 + H^+$: 339.0900, found: 339.0898.

Ethyl 2-(1-cyano-2-(4-fluorophenyl)indolizin-3-yl)acetate (2n):



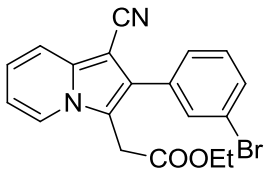
Brown solid. m.p.: 109 – 111 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (1H, d, J = 7.0 Hz), 7.69 (1H, d, J = 9.0 Hz), 7.56 (2H, m), 7.16 (3H, m), 6.87 (1H, td, J = 7.0, 1.0 Hz), 4.22 (2H, q, J = 7.0 Hz), 3.88 (2H, s), 1.28 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.2, 162.77 (d, J = 247 Hz), 138.1, 131.4 (d, J = 8 Hz), 130.4, 128.0 (d, J = 4 Hz), 123.8, 122.7, 117.8, 116.6, 115.9 (d, J = 21 Hz), 115.3, 113.5, 81.9, 61.8, 31.0, 14.2. HRMS Calcd. For $C_{19}H_{15}FN_2O_2$ + H^+: 323.1196, found: 323.1191.

Ethyl 2-(2-(4-bromophenyl)-1-cyanoindolizin-3-yl)acetate (2o):



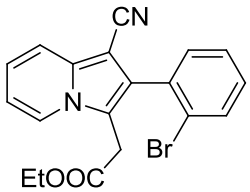
Brown solid. m.p.: 128 – 130 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (1H, d, J = 7.0 Hz), 7.69 (1H, d, (1H, d, J = 9.0 Hz), 7.63 (2H, d, J = 8.5 Hz), 7.46 (2H, d, J = 8.0 Hz), 7.15 (1H, dd, J = 8.5, 7.0 Hz), 6.87 (1H, t, J = 7.0 Hz), 4.22 (2H, q, J = 7.0 Hz), 3.88 (2H, s), 1.28 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.1, 138.2, 132.1, 131.2, 130.9, 130.6, 123.9, 122.8, 122.7, 117.9, 116.5, 115.3, 113.6, 81.8, 61.9, 31.0, 14.2. HRMS Calcd. For $C_{19}H_{15}BrN_2O_2$ + H^+: 383.0395, found: 383.0386.

Ethyl 2-(2-(3-bromophenyl)-1-cyanoindolizin-3-yl)acetate (2p):



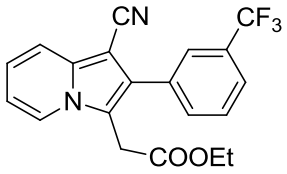
Brown solid. m.p.: 107 – 109 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (1H, d, J = 7.0 Hz), 7.60 (1H, t, J = 2.0 Hz), 7.70 (1H, d, J = 9.0 Hz), 7.55 (2H, m), 7.37 (1H, t, J = 8.0 Hz), 7.16 (1H, dd, J = 8.5, 7.0 Hz), 6.88 (1H, td, J = 7.0, 1.0 Hz), 4.23 (2H, q, J = 7.0 Hz), 3.89 (2H, s), 1.31 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.0, 138.2, 134.1, 132.5, 131.3, 130.4, 130.1, 128.4, 123.9, 122.9, 122.8, 117.9, 116.3, 115.6, 113.6, 81.9, 61.9, 31.1, 14.2. HRMS Calcd. For $C_{19}H_{15}BrN_2O_2$ + H^+: 383.0395, found: 383.0386.

Ethyl 2-(2-(2-bromophenyl)-1-cyanoindolizin-3-yl)acetate (2q):



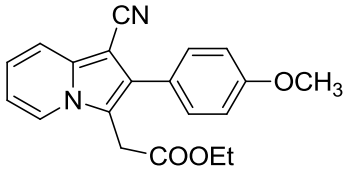
Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (1H, d, J = 7.0 Hz), 7.70 (2H, m), 7.39 (2H, m), 7.29 (1H, td, J = 7.0, 2.5 Hz), 7.14 (1H, ddd, J = 9.0, 7.0, 0.5 Hz), 6.86 (1H, td, J = 7.0, 1.0 Hz), 4.12 (2H, m), 3.76 (2H, s), 1.21 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.8, 137.7, 133.1, 133.0, 132.6, 130.7, 130.2, 127.5, 124.4, 124.0, 122.6, 117.9, 116.5, 116.2, 113.3, 81.2, 61.6, 30.9, 14.1. HRMS Calcd. For $C_{19}H_{15}BrN_2O_2$ + H^+: 383.0395, found: 383.0386.

Ethyl 2-(1-cyano-2-(3-(trifluoromethyl)phenyl)indolizin-3-yl)acetate (2r):



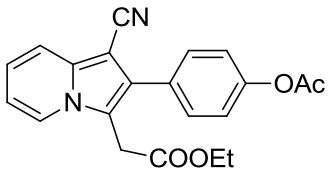
Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (1H, d, J = 7.0 Hz), 7.89 (1H, s), 7.82 (1H, d, J = 7.5 Hz), 7.70 (2H, m), 7.64 (1H, t, J = 7.5 Hz), 7.18 (1H, ddd, J = 9.0, 7.0, 0.5Hz), 6.90 (1H, td, J = 7.0, 1.0 Hz), 4.24 (2H, q, J = 7.0 Hz), 3.88 (2H, s), 1.29 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.9, 138.2, 133.1, 132.9, 131.2 (q, J = 33 Hz), 130.1, 129.5, 126.4 (q, J = 4 Hz), 125.1 (q, J = 271 Hz), 124.9 (q, J = 4 Hz), 124.0, 123.0, 117.9, 116.3, 115.6, 113.7, 81.9, 62.0, 31.2, 14.0. HRMS Calcd. For $C_{20}H_{15}F_3N_2O_2 + H^+$: 373.1164, found: 373.1154.

Ethyl 2-(1-cyano-2-(4-methoxyphenyl)indolizin-3-yl)acetate (2s):



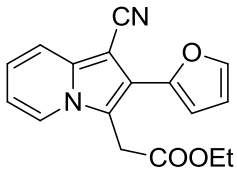
Brown solid. m.p.: 132 – 134 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (1H, d, J = 7.0 Hz), 7.67 (1H, d, J = 9.0 Hz), 7.52 (2H, d, J = 8.5 Hz), 7.11 (1H, ddd, J = 9.0, 7.0, 0.5 Hz), 7.02 (2H, d, J = 9.0 Hz), 6.84 (1H, td, J = 7.0, 1.0 Hz), 4.22 (2H, q, J = 7.0 Hz), 3.90 (2H, s), 3.86 (3H, s), 1.28 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.4, 159.6, 138.0, 131.6, 130.8, 124.3, 123.8, 122.4, 117.7, 116.9, 115.0, 114.4, 113.2, 81.8, 61.7, 55.4, 31.1, 14.2. HRMS Calcd. For $C_{20}H_{18}N_2O_3 + H^+$: 335.1396, found: 335.1394.

Ethyl 2-(2-(4-acetoxyphenyl)-1-cyanoindolizin-3-yl)acetate (2t):



Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (1H, d, J = 7.0 Hz), 7.70 (1H, d, J = 9.0 Hz), 7.62 (2H, d, J = 8.5 Hz), 7.23 (2H, d, J = 8.5 Hz), 7.15 (1H, m), 6.87 (1H, td, J = 7.0, 1.0 Hz), 4.22 (2H, q, J = 7.0 Hz), 3.92 (2H, s), 2.34 (3H, s), 1.28 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.5, 169.2, 150.6, 138.2, 130.7, 129.6, 123.8, 122.7, 122.1, 117.9, 116.6, 115.4, 114.0, 113.5, 81.9, 61.8, 29.7, 21.2, 14.2. HRMS Calcd. For $C_{21}H_{18}N_2O_4 + H^+$: 363.1345, found: 363.1338.

Ethyl 2-(1-cyano-2-(furan-2-yl)indolizin-3-yl)acetate (2u):

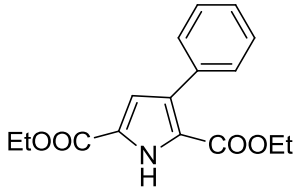


Brown solid. m.p.: 130 – 132 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (1H, d, J = 7.0 Hz), 7.64 (1H, d, J = 8.5 Hz), 7.55 (1H, dd, J = 2.0, 0.5 Hz), 7.11 (1H, ddd, J = 8.5, 7.0, 1.0 Hz), 7.04 (1H, dd, J = 3.5, 0.5 Hz), 6.83 (1H, td, J = 7.0, 1.0 Hz), 6.54 (1H, dd, J = 3.5, 2.0 Hz), 4.24 (2H, s), 4.18 (2H, q, J = 7.0 Hz), 1.24 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.1, 147.2, 142.5, 138.5, 123.5, 122.8, 120.5, 117.7, 116.7, 114.6, 113.5, 111.7, 119.3, 79.2, 61.6, 31.2, 14.1. HRMS Calcd. For $C_{17}H_{14}N_2O_3 + H^+$: 295.1083, found: 295.1077.

V. General Procedure for the Synthesis of Pyrroles

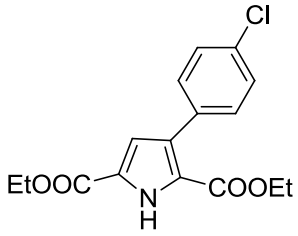
To a solution of 2-isocyanoacetate (**8**, 0.3 mmol, 1.0 equiv) and DBU (0.3 mmol, 1.0 equiv) in toluene (1 mL) was added MBHAs (0.3 mmol, 1.0 equiv) in toluene (1 mL) dropwise and then the mixture was stirred at room temperature for 2h. Water (5 mL) was added to it and the mixture was extracted three times with EtOAc (10 mL × 3). The combined organic layers were washed with water (10 mL × 3) and brine (10 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuum. Purification of the residue by chromatography (silica gel) affords the product.

Diethyl 3-phenyl-1H-pyrrole-2,5-dicarboxylate (3a):



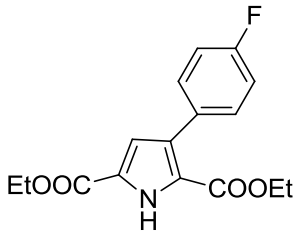
Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.50 (1H, s), 7.59 (1H, d, J = 3.5 Hz), 7.32 (5H, m), 4.12 (4H, m), 1.10 (3H, t, J = 7.5 Hz), 1.07 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.8, 160.9, 133.7, 132.3, 130.1, 127.1, 126.9, 126.7, 121.0, 117.3, 60.5, 59.8, 13.9, 13.8. HRMS Calcd. For $C_{16}H_{17}NO_4 + H^+$: 288.1236, found: 288.1239.

Diethyl 3-(4-chlorophenyl)-1H-pyrrole-2,5-dicarboxylate (3b):



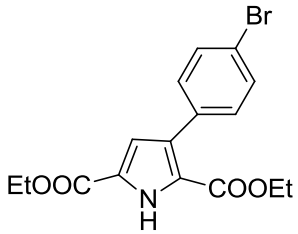
Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.64 (1H, s), 7.58 (1H, d, J = 3.0 Hz), 7.32 (2H, d, J = 8.0 Hz), 7.26 (2H, d, J = 8.0 Hz), 4.14 (4H, m), 1.15 (3H, t, J = 7.0 Hz), 1.11 (3H, t, J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.7, 160.8, 133.1, 132.2, 131.6, 131.0, 127.2, 126.9, 121.0, 117.1, 60.7, 59.9, 14.1, 13.9. HRMS Calcd. For $C_{16}H_{16}ClNO_4 + H^+$: 322.0846, found: 322.0840.

Diethyl 3-(4-fluorophenyl)-1H-pyrrole-2,5-dicarboxylate (3c):



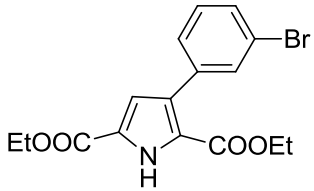
Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.66 (1H, s), 7.58 (1H, d, J = 3.5 Hz), 7.29 (2H, m), 7.04 (2H, t, J = 8.5 Hz), 4.14 (4H, m), 1.42 (3H, t, J = 7.0 Hz), 1.09 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.8, 162.3 (d, J = 244 Hz), 160.9, 131.9 (d, J = 8.0 Hz), 131.2, 129.5 (d, J = 4.0 Hz), 126.9, 121.1, 117.2, 113.9 (d, J = 21 Hz), 60.7, 59.9, 14.1, 13.9. HRMS Calcd. For $C_{16}H_{16}FNO_4 + H^+$: 306.1142, found: 306.1136.

Diethyl 3-(4-bromophenyl)-1H-pyrrole-2,5-dicarboxylate (3d):



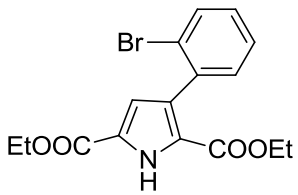
Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.59 (1H, s), 7.58 (1H, d, J = 3.5 Hz), 7.47 (2H, d, J = 8.0 Hz), 7.21 (2H, d, J = 8.0 Hz), 4.15 (4H, m), 1.52 (3H, t, J = 7.0 Hz), 1.11 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.7, 160.8, 132.7, 131.9, 131.0, 130.1, 126.9, 121.4, 121.0, 117.1, 60.7, 59.9, 14.1,13.9. HRMS Calcd. For $C_{16}H_{16}BrNO_4 + H^+$: 366.0341, found: 366.0338.

Diethyl 3-(3-bromophenyl)-1H-pyrrole-2,5-dicarboxylate (3e):



Yellow solid. m.p.: 91 – 93 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.52 (1H, s), 7.62 (1H, d, J = 3.5 Hz), 7.50 (1H, s), 7.47 (1H, d, J = 8.0 Hz), 7.28 (1H, d, J = 8.0 Hz), 7.23 (1H, t, J = 8.0 Hz), 4.15 (4H, m), 1.13 (6H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.6, 160.8, 135.8, 133.2, 130.2, 130.1, 129.0, 128.4, 126.9, 121.2, 120.8, 117.3, 60.8, 60.3, 14.0, 13.8. HRMS Calcd. For $C_{16}H_{16}BrNO_4 + H^+$: 366.0341, found: 366.0338.

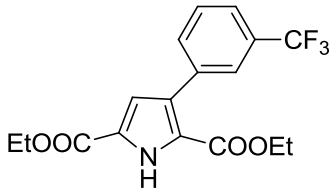
Diethyl 3-(2-bromophenyl)-1H-pyrrole-2,5-dicarboxylate (3f):



Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.75 (1H, s), 7.62 (1H, d, J = 3.0 Hz), 7.59 (1H, dd, J =

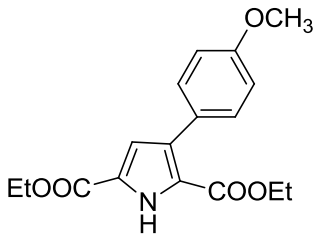
8.0, 1.0 Hz), 7.30 (1H, td, J = 7.5, 1.0 Hz), 7.25 (1H, dd, J = 7.5, 2.0 Hz), 7.18 (1H, m), 4.09 (4H, m), 1.06 (3H, t, J = 7.0 Hz), 1.00 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.6, 160.8, 136.0, 131.7, 131.2, 130.5, 128.6, 126.7, 126.3, 124.2, 121.4, 117.5, 60.6, 59.8, 13.9, 13.7. HRMS Calcd. For $C_{16}H_{16}BrNO_4 + H^+$: 366.0341, found: 366.0338.

Diethyl 3-(3-(trifluoromethyl)phenyl)-1H-pyrrole-2,5-dicarboxylate (3g):



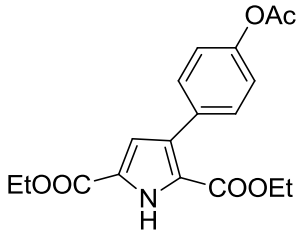
Yellow solid. m.p.: 49 – 51 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.83 (1H, s), 7.63 (1H, d, J = 3.5 Hz), 7.59 (2H, m), 7.52 (1H, d, J = 7.5 Hz), 7.46 (1H, t, J = 7.5 Hz), 4.11 (4H, m), 1.08 (3H, t, J = 7.0 Hz), 1.02 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.7, 161.0, 134.7, 133.7, 130.3, 129.4 (q, J = 32 Hz), 127.3, 127.2, 124.4 (q, J = 271 Hz), 123.8 (q, J = 4 Hz), 122.3, 121.3, 117.2, 60.9, 60.0, 13.9, 13.6. HRMS Calcd. For $C_{17}H_{16}F_3NO_4 + H^+$: 356.1110, found: 356.1104.

Diethyl 3-(4-methoxyphenyl)-1H-pyrrole-2,5-dicarboxylate (3h):



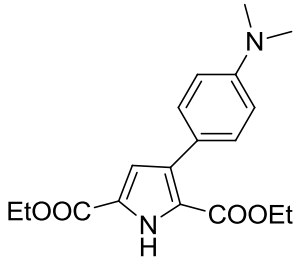
Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.67 (1H, s), 7.58 (1H, d, J = 3.5 Hz), 7.29 (2H, d, J = 9.0 Hz), 6.91 (2H, d, J = 9.0 Hz), 4.16 (4H, m), 3.84 (3H, s), 1.18 (3H, t, J = 7.0 Hz), 1.13 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.9, 161.0, 158.8, 132.3, 131.4, 126.9, 125.6, 120.8, 117.0, 112.5, 60.5, 59.8, 55.2, 14.2, 14.0. HRMS Calcd. For $C_{17}H_{19}NO_5 + H^+$: 318.1341, found: 318.1340.

Diethyl 3-(4-acetoxyphenyl)-1H-pyrrole-2,5-dicarboxylate (3i):



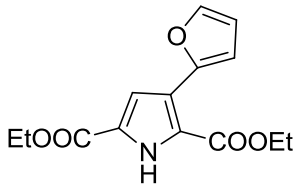
Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.73 (1H, s), 7.59 (1H, d, J = 3.5 Hz), 7.32 (2H, d, J = 8.5 Hz), 7.07 (2H, d, J = 8.5 Hz), 4.12 (4H, m), 2.30 (3H, s), 1.12 (3H, t, J = 7.0 Hz), 1.07 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.4, 163.9, 161.1, 149.9, 131.5, 131.2, 131.1, 127.0, 121.2, 120.1, 117.3, 60.7, 59.9, 21.2, 13.9, 13.7. HRMS Calcd. For $C_{18}H_{19}NO_6 + H^+$: 346.1291, found: 346.1287.

Diethyl 3-(4-(dimethylamino)phenyl)-1H-pyrrole-2,5-dicarboxylate (3j):



Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.45 (1H, s), 7.57 (1H, d, J = 3.5 Hz), 7.27 (2H, d, J = 8.5 Hz), 6.75 (2H, d, J = 8.5 Hz), 4.19 (4H, m), 2.98 (6H, s), 1.20 (3H, t, J = 7.0 Hz),1.18 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.9, 160.9, 149.9, 133.1, 131.2, 126.9, 120.9, 120.5, 116.9, 111.3, 60.4, 59.7, 40.7, 14.2, 14.1. HRMS Calcd. For $C_{18}H_{22}N_2O_4$ + H^+: 331.1658, found: 331.1652.

Diethyl 3-(furan-2-yl)-1H-pyrrole-2,5-dicarboxylate (3k):

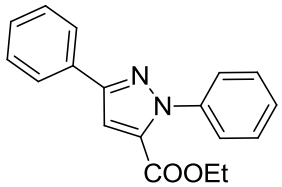


Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.78 (1H, s), 7.56 (1H, d, J = 3.5 Hz), 7.50 (1H, dd, J = 2.0, 1.0 Hz), 6.54 (1H, dd, J = 3.0, 1.0 Hz), 6.48 (1H, dd, J = 3.0, 2.0 Hz), 4.24 (2H, q, J = 7.0 Hz), 4.20 (2H, q, J = 7.0 Hz), 1.22 (6H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.5, 160.6, 145.4, 141.8, 126.9, 122.3, 120.3, 117.8, 110.9, 110.7, 60.9, 60.1, 14.2, 14.1. HRMS Calcd. For $C_{14}H_{15}NO_5$ + H^+: 278.1028, found: 278.1020.

VI. General Procedure for the Synthesis of Pyrazoles

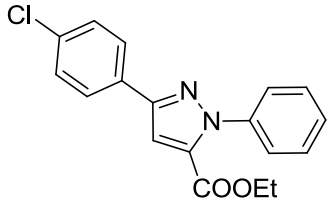
A mixture of MBHAs (0.3 mmol, 1.0 equiv) and phenylhydrazine (**9**, 0.3 mmol, 1.0 equiv) was stirred in MeOH (2 mL) at 65 ^{o}C overnight. Once starting material was consumed (monitored by TLC), the organic solvent was removed and the residue was purified by column chromatography (silica gel) to give the target compound.

Ethyl 1,3-diphenyl-1H-pyrazole-5-carboxylate (4a):[2]



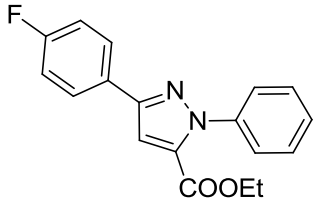
Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (2H, m), 7.45 (7H, m), 7.36 (1H, tt, J = 7.0, 1.5 Hz), 7.34 (1H, s), 4.27 (2H, q, J = 7.0 Hz), 1.27 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 151.5, 140.4, 134.7, 132.2, 128.8, 128.7, 128.6, 128.4, 126.1, 125.8, 109.4, 61.2, 14.1. HRMS Calcd. For $C_{18}H_{16}N_2O_2$ + H^+: 293.1290, found: 293.1282.

Ethyl 3-(4-chlorophenyl)-1-phenyl-1H-pyrazole-5-carboxylate (4b):



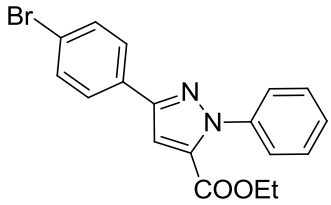
Yellow solid. m.p.: 61 – 63 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (2H, d, J = 8.5 Hz), 7.48 (5H, m), 7.39 (2H, d, J = 8.5 Hz), 7.30 (1H, s), 4.27 (2H, q, J = 7.0 Hz), 1.27 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.0, 150.4, 140.3, 134.9, 134.2, 130.7, 128.9, 128.8, 128.6, 127.1, 126.1, 109.3, 61.3, 14.0. HRMS Calcd. For $C_{18}H_{15}ClN_2O_2 + H^+$: 327.0900, found: 327.0898.

Ethyl 3-(4-fluorophenyl)-1-phenyl-1H-pyrazole-5-carboxylate (4c):



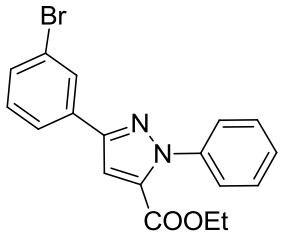
Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (2H, m), 7.48 (5H, m), 7.28 (1H, s), 7.11 (2H, t, J = 9.0 Hz), 4.27 (2H, q, J = 7.0 Hz), 1.27 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.9 (d, J = 245 Hz), 159.0, 150.6, 140.3, 134.8, 128.7, 128.6, 128.4 (d, J = 4 Hz), 127.5 (d, J = 8 Hz), 126.1, 115.7 (d, J = 21 Hz), 109.2, 61.3, 14.0. HRMS Calcd. For $C_{18}H_{15}FN_2O_2 + H^+$: 311.1196, found: 311.1189.

Ethyl 3-(4-bromophenyl)-1-phenyl-1H-pyrazole-5-carboxylate (4d):



Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (2H, d, J = 8.5 Hz), 7.55 (2H, d, J = 8.5 Hz), 7.48 (5H, m), 7.30 (1H, s), 4.27 (2H, q, J = 7.0 Hz), 1.26 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.0, 150.4, 140.3, 134.9, 131.9, 131.1, 128.8, 128.5, 127.3, 126.1, 122.4, 109.3, 61.3, 14.0. HRMS Calcd. For $C_{18}H_{15}BrN_2O_2 + H^+$: 371.0395, found: 371.0391.

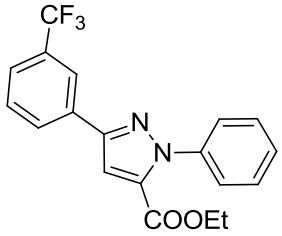
Ethyl 3-(3-bromophenyl)-1-phenyl-1H-pyrazole-5-carboxylate (4e):



Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (1H, t, J = 1.5 Hz), 7.79 (1H, d, J = 8.0 Hz), 7.48 (6H, m), 7.31 (1H, s), 7.29 (1H, t, J = 8.0 Hz), 4.27 (2H, q, J = 7.0 Hz), 1.27 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.9, 150.0, 140.2, 134.2, 131.3, 130.3, 129.0, 128.8, 128.7,

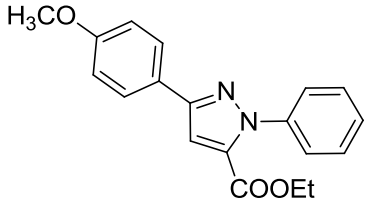
128.6, 128.2, 126.1, 124.3, 109.5, 61.3, 14.0. HRMS Calcd. For $C_{18}H_{15}BrN_2O_2 + H^+$: 371.0395, found: 371.0391.

Ethyl 1-phenyl-3-(3-(trifluoromethyl)phenyl)-1H-pyrazole-5-carboxylate (4f):



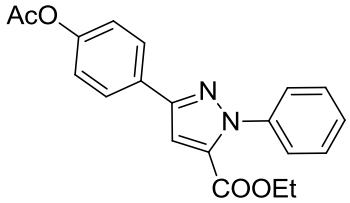
Yellow solid. m.p.: 96 – 98 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (1H, s), 8.06 (1H, d, J = 7.5 Hz), 7.61 (1H, d, J = 7.5 Hz), 7.54 (1H, t, J = 7.5 Hz), 7.49 (5H, m), 7.37 (1H, s), 4.28 (2H, q, J = 7.5 Hz), 1.28 (3H, t, J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.9, 150.0, 140.2, 135.0, 133.0, 131.2 (d, J = 32 Hz), 129.2, 128.9, 128.6, 128.2, 126.1, 124.9 (q, J = 4 Hz), 124.1 (q, J = 271 Hz), 122.5 (q, J = 4 Hz), 109.5, 61.4, 14.0. HRMS Calcd. For $C_{19}H_{15}F_3N_2O_2 + H^+$: 361.1164, found: 361.1155.

Ethyl 3-(4-methoxyphenyl)-1-phenyl-1H-pyrazole-5-carboxylate (4g):



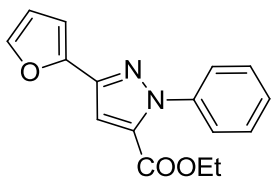
Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (2H, d, J = 9.0 Hz), 7.47 (5H, m), 7.26 (1H, s), 6.95 (2H, d, J = 9.0 Hz), 4.26 (2H, q, J = 7.0 Hz), 3.84 (3H, s), 1.26 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.8, 159.2, 151.3, 140.4, 134.6, 128.6, 128.5, 127.1, 126.1, 124.9, 114.1, 108.9, 61.2, 55.3, 14.0. HRMS Calcd. For $C_{19}H_{18}N_2O_2 + H^+$: 323.1396, found: 323.1394.

Ethyl 3-(4-acetoxyphenyl)-1-phenyl-1H-pyrazole-5-carboxylate (4h):



Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (2H, d, J = 8.5 Hz), 7.48 (5H, m), 7.29 (1H, s), 7.16 (2H, d, J = 8.5 Hz), 4.26 (2H, q, J = 7.0 Hz), 2.31 (3H, s), 1.26 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.4, 159.1, 150.8, 150.7, 140.3, 134.8, 129.9, 128.7, 128.6, 126.9, 126.1, 121.9, 109.3, 61.2, 21.2, 14.0. HRMS Calcd. For $C_{20}H_{18}N_2O_2 + H^+$: 351.1345, found: 351.1338.

Ethyl 3-(furan-2-yl)-1-phenyl-1H-pyrazole-5-carboxylate (4i):

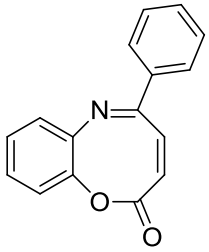


Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (6H, m), 7.24 (1H, s), 6.78 (1H, d, J = 3.0 Hz), 6.49 (1H, dd, J = 3.0, 2.0 Hz), 4.25 (2H, q, J = 7.0 Hz), 1.26 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.9, 147.6, 144.1, 142.4, 140.1, 134.4, 128.8, 128.6, 126.2, 111.5, 109.1, 106.8, 61.3, 14.0. HRMS Calcd. For $C_{16}H_{14}N_2O_3 + H^+$: 283.1083, found: 283.1080.

VII. General Procedure for the Synthesis of Benzo[b][1,6]oxazocin-2-ones

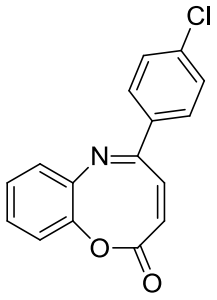
A mixture of MBHAs (0.3 mmol, 1.0 equiv) and 2-aminophenol (**10**, 0.3 mmol, 1.0 equiv) was stirred in MeOH (2 mL) at room temperature for 15 min. Then Na_2CO_3 (0.3 mmol, 1.0 equiv) was added and the mixture was heated to 40 ^{o}C for 2h. Once the starting MBHAs disappeared, the organic solvent was removed and the residue was purified by column chromatography (silica gel) to give the product.

(3Z,5E)-5-Phenyl-2H-benzo[b][1,6]oxazocin-2-one (5a):



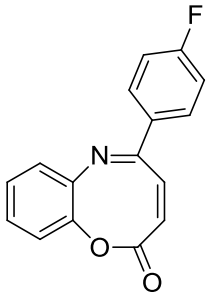
Yellow solid. m.p.: 151 – 153 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (1H, d, J = 16.5 Hz), 7.77 (1H, d, J = 7.5 Hz), 7.67 (2H, d, J = 7.0 Hz), 7.53 (1H, d, J = 16.5 Hz), 7.47 (1H, t, J = 7.0 Hz), 7.40 (4H, m), 7.30 (1H, d, J = 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.1, 149.6, 146.0, 140.4, 135.8, 131.9, 130.6, 129.9, 129.0, 128.9, 128.1, 125.7, 121.2, 116.3. HRMS Calcd. For $C_{16}H_{11}NO_2 + H^+$: 250.0868, found: 250.0867.

(3Z,5E)-5-(4-Chlorophenyl)-2H-benzo[b][1,6]oxazocin-2-one (5b):



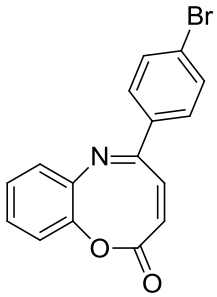
Yellow solid. m.p.: 148 – 150 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (1H, d, J = 16.5 Hz), 7.77 (1H, dd, J = 8.0, 1.5 Hz), 7.59 (2H, dt, J = 9.0, 2.0 Hz), 7.48 (2H, m), 7.37 (3H, m), 7.31 (1H, dd, J = 8.5, 1.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.0, 149.4, 146.1, 138.9, 135.8, 134.4, 131.9, 130.7, 129.2, 129.0, 125.7, 121.8, 116.3. HRMS Calcd. For $C_{16}H_{10}ClNO_2 + H^+$: 284.0478, found: 284.0468.

(3Z,5E)-5-(4-Fluorophenyl)-2H-benzo[b][1,6]oxazocin-2-one (5c):



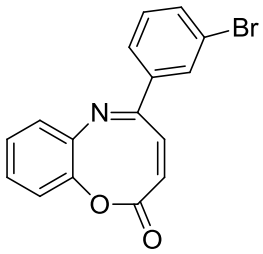
Yellow solid. m.p.: 141 – 143 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (1H, d, J = 16.5 Hz), 7.76 (1H, dd, J = 16.5 Hz), 7.64 (2H, m), 7.47 (1H, td, J = 8.5, 2.0 Hz), 7.43 (1H, d, J = 16.5 Hz), 7.37 (1H, m), 7.30 (1H, dd, J = 8.0, 1.0 Hz), 7.10 (2H, t, J = 8.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.7 (d, J = 249 Hz), 153.1, 149.4, 146.0, 139.1, 132.0 (d, J = 3 Hz), 131.9, 130.6 129.9 (d, J = 8 Hz), 128.9, 125.7, 120.9 (d, J = 2 Hz), 116.3, 116.1 (d, J = 22 Hz) . HRMS Calcd. For $C_{16}H_{10}FNO_2 + H^+$: 268.0774, found: 268.0771.

(3Z,5E)-5-(4-Bromophenyl)-2H-benzo[b][1,6]oxazocin-2-one (5d):



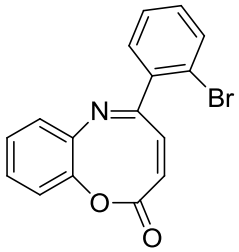
Yellow solid. m.p.: 137 – 139 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (1H, d, J = 16.5 Hz), 7.76 (1H, dd, J = 8.0, 1.0 Hz), 7.50 (6H, m), 7.38 (1H, t, J = 7.5 Hz), 7.30 (1H, d, J = 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.0, 149.3, 146.0, 138.9, 134.7, 132.2, 131.9, 130.8, 129.4, 129.0, 125.7, 124.1, 121.8, 116.4. HRMS Calcd. For $C_{16}H_{10}BrNO_2 + H^+$: 327.9973, found: 327.9969.

(3Z,5E)-5-(3-Bromophenyl)-2H-benzo[b][1,6]oxazocin-2-one (5e):



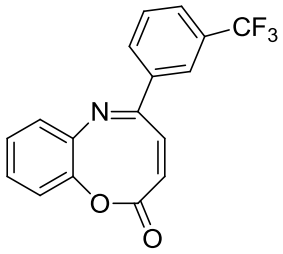
Yellow solid. m.p.: >250 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (1H, d, J = 16.5 Hz), 7.78 (2H, m), 7.57 (1H, d, J = 7.5 Hz), 7.48 (3H, m), 7.39 (1H, t, J = 7.5 Hz), 7.28 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.0, 149.1, 146.1, 138.6, 137.8, 132.6, 131.9, 130.9, 130.7, 130.4, 129.1, 126.6, 125.7, 123.1, 122.5, 116.3. HRMS Calcd. For $C_{16}H_{10}BrNO_2 + H^+$: 327.9973, found: 327.9969.

(3Z,5E)-5-(2-Bromophenyl)-2H-benzo[b][1,6]oxazocin-2-one (5f):



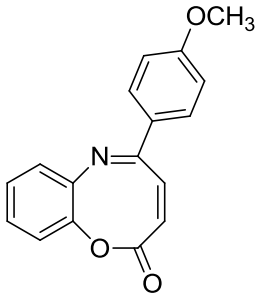
Yellow solid. m.p.: 148 – 150 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50 (1H, d, J = 16.0 Hz), 7.82 (1H, dd, J = 8.0, 1.0 Hz), 7.79 (1H, dd, J = 8.0, 1.0 Hz), 7.63 (1H, dd, J = 8.0, 1.0 Hz), 7.48 (2H, m), 7.38 (2H, m), 7.31 (1H, dd, J = 8.0, 1.0 Hz), 7.23 (1H, td, J = 8.0, 1.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.1, 149.3, 146.1, 138.6, 135.7, 133.4, 131.9, 130.9, 130.8, 129.3, 127.7, 127.6, 125.7, 125.6, 123.6, 116.3. HRMS Calcd. For $C_{16}H_{10}BrNO_2 + H^+$: 327.9973, found: 327.9969.

(3Z,5E)-5-(3-(Trifluoromethyl)phenyl)-2H-benzo[b][1,6]oxazocin-2-one (5g):



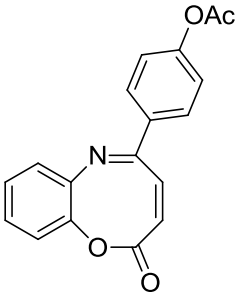
Yellow solid. m.p.: 158 – 160 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (1H, d, J = 16.0 Hz), 7.90 (1H, s), 7.83 (1H, d, J = 7.5 Hz), 7.79 (1H, dd, J = 8.0, 1.5 Hz), 7.62 (1H, d, J = 7.5 Hz), 7.52 (3H, m), 7.40 (1H, td, J = 7.5, 1.0 Hz), 7.32 (1H, dd, J = 8.0, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.0, 149.1, 146.1, 138.6, 136.5, 131.9, 131.5 (d, J = 32 Hz), 131.1, 130.9, 129.4, 129.2, 126.2 (q, J = 4 Hz), 125.8, 124.7 (q, J = 4 Hz), 123.9 (q, J = 271 Hz), 122.9, 116.4. HRMS Calcd. For $C_{17}H_{10}F_3NO_2 + H^+$: 318.0742, found: 318.0733.

(3Z,5E)-5-(4-Methoxyphenyl)-2H-benzo[b][1,6]oxazocin-2-one (5h):



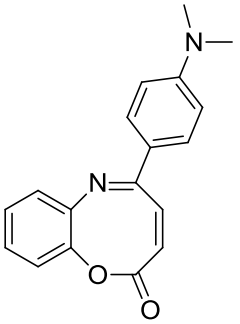
Yellow solid. m.p.: 166 – 168 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (1H, d, J = 16.0 Hz), 7.75 (1H, dd, J = 8.0, 1.5 Hz), 7.62 (2H, d, J = 8.5 Hz), 7.44 (1H, td, J = 7.5, 1.5 Hz), 7.40 (1H, d, J = 16.0 Hz), 7.36 (1H, td, J = 8.0, 1.5 Hz), 7.29 (1H, dd, J = 8.5, 1.0 Hz), 6.94 (2H, d, J = 8.5 Hz), 3.85 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.2, 153.3, 149.8, 145.9, 140.1, 132.5, 132.1, 130.1, 129.8, 128.7, 125.6, 118.8, 116.3, 114.5, 55.4. HRMS Calcd. For $C_{17}H_{13}NO_3 + H^+$: 280.0974, found: 280.0972.

4-((3Z,5E)-2-Oxo-2H-benzo[b][1,6]oxazocin-5-yl)phenyl acetate (5i):



Yellow solid. m.p.: 169 – 171 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (1H, d, J = 16.0 Hz), 7.77 (1H, dd, J = 8.0, 1.5 Hz), 7.68 (2H, d, J = 8.5 Hz), 7.47 (2H, m), 7.38 (1H, td, J = 8.0, 1.0 Hz), 7.30 (1H, dd, J = 8.0, 1.0 Hz), 7.15 (2H, d, J = 8.5 Hz), 2.32 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.2, 153.1, 151.8, 149.5, 146.0, 139.3, 133.6, 131.9, 130.6, 129.2, 128.9, 125.7, 122.2, 121.3, 116.3, 21.2. HRMS Calcd. For $C_{18}H_{13}NO_4 + H^+$: 308.0923, found: 308.0920.

(3Z,5E)-5-(4-(Dimethylamino)phenyl)-2H-benzo[b][1,6]oxazocin-2-one (5j):

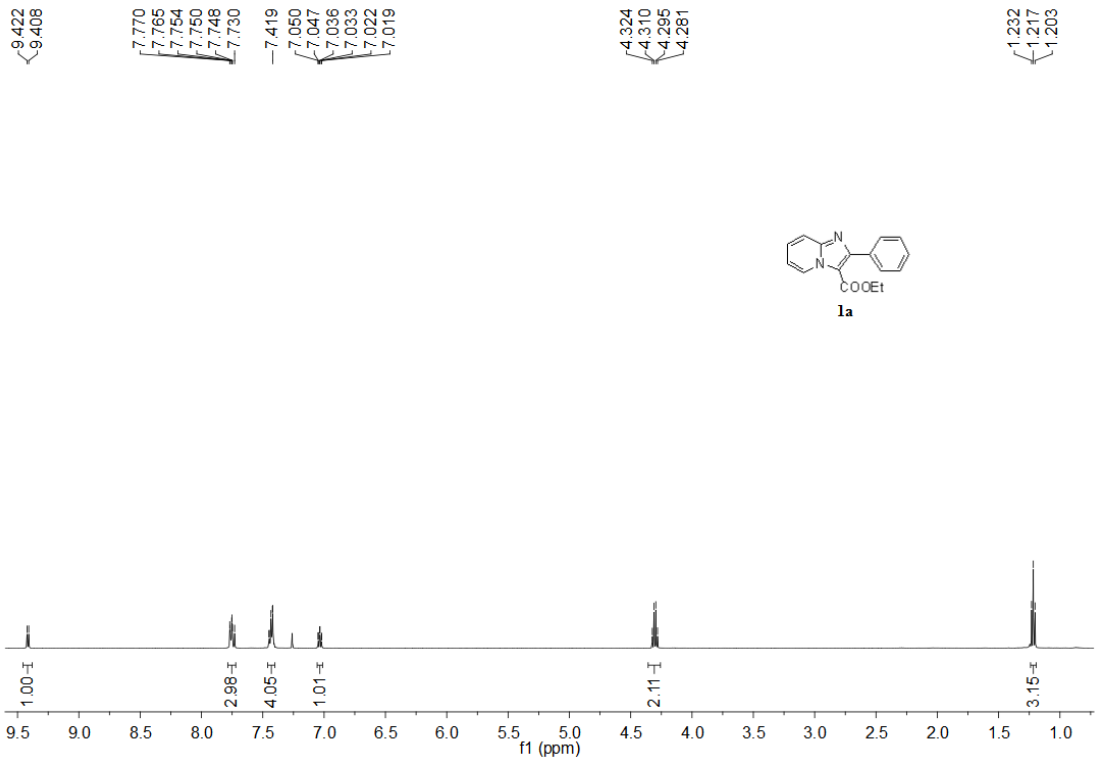


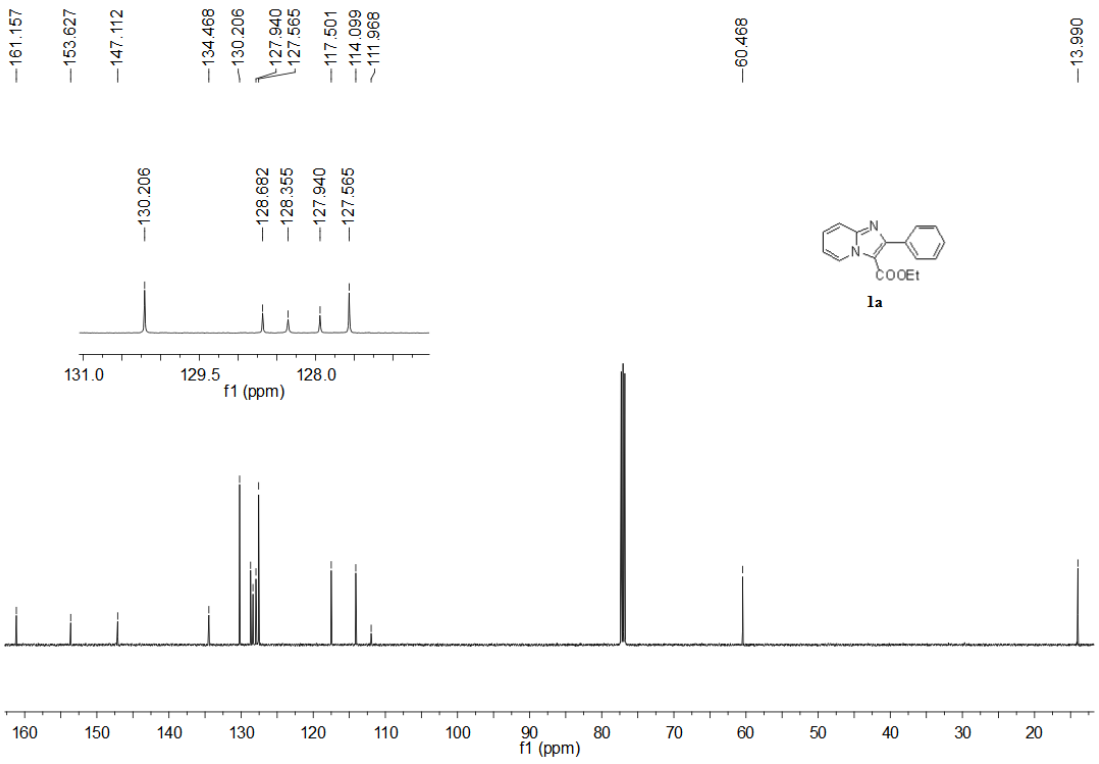
Yellow solid. m.p.: 70 – 72 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (1H, d, J = 16.0 Hz), 7.72 (1H, dd, J = 8.0, 1.5 Hz), 7.57 (2H, d, J = 9.0 Hz), 7.39 (1H, td, J = 8.0, 1.5 Hz), 7.33 (2H, m), 7.27 (1H, m), 6.70 (2H, d, J = 9.0 Hz), 3.04 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.6, 151.6, 150.0, 145.8, 141.0, 132.4, 130.0, 129.3, 128.3, 125.5, 123.9, 116.2, 115.8, 111.9, 40.2. HRMS Calcd. For $C_{18}H_{16}N_2O_2 + H^+$: 293.1290, found: 293.1285.

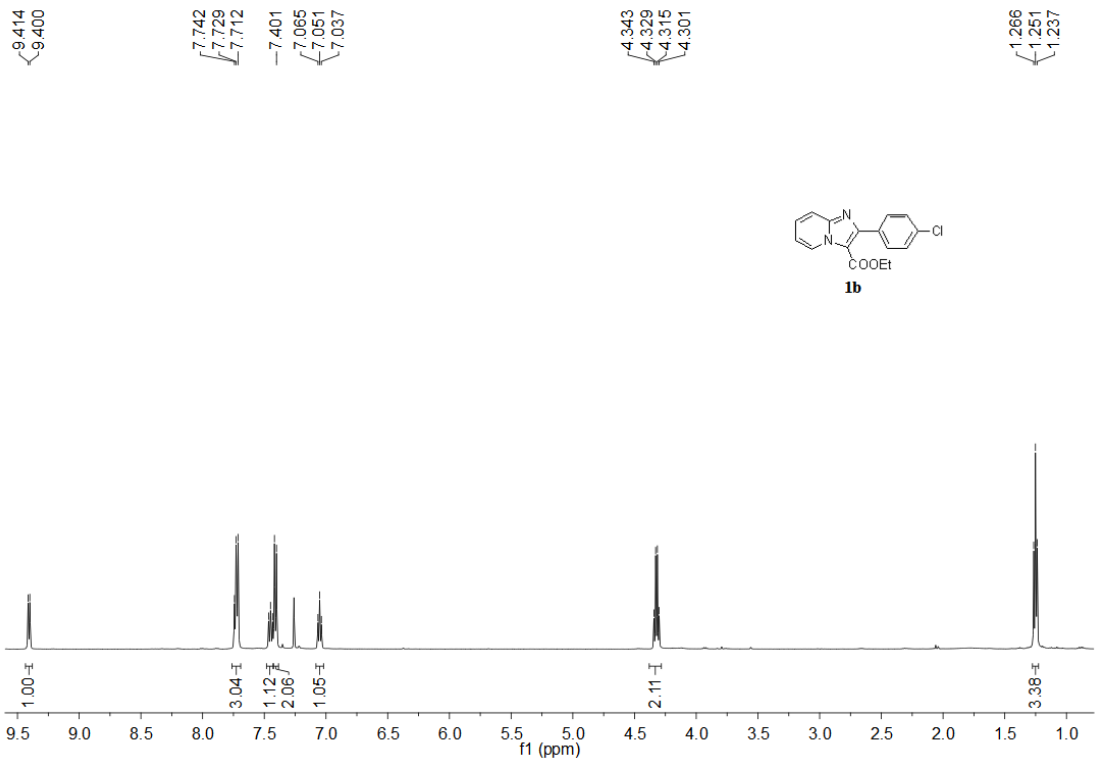
VIII. Reference

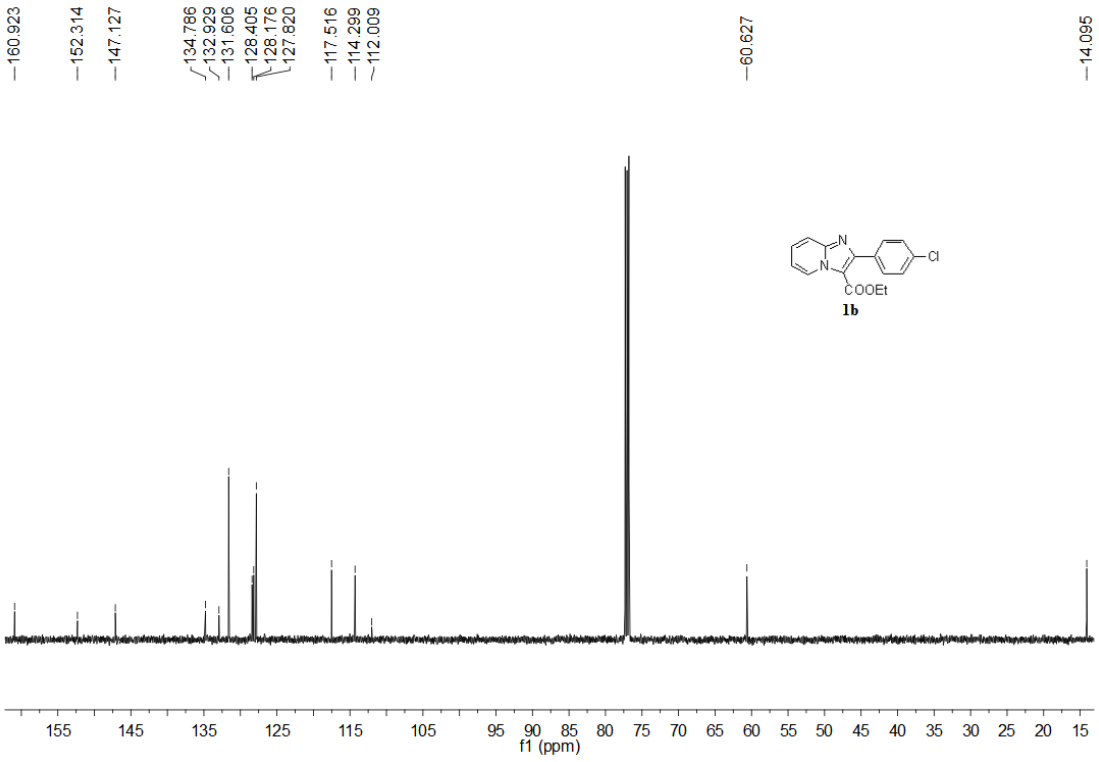
1 Kuan, H. H.; Reddy, R. J.; Chen, K. *Tetrahedron*, **2010**, *66*, 9875 – 9879.
2 Yang, X.; Shui, S.; Chen, X.; He, H.; Wu, F. *Journal of Fluorine Chemistry*, **2010**, *131*, 426 – 432.

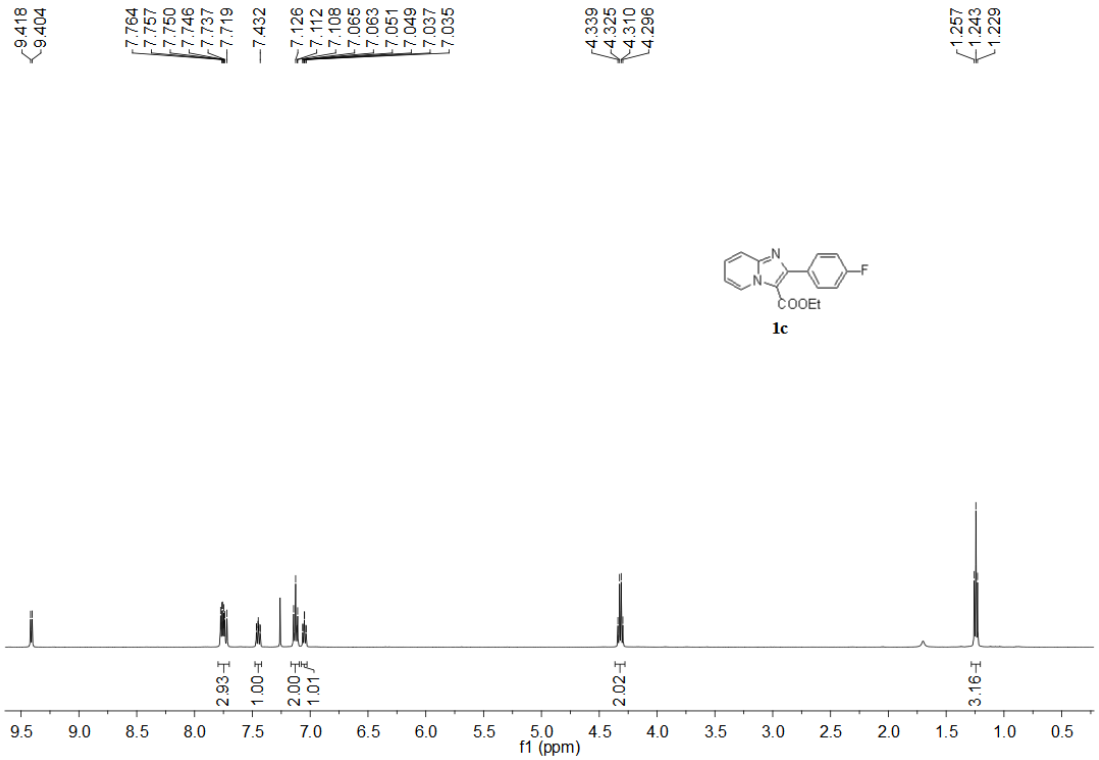
IX. ^{1}H NMR and ^{13}C NMR Spectra.

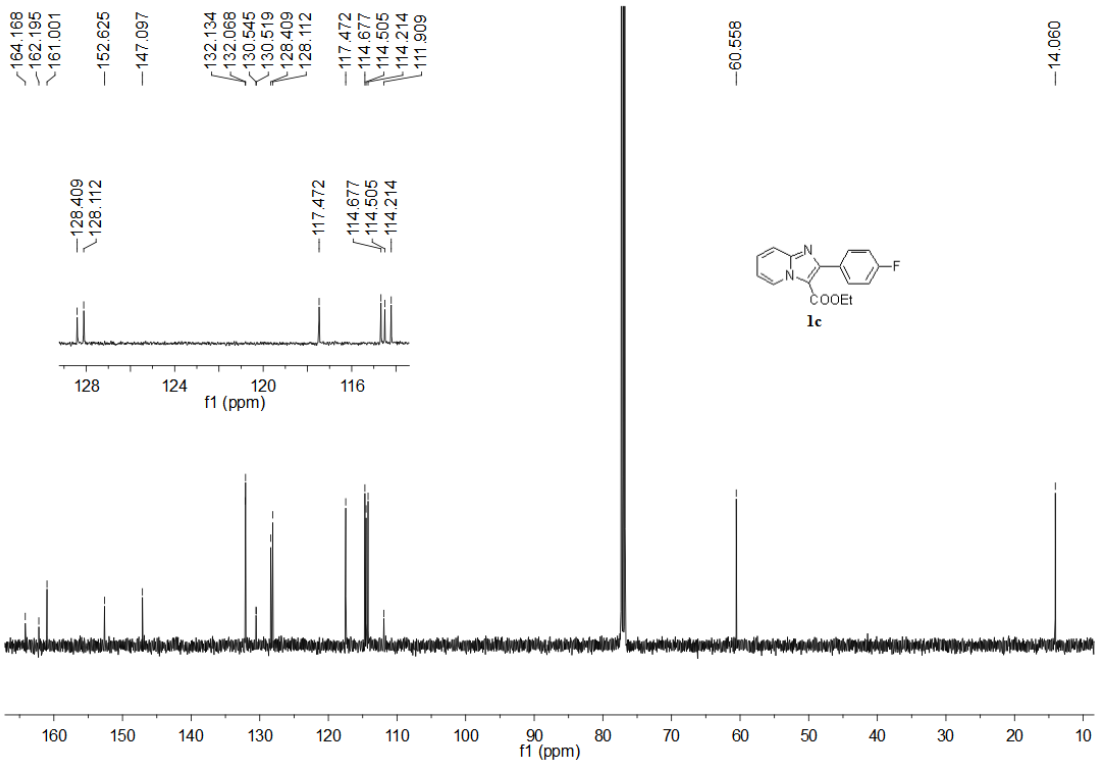





9.414
9.400
7.742
7.729
7.712
7.401
7.065
7.051
7.037
4.343
4.329
4.315
4.301
1.266
1.251
1.237
Cl
COOEt
1b
1.00
3.04
1.12
2.06
1.05
2.11
3.38
f1 (ppm)


160.923
152.314
147.127
134.786
132.929
131.606
128.405
128.176
127.820
117.516
114.299
112.009
60.627
14.095
Cl
COOEt
1b
f1 (ppm)


9.418
9.404
7.764
7.757
7.750
7.746
7.737
7.719
7.432
7.126
7.112
7.108
7.065
7.063
7.051
7.049
7.037
7.035
4.339
4.325
4.310
4.296
1.257
1.243
1.229
N
N
F
COOEt
1c
2.93
1.00
2.00
1.01
2.02
3.16
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
f1 (ppm)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161.001
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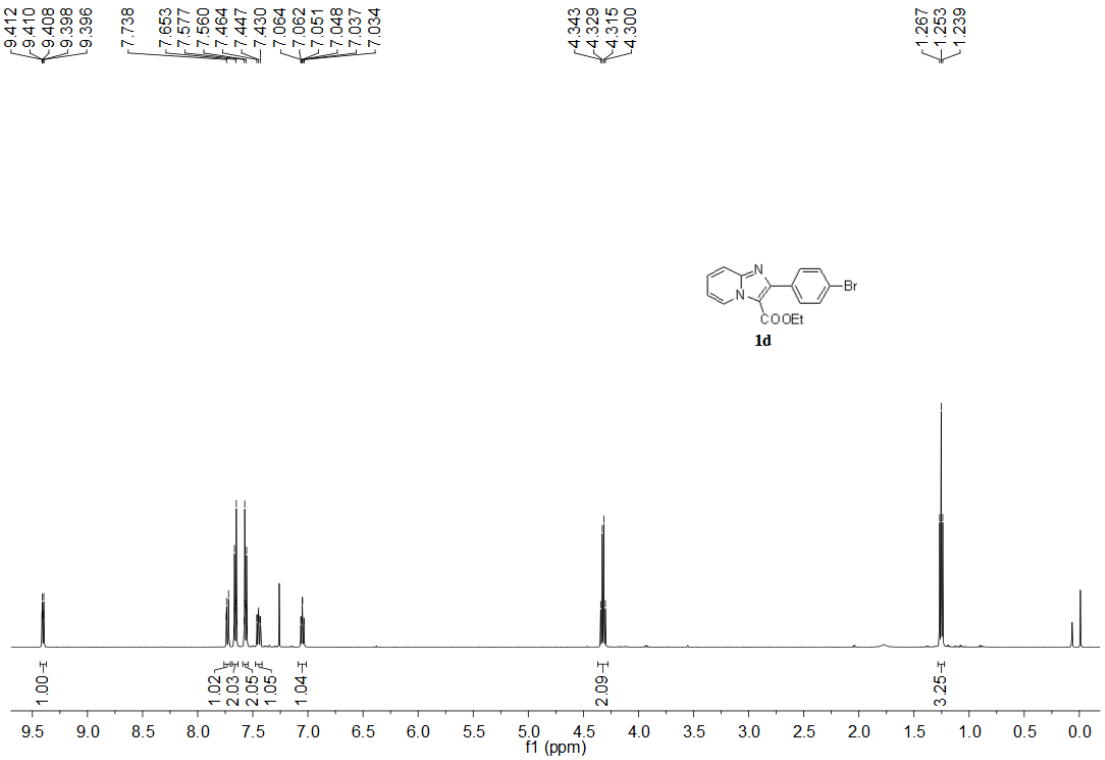
147.097
132.134
132.068
130.545
130.519
128.409
128.112
117.472
114.677
114.505
114.214
111.909
60.558
14.060
128.409
128.112
117.472
114.677
114.505
114.214
128 124 120 116
f1 (ppm)
N
N
F
COOEt
1c
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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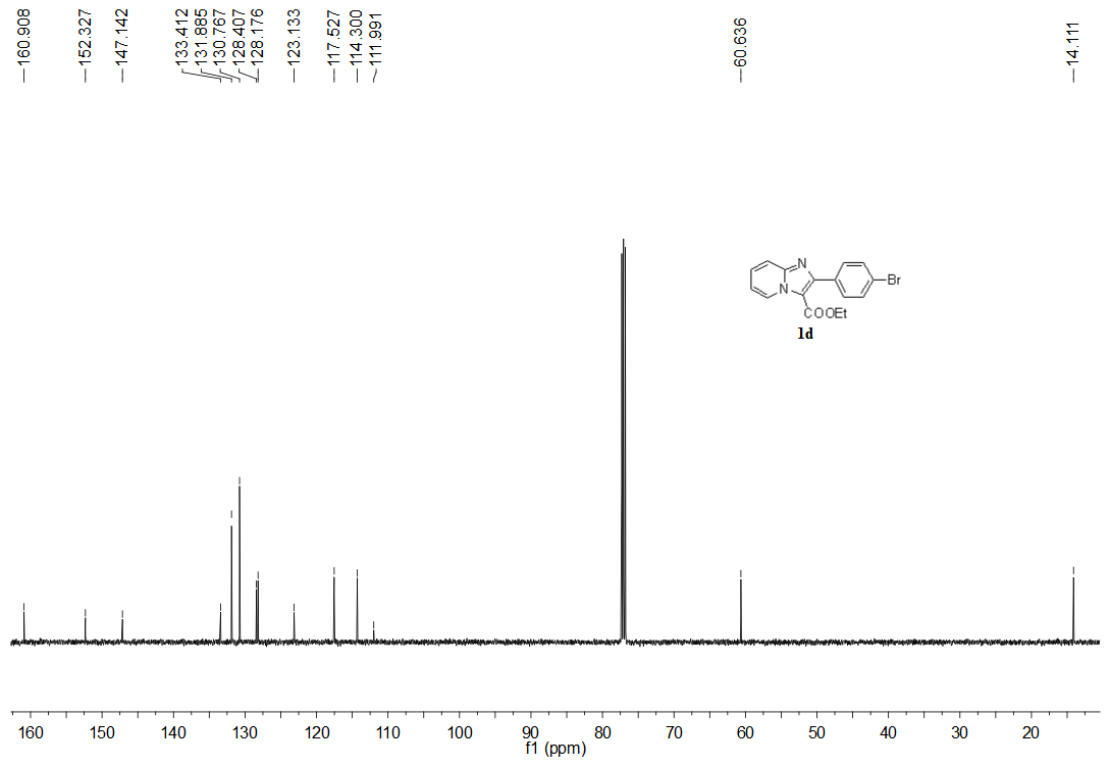
9.410
9.408
9.398
9.396
7.738
7.653
7.577
7.560
7.464
7.447
7.430
7.064
7.062
7.051
7.048
7.037
7.034
4.343
4.329
4.315
4.300
1.267
1.253
1.239
Br
N
COOEt
1d
1.00
1.02
2.03
2.05
1.05
1.04
2.09
3.25
f1 (ppm)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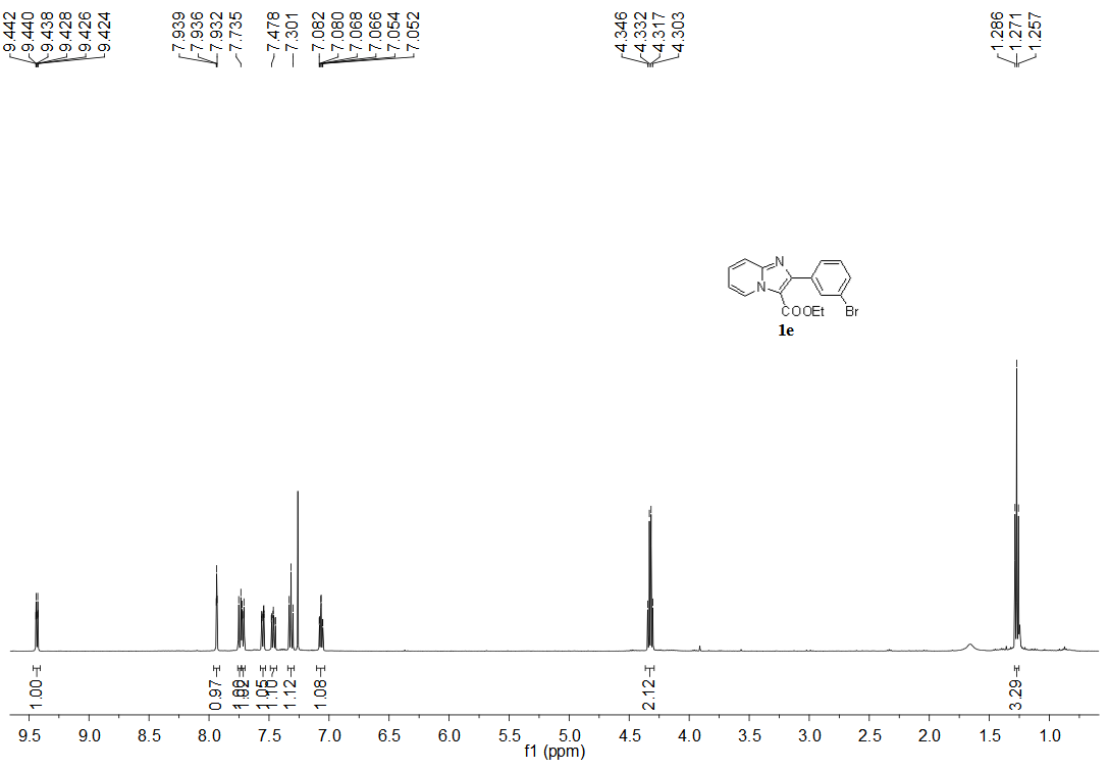
152.327
147.142
133.412
131.885
130.767
128.407
128.176
123.133
117.527
114.300
111.991
60.636
14.111
Br
N
COOEt
1d
f1 (ppm)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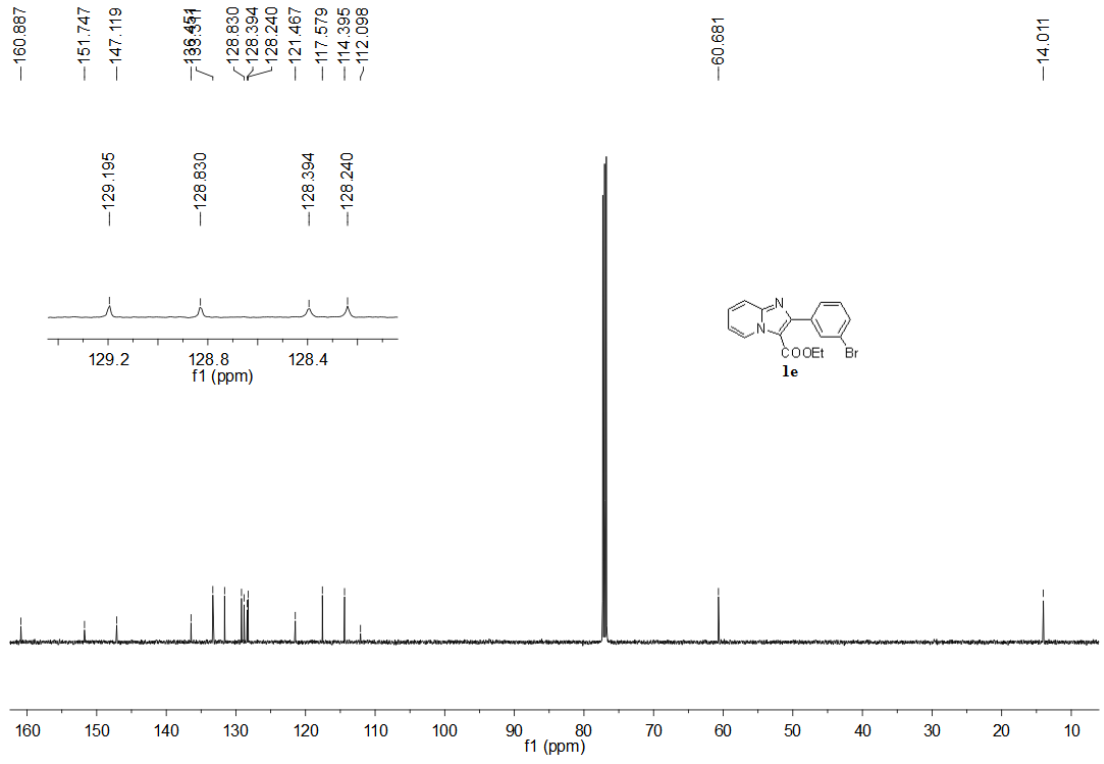
9.440
9.438
9.428
9.426
9.424
7.939
7.936
7.932
7.735
7.478
7.301
7.082
7.080
7.068
7.066
7.054
7.052
4.346
4.332
4.317
4.303
1.286
1.271
1.257
COOEt
Br
1e
1.00
0.97
1.12
1.08
2.12
3.29
f1 (ppm)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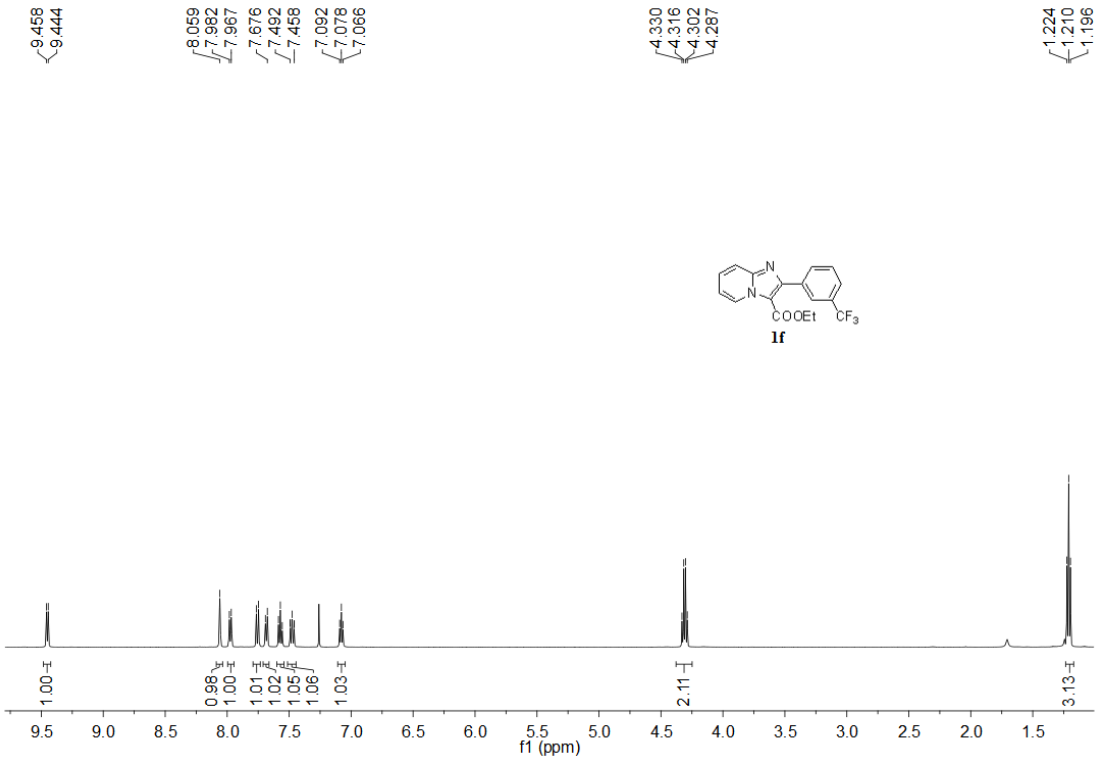
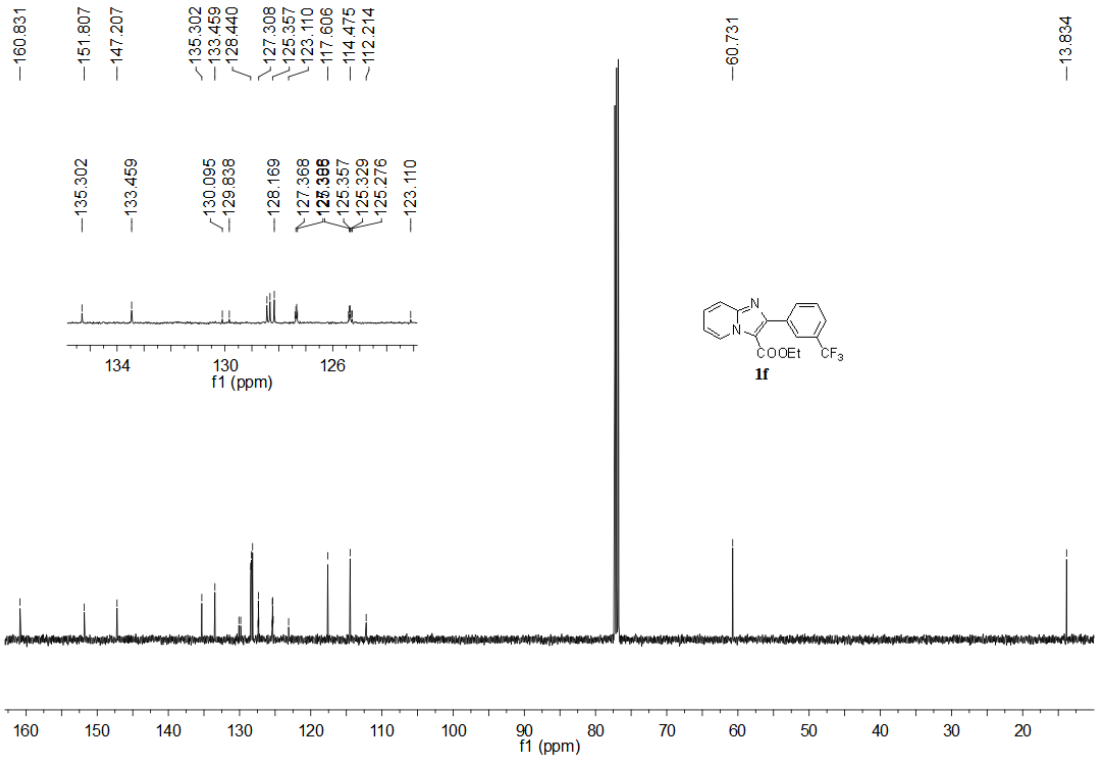
151.747
147.119
128.830
128.394
128.240
121.467
117.579
114.395
112.098
60.681
14.011
129.195
128.830
128.394
128.240
129.2
128.8
128.4
f1 (ppm)
COOEt
Br
1e
f1 (ppm)


9.458
9.444
8.059
7.982
7.967
7.676
7.492
7.458
7.092
7.078
7.066
4.330
4.316
4.302
4.287
1.224
1.210
1.196
COOEt
CF3
1f
1.00
0.98
1.00
1.01
1.02
1.05
1.06
1.03
2.11
3.13
f1 (ppm)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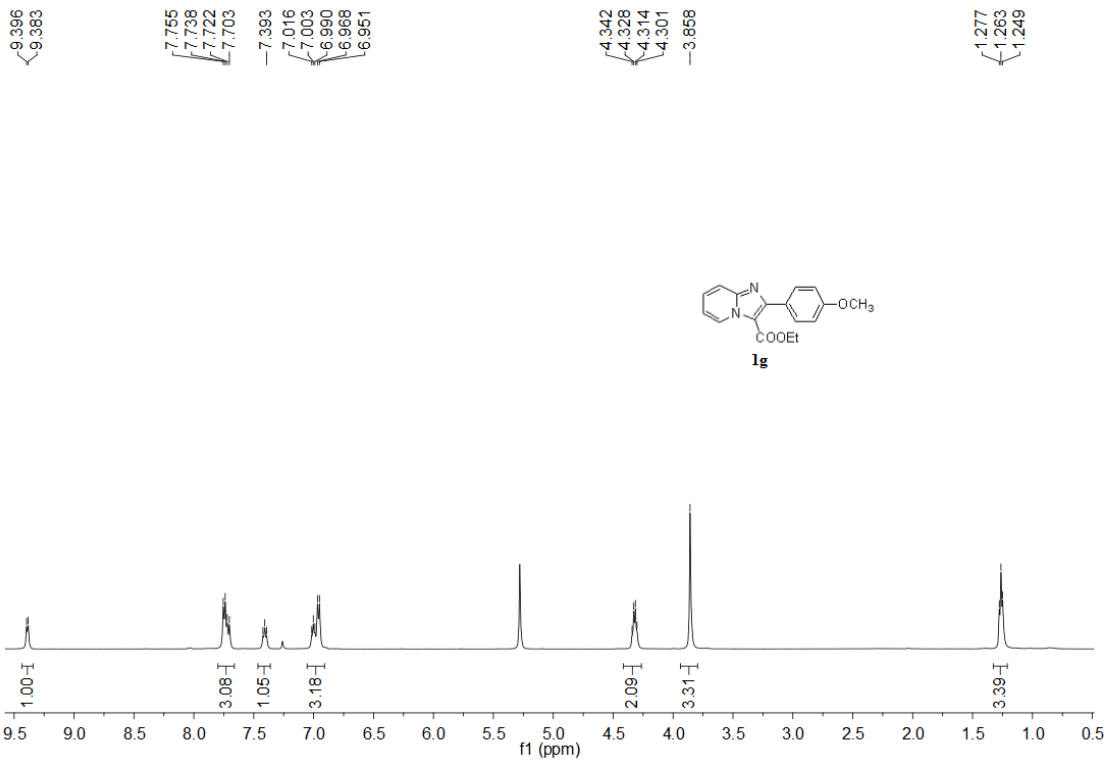
151.807
147.207
135.302
133.459
128.440
127.308
125.357
123.110
117.606
114.475
112.214
60.731
13.834
130.095
129.838
128.169
127.368
125.366
125.357
125.329
125.276
COOEt
CF3
1f
f1 (ppm)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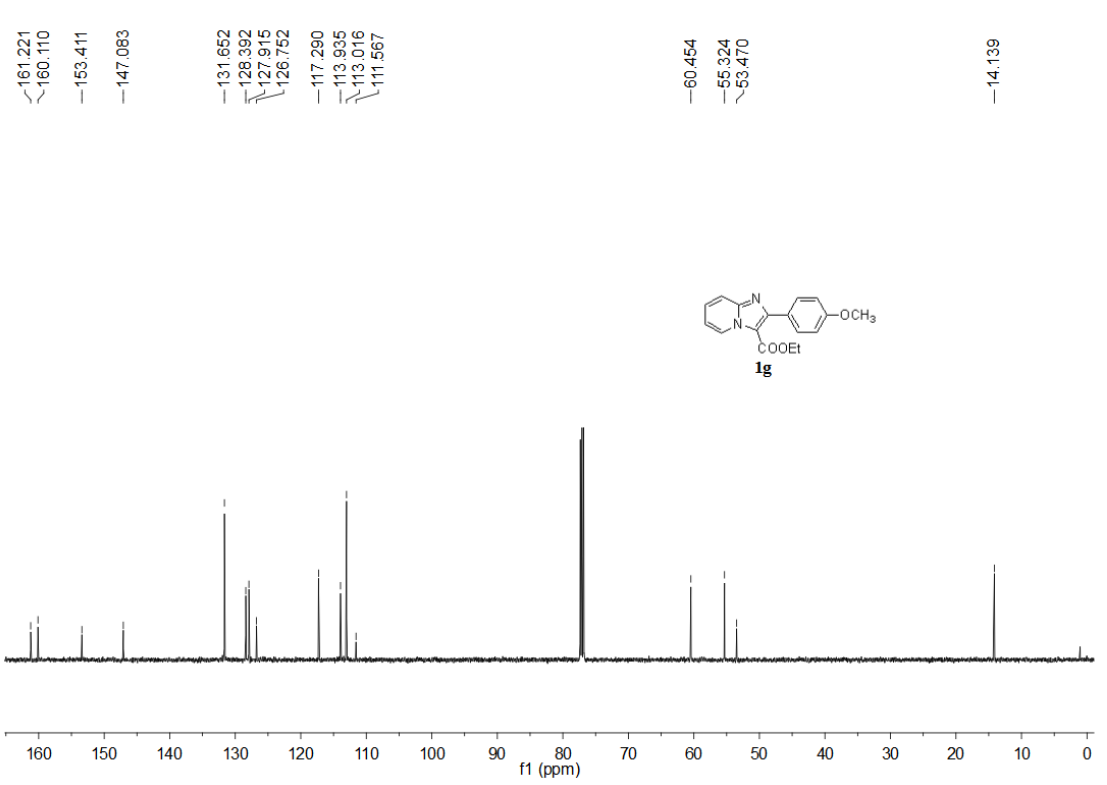
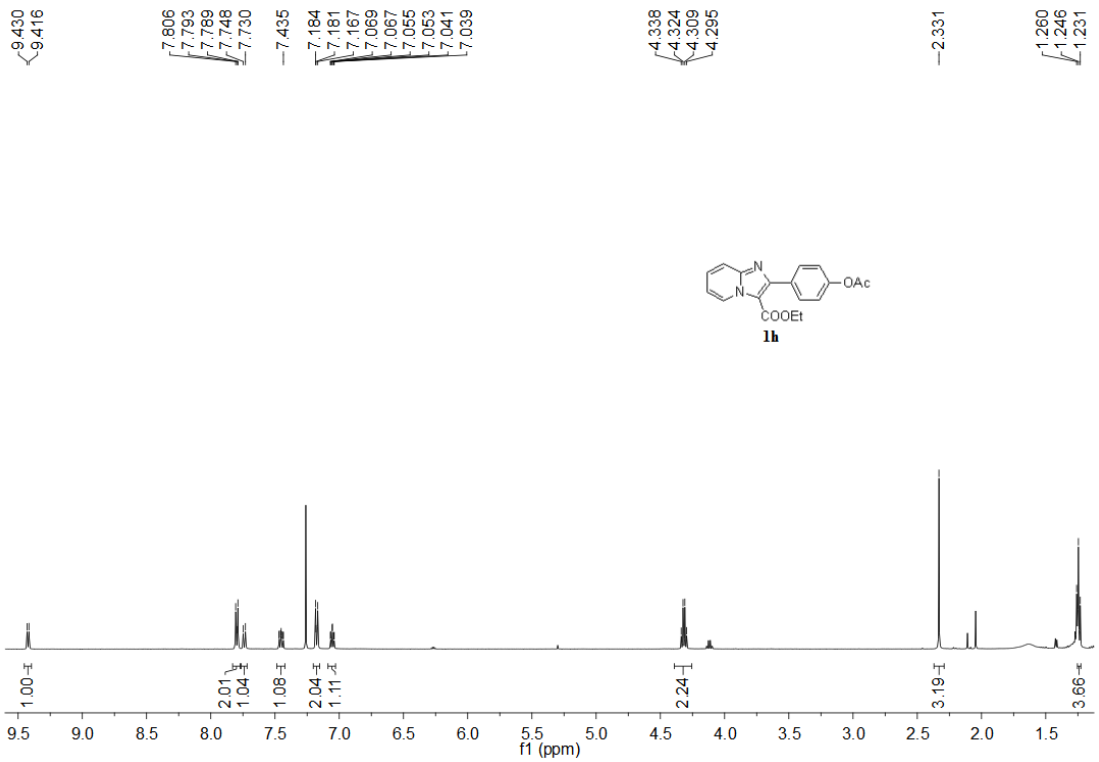
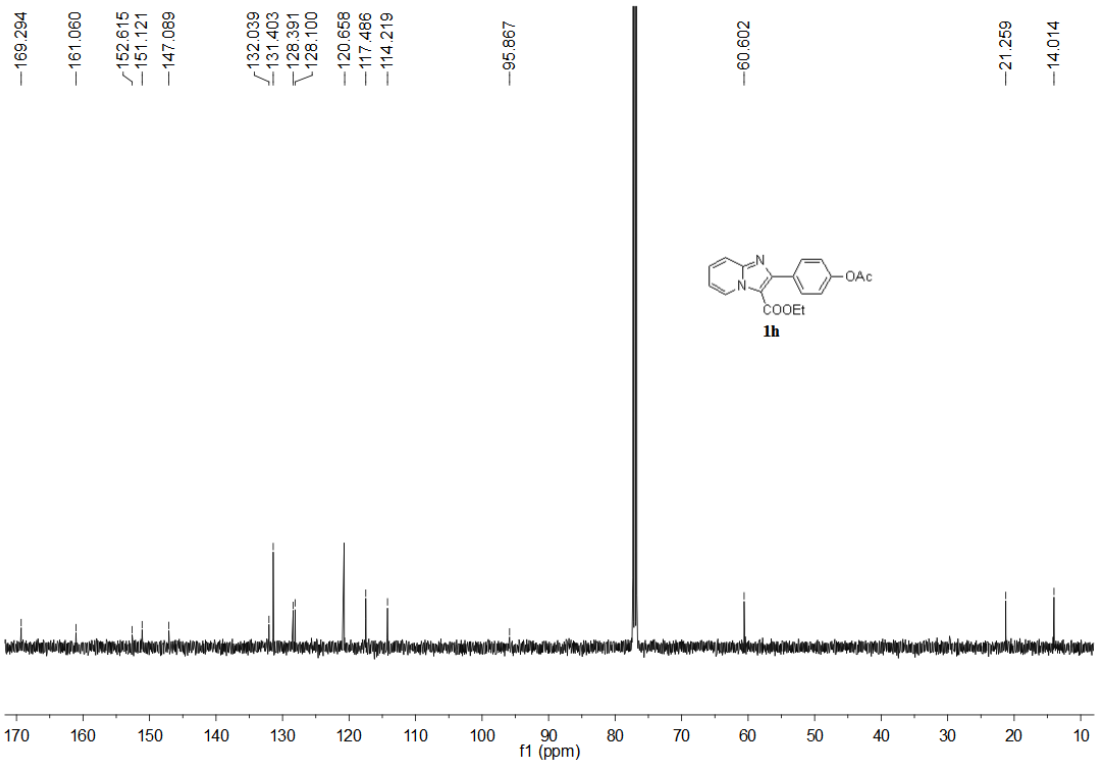
9.383
7.755
7.738
7.722
7.703
7.393
7.016
7.003
6.990
6.968
6.951
4.342
4.328
4.314
4.301
3.858
1.277
1.263
1.249
OCH3
COOEt
1g
1.00
3.08
1.05
3.18
2.09
3.31
3.39
f1 (ppm)


161.221
160.110
153.411
147.083
131.652
128.392
127.915
126.752
117.290
113.935
113.016
111.567
60.454
55.324
53.470
14.139
OCH3
COOEt
1g
f1 (ppm)


9.430
9.416
7.806
7.793
7.789
7.748
7.730
7.435
7.184
7.181
7.167
7.069
7.067
7.055
7.053
7.041
7.039
4.338
4.324
4.309
4.295
2.331
1.260
1.246
1.231
OAc
COOEt
1h
1.00
2.01
1.04
1.08
2.04
1.11
2.24
3.19
3.66
f1 (ppm)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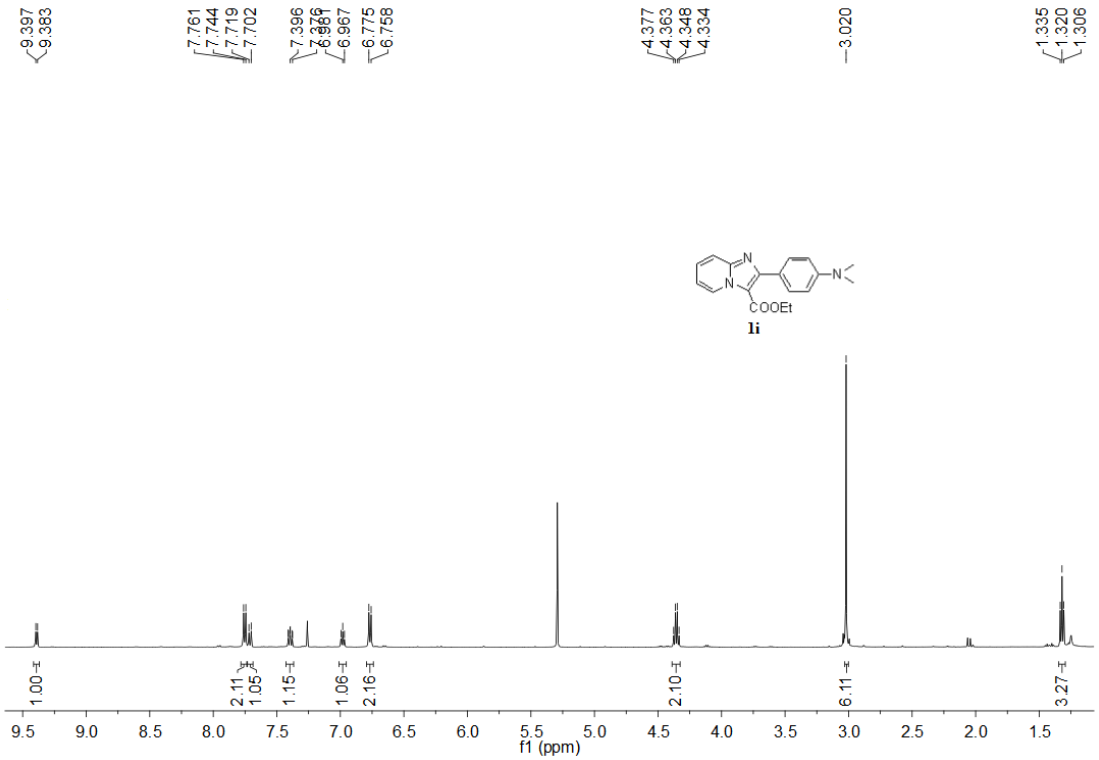
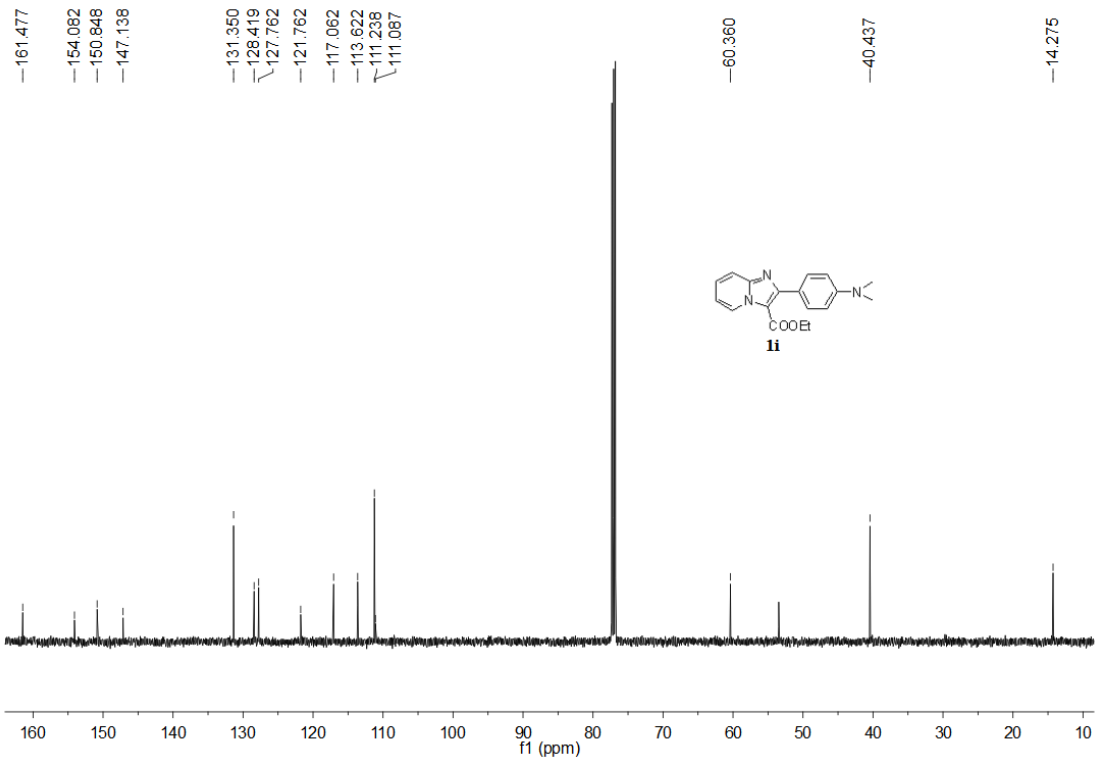
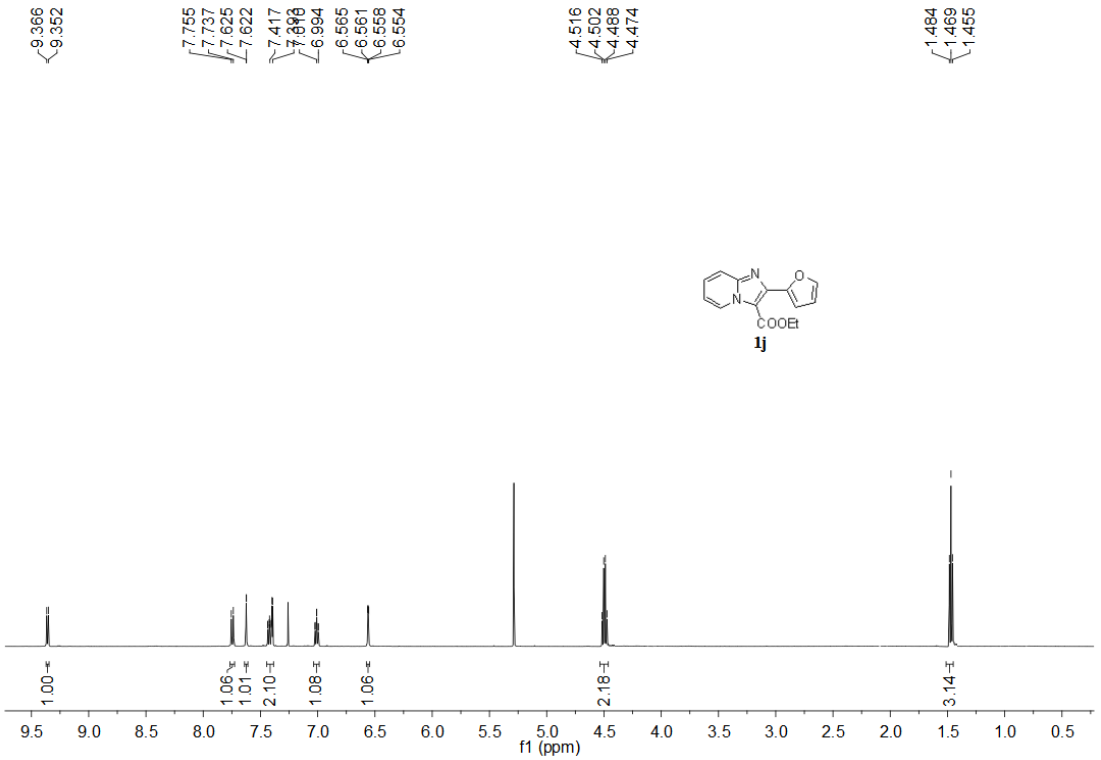
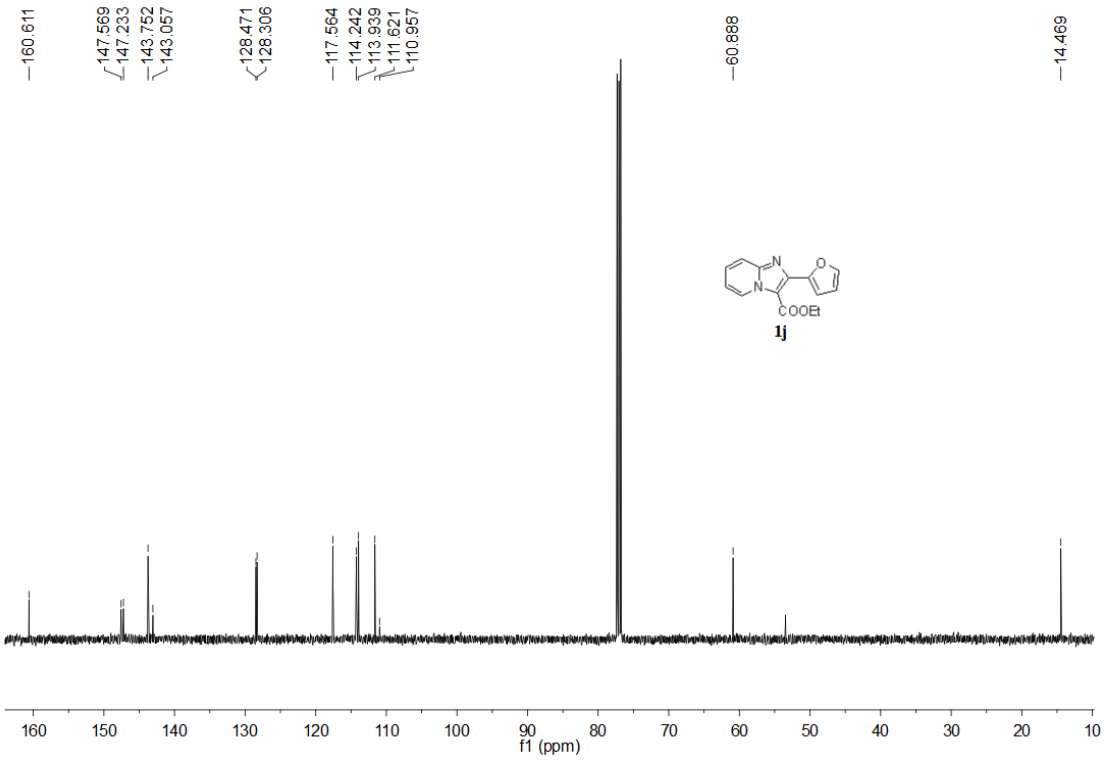
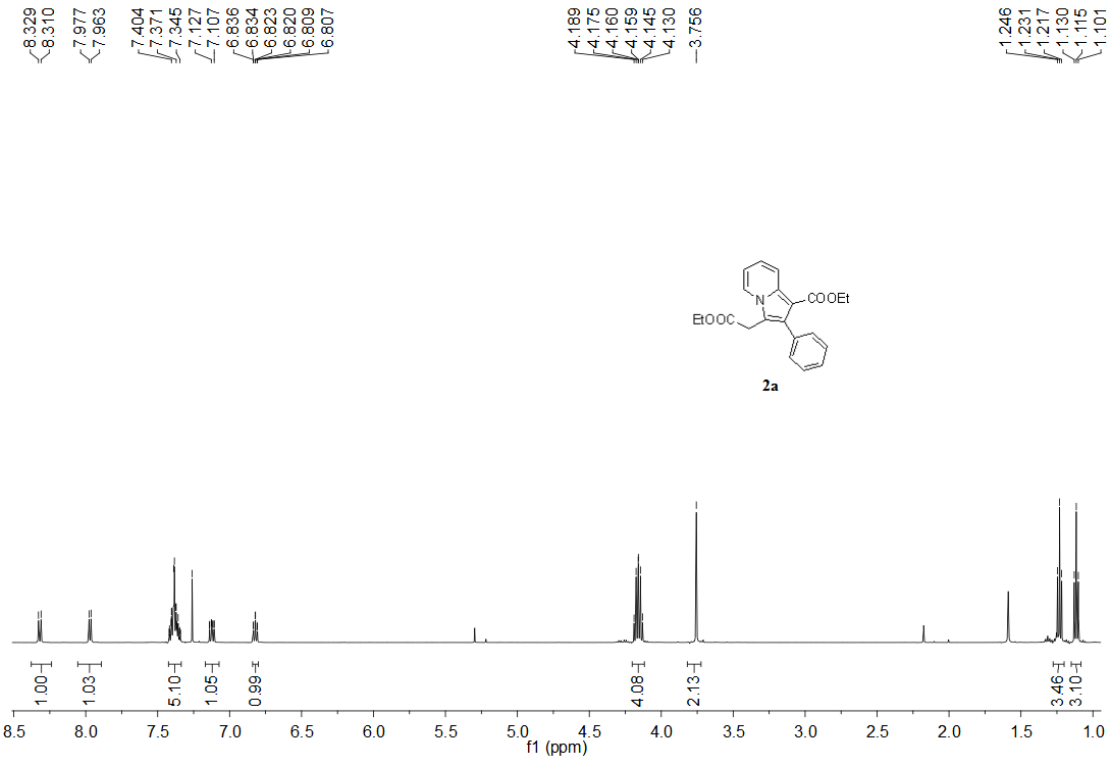
161.060
152.615
151.121
147.089
132.039
131.403
128.391
128.100
120.658
117.486
114.219
95.867
60.602
21.259
14.014
OAc
COOEt
1h
f1 (ppm)

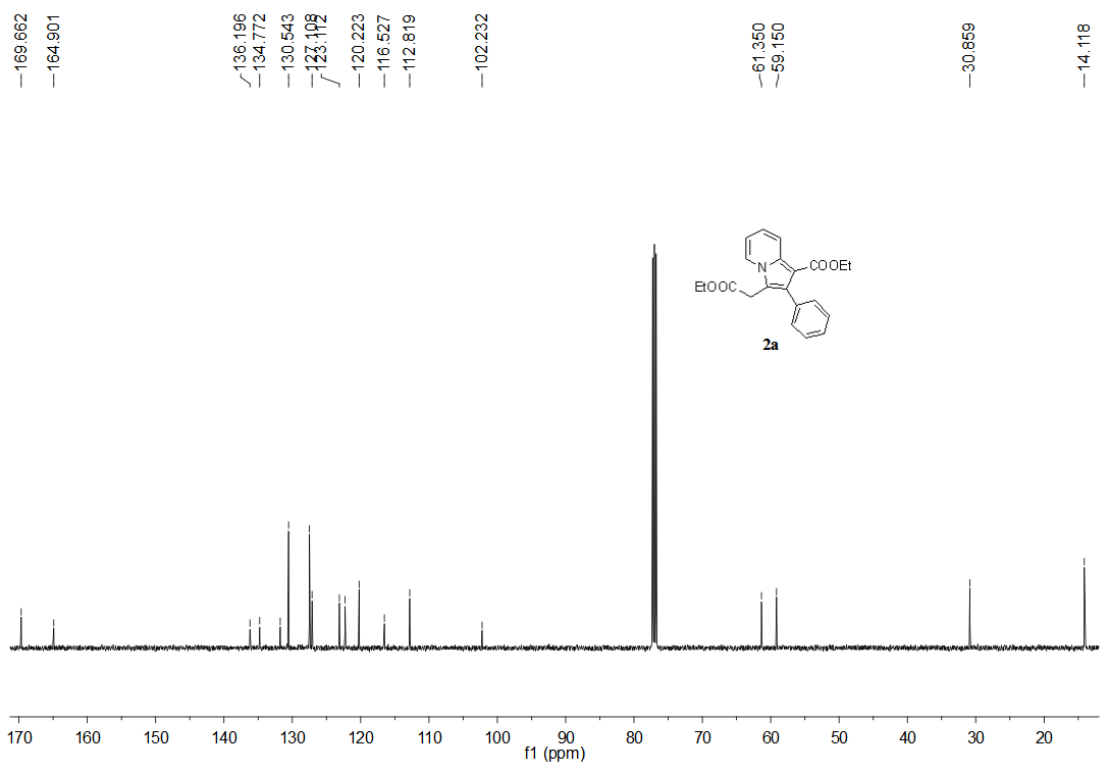

9.397
9.383
7.761
7.744
7.719
7.702
7.396
7.376
6.967
6.775
6.758
4.377
4.363
4.348
4.334
3.020
1.335
1.320
1.306
COOEt
1i
1.00
2.11
1.05
1.15
1.06
2.16
2.10
6.11
3.27
f1 (ppm)

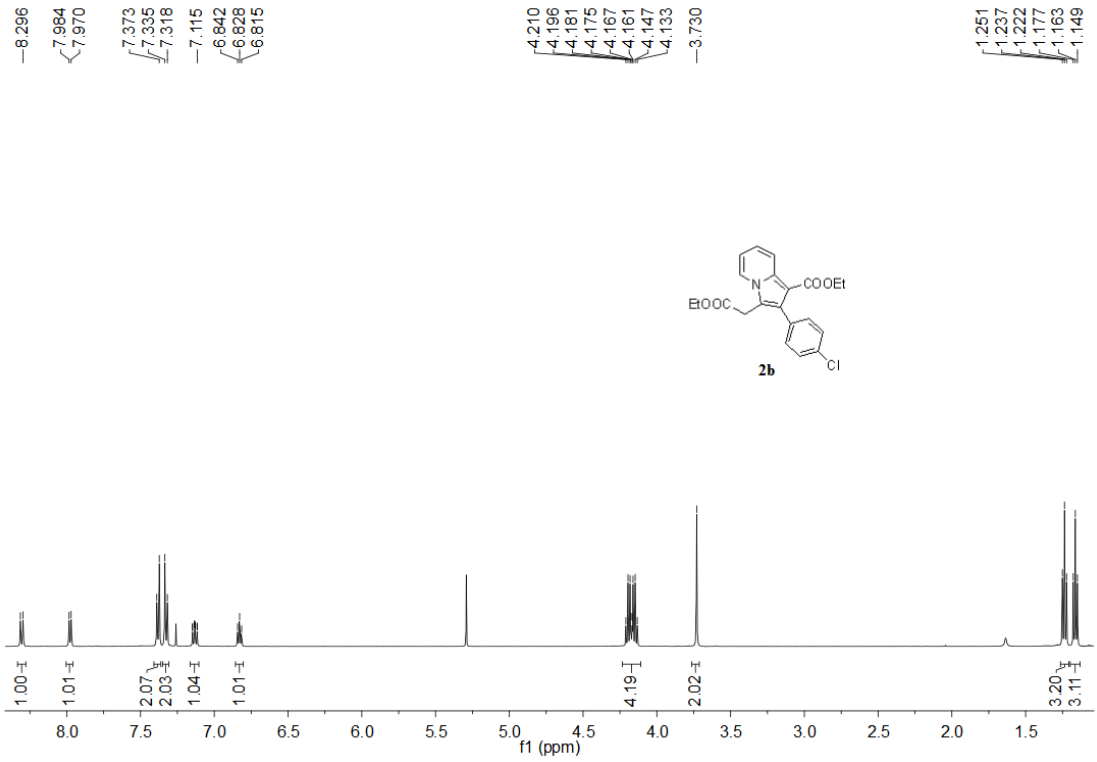

161.477
154.082
150.848
147.138
131.350
128.419
127.762
121.762
117.062
113.622
111.238
111.087
60.360
40.437
14.275
COOEt
1i
f1 (ppm)


9.366
9.352
7.755
7.737
7.625
7.622
7.417
6.994
6.565
6.561
6.558
6.554
4.516
4.502
4.488
4.474
1.484
1.469
1.455
COOEt
1j
1.00
1.06
1.01
2.10
1.08
1.06
2.18
3.14
f1 (ppm)


160.611
147.569
147.233
143.752
143.057
128.471
128.306
117.564
114.242
113.939
111.621
110.957
60.888
14.469
COOEt
1j
f1 (ppm)


8.329
8.310
7.977
7.963
7.404
7.371
7.345
7.127
7.107
6.836
6.834
6.823
6.820
6.809
6.807
4.189
4.175
4.160
4.159
4.145
4.130
3.756
1.246
1.231
1.217
1.130
1.115
1.101
COOEt
EtOOC
2a
1.00
1.03
5.10
1.05
0.99
4.08
2.13
3.46
3.10
f1 (ppm)


169.662
164.901
136.196
134.772
130.543
127.108
123.112
120.223
116.527
112.819
102.232
61.350
59.150
30.859
14.118
COOEt
EtOOC
2a
f1 (ppm)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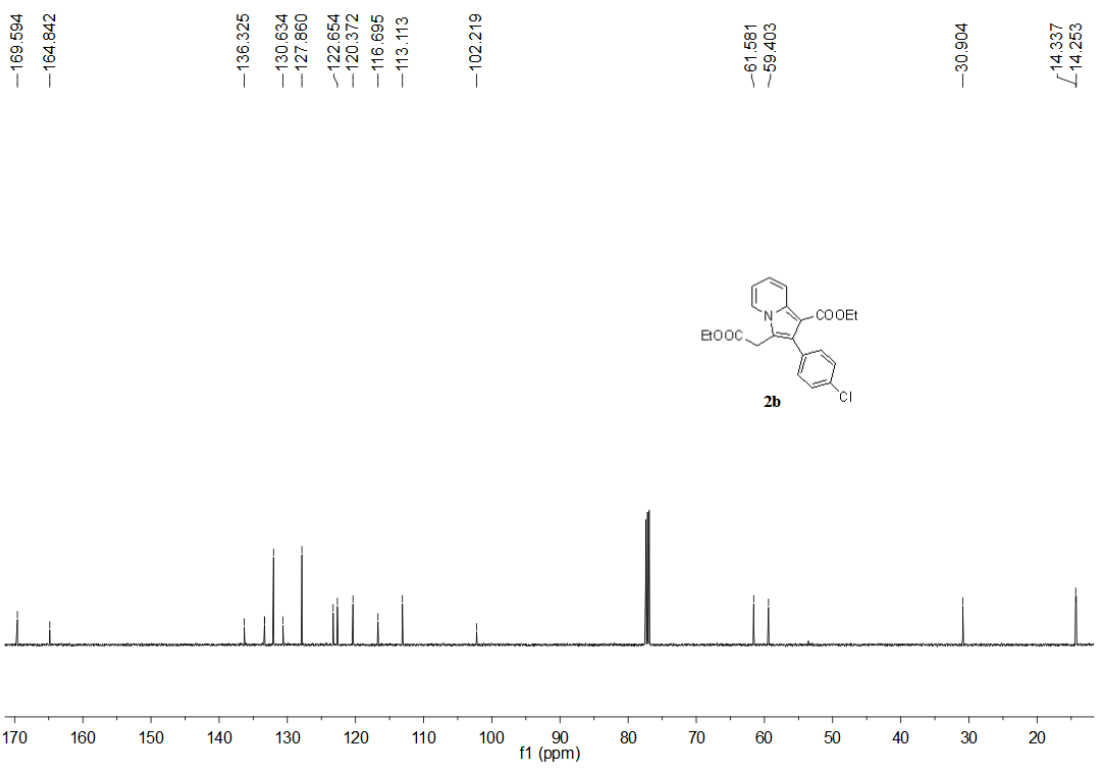
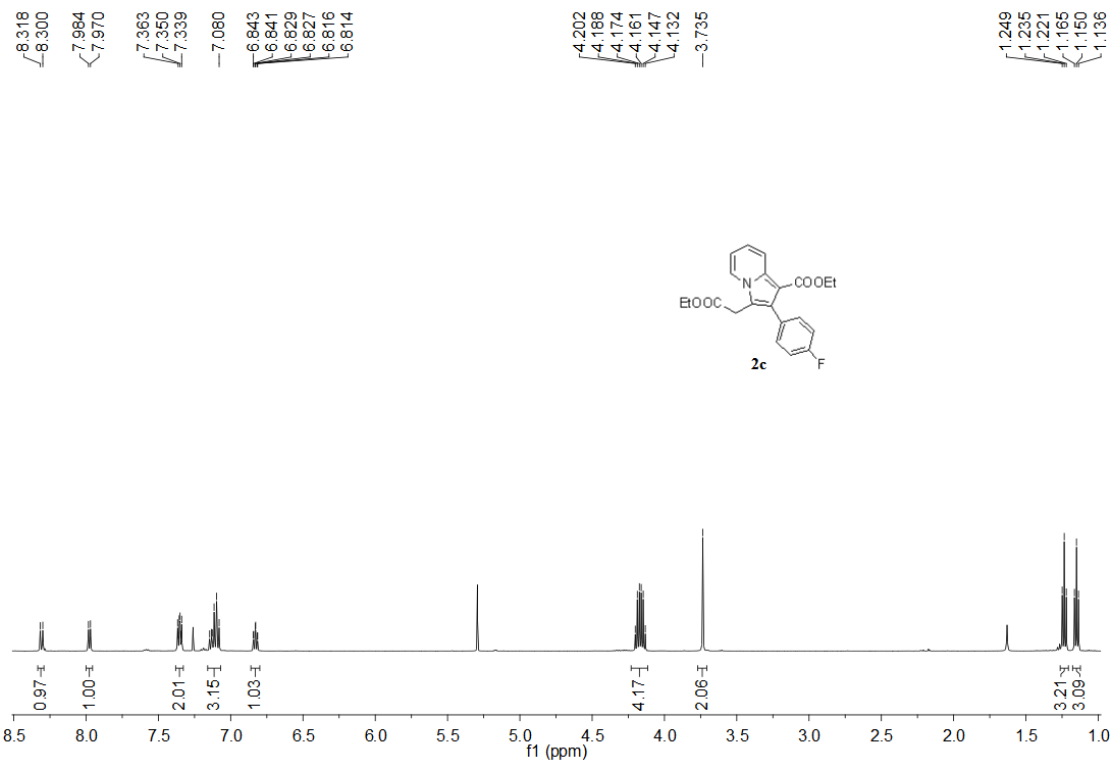
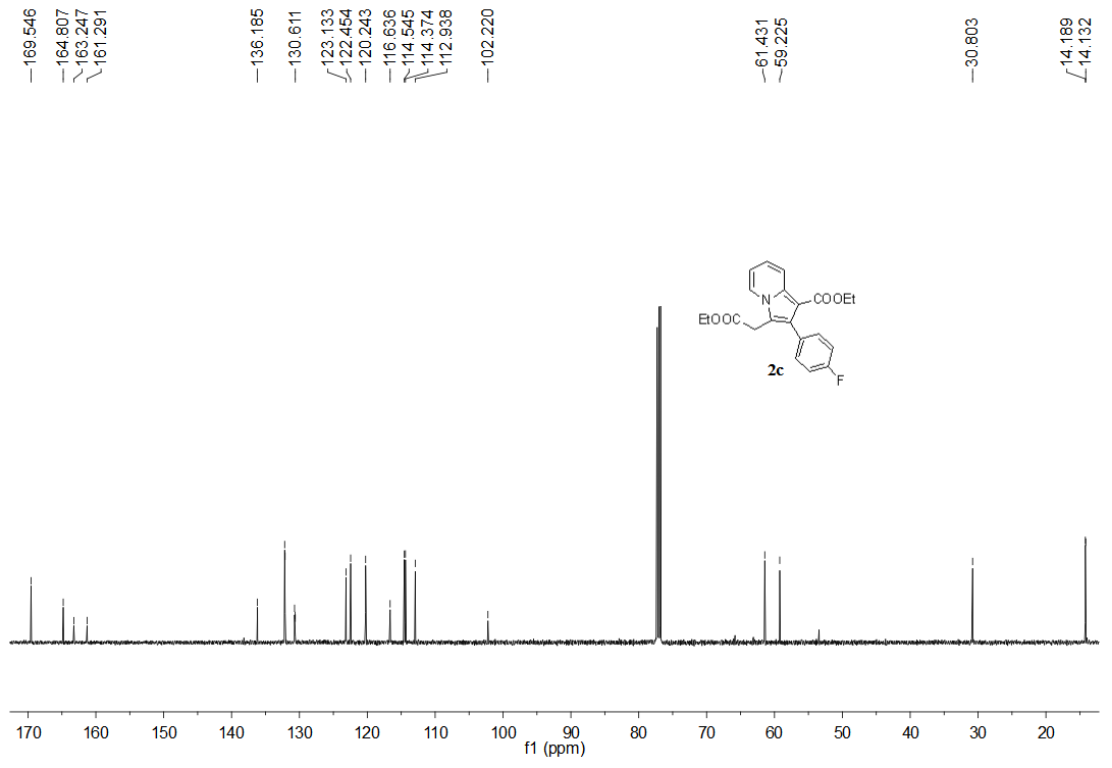
7.984
7.970
7.373
7.335
7.318
7.115
6.842
6.828
6.815
4.210
4.196
4.181
4.175
4.167
4.161
4.147
4.133
3.730
1.251
1.237
1.222
1.177
1.163
1.149
COOEt
EtOOC
Cl
2b
1.00
1.01
2.07
2.03
1.04
1.01
4.19
2.02
3.20
3.11
f1 (ppm)


169.594
164.842
136.325
130.634
127.860
122.654
120.372
116.695
113.113
102.219
61.581
59.403
30.904
14.337
14.253
COOEt
EtOOC
Cl
2b
f1 (ppm)


8.318
8.300
7.984
7.970
7.363
7.350
7.339
7.080
6.843
6.841
6.829
6.827
6.816
6.814
4.202
4.188
4.174
4.161
4.147
4.132
3.735
1.249
1.235
1.221
1.165
1.150
1.136
COOEt
EtOOC
F
2c
0.97
1.00
2.01
3.15
1.03
4.17
2.06
3.21
3.09
f1 (ppm)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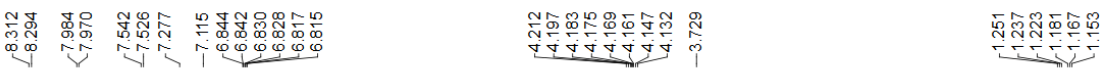
164.807
163.247
161.291
136.185
130.611
123.133
122.454
120.243
116.636
114.545
114.374
112.938
102.220
61.431
59.225
30.803
14.189
14.132
COOEt
EtOOC
F
2c
f1 (ppm)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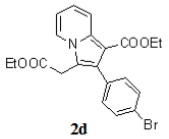
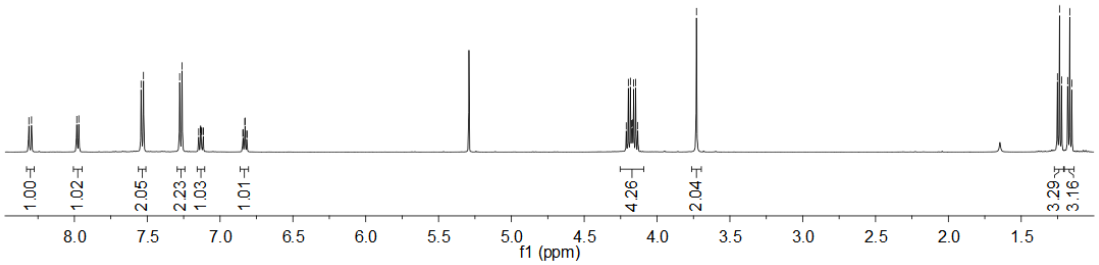
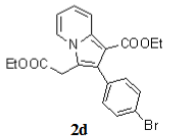
7.970
7.542
7.526
7.277
7.115
6.844
6.842
6.830
6.828
6.817
6.815
4.212
4.197
4.183
4.175
4.169
4.161
4.147
4.132
3.729
1.251
1.237
1.223
1.181
1.167
1.153


N
COOEt
EtOOC
Br

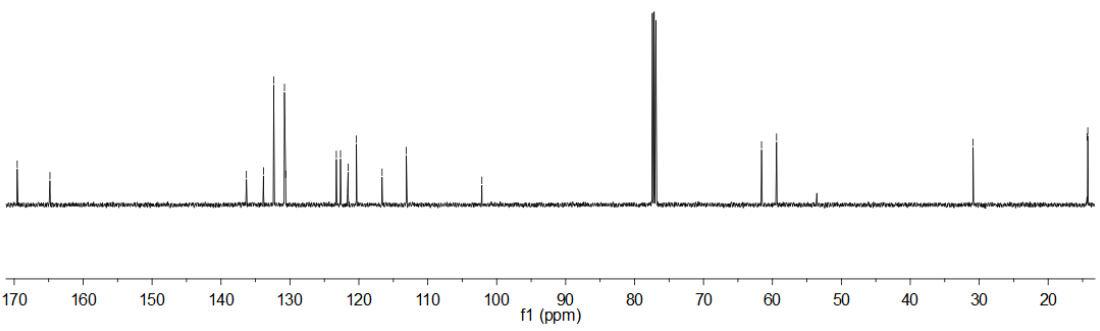
2d


1.00
1.02
2.05
2.23
1.03
1.01
4.26
2.04
3.29
3.16
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
f1 (ppm)

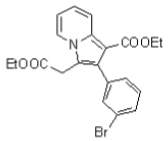

169.565
164.813
136.315
133.843
132.357
130.793
130.615
122.661
121.565
120.359
116.630
113.112
102.150
61.577
59.402
30.887
14.334
14.246


N
COOEt
EtOOC
Br

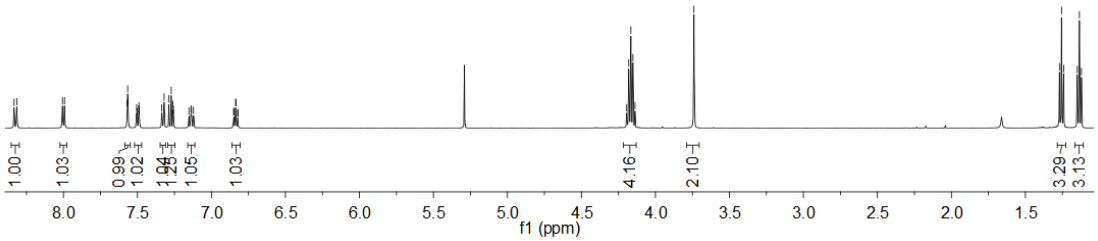
2d


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

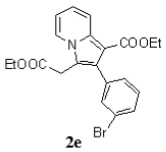

8.315
8.007
7.993
7.568
7.492
7.487
7.260
7.121
6.850
6.848
6.837
6.835
6.823
6.821
4.194
4.180
4.166
4.152
4.138
3.740
1.270
1.256
1.241
1.149
1.135
1.121


COOEt
EtOOC
Br

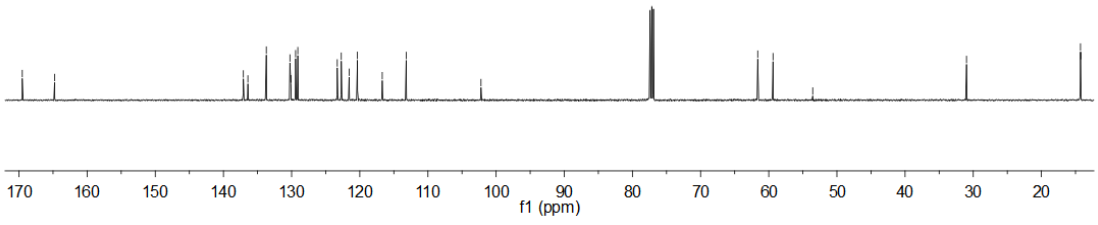
2e

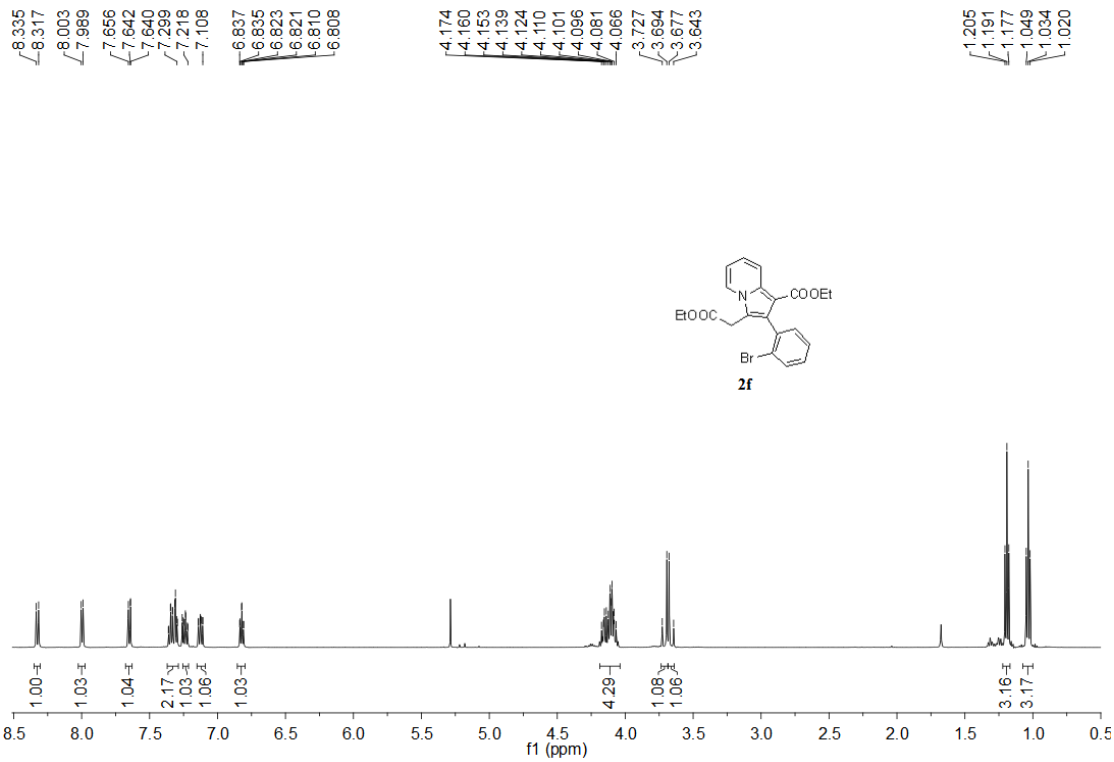

1.00
1.03
0.99
1.02
1.04
1.05
1.03
4.16
2.10
3.29
3.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


169.512
164.769
137.077
136.415
133.712
130.107
121.564
120.343
116.702
113.192
102.216
61.618
59.376
53.551
30.989
14.265
14.220


COOEt
EtOOC
Br

2e


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


8.335
8.317
8.003
7.989
7.656
7.642
7.640
7.299
7.218
7.108
6.837
6.835
6.823
6.821
6.810
6.808
4.174
4.160
4.153
4.139
4.124
4.110
4.101
4.096
4.081
4.066
3.727
3.694
3.677
3.643
1.205
1.191
1.177
1.049
1.034
1.020
COOEt
EtOOC
Br
2f
1.00
1.03
1.04
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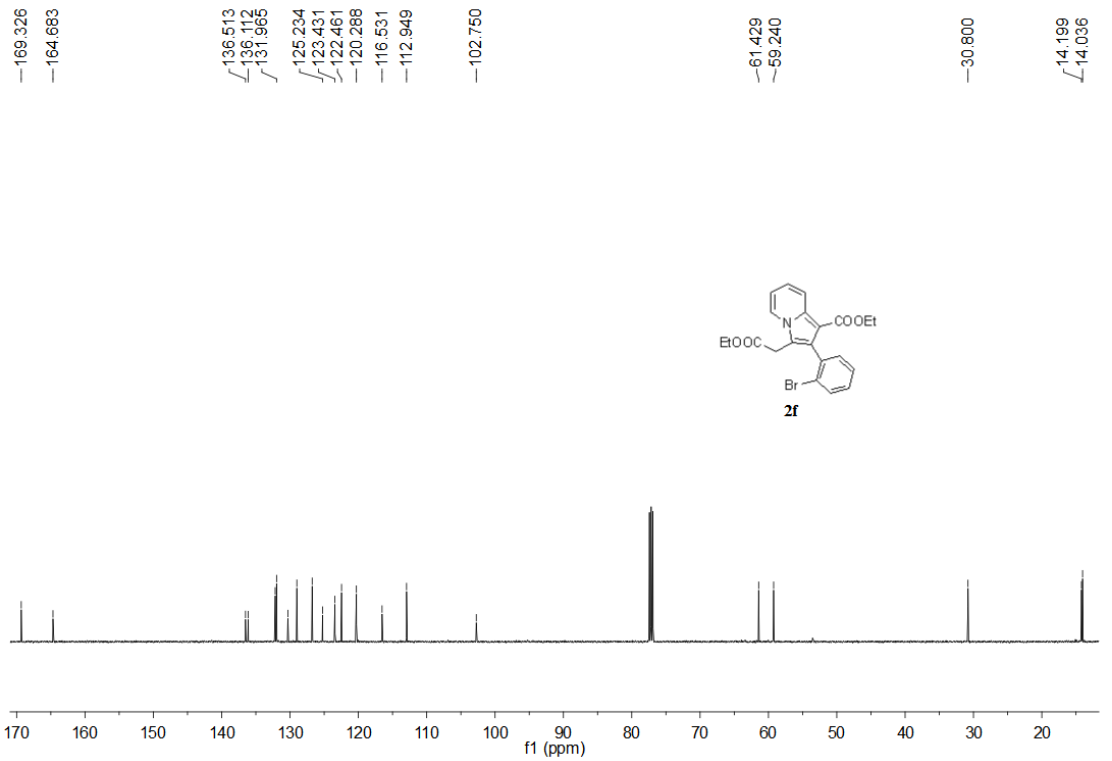
1.03
1.06
1.03
4.29
1.08
1.06
3.16
3.17
f1 (ppm)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122.461
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116.531
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59.240
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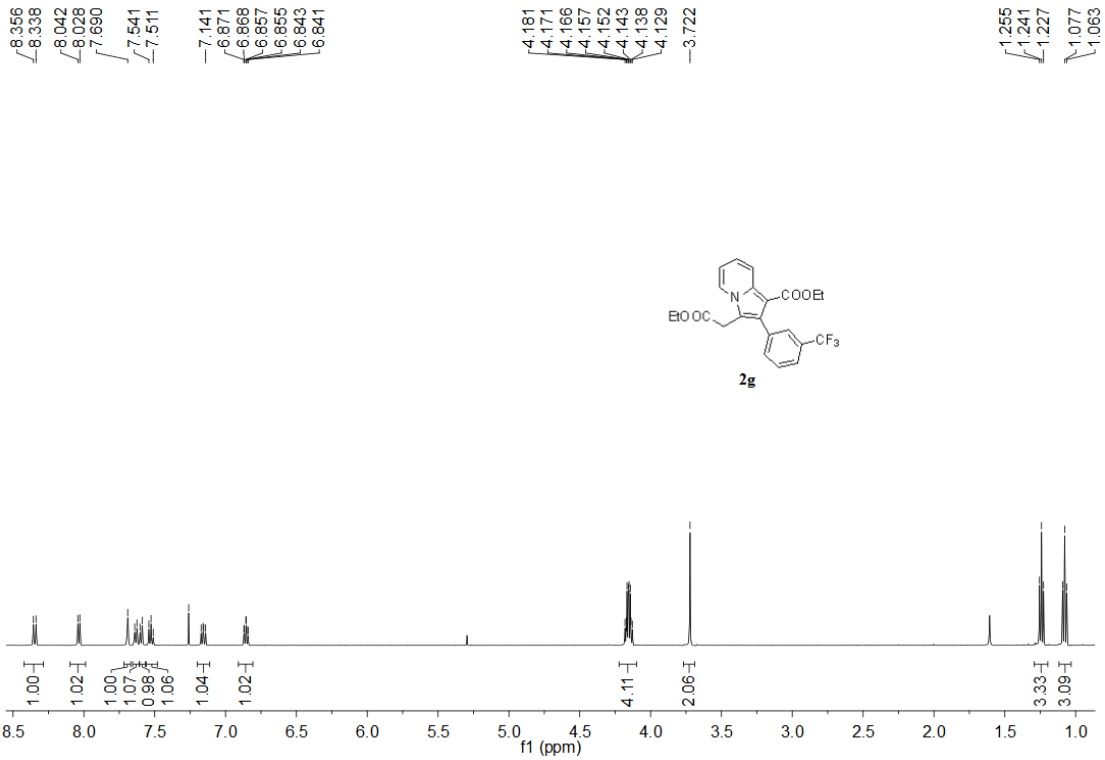
14.199
14.036
COOEt
EtOOC
Br
2f
f1 (ppm)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6.843
6.841
4.181
4.171
4.166
4.157
4.152
4.143
4.138
4.129
3.722
1.255
1.241
1.227
1.077
1.063
COOEt
EtOOC
CF3
2g
1.00
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1.00
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0.98
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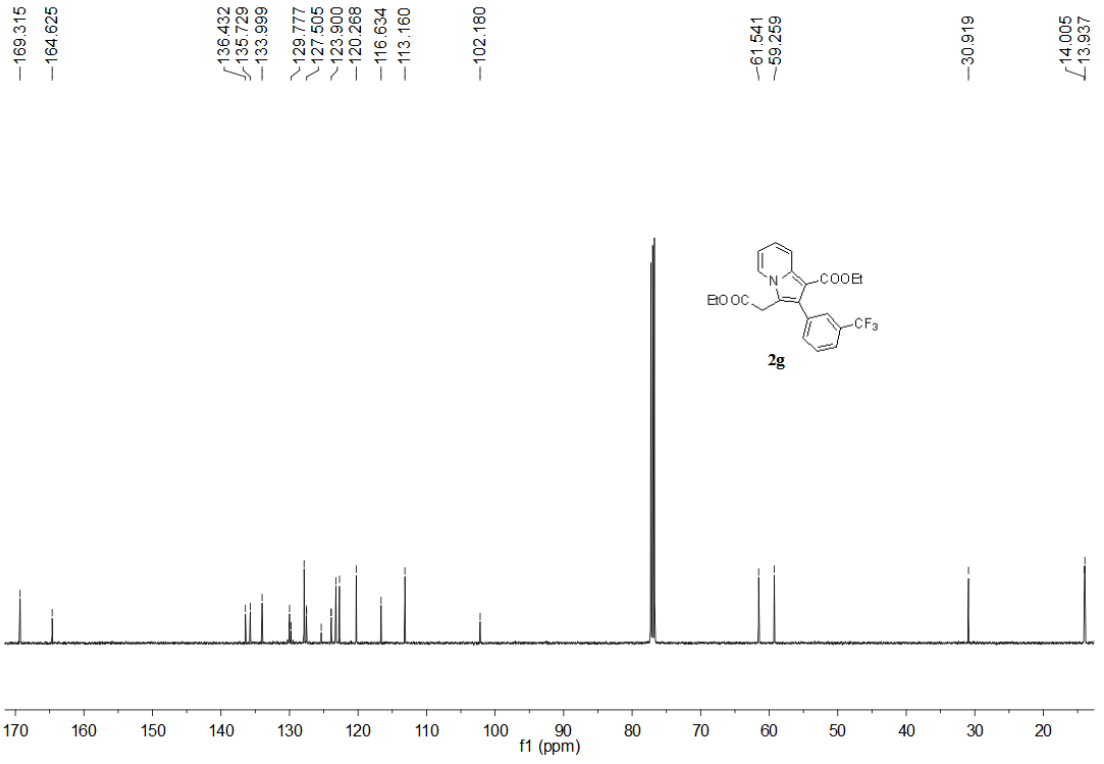
1.04
1.02
4.11
2.06
3.33
3.09
f1 (ppm)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123.900
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102.180
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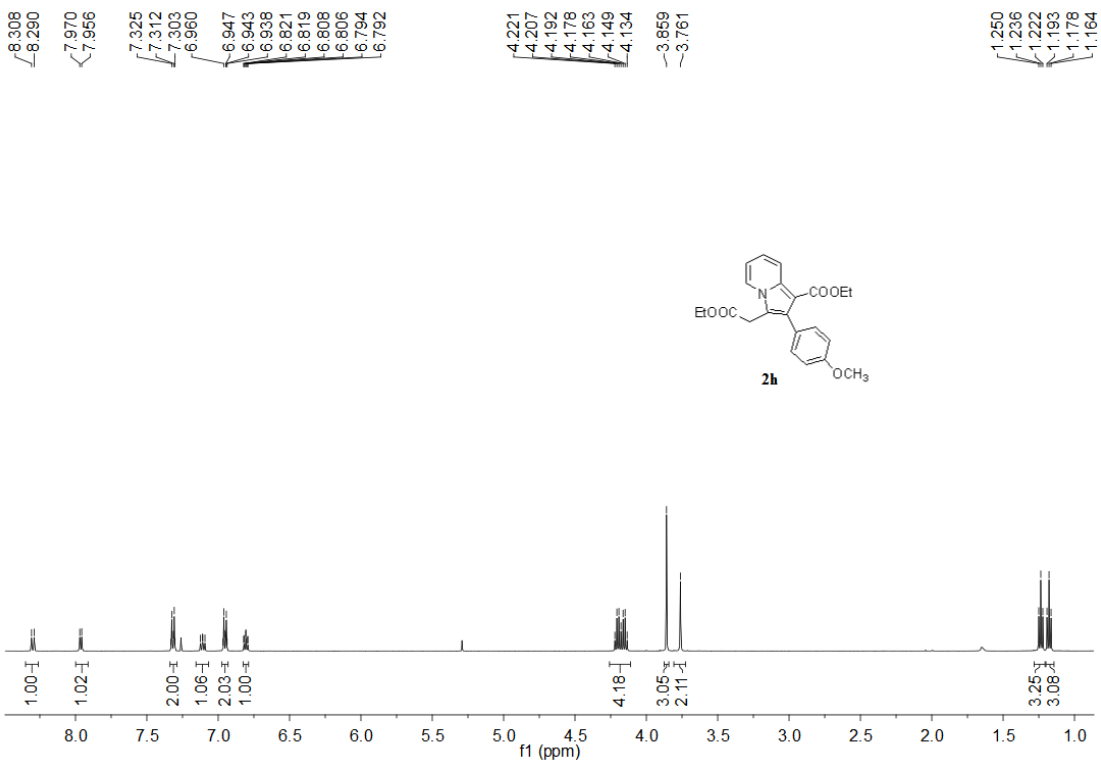
59.259
30.919
14.005
13.937
COOEt
EtOOC
CF3
2g
f1 (ppm)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7.312
7.303
6.960
6.947
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6.938
6.821
6.819
6.808
6.806
6.794
6.792
4.221
4.207
4.192
4.178
4.163
4.149
4.134
3.859
3.761
1.250
1.236
1.222
1.193
1.178
1.164
COOEt
EtOOC
OCH3
2h
1.00
1.02
2.00
1.06
2.03
1.00
4.18
3.05
2.11
3.25
3.08
8.0
7.5
7.0
6.5
6.0
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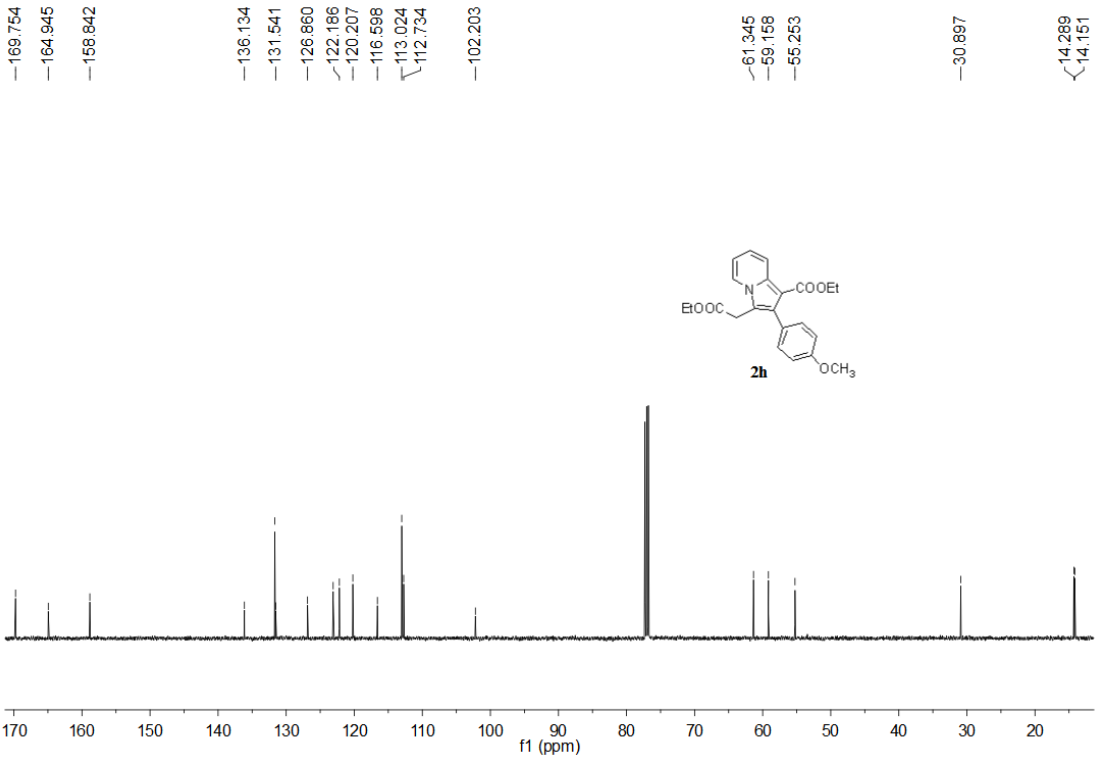
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)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102.203
61.345
59.158
55.253
30.897
14.289
14.151
COOEt
EtOOC
OCH3
2h
170
160
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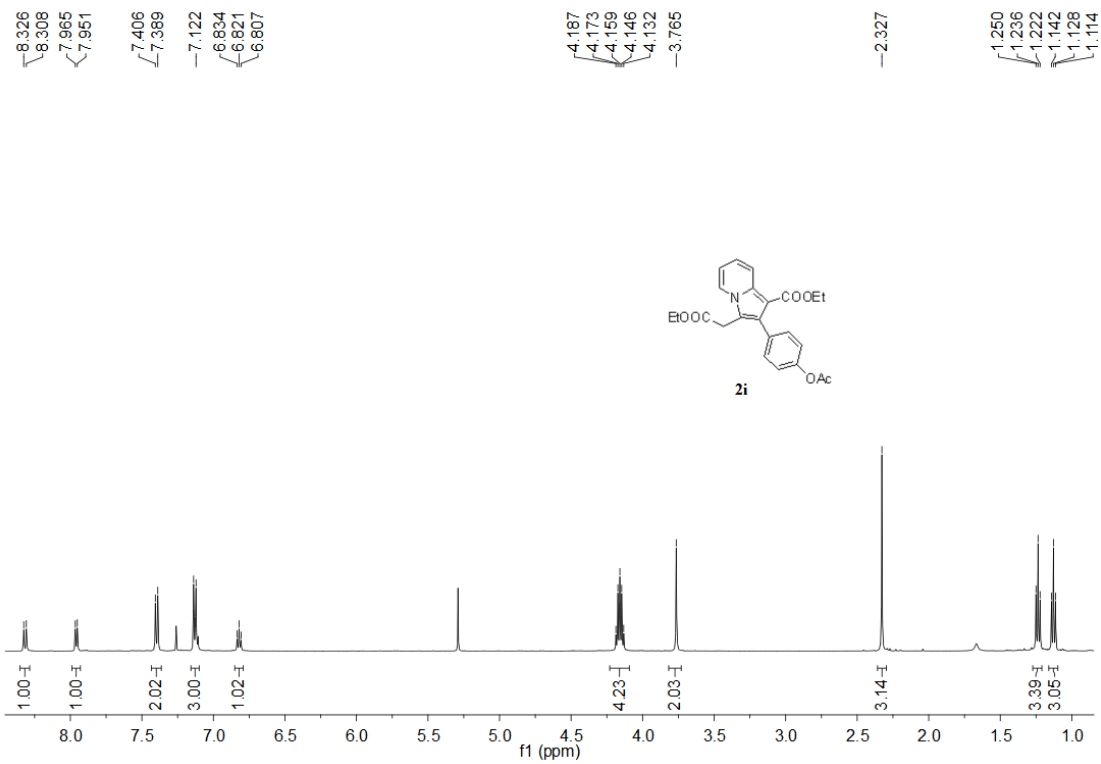
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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6.834
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6.807
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4.173
4.159
4.146
4.132
3.765
2.327
1.250
1.236
1.222
1.142
1.128
1.114
COOEt
EtOOC
OAc
2i
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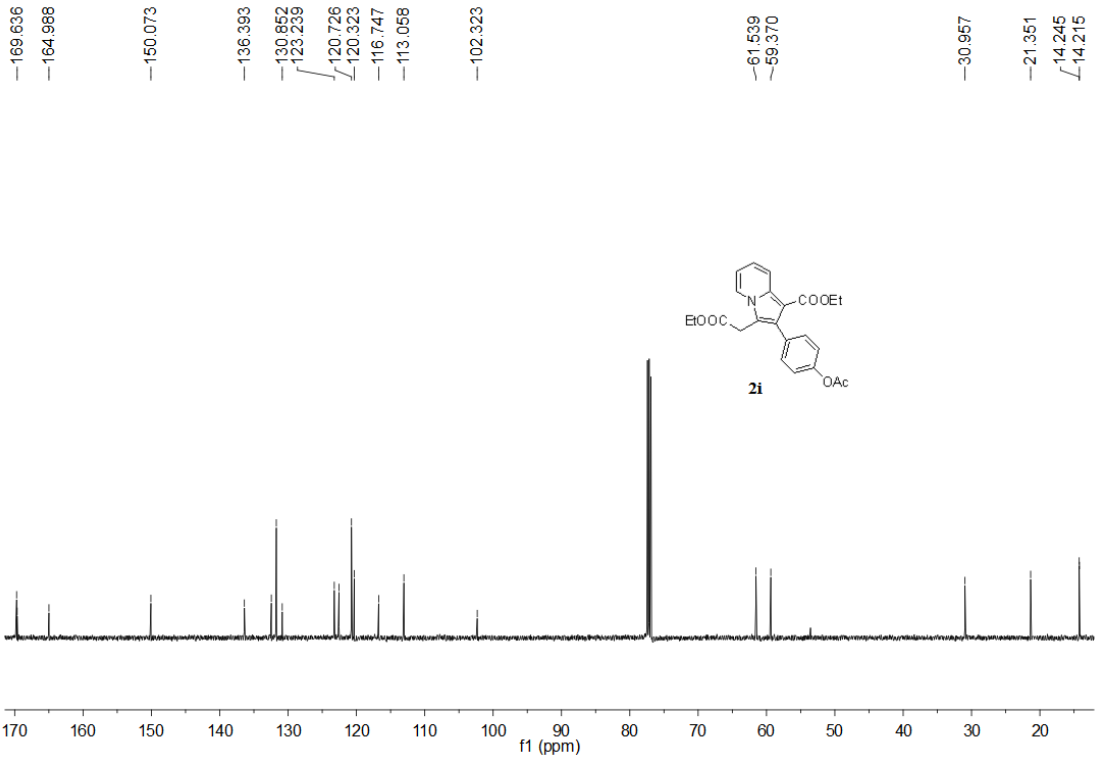
1.00
2.02
3.00
1.02
4.23
2.03
3.14
3.39
3.05
f1 (ppm)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120.323
116.747
113.058
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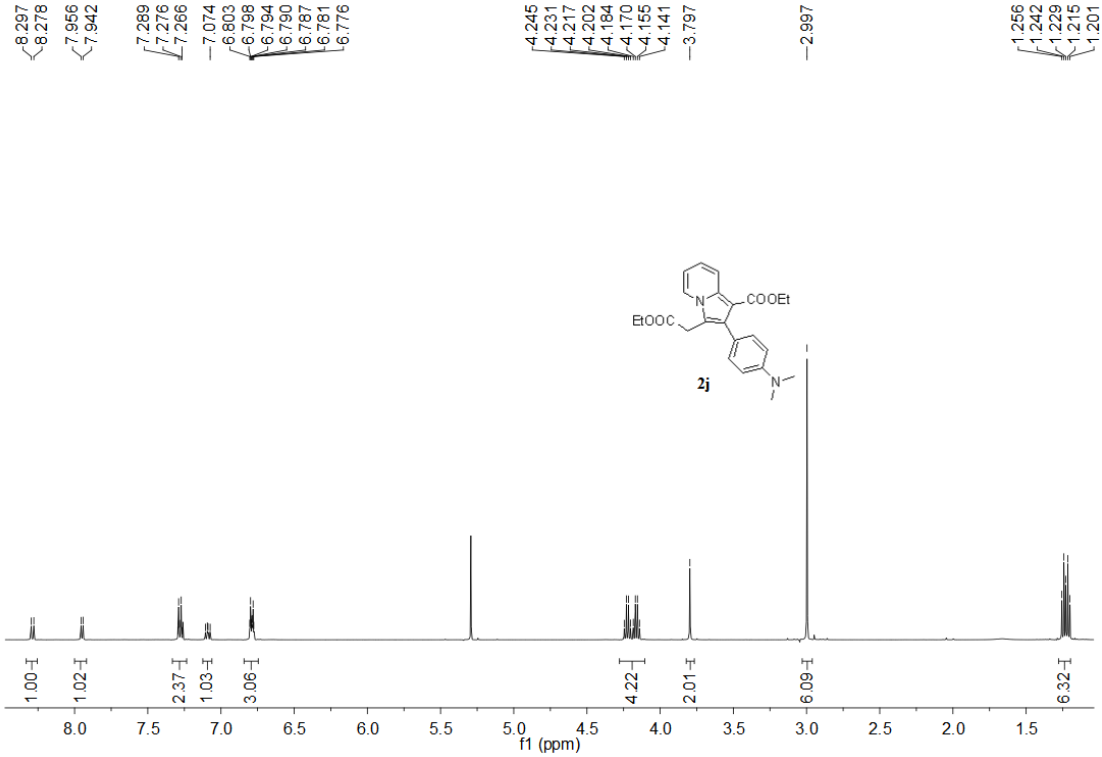
30.957
21.351
14.245
14.215
COOEt
EtOOC
OAc
2i
f1 (ppm)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7.266
7.074
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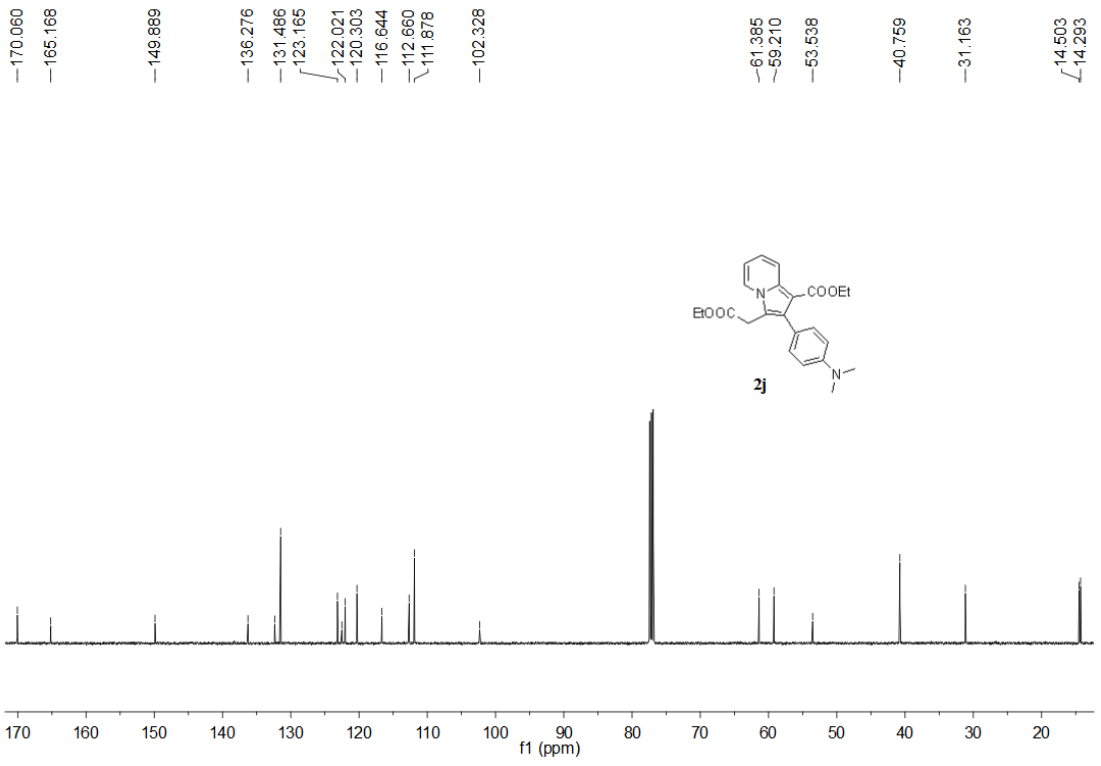
6.794
6.790
6.787
6.781
6.776
4.245
4.231
4.217
4.202
4.184
4.170
4.155
4.141
3.797
2.997
1.256
1.242
1.229
1.215
1.201
COOEt
EtOOC
N
2j
1.00
1.02
2.37
1.03
3.06
4.22
2.01
6.09
6.32
f1 (ppm)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122.021
120.303
116.644
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111.878
102.328
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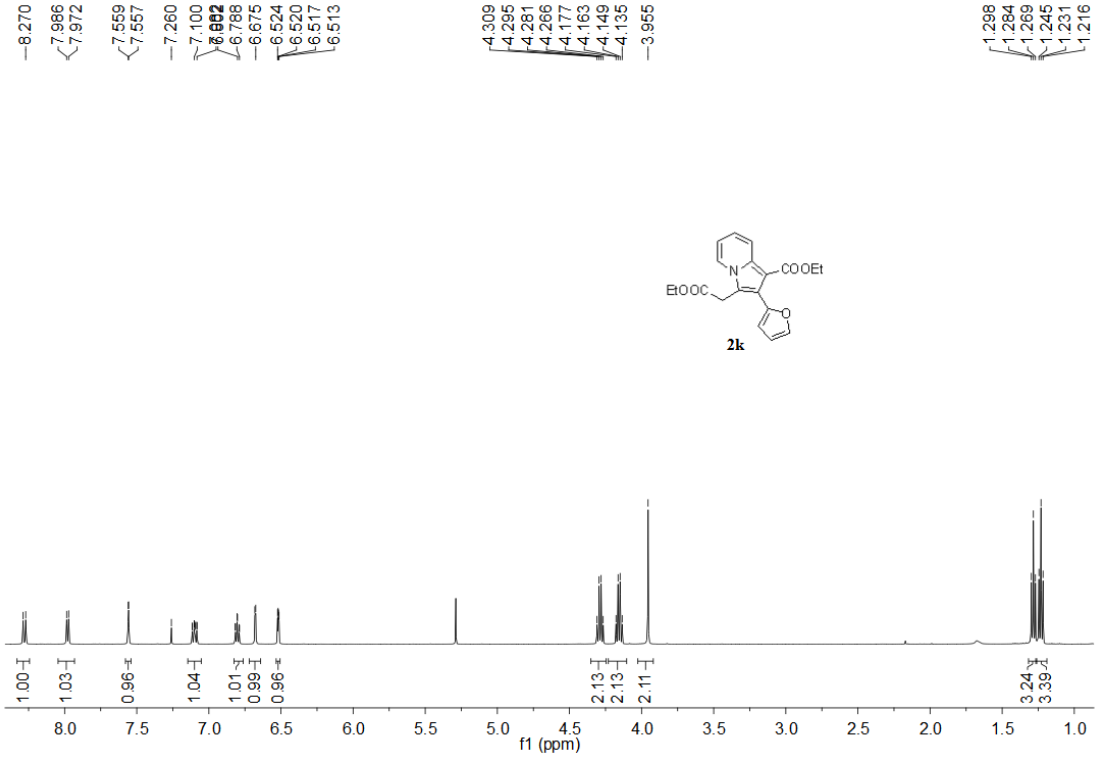
53.538
40.759
31.163
14.503
14.293
COOEt
EtOOC
N
2j
f1 (ppm)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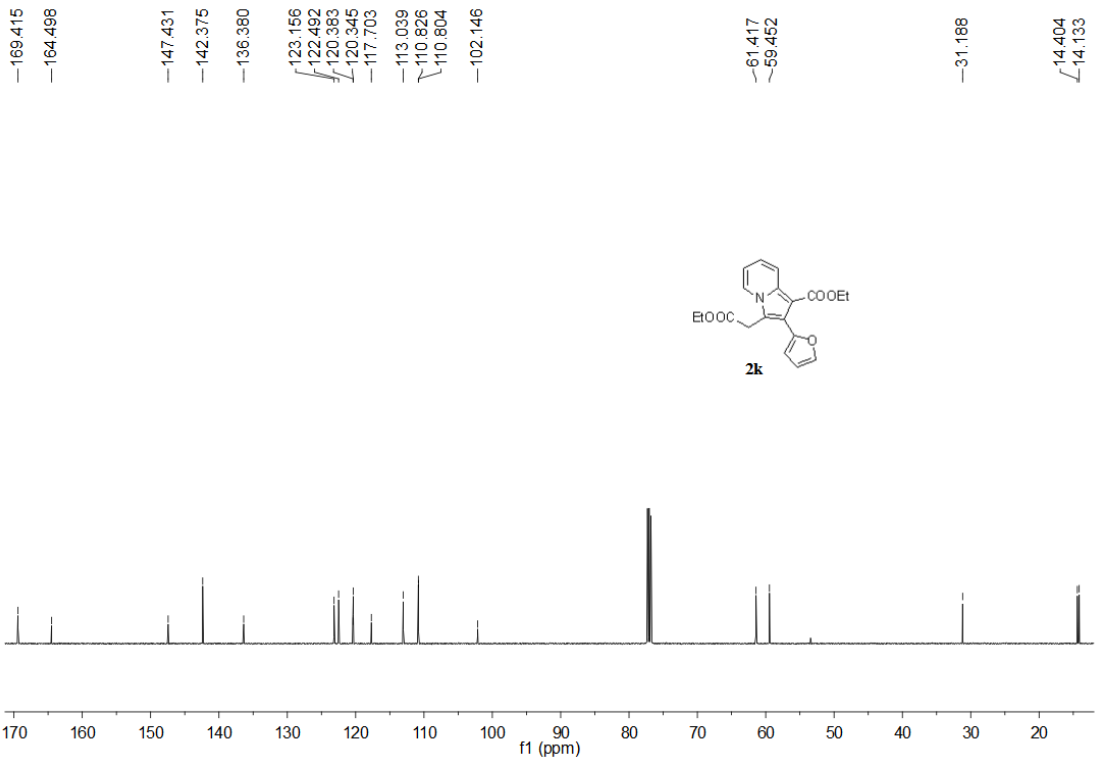
6.788
6.675
6.524
6.520
6.517
6.513
4.309
4.295
4.281
4.266
4.177
4.163
4.149
4.135
3.955
1.298
1.284
1.269
1.245
1.231
1.216
EtOOC
COOEt
2k
1.00
1.03
0.96
1.04
1.01
0.99
0.96
2.13
2.13
2.11
3.24
3.39
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)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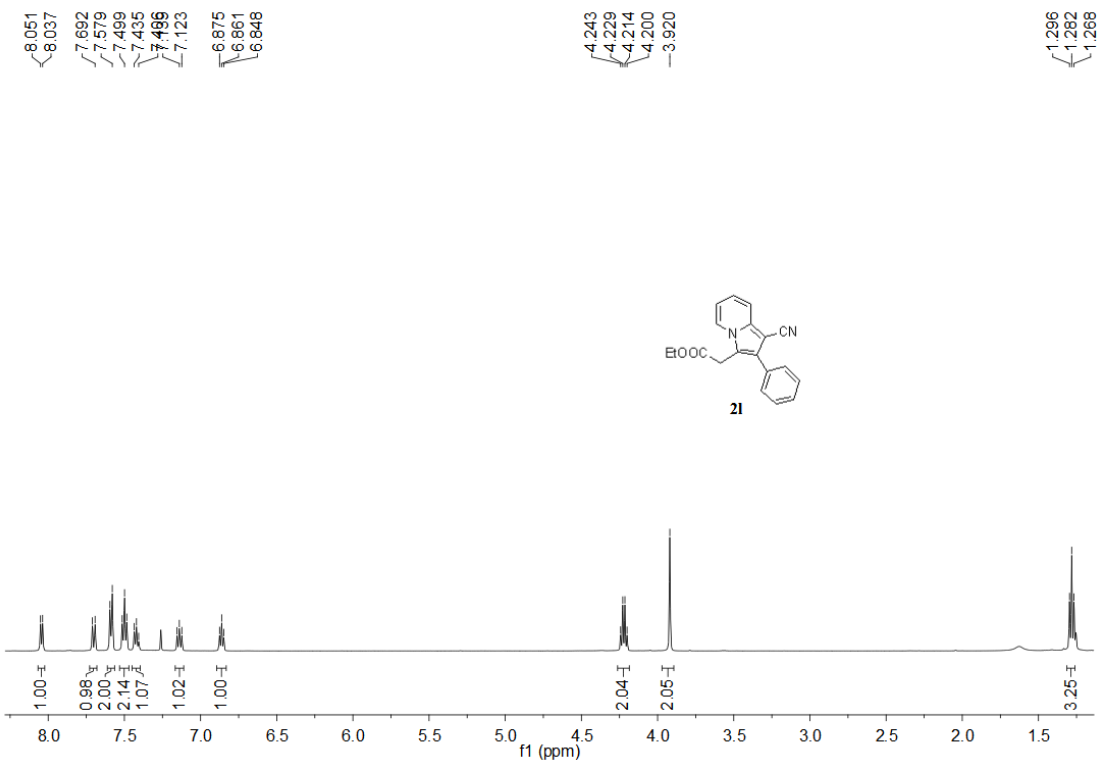
120.383
120.345
117.703
113.039
110.826
110.804
102.146
61.417
59.452
31.188
14.404
14.133
EtOOC
COOEt
2k
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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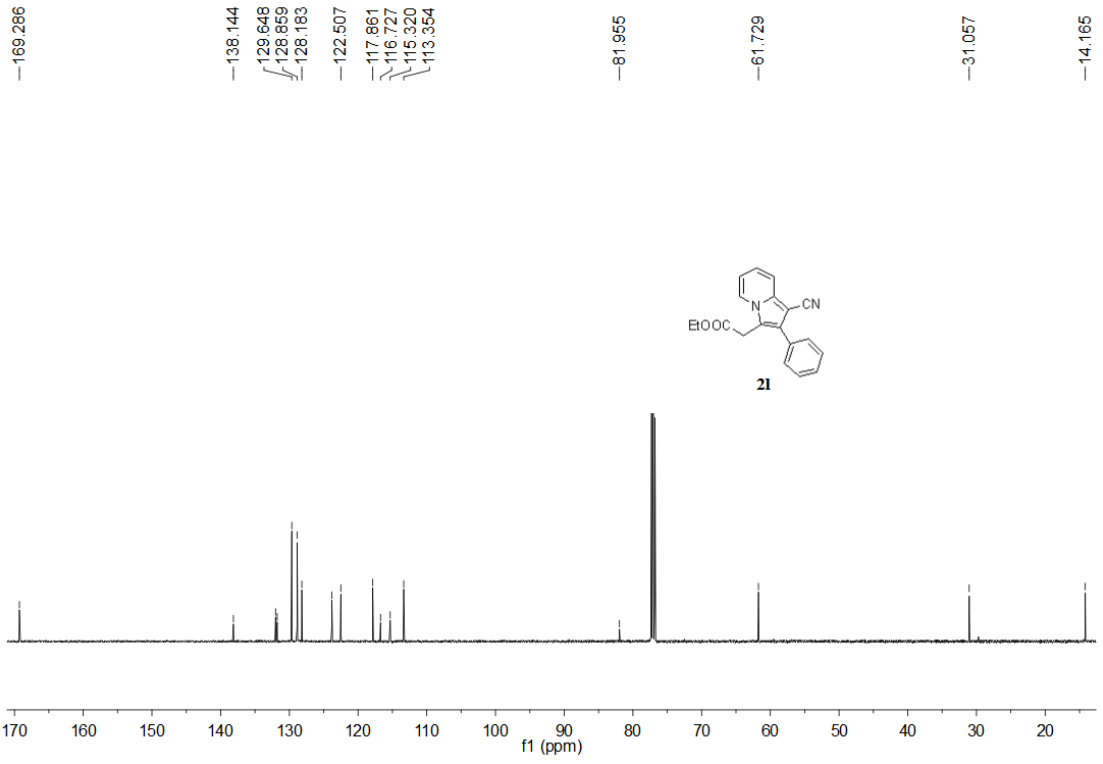
7.579
7.499
7.435
7.123
6.875
6.861
6.848
4.243
4.229
4.214
4.200
3.920
1.296
1.282
1.268
EtOOC
CN
N
21
1.00
0.98
2.00
2.14
1.07
1.02
1.00
2.04
2.05
3.25
f1 (ppm)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122.507
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116.727
115.320
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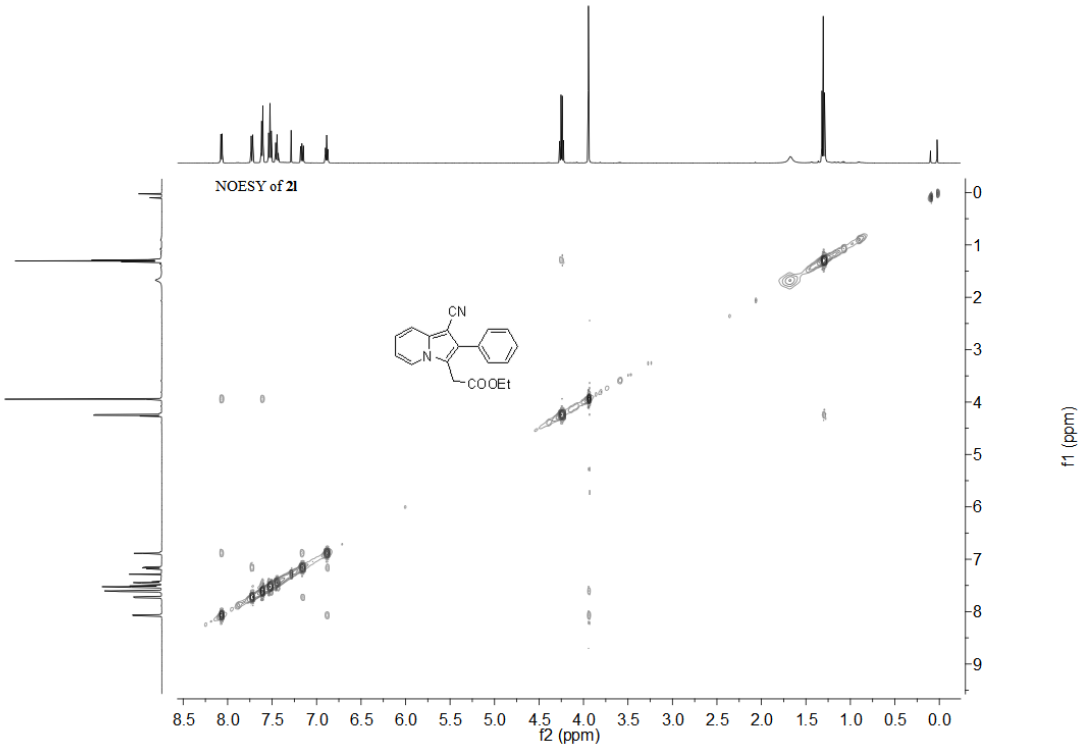
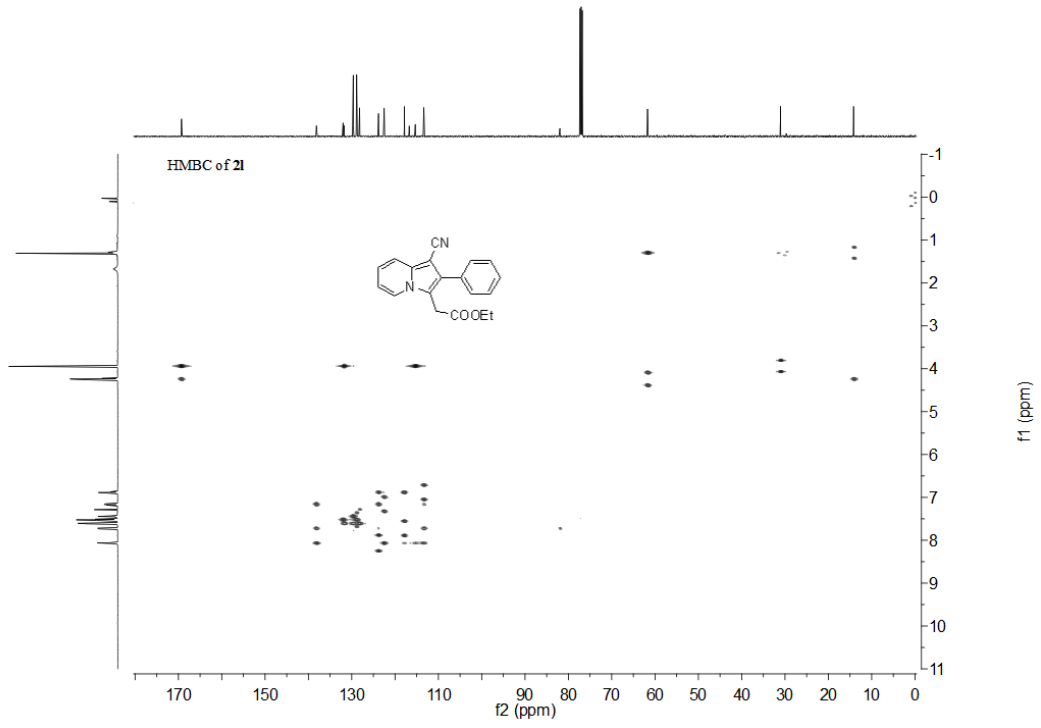
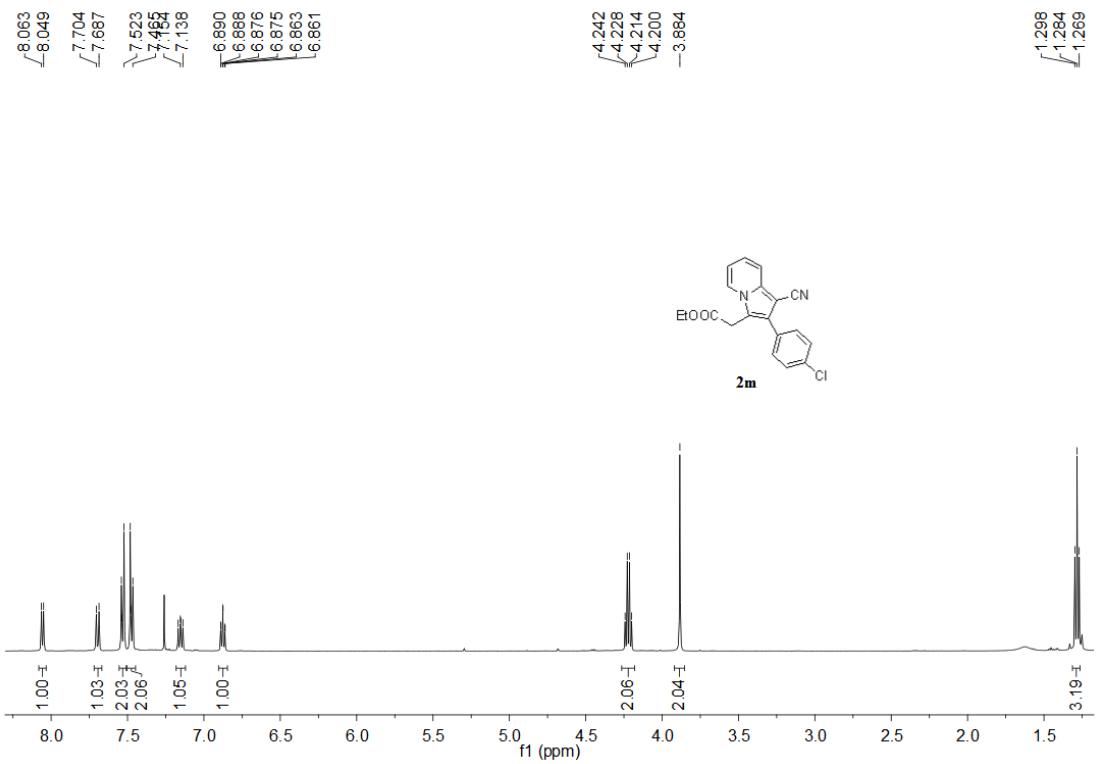
81.955
61.729
31.057
14.165
EtOOC
CN
N
21
f1 (ppm)


NOESY of 2l
CN
COOEt
f2 (ppm)
f1 (ppm)


HMBC of 2l
CN
COOEt
f2 (ppm)
f1 (ppm)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7.138
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6.888
6.876
6.875
6.863
6.861
4.242
4.228
4.214
4.200
3.884
1.298
1.284
1.269
CN
EtOOC
Cl
2m
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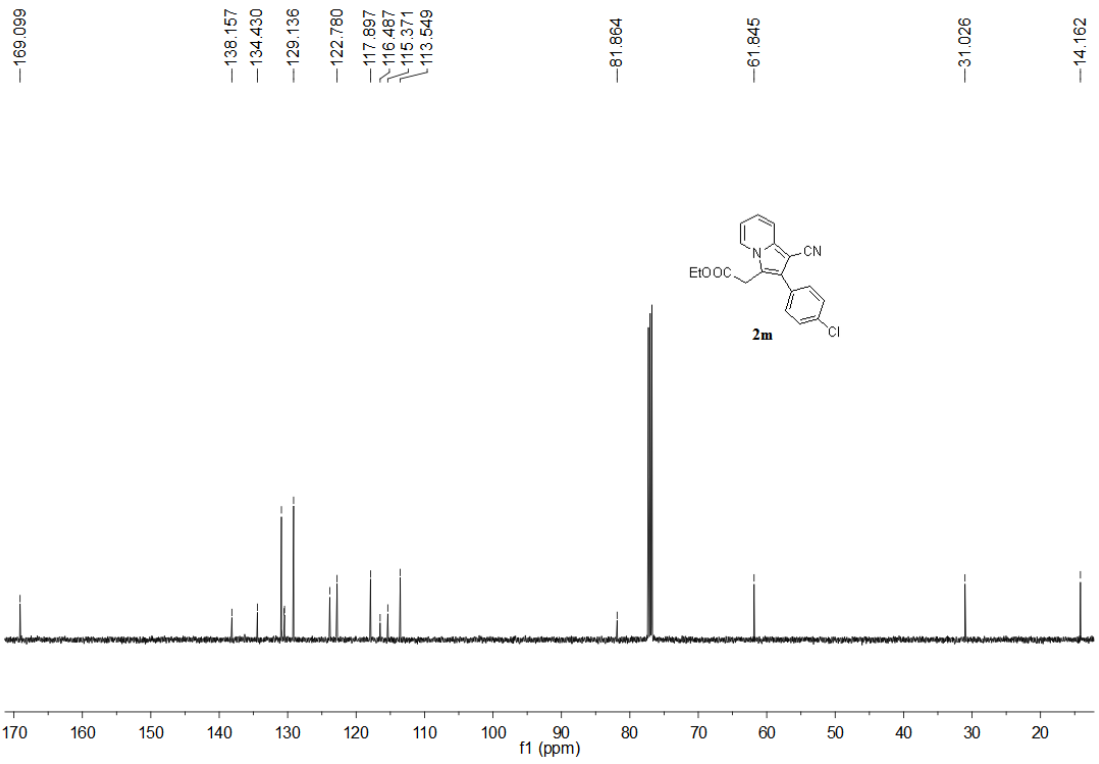
1.03
2.03
2.06
1.05
1.00
2.06
2.04
3.19
f1 (ppm)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113.549
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61.845
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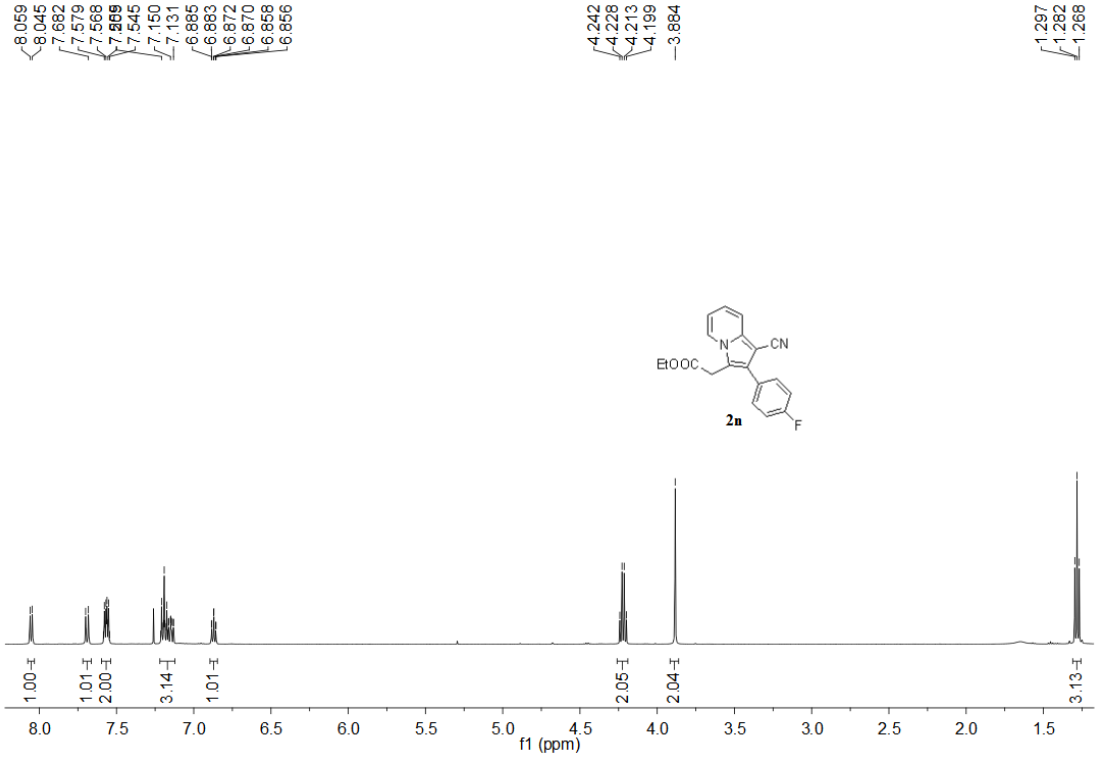
14.162
CN
EtOOC
Cl
2m
f1 (ppm)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7.131
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6.870
6.858
6.856
4.242
4.228
4.213
4.199
3.884
1.297
1.282
1.268
CN
EtOOC
N
F
2n
1.00
1.01
2.00
3.14
1.01
2.05
2.04
3.13
8.0
7.5
7.0
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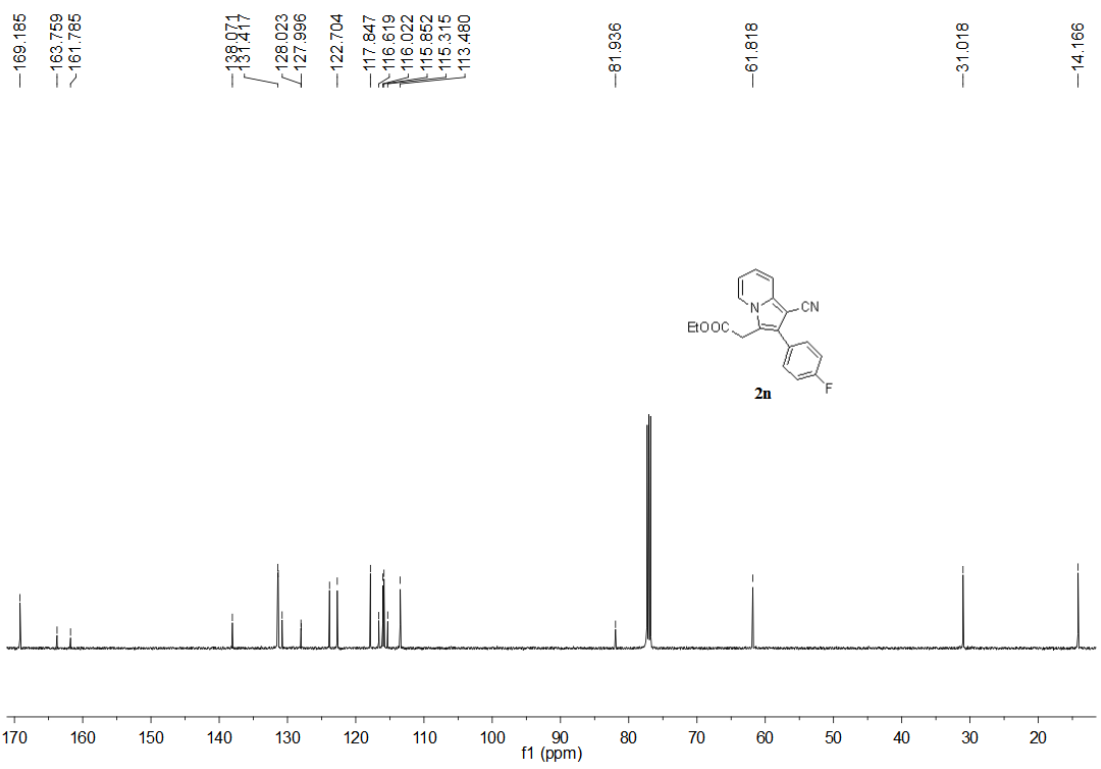
3.0
2.5
2.0
1.5
f1 (ppm)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127.996
122.704
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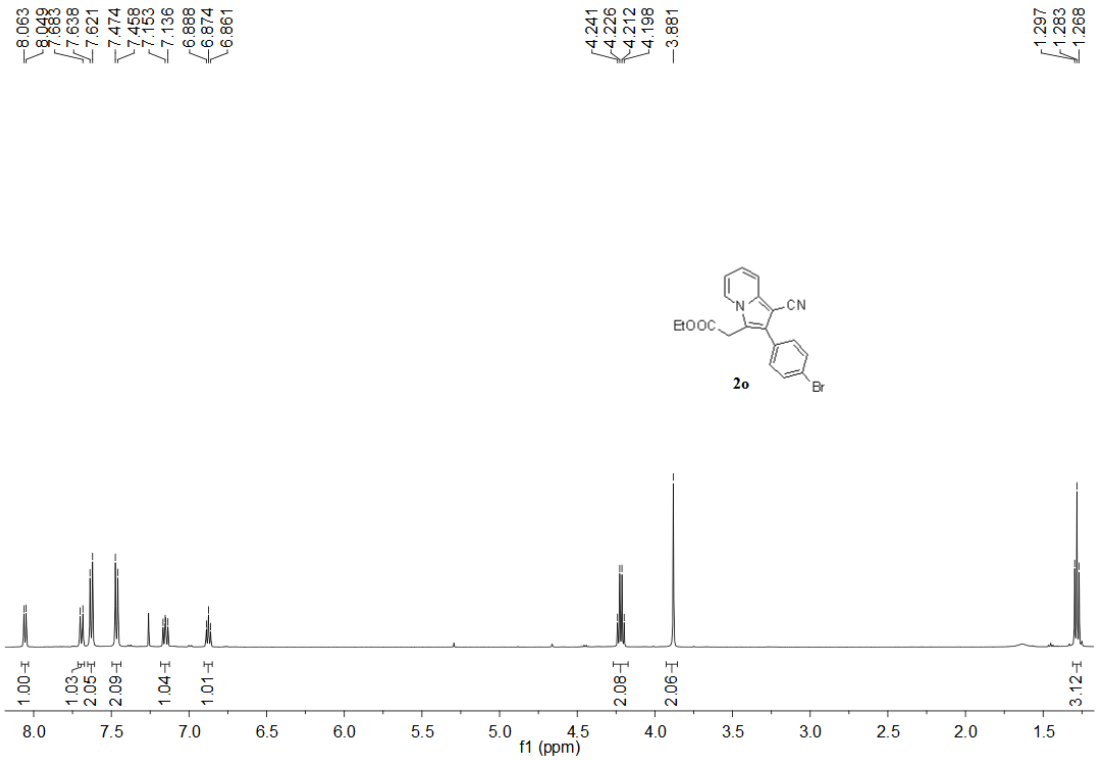
116.619
116.022
115.852
115.315
113.480
81.936
61.818
31.018
14.166
CN
EtOOC
N
F
2n
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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4.241
4.226
4.212
4.198
3.881
1.297
1.283
1.268
EtOOC
CN
N
Br
2o
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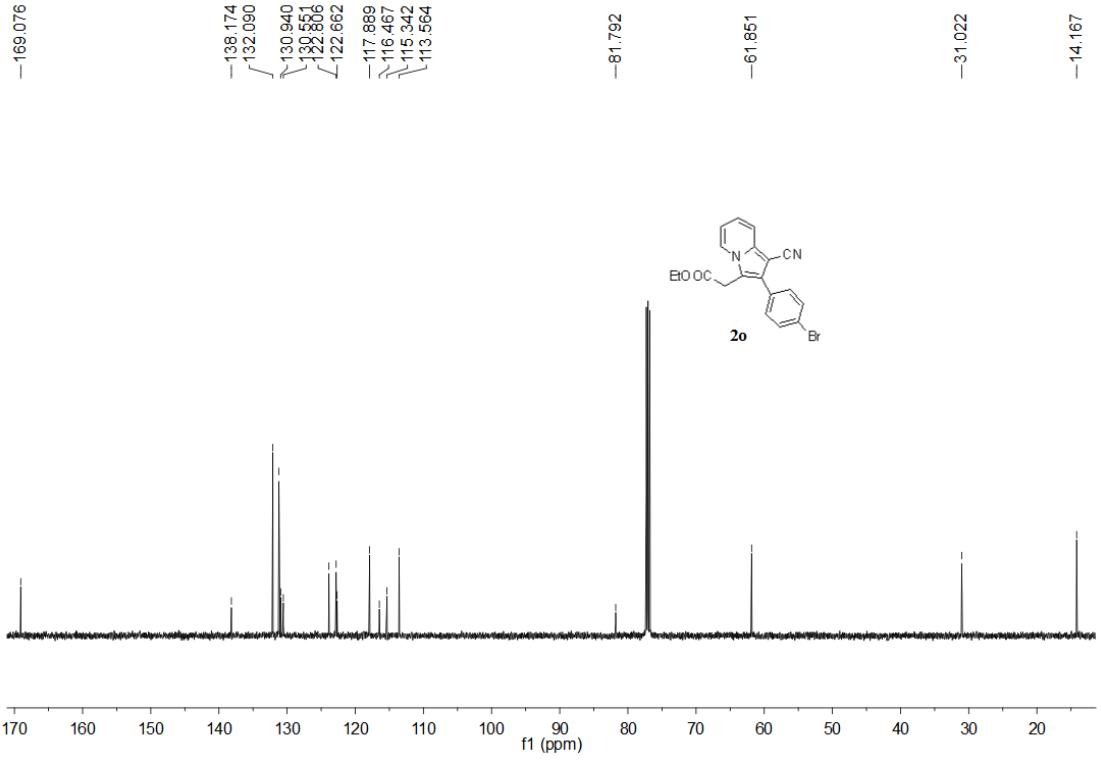
1.03
2.05
2.09
1.04
1.01
2.08
2.06
3.12
f1 (ppm)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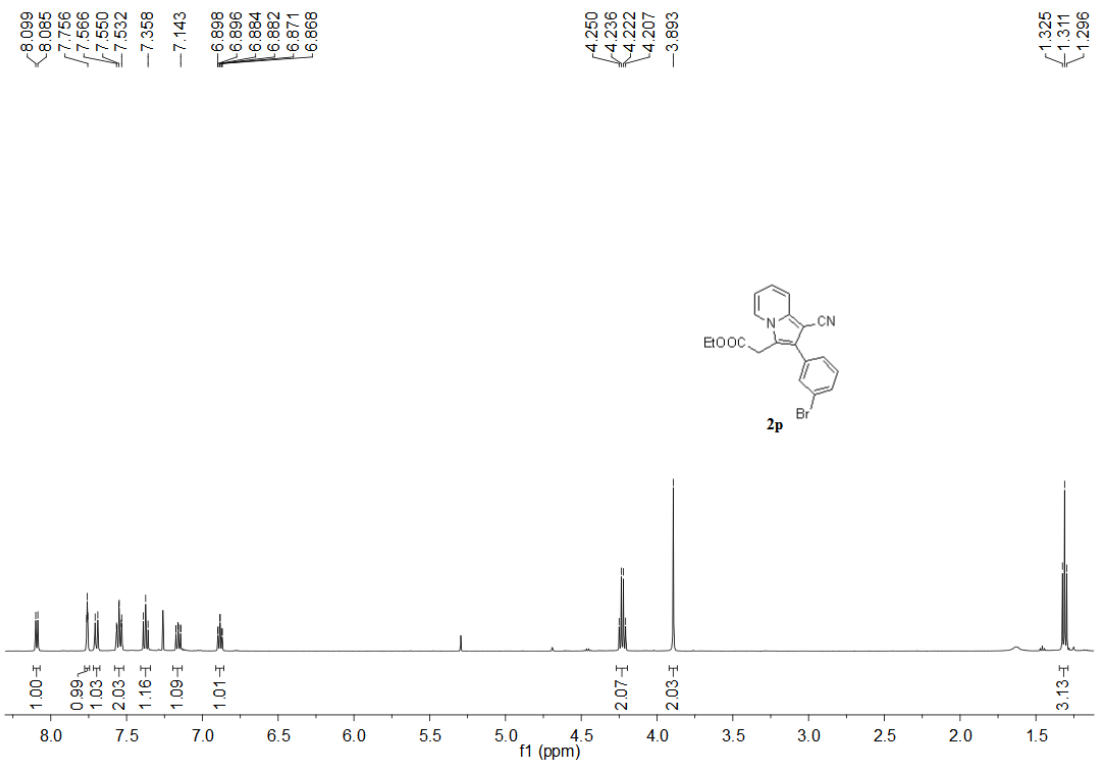
EtOOC
CN
N
Br
2o
f1 (ppm)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7.143
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6.868
4.250
4.236
4.222
4.207
3.893
1.325
1.311
1.296
CN
EtOOC
N
Br
2p
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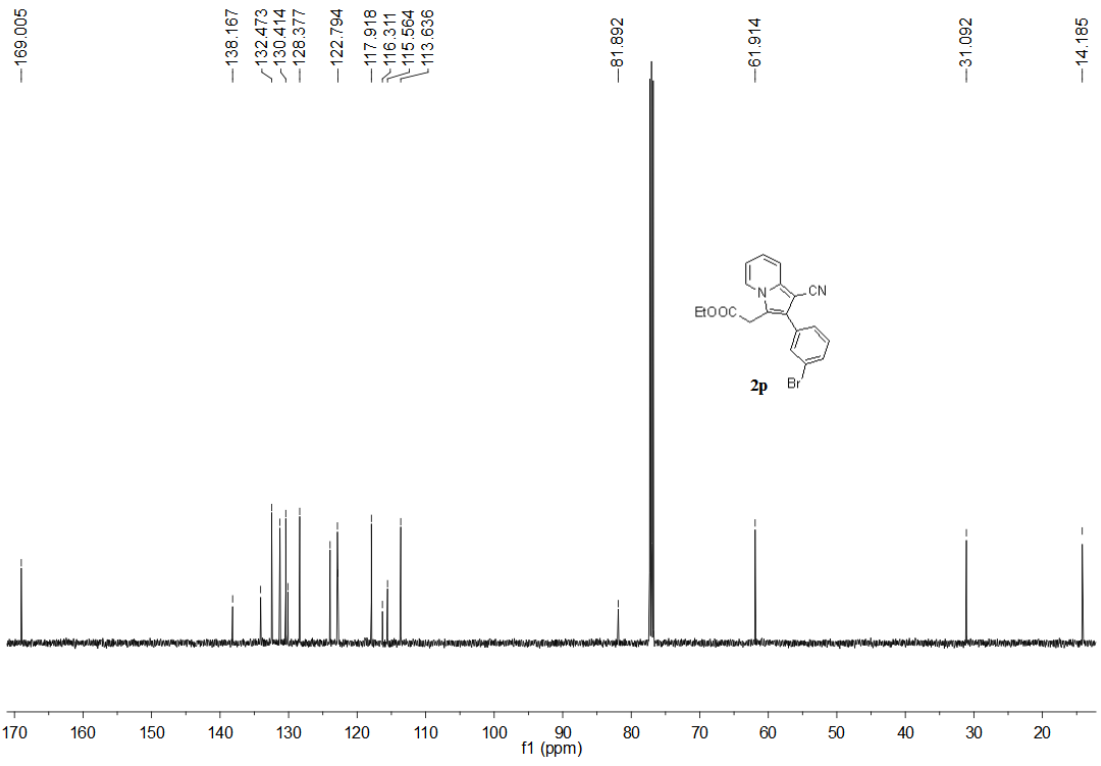
2.03
1.16
1.09
1.01
2.07
2.03
3.13
f1 (ppm)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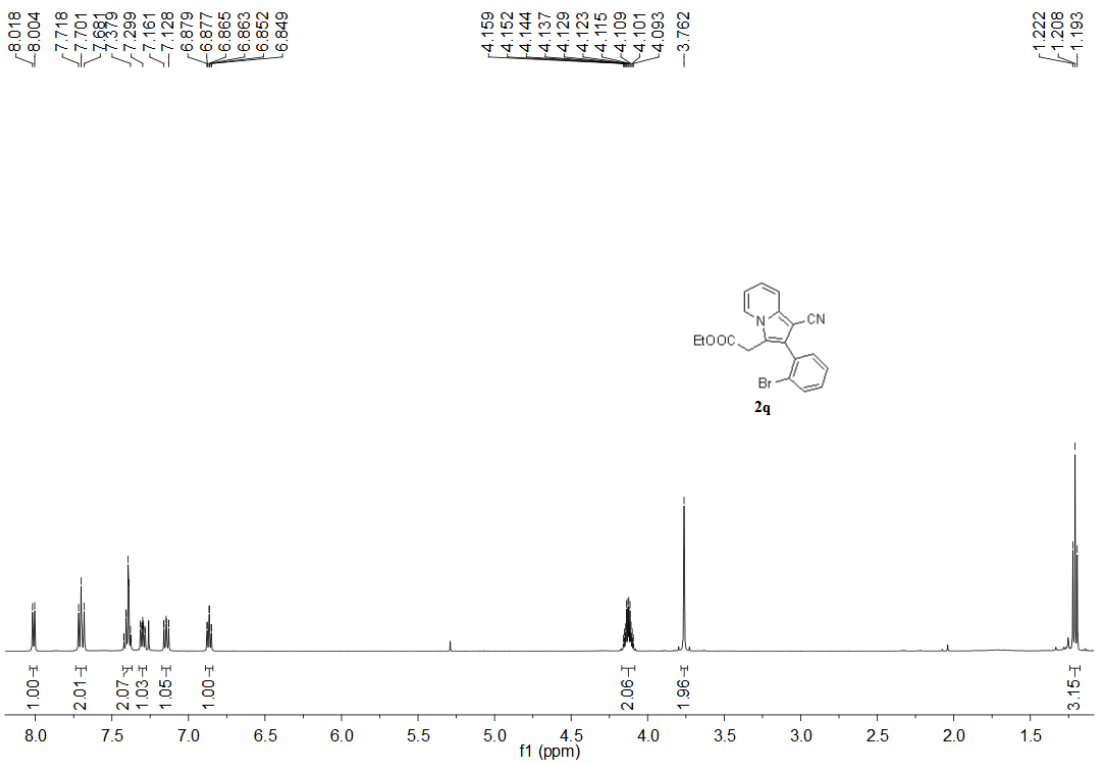
CN
EtOOC
N
Br
2p
f1 (ppm)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6.863
6.852
6.849
4.159
4.152
4.144
4.137
4.129
4.123
4.115
4.109
4.101
4.093
3.762
1.222
1.208
1.193
CN
EtOOC
N
Br
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1.00
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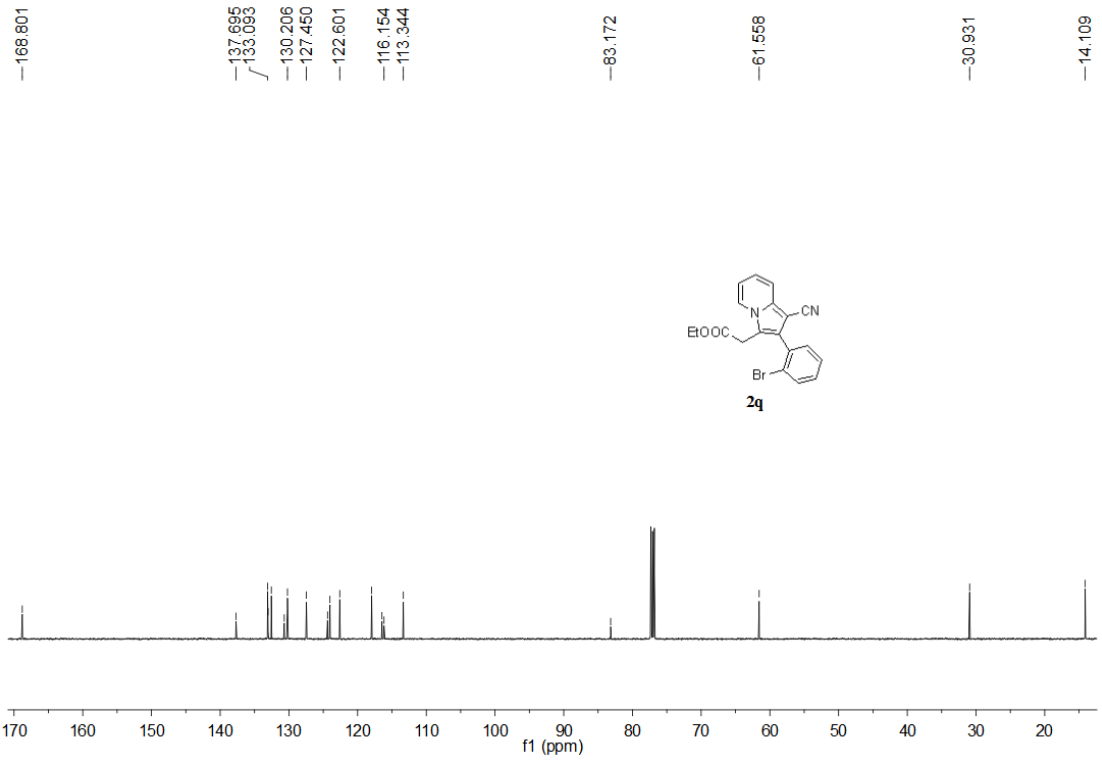
3.15
f1 (ppm)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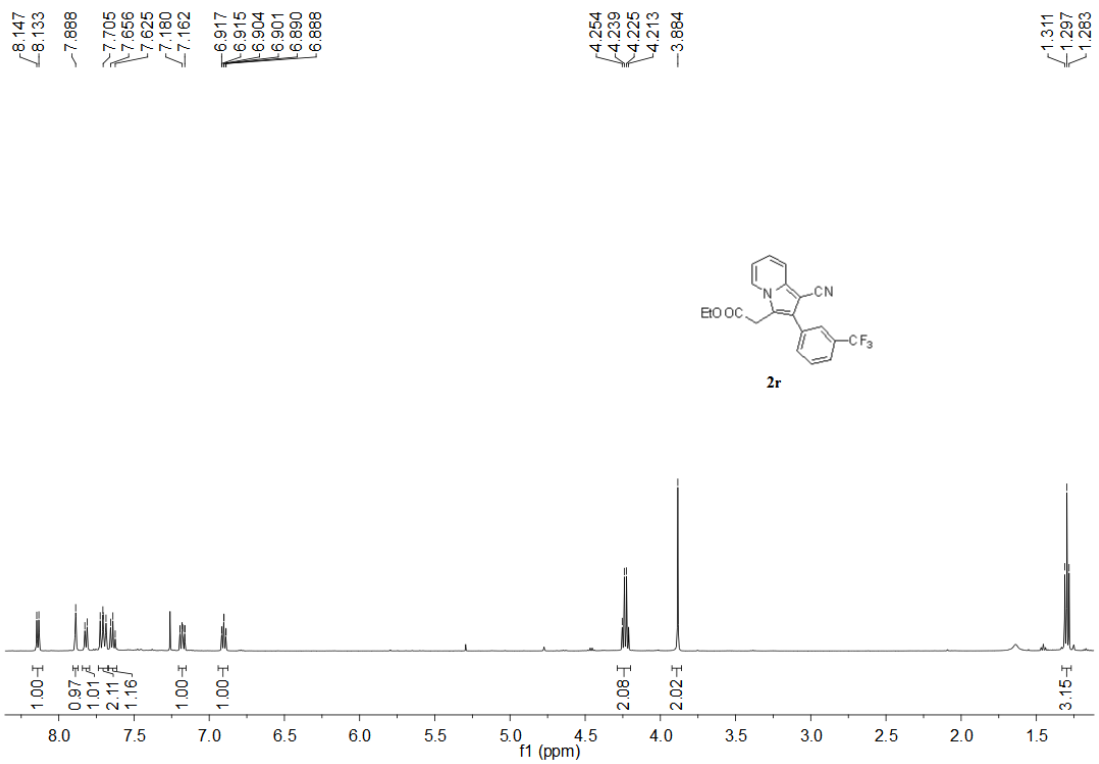
CN
EtOOC
N
Br
2q
f1 (ppm)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4.254
4.239
4.225
4.213
3.884
1.311
1.297
1.283
CN
EtO OC
CF3
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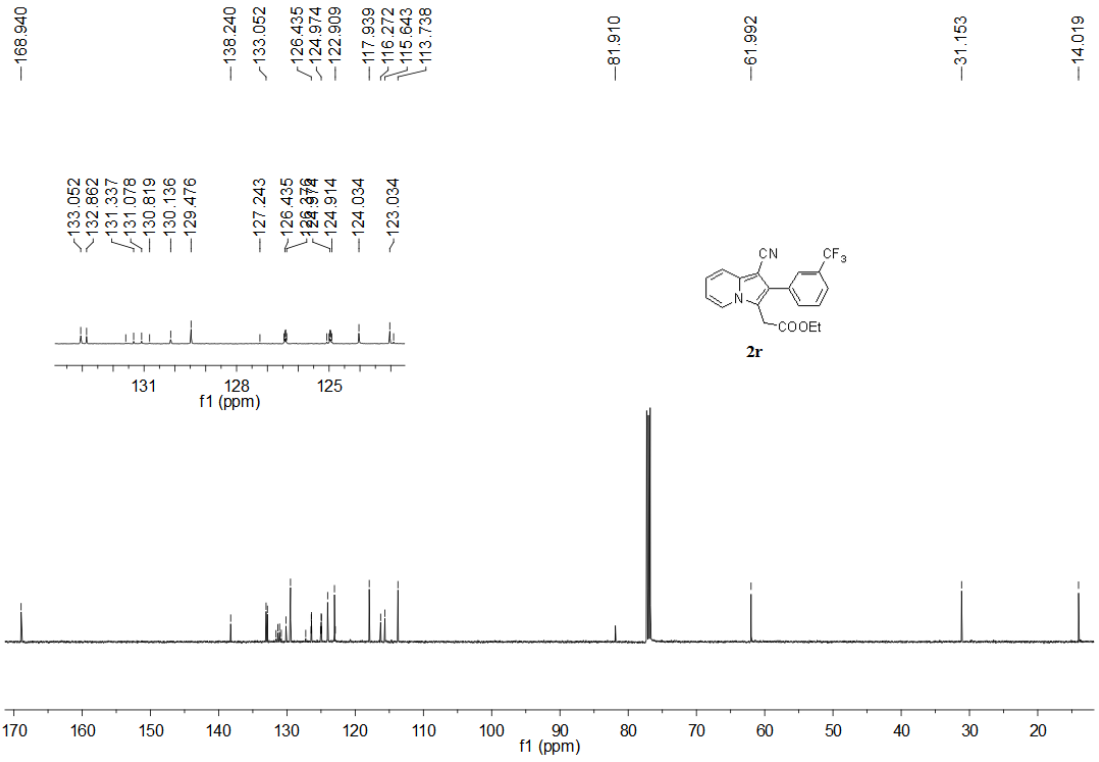
2.08
2.02
3.15
f1 (ppm)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14.019
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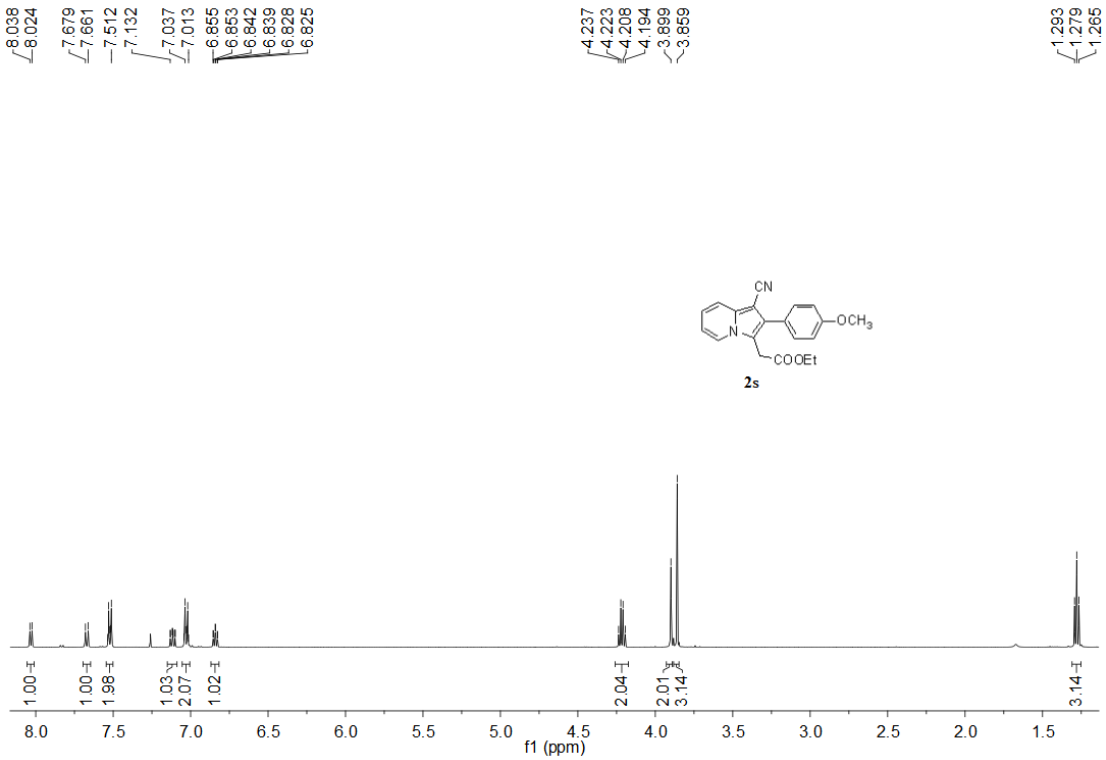
CF3
COOEt
2r
f1 (ppm)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4.237
4.223
4.208
4.194
3.899
3.859
1.293
1.279
1.265
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OCH3
COOEt
2s
1.00
1.00
1.98
1.03
2.07
1.02
2.04
2.01
3.14
3.14
8.0
7.5
7.0
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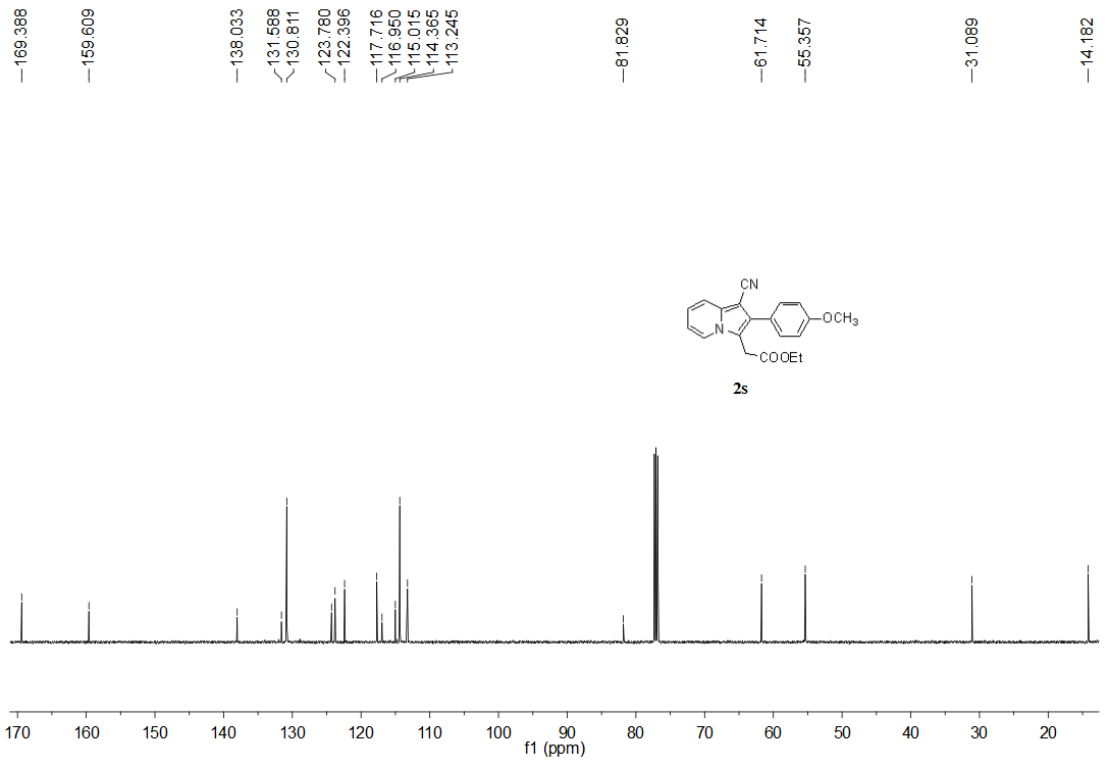
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55.357
31.089
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CN
OCH3
COOEt
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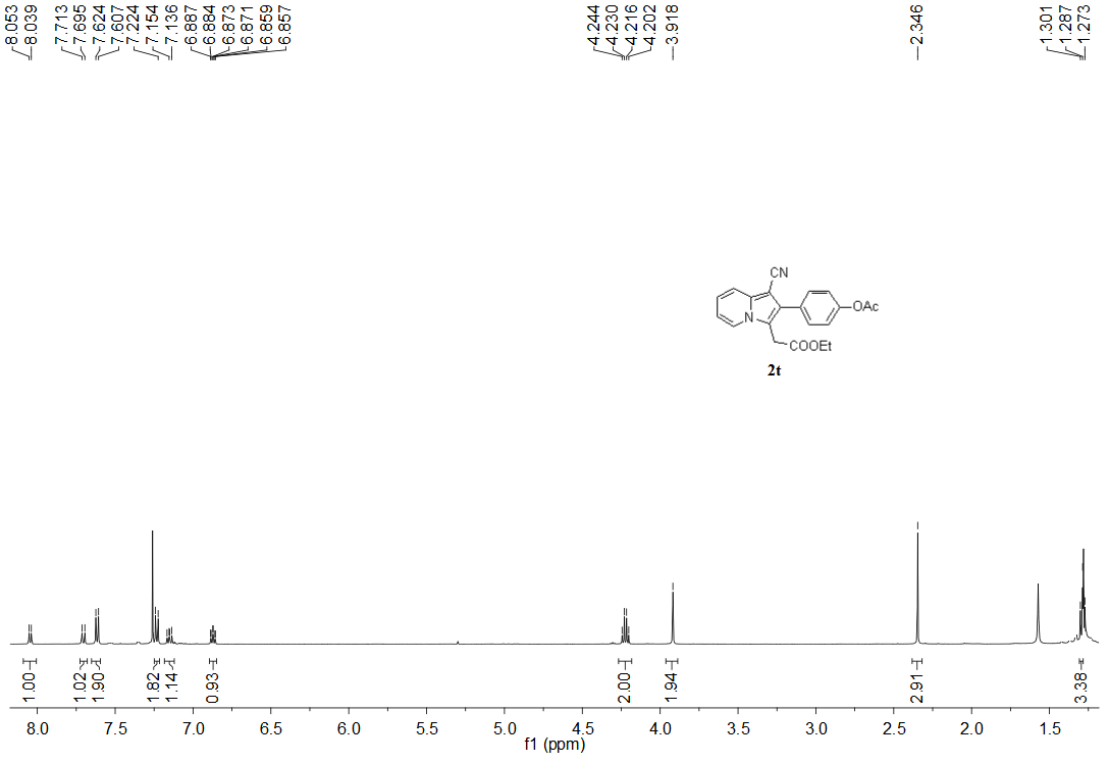
f1 (ppm)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6.871
6.859
6.857
4.244
4.230
4.216
4.202
3.918
2.346
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1.287
1.273
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OAc
N
COOEt
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1.02
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1.82
1.14
0.93
2.00
1.94
2.91
3.38
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7.0
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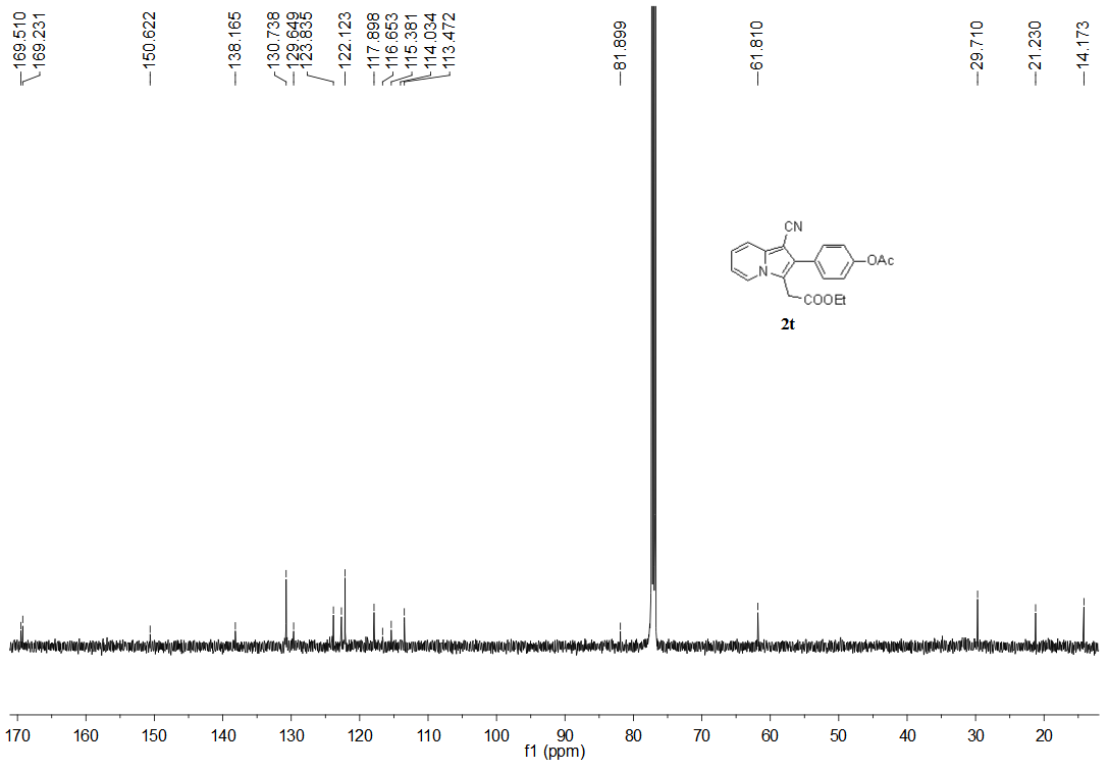
1.5
f1 (ppm)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OAc
N
COOEt
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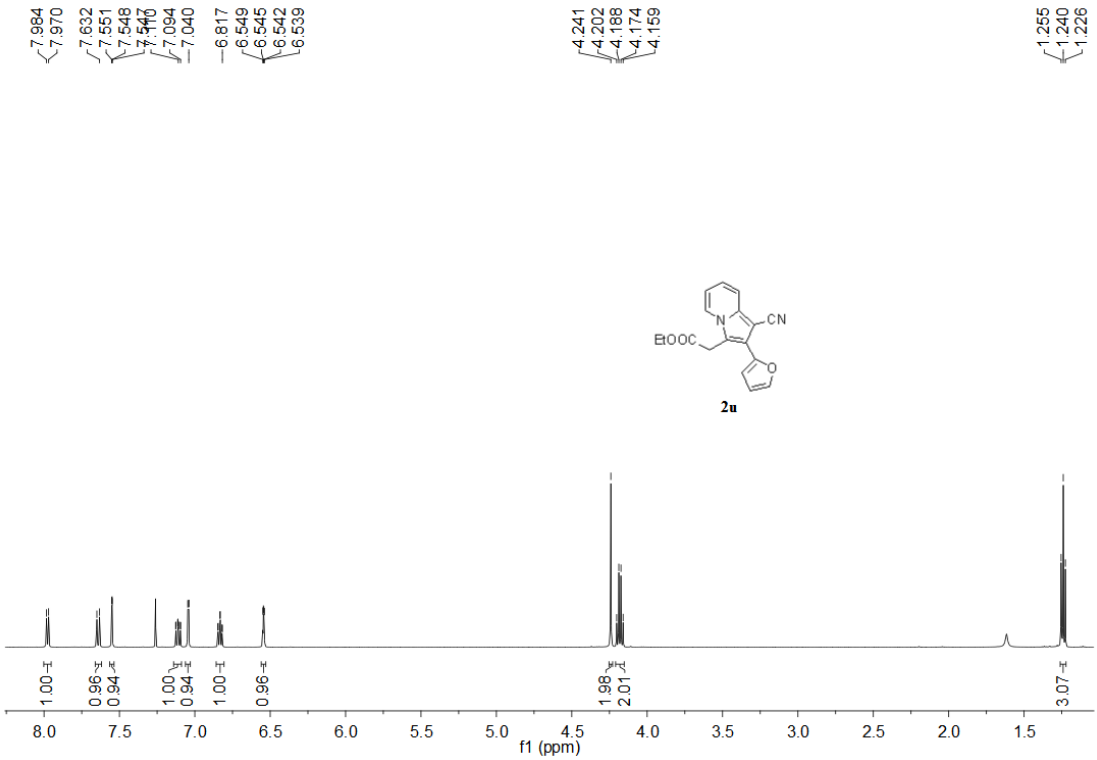
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6.542
6.539
4.241
4.202
4.188
4.174
4.159
1.255
1.240
1.226
CN
EtOOC
O
2u
1.00
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0.94
1.00
0.94
1.00
0.96
1.98
2.01
3.07
8.0
7.5
7.0
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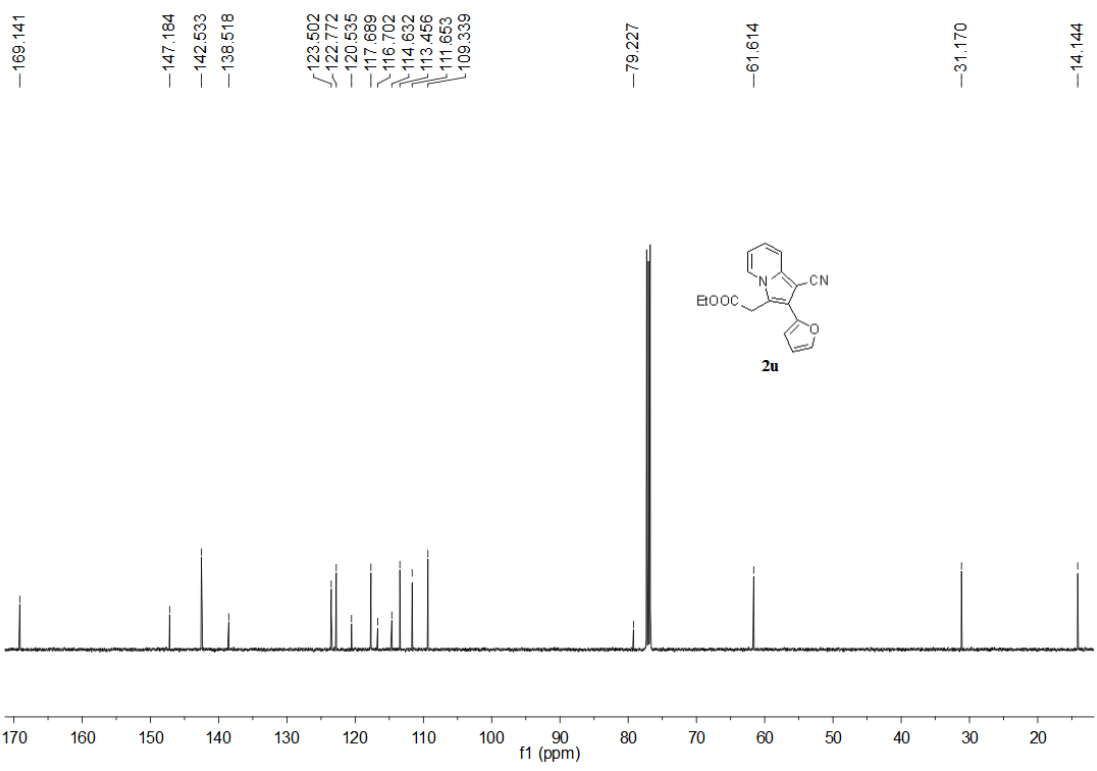
f1 (ppm)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31.170
14.144
CN
EtOOC
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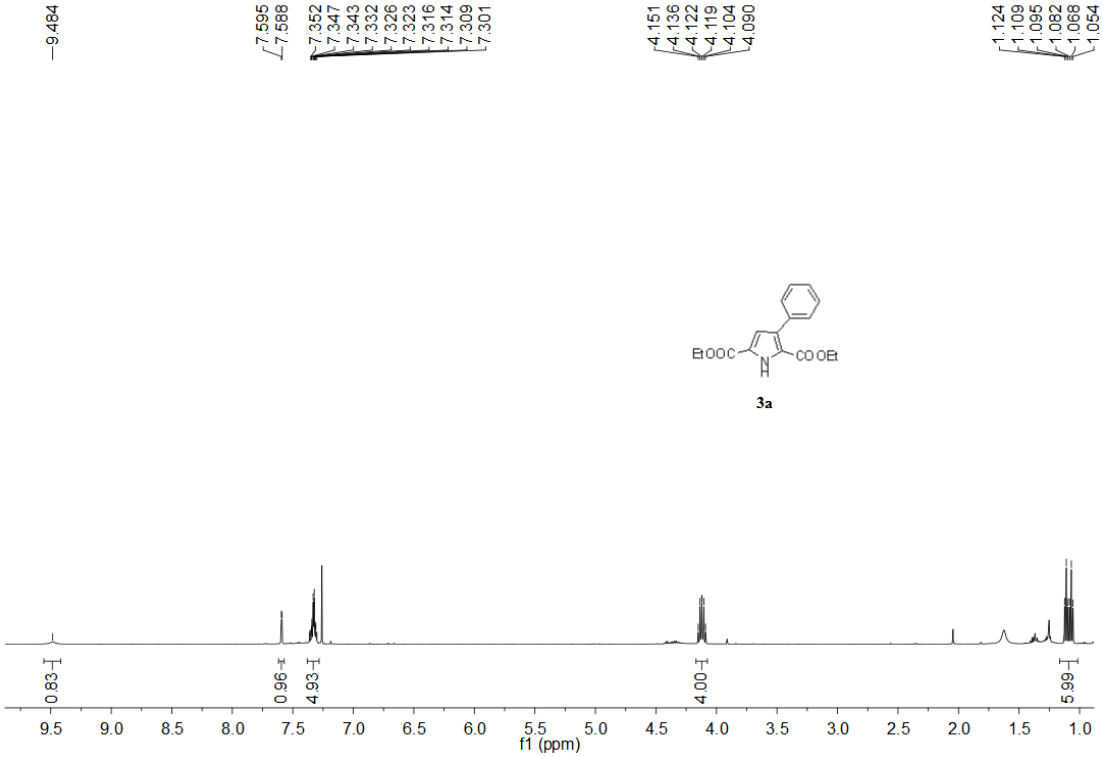
f1 (ppm)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7.309
7.301
4.151
4.136
4.122
4.119
4.104
4.090
1.124
1.109
1.095
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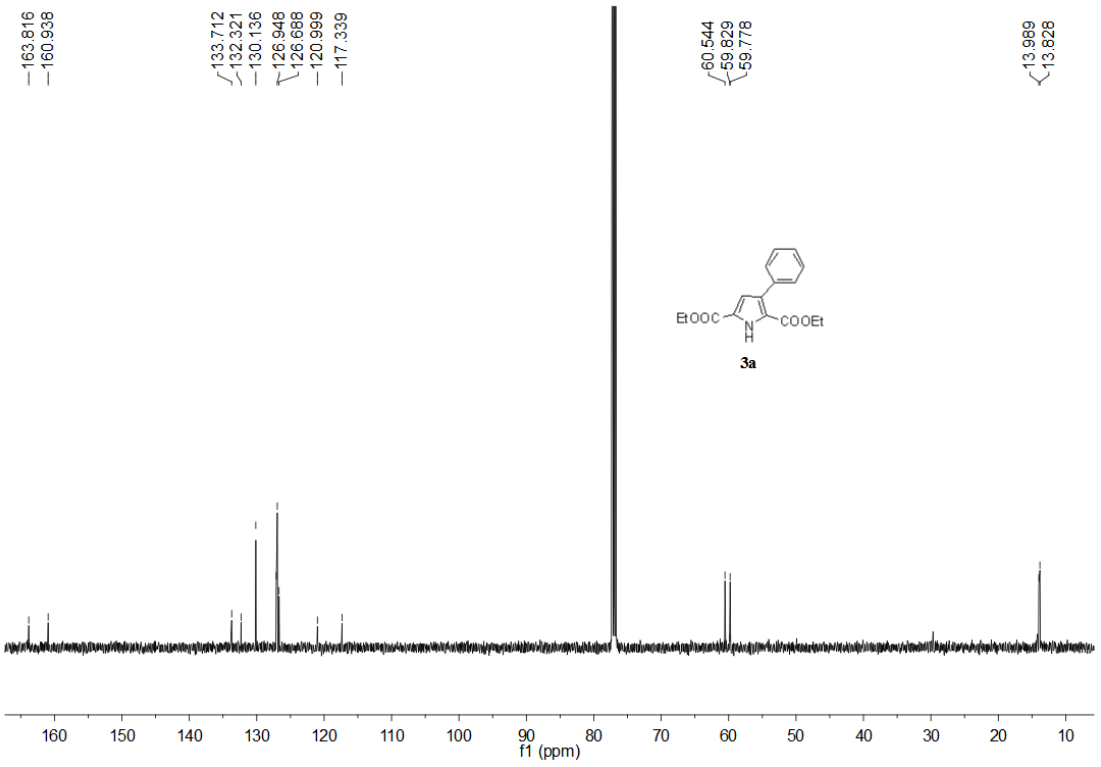
f1 (ppm)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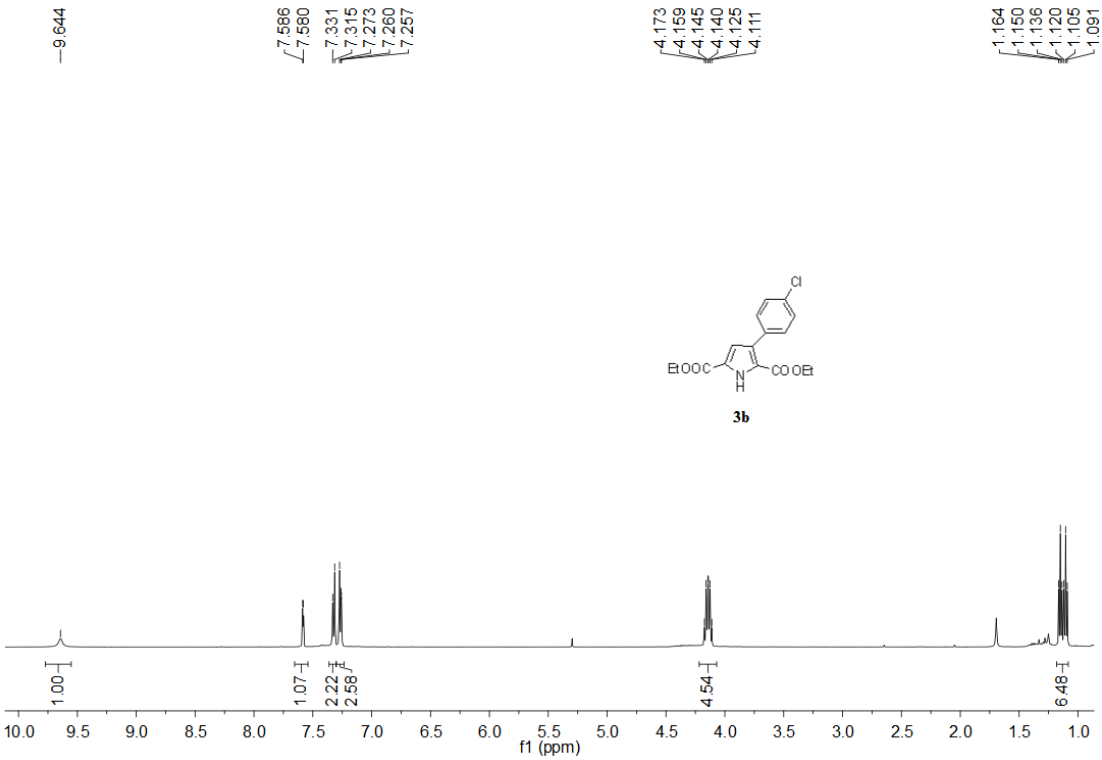
13.828
EtOOC
COOEt
3a
f1 (ppm)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7.580
7.331
7.315
7.273
7.260
7.257
4.173
4.159
4.145
4.140
4.125
4.111
1.164
1.150
1.136
1.120
1.105
1.091
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CO OEt
N
H
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2.58
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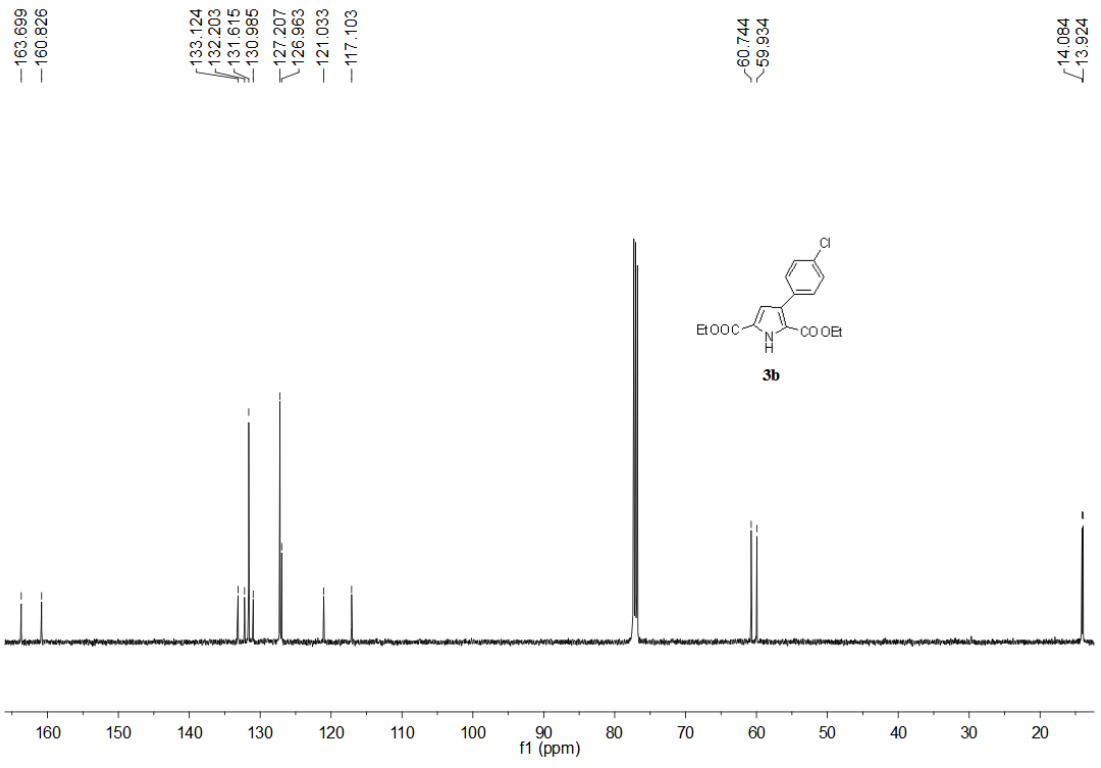
f1 (ppm)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13.924
Cl
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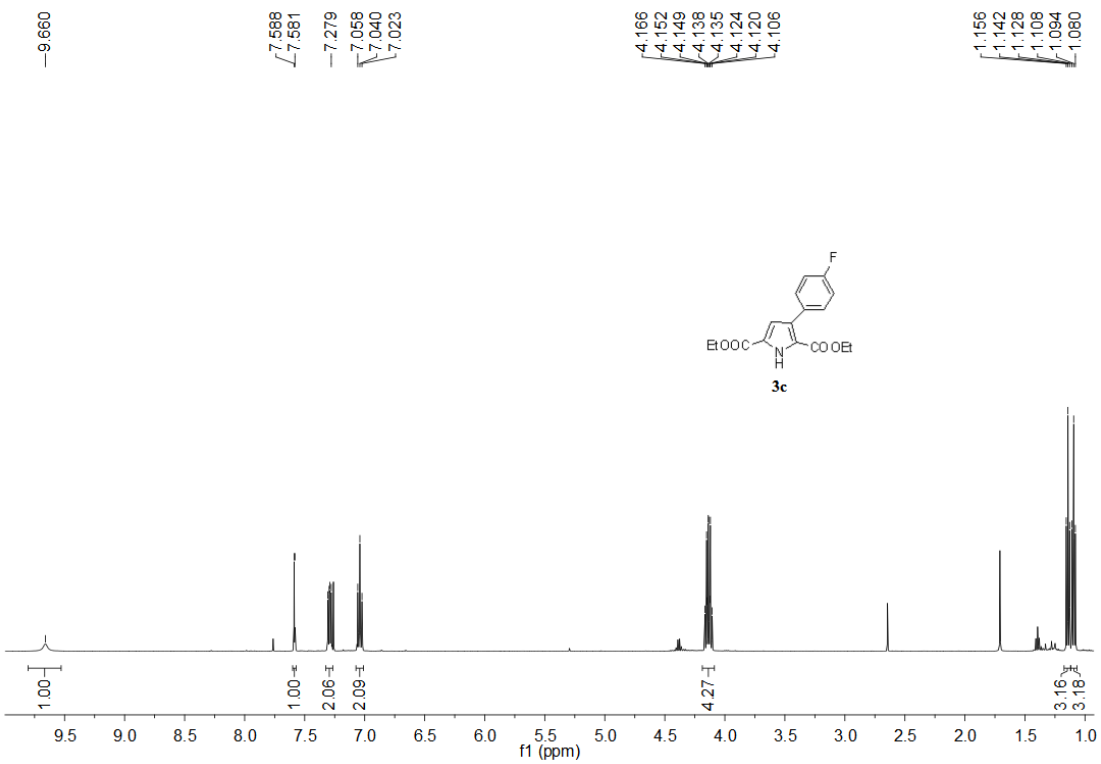
CO OEt
N
H
3b
f1 (ppm)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4.149
4.138
4.135
4.124
4.120
4.106
1.156
1.142
1.128
1.108
1.094
1.080
F
EtOOC
COOEt
N
H
3c
1.00
1.00
2.06
2.09
4.27
3.16
3.18
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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4.5
4.0
3.5
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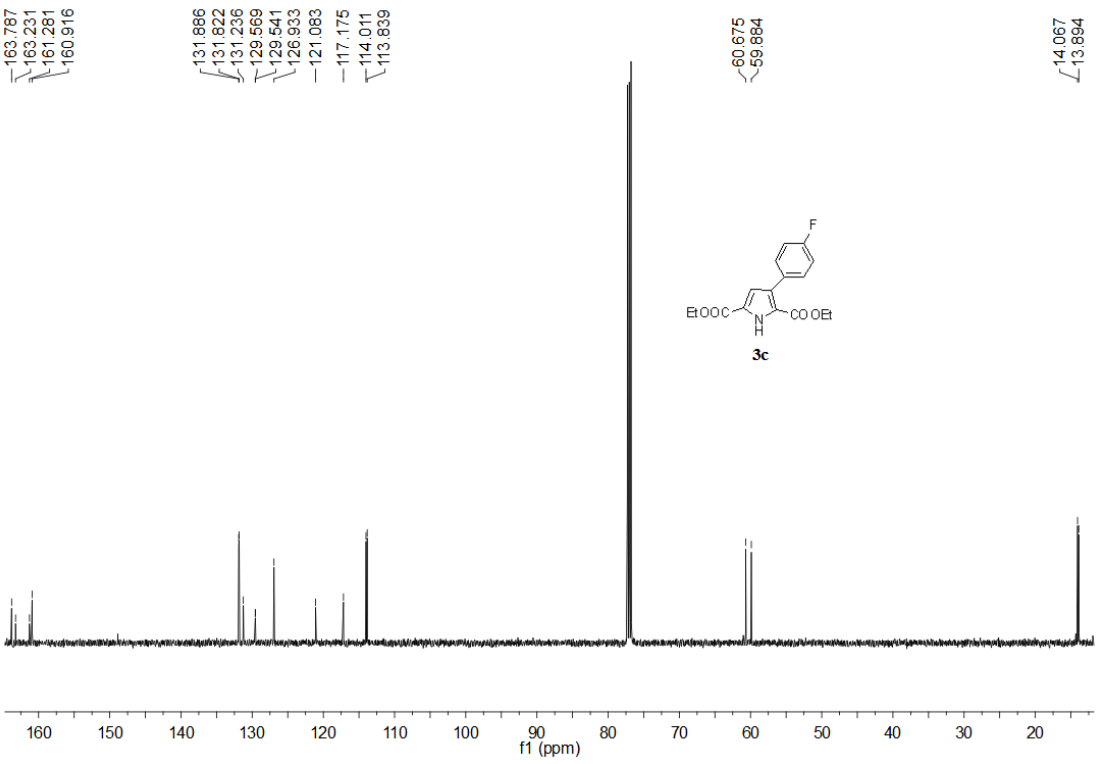
1.0
f1 (ppm)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117.175
114.011
113.839
60.675
59.884
14.067
13.894
F
EtOOC
COOEt
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H
3c
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110
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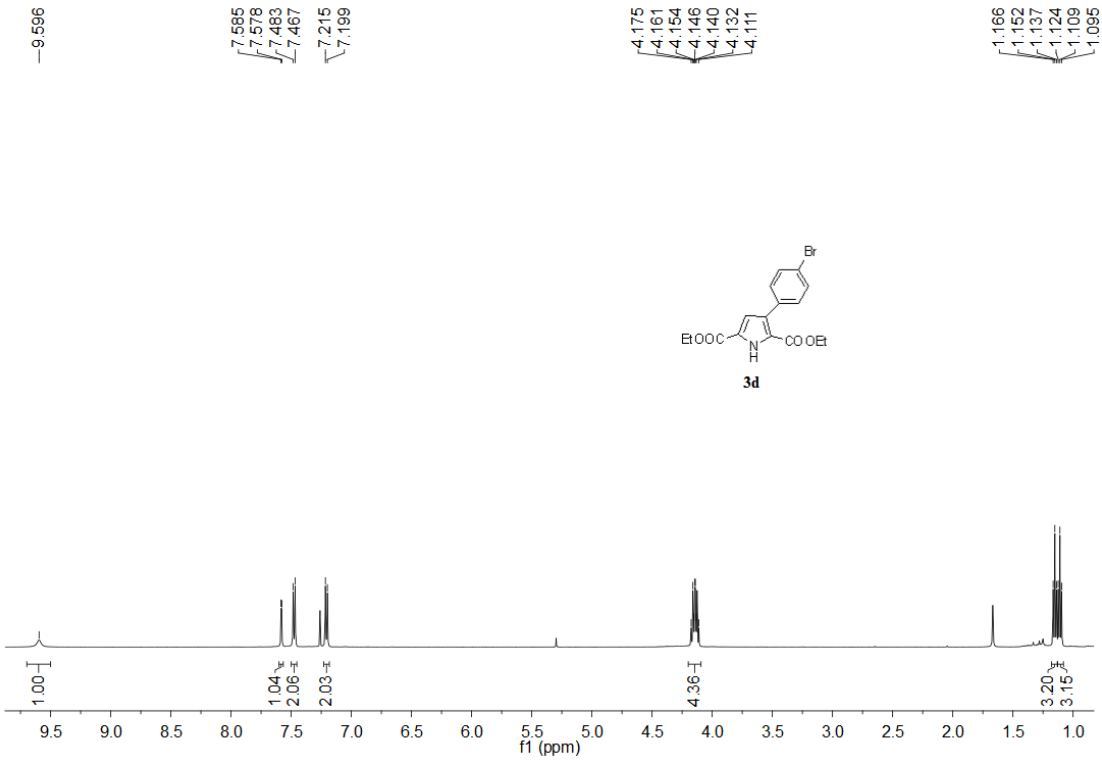
90
80
70
60
50
40
30
20
f1 (ppm)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4.154
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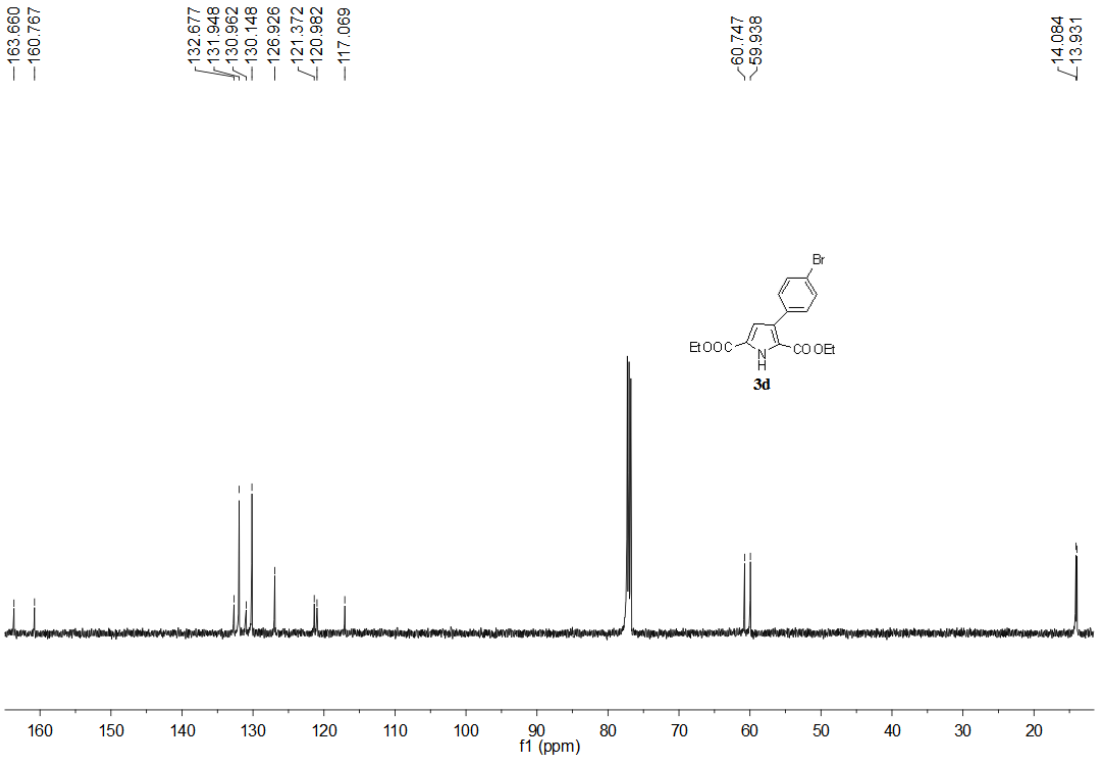
4.140
4.132
4.111
1.166
1.152
1.137
1.124
1.109
1.095
Br
EtOOC
CO OEt
N
H
3d
1.00
1.04
2.06
2.03
4.36
3.20
3.15
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)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Br
EtOOC
CO OEt
N
H
3d
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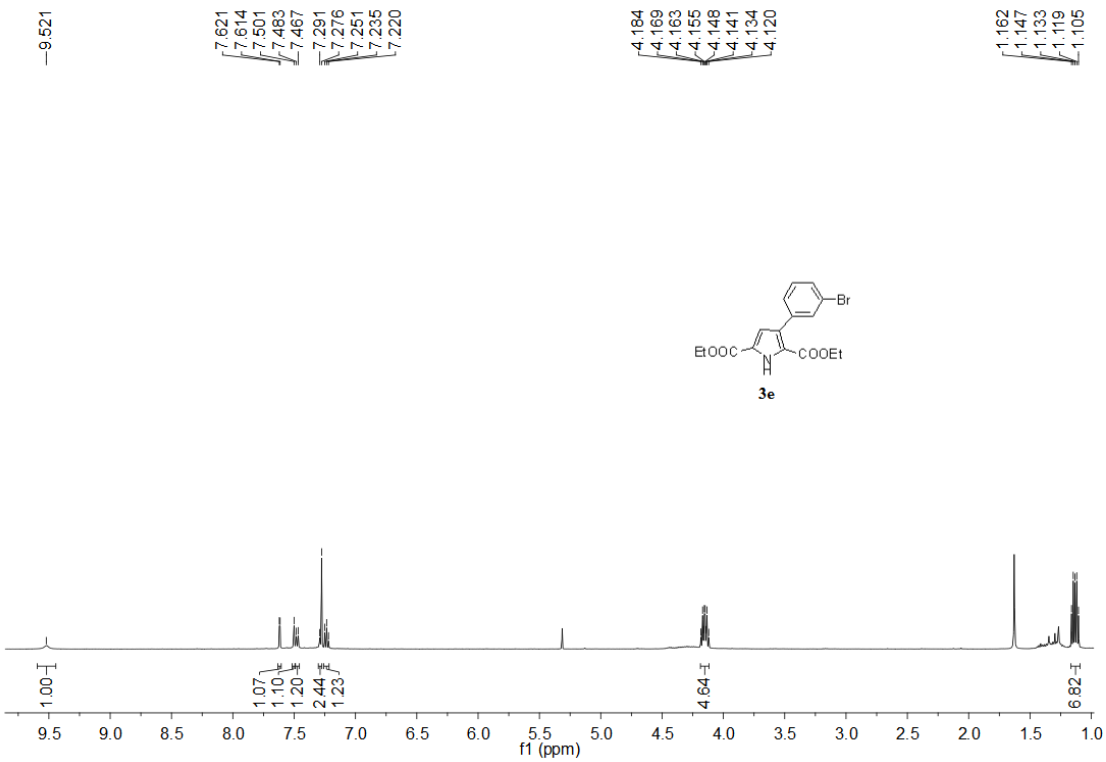
f1 (ppm)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7.235
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4.163
4.155
4.148
4.141
4.134
4.120
1.162
1.147
1.133
1.119
1.105
Br
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COOEt
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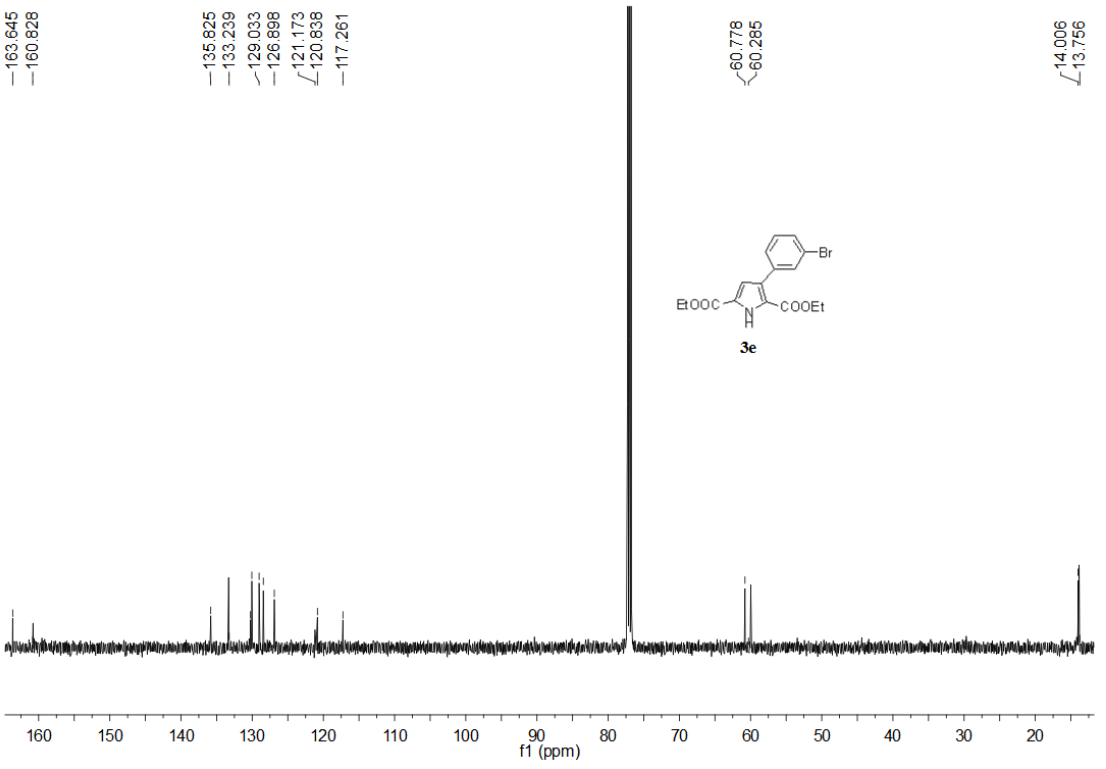
f1 (ppm)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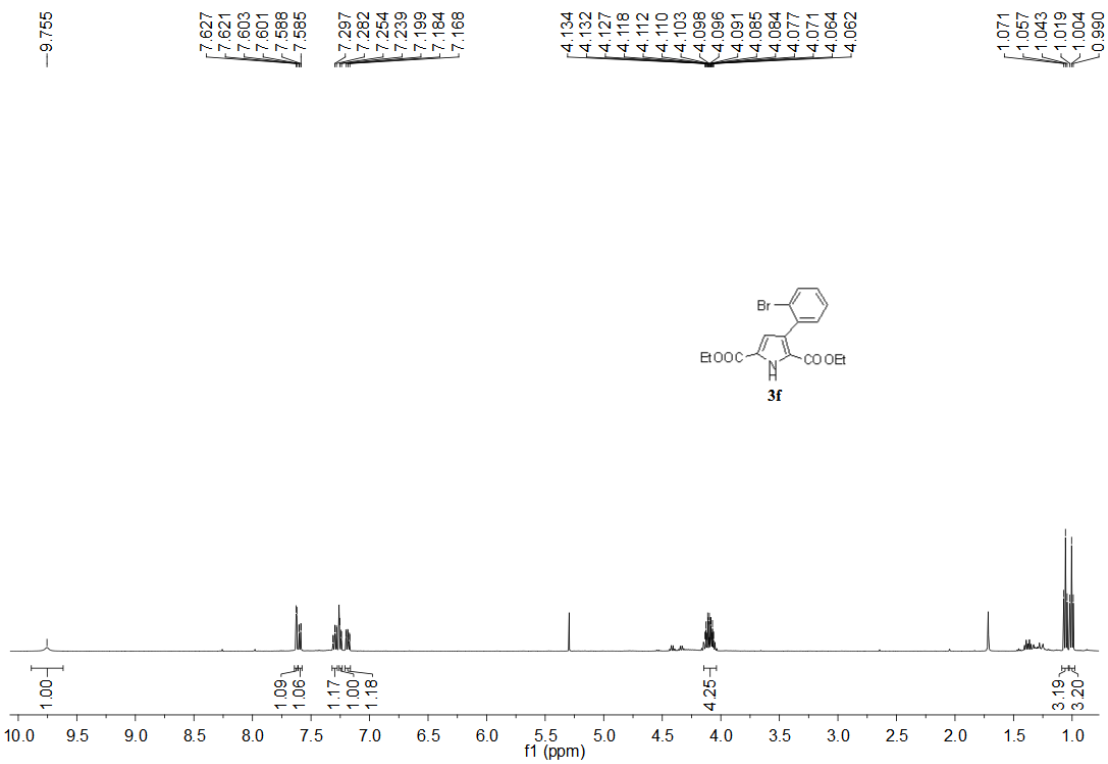
COOEt
3e
f1 (ppm)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7.184
7.168
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4.132
4.127
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4.112
4.110
4.103
4.098
4.096
4.091
4.085
4.084
4.077
4.071
4.064
4.062
1.071
1.057
1.043
1.019
1.004
0.990
Br
EtOOC
COOEt
N
H
3f
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1.09
1.06
1.17
1.00
1.18
4.25
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3.20
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9.0
8.5
8.0
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7.0
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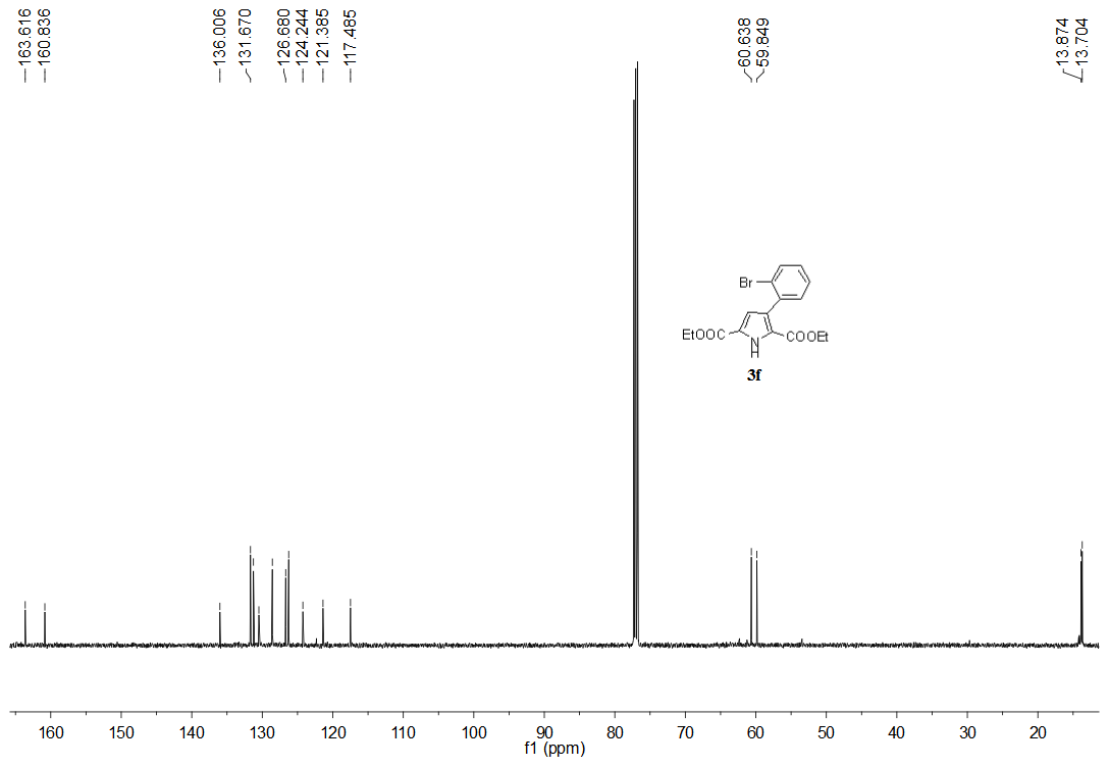
f1 (ppm)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COOEt
N
H
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130
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110
100
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80
70
60
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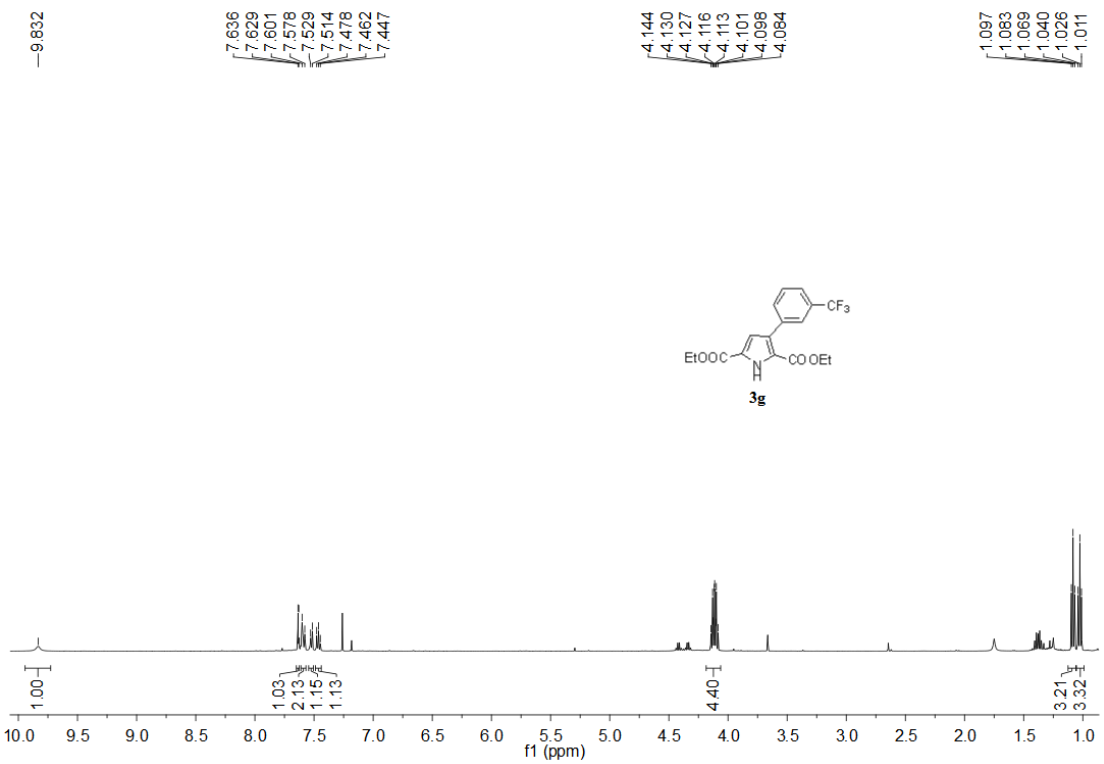
40
30
20
f1 (ppm)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4.113
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4.098
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1.083
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1.040
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1.011
CF3
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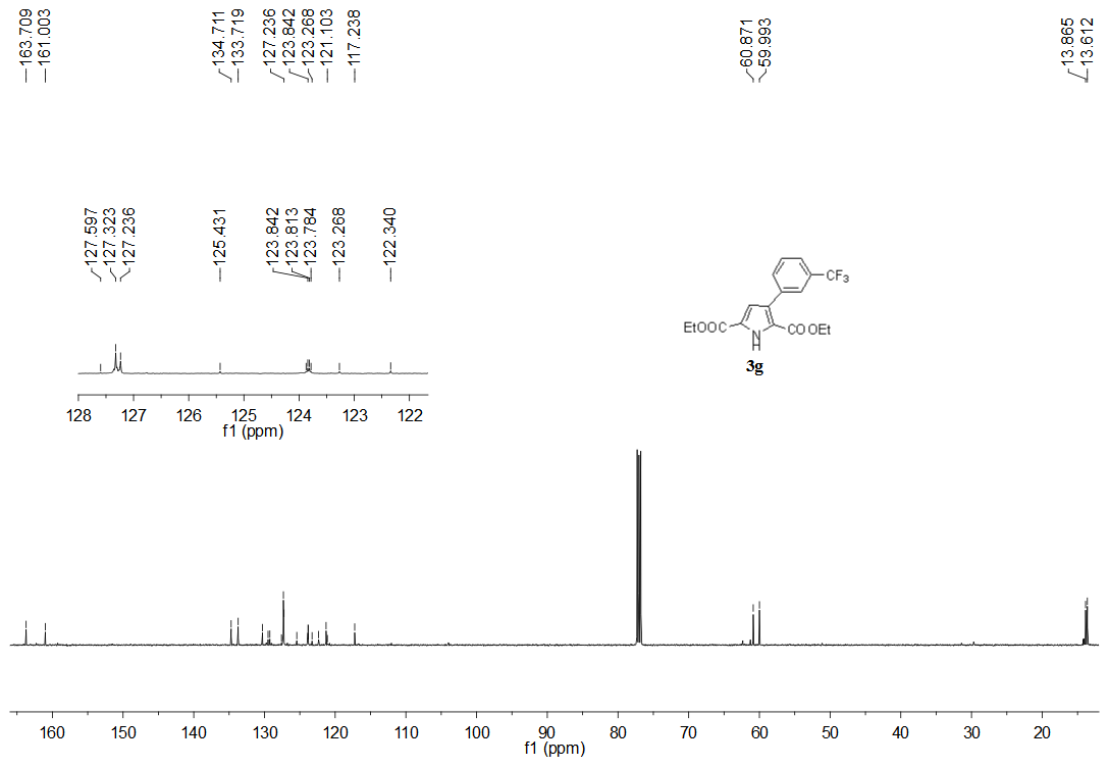
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CF3
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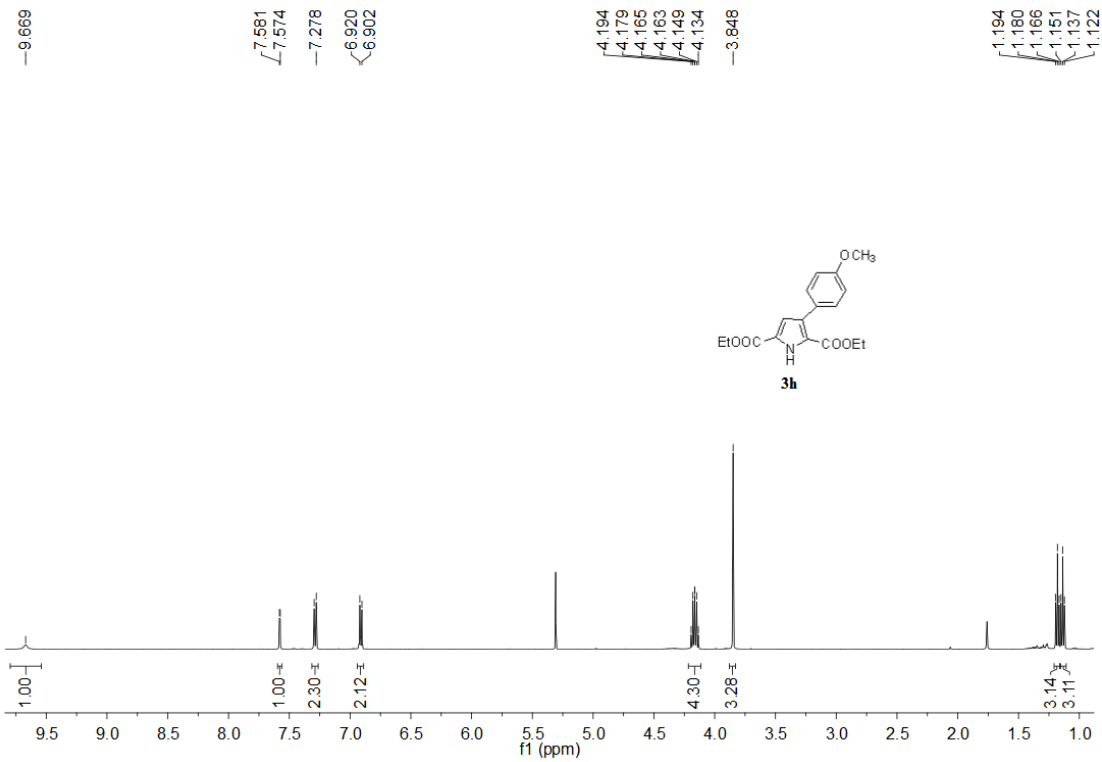
CO OEt
3g
f1 (ppm)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1.194
1.180
1.166
1.151
1.137
1.122
OCH3
EtOOC
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H
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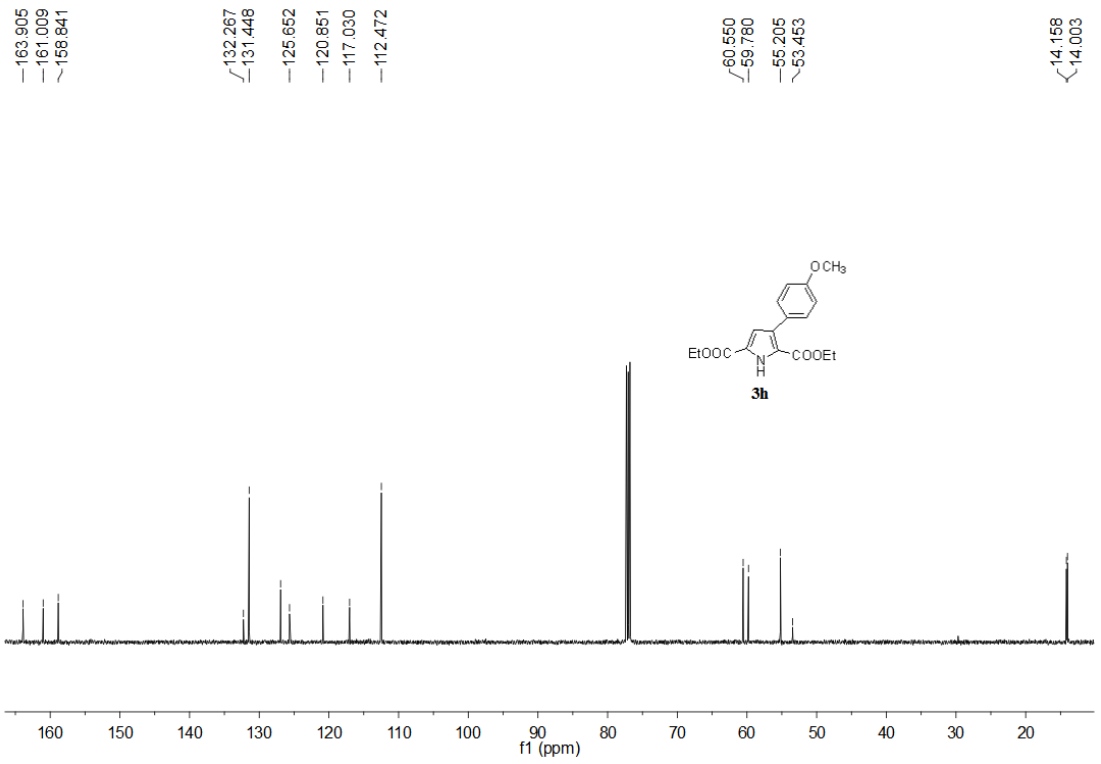
f1 (ppm)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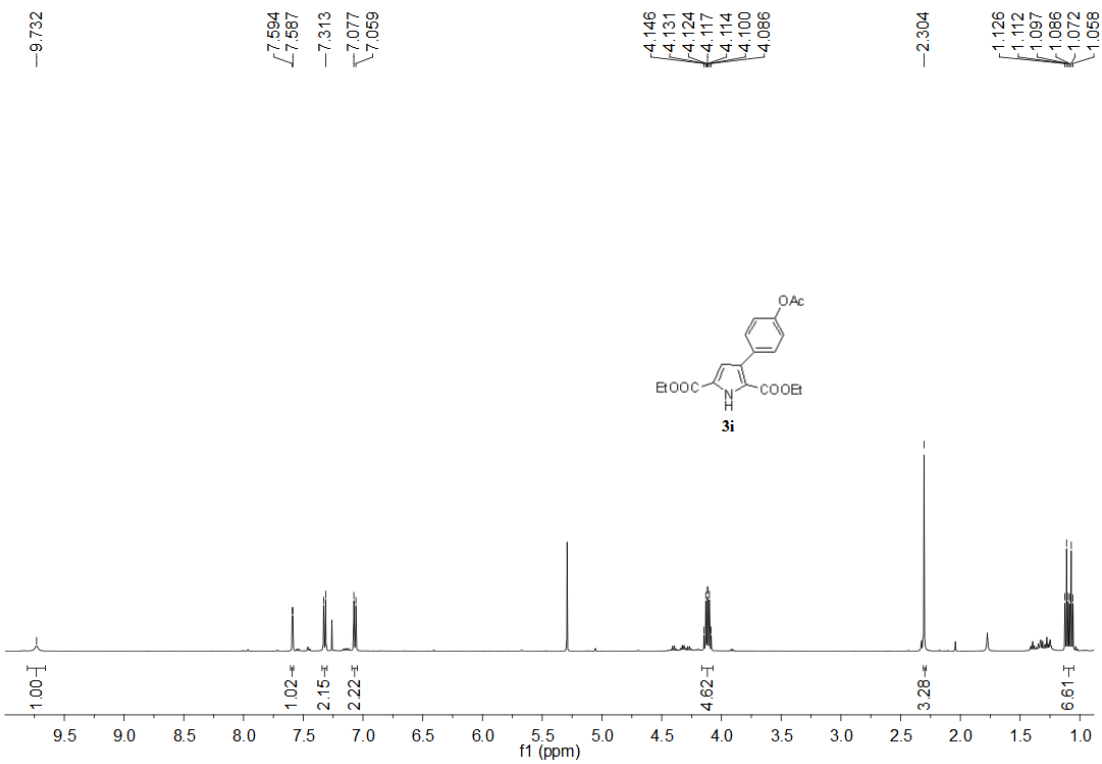
f1 (ppm)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2.304
1.126
1.112
1.097
1.086
1.072
1.058
OAc
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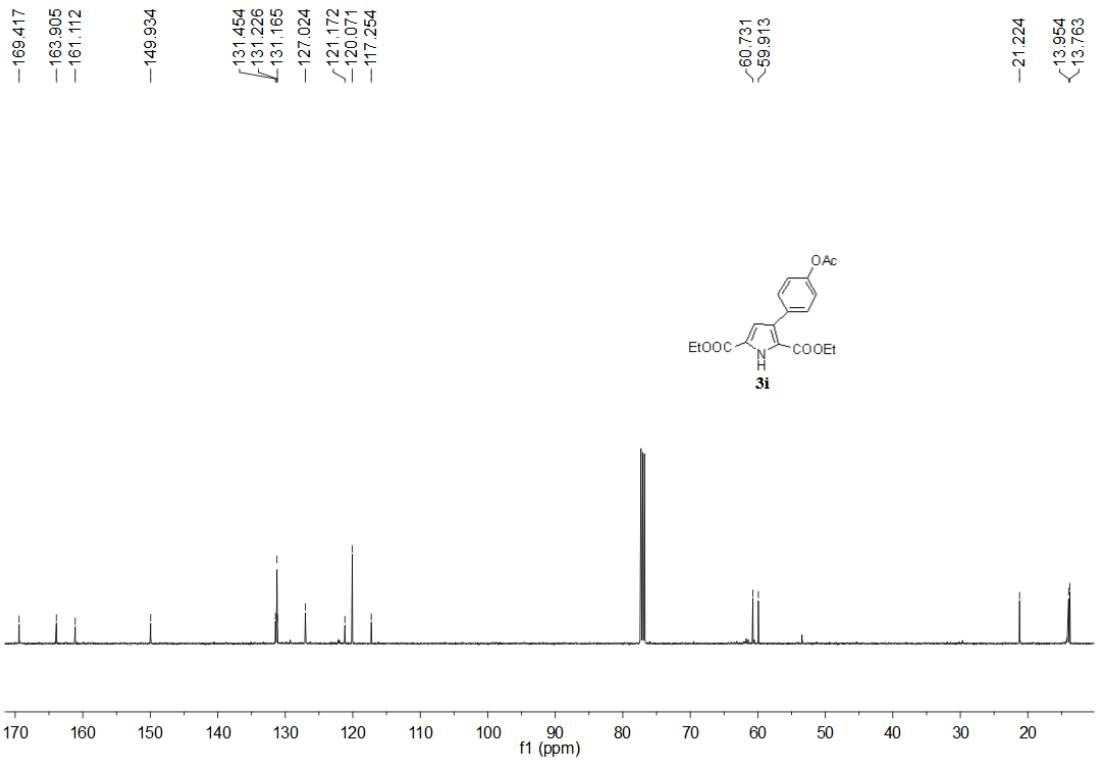
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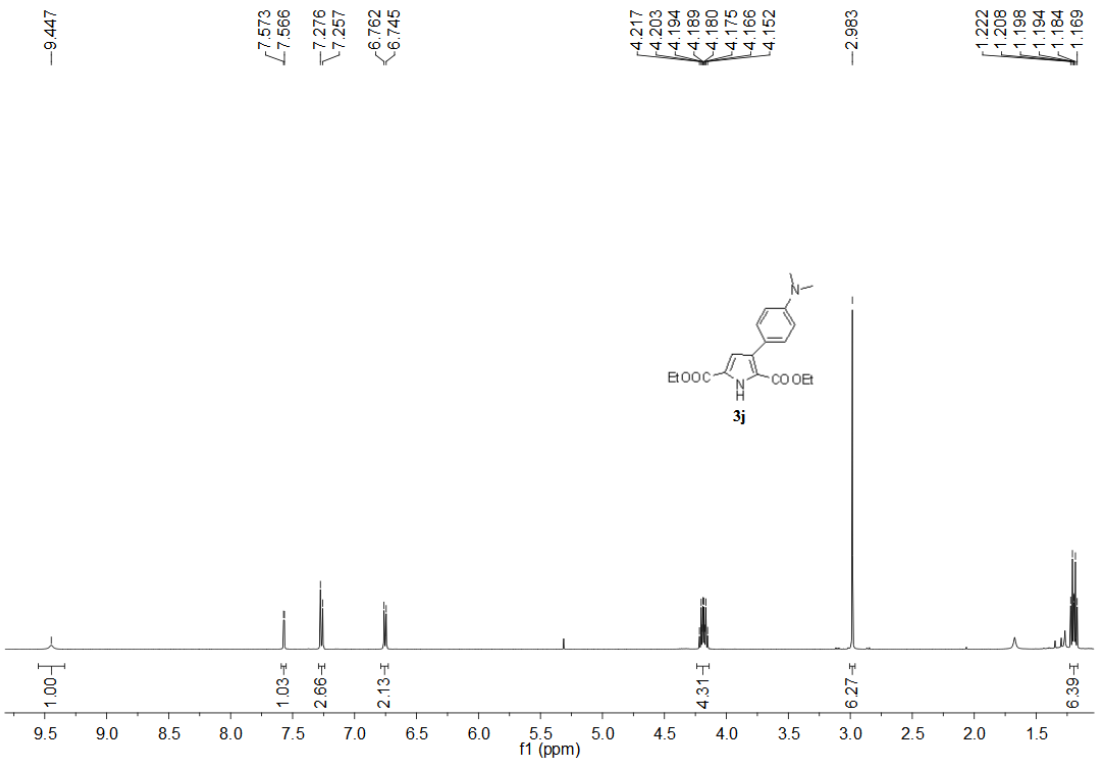
COOEt
H
N
3i
f1 (ppm)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4.175
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1.208
1.198
1.194
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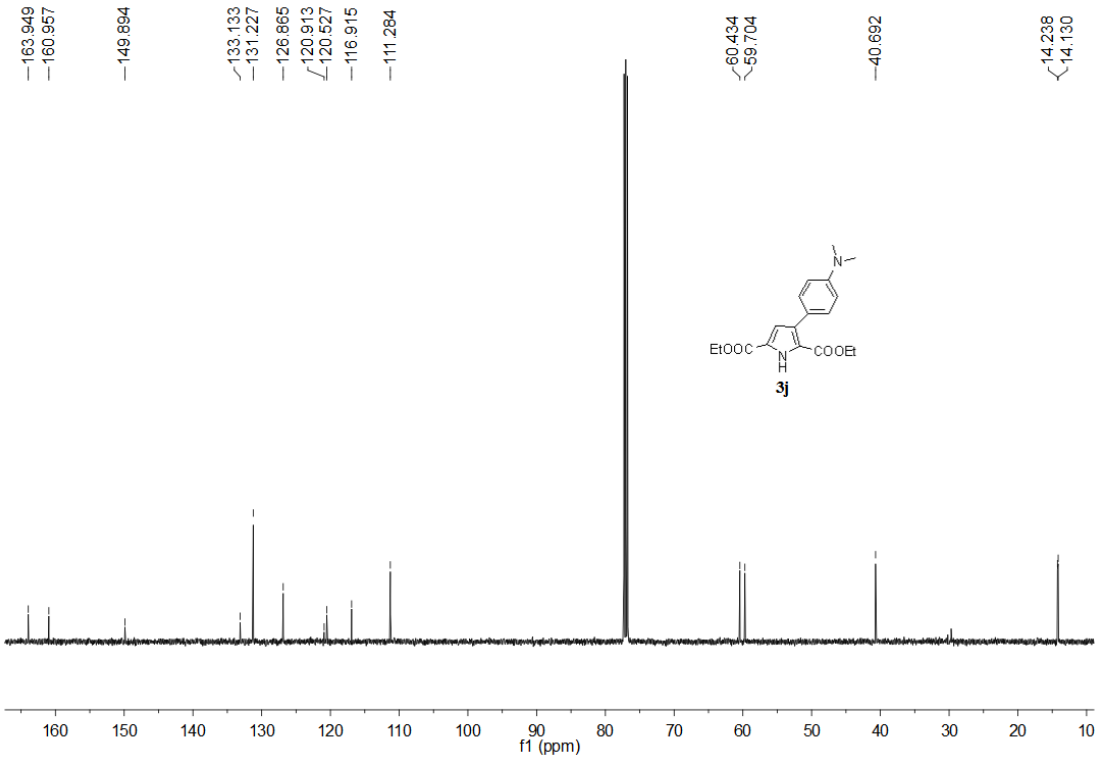
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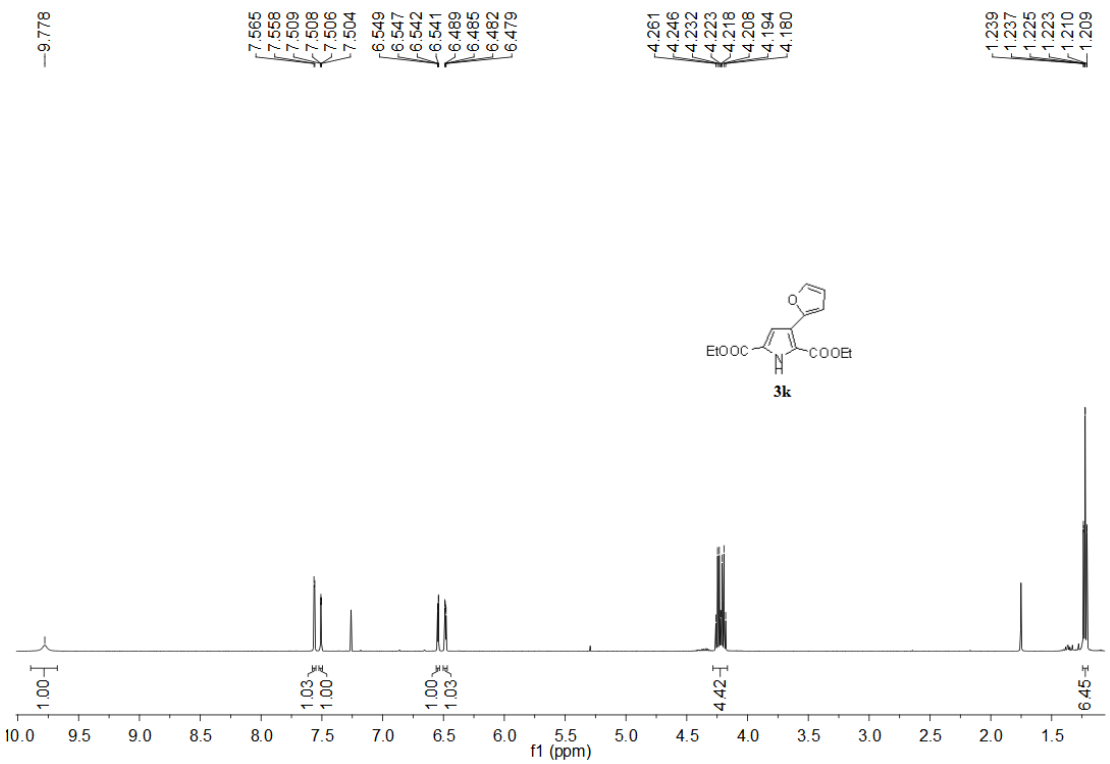
COOEt
3j
f1 (ppm)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6.479
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4.246
4.232
4.223
4.218
4.208
4.194
4.180
1.239
1.237
1.225
1.223
1.210
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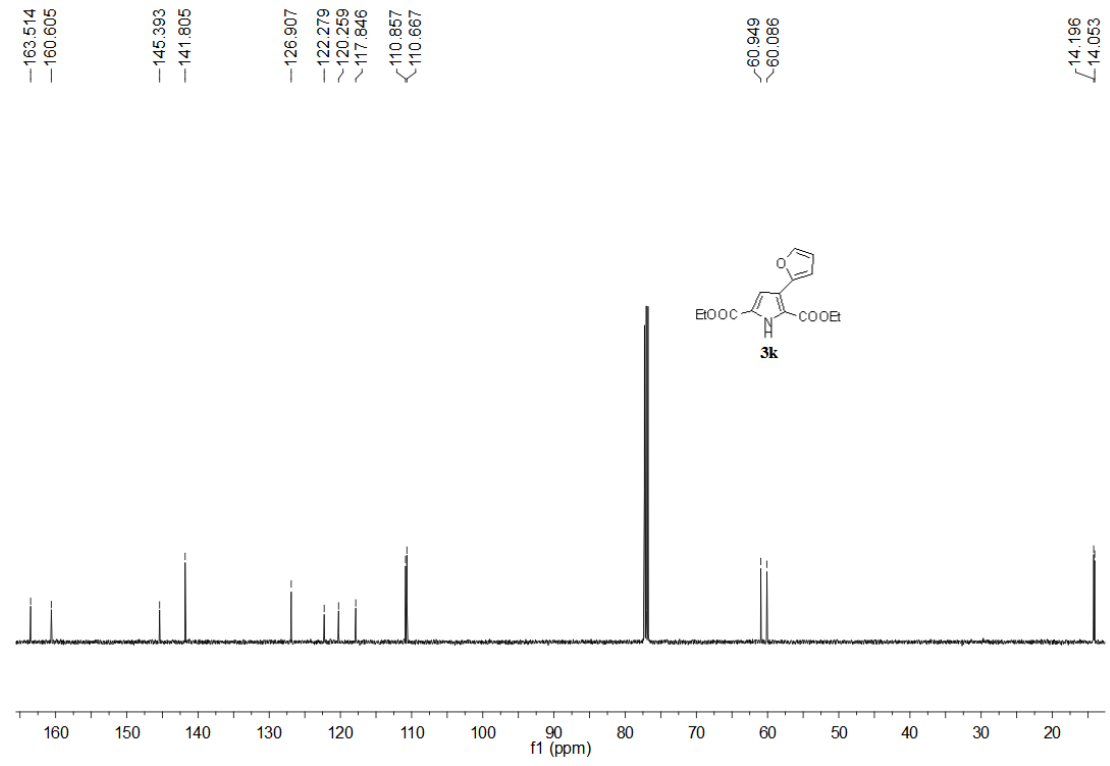
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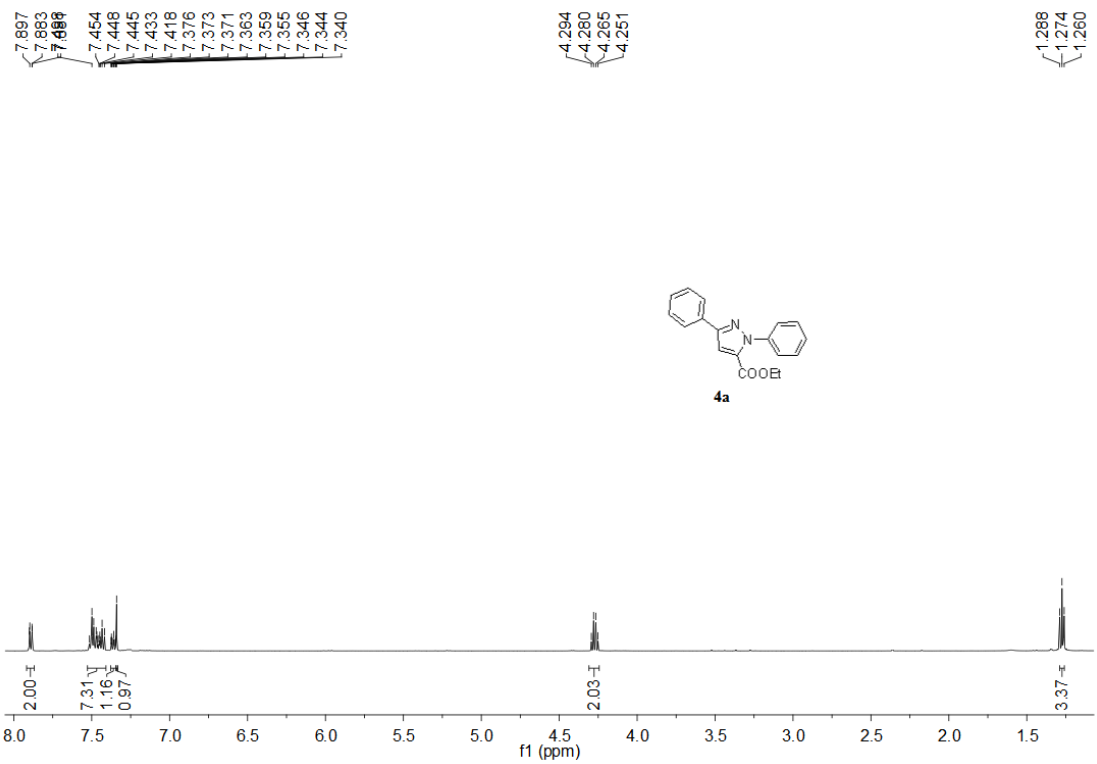
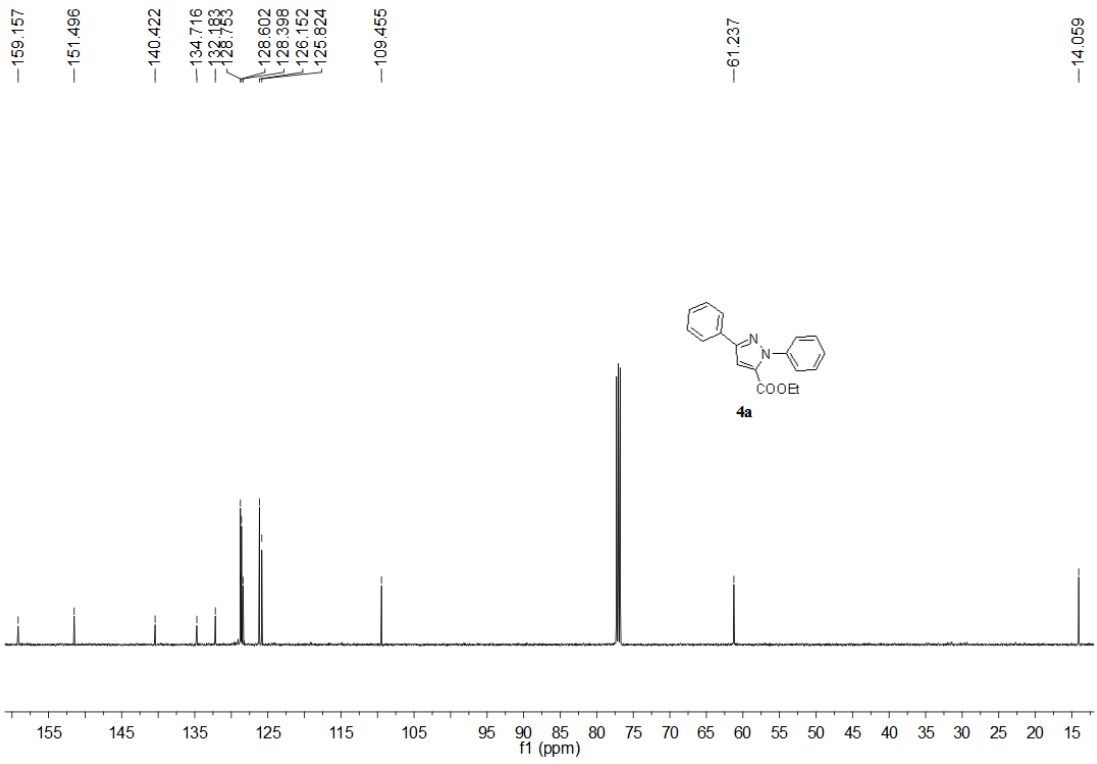
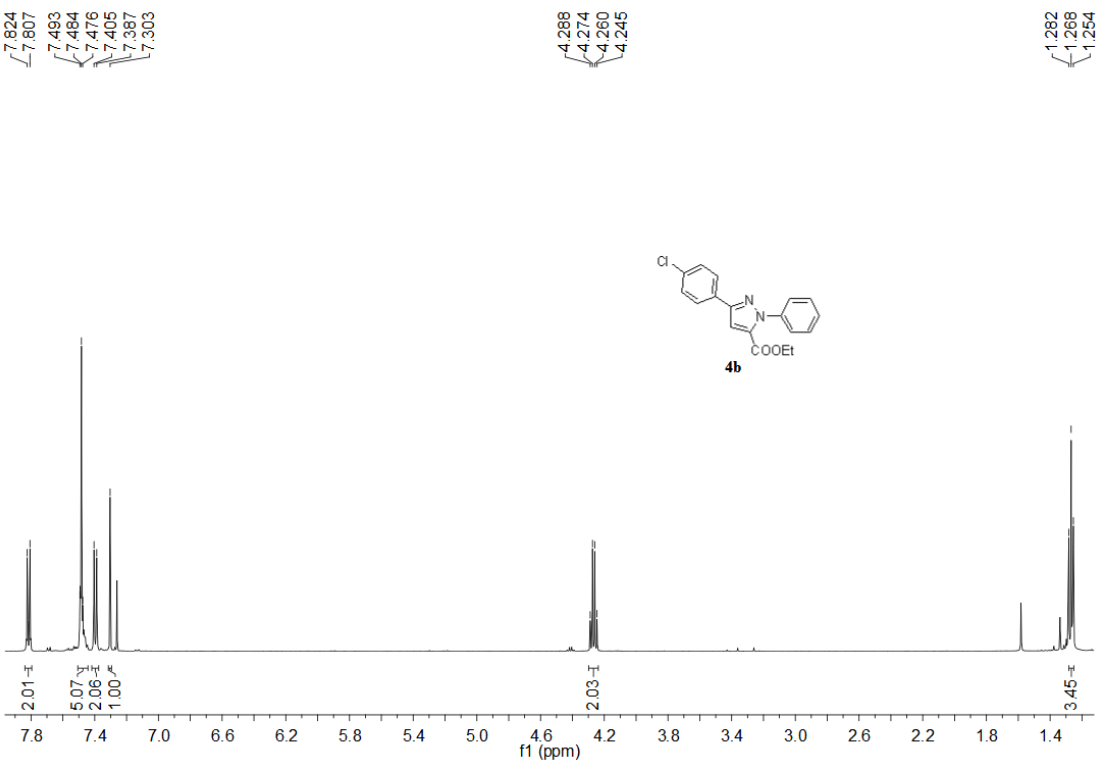
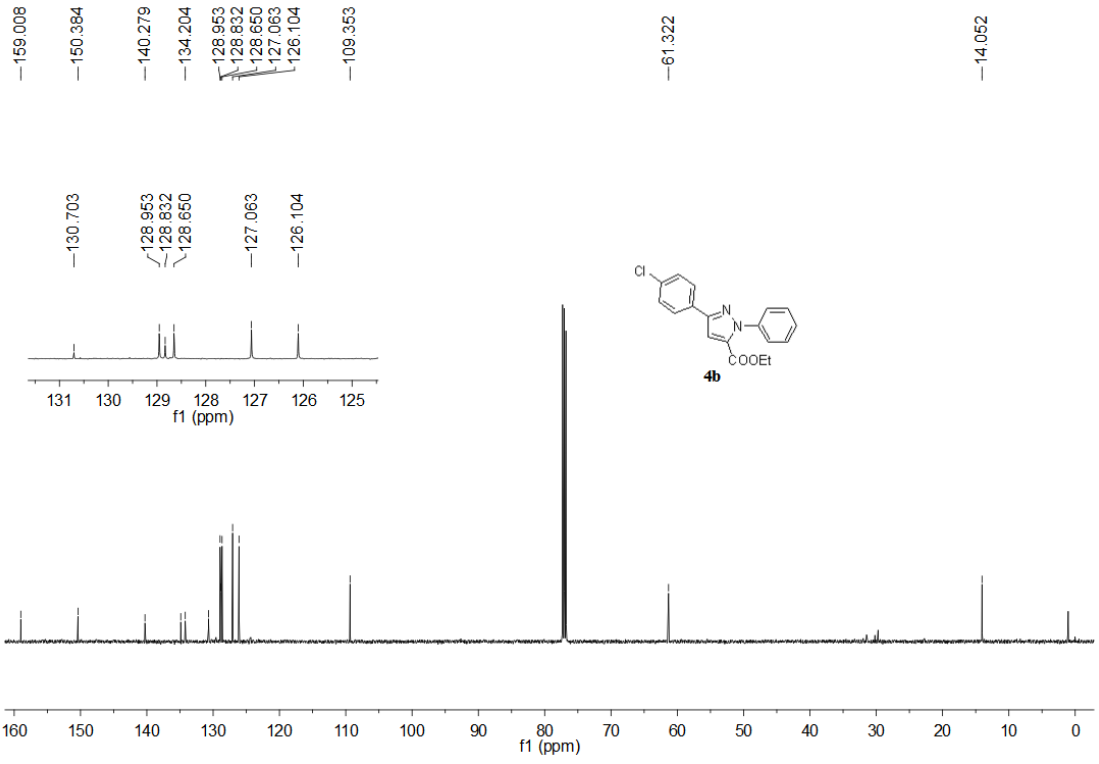
126.907
122.279
120.259
117.846
110.857
110.667
60.949
60.086
14.196
14.053
EtOOC
COOEt
3k
f1 (ppm)


7.897
7.883
7.454
7.448
7.445
7.433
7.418
7.376
7.373
7.371
7.363
7.359
7.355
7.346
7.344
7.340
4.294
4.280
4.265
4.251
1.288
1.274
1.260
COOEt
4a
2.00
7.31
1.16
0.97
2.03
3.37
f1 (ppm)


159.157
151.496
140.422
134.716
132.183
128.753
128.602
128.398
126.152
125.824
109.455
61.237
14.059
COOEt
4a
f1 (ppm)


7.824
7.807
7.493
7.484
7.476
7.405
7.387
7.303
4.288
4.274
4.260
4.245
1.282
1.268
1.254
Cl
N
N
COOEt
4b
2.01
5.07
2.06
1.00
2.03
3.45
7.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
f1 (ppm)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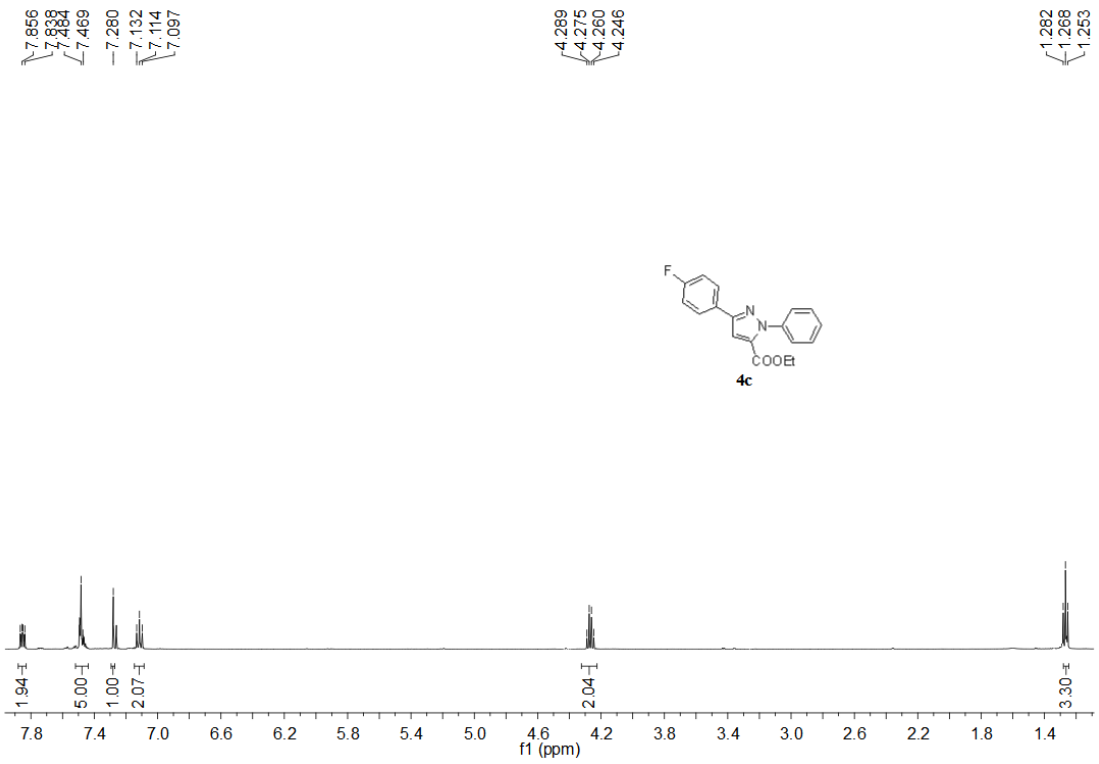
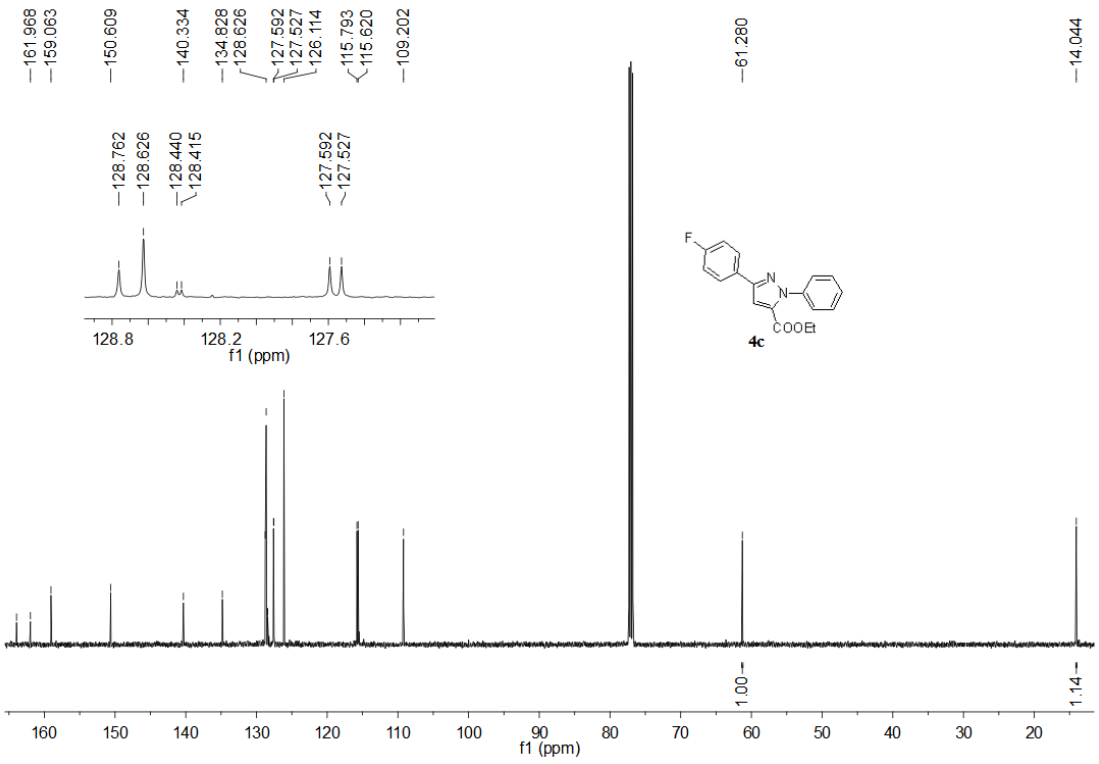
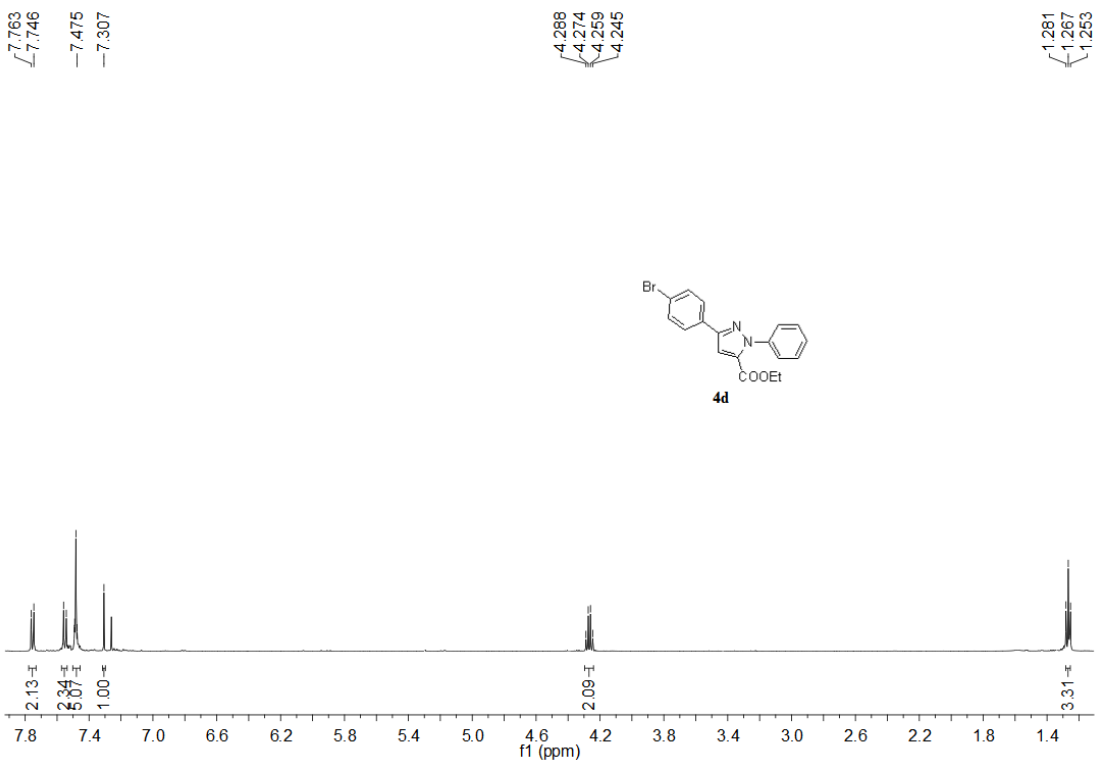
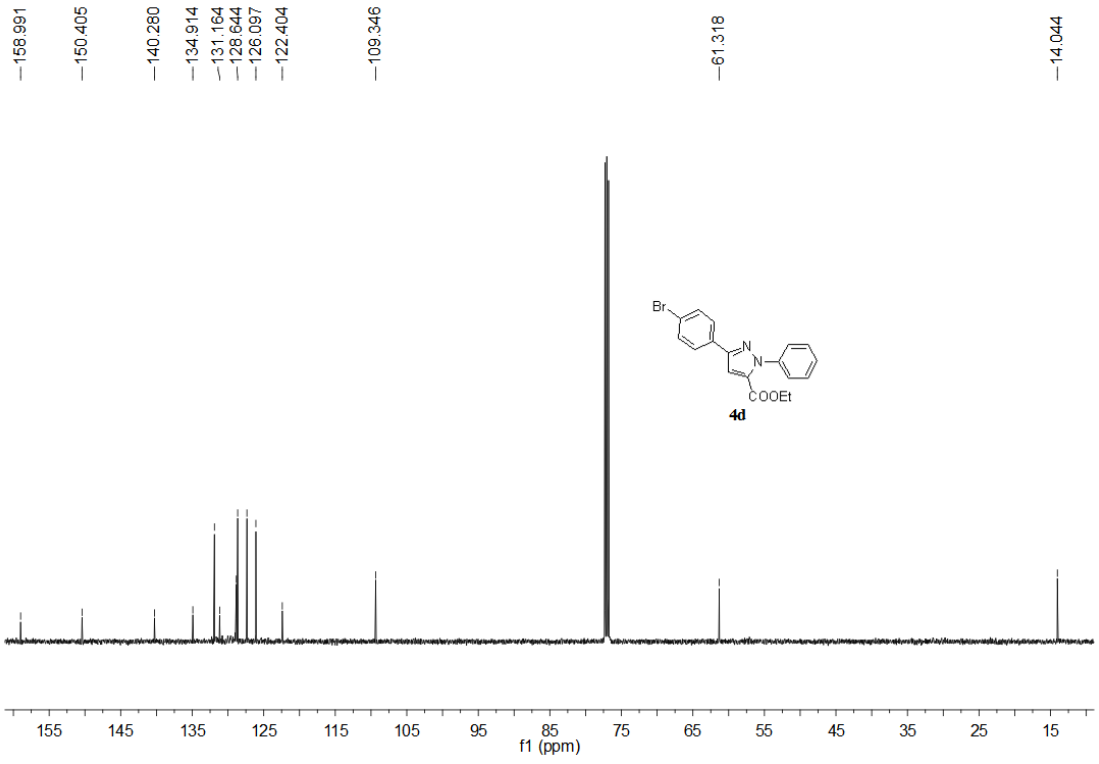
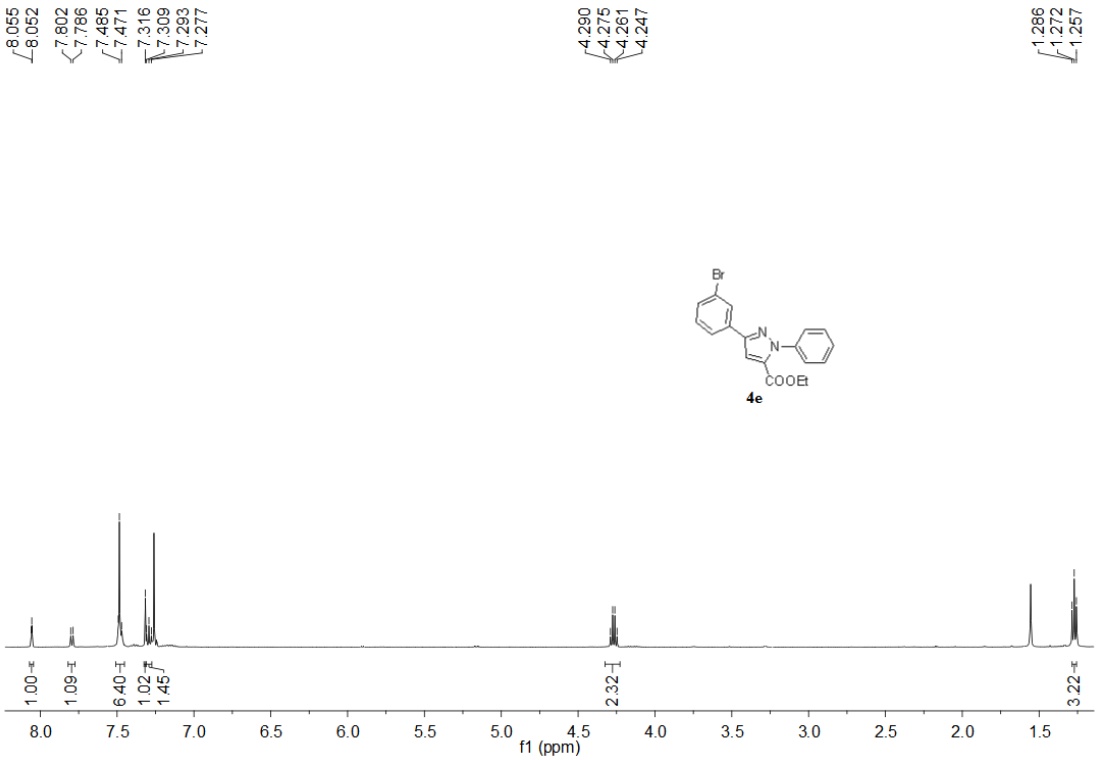
150.384
140.279
134.204
128.953
128.832
128.650
127.063
126.104
109.353
61.322
14.052
130.703
128.953
128.832
128.650
127.063
126.104
131
130
129
128
127
126
125
f1 (ppm)
Cl
N
N
COOEt
4b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

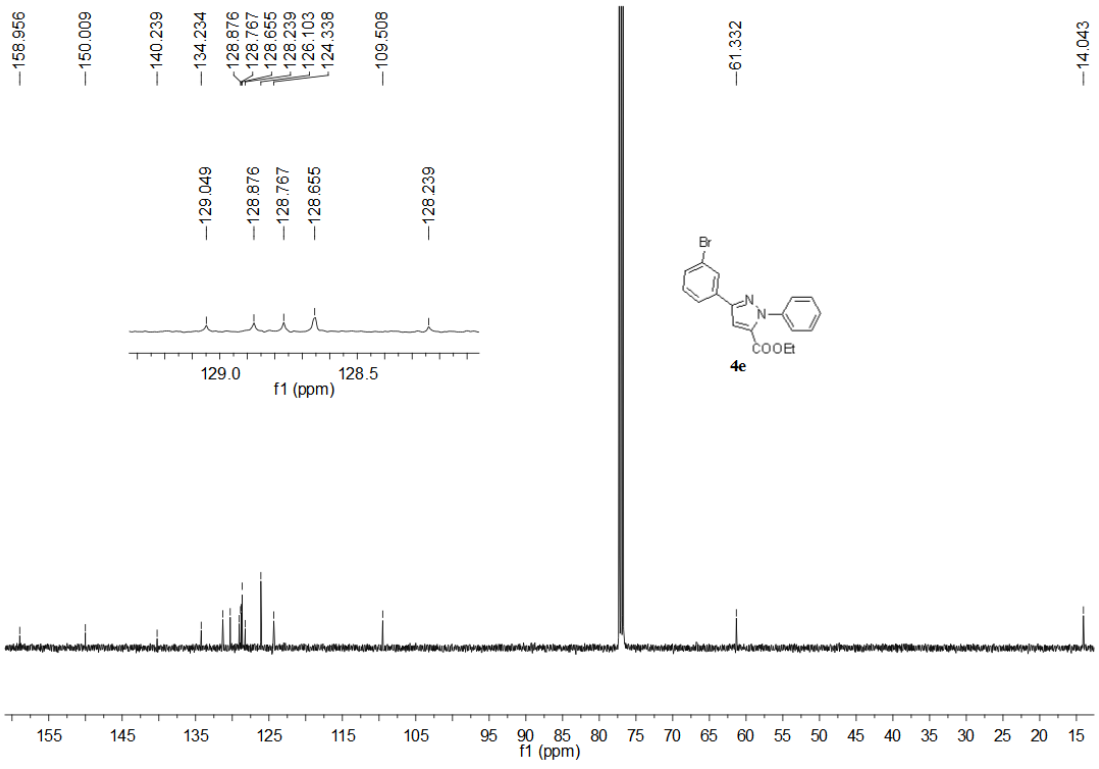

7.856
7.838
7.484
7.469
7.280
7.132
7.114
7.097
4.289
4.275
4.260
4.246
1.282
1.268
1.253
F
N
N
COOEt
4c
1.94
5.00
1.00
2.07
2.04
3.30
7.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
f1 (ppm)

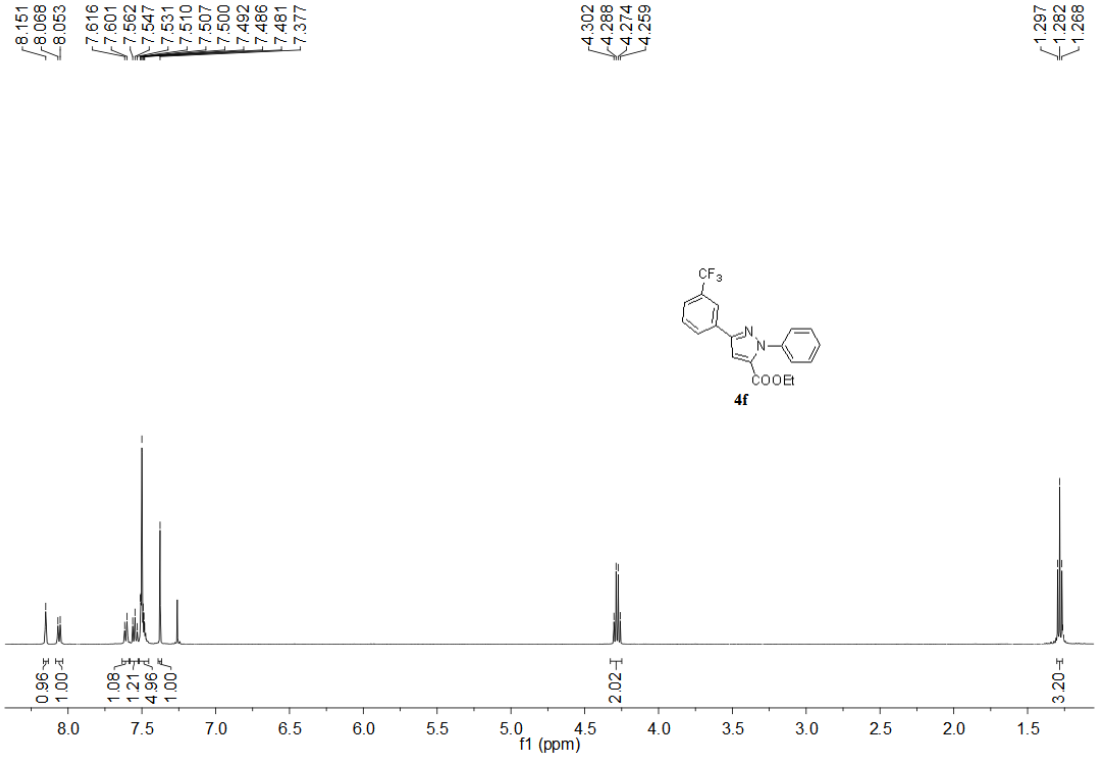

161.968
159.063
150.609
140.334
134.828
128.626
127.592
127.527
126.114
115.793
115.620
109.202
61.280
14.044
128.762
128.626
128.440
128.415
127.592
127.527
128.8
128.2
127.6
f1 (ppm)
F
N
N
COOEt
4c
1.00
1.14
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


7.763
7.746
7.475
7.307
4.288
4.274
4.259
4.245
1.281
1.267
1.253
Br
N
N
COOEt
4d
2.13
2.34
5.07
1.00
2.09
3.31
7.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
f1 (ppm)


158.991
150.405
140.280
134.914
131.164
128.644
126.097
122.404
109.346
61.318
14.044
Br
N
N
COOEt
4d
155
145
135
125
115
105
95
85
75
65
55
45
35
25
15
f1 (ppm)


8.055
8.052
7.802
7.786
7.485
7.471
7.316
7.309
7.293
7.277
4.290
4.275
4.261
4.247
1.286
1.272
1.257
Br
N
N
COOEt
4e
1.00
1.09
6.40
1.02
1.45
2.32
3.22
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
f1 (ppm)


158.956
150.009
140.239
134.234
128.876
128.767
128.655
128.239
126.103
124.338
109.508
61.332
14.043
129.049
128.876
128.767
128.655
128.239
129.0
128.5
f1 (ppm)
Br
N
N
COOEt
4e
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)


8.151
8.068
8.053
7.616
7.601
7.562
7.547
7.531
7.510
7.507
7.500
7.492
7.486
7.481
7.377
4.302
4.288
4.274
4.259
1.297
1.282
1.268
CF3
N
N
COOEt
4f
0.96
1.00
1.08
1.21
4.96
1.00
2.02
3.20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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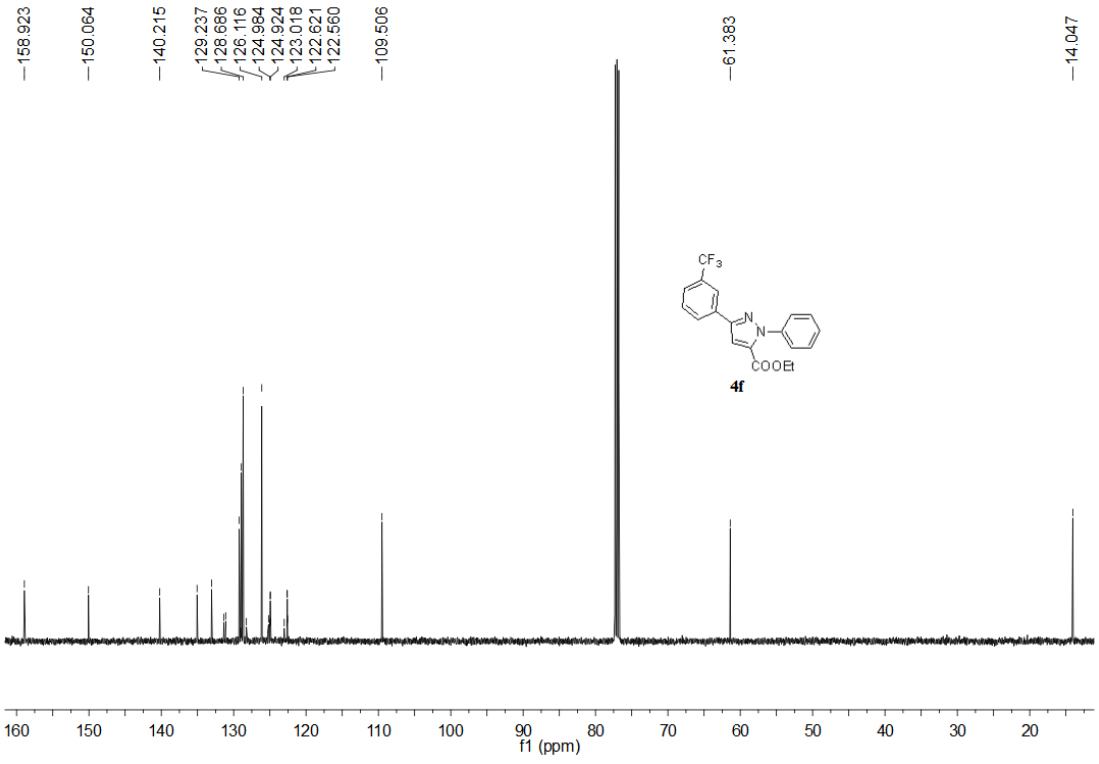
3.0
2.5
2.0
1.5
f1 (ppm)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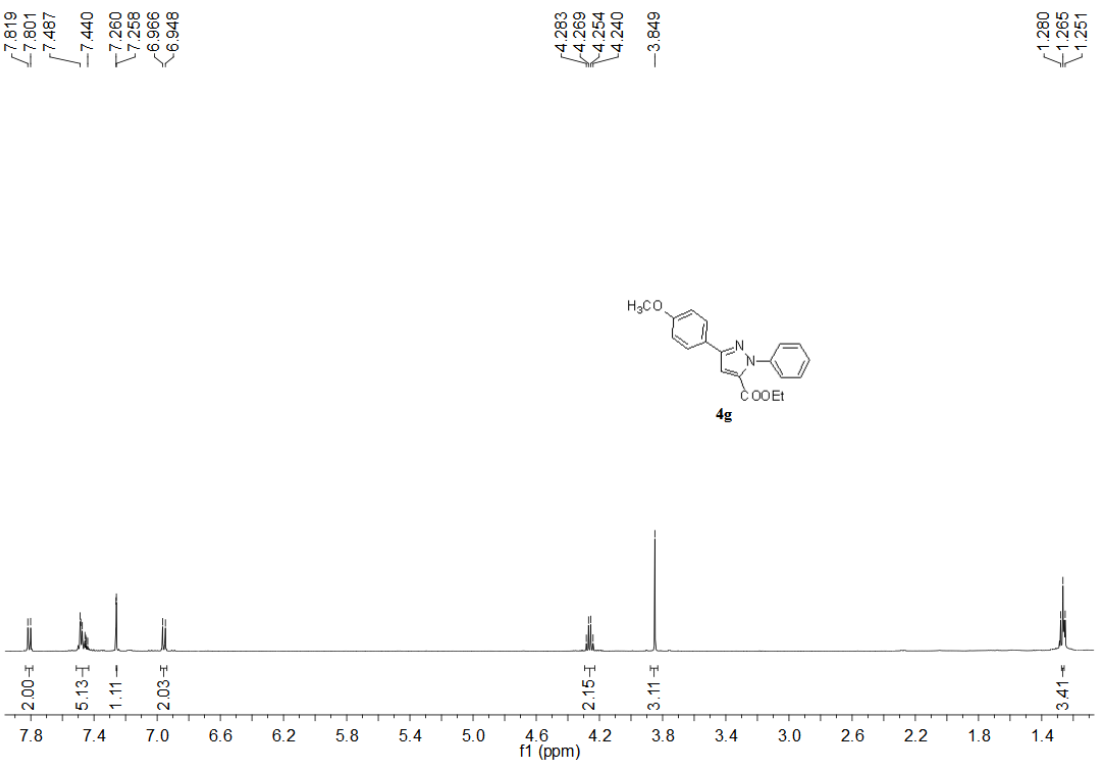
150.064
140.215
129.237
128.686
126.116
124.984
124.924
123.018
122.621
122.560
109.506
61.383
14.047
CF3
N
N
COOEt
4f
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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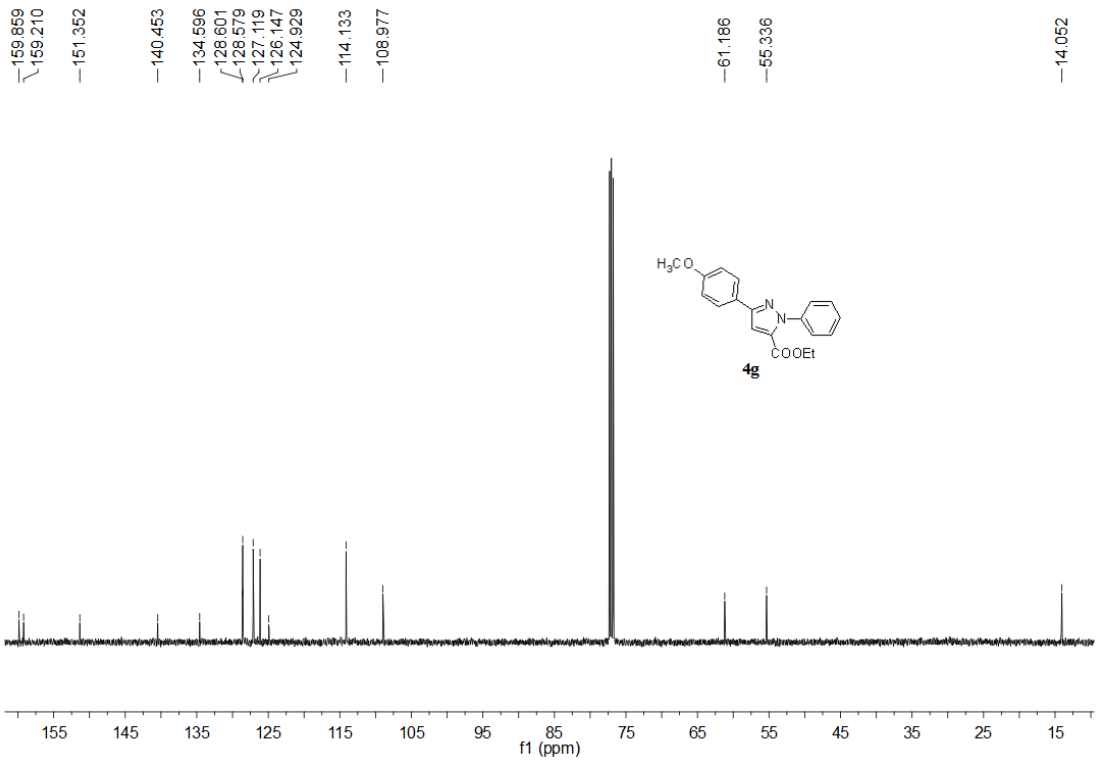
7.801
7.487
7.440
7.260
7.258
6.966
6.948
4.283
4.269
4.254
4.240
3.849
1.280
1.265
1.251
H3CO
N
N
COOEt
4g
2.00
5.13
1.11
2.03
2.15
3.11
3.41
7.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
f1 (ppm)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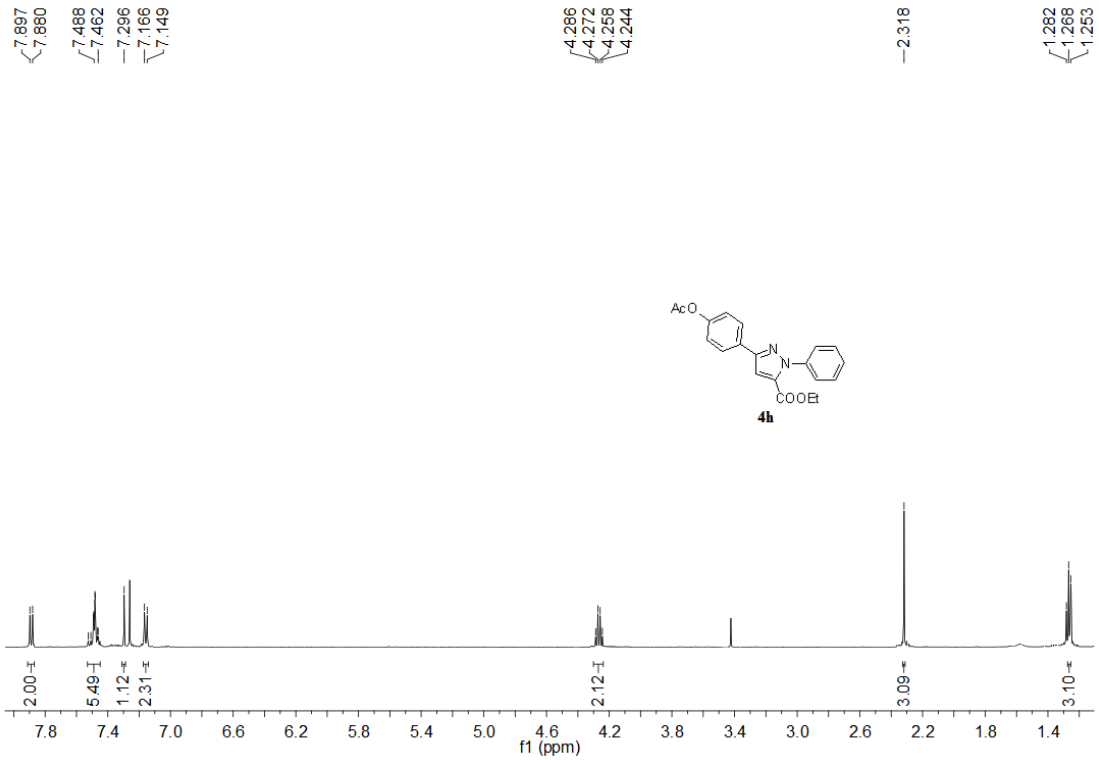
151.352
140.453
134.596
128.601
128.579
127.119
126.147
124.929
114.133
108.977
61.186
55.336
14.052
H3CO
N
N
COOEt
4g
155
145
135
125
115
105
95
85
75
65
55
45
35
25
15
f1 (ppm)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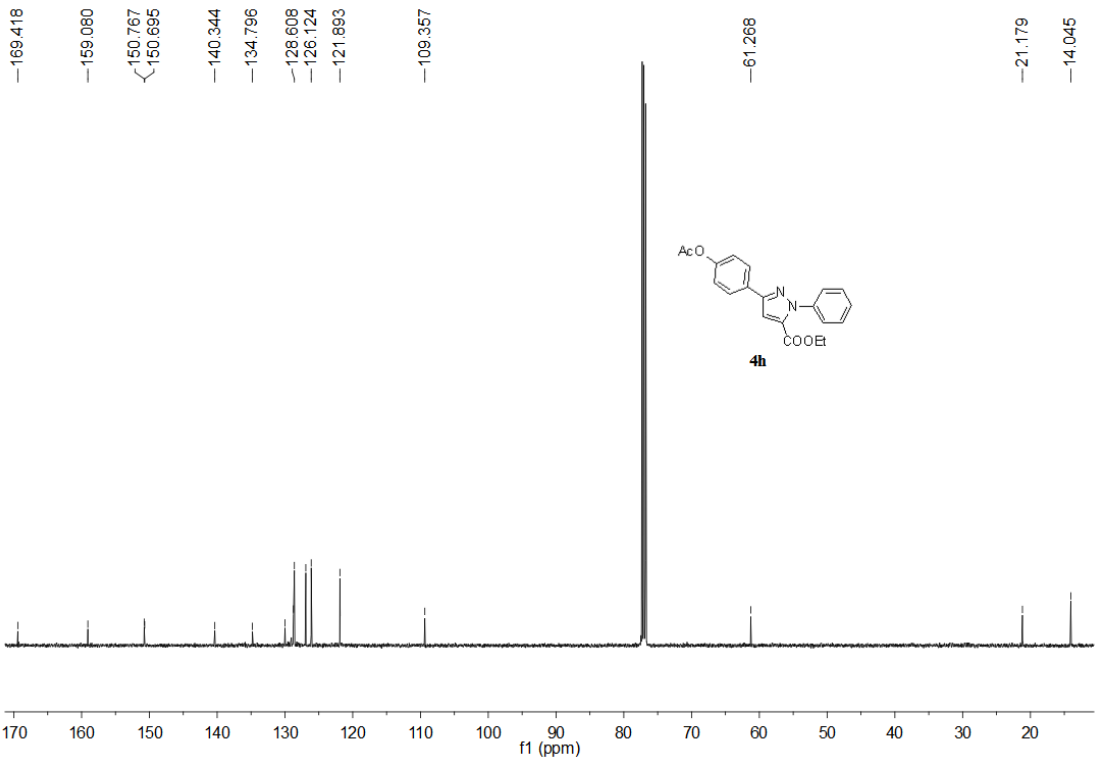
7.462
7.296
7.166
7.149
4.286
4.272
4.258
4.244
2.318
1.282
1.268
1.253
AcO
N
N
COOEt
4h
2.00
5.49
1.12
2.31
2.12
3.09
3.10
7.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
f1 (ppm)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159.080
150.767
150.695
140.344
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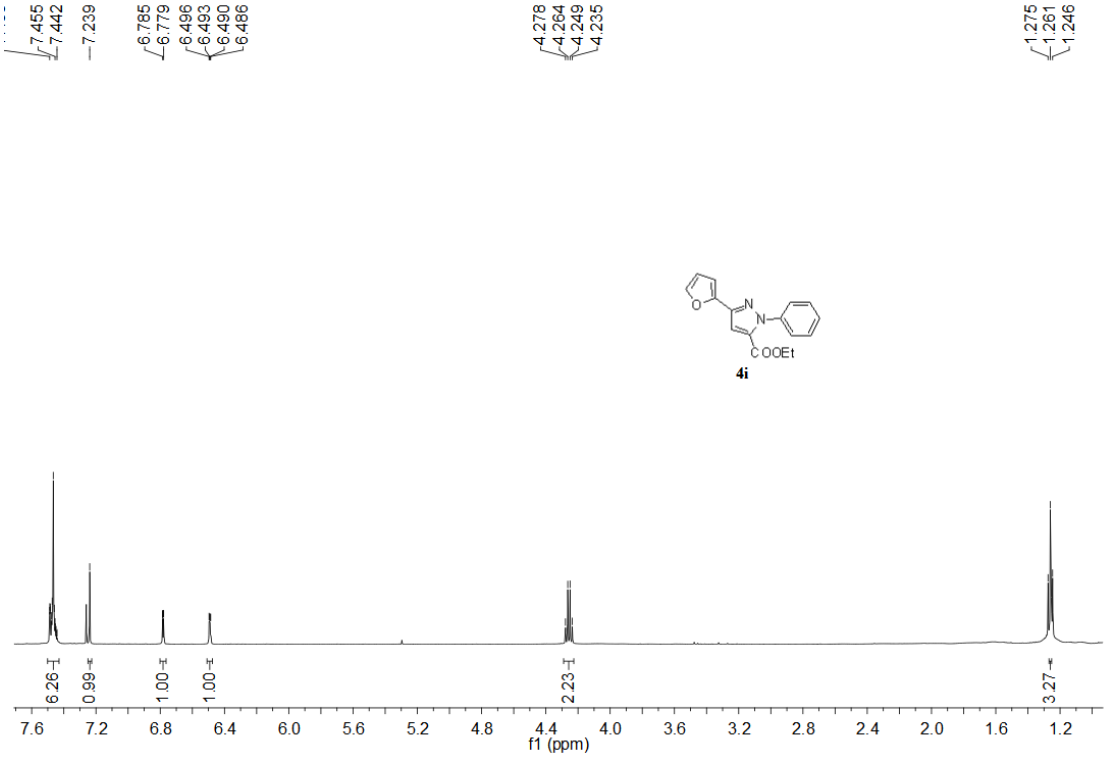
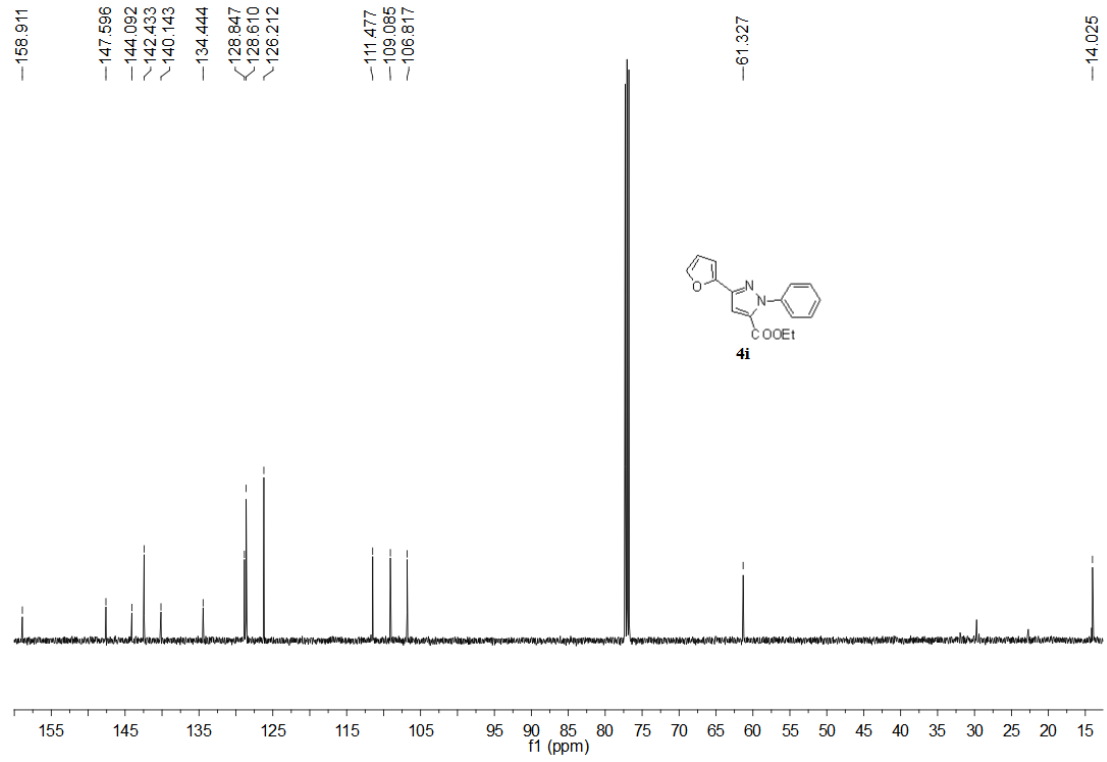
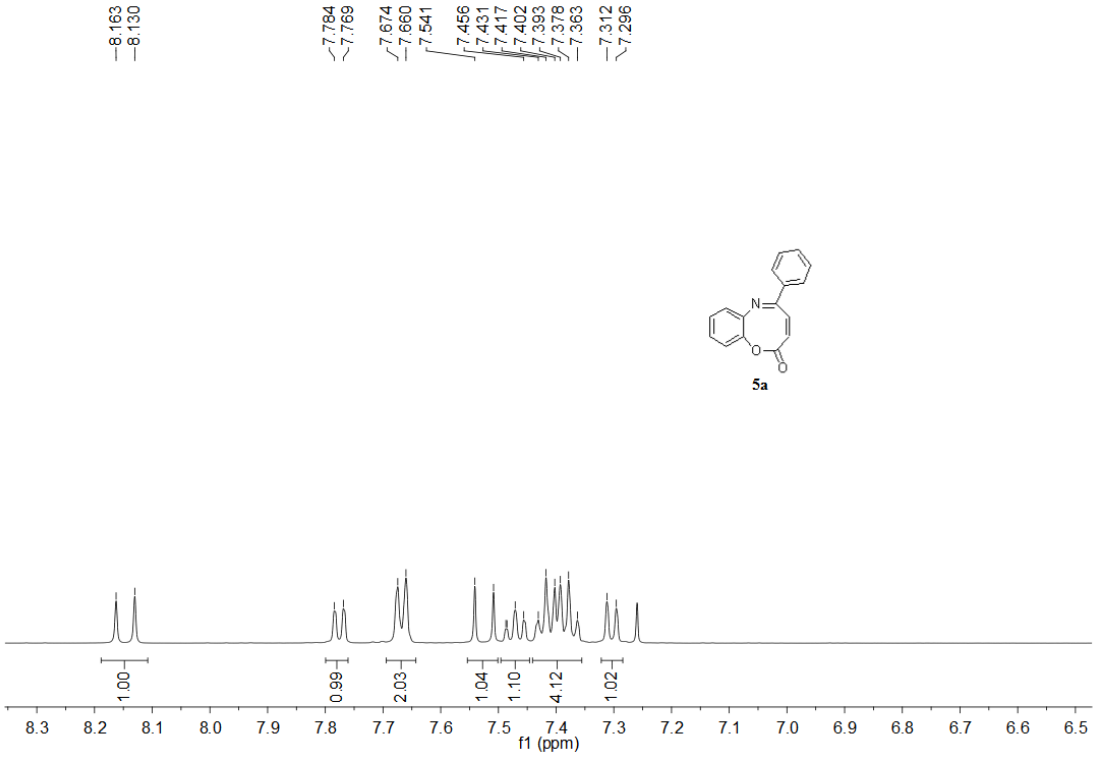
128.608
126.124
121.893
109.357
61.268
21.179
14.045
AcO
N
N
COOEt
4h
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


7.455
7.442
7.239
6.785
6.779
6.496
6.493
6.490
6.486
4.278
4.264
4.249
4.235
1.275
1.261
1.246
COOEt
4i
6.26
0.99
1.00
1.00
2.23
3.27
f1 (ppm)


158.911
147.596
144.092
142.433
140.143
134.444
128.847
128.610
126.212
111.477
109.085
106.817
61.327
14.025
COOEt
4i
f1 (ppm)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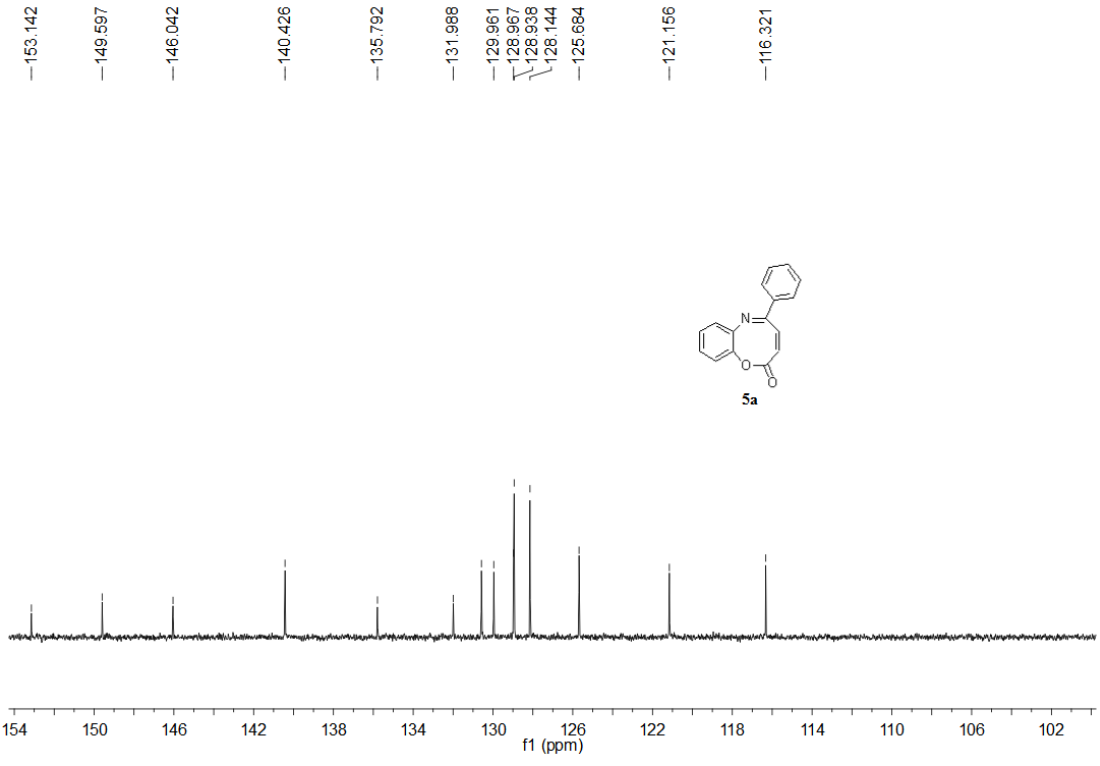
8.130
7.784
7.769
7.674
7.660
7.541
7.456
7.431
7.417
7.402
7.393
7.378
7.363
7.312
7.296
5a
1.00
0.99
2.03
1.04
1.10
4.12
1.02
f1 (ppm)


153.142
149.597
146.042
140.426
135.792
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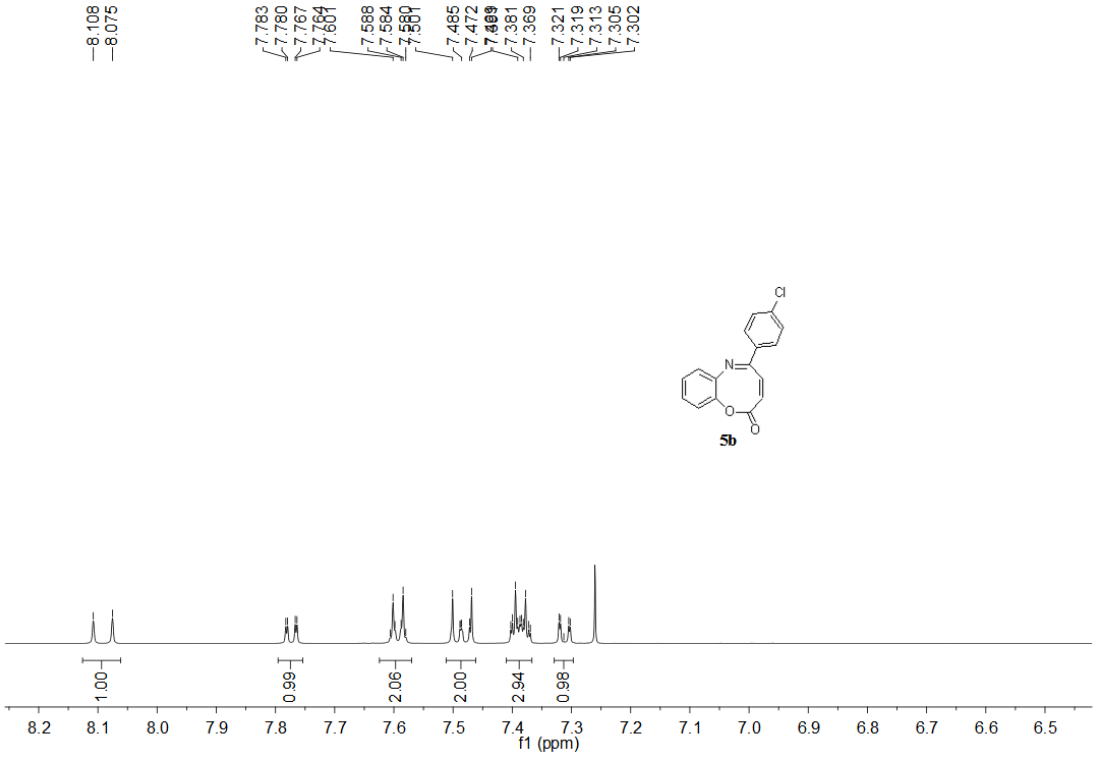
129.961
128.967
128.938
128.144
125.684
121.156
116.321
5a
f1 (ppm)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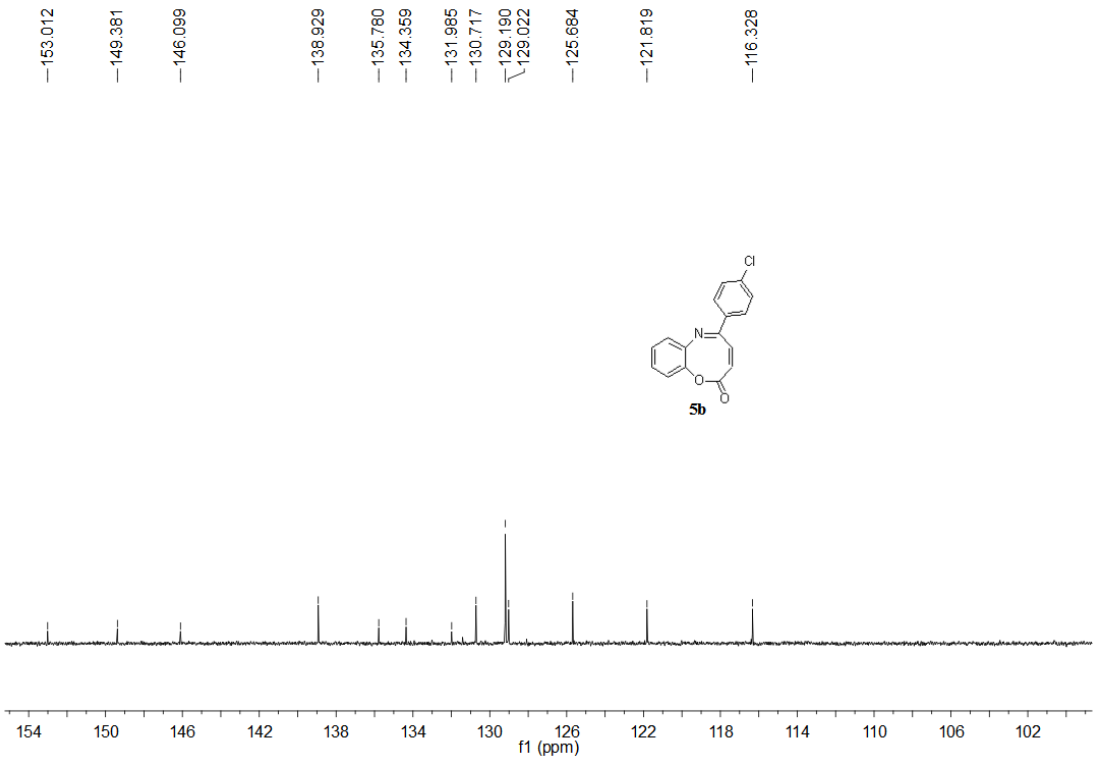
7.780
7.767
7.764
7.601
7.588
7.584
7.580
7.501
7.485
7.472
7.381
7.369
7.321
7.319
7.313
7.305
7.302
Cl
N
O
O
5b
1.00
0.99
2.06
2.00
2.94
0.98
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
f1 (ppm)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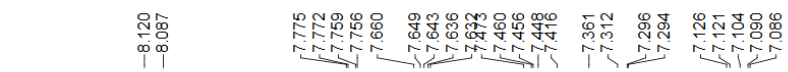
134.359
131.985
130.717
129.190
129.022
125.684
121.819
116.328
Cl
N
O
O
5b
154
150
146
142
138
134
130
126
122
118
114
110
106
102
f1 (ppm)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7.756
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7.643
7.636
7.460
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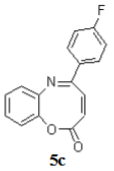
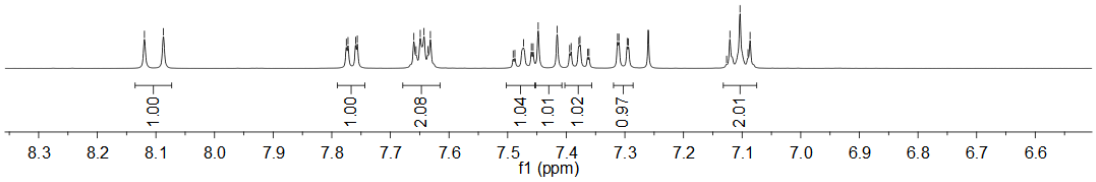
7.294
7.126
7.121
7.104
7.090
7.086


F
N
O
O

5c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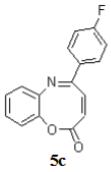
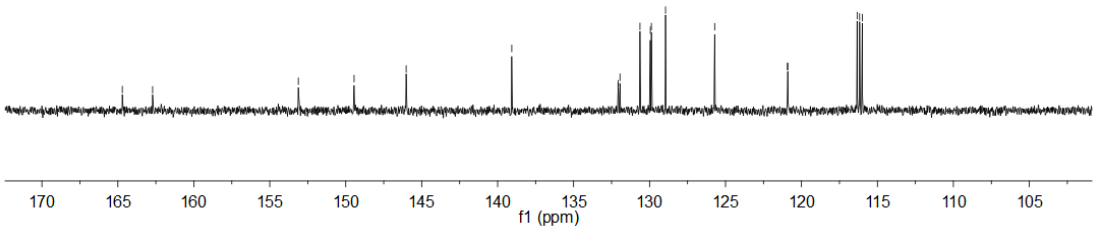
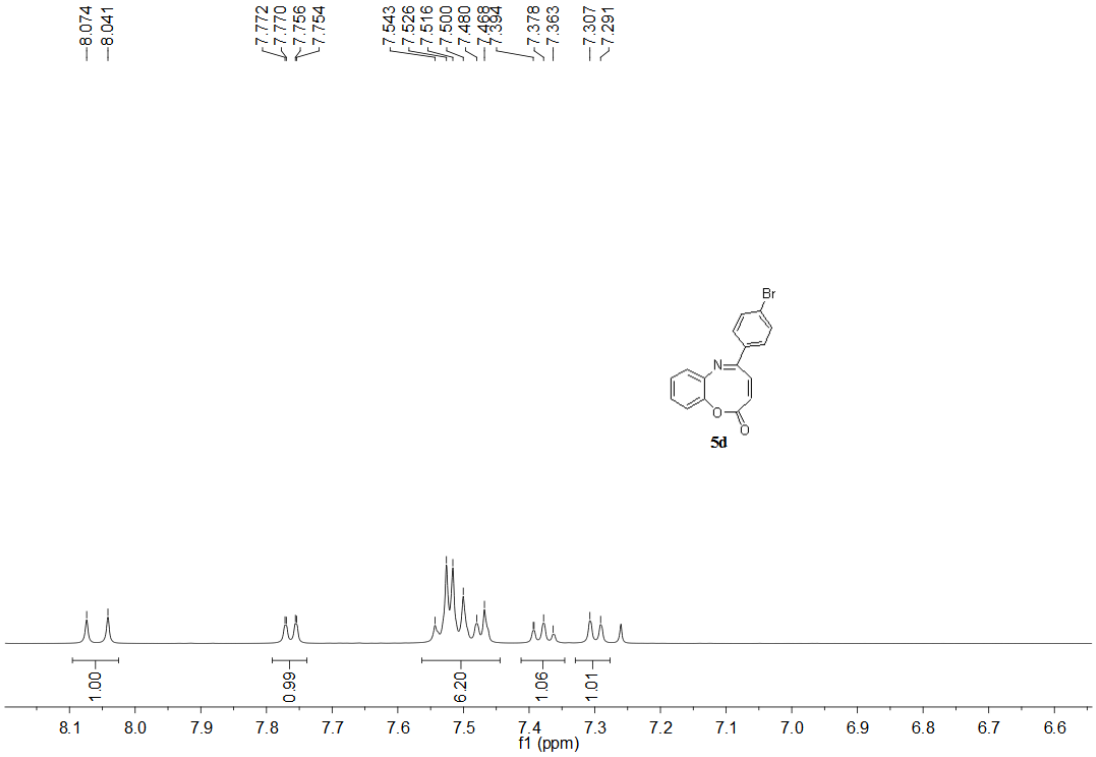
1.00
2.08
1.04
1.01
1.02
0.97
2.01
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
f1 (ppm)


164.707
162.713
153.119
149.449
146.022
139.070
132.077
132.054
131.948
130.630
129.881
128.948
125.714
120.923
120.903
116.336
116.171
115.997


F
N
O
O

5c


170
165
160
155
150
145
140
135
130
125
120
115
110
105
f1 (ppm)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8.041
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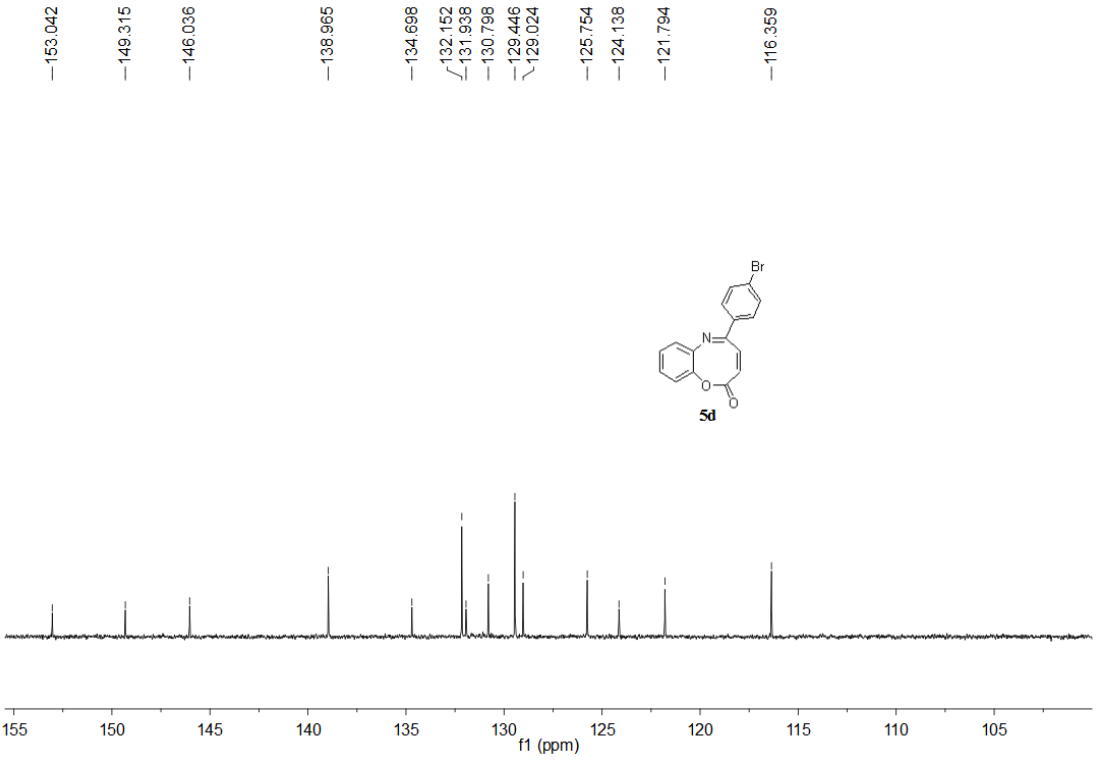
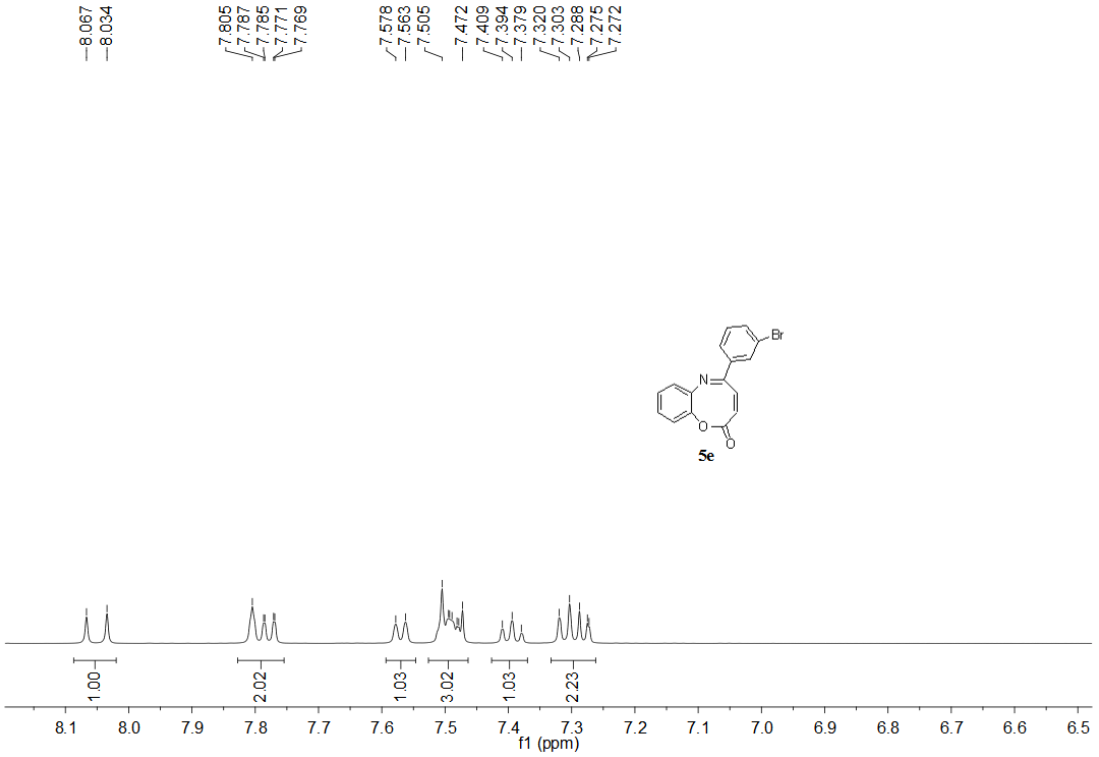
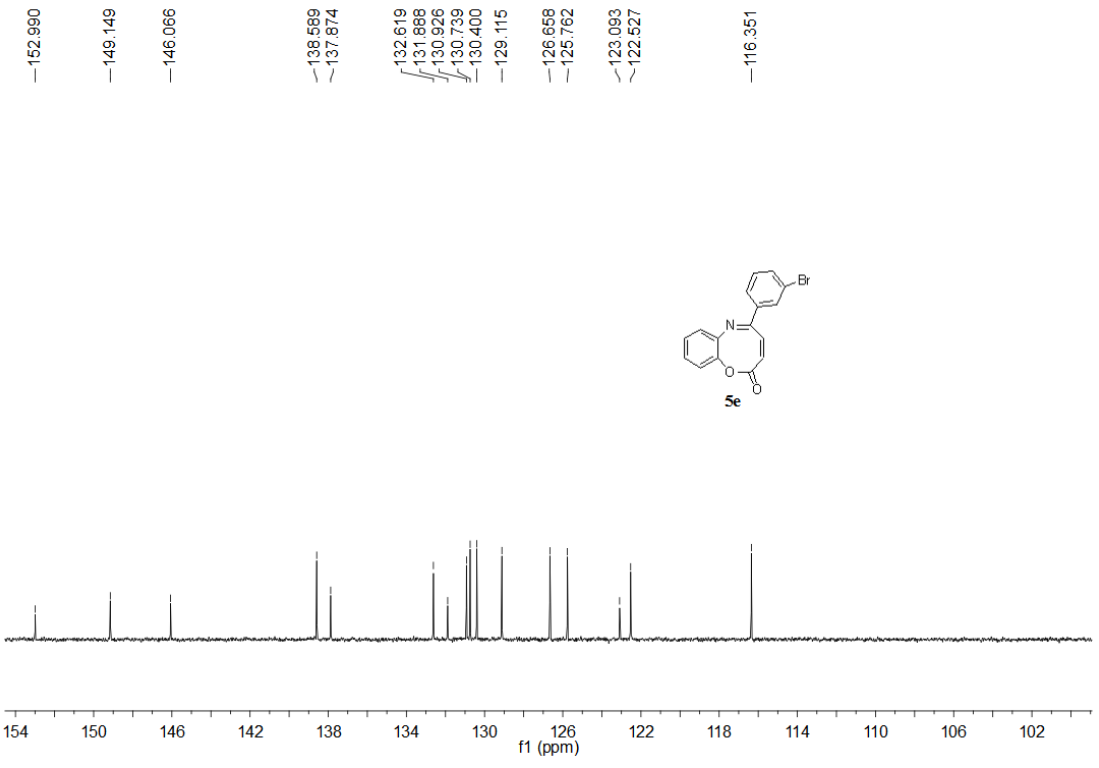
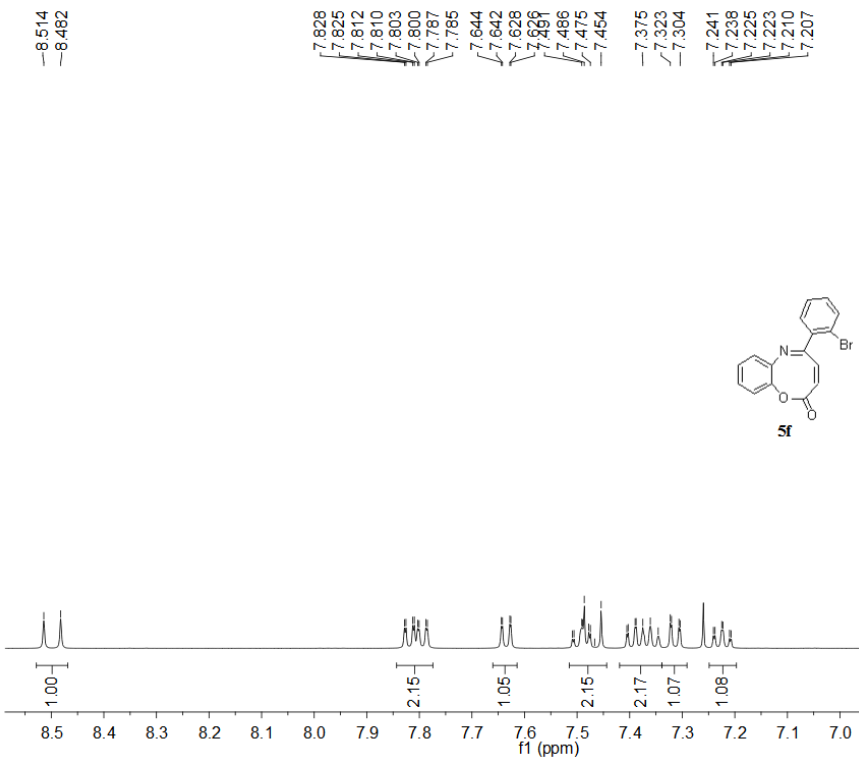
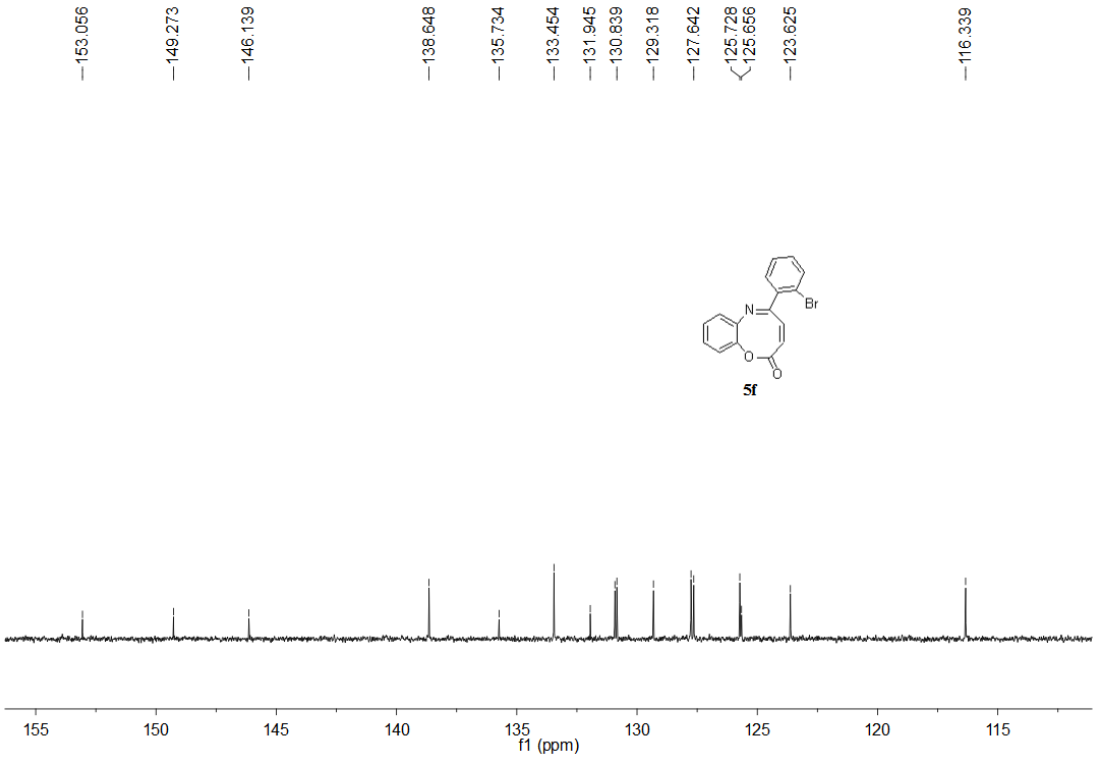
7.770
7.756
7.754
7.543
7.526
7.516
7.500
7.480
7.468
7.394
7.378
7.363
7.307
7.291
Br
N
O
O
5d
1.00
0.99
6.20
1.06
1.01
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
f1 (ppm)

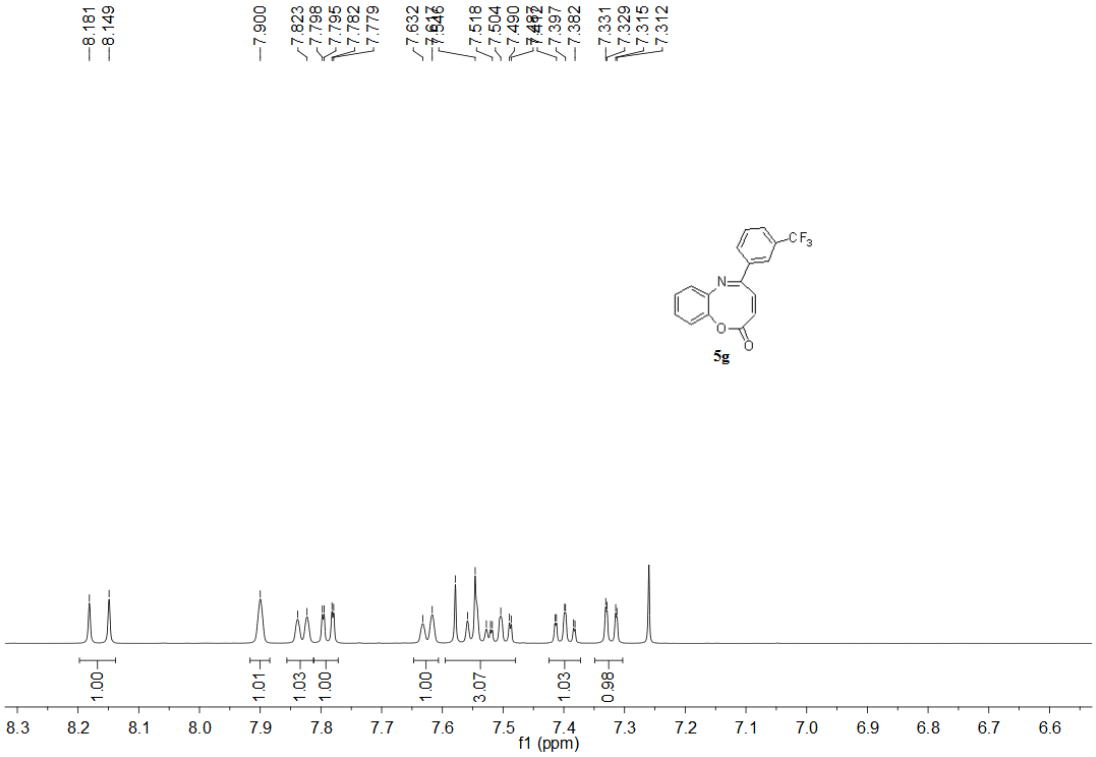

153.042
149.315
146.036
138.965
134.698
132.152
131.938
130.798
129.446
129.024
125.754
124.138
121.794
116.359
Br
N
O
O
5d
155
150
145
140
135
130
125
120
115
110
105
f1 (ppm)

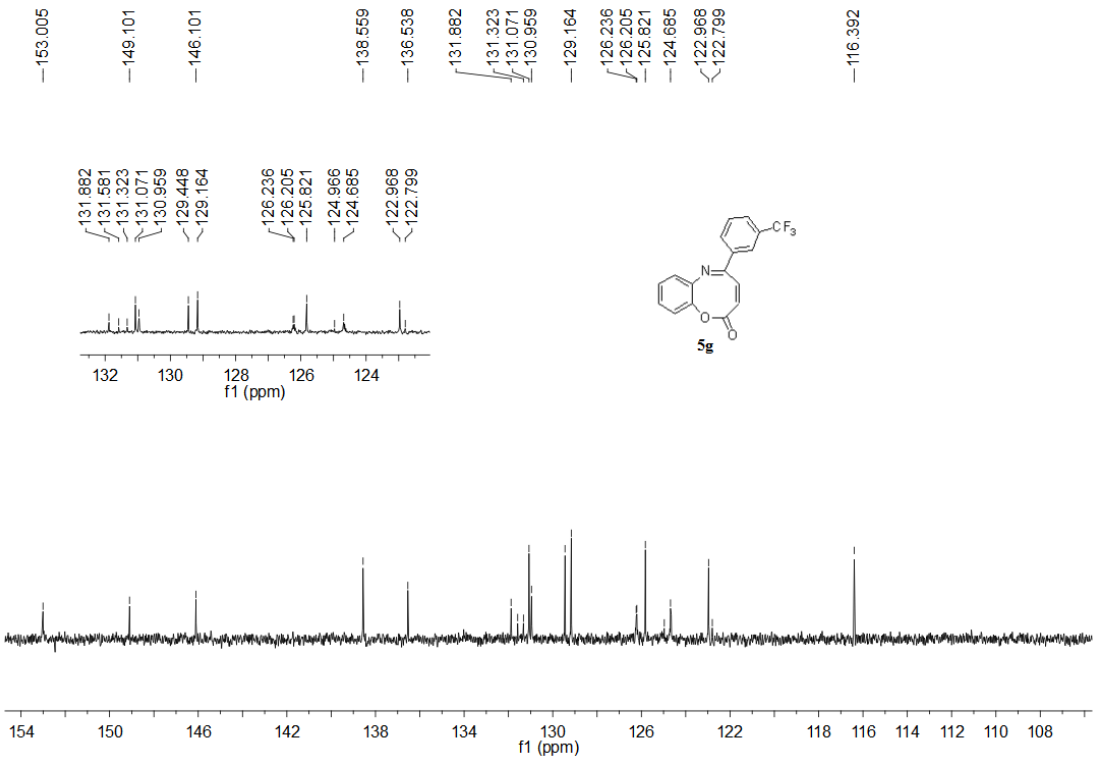

8.067
8.034
7.805
7.787
7.785
7.771
7.769
7.578
7.563
7.505
7.472
7.409
7.394
7.379
7.320
7.303
7.288
7.275
7.272
Br
N
O
O
5e
1.00
2.02
1.03
3.02
1.03
2.23
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
f1 (ppm)

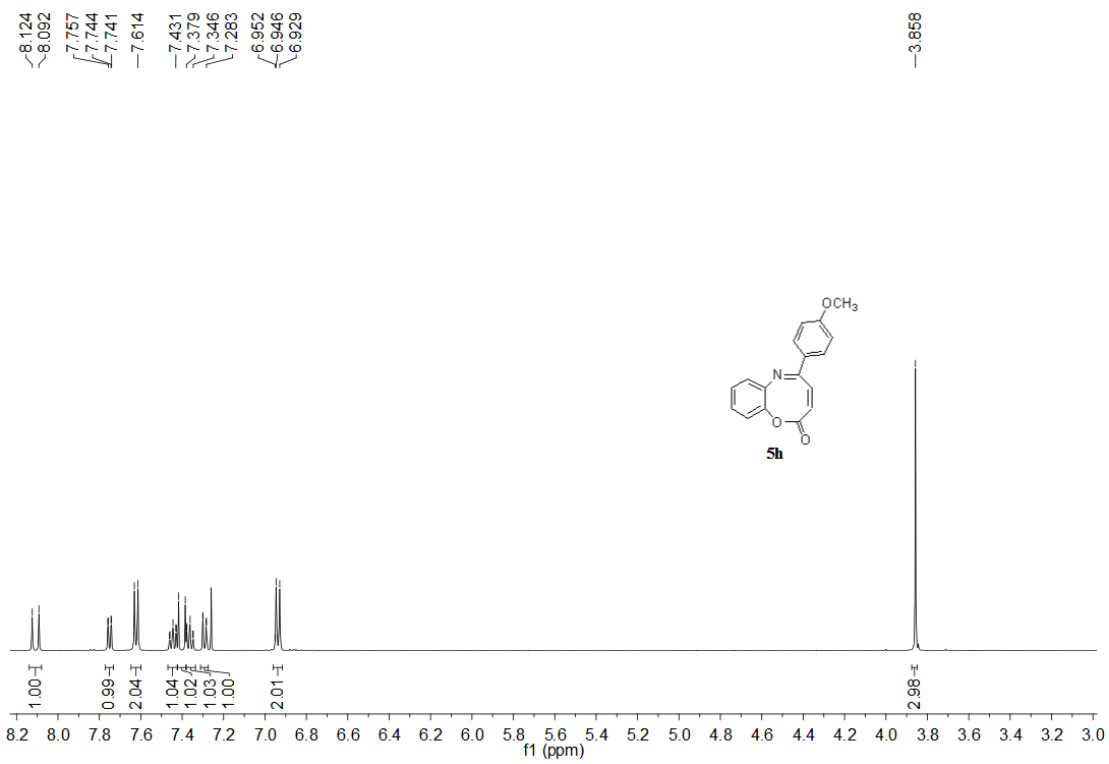

152.990
149.149
146.066
138.589
137.874
132.619
131.888
130.926
130.739
130.400
129.115
126.658
125.762
123.093
122.527
116.351
Br
N
O
O
5e
154
150
146
142
138
134
130
126
122
118
114
110
106
102
f1 (ppm)

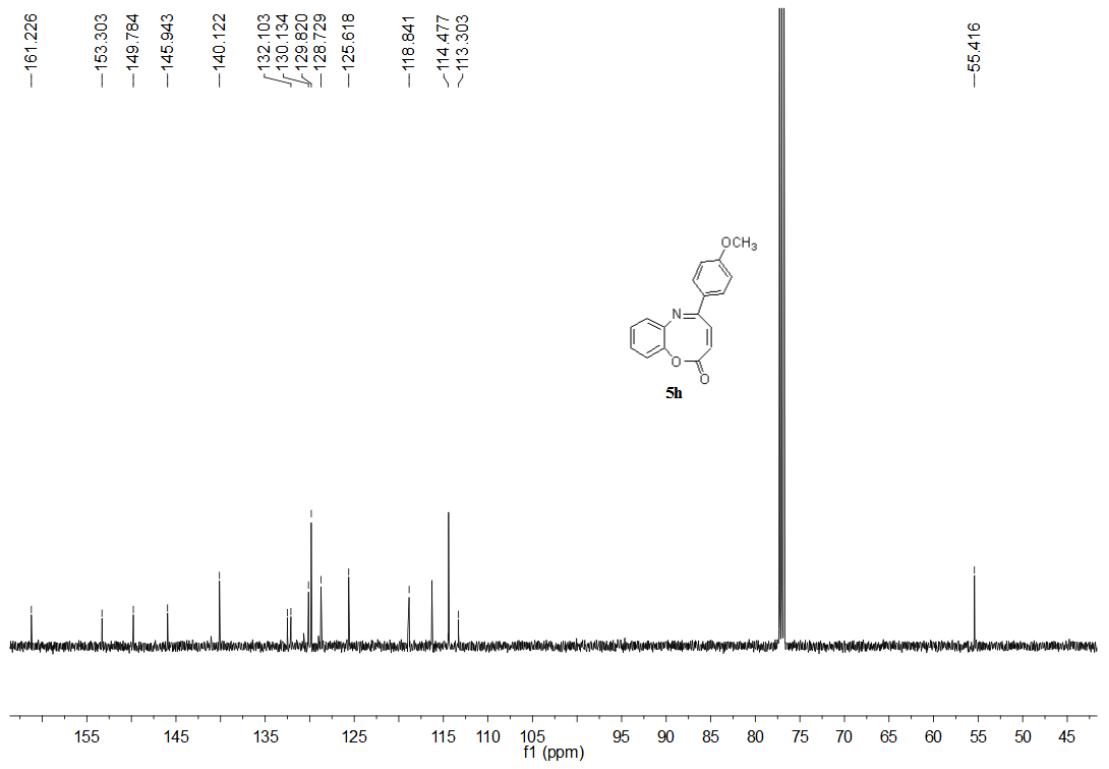

8.514
8.482
7.828
7.825
7.812
7.810
7.803
7.800
7.787
7.785
7.644
7.642
7.628
7.626
7.491
7.486
7.475
7.454
7.375
7.323
7.304
7.241
7.238
7.225
7.223
7.210
7.207
Br
N
O
O
5f
1.00
2.15
1.05
2.15
2.17
1.07
1.08
8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
f1 (ppm)

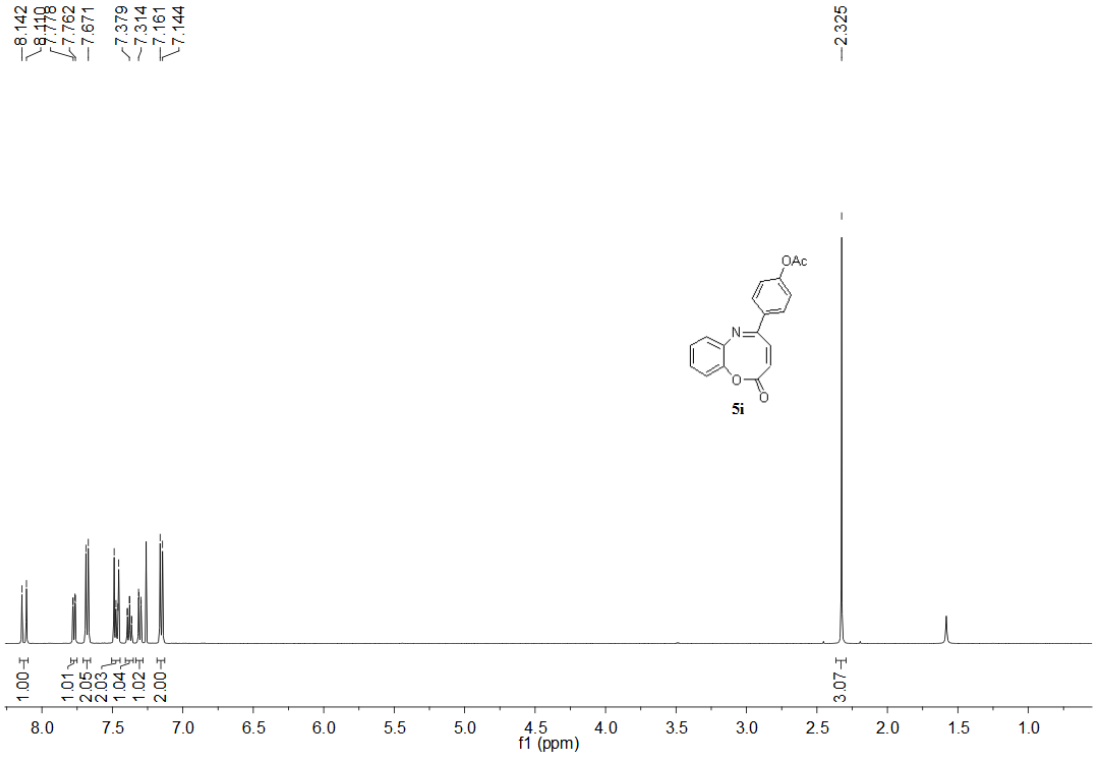

153.056
149.273
146.139
138.648
135.734
133.454
131.945
130.839
129.318
127.642
125.728
125.656
123.625
116.339
Br
N
O
O
5f
155 150 145 140 135 130 125 120 115
f1 (ppm)

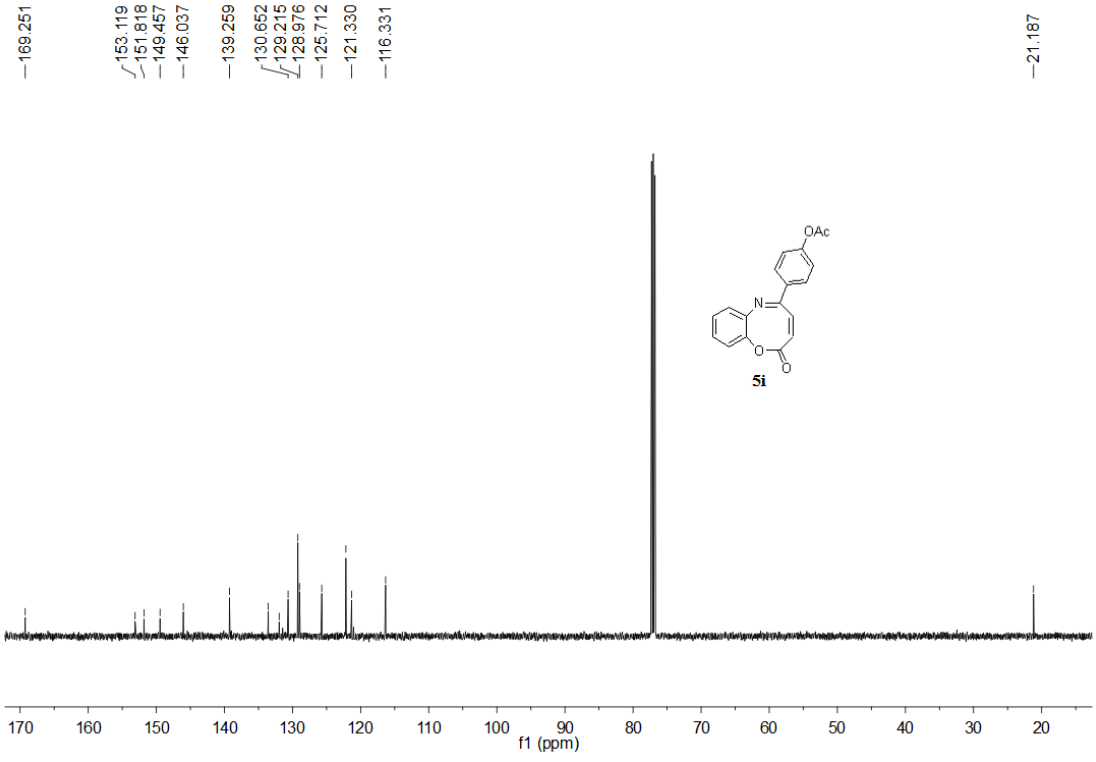

8.181
8.149
7.900
7.823
7.798
7.795
7.782
7.779
7.632
7.518
7.504
7.490
7.397
7.382
7.331
7.329
7.315
7.312
CF3
N
O
O
5g
1.00
1.01
1.03
1.00
1.00
3.07
1.03
0.98
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
f1 (ppm)

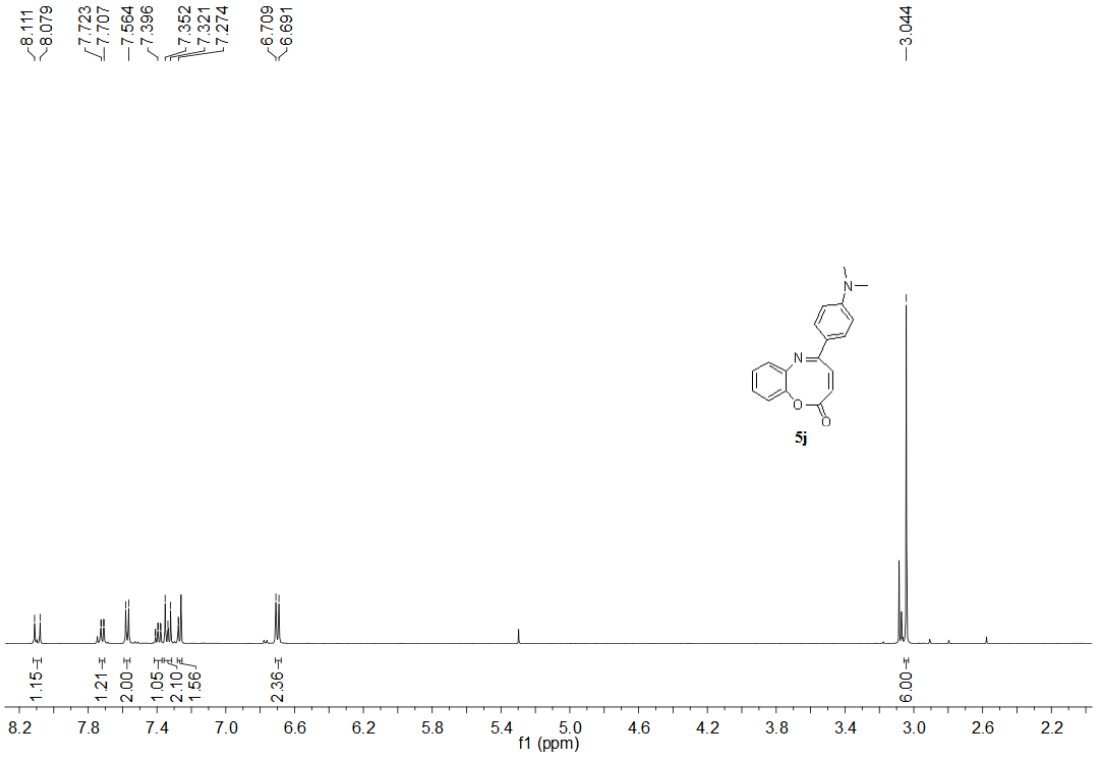

153.005
149.101
146.101
138.559
136.538
131.882
131.323
131.071
130.959
129.164
126.236
126.205
125.821
124.685
122.968
122.799
116.392
131.882
131.581
131.323
131.071
130.959
129.448
129.164
126.236
126.205
125.821
124.966
124.685
122.968
122.799
CF3
N
O
O
5g
132
130
128
126
124
f1 (ppm)
154
150
146
142
138
134
130
126
122
118
116
114
112
110
108
f1 (ppm)

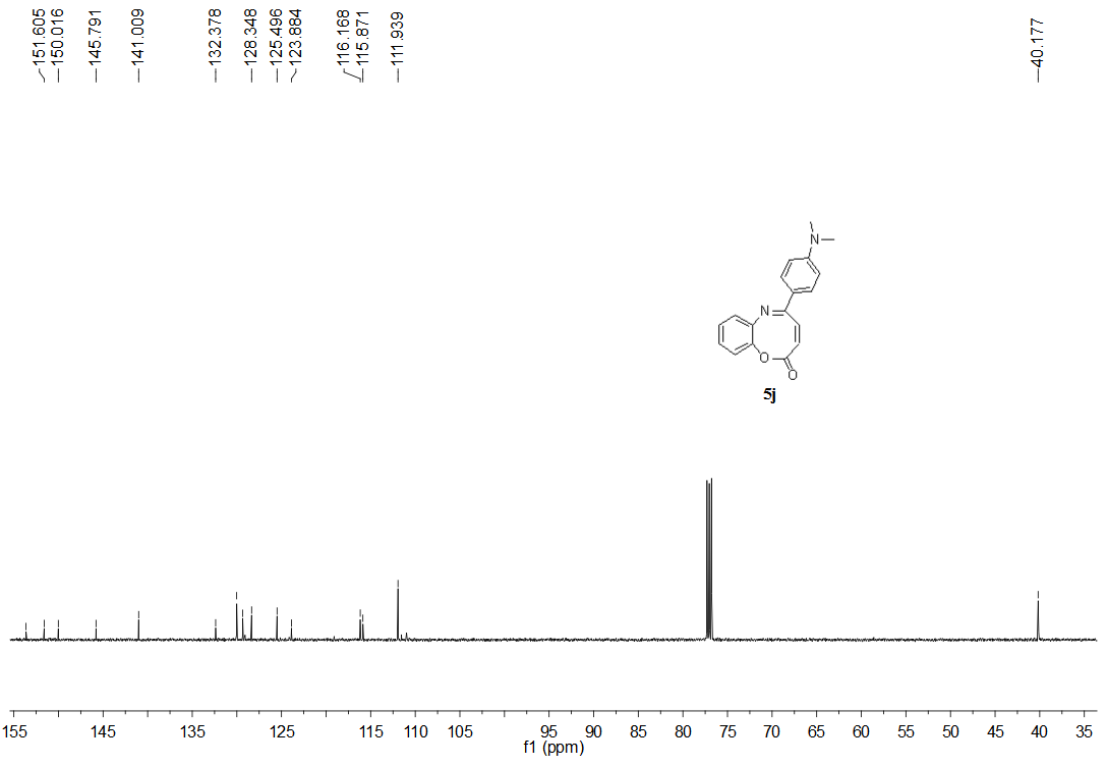

8.124
8.092
7.757
7.744
7.741
7.614
7.431
7.379
7.346
7.283
6.952
6.946
6.929
3.858
OCH3
N
O
O
5h
1.00
0.99
2.04
1.04
1.02
1.03
1.00
2.01
2.98
f1 (ppm)


161.226
153.303
149.784
145.943
140.122
132.103
130.134
129.820
128.729
125.618
118.841
114.477
113.303
55.416
OCH3
N
O
O
5h
f1 (ppm)


8.142
8.140
7.778
7.762
7.671
7.379
7.314
7.161
7.144
2.325
OAc
N
O
O
5i
1.00
1.01
2.05
2.03
1.04
1.02
2.00
3.07
f1 (ppm)


169.251
153.119
151.818
149.457
146.037
139.259
130.652
129.215
128.976
125.712
121.330
116.331
21.187
OAc
N
O
O
5i
f1 (ppm)


8.111
8.079
7.723
7.707
7.564
7.396
7.352
7.321
7.274
6.709
6.691
3.044
5j
1.15
1.21
2.00
1.05
2.10
1.56
2.36
6.00
f1 (ppm)


151.605
150.016
145.791
141.009
132.378
128.348
125.496
123.884
116.168
115.871
111.939
40.177
5j
f1 (ppm)