Supporting Information

[N,P]-pyrrole $PdCl_2$ complexes catalyzed the formation of Dibenzo-α-pyrones and lactam analogues

J.V. Suárez Meneses,[1] A. Oukhrib,[2,3] M. Gouygou,[2,3] M. Urrutigoïty,[2,3] J.C. Daran,[2] M. C. Ortega-Alfaro,[4] J.G. López-Cortés.[1,*]

[1] Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán, C.P. 04510 México, D.F. México.

[2] CNRS, LCC (Laboratoire de Chimie de Coordination), 205, route de Narbonne, 31077-Toulouse, France

[3] Université de Toulouse, UPS, INPT, LCC, 31077 Toulouse, France

[4] Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán, C.P. 04510 México, D.F. México.

Table of Contents

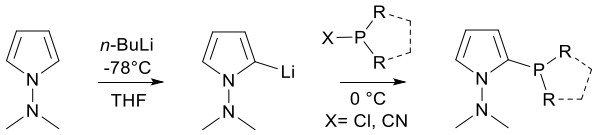
1. General considerations S2
2. Experimental procedures and characterization data S2
3. General synthesis of ligand bidentate [N,P] based on pyrrole S2
4. General procedure for complexation reaction S4
5. General synthesis of the esters S6
6. General procedure for catalytic reactions under microwave S11
7. General procedure for the synthesis of amide substrates S15
8. Preparation of 2-Iodobenzamide 9a–e. S16
9. Preparation of 2-Iodobenzamide 9f–g. S16
10. Synthesis of benzolactams 10a-g S19
11. ^{1}H, ^{13}C and ^{31}P NMR spectra and NMR spectra of Palladium Complexes S22
12. Compounds prepared for the coupling reaction S33
13. Compounds prepared by aryl-aryl coupling reaction S53
14. X-Ray data for complex 3d S68
15. References S70

1. General Considerations

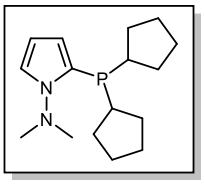
All operations were carried out under an inert atmosphere of nitrogen or argon gas using standard Schlenk techniques. Anhydrous THF was obtained by distillation under an inert atmosphere over sodium and benzophenone. Column chromatography was performed using 70–230 mesh silica gel. All reagents and solvents were obtained from commercial suppliers and used without further purification. All compounds were characterized by IR spectra, recorded on a Perkin-Elmer 283B or 1420 spectrophotometer, by means of film and KBr techniques, and all data are expressed in wave numbers (cm^{-1}). Melting points were obtained on a Melt-Temp II apparatus and are uncorrected. NMR spectra were measured with a JEOL Eclipse +300 and a Varian Gemini (200 MHz), using $CDCl_3$ and C_2D_6SO as solvents. Chemical shifts are in ppm (δ), relative to TMS. The MS-FAB$^+$ and MS-EI spectra were obtained on a JEOL SX 102A, *the values of the signals are expressed in mass/charge units (m/z), followed by the relative intensity with reference to a 100% base peak.*

2. Experimental Procedure and Characterization Data

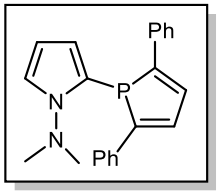
3. General synthesis of ligand bidentate [N,P] based on pyrrole.



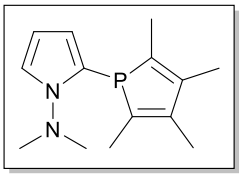
A solution of *N*,*N*-dimethyl-1*H*-pyrrol-1-amine (8.3 mmol, 1equiv) in anhydrous THF (15 mL) under nitrogen atmosphere, was cooled at -78 °C and then *n*-butyl lithium (9.9 mmol, 1.2 equiv. Sol. 2.5 M in *n*-hexane) was added dropwise by syringe. The mixture was gradually warmed to room temperature. After reaching this temperature, the reaction mixture was cooled at 0 ºC, followed by the addition of chlorodiphenylphosphine (8.3 mmol, 1equiv) and stirring at room temperature for 2 h. The solvent was evaporated at reduced pressure and the crude was purified by column chromatography. Elution with hexane/ethyl acetate.



2-(dicyclopentylphosphino)-*N*,*N*-dimethyl-1*H*-pyrrol-1-amine (2b). Colorless oil (50 %). ^{1}H NMR (300.53 MHz, $CDCl_3$) δ 7.06 (s, 1H, $H^{2}_{pyrrole}$), 6.17 (d, *J*= 8.1 Hz, 2H, $H^{3,4}_{pyrrole}$), 2.82 (s, 6H, H^{1}), 2.28 – 2.21 (m, 2H, $H^{10,12}$), 1.94 – 1.90 (m, 2H, $H^{6,11}$), 1.67 – 1.24 (m, 14H, $H^{7,8,9,10,12,13,14,15}$). ^{13}C NMR (75.58 MHz, $CDCl_3$) δ 128.9 (d, *J*= 6.2 Hz, $C_{ipso}{}^{5}_{pyrrole}$), 115.5 $C^{2}_{pyrrole}$, 112.3 (d, *J*= 2.6 Hz, $C^{3}_{pyrrole}$), 107.6 (d, *J*= 3.0 Hz, $C^{4}_{pyrrole}$), 48.1 $C^{1}_{\text{-N-(CH3)2}}$, 36.9 (d, *J*= 6.4 Hz, $C^{6,\ 11}_{cyclopenthyl}$), 31.2 (d, *J* = 6.1 Hz, $C^{10,12}_{cyclopenthyl}$), 31.0 (d, *J*= 2.8 Hz, $C^{7,15}_{cyclopenthyl}$), 26.7 (d, *J*= 7.9 Hz, $C^{9,13}_{cyclopenthyl}$), 25.8 (d, *J* = 6.5 *H*z, $C^{8,\ 14}_{cyclopenthyl}$). ^{31}P NMR (50 MHz, $CDCl_3$) δ -25.71. IR (KBr, cm^{-1}) νmax: 3096 (=C-H), 2946 (-CH). MS (DART): m/z (% x10^6): 279.12512 [M^{+1}] (18). HRMS (DART): calcd for $C_{16}H_{28}N_2P$ [M+] 279.1990; found 279.19851.

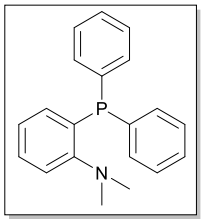


2-(2,5-diphenyl-1*H*-phosphol-1-yl)-*N*,*N*-dimethyl-1*H*-pyrrol-1-amine (2c). Yellow solid. (45 %). m.p: 64-66 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$) δ 7.55 (d, *J*= 7.8 Hz, 4H, $H_{ortho\text{-}phenyl}$), 7.29 – 7.13 (m, 8H, $H_{aromatic,}$ $H_{\beta\text{-}phosphole}$), 6.96 (s, 1H, $H^{2}_{pyrrole}$), 6.30-6.27 (m, 1H, $H^{4}_{pyrrole}$), 6.07 (q, *J*= 2.9 Hz, 1H, $H^{3}_{pyrrole}$), 2.48 (s, 6H, $H^{1}_{\text{-N-(CH3)2}}$). ^{13}C NMR (75.58 MHz, $CDCl_3$) δ 150.3 (d, *J*= 5.1 Hz, $C_{ipso}\alpha\text{-}_{phosphole}$), 137.1 (d, *J*= 16.6 Hz, $C_{ipso\text{-}phenyl}$), 131.1 (d, *J* = 12.5 Hz, $C_{\beta\text{-}phosphole}$), 128.6 $C_{para\text{-}phenyl}$, 126.8 $C_{meta\text{-}phenyl}$, 126.4 (d, *J*= 9.4 Hz, $C_{ortho\text{-}phenyl}$), 118.5 $C^{2}_{pyrrole}$, 118.3 (d, *J*= 3.6 Hz, $C_{ipso}{}^{5}_{pyrrole}$, 116.9 $C^{4}_{pyrrole}$, 108.5 (d, *J*= 9.4 Hz, $C^{3}_{pyrrole}$), 47.9 $C^{1}_{\text{-N-(CH3)}}$. ^{31}P NMR (50 MHz, $CDCl_3$) δ -27.02. IR (KBr, cm^{-1}) ν_{max}: 3056 (=C-H), 2960 (-CH), 1591(C=C_{arom}), 756 (Ph $_{arom\ monosust}$). MS (DART): *m/z (%* x10^6*)*: 345 [M^{+}] (35).



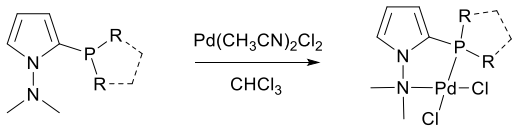
***N*,*N*-dimethyl-2-(2,3,4,5-tetramethyl-1*H*-phosphol-1-yl)-1*H* pyrrol-1-amine (2d).** Yellow solid. (43 %). m.p: 58-60 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$) δ 6.98 (q, *J*= 2.6 Hz, 1H, $H^{2}_{pyrrole}$), 6.05 (t, *J*= 3.0 Hz, 1H, $H^{4}_{pyrrole}$), 5.70 (dd, *J*= 2.2, 1.1 Hz, 1H, $H^{3}_{pyrrole}$), 2.74 (s, 6H, $H^{1}_{\text{-N-(CH3)2}}$) 1.93 (d, *J*= 10.7 Hz, 6H,

$H^{7,13}{}_{CH3CP}$), 1.82 (d, *J*= 1.9 Hz, 6H, $H^{9,11}{}_{CH3}$). ^{13}C NMR (75.58 MHz, $CDCl_3$) δ 142.2 (d, *J*= 13.3 Hz, $C_{ipso}\alpha$-$_{phosphole}$), 133.6 (d, *J*= 5.2 Hz, C_{ipso} β-phosphole), 122.9 $C_{ipso}{}^{5}{}_{pyrrole}$), 116.5 $C^{2}{}_{pyrrole}$, 111.5 (d, *J*= 3.4 Hz,$C^{4}{}_{pyrrole}$, 108.5 (d, *J*= 3.9 Hz, $C^{3}{}_{pyrrole}$), 48.2 $C^{1}{}_{\text{-N-(CH3)}}$, 14.0 (d, *J*= 3.2 Hz, $C^{7,13}{}_{CH3CP}$), 13.2 (d, *J*= 21.5 Hz, $C^{9,11}{}_{CH3}$). ^{31}P NMR (50 MHz, $CDCl_3$) δ -12.25. IR (KBr, cm^{-1}) ν_{max}: 2909 (-CH), 1512(C=C_{arom}). MS (DART): *m/z (%* x10^6*)*: 249.08447 [M^{+1}] (16). HRMS (DART): calcd for $C_{14}H_{22}N_2P$ [M+] 249.15206; found 249.15144.

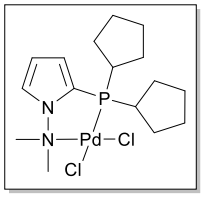


2-(diphenylphosphino)-*N*,*N*-dimethylaniline (4)[1]. White solid. (75 %). m.p: 110-112 °C. ^1H NMR (300.53 MHz, $CDCl_3$) δ 7.31-7.21 (m, 12H, $H^{3,6,9,10,11}{}_{aromatic}$), 6.98 (t, *J*= 7.4 Hz, 1H, $H^{4}{}_{aromatic}$), 6.80 (m, 1H, $H^{5}{}_{aromatic}$), 2.60 (s, 6H, $H^{1}{}_{\text{-N-(CH3)2}}$). ^{13}C NMR (75.58 MHz, $CDCl_3$) δ 158.1 (d, *J*= 19.5 Hz, $C^{2}{}_{ipsoN\text{-}aromatic}$), 138.3 (d, *J*= 11.8 Hz, $C^{8}{}_{ipsoP\text{-}aromatic}$), 134.4 $C^{6}{}_{N\text{-}aromatic}$, 133.9 (d, *J*= 20 Hz, $C^{9,13}{}_{P\text{-}aromatic}$, 129.9 $C^{4}{}_{N\text{-}aromatic}$, 128.4 (d, *J*= 2.0 Hz, $C^{10,12}{}_{P\text{-}aromatic}$), 128.3 $C^{11}{}_{P\text{-}aromatic}$, 124.5 $C^{3}{}_{N\text{-}aromatic}$, 120.7 (d, *J*= 2.6 Hz, $C^{5}{}_{N\text{-}aromatic}$), 45.6 (d, *J*= 3.4 Hz, $C^{1}{}_{\text{-N-(CH3)}}$). ^{31}P NMR (50 MHz, $CDCl_3$) δ -14.49. IR (KBr, cm^{-1}) ν_{max}: 3056 (=C-H), 2960 (-CH), 1591(C=C_{arom}), 756 (Ph arom monosust). MS (DART): *m/z (%* x10^3*)*: 306 [M^{+1}] (1200). HRMS (DART): calcd for $C_{20}H_{21}NP$ [M+] 306.14116; found 306.14179.

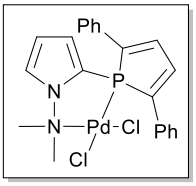
4. General procedure for complexation reaction



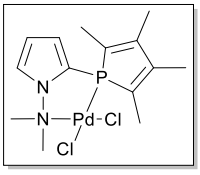
To a solution of **ligand** (0.5 mmol) in chloroform (15 mL) was added [$Pd(CH_3CN)_2Cl_2$] (0.5 mmol), then the mixture was stirred for 4 h at room temperature. The solvent was removed under vacuum leaving a yellow residue which was dissolved in dichloromethane. The resulting solution was filtered through celite and finally it is concentrated to a minimum and hexane was added to precipitate the complex, which was filtered, washed with hexane, and dried under vacuum.



Palladium dichloro[2-(dicyclopentylphosphino-k*P*)-*N*,*N*-dimethyl-1*H*-pyrrol-1-amine-k*N*] (3b). Yellow solid. (95 %). m.p: 280 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$) δ 7.26-7.23 (m, 1H, $H^{2}_{pyrrole}$), 6.63-6.61 (m, 1H, $H^{4}_{pyrrole}$), 6.34-6.32 (m, 1H, $H^{3}_{pyrrole}$), 3.66 (s, 6H, H^{1}), 2.67 (m, 2H, $H^{10,12}$), 2.38 – 2.30 (m, 2H, $H^{6,11}$), 2.05–1.66 (m, 14H, $H^{7,8,9,10,12,13,14,15}$). ^{13}C NMR (75.58 MHz, $CDCl_3$) δ 120.2 (d, *J*= 6.2 Hz, $C^{5}_{ipso\text{-}pyrrole}$), 119.4 $C^{2}_{pyrrole}$, 116.4 (t, *J*= 7.7, 6.4 Hz, $C^{4}_{pyrrole}$), 111.4 $C^{3}_{pyrrole}$), 57.2 $C^{1}_{\text{-N-(CH3)2}}$, 37.8 (d, *J*= 37.4 Hz, $C^{6,\,11}_{cyclopenthyl}$), 29.7 (d, *J* = 2.7 Hz, $C^{10,12}_{cyclopenthyl}$), 29.3 (d, *J*= *2.9 Hz*, $C^{7,15}_{cyclopenthyl}$), 26.4 (d, *J*= 10.1 Hz, $C^{9,13}_{cyclopenthyl}$), 25.6 (d, *J*= 12.2 Hz, $C^{8,\,14}_{cyclopenthyl}$). ^{31}P NMR (50 MHz, $CDCl_3$) δ 40.54. IR (KBr, cm^{-1}) νmax: 3103 (=C-H), 2952 (-CH). MS (FAB^{+}): m/z (100 %): 421 [M^{+1}-Cl] (55). HRMS (FAB^{+}): calcd for $C_{16}H_{27}ClN_2PPd$ [M+] 421.0633; found 421.0639.

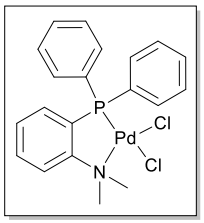


Palladium dichloro[2-(2,5-diphenyl-1*H*-phosphol-1-yl-k*P*)-*N*,*N*-dimethyl-1*H*-pyrrol-1-amine-k*N*] (3c). Orange solid. (86 %). m.p: 280 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$) δ 7.88 (d, *J*= 7.6 Hz, 4H, $H_{ortho\text{-}phenyl}$), 7.62 – 7.08 (m, 10H, $H_{aromatic,}$ $H_{\beta\text{-}phosphole}$, $H^{2}_{pyrrole}$), 6.52 (m, 1H, $H^{4}_{pyrrole}$), 6.17 (m, 1H, $H^{3}_{pyrrole}$), 3.70 (s, 6H, $H^{1}_{\text{-N-(CH3)2}}$). ^{31}P NMR (50 MHz, $CDCl_3$) δ 16.5.). MS (FAB^{+}): m/z (100 %): 487 [M^{+1}-Cl] (5). HRMS (FAB^{+}): calcd for $C_{22}H_{21}ClN_2PPd$ [M+] 487.0162; found 487.0170.



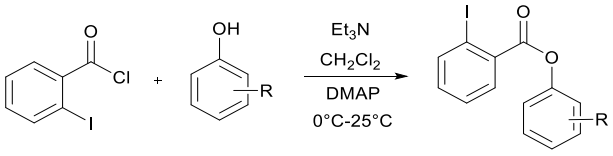
Palladium dichloro[*N*,*N*-dimethyl-2-(2,3,4,5-tetramethyl-1*H*-phosphol-1-yl-k*P*)-1*H*-pyrrol-1-amine-k*N*] (3d). Yellow solid. (94 %). m.p: 280 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$) δ 7.30 (m, 1H, $H^{2}_{pyrrole}$), 6.59 (m, 1H, $H^{4}_{pyrrole}$), 6.05 (m, 1H, $H^{3}_{pyrrole}$), 3.72 (s, 6H, $H^{1}_{\text{-N-(CH3)2}}$) 2.06 - 1.97 (m, 12H, $H^{7,9,11,13}_{CH3CP}$). ^{13}C NMR (75.58 MHz, $CDCl_3$) δ 150.2 (d, *J*= 21.5 Hz, $C\alpha\text{-}_{phosphole}$), 124.9, 124.1 $C_{\beta\text{-}phosphole}$, 1117.8 (d, *J*= 6.8 Hz, $C^{2}_{pyrrole}$), 116.9 $C^{5}_{ipso\text{-}pyrrole}$, 116.6 (d, *J*= 7.2 Hz,$C^{4}_{pyrrole}$), 110.8 (d, *J*= 2.9 Hz, $C^{3}_{pyrrole}$), 57.2 $C^{1}_{\text{-N-(CH3)}}$, 14.5 (d, *J*= 14.2 Hz, $C^{7,13}_{CH3CP}$), 11.4 (d, *J*= 17.0 Hz,

$C^{9,11}{}_{CH3}$). ^{31}P NMR (50 MHz, $CDCl_3$) δ 28.91. IR (KBr, cm^{-1}) νmax: 3128 (=C-H), 2912 (-CH). MS (FAB^+) m/z (100 %): 391 [M^{+1}-Cl] (5). HRMS (FAB^+): calcd for $C_{14}H_{21}ClN_2PPd$ [M+] 391.0170; found 391.0170.



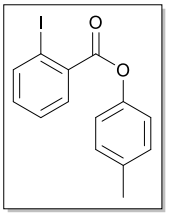
Palladium dichloro[2-(diphenylphosphino-k*P*)-*N*,*N*-dimethylaniline-k*N*] (5).[1] Yellow solid. (75 %). m.p: 280 °C. ^1H NMR (300.53 MHz, $CDCl_3$) δ 7.59 (m, 4H, $H^{9,19,13,15}{}_{aromatic}$), 7.73 (s, 2H, $H^{10,17}{}_{aromatic}$), 7.61-7.56 (m, 2H, $H^{5,3}{}_{aromatic}$), 7.51-7.38 (m, 6H, $H^{4,6,11,12,16,18}{}_{aromatic}$), 3.56 (s, 6H, $H^1{}_{-N-(CH3)2}$). ^{13}C NMR (75.58 MHz, $CDCl_3$) δ 160.9 (d, *J* = 17.2 Hz, $C^2{}_{ipsoN-aromatic}$), 134.7 (d, *J* = 2.2 Hz, $C^{8,14}{}_{ipsoP-aromatic}$), 133.8 (d, *J*= 11.3 Hz, $C^{11,12,16,18}{}_{P-aromatic}$), 136.6 $C^{10,17}{}_{P-Aromatic}$, 133.7 $C^9{}_{P-aromatic}$, 128.9 $C^3{}_{aromatic}$, 128.4 (d, *J* = 2.0 Hz, $C^{12}{}_{P-aromatic}$), 132.4 (d, *J*= 3.2 Hz, $C^6{}_{N-aromatic}$), 130.3 (d, *J* = 6.7 Hz, $C^7{}_{N-aromatic}$), 129.2 (d, *J*= 12.2 Hz, $C^{9,13,15,19}{}_{P-aromatic}$), 128.2 $C^4{}_{N-aromatic}$, 127.3 $C^5{}_{N-aromatic,}$ 122.6 (d, *J*= 12.4 Hz, $C^3{}_{N-aromatic}$), 55.5 $C^1{}_{-N-(CH3)}$. ^{31}P NMR (50 MHz, $CDCl_3$) δ 42.11. IR (KBr, cm^{-1}) ν_{max}: 3052 (=C-H), 2983(-CH), 1578(C=C_{arom}), 687 (Ph $_{arom\ monosust}$). MS (FAB^+): m/z (100 %): 448 [M^{+1}-Cl] (10). HRMS (FAB^+): calcd for $C_{20}H_{20}ClNPPd$ [M+] 448.0063; found 448.0061.

5. General synthesis of the esters:

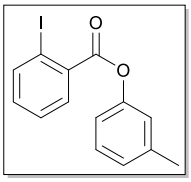


To a solution of the corresponding phenol (1.84 mmol, 1 equiv) in anhydrous dichloromethane (20 mL) at 0 ºC, was added dropwise a solution of triethylamine (2.75 mmol, 1,5 equiv) and a catalytic amount of 4-DMAP in anhydrous dichloromethane (5 mL). After stirring for 30 min at 0 °C a solution of the appropriate 2-iodobenzyl chloride (1.84 mmol, 1.0 equiv.) dissolved in anhydrous dichloromethane (5 ml) was added to the reaction mixture was allowed to warm to room temperature and stirred for 3 h. The mixture was extracted with CH_2Cl_2, the organic phase was washed with a saturated solution of $NaHCO_3$, the organic phase was dried with sodium sulfate and the solvent was

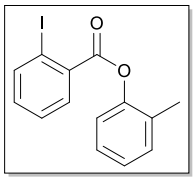
evaporated under vacuum. The crude product was purified by flash chromatography using silica-gel and hexane-ethyl acetate 95:5 as eluent.



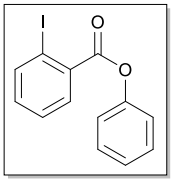
***p*-tolyl-2-iodobenzoate (6a)**: White solid. Yield (95 %). m.p: 40-42 ° C. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm): δ 8.07-7.92 (m, 2H, $H_{arom}^{2,5}$), 7.43 (t, *J*= 7.6 Hz, 1H, H_{arom}^{4}), 7.26-7.07 (m, 5H, $H_{arom}^{3,9,10,13,14}$), 2.35 (s, 3H, $H_{CH_3}^{12}$). ^{13}C NMR (75.58 MHz, $CDCl_3$, ppm): δ 165.2 ^{7}C=O, 148.5 $C_{arom}^{8}{}_{(ipso)}$, 141.6 C_{arom}^{2}, 135.8 $C_{arom}^{11}{}_{(ipso)}$, 134.4 $C_{arom}^{6}{}_{(ipso)}$, 133.2 C_{arom}^{3}, 131.5 C_{arom}^{5}, 130.1 $C_{arom}^{10,13}$, 128.1 C_{arom}^{4}, 121.3 $C_{arom}^{9,14}$, 94.7 $C_{arom}^{1}{}_{(ipso)}$, 21.0 C_{arom}^{12}. IR (KBr, cm^{-1}) ν_{max}: 3084 (=C-H), 1734 (C=O), 1578 (C=C_{arom}), 738 (Ph $_{arom\ 1,2\ disust}$). MS (DART): *m/z (% x10^{3})*: 338 [M^{+}] (592).



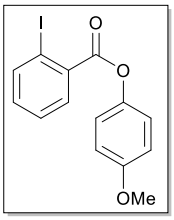
***m*-tolyl-2-iodobenzoate (6b)[2]**: Colorless oil. Yield (93 %). ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm): δ 8.01 (t, *J*= 7.0 Hz, 2H, $H_{arom}^{2,5}$), 7.42 (t, *J*= 7.6 Hz, 1H, H_{arom}^{4}), 7.29 (t, *J*= 7.9 Hz, 1H, H_{arom}^{3}), 7.16 (td, *J*= 7.8, 1.4 Hz, 1H, H_{arom}^{12}), 7.07 (m, 3H, $H_{arom}^{7,9,13}$), 2.37 (s, 3H, $H_{CH_3}^{11}$). ^{13}C NMR (75.58 MHz, $CDCl_3$, ppm): δ 165.0 ^{7}C=O, 150.7 $C_{arom}^{8}{}_{(ipso)}$, 141.7 C_{arom}^{2}, 139.8 $C_{arom}^{10}{}_{(ipso)}$, 134.3 $C_{arom}^{6}{}_{(ipso)}$, 133.3 C_{arom}^{3}, 131.6 C_{arom}^{5}, 129.3 C_{arom}^{12}, 128.2 C_{arom}^{4}, 127.0 C_{arom}^{13}, 122.2 C_{arom}^{9}, 118.6 C_{arom}^{14}, 94.7 $C_{arom}^{1}{}_{(ipso)}$, 21.5 C_{CH3}^{11}. IR (KBr, cm^{-1}) ν_{max}: 3059 (=C-H), 1740 (C=O), 1580 (C=C_{arom}), 734 (Ph $_{arom\ 1,2\ disust}$). MS (DART): *m/z (% x10^{6})*: 339 [M^{+}] (32).



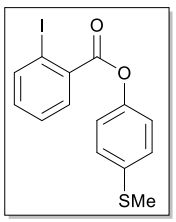
***o*-tolyl-2-iodobenzoate (6c):** Colorless oil. Yield (91 %). ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm): δ 8.11-8.00 (m, 2H, $H_{arom}^{2,5}$), 7.45 (t, *J*= 7.6 Hz, 1H, H_{arom}^{4}), 7.31-7.12 (m, 5H, $H_{arom}^{3,11,12,13,14}$), 2.26 (s, 3H, $H_{CH_3}^{10}$). ^{13}C NMR (75.58 MHz, $CDCl_3$, ppm): δ 164.7 ^{7}C=O, 149.4 $C_{arom}^{8}{}_{(ipso)}$, 141.8 C_{arom}^{2}, 134.2 $C_{arom}^{6}{}_{(ipso)}$, 133.3 C_{arom}^{3}, 131.4 $C_{arom}^{5,11}$ (d, *J*= 10.2 Hz), 130.3 $C_{arom}^{9}{}_{(ipso)}$, 128.2 C_{arom}^{4}, 127.2 C_{arom}^{12}, 126.4 C_{arom}^{13}, 122.0 C_{arom}^{14}, 94.9 $C_{arom}^{1}{}_{(ipso)}$, 16.6 C_{CH3}^{10}. IR (KBr, cm^{-1}) ν_{max}: 3059 (=C-H), 1740 (C=O), 1580 (C=C_{arom}), 737 (Ph $_{arom\ 1,2\ disust}$). MS (DART): *m/z (% x10^{3})*: 338.9570 [M^{+}] (592).



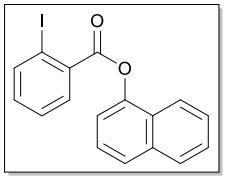
phenyl-2-iodobenzoate (6d)[3]: Colorless oil. Yield: (91 %). ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm): δ 8.01-7.97 (m, 2H, $H_{arom}^{2,5}$), 7.39 (t, *J*= 7.8 Hz, 3H, $H_{arom}^{10,11,12}$), 7.30-7.19 (m, 3H, $H_{arom}^{4,9,13}$), 7.13 (td, *J*= 7.9, 1,6 Hz, 1H, H_{arom}^{3}). ^{13}C NMR (75.58 MHz, $CDCl_3$, ppm): δ 165.0 ^{7}C=O, 150.8 $C_{arom}^{8}{}_{(ipso)}$, 141.7 C_{arom}^{2}, 134.2 $C_{arom}^{6}{}_{(ipso)}$, 133.4 C_{arom}^{3}, 131.6 C_{arom}^{5}, 129.7 $C_{arom}^{10,12}$, 128.2 C_{arom}^{4}, 126.3 C_{arom}^{11}), 121.7 $C_{arom}^{9,13}$ 94.8 $C_{arom}^{1}{}_{(ipso)}$. IR (KBr, cm^{-1}) ν_{max}: 3064 (=C-H), 1738 (C=O), 1584 (C=C_{arom}), 735 (Ph $_{arom\ 1,2\ disust}$). MS (DART): *m/z (% x10^3)*: 324.1172 [M^+] (593).



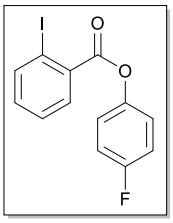
4-methoxyphenyl-2-iodobenzoate (6e)[3]. White solid. Yield (95 %).m.p: 108-110 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm): δ 8.03 (dd, , *J*= 11.0, 7.9 Hz, 2H, $H_{arom}^{2,5}$), 7.46 (t, *J*= 7.6 Hz, 1H, H_{arom}^{4}), 7.31-7.10 (m, 3H, $H_{arom}^{3,\ 9,\ 14}$) 6.94 (d, *J* = 9.0 Hz, 1H, $H_{arom}^{10,13}$), 3.81 (s, 3H, $H_{OCH_3}^{12}$). ^{13}C NMR (75.58 MHz, $CDCl_3$, ppm): δ 165.3 ^{7}C=O, 157.5 $C_{arom}^{11}{}_{(ipso)}$, 144.2 $C_{arom}^{8}{}_{(ipso)}$, 141.6 C_{arom}^{1}, 134.3 $C_{arom}^{6}{}_{(ipso)}$, 133.2 C_{arom}^{3}, 131.5 C_{arom}^{5}, 128.1 C_{arom}^{4}, 122.4 $C_{arom}^{9,14}$, 114.6 $C_{arom}^{10,13}$, 94.6 $C_{arom}^{1}{}_{(ipso)}$., 55.7 C $_{OCH_3}{}^{12}$. IR (KBr, cm^{-1}) ν_{max}: 3077 (=C-H), 1736 (C=O), 1577 (C=C_{arom}), 745 (Ph $_{arom\ 1,2\ disust}$). MS (DART): *m/z (% x10^3)*: 354.9477 [M^+] (7653).



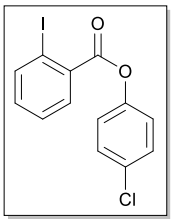
4-(methylthio)phenyl-2-iodobenzoate(6f). White solid. Yield (92 %).m.p: 78-80 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm): δ 8.00 (t, , *J*= 8.1 Hz, 2H, $H_{arom}^{2,5}$), 7.42 (t, *J*= 7.6 Hz, 1H, H_{arom}^{4}), 7.29 (d, *J*= 8.7 Hz, 2H, $H_{arom}^{10,13}$), 7.17 (d, *J*= 8.6 Hz, 3H, $H_{arom}^{3,9,14}$), 2.45 (s, 3H, $H_{SCH_3}^{12}$). ^{13}C NMR (75.58 MHz, $CDCl_3$, ppm): δ 164.9 ^{7}C=O, 148.4 $C_{arom}^{8}{}_{(ipso)}$, 141.7 C_{arom}^{2}, 136.2 $C_{arom}^{6}{}_{(ipso)}$, 134.1 $C_{arom}^{11}{}_{(ipso)}$, 133.4 C_{arom}^{3}, 131.6 C_{arom}^{5}, 128.2 C_{arom}^{4}, 128.0 $C_{arom}^{10,13}$, 122.2$C_{arom}^{9,14}$, 94.7 $C_{arom}^{1}{}_{(ipso)}$, 16.6 C $_{SCH_3}{}^{12}$. IR (KBr, cm^{-1}) ν_{max}: 3062 (=C-H), 1737 (C=O), 1576 (C=C_{arom}), 744 (Ph $_{arom\ 1,2\ disust}$).). MS (DART): *m/z (% x10^3)*: 371 [M^+] (2700).



Naphthalen-1-yl 2-iodobenzoate (6g)[4]: White solid. Yield: (93 %). mp: 60-62 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm): δ 8.24 (dd, *J*= 7.8, 1.2 Hz, 1H, H_{arom}^{10}), 8.11 (d, *J*= 7.9 Hz, 1H, H_{arom}^{13}), 8.03-7.92 (m, 1H, H_{arom}^{2}), 7.90-7.86 (m, 1H, H_{arom}^{5}) 7.78 (d, *J*= 8.1 Hz, 1H, H_{arom}^{3}), 7.58-7.46 (m, 4H, $H_{arom}^{4,11,12,15}$), 7.42 (d, *J*= 7.4 Hz,1H, H_{arom}^{16}), 7.29-7.19 (m, 1H, H_{arom}^{17}). ^{13}C NMR (75.58 MHz, $CDCl_3$, ppm): δ 164.8 ^{7}C=O, 146.7 $C_{arom}^{8}{}_{(ipso)}$, 142.0 C_{arom}^{2}, 134.8 $C_{arom}^{6}{}_{(ipso)}$, 134.0 $C_{arom}^{9}{}_{(ipso)}$, 133.4 C_{arom}^{3}, 131.7 C_{arom}^{5}, 128.2 (d, *J* =7.8 Hz, $C_{arom}^{13,15}$),126.9 $C_{arom}^{14}{}_{(ipso)}$, 126.6 (d, *J*= 4.9 Hz, $C_{arom}^{12,16}$), 126.4 C_{arom}^{4}, 125.5 C_{arom}^{11}, 121.4 C_{arom}^{10}, 118.2 C_{arom}^{17}, 95.0 $C_{arom}^{1}{}_{(ipso)}$. IR (KBr, cm^{-1}) ν_{max}: 3056 (=C-H), 1741 (C=O), 1578 (C=C_{arom}), 733 (Ph $_{arom\ 1,2\ disust}$).). MS (DART): *m/z (% x10^{3})*: 375 [M^{+}] (5300).

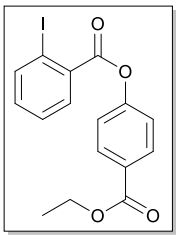


4-fluorophenyl-2-iodobenzoate (6h). Colorless oil. Yield (89 %). ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm): δ 8.07 (t, *J*= 8.4 Hz, 2H, $H_{arom}^{2,5}$), 7.49 (t, *J*=7.6 Hz, 1H, H_{arom}^{4}), 7.26 (m, 5H, $H_{arom}^{3,9,10,11,12}$). ^{13}C NMR (75.58 MHz, $CDCl_3$, ppm): δ 164.9 ^{7}C=O, 160.42 (d, *J* = 244.6 Hz, $C_{arom}^{11}{}_{(ipso)}$,), 146.5 (d, *J*= 2.9 Hz, $C_{arom}^{8}{}_{(ipso)}$), 141.7 C_{arom}^{2}, 133.9 $C_{arom}^{6}{}_{(ipso)}$, 133.5 C_{arom}^{3}, 131.6 C_{arom}^{5}, 128.2 C_{arom}^{4}, 123.1 (d, *J* = 8.5 Hz, $C_{arom}^{9,13}$), 116.4 C_{arom}^{12}, 116.1 C_{arom}^{10}, 94.8 $C_{arom}^{1}{}_{(ipso)}$. IR (KBr, cm^{-1}) ν_{max}: 3068 (=C-H), 1740 (C=O), 1498 (C=C_{arom}), 735 (Ph $_{arom\ 1,2\ disust}$). MS (DART): *m/z (% x10^{6})*: 343 [M^{+}] (20).

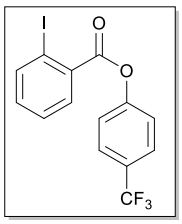


4-chlorophenyl-2-iodobenzoate (6i). White solid. Yield (90 %), m.p: 54-56 ° C. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm): δ 8.10-8.793 (m, 2H, $H_{arom}^{2,5}$), 7.46 (t, *J*= 7.6 Hz, 1H, H_{arom}^{4}), 7.38 (d, *J*= 8.8 Hz, 2H, $H_{arom}^{10,12}$), 7.20 (d, *J*= 8.7 Hz, 2H, $H_{arom}^{9,13}$). ^{13}C NMR (75.58 MHz, $CDCl_3$, ppm): δ 164.6 ^{7}C=O, 149 $C_{arom}^{8}{}_{(ipso)}$, 141.8 C_{arom}^{2}, 133.7 $C_{arom}^{6}{}_{(ipso)}$, 133.5 C_{arom}^{3}, 131.6 C_{arom}^{5}, 131.5 $C_{arom}^{11}{}_{(ipso)}$, 129.6 $C_{arom}^{10,12}$, 128.2 C_{arom}^{4}, 123.0 $C_{arom}^{9,13}$), 94.8 $C_{arom}^{1}{}_{(ipso)}$. IR (KBr, cm^{-1}) ν_{max}: 3064 (=C-H), 1736 (C=O), 1584 (C=C_{arom}), 806 (Ph $_{arom\ 1,4\ disust}$), 733 (Ph $_{arom\ 1,2\ disust}$). MS (DART):

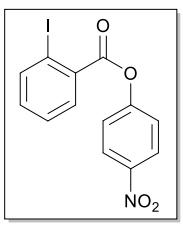
m/z (% x10^3): 358.9009 [M^+] (719.2), 360.8958 [M^{+2}] (300).



4-(ethoxycarbonyl)phenyl-2-iodobenzoate (6j). White solid. Yield (96 %), m.p: 48-50 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm): δ 8.13 (d, *J* = 8.6 Hz, 2H, $H_{arom}^{10,15}$), 8.04 (t, *J* = 6.8 Hz, 2H, $H_{arom}^{2,5}$), 7.46 (t, *J* = 7.6 Hz, 1H, H_{arom}^{4}), 7.34 (d, *J* = 8.6 Hz, 2H, $H_{arom}^{9,16}$). 7.21 (t, *J* = 7.6 Hz, 1H, H_{arom}^{3}), 4.38 (q, *J* = 7.1 Hz, 2H, $H_{CH_2}^{13}$), 1.39 (d, *J* = 7.1 Hz, 3H, $H_{CH_3}^{14}$). ^{13}C NMR (75.58 MHz, $CDCl_3$, ppm): δ 165.8 ^{7}C=O, 164.2 ^{12}C=O, 154.21 $C_{arom}^{8}{}_{(ipso)}$, 141.8 C_{arom}^{2}, 133.6 $C_{arom}^{6}{}_{(ipso)}$, 133.5 C_{arom}^{3}, 131.7 C_{arom}^{5}, 131.2 $C_{arom}^{10,15}$, 128.4 $C_{arom}^{11}{}_{(ipso)}$, 128.2 C_{arom}^{4}, 121.6 $C_{arom}^{9,16}$, 94.8 $C_{arom}^{1}{}_{(ipso)}$, 61.2 $C_{CH_2}^{13}$, 14.4 $C_{CH_3}^{14}$. IR (KBr, cm^{-1}) ν_{max}: 3104 (=C-H), 1741 (C=O), 1666 (C=O), 1570 (C=C_{arom}), 741 (Ph $_{arom\ 1,2\ disust}$). MS (DART): *m/z (%* x10^6*)*: 396 [M^+] (15.5).



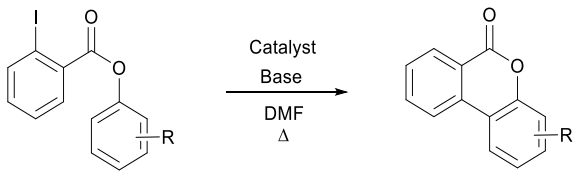
4-(trifluoromethyl)phenyl-2-iodobenzoate (6k). White solid. Yield (90 %), m.p: 42-44 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm): δ 8.06 (td, *J* = 8.4, 8.0, 1.2 Hz, 2H, $H_{arom}^{2,5}$), 7.71 (d, *J* = *8.5* Hz, 2H, $H_{arom}^{11,12}$), 7.49 (td, *J* = 7.7, 1.1 Hz, 1H, H_{arom}^{4}), 7.39 (d, *J* = 8.4 Hz, 2H, $H_{arom}^{9,10}$), 7.24 (td, *J* = 7.7, 1.7 Hz, 1H, H_{arom}^{3}). ^{13}C NMR (75.58 MHz, $CDCl_3$, ppm): δ 164.3 ^{7}C=O, 153.1 $C_{arom}^{8}{}_{(ipso)}$, 141.9 C_{arom}^{2}, 133.6 C_{arom}^{3}, 133.4 $C_{arom}^{6}{}_{(ipso)}$, 131.7 C_{arom}^{5}, 129.3-127.8 $C_{arom}^{11}{}_{(ipso)}$, 128.2 C_{arom}^{4}, 127.0 $C_{arom}^{10,13}$(q, *J*= 3.7 Hz), 122.2 $C_{arom}^{9,14}$), 125.7 $C_{CF_3}^{12}{}_{(ipso)}$, 94.8 $C_{arom}^{1}{}_{(ipso)}$. IR (KBr, cm^{-1}) ν_{max}: 1739 (C=O), 1579 (C=C_{arom}), 815 (Ph $_{arom\ 1,4\ disust}$), 738 (Ph $_{arom\ 1,2\ disust}$) MS (DART): *m/z (%* x10^3*)*: 393 [M^+] (4800).



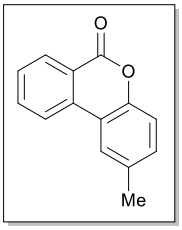
4-nitrophenyl 2-iodobenzoate (6l)[5]: Yelow solid. Yield (90 %), m.p: 100-102 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm): δ 8.33 (d, *J* = 9.0 Hz, 2H, $H_{arom}^{10,12}$), 8.08 (m, 2H, $H_{arom}^{2,5}$), 7.49 (m, 3H, $H_{arom}^{4,9,13}$), 7.28 (t, *J* = 7.6 Hz, 1H, H_{arom}^{3}). ^{13}C NMR (75.58 MHz, $CDCl_3$, ppm): δ 163.8 ^{7}C=O, 155.4 $C_{arom}^{8}{}_{(ipso)}$, 145.5 $C_{arom}^{11}{}_{(ipso)}$, 142.0 C_{arom}^{2}, 133.9 C_{arom}^{3}, 133.0 $C_{arom}^{6}{}_{(ipso)}$, 131.8 C_{arom}^{5}, 128.3

C_{arom}^{4}, 125.3 $C_{arom}^{10,12}$, 122.6 $C_{arom}^{9,13}$, 95.0 $C_{arom}^{1}{}_{(ipso)}$. IR (KBr, cm^{-1}) ν_{max}: 3116 (=C-H), 1743 (C=O), 1589 (C=C_{arom}), 736 (Ph $_{arom\ 1,2\ disust}$). MS (DART): *m/z (%* $x10^{3}$*)*: 369.9206 [M^{+}] (442).

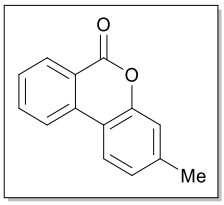
6. General procedure for catalytic reactions under microwave



A 30 mL microwave-transparent process vial was filled with the substrate (0.62 mmol, 1 equiv), base (0.74 mmol 1.2 equiv) and the palladium complex **X-PdCl₂** (l mol %) in 10 ml of solvent (DMF). The vial is sealed with PEEK snap caps and standard PTFE coated silicone septa. The reaction mixture was then exposed to microwave heating to the desired temperature. The reaction vial is thereafter cooled to room temperature and the mixture is diluted with 30 mL of water and extracted with 3 × 20 mL of hexane. The combined organic layers are dried over anhydrous sodium sulfate. The crude product is finally purified by flash column chromatography on silica-gel using ethyl acetate/hexanes mixtures.

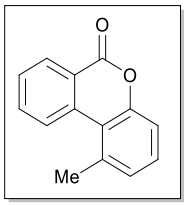


2-methyl-6H-benzo[c]chromen-6-one (7a)[6]. White solid. Yield (94 %).m.p: 126-128 °C.^{1}H NMR (300.53 MHz, $CDCl_3$, ppm) δ 8.36-8.34 (d, *J*= 7.1 Hz, 1H, H^{1}), 8.05 (d, *J*= 6.3 Hz, 1H, H^{4}), 7.80-7.78 (m, 2H, $H^{3,13}$), 7.56-7.51 (t, *J*= 7.2 Hz, 1H, H^{2}), 7.26-7.22 (m, $2H^{9,10}$), 2.44 (s, 3H, H^{12}). ^{13}C NMR (75.58 MHz, $CDCl_3$) δ 161.4 ^{7}C=O, 149.3 $C_{arom}^{8}{}_{(ipso)}$, 134.8 $C_{arom}^{5}{}_{(ipso)}$, 134.7 C_{arom}^{3}, 134.1 $C_{arom}^{11}{}_{(ipso),}$ 131.3 C_{arom}^{2}, 130.5 C_{arom}^{10}, 128.7 C_{arom}^{1}, 122.7 C_{arom}^{4}, 121.6 C_{arom}^{13}, 121.2 $C_{arom}^{6}{}_{(ipso),}$ 117.6 $C_{arom}^{14}{}_{(ipso),}$ 117.4 C_{arom}^{9}, 21.1 C_{CH3}^{12}. IR (KBr, cm^{-1}) νmax: 3056 (=C-H), 1712 (C=O), 1602 (C=C_{arom}), 769 (Ph $_{arom\ 1,2\ disust}$). MS (DART): m/z (% $x10^{3}$): 211.0568 [M^{+1}] (880).

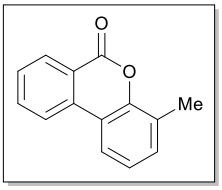


3-methyl-6*H*-benzo[c]chromen-6-one (7b)[7]. White solid. Yield (86). m.p. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm) δ 8.39 (dd, *J* = 8.0, 1.0 Hz, 1H, H^{1}), 8.09 (d, *J* = 8.1 Hz, 1H, H^{4}), 7.94 (d, *J* =

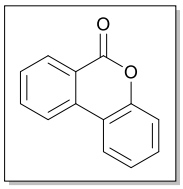
8.1 Hz, 1H, H^{11}), 7.81 (td, *J* = 7.9, 1.4 Hz, 1H, H^{3}), 7.55 (td, *J* = 7.6, 1.1 Hz, 1H, H^{2}), 7.18 (s,1H, H^{9}), 7.15 (d, *J* = 8.1 Hz, 1H, H^{13}), 2.46 (s, 3H, $H_{CH3}{}^{14}$). ^{13}C NMR (75.58 MHz, $CDCl_3$) δ 161.5 $^{7}C{=}O$, 151.4 $C_{arom}{}^{8}{}_{(ipso)}$, 141.4 $C_{arom}{}^{10}{}_{(ipso)}$, 135.1 $C_{arom}{}^{5}{}_{(ipso),}$ 134.9 $C_{arom}{}^{3}$, 130.7 $C_{arom}{}^{2}$, 128.5 $C_{arom}{}^{1}$, 125.8 $C_{arom}{}^{4}$, 122.6 $C_{arom}{}^{13}$, 121.6 $C_{arom}{}^{12}$ 121.0 $C_{arom}{}^{6}{}_{(ipso),}$ 118.0 $C_{arom}{}^{9}$, 115.6 $C_{arom}{}^{14}{}_{(ipso),}$ 21.6 $C_{CH3}{}^{11}$. IR (KBr, cm^{-1}) νmax: 3043 (=C-H), 1710 (C=O), 760 (Ph $_{arom\ 1,2\ disust}$). MS (DART): m/z (% x10^3): 211.074 [M^{+1}] (530).



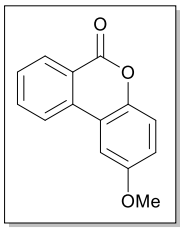
1-methyl-6*H*-benzo[c]chromen-6-one (7b')[7]. White solid. Yield (86 %). ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm) δ 8.51 (dd, *J* = 7.9, 1.3 Hz, 1H, H^{1}), 8.40 (d, *J* = 8.4 Hz, 1H, H^{4}), 7.84 (td, *J* = 7.8, 1.6 Hz, 1H, H^{3}), 7.60 (td, *J* = 7.6, 1.0 Hz, 1H, H^{2}), 7.39 – 7.33 (m, 1H, H^{10}), 7.28 (dd, *J* = 8.2, 1.0 Hz, 1H, H^{9}), 7.18 (d, *J* = 7.4 Hz, 1H, H^{11}), 2.91 (s, 3H, H^{13}). ^{13}C NMR (75.58 MHz, $CDCl_3$) δ 161.3 $^{7}C{=}O$, 152.3 $C_{arom}{}^{8}{}_{(ipso)}$, 136.3 $C_{arom}{}^{12}{}_{(ipso)}$, 136.1 $C_{arom}{}^{5}{}_{(ipso)}$, 134.4 $C_{arom}{}^{3}$, 130.9 $C_{arom}{}^{2}$, 129.4 $C_{arom}{}^{11}$, 128.9 $C_{arom}{}^{10}$, 128.2 $C_{arom}{}^{1}$, 126.3 $C_{arom}{}^{4}$, 122.2 $C_{arom}{}^{6}{}_{(ipso),}$ 117.6 $C_{arom}{}^{14}{}_{(ipso),}$ 116.3 $C_{arom}{}^{9}$, 25.6 $C_{CH3}{}^{13.}$ MS (DART): m/z (% x10^3): 211.0754 [M^{+1}] (530).



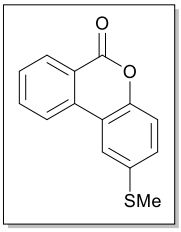
4-Methyl-6H-benzo[c]chromen-6-one (7c)[6]: White solid. Yield (88 %).m.p: 132-134 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm) δ 8.32 (d, *J*=7.9 Hz, 1H, H^{1}), 8.00 (d, *J*=8.1 Hz, 1H, H^{4}), 7.86-7.69 (m, 2H, $H^{3,13}$), 7.51 (t, *J*= 7.6 Hz, 1H, H^{2}), 7.26 (d, *J*=7.4 Hz, 1H, H^{11}), 7.15 (t, *J*= 7.6 Hz, 1H, H^{12}), 2.43 (s, 3H, H^{10}). ^{13}C NMR (75.58 MHz, $CDCl_3$) ppm 161.1 $^{7}C{=}O$, 149.5 $C_{arom}{}^{8}{}_{(ipso)}$, 135.0 $C_{arom}{}^{5}{}_{(ipso)}$, 134.7 $C_{arom}{}^{3}$, 131.7 $C_{arom}{}^{11}$, 130.3 $C_{arom}{}^{2}$, 128.6 $C_{arom}{}^{1}$, 126.9 $C_{arom}{}^{6}{}_{(ipso)}$, 123.9 $C_{arom}{}^{4}$, 121.8 $C_{arom}{}^{12}$, 120.9 $C_{arom}{}^{14}{}_{(ipso)}$, 120.3 $C_{arom}{}^{13}$, 117.6 $C_{arom}{}^{9}{}_{(ipso)}$, 16.0 $C_{CH3}{}^{10}$. IR (KBr, cm^{-1}) νmax: 3065 (=C-H), 1721 (C=O), 1599 (C=C_{arom}), 751 (Ph $_{arom\ 1,2\ disust}$). MS (DART): m/z (% x10^3): 211.0487 [M^{+1}] (218).



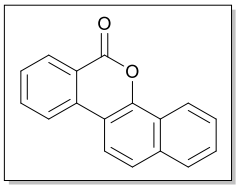
6H-benzo[c]chromen-6-one (7d)[7]. White solid. Yield (85 %). m.p: 94-96 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm) δ 8.35 (d, *J*= 7.9 Hz, 1H, H^1), 8.05 (d, *J*= 8.1 Hz, 1H, H^4), 7.99 (d, *J*= 7.7 Hz, 1H, H^{12}), 7.78 (t, *J*= 7.6 Hz, 1H, H^3), 7.54 (t, *J*= 7.6 Hz, 1H, H^2), 7.44 (t, *J*= 7.7 Hz, 1H, H^{10}), 7.37-7.25 (m, 2H, $H^{9,11}$). ^{13}C NMR (75.58 MHz, $CDCl_3$) δ 161.1 ^{7}C=O, 151.2 $C_{arom}{}^{8}{}_{(ipso)}$, 134.8 $C_{arom}{}^{3}$, 134.7 $C_{arom}{}^{5}{}_{(ipso)}$, 130.5 $C_{arom}{}^{10}$, 130.4 $C_{arom}{}^{2}$, 128.8 $C_{arom}{}^{1}$, 124.5 $C_{arom}{}^{4}$, 122.7 $C_{arom}{}^{12}$, 121.7 $C_{arom}{}^{11}$, 121.2 $C_{arom}{}^{6}{}_{(ipso)}$, 118.0 $C_{arom}{}^{13}{}_{(ipso)}$, 117.8 $C_{arom}{}^{9}$. IR (KBr, cm-1) νmax: 3060 (=C-H), 1730 (C=O), 1580 (C=Carom). MS (EI) m/z: 196 (M^+).



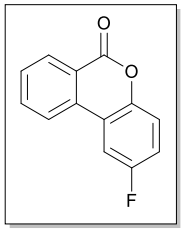
2-Methoxy-6H-benzo[c]chromen-6-one (7e)[7]: White solid Yield (96 %) m.p: 122-124 °C.^{1}H NMR (300.53 MHz, $CDCl_3$, ppm) δ 8.41 (d, *J*=7.8 Hz, 1H, H^1), 8.08 (d, *J*= 8.1 Hz, 1H, H^4), 7.83 (t, *J*= 7.6, Hz, 1H, H^3), 7.60 (t, *J*= 7.6 Hz, 1H, H^2), 7.50 (d, *J*= 2.6 Hz, 1H, H^{13}), 7.34-7.25 (m, 1H, H^9), 7.06 (dd, *J*= 9, 2.7 Hz, 1H, H^{10}), 3.91 (s, 3H, H^{12}). ^{13}C NMR (75.58 MHz, $CDCl_3$) ppm 161.3 ^{7}C=O, 156.3 $C_{arom}{}^{11}{}_{(ipso),}$ 145.6 $C_{arom}{}^{8}{}_{(ipso)}$, 134.8 $C_{arom}{}^{3}$, 134.7 $C_{arom}{}^{5}{}_{(ipso),}$ 130.7 $C_{arom}{}^{2}$, 129.0 $C_{arom}{}^{1}$, 121.7 $C_{arom}{}^{4}$, 121.4 $C_{arom}{}^{6}{}_{(ipso),}$ 118.7 $C_{arom}{}^{9}$, 118.6 $C_{arom}{}^{14}{}_{(ipso)}$, 117.1 $C_{arom}{}^{10}$, 106.4 $C_{arom}{}^{13}$, 55.8 C^{12}. IR (KBr, cm^{-1}) νmax: 3073 (=C-H), 1709 (C=O), 1607 (C=C_{arom}), 761 (Ph $_{arom\ 1,2\ disust}$). MS (DART): m/z (% x10^3): 227.0415 [M^{+1}] (312).



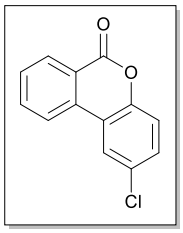
2-(methylthio)-6H-benzo[c]chromen-6-one (7f). White solid. Yield (90 %).m.p: 126-128 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm) δ 8.34 (d, *J*= 7.9 Hz, 1H, H^1), 8.01 (d, *J*= 8.1 Hz, 1H, H^4), 7.88-7.73 (m, 2H, $H^{3,13}$), 7.56 (t, *J*= 7.6 Hz, 1H, H^2), 7.33 (dd, *J*= 8.6, 2.0 Hz, 1H, H^{10}), 7.23 (d, *J*= 8.6 Hz, 1H, H^9), 2.55 (s, 3H, $H_{CH3}{}^{12}$). ^{13}C NMR (75.58 MHz, $CDCl_3$) δ 160.9 ^{7}C=O, 149.2 $C_{arom}{}^{8}{}_{(ipso)}$, 134.9 $C_{arom}{}^{3}$, 134.5 $C_{arom}{}^{5}{}_{(ipso)}$, 134.0 $C_{arom}{}^{11}{}_{(ipso)}$, 131.6 $C_{arom}{}^{2}$, 129.4 $C_{arom}{}^{1}$, 129.1 $C_{arom}{}^{10}$, 121.6 $C_{arom}{}^{4}$, 121.2 $C_{arom}{}^{6}{}_{(ipso),}$ 121.1 $C_{arom}{}^{13}$, 118.4 $C_{arom}{}^{14}{}_{(ipso)}$, 118.2 $C_{arom}{}^{9}$, 16.9.1 $C_{CH3}{}^{12}$. IR. (KBr, cm^{-1}) ν_{max}: 3065 (=C-H), 1711 (C=O), 1560 (C=C_{arom}), 764 (Ph $_{arom\ 1,2\ disust}$). MS (DART): m/z (% x10^3): 243 [M^{+1}] (3300).



6H-Dibenzo[c,h]chromen-6-one (7g)[4]: White solid. Yield (79 %).m.p: 184-186 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm) δ 8.59 (d, *J*=8.8Hz, 1H, H^{1}), 8.47 (d, *J*=7.9 Hz, 1H, H^{10}), 8.20 (d, *J*=8.1Hz, 1H, H^{4}), 8.06 (d, *J*=8.8 Hz, 1H, H^{13}), 7.89 – 7.84 (m, 2H, $H^{3,16}$), 7.77 (d, *J*=8.8 Hz, 1H, H^{15}), 7.66–7.58 (m, 3$H^{2,11,12}$). ^{13}C NMR (75.58 MHz, $CDCl_3$) ppm 161.3 ^{7}C=O, 147.3 $C_{arom}{}^{8}{}_{(ipso)}$, 135.4 $C_{arom}{}^{5}{}_{(ipso),}$ 135.0 $C_{arom}{}^{3}$, 134.3 $C_{arom}{}^{14}{}_{(ipso),}$ 130.7 $C_{arom}{}^{2}$, 128.6 $C_{arom}{}^{13}$, 127.9 $C_{arom}{}^{1}$, 127.7 $C_{arom}{}^{12}$, 127.1 $C_{arom}{}^{4}$, 124.5 $C_{arom}{}^{11}$, 123.9 $C_{arom}{}^{6}{}_{(ipso)}$, 122.3 $C_{arom}{}^{15}$, 122.0 $C_{arom}{}^{10}$, 121.2 $C_{arom}{}^{17}{}_{(ipso),}$ 119.2 $C_{arom}{}^{16}$, 113.0 $C_{arom}{}^{9}{}_{(ipso)}$. IR. (KBr, cm^{-1}) ν_{max}: 3046 (=C-H), 1682 (C=O), 1575(C=C_{arom}), 761 (Ph $_{arom\ 1,2\ disust}$). MS (DART): m/z (% x10^{3}): 247 [M^{+1}] (3400).

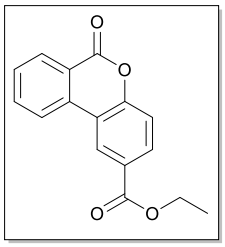


2-fluoro-6H-benzo[c]chromen-6-one (7h)[7]. White solid. Yield (77 %). m.p: 150-152 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm) δ 8.39 (dd, *J*= 7.9 Hz, 1H, H^{1}), 8.01 (d, *J* = 8.0 Hz, 1H, H^{4}), 7.85 (d, *J*= 7.7 Hz, 1H, H^{3}), 7.69 (dd, *J*= 9.1, 2.7 Hz, 1H, H^{12}), 7.62 (t, *J*= 7.6 Hz, 1H, H^{2}), 7.33 (m, 1H, H^{10}), 7.23-7.13 (m, 1H, H^{9}). ^{13}C NMR (75.58 MHz, $CDCl_3$) δ 160.8 (d, *J*= 6.9 Hz, ^{7}C=O), 157.7 $C_{arom}{}^{12}{}_{(ipso)}$, 147.4 (d, *J*= 2.1 Hz, $C_{arom}{}^{8}{}_{(ipso)}$), 135.0 $C_{arom}{}^{3}$, 133.9 (d, *J* = 2.6 Hz, $C_{arom}{}^{4}$), 130.7 $C_{arom}{}^{2}$, 129.6 $C_{arom}{}^{1}$, 121.9 $C_{arom}{}^{4}$, 121.2 $C_{arom}{}^{6}{}_{(ipso)}$, 119.3 (d, *J*= 8.6 Hz, $C_{arom}{}^{9}$), 119.2 $C_{arom}{}^{13}{}_{(ipso)}$,117.8 (d, *J* = 24.26 Hz, $C_{arom}{}^{10}$), 108.6 (d, *J* = 24.86 Hz, $C_{arom}{}^{12}$). IR (KBr, cm^{-1}) νmax: 3065 (=C-H), 1717 (C=O), 1603 (C=C_{arom}), 817 (Ph $_{arom\ 1,4\ disust}$).. MS (DART): m/z (% x10^{3}): 215.0253 [M^{+1}] (692).



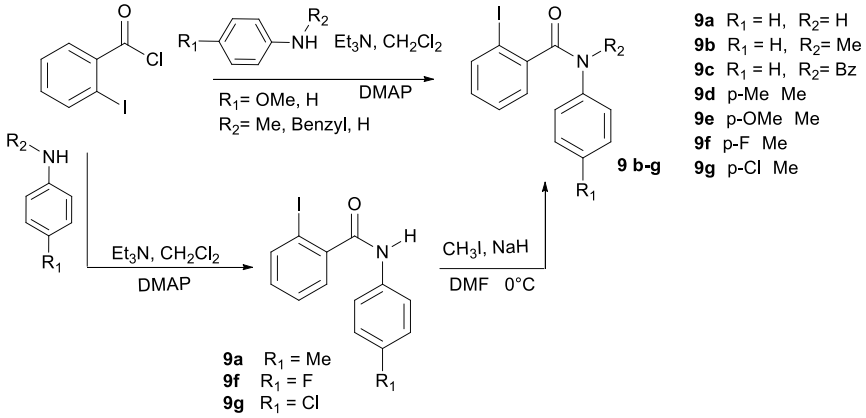
2-chloro-6H-benzo[c]chromen-6-one (7i)[7]. White solid. Yield (71 %). m.p: 178-180 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm) δ 8.38 (d, *J*= 7.9 Hz, 1H, H^{1}), 8.03 (d, *J*= 8.1 Hz, 1H, H^{4}), 7.97 (d, *J*= 2.0 Hz, 1H, H^{11}), 7.84 (t, *J*= 7.7 Hz, 1H, H^{3}), 7.62 (t, *J*= 7.6 Hz, 1H, H^{2}), 7.41 (dd, *J*= 8.8, 2.2 Hz, 1H, H^{10}), 7.29 (d, *J*= 8.8 Hz, 1H, H^{9}). ^{13}C NMR (75.58 MHz, $CDCl_3$) δ 160.6 ^{7}C=O, 149.6 $C_{arom}{}^{8}{}_{(ipso)}$, 135.1 $C_{arom}{}^{3}$, 133.5 $C_{arom}{}^{5}{}_{(ipso)}$, 130.7 $C_{arom}{}^{2}$, 130.4

C_{arom}^{10}, 130.1 $C_{arom}^{11}{}_{(ipso)}$, 129.6 C_{arom}^{1}, 122.6 C_{arom}^{4}, 121.8 C_{arom}^{12}, 121.2 $C_{arom}^{6}{}_{(ipso)}$, 119.3 $C_{arom}^{13}{}_{(ipso)}$, 119.2 C_{arom}^{9}. IR (KBr, cm^{-1}) νmax: 3068 (=C-H), 1727 (C=O), 1602 (C=C_{arom}), 806 (Ph $_{arom\ 1,4\ disust}$), 712 (Ph $_{arom\ 1,2\ disust}$). MS (DART): m/z (% x10^3): 230.9918 [M^+] (383), 232.9890 [M^{+2}] (120).



2-chloro-6H-benzo[c]chromen-6-one (7j)[8]. White solid. Yield (38 %). m.p: 134-136 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm): δ 8.76 (d, *J* = 1.2 Hz, 1H, H_{arom}^{15}), 8.40 (d, *J* = 6.4 Hz, 1H, H_{arom}^{1}), 8.21 (d, *J* = 6.4 Hz, 1H, H_{arom}^{4}), 8.13 (dd, *J* = 6.8, 1.2 Hz, 1H, H_{arom}^{10}), 7.87 (t, *J* = 7.0 Hz, 1H, H_{arom}^{3}). 7.63 (t, *J* = 7.0 Hz, 1H, H_{arom}^{2}), 7.39 (d, *J* = 6.8 Hz, 1H, H_{arom}^{9}), 4.44 (q, *J* = 5.6 Hz, 2H, H $_{CH_3CH_2O,}$ H^{13}), 1.39 (t, *J* = 5.2 Hz, 3H, H $_{CH_3CH_2O,}$ H^{14}). ^{13}C NMR (75.58 MHz, $CDCl_3$, ppm): δ 165.5 ^{12}C=O, 164.2 ^{7}C=O, 154.1 $C_{arom}^{8}{}_{(ipso)}$, 135.1 C_{arom}^{3}, 134.1 $C_{arom}^{5}{}_{(ipso)}$, 131.4 C_{arom}^{2}, 130.6 C_{arom}^{15}, 129.4 C_{arom}^{10}, 126.8 $C_{arom}^{11}{}_{(ipso)}$, 124.9 C_{arom}^{4}, 122.0 C_{arom}^{1}, 121.1 $C_{arom}^{6}{}_{(ipso)}$, 117.9 $C_{arom}^{16}{}_{(ipso)}$, 117.9 C_{arom}^{9}, 61.4 $C_{CH_2}^{13}$, 14.4 $C_{CH_3}^{14}$. IR (KBr, cm^{-1}) νmax: 3062 (=C-H), 1719 (C=O). MS (DART): m/z (% x103): 268.0735 [M^+] (383).

7. General procedure for the synthesis of amide substrates



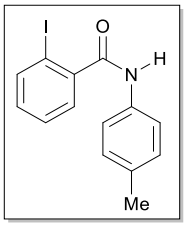
8. Preparation of 2-Iodobenzamide 9a–e.

In a 50mL round-bottom flask equipped with a magnetic stirrer the corresponding amine (1.5 equiv) is added and dichloromethane (20 ml). The flask is purged with nitrogen and placed in an ice bath; triethylamine (2 equiv) is added for a time reaction of 30 minutes. The appropriate iodobenzyl chloride (1.0 equiv.) dissolved in dichloromethane (10 ml)

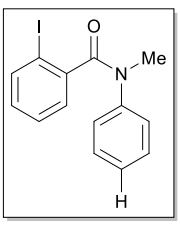
and DMAP (0.05 equiv) are then added. The reaction is allowed to stir and warm to room temperature. The mixture is extracted using CH_2Cl_2/Brine. The organic layers are dried using Na_2SO_4, filtered and the volatiles are evaporated under vacuum. The residue is then purified via column chromatography using ethyl acetate/hexanes mixtures.

9. Preparation of 2-Iodobenzamide 9f–g.

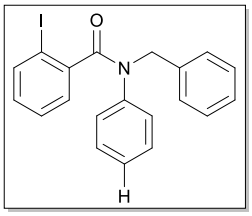
To a suspension of 60% NaH (15 mmol) in DMF (10 ml), the amide **9** (6 mmol) in DMF (10 ml) was added slowly under argon at 0 °C. After that, iodomethane (9 mmol) in DMF (5 ml) was added dropwise at 0 °C. After stirred at room temperature for 2 h, the solution was diluted with CH_2Cl_2, then washed with water (3×50 ml). The organic layer dried (Na_2SO_4), and evaporated under reduced pressure. The crude material was purified by chromatography (hexane/ethyl acetate).



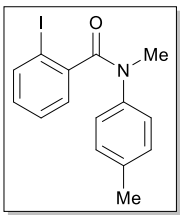
2-iodo-*N*-(*p*-tolil)benzamide (9a)[9].White solid, Yield 94 %; ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm) δ 7.91 (dd, *J* = 8.0, 1.2 Hz, 1H, H_{arom}^2), 7.55–7.51 (m, 3H, $H_{arom}^{5,9,14}$), 7.49 (s, 1H, H^{15}), 7.43 (dt, *J* = 7.6, 0.8 Hz, 1H, H^4), 7.20 (d, *J*= 8.0 Hz, 2H, $H^{10,13}$), 7.15 (td, J= 7.6, 1.6 Hz, 1H, H_{arom}^3), 2.37 (s, 3H, H_{CH3}^{12}); ^{13}C NMR (75.58 MHz, $CDCl_3$) δ 167.2 ^{7}C=O, 142.2 $C_{arom}^{6}{}_{(ipso)}$, 140.0 C_{arom}^2, 135.0 $C_{arom}^{8}{}_{(ipso)}$, 134.6 $C_{arom}^{11}{}_{(ipso)}$, 131.4 C_{arom}^3, 129.6 $C_{arom}^{10,13}$, 128.5 C_{arom}^5, 128.3 C_{arom}^4, 120.2 $C_{arom}^{9,14}$, 92.5 $C_{arom}^{1}{}_{(ipso)}$, 21.0 C_{CH3}^{12}. IR (KBr, cm^{-1}) νmax: 3417 (-N-H), 3019 (=C-H), 1671 (C=O). MS (DART): m/z (% x10^3): 338.0041 [M^+] (370).



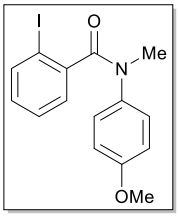
2-iodo-*N*-methyl-*N*-phenylbenzamide (9b)[10]. White solid, Yield (94%). mp 94-96 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm) δ 7.55 (d, *J* = 7.8 Hz, 1H, H^2), 7.25-6.86 (m, 7H, $H^{3,4,5,10,11}$), 6.73 (t, *J* = 6.4 Hz, 2H, H^{12}), 3.41 (s, 3H, H^8). ^{13}C NMR (75.58 MHz, $CDCl_3$) δ 170.2 ^{7}C=O, 143.3 $C_{arom}^{6}{}_{(ipso)}$, 142.5 $C_{arom}^{9}{}_{(ipso)}$, 139.2 C_{arom}^2, 129.9 C_{arom}^5, 129.0 C_{arom}^{11}, 128.7 C_{arom}^3, 127.4 C_{arom}^4, 127.2 C_{arom}^{12}, 127.1 C_{arom}^{10}, 93.8 $C_{arom}^{1}{}_{(ipso)}$, 37.5 C_{CH3}^8. IR (KBr) cm^{-1}: 3054 (=C-H), 1642 (C=O); 1588 (C=C_{arom}), 695 (Ph $_{arom\ 1,2\ disust}$). MS (DART): m/z (% x10^3): 338 [M^{+1}] (1300).



***N*-benzyl-2-iodo-*N*-phenylbenzamide (9c).** Colorless oil. Yield (95%) ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm) δ 7.62 (d, *J* = 7.9 Hz, 1H, H^{2}), 7.36 (d, *J*= 6.3 Hz, 3H, H^{14}), 7.32-7.19 (m, 3H, $H^{3,4,5}$), 7.10-6.93 (m, 7H, $H^{10,11,12,15}$), 6.84 (td, *J* = 6.9, 2.1 Hz, 1H, H^{16}), 5.13 (s, 3H, H^{8}). ^{13}C NMR (75.58 MHz, $CDCl_3$, ppm) δ 170.1 ^{7}C=O, 142.2 $C_{arom}{}^{6}{}_{(ipso)}$, 141.6 $C_{arom}{}^{13}{}_{(ipso)}$, 139.2 $C_{arom}{}^{2}$, 137.0 $C_{arom}{}^{9}{}_{(ipso)}$, 129.7 $C_{arom}{}^{5}$, 129 (d, *J* = 9.7 Hz, $C_{arom}{}^{11,15}$), 128.5 $C_{arom}{}^{3}$, 128.5 $C_{arom}{}^{10,12}$, 128.2 $C_{arom}{}^{14}$, 127.5 (d, *J*= 7.8 Hz, $C_{arom}{}^{16}$), 127.3 $C_{arom}{}^{4}$, 93.9 $C_{arom}{}^{1}{}_{(ipso)}$, 53.0 $C_{CH_2}{}^{8}$. IR (KBr) cm^{-1}: 3058 (=C-H), 1643 (C=O); 1588 (C=C_{arom}), 694 ($Ph_{\text{arom 1,2 disust}}$). MS (DART): m/z (% x$10^{3}$): 414 [$M^{+1}$] (2000).

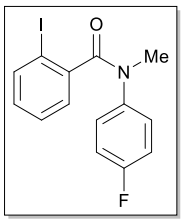


2-iodo-*N*-methyl-*N*-(*p*-tolyl)benzamide (9d).[10] White solid. Yield (93 %), mp 78-80°C. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm) δ 7.67 (d, *J* = 8.0 Hz, 1H, H^{2}), 7.24 (d, *J* = 8.2 Hz, 2H, H^{10}), 7.21-7.11 (m, 3H, $H^{3,5}$), 7.04 (d, *J* = 8.1 Hz, 2H, H^{11}), 6.95-6.83 (m, 1H, H^{4}), 3.59 (s, 3H, H^{8}), 2.22 (s, 3H, H^{13}). ^{13}C NMR (75.58 MHz, $CDCl_3$) δ 170.2 ^{7}C=O, 140.1 $C_{arom}{}^{6}{}_{(ipso)}$, 139.4 $C_{arom}{}^{2}$, 132.5 $C_{arom}{}^{12}{}_{(ipso)}$, 131.0 $C_{arom}{}^{5}$, 130.2 $C_{arom}{}^{9}{}_{(ipso)}$, 130.1 $C_{arom}{}^{10}$, 129.7 $C_{arom}{}^{11}$, 128.2 $C_{arom}{}^{3}$, 127.6 $C_{arom}{}^{4}$, 92.7 $C_{arom}{}^{1}{}_{(ipso)}$, 41.5 $C_{CH_3}{}^{8}$, 21.2 $C_{CH_3}{}^{13}$. IR (KBr) cm^{-1}: 3085 (=C-H), 1694 (C=O); 1583 (C=C_{arom}), 755 ($Ph_{\text{arom 1,2 disust}}$). MS (DART): m/z (% x$10^{3}$): 352 [$M^{+1}$] (1300).

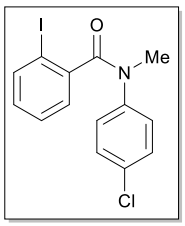


2-iodo-*N*-(4-methoxyphenyl)-*N*-methylbenzamide (9e).[10] Colorless oil. Yield (98%). ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm) δ 7.60 (dd, *J* = 7.8, 1.2 Hz, 1H, H^{2}), 7.11 (d, *J* = 9.0 Hz, 2H, H^{10}), 7.07-704 (m, 2H, $H^{3,5}$), 6.78 (td, *J* = 7.7, 2.1 Hz, 1H, H^{4}), 6.66 (d, *J*= 8.9 Hz, 2H, H^{11}), 3.62 (s, 3H, H^{8}), 3.44 (s, 3H, H^{13}). ^{13}C NMR (75.58 MHz, $CDCl_3$) δ 170.3 ^{7}C=O, 158.2 $C_{arom}{}^{12}{}_{(ipso)}$, 142.6 $C_{arom}{}^{6}{}_{(ipso)}$, 139.0 $C_{arom}{}^{2}$, 136.0 $C_{arom}{}^{9}{}_{(ipso)}$, 129.6 $C_{arom}{}^{5}$, 128.4 $C_{arom}{}^{3}$, 128.2 $C_{arom}{}^{10}$, 127.4 $C_{arom}{}^{4}$, 114.1 $C_{arom}{}^{11}$, 93.6 $C_{arom}{}^{1}{}_{(ipso)}$, 55.3 $C_{CH_3}{}^{13}$, 37.59 $C_{CH_3}{}^{8}$. IR (KBr) cm^{-1}: 3043 (=C-H), 1648

(C=O); 1579 (C=C_{arom}), 739 (Ph $_{arom\ 1,2\ disust}$). MS (DART): m/z (% x10^3): 368 [M^{+1}] (5800).

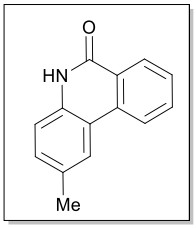


***N*-(4-fuorophenyl)-2-iodo-*N*-methylbenzamide (9f).** White solid. Yield (79%). mp 100-102 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm) δ 7.65 (d, *J* = 7.9 Hz, 1H, H^2), 7.23-7.10 (m, 4H, $H^{4,10}$), 7.04 (dd, *J* = 7.6, 1.4 Hz, 1H, H^3), 6.87 (t, *J* = 8.5 Hz, 1H, $H^{2,11}$), 3.48 (s, 3H, H^8). ^{13}C NMR (75.58 MHz, $CDCl_3$, ppm) δ 170.2 ^{7}C=O, 162.7 and 159.4 (d, *J*= 247.7 Hz, $C_{arom}{}^{12}{}_{(ipso)}$), 142.2 $C_{arom}{}^{6}{}_{(ipso)}$, 139.3 $C_{arom}{}^{2}$, 139.2 $C_{arom}{}^{9}{}_{(ipso)}$, 129.9 $C_{arom}{}^{5}$, 128.9 (d, J = 8.6 Hz, $C_{arom}{}^{10}$), 128.4 $C_{arom}{}^{3}$, 127.5 $C_{arom}{}^{4}$, 115.9 (d, *J*= 22.7 Hz, $C_{arom}{}^{11}$), 93.5 $C_{arom}{}^{1}{}_{(ipso)}$, 37.4 $C_{CH3}{}^{8}$. IR (KBr) cm^{-1}: 3118 (=C-H), 1642 (C=O); 1581 (C=C_{arom}), 682 (Ph $_{arom\ 1,2\ disust}$). MS (DART): m/z (% x10^3): 356 [M^{+1}] (8000).



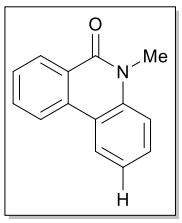
***N*-(4-chlorophenyl)-2-iodo-*N*-methylbenzamide (9g).[10]** White solid. Yield (62 %). mp 90-92 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm) δ 7.64 (d, *J* = 7.9 Hz, 1H, H^2), 7.09-7.33 (m, 6H, $H^{4,5,10,11}$), 6.87 (t, *J*= 7.4 Hz, 1H, H^3), 3.50 (s, 3H, H^8). ^{13}C NMR (75.58 MHz, $CDCl_3$, ppm) δ 170.0 ^{7}C=O, 142.1 $C_{arom}{}^{6}{}_{(ipso)}$, 141.7 $C_{arom}{}^{9}{}_{(ipso)}$, 139.2 $C_{arom}{}^{2}$, 132.7 $C_{arom}{}^{12}{}_{(ipso)}$, 130.1 $C_{arom}{}^{5}$, 129.2 $C_{arom}{}^{11}$, 128.5 $C_{arom}{}^{3}$, 128.4 $C_{arom}{}^{10}$, 127.6 $C_{arom}{}^{4}$, 93.5 $C_{arom}{}^{1}{}_{(ipso)}$, 37.4 $C_{CH3}{}^{8}$. IR (KBr) cm^{-1}: 3059 (=C-H), 1636 (C=O); 1583 (C=C_{arom}), 740 (Ph $_{arom\ 1,2\ disust}$). MS (DART): m/z (% x10^3): 372 [M^{+1}] (4200).

10. Synthesis of benzolactams 10a-g

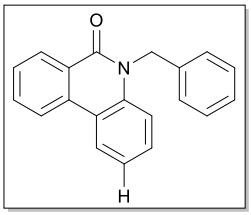


2-Methylphenanthridin-6(5H)-one (10a).[11] White powder. Yield (36 %). mp 256-258 °C; ^{1}H NMR (300.53 MHz, DMSO-d_6): 11.60 (s, 1H, H^{15}), 8.47 (d, 1H, *J*= 7.8 Hz, H^1), 8.30 (d, 1H, *J*= 7.8 Hz, H^4), 8.19 (s, 1H, H^{13}), 7.83 (t, 1H, *J*= 7.8 Hz, H^3), 7.61 (t, 1H, *J*= 7.8 Hz, H^2), 7.24-7.31 (m, 2H, $H^{9,10}$), 2.40 (s, 3H, H^{12}). ^{13}C NMR (75.58 MHz, DMSO-d_6) 160.7 ^{7}C=O, 134.4 $C_{arom}{}^{5}{}_{(ipso)}$, 134.2 $C_{arom}{}^{8}{}_{(ipso)}$, 132.7 $C_{arom}{}^{3}$, 131.2 $C_{arom}{}^{2}$, 130.6 $C_{arom}{}^{11}{}_{(ipso)}$, 127.8 $C_{arom}{}^{10}$, 127.5 $C_{arom}{}^{9}$, 125.7 $C_{arom}{}^{6}{}_{(ipso)}$,, 123.1 $C_{arom}{}^{4}$, 122.6 $C_{arom}{}^{13}$, 117.4 $C_{arom}{}^{14}{}_{(ipso)}$, 116.0 $C_{arom}{}^{9}$, 20.7 $C_{CH3}{}^{12}$. IR (KBr) ν (cm−1)

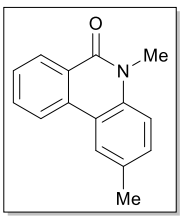
3012 (=C-H), 1657 (C=O); 1608 (C=C_{arom}), 770 740 (Ph $_{arom\ 1,2\ disust}$). MS (DART): m/z (% x10^3): 209.08402 [M^{+1}] (3200).



5-methylphenanthridin-6(5*H*)-one (10b).[10] White solid. Yield (79 %). mp 108-110°C. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm): δ 8.52 (d, *J*= 7.2 Hz,1H, H^{13}), 8.19 (dd, *J*=7.9, 1.6 Hz, 2H, $H^{1,4}$), 7.70 (td, *J* = 7.6 Hz, 1H, H^3), 7.60-7.45 (m, 2H, $H^{2,11}$), 7.33 (d, *J* = 8.4Hz, 1H, H^{10}), 7.26 (t, *J*= 7.7 Hz, 1H, H^{12}), 3.76 (s, 3H, H^8). ^{13}C NMR (75.58 MHz, $CDCl_3$, ppm): δ 161.6 ^{7}C=O, 137.9 $C_{arom}{}^{5}{}_{(ipso)}$, 133.5 $C_{arom}{}^{9}{}_{(ipso)}$, 132.3 $C_{arom}{}^{3}$, 129.5 $C_{arom}{}^{2}$, 128.8 $C_{arom}{}^{1}$, 127.9 $C_{arom}{}^{11}$, 125.5 $C_{arom}{}^{6}{}_{(ipso)}$, 123.2 $C_{arom}{}^{13}$, 122.4 $C_{arom}{}^{12}$, 121.6 $C_{arom}{}^{4}$, 119.2 $C_{arom}{}^{14}{}_{(ipso)}$, 115.0 $C_{arom}{}^{10}$, 29.9 $C_{CH3}{}^{8}$. IR (KBr) cm^{-1}: 3071 (=C-H), 1641 (C=O); 1583 (C=C_{arom}), 717 (Ph $_{arom\ 1,2\ disust}$. MS (DART): m/z (% x10^3): 210 [M^{+1}] (7000).

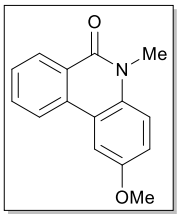


5-benzylphenanthridin-6(5*H*)-one (10c). White solid. Yield (73 %); mp 120-122 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm): δ 8.61 (dd, *J*= 8.0, 1.5 Hz, 1H, H^{17}), 8.22 (t, *J*= 7.5, 2H, $H^{1,4,}$), 7.73 (td, *J* = 8.1, 7.6, 1.5 Hz, 1H, H^3), 7.57 (t, *J* = 7.8, Hz, 1H, H^2), 7.46-709 (m, 8H, $H^{10,11,12,14,15,16}$), 5.63 (s, 2H, H^8). ^{13}C NMR (75.58 MHz, $CDCl_3$, ppm): δ 161.9 ^{7}C=O, 137.3 $C_{arom}{}^{5}{}_{(ipso)}$, 136.6 $C_{arom}{}^{13}{}_{(ipso)}$, 133.8 $C_{arom}{}^{9}{}_{(ipso)}$, 132.7 $C_{arom}{}^{3}$, 129.6 $C_{arom}{}^{2}$, 129.2 $C_{arom}{}^{15}$, 128.8 $C_{arom}{}^{11}$, 128.1 $C_{arom}{}^{1}$, 127.2 $C_{arom}{}^{12}$, 126.6 $C_{arom}{}^{10}$, 125.4 $C_{arom}{}^{6}{}_{(ipso)}$, 123.3 $C_{arom}{}^{17}$, 122.6 $C_{arom}{}^{4}$, 121.7 $C_{arom}{}^{16}$, 119.5 $C_{arom}{}^{18}{}_{(ipso)}$, 116.0 $C_{arom}{}^{14}$, 46.5 $C_{CH2}{}^{8}$. IR (KBr) cm^{-1}: 3070 (=C-H), 1637 (C=O); 1582 (C=C_{arom}), 720 (Ph $_{arom\ 1,2\ disust}$. MS (DART): m/z (% x10^3): 286 [M^{+1}] (7000).

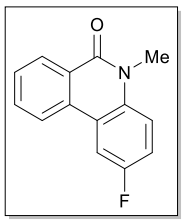


2,5-dimethylphenanthridin-6(5*H*)-one (10d).[10] White solid. Yield (80 %). mp: 114-116 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm): δ 8.51 (dd, *J* = 8.1, 1.5 Hz, 1H, H^1), 8.18 (dd, *J* = 8.2, 1.2 Hz, 1H, H^4), 7.97 (s, 1H, H^{14}), 7.69 (td, *J*= 8.4, 7.2, 1.5 Hz, 1H, H^3), 7.53 (td, *J*= 8.3, 7.1, 1.1 Hz, 1H, H^2), 7.29 (dd, *J*= 8.5, 2.1 Hz, 1H, H^{10}), 7.21 (d, *J* = 8.5 Hz, 1H, H^{11}), 3.73 (s, 3H, H^8), 2.44 (s, 3H, H^{13}). ^{13}C NMR (75.58 MHz, $CDCl_{3,}$ ppm): δ 161.4 ^{7}C=O,

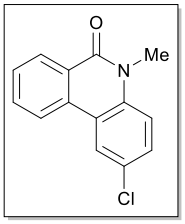
135.8 $C_{arom}^{5}{}_{(ipso)}$, 133.4 $C_{arom}^{9}{}_{(ipso)}$, 132.2 C_{arom}^{3}, 131.8 $C_{arom}^{12}{}_{(ipso)}$, 130.5 C_{arom}^{2}, 128.8 C_{arom}^{1}, 127.7 C_{arom}^{11}, 125.6 $C_{arom}^{6}{}_{(ipso)}$, 123.3 C_{arom}^{4}, 121.5 C_{arom}^{14}, 119.0 $C_{arom}^{15}{}_{(ipso)}$, 114.9 C_{arom}^{10}, 29.9 C_{CH3}^{8}, 21.0 C_{CH3}^{13}. IR (KBr) cm^{-1}: 1630 (C=O); 1579 (C=C_{arom}), 719 (Ph $_{arom\ 1,2\ disust}$). MS (DART): m/z (% $x10^{6}$): 224 [M^{+1}] (13).



2-methoxy-5-methylphenanthridin-6(5*H*)-one (10e)[10]. White solid. Yield (97%). 122-124 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm): δ 8.54 (dd, *J*= 7.9, 1.2 Hz, 1H, H^{1}), 8.18 (d, *J*= 7.4 Hz, 1H, H^{4}), 7.83-7.67 (m, 2H, $H^{3,14}$), 7.58 (td, *J*= 7.7, 1.2 Hz, 1H, H^{2}), 7.37-7.25 (m, 1H, H^{10}), 7.12 (dd, *J* = 9.1, 2.8 Hz, 1H, H^{11}), 3.92 (s, 3H, H^{8}), 3.77 (s, 3H, H^{13}). ^{13}C NMR (75.58 MHz, $CDCl_3$, ppm): δ 161.1 ^{7}C=O, 155.1 $C_{arom}^{12}{}_{(ipso)}$, 133.2 $C_{arom}^{5}{}_{(ipso)}$, 132.3 $C_{arom}^{9}{}_{(ipso)}$, 132.2 C_{arom}^{3}, 129.0 C_{arom}^{2}, 128.1 C_{arom}^{1}, 125.9 $C_{arom}^{6}{}_{(ipso)}$, 121.7 C_{arom}^{4}, 120.2 $C_{arom}^{15}{}_{(ipso)}$, 116.5 C_{arom}^{10}, 116.2 C_{arom}^{11}, 107.1 C_{arom}^{14}, 55.7 C_{CH3}^{13}, 30.1 C_{CH3}^{8}. IR (KBr) cm^{-1}: 1630 (C=O); 1578 (C=C_{arom}), 719 (Ph $_{arom\ 1,2\ disust}$). MS (DART): m/z (% $x10^{6}$): 240 [M^{+1}] (16).



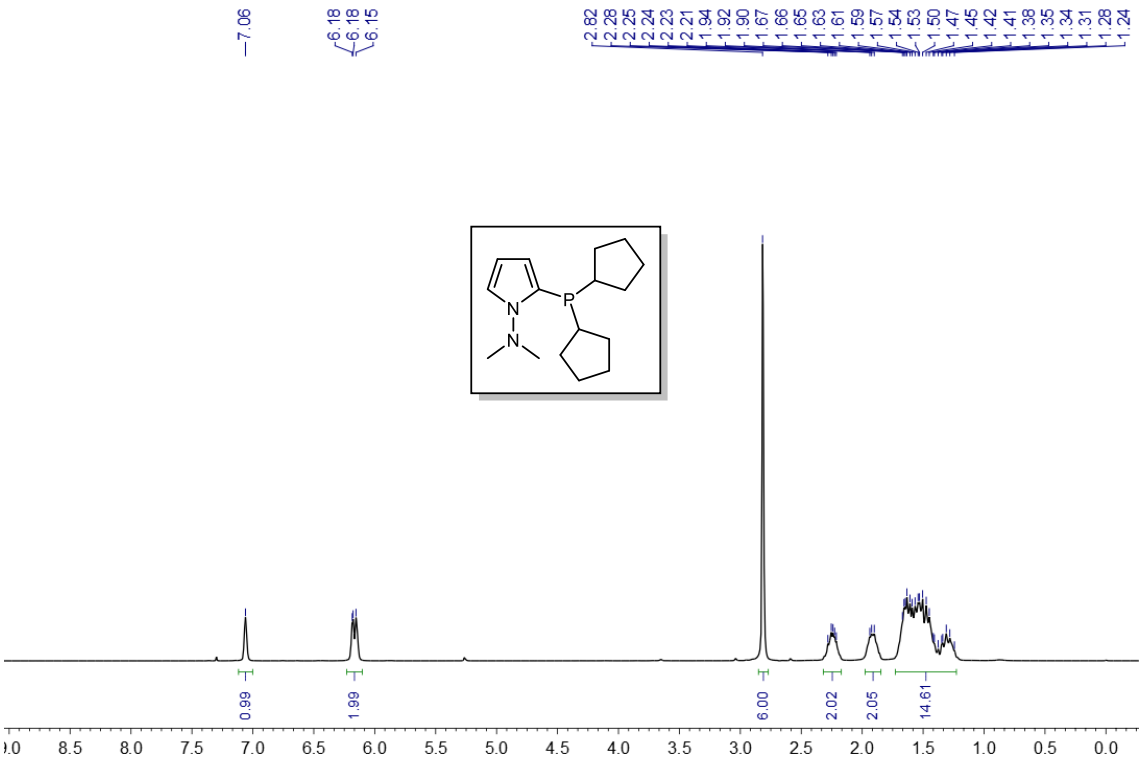
2-fluoro-5-methylphenanthridin-6(5*H*)-one (10f). White solid. Yield (87%). mp 120-122 °C. ^{1}H NMR (300.53 MHz, $CDCl_3$, ppm): δ 8.48 (d, *J*= 7.4 Hz, 1H, H^{1}), 8.02 (d, *J*= 8.1 Hz, 1H, H^{4}), 7.78 (dd, *J*= 9.7, 2.6 Hz 1H, H^{13}), 7.70 (t, *J*= 7.1 Hz, 1H, H^{3}), 7.57 (t, *J*= 7.3 Hz, 1H, H^{2}), 7.29-7.25 (m, 1H, H^{10}), 7.19 (td, *J*= 9.3, 8.4, 2.7 Hz, 1H, H^{11}), 3.72 (s, 3H, H^{11}). ^{13}C NMR (75.58 MHz, $CDCl_3$, ppm): δ 161.1 ^{7}C=O, 158.4 (d, *J*= 242 Hz, $C_{arom}^{12}{}_{(ipso)}$), 134.3 (d, *J* = 1.9 Hz, $C_{arom}^{5}{}_{(ipso)}$), 132.5 $C_{arom}^{9}{}_{(ipso)}$, 132.4 C_{arom}^{3}, 128.9 C_{arom}^{2}, 128.6 C_{arom}^{1}, 125.7 $C_{arom}^{6}{}_{(ipso)}$, 121.7 C_{arom}^{4}, 120.5 (d, *J*= 7.9 Hz, $C_{arom}^{14}{}_{(ipso)}$), 116.8 C_{arom}^{10}, 116.6-116.0 (m, C_{arom}^{13}), 109.1 (d, *J* = 23.7 Hz, C_{arom}^{11}), 30.1 C_{CH3}^{8}. IR (KBr) cm^{-1}: 1630 (C=O); 1578 (C=C_{arom}), 718 (Ph $_{arom\ 1,2\ disust}$) MS (DART): m/z (% $x10^{3}$): 228 [M^{+1}] (4000).

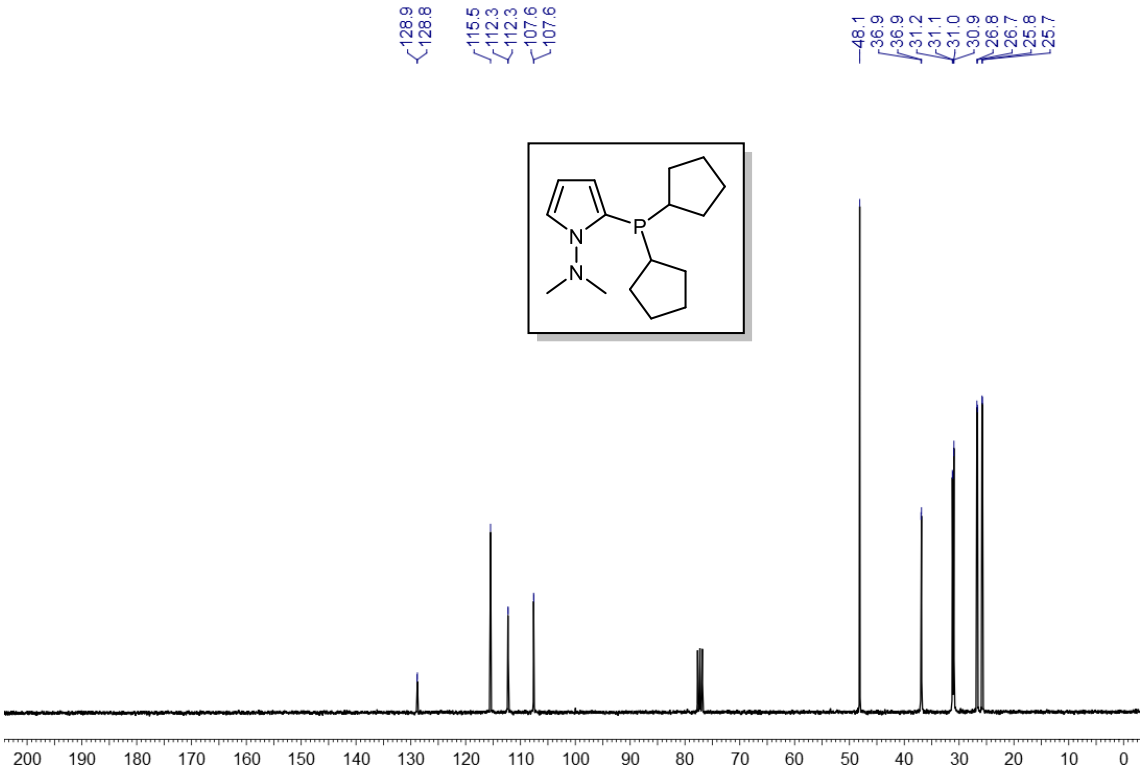


2-Chloro-5-methylphenanthridin-6(5*H*)-one (10g)[10]. White solid. Yield (90%). mp 130-132 °C. ^{1}H NMR (300.53 MHz,

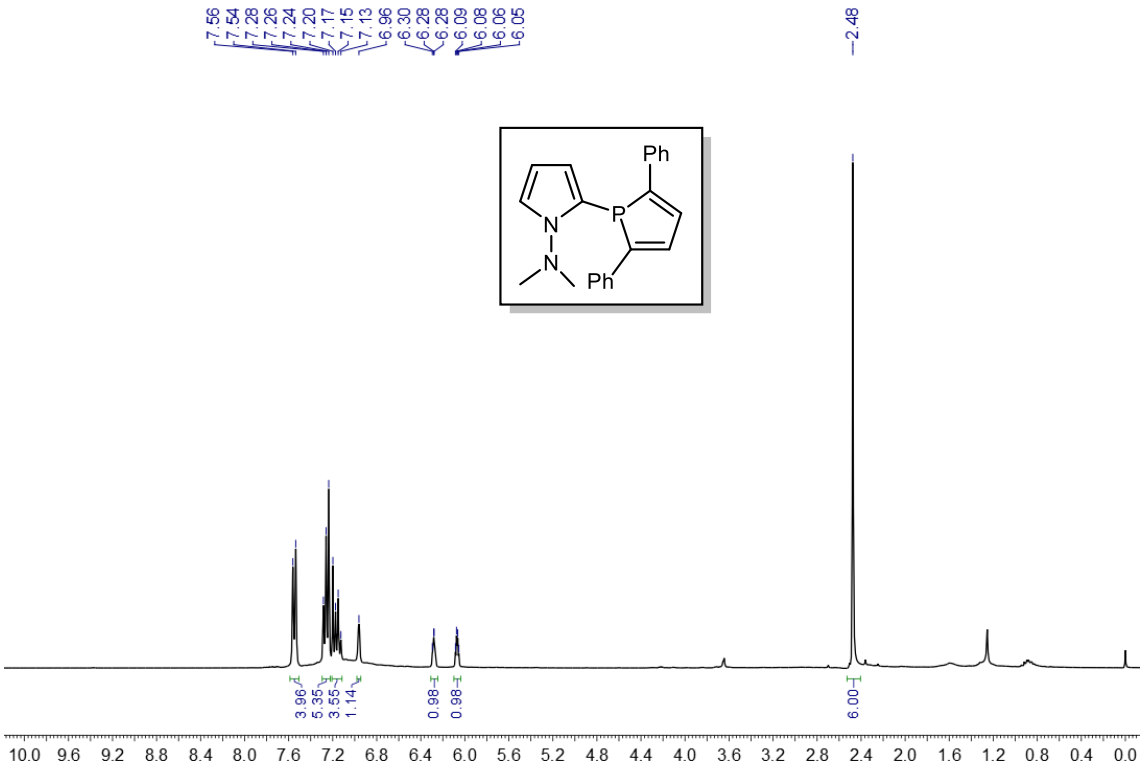
$CDCl_3$, ppm): δ 8.49 (dd, *J* = 7.9, 1.5 Hz, 1H, H^1), 8.10-808 (m, 2H, $H^{4,13}$), 7.73 (td, *J* = 8.2, 1.5 Hz, 1H, H^3), 7.59 (td, *J* = 8.2, 1.5 Hz, 1H, H^2), 7.43 (dd, *J* = 9.0, 2.4 Hz 1H, H^{11}), 7.26 (d, *J* = 8.9 Hz, 1H, H^{10}), 3.73 (s, 3H, H^8). ^{13}C NMR (75.58 MHz, $CDCl_3$, ppm): δ 161.2 ^7C=O, 136.5 $C_{arom}{}^5{}_{(ipso)}$, 132.6 $C_{arom}{}^3$, 132.2 $C_{arom}{}^9{}_{(ipso)}$, 129.3 $C_{arom}{}^2$, 128.9 $C_{arom}{}^{11}$, 128.6 $C_{arom}{}^1$, 128.1 $C_{arom}{}^{12}{}_{(ipso)}$, 125.6 $C_{arom}{}^6{}_{(ipso)}$, 122.9 $C_{arom}{}^4$, 121.6 $C_{arom}{}^{13}$, 120.5 $C_{arom}{}^{14}{}_{(ipso)}$, 116.3 $C_{arom}{}^{10}$, 30.1 $C_{CH3}{}^8$. IR (KBr) cm^{-1}: 1639 (C=O); 1589 (C=C_{arom}), 730 (Ph $_{arom\ 1,2\ disust}$. MS (DART): m/z (% $x10^3$): 244 [M^{+1}] (5800).

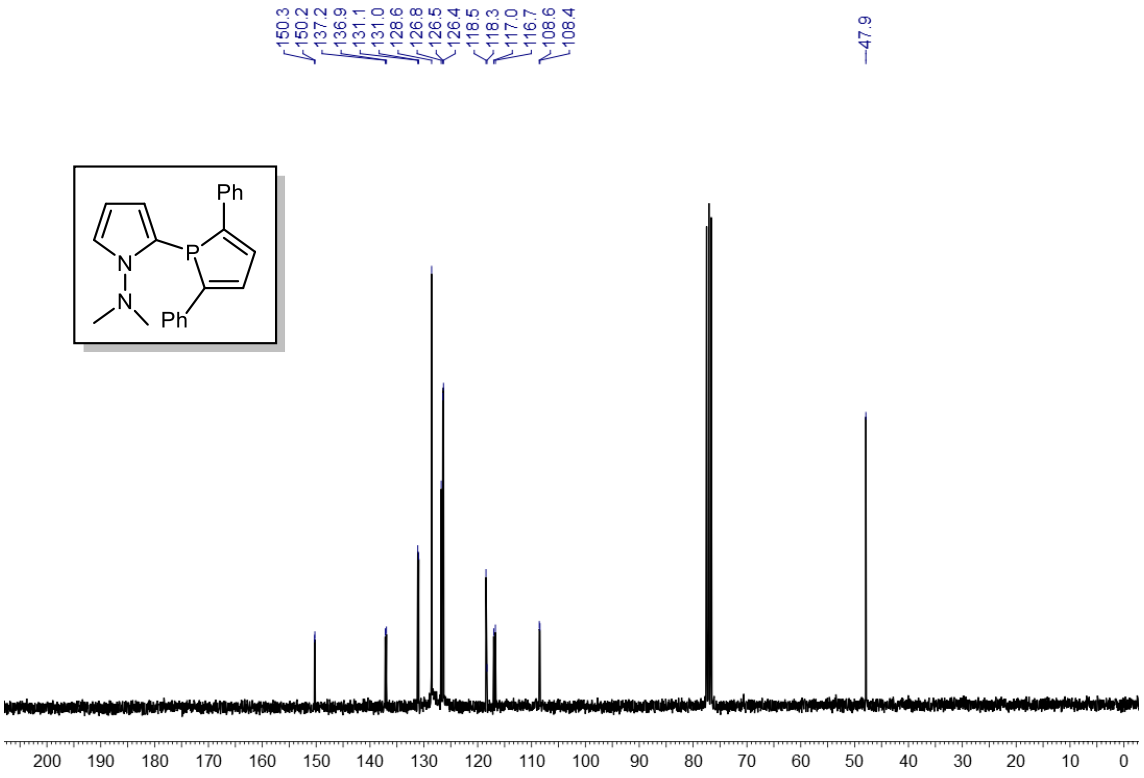
11. ^{1}H, ^{13}C and ^{31}P NMR spectra and NMR spectra of Palladium Complexes

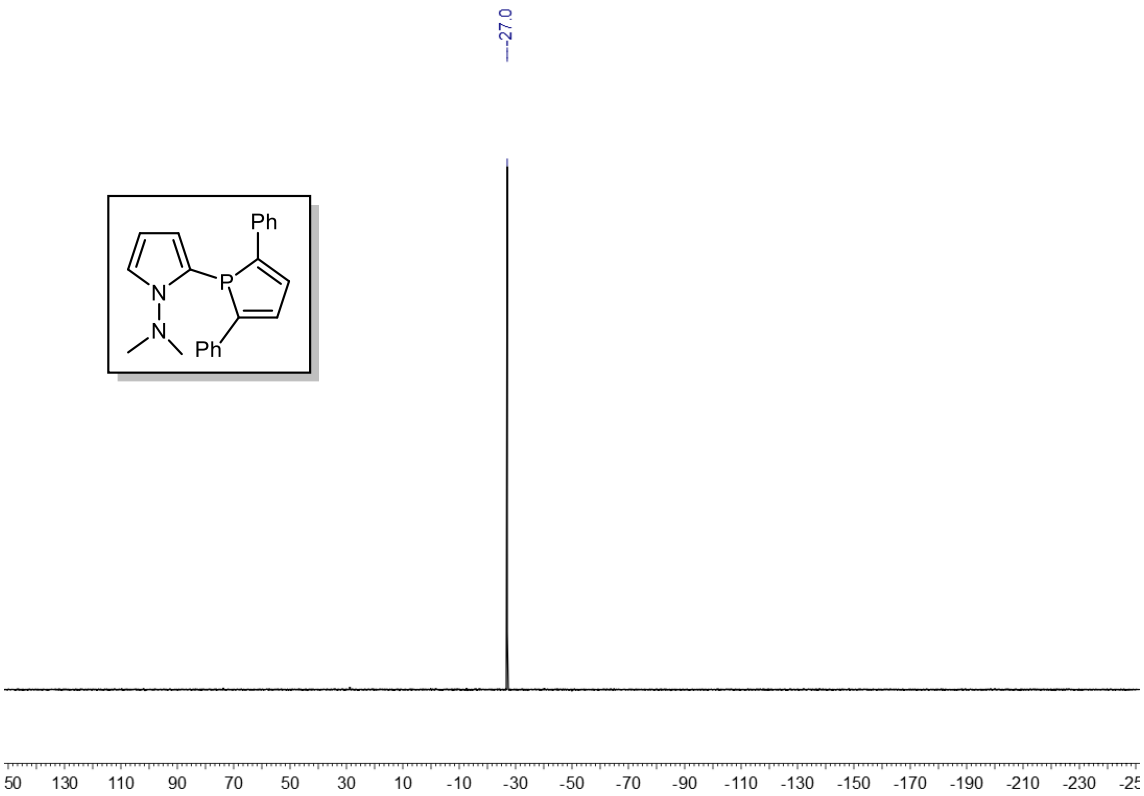


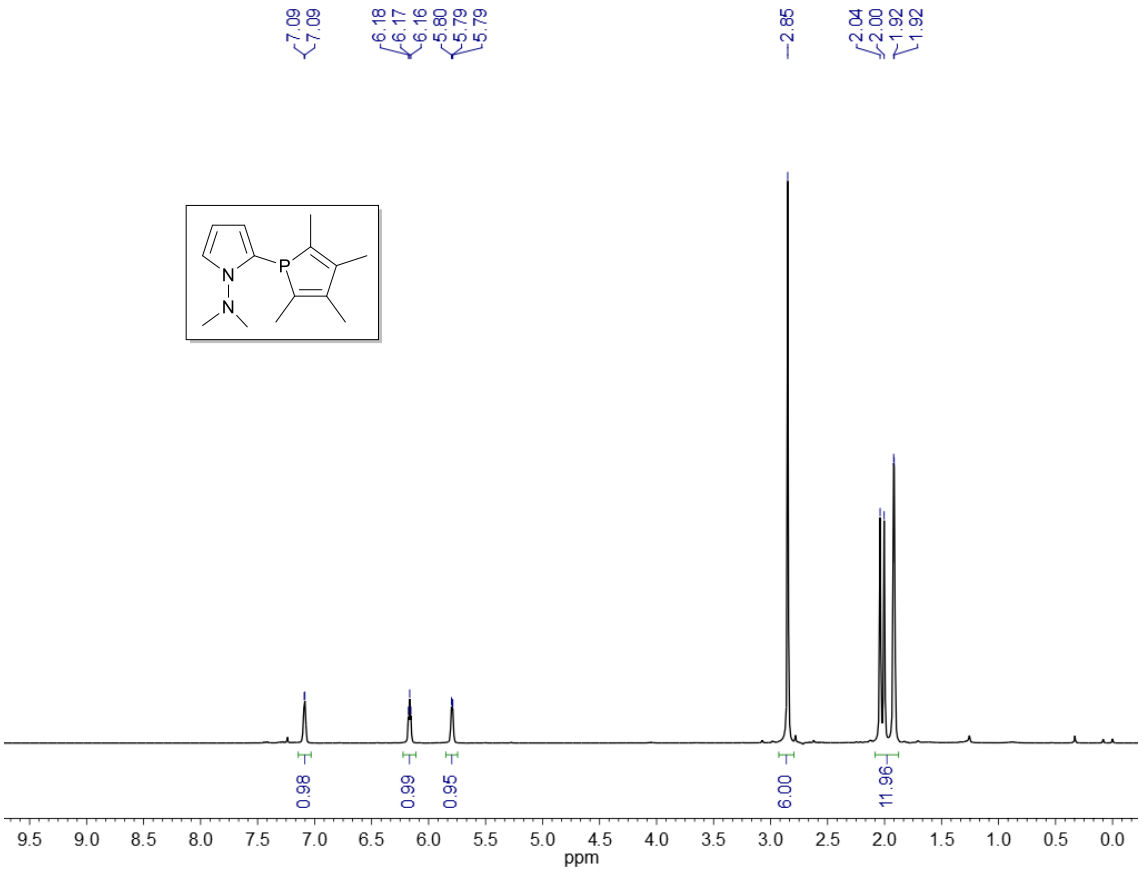


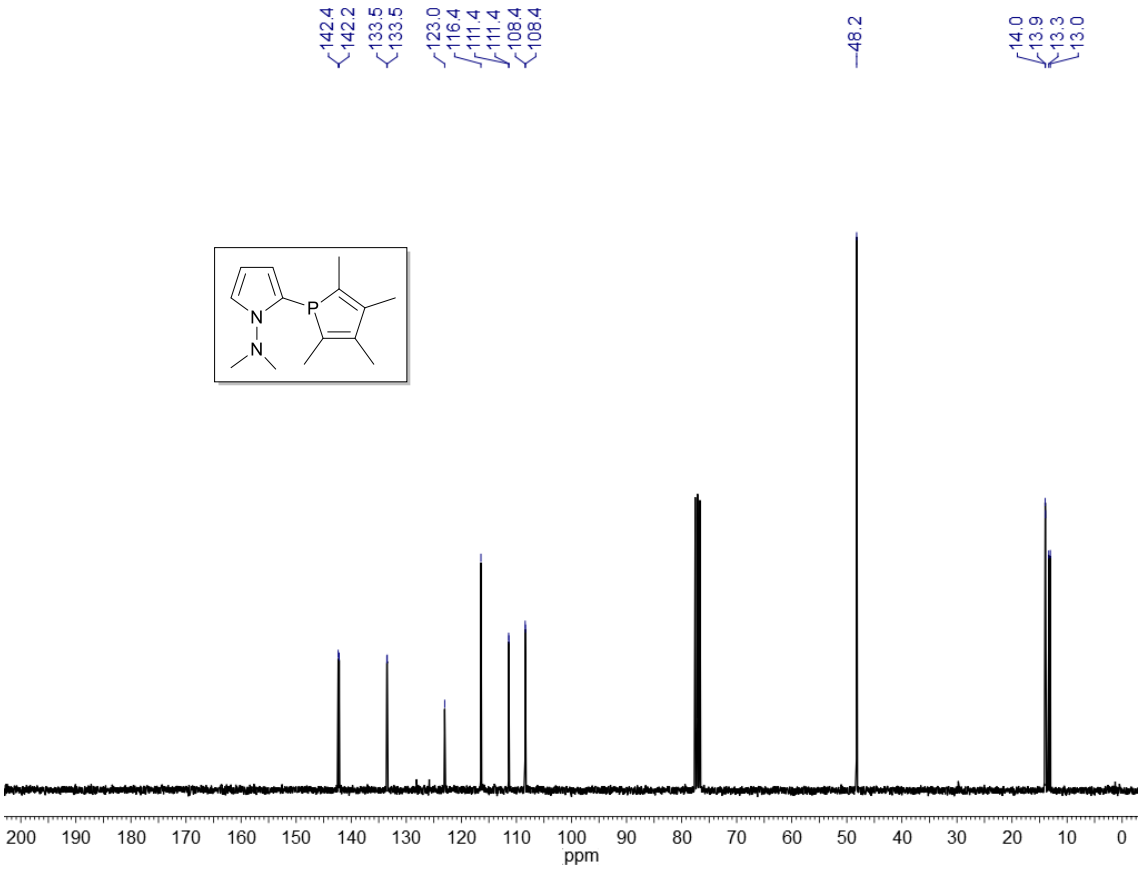

-25.7
N
N
P
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230

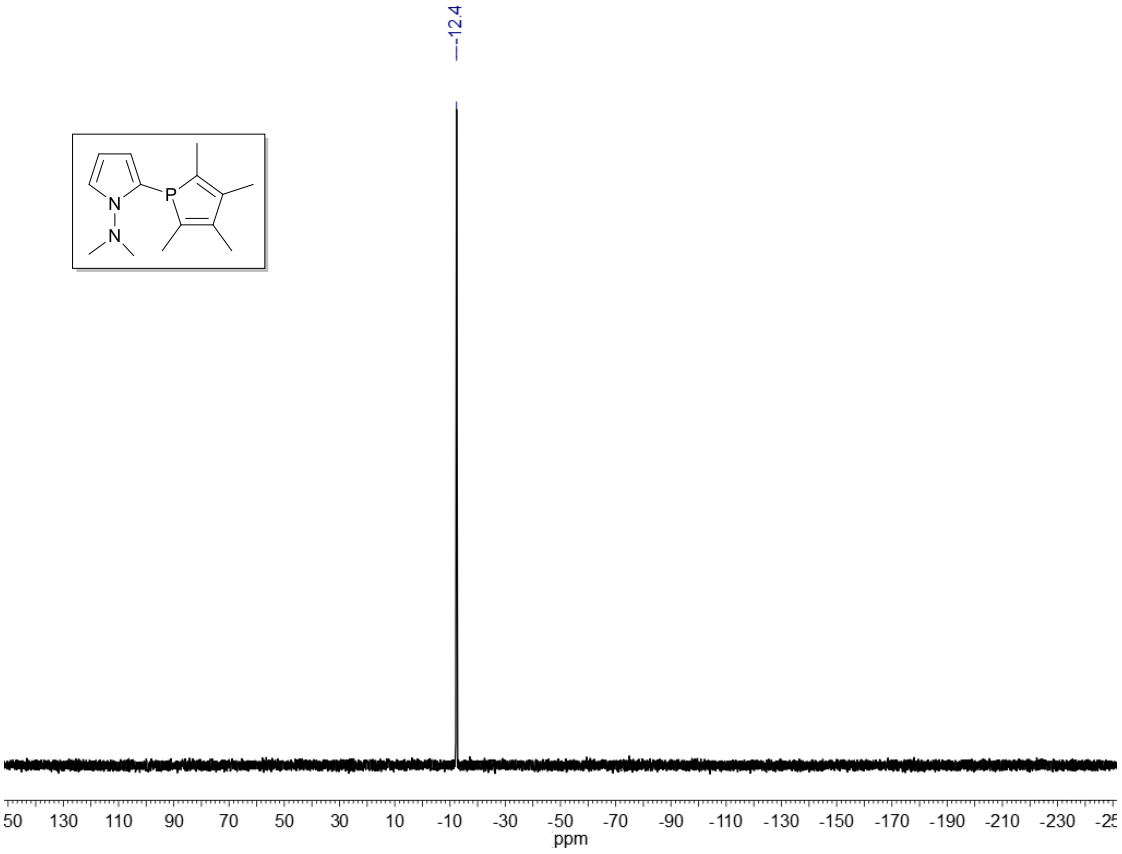

7.56
7.54
7.28
7.26
7.24
7.20
7.17
7.15
7.13
6.96
6.30
6.28
6.28
6.09
6.08
6.06
6.05
2.48
Ph
N
N
P
Ph
3.96
5.35
3.55
1.14
0.98
0.98
6.00
10.0 9.6 9.2 8.8 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4 0.0

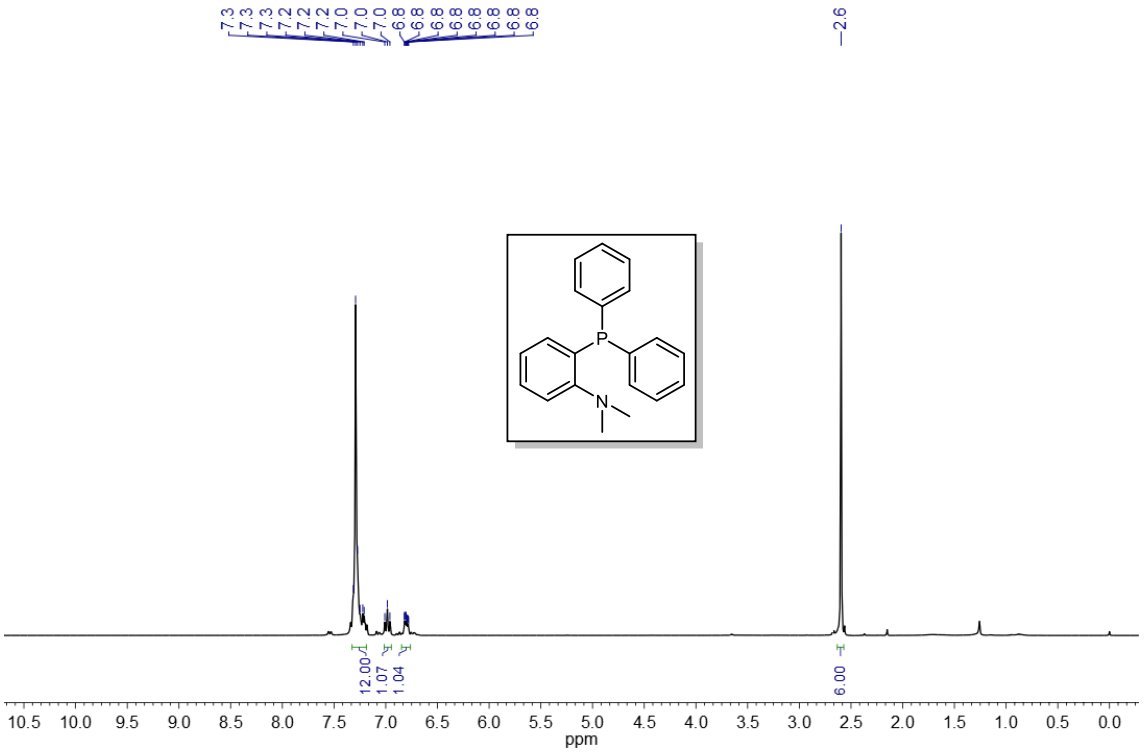

150.3
150.2
137.2
136.9
131.1
131.0
128.6
126.8
126.5
126.4
118.5
118.3
117.0
116.7
108.6
108.4
47.9
Ph
N
P
N
Ph
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

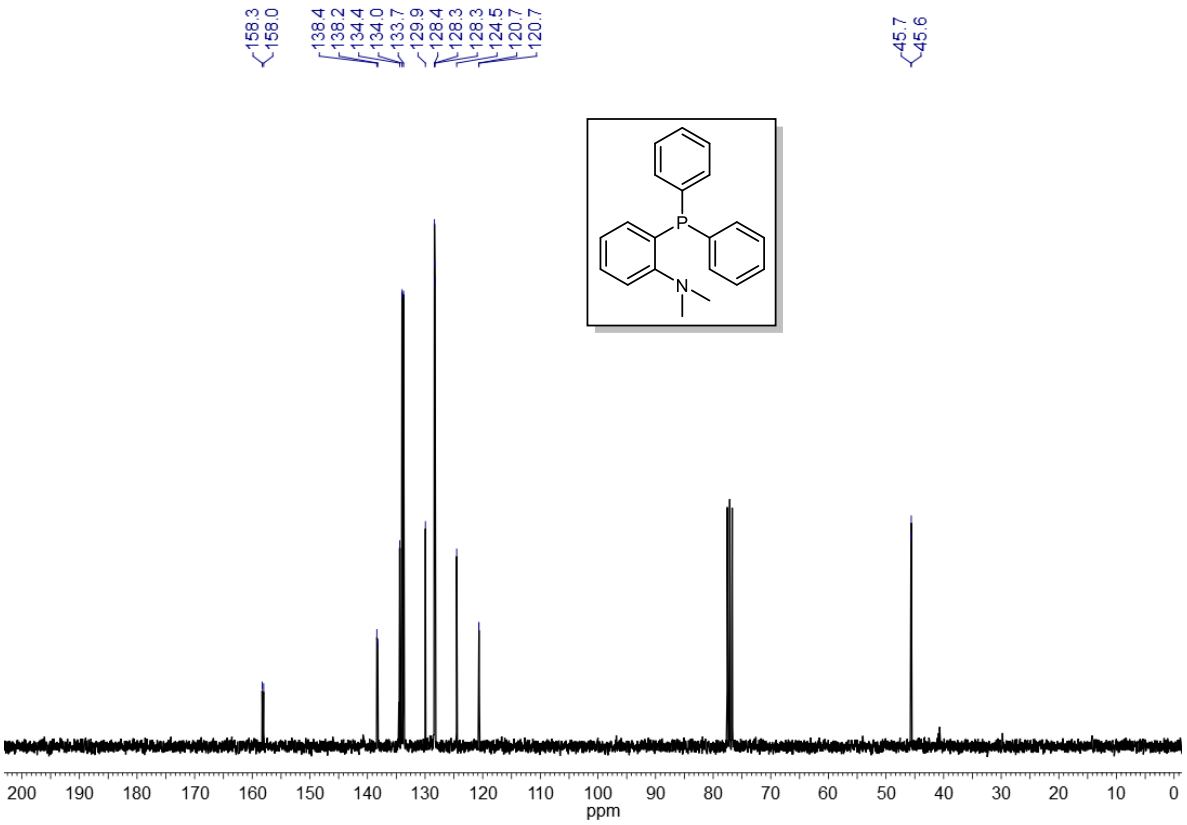

27.0
Ph
N
P
N
Ph
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230

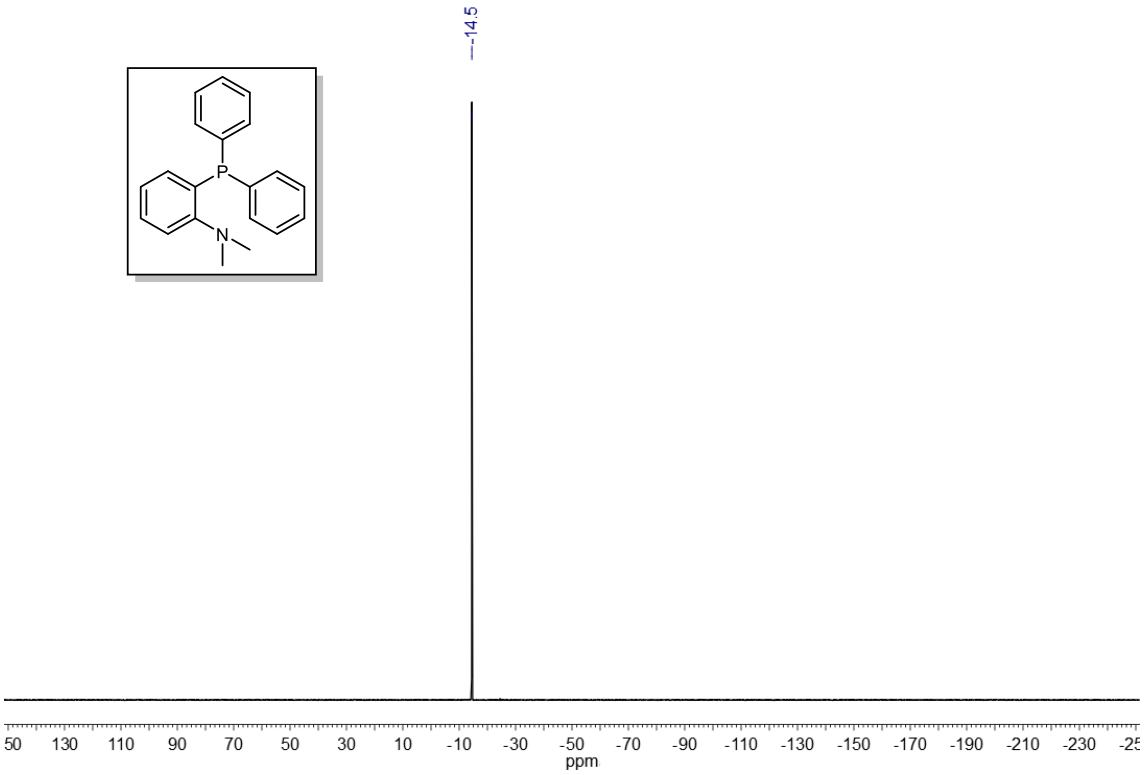

7.09
7.09
6.18
6.17
6.16
5.80
5.79
5.79
2.85
2.04
2.00
1.92
1.92
N
N
P
0.98
0.99
0.95
6.00
11.96
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

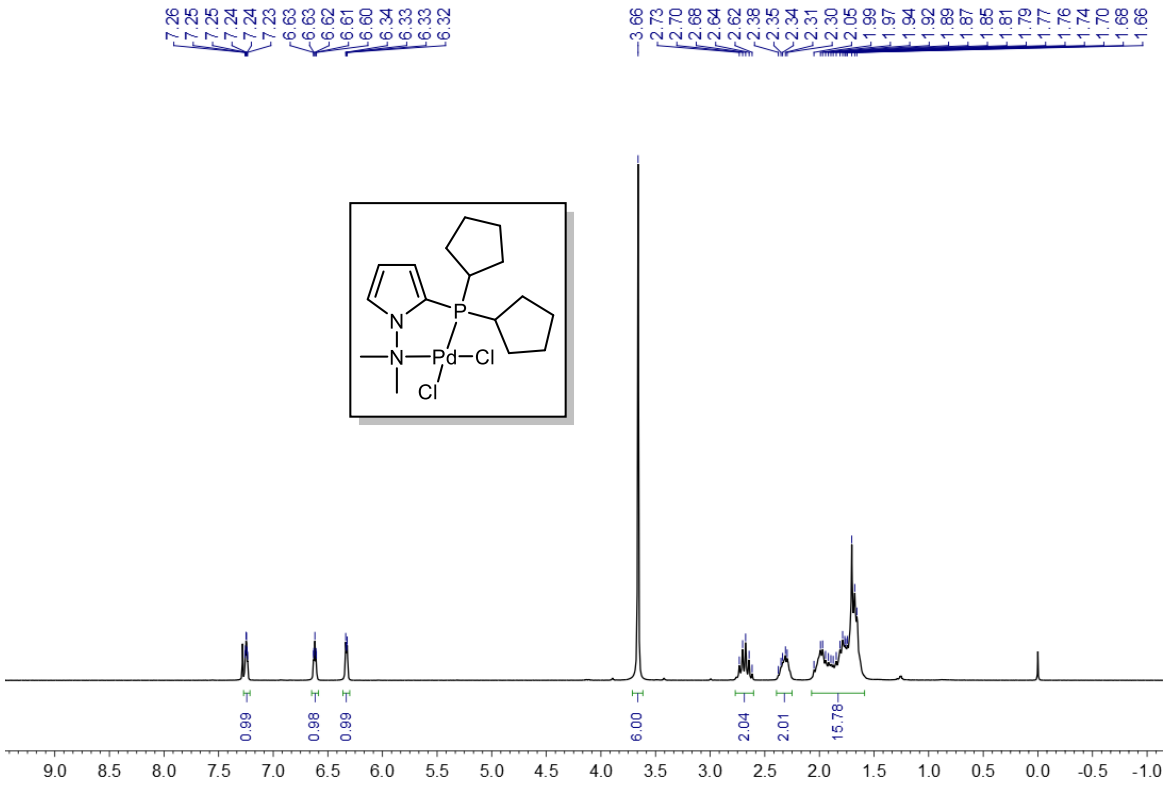

142.4
142.2
133.5
133.5
123.0
116.4
111.4
111.4
108.4
108.4
48.2
14.0
13.9
13.3
13.0
N
N
P
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

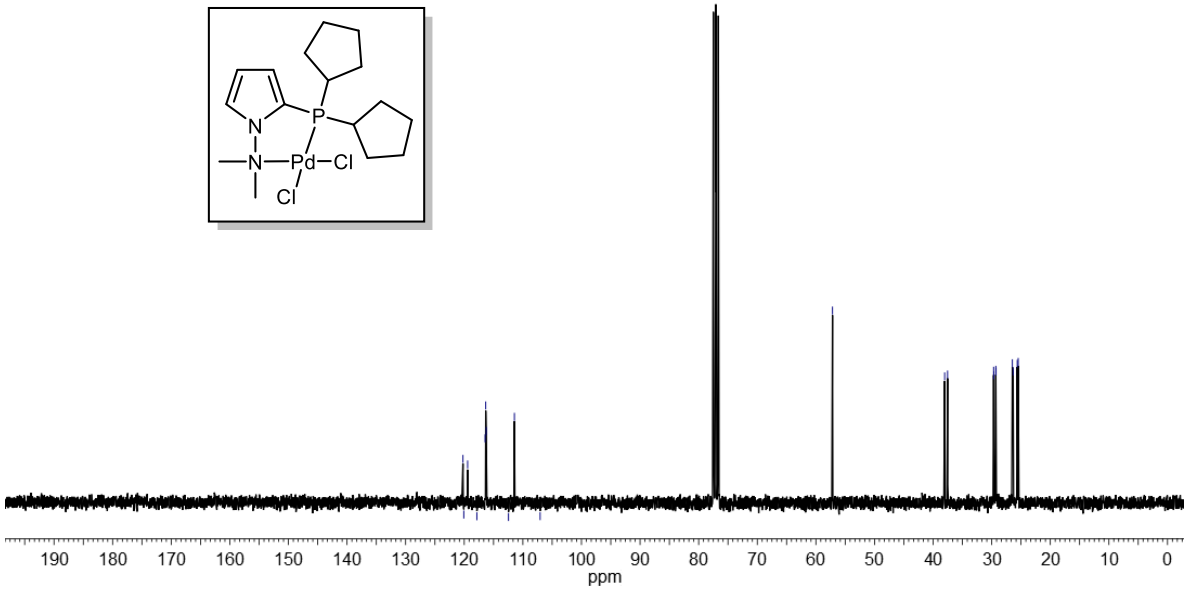

12.4
N
N
P
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
ppm

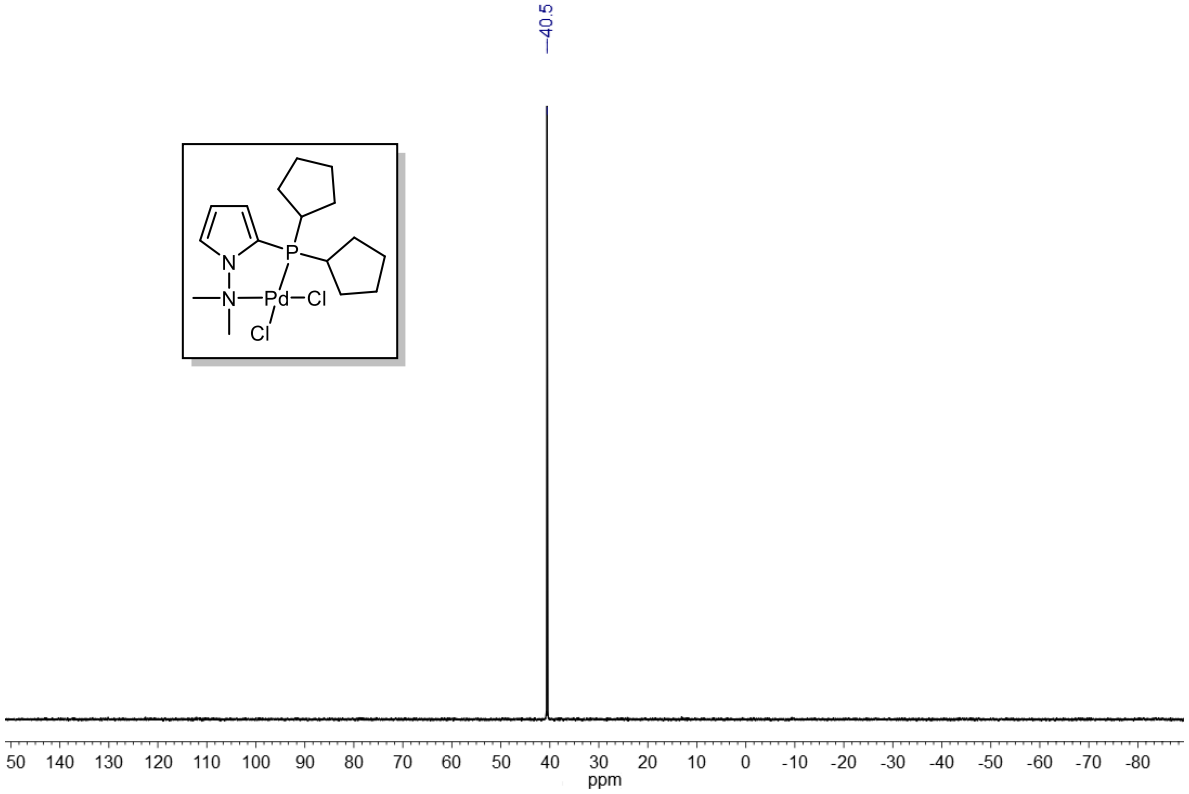

7.3
7.3
7.3
7.2
7.2
7.2
7.0
7.0
7.0
6.8
6.8
6.8
6.8
6.8
6.8
6.8
2.6
P
N
12.00
1.07
1.04
6.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

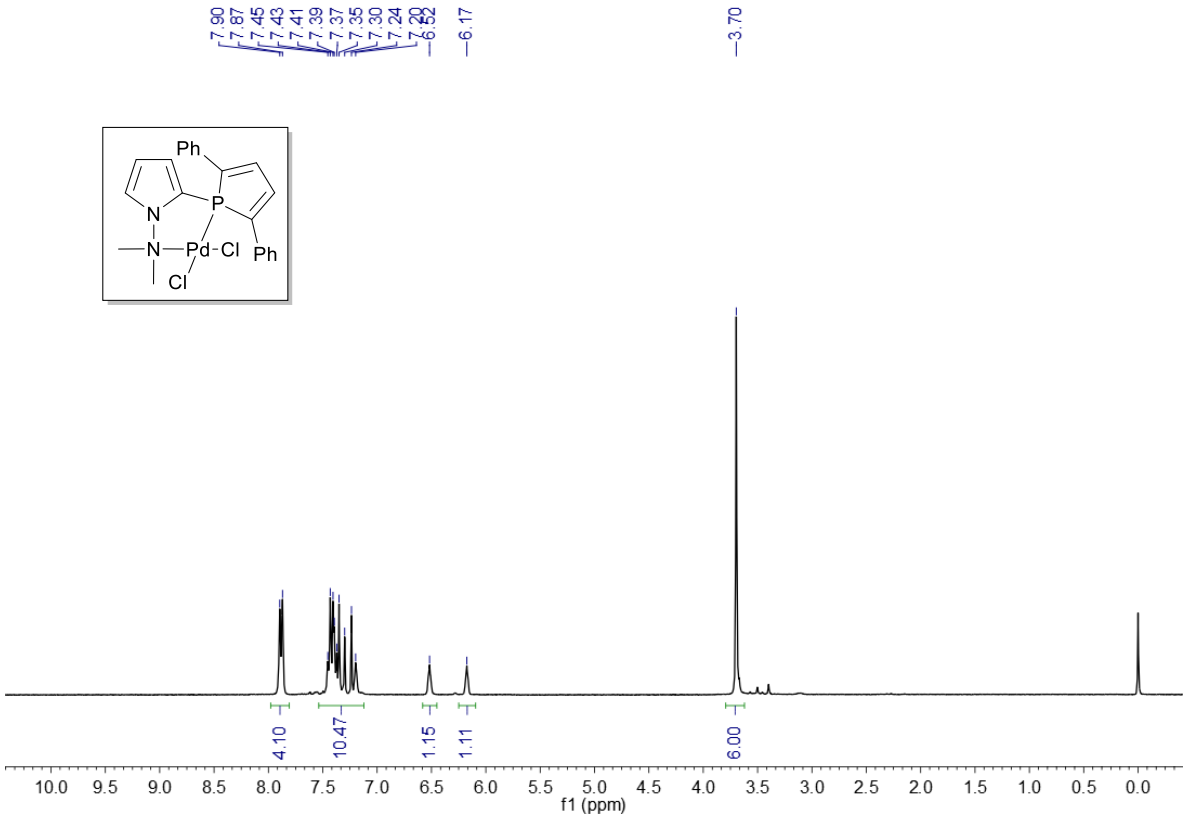

158.3
158.0
138.4
138.2
134.4
134.0
133.7
129.9
128.4
128.3
124.5
120.7
120.7
45.7
45.6
P
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

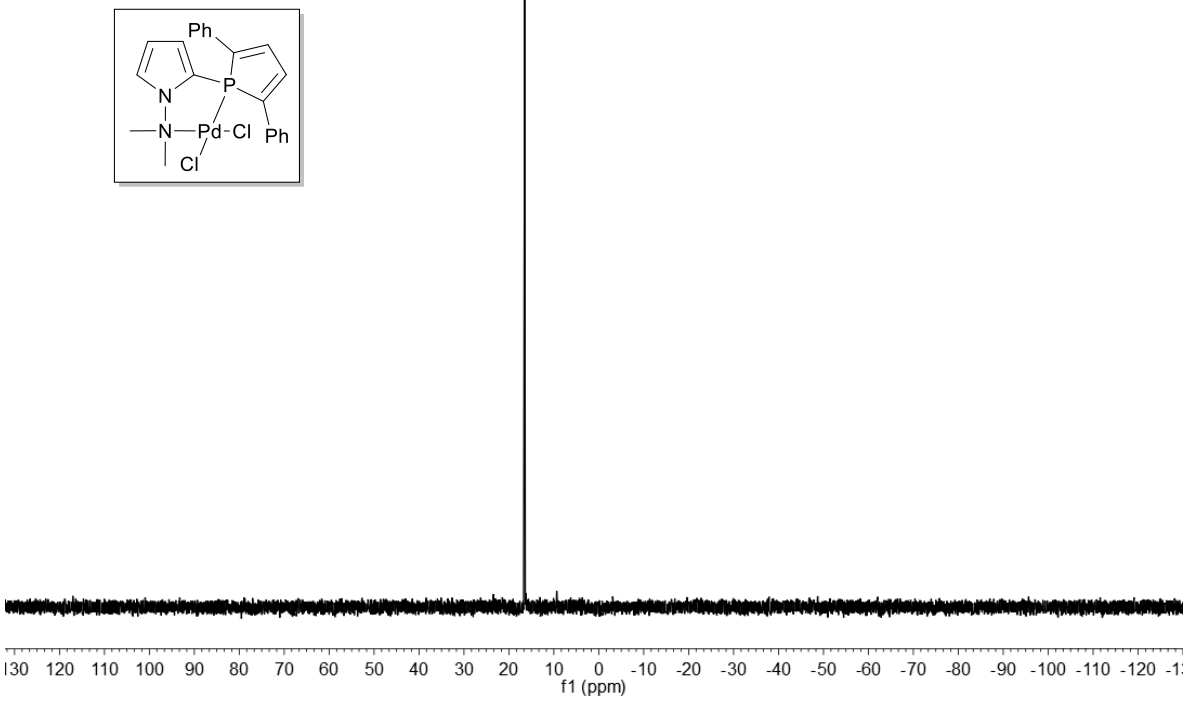

-14.5
P
N
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
ppm

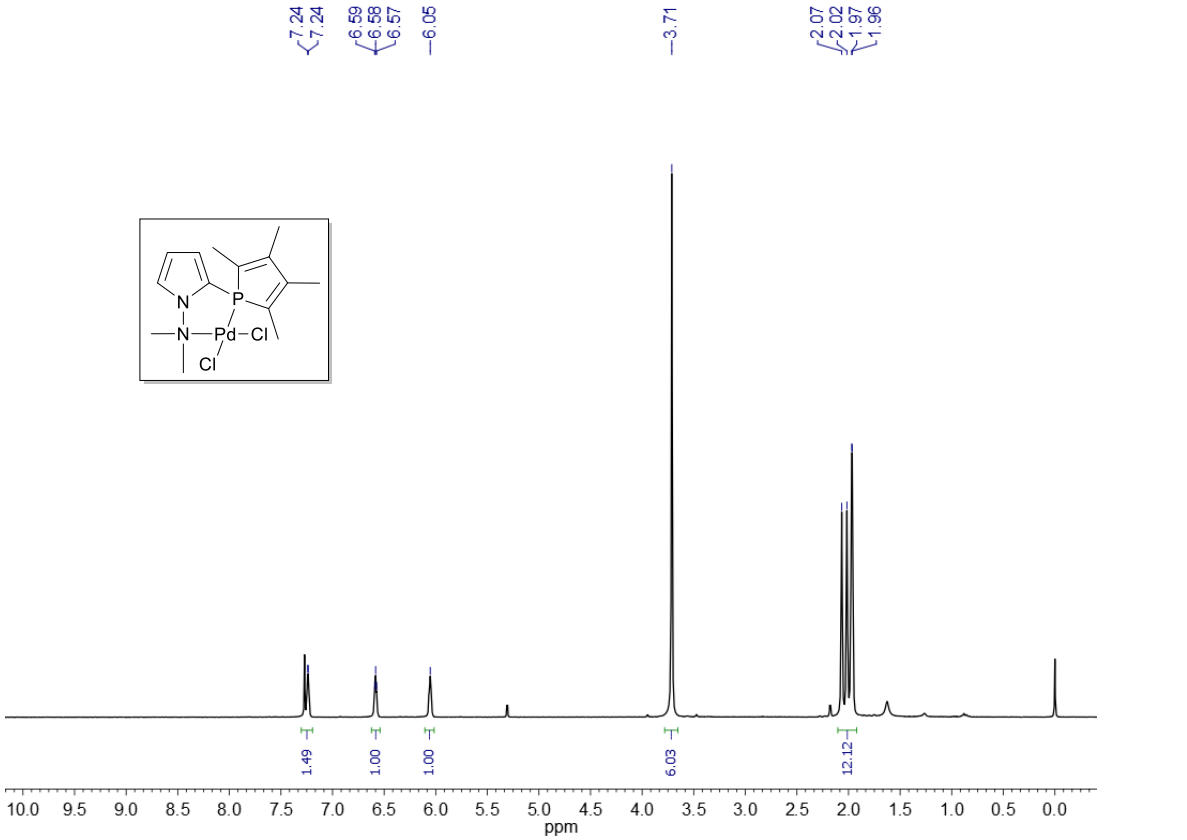

7.26
7.25
7.25
7.24
7.24
7.23
6.63
6.63
6.62
6.61
6.60
6.34
6.33
6.32
3.66
2.73
2.70
2.68
2.64
2.62
2.38
2.35
2.34
2.31
2.30
2.05
1.99
1.97
1.94
1.92
1.89
1.87
1.85
1.81
1.79
1.77
1.76
1.74
1.70
1.68
1.66
N
P
N
Pd
Cl
Cl
0.99
0.98
0.99
6.00
2.04
2.01
15.78
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

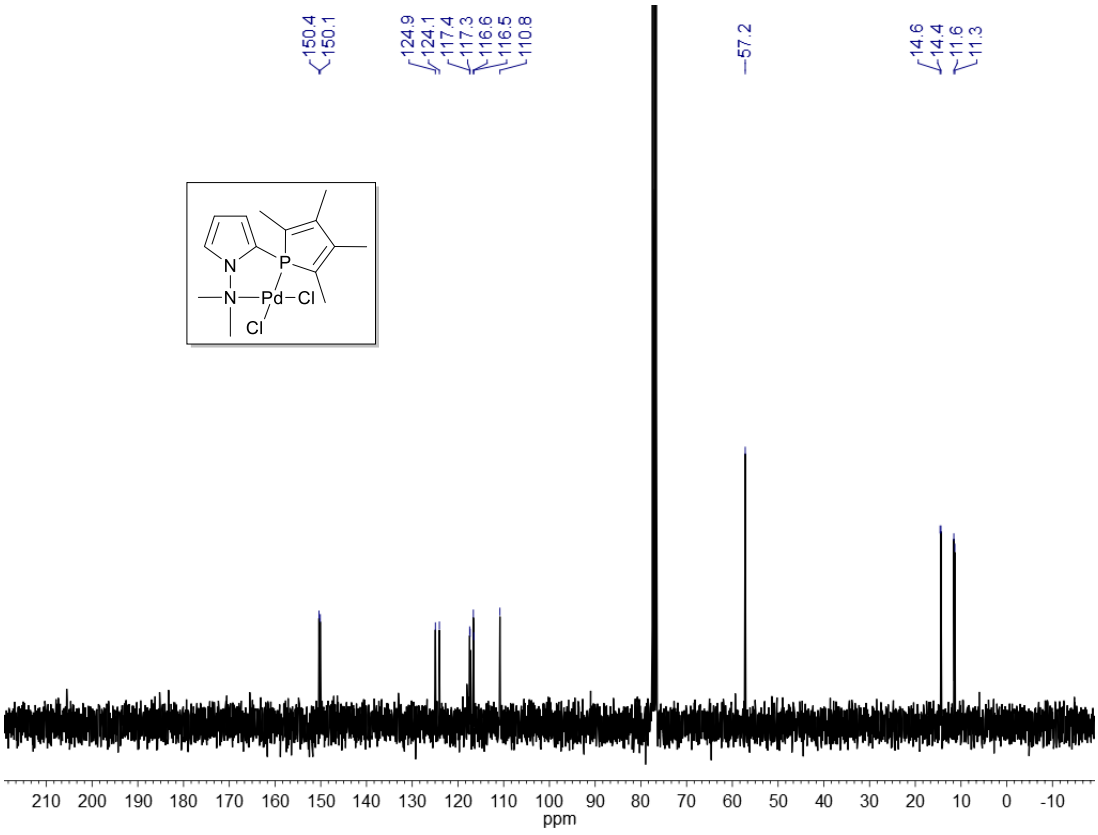

120.2
120.1
119.4
117.8
116.4
116.3
116.3
112.5
111.4
107.1
57.2
38.0
37.5
29.7
29.6
29.3
29.3
26.5
26.3
25.6
25.5
N
P
N
Pd
Cl
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

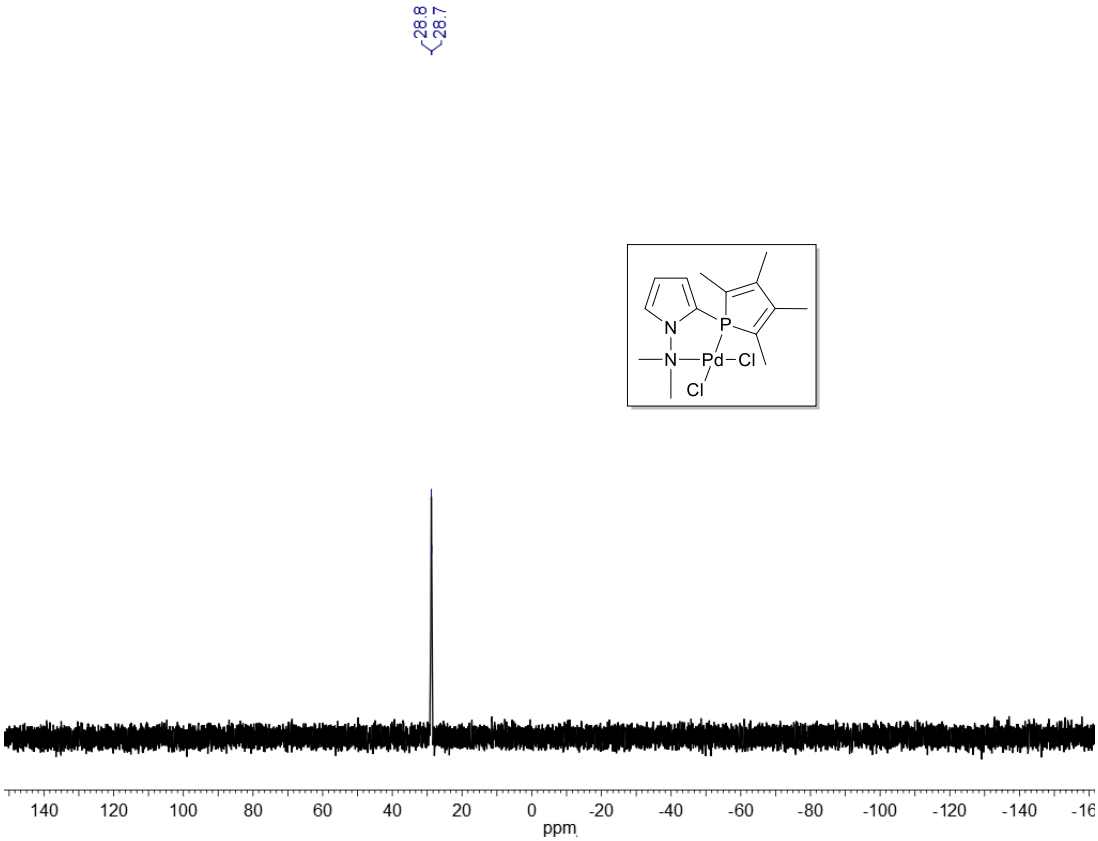

40.5
N
P
N
Pd
Cl
Cl
50 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
ppm

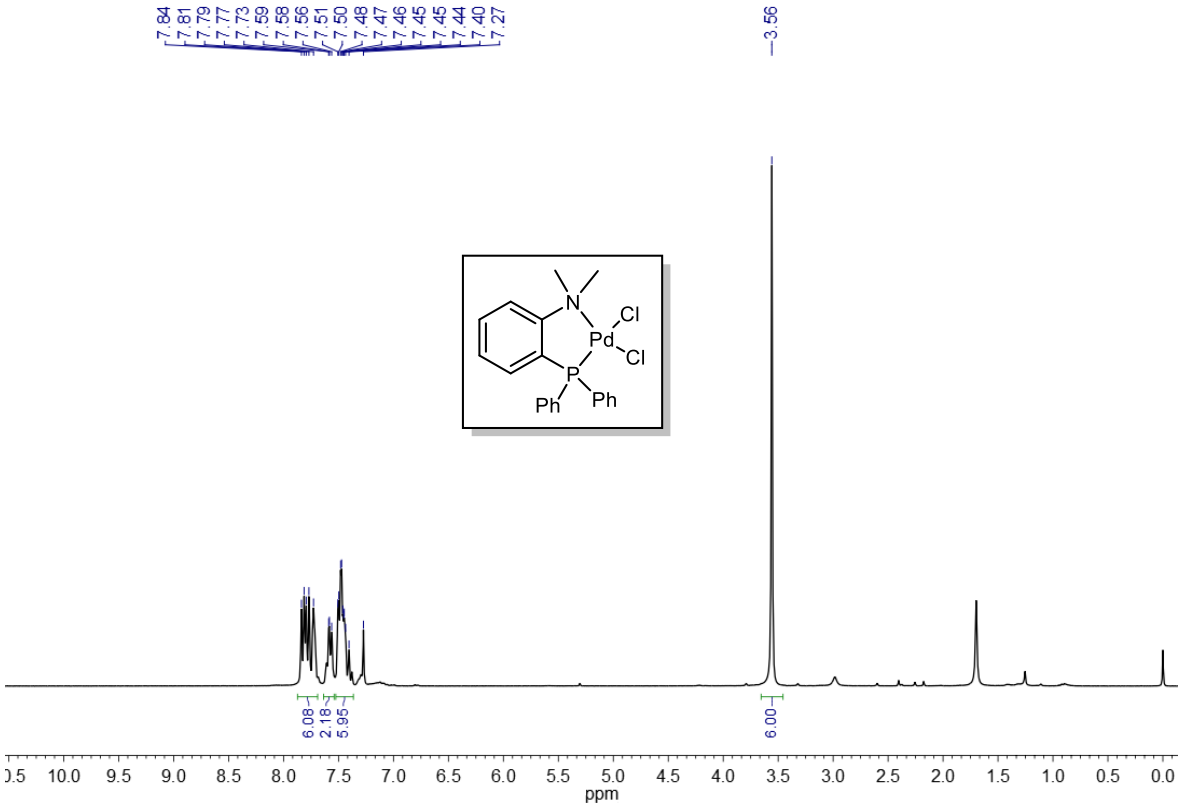

7.90
7.87
7.45
7.43
7.41
7.39
7.37
7.35
7.30
7.24
6.17
3.70
Ph
N
P
N
Pd
Cl
Ph
Cl
4.10
10.47
1.15
1.11
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

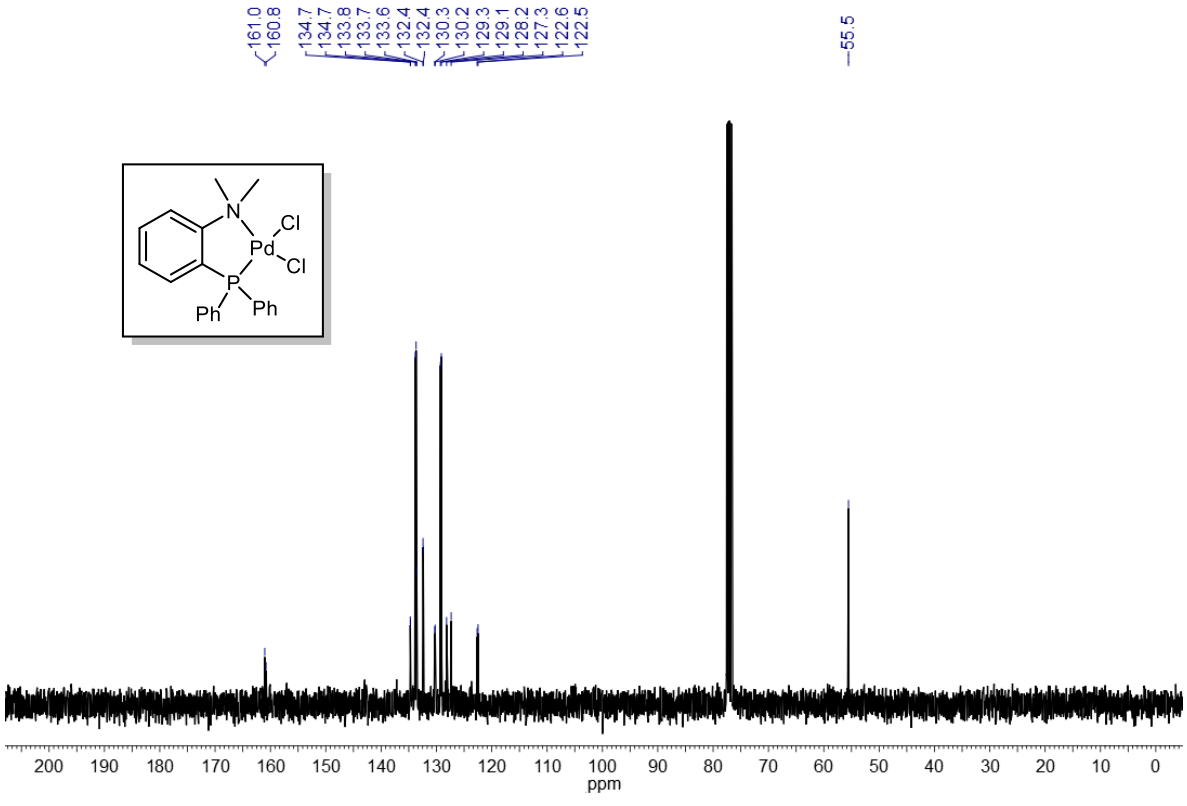

16.5
Ph
N
P
N
Pd
Cl
Ph
Cl
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)

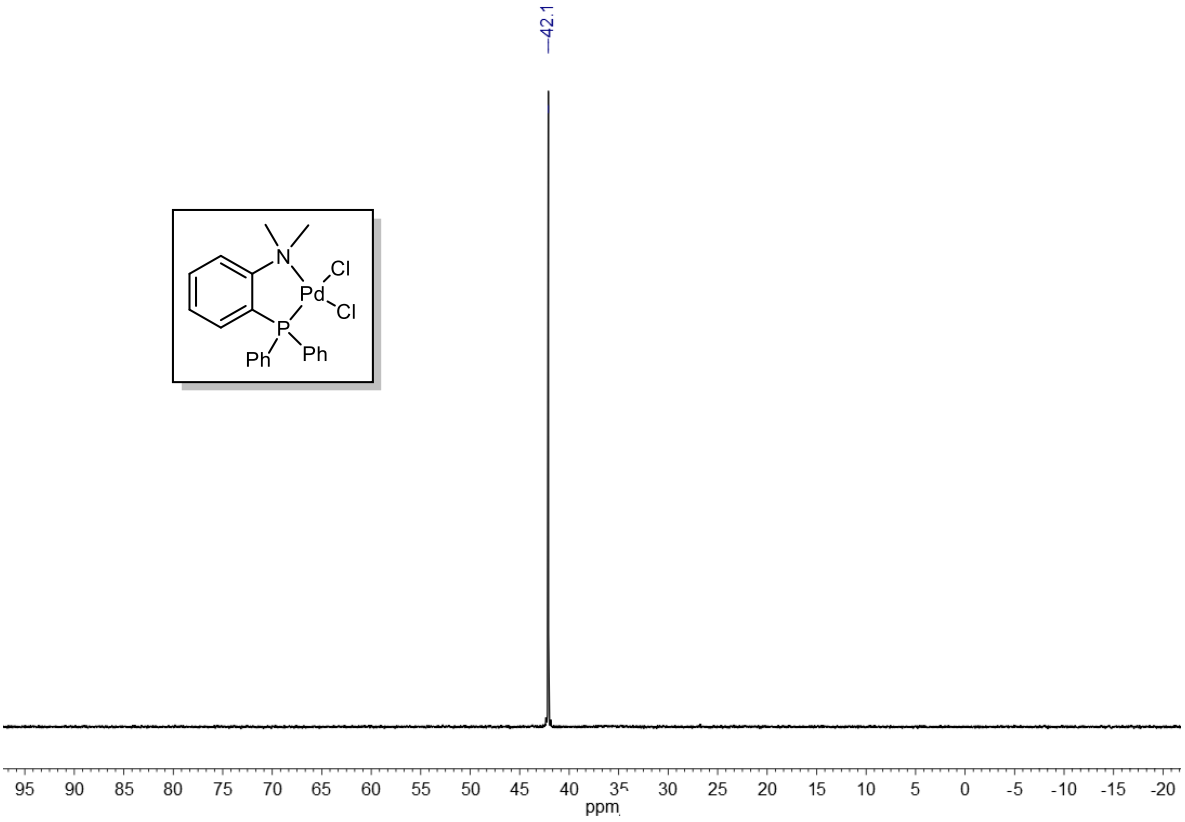

7.24
7.24
6.59
6.58
6.57
6.05
3.71
2.07
2.02
1.97
1.96
N
P
N
Pd
Cl
Cl
1.49
1.00
1.00
6.03
12.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


150.4
150.1
124.9
124.1
117.4
117.3
116.6
116.5
110.8
57.2
14.6
14.4
11.6
11.3
N
P
N
Pd
Cl
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

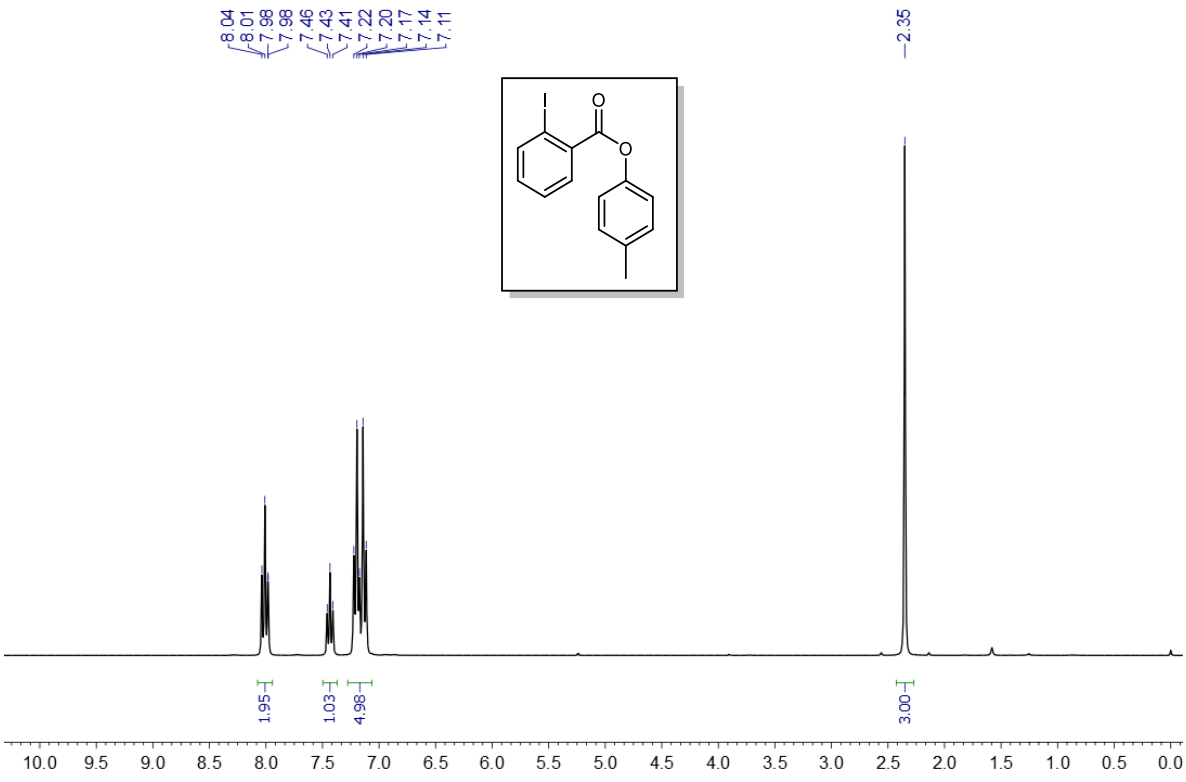

28.8
28.7
N
P
N
Pd
Cl
Cl
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -16
ppm

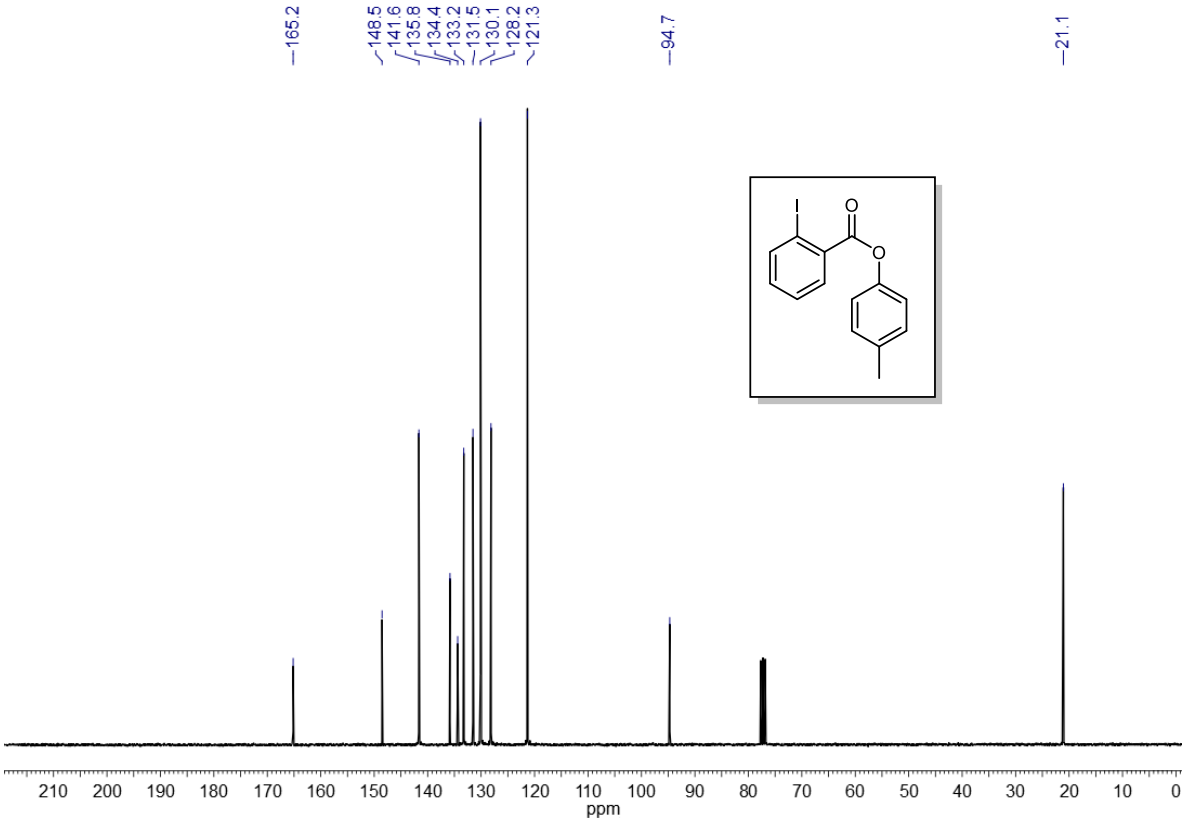

7.84
7.81
7.79
7.77
7.73
7.59
7.58
7.56
7.51
7.50
7.48
7.47
7.46
7.45
7.45
7.44
7.40
7.27
3.56
N
Cl
Pd
Cl
P
Ph
Ph
6.08
2.18
5.95
6.00
ppm

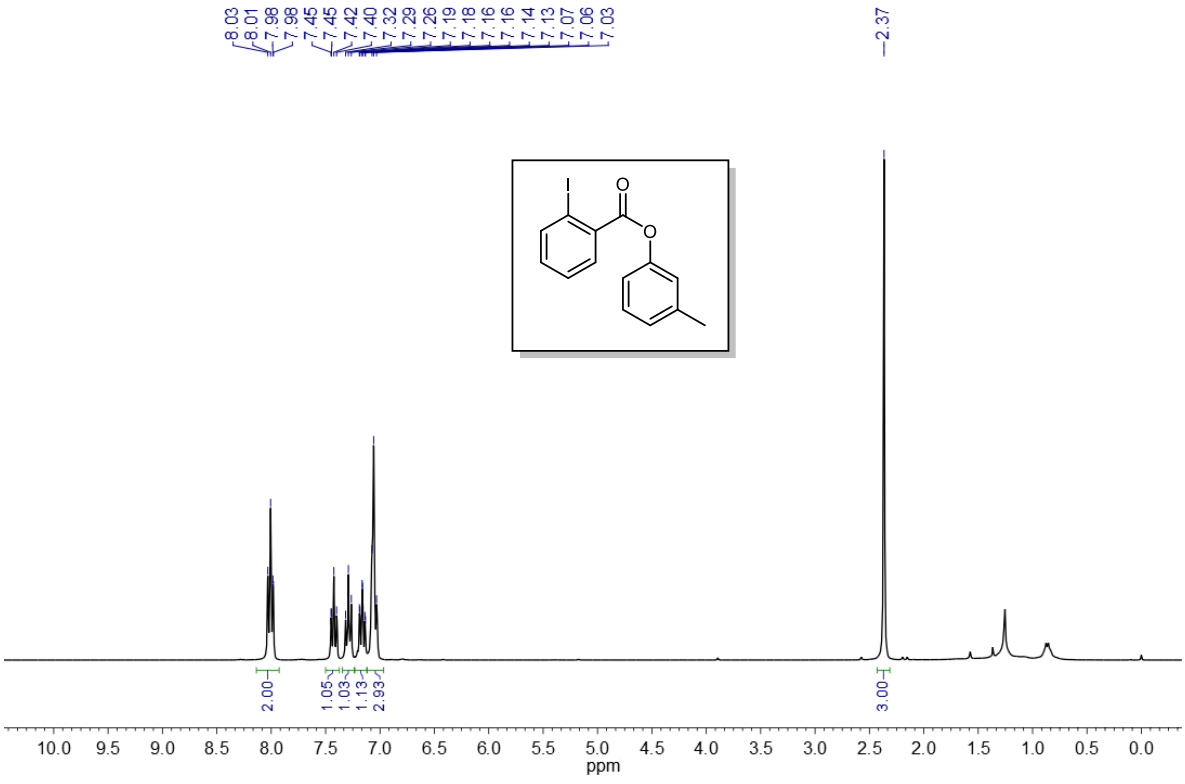

161.0
160.8
134.7
134.7
133.8
133.7
133.6
132.4
132.4
130.3
130.2
129.3
129.1
128.2
127.3
122.6
122.5
55.5
N
Cl
Pd
Cl
P
Ph
Ph
ppm

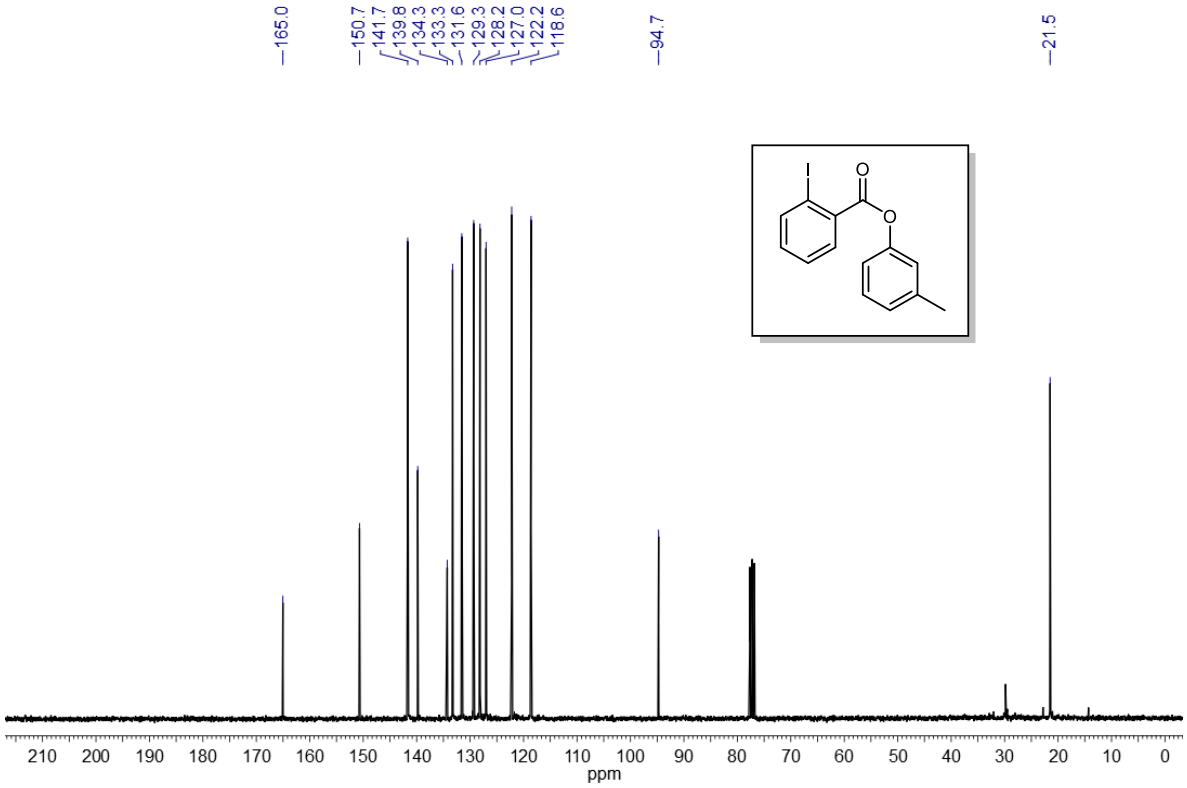


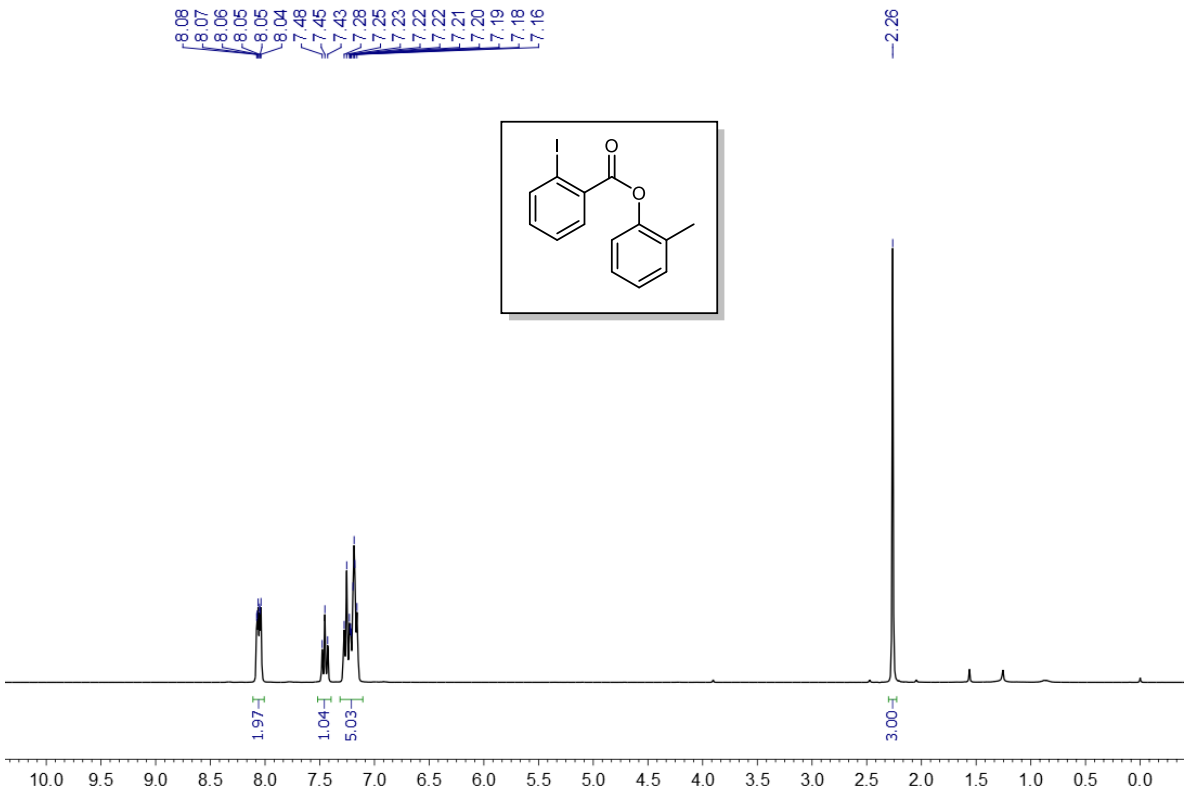
12. Compounds prepared for the coupling reaction

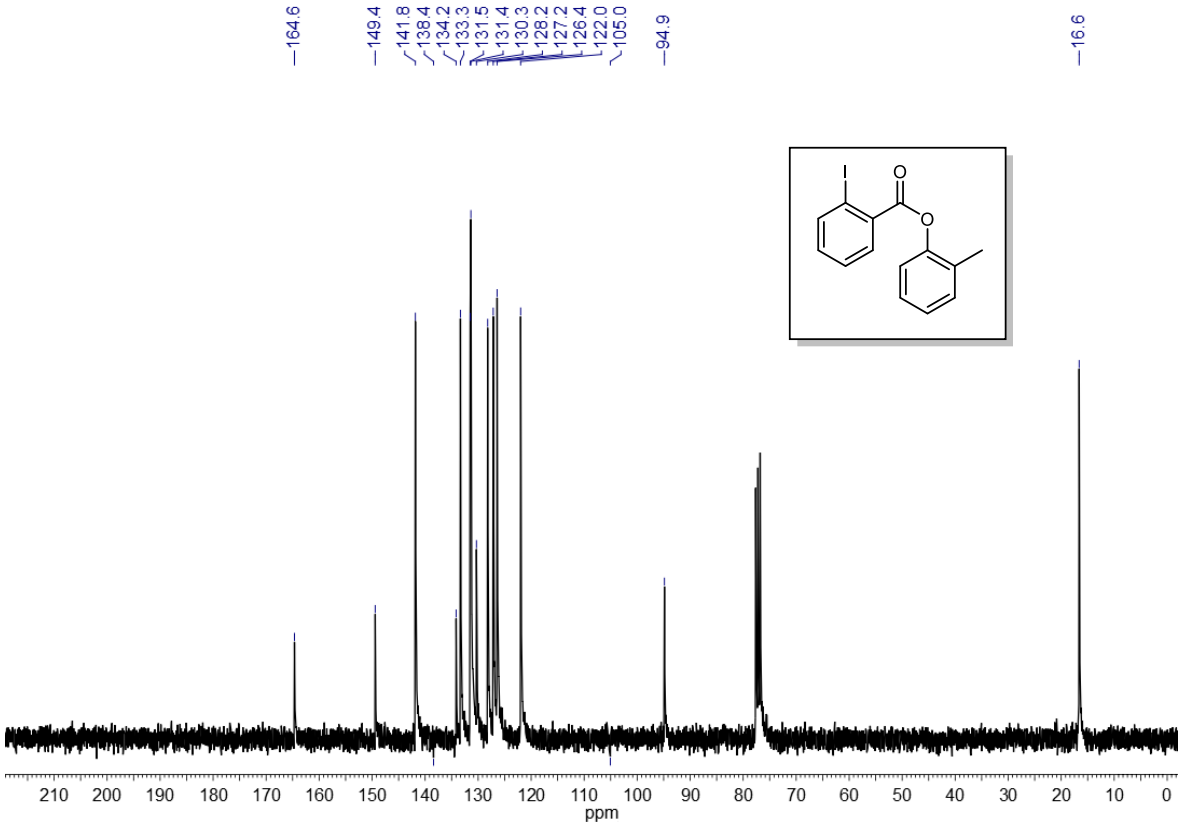


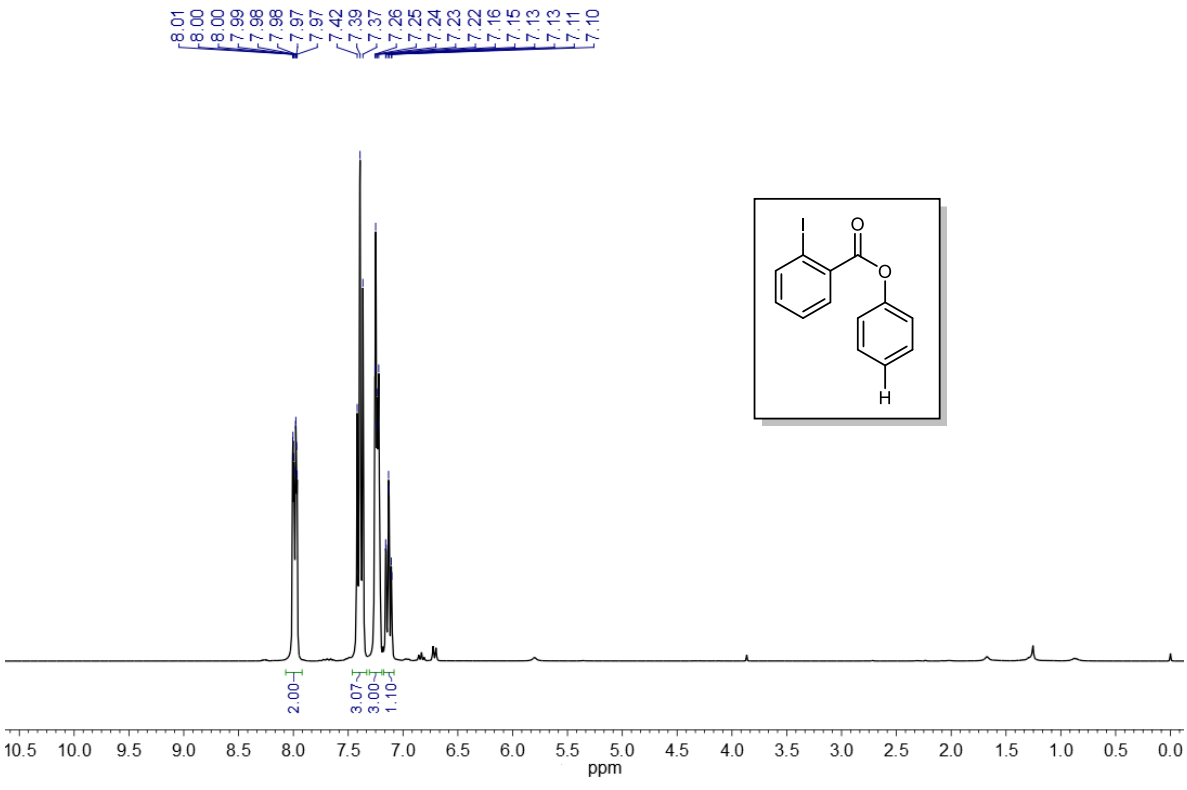

165.2
148.5
141.6
135.8
134.4
133.2
131.5
130.1
128.2
121.3
94.7
21.1
I
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

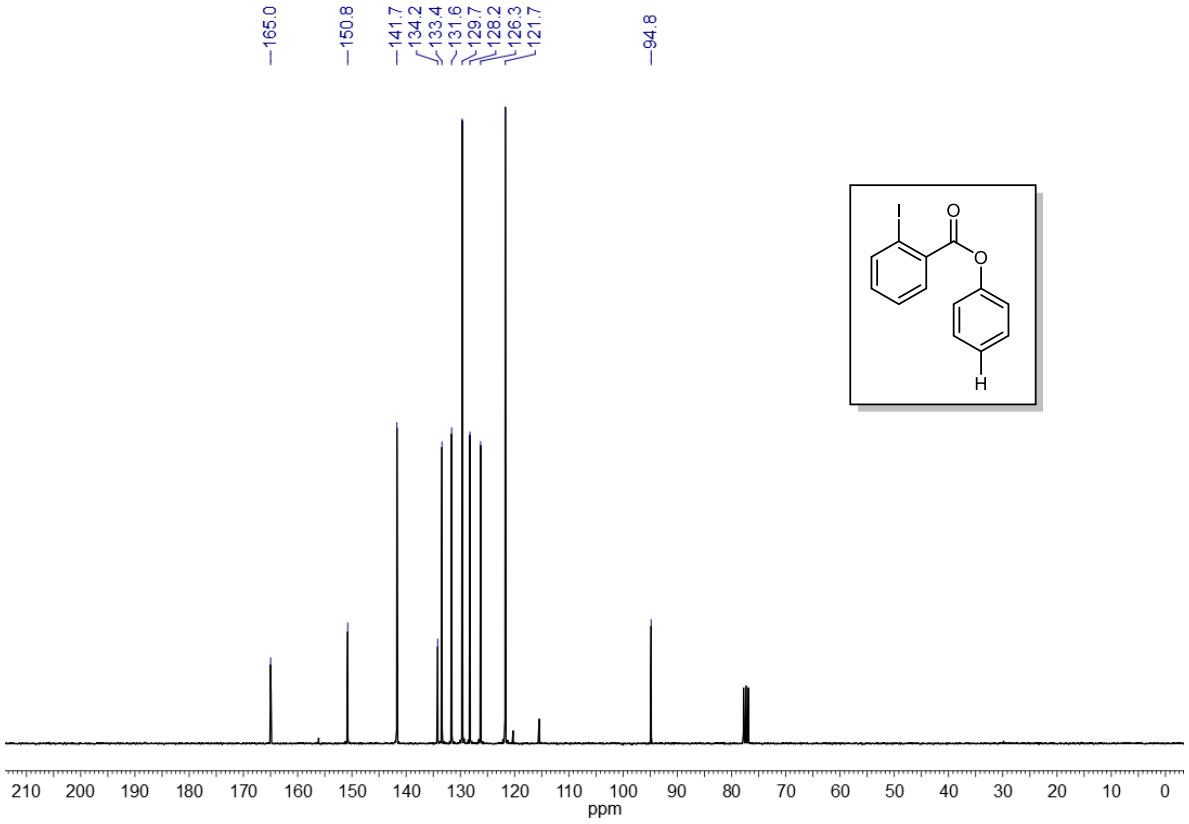

8.03
8.01
7.98
7.98
7.45
7.45
7.42
7.40
7.32
7.29
7.26
7.19
7.18
7.16
7.16
7.14
7.13
7.07
7.06
7.03
2.37
I
O
O
2.00
1.05
1.03
1.13
2.93
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

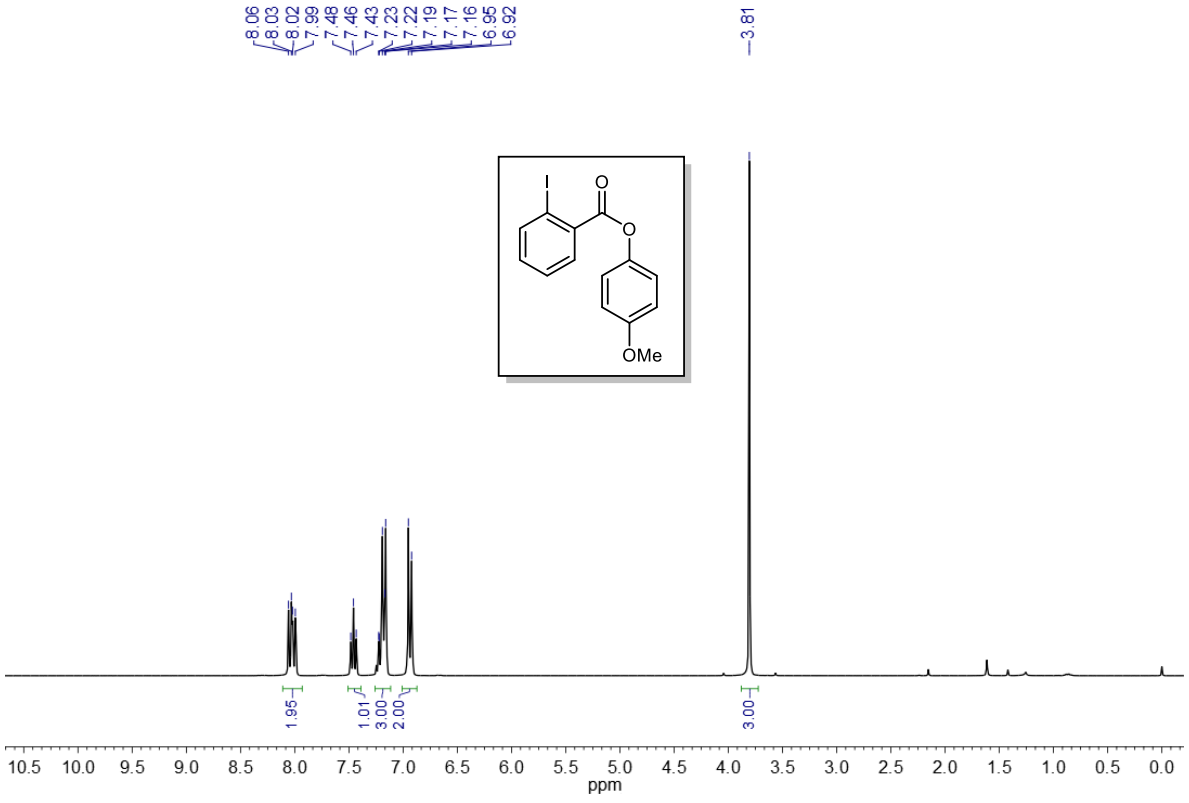

165.0
150.7
141.7
139.8
134.3
133.3
131.6
129.3
128.2
127.0
122.2
118.6
94.7
21.5
I
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

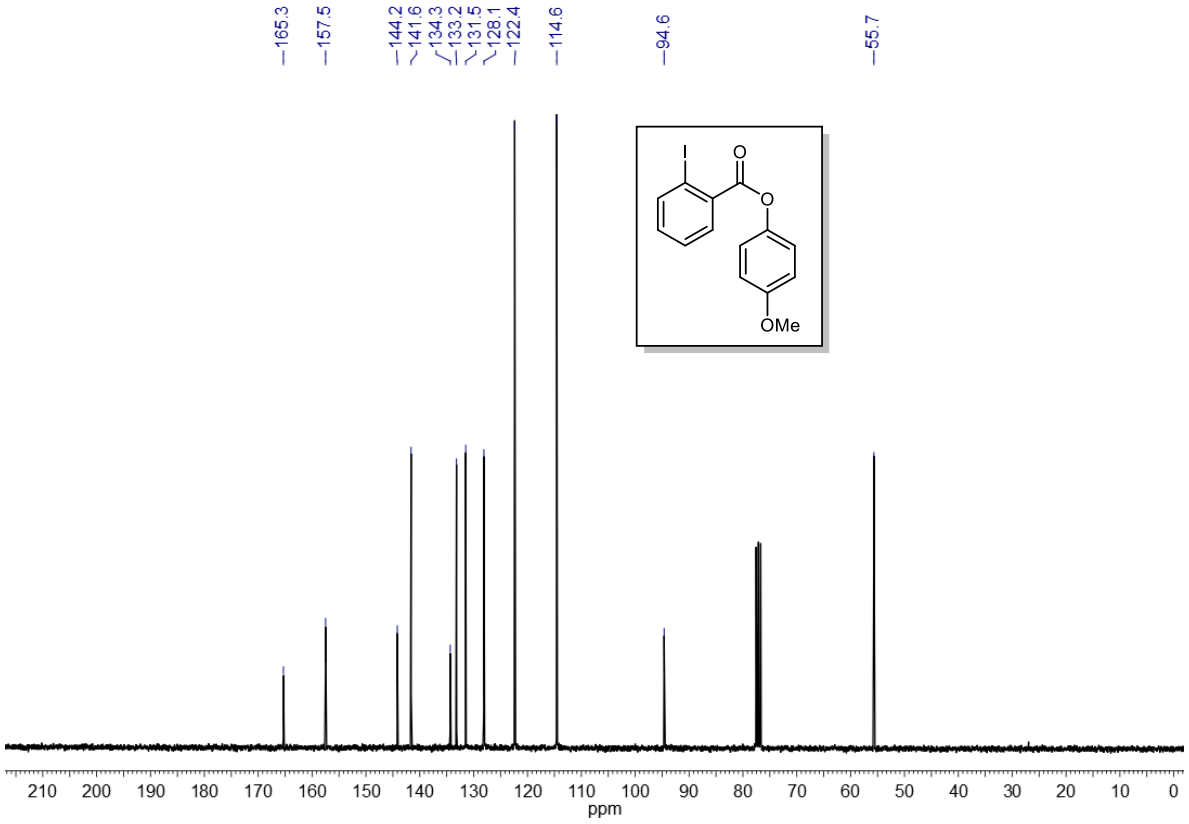

8.08
8.07
8.06
8.05
8.05
8.04
7.48
7.45
7.43
7.28
7.25
7.23
7.22
7.22
7.21
7.20
7.19
7.18
7.16
2.26
I
O
O
1.97
1.04
5.03
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

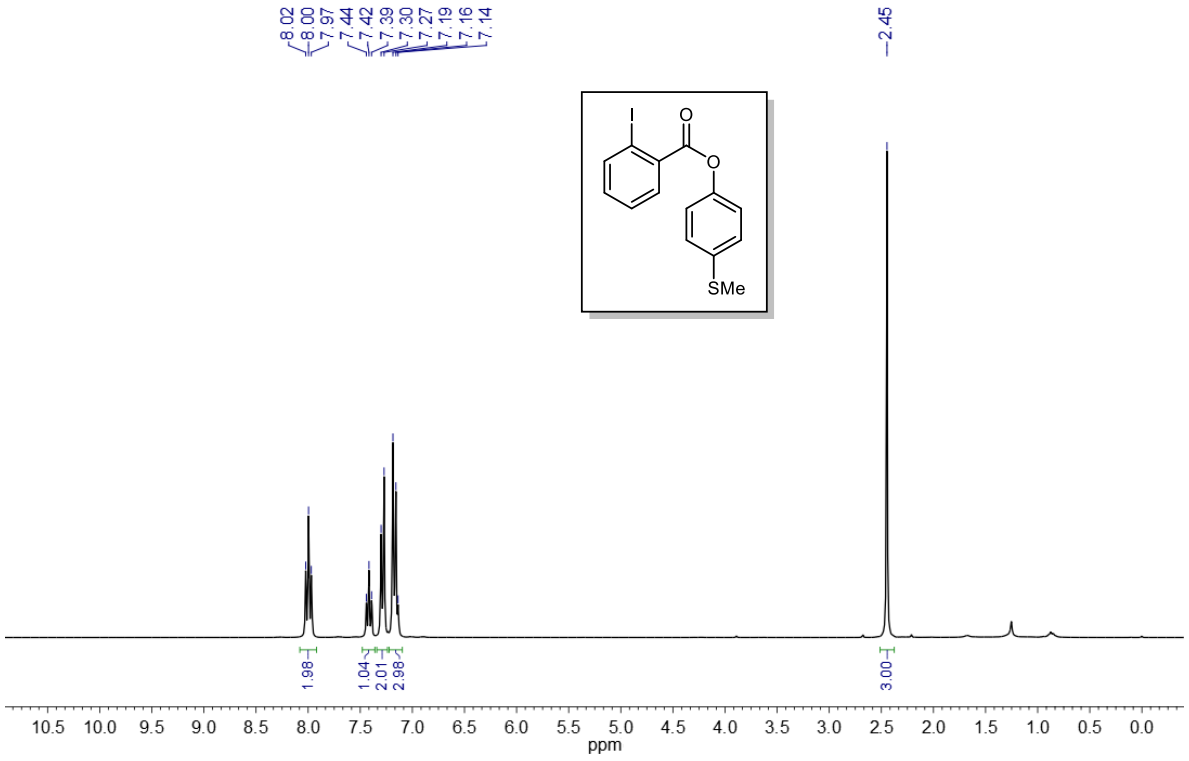

164.6
149.4
141.8
138.4
134.2
133.3
131.5
131.4
130.3
128.2
127.2
126.4
122.0
105.0
94.9
16.6
I
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

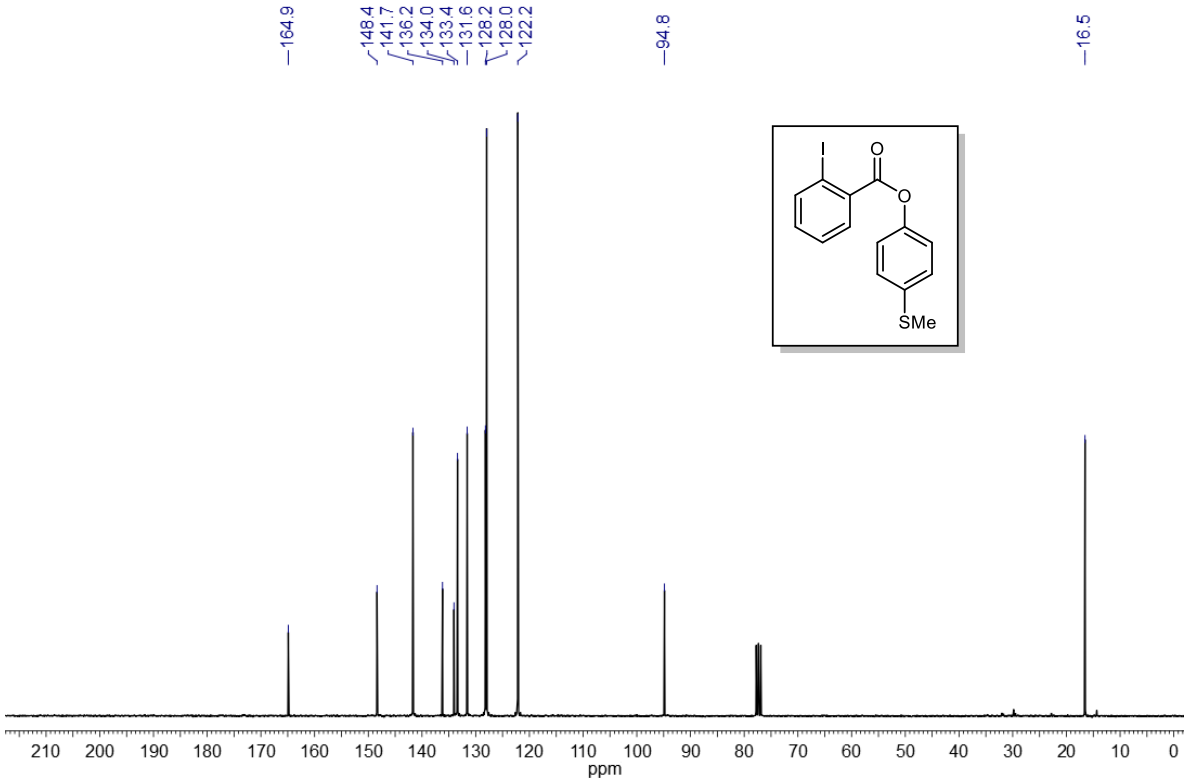

8.01
8.00
8.00
7.99
7.98
7.98
7.97
7.97
7.42
7.39
7.37
7.26
7.25
7.24
7.23
7.22
7.16
7.15
7.13
7.13
7.11
7.10
I
O
O
H
2.00
3.07
3.00
1.10
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

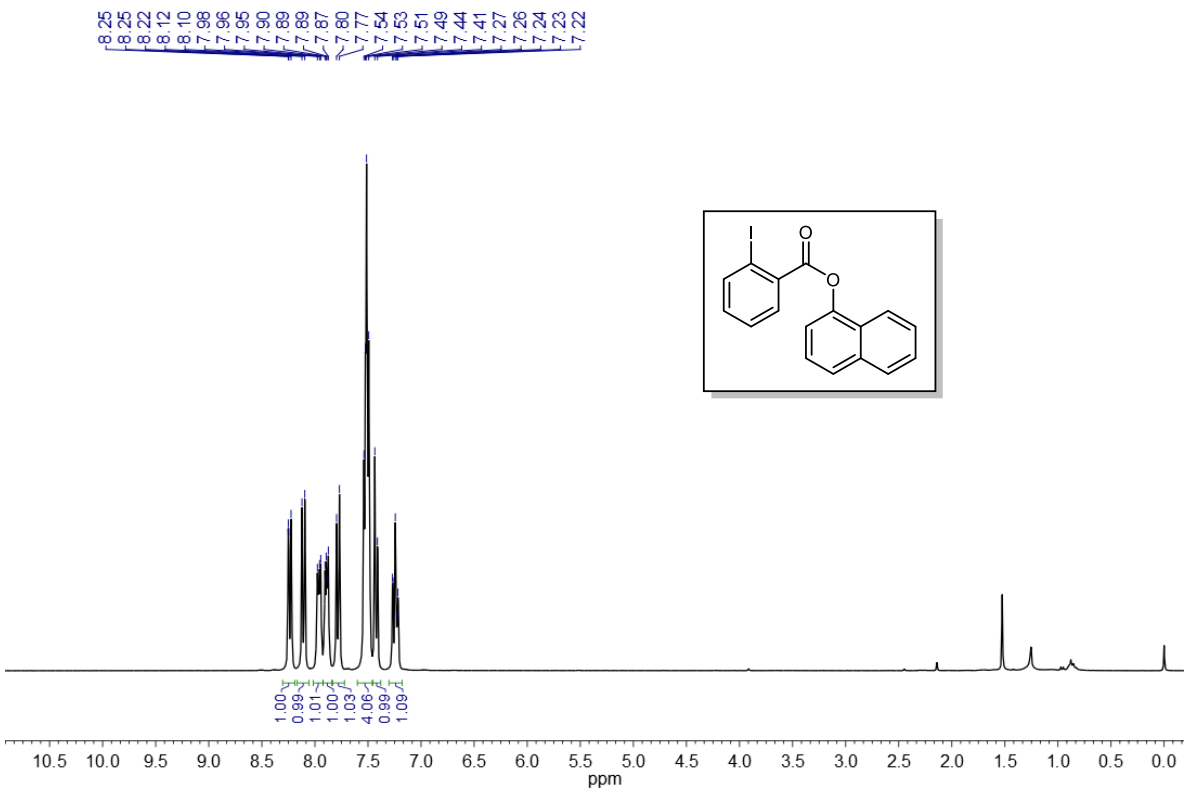

165.0
150.8
141.7
134.2
133.4
131.6
129.7
128.2
126.3
121.7
94.8
I
O
O
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

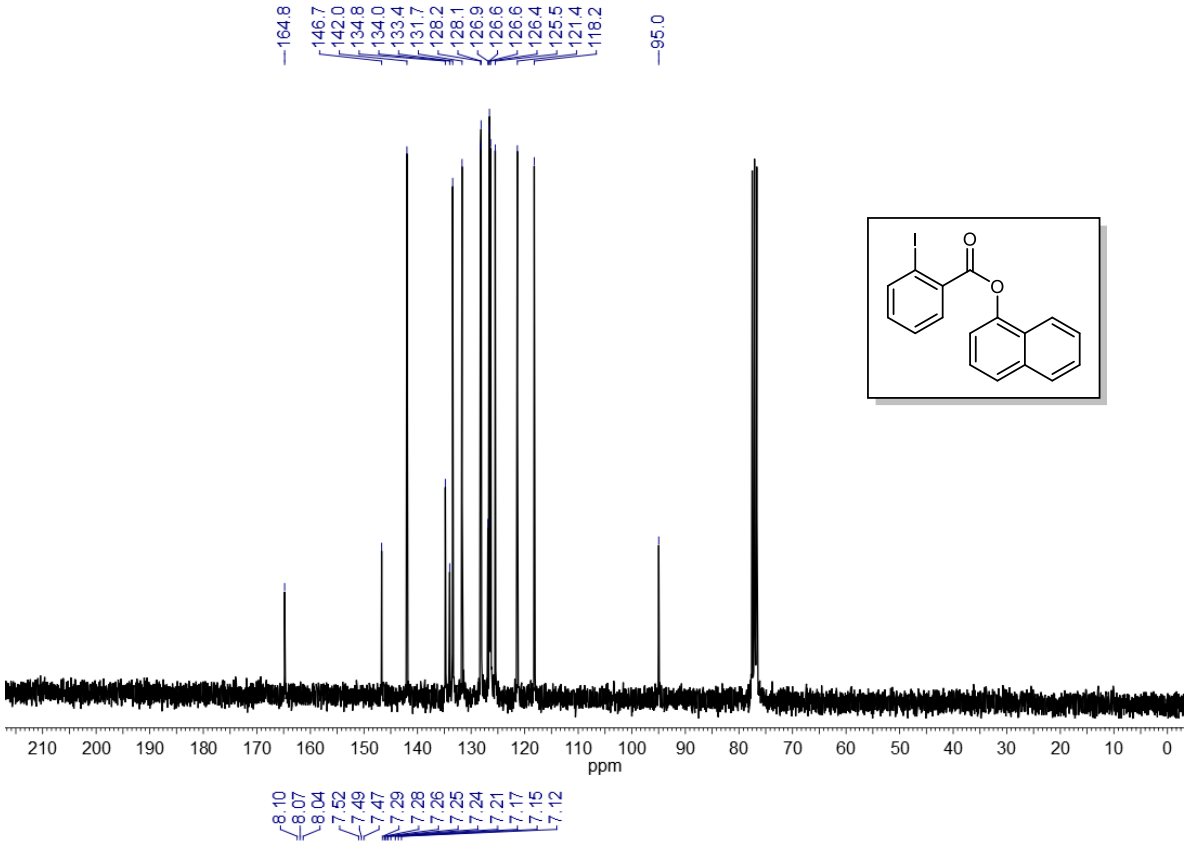

8.06
8.03
8.02
7.99
7.48
7.46
7.43
7.23
7.22
7.19
7.17
7.16
6.95
6.92
3.81
I
O
O
OMe
1.95
1.01
3.00
2.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

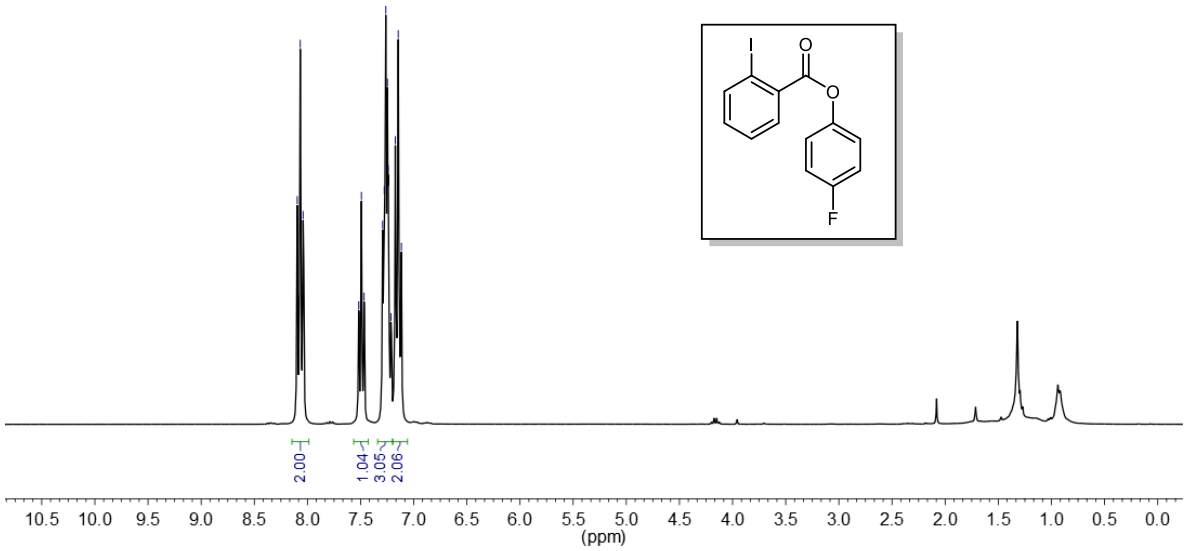

165.3
157.5
144.2
141.6
134.3
133.2
131.5
128.1
122.4
114.6
94.6
55.7
I
O
O
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

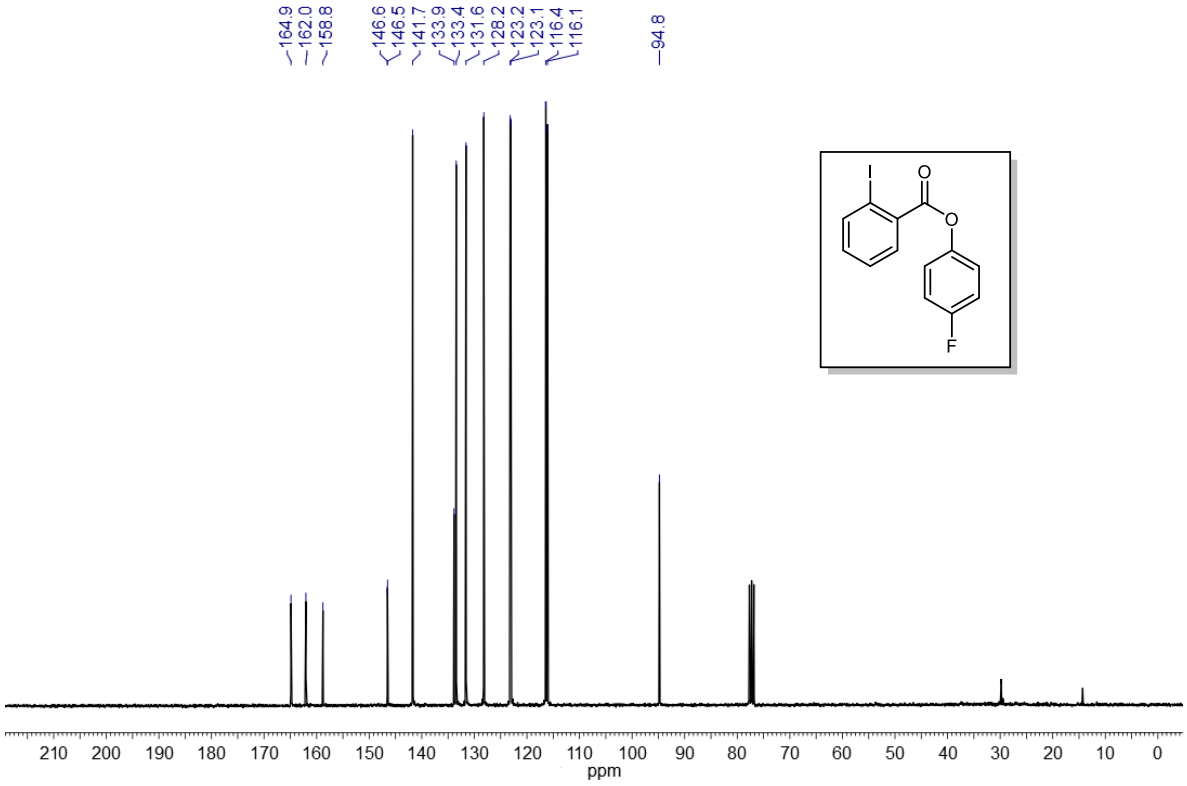

8.02
8.00
7.97
7.44
7.42
7.39
7.30
7.27
7.19
7.16
7.14
2.45
I
O
O
SMe
1.98
1.04
2.01
2.98
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

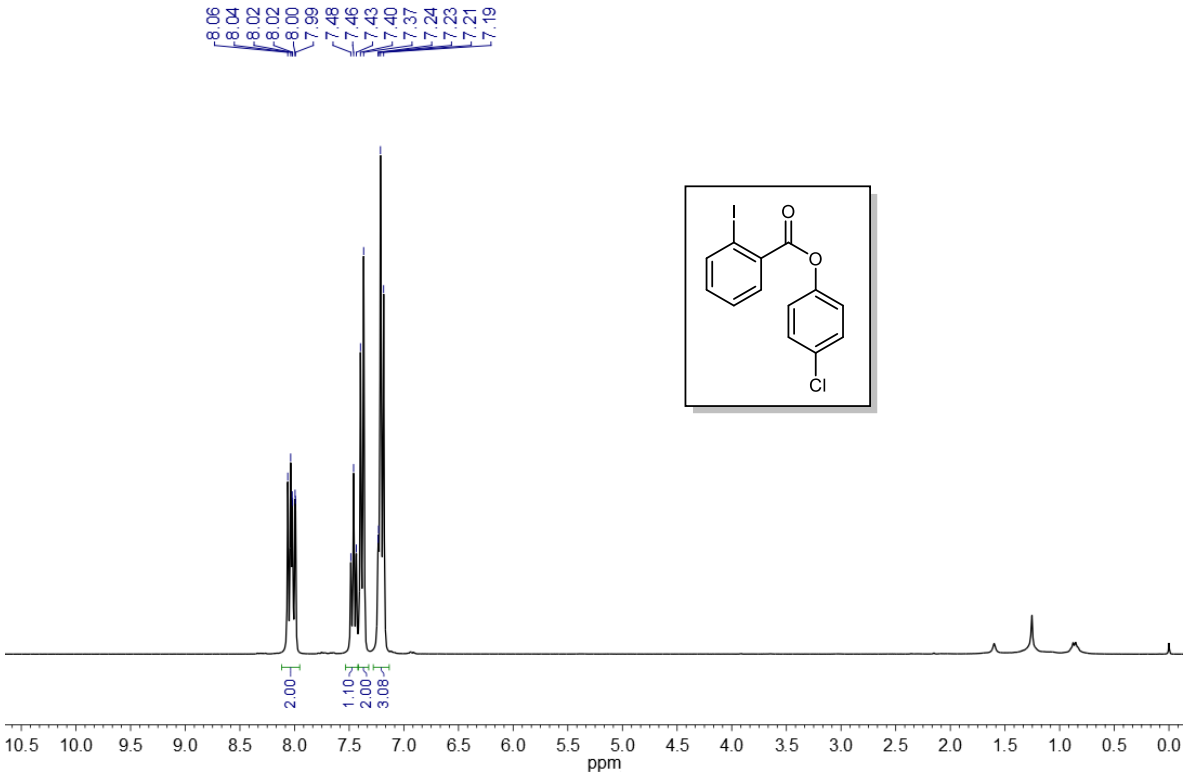

164.9
148.4
141.7
136.2
134.0
133.4
131.6
128.2
128.0
122.2
94.8
16.5
I
O
O
SMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

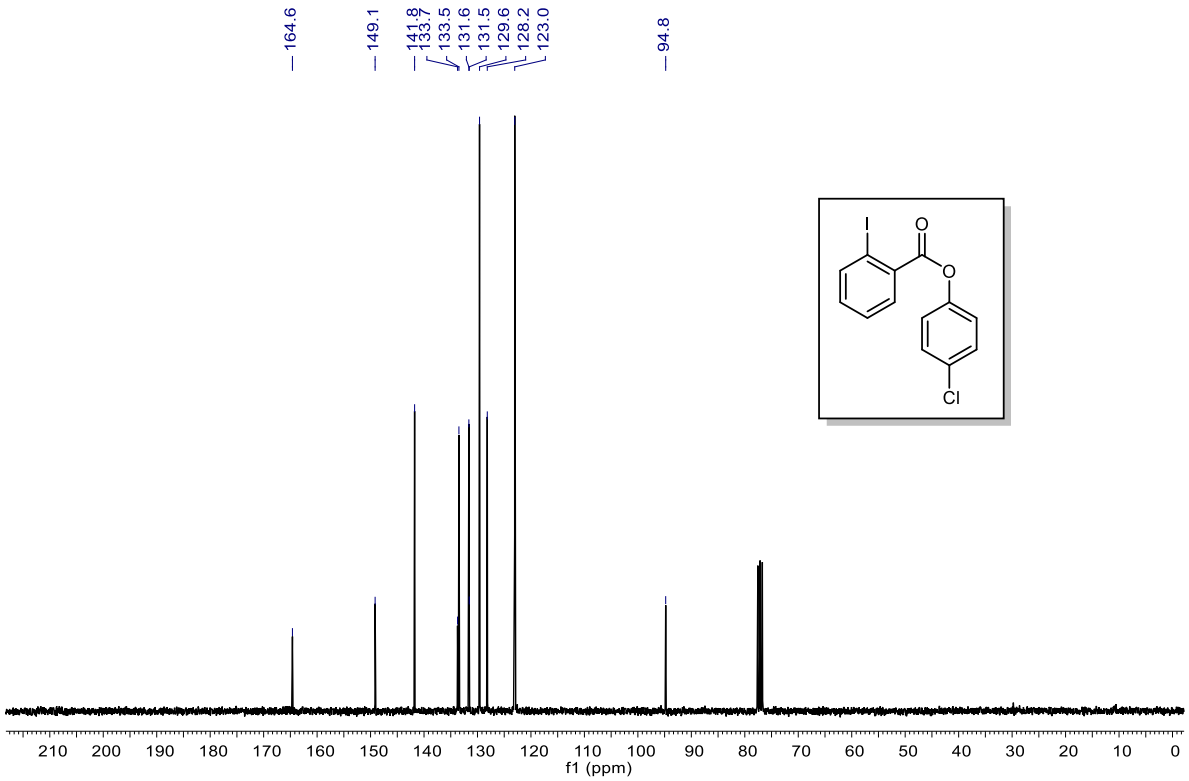

8.25
8.25
8.22
8.12
8.10
7.98
7.96
7.95
7.90
7.89
7.89
7.87
7.80
7.77
7.54
7.53
7.51
7.49
7.44
7.41
7.27
7.26
7.24
7.23
7.22
I
O
O
1.00
0.99
1.01
1.00
1.03
4.06
0.99
1.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

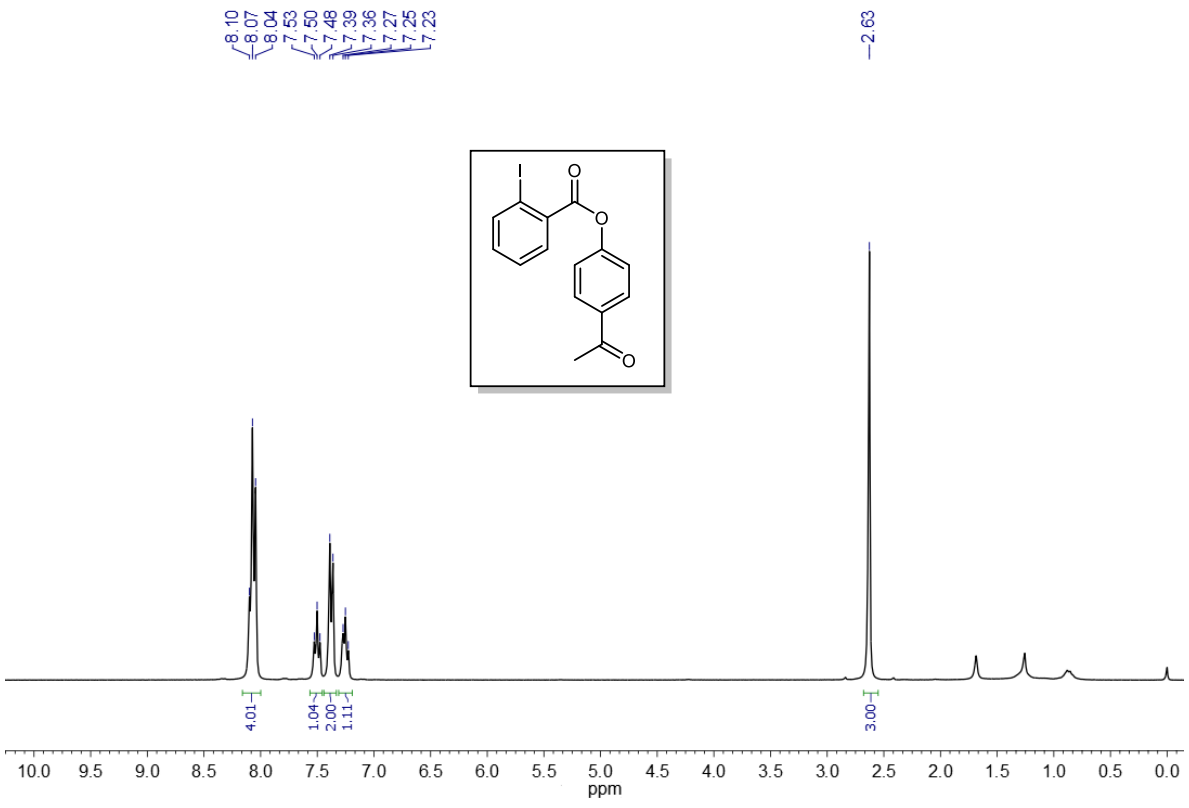

164.8
146.7
142.0
134.8
134.0
133.4
131.7
128.2
128.1
126.9
126.6
126.6
126.4
125.5
121.4
118.2
95.0
I
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm
8.10
8.07
8.04
7.52
7.49
7.47
7.29
7.28
7.26
7.25
7.24
7.21
7.17
7.15
7.12

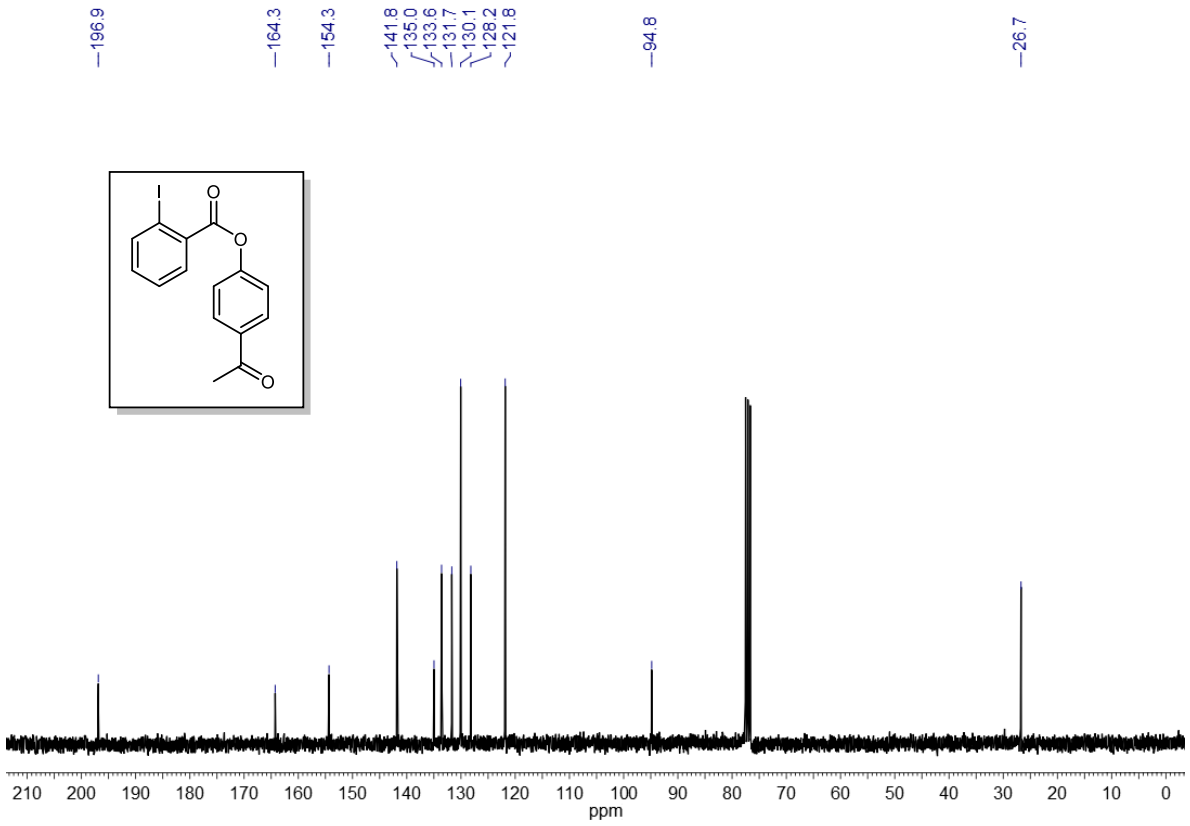

I
O
O
F
2.00
1.04
3.05
2.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

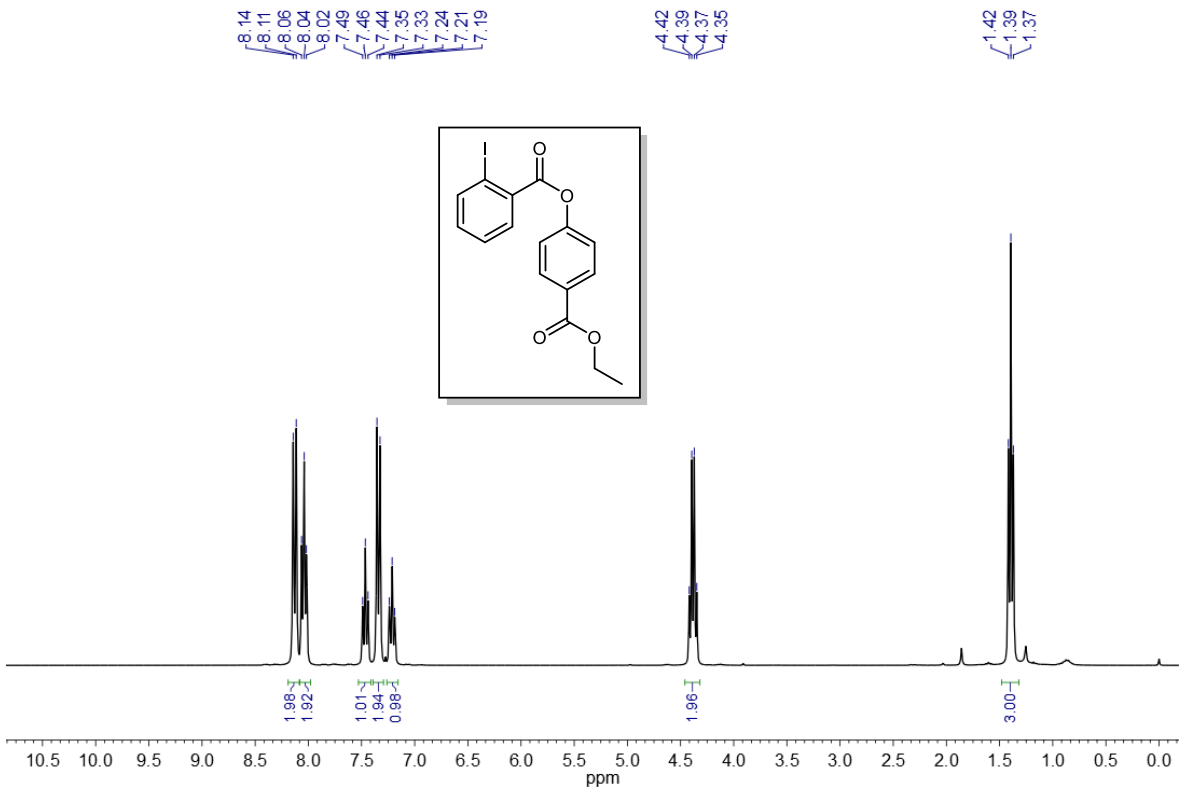

164.9
162.0
158.8
146.6
146.5
141.7
133.9
133.4
131.6
128.2
123.2
123.1
116.4
116.1
94.8
I
O
O
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

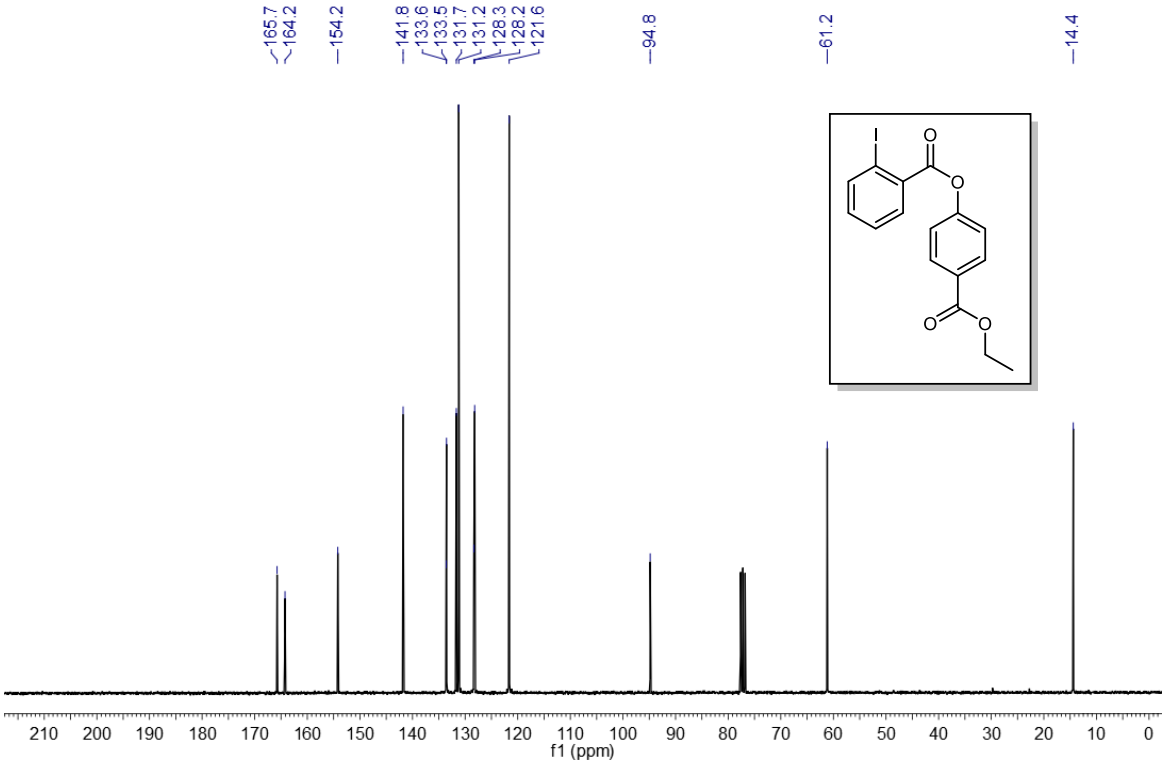

8.06
8.04
8.02
8.02
8.00
7.99
7.48
7.46
7.43
7.40
7.37
7.24
7.23
7.21
7.19
I
O
O
Cl
2.00
1.10
2.00
3.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

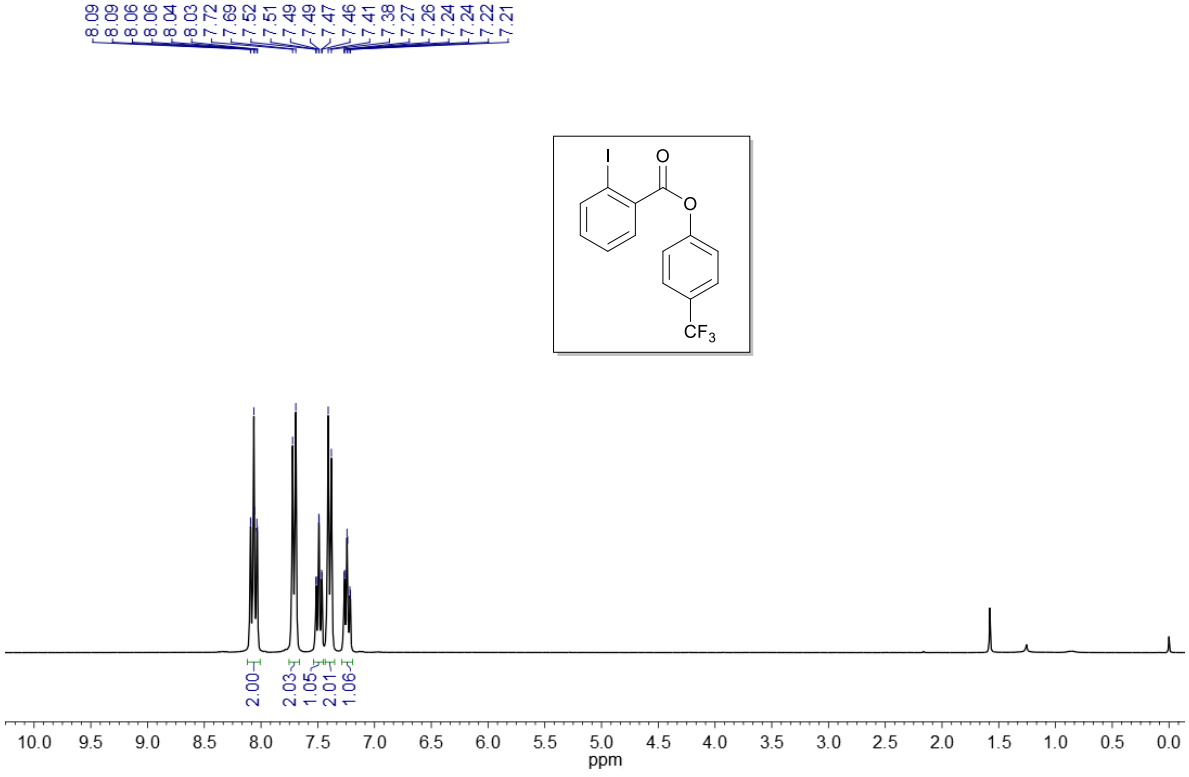

164.6
149.1
141.8
133.7
133.5
131.6
131.5
129.6
128.2
123.0
94.8
I
O
O
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

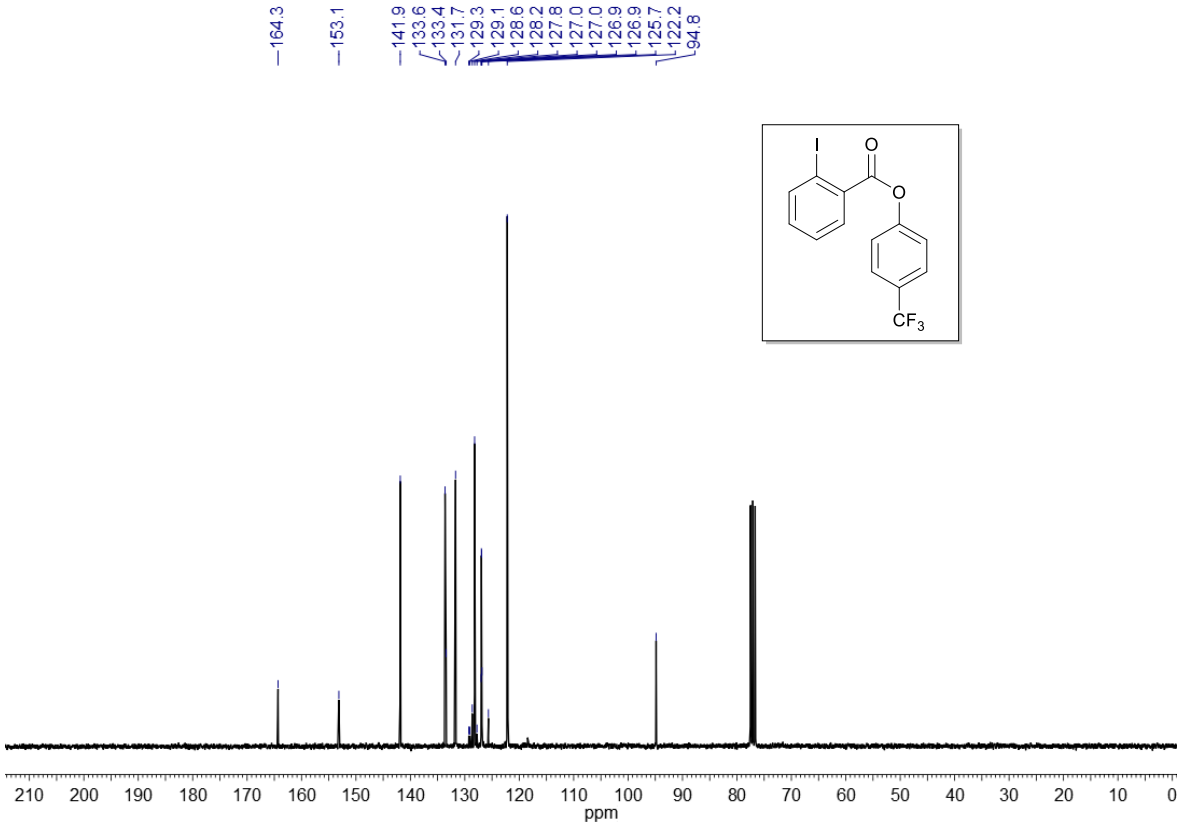

8.10
8.07
8.04
7.53
7.50
7.48
7.39
7.36
7.27
7.25
7.23
2.63
I
O
O
O
4.01
1.04
2.00
1.11
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

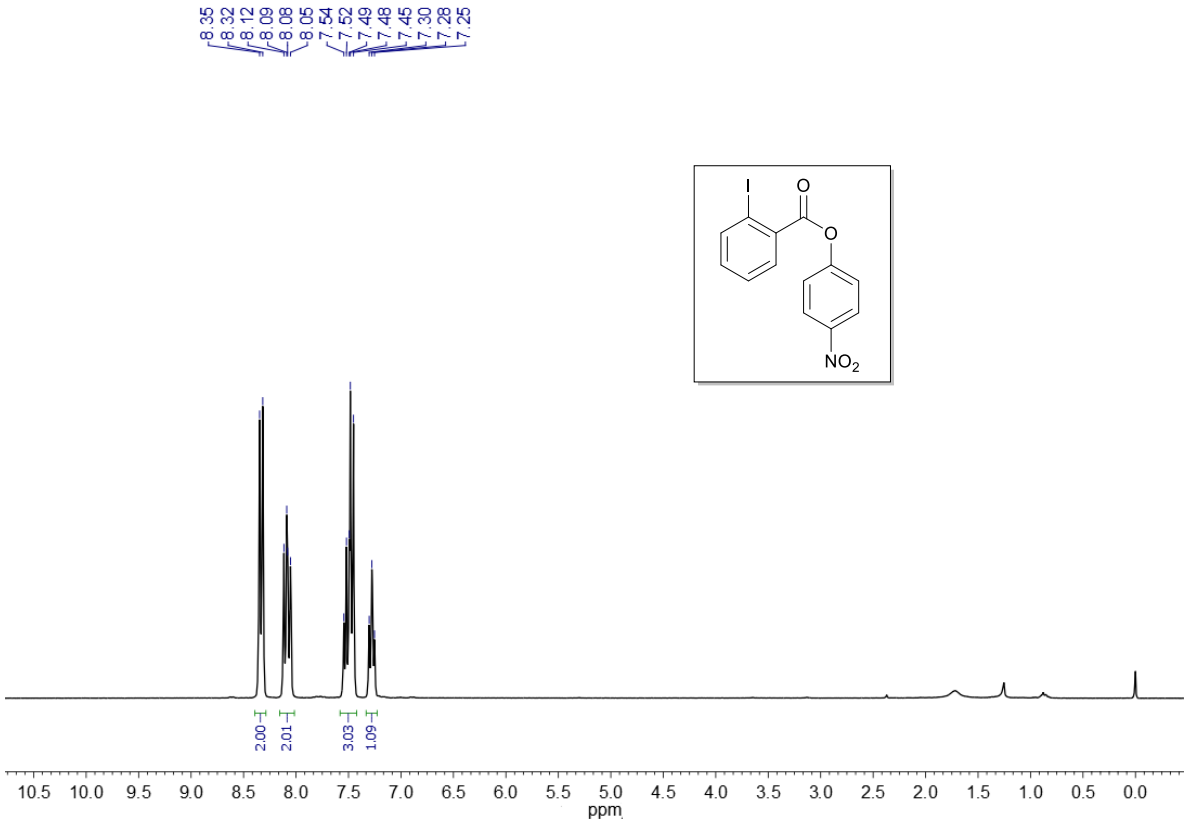

196.9
164.3
154.3
141.8
135.0
133.6
131.7
130.1
128.2
121.8
94.8
26.7
I
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

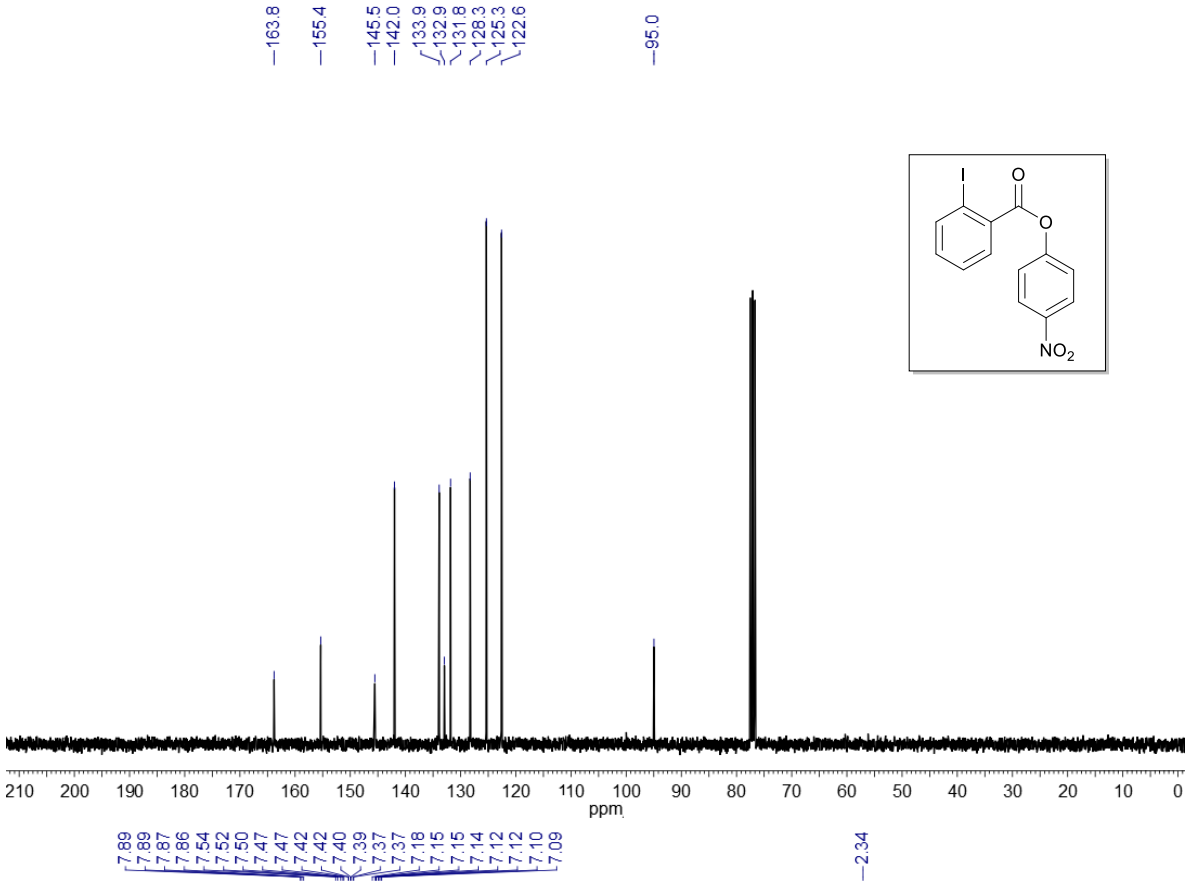

8.14
8.11
8.06
8.04
8.02
7.49
7.46
7.44
7.35
7.33
7.24
7.21
7.19
4.42
4.39
4.37
4.35
1.42
1.39
1.37
I
O
O
O
O
1.98
1.92
1.01
1.94
0.98
1.96
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

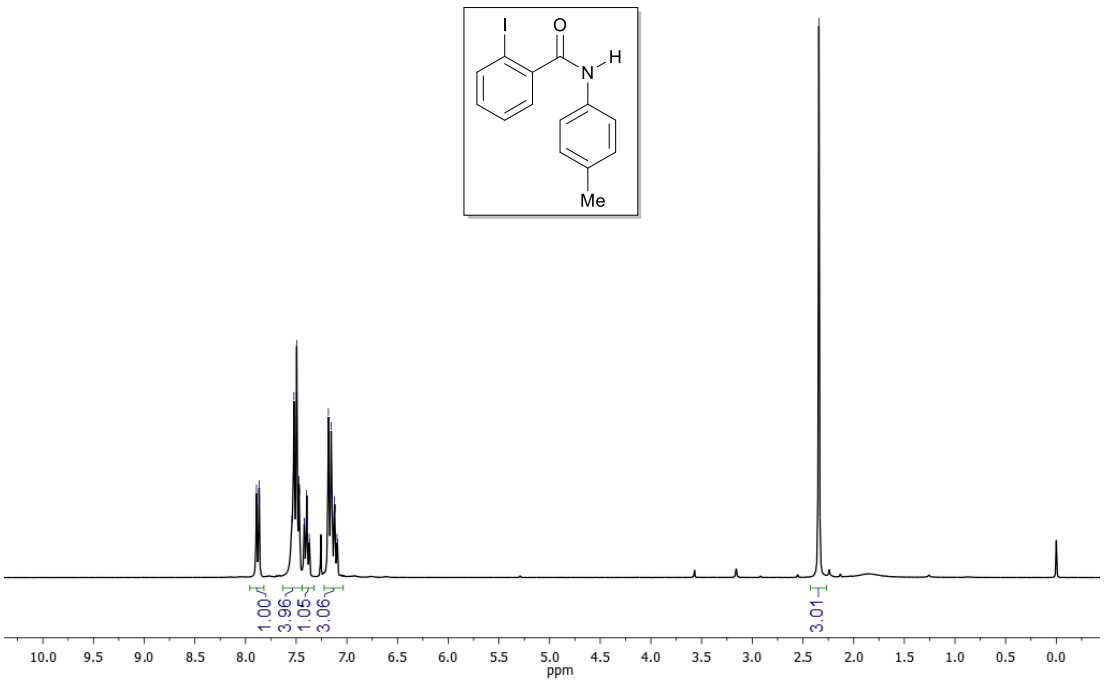

165.7
164.2
154.2
141.8
133.6
133.5
131.7
131.2
128.3
128.2
121.6
94.8
61.2
14.4
I
O
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

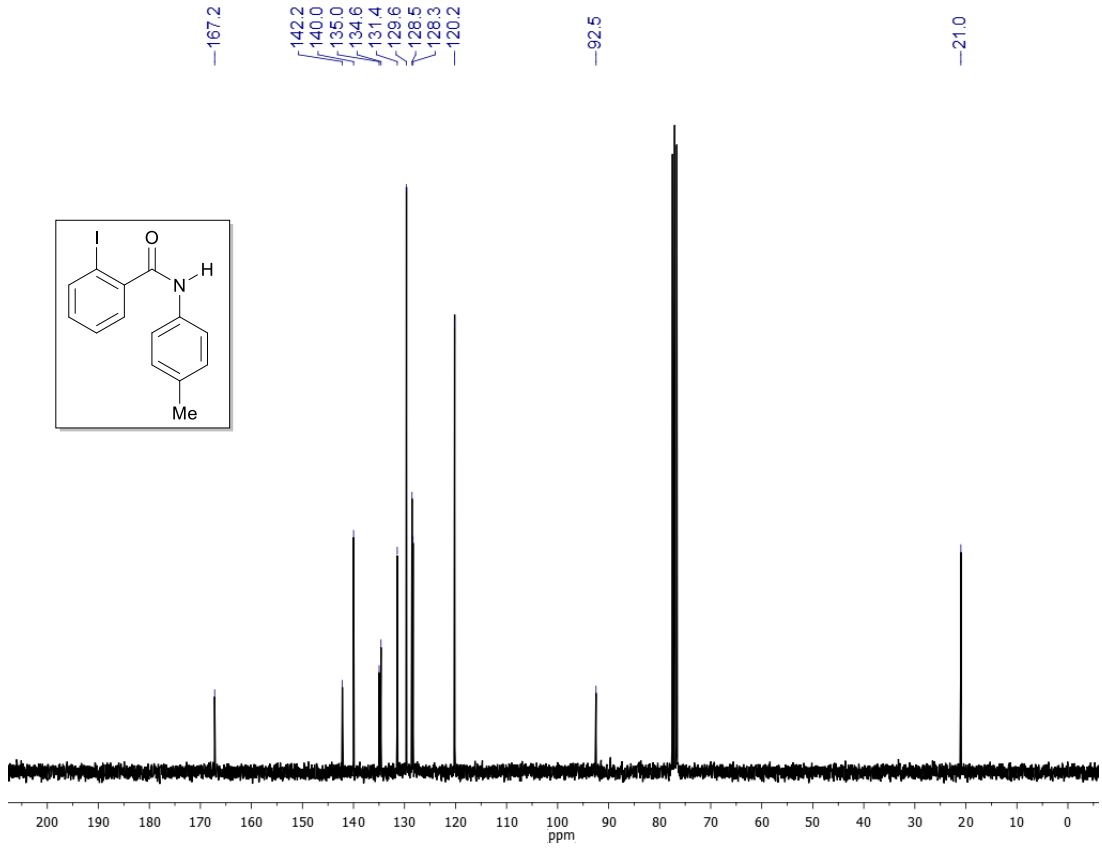

8.09
8.09
8.06
8.06
8.04
8.03
7.72
7.69
7.52
7.51
7.49
7.49
7.47
7.46
7.41
7.38
7.27
7.26
7.24
7.24
7.22
7.21
I
O
O
CF3
2.00
2.03
1.05
2.01
1.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

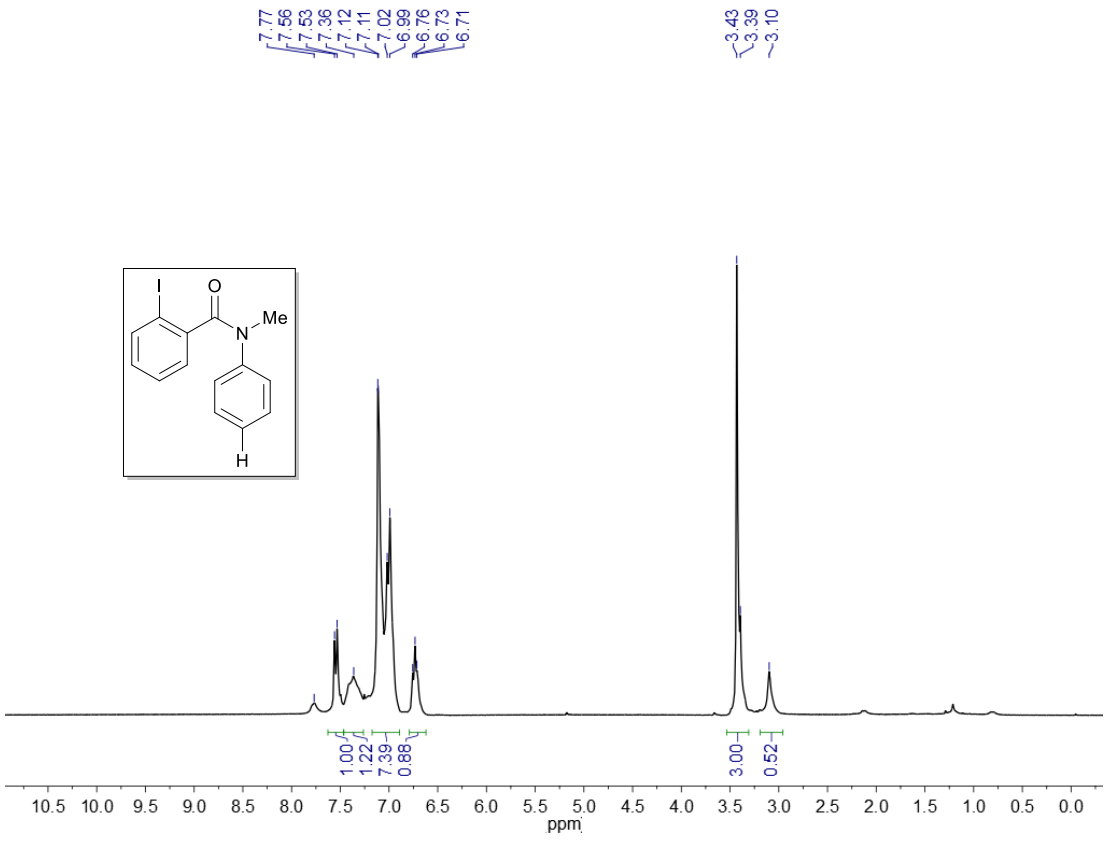

164.3
153.1
141.9
133.6
133.4
131.7
129.3
129.1
128.6
128.2
127.8
127.0
127.0
126.9
126.9
125.7
122.2
94.8
I
O
O
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

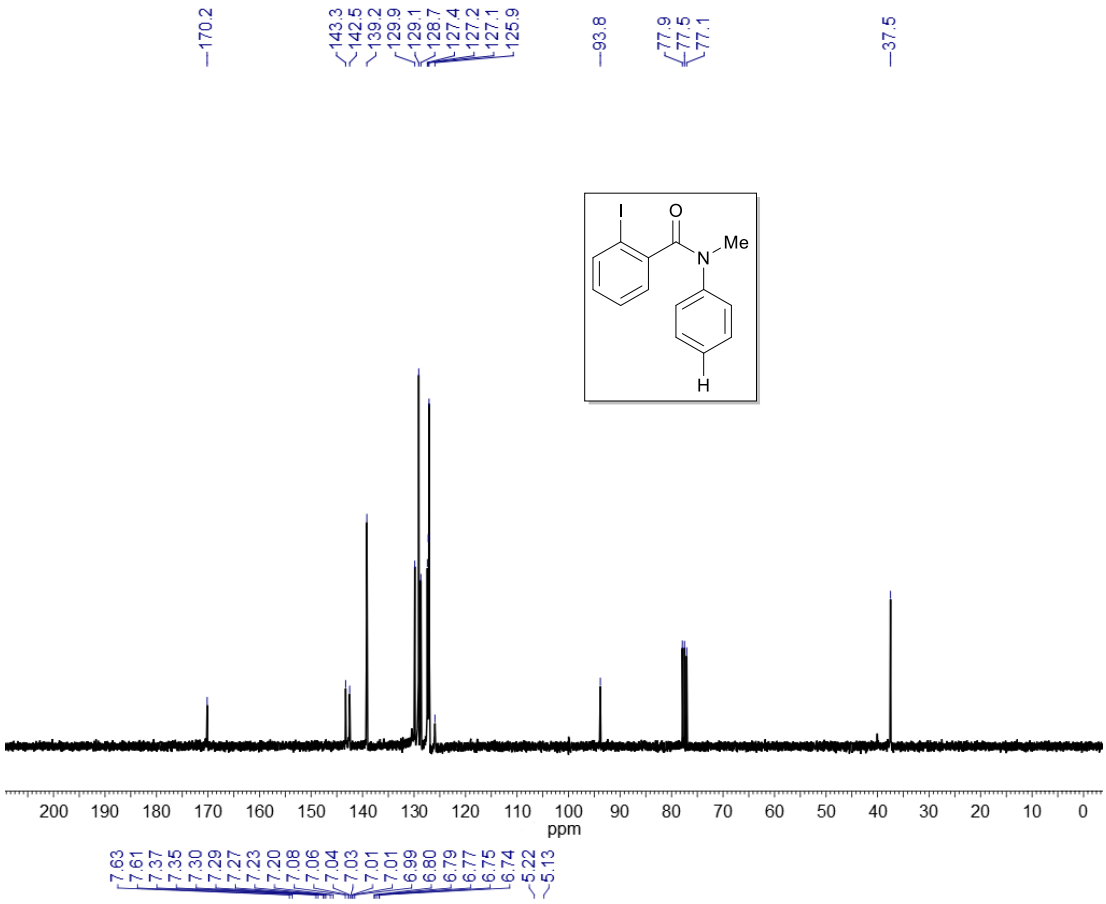

8.35
8.32
8.12
8.09
8.08
8.05
7.54
7.52
7.49
7.48
7.45
7.30
7.28
7.25
I
O
O
NO2
2.00
2.01
3.03
1.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

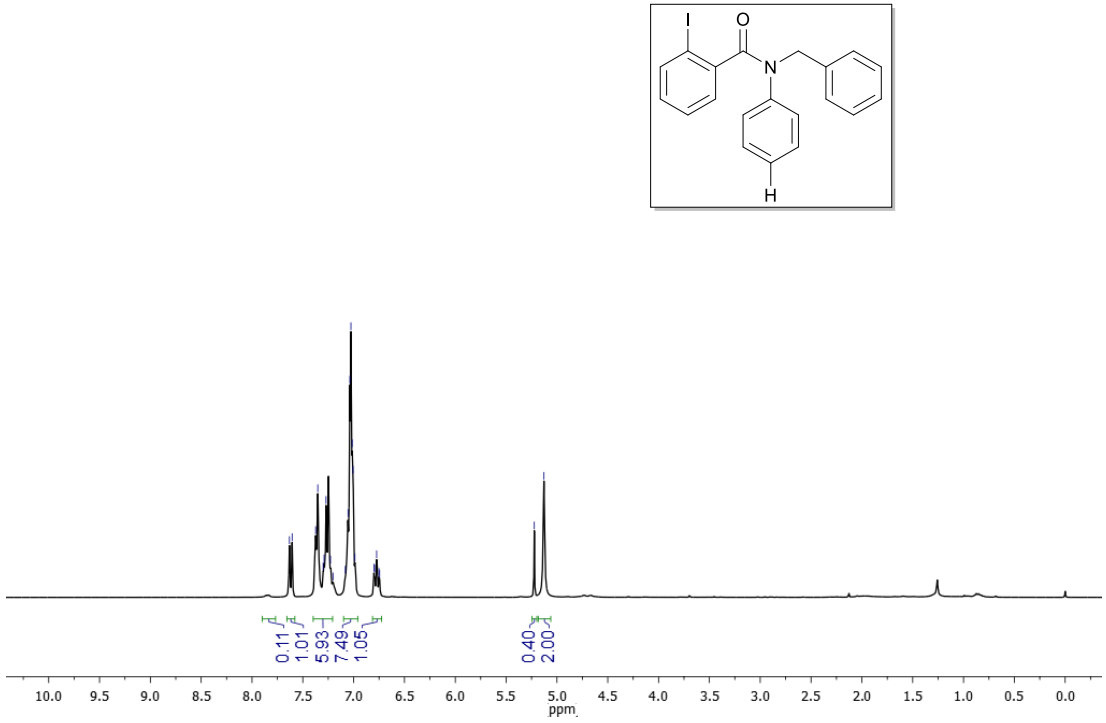

163.8
155.4
145.5
142.0
133.9
132.9
131.8
128.3
125.3
122.6
95.0
I
O
O
NO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm
7.89
7.89
7.87
7.86
7.54
7.52
7.50
7.47
7.47
7.42
7.42
7.40
7.39
7.37
7.37
7.18
7.15
7.15
7.14
7.12
7.12
7.10
7.09
2.34

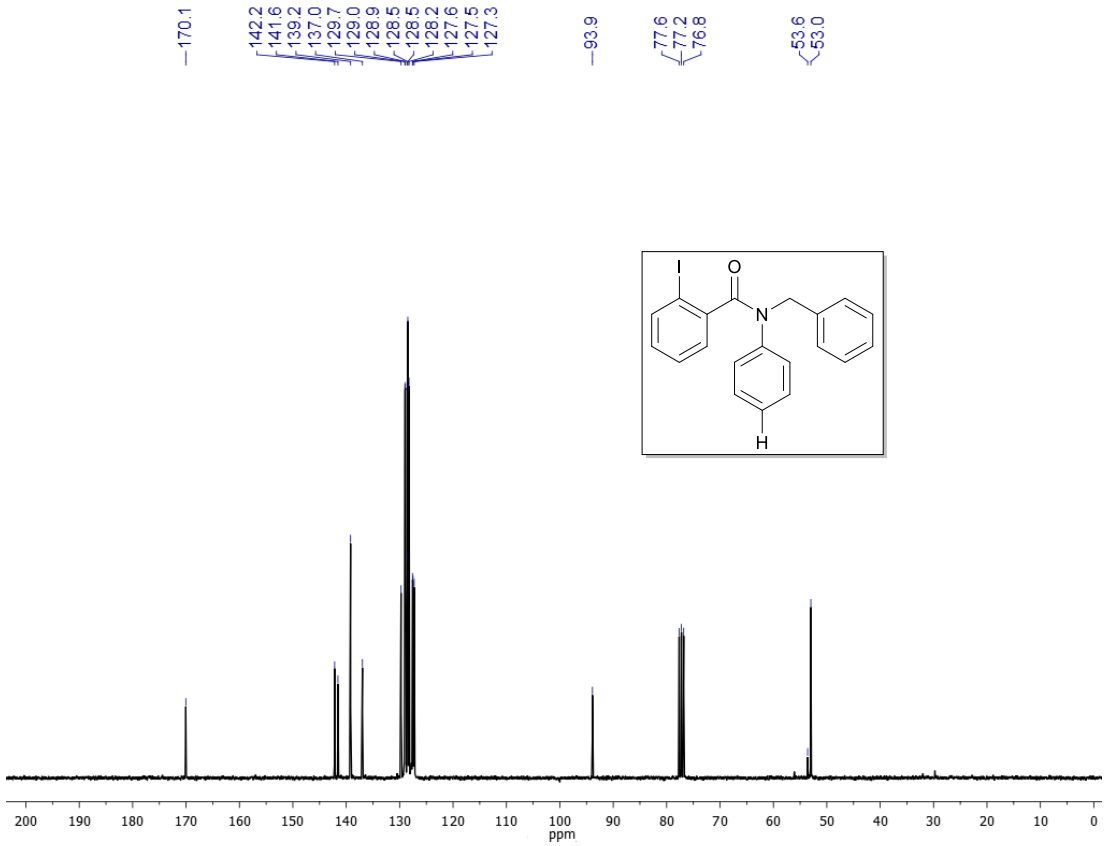

I
O
N
H
Me
1.00
3.96
1.05
3.06
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

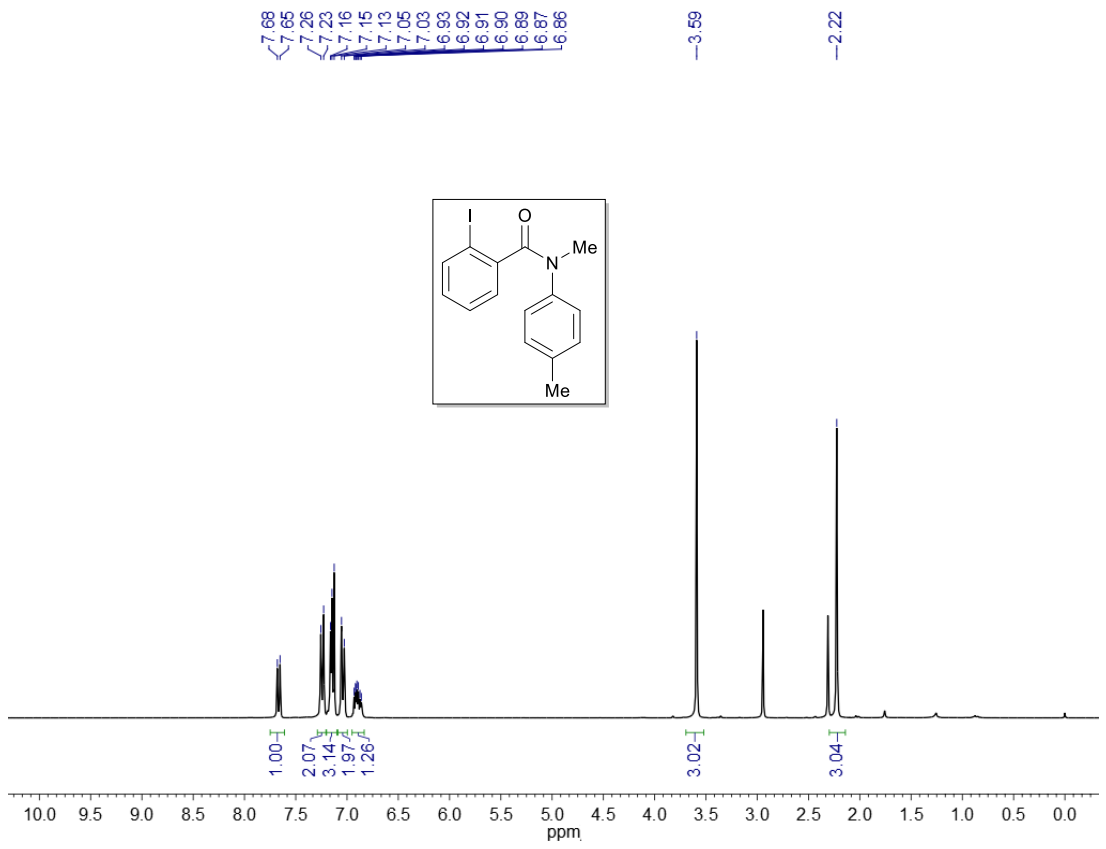

167.2
142.2
140.0
135.0
134.6
131.4
129.6
128.5
128.3
120.2
92.5
21.0
I
O
N
H
Me
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

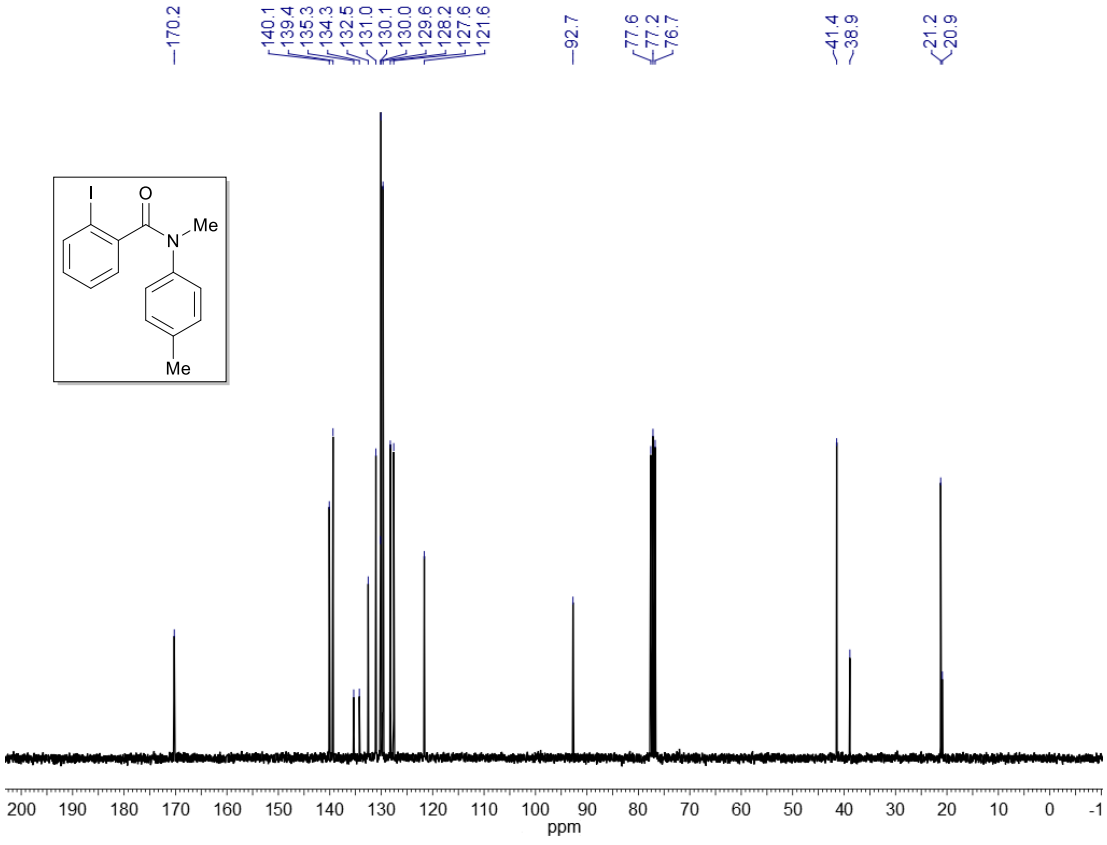

7.77
7.56
7.53
7.36
7.12
7.11
7.02
6.99
6.76
6.73
6.71
3.43
3.39
3.10
I
O
N
Me
H
1.00
1.22
7.39
0.88
3.00
0.52
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

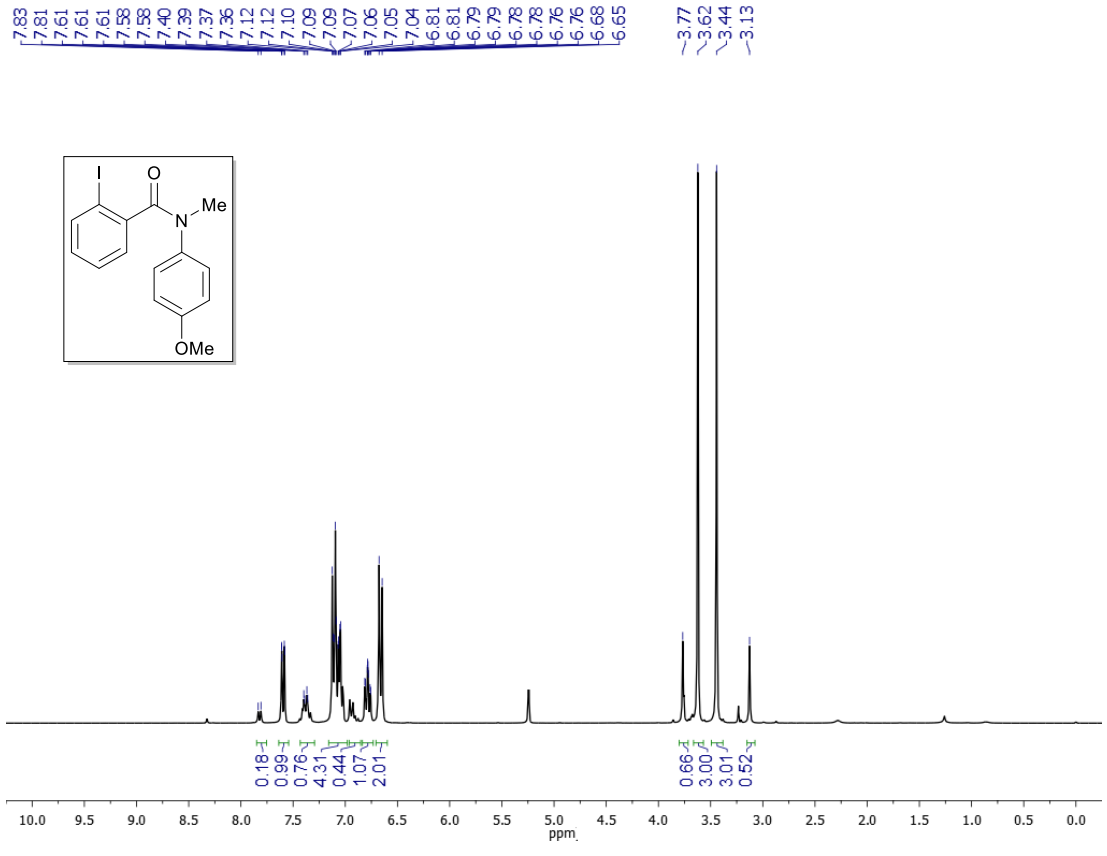

170.2
143.3
142.5
139.2
129.9
129.1
128.7
127.4
127.2
127.1
125.9
93.8
77.9
77.5
77.1
37.5
I
O
N
Me
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm
7.63
7.61
7.37
7.35
7.30
7.29
7.27
7.23
7.20
7.08
7.06
7.04
7.03
7.01
7.01
6.99
6.80
6.79
6.77
6.75
6.74
5.22
5.13

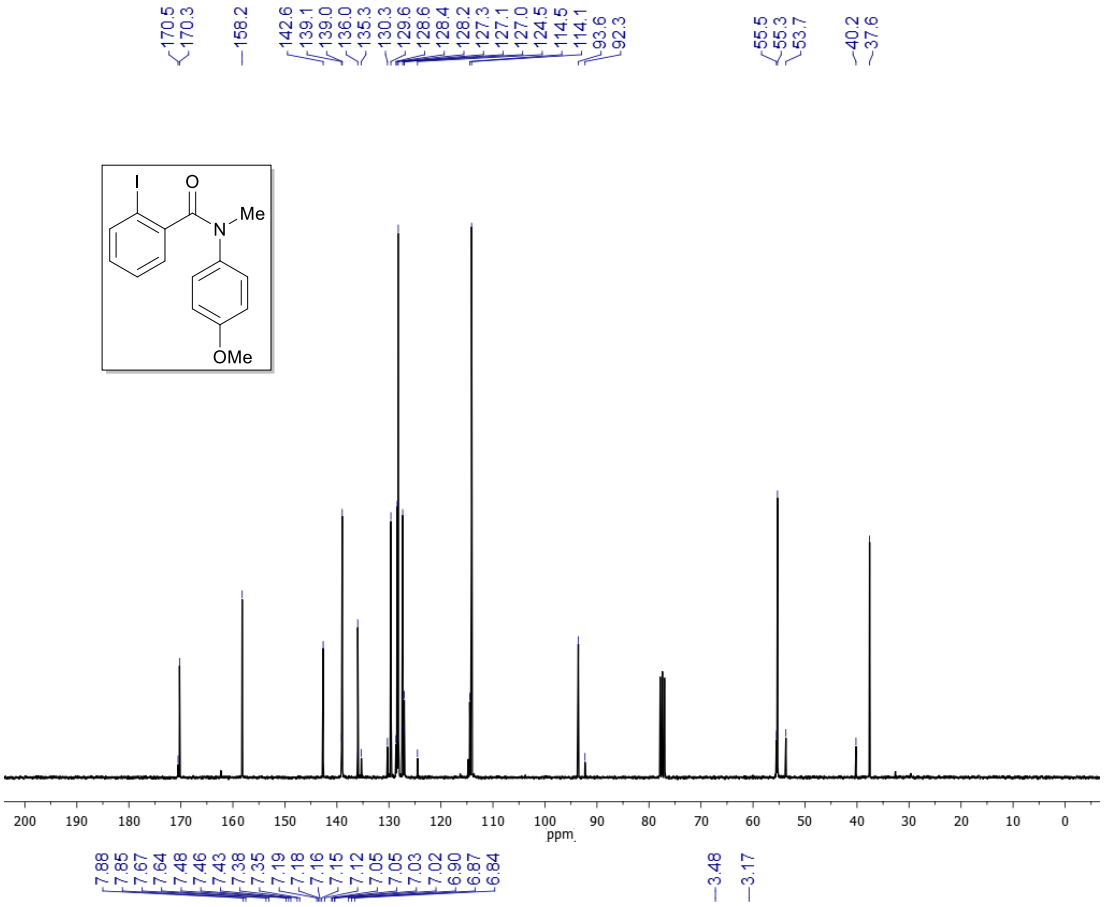

I
O
N
H
0.11
1.01
5.93
7.49
1.05
0.40
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

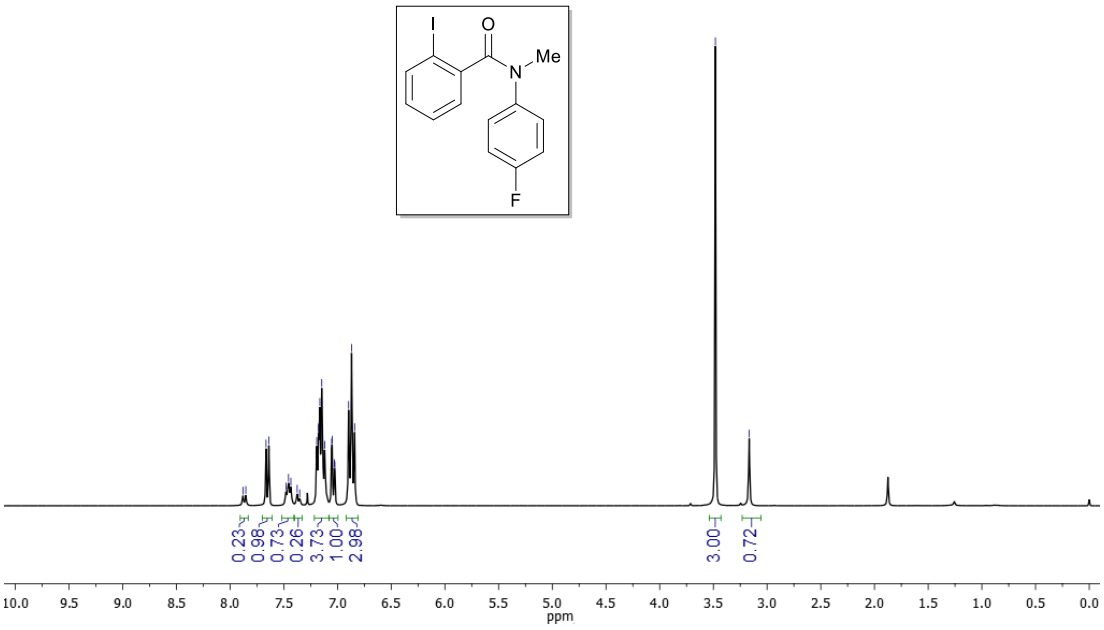

170.1
142.2
141.6
139.2
137.0
129.7
129.0
128.9
128.5
128.5
128.2
127.6
127.5
127.3
93.9
77.6
77.2
76.8
53.6
53.0
I
O
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

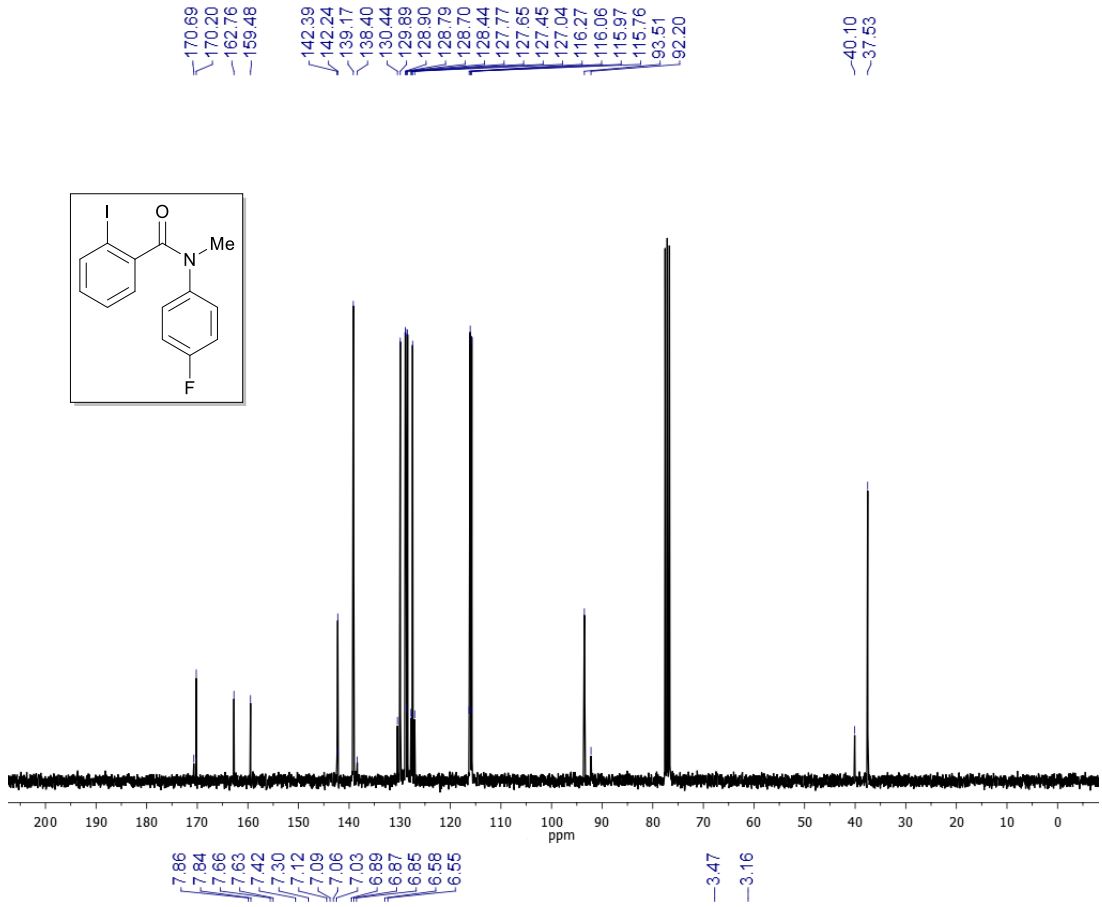

7.68
7.65
7.26
7.23
7.16
7.15
7.13
7.05
7.03
6.93
6.92
6.91
6.90
6.89
6.87
6.86
3.59
2.22
I
O
N
Me
Me
1.00
2.07
3.14
1.97
1.26
3.02
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

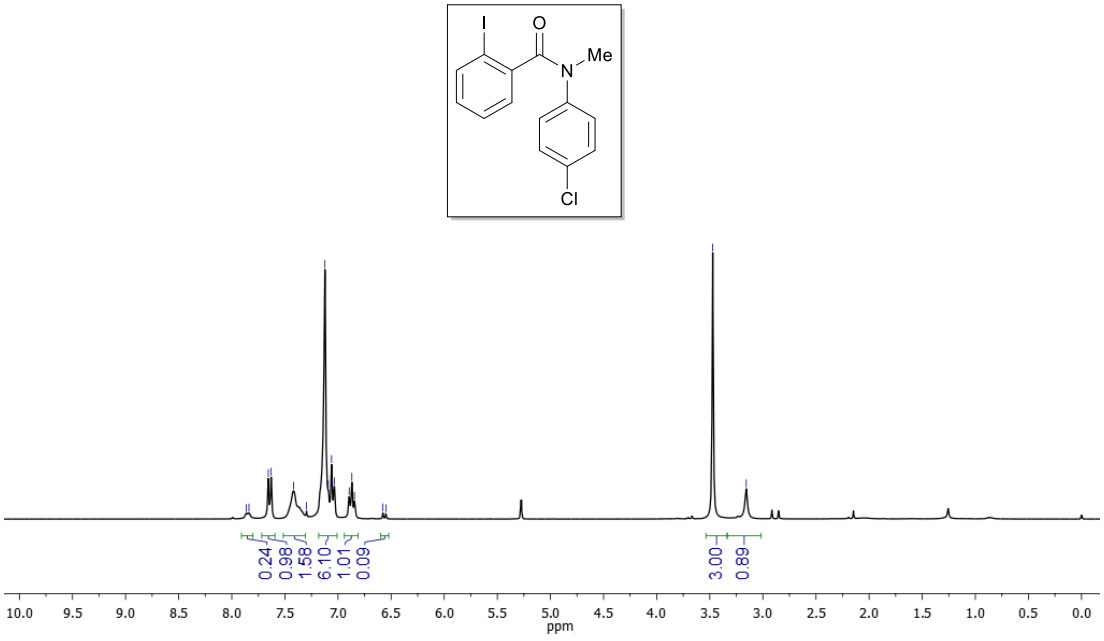

170.2
140.1
139.4
135.3
134.3
132.5
131.0
130.1
130.0
129.6
128.2
127.6
121.6
92.7
77.6
77.2
76.7
41.4
38.9
21.2
20.9
I
O
N
Me
Me
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
ppm

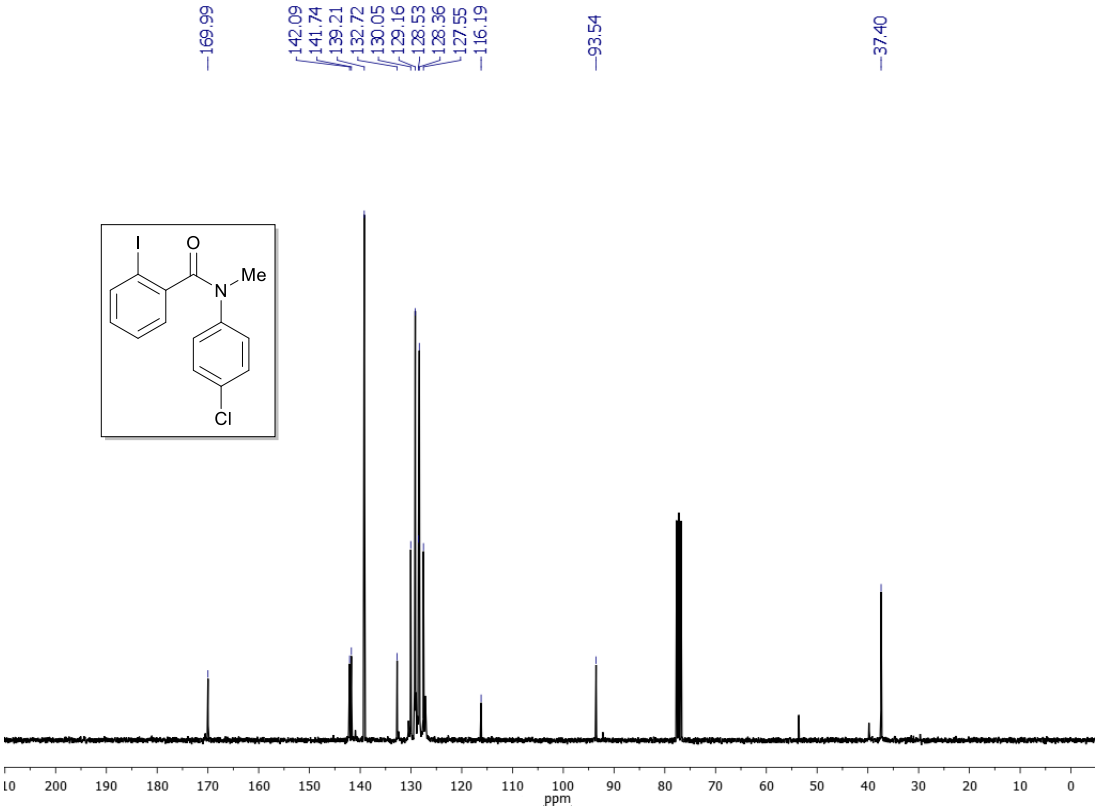

7.83
7.81
7.61
7.61
7.61
7.58
7.58
7.40
7.39
7.37
7.36
7.12
7.10
7.09
7.09
7.07
7.06
7.05
7.04
6.81
6.81
6.79
6.79
6.78
6.78
6.76
6.76
6.68
6.65
3.77
3.62
3.44
3.13
I
O
N
Me
OMe
0.18
0.99
0.76
4.31
0.44
1.07
2.01
0.66
3.00
3.01
0.52
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


170.5
170.3
158.2
142.6
139.1
139.0
136.0
135.3
130.3
129.6
128.6
128.4
128.2
127.3
127.1
127.0
124.5
114.5
114.1
93.6
92.3
55.5
55.3
53.7
40.2
37.6
I
O
N
Me
OMe
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm
7.88
7.85
7.67
7.64
7.48
7.46
7.43
7.38
7.35
7.19
7.18
7.16
7.15
7.12
7.05
7.05
7.03
7.02
6.90
6.87
6.84
3.48
3.17

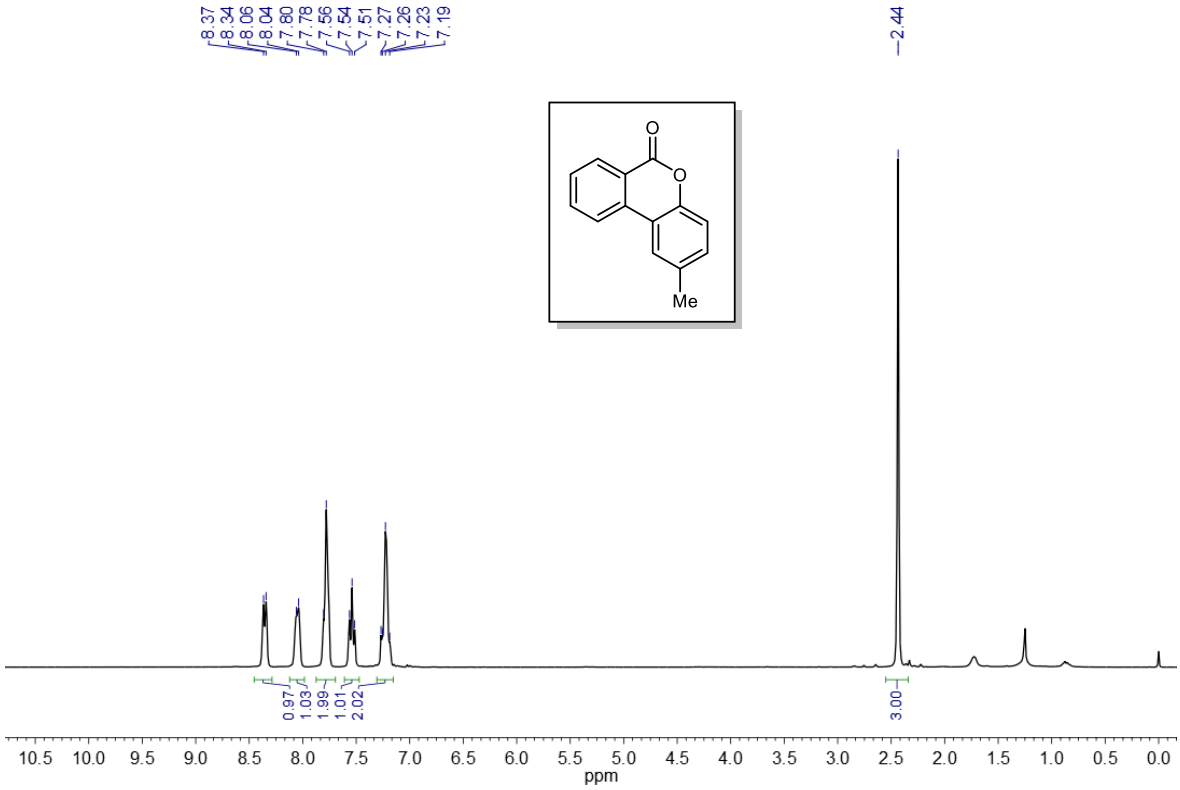

I
O
N
Me
F
0.23
0.98
0.73
0.26
3.73
1.00
2.98
3.00
0.72
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

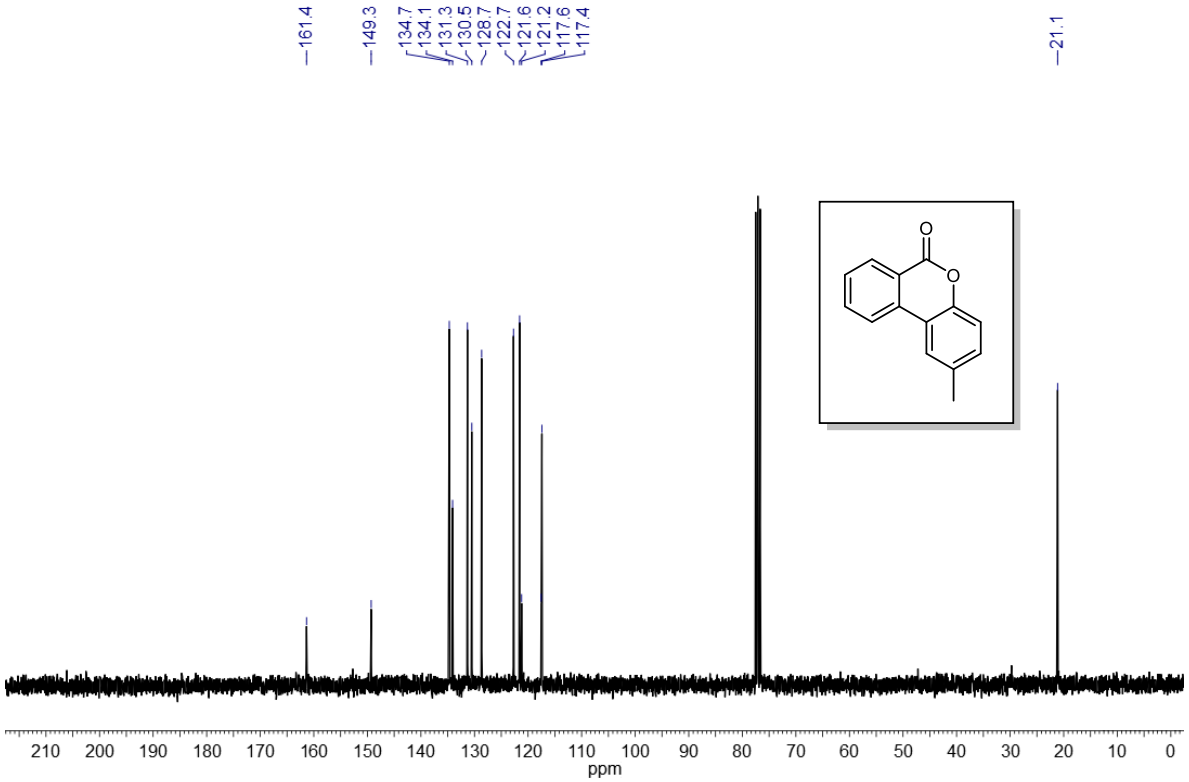

170.69
170.20
162.76
159.48
142.39
142.24
139.17
138.40
130.44
129.89
128.90
128.79
128.70
128.44
127.77
127.65
127.45
127.04
116.27
116.06
115.97
115.76
93.51
92.20
40.10
37.53
I
O
N
Me
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm
7.86
7.84
7.66
7.63
7.42
7.30
7.12
7.09
7.06
7.03
6.89
6.87
6.85
6.58
6.55
3.47
3.16

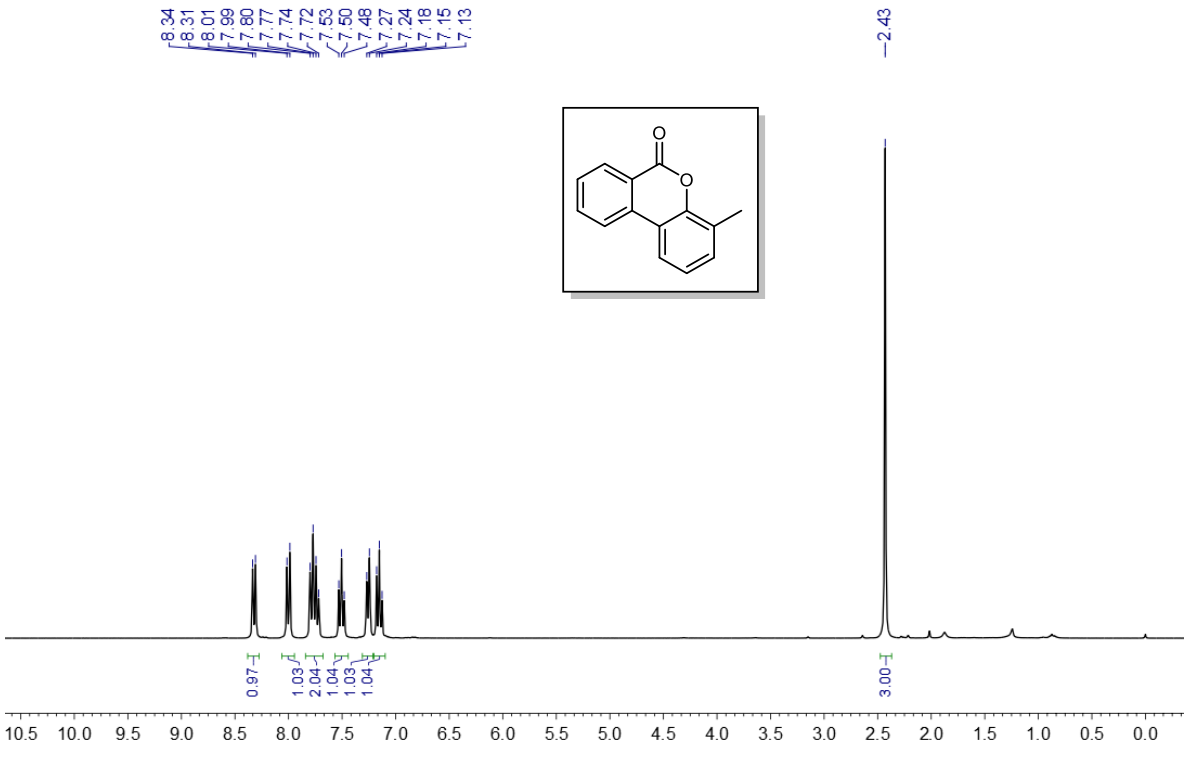

I
O
N
Me
Cl
0.24
0.98
1.58
6.10
1.01
0.09
3.00
0.89
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

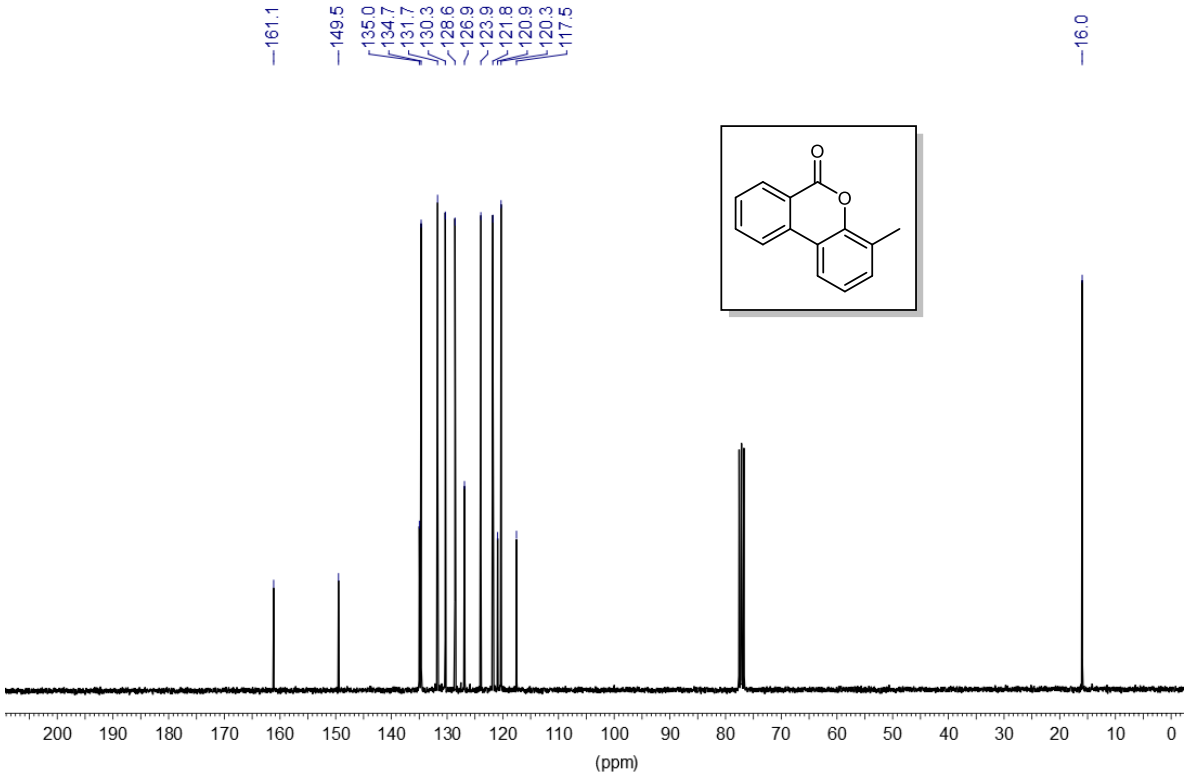


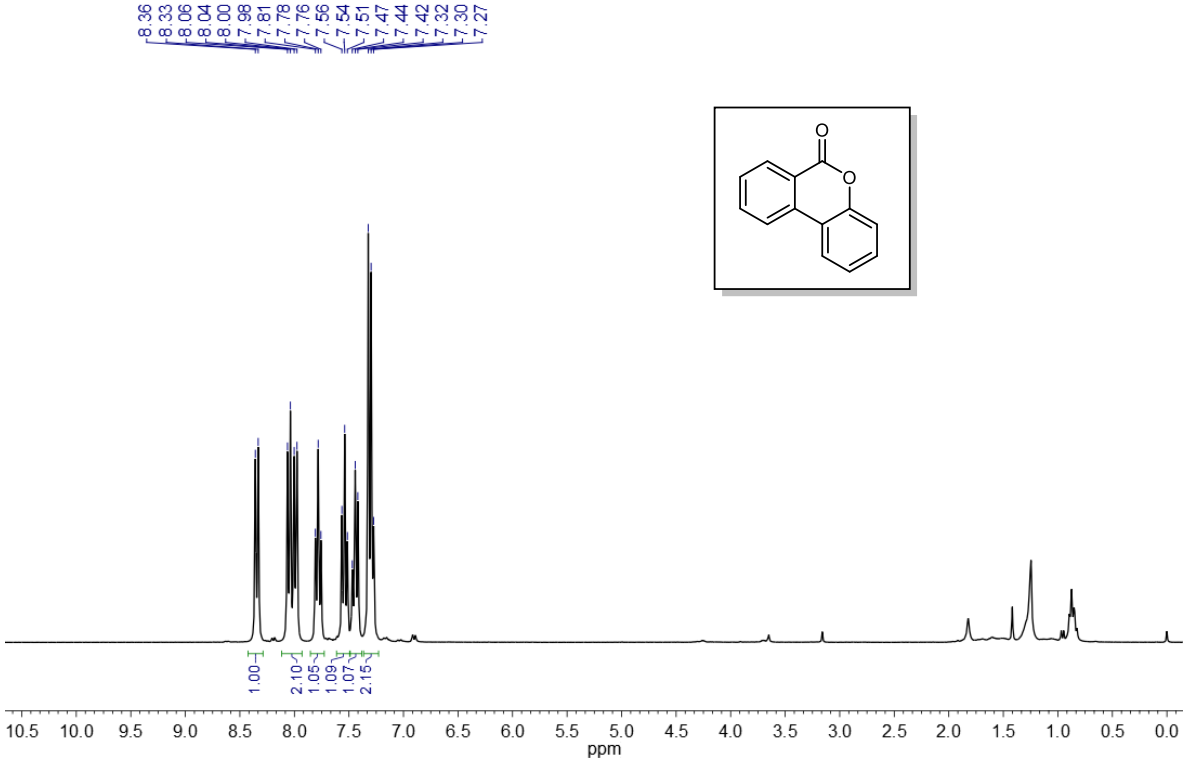
13. Compounds prepared by aryl-aryl coupling reaction

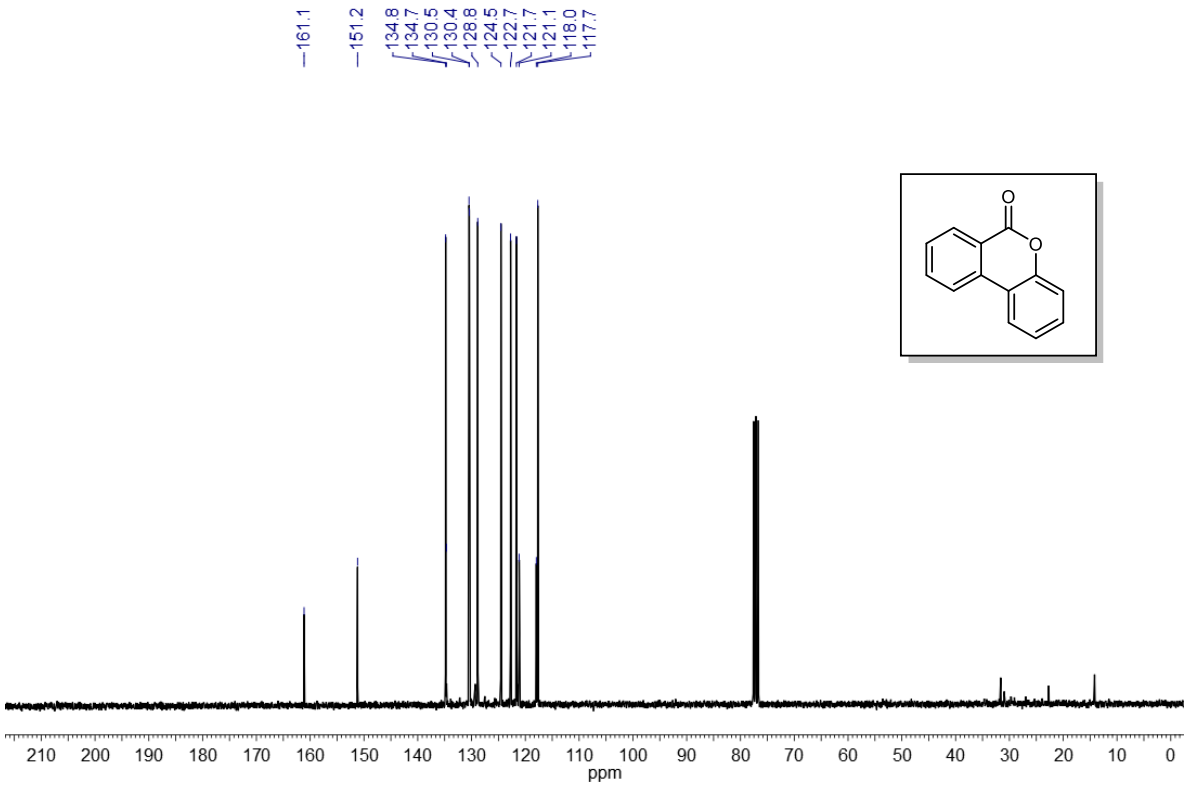


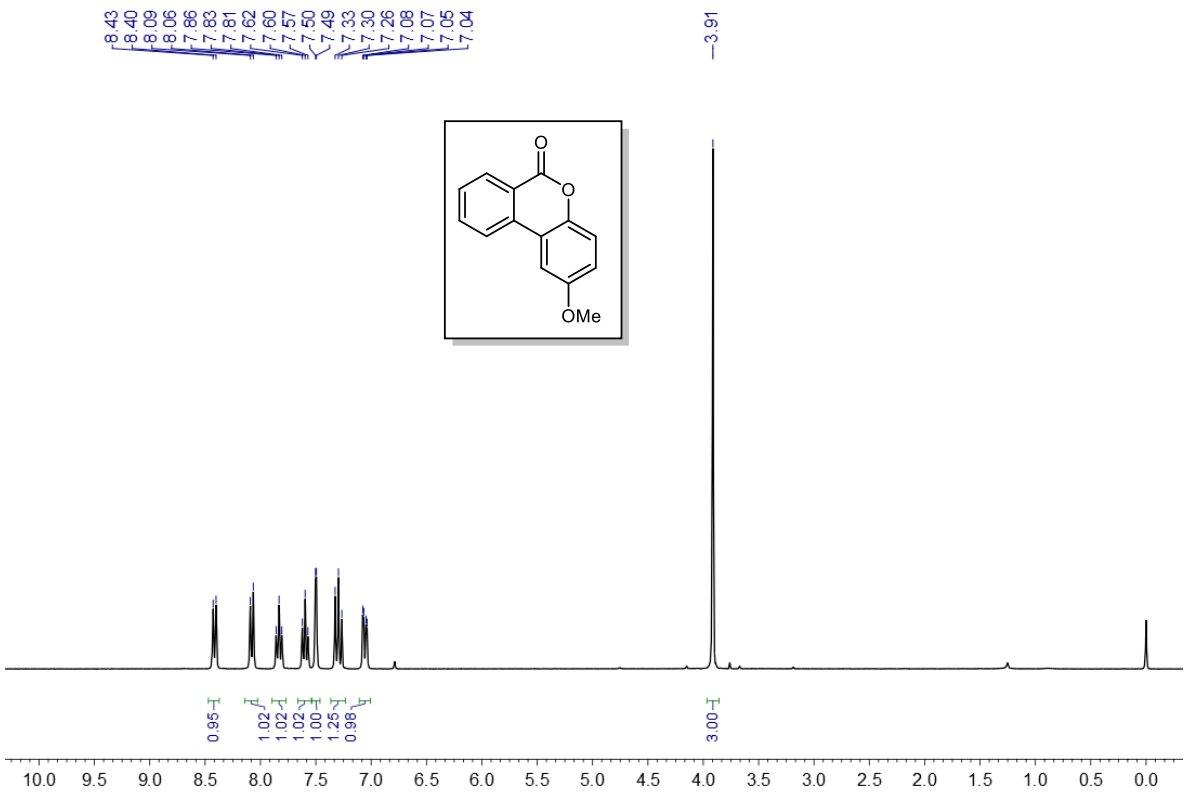

161.4
149.3
134.7
134.1
131.3
130.5
128.7
122.7
121.6
121.2
117.6
117.4
21.1
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

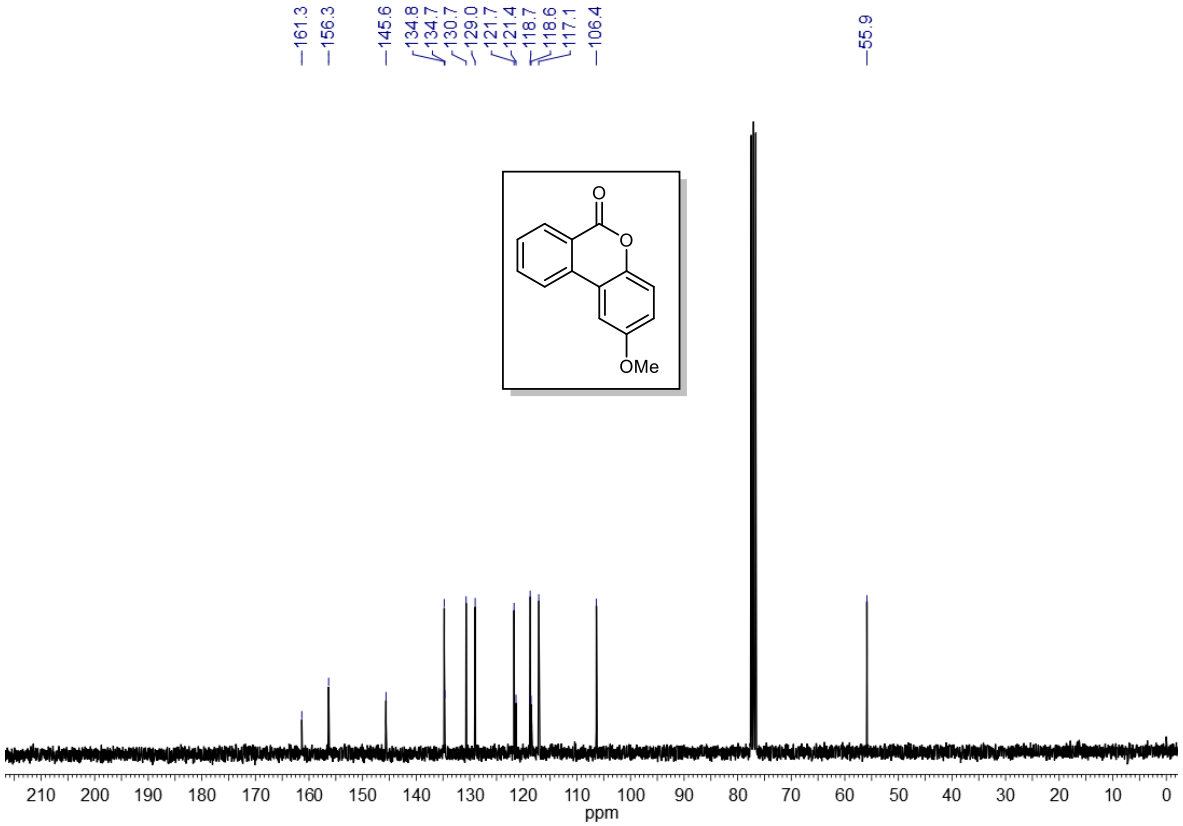

8.34
8.31
8.01
7.99
7.80
7.77
7.74
7.72
7.53
7.50
7.48
7.27
7.24
7.18
7.15
7.13
2.43
O
O
0.97
1.03
2.04
1.04
1.03
1.04
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

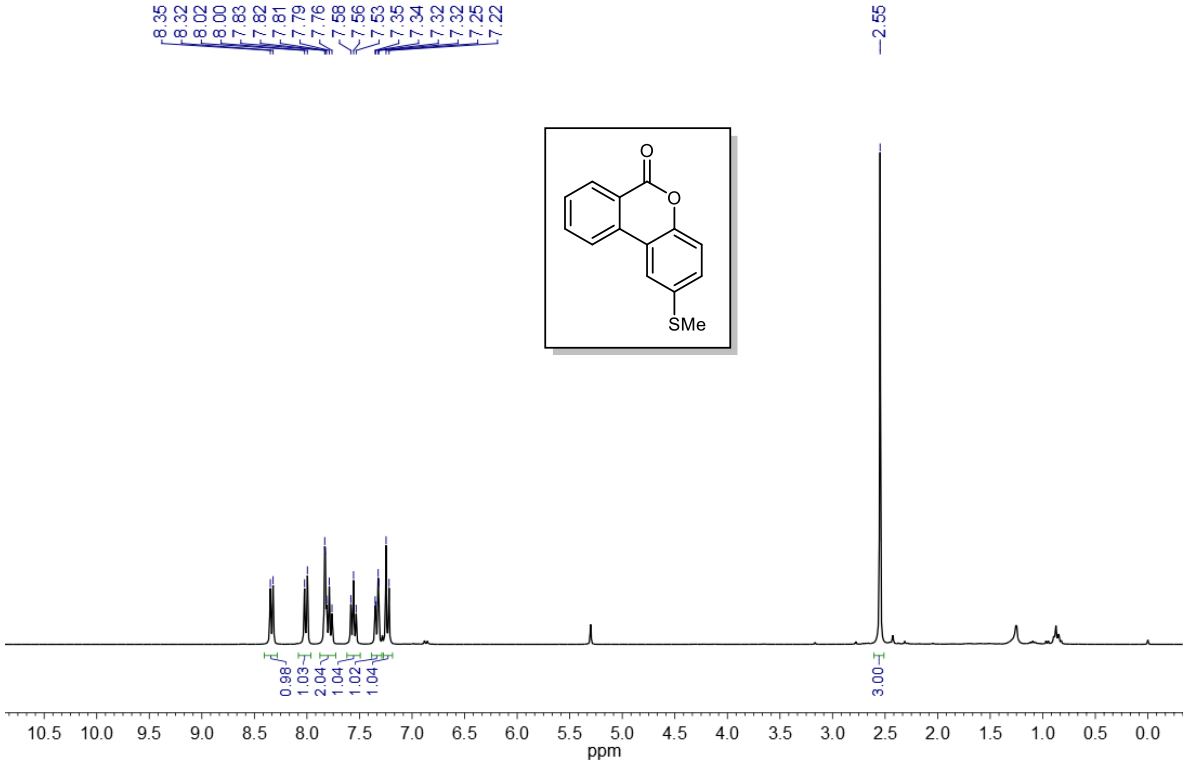

161.1
149.5
135.0
134.7
131.7
130.3
128.6
126.9
123.9
121.8
120.9
120.3
117.5
16.0
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

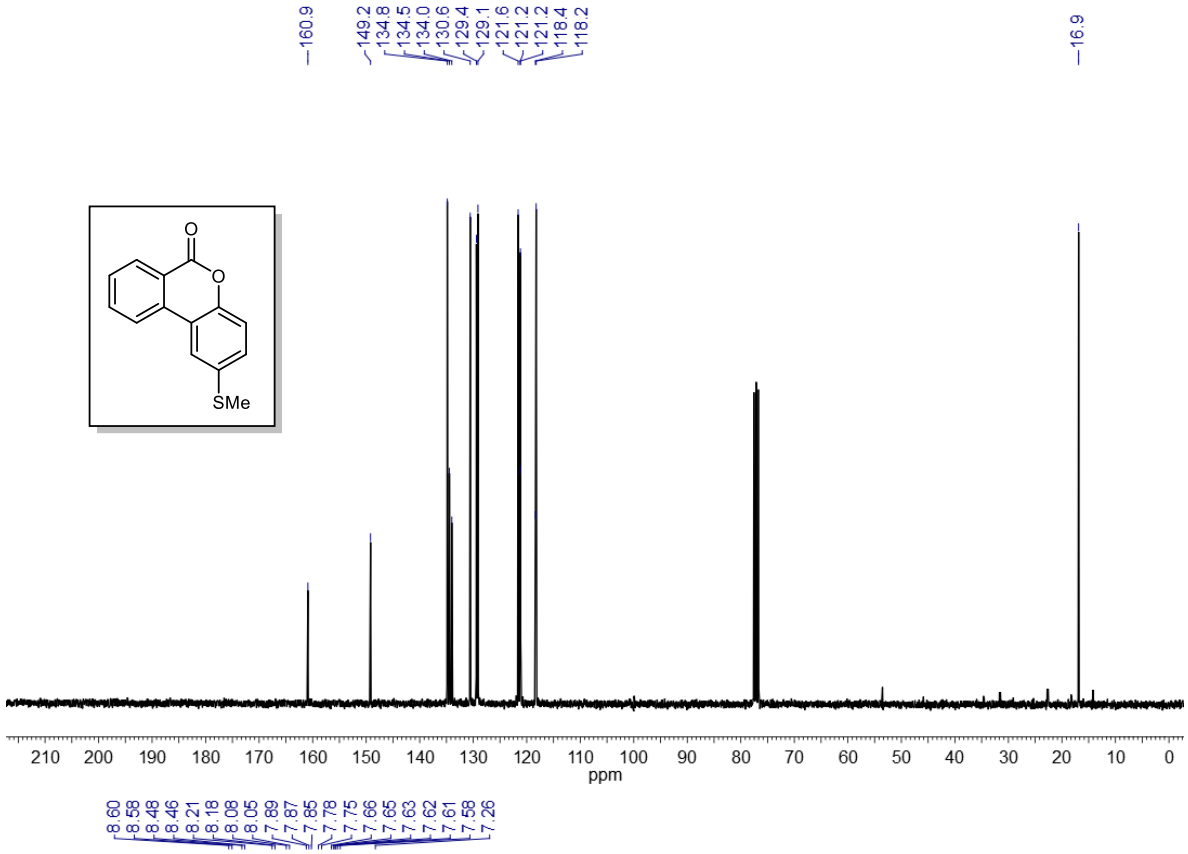

8.36
8.33
8.06
8.04
8.00
7.98
7.81
7.78
7.76
7.56
7.54
7.51
7.47
7.44
7.42
7.32
7.30
7.27
O
O
1.00
2.10
1.05
1.09
1.07
2.15
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

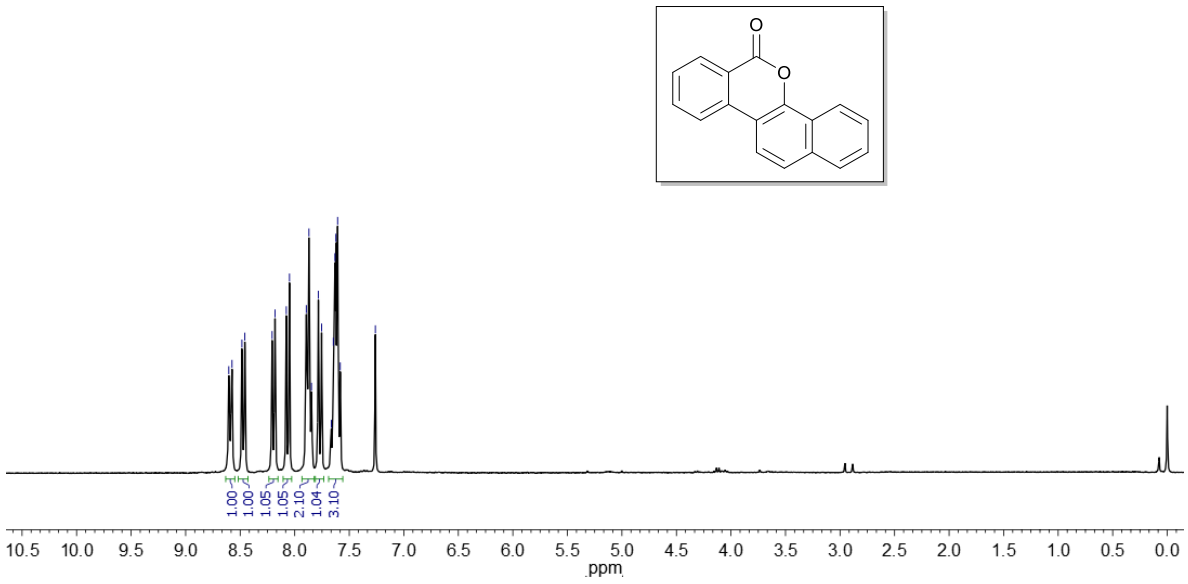

161.1
151.2
134.8
134.7
130.5
130.4
128.8
124.5
122.7
121.7
121.1
118.0
117.7
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

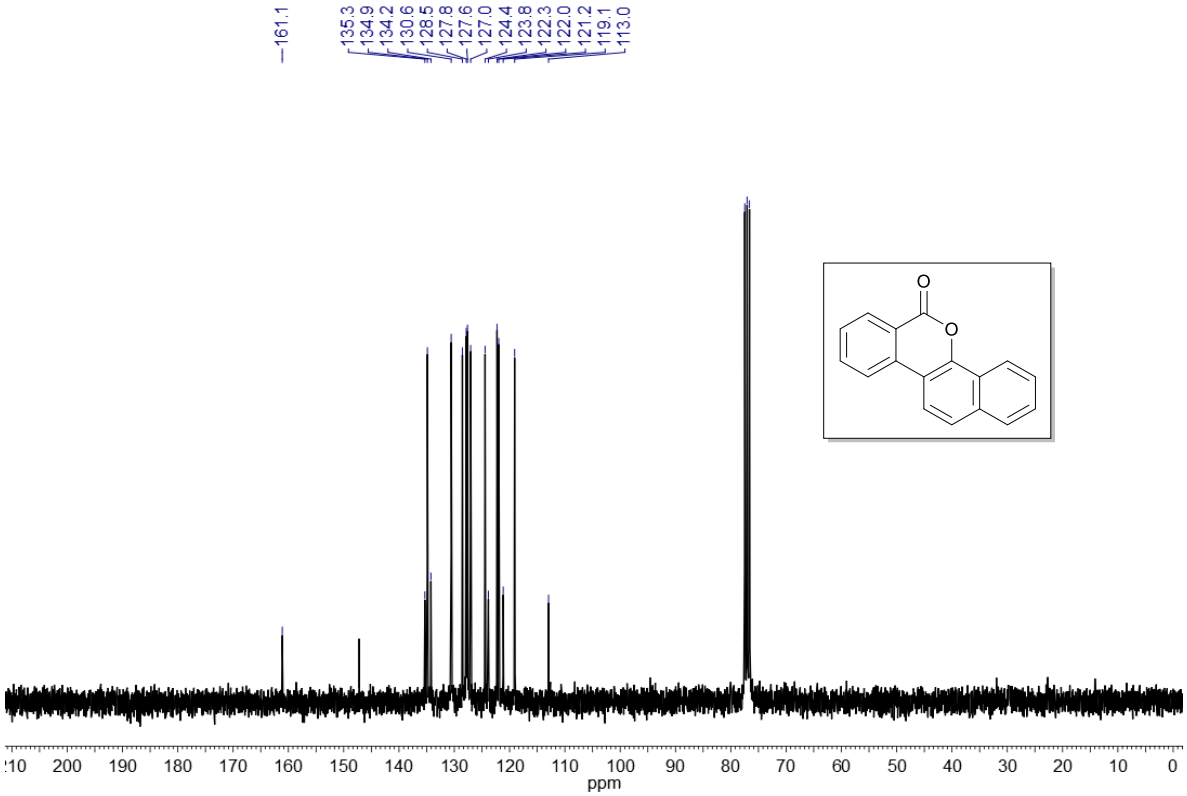

8.43
8.40
8.09
8.06
7.86
7.83
7.81
7.62
7.60
7.57
7.50
7.49
7.33
7.30
7.26
7.08
7.07
7.05
7.04
3.91
O
O
OMe
0.95
1.02
1.02
1.02
1.00
1.25
0.98
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

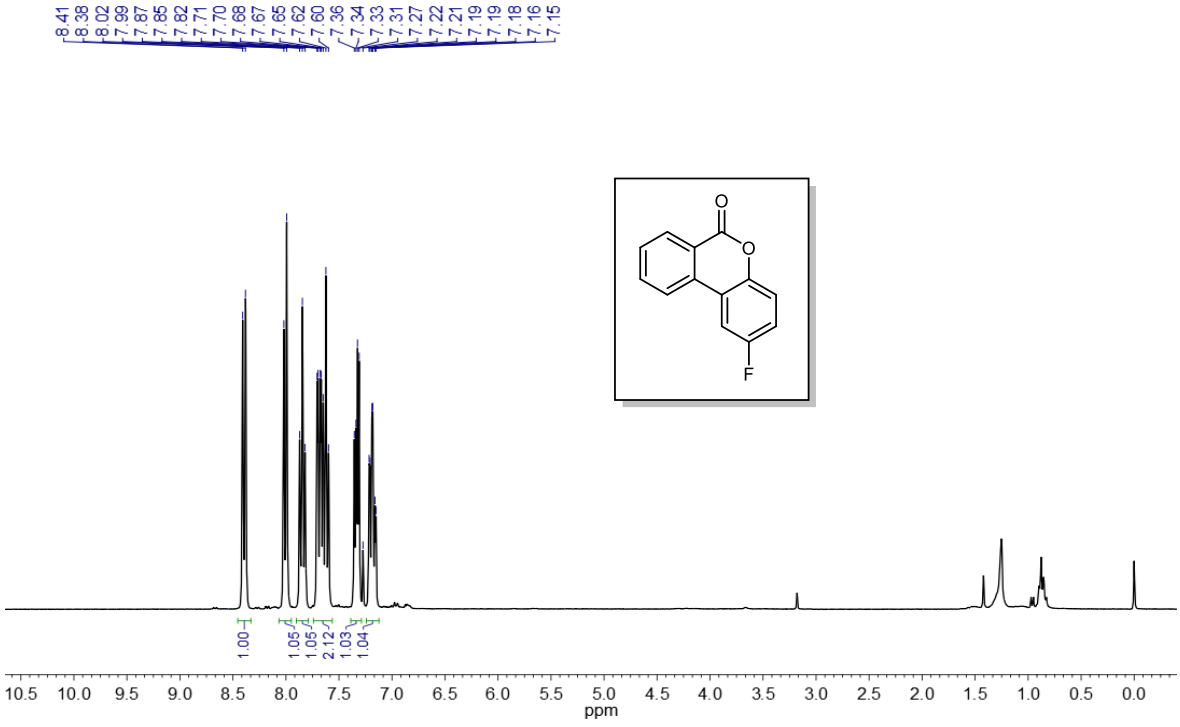

161.3
156.3
145.6
134.8
134.7
130.7
129.0
121.7
121.4
118.7
118.6
117.1
106.4
55.9
O
O
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

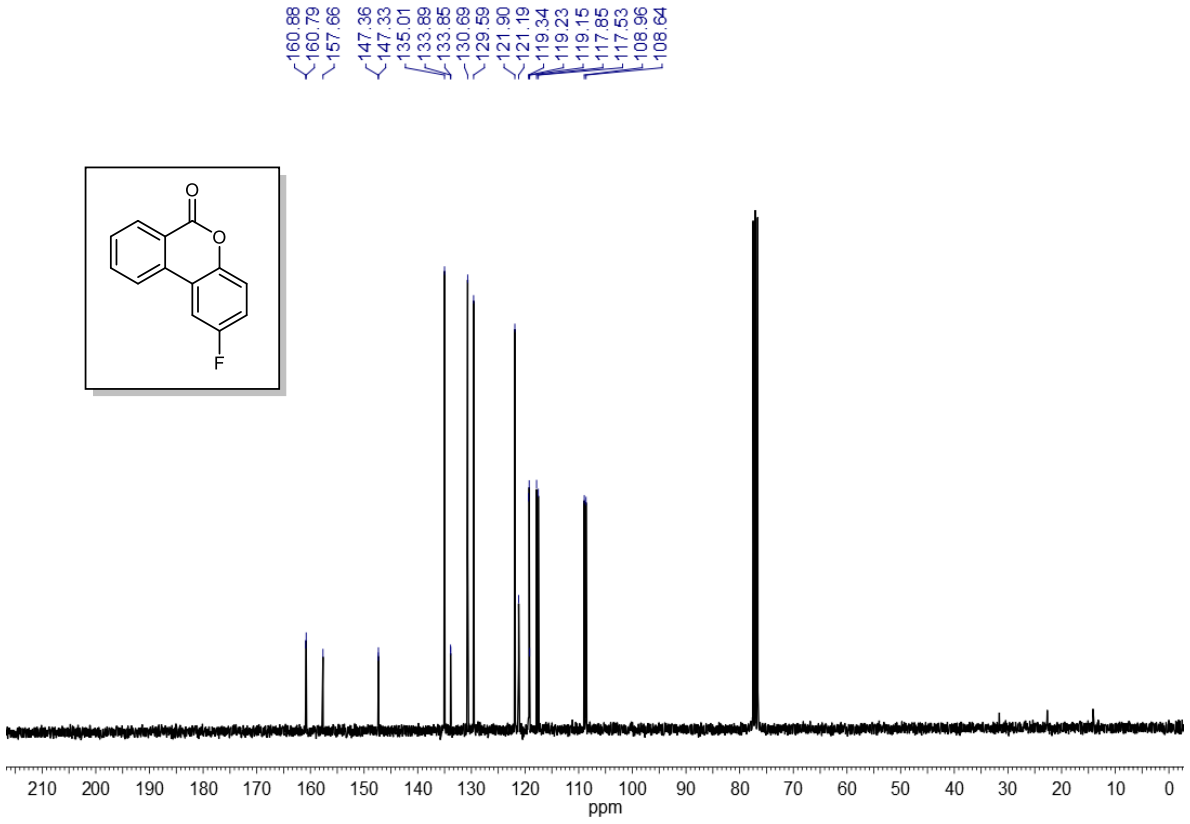

8.35
8.32
8.02
8.00
7.83
7.82
7.81
7.79
7.76
7.58
7.56
7.53
7.35
7.34
7.32
7.32
7.25
7.22
2.55
O
O
SMe
0.98
1.03
2.04
1.04
1.02
1.04
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

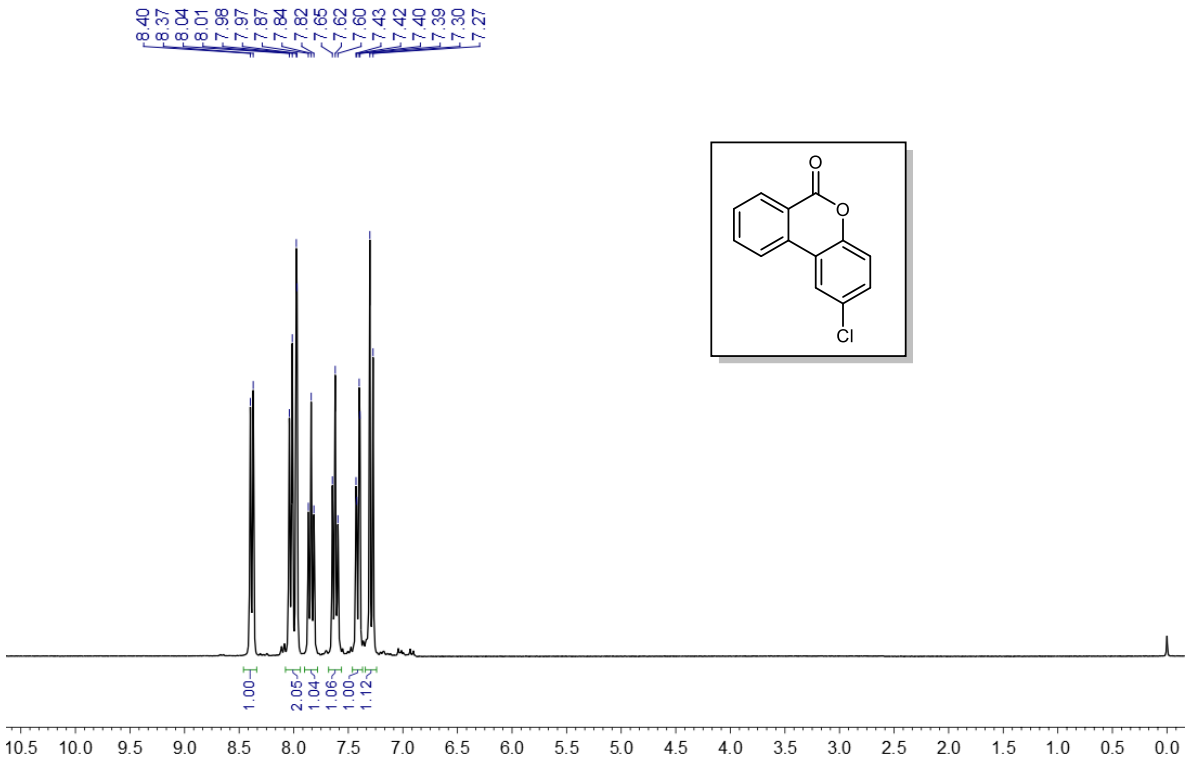

160.9
149.2
134.8
134.5
134.0
130.6
129.4
129.1
121.6
121.2
121.2
118.4
118.2
16.9
O
O
SMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm
8.60
8.58
8.48
8.46
8.21
8.18
8.08
8.05
7.89
7.87
7.85
7.78
7.75
7.66
7.65
7.63
7.62
7.61
7.58
7.26

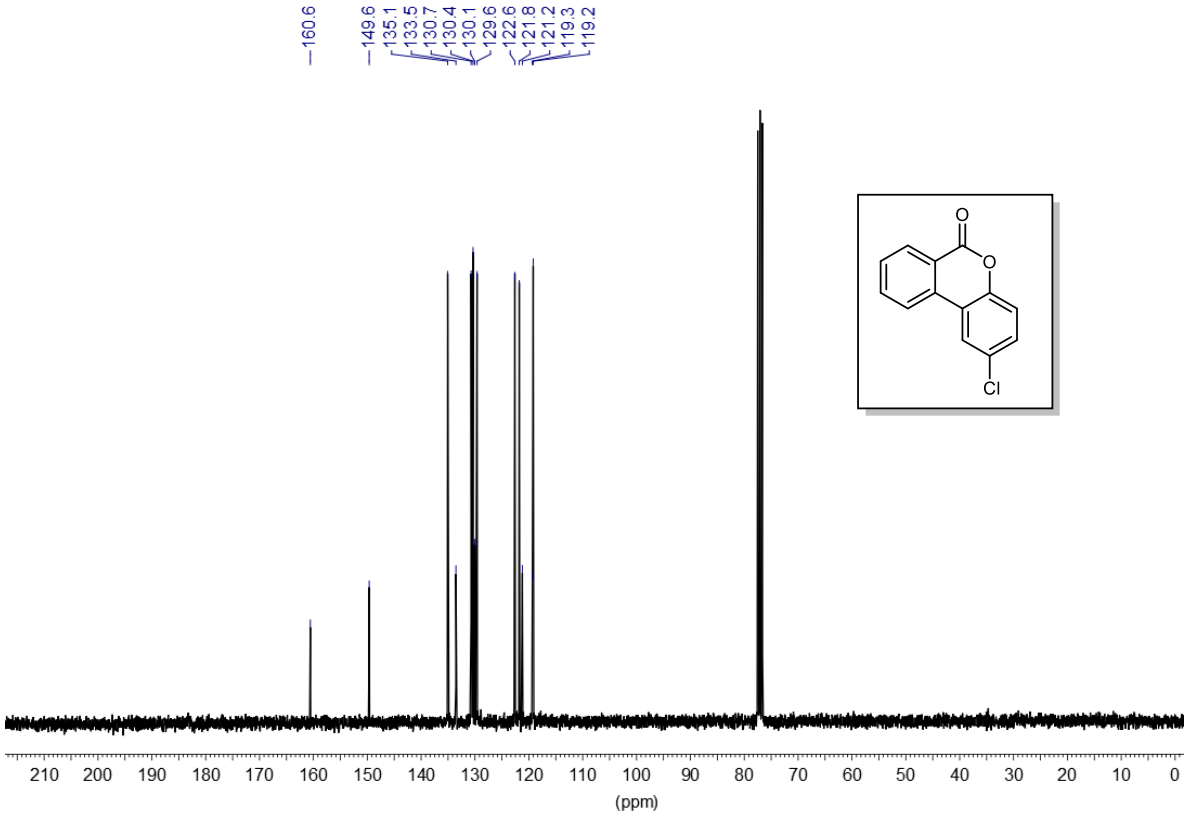

O
O
1.00
1.00
1.05
1.05
2.10
1.04
3.10
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

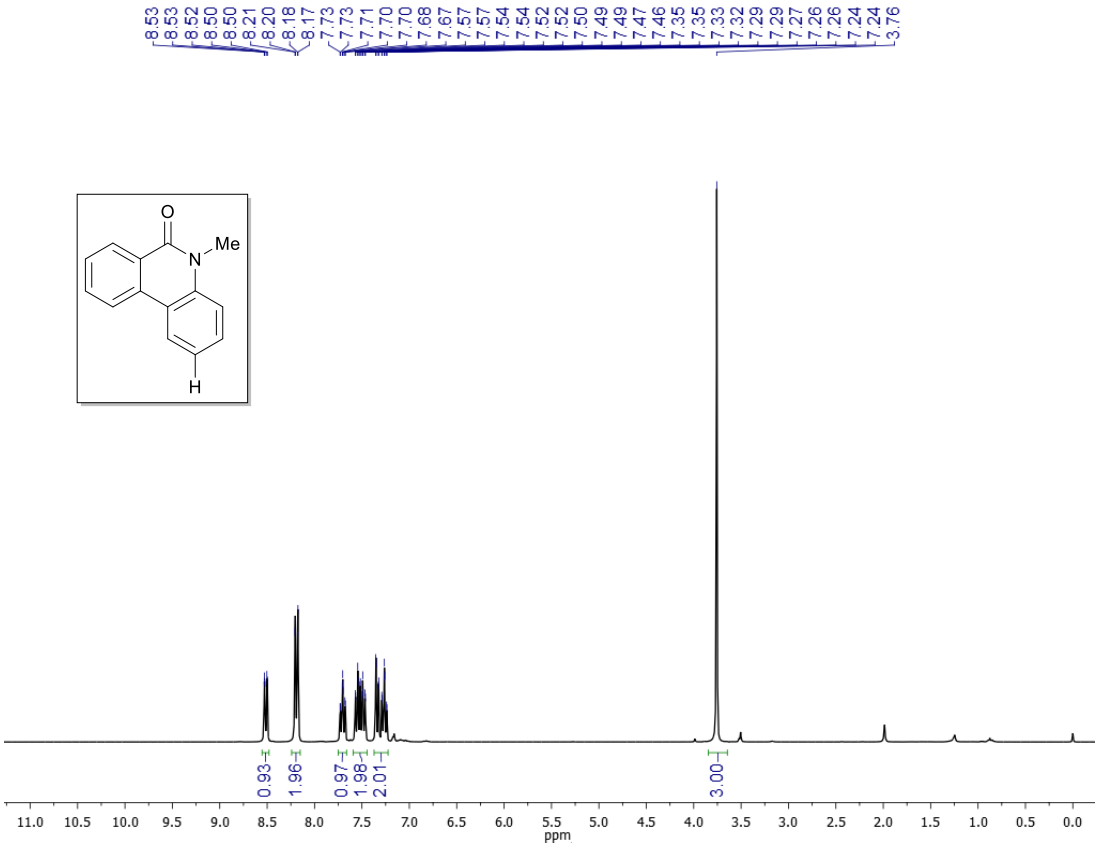

161.1
135.3
134.9
134.2
130.6
128.5
127.8
127.6
127.0
124.4
123.8
122.3
122.0
121.2
119.1
113.0
O
O
ppm

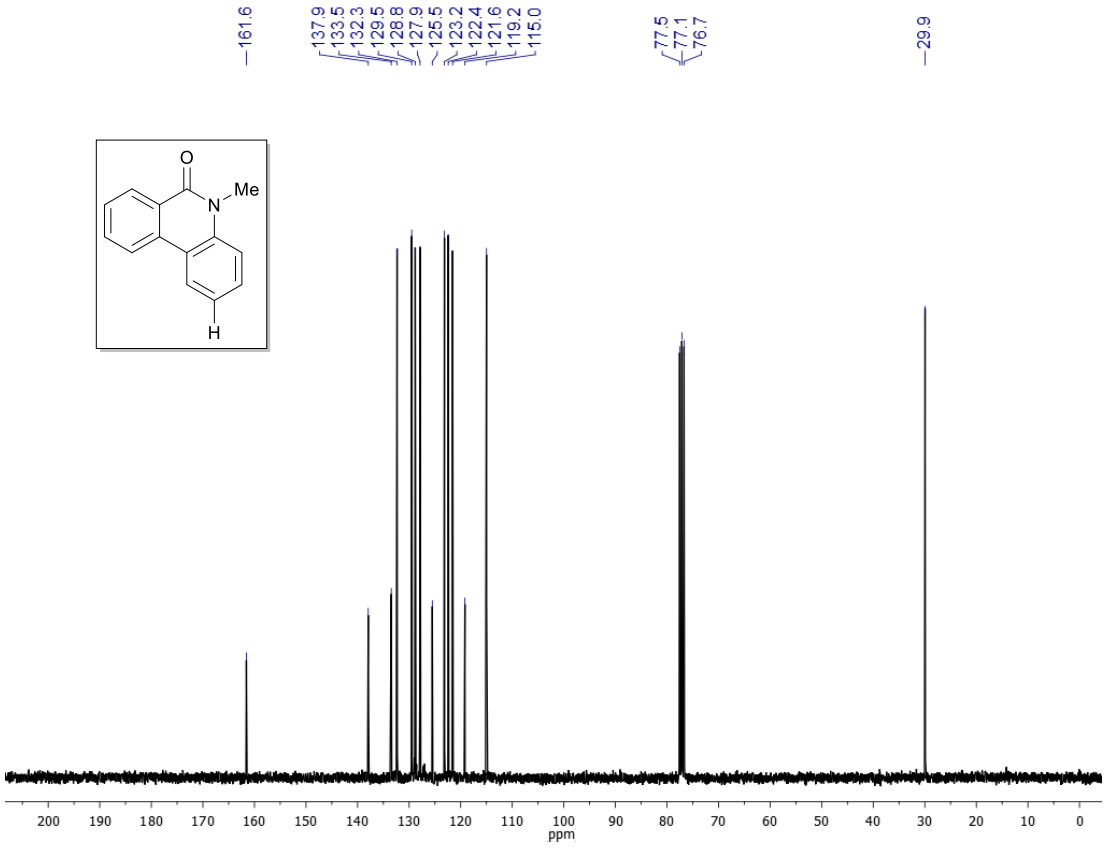

8.41
8.38
8.02
7.99
7.87
7.85
7.82
7.71
7.70
7.68
7.67
7.65
7.62
7.60
7.36
7.34
7.33
7.31
7.27
7.22
7.21
7.19
7.19
7.18
7.16
7.15
O
O
F
1.00
1.05
1.05
2.12
1.03
1.04
ppm

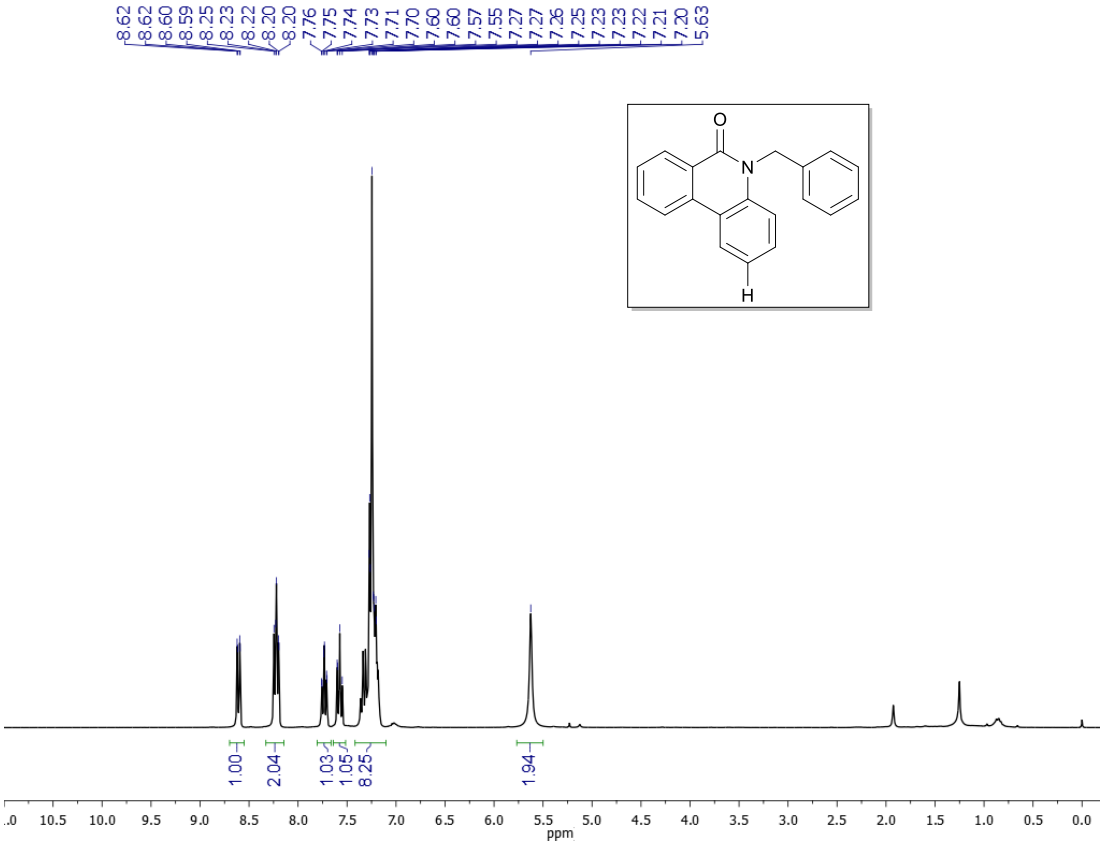

160.88
160.79
157.66
147.36
147.33
135.01
133.89
133.85
130.69
129.59
121.90
121.19
119.34
119.23
119.15
117.85
117.53
108.96
108.64
O
O
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

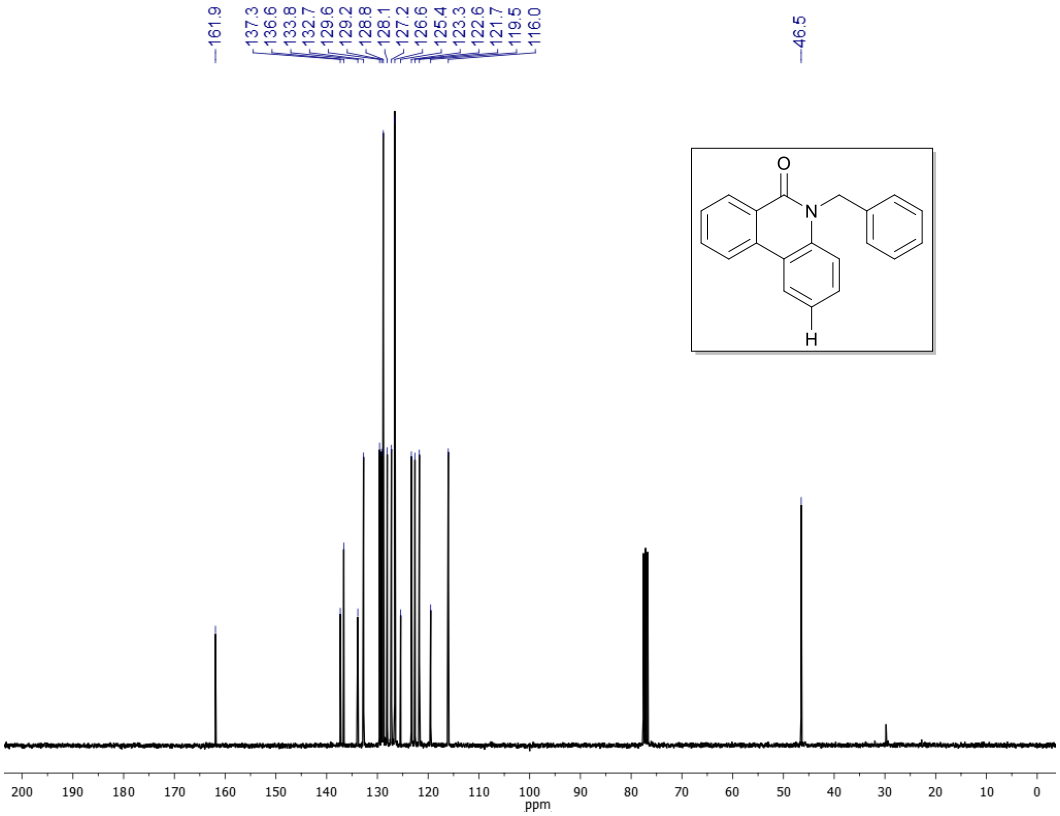

8.40
8.37
8.04
8.01
7.98
7.97
7.87
7.84
7.82
7.65
7.62
7.60
7.43
7.42
7.40
7.39
7.30
7.27
O
O
Cl
1.00
2.05
1.04
1.06
1.00
1.12
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

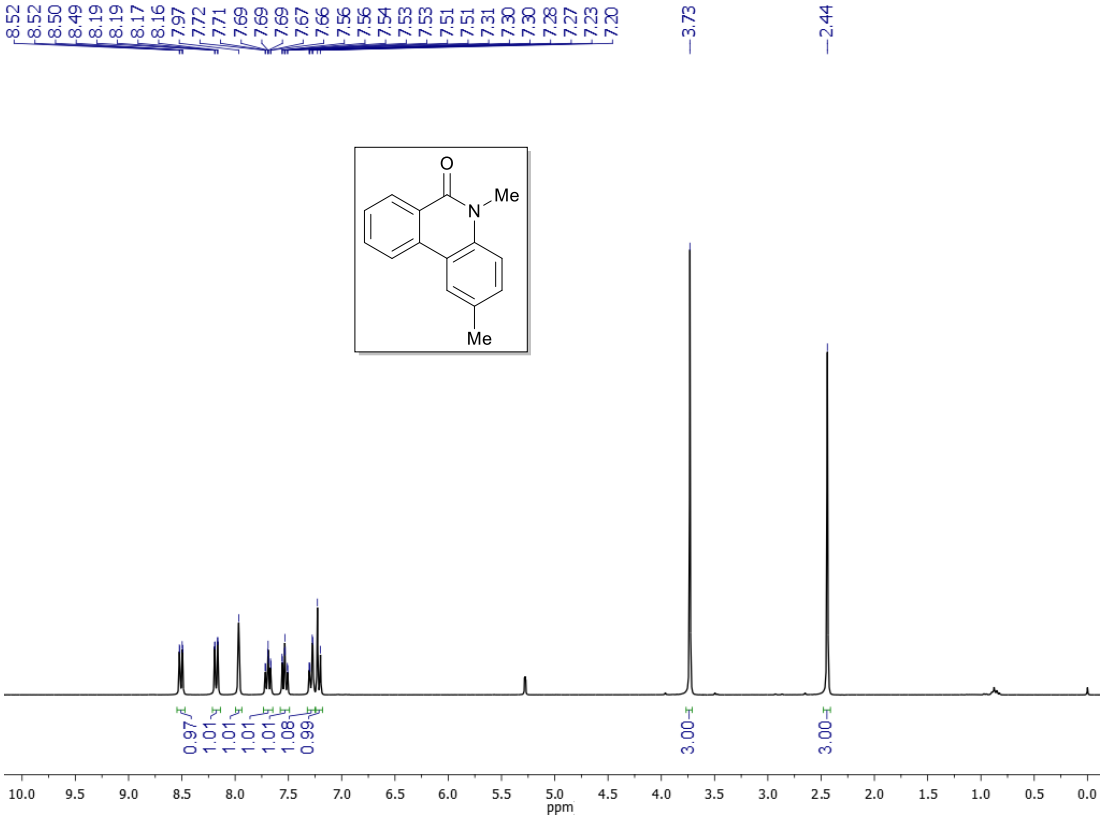

160.6
149.6
135.1
133.5
130.7
130.4
130.1
129.6
122.6
121.8
121.2
119.3
119.2
O
O
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

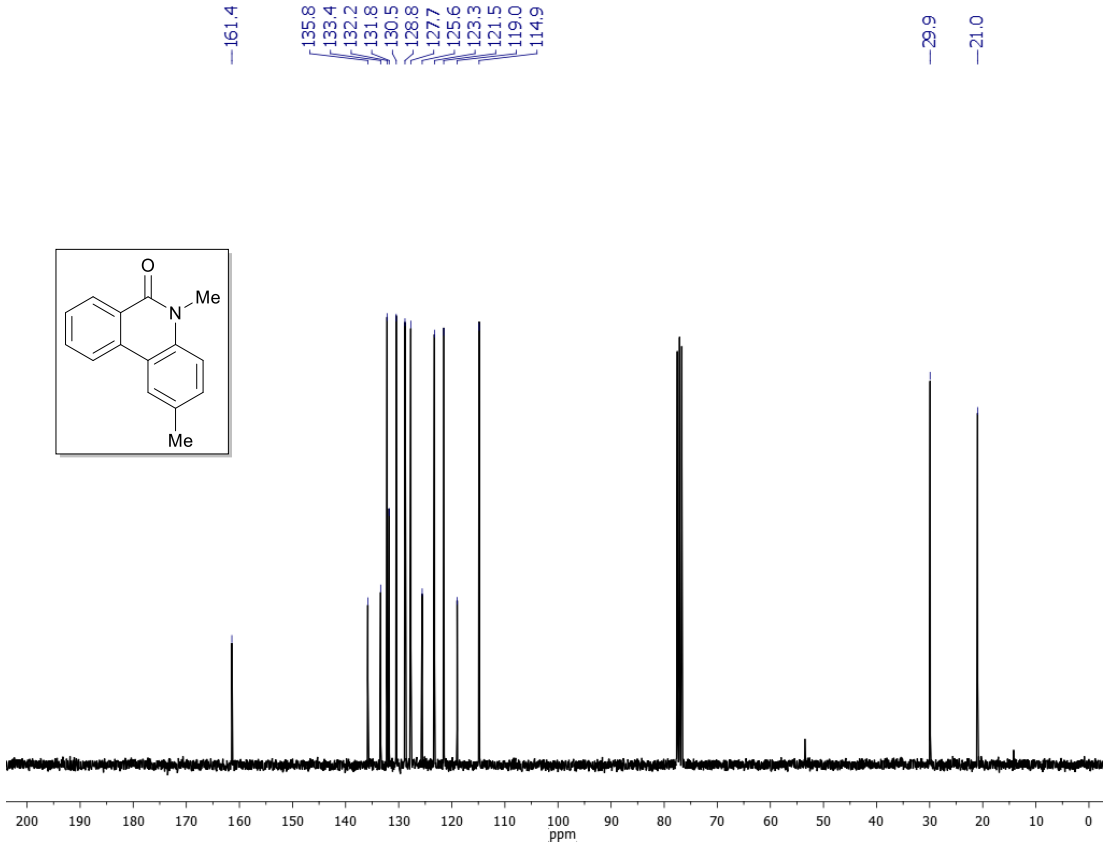

8.53
8.53
8.52
8.50
8.50
8.21
8.20
8.18
8.17
7.73
7.73
7.71
7.70
7.70
7.68
7.67
7.57
7.57
7.54
7.54
7.52
7.52
7.50
7.49
7.49
7.47
7.46
7.35
7.35
7.33
7.32
7.29
7.29
7.27
7.26
7.26
7.24
7.24
3.76
O
N
Me
H
0.93
1.96
0.97
1.98
2.01
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

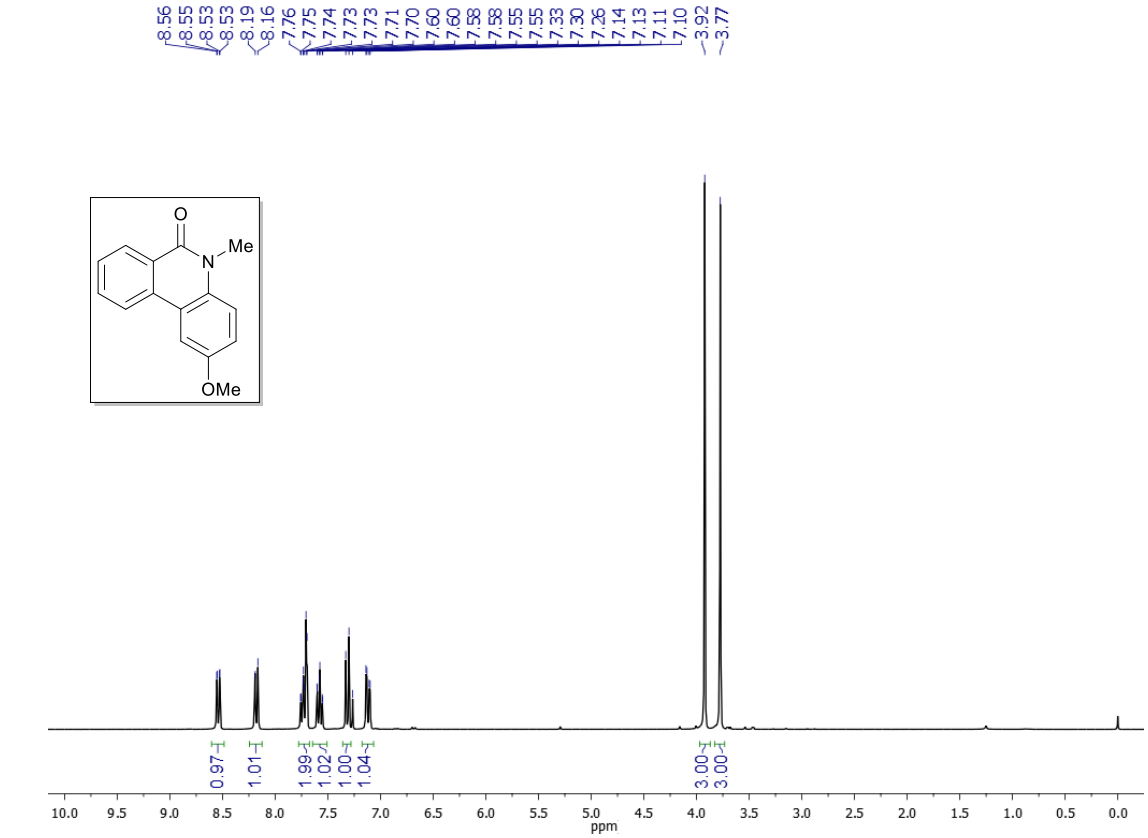

161.6
137.9
133.5
132.3
129.5
128.8
127.9
125.5
123.2
122.4
121.6
119.2
115.0
77.5
77.1
76.7
29.9
O
N
Me
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

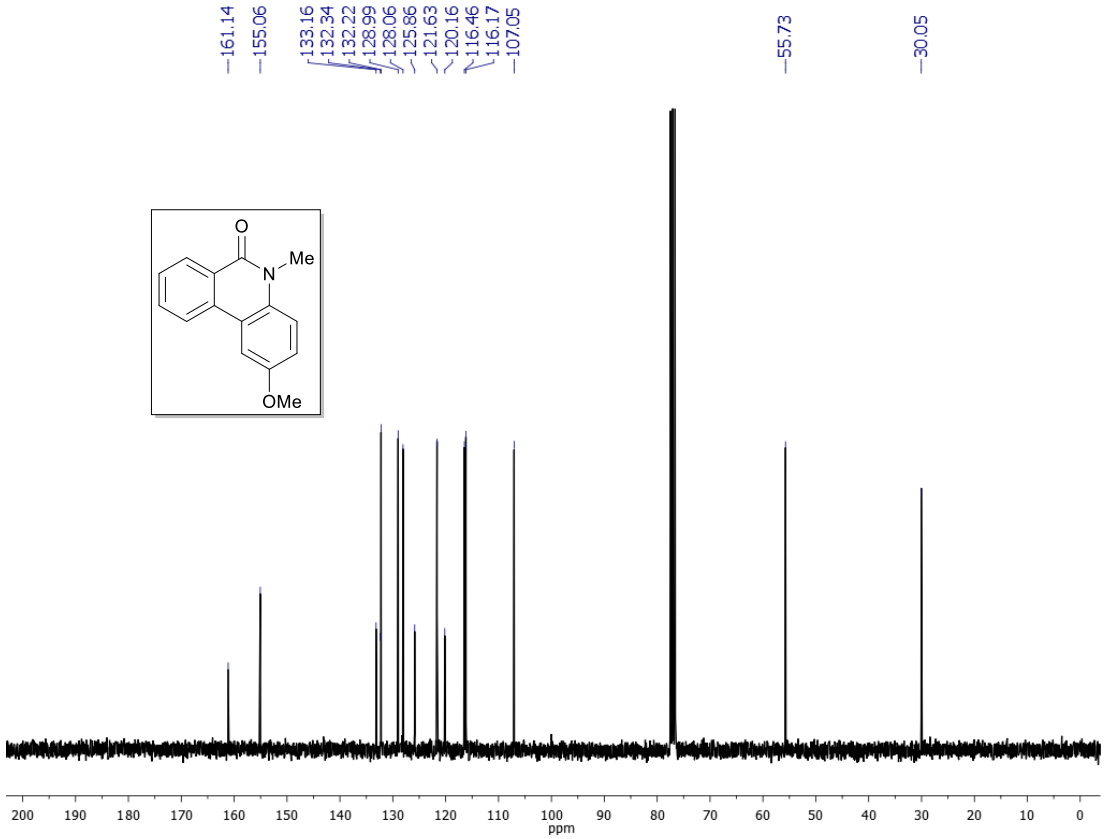

8.62
8.62
8.60
8.59
8.25
8.23
8.22
8.20
8.20
7.76
7.75
7.74
7.73
7.71
7.70
7.60
7.60
7.57
7.55
7.27
7.27
7.26
7.25
7.23
7.23
7.22
7.21
7.20
5.63
O
N
H
1.00
2.04
1.03
1.05
8.25
1.94
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

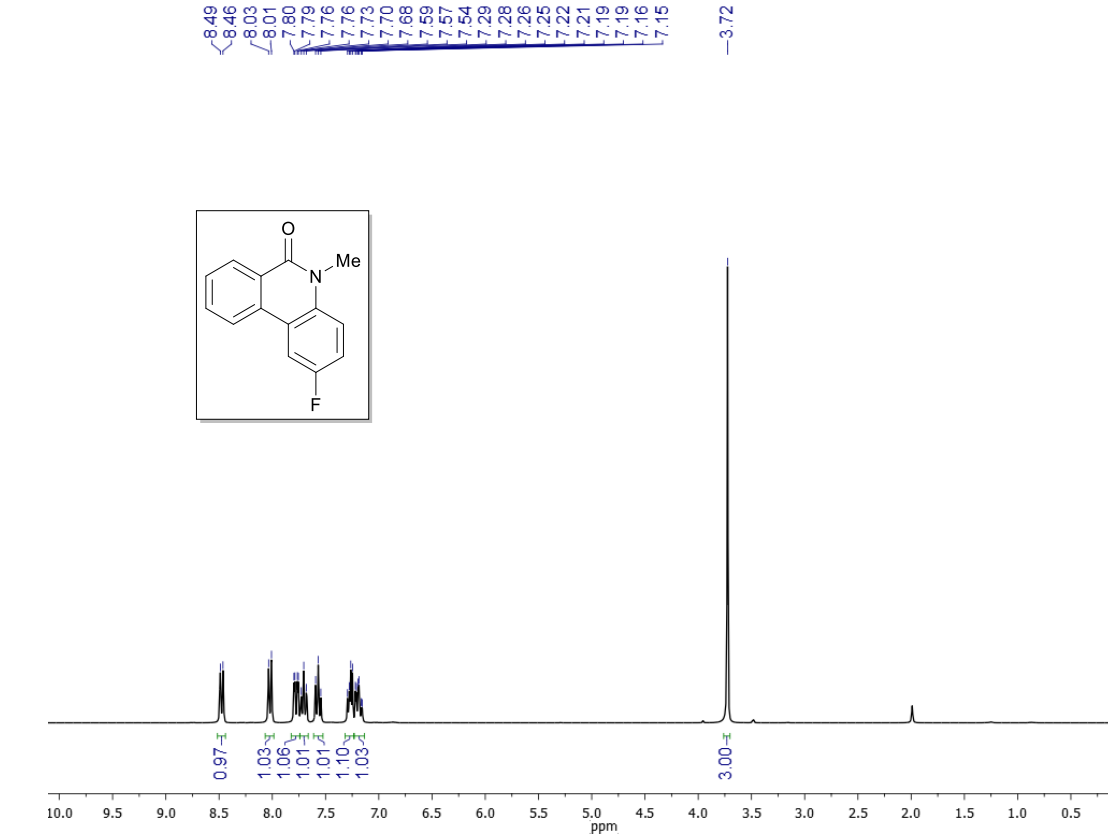

161.9
137.3
136.6
133.8
132.7
129.6
129.2
128.8
128.1
127.2
126.6
125.4
123.3
122.6
121.7
119.5
116.0
46.5
O
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

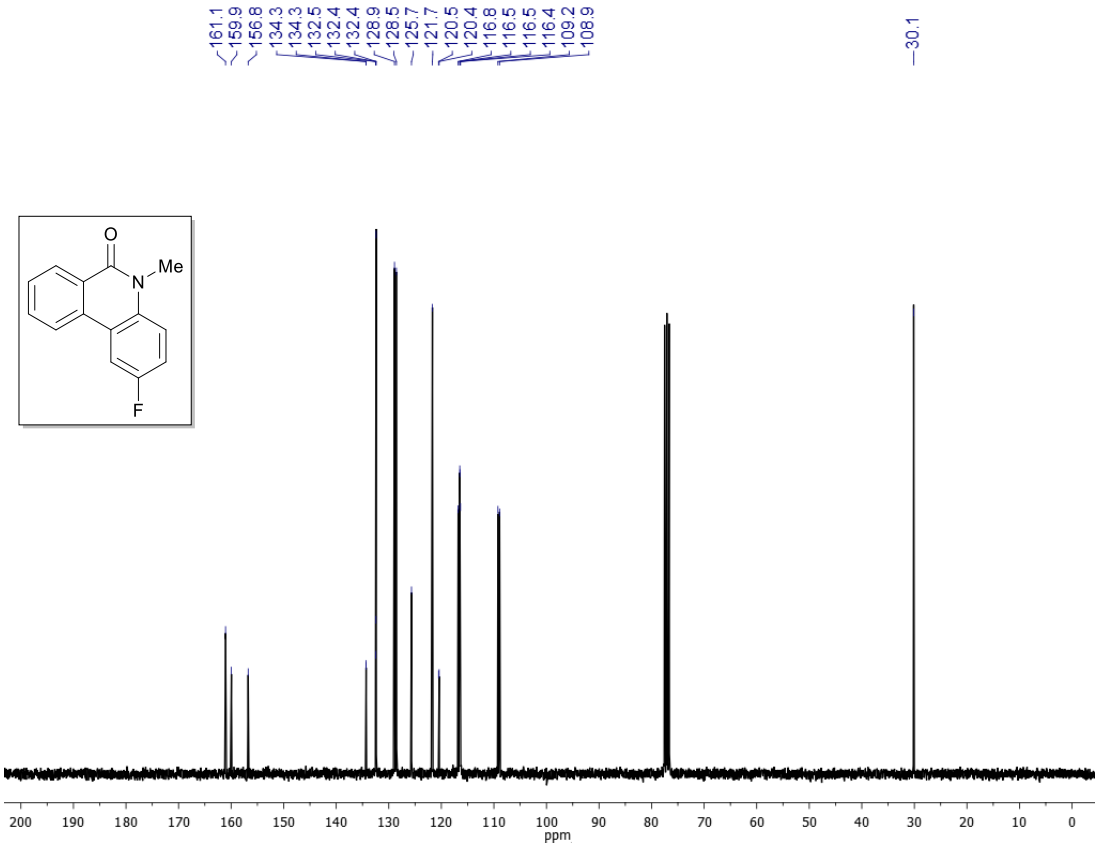

8.52
8.52
8.50
8.49
8.19
8.19
8.17
8.16
7.97
7.72
7.71
7.69
7.69
7.69
7.67
7.66
7.56
7.56
7.54
7.53
7.53
7.51
7.51
7.31
7.30
7.30
7.28
7.27
7.23
7.20
3.73
2.44
O
N
Me
Me
0.97
1.01
1.01
1.01
1.01
1.08
0.99
3.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

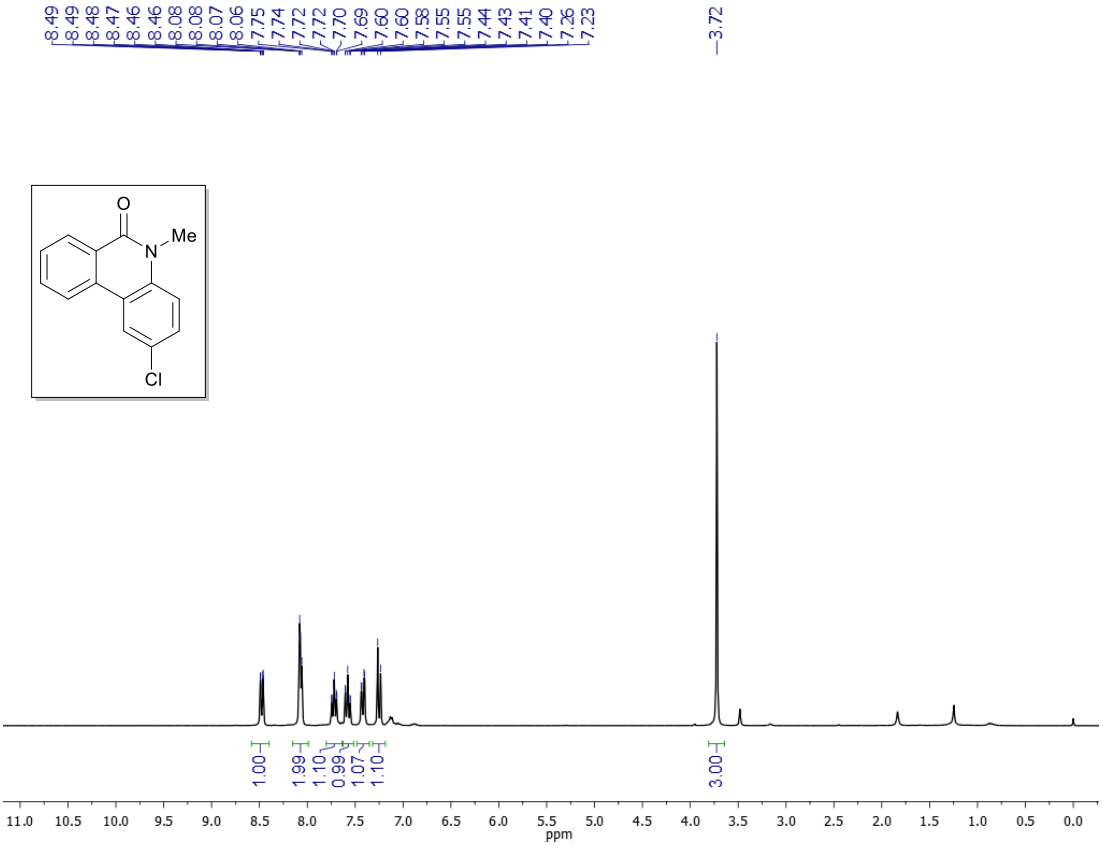

161.4
135.8
133.4
132.2
131.8
130.5
128.8
127.7
125.6
123.3
121.5
119.0
114.9
29.9
21.0
O
N
Me
Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

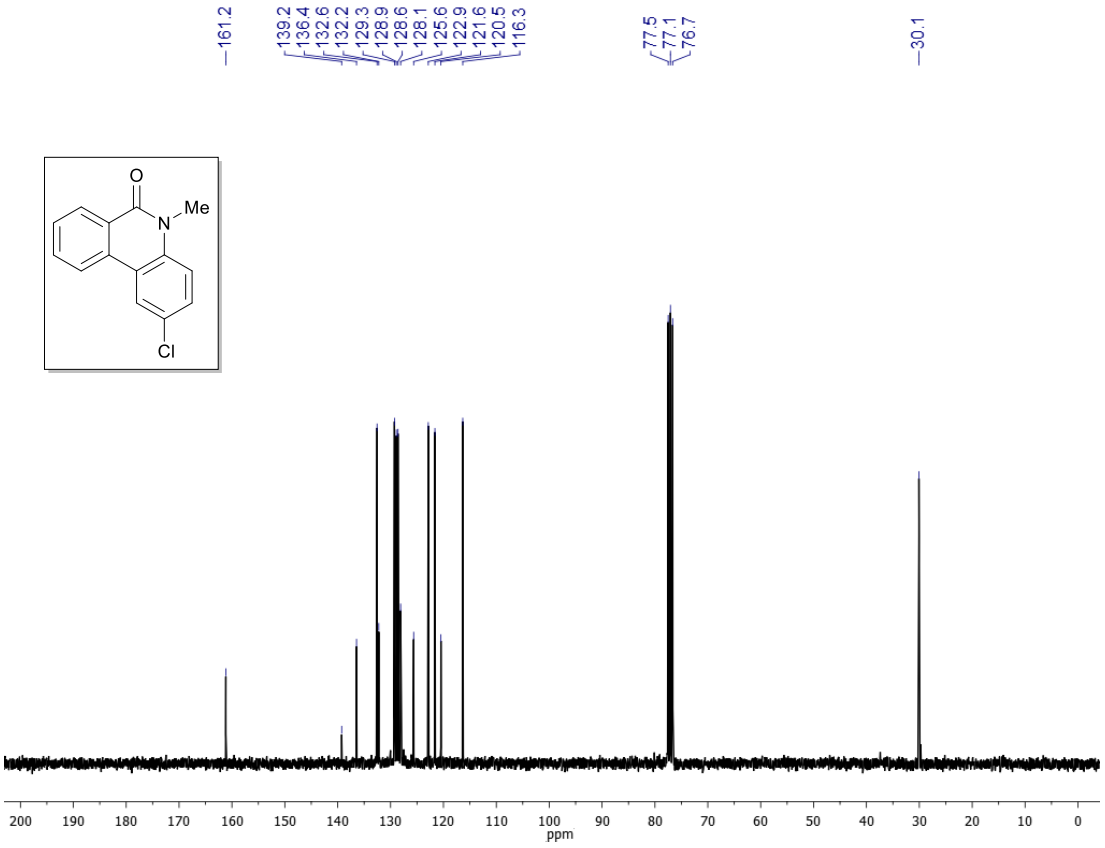

8.56
8.55
8.53
8.53
8.19
8.16
7.76
7.75
7.74
7.73
7.73
7.71
7.70
7.60
7.60
7.58
7.58
7.55
7.55
7.33
7.30
7.26
7.14
7.13
7.11
7.10
3.92
3.77
O
N
Me
OMe
0.97
1.01
1.99
1.02
1.00
1.04
3.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


161.14
155.06
133.16
132.34
132.22
128.99
128.06
125.86
121.63
120.16
116.46
116.17
107.05
55.73
30.05
O
N
Me
OMe
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


8.49
8.46
8.03
8.01
7.80
7.79
7.76
7.76
7.73
7.70
7.68
7.59
7.57
7.54
7.29
7.28
7.26
7.25
7.22
7.21
7.19
7.19
7.16
7.15
3.72
O
N
Me
F
0.97
1.03
1.06
1.01
1.01
1.10
1.03
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


161.1
159.9
156.8
134.3
134.3
132.5
132.4
132.4
128.9
128.5
125.7
121.7
120.5
120.4
116.8
116.5
116.5
116.4
109.2
108.9
30.1
O
N
Me
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


8.49
8.49
8.48
8.47
8.46
8.46
8.08
8.08
8.07
8.06
7.75
7.74
7.72
7.72
7.70
7.69
7.60
7.60
7.58
7.55
7.55
7.44
7.43
7.41
7.40
7.26
7.23
3.72
O
N
Me
Cl
1.00
1.99
1.10
0.99
1.07
1.10
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


161.2
139.2
136.4
132.6
132.2
129.3
128.9
128.6
128.1
125.6
122.9
121.6
120.5
116.3
77.5
77.1
76.7
30.1
O
N
Me
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

14. X-Ray data for complex 3d

Table 1. Crystal data and structure refinement for **3d**.

Identification code	**3d**	
Empirical formula	$C_{14}H_{21}Cl_2N_2PPd$	
Formula weight	425.60	
Temperature	181(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1/n	
Unit cell dimensions	a = 11.598(5) Å	α= 90.000(5)°.
	b = 13.656(5) Å	β= 117.992(5)°.
	c = 12.222(5) Å	γ = 90.000(5)°.
Volume	1709.3(12) $Å^3$	
Z	4	
Density (calculated)	1.654 Mg/m^3	
Absorption coefficient	1.483 mm^{-1}	
F(000)	856	
Crystal size	0.250 x 0.150 x 0.070 mm^3	
Theta range for data collection	2.983 to 26.370°.	
Index ranges	-14<=h<=14, -17<=k<=17, -15<=l<=15	
Reflections collected	10189	
Independent reflections	3480 [R(int) = 0.0202]	
Completeness to theta = 26.400°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.88326	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3480 / 0 / 187	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0224, wR2 = 0.0520	
R indices (all data)	R1 = 0.0287, wR2 = 0.0549	
Largest diff. peak and hole	0.352 and -0.335 e.$Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for **3d**.

Pd(1)-P(1)	2.1952(8)	Pd(1)-N(1)	2.1331(19)
Pd(1)-Cl(1)	2.3806(9)	Pd(1)-Cl(2)	2.2718(9)
P(1)-C(11)	1.792(2)	P(1)-C(21)	1.779(2)
P(1)-C(14)	1.799(2)	N(1)-N(2)	1.441(3)
N(1)-C(2)	1.492(3)	N(2)-C(24)	1.365(3)
N(1)-C(1)	1.492(3)	N(2)-C(21)	1.378(3)
C(11)-C(12)	1.351(3)	C(13)-C(131)	1.501(3)
C(11)-C(111)	1.493(3)	C(14)-C(141)	1.491(3)
C(12)-C(121)	1.491(3)	C(21)-C(22)	1.373(3)
C(12)-C(13)	1.499(3)	C(22)-C(23)	1.398(3)
C(13)-C(14)	1.342(3)	C(23)-C(24)	1.361(4)

N(1)-Pd(1)-P(1)	87.62(6)	N(1)-Pd(1)-Cl(1)	92.59(6)
N(1)-Pd(1)-Cl(2)	173.84(5)	P(1)-Pd(1)-Cl(1)	174.29(2)
P(1)-Pd(1)-Cl(2)	87.18(4)	Cl(2)-Pd(1)-Cl(1)	92.92(4)
C(21)-P(1)-C(11)	108.94(10)	N(2)-N(1)-C(2)	108.55(18)
C(21)-P(1)-C(14)	109.74(10)	N(2)-N(1)-C(1)	107.96(18)
C(11)-P(1)-C(14)	95.05(11)	C(2)-N(1)-C(1)	110.30(19)
C(21)-P(1)-Pd(1)	100.13(8)	N(2)-N(1)-Pd(1)	110.26(13)
C(11)-P(1)-Pd(1)	125.98(8)	C(2)-N(1)-Pd(1)	110.33(15)
C(14)-P(1)-Pd(1)	116.76(8)	C(1)-N(1)-Pd(1)	109.39(15)

C(21)-N(2)-N(1)	123.03(18)	C(24)-N(2)-N(1)	127.17(19)
C(24)-N(2)-C(21)	109.8(2)		
C(12)-C(11)-P(1)	107.19(17)	C(13)-C(14)-P(1)	107.19(17)
C(111)-C(11)-P(1)	122.21(17)	C(141)-C(14)-P(1)	122.60(17)
C(22)-C(21)-P(1)	136.24(19)	N(2)-C(21)-P(1)	117.03(16)
C(22)-C(21)-N(2)	106.69(19)	C(23)-C(24)-N(2)	107.5(2)
C(12)-C(11)-C(111)	130.6(2)	C(14)-C(13)-C(131)	124.2(2)
C(11)-C(12)-C(121)	125.5(2)	C(12)-C(13)-C(131)	120.4(2)
C(11)-C(12)-C(13)	115.2(2)	C(13)-C(14)-C(141)	130.2(2)
C(121)-C(12)-C(13)	119.3(2)	C(21)-C(22)-C(23)	107.9(2)
C(14)-C(13)-C(12)	115.37(19)	C(24)-C(23)-C(22)	108.2(2)

15. References

[1] D. M. Roundhill, S. G. N. Roundhill, W. B. Beaulieu, U. Bagchi, *Inorganic Chemistry,* **1980**, *19*, 3365.

[2] K. Maeda, T. Matsukihira, S. Saga, Y. Takeuchi, T. Harayama, Y. Horino, H. Abe, *Heterocycles*, **2014**, *88*, 2151.

[3] R. J. Perry, B. D. Wilson, S. R. Turner, R. W. Blevins, *Macromolecules*, **1995**, *28*, 3509.

[4] T. Harayama, H. Yasuda, T. Akiyama, Y. Takeuchi, H. Abe, *Chem. Pharm. Bull*., 2000, *48*, 861.

[5] J. L. Wardell, J. M. S. Skakle, J. N. Low, C. Glidewell, *Acta Cryst.* **2005**, E61, o3334

[6] J. Luo; Y. Lu, S. Liu, J. Liu,G-J. Deng, *Adv. Synth. Catal.* **2011**, *353*, 2604.

[7] Y. Li, Y.-J. Ding, J.-Y. Wang, Y.-M. Su, X.-S. Wang, *Org. Lett.*, **2013**, *15*, 2574.

[8] X. Shang, L. Xu, W. Yang, J. Zhou, M. Miao, H. Ren, *Eur. J. Org. Chem.* **2013**, 5475.

[9] K. Devab, R. Maurya, *RSC Adv.,* **2015**, 5, 13102.

[10] G. Zhang, X. Zhao, Y. Yan, C. Ding, *Eur. J. Org. Chem*. **2012**, 669.

[11] E. Dubost, R. Magnelli, T. Cailly, R. Legay, F. Fabis, S. Rault, *Tetrahedron*, **2010**, 66, 5008