Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

$FeCl_3$ Mediated Synthesis of Substituted Indenones by Formal [2+2] Cycloaddition/Ring Opening of *o*-Keto-Cinnamates.

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General Information

All reactions were carried out under nitrogen or argon atmosphere with dry solvents under anhydrous conditions, unless otherwise mentioned. Anhydrous THF and diethyl ether were distilled from sodium- benzophenone and dichloromethane was distilled from calcium hydride. Yields refer to chromatographically pure material, unless otherwise stated.

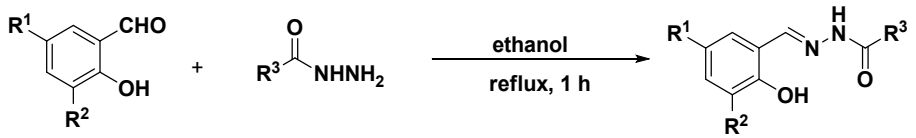
Reaction were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel plates (60F-254) using UV light as a visualizing agent and an p - anisaldehyde or ninhydrine stain, and heat as developing agents. Merck silica gel (particle size 100-200 and 230-400 mesh) was used for flash column chromatography.

Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. NMR spectra were recorded on either a Bruker Avance 200 (^{1}H: 200 MHz, ^{13}C: 50MHz), Bruker Avance 400 (^{1}H: 400 MHz, ^{13}C: 100MHz), Bruker Avance 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz), JEOL ECX 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) Mass spectrometric data were obtained using WATERS-Q-Tof Premier-ESI-MS.

The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of a doublet of a doublet, dm = doublet of a multiplet, m = multiplet, br = broad.

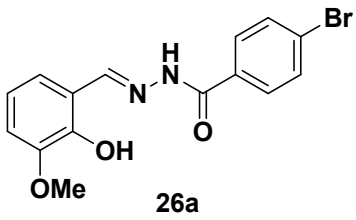
A) General procedure for the Preparation of hydrazones.

The carbohydrazides was added at room temperature to a solution of the desired aldehyde in ethanol. The reaction mixture was refluxed for 30 min., poured on ice and the resulting solid was filtered, washed with water and solid was taken in to round bottom flask, added methanol and refluxed for another 15 min. Solid was filtered again, washed with methanol and dried under vacuum.



24a) R^1 = H, R^2 = OMe **25a**) R^3 = (*p*-Br)Ph **26a**) R^1 = H, R^2 = OMe, R^3 = (*p*-Br)Ph
24b) R^1 = Cl, R^2 = H **25b**) R^3 = α- napthaline **26b**) R^1 = Cl, R^2 = H, R^3 = α- napthaline
24c) R^1 = -OAc, R^2 = H **25c)** R^3 = Ph **26c**) R^1 = -OAc,R^2 = H, R^3 = Ph

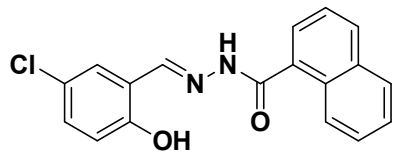
Compound 26a: According to the general procedure **A** for the preparation of hydrazones,



26a

aldehyde **24a** (500 mg, 3.28 mmol) and hydrazide **25a**[1a] (700 mg, 3.28 mmol) in ethanol (15 ml), were used to furnish the product **26a** (1.0 gm, 89%) as a light yellow solid; **IR** (neat): ν_{max}/cm^{-1} 3561, 3215, 3083, 1654, 1622, 1606, 1589, 1574, 1479, 1241, 1072; **^{1}H NMR** (400 MHz, $DMSOd_6$) δ 3.82 (s, 3H), 6.87 (t, *J* = 7.9 Hz, 1H), 7.04 (d, *J* = 7.9 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.81 - 7.97 (m, 2H), 8.66 (s, 1H), 10.88 (br. s., 1H), 12.14 (br. s., 1H); **^{13}C NMR** (100 MHz, $DMSOd_6$) δ 55.8, 113.8, 119.0, 119.1, 120.7, 125.8, 129.8, 131.6, 132.0, 147.2, 148.0, 148.3, 161.9; **HRMS:** m/z calcd for $C_{15}H_{14}BrN_2O_3$ $[(M+H)^+]$: 349.0188; Found: 349.0189.

Compound 26b: According to the general procedure **A** for the preparation of hydrazones,

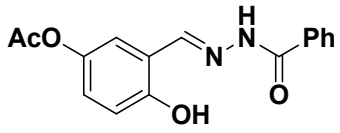


26b

aldehyde **24b** (390 mg, 2.50 mmol) and hydrazide **25b**[1b] (500 mg, 2.50 mmol) in ethanol (15 ml), were used to furnish the product **26b** (729 mg, 90%) (1:6 diastereomeric ratio) as a white solid; **IR** (neat): ν_{max}/cm^{-1} 3153, 3008, 1643, 1621, 1591, 1566, 1478, 1310, 1295, 1254, 798, 729; **^{1}H NMR** (400 MHz, $DMSOd_6$) δ 6.98 (d, *J* = 8.7 Hz, 1H), 7.61 (d, *J* = 6.6 Hz, 3H), 7.71 (br. s., 1H), 7.80 (d, *J* = 6.7 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 8.25 (d, *J* = 7.53 Hz, 1H), 8.54 (br. s., 1H), 11.24 (br. s., 1H),

12.32 (br. s., 1H); **^{13}C NMR** (100 MHz, DMSOd_6) δ 118.3, 120.8, 123.1, 125.0, 125.1, 126.2, 126.5, 127.2, 127.6, 128.4, 130.0, 130.9, 130.9, 132.1, 133.2, 145.7, 156.1, 164.6; **HRMS:** m/z calcd for $C_{18}H_{14}ClN_2O_2$ [$(M+H)^+$]: 325.0744; Found: 325.0745.

Compound 26c: According to the general procedure **A** for the preparation of hydrazones,

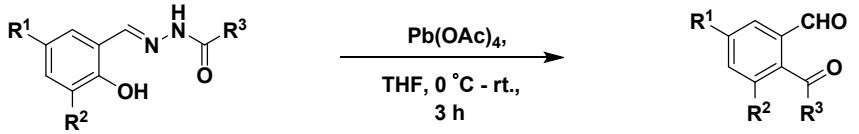


26c

aldehyde **24c** (60 mg, 0.33 mmol) and hydrazide **25c**[1a] (45 mg, 0.33 mmol) in ethanol (3 ml), were used to furnish the product **26c** (84 mg, 84%) as a light yellow solid; **IR** (neat): ν_{max}/cm$^-$ 3241, 3060, 1759, 1655, 1543, 1488, 1369, 1278, 1209, 1142; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 2.21 (s, 3H), 6.90 (d, *J* = 8.6 Hz, 1H), 7.01 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.34 (d, *J* = 2.7 Hz, 1H), 7.43 - 7.65 (m, 3H), 7.90 (d, *J* = 7.2 Hz, 2H), 8.60 (s, 1H), 11.04 (br. s., 1H), 12.09 (br. s., 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 20.8, 117.0, 119.4, 121.1, 124.7, 127.7, 128.5, 132.0, 132.8, 142.8, 146.4, 154.8, 162.9, 169.5; **HRMS:** m/z calcd for $C_{16}H_{15}N_2O_4$ [$(M+H)^+$]: 299.1032; Found: 299.1036.

B) General procedure for the Preparation of keto-aldehyde

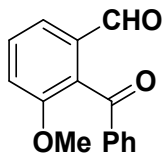
At room temperature, the appropriate hydrazone was dissolved in tetrahydrofuran (analytical grade). At 0°C, lead tetra acetate was gradually added to the solution. The resulting mixture was stirred during 3 - 4 h at rt. Progress of the reaction was monitored by the evolution of nitrogen. The solvent was removed under reduce pressure. Ethyl acetate was added to the residue. The suspension was filtered over celite. The organic layer was washed with a saturated solution of NaHCO3, with brine and dried over Na_2SO_4.The solvent was removed under vacuo and the residue was purified on a silica gel column using EtOAc-hexane as eluent to furnished product.



26d) R^1 = H, R^2 = OMe, R^3 = Ph
26e) R^1 = H, R^2 = H, R^3 = (*o*-Br)Ph
26f) R^1 = Cl, R^2 = H, R^3 = (*p*-OMe)Ph
26g) R^1 = Cl, R^2 = H, R^3 = (*p*-Br)Ph
26a) R^1 = H, R^2 = OMe, R^3 = (*p*-Br)Ph
26h) R^1 = H, R^2 = H, R^3 = 3,4 dichloro benzene
26b) R^1 = Cl, R^2 = H, R^3 = α- napthaline
26c) R^1 = OAc, R^2 = H, R^3 = Ph

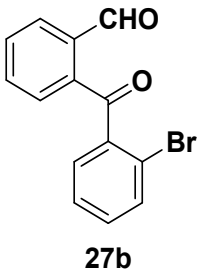
27a) R^1 = H, R^2 = OMe, R^3 = Ph
27b) R^1 = H, R^2 = H, R^3 = (*o*-Br)Ph
27c) R^1= Cl, R^2 = H, R^3 = (*p*-OMe)Ph
27d) R^1 = Cl, R^2= H, R^3 = (*p*-Br)Ph
27e) R^1 = H, R^2 = OMe,R^3 = (*p*-Br)Ph
27f) R^1 = H, R^2 = H, R^3 = 3,4 dichloro benzene
27g) R^1 = Cl, R^2 = H, R^3 = α- napthaline
27h) R^1 = OAc, R^2 = H, R^3 = Ph

Compound 27a: According to the general procedure **B** for the preparation of keto-aldehyde, compound **26d**[2a] (680 mg, 2.52 mmol) and $Pb(OAc)_4$ (1.67 gm, 3.78 mmol) in THF (15ml), were used to furnish the product **27a** (478 mg, 79%) as a light yellow solid. *Rf* = 0.33 (EtOAc-hexane 20:80); **IR** (neat): ν_{max}/cm^{-1} 3087, 2941, 1697, 1676, 1594, 1580, 1468, 1268, 953, 927 ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.76 (s, 3H), 7.26 (d, *J* = 9.2 Hz, 1H), 7.39 - 7.47 (m, 2H), 7.52 - 7.63 (m, 3H), 7.79 (d, *J* = 7.8 Hz, 2H), 9.87 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 56.2, 116.8, 123.0, 128.6, 129.0, 130.4, 130.7, 133.5, 135.3, 137.3, 157.0, 190.4, 195.8; **HRMS:** m/z calcd for $C_{15}H_{13}O_3$ $[(M+H)^+]$: 214.0865; Found: 241.0866.



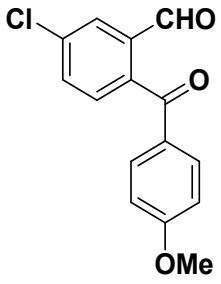
27a

Compound 27b: According to the general procedure **B** for the preparation of keto-aldehyde, compound **26e** (210 mg, 0.66 mmol) and $Pb(OAc)_4$ (439 mg, 0.99 mmol) in THF (15ml), were used to furnished the product **27b** (141 mg, 74%) as a light yellow solid. *Rf* = 0.29 (EtOAc-hexane 10:90); **IR** (neat): ν_{max}/cm^{-1} 3065, 1697, 1668, 1587, 1429, 1290, 1248, 1195, 1027, 930, 766, 739; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 - 7.49 (m, 4H), 7.57 - 7.61 (m, 1H), 7.64 - 7.70 (m, 2H), 8.00 (dd, *J* = 7.7, 1.3 Hz, 1H), 10.34 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 120.6, 127.4, 129.0, 130.7, 130.7, 132.4, 132.5, 132.8, 133.8, 136.9, 139.4, 139.9, 191.5, 196.3; **HRMS:** m/z calcd for $C_{14}H_{10}BrO_2$ $[(M+H)^+]$: 288.9864; Found: 288.9860.



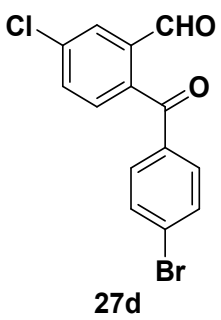
27b

Compound 27c: According to the general procedure **B** for the preparation of keto-aldehyde, compound[2b] **26f** (475 mg, 1.56 mmol) and $Pb(OAc)_4$ (1.03 gm, 2.34 mmol) in THF (15ml), were used to furnish the product **27c** (309 mg, 72%) as a light yellow solid. *Rf* = 0.33 (EtOAc-hexane 10:90); **IR** (neat): ν_{max}/cm^{-1} 3074, 1697, 1628, 1598, 1584, 1569, 1508, 1282, 1295, 1260, 1181, 1150, 1018; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.88 (s, 3H), 6.93 - 6.97 (m, *J* = 8.9 Hz, 2H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.59 - 7.65 (m, 1H), 7.76 - 7.80 (m, *J* = 9.2 Hz, 2H), 7.99 (s, 1H), 9.97 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 55.6, 114.1, 129.0, 129.8, 130.3, 132.5, 133.0, 136.7, 137.0, 140.1, 164.3, 189.2, 193.6; **HRMS:** m/z calcd for $C_{15}H_{12}ClO_3$ $[(M+H)^+]$: 275.0475; Found: 275.0475.



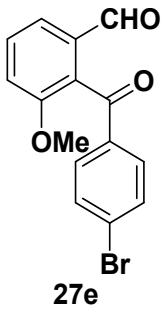
27c

Compound 27d: According to the general procedure **B** for the preparation of keto-aldehyde, compound[2c] **26g** (500 mg, 1.42 mmol) and $Pb(OAc)_4$ (944 mg, 2.13 mmol) in THF (15ml), were used to furnish the product **27d** (339 mg, 72%) as a yellow solid. *Rf* = 0.36 (EtOAc-hexane 10:90); **IR** (neat): ν_{max}/cm^{-1} 2967, 1697, 1668, 1459, 1270, 1187; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.1 Hz, 1H), 7.61 - 7.68 (m, 6H), 7.99 (t, *J* = 2.0 Hz, 1H), 9.97 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 129.3, 130.1, 130.4, 131.3, 132.1, 133.2, 135.5, 136.9, 137.6, 138.7, 189.1, 194.3; **HRMS:** m/z calcd for $C_{14}H_9BrClO_3$ $[(M+H)^+]$: 322.9474; Found: 322.9478.



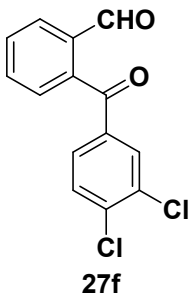
27d

Compound 27e: According to the general procedure **B** for the preparation of keto-aldehyde, compound **26a** (400 mg, 1.15 mmol) and $Pb(OAc)_4$ (763 mg, 1.72 mmol) in THF (15ml), were used to furnish the product **27e** (260 mg, 71%) as a light yellow solid. *Rf* = 0.29 (EtOAc-hexane 20:80); **IR** (neat): ν_{max}/cm^{-1} 3087, 2940, 1698, 1679, 1583, 1468, 1438, 1268, 1067, 924; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.76 (s, 3H), 7.26 (d, *J* = 8.3 Hz, 1H), 7.55 - 7.59 (m, 3H), 7.61 - 7.67 (m, 3H), 9.87 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 56.2, 116.9, 123.8, 128.6, 129.4, 130.4, 131.0, 131.9, 135.4, 136.1, 157.0, 190.4, 194.8; **HRMS:** m/z calcd for $C_{15}H_{12}BrO_3$ $[(M+H)^+]$: 318.9970; Found: 318.9970.



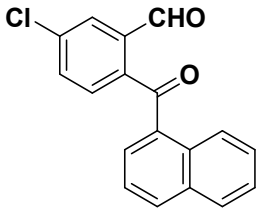
27e

Compound 27f: According to the general procedure **B** for the preparation of keto-aldehyde, compound[2d] **26h** (500 mg, 1.62 mmol) and Pb $(OAc)_4$ (1.08gm, 2.43 mmol) in THF (15 ml), were used to furnish the product **27f** (342 mg, 76%) as a light yellow solid. *Rf* = 0.3 (EtOAc-hexane 20:80); **IR** (neat): ν_{max}/cm^{-} 2969, 1712, 1665, 1488, 1285, 1250, 1054 ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 - 7.49 (m, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.57 - 7.62 (m, 1H), 7.70 - 7.78 (m, 2H), 7.84 (d, *J* = 1.9 Hz, 1H), 8.00 - 8.04 (m, 1H), 10.00 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 128.4, 128.5, 130.7, 130.9, 131.2, 131.5, 133.3, 133.7, 135.1, 136.5, 138.1, 139.7, 190.5, 194.4; **HRMS:** m/z calcd for $C_{15}H_{13}O_3$ $[(M+H)^+]$: 278.9980; Found: 278.9980.



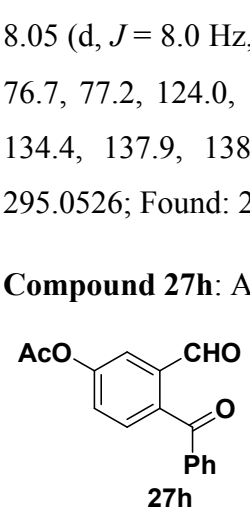
27f

Compound 27g: According to the general procedure **B** for the preparation of keto-aldehyde, compound **26b** (530 mg, 1.63 mmol) and $Pb(OAc)_4$ (1.08 gm, 2.44 mmol) in THF (15ml), were used to furnish the product **27g** (421 mg, 88%) as a colorless oil. *Rf* = 0.24 (EtOAc-hexane 20:80); **IR** (neat): ν_{max}/cm^{-1} 3068, 2888, 1692, 1650, 1583, 1559, 1509, 1280, 1240, 1188, 1088, 946, 780; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 - 7.46 (m, 1H), 7.47 - 7.50 (m, 1H), 7.54 - 7.60 (m, 3H), 7.63 (d, *J* = 6.9 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 1.7 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 8.69 (d, *J* = 8.6 Hz, 1H), 10.12 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 76.7, 77.2, 124.0, 125.6, 126.9, 128.5, 128.5, 129.0, 130.8, 131.5, 131.8, 132.7, 133.8, 133.9, 134.4, 137.9, 138.0, 140.6, 189.6, 196.6; **HRMS:** m/z calcd for $C_{18}H_{12}ClO_2$ $[(M+H)^+]$: 295.0526; Found: 295.0520.



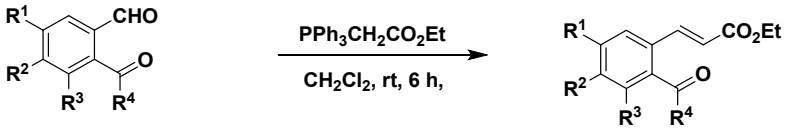
27g

Compound 27h: According to the general procedure **B** for the preparation of keto-aldehyde, compound **26c** (64 mg, 0.21 mmol) and Pb $(OAc)_4$ (142 mg, 0.32 mmol) in THF (5 ml), were used to furnish the product **27h** (49 mg, 85%) as a light yellow solid. *Rf* = 0.34 (EtOAc-hexane 20:80); **IR** (neat): ν_{max}/cm^{-} 2853, 1769, 1698, 1662, 1597, 1448, 1275, 1194; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 7.42 (dd, *J* = 8.0, 2.3 Hz, 1H), 7.47 - 7.51 (m, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.59 - 7.66 (m, 1H), 7.78 (d, *J* = 2.3 Hz, 1H), 7.80 - 7.87 (m, 2H), 10.03 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.1, 122.5, 126.2, 128.7, 130.1, 130.7, 133.8, 137.0, 137.4, 138.6, 152.4, 168.7, 189.5, 189.5, 195.4; **HRMS (EI):** m/z calcd for $C_{16}H_{12}O_4$ $[M]^+$: 268.0736; Found: 268.0722.



27h

C) **General procedure for the preparation of keto-ester**

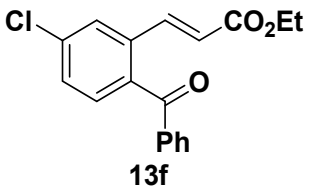


27j) R^1 = Cl, R^2 = H, R^3 = H, R^4 = Ph
27k) R^1 = H, R^2 = OMe, R^3 = H, R^4 = Ph
27a) R^1 = H, R^2 = H, R^3 = OMe, R^4 = Ph
27b) R^1 = H, R^2 = H, R^3 = H, R^4 = (o-Br)Ph
27c) R^1 = Cl, R^2 = H, R^3 = H, R^4 = (p-OMe)Ph
27d) R^1 = Cl, R^2 = H, R^3 = H, R^4 = (p-Br)Ph
27e) R^1 = H, R^2 = H, R^3 = OMe, R^4 = (p-Br)Ph
27f) R^1 = H, R^2 = H, R^3 = H, R^4 = 3,4 dichlorobenzene
27g) R^1 = Cl, R^2 = H, R^3 = H, R^4 = α- napthaline
27i) R^1 = H, R^2 = H, R^3 = H, R^4 = thiophene
27h) R^1 = OAc, R^2 = H, R^3 = H, R^4 = Ph

13f) R^1 = Cl, R^2 = H, R^3 = H, R^4 = Ph
13i) R^1 = H, R^2 = OMe, R^3 = H, R^4 = Ph
13j) R^1 = H, R^2 = H, R^3 = OMe, R^4 = Ph
13l) R^1 = H, R^2 = H, R^3 = H, R^4 = (o-Br)Ph
13n) R^1 = Cl, R^2 = H, R^3 = H, R^4 = (p-OMe)Ph
13o) R^1 = Cl, R^2 = H, R^3 = H, R^4 = (p-Br)Ph
13p) R^1 = H, R^2 = H, R^3 = OMe, R^4 = (p-Br)Ph
13q) R^1 = H, R^2 = H, R^3 = H, R^4 = 3,4 dichlorobenzene
13r) R^1 = Cl, R^2 = H, R^3 = H, R^4 = α- napthaline
13s) R^1 = H, R^2 = H, R^3 = H, R^4 = thiophene
15) R^1 = OAc, R^2 = H, R^3 = H, R^4 = Ph

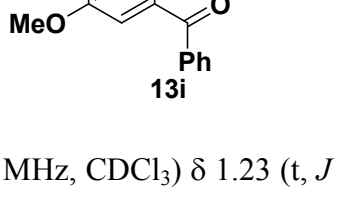
To a stirred solution of the aldehyde which was prepared according to reported literature procedure[3] in CH_2Cl_2 was added $Ph_3P{=}CHCO_2Et$ and the reaction mixture was stirred for 6 h at RT. Evaporation of the solvent under reduced pressure and the crude product was purified on silica gel column chromatography using EtOAc-hexane as an eluent to furnish the product.

Compound 13f: According to the general procedure **C** for wittig reaction, compound **27j**[3a] (193 mg, 0.77 mmol) and $Ph_3P{=}CHCO_2Et$ (821 mg, 2.4 mmol) in CH_2Cl_2 (15 ml), were used to furnish the product **13f** (215 mg, 89%) as a white solid. *Rf* = 0.20 (EtOAc-hexane 10:90); **IR** (neat): ν_{max}/cm^{-1} 2979, 1713, 1655, 1598, 1509, 1314, 1285, 1257, 1177, 1149, 1029, 933; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.25 (t, *J* = 7.2 Hz, 3H), 4.17 (q, *J* = 7.2 Hz, 2H), 6.36 (d, *J* = 15.7 Hz, 1H), 7.33 - 7.42 (m, 2H), 7.43 - 7.50 (m, 2H), 7.57 - 7.63 (m, 1H), 7.69 (dd, *J* = 8.7, 7.0 Hz, 2H), 7.73 - 7.81 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 14.1, 60.6, 122.1, 127.2, 128.6, 129.0, 130.2, 130.7, 133.7, 135.9, 137.0, 137.0, 137.3, 140.3, 165.8, 196.0; **HRMS:** m/z calcd for $C_{18}H_{16}ClO_3$ [$(M+H)^+$]: 315.0788; Found: 315.0784.



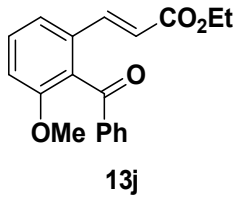
13f

Compound 13i: According to the procedure **C** for wittig reaction, compound **27k**[3b] (900 mg, 3.75 mmol) and $Ph_3P{=}CHCO_2Et$ (2.61 gm, 7.5 mmol) in CH_2Cl_2 (20 ml), were used to furnish the product **13i** (1.03 gm, 89%) as a white solid. *Rf* = 0.30 (EtOAc-hexane 20:80); **IR** (neat): ν_{max}/cm^{-1} 2979, 1712, 1665, 1638, 1574, 1469, 1261, 1183, 1033; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.23 (t, *J* = 7.2 Hz, 3H), 3.82 (s, 3H), 4.14 (q, *J* = 7.4 Hz, 2H), 6.26 (d, *J* = 15.5 Hz, 1H), 6.89 (d, *J* = 2.9 Hz, 1H), 7.04 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.40 - 7.50 (m, 2H), 7.52 - 7.66 (m, 2H), 7.68 (d, *J* = 9.2 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 14.2, 55.5, 60.3, 113.7, 116.6, 118.5, 125.9, 128.5, 128.6, 130.3, 133.6, 137.0, 141.0, 141.1, 160.2, 166.5, 196.9; **HRMS:** m/z calcd for $C_{19}H_{19}O_4$ [$(M+H)^+$]: 311.1283; Found: 311.1286.



13i

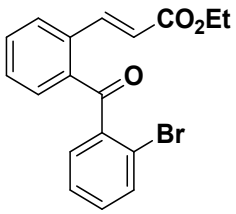
Compound 13j: According to the procedure **C** for wittig reaction, compound **27a** (110 mg, 0.46 mmol) and $Ph_3P{=}CHCO_2Et$ (479 mg, 1.37 mmol) in CH_2Cl_2 (15 ml), were used to furnish the product **13j** (122 mg, 86%) as a white solid. *Rf* = 0.40 (EtOAc-hexane 20:80); **IR** (neat): ν_{max}/cm^{-1} 2979, 1713, 1670, 1638, 1574, 1469, 1261, 1183, 1033; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.22 (t, *J* = 7.0 Hz,



13j

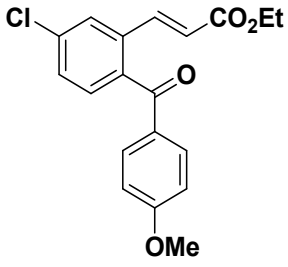
3H), 3.70 (s, 3H), 4.12 - 4.16 (m, 2H), 6.36 (d, *J* = 16.0 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.41 - 7.46 (m, 4H), 7.55 - 7.59 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 14.1, 55.8, 60.5, 112.2, 118.8, 121.3, 128.6, 129.5, 129.8, 130.4, 133.6, 133.6, 137.4, 140.6, 156.9, 166.2, 196.6; **HRMS:** m/z calcd for $C_{19}H_{19}O_4$ [$(M+H)^+$]: 311.1283; Found: 311.1286.

Compound 13l: According to the procedure **C** for wittig reaction, compound **27b** (100 mg, 0.35 mmol) and $Ph_3P{=}CHCO_2Et$ (363 mg, 1.04 mmol) in CH_2Cl_2 (10 ml), were used to furnish the product **13l** (113 mg, 90%) as a colourless oil. *Rf* = 0.33 (EtOAc-hexane 20:80); **IR** (neat): ν_{max}/cm^{-1} 2980, 1712, 1668, 1635, 1465, 1366, 1294, 1271, 1179, 1027; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.10 Hz, 3H), 4.24 (q, *J* = 7.2 Hz, 2H), 6.35 (d, *J* = 15.8 Hz, 1H), 7.31 - 7.43 (m, 5H), 7.53 - 7.58 (m, 1H), 7.66 (d, *J* = 7.3 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 1H), 8.15 (d, *J* = 16.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.2, 60.5, 120.4, 121.3, 127.3, 128.1, 129.1, 130.3, 131.3, 132.0, 132.4, 133.6, 136.0, 137.1, 140.6, 143.0, 166.3, 196.8; **HRMS:** m/z calcd for $C_{18}H_{16}BrO_3$ [$(M+H)^+$]: 359.0283; Found: 359.0282.



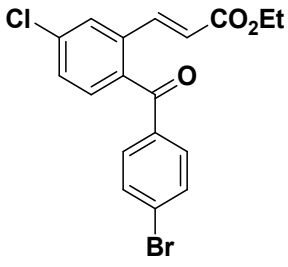
13l

Compound 13n: According to the procedure **C** for wittig reaction, compound **27c** (86 mg, 0.27 mmol) and $Ph_3P{=}CHCO_2Et$ (281 mg, 0.81 mmol) in CH_2Cl_2 (7 ml), were used to furnish the product **13n** (82 mg, 89%) as a white solid. *Rf* = 0.30 (EtOAc-hexane 20:80); **IR** (neat): ν_{max}/cm^{-1} 2979, 1714, 1655, 1598, 1508, 1421, 1314, 1285, 1257, 1177, 1149; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.25 (t, *J* = 7.2 Hz, 3H), 3.86 (s, 3H), 4.17 (q, *J* = 7.2 Hz, 2H), 6.36 (d, *J* = 15.9 Hz, 1H), 6.92 (d, *J* = 9.1 Hz, 2H), 7.30 - 7.46 (m, 2H), 7.55 - 7.70 (m, 2H), 7.75 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.1, 55.5, 60.6, 113.9, 121.9, 127.0, 129.0, 129.9, 130.2, 132.7, 135.4, 136.4, 138.1, 140.3, 164.1, 165.9, 194.6; **HRMS:** m/z calcd for $C_{19}H_{18}ClO_4$ [$(M+H)^+$]: 345.0894; Found: 345.0890.



13n

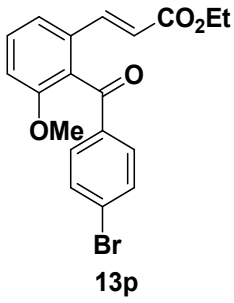
Compound 13o: According to the procedure **C** for wittig reaction, compound **27d** (278 mg, 0.87 mmol) and $Ph_3P{=}CHCO_2Et$ (904 mg, 2.60 mmol) in CH_2Cl_2 (10 ml), were used to furnish the product **13o** (290 mg, 85%) as a white solid. *Rf* = 0.20 (EtOAc-hexane 10:90); **IR** (neat): ν_{max}/cm^{-1} 2979, 1713, 1663, 1638, 1584, 1395, 1312, 1280, 1179, 931; **^{1}H NMR** (500 MHz, $CDCl_3$)



13o

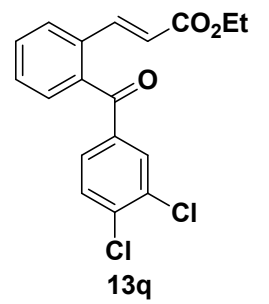
δ 1.27 (t, *J* = 7.2 Hz, 3H), 4.20 (q, *J* = 7.1 Hz, 2H), 6.37 (d, *J* = 16.0 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.42 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.57 - 7.68 (m, 5H), 7.70 (d, *J* = 2.0 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 14.2, 60.8, 122.4, 127.4, 129.1, 130.6, 131.6, 132.0, 135.8, 136.0, 136.8, 137.3, 140.1, 165.8, 195.0; **HRMS:** m/z calcd for $C_{18}H_{15}BrClO_3$ [$(M+H)^+$]: 392.9893; Found: 392.9897.

Compound 13p: According to the procedure **C** for wittig reaction, compound **27e** (130 mg, 0.41 mmol) and $Ph_3P{=}CHCO_2Et$ (428 mg, 1.23 mmol) in CH_2Cl_2 (10 ml), were used to furnish the product **13p** (140 mg, 88%) as a white solid. *Rf* = 0.30 (EtOAc-hexane 20:80); **IR** (neat): ν_{max}/cm^{-1} 2979, 1712, 1672, 1583, 1574, 1470, 1262, 1184, 1068; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.2 Hz, 3H), 3.70 (s, 3H), 4.15 (q, *J* = 7.2 Hz, 2H), 6.36 (d, *J* = 15.8 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.37 - 7.46 (m, 2H), 7.54 - 7.60 (m, *J* = 8.7 Hz, 2H), 7.62 - 7.68 (m, *J* = 8.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.2, 55.8, 60.6, 112.1, 118.9, 121.6, 129.0, 129.1, 130.7, 130.9, 132.0, 133.6, 136.2, 140.3, 156.8, 166.1, 195.6; **HRMS:** m/z calcd for $C_{19}H_{18}BrO_4$ [$(M+H)^+$]: 389.0388; Found: 389.0381.



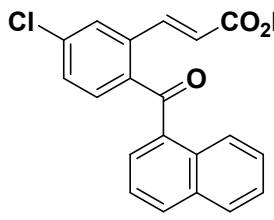
13p

Compound 13q: According to the procedure **C** for wittig reaction, compound **27f** (1.05 gm, 3.76 mmol) and $Ph_3P{=}CHCO_2Et$ (2.62 gm, 7.52 mmol) in CH_2Cl_2 (15 ml), were used to furnish the product **13q** (1.2 gm, 91%) as a white solid. *Rf* = 0.33 (EtOAc-hexane 20:80); **IR** (neat): ν_{max}/cm^{-1} 3078, 1714, 1663, 1636, 1578, 1556, 1461, 1386, 1314, 1242, 1184; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.27 (t, *J* = 7.2 Hz, 3H), 4.20 (q, *J* = 7.1 Hz, 2H), 6.37 (d, *J* = 15.9 Hz, 1H), 7.38 - 7.42 (m, 1H), 7.45 - 7.49 (m, 1H), 7.52 - 7.62 (m, 3H), 7.67 - 7.77 (m, 2H), 7.88 (d, *J* = 1.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.2, 60.6, 121.5, 127.5, 129.1, 129.3, 130.7, 131.3, 132.0, 133.3, 134.1, 136.9, 138.0, 138.2, 141.2, 166.1, 194.7; **HRMS:** m/z calcd for $C_{18}H_{18}Cl_2NO_3$ [$(M+NH_4)^+$]: 366.0664; Found: 366.0660.



13q

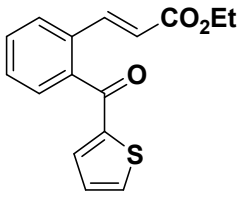
Compound 13r: According to the procedure **C** for wittig reaction, compound **27g** (294 mg, 0.83 mmol) and $Ph_3P{=}CHCO_2Et$ (866 mg, 2.49 mmol) in CH_2Cl_2 (15 ml), were used to furnish the product **13r** (284 mg, 94%) as a white solid. *Rf* = 0.40 (EtOAc-hexane 20:80); **IR** (neat): ν_{max}/cm^{-1} 3060, 3001, 2894,



13r

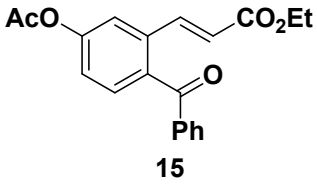
1699, 1650, 1509, 1475, 1296, 1281, 1039, 921; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.20 (t, *J* = 7.1 Hz, 3H), 4.14 (q, *J* = 7.1 Hz, 2H), 6.35 (d, *J* = 15.8 Hz, 1H), 7.31 - 7.42 (m, 2H), 7.42 - 7.47 (m, 1H), 7.52 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.58 (td, *J* = 7.6, 1.6 Hz, 2H), 7.68 (d, *J* = 2.1 Hz, 1H), 7.78 - 7.97 (m, 2H), 8.03 (d, *J* = 8.0 Hz, 1H), 8.40 - 8.58 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.1, 60.6, 76.3, 76.7, 77.3, 77.7, 122.2, 124.2, 125.6, 126.8, 127.7, 128.2, 128.5, 129.0, 130.9, 131.0, 132.2, 133.4, 133.9, 135.3, 137.1, 137.8, 138.3, 141.2, 165.9, 197.6; **HRMS:** m/z calcd for $C_{22}H_{18}ClO_3$ $[(M+H)^+]$: 365.0944; Found: 365.0941.

Compound 13s: According to the procedure **C** for wittig reaction, compound **27i**[3c] (215 mg, 1.0 mmol) and $Ph_3P{=}CHCO_2Et$ (1.04 gm, 3 mmol) in CH_2Cl_2 (10 ml), were used to furnish the product **13s** (268 mg, 94%) as a white solid. *Rf* = 0.26 (EtOAc-hexane 20:80); **IR** (neat): ν_{max}/cm^{-1} 1712, 1638, 1594, 1513, 1411, 1315, 1291, 1181, 1043, 977, 767, 727; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.25 (t, *J* = 7.2 Hz, 3H), 4.17 (q, *J* = 7.4 Hz, 2H), 6.38 (d, *J* = 16.04 Hz, 1H), 7.07 - 7.11 (m, 1H), 7.37 - 7.40 (m, 1H), 7.41 - 7.44 (m, 1H), 7.48 - 7.53 (m, 2H), 7.69 - 7.74 (m, 2H), 7.80 (d, *J* = 16.0 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 14.1, 60.4, 120.8, 127.1, 128.2, 128.6, 129.1, 130.7, 133.3, 135.5, 135.9, 139.0, 141.3, 144.2, 166.2, 188.8; **HRMS:** m/z calcd for $C_{16}H_{15}O_3S$ $[(M+H)^+]$: 287.0742; Found: 287.0745.



13s

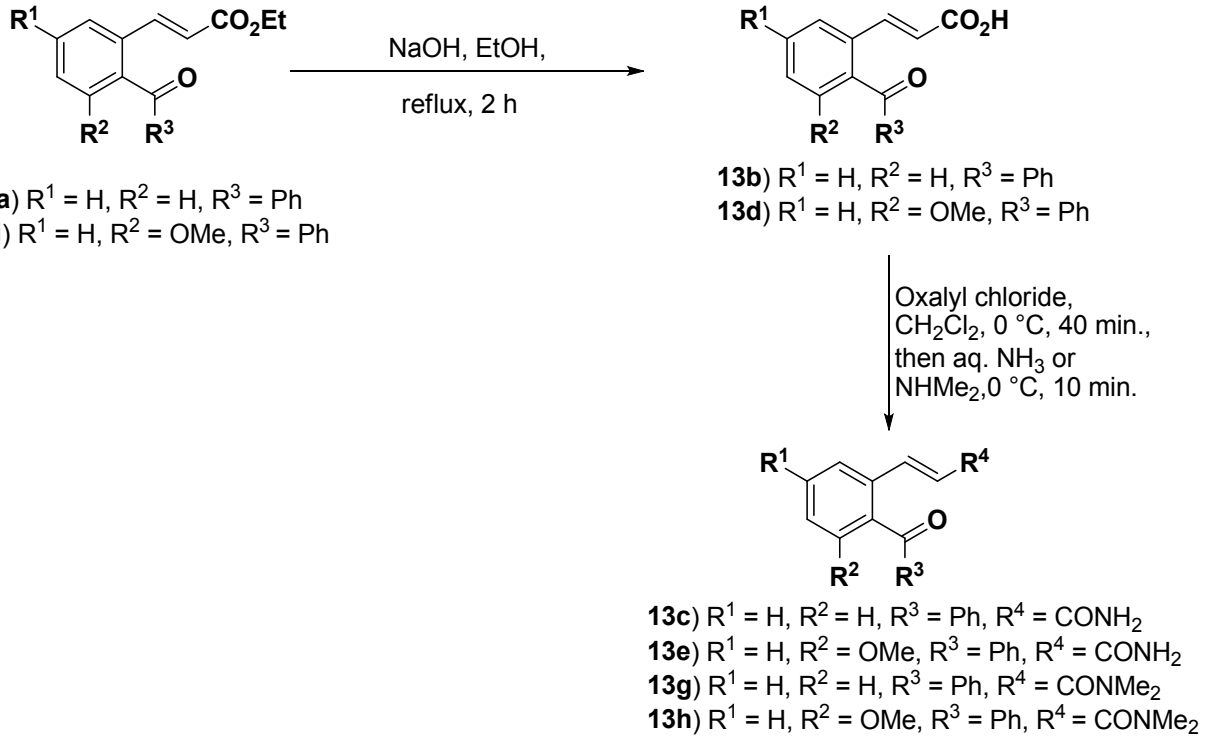
Compound 15: According to the procedure **C** for wittig reaction, compound **27h** (42 mg, 0.16 mmol) and $Ph_3P{=}CHCO_2Et$ (162 mg, 0.47 mmol) in CH_2Cl_2 (5 ml), were used to furnish the product **15** (48 mg, 90%) as a colourless oil. *Rf* = 0.4 (EtOAc-hexane 20:80); **IR** (neat): ν_{max}/cm^{-} 2925, 1769, 1713, 1661, 1638, 1368, 1316, 1266, 1195; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.26 (s, 3H), 2.35 (s, 3H), 4.18 (q, *J* = 7.2 Hz, 2H), 6.35 (d, *J* = 15.9 Hz, 1H), 7.17 - 7.21 (m, 1H), 7.44 - 7.51 (m, 4H), 7.57 - 7.63 (m, 1H), 7.75 (d, *J* = 15.9 Hz, 1H), 7.80 (dd, *J* = 8.4, 1.1 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.2, 21.1, 60.6, 120.3, 121.9, 122.2, 128.6, 130.4, 130.9, 133.6, 136.1, 136.6, 137.3, 140.9, 152.3, 166.0, 168.9, 196.2; **HRMS (EI):** m/z calcd for $C_{20}H_{18}O_5$ $[M]^+$: 338.1154; Found: 338.1145.



15

D) General procedure for the preparation of keto-acid and keto-amid.

Step 1: To a solution of keto-ester in EtOH was added NaOH (3eq. dissolve in water) at room temperature and reflux for 2h, the mixture was adjusted to pH 1.0 with1N HCl, and then extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo and crude acid was directly used for next step. **Step 2**: To a solution of acid in CH_2Cl_2 were added Dimethylformamide (DMF) (1 drop) and oxalyl chloride at 0°C under argon atmosphere. After 40 min. of stirring, the mixture was concentrated in vacuo to afford the crude acid chloride as yellow oil and crude product was employed directly in the following reaction. A solution of the crude acid chloride in $CH_2Cl_2$was poured into 28% aqueous NH_3solution or $NHMe_2$1M solution in THF at 0 °C under an argon atmosphere. After 10 min of stirring, the mixture was extracted with CH_2Cl_2, washed with brine, dried over Na_2SO_4, filtered and the solvent was removed under vacuo and the residue was purified on a silica gel column using EtOAc-hexane to furnish product.

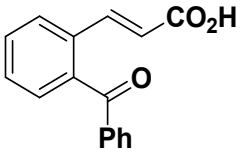


13a) R^1 = H, R^2 = H, R^3 = Ph
13j) R^1 = H, R^2 = OMe, R^3 = Ph

13b) R^1 = H, R^2 = H, R^3 = Ph
13d) R^1 = H, R^2 = OMe, R^3 = Ph

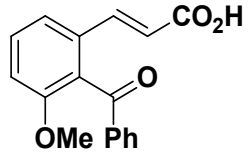
13c) R^1 = H, R^2 = H, R^3 = Ph, R^4 = $CONH_2$
13e) R^1 = H, R^2 = OMe, R^3 = Ph, R^4 = $CONH_2$
13g) R^1 = H, R^2 = H, R^3 = Ph, R^4 = $CONMe_2$
13h) R^1 = H, R^2 = OMe, R^3 = Ph, R^4 = $CONMe_2$

Compound 13b: According to the general procedure **D** (step-I[st]), compound **13a**[3d,e] (200 mg, 0.71 mmol) and NaOH (86 mg, 2.14 mmol), in ethanol (5ml) were used to furnish the product **13b** (125 mg, 70%) as a white solid. *Rf* = 0.40 (EtOAc-hexane 80:20); **IR** (neat): ν_{max}/cm^{-1} 3450, 3200, 2923, 1698, 1661, 1595, 1448, 1315, 1270, 928; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.38 (d, *J* = 15.9 Hz, 1H), 7.44 - 7.50 (m, 4H), 7.54 - 7.57 (m, 1H), 7.59 - 7.63 (m, 1H), 7.75 - 7.82 (m, 3H), 7.86 (d, *J* = 15.9 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 119.8, 127.4, 128.6, 129.3, 129.5, 130.4, 130.8, 133.6, 133.6, 137.2, 139.5, 144.1, 171.1, 197.1; **HRMS:** m/z calcd for $C_{16}H_{13}O_3$ [$(M+H)^+$]: 253.0865; Found: 253.0870.



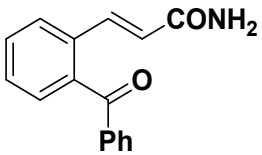
13b

Compound 13d: According to the general procedure **D** (step-I[st]), compound **13j** (279 mg, 0.90 mmol) and NaOH (108 mg, 2.70 mmol), in ethanol (5ml) were used to furnish the product **13d** (175 mg, 69%) as a light yellow solid. *Rf* = 0.46 (EtOAc-hexane 80:20); **IR** (neat): ν_{max}/cm^{-1} 3350, 2923, 1668, 1572, 1468, 1266, 1068; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.71 (s, 3H), 6.35 (d, *J* = 15.9 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.44 (td, *J* = 7.8, 4.0 Hz, 3H), 7.51 (d, *J* = 15.3 Hz, 1H), 7.56 - 7.60 (m, 1H), 7.79 (d, *J* = 7.3 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 55.9, 112.6, 119.0, 120.1, 128.7, 129.5, 130.0, 130.5, 133.8, 137.3, 143.0, 156.9, 170.4, 196.5; **HRMS:** m/z calcd for $C_{17}H_{15}O_4$ [$(M+H)^+$]: 283.0970; Found: 283.0977.



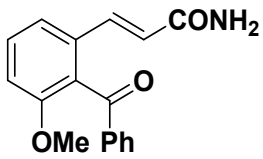
13d

Compound 13c: According to the general procedure **D** (step 2[nd]), crude acid **13b** (98 mg, 0.39 mmol) in CH_2Cl_2 (5 ml), Dimethylformamide (DMF) (1 drop) and oxalyl chloride (0.1 ml, 1.17 mmol), then 5 ml 28% aqueous NH_3 solution afforded product **13g** (68 mg, 70%) as a yellow solid. *Rf* = 0.40 (EtOAc-hexane 70:30); **IR** (neat): ν_{max}/cm^{-1} 3348, 3135, 1663, 1611, 1448, 1390, 1272; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.99 (br. s., 2H), 6.39 (d, *J* = 15.9 Hz, 1H), 7.36 - 7.47 (m, 4H), 7.50 (td, *J* = 7.02, 2.44 Hz, 1H), 7.55 - 7.65 (m, 2H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.74 - 7.82 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 122.9, 127.4, 128.5, 128.8, 129.1, 130.3, 130.7, 133.6, 134.1, 137.1, 139.1, 139.1, 167.6, 197.5; **HRMS:** m/z calcd for $C_{16}H_{13}NO_2$ [$(M+H)^+$]: 252.1025; Found: 252.1025.



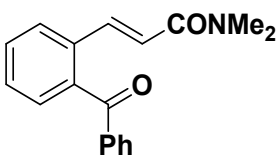
13c

Compound 13e: According to the general procedure **D** (step 2nd), crude acid **13d** (125 mg, 0.44 mmol) in CH_2Cl_2 (5 ml), Dimethylformamide (DMF) (1 drop) and oxalyl chloride (0.14 ml, 1.33 mmol), then 10 ml 28% aqueous NH_3 solution afforded product **13e** (90 mg, 73%) as a white solid. *Rf* = 0.25 (EtOAc-hexane 50:50); **IR** (neat): ν_{max}/cm^{-1} 3400, 3331, 3185, 2926, 1666, 1633, 1576, 1469, 1386, 1269, 1068; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.70 (s, 3H), 5.71 (br. s., 1H), 6.36 (d, *J* = 14.7 Hz, 1H), 6.99 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 14.7 Hz, 1H), 7.42 (t, *J* = 7.3 Hz, 3H), 7.55 - 7.59 (m, 1H), 7.78 (d, *J* = 7.3 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 55.9, 111.9, 119.3, 123.1, 128.7, 129.4, 129.5, 130.4, 132.0, 133.7, 133.8, 137.2, 138.4, 156.9, 167.3, 197.0; **HRMS:** m/z calcd for $C_{17}H_{16}NO_3$ [$(M+H)^+$]: 282.1130; Found: 282.1136.



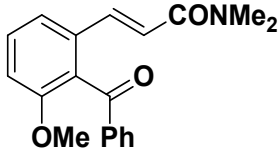
13e

Compound 13g: According to the general procedure **D** (step 2nd), crude acid **13b** (115 mg, 0.46 mmol) in CH_2Cl_2 (5 ml), Dimethylformamide (DMF) (1 drop) and oxalyl chloride (0.12 ml, 1.37 mmol), then 5 ml $NHMe_2$ (1M solution in THF), afforded product **13g** (90 mg, 70%) as a yellow solid. *Rf* = 0.20 (EtOAc-hexane 50:50); **IR** (neat): ν_{max}/cm^{-1} 3454, 3060, 2926, 1653, 1611, 1596, 1579, 1491, 1395, 1278, 1141, 973, 928 ; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.70 (s, 3 H), 5.71 (br. s., 1H), 6.36 (d, *J* = 14.66 Hz, 1H), 6.99 (d, *J* = 7.94 Hz, 1H), 7.35 (d, *J* = 14.66 Hz, 1H), 7.42 (t, *J* = 7.33 Hz, 3H), 7.54 - 7.58 (m, 1H), 7.78 (d, *J* = 7.33 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 36.0, 37.4, 121.2, 127.7, 128.4, 128.5, 128.6, 130.2, 130.3, 133.5, 134.6, 137.0, 139.1, 139.2, 166.3, 197.6; **HRMS:** m/z calcd for $C_{18}H_{18}NO_2$ [$(M+H)^+$]: 280.1338; Found: 280.1339.

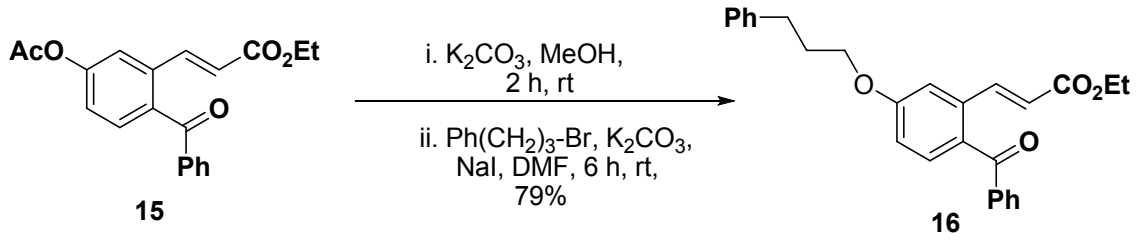


13g

Compound 13h: According to the general procedure **D** (step 2nd), crude acid **13d** (118 mg, 0.42 mmol) in CH_2Cl_2 (5 ml), Dimethylformamide (DMF) (1 drop) and oxalyl chloride (0.11 ml, 1.26 mmol), then 5 ml $NHMe_2$ (1M solution in THF), afforded product **13h** (93 mg, 72%) as a white solid. *Rf* = 0.24 (EtOAc-hexane 50:50); **IR** (neat): ν_{max}/cm^{-1} 3454, 3063, 2934, 1667, 1653, 1609, 1596, 1573, 1469, 1365, 1259, 1144, 1068, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.95 (s, 6H), 3.70 (s, 3H), 6.70 (d, *J* = 15.6 Hz, 1H), 6.96 (d, *J* = 8.5 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.30 - 7.46 (m, 4H), 7.51 - 7.57 (m, 1H), 7.72 - 7.86 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 36.4, 55.9, 111.5, 119.8, 121.6, 128.6, 129.1, 129.5, 130.2, 133.6, 134.6, 137.2, 138.4, 156.9, 166.1, 197.0; **HRMS:** m/z calcd for $C_{19}H_{20}NO_3$ [$(M+H)^+$]: 310.1443; Found: 310.1441.

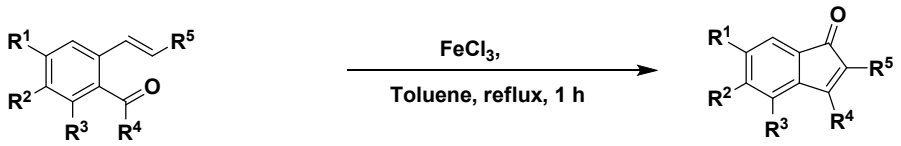


13h



Compound 16: **Step 1**- Compound **15** (40 mg, 0.12 mmol) was dissolved in methanol (2 ml) and added K_2CO_3 (25 mg, 0.18 mmol) at room temperature and stirred resultant reaction mixture for 2 h. Then reaction was quenched with water and extracted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered and the solvent was removed under vacuo and this hydrolysed product was used for next step without further purification. **Step 2** - Crude ester, K_2CO_3 (49 mg, 0.36 mmol) and NaI (5.4 mg, 0.036 mmol) was dissolved in DMF and bromide (71 mg, 0.36 mmol) was added in reaction mixture. After 6 h reaction was quenched with water and extracted with diethyl ether, washed with brine, dried over Na_2SO_4, filtered and the solvent was removed under vacuo pressure and the crude product was purified on silica gel column chromatography using EtOAc-hexane as an eluent to furnish the product **16** (39 mg, 79%) as a colourless oil. *Rf* = 0.3 (EtOAc-hexane 20:80); **IR** (neat): ν_{max}/cm^{-} 2925, 1769, 1713, 1661, 1638, 1596, 1570, 1316, 1266, 1195; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.25 - 1.30 (m, 3H), 2.10 - 2.20 (m, 2H), 2.83 (t, *J* = 7.5 Hz, 2H), 4.04 (t, *J* = 6.3 Hz, 2H), 4.19 (q, *J* = 6.9 Hz, 2H), 6.32 (d, *J* = 15.9 Hz, 1H), 6.90 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.17 (d, *J* = 2.27 Hz, 1H), 7.18 - 7.24 (m, 3H), 7.26 - 7.34 (m, 2H), 7.39 - 7.47 (m, 3H), 7.53 - 7.60 (m, 1H), 7.76 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.87 (d, *J* = 15.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.2, 30.6, 32.0, 60.5, 67.2, 113.1, 114.8, 121.0, 126.1, 128.4, 128.5, 130.2, 131.4, 132.4, 132.9, 137.1, 138.2, 141.1, 142.5, 161.1, 166.3, 196.4; **LCMS:** m/z calcd for $C_{27}H_{26}O_4$ $[M]^+$: 338.1145; Found: 338.1145.

E) General procedure for the cyclisation reaction

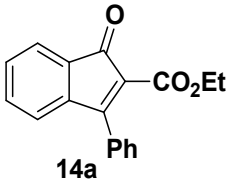


13a) R^1 = H, R^2 = H, R^3 = H, R^4 = Ph, R^5 = CO_2Et
13b) R^1 = H, R^2 = H, R^3 = H, R^4 = Ph, R^5 = CO_2H
13c) R^1 = H, R^2 = H, R^3 = H, R^4 = Ph, R^5 = $CONH_2$
13d) R^1 = H, R^2 = H, R^3 = OMe, R^4 = Ph, R^5 = CO_2H
13e) R^1 = H, R^2 = H, R^3 = OMe, R^4 = Ph, R^5 = $CONH_2$
13f) R^1 = Cl, R^2 = H, R^3 = H, R^4 = Ph, R^5 = CO_2Et
13g) R^1 = H, R^2 = H, R^3 = H, R^4 = Ph, R^5 = $CONMe_2$
13h) R^1 = H, R^2 = H, R^3 = OMe, R^4 = Ph, R^5 = $CONMe_2$
13i) R^1 = H, R^2 = OMe, R^3 = H, R^4 = Ph, R^5 = CO_2Et
13j) R^1 = H, R^2 = H, R^3 = OMe, R^4 = Ph, R^5 = CO_2Et
13k) R^1 = H, R^2 = H, R^3 = H, R^4 = (p-Br)Ph, R^5 =CO_2Et
13l) R^1 = H, R^2 = H, R^3 = H, R^4 = (o-Br)Ph, R^5 = CO_2Et
13m) R^1 = H, R^2 = H, R^3 = H, R^4 = (p-OMe)Ph, R^5 = CO_2Et
13n) R^1 = Cl, R^2 = H, R^3 = H, R^4 = (p-OMe)Ph, R^5 = CO_2Et
13o) R^1 = Cl, R^2 = H, R^3 = H, R^4 = (p-Br)Ph, R^5 = CO_2Et
13p) R^1 = H, R^2 = H, R^3 = OMe, R^4 = (p-OMe)Ph, R^5 = CO_2Et
13q) R^1 = H, R^2 = H, R^3 = H, R^4 = 3,4-dichlorophenyl, R^5 = CO_2Et
13r) R^1 = Cl, R^2 = H, R^3 = H, R^4 = α- napthaline, R^5 = CO_2Et
13s) R^1 = H, R^2 = H, R^3 = H, R^4 = thiophene, R^5 = CO_2Et
16) R^1 = -$O(CH_2)_3Ph$, R^2 = H, R^3 = H, R^4 = Ph, R^5 = CO_2Et

14a) R^1 = H, R^2 = H, R^3 = H, R^4 = Ph, R^5 = CO_2Et
14b) R^1 = H, R^2 = H, R^3 = H, R^4 = Ph, R^5 = CO_2H
14c) R^1 = H, R^2 = H, R^3 = H, R^4 = Ph, R^5 = $CONH_2$
14d) R^1 = H, R^2 = H, R^3 = OMe, R^4 = Ph, R^5 = CO_2H
14e) R^1 = H, R^2 = H, R^3 = OMe, R^4 = Ph, R^5 = $CONH_2$
14f) R^1 = Cl, R^2 = H, R^3 = H, R^4 = Ph, R^5 = CO_2Et
14g) R^1 = H, R^2 = H, R^3 = H, R^4 = Ph, R^5 = $CONMe_2$
14h) R^1 = H, R^2 = H, R^3 = OMe, R^4 = Ph, R^5 = $CONMe_2$
14i) R^1 = H, R^2 = OMe, R^3 = H, R^4 = Ph, R^5 = CO_2Et
14j) R^1 = H, R^2 = H, R^3 = OMe, R^4 = Ph, R^5 = CO_2Et
14k) R^1 = H, R^2 = H, R^3 = H, R^4 = (p-Br)Ph, R^5 =CO_2Et
14l) R^1 = H, R^2 = H, R^3 = H, R^4 = (o-Br)Ph, R^5 = CO_2Et
14m) R^1 = H, R^2 = H, R^3 = H, R^4 = (p-OMe)Ph, R^5 = CO_2Et
14n) R^1 = Cl, R^2 = H, R^3 = H, R^4 = (p-OMe)Ph, R^5 = CO_2Et
14o) R^1 = Cl, R^2 = H, R^3 = H, R^4 = (p-Br)Ph, R^5 = CO_2Et
14p) R^1 = H, R^2 = H, R^3 = OMe, R^4 = (p-OMe)Ph, R^5 = CO_2Et
14q) R^1 = H, R^2 = H, R^3 = H, R^4 = 3,4-dichlorophenyl, R^5 = CO_2Et
14r) R^1 = Cl, R^2 = H, R^3 = H, R^4 = α- napthaline, R^5 = CO_2Et
14s) R^1 = H, R^2 = H, R^3 = H, R^4 = thiophene, R^5 = CO_2Et
7) R^1 = -$O(CH_2)_3Ph$, R^2 = H, R^3 = H, R^4 = Ph, R^5 = CO_2Et

Under argon atmosphere to a magnetically stirred solution of keto-ester/amide/acid, in toluene was added $FeCl_3$ (2 eqv.) and refluxed for 1 h. When completion of the reaction was noticed by TLC, the reaction mixture was allow to come room temperature and added saturated solution of $NaHCO_3$ and reaction mixture filtered through a sintered funnel. The reaction mixture was then extracted with ethyl acetate. The combined organic extract was washed with brine and dried over Na_2SO_4. Evaporation of solvent and purification of residue on a silica gel column using EtOAc-hexane as eluent, afforded cyclised product.

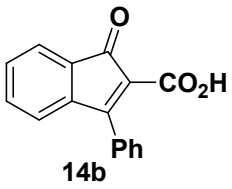
Compound 14a: According to the general procedure **E** for cyclization reaction, compound **13a**[3d]



14a

(30 mg, 0.11 mmol) and $FeCl_3$ (36 mg, 0.22 mmol), in toluene (5 ml) were used to furnished the product **14a** (26 mg, 87%) as a yellow semisolid. *Rf* = 0.29 (EtOAc-hexane 10:90); **IR** (neat): ν_{max}/cm^{-1} 2917, 1731, 1711, 1450, 1456, 1340, 1226, 1050; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.17 (t, *J* = 7.1 Hz, 3H), 4.21 (q, *J* = 7.3 Hz, 2H), 7.17 - 7.22 (m, 1H), 7.39 - 7.44 (m, 2H), 7.46 - 7.57 (m, 5H), 7.59 - 7.63 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 13.9, 60.9, 123.4, 123.4, 124.4, 128.1, 128.4, 130.4, 130.5, 131.0, 131.5, 133.5, 143.1, 163.0, 164.9, 192.1; **HRMS:** m/z calcd for $C_{18}H_{15}O_3$ [$(M+H)^+$]: 279.1021; Found: 279.1029.

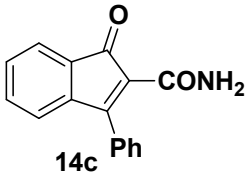
Compound 14b: According to the general procedure **E** for cyclization reaction, compound **13b**



14b

(30 mg, 0.12 mmol) and $FeCl_3$ (39 mg, 0.24 mmol), in toluene (5 ml) were used to furnish the product **14b** (21 mg, 71%) as a red solid. *Rf* = 0.44 (EtOAc); **IR** (neat): ν_{max}/cm^{-1} 3061, 2924, 1716, 1683, 1563, 1458, 1396, 1363, 1333, 1133; **^{1}H NMR** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.4 Hz, 1H), 7.46 - 7.52 (m, 2H), 7.53 - 7.60 (m, 3H), 7.67 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 118.4, 124.4, 125.4, 128.3, 129.1, 130.0, 130.1, 131.8, 132.3, 134.9, 143.4, 161.2, 172.0, 198.2; **HRMS:** m/z calcd for $C_{16}H_9O_2$ [$(M+H- H_2O)^+$]: 233.0603; Found: 233.0603.

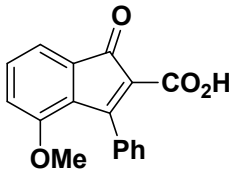
Compound 14c: According to the general procedure **E** for cyclization reaction, compound **13c**



14c

(40 mg, 0.16 mmol) and $FeCl_3$ (52 mg, 0.32 mmol), in toluene (5 ml) were used to furnish the product **14c** (30 mg, 76%) as a red solid. *Rf* = 0.33 (EtOAc-hexane 70:30); **IR** (neat): ν_{max}/cm^{-1} 3416, 3330, 2923, 2851, 1699, 1672, 1592, 1457, 1361, 1291, 1193; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.60 (br. s., 1H), 7.15 (dd, *J* = 5.8, 2.1 Hz, 1H), 7.36 - 7.47 (m, 2H), 7.51 (m, 3H), 7.54 - 7.63 (m, 3H), 7.78 (br. s., 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 122.3, 123.5, 124.0, 128.0, 128.6, 130.3, 130.5, 131.3, 131.4, 134.1, 143.7, 162.8, 169.0, 196.4; **HRMS:** m/z calcd for $C_{16}H_{11}NO_2Na$ [$(M+Na)^+$]: 272.0687; Found: 272.0686.

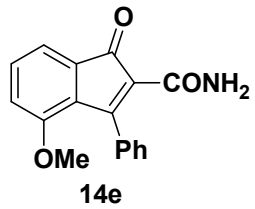
Compound 14d: According to the general procedure **E** for cyclization reaction, compound **13d**



14d

(42 mg, 0.15 mmol) and $FeCl_3$ (49 mg, 0.30 mmol), in toluene (5 ml) were used to furnish the product **14d** (30 mg, 72%) as a red semisolid. *Rf* = 0.29 (EtOAc-hexane 50:50); **IR** (neat): ν_{max}/cm^{-1} 3422, 2924, 2853, 1719, 1598, 1486, 1463, 1269, 1044; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.61 (br. s., 3H), 7.05 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 6.3 Hz, 1H), 7.45 (br. s., 4H), 7.51 (br. s., 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 55.7, 117.1, 118.3, 120.7, 124.5, 127.1, 127.2, 127.9, 130.4, 131.8, 132.5, 135.0, 156.5, 161.3, 174.7, 197.7; **HRMS:** m/z calcd for $C_{17}H_{13}O_4$ [$(M+H)^+$]: 281.0814; Found: 281.0820.

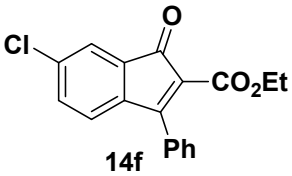
Compound 14e: According to the general procedure **E** for cyclization reaction, compound **13e**



14e

(34 mg, 0.12 mmol) and $FeCl_3$ (39 mg, 0.24 mmol), in toluene (5 ml) were used to furnish the product **14e** (26 mg, 74%) as a yellow solid. *Rf* = 0.30 (EtOAc-hexane 50:50); **IR** (neat): ν_{max}/cm^{-1} 3380, 3149, 1694, 1672, 1550, 1477, 1365, 1294, 1270, 1138; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.56 (s, 3H), 5.76 (br. s., 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 7.23 (d, *J* = 6.8 Hz, 1H), 7.38 - 7.50 (m, 6H), 7.77 (br. s., 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 55.6, 116.4, 120.0, 122.1, 127.1, 127.3, 129.2, 132.2, 133.9, 134.1, 155.8, 162.9, 171.4, 178.0, 196.1; **HRMS:** m/z calcd for $C_{17}H_{13}NNaO_3$ $[(M+Na)^+]$: 302.0793; Found: 302.0790.

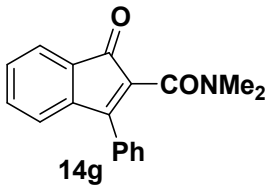
Compound 14f: According to the general procedure **E** for cyclization reaction, compound **13f**



14f

(42 mg, 0.13 mmol) and $FeCl_3$ (42 mg, 0.26 mmol), in toluene (5 ml) were used to furnish the product **14f** (39 mg, 93%) as a yellow solid. *Rf* = 0.29 (EtOAc-hexane 10:90); **IR** (neat): ν_{max}/cm^{-1} 2977, 2931, 1734, 1716, 1602, 1562, 1417, 1339, 1216, 1129, 1029; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.17 (t, *J* = 7.02 Hz, 3H), 4.20 (q, *J* = 6.9 Hz, 2H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.39 (dd, *J* = 7.9, 2.0 Hz, 1H), 7.52 (s, 5H), 7.56 (d, *J* = 2.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13.9, 61.0, 124.0, 124.4, 128.0, 128.5, 130.7, 131.1, 132.1, 132.9, 137.4, 141.2, 162.6, 164.7, 190.7; **HRMS:** m/z calcd for $C_{18}H_{14}ClO_3$ $[(M+H)^+]$: 313.0631; Found: 313.0637.

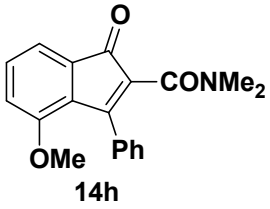
Compound 14g: According to the general procedure **E** for cyclization reaction, compound



14g

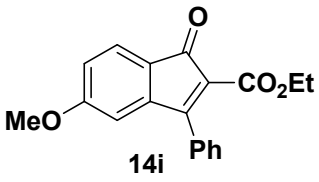
13g[3d,e] (36 mg, 0.13 mmol) and $FeCl_3$ (42 mg, 0.26 mmol), in toluene (5 ml) were used to furnish the product **14g** (27 mg, 76%) as a yellow semisolid. *Rf* = 0.40 (EtOAc-hexane 50:50); **IR** (neat): ν_{max}/cm^{-1} 2926, 1707 1633, 1585, 1500, 1456, 1414, 1397, 1315, 1196, 1102; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.77 (s, 3H), 3.00 (s, 3H), 7.29 - 7.36 (m, 2H), 7.39 - 7.43 (m, 1H), 7.47 - 7.53 (m, 3H), 7.58 (d, *J* = 6.7 Hz, 1H), 7.62 (dd, *J* = 4.0, 2.6 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 34.5, 37.8, 122.4, 123.5, 127.7, 129.0, 129.8, 129.9, 130.6, 130.7, 131.6, 133.4, 143.5, 157.1, 164.7, 193.3; **HRMS:** m/z calcd for $C_{18}H_{15}NNaO_2$ $[(M+Na)^+]$: 300.1000; Found: 300.1004.]

Compound 14h: According to the general procedure **E** for cyclization reaction, compound **13h** (36 mg, 0.13 mmol) and $FeCl_3$ (42 mg, 0.26 mmol), in toluene (5 ml) were used to furnish the product **14h** (31 mg, 74%) as a brown semisolid. *Rf* = 0.40 (EtOAc-hexane 50:50); **IR** (neat): ν_{max}/cm^{-1} 2923, 2850, 1704, 1633, 1609, 1479, 1272, 1115, 1050; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.67 (s, 3H), 2.91 (s, 3H), 3.65 (s, 3H), 7.01 (d, *J* = 8.5 Hz, 1H), 7.21 - 7.24 (m, 1H), 7.29 - 7.33 (m, 1H), 7.37 - 7.42 (m, 3H), 7.52 - 7.56 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 29.7, 34.4, 37.7, 55.6, 116.4, 119.5, 127.6, 127.9, 128.1, 129.8, 130.1, 132.1, 132.8, 133.4, 154.6, 159.1, 164.7, 193.2; **HRMS:** m/z calcd for $C_{19}H_{17}NO_3$ [$(M-H)^+$]: 307.1208; Found: 307.1208.



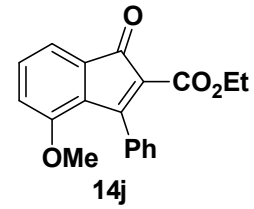
14h

Compound 14i: According to the general procedure **E** for cyclization reaction, compound **13i** (30 mg, 0.96 mmol) and $FeCl_3$ (31 mg, 0.19 mmol), in toluene (5 ml) were used to furnish the product **14i** (24 mg, 80%) as a red solid. *Rf* = 0.30 (EtOAc-hexane 20:80); **IR** (neat): ν_{max}/cm^{-1} 1730, 1705, 1614, 1479, 1244, 1129; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.16 (t, *J* = 7.2 Hz, 3H), 3.83 (s, 3H), 4.20 (q, *J* = 6.9 Hz, 2H), 6.73 (s, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 7.50 (s, 5H), 7.57 (d, *J* = 8.0 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 13.9, 55.8, 60.9, 112.3, 112.5, 123.1, 125.4, 125.9, 128.1, 128.4, 130.3, 131.4, 145.8, 162.5, 163.1, 164.4, 190.7; **HRMS:** m/z calcd for $C_{19}H_{16}O_4Na$ [$(M+Na)^+$]: 331.0946; Found: 331.0943.



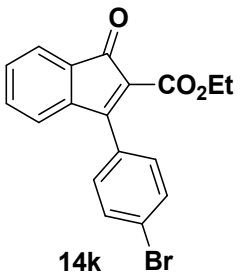
14i

Compound 14j: According to the general procedure **E** for cyclization reaction, compound **13j** (32 mg, 0.10 mmol) and $FeCl_3$ (33 mg, 0.20 mmol), in toluene (5 ml) were used to furnish the product **14j** (27 mg, 85%) as a red solid. *Rf* = 0.30 (EtOAc-hexane 20:80); **IR** (neat): ν_{max}/cm^{-1} 1730, 1705, 1608, 1479, 1336, 1274, 1274, 1223, 1129, 1049; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.06 (t, *J* = 7.2 Hz, 3H), 3.59 (s, 3H), 4.11 (q, *J* = 7.2 Hz, 2H), 6.98 (d, *J* = 8.6 Hz, 1H), 7.24 (dd, *J* = 7.2, 0.9 Hz, 1H), 7.32 - 7.40 (m, 2H), 7.40 - 7.45 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 13.8, 29.7, 55.5, 60.6, 116.3, 119.1, 124.5, 127.3, 127.4, 127.6, 129.3, 132.4, 133.5, 134.1, 155.4, 163.0, 167.1, 192.1; **HRMS:** m/z calcd for $C_{19}H_{16}O_4Na$ [$(M+Na)^+$]: 331.0946; Found: 331.0943.



14j

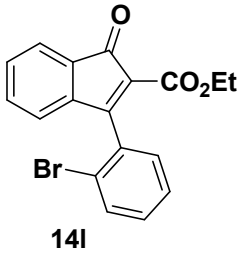
Compound 14k: According to the general procedure **E** for cyclization reaction, compound **13k**[3e]



14k

(50 mg, 0.14 mmol) and $FeCl_3$ (46 mg, 0.28 mmol), in toluene (5 ml) were used to furnish the product **14k** (42 mg, 84%) as a yellow solid. *Rf* = 0.30 (EtOAc-hexane 20:80); **IR** (neat): ν_{max}/cm^{-1} 2926, 1734, 1715, 1588, 1487, 1456, 1369, 1337, 1226, 1010; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.21 (t, *J* = 7.1 Hz, 3H), 4.22 (q, *J* = 7.3 Hz, 2H), 7.11 - 7.18 (m, 1H), 7.36 - 7.50 (m, 4H), 7.58 - 7.63 (m, 1H), 7.63 - 7.71 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.0, 61.1, 123.2, 123.6, 124.4, 124.9, 129.7, 130.3, 131.3, 131.7, 133.6, 142.7, 162.8, 163.9, 191.8; **HRMS:** m/z calcd for $C_{18}H_{13}BrNaO_3$ [$(M+Na)^+$]: 378.9940; Found: 378.9940.

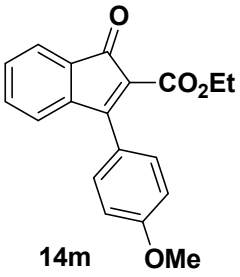
Compound 14l: According to the general procedure **E** for cyclization reaction, compound **13l**



14l

(36 mg, 0.1 mmol) and $FeCl_3$ (33 mg, 0.2 mmol), in toluene (5 ml) were used to furnish the product **14l** (30 mg, 84%) as a brown solid. *Rf* = 0.34 (EtOAc-hexane 20:80); **IR** (neat): ν_{max}/cm^{-1} 2977, 1735, 1698, 1588, 1368, 1338, 1229, 1113, 1018, 753; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.06 (t, *J* = 7.1 Hz, 3 H), 4.09 - 4.18 (m, 2H), 6.90 (dd, *J* = 5.8, 2.4 Hz, 1H), 7.27 - 7.36 (m, 2H), 7.37 - 7.47 (m, 3H), 7.61 (dd, *J* = 5.6, 2.6 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13.7, 60.7, 121.0, 123.5, 124.7, 127.2, 128.6, 129.9, 130.6, 131.4, 132.9, 133.8, 133.9, 142.8, 161.8, 166.3, 191.8; **HRMS:** m/z calcd for $C_{18}H_{14}O_3Br$ [$(M+H)^+$]: 357.0126; Found: 357.0121.

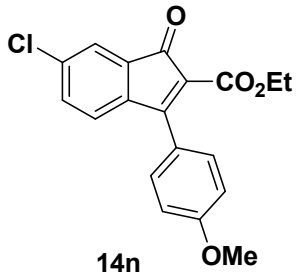
Compound 14m: According to the general procedure **E** for cyclization reaction, compound



14m

13m[3e] (40 mg, 0.13 mmol) and $FeCl_3$ (42 mg, 0.26 mmol), in toluene (5 ml) were used to furnish the product **14m** (33 mg, 83%) as a yellow semisolid. *Rf* = 0.20 (EtOAc-hexane 10:90); **IR** (neat): ν_{max}/cm^{-1} 2932, 1731, 1712, 1604, 1509, 1420, 1368, 1335, 1223, 1256, 1178, 1026; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.22 - 1.26 (m, 3H), 3.90 (s, 3H), 4.24 (q, *J* = 7.1 Hz, 2H), 6.97 - 7.10 (m, 2H), 7.28 (d, *J* = 2.1 Hz, 1H), 7.37 - 7.45 (m, 2H), 7.51 - 7.58 (m, 2H), 7.58 - 7.63 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.2, 55.5, 61.0, 114.0, 123.4, 123.5, 123.8, 125.4, 130.4, 131.0, 131.0, 133.4, 143.2, 161.8, 163.6, 164.7, 192.3; **HRMS:** m/z calcd for $C_{19}H_{17}O_4$ [$(M+H)^+$]: 309.1127; Found: 309.1121.

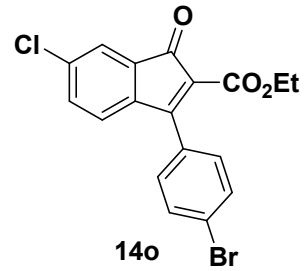
Compound 14n: According to the general procedure **E** for cyclization reaction, compound **13n**



14n

(35mg, 0.1 mmol) and $FeCl_3$ (33 mg, 0.2 mmol), in toluene (5 ml) were used to furnish the product **14n** (30 mg, 87%) as a yellow solid. *Rf* = 0.33 (EtOAc-hexane 20:80); **IR** (neat): ν_{max}/cm^{-1} 2933, 1732, 1714, 1604, 1509, 1419, 1341, 1257, 1220, 1178, 1127, 1026; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.23 (t, *J* = 7.2 Hz, 3H), 3.90 (s, 3H), 4.24 (q, *J* = 7.2 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.39 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.48 - 7.60 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 14.1, 55.5, 61.0, 114.0, 123.2, 123.3, 123.8, 124.4, 130.3, 132.4, 132.6, 137.3, 141.1, 161.9, 163.1, 164.4, 179.3, 190.8; **HRMS:** m/z calcd for $C_{19}H_{15}ClO_4Na$ [$(M+Na)^+$]: 365.0557; Found: 365.0555.

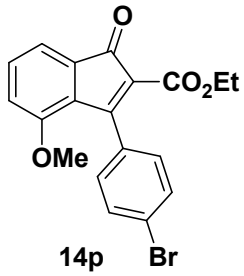
Compound 14o: According to the general procedure **E** for cyclization reaction, compound **13o**



14o

(50 mg, 0.13 mmol) and $FeCl_3$ (42 mg, 0.26 mmol), in toluene (5 ml) were used to furnish the product **14o** (45 mg, 90%) as a yellow solid. *Rf* = 0.30 (EtOAc-hexane 10:90); **IR** (neat): ν_{max}/cm^{-1} 2923, 1731, 1687, 1588, 1486, 1419, 1396, 1236, 1126, 1026; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.20 (t, *J* = 7.2 Hz, 3H), 4.20 (d, *J* = 7.2 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 1H), 7.36 - 7.40 (m, 4 H), 7.55 (d, *J* = 1.8 Hz, 1H), 7.65 (d, *J* = 8.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.0, 61.2, 124.1, 124.2, 124.4, 125.2, 129.7, 129.9, 131.8, 133.0, 137.7, 140.7, 162.4, 163.7, 190.4; **HRMS:** m/z calcd for $C_{18}H_{13}BrClO_3$ [$(M+H)^+$]: 390.9737; Found: 390.9730.

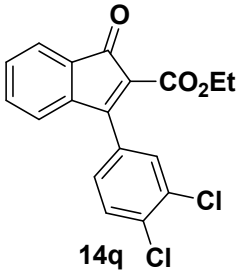
Compound 14p: According to the general procedure **E** for cyclization reaction, compound **13p**



14p

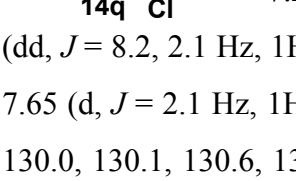
(30 mg, 0.08 mmol) and $FeCl_3$ (26 mg, 0.16 mmol), in toluene (5 ml) were used to furnish the product **14p** (25 mg, 84%) as a yellow solid. *Rf* = 0.25 (EtOAc-hexane 20:80); **IR** (neat): ν_{max}/cm^{-1} 2923, 1731, 1715, 1608, 1480, 1335, 1276, 1223, 1335, 1130, 1049 ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.12 (t, *J* = 7.10 Hz, 3H), 3.62 (s, 3H), 4.13 (q, *J* = 7.2 Hz, 2H), 6.99 (d, *J* = 7.8 Hz, 1H), 7.24 (m, 1H), 7.29 - 7.34 (m, 2H), 7.38 (dd, *J* = 8.5, 7.1 Hz, 1H), 7.51 - 7.57 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13.9, 55.5, 60.8, 116.4, 119.0, 120.5, 123.5, 124.5, 127.2, 129.3, 130.5, 132.2, 132.9, 133.7, 155.3, 165.9, 191.8; **HRMS:** m/z calcd for $C_{19}H_{15}BrNaO_4$ [$(M+Na)^+$]: 409.0051; Found: 409.0056.

Compound 14q: According to the general procedure **E** for cyclization reaction, compound **13q** (60 mg, 0.17 mmol) and $FeCl_3$ (56 mg, 0.34 mmol), in toluene (5 ml) were used to furnish the product **14q** (51 mg, 85%) as a white solid. *Rf* = 0.3 (EtOAc-hexane 5:95); **IR** (neat): ν_{max}/cm^{-1} 3084, 2987, 1733, 1686, 1571, 1461, 1371, 1338, 1230, 1113; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.23 (t, *J* = 7.2 Hz, 3H), 4.24 (q, *J* = 7.1 Hz, 2H), 7.14 (dt, *J* = 6.1, 1.1 Hz, 1H), 7.38 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.42 - 7.47 (m, 2H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.62 (d, *J* = 5.7 Hz, 1H), 7.65 (d, *J* = 2.1 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 14.0, 61.2, 123.1, 123.8, 124.8, 127.5, 130.0, 130.1, 130.6, 131.2, 131.5, 133.0, 133.8, 134.6, 142.5, 162.3, 162.4, 191.5; **HRMS:** m/z calcd for $C_{19}H_{16}O_4Na$ [$(M+Na)^+$]: 347.0242; Found: 347.0241.



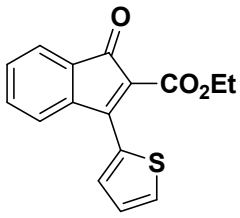
14q

Compound 14r: According to the general procedure **E** for cyclization reaction, compound **13r** (100 mg, 0.27 mmol) and $FeCl_3$ (88 mg, 0.54 mmol), in toluene (5 ml) were used to furnish the product **14r** (93 mg, 93%) as a yellow solid. *Rf* = 0.40 (EtOAc-hexane 20:80); **IR** (neat): ν_{max}/cm^{-1} 3066, 2979, 1734, 1692, 1556, 1418, 1367, 1340, 1262, 1130, 801, 778; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 0.76 (t, *J* = 7.2 Hz, 3H), 3.94 (dd, *J* = 7.4, 3.4 Hz, 2H), 6.80 (d, *J* = 8.0 Hz, 1H), 7.30 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.44 - 7.47 (m, 1H), 7.48 - 7.51 (m, 1H), 7.52 - 7.56 (m, 1H), 7.56 - 7.64 (m, 2H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13.4, 60.6, 76.8, 77.3, 123.9, 124.7, 124.9, 125.1, 125.1, 125.7, 126.5, 126.8, 128.6, 129.5, 130.1, 130.2, 131.7, 133.1, 133.4, 137.6, 141.9, 161.9, 165.8, 190.6; **HRMS:** m/z calcd for $C_{22}H_{16}ClO_3$ [$(M+H)^+$]: 363.0788; Found: 363.0786.



14r

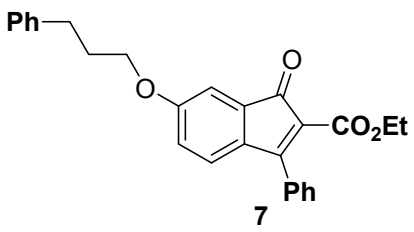
Compound 14s: According to the general procedure **E** for cyclization reaction, compound **13s** (53 mg, 0.18 mmol) and $FeCl_3$ (59 mg, 0.36 mmol), in toluene (5 ml) were used to furnish the product **14s** (44 mg, 83%) as a yellow solid. *Rf* = 0.24 (EtOAc-hexane 20:80); **IR** (neat): ν_{max}/cm^{-1} 2924, 2853, 1728, 1710, 1458, 1375, 1230, 1110, 1020, 909, 816; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.33 (t, *J* = 7.1 Hz, 3H), 4.35 (q, *J* = 7.1 Hz, 2H), 7.27 (s, 1H), 7.40 - 7.44 (m, 1H), 7.48 (td, *J* = 7.4, 1.4 Hz, 1H), 7.62 (dd, *J* = 6.9, 0.9 Hz, 1H), 7.65 (d, *J* = 7.1 Hz, 1H), 7.71 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.78 (dd, *J* = 3.7, 1.1 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$)



14s

δ 14.1, 61.4, 76.7, 77.3, 123.4, 123.6, 128.0, 130.7, 130.8, 131.3, 132.2, 132.3, 133.3, 142.4, 154 .7, 163.8, 191.7; **HRMS:** m/z calcd for $C_{16}H_{13}O_3S[(M+H)^+]$: 285.0585; Found: 285.0582.

Compound 7: According to the general procedure **E** for cyclization reaction, compound **16** (25 mg, 0.06 mmol) and $FeCl_3$ (19 mg, 0.12 mmol), in toluene (5 ml) were used to furnish the product **7** (21 mg, 84%) as a dark red solid. *Rf* = 0.3 (EtOAc-hexane 20:80); **IR** (neat): ν_{max}/cm^{-1} 2925, 1731, 1772, 1611, 1442, 1342, 1285, 1221, 1113; **^{1}H NMR** (400 MHz, $CDCl_3$) 1.15 (t, *J* = 7.0 Hz, 3H), 2.12 (dd, *J* = 7.9, 7.0 Hz, 2H), 2.81 (t, *J* = 7.5 Hz, 2H), 4.01 (t, *J* = 6.3 Hz, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 6.81 (dd, *J* = 8.1, 2.3 Hz, 1H), 7.06 (d, *J* = 8.1 Hz, 1H), 7.16 - 7.24 (m, 4H), 7.26 - 7.35 (m, 2H), 7.46 - 7.57 (m, 5H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 13.9, 30.6, 32.0, 60.6, 67.6, 111.1, 117.4, 122.6, 124.9, 126.1, 128.0, 128.3, 128.5, 130.4, 131.9, 133.0, 134.5, 141.1, 162.3, 162.9, 167.2, 191.9; **HRMS (EI):** m/z calcd for $C_{27}H_{24}O_4$ $[M]^+$: 412.1675; Found: 412.1675.



7

Reference:

(1) (a) M. -C. Hung, J. -L. Liao, S. -A. Chen and S. -H. Chen, A. -C. Su, *J. Am. Chem. Soc.*, 2005, **127**, 14576; (b) A. Harikishore, M. L. Leow, M. Niang, S. Rajan, K. K. Pasunooti, P. R. Preiser, X. Liu and H. S. Yoon, *ACS Med. Chem. Lett.* 2013, **4**, 1097.

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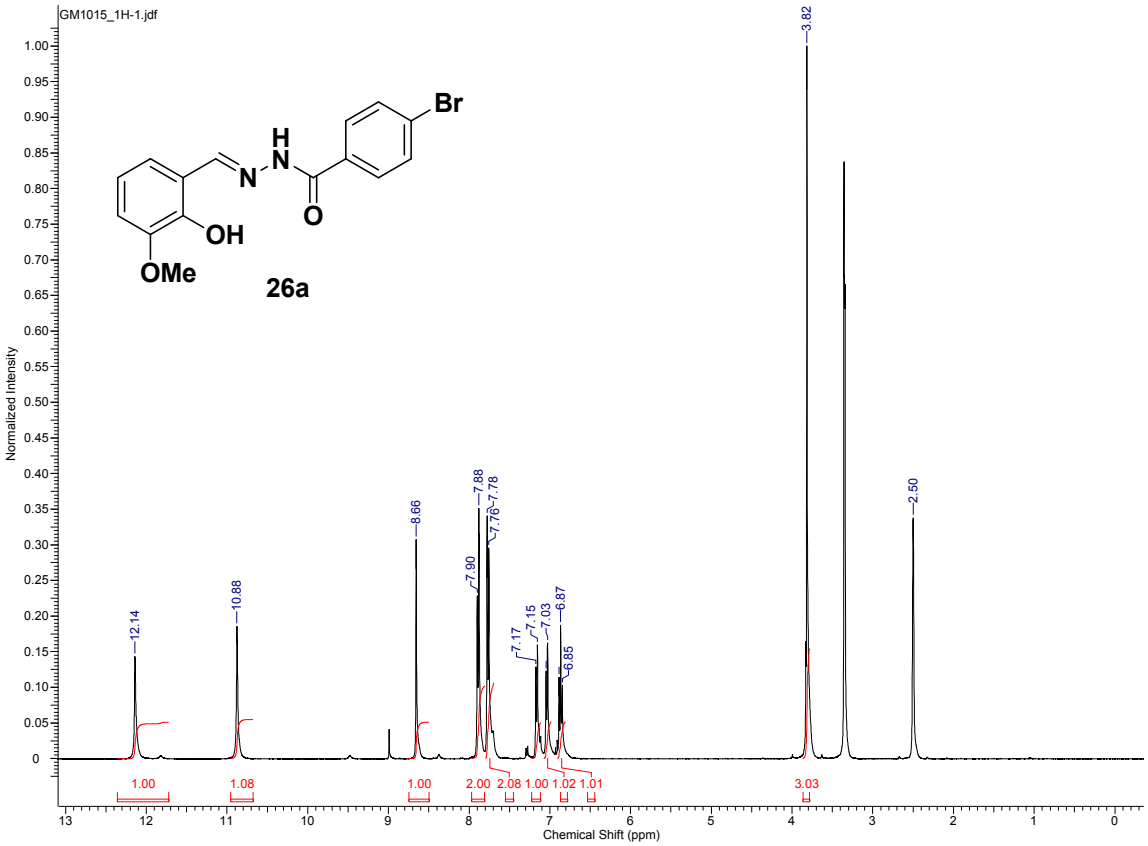
(3) (a) J. Jacq, *Sel. Org. React Database (SORD)* 2009, 20140701; (b) J. Jacq, C. Einhorn and J. Einhorn, *Org. Lett.* 2008, **17**, 3757; (c) D. Li, G. Qiann and Z. Y. Wang, *Polymer* 2013, **54,** 5543; (d) D. H. Dethe and G. Murhade *Org. Lett.* 2013, **15**, 429; (e) D. H. Dethe and G. M. Murhade *Chem. Commun.* 2013, **49**, 8051.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H
N
N
O
OH
OMe
26a
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Chemical Shift (ppm)
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10.88
8.66
7.90
7.88
7.78
7.76
7.17
7.15
7.03
6.87
6.85
3.82
2.50
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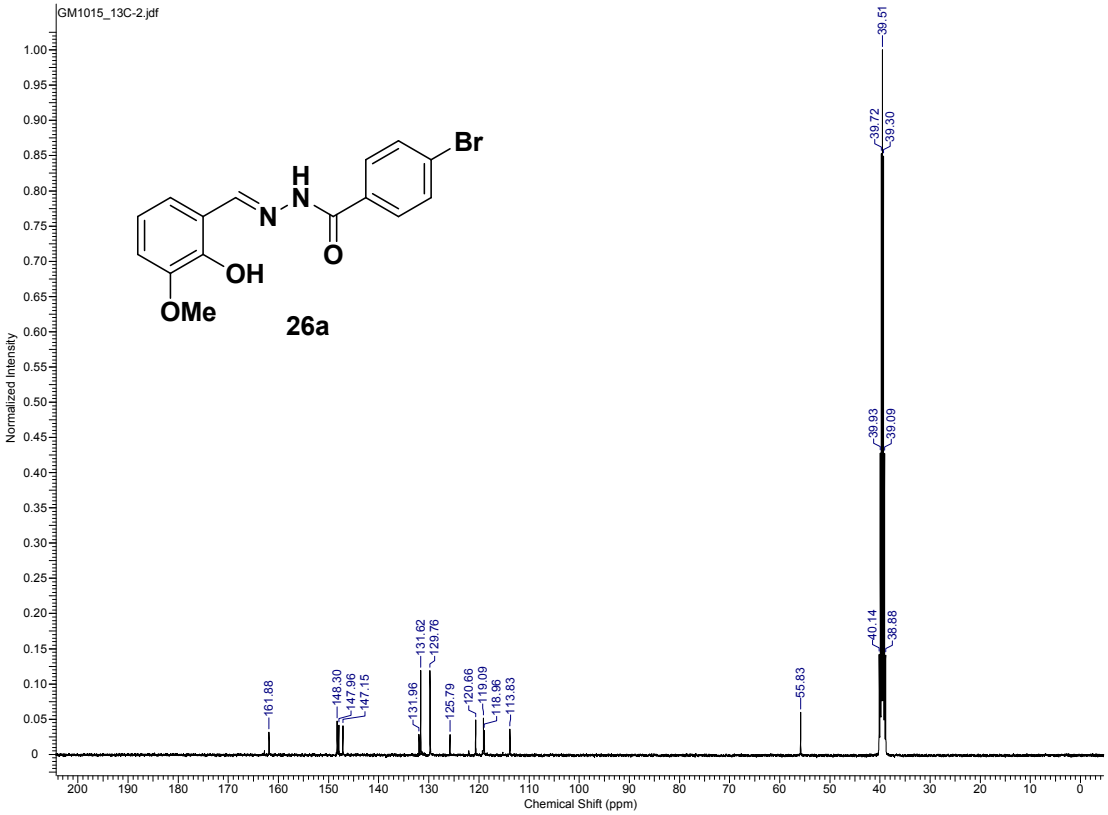
1.08
1.00
2.00
2.08
1.00
1.02
1.01
3.03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Br
H
N
N
O
OH
OMe
26a
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147.96
147.15
131.96
131.62
129.76
125.79
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40.14
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39.72
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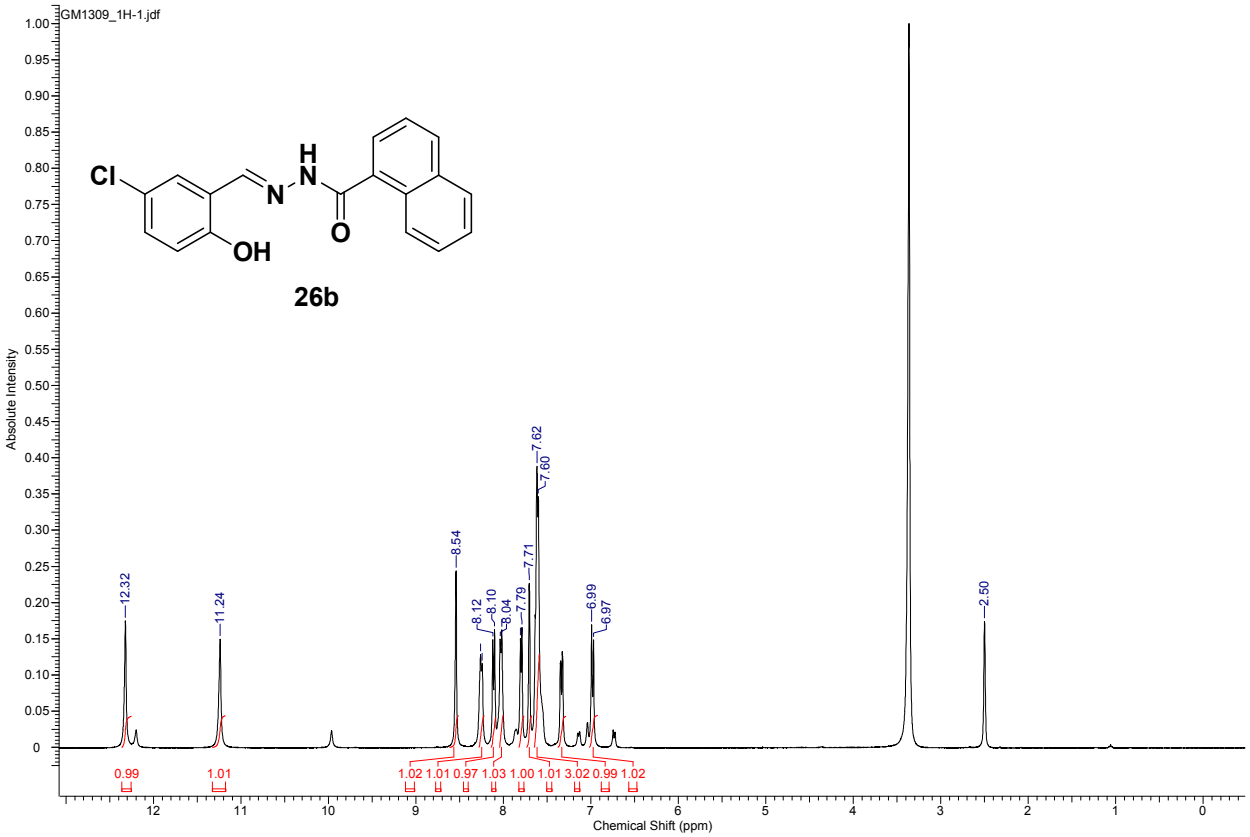
39.30
39.09
38.88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H
N
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8.12
8.10
8.04
7.79
7.71
7.62
7.60
6.99
6.97
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1.02
1.01
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1.00
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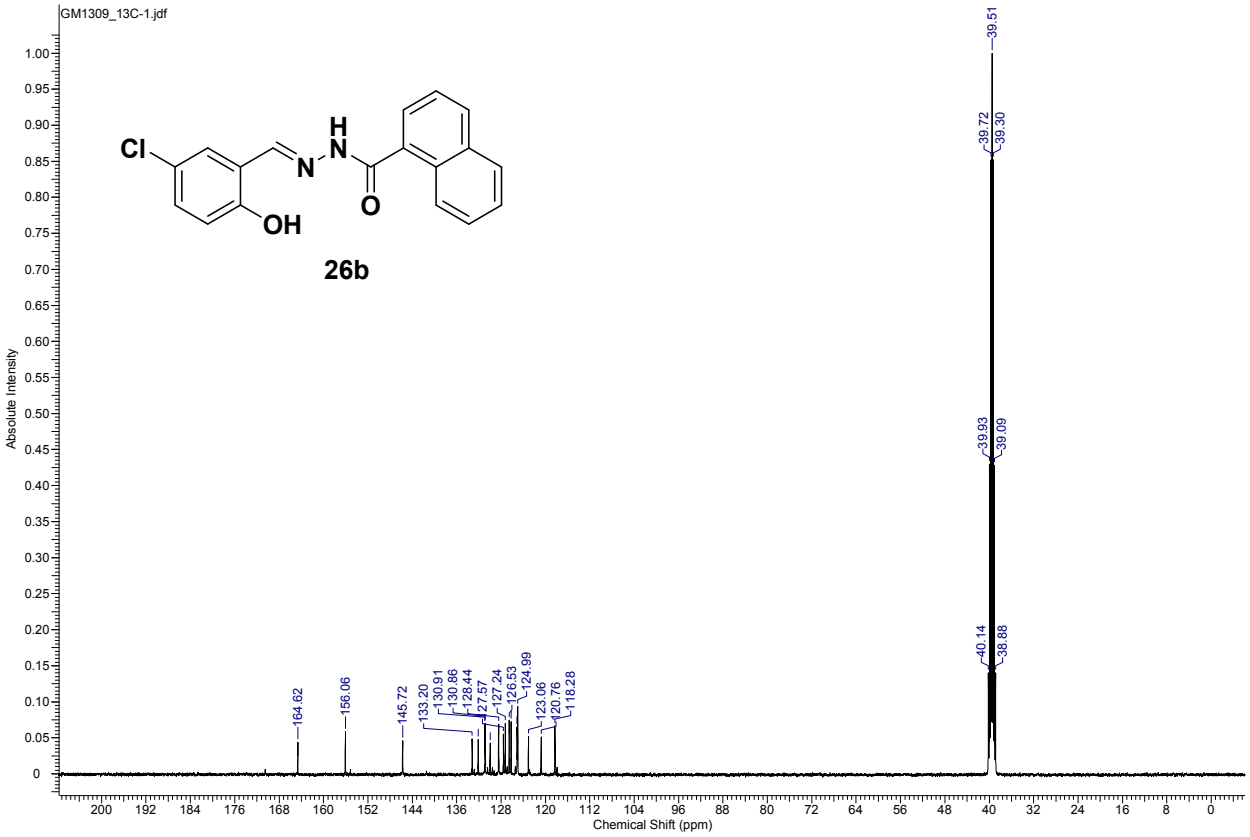
1.02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H
N
O
26b
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145.72
133.20
130.91
130.86
128.44
127.57
127.24
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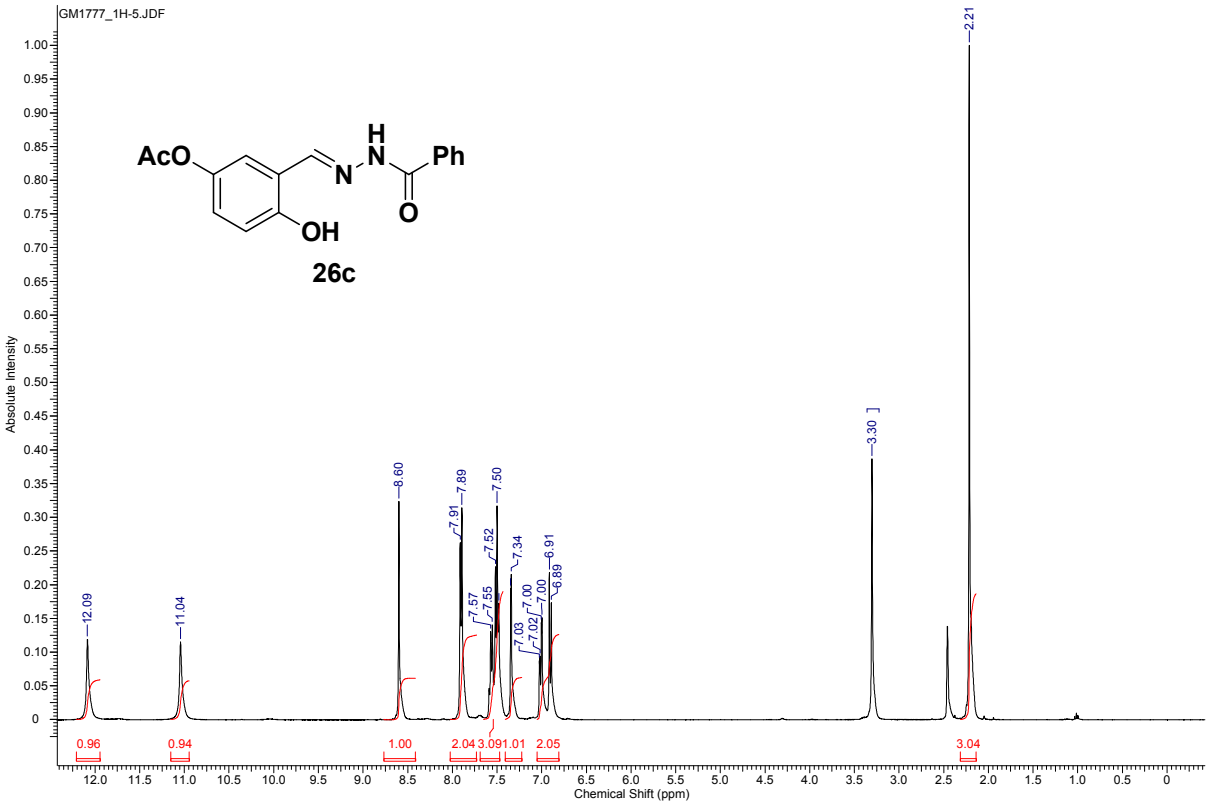
39.72
39.51
39.30
39.09
38.88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N
Ph
O
OH
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Chemical Shift (ppm)
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7.89
7.57
7.55
7.52
7.50
7.34
7.03
7.02
7.00
7.00
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1.00
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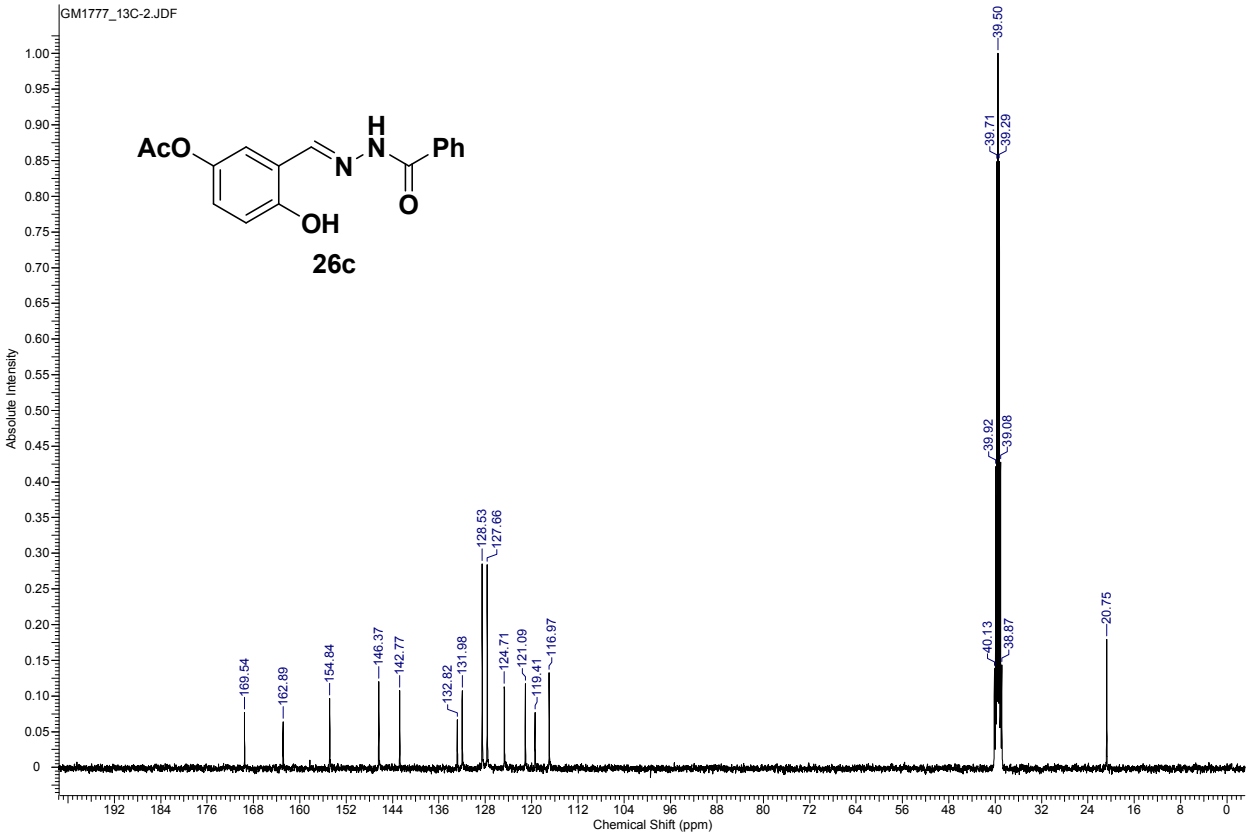
3.04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N
Ph
O
OH
26c
Absolute Intensity
Chemical Shift (ppm)
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142.77
132.82
131.98
128.53
127.66
124.71
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119.41
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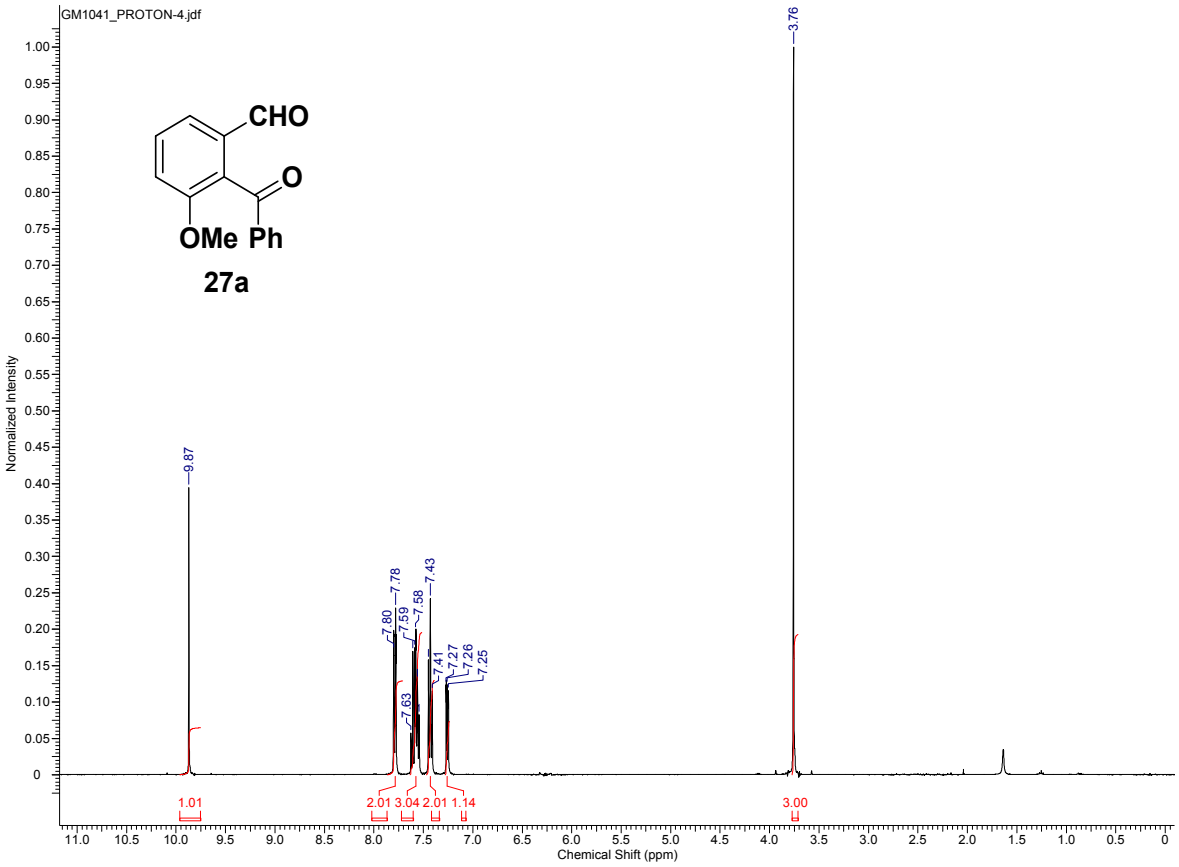
39.29
39.92
39.08
40.13
38.87
20.75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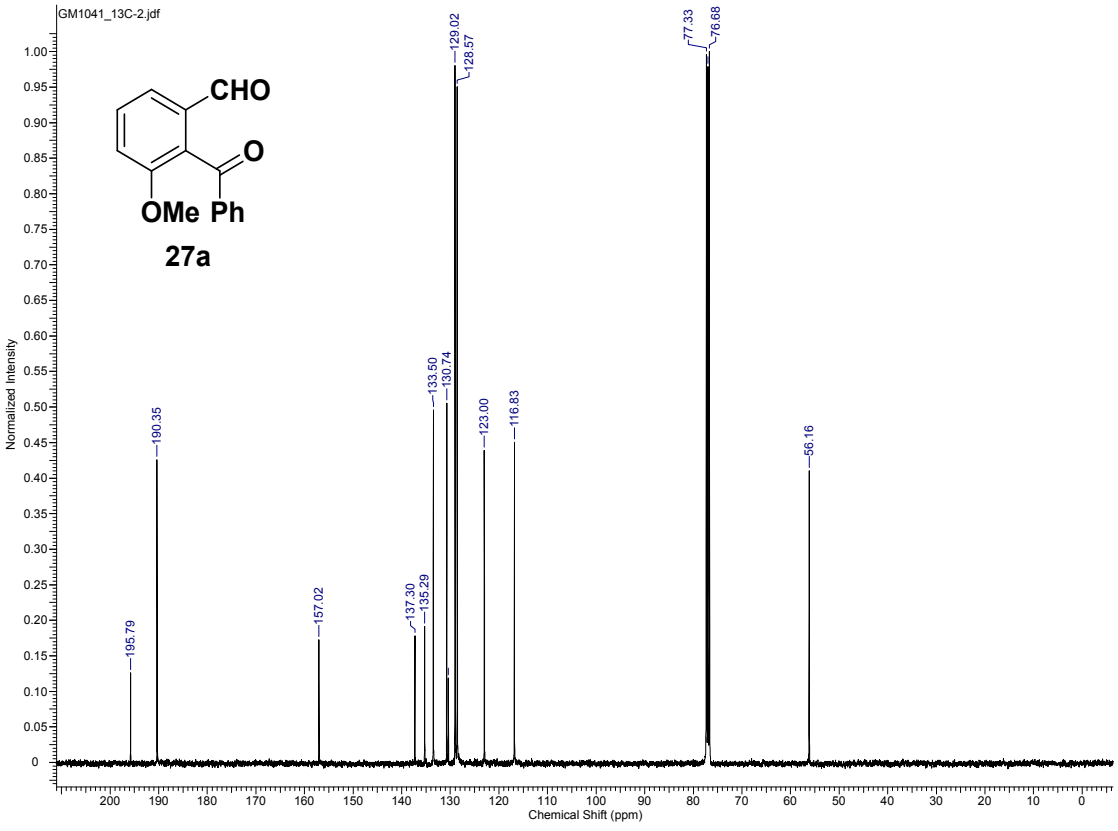
2.01
3.04
2.01
1.14
3.00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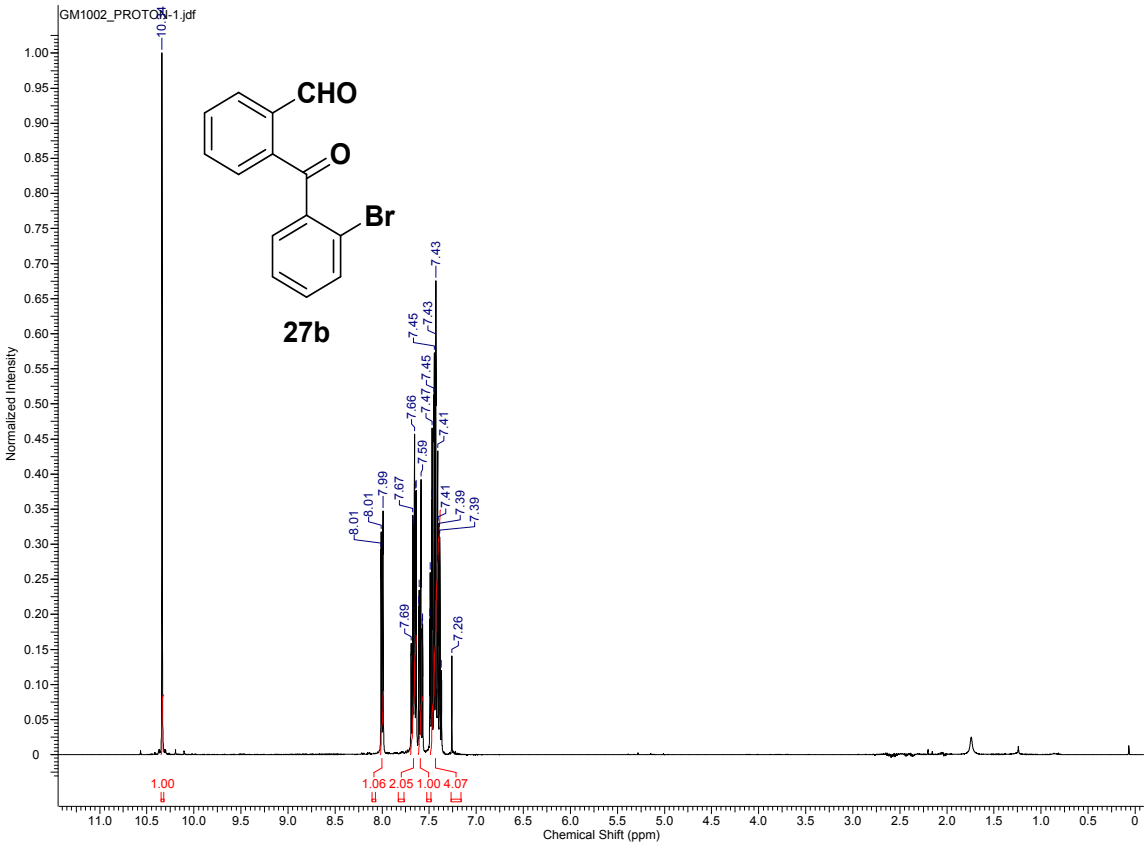
77.33
76.68
56.16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7.26
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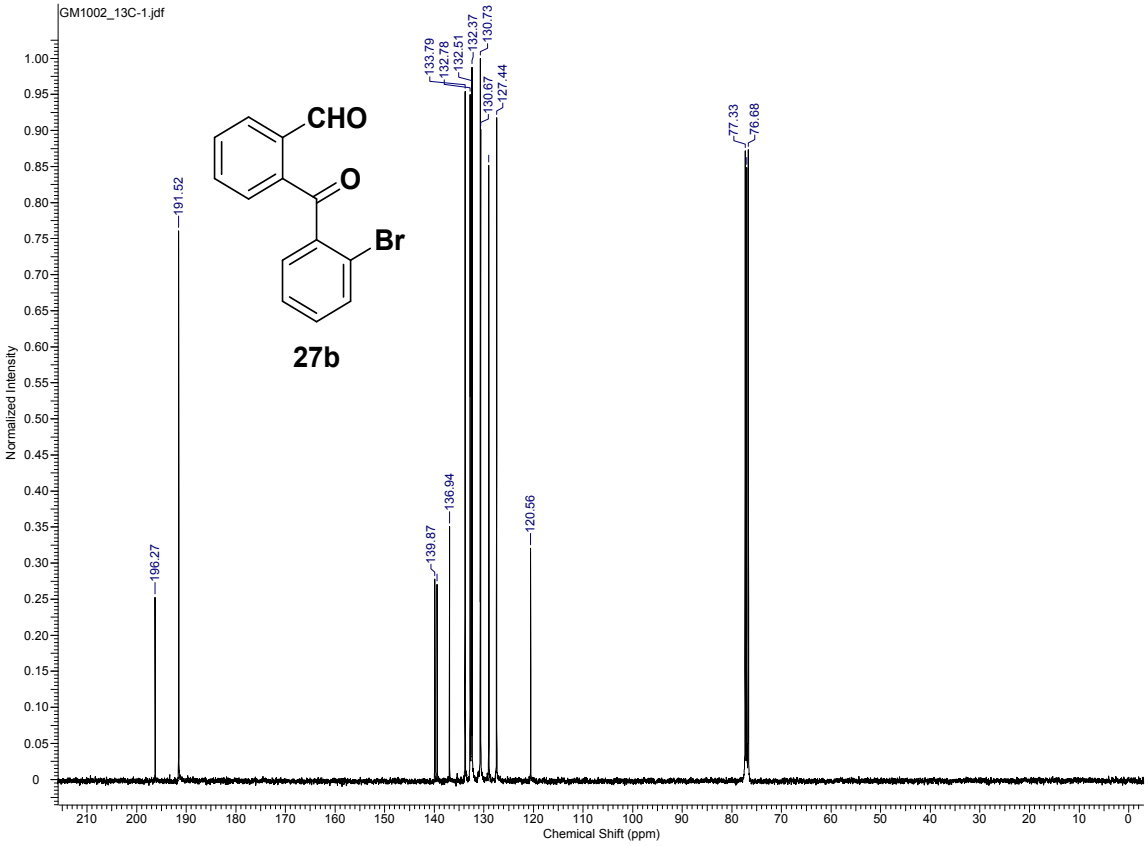
1.06
2.05
1.00
4.07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O
Br
27b
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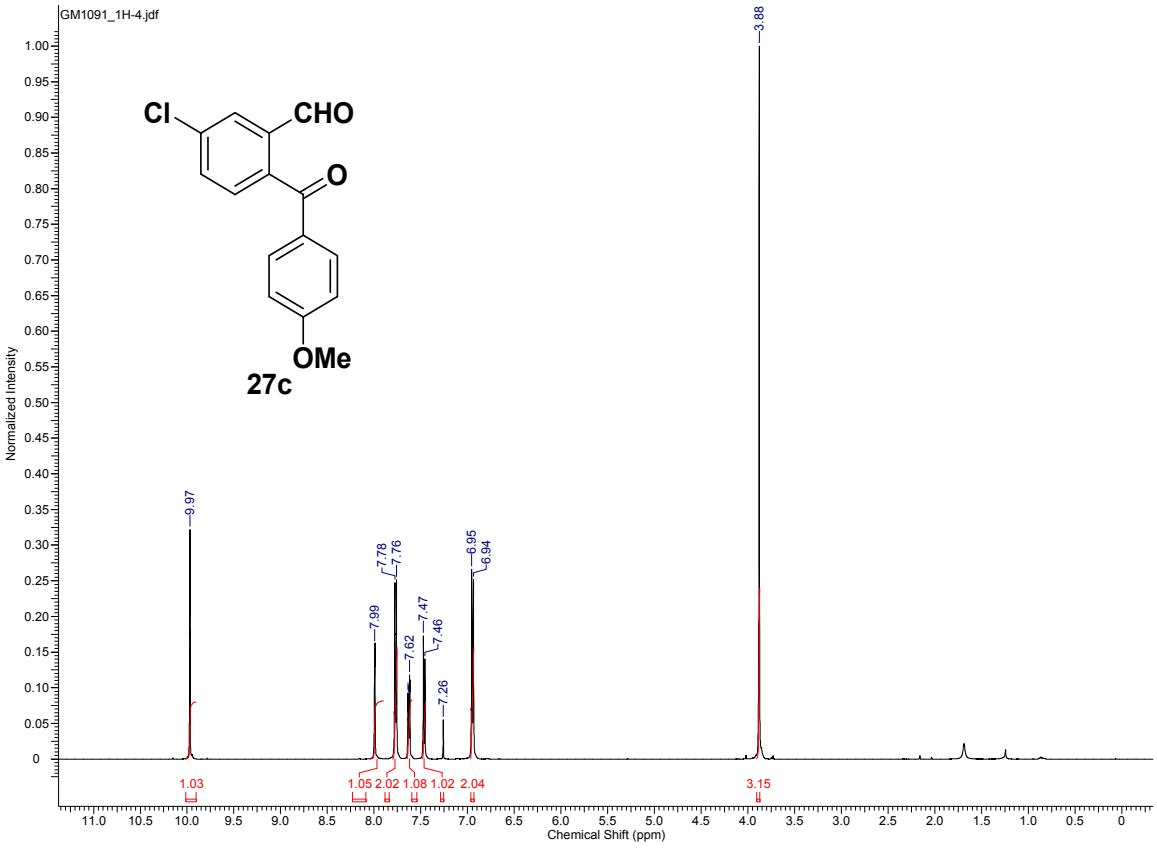
76.68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6.94
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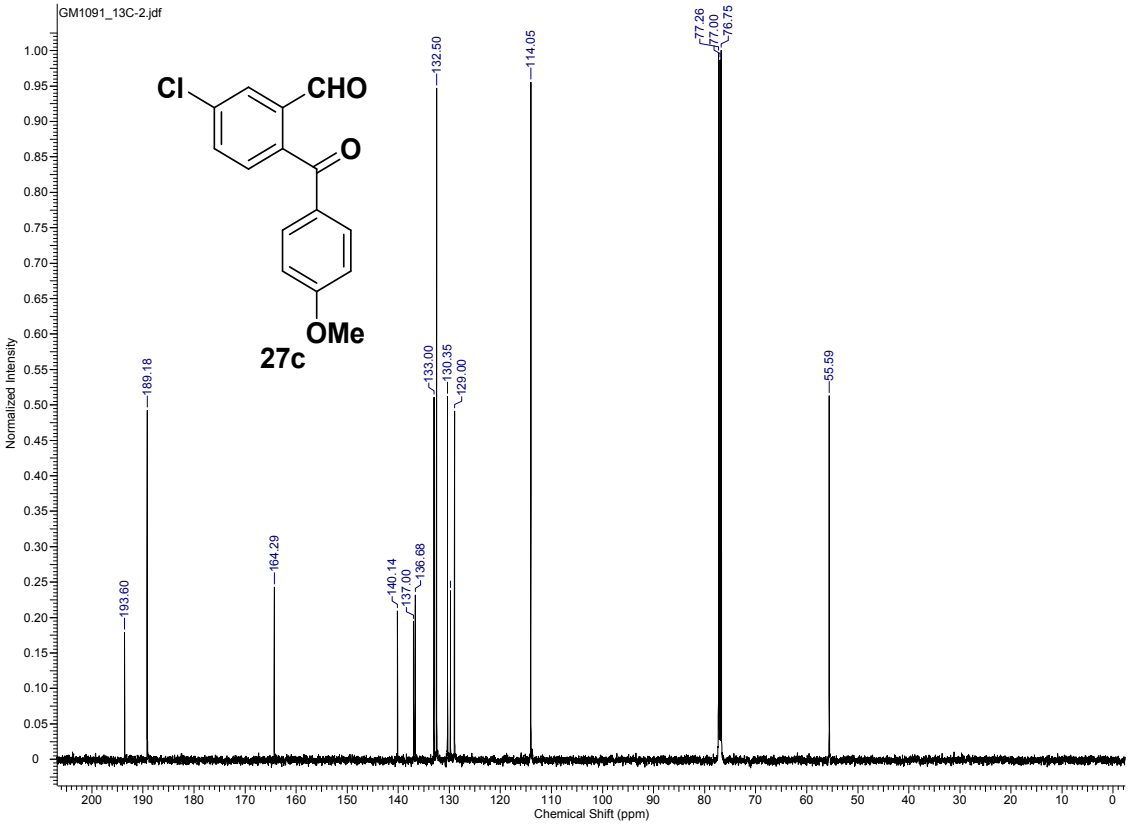
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CHO
O
OMe
27c
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Chemical Shift (ppm)
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133.00
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77.00
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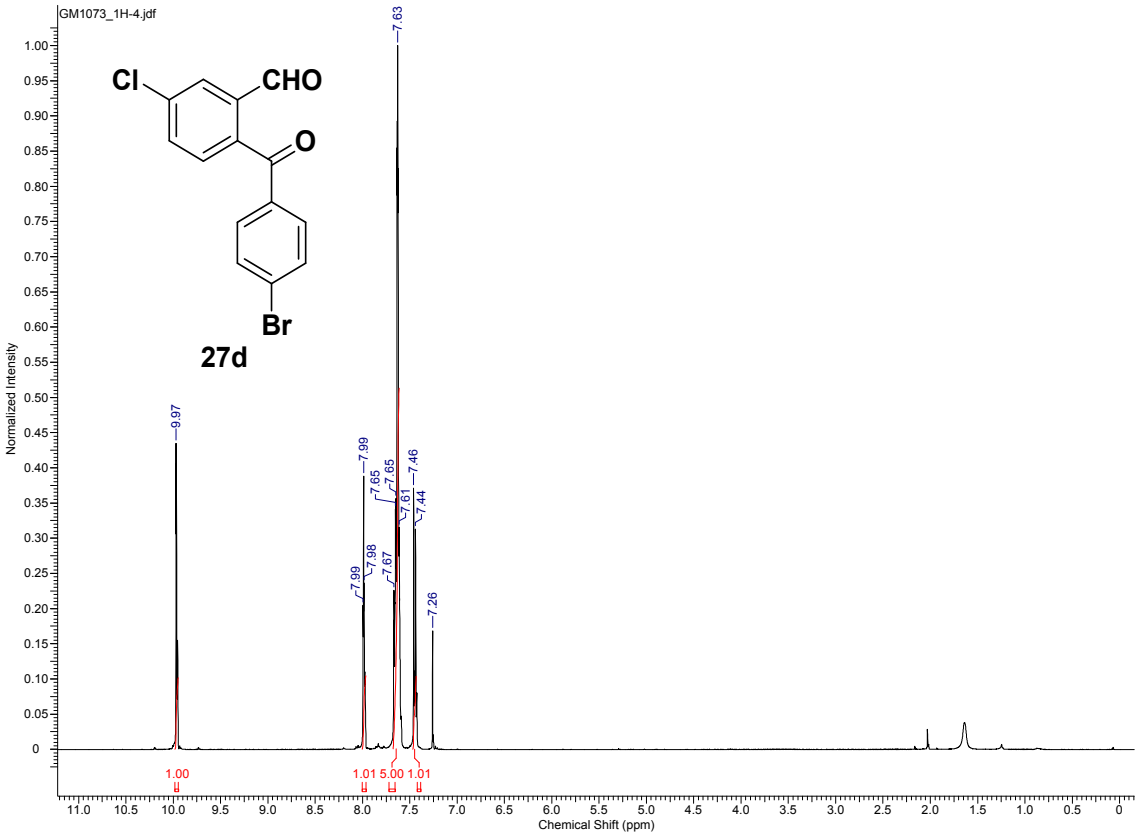
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CHO
O
Br
27d
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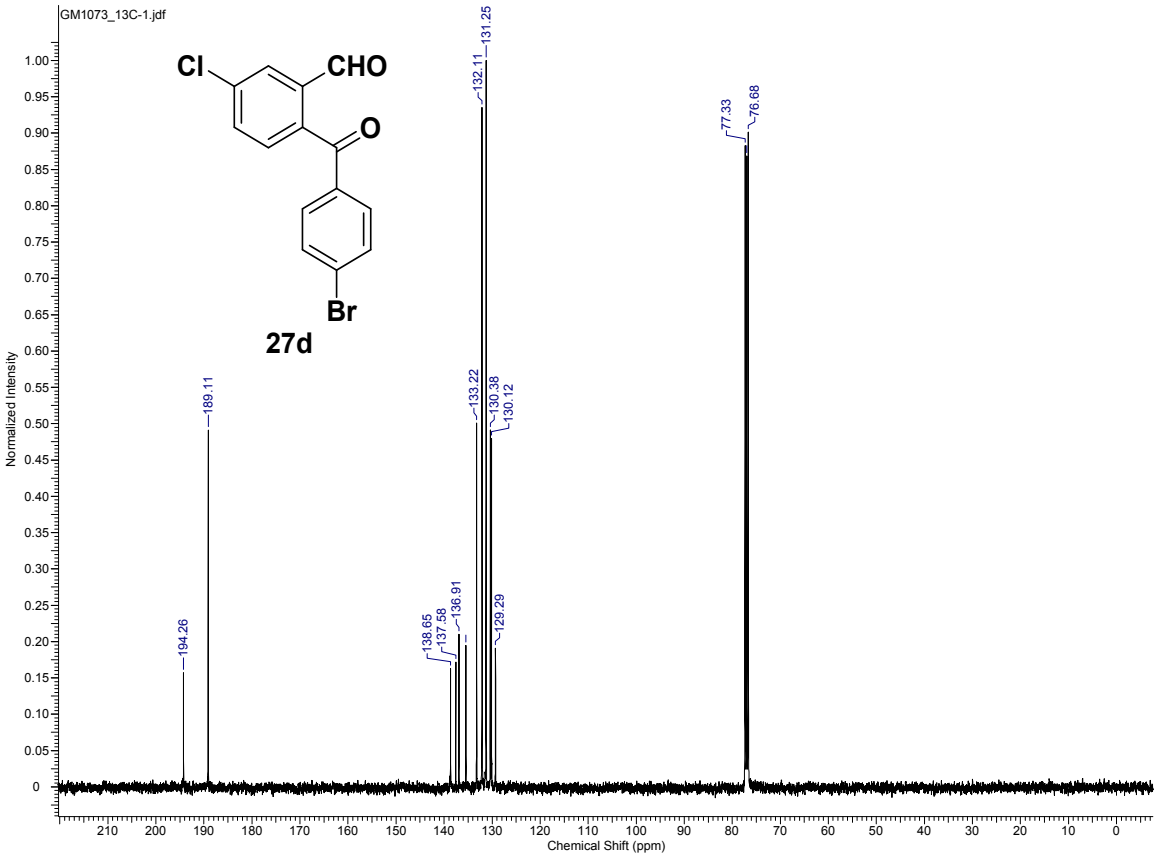
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CHO
O
Br
27d
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Chemical Shift (ppm)
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131.25
130.38
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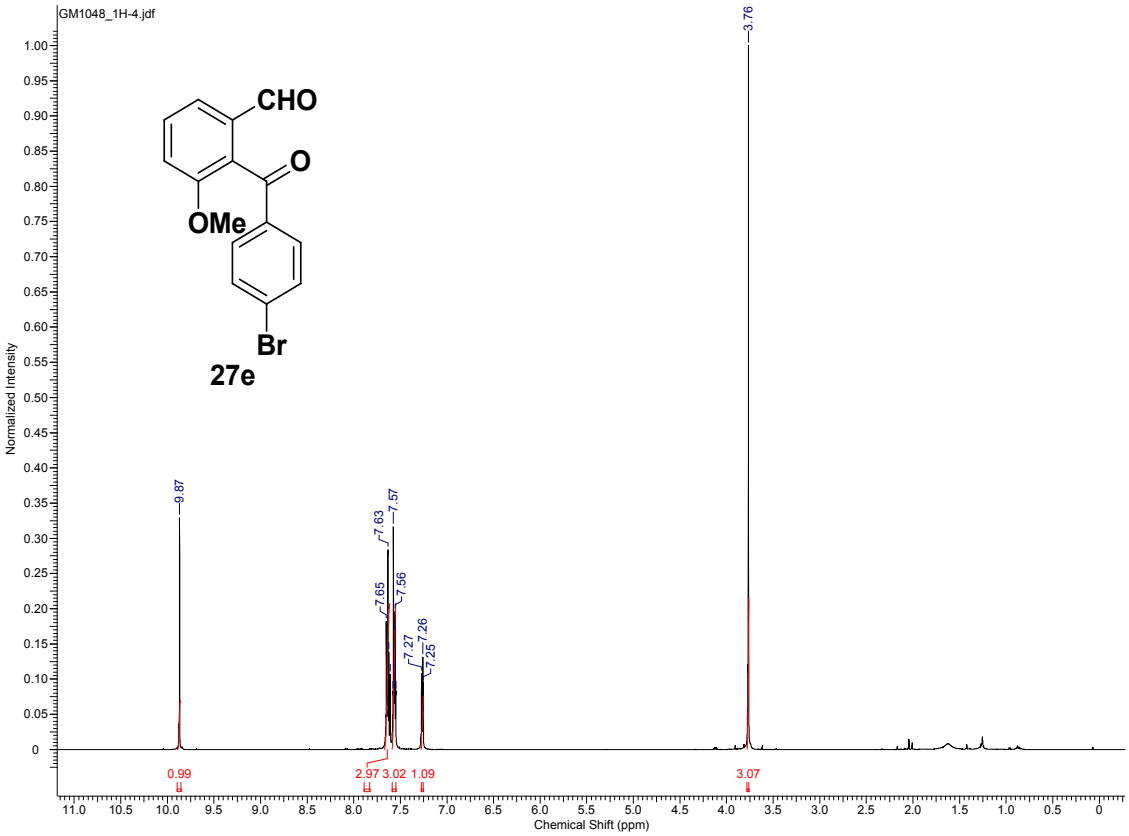
129.29
77.33
76.68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Br
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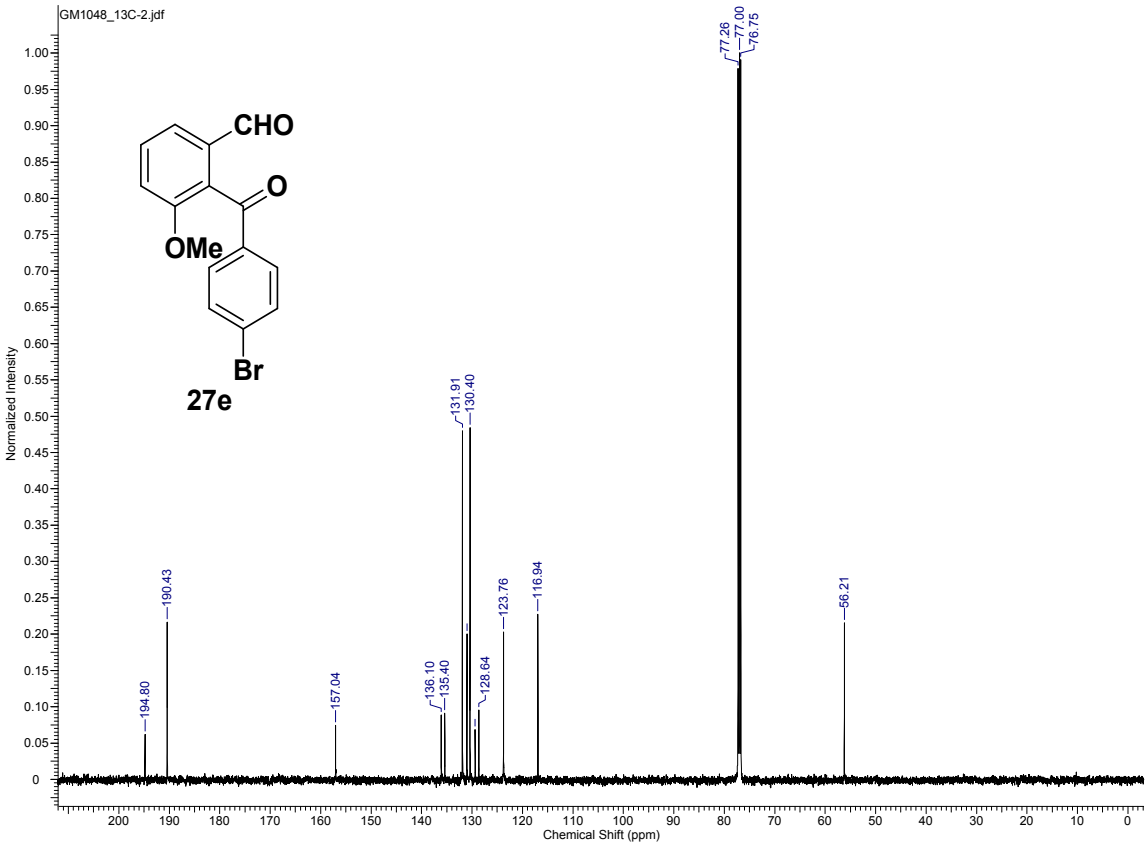
3.02
1.09
3.07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Br
27e
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123.76
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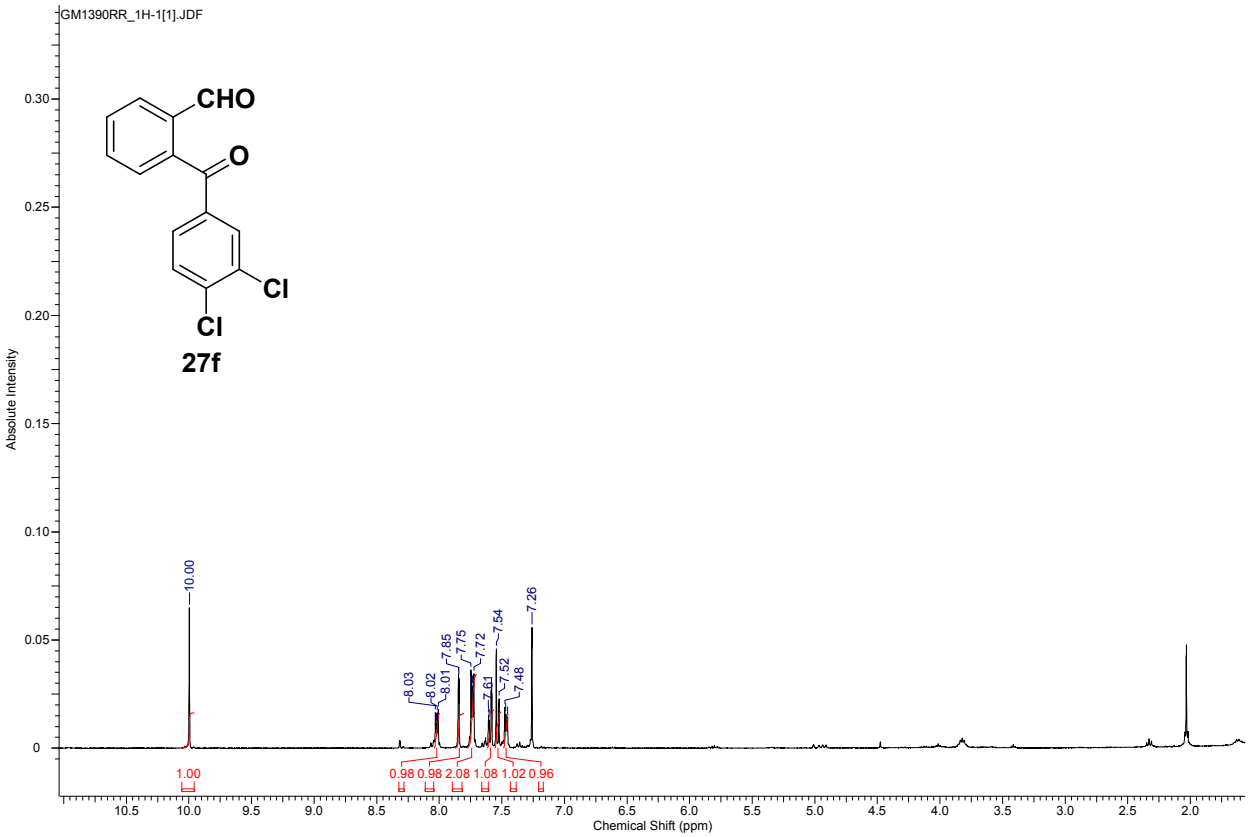
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O
Cl
Cl
27f
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7.26
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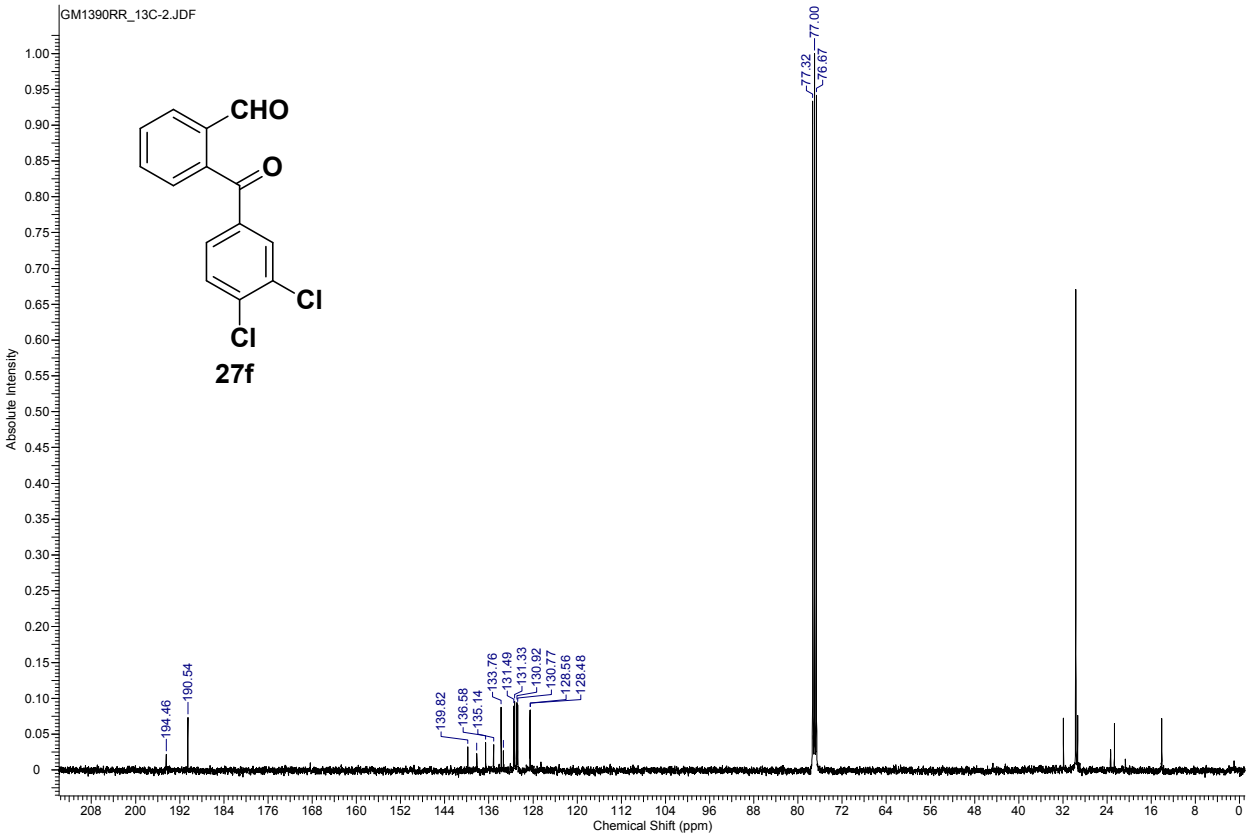
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Cl
Cl
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Chemical Shift (ppm)
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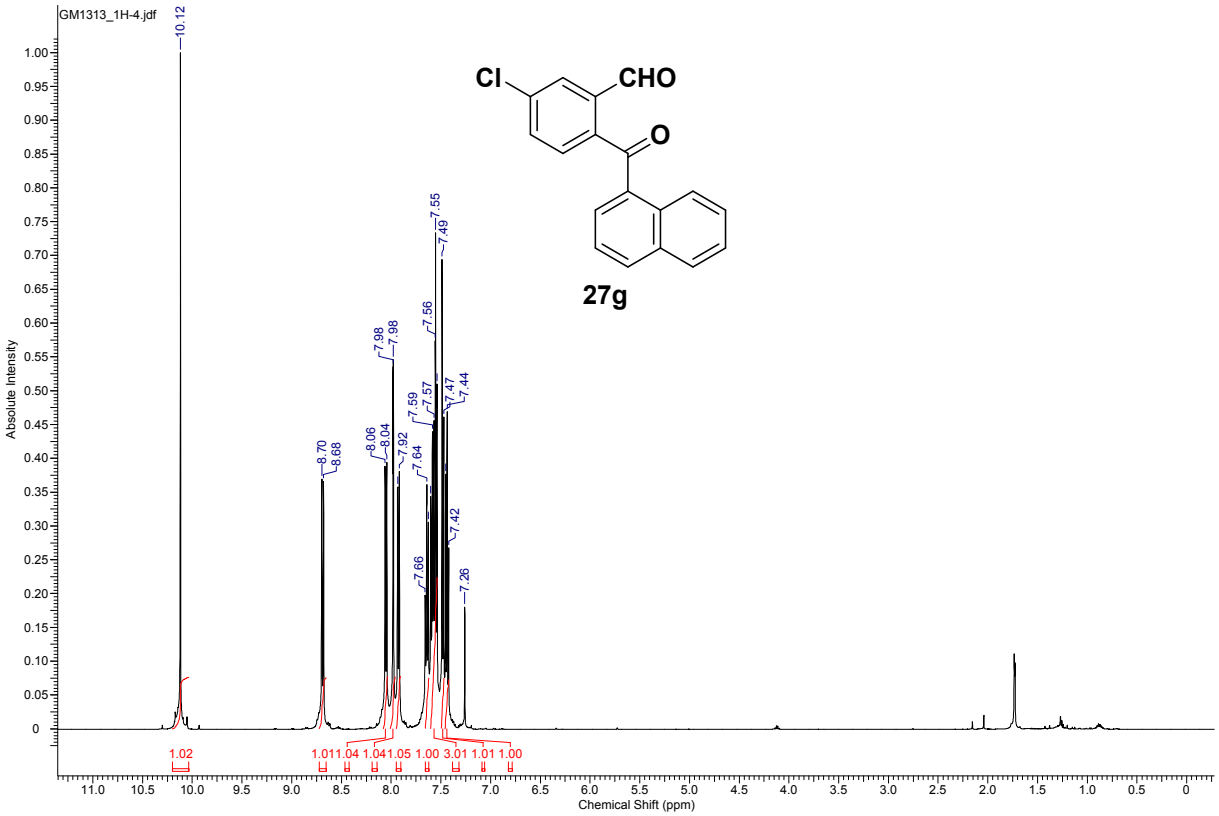
77.00
76.67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7.57
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7.44
7.42
7.26
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1.05
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1.01
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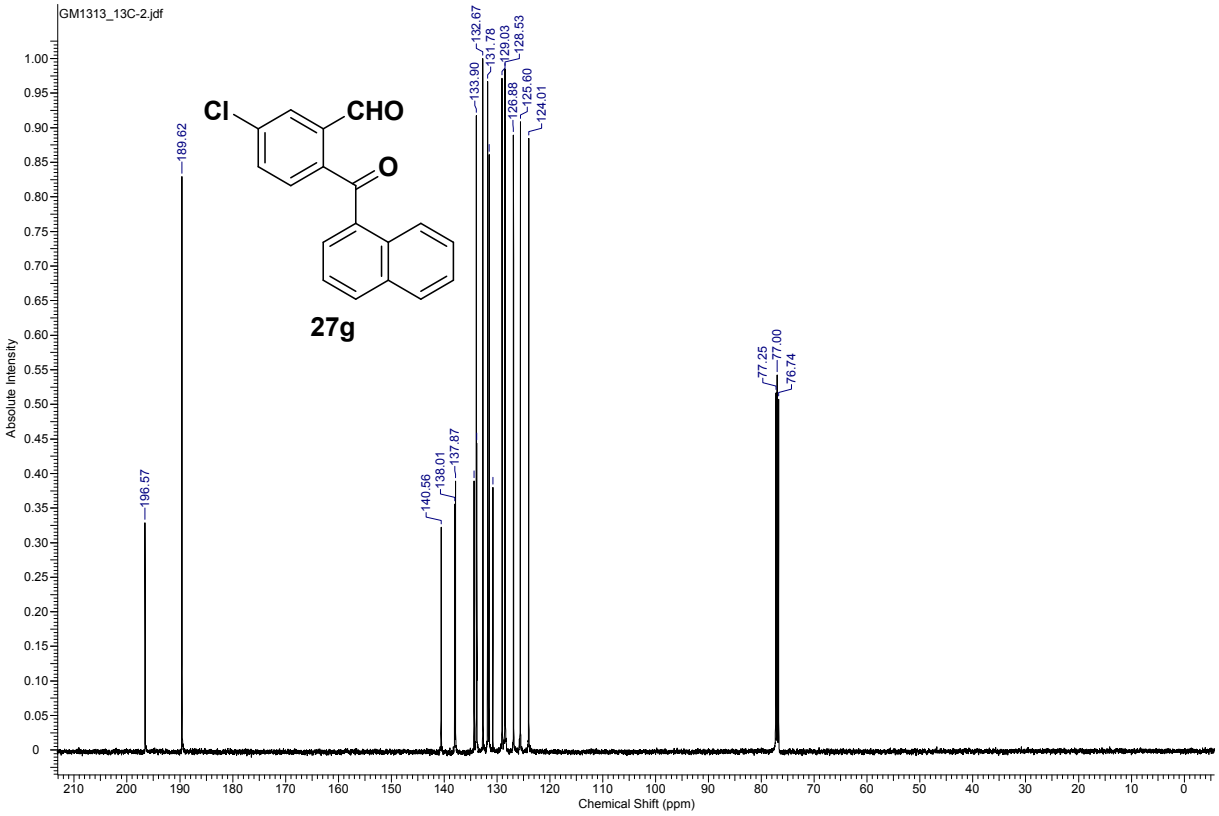
Absolute Intensity
Chemical Shift (ppm)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77.00
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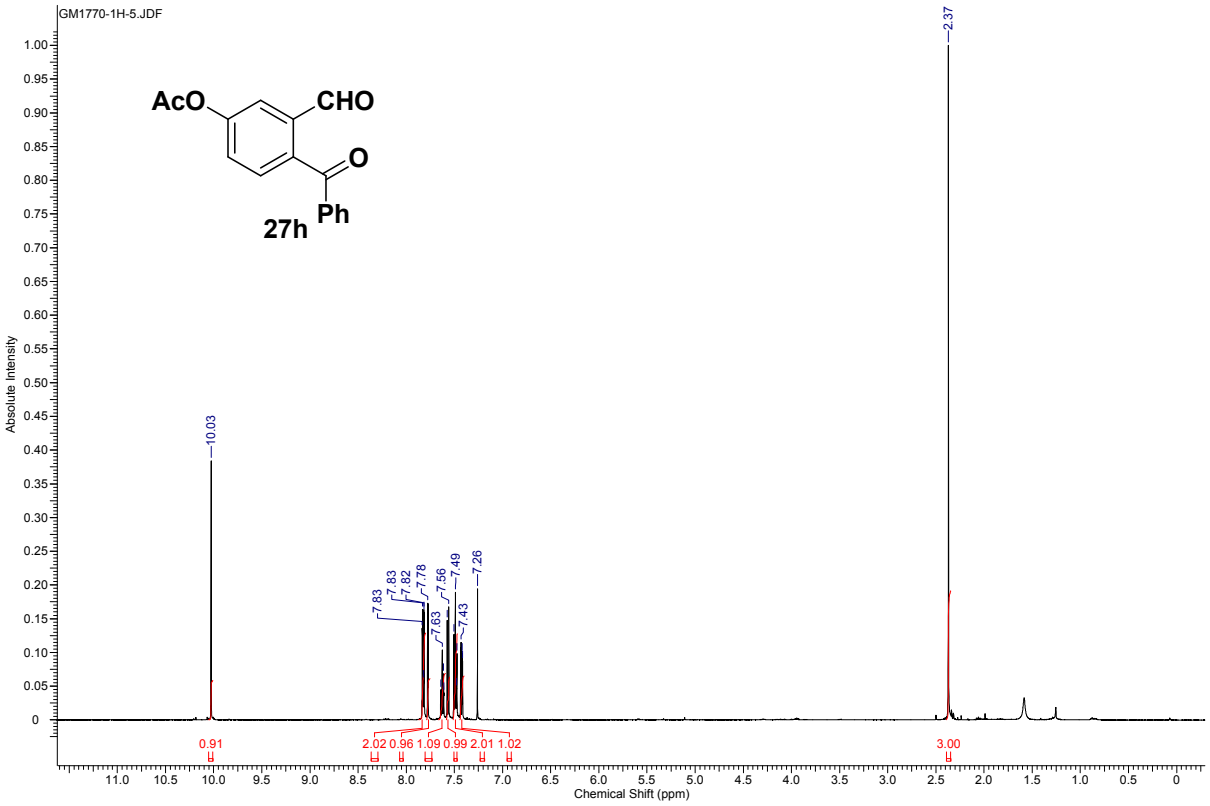
Absolute Intensity
Chemical Shift (ppm)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Ph
27h
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7.63
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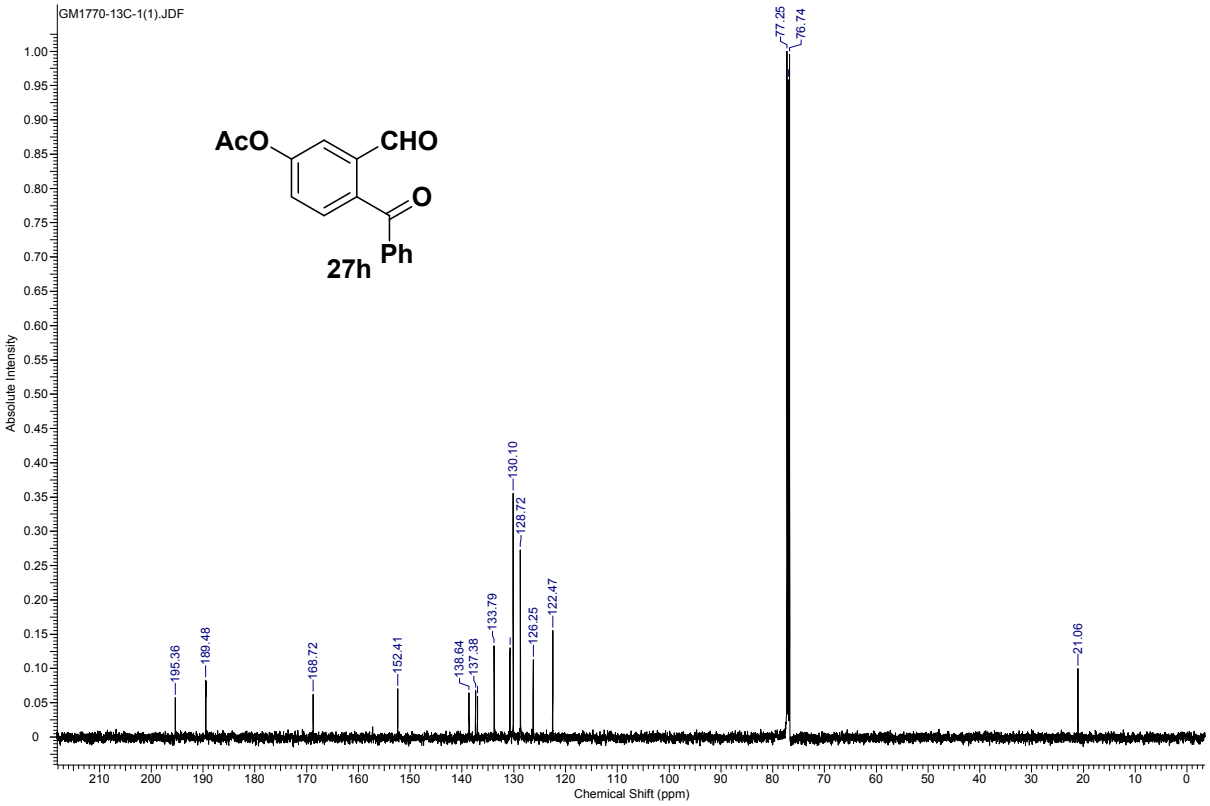
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Ph
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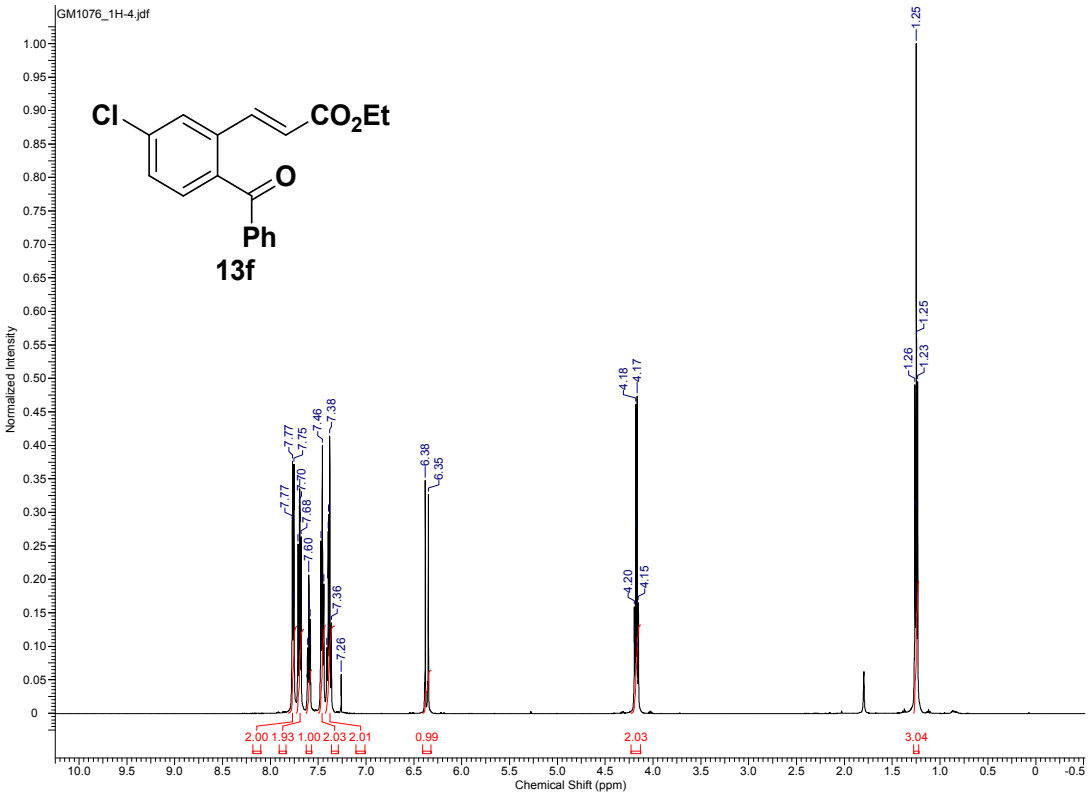
122.47
21.06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CO2Et
O
Ph
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6.35
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4.17
4.15
1.26
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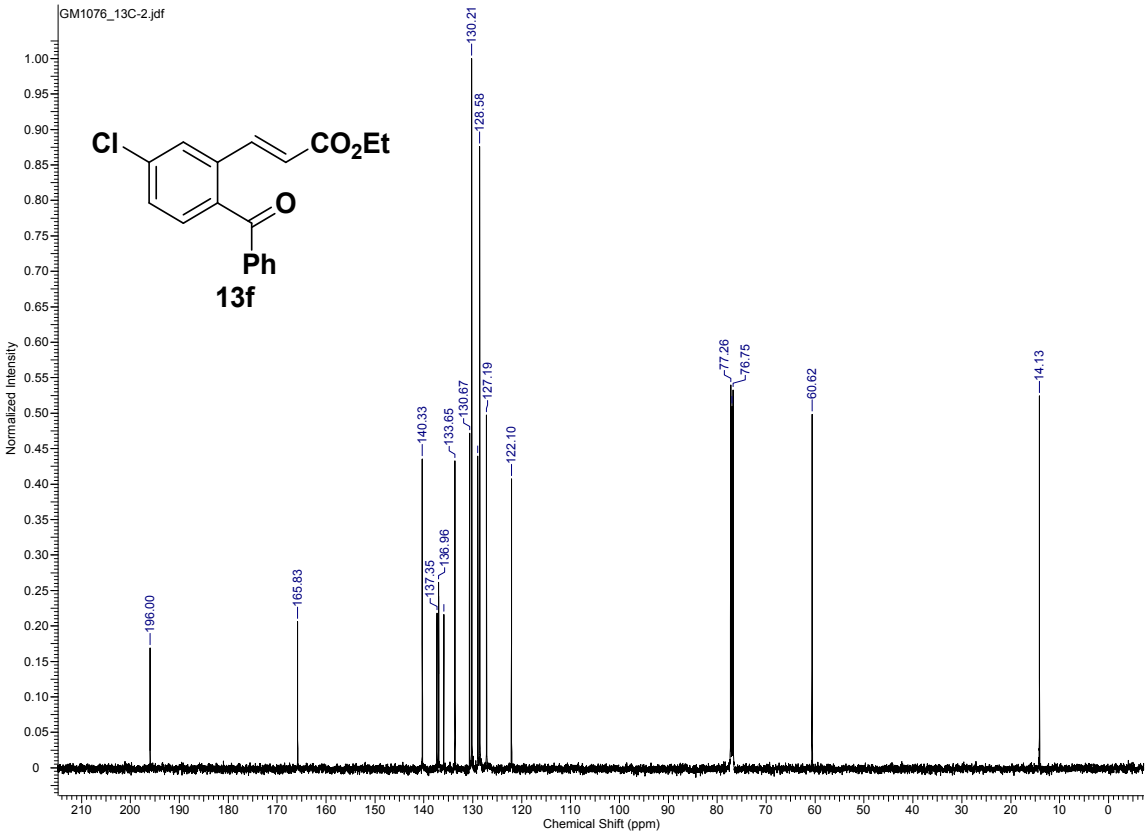
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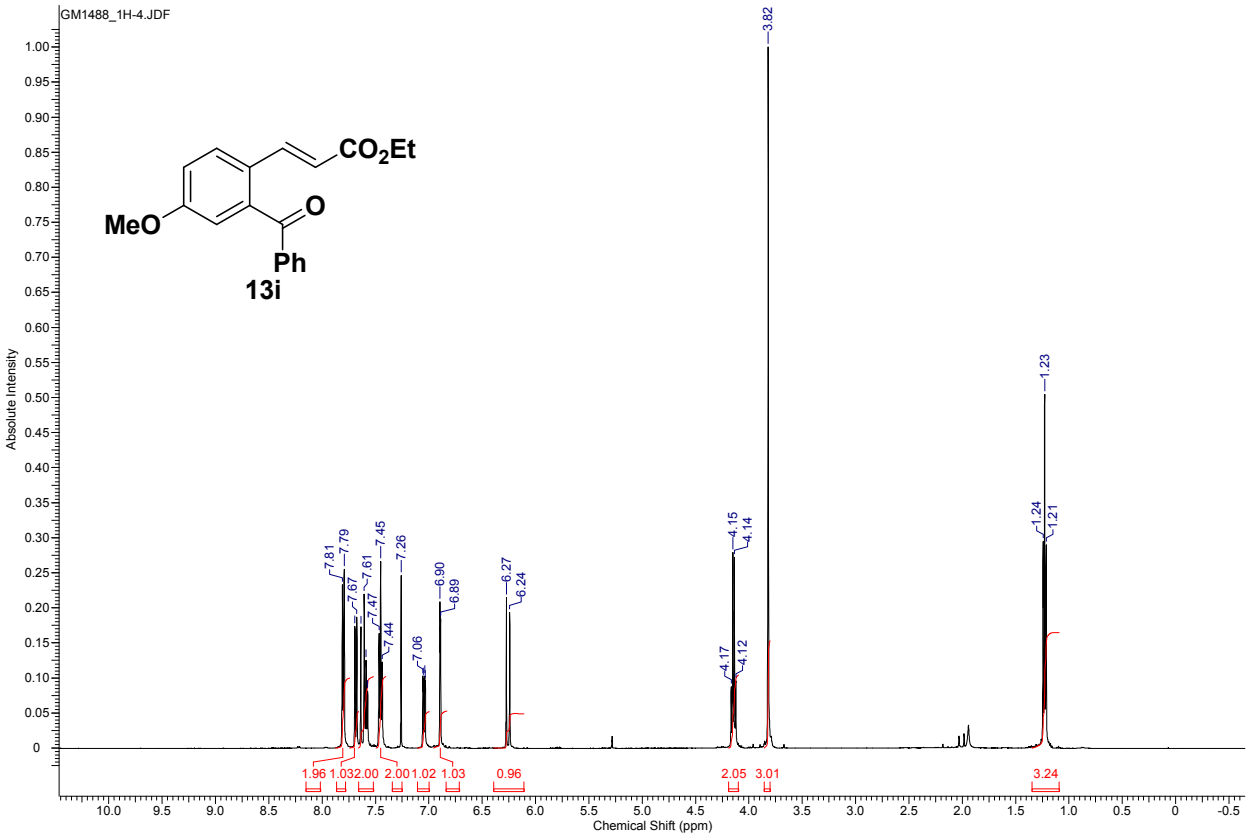
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Ph
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4.15
4.14
4.17
4.12
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7.67
7.61
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7.26
7.06
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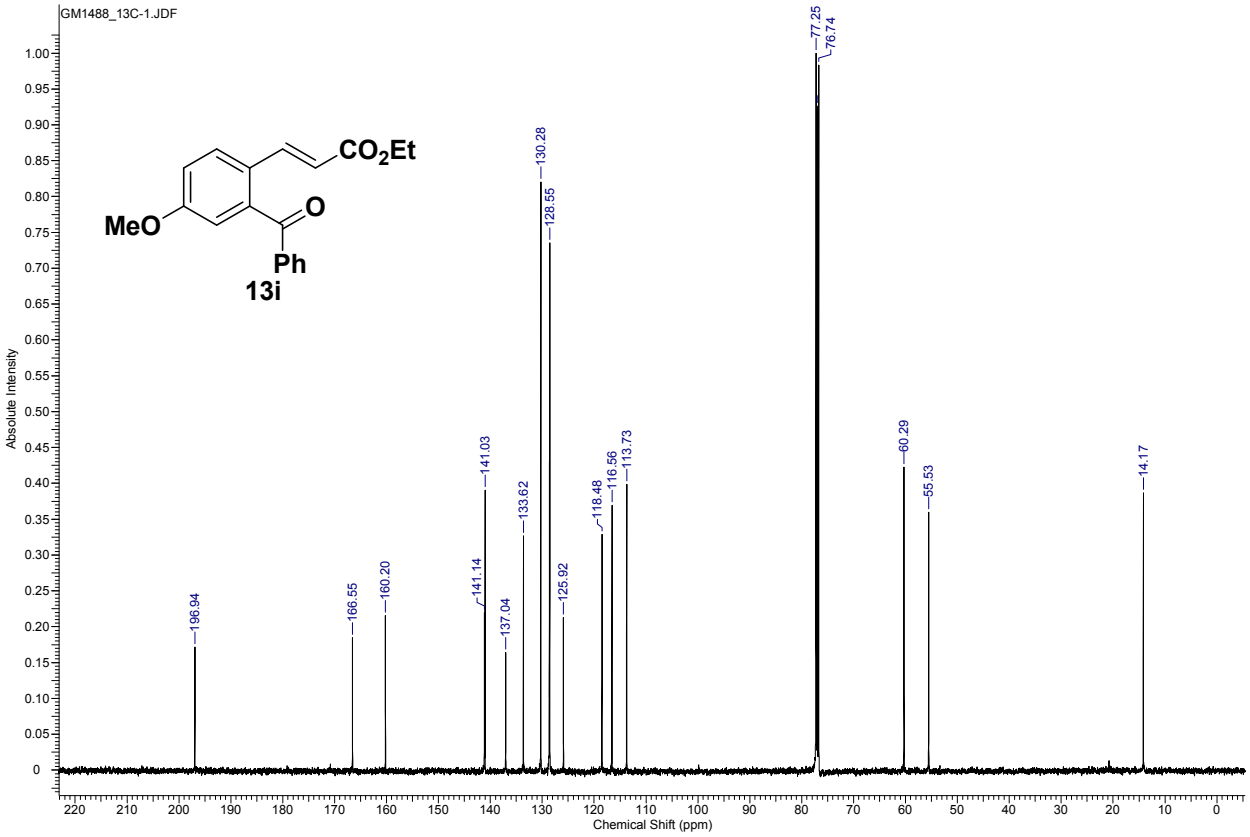
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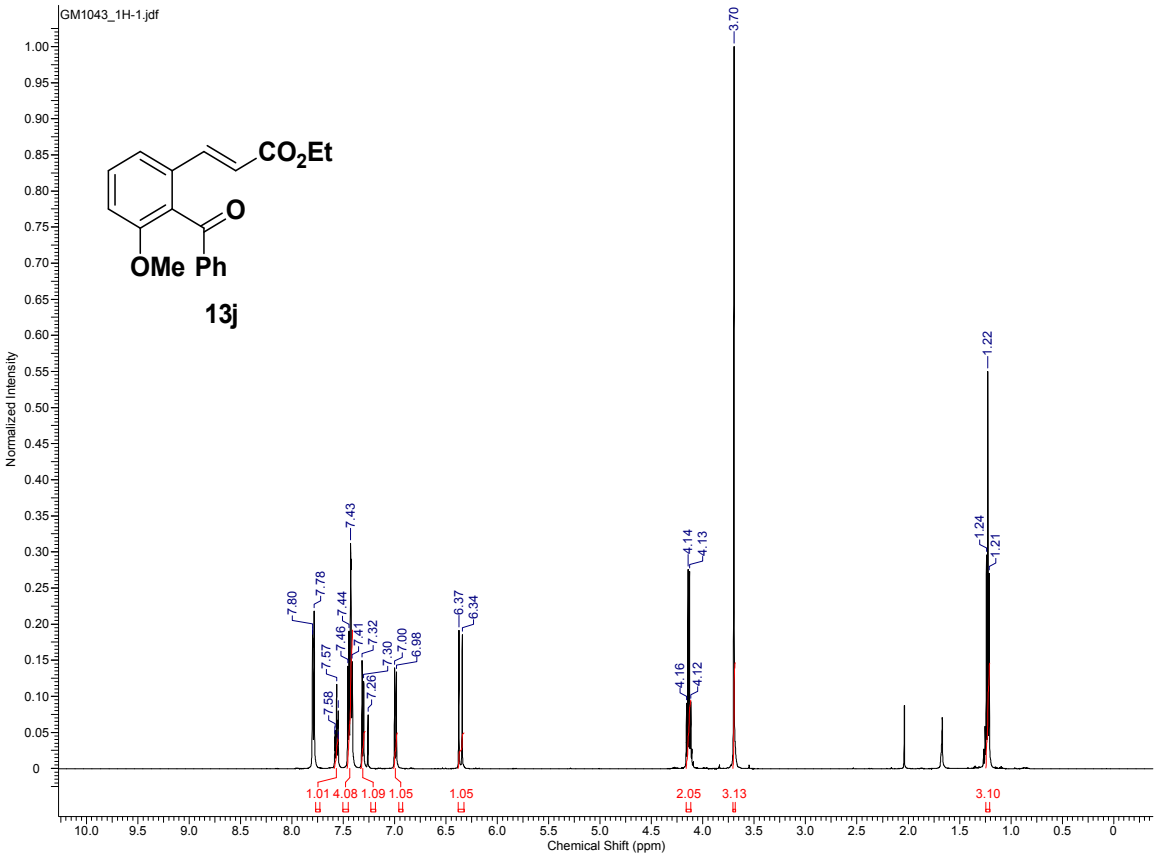
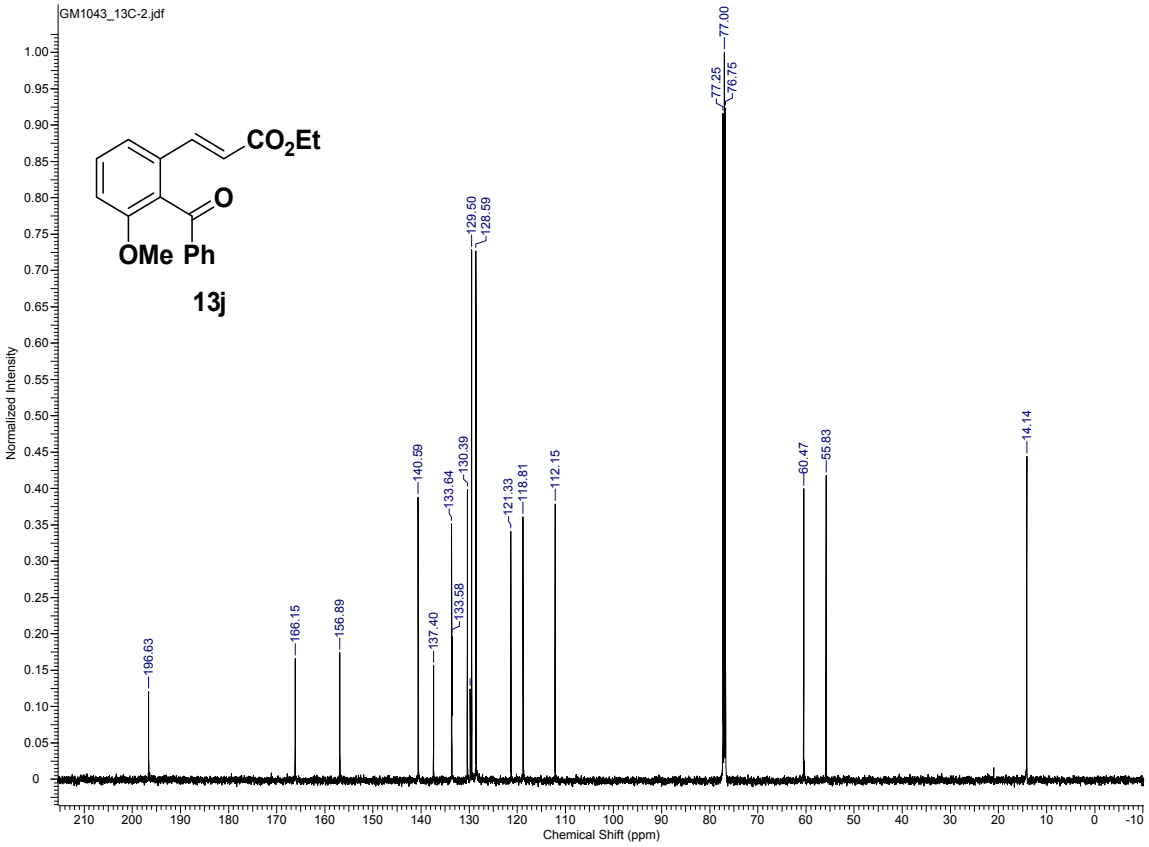
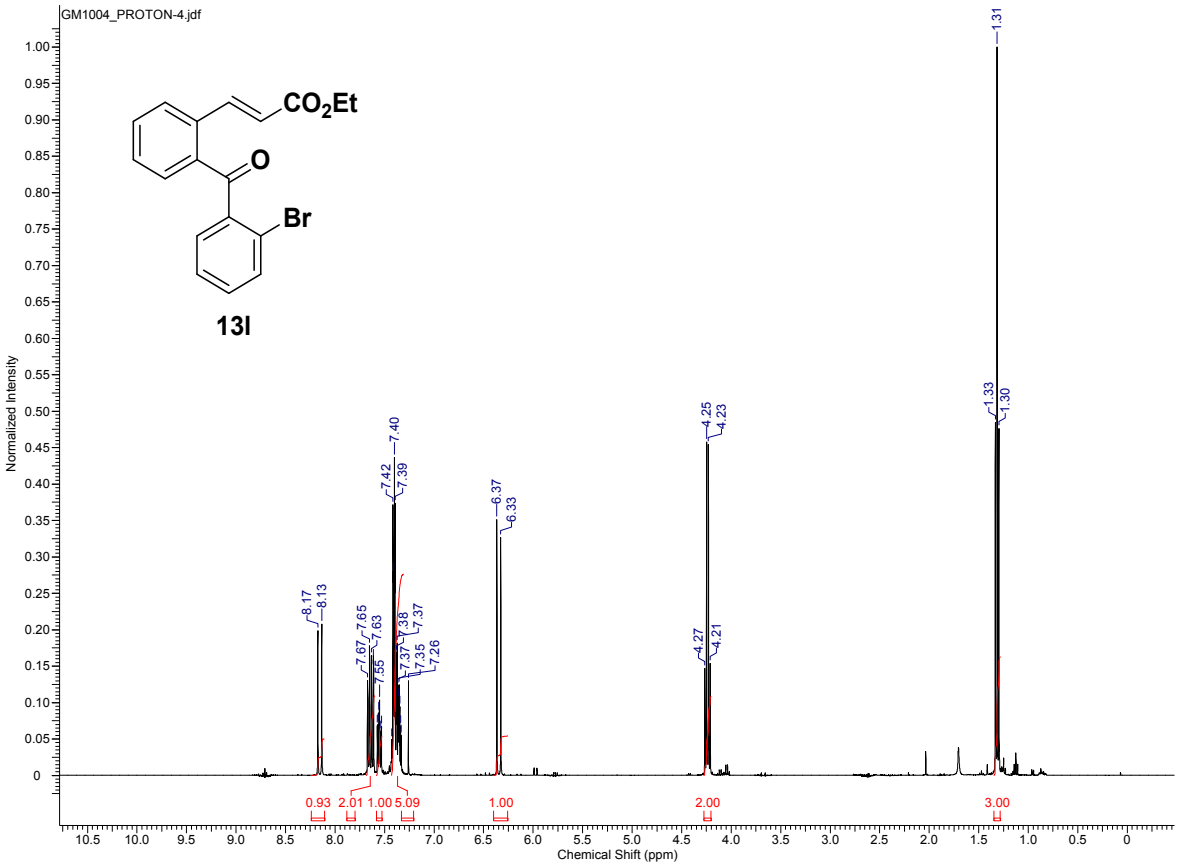
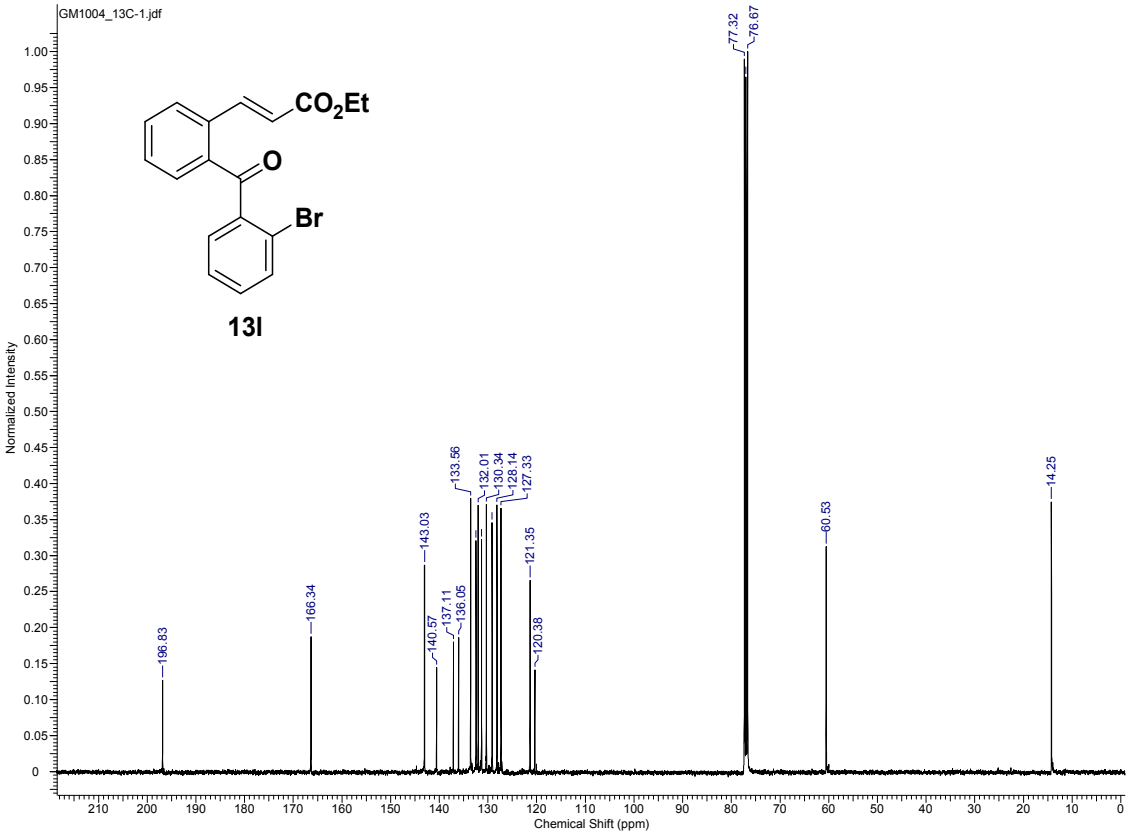
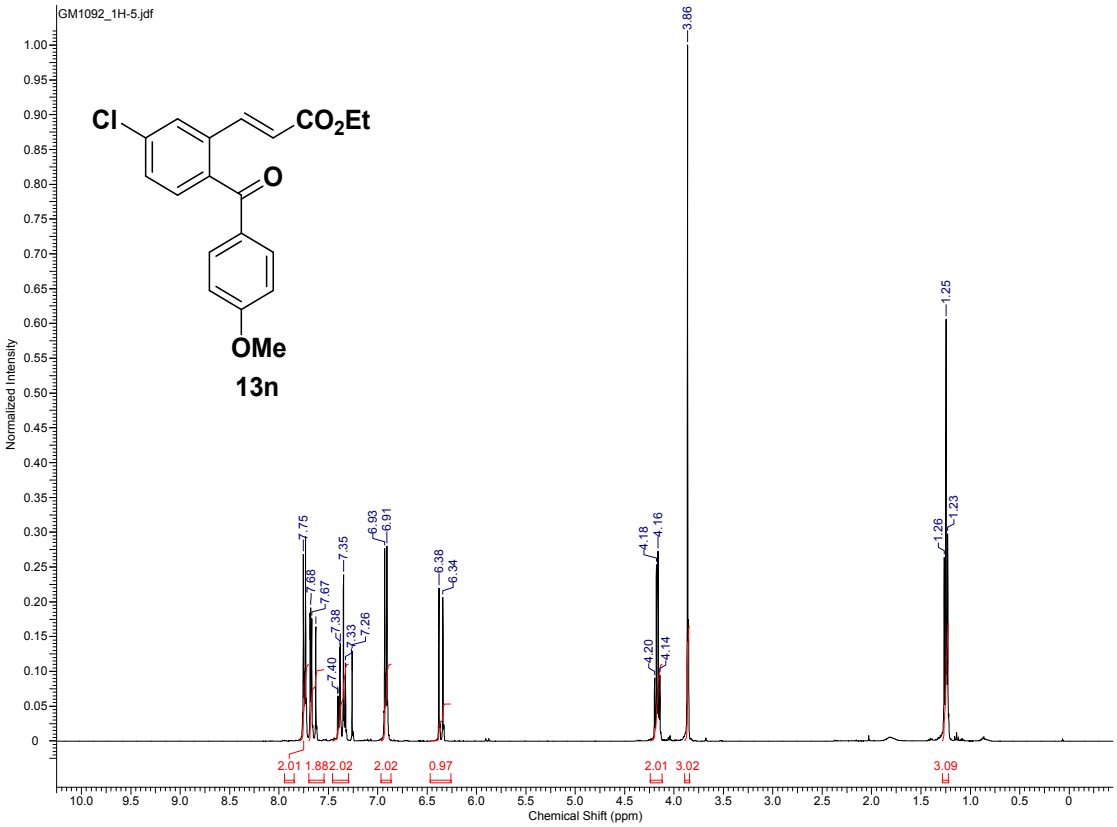
Ph
13i
Absolute Intensity
Chemical Shift (ppm)
77.25
76.74
130.28
128.55
141.03
133.62
125.92
118.48
116.56
113.73
60.29
55.53
14.17
196.94
166.55
160.20
141.14
137.04

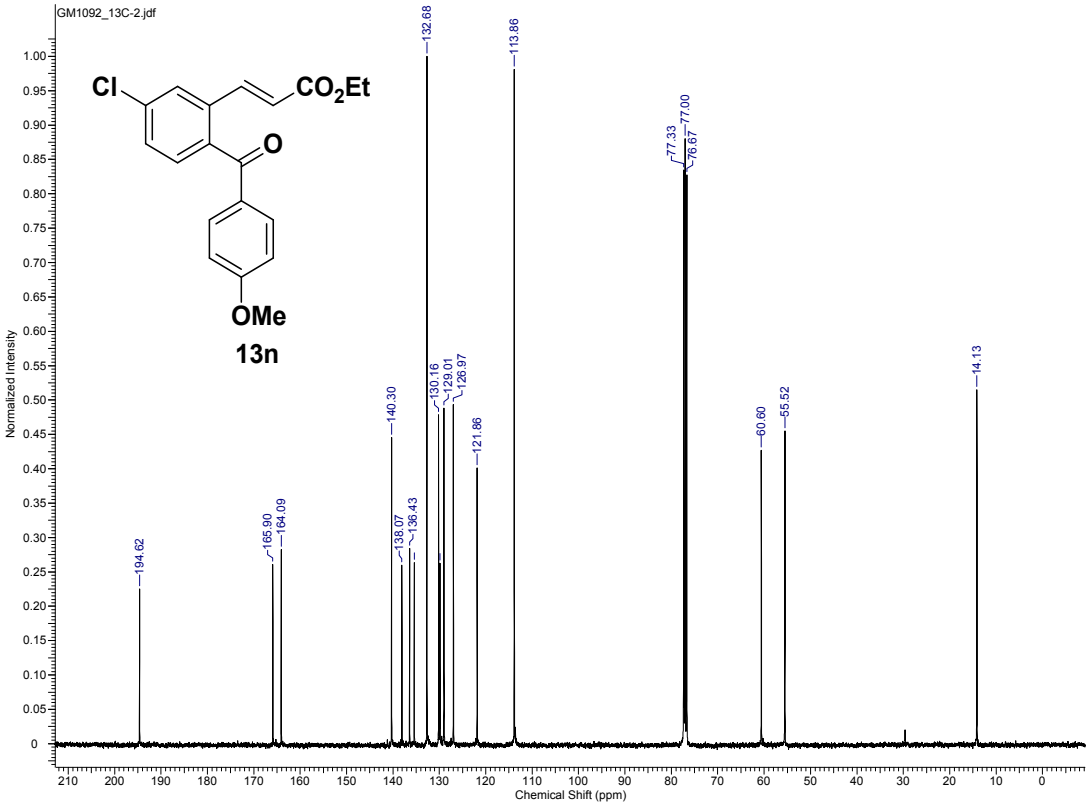

GM1043_1H-1.jdf
CO2Et
O
OMe Ph
13j
Normalized Intensity
Chemical Shift (ppm)
7.80
7.78
7.57
7.46
7.44
7.43
7.41
7.32
7.30
7.26
7.00
6.98
6.37
6.34
4.16
4.14
4.13
4.12
3.70
1.24
1.22
1.21
1.01 4.08 1.09 1.05
1.05
2.05
3.13
3.10

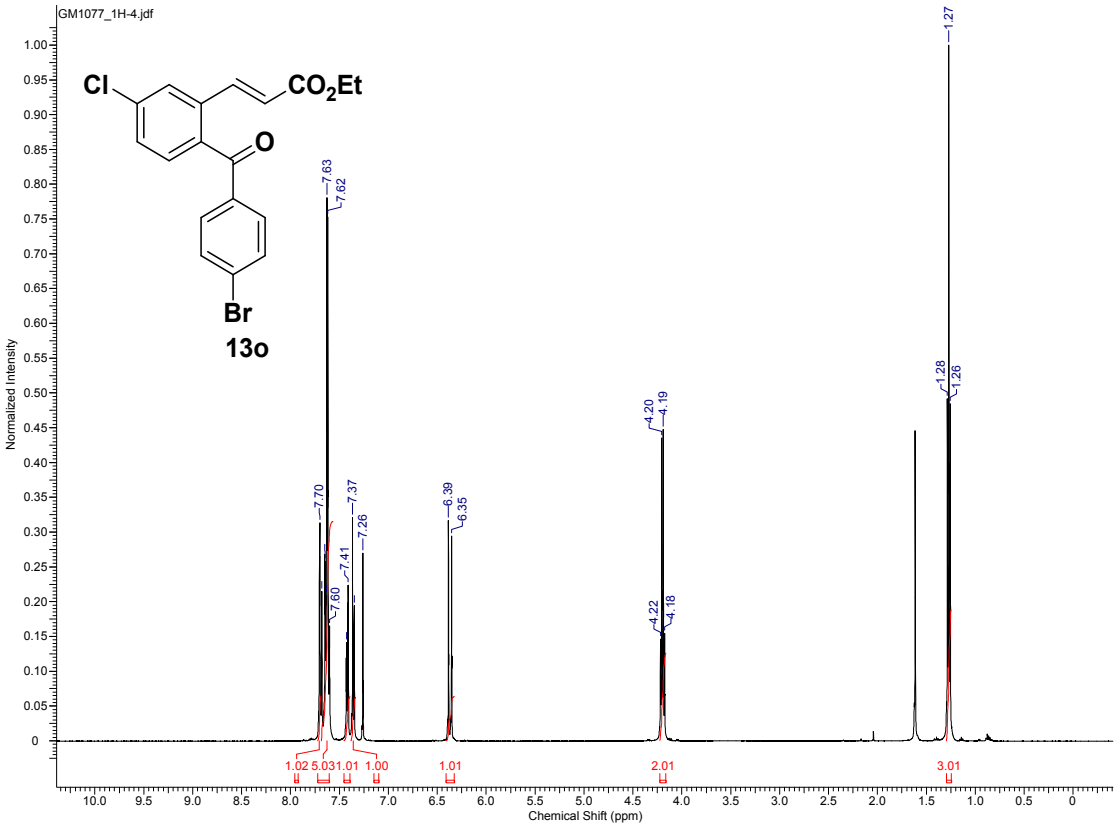

GM1043_13C-2.jdf
CO2Et
O
OMe Ph
13j
Normalized Intensity
Chemical Shift (ppm)
196.63
166.15
156.89
140.59
137.40
133.64
133.58
130.39
129.50
128.59
121.33
118.81
112.15
77.25
77.00
76.75
60.47
55.83
14.14

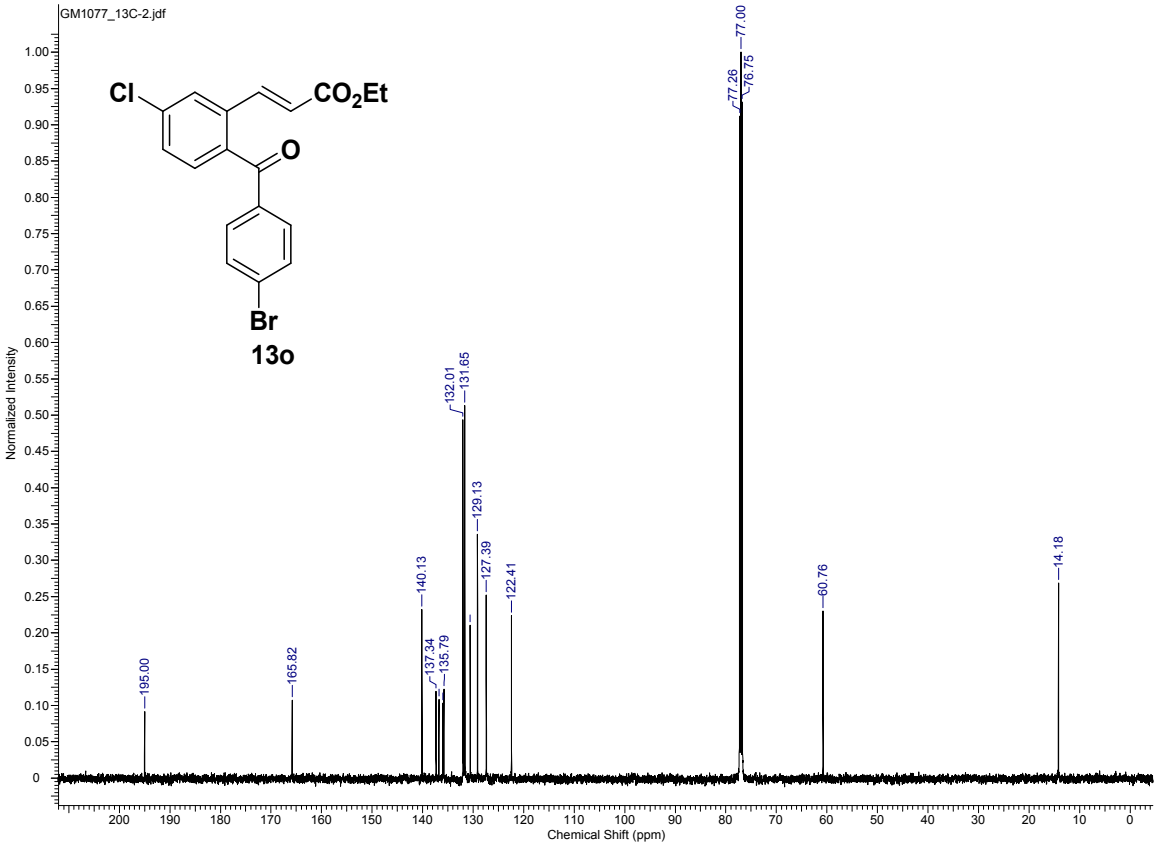

GM1004_PROTON-4.jdf
CO2Et
O
Br
13l
Normalized Intensity
Chemical Shift (ppm)
1.31
1.33
1.30
4.25
4.23
4.27
4.21
7.40
7.42
7.39
6.37
6.33
8.17
8.13
7.67
7.65
7.63
7.55
7.38
7.37
7.35
7.26
0.93
2.01
1.00
5.09
1.00
2.00
3.00

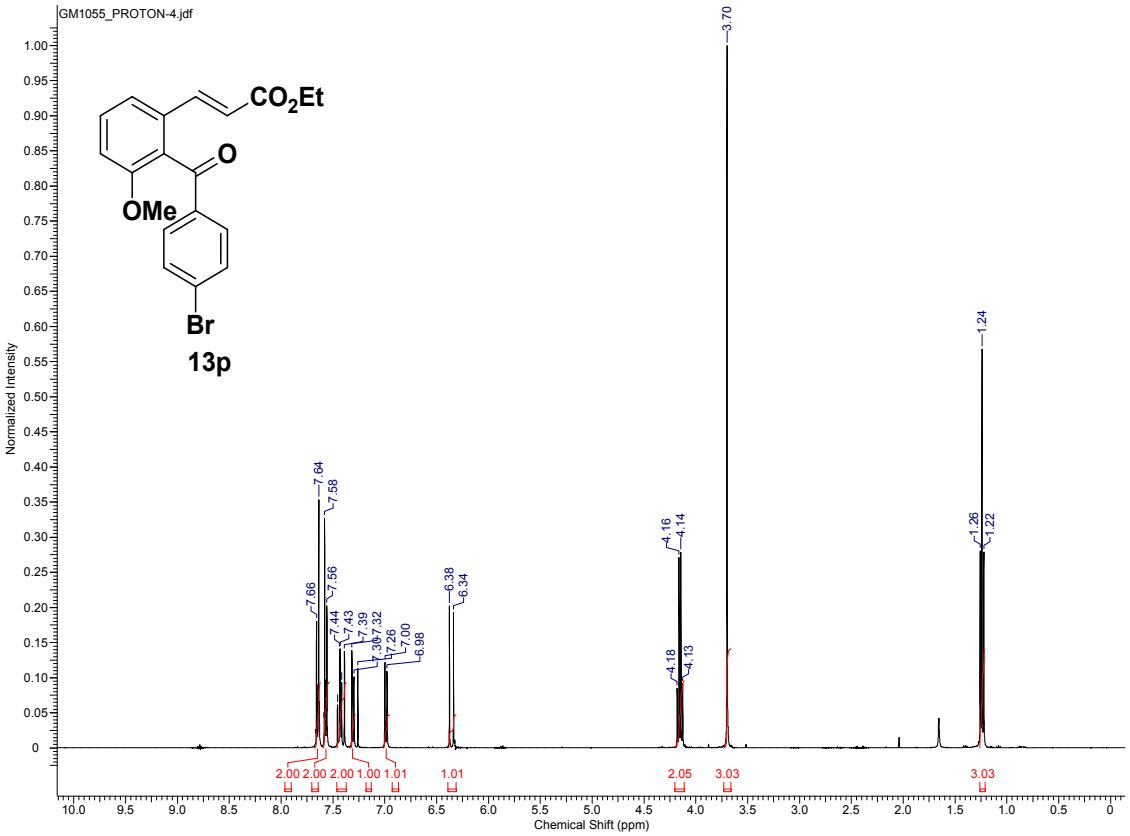

GM1004_13C-1.jdf
CO2Et
O
Br
13l
Normalized Intensity
Chemical Shift (ppm)
77.32
76.67
133.56
132.01
130.34
128.14
127.33
143.03
121.35
140.57
137.11
136.05
120.38
166.34
196.83
60.53
14.25

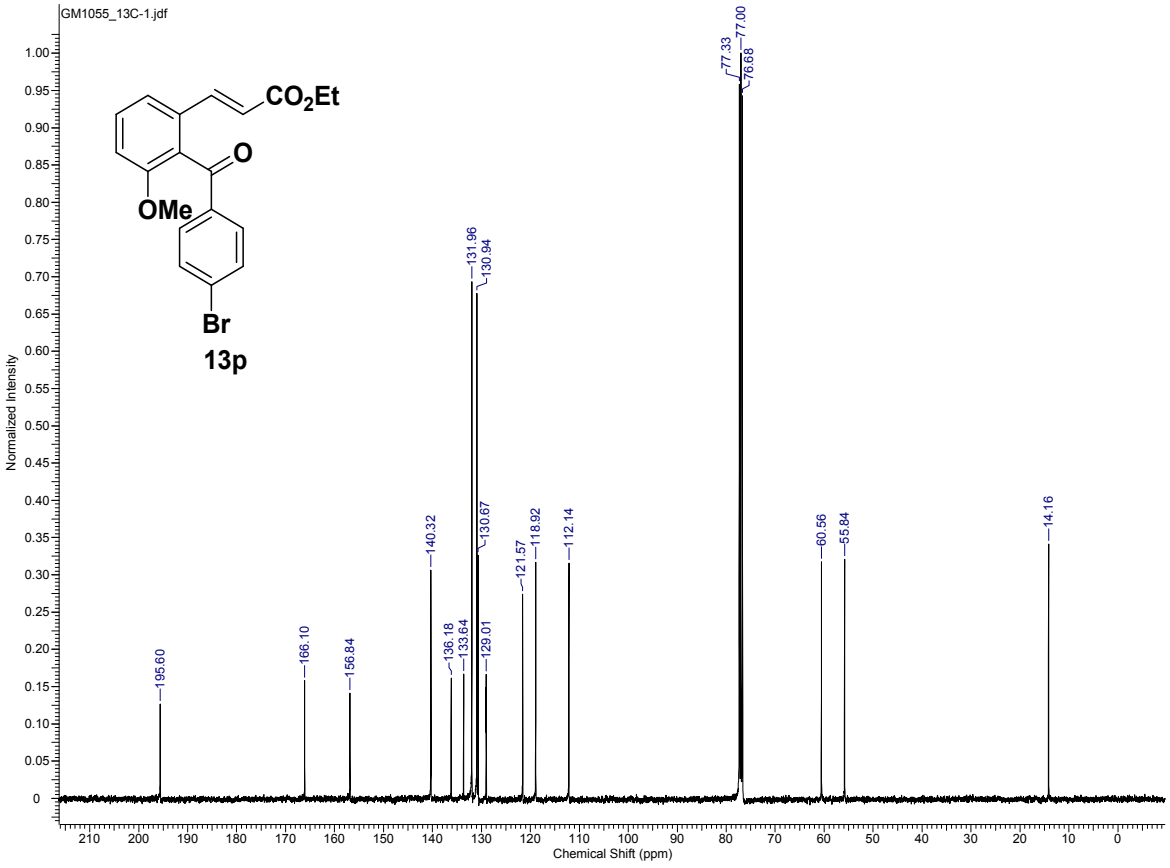

GM1092_1H-5.jdf
Cl
CO2Et
O
OMe
13n
Normalized Intensity
Chemical Shift (ppm)
7.75
7.68
7.67
7.40
7.38
7.35
7.33
7.26
6.93
6.91
6.38
6.34
4.18
4.16
4.20
4.14
3.86
1.26
1.25
1.23
2.01
1.88
2.02
2.02
0.97
2.01
3.02
3.09

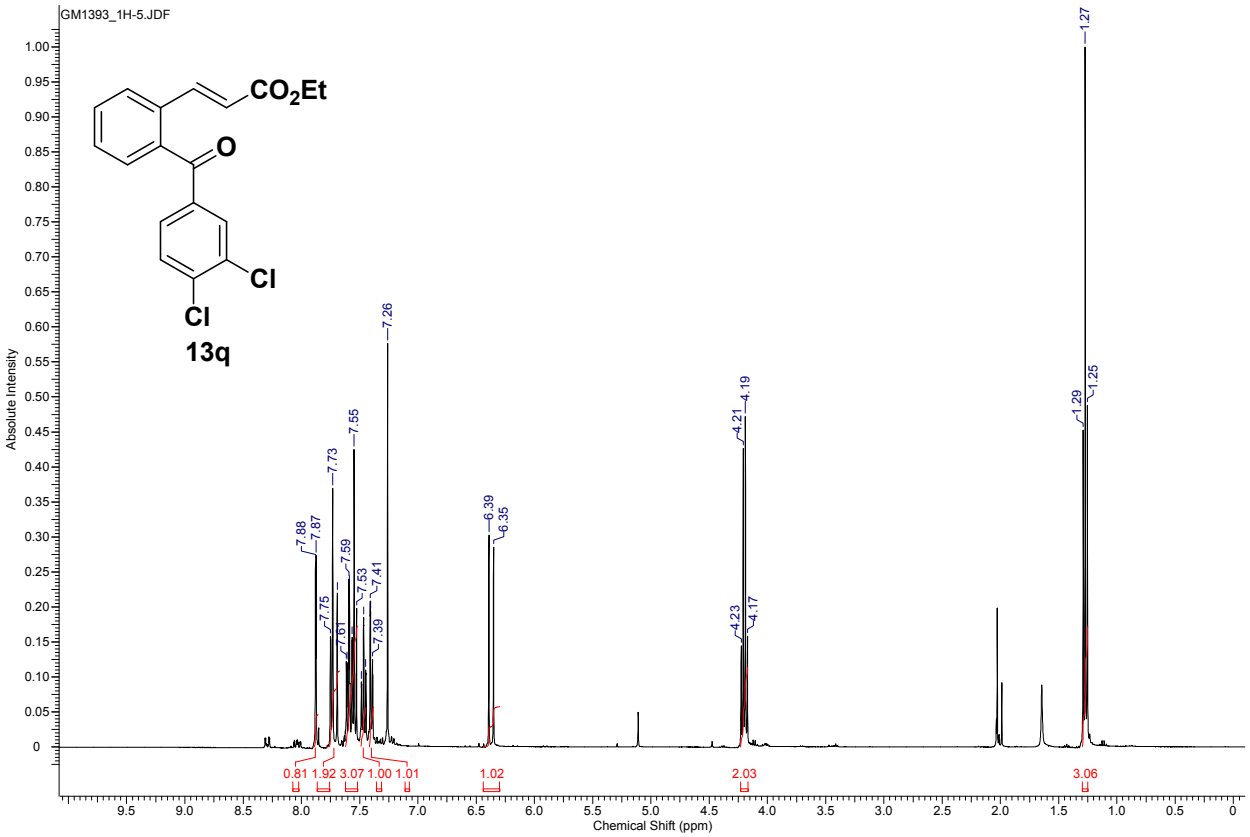

GM1092_13C-2.jdf
Cl
CO2Et
O
OMe
13n
Normalized Intensity
Chemical Shift (ppm)
194.62
165.90
164.09
140.30
138.07
136.43
132.68
130.16
129.01
126.97
121.86
113.86
77.33
77.00
76.67
60.60
55.52
14.13

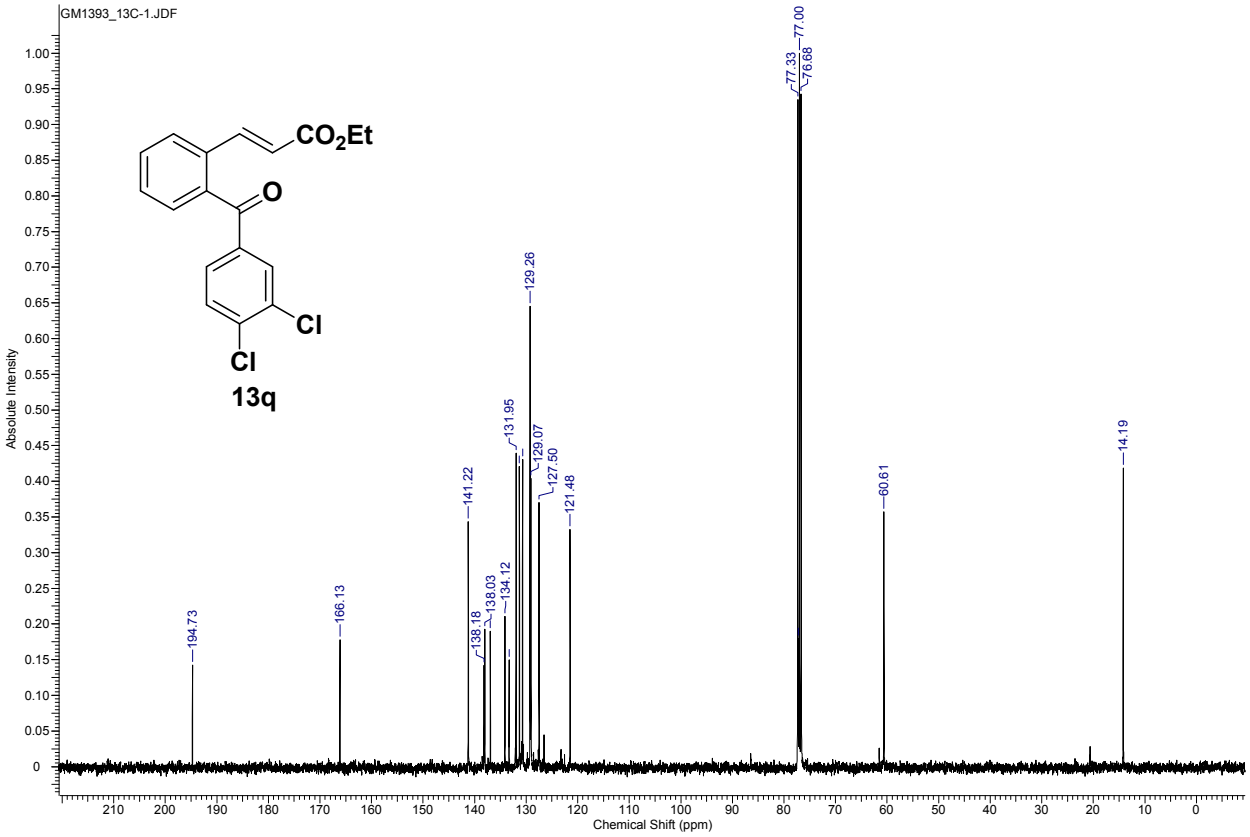

GM1077_1H-4.jdf
Cl
CO2Et
O
Br
13o
Normalized Intensity
Chemical Shift (ppm)
7.63
7.62
7.70
7.37
7.26
7.41
7.60
6.39
6.35
4.20
4.19
4.22
4.18
1.27
1.28
1.26
1.02
5.03
1.01
1.00
1.01
2.01
3.01

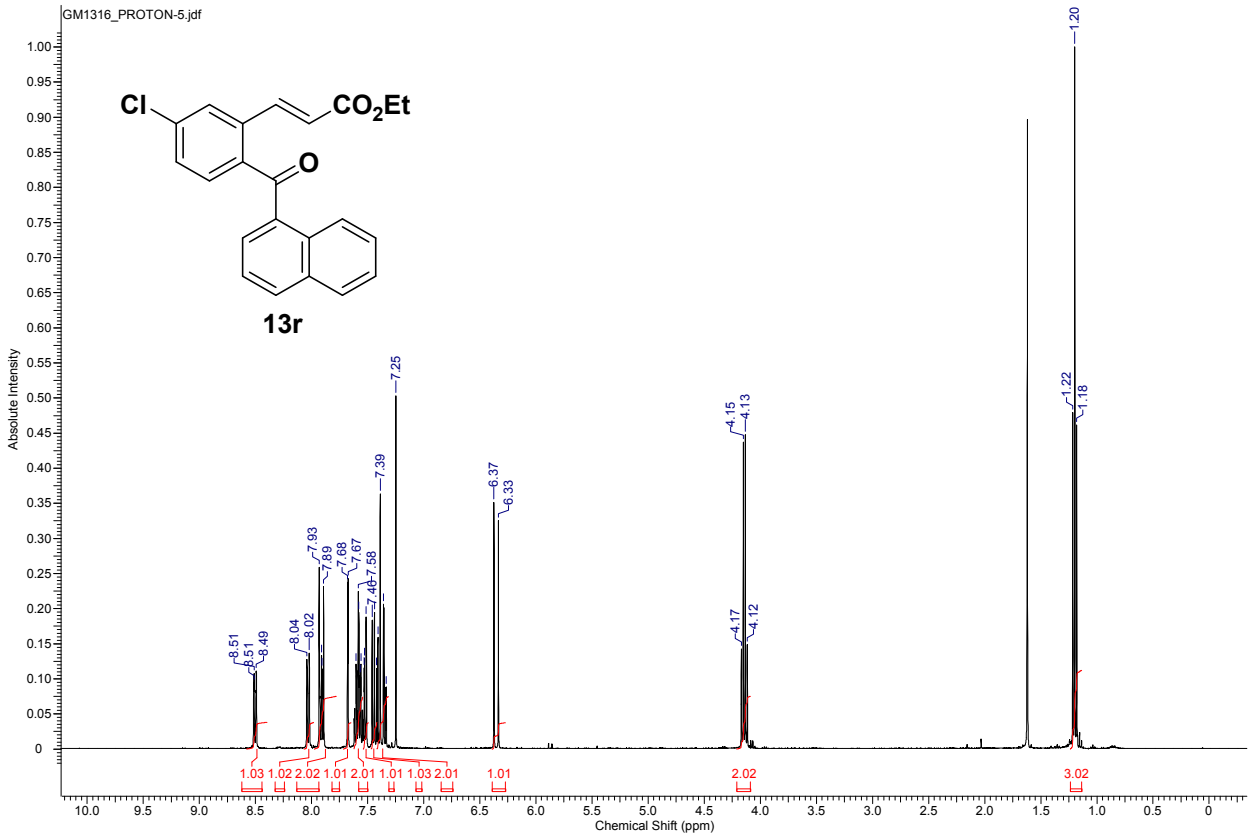

GM1077_13C-2.jdf
Cl
CO2Et
O
Br
13o
Normalized Intensity
Chemical Shift (ppm)
77.00
77.26
76.75
132.01
131.65
129.13
127.39
122.41
140.13
137.34
135.79
195.00
165.82
60.76
14.18

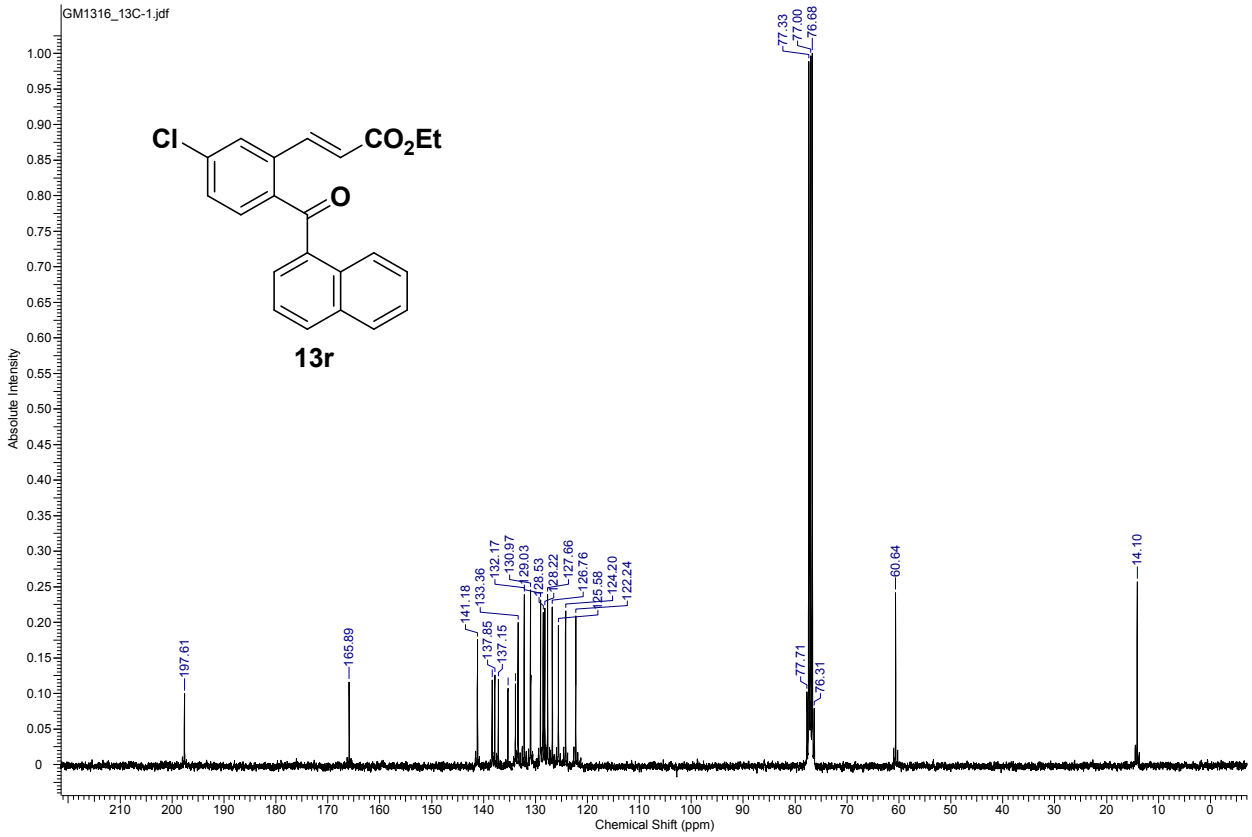

GM1055_PROTON-4.jdf
CO2Et
O
OMe
Br
13p
Normalized Intensity
Chemical Shift (ppm)
7.66
7.64
7.58
7.56
7.44
7.43
7.39
7.38
7.32
7.26
7.00
6.98
6.38
6.34
4.18
4.16
4.14
4.13
3.70
1.26
1.24
1.22
2.00 2.00 2.00 1.00 1.01 1.01 2.05 3.03 3.03

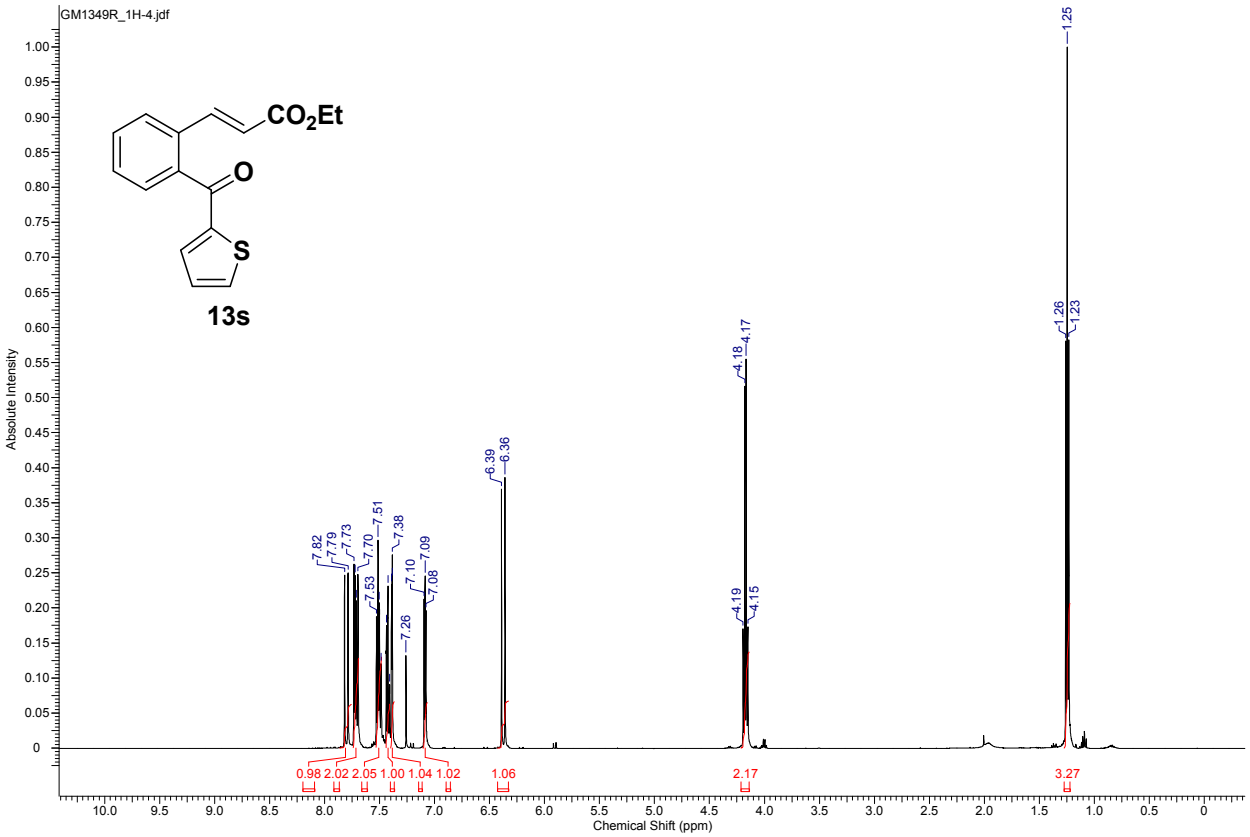

GM1055_13C-1.jdf
CO2Et
O
OMe
Br
13p
Normalized Intensity
Chemical Shift (ppm)
195.60
166.10
156.84
140.32
136.18
133.64
131.96
130.94
130.67
129.01
121.57
118.92
112.14
77.33
77.00
76.68
60.56
55.84
14.16

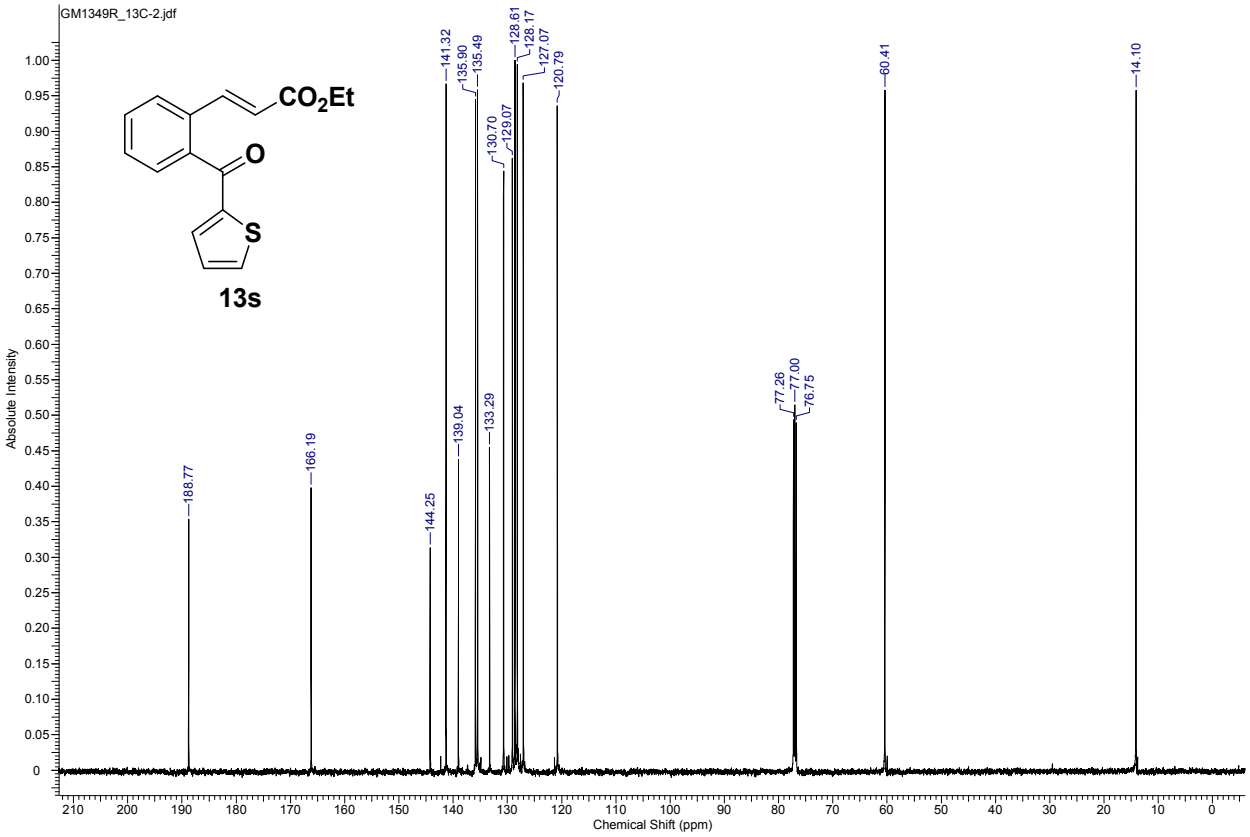

GM1393_1H-5.JDF
CO2Et
O
Cl
Cl
13q
Absolute Intensity
Chemical Shift (ppm)
7.88
7.87
7.76
7.73
7.61
7.59
7.55
7.53
7.41
7.39
7.26
6.39
6.35
4.23
4.21
4.19
4.17
1.29
1.27
1.25
0.81
1.92
3.07
1.00
1.01
1.02
2.03
3.06

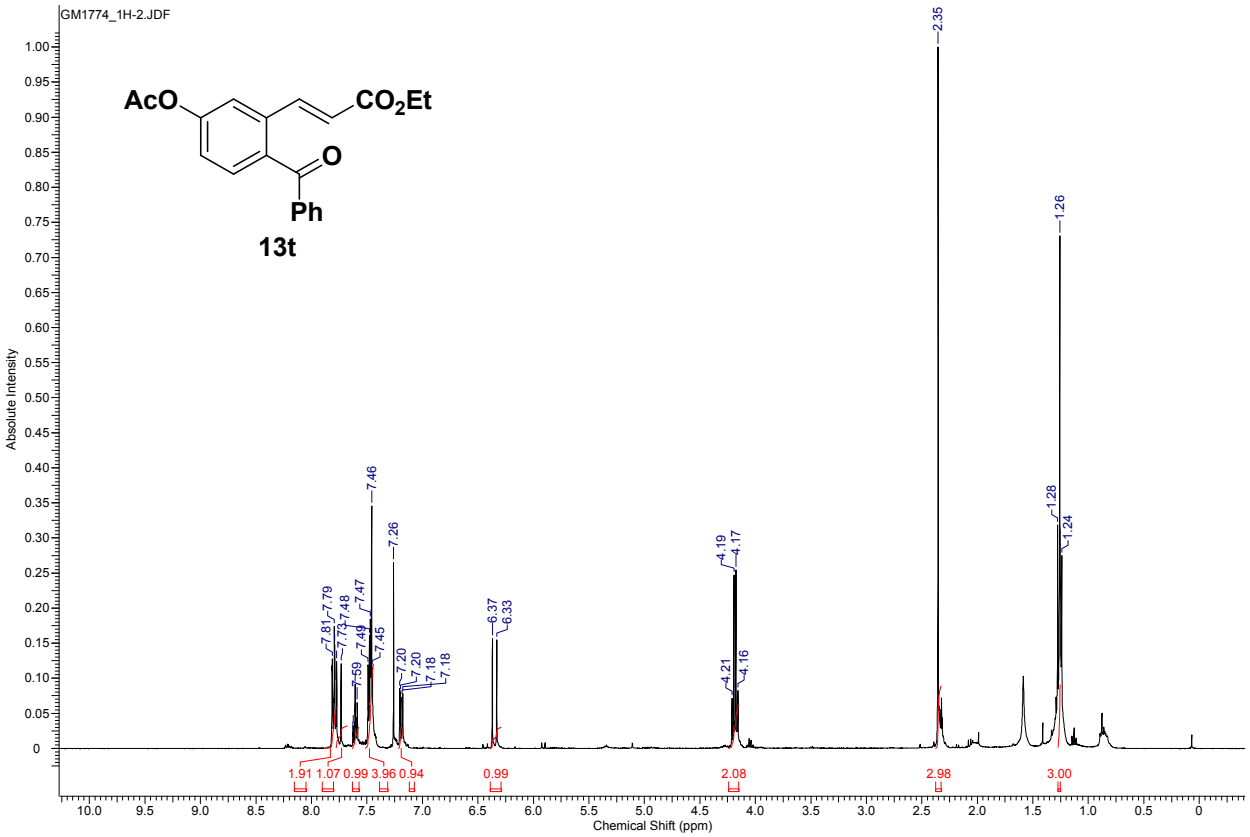

GM1393_13C-1.JDF
CO2Et
O
Cl
Cl
13q
Absolute Intensity
Chemical Shift (ppm)
194.73
166.13
141.22
138.18
138.03
134.12
131.95
129.26
129.07
127.50
121.48
77.33
77.00
76.68
60.61
14.19

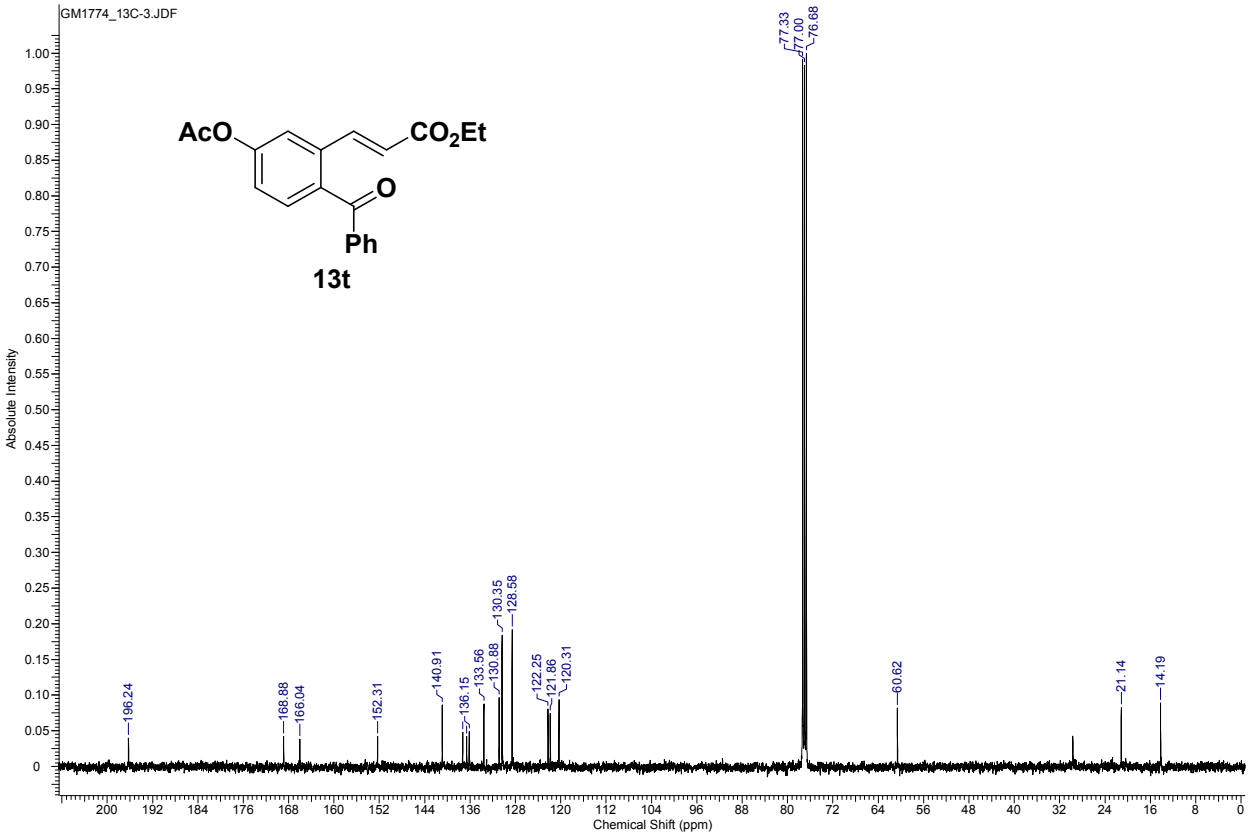

GM1316_PROTON-5.jdf
Cl
CO2Et
O
13r
Absolute Intensity
Chemical Shift (ppm)
8.51
8.51
8.49
8.04
8.02
7.93
7.89
7.68
7.67
7.58
7.48
7.39
7.25
6.37
6.33
4.17
4.15
4.13
4.12
1.22
1.20
1.18
1.03 1.02 2.02 1.01 2.01 1.01 1.03 2.01
1.01
2.02
3.02

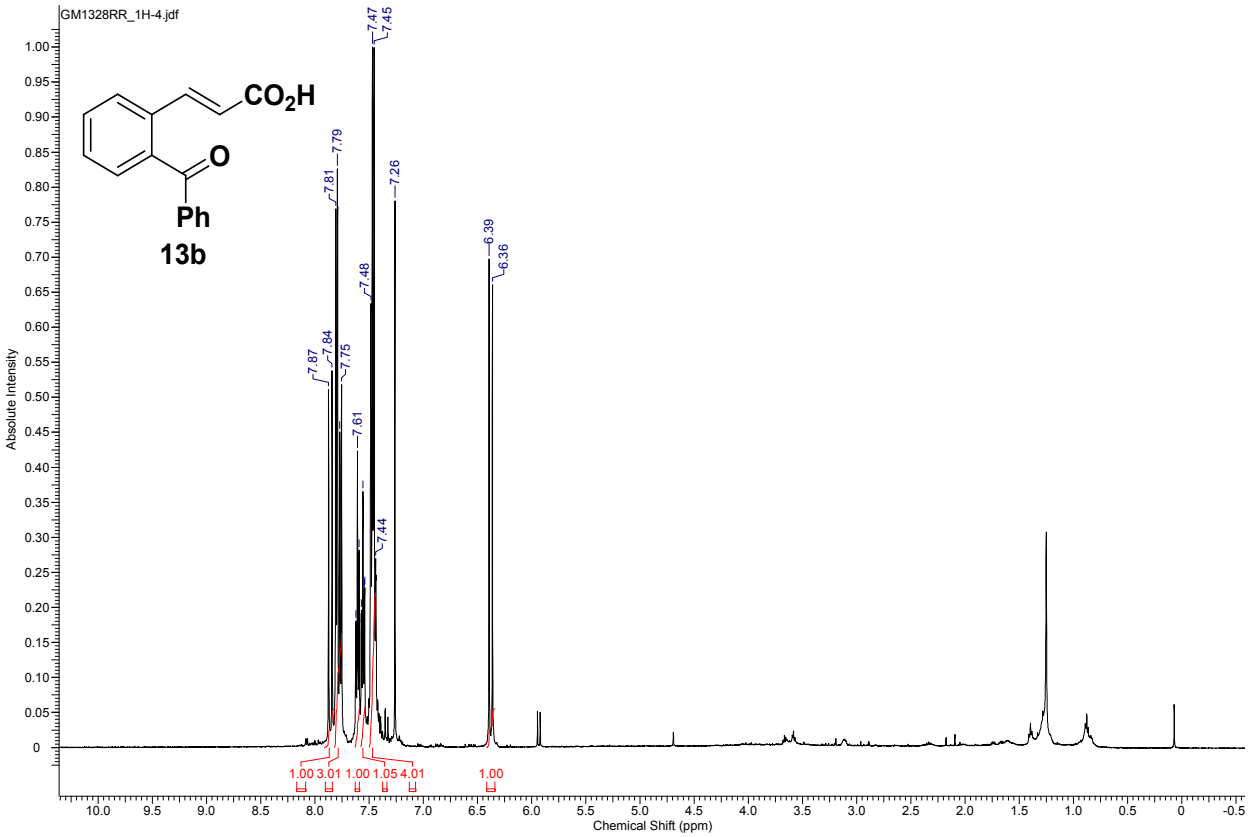

GM1316_13C-1.jdf
Cl
CO2Et
O
13r
Absolute Intensity
Chemical Shift (ppm)
197.61
165.89
141.18
137.85
137.15
133.36
132.17
130.97
129.03
128.53
128.22
127.66
126.76
125.58
124.20
122.24
77.33
77.00
76.68
77.71
76.31
60.64
14.10

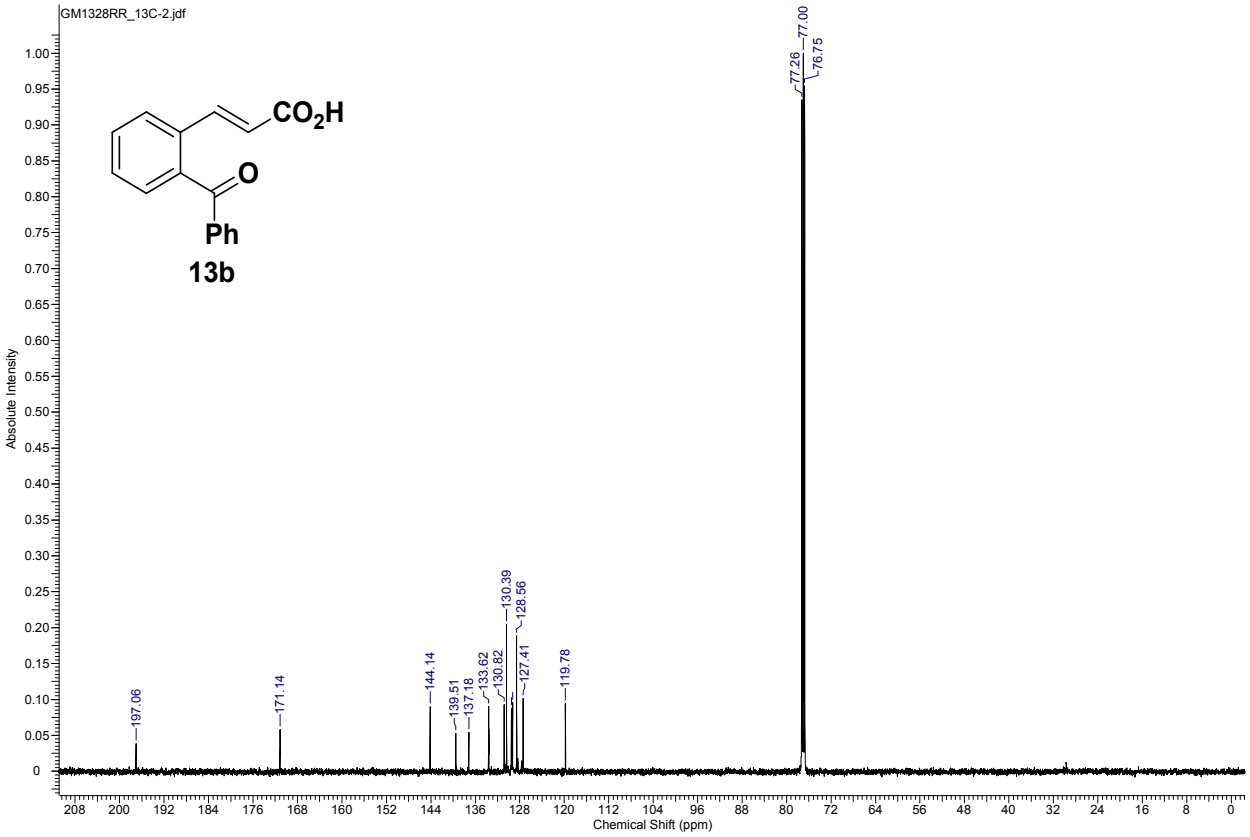

GM1349R_1H-4.jdf
CO2Et
O
S
13s
Absolute Intensity
Chemical Shift (ppm)
1.25
1.26
1.23
4.18
4.17
4.19
4.15
6.39
6.36
7.82
7.79
7.73
7.70
7.51
7.53
7.38
7.10
7.09
7.08
7.26
0.98 2.02 2.05 1.00 1.04 1.02
1.06
2.17
3.27

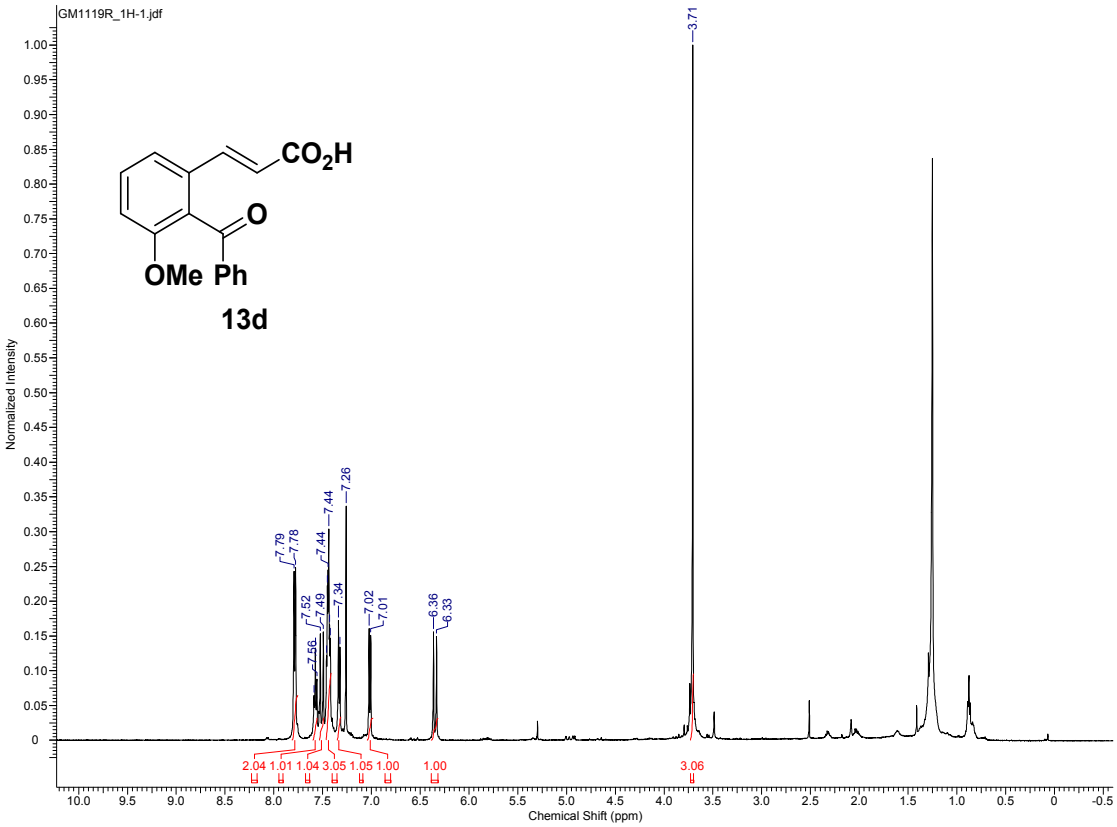

GM1349R_13C-2.jdf
CO2Et
O
S
13s
Absolute Intensity
Chemical Shift (ppm)
188.77
166.19
144.25
141.32
139.04
135.90
135.49
133.29
130.70
129.07
128.61
128.17
127.07
120.79
77.26
77.00
76.75
60.41
14.10

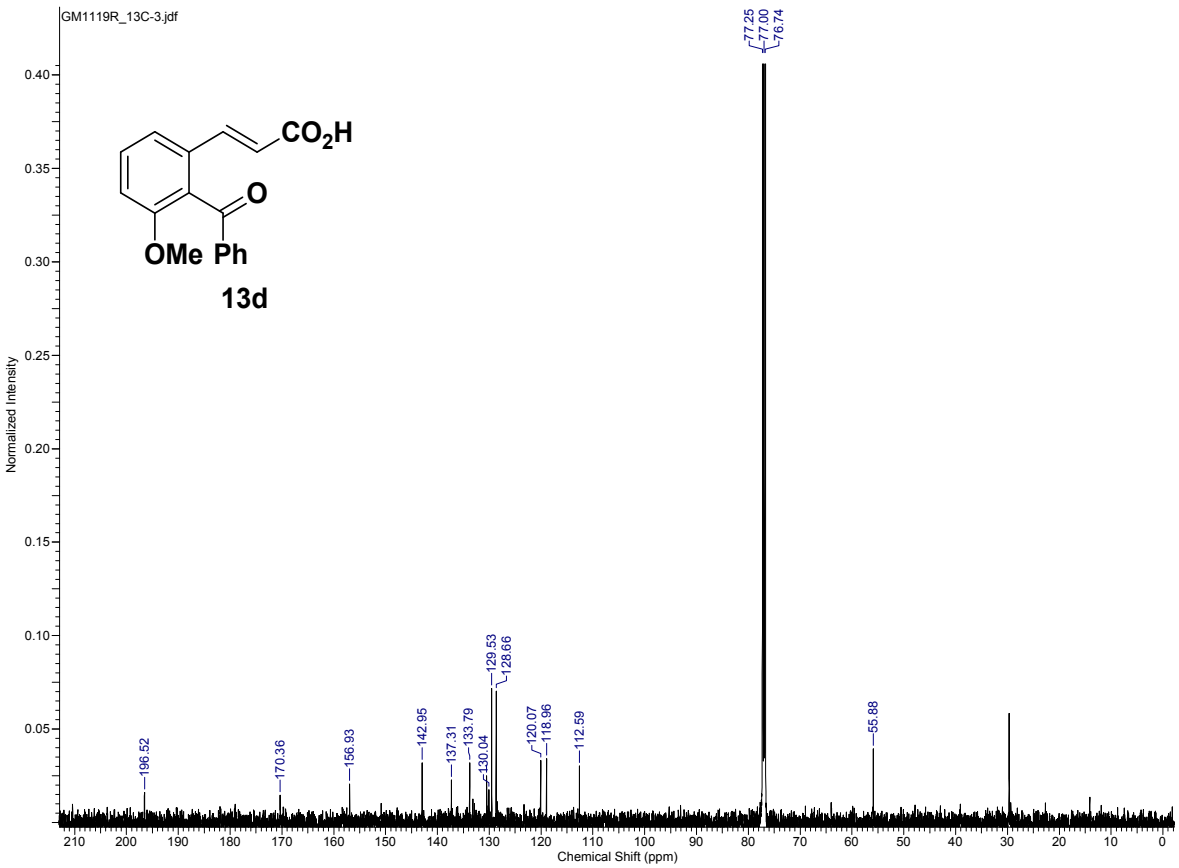

GM1774_1H-2.JDF
AcO
CO2Et
O
Ph
13t
Absolute Intensity
Chemical Shift (ppm)
2.35
1.26
1.28
1.24
7.46
7.26
7.81
7.79
7.73
7.48
7.47
7.49
7.45
7.59
7.20
7.20
7.18
7.18
6.37
6.33
4.19
4.17
4.21
4.16
1.91
1.07
0.99
3.96
0.94
0.99
2.08
2.98
3.00

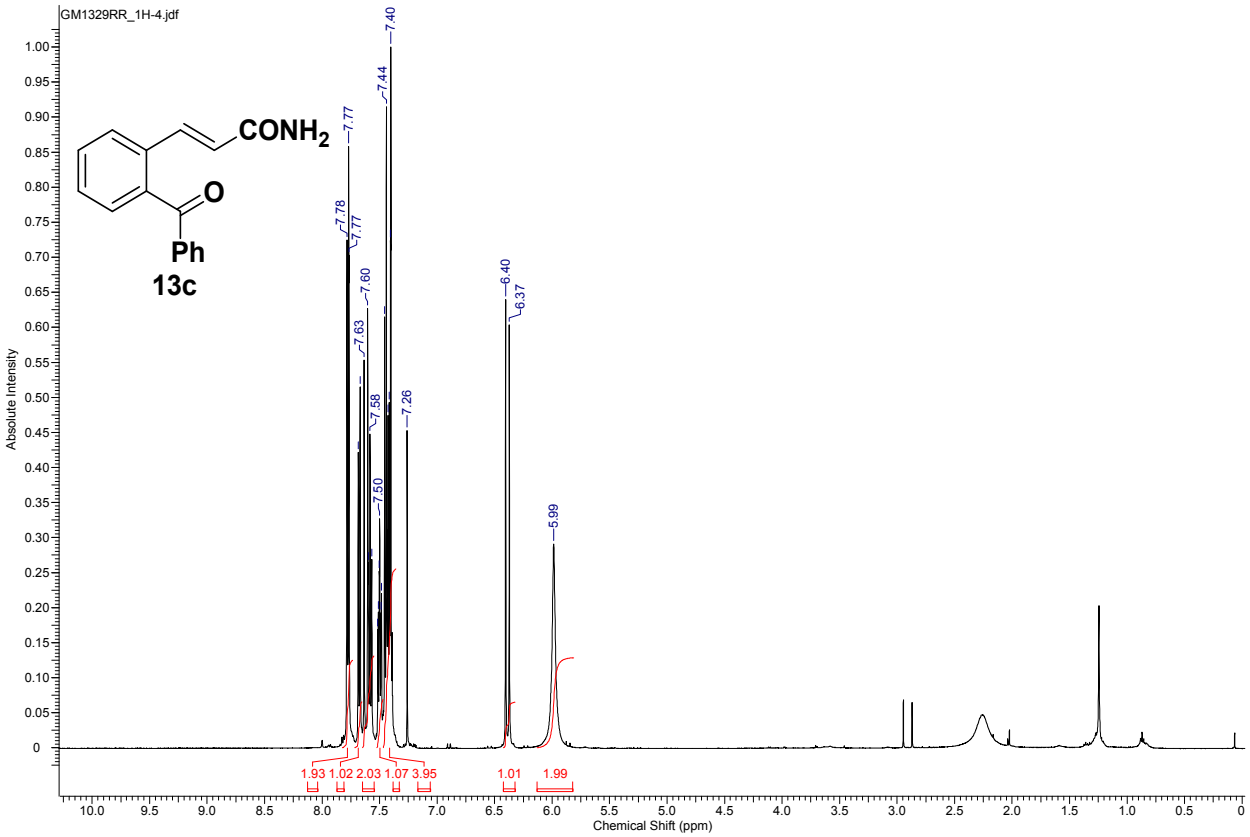

GM1774_13C-3.JDF
AcO
CO2Et
O
Ph
13t
Absolute Intensity
Chemical Shift (ppm)
77.33
77.00
76.68
196.24
168.88
166.04
152.31
140.91
136.15
133.56
130.88
130.35
128.58
122.25
121.86
120.31
60.62
21.14
14.19

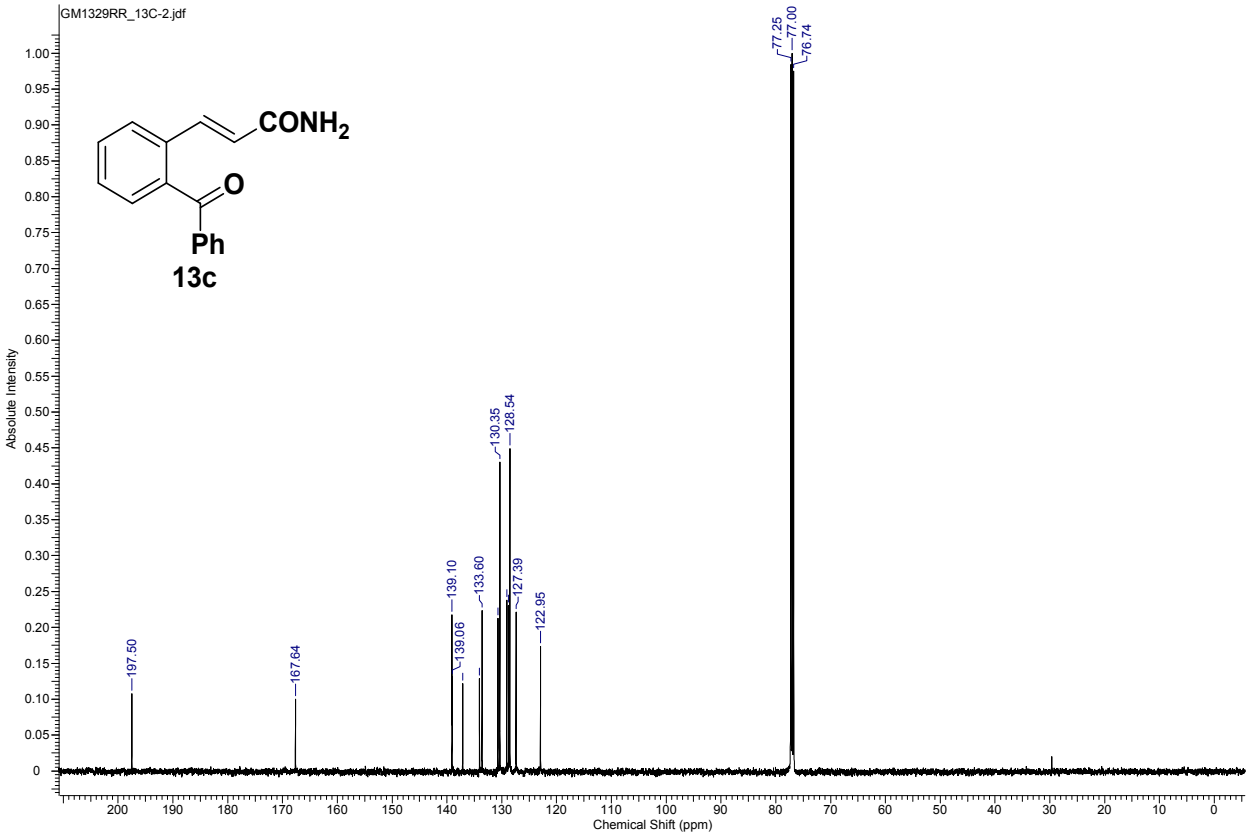

GM1328RR_1H-4.jdf
CO2H
O
Ph
13b
7.87
7.84
7.81
7.79
7.75
7.61
7.48
7.47
7.45
7.44
7.26
6.39
6.36
1.00 3.01 1.00 1.05 4.01 1.00
Absolute Intensity
Chemical Shift (ppm)

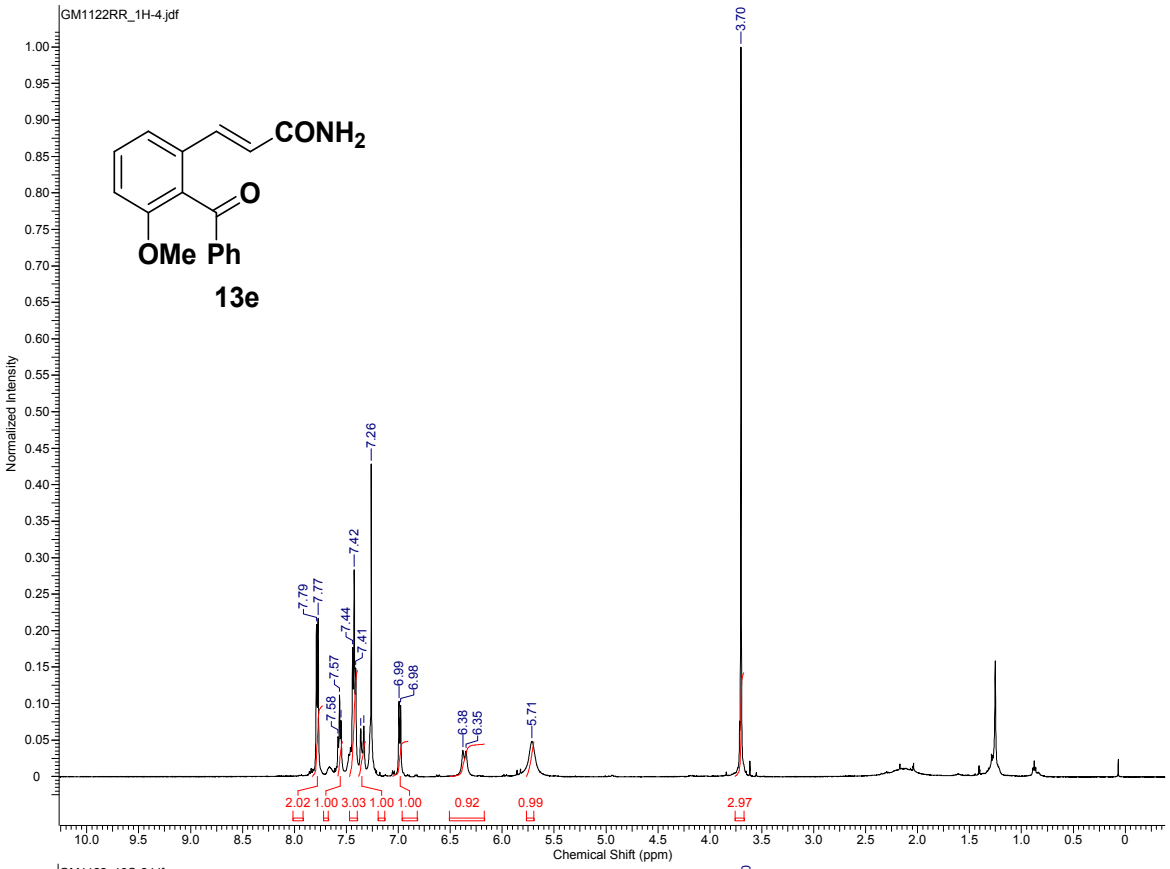

GM1328RR_13C-2.jdf
CO2H
O
Ph
13b
197.06
171.14
144.14
139.51
137.18
133.62
130.82
130.39
128.56
127.41
119.78
77.26
77.00
76.75
Absolute Intensity
Chemical Shift (ppm)

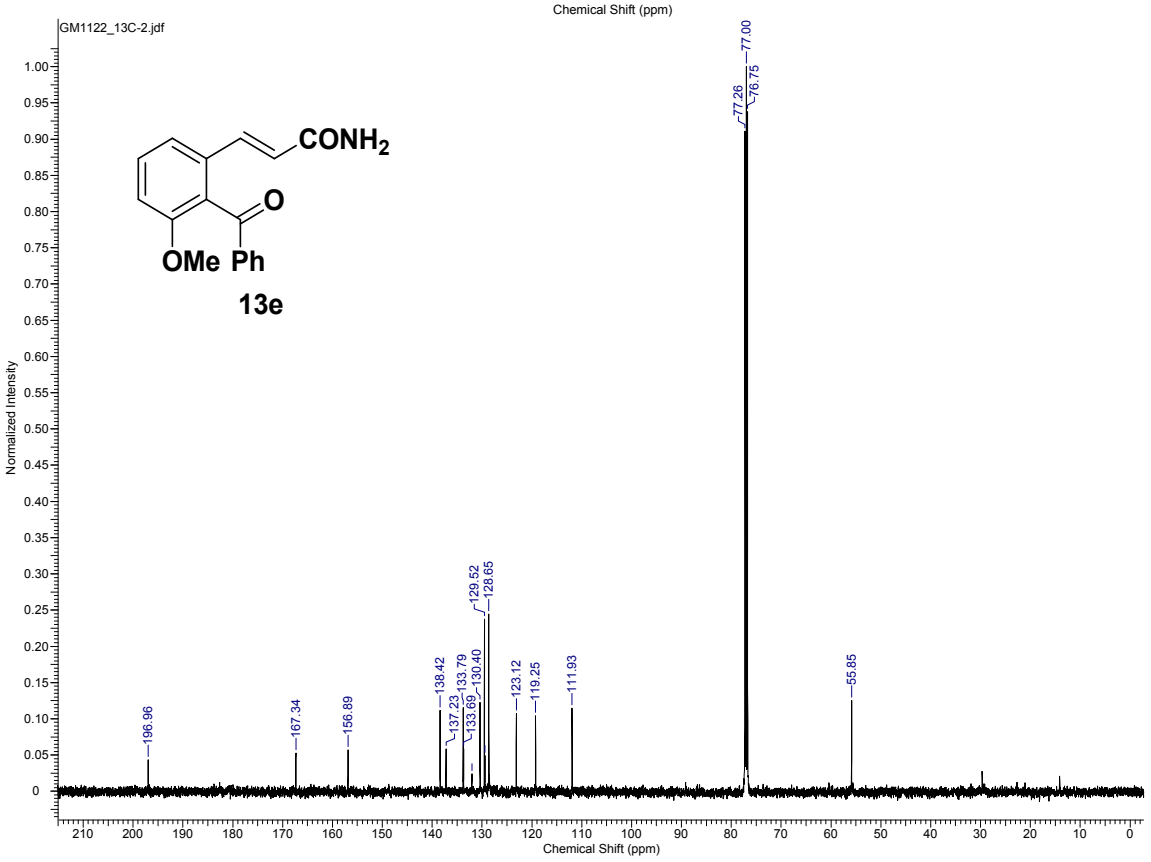

GM1119R_1H-1.jdf
CO2H
O
OMe Ph
13d
Normalized Intensity
Chemical Shift (ppm)
3.71
7.79
7.78
7.44
7.44
7.26
7.52
7.49
7.34
7.56
7.02
7.01
6.36
6.33
2.04 1.01 1.04 3.05 1.05 1.00
1.00
3.06

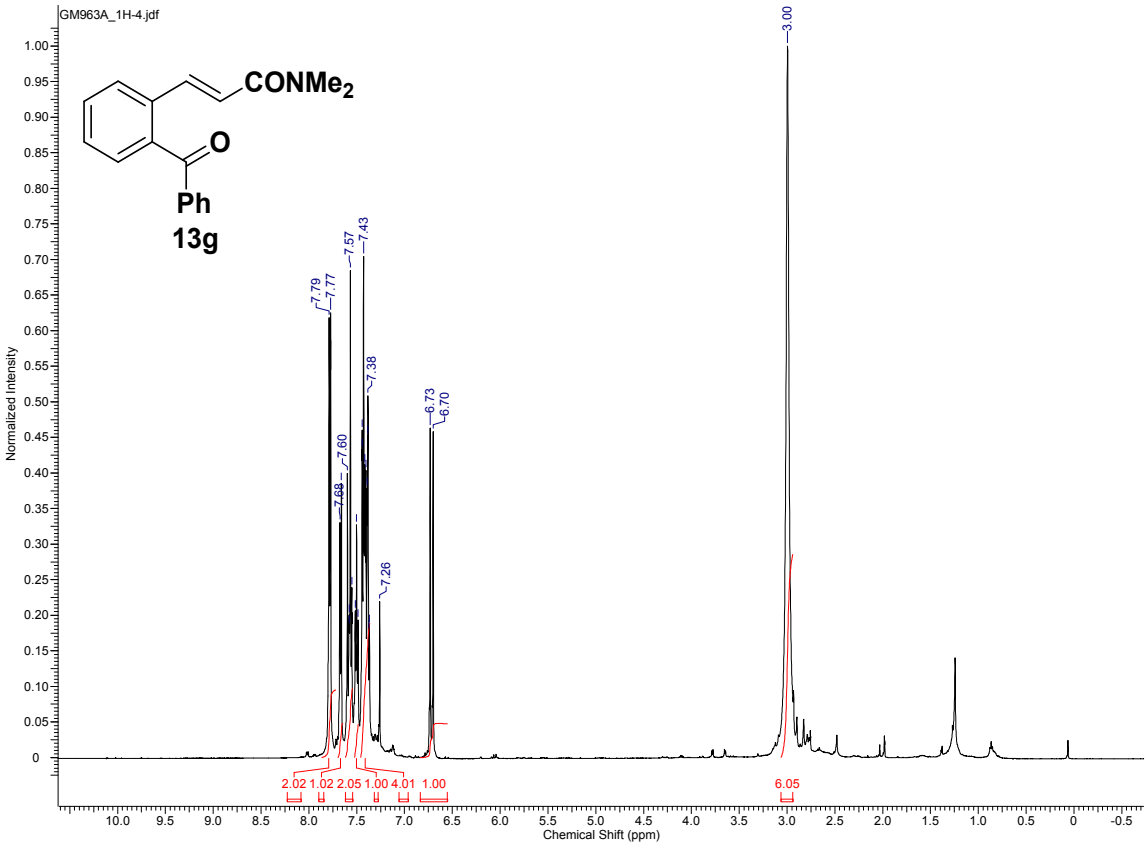

GM1119R_13C-3.jdf
CO2H
O
OMe Ph
13d
Normalized Intensity
Chemical Shift (ppm)
77.25
77.00
76.74
196.52
170.36
156.93
142.95
137.31
133.79
130.04
129.53
128.66
120.07
118.96
112.59
55.88


GM1329RR_1H-4.jdf
CONH2
O
Ph
13c
Absolute Intensity
Chemical Shift (ppm)
7.78
7.77
7.77
7.60
7.63
7.58
7.50
7.40
7.44
7.26
6.40
6.37
5.99
1.93 1.02 2.03 1.07 3.95
1.01
1.99


GM1329RR_13C-2.jdf
CONH2
O
Ph
13c
Absolute Intensity
Chemical Shift (ppm)
77.25
77.00
76.74
130.35
128.54
139.10
133.60
127.39
122.95
139.06
197.50
167.64


GM1122RR_1H-4.jdf
CONH2
O
OMe Ph
13e
Normalized Intensity
Chemical Shift (ppm)
3.70
7.79
7.77
7.57
7.58
7.42
7.44
7.41
7.26
6.99
6.98
6.38
6.35
5.71
2.02 1.00 3.03 1.00 1.00 0.92 0.99 2.97


GM1122_13C-2.jdf
CONH2
O
OMe Ph
13e
Normalized Intensity
Chemical Shift (ppm)
77.26
77.00
76.75
196.96
167.34
156.89
138.42
137.23
133.79
133.69
130.40
129.52
128.65
123.12
119.25
111.93
55.85


GM963A_1H-4.jdf
CONMe2
O
Ph
13g
Normalized Intensity
Chemical Shift (ppm)
7.79
7.77
7.57
7.43
7.38
7.60
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7.26
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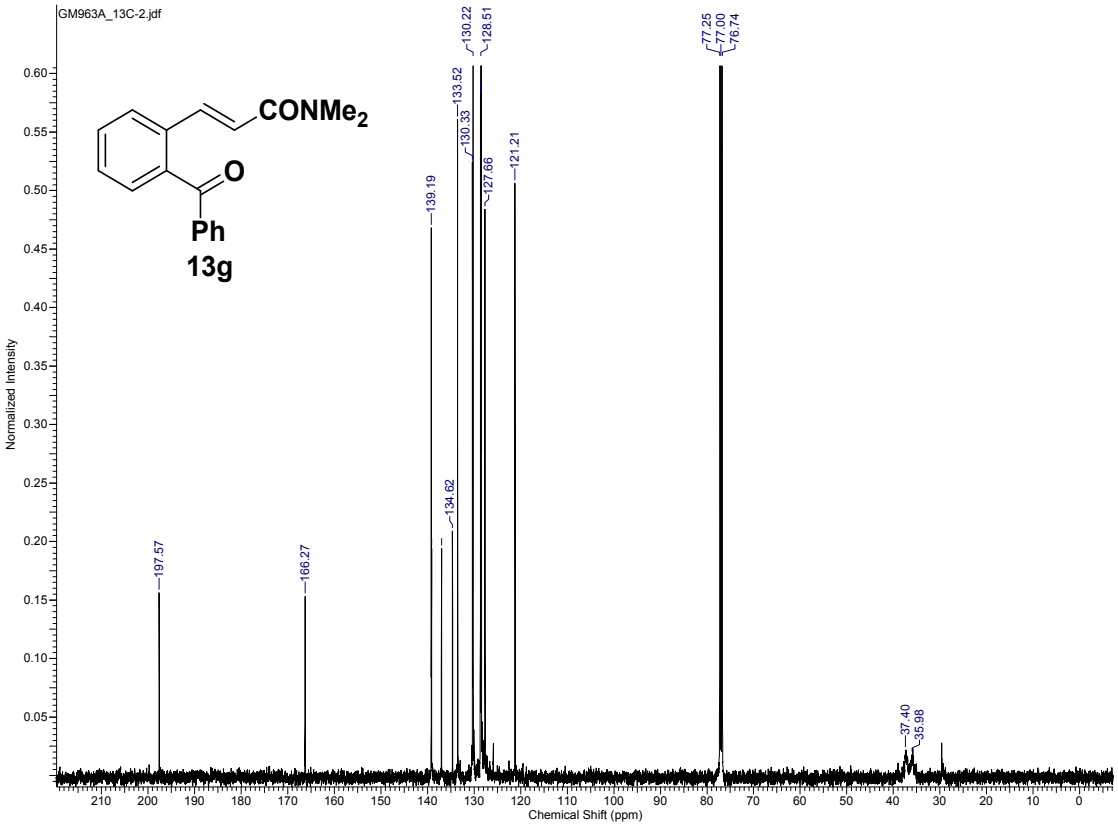
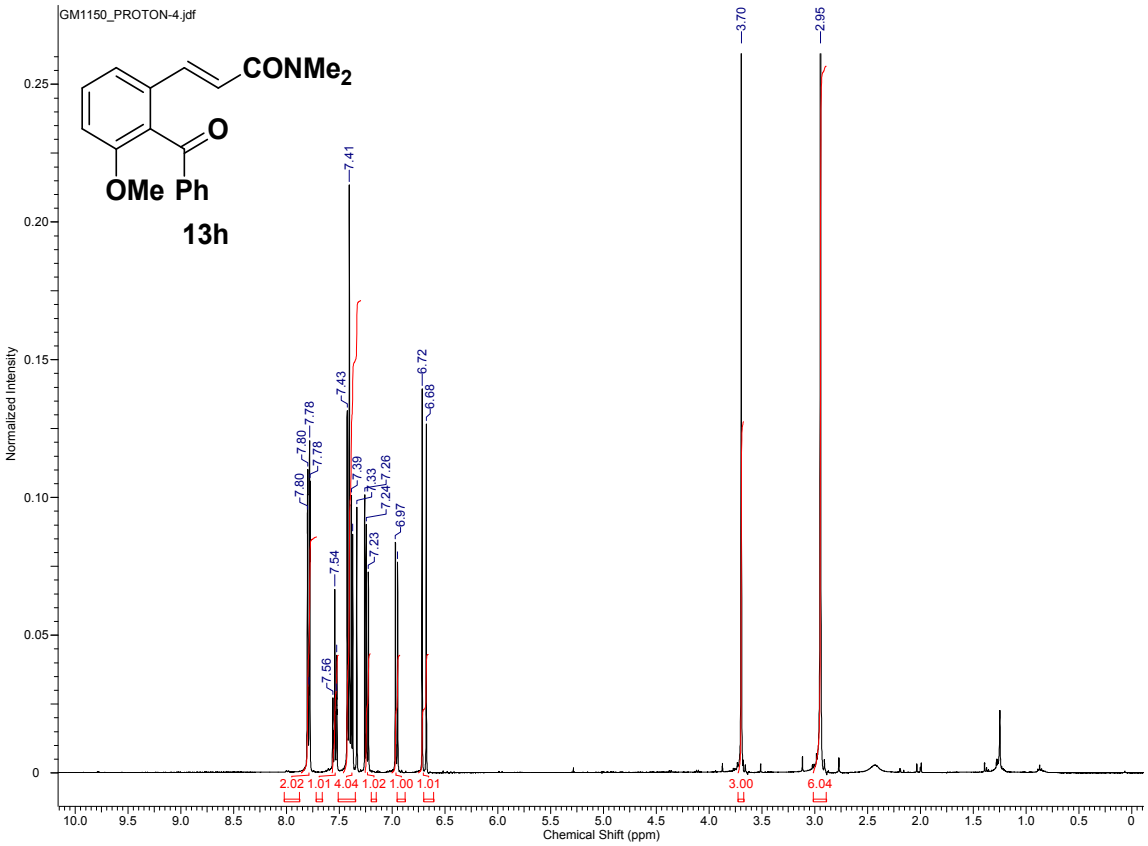
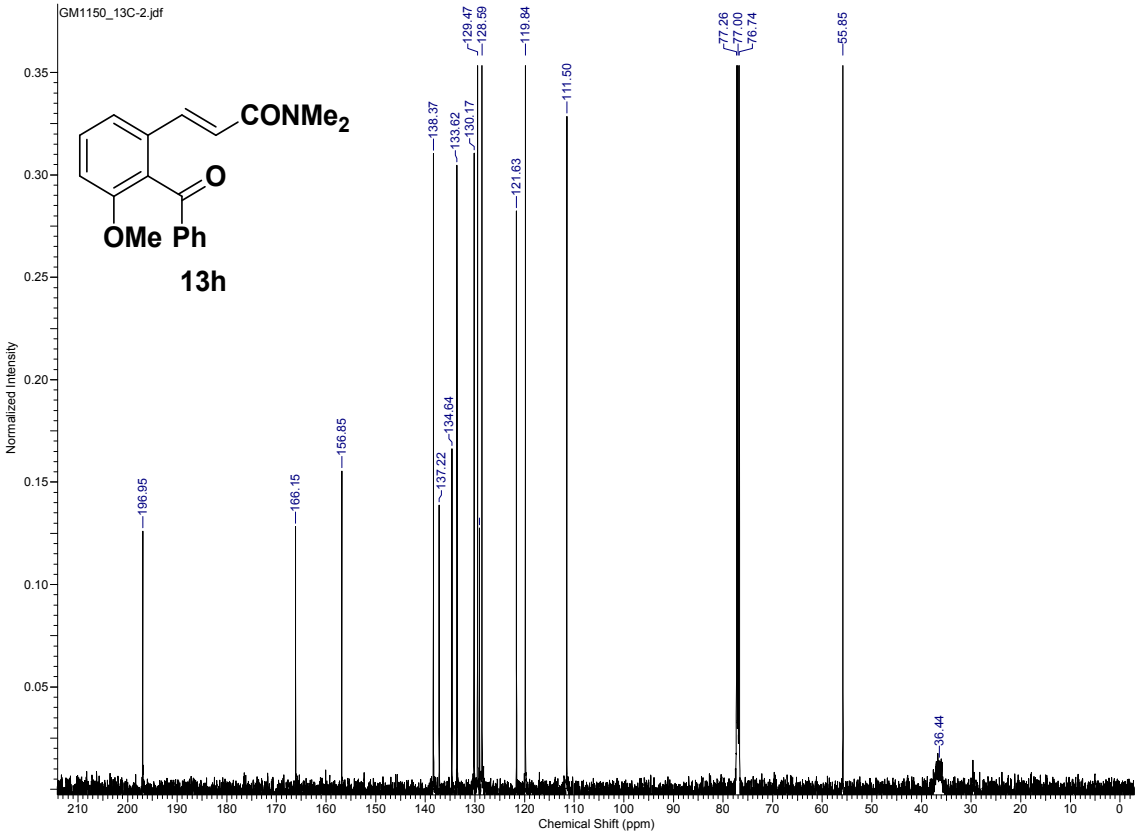
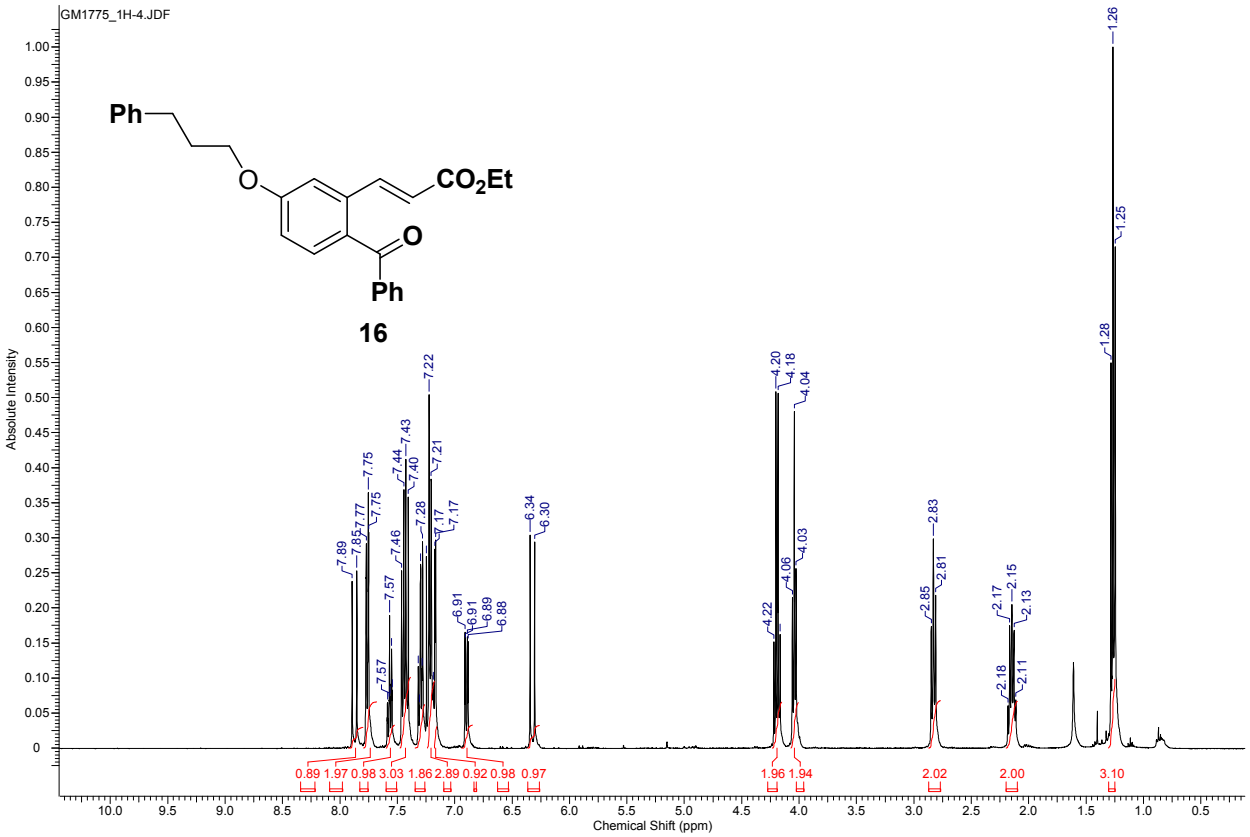
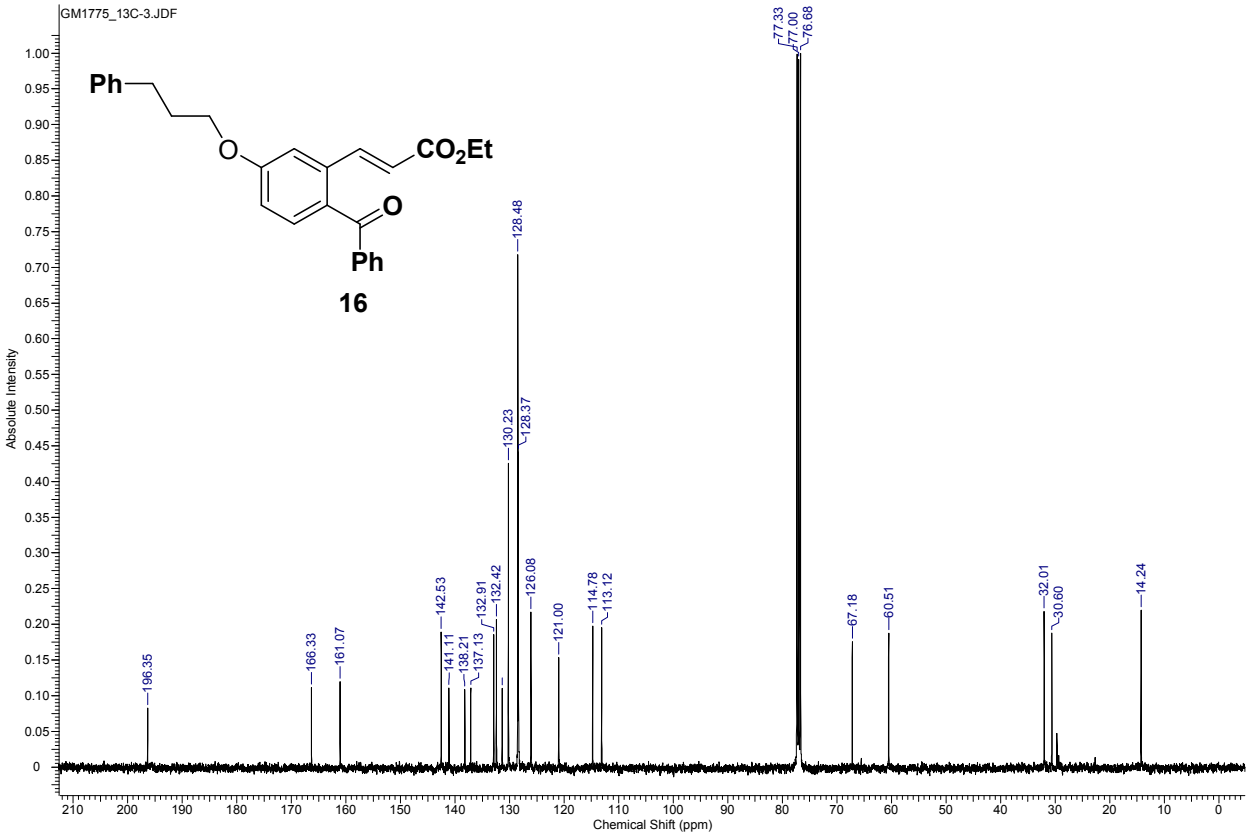
6.70
3.00
2.02 1.02 2.05 1.00 4.01 1.00
6.05

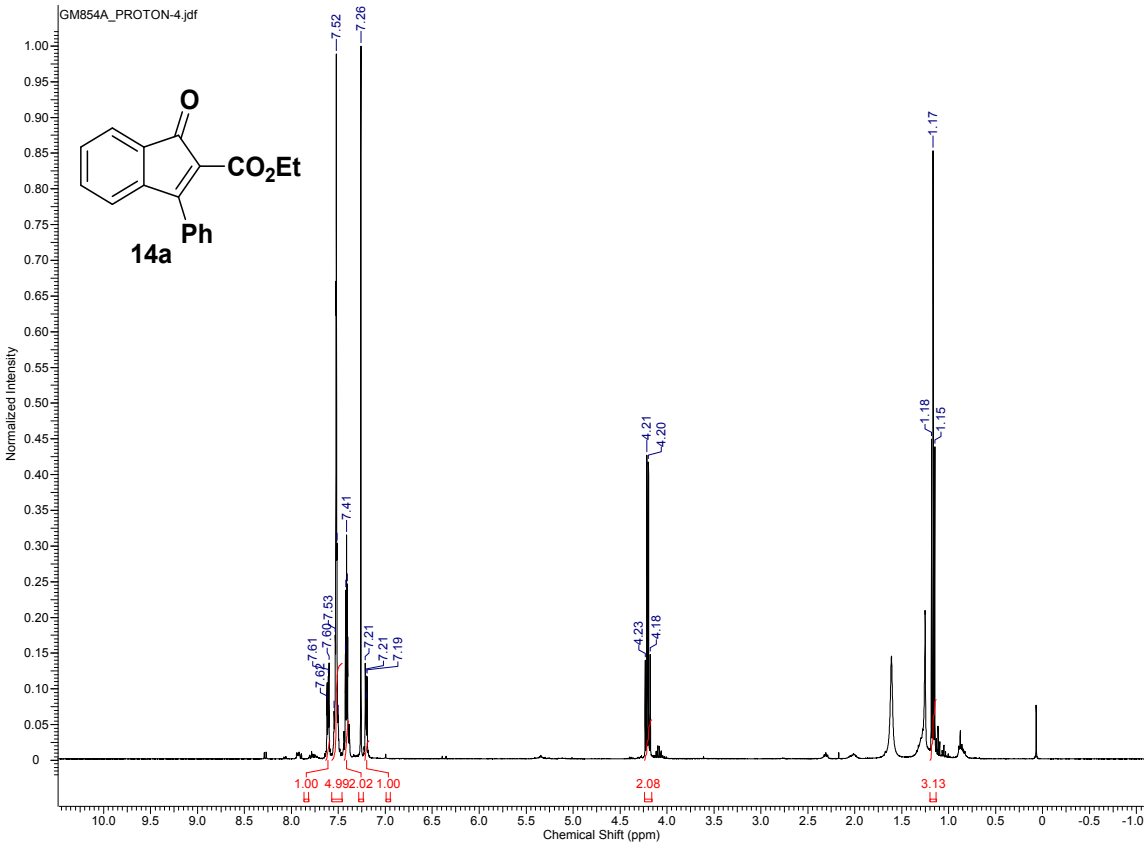

GM963A_13C-2.jdf
CONMe2
O
Ph
13g
Normalized Intensity
Chemical Shift (ppm)
130.22
128.51
133.52
130.33
127.66
121.21
139.19
134.62
77.25
77.00
76.74
197.57
166.27
37.40
35.98

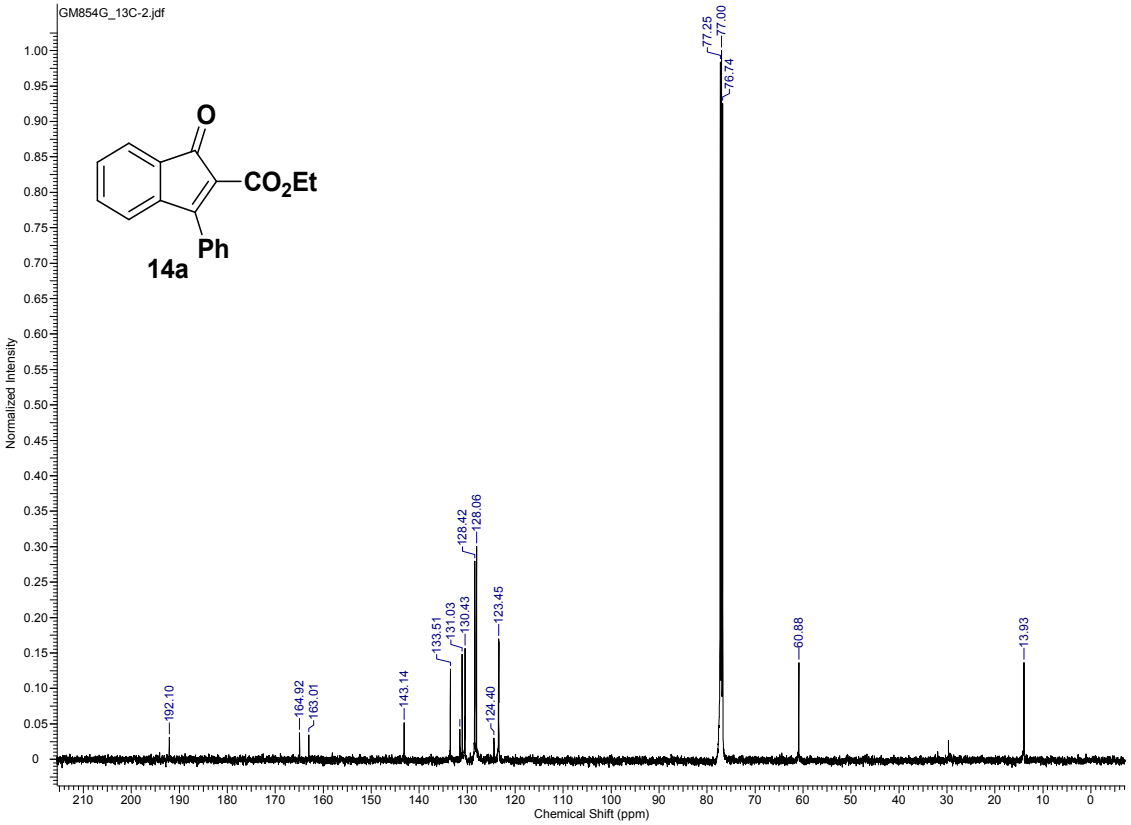

GM1150_PROTON-4.jdf
CONMe2
O
OMe Ph
13h
Normalized Intensity
Chemical Shift (ppm)
3.70
2.95
7.41
7.80
7.78
7.43
7.39
7.33
7.26
7.24
6.97
7.23
7.54
7.56
6.72
6.68
2.02 1.01 4.04 1.02 1.00 1.01
3.00
6.04

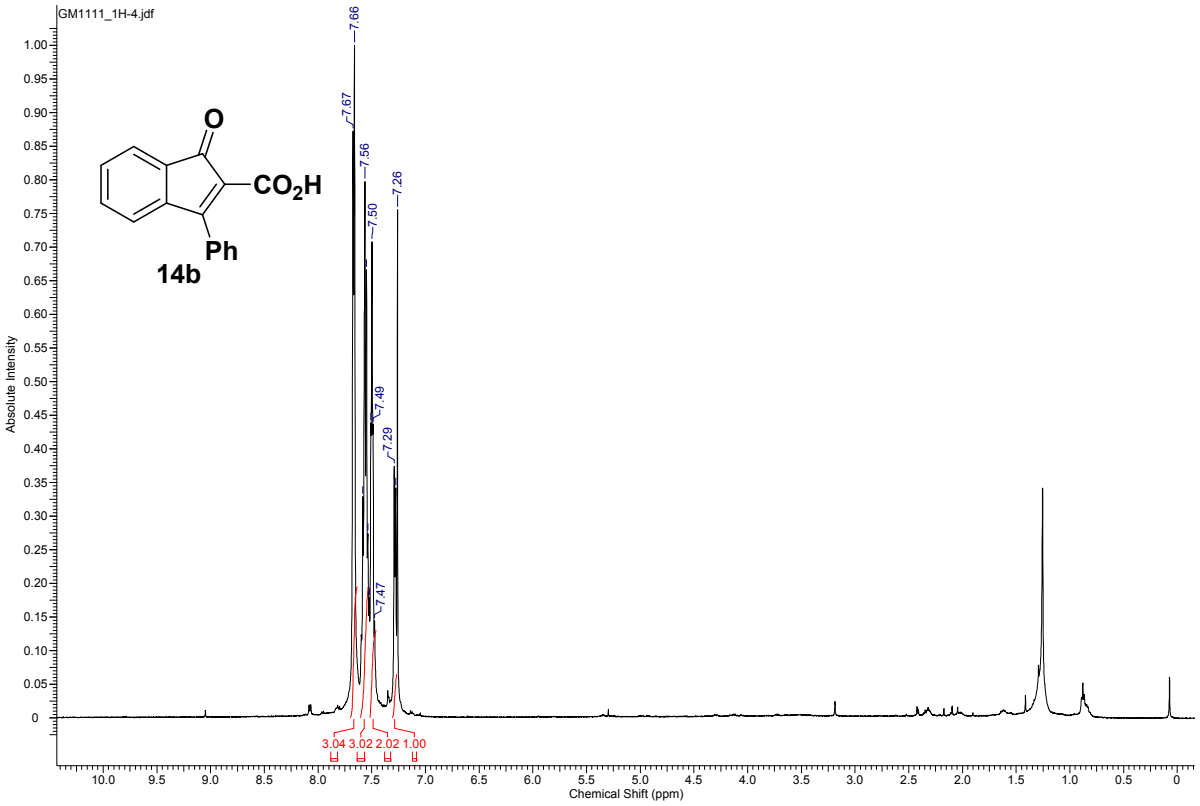

GM1150_13C-2.jdf
CONMe2
O
OMe Ph
13h
Normalized Intensity
Chemical Shift (ppm)
196.95
166.15
156.85
138.37
137.22
134.64
133.62
130.17
129.47
128.59
121.63
119.84
111.50
77.26
77.00
76.74
55.85
36.44

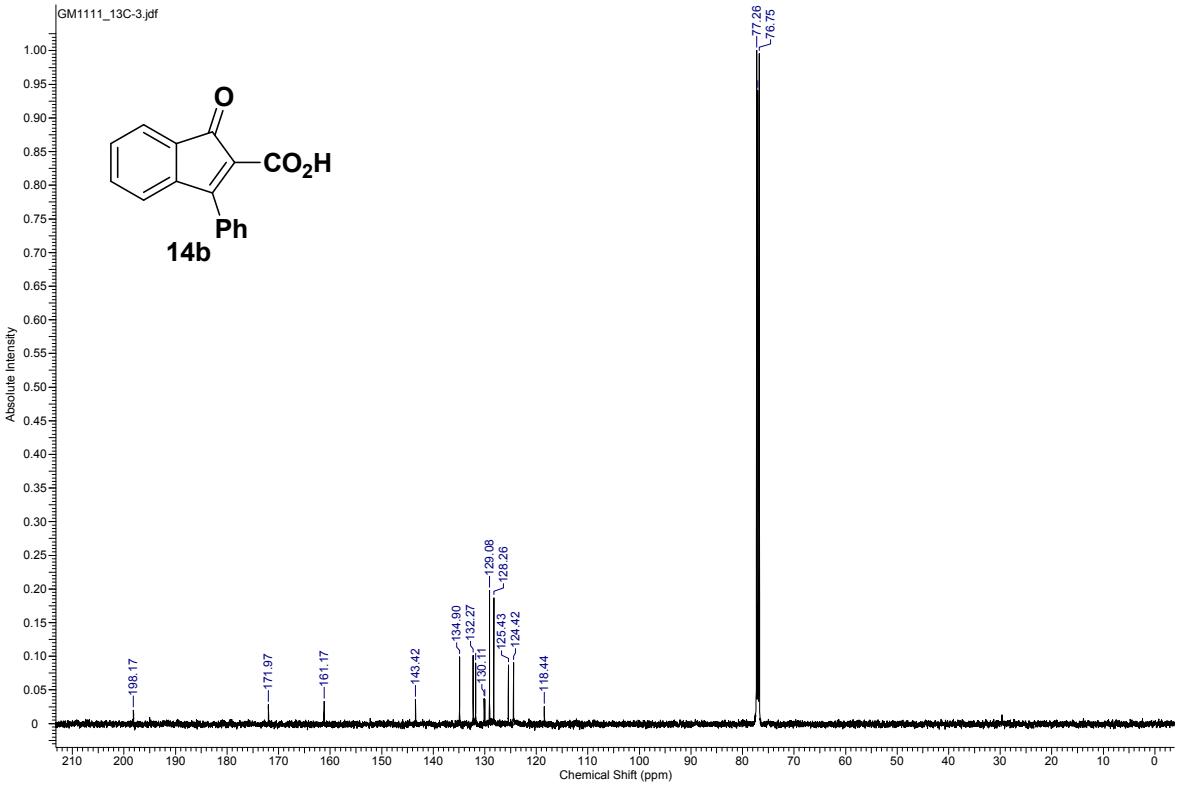

GM1775_1H-4.JDF
Ph
O
CO2Et
O
Ph
16
Absolute Intensity
Chemical Shift (ppm)
0.89 1.97 0.98 3.03 1.86 2.89 0.92 0.98 0.97
1.96 1.94
2.02
2.00
3.10

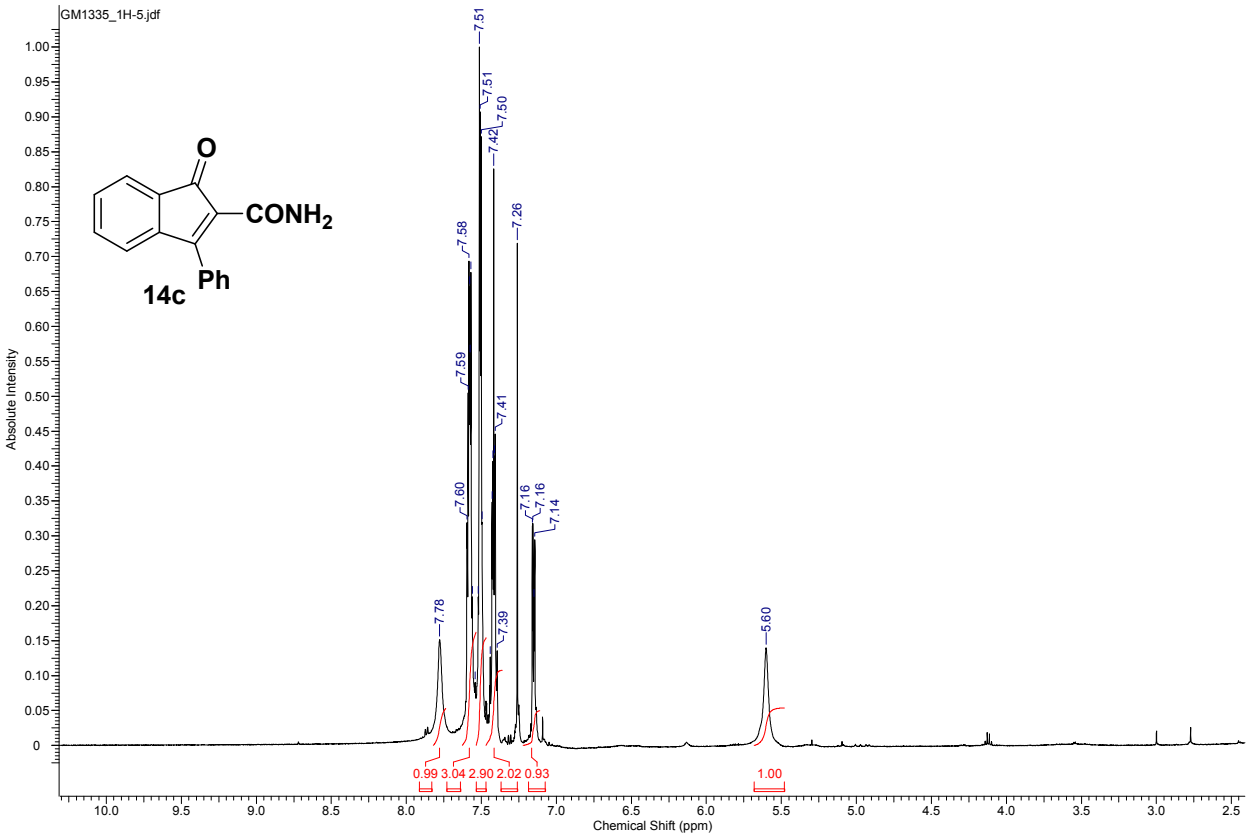

GM1775_13C-3.JDF
Ph
O
CO2Et
O
Ph
16
Absolute Intensity
Chemical Shift (ppm)

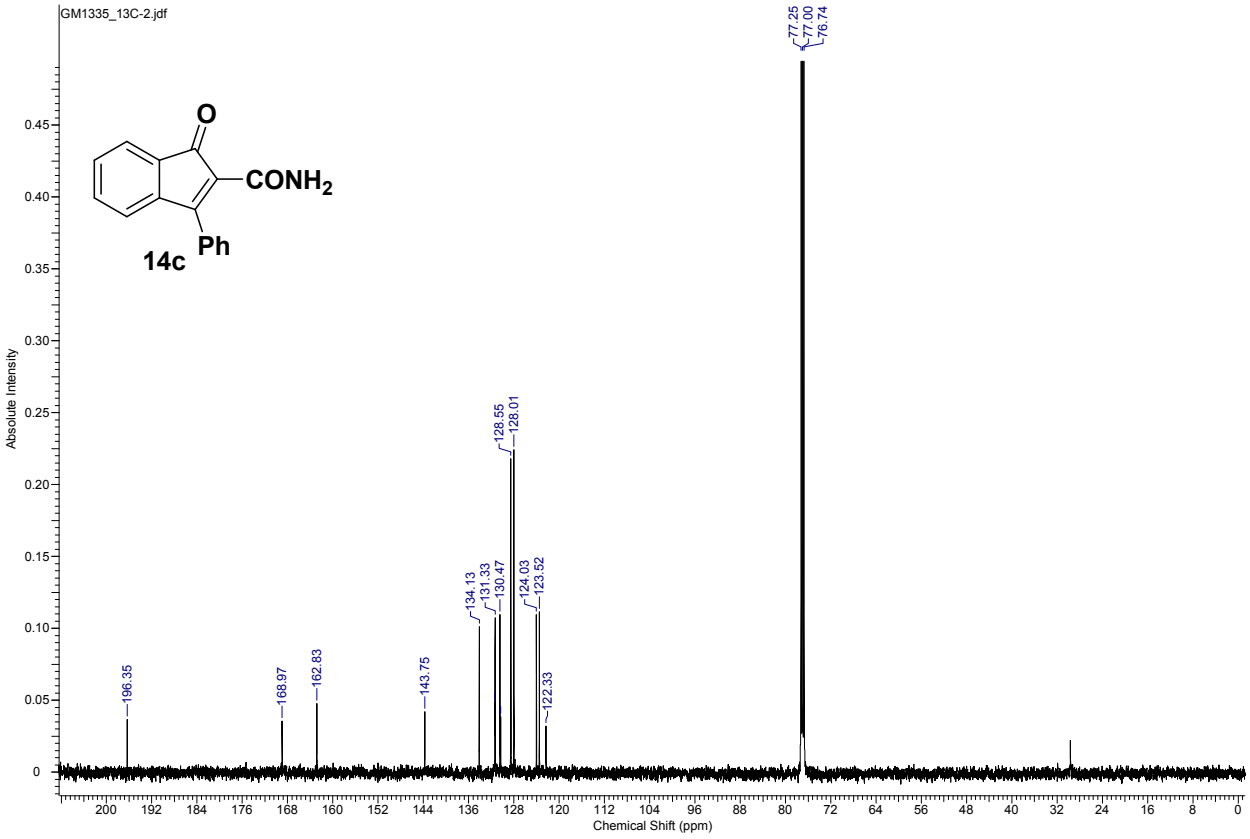

GM854A_PROTON-4.jdf
O
CO2Et
Ph
14a
Normalized Intensity
Chemical Shift (ppm)
7.52
7.26
7.61
7.60
7.53
7.41
7.21
7.21
7.19
4.23
4.21
4.20
4.18
1.18
1.17
1.15
1.00
4.99
2.02
1.00
2.08
3.13

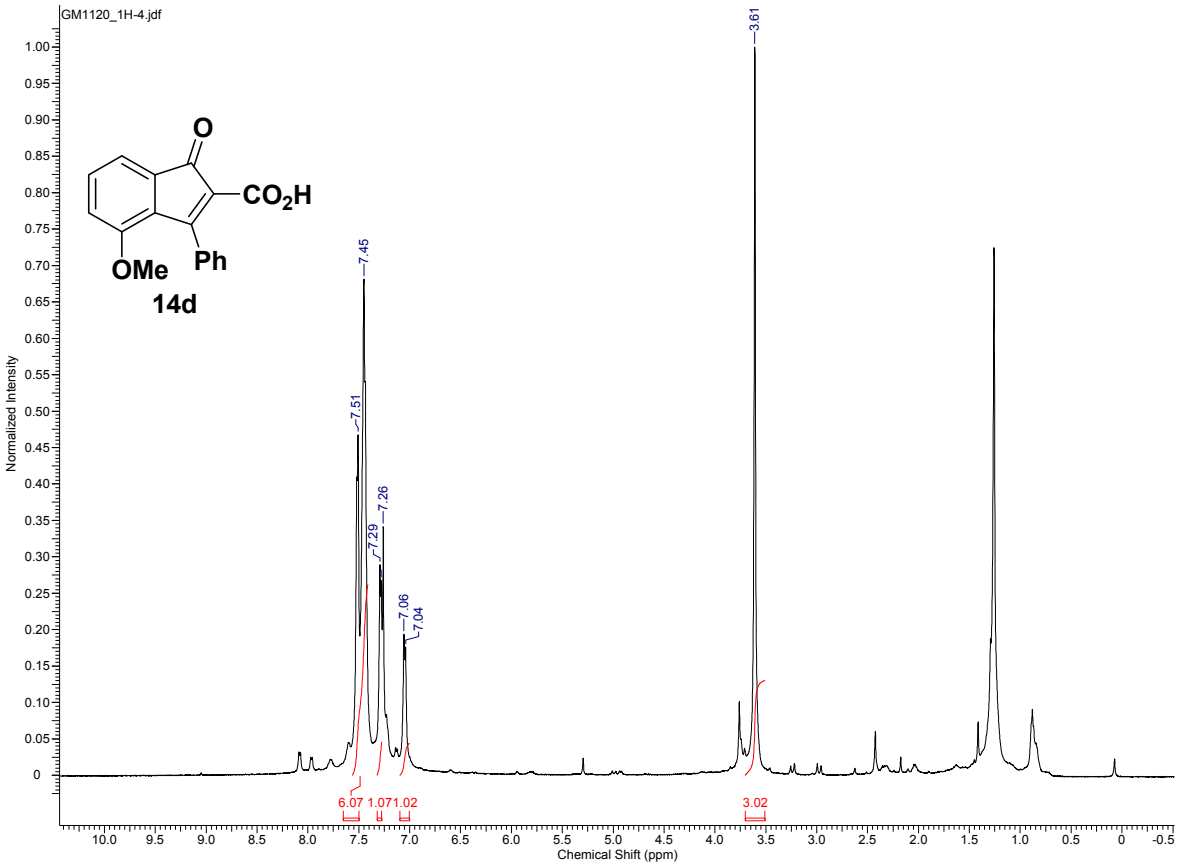

GM854G_13C-2.jdf
O
CO2Et
Ph
14a
Normalized Intensity
Chemical Shift (ppm)
77.25
77.00
76.74
192.10
164.92
163.01
143.14
133.51
131.03
130.43
128.42
128.06
123.45
124.40
60.88
13.93

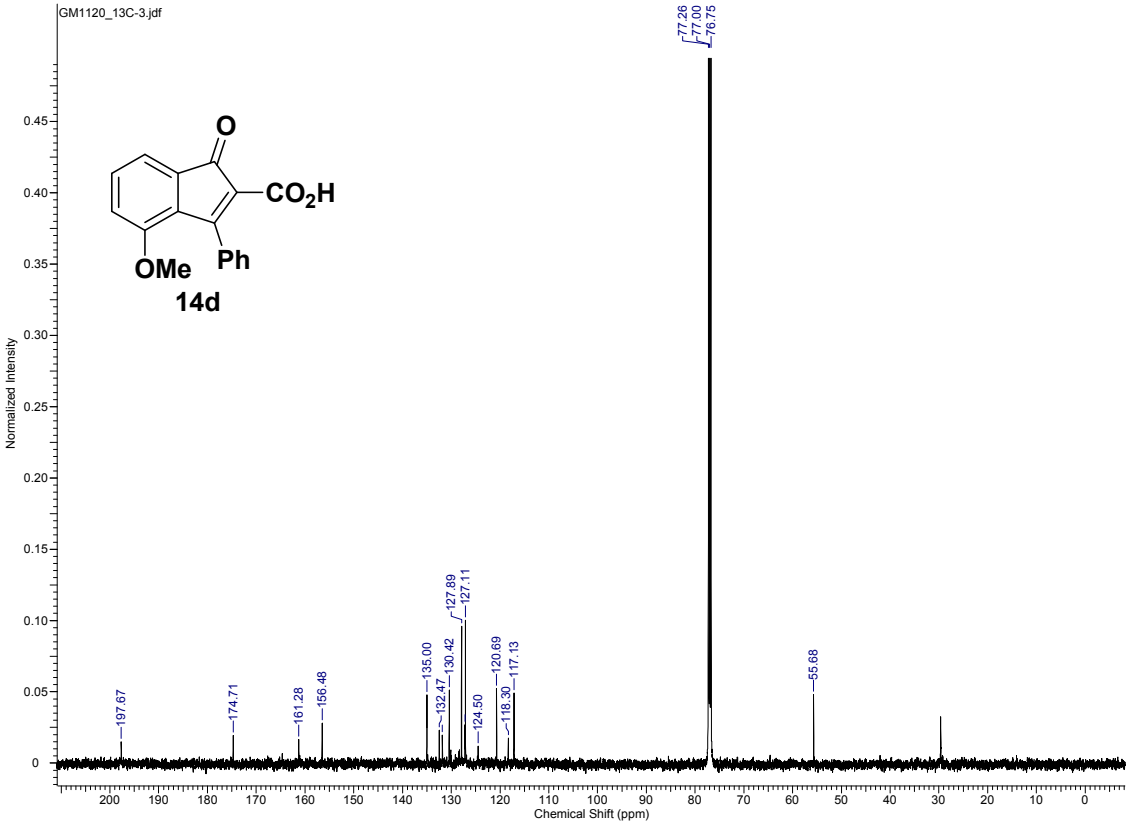

GM1111_1H-4.jdf
O
CO2H
Ph
14b
7.66
7.67
7.56
7.50
7.26
7.49
7.29
7.47
3.04 3.02 2.02 1.00
Absolute Intensity
Chemical Shift (ppm)

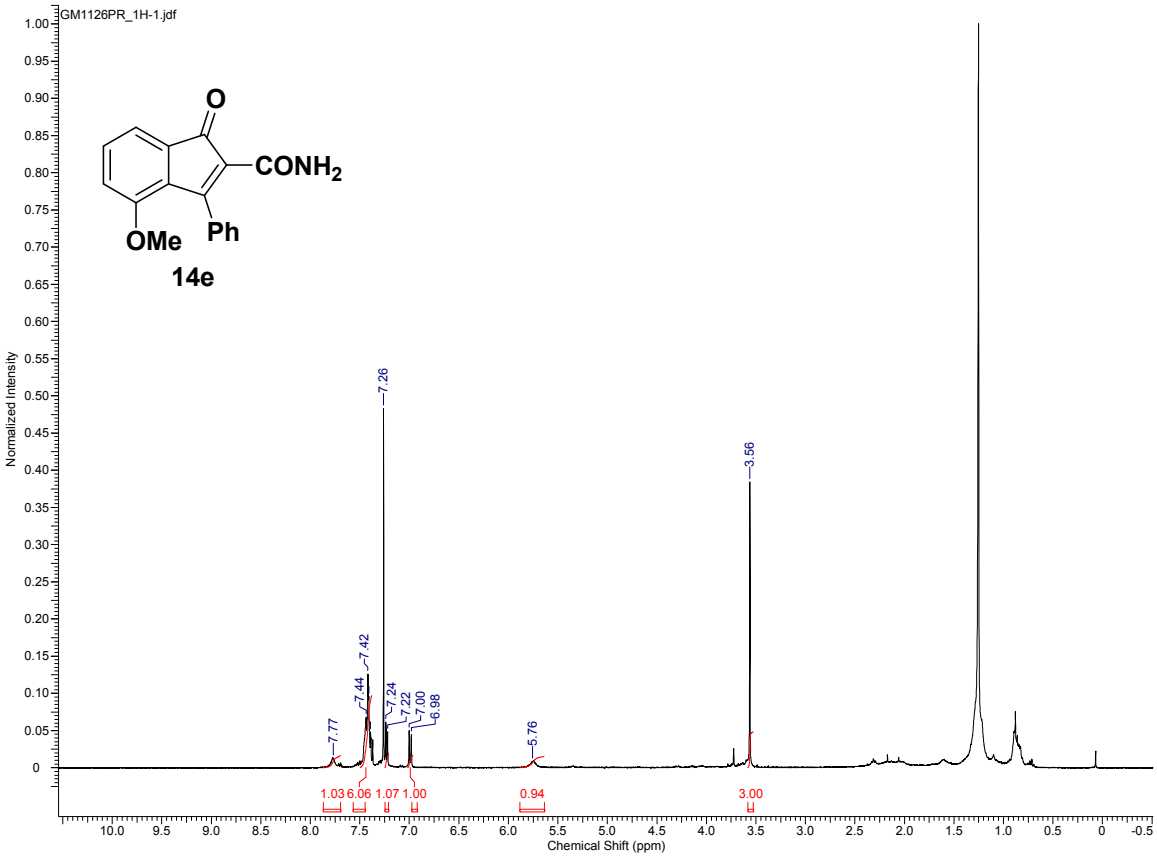

GM1111_13C-3.jdf
O
CO2H
Ph
14b
77.26
76.75
129.08
128.26
134.90
132.27
130.11
125.43
124.42
198.17
171.97
161.17
143.42
118.44
Absolute Intensity
Chemical Shift (ppm)

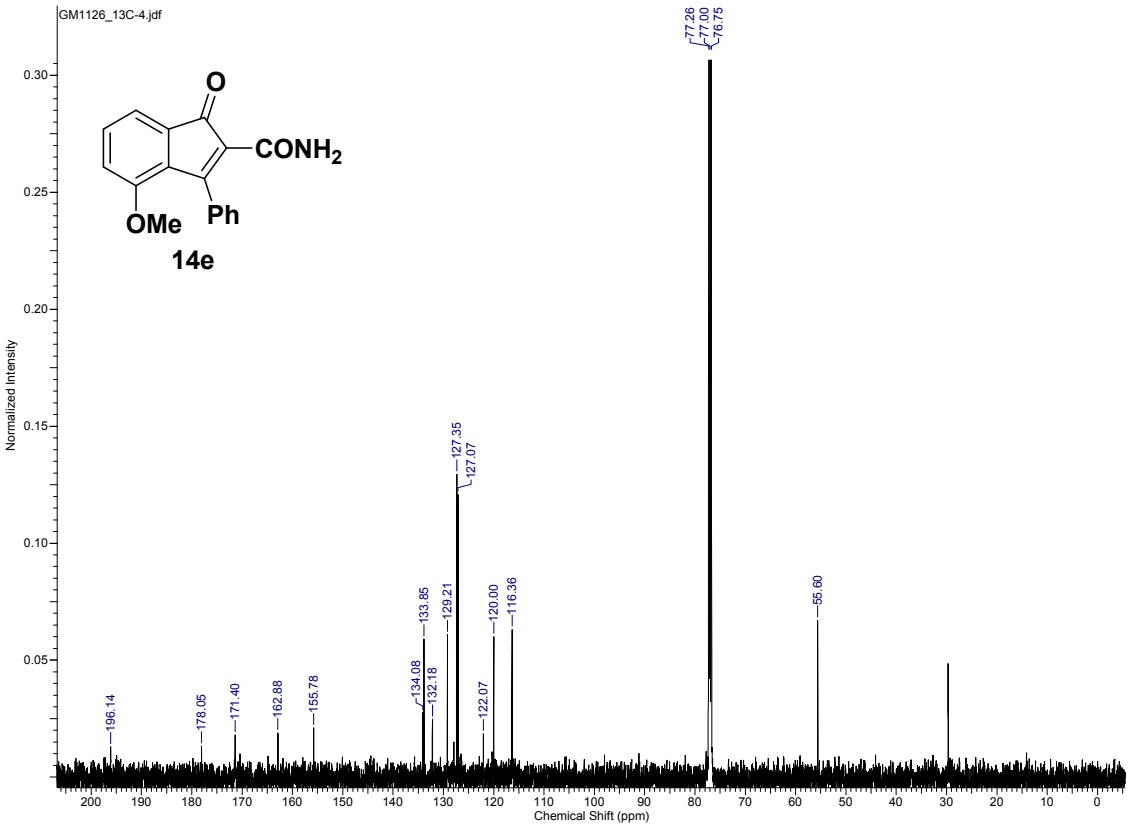

GM1335_1H-5.jdf
O
CONH2
Ph
14c
Absolute Intensity
Chemical Shift (ppm)
7.78
7.60
7.59
7.58
7.51
7.51
7.50
7.42
7.41
7.39
7.26
7.16
7.16
7.14
5.60
0.99 3.04 2.90 2.02 0.93
1.00

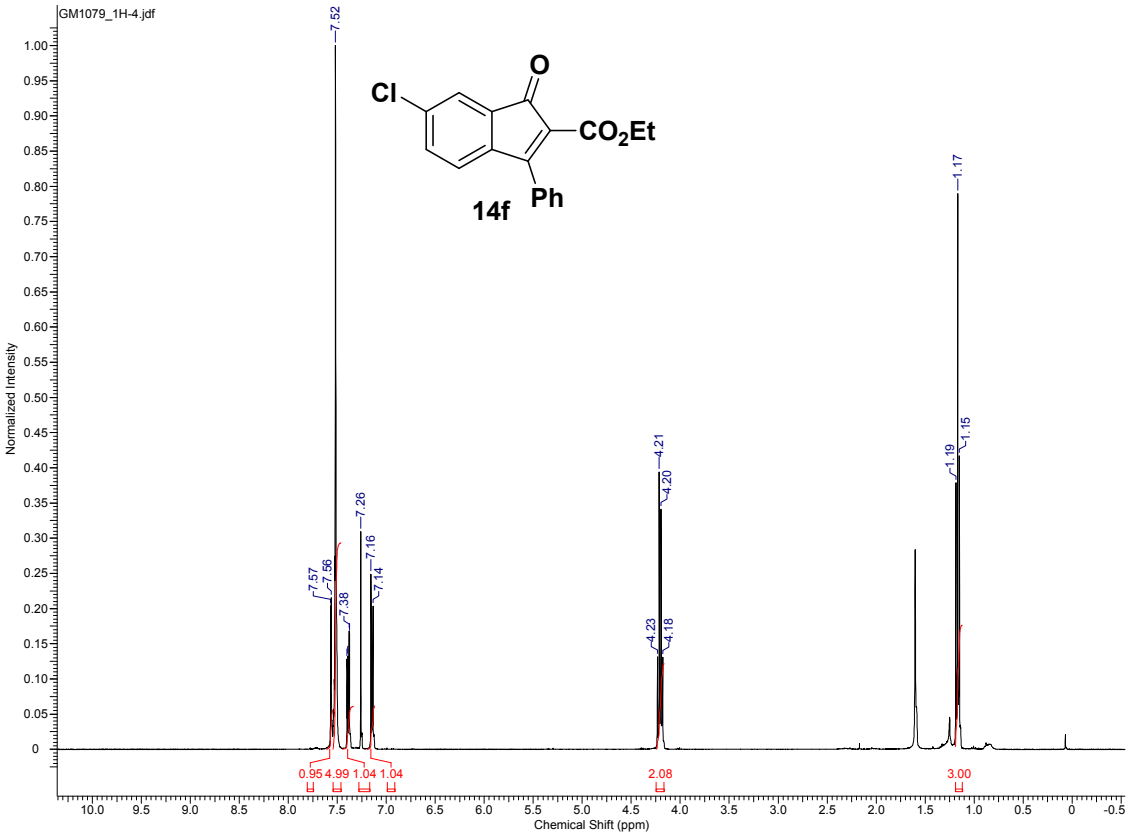

GM1335_13C-2.jdf
O
CONH2
Ph
14c
Absolute Intensity
Chemical Shift (ppm)
196.35
168.97
162.83
143.75
134.13
131.33
130.47
128.55
128.01
124.03
123.52
122.33
77.25
77.00
76.74

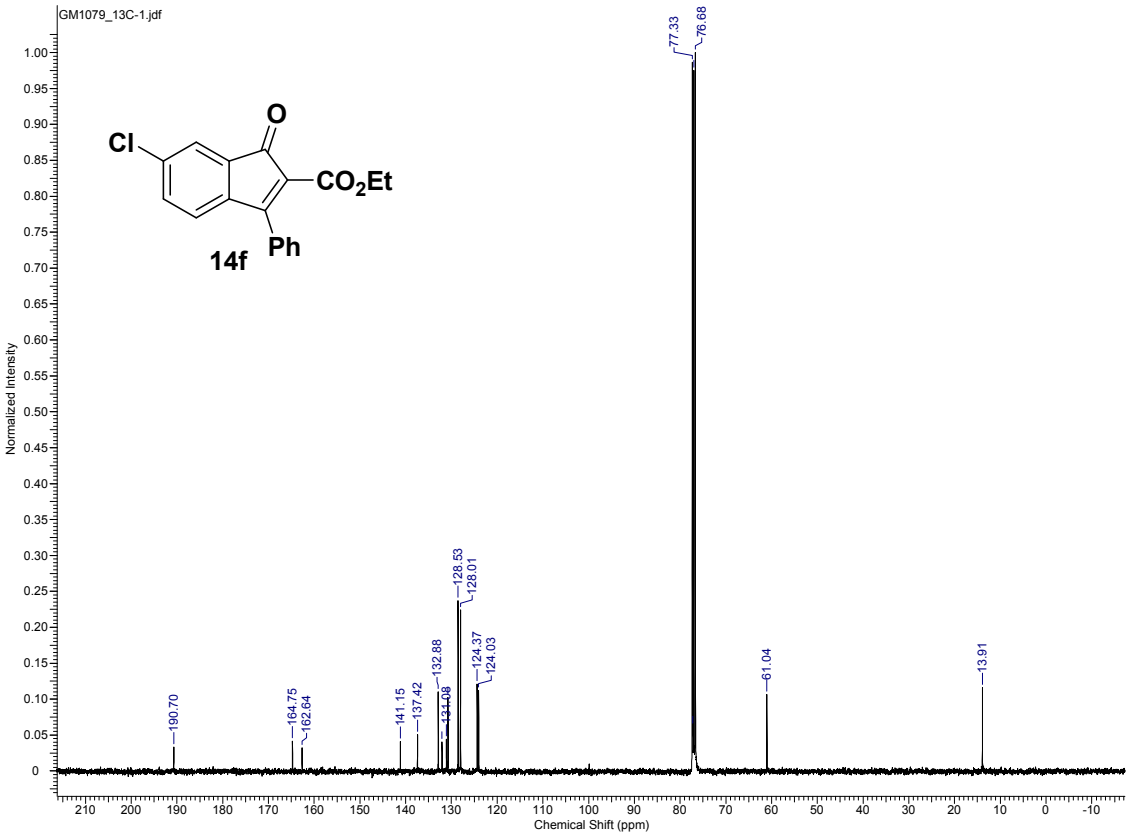

GM1120_1H-4.jdf
O
CO2H
OMe
Ph
14d
Normalized Intensity
Chemical Shift (ppm)
7.45
7.51
7.26
7.29
7.06
7.04
3.61
6.07
1.07
1.02
3.02

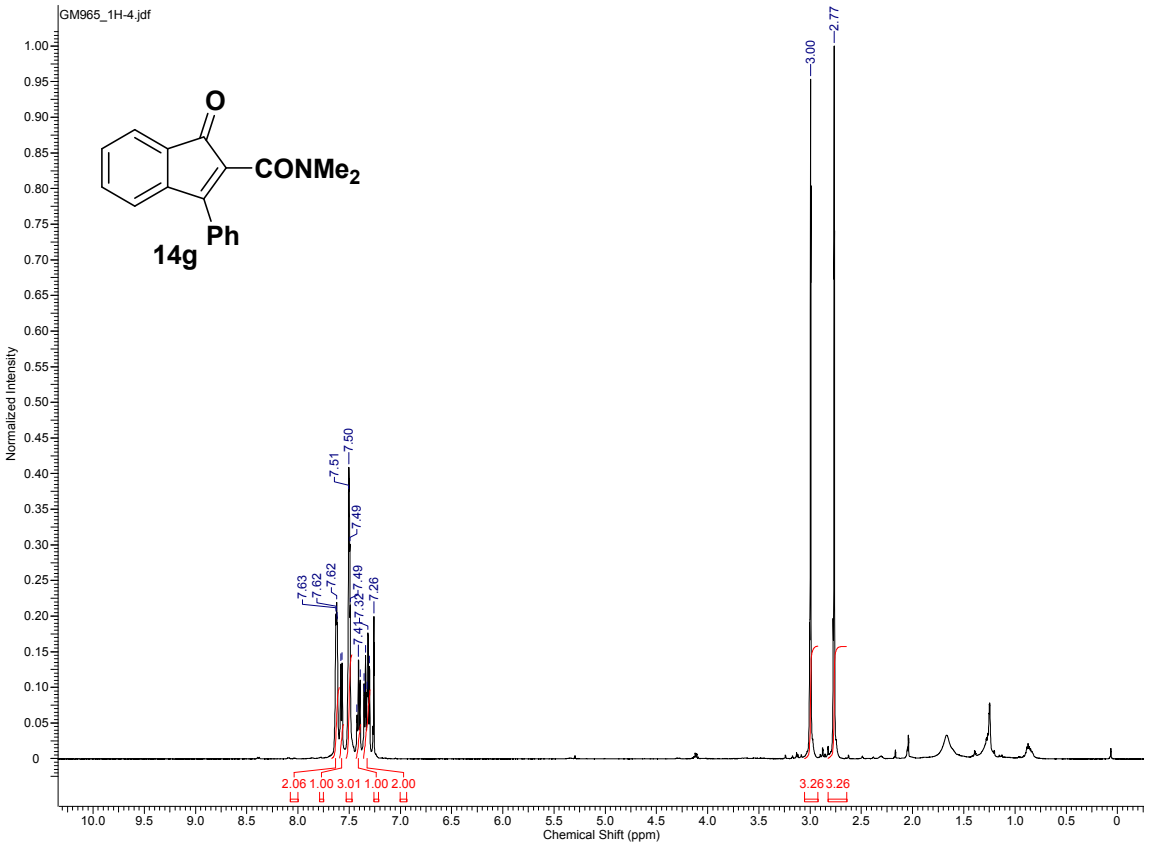

GM1120_13C-3.jdf
O
CO2H
OMe
Ph
14d
Normalized Intensity
Chemical Shift (ppm)
77.26
77.00
76.75
197.67
174.71
161.28
156.48
135.00
132.47
130.42
127.89
127.11
124.50
120.69
118.30
117.13
55.68

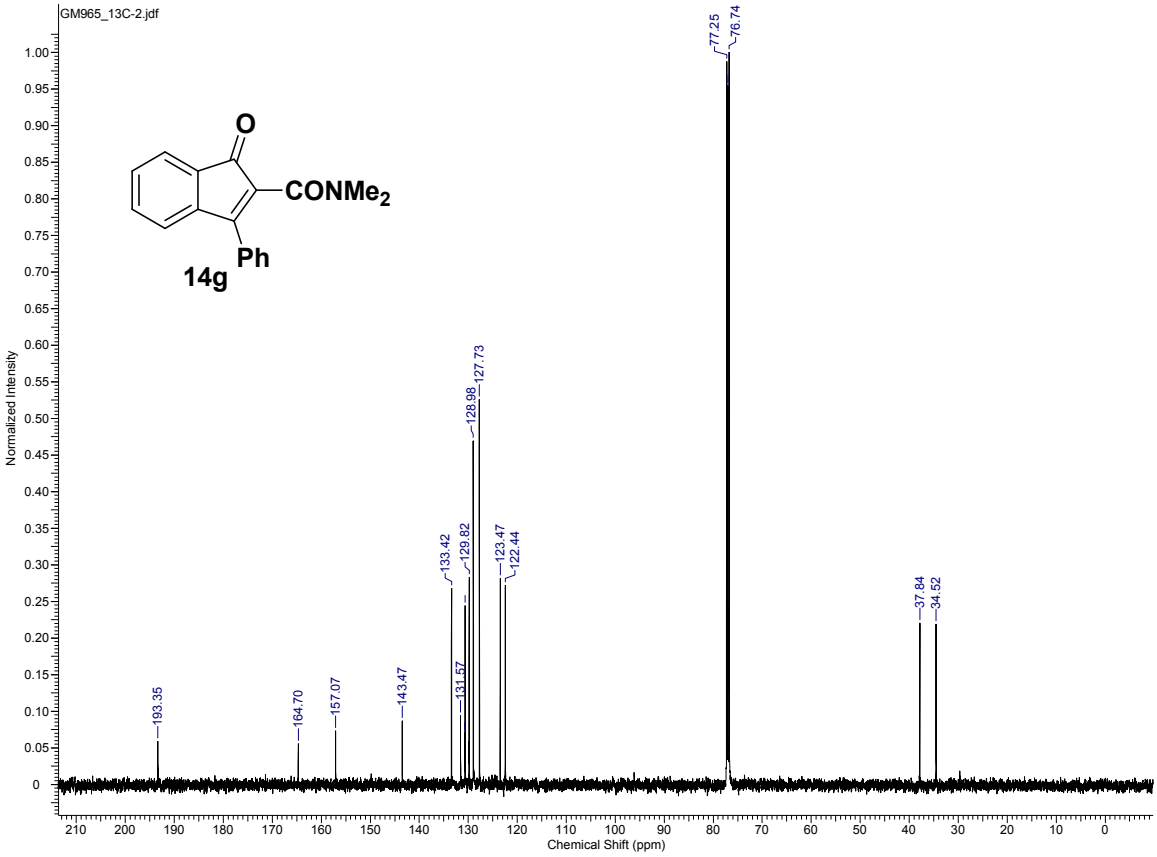

GM1126PR_1H-1.jdf
O
CONH2
OMe
Ph
14e
Normalized Intensity
Chemical Shift (ppm)
7.26
3.56
7.77
7.44
7.42
7.24
7.22
7.00
6.98
5.76
1.03
6.06
1.07
1.00
0.94
3.00

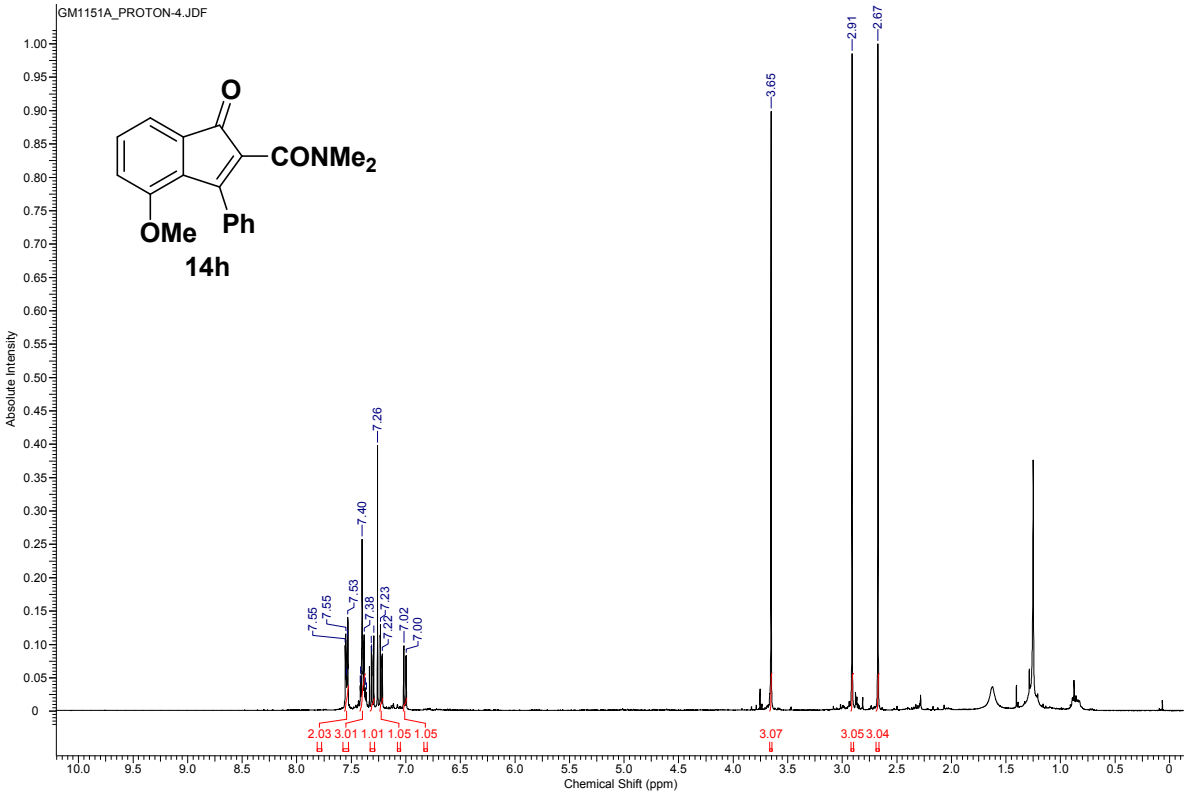

GM1126_13C-4.jdf
O
CONH2
OMe
Ph
14e
Normalized Intensity
Chemical Shift (ppm)
77.26
77.00
76.75
127.35
127.07
133.85
129.21
120.00
116.36
55.60
134.08
132.18
122.07
196.14
178.05
171.40
162.88
155.78

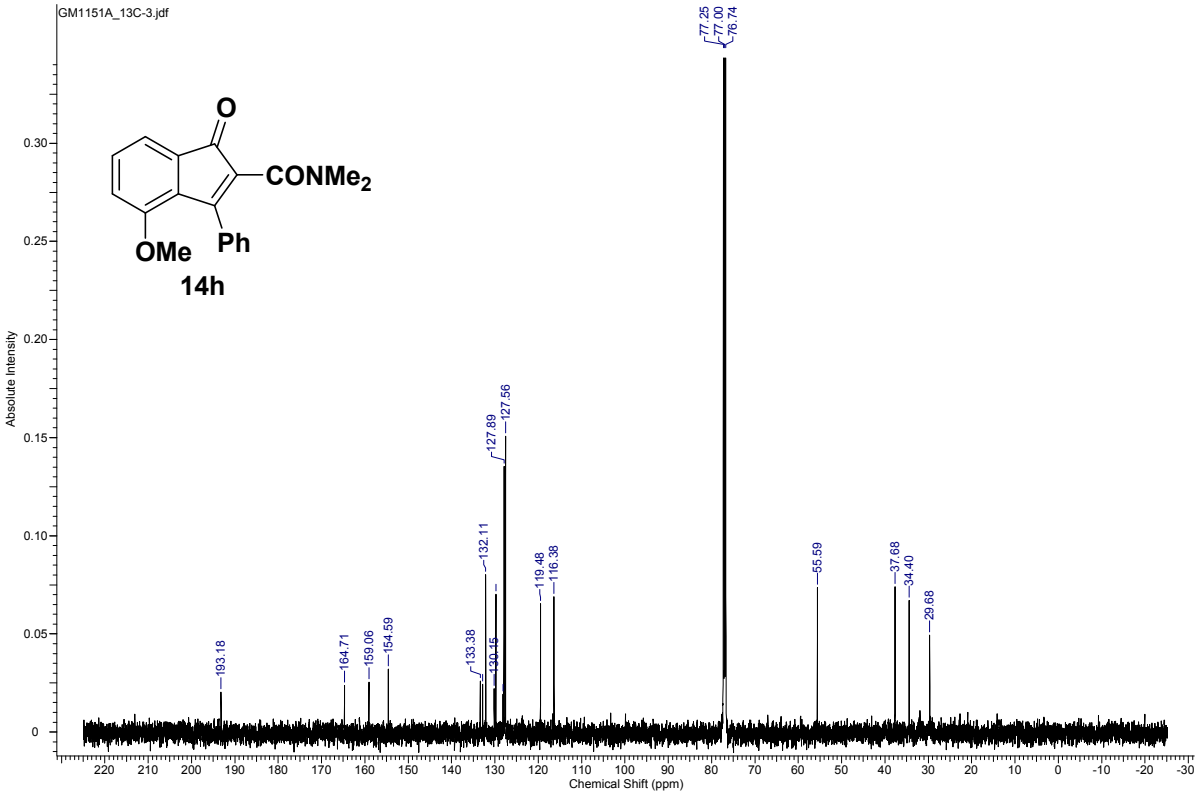

GM1079_1H-4.jdf
Cl
O
CO2Et
Ph
14f
Normalized Intensity
Chemical Shift (ppm)
7.52
7.57
7.56
7.38
7.26
7.16
7.14
4.23
4.21
4.20
4.18
1.19
1.17
1.15
0.95
4.99
1.04
1.04
2.08
3.00

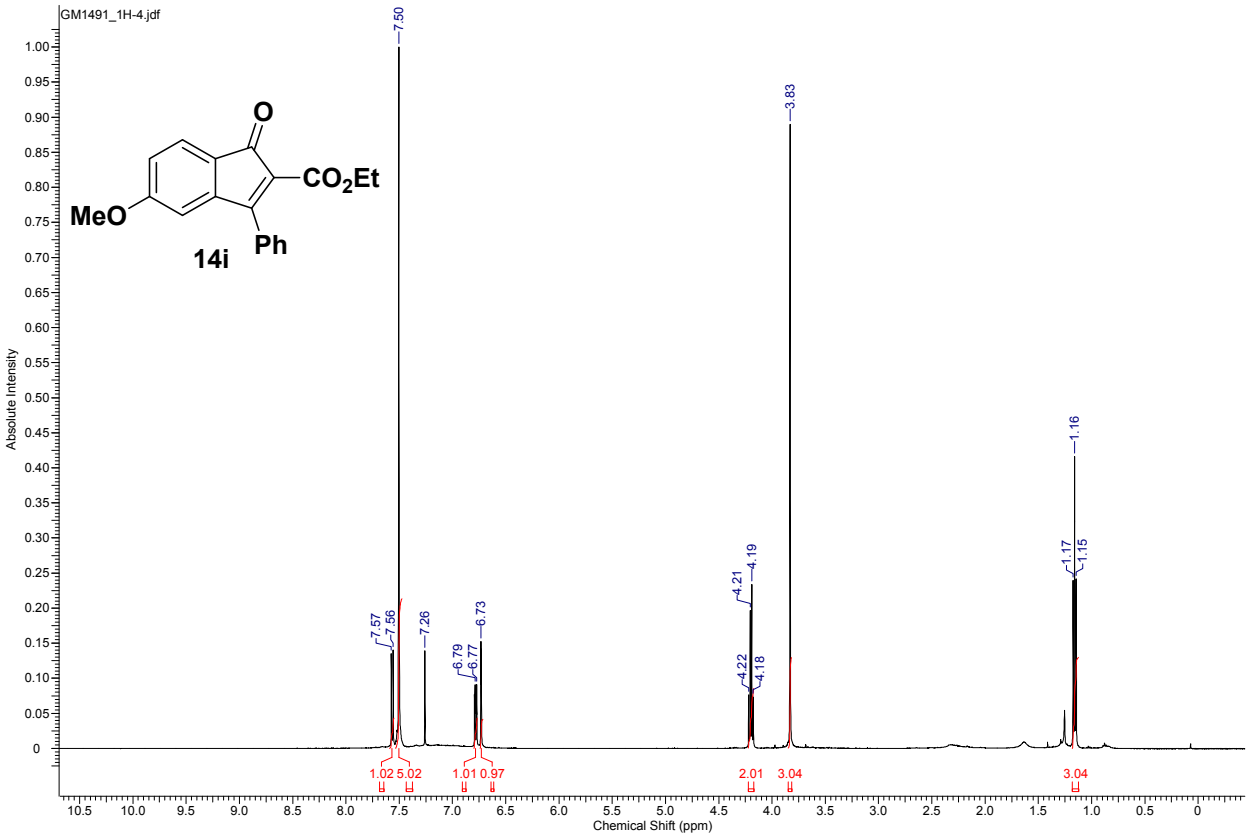

GM1079_13C-1.jdf
Cl
O
CO2Et
Ph
14f
Normalized Intensity
Chemical Shift (ppm)
77.33
76.68
190.70
164.75
162.64
141.15
137.42
132.88
131.08
128.53
128.01
124.37
124.03
61.04
13.91

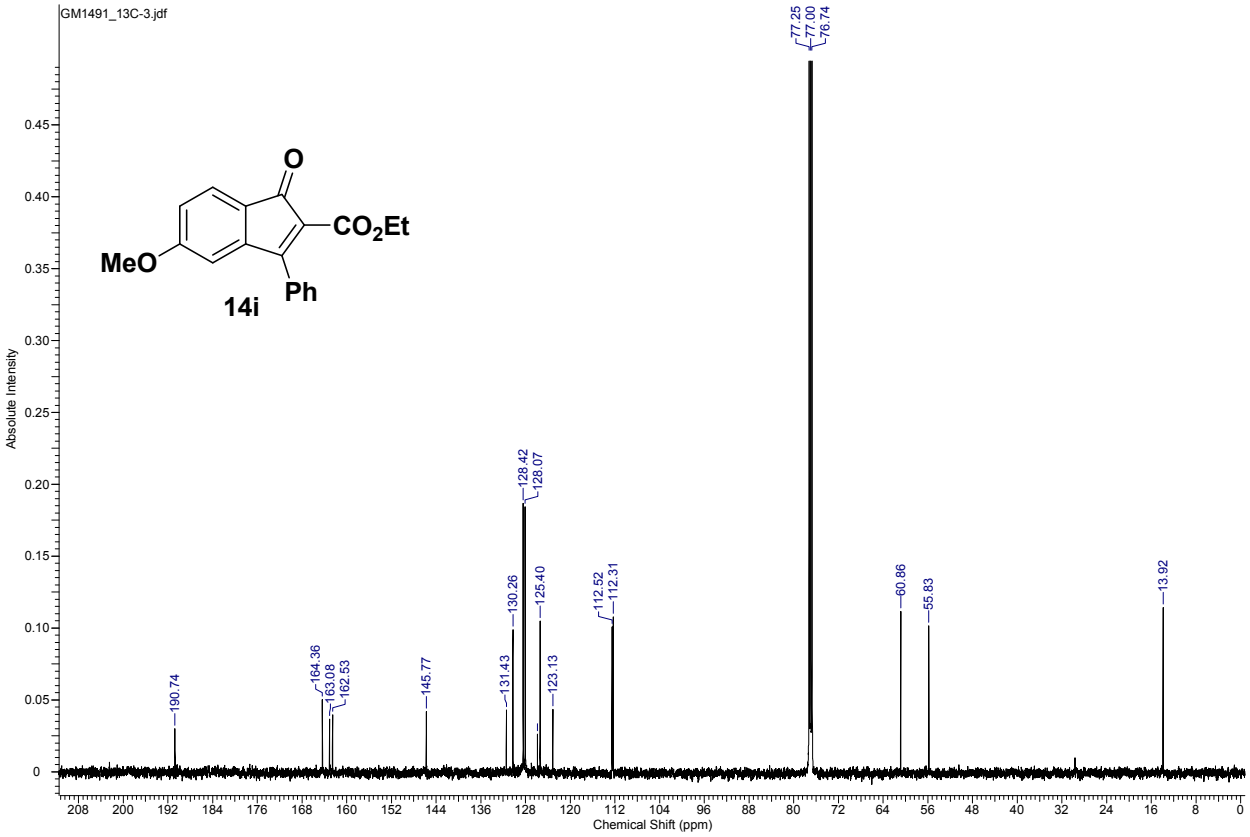

GM965_1H-4.jdf
O
CONMe2
Ph
14g
Normalized Intensity
Chemical Shift (ppm)
3.00
2.77
7.51
7.50
7.49
7.63
7.62
7.62
7.49
7.26
2.06 1.00 3.01 1.00 2.00
3.26 3.26

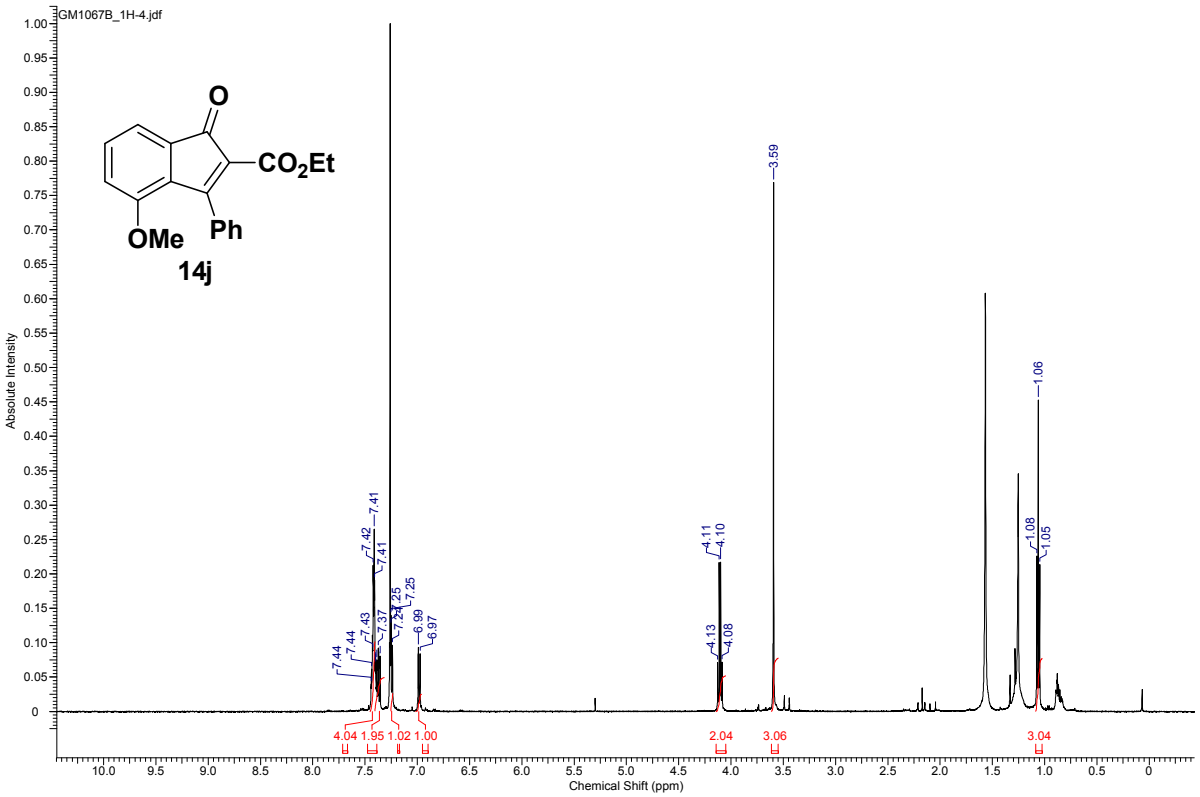

GM965_13C-2.jdf
O
CONMe2
Ph
14g
Normalized Intensity
Chemical Shift (ppm)
77.25
76.74
128.98
127.73
133.42
129.82
123.47
122.44
37.84
34.52
193.35
164.70
157.07
143.47
131.57

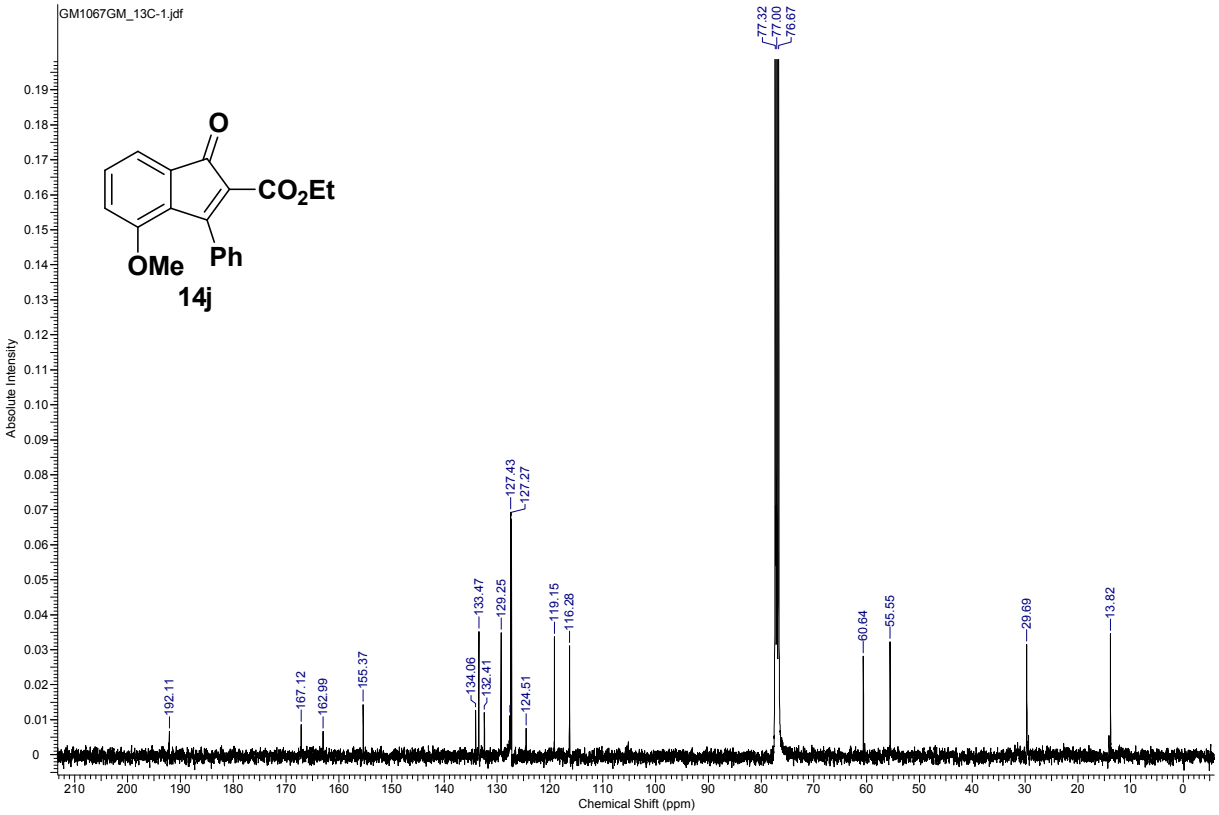

GM1151A_PROTON-4.JDF
O
CONMe2
OMe
Ph
14h
Absolute Intensity
Chemical Shift (ppm)
7.55
7.55
7.53
7.40
7.38
7.26
7.23
7.22
7.02
7.00
3.65
2.91
2.67
2.03 3.01 1.01 1.01 1.05 1.05
3.07
3.05 3.04

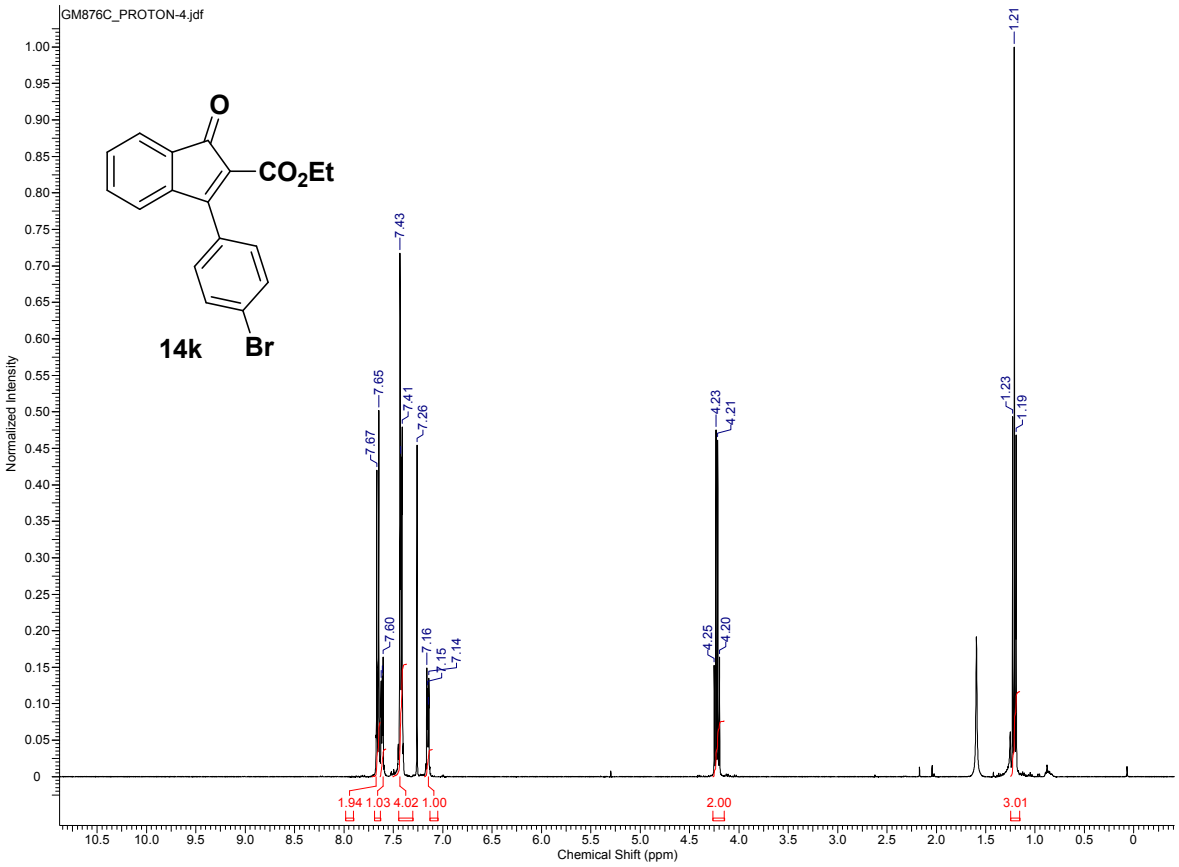

GM1151A_13C-3.jdf
O
CONMe2
OMe
Ph
14h
Absolute Intensity
Chemical Shift (ppm)
77.25
77.00
76.74
193.18
164.71
159.06
154.59
133.38
130.15
132.11
127.89
127.56
119.48
116.38
55.59
37.68
34.40
29.68

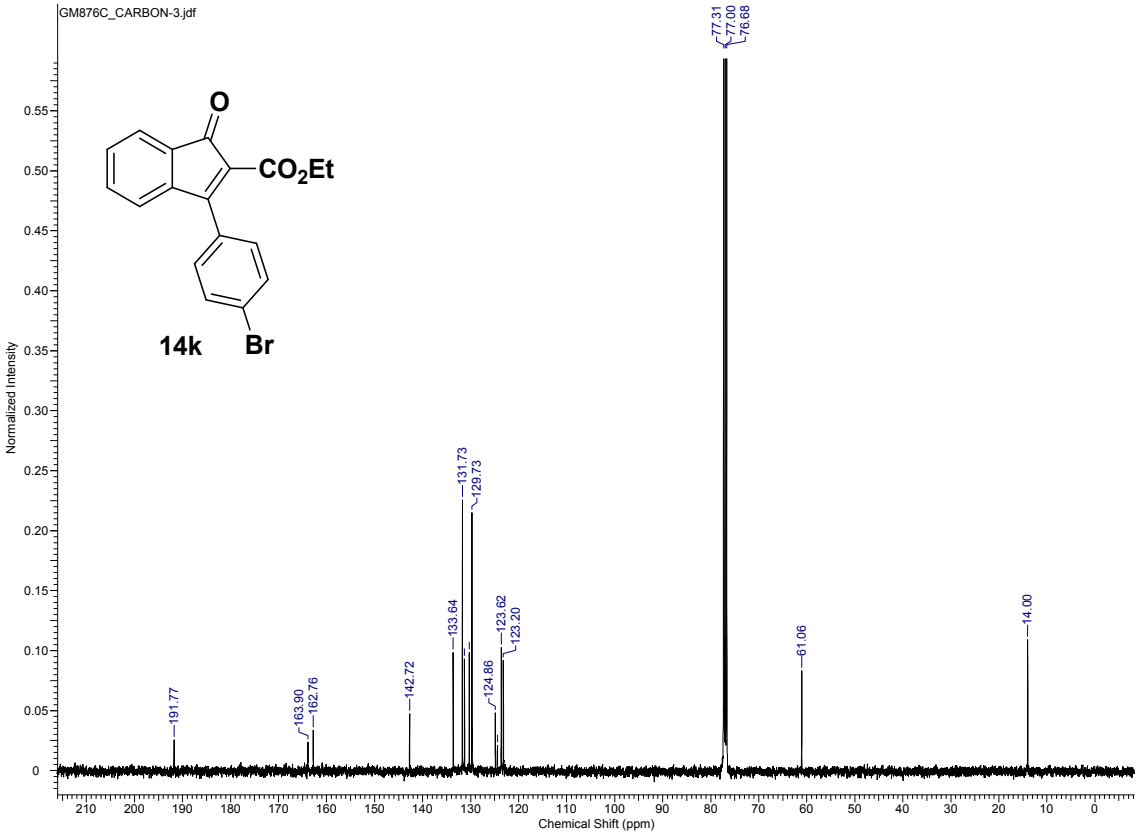

GM1491_1H-4.jdf
O
CO2Et
MeO
Ph
14i
Absolute Intensity
Chemical Shift (ppm)
7.50
3.83
1.16
1.17
1.15
4.21
4.19
4.22
4.18
7.57
7.56
7.26
6.73
6.79
6.77
1.02
5.02
1.01
0.97
2.01
3.04
3.04

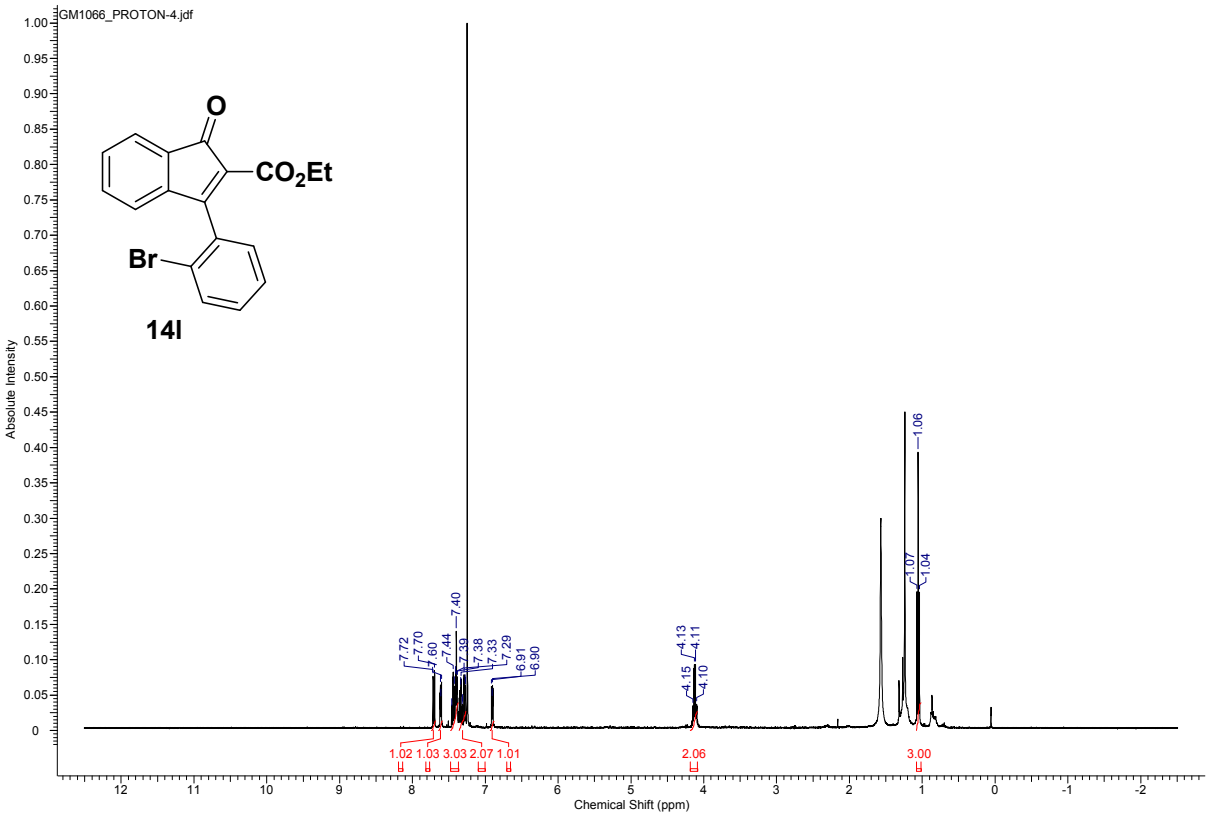

GM1491_13C-3.jdf
O
CO2Et
MeO
Ph
14i
Absolute Intensity
Chemical Shift (ppm)
77.25
77.00
76.74
128.42
128.07
130.26
125.40
112.52
112.31
60.86
55.83
13.92
190.74
164.36
163.08
162.53
145.77
131.43
123.13

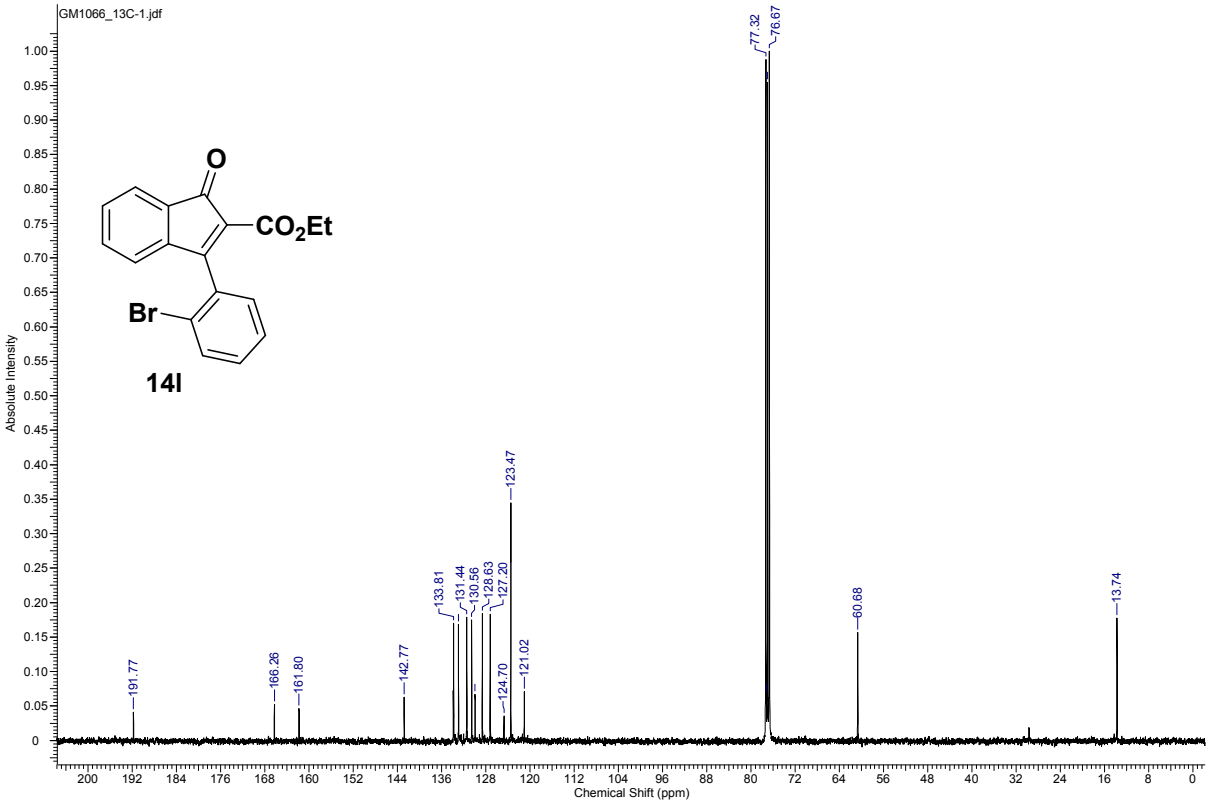

GM1067B_1H-4.jdf
O
CO2Et
OMe
Ph
14j
Absolute Intensity
Chemical Shift (ppm)
7.44
7.44
7.43
7.42
7.41
7.41
7.37
7.25
7.25
6.99
6.97
4.13
4.11
4.10
4.08
3.59
1.08
1.06
1.05
4.04
1.95
1.02
1.00
2.04
3.06
3.04

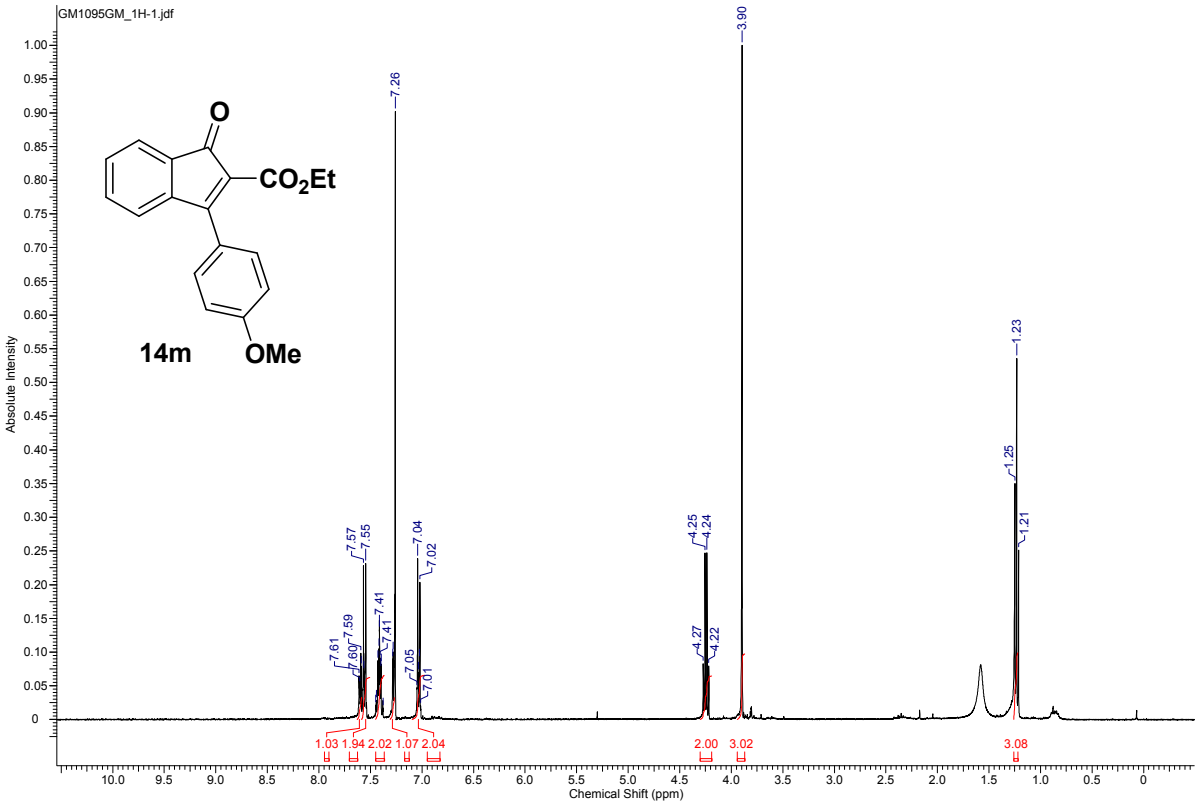

GM1067GM_13C-1.jdf
O
CO2Et
OMe
Ph
14j
Absolute Intensity
Chemical Shift (ppm)
77.32
77.00
76.67
192.11
167.12
162.99
155.37
134.06
133.47
132.41
129.25
127.43
127.27
124.51
119.15
116.28
60.64
55.55
29.69
13.82

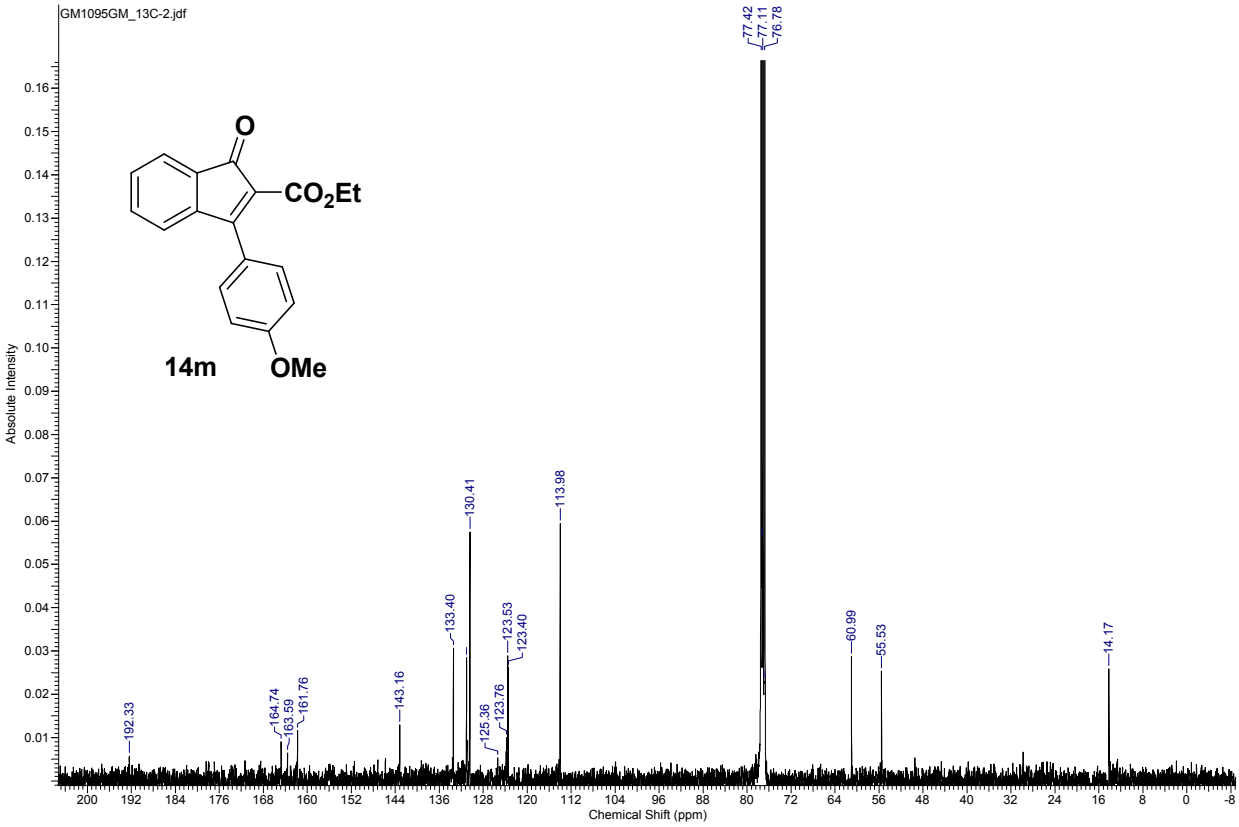

GM876C_PROTON-4.jdf
O
CO2Et
14k
Br
Normalized Intensity
Chemical Shift (ppm)
1.21
7.43
7.65
7.67
7.41
7.26
4.23
4.21
1.23
1.19
7.60
7.16
7.15
7.14
4.25
4.20
1.94
1.03
4.02
1.00
2.00
3.01

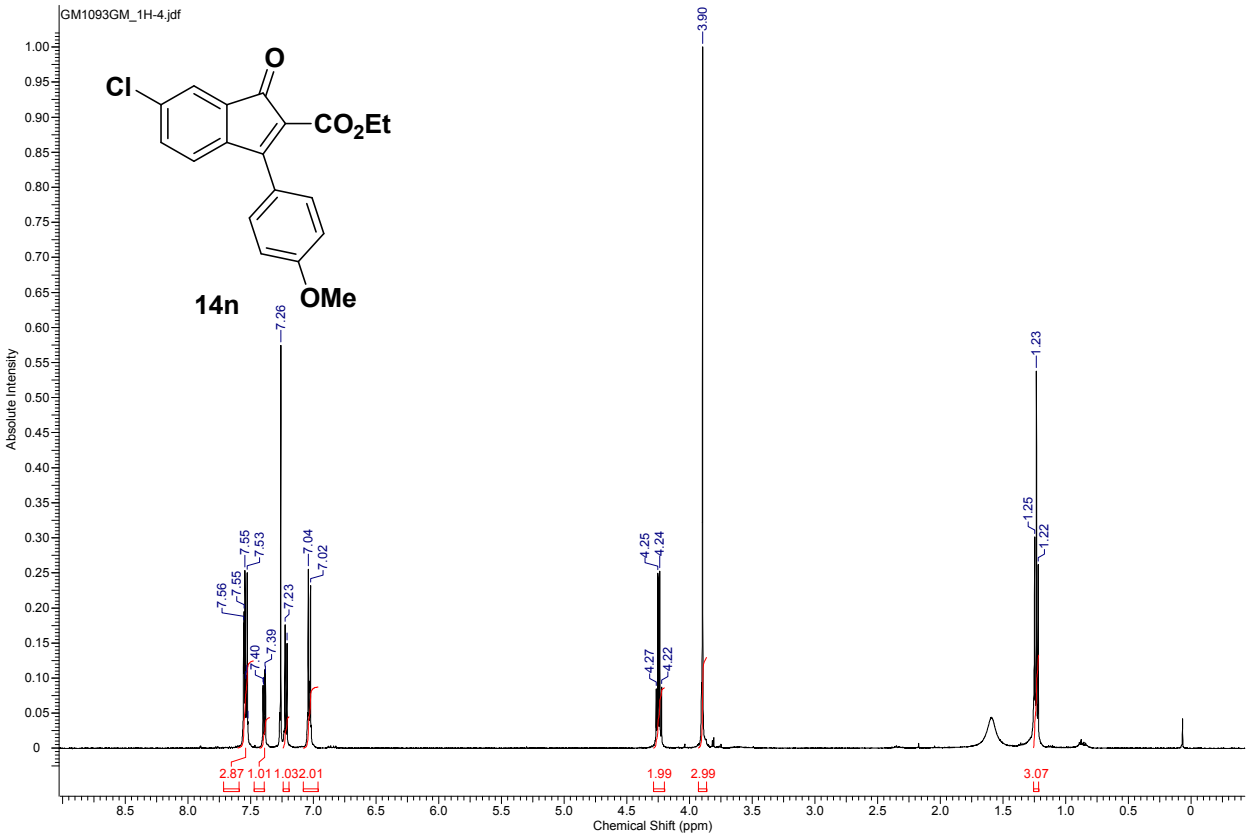

GM876C_CARBON-3.jdf
O
CO2Et
14k
Br
Normalized Intensity
Chemical Shift (ppm)
77.31
77.00
76.68
131.73
129.73
133.64
123.62
123.20
124.86
142.72
191.77
163.90
162.76
61.06
14.00

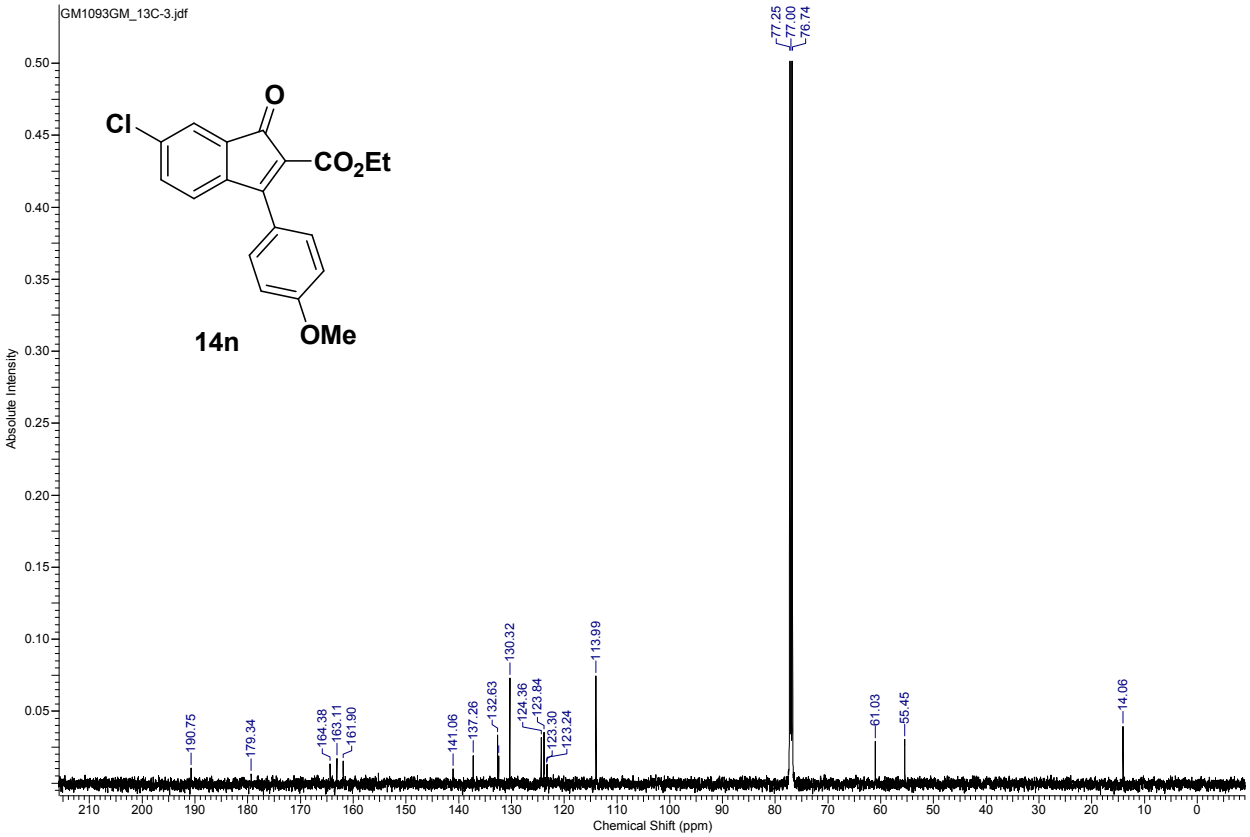

GM1066_PROTON-4.jdf
O
CO2Et
Br
14l
Absolute Intensity
Chemical Shift (ppm)
7.72
7.70
7.60
7.44
7.40
7.38
7.33
7.29
6.91
6.90
4.15
4.13
4.11
4.10
1.07
1.06
1.04
1.02
1.03
3.03
2.07
1.01
2.06
3.00

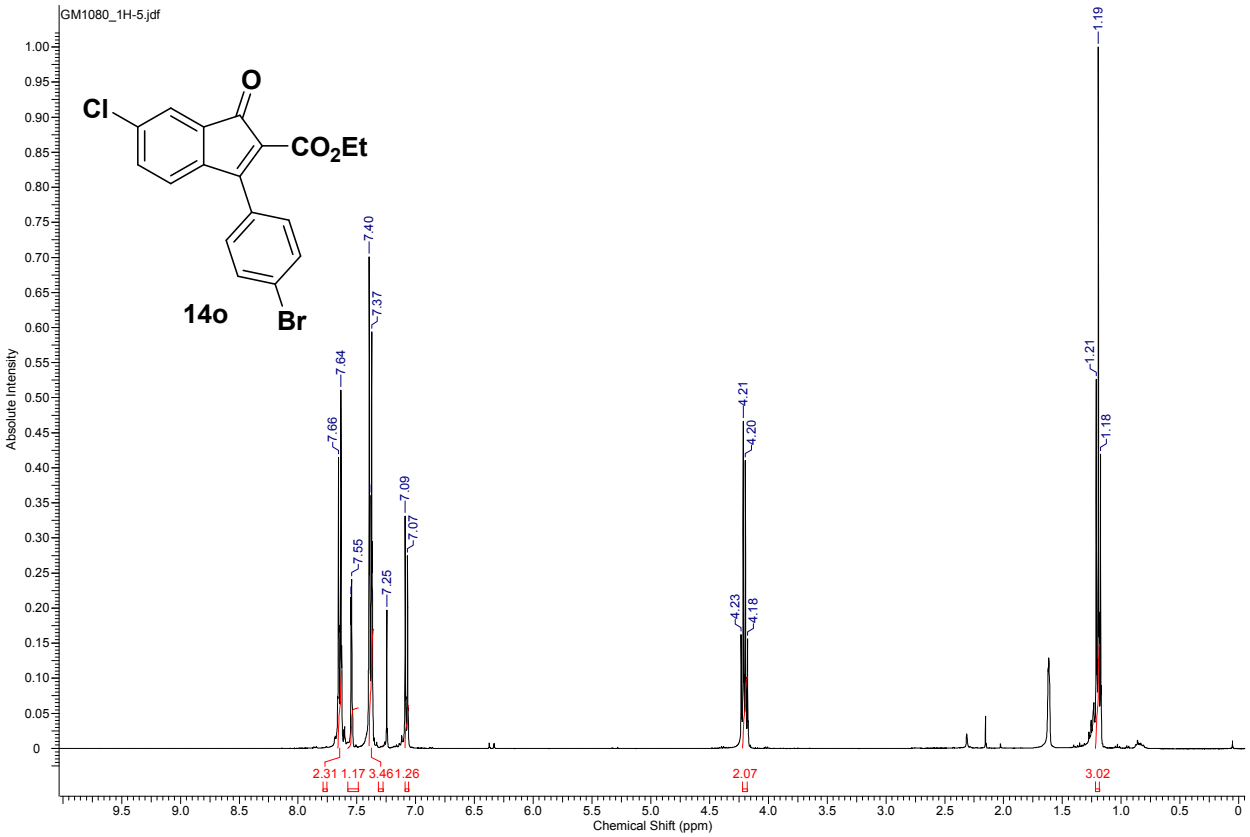

GM1066_13C-1.jdf
O
CO2Et
Br
14l
Absolute Intensity
Chemical Shift (ppm)
77.32
76.67
123.47
133.81
131.44
130.56
128.63
127.20
121.02
124.70
142.77
191.77
166.26
161.80
60.68
13.74

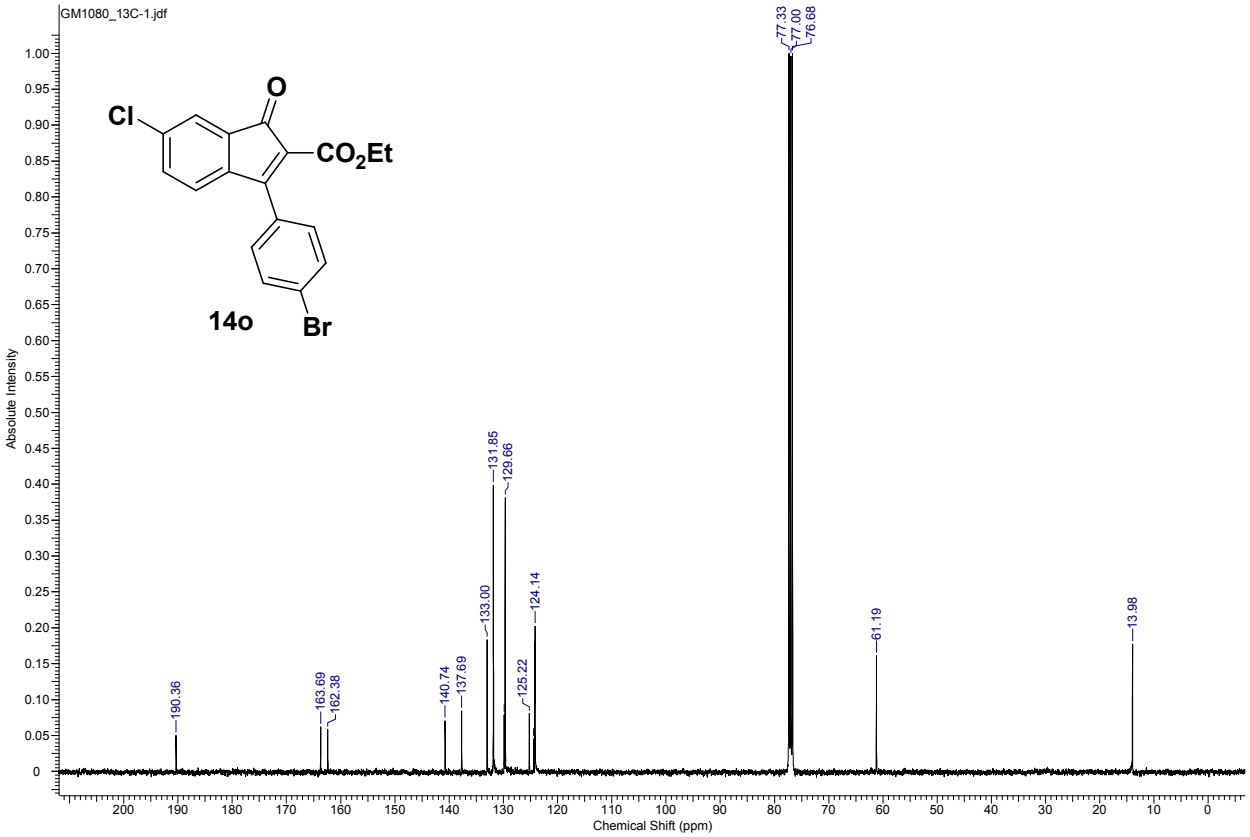

GM1095GM_1H-1.jdf
O
CO2Et
14m
OMe
Absolute Intensity
Chemical Shift (ppm)
7.26
3.90
1.23
1.25
1.21
7.57
7.55
7.04
7.02
7.61
7.59
7.60
7.41
7.41
7.05
7.01
4.25
4.24
4.27
4.22
1.03 1.94 2.02 1.07 2.04
2.00 3.02
3.08

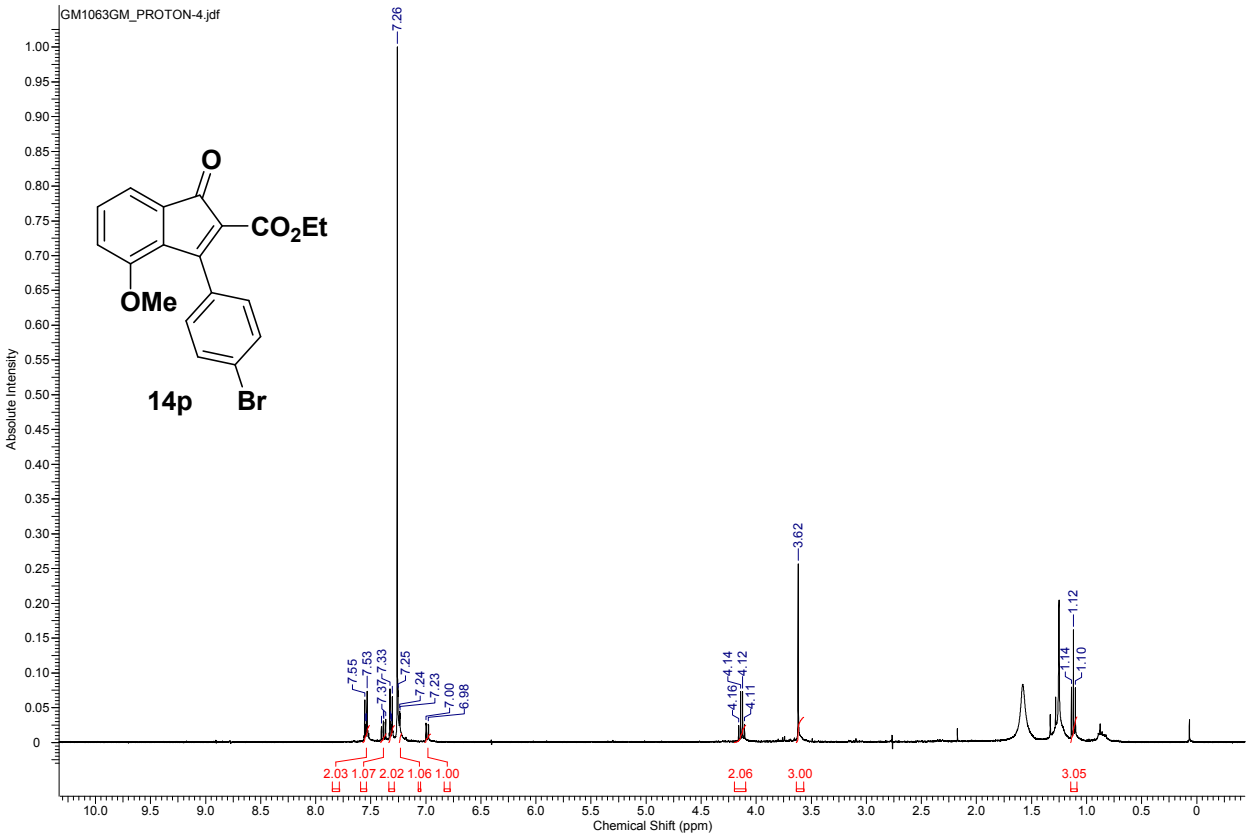

GM1095GM_13C-2.jdf
O
CO2Et
14m
OMe
Absolute Intensity
Chemical Shift (ppm)
77.42
77.11
76.78
130.41
113.98
133.40
123.53
123.40
143.16
164.74
163.59
161.76
192.33
125.36
123.76
60.99
55.53
14.17

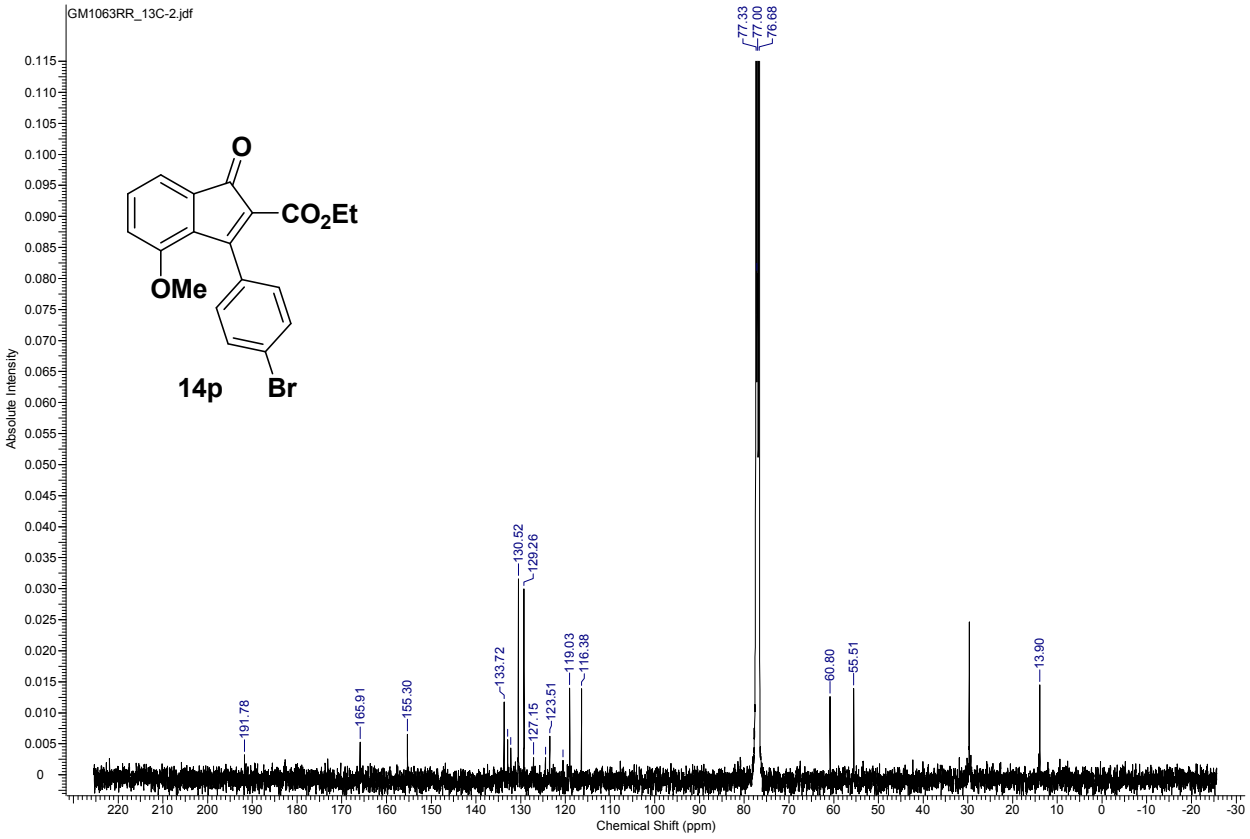

GM1093GM_1H-4.jdf
Cl
O
CO2Et
OMe
14n
Absolute Intensity
Chemical Shift (ppm)
7.56
7.55
7.55
7.53
7.40
7.39
7.26
7.23
7.04
7.02
4.25
4.24
4.27
4.22
3.90
1.25
1.23
1.22
2.87
1.01
1.03
2.01
1.99
2.99
3.07

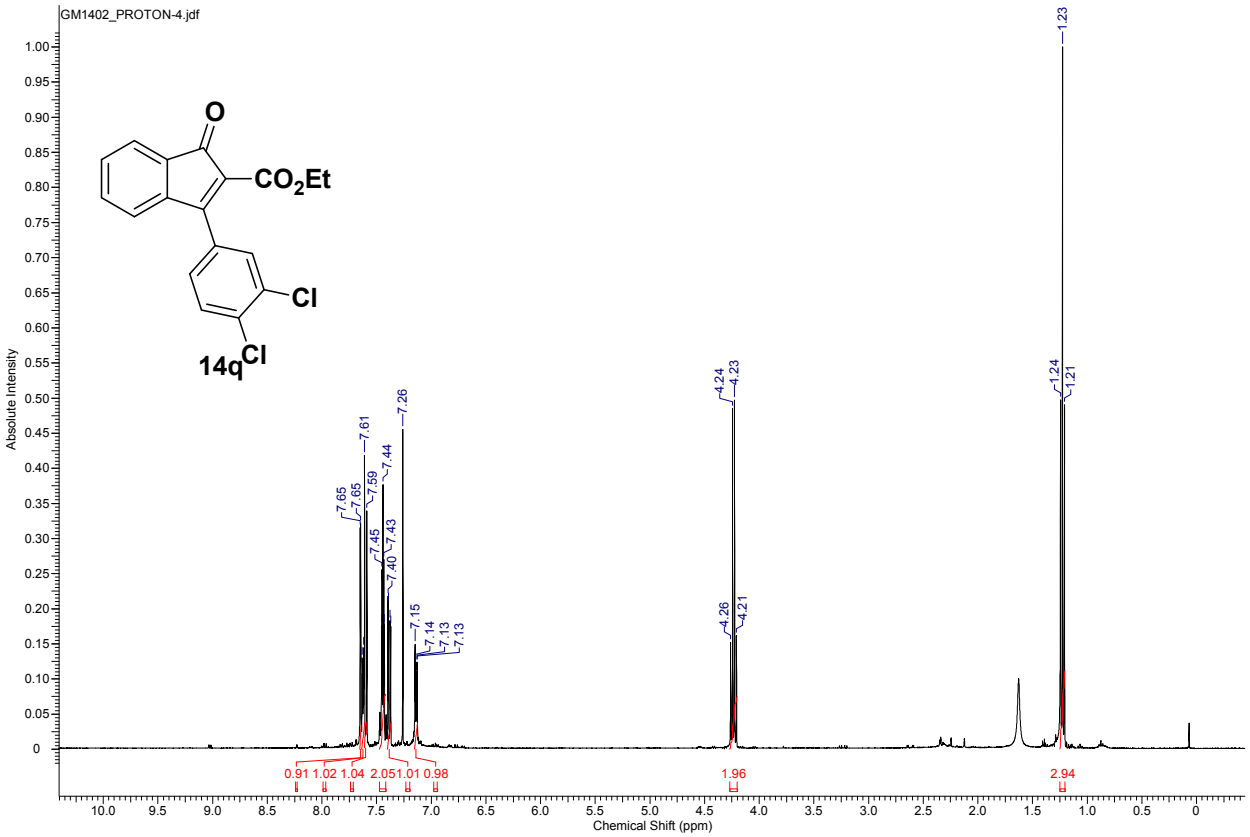

GM1093GM_13C-3.jdf
Cl
O
CO2Et
OMe
14n
Absolute Intensity
Chemical Shift (ppm)
77.25
77.00
76.74
190.75
179.34
164.38
163.11
161.90
141.06
137.26
132.63
130.32
124.36
123.84
123.30
123.24
113.99
61.03
55.45
14.06

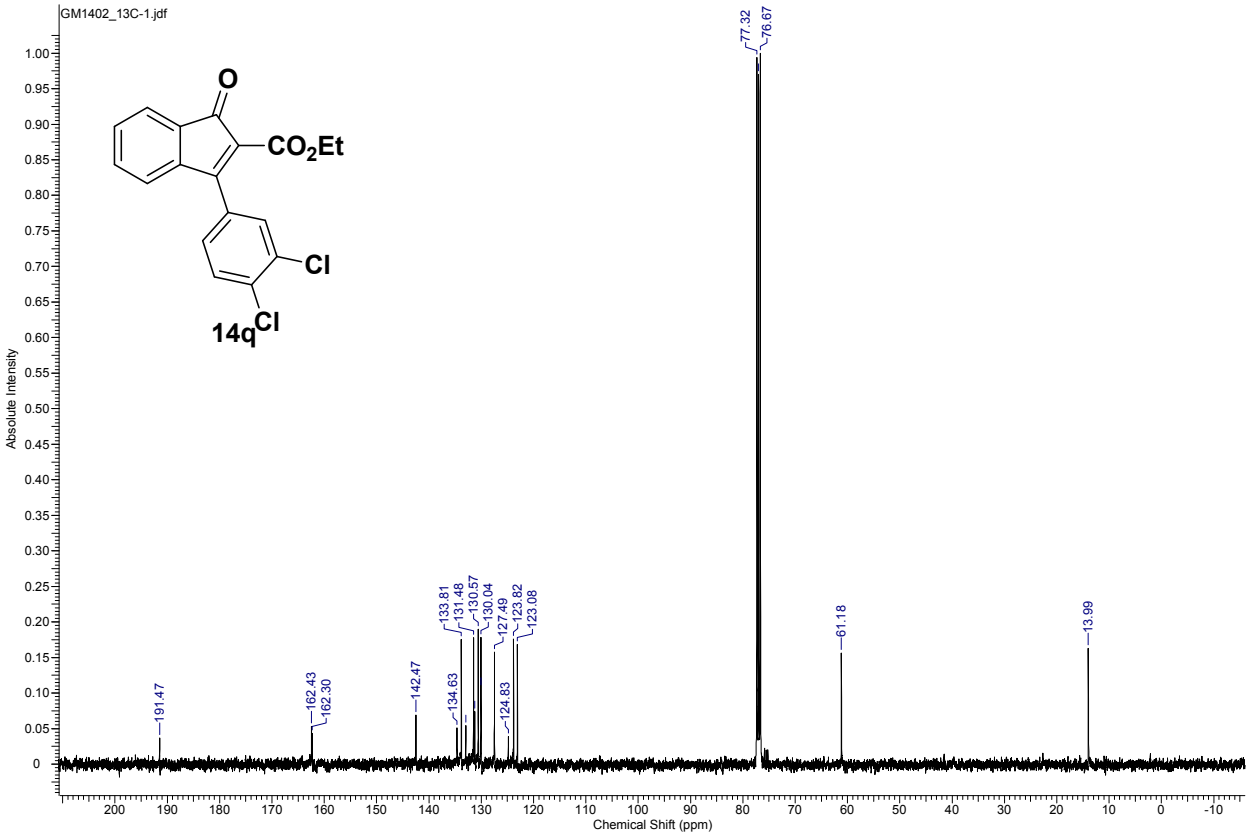

GM1080_1H-5.jdf
Cl
O
CO2Et
Br
14o
Absolute Intensity
Chemical Shift (ppm)
7.66
7.64
7.55
7.40
7.37
7.25
7.09
7.07
4.23
4.21
4.20
4.18
1.21
1.19
1.18
2.31
1.17
3.46
1.26
2.07
3.02

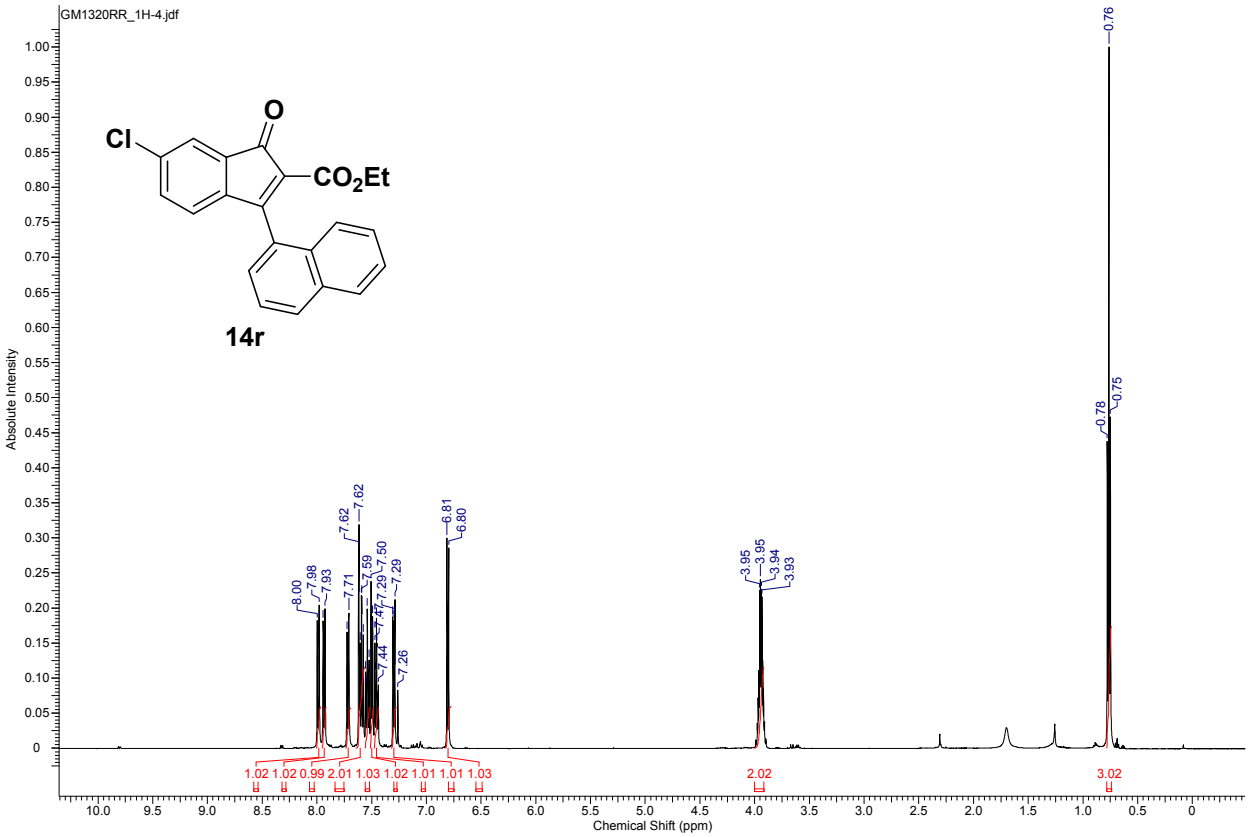

GM1080_13C-1.jdf
Cl
O
CO2Et
Br
14o
Absolute Intensity
Chemical Shift (ppm)
190.36
163.69
162.38
140.74
137.69
133.00
131.85
129.66
125.22
124.14
77.33
77.00
76.68
61.19
13.98

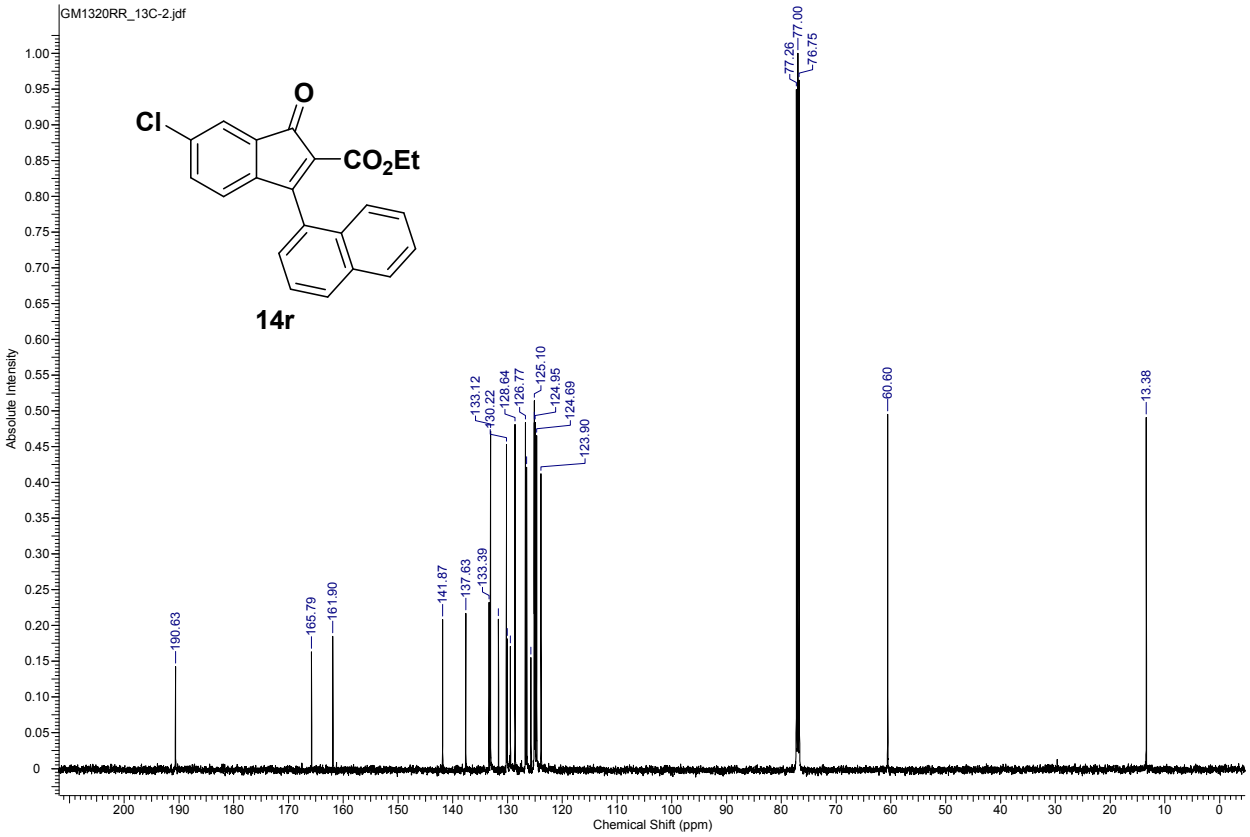

GM1063GM_PROTON-4.jdf
O
CO2Et
OMe
14p
Br
Absolute Intensity
Chemical Shift (ppm)
7.26
7.55
7.53
7.33
7.37
7.25
7.24
7.23
7.00
6.98
4.16
4.14
4.12
4.11
3.62
1.12
1.14
1.10
2.03 1.07 2.02 1.06 1.00
2.06
3.00
3.05


GM1063RR_13C-2.jdf
O
CO2Et
OMe
14p
Br
Absolute Intensity
Chemical Shift (ppm)
77.33
77.00
76.68
191.78
165.91
155.30
133.72
130.52
129.26
127.15
123.51
119.03
116.38
60.80
55.51
13.90


GM1402_PROTON-4.jdf
O
CO2Et
Cl
14qCl
Absolute Intensity
Chemical Shift (ppm)
7.65
7.65
7.61
7.59
7.45
7.44
7.43
7.40
7.26
7.15
7.14
7.13
7.13
4.24
4.23
4.26
4.21
1.23
1.24
1.21
0.91 1.02 1.04 2.05 1.01 0.98
1.96
2.94


GM1402_13C-1.jdf
O
CO2Et
Cl
14qCl
Absolute Intensity
Chemical Shift (ppm)
77.32
76.67
191.47
162.43
162.30
142.47
134.63
133.81
131.48
130.57
130.04
127.49
124.83
123.82
123.08
61.18
13.99


GM1320RR_1H-4.jdf
Cl
O
CO2Et
14r
Absolute Intensity
Chemical Shift (ppm)
0.76
0.78
0.75
7.62
7.62
6.81
6.80
8.00
7.98
7.93
7.71
7.59
7.50
7.29
7.29
7.47
7.44
7.26
3.95
3.95
3.94
3.93
1.02 1.02 0.99 2.01 1.03 1.02 1.01 1.01 1.03
2.02
3.02


GM1320RR_13C-2.jdf
Cl
O
CO2Et
14r
Absolute Intensity
Chemical Shift (ppm)
77.26
77.00
76.75
133.12
130.22
128.64
126.77
125.10
124.95
124.69
123.90
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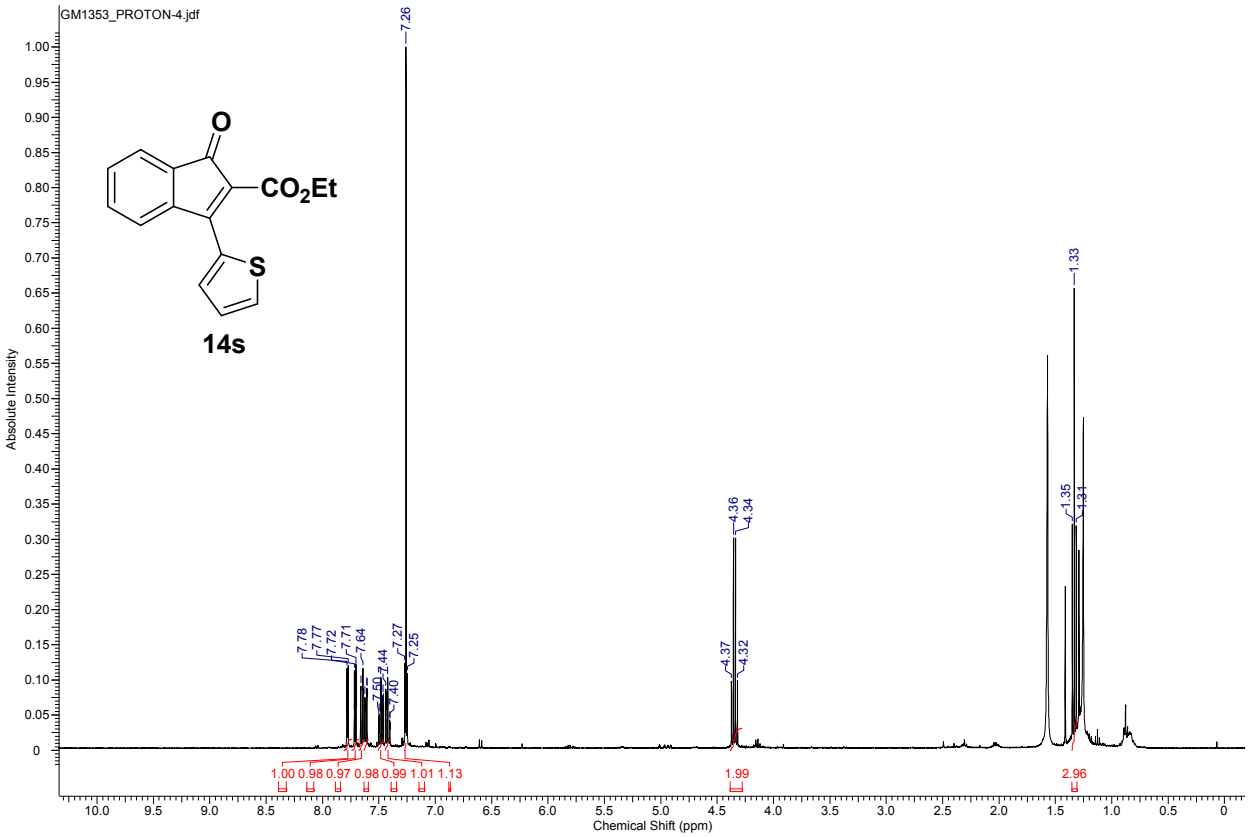
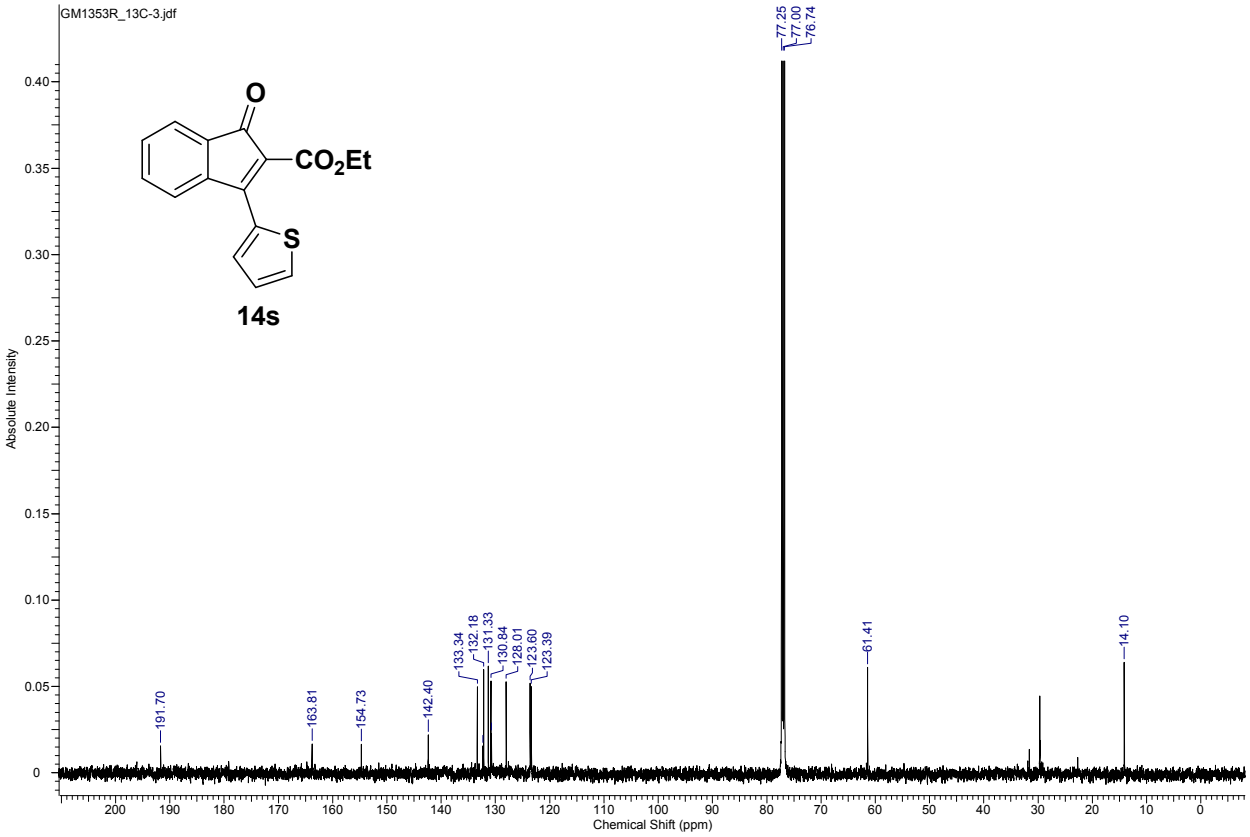
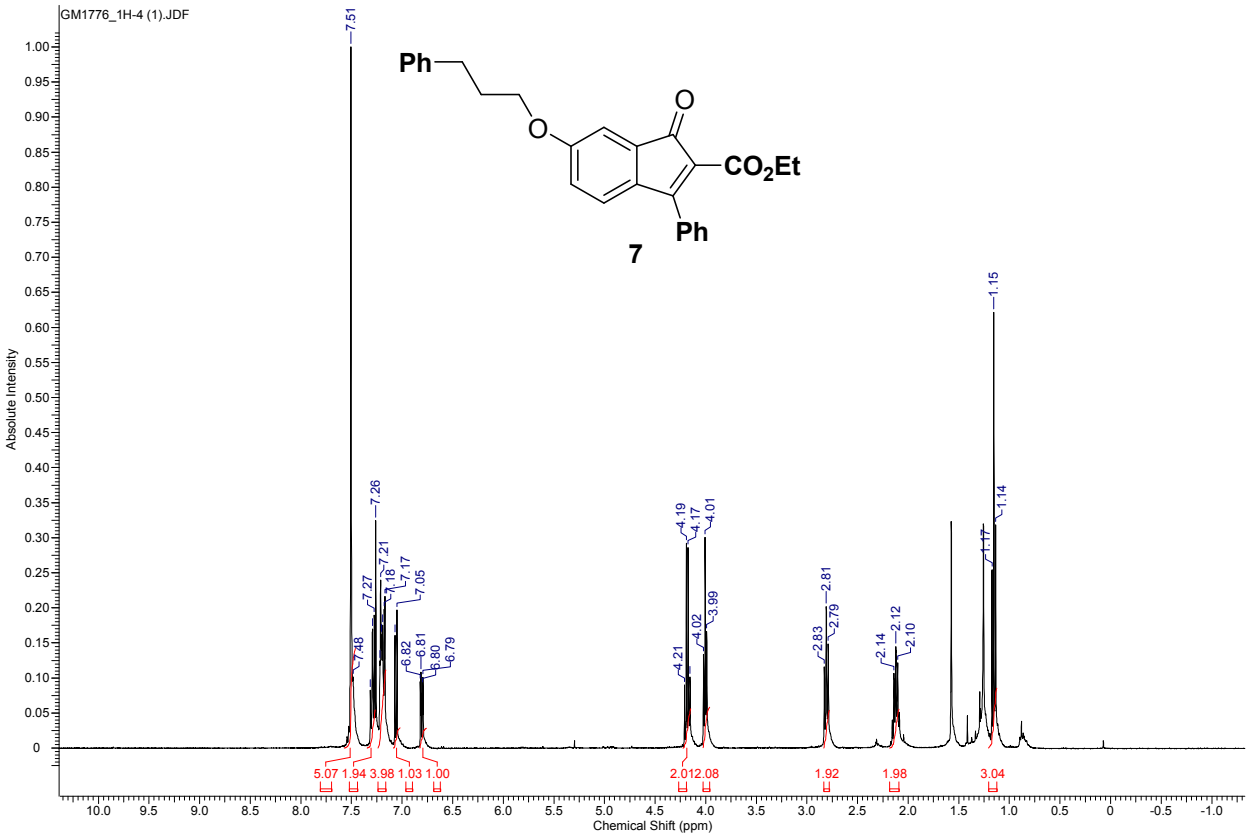
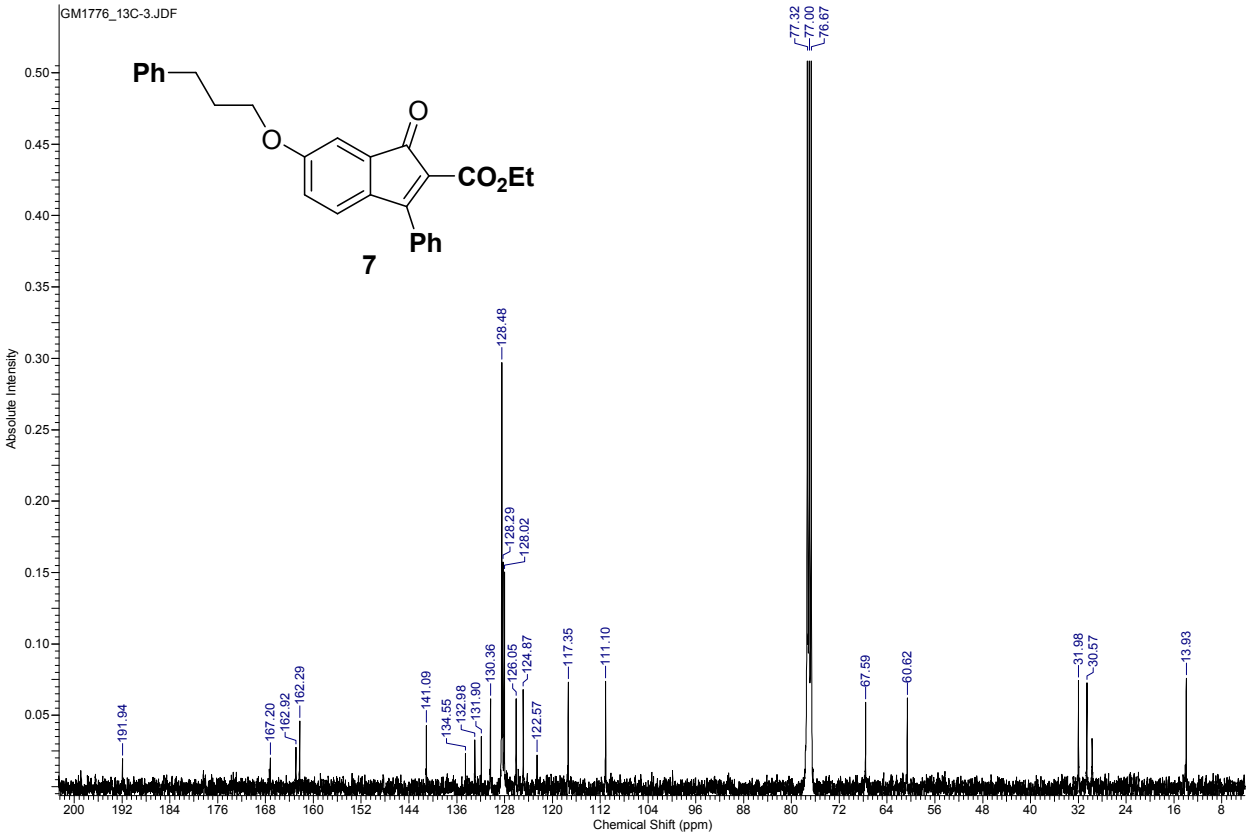
190.63
165.79
161.90
141.87
137.63
133.39


GM1353_PROTON-4.jdf
O
CO2Et
S
14s
Absolute Intensity
Chemical Shift (ppm)
7.26
7.78
7.77
7.72
7.71
7.64
7.44
7.40
7.27
7.25
4.36
4.34
4.37
4.32
1.33
1.35
1.34
1.00 0.98 0.97 0.98 0.99 1.01 1.13
1.99
2.96


GM1353R_13C-3.jdf
O
CO2Et
S
14s
Absolute Intensity
Chemical Shift (ppm)
77.25
77.00
76.74
191.70
163.81
154.73
142.40
133.34
132.18
131.33
130.84
128.01
123.60
123.39
61.41
14.10


GM1776_1H-4 (1).JDF
Ph
O
O
CO2Et
Ph
7
Absolute Intensity
Chemical Shift (ppm)
7.51
7.26
7.27
7.21
7.18
7.17
7.05
7.48
6.82
6.81
6.80
6.79
4.19
4.17
4.01
4.21
4.02
3.99
2.83
2.81
2.79
2.14
2.12
2.10
1.15
1.17
1.14
5.07 1.94 3.98 1.03 1.00
2.01 2.08
1.92
1.98
3.04


GM1776_13C-3.JDF
Ph
O
O
CO2Et
Ph
7
Absolute Intensity
Chemical Shift (ppm)
77.32
77.00
76.67
128.48
128.29
128.02
191.94
167.20
162.92
162.29
141.09
134.55
132.98
131.90
130.36
126.05
124.87
122.57
117.35
111.10
67.59
60.62
31.98
30.57
13.93