Supporting Information

Pd(II)-Catalyzed Direct C5-Arylation of Azole-4-carboxylates through Double C-H Bond Cleavage

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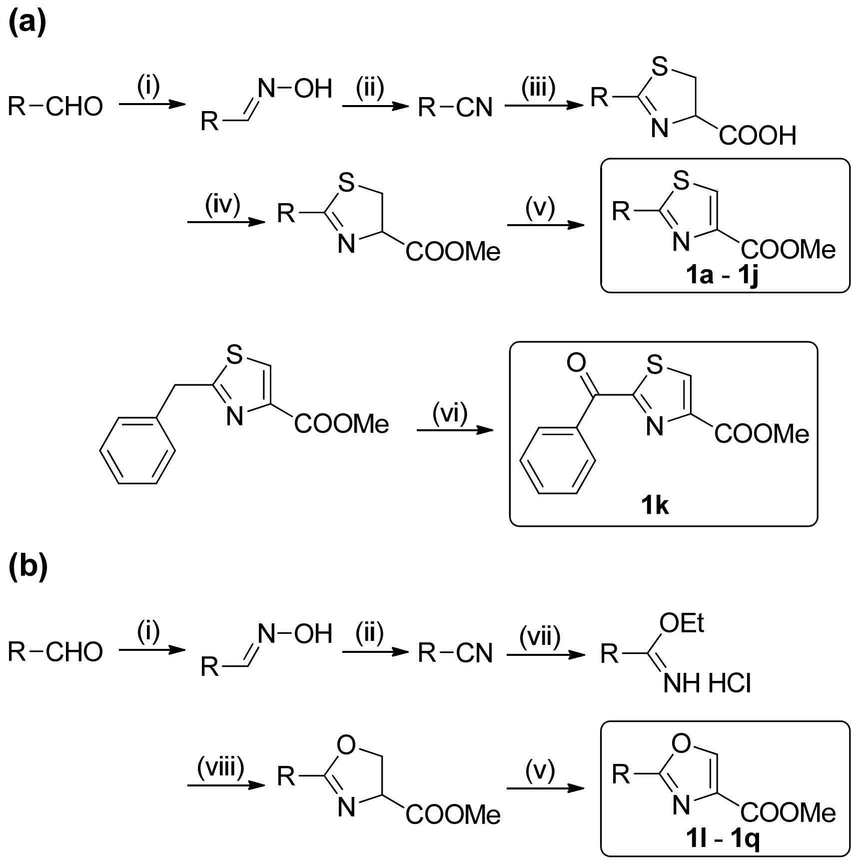
1. *General Information*

Melting point (mp) was measured on a microscopic melting point apparatus. ^{1}H and ^{13}C NMR spectra were collected on BRUKER AV-300 (300MHz) spectrometer using $CDCl_3$ or DMSO as solvent. Chemical shifts of ^{1}H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm) with the solvent resonance as an internal standard ($CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ = 2.50 ppm). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet), coupling constant (Hz), and integration. Chemical shifts of ^{13}C NMR were reported in ppm with the solvent as the internal standard ($CDCl_3$: δ = 77.0 ppm; DMSO-d_6: δ = 40.5 ppm). Infrared spectra (IR) were recorded on a Thermo Scientific iS10 FT/IR spectrometer; absorptions are reported in reciprocal centimeters. High Resolution Mass measurement was performed on Agilent QTOF 6520 mass spectrometer with electron spray ionization (ESI) as the ion source. High Performance Liquid Chromatography (HPLC) was performed on Agilent 1260 eluting with acetonitrile and water. The peaks were detected by UV light of irradiation (254 nm).

2. *Materials*

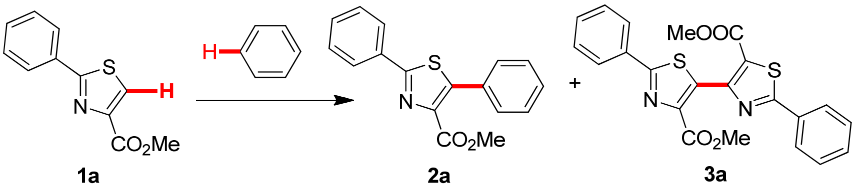
Palladium(II) catalysts, oxidants (except IOAc), additives and arenes are commercially available. IOAc was prepared *in situ* using I_2 and $PhI(OAc)_2$ according to previous literatures.[1] As shown in *Scheme S1*, Thiazole-4-carboxylate and oxazole-4-carboxylate substrates were synthesized from corresponding aldehydes or nitriles by our recently disclosed methods.[2] Unless otherwise indicated, all other reagents and solvents were obtained from commercial suppliers and used as received.



Scheme S1. Preparation of Thiazole-4-carboxylate **(a)** and oxazole-4-carboxylate **(b)**. *Reaction Conditions*: (i) NH_2OH-HCl, Na_2CO_3, MeOH/H_2O, reflux; (ii) Ac_2O, reflux; (iii) L-cysteine, $NaHCO_3$, EtOH/H_2O, rt or reflux; (iv) MeI, $KHCO_3$, DMF, 0 °C to rt; (v) $Cu(OAc)_2$, DMF, 120 ^{0}C; (vi) O_2, K_2CO_3, MS, DMF, 100 °C; (vii) HCl (g), EtOH, 0 °C to rt; (viii) methyl L-serine hydrochloride, NEt_3, CH_2Cl_2, 0 °C to rt.

3. *Screening of Reaction Conditions*

Table S1. Screening of Reaction Conditions[a]



Entry	Pd(II)	Oxidant	Additive (equiv)	Solvent	Benzene (mL)	Temp. (°C)	Yield (%)[b] (**2a** / **3a** / **1a**)
1	$Pd(OAc)_2$	AgOAc	-	-	1.5	80	44 / 38 / trace
2	$Pd(OAc)_2$	AgOAc	-	-	1.5	100	59 /27 / trace
3	$Pd(OAc)_2$	AgOAc	-	-	1.5	120	62 / 25 / 0
4	$PdCl_2$	AgOAc	-	-	1.5	120	69 / 11 / 5
5	$PdCl_2(MeCN)_2$	AgOAc	-	-	1.5	120	54 / 16 / 12
6	$Pd(OCOCF_3)_2$	AgOAc	-	-	1.5	120	36 / 40 / 15
7	$PdCl_2$	$AgCO_3$	-	-	1.5	120	0 / 8 / 86
8	$PdCl_2$	$Cu(OAc)_2$	-	-	1.5	120	21 / 27 / 47
9	$PdCl_2$	*p*-BQ	-	-	1.5	120	0 / 0 / 94
10	$PdCl_2$	Ag_2O	-	-	1.5	120	0 / trace / 94
11[c]	$PdCl_2$	IOAc	-	-	1.5	120	0 / 0 / 53

12	$PdCl_2$	$K_2S_2O_8$	-	-	1.5	120	0 / trace / 90
13	$Pd(OAc)_2$	$AgCO_3$	-	-	1.5	120	46 / 39 / 7
14	$Pd(OAc)_2$	$Cu(OAc)_2$	-	-	1.5	120	6 / 42 / 44
15	$Pd(OAc)_2$	*p*-BQ	-	-	1.5	120	0 / 26 / 68
16	$Pd(OAc)_2$	Ag_2O	-	-	1.5	120	trace / 93 / 0
17[d]	$Pd(OAc)_2$	IOAc	-	-	1.5	120	0 / trace / 56
18	$Pd(OAc)_2$	$K_2S_2O_8$	-	-	1.5	120	trace / 25 / 65
19	$PdCl_2$	AgOAc	K_2CO_3 (1)	-	1.5	120	0 / 82 / 5
20	$PdCl_2$	AgOAc	Cs_2CO_3 (1)	-	1.5	120	0 / 84 / 9
21	$PdCl_2$	AgOAc	KOAc (2)	-	1.5	120	0 / 35 / 53
22	$PdCl_2$	AgOAc	p-TsOH (1)	-	1.5	120	31 / 27 / 32
23	$PdCl_2$	AgOAc	AcOH (1)	-	1.5	120	66 / 18 / 6
24	$PdCl_2$	AgOAc	TFA (1)	-	1.5	120	38 / 19 / 33
25	$PdCl_2$	AgOAc	PivOH (1)	-	1.5	120	77 / 15 / 5
26	$PdCl_2$	AgOAc	PivOH (2)	-	1.5	120	79 / 13 / 6
27	$PdCl_2$	AgOAc	PivOH (4)	-	1.5	120	71 / 16 / 5
28	$PdCl_2$	AgOAc	DMSO (5%, v/v)	-	1.5	120	25 / 58 / 8
29	$PdCl_2$	AgOAc	DMSO (10%, v/v)	-	1.5	120	33 / 62 / trace
30	$Pd(OAc)_2$	AgOAc	DMSO (5%, v/v)	-	1.5	120	21 / 60 / 10
31	$Pd(OAc)_2$	AgOAc	DMSO (10%, v/v)	-	1.5	120	22 / 62 / 0
32	$PdCl_2$	AgOAc	DMSO (10%, v/v)	-	1.5	100	29 / 55 / 8
33	$Pd(OAc)_2$	AgOAc	DMSO (10%, v/v)	-	1.5	100	42 / 50 / 0
34	$PdCl_2$	AgOAc	-	AcOH (1 ml)	0.5	120	15 / 27 / 43
35	$PdCl_2$	AgOAc	-	EtCOOH (1 ml)	0.5	120	23 / 45 / 21
36	$PdCl_2$	AgOAc	-	PivOH (1 g)	0.5	120	33 / 51 / 8
37	$PdCl_2$	AgOAc	-	-	1	120	51 / 28 / 7
38	$PdCl_2$	AgOAc	-	PivOH (0.5 g)	1	120	45 / 47 / 0

39	$PdCl_2$	AgOAc	-	PivOH (0.25 g)	1	120	57 / 35 / 0
40	$PdCl_2$	AgOAc	PivOH (4)	-	1	120	51 / 36 / 0
41	$PdCl_2$	AgOAc	PivOH (2)	-	1	120	65 / 28 / trace
42	$PdCl_2$	AgOAc	PivOH (1)	-	1	120	63 / 26 / trace
43	$PdCl_2$	AgOAc	PivOH (2)	-	2	120	76 / 13 /trace
44	$PdCl_2$	AgOAc	PivOH (2)	-	1.5	140	43 / 37 / 6
45	$PdCl_2$	AgOAc	PivOH (2)	-	2	140	42 / 41 / 6
46	$Pd(OAc)_2$	AgOAc	PivOH (2)	-	1.5	120	76 / 16 / 0

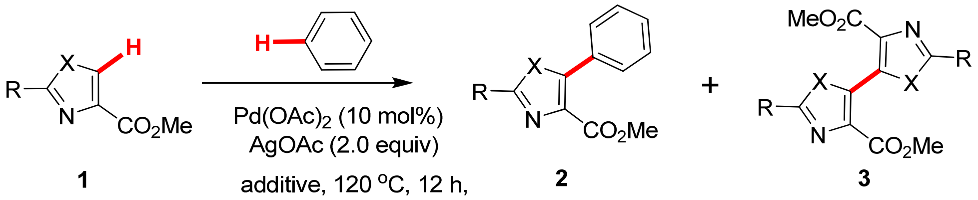
[a] Reaction conditions: methyl 2-phenylthiazole-4-carboxylate **1a** (0.5 mmol), Pd(II) catalyst (0.05 mmol), oxidant (1 mmol), additive and/or solvent in benzene for 12 h. [b] Isolated yield. [c] Afford 45 % of 5-iodination product. [d] Afford 39 % of 5-iodination product.

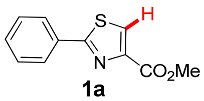
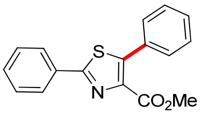
4. *Direct Arylation of Azole-4-carboxylates (1) with Benzene through Double C-H cleavage*

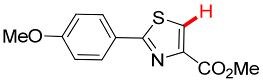
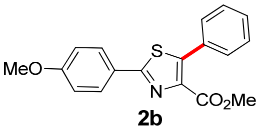
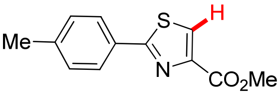
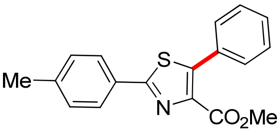
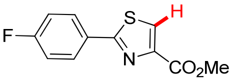
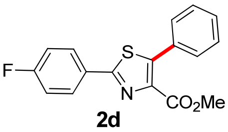
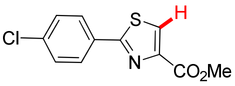
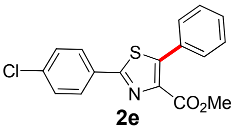
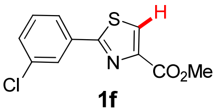
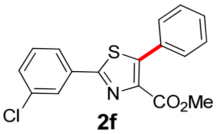
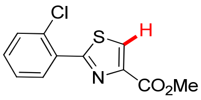
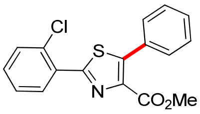
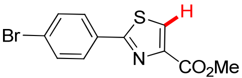
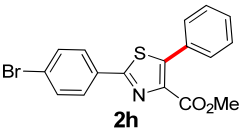
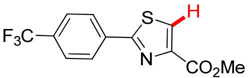
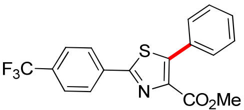
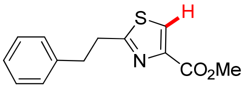
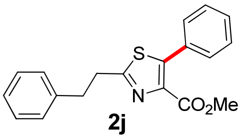
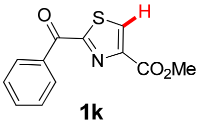
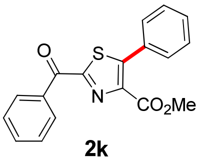
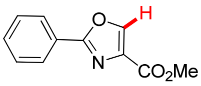
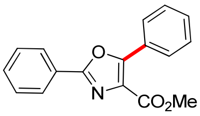
4.1 General Procedure for the Direct Arylation ofAzole-4-carboxylates 1 with Benzene

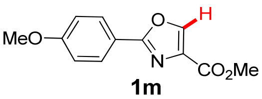
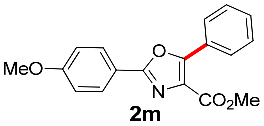
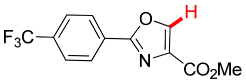
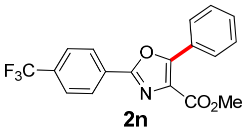
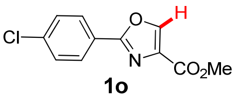
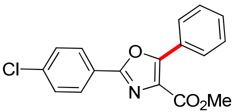
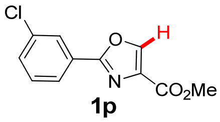
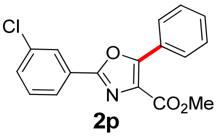
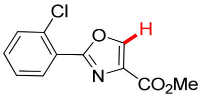
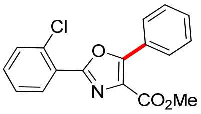
A reaction tube was charged with azole-4-carboxylate (0.5 mmol, 1 equiv.), Pd(II)-catalyst (0.05 mmol, 0.1 equiv.), AgOAc (1 mmol, 2 equiv.), PivOH (1 mmol, 2 equiv.) or DMSO (0.15 ml, 10%, v/v), and benzene (1.5 mL). The reaction mixture was vigorously stirred at 120°C (oil temperature). After stirring for 12 hours, the mixture was cooled to room temperature, diluted with ethyl acetate and filtered. The filtrate was washed with saturated $NaHCO_3$, water and brine, dried over Na_2SO_4, and concentrated *in vacuo* to give dark residue, which was purified by flash chromatography on silica gel to afford the arylated products **2** as summarized in *Table S2*.

Table S2. Scope of Azole-4-carboxylates in the Direct Arylation[a]



Entry	Substrate	Product	Catalyst	Yield (%) [b] (**2** / **1**)
1	 **1a**	 **2a**	$PdCl_2$ $Pd(OAc)_2$	79/trace 76/trace

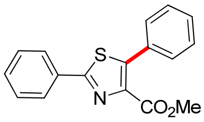
2	 **1b**	 **2b**	$PdCl_2$ $Pd(OAc)_2$	56/6 68/0
3	 **1c**	 **2c**	$PdCl_2$ $Pd(OAc)_2$	48/26 69/trace
4	 **1d**	 **2d**	$PdCl_2$ $Pd(OAc)_2$	81/0 81/0
5	 **1e**	 **2e**	$PdCl_2$ $Pd(OAc)_2$	78/0 82/0
6	 **1f**	 **2f**	$Pd(OAc)_2$	83/0
7	 **1g**	 **2g**	$Pd(OAc)_2$	79/0
8	 **1h**	 **2h**	$Pd(OAc)_2$	[c] 64/0 [d] 37/0
9	 **1i**	 **2i**	$PdCl_2$ $Pd(OAc)_2$	83/0 84/0
10	 **1j**	 **2j**	$PdCl_2$ $Pd(OAc)_2$	72/trace 75/trace
11	 **1k**	 **2k**	$PdCl_2$ $Pd(OAc)_2$	73/19 77/trace
12	 **1l**	 **2l**	$PdCl_2$ $Pd(OAc)_2$	76/12 81/0

13	 **1m**	 **2m**	$PdCl_2$ $Pd(OAc)_2$	79/0 81/0
14	 **1n**	 **2n**	$PdCl_2$ $Pd(OAc)_2$	82/4 84/0
15	 **1o**	 **2o**	$PdCl_2$ $Pd(OAc)_2$	74/13 78/0
16	 **1p**	 **2p**	$PdCl_2$ $Pd(OAc)_2$	77/8 81/0
17	 **1q**	 **2q**	$Pd(OAc)_2$	78/0

[a] Reaction conditions: methyl azole-4-carboxylates **1** (0.5 mmol), Pd(II) catalyst (0.05 mmol), AgOAc (1 mmol), PivOH (1 mmol) in benzene (1.5 mL) at 120 °C for 12 h. [b] Isolated yield. [c] DMSO (0.15 ml) was used as the additive instead of PivOH at 100°C. [d] DMSO (0.15 mL) was used as the additive instead of PivOH at 120°C.

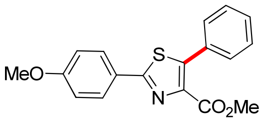
4.2 Characterization of the Arylated Products (2a-2q)

Methyl 2,5-Diphenylthiazole-4-carboxylate (2a)



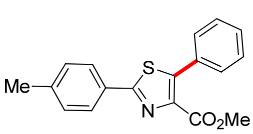
Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.78 (s, 3H), 7.35-7.38 (m, 6H), 7.45-7.48 (m, 2H), 7.89-7.92 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 160.8, 144.5, 139.0, 130.9, 128.8, 128.4, 128.0, 127.4, 127.2, 126.4, 124.9, 50.4 ppm; IR (KBr): 2950, 1720, 1468, 1336, 1329, 1211, 1014, 762, 748, 686 cm^{-1}; HRMS (ESI) calcd for $[C_{17}H_{13}NO_2S+Na]^+$ 318.0565, found 318.0572.

Methyl 2-(*p*-Methoxylphenyl)-5-phenylthiazole-4-carboxylate (2b)



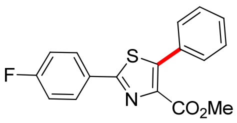
Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.85 (s, 3H), 3.87 (s, 3H), 6.96 (d, J = 8.6 Hz, 2H), 7.42-7.44 (m, 3H), 7.53-7.55 (m, 2H), 7.92 (d, J = 8.6 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 162.7, 161.7, 130.4, 129.9, 129.1, 128.5, 128.3, 128.2, 126.5, 125.6, 114.3, 55.4, 52.2 ppm; IR (KBr) 2932, 1724, 1609, 1469, 1249, 1211, 1174, 1038, 830, 796, 751, 692 cm^{-1}; HRMS (ESI) calcd for $[C_{18}H_{15}NO_3S+Na]^+$ 348.0670, found 318.0678.

Methyl 2-(*p*-Methylphenyl)-5-phenylthiazole-4-carboxylate (2c)



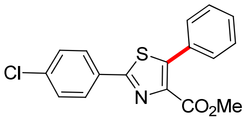
Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.41 (s, 3H), 3.86 (s, 3H), 7.26 (d, J = 8.1 Hz, 2H), 7.43-7.45 (m, 3H), 7.53-7.56 (m, 2H), 7.88 (d, J = 8.1 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 162.7, 146.0, 141.1, 140.7, 130.4, 130.1, 129.9, 129.7, 129.2, 128.2, 126.7, 52.2, 21.5 ppm; IR (KBr) 2944, 2914, 1718, 1602, 1471, 1329, 1202, 1014, 970, 818, 755, 695 cm^{-1}; HRMS (ESI) calcd for $[C_{18}H_{15}NO_2S+Na]^+$ 332.0721, found 332.0729.

Methyl 2-(*p*-Fluorophenyl)-5-phenylthiazole-4-carboxylate (2d)



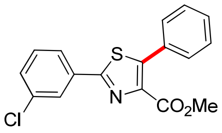
Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.86 (s, 3H), 7.12-7.18 (m, 2H), 7.43-7.46 (m, 3H), 7.53-7.56 (m, 2H), 7.95-8.00 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 164.9, 162.6, 146.4, 140.8, 130.1, 129.9, 129.3, 129.1, 128.8, 128.7, 128.3, 116.3, 116.0, 52.3 ppm; IR (KBr) 3056, 2943, 1729, 1601, 1468, 1347, 1170, 1158, 1010, 844, 760, 700 cm^{-1}; HRMS (ESI) calcd for $[C_{17}H_{12}FNO_2S+Na]^+$ 336.0470, found 336.0479.

Methyl 2-(*p*-Chlorophenyl)-5-phenylthiazole-4-carboxylate (2e)



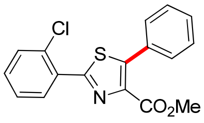
White solid, m.p. 111-112 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.86 (s, 3H), 7.42-7.46 (m, 5H), 7.53-7.56 (m, 2H), 7.93 (d, J = 8.6 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7, 162.5, 146.6, 141.0, 136.7, 131.2, 130.1, 129.9, 129.4, 129.3, 128.3, 127.9, 52.3 ppm; IR (KBr) 2944, 1724, 1466, 1345, 1201, 1171, 1087, 1014, 967, 843, 761, 698 cm^{-1}; HRMS (ESI) calcd for $[C_{17}H_{12}ClNO_2S+Na]^+$ 352.0175, found 352.0182.

Methyl 2-(*m*-Chlorophenyl)-5-phenylthiazole-4-carboxylate (2f)



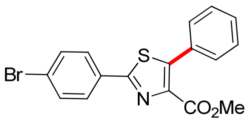
White solid, m.p. 121-122 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.87 (s, 3H), 7.39-7.46 (m, 5H), 7.53-7.56 (m, 2H), 7.82-7.85 (m, 1H), 8.01 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 162.5, 146.9, 141.0, 135.2, 134.3, 130.6, 130.3, 130.0, 129.9, 129.4, 128.3, 126.6, 124.9, 52.3 ppm; IR (KBr) 3056, 2944, 1727, 1567, 1452, 1333, 1248, 1197, 1168, 1021, 993, 882, 784, 759, 746, 696, 677 cm^{-1}; HRMS (ESI) calcd for $[C_{17}H_{12}ClNO_2S+Na]^+$ 352.0175, found 352.0184.

Methyl 2-(*o*-Chlorophenyl)-5-phenylthiazole-4-carboxylate (2g)



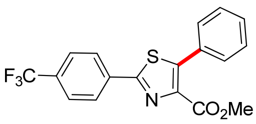
White solid, m.p. 136-138 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.87 (s, 3H), 7.38-7.52 (m, 6H), 7.56-7.59 (m, 2H), 8.30-8.32 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.7, 161.5, 147.7, 139.6, 132.1, 131.3, 131.1, 130.9, 130.5, 130.1, 130.0, 129.3, 128.3, 127.2, 52.2 ppm; IR (KBr) 2944, 1721, 1481, 1434, 1338, 1208, 1066, 1017, 761, 750, 688 cm^{-1}; HRMS (ESI) calcd for $[C_{17}H_{12}ClNO_2S+Na]^+$ 352.0175, found 352.0184.

Methyl 2-(*p*-Bromophenyl)-5-phenylthiazole-4-carboxylate (2h)



White solid, m.p. 120-122 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.78 (s, 3H), 7.36-7.38 (m, 3H), 7.45-7.48 (m, 2H), 7.52 (d, J = 8.3 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8, 162.5, 146.6, 141.0, 132.2, 131.6, 130.1, 129.9, 129.4, 128.3, 128.1, 125.1, 52.3 ppm; IR (KBr) 2944, 1723, 1466, 1346, 1200, 1171, 1066, 1013, 966, 843, 761, 697 cm^{-1}; HRMS (ESI) calcd for $[C_{17}H_{12}BrNO_2S+Na]^+$ 395.9670, found 395.9671.

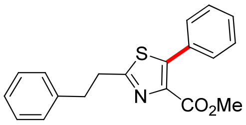
Methyl 2-(*p*-Trifluoromethylphenyl)-5-phenylthiazole-4-carboxylate (2i)



White solid, m.p. 126-127.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.79 (s, 3H), 7.37-7.39 (m, 3H), 7.46-7.49 (m, 2H), 7.64 (d, J = 8.2 Hz, 2H), 8.02 (d, J =

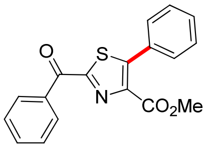
8.2 Hz, 2H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) δ 164.1, 162.5, 147.3, 141.3, 135.8, 132.4, 132.0, 129.9, 129.5, 128.3, 127.0, 126.1, 126.0, 125.6, 122.0, 52.3 ppm; IR (KBr) 2950, 1725, 1470, 1322, 1203, 1172, 1065, 860, 762, 705, 698 cm^{-1}; HRMS (ESI) calcd for [$C_{18}H_{12}F_3NO_2S$+Na]$^+$ 386.0439, found 386.0448.

Methyl 2-Phenylethyl-5-phenylthiazole-4-carboxylate (2j)



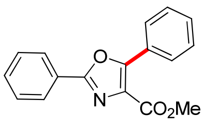
Colorless oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.07 (t, *J* = 8.5 Hz, 2H), 3.29 (t, *J* = 8.5 Hz, 2H), 3.77 (s, 3H), 7.16-7.26 (m, 5H), 7.34-7.39 (m, 5H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) δ 168.5, 162.5, 146.6, 39.9, 138.3, 130.4, 129.9, 129.1, 128.6, 128.5, 128.2, 126.6, 52.2, 35.9, 35.2 ppm; IR (KBr) 3027, 2950, 1720, 1475, 1327, 1070, 1006, 754, 695 cm^{-1}; HRMS (ESI) calcd for [$C_{19}H_{17}NO_2S$+Na]$^+$ 346.0878, found 346.0884.

Methyl 2-Benzoyl-5-phenylthiazole-4-carboxylate (2k)



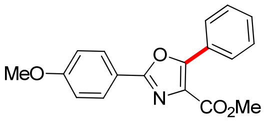
White solid, m.p. 105-106 ^{o}C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.79 (s, 3H), 7.39-7.41 (m, 3H), 7.45-7.50 (m, 4H), 7.59 (t, *J* = 7.4 Hz, 1H), 8.48 (d, *J* = 7.4 Hz, 2H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) δ 183.5, 165.2, 162.3, 152.6, 134.5, 134.0, 131.3, 130.0, 129.9, 129.6, 128.9, 128.6, 128.4, 52.4 ppm; IR (KBr) 3056, 2956, 1729, 1639, 1459, 1297, 1202, 1173, 901, 754, 713, 697 cm^{-1}; HRMS (ESI) calcd for [$C_{18}H_{13}NO_3S$+Na]$^+$ 346.0514, found 346.0521.

Methyl 2,5-Diphenyloxazole-4-carboxylate (2l)



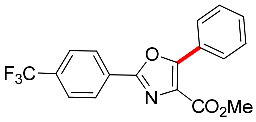
Colorless oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.91 (s, 3H), 7.42-7.46 (m, 6H), 8.06-8.10 (m, 4H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) δ 162.7, 159.8, 155.3, 131.1, 130.3, 128.8, 128.4, 128.0, 127.0, 126.8, 126.3, 52.3 ppm; IR (KBr) 2923, 1713, 1563, 1492, 1358, 1227, 1099, 775, 708, 686 cm^{-1}; HRMS (ESI) calcd for [$C_{17}H_{13}NO_3$+Na]$^+$ 302.0793, found 302.0801.

Methyl 2-(*p*-Methoxylphenyl)-5-phenyloxazole-4-carboxylate (2m)



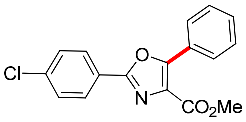
White solid, m.p. 114-115 ^{o}C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.81 (s, 3H), 3.90 (s, 3H), 6.92 (d, *J* = 8.9 Hz, 2H), 7.39-7.45 (m, 3H), 8.00-8.08 (m, 4H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) δ 162.8, 162.0, 159.9, 154.8, 130.2, 128.6, 128.4, 128.3, 127.8, 127.2, 119.0, 114.3, 55.4, 55.3 ppm; IR (KBr) 2923, 1724, 1615, 1506, 1356, 1257, 1214, 1105, 1023, 831, 762, 737, 682 cm^{-1}; HRMS (ESI) calcd for [$C_{18}H_{15}NO_4$+Na]$^+$ 332.0899, found 302.0905.

Methyl 2-(*p*-Trifluoromethylphenyl)-5-phenyloxazole-4-carboxylate (2n)



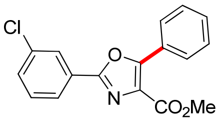
White solid, m.p. 111-112 ^{o}C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.90 (s, 3H), 7.42-7.45 (m, 3H), 7.67 (d, *J* = 8.2 Hz, 2H), 8.04-8.07 (m, 2H), 8.19 (d, *J* = 8.2 Hz, 2H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) δ 162.3, 158.2, 155.9, 132.8, 132.4, 130.6, 129.4, 128.5, 128.2, 127.0, 126.6, 125.9, 125.8, 125.5, 121.9, 52.4 ppm; IR (KBr) 2920, 1723, 1492, 1326, 1221, 1063, 1012, 853, 769, 708 cm^{-1}; HRMS (ESI) calcd for [$C_{18}H_{12}F_3NO_3$+Na]$^+$ 370.0667, found 370.0673.

Methyl 2-(*p*-Chlorophenyl)-5-phenyloxazole-4-carboxylate (2o)



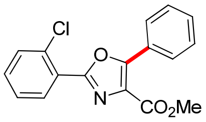
White solid, m.p. 123-124 ^{o}C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.90 (s, 3H), 7.38-7.45 (m, 5H), 8.00-8.06 (m, 4H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) δ 162.5, 158.8, 155.4, 137.3, 130.5, 129.2, 128.5, 128.4, 128.1, 126.8, 124.8, 52.4 ppm; IR (KBr) 2920, 1724, 1607, 1491, 1405, 1221, 1088, 1010, 835, 814, 759, 730, 683 cm^{-1}; HRMS (ESI) calcd for [$C_{17}H_{12}ClNO_3$+Na]$^+$ 336.0403, found 336.0409.

Methyl 2-(*m*-Chlorophenyl)-5-phenyloxazole-4-carboxylate (2p)



White solid, m.p. 106-108 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.92 (s, 3H), 7.36-7.47 (m, 5H), 7.97 (d, J = 7.2 Hz, 1H), 8.05-8.09 (m, 3H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): δ 162.4, 158.3, 155.6, 135.0, 131.1, 130.5, 130.1, 128.5, 128.4, 128.1, 128.1, 127.9, 126.7, 124.8, 52.4 ppm; IR (KBr) 3080, 2950, 2920, 1720, 1561, 1494, 1228, 1111, 879, 819, 722, 689 cm^{-1}; HRMS (ESI) calcd for [$C_{17}H_{12}ClNO_3$+Na]$^+$ 336.0403, found 336.0411.

Methyl 2-(*o*-Chlorophenyl)-5-phenyloxazole-4-carboxylate (2q)



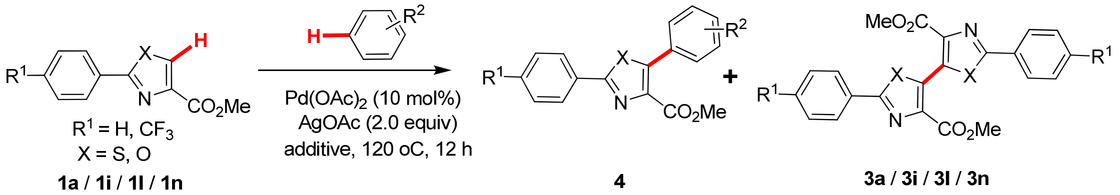
White solid, m.p. 104-105 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.92 (s, 3H), 7.13-7.24 (m, 2H), 7.42-7.46 (m, 4H), 8.07-8.13 (m, 3H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) δ 162.6, 162.0, 158.6, 132.8, 132.7, 130.5, 130.0, 128.5, 128.4, 126.8, 124.4, 124.3, 117.0, 116.8, 52.4 ppm; IR (KBr) 2923, 1718, 1495, 1442, 1240, 1220, 1098, 1014, 812, 766, 737, 683 cm^{-1}; HRMS (ESI) calcd for [$C_{17}H_{12}ClNO_3$+Na]$^+$ 336.0403, found 336.0409.

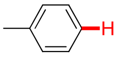
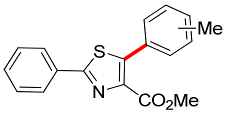
5. *Arylation of Azole-4-carboxylates 1a/1i/1l/1n with Other Arenes*

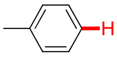
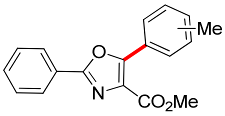
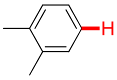
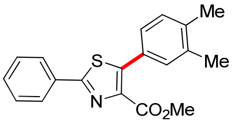
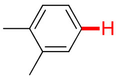
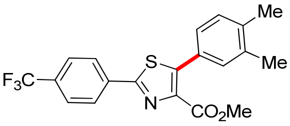
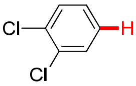
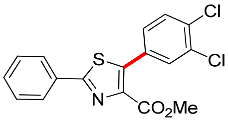
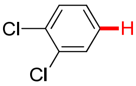
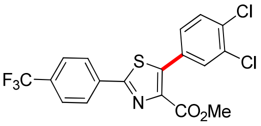
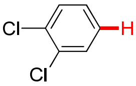
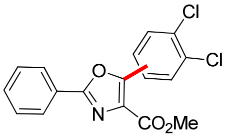
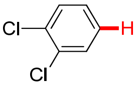
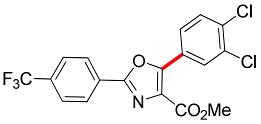
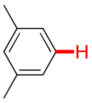
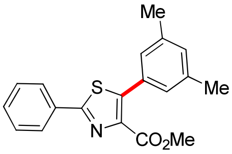
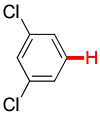
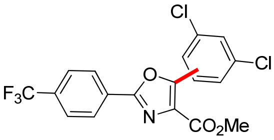
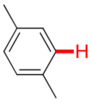
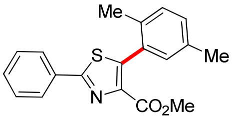
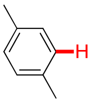
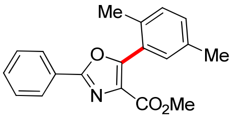
5.1 General Procedure for the Arylation of Azole-4-carboxylates 1a/1i/1l/1n with Other Arenes

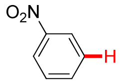
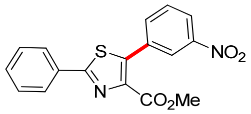
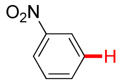
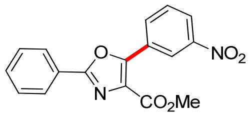
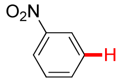
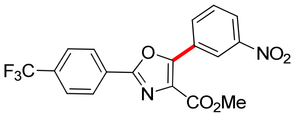
A reaction tube was charged with azole-4-carboxylate (0.5 mmol, 1 equiv.), Pd(II)-catalyst (0.05 mmol, 0.1 equiv.), AgOAc (1 mmol, 2 equiv.), PivOH (1 mmol, 2 equiv.) or DMSO (0.15 mL, 10%, v/v), and arene (1.5 mL). The reaction mixture was vigorously stirred at 120 °C (oil temperature). After stirring for 12 hours, the mixture was cooled to room temperature, diluted with ethyl acetate and filtered. The filtrate was washed with saturated NaHCO$_3$, water and brine, dried over Na$_2$SO$_4$, and concentrated *in vacuo* to give dark residue, which was purified by flash chromatography on silica gel to afford the arylated products **4** as summarized in *Table S3*. Isomers of **4a** and **4b** were isolated via HPLC.

Table S3. Scope of Arenes in the Direct Arylation^a



Entry	Arene	Product	Additive	Yield (%) ^{b} (**4**/**1**)
1		 **4a-I / 4a-II**	PivOH	61/ trace (1,3/1,4 = 1:1.4^c)

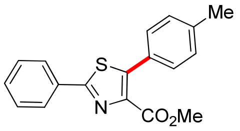
2		 **4b-I / 4b-II**	PivOH	77/0 (1,3/1,4 = 1:1.4[c])
3		 **4c**	PivOH	56/ trace
4		 **4d**	PivOH	73/0
5		 **4e**	PivOH	56/0
6		 **4f**	PivOH	68/0
7		 **4g-I / 4g-II**	PivOH	78/0 (1,2,3/1,2,4=1:4.8[c])
8		 **4h**	PivOH	72/7
9		 **4i**	PivOH DMSO[d] DMSO[e]	39/0 56/0 61/0
10		 **4j-I / 4j-II**	PivOH	63/0 (1,2,4/1,3,5=1:2.1[c])
11		 **4k**	PivOH DMSO[d] DMSO[e]	9/trace 37/0 60/0
12		 **4l**	PivOH DMSO[d] DMSO[e]	21/0 44/0 51/0

13		 **4m**	PivOH	44/0
14		 **4n**	PivOH	56/0
15		 **4o**	PivOH	60/0

[a] Reaction conditions: methyl azole-4-carboxylates **1** (0.5 mmol), $Pd(OAc)_2$ (0.05 mmol), AgOAc (1 mmol), and PivOH (1 mmol) or DMSO (0.15 mL) in arene (1.5 ml) at 120 °C for 12 h. [b] Isolated yield. [c] Determined by HPLC. [d] Conducted at 120 °C. [e] Conducted at 100 °C.

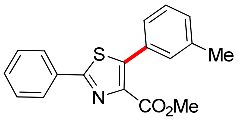
5.2 Characterization of the Arylated Products (4a-4o)

Methyl 2-Phenyl-5-(4-methylphenyl)thiazole-4-carboxylate (4a-I)



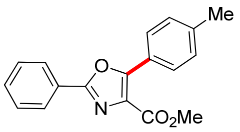
Colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 2.42 (s, 3H), 3.87 (s, 3H), 7.25 (d, J = 6.3 Hz, 2H), 7.44-7.46 (m, 5H), 7.96-7.99 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8, 161.8, 145.8, 138.5, 131.8, 129.6, 128.8, 128.2, 128.0, 127.9, 126.3, 125.8, 51.3, 20.4 ppm; IR (KBr) 3015, 2950, 1728, 1466, 1203, 1010, 763, 690 cm^{-1}; HRMS (ESI) calcd for $[C_{18}H_{15}NO_2S + H]^+$ 310.0902, found 310.0900.

Methyl 2-Phenyl-5-(3-methylphenyl)thiazole-4-carboxylate (4a-II)



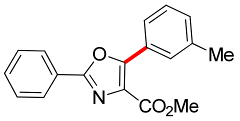
Colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 2.42 (s, 3H), 3.87 (s, 3H), 7.30-7.35 (m, 4H), 7.45-7.47 (m, 3H), 7.97-8.00 (m, 2H) ppm; J = 2.0 Hz, 1H), 7.65 (d, J = 8.2 Hz, 2H), 8.01 (d, J = 8.2 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0, 161.7, 145.6, 139.8, 137.0, 131.8, 129.6, 129.5, 129.2, 129.1, 128.0, 127.2, 126.0, 125.8, 51.3, 20.4 ppm; IR (KBr) 3038, 2962, 1727, 1465, 1202, 1168, 763, 689 cm^{-1}; HRMS (ESI) calcd for $[C_{18}H_{15}NO_2S + H]^+$ 310.0902, found 310.0899.

Methyl 2-Phenyl-5-(4-methylphenyl)oxazole-4-carboxylate (4b-I)



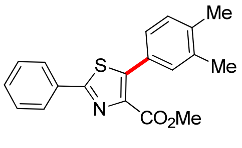
Colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 2.44 (s, 3H), 3.98 (s, 3H), 7.32 (d, J = 8.2 Hz, 2H), 7.49-7.51 (m, 3H), 8.05 (d, J = 8.2 Hz, 2H), 8.14-8.17 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.5, 156.0, 154.7, 139.8, 130.0, 128.2, 127.8, 127.4, 125.8, 125.5, 123.2, 51.3, 20.6 ppm; IR (KBr) 3074, 2950, 2914, 1720, 1561, 1449, 1221, 1096, 784, 710, 689 cm^{-1}; HRMS (ESI) calcd for $[C_{18}H_{15}NO_3 + H]^+$ 294.1130, found 294.1128.

Methyl 2-Phenyl-5-(3-methylphenyl)oxazole-4-carboxylate (4b-II)



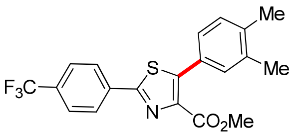
Colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 2.46 (s, 3H), 3.98 (s, 3H), 7.30 (d, J = 7.5 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.49-7.51 (m, 3H), 7.94 (s, 1H), 7.95 (d, J = 7.5 Hz, 1H), 8.15-8.18 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.7, 158.8, 154.5, 143.7, 137.2, 130.2, 130.1, 127.9, 127.8, 127.4, 126.9, 125.9, 125.4, 124.7, 51.4, 20.5 ppm; IR (KBr) 3068, 2956, 1714, 1564, 1443, 1225, 1104, 792, 701, 695 cm^{-1}; HRMS (ESI) calcd for $[C_{18}H_{15}NO_3+H]^+$ 294.1130, found 294.1127.

Methyl 2-Phenyl-5-(3,4-dimethylphenyl)thiazole-4-carboxylate (4c)



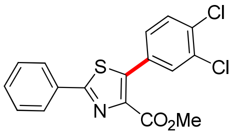
Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.24 (s, 6H), 3.80 (s, 3H), 7.13 (d, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.24 (s, 1H), 7.37-7.39 (m, 3H), 7.89-7.92 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 162.8, 138.1, 136.6, 132.9, 130.9, 130.5, 129.9, 129.6, 129.0, 128.3, 127.6, 127.4, 126.8, 52.2, 19.8, 19.7 ppm; IR (KBr): 2920, 1723, 1473, 1338, 1216, 1039, 969, 818, 777, 757, 682 cm^{-1}; HRMS (ESI) calcd for $[C_{19}H_{17}NO_2S+Na]^+$ 346.0878, found 346.0887.

Methyl 2-(*p*-Trifluoromethylphenyl)-5-(3,4-dimethylphenyl)thiazole-4-carboxylate (4d)



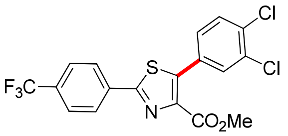
Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.22 (s, 6H), 3.79 (s, 3H), 7.11 (d, *J* = 7.9 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 7.22 (s, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.99 (d, *J* = 8.3 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.6, 162.6, 147.8, 140.9, 138.5, 136.7, 135.9, 132.3, 131.9, 130.9, 129.9, 129.6, 128.3, 127.3, 127.2, 126.9, 126.1, 126.0, 125.9, 125.6, 122.0, 52.3, 19.7, 19.6 ppm; IR (KBr) 2920, 1725, 1616, 1467, 1322, 1205, 1111, 1068, 839, 781 cm^{-1}; HRMS (ESI) calcd for $[C_{20}H_{16}F_3NO_2S+Na]^+$ 414.0752, found 414.0753.

Methyl 2-Phenyl-5-(3,4-dichlorophenyl)thiazole-4-carboxylate (4e)



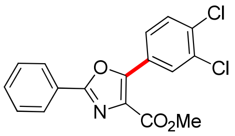
White solid, m.p. 144-146 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.89 (s, 3H), 7.40 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.47-7.49 (m, 3H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.66 (d, *J* = 2.0 Hz, 1H), 7.96-7.99 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 162.3, 143.3, 141.5, 138.4, 133.7, 132.5, 132.4, 131.7, 131.0, 130.2, 129.3, 129.1, 126.8, 52.4 ppm; IR (KBr) 2922, 1719, 1467, 1384, 1337, 1221, 1033, 820, 760, 684 cm^{-1}; HRMS (ESI) calcd for $[C_{17}H_{11}Cl_2NO_2S+Na]^+$ 385.9785, found 385.9790.

Methyl 2-(*p*-Trifluoromethylphenyl)-5-(3,4-dichlorophenyl)thiazole-4-carboxylate (4f)



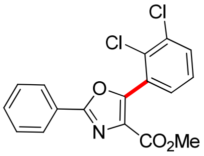
White solid, m.p. 137-139 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.81 (s, 3H), 7.32 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.58 (d, *J* = 2.0 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 8.01 (d, *J* = 8.2 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8, 162.1, 144.2, 141.9, 135.5, 134.0, 132.8, 132.7, 131.7, 130.4, 129.7, 129.3, 127.1, 126.2, 126.1, 125.5, 121.9, 52.6 ppm; IR (KBr) 2956, 1722, 1614, 1466, 1324, 1212, 1106, 1068, 1025, 841 cm^{-1}; HRMS (ESI) calcd for $[C_{18}H_{10}Cl_2F_3NO_2S+Na]^+$ 453.9659, found 453.9665.

Methyl 2-Phenyl-5-(3,4-dichlorophenyl)oxazole-4-carboxylate (4g-I)



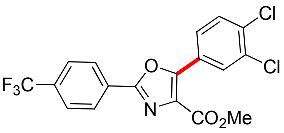
White solid, m.p. 150-152 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.01 (s, 3H), 7.49-7.53 (m, 3H), 7.58 (d, *J* = 8.5 Hz, 1H), 8.09 (dd, *J* = 8.5, 2.0 Hz, 1H), 8.14-8.17 (m, 2H), 8.33 (d, *J* = 2.0 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.4, 160.1, 152.6, 134.5, 132.9, 131.4, 130.5, 129.9, 128.9, 127.4, 127.2, 126.9, 126.8, 125.9, 52.6 ppm; IR (KBr) 2920, 1714, 1564, 1471, 1349, 1224, 1108, 1031, 789, 710, 685 cm^{-1}; HRMS (ESI) calcd for $[C_{17}H_{11}Cl_2NO_3+Na]^+$ 370.0014, found 370.0014.

Methyl 2-Phenyl-5-(2,3-dichlorophenyl)oxazole-4-carboxylate (4g-II)



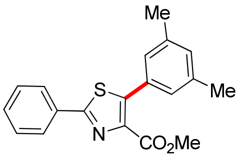
White solid, m.p. 136-138 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.88 (s, 3H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.47-7.53 (m, 4H), 7.64 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.13-8.16 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.8, 161.4, 152.0, 134.0, 132.9, 132.4, 131.4, 130.9, 130.6, 129.0, 128.9, 127.1, 127.0, 126.2, 52.3 ppm; IR (KBr) 2923, 1721, 1456, 1366, 1259, 1234, 1101, 784, 713, 684 cm^{-1}; HRMS (ESI) calcd for $[C_{17}H_{11}Cl_2NO_3+Na]^+$ 370.0014, found 370.0016.

Methyl 2-(*p*-Trifluoromethylphenyl)-5-(3,4-dichlorophenyl)oxazole-4-carboxylate (4h)



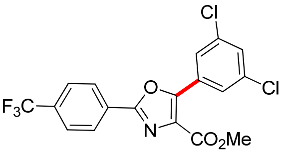
White solid, m.p. 169-170 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.93 (s, 3H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 8.00 (dd, *J* = 8.5, 2.0 Hz, 1H), 8.19 (d, *J* = 8.3 Hz, 2H), 8.24 (d, *J* = 2.0 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.1, 158.6, 153.3, 134.9, 133.2, 133.0, 132.8, 130.6, 130.0, 129.2, 129.0, 127.5, 127.2, 126.4, 126.0, 125.9, 125.4, 121.8, 52.7 ppm; IR (KBr) 2920, 1715, 1567, 1475, 1322, 1225, 1113, 848, 786, 709 cm^{-1}; HRMS (ESI) calcd for $[C_{18}H_{10}Cl_2F_3NO_3+H]^+$ 416.0063, found 416.0057.

Methyl 2-Phenyl-5-(3,5-dimethylphenyl)thiazole-4-carboxylate (4i)



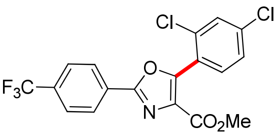
Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 6H), 3.87 (s, 3H), 7.07 (s, 1H), 7.15 (s, 2H), 7.44-7.46 (m, 3H), 7.96-7.99 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 162.8, 146.7, 137.8, 132.8, 131.0, 130.5, 130.0, 129.0, 127.6, 126.8, 126.3, 52.2, 21.3 ppm; IR (KBr) 2926, 1731, 1464, 1381, 1275, 1260, 1207, 1166, 764, 750, 689 cm^{-1}; HRMS (ESI) calcd for $[C_{19}H_{17}NO_2S+Na]^+$ 346.0878, found 346.0883.

Methyl 2-(*p*-Trifluoromethylphenyl)-5-(3,5-dichlorophenyl)oxazole-4-carboxylate (4j-I)



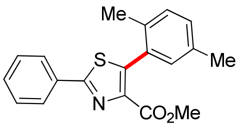
White solid, m.p. 137-138 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.95 (s, 3H), 7.41 (t, *J* = 1.8 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 8.05 (d, *J* = 1.8 Hz, 2H), 8.21 (d, *J* = 8.3 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.95, 158.9, 152.7, 135.4, 133.3, 132.9, 130.3, 129.7, 129.2, 128.9, 127.2, 126.5, 126.0, 125.9, 125.4, 121.8, 52.7 ppm; IR (KBr) 3091, 2956, 1715, 1552, 1329, 1226, 1112, 1066, 804, 711, 662 cm^{-1}; HRMS (ESI) calcd for $[C_{18}H_{10}Cl_2F_3NO_3+H]^+$ 416.0063, found 416.0063.

Methyl 2-(*p*-Trifluoromethylphenyl)-5-(2,4-dichlorophenyl)oxazole-4-carboxylate (4j-II)



Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.90 (s, 3H), 7.41 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.56-7.59 (m, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 8.26 (d, *J* = 8.3 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.5, 159.0, 151.2, 136.5, 134.2, 132.2, 132.1, 131.8, 130.3, 129.1, 128.4, 126.2, 126.1, 125.0, 124.9, 124.5, 124.0, 120.9, 51.4 ppm; IR (KBr) 2920, 1720, 1622, 1470, 1322, 1169, 1117, 1070, 853, 800 cm^{-1}; HRMS (ESI) calcd for $[C_{18}H_{10}Cl_2F_3NO_3+H]^+$ 416.0063, found 416.0065.

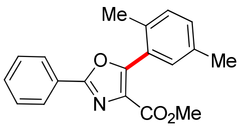
Methyl 2-Phenyl-5-(2,5-dimethylphenyl)thiazole-4-carboxylate (4k)



Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.19 (s, 3H), 2.35 (s, 3H), 3.81 (s, 3H), 7.10-7.18 (m, 3H), 7.45-7.48 (m, 3H), 7.98-8.01 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 162.2, 135.0, 134.2, 132.8, 130.6, 130.1, 130.0, 129.8, 129.0, 126.8, 52.2, 20.9, 19.6 ppm; IR (KBr) 2950, 2914, 1728, 1468, 1330, 1291, 1236, 1206, 1036, 972, 774, 731, 690 cm^{-1}; HRMS Calcd for $[C_{19}H_{17}NO_2S+H]^+$

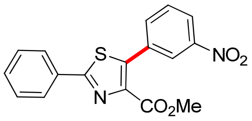
324.1058, found 324.1062.

Methyl 2-Phenyl-5-(2,5-dimethylphenyl)oxazole-4-carboxylate (4l)



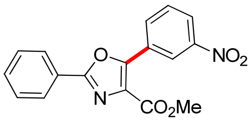
Colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 2.23 (s, 3H), 2.31 (s, 3H), 3.81 (s, 3H), 7.15 (s, 2H), 7.19 (s, 1H), 7.39-7.42 (m, 3H), 8.05-8.07 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.2, 160.6, 156.1, 135.0, 134.9, 131.3, 131.2, 130.4, 129.5, 128.8, 126.8, 126.7, 126.6, 52.1, 20.9, 19.7 ppm; IR (KBr) 2926, 1720, 1602, 1494, 1437, 1353, 1221, 1096, 1034, 814, 711, 686 cm^{-1}; HRMS (ESI) calcd for $[C_{19}H_{17}NO_3+Na]^+$ 330.1106, found 330.1114.

Methyl 2-Phenyl-5-(3-nitrophenyl)thiazole-4-carboxylate (4m)



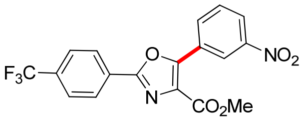
White solid, m.p. 186-188 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 3.89 (s, 3H), 7.48-7.50 (m, 3H), 7.64 (t, J = 8.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.98-8.01 (m, 2H), 8.31 (dd, J = 8.0, 1.7 Hz, 1H), 8.43 (d, J = 1.7 HZ, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.2, 162.2, 148.0, 141.8, 136.0, 132.3, 131.1, 129.2, 129.1, 127.2, 126.9, 125.0, 124.0, 52.5 ppm; IR (KBr): 2922, 1716, 1531, 1467, 1354, 1218, 1031, 763, 742, 686 cm^{-1}; HRMS (ESI) calcd for $[C_{17}H_{12}N_2O_4S+Na]^+$ 363.0415, found 363.0418.

Methyl 2-Phenyl-5-(3-nitrophenyl)oxazole-4-carboxylate (4n)



Light yellow solid, m.p. 155-157 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 4.03 (s, 3H), 7.53-7.55 (m, 3H), 7.71 (t, J = 8.2 Hz, 1H), 8.18-8.21 (m, 2H), 8.33 (dd, J = 8.2, 1.8 Hz, 1H), 8.74 (d, J = 8.2 Hz, 1H), 9.09 (d, J= 1.8 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.4, 160.6, 152.4, 148.4, 133.9, 131.6, 129.6, 129.0, 128.5, 127.0, 125.8, 124.6, 123.2, 52.7 ppm; IR (KBr) 2922, 1720, 1531, 1348, 1236, 1115, 817, 741, 710 cm^{-1}; HRMS (ESI) calcd for $[C_{17}H_{12}N_2O_5+Na]^+$ 347.0644, found 347.0648.

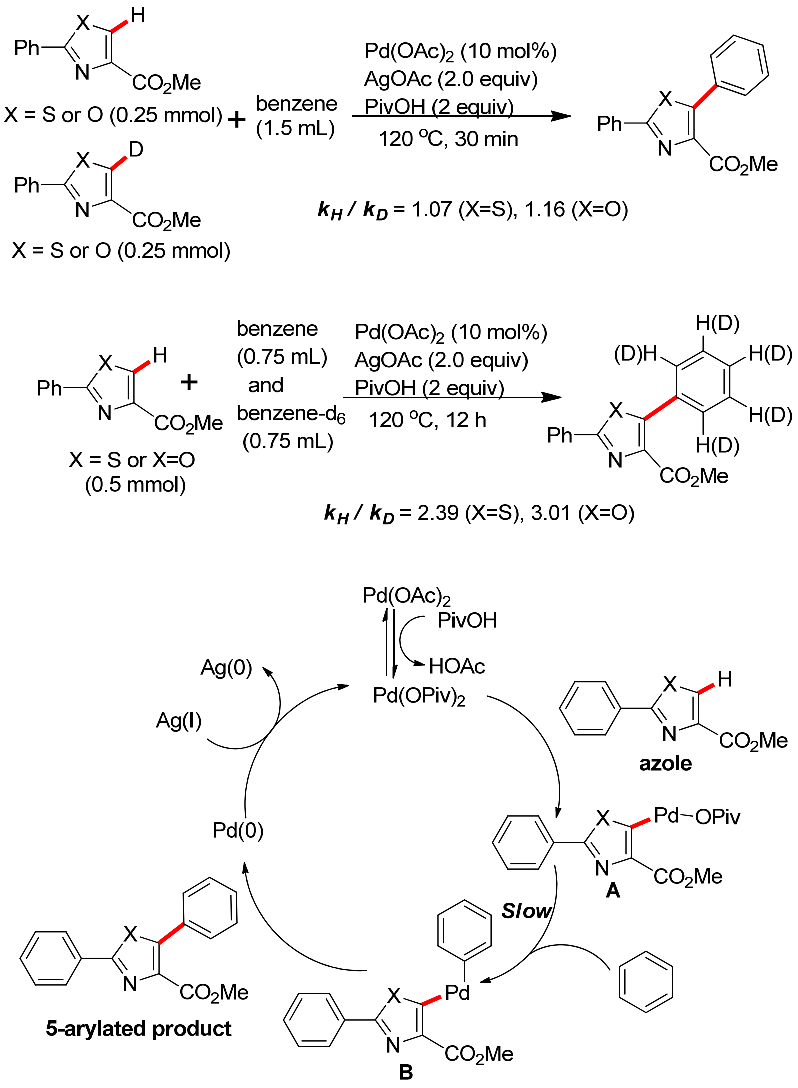
Methyl 2-(p-Trifluoromethylphenyl)-5-(3-nitrophenyl)oxazole-4-carboxylate (4o)



Light yellow solid, m.p. 138-139 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 4.03 (s, 3H), 7.69-7.80 (m, 3H), 8.28-8.36 (m, 3H), 8.56 (d, J = 7.9 Hz, 1H), 9.06 (d, J = 1.7 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.0, 158.1, 152.0, 147.4, 133.0, 132.4, 131.9, 128.9, 128.7, 128.2, 128.0, 127.2, 126.3, 125.1, 125.0, 124.9, 124.4, 123.9, 122.7, 122.3, 120.8, 51.8 ppm; IR (KBr) 2956, 1725, 1532, 1324, 1229, 1183, 1121, 1065, 852, 740, 710 cm^{-1}; HRMS (ESI) calcd for $[C_{18}H_{11}F_3N_2O_5+Na]^+$ 415.0518, found 415.0518.

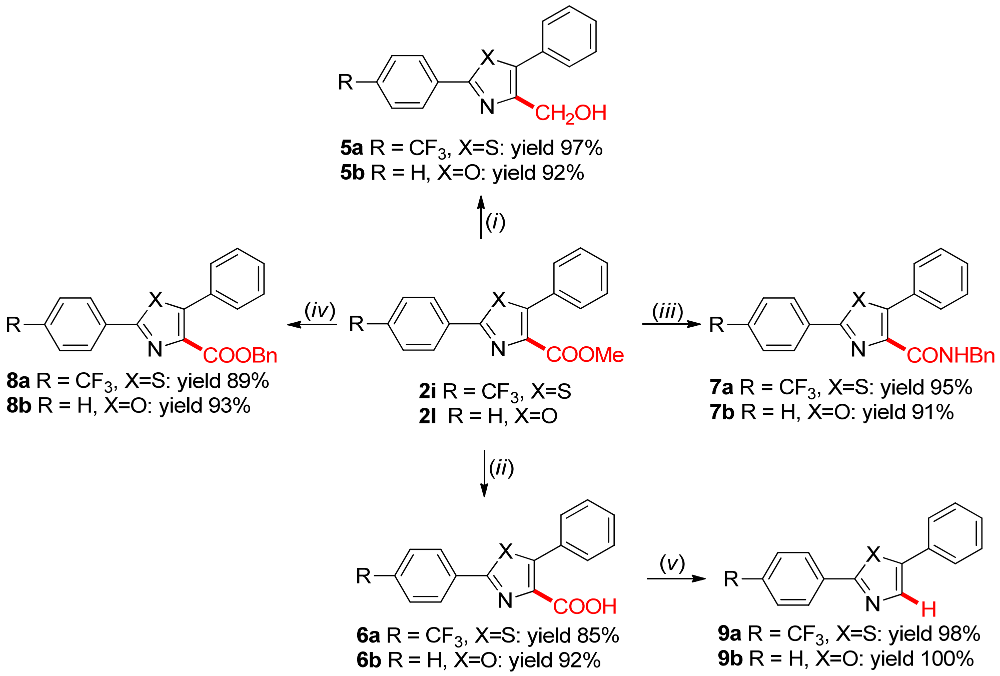
6. Mechanism Studies

To gain mechanistic insights of this process, we performed kinetic isotope effect studies (Scheme S3). By comparing the the initial rates of benzene to those of benzene-d_6, the k_H / k_D values (by ^{1}H NMR) were determined to be 2.39 and 3.01 for thiazole and oxazole, respectively. The k_H / k_D values (by ^{1}H NMR) of H/D-azoles were determined to be 1.07 and 1.16 for thiazole and oxazole, respectively. The results suggest that the second C-H bond cleavage could be a rate-limiting step of the reaction. Thus, a plausible mechanism for the direct arylation of azoles is set out to be in Scheme 1. This process is initiated by a palladation of azole at C5 to give palladium intermediate **A**. In the presence of unactivated arene, the C5-palladated species **A** inserts slowly into arene, and reductive elimination produced the arylated product, along with Pd(0) which is reoxidized by Ag(I) to complete the catalytic cycle.



Scheme S2. Mechanism Studies.

7. *Derivation of the Arylated Products 2i and 2l*

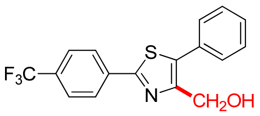


Scheme S3. Derivation of the 5-Arylation Products. *Reaction conditions:* (i) $LiAlH_4$, THF, 0 °C; (ii) 20 % KOH (aq), MeOH, r.t. to 60°C; (iii) $BnNH_2$, 100°C; (iv) BnOH, $KHCO_3$, 100 °C; (v) Ag_2CO_3 (20 mol%), AcOH (5 mol%), DMSO, 120 °C.

7.1 Reduction of the Arylated Products

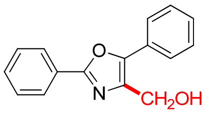
To a mixture of the arylation product **2i** or **2l** (0.2 mmol, 1 equiv.) and THF (2 mL) was added $LiAlH_4$ (0.5 mmol, 2.5 equiv.) at 0 °C. After stirring for 10 min, the reaction mixture was quenched with 0.2 ml water, diluted with ethyl acetate, washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo* to give crude product, which was purified by flash chromatography on silica gel to afford the reduction derivative **5a** or **5b**.

2-(4-Trifluoromethylphenyl)-5-phenylthiazole-4-methanol (5a)



White solid, m.p. 106.5-107.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.86 (brs, 1H), 4.82 (s, 2H), 7.39-7.53 (m, 5H), 7.70 (d, J = 8.2 Hz, 2H), 8.06 (d, J = 8.2 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 151.8, 136.3, 131.9, 131.5, 130.6, 129.2, 129.0, 128.8, 126.5, 126.0, 125.9, 125.7, 122.1, 58.9 ppm; IR (KBr) 3297, 2926, 1617, 1451, 1324, 1131, 1070, 843, 750, 696 cm^{-1}; HRMS (ESI) calcd for $[C_{17}H_{12}F_3NOS+Na]^+$ 358.0489, found 358.0495.

2,5-Diphenyloxazole-4-methanol (5b)

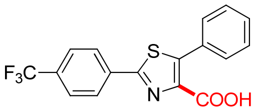


White solid, m.p. 117-118 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.96 (brs, 1H), 4.79 (s, 2H), 7.32 (t, J = 7.2 Hz, 1H), 7.37-7.44 (m, 5H), 7.66 (d, J = 7.2 Hz, 2H), 8.00-8.03 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 147.4, 136.3, 130.5, 128.9, 128.8, 128.6, 128.1, 127.0, 126.4, 126.1, 57.0 ppm; IR (KBr) 3252, 2932, 1593, 1548, 1487, 1445, 1026, 777, 705, 688 cm^{-1}; HRMS (ESI) calcd for $[C_{16}H_{13}NO_2+Na]^+$ 274.0844, found 274.0848.

7.2 Hydrolysis of the Arylated Products

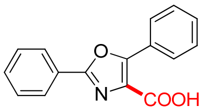
To a mixture of the arylated product **2i** or **2l** (1 mmol, 1 equiv.) and MeOH (5 ml) was added 20% KOH (aq) (4 mL) at room temperature. After stirring at 60 °C for 3 hours, the reaction mixture was concentrated *in vacuo* to remove MeOH, cooled to 0 °C, adjusted pH value to 2.0 with 3M HCl (aq), and then filtered. The filter cake was washed with water and petrol ether to give crude product, which was purified by recrystallization to afford the hydrolysis derivative **6a** or **6b**.

2-(4-Trifluoromethylphenyl)-5-phenylthiazole-4-carboxylic Acid (6a)



White solid, m.p. 150-151 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.50 (m, 3H), 7.59-7.62 (m, 2H), 7.92 (d, J = 8.3 Hz, 2H), 8.20 (d, J = 8.3 Hz, 2H), 13.21 (brs, 1H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 163.4, 163.1, 145.6, 143.0, 136.2, 131.1, 130.7, 130.3, 130.1, 129.8, 128.8, 127.4, 126.7, 126.2 ppm; IR (KBr) 3434, 3003, 2826, 1693, 1614, 1474, 1327, 1067, 847, 752, 695 cm^{-1}; HRMS (ESI) calcd for $[C_{17}H_{10}F_3NO_2S+H]^+$ 350.0463, found 350.0468.

2,5-Diphenyloxazole-4-carboxylic Acid (6b)

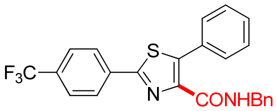


White solid, m.p. 177-181 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49-7.60 (m, 6H), 8.09-8.15 (m, 4H), 13.30 (brs, 1H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 163.5, 159.2, 154.3, 131.6, 130.6, 129.7, 129.2, 128.9, 128.8, 127.3, 126.8, 126.5 ppm; IR (KBr) 3451, 3050, 2909, 1713, 1560, 1492, 1216, 1109, 779, 709, 687 cm^{-1}; HRMS (ESI) calcd for $[C_{16}H_{11}NO_3+H]^+$ 266.0817, found 266.0825.

7.3 Ammonolysis of the Arylated Products

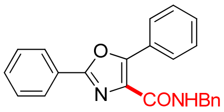
A mixture of the aryled product **2i** or **2l** (0.2 mmol, 1 equiv.) and benzylamine (1 mL) was stirred at 100 °C. After stirring for 12 hours, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, washed with 3M HCl (aq), water and brine, dried over Na_2SO_4, and concentrated *in vacuo* to give crude product, which was purified by flash chromatography on silica gel to afford the ammonolysis derivative **7a** or **7b**.

***N*-Benzyl 2-(4-Trifluoromethylphenyl)-5-phenylthiazole-4-formamide (7a)**



White solid, m.p. 169-170 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.56 (d, J = 6.0 Hz, 2H), 7.21-7.31 (m, 5H), 7.35-7.37 (m, 3H), 7.60-7.64 (m, 4H), 7.80 (brs, 1H), 7.95 (d, J = 8.3 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.9, 161.2, 144.7, 142.8, 138.4, 135.8, 132.4, 131.9, 130.4, 129.9, 129.4, 128.7, 128.2, 127.9, 127.5, 126.7, 126.2, 126.1, 126.0, 125.6, 122.0, 43.3 ppm; IR (KBr) 3310, 2909, 1650, 1544, 1328, 1125, 1068, 851, 756, 694 cm^{-1}; HRMS (ESI) calcd for $[C_{24}H_{17}F_3N_2OS+H]^+$ 439.1092, found 439.1095.

***N*-Benzyl 2,5-Diphenyloxazole-4-formamide (7b)**

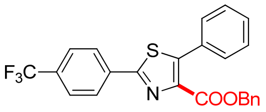


White solid, m.p. 125-127 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.61 (d, J = 6.0 Hz, 2H), 7.18-7.45 (m, 11H), 7.69 (brs, 1H), 7.99-8.03 (m, 2H), 8.34 (dd, J = 7.0, 2.1 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3, 158.5, 152.4, 138.4, 131.0, 130.3, 129.9, 128.9, 128.7, 128.4, 128.3, 127.9, 127.5, 127.4, 126.6, 126.5, 43.3 ppm; IR (KBr) 3323, 3068, 2926, 1643, 1512, 1232, 1219, 775, 748, 706, 687 cm^{-1}; HRMS (ESI) calcd for $[C_{23}H_{18}N_2O_2+H]^+$ 355.1447, found 355.1450.

7.4 Transesterification of the Arylated Products

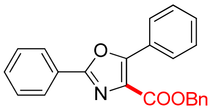
A mixture of the arylated product **2i** or **2l** (0.2 mmol, 1 equiv.), $KHCO_3$ (0.4 mmol, 2 equiv.) and phenylmethanol (1 mL) was stirred at 100 °C. After stirring for 6 hours, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo* to give crude product, which was purified by flash chromatography on silica gel to afford the ammonolysis derivative **8a** or 8**b**.

Benzyl 2-(4-Trifluoromethylphenyl)-5-phenylthiazole-4-carboxylate (8a)



White solid, m.p. 106-108 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.21 (s, 2H), 7.11-7.14 (m, 2H), 7.21-7.23 (m, 3H), 7.27-7.35 (m, 3H), 7.40 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 8.04 (d, *J* = 8.2 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.1, 161.9, 146.8, 141.8, 135.9, 135.3, 132.4, 132.0, 130.0, 129.9, 129.4, 128.4, 128.3, 128.2, 127.0, 126.1, 126.0, 125.9, 125.6, 122.0, 67.0 ppm; IR (KBr): 2920, 1727, 1611, 1463, 1324, 1195, 1067, 849, 740, 692 cm^{-1}; HRMS (ESI) calcd for $[C_{24}H_{16}F_3NO_2S+H]^+$ 440.0932, found 440.0934.

Benzyl 2,5-Diphenyloxazole-4-carboxylate (8b)

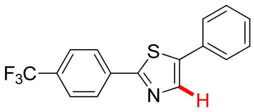


Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.33 (s, 2H), 7.22-7.29 (m, 3H), 7.32-7.38 (m, 8H), 7.93-7.96 (m, 2H), 8.03-8.06 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.1, 159.9, 155.3, 135.7, 131.1, 130.3, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 127.1, 126.9, 126.5, 66.9 ppm; IR (KBr) 3044, 2926, 1709, 1562, 1489, 1350, 1221, 1108, 1006, 748, 708, 688 cm^{-1}; HRMS (ESI) calcd for $[C_{23}H_{17}NO_3+Na]^+$ 378.1106, found 378.1109.

7.5 Decarboxylation of the Hydrolysis Derivatives[3]

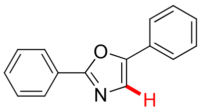
A mixture of the hydrolysis derivative **6a** or **6b** (0.2 mmol, 1 equiv.), Ag_2CO_3 (0.04 mmol, 0.2 equiv.), AcOH (0.01 mmol, 0.05 equiv.) and DMSO (2 ml) was stirred at 120 °C. After stirring for 24 hours, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, and filtered. The filtrate was washed with saturated $NaHCO_3$, water and brine, dried over Na_2SO_4, and concentrated *in vacuo* to give crude product, which was purified by flash chromatography on silica gel to afford the 4-unsubstituted derivative **9a** or **9b**.

2-(4-Trifluoromethylphenyl)-5-phenylthiazole (9a)



White solid, m.p. 150-151 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27-7.37 (m, 3H), 7.52 (dd, *J* = 6.9, 1.9 Hz, 2H), 7.61 (d, *J* = 8.3, 2H), 7.97-7.99 (m, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0, 140.6, 139.6, 136.7, 131.7, 131.3, 131.0, 129.2, 128.7, 126.8, 126.5, 126.1, 126.0, 125.9, 125.7, 122.1 ppm; IR (KBr) 2920, 1614, 1450, 1327, 1169, 1107, 1070, 846, 835, 756, 687 cm^{-1}; HRMS (ESI) calcd for $[C_{16}H_{10}F_3NS+H]^+$ 306.0564, found 306.0568.

2,5-Diphenyloxazole (9b)



White solid, m.p. 78-80 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (t, J = 7.3 Hz, 1H), 7.42-7.52 (m, 6H), 7.73 (dd, *J* = 7.3, 1.3 Hz, 2H), 8.13 (dd, *J* = 7.9, 1.7 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.2, 151.3, 130.3, 128.9, 128.8, 128.4, 128.1, 127.5, 126.3, 124.2, 123.5 ppm; IR (KBr) 2920, 1585, 1481, 1445, 1133, 1027, 760, 707, 686 cm^{-1}; HRMS (ESI) calcd for $[C_{15}H_{11}NO+H]^+$ 222.0919, found 222.0918.

References

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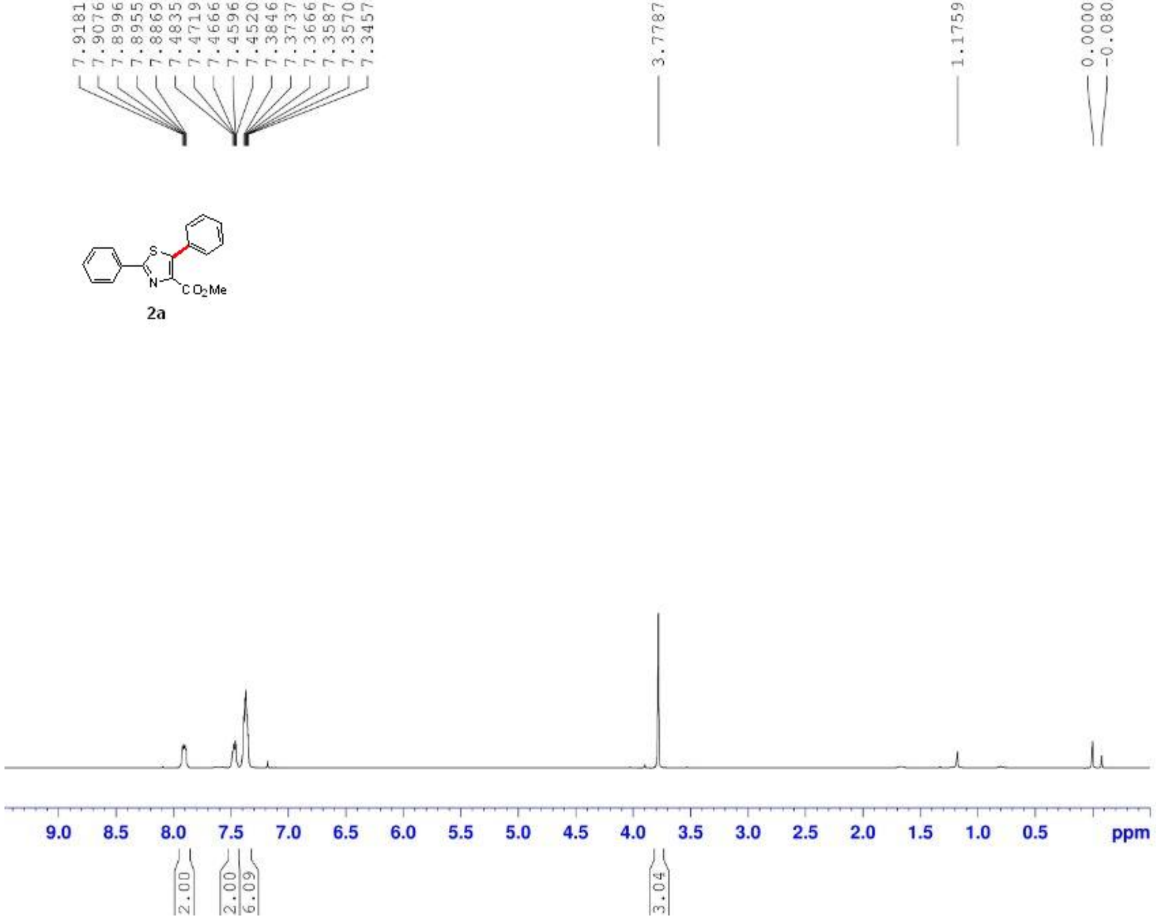
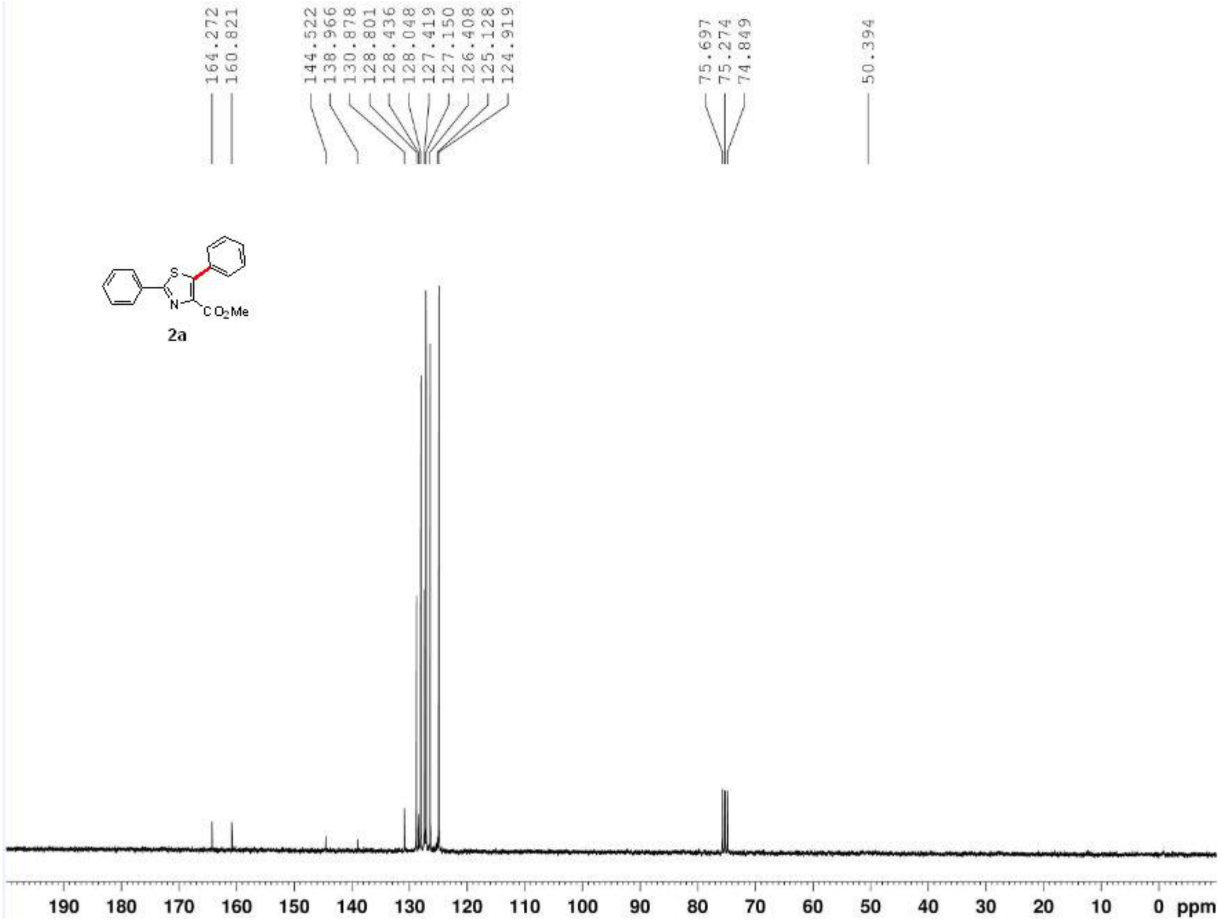
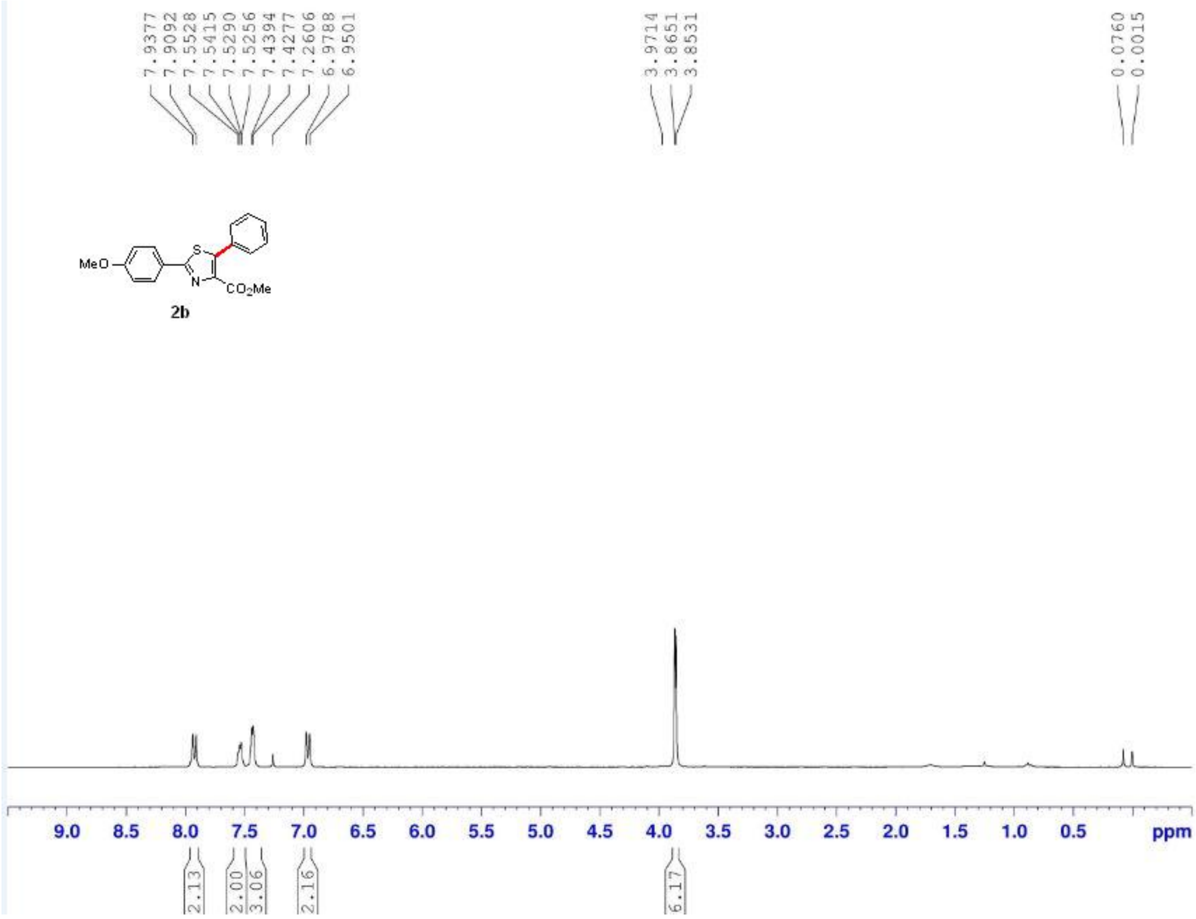
^{1}H NMR and ^{13}C NMR Spectra



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N
CO2Me
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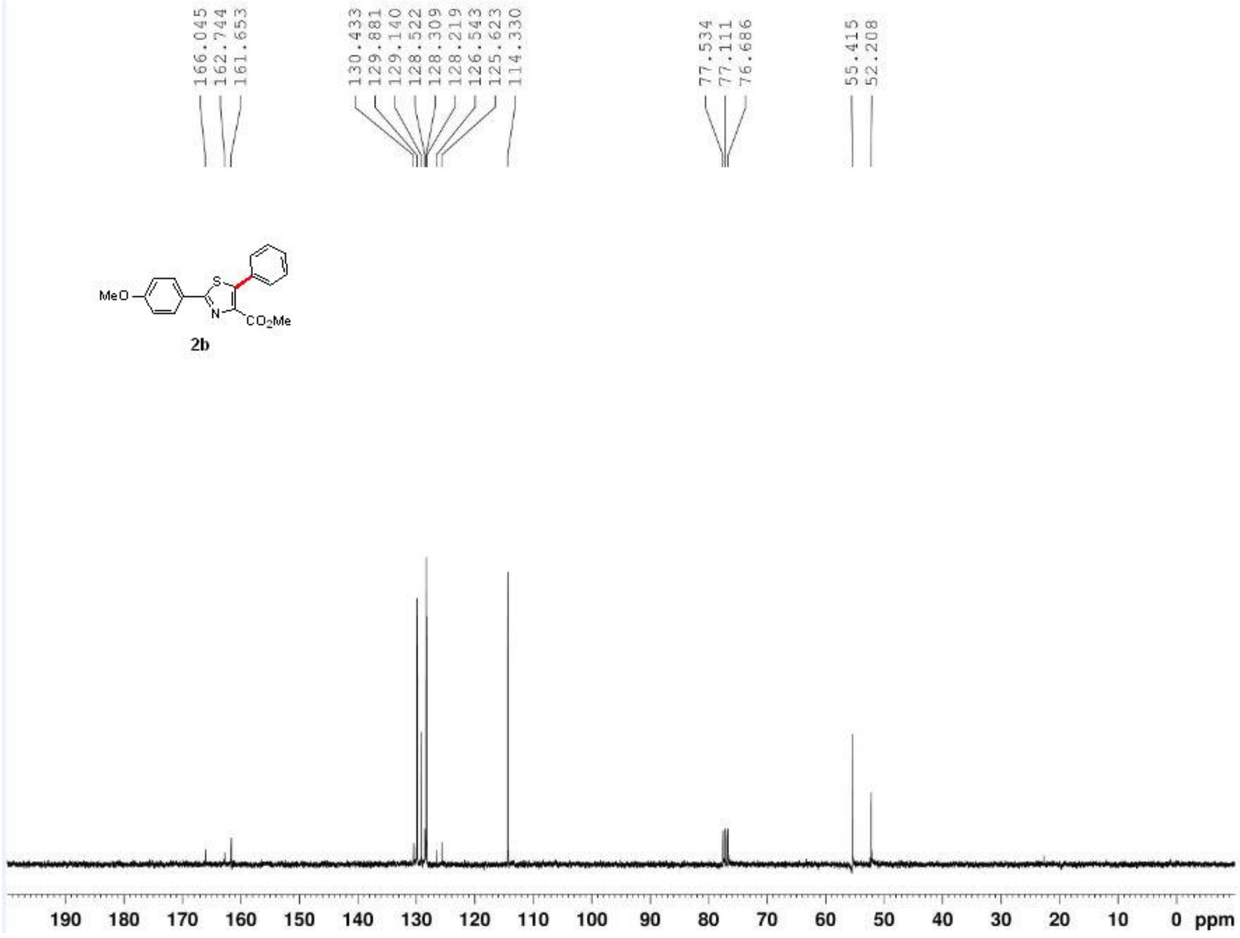
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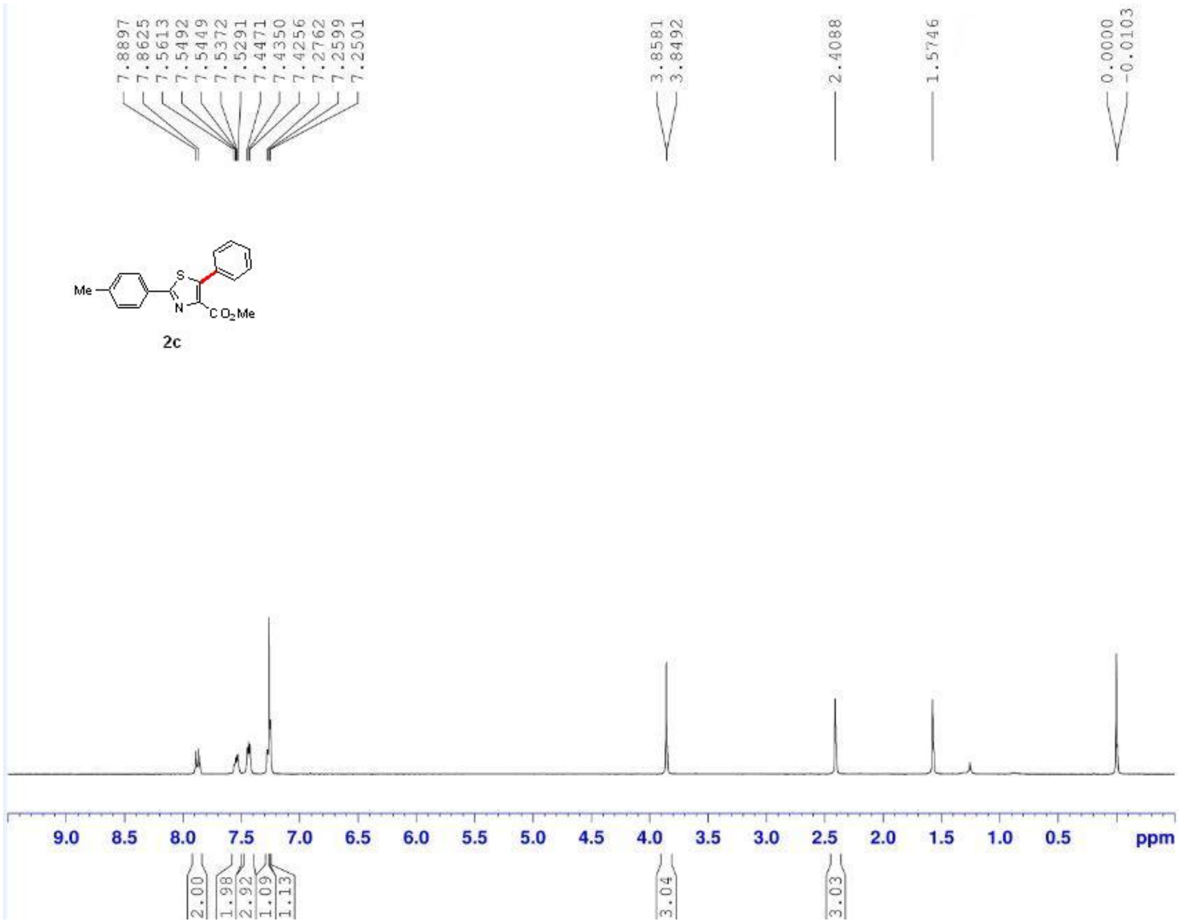
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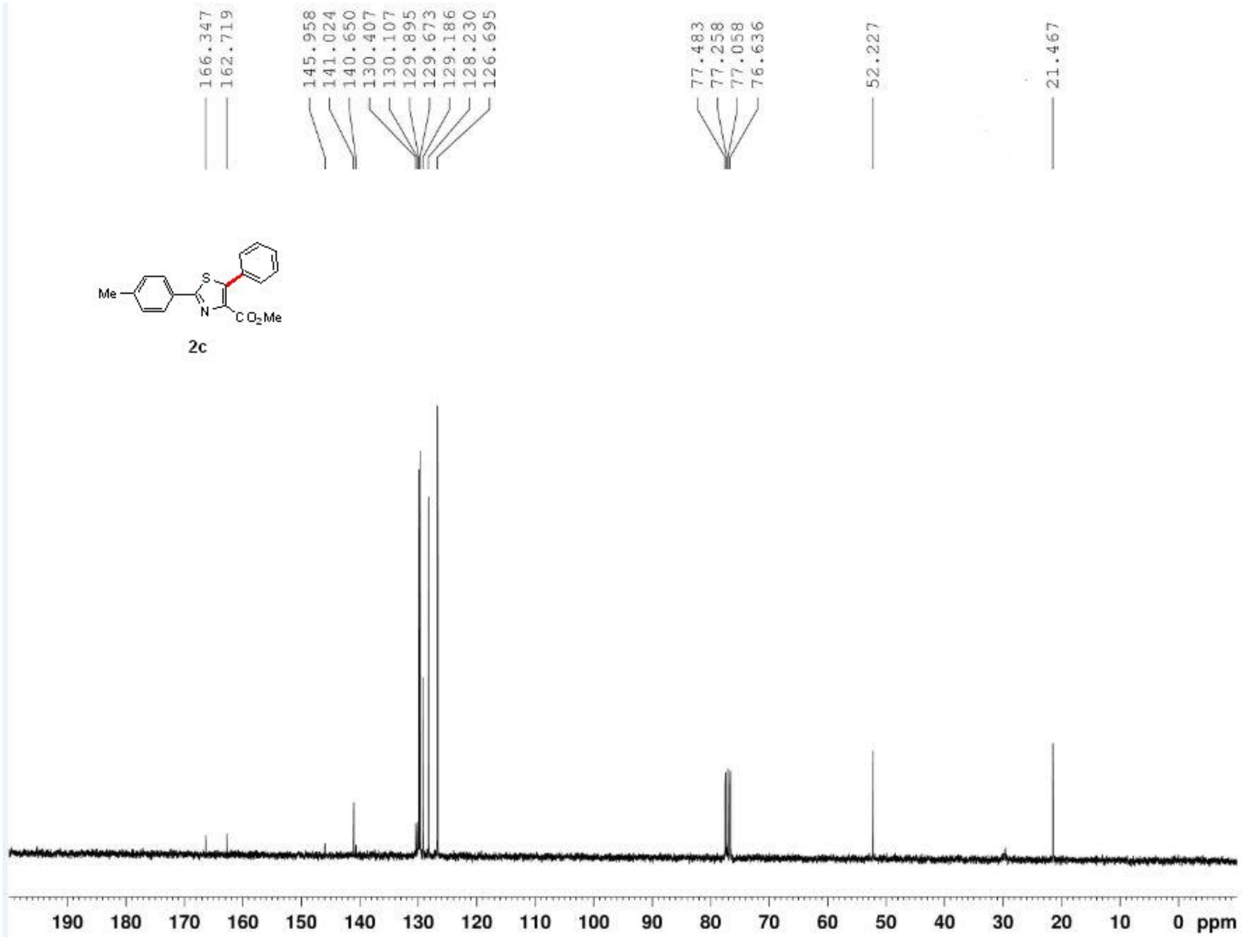
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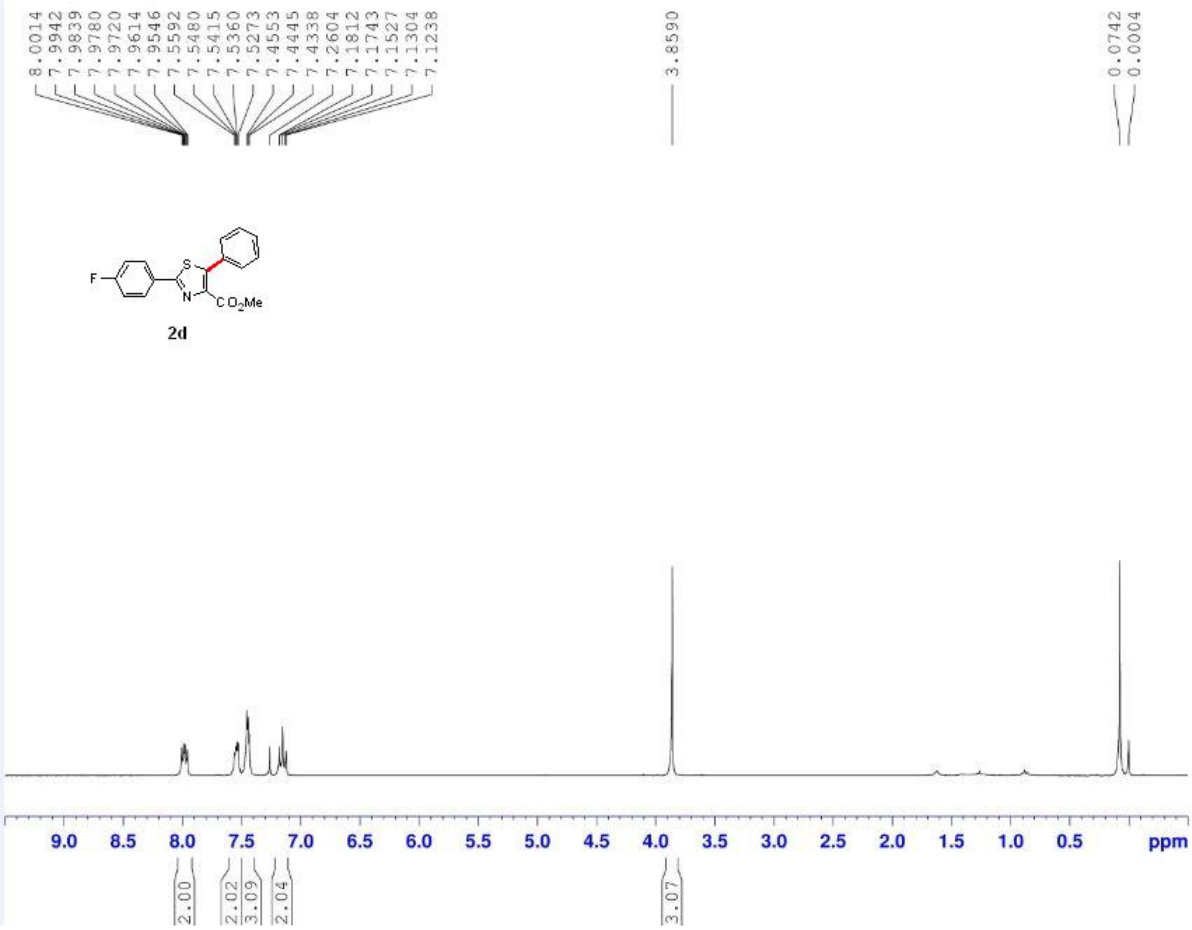
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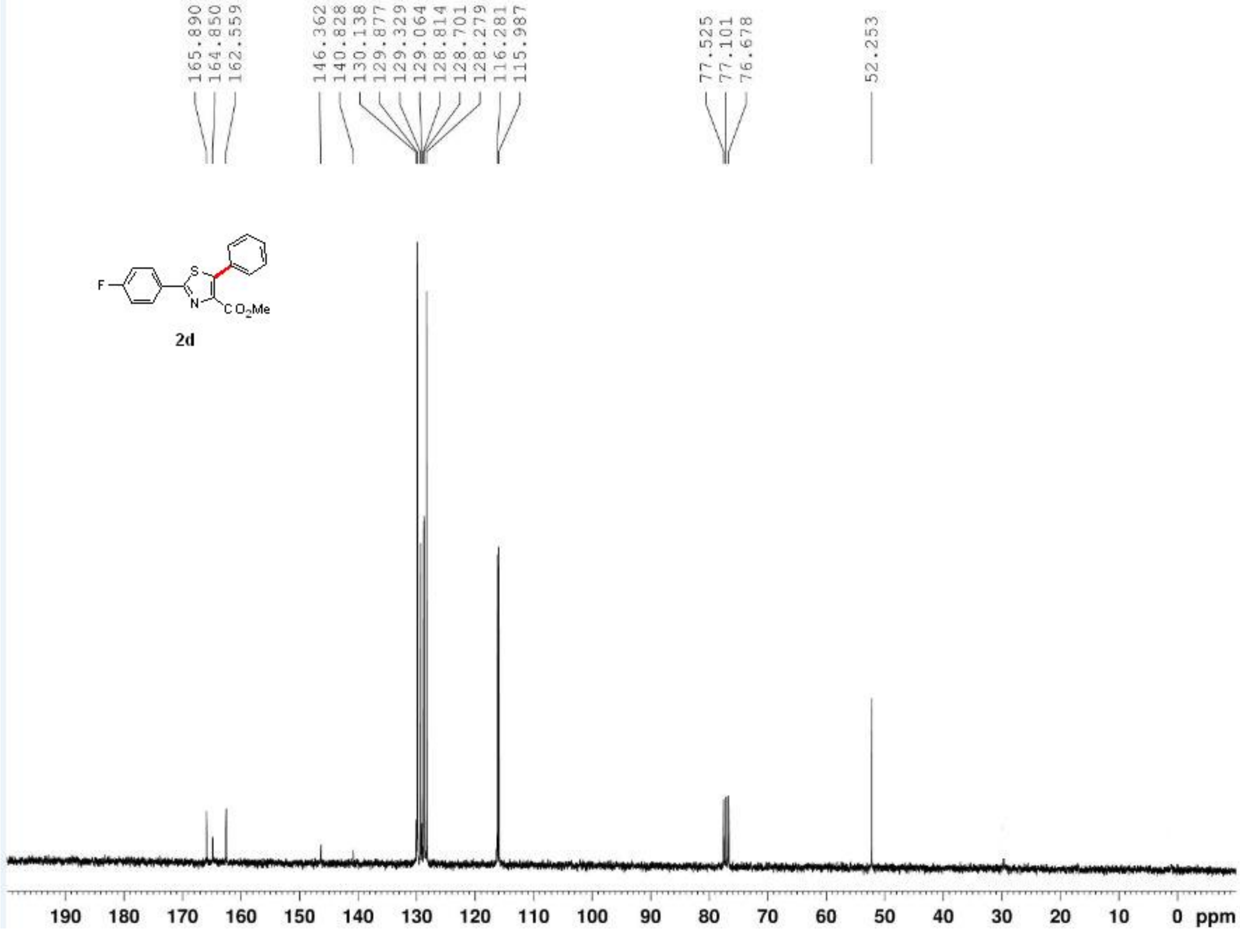
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2d
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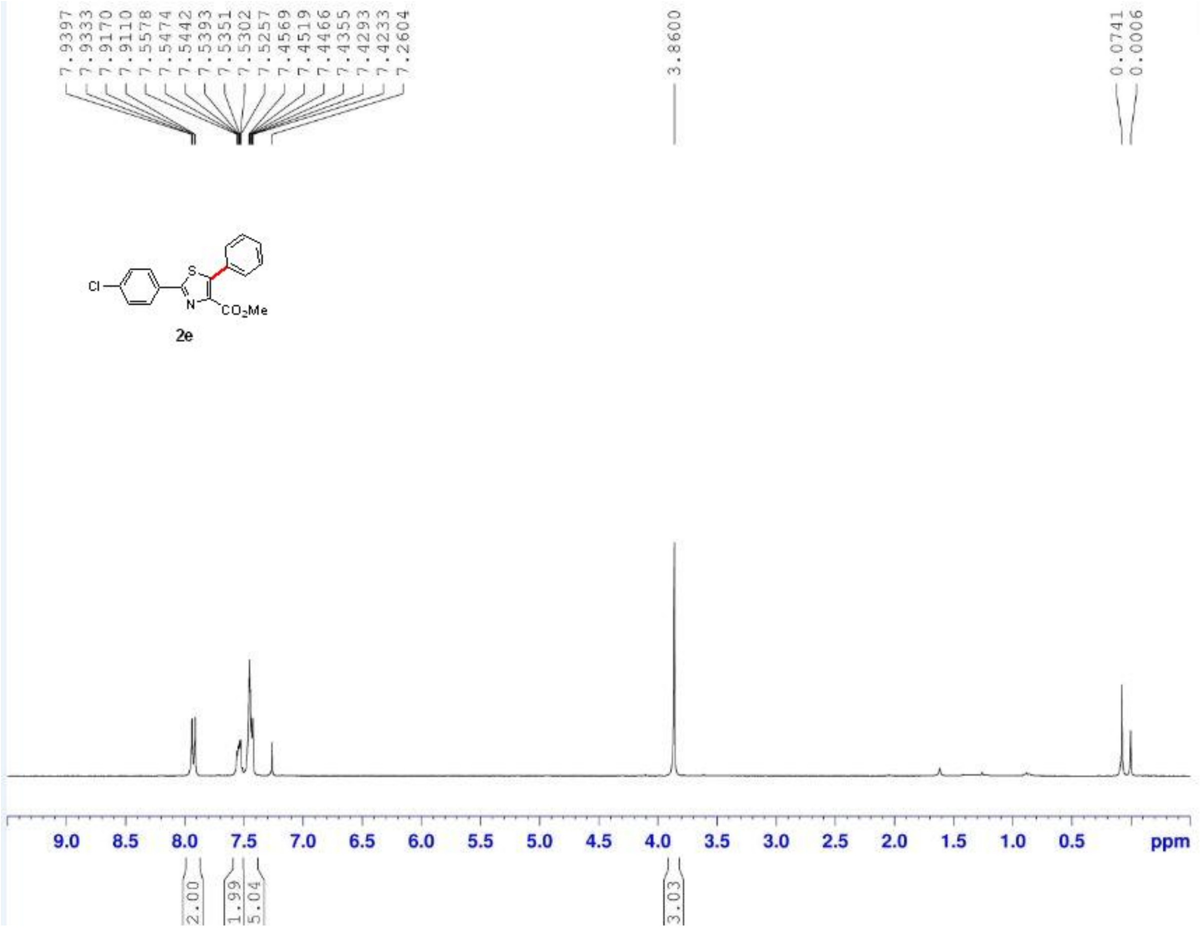
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CO2Me
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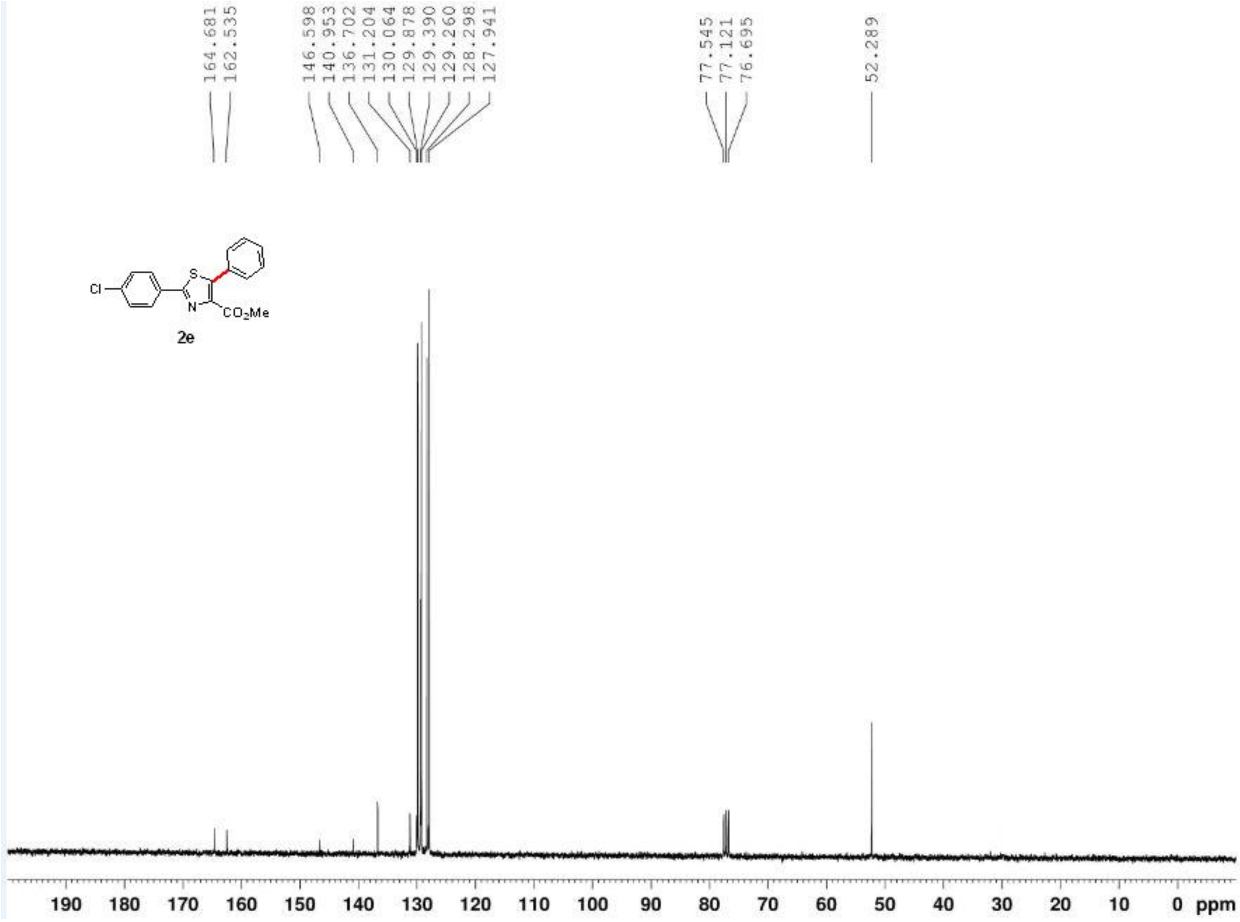
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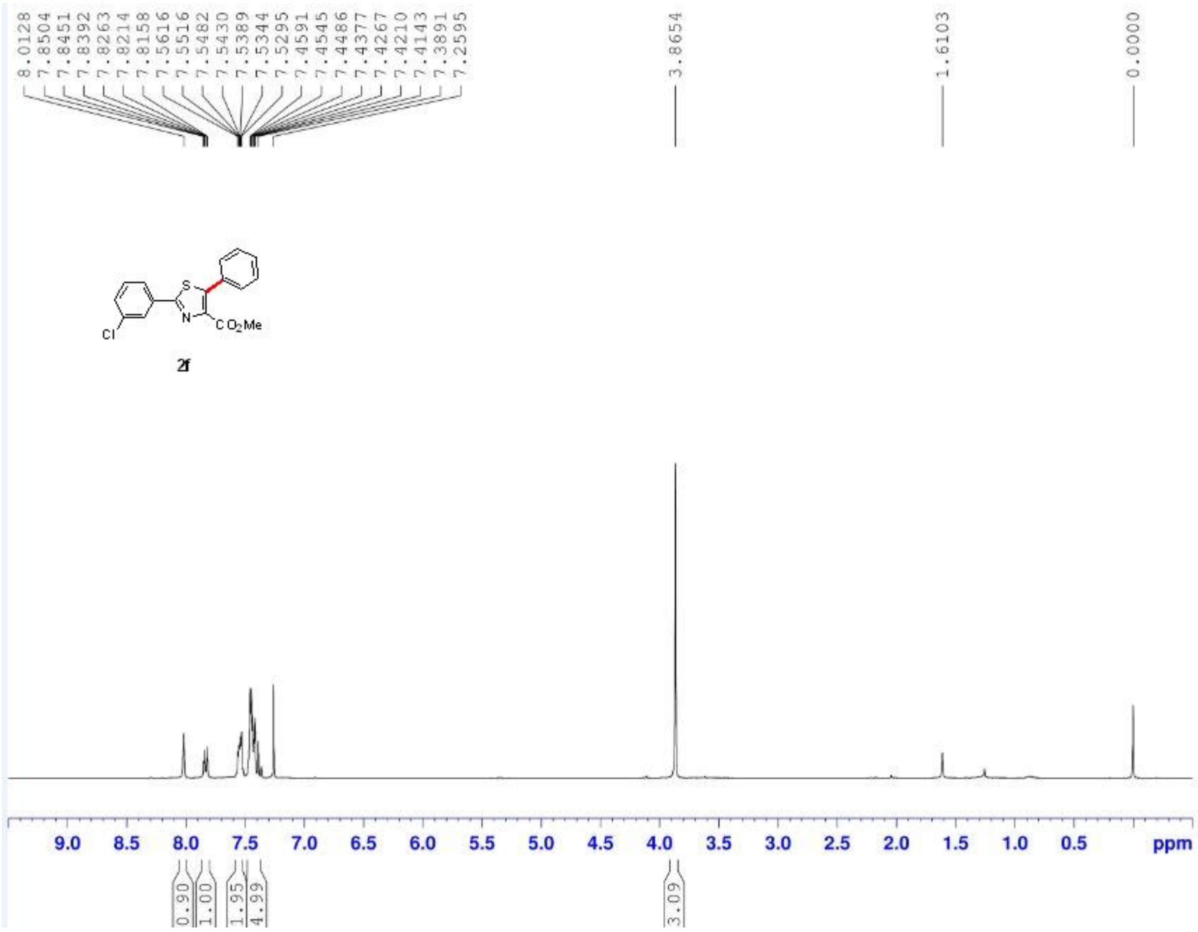
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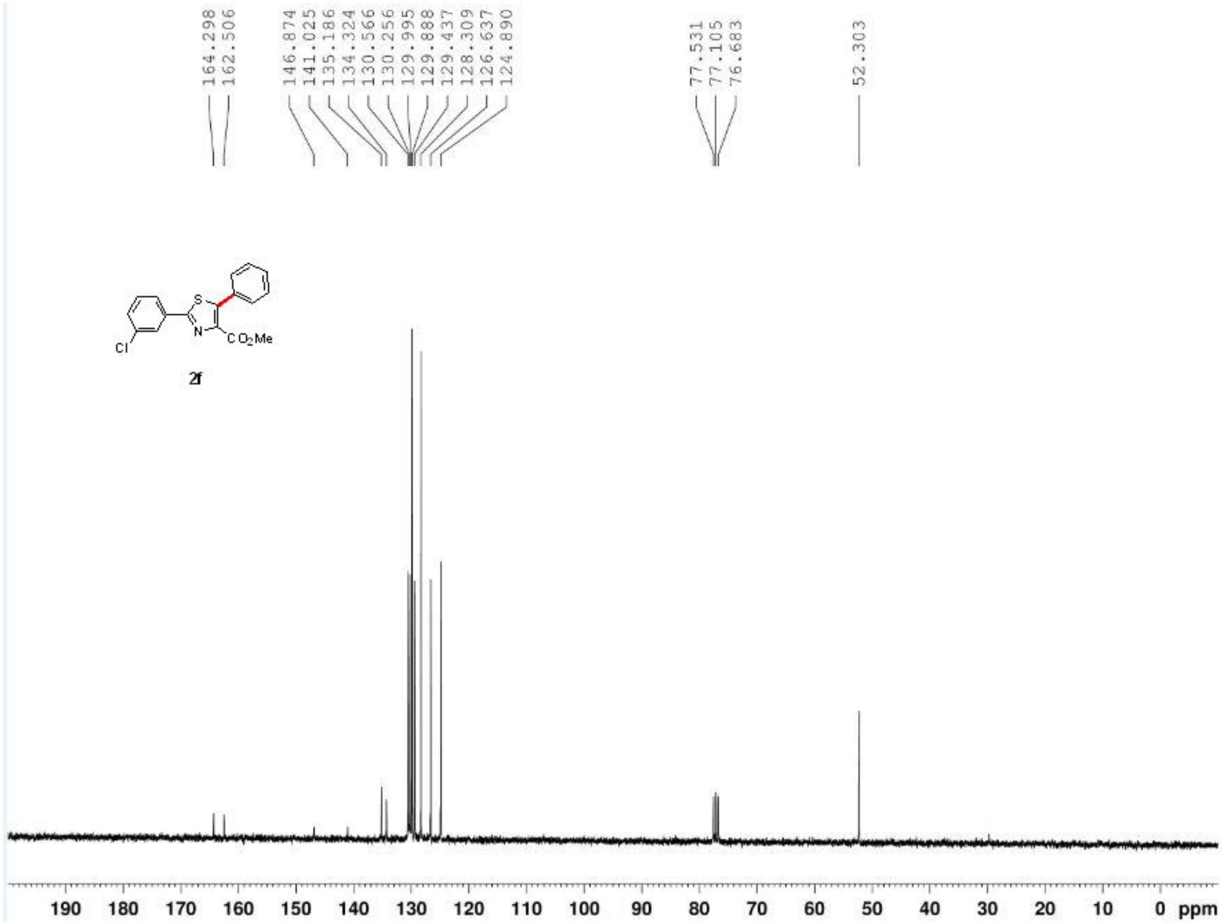
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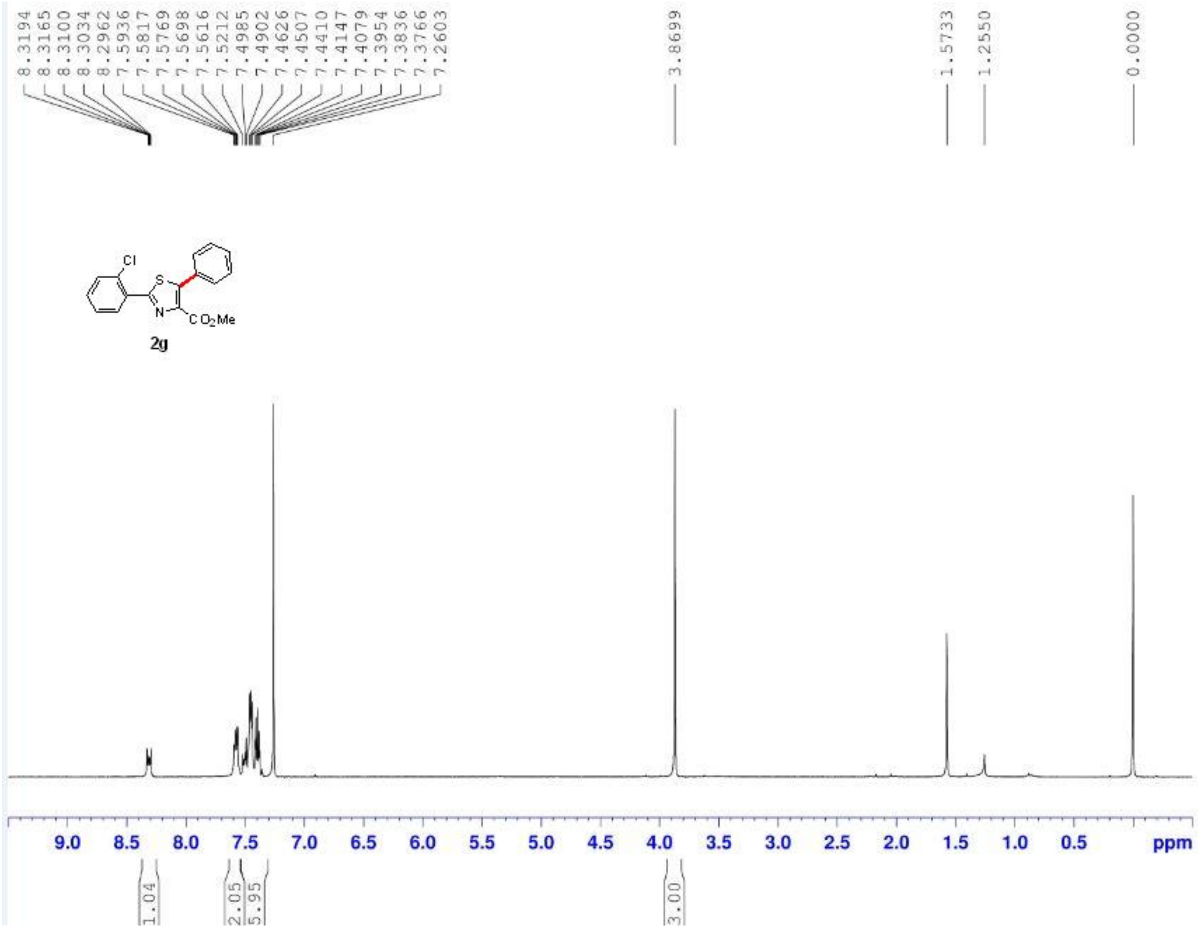
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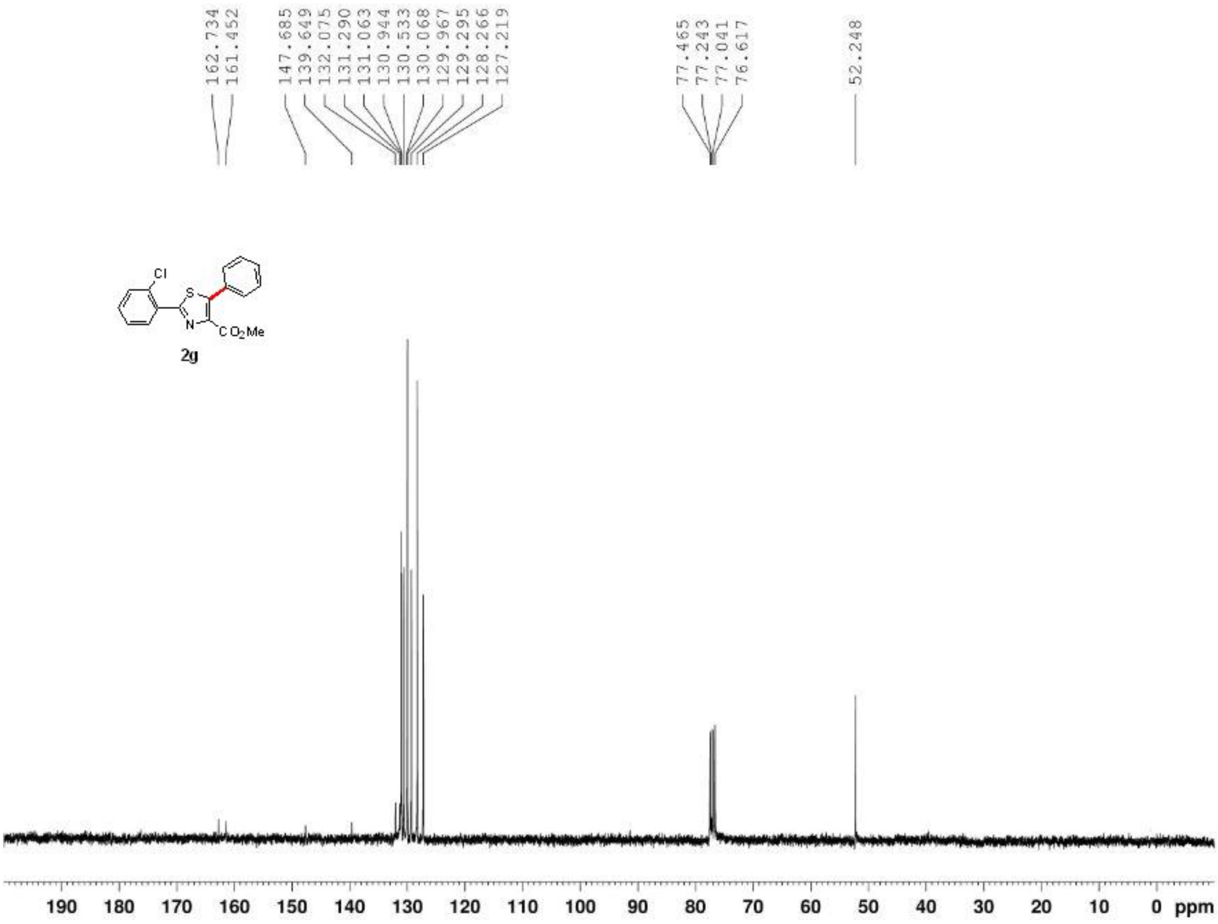
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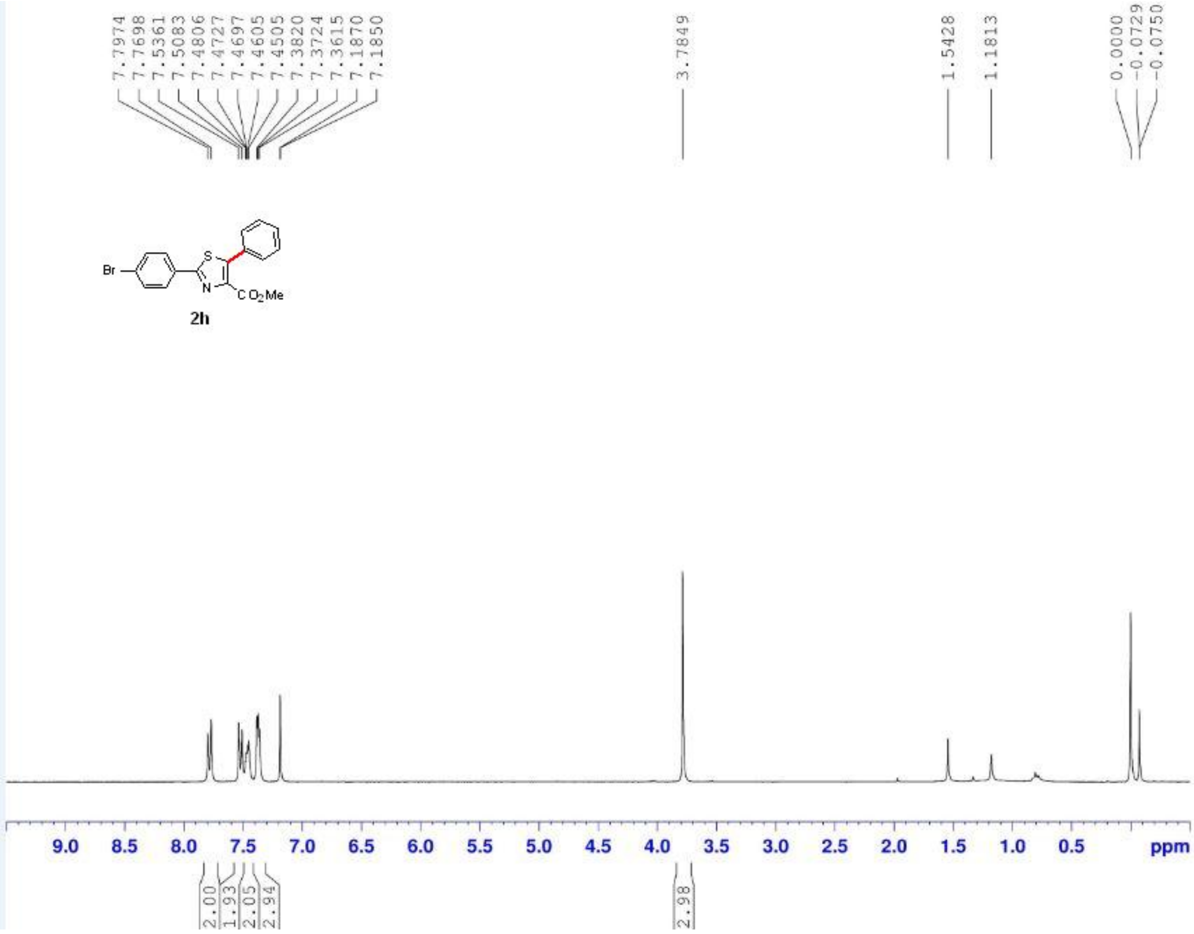
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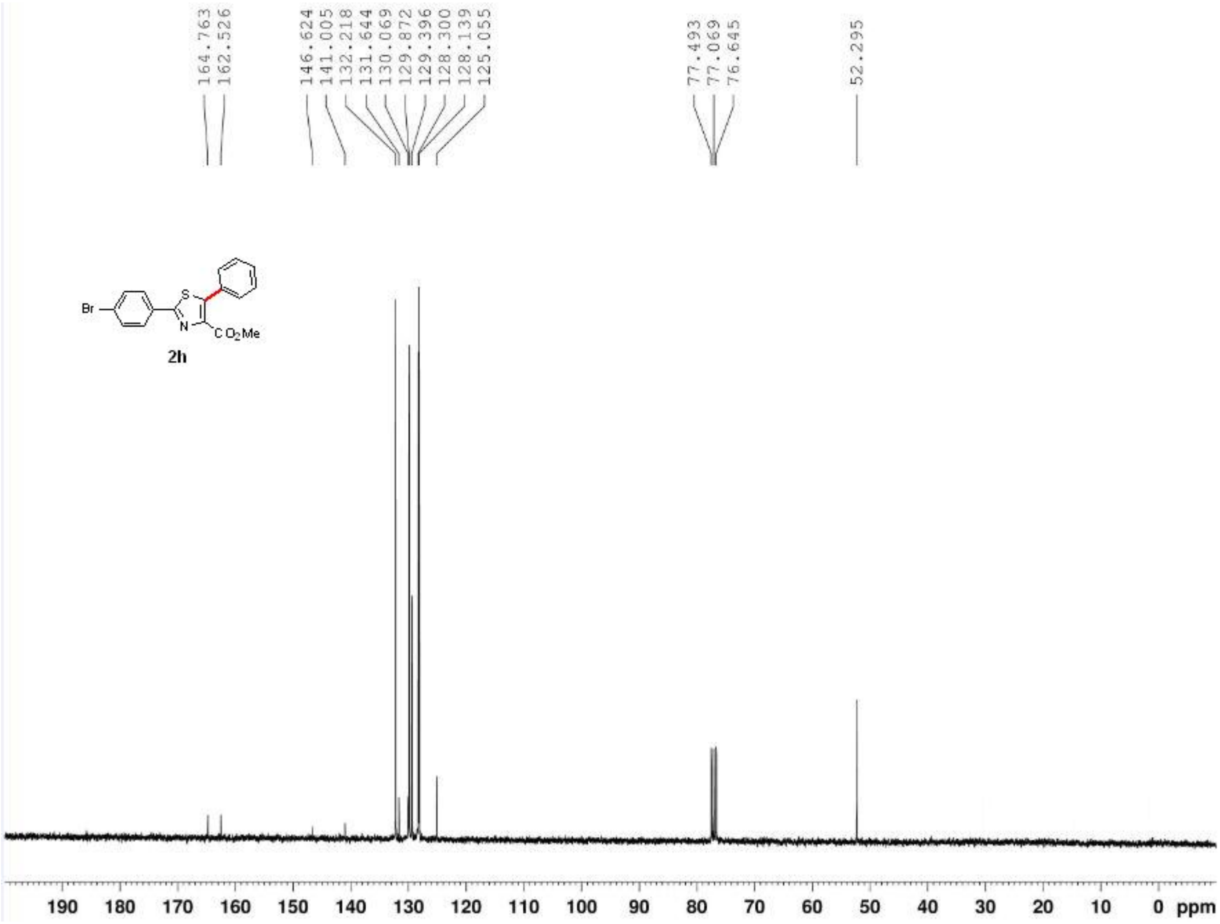
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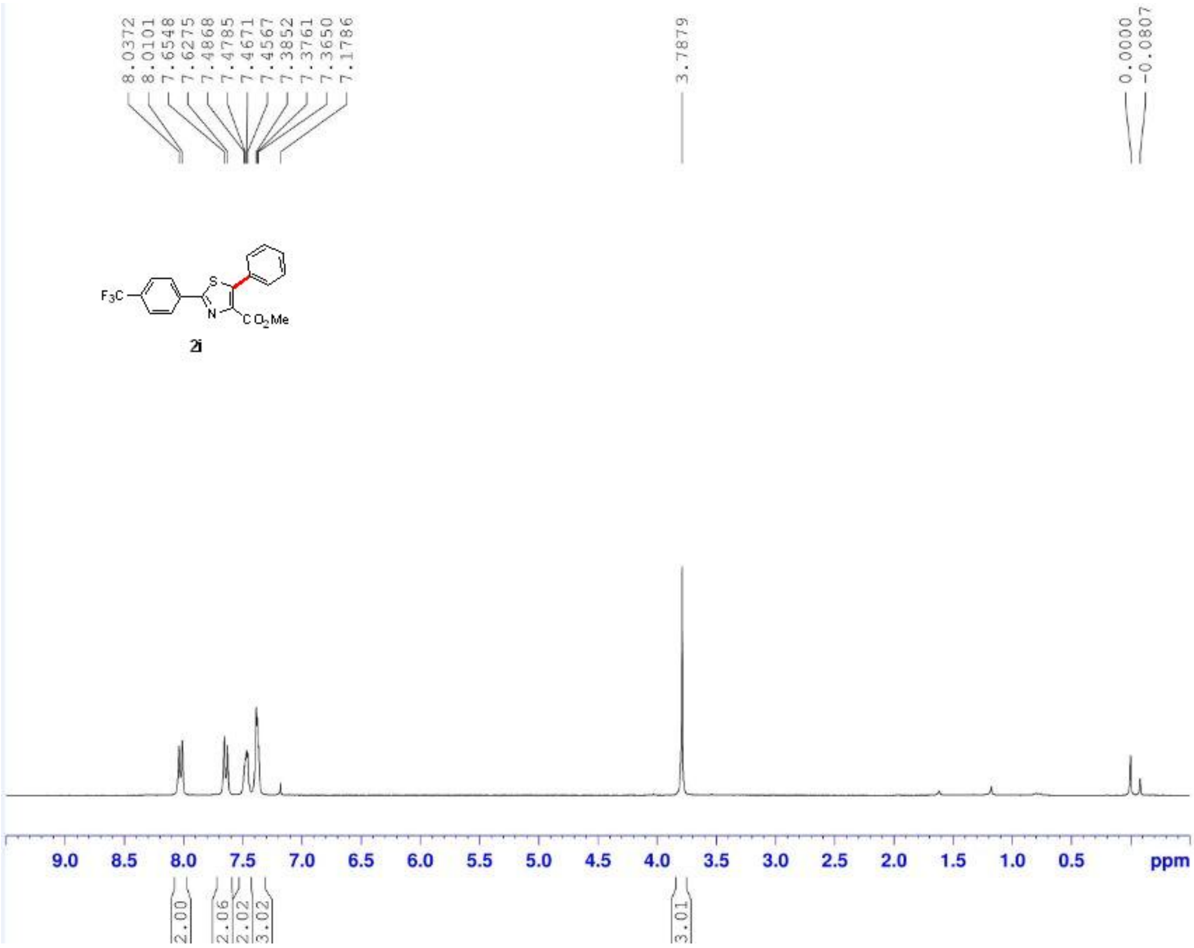
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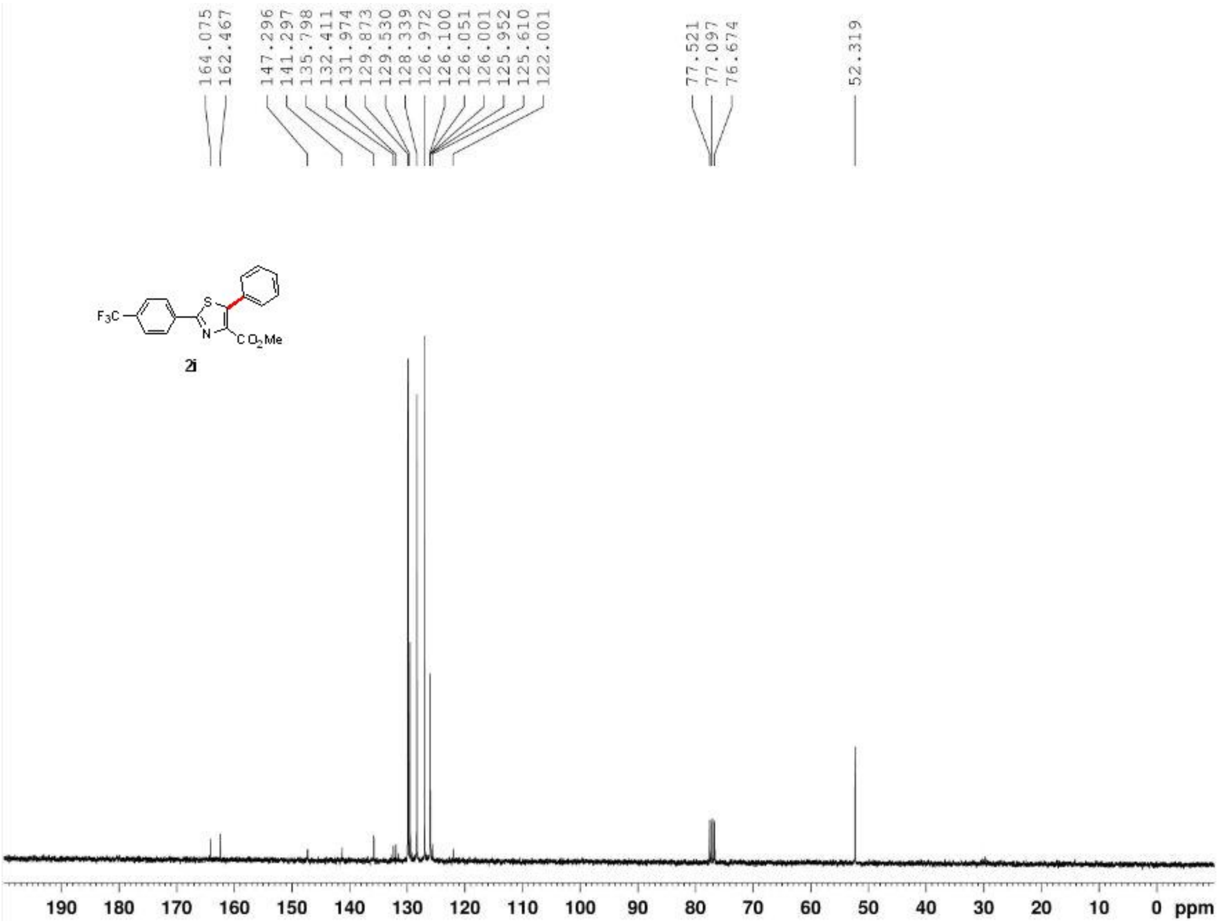
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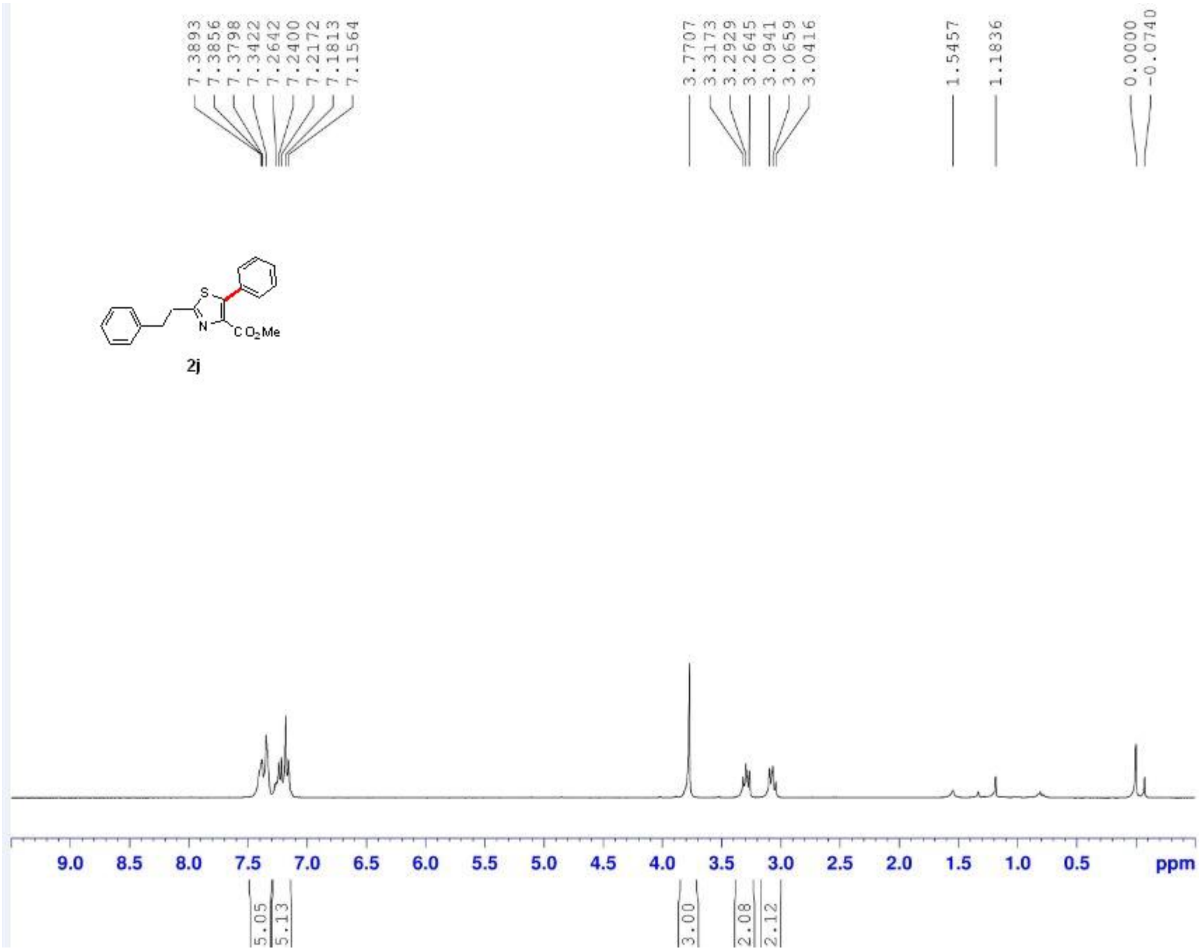
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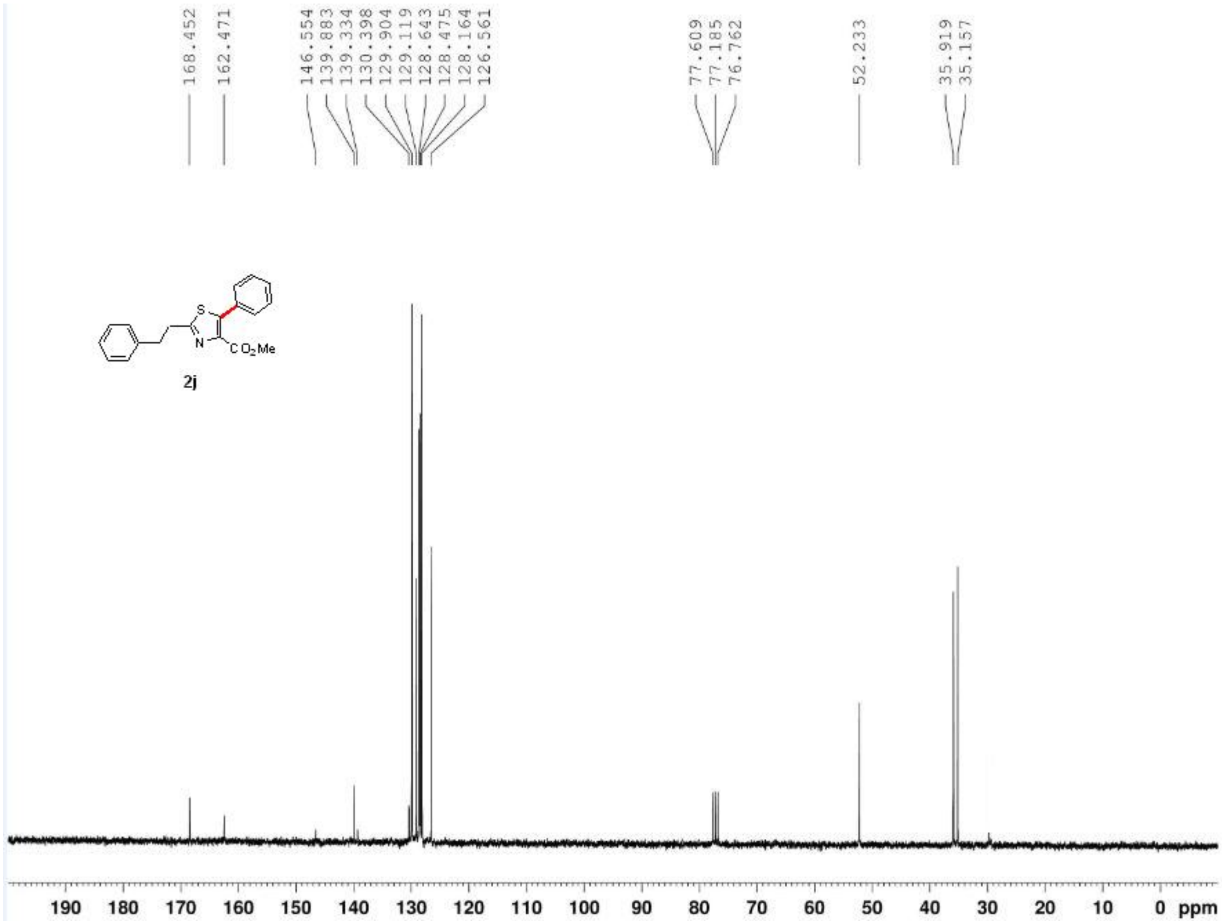
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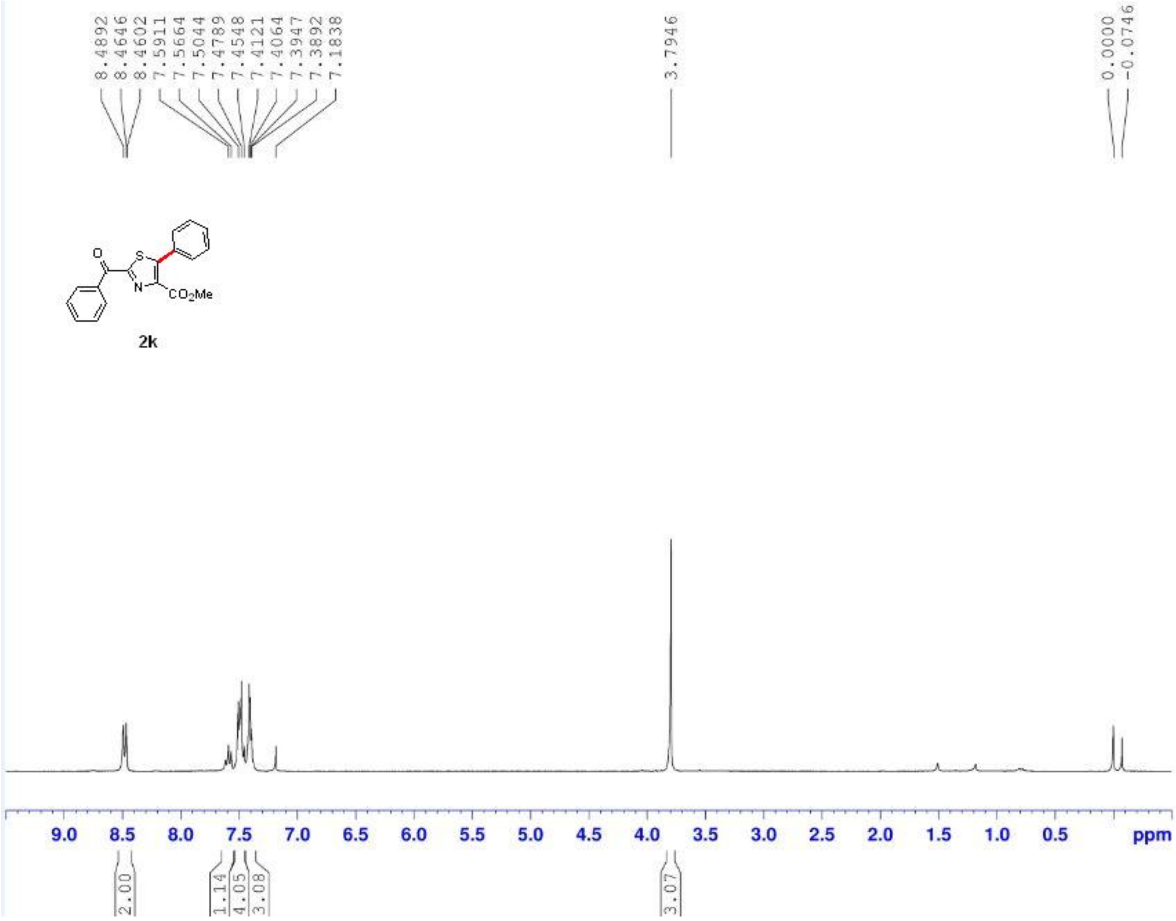
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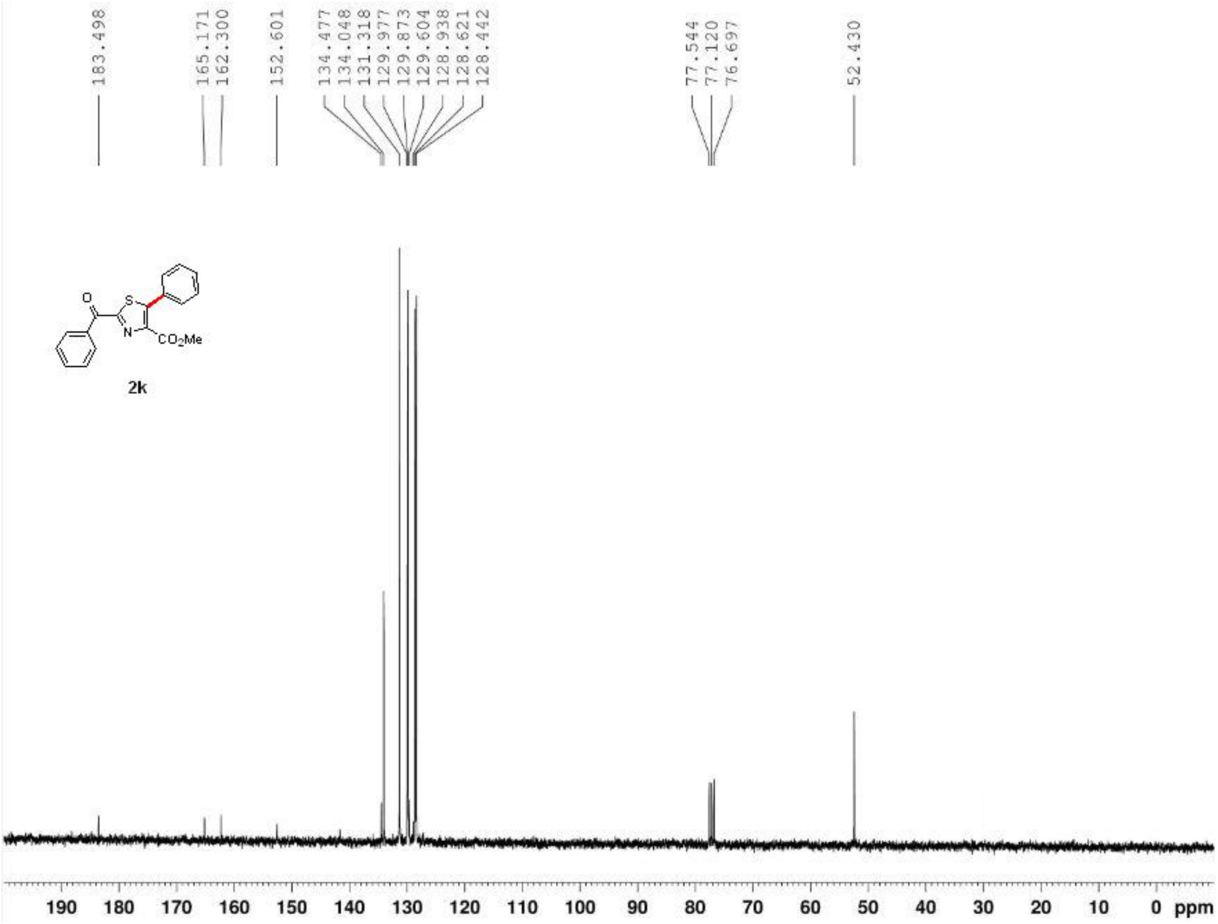
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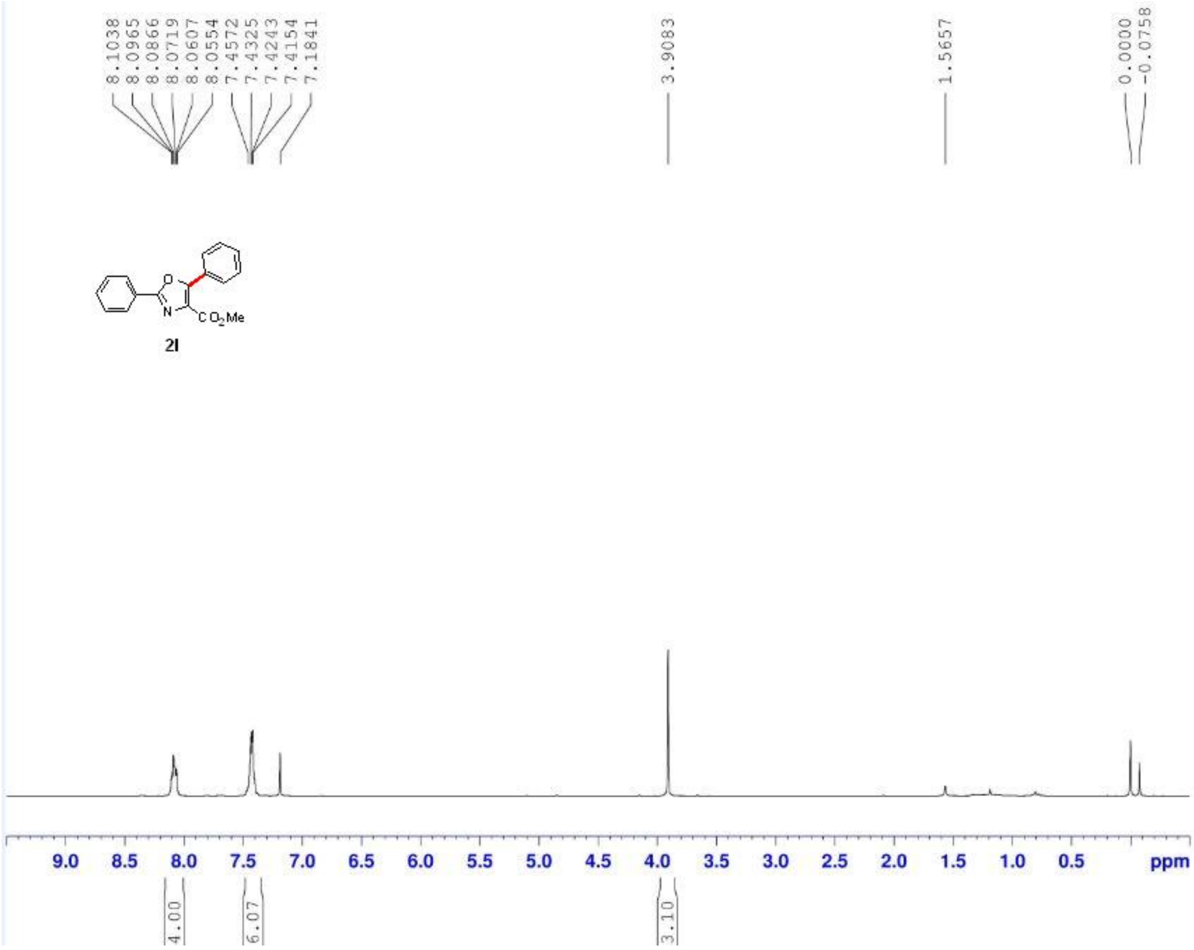
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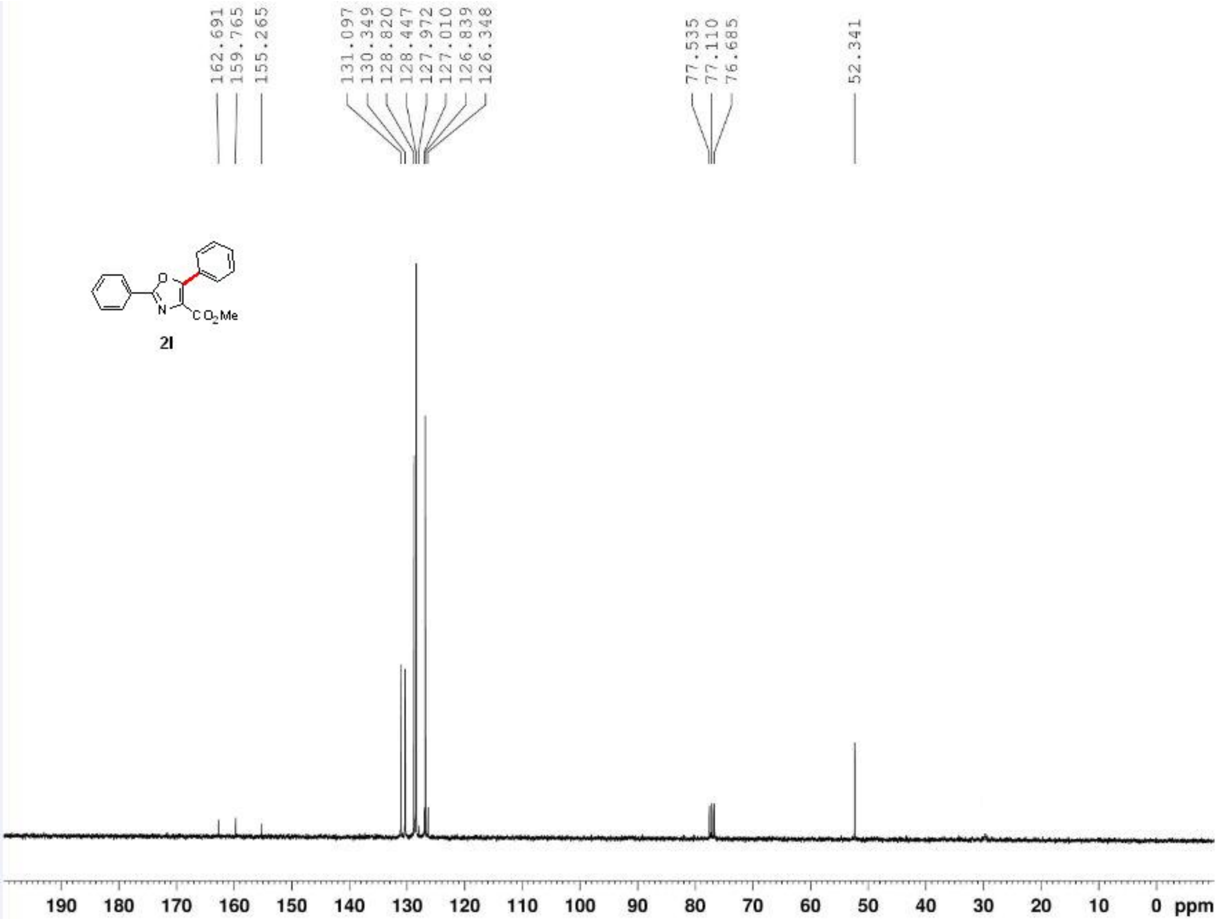
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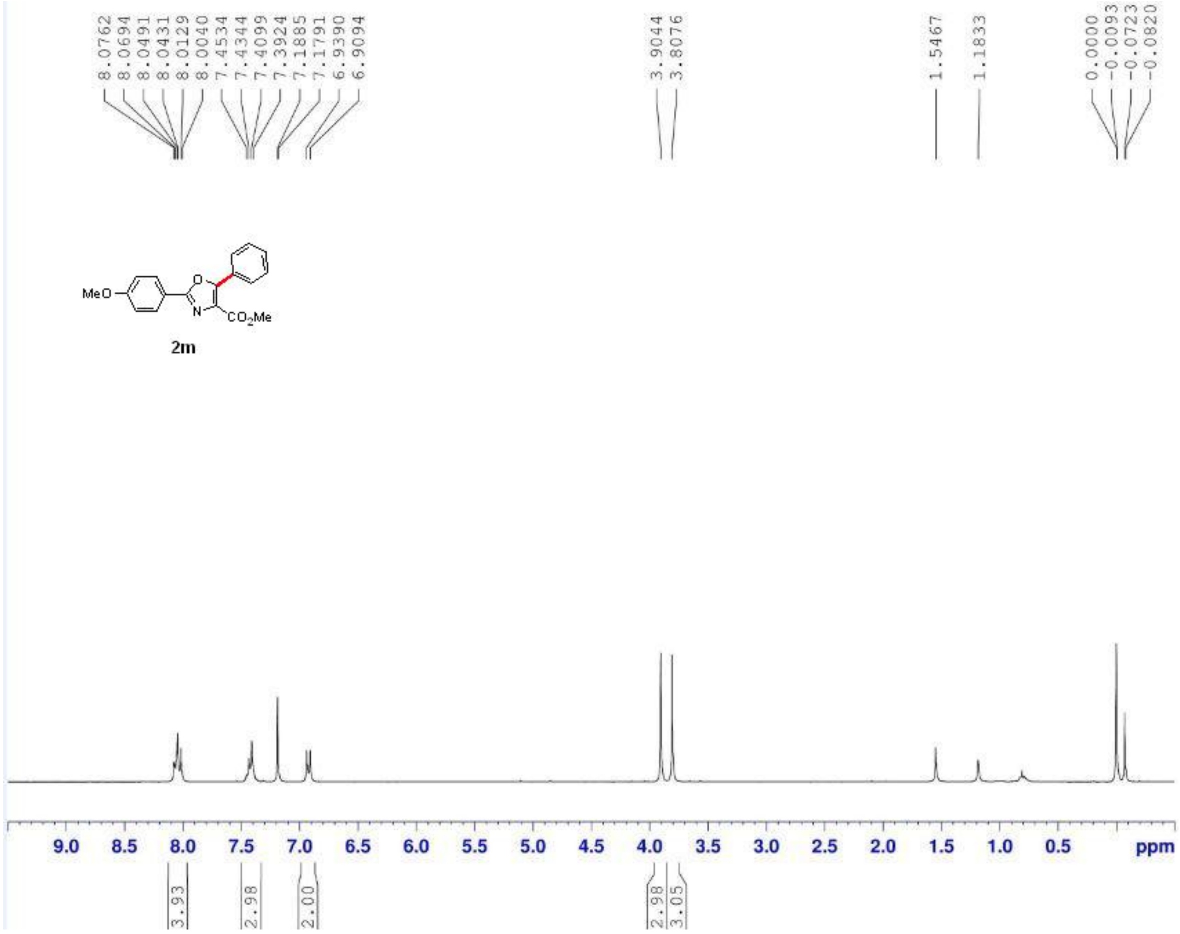
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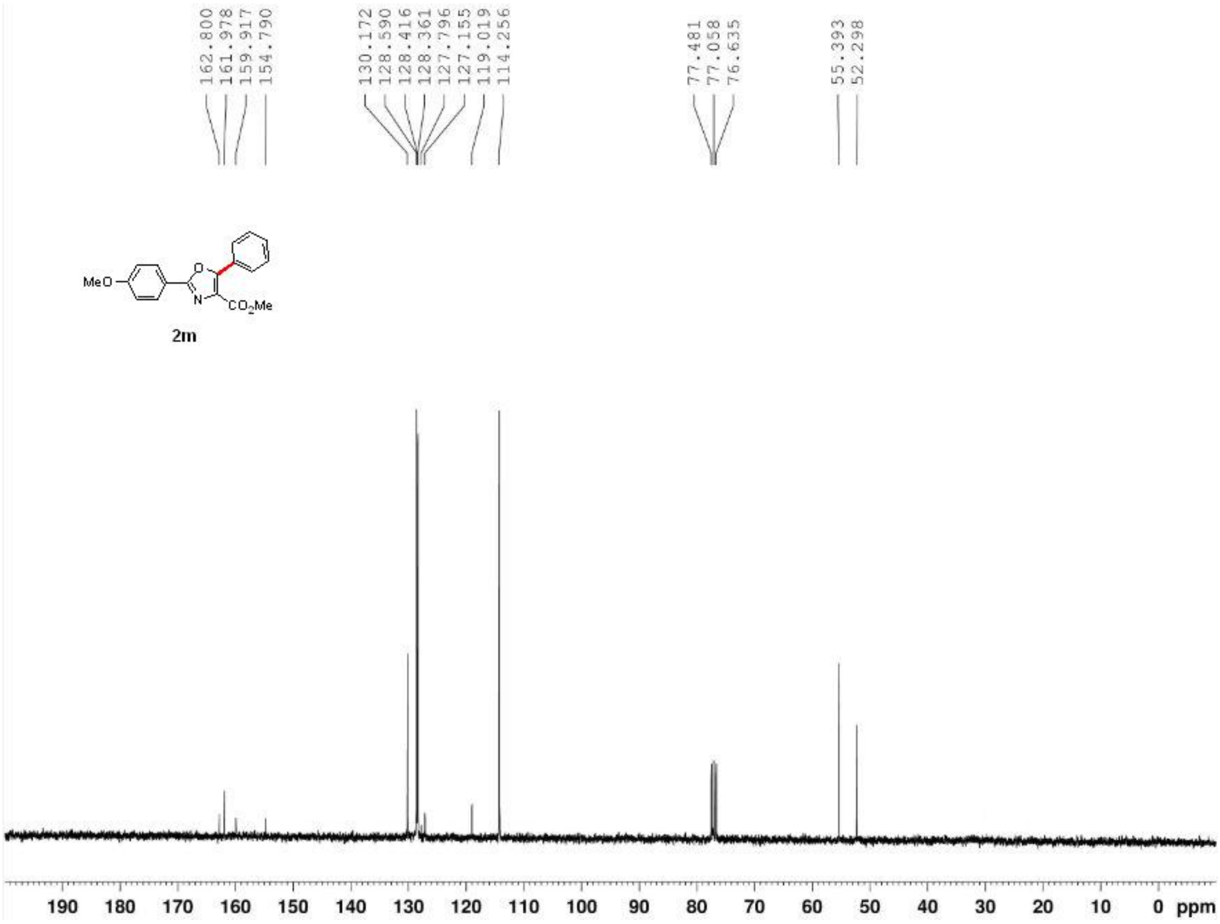
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77.058
76.635
55.393
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MeO
O
N
CO2Me
2m
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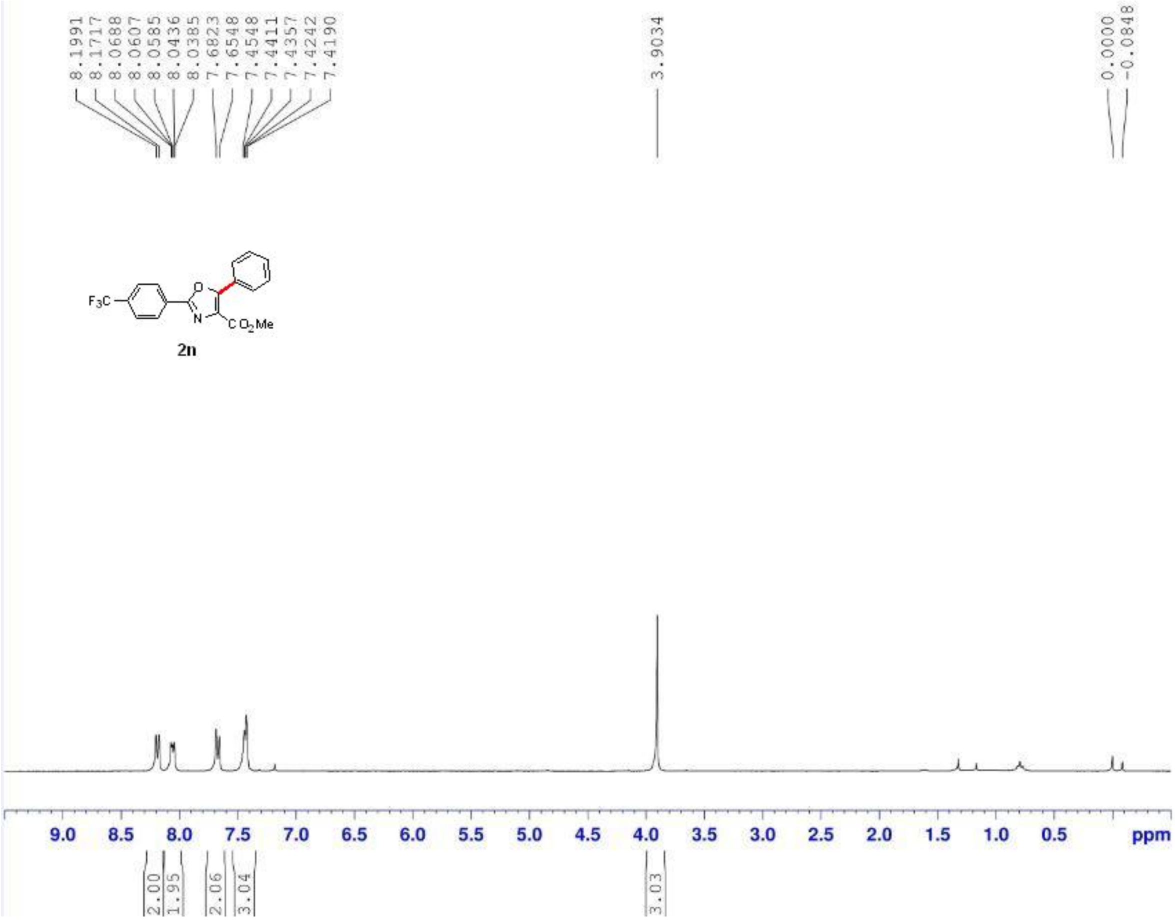
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7.4357
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N
CO2Me
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4.0
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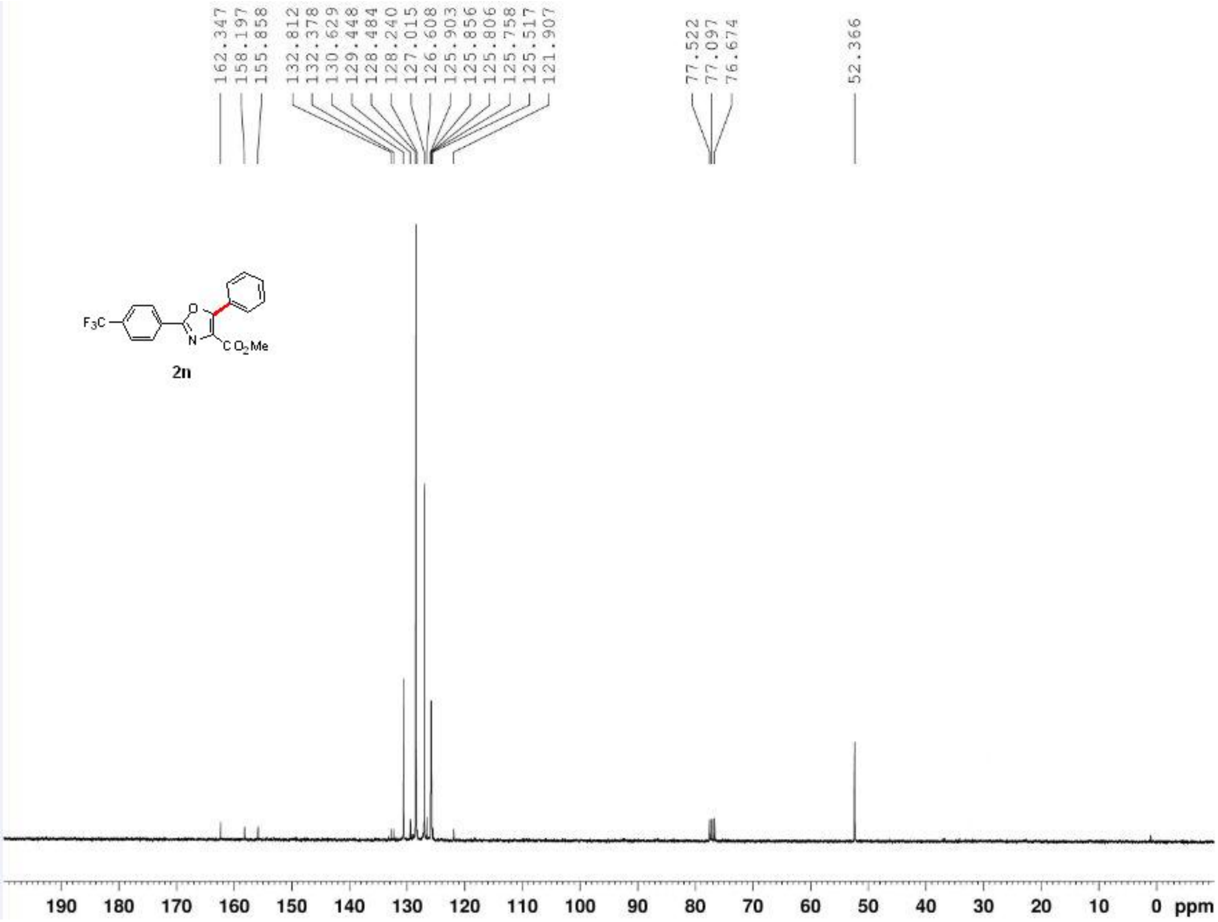
3.03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CO2Me
2n
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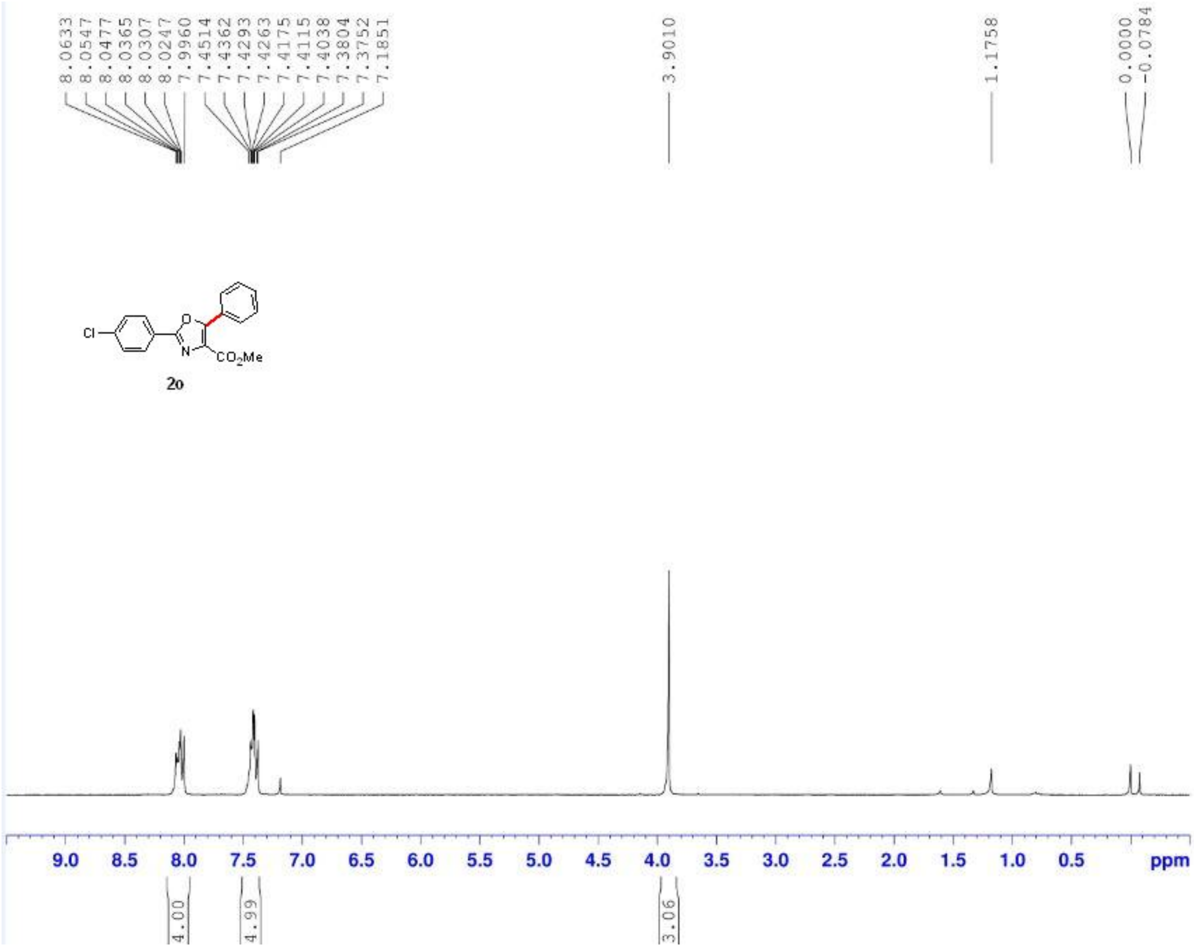
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7.4115
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7.1851
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7.0
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6.0
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5.0
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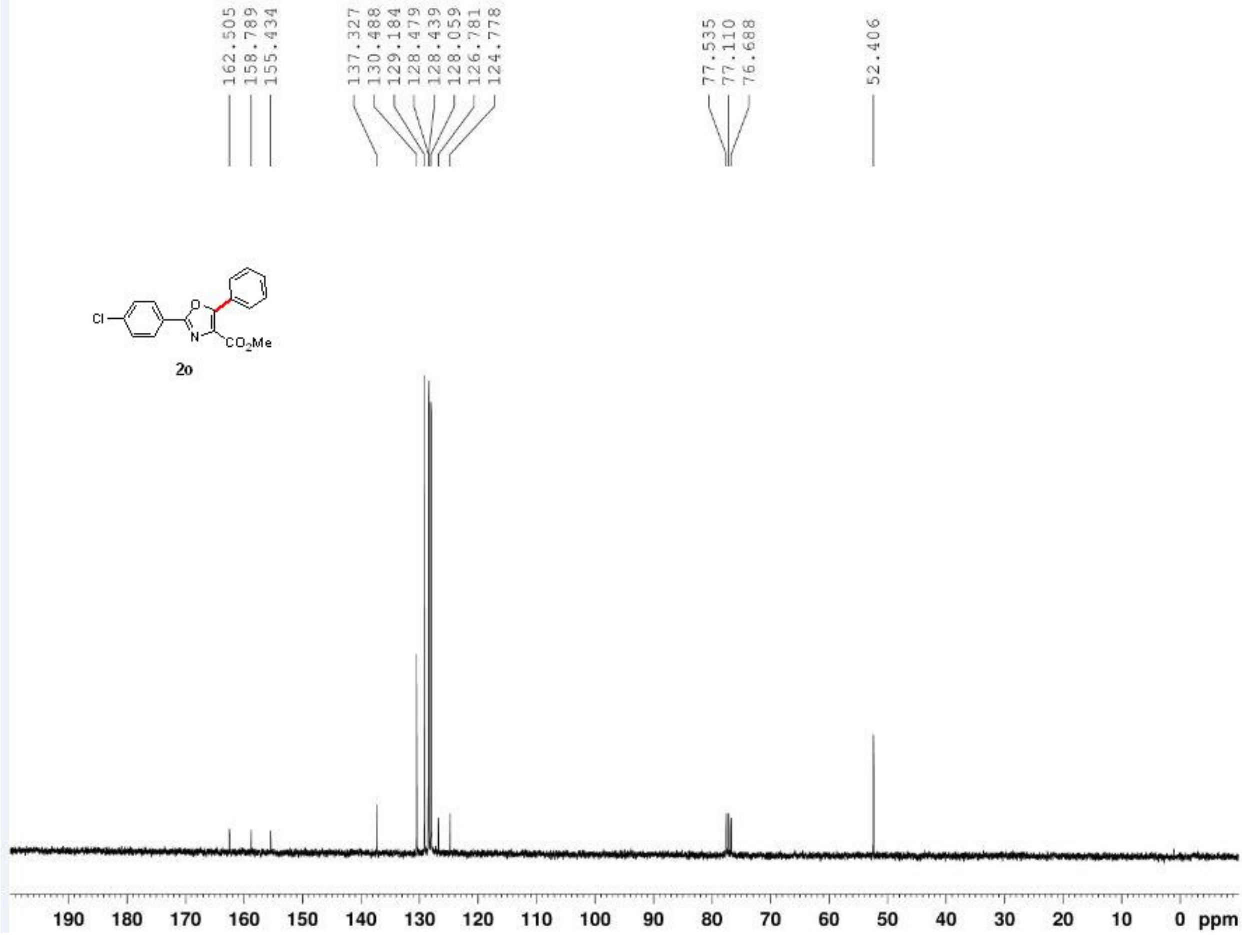
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2o
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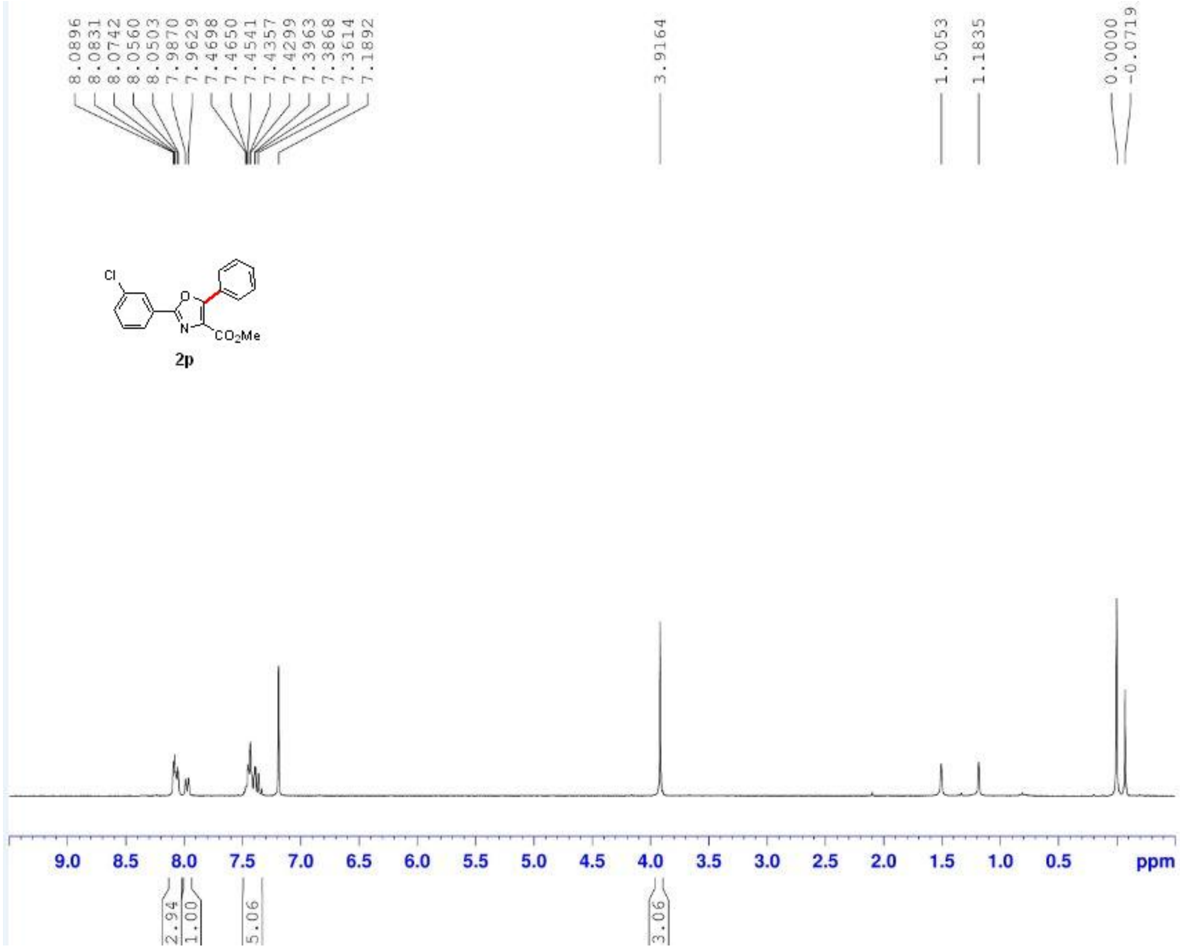
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7.3868
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7.1892
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N
CO2Me
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8.0
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7.0
6.5
6.0
5.5
5.0
4.5
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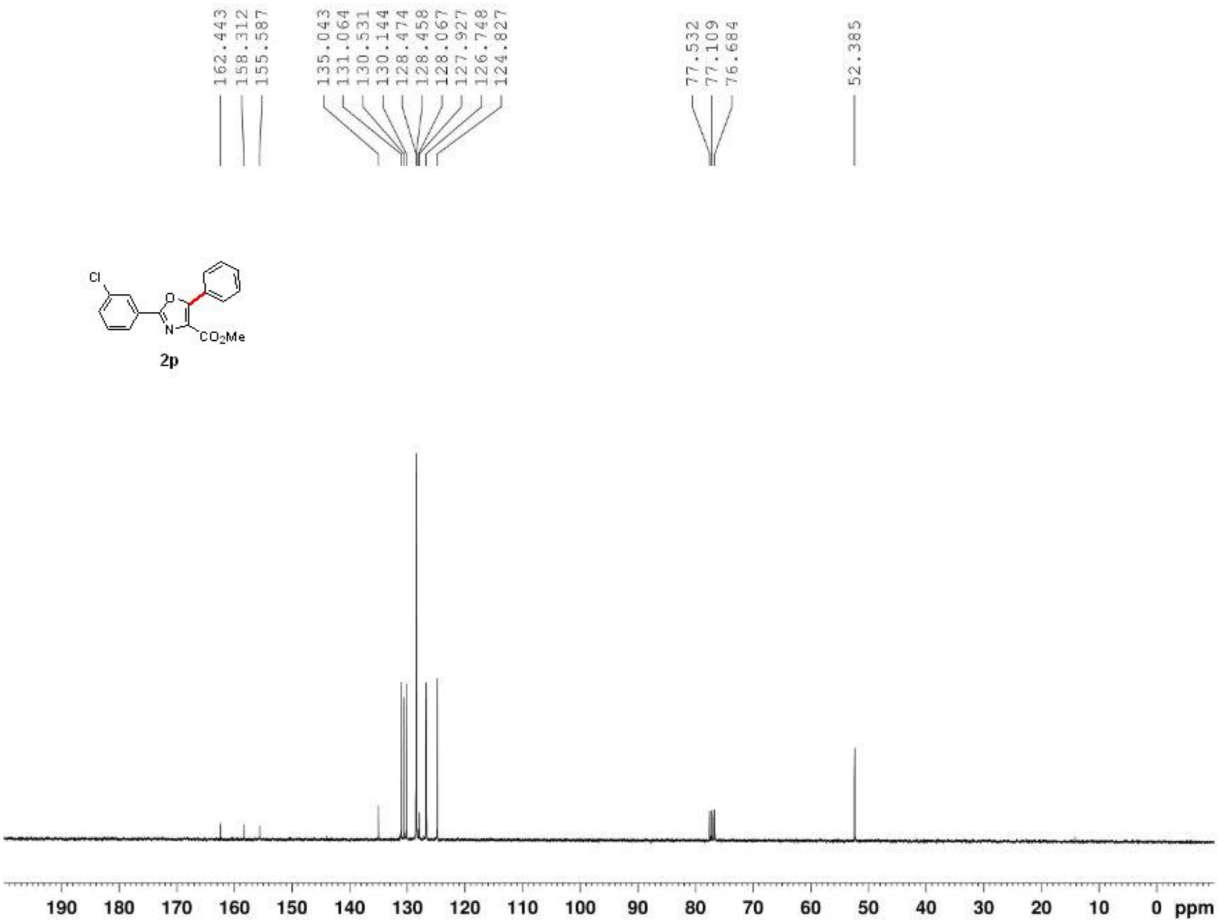
3.06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77.532
77.109
76.684
52.385
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O
N
CO2Me
2p
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140
130
120
110
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80
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60
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20
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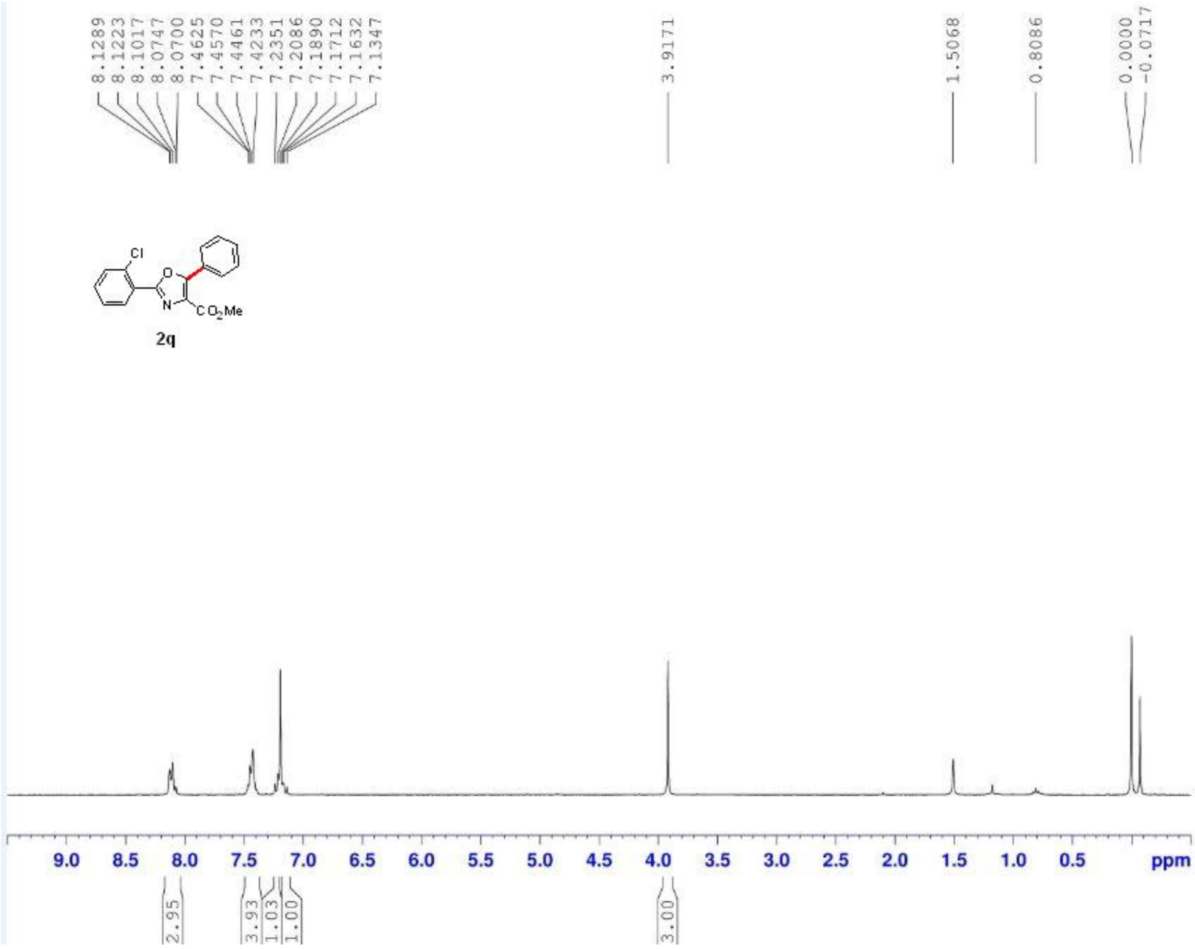
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N
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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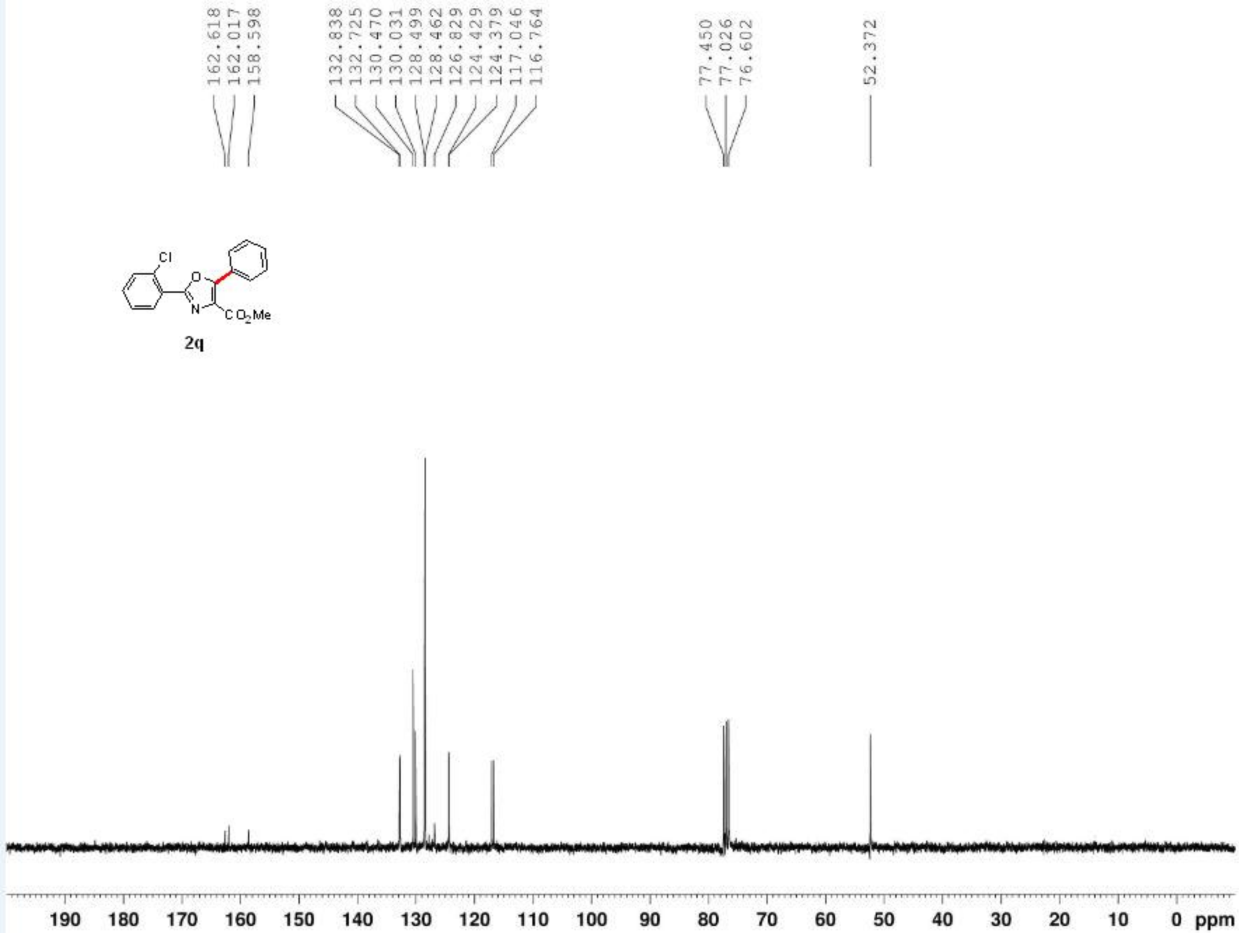
3.00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77.026
76.602
52.372
Cl
O
N
CO2Me
2q
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150
140
130
120
110
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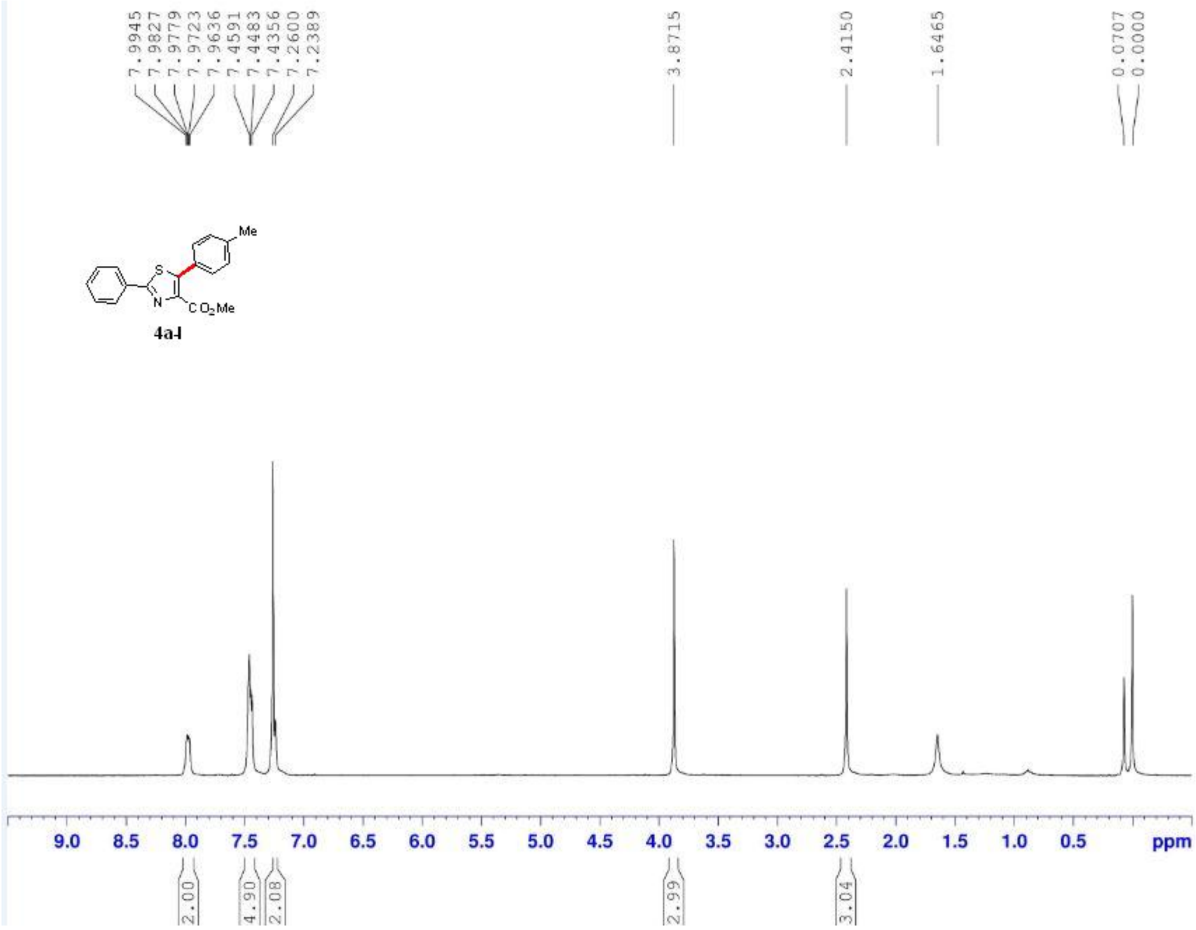
0 ppm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2.4150
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0.0000
Me
S
N
CO_2Me
4a-l
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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1.5
1.0
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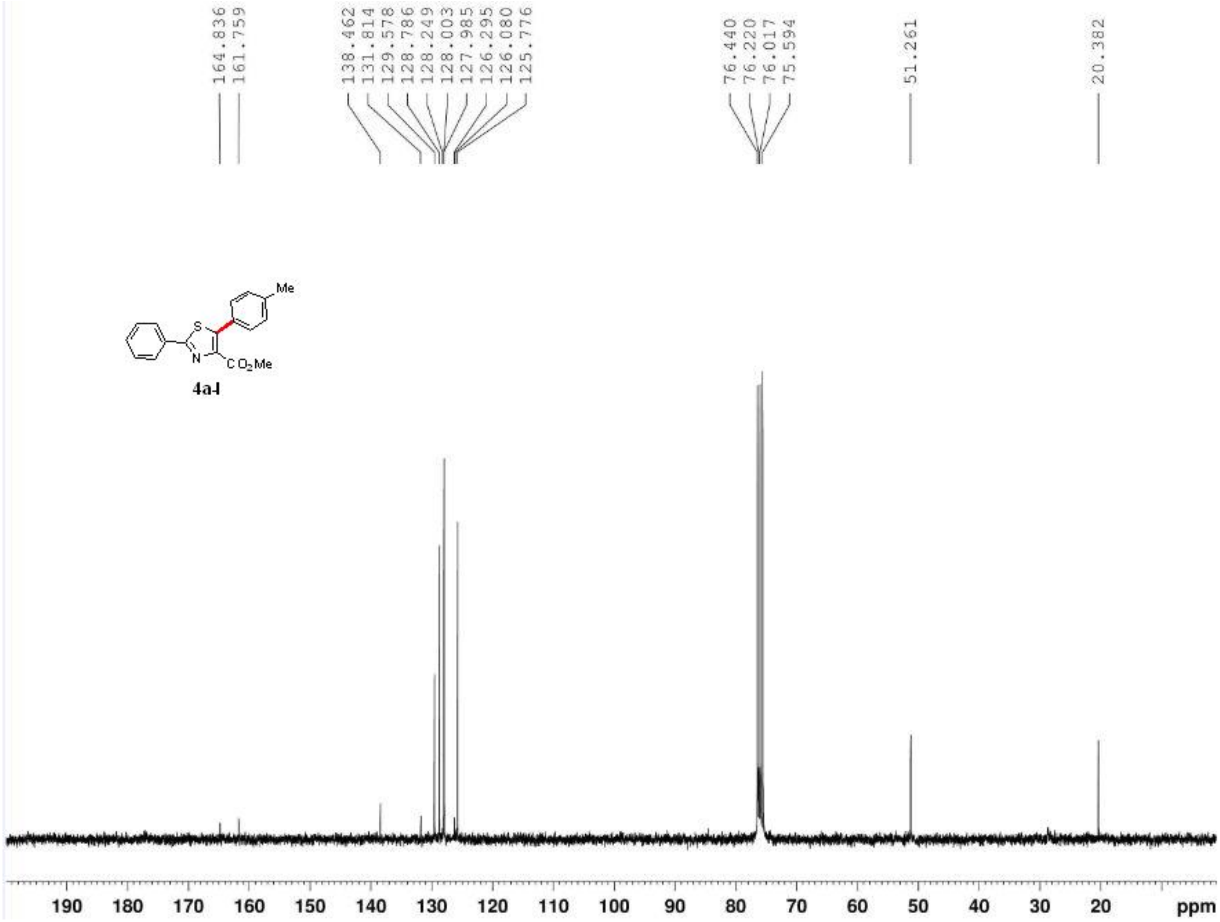
2.08
2.99
3.04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76.017
75.594
51.261
20.382
Me
S
N
CO_2Me
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150
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120
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80
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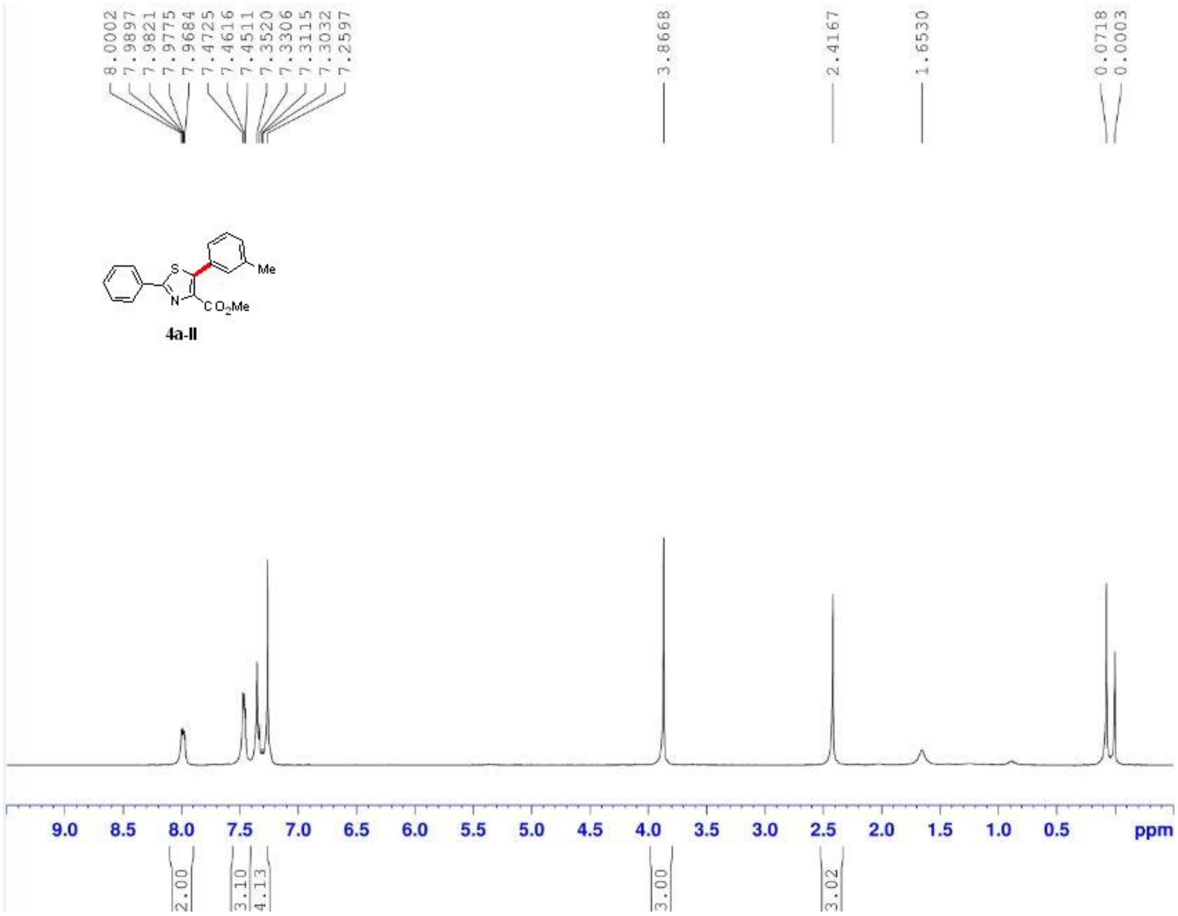
40
30
20
ppm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S
N
Me
CO2Me
4a-II
9.0
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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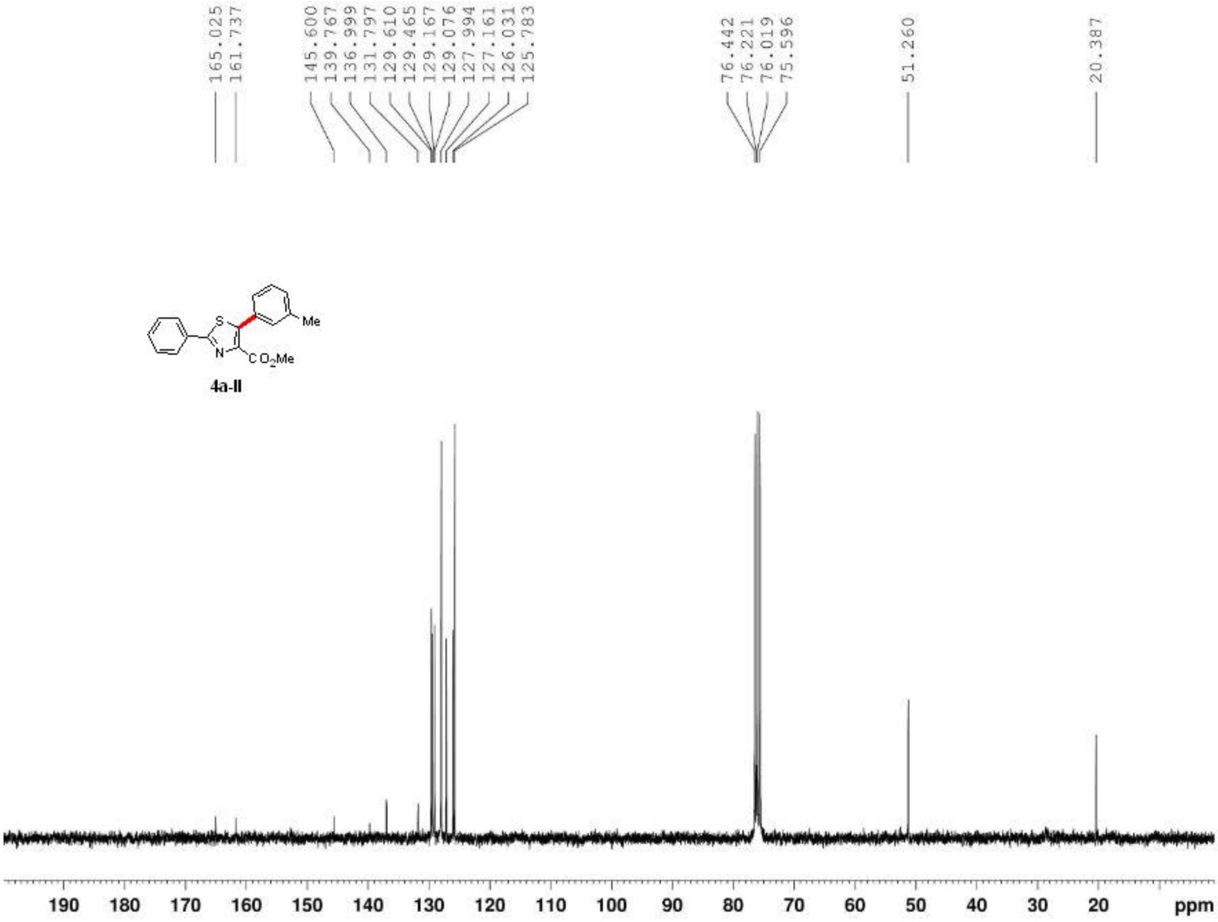
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76.221
76.019
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20.387
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N
Me
CO2Me
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80
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20
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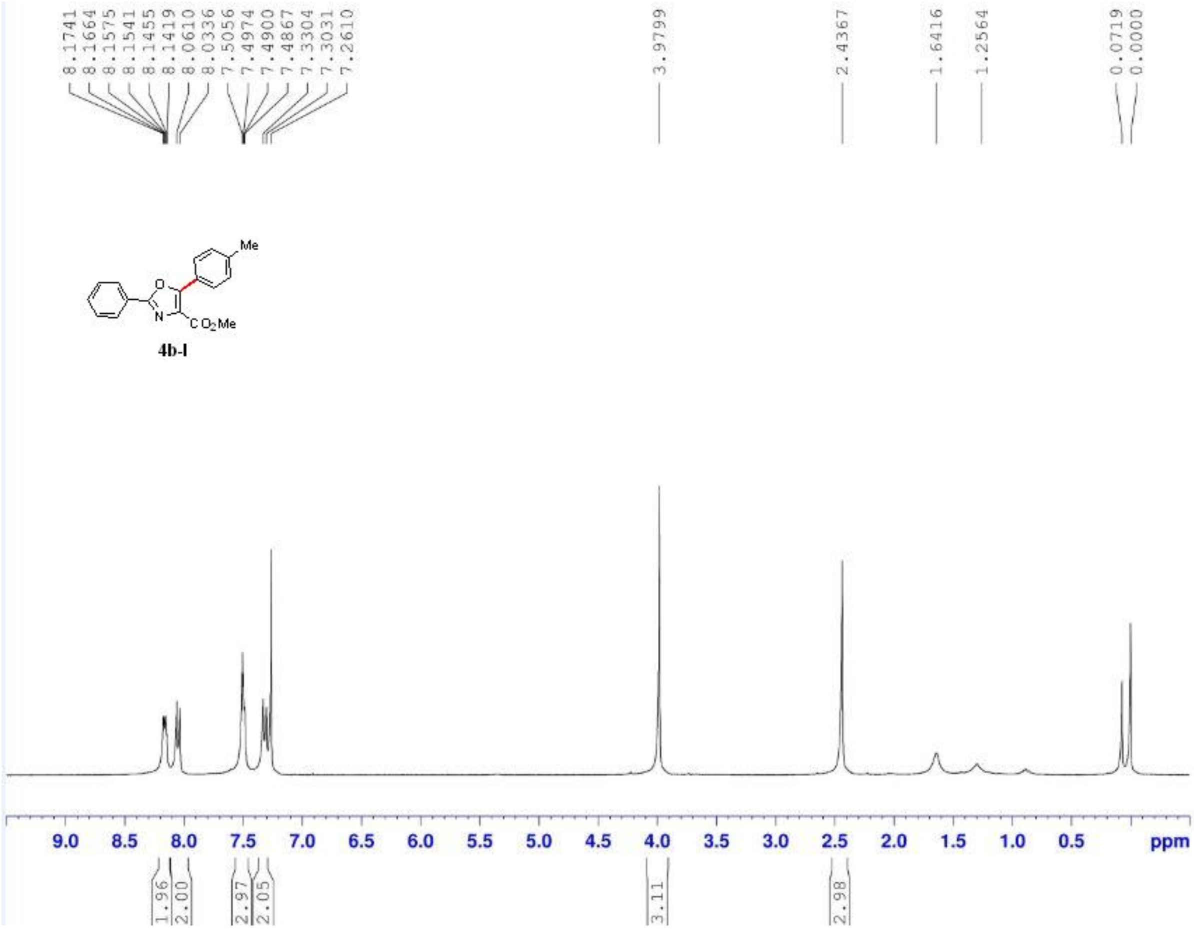
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7.4867
7.3304
7.3031
7.2610
3.9799
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1.2564
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0.0000
Me
O
N
CO2Me
4b-l
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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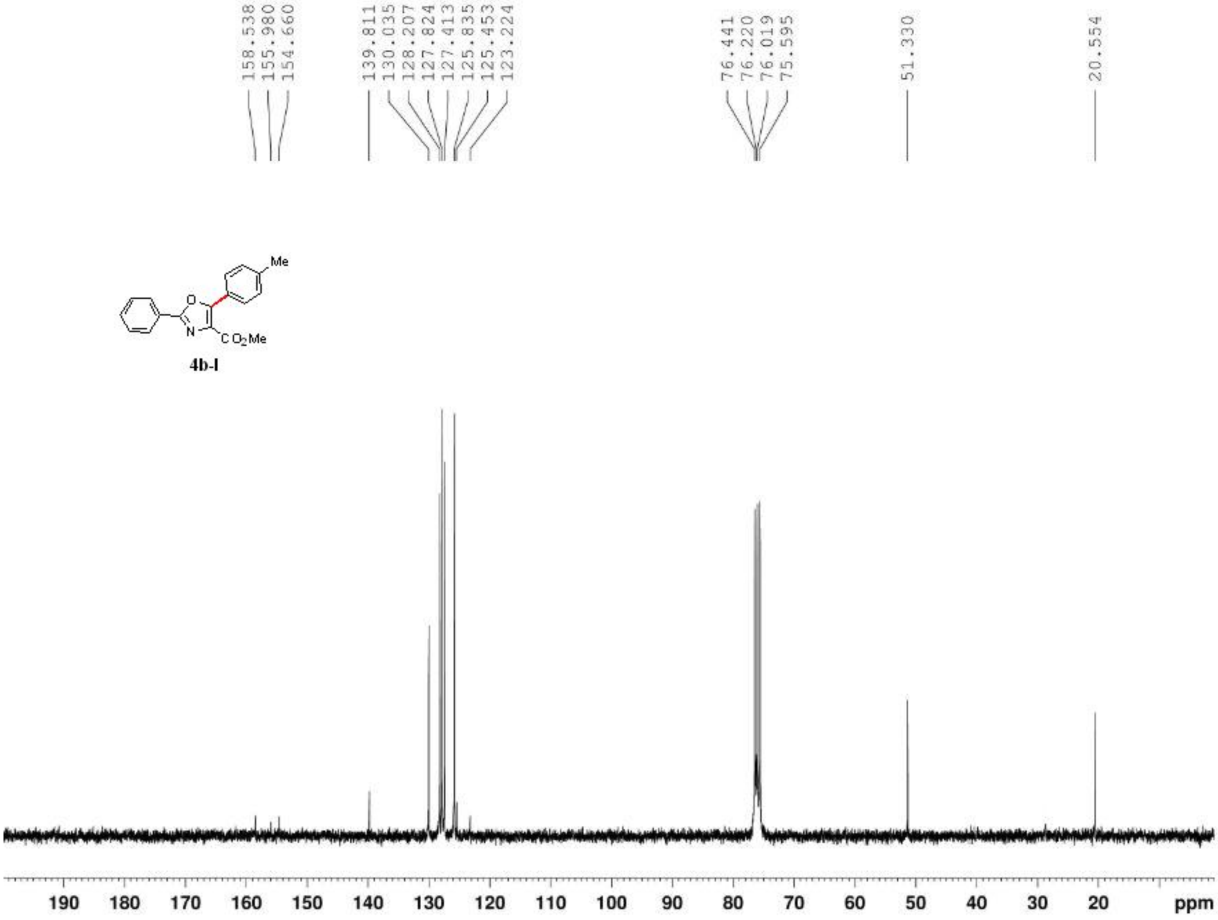
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75.595
51.330
20.554
Me
O
N
CO2Me
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150
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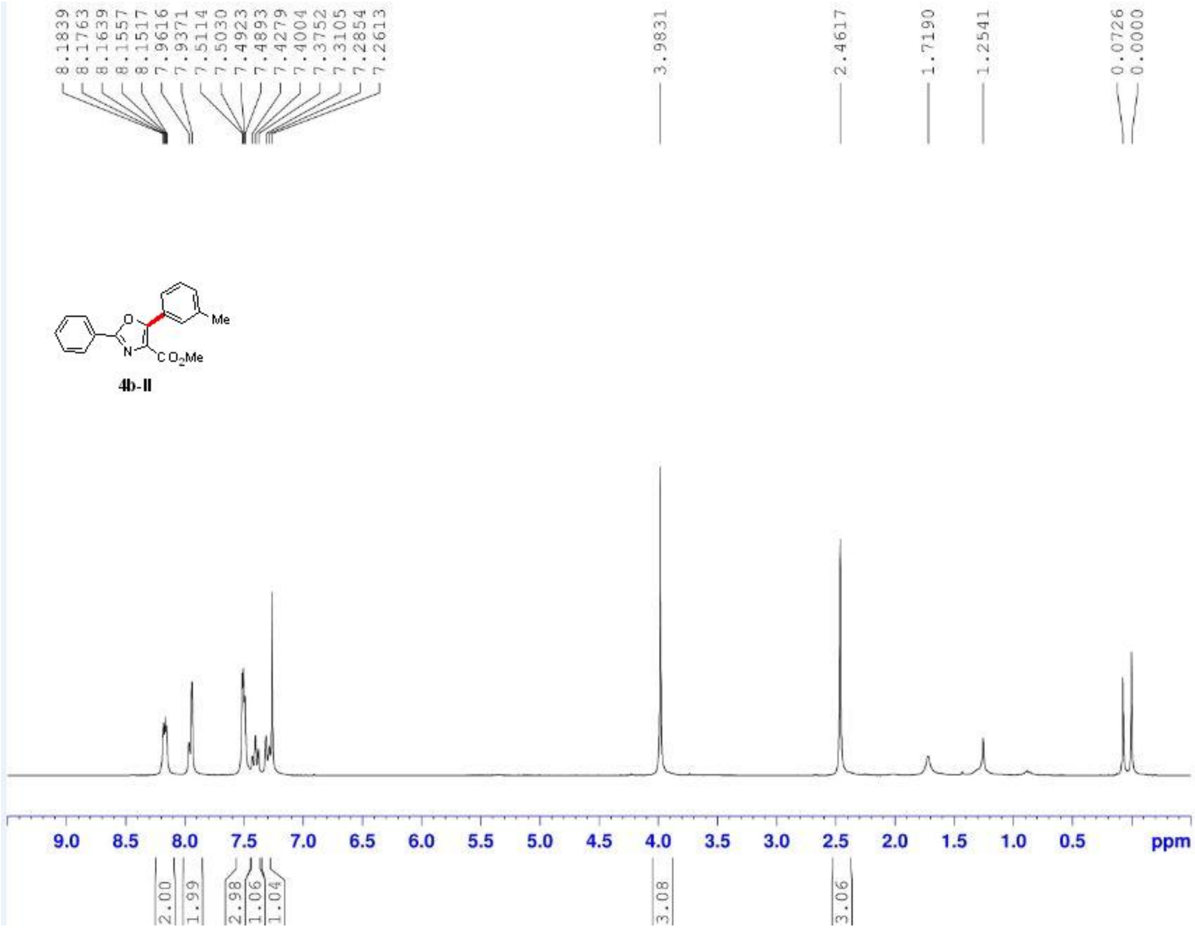
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7.2613
3.9831
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Me
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6.5
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5.5
5.0
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3.5
3.0
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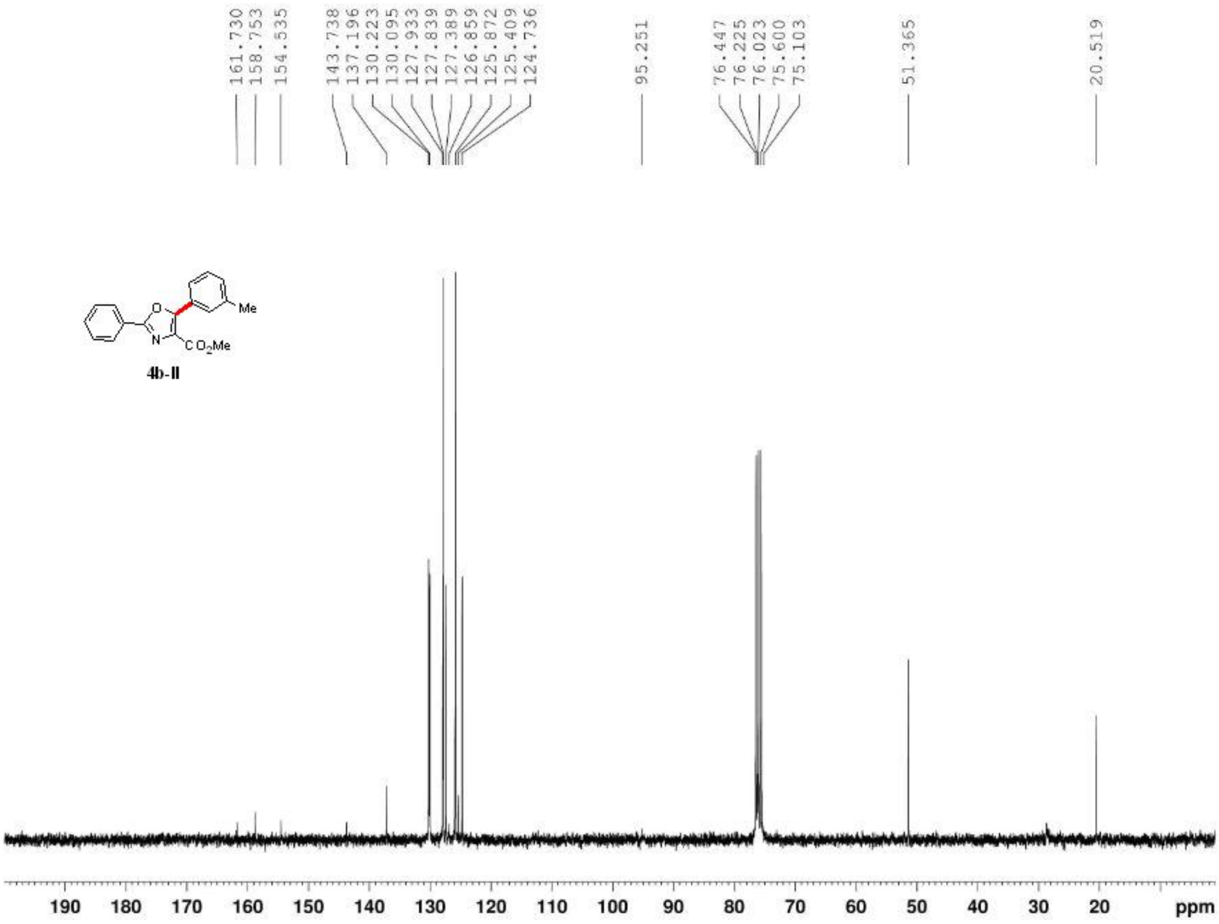
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125.409
124.736
95.251
76.447
76.225
76.023
75.600
75.103
51.365
20.519
O
N
Me
CO2Me
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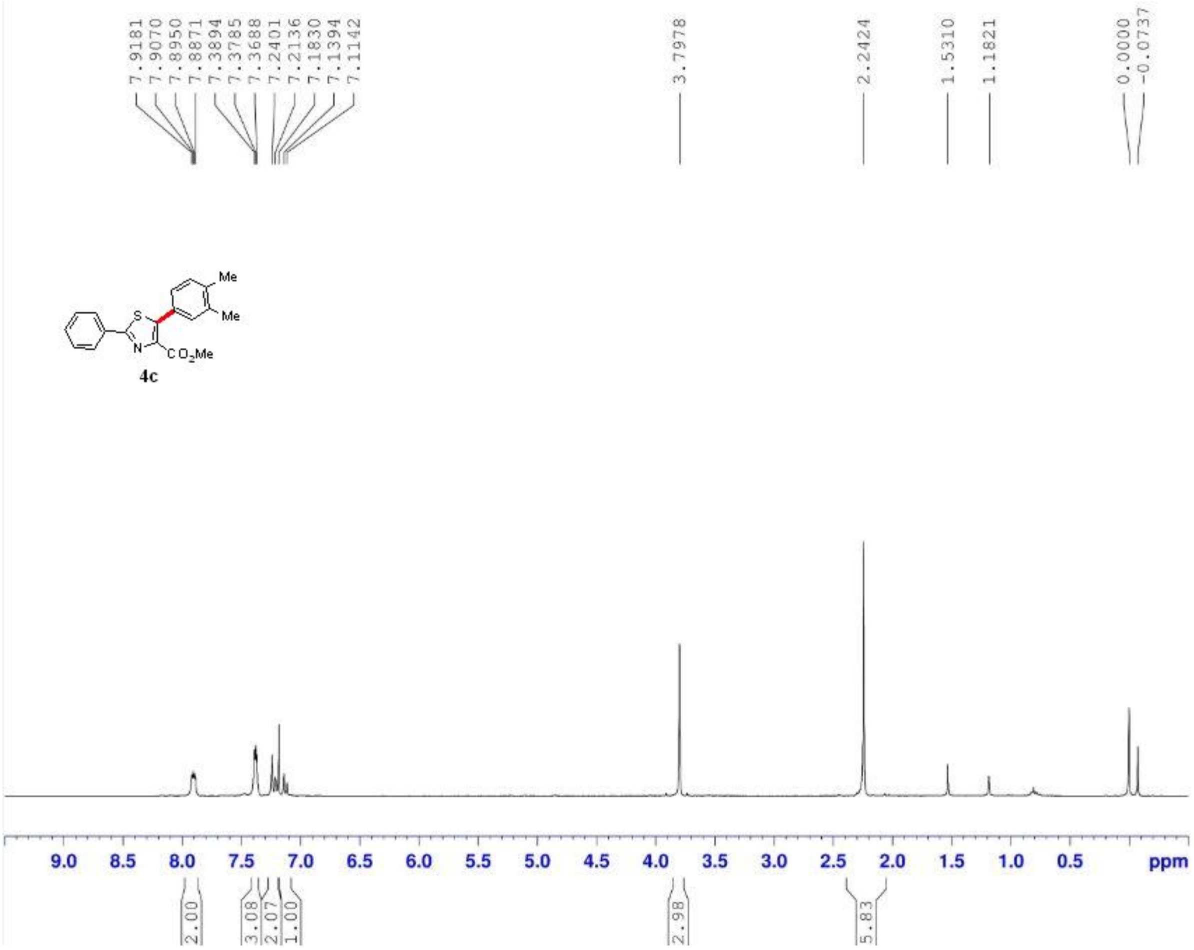
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7.1142
3.7978
2.2424
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1.1821
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Me
S
N
CO2Me
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8.0
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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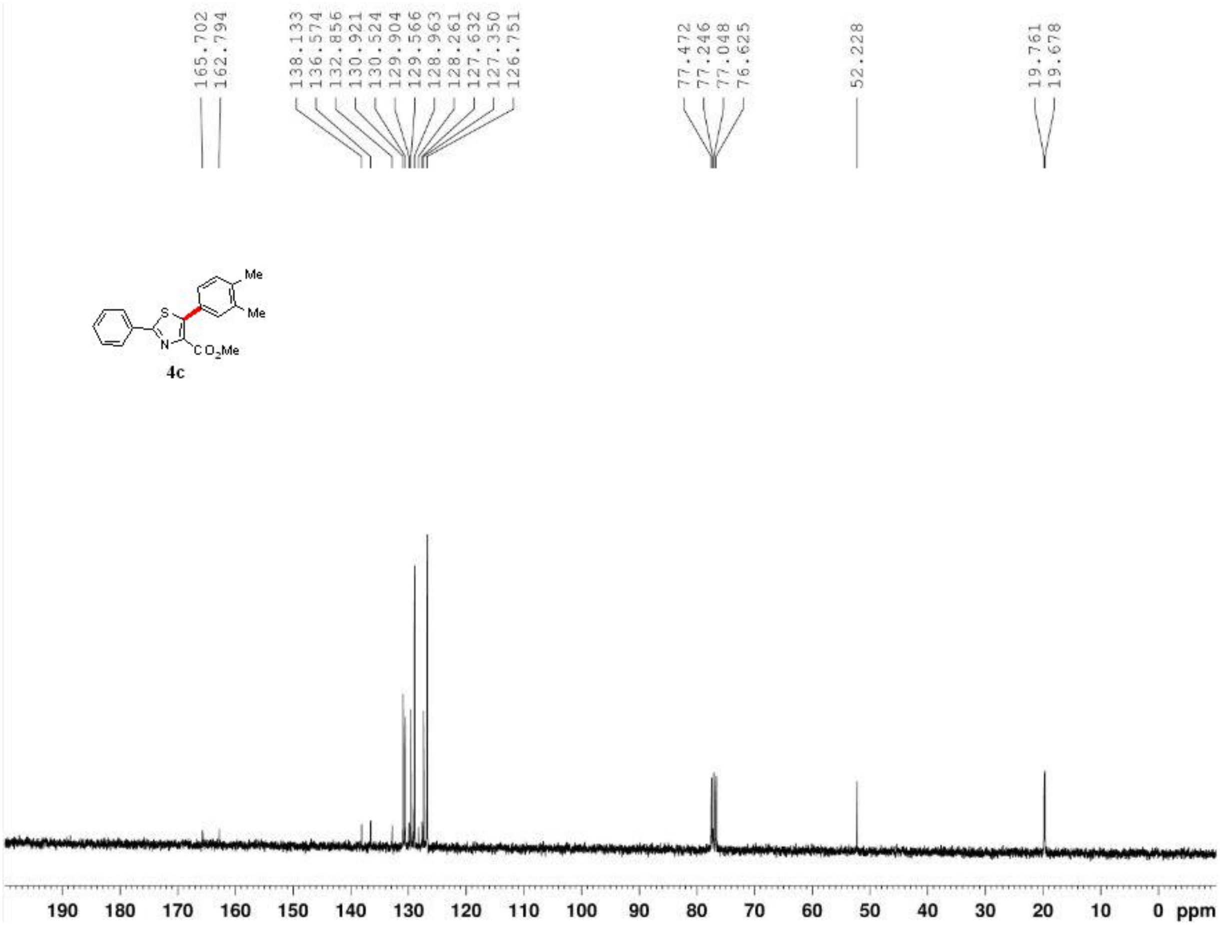
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127.632
127.350
126.751
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77.246
77.048
76.625
52.228
19.761
19.678
Me
Me
S
N
CO2Me
190
180
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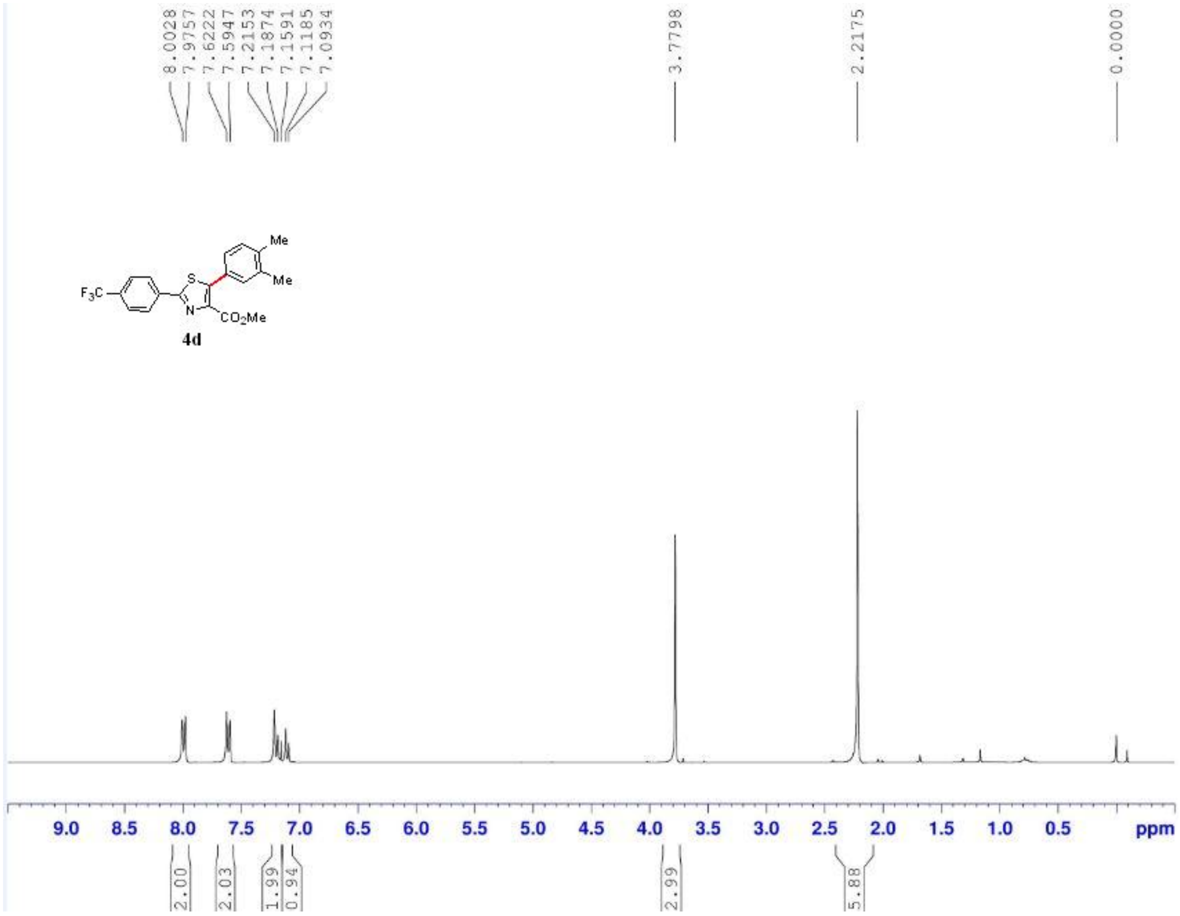
ppm

4c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2.2175
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Me
F_3C
S
N
CO_2Me
4d
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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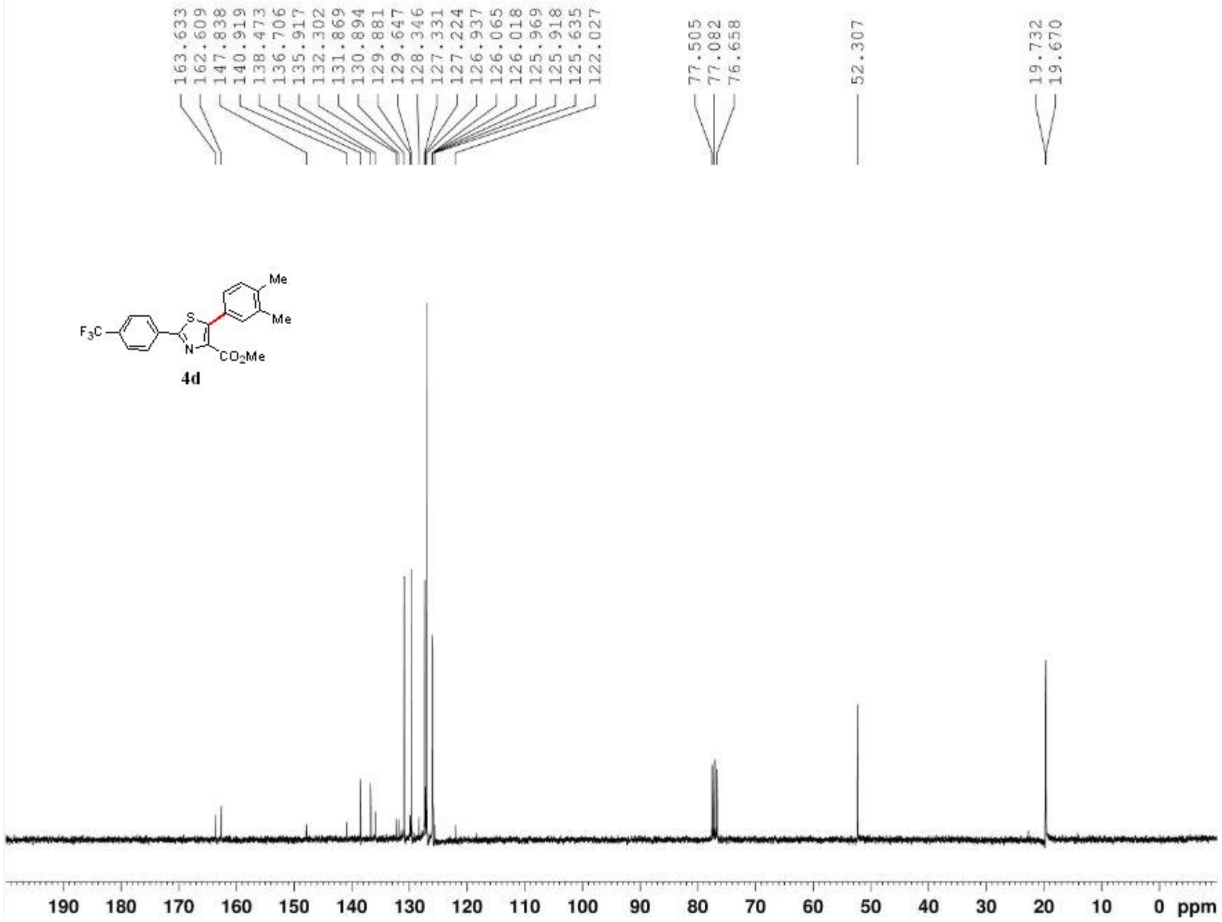
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122.027
77.505
77.082
76.658
52.307
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19.670
Me
Me
F_3C
S
N
CO_2Me
4d
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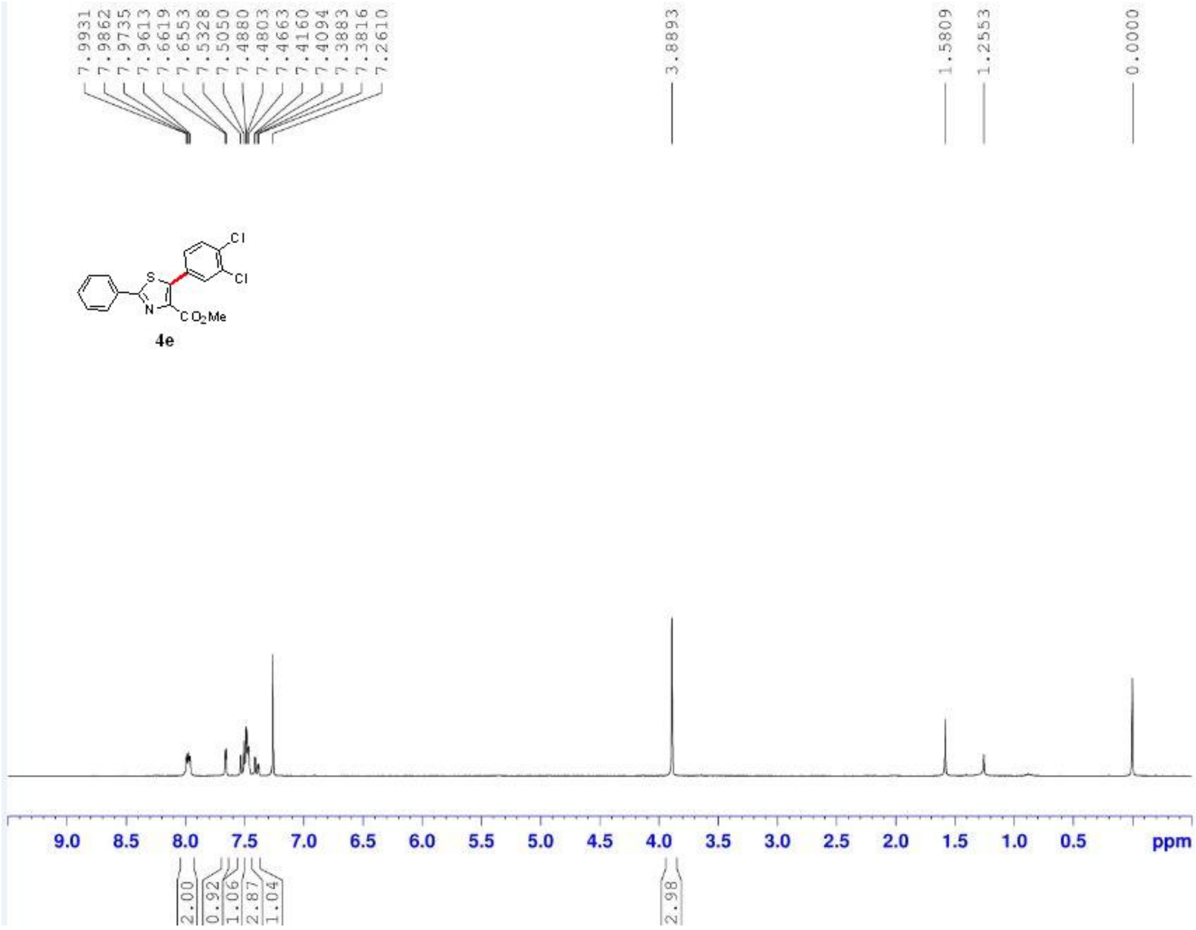
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7.4160
7.4094
7.3883
7.3816
7.2610
3.8893
1.5809
1.2553
0.0000
S
N
Cl
Cl
CO2Me
4e
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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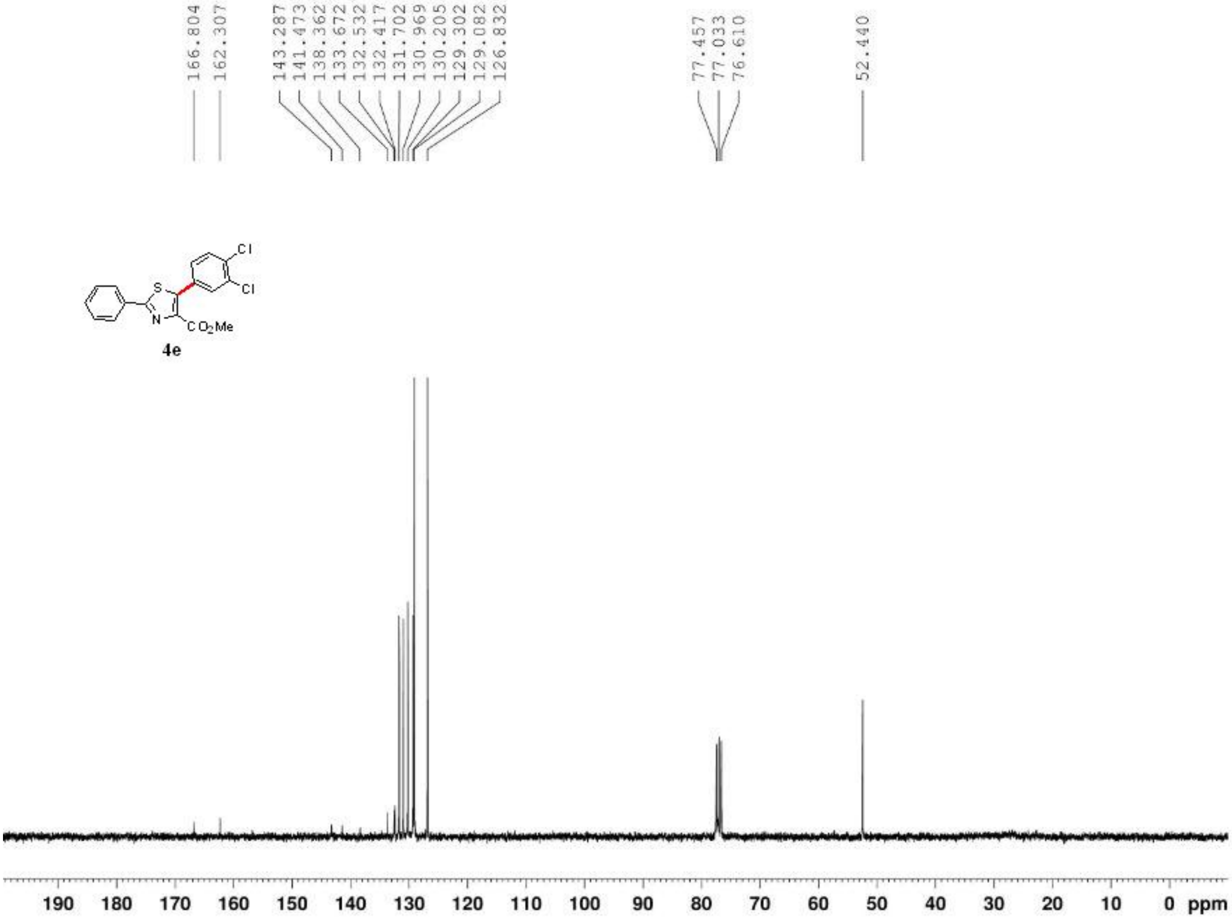
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126.832
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77.033
76.610
52.440
S
N
Cl
Cl
CO2Me
4e
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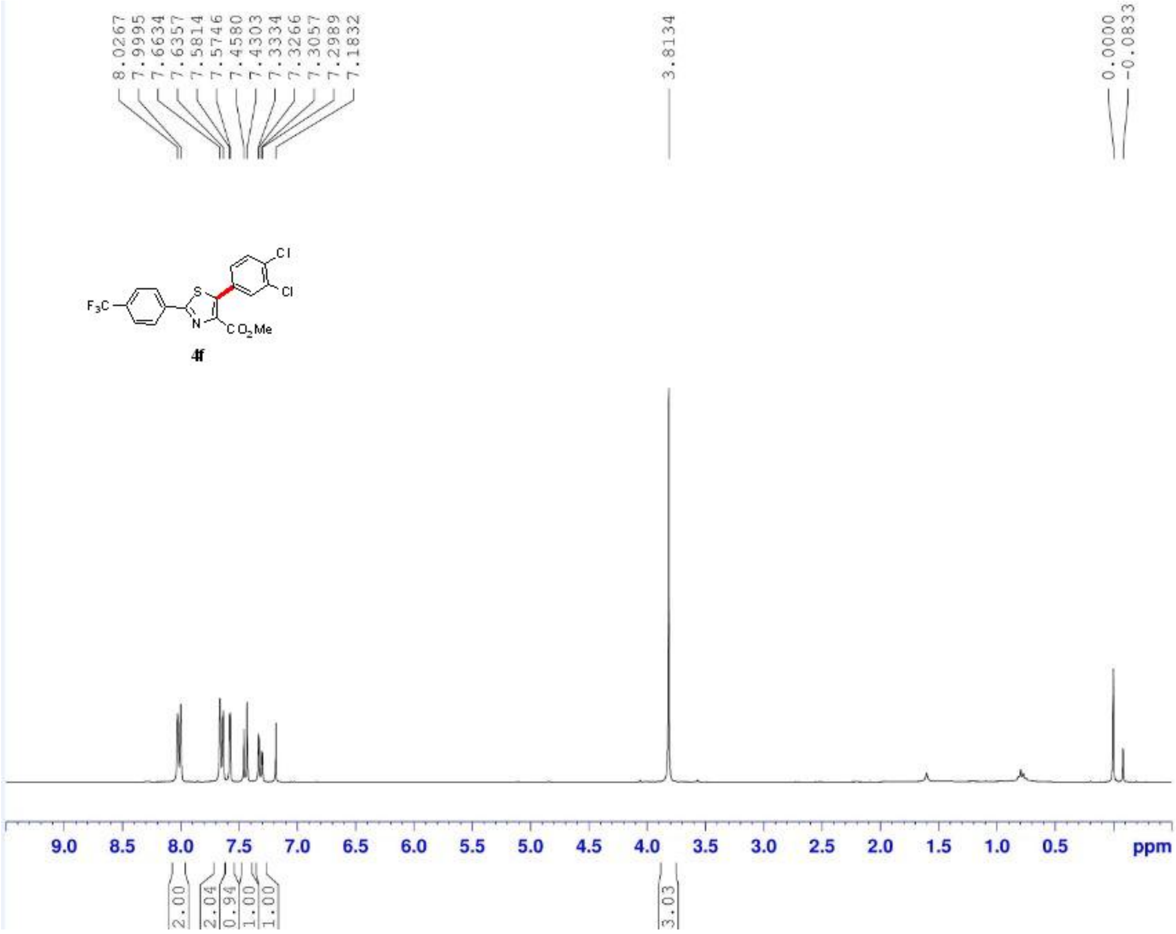
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7.2989
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F_3C
S
N
Cl
Cl
CO_2Me
4f
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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1.0
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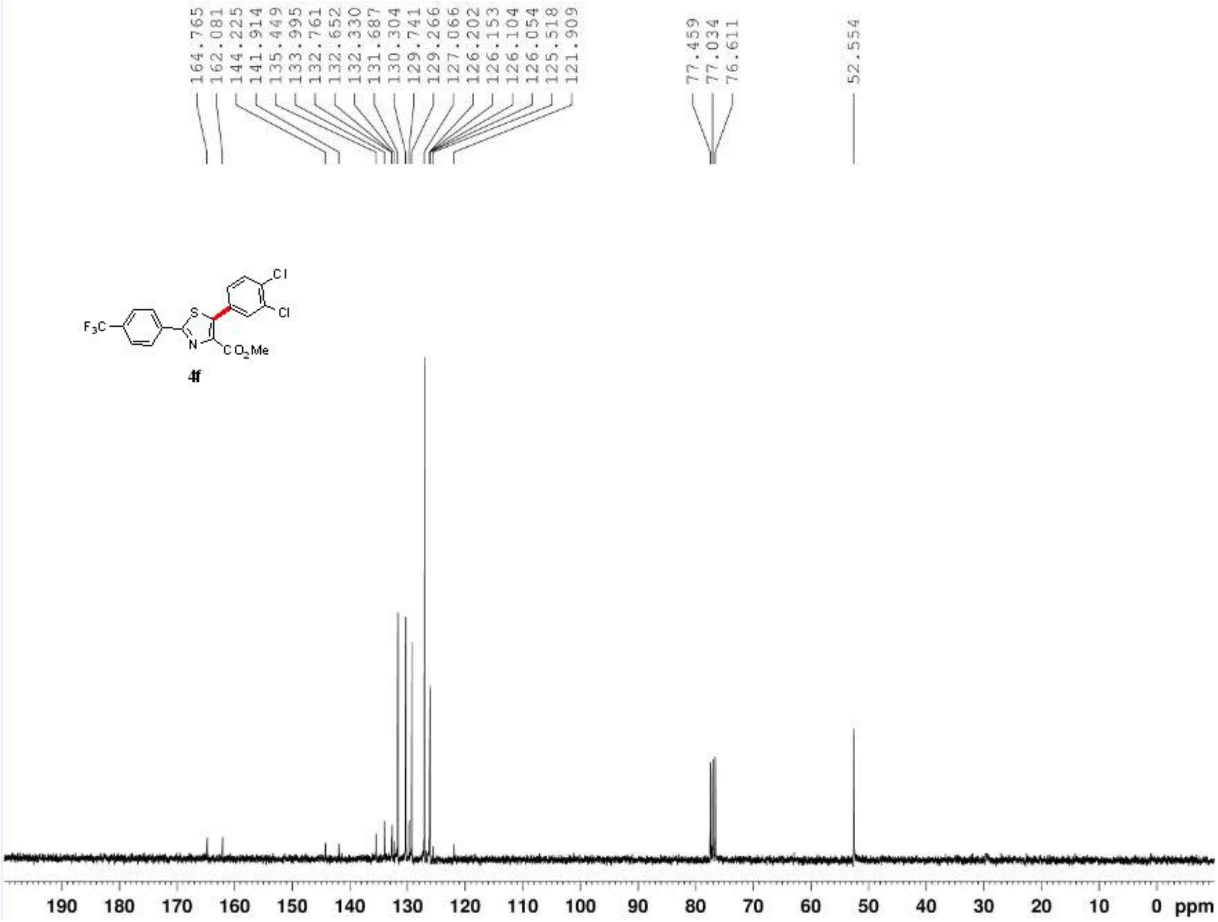
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52.554
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S
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CO_2Me
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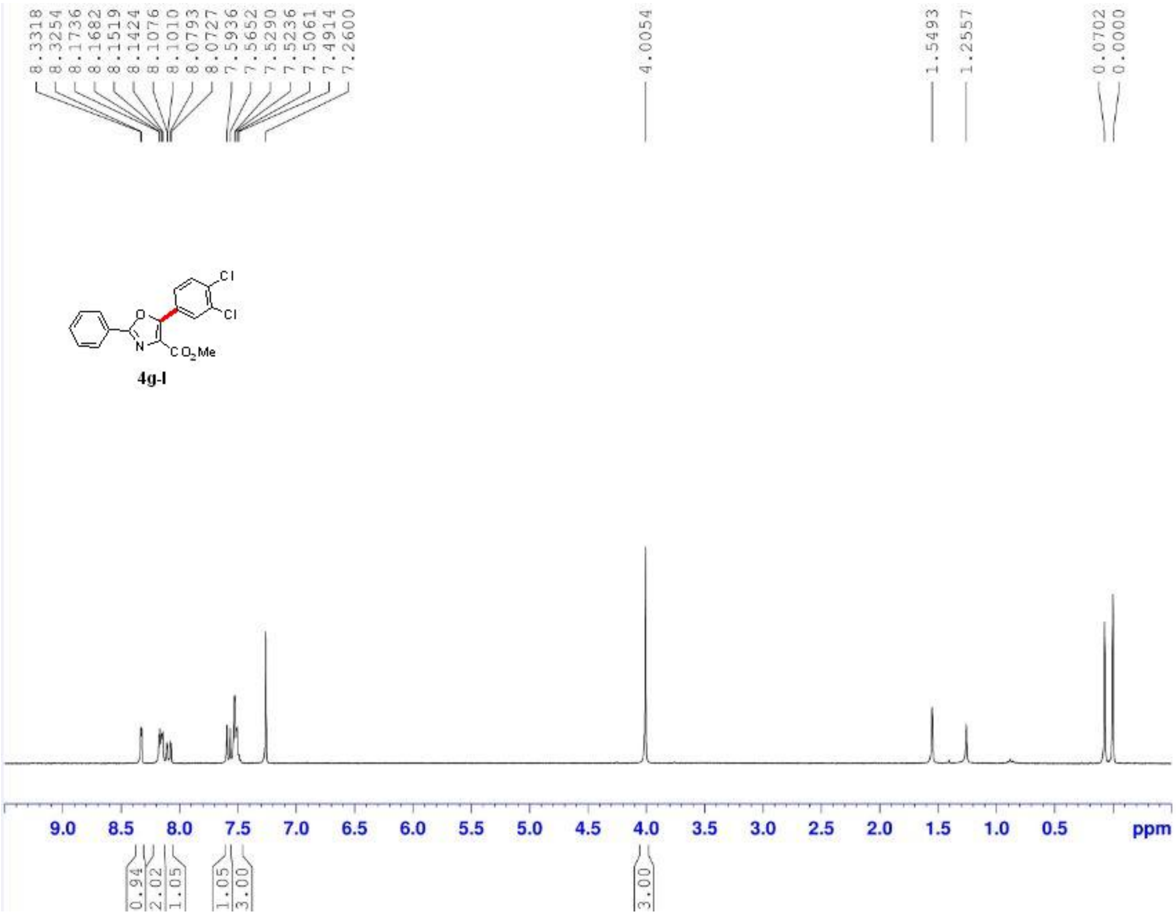
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8.0727
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Cl
O
N
CO2Me
4g-I
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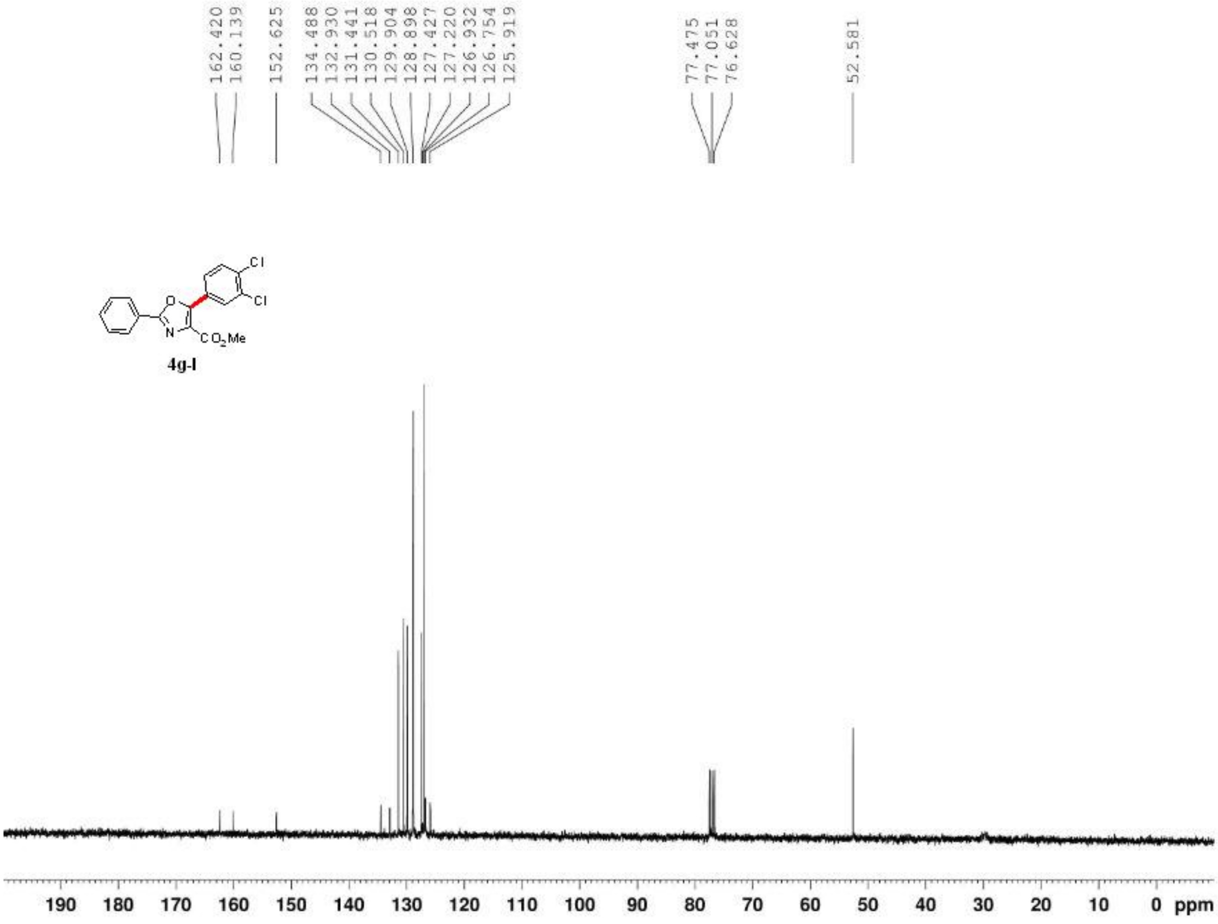
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77.475
77.051
76.628
52.581
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Cl
O
N
CO2Me
4g-I
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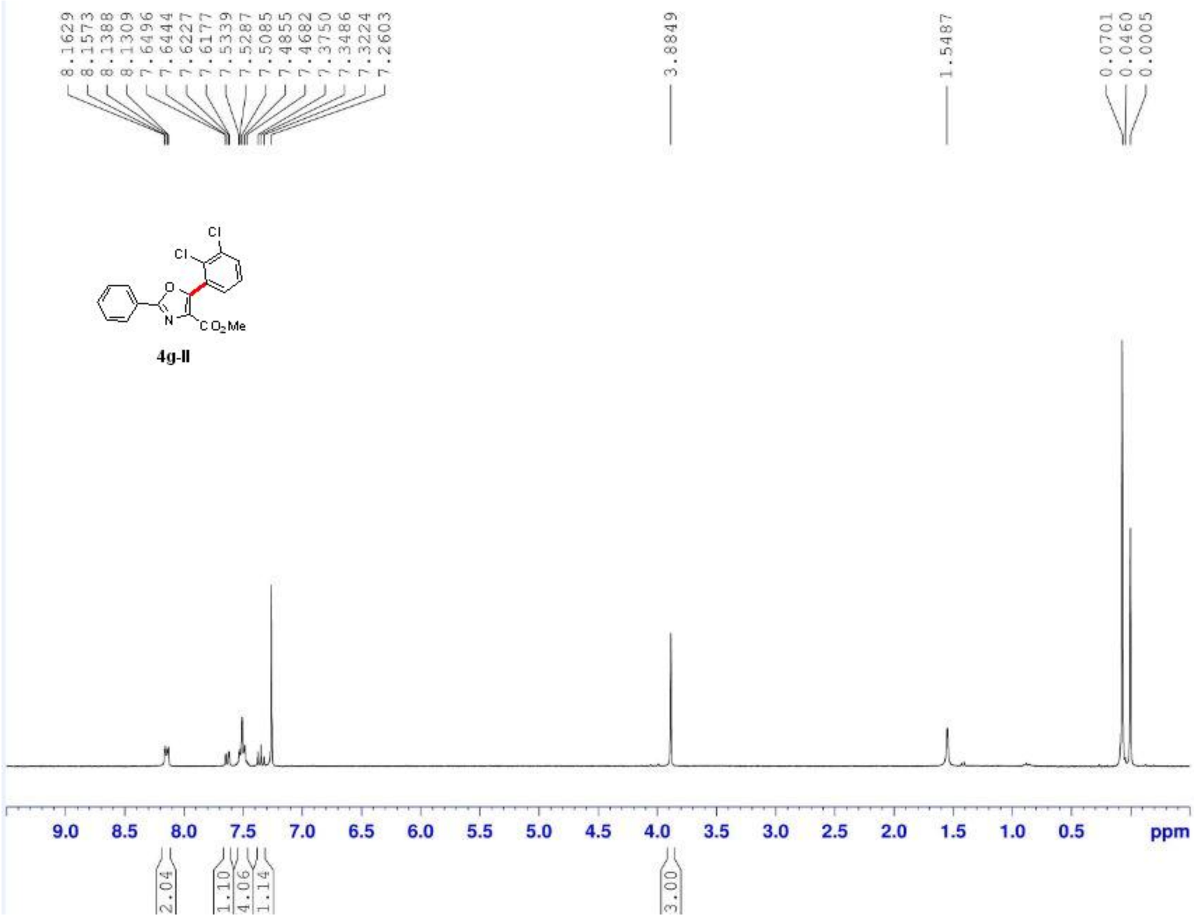
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7.3224
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Cl
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N
CO2Me
4g-II
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8.0
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
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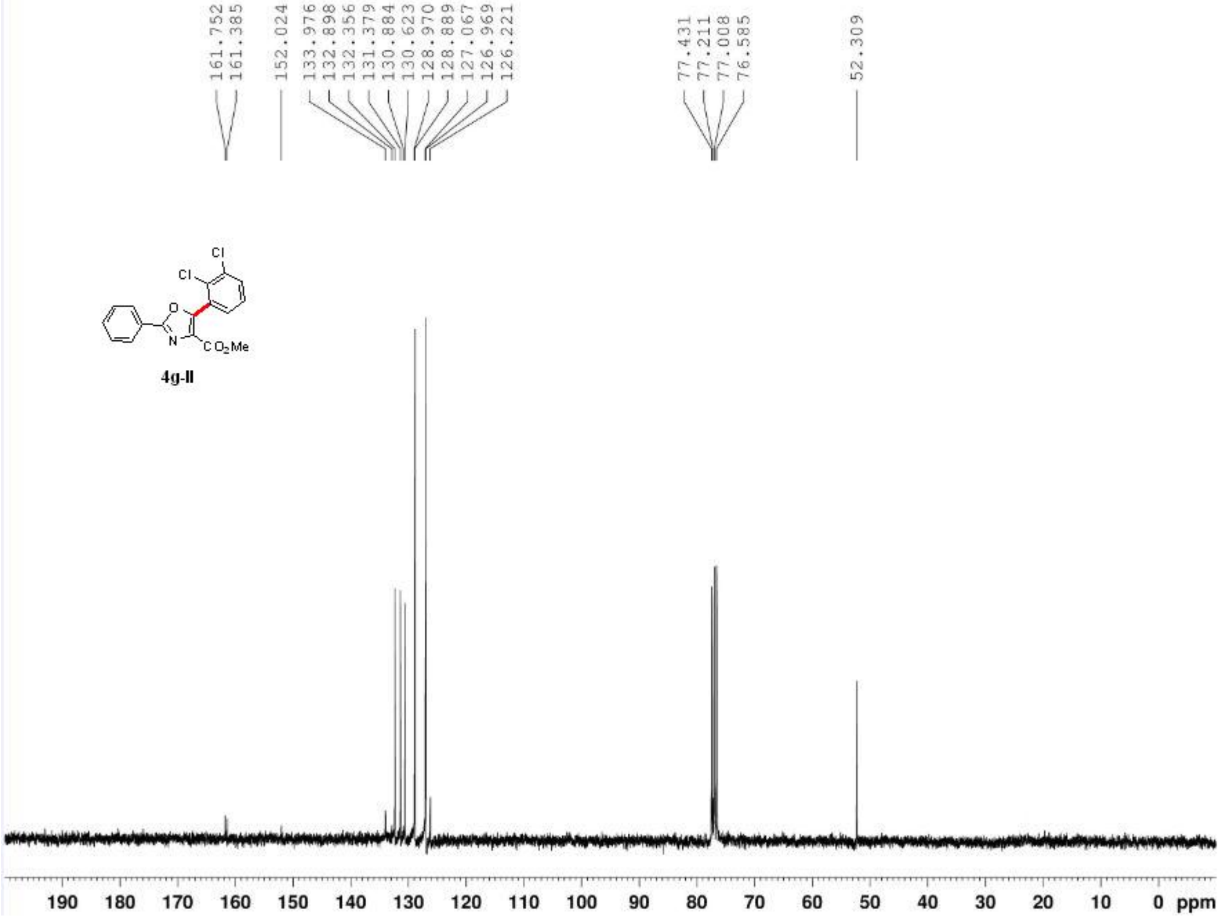
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77.211
77.008
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Cl
O
N
CO2Me
4g-II
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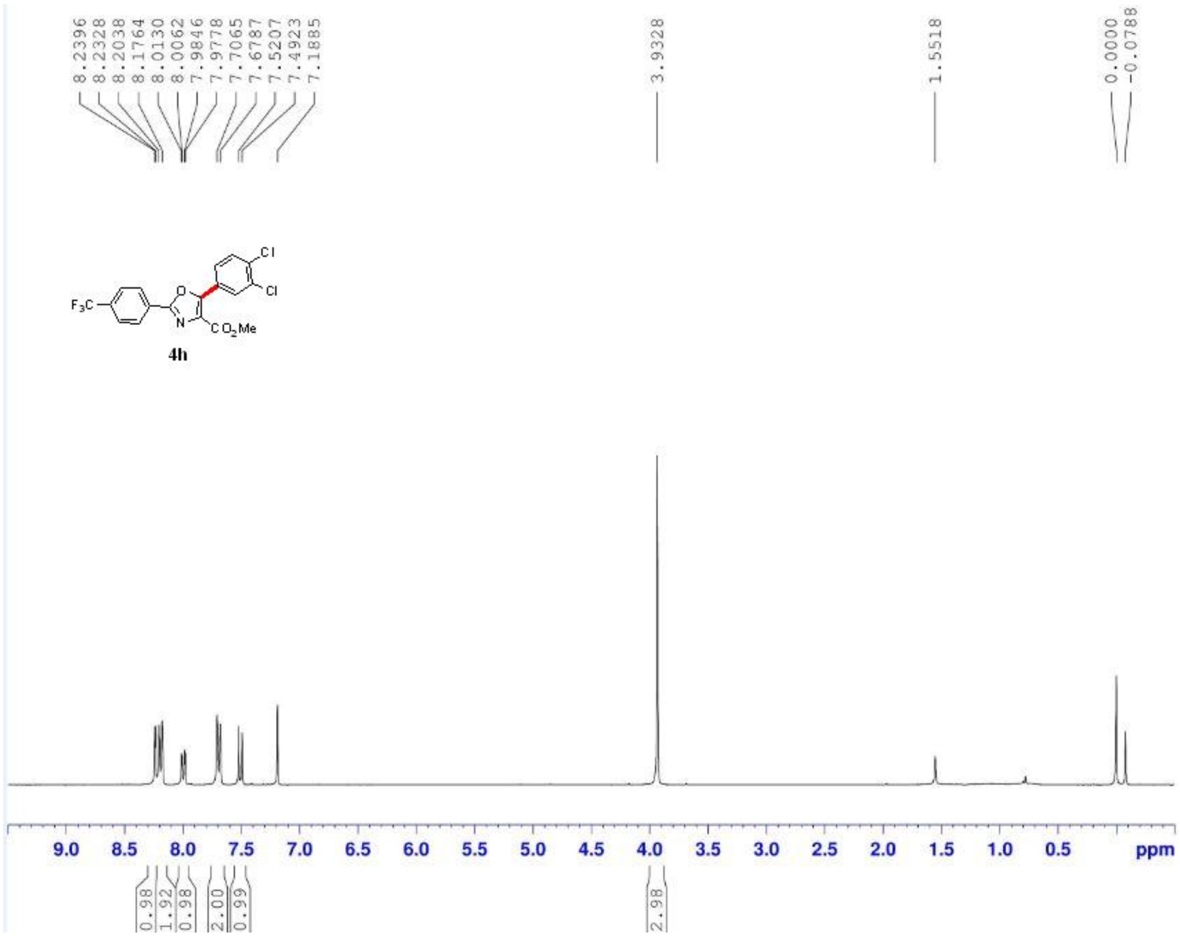
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7.1885
3.9328
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O
N
Cl
Cl
CO_2Me
4h
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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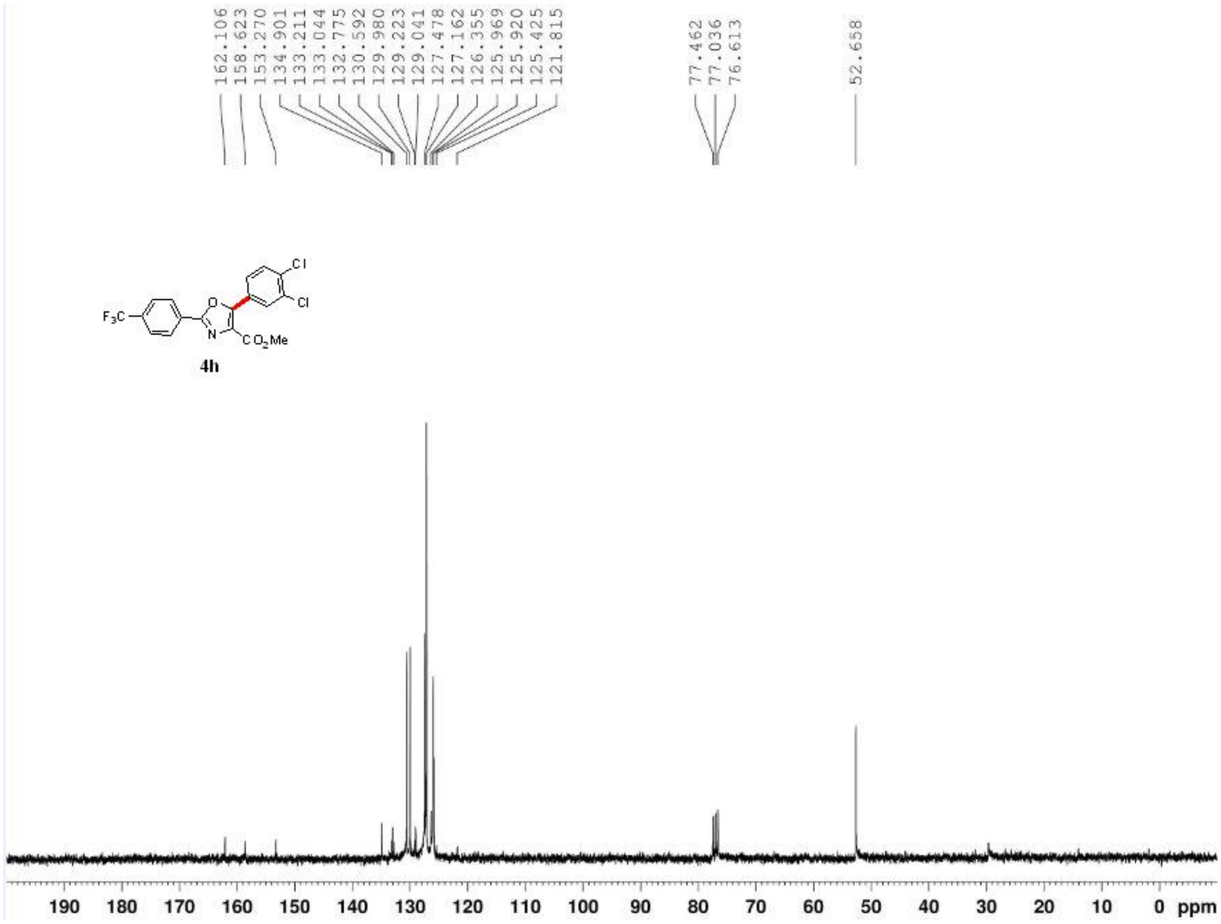
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126.355
125.969
125.920
125.425
121.815
77.462
77.036
76.613
52.658
F_3C
O
N
Cl
Cl
CO_2Me
4h
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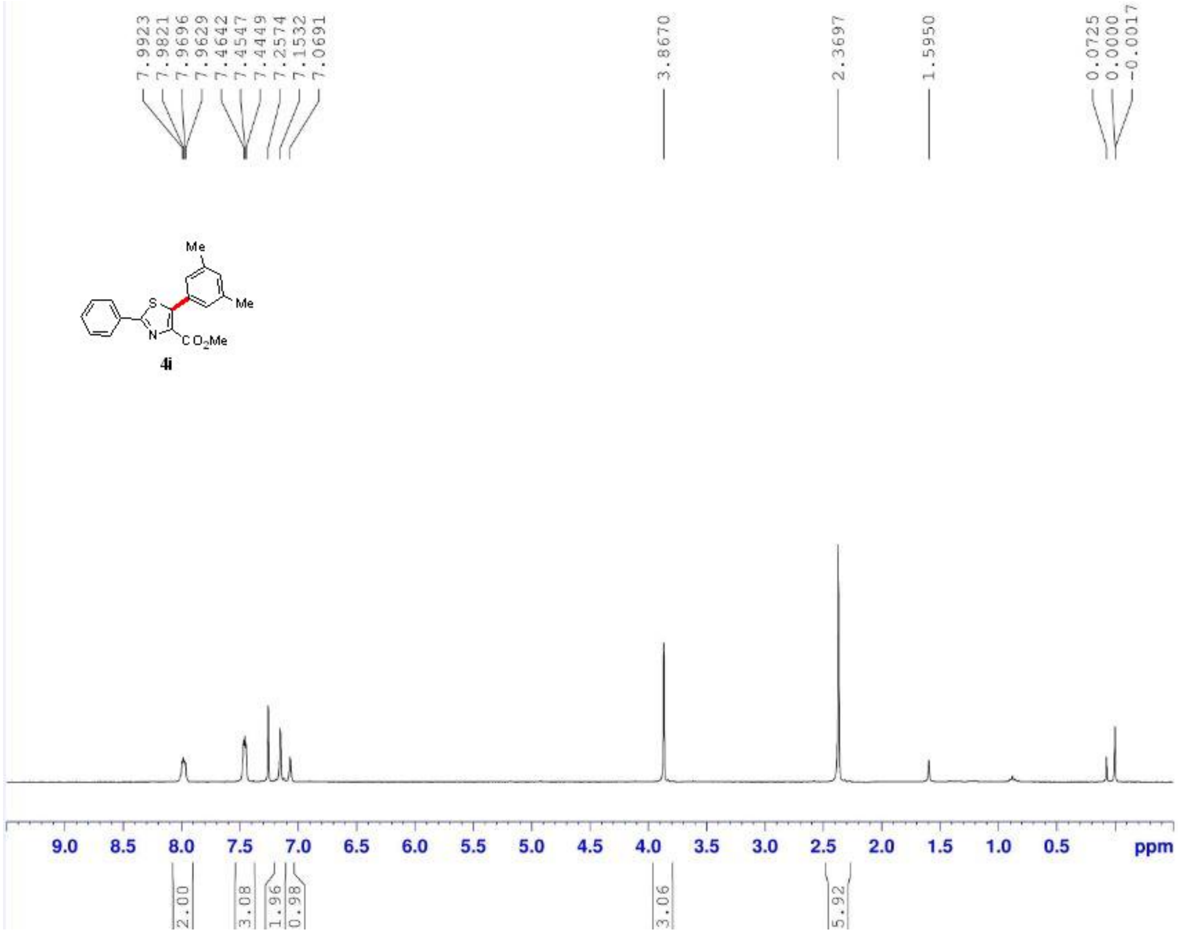
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-0.0017
Me
Me
S
N
CO2Me
4i
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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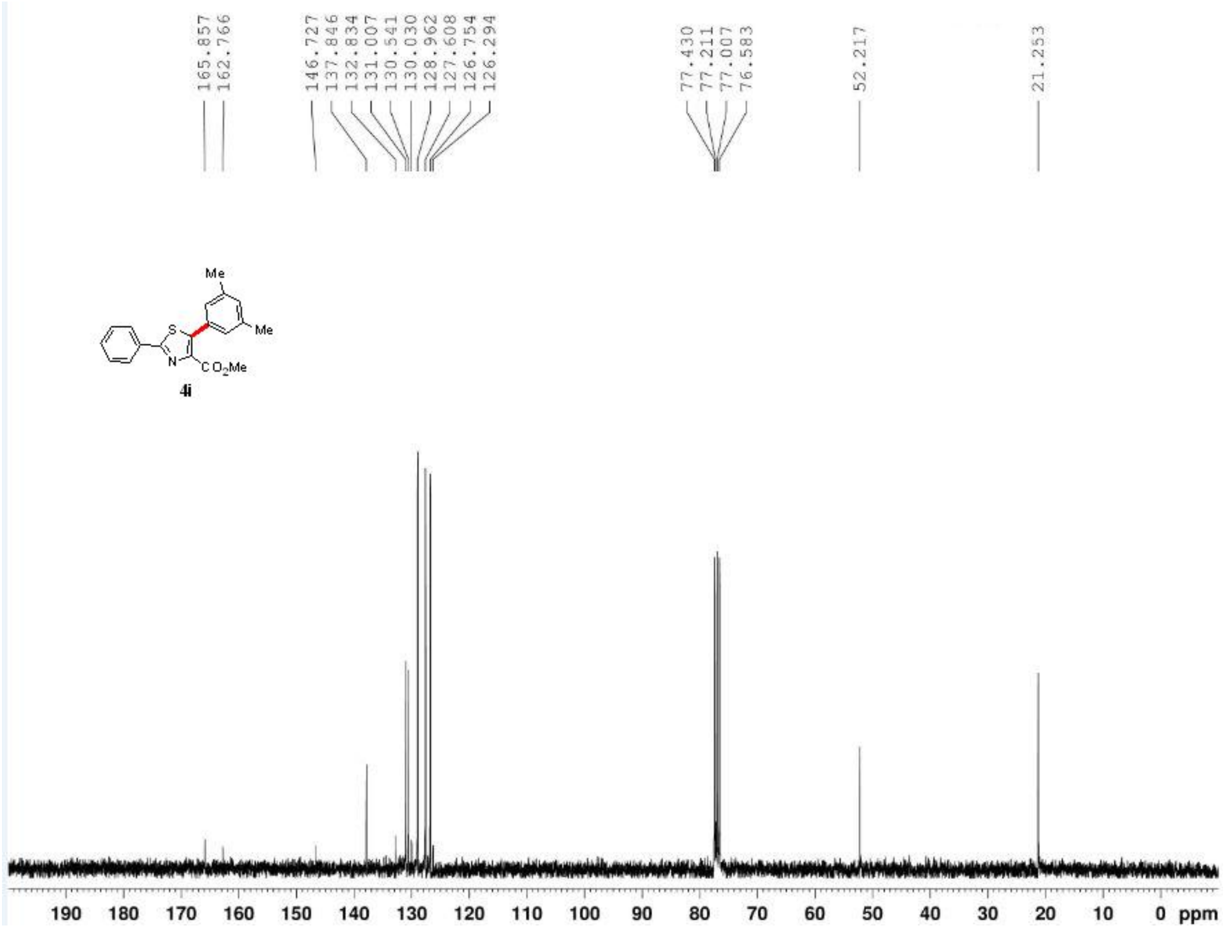
5.92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77.430
77.211
77.007
76.583
52.217
21.253
Me
Me
S
N
CO2Me
4i
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180
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160
150
140
130
120
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100
90
80
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60
50
40
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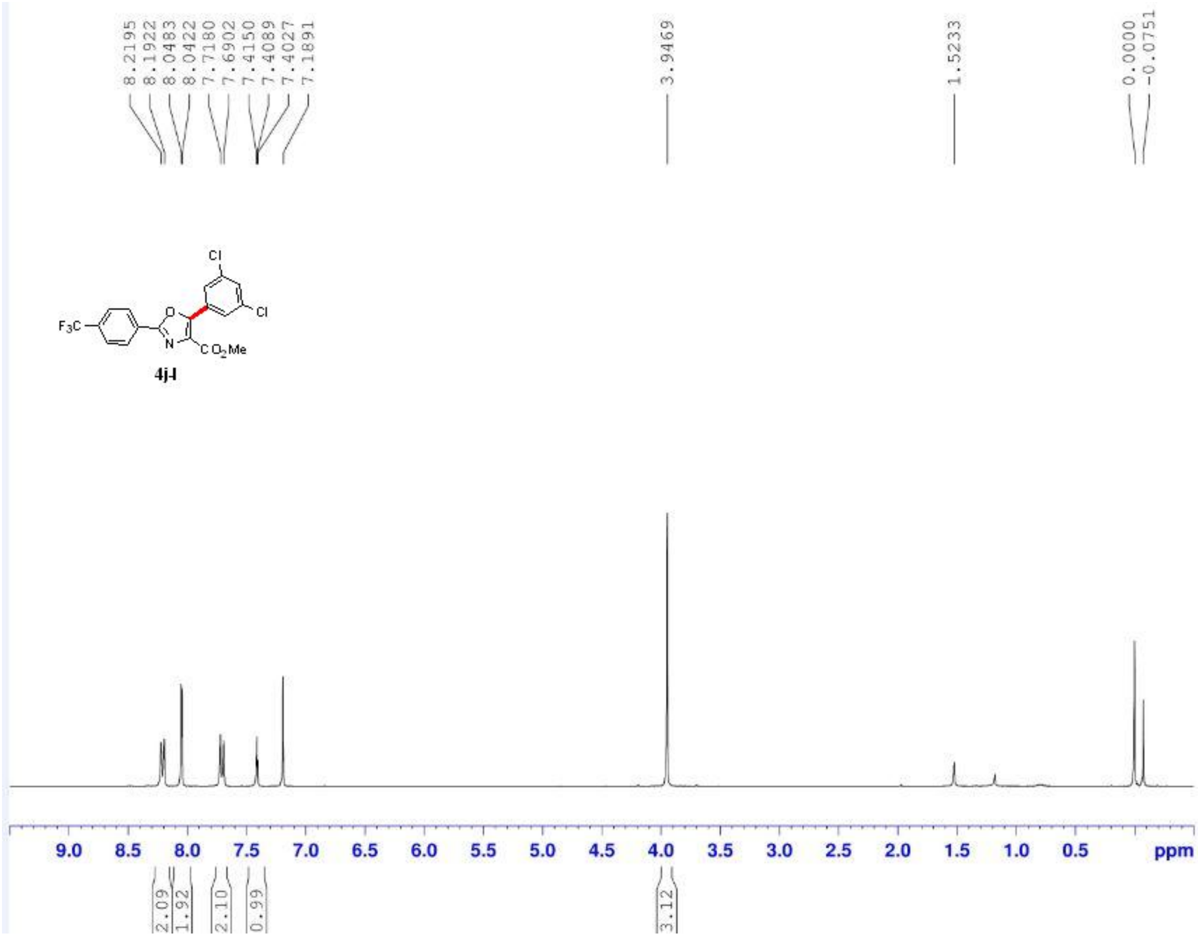
20
10
0
ppm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7.4150
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7.4027
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3.9469
1.5233
0.0000
-0.0751
Cl
Cl
F3C
O
N
CO2Me
4j-l
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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1.5
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0.99
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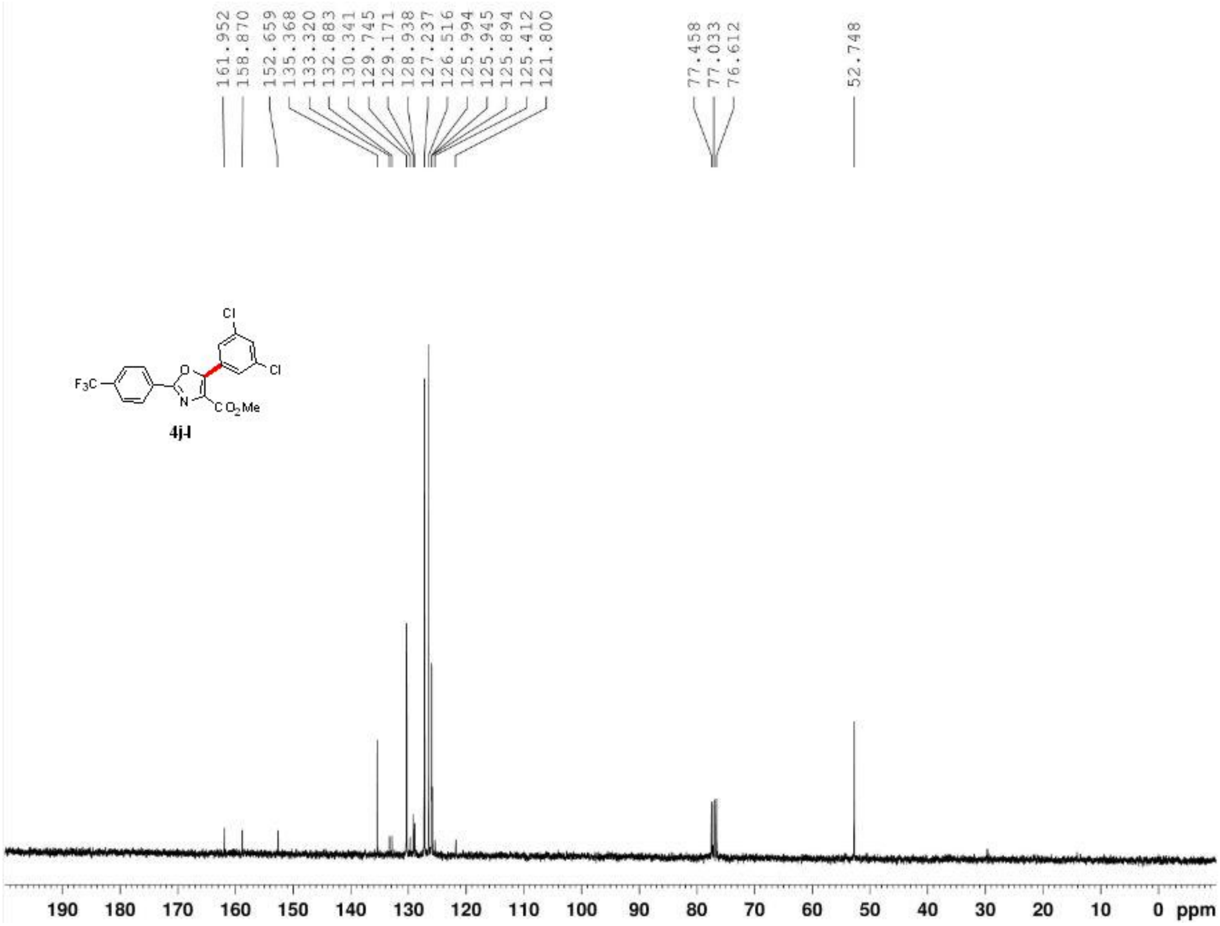
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125.945
125.894
125.412
121.800
77.458
77.033
76.612
52.748
Cl
Cl
F3C
O
N
CO2Me
4j-l
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140
130
120
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20
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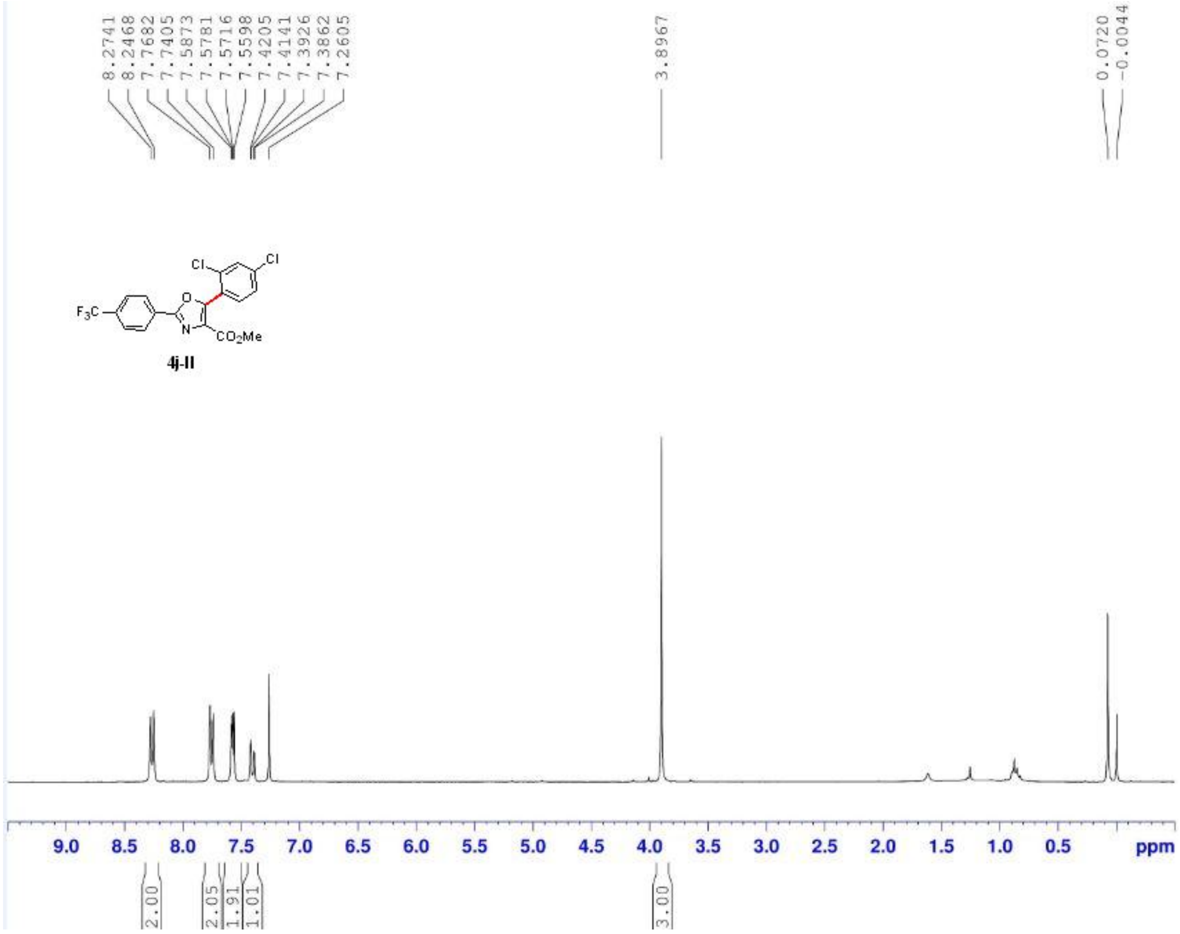
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7.4205
7.4141
7.3926
7.3862
7.2605
3.8967
0.0720
-0.0044
Cl
Cl
O
F3C
N
CO2Me
4j-II
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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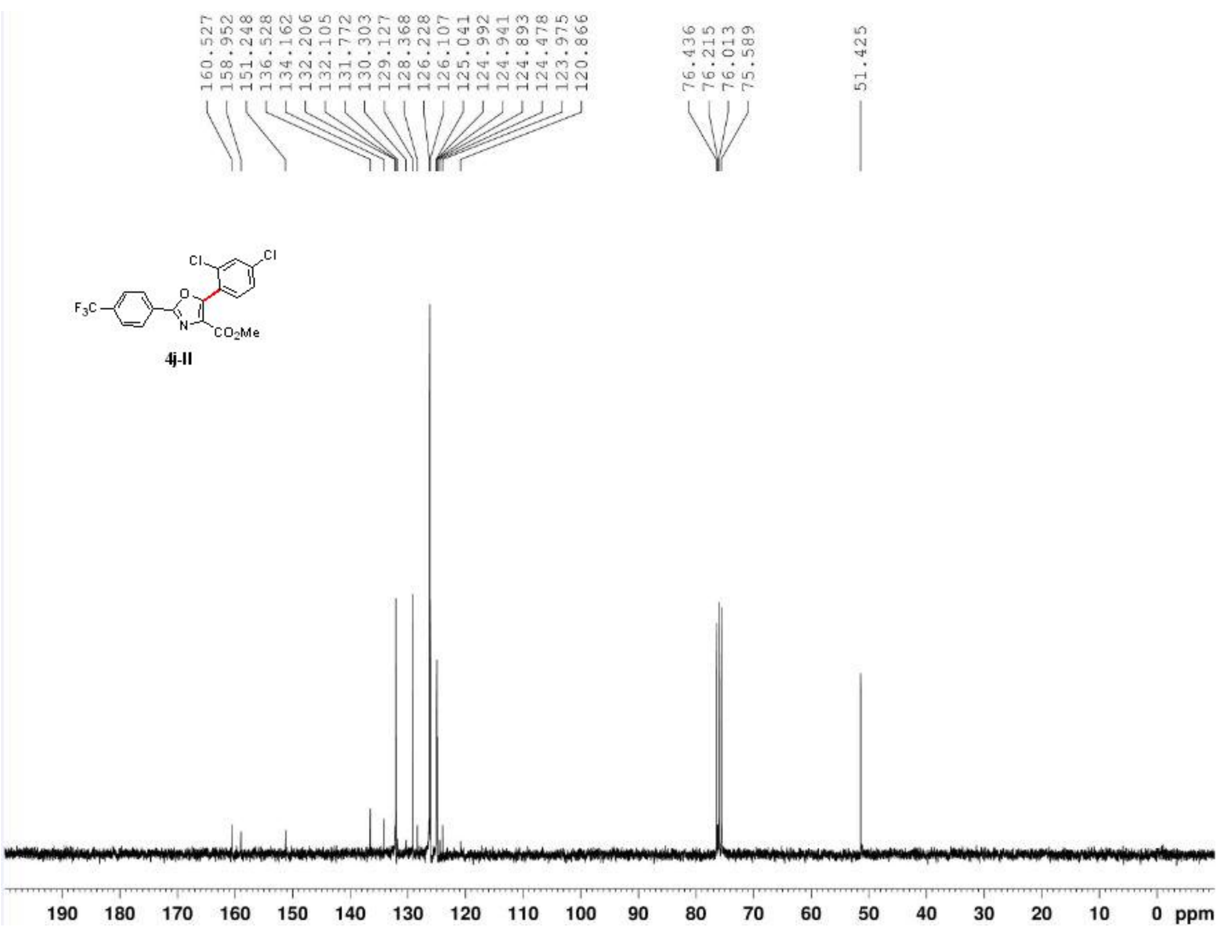
1.91
1.01
3.00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124.941
124.893
124.478
123.975
120.866
76.436
76.215
76.013
75.589
51.425
Cl
Cl
O
F3C
N
CO2Me
4j-II
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140
130
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20
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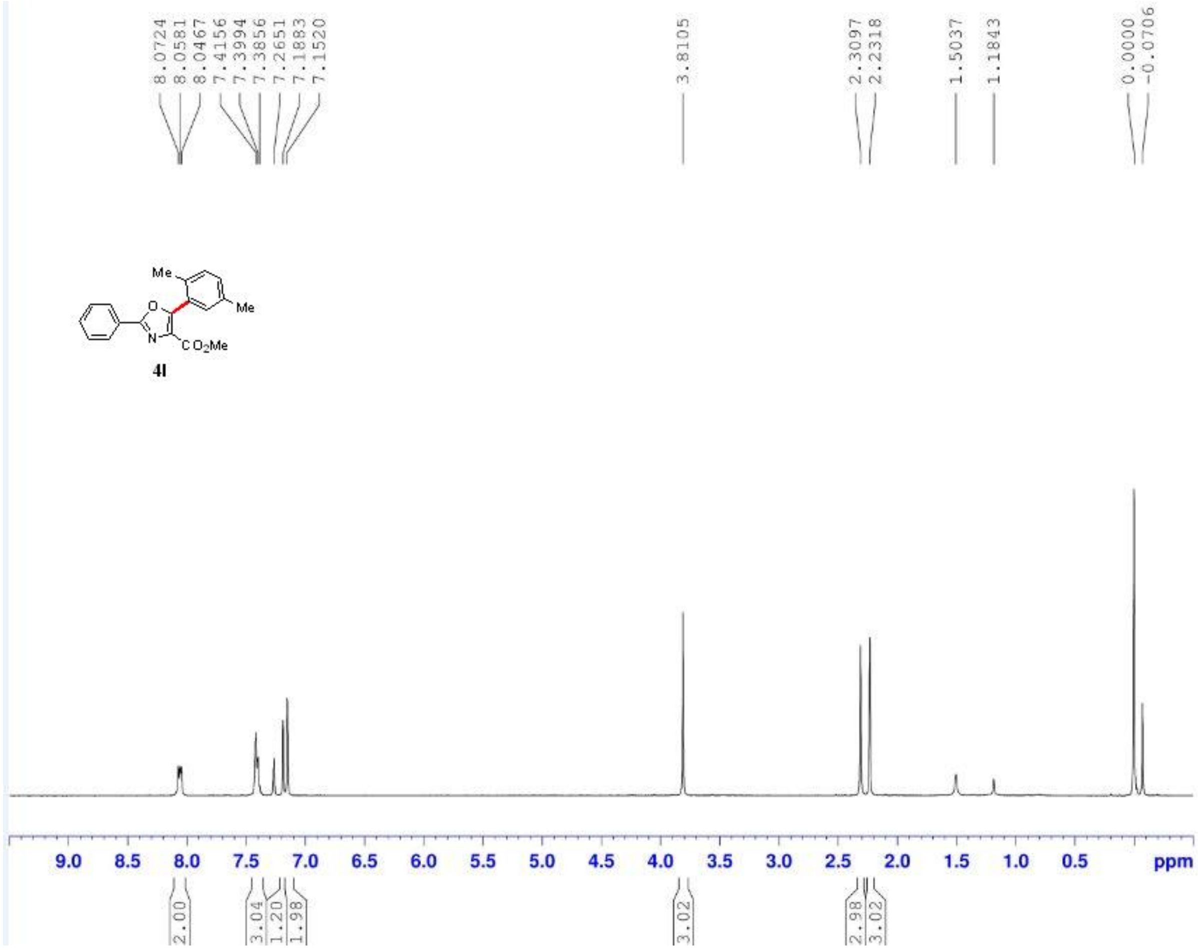
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2.2318
1.5037
1.1843
0.0000
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Me
O
Me
N
CO2Me
4l
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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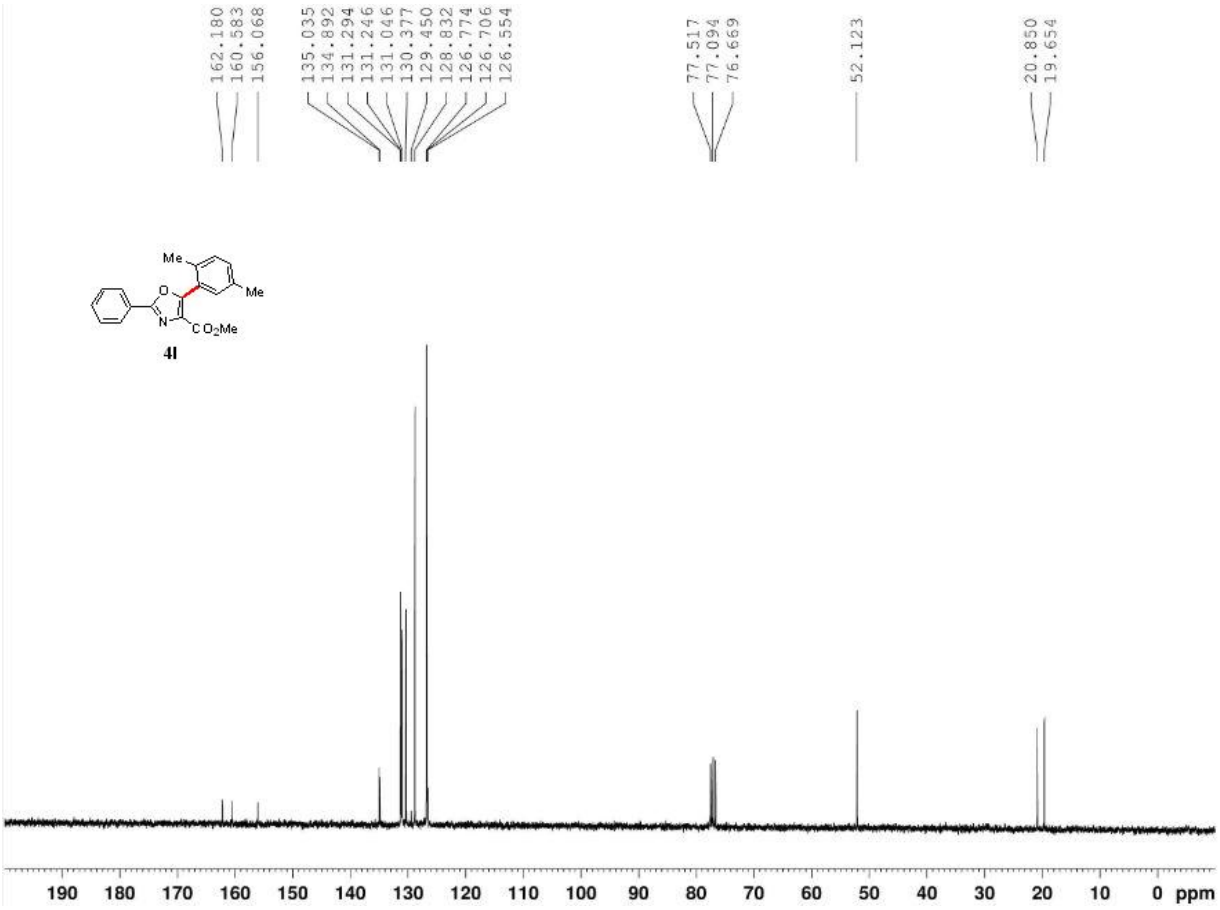
3.02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126.706
126.554
77.517
77.094
76.669
52.123
20.850
19.654
Me
O
Me
N
CO2Me
4l
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140
130
120
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80
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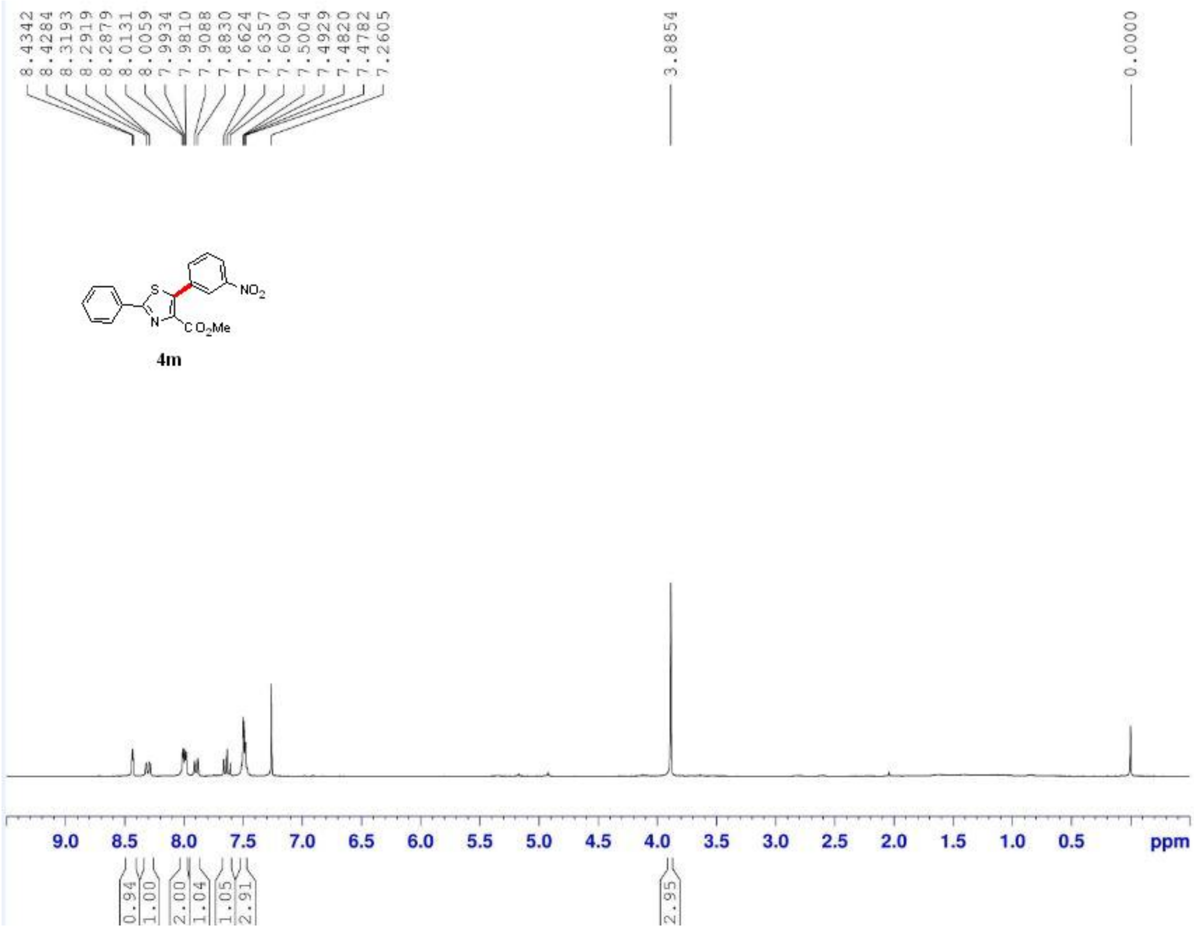
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7.8830
7.6624
7.6357
7.6090
7.5004
7.4929
7.4820
7.4782
7.2605
3.8854
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S
N
NO$_2$
CO$_2$Me
4m
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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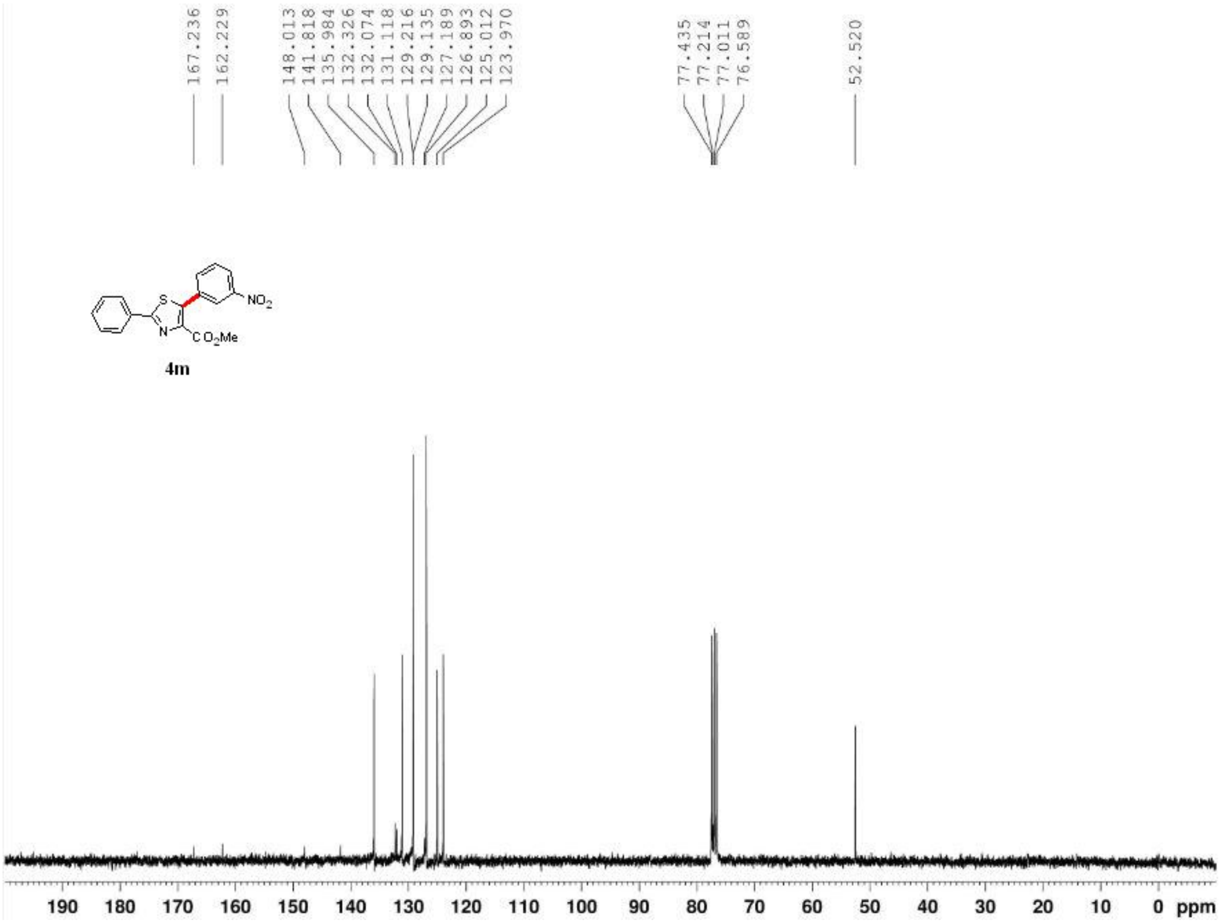
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125.012
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77.214
77.011
76.589
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N
NO$_2$
CO$_2$Me
4m
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20
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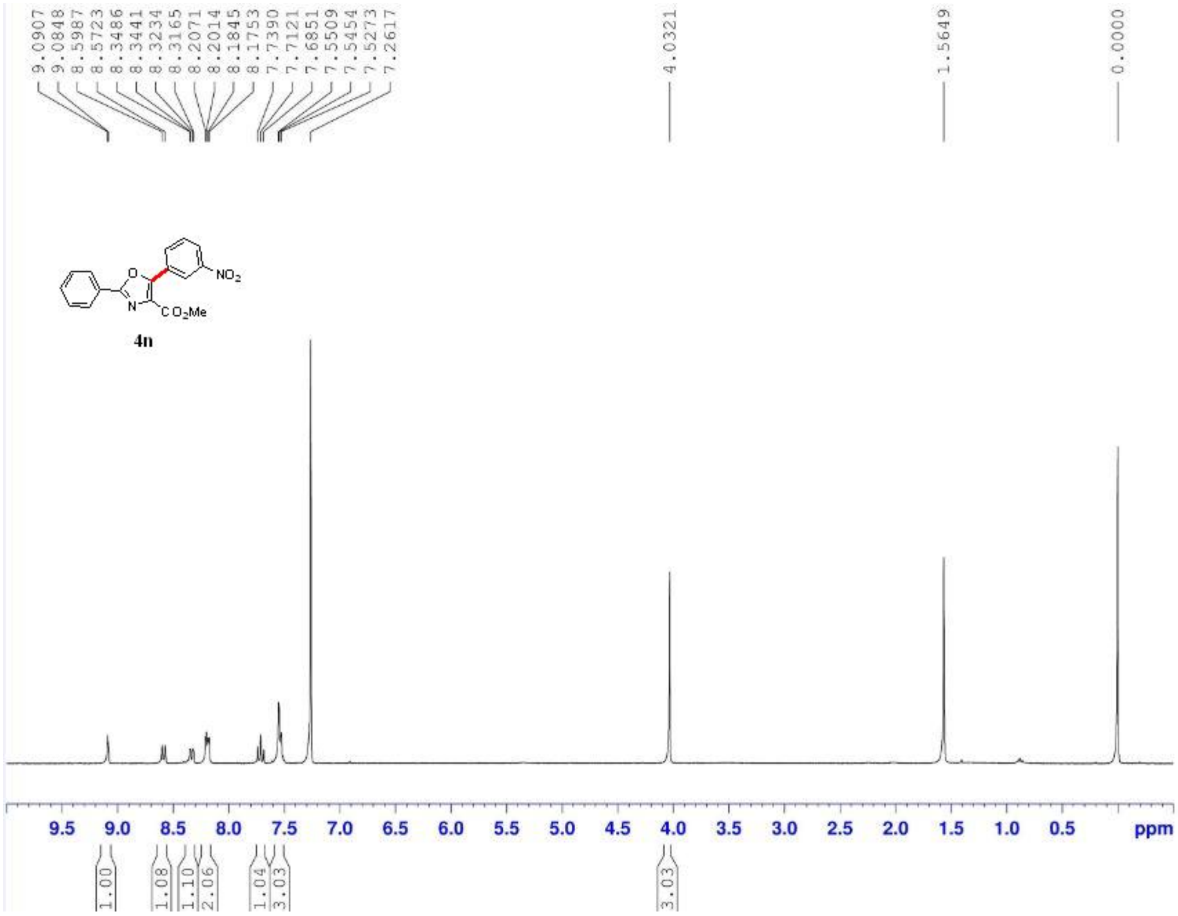
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7.5273
7.2617
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O
N
CO2Me
4n
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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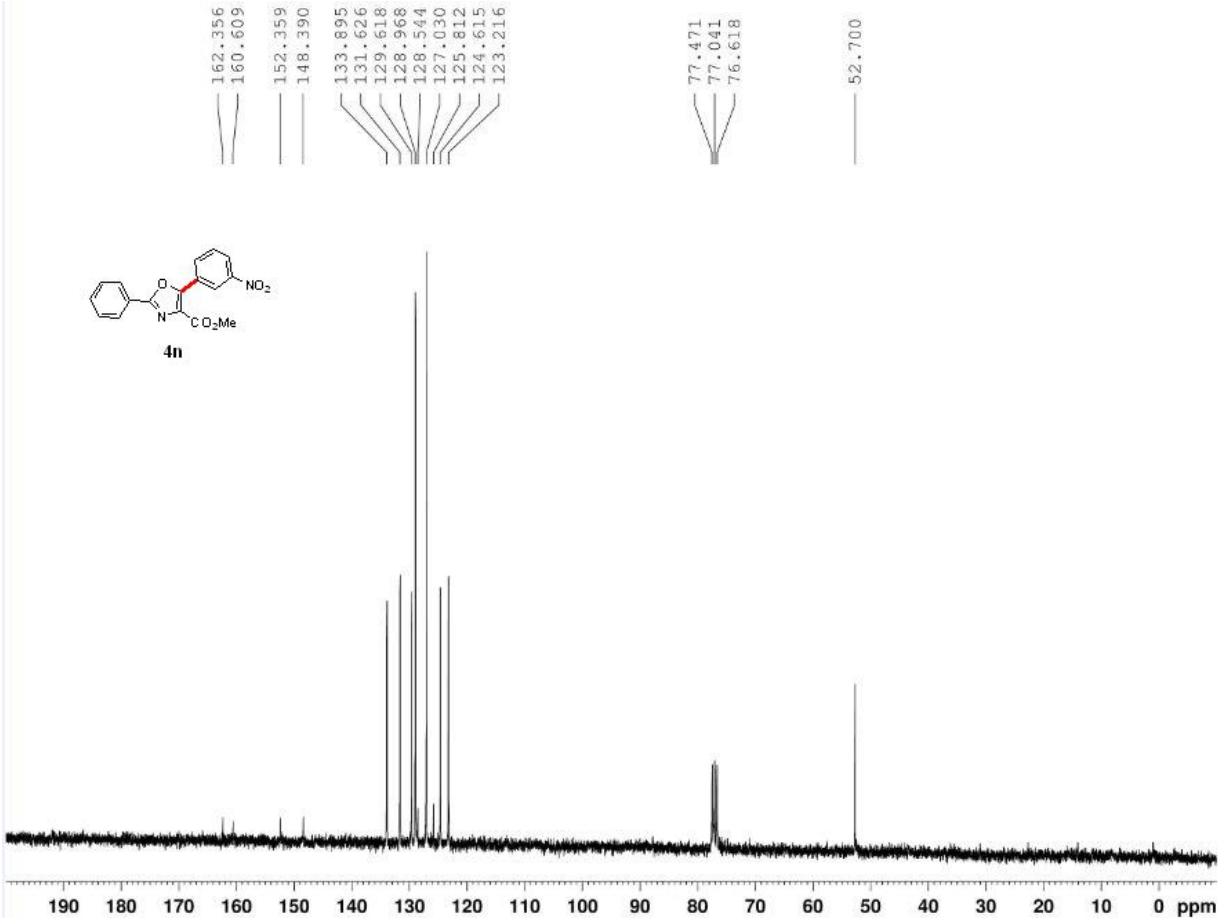
3.03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124.615
123.216
77.471
77.041
76.618
52.700
NO2
O
N
CO2Me
4n
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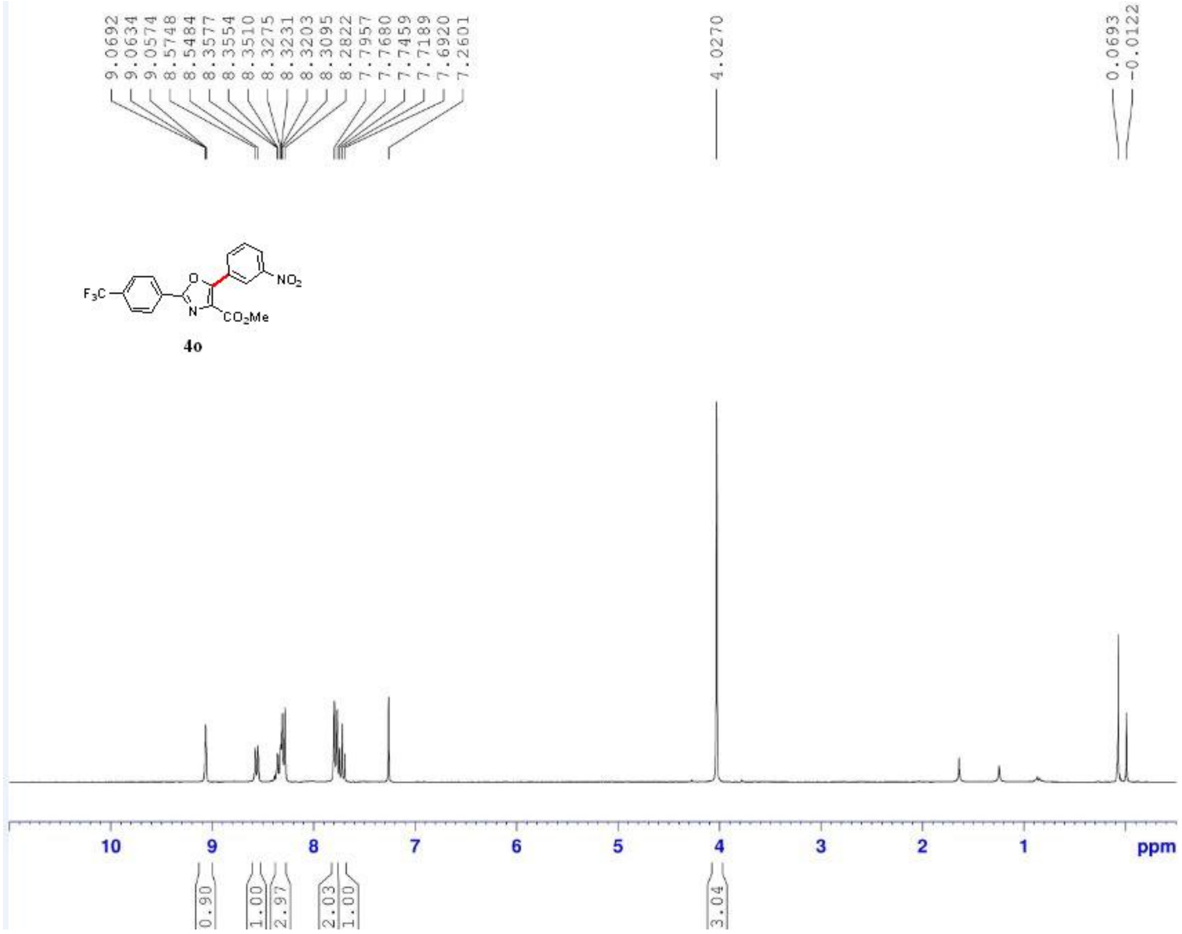
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7.7680
7.7459
7.7189
7.6920
7.2601
4.0270
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F3C
O
N
NO2
CO2Me
10
9
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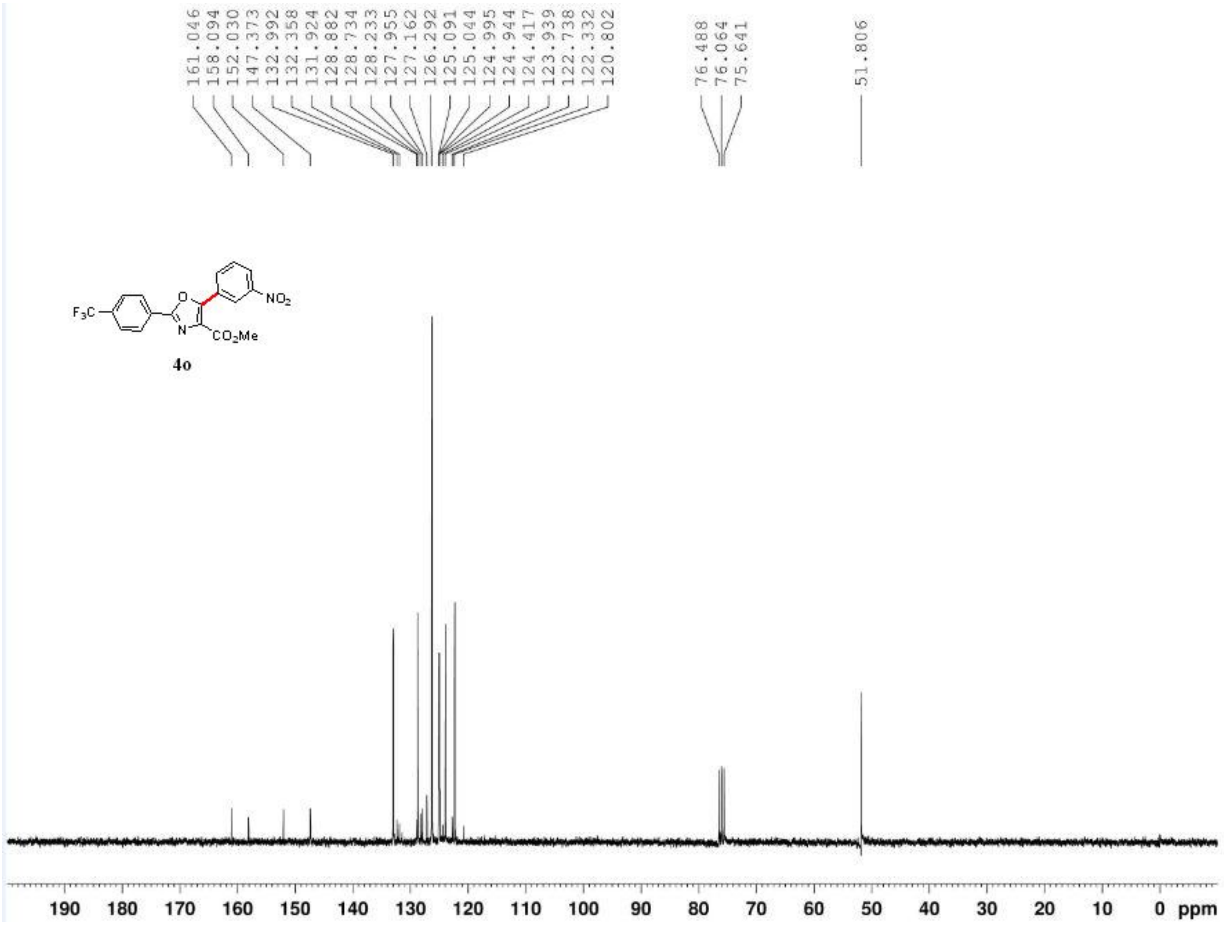
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124.417
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75.641
51.806
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N
NO2
CO2Me
190
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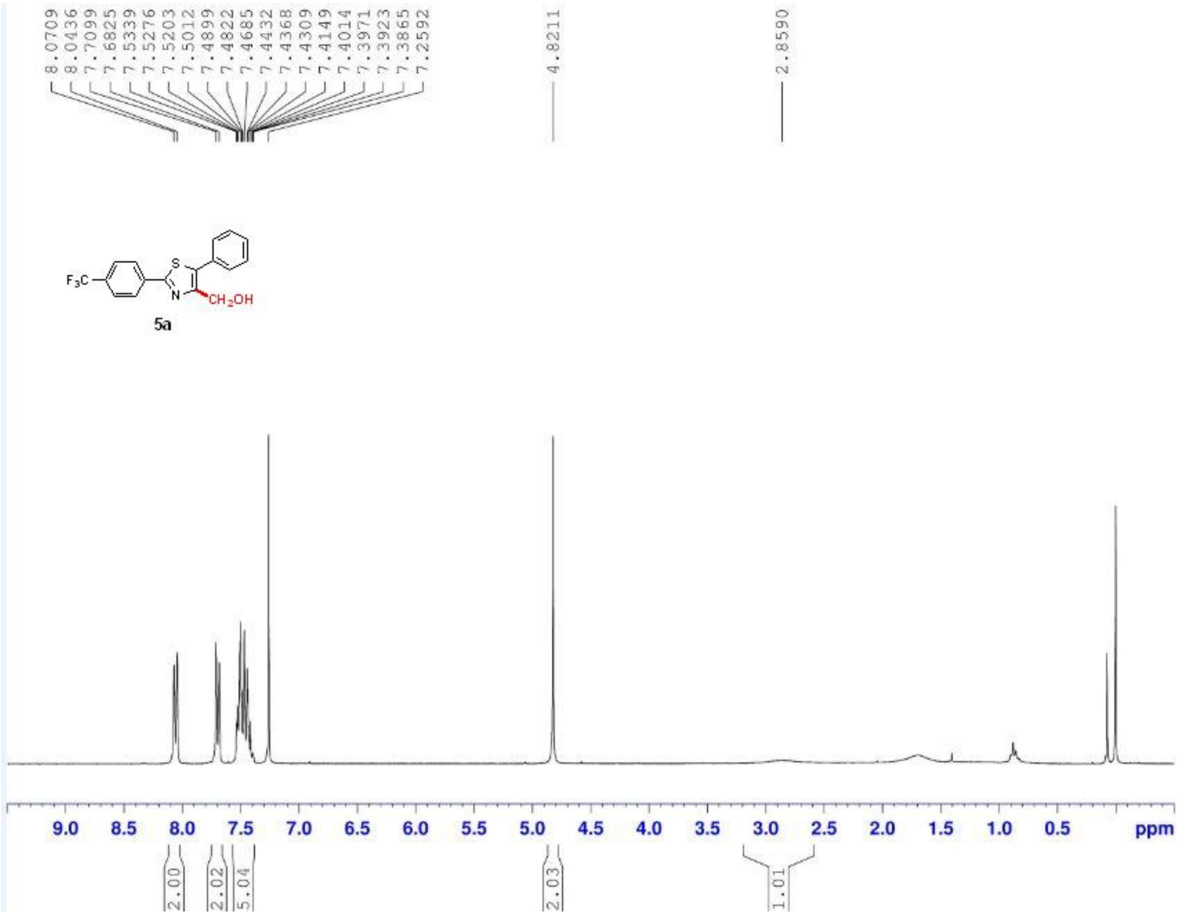
4o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7.3865
7.2592
4.8211
2.8590
F3C
S
N
CH2OH
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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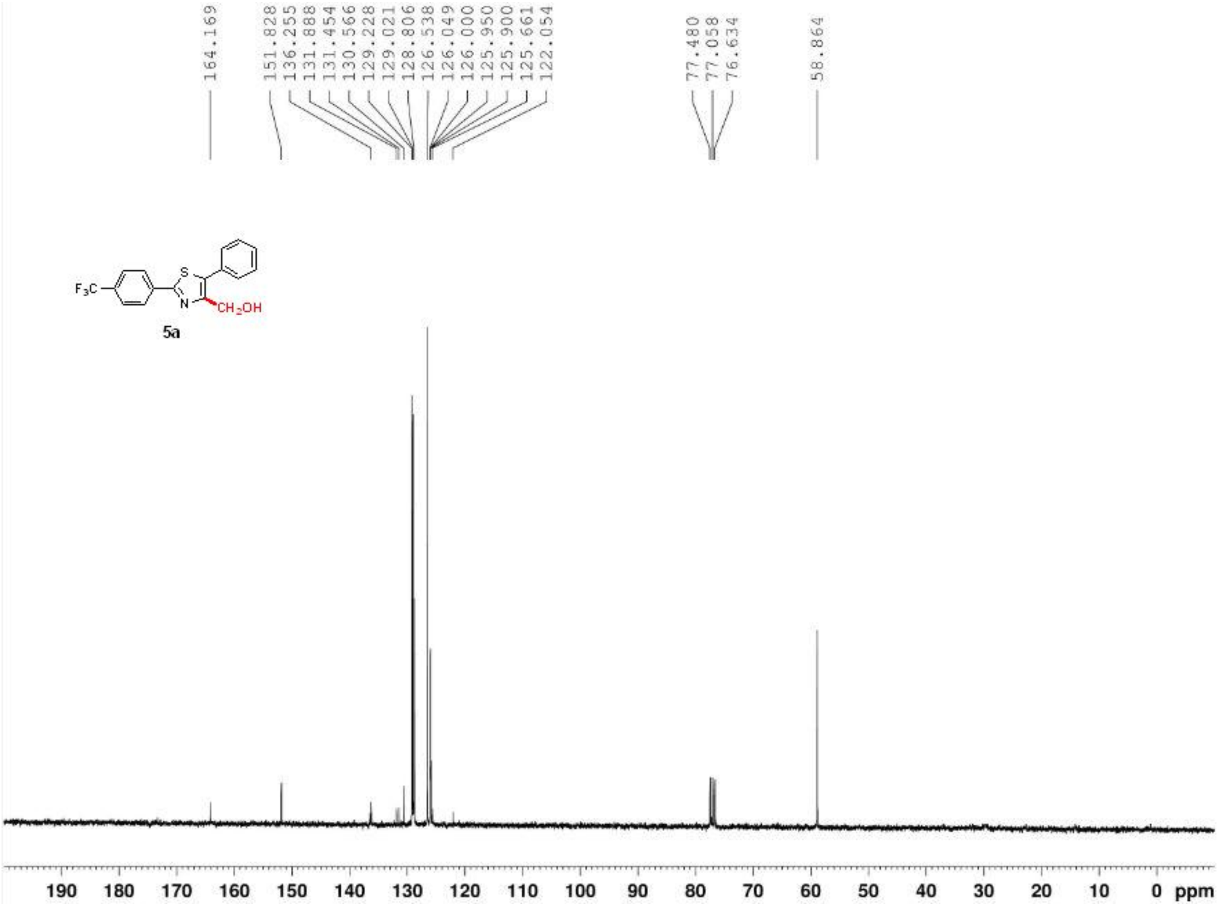
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77.058
76.634
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N
CH2OH
5a
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120
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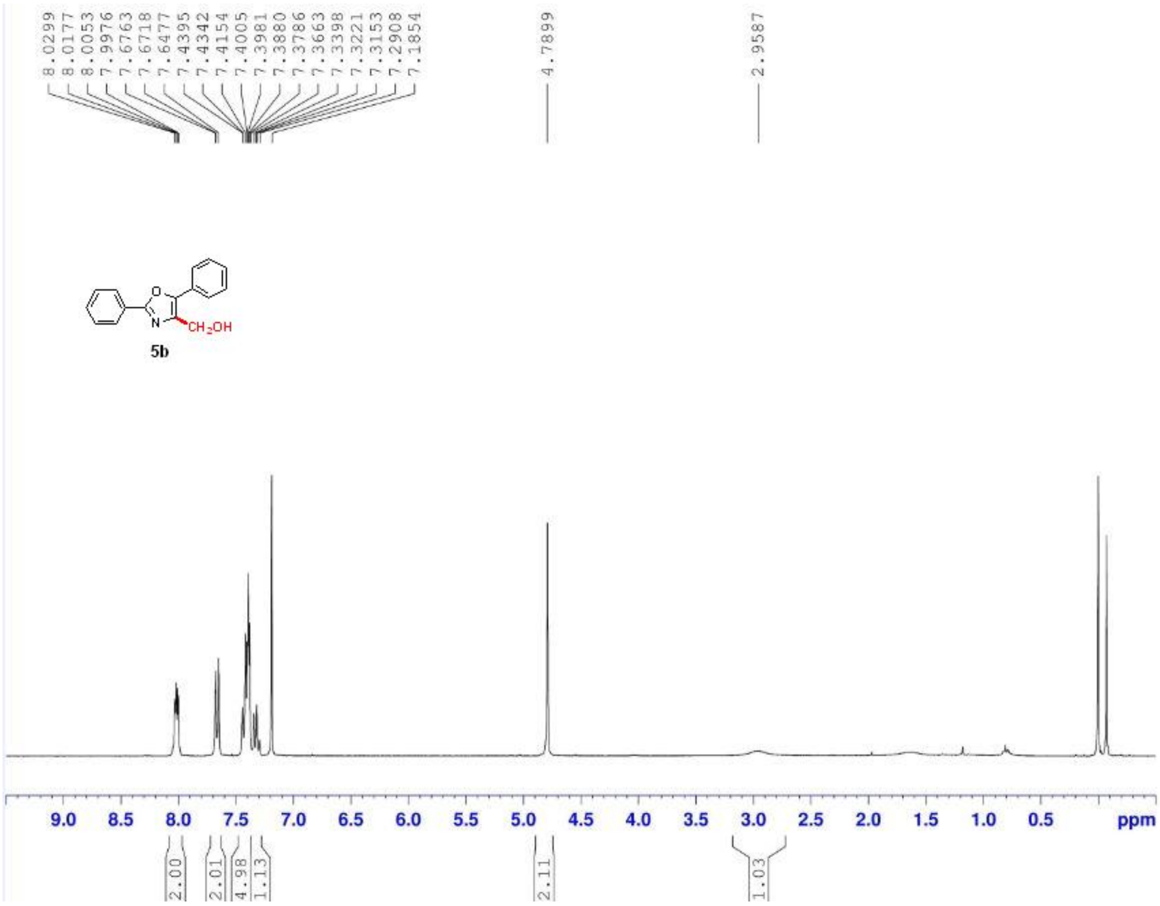
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7.2908
7.1854
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O
N
CH$_2$OH
5b
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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1.0
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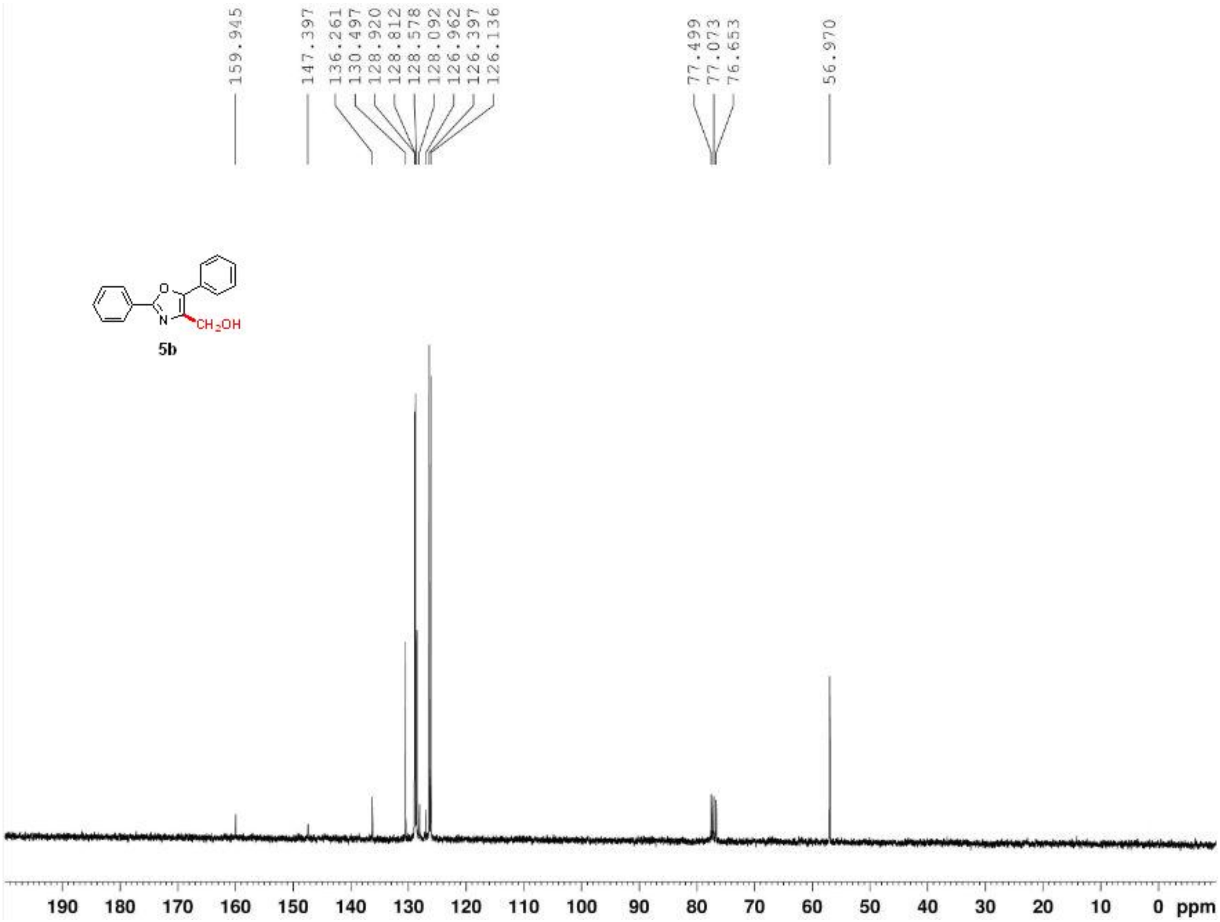
2.11
1.03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77.499
77.073
76.653
56.970
O
N
CH$_2$OH
5b
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100
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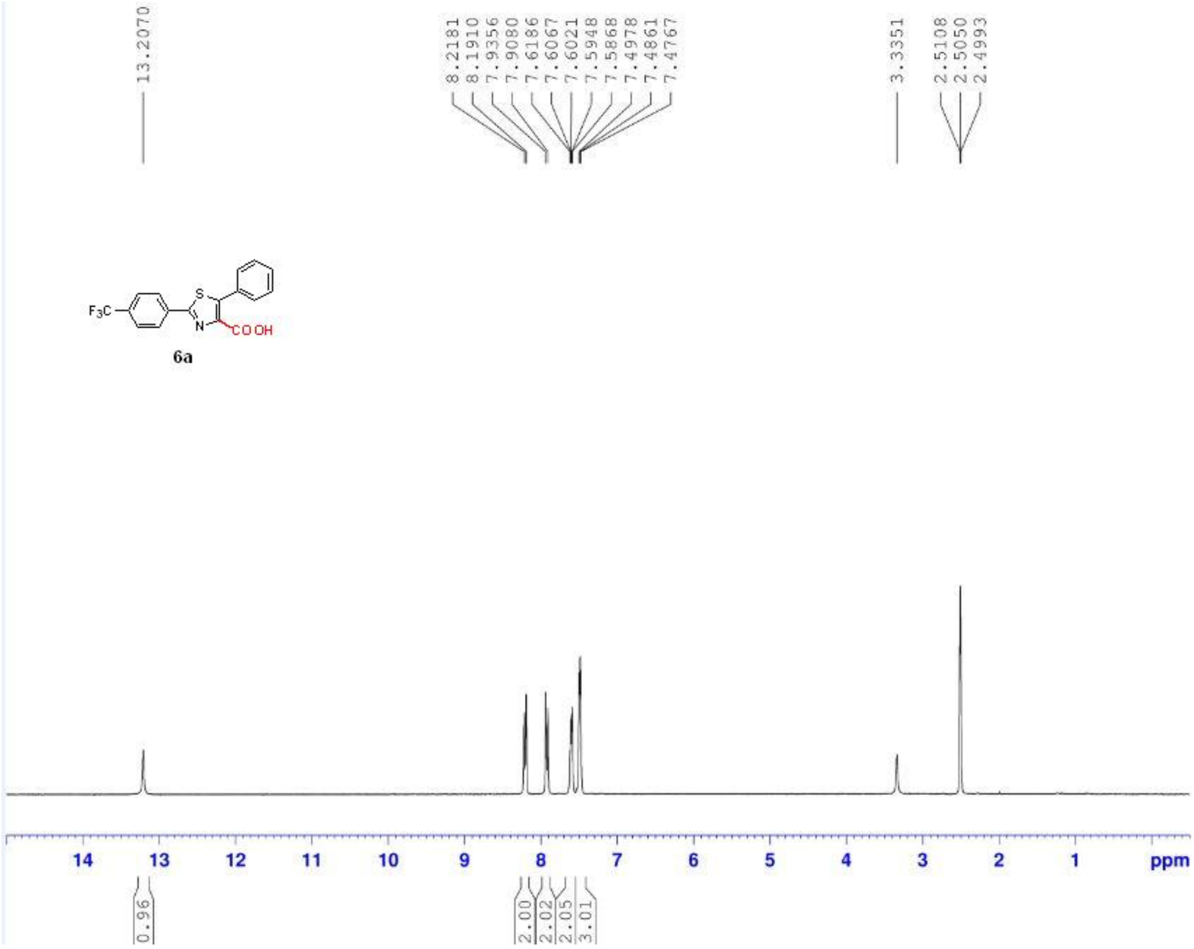
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7.4978
7.4861
7.4767
3.3351
2.5108
2.5050
2.4993
F3C
S
N
COOH
6a
14
13
12
11
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7
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5
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2
1
ppm
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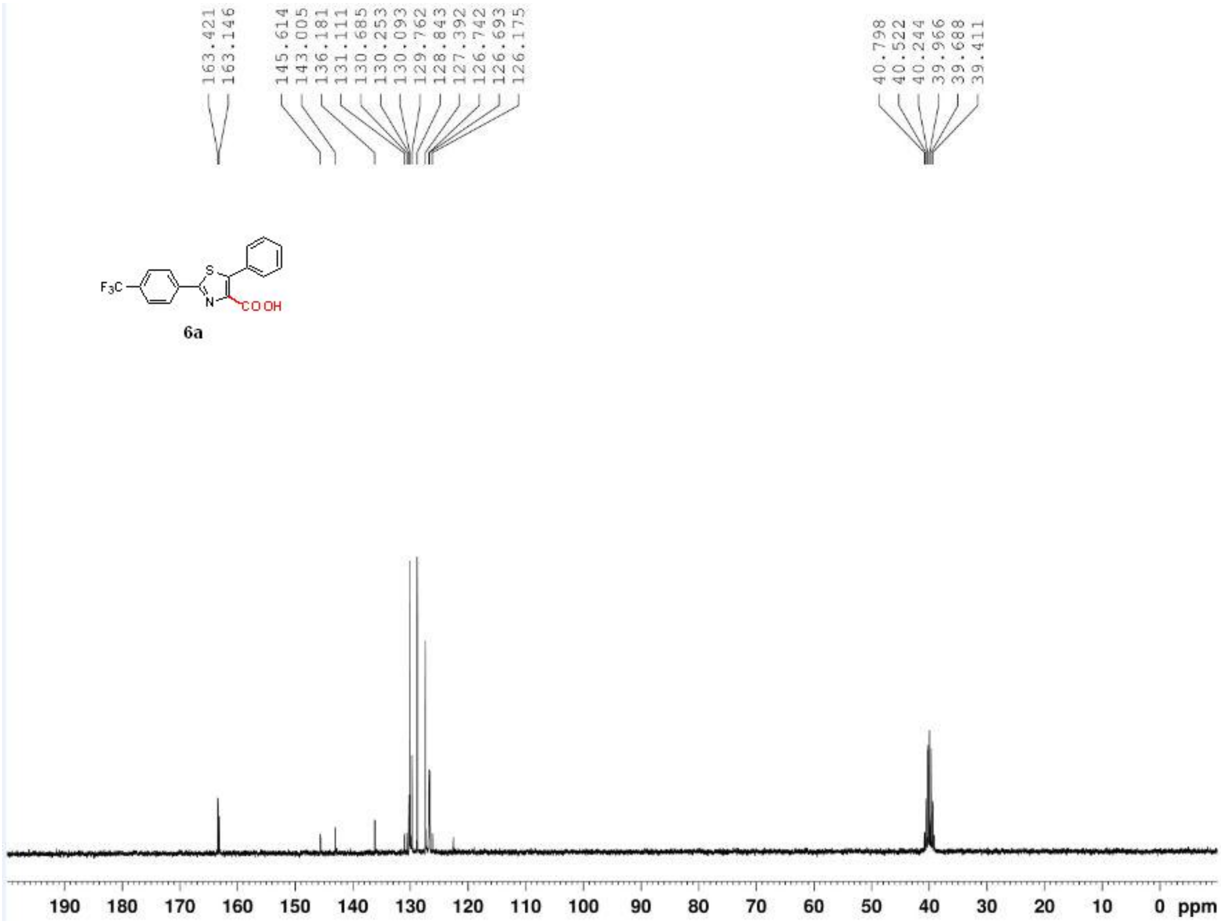
3.01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130.685
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127.392
126.742
126.693
126.175
40.798
40.522
40.244
39.966
39.688
39.411
F3C
S
N
COOH
6a
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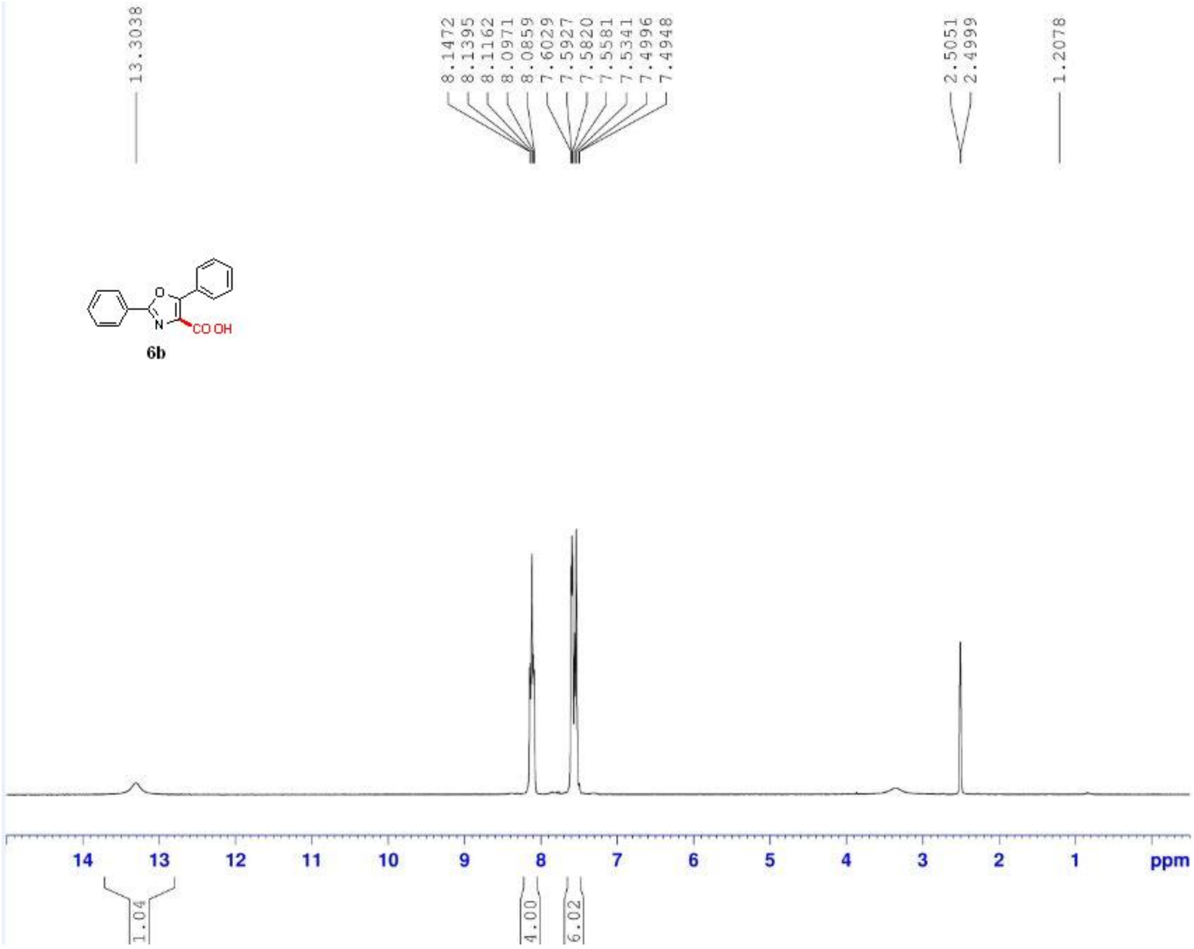
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7.4996
7.4948
2.5051
2.4999
1.2078
O
N
COOH
6b
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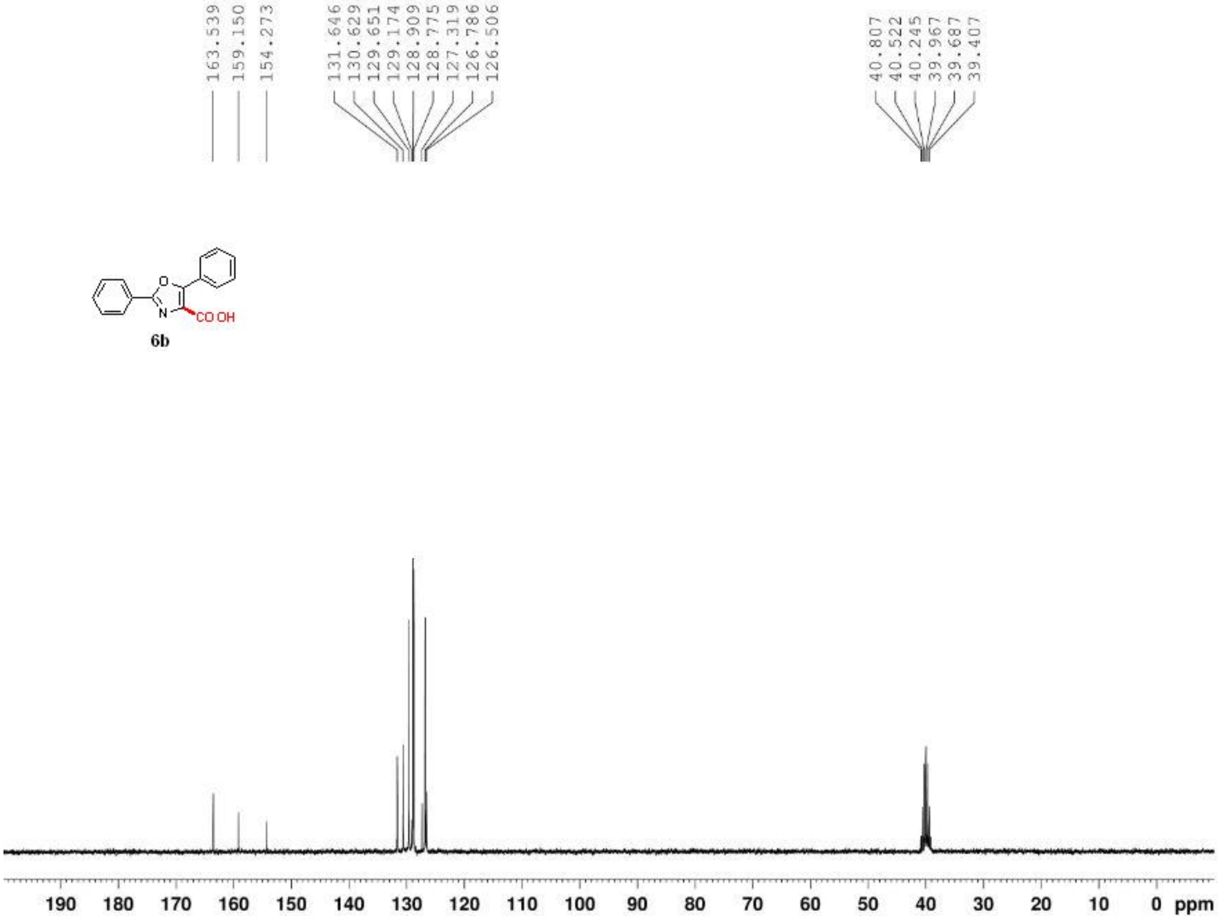
6.02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40.522
40.245
39.967
39.687
39.407
O
N
COOH
6b
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180
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150
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130
120
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100
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80
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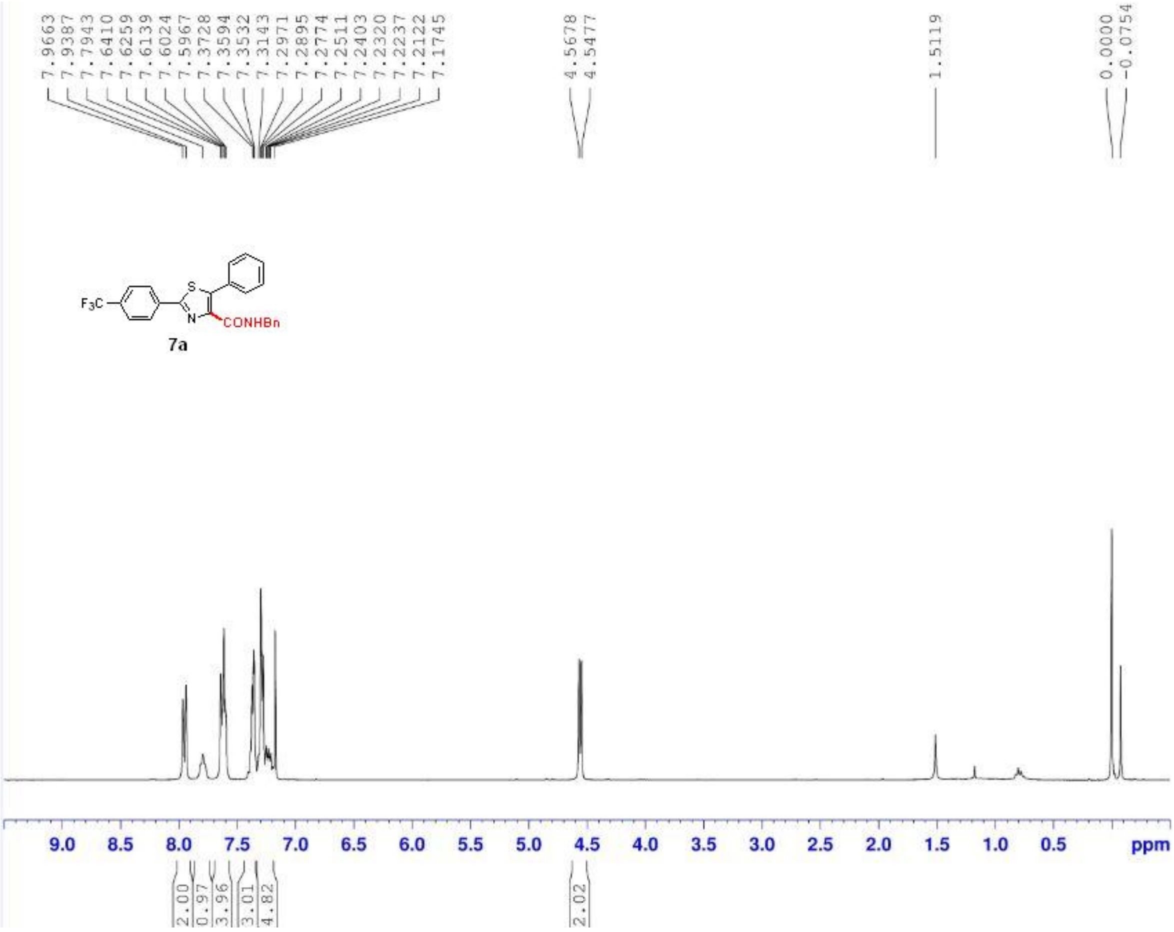
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7.3532
7.3143
7.2971
7.2895
7.2774
7.2511
7.2403
7.2320
7.2237
7.2122
7.1745
4.5678
4.5477
1.5119
0.0000
-0.0754
F3C
S
N
CONHBn
7a
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.0
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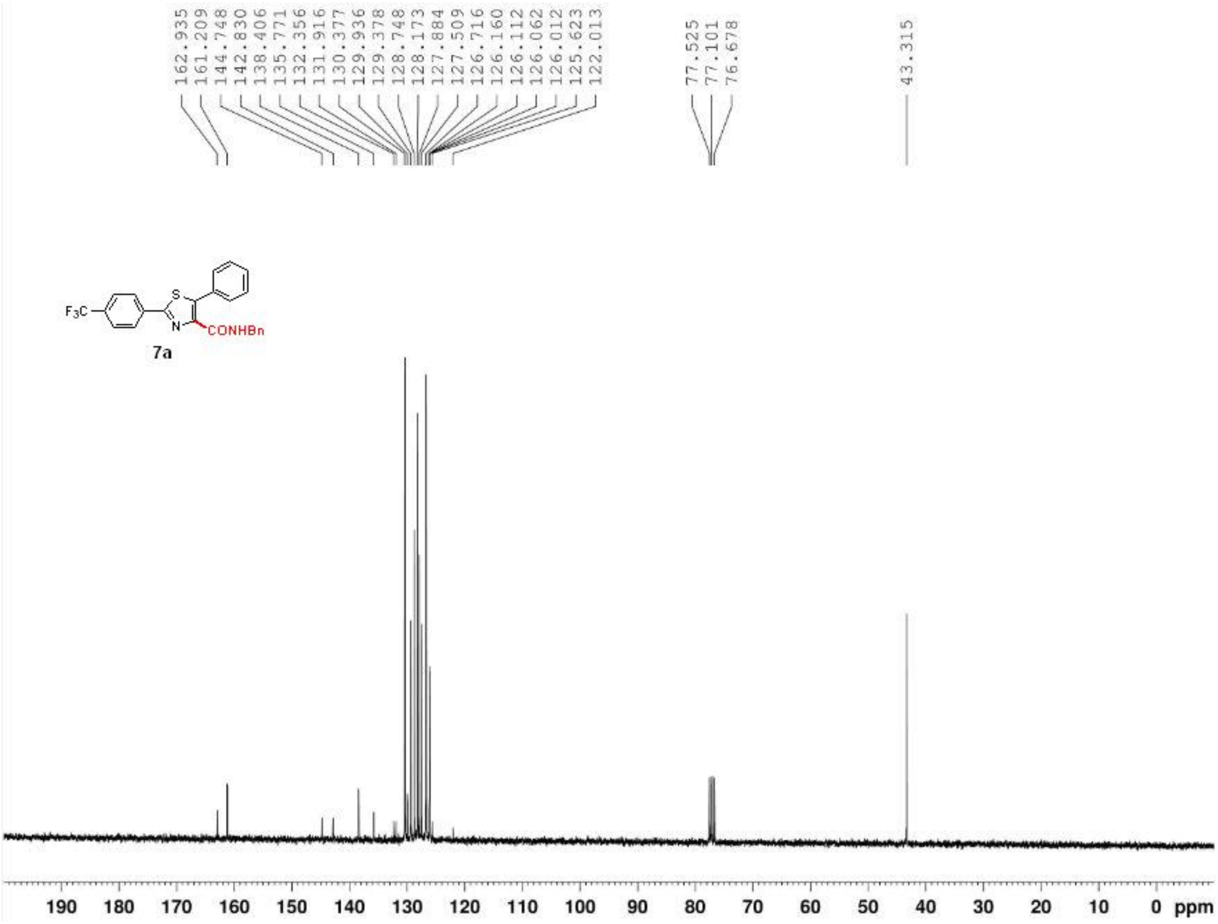
3.01
4.82
2.02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128.173
127.884
127.509
126.716
126.160
126.112
126.062
126.012
125.623
122.013
77.525
77.101
76.678
43.315
F3C
S
N
CONHBn
7a
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140
130
120
110
100
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80
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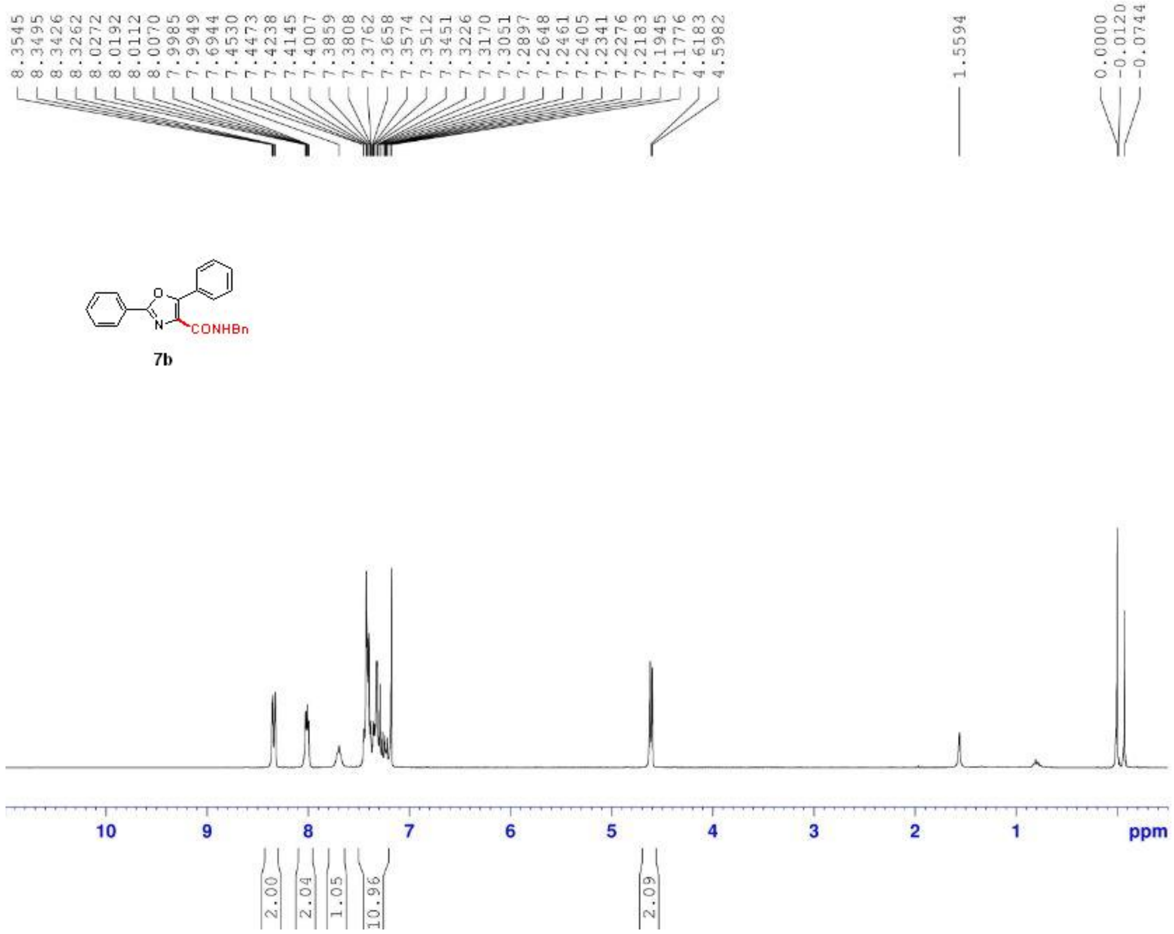
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7.4530
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7.4145
7.4007
7.3859
7.3808
7.3762
7.3658
7.3574
7.3512
7.3451
7.3226
7.3170
7.3051
7.2897
7.2648
7.2461
7.2405
7.2341
7.2276
7.2183
7.1945
7.1776
4.6183
4.5982
1.5594
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-0.0120
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O
N
CONHBn
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4
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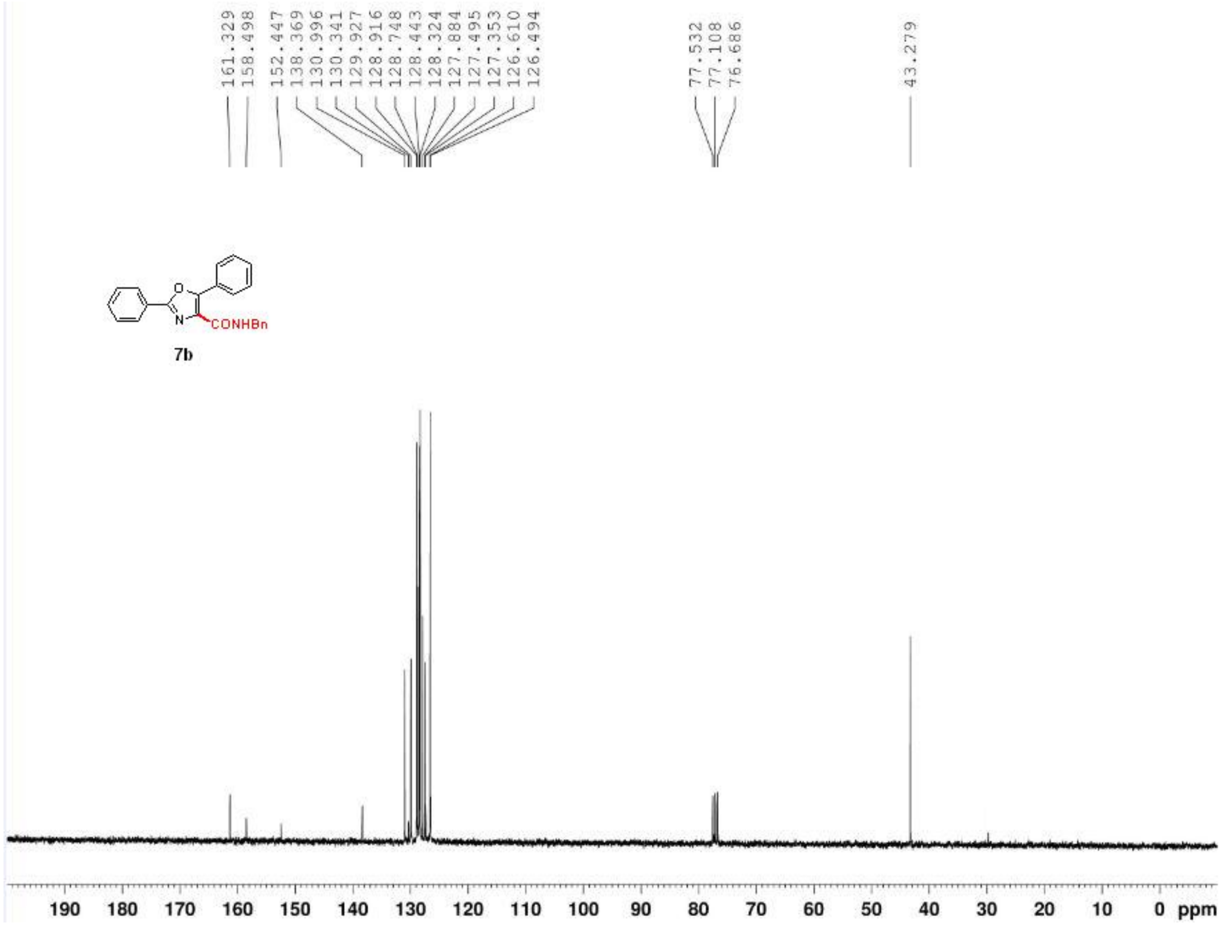
2.09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127.353
126.610
126.494
77.532
77.108
76.686
43.279
O
N
CONHBn
7b
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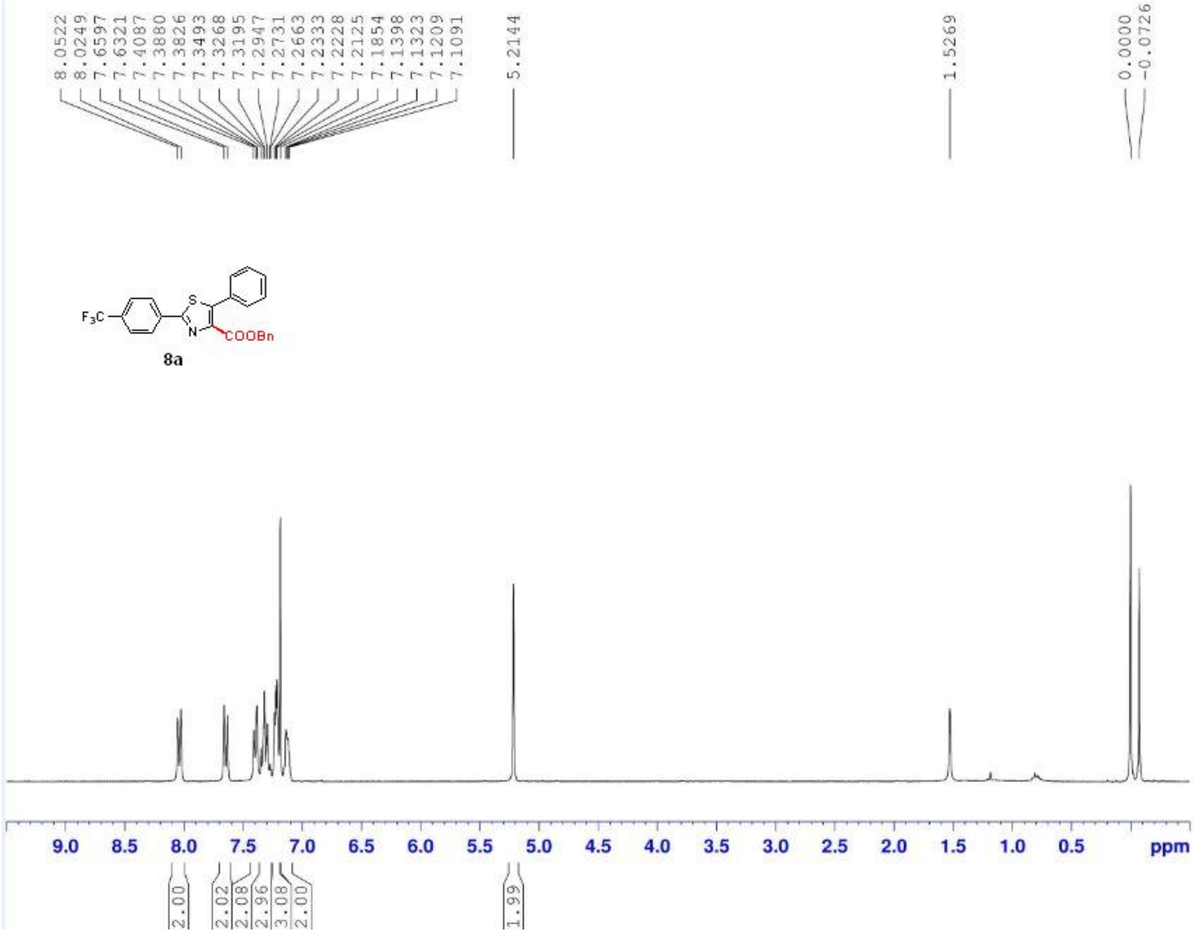
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7.3268
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7.2947
7.2731
7.2663
7.2333
7.2228
7.2125
7.1854
7.1398
7.1323
7.1209
7.1091
5.2144
1.5269
0.0000
-0.0726
F$_3$C
S
N
COOBn
8a
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.0
0.5
ppm
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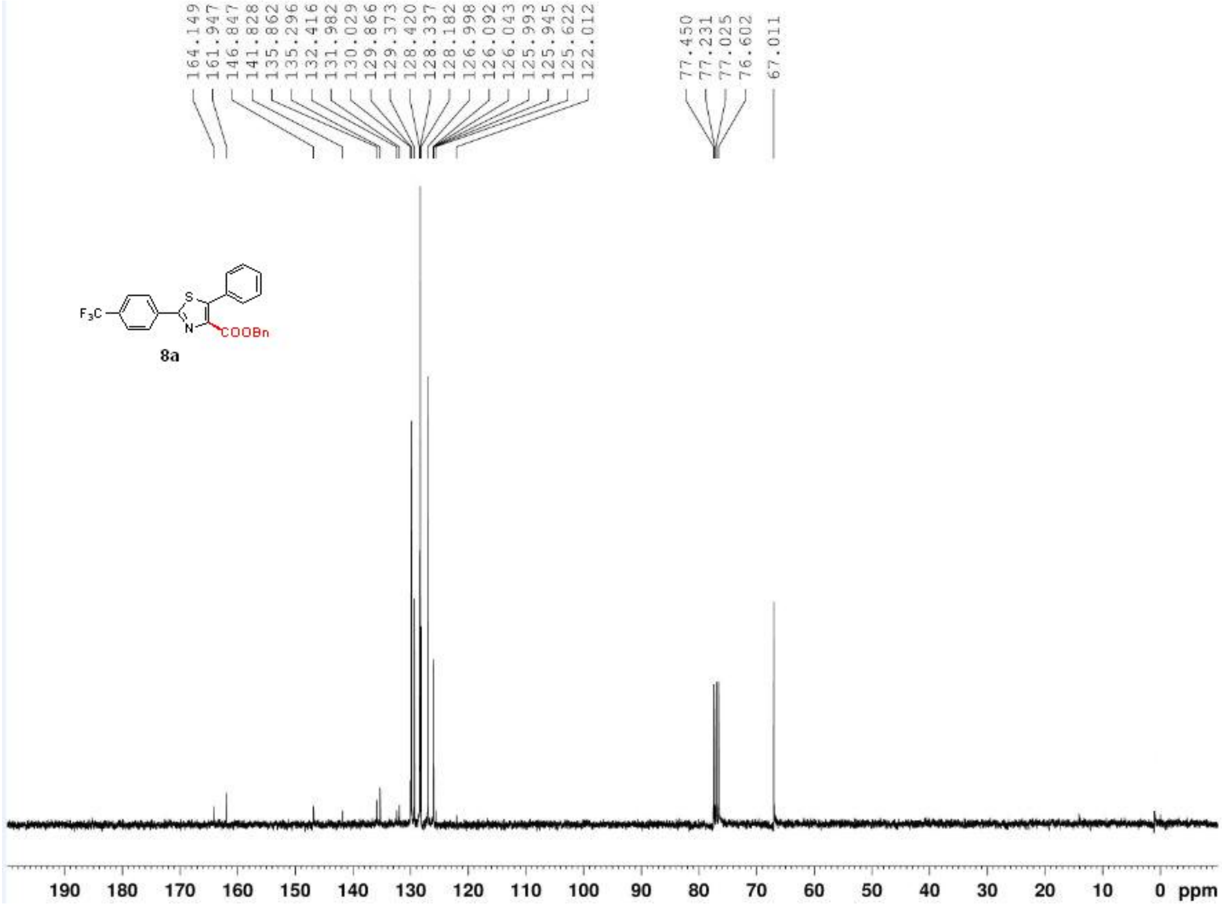
2.02
2.08
2.96
3.08
2.00
1.99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130.029
129.866
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128.420
128.337
128.182
126.998
126.092
126.043
125.993
125.945
125.622
122.012
77.450
77.231
77.025
76.602
67.011
F$_3$C
S
N
COOBn
8a
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170
160
150
140
130
120
110
100
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80
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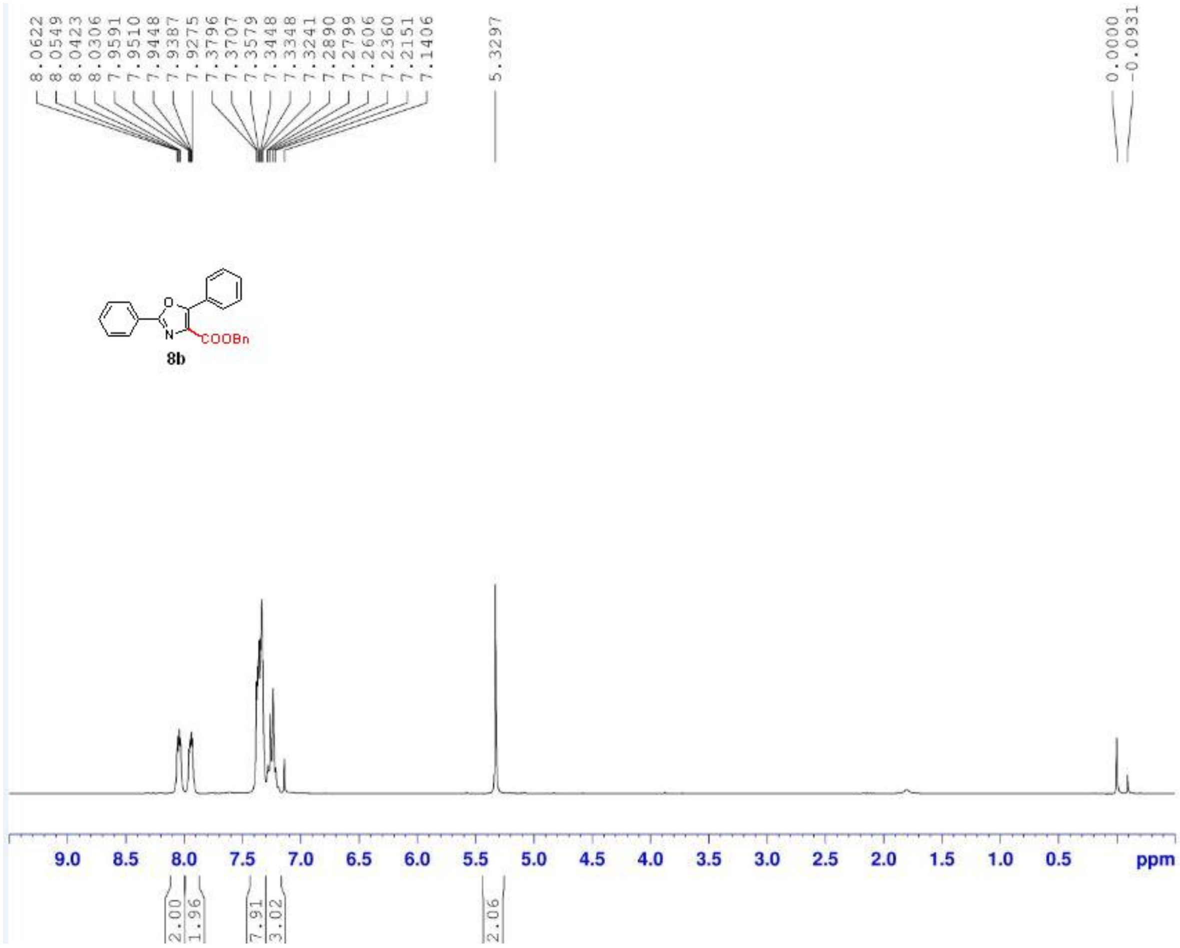
50
40
30
20
10
0
ppm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7.3579
7.3448
7.3348
7.3241
7.2890
7.2799
7.2606
7.2360
7.2151
7.1406
5.3297
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-0.0931
O
N
COOBn
8b
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.0
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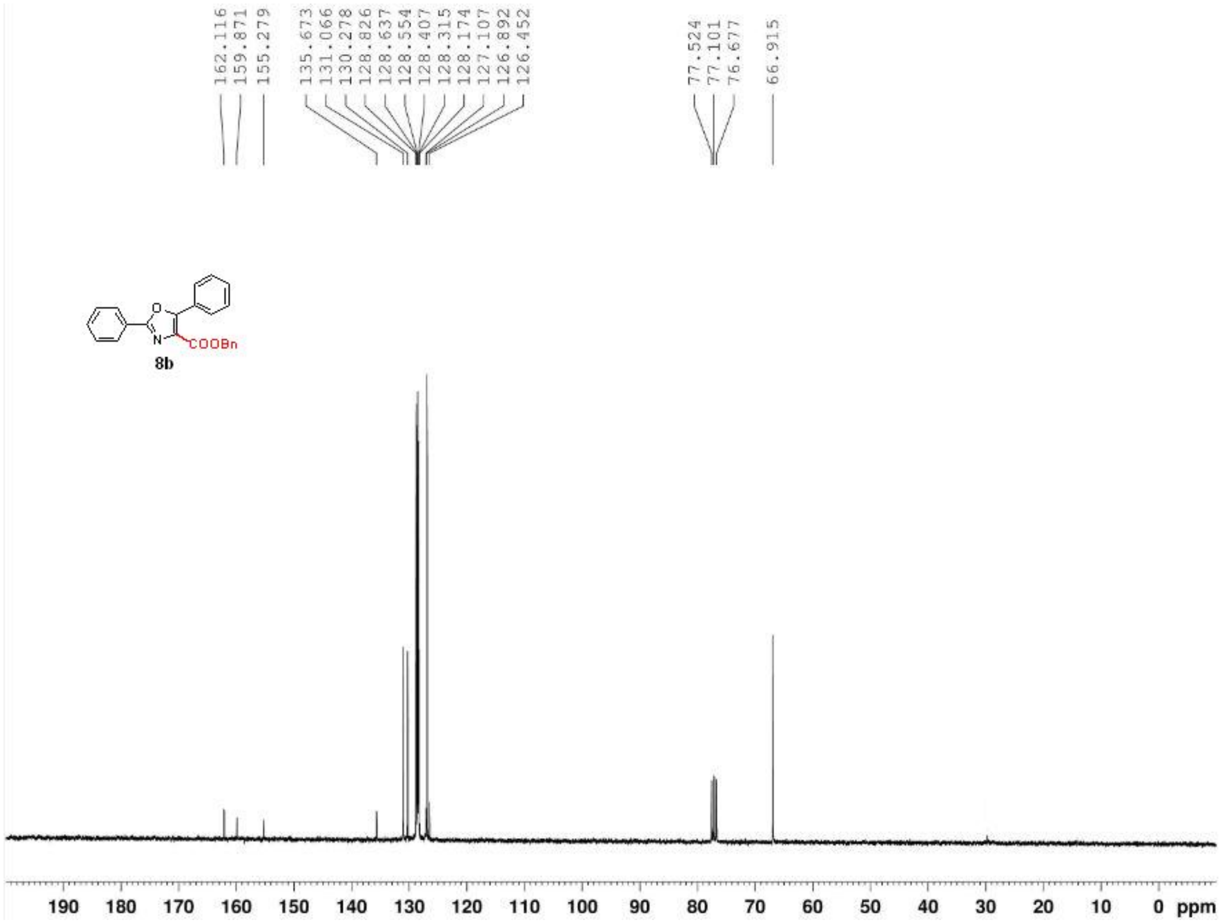
1.96
7.91
3.02
2.06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128.407
128.315
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127.107
126.892
126.452
77.524
77.101
76.677
66.915
O
N
COOBn
8b
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120
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100
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80
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60
50
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20
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0
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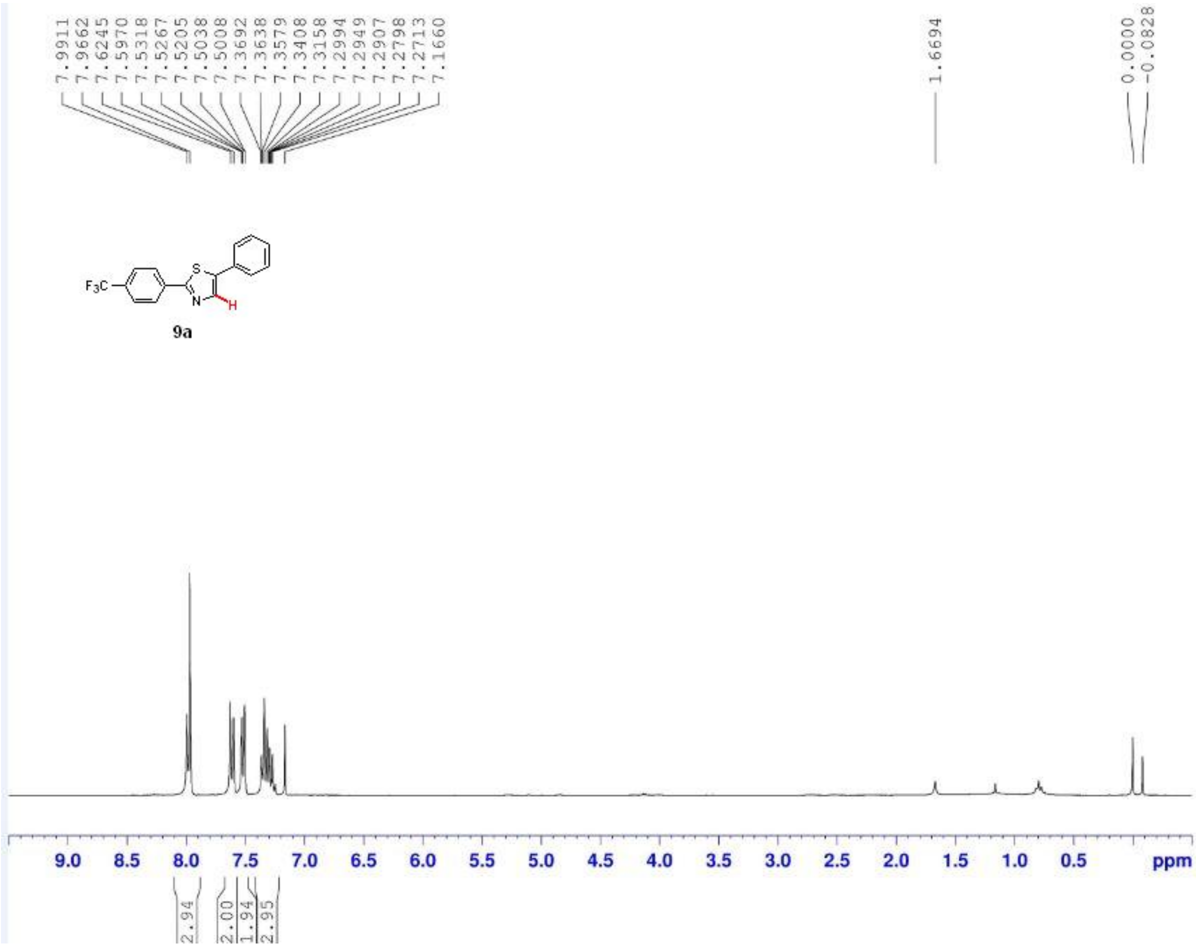
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7.3579
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7.2994
7.2949
7.2907
7.2798
7.2713
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-0.0828
F3C
S
N
H
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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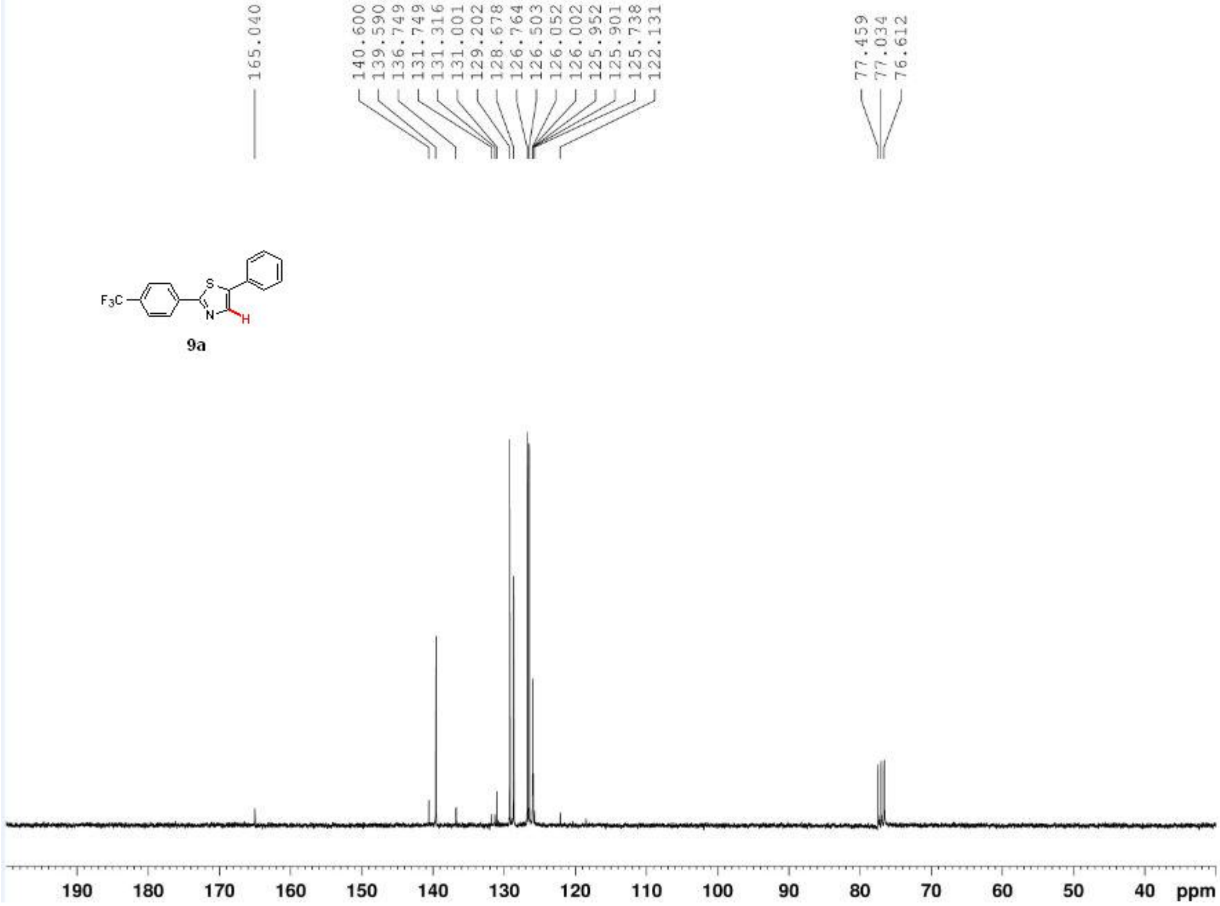
9a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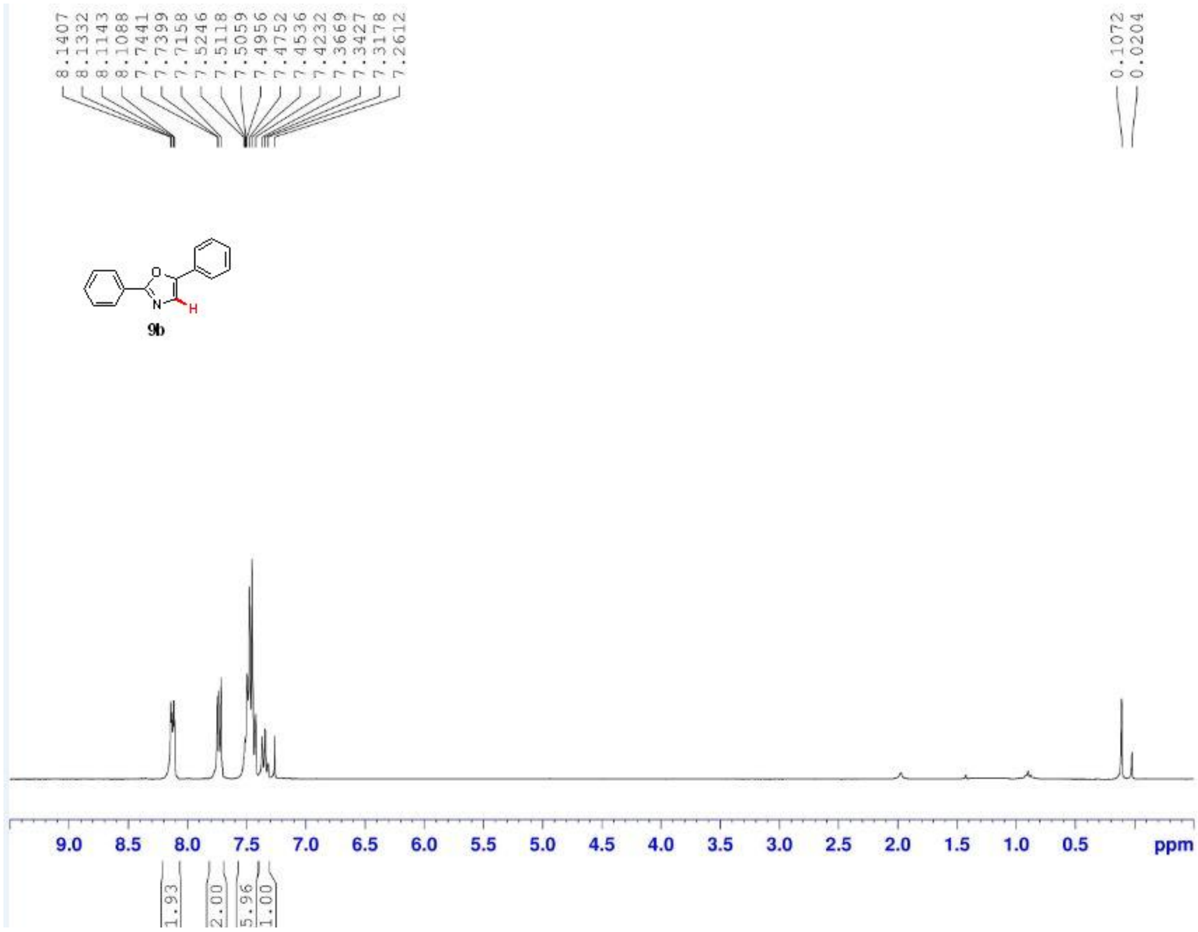
126.052
126.002
125.952
125.901
125.738
122.131
77.459
77.034
76.612
F3C
S
N
H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

9a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7.4752
7.4536
7.4232
7.3669
7.3427
7.3178
7.2612
0.1072
0.0204
O
N
H
9b
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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ppm
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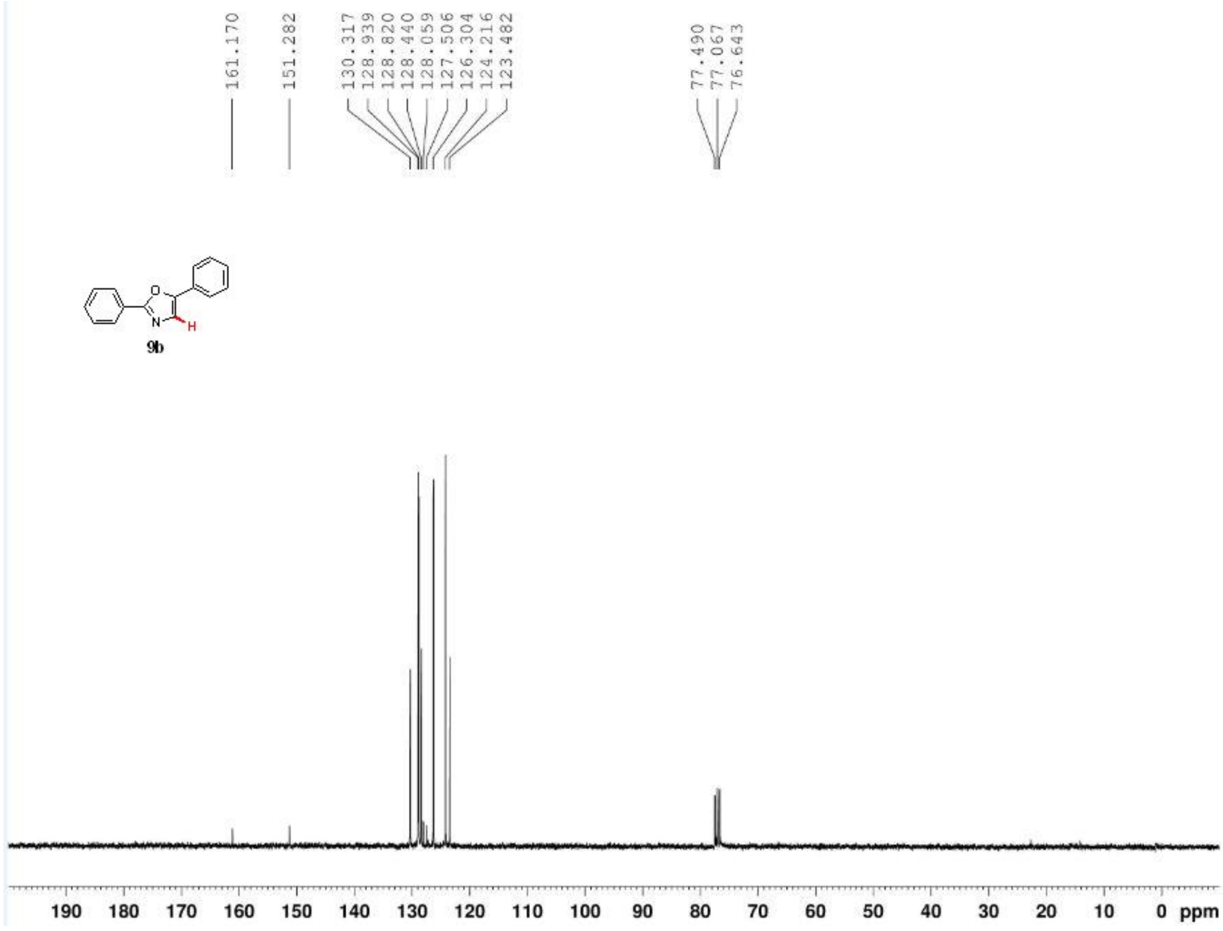
1.00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124.216
123.482
77.490
77.067
76.643
O
N
H
9b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm