

Decarboxylative Amination of Benzoic Acids Bearing Electron-Donating Substituents and Non-Activated Amines

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Supporting Information

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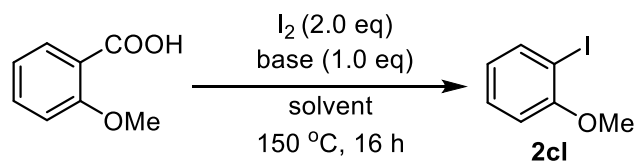
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General information.

All reactions were carried out under an argon atmosphere using standard Schlenk-Lines. ^1H , ^{13}C and ^{19}F NMR spectra were acquired on 400 MHz, 100 MHz, 376 MHz on JOEL-ZETA 400 MHz or Bruker-AVANCE III-400 MHz spectrometer (400 MHz for ^1H ; 100 MHz for ^{13}C ; 376 MHz for ^{19}F). ^1H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 ppm and ^{19}F NMR chemical shifts were determined relative to CFCl_3 as inter standard. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. All reactions were monitored by TLC with 0.25 mm coated commercial silica gel plates (TLC Silica Gel 60 F₂₅₄). Flash column chromatograph was carried out using 300-400 mesh silica gel at medium pressure. Infrared (IR) data were recorded as films on potassium bromide plates on a Bruker Tensor 27 FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). Mass spectra were acquired on a Bruker Daltonics MicroTof-Q II mass spectrometer or Agilent 7890B-5977A mass spectrometer.

Materials. All reagents were received from commercial sources unless otherwise noted. Solvents were freshly dried and degassed according to the purification handbook *Purification of Laboratory Chemicals* before using.

Table S1. Optimization of reaction conditions for decarboxylative iodization of aryl carboxylic acid.^{a,b}



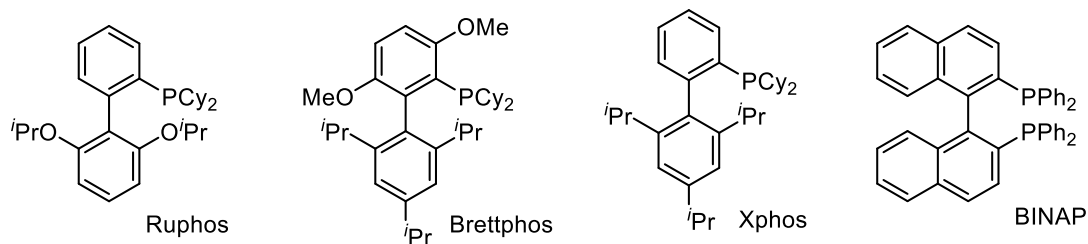
entry	base	solvent	yield (2cl , %) ^b
1	K_3PO_4	CH_3CN	94 (25 ^c)
2	K_3PO_4	toluene	36
3	Li_2CO_3	toluene	trace
4	K_2CO_3	toluene	83
5	Cs_2CO_3	toluene	94
6	Cs_2CO_3	C_6H_5Cl	59

^a Reaction conditions: *o*-methoxybenzoic acid (0.10 mmol), I_2 (0.20 mmol), base (1.0 equiv, anhydrous) in solvent (1.0 mL) at 150 °C for 16 h; ^b Yields were determined by 1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard; ^c No drying treatment.

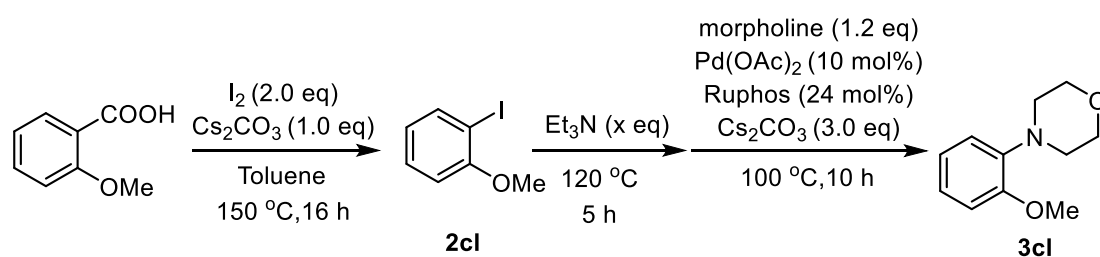
Caution: decarboxylation iodization is sensitive to water, and anhydrous inorganic base is necessary.

Table S2. Optimization of reaction conditions for palladium-catalyzed C-N coupling.^{a,b}

entry	[Pd]	[L]	base	x (eq)	solvent	temp. (°C)	yield (3cl , %)
1	Pd(OAc) ₂	Ruphos	K ₃ PO ₄	2.0	MeCN	120	< 4
2	Pd(OAc) ₂	Ruphos	K ₃ PO ₄	2.0	toluene	120	7
3	Pd(OAc) ₂	Ruphos	K ₂ CO ₃	2.0	toluene	120	< 4
4	Pd(OAc) ₂	Ruphos	Li ₂ CO ₃	2.0	toluene	120	< 3
5	Pd(OAc) ₂	Ruphos	Cs ₂ CO ₃	2.0	toluene	120	18
6	Pd(OAc) ₂	Ruphos	Cs ₂ CO ₃	3.0	toluene	120	87
7	PdCl ₂	Ruphos	Cs ₂ CO ₃	3.0	toluene	120	12
8	Pd(TFA) ₂	Ruphos	Cs ₂ CO ₃	3.0	toluene	120	86
9	Pd(OAc) ₂	P(^t Bu) ₃	Cs ₂ CO ₃	3.0	toluene	120	ND
10	Pd(OAc) ₂	P(<i>o</i> -tol) ₃	Cs ₂ CO ₃	3.0	toluene	120	ND
11	Pd(OAc) ₂	BINAP	Cs ₂ CO ₃	3.0	toluene	120	78
12	Pd(OAc) ₂	Xantphos	Cs ₂ CO ₃	3.0	toluene	120	36
13	Pd(OAc) ₂	Brettphos	Cs ₂ CO ₃	3.0	toluene	120	60
14	Pd(OAc) ₂	Xphos	Cs ₂ CO ₃	3.0	toluene	120	36
15	Pd(OAc)₂	Ruphos	Cs₂CO₃	3.0	toluene	100	97
16	Pd(OAc) ₂	Ruphos	Cs ₂ CO ₃	3.0	toluene	80	52



^a Reaction conditions: *o*-iodoanisole (0.10 mmol), morpholine (0.12 mmol, 1.2 equiv), [Pd] (10 mol%), [L] (24 mol%), and anhydrous base in solvent (1.0 mL) at setting temperature for 10 h; ^b Yields were determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

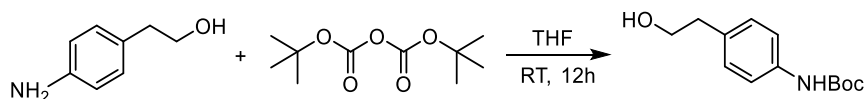
Table S3. Optimization of reaction conditions for quenching experiment. ^{a,b}

Entry	Et_3N (x eq)	yield (3cl , %) ^b
1	0	0
2	3.0	60
3	4.0	71
4	5.0	78
5	6.0	81
6	8.0	88
7	10.0	56

^a Reaction conditions: *o*-methoxybenzoic acid (0.10 mmol), I_2 (0.20 mmol), Cs_2CO_3 (1.0 equiv, anhydrous) in toluene (1.0 mL) at 150 °C for 16 h; then the reaction was quenched by x equiv Et_3N at 120 °C for 5 h; after filtration, morpholine (0.12 mmol, 1.2 equiv), $Pd(OAc)_2$ (10 mol%), RuPhos (24 mol%), Cs_2CO_3 (3.0 equiv, anhydrous) were added to the filtrate at the 100 °C for another 10 h; ^b Yields were determined by 1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

Preparation of substrates

The substrate was prepared following literature procedures: [1]

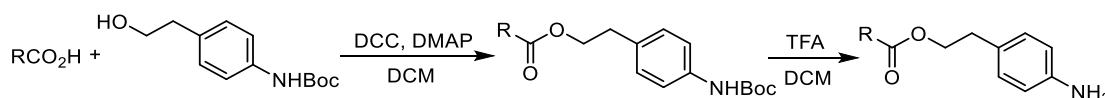


Di-*tert*-butyl dicarbonate (23.42 ml, 100 mmol) was added into a solution of 2-(4-aminophenyl)ethanol (6.86 g, 50 mmol) in 250 mL THF. The reaction mixture was stirred at room temperature overnight. The organic phase was concentrated by reduced vacuum, and then precipitated in hexanes. The precipitate was filtered and dried under high vacuum to yield white solid (11.15 g, 94%).

Tert-butyl (4-(2-hydroxyethyl)phenyl)carbamate

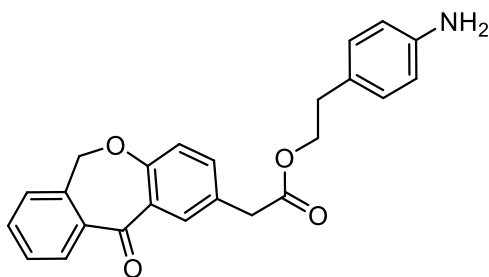
White solid (11.15 g, 94%). Mp: 107-108 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.28 (d, *J* = 8.1 Hz, 2 H), 7.12 (d, *J* = 8.2 Hz, 2 H), 6.55 (s, 1 H), 3.79 (t, *J* = 6.6 Hz, 2 H), 2.79 (t, *J* = 6.6 Hz, 2 H), 1.64 (s, 1 H), 1.50 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃) δ 153.0, 136.9, 133.2, 129.6, 119.1, 63.8, 38.6, 28.4, 27.5 ppm.

These substrates were prepared following the literature procedure: [2]



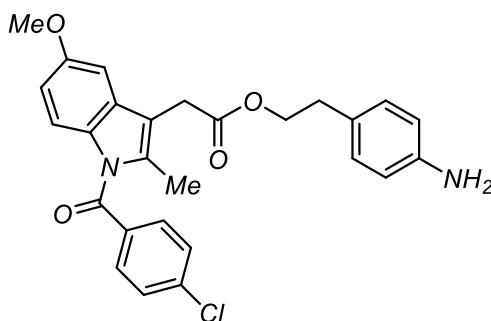
Complex carboxylic acid (5.0 mmol), *tert*-butyl (4-(2-hydroxyethyl)phenyl)carbamate (5.0 mmol, 1.0 equiv), DCC (7.5 mmol, 1.5 equiv) and DMAP (0.5 mmol, 10 mmol%) in DCM (30 mL) in 100mL round bottom flask were stirred at RT for 12 h. After the reaction, the mixture was filtered and the filtrate was concentrated by reduced vacuum. Then crude compound was subjected to 20% of TFA in DCM (v/v, 20 mL) at room temperature for 30 min. After the concentration under reduced vacuum, the mixture was dissolved in water and treated with saturated NaHCO₃ to adjust the pH to 8, subsequently extracted with EtOAc for three times. The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified on a silica gel column chromatograph to afford the corresponding complex aniline substrates.

4-Aminophenethyl-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate 1cp



Yellow oil (1.31 g, 67%). Eluent: ethyl acetate/petroleum ether (2:1, $R_f = 0.3$). ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 2.4$ Hz, 1 H), 7.89 (d, $J = 7.8$ Hz, 1 H), 7.55 (t, $J = 7.4$ Hz, 1 H), 7.47 (t, $J = 7.6$ Hz, 1 H), 7.36 (dd, $J = 8.0, 3.0$ Hz, 2 H), 7.00 (d, $J = 8.5$ Hz, 1 H), 6.94 (d, $J = 8.1$ Hz, 2 H), 6.59 (d, $J = 8.0$ Hz, 2 H), 5.18 (s, 2 H), 4.24 (t, $J = 7.1$ Hz, 2 H), 3.61 (s, 2 H), 3.44 (br, 2 H), 2.80 (t, $J = 7.1$ Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.0, 171.5, 160.5, 145.0, 140.6, 136.5, 135.7, 132.9, 132.6, 129.9, 129.6, 129.4, 128.0, 127.9, 127.6, 125.2, 121.1, 115.4, 73.7, 66.0, 40.4, 34.3 ppm. IR (KBr): $\nu = 3369, 2929, 1727, 1643, 1611, 1517, 1489, 1412, 1300, 1139, 1011, 827, 763, 698, 641, 554, 506$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{24}\text{H}_{21}\text{NO}_4$ $[\text{M}+\text{H}]^+$ calcd 388.1549, found 388.1543.

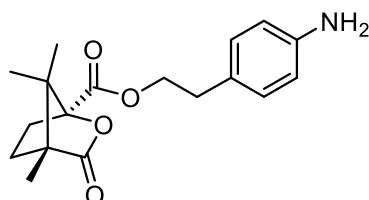
4-Aminophenethyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate 1cq



Yellow solid (1.84 g, 77%). Mp: 121-122 °C. Eluent: ethyl acetate/petroleum ether (2:1, $R_f = 0.3$). ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, $J = 8.1$ Hz, 2 H), 7.46 (d, $J = 8.2$ Hz, 2 H), 6.94 (d, $J = 2.5$ Hz, 1 H), 6.89 (t, $J = 8.4$ Hz, 3 H), 6.67 (dd, $J = 9.0, 2.5$ Hz, 1 H), 6.54 (d, $J = 8.1$ Hz, 2 H), 4.25 (t, $J = 6.9$ Hz, 2 H), 3.81 (s, 3 H), 3.63 (s, 2 H), 3.53 (br, 2 H), 2.78 (t, $J = 6.9$ Hz, 2 H), 2.32 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.9, 168.4, 156.2, 145.0, 139.3, 136.0, 134.1, 131.3, 130.9, 130.8, 129.8, 129.2, 127.5, 115.3, 115.1, 112.8, 111.8, 101.4, 66.0, 55.8, 34.3, 30.5, 13.5 ppm. IR (KBr): ν

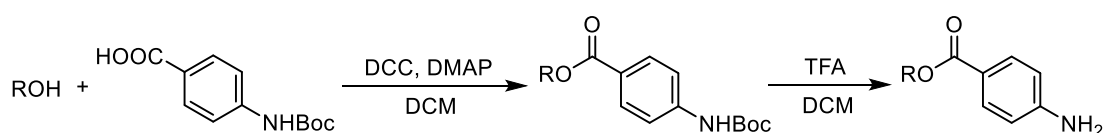
= 3369, 2929, 1726, 1677, 1517, 1476, 1356, 1219, 1164, 1142, 1066, 925, 828, 753, 733, 700, 551, 481 cm^{-1} . HRMS (ESI): m/z for $\text{C}_{27}\text{H}_{25}\text{ClN}_2\text{O}_4$ $[\text{M}+\text{H}]^+$ calcd 477.1581, found 477.1575.

4-Aminophenethyl(1S,4R)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate 1cr



Yellow solid (0.96 g, 60%). Mp: 95-96 °C. Eluent: ethyl acetate/petroleum ether (2:1, $R_f = 0.3$). ^1H NMR (400 MHz, CDCl_3) δ 6.99 (d, $J = 8.3$ Hz, 2 H), 6.61 (d, $J = 8.2$ Hz, 2 H), 4.32-4.40 (m, 2 H), 3.60 (br, 2 H), 2.87 (t, $J = 7.1$ Hz, 2 H), 2.31-2.39 (m, 1 H), 1.93-2.00 (m, 1 H), 1.83-1.89 (m, 1 H), 1.61-1.68 (m, 1 H), 1.08 (s, 3 H), 0.96 (s, 3 H), 0.86 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.3, 167.5, 145.2, 129.9, 126.9, 115.4, 91.3, 66.4, 54.9, 54.2, 34.2, 30.7, 29.0, 16.8, 16.7, 9.8 ppm. IR (KBr): $\nu = 2966, 1781, 1743, 1626, 1518, 1312, 1269, 1169, 1105, 1062, 931, 822, 797, 734, 554$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{18}\text{H}_{23}\text{NO}_4$ $[\text{M}+\text{H}]^+$ calcd 318.1705, found 318.1698.

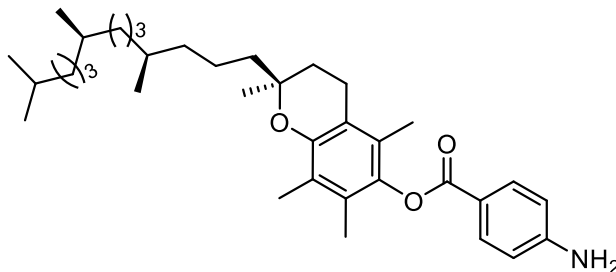
The substrate was prepared following literature procedures: ^[2-3]



4-((*Tert*-butoxycarbonyl)amino)benzoic acid (5.0 mmol), phenol (5.0 mmol, 1.0 equiv), DCC (7.5 mmol, 1.5 equiv) and DMAP (0.5 mmol, 10 mmol%) in DCM (30 mL) in 100mL round bottom flask were stirred at RT for 12 h. After the reaction, the mixture was filtered and the filtrate was concentrated by reduced vacuum. Then crude compound was subjected to 20% of TFA in DCM (v/v, 20 mL) at room temperature for 30 min. After the concentration under reduced vacuum, the mixture was dissolved in water and treated with saturated NaHCO_3 to adjust the pH to 8, subsequently extracted with EtOAc for three times. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The

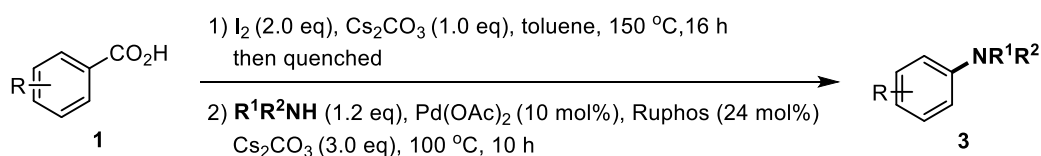
residue was purified on a silica gel column chromatograph to afford the corresponding complex aniline substrates.

(S)-2,5,7,8-Tetramethyl-2-((4S,8R)-4,8,12-trimethyltridecyl)chroman-6-yl 4-aminobenzoate 1cs



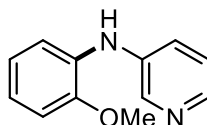
Yellow oil (1.23 g, 45%). Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.3$). ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, $J = 8.6$ Hz, 2 H), 6.68 (d, $J = 8.4$ Hz, 2 H), 3.97 (br, 2 H), 2.62 (t, $J = 6.9$ Hz, 2 H), 2.16 (s, 1 H), 2.13 (s, 3 H), 2.06 (s, 3 H), 2.02 (s, 3 H), 1.73-1.87 (m, 3 H), 1.55 (dq, $J = 13.0, 6.7$ Hz, 3 H), 1.24-1.30 (m, 14 H), 1.16 (t, $J = 7.0$ Hz, 3 H), 0.86-0.89 (m, 16 H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.4, 151.5, 149.4, 140.9, 132.4, 127.3, 125.5, 123.1, 118.9, 117.5, 114.0, 39.5, 37.7, 37.6, 37.5, 37.4, 32.9, 28.1, 24.9, 24.6, 24.3, 23.9, 23.8, 22.9, 22.8, 21.2, 20.9, 20.8, 19.9, 19.8, 19.7, 13.2, 12.3, 12.0 ppm. IR (KBr): $\nu = 3334, 2925, 2867, 1733, 1702, 1592, 1528, 1459, 1412, 1288, 1230, 1155, 1096, 859, 769, 701$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{36}\text{H}_{55}\text{NO}_3$ $[\text{M}+\text{H}]^+$ calcd 550.4260, found 550.4253.

General procedure for decarboxylative amination



Aromatic carboxylic acid (0.5 mmol), I₂ (1.0 mmol, 2.0 equiv) and Cs₂CO₃ (0.5 mmol, 1.0 equiv, anhydrous) were placed into an oven-dried 25 mL Schlenk tube that was equipped with a stirring bar under argon atmosphere. Freshly distilled toluene (3.0 mL) was added to the Schlenk tube. The reaction was stirred at 150 °C for 16 h and then quenched by NEt₃ (4.0 mmol, 8.0 equiv) at 120 °C for 5 h. Subsequently, after the filtration, the filtrate was added to another Schlenk tube charged with Pd(OAc)₂ (10 mol%), Ruphos (24 mol%), amines (0.6 mmol, 1.2 equiv) and Cs₂CO₃ (1.5 mmol, 3.0 equiv, anhydrous) under argon atmosphere. The mixture was stirred at 100 °C for 10 h. After the reaction, the solution was filtered and washed with ethyl acetate for three times. The combined solvents were removed under vacuum, and the residue was purified by column chromatography to obtain the desired aromatic amines.

N-(2-Methoxyphenyl)pyridin-3-amine 3aa



Yellow solid (87.1 mg, 87%). Mp: 81-82 °C. Eluent: ethyl acetate/petroleum ether (1:1, R_f = 0.6). ¹H NMR (400 MHz, CDCl₃) δ 8.46 (d, *J* = 2.8 Hz, 1 H), 8.18 (d, *J* = 4.5 Hz, 1 H), 7.48 (d, *J* = 8.3 Hz, 1 H), 7.24-7.30 (m, 1 H), 7.18 (dd, *J* = 8.3, 4.6 Hz, 1 H), 6.87-6.95 (m, 3 H), 6.24 (s, 1 H), 3.89 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 148.8, 142.0, 140.8, 139.5, 131.7, 124.0, 123.6, 121.2, 120.9, 115.3, 110.8, 55.6 ppm.

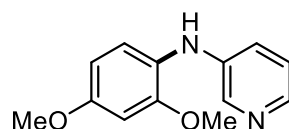
The spectroscopic data were matched with those reported in the literature.^[4]

Gram-scale synthesis of *N*-(2-methoxyphenyl)pyridin-3-amine 3aa

To a mixture of *o*-methoxybenzoic acid (7.5 mmol), I₂ (15.0 mmol, 2.0 equiv) and Cs₂CO₃ (7.5 mmol, 1.0 equiv, anhydrous) in an oven-dried 100 mL Schlenk tube was added freshly distilled toluene (45.0 mL) under argon atmosphere. The reaction was

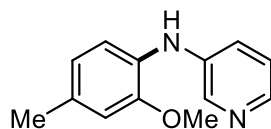
stirred at 150 °C for 16 h and then quenched by NEt₃ (60.0 mmol, 8.0 equiv) at 120 °C for 5 h. Subsequently, after the filtration, the filtrate was added to another Schlenk tube charged with Pd(OAc)₂ (10 mol%), Ruphos (24 mol%), amines (9.0 mmol, 1.2 equiv) and Cs₂CO₃ (22.5 mmol, 3.0 equiv, anhydrous) under argon atmosphere. The mixture was stirred at 100 °C for 10 h. After the reaction, the solution was filtered and washed with ethyl acetate for three times. The combined solvents were removed under vacuum, and the residue was purified by column chromatography to obtain *N*-(2-methoxyphenyl)pyridin-3-amine **3aa** as a yellow solid (1.27 g, 85%).

***N*-(2,4-Dimethoxyphenyl)pyridin-3-amine 3ab**



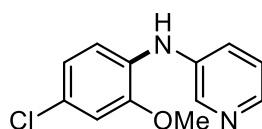
Yellow solid (82.9 mg, 72%). Mp: 93-94 °C. Eluent: ethyl acetate/petroleum ether (1:1, R_f = 0.4). ¹H NMR (400 MHz, CDCl₃) δ 8.29 (s, 1 H), 8.05 (d, *J* = 4.7 Hz, 1 H), 7.24 (d, *J* = 10.5 Hz, 1 H), 7.15 (d, *J* = 8.6 Hz, 1 H), 7.11-7.12 (m, 1 H), 6.46-6.57 (m, 1 H), 6.43 (dt, *J* = 8.6, 2.1 Hz, 1 H), 5.77 (s, 1 H), 3.80 (s, 3 H), 3.78 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 156.1, 151.8, 141.4, 140.8, 139.0, 124.2, 123.7, 121.8, 120.0, 103.9, 99.6, 55.7 ppm. The spectroscopic data were matched with those reported in the literature.^[5]

***N*-(2-Methoxy-4-methylphenyl)pyridin-3-amine 3ac**



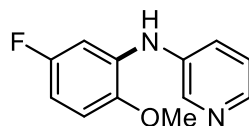
Yellow oil (99.6 mg, 93%). Eluent: ethyl acetate/petroleum ether (1:1, R_f = 0.3). ¹H NMR (400 MHz, CDCl₃) δ 8.38 (d, *J* = 2.9 Hz, 1 H), 8.12 (dd, *J* = 4.7, 1.4 Hz, 1 H), 7.38-7.41 (m, 1 H), 7.14 (dd, *J* = 8.2, 4.7 Hz, 2 H), 6.72 (d, *J* = 12.9 Hz, 2 H), 6.02 (s, 1 H), 3.86 (s, 3 H), 2.33 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 149.3, 141.4, 140.3, 140.0, 131.7, 128.7, 123.7, 123.2, 121.1, 116.6, 112.0, 55.7, 21.3 ppm. IR (KBr): ν = 2923, 1524, 1261, 801, 764, 750 cm⁻¹. HRMS (ESI): *m/z* for C₁₃H₁₄N₂O [M+H]⁺ calcd 215.1184, found 215.1181.

***N*-(4-Chloro-2-methoxyphenyl)pyridin-3-amine 3ad**



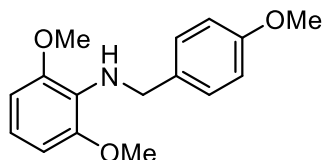
Yellow solid (84.5 mg, 72%). Mp: 78-79 °C. Eluent: ethyl acetate/petroleum ether (1:1, $R_f = 0.3$). ^1H NMR (400 MHz, CDCl_3) δ 8.40 (s, 1 H), 8.18 (s, 1 H), 7.43 (d, $J = 8.2$ Hz, 1 H), 7.18 (dd, $J = 8.3, 4.6$ Hz, 1 H), 7.12 (d, $J = 8.2$ Hz, 1 H), 6.83-6.87 (m, 2 H), 6.08 (s, 1 H), 3.87 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.3, 142.3, 140.9, 139.2, 130.5, 125.7, 124.5, 123.9, 120.7, 115.7, 111.6, 56.0 ppm. IR (KBr): $\nu = 2925, 2851, 1580, 1515, 1245, 1029, 891, 853, 838, 793, 708$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{12}\text{H}_{11}\text{ClN}_2\text{O}$ $[\text{M}+\text{H}]^+$ calcd 235.0638, found 235.0637.

***N*-(5-Fluoro-2-methoxyphenyl)pyridin-3-amine 3ae**



Yellow solid (82.9 mg, 76%). Mp: 70-71 °C. Eluent: ethyl acetate/petroleum ether (1:1, $R_f = 0.2$). ^1H NMR (400 MHz, CDCl_3) δ 8.47 (s, 1 H), 8.24 (s, 1 H), 7.52 (s, 1 H), 7.22 (s, 1 H), 6.93 (s, 1 H), 6.78 (s, 1 H), 6.54 (s, 1 H), 6.36 (s, 1 H), 3.88 (s, 3 H); ^{19}F NMR (376 MHz, CDCl_3) δ -121.3 (m, 1 F); ^{13}C NMR (100 MHz, CDCl_3) δ 157.5 (d, $J = 242.4$ Hz), 144.5, 143.1, 141.9, 138.4, 133.4, 125.4, 123.9, 111.1 (d, $J = 10.1$ Hz), 105.6 (d, $J = 20.2$ Hz), 101.5 (d, $J = 10.1$ Hz), 56.2 ppm. IR (KBr): $\nu = 2936, 1617, 1580, 1525, 1479, 1444, 1408, 1246, 1210, 1108, 1030, 984, 846, 789, 711$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{12}\text{H}_{11}\text{FN}_2\text{O}$ $[\text{M}+\text{H}]^+$ calcd 219.0934, found 219.0938.

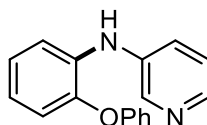
2,6-Dimethoxy-*N*-(4-methoxybenzyl)aniline 3af



Yellow oil (54.7 mg, 40%). Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.3$). ^1H NMR (400 MHz, CDCl_3) δ 7.27 (d, $J = 8.6$ Hz, 2 H), 6.77-6.87 (m, 3 H), 6.55 (d, $J = 8.3$ Hz, 2 H), 4.36 (s, 2 H), 4.12 (s, 1 H), 3.82 (s, 6 H), 3.78 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.6, 151.1, 133.5, 129.3, 127.4, 120.1, 113.7, 104.9, 56.1, 55.3,

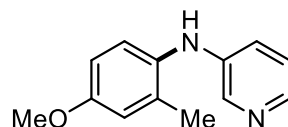
50.9 ppm. IR (KBr): $\nu = 2224, 1605, 1508, 1303, 1258, 1172, 1024, 834, 683, 548$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{16}\text{H}_{19}\text{NO}_3$ $[\text{M}+\text{H}]^+$ calcd 274.1443, found 274.1438.

***N*-(2-Phenoxyphenyl)pyridin-3-amine 3ag**



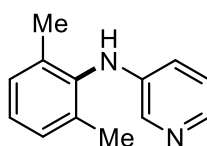
Yellow solid (43.3 mg, 33%). Mp: 54-55 °C. Eluent: ethyl acetate/petroleum ether (1:1, $R_f = 0.6$). ^1H NMR (400 MHz, CDCl_3) δ 8.42 (d, $J = 2.8$ Hz, 1 H), 8.18 (dd, $J = 4.7, 1.4$ Hz, 1 H), 7.46 (qd, $J = 8.2, 2.8$ Hz, 1 H), 7.32 (td, $J = 7.4, 1.6$ Hz, 3 H), 7.17 (dd, $J = 8.3, 4.7$ Hz, 1 H), 7.03-7.11 (m, 2 H), 6.98-7.02 (m, 2 H), 6.93 (dd, $J = 8.0, 1.7$ Hz, 1 H), 6.85-6.90 (m, 1 H), 6.16 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.0, 145.9, 142.6, 141.3, 139.1, 134.4, 130.0, 124.9, 124.4, 123.8, 123.5, 121.5, 119.7, 118.1, 116.4 ppm. IR (KBr): $\nu = 2922, 1577, 1519, 1486, 1453, 1407, 1239, 1214, 794, 748, 708, 691$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ calcd 263.1184, found 263.1181.

***N*-(4-Methoxy-2-methylphenyl)pyridin-3-amine 3ah**



White solid (88.9 mg, 83%). Mp: 94-95 °C. Eluent: ethyl acetate/petroleum ether (1:1, $R_f = 0.3$). ^1H NMR (400 MHz, CDCl_3) δ 8.11 (d, $J = 2.9$ Hz, 1 H), 8.00 (dd, $J = 4.7, 1.4$ Hz, 1 H), 7.11 (d, $J = 8.6$ Hz, 1 H), 7.06 (dd, $J = 8.3, 4.6$ Hz, 1 H), 6.90-6.93 (m, 1 H), 6.81 (d, $J = 3.0$ Hz, 1 H), 6.73 (dd, $J = 8.6, 3.0$ Hz, 1 H), 5.41 (s, 1 H), 3.80 (s, 3 H), 2.20 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.1, 142.9, 139.8, 137.5, 134.9, 132.2, 125.8, 123.8, 120.4, 116.6, 112.2, 55.5, 18.3 ppm. IR (KBr): $\nu = 1584, 1498, 1289, 1218, 1046, 794, 764, 750, 708$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ calcd 215.1184, found 215.1179.

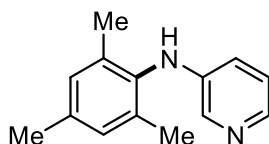
***N*-(2,6-Dimethylphenyl)pyridin-3-amine 3ai**



Yellow solid (59.5 mg, 60%). Mp: 111-112 °C. Eluent: ethyl acetate/petroleum ether

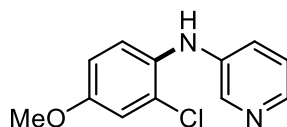
(1:1, $R_f = 0.4$). ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 2.9$ Hz, 1 H), 7.99 (d, $J = 3.5$ Hz, 1 H), 7.12 (s, 3 H), 7.03 (dd, $J = 8.3, 4.6$ Hz, 1 H), 6.64 (d, $J = 8.2$ Hz, 1 H), 5.46 (s, 1 H), 2.20 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.7, 139.4, 137.0, 136.7, 136.1, 128.8, 126.5, 123.9, 119.1, 18.4 ppm. The spectroscopic data were matched with those reported in the literature.^[6]

***N*-Mesitylpyridin-3-amine 3aj**



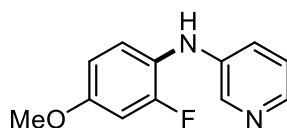
Yellow solid (80.7 mg, 76%). Mp: 97-98 °C. Eluent: ethyl acetate/petroleum ether (1:1, $R_f = 0.3$). ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, $J = 2.9$ Hz, 1 H), 8.00 (d, $J = 4.7$ Hz, 1 H), 7.04 (dd, $J = 8.3, 4.7$ Hz, 1 H), 6.97 (s, 2 H), 6.65 (d, $J = 8.3$ Hz, 1 H), 5.39 (s, 1 H), 2.33 (s, 3 H), 2.18 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.0, 139.2, 136.5, 136.1, 136.0, 134.3, 129.4, 123.8, 118.8, 20.9, 18.2 ppm. The spectroscopic data were matched with those reported in the literature.^[7]

***N*-(2-Chloro-4-methoxyphenyl)pyridin-3-amine 3ak**



Yellow solid (89.2 mg, 76%). Mp: 55-56 °C. Eluent: ethyl acetate/petroleum ether (1:1, $R_f = 0.5$). ^1H NMR (400 MHz, CDCl_3) δ 8.31 (s, 1 H), 8.13 (s, 1 H), 7.17-7.27 (m, 2 H), 7.14 (dd, $J = 8.5, 4.5$ Hz, 1 H), 6.97 (d, $J = 2.7$ Hz, 1 H), 6.78 (d, $J = 8.9$ Hz, 1 H), 5.76 (s, 1 H), 3.77 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.6, 141.8, 140.5, 139.6, 131.8, 126.3, 123.9, 123.1, 121.4, 115.4, 113.9, 55.9 ppm. IR (KBr): $\nu = 2923, 1583, 1512, 1494, 1281, 1251, 1210, 1045, 858, 841, 798, 708$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{12}\text{H}_{11}\text{ClN}_2\text{O}$ $[\text{M}+\text{H}]^+$ calcd 235.0638, found 235.0642.

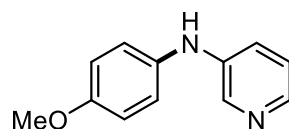
***N*-(2-Fluoro-4-methoxyphenyl)pyridin-3-amine 3al**



Yellow oil (72.0 mg, 66%). Eluent: ethyl acetate/petroleum ether (1:1, $R_f = 0.2$). ^1H NMR (400 MHz, CDCl_3) δ 8.27 (s, 1 H), 8.10 (s, 1 H), 7.12-7.23 (m, 3 H), 6.72 (dd, J

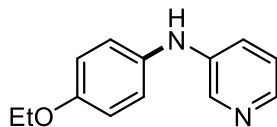
= 12.2, 2.8 Hz, 1 H), 6.66 (dq, $J = 8.8, 2.9, 1.3$ Hz, 1 H), 5.52 (s, 1 H), 3.79 (s, 3 H); ^{19}F NMR (376 MHz, CDCl_3) δ -124 (m, 1 F); ^{13}C NMR (100 MHz, CDCl_3) δ 148.9, 141.9, 141.0, 138.3, 123.0 (d, $J = 242.4$ Hz), 121.3, 120.9, 115.3, 110.8, 110.0 (d, $J = 2.0$ Hz), 102.8 (d, $J = 20.2$ Hz), 55.9 ppm. IR (KBr): $\nu = 2923, 2851, 1582, 1514, 1287, 1244, 1155, 1117, 1030, 795, 749, 708$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{12}\text{H}_{11}\text{FN}_2\text{O}$ $[\text{M}+\text{H}]^+$ calcd 219.0934, found 219.0931.

***N*-(4-Methoxyphenyl)pyridin-3-amine 3am**



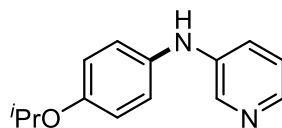
Yellow solid (57.1 mg, 57%). Mp: 125-126 °C. Eluent: ethyl acetate/petroleum ether (1:1, $R_f = 0.3$). ^1H NMR (400 MHz, CDCl_3) δ 8.23 (s, 1 H), 8.04 (s, 1 H), 7.19 (d, $J = 8.3$ Hz, 1 H), 7.06 (d, $J = 8.9$ Hz, 3 H), 6.86 (d, $J = 7.0$ Hz, 2 H), 5.75 (s, 1 H), 3.79 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.0, 142.0, 140.4, 138.2, 134.4, 123.9, 122.8, 121.3, 114.9, 55.7 ppm. The spectroscopic data were matched with those reported in the literature.^[4]

***N*-(4-Ethoxyphenyl)pyridin-3-amine 3an**



Yellow solid (78.2 mg, 73%). Mp: 107-108 °C. Eluent: ethyl acetate/petroleum ether (1:1, $R_f = 0.4$). ^1H NMR (400 MHz, CDCl_3) δ 8.22 (d, $J = 2.8$ Hz, 1 H), 8.03 (d, $J = 4.6$ Hz, 1 H), 7.18 (dq, $J = 8.3, 2.9$ Hz, 1 H), 7.02-7.10 (m, 3 H), 6.82-6.88 (m, 2 H), 5.78 (s, 1 H), 4.00 (q, $J = 7.0$ Hz, 2 H), 1.40 (t, $J = 7.0$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.3, 142.0, 140.4, 138.2, 134.3, 123.8, 122.8, 121.3, 115.6, 63.9, 15.0 ppm. The spectroscopic data were matched with those reported in the literature.^[8]

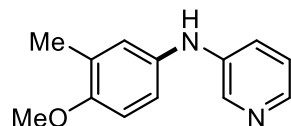
***N*-(4-Isopropoxyphenyl)pyridin-3-amine 3ao**



Yellow solid (99.3 mg, 87%). Mp: 133-134 °C. Eluent: ethyl acetate/petroleum ether

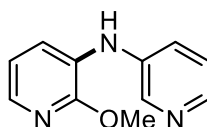
(5:1, $R_f = 0.4$). ^1H NMR (400 MHz, CDCl_3) δ 8.23 (d, $J = 2.9$ Hz, 1 H), 8.04 (dd, $J = 4.6, 1.3$ Hz, 1 H), 7.20 (dq, $J = 8.4, 2.9$ Hz, 1 H), 7.08 (dd, $J = 8.3, 4.6$ Hz, 1 H), 7.01-7.06 (m, 2 H), 6.82-6.87 (m, 2 H), 5.73 (s, 1 H), 4.43-4.52 (m, 1 H), 1.32 (d, $J = 6.1$ Hz, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.2, 141.9, 140.5, 138.3, 134.4, 123.8, 122.7, 121.3, 117.2, 70.6, 22.2 ppm. IR (KBr): $\nu = 3252, 3180, 3042, 2976, 1575, 1509, 1482, 1327, 1276, 1240, 1121, 957, 764, 750, 701$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ calcd 229.1341, found 229.1340.

***N*-(4-Methoxy-3-methylphenyl)pyridin-3-amine 3ap**



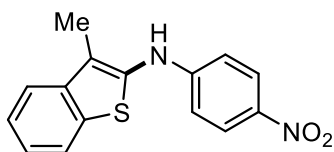
Yellow solid (63.2 mg, 59%). Mp: 122-123 °C. Eluent: ethyl acetate/petroleum ether (1:1, $R_f = 0.4$). ^1H NMR (400 MHz, CDCl_3) δ 8.24 (d, $J = 2.8$ Hz, 1 H), 8.04 (d, $J = 4.5$ Hz, 1 H), 7.18-7.21 (m, 1 H), 7.08 (dd, $J = 8.3, 4.7$ Hz, 1 H), 6.94 (d, $J = 6.1$ Hz, 2 H), 6.78 (d, $J = 9.3$ Hz, 1 H), 5.71 (s, 1 H), 3.81 (s, 3 H), 2.20 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.3, 142.0, 140.4, 138.3, 134.0, 128.0, 124.4, 123.8, 121.2, 119.6, 111.0, 55.8, 16.4 ppm. IR (KBr): $\nu = 1580, 1502, 1482, 1255, 1225, 1127, 1033, 795, 764, 750, 707$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ calcd 215.1184, found 215.1181.

2-Methoxy-*N*-(pyridin-3-yl)pyridin-3-amine 3aq



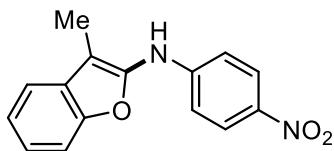
Yellow solid (45.3 mg, 45%). Mp: 67-68 °C. Eluent: ethyl acetate/petroleum ether (1:1, $R_f = 0.4$). ^1H NMR (400 MHz, CDCl_3) δ 8.41 (d, $J = 2.9$ Hz, 1 H), 8.18 (dd, $J = 4.7, 1.4$ Hz, 1 H), 7.67 (dd, $J = 5.0, 1.6$ Hz, 1 H), 7.42 (dq, $J = 8.2, 2.9$ Hz, 1 H), 7.37 (dd, $J = 7.7, 1.6$ Hz, 1 H), 7.17 (dd, $J = 8.3, 4.7$ Hz, 1 H), 6.77 (dd, $J = 7.7, 5.0$ Hz, 1 H), 6.17 (s, 1 H), 3.99 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.7, 143.0, 141.3, 138.4, 137.1, 127.2, 125.0, 123.9, 119.7, 117.0, 53.7 ppm. IR (KBr): $\nu = 1573, 1464, 1418, 1388, 1244, 1188, 1113, 1017, 783, 755, 709$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ calcd 202.0980, found 202.0978.

3-Methyl-*N*-(4-nitrophenyl)benzo[*b*]thiophen-2-amine 3ar



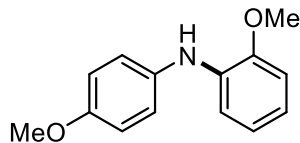
Yellow solid (49.7 mg, 35%). Mp: 133-134 °C. Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.5$). ^1H NMR (400 MHz, CDCl_3) δ 8.11 (d, $J = 9.0$ Hz, 2 H), 7.76 (d, $J = 7.6$ Hz, 1 H), 7.68 (d, $J = 7.9$ Hz, 1 H), 7.36-7.44 (m, 2 H), 6.75 (d, $J = 9.2$ Hz, 2 H), 6.06 (s, 1 H), 2.26 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.6, 140.2, 138.9, 136.9, 135.2, 126.3, 125.5, 125.3, 124.6, 122.7, 122.3, 113.2, 11.3 ppm. IR (KBr): $\nu = 3337$, 1584, 1498, 1320, 1301, 1272, 1179, 1111, 839, 751, 728, 691, 486 cm^{-1} . HRMS (ESI): m/z for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$ calcd 285.0698, found 285.0694.

3-Methyl-*N*-(4-nitrophenyl)benzofuran-2-amine 3as



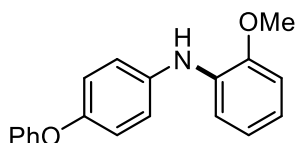
Yellow solid (60.3 mg, 45%). Mp: 59-60 °C. Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.4$). ^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, $J = 9.1$ Hz, 2 H), 7.50 (d, $J = 7.1$ Hz, 1 H), 7.40 (d, $J = 7.8$ Hz, 1 H), 7.26-7.32 (m, 2 H), 6.80 (d, $J = 8.9$ Hz, 2 H), 6.23 (s, 1 H), 2.15 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.6, 149.8, 144.5, 140.8, 129.7, 126.2, 124.6, 122.9, 119.4, 113.7, 111.1, 106.7, 8.0 ppm. IR (KBr): $\nu = 3346$, 1593, 1501, 1323, 1304, 1111, 841, 747 cm^{-1} . HRMS (ESI): m/z for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ calcd 269.0926, found 269.0921.

2-Methoxy-*N*-(4-methoxyphenyl)aniline 3aw



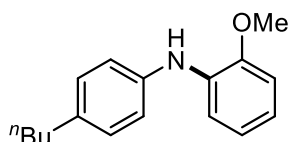
Yellow oil (86.0 mg, 75%). Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.8$). ^1H NMR (400 MHz, CDCl_3) δ 7.14 (d, $J = 8.6$ Hz, 2 H), 7.07 (d, $J = 7.5$ Hz, 1 H), 6.91 (d, $J = 5.8$ Hz, 1 H), 6.88 (s, 1 H), 6.87 (s, 1 H), 6.84 (d, $J = 7.5$ Hz, 1 H), 6.79 (t, $J = 7.5$ Hz, 1 H), 6.00 (s, 1 H), 3.90 (s, 3 H), 3.81 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.4, 147.5, 135.5, 135.2, 122.9, 121.1, 118.7, 114.7, 112.7, 110.3, 55.7 ppm. The spectroscopic data were matched with those reported in the literature.^[9]

2-Methoxy-*N*-(4-phenoxyphenyl)aniline 3ax



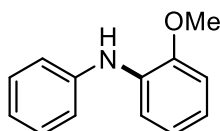
Yellow oil (109.3 mg, 75%). Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.8$). ^1H NMR (400 MHz, CDCl_3) δ 7.41-7.52 (m, 2 H), 7.38 (d, $J = 7.3$ Hz, 1 H), 7.27 (d, $J = 6.5$ Hz, 2 H), 7.17-7.23 (m, 2 H), 7.10-7.17 (m, 3 H), 7.04 (dd, $J = 6.3, 3.0$ Hz, 1 H), 6.98-7.02 (m, 2 H), 6.28 (s, 1 H), 3.98 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 151.4, 148.2, 138.7, 134.0, 130.0, 122.9, 121.2, 120.8, 119.8, 118.2, 114.1, 110.7, 55.8 ppm. IR (KBr): $\nu = 3404, 1596, 1502, 1485, 1457, 1218, 1114, 1025, 864, 835, 778, 738, 690, 504$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{19}\text{H}_{17}\text{NO}_2$ $[\text{M}+\text{H}]^+$ calcd 292.1338, found 292.1335.

N-(4-butylphenyl)-2-methoxyaniline 3ay



Yellow oil (94.5 mg, 74%). Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.8$). ^1H NMR (400 MHz, CDCl_3) δ 7.33 (d, $J = 6.1$ Hz, 1 H), 7.17 (s, 4 H), 6.90 (dd, $J = 15.4, 8.1$ Hz, 3 H), 6.18 (s, 1 H), 3.94 (s, 3 H), 2.65 (t, $J = 7.7$ Hz, 2 H), 1.68 (dt, $J = 15.6, 7.3$ Hz, 2 H), 1.41-1.50 (m, 2 H), 0.98-1.10 (m, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.1, 140.3, 136.3, 133.9, 129.3, 121.0, 119.6, 119.4, 114.0, 110.6, 55.7, 35.2, 34.0, 22.6, 14.2 ppm. The spectroscopic data were matched with those reported in the literature.^[10]

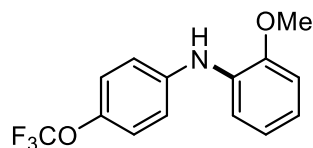
2-Methoxy-*N*-phenylaniline 3az



Yellow oil (76.7 mg, 77%). Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.8$). ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.48 (m, 3 H), 7.28 (d, $J = 7.4$ Hz, 2 H), 7.07 (t, $J = 7.3$ Hz, 1 H), 7.00 (dd, $J = 6.3, 2.4$ Hz, 3 H), 6.30 (s, 1 H), 3.96 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.5, 143.0, 133.2, 129.5, 121.4, 121.1, 120.2, 118.8, 114.9, 110.8, 55.8 ppm. The spectroscopic data were matched with those reported in the

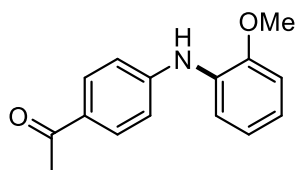
literature.^[10]

2-Methoxy-*N*-(4-(trifluoromethoxy)phenyl)aniline 3ba



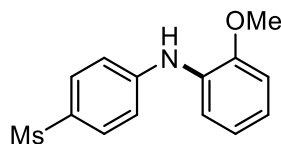
Yellow oil (110.5 mg, 78%). Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.8$). ^1H NMR (400 MHz, CDCl_3) δ 7.31 (s, 1 H), 7.13-7.19 (m, 4 H), 6.94 (s, 3 H), 6.20 (s, 1 H), 3.91 (s, 3 H); ^{19}F NMR (376 MHz, CDCl_3) δ -58.1 (s, 3 F); ^{13}C NMR (100 MHz, CDCl_3) δ 148.7, 143.0, 141.9, 132.5, 122.4, 121.0, 120.8, 120.7 (q, $J = 262.6$ Hz), 118.9, 115.4, 110.8, 55.6 ppm. IR (KBr): $\nu = 1594, 1505, 1460, 1256, 1197, 1150, 1114, 1027, 918, 835, 809, 780, 739, 503, 449$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{14}\text{H}_{12}\text{F}_3\text{NO}_2$ $[\text{M}+\text{H}]^+$ calcd 284.0898, found 284.0889.

1-(4-((2-Methoxyphenyl)amino)phenyl)ethan-1-one 3bb



Yellow oil (105.0 mg, 87%). Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.6$). ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 8.7$ Hz, 2 H), 7.40 (d, $J = 7.8$ Hz, 1 H), 7.07 (d, $J = 8.8$ Hz, 2 H), 6.98-7.02 (m, 1 H), 6.89-6.97 (m, 2 H), 6.49 (s, 1 H), 3.86 (s, 3 H), 2.52 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.6, 149.8, 148.1, 130.6, 130.3, 129.1, 122.7, 120.8, 118.3, 115.1, 111.1, 55.7, 26.3 ppm. The spectroscopic data were matched with those reported in the literature.^[11]

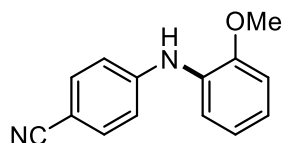
2-Methoxy-*N*-(4-(methylsulfonyl)phenyl)aniline 3bc



Yellow solid (104.0 mg, 75%). Mp: 114-115 °C. Eluent: ethyl acetate/petroleum ether (1:1, $R_f = 0.7$). ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, $J = 8.7$ Hz, 2 H), 7.35 (d, $J = 8.4$ Hz, 1 H), 7.08 (d, $J = 8.8$ Hz, 2 H), 7.03 (t, $J = 7.7$ Hz, 1 H), 6.90-6.99 (m, 2 H), 6.50 (s, 1 H), 3.84 (s, 3 H), 3.00 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.4, 148.7, 130.0, 129.6, 129.3, 123.5, 120.8, 119.2, 115.2, 111.3, 55.7, 45.0 ppm. The

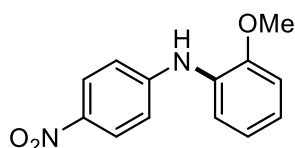
spectroscopic data were matched with those reported in the literature.^[12]

4-((2-Methoxyphenyl)amino)benzonitrile **3bd**



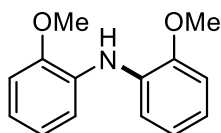
White solid (85.2 mg, 76%). Mp: 107-108 °C. Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.4$). ^1H NMR (400 MHz, CDCl_3) δ 7.45 (dd, $J = 8.8, 1.8$ Hz, 2 H), 7.35 (d, $J = 1.9$ Hz, 1 H), 7.00-7.06 (m, 3 H), 6.91-6.96 (m, 2 H), 6.40 (s, 1 H), 3.86 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.2, 147.7, 133.8, 129.6, 123.4, 120.8, 120.1, 118.9, 115.6, 111.2, 101.5, 55.8 ppm. IR (KBr): $\nu = 3319, 2215, 1587, 1517, 1458, 1338, 1245, 1173, 1112, 1027, 822, 742, 542$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ calcd 225.1028, found 225.1025.

2-Methoxy-*N*-(4-nitrophenyl)aniline **3be**



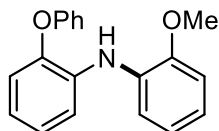
Reddish brown solid (73.3 mg, 60%). Mp: 109-110 °C. Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.5$). ^1H NMR (400 MHz, CDCl_3) δ 8.12 (t, $J = 8.2$ Hz, 2 H), 7.31-7.44 (m, 1 H), 7.08 (t, $J = 7.7$ Hz, 1 H), 7.02 (t, $J = 8.2$ Hz, 2 H), 6.96 (t, $J = 7.7$ Hz, 2 H), 6.54 (s, 1 H), 3.88 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.5, 149.7, 139.9, 129.1, 126.2, 124.2, 120.9, 119.7, 114.3, 111.3, 55.8 ppm. The spectroscopic data were matched with those reported in the literature.^[13]

Bis(2-methoxyphenyl)amine **3bf**



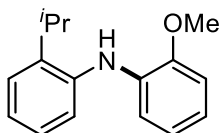
Yellow oil (91.7 mg, 80%). Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.8$). ^1H NMR (400 MHz, CDCl_3) δ 7.56 (d, $J = 7.7$ Hz, 2 H), 7.02-7.09 (m, 2 H), 7.02 (s, 2 H), 7.00 (s, 2 H), 6.70 (s, 1 H), 3.97 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.2, 132.7, 121.0, 120.4, 115.6, 110.8, 55.8 ppm. The spectroscopic data were matched with those reported in the literature.^[9]

2-Methoxy-*N*-(2-phenoxyphenyl)aniline **3bg**



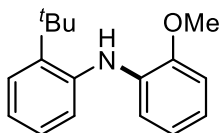
Yellow solid (109.3 mg, 75%). Mp: 78-79 °C. Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.8$). ^1H NMR (400 MHz, CDCl_3) δ 7.57 (dd, $J = 8.1, 1.5$ Hz, 1 H), 7.50 (dd, $J = 6.7, 2.7$ Hz, 1 H), 7.37-7.43 (m, 2 H), 7.16-7.18 (m, 1 H), 7.14-7.16 (m, 2 H), 7.12 (q, $J = 1.5$ Hz, 1 H), 7.04 (dd, $J = 8.0, 1.6$ Hz, 1 H), 6.98 (qd, $J = 7.0, 4.2$ Hz, 2 H), 6.94 (dd, $J = 7.0, 5.1$ Hz, 2 H), 6.59 (s, 1 H), 3.85 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.6, 149.4, 145.9, 135.4, 132.2, 129.9, 124.4, 123.2, 120.9, 120.8, 120.5, 119.9, 118.1, 116.7, 116.2, 110.9, 55.7 ppm. IR (KBr): $\nu = 1600, 1526, 1489, 1242, 1215, 1117, 1028, 856, 748, 691$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{19}\text{H}_{17}\text{NO}_2$ $[\text{M}+\text{H}]^+$ calcd 292.1338, found 292.1334.

2-Isopropyl-*N*-(2-methoxyphenyl)aniline 3bh



Yellow oil (84.5 mg, 70%). Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.9$). ^1H NMR (400 MHz, CDCl_3) δ 7.45 (td, $J = 7.6, 1.7$ Hz, 2 H), 7.28 (td, $J = 7.5, 1.7$ Hz, 1 H), 7.20 (td, $J = 7.5, 1.4$ Hz, 1 H), 7.06 (dd, $J = 7.6, 1.9$ Hz, 1 H), 6.96-7.01 (m, 1 H), 6.88-6.96 (m, 2 H), 6.08 (s, 1 H), 4.01 (s, 3 H), 3.28-3.38 (m, 1 H), 1.39 (d, $J = 6.9$ Hz, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.9, 141.4, 139.6, 135.3, 126.6, 126.3, 123.7, 122.4, 121.2, 118.9, 113.8, 110.5, 55.8, 28.0, 23.3 ppm. IR (KBr): $\nu = 2960, 1594, 1510, 1491, 1449, 1292, 1236, 1114, 1030, 743$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{16}\text{H}_{19}\text{NO}$ $[\text{M}+\text{H}]^+$ calcd 242.1545, found 242.1543.

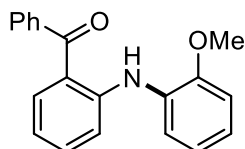
2-(*Tert*-butyl)-*N*-(2-methoxyphenyl)aniline 3bi



Yellow oil (76.6 mg, 60%). Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.9$). ^1H NMR (400 MHz, CDCl_3) δ 7.50 (dd, $J = 26.1, 7.8$ Hz, 2 H), 7.27 (q, $J = 6.1$ Hz, 1 H), 7.16 (t, $J = 7.3$ Hz, 1 H), 6.97 (d, $J = 4.5$ Hz, 2 H), 6.82-6.93 (m, 2 H), 6.18 (s, 1 H),

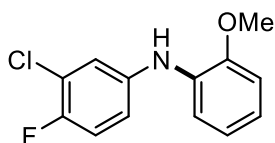
4.00 (s, 3 H), 1.54 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.7, 143.6, 141.0, 135.8, 127.2, 127.0, 125.9, 123.8, 121.2, 118.3, 113.0, 110.4, 55.9, 35.0, 30.8 ppm. IR (KBr): $\nu = 2954, 2928, 1593, 1508, 1445, 1226, 1113, 1029, 802, 756, 737\text{ cm}^{-1}$. HRMS (ESI): m/z for $\text{C}_{17}\text{H}_{21}\text{NO}$ $[\text{M}+\text{H}]^+$ calcd 256.1701, found 256.1697.

(2-((2-Methoxyphenyl)amino)phenyl)(phenyl)methanone 3bj



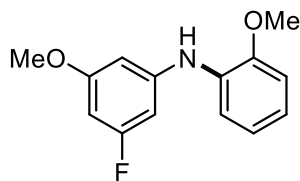
Yellow oil (97.1 mg, 64%). Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.7$). ^1H NMR (400 MHz, CDCl_3) δ 10.20 (s, 1 H), 7.78 (dd, $J = 7.5, 2.3$ Hz, 2 H), 7.59 (s, 1 H), 7.57 (s, 1 H), 7.55 (s, 1 H), 7.53 (d, $J = 2.7$ Hz, 1 H), 7.50 (s, 1 H), 7.47 (d, $J = 7.0$ Hz, 1 H), 7.34-7.43 (m, 1 H), 7.03-7.09 (m, 1 H), 6.93-7.02 (m, 2 H), 6.70-6.80 (m, 1 H), 3.94 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.9, 151.3, 147.3, 139.9, 135.0, 134.2, 131.7, 130.2, 129.8, 128.3, 123.3, 121.0, 120.7, 119.7, 117.0, 115.2, 111.4, 55.9 ppm. The spectroscopic data were matched with those reported in the literature.^[14]

3-Chloro-4-fluoro-N-(2-methoxyphenyl)aniline 3bk



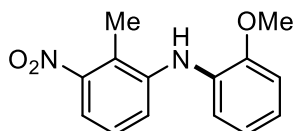
Yellow oil (69.2 mg, 55%). Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.7$). ^1H NMR (400 MHz, CDCl_3) δ 7.17-7.24 (m, 2 H), 7.05 (t, $J = 8.7$ Hz, 1 H), 6.95-7.00 (m, 1 H), 6.93 (d, $J = 1.9$ Hz, 3 H), 6.09 (s, 1 H), 3.90 (s, 3 H); ^{19}F NMR (376 MHz, CDCl_3) δ -125.4 (m, 1 F); ^{13}C NMR (100 MHz, CDCl_3) 153.1 (d, $J = 242.4$ Hz), 148.6, 139.9 (d, $J = 3.0$ Hz), 132.6, 121.3 (d, $J = 20.2$ Hz), 121.0, 120.9, 120.3, 118.3 (d, $J = 3.0$ Hz), 117.0 (d, $J = 11.1$ Hz), 115.1, 110.8, 55.7 ppm. IR (KBr): $\nu = 1598, 1514, 1498, 1460, 1244, 1221, 1115, 1029, 813, 746, 533\text{ cm}^{-1}$. HRMS (ESI): m/z for $\text{C}_{13}\text{H}_{11}\text{ClFNO}$ $[\text{M}+\text{H}]^+$ calcd 252.0591, found 252.0586.

3-Fluoro-5-methoxy-N-(2-methoxyphenyl)aniline 3bl



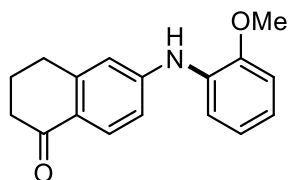
Yellow oil (105.1 mg, 85%). Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.6$). ^1H NMR (400 MHz, CDCl_3) δ 7.35-7.47 (m, 1 H), 6.87-7.05 (m, 3 H), 6.44-6.58 (m, 2 H), 6.11-6.33 (m, 2 H), 3.90 (s, 3 H), 3.80 (d, $J = 7.0$ Hz, 3 H); ^{19}F NMR (376 MHz, CDCl_3) δ -111.2 (m, 1 F); ^{13}C NMR (100 MHz, CDCl_3) δ 164.7 (d, $J = 243.4$ Hz), 161.8 (d, $J = 13.1$ Hz), 149.2, 145.6 (d, $J = 13.1$ Hz), 131.7, 121.5, 120.9, 117.0, 110.9, 98.9, 96.9 (d, $J = 25.3$ Hz), 93.9 (d, $J = 25.3$ Hz), 55.7, 55.5 ppm. IR (KBr): $\nu = 3410, 2938, 1589, 1491, 1460, 1250, 1157, 1129, 821, 744, 672, 447$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{14}\text{H}_{14}\text{FNO}_2$ $[\text{M}+\text{H}]^+$ calcd 248.1087, found 248.1079.

***N*-(2-Methoxyphenyl)-2-methyl-3-nitroaniline 3bm**



Yellow solid (96.9 mg, 75%). Mp: 100-101 °C. Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.7$). ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, $J = 8.1$ Hz, 1 H), 7.39 (d, $J = 8.1$ Hz, 1 H), 7.21 (t, $J = 8.1$ Hz, 1 H), 7.03 (d, $J = 6.8$ Hz, 1 H), 6.95 (d, $J = 3.5$ Hz, 2 H), 6.87-6.93 (m, 1 H), 6.00 (s, 1 H), 3.92 (s, 3 H), 2.39 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.9, 148.9, 143.4, 132.3, 126.8, 122.8, 122.1, 121.5, 121.0, 117.0, 116.3, 110.9, 55.8, 13.6 ppm. IR (KBr): $\nu = 3414, 1597, 1524, 1464, 1352, 1244, 1116, 1028, 851, 802, 778, 737$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ calcd 259.1083, found 259.1081.

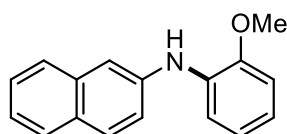
6-((2-Methoxyphenyl)amino)-3,4-dihydronaphthalen-1(2H)-one 3bn



Yellow solid (93.6 mg, 70%). Mp: 52-53 °C. Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.3$). ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 8.6$ Hz, 1 H), 7.38 (dd, $J = 7.7, 1.8$ Hz, 1 H), 6.98-7.05 (m, 1 H), 6.96 (dd, $J = 9.4, 1.8$ Hz, 1 H), 6.87-6.94 (m, 2

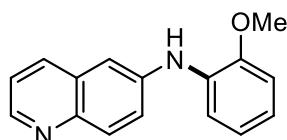
H), 6.83 (s, 1 H), 6.45 (s, 1 H), 3.83 (s, 3 H), 2.82 (t, $J = 6.3$ Hz, 2 H), 2.47-2.65 (m, 2 H), 2.06 (q, $J = 6.0$ Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.0, 150.0, 148.3, 146.9, 130.2, 129.5, 125.2, 122.8, 120.8, 118.8, 114.3, 113.6, 111.1, 55.7, 39.0, 30.3, 23.5 ppm. IR (KBr): $\nu = 3318, 2936, 1659, 1582, 1520, 1350, 1284, 1245, 1183, 1115, 1026, 897, 823, 746, 701, 657$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{17}\text{H}_{17}\text{NO}_2$ $[\text{M}+\text{H}]^+$ calcd 268.1338, found 268.1335.

***N*-(2-Methoxyphenyl)naphthalen-2-amine 3bo**



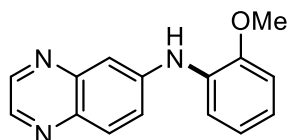
Yellow solid (99.7 mg, 80%). Mp: 57-58 °C. Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.8$). ^1H NMR (400 MHz, CDCl_3) δ 7.83-7.92 (m, 2 H), 7.80 (d, $J = 8.1$ Hz, 1 H), 7.67 (s, 1 H), 7.62 (d, $J = 7.4$ Hz, 1 H), 7.55 (t, $J = 7.5$ Hz, 1 H), 7.39-7.48 (m, 2 H), 6.99-7.12 (m, 3 H), 6.49 (s, 1 H), 3.97 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.8, 140.7, 134.9, 133.0, 129.5, 129.4, 127.9, 126.9, 126.7, 123.8, 121.1, 121.0, 120.7, 115.5, 112.4, 110.9, 55.8 ppm. The spectroscopic data were matched with those reported in the literature.^[10]

***N*-(2-Methoxyphenyl)quinolin-6-amine 3bp**



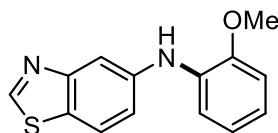
White solid (108.9 mg, 87%). Mp: 142-143 °C. Eluent: ethyl acetate/petroleum ether (1:1, $R_f = 0.5$). ^1H NMR (400 MHz, CDCl_3) δ 8.69 (dd, $J = 4.3, 1.7$ Hz, 1 H), 7.98 (d, $J = 9.0$ Hz, 1 H), 7.90 (d, $J = 7.8$ Hz, 1 H), 7.46 (dt, $J = 9.2, 2.9$ Hz, 2 H), 7.40 (d, $J = 2.6$ Hz, 1 H), 7.25 (dd, $J = 8.3, 4.3$ Hz, 1 H), 6.90-6.96 (m, 3 H), 6.42 (s, 1 H), 3.86 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.1, 147.7, 144.5, 141.3, 134.5, 131.9, 130.6, 129.7, 123.8, 121.6, 121.4, 120.9, 116.3, 110.9, 110.0, 55.7 ppm. IR (KBr): $\nu = 1624, 1596, 1527, 1502, 1438, 1378, 1295, 1250, 1115, 1028, 831, 747$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ calcd 251.1184, found 251.1180.

***N*-(2-Methoxyphenyl)quinoxalin-6-amine 3bq**



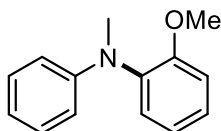
Yellow solid (111.8 mg, 89%). Mp: 41-42 °C. Eluent: ethyl acetate/petroleum ether (1:1, $R_f = 0.5$). ^1H NMR (400 MHz, CDCl_3) δ 8.61 (t, $J = 2.1$ Hz, 1 H), 8.52 (t, $J = 2.1$ Hz, 1 H), 7.88 (d, $J = 9.1$ Hz, 1 H), 7.64 (t, $J = 2.3$ Hz, 1 H), 7.51 (dt, $J = 7.7, 1.9$ Hz, 1 H), 7.42 (dt, $J = 9.0, 2.3$ Hz, 1 H), 6.85-6.99 (m, 3 H), 6.63 (s, 1 H), 3.79 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.7, 145.2, 145.1, 145.0, 141.6, 139.0, 130.5, 130.3, 123.9, 122.7, 120.9, 118.1, 111.0, 109.0, 55.7 ppm. IR (KBr): $\nu = 3402, 3271, 2927, 1621, 1595, 1529, 1501, 1349, 1251, 1229, 1116, 1028, 868, 824, 778, 745, 415$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ calcd 252.1137, found 252.1134.

***N*-(2-Methoxyphenyl)benzo[d]thiazol-5-amine 3br**



Yellow solid (110.2 mg, 86%). Mp: 101-102 °C. Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.5$). ^1H NMR (400 MHz, CDCl_3) δ 8.92 (s, 1 H), 7.94 (d, $J = 2.2$ Hz, 1 H), 7.77 (d, $J = 8.6$ Hz, 1 H), 7.36-7.42 (m, 1 H), 7.23 (dd, $J = 8.6, 2.2$ Hz, 1 H), 6.87-6.94 (m, 3 H), 6.36 (s, 1 H), 3.87 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.9, 154.8, 148.6, 142.1, 132.8, 126.0, 122.2, 121.0, 120.7, 118.9, 115.2, 111.6, 110.8, 55.7 ppm. IR (KBr): $\nu = 3401, 3063, 2931, 2833, 1590, 1557, 1508, 1430, 1228, 1113, 1025, 860, 804, 729, 635, 423$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{OS}$ $[\text{M}+\text{H}]^+$ calcd 257.0749, found 257.0745.

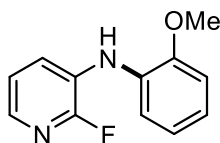
2-Methoxy-*N*-methyl-*N*-phenylaniline 3bs



Yellow oil (89.6 mg, 84%). Eluent: ethyl acetate/petroleum ether (10:1, $R_f = 0.8$). ^1H NMR (400 MHz, CDCl_3) δ 7.30 (dt, $J = 10.5, 1.9$ Hz, 1 H), 7.25-7.27 (m, 1 H), 7.20-7.25 (m, 2 H), 7.03 (t, $J = 8.3$ Hz, 2 H), 6.79 (t, $J = 7.3$ Hz, 1 H), 6.73 (dd, $J = 7.8, 1.1$ Hz, 2 H), 3.82 (s, 3 H), 3.29 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.2,

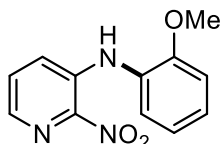
149.6, 137.0, 129.4, 128.9, 127.2, 121.5, 117.4, 113.6, 112.8, 55.8, 39.2 ppm. The spectroscopic data were matched with those reported in the literature.^[15]

2-Fluoro-*N*-(2-methoxyphenyl)pyridin-3-amine **3bt**



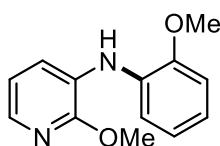
Yellow oil (105.8 mg, 97%). Eluent: ethyl acetate/petroleum ether (1:1, $R_f = 0.9$). ^1H NMR (400 MHz, CDCl_3) δ 7.63 (dd, $J = 10.3, 6.2$ Hz, 2 H), 7.26 (dd, $J = 8.0, 1.7$ Hz, 1 H), 7.02 (dd, $J = 7.7, 4.9$ Hz, 1 H), 6.94-6.99 (m, 1 H), 6.91 (dd, $J = 6.7, 3.9$ Hz, 2 H), 6.24 (s, 1 H), 3.85 (s, 3 H). ^{19}F NMR (376 MHz, CDCl_3) δ -83.9 (m, 1 F); ^{13}C NMR (100 MHz, CDCl_3) δ 153.9 (d, $J = 232.3$ Hz), 149.7, 136.1 (d, $J = 20.2$ Hz), 130.1, 127.4 (d, $J = 20.20$ Hz), 123.6 (d, $J = 5.05$ Hz), 122.5, 121.7 (d, $J = 10.1$ Hz), 120.8, 117.1, 111.1, 55.7 ppm. IR (KBr): $\nu = 3418, 1597, 1573, 1514, 1456, 1440, 1230, 1172, 1108, 1025, 828, 789, 737, 449$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{12}\text{H}_{11}\text{FN}_2\text{O}$ $[\text{M}+\text{H}]^+$ calcd 219.0934, found 219.0928.

N-(2-Methoxyphenyl)-2-nitropyridin-3-amine **3bu**



Reddish brown solid (88.3 mg, 72%). Mp: 134-135 °C. Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.5$). ^1H NMR (400 MHz, CDCl_3) δ 9.12 (s, 1 H), 7.96 (dd, $J = 4.0, 1.5$ Hz, 1 H), 7.61 (dd, $J = 8.6, 1.5$ Hz, 1 H), 7.35 (dd, $J = 8.6, 4.0$ Hz, 1 H), 7.29 (dd, $J = 7.6, 1.6$ Hz, 1 H), 7.19-7.24 (m, 1 H), 6.99 (t, $J = 8.3$ Hz, 2 H), 3.84 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.0, 142.2, 138.6, 137.2, 129.9, 126.9, 126.6, 125.9, 124.0, 120.9, 111.9, 55.8 ppm. IR (KBr): $\nu = 3364, 2924, 1592, 1505, 1483, 1253, 1140, 1116, 1047, 1024, 891, 848, 807, 751, 637$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_3$ $[\text{M}+\text{H}]^+$ calcd 246.0879, found 246.0872.

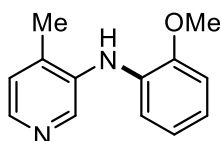
2-Methoxy-*N*-(2-methoxyphenyl)pyridin-3-amine **3bv**



Yellow oil (105.9 mg, 92%). Eluent: ethyl acetate/petroleum ether (1:1, $R_f = 0.9$). ^1H

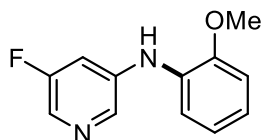
NMR (400 MHz, CDCl₃) δ 7.66 (dd, J = 5.0, 1.6 Hz, 1 H), 7.50 (dd, J = 7.8, 1.6 Hz, 1 H), 7.34 (dd, J = 6.8, 2.1 Hz, 1 H), 6.91 (q, J = 4.1 Hz, 3 H), 6.77-6.82 (m, 1 H), 6.49 (s, 1 H), 4.04 (s, 3 H), 3.87 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 153.9, 149.4, 135.9, 131.2, 127.9, 121.3, 120.8, 119.3, 117.0, 116.4, 110.8, 55.7, 53.6 ppm. IR (KBr): ν = 3416, 2948, 1579, 1517, 1482, 1452, 1395, 1241, 1113, 1019, 782, 741 cm⁻¹. HRMS (ESI): m/z for C₁₃H₁₄N₂O₂ [M+H]⁺ calcd 231.1134, found 231.1129.

***N*-(2-Methoxyphenyl)-4-methylpyridin-3-amine 3bw**



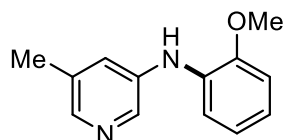
Yellow oil (97.5 mg, 91%). Eluent: ethyl acetate/petroleum ether (1:1, R_f = 0.5). ¹H NMR (400 MHz, CDCl₃) δ 8.52 (s, 1 H), 8.16 (d, J = 4.9 Hz, 1 H), 7.11 (d, J = 4.9 Hz, 1 H), 6.88-6.93 (m, 2 H), 6.83-6.85 (m, 2 H), 5.80 (s, 1 H), 3.90 (s, 3 H), 2.26 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 148.2, 143.6, 142.1, 138.7, 137.9, 133.2, 125.7, 121.0, 120.3, 114.6, 110.6, 55.7, 17.5 ppm. IR (KBr): ν = 2929, 1600, 1562, 1512, 1456, 1410, 1320, 1243, 1115, 1028, 822, 746, 728 cm⁻¹. HRMS (ESI): m/z for C₁₃H₁₄N₂O [M+H]⁺ calcd 215.1184, found 215.1188.

5-Fluoro-*N*-(2-methoxyphenyl)pyridin-3-amine 3bx



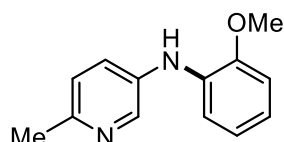
White solid (106.9 mg, 98%). Mp: 76-77 °C. Eluent: ethyl acetate/petroleum ether (1:1, R_f = 0.8). ¹H NMR (400 MHz, CDCl₃) δ 8.20 (dd, J = 2.3, 1.4 Hz, 1 H), 7.98 (d, J = 2.4 Hz, 1 H), 7.28 (dd, J = 8.1, 1.7 Hz, 1 H), 7.16-7.20 (m, 1 H), 6.96-7.03 (m, 1 H), 6.91-6.95 (m, 2 H), 6.29 (s, 1 H), 3.88 (s, 3 H); ¹⁹F NMR (376 MHz, CDCl₃) δ -126.8 (m, 1 F); ¹³C NMR (100 MHz, CDCl₃) δ 160.1 (d, J = 252.5 Hz), 149.5, 141.4 (d, J = 6.1 Hz), 135.9 (d, J = 3.0 Hz), 130.4, 129.1 (d, J = 76.8 Hz), 122.6, 121.0, 117.0, 111.1, 109.5 (d, J = 22.2 Hz), 55.7 ppm. The spectroscopic data were matched with those reported in the literature.^[16]

***N*-(2-Methoxyphenyl)-5-methylpyridin-3-amine 3by**



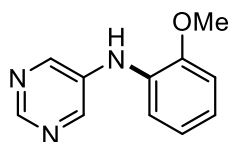
Yellow oil (103.9 mg, 97%). Eluent: ethyl acetate/petroleum ether (1:1, $R_f = 0.5$). ^1H NMR (400 MHz, CDCl_3) δ 8.26 (s, 1 H), 8.01 (s, 1 H), 7.27 (s, 2 H), 6.90 (s, 3 H), 6.12 (s, 1 H), 3.88 (s, 3 H), 2.28 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.8, 142.8, 139.2, 138.2, 133.5, 132.0, 124.9, 121.1, 120.9, 115.3, 110.8, 55.7, 18.5 ppm. IR (KBr): $\nu = 3395, 3250, 3038, 2925, 1587, 1524, 1459, 1298, 1251, 1180, 1116, 1027, 850, 743, 708\text{ cm}^{-1}$. HRMS (ESI): m/z for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ calcd 215.1184, found 215.1181.

***N*-(2-Methoxyphenyl)-6-methylpyridin-3-amine 3b**



Yellow solid (99.6 mg, 93%). Mp: 108-109 °C. Eluent: ethyl acetate/petroleum ether (1:1, $R_f = 0.5$). ^1H NMR (400 MHz, CDCl_3) δ 8.34 (d, $J = 2.8$ Hz, 1 H), 7.40 (dd, $J = 8.3, 2.8$ Hz, 1 H), 7.14 (dd, $J = 5.6, 3.5$ Hz, 1 H), 7.05 (d, $J = 8.3$ Hz, 1 H), 6.83-6.89 (m, 3 H), 6.06 (s, 1 H), 3.88 (s, 3 H), 2.49 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.1, 148.3, 141.1, 136.7, 132.8, 126.5, 123.3, 121.0, 120.4, 114.0, 110.7, 55.7, 23.6 ppm. IR (KBr): $\nu = 3402, 3005, 2936, 1594, 1515, 1492, 1459, 1243, 1115, 1027, 822, 742, 723, 648\text{ cm}^{-1}$. HRMS (ESI): m/z for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ calcd 215.1184, found 215.1180.

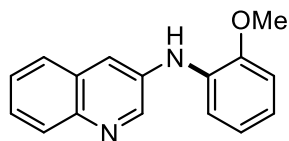
***N*-(2-Methoxyphenyl)pyrimidin-5-amine 3ca**



White solid (82.5 mg, 82%). Mp: 105-106 °C. Eluent: ethyl acetate/petroleum ether (1:1, $R_f = 0.4$). ^1H NMR (400 MHz, CDCl_3) δ 8.73 (s, 1 H), 8.53 (s, 2 H), 7.22 (d, $J = 6.8$ Hz, 1 H), 6.94-7.00 (m, 1 H), 6.86-6.93 (m, 2 H), 6.19 (s, 1 H), 3.85 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.9, 149.4, 145.3, 138.2, 130.1, 122.7, 121.0, 116.5, 111.2, 55.7 ppm. IR (KBr): $\nu = 1573, 1522, 1424, 1250, 1122, 1026, 750, 723\text{ cm}^{-1}$.

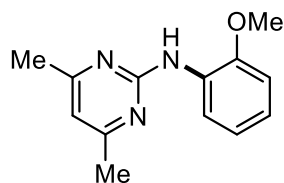
HRMS (ESI): m/z for $C_{11}H_{11}N_3O$ $[M+H]^+$ calcd 202.0980, found 202.0978.

***N*-(2-Methoxyphenyl)quinolin-3-amine 3cb**



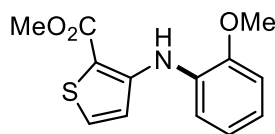
Yellow solid (107.6 mg, 86%). Mp: 68-69 °C. Eluent: ethyl acetate/petroleum ether (1:1, R_f = 0.5). 1H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, J = 2.6 Hz, 1 H), 8.03 (d, J = 7.8 Hz, 1 H), 7.77 (s, 1 H), 7.62 (d, J = 8.0 Hz, 1 H), 7.39-7.52 (m, 3 H), 6.83-7.02 (m, 3 H), 6.46 (s, 1 H), 3.87 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 145.8, 143.7, 136.8, 131.6, 129.1, 129.0, 127.2, 126.6, 126.6, 121.6, 121.0, 117.3, 115.7, 110.9, 55.7 ppm. The spectroscopic data were matched with those reported in the literature.^[17]

***N*-(2-Methoxyphenyl)-4,6-dimethylpyrimidin-2-amine 3cc**



Yellow solid (57.3 mg, 50%). Mp: 100-101 °C. Eluent: ethyl acetate/petroleum ether (5:1, R_f = 0.4). 1H NMR (400 MHz, $CDCl_3$) δ 8.63 (dd, J = 7.9, 1.8 Hz, 1 H), 7.70 (s, 1 H), 6.85-7.00 (m, 2 H), 6.87 (dd, J = 7.9, 1.7 Hz, 1 H), 6.47 (s, 1 H), 3.87 (s, 3 H), 2.37 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 159.9, 147.8, 129.8, 121.2, 120.9, 118.2, 111.6, 109.9, 55.7, 24.1 ppm. The spectroscopic data were matched with those reported in the literature.^[18]

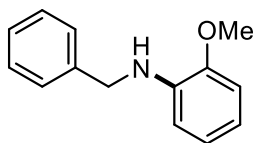
Methyl 3-((2-methoxyphenyl)amino)thiophene-2-carboxylate 3cd



Yellow oil (102.7 mg, 78%). Eluent: ethyl acetate/petroleum ether (5:1, R_f = 0.5). 1H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1 H), 7.34 (dd, J = 9.5, 6.6 Hz, 2 H), 7.18 (d, J = 5.6 Hz, 1 H), 6.95-7.01 (m, 1 H), 6.91 (dd, J = 12.0, 7.6 Hz, 2 H), 3.88 (s, 3 H), 3.87 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 150.7, 149.7, 131.9, 131.1, 122.6, 120.8, 118.1, 117.8, 110.9, 103.7, 55.8, 51.6 ppm. IR (KBr): ν = 2949, 1669, 1598,

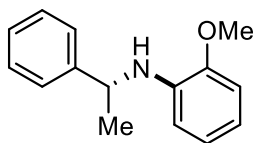
1562, 1503, 1445, 1396, 1254, 1236, 1087, 1030, 776, 743, 454 cm^{-1} . HRMS (ESI): m/z for $\text{C}_{13}\text{H}_{13}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$ calcd 264.0694, found 264.0688.

***N*-Benzyl-2-methoxyaniline 3ce**



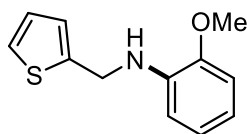
Yellow oil (66.1 mg, 62%). Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.8$). ^1H NMR (400 MHz, CDCl_3) δ 7.53 (d, $J = 6.8$ Hz, 2 H), 7.48 (t, $J = 7.4$ Hz, 2 H), 7.41 (t, $J = 7.1$ Hz, 1 H), 6.96-7.03 (m, 1 H), 6.93 (dd, $J = 8.0, 1.5$ Hz, 1 H), 6.84 (td, $J = 7.6, 1.6$ Hz, 1 H), 6.75 (dd, $J = 7.8, 1.6$ Hz, 1 H), 4.79 (s, 1 H), 4.48 (s, 2 H), 3.96 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.1, 139.9, 138.4, 128.9, 127.8, 127.4, 121.6, 116.9, 110.3, 109.7, 55.6, 48.3 ppm. The spectroscopic data were matched with those reported in the literature.^[19]

(*R*)-2-Methoxy-*N*-(1-phenylethyl)aniline 3cf



Yellow solid (63.6 mg, 56%). Mp: 74-75 $^{\circ}\text{C}$. Eluent: ethyl acetate/petroleum ether (20:1, $R_f = 0.5$). ^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, $J = 8.1$ Hz, 2 H), 7.38 (t, $J = 7.4$ Hz, 2 H), 7.26-7.32 (m, 1 H), 6.84 (d, $J = 7.8$ Hz, 1 H), 6.78 (t, $J = 7.6$ Hz, 1 H), 6.69 (t, $J = 7.7$ Hz, 1 H), 6.43 (d, $J = 7.6$ Hz, 1 H), 4.71 (s, 1 H), 4.55 (q, $J = 6.8$ Hz, 1 H), 3.94 (s, 3 H), 1.62 (d, $J = 6.6$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.7, 145.6, 137.4, 128.8, 127.0, 126.0, 121.3, 116.5, 111.2, 109.4, 55.6, 53.5, 25.4 ppm. The spectroscopic data were matched with those reported in the literature.^[20]

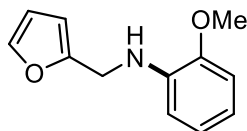
2-Methoxy-*N*-(thiophen-2-ylmethyl)aniline 3cg



Yellow oil (80.0 mg, 73%). Eluent: ethyl acetate/petroleum ether (10:1, $R_f = 0.6$). ^1H NMR (400 MHz, CDCl_3) δ 7.27 (d, $J = 3.7$ Hz, 1 H), 7.09 (s, 1 H), 7.01-7.06 (m, 1 H), 6.95 (t, $J = 6.9$ Hz, 1 H), 6.86 (d, $J = 6.7$ Hz, 1 H), 6.78 (q, $J = 7.5$ Hz, 2 H), 4.74 (s, 1 H), 4.59 (s, 2 H), 3.89 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.1, 143.4, 137.8,

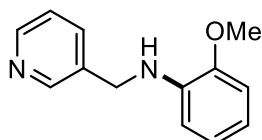
127.0, 125.1, 124.7, 121.4, 117.4, 110.5, 109.7, 55.6, 43.4 ppm. The spectroscopic data were matched with those reported in the literature.^[21]

N-(Furan-2-ylmethyl)-2-methoxyaniline 3ch



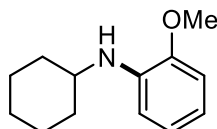
Yellow oil (76.2 mg, 75%). Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.8$). ^1H NMR (400 MHz, CDCl_3) δ 7.43 (s, 1 H), 6.91-7.00 (m, 1 H), 6.86 (dd, $J = 8.0, 4.2$ Hz, 1 H), 6.76-6.82 (m, 2 H), 6.38 (d, $J = 2.0$ Hz, 1 H), 6.31 (d, $J = 3.6$ Hz, 1 H), 4.70 (s, 1 H), 4.40 (s, 2 H), 3.89 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.2, 147.2, 142.0, 137.8, 121.4, 117.3, 110.5, 110.4, 109.7, 107.1, 55.6, 41.3 ppm. The spectroscopic data were matched with those reported in the literature.^[22]

2-Methoxy-N-(pyridin-3-ylmethyl)aniline 3ci



Yellow oil (81.4 mg, 76%). Eluent: ethyl acetate/petroleum ether (1:1, $R_f = 0.5$). ^1H NMR (400 MHz, CDCl_3) δ 8.62 (s, 1 H), 8.50 (d, $J = 4.9$ Hz, 1 H), 7.68 (d, $J = 8.0$ Hz, 1 H), 7.23 (dd, $J = 7.7, 4.7$ Hz, 1 H), 6.76-6.95 (m, 2 H), 6.69 (td, $J = 7.7, 1.6$ Hz, 1 H), 6.54 (d, $J = 7.6$ Hz, 1 H), 4.67 (s, 1 H), 4.36 (s, 2 H), 3.84 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.3, 148.7, 147.0, 137.7, 135.3, 135.2, 123.7, 121.4, 117.3, 110.2, 109.6, 55.5, 45.6 ppm. The spectroscopic data were matched with those reported in the literature.^[23]

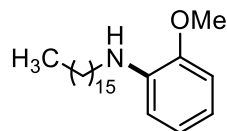
N-Cyclohexyl-2-methoxyaniline 3cj



Yellow oil (56.4 mg, 55%). Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.8$). ^1H NMR (400 MHz, CDCl_3) δ 6.92 (t, $J = 7.6$ Hz, 1 H), 6.82 (d, $J = 8.4$ Hz, 1 H), 6.69 (d, $J = 14.3$ Hz, 2 H), 4.21 (s, 1 H), 3.89 (s, 3 H), 3.28-3.37 (m, 1 H), 2.15 (d, $J = 8.9$ Hz, 2 H), 1.84 (d, $J = 13.4$ Hz, 2 H), 1.45 (q, $J = 12.7$ Hz, 2 H), 1.27-1.33 (m, 2 H), 1.22-1.27 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.9, 137.4, 121.4, 115.9, 110.3,

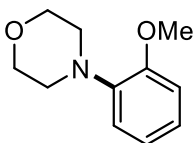
109.7, 55.5, 51.5, 33.6, 26.2, 25.3 ppm. The spectroscopic data were matched with those reported in the literature.^[4]

***N*-hexadecyl-2-methoxyaniline 3ck**



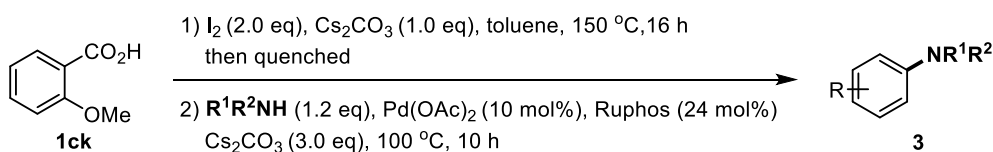
White solid (107.7 mg, 62%). Mp: 55-56 °C. Eluent: ethyl acetate/petroleum ether (10:1, $R_f = 0.6$). ^1H NMR (400 MHz, CDCl_3) δ 6.91 (t, $J = 7.6$ Hz, 1 H), 6.79 (d, $J = 7.9$ Hz, 1 H), 6.69 (t, $J = 7.7$ Hz, 1 H), 6.64 (d, $J = 7.8$ Hz, 1 H), 4.21 (s, 1 H), 3.87 (s, 3 H), 3.15 (t, $J = 7.2$ Hz, 2 H), 1.66-1.73 (m, 3 H), 1.42-1.51 (m, 3 H), 1.30-1.34 (m, 22 H), 0.94 (t, $J = 6.7$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.8, 138.6, 121.4, 116.2, 109.8, 109.4, 55.4, 43.9, 32.1, 29.7-29.9 (m, 10 C), 29.6, 27.4, 22.9, 14.3 ppm. IR (KBr): $\nu = 2917, 2847, 1602, 1521, 1468, 1224, 1026, 730$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{23}\text{H}_{41}\text{NO}$ $[\text{M}+\text{H}]^+$ calcd 348.3266, found 348.3262.

4-(2-Methoxyphenyl)morpholine 3cl



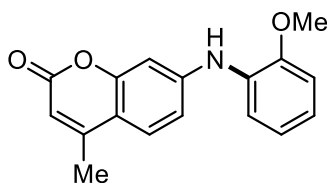
Yellow oil (82.1 mg, 85%). Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.5$). ^1H NMR (400 MHz, CDCl_3) δ 6.97-7.04 (m, 1 H), 6.90-6.94 (m, 2 H), 6.86 (d, $J = 7.8$ Hz, 1 H), 3.86-3.91 (m, 4 H), 3.85 (s, 3 H), 3.02-3.09 (m, 4 H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.3, 141.2, 123.3, 121.1, 118.1, 111.4, 67.3, 55.5, 51.3 ppm. The spectroscopic data were matched with those reported in the literature.^[24]

Decarboxylative amination modifications of complex bioactive molecules



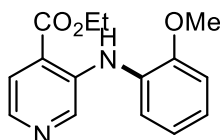
o-Methoxybenzoic acid (0.5 mmol), I_2 (1.0 mmol, 2.0 equiv) and Cs_2CO_3 (0.5 mmol, 1.0 equiv, anhydrous) were placed into an oven-dried 25 mL Schlenk tube that was equipped with a stirring bar under argon atmosphere. Freshly distilled toluene (3.0 mL) was added to the Schlenk tube. The reaction was stirred at 150 °C for 16 h and then quenched by NEt_3 (4.0 mmol, 8.0 equiv) at 120 °C for 5 h. Subsequently, after the filtration, the filtrate was added to another Schlenk tube charged with $Pd(OAc)_2$ (10 mol%), Ruphos (24 mol%), complex bioactive amines (0.6 mmol, 1.2 equiv) and Cs_2CO_3 (1.5 mmol, 3.0 equiv, anhydrous) under argon atmosphere. The mixture was stirred at 100 °C for 10 h. After the reaction, the solution was filtered and washed with ethyl acetate for three times. The combined solvents were removed under vacuum, and the residue was purified by column chromatography to obtain the desired *N*-aryl complex bioactive anilines.

7-((2-Methoxyphenyl)amino)-4-methyl-2H-chromen-2-one **3cm**



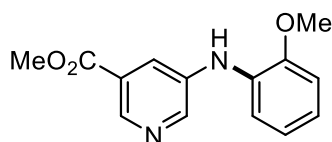
Yellow solid (122.4 mg, 87%). Mp: 160-161 °C. Eluent: ethyl acetate/petroleum ether (2:1, $R_f = 0.4$). 1H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, $J = 13.6, 8.2$ Hz, 2 H), 6.96-7.04 (m, 2 H), 6.93 (t, $J = 7.9$ Hz, 3 H), 6.43 (s, 1 H), 6.04 (s, 1 H), 3.87 (s, 3 H), 2.35 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 155.5, 152.7, 149.8, 147.2, 130.1, 125.6, 122.9, 120.9, 118.3, 113.3, 112.9, 111.1, 110.9, 102.1, 55.7, 18.6 ppm. The spectroscopic data were matched with those reported in the literature.^[25]

Ethyl 3-((2-methoxyphenyl)amino)isonicotinate **3cn**



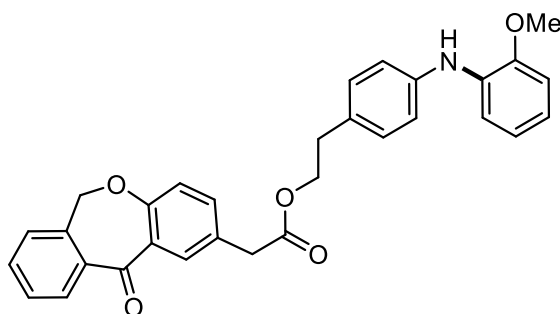
Yellow solid (113.0 mg, 83%). Mp: 57-58 °C. Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.4$). ^1H NMR (400 MHz, CDCl_3) δ 9.09 (s, 1 H), 8.68 (s, 1 H), 8.01 (d, $J = 5.2$ Hz, 1 H), 7.69 (d, $J = 5.2$ Hz, 1 H), 7.41 (d, $J = 8.2$ Hz, 1 H), 7.07 (t, $J = 7.8$ Hz, 1 H), 6.93 (t, $J = 8.0$ Hz, 2 H), 4.38 (q, $J = 7.2$ Hz, 2 H), 3.86 (s, 3 H), 1.40 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.3, 151.7, 141.8, 138.9, 138.1, 128.8, 124.5, 123.3, 121.1, 120.8, 117.8, 111.4, 61.5, 55.8, 14.3 ppm. IR (KBr): $\nu = 3333$, 1694, 1597, 1563, 1510, 1419, 1296, 1254, 1222, 1177, 1118, 1099, 1026, 788, 747, 711 cm^{-1} . HRMS (ESI): m/z for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_3$ $[\text{M}+\text{Na}]^+$ calcd 295.1059, found 295.1057.

Methyl 5-((2-methoxyphenyl)amino)nicotinate 3co



White solid (109.8 mg, 85%). Mp: 134-135 °C. Eluent: ethyl acetate/petroleum ether (1:1, $R_f = 0.5$). ^1H NMR (400 MHz, CDCl_3) δ 8.71 (s, 1 H), 8.54 (s, 1 H), 8.00 (d, $J = 1.7$ Hz, 1 H), 7.27 (d, $J = 8.1$ Hz, 1 H), 6.83-7.05 (m, 3 H), 6.29 (s, 1 H), 3.90 (s, 3 H), 3.86 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 149.3, 143.6, 142.4, 139.8, 130.7, 126.3, 123.6, 122.2, 121.0, 116.4, 111.0, 55.7, 52.5 ppm. IR (KBr): $\nu = 3372$, 2951, 1724, 1588, 1527, 1455, 1303, 1266, 1243, 1113, 1020, 768, 745, 700, 454 cm^{-1} . HRMS (ESI): m/z for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ calcd 259.1083, found 259.1079.

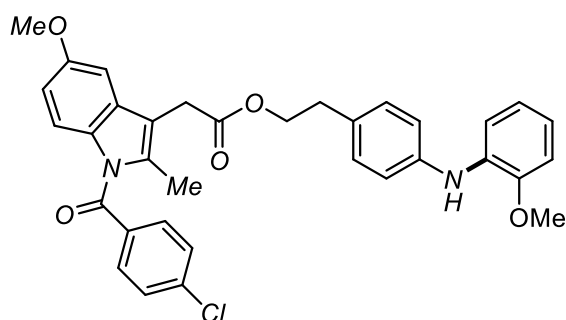
3-((2-methoxyphenyl)amino)phenethyl-2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate 3cp



Yellow oil (167.8 mg, 68%). Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.3$). ^1H NMR (400 MHz, CDCl_3) δ 8.12 (d, $J = 2.4$ Hz, 1 H), 7.89 (d, $J = 7.7$ Hz, 1 H), 7.54 (t, $J = 7.4$ Hz, 1 H), 7.45 (t, $J = 7.6$ Hz, 1 H), 7.38 (dd, $J = 8.4$, 2.3 Hz, 1 H), 7.34 (d, $J = 7.5$ Hz, 1 H), 7.25 (dd, $J = 6.0$, 2.0 Hz, 1 H), 7.07 (s, 4 H), 7.02 (d, $J = 8.4$ Hz, 1 H),

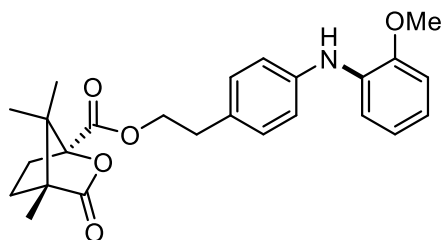
6.82-6.89 (m, 3 H), 6.08 (s, 1 H), 5.16 (s, 2 H), 4.30 (t, $J = 7.0$ Hz, 2 H), 3.87 (s, 3 H), 3.63 (s, 2 H), 2.88 (t, $J = 7.0$ Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.0, 171.5, 160.6, 148.2, 141.3, 140.6, 136.6, 136.4, 135.7, 133.2, 132.9, 132.5, 130.4, 130.0, 129.8, 129.6, 127.9, 125.2, 121.3, 121.1, 119.1, 118.9, 114.6, 110.6, 73.7, 65.8, 55.7, 40.4, 34.5 ppm. IR (KBr): $\nu = 2955, 2921, 2851, 1732, 1647, 1599, 1520, 1459, 1300, 1242, 1016, 829, 737, 702, 642$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{31}\text{H}_{27}\text{NO}_5$ $[\text{M}+\text{H}]^+$ calcd 494.1967, found 494.1959.

4-((2-Methoxyphenyl)amino)phenethyl-2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate 3cq



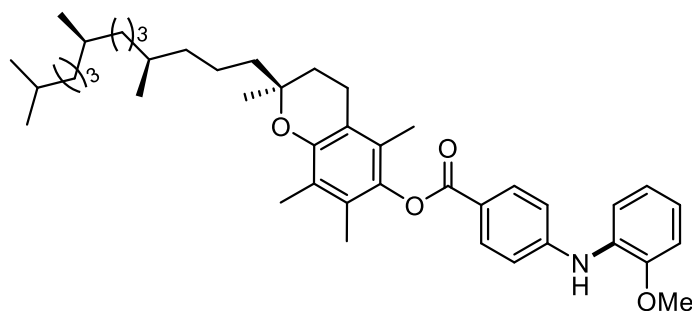
Yellow solid (183.7 mg, 63%). Mp: 39-40 °C. Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.4$). ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, $J = 1.9$ Hz, 1 H), 7.61 (d, $J = 1.9$ Hz, 1 H), 7.44 (d, $J = 2.0$ Hz, 1 H), 7.42 (d, $J = 2.0$ Hz, 1 H), 7.19-7.23 (m, 1 H), 7.00 (s, 4 H), 6.94 (d, $J = 2.6$ Hz, 1 H), 6.88 (dd, $J = 9.3, 4.4$ Hz, 2 H), 6.82-6.86 (m, 2 H), 6.67 (dd, $J = 9.0, 2.5$ Hz, 1 H), 6.01-6.13 (m, 1 H), 4.30 (t, $J = 6.8$ Hz, 2 H), 3.88 (s, 3 H), 3.81 (s, 3 H), 3.64 (s, 2 H), 2.85 (t, $J = 6.9$ Hz, 2 H), 2.32 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.9, 168.4, 156.2, 148.2, 141.2, 139.3, 136.0, 134.0, 133.2, 131.3, 130.9, 130.8, 130.4, 129.7, 129.2, 120.9, 119.8, 118.9, 115.1, 114.4, 112.7, 111.7, 110.6, 101.4, 65.8, 55.8, 55.7, 34.4, 30.5, 13.5 ppm. IR (KBr): $\nu = 2955, 2921, 2851, 1733, 1682, 1598, 1521, 1459, 1317, 1237, 1170, 1114, 835, 739$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{34}\text{H}_{31}\text{ClN}_2\text{O}_5$ $[\text{M}+\text{H}]^+$ calcd 583.2000, found 583.1993.

4-((2-Methoxyphenyl)amino)phenethyl-(1S,4R)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate 3cr



Yellow solid (180.0 mg, 85%). Mp: 37-38 °C. Eluent: ethyl acetate/petroleum ether (5:1, $R_f = 0.3$). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.21-7.25 (m, 1 H), 7.13 (d, $J = 8.4$ Hz, 2 H), 7.08 (d, $J = 7.8$ Hz, 2 H), 6.83-6.89 (m, 3 H), 6.11 (s, 1 H), 4.43 (t, $J = 7.0$ Hz, 2 H), 3.87 (s, 3 H), 2.95 (t, $J = 7.0$ Hz, 2 H), 2.36 (td, $J = 13.6, 10.1$ Hz, 1 H), 1.99 (td, $J = 13.5, 9.6$ Hz, 1 H), 1.84-1.93 (m, 1 H), 1.66 (td, $J = 13.3, 9.3$ Hz, 1 H), 1.09 (s, 3 H), 0.97 (s, 3 H), 0.87 (s, 3 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 178.3, 167.5, 148.2, 141.4, 133.2, 129.9, 120.9, 119.9, 119.1, 114.3, 110.6, 91.2, 66.2, 55.7, 54.9, 54.2, 34.4, 30.7, 29.0, 16.8, 16.7, 9.8 ppm. IR (KBr): $\nu = 2956, 2921, 2851, 1788, 1748, 1599, 1521, 1460, 1243, 1170, 1109, 932, 739$ cm^{-1} . HRMS (ESI): m/z for $\text{C}_{25}\text{H}_{29}\text{NO}_5$ $[\text{M}+\text{H}]^+$ calcd 424.2124, found 424.2119.

(S)-2,5,7,8-Tetramethyl-2-((4R,6R)-4,6,8-trimethylnonyl)chroman-6-yl-4-((2-methoxyphenyl)amino)benzoate 3cs

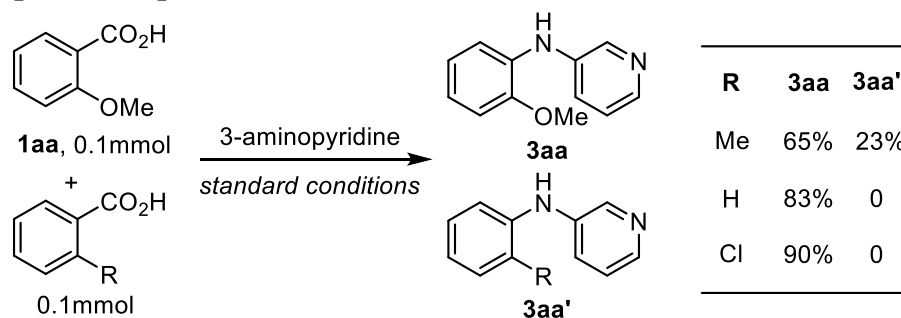


Yellow solid (263.9 mg, 88%). Mp: 55-56 °C. Eluent: ethyl acetate/petroleum ether (1:1, $R_f = 0.3$). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.14-8.22 (m, 2 H), 7.48 (dd, $J = 7.6, 1.8$ Hz, 1 H), 7.12-7.21 (m, 2 H), 6.92-7.08 (m, 3 H), 6.50 (s, 1 H), 3.91 (s, 3 H), 2.66 (t, $J = 6.9$ Hz, 2 H), 2.18 (s, 3 H), 2.13 (s, 3 H), 2.08 (s, 3 H), 1.87 (td, $J = 13.8, 12.5, 6.9$ Hz, 2 H), 1.46 (t, $J = 5.4$ Hz, 4 H), 1.31 (d, $J = 4.9$ Hz, 12 H), 1.09-1.25 (m, 7 H), 0.91-0.94 (m, 13 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 165.2, 149.9, 149.5, 148.3, 140.9, 132.2, 130.5, 127.3, 125.5, 123.1, 122.7, 120.9, 120.5, 118.2, 117.5, 115.3, 111.1, 55.7, 39.6, 37.7, 37.6, 37.5, 33.0, 28.2, 25.0, 24.6, 24.3, 23.9, 22.9, 22.8, 21.2, 20.8,

20.0, 19.9, 19.8, 13.2, 12.4, 12.0 ppm. IR (KBr): $\nu = 2925, 2866, 1716, 1591, 1525, 1460, 1275, 1237, 1171, 1089, 762, 742, 699, 500 \text{ cm}^{-1}$. HRMS (ESI): m/z for $\text{C}_{39}\text{H}_{53}\text{NO}_4$ $[\text{M}+\text{H}]^+$ calcd 656.4679, found 656.4670.

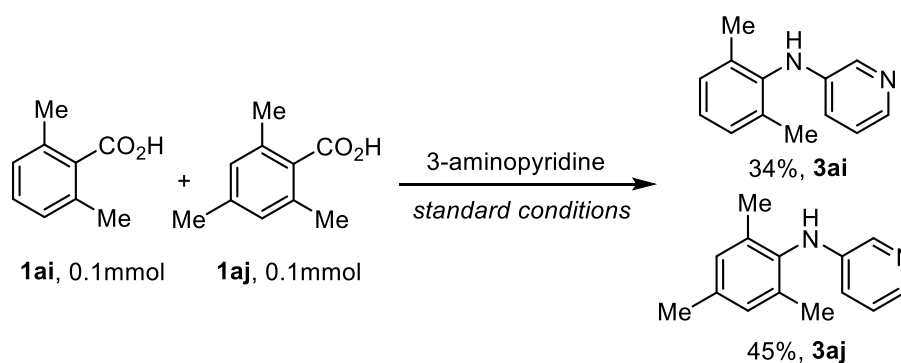
Preliminary mechanism studies

A. Competition experiments: *ortho*-substituents



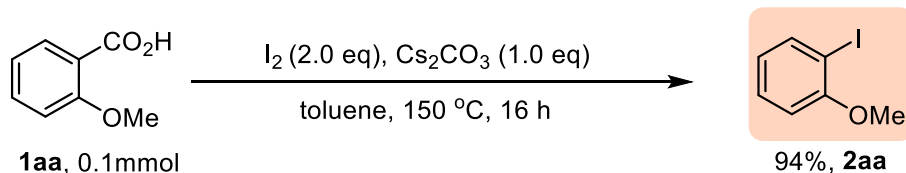
2-Methoxybenzoic acid (0.1 mmol), *ortho*-substituted benzoic acid (0.1 mmol, methyl, hydrogen, fluoro, chloro), I₂ (0.4 mmol, 2.0 equiv) and Cs₂CO₃ (0.2 mmol, 1.0 equiv, anhydrous) were placed into an oven-dried 25 mL Schlenk tube that was equipped with a stirring bar under argon atmosphere. Freshly distilled toluene (2.0 mL) was added to the Schlenk tube. The reaction was stirred at 150 °C for 16 h and then quenched by NEt₃ (1.6 mmol, 8.0 equiv) at 120 °C for 5 h. Subsequently, after the filtration, the filtrate was added to another Schlenk tube charged with Pd(OAc)₂ (10 mol%), Ruphos (24 mol%), amines (0.24 mmol, 1.2 equiv) and Cs₂CO₃ (0.6 mmol, 3.0 equiv, anhydrous) under argon atmosphere. The mixture was stirred at 100 °C for 10 h. After the reaction, the solution was filtered and washed with ethyl acetate for three times. The combined solvents were removed under vacuum, and the crude residue was analyzed by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. This reaction afforded 65:23 mixed products for 2-methoxybenzoic acid and 2-methylbenzoic acid, and single product *N*-(2-methoxyphenyl)pyridin-3-amine **3aa** in 83%, 90% yields, respectively, for the sequences containing with hydrogen and chloro-substituted benzoic acids.

B. Competition experiments: differences in electronic effects



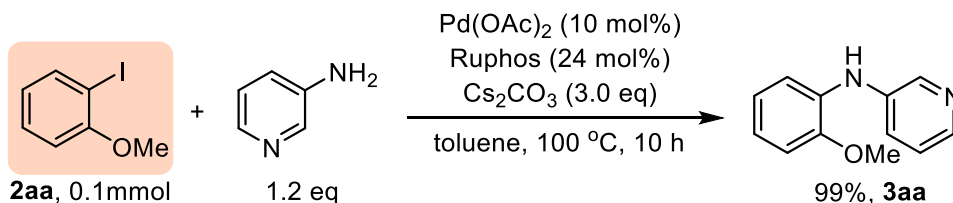
2,6-Dimethylbenzoic acid (0.1 mmol, **1ai**), 2,4,6-trimethylbenzoic acid (0.1 mmol, **1aj**), I₂ (0.4 mmol, 2.0 equiv) and Cs₂CO₃ (0.2 mmol, 1.0 equiv, anhydrous) were placed into an oven-dried 25 mL Schlenk tube that was equipped with a stirring bar under argon atmosphere. Freshly distilled toluene (2.0 mL) was added to the Schlenk tube. The reaction was stirred at 150 °C for 16 h and then quenched by NEt₃ (1.6 mmol, 8.0 equiv) at 120 °C for 5 h. Subsequently, after the filtration, the filtrate was added to another Schlenk tube charged with Pd(OAc)₂ (10 mol%), Ruphos (24 mol%), amines (0.24 mmol, 1.2 equiv) and Cs₂CO₃ (0.6 mmol, 3.0 equiv, anhydrous) under argon atmosphere. The mixture was stirred at 100 °C for 10 h. After the reaction, the solution was filtered and washed with ethyl acetate for three times. The combined solvents were removed under vacuum, and the crude residue was analyzed by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. This reaction afforded *N*-(2,6-dimethylphenyl)pyridin-3-amine **3ai** in 34% yield and *N*-mesitylpyridin-3-amine **3aj** in 45% yield.

C. Control experiments: decarboxylative iodination



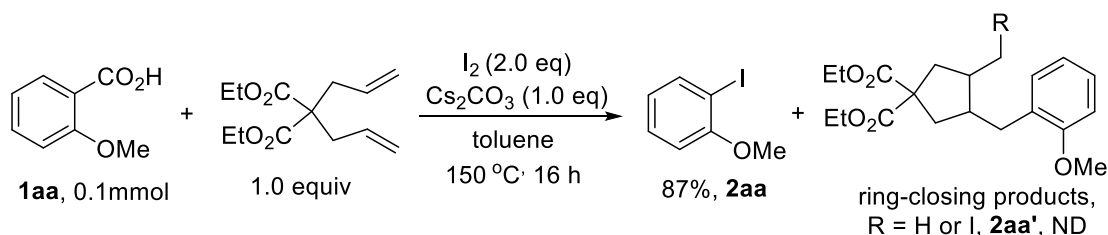
2-Methoxybenzoic acid (0.1 mmol), I₂ (0.2 mmol, 2.0 equiv) and Cs₂CO₃ (0.1 mmol, 1.0 equiv, anhydrous) were placed into an oven-dried 25 mL Schlenk tube that was equipped with a stirring bar under argon atmosphere. Freshly distilled toluene (1.0 mL) was added to the Schlenk tube. The reaction was stirred at 150 °C for 16 h and then quenched by NEt₃ (0.8 mmol, 8.0 equiv) at 120 °C for 5 h. After the reaction, the solution was filtered and washed with ethyl acetate for three times. The combined solvents were removed under vacuum, and the crude residue was analyzed by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. This reaction successfully afforded the desired *o*-methoxyiodobenzene **2aa** in 94% yield.

D. Control experiments: Buchwald-Hartwig amination



25 mL Schlenk tube charged with Pd(OAc)₂ (10 mol%), Ruphos (24 mol%) and Cs₂CO₃ (0.3 mmol, 3.0 equiv, anhydrous) was added *o*-methoxyiodobenzene (0.10 mmol), 3-aminopyridine (0.12 mmol, 1.2 equiv) and 1mL toluene under argon atmosphere. The mixture was stirred at 100 °C for 10 h. After the reaction, the solution was filtered and washed with ethyl acetate for three times. The combined solvents were removed under vacuum, and the crude residue was analyzed by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. This reaction successfully afforded the desired *N*-(2-methoxyphenyl)pyridin-3-amine **3aa** in 99% yield.

E. Radical exclusion experiment



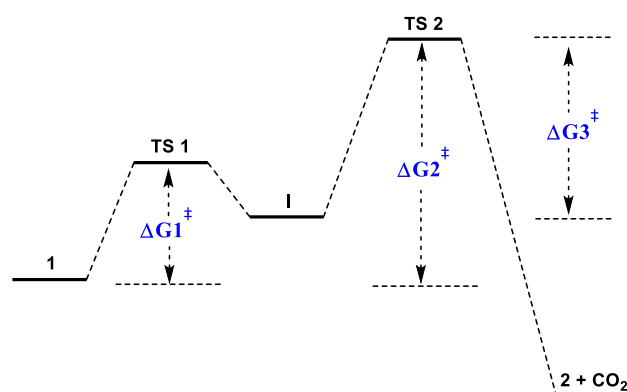
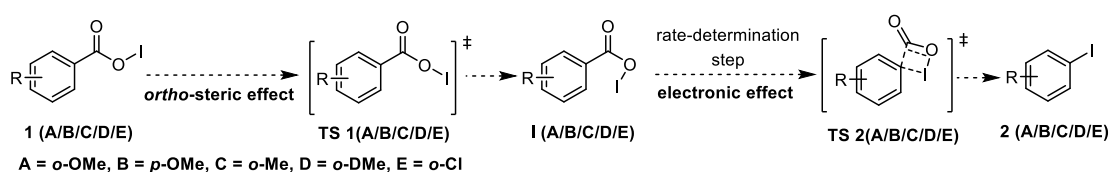
2-Methoxybenzoic acid (0.1 mmol), I₂ (0.2 mmol, 2.0 equiv) and Cs₂CO₃ (0.1 mmol, 1.0 equiv, anhydrous) were placed into an oven-dried 25 mL Schlenk tube that was equipped with a stirring bar under argon atmosphere. Freshly distilled toluene (1.0 mL) and diallylmalonate (1.0 equiv) were added to the Schlenk tube. The reaction was stirred at 150 °C for 16 h and then quenched by NEt₃ (0.8 mmol, 8.0 equiv) at 120 °C for 5 h. After the reaction, the solution was filtered and washed with ethyl acetate for three times. The combined solvents were removed under vacuum, and the crude residue was analyzed by GC-MS and ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. This reaction successfully afforded the desired *o*-methoxyiodobenzene **2aa** in 87% yield and no cyclization adducts were observed, suggesting that a radical mechanism is excluded in current decarboxylative iodination.

Theoretical calculation for decarboxylative iodination

A. Computational methods

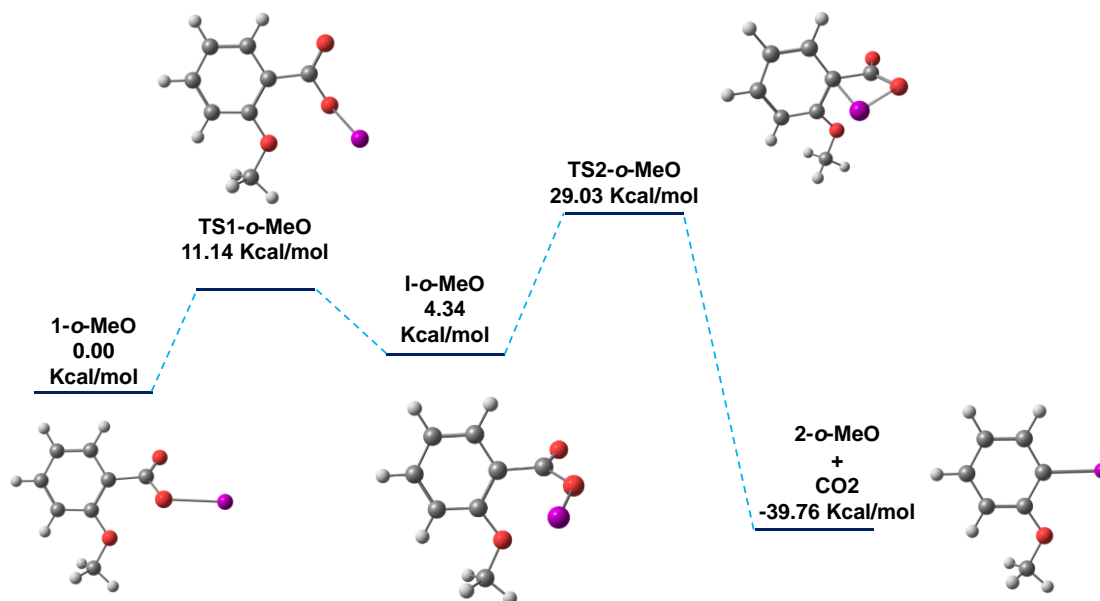
All calculations were performed with the Gaussian 09 package [26]. Geometry optimizations were performed with the dispersion-corrected density functional method B3LYP-D3 [27-29] with solvent effects in acetonitrile represented by the SMD solvation model [30]. The 6-311++G(d,p) basis set [31-33] was used for C, H, O and Cl atoms and the SDD basis set [34-35] was used for I. Normal vibrational mode analysis at the same level of theory confirmed that the optimized structures are minima (zero imaginary frequency) or saddle points (one imaginary frequency). The relative energies and free energies (at 298.15K, 1 atm) are in kcal/mol.

The decarboxylative iodination was modelled starting from the benzoyl hypoiodite **1**. An initial rotation provides intermediate **I** via transition state **TS 1**. The decarboxylation step proceeds from intermediate **I** via transition state **TS 2**. The resulting overall energy diagram is shown below:

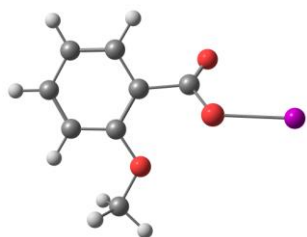


Scheme S1. Energies measured in kcal/mol for DFT modelling using a toluene solvent correction.

B. Coordinates and energies of computed structures



1-*o*-MeO

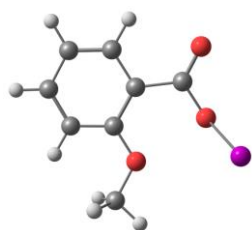


E = -546.292571

G = -546.197526

C	-1.54591100	-0.66041600	0.09001700
C	-2.18858800	0.59685100	0.04070700
C	-2.29570800	-1.83087600	-0.06604300
C	-3.57140600	0.64108800	-0.18045200
C	-3.66523500	-1.77903600	-0.29752900
C	-4.29450800	-0.53654800	-0.35511200
H	-4.23172300	-2.69273800	-0.42662300
H	-5.36230400	-0.47565300	-0.53165600
O	0.63467600	0.04337800	-0.37077200
H	-4.08888500	1.58914300	-0.21325900
O	-1.42849100	1.69632500	0.25180700
C	-2.05648500	2.98325800	0.28375000
H	-2.80424500	3.03743100	1.07999300
H	-1.25568300	3.69110900	0.48602500
H	-2.51890400	3.22031200	-0.67845300
C	-0.08300200	-0.83376800	0.34926200
O	0.38282500	-1.69033500	1.06618800
I	2.70828500	0.04784700	-0.12218600
H	-1.78437100	-2.78376200	-0.00553800

TS1-*o*-MeO

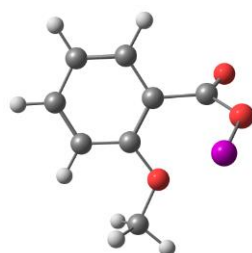


E = -546.276713

G = -546.179778

C	-1.44221700	-0.72886400	0.20823500
C	-1.64067400	0.67925200	0.20212000
C	-2.51172400	-1.55941300	-0.17690500
C	-2.88805800	1.19045600	-0.19106400
C	-3.73932900	-1.04656600	-0.55812000
C	-3.91963200	0.33845500	-0.56311300
H	-4.54378000	-1.70965900	-0.85043500
H	-4.87242000	0.76317500	-0.85821000
O	0.84400400	-0.64144600	1.06341400
H	-3.05695500	2.25727800	-0.20169800
O	-0.62124500	1.47711800	0.57484300
C	-0.75799300	2.90044800	0.47978900
H	-1.53461700	3.26764800	1.15568400
H	0.20731600	3.30002700	0.78223100
H	-0.97745400	3.20647100	-0.54651500
C	-0.18429600	-1.42229100	0.57731000
O	-0.04999200	-2.62547800	0.54929700
I	2.23104600	0.07082200	-0.31474200
H	-2.34614100	-2.62889200	-0.16967700

I-*o*-MeO



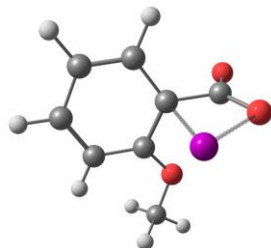
E = -546.286051

G = -546.190615

C	-1.20963300	-0.77195500	0.28737700
C	-1.48881800	0.60540400	0.36702800
C	-1.98691700	-1.59581800	-0.52778200
C	-2.51559900	1.14396000	-0.41276100
C	-3.00404600	-1.05729800	-1.31137200
C	-3.25883900	0.31134700	-1.24939200
H	-3.59076800	-1.69828000	-1.95736400
H	-4.05058700	0.74316000	-1.85068000
O	1.15026400	-1.00666500	1.00444300
H	-2.74503700	2.19930500	-0.36821100

O	-0.72656600	1.31454900	1.23728500
C	-0.87156700	2.73885800	1.28751900
H	-1.87294300	3.01934600	1.62491000
H	-0.13389800	3.08215100	2.00923400
H	-0.66695300	3.18571200	0.31070600
C	-0.14438000	-1.39423200	1.12297800
O	-0.34872700	-2.27217300	1.93109600
I	1.90779900	0.15017300	-0.56557000
H	-1.77411000	-2.65788600	-0.55754100

TS2-*o*-MeO

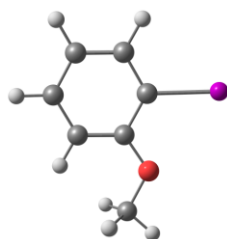


E = -546.245523

G = -546.151269

C	-0.65503800	0.25583500	0.86521600
C	-1.45578000	0.01142700	-0.31997300
C	-0.65372800	-0.72155200	1.89708900
C	-1.96056700	-1.27866500	-0.55735700
C	-1.16963000	-1.96763500	1.65623100
C	-1.79984700	-2.24566900	0.41362800
H	-1.10721900	-2.74385900	2.40784000
H	-2.20284500	-3.23605800	0.23901800
O	0.86102400	2.03378100	0.49205800
H	-2.50502100	-1.50241600	-1.46304000
O	-1.65900800	1.06456100	-1.08691800
C	-2.35729400	0.92789400	-2.34678600
H	-3.37898500	0.58591300	-2.17562800
H	-2.36093000	1.92516000	-2.77615000
H	-1.81951300	0.23604400	-2.99675900
C	-0.18138200	1.68641600	1.13272500
O	-0.84796200	2.36537100	1.92383500
I	1.66253500	-0.34908900	-0.43675900
H	-0.17269900	-0.48110000	2.83649800

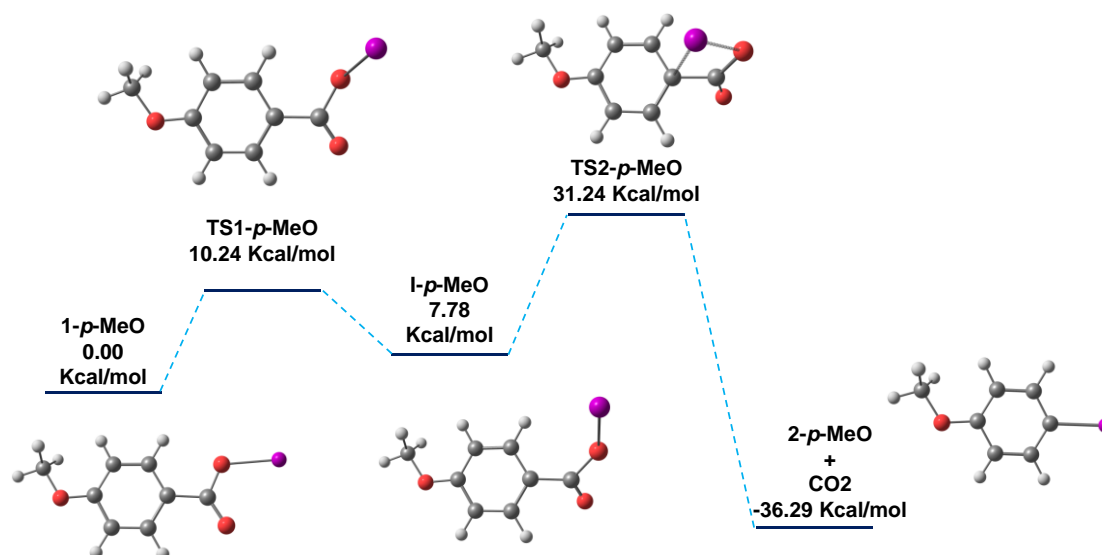
2-*o*-MeO



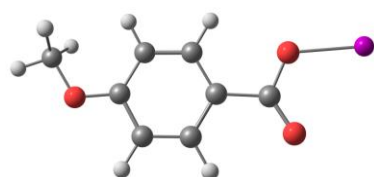
E = -546.341027

G = -546.260891

C	0.32263000	-0.54575100	0.00003000
C	1.28886300	0.47457800	0.00012100
C	0.69007600	-1.88515900	0.00005500
C	2.64107900	0.10736700	0.00024000
C	2.04147600	-2.23761000	0.00017400
C	3.00881600	-1.23769200	0.00026600
H	2.32370000	-3.28332200	0.00019100
H	4.06128100	-1.49616400	0.00035900
H	3.40877800	0.86878800	0.00031400
O	0.84930100	1.75729600	0.00008300
C	1.80832600	2.81953600	0.00015700
H	2.43601400	2.78449600	-0.89500300
H	1.22489400	3.73774900	0.00009700
H	2.43585700	2.78451300	0.89542700
I	-1.76266800	-0.03342100	-0.00015600
H	-0.07113900	-2.65470800	-0.00001600



1-*p*-MeO



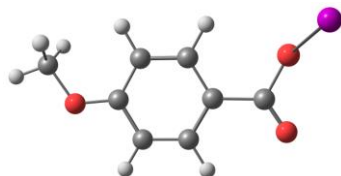
E = -546.300315

G = -546.204618

C	1.01808900	0.48113900	0.00000700
C	1.88366700	1.58849500	0.00009600
C	1.56310600	-0.80750600	0.00000900
C	3.25369600	1.40864900	0.00019800
C	2.94043500	-0.99935400	0.00010200
C	3.79456300	0.11202500	0.00021000
H	3.33354000	-2.00598400	0.00007800
O	-1.14408400	-0.41632700	-0.00015600
H	3.92901900	2.25542900	0.00027800

C	-0.44403800	0.74040500	-0.00008600
O	-0.95138600	1.84179500	-0.00005600
I	-3.21868100	-0.29867400	-0.00023800
H	0.90895500	-1.66889600	-0.00007400
O	5.14621300	0.03889700	0.00027900
C	5.77327800	-1.25076700	0.00089200
H	5.50378900	-1.81790400	-0.89434500
H	6.84337000	-1.05601700	0.00128500
H	5.50303300	-1.81741600	0.89620900
H	1.46568900	2.58705400	0.00009700

TS1-*p*-MeO

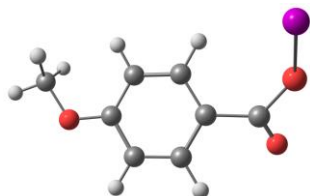


E = -546.284987

G = -546.188302

C	-0.70074200	0.96183900	0.23340600
C	-1.65484000	1.73261400	-0.45869000
C	-1.07644100	-0.29017500	0.73647400
C	-2.93653800	1.25907500	-0.64782200
C	-2.36549400	-0.77576400	0.55645900
C	-3.30386800	-0.00169500	-0.14187400
H	-2.62826200	-1.74352900	0.95910600
O	1.56074700	0.63217700	1.02127200
H	-3.67659400	1.83922600	-1.18505300
C	0.65492400	1.49997200	0.41634500
O	1.00213900	2.62741600	0.15194900
I	2.60660400	-0.66922100	-0.22537400
H	-0.35672800	-0.88668300	1.28087200
O	-4.57895100	-0.37755000	-0.37912600
C	-5.03257000	-1.65248200	0.09871700
H	-4.97037100	-1.70568400	1.18883900
H	-6.07184300	-1.72801100	-0.21251700
H	-4.45442100	-2.46514400	-0.34900300
H	-1.36985000	2.70189200	-0.84829000

I-*p*-MeO



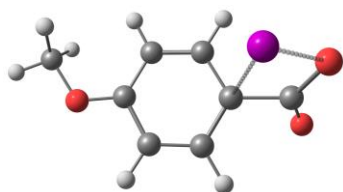
E = -546.287640

G = -546.192227

C	-0.52201600	1.10037600	0.16165300
C	-1.44771700	1.68825000	-0.71670900
C	-0.90162700	-0.02973200	0.89161600

C	-2.69992500	1.13095000	-0.89259500
C	-2.16864900	-0.58379100	0.74269800
C	-3.07169000	-0.01079600	-0.16287900
H	-2.43916200	-1.44788000	1.33250300
O	1.91099300	1.04024800	0.60893500
H	-3.41345500	1.56355500	-1.58293800
C	0.77957600	1.76859600	0.36441100
O	0.92986600	2.97151100	0.38771400
I	2.31317600	-0.85314800	-0.19729700
H	-0.21930900	-0.47316000	1.60547300
O	-4.31986900	-0.47805400	-0.39840300
C	-4.77089200	-1.64278400	0.30645100
H	-4.78842500	-1.46555200	1.38532500
H	-5.78194200	-1.82730000	-0.04947900
H	-4.13869400	-2.50593900	0.08077900
H	-1.16761300	2.57706800	-1.26878000

TS2-*p*-MeO

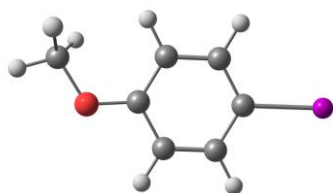


E = -546.249405

G = -546.154832

C	-0.13664900	1.17794900	-0.04528800
C	0.56652200	1.34713700	1.18219200
C	0.57496500	0.66319000	-1.17789400
C	1.82421700	0.83892700	1.32375500
C	1.85944400	0.18748600	-1.05465500
C	2.48607300	0.24008200	0.20717000
H	2.36972200	-0.21819800	-1.91561000
O	-2.38622700	1.10718500	-0.78404800
H	2.36171900	0.89551600	2.26168600
C	-1.48468400	1.85446700	-0.27655800
O	-1.58188800	3.05680200	-0.00110900
I	-1.47079300	-1.22315600	0.13993300
H	0.07563800	0.64243500	-2.13845200
O	3.70395700	-0.20920200	0.46050000
C	4.49297500	-0.81976000	-0.58650600
H	4.68386500	-0.09935200	-1.38343800
H	5.42503600	-1.10601000	-0.10829000
H	3.98213300	-1.70155600	-0.97679400
H	0.07002300	1.83930200	2.00839700

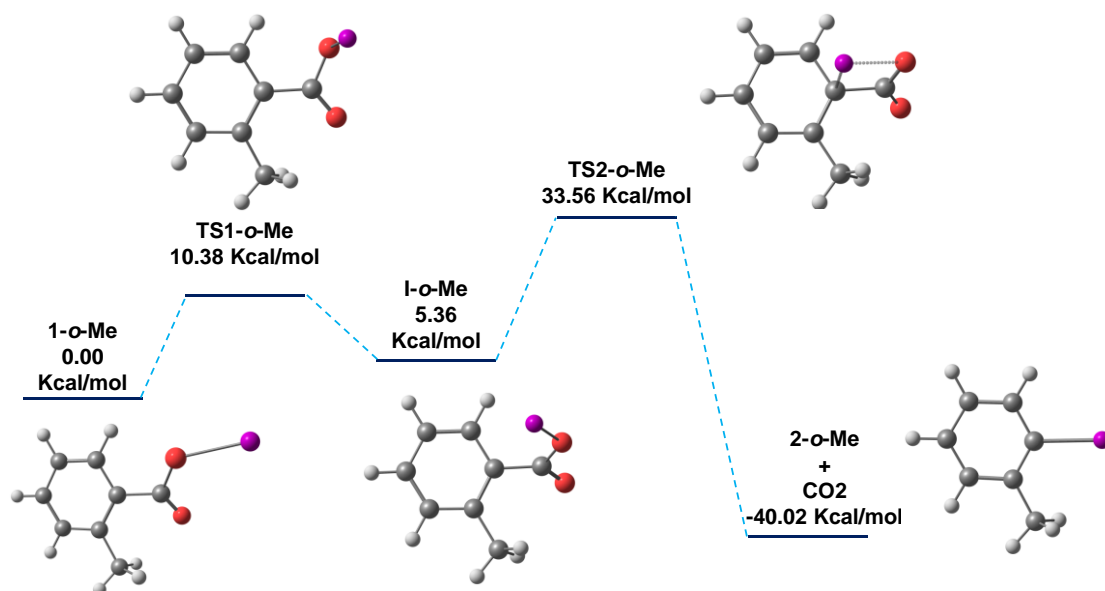
2-*p*-MeO



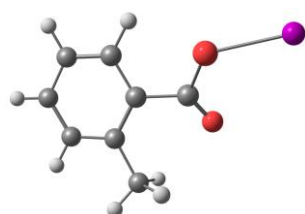
E = -546.342342

G = -546.262454

C	0.18389500	0.07562800	-0.00005100
C	-0.41528500	1.33597800	0.00005500
C	-0.58812900	-1.07829400	-0.00016100
C	-1.80077500	1.43138200	0.00006100
C	-1.98259300	-0.98164900	-0.00017200
C	-2.59389600	0.27600100	-0.00005900
H	-2.56665900	-1.89134700	-0.00028000
H	-2.28490200	2.40059300	0.00015700
I	2.32944300	-0.07821400	-0.00004400
H	-0.12676100	-2.05722500	-0.00024700
O	-3.93983300	0.48067500	-0.00011800
C	-4.80628600	-0.65776300	0.00055000
H	-4.65447000	-1.26912800	0.89532600
H	-5.81849200	-0.25866600	0.00091500
H	-4.65530600	-1.26955500	-0.89407800
H	0.18320900	2.23758700	0.00015400



1-o-Me



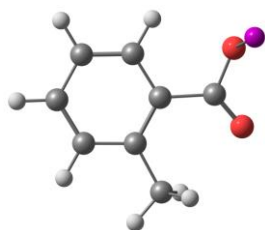
E = -471.062670

G = -470.970195

C	-1.66354600	-0.07435600	0.08766800
C	-2.72403900	0.83877500	-0.10317000
C	-1.91287500	-1.45140100	0.18752000

C	-4.01879600	0.31373000	-0.18287600
C	-3.21141200	-1.94161100	0.12308500
C	-4.26768700	-1.05221700	-0.06640200
H	-3.39533700	-3.00526100	0.21527000
H	-5.28585100	-1.41975000	-0.12626600
O	0.60148300	-0.49319700	-0.26776900
H	-4.84844600	0.99431200	-0.33953600
C	-0.25990300	0.42341400	0.22466900
O	0.07041700	1.48539700	0.69952300
I	2.64340400	-0.12870500	-0.05612600
H	-1.08231200	-2.12953700	0.33123300
C	-2.52002200	2.32762800	-0.23297200
H	-3.43719000	2.80659800	-0.57872400
H	-2.23960100	2.76723700	0.72690600
H	-1.71717600	2.56640400	-0.93336900

TS1-*o*-Me

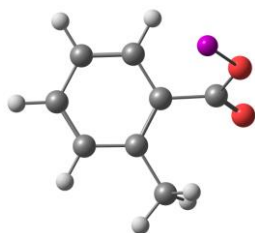


E = -471.047336

G = -470.953661

C	-1.40270700	0.10856800	0.36268300
C	-2.55386400	0.65069900	-0.26269700
C	-1.34178700	-1.26418400	0.66220400
C	-3.59816300	-0.22835000	-0.56913600
C	-2.39866100	-2.10955100	0.35676100
C	-3.53166800	-1.58601100	-0.26492500
H	-2.33955000	-3.16380800	0.59858700
H	-4.36437500	-2.23359700	-0.51528900
O	0.87561800	0.26998400	1.15381600
H	-4.48333300	0.16313400	-1.05787000
C	-0.24917900	0.96809800	0.71727900
O	-0.23203300	2.17410300	0.72012500
I	2.28943100	-0.22632400	-0.28878900
H	-0.45705400	-1.65613600	1.14421300
C	-2.69875600	2.10683300	-0.62244200
H	-1.85284000	2.45782000	-1.21765400
H	-3.61737800	2.26633200	-1.18877400
H	-2.72526500	2.73211000	0.27273700

I-*o*-Me

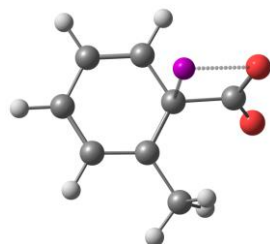


E = -471.052974

G = -470.961652

C	-1.22047700	0.27298600	0.44373600
C	-2.18113200	0.46753400	-0.56494500
C	-1.18418800	-0.90932600	1.19090800
C	-3.08009500	-0.57468500	-0.81157100
C	-2.10584700	-1.92127900	0.94372700
C	-3.05154400	-1.75279200	-0.06635600
H	-2.08157100	-2.83173600	1.53024900
H	-3.76791400	-2.53880000	-0.27633400
O	1.06363800	1.15856300	0.76917100
H	-3.81727000	-0.45720700	-1.59820900
C	-0.27918200	1.37354400	0.79977900
O	-0.61916800	2.47207800	1.17451700
I	1.98776300	-0.38869200	-0.29877300
H	-0.43860500	-1.03206000	1.96773600
C	-2.23859000	1.74208700	-1.37023600
H	-2.94069500	1.64516900	-2.19906700
H	-2.55596900	2.58157900	-0.74664500
H	-1.25906800	2.00016500	-1.78250300

TS2-*o*-Me

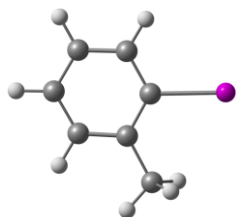


E = -471.007790

G = -470.916714

C	0.85010000	0.44520500	-0.39547600
C	1.62696100	0.12157600	0.77743400
C	0.89751200	-0.42078800	-1.54518400
C	2.23736600	-1.11740300	0.81806700
C	1.55224100	-1.63070800	-1.47615800
C	2.20231700	-1.98350800	-0.28761800
H	1.56712300	-2.29718000	-2.32845400
H	2.71309900	-2.93722500	-0.22307900
O	-0.94907700	1.90694900	-0.85265600
H	2.77760300	-1.41794300	1.70770100
C	0.30255700	1.85663900	-0.62366800
O	1.10200300	2.79972400	-0.62189500
I	-1.54938700	-0.47491200	0.25440200
H	0.39247900	-0.10377800	-2.44912900
C	1.71037000	1.09529800	1.90661800
H	2.30012400	0.69755500	2.73161800
H	2.15650500	2.03098200	1.55513600
H	0.71063500	1.34665400	2.27519900

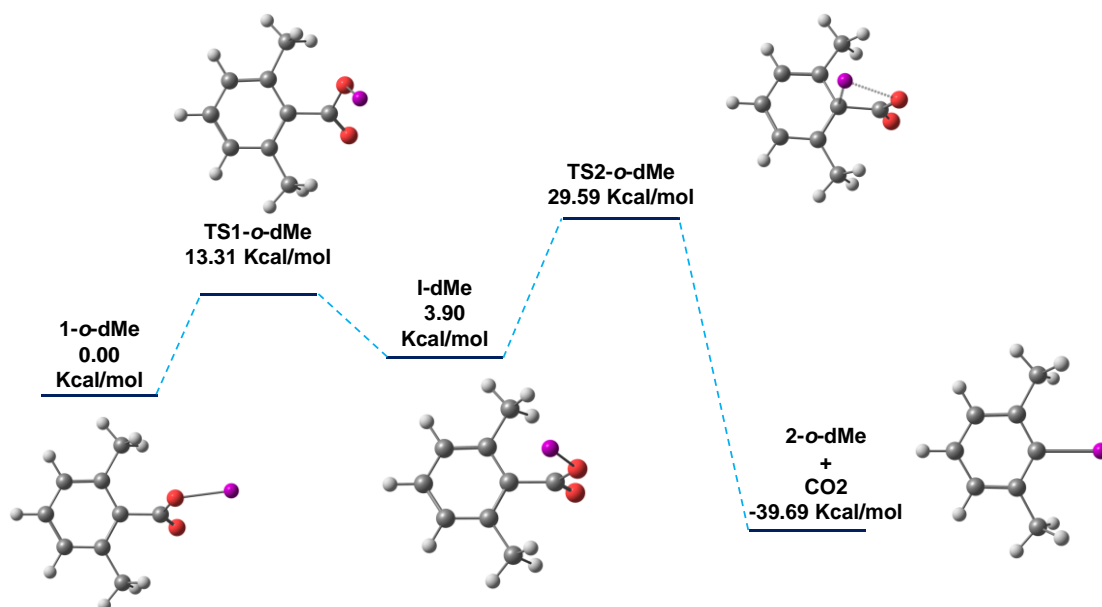
2-*o*-Me



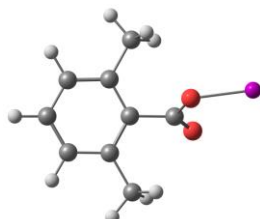
E = -471.110958

G = -471.033977

C	0.54520100	-0.20702200	-0.00006100
C	1.28878300	0.98057300	-0.00018700
C	1.14343700	-1.46503500	-0.00009700
C	2.68553100	0.84433100	-0.00035800
C	2.53432700	-1.56152600	-0.00026800
C	3.30623600	-0.40212700	-0.00040100
H	3.00242100	-2.53899100	-0.00029400
H	4.38819500	-0.46566700	-0.00053800
H	3.29175300	1.74379800	-0.00046200
I	-1.61708500	-0.14584900	0.00020100
H	0.53820200	-2.36214500	0.00000600
C	0.66282900	2.35053500	-0.00013300
H	1.42930500	3.12638900	-0.00026500
H	0.02866400	2.49410200	-0.87942000
H	0.02892800	2.49414500	0.87933900



1-DMeO

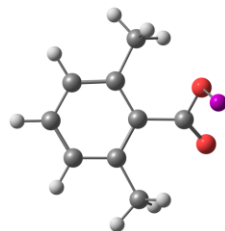


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C	-2.06554100	-1.27552000	0.13671100
C	-3.82281400	0.85562300	-0.39355000
C	-3.41624200	-1.51236700	-0.13362400
C	-4.28552600	-0.45850800	-0.40241900
H	-3.78469700	-2.53211700	-0.13770300
H	-5.32817600	-0.66143200	-0.61976200
O	0.59774900	-0.15297000	-0.43338400
H	-4.50468100	1.67115100	-0.60718600
C	-0.19766100	0.36033400	0.51873100
O	0.17340700	0.96919100	1.49211400
I	2.67493400	-0.02829900	-0.16748300
C	-1.99040100	2.56669200	-0.08796700
H	-2.76208000	3.24972400	-0.44462400
H	-1.70756400	2.86542700	0.92465100
H	-1.10649300	2.69380000	-0.71957300
C	-1.12797800	-2.42737400	0.41013900
H	-1.68730200	-3.34807100	0.58026300
H	-0.45165400	-2.58637300	-0.43335800
H	-0.50574300	-2.24201600	1.29017700

TS1-DMeO



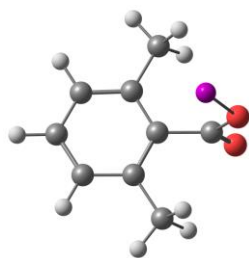
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C	-2.14935200	1.13803000	-0.13897600
C	-1.81725200	-1.27505500	0.25424600
C	-3.30978500	0.83399500	-0.85463500
C	-3.00265600	-1.52103200	-0.44282900
C	-3.73799900	-0.48100100	-1.00191800
H	-3.35023400	-2.54259300	-0.54784600
H	-4.64839200	-0.69570700	-1.55036000
O	0.88200900	-0.51586400	0.97712600
H	-3.88391600	1.64056400	-1.29638800
C	-0.14871200	0.39938200	1.14654000
O	0.00096600	1.35029900	1.87087100
I	2.31262200	-0.02743500	-0.44593300
C	-1.73974100	2.58541100	-0.00313200
H	-2.32814600	3.20759200	-0.67885300
H	-1.89462800	2.94194400	1.01742900
H	-0.68220100	2.73460200	-0.23211300
C	-1.06929000	-2.45235900	0.83600200
H	-1.71716200	-3.33004800	0.86488900

H	-0.19139400	-2.69304000	0.23242100
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I-DMeO

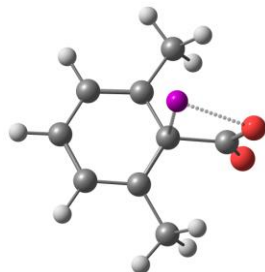


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C	-1.64283600	-1.23029900	0.01831100
C	-2.60268200	1.21066400	-0.99144800
C	-2.60323800	-1.20633000	-0.99579200
C	-3.07903600	0.00318900	-1.49692900
H	-2.97926900	-2.14289500	-1.39223900
H	-3.82519400	0.00477700	-2.28347800
O	1.14470700	-0.00293100	1.35657000
H	-2.97827800	2.14882700	-1.38451800
C	-0.18509700	-0.00321100	1.63346600
O	-0.47151300	-0.00492100	2.80713300
I	1.90601600	0.00091500	-0.59235200
C	-1.10533200	2.53217100	0.56568500
H	-1.63380600	3.38357700	0.13588700
H	-1.20722500	2.58237700	1.65318900
H	-0.04180700	2.64719600	0.33239300
C	-1.10695500	-2.53406500	0.55712200
H	-1.63302400	-3.38384100	0.12120000
H	-0.04240000	-2.64718400	0.32769500
H	-1.21324900	-2.58944000	1.64397300

TS2-DMeO



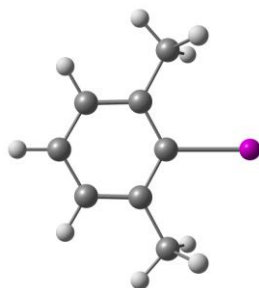
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C	1.26319400	-0.20394800	1.25754500
C	1.26317300	-0.20393500	-1.25756200
C	1.73972900	-1.50020700	1.22462800

C	1.73970900	-1.50019400	-1.22466800
C	1.95481400	-2.14606600	-0.00002500
H	1.97166000	-2.01295100	-2.14994400
H	2.33666700	-3.16053700	-0.00003400
O	-0.78185700	2.08432600	-0.00003500
H	1.97169400	-2.01297500	2.14989500
C	0.47490600	1.87810000	0.00000600
O	1.38139500	2.71993000	0.00004200
I	-1.63681900	-0.43500000	0.00001000
C	1.10970000	0.56444800	2.53170400
H	1.33469400	-0.05728300	3.39727800
H	1.78678400	1.42506800	2.52804800
H	0.09574000	0.96089400	2.63381400
C	1.10966600	0.56448000	-2.53170800
H	1.33461900	-0.05724500	-3.39729700
H	0.09571700	0.96096100	-2.63378500
H	1.78677800	1.42507900	-2.52805900

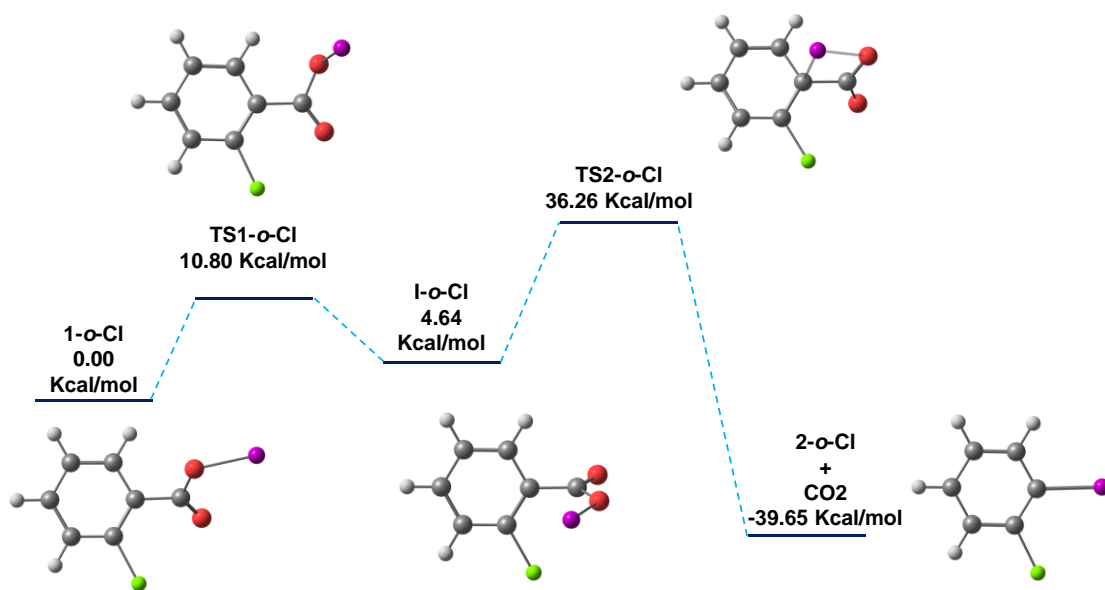
2-DMeO



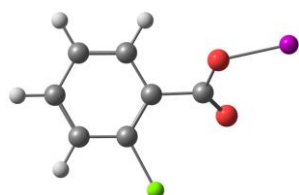
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C	-1.19960100	1.23492900	-0.00000700
C	-2.60088000	-1.20329200	0.00000000
C	-2.60083900	1.20335600	0.00000000
C	-3.29711400	0.00004400	0.00000100
H	-3.14296900	2.14250300	0.00000300
H	-4.38109800	0.00006200	0.00000200
H	-3.14304400	-2.14242000	0.00000300
I	1.64042600	-0.00001200	0.00000000
C	-0.48947200	-2.56450200	0.00000600
H	-1.20964600	-3.38355100	0.00001700
H	0.15161700	-2.67188600	-0.87925100
H	0.15162000	-2.67186500	0.87926300
C	-0.48936700	2.56448000	0.00000500
H	-1.20950000	3.38356500	-0.00005100
H	0.15167500	2.67183400	0.87930200
H	0.15178500	2.67180600	-0.87921100



1-*o*-Cl

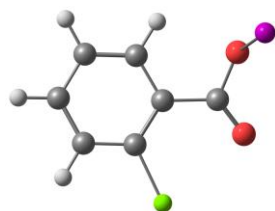


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C	-1.48919600	-0.33886400	0.15260300
C	-2.60274400	0.48521200	-0.06447300
C	-1.67960100	-1.72648800	0.21042800
C	-3.87455000	-0.06259300	-0.20295700
C	-2.94981900	-2.27683100	0.08807400
C	-4.04677800	-1.44238800	-0.11823300
H	-3.08106400	-3.34994300	0.14970600
H	-5.04111900	-1.86019200	-0.22054800
O	0.76429400	-0.50338100	-0.33680200
H	-4.72007600	0.58950600	-0.37887100
C	-0.11554800	0.21431900	0.38530400
O	0.16005000	1.13488400	1.11332600
I	2.79871300	-0.09561400	-0.09491500
H	-0.81904200	-2.36353200	0.36723100
Cl	-2.44210800	2.22855600	-0.22374500

TS1-*o*-Cl

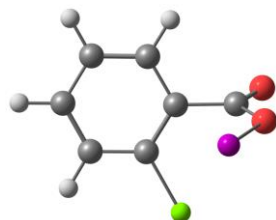


E = -891.335385

G = -891.279680

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C	2.41045500	-0.30491400	-0.13798200
C	1.13251500	1.59808500	0.61438200
C	3.43446600	0.55015200	-0.53579900
C	2.15727700	2.45092200	0.23078600
C	3.31097000	1.92385600	-0.34655800
H	2.05530200	3.51878100	0.37806300
H	4.11791200	2.57700800	-0.65672600
O	-1.04943200	0.05945900	1.17501200
H	4.32235800	0.13723800	-0.99628400
C	0.11149800	-0.65358000	0.91429900
O	0.16042900	-1.83501800	1.13443900
I	-2.48111400	0.10587100	-0.33294900
H	0.23234200	1.99615600	1.06070700
Cl	2.65489200	-2.01475200	-0.45574400

I-o-Cl

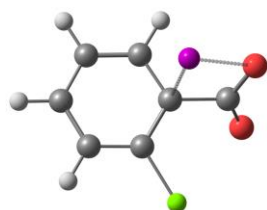


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G = -891.289494

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C	-1.68284000	0.48869100	-0.47395900
C	-1.61734600	-1.20897300	1.23364000
C	-2.65389800	-0.22533700	-1.16715500
C	-2.58340700	-1.93444300	0.54349000
C	-3.09945500	-1.44194600	-0.65463500
H	-2.93477500	-2.87777100	0.94272100
H	-3.85408600	-2.00079800	-1.19479100
O	1.16386300	0.74313200	1.15521600
H	-3.05540100	0.16932000	-2.09131900
C	-0.14027900	0.78593600	1.50782400
O	-0.41383500	1.45737200	2.47258000
I	1.92023600	-0.46445400	-0.37867600
H	-1.21235800	-1.58345900	2.16612600
Cl	-1.12710000	2.02918100	-1.11996200

TS2-o-Cl

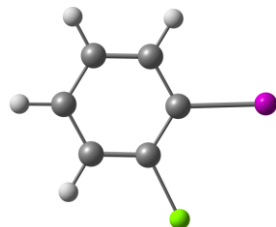


E = -891.292963

G = -891.239112

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C	1.58640100	0.14132700	-0.40309300
C	0.40633000	0.92668700	1.60994600
C	2.04905900	1.41940100	-0.61825300
C	0.90608900	2.19427600	1.40422700
C	1.70904800	2.43999900	0.28613600
H	0.68333700	2.98987300	2.10247200
H	2.09766500	3.43623400	0.11254600
O	-0.91278400	-1.78379000	1.24725700
H	2.68626300	1.63261400	-1.46598600
C	0.33338300	-1.56012400	1.14235700
O	1.26601300	-2.30970000	1.43923600
I	-1.67495600	0.20292100	-0.45608800
H	-0.20525300	0.69415600	2.47252000
Cl	2.04191200	-1.13664400	-1.47564900

2-*o*-Cl



E = -891.399628

G = -891.360076

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C	-1.31213200	0.67527800	-0.00005000
C	-0.98789600	-1.71747300	0.00002700
C	-2.69515900	0.48305600	-0.00002600
C	-2.36762100	-1.90539900	0.00001300
C	-3.22159600	-0.80429700	-0.00000400
H	-2.76778900	-2.91201900	0.00004600
H	-4.29604100	-0.94139400	0.00000600
H	-3.34763500	1.34681800	-0.00005100
I	1.68320200	-0.23253800	0.00001600
H	-0.32702400	-2.57421700	0.00004100
Cl	-0.72049900	2.32857600	-0.00003200

CO₂

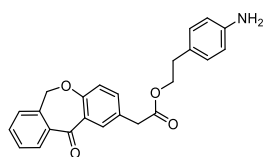
O	1.15611800	-0.00054300	0.00000000
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O	-1.15611800	0.00027500	0.00000000

References

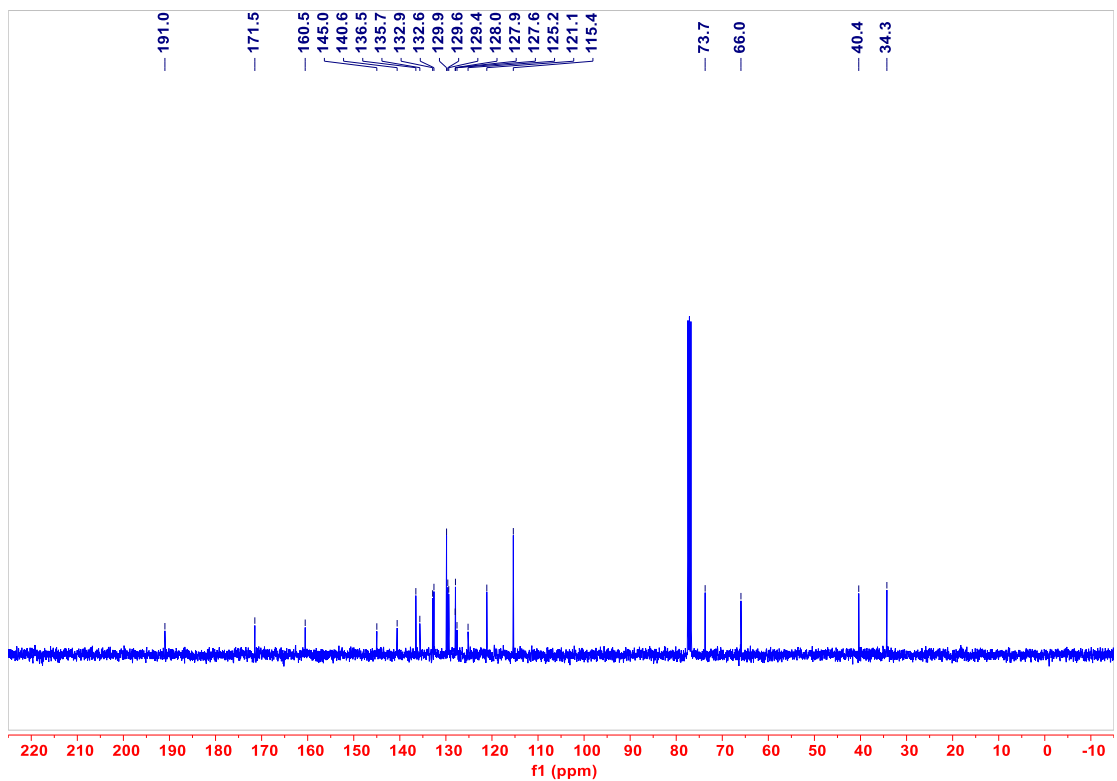
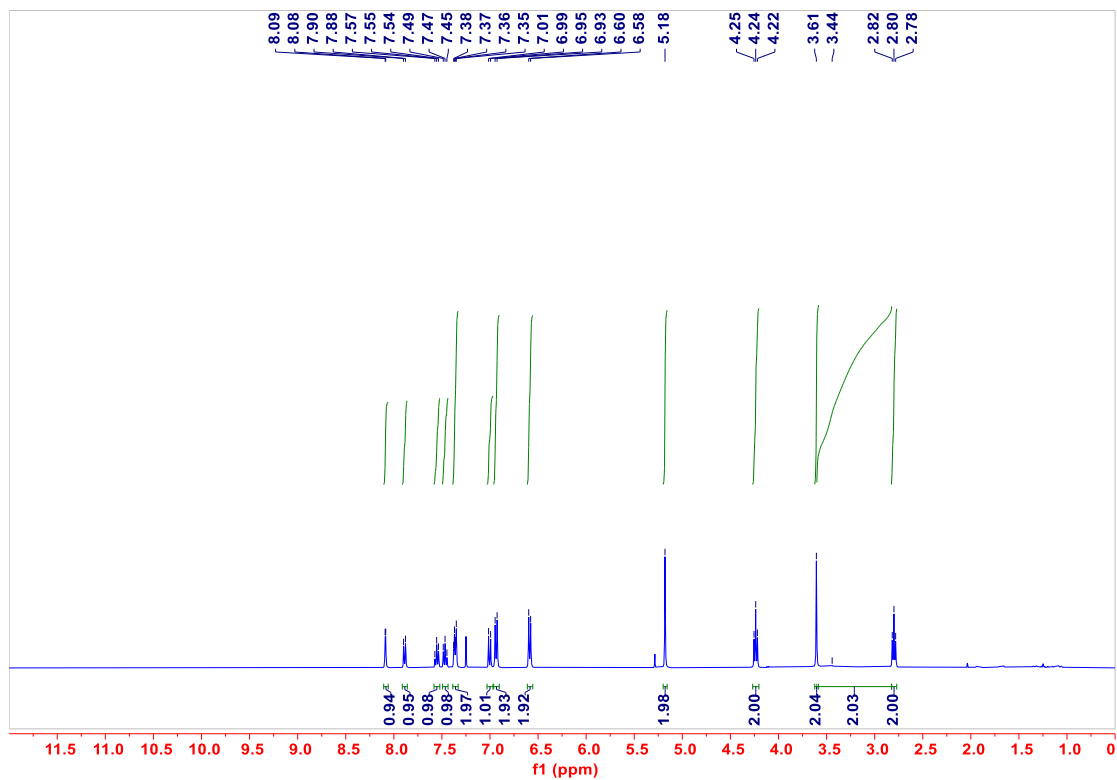
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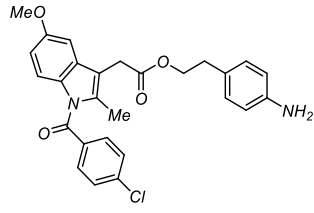
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^1H , ^{19}F , ^{13}C NMR spectra of corresponding compounds

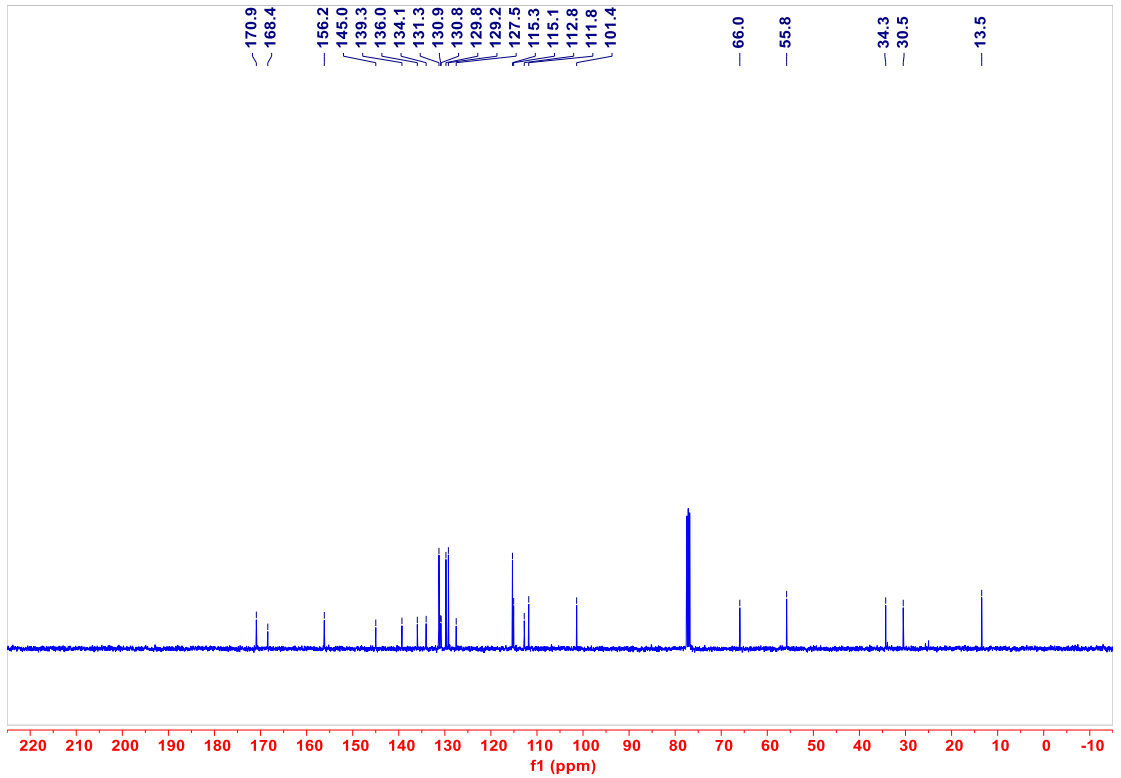
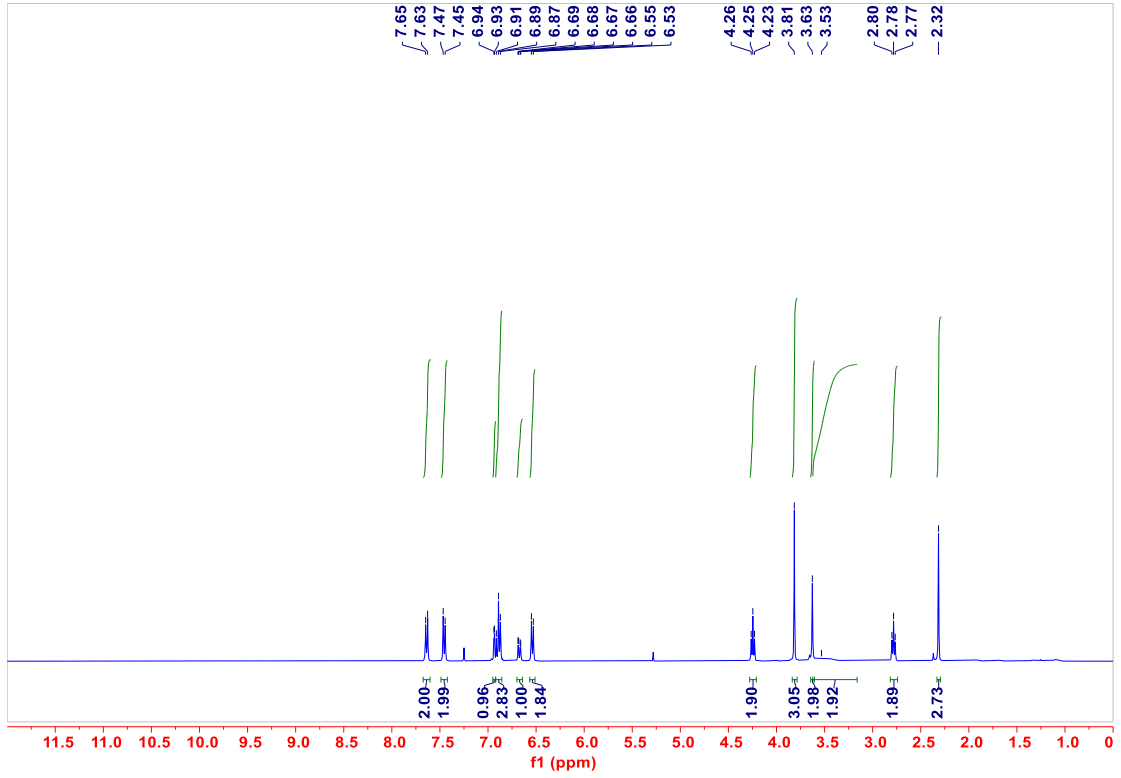


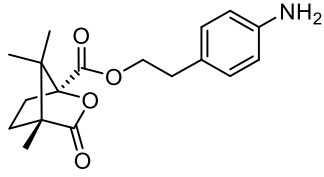
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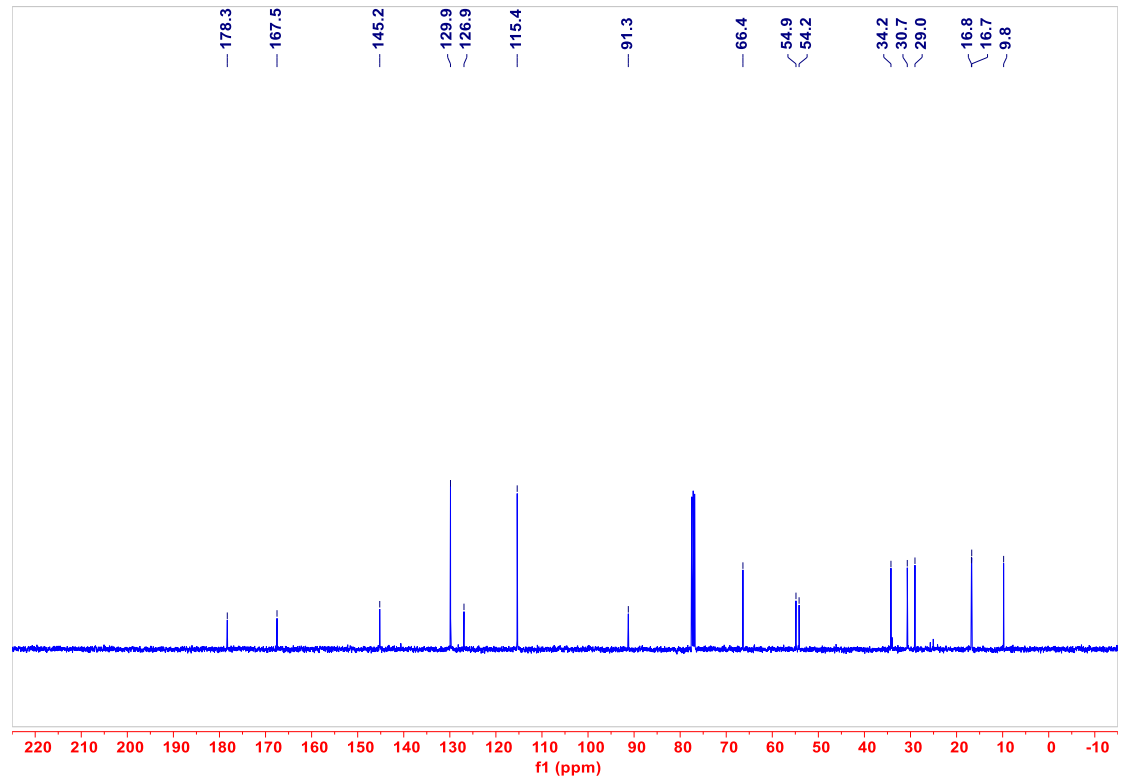
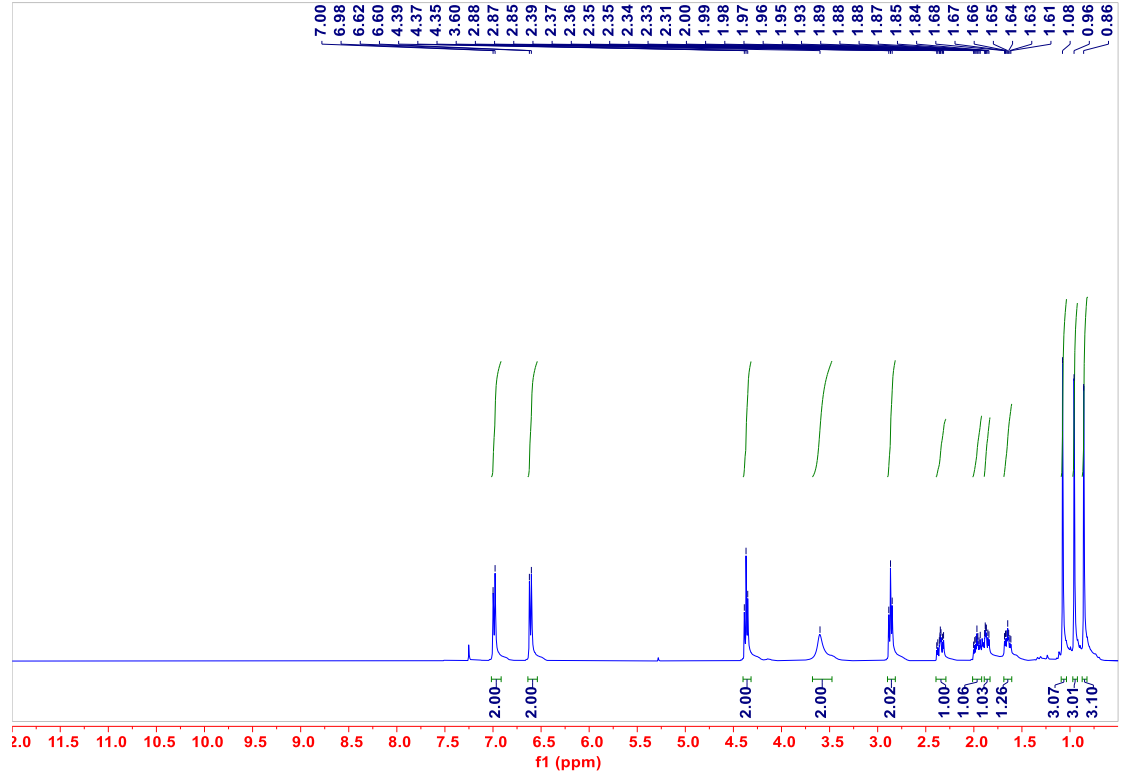


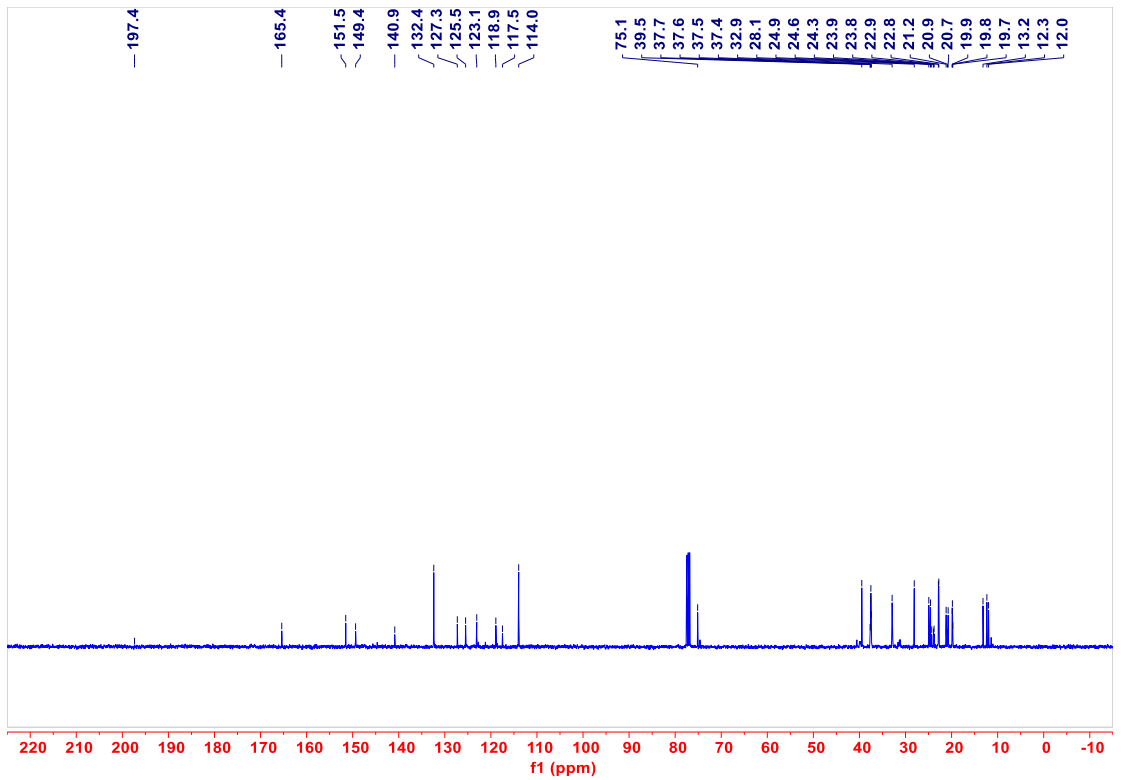
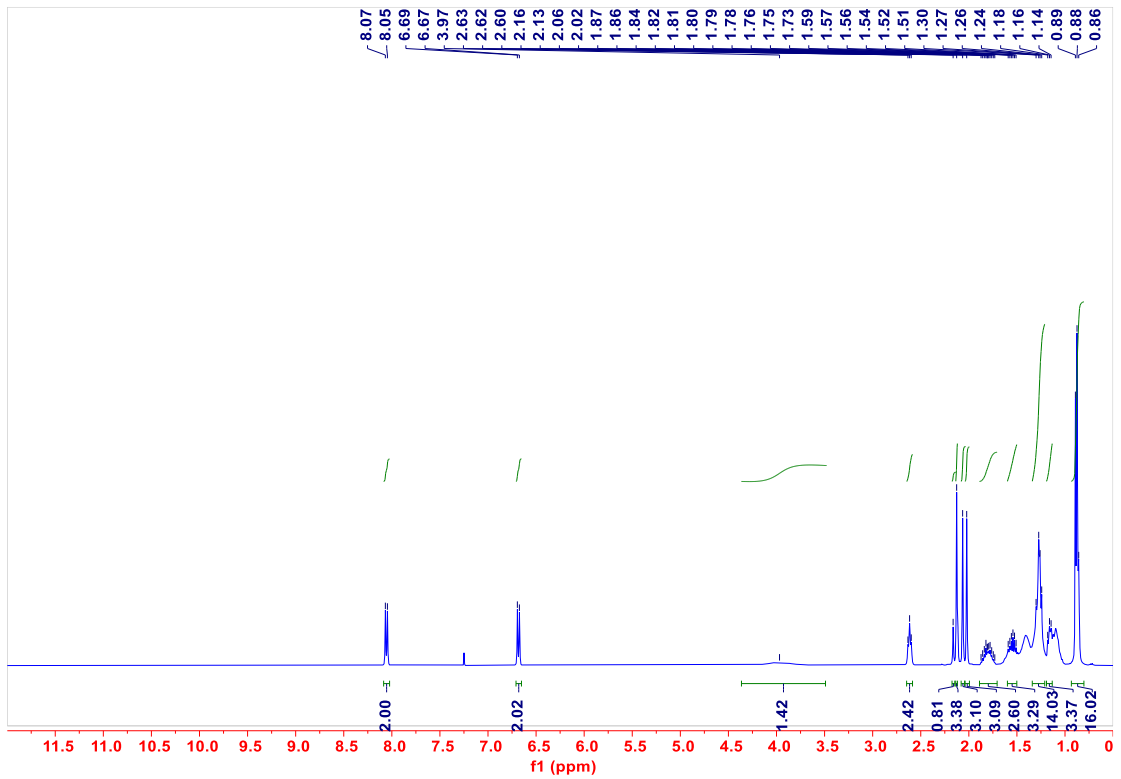
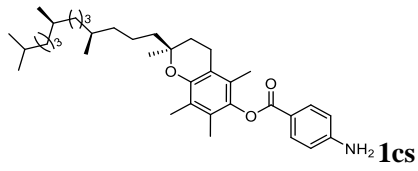
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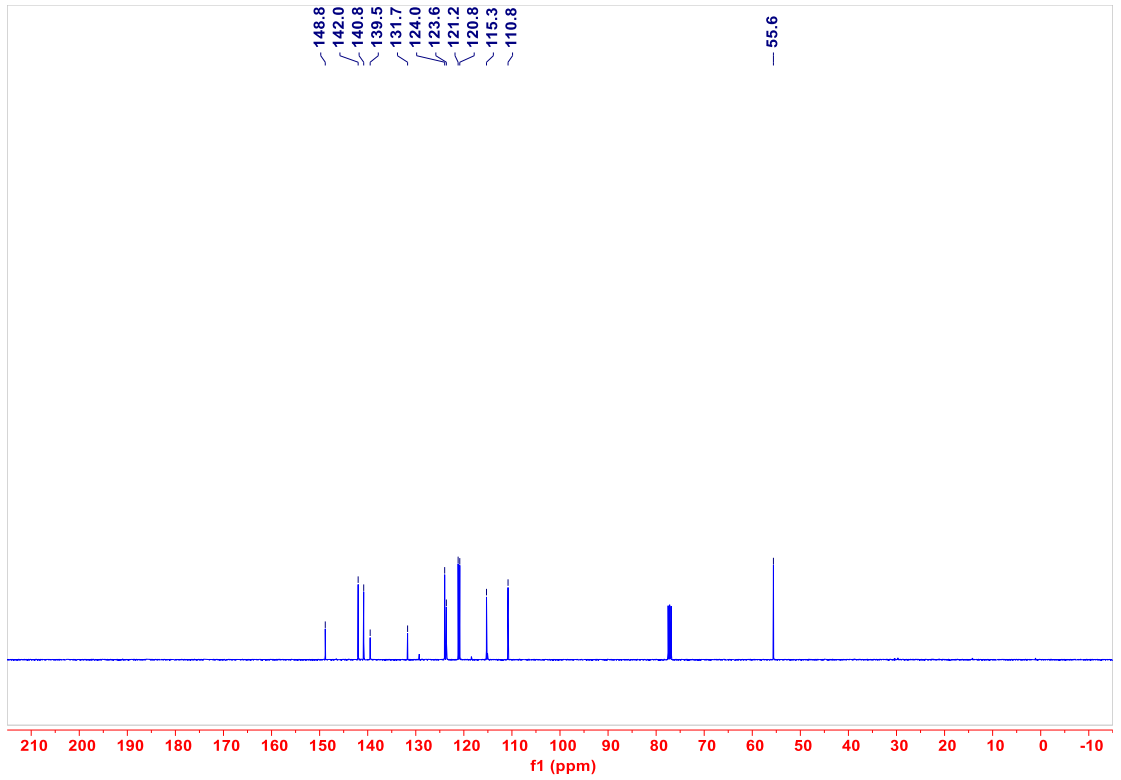
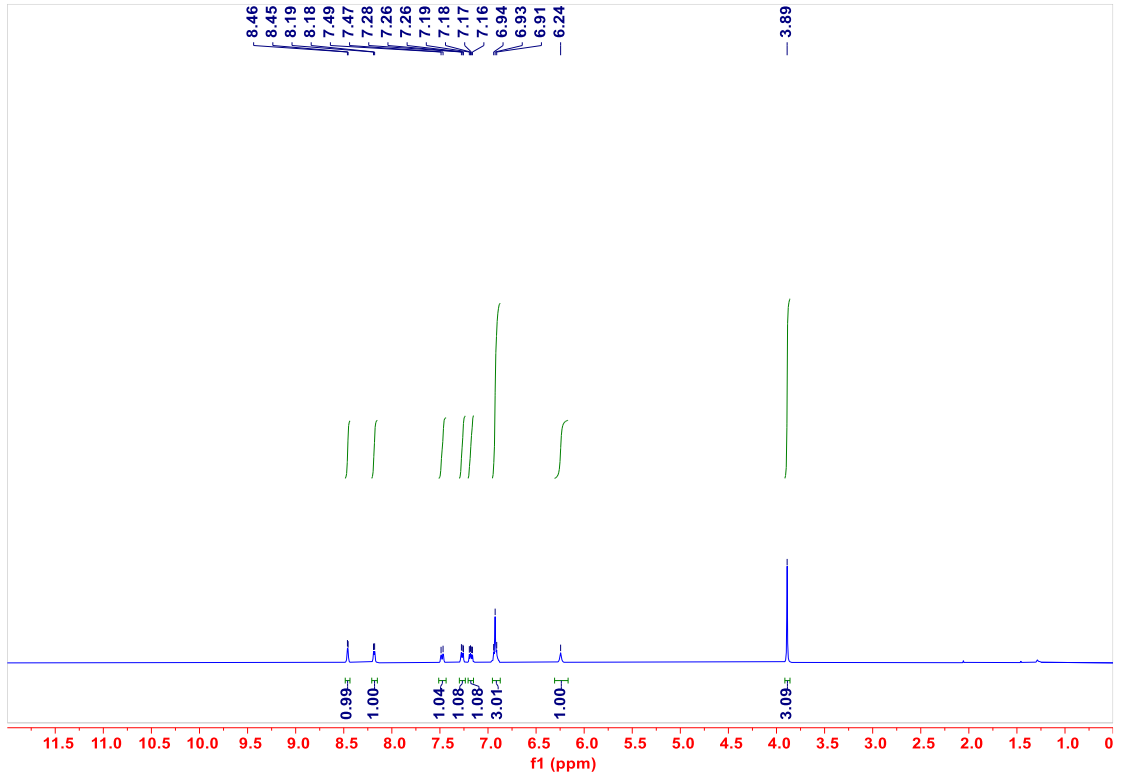
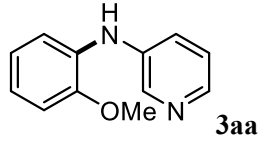


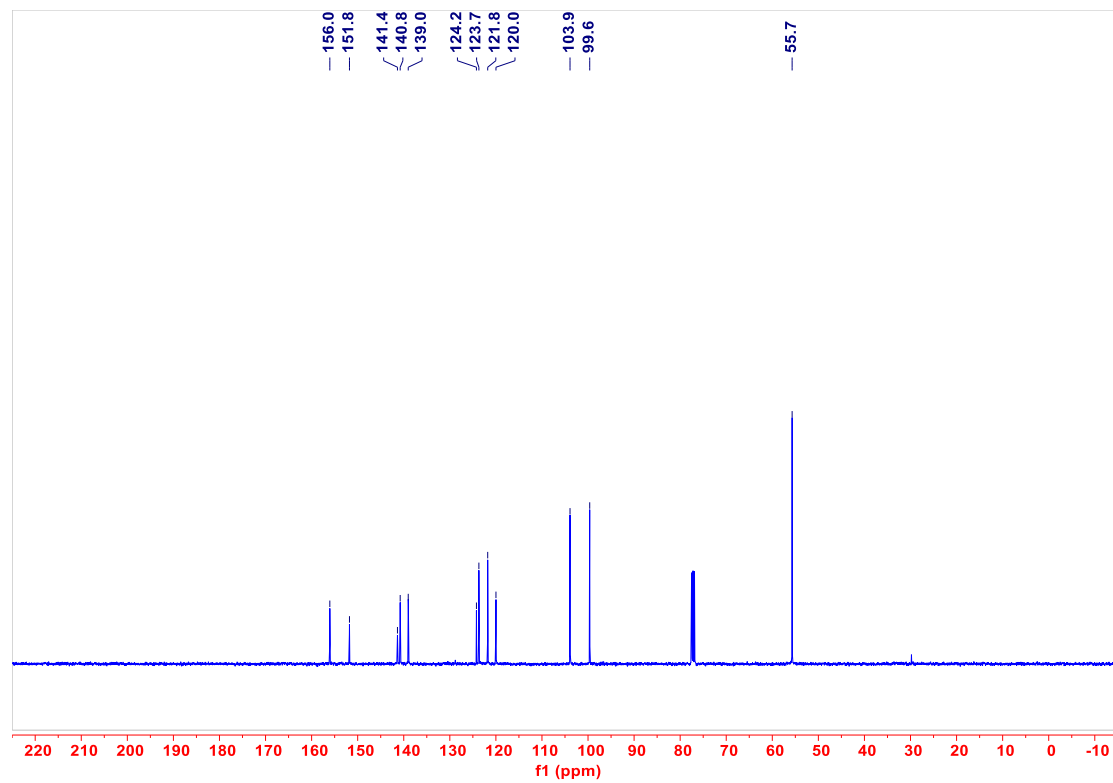
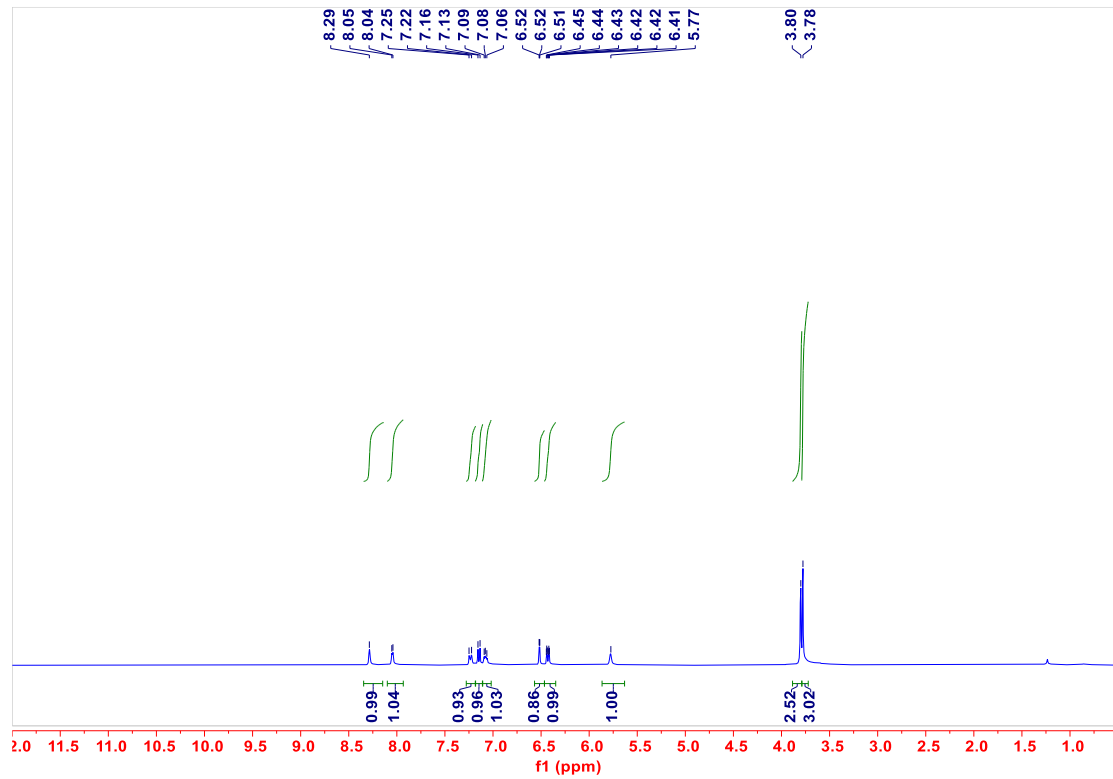
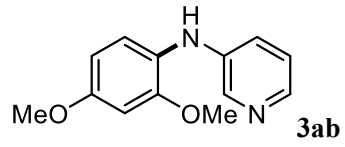


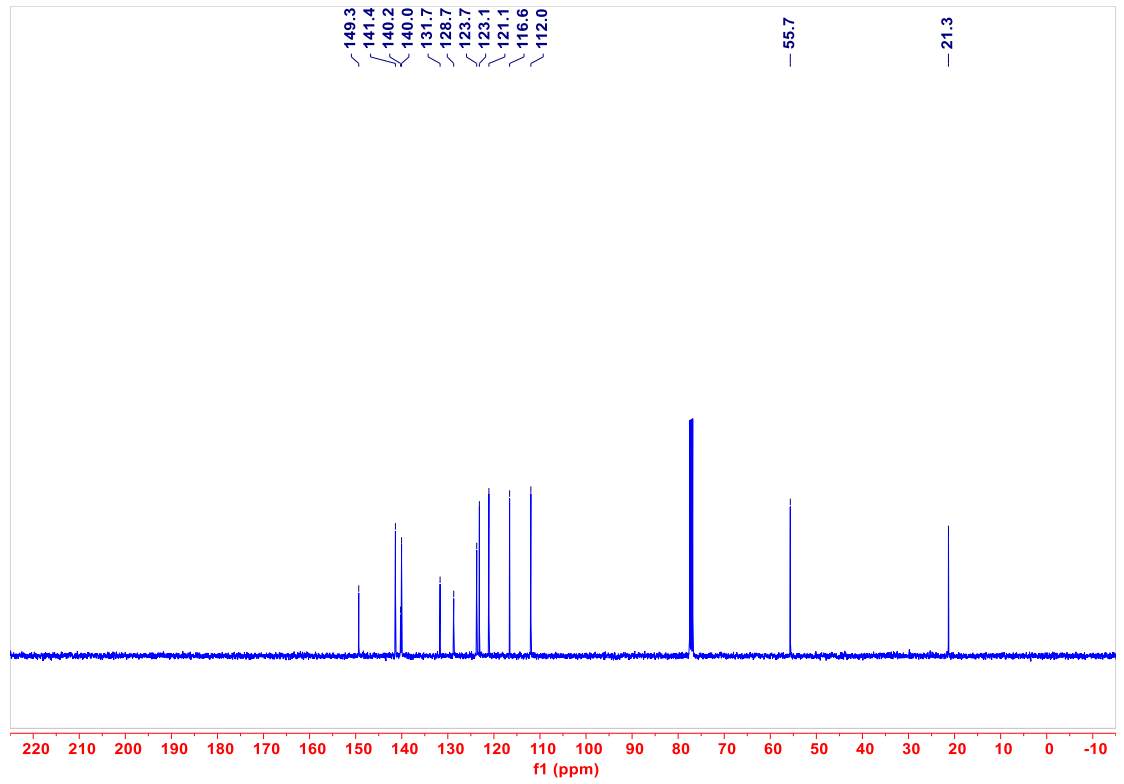
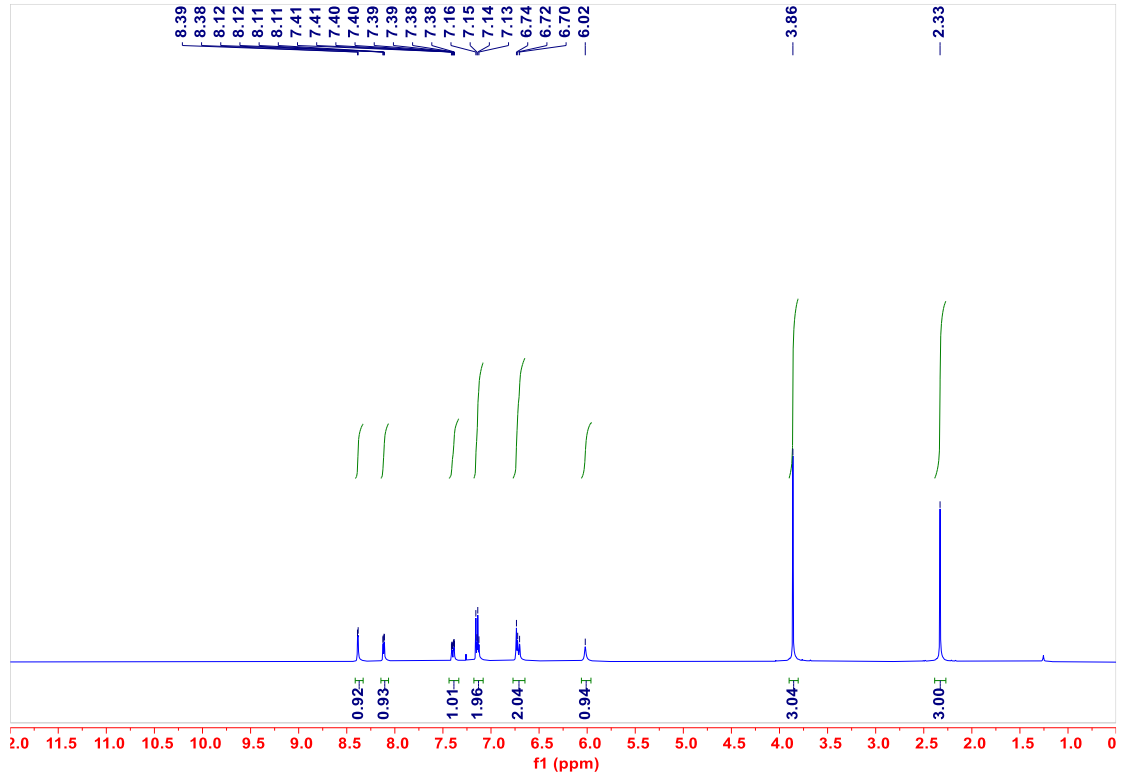
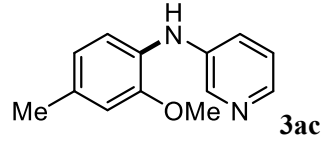
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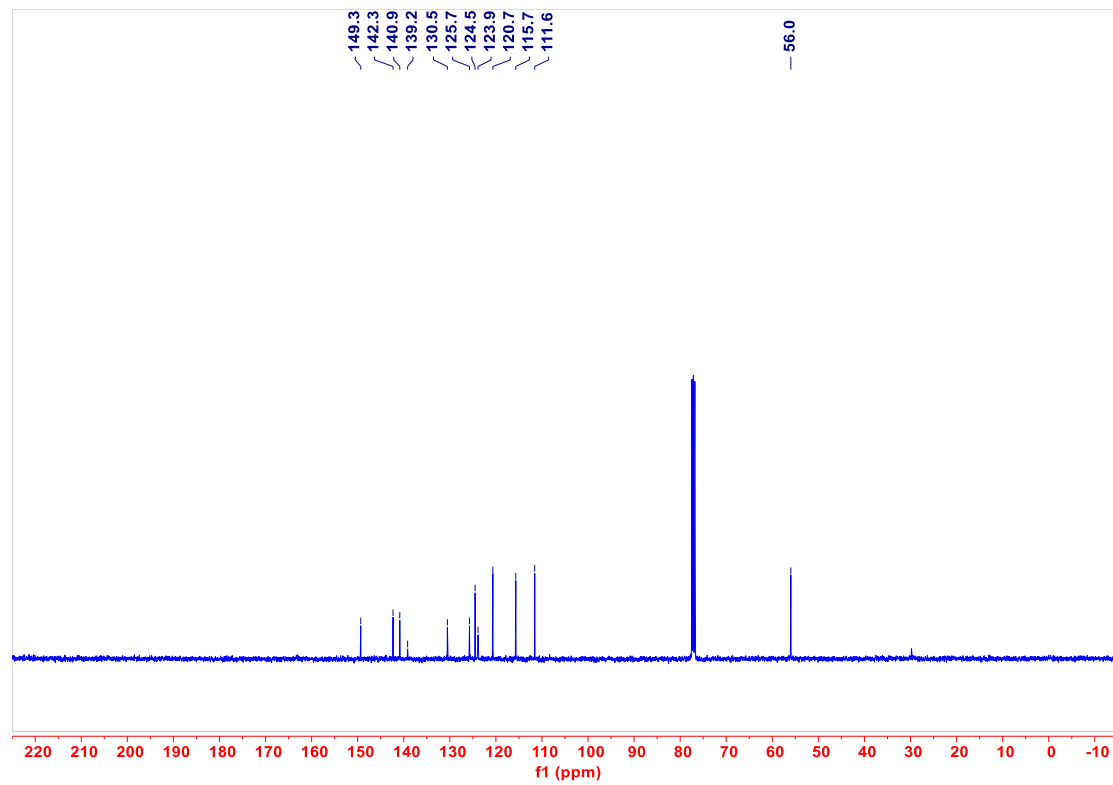
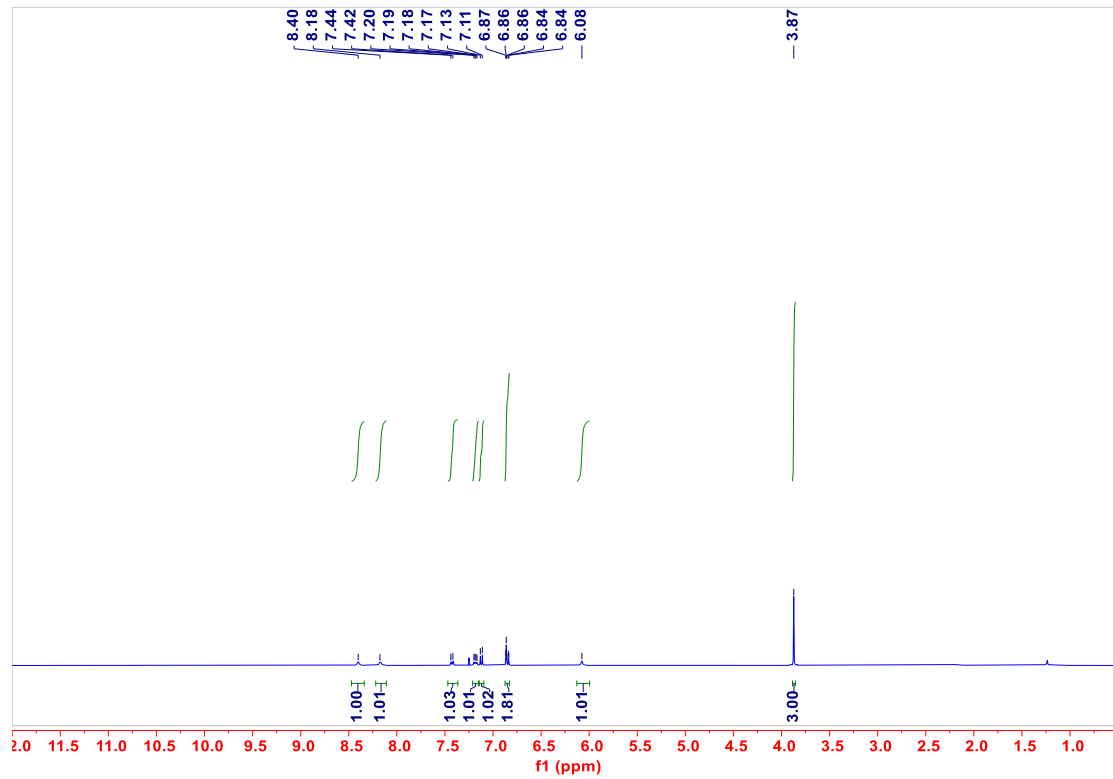
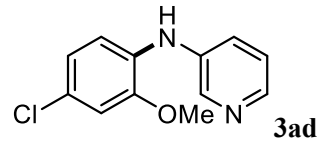


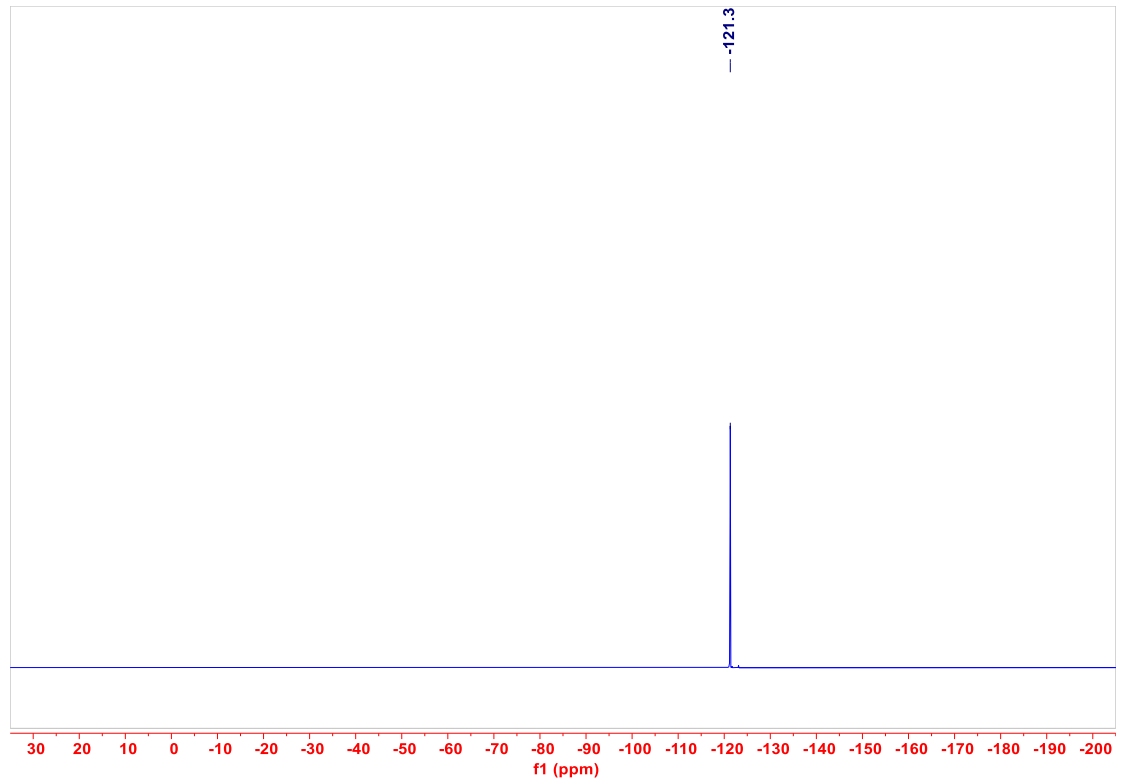
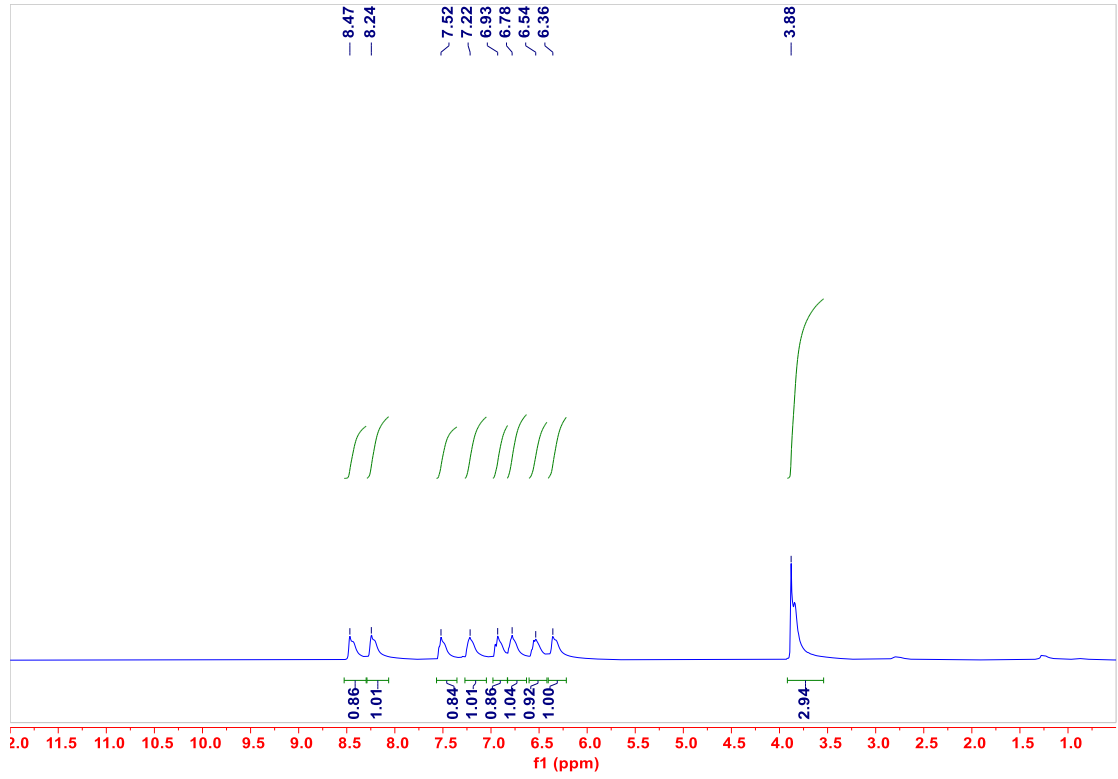
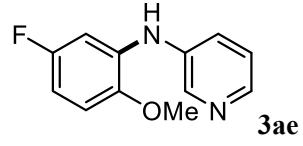


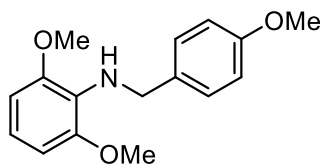
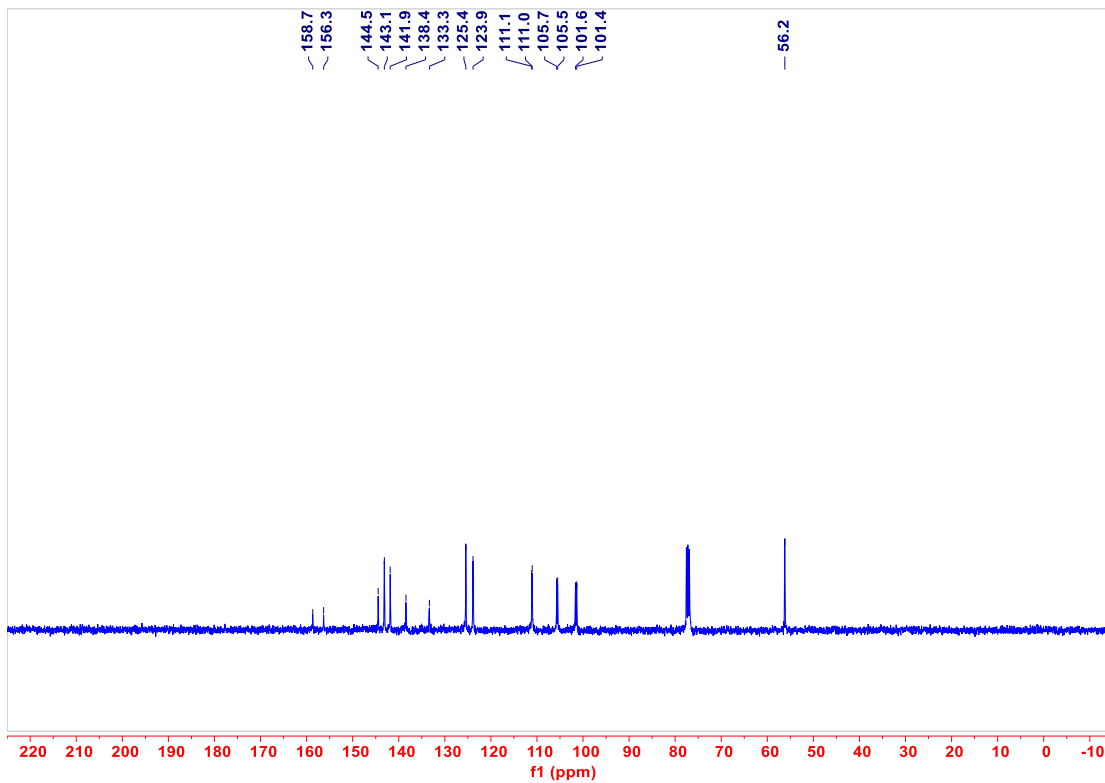




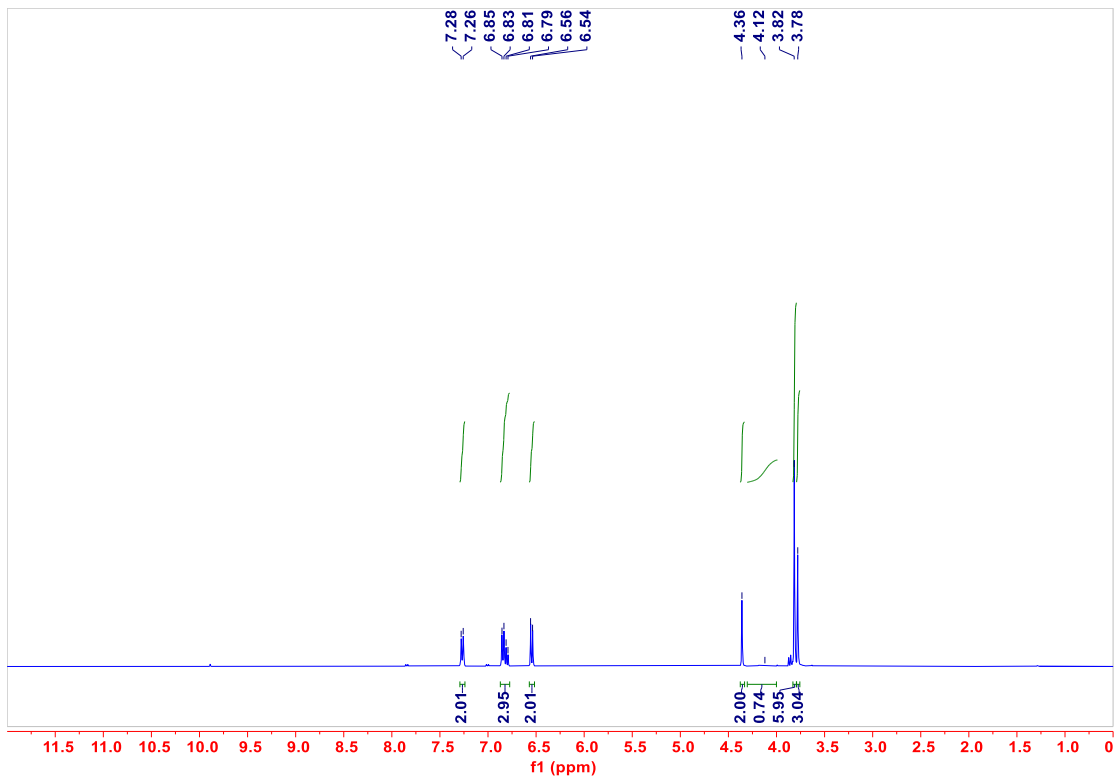


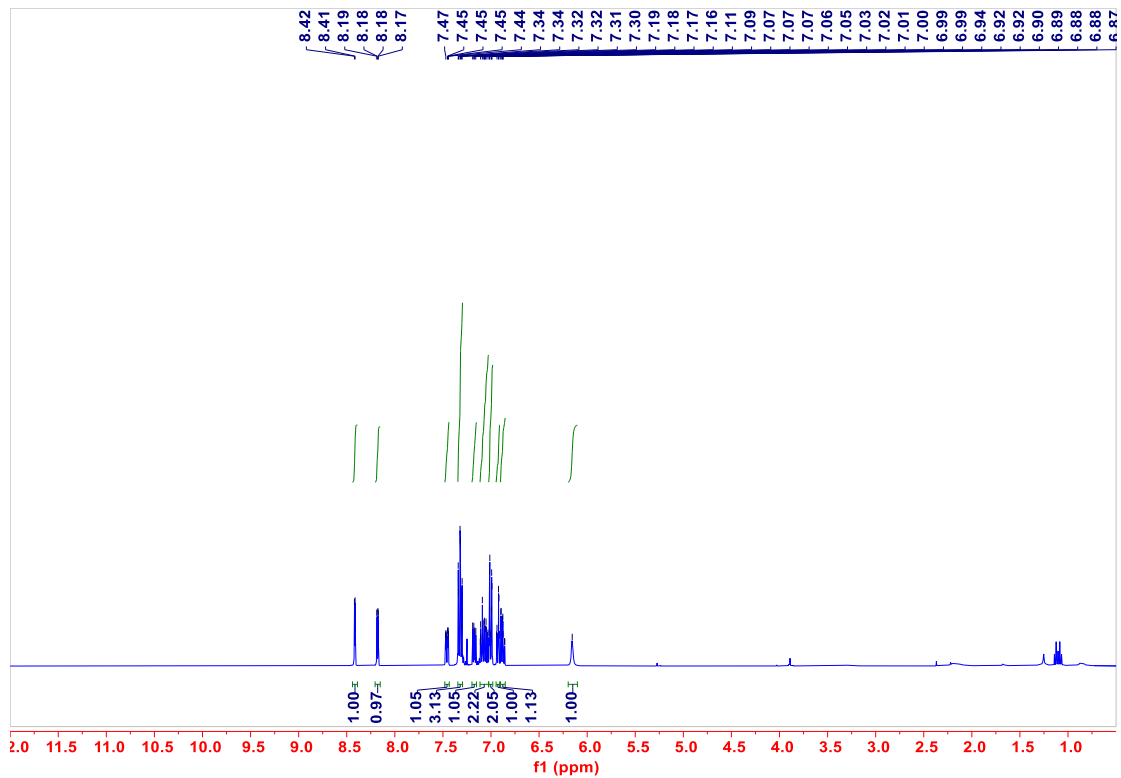
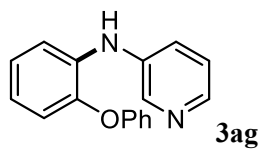
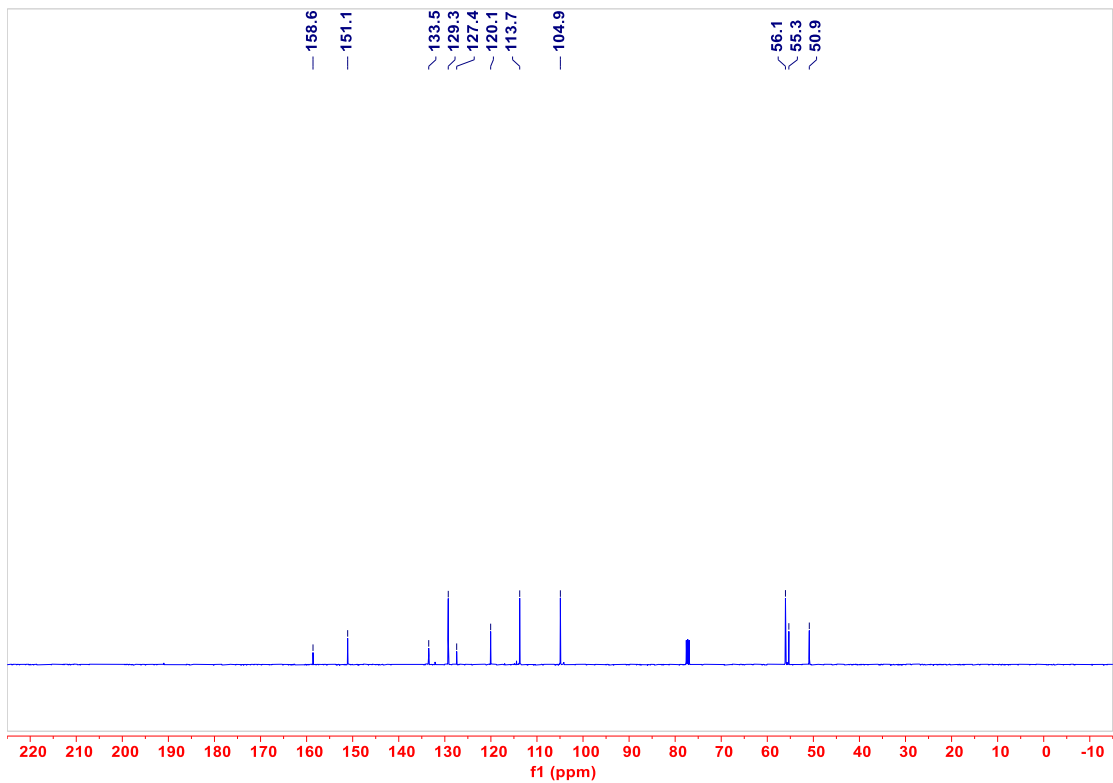


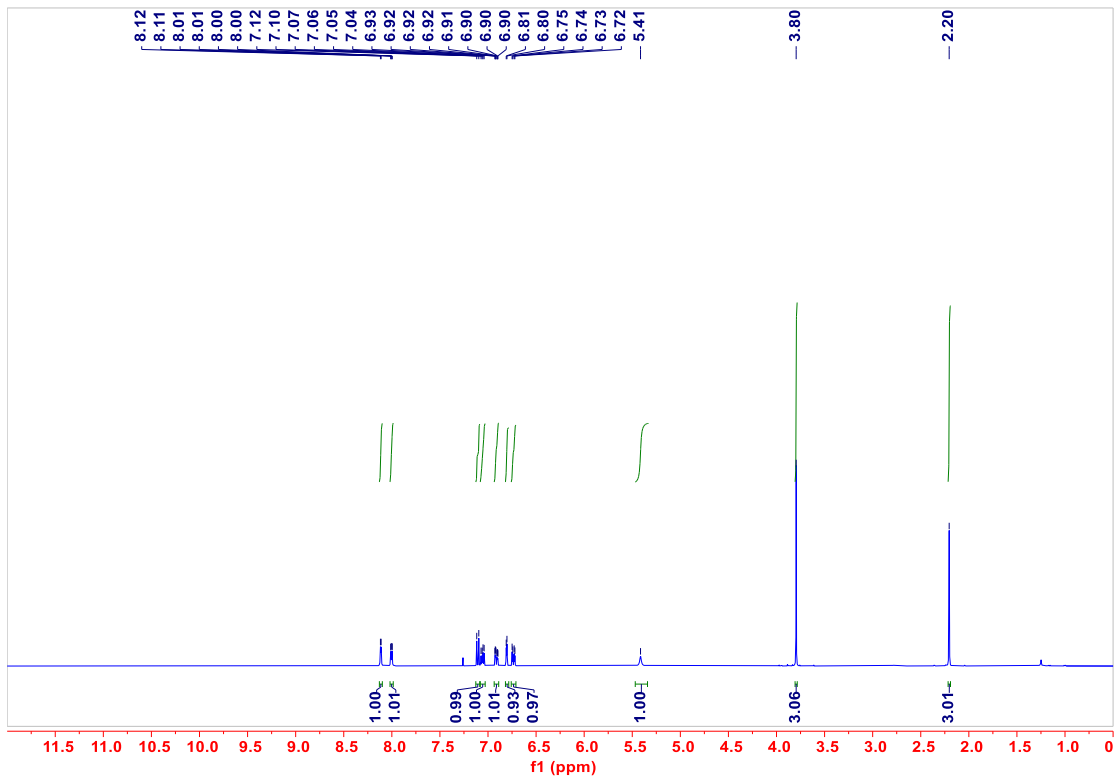
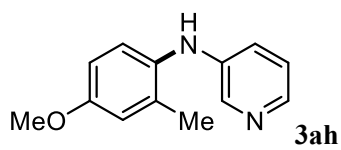
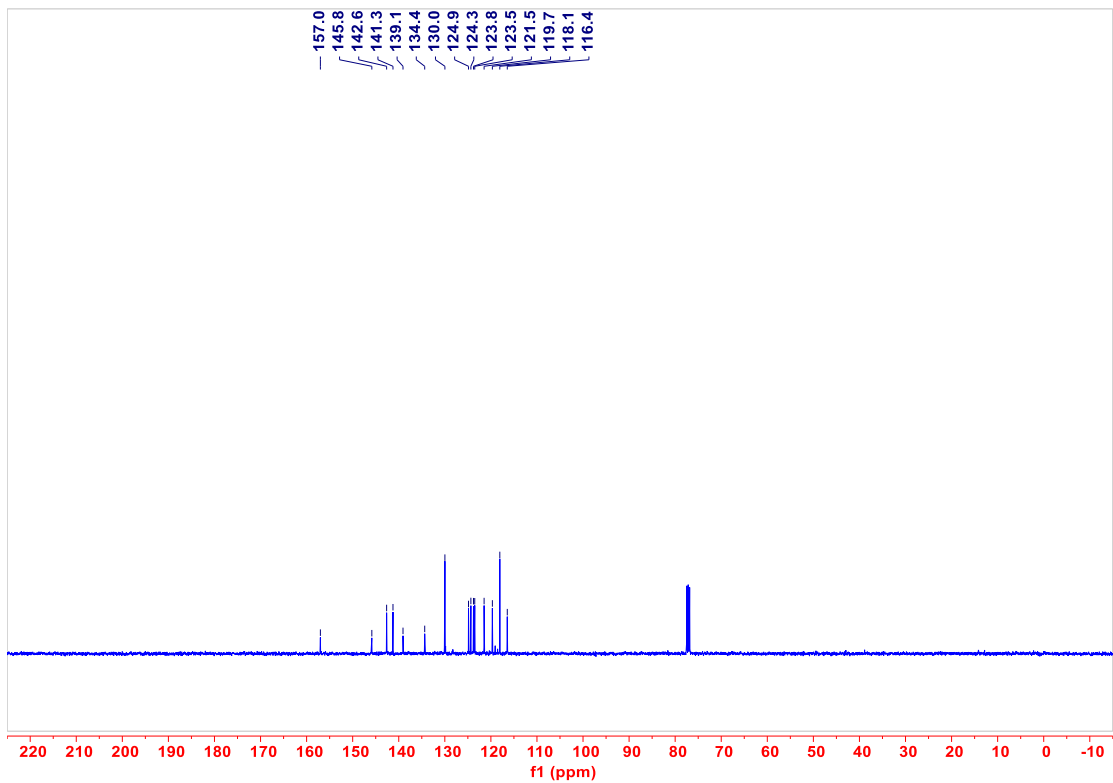


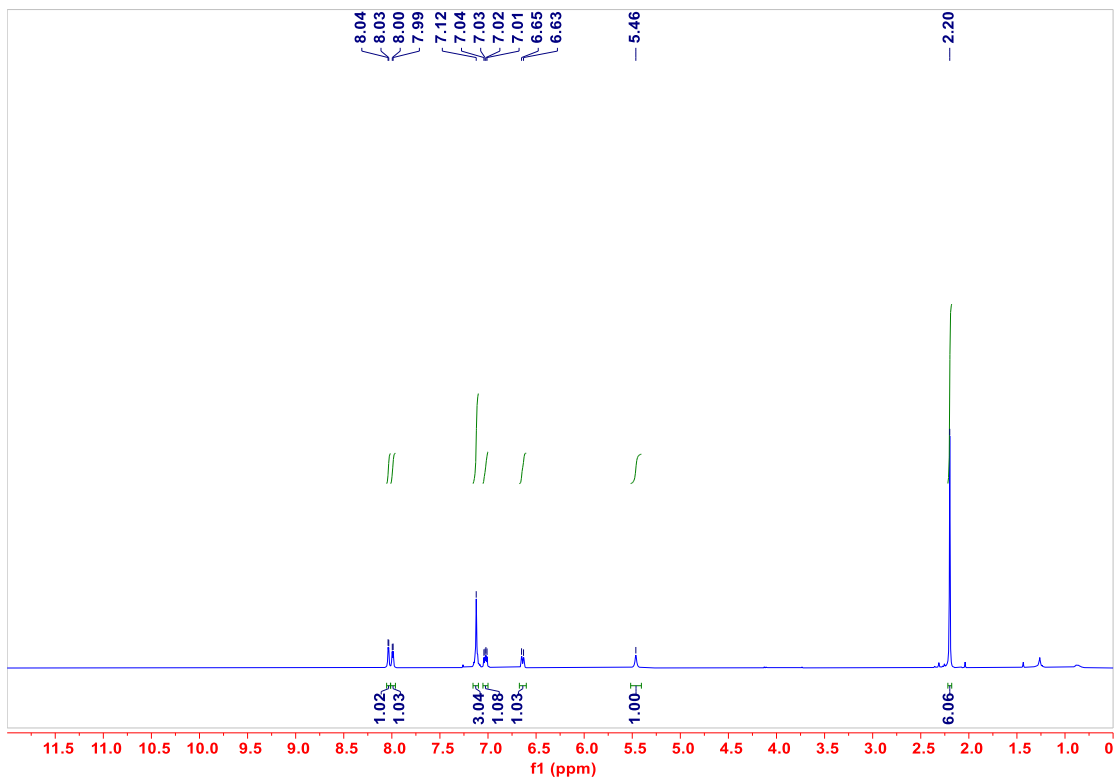
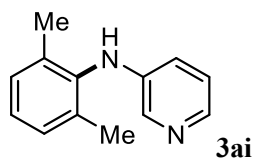
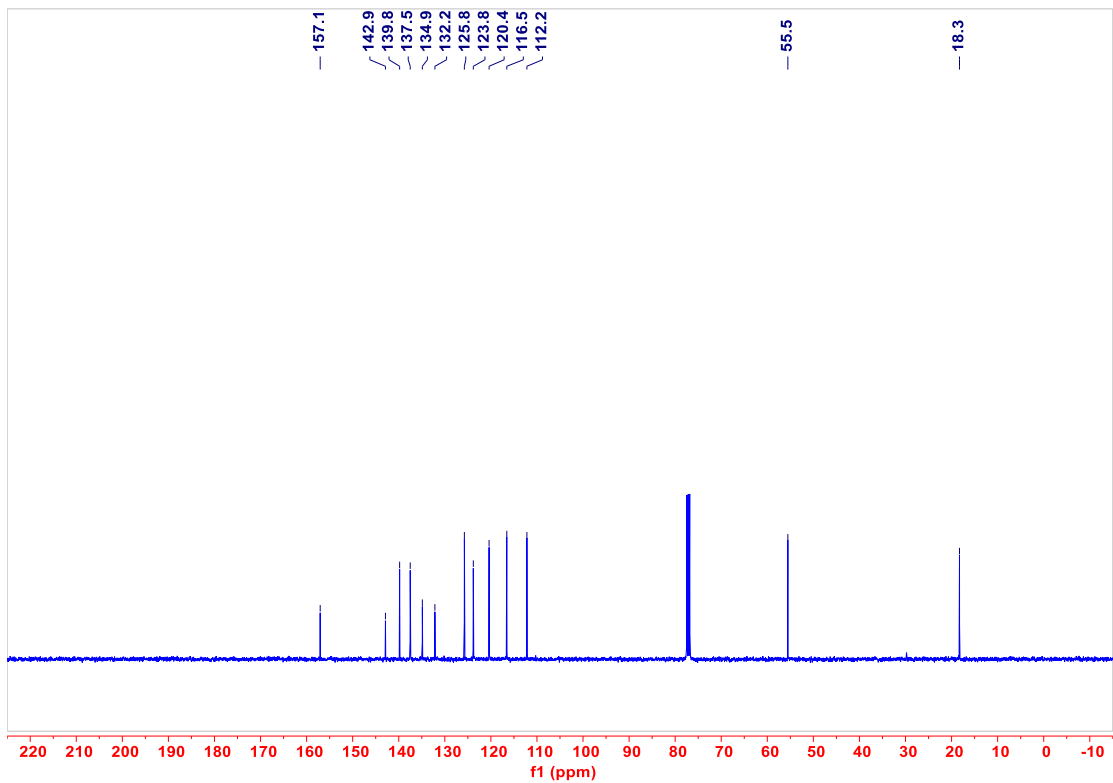


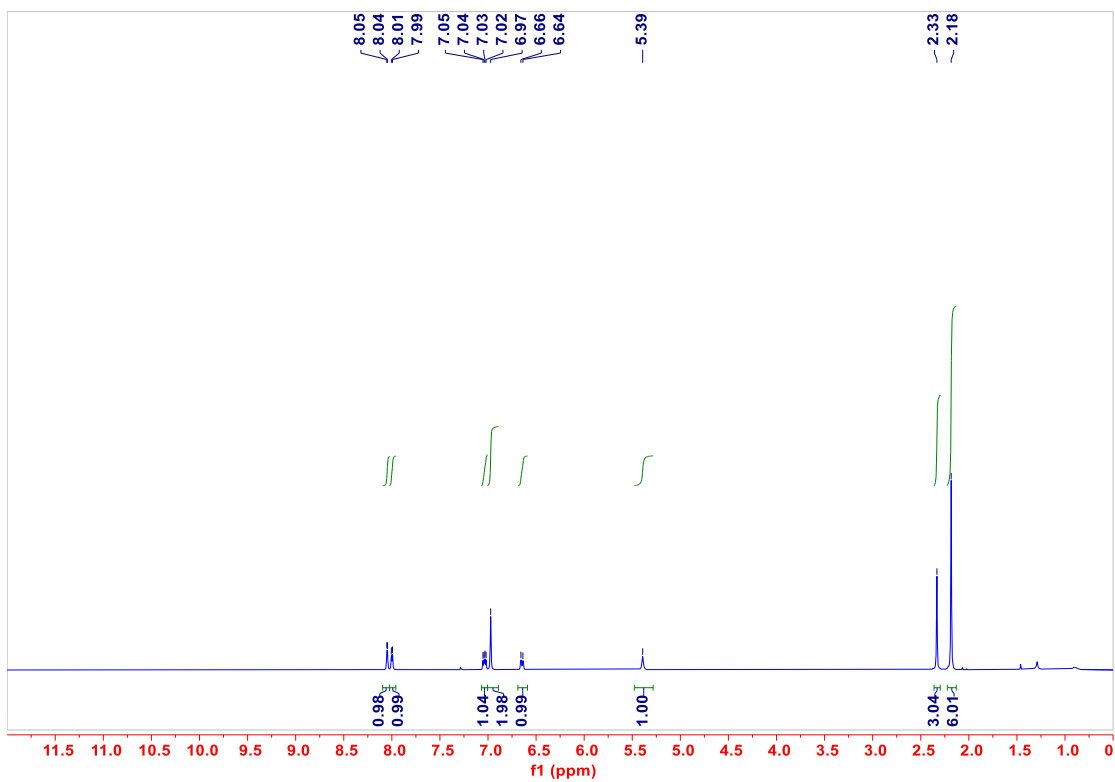
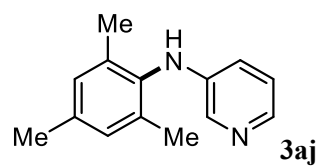
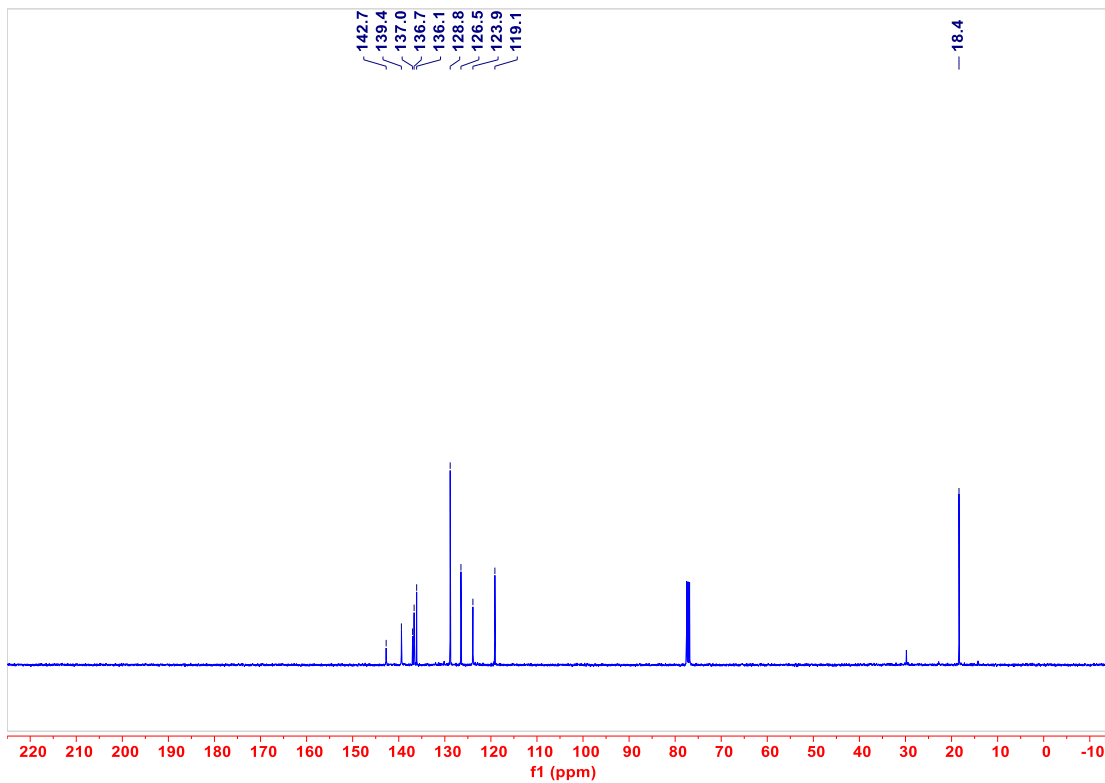
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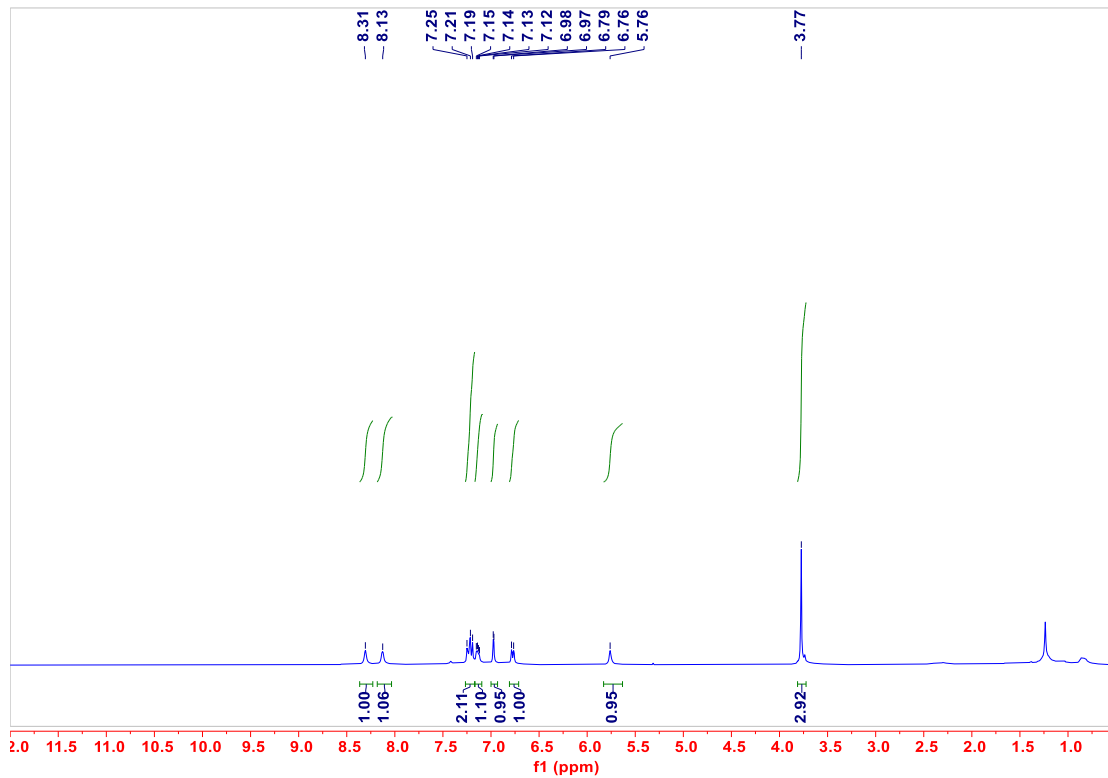
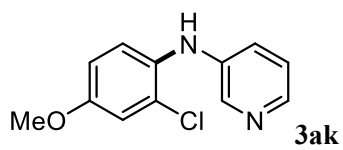
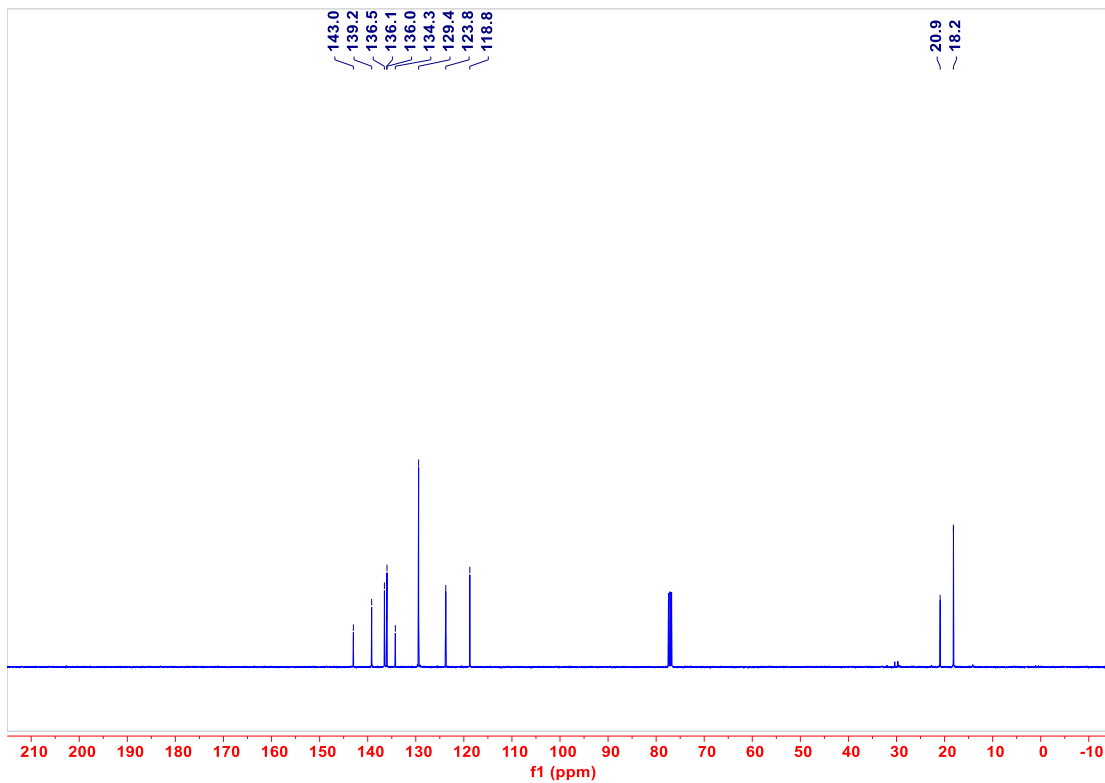


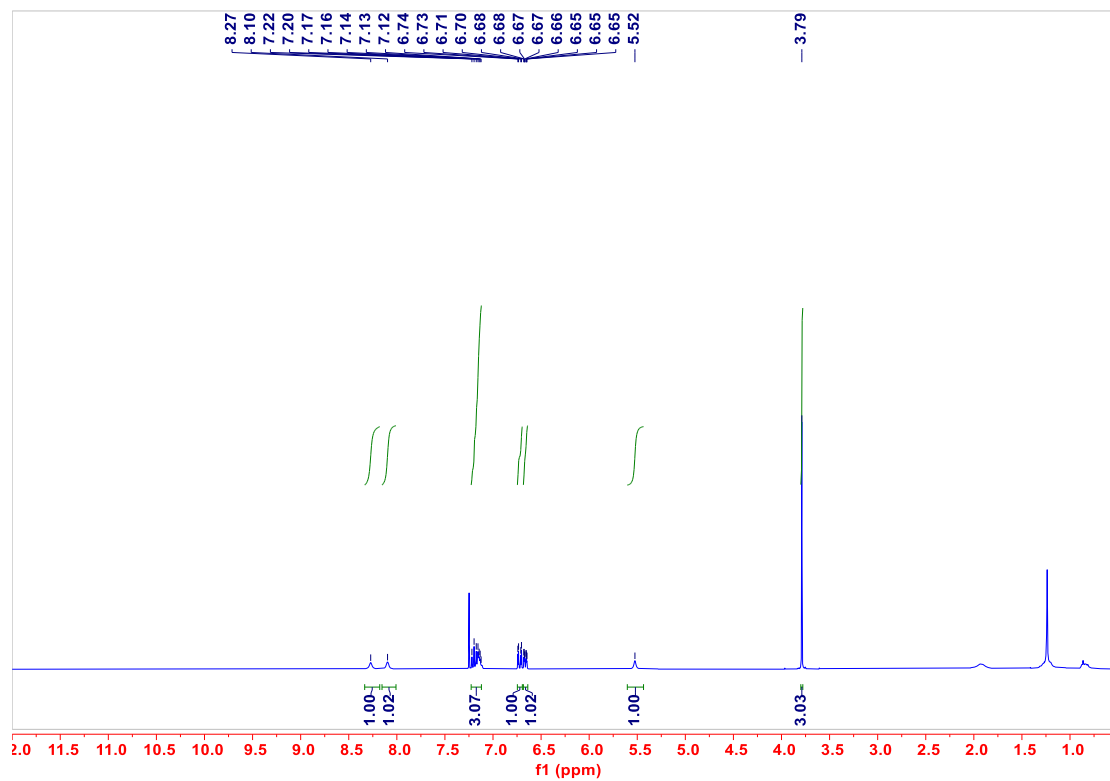
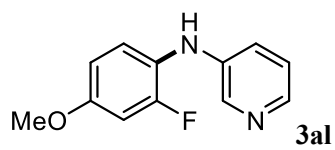
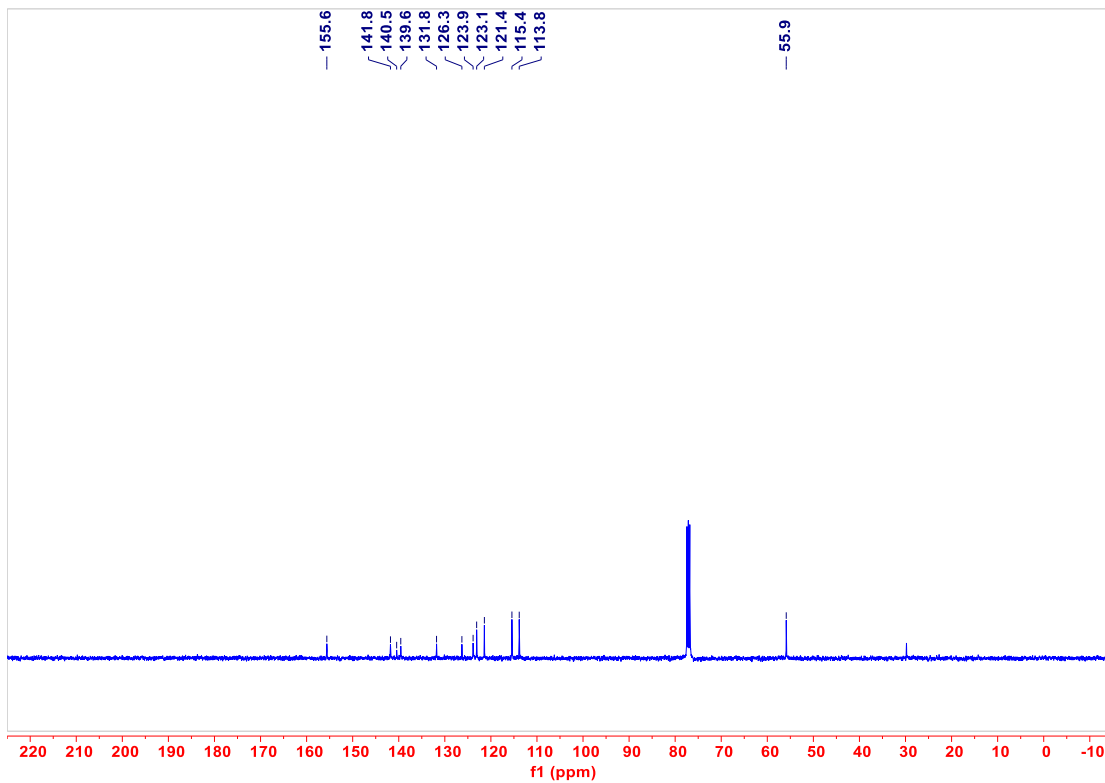


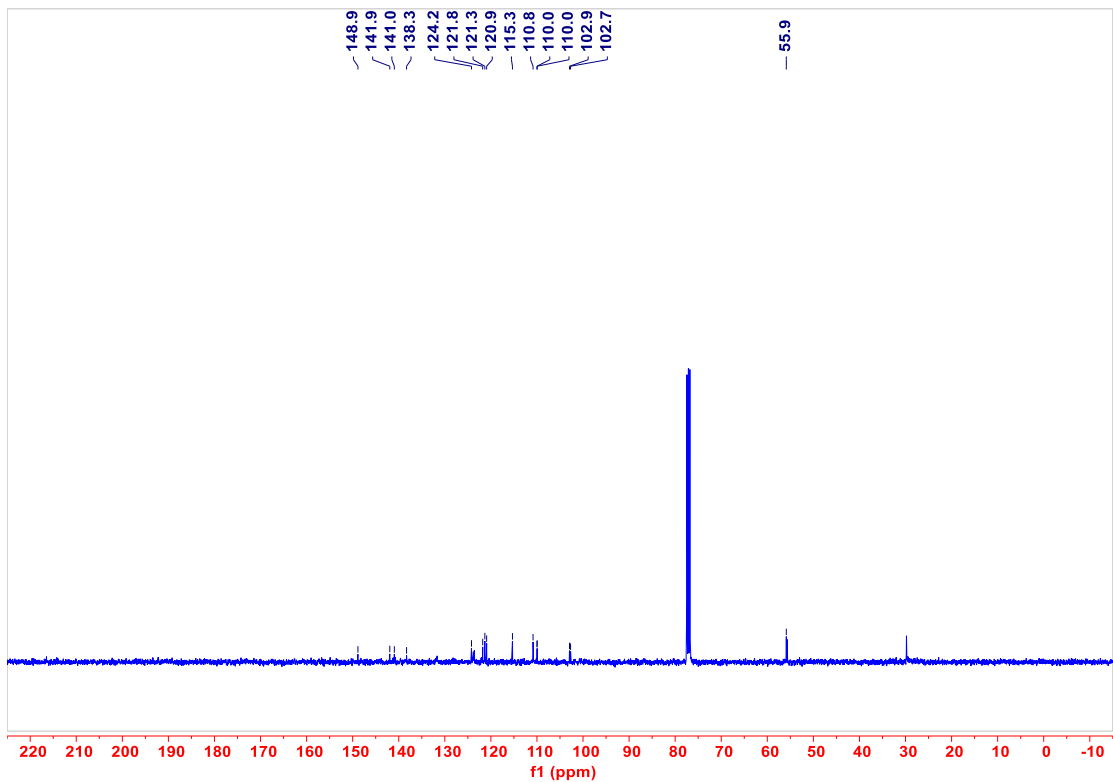
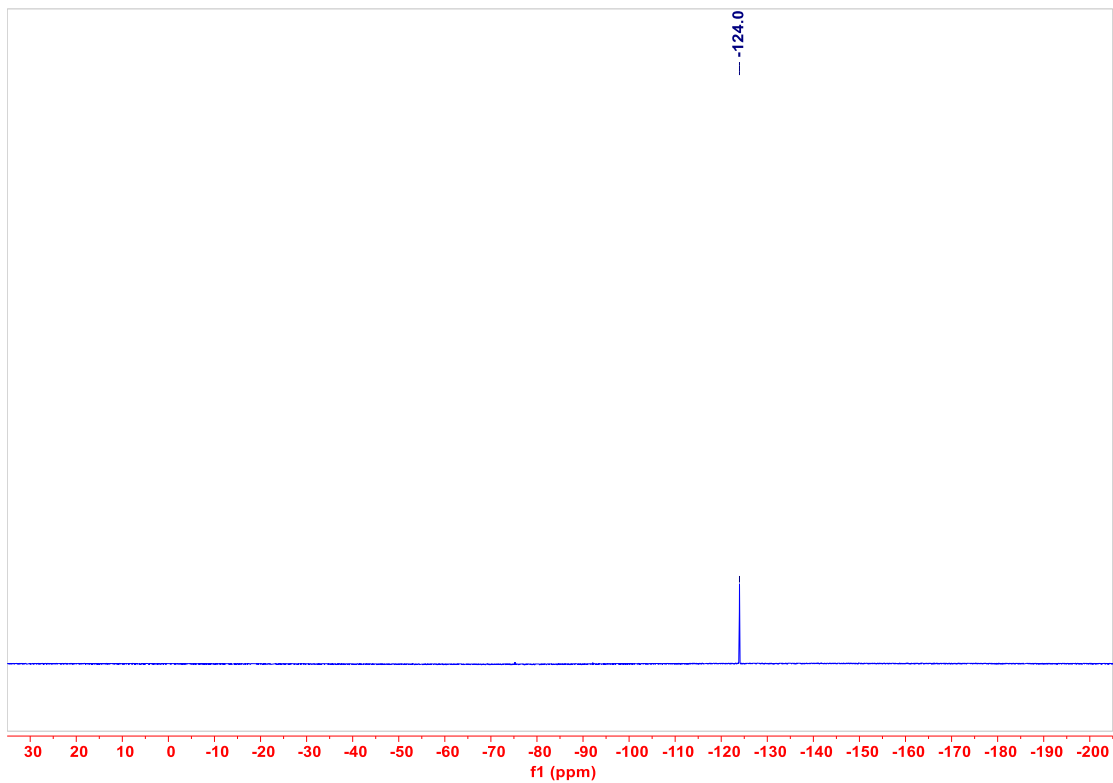


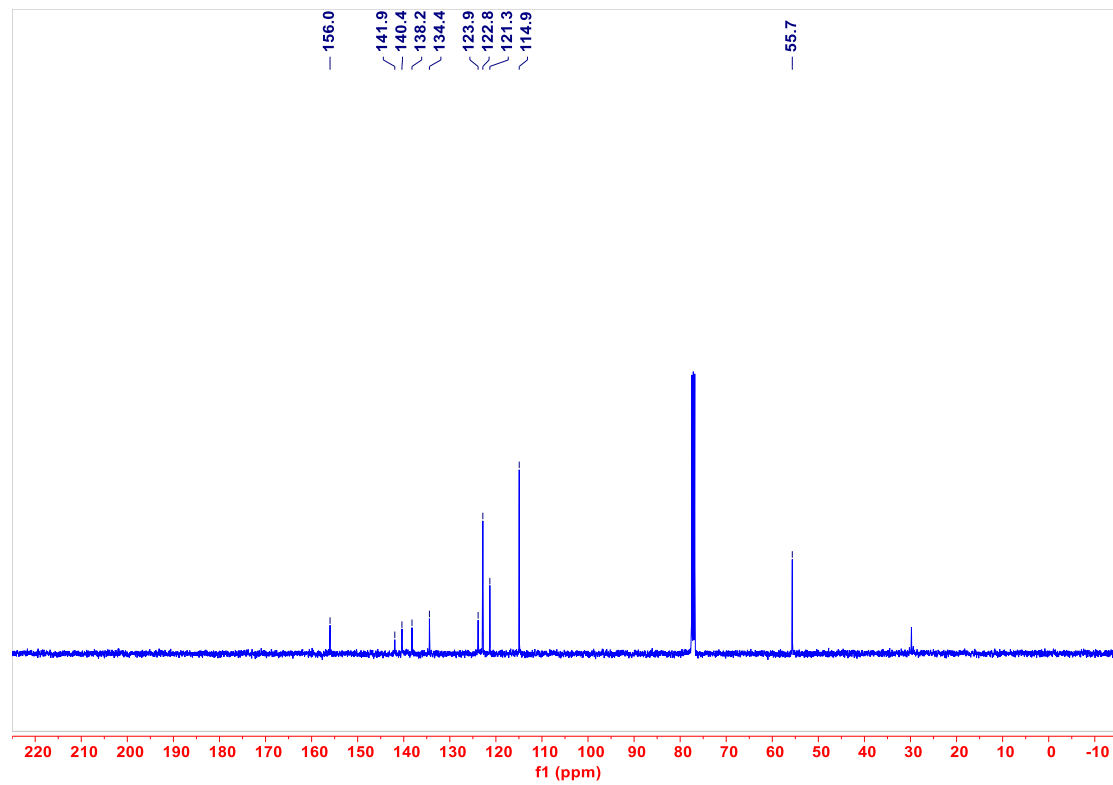
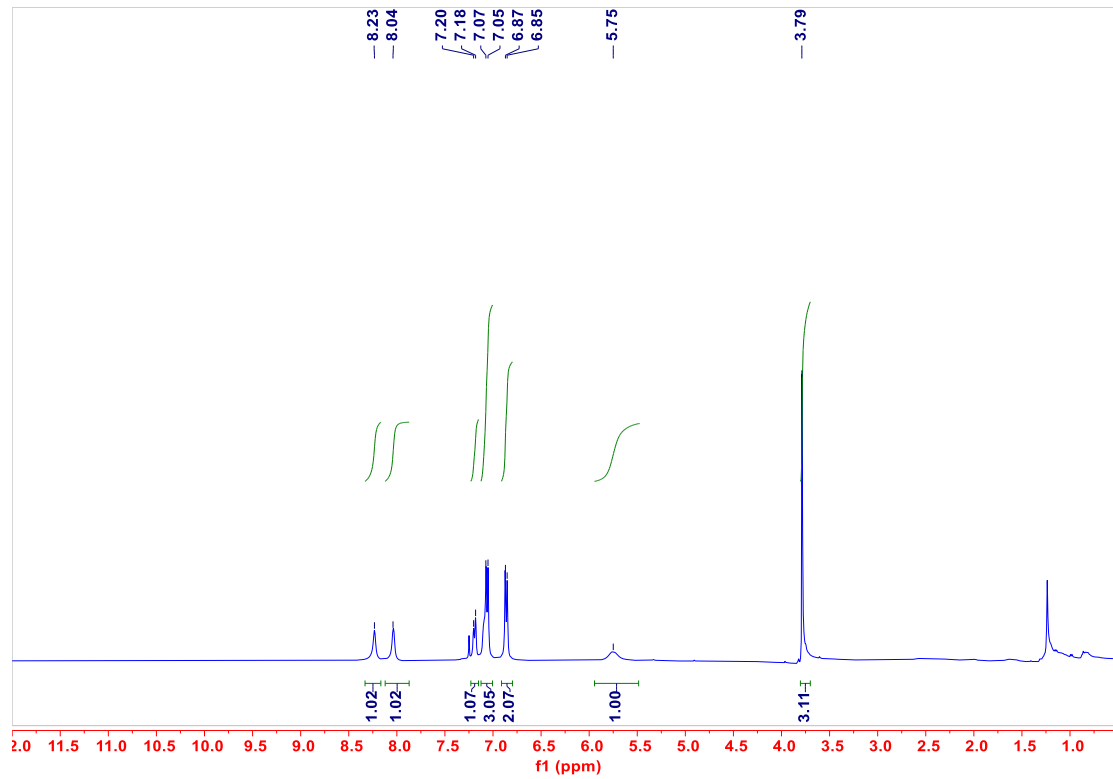
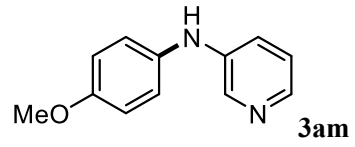


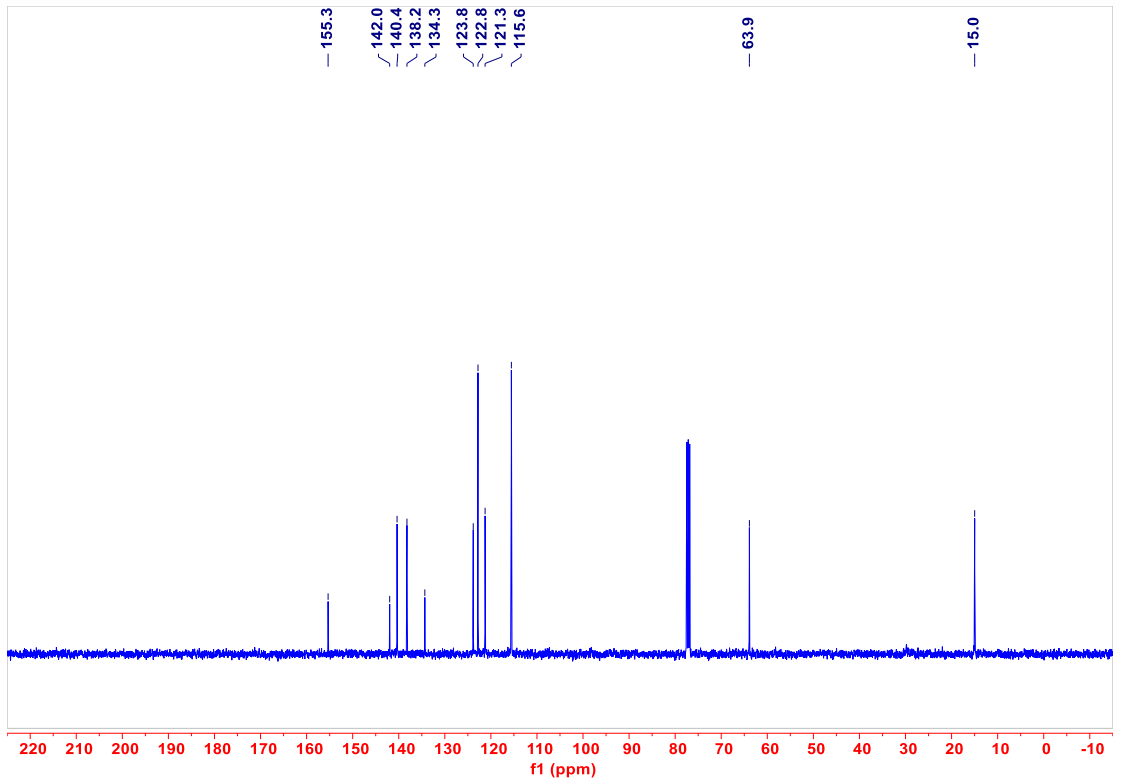
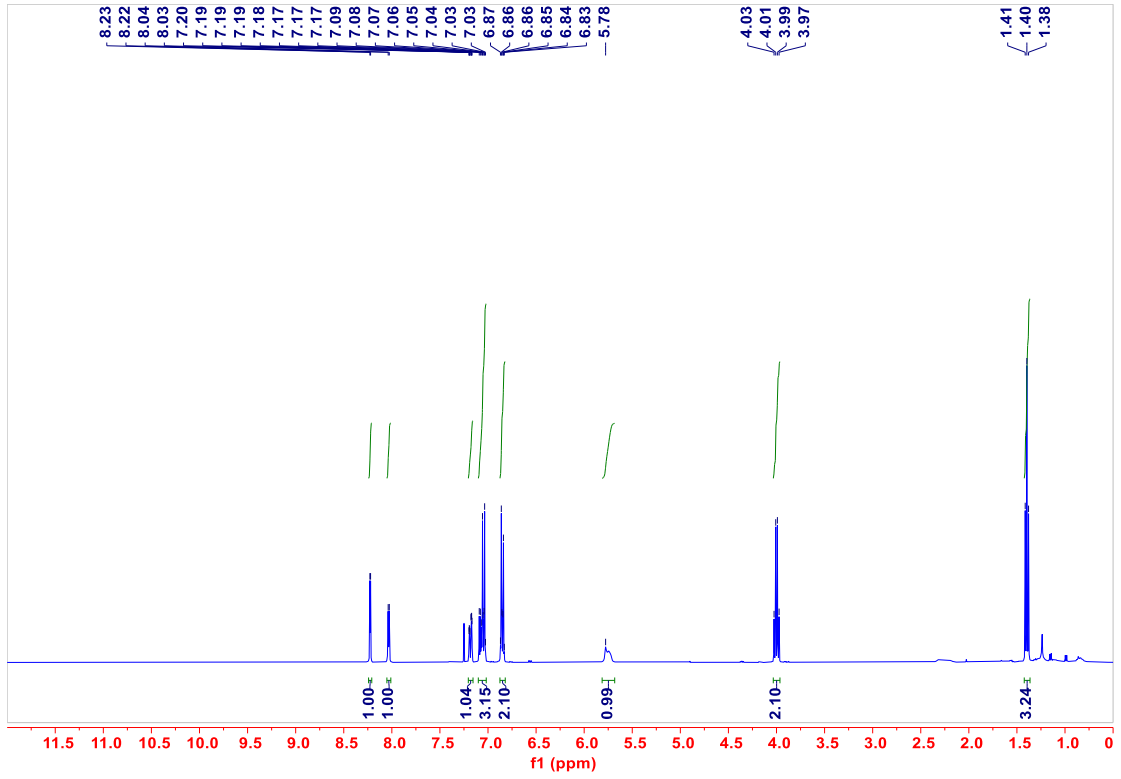
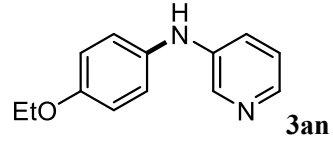


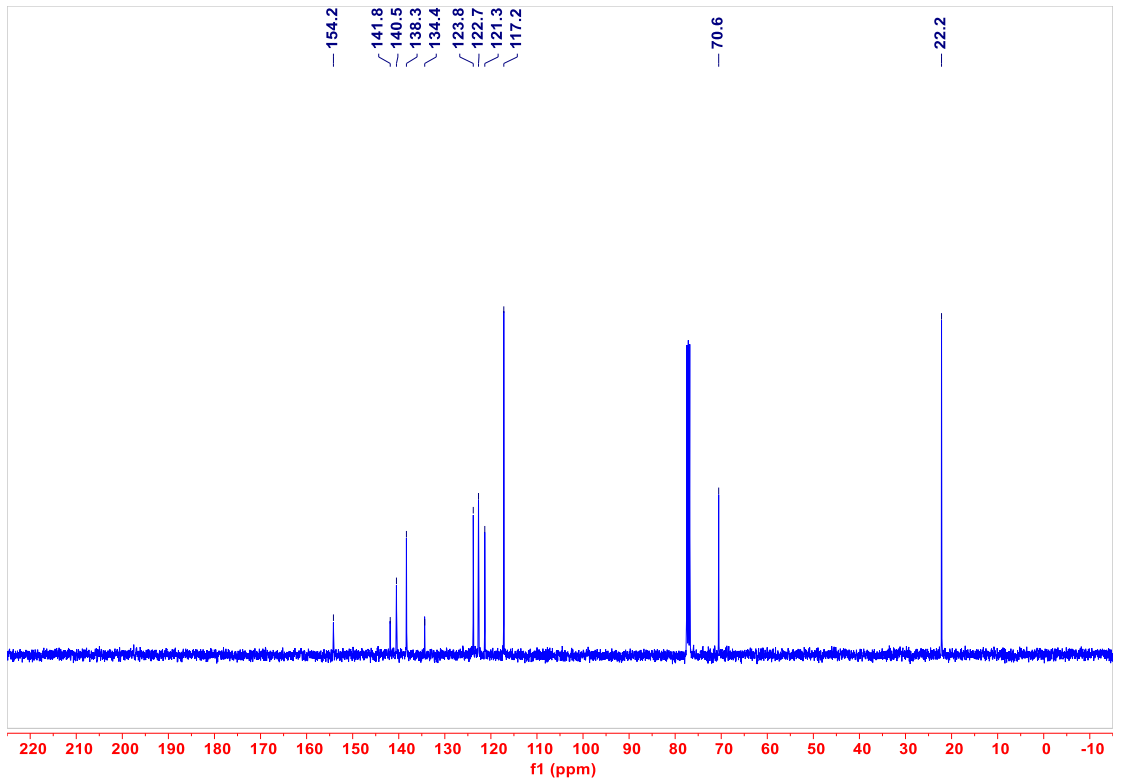
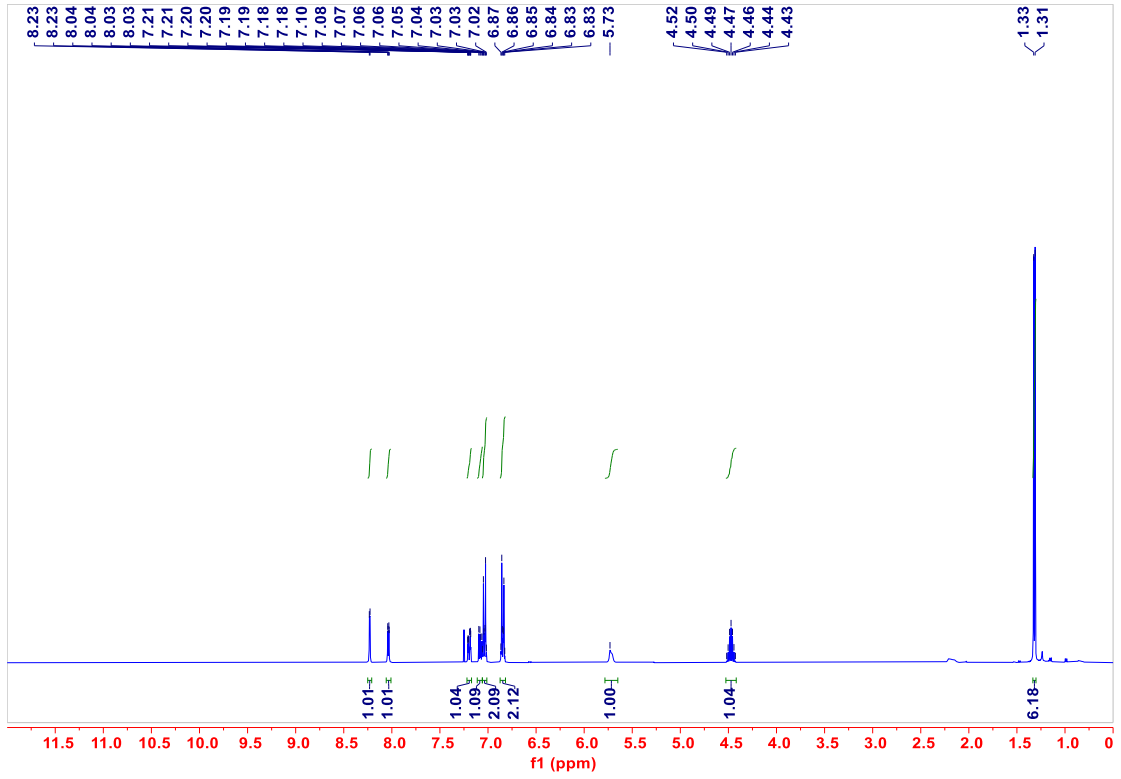
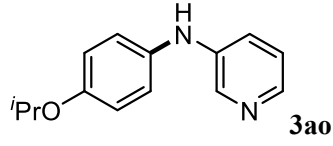


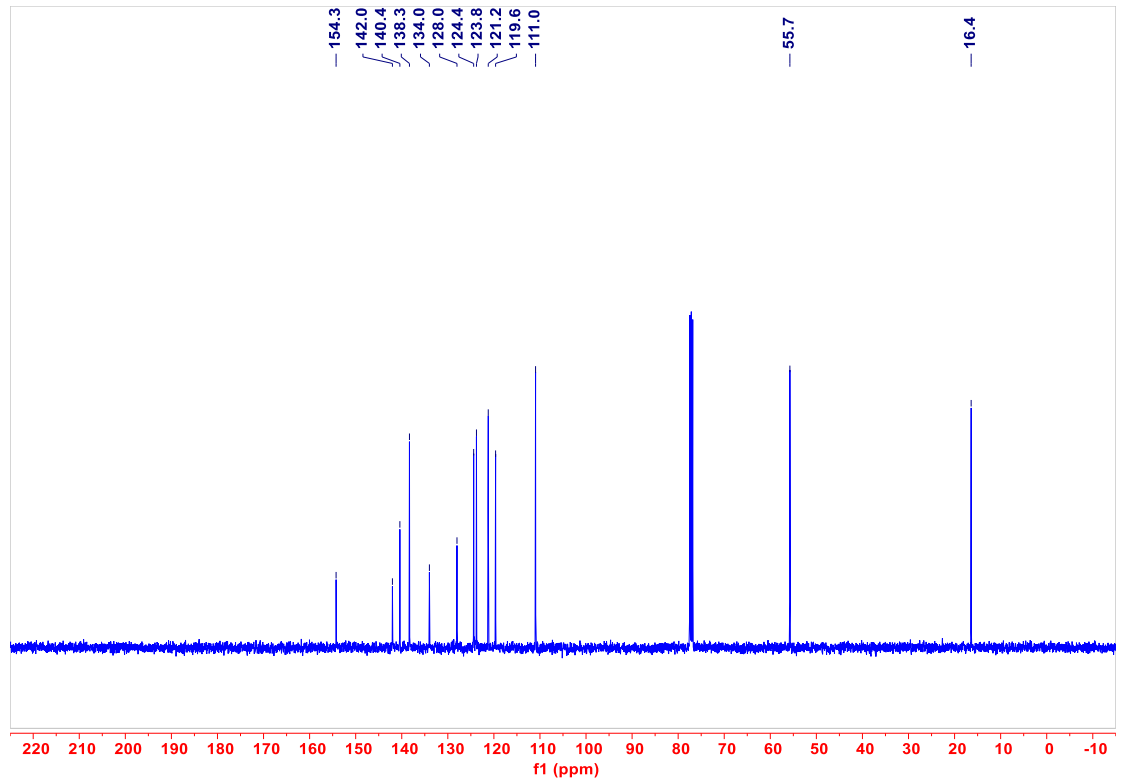
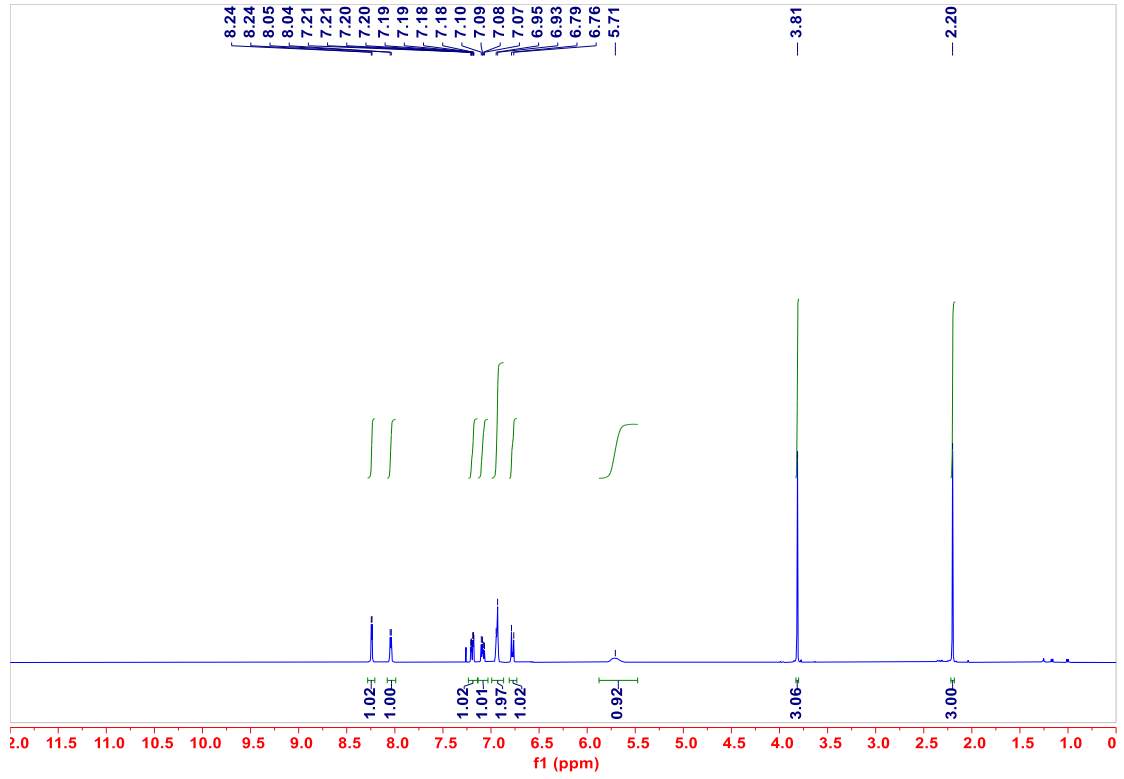
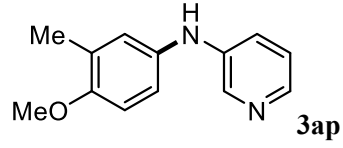


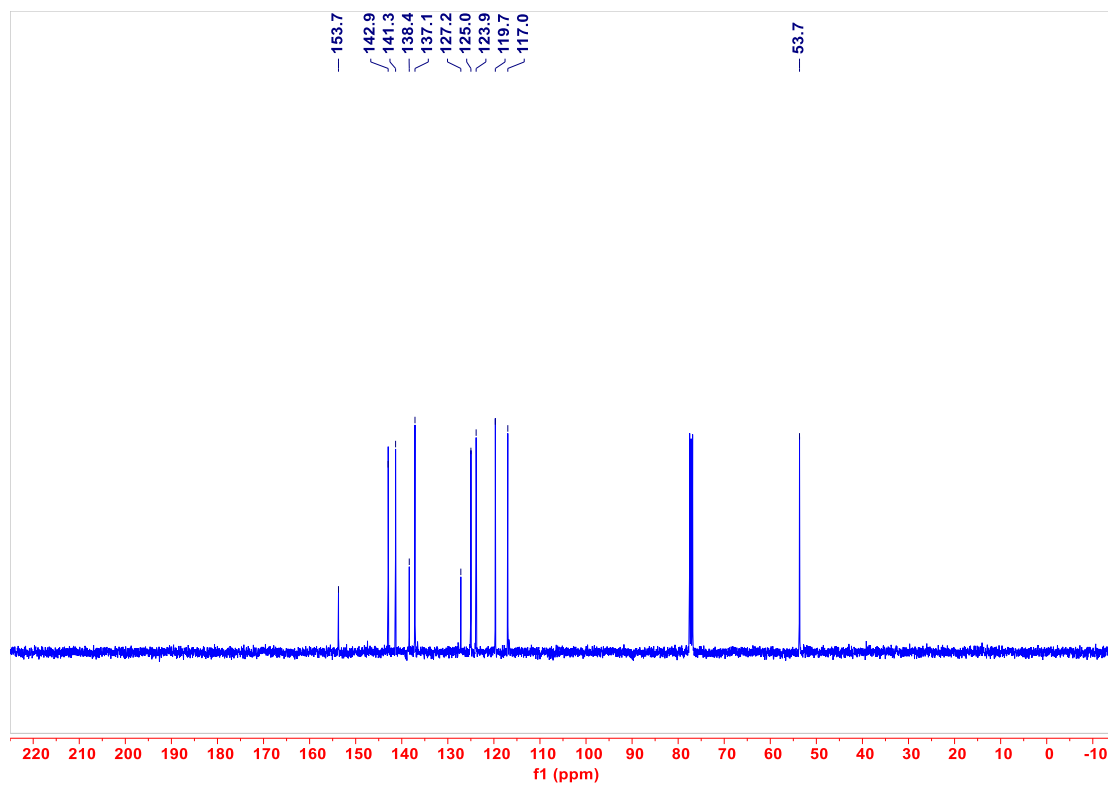
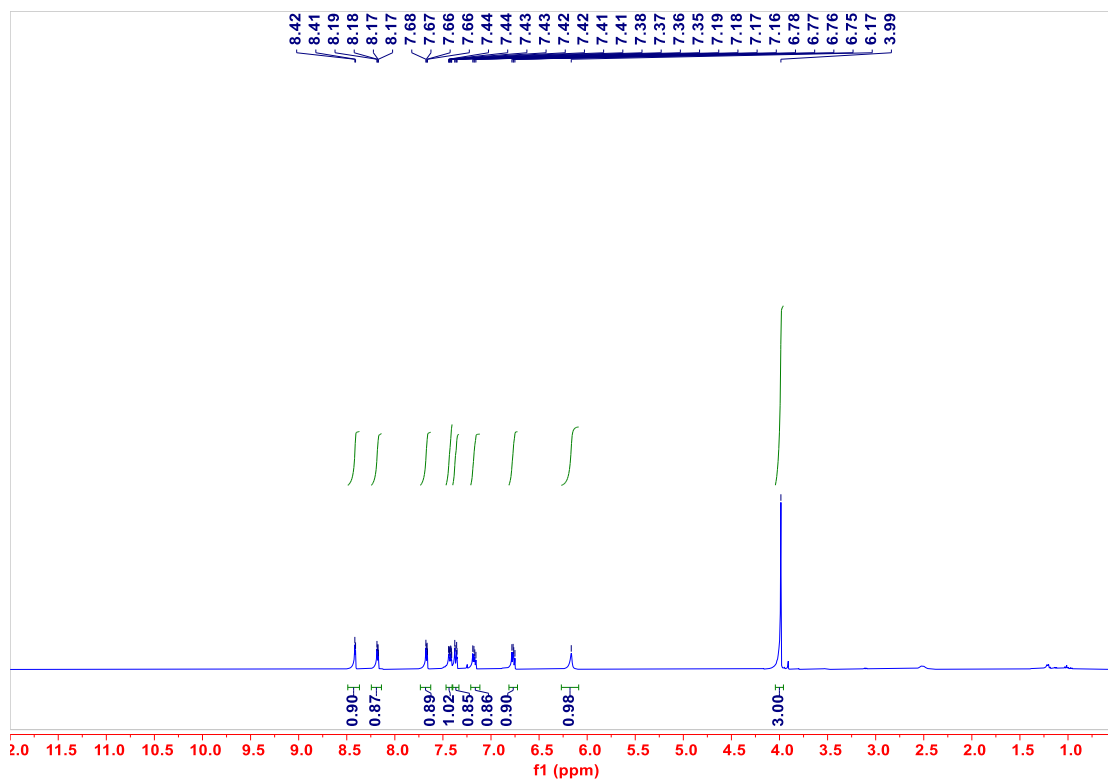
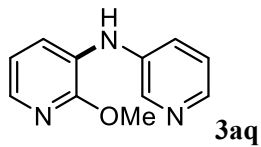


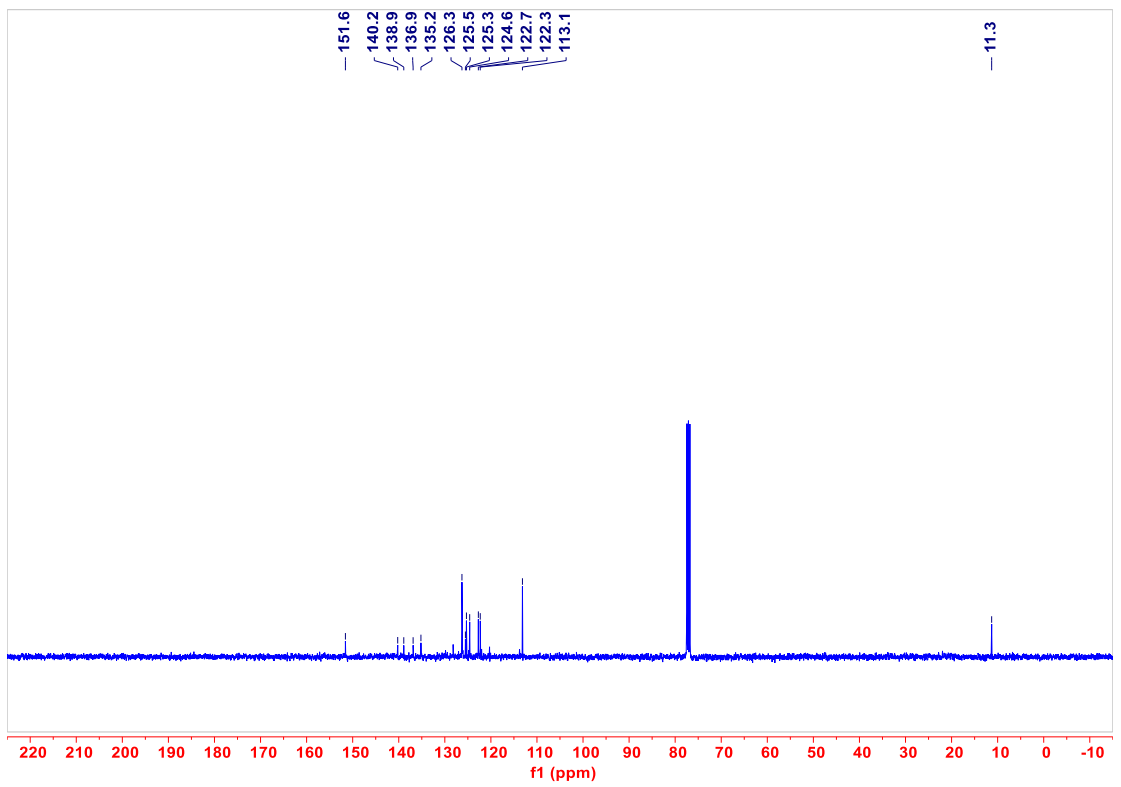
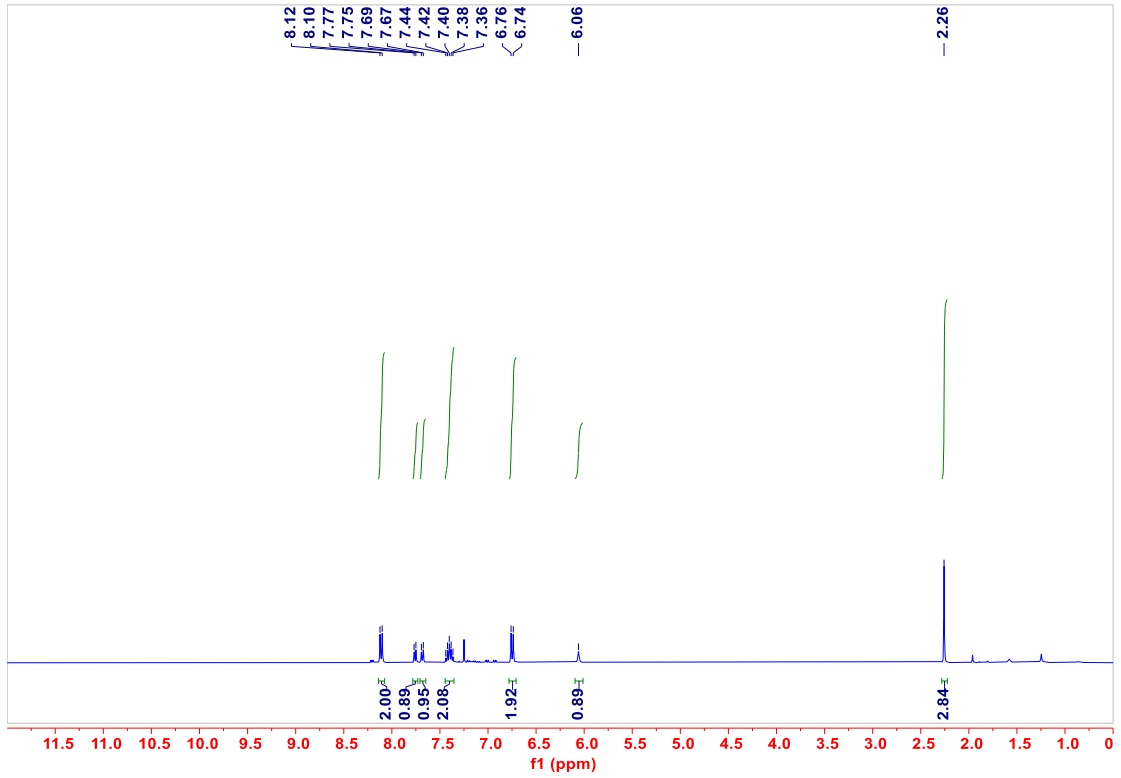
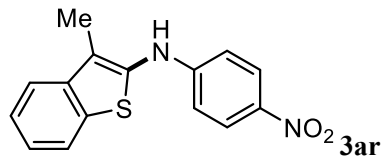


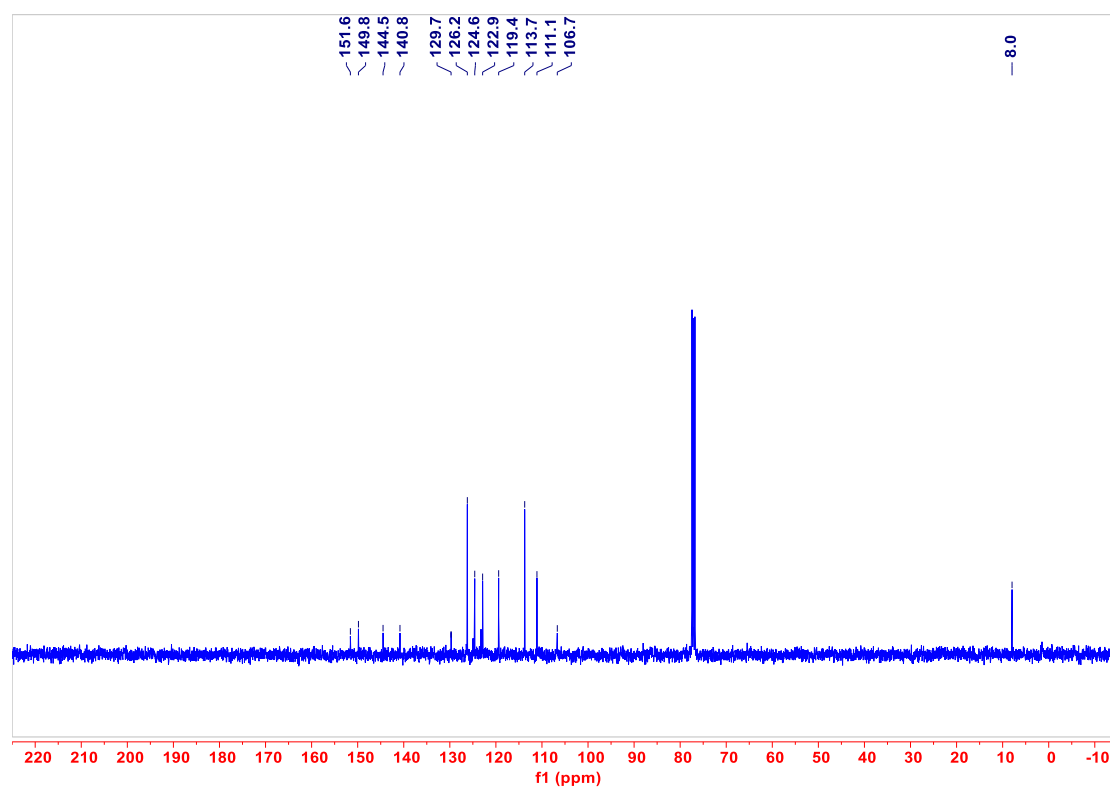
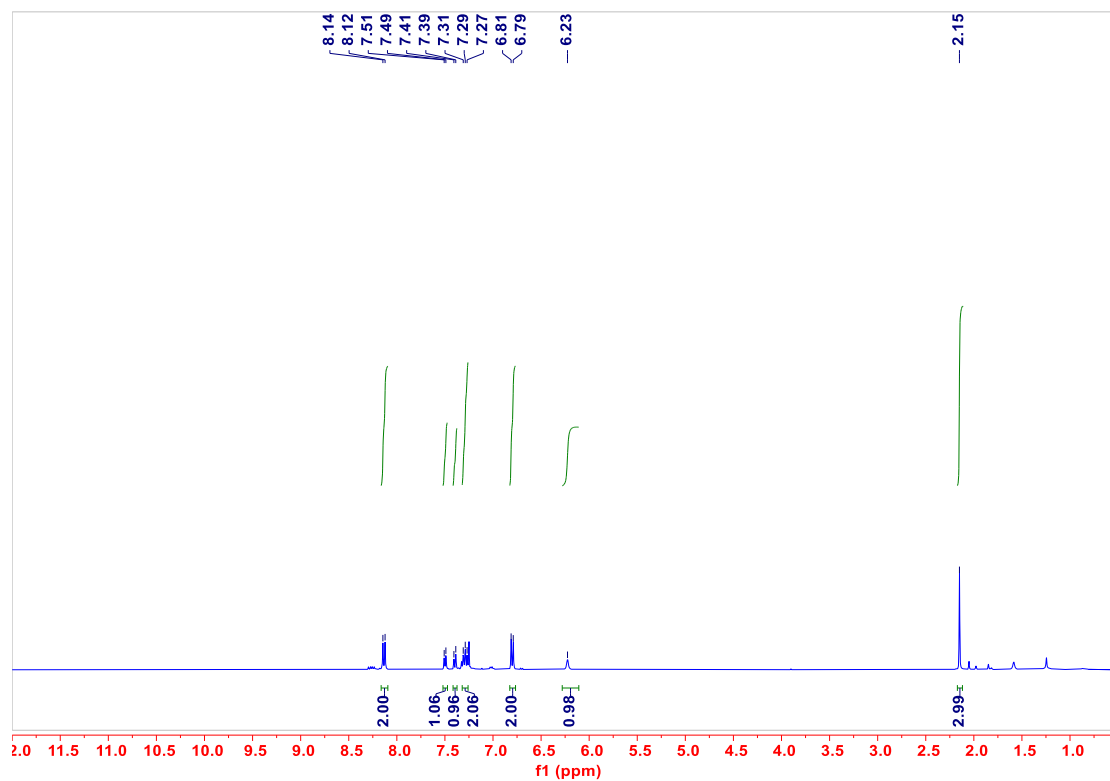
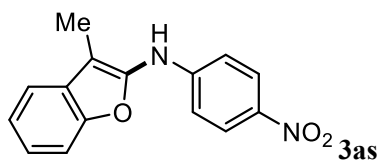


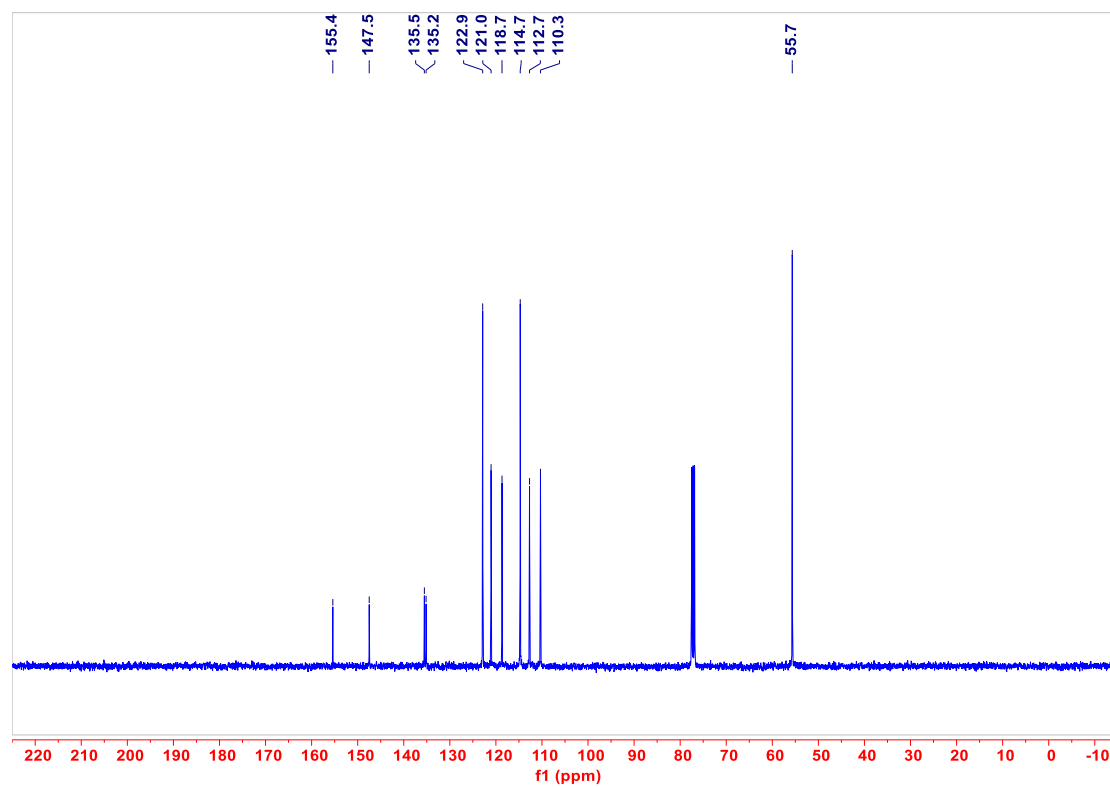
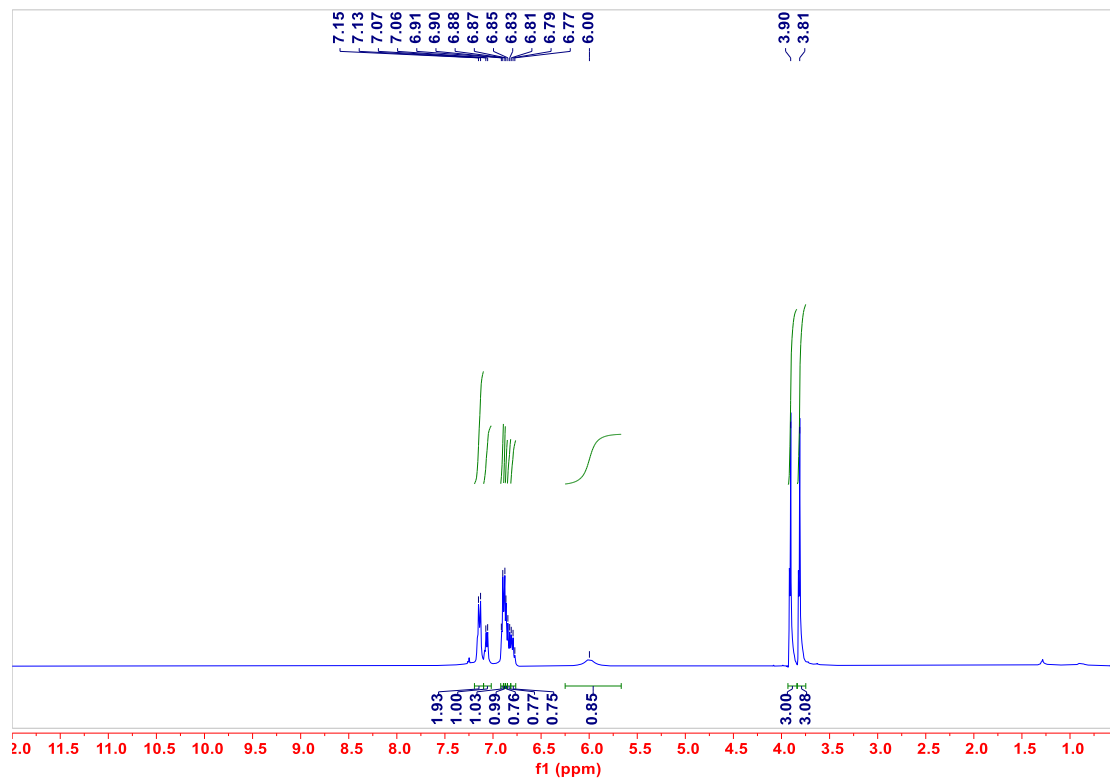
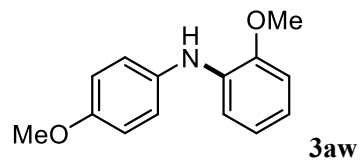


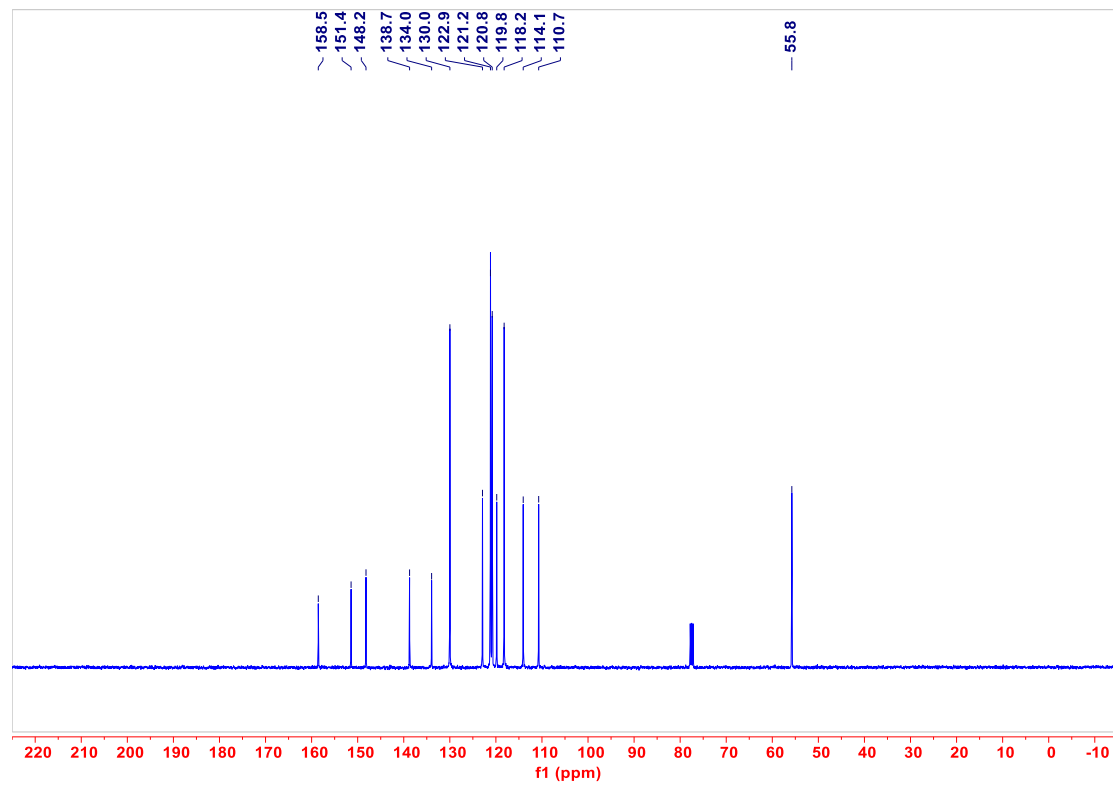
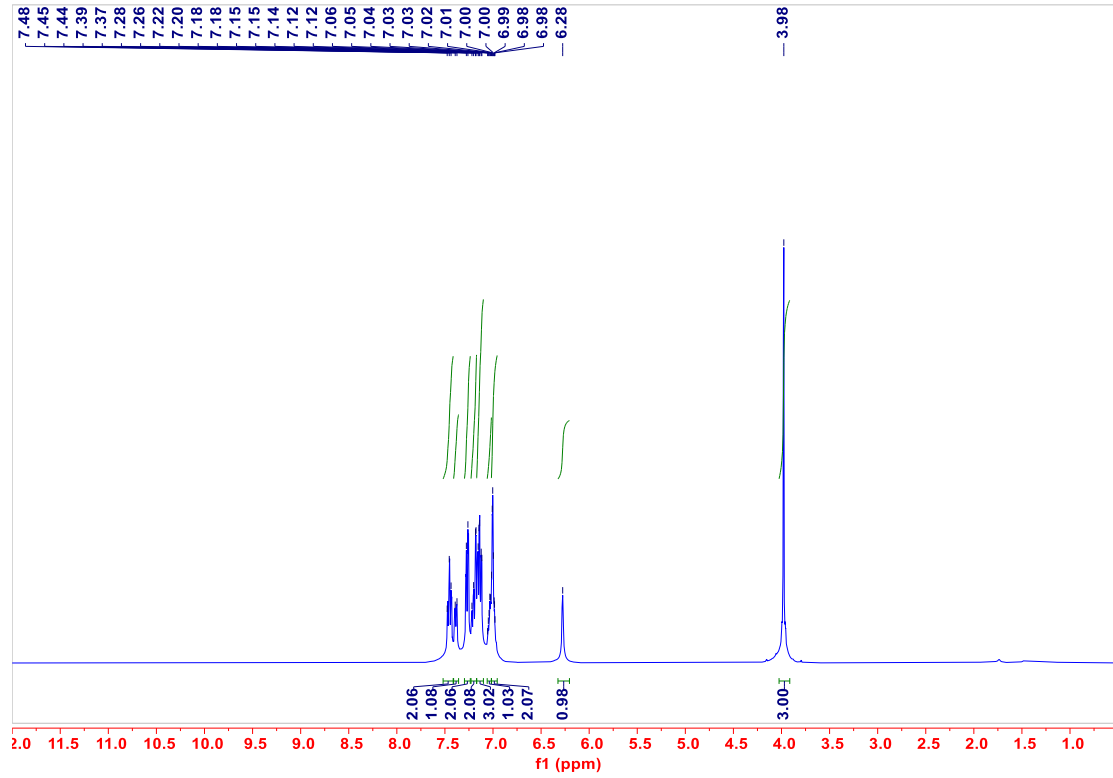
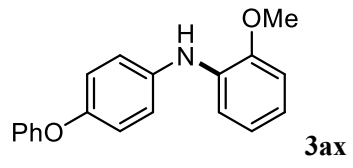


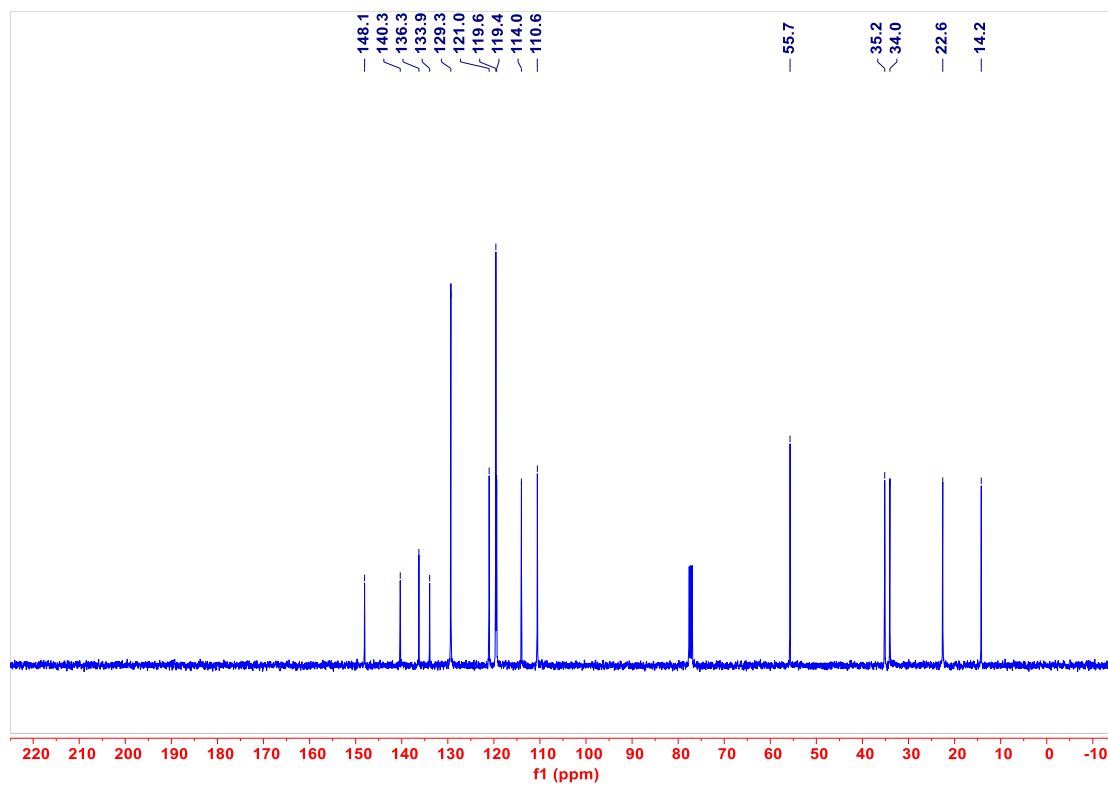
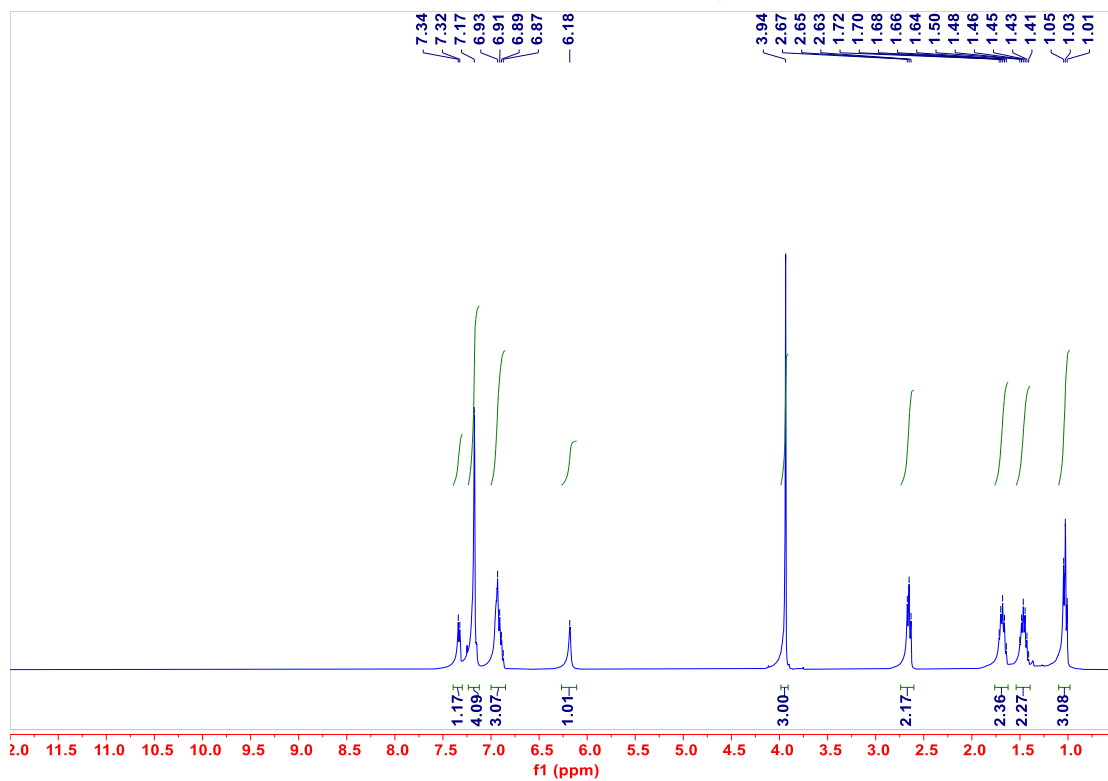
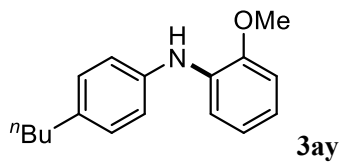


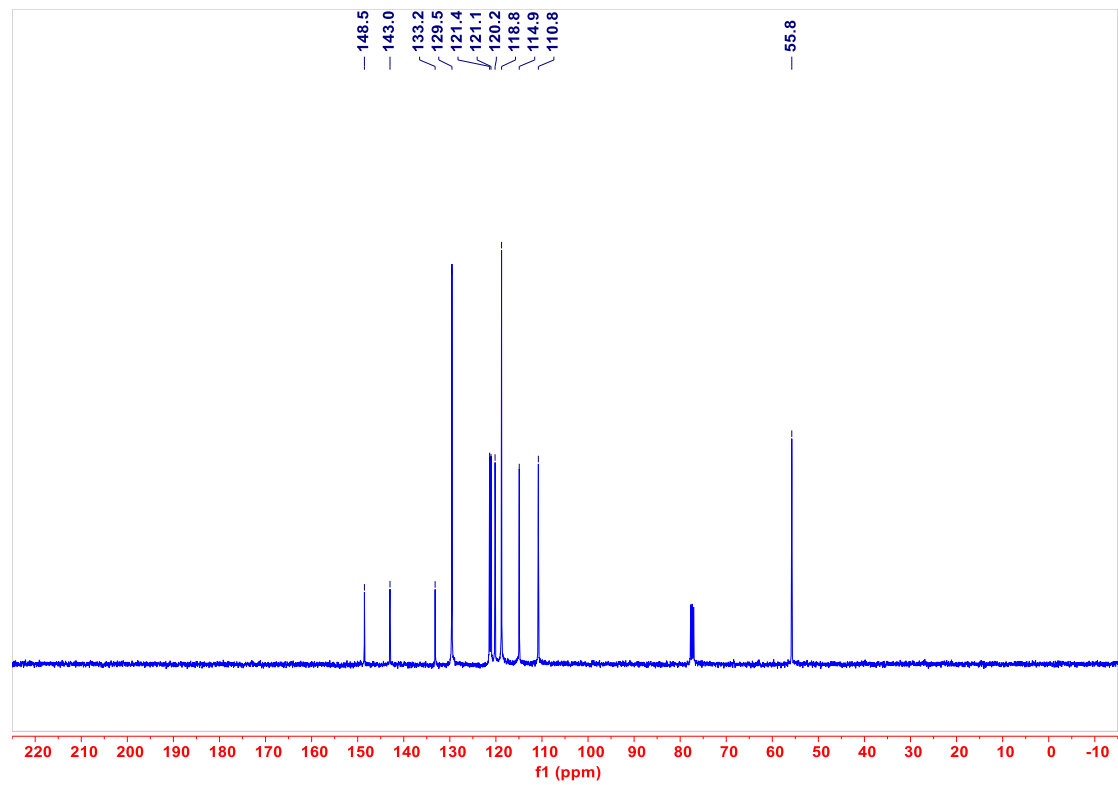
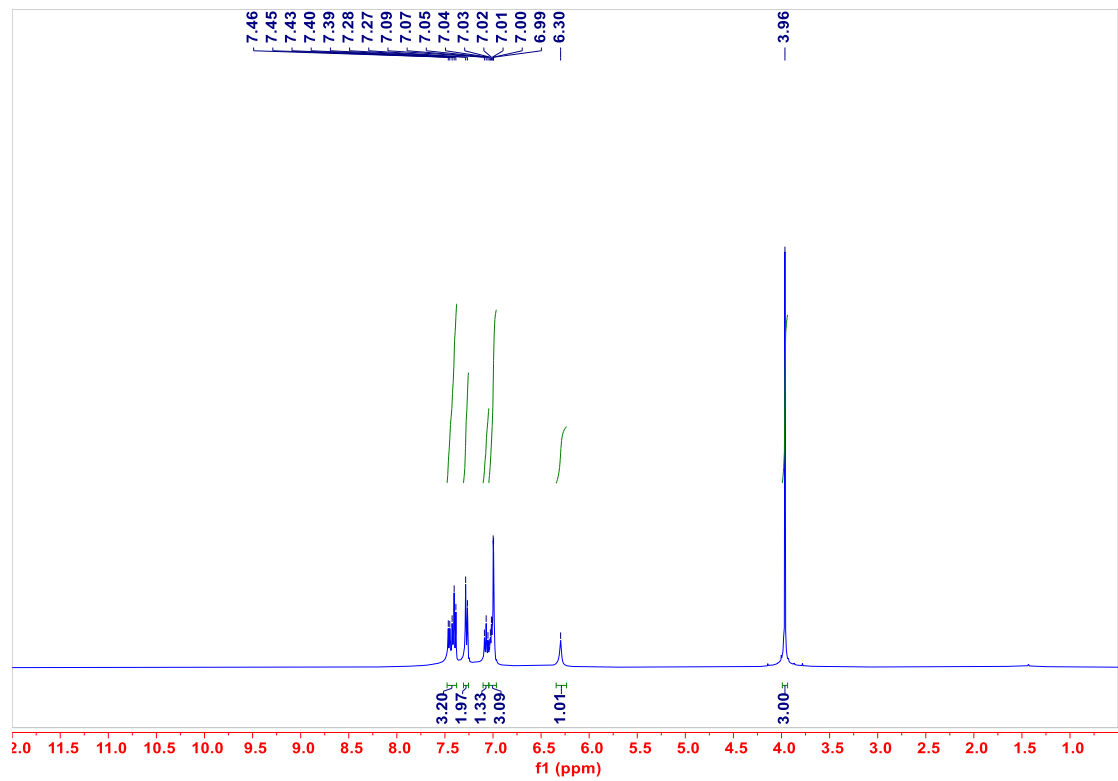
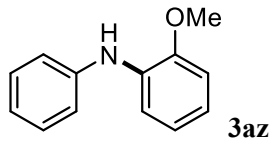


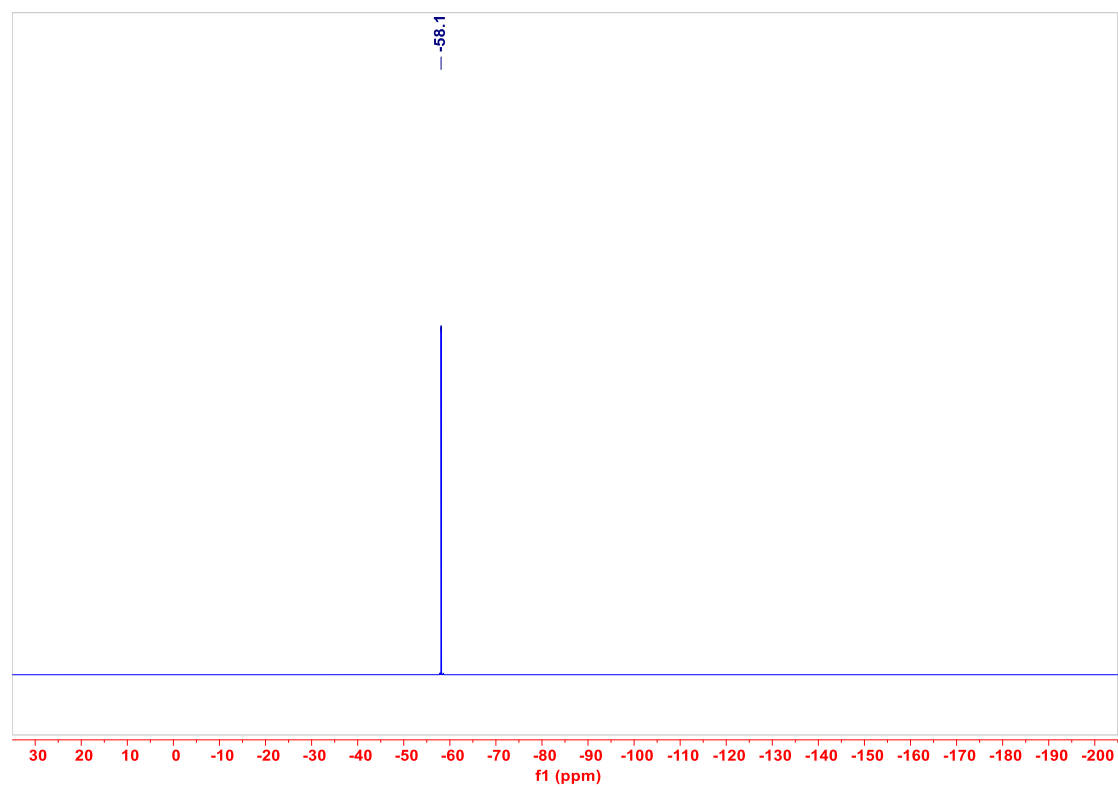
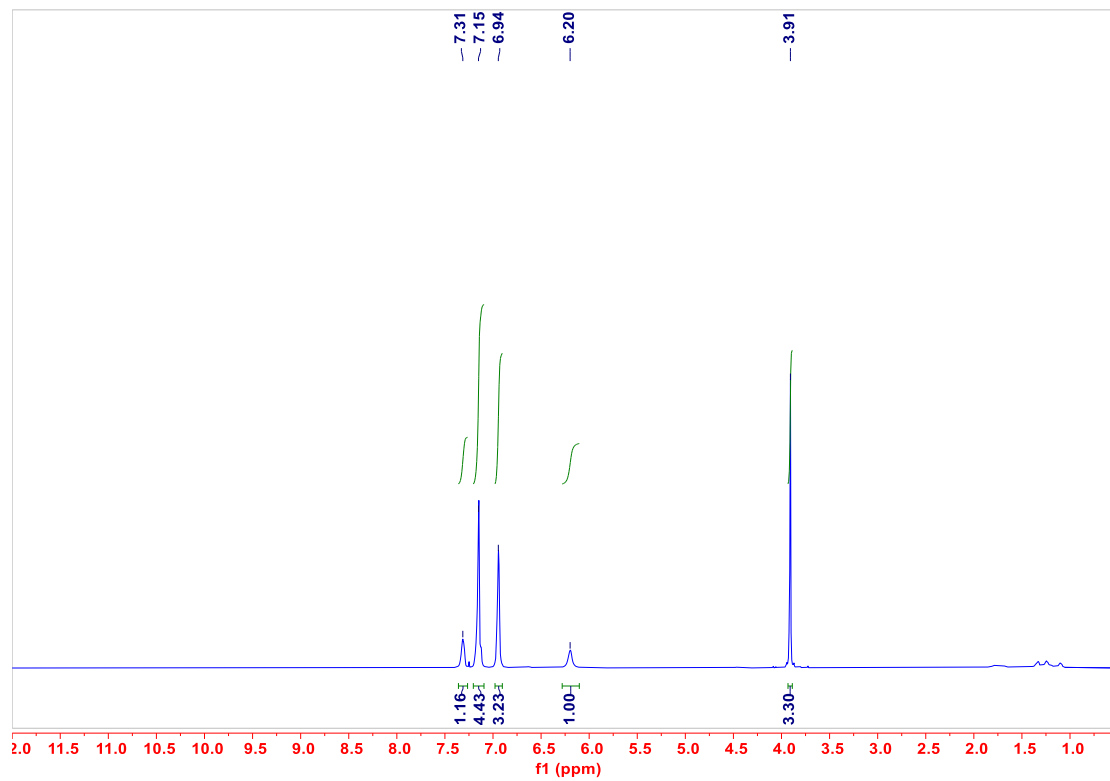
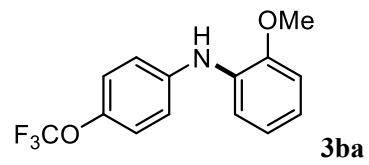


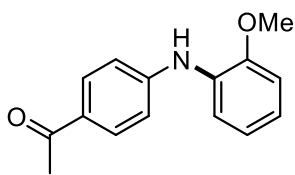
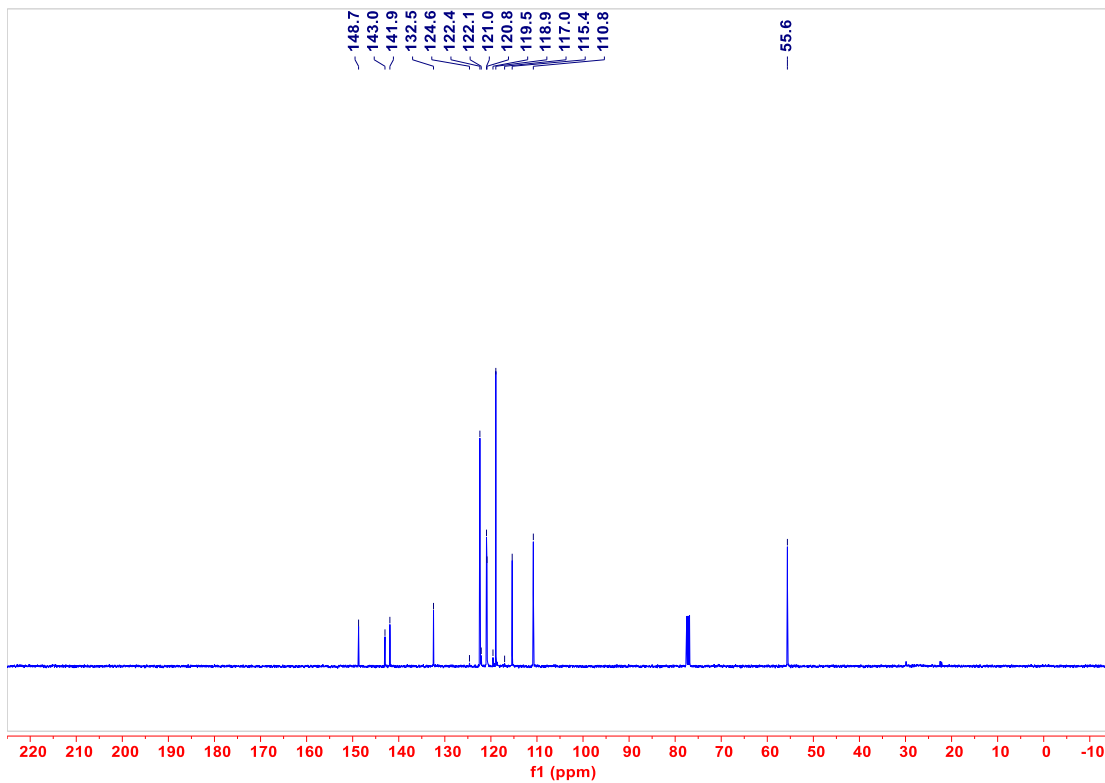




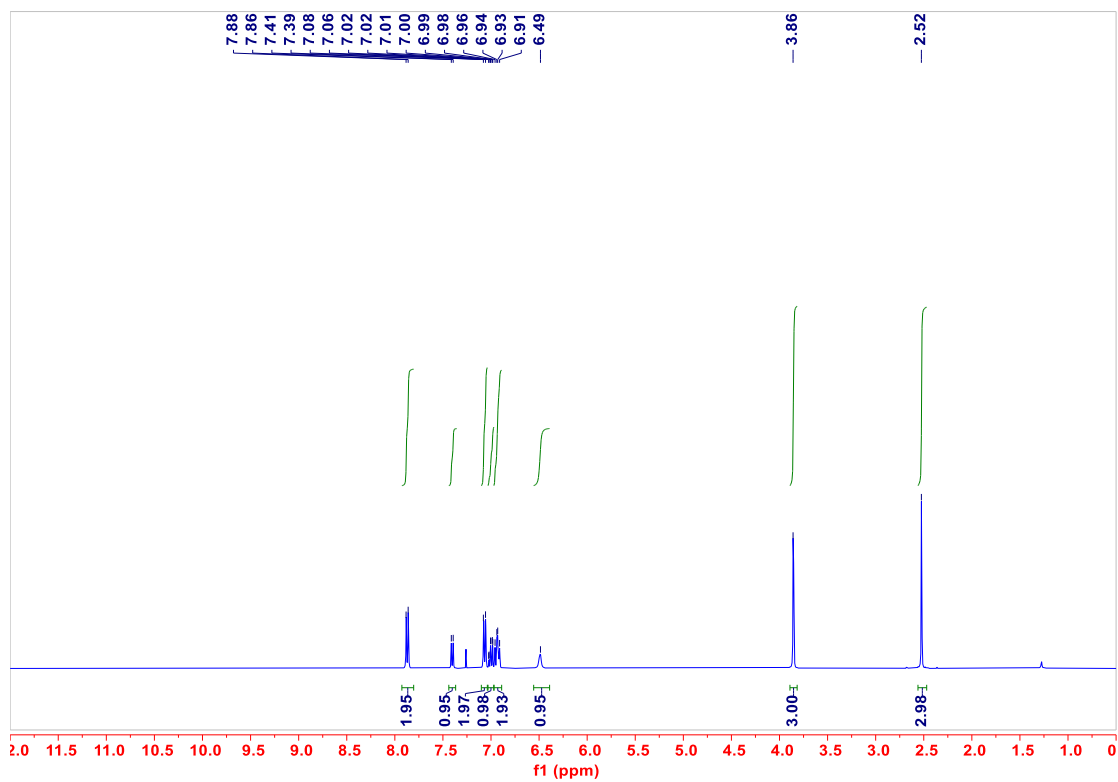


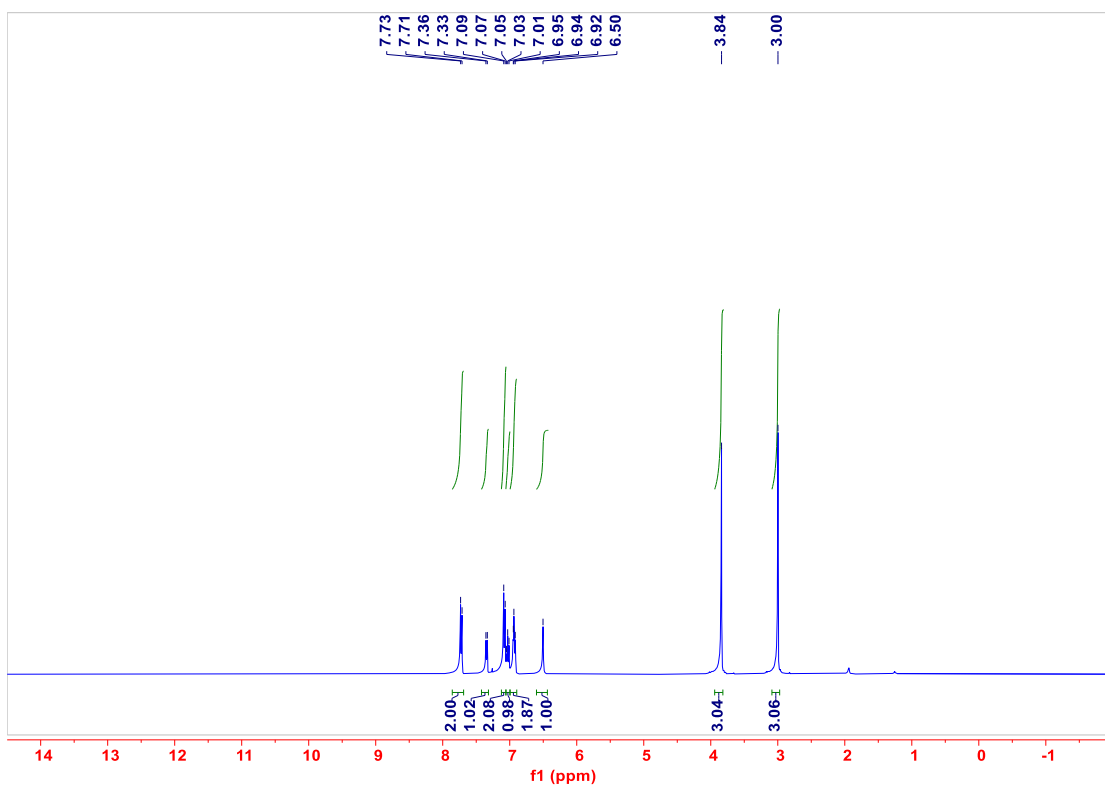
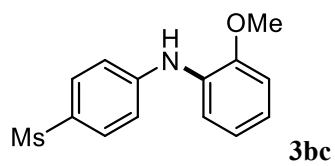
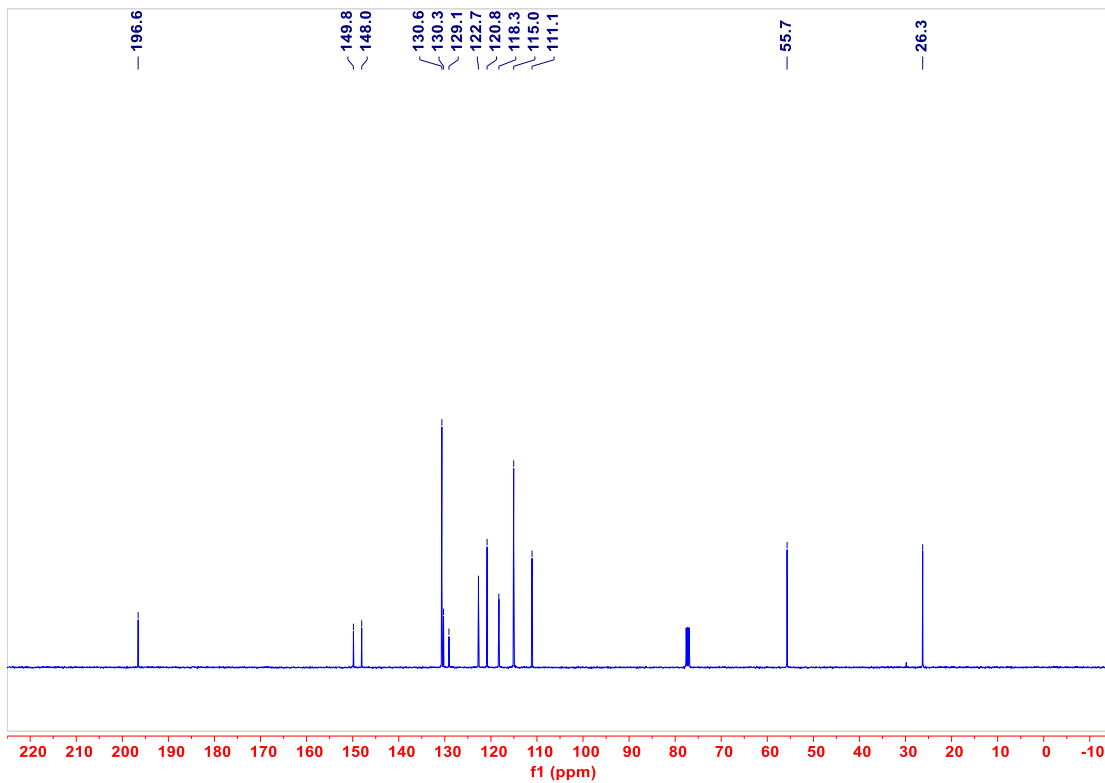


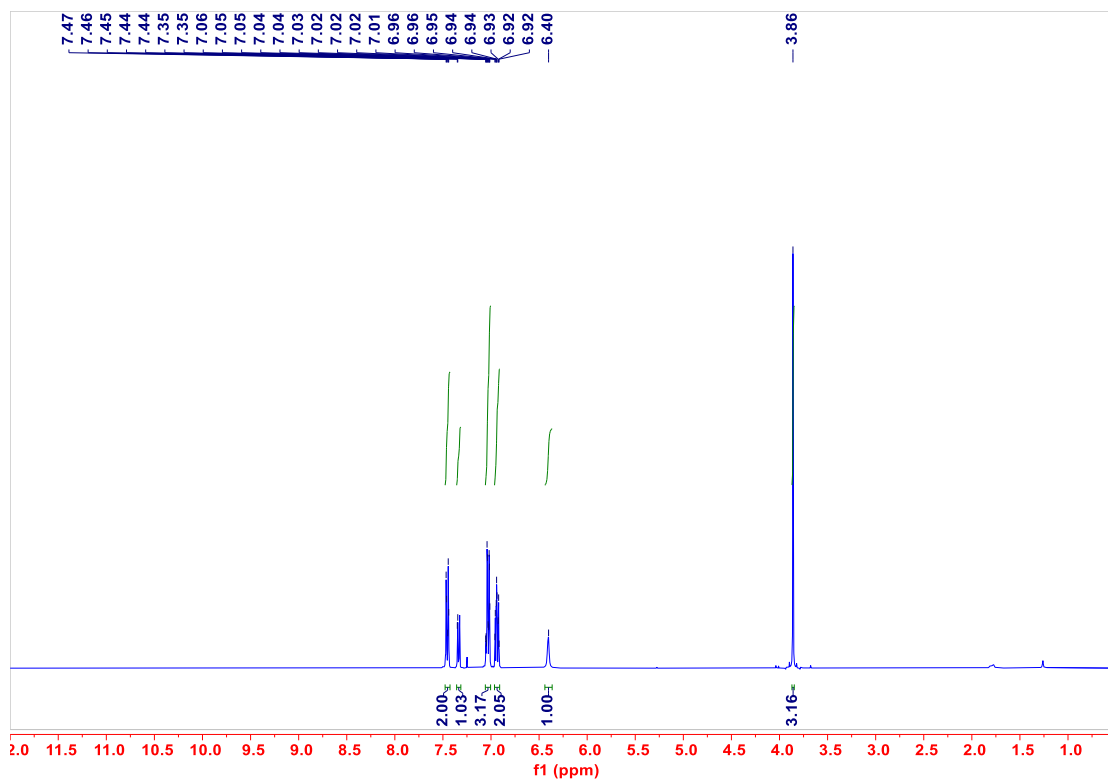
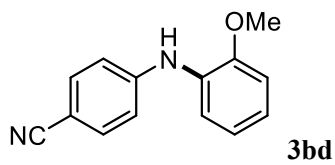
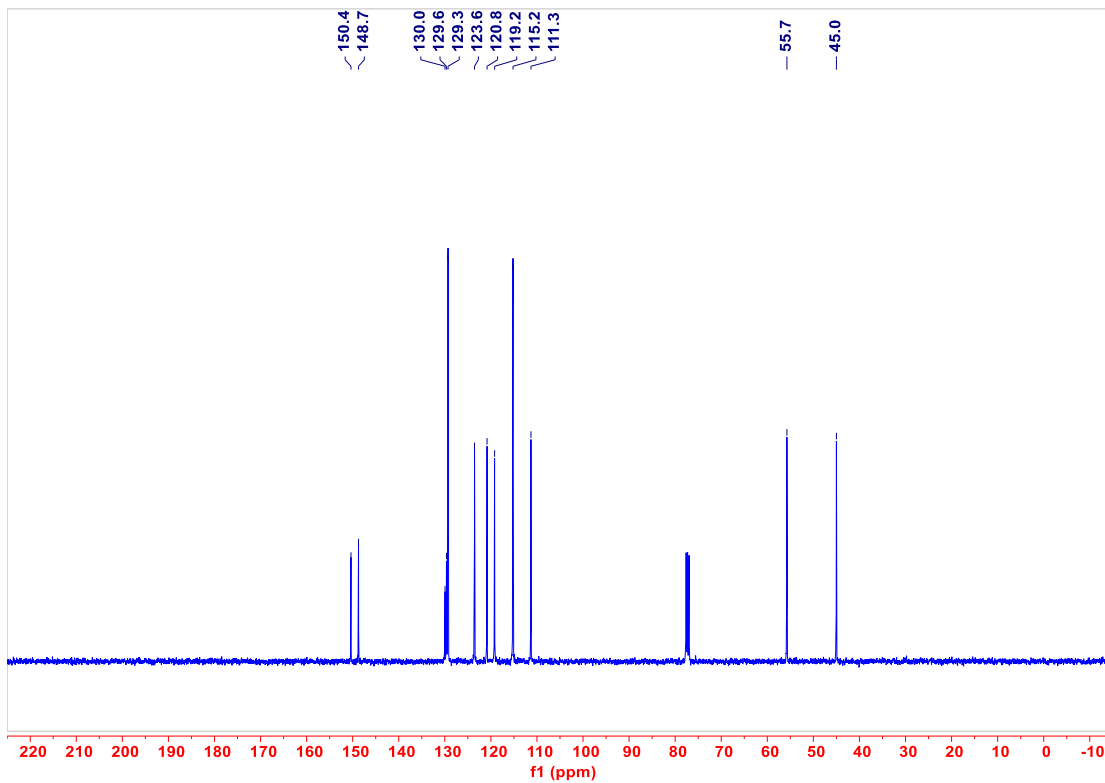


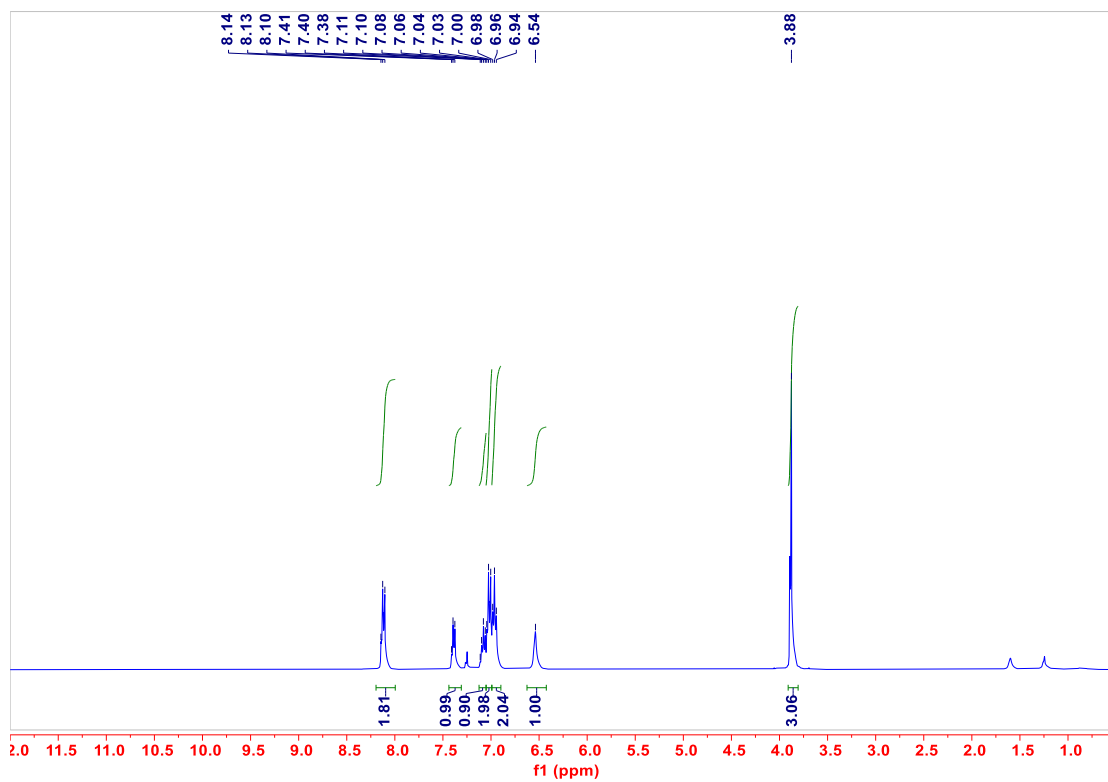
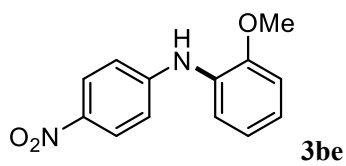
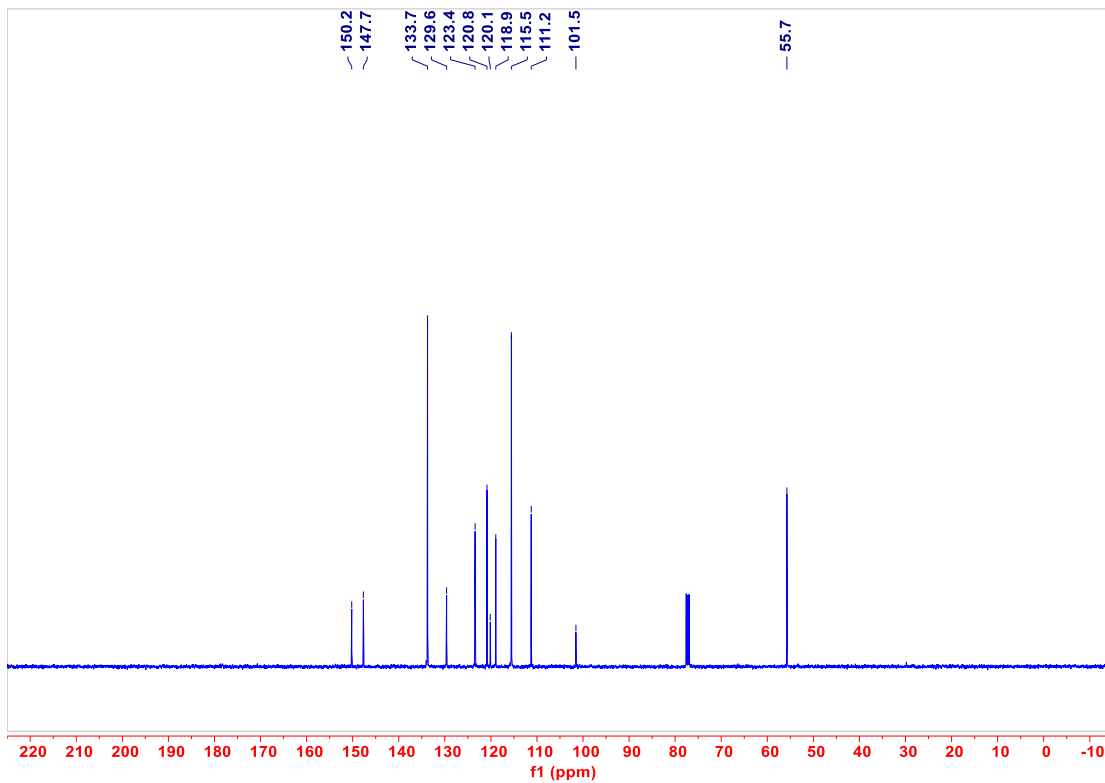


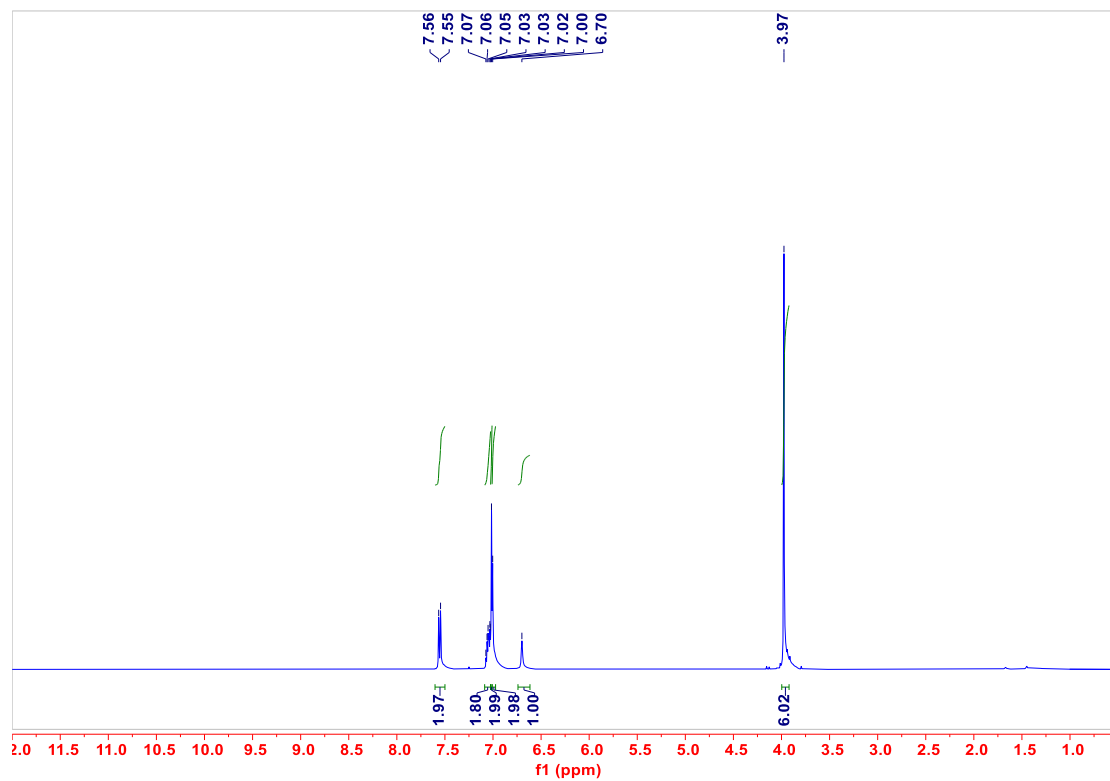
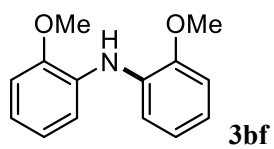
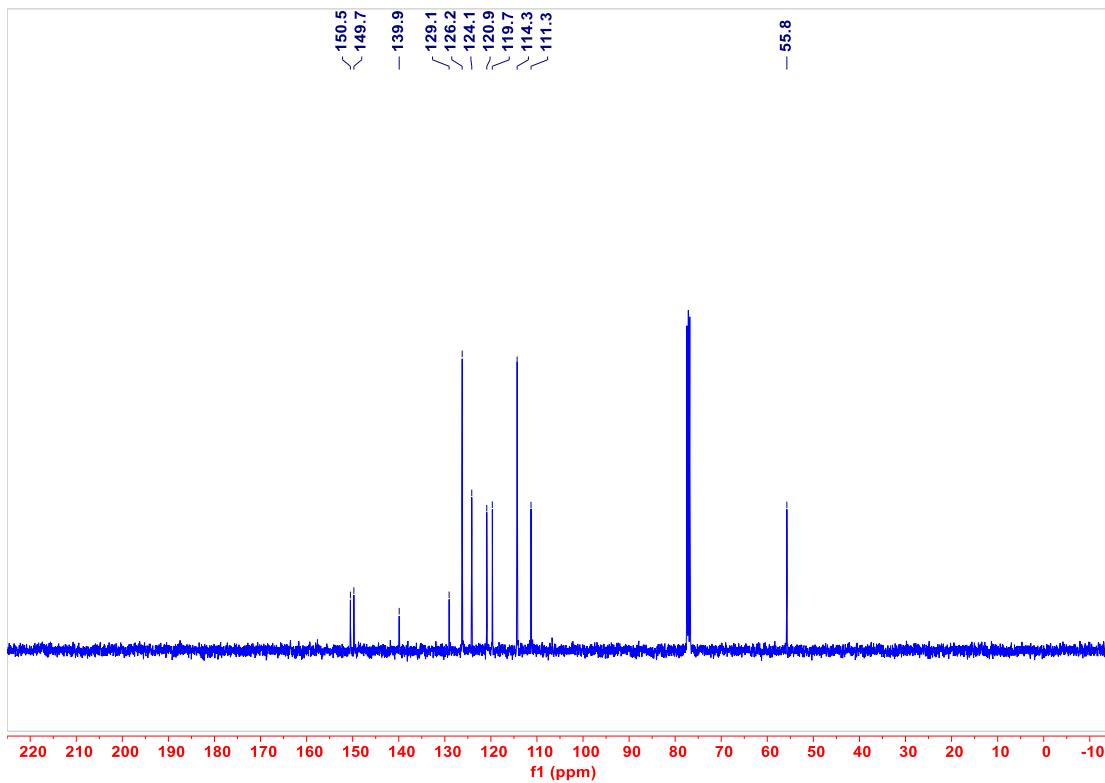
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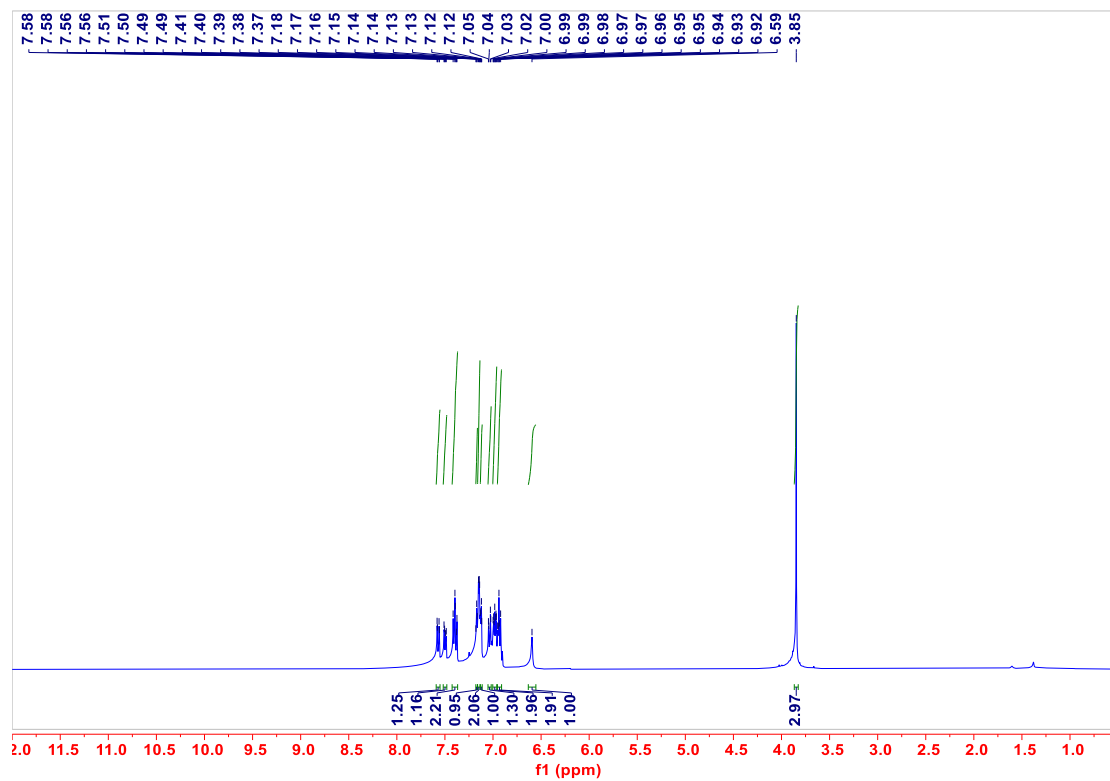
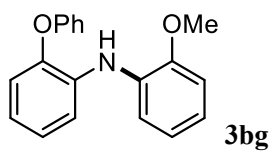
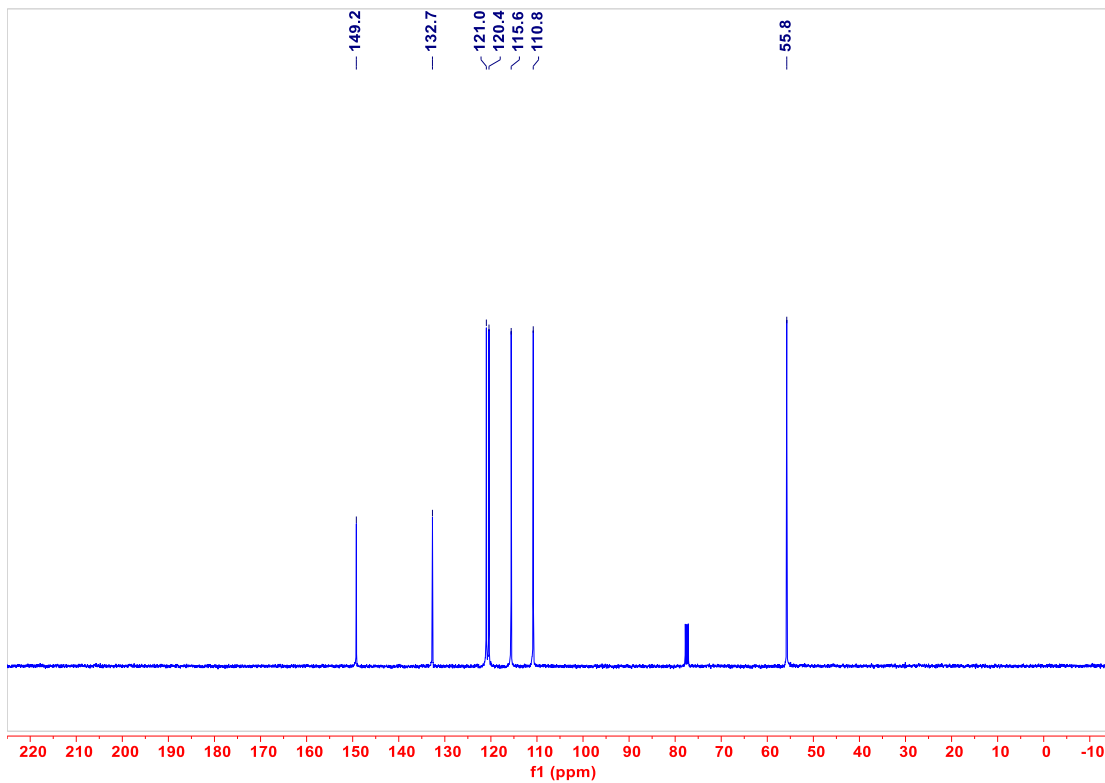


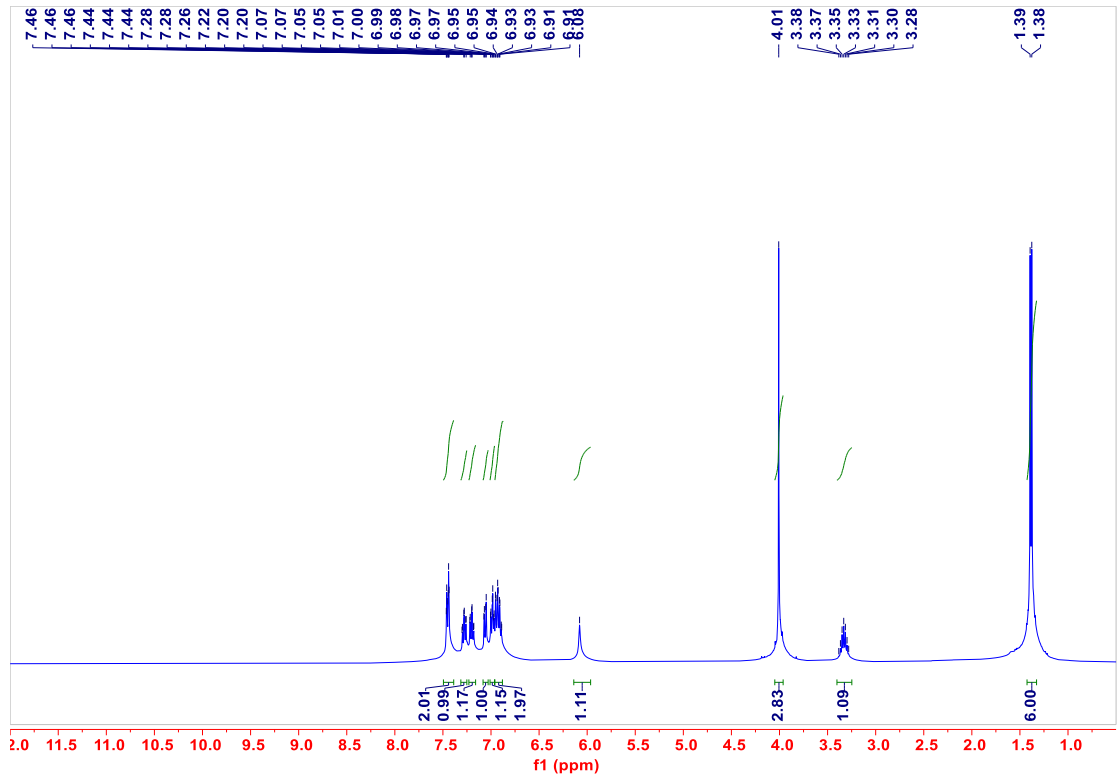
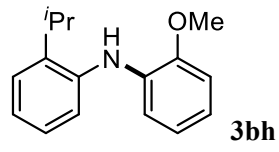
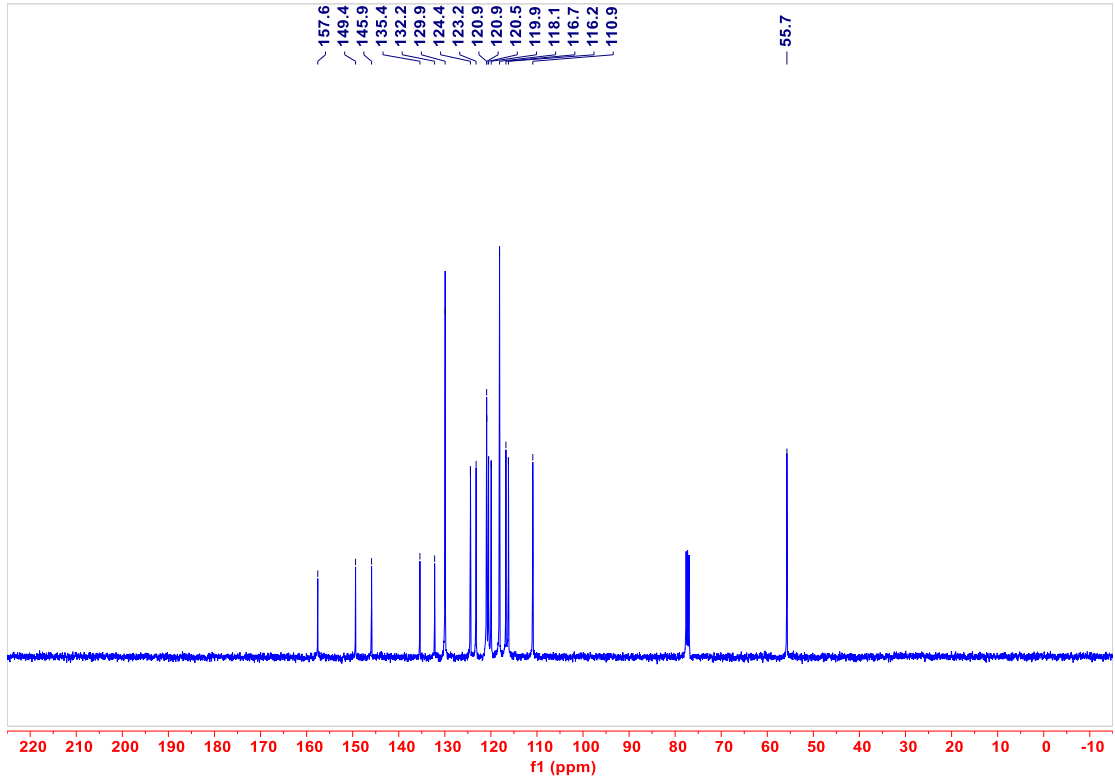


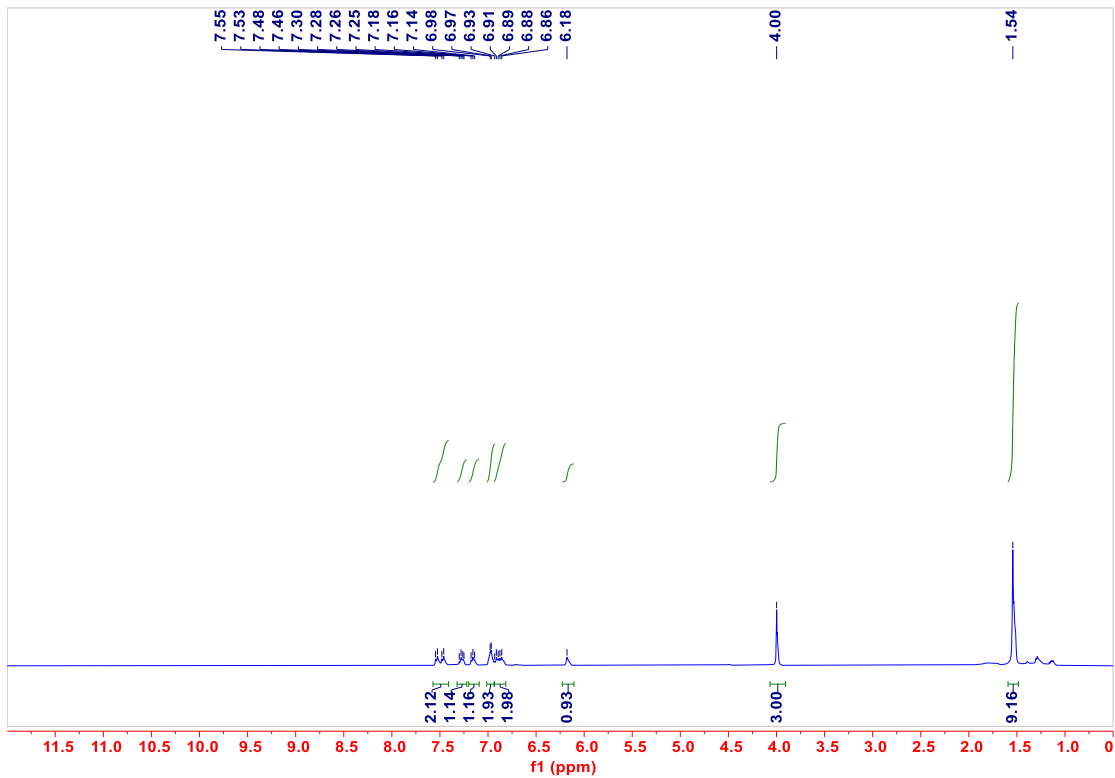
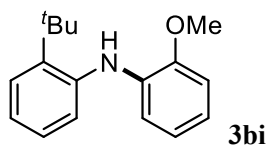
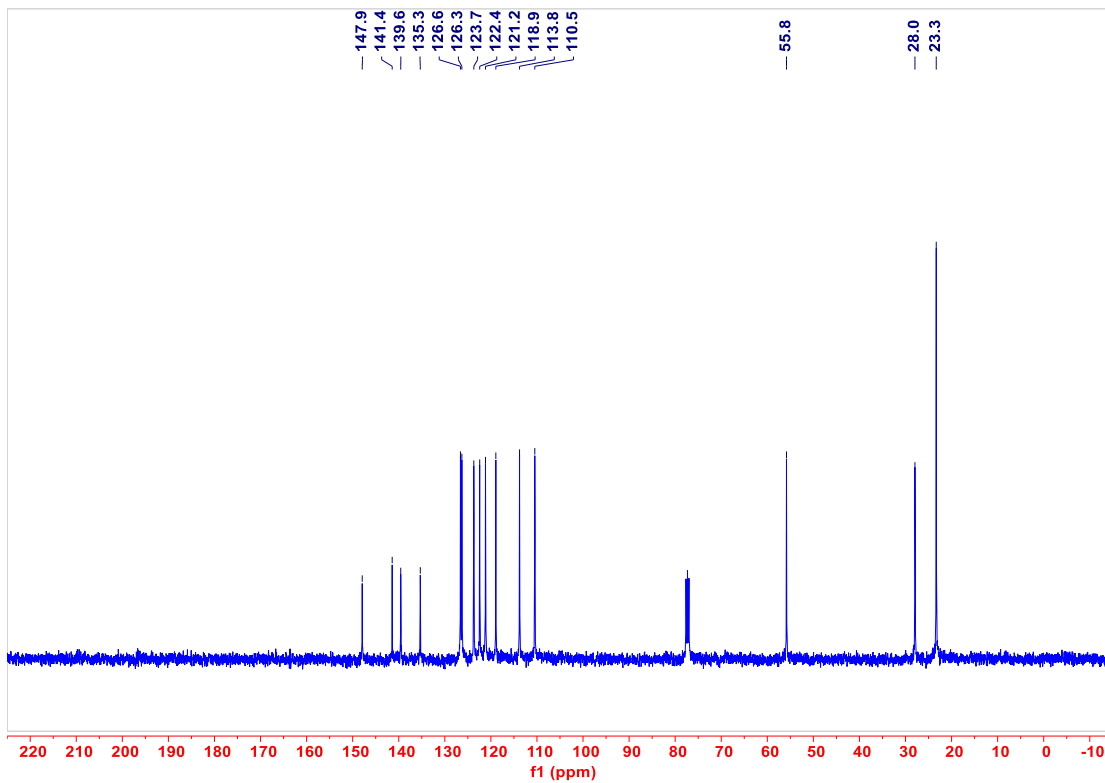


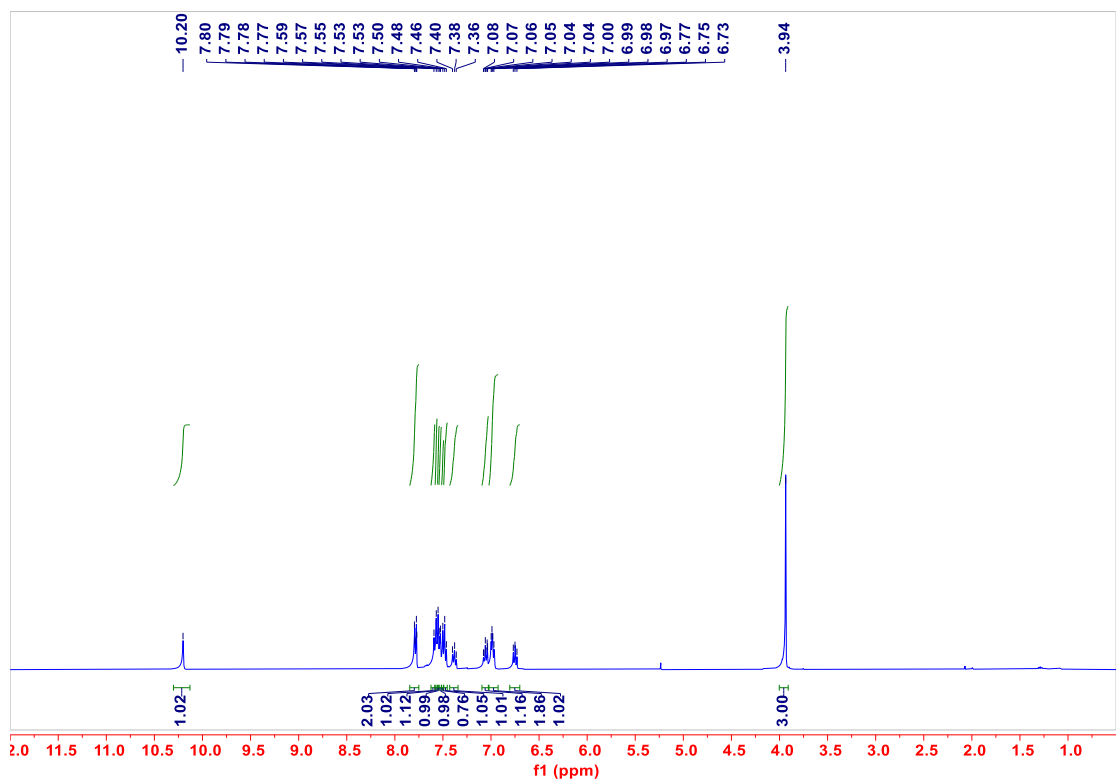
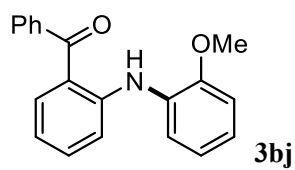
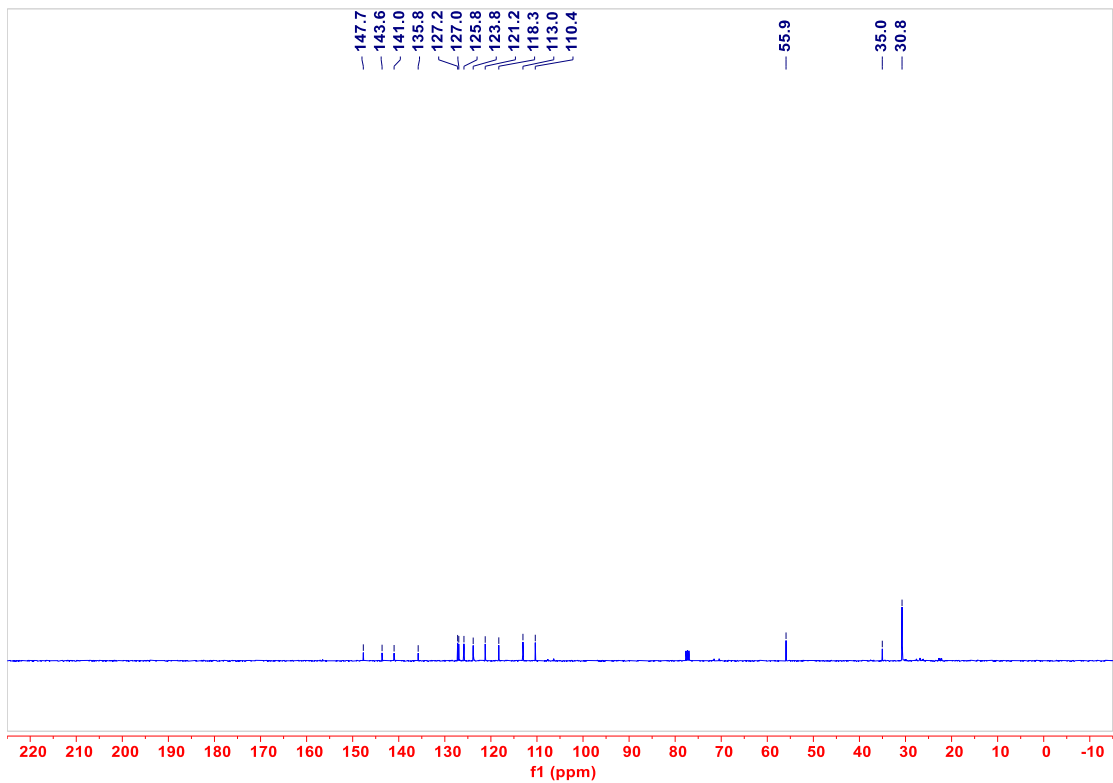


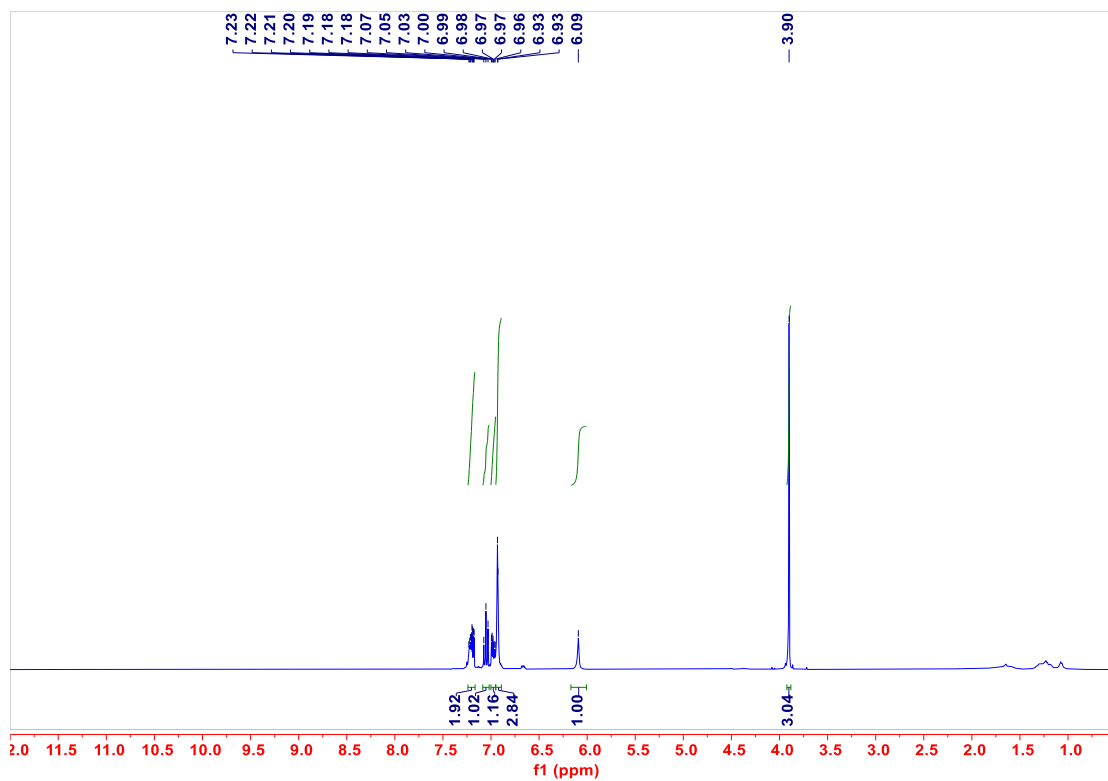
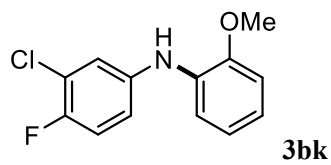
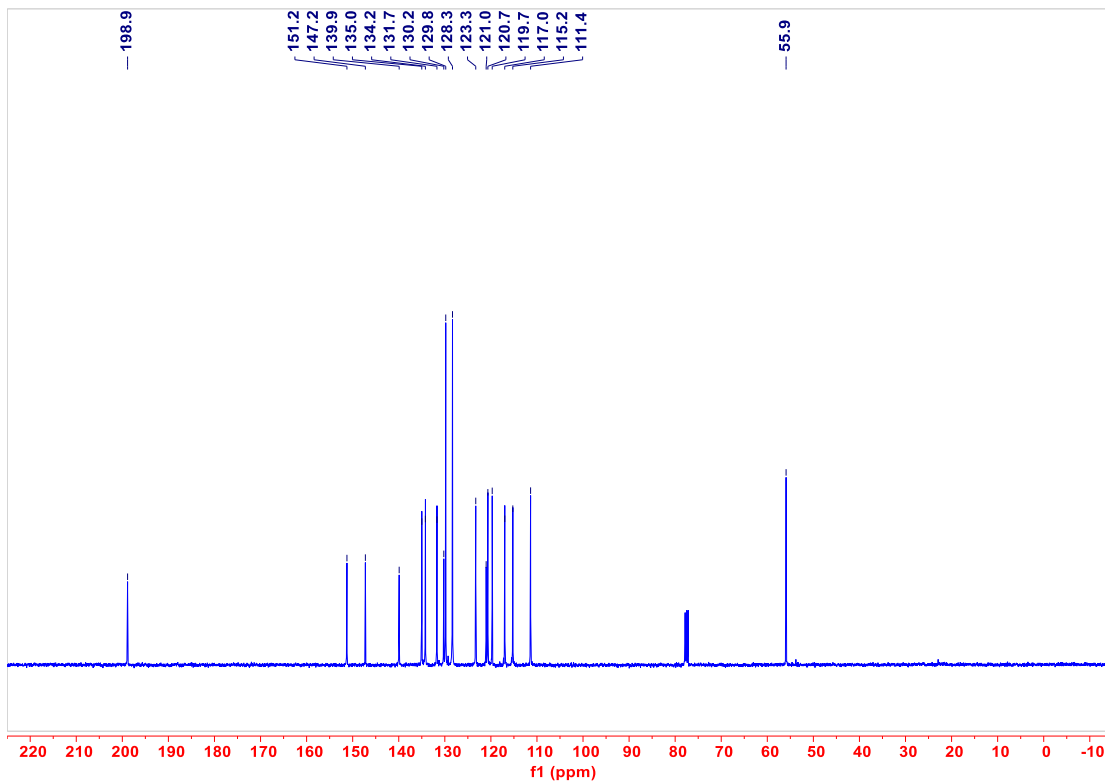


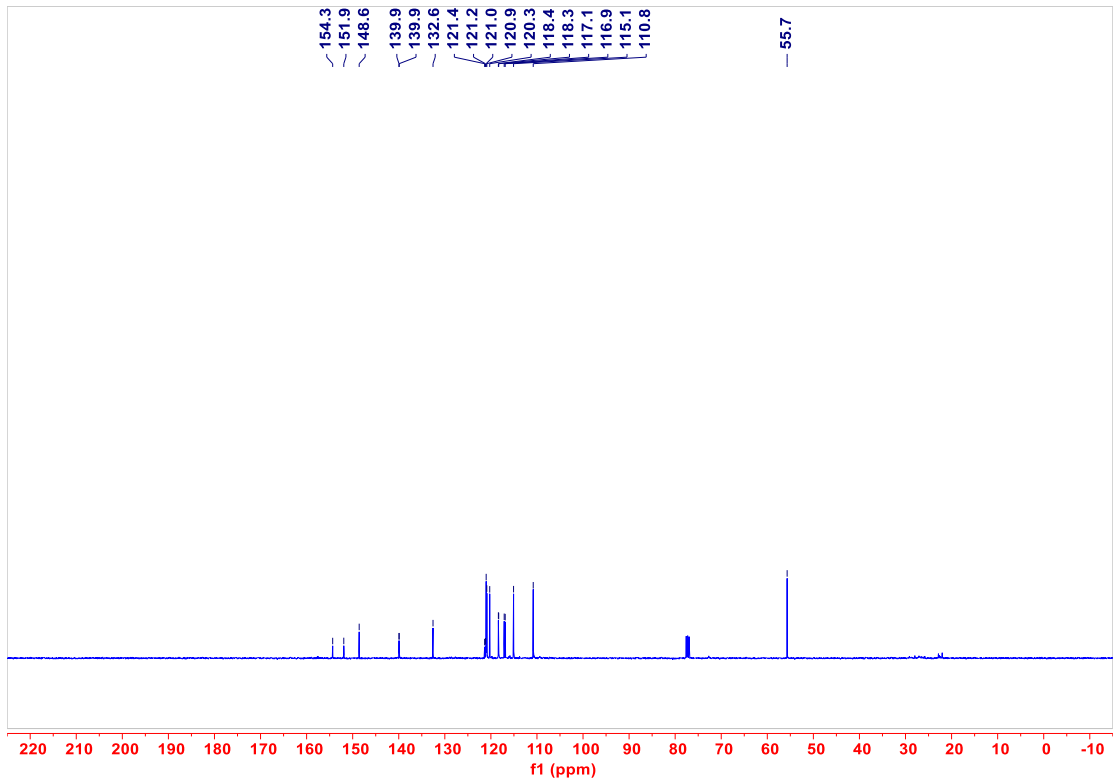
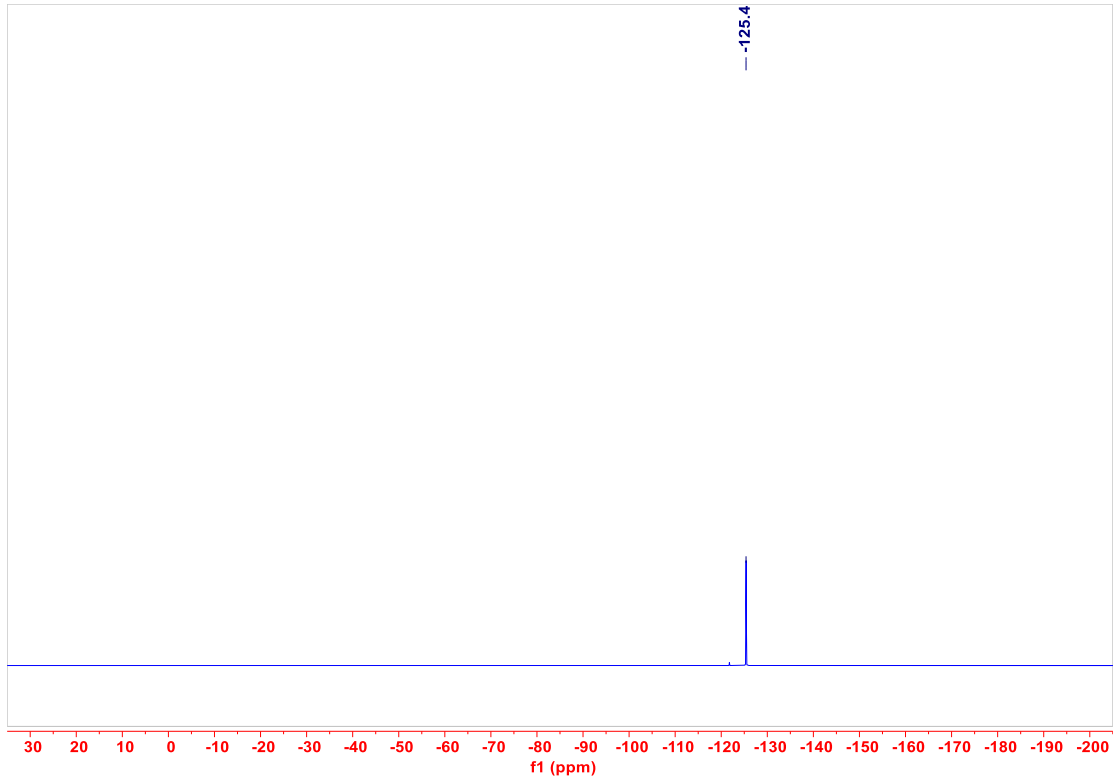


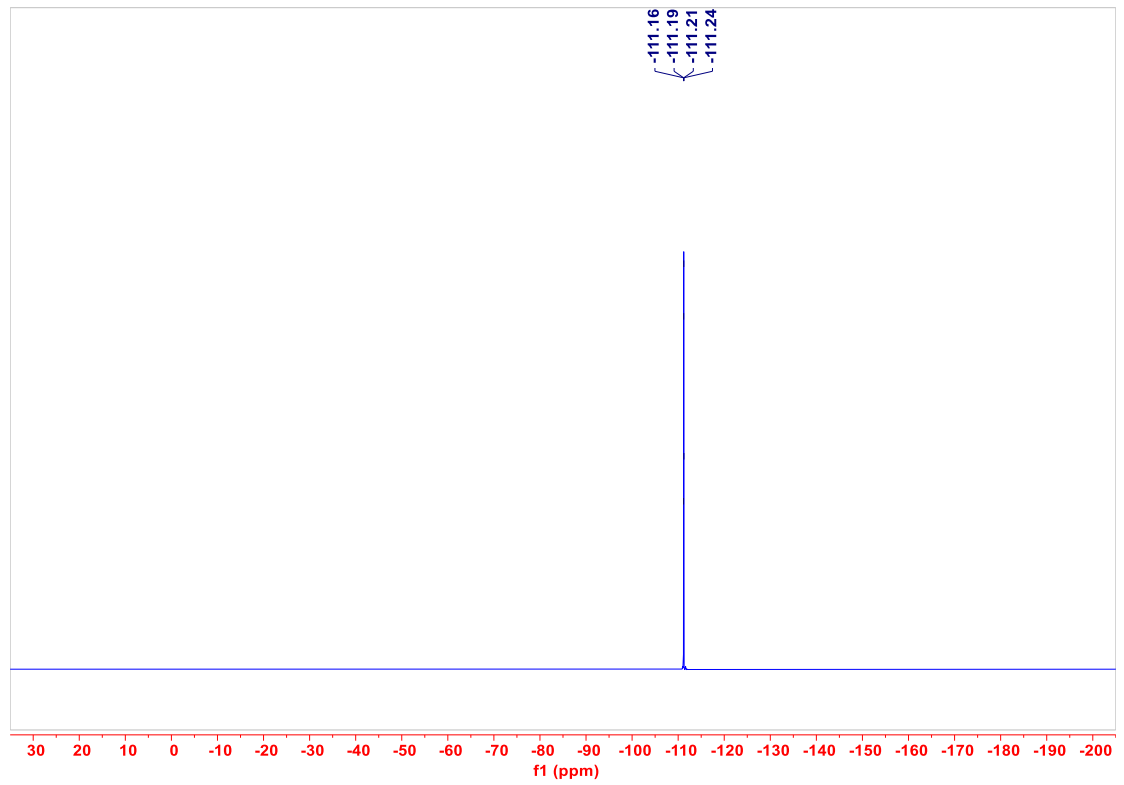
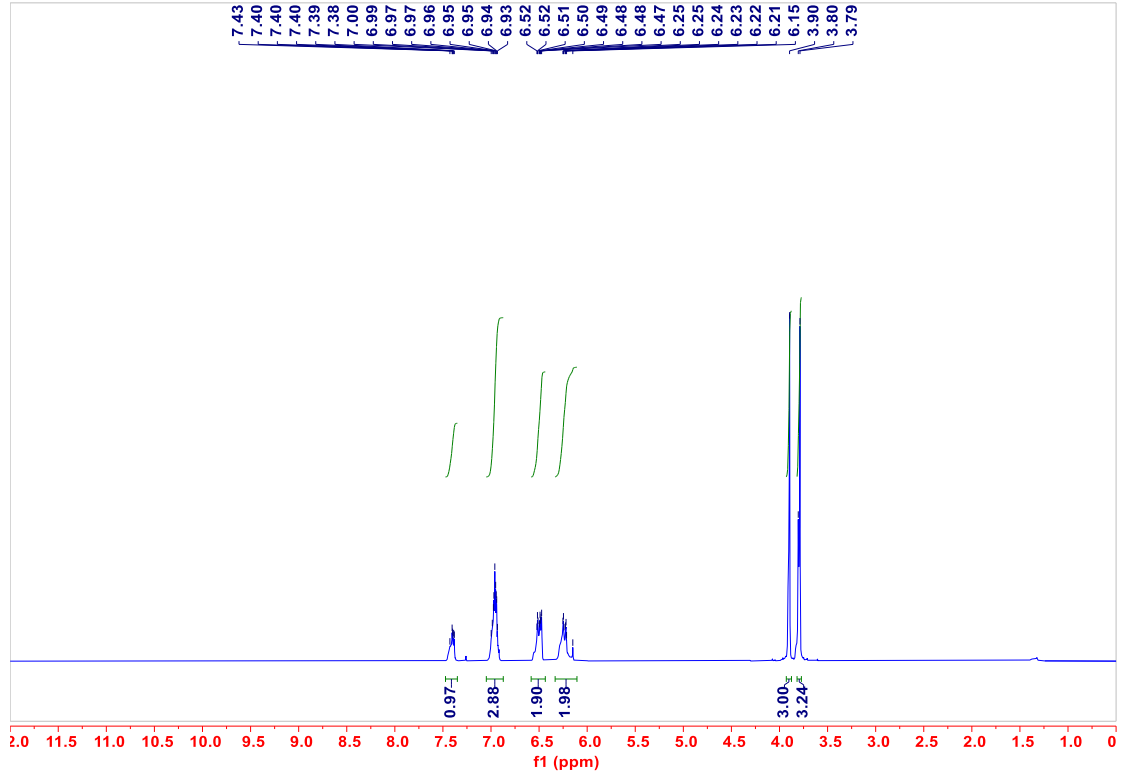
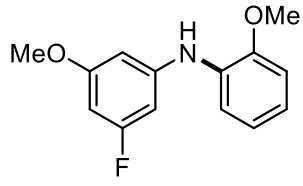


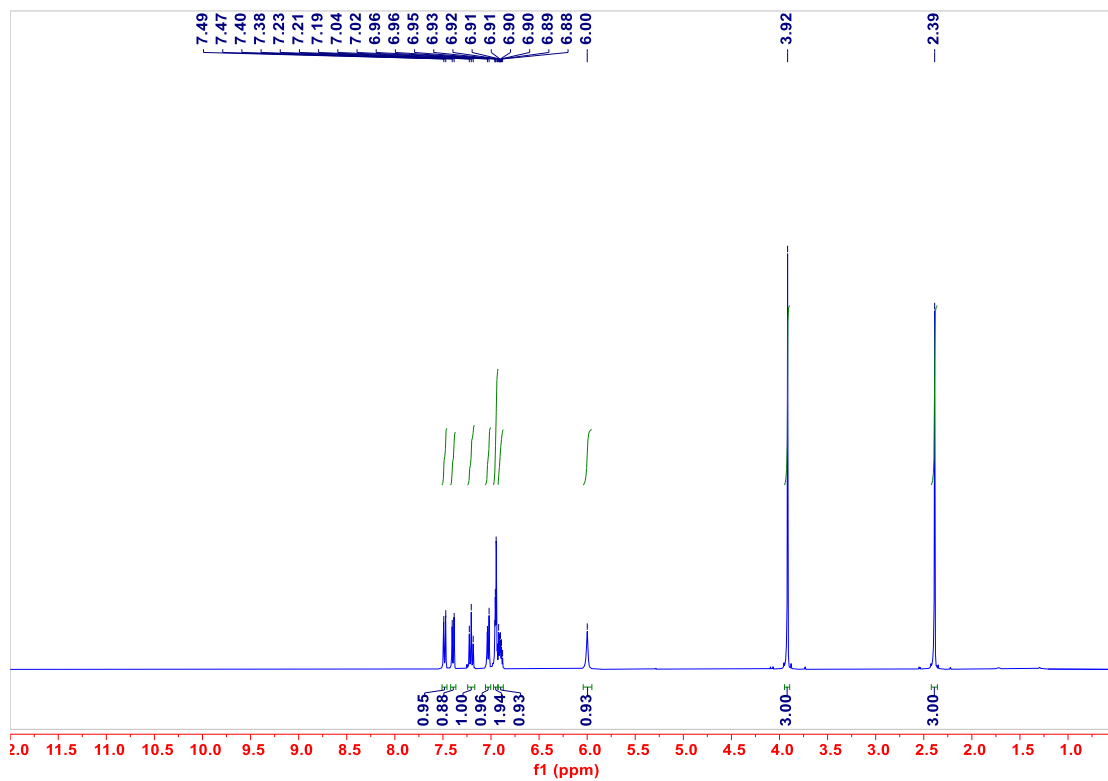
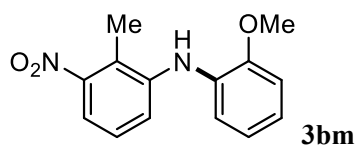
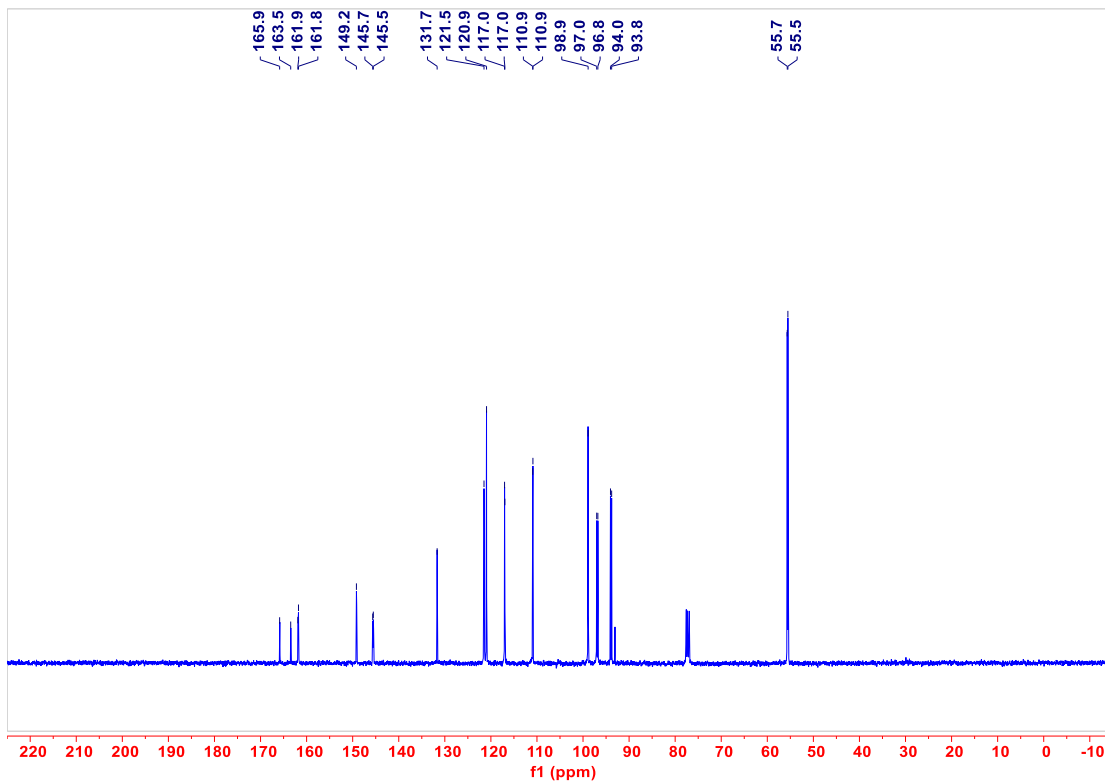


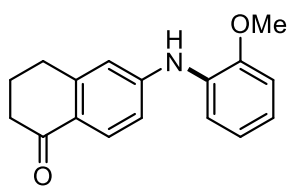
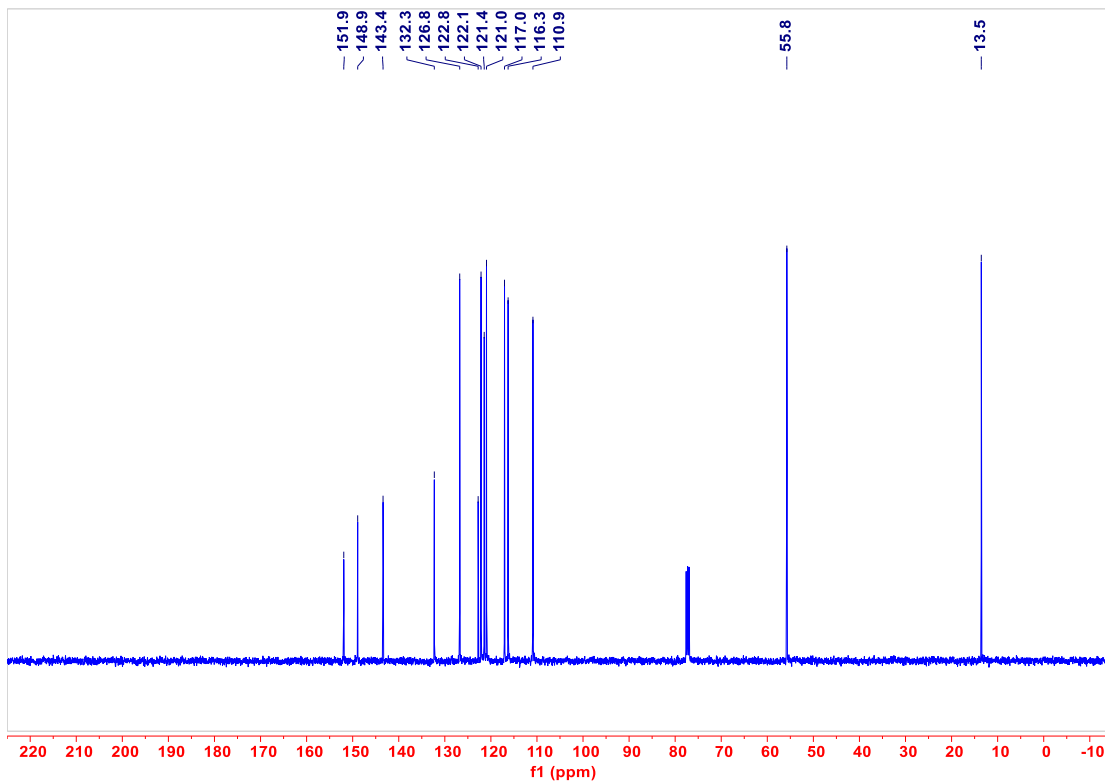




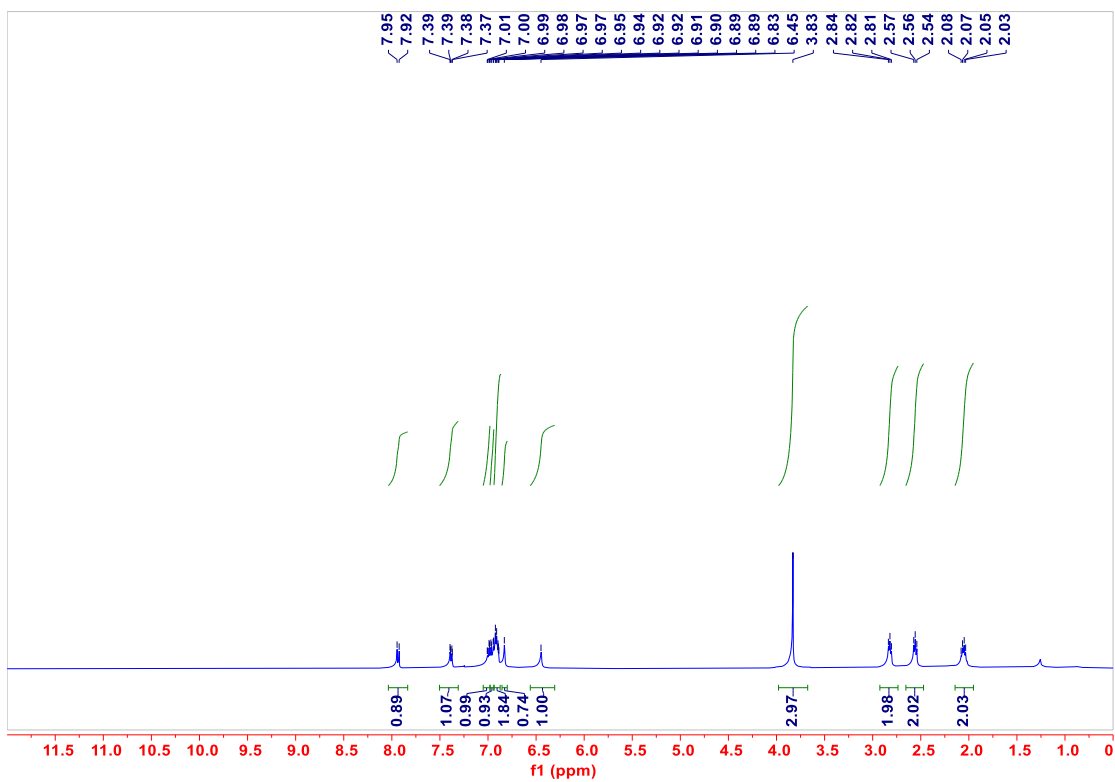


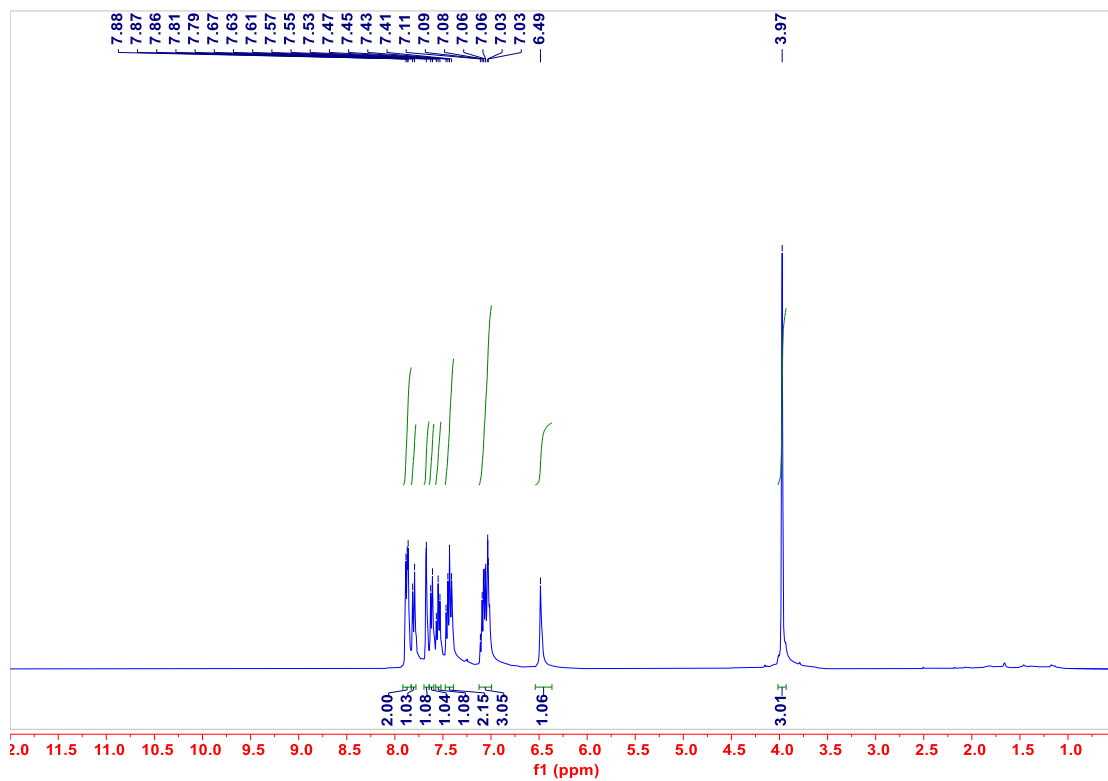
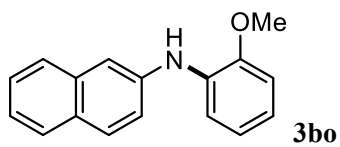
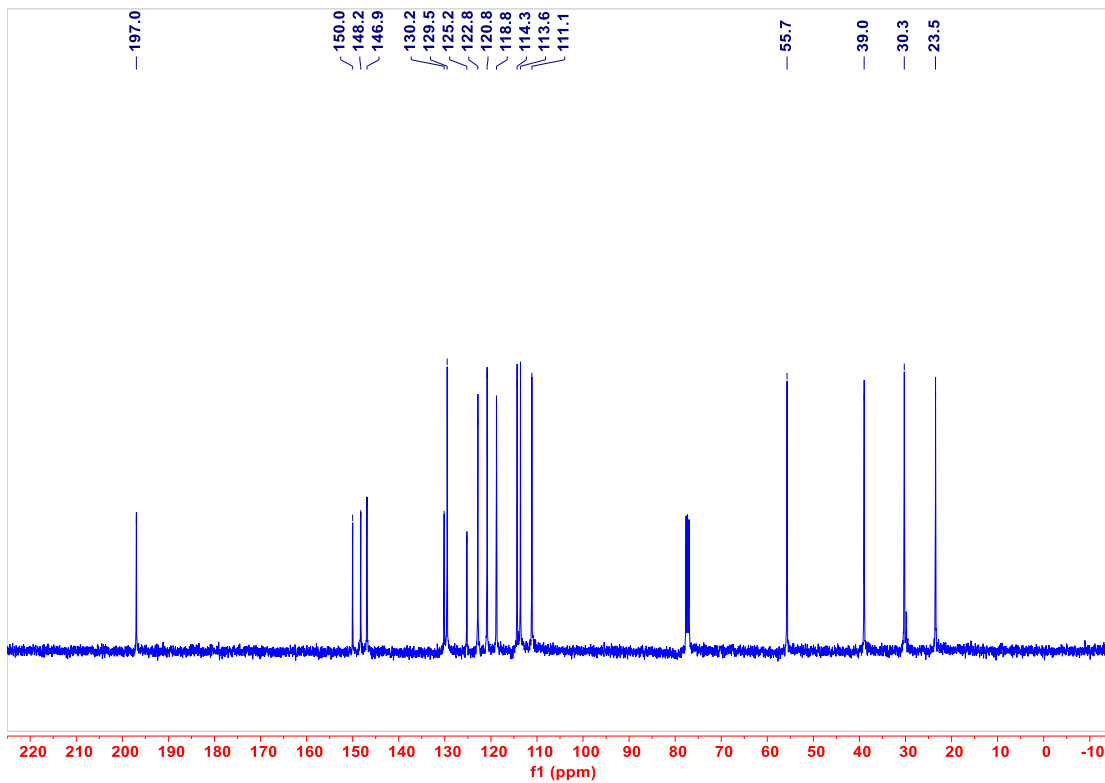


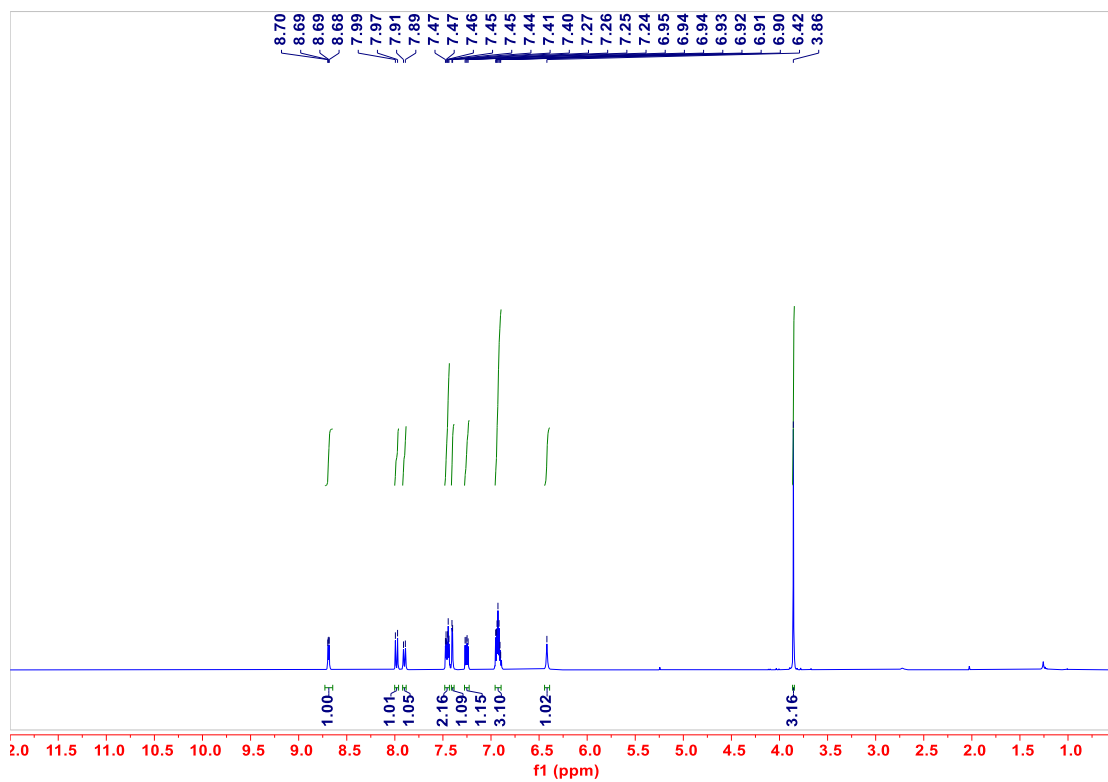
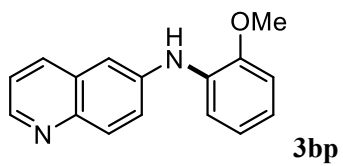
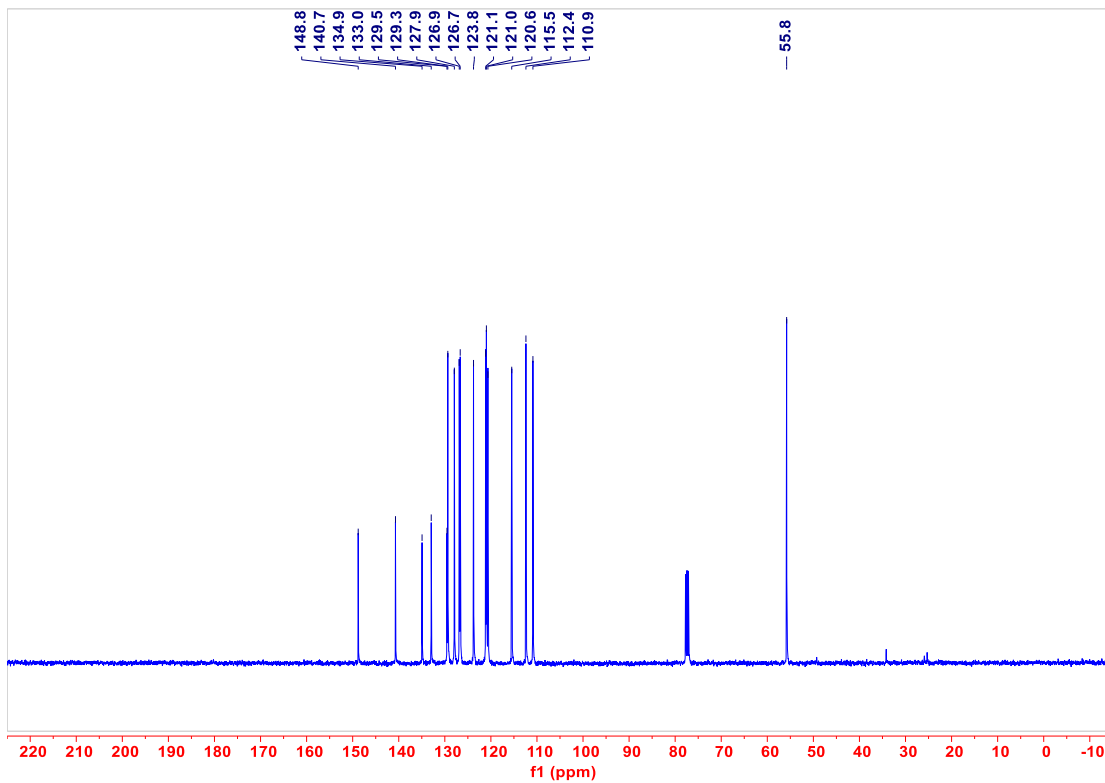


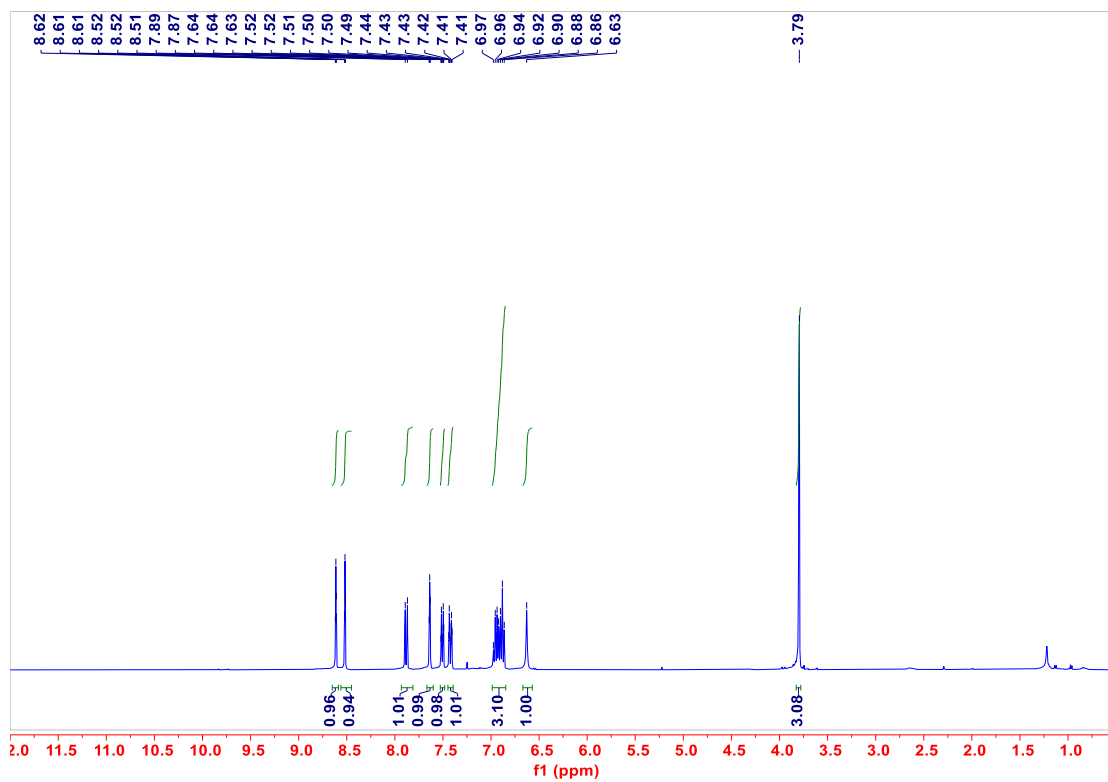
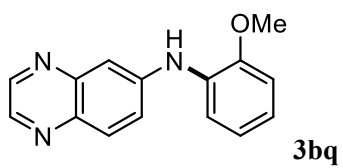
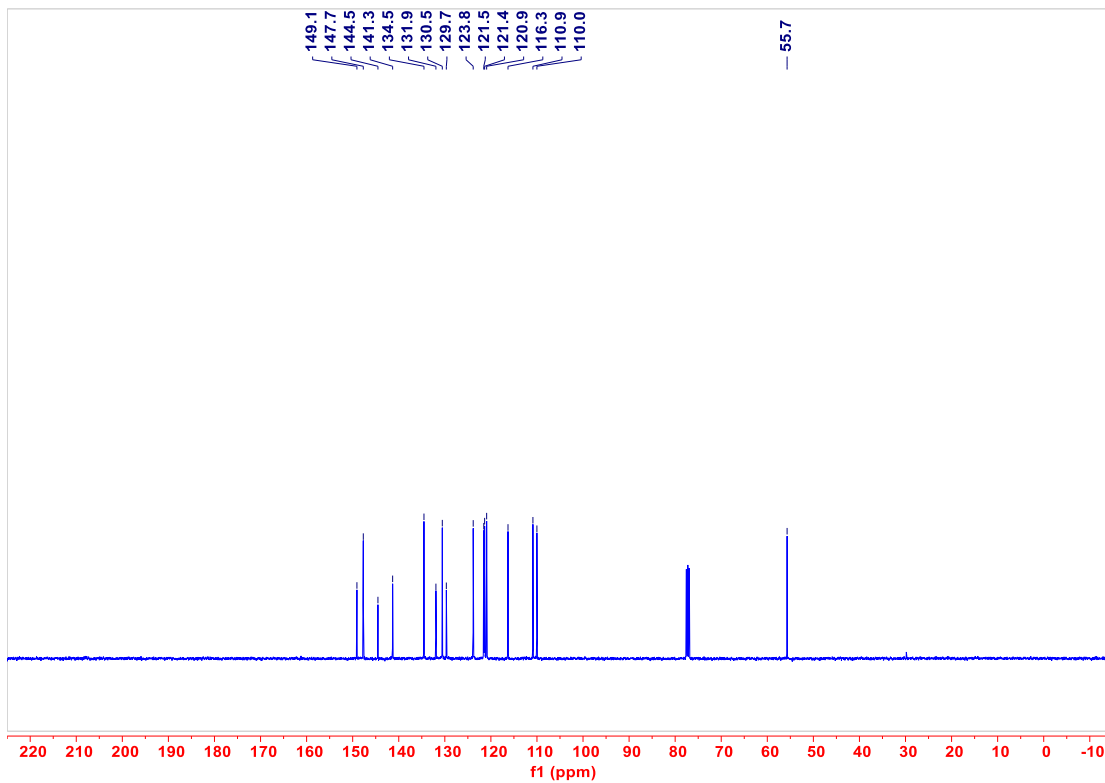


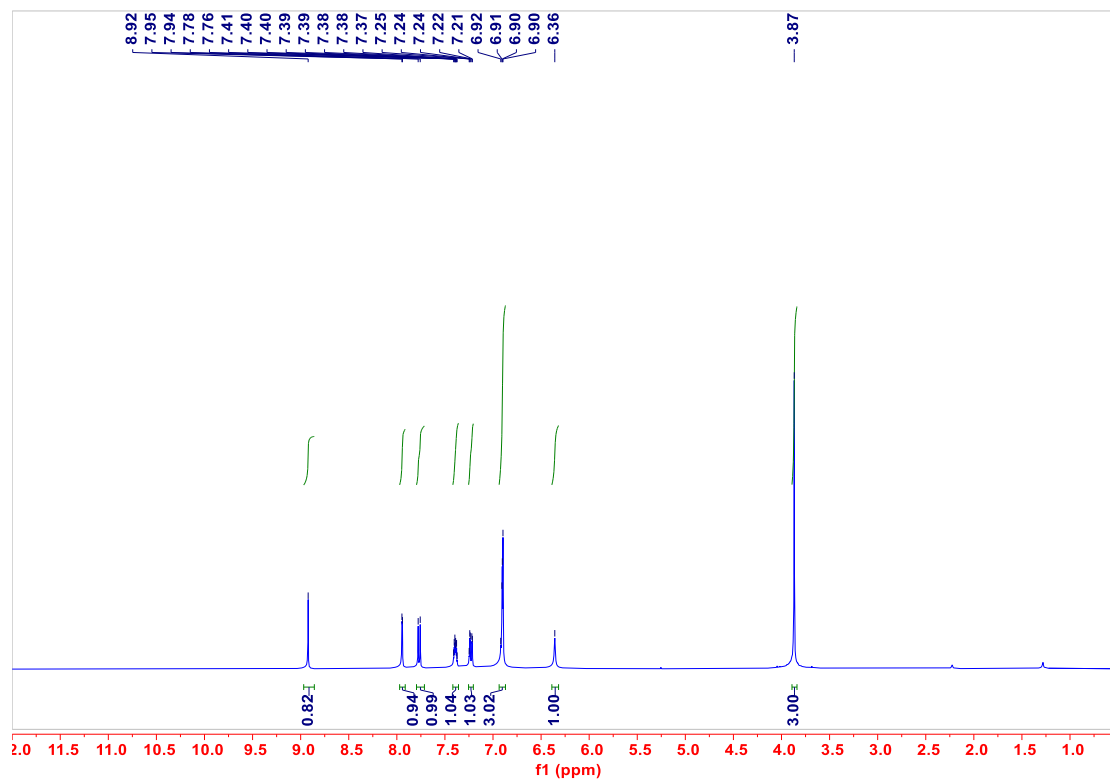
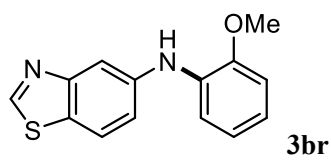
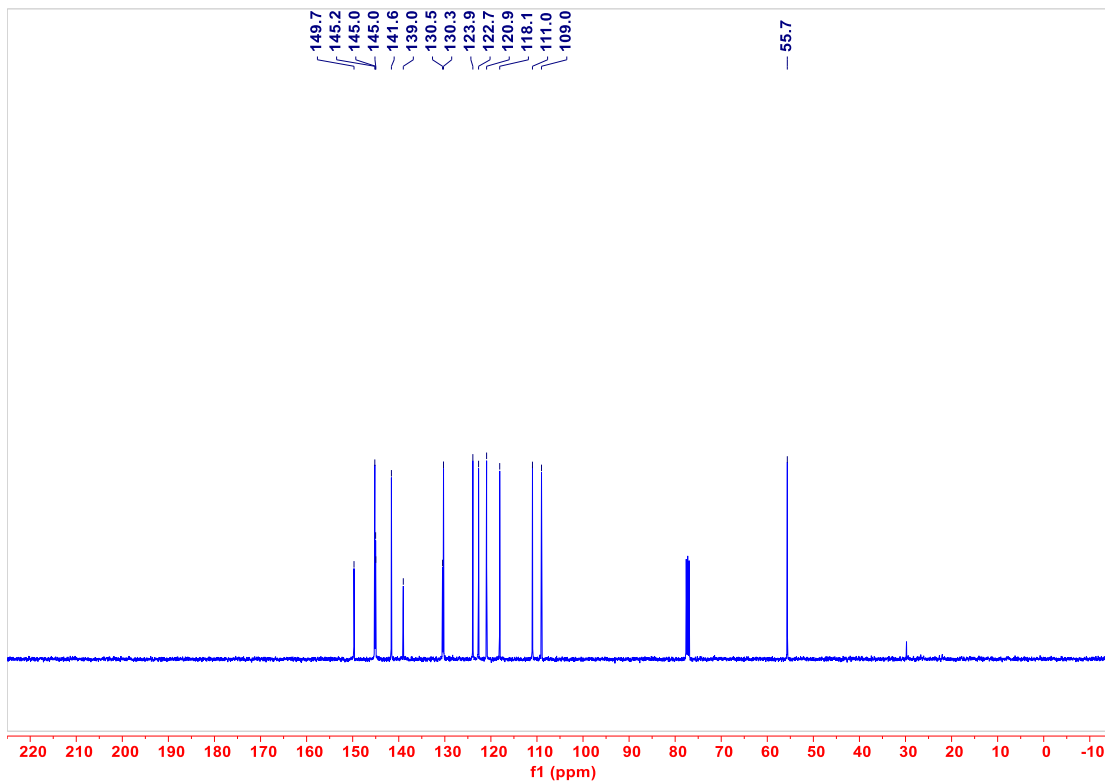
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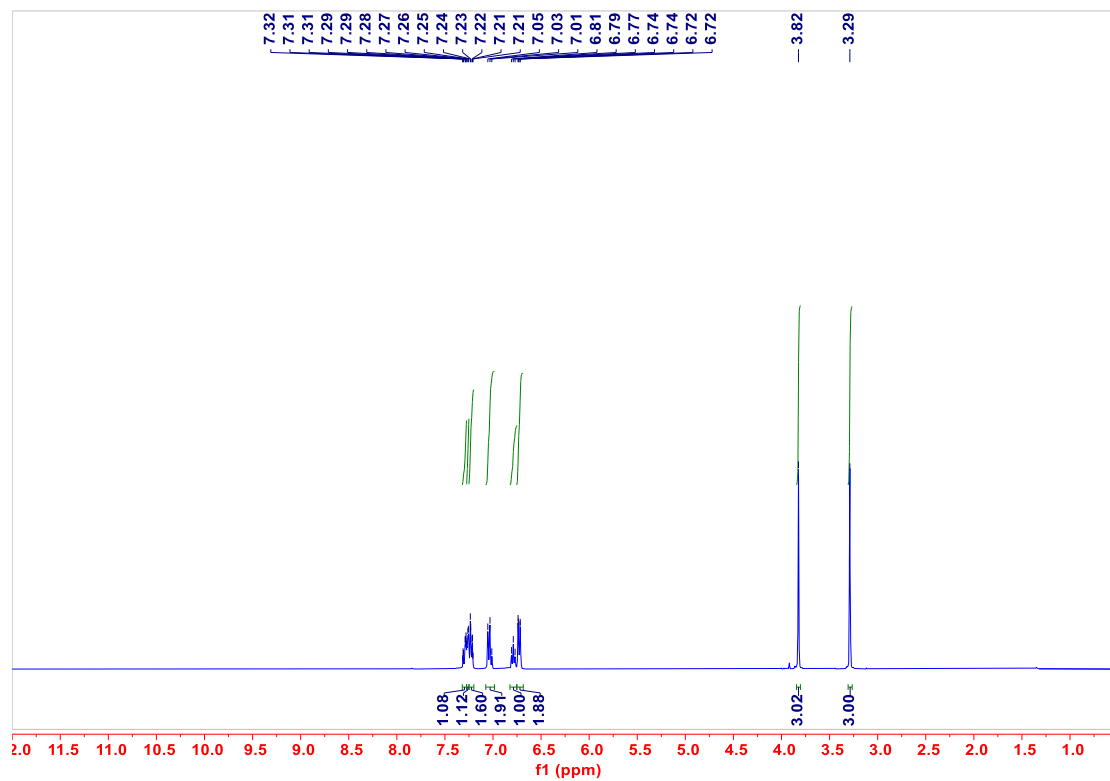
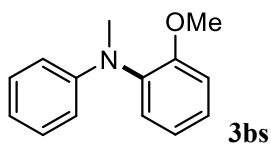
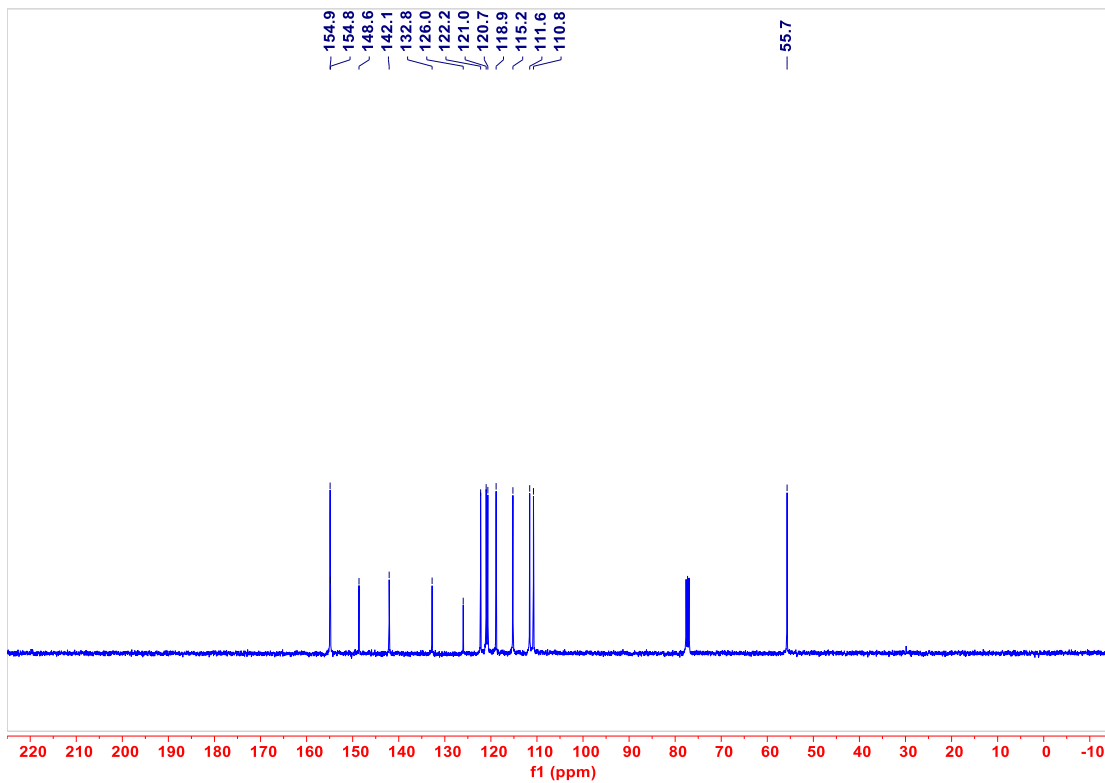


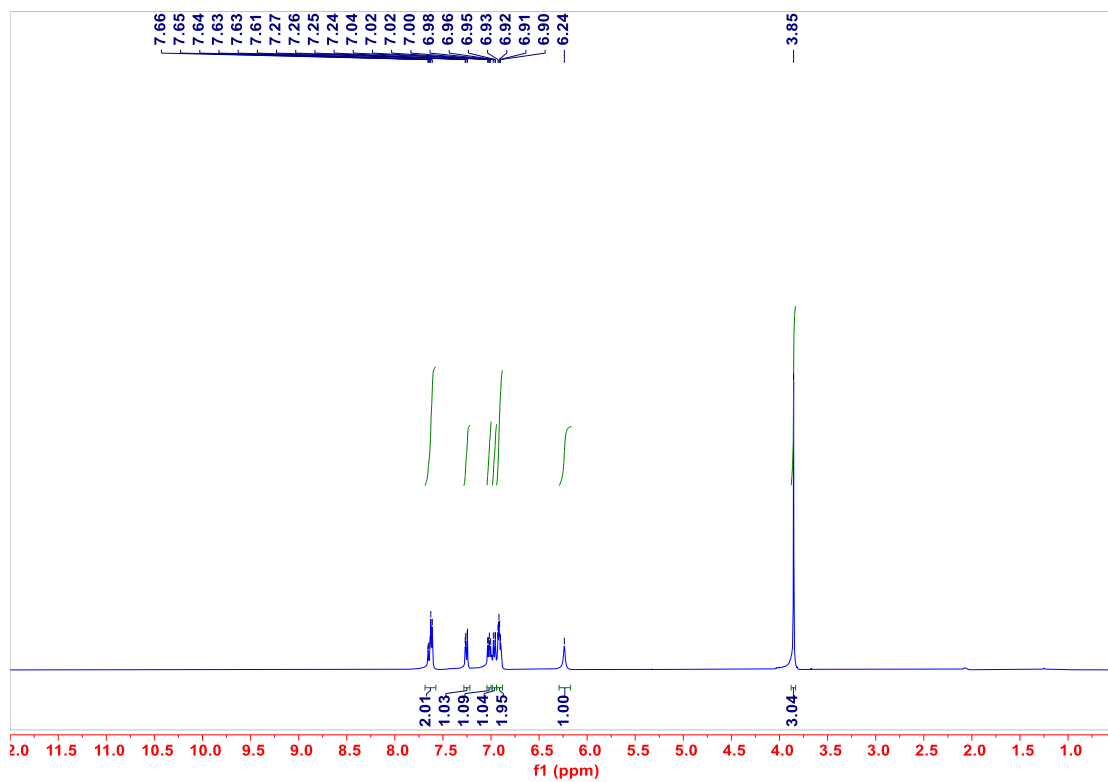
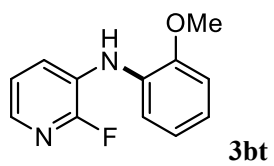
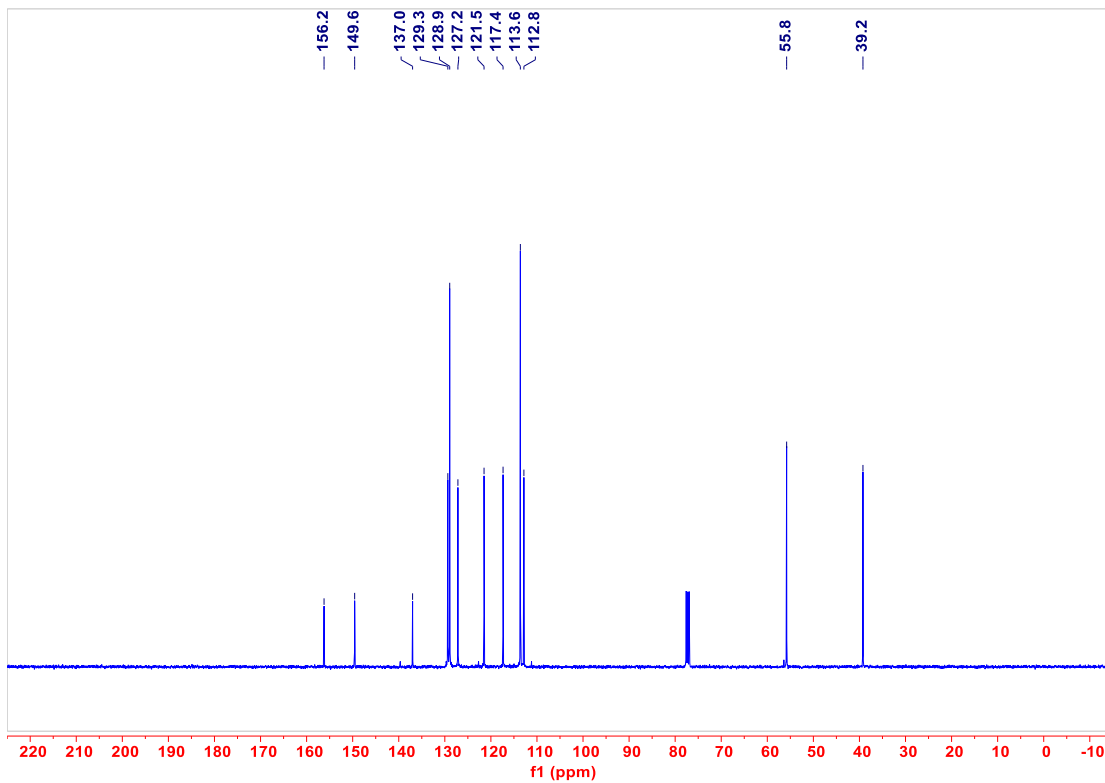


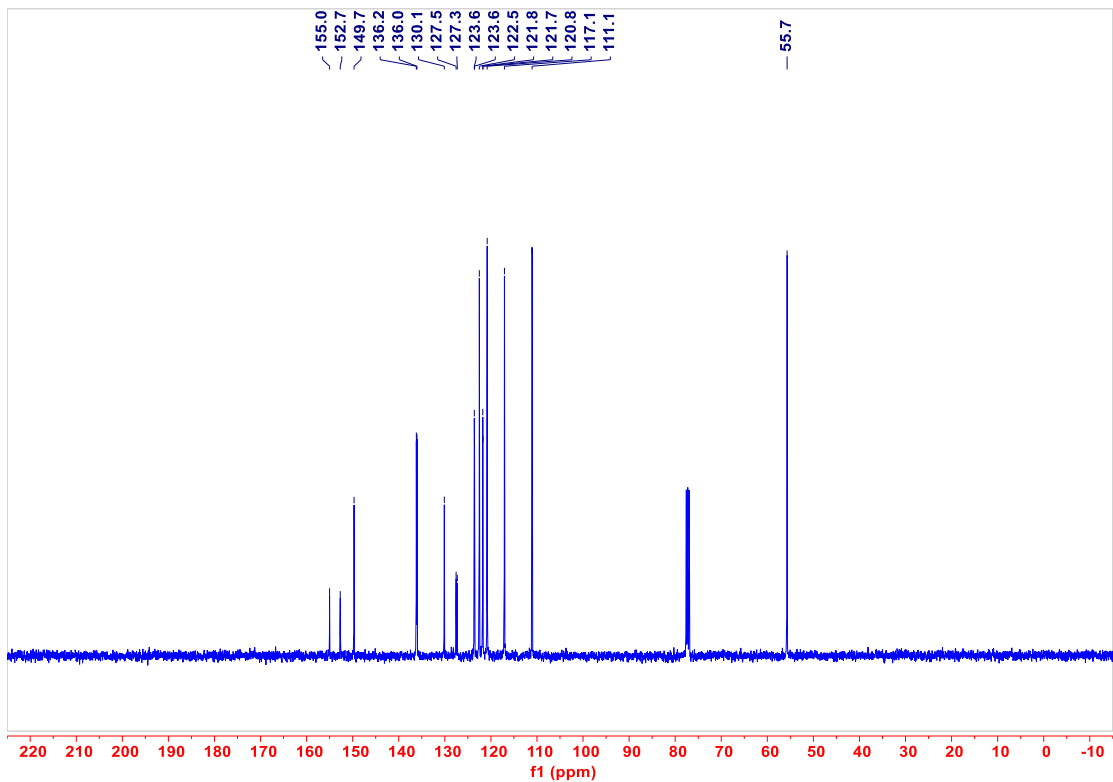
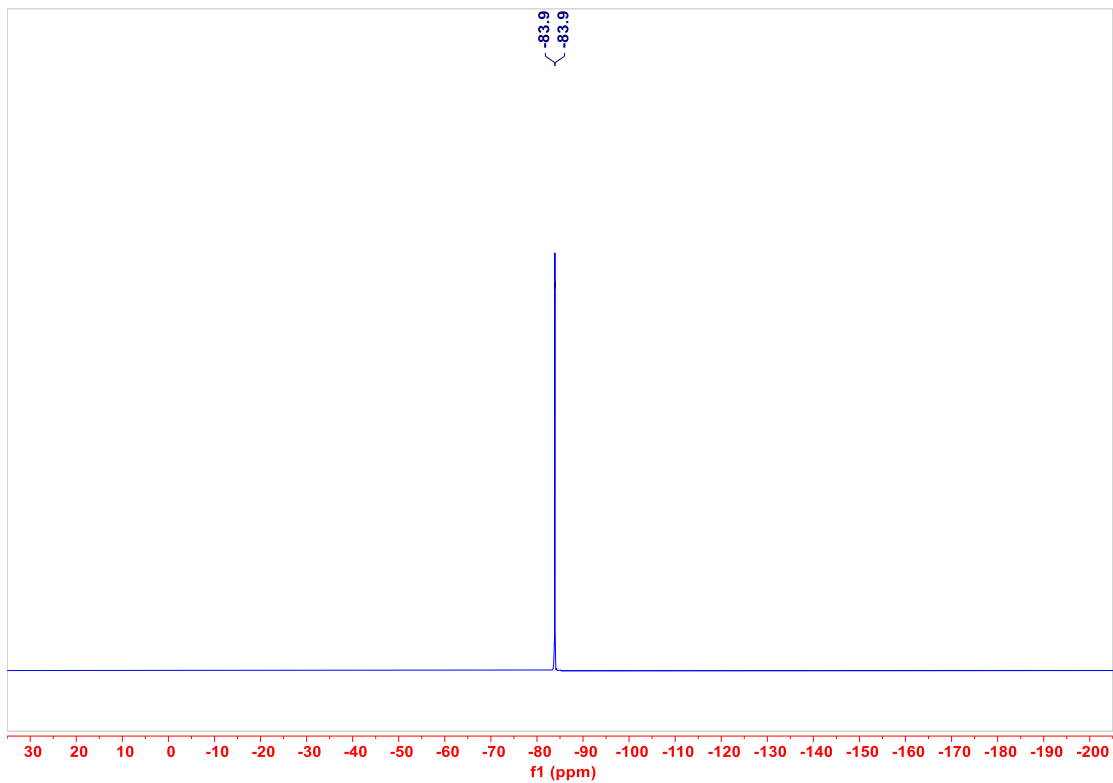


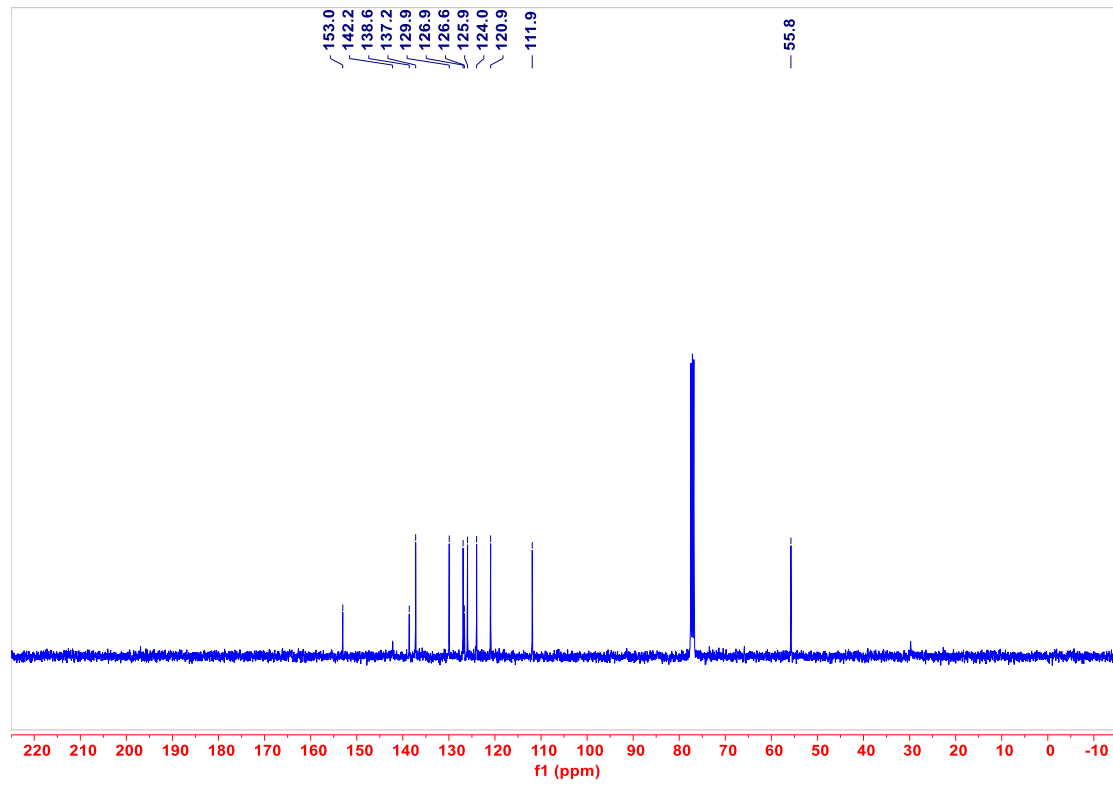
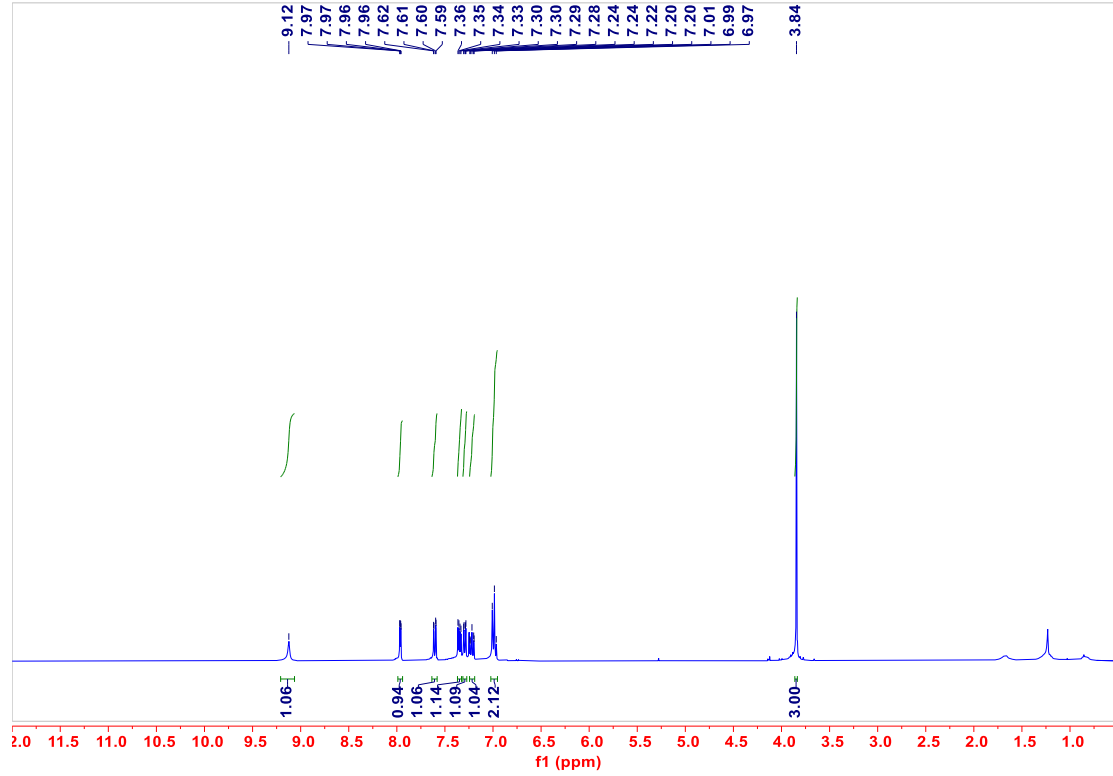
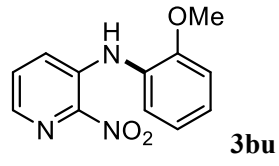


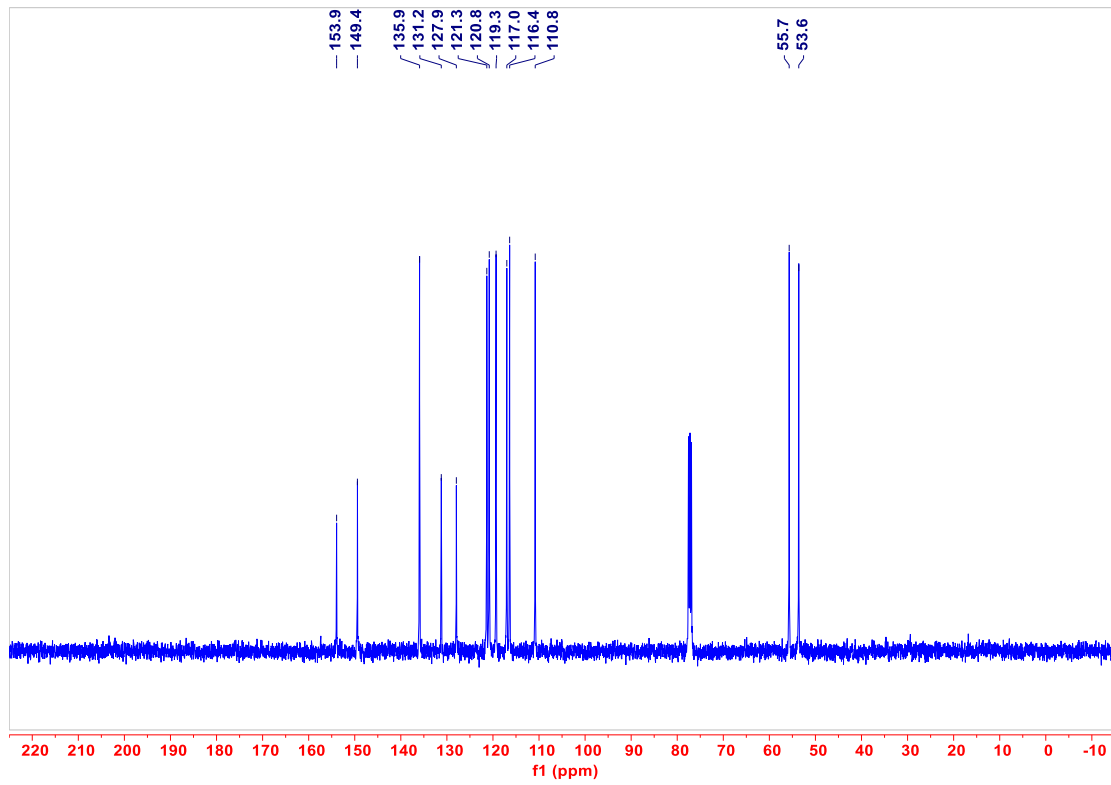
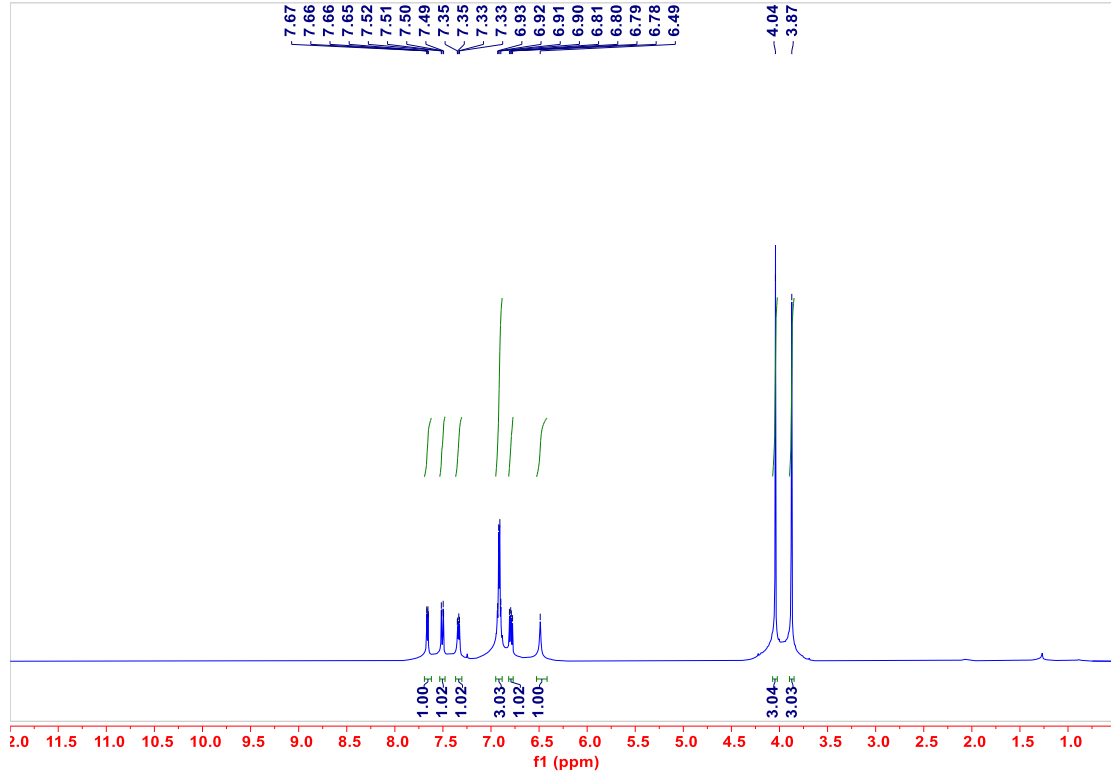
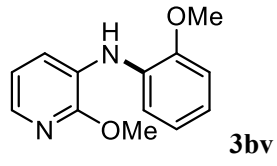


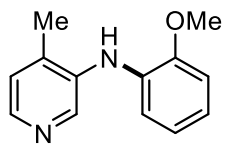




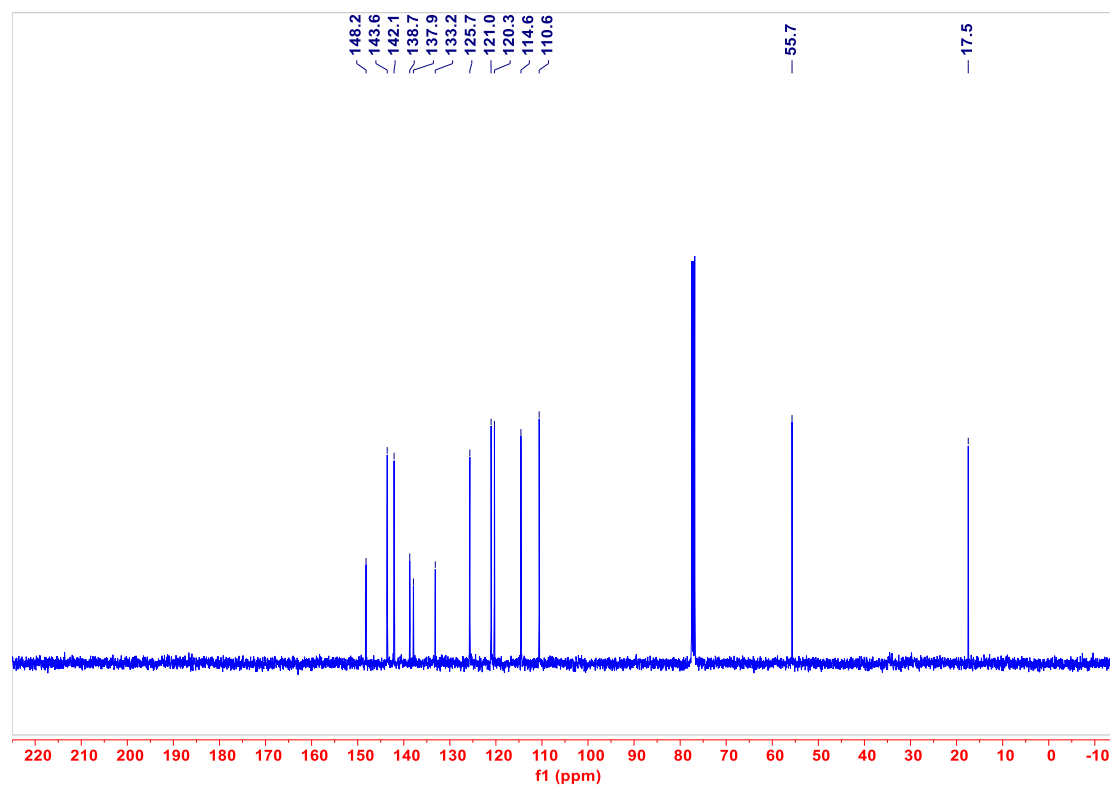
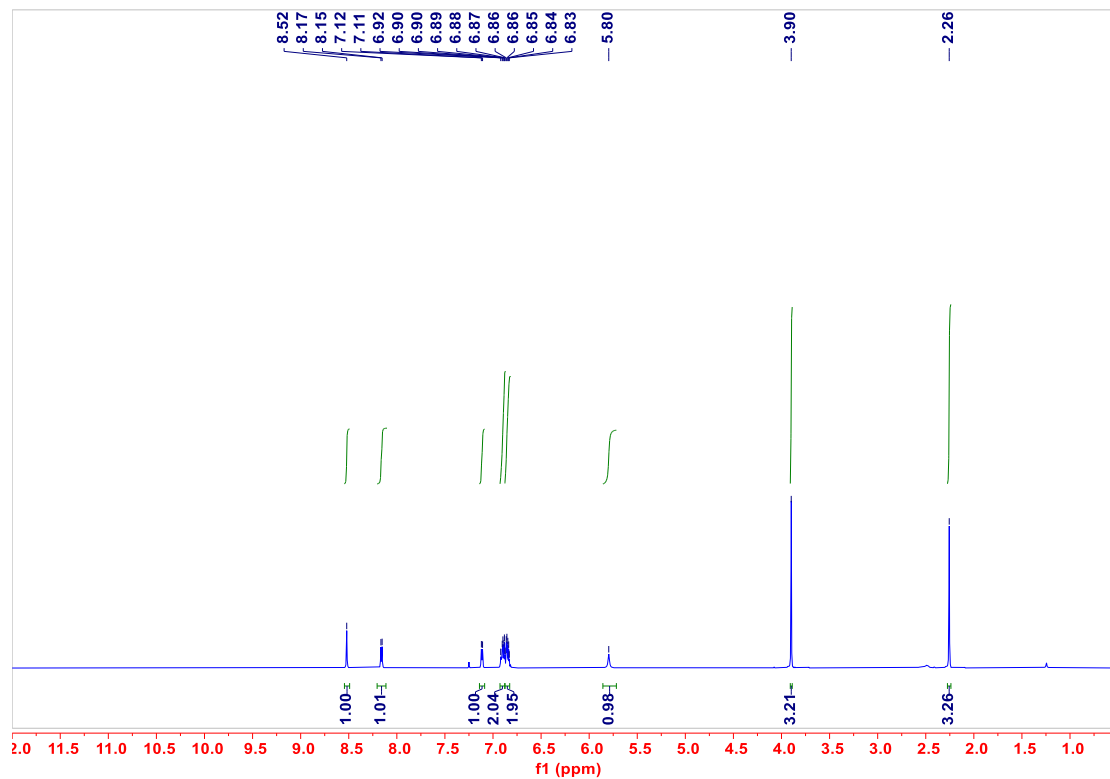


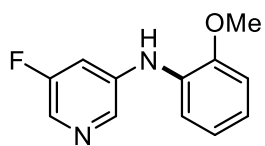




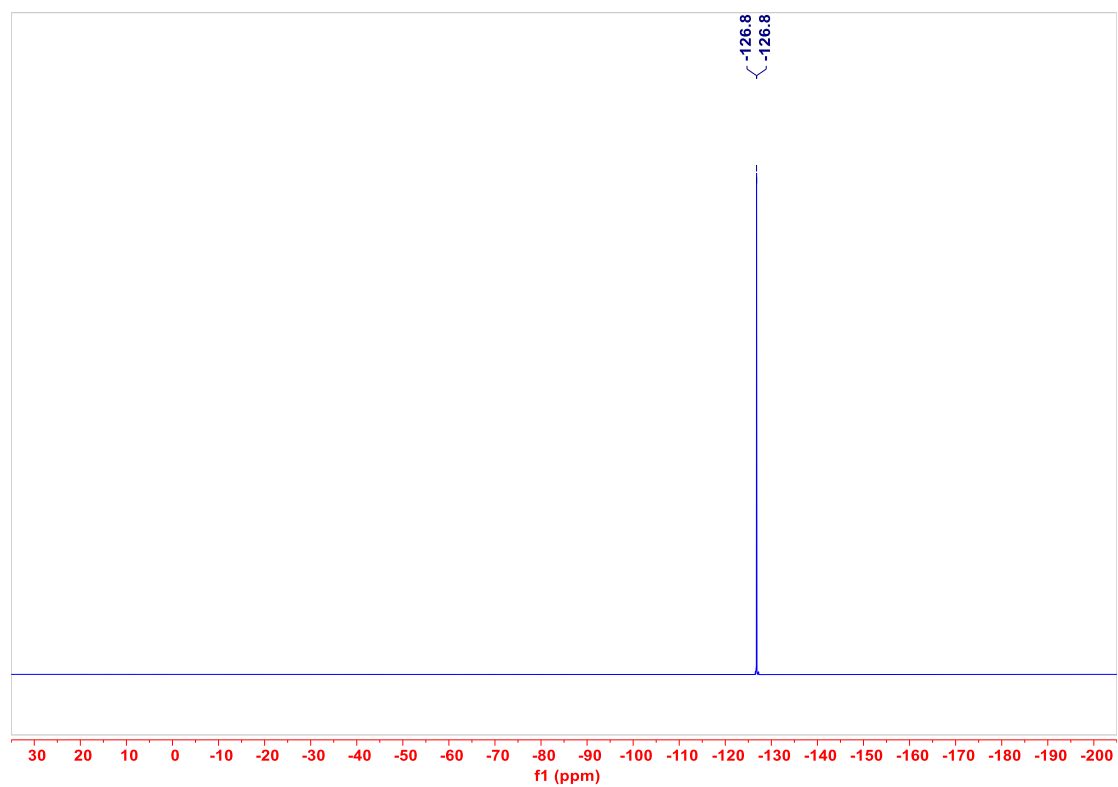
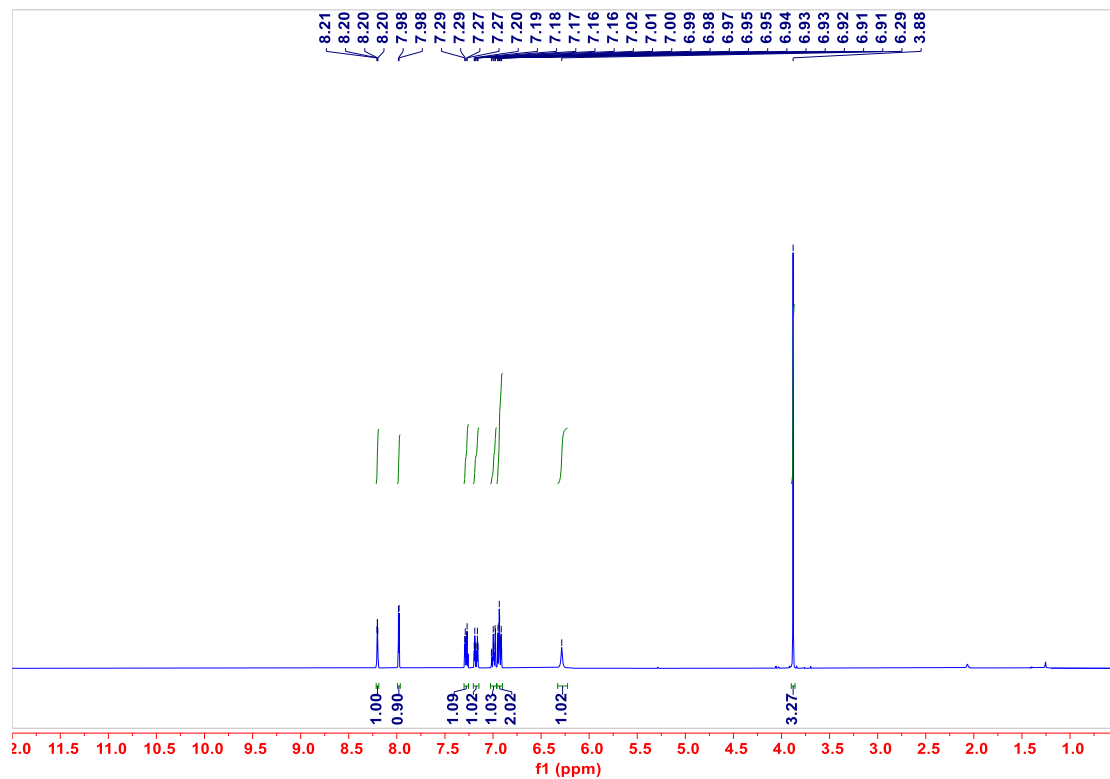


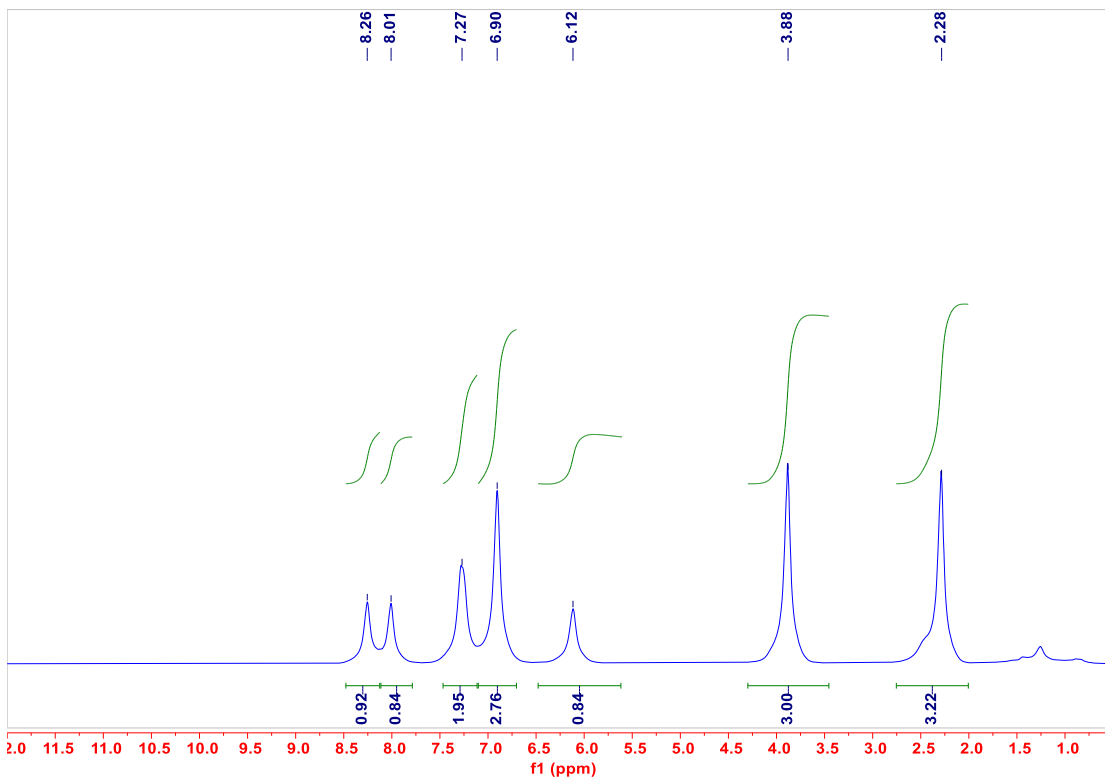
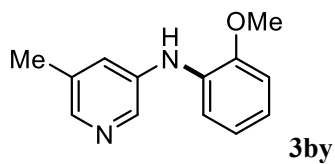
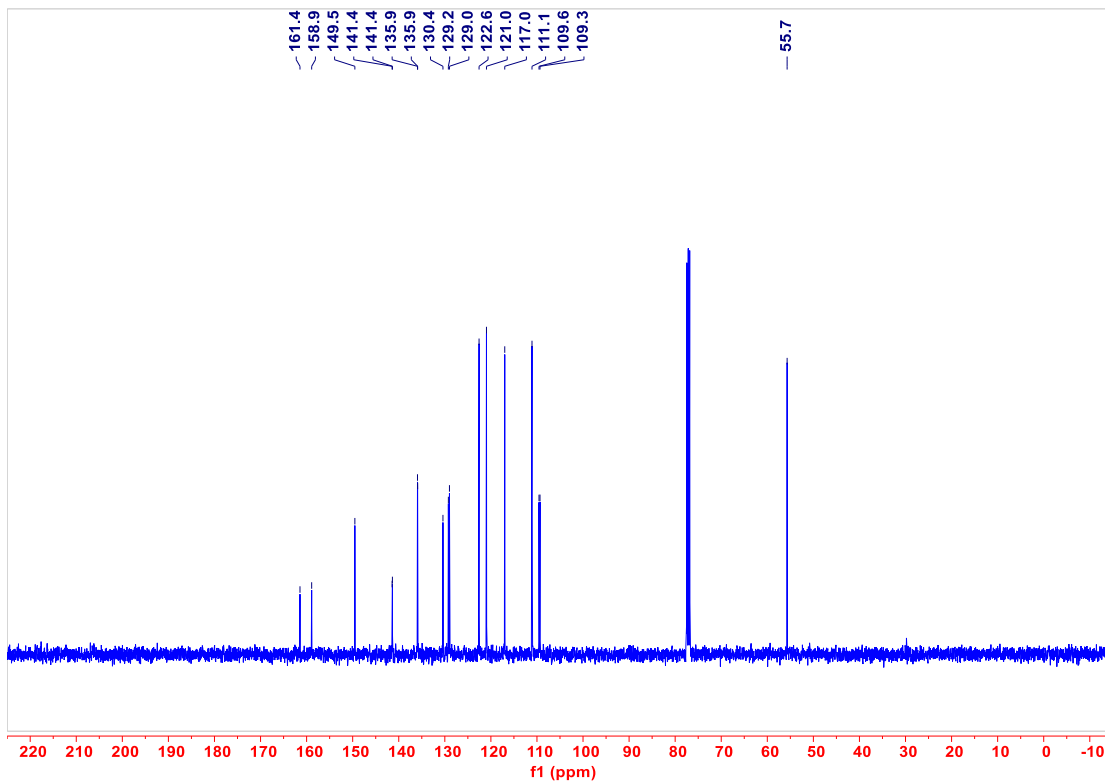
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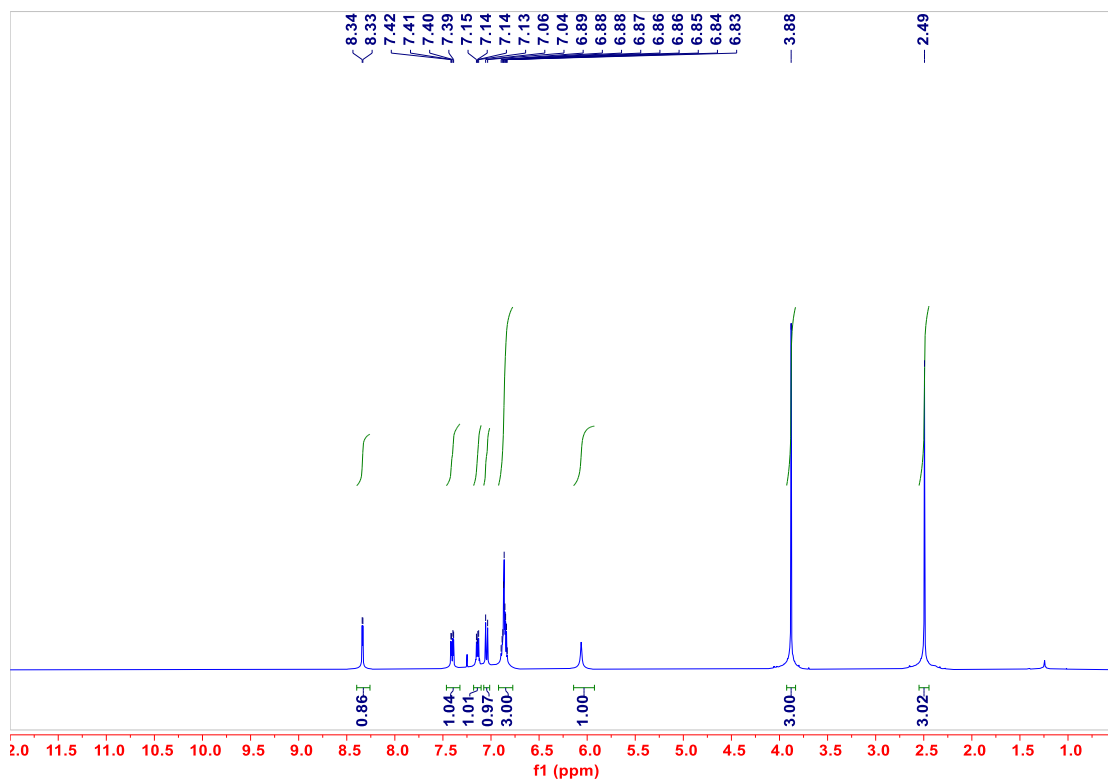
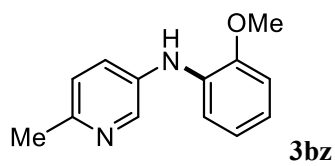
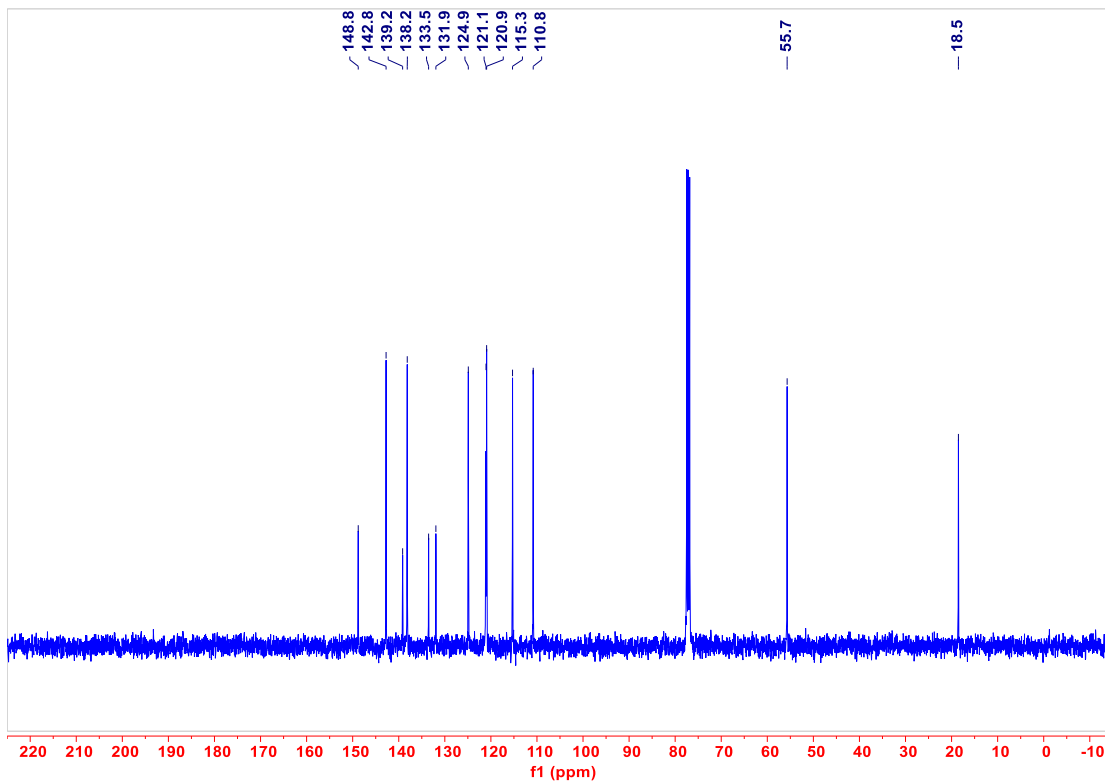


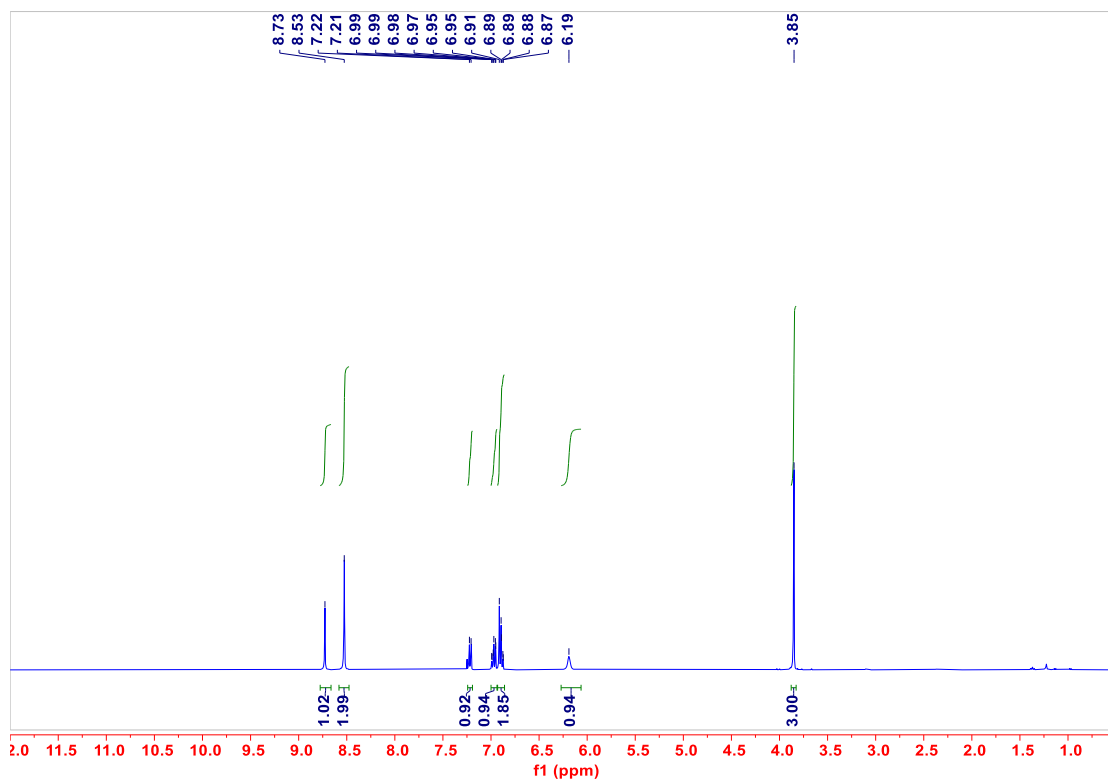
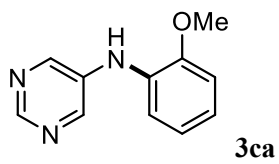
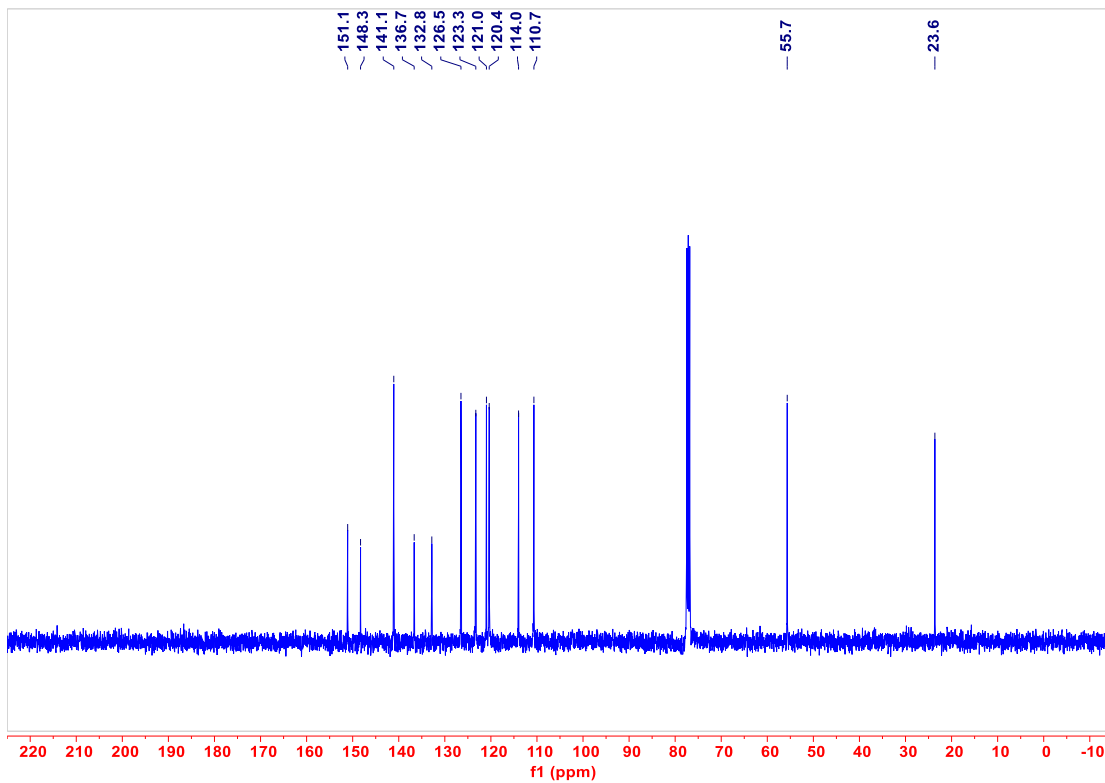


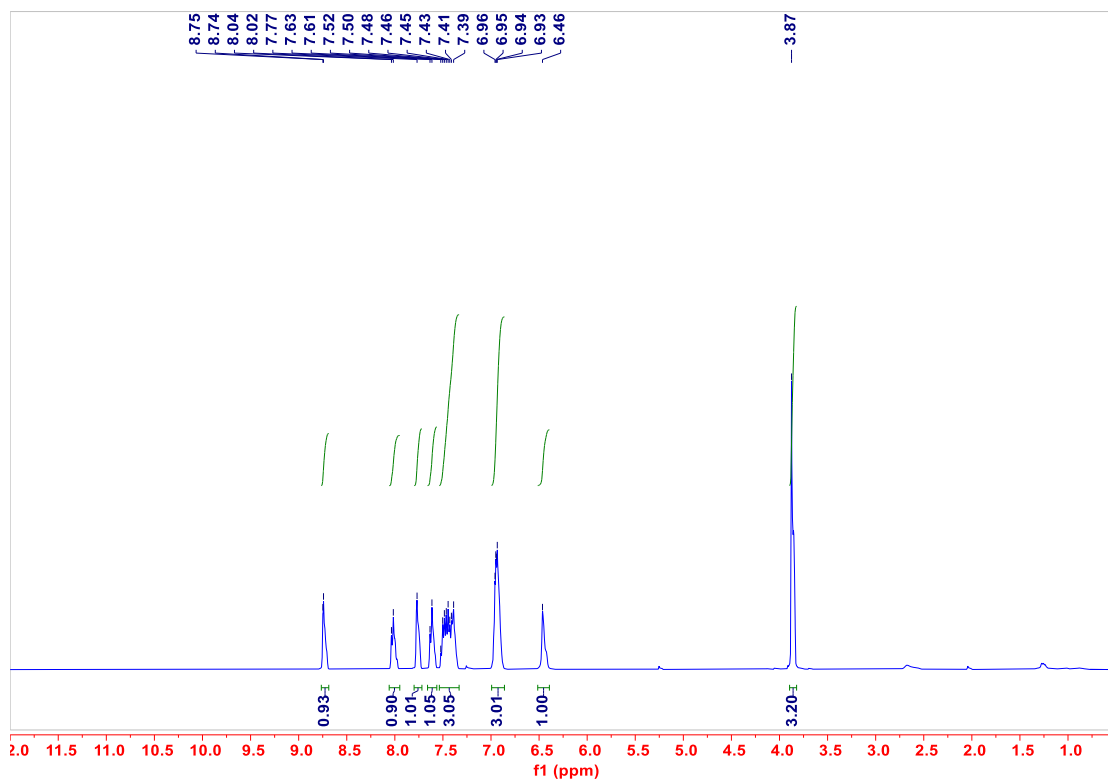
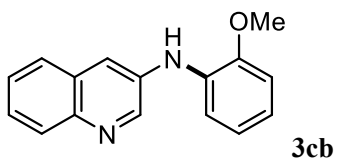
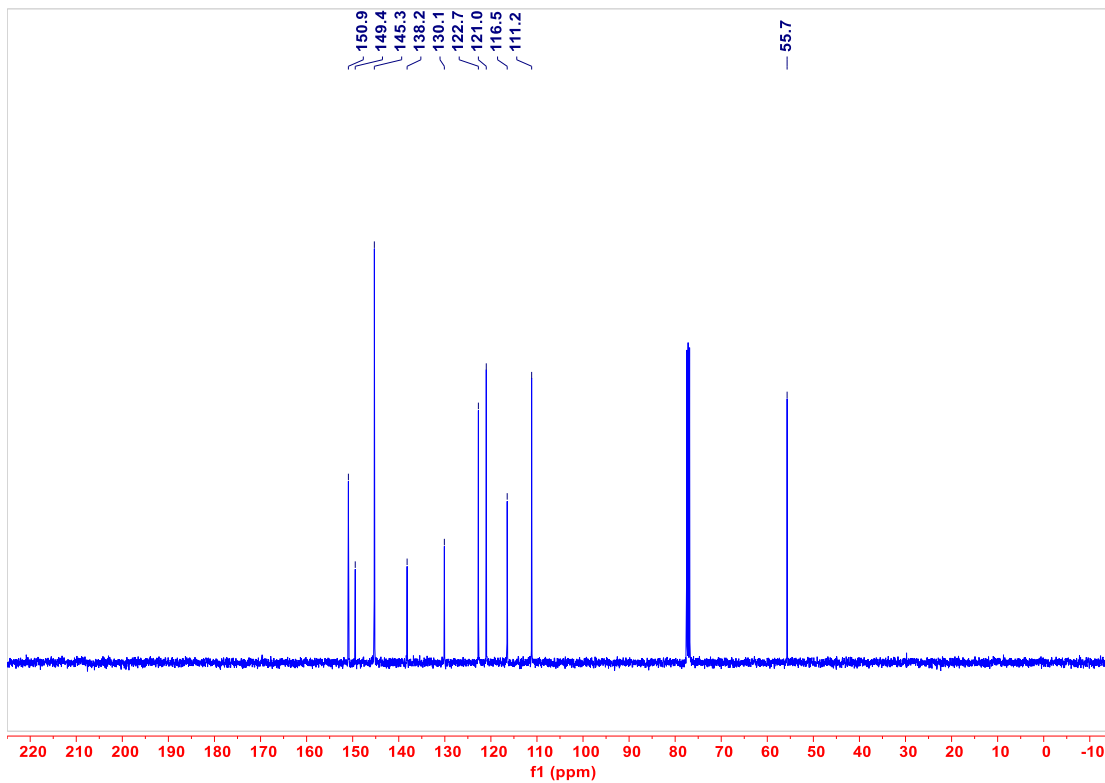
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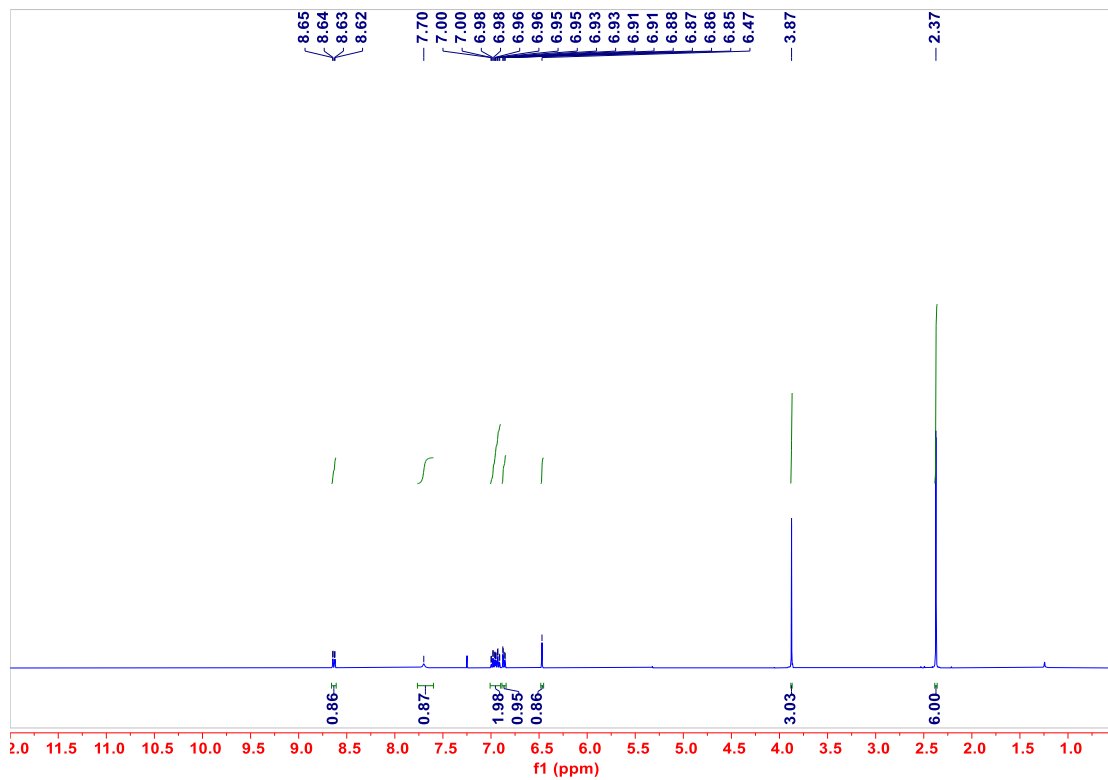
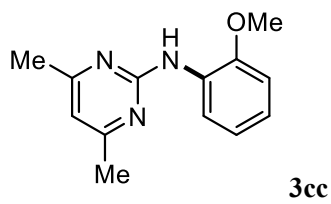
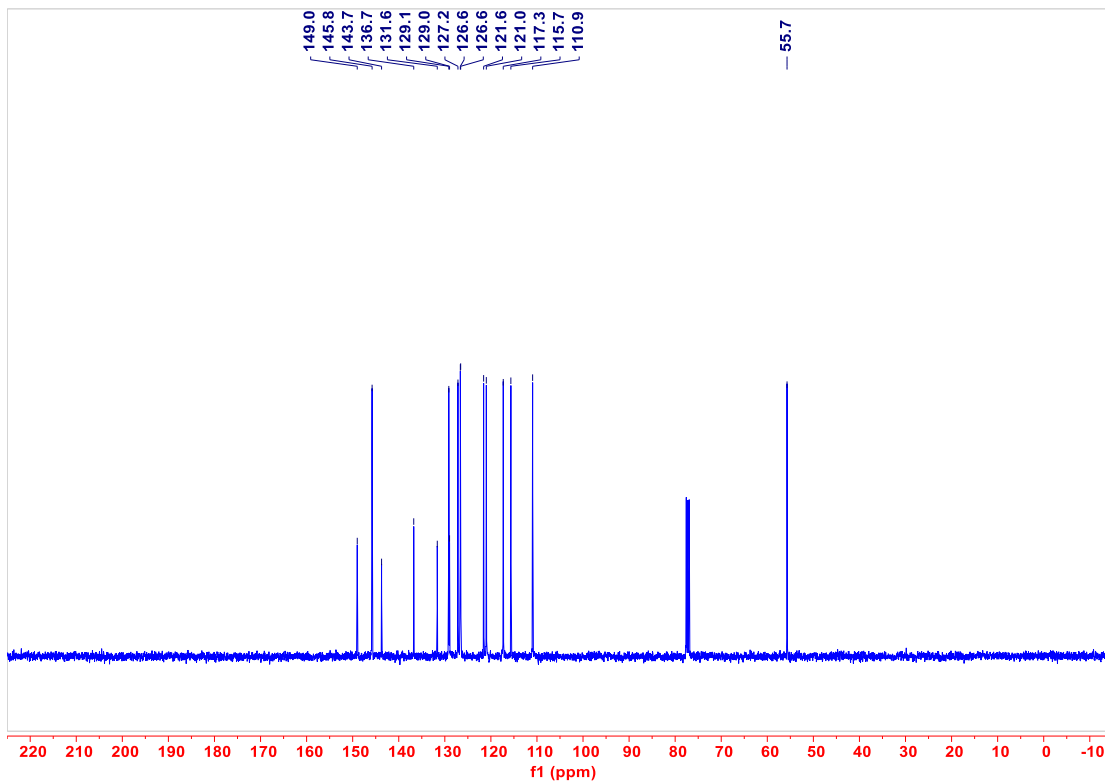


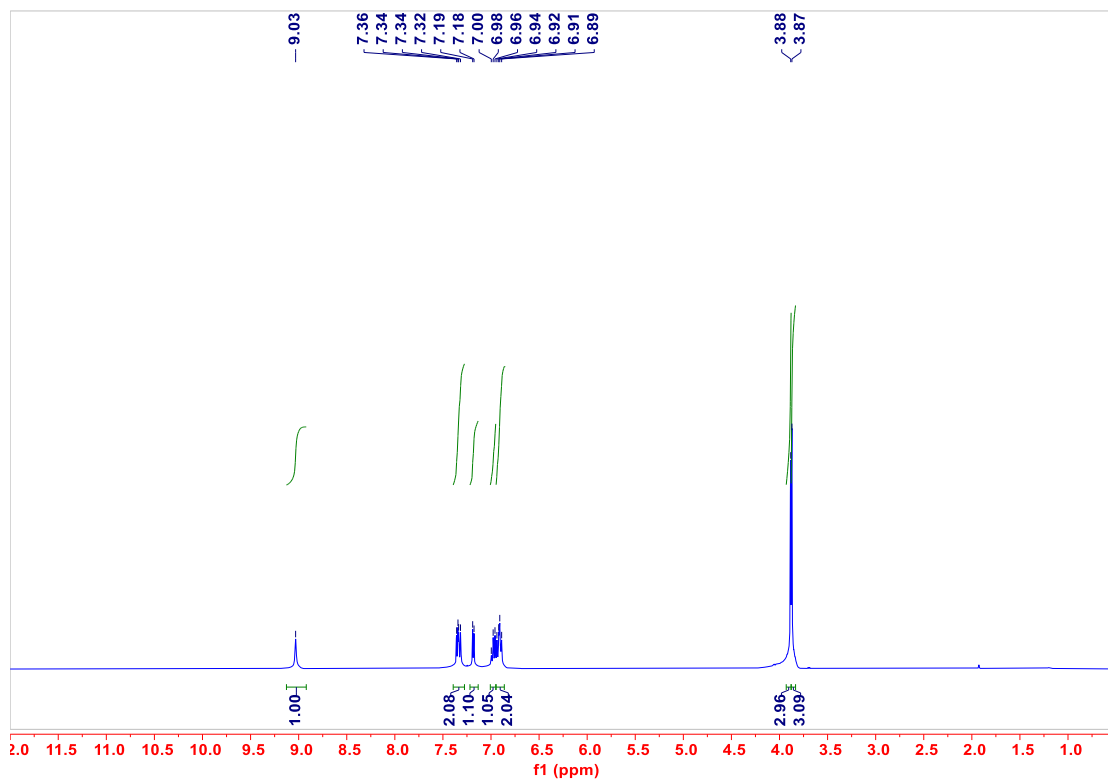
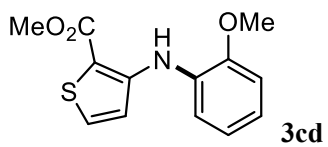
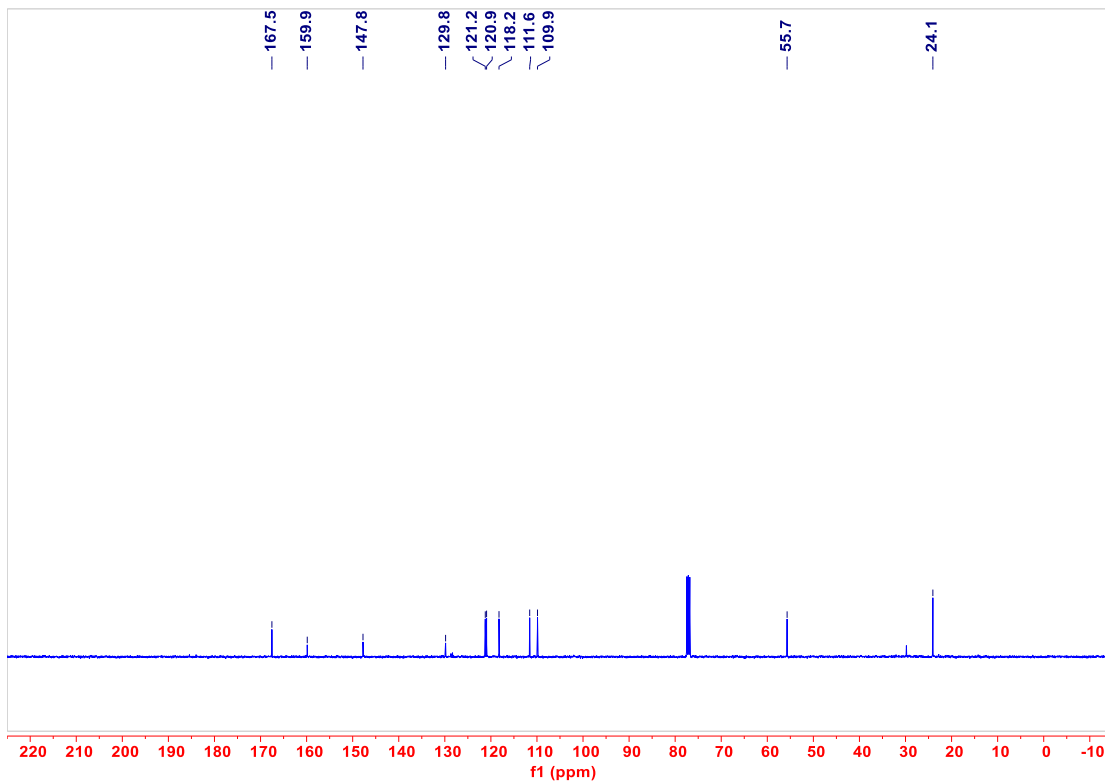


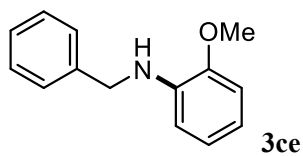
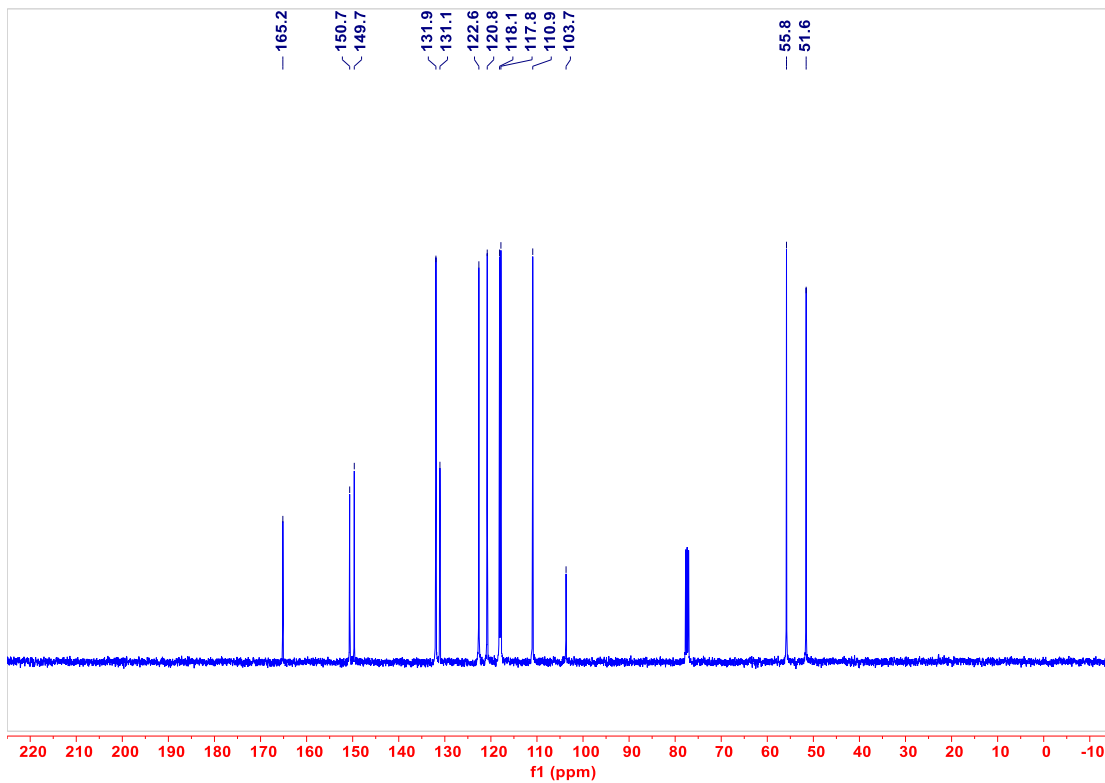




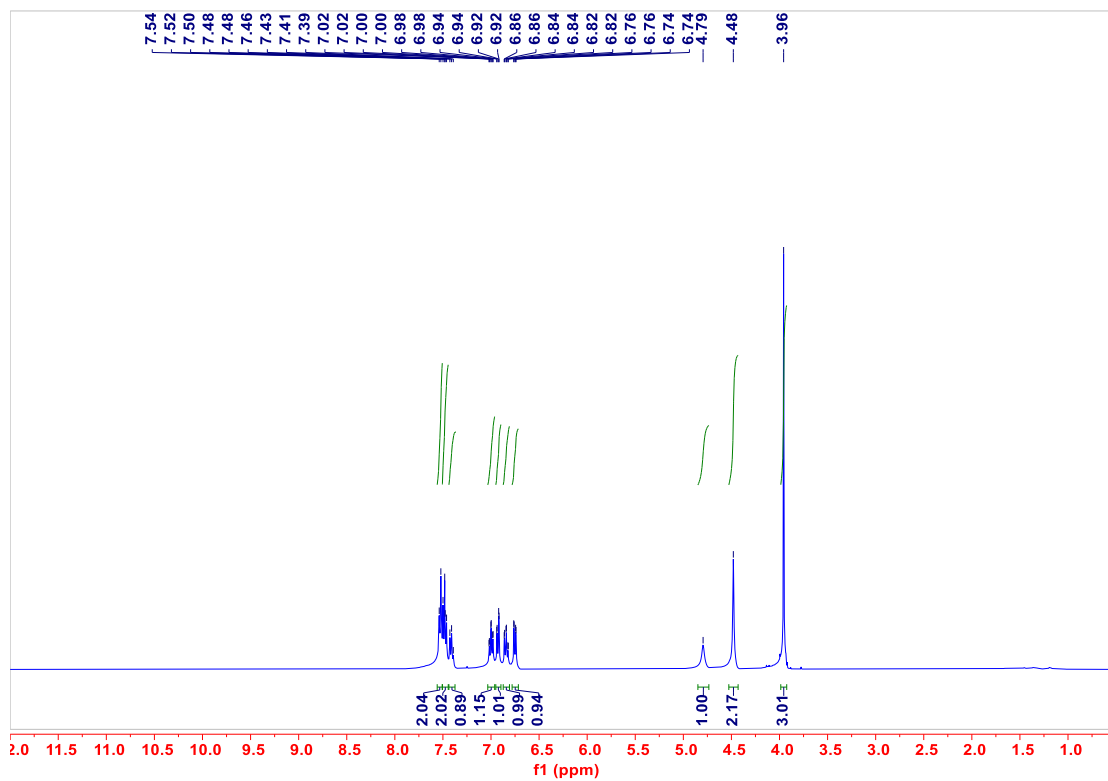


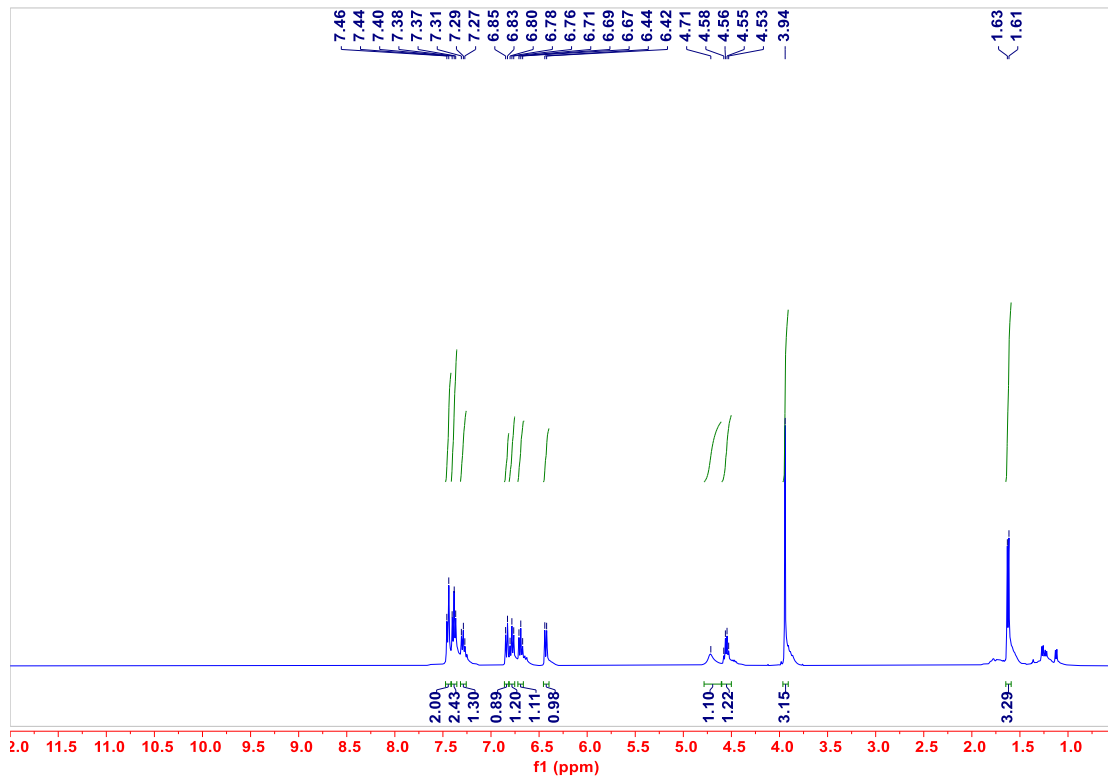
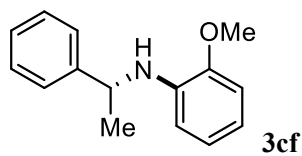
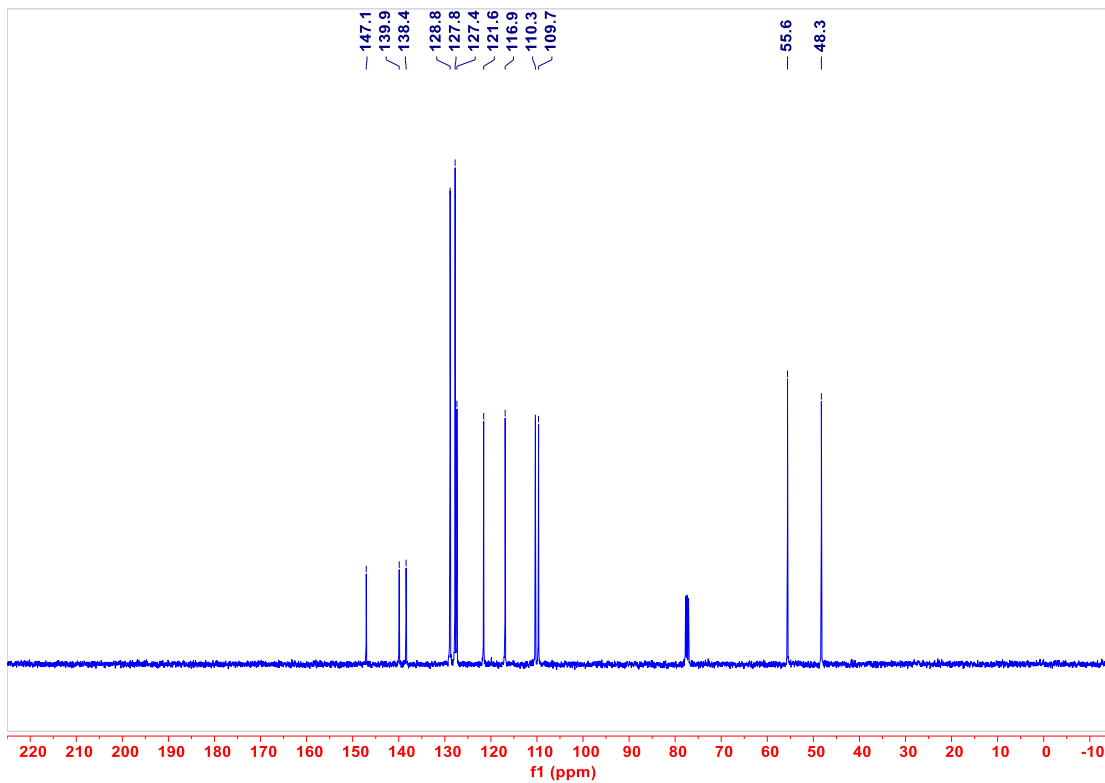


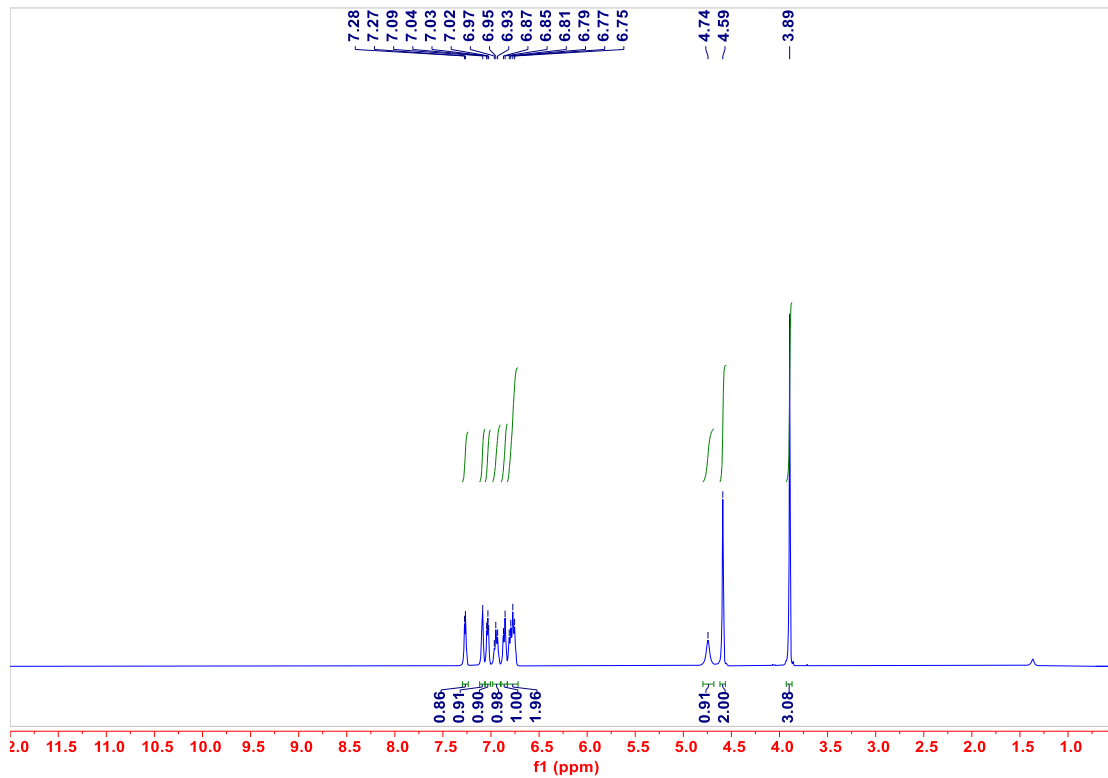
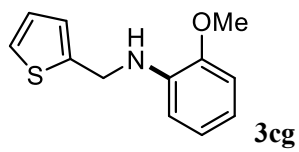
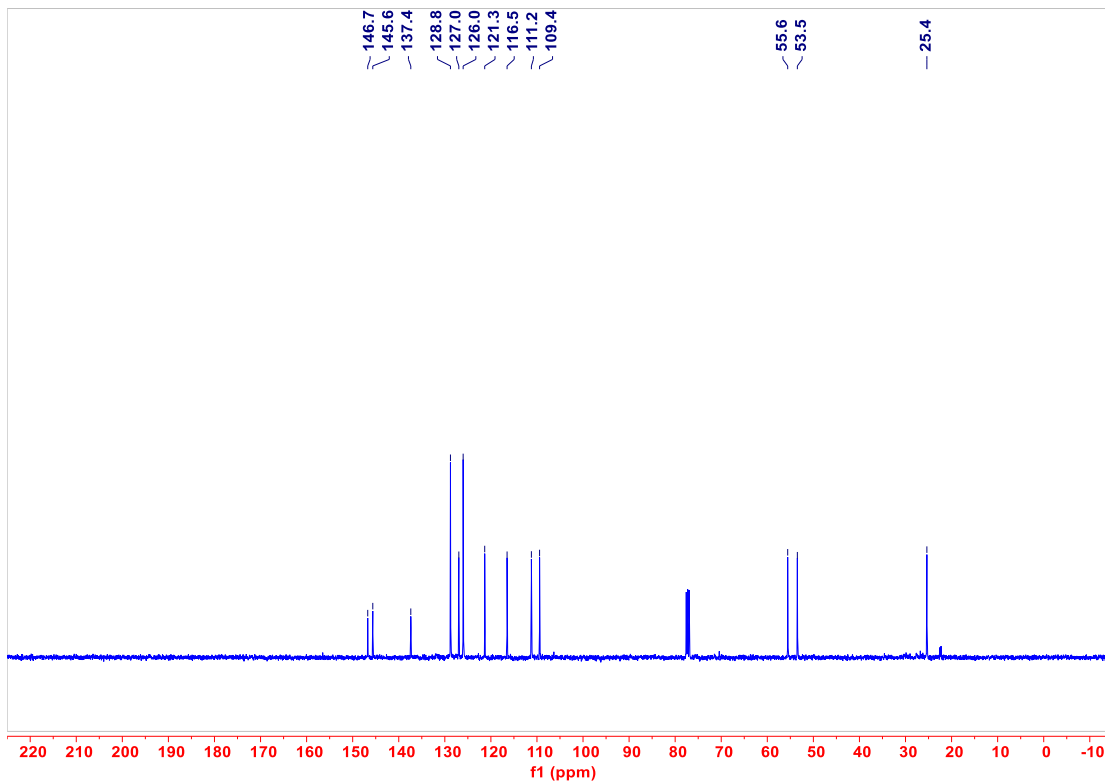


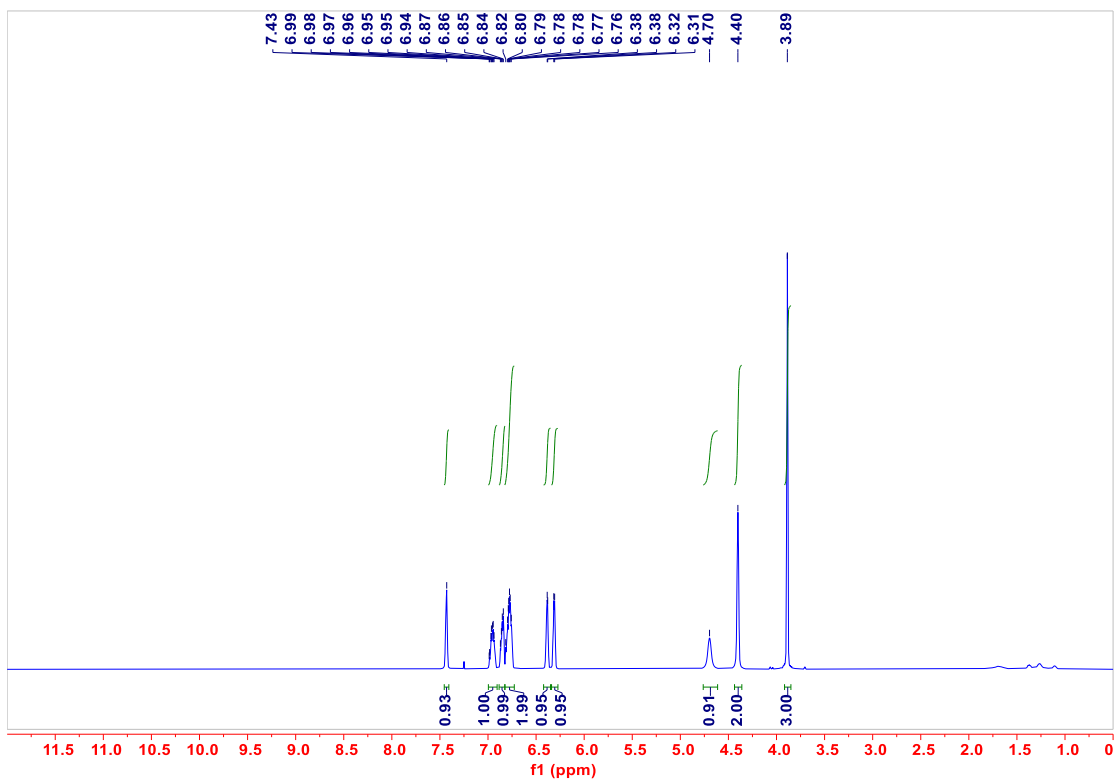
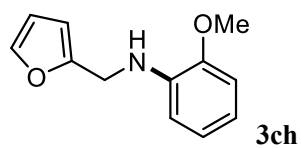
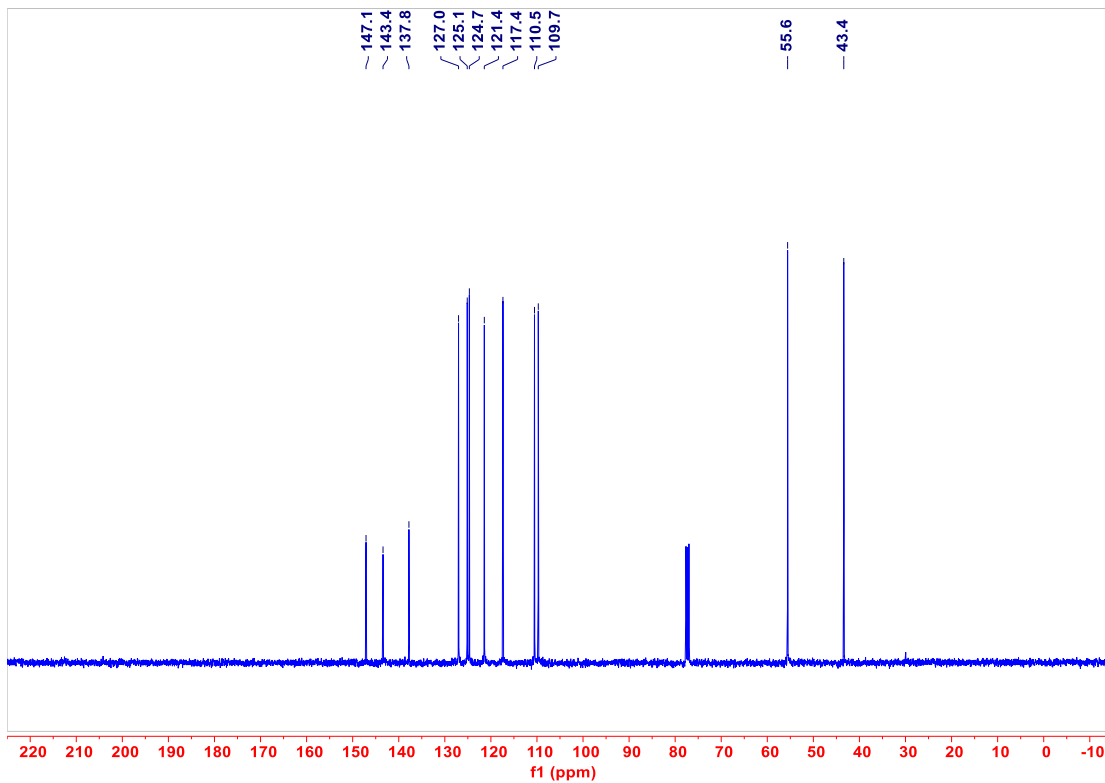


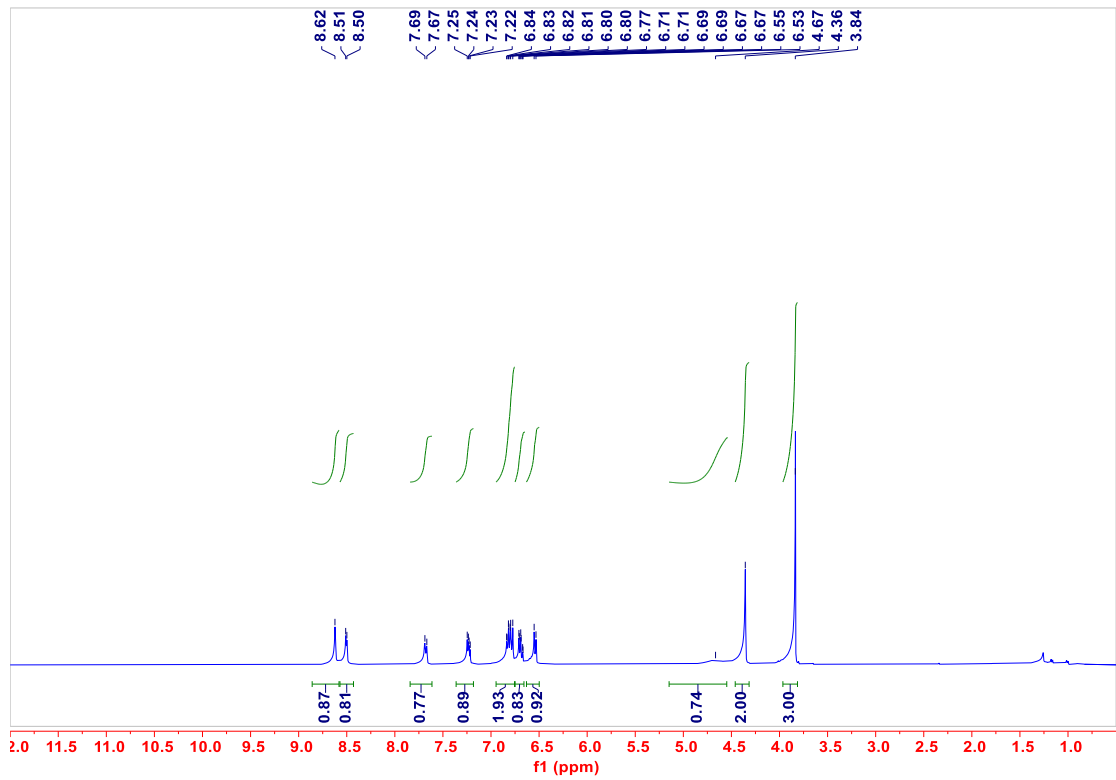
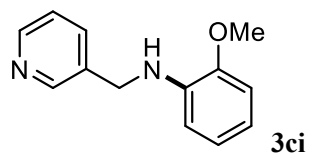
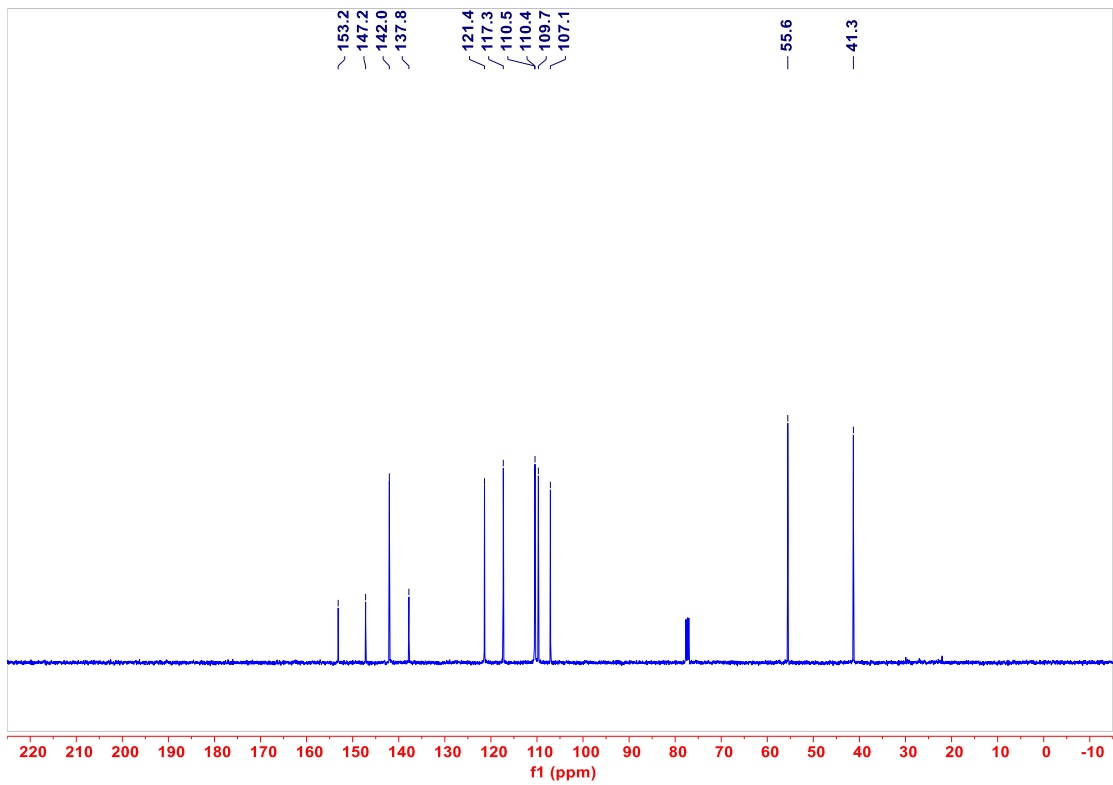
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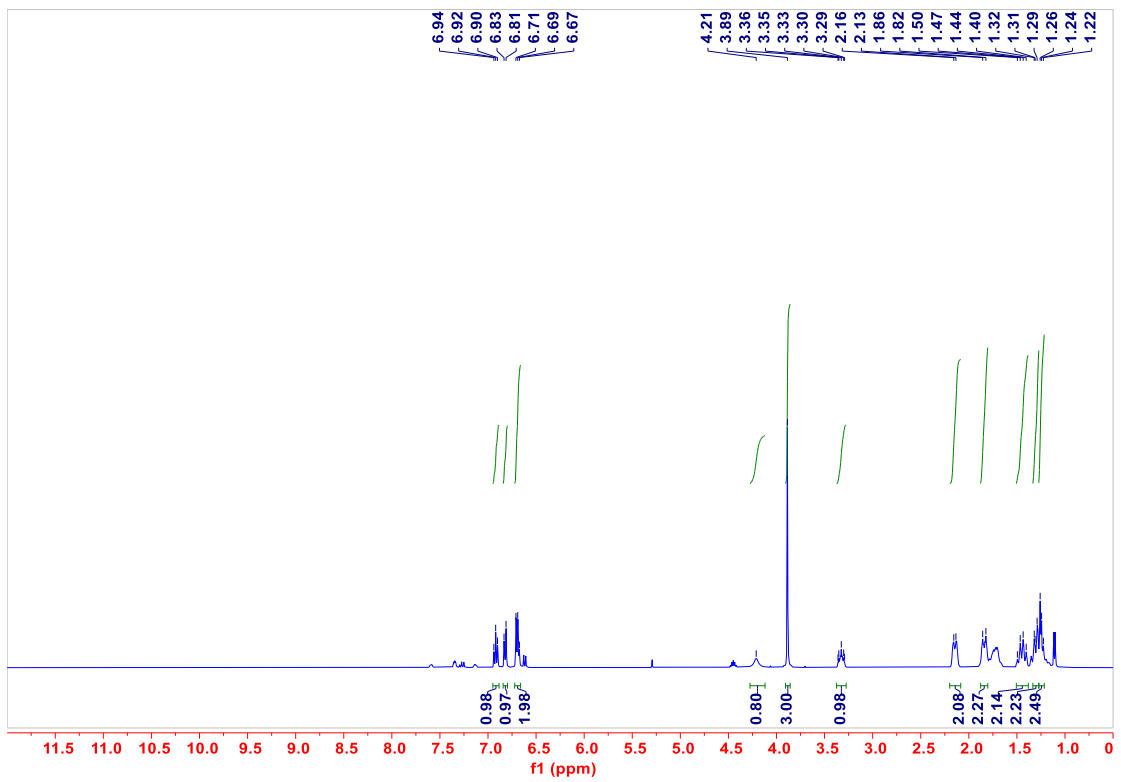
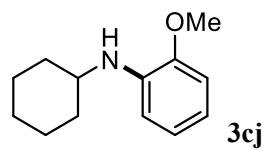
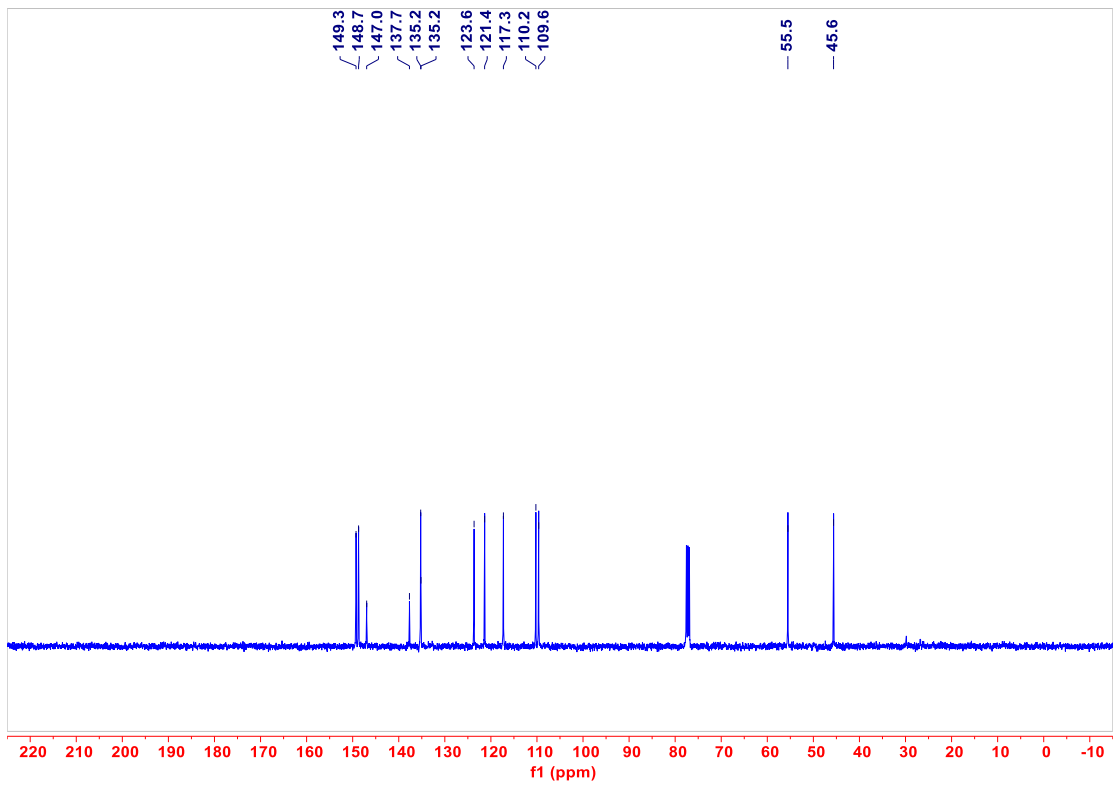


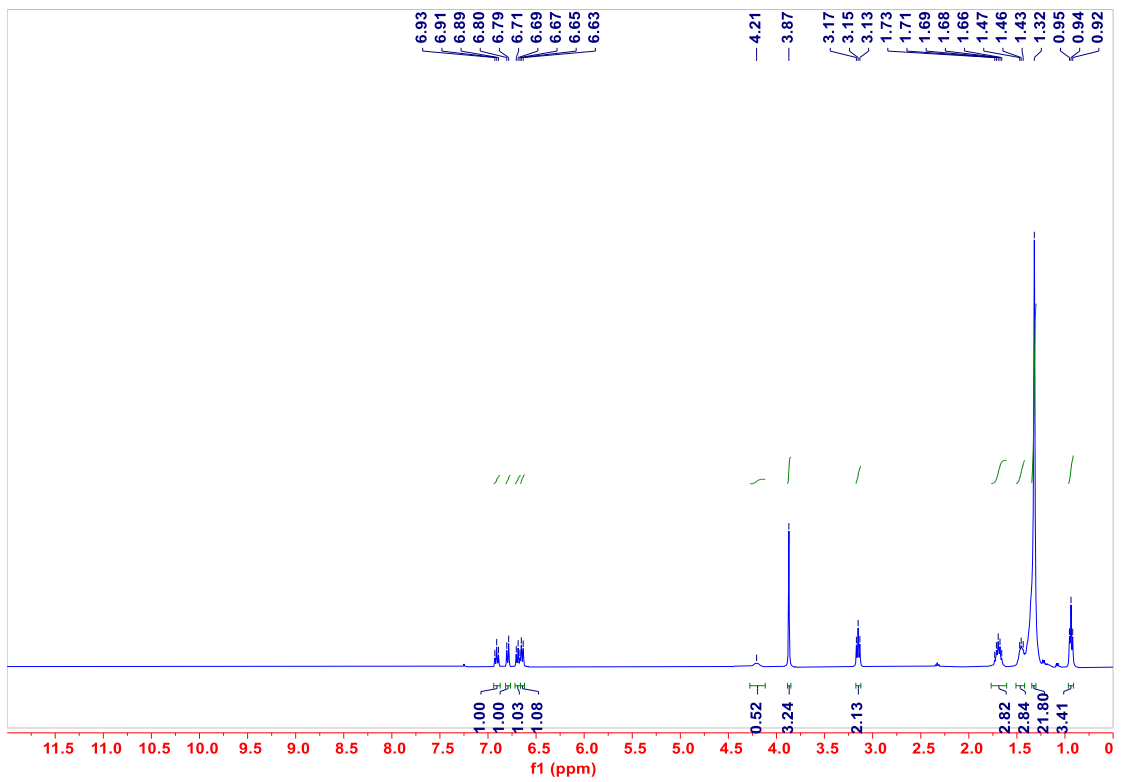
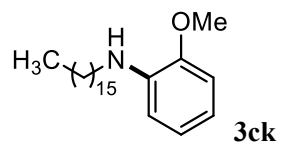
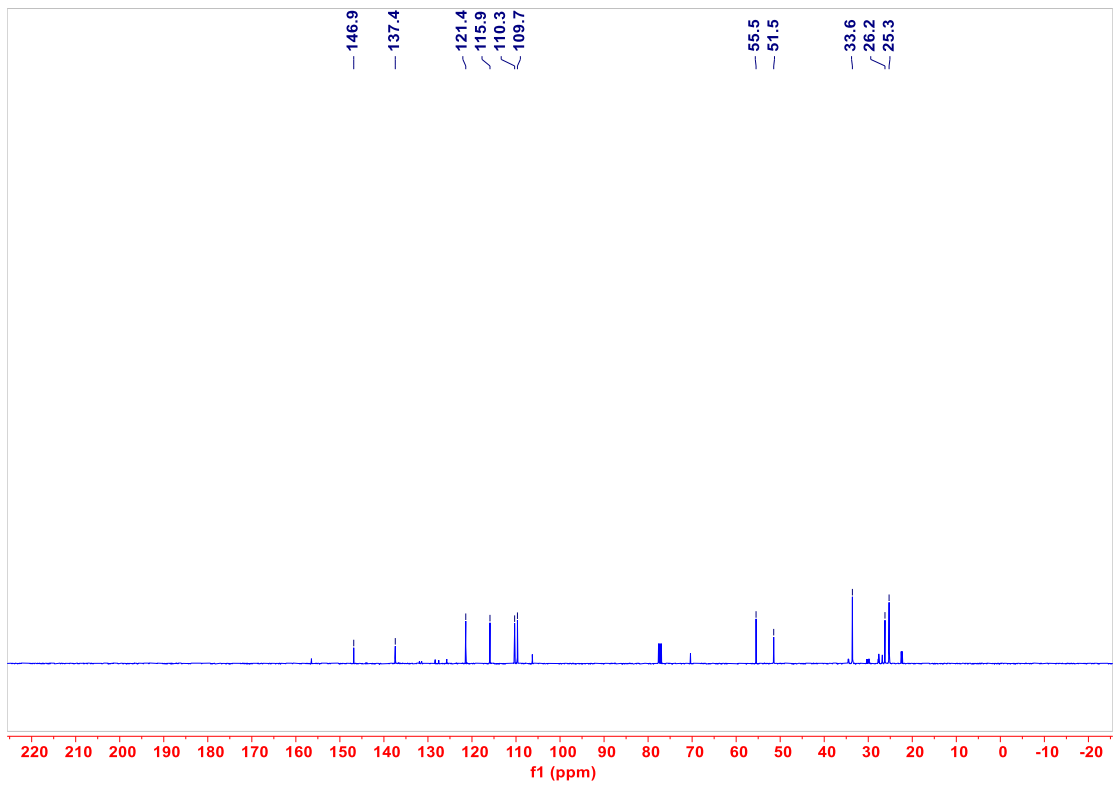


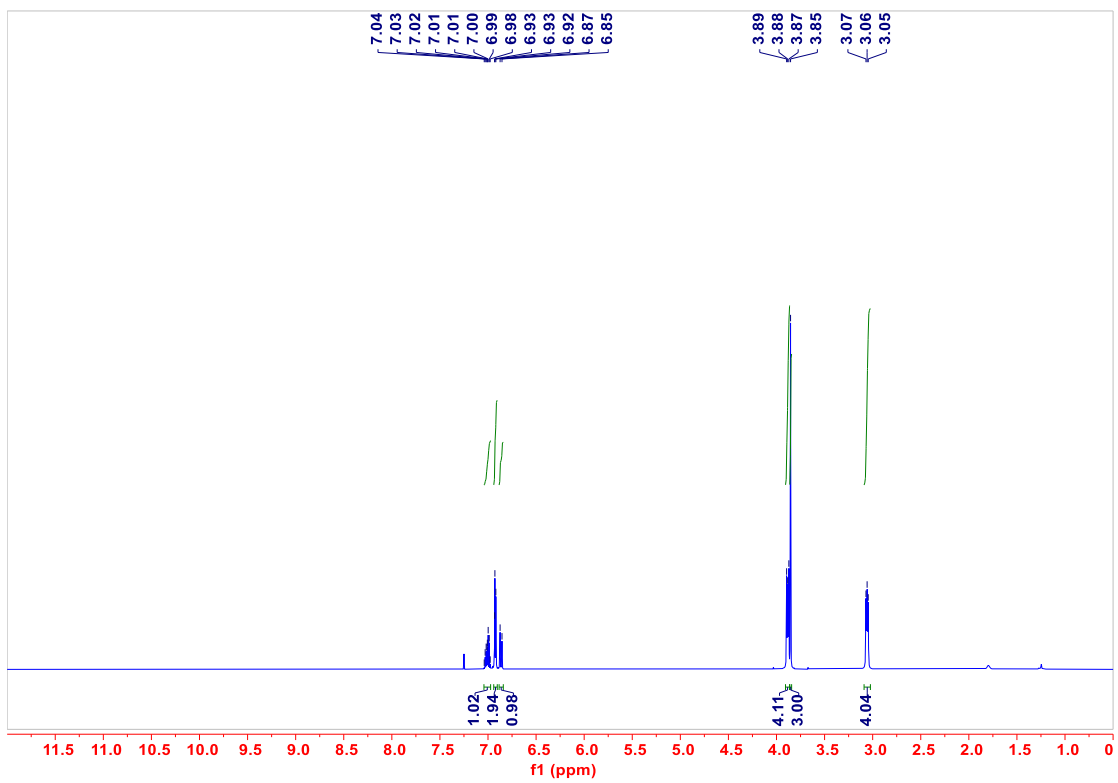
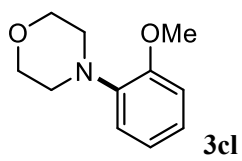
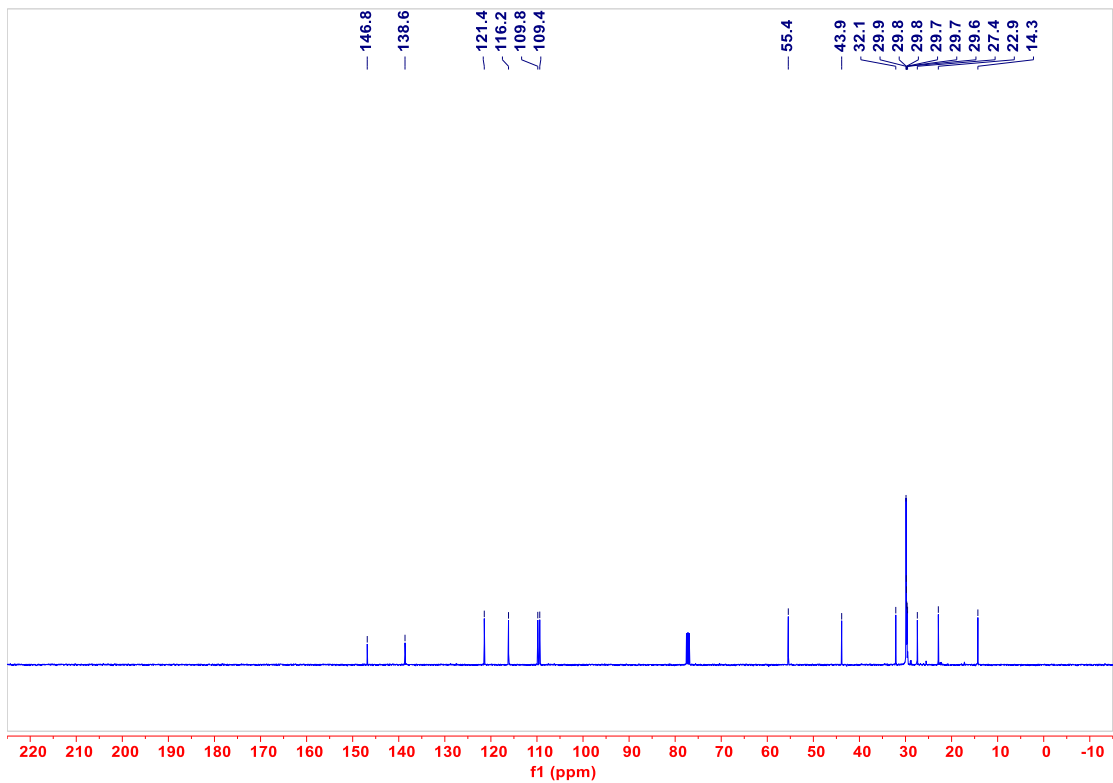


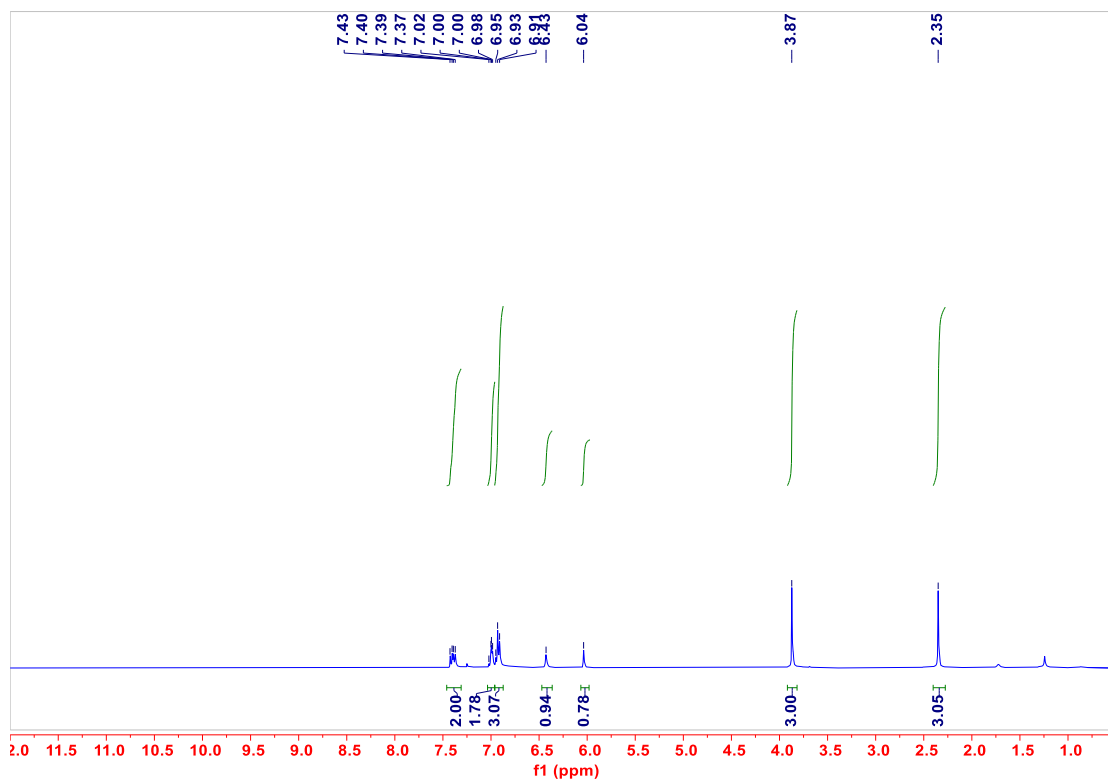
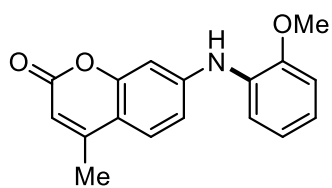
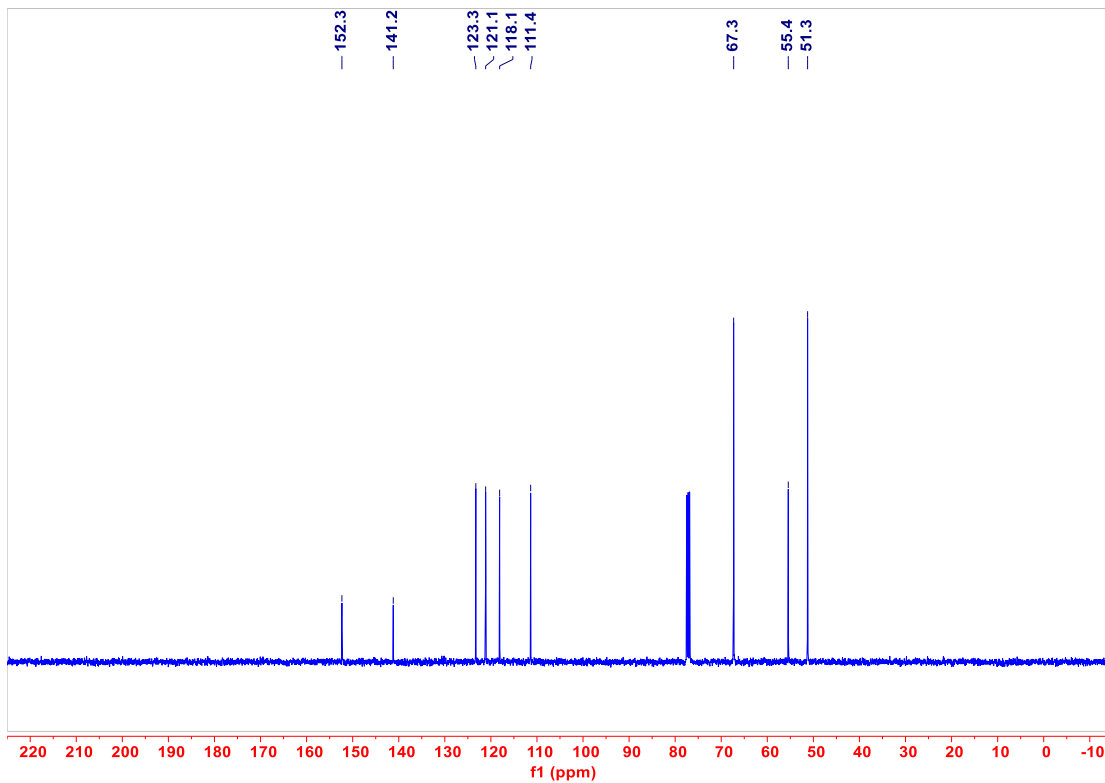


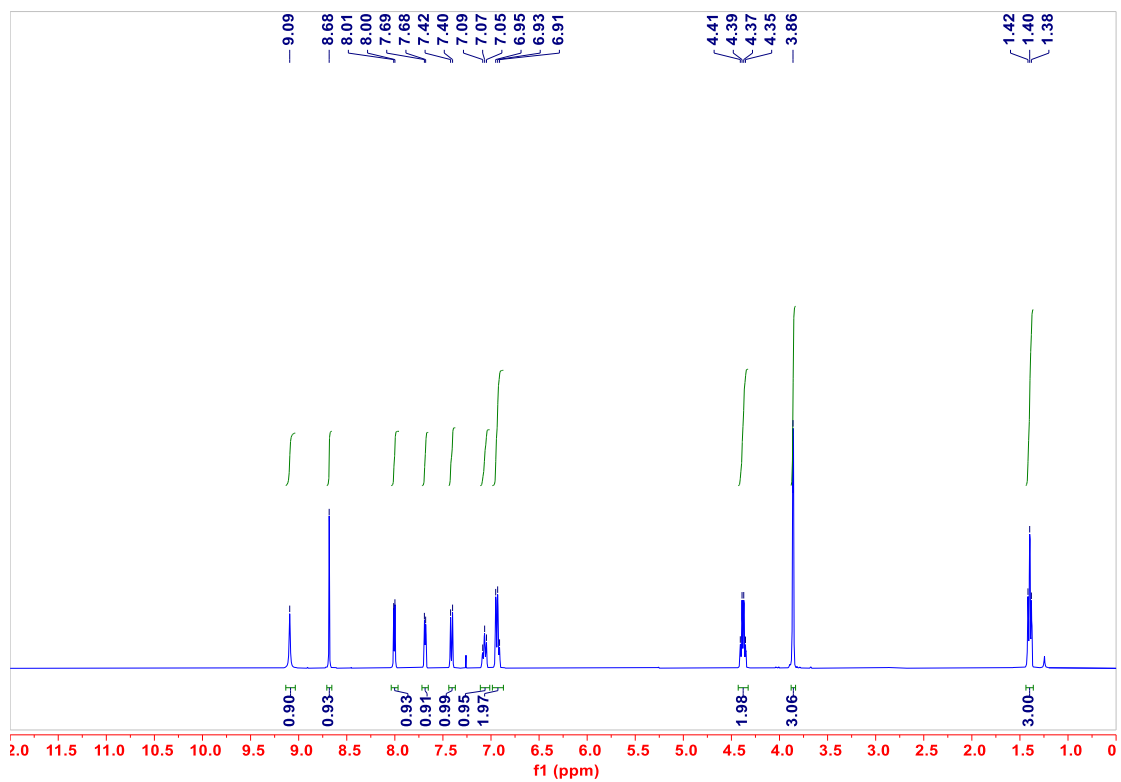
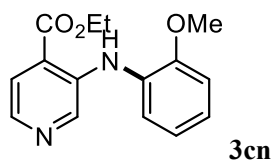
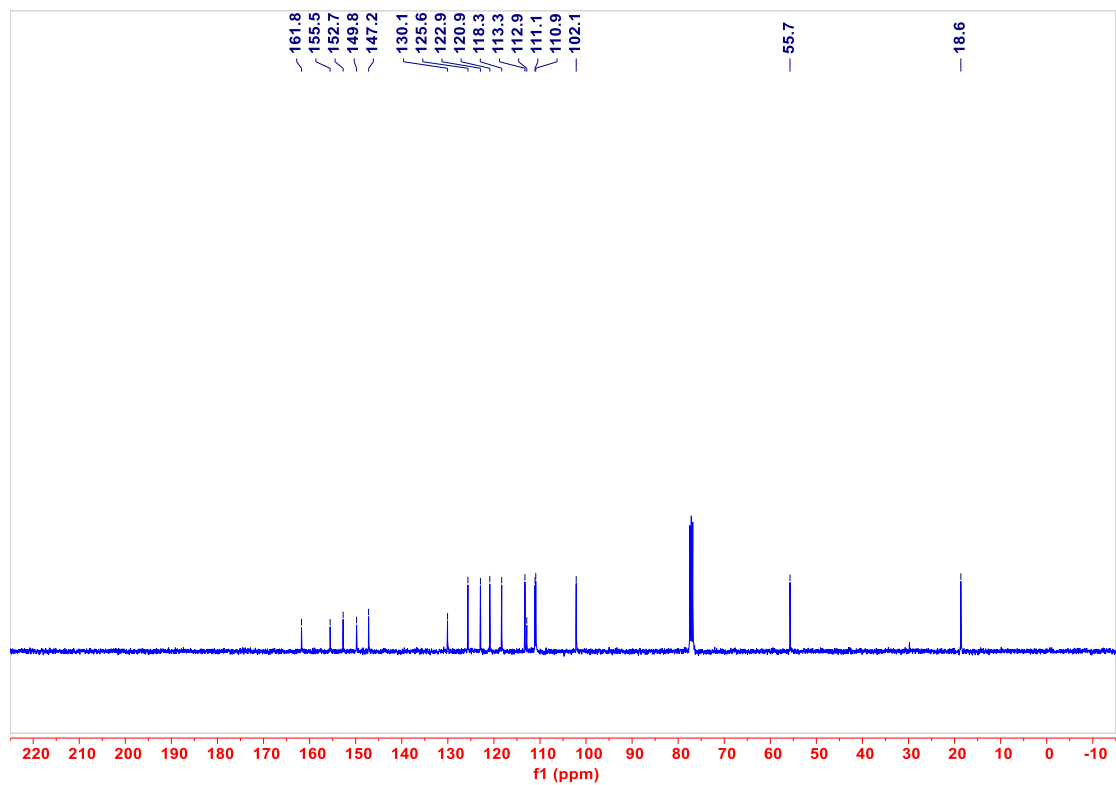


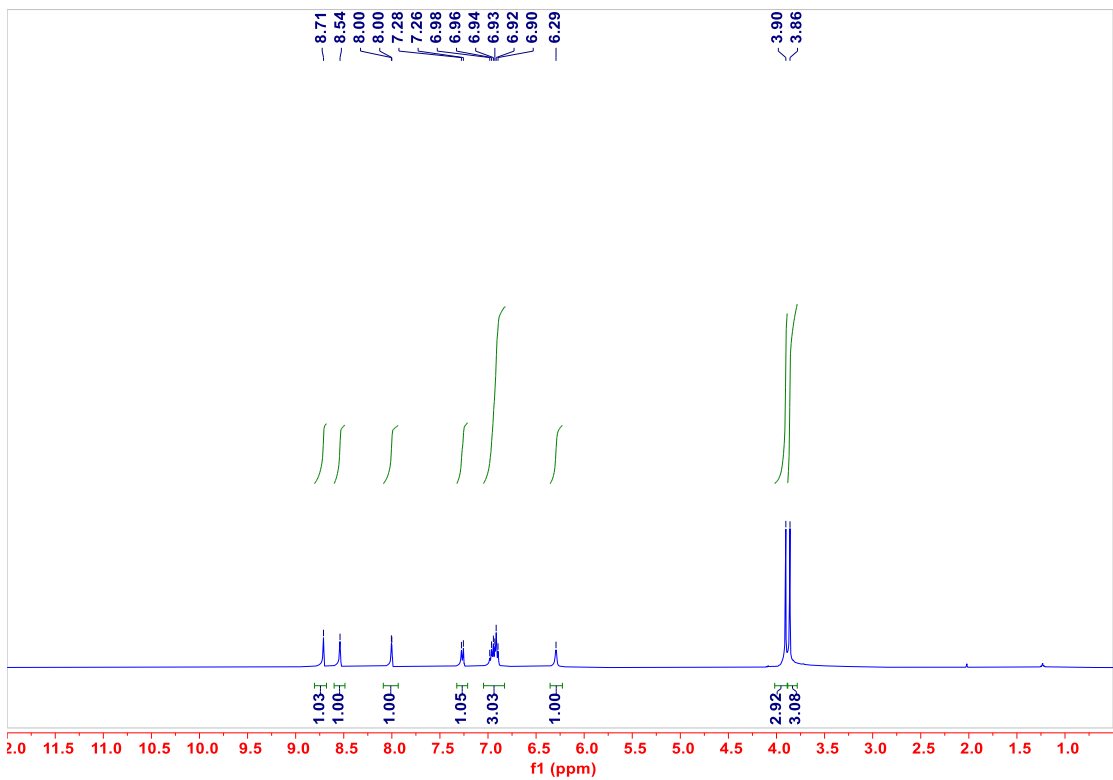
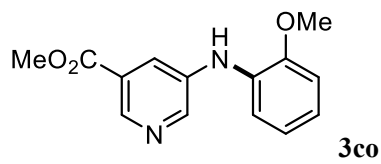
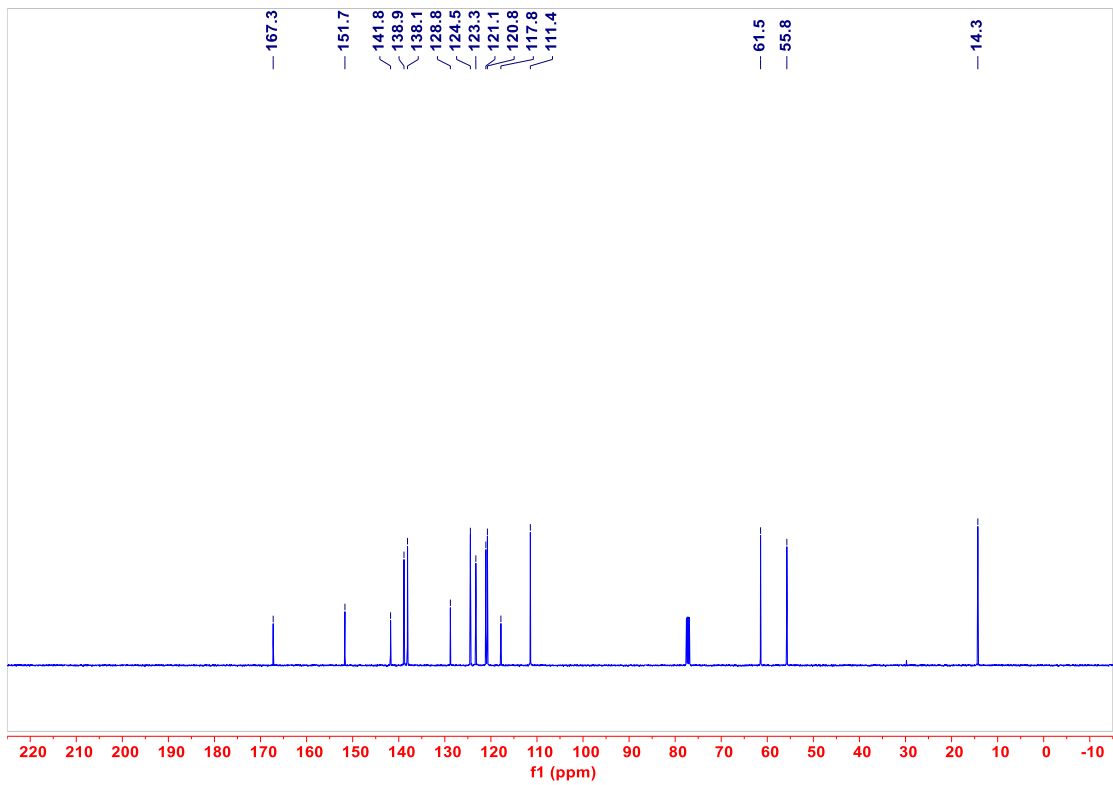


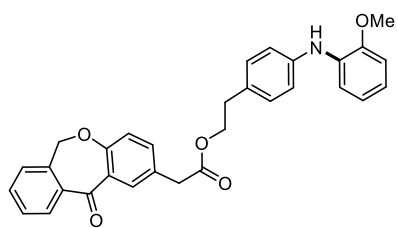
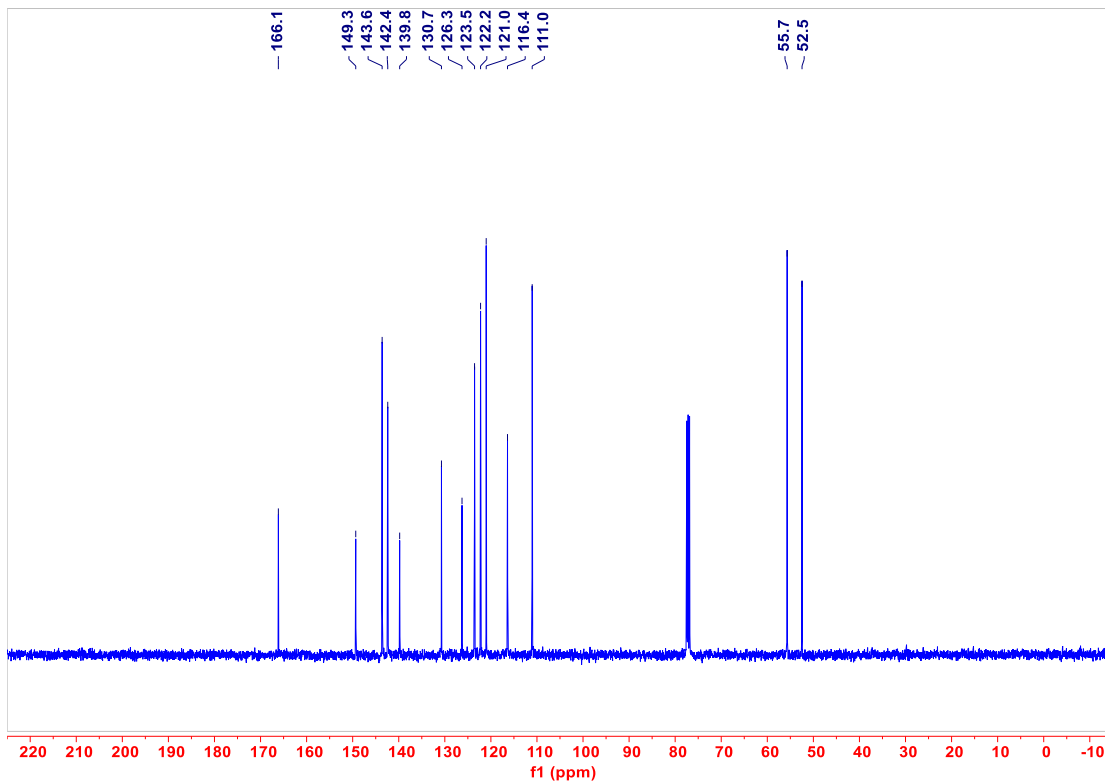




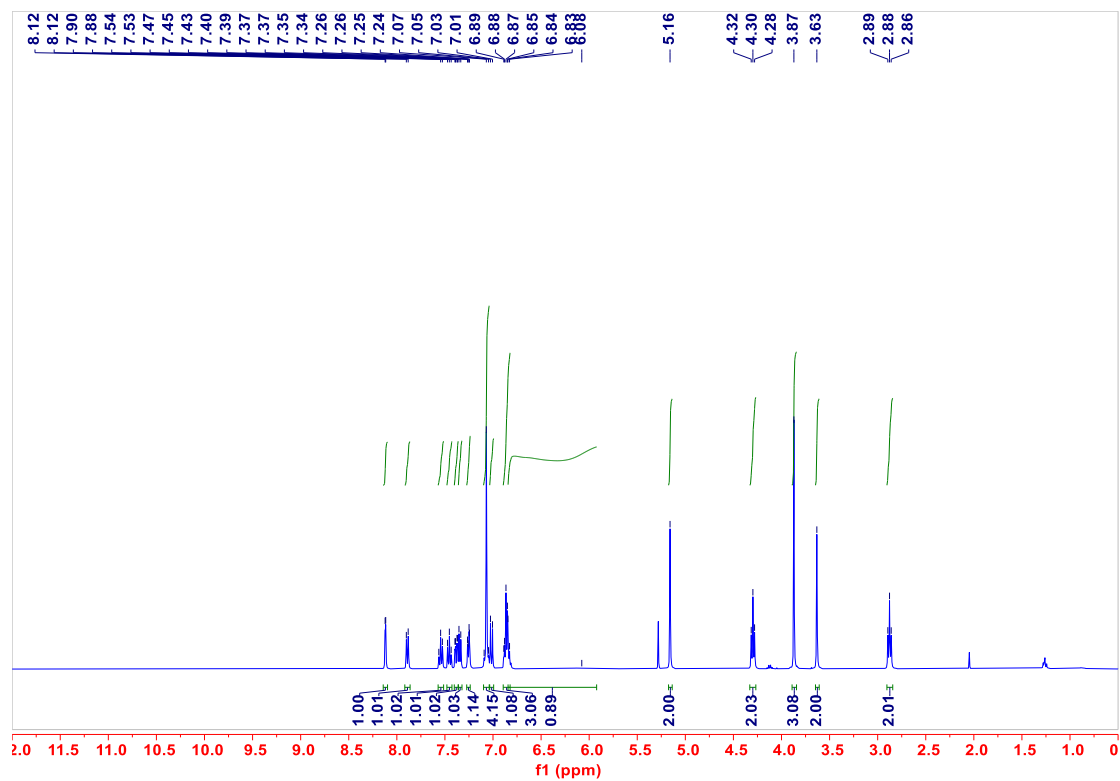


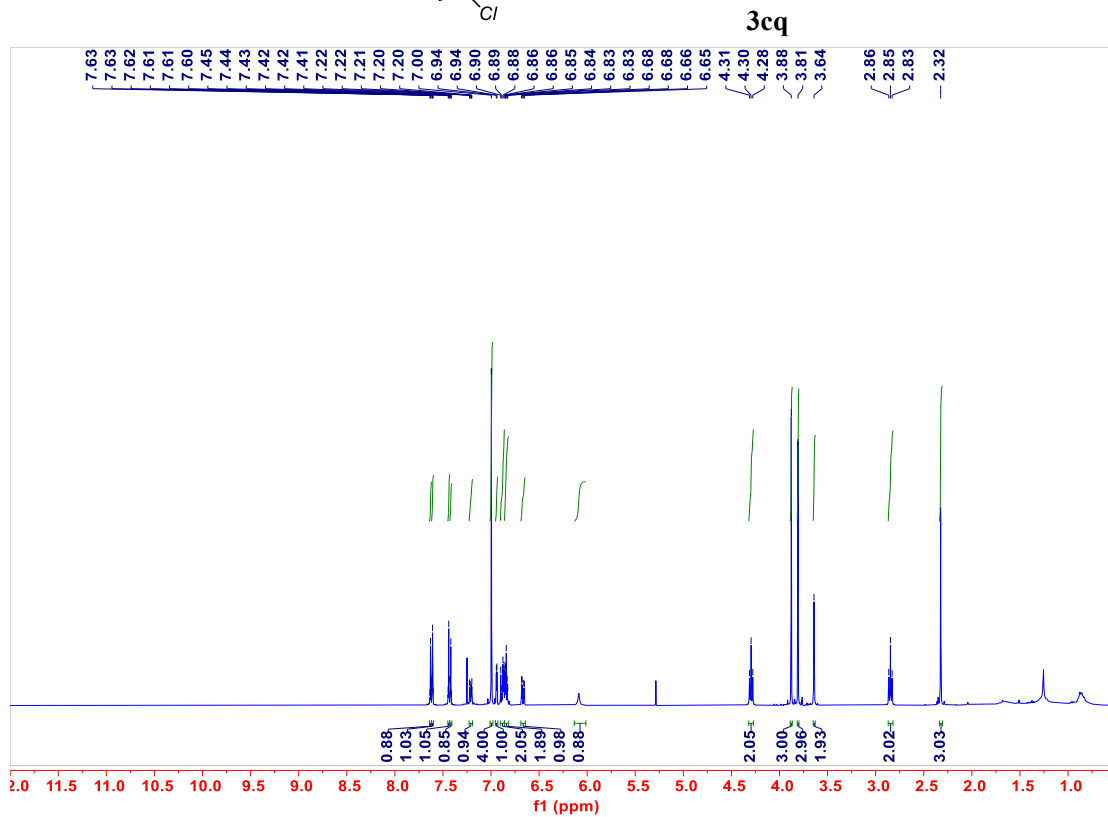
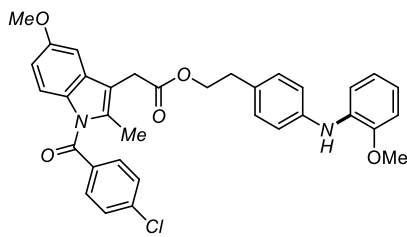
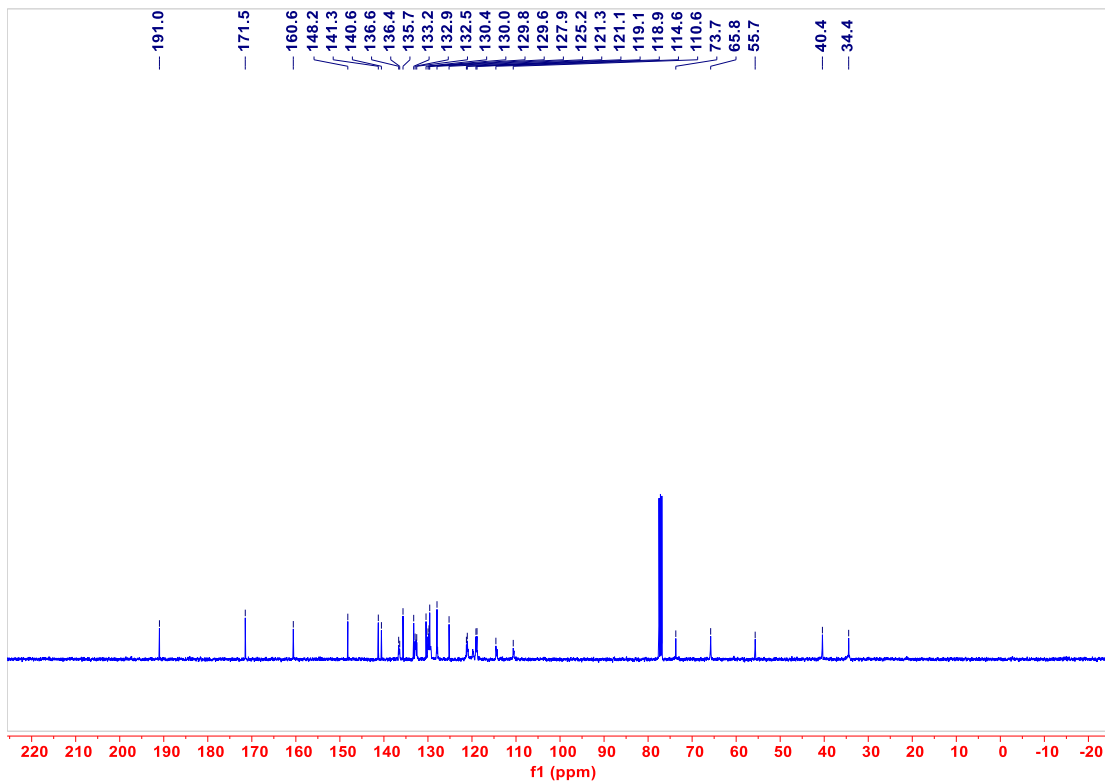


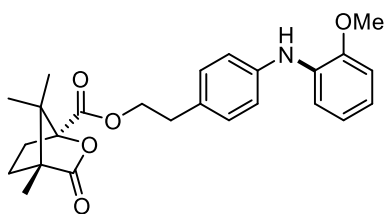
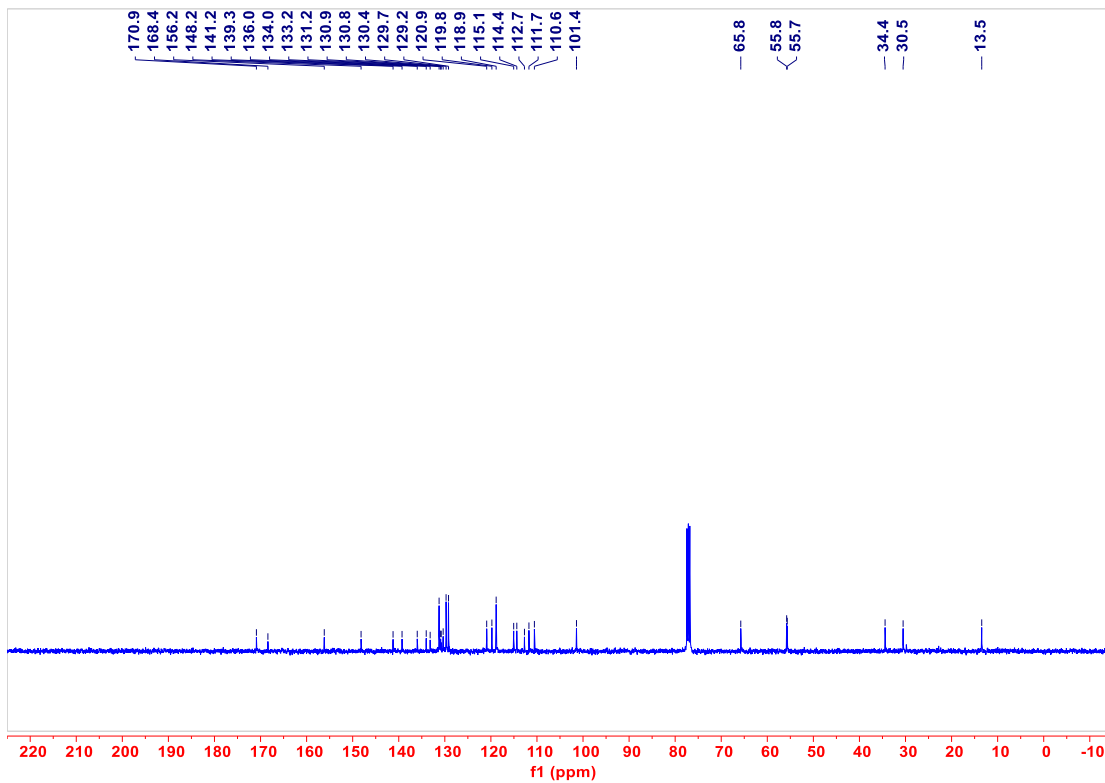




3cp







3cr

