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Supplementary Information

Ruthenium(II)-Catalyzed Intermolecular Synthesis of 2-Arylindolines through C-H Activation/Oxidative Cyclization Cascade

Manash Kumar Manna,[ab] Samir Kumar Bhunia,[ab] and Ranjan Jana*[ab]

[a]Organic and Medicinal Chemistry Division, CSIR-Indian Institute of Chemical Biology

4 Raja S. C. Mullick Road, Jadavpur, Kolkata-700032, West Bengal, India

[b]Academy of Scientific and Innovative Research (AcSIR), Kolkata-700032, West Bengal, India

E-mail: rjana@iicb.res.in

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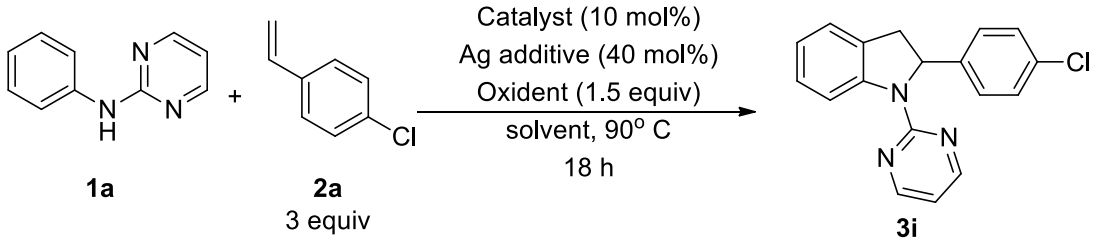
General Information: All manipulations with air-sensitive reagents were carried out under a dry nitrogen atmosphere. Unless otherwise stated, all commercial reagents were used without additional purification. Solvents were dried using standard methods and distilled before use. The starting material *N*-aryl pyrimidines[1], deuterated N-phenyl pyrimidine (**1a-d$_5$**)[2] and Ru(OAc)2(*p*-cymene)[3] were prepared using literature reported method. TLC was performed on silica gel plates (Merck silica gel 60, f_{254}), and the spots were visualized with UV light (254 and 365 nm) or by charring the plate dipped in $KMnO_4$ or vanillin charring solution. ^{1}H NMR was recorded at 300 MHz (Bruker-DPX) and 600 MHz (Bruker-Avance) frequency and ^{13}C NMR spectra were recorded at 75 MHz (Bruker-DPX) and 150 MHz (Bruker-Avance) frequency in $CDCl_3$ solvent using TMS as the internal standard. Chemical shifts were measured in parts per million (ppm) referenced to 0.0 ppm for tetramethylsilane. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br. = broad. Coupling constants, *J* were reported in Hertz unit (Hz). HRMS (m/z) were measured using EI and ESI techniques (JEOL-JMS 700 and Q-Tof Micro mass spectrometer respectively). Infrared (IR) spectra were recorded on Fourier Transform Infrared Spectroscopy (Bruker Tensor 27), only intense peaks were reported.

Optimization Details:

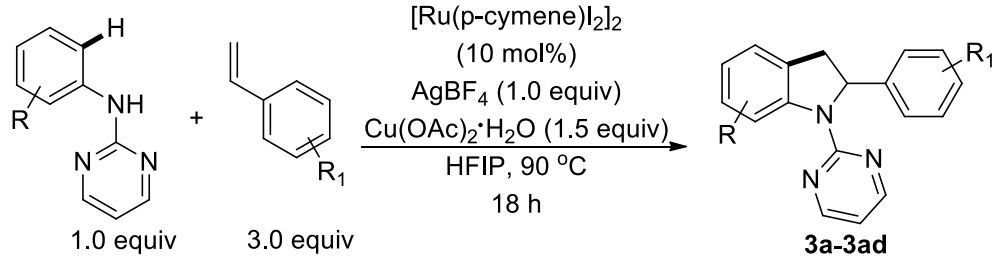


Entry no.	Catalyst	Silver additives	Oxidant	Additives	Solvent	Yield
1	[Ru(*p*-cymene)Cl_2]$_2$	$AgSbF_6$	$Cu(OAc)_2$		DCE	34%
2	[Ru(*p*-cymene)Cl_2]$_2$	$AgSbF_6$	$K_2S_2O_8$		DCE	17%
3	[Ru(*p*-cymene)Cl_2]$_2$	$AgSbF_6$	$(NH_4)_2S_2O_8$		DCE	Trace
4	[Ru(*p*-cymene)Cl_2]$_2$	$AgSbF_6$	Ag_2O		DCE	Trace

5	$[Ru(p\text{-cymene})Cl_2]_2$	$AgSbF_6$	$Mn(OAc)_2$		DCE	Trace
6	$[Ru(p\text{-cymene})Cl_2]_2$	$AgSbF_6$	AgOAc		DCE	8%
7	$[Ru(p\text{-cymene})Cl_2]_2$	$AgSbF_6$	CuO		DCE	23%
8	$[Ru(p\text{-cymene})Cl_2]_2$	$AgSbF_6$	$Cu(OTf)_2$		DCE	Trace
9	$[Ru(p\text{-cymene})Cl_2]_2$	$AgSbF_6$	$PhI(OAc)_2$		DCE	ND
10	$[Ru(p\text{-cymene})Cl_2]_2$	$AgSbF_6$	$Cu(OAc)_2$		1,4-Dioxane	15%
11	$[Ru(p\text{-cymene})Cl_2]_2$	$AgSbF_6$	$Cu(OAc)_2$		MeOH	12%
12	$[Ru(p\text{-cymene})Cl_2]_2$	$AgSbF_6$	$Cu(OAc)_2$		Isopropanol	6%
13	$[Ru(p\text{-cymene})Cl_2]_2$	$AgSbF_6$	$Cu(OAc)_2$		AcOH	Trace
14	$[Ru(p\text{-cymene})Cl_2]_2$	$AgSbF_6$	$Cu(OAc)_2$		THF	11%
15	$[Ru(p\text{-cymene})Cl_2]_2$	$AgSbF_6$	$Cu(OAc)_2$		Toluene	14%
16	$[Ru(p\text{-cymene})Cl_2]_2$	$AgSbF_6$	$Cu(OAc)_2$		DME	18%
17	$[Ru(p\text{-cymene})Cl_2]_2$	$AgSbF_6$	$Cu(OAc)_2$		*Tert*-Amyl alcohol	17%
18	$[Ru(p\text{-cymene})Cl_2]_2$	$AgSbF_6$	$Cu(OAc)_2$		Acetone	22%
19	$[Ru(p\text{-cymene})Cl_2]_2$	$AgSbF_6$	$Cu(OAc)_2$		Acetonitrile	ND
20	$[Ru(p\text{-cymene})Cl_2]_2$	$AgSbF_6$	$Cu(OAc)_2$		TFE	38%
21	$[Ru(p\text{-cymene})Cl_2]_2$	$AgSbF_6$	$Cu(OAc)_2$		HFIP	45%
22	$[Ru(p\text{-cymene})Cl_2]_2$	AgOTf	$Cu(OAc)_2$		HFIP	32%
23	$[Ru(p\text{-cymene})Cl_2]_2$	$Ag(NTf)_2$	$Cu(OAc)_2$		HFIP	37%
24	$[Ru(p\text{-cymene})Cl_2]_2$	$AgPF_6$	$Cu(OAc)_2$		HFIP	43%
25	$[Ru(p\text{-cymene})Cl_2]_2$	$AgBF_4$	$Cu(OAc)_2$		HFIP	48%
26	$[Ru(p\text{-cymene})Cl_2]_2$	$AgBF_4$	$Cu(OAc)_2$	$NaBF_4$ (1 equiv)	HFIP	43%
27	$[Ru(p\text{-cymene})Cl_2]_2$	$AgBF_4$	$Cu(OAc)_2$	$TBABF_4$ (1 equiv)	HFIP	33%
28	$[Ru(p\text{-cymene})Cl_2]_2$	$AgBF_4$	$Cu(OAc)_2$	$TBAPF_6$ (1 equiv)	HFIP	28%
29	$[Ru(p\text{-cymene})Cl_2]_2$	$AgBF_4$	$Cu(OAc)_2$	HBF_4 (1 equiv)	HFIP	35%

30	[Ru(*p*-cymene)Cl_2]$_2$	$AgBF_4$ (0.5 equiv)	$Cu(OAc)_2$		HFIP	51%
31	[Ru(*p*-cymene)Cl_2]$_2$	$AgBF_4$ (1 equiv)	$Cu(OAc)_2$		HFIP	58%
32	**[Ru(*p*-cymene)I_2]$_2$**	**$AgBF_4$ (1 equiv)**	**$Cu(OAc)_2$**		**HFIP**	**74%**
33	[Ru(*p*-cymene)I_2]$_2$	$AgBF_4$ (0.5 equiv)	$Cu(OAc)_2$		HFIP	65%
34	[Ru(*p*-cymene)I_2]$_2$	$AgBF_4$ (1 equiv)	$Cu(OAc)_2$ (1 equiv)		HFIP	67%
35	[Ru(*p*-cymene)I_2]$_2$ (5 mol%)	$AgBF_4$ (1 equiv)	$Cu(OAc)_2$		HFIP	65%
36	[Cp*$RhCl_2$]$_2$ (5 mol%)	$AgSbF_6$	$Cu(OAc)_2$		DCE	12%
37	[Cp*$IrCl_2$]$_2$ (5 mol%)	$AgSbF_6$	$Cu(OAc)_2$		DCE	Trace
38	$Pd(OAc)_2$		$Cu(OAc)_2$		DCE	ND

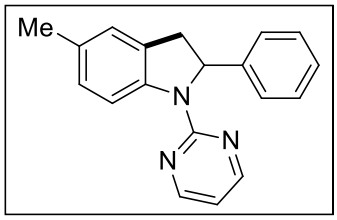
General Experimental Procedure for Ruthenium-Catalyzed Indoline Synthesis from the Corresponding *N*-aryl pyrimidines and Vinyl Arenes:



A mixture of *N*-aryl pyrimidine (0.2 mmol), [Ru(*p*-cymene)I_2]$_2$ (0.02 mmol, 10 mol %), $AgBF_4$ (0.2 mmol, 1 equiv) and $Cu(OAc)_2.H_2O$ (0.3 mmol, 1.5 equiv) was taken in a 15-mL pressure tube and the reaction tube was purged with nitrogen for 30 seconds. To this reaction

mixture, hexafluoroisopropanol (HFIP) (1.0 mL) and the corresponding styrene (0.6 mmol) was added via syringe and the closed reaction mixture was allowed to stir at 90 ^{o}C for 18 h. After completion as indicated by TLC, the reaction the reaction mixture was cooled to ambient temperature. The reaction mixture was quenched with 20 mL saturated solution of Na_2S and extracted with ethyl acetate (3x20 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography using ethyl acetate/hexane as eluent to afford the desired indoline product.

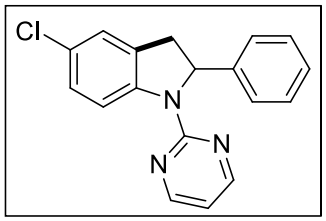
Spectral Data:



5-methyl-2-phenyl-1-(pyrimidin-2-yl)indoline, 3a, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 19:1 hexane/ethyl acetate) afforded the desired product as a white solid, (37 mg, 65%), mp 90-92 ºC.

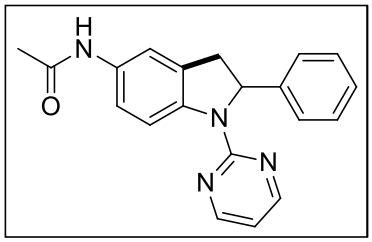
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.38 (d, *J* = 4.8 Hz, 2H), 8.34 (d, *J* = 8.1 Hz, 1H), 7.15-7.25 (m, 5H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.98 (s, 1H), 6.59 (t, *J* = 4.8 Hz, 1H), 5.92 (dd, J_1 = 10.5 Hz, J_2 = 2.4 Hz, 1H), 3.76 (dd, J_1 = 15.9 Hz, J_2 = 10.2 Hz, 1H), 2.98 (dd, J_1 = 15.9 Hz, J_2 = 2.4 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.0, 157.4, 144.3, 141.6, 131.5, 130.5, 128.5, 127.8, 126.8, 125.6, 125.5, 115.4, 111.5, 62.7, 37.8, 21.0; IR (neat): υ_{max} 1579, 1548, 1491, 1461, 1243, 798, 699 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{19}H_{18}N_3$ $[M + H]^+$: 288.1501; found: 288.1501.



5-chloro-2-phenyl-1-(pyrimidin-2-yl)indoline, 3b, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 19:1 hexane/ethyl acetate) afforded the desired product as a white solid, (47 mg, 76%), mp 124-126 ºC.

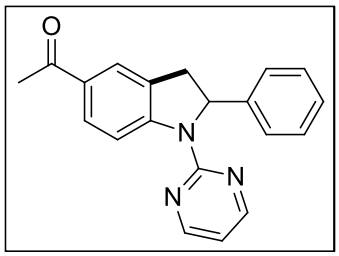
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.45 (d, J = 8.4 Hz, 1H), 8.42 (d, J = 4.8 Hz, 2H), 7.24-7.29 (m, 6H), 7.15 (s, 1H), 6.67 (t, J = 4.8 Hz, 1H), 5.98 (dd, J_1 = 10.5 Hz, J_2 = 2.4 Hz, 1H), 3.78 (dd, J_1 = 16.2 Hz, J_2 = 10.5 Hz, 1H), 3.03 (dd, J_1 = 16.2 Hz, J_2 = 2.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.8, 157.5, 143.8, 142.6, 132.4, 128.5, 127.3, 127.0, 126.6, 125.5, 124.9, 116.5, 112.1, 62.9, 37.5; IR (neat): υ_{max} 1580, 1552, 1485, 1410, 1240, 790, 699 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{18}H_{15}N_3Cl$ $[M + H]^+$: 308.0955; found: 308.0955.



N-(2-phenyl-1-(pyrimidin-2-yl)indolin-5-yl)acetamide, 3c, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 2:8 hexane/ethyl acetate) afforded the desired product as a white solid, (40 mg, 61%), mp 198-200 ºC.

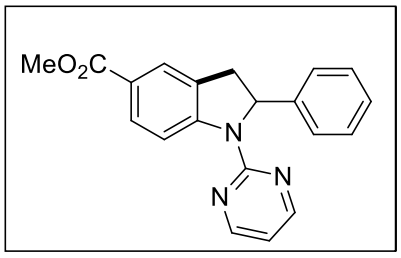
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.37-8.40 (m, 3H), 7.52 (s, 1H), 7.17-7.23 (m, 7H), 6.61 (t, J = 4.8 Hz, 1H), 5.92 (dd, J_1 = 10.5 Hz, J_2 = 2.4 Hz, 1H), 3.76 (dd, J_1 = 16.2 Hz, J_2 = 2.4 Hz, 1H), 3.00 (dd, J_1 = 16.2 Hz, J_2 = 2.4 Hz, 1H), 2.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.3, 158.9, 157.4, 144.0, 140.6, 132.4, 131.3, 128.5, 126.9, 125.5, 119.2, 117.6, 115.6, 111.7, 62.8, 37.8, 24.4; IR (neat): υ_{max} 3422, 1652, 1577, 1553, 1494, 1417, 1303, 789, 701 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{20}H_{18}N_4ONa$ $[M + Na]^+$: 353.1378; found: 353.1378.



1-(2-phenyl-1-(pyrimidin-2-yl)indolin-5-yl)ethanone, 3d, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 1:1 hexane/ethyl acetate) afforded the desired product as a white solid, (54 mg, 86%), mp 176-178 ^oC.

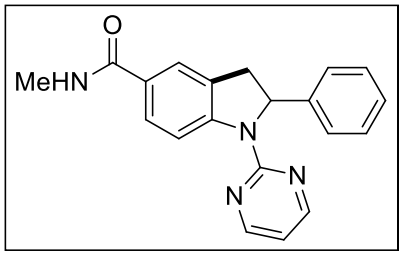
^1H NMR (300 MHz, $CDCl_3$): δ 8.53 (d, J = 8.4 Hz, 1H), 8.44 (d, J = 4.8 Hz, 2H), 7.95 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.80 (s, 1H), 7.18-7.25 (m, 5H), 6.72 (t, J = 4.8 Hz, 1H), 6.00 (dd, J_1 = 10.5 Hz, J_2 = 2.4 Hz, 1H), 3.79 (dd, J_1 = 16.2 Hz, J_2 = 10.5 Hz, 1H), 3.07 (dd, J_1 = 16.5 Hz, J_2 = 2.7 Hz, 1H), 2.58 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.8, 158.7, 157.4, 148.1, 143.6, 131.2, 130.8, 129.6, 128.5, 127.0, 125.3, 124.9, 114.5, 112.9, 63.3, 37.2, 26.4; IR (neat): υ_{max} 1669, 1578, 1489, 1451, 1252, 970, 795 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{20}H_{17}N_3ONa$ [M + Na]$^+$: 338.1269; found: 338.1266.



Methyl 2-phenyl-1-(pyrimidin-2-yl)indoline-5-carboxylate, 3e, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 1:1 hexane/ethyl acetate) afforded the desired product as a white solid, (50 mg, 75%), mp 162-164 ^oC.

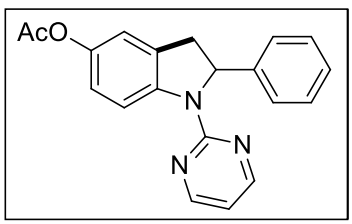
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.53 (d, *J* = 8.4 Hz, 1H), 8.44 (d, *J* = 4.8 Hz, 2H), 8.03 (dd, J_1 = 8.7 Hz, J_2 = 2.1 Hz, 1H), 7.84 (s, 1H), 7.20-7.25 (m, 5H), 6.71 (t, *J* = 4.5 Hz, 1H), 5.99 (dd, J_1 = 10.5 Hz, J_2 = 2.7 Hz, 1H), 3.90 (s, 3H), 3.79 (dd, J_1 = 16.2 Hz, J_2 = 10.5 Hz, 1H), 3.07 (dd, J_1 = 16.2 Hz, J_2 = 2.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.1, 158.8, 157.5, 148.0, 143.7, 130.6, 130.3, 128.5, 127.1, 126.2, 125.5, 123.4, 114.7, 112.8, 63.4, 51.8, 37.3; IR (neat): υ_{max} 1705, 1578, 1487, 1457, 1287, 766, 704 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{20}H_{17}N_3O_2Na$ [M + Na]$^+$: 354.1218; found: 354.1211.



N-methyl-2-phenyl-1-(pyrimidin-2-yl)indoline-5-carboxamide, 3f, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 3:7 hexane/ethyl acetate) afforded the desired product as a white solid, (44 mg, 66%), mp 172-174 ^{o}C.

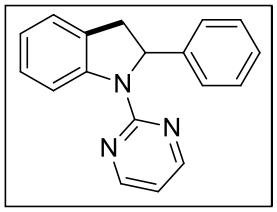
^{1}H NMR (300 MHz, d_6-DMSO): δ 8.54 (d, *J* = 4.5 Hz, 2H), 8.42 (d, *J* = 8.4 Hz, 1H), 8.26 (d, *J* = 4.8 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.68 (s, 1H), 7.13-7.27 (m, 5H), 6.90 (t, *J* = 4.8 Hz, 1H), 5.99 (dd, J_1 = 9.3 Hz, J_2 = 2.4 Hz, 1H), 3.82 (dd, J_1 = 16.5 Hz, J_2 = 10.5 Hz, 1H), 2.92 (dd, J_1 = 16.5 Hz, J_2 = 2.1 Hz, 1H), 2.76 (d, *J* = 4.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.2, 158.8, 157.5, 146.7, 143.8, 130.9, 128.5, 128.0, 127.1, 126.7, 125.4, 123.9, 114.8, 112.6, 63.2, 37.4, 26.8; IR (neat): υ_{max} 3323, 1632, 1578, 1551, 1485, 1456, 1416, 1292, 763, 699 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{20}H_{18}N_4ONa$ [M + Na]$^+$: 353.1378; found: 353.1384.



2-phenyl-1-(pyrimidin-2-yl)indolin-5-yl acetate, 3g, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 6:4 hexane/ethyl acetate) afforded the desired product as a white solid, (38 mg, 57%), mp 140-142 ºC.

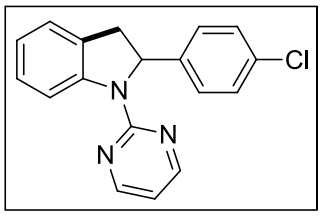
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.46 (d, *J* = 8.7 Hz, 1H), 8.38 (d, *J* = 4.8 Hz, 2H), 7.17-7.25 (m, 5H), 6.97 (d, *J* = 8.7 Hz, 1H), 6.90 (s, 1H), 6.62 (t, *J* = 4.8 Hz, 1H), 5.59 (dd, J_1 = 10.5 Hz, J_2 = 2.7 Hz, 1H), 3.78 (dd, J_1 = 16.2 Hz, J_2 = 2.7 Hz, 1H), 3.01 (dd, J_1 = 16.2 Hz, J_2 = 2.7 Hz, 1H) 2.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.0, 158.9, 157.4, 145.5, 144.0, 141.7, 131.7, 128.5, 126.9, 125.5, 120.0, 118.3, 115.9, 111.9, 63.0, 37.7, 21.2; IR (neat): υ_{max} 1747, 1582, 1552, 1490, 1424, 1219, 898, 802 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{20}H_{17}N_3O_2Na$ $[M + Na]^+$: 354.1218; found: 354.1220.



2-phenyl-1-(pyrimidin-2-yl)indoline, 3h, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 19:1 hexane/ethyl acetate) afforded the desired product as a white solid, (42 mg, 76%), mp 110-112 ºC. The same reaction was performed in 1.0 mmole scale by lowering the catalyst loading (7.5 mol%) and the desired compound obtained with comparable yield.

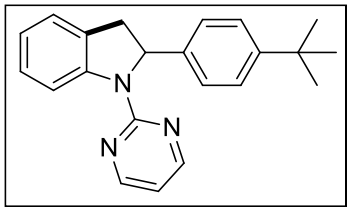
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.49 (d, *J* = 8.1 Hz, 1H), 8.42 (d, *J* = 4.8 Hz, 2H), 7.17-7.34 (m, 7H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.65 (t, *J* = 4.8 Hz, 1H), 5.96 (dd, J_1 = 10.2 Hz, J_2 = 2.4 Hz, 1H), 3.81 (dd, J_1 = 15.9 Hz, J_2 = 10.2 Hz, 1H), 3.05 (dd, J_1 = 15.9 Hz, J_2 = 2.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.1, 157.4, 144.2, 143.9, 130.4, 128.4, 127.4, 126.8, 125.5, 124.8, 122.0, 115.6, 111.7, 62.7, 37.8; IR (neat): υ_{max} 1579, 1548, 1489, 1443, 799, 752 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{18}H_{16}N_3$ $[M + H]^+$: 274.1344; found: 274.1347.



2-(4-chlorophenyl)-1-(pyrimidin-2-yl)indoline, 3i, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 19:1 hexane/ethyl acetate) afforded the desired product as a white solid, (45 mg, 74%), mp 112-114 ºC.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.47 (d, J = 8.1 Hz, 1H), 8.40 (d, J = 4.8 Hz, 2H), 7.30 (t, J = 7.8 Hz, 1H), 7.16-7.19 (m, 5H), 6.99 (td, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 6.64 (t, J = 4.8 Hz, 1H), 5.89 (dd, J_1 = 10.5 Hz, J_2 = 2.7 Hz, 1H), 3.77 (dd, J_1 = 15.9 Hz, J_2 = 10.5 Hz, 1H), 2.98 (dd, J_1 = 16.2 Hz, J_2 = 2.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.0, 157.5, 143.7, 142.9, 132.5, 130.0, 128.6, 127.6, 127.1, 124.9, 122.1, 115.7, 112.0, 62.2, 37.7; IR (neat): υ_{max} 1582, 1550, 1491, 1445, 1084, 794, 748 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{18}H_{15}N_3Cl$ $[M + H]^+$: 308.0955; found: 308.0950.

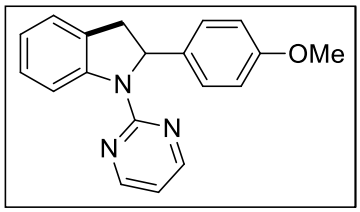


2-(4-(tert-butyl)phenyl)-1-(pyrimidin-2-yl)indoline, 3j, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 19:1 hexane/ethyl acetate) afforded the desired product as a white solid, (40 mg, 60%), mp 90-92 ºC.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43-8.47 (m, 3H), 7.24-7.32 (m, 3H), 7.17-7.20 (m, 3H), 6.99 (td, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1H), 6.66 (t, J = 4.8 Hz, 1H), 5.98 (dd, J_1 = 10.2 Hz, J = 2.1 Hz, 1H), 3.78 (dd, $_{J1}$ = 15.9 Hz, J_2 = 9.9 Hz, 1H), 3.05 (d, J = 15.6 Hz, 1H), 1.27 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.2, 157.5, 149.5, 143.8, 141.0, 130.7, 127.3, 125.3, 125.2, 124.9, 122.0,

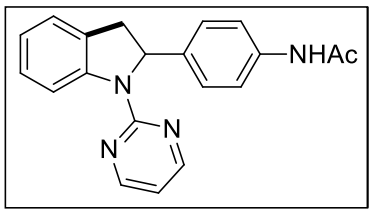
115.8, 111.7, 62.4, 37.8, 34.4, 31.4; IR (neat): υ_{max} 1584, 1547, 1492, 1445, 790, 742 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{22}H_{23}N_3Na$ $[M + Na]^+$: 352.1790; found: 352.1792.



2-(4-methoxyphenyl)-1-(pyrimidin-2-yl)indoline, 3k, Table 2

The same general procedure was followed except $AgSbF_6$.(40 mol%) was used instead of $AgBF_4$ (1 equiv) and DCE was used as a solvent instead of HFIP. Column chromatography (SiO_2, eluting with 19:1 hexane/ethyl acetate) afforded the desired product as a white solid, (28 mg, 46%), mp 114-116 ºC.

^1H NMR (300 MHz, $CDCl_3$): δ 8.44 (d, *J* = 8.4 Hz, 1H), 8.40 (d, *J* = 4.8 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 1H), 7.16-7.25 (m, 3H), 6.97 (t, *J* = 7.2 Hz, 1H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.62 (t, *J* = 4.8 Hz, 1H), 5.89 (dd, J_1 = 10.5 Hz, J_2 = 2.4 Hz, 1H), 3.71-3.79 (m, 4H), 3.00 (dd, J_1 = 16.2 Hz, J_2 = 2.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.0, 158.4, 157.4, 143.7, 136.3, 130.5, 127.3, 126.7, 124.8, 121.9, 115.6, 113.7, 111.7, 62.1, 55.1, 37.9; IR (neat): υ_{max} 1580, 1551, 1487, 1446, 1241, 1029, 845, 761 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{19}H_{17}N_3ONa$ $[M + Na]^+$: 326.1269; found: 326.1268.

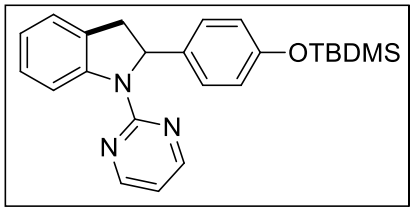


N-(4-(1-(pyrimidin-2-yl)indolin-2-yl)phenyl)acetamide, 3l, Table 2

The same general procedure was followed except $AgSbF_6$ (40 mol%) was used instead of $AgBF_4$ (1 equiv) and DCE was used as a solvent instead of HFIP. Column chromatography (SiO_2,

eluting with 4:6 hexane/ethyl acetate) afforded the desired product as a white solid, (28 mg, 42%), mp 222-224 ºC.

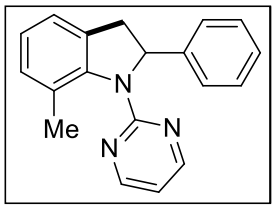
^{1}H NMR (300 MHz, d_6-DMSO): δ 9.86 (br. s, 1H), 8.49 (d, *J* = 4.8 Hz, 2H), 8.39 (d, *J* = 8.1 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.20-7.27 (m, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.95 (t, *J* = 7.2 Hz, 1H), 6.83 (t, *J* = 4.8 Hz, 1H), 5.87 (dd, J_1 = 10.5 Hz, J_2 = 2.4 Hz, 1H), 3.75 (dd, J_1 = 16.2 Hz, J_2 = 10.2 Hz, 1H) 2.88 (d, *J* = 15.9 Hz, 1H), 1.98 (s, 3H); ^{13}C NMR (75 MHz, d_6-DMSO): δ 168.2, 158.5, 157.9, 143.4, 138.7, 138.0, 130.4, 127.2, 125.5, 125.0, 122.0, 119.3, 115.3, 112.3, 61.8, 37.5, 23.9; IR (neat): υ_{max} 3325, 1662, 1582, 1535, 1491, 1445, 1310, 834, 792, 750 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{20}H_{19}N_4O$ $[M + H]^+$: 331.1559; found: 331.1554.



2-(4-((tert-butyldimethylsilyl)oxy)phenyl)-1-(pyrimidin-2-yl)indoline, 3m, Table 2

The same general procedure was followed except $AgSbF_6$.(40 mol%) was used instead of $AgBF_4$ (1 equiv) and DCE was used as a solvent instead of HFIP. Column chromatography (SiO_2, eluting with 19:1 hexane/ethyl acetate) afforded the desired product as a white solid, (39 mg, 48%), mp 88-90 ºC.

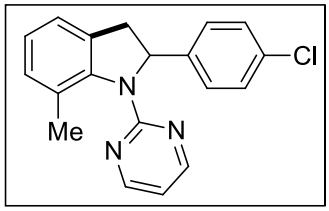
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.46 (d, *J* = 8.1 Hz, 1H), 8.41 (d, *J* = 4.8 Hz, 2H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.69 (d, *J* = 8.4 Hz, 2H), 6.62 (t, *J* = 4.8 Hz, 1H), 5.89 (dd, J_1 = 10.2 Hz, J_2 = 2.4 Hz, 1H), 3.75 (dd, J_1 = 15.9 Hz, J_2 = 10.2 Hz, 1H), 3.02 (dd, J_1 = 15.9 Hz, J_2 = 2.4 Hz, 1H), 0.95 (s, 9H), 0.15 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.7, 157.0, 154.0, 143.5, 136.5, 130.3, 126.9, 126.3, 124.4, 121.5, 119.4, 115.3, 111.3, 61.8, 37.5, 25.3, 17.7, -4.8; IR (neat): υ_{max} 1582, 1550, 1490, 1444, 1257, 916, 838, 782 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{24}H_{30}N_3OSi$ $[M + H]^+$: 404.2158; found: 404.2153.



7-methyl-2-phenyl-1-(pyrimidin-2-yl)indoline, 3n, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a white solid, (37 mg, 64%), mp 188-190 ^oC.

^1H NMR (300 MHz, $CDCl_3$): δ 8.43 (d, J = 4.8 Hz, 2H), 7.17-7.36 (m, 5H), 7.08 (dd, J_1 = 6.6 Hz, J_2 = 1.8 Hz, 1H), 6.94-7.02 (m, 2H), 6.70 (t, J = 4.8 Hz, 1H), 5.95 (d, J = 9.0 Hz, 1H), 3.85 (dd, J_1 = 15.3 Hz, J_2 = 9.0 Hz, 1H), 2.94 (d, J = 15.3 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.1, 157.7, 143.5, 142.4, 132.4, 129.6, 128.5, 128.1, 127.0, 125.4, 124.4, 122.2, 112.6, 66.9, 38.8, 21.0; IR (neat): υ_{max} 1576, 1545, 1473, 11433, 1283, 757, 697 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{19}H_{17}N_3Na$ $[M + Na]^+$: 310.1320; found: 310.1321.

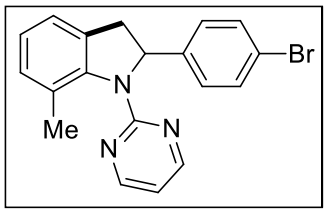


2-(4-chlorophenyl)-7-methyl-1-(pyrimidin-2-yl)indoline, 3o, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a white solid, (44 mg, 68%), mp 192-194 ^oC.

^1H NMR (300 MHz, $CDCl_3$): δ 8.44 (d, J = 4.5 Hz, 2H), 7.23-7.30 (m, 4H), 7.10 (d, J = 6.9 Hz, 1H), 6.99-7.11 (m, 2H), 6.73 (t, J = 4.5 Hz, 1H), 5.91 (d, J = 9.0 Hz, 1H), 3.85 (dd, J_1 = 15.6 Hz, J_2 = 9.3 Hz, 1H), 2.90 (d, J = 15.6 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.0,

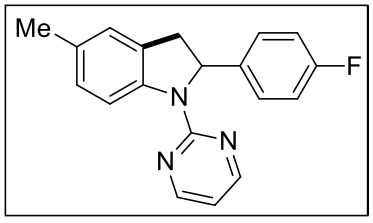
157.8, 142.2, 142.1, 132.7, 132.1, 129.8, 128.6, 128.2, 127.0, 124.5, 122.2, 112.8, 66.4, 38.7, 21.0; IR (neat): υ_{max} 1574, 1550, 1468, 1428, 1281, 1088, 806, 771 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{19}H_{17}N_3Cl$ $[M + H]^+$: 322.1111; found: 322.1109.



2-(4-bromophenyl)-7-methyl-1-(pyrimidin-2-yl)indoline, 3p, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a white solid, (45 mg, 62%), mp 180-182 ^oC.

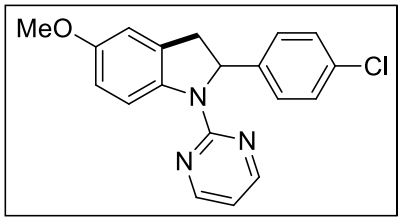
^1H NMR (300 MHz, $CDCl_3$): δ 8.44 (d, *J* = 4.8 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 6.6 Hz, 1H), 6.96-7.03 (m, 2H), 6.72 (t, *J* = 4.8 Hz, 1H), 5.89 (d, *J* = 9.0 Hz, 1H), 3.85 (dd, J_1 = 15.6 Hz, J_2 = 9.0 Hz, 1H), 2.90 (d, *J* = 15.0 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.0, 157.8, 142.6, 142.2, 132.1, 131.6, 129.8, 128.2, 127.4, 124.5, 122.2, 120.8, 112.8, 66.5, 38.6, 21.0; IR (neat): υ_{max} 1574, 1549, 1468, 1427, 1281, 806, 771 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{19}H_{16}N_3Br$ $[M]^+$: 365.0528; found: 365.0525.



2-(4-fluorophenyl)-5-methyl-1-(pyrimidin-2-yl)indoline, 3q, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 19:1 hexane/ethyl acetate) afforded the desired product as a white solid, (41 mg, 67%), mp 120-122 ^oC.

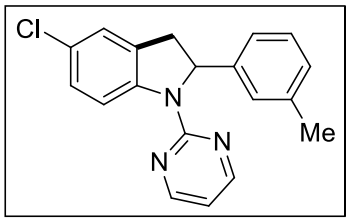
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.40 (d, *J* = 4.8 Hz, 2H), 8.34 (d, *J* = 8.4 Hz, 1H), 7.22-7.24 (m, 2H), 7.11 (d, *J* = 8.4 Hz, 1H), 7.01 (s, 1H), 6.91-6.95 (m, 2H), 6.63 (t, *J* = 4.8 Hz, 1H), 5.91 (d, *J* = 10.2 Hz, 1H), 3.76 (dd, J_1 = 16.2 Hz, J_2 =10.8 Hz, 1H), 2.97 (dd, J_1 = 15.6 Hz, J_2 = 1.8 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 161.7 (d, J_{C-F} = 243.0 Hz), 158.9, 157.4, 141.4, 140.0 (d, J_{C-F} = 3.0 Hz), 131.6, 130.3, 127.9, 127.2 (d, J_{C-F} = 8.0 Hz), 125.6, 115.5, 115.2 (J_{C-F} = 21.3 Hz), 111.6, 62.1, 37.8, 20.9; IR (neat): υ_{max} 1580, 1498, 1459, 1414, 1218, 826. HRMS (ESI, m/z) calcd. for $C_{19}H_{17}FN_3$ $[M + H]^+$: 306.1407; found: 306.1400.



2-(4-chlorophenyl)-5-methoxy-1-(pyrimidin-2-yl)indoline, 3r, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a white solid, (27 mg, 40%), mp 132-134 ^{o}C.

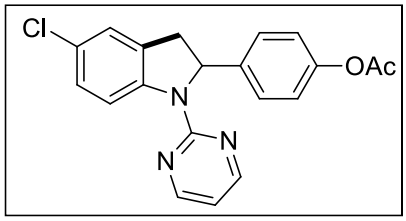
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.35-8.40 (m, 3H), 7.18-7.24 (m, 4H), 6.85 (dd, J_1 = 8.7 Hz, J_2 = 2.7 Hz, 1H), 6.79 (s, 1H), 6.62 (t, *J* = 4.8 Hz, 1H), 5.90 (dd, J_1 = 10.2 Hz, J_2 = 2.4 Hz, 1H), 3.82 (s, 3H), 3.78 (dd, J_1 = 15.9 Hz, J_2 = 10.2 Hz, 1H), 2.96 (dd, J_1 = 16.2 Hz, J_2 = 2.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.7, 157.4, 155.4, 142.8, 137.4, 132.5, 131.6, 128.6, 127.0, 116.2, 112.0, 114.4, 111.3, 62.2, 55.7, 37.8; IR (neat): υ_{max} 1584, 1549, 1493, 1428, 1256, 1035, 797 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{19}H_{17}N_3OCl$ $[M + H]^+$: 338.1060; found: 338.1064.



5-chloro-1-(pyrimidin-2-yl)-2-(*m*-tolyl)indoline, 3s, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a gummy liquid, (45 mg, 70%),

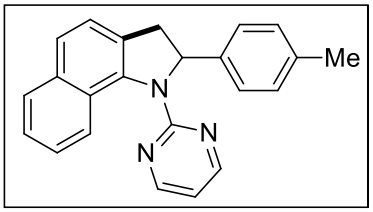
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.40-8.42 (m, 3H), 7.23 (d, *J* = 9.0 Hz, 1H), 7.10-7.15 (m, 2H), 6.99-7.03 (m, 3H), 6.65 (t, *J* = 4.8 Hz, 1H), 5.91 (dd, J_1 = 10.2 Hz, J_2 = 2.4 Hz, 1H), 3.74 (dd, J_1 = 16.2 Hz, J_2 = 10.5 Hz, 1H), 2.99 (dd, J_1 = 16.2 Hz, J_2 = 2.4 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.9, 157.5, 143.8, 142.7, 138.2, 132.5, 128.5, 127.9, 127.3, 126.6, 126.1, 125.0, 122.4, 116.5, 112.1, 62.9, 37.7, 21.6; IR (neat): υ_{max} 1580, 1550, 1484, 1409, 1167, 790 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{19}H_{17}N_3Cl$ $[M + H]^+$: 322.1111; found: 322.1112.



4-(5-chloro-1-(pyrimidin-2-yl)indolin-2-yl)phenyl acetate, 3t, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 6:4 hexane/ethyl acetate) afforded the desired product as a white solid, (38 mg, 52%), mp 160-162 ºC.

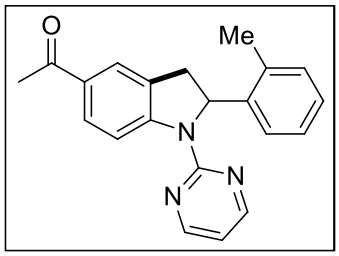
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.53 (d, *J* = 2.1 Hz, 1H), 8.42 (d, *J* = 4.8 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 1H), 6.94-6.97 (m, 3H), 6.69 (t, *J* = 4.8 Hz, 1H), 5.95 (dd, J_1 = 10.5 Hz, J_2 = 2.7 Hz, 1H), 3.71 (dd, J_1 = 15.9 Hz, J_2 = 9.9 Hz, 1H), 2.99 (dd, J_1 = 16.2 Hz, J_2 = 2.7 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.5, 158.6, 157.5, 149.5, 144.8, 141.3, 133.0, 128.7, 126.6, 125.4, 121.7, 121.5, 115.9, 112.4, 62.7, 37.1, 21.1; IR (neat): υ_{max} 1756, 1582, 1489, 1443, 1213, 909, 796 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{20}H_{16}N_3O_2ClNa$ $[M + Na]^+$: 388.0829; found: 388.0826.



1-(pyrimidin-2-yl)-2-(*p*-tolyl)-2,3-dihydro-1H-benzo[g]indole, 3u, Table 2

The same general procedure was followed except $AgSbF_6$.(40 mol%) was used instead of $AgBF_4$ (1 equiv) and DCE was used as a solvent instead of HFIP. Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a white solid, (38 mg, 56%), mp 216-218 ºC.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (d, J = 4.8 Hz, 2H), 7.86 (dd, J_1 = 8.0 Hz, J_2 = 2.1 Hz, 1H), 7.76 (dd, J_1 = 8.1 Hz, J_2 = 2.4 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.26-7.47 (m, 5H), 7.07 (d, J = 7.5 Hz, 2H), 6.74 (t, J = 4.8 Hz, 1H), 6.10 (d, J = 9.0 Hz, 1H), 4.07 (dd, J_1 = 15.6 Hz, J_2 = 9.0 Hz, 1H), 3.07 (dd, J_1 = 15.6 Hz, J_2 = 1.5 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.7, 157.7, 140.7, 139.3, 136.6, 134.0, 129.3, 129.1, 128.5, 126.1, 125.5, 125.4, 124.9, 124.8, 124.4, 123.0, 112.9, 67.8, 39.5, 21.1; IR (neat): υ_{max} 1577, 1433, 1284, 808 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{23}H_{20}N_3$ $[M + H]^+$: 338.1657; found: 338.1651.

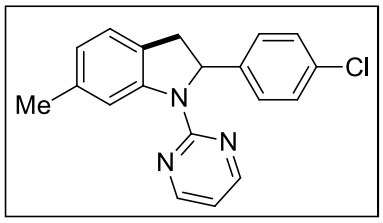


1-(1-(pyrimidin-2-yl)-2-(o-tolyl)indolin-5-yl)ethanone, 3v, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 6:4 hexane/ethyl acetate) afforded the desired product as a white solid, (29 mg, 44%), mp 144-146 ºC.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.57 (d, J = 8.4 Hz, 1H), 8.43 (d, J = 4.8 Hz, 2H), 7.96 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.78 (s, 1H), 7.19 (d, J = 7.5 Hz, 1H), 7.10 (td, J_1 = 7.2 Hz, J_2 = 1.8 Hz, 1H), 6.88-6.98 (m, 2H), 6.71 (t, J = 4.8 Hz, 1H), 6.14 (dd, J_1 = 10.5 Hz, J_2 = 3.0 Hz, 1H), 3.80 (dd, J_1 = 15.9 Hz, J_2 = 10.5 Hz, 1H), 2.94 (dd, J_1 = 16.2 Hz, J_2 = 3.0 Hz, 1H), 2.58 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.9, 158.7, 157.5, 148.5, 141.8, 134.2, 131.2, 130.8, 130.6, 129.7, 126.8, 126.1, 125.1, 123.4, 114.5, 112.9, 60.5, 36.1, 26.4, 19.5; IR (neat): υ_{max}

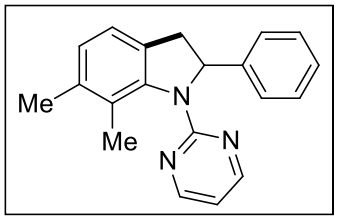
1675, 1578, 1489, 1452, 1257, 971 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{21}H_{19}N_3ONa$ $[M + Na]^+$: 352.1426; found: 352.1419.



2-(4-chlorophenyl)-6-methyl-1-(pyrimidin-2-yl)indoline, 3w, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 19:1 hexane/ethyl acetate) afforded the desired product as a white solid, (35 mg, 55%), mp 196-198 ^oC.

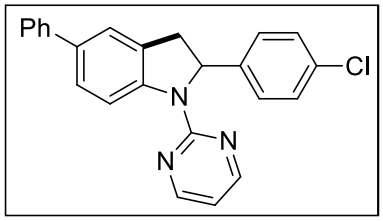
^1H NMR (300 MHz, $CDCl_3$): δ 8.42 (d, J = 4.8 Hz, 2H), 8.31 (s, 1H), 7.17-7.23 (m, 4H), 7.06 (d, J = 7.5 Hz, 1H), 6.83 (d, J = 7.5 Hz, 1H), 6.66 (t, J = 4.8 Hz, 1H), 5.90 (dd, J_1 = 10.5 Hz, J_2 = 2.7 Hz, 1H), 3.74 (dd, J_1 = 15.9 Hz, J_2 = 10.2 Hz, 1H), 2.94 (dd, J_1 = 16.5 Hz, J_2 = 2.4 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.9, 157.4, 143.8, 142.9, 137.4, 132.4, 128.6, 127.1, 127.0, 124.5, 122.9, 116.3, 111.8, 62.5, 37.3, 22.0; IR (neat): υ_{max} 1582, 1501, 1461, 1084, 794 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{19}H_{17}N_3Cl$ $[M + H]^+$: 322.1111; found: 322.1116.



6,7-dimethyl-2-phenyl-1-(pyrimidin-2-yl)indoline, 3x, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a white solid, (30 mg, 50%), mp 200-202 ^oC.

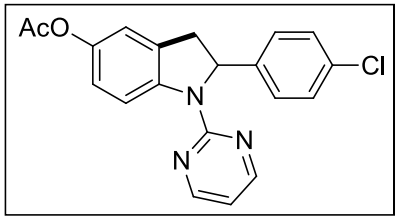
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.42 (d, *J* = 4.8 Hz, 2H), 7.25-7.37 (m, 4H), 7.17-7.22 (m, 1H), 6.87-6.93 (m, 2H), 6.70 (t, *J* = 4.8 Hz, 1H), 5.98 (d, *J* = 8.7 Hz, 1H), 3.82 (dd, J_1 = 15.3 Hz, J_2 = 8.7 Hz, 1H), 2.92 (d, *J* = 15.3 Hz, 1H), 2.32 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.5, 157.7, 143.7, 142.8, 136.1, 130.1, 128.5, 127.2, 127.0, 126.2, 125.6, 121.7, 112.5, 67.4, 38.7, 20.1, 17.9; IR (neat): υ_{max} 1577, 1547, 1430, 1282, 1049, 800, 753, 700 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{20}H_{20}N_3$ $[M + H]^+$: 302.1657; found: 302.1655.



2-(4-chlorophenyl)-5-phenyl-1-(pyrimidin-2-yl)indoline, 3y, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a white solid, (48 mg, 63%), mp 140-142 ^{o}C.

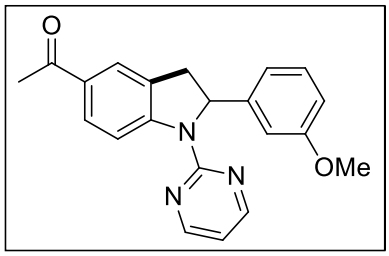
^{1}H NMR (300 MHz, d_6-DMSO): δ 8.52 (d, *J* = 4.8 Hz, 2H), 8.47 (d, *J* = 8.1 Hz, 1H), 7.54-7.66 (m, 4H), 7.40-7.45 (m, 2H), 7.28-7.33 (m, 3H), 7.18-7.21 (m, 2H), 6.87 (t, *J* = 4.8 Hz, 1H), 5.96 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 3.85 (dd, J_1 = 16.5 Hz, J_2 = 10.5 Hz, 1H), 2.95 (dd, J_1 = 17.1 Hz, J_2 = 2.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.8, 157.5, 143.1, 142.7, 141.0, 135.2, 132.5, 130.7, 128.7, 128.6, 127.0, 126.7, 126.6, 126.5, 123.5, 115.7, 112.0, 62.4, 37.7; IR (neat): υ_{max} 1580, 1547, 1486, 1411, 1087, 826, 761, 692 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{24}H_{18}N_3Cl$ $[M]^+$: 383.1189; found: 383.1185.



2-(4-chlorophenyl)-1-(pyrimidin-2-yl)indolin-5-yl acetate, 3z, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 6:4 hexane/ethyl acetate) afforded the desired product as a white solid, (44 mg, 60%), mp 190-192 ^oC.

^1H NMR (300 MHz, $CDCl_3$): δ 8.47 (d, *J* = 8.7 Hz, 1H), 8.40 (d, *J* = 4.8 Hz, 2H), 7.17-7.24 (m, 4H), 6.99 (d, *J* = 8.7 Hz, 1H), 6.93 (s, 1H), 6.66 (t, *J* = 4.8 Hz, 1H), 5.91 (dd, J_1 = 10.5 Hz, J_2 = 2.7 Hz, 1H), 3.78 (dd, J_1 = 16.2 Hz, J_2 = 10.5 Hz, 1H), 2.99 (dd, J_1 = 16.5 Hz, J_2 = 3.0 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.9, 158.7, 157.4, 145.5, 142.5, 141.4, 132.5, 131.3, 128.6, 127.0, 120.1, 118.3, 115.9, 112.0, 62.4, 37.5, 21.1; IR (neat): υ_{max} 1756, 1582, 1489, 1442, 1214, 908, 795 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{20}H_{17}N_3O_2Cl$ $[M + H]^+$: 366.1009; found: 366.1011.

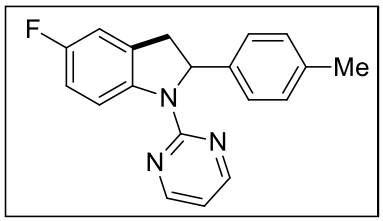


1-(2-(3-methoxyphenyl)-1-(pyrimidin-2-yl)indolin-5-yl)ethanone, 3aa, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 4:6 hexane/ethyl acetate) afforded the desired product as a white solid, (38 mg, 55%), mp 128-130 ^oC.

^1H NMR (300 MHz, $CDCl_3$): δ 8.48 (d, *J* = 8.7 Hz, 1H), 8.45 (d, *J* = 4.8 Hz, 2H), 7.94 (dd, J_1 = 8.7 Hz, J_2 = 1.8 Hz, 1H), 7.79 (s, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 6.71-6.82 (m, 4H), 5.97 (dd, J_1 = 10.5 Hz, J_2 = 2.7 Hz, 1H), 3.78 (dd, J_1 = 16.2 Hz, J_2 = 10.5 Hz, 1H), 3.72 (s, 3H), 3.07 (dd, J_1 = 16.2 Hz, J_2 = 2.7 Hz, 1H), 2.58 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.9, 159.7, 158.8, 157.5, 148.2, 145.4, 131.3, 130.9, 129.7, 124.9, 117.6, 114.6, 113.0, 111.9, 111.5, 63.3, 55.1,

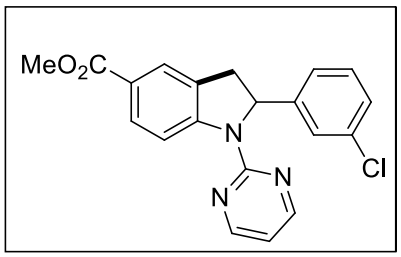
37.2, 26.4; IR (neat): υ_{max} 1667, 1579, 1488, 1449, 1419, 1260, 968, 795 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{21}H_{19}N_3O_2Na$ $[M + Na]^+$: 368.1375; found: 368.1380.



5-fluoro-1-(pyrimidin-2-yl)-2-(*p*-tolyl)indoline, 3ab, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 19:1 hexane/ethyl acetate) afforded the desired product as a white solid, (24 mg, 40%), mp 104-106 ^oC.

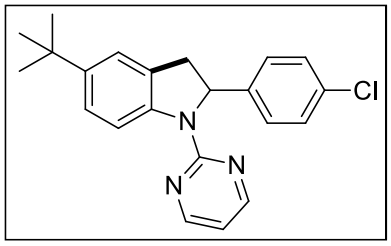
^1H NMR (300 MHz, d_6-DMSO): δ 8.49 (d, J = 4.8 Hz, 2H), 8.34-8.39 (m, 1H), 7.00-7.10 (m, 6H), 6.83 (t, J = 4.8 Hz, 1H), 5.92 (dd, J_1 = 8.4 Hz, J_2 = 2.1 Hz, 1H), 3.77 (dd, J_1 = 16.5 Hz, J_2 10.5 Hz, 1H), 2.87 (d, J = 16.5 Hz, 1H), 2.21 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.9, 158.5 (d, $J_{C\text{-}F}$ = 239.3 Hz), 157.5, 140.9, 140.0 (d, $J_{C\text{-}F}$ = 2.0 Hz), 136.6, 132.4 (d, $J_{C\text{-}F}$ = 8.3 Hz), 129.2, 125.4, 116.2 (d, $J_{C\text{-}F}$ = 7.5 Hz), 113.3 (d, $J_{C\text{-}F}$ = 21.8 Hz), 112.2 (d, $J_{C\text{-}F}$ = 24.0 Hz), 111.7, 62.7, 37.8, 21.1; IR (neat): υ_{max} 1586, 1552, 1493, 1428, 1177, 818, 756 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{19}H_{17}N_3F$ $[M + H]^+$: 306.1407; found: 306.1413.



Methyl 2-(3-chlorophenyl)-1-(pyrimidin-2-yl)indoline-5-carboxylate, 3ac, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 3:7 hexane/ethyl acetate) afforded the desired product as a white solid, (41 mg, 56%), mp 162-164 ºC.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.52 (d, J = 8.4 Hz, 1H), 8.45 (d, J = 4.8 Hz, 2H), 8.03 (dd, J_1 = 8.7 Hz, J_2 = 1.8 Hz, 1H), 7.84 (s, 1H), 7.21 (s, 1H), 7.07-7.18 (m, 3H), 6.74 (t, J = 4.8 Hz, 1H), 5.93 (dd, J_1 = 10.5 Hz, J_2 = 2.7 Hz, 1H), 3.90 (s, 3H), 3.78 (dd, J_1 = 16.2 Hz, J_2 = 10.5 Hz, 1H), 3.04 (dd, J_1 = 16.2 Hz, J_2 = 2.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.0, 158.6, 157.5, 147.8, 145.9, 134.3, 130.4, 130.1, 129.9, 127.3, 126.2, 125.8, 123.60, 123.57, 114.8, 113.0, 62.9, 51.9, 37.1; IR (neat): υ_{max} 1709, 1583, 1458, 1424, 1279, 980, 767 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{20}H_{16}N_3O_2ClNa$ $[M + Na]^+$: 388.0829; found: 388.0824.



5-(tert-butyl)-2-(4-chlorophenyl)-1-(pyrimidin-2-yl)indoline, 3ad, Table 2

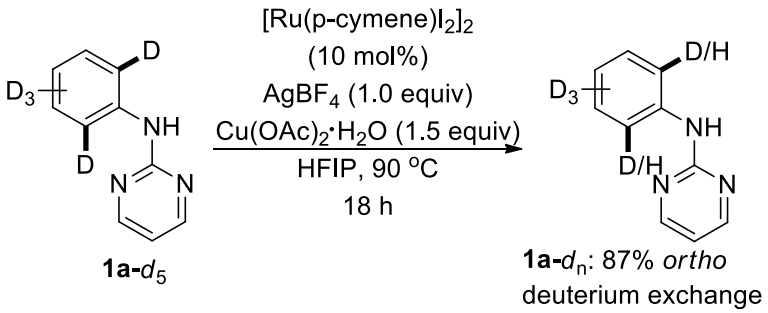
The same general procedure was followed. Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a white solid, (44 mg, 60%), mp 100-102 ºC.

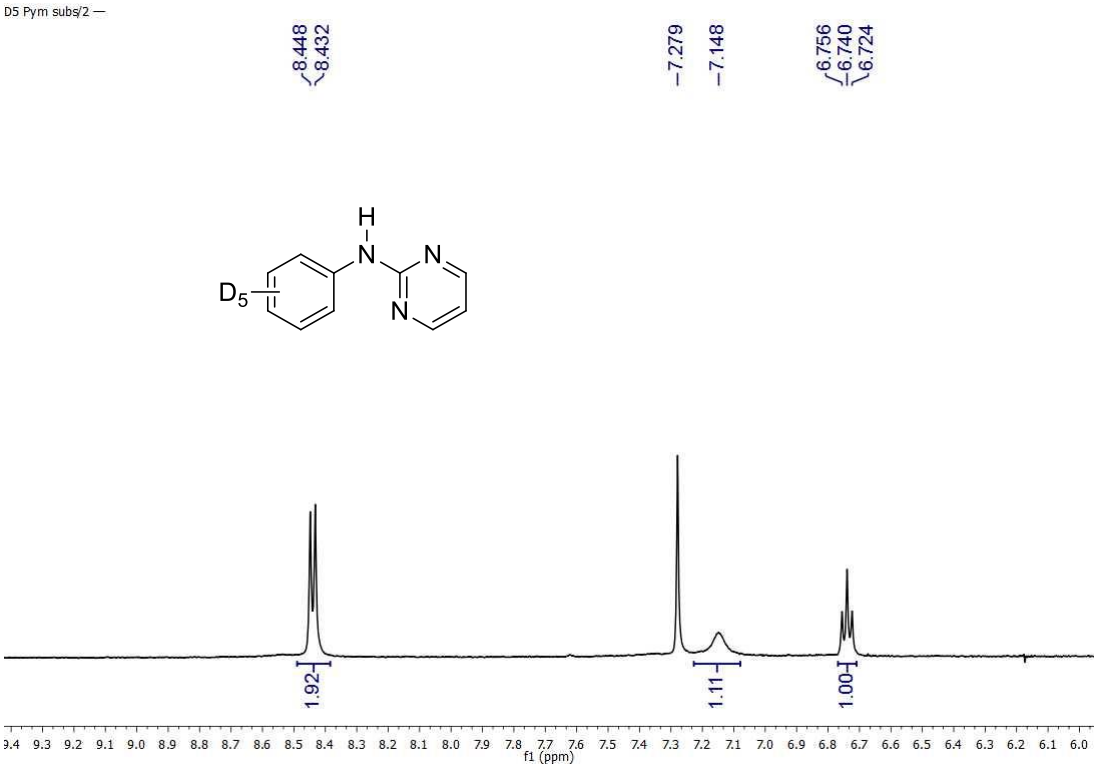
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.38 (d, J = 4.8 Hz, 2H), 8.33 (d, J = 8.7 Hz, 1H), 7.31 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.16-7.20 (m, 5H), 6.62 (t, J = 4.8 Hz, 1H), 5.87 (dd, J_1 = 10.5 Hz, J_2 = 2.7 Hz, 1H), 3.78 (dd, J_1 = 15.6 Hz, J_2 = 10.2 Hz, 1H), 2.97 (dd, J_1 = 15.9 Hz, J_2 = 2.7 Hz, 1H), 1.32(s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.9, 157.4, 145.2, 143.0, 141.2, 132.3, 129.7, 128.5, 127.1, 124.2, 121.9, 115.1, 111.7, 62.2, 37.9, 34.3, 31.6; IR (neat): υ_{max} 1580, 1548, 1496, 1465, 1414, 1266, 827, 792 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{22}H_{23}N_3Cl$ $[M + H]^+$: 364.1581; found: 364.1582.

Mechanistic Study:

(a) H/D Exchange Experiment:

A mixture of d_5 *N*-phenyl pyrimidine (0.2 mmol), [Ru(*p*-cymene)I_2]$_2$ (0.02 mmol, 10 mol %), $AgBF_4$ (0.2 mmol, 1 equiv) and $Cu(OAc)_2.H_2O$ (0.3 mmol, 1.5 equiv) was taken in a 15-mL pressure tube and the reaction tube was purged with nitrogen for 30 seconds. To this reaction mixture, hexafluoroisopropanol (HFIP) (1.0 mL) was added via syringe and the closed reaction mixture was allowed to stir at 90 ^oC in absence of olefins. After 18 h, the reaction mixture was cooled to ambient temperature. The reaction mixture was quenched with 20 mL saturated solution of Na_2S and extracted with ethyl acetate (3x20 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude starting material was purified by column chromatography using ethyl acetate/hexane as eluent and H/D exchange was determined by ^1H NMR analysis.

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6.740
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H
N
N
N
D5
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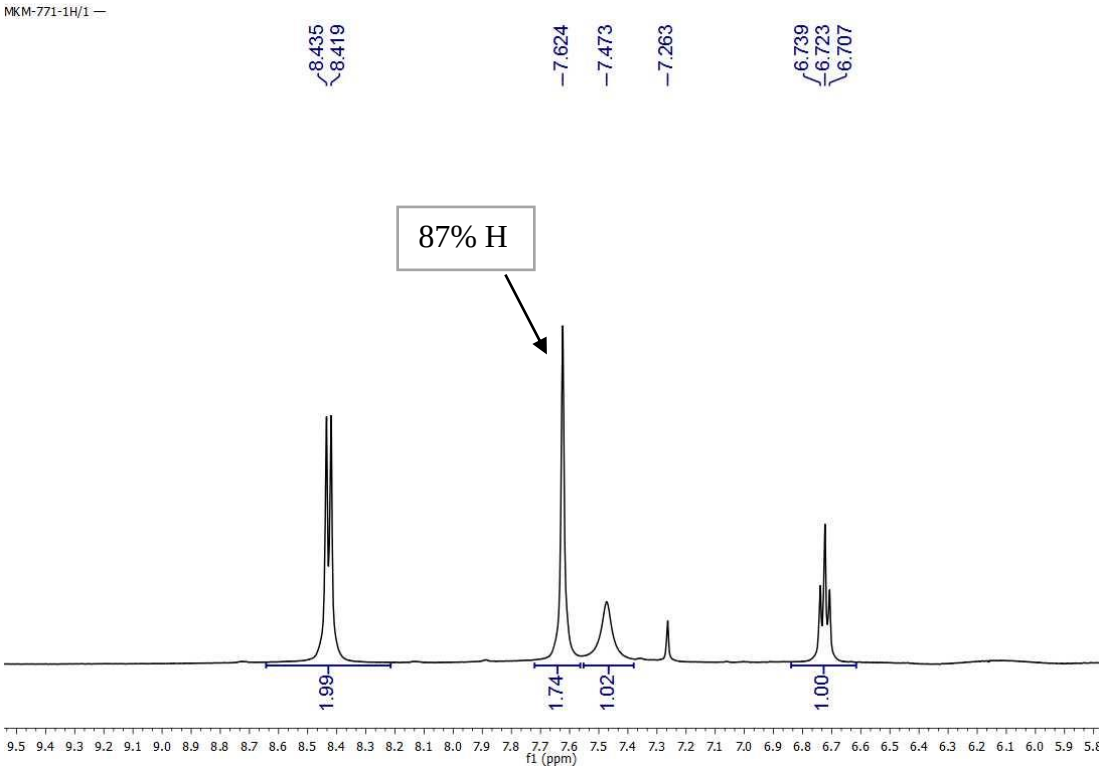
1.11
1.00
f1 (ppm)


MKM-771-1H/1 —
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7.624
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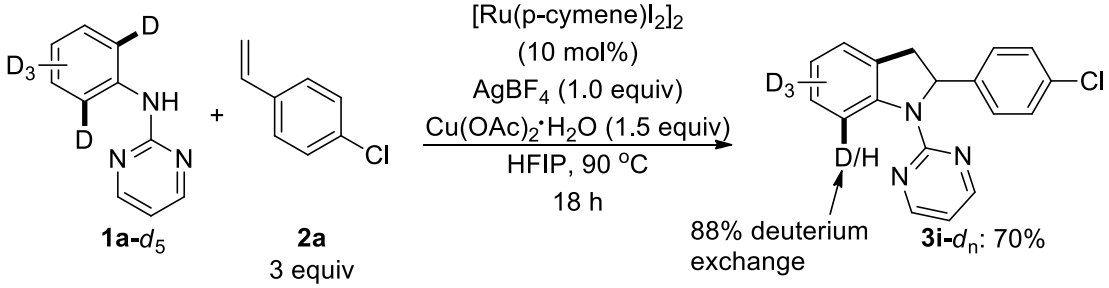
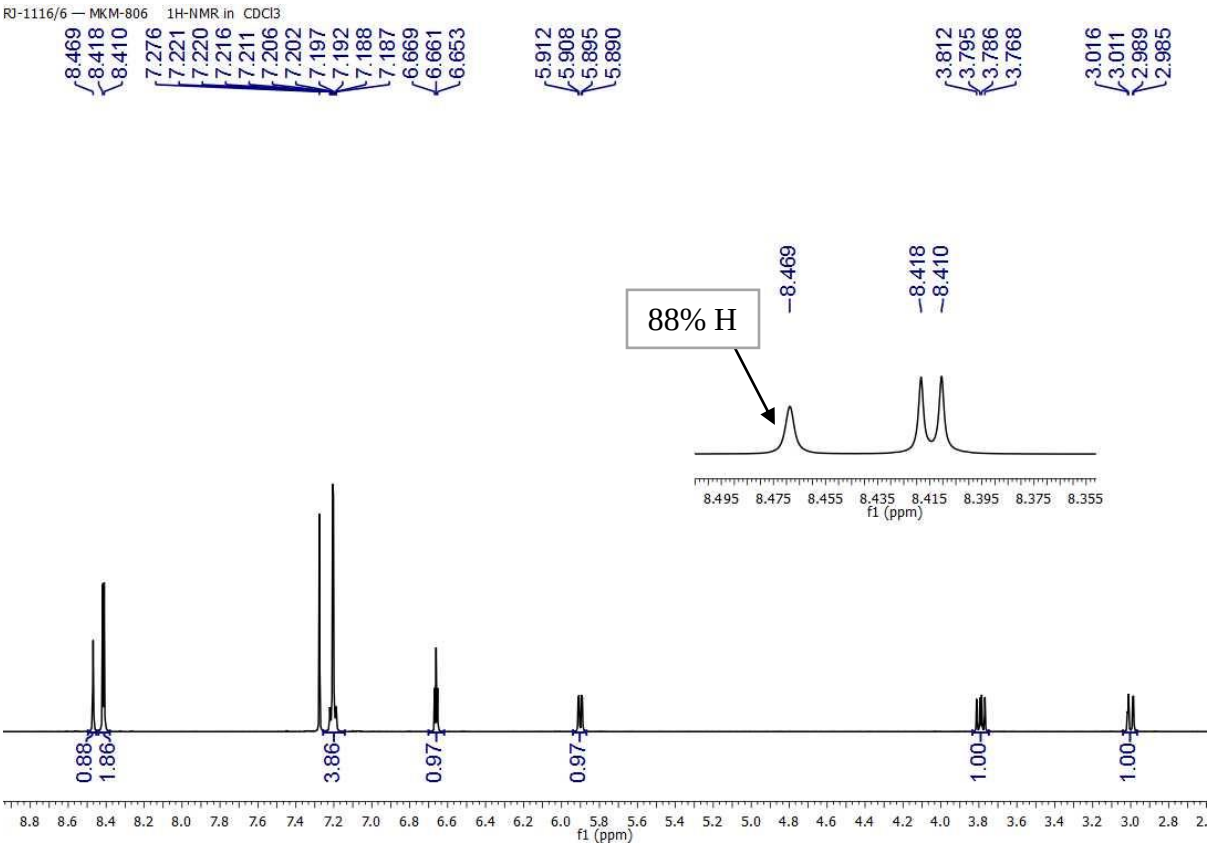
7.263
6.739
6.723
6.707
87% H
1.99
1.74
1.02
1.00
f1 (ppm)

(b) Procedure for C-7 H/D Exchange Experiment in the Product:

A mixture of d_5 *N*-phenyl pyrimidine (0.2 mmol), [Ru(*p*-cymene)I_2]$_2$ (0.02 mmol, 10 mol %), $AgBF_4$ (0.2 mmol, 1 equiv) and $Cu(OAc)_2.H_2O$ (0.3 mmol, 1.5 equiv) was taken in a 15-mL pressure tube and the reaction tube was purged with nitrogen for 30 seconds. To this reaction mixture, hexafluoroisopropanol (HFIP) (1.0 mL) and the corresponding styrene (0.6 mmol) were added via syringe and the closed reaction mixture was allowed to stir at 90 ^oC for 18 h. After completion as indicated by TLC, the reaction the reaction mixture was cooled to ambient temperature. The reaction mixture was quenched with 20 mL saturated solution of Na_2S and extracted with ethyl acetate (3x20 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography using ethyl acetate/hexane as eluent to afford the desired indoline product. The H/D exchange at the C7 position of the product was determined by ^1H NMR analysis.

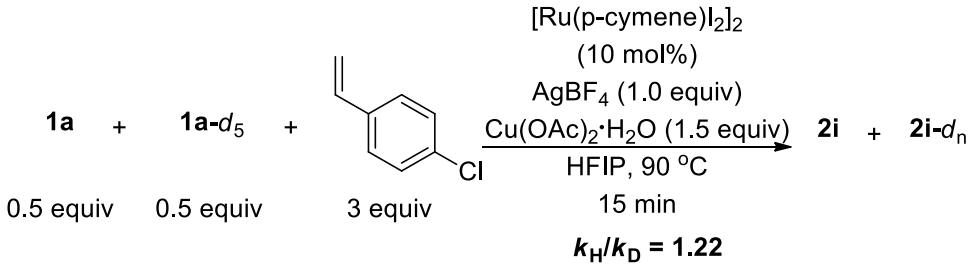


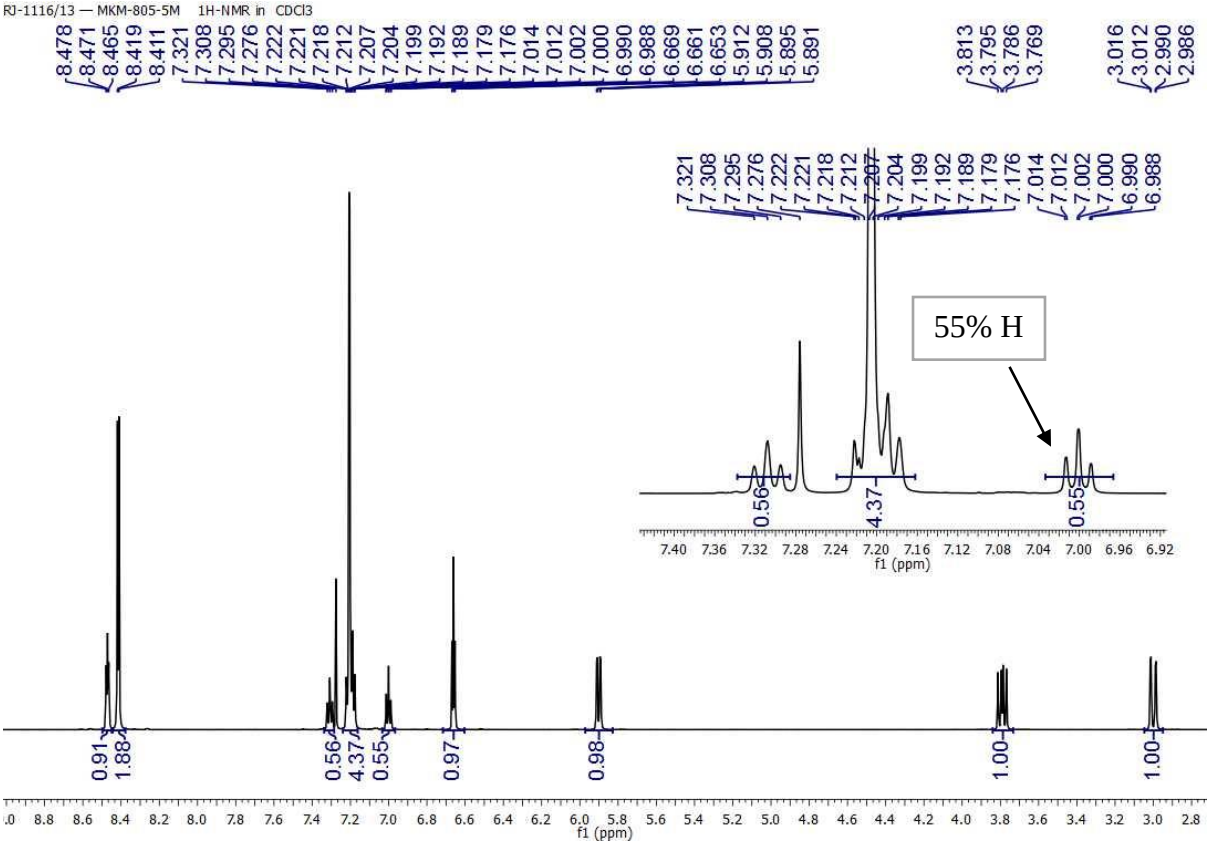


(c) Intermolecular Kinetic Experiment through competitive reaction:

A mixture of *N*-phenyl pyrimidine (0.1 mmol), d_5-*N*-phenyl pyrimidine (0.1 mmol), [Ru(*p*-cymene)I_2]$_2$ (0.02 mmol, 10 mol %), $AgBF_4$ (0.2 mmol, 1 equiv) and $Cu(OAc)_2.H_2O$ (0.3 mmol, 1.5 equiv) was taken in a 15-mL pressure tube and the reaction tube was purged with nitrogen for 30 seconds. To this reaction mixture, hexafluoroisopropanol (HFIP) (1.0 mL) and the corresponding styrene (0.6 mmol) were added via syringe and the closed reaction mixture was allowed to stir at 90 ^oC. After 15 min, the reaction the reaction mixture was cooled to ambient temperature. The reaction mixture was quenched with 20 mL saturated solution of Na_2S and extracted with ethyl acetate (3x20 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography

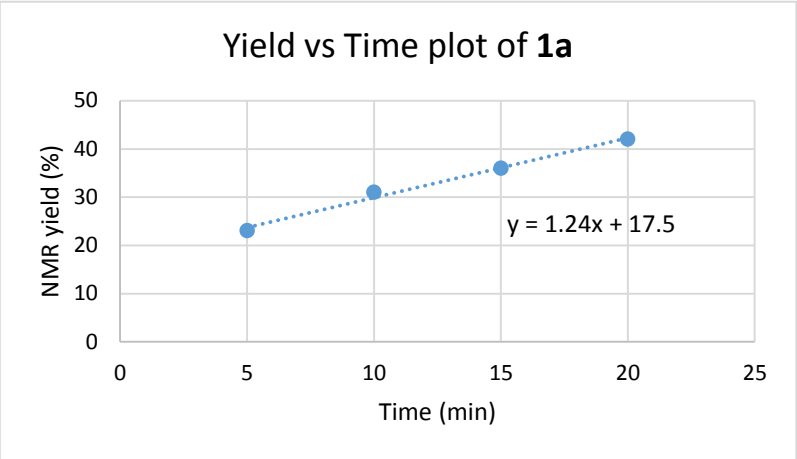
using ethyl acetate/hexane as eluent to afford the desired indoline product. The k_H/k_D value was determined by ^{1}H NMR analysis.



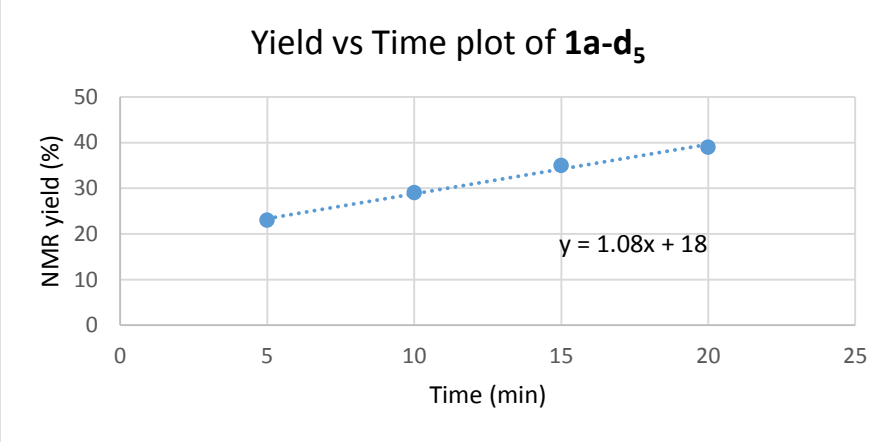


Intermolecular Kinetic Experiment through parallel reaction:

Time (min)	5	10	15	20
NMR yield of 2i (%)	23	31	36	42

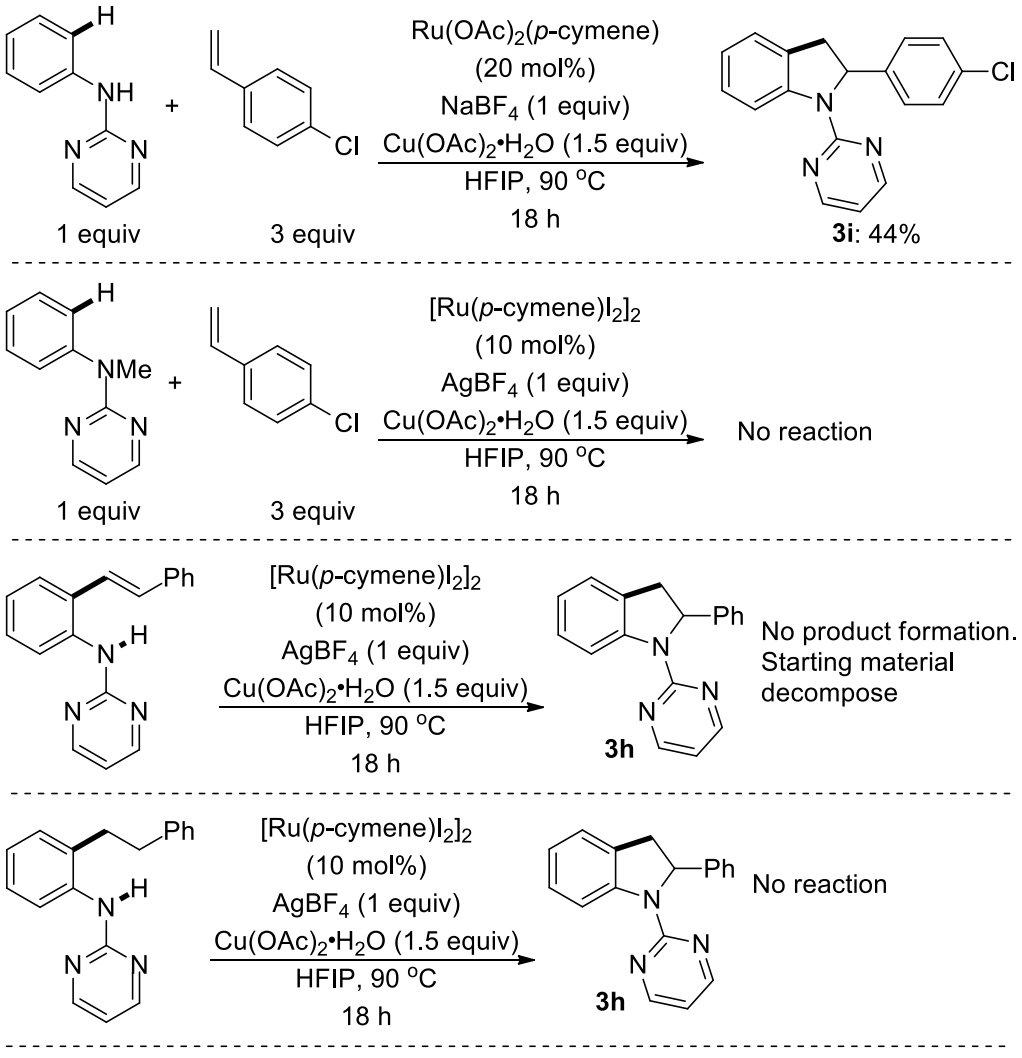


Time (min)	5	10	15	20
NMR yield of 2i-*d*n (%)	23	29	35	39



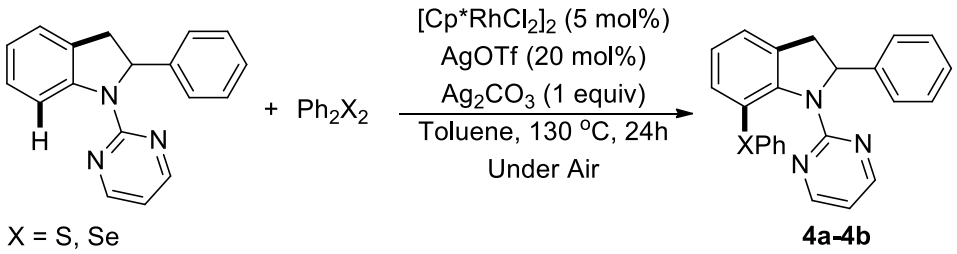
Kinetic Isotopic Effect = k_H/k_D = 1.24/1.08 = 1.15

Control experiments:

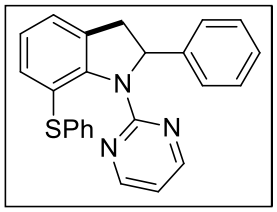


Product Derivatization:

General Experimental Procedure for Rh(III)-Catalyzed C7-Thiolation and Selenation of Indolines:[4]



In an oven dried reaction tube 2-phenyl-1-(pyrimidin-2-yl)indoline, **3h**, (0.2 mmol), diphenyldisulfide or diphenyldiselenide (0.2 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), AgOTf (20 mol%), Ag_2CO_3 (1 equiv) were taken and dry toluene (1.0 mL) was added to it. The reaction vessel was sealed under air and heated at 130 ^oC for 24 h. After completion the reaction, the reaction vessel was cooled to ambient temperature. The reaction mixture was diluted with CH_2Cl_2 and transferred to a round-bottom flask. Silica gel was added to mixture and the solvent was evaporated. Then the mixture was subjected for column chromatography for further purification.

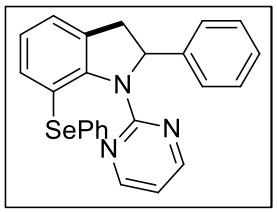


2-phenyl-7-(phenylthio)-1-(pyrimidin-2-yl)indoline, 4a, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 7:3 hexane/ethyl acetate) afforded the desired product as a white solid, (60 mg, 78%), mp 140-142 ^oC.

^1H NMR (600 MHz, $CDCl_3$): δ 8.46 (d, J = 4.8 Hz, 2H), 7.49 (d, J = 7.2 Hz, 2H), 7.32 (t, J = 7.2 Hz, 2H), 7.16-7.26 (m, 7H), 7.06 (d, J = 7.2 Hz, 1H), 6.93 (t, J = 7.2 Hz, 1H), 6.76 (t, J = 4.2 Hz, 1H), 6.05 (d, J = 9.0 Hz, 1H), 3.95 (dd, J_1 = 15.6 Hz, J_2 = 9.6 Hz, 1H), 3.05 (d, J = 15.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 160.7, 157.5, 143.9, 143.1, 138.9, 123.9, 132.2, 131.0, 128.8,

128.5, 127.1, 126.52, 126.45, 125.5, 124.9, 123.7, 113.2, 65.9, 39.0; IR (neat): υ_{max} 1577, 1551, 1460, 1426, 1284, 1057, 743 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{24}H_{20}N_3S$ $[M + H]^+$: 382.1378; found: 382.1375.



2-phenyl-7-(phenylselanyl)-1-(pyrimidin-2-yl)indoline, 4b, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 7:3 hexane/ethyl acetate) afforded the desired product as a white solid, (62 mg, 72%), mp 140-142 ^oC.

^1H NMR (600 MHz, $CDCl_3$): δ 8.46 (d, J = 4.8 Hz, 2H), 7.51 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 2H), 7.45-7.47 (m, 2H), 7.33-7.36 (m, 2H), 7.20-7.28 (m, 5H), 7.03 (d, J = 7.2 Hz, 1H), 6.84 (t, J = 7.8 Hz, 1H), 6.76 (t, J = 4.8 Hz, 1H), 6.11 (d, J = 9.6 Hz, 1H), 3.93 (dd, J_1 = 15.6 Hz, J_2 = 9.0 Hz, 1H), 3.04 (d, J = 9.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 160.5, 157.6, 144.0, 143.1, 135.0, 133.9, 132.8, 132.3, 129.0, 128.6, 127.1, 125.5, 124.9, 123.5, 123.2, 113.1, 65.0, 39.0; IR (neat): υ_{max} 1575, 1547, 1460, 1426, 1284, 1056, 737 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{24}H_{20}N_3Se$ $[M + H]^+$: 430.0822; found: 430.0826.

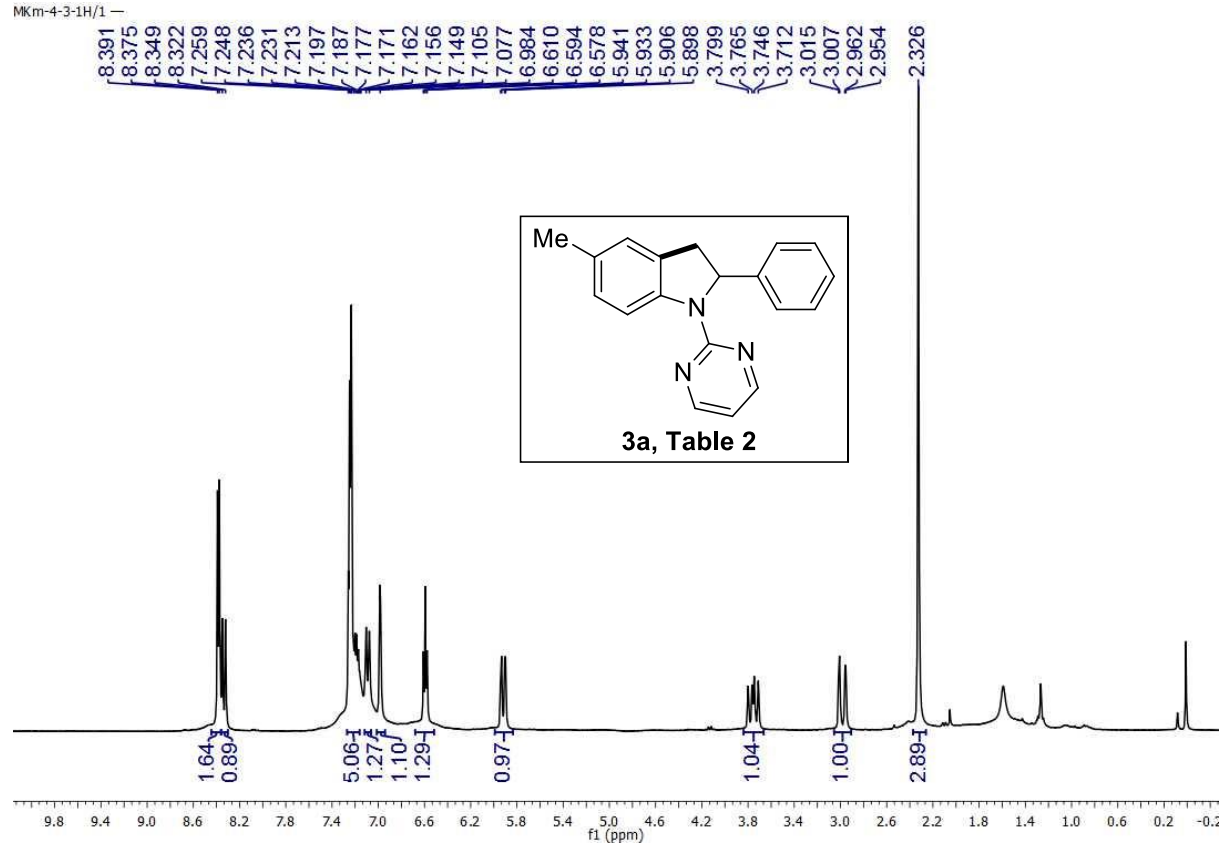
References:

(1) N. K. Mishra, M. Choi, H. Jo, Y. Oh, S. Sharma, S. H. Han, T. Jeong, S. Han, S. Y. Lee and I. S. Kim, *Chem. Commun*, 2015, **51**, 17229-17232.

(2) J. W. Shaw, D. H. Grayson and I. Rozas, *ARKIVOC*, 2014, 161-174.

(3) D. A. Tocher, R. O. Gould and T. A. Stephenson, *J. Chem. Soc. Dalton Trans*, 1983, 1571-1581.

(4) W. Xie, B. Li and B. Wang, *J. Org. Chem*, 2016, **81**, 396-403.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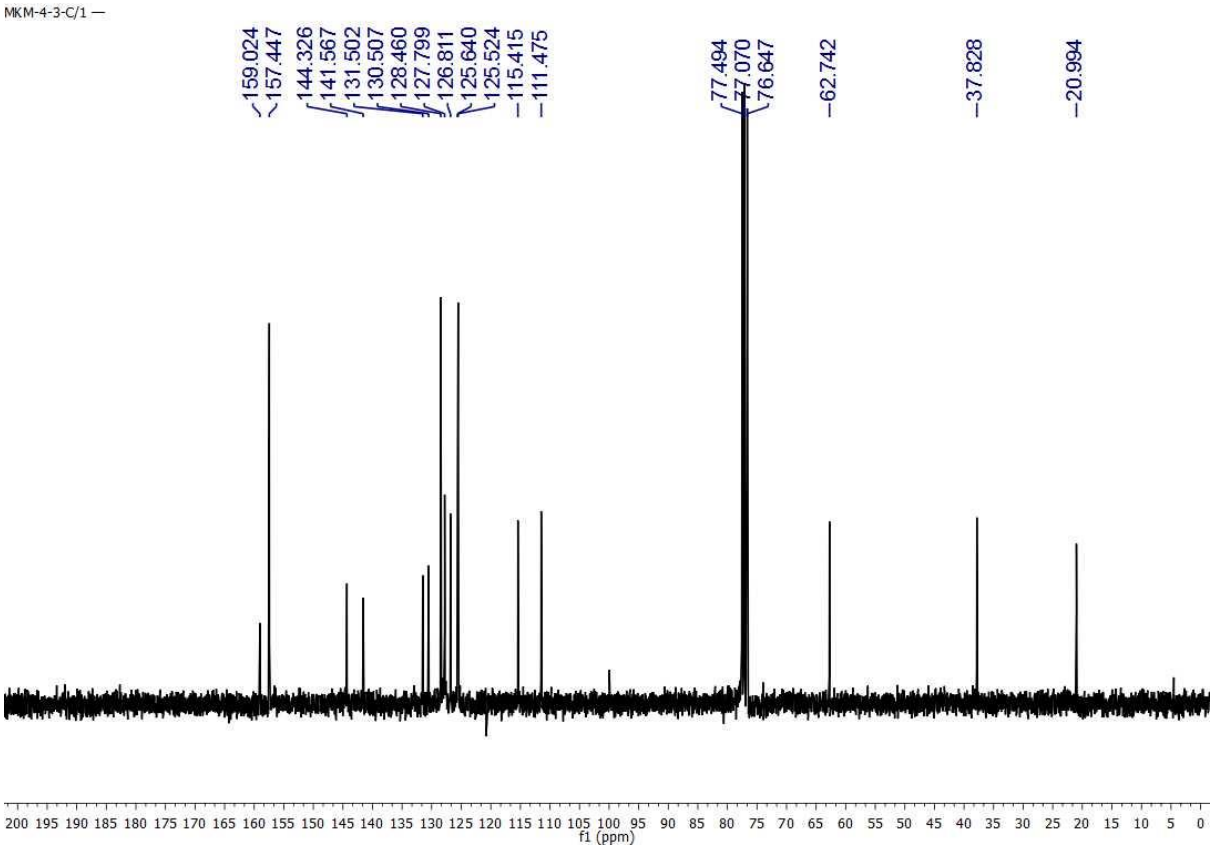
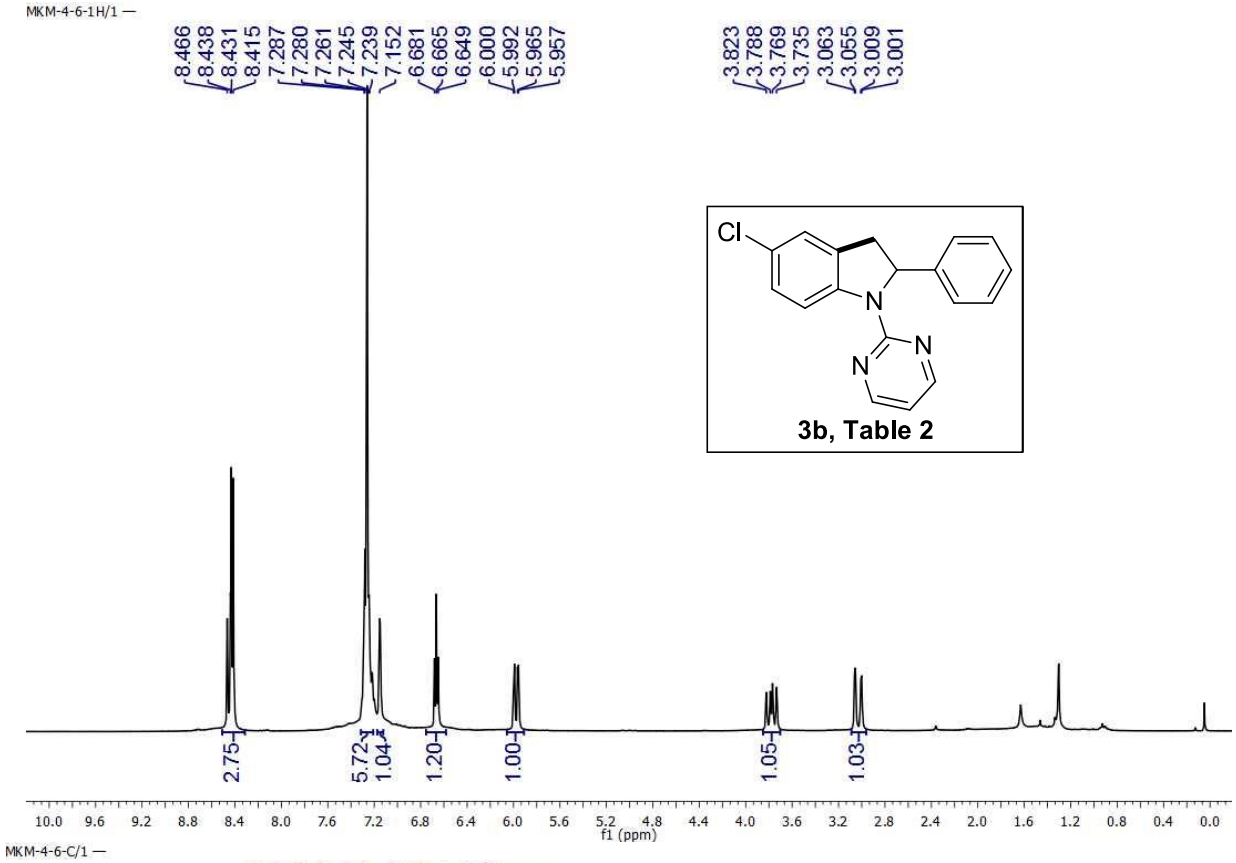
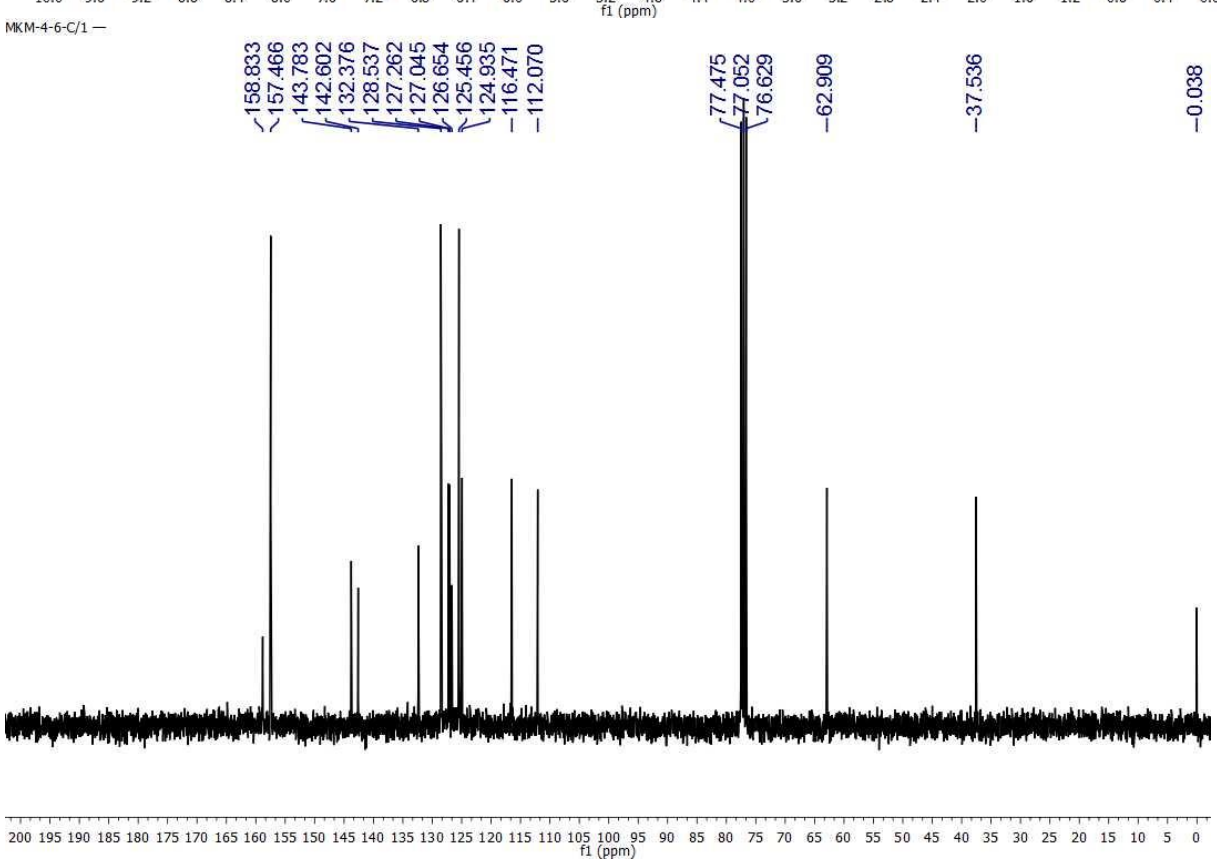
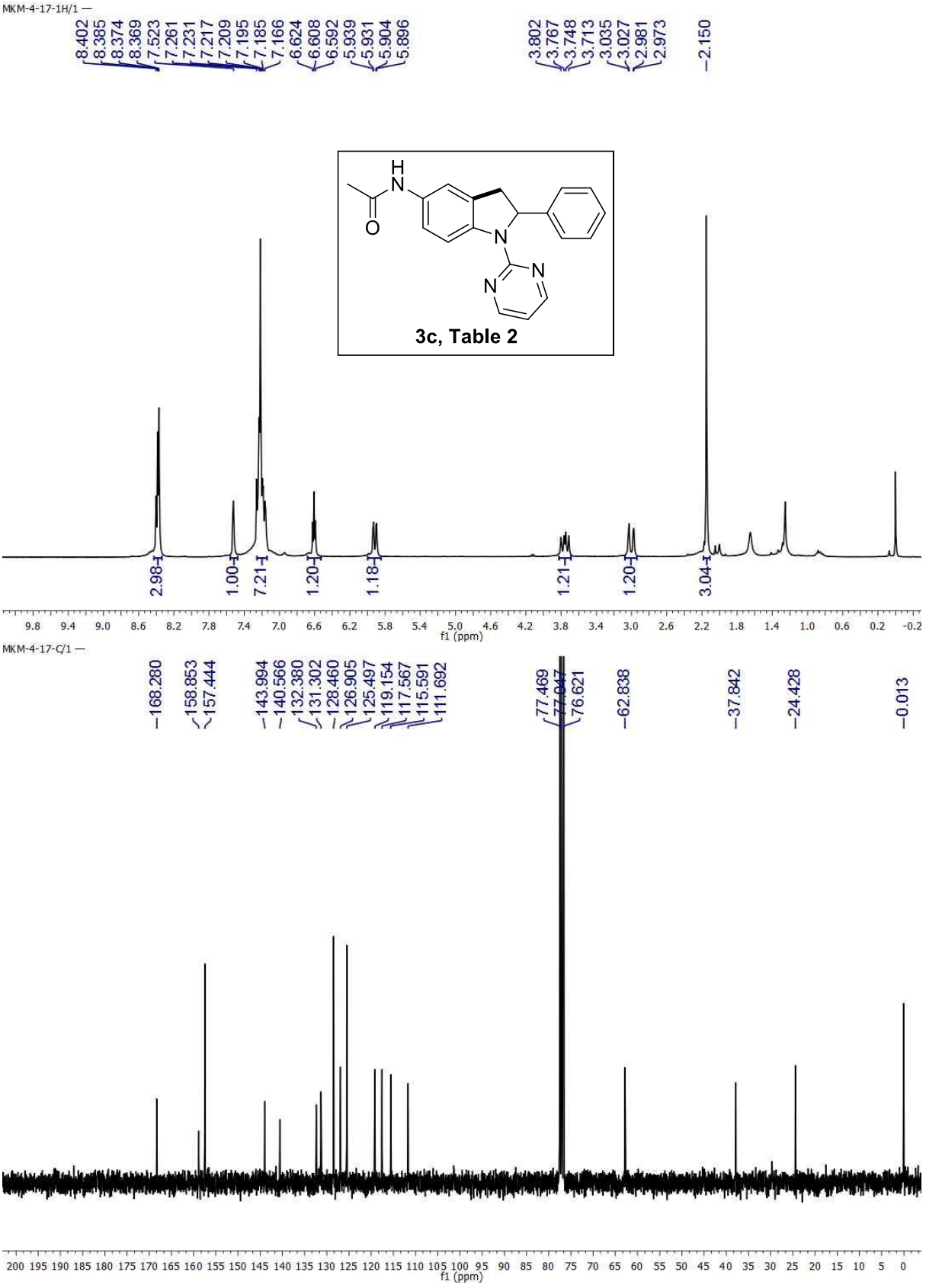
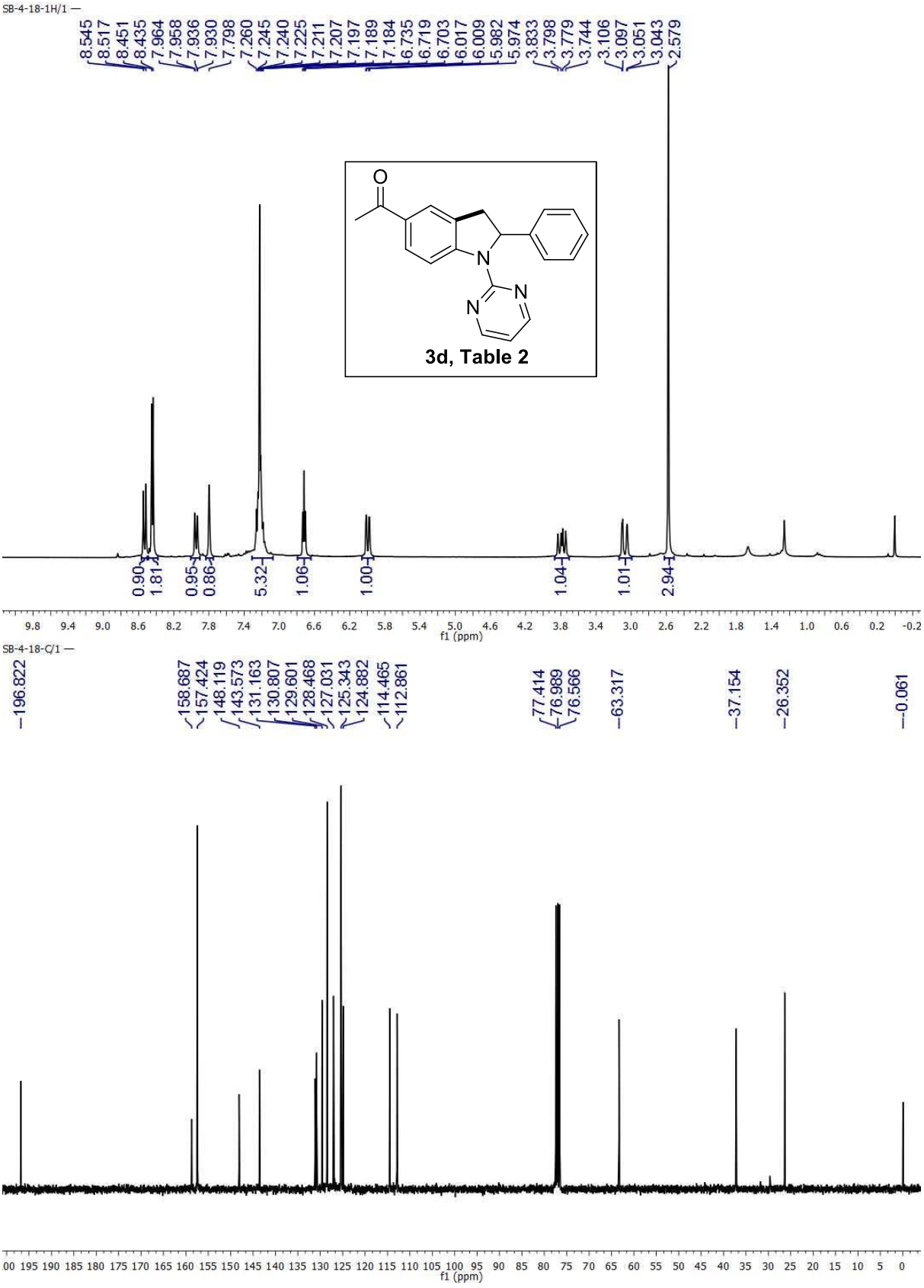
8.391
8.375
8.349
8.322
7.259
7.248
7.236
7.231
7.213
7.197
7.187
7.177
7.171
7.162
7.156
7.149
7.105
7.077
6.984
6.610
6.594
6.578
5.941
5.933
5.906
5.898
3.799
3.765
3.746
3.712
3.015
3.007
2.962
2.954
2.326
Me
N
N
N
3a, Table 2
1.64
0.89
5.06
1.27
1.10
1.29
0.97
1.04
1.00
2.89
f1 (ppm)


MKM-4-3-C/1
159.024
157.447
144.326
141.567
131.502
130.507
128.460
127.799
126.811
125.640
125.524
115.415
111.475
77.494
77.070
76.647
62.742
37.828
20.994
f1 (ppm)


MKM-4-6-1H/1
8.466
8.438
8.431
8.415
7.287
7.280
7.261
7.245
7.239
7.152
6.681
6.665
6.649
6.000
5.992
5.965
5.957
3.823
3.788
3.769
3.735
3.063
3.055
3.009
3.001
Cl
N
N
N
3b, Table 2
2.75
5.72
1.04
1.20
1.00
1.05
1.03
f1 (ppm)


MKM-4-6-C/1
158.833
157.466
143.783
142.602
132.376
128.537
127.262
127.045
126.654
125.456
124.935
116.471
112.070
77.475
77.052
76.629
62.909
37.536
0.038
f1 (ppm)


MKM-4-17-1H/1
8.402
8.385
8.374
8.369
7.523
7.261
7.231
7.217
7.209
7.195
7.185
7.166
6.624
6.608
6.592
5.939
5.931
5.904
5.896
3.802
3.767
3.748
3.713
3.035
3.027
2.981
2.973
2.150
3c, Table 2
2.98
1.00
7.21
1.20
1.18
1.21
1.20
3.04
f1 (ppm)
MKM-4-17-C/1
168.280
158.853
157.444
143.994
140.566
132.380
131.302
128.460
126.905
125.497
119.154
117.567
115.591
111.692
77.469
77.047
76.621
62.838
37.842
24.428
0.013
f1 (ppm)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8.517
8.451
8.435
7.964
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7.930
7.798
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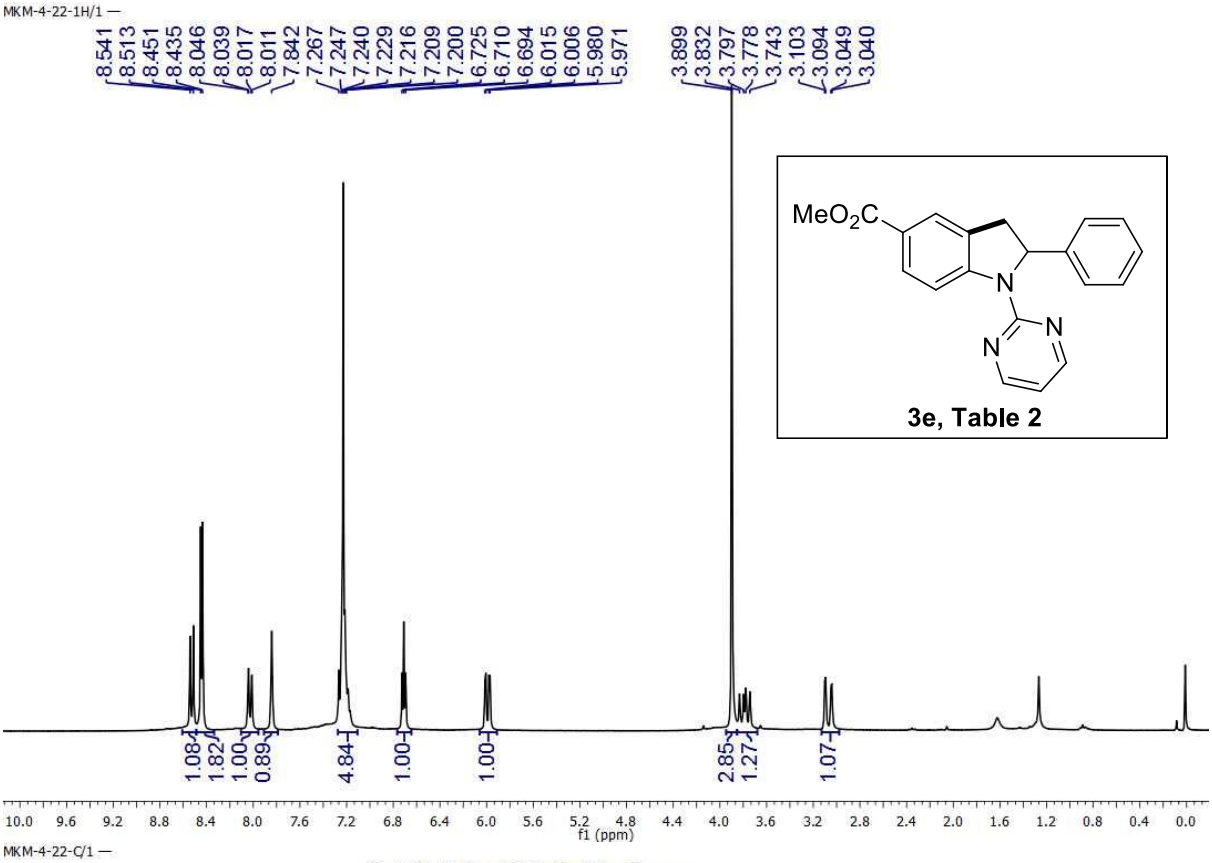
7.245
7.240
7.225
7.211
7.207
7.197
7.189
7.184
6.735
6.719
6.703
6.017
6.009
5.982
5.974
3.833
3.798
3.779
3.744
3.106
3.097
3.051
3.043
2.579
O
N
N
N
3d, Table 2
0.90
1.81
0.95
0.86
5.32
1.06
1.00
1.04
1.01
2.94
f1 (ppm)
SB-4-18-C/1
196.822
158.687
157.424
148.119
143.573
131.163
130.807
129.601
128.468
127.031
125.343
124.882
114.465
112.861
77.414
76.989
76.566
63.317
37.154
26.352
0.061
f1 (ppm)


MKM-4-22-1H/1
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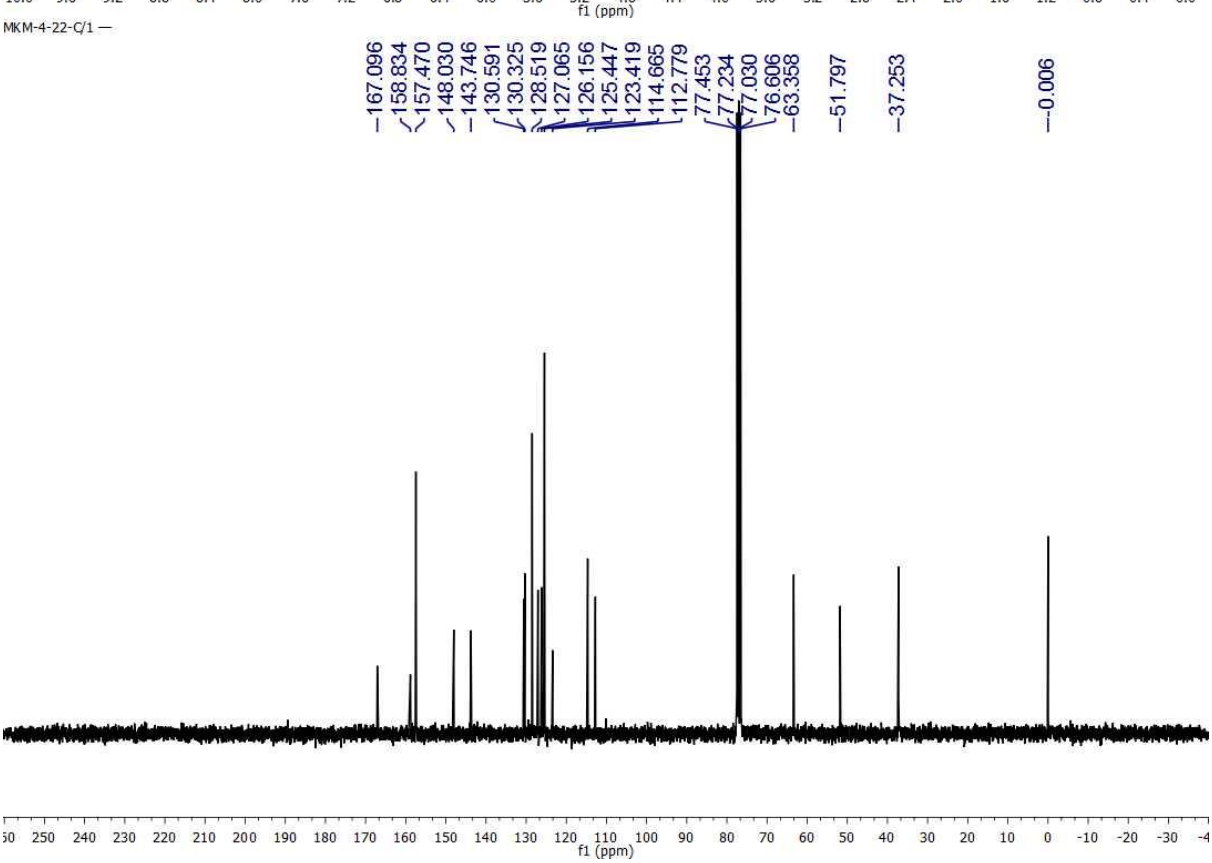
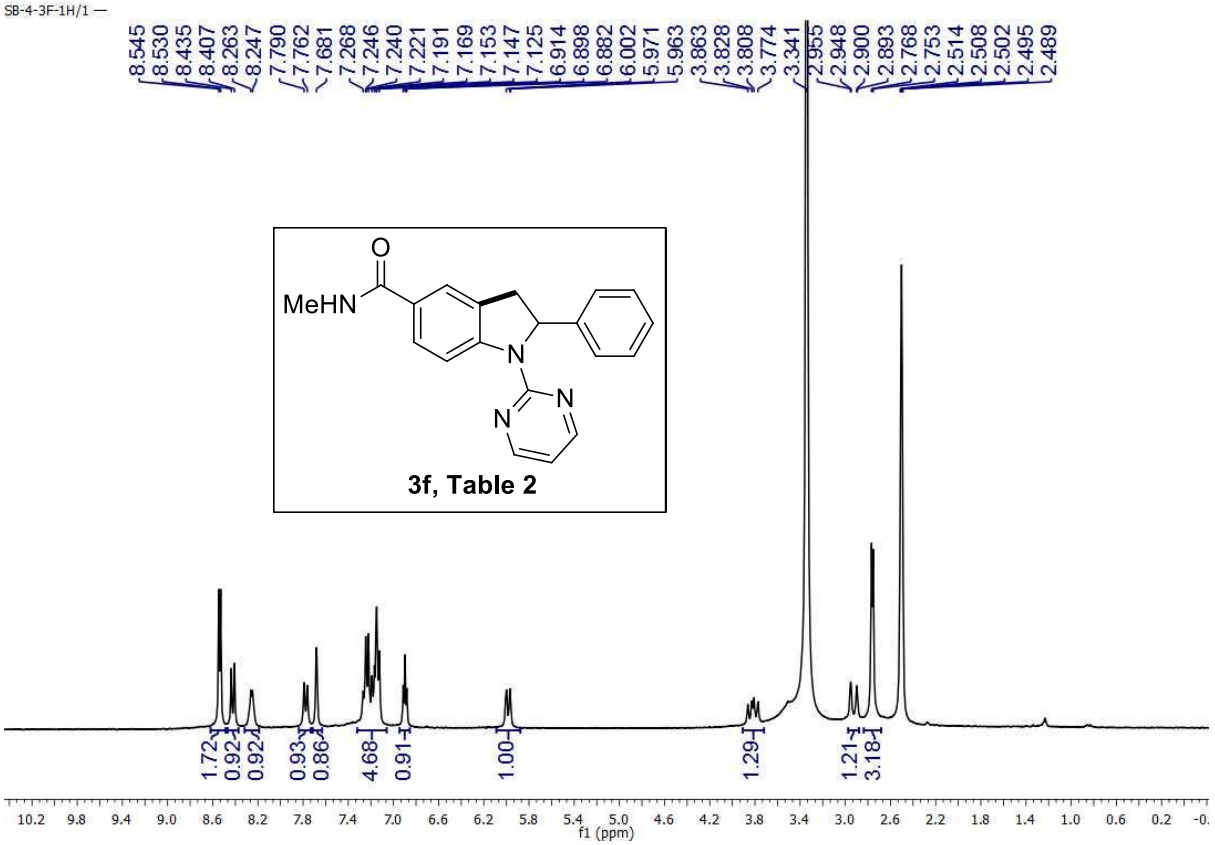
8.513
8.451
8.435
8.046
8.039
8.017
8.011
7.842
7.267
7.247
7.240
7.229
7.216
7.209
7.200
6.725
6.710
6.694
6.015
6.006
5.980
5.971
3.899
3.832
3.797
3.778
3.743
3.103
3.094
3.049
3.040
1.08
1.82
1.00
0.89
4.84
1.00
1.00
2.85
1.27
1.07
f1 (ppm)

MeO2C
N
N
N

3e, Table 2


MKM-4-22-C/1
167.096
158.834
157.470
148.030
143.746
130.591
130.325
128.519
127.065
126.156
125.447
123.419
114.665
112.779
77.453
77.234
77.030
76.606
63.358
51.797
37.253
0.006
f1 (ppm)


SB-4-3F-1H/1
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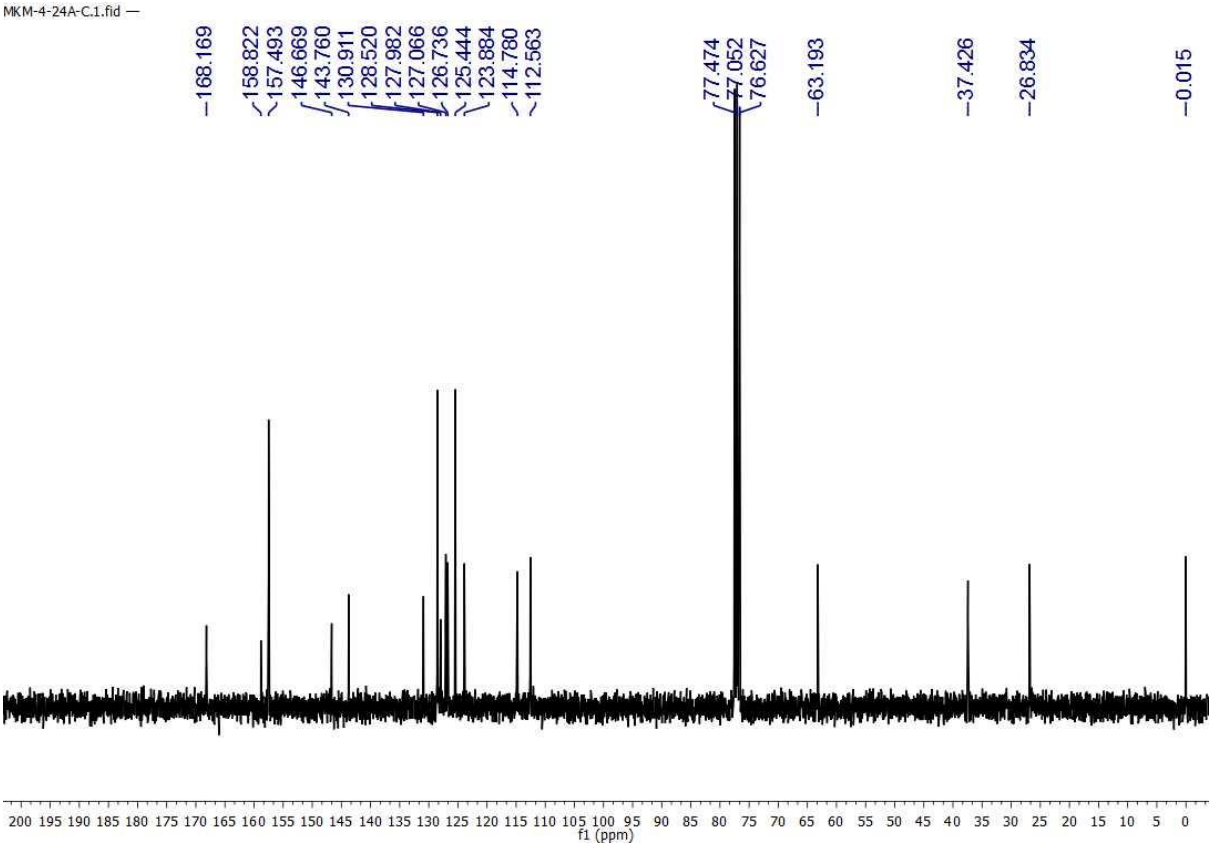
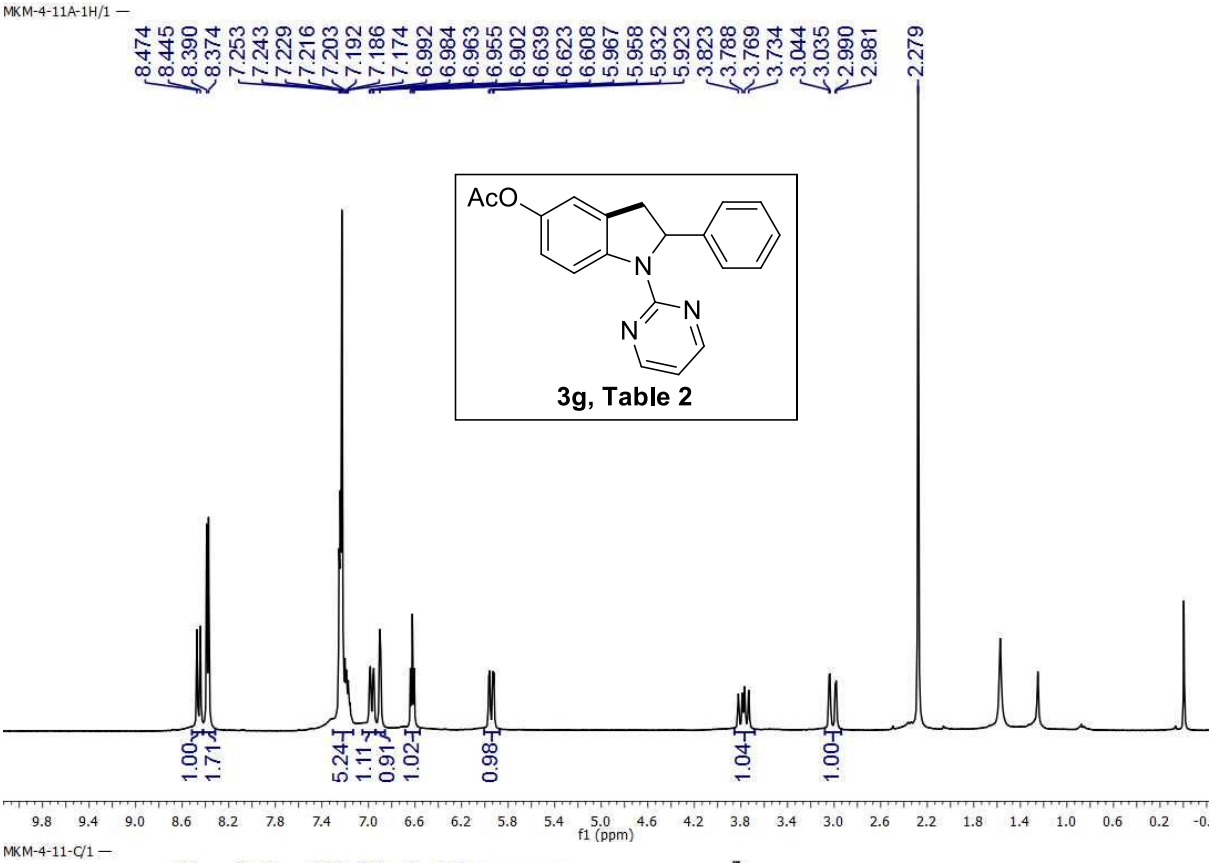
8.530
8.435
8.407
8.263
8.247
7.790
7.762
7.681
7.268
7.246
7.240
7.221
7.191
7.169
7.153
7.147
7.125
6.914
6.898
6.882
6.002
5.971
5.963
3.863
3.828
3.808
3.774
3.341
2.955
2.948
2.900
2.893
2.768
2.753
2.514
2.508
2.502
2.495
2.489
O
MeHN
N
N
N
3f, Table 2
1.72
0.92
0.92
0.93
0.86
4.68
0.91
1.00
1.29
1.21
3.18
f1 (ppm)


MKM-4-24A-C.1.fid
168.169
158.822
157.493
146.669
143.760
130.911
128.520
127.982
127.066
126.736
125.444
123.884
114.780
112.563
77.474
77.052
76.627
63.193
37.426
26.834
0.015
f1 (ppm)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8.445
8.390
8.374
7.253
7.243
7.229
7.216
7.203
7.192
7.186
7.174
6.992
6.984
6.963
6.955
6.902
6.639
6.623
6.608
5.967
5.958
5.932
5.923
3.823
3.788
3.769
3.734
3.044
3.035
2.990
2.981
2.279
AcO
N
N
N
3g, Table 2
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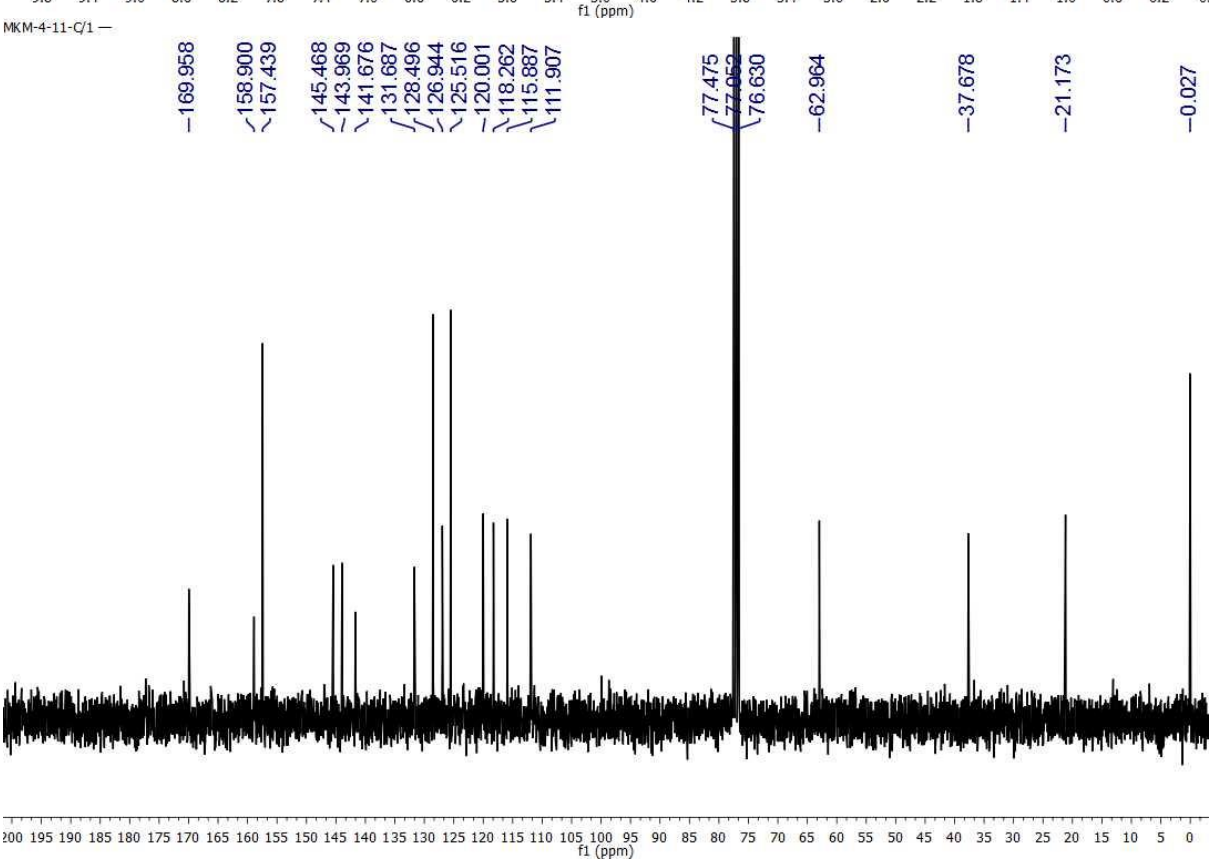
1.71
5.24
1.11
0.91
1.02
0.98
1.04
1.00
f1 (ppm)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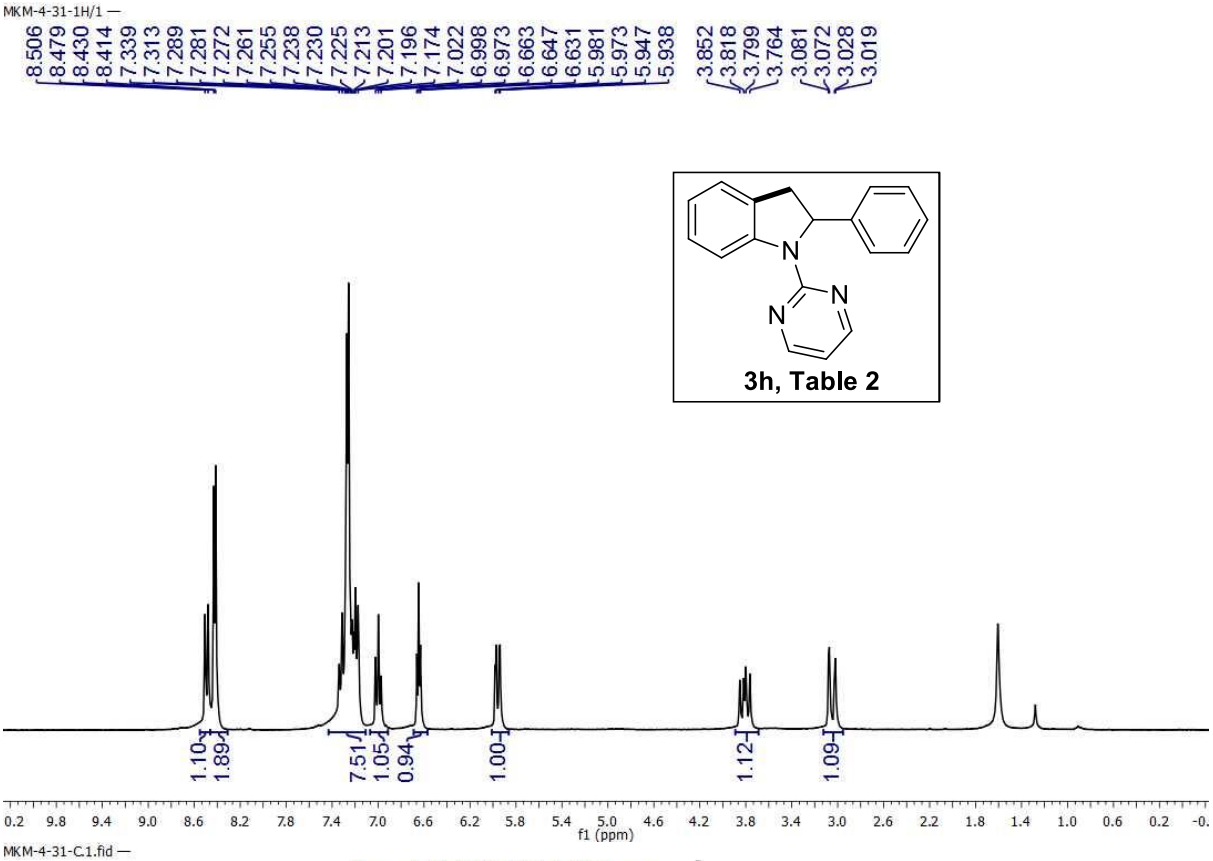
169.958
158.900
157.439
145.468
143.969
141.676
131.687
128.496
126.944
125.516
120.001
118.262
115.887
111.907
77.475
77.052
76.630
62.964
37.678
21.173
0.027
f1 (ppm)


MKM-4-31-1H/1
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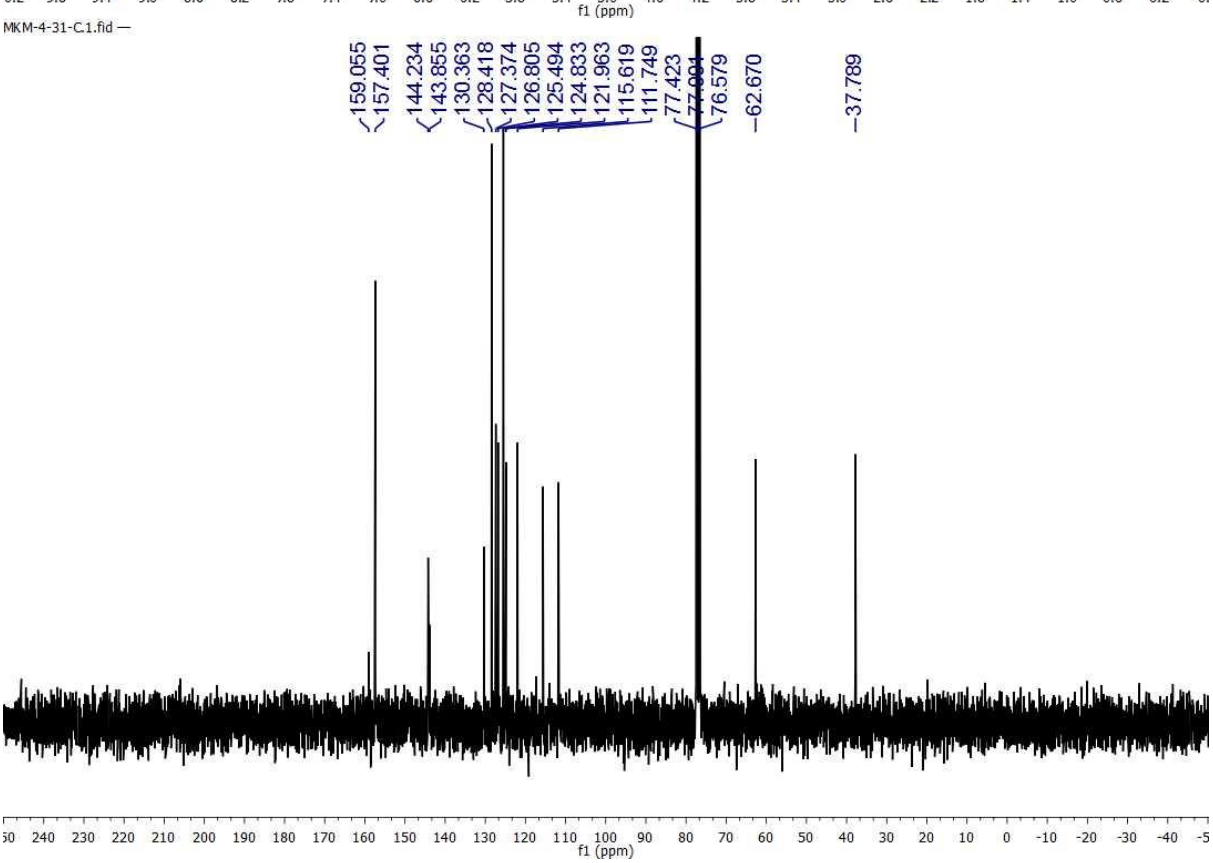
8.479
8.430
8.414
7.339
7.313
7.289
7.281
7.272
7.261
7.255
7.238
7.230
7.225
7.213
7.201
7.196
7.174
7.022
6.998
6.973
6.663
6.647
6.631
5.981
5.973
5.947
5.938
3.852
3.818
3.799
3.764
3.081
3.072
3.028
3.019
3h, Table 2
1.10
1.89
7.51
1.05
0.94
1.00
1.12
1.09
f1 (ppm)


MKM-4-31-C.1.fid
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157.401
144.234
143.855
130.363
128.418
127.374
126.805
125.494
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121.963
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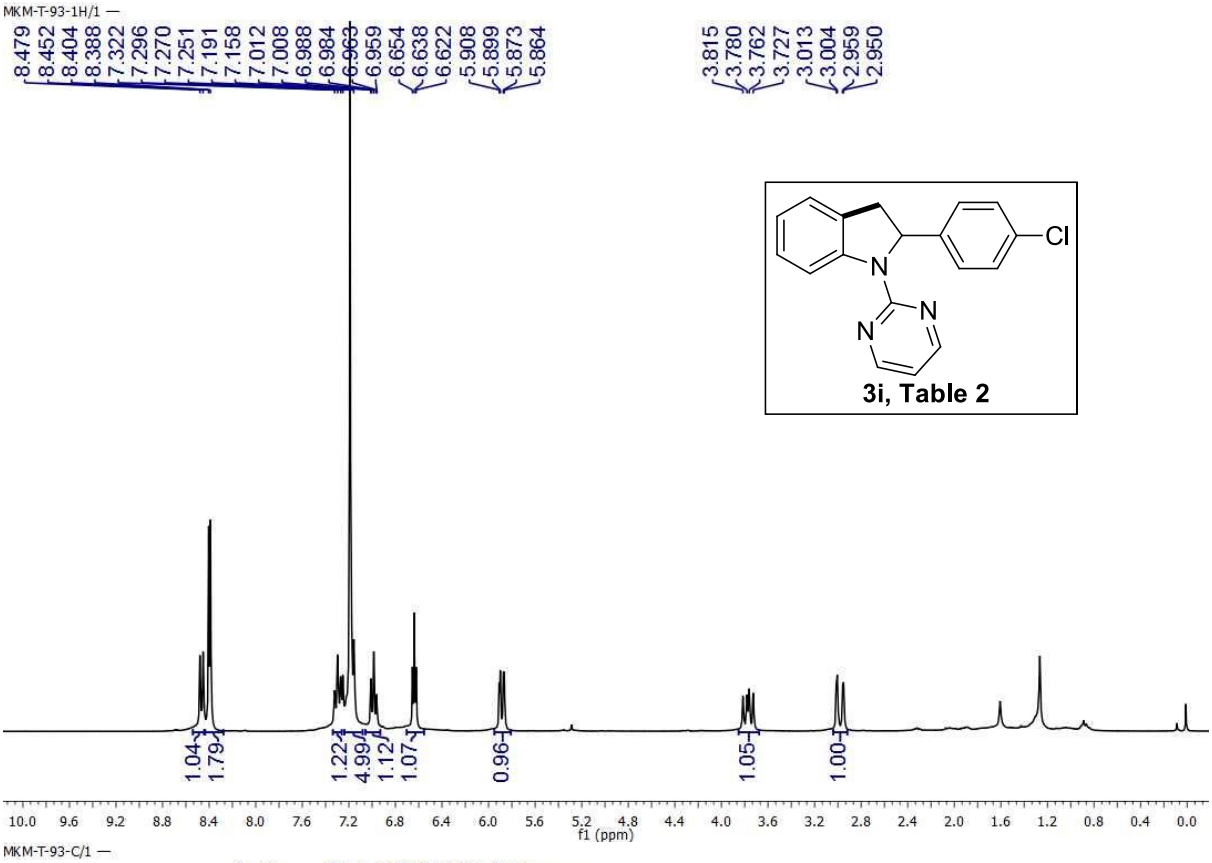
111.749
77.423
76.579
62.670
37.789
f1 (ppm)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8.452
8.404
8.388
7.322
7.296
7.270
7.251
7.191
7.158
7.012
7.008
6.988
6.984
6.963
6.959
6.654
6.638
6.622
5.908
5.899
5.873
5.864
3.815
3.780
3.762
3.727
3.013
3.004
2.959
2.950
Cl
N
N
N
3i, Table 2
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1.79
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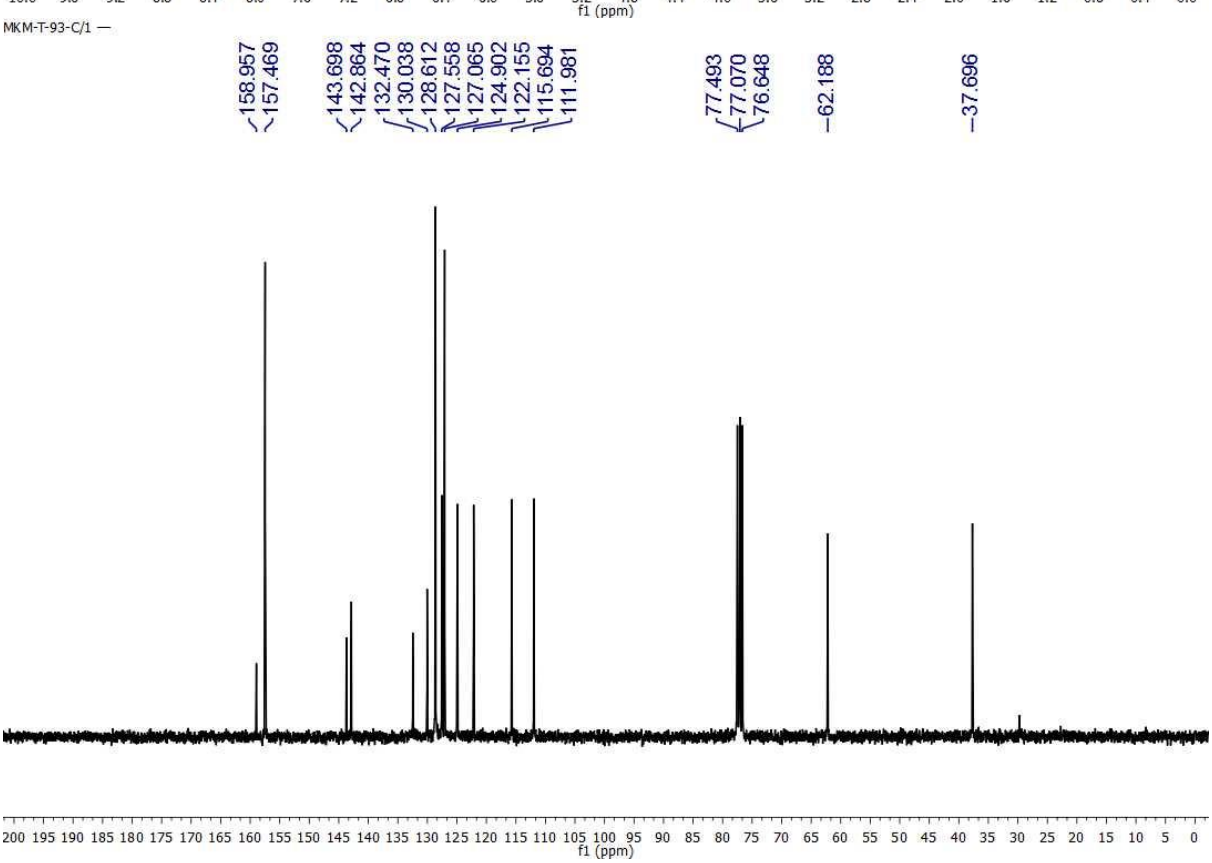
4.99
1.12
1.07
0.96
1.05
1.00
f1 (ppm)


MKM-T-93-C/1
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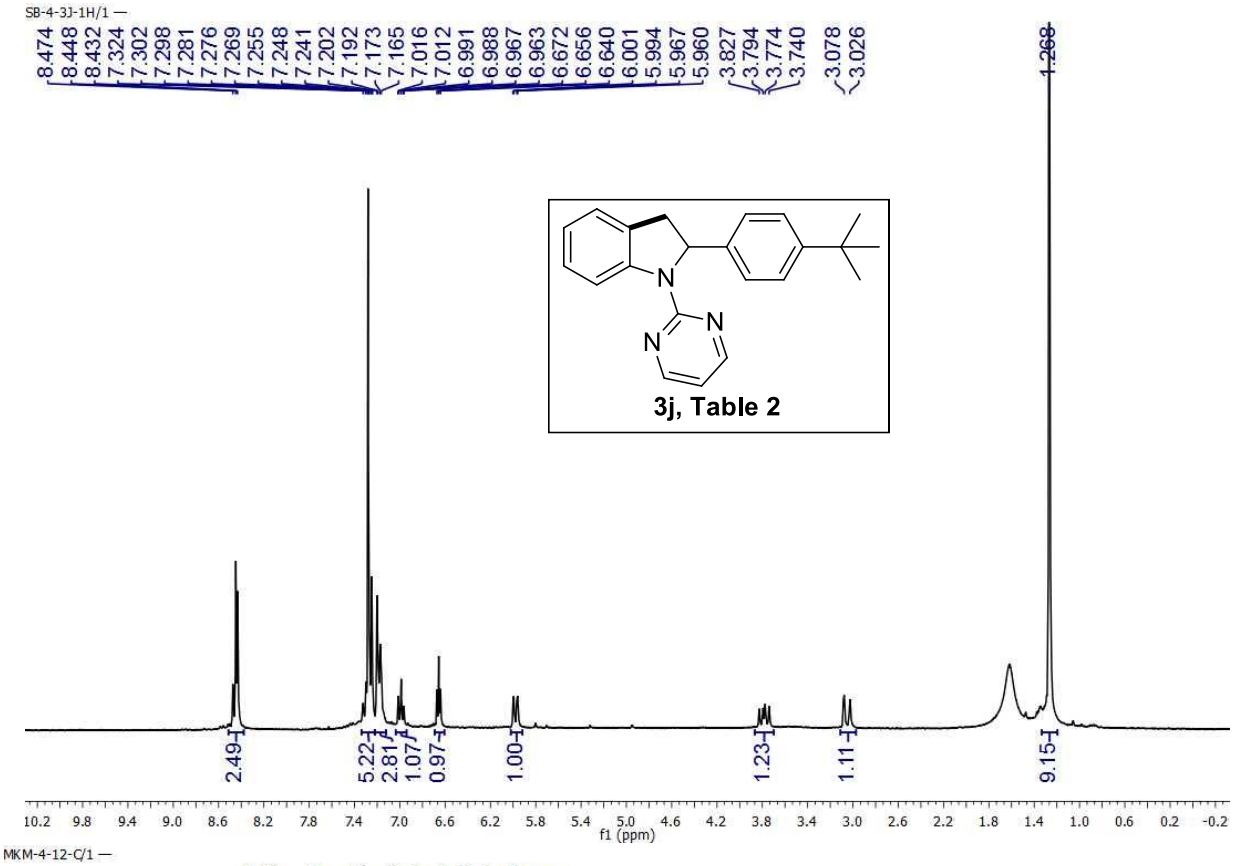
157.469
143.698
142.864
132.470
130.038
128.612
127.558
127.065
124.902
122.155
115.694
111.981
77.493
77.070
76.648
62.188
37.696
f1 (ppm)


SB-4-3J-1H/1
8.474
8.448
8.432
7.324
7.302
7.298
7.281
7.276
7.269
7.255
7.248
7.241
7.202
7.192
7.173
7.165
7.016
7.012
6.991
6.988
6.967
6.963
6.672
6.656
6.640
6.001
5.994
5.967
5.960
3.827
3.794
3.774
3.740
3.078
3.026
1.268
3j, Table 2
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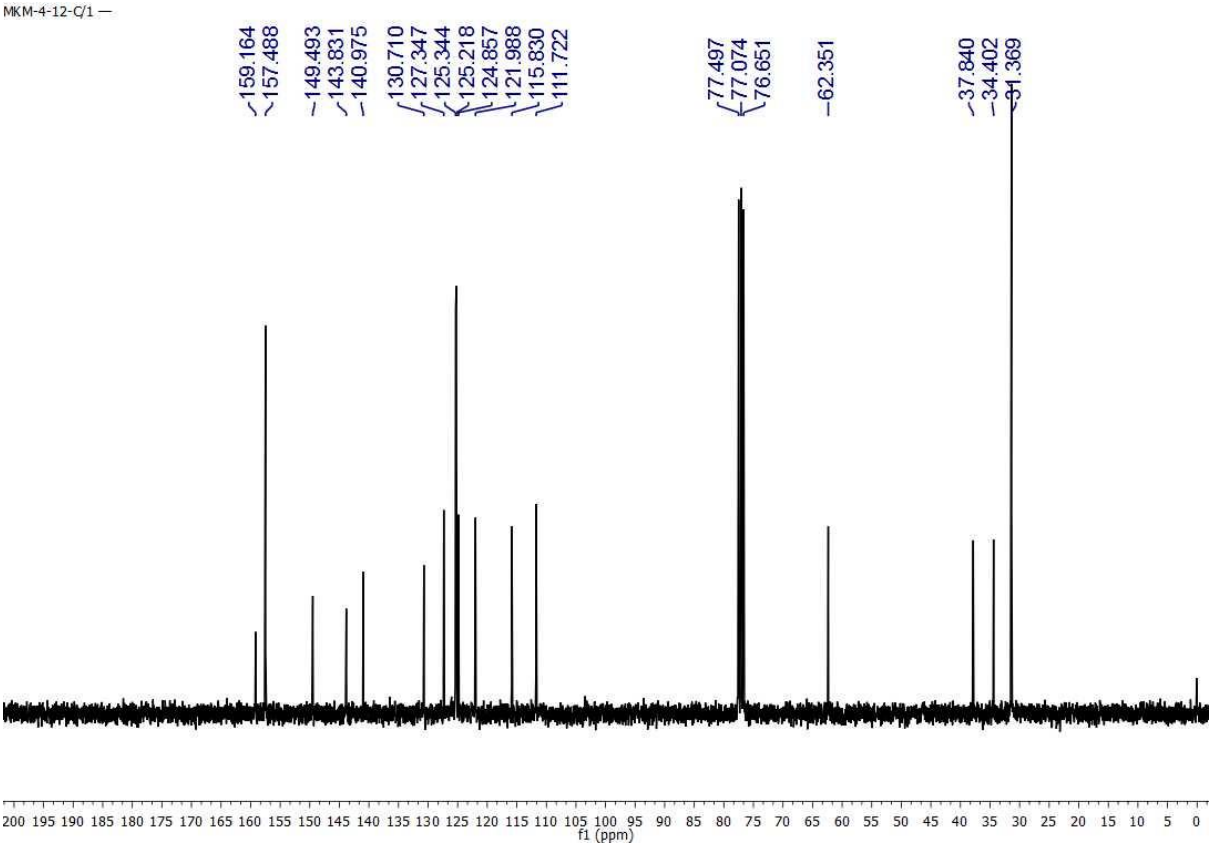
5.22
2.81
1.07
0.97
1.00
1.23
1.11
9.15
f1 (ppm)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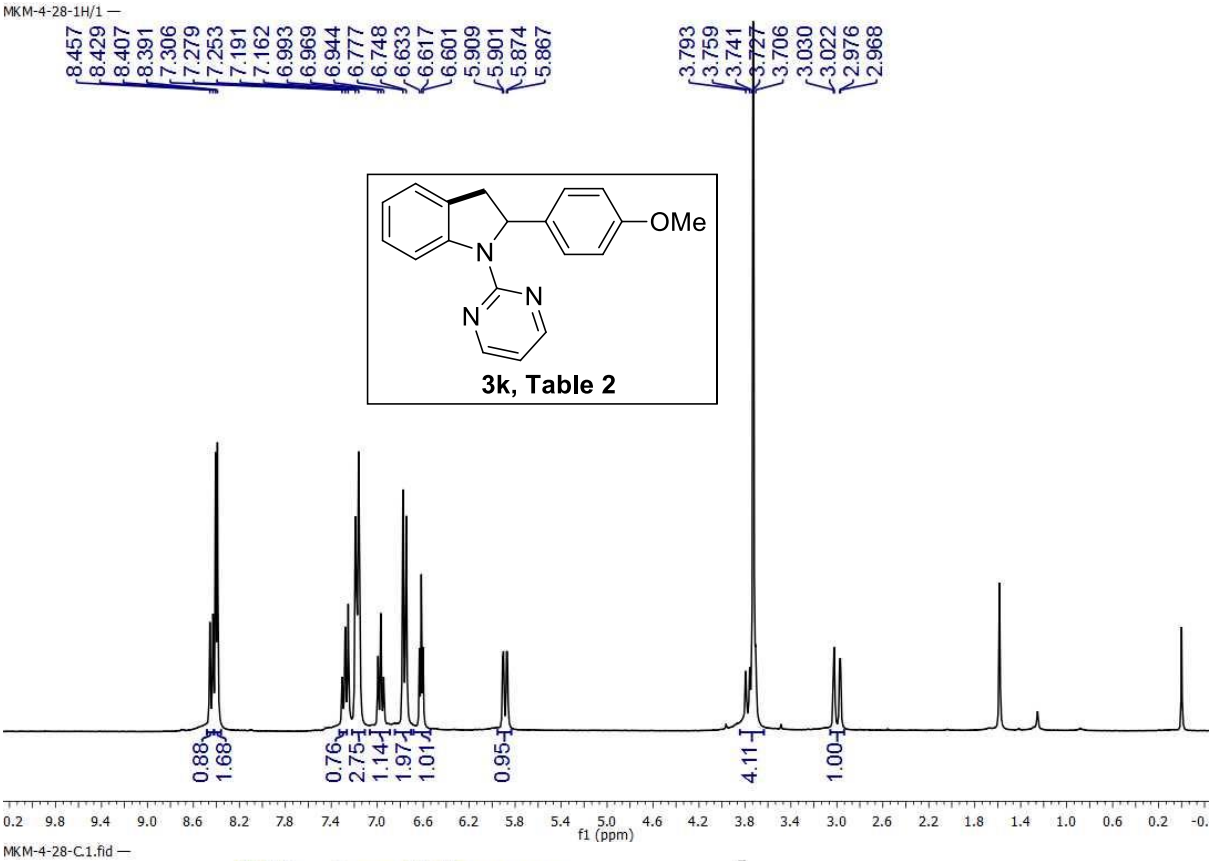
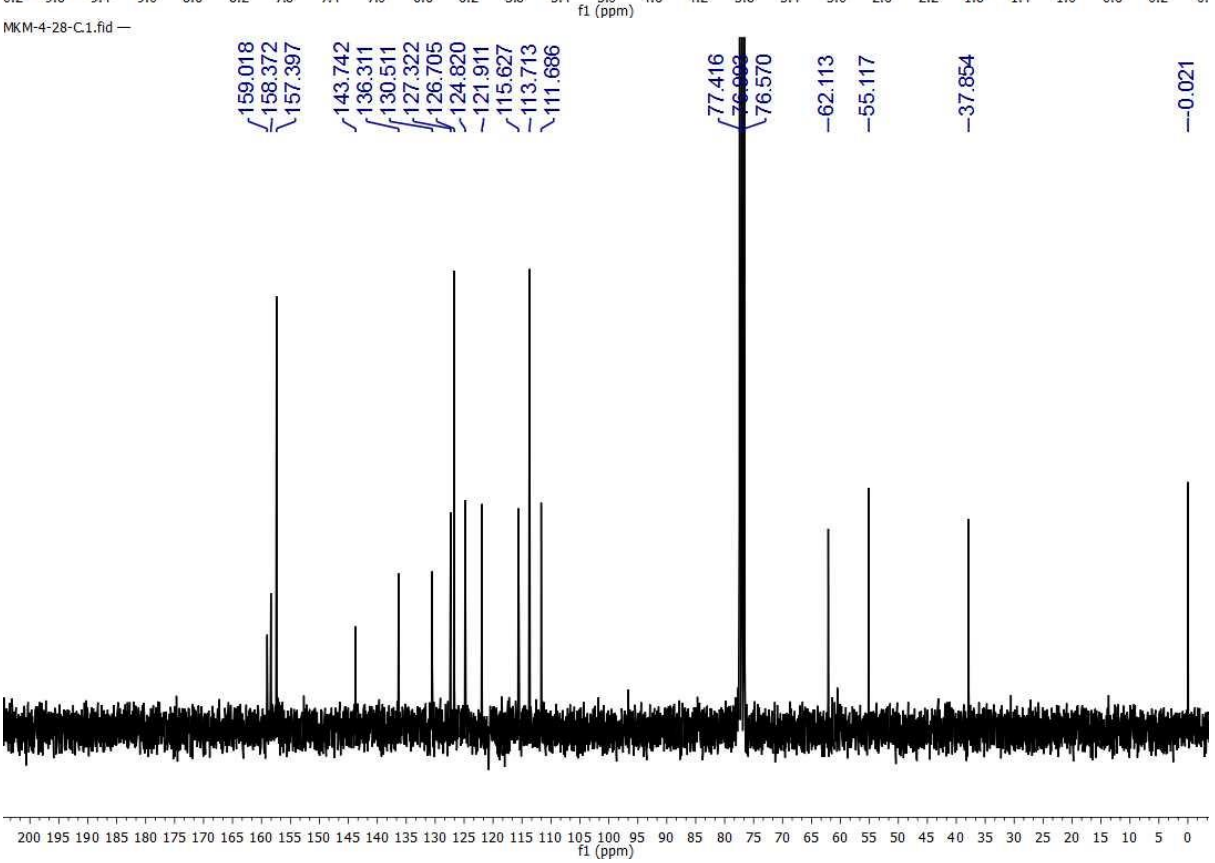
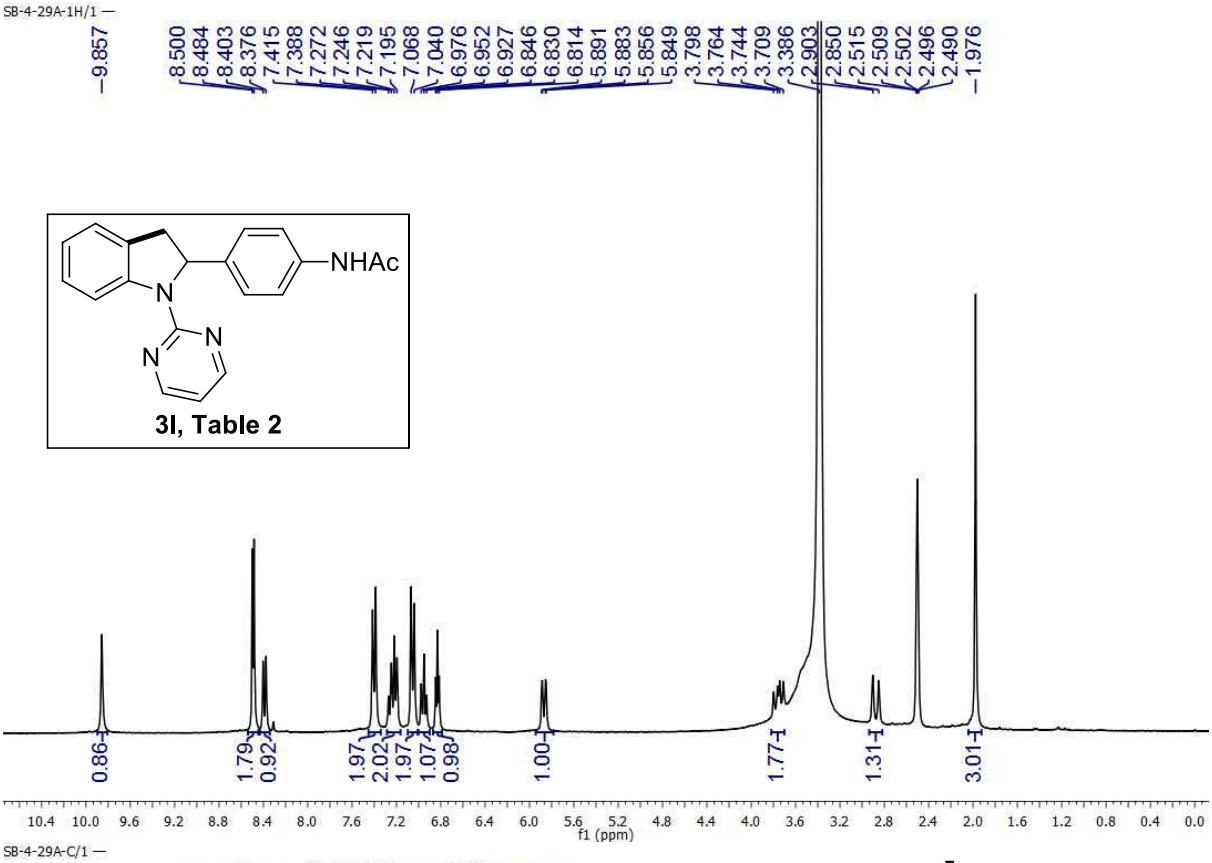
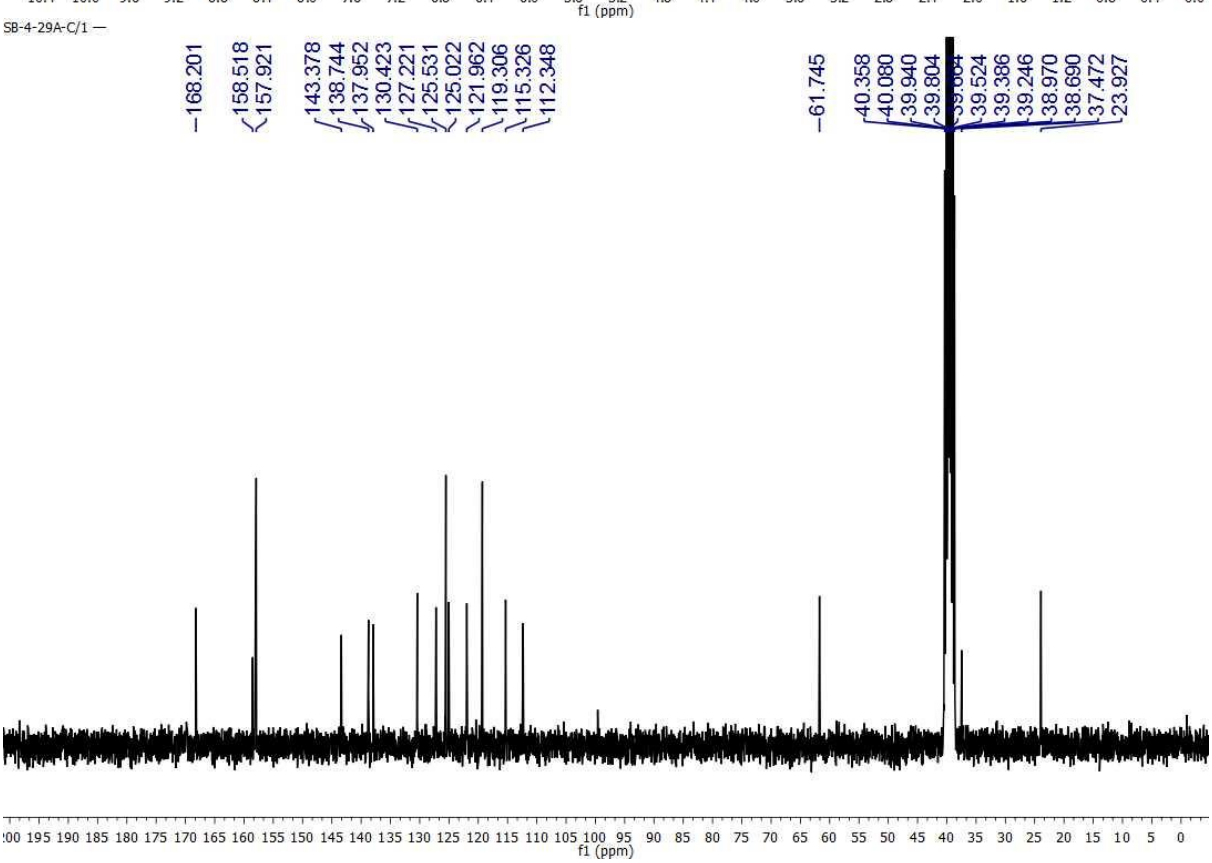
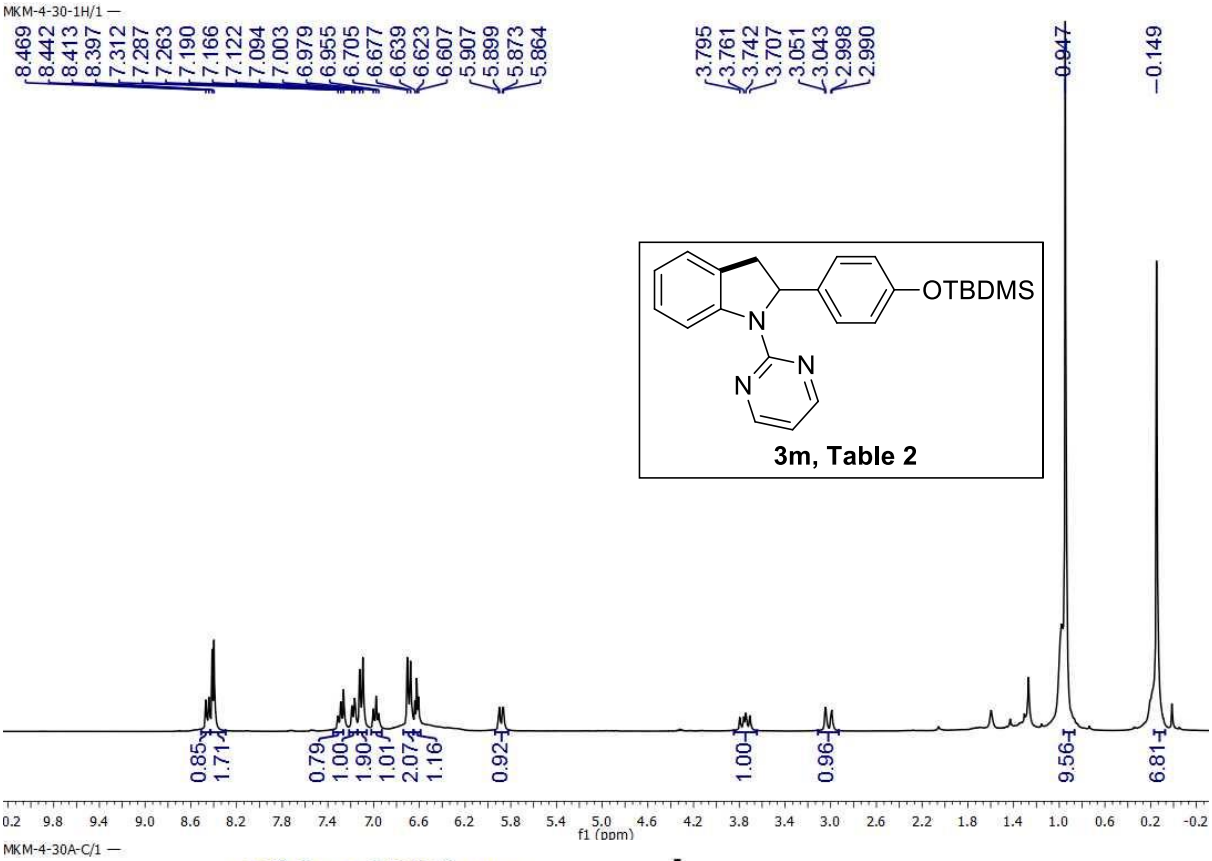
159.164
157.488
149.493
143.831
140.975
130.710
127.347
125.344
125.218
124.857
121.988
115.830
111.722
77.497
77.074
76.651
62.351
37.840
34.402
31.369
f1 (ppm)

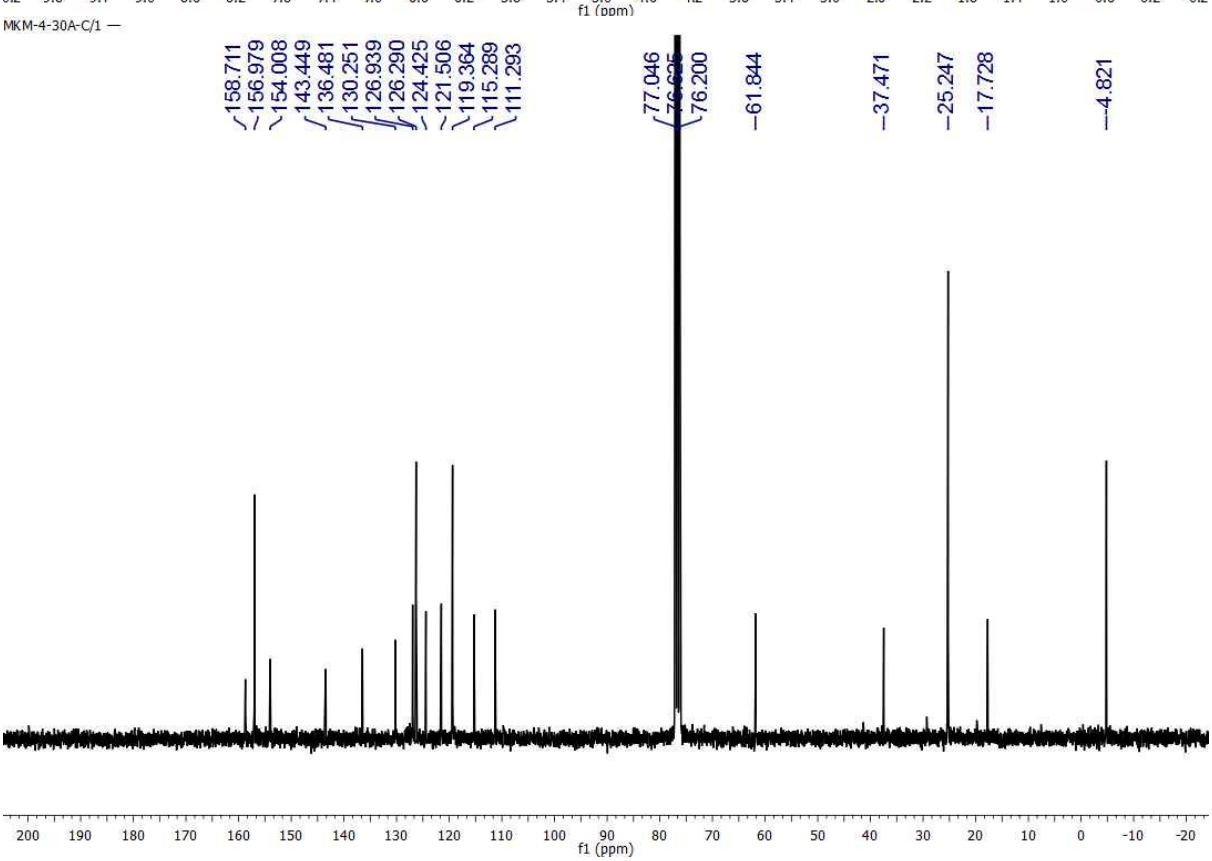

MKM-4-28-1H/1
8.457
8.429
8.407
8.391
7.306
7.279
7.253
7.191
7.162
6.993
6.969
6.944
6.777
6.748
6.633
6.617
6.601
5.909
5.901
5.874
5.867
3.793
3.759
3.741
3.727
3.706
3.030
3.022
2.976
2.968
OMe
N
N
N
3k, Table 2
0.88
1.68
0.76
2.75
1.14
1.97
1.01
0.95
4.11
1.00
f1 (ppm)

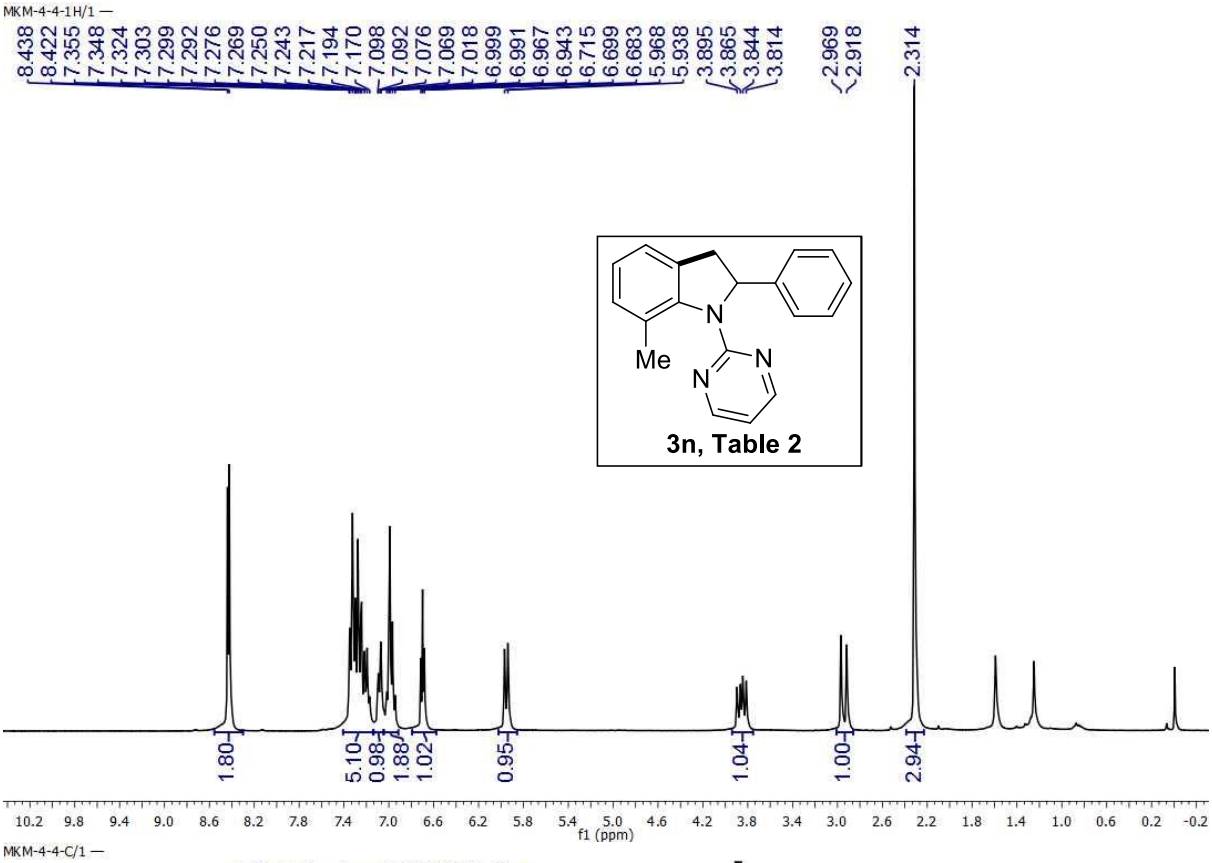

MKM-4-28-C.1.fid
159.018
158.372
157.397
143.742
136.311
130.511
127.322
126.705
124.820
121.911
115.627
113.713
111.686
77.416
76.993
76.570
62.113
55.117
37.854
0.021
f1 (ppm)

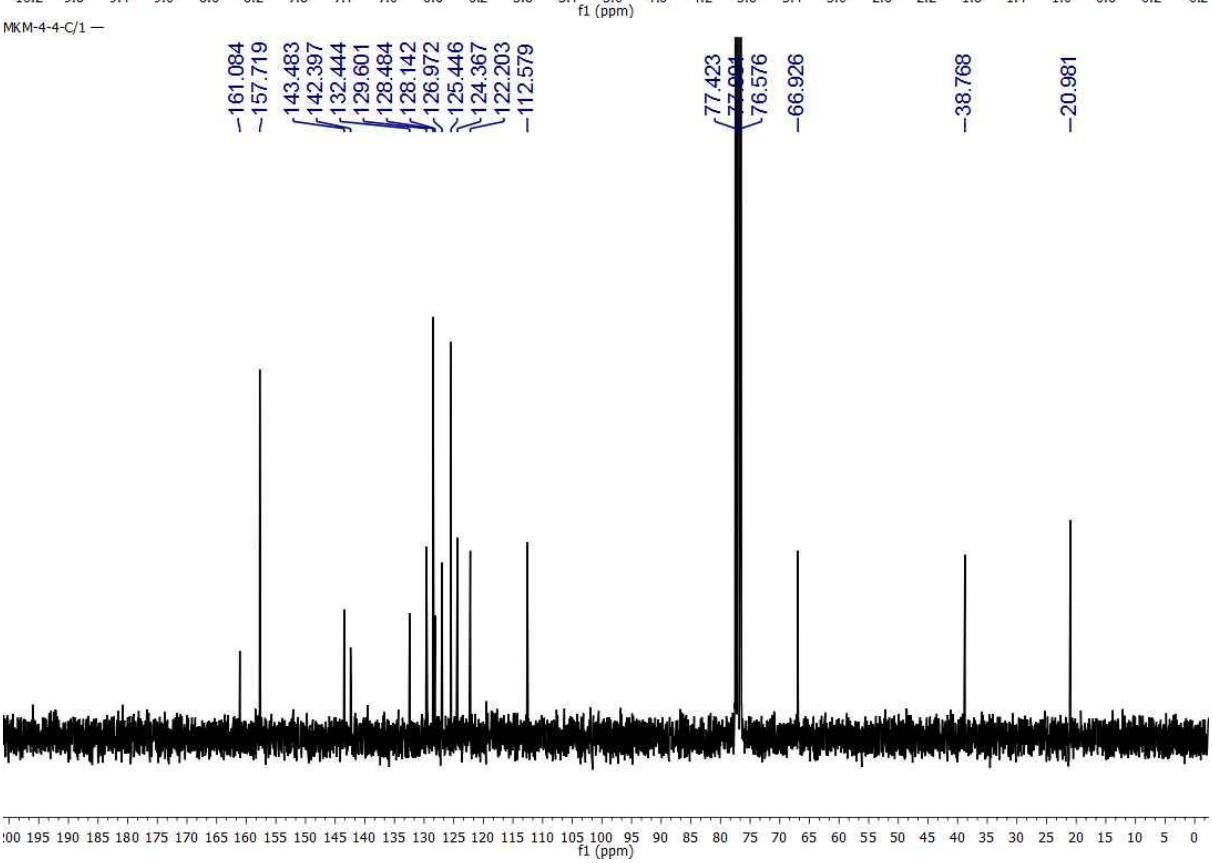

SB-4-29A-1H/1
9.857
8.500
8.484
8.403
8.376
7.415
7.388
7.272
7.246
7.219
7.195
7.068
7.040
6.976
6.952
6.927
6.846
6.830
6.814
5.891
5.883
5.856
5.849
3.798
3.764
3.744
3.709
3.386
2.903
2.850
2.515
2.509
2.502
2.496
2.490
1.976
NHAc
N
N
N
3l, Table 2
0.86
1.79
0.92
1.97
2.02
1.97
1.07
0.98
1.00
1.77
1.31
3.01
f1 (ppm)

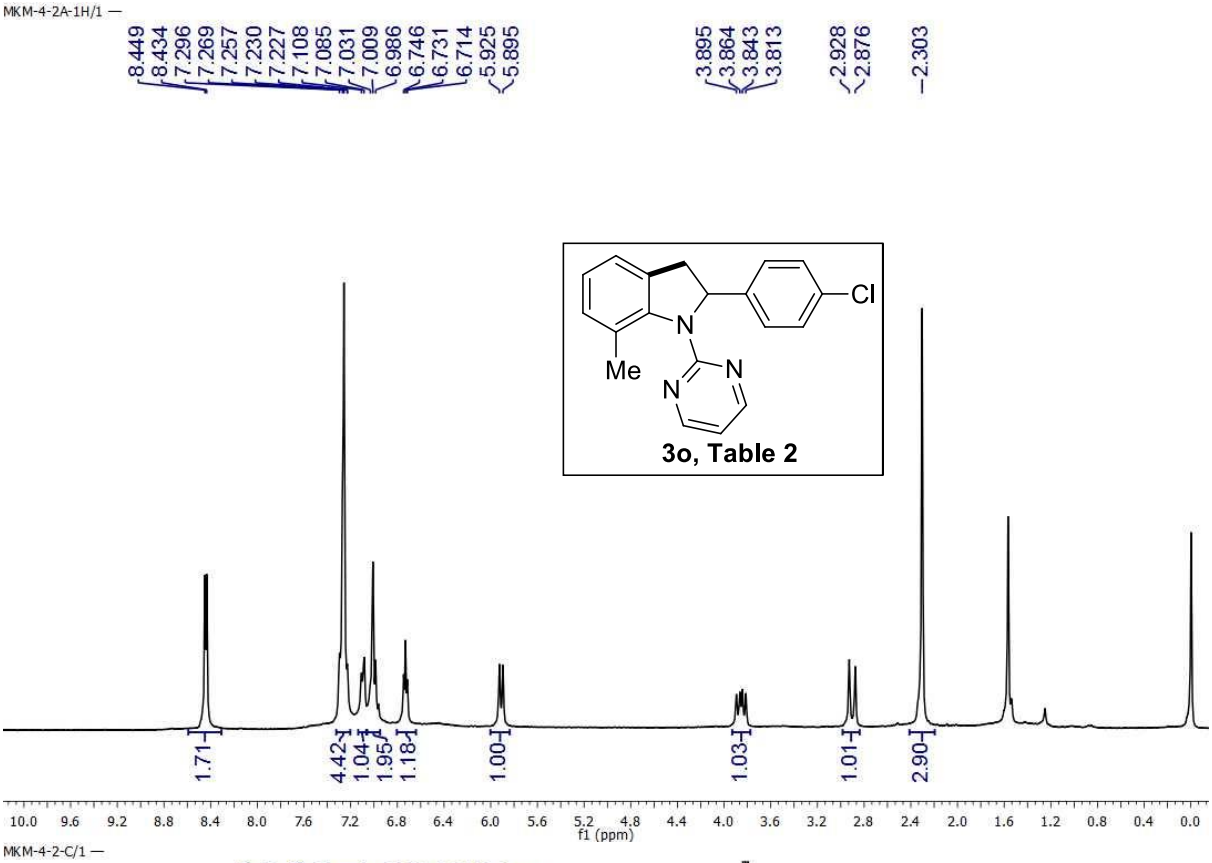

SB-4-29A-C/1
168.201
158.518
157.921
143.378
138.744
137.952
130.423
127.221
125.531
125.022
121.962
119.306
115.326
112.348
61.745
40.358
40.080
39.940
39.804
39.664
39.524
39.386
39.246
38.970
38.690
37.472
23.927
f1 (ppm)

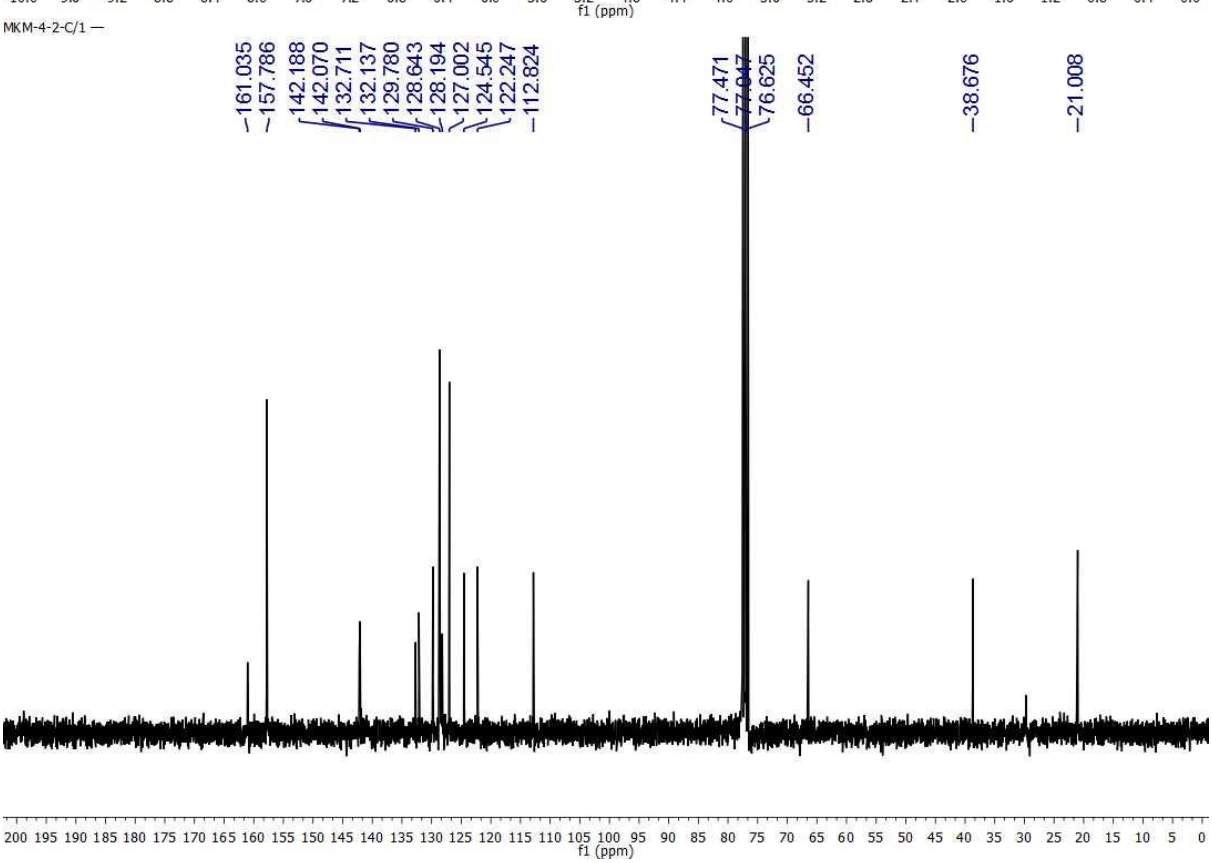

MKM-4-30-1H/1
8.469
8.442
8.413
8.397
7.312
7.287
7.263
7.190
7.166
7.122
7.094
7.003
6.979
6.955
6.705
6.677
6.639
6.623
6.607
5.907
5.899
5.873
5.864
3.795
3.761
3.742
3.707
3.051
3.043
2.998
2.990
0.947
-0.149
OTBDMS
N
N
N
3m, Table 2
0.85
1.71
0.79
1.00
1.90
1.01
2.07
1.16
0.92
1.00
0.96
9.56
6.81
f1 (ppm)

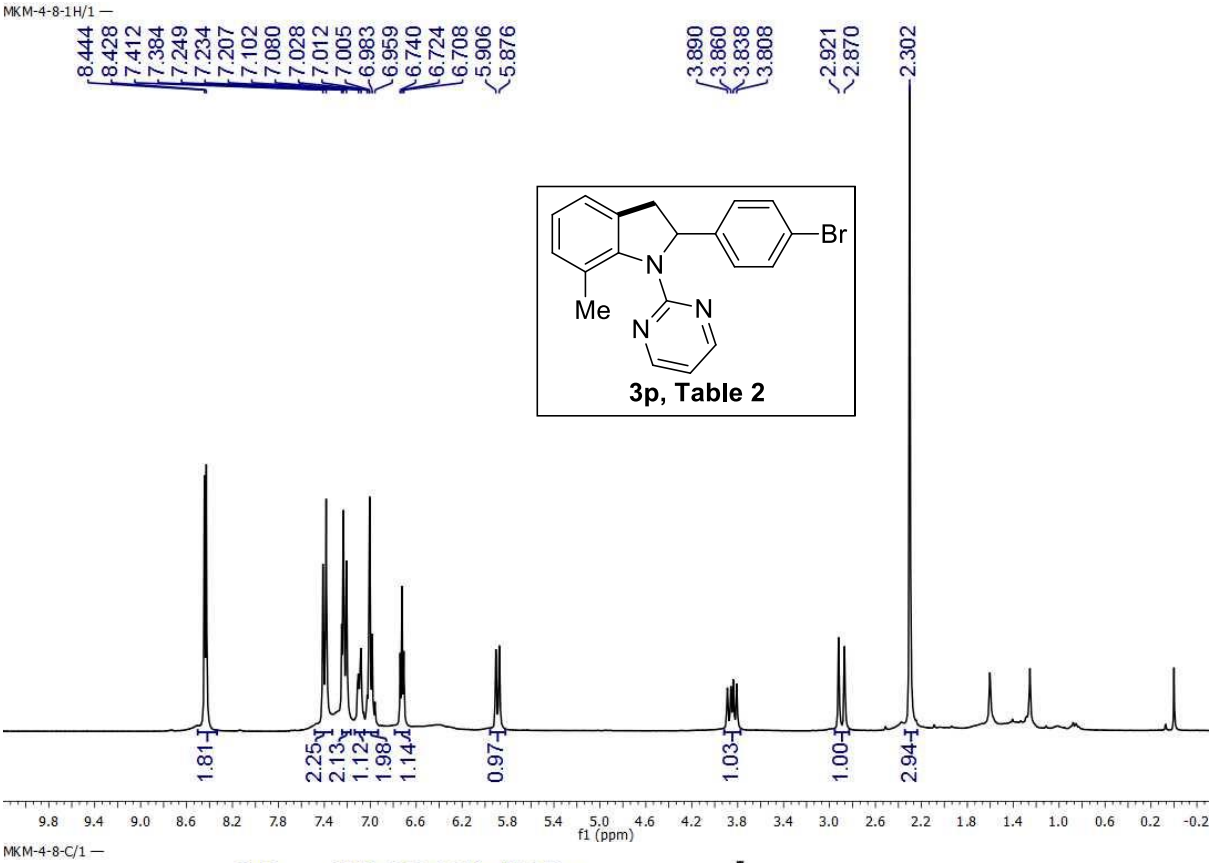

MKM-4-30A-C/1
158.711
156.979
154.008
143.449
136.481
130.251
126.939
126.290
124.425
121.506
119.364
115.289
111.293
77.046
76.625
76.200
61.844
37.471
25.247
17.728
4.821
f1 (ppm)

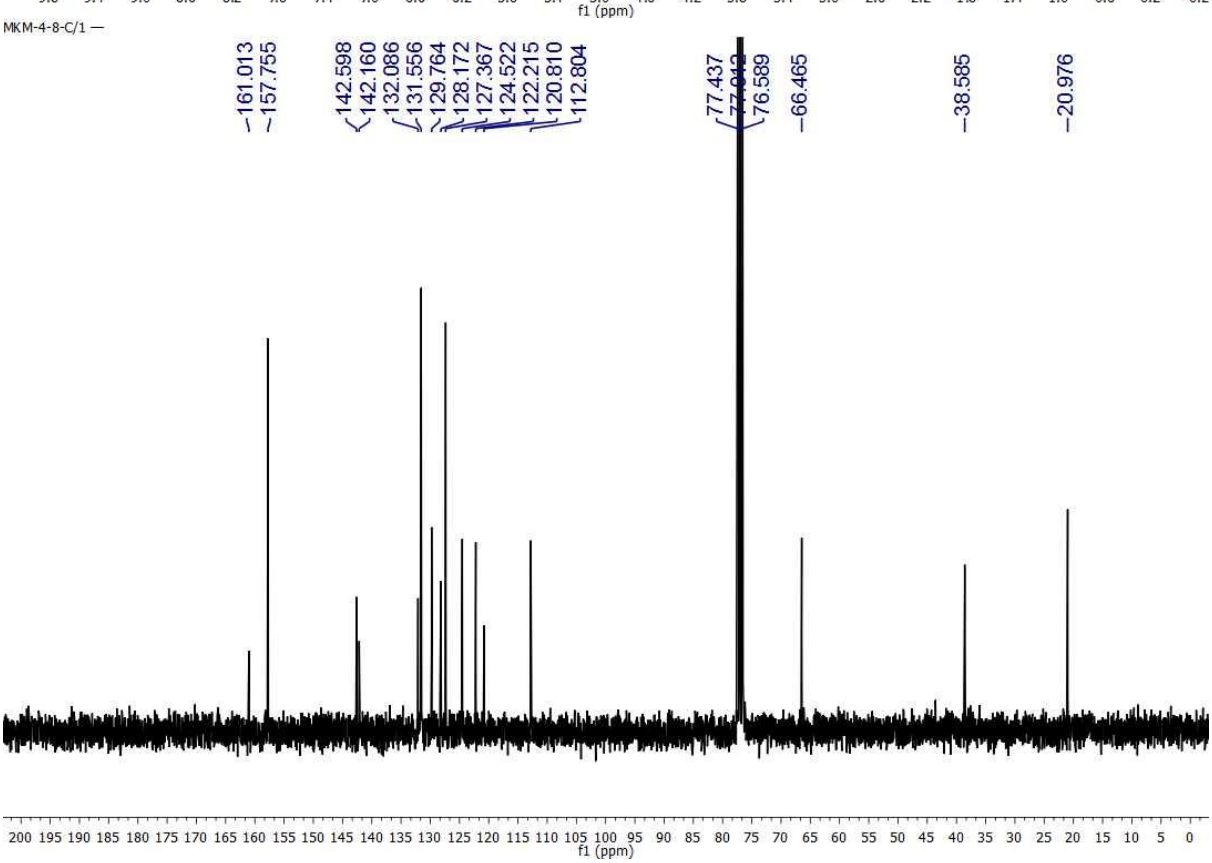

MKM-4-4-1H/1
8.438
8.422
7.355
7.348
7.324
7.303
7.299
7.292
7.276
7.269
7.250
7.243
7.217
7.194
7.170
7.098
7.092
7.076
7.069
7.018
6.999
6.991
6.967
6.943
6.715
6.699
6.683
5.968
5.938
3.895
3.865
3.844
3.814
2.969
2.918
2.314
Me
N
N
N
3n, Table 2
1.80
5.10
0.98
1.88
1.02
0.95
1.04
1.00
2.94
f1 (ppm)

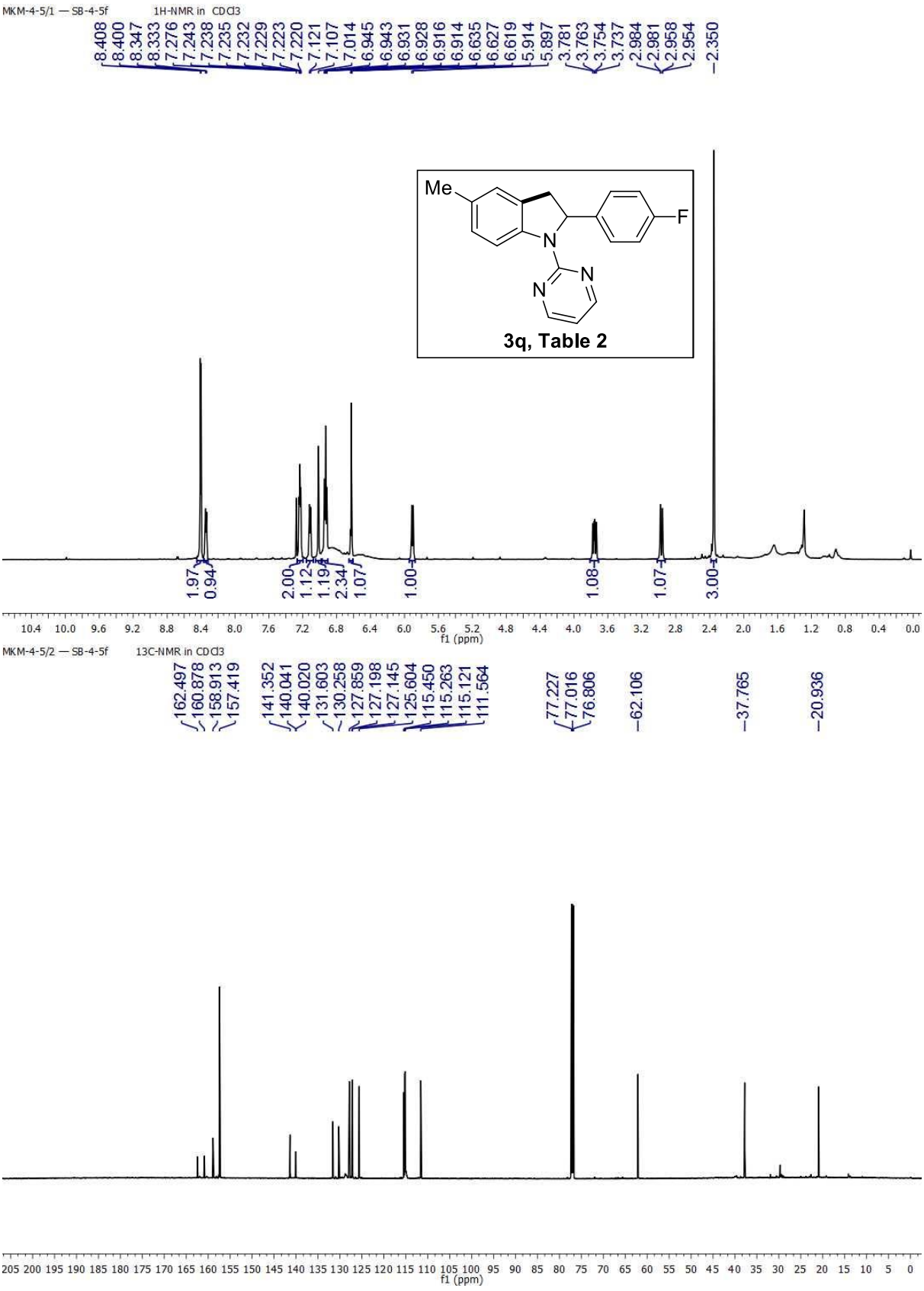

MKM-4-4-C/1
161.084
157.719
143.483
142.397
132.444
129.601
128.484
128.142
126.972
125.446
124.367
122.203
112.579
77.423
77.004
76.576
66.926
38.768
20.981
f1 (ppm)

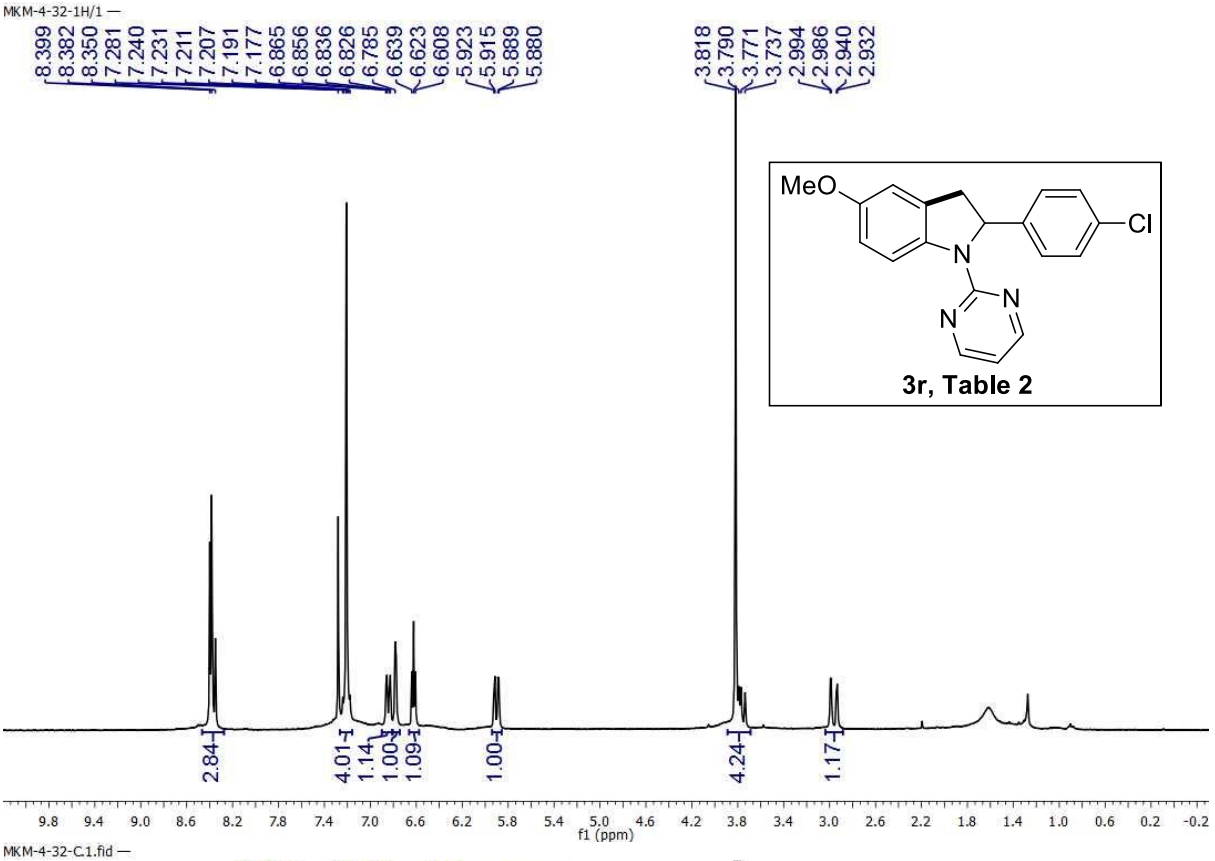

MKM-4-2A-1H/1
8.449
8.434
7.296
7.269
7.257
7.230
7.227
7.108
7.085
7.031
7.009
6.986
6.746
6.731
6.714
5.925
5.895
3.895
3.864
3.843
3.813
2.928
2.876
2.303
Cl
N
Me
N
N
3o, Table 2
1.71
4.42
1.04
1.95
1.18
1.00
1.03
1.01
2.90
f1 (ppm)

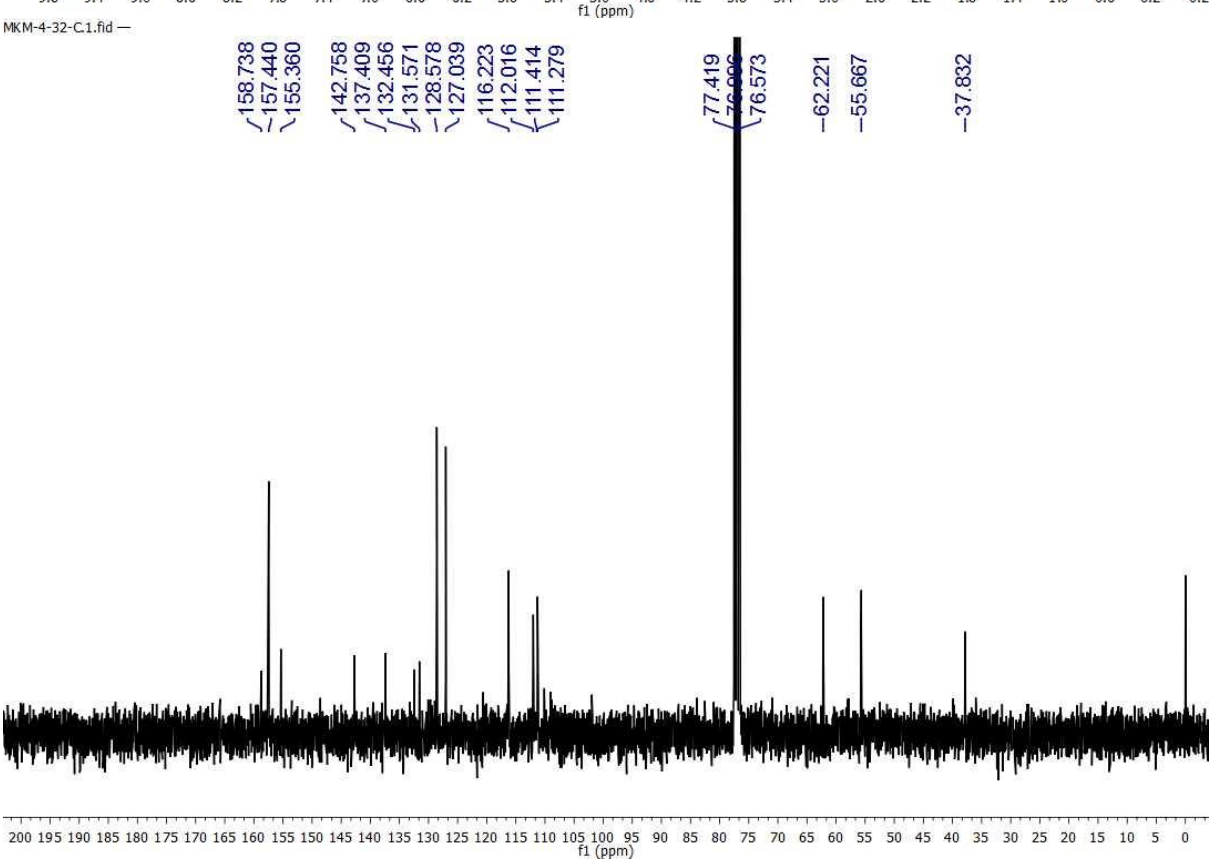

MKM-4-2-C/1
161.035
157.786
142.188
142.070
132.711
132.137
129.780
128.643
128.194
127.002
124.545
122.247
112.824
77.471
77.047
76.625
66.452
38.676
21.008
f1 (ppm)

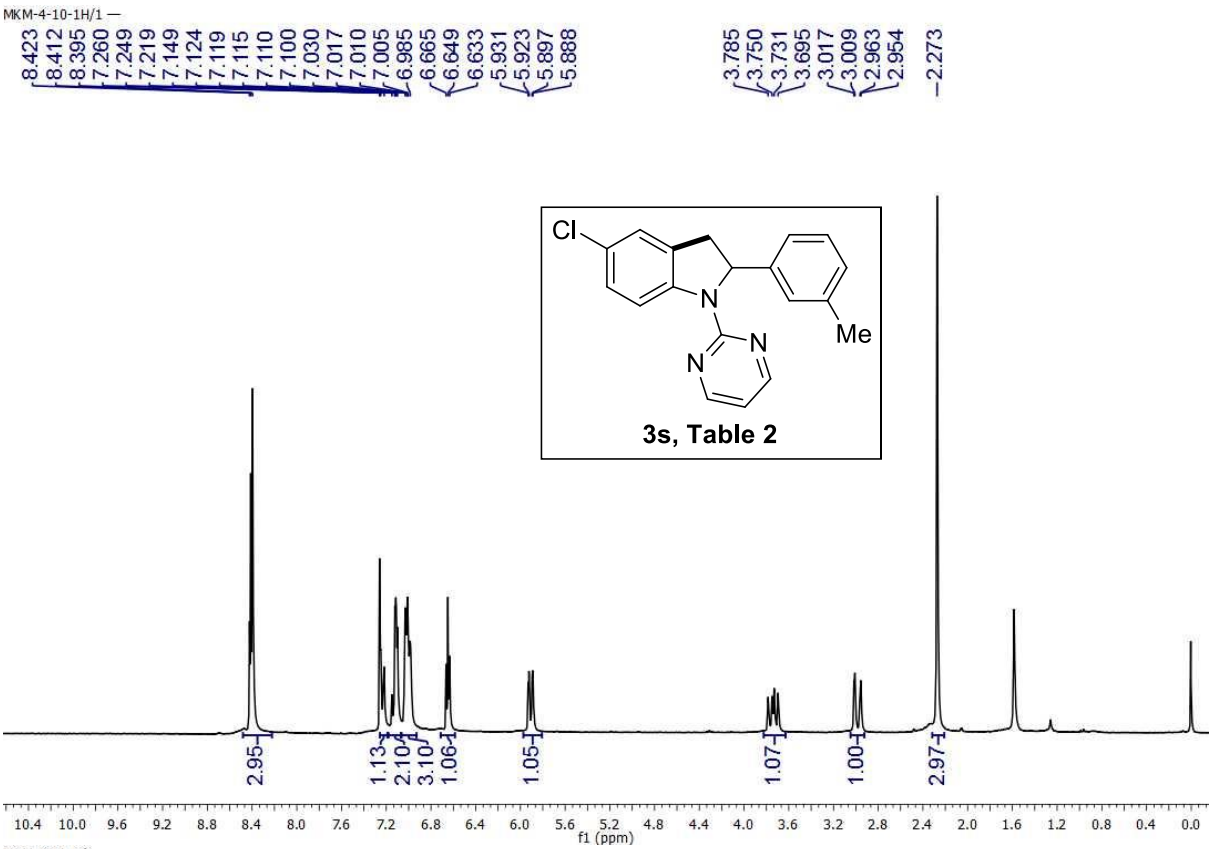

MKM-4-8-1H/1
8.444
8.428
7.412
7.384
7.249
7.234
7.207
7.102
7.080
7.028
7.012
7.005
6.983
6.959
6.740
6.724
6.708
5.906
5.876
3.890
3.860
3.838
3.808
2.921
2.870
2.302
Br
N
Me
N
N
3p, Table 2
1.81
2.25
2.13
1.12
1.98
1.14
0.97
1.03
1.00
2.94
f1 (ppm)

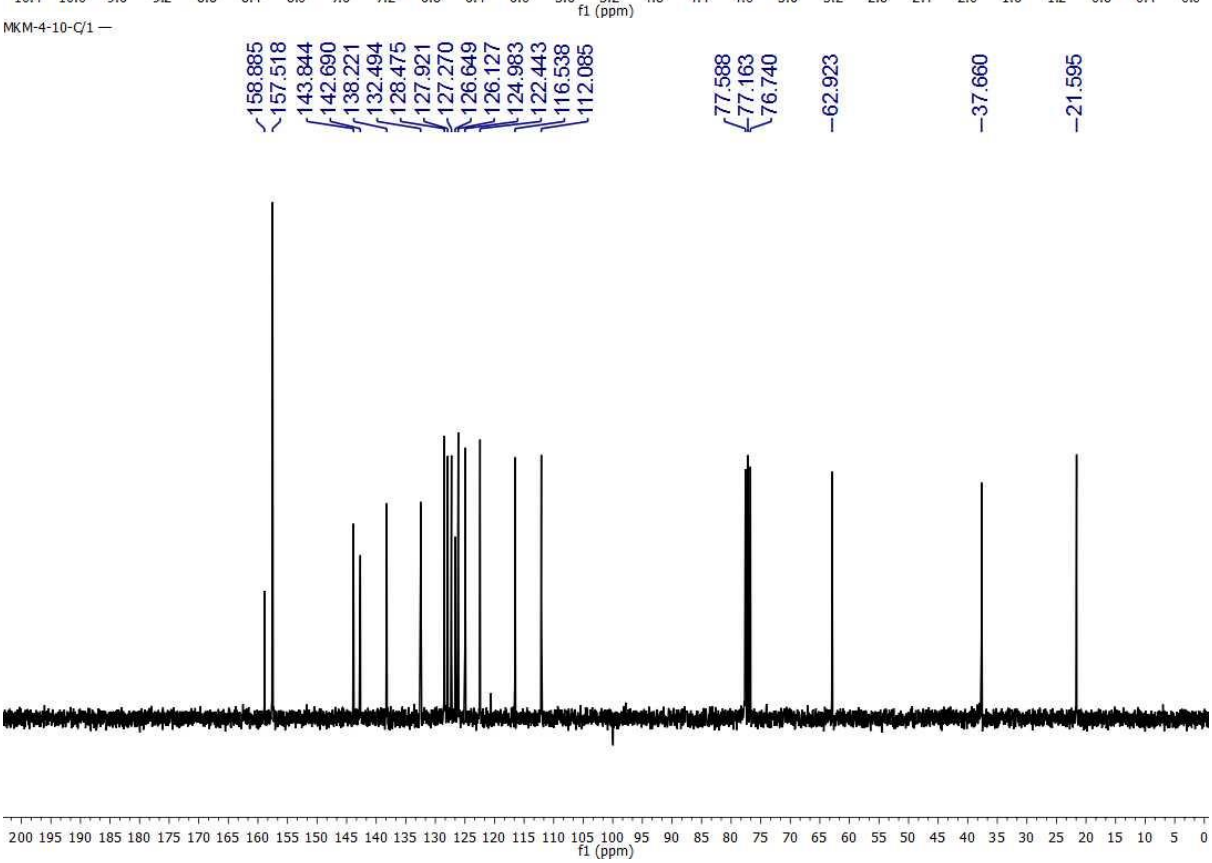

MKM-4-8-C/1
161.013
157.755
142.598
142.160
132.086
131.556
129.764
128.172
127.367
124.522
122.215
120.810
112.804
77.437
76.589
66.465
38.585
20.976
f1 (ppm)

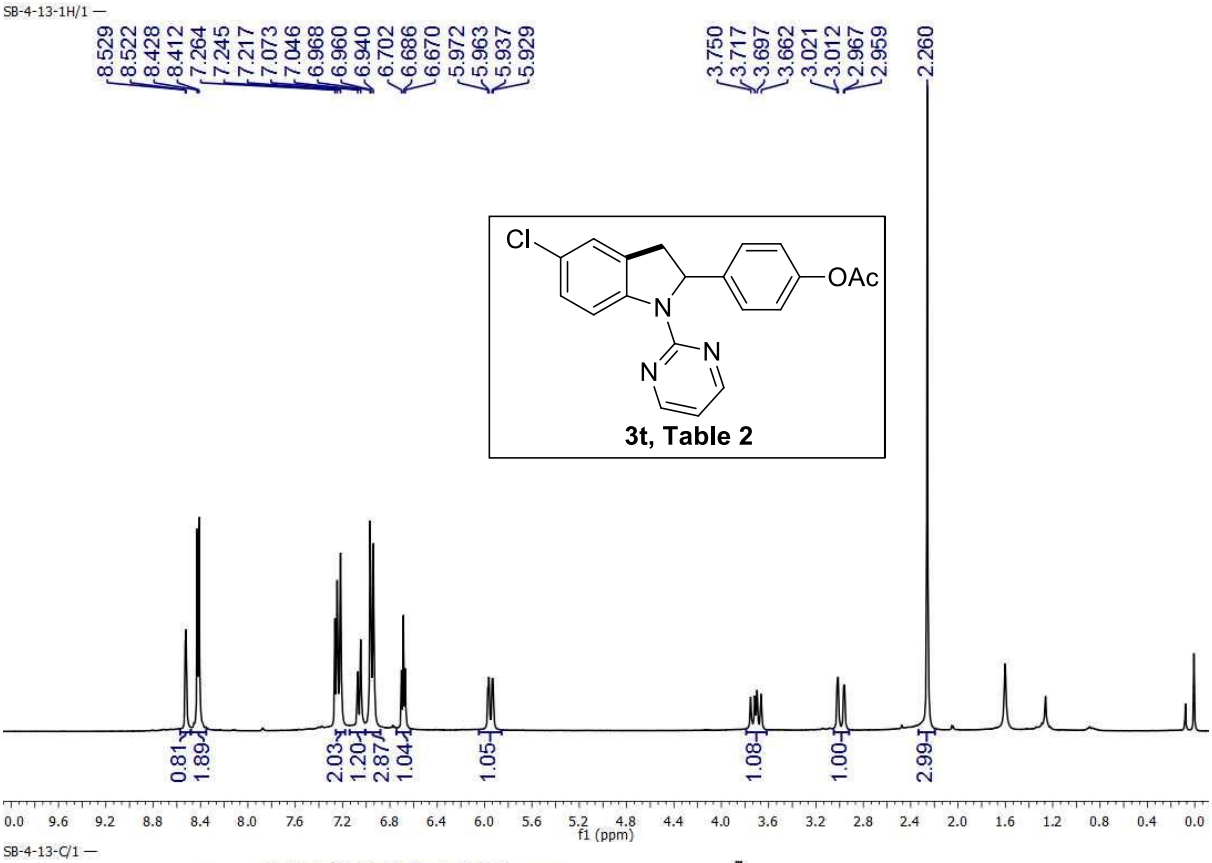

MKM-4-5/1 — SB-4-5f 1H-NMR in CDCl3
8.408
8.400
8.347
8.333
7.276
7.243
7.238
7.235
7.232
7.229
7.223
7.220
7.121
7.107
7.014
6.945
6.943
6.931
6.928
6.916
6.914
6.635
6.627
6.619
5.914
5.897
3.781
3.763
3.754
3.737
2.984
2.981
2.958
2.954
2.350
Me
F
N
N
N
3q, Table 2
1.97
0.94
2.00
1.12
1.19
2.34
1.07
1.00
1.08
1.07
3.00
f1 (ppm)
MKM-4-5/2 — SB-4-5f 13C-NMR in CDCl3
162.497
160.878
158.913
157.419
141.352
140.041
140.020
131.603
130.258
127.859
127.198
127.145
125.604
115.450
115.263
115.121
111.564
77.227
77.016
76.806
62.106
37.765
20.936
f1 (ppm)

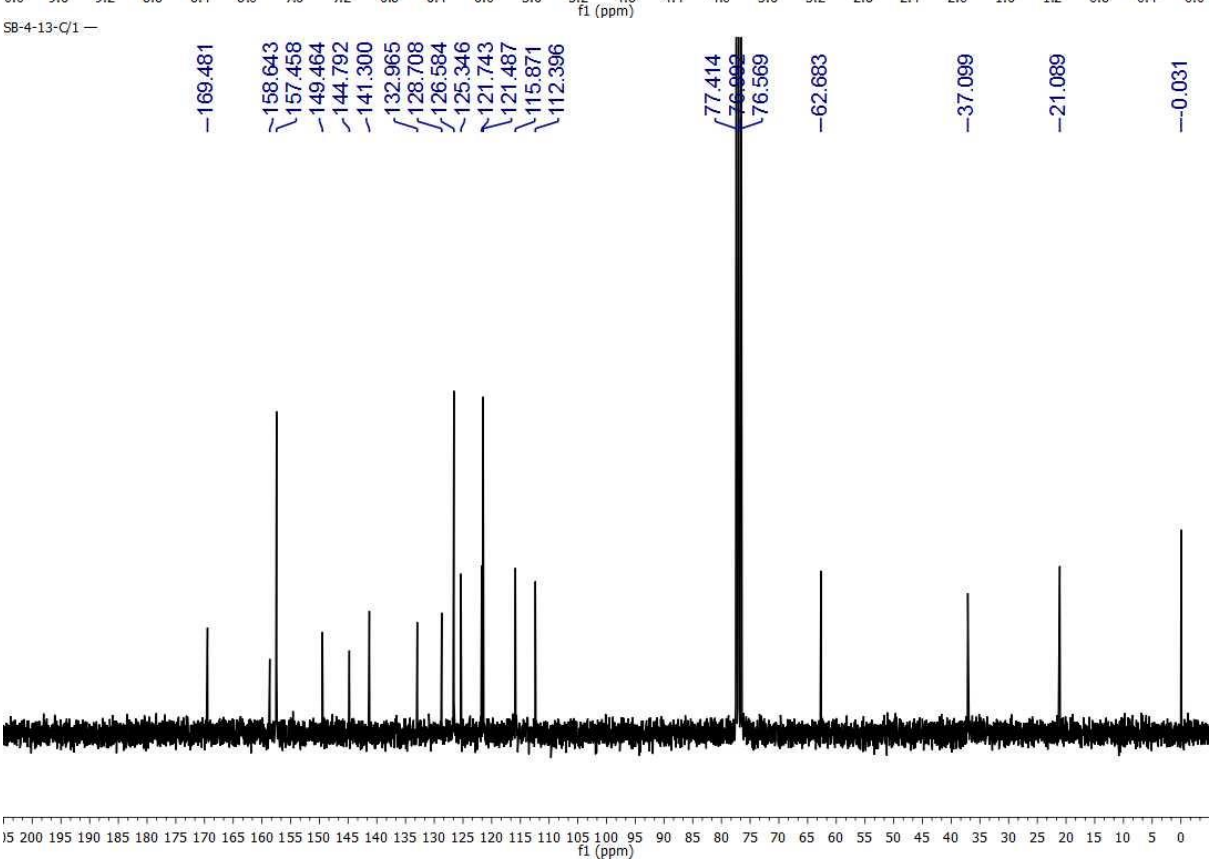

MKM-4-32-1H/1
8.399
8.382
8.350
7.281
7.240
7.231
7.211
7.207
7.191
7.177
6.865
6.856
6.836
6.826
6.785
6.639
6.623
6.608
5.923
5.915
5.889
5.880
3.818
3.790
3.771
3.737
2.994
2.986
2.940
2.932
MeO
Cl
N
N
N
3r, Table 2
2.84
4.01
1.14
1.00
1.09
1.00
4.24
1.17
f1 (ppm)

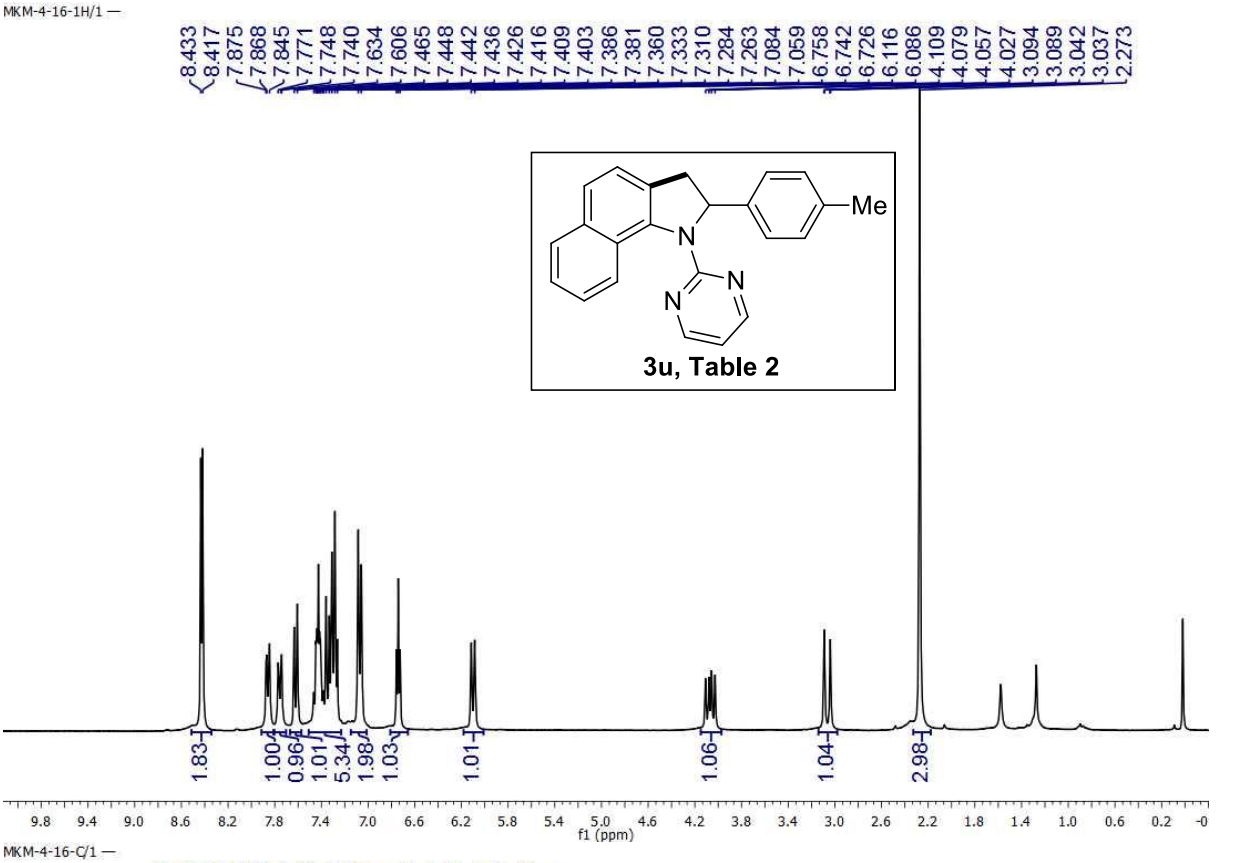

MKM-4-32-C.1.fid
158.738
157.440
155.360
142.758
137.409
132.456
131.571
128.578
127.039
116.223
112.016
111.414
111.279
77.419
76.996
76.573
62.221
55.667
37.832
f1 (ppm)

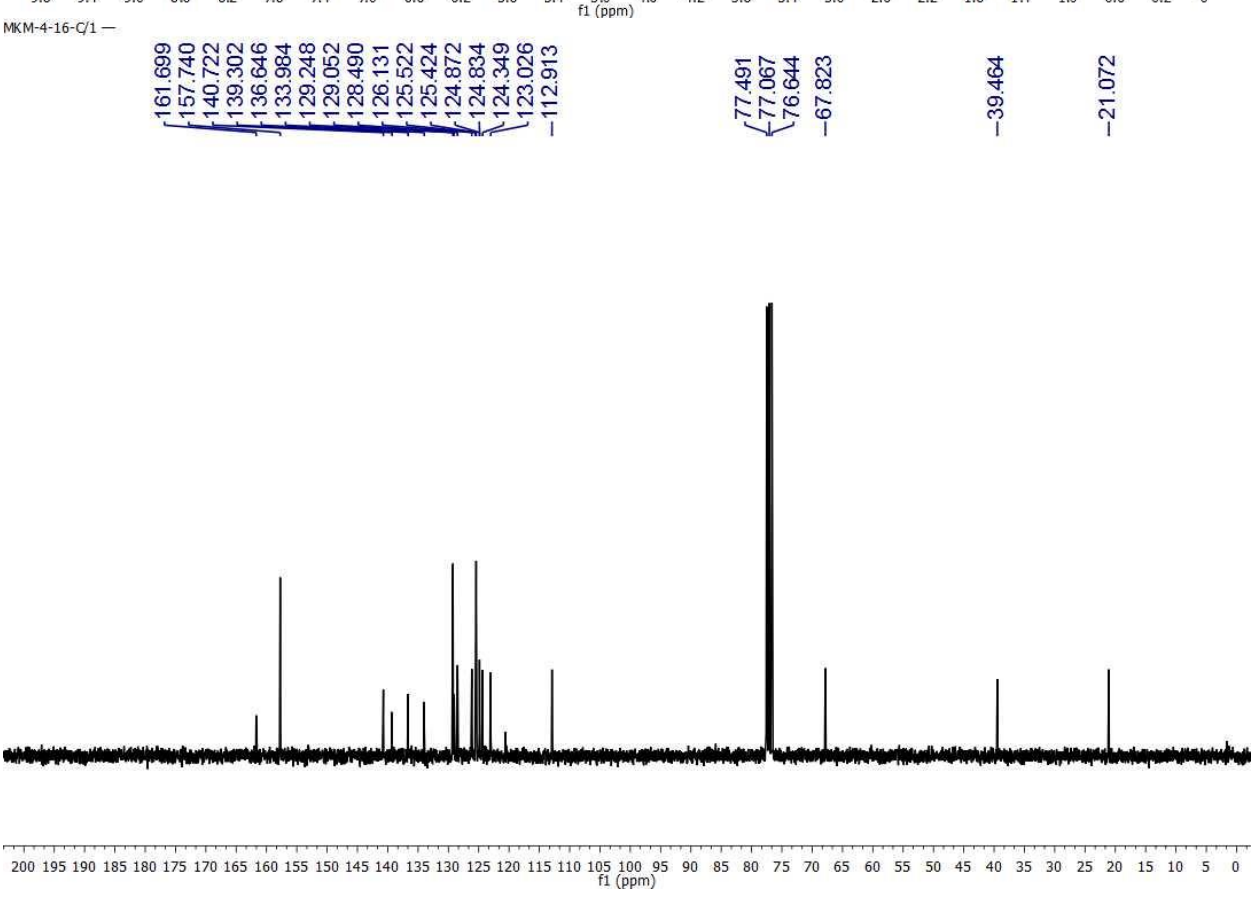

MKM-4-10-1H/1
8.423
8.412
8.395
7.260
7.249
7.219
7.149
7.124
7.119
7.115
7.110
7.100
7.030
7.017
7.010
7.005
6.985
6.665
6.649
6.633
5.931
5.923
5.897
5.888
3.785
3.750
3.731
3.695
3.017
3.009
2.963
2.954
2.273
Cl
N
N
N
Me
3s, Table 2
2.95
1.13
2.10
3.10
1.06
1.05
1.07
1.00
2.97
f1 (ppm)

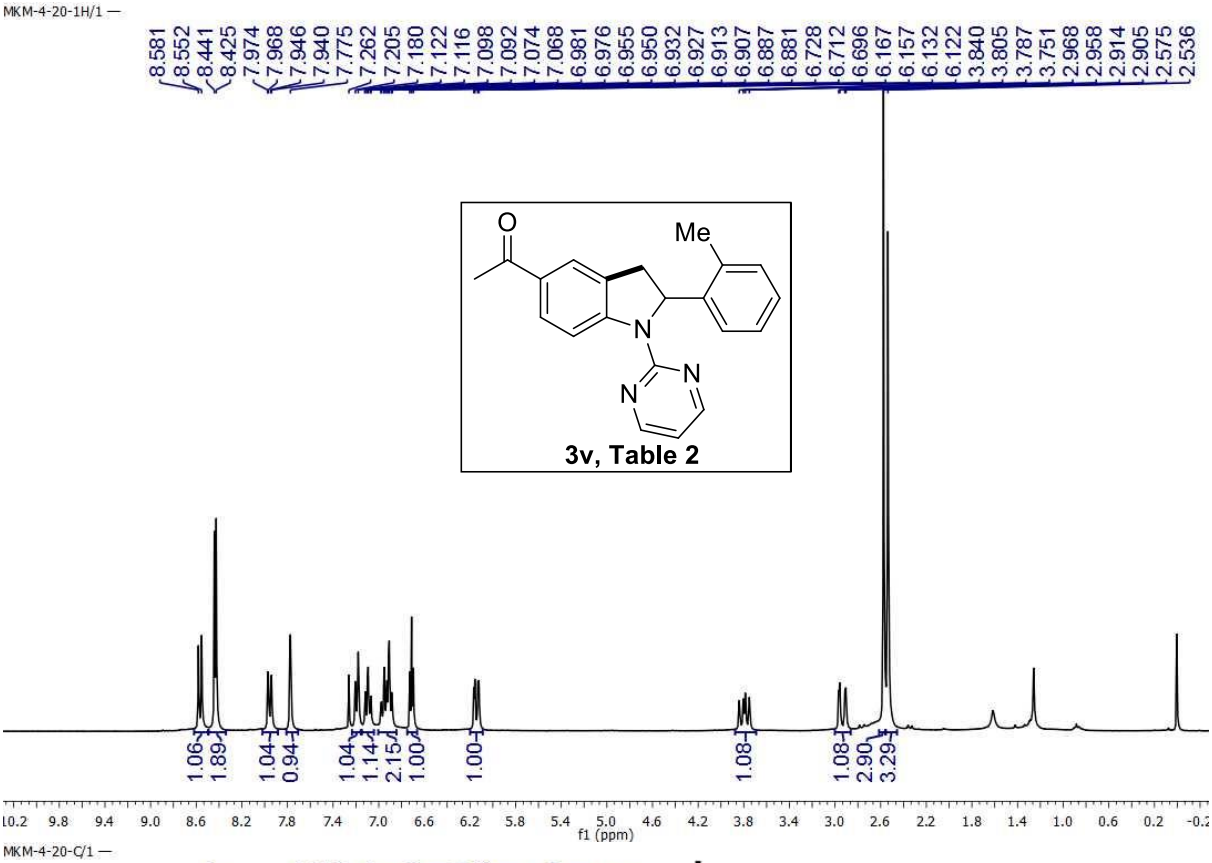

MKM-4-10-C/1
158.885
157.518
143.844
142.690
138.221
132.494
128.475
127.921
127.270
126.649
126.127
124.983
122.443
116.538
112.085
77.588
77.163
76.740
62.923
37.660
21.595
f1 (ppm)

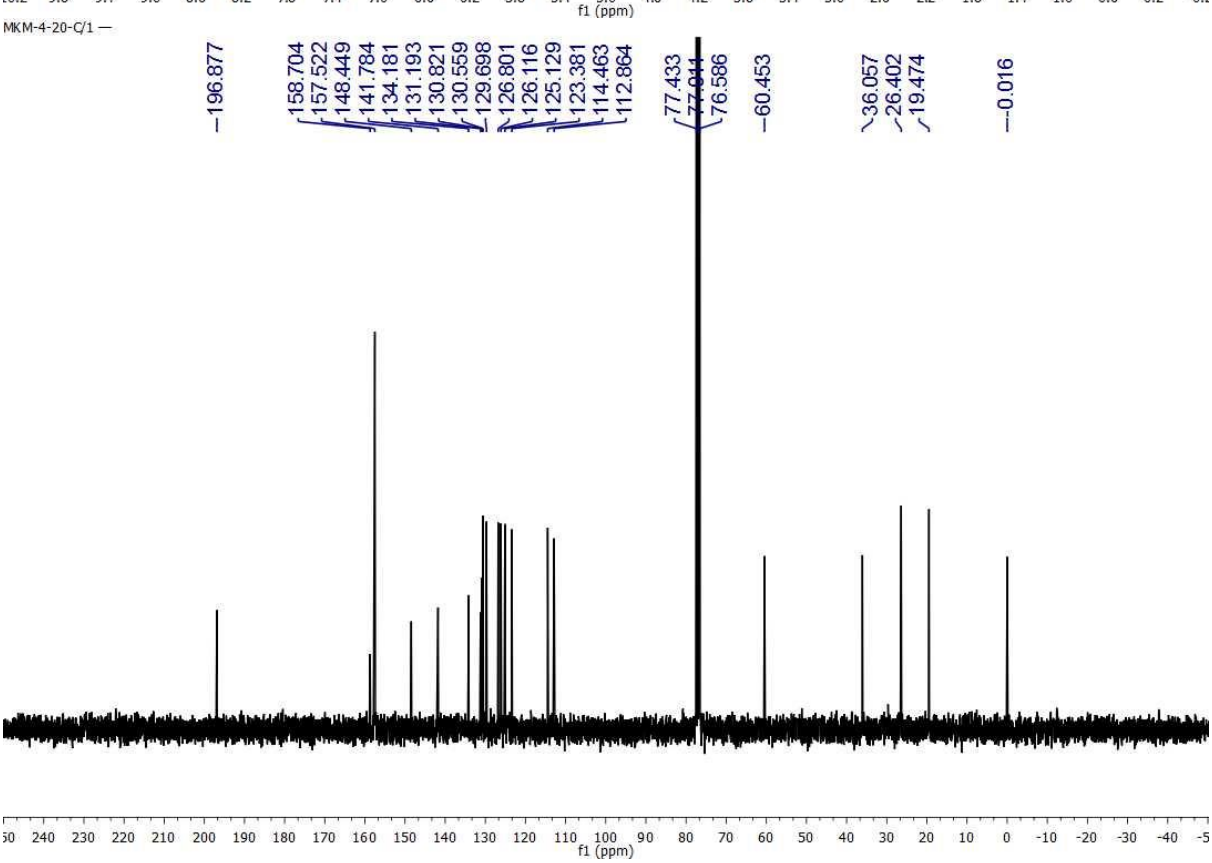

SB-4-13-1H/1
8.529
8.522
8.428
8.412
7.264
7.245
7.217
7.073
7.046
6.968
6.960
6.940
6.702
6.686
6.670
5.972
5.963
5.937
5.929
3.750
3.717
3.697
3.662
3.021
3.012
2.967
2.959
2.260
Cl
OAc
N
N
N
3t, Table 2
0.81
1.89
2.03
1.20
2.87
1.04
1.05
1.08
1.00
2.99
f1 (ppm)

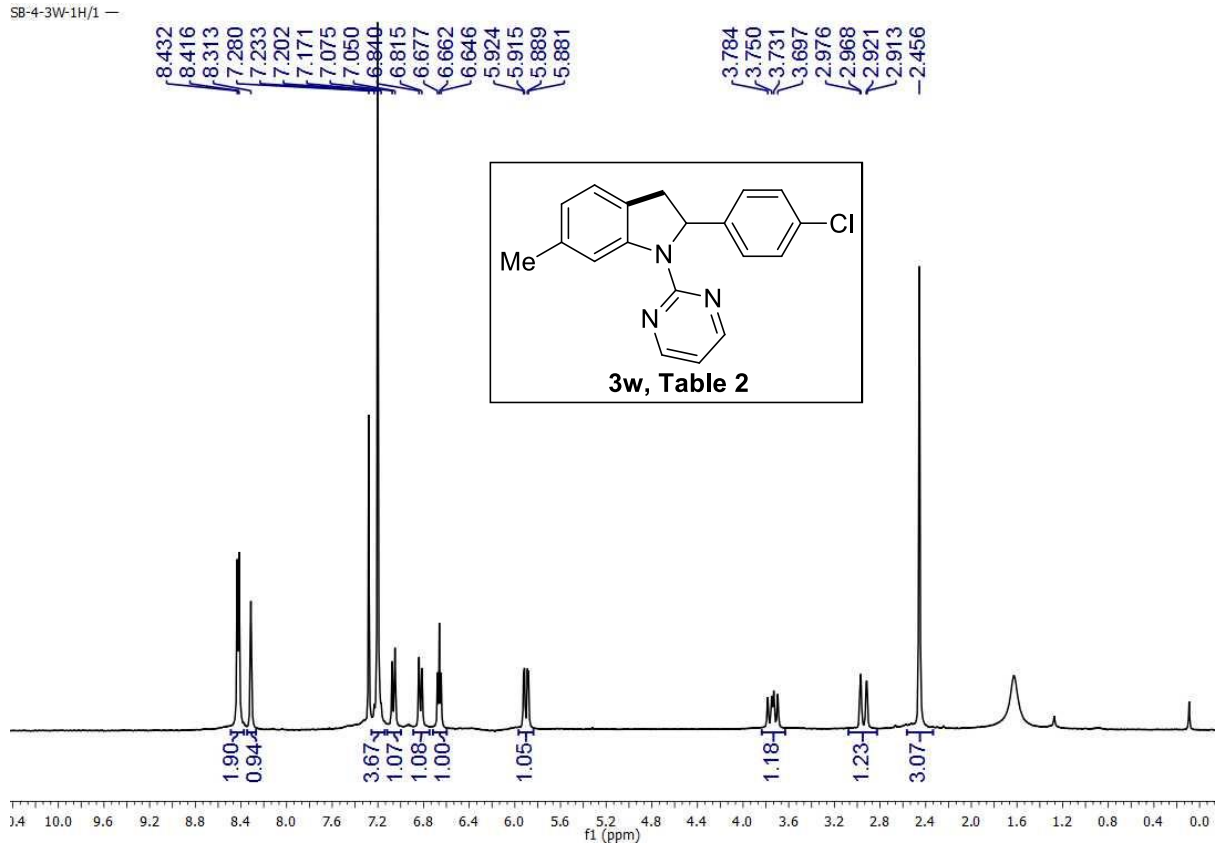

SB-4-13-C/1
169.481
158.643
157.458
149.464
144.792
141.300
132.965
128.708
126.584
125.346
121.743
121.487
115.871
112.396
77.414
76.569
62.683
37.099
21.089
0.031
f1 (ppm)

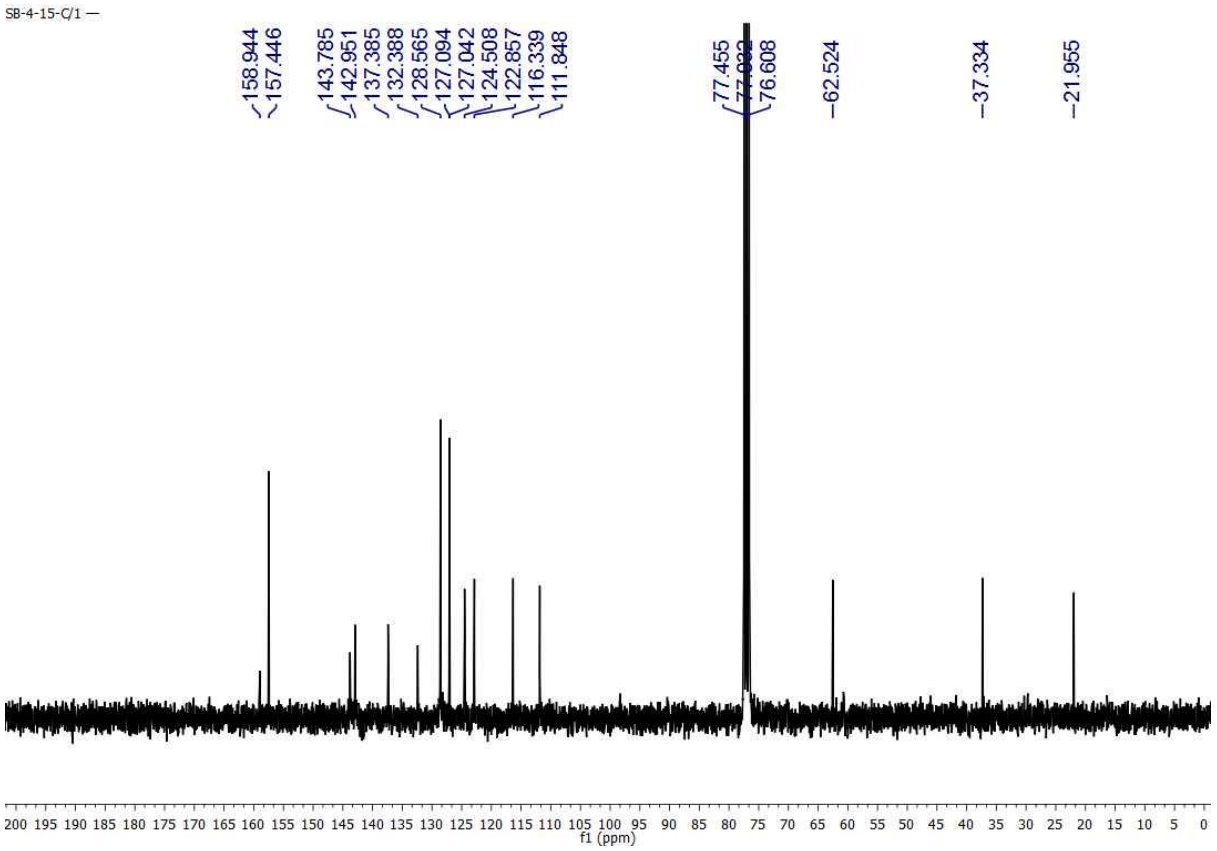

MKM-4-16-1H/1
8.433
8.417
7.875
7.868
7.845
7.771
7.748
7.740
7.634
7.606
7.465
7.448
7.442
7.436
7.426
7.416
7.409
7.403
7.386
7.381
7.360
7.333
7.310
7.284
7.263
7.084
7.059
6.758
6.742
6.726
6.116
6.086
4.109
4.079
4.057
4.027
3.094
3.089
3.042
3.037
2.273
Me
N
N
N
3u, Table 2
1.83
1.00
0.96
1.01
5.34
1.98
1.03
1.01
1.06
1.04
2.98
f1 (ppm)

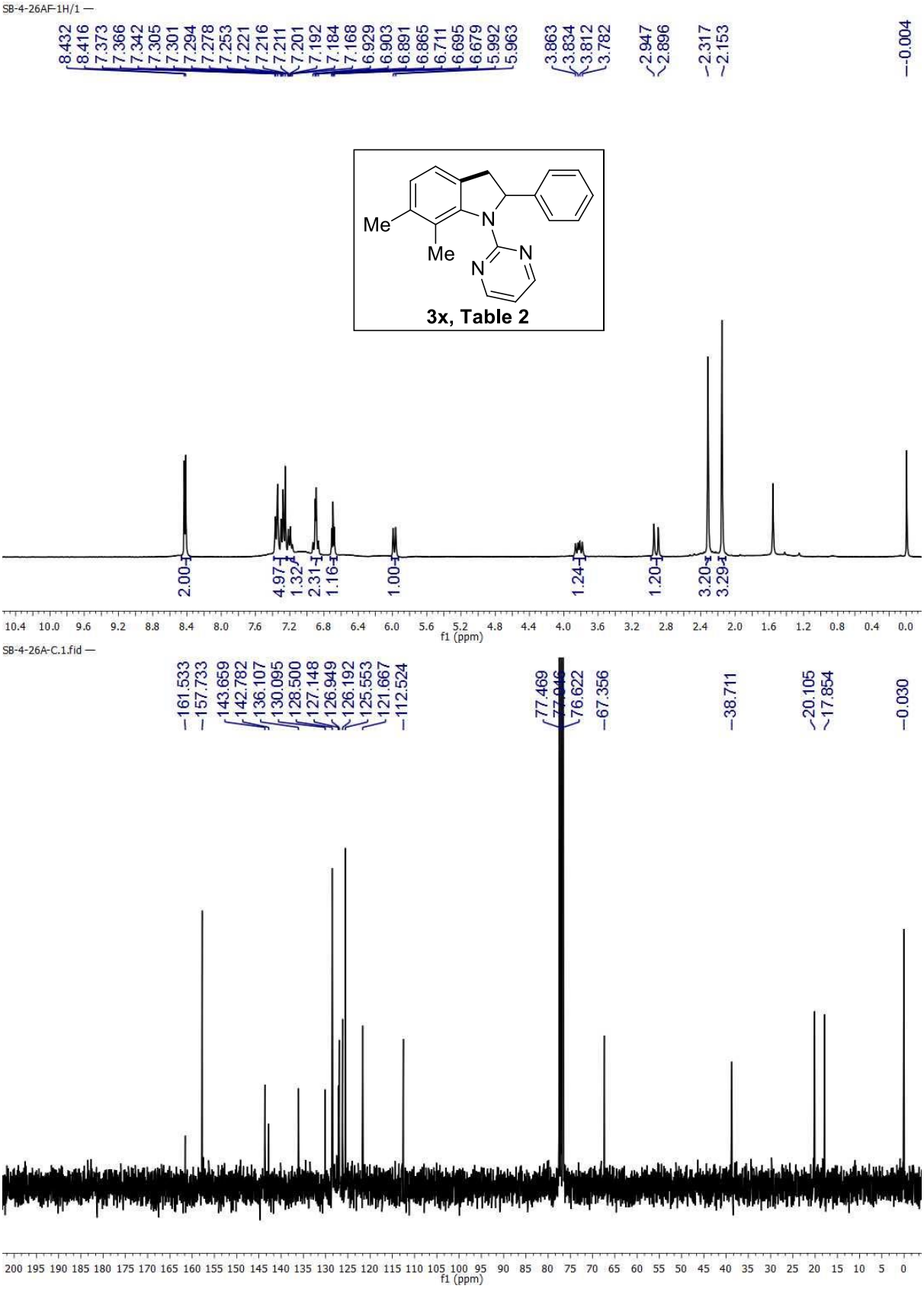

MKM-4-16-C/1
161.699
157.740
140.722
139.302
136.646
133.984
129.248
129.052
128.490
126.131
125.522
125.424
124.872
124.834
124.349
123.026
112.913
77.491
77.067
76.644
67.823
39.464
21.072
f1 (ppm)

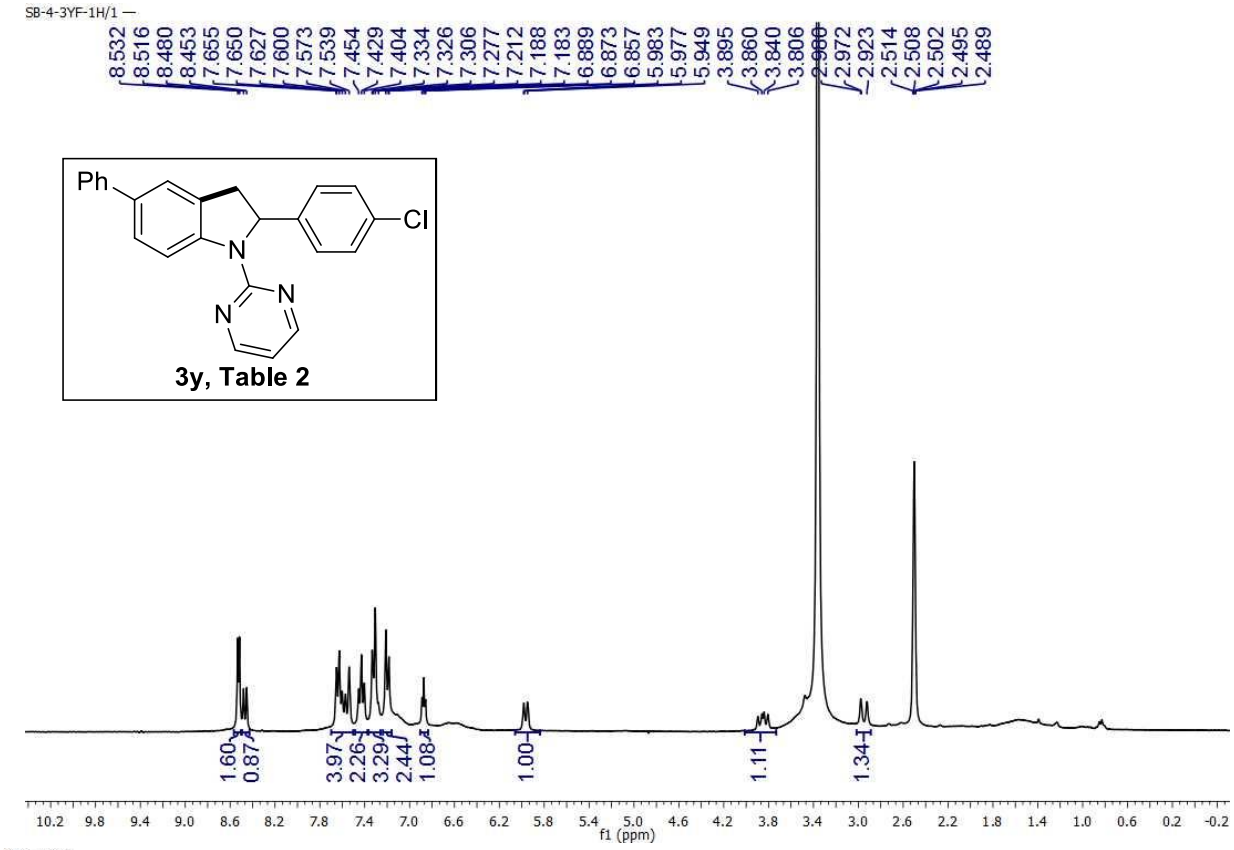

MKM-4-20-1H/1
8.581
8.552
8.441
8.425
7.974
7.968
7.946
7.940
7.775
7.262
7.205
7.180
7.122
7.116
7.098
7.092
7.074
7.068
6.981
6.976
6.955
6.950
6.932
6.927
6.913
6.907
6.887
6.881
6.728
6.712
6.696
6.167
6.157
6.132
6.122
3.840
3.805
3.787
3.751
2.968
2.958
2.914
2.905
2.575
2.536
O
Me
N
N
N
3v, Table 2
1.06
1.89
1.04
0.94
1.04
1.14
2.15
1.00
1.00
1.08
1.08
2.90
3.29
f1 (ppm)

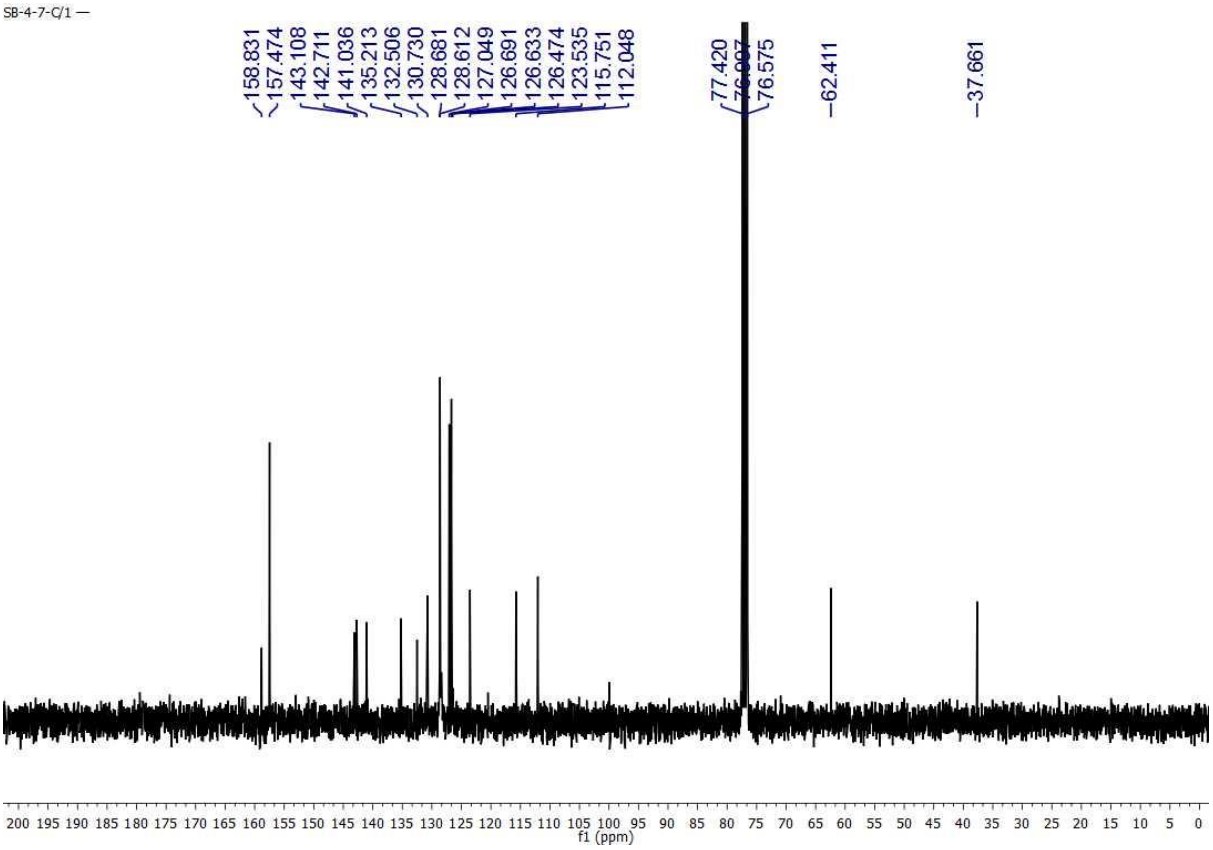

MKM-4-20-C/1
196.877
158.704
157.522
148.449
141.784
134.181
131.193
130.821
130.559
129.698
126.801
126.116
125.129
123.381
114.463
112.864
77.433
77.011
76.586
60.453
36.057
26.402
19.474
0.016
f1 (ppm)

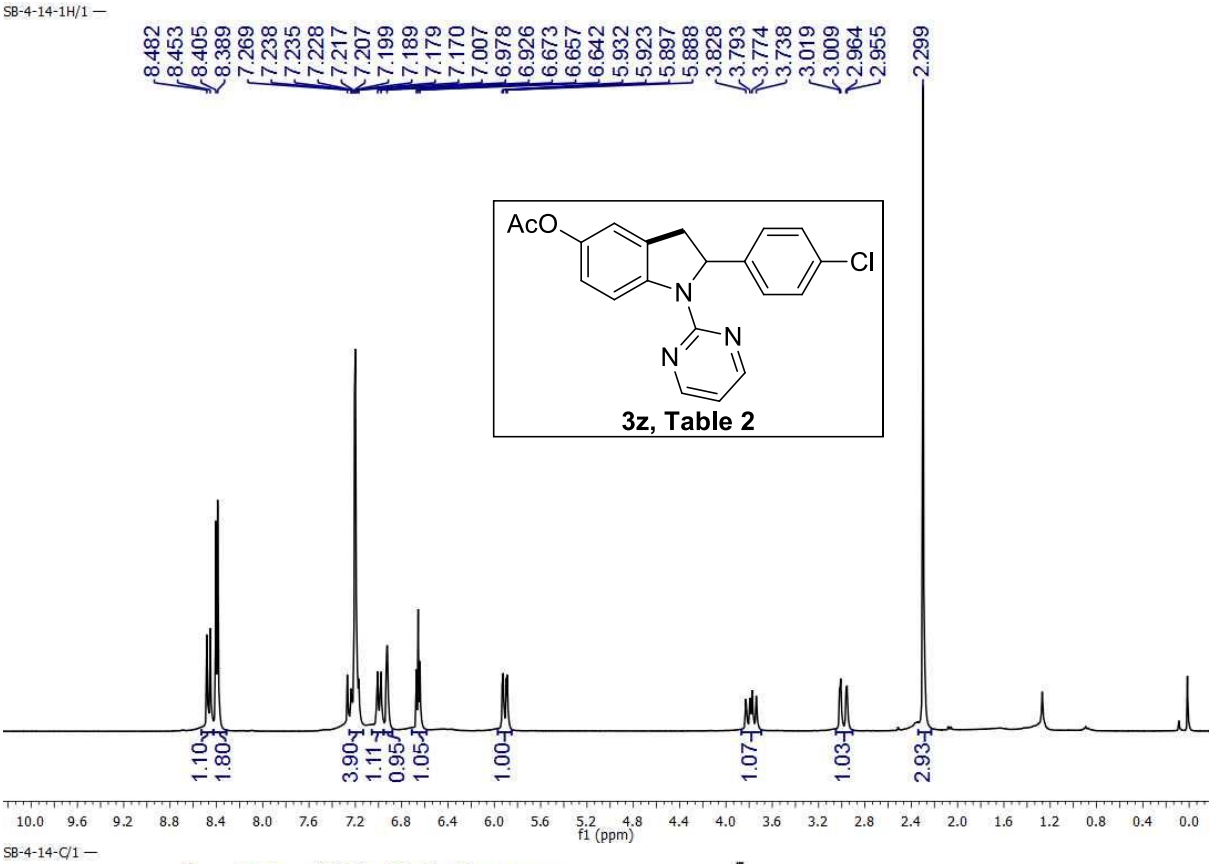

SB-4-3W-1H/1
8.432
8.416
8.313
7.280
7.233
7.202
7.171
7.075
7.050
6.840
6.815
6.677
6.662
6.646
5.924
5.915
5.889
5.881
3.784
3.750
3.731
3.697
2.976
2.968
2.921
2.913
2.456
Me
N
N
N
Cl
3w, Table 2
1.90
0.94
3.67
1.07
1.08
1.00
1.05
1.18
1.23
3.07
f1 (ppm)

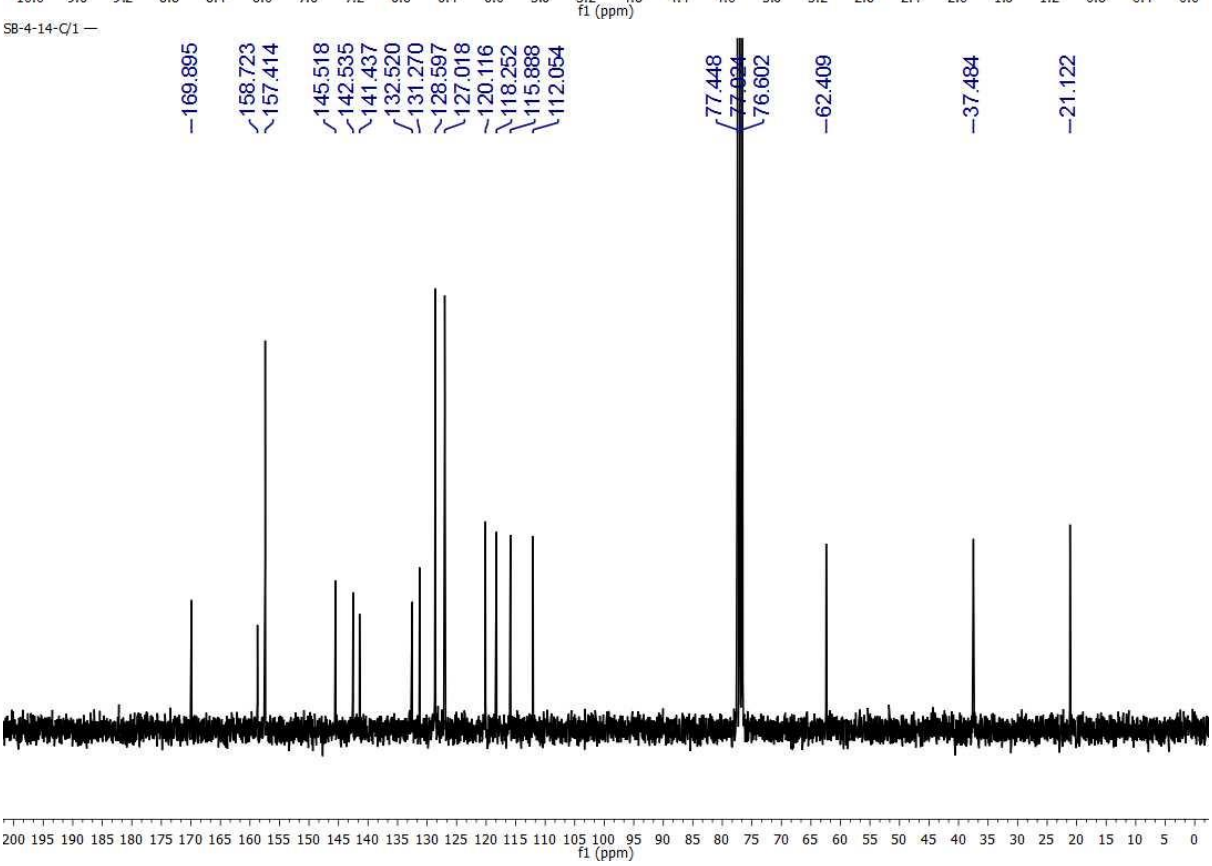

SB-4-15-C/1
158.944
157.446
143.785
142.951
137.385
132.388
128.565
127.094
127.042
124.508
122.857
116.339
111.848
77.455
77.033
76.608
62.524
37.334
21.955
f1 (ppm)

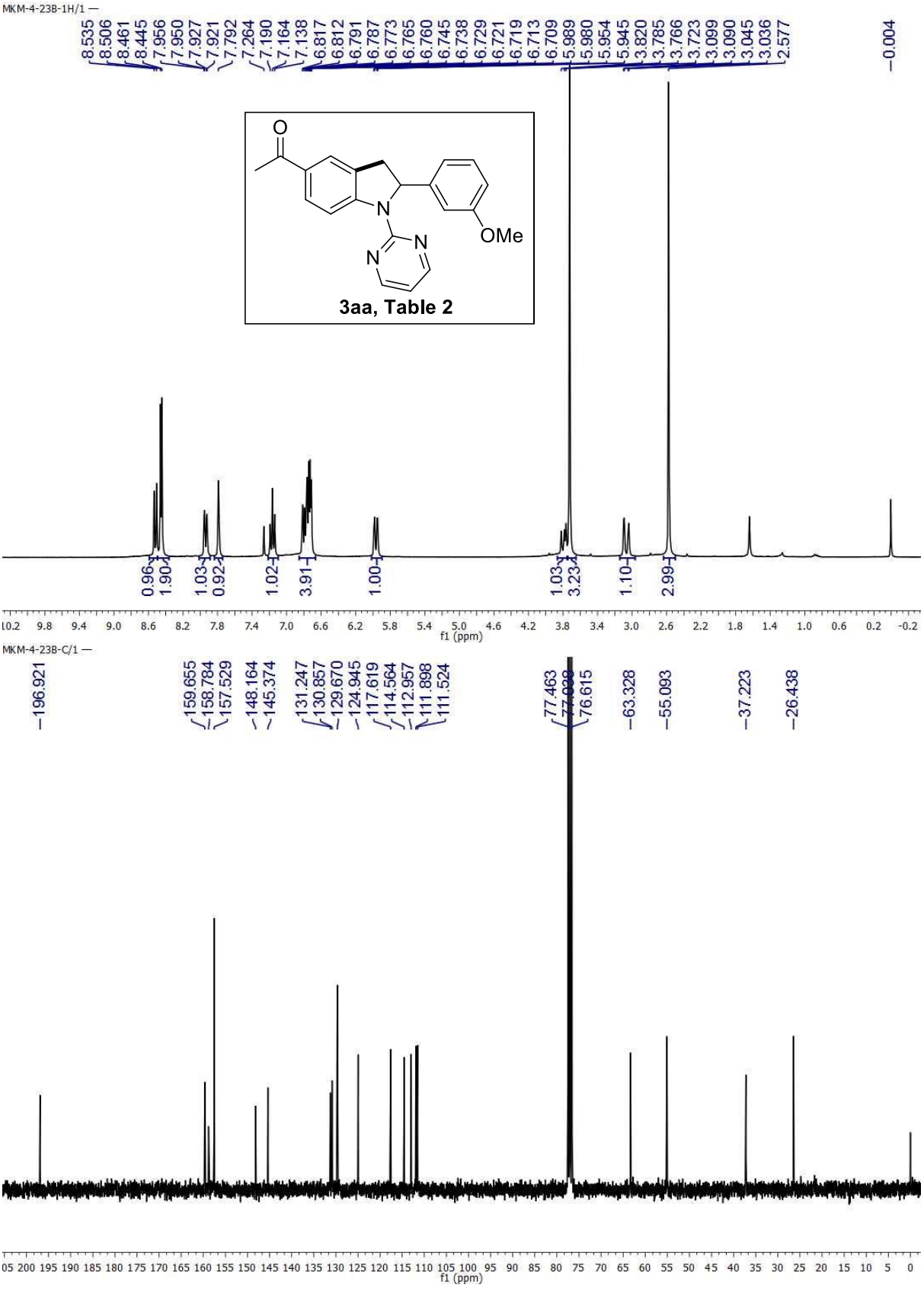

SB-4-26AF-1H/1
8.432
8.416
7.373
7.366
7.342
7.305
7.301
7.294
7.278
7.253
7.221
7.216
7.211
7.201
7.192
7.184
7.168
6.929
6.903
6.891
6.865
6.711
6.695
6.679
5.992
5.963
3.863
3.834
3.812
3.782
2.947
2.896
2.317
2.153
0.004
Me
Me
N
N
N
3x, Table 2
2.00
4.97
1.32
2.31
1.16
1.00
1.24
1.20
3.20
3.29
f1 (ppm)
SB-4-26A-C.1.fid
161.533
157.733
143.659
142.782
136.107
130.095
128.500
127.148
126.949
126.192
125.553
121.667
112.524
77.469
77.046
76.622
67.356
38.711
20.105
17.854
0.030
f1 (ppm)

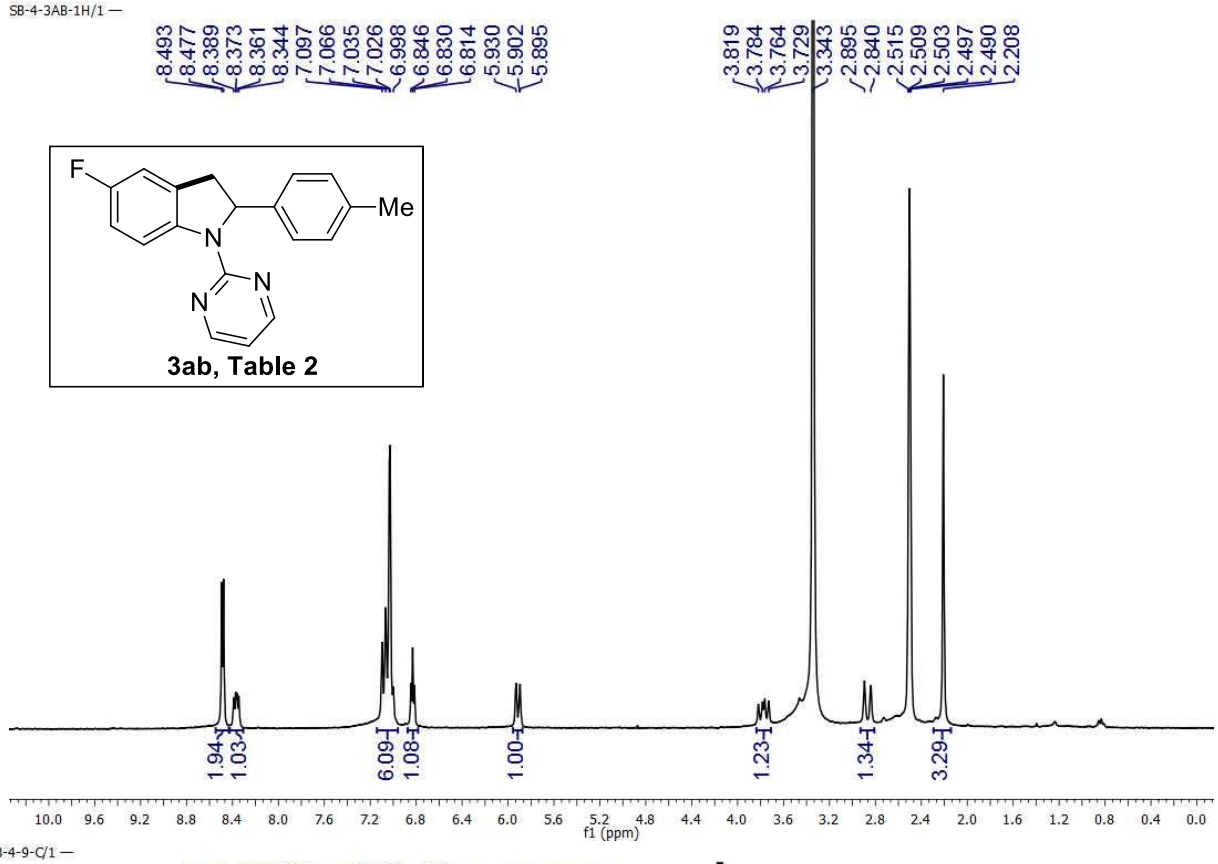

SB-4-3YF-1H/1
8.532
8.516
8.480
8.453
7.655
7.650
7.627
7.600
7.573
7.539
7.454
7.429
7.404
7.334
7.326
7.306
7.277
7.212
7.188
7.183
6.889
6.873
6.857
5.983
5.977
5.949
3.895
3.860
3.840
3.806
2.972
2.923
2.514
2.508
2.502
2.495
2.489
Ph
Cl
N
N
N
3y, Table 2
1.60
0.87
3.97
2.26
3.29
2.44
1.08
1.00
1.11
1.34
f1 (ppm)

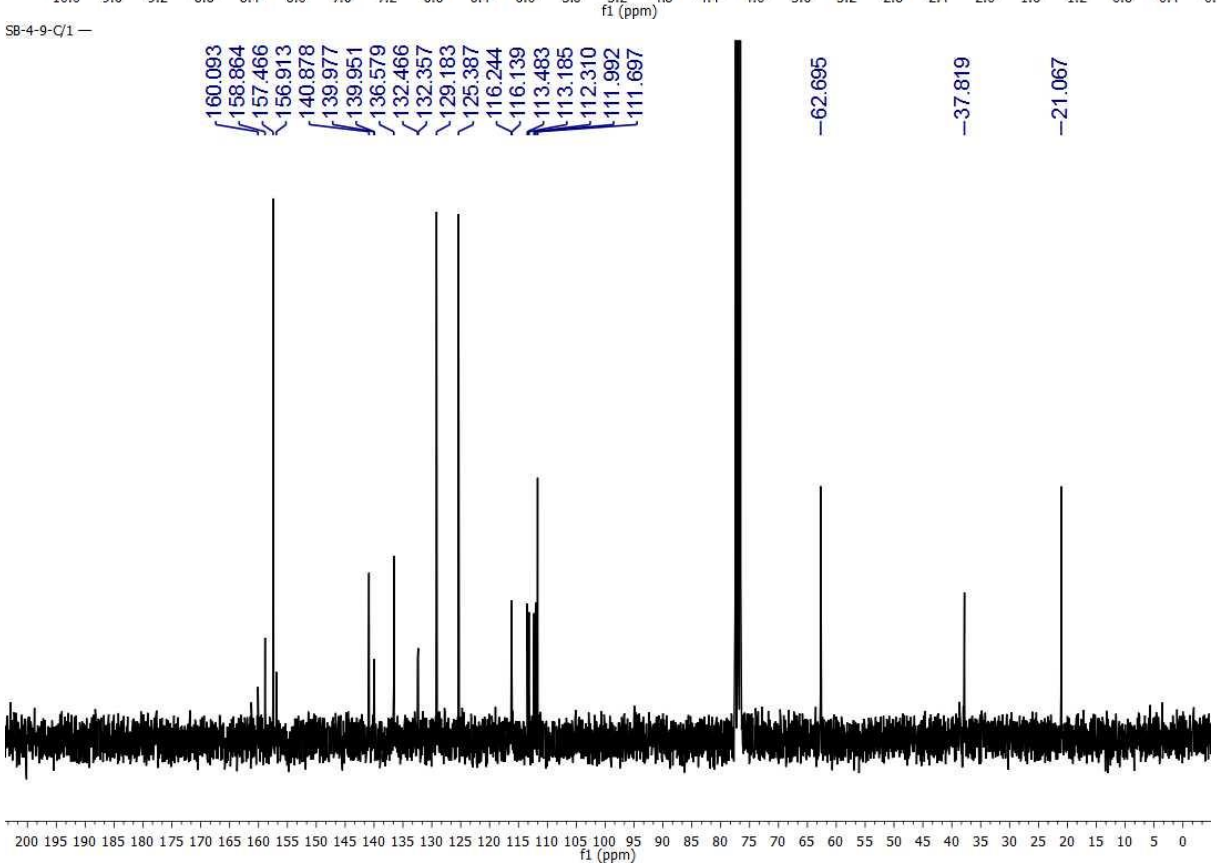

SB-4-7-C/1
158.831
157.474
143.108
142.711
141.036
135.213
132.506
130.730
128.681
128.612
127.049
126.691
126.633
126.474
123.535
115.751
112.048
77.420
76.007
76.575
62.411
37.661
f1 (ppm)

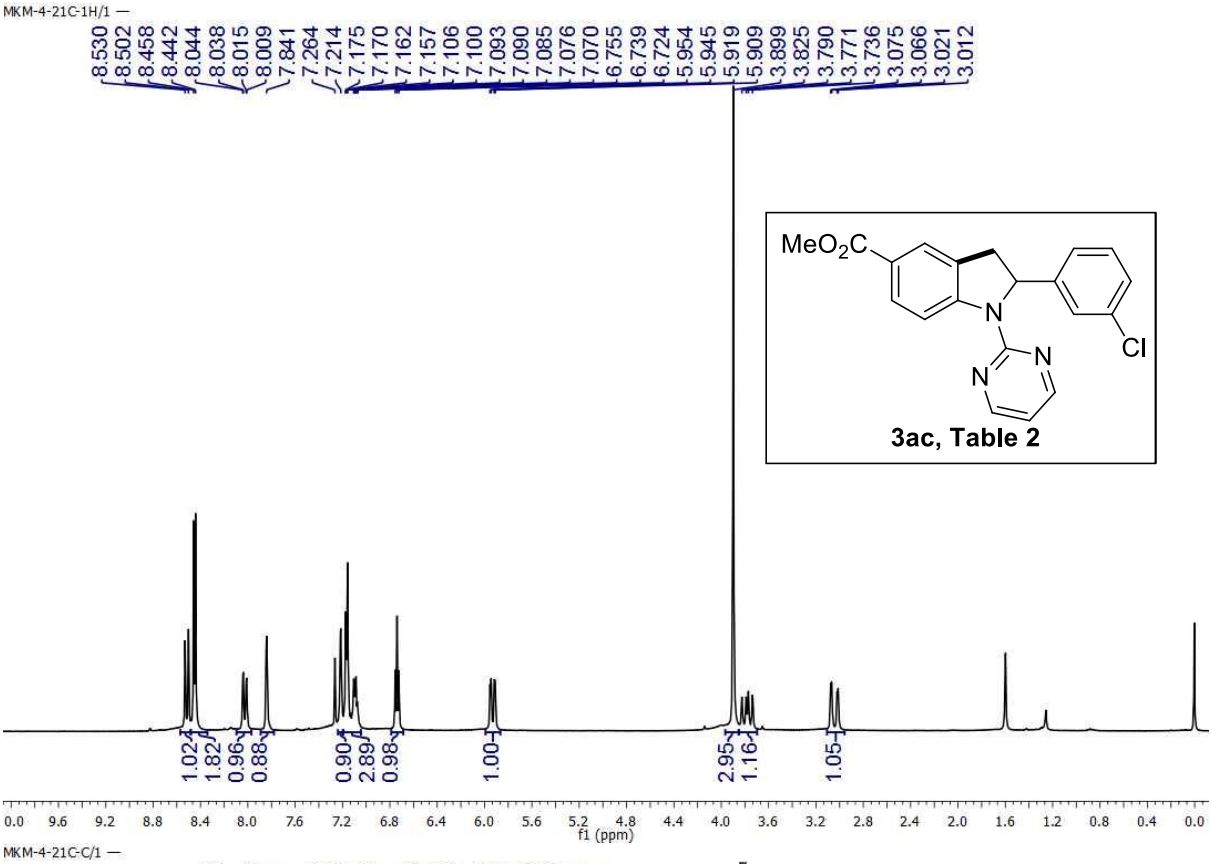

SB-4-14-1H/1
8.482
8.453
8.405
8.389
7.269
7.238
7.235
7.228
7.217
7.207
7.199
7.189
7.179
7.170
7.007
6.978
6.926
6.673
6.657
6.642
5.932
5.923
5.897
5.888
3.828
3.793
3.774
3.738
3.019
3.009
2.964
2.955
2.299
AcO
Cl
N
N
N
3z, Table 2
1.10
1.80
3.90
1.11
0.95
1.05
1.00
1.07
1.03
2.93
f1 (ppm)

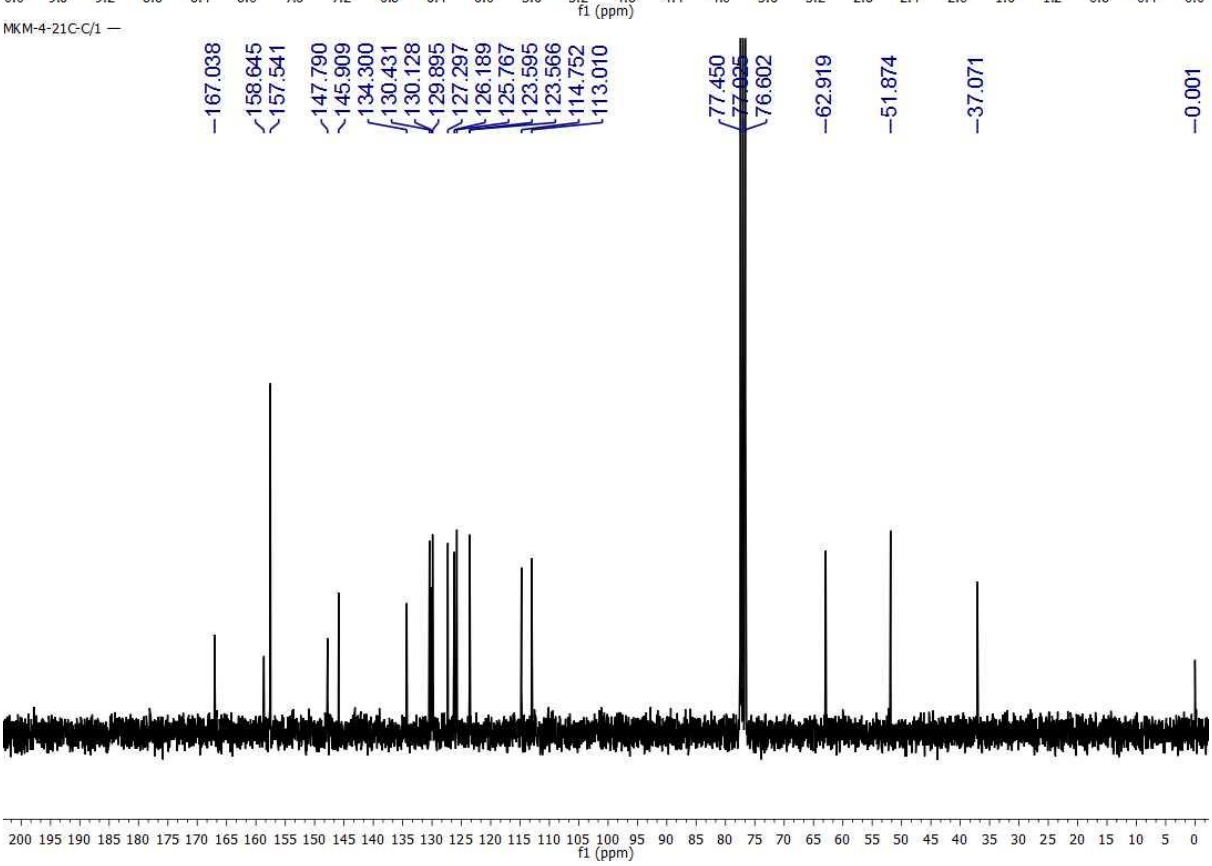

SB-4-14-C/1
169.895
158.723
157.414
145.518
142.535
141.437
132.520
131.270
128.597
127.018
120.116
118.252
115.888
112.054
77.448
76.602
62.409
37.484
21.122
f1 (ppm)

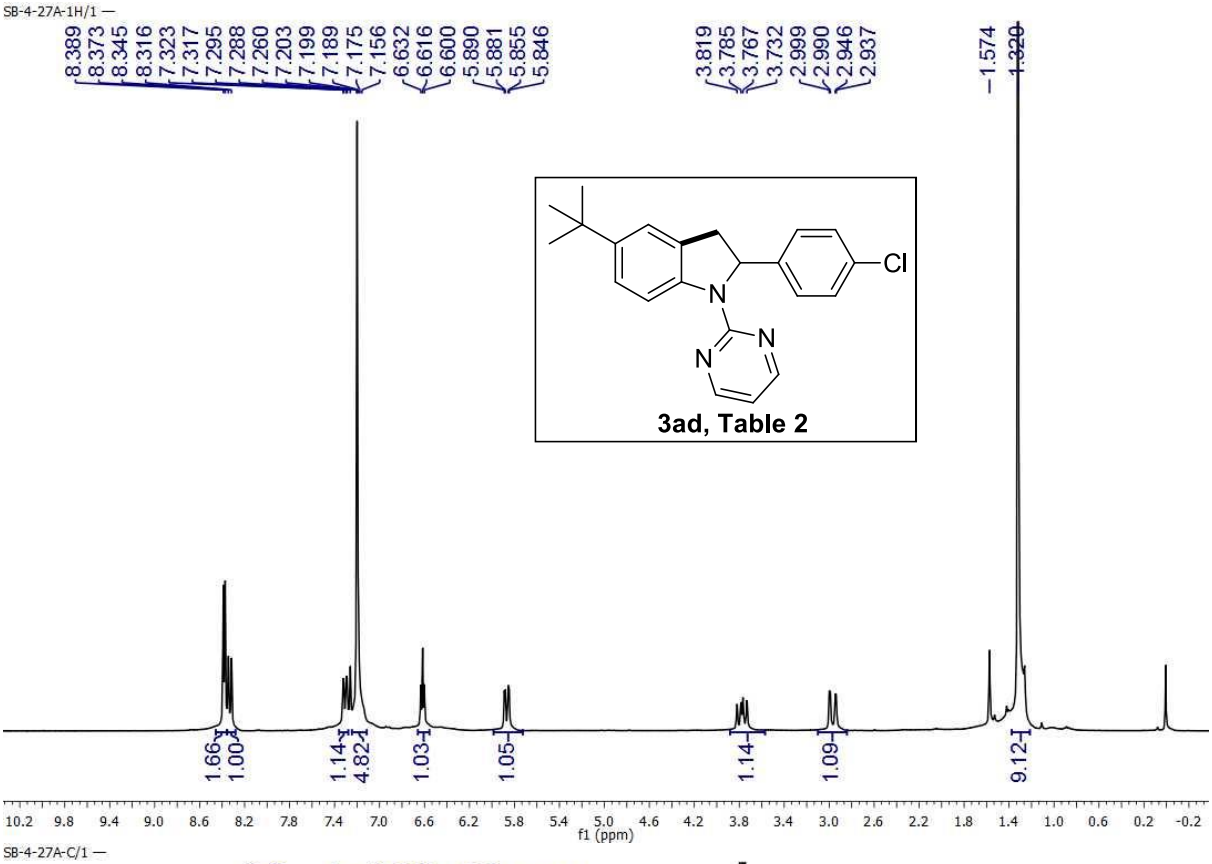

MKM-4-23B-1H/1
8.535
8.506
8.461
8.445
7.956
7.950
7.927
7.921
7.792
7.264
7.190
7.164
7.138
6.817
6.812
6.791
6.787
6.773
6.765
6.760
6.745
6.738
6.729
6.721
6.719
6.713
6.709
5.989
5.980
5.954
5.945
3.820
3.785
3.766
3.723
3.099
3.090
3.045
3.036
2.577
0.004
O
N
N
N
OMe
3aa, Table 2
0.96
1.90
1.03
0.92
1.02
3.91
1.00
1.03
3.23
1.10
2.99
f1 (ppm)
MKM-4-23B-C/1
196.921
159.655
158.784
157.529
148.164
145.374
131.247
130.857
129.670
124.945
117.619
114.564
112.957
111.898
111.524
77.463
77.039
76.615
63.328
55.093
37.223
26.438
f1 (ppm)

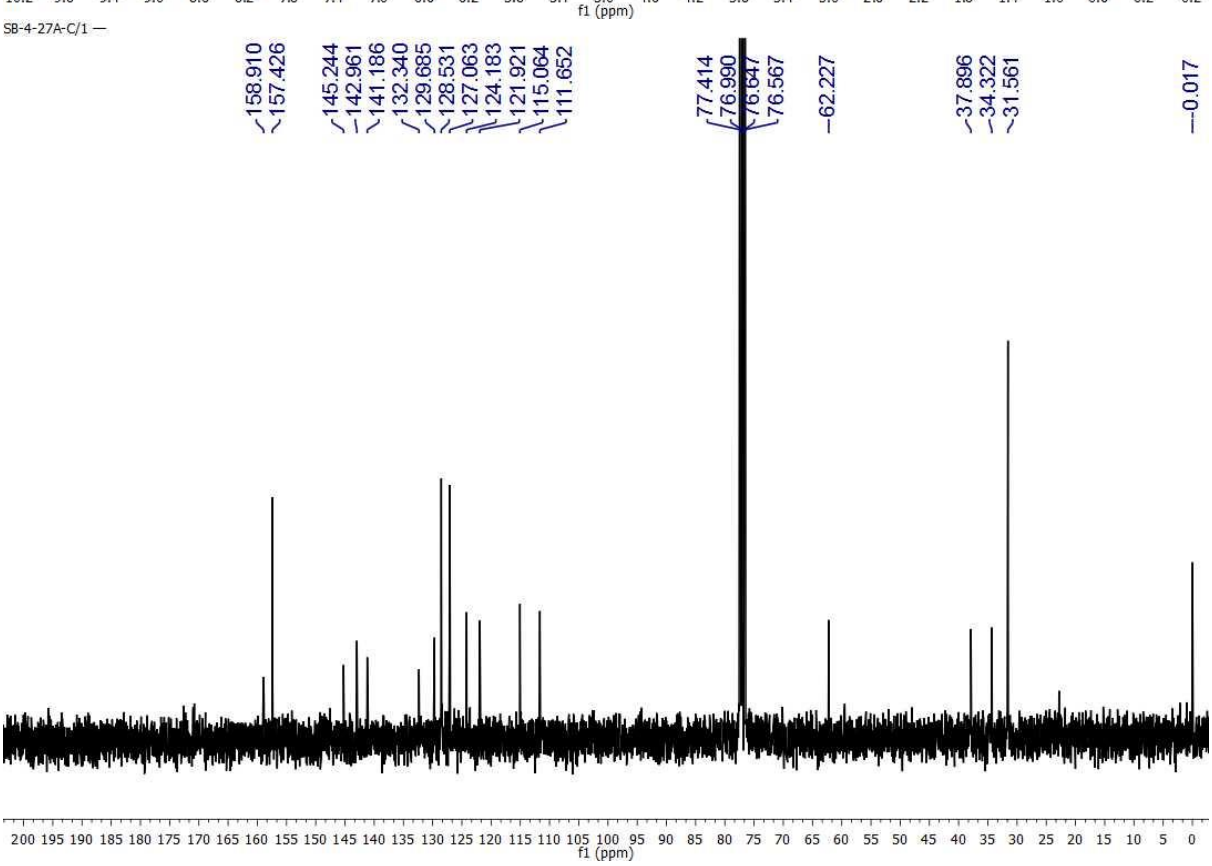

SB-4-3AB-1H/1
8.493
8.477
8.389
8.373
8.361
8.344
7.097
7.066
7.035
7.026
6.998
6.846
6.830
6.814
5.930
5.902
5.895
3.819
3.784
3.764
3.729
3.343
2.895
2.840
2.515
2.509
2.503
2.497
2.490
2.208
F
Me
N
N
N
3ab, Table 2
1.94
1.03
6.09
1.08
1.00
1.23
1.34
3.29
f1 (ppm)


SB-4-9-C/1
160.093
158.864
157.466
156.913
140.878
139.977
139.951
136.579
132.466
132.357
129.183
125.387
116.244
116.139
113.483
113.185
112.310
111.992
111.697
62.695
37.819
21.067
f1 (ppm)

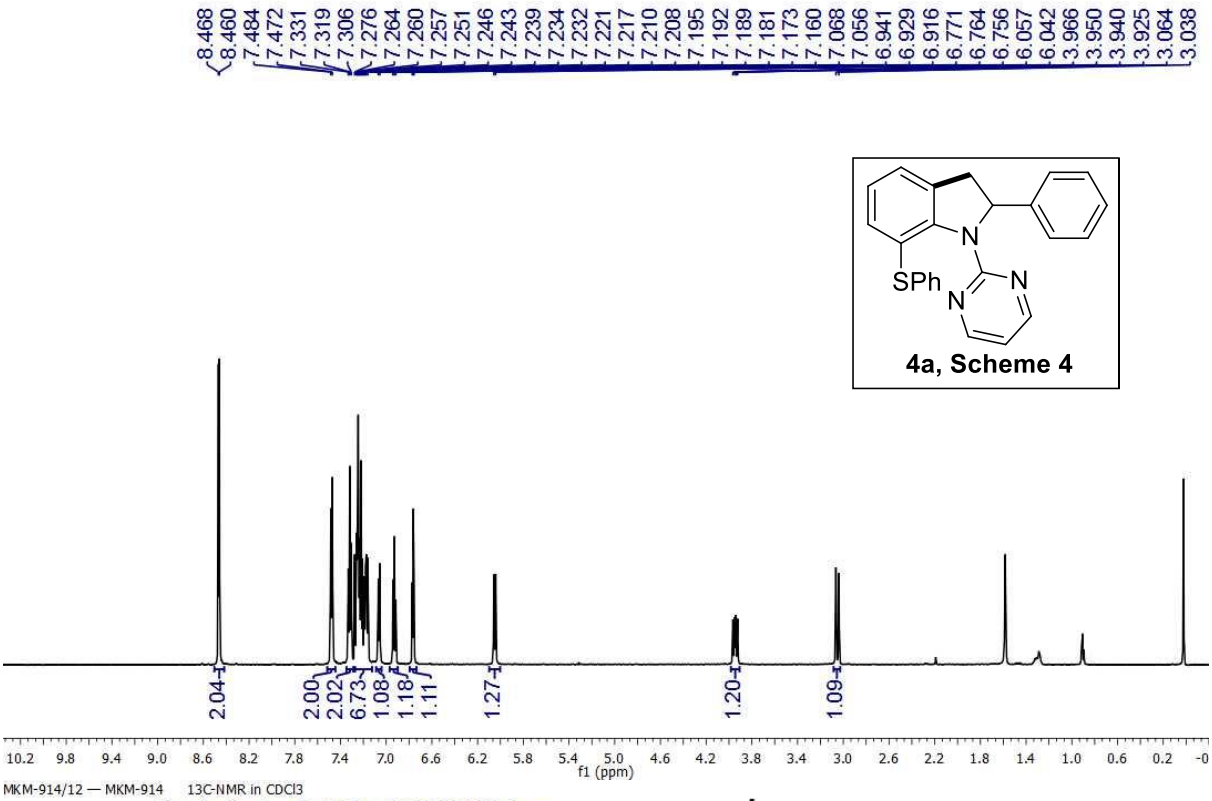

MKM-4-21C-1H/1
8.530
8.502
8.458
8.442
8.044
8.038
8.015
8.009
7.841
7.264
7.214
7.175
7.170
7.162
7.157
7.106
7.100
7.093
7.090
7.085
7.076
7.070
6.755
6.739
6.724
5.954
5.945
5.919
5.909
3.899
3.825
3.790
3.771
3.736
3.075
3.066
3.021
3.012
MeO2C
N
N
N
Cl
3ac, Table 2
1.024
1.82
0.96
0.88
0.90
2.89
0.98
1.00
2.95
1.16
1.05
f1 (ppm)


MKM-4-21C-C/1
167.038
158.645
157.541
147.790
145.909
134.300
130.431
130.128
129.895
127.297
126.189
125.767
123.595
123.566
114.752
113.010
77.450
77.035
76.602
62.919
51.874
37.071
0.001
f1 (ppm)

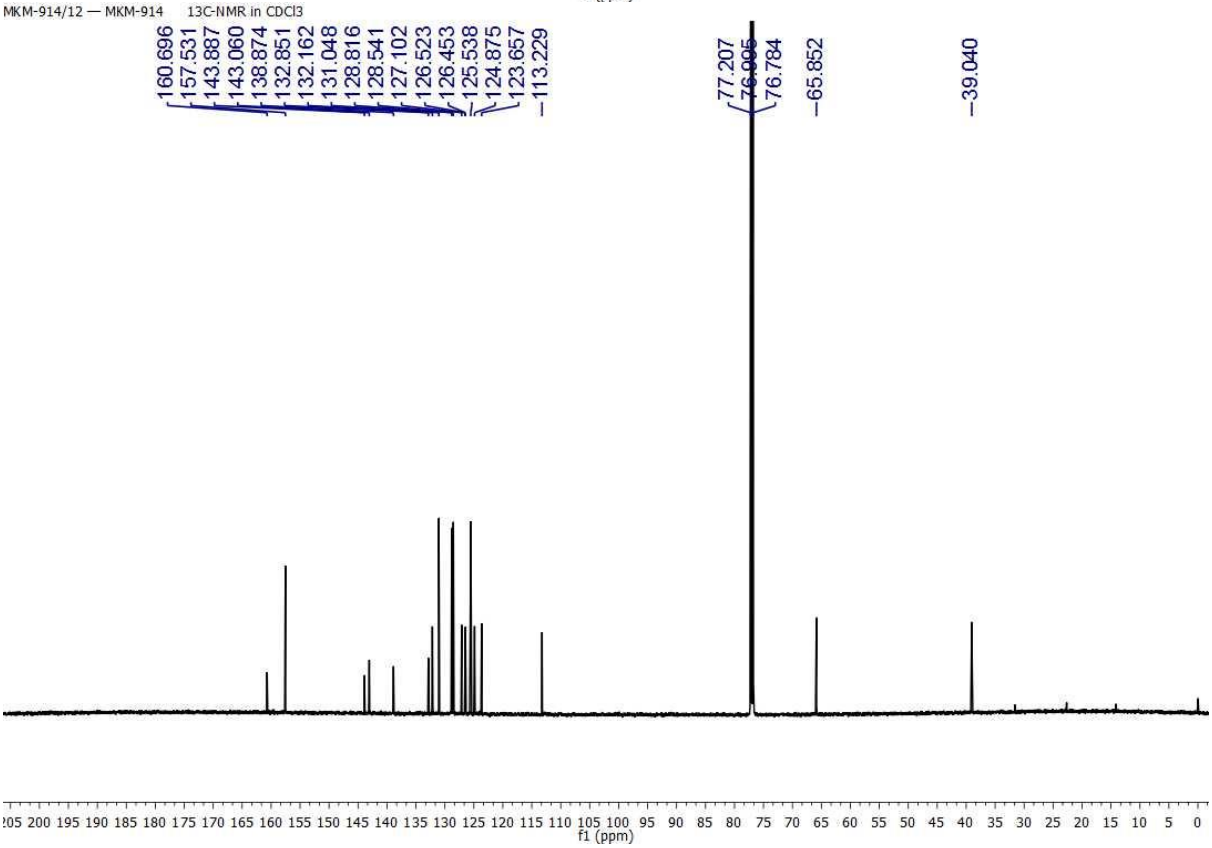

SB-4-27A-1H/1
8.389
8.373
8.345
8.316
7.323
7.317
7.295
7.288
7.260
7.203
7.199
7.189
7.175
7.156
6.632
6.616
6.600
5.890
5.881
5.855
5.846
3.819
3.785
3.767
3.732
2.999
2.990
2.946
2.937
1.574
1.329
Cl
N
N
N
3ad, Table 2
1.66
1.00
1.14
4.82
1.03
1.05
1.14
1.09
9.12
f1 (ppm)

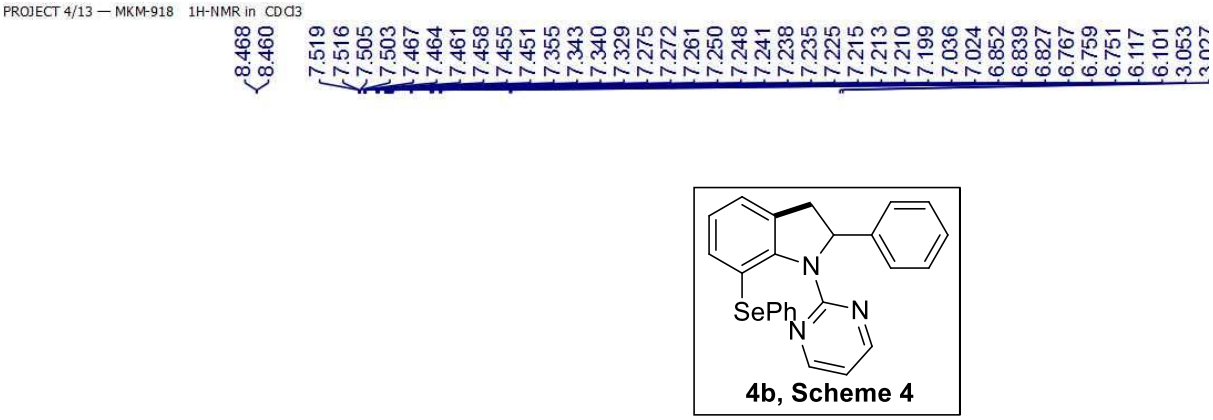

SB-4-27A-C/1
158.910
157.426
145.244
142.961
141.186
132.340
129.685
128.531
127.063
124.183
121.921
115.064
111.652
77.414
76.990
76.647
76.567
62.227
37.896
34.322
31.561
0.017
f1 (ppm)

PROJECT 4/11 — MKM-914 1H-NMR in CDCl3



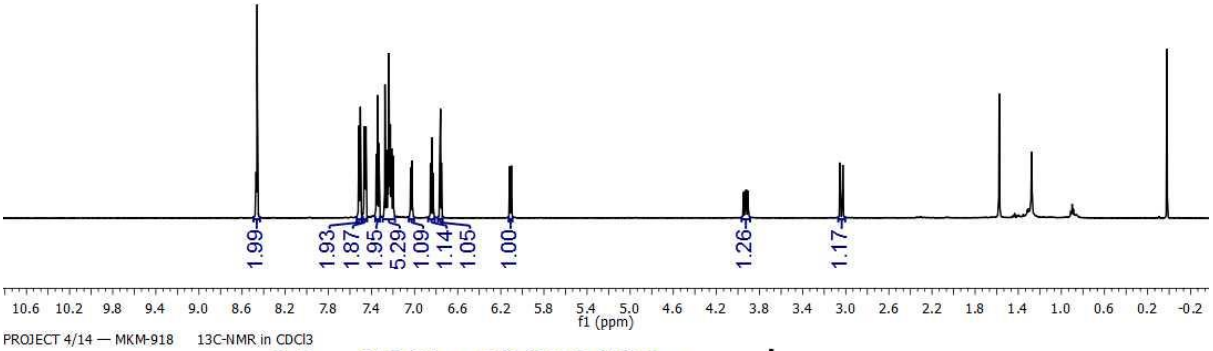
MKM-914/12 — MKM-914 13C-NMR in CDCl3

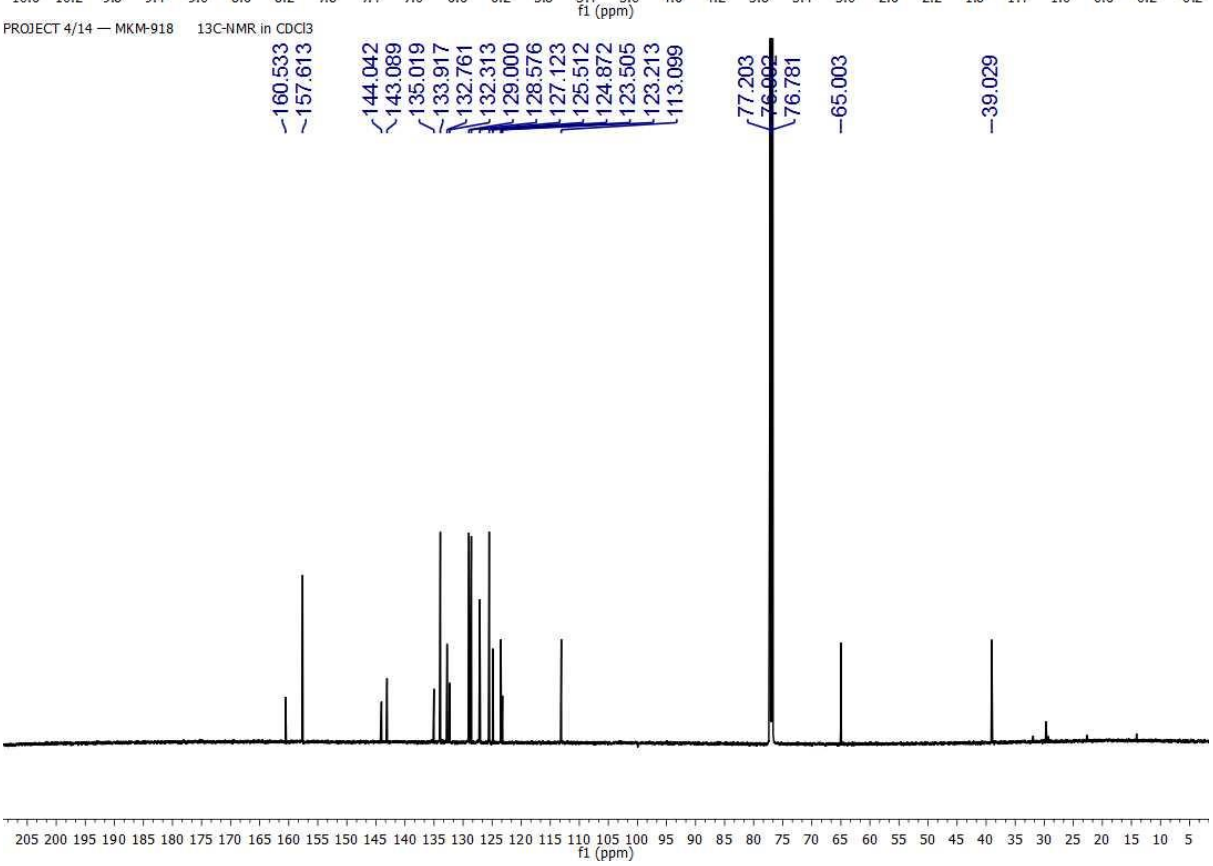



PROJECT 4/13 — MKM-918 1H-NMR in CDCl3
8.468
8.460
7.519
7.516
7.505
7.503
7.467
7.464
7.461
7.458
7.455
7.451
7.355
7.343
7.340
7.329
7.275
7.272
7.261
7.250
7.248
7.241
7.238
7.235
7.225
7.215
7.213
7.210
7.199
7.036
7.024
6.852
6.839
6.827
6.767
6.759
6.751
6.117
6.101
3.053

SePh
N
N
N

4b, Scheme 4


1.99
1.93
1.87
1.95
5.29
1.09
1.14
1.05
1.00
1.26
1.17
10.6 10.2 9.8 9.4 9.0 8.6 8.2 7.8 7.4 7.0 6.6 6.2 5.8 5.4 5.0 4.6 4.2 3.8 3.4 3.0 2.6 2.2 1.8 1.4 1.0 0.6 0.2 -0.2
f1 (ppm)


PROJECT 4/14 — MKM-918 13C-NMR in CDCl3
160.533
157.613
144.042
143.089
135.019
133.917
132.761
132.313
129.000
128.576
127.123
125.512
124.872
123.505
123.213
113.099
77.203
76.002
76.781
65.003
39.029
205 200 195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)