Electronic Supplementary Material (ESI) for ChemComm.

Rhodium(III)-Catalyzed C7-Position C-H Alkenylation and Alkynylation of Indolines

Xiao-Fei Yang, Xu-Hong Hu, Chao Feng, and Teck-Peng Loh

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371

teckpeng@ntu.edu.sg

Supporting Information

Table of Contents **Page No.**

General information

$[RhCp^*Cl_2]_2$, $Cu(OAc)_2$, $Cu(OTf)_2$ and solvents were purchased from commercial suppliers and used as received unless otherwise noted. All reactions were carried out using 8mL sample vial or standard Schlenk technic. Reactions were monitored through thin layer chromatography [Merck 60 F254 precoated silica gel plate (0.2 mm thickness)]. Subsequent to elution, spots were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible using basic solution of potassium permanganate. Flash chromatography was performed using Merck silica gel 60 with distilled solvents. HRMS spectra were recorded on a Waters Q–Tof Permier Spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded using Bruker Avance 400 MHz spectrometers. Chemical shifts for ^1H NMR and ^{13}C NMR spectra were recorded using Bruker Avance 400 MHz spectrometers. Chemical shifts for ^1H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of $SiMe_4$ (δ 0.00, singlet). Multiplicities were given as: s (singlet); brs (broad singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); ddd (doublets of doublets of doublet); td (triplet of doublet); m (multiplets); ddt (doublet of doublet of triplet) and etc. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.00, triplet).

Experimental section

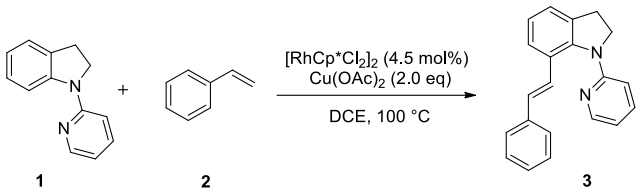
Substrate synthesis

1 were synthesized using reported method.[1]

Alkynyliodonium reagent was synthesized following the reported method.[2]

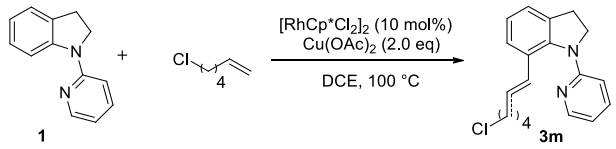
Rh(III) catalyzed C-H alkenylation of indoline

General reaction procedure A



Synthetic procedure: The indoline **1** (0.14 mmol, 1 equiv.), styrene (0.70 mmol, 5.0 equiv.), $[RhCp^*Cl_2]_2$ (0.006 mmol, 4.5 mol%), $Cu(OAc)_2$ (0.28 mmol, 2.0 equiv.) and DCE (1.0 mL) were placed in a 4 mL glass vial under N_2. After stirring at 100 ℃ for 12 hours. Removal of the solvent in vacuo and purified by column chromatography afforded the desired product **3**.

General reaction procedure B



Synthetic procedure: The indoline **1** (0.14 mmol, 1 equiv.), 6-chlorohex-1-ene (0.70 mmol, 5.0 equiv.), $[RhCp^*Cl_2]_2$ (0.014 mmol, 10 mol%), $Cu(OAc)_2$ (0.28 mmol, 2.0 equiv.) and DCE (1.0 mL) were placed in a 4 mL glass vial under N_2. After stirring at 100 ℃ for 24 hours. Removal of the solvent in vacuo and purified by column chromatography afforded the desired product **3m**.

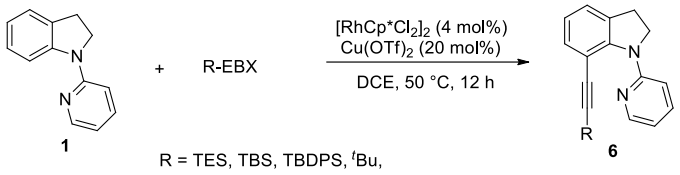
Rh(III) catalyzed C-H alkynylation of indoline

General reaction procedure C

Synthetic procedure: The indoline **1** (0.14 mmol, 1 equiv.), alkynyliodonium reagent (0.18 mmol, 1.1 equiv.), $[RhCp^*Cl_2]_2$ (0.0056 mmol, 4 mol%), $Cu(OTf)_2$ (0.016 mmol, 12 mol%) and DCE (1.0 mL) were placed in a 4 mL glass vial under N_2. After stirring at 50 ℃ for 12 hours, saturated $NaHCO_3$

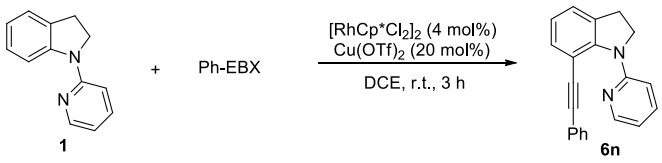
solution (2 mL) was added and the resulting mixture was extracted with dichloromethane (2x5 mL). Removal of the solvent in vacuo and purified by column chromatography afforded the desired product **6a**.

General reaction procedure D



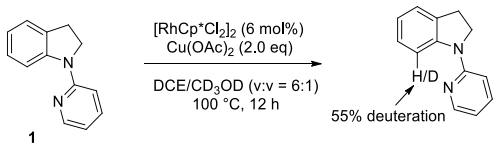
Synthetic procedure: The indoline **1** (0.14 mmol, 1 equiv.), alkynyliodonium reagent (0.36 mmol, 2.5 equiv.), $[RhCp^*Cl_2]_2$ (0.0056 mmol, 4 mol%), $Cu(OTf)_2$ (0.028 mmol, 20 mol%) and DCE (1.0 mL) were placed in a 4 mL glass vial under N_2. After stirring at 50 ℃ for 12 hours, saturated $NaHCO_3$ solution (2 mL) was added and the resulting mixture was extracted with dichloromethane (2x5 mL). Removal of the solvent in vacuo and purified by column chromatography afforded the desired product **6**.

General reaction procedure E



Synthetic procedure: The indoline **1** (0.14 mmol, 1 equiv.), alkynyliodonium reagent (0.36 mmol, 2.5 equiv.), $[RhCp^*Cl_2]_2$ (0.0056 mmol, 4 mol%), $Cu(OTf)_2$ (0.028 mmol, 20 mol%) and DCE (1.0 mL) were placed in a 4 mL glass vial under N_2. After stirring at room temperature for 3 hours, saturated $NaHCO_3$ solution (2 mL) was added and the resulting mixture was extracted with dichloromethane (2x5 mL). Removal of the solvent in vacuo and purified by column chromatography afforded the desired product **6n**.

H/D exchange experiment



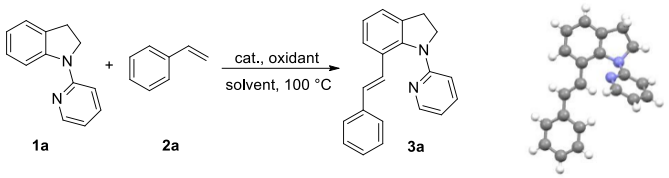
Synthetic procedure: The indoline **1** (0.14 mmol, 1 equiv.), $[RhCp^*Cl_2]_2$ (0.006 mmol, 4.5 mol%), $Cu(OAc)_2$ (0.28 mmol, 2.0 equiv.) and DCE/CD_3OD 1 mL (v:v = 6:1) were placed in a 4 mL glass vial under N_2. After stirring at 100 ℃ for 12 hours. Removal of the solvent in vacuo and purified by column chromatography.

Preparation of rhodacycle complex 1

Preparation of a rhodacycle complex 1 was carried out according to the reported Jones' procedure: A solution of indoline **1** (0.14 mmol), $[RhCp^*Cl_2]_2$ (0.063 mmol) and NaOAc (0.39 mmol) in CH_2Cl_2 (3 mL) was stirred at room temperature under N_2 atmosphere for 24 h. The crude mixture was filtered through a pad of celite washing with CH_2Cl_2 (5 mL x 2) and concentrated under reduced pressure. After recrystallization from CH_2Cl_2/hexane, rhodacycle complex 1 was obtained as a red crystal (41.3 mg, 63%).

Optimaization of reaction condition

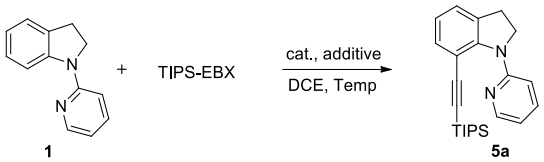
Table S1



Entry	Cat.	Oxidant	Solvent	Yield[b] (%)
1	$[RhCp^*Cl_2]_2$	AgOAc	DCE	48
2	$[RhCp^*Cl_2]_2$	BQ	DCE	N.R.
3	$[RhCp^*Cl_2]_2$	Ag_2CO_3	DCE	N.R.
4	$[RhCp^*Cl_2]_2$	Ag_2O	DCE	trace
5	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2$	DCE	83
6	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2$	Toluene	47
7	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2$	THF	58
8	$[Ru(p\text{-cymene})Cl_2]_2$	$Cu(OAc)_2$	DCE	N.R.
9	$Pd(OAc)_2$	BQ	DCE	N.R.
10	-	$Cu(OAc)_2$	DCE	N.R.

[a]The reactions were carried out at 100 ℃ using **1a** (0.14 mmol), **2a** (0.7 mmol), oxidant (0.28 mmol), catalyst (0.006 mmol) in solvent (1 mL) for 12 h. [b]Isolated yields.

Table S2



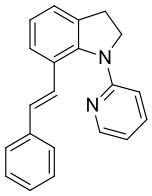
1 5a

entry	cat.	additives	Temp (℃)	yield[b] (%)
1	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2$	50	24
2	$[RhCp^*Cl_2]_2$	$Cu(OTf)_2$	50	77
3	$[RhCp^*Cl_2]_2$	$Cu(OTf)_2$	r.t.	33
4	$[RhCp^*Cl_2]_2$	$Zn(OTf)_2$	50	74
5	$[RhCp^*Cl_2]_2$	$AgSbF_6$	50	46
6	$[RhCp^*Cl_2]_2$	$AgNTf_2$	50	52
7	$[RhCp^*Cl_2]_2$	-	50	N.R.
8	-	$Cu(OTf)_2$	50	N.R.
9	$[RhCp^*(CH_3CN)_3]\ (SbF_6)_2$	$Cu(OTf)_2$	50	71
10	$[Ru(p\text{-cymene})Cl_2]_2$	$Cu(OTf)_2$	50	N.R.
11	$Pd(OAc)_2$	$Cu(OTf)_2$	50	-

[a] Unless otherwise noted, the reactions were carried out at 50 ℃ using 1 (0.14 mmol), alknye (0.18 mmol),additives (0.16 mmol), catalyst (0.0056 mmol) in solvent (1 mL) for 12 h. [b] Isolated yields.

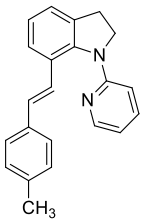
^{1}H and ^{13}C NMR Spectra of Products

(*E*)-1-(pyridin-2-yl)-7-styrylindoline (3a)



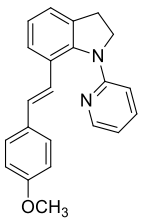
Following the general reaction procedure A, **3a** was obtained as a yellow solid (34.6 mg, 0.116 mmol, Yield: 83%); m.p. = 134-136 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.29 (m, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.41 – 7.31 (m, 1H), 7.28 – 7.14 (m, 6H), 7.02 (d, *J* = 7.9 Hz, 1H), 6.97 (d, *J* = 16.4 Hz, 1H), 6.83 – 6.70 (m, 3H), 4.40 (t, *J* = 7.9 Hz, 2H), 3.08 (t, *J* = 7.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.99, 147.93, 143.17, 137.63, 136.80 × 2, 135.39, 128.55 × 2, 127.83, 127.38, 126.38 × 2, 125.04, 125.67, 123.99, 123.09, 115.66, 111.15, 54.23, 29.38; HRMS (ESI): m/z calculated for $[C_{21}H_{19}N_2]^+$ [M + H]$^+$: 299.1548, Found: 299.1545; FTIR (NaCl): ν 3442, 2916, 1583, 1463, 1429, 1327, 972, 732, 690 cm^{-1}

(*E*)-7-(4-methylstyryl)-1-(pyridin-2-yl)indoline (3b)



Following the general reaction procedure A, **3b** was obtained as a yellow solid (27.5 mg, 0.088 mmol, Yield: 63%); m.p. = 127-129 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.29 (m, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.18 – 6.90 (m, 7H), 6.76 – 6.66 (m, 3H), 4.40 (t, *J* = 8.0 Hz, 2H), 3.07 (t, *J* = 8.0 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.00, 147.92, 143.04, 137.22, 136.65, 135.34, 134.81, 129.23 × 2, 127.72, 126.26 × 2, 125.37, 125.21, 124.50, 123.72, 123.03, 115.52, 111.06, 54.13, 29.35, 21.16; HRMS (ESI): m/z calculated for $[C_{22}H_{21}N_2]^+$ [M + H]$^+$: 313.1705, Found: 313.1703; FTIR (NaCl): ν 3583, 2916, 1583, 1465, 1429, 1371, 970, 806, 771 cm^{-1}

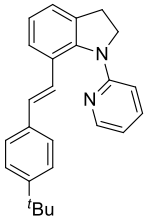
(*E*)-7-(4-methoxystyryl)-1-(pyridin-2-yl)indoline (3c)



Following the general reaction procedure A, **3c** was obtained as a yellow solid (30.8 mg, 0.093 mmol, Yield: 67%); m.p. = 97-99 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.35 (m, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.43 – 7.35 (m, 1H), 7.21 – 7.14 (m, 3H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 16.3 Hz, 1H), 6.84 – 6.71 (m, 4H), 6.65 (d, *J* = 16.3 Hz, 1H), 4.44 (t, *J* = 8.0 Hz, 2H), 3.80 (s, 3H), 3.10 (t, *J* = 8.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.12, 157.98, 147.88, 142.88, 136.64, 135.35, 130.40, 127.53, 127.39,

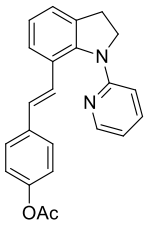
125.38, 124.35 × 2, 124.30, 123.54, 123.07, 115.49, 113.98 × 2, 111.11, 55.22, 54.14, 29.37; HRMS (ESI): m/z calculated for $[C_{22}H_{21}N_2O]^+$ $[M + H]^+$: 329.1654, Found: 329.1651; FTIR (NaCl): ν 3053, 2985, 2304, 1604, 1583, 1510, 1465, 1265, 1174, 1033, 894cm^{-1}

(*E*)-7-(4-(tert-butyl)styryl)-1-(pyridin-2-yl)indoline (3d)



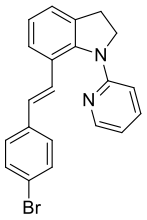
Following the general reaction procedure A, **3d** was obtained as a white solid (46.6 mg, 0.13 mmol, Yield: 94%); m.p. = 165-167 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.30 (m, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.36 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.31 – 7.23 (m, 2H), 7.14 (d, *J* = 8.3 Hz, 3H), 7.07 – 6.92 (m, 2H), 6.78 – 6.69 (m, 3H), 4.40 (t, *J* = 7.9 Hz, 2H), 3.06 (t, *J* = 7.9 Hz, 2H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.03, 150.44, 147.93, 143.02, 136.71, 135.35, 134.78, 127.56, 126.07 × 2, 125.46, 125.43 × 2, 125.25, 124.44, 123.71, 123.04, 115.52, 110.96, 54.13, 34.51, 31.21 × 3, 29.33; HRMS (ESI): m/z calculated for $[C_{25}H_{27}N_2]^+$ $[M + H]^+$: 355.2174, Found: 355.2171; FTIR (NaCl): ν 2960, 2916, 1581, 1465, 1429, 1363, 1153, 819, 771 cm^{-1}

(*E*)-4-(2-(1-(pyridin-2-yl)indolin-7-yl)vinyl)phenyl acetate (3e)



Following the general reaction procedure A, **3e** was obtained as a yellow solid (46.4 mg, 0.13 mmol, Yield: 93%); m.p. = 96-98 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.28 (m, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.35 – 7.39 (m, 1H), 7.20 – 7.15 (m, 3H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.98 – 6.92 (m, 3H), 6.79 – 6.73 (m, 2H), 6.70 (d, *J* = 5.7 Hz, 1H), 4.39 (t, *J* = 7.9 Hz, 2H), 3.07 (t, *J* = 7.9 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.41, 157.93, 149.79, 147.92, 143.14, 136.75, 135.37, 135.33, 127.19 × 2, 126.64, 126.55, 124.79, 124.54, 123.98, 123.02, 121.58 × 2, 115.65, 110.98, 54.15, 29.28, 21.05; HRMS (ESI): m/z calculated for $[C_{23}H_{21}N_2O_2]^+$ $[M + H]^+$: 357.1603, Found: 357.1601; FTIR (NaCl): ν 3412, 3049, 1759, 1583, 1504, 1469, 1433, 1369, 1193, 1165, 1014 cm^{-1}

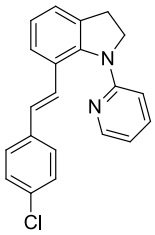
(*E*)-7-(4-bromostyryl)-1-(pyridin-2-yl)indoline (3f)



Following the general reaction procedure A, **3f** was obtained as a yellow solid (43.2 mg, 0.115 mmol,

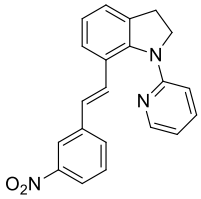
Yield: 82%); m.p. = 117-119 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.27 (m, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.39 – 7.31 (m, 3H), 7.17 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 16.4 Hz, 1H), 6.75 – 6.70 (m, 3H), 4.38 (t, *J* = 8.0 Hz, 2H), 3.08 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.89, 147.96, 143.21, 136.67, 136.53, 135.32, 131.58 × 2, 127.72 × 2, 127.14, 126.31, 124.59, 124.51, 124.17, 123.00, 120.98, 115.68, 111.02, 54.14, 29.27; HRMS (ESI): m/z calculated for $[C_{21}H_{18}BrN_2]^+$ $[M + H]^+$: 377.0653, Found: 377.0650; FTIR (NaCl): ν 3421, 2848, 1635, 1585, 1463, 1429, 1261, 1151, 1070, 810 cm^{-1}

(*E*)-7-(4-chlorostyryl)-1-(pyridin-2-yl)indoline (3g)



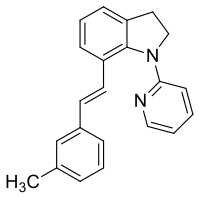
Following the general reaction procedure A, **3g** was obtained as a yellow solid (36.3 mg, 0.11 mmol, Yield: 78%); m.p. = 94-96 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.28 (m, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.36 (ddd, *J* = 8.5, 7.7, 2.0 Hz, 1H), 7.20 – 7.16 (m, 3H), 7.14 – 7.07 (m, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 16.4 Hz, 1H), 6.80 – 6.65 (m, 3H), 4.38 (t, *J* = 8.0 Hz, 2H), 3.08 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.88, 147.92, 143.18, 136.72, 136.09, 135.33, 132.85, 128.66 × 2, 127.41 × 2, 127.01, 126.34, 124.60, 124.56, 124.15, 123.03, 115.69, 111.08, 54.18, 29.29; HRMS (ESI): m/z calculated for $[C_{21}H_{18}ClN_2]^+$ $[M + H]^+$: 333.1159, Found: 333.1153; FTIR (NaCl): ν 3047, 2916, 2846, 1581, 1444, 1371, 1261, 1091, 970,864, 813 cm^{-1}

(*E*)-7-(3-nitrostyryl)-1-(pyridin-2-yl)indoline (3h)



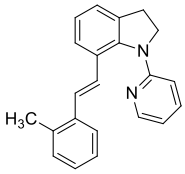
Following the general reaction procedure A, **3h** was obtained as a yellow solid (41.1 mg, 0.12 mmol, Yield: 85%); m.p. = 133-135 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.30 (m, 1H), 8.13 – 7.89 (m, 2H), 7.50 – 7.33 (m, 4H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 16.4 Hz, 1H), 6.90 (d, *J* = 16.4 Hz, 1H), 6.82 – 6.72 (m, 2H), 4.38 (t, *J* = 8.0 Hz, 2H), 3.12 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.81, 148.60, 148.06, 143.57, 139.57, 136.85, 135.32, 131.71, 129.68, 129.34, 124.90, 124.88, 124.77, 123.70, 122.97, 121.66, 120.91, 116.05, 111.23, 54.24, 29.25; HRMS (ESI): m/z calculated for $[C_{21}H_{18}N_3O_2]^+$ $[M + H]^+$: 344.1399, Found: 344.1395; FTIR (NaCl): ν 2954, 2848, 1583, 1519, 1429, 1348, 1263, 960 cm^{-1}

(*E*)-7-(3-methylstyryl)-1-(pyridin-2-yl)indoline (3i)



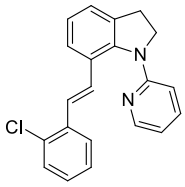
Following the general reaction procedure A, **3i** was obtained as a yellow oil (36.7 mg, 0.12 mmol, Yield: 84%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 – 8.20 (m, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.36 (ddd, *J* = 8.4, 7.8, 2.0 Hz, 1H), 7.20 – 7.06 (m, 2H), 7.06 – 6.89 (m, 5H), 6.75 – 6.71 (m, 3H), 4.40 (t, *J* = 8.0 Hz, 2H), 3.08 (t, *J* = 8.0 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.93, 147.84, 143.07, 138.00, 137.51, 136.80, 135.32, 128.38, 128.15, 127.86, 127.15, 126.13, 125.03, 124.55, 123.85, 123.44, 123.04, 115.56, 111.16, 54.17, 29.33, 21.29; HRMS (ESI): m/z calculated for $[C_{22}H_{21}N_2]^+$ [M + H]$^+$: 313.1705, Found: 313.1703; FTIR (NaCl): ν 3047, 2916, 1693, 1583, 1427, 1263, 1153, 1056, 856 cm^{-1}

(*E*)-7-(2-methylstyryl)-1-(pyridin-2-yl)indoline (3j)



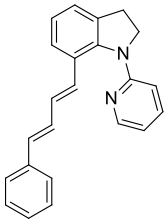
Following the general reaction procedure A, **3j** was obtained as yellow solid (33.7 mg, 0.11 mmol, Yield: 77%); m.p. = 104-106 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 – 8.28 (m, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.42 – 7.34 (m, 1H), 7.21 – 6.98 (m, 7H), 6.82 – 6.61 (m, 3H), 4.40 (t, *J* = 8.0 Hz, 2H), 3.07 (t, *J* = 8.0 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.85, 147.89, 143.02, 136.73, 136.48, 135.60, 135.43, 130.16, 127.54, 127.23, 126.01, 125.96, 125.56, 125.21, 125.15, 123.87, 123.10, 115.62, 111.16, 54.22, 29.31, 19.72; HRMS (ESI): m/z calculated for $[C_{22}H_{21}N_2]^+$ [M + H]$^+$: 313.1705, Found: 313.1707; FTIR (NaCl): ν 3421, 1637, 1583, 1463, 1429, 1371, 1263, 1153, 1056, 985, 970 cm^{-1}

(*E*)-7-(2-chlorostyryl)-1-(pyridin-2-yl)indoline (3k)



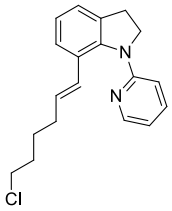
Following the general reaction procedure A, **3k** was obtained as a yellow oil (43.2 mg, 0.13 mmol, Yield: 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 3.5 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.45 – 7.28 (m, 3H), 7.20 – 7,14 (m, 2H), 7.12 – 7.01 (m, 3H), 6.82 – 6.65 (m, 3H), 4.39 (t, *J* = 8.0 Hz, 2H), 3.09 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.99, 147.89, 143.33, 136.86, 135.59, 135.29, 133.18, 129.58, 128.83, 128.21, 126.76, 126.30, 124.99, 124.79, 124.34, 123.72, 123.13, 115.71, 111.07, 54.23, 29.29; HRMS (ESI): m/z calculated for $[C_{21}H_{18}ClN_2]^+$ [M + H]$^+$: 333.1159, Found: 333.1151; FTIR (NaCl): ν 3053, 2956, 1583, 1469, 1429, 1261, 1153, 1051, 1033, 970 cm^{-1}

7-((1*E*, 3*E*)-4-phenylbuta-1,3-dien-1-yl)-1-(pyridin-2-yl)indoline (3l)



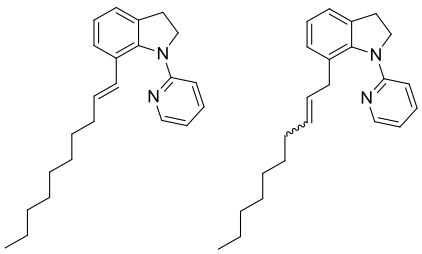
Following the general reaction procedure A, **3l** was obtained as a yellow solid (29.5 mg, 0.09 mmol, Yield: 65%); m.p. = 138-140 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31– 8.30 (m, 1H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.20 – 7.13 (m, 2H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.82 (dd, *J* = 15.4, 10.5 Hz, 1H), 6.78 – 6.68 (m, 3H), 6.57 (d, *J* = 15.4 Hz, 1H), 6.34 (d, *J* = 15.4 Hz, 1H), 4.39 (t, *J* = 7.9 Hz, 2H), 3.05 (t, *J* = 7.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.02, 147.88, 142.92, 137.29, 136.72, 135.49, 132.41, 130.15, 129.54, 128.73, 128.54 × 2, 127.41, 126.28 × 2, 125.32, 124.39, 123.88, 123.16, 115.65, 110.98, 54.25, 29.30; HRMS (ESI): m/z calculated for $[C_{23}H_{21}N_2]^+$ $[M + H]^+$: 325.1705, Found: 325.1706; FTIR (NaCl): ν 3442, 2916, 1587, 1463, 1429, 1361, 1263, 987 cm^{-1}

(*E*)-7-(6-chlorohex-1-en-1-yl)-1-(pyridin-2-yl)indoline (3m)



Following the general reaction procedure B, **3m** was obtained as a colorless oil (22.7 mg, 0.07 mmol, Yield: 52%); ^{1}H NMR (400 MHz, $CDCl_3$) *E* form δ 8.36 – 8.20 (m, 1H), 7.42 (ddd, *J* = 8.5, 7.2, 2.0 Hz, 1H), 7.26 (m, 1H), 7.12 (dd, *J* = 7.2, 2.0 Hz, 1H), 6.97 (t, *J* = 7.2 Hz, 1H), 6.75 (dd, *J* = 7.2, 4.9 Hz, 1H), 6.64 (d, *J* = 8.5 Hz, 1H), 6.13 – 5.98 (m, 2H), 4.37 (t, *J* = 7.9 Hz, 2H), 3.46 (t, *J* = 6.7 Hz, 2H), 3.04 (t, *J* = 7.9 Hz, 2H), 2.07 (m, 2H), 1.71-1.65 (m, 2H), 1.50 – 1.37 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.01, 147.94, 142.43, 136.41, 135.37, 129.80, 128.15, 125.67, 124.83, 123.34, 123.10, 115.42, 111.33, 54.21, 44.88, 32.18, 31.92, 29.39, 26.39; HRMS (ESI): m/z calculated for $[C_{19}H_{22}N_2]^+$ $[M + H]^+$: 313.1472, Found: 313.1469; FTIR (NaCl): ν 2954, 2850, 1585, 1469, 1431, 1056, 975, 771, 740 cm^{-1}

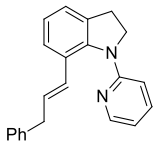
3n



Following the general reaction procedure B, **3n** was obtained as a colorless oil (15.9 mg, 0.05 mmol, Yield: 34%); ^{1}H NMR (*E* and major positional isomer, 400 MHz, $CDCl_3$) δ 8.31 – 8.25 (m, 1H), 7.53 –

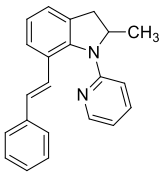
7.37 (m, 1H), 7.31 – 7.08 (m, 2H), 6.96 (td, *J* = 7.5, 2.7 Hz, 1H), 6.75 (m, 1H), 6.64 (m, 1H), 6.09 -6.01 (m, 1H), 5.47 – 5.31 (m, 1H), 4.41 – 4.32 (m, 2H), 3.22 – 2.96 (m, 2H), 2.11 – 1.84 (m, 2H), 1.34 – 1.18 (m, 12H), 0.87 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (*E* and major positional isomer, 101 MHz, $CDCl_3$) δ 158.46, 157.90, 147.99, 147.75, 143.58, 142.28, 136.86, 136.38, 135.32, 134.63, 132.58, 131.11, 129.08, 128.23, 127.46, 127.39, 126.01, 124.79, 123.17, 123.12, 123.10, 122.50, 115.43, 115.28, 111.44, 111.34, 54.90, 54.17, 36.01, 33.08, 32.53, 31.88, 31.86, 29.90, 29.47, 29.40, 29.24, 29.23, 29.224, 29.16, 29.15, 29.12, 27.18, 22.66, 22.65, 14.09; HRMS (ESI): m/z calculated for $[C_{23}H_{31}N_2]^+$ $[M + H]^+$: 335.2487, Found: 335.2489; FTIR (NaCl): ν 2924, 2854, 1585, 1469,1431, 1369, 1153, 1056, 972, 771 cm^{-1}

(*E*)-7-(3-phenylprop-1-en-1-yl)-1-(pyridin-2-yl)indoline (3o)



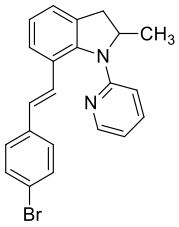
Following the general reaction procedure B, **3o** was obtained as a colorless oil (21.9 mg, 0.07 mmol, Yield: 50%); ^{1}H NMR (400 MHz, $CDCl_3$) major δ 8.31-8.29 (m, 1H), 7.53 – 7.49 (m, 1H), 7.34 – 7.10 (m, 7H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.82 – 6.76 (m, 1H), 6.68 (d, *J* = 8.2 Hz, 1H), 6.30 (d, *J* = 15.9 Hz, 1H), 6.24 (dt, *J* = 15.9, 6.2 Hz, 1H), 4.27 (t, *J* = 7.9 Hz, 2H), 3.32 (d, *J* = 6.2 Hz, 2H), 3.08 (t, *J* = 7.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.48, 148.06, 143.81, 137.69, 137.03, 134.72, 131.38, 128.65, 128.51, 128.45 × 2, 128.37, 126.94, 126.07 × 2, 123.27, 122.83, 115.66, 111.57, 54.99, 36.57, 29.94; HRMS (ESI): m/z calculated for $[C_{22}H_{21}N_2]^+$ $[M + H]^+$: 313.1705.1705, Found: 313.1701; FTIR (NaCl): ν 2920, 1643, 1465, 1431, 1369, 1153, 1056, 968, 698 cm^{-1}

(*E*)-2-methyl-1-(pyridin-2-yl)-7-styrylindoline (3p)



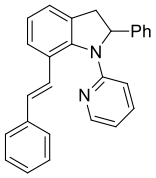
Following the general reaction procedure A, **3p** was obtained as a yellow oil (40.6 mg, 0.13 mmol, Yield: 95%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 – 8.23 (m, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.34 (ddd, *J* = 8.5, 7.8, 2.0 Hz, 1H), 7.26 – 7.10 (m, 6H), 7.08 – 6.87 (m, 2H), 6.78 – 6.68 (m, 3H), 4.88 – 4.63 (m, 1H), 3.43 (dd, *J* = 15.5, 8.5 Hz, 1H), 2.51 (d, *J* = 15.5 Hz, 1H), 1.47 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.84, 148.03, 141.94, 137.62, 136.67, 134.11, 128.45 × 2, 127.50, 127.26, 126.43, 126.33 × 2, 125.45, 124.41, 124.39, 123.06, 115.68, 110.53, 61.63, 36.75, 22.45; HRMS (ESI): m/z calculated for $[C_{22}H_{21}N_2]^+$ $[M + H]^+$: 313.1705, Found: 313.1702; FTIR (NaCl): ν 3442, 3051, 2972, 2920, 1581, 1467, 1429, 1265, 1153, 1060, 983, 968, 910 cm^{-1}

(*E*)-7-(4-bromostyryl)-2-methyl-1-(pyridin-2-yl)indoline (3q)



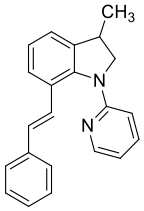
Following the general reaction procedure A, **3q** was obtained as a yellow oil (49.2 mg, 0.13 mmol, Yield: 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.25 (m, 1H), 7.51 – 7.41 (m, 1H), 7.39 – 7.31 (m, 3H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.11 – 6.98 (m, 3H), 6.89 (d, *J* = 16.4 Hz, 1H), 6.82 – 6.59 (m, 3H), 4.83 – 4.70 (m, 1H), 3.45 (dd, *J* = 15.0, 8.5 Hz, 1H), 2.51 (d, *J* = 15.0Hz, 1H), 1.47 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.81, 148.08, 142.06, 136.69, 136.61, 134.13, 131.57 × 2, 127.77 × 2, 127.25, 126.13, 125.04, 124.69, 124.44, 123.08, 120.95, 115.81, 110.56, 61.72, 36.77, 22.49; HRMS (ESI): m/z calculated for $[C_{22}H_{20}BrN_2]^+$ $[M + H]^+$: 391.0810, Found: 391.0806; FTIR (NaCl): ν 3074, 2970, 1581, 1444, 1365, 1334, 1303, 1072, 864, 692 cm^{-1}

(*E*)-2-phenyl-1-(pyridin-2-yl)-7-styrylindoline (3r)



Following the general reaction procedure A, **3r** was obtained as a yellow oil (39.3 mg, 0.11mmol, Yield: 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.23 (m, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 3H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.24 – 7.14 (m, 6H), 7.12 – 6.98 (m, 3H), 6.92 (d, *J* = 16.3 Hz, 1H), 6.77 – 6.73 (m, 2H), 5.67 (d, *J* = 8.8 Hz, 1H), 3.85 (dd, *J* = 15.5, 8.8 Hz, 1H), 2.93 (d, *J* = 15.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.83, 148.10, 144.35, 142.89, 137.69, 136.93, 133.14, 128.63 × 2, 128.51 × 2, 127.62, 127.33, 127.04, 126.58, 126.39 × 2, 125.58 × 2, 125.24, 124.61, 124.24, 123.52, 116.17, 110.74, 68.45, 38.83; HRMS (ESI): m/z calculated for $[C_{27}H_{23}N_2]^+$ $[M + H]^+$: 375.1861, Found: 375.1864; FTIR (NaCl): ν 3061, 3028, 2956, 2916, 2846, 2245, 1583, 1568, 1556, 1446, 1371, 1265, 1244, 1153, 1060, 968 cm^{-1}

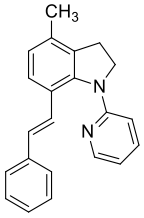
(*E*)-3-methyl-1-(pyridin-2-yl)-7-styrylindoline (3s)



Following the general reaction procedure A, **3s** was obtained as a yellow oil (39.8 mg, 0.13 mmol, Yield: 91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 – 8.19 (m, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.41 – 7.32 (m, 1H), 7.28 – 7.10 (m, 6H), 7.04 (t, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 16.4 Hz, 1H), 6.79 – 6.71 (m, 3H), 4.55 (dd, *J* = 10.8, 8.2 Hz, 1H), 3.92 (dd, *J* = 10.8, 6.9 Hz, 1H), 3.49 – 3.31 (m, 1H), 1.28 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.17, 147.98, 142.78, 140.58, 137.59, 136.77, 128.49 × 2, 127.77, 127.32, 126.32 × 2, 126.29, 125.01, 124.68, 123.21, 122.75, 115.53, 110.78, 62.04, 36.06,

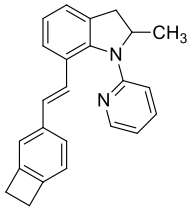
19.12; HRMS (ESI): m/z calculated for $[C_{22}H_{21}N_2]^+$ [M + H]$^+$: 313.1705, Found: 313.1704; FTIR (NaCl): ν 3583, 3406, 2956, 2918, 1581, 1469, 1263, 1153, 1072, 910 cm^{-1}

(*E*)-4-methyl-1-(pyridin-2-yl)-7-styrylindoline (3t)



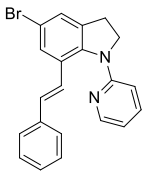
Following the general reaction procedure A, **3t** was obtained as a yellow oil (29.3 mg, 0.09 mmol, Yield: 67%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.29 (m, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.31 (m, 1H), 7.26 – 7.10 (m, 5H), 6.93 (d, *J* = 16.4 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.80 – 6.65 (m, 3H), 4.41 (t, *J* = 8.0 Hz, 2H), 2.98 (t, *J* = 8.0 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.11, 147.90, 142.79, 137.75, 136.67, 133.77, 133.64, 128.47 × 2, 127.13, 126.90, 126.36, 126.22 × 2, 124.61, 124.40, 122.46, 115.52, 111.12, 53.94, 28.06, 18.74; HRMS (ESI): m/z calculated for $[C_{22}H_{21}N_2]^+$ [M + H]$^+$: 313.1705, Found: 313.1703; FTIR (NaCl): ν 3053, 2916, 2850, 2218, 1593, 1433, 1325, 1300, 1267, 1153, 1058, 968, 908, 692 cm^{-1}

(*E*)-7-(2-(bicyclo[4.2.0]octa-1(6),2,4-trien-3-yl)vinyl)-2-methyl-1-(pyridin-2-yl)indoline (3u)



Following the general reaction procedure A, **3u** was obtained as a yellow oil (39.8 mg, 0.12 mmol, Yield: 84%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.28 (m, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.34 (ddd, *J* = 8.5, 7.8, 2.0 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.09 – 6.89 (m, 5H), 6.75 – 6.62 (m, 3H), 4.80 (qd, *J* = 8.5, 6.6 Hz, 1H), 3.43 (dd, *J* = 15.5, 8.5 Hz, 1H), 3.10 – 3.09 (m, 4H), 2.50 (d, *J* = 15.5 Hz, 1H), 1.46 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.84, 147.96, 145.99, 145.33, 141.77, 136.69, 136.52, 134.13, 128.79, 125.86, 125.06 × 2, 124.31, 124.14, 123.12, 122.51, 119.91, 115.60, 110.56, 61.61, 36.77, 29.39, 29.21, 22.43; HRMS (ESI): m/z calculated for $[C_{24}H_{23}N_2]^+$ [M + H]$^+$: 339.1861, Found: 339.1860; FTIR (NaCl): ν 3064, 2964, 2924, 2245, 1583, 1469, 1429, 1153 cm^{-1}

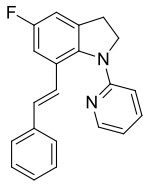
(*E*)-5-bromo-1-(pyridin-2-yl)-7-styrylindoline (3v)



Following the general reaction procedure A, **3v** was obtained as a yellow oil (32.6 mg, 0.09 mmol, Yield: 62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.24 (m, 1H), 7.58 (d, *J* = 2.0 Hz, 1H), 7.39 (ddd, *J*

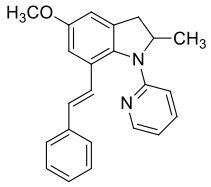
= 8.5, 7.3, 2.0 Hz, 1H), 7.28 – 7.11 (m, 6H), 6.94 (d, *J* = 16.3 Hz, 1H), 6.77 (m, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 6.64 (d, *J* = 16.3 Hz, 1H), 4.36 (t, *J* = 8.0 Hz, 2H), 3.07 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.57, 148.00, 142.32, 137.47, 137.11, 136.90 × 2, 128.74, 128.55 × 2, 127.67, 127.12, 126.70, 126.43, 125.13 × 2, 116.06, 115.41, 111.24, 54.32, 29.12; HRMS (ESI): m/z calculated for $[C_{21}H_{18}BrN_2]^+$ $[M + H]^+$: 377.0653, Found: 377.0650; FTIR (NaCl): ν 30552958, 1589, 1469, 1431, 1323, 1153, 1056, 964, 910, 864,732 cm^{-1}

(*E*)-5-fluoro-1-(pyridin-2-yl)-7-styrylindoline (3w)



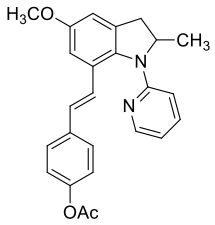
Following the general reaction procedure A, **3w** was obtained as a yellow solid (38.1 mg, 0.12 mmol, Yield: 86%); m.p. = 163-165 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.27 (m, 1H), 7.46 – 7.33 (m, 1H), 7.28 – 7.11 (m, 6H), 6.95 (d, *J* = 16.3 Hz, 1H), 6.91 – 6.84 (m, 1H), 6.81 -6.65 (m, 3H), 4.40 (t, *J* = 7.9 Hz, 2H), 3.04 (t, *J* = 7.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.50 (d, *J* = 240.6 Hz), 158.19, 147.97, 139.39, 137.42 (d, *J* = 8.9 Hz), 137.09, 136.88, 128.80, 128.54 × 2, 127.67, 126.45 × 2, 126.19 (d, *J* = 8.9 Hz), 125.31 (d, *J* = 2.3 Hz), 115.68, 111.45 (d, *J* = 24.4 Hz), 110.65, 109.94 (d, *J* = 24.4 Hz), 54.62, 29.63; ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.67; HRMS (ESI): m/z calculated for $[C_{21}H_{18}FN_2]^+$ $[M + H]^+$: 317.1454, Found: 317.1453; FTIR (NaCl): ν 2954, 2916, 2848, 1463, 1431, 1263, 1176 cm^{-1}

(*E*)-5-methoxy-2-methyl-1-(pyridin-2-yl)-7-styrylindoline (3x)



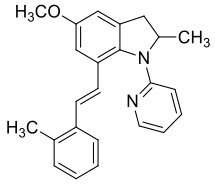
Following the general reaction procedure A, **3x** was obtained as a yellow solid (45.0 mg, 0.13 mmol, Yield: 94%); m.p. = 122-124 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.26 (m, 1H), 7.34 (ddd, *J* = 8.5, 7.2, 2.0 Hz, 1H), 7.27 – 7.13 (m, 5H), 7.02 – 6.97 (m, 2H), 6.83 – 6.75 (m, 2H), 6.72 – 6.63 (m, 2H), 4.83 (qd, *J* = 8.5, 6.6 Hz, 1H), 3.85 (s, 3H), 3.41 (dd, *J* = 15.5, 8.3 Hz, 1H), 2.45 (d, *J* = 15.5 Hz, 1H), 1.45 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.38, 156.41, 147.98, 137.45, 136.75, 135.94 × 2, 128.48 × 2, 127.91, 127.39, 126.40 × 3, 126.17, 115.24, 111.63, 109.93, 108.14, 61.87, 55.71, 37.05, 22.31; HRMS (ESI): m/z calculated for $[C_{23}H_{23}N_2O]^+$ $[M + H]^+$: 343.1810, Found: 343.1807; FTIR (NaCl): ν 3417, 2956, 2918, 1593, 1469, 1429, 1265, 1199, 1143, 1043, 736, 692 cm^{-1}

(*E*)-4-(2-(5-methoxy-2-methyl-1-(pyridin-2-yl)indolin-7-yl)vinyl)phenyl acetate (3y)



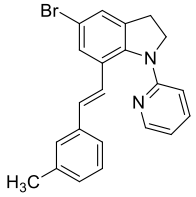
Following the general reaction procedure A, **3y** was obtained as a yellow oil (42.6 mg, 0.11 mmol, Yield: 76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.25 (m, 1H), 7.35 (ddd, *J* = 8.9, 7.2, 2.0 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.03 – 6.88 (m, 4H), 6.83 – 6.61 (m, 4H), 4.85 – 4.78 (m, 1H), 3.85 (s, 3H), 3.41 (dd, *J* = 15.6, 8.3 Hz, 1H), 2.45 (d, *J* = 15.6 Hz, 1H), 2.27 (s, 3H), 1.45 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.41, 158.39, 156.41, 149.87, 148.03, 136.79, 135.99, 135.96, 135.29, 127.32 × 2, 126.82, 126.44, 126.23, 121.59 × 2, 115.31, 111.72, 109.89, 108.14, 61.90, 55.73, 37.05, 22.34, 21.06; HRMS (ESI): m/z calculated for $[C_{25}H_{25}N_2O_3]^+$ $[M + H]^+$: 401.1865, Found: 401.1863; FTIR (NaCl): ν 3429, 3417, 2843, 1761, 1587, 1504, 1469, 1429, 1193, 1165, 1143 cm^{-1}

(*E*)-5-methoxy-2-methyl-7-(2-methylstyryl)-1-(pyridin-2-yl)indoline (3z)



Following the general reaction procedure A, **3z** was obtained as a yellow solid (40.4 mg, 0.11 mmol, Yield: 81%); m.p. = 88-90 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.26 (m, 1H), 7.39 – 7.31 (m, 1H), 7.22 – 7.18 (m, 2H), 7.13 – 6.96 (m, 4H), 6.84 – 6.76 (m, 1H), 6.72 – 6.67 (m, 3H), 4.88 – 4.81 (m, 1H), 3.86 (s, 3H), 3.42 (dd, *J* = 15.6, 8.3 Hz, 1H), 2.46 (d, *J* = 15.6 Hz, 1H), 2.28 (s, 3H), 1.45 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.29, 156.49, 148.09, 136.77, 136.49, 136.08, 135.88, 135.72, 130.22, 127.45, 127.37, 127.14, 126.29, 126.07, 125.40, 115.33, 111.19, 110.12, 109.33, 61.92, 55.80, 37.09, 22.40, 19.75; HRMS (ESI): m/z calculated for $[C_{24}H_{25}N_2O]^+$ $[M + H]^+$: 357.1967, Found: 357.1968; FTIR (NaCl): ν 3419, 1595, 1467, 1429, 1334, 1145, 1043, 968 cm^{-1}

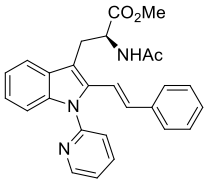
(*E*)-5-bromo-7-(3-methylstyryl)-1-(pyridin-2-yl)indoline (3aa)



Following the general reaction procedure A, **3aa** was obtained as a yellow solid (43.7 mg, 0.11 mmol, Yield: 80%); m.p. = 99-101 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 – 8.30 (m, 1H), 7.60 (d, *J* = 1.5 Hz, 1H), 7.43 (td, *J* = 7.8, 1.5 Hz, 1H), 7.28 – 7.27 (m, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.04 – 7.02 (m, 3H), 6.95 (d, *J* = 16.3 Hz, 1H), 6.80 (ddd, *J* = 7.8, 5.0, 0.7 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 6.65 (d, *J* = 16.3 Hz, 1H), 4.40 (t, *J* = 8.0 Hz, 2H), 3.10 (t, *J* = 8.0 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.62, 148.04, 142.31, 138.10, 137.48, 137.09, 136.90, 128.81, 128.50, 128.45, 127.29, 127.08, 126.63, 126.51, 124.98, 123.57, 116.00, 115.40, 111.26, 54.30, 29.14, 21.29; HRMS (ESI): m/z calculated for $[C_{22}H_{20}BrN_2]^+$ $[M + H]^+$: 391.0810, Found: 391.0812; FTIR (NaCl): ν 3431, 3419, 2916,

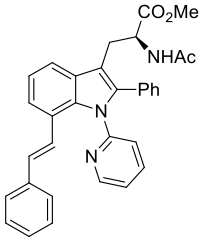
1591, 1469, 1433, 1323, 1265, 964 cm^{-1}

(*S*, *E*)-methyl 2-acetamido-3-(1-(pyridin-2-yl)-2-styryl-1H-indol-3-yl)propanoate (5a)



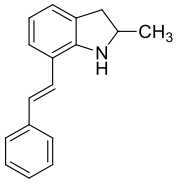
Following the general reaction procedure A, **5a** was obtained as a colorless oil (38.5 mg, 0.11 mmol, Yield: 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (dd, *J* = 4.9, 0.9 Hz, 1H), 7.87 (td, *J* = 7.7, 1.8 Hz, 1H), 7.57 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.44 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.38 (ddd, *J* = 7.7, 4.9, 0.9 Hz, 1H), 7.35 – 7.30 (m, 5H), 7.27 – 7.17 (m, 3H), 7.10 (d, *J* = 16.7 Hz, 1H), 6.37 (d, *J* = 16.7 Hz, 1H), 6.14 (d, *J* = 7.9 Hz, NH), 5.02 (dt, *J* = 7.9, 5.6 Hz, 1H), 3.67 – 3.50 (m, 5H), 1.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.21, 169.72, 152.14, 149.52, 138.35, 138.34, 136.91, 134.89, 132.24, 129.00, 128.71 × 2, 127.91, 126.21 × 2, 123.82, 122.36, 122.34, 121.19, 118.68, 116.69, 112.71, 110.90, 52.83, 52.48, 27.42, 23.13; HRMS (ESI): m/z calculated for $[C_{27}H_{26}N_3O_3]^+$ $[M + H]^+$: 440.1974, Found: 440.1971; FTIR (NaCl): ν 3417, 3052, 1745, 1645, 1469, 1371, 1265, 1226, 698 cm^{-1}

(*S*, *E*)-methyl 2-acetamido-3-(2-phenyl-1-(pyridin-2-yl)-7-styryl-1H-indol-3-yl)propanoate (5b)



Following the general reaction procedure A, **5b** was obtained as a colorless oil (31.0 mg, 0.06 mmol, Yield: 43%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 – 8.50 (m, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.58 (td, *J* = 7.7, 1.9 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.36 – 7.11 (m, 10H), 7.02 – 7.00 (m, 3H), 6.80 (d, *J* = 16.0 Hz, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 5.77 (d, *J* = 7.8 Hz, NH), 4.96 – 4.72 (m, 1H), 3.59 – 3.26 (m, 5H), 1.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.13, 169.63, 153.06, 148.96, 139.80, 137.75, 137.41, 134.80, 131.40, 130.96 × 2, 129.52, 129.34, 128.36 × 2, 128.26 × 2, 128.07, 127.22, 126.17 × 2, 125.63, 124.58, 123.29, 123.10, 121.91, 121.06, 118.58, 109.30, 52.59, 52.14, 26.54, 23.04; HRMS (ESI): m/z calculated for $[C_{33}H_{30}N_3O_3]^+$ $[M + H]^+$: 516.2287, Found: 516.2283; FTIR (NaCl): ν 3583, 3425, 3055, 2918, 2247, 1745, 1585, 1469, 1371, 1265, 1217, 964 cm^{-1}

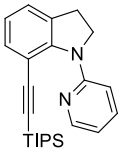
(*E*)-2-methyl-7-styrylindoline (3p')



Following the reported method[3], **3p'** was obtained as a colorless oil (28.6 mg, 0.12 mmol, Yield: 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.23 (dt, *J* = 16.9, 7.7 Hz, 2H), 7.11 – 6.92 (m, 3H), 6.72 (t, *J* = 7.7 Hz, 1H), 4.29 – 3.78 (m, 1H), 3.17 (dd, *J* = 15.4, 7.8 Hz,

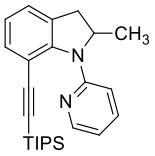
1H), 2.67 (dd, *J* = 15.4, 7.8 Hz, 1H), 1.33 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.68, 137.82, 129.69, 128.61 × 2, 128.54, 127.28, 126.24 × 2, 125.43, 125.22, 123.84, 119.36, 119.05, 55.29, 37.68, 22.38; HRMS (ESI): m/z calculated for $[C_{17}H_{18}N]^+$ $[M + H]^+$: 236.1439, Found: 236.1433; FTIR (NaCl): ν 3369, 2958, 1629, 1597, 1452, 1257, 1058, 960 690 cm^{-1}

1-(pyridin-2-yl)-7-((triisopropylsilyl)ethynyl)indoline (6a)



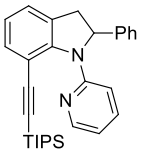
Following the general reaction procedure C, **6a** was obtained as a yellow solid (40.6 mg, 0.11 mmol, Yield: 77%); m.p. = 44-46 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 5.0, 1.7 Hz, 1H), 7.50 – 7.42 (m, 1H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.18 (dd, *J* = 7.3, 0.9 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.86 (t, *J* = 7.3 Hz, 1H), 6.77 (dd, *J* = 7.3, 5.0 Hz, 1H), 4.34 (t, *J* = 8.2 Hz, 2H), 3.07 (t, *J* = 8.2 Hz, 2H), 1.00 – 0.85 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.04, 147.57, 146.07, 136.12, 134.84, 132.59, 125.10, 121.50, 115.93, 112.88, 109.44, 104.40, 99.74, 53.83, 28.73, 18.51 × 6, 11.11 × 3; HRMS (ESI): m/z calculated for $[C_{24}H_{33}N_2Si]^+$ $[M + H]^+$: 377.2413, Found: 377.2417; FTIR (NaCl): ν 3410, 2941, 2862, 2144, 1705, 1593, 1579, 1469, 1433, 1381, 1153, 1064, 883, 673 cm^{-1}

2-methyl-1-(pyridin-2-yl)-7-((triisopropylsilyl)ethynyl)indoline (6b)



Following the general reaction procedure C, **6b** was obtained as a yellow solid (44.8 mg, 0.11 mmol, Yield: 82%); m.p. = 92-94 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H), 7.44 (ddd, *J* = 8.5, 7.2, 1.9 Hz, 1H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.18 (dd, *J* = 7.2, 0.9 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 1H), 6.87 (t, *J* = 7.2 Hz, 1H), 6.76 (ddd, *J* = 7.2, 4.9, 0.9 Hz, 1H), 4.68 (dqd, *J* = 8.7, 6.5, 1.9 Hz, 1H), 3.41 (dd, *J* = 15.5, 8.7 Hz, 1H), 2.50 (dd, *J* = 15.5, 1.9 Hz, 1H), 1.43 (d, *J* = 6.5 Hz, 3H), 1.02 – 0.84 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.88, 147.75, 145.23, 136.07, 133.61, 132.41, 125.52, 121.58, 115.99, 112.39, 110.28, 104.48, 99.21, 61.42, 36.54, 22.31, 18.55 × 3, 18.50 × 3, 11.14 × 3; HRMS (ESI): m/z calculated for $[C_{25}H_{35}N_2Si]^+$ $[M + H]^+$: 391.2570, Found: 391.2563; FTIR (NaCl): ν 3446, 3412, 2146, 1593, 1579, 1469, 1435, 1381, 883, 769 cm^{-1}

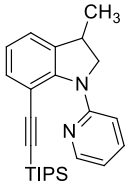
2-phenyl-1-(pyridin-2-yl)-7-((triisopropylsilyl)ethynyl)indoline (6c)



Following the general reaction procedure C, **6c** was obtained as a white solid (56.4 mg, 0.12 mmol, Yield: 89%); m.p. = 96-98 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (ddd, *J* = 5.0, 1.9, 0.8 Hz, 1H), 7.44 (ddd, *J* = 8.5, 7.2, 1.9 Hz, 1H), 7.42 – 7.39 (m, 2H), 7.35 – 7.17 (m, 4H), 7.09 (dd, *J* = 7.2, 0.8 Hz, 1H), 6.92 – 6.84 (m, 2H), 6.76 (ddd, *J* = 7.2, 5.0, 0.8 Hz, 1H), 5.64 (d, *J* = 8.7 Hz, 1H), 3.82 (dd, *J* = 15.5, 8.7 Hz, 1H), 2.91 (dd, *J* = 15.5, 1.4 Hz, 1H), 1.05 – 0.84 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ

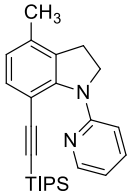
155.91, 147.88, 146.06, 143.93, 136.31, 132.68, 132.19, 128.48 × 2, 126.92, 125.65 × 2, 125.28, 122.27, 116.19, 111.75, 110.84, 104.34, 99.08, 67.79, 38.69, 18.54 × 3, 18.46 × 3, 11.14 × 3; HRMS (ESI): m/z calculated for $[C_{30}H_{37}N_2Si]^+$ $[M + H]^+$: 453.2726, Found: 453.2725; FTIR (NaCl): ν 3412, 2941, 2864, 2146, 1797, 1583, 1469, 1433, 1379, 1253, 1153, 1060, 883, 771 cm^{-1}

3-methyl-1-(pyridin-2-yl)-7-((triisopropylsilyl)ethynyl)indoline (6d)



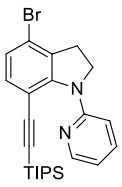
Following the general reaction procedure C, **6d** was obtained as a yellow oil (34.4 mg, 0.09mmol, Yield: 63%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 5.0 Hz, 1H), 7.46 (ddd, *J* = 8.4, 7.3, 1.9 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.14 (d, *J* = 7.3 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.89 (t, *J* = 7.3 Hz, 1H), 6.76 (dd, *J* = 7.3, 5.0 Hz, 1H), 4.48 (dd, *J* = 10.7, 8.7 Hz, 1H), 3.89 (dd, *J* = 10.7, 7.1 Hz, 1H), 3.46 – 3.32 (m, 1H), 1.28 (d, *J* = 6.9 Hz, 3H), 0.97 – 0.83 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.07, 147.62, 145.58, 140.01, 136.12, 132.68, 123.92, 121.62, 115.83, 112.61, 109.43, 104.29, 99.63, 61.72, 35.44, 19.33, 18.50 × 6, 11.10 × 3; HRMS (ESI): m/z calculated for $[C_{25}H_{35}N_2Si]^+$ $[M + H]^+$: 391.2570, Found: 391.2575; FTIR (NaCl): ν 3583, 3412, 2956, 2916, 2144, 1703, 1593, 1435, 1325, 1153, 1074, 997, 883, 713 cm^{-1}

4-methyl-1-(pyridin-2-yl)-7-((triisopropylsilyl)ethynyl)indoline (6e)



Following the general reaction procedure C, **6e** was obtained as a yellow solid (37.2 mg, 0.10 mmol, Yield: 68%); m.p. = 55-57 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.22 (m, 1H), 7.45 (ddd, *J* = 8.4, 7.9, 2.0 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.76 (ddd, *J* = 7.9, 5.0, 0.8 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 4.35 (t, *J* = 8.3 Hz, 2H), 2.97 (t, *J* = 8.3 Hz, 2H), 2.24 (s, 3H), 0.99 – 0.82 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.06, 147.56, 145.62, 135.98, 134.98, 133.12, 132.51, 122.92, 115.77, 112.87, 106.85, 104.50, 98.75, 53.55, 27.45, 18.85, 18.49 × 6, 11.11 × 3; HRMS (ESI): m/z calculated for $[C_{25}H_{35}N_2Si]^+$ $[M + H]^+$: 391.2570, Found: 391.2561; FTIR (NaCl): ν 2941, 2864, 2304, 2148, 1593, 1573, 1469, 1433, 1153, 894 cm^{-1}

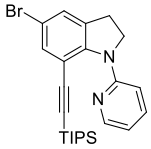
4-bromo-1-(pyridin-2-yl)-7-((triisopropylsilyl)ethynyl)indoline (6f)



Following the general reaction procedure C, **6f** was obtained as a yellow oil (46.4 mg, 0.10 mmol, Yield: 73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ8.29 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.49 (ddd, *J* = 8.4, 7.2, 1.1

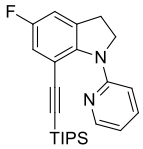
Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.81 (ddd, *J* = 7.2, 4.9, 1.1 Hz, 1H), 4.34 (t, *J* = 8.4 Hz, 2H), 3.09 (t, *J* = 8.4 Hz, 2H), 0.94 – 0.91 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.59, 147.72, 146.81, 136.17, 134.92, 134.01, 124.23, 119.92, 116.61, 113.19, 107.86, 103.47, 100.70, 53.08, 30.18, 18.47 × 6, 11.05 × 3; HRMS (ESI): m/z calculated for $[C_{24}H_{32}BrN_2Si]^+$ $[M + H]^+$: 455.1518, Found: 455.1511; FTIR (NaCl): ν 2953, 2916, 2146, 1732, 1568, 1435, 1317, 1153, 1062, 993, 883, 738 cm^{-1}

5-bromo-1-(pyridin-2-yl)-7-((triisopropylsilyl)ethynyl)indoline (6g)



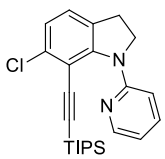
Following the general reaction procedure C, **6g** was obtained as a yellow oil (49.6 mg, 0.11 mmol, Yield: 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.20 (m, 1H), 7.48 (ddd, *J* = 8.4, 7.2, 2.0 Hz, 1H), 7.38 (d, *J* = 2.0 Hz, 1H), 7.25 (s, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.80 (ddd, *J* = 7.2, 5.0, 0.8 Hz, 1H), 4.32 (t, *J* = 8.3 Hz, 2H), 3.07 (t, *J* = 8.3 Hz, 2H), 0.98 – 0.83 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.63, 147.75, 145.33, 136.95, 136.22, 134.48, 128.15, 116.41, 112.95, 112.85, 110.68, 102.85, 101.27, 53.99, 28.51, 18.49 × 6, 11.06 × 3; HRMS (ESI): m/z calculated for $[C_{24}H_{32}BrN_2Si]^+$ $[M + H]^+$: 455.1518, Found: 455.1516; FTIR (NaCl): ν 3001, 2954, 2862, 2146, 1705, 1593, 1573, 1469, 1435, 1319, 1153, 997, 881, 866, 717 cm^{-1}

5-fluoro-1-(pyridin-2-yl)-7-((triisopropylsilyl)ethynyl)indoline (6h)



Following the general reaction procedure C, **6h** was obtained as a yellow solid (40.8 mg, 0.10 mmol, Yield: 74%); m.p. = 44-46 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.26 (m, 1H), 7.49 – 7.44 (m, 1H), 7.01 – 6.85 (m, 3H), 6.77 (dd, *J* = 6.9, 5.2 Hz, 1H), 4.35 (t, *J* = 8.2 Hz, 2H), 3.05 (t, *J* = 8.2 Hz, 2H), 0.94 – 0.94 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.66 (d, *J* = 240.6 Hz), 156.16, 147.68, 142.58, 136.95 (d, *J* = 8.9 Hz), 136.20, 117.64 (d, *J* = 24.2 Hz), 115.91, 113.30 (d, *J* = 24.2 Hz), 112.31, 110.11 (d, *J* = 10.0 Hz), 103.08 (d, *J* = 2.5 Hz), 100.66, 54.27, 29.06 (d, *J* = 1.9 Hz), 18.45 × 6, 11.04 × 3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -122.41; HRMS (ESI): m/z calculated for $[C_{24}H_{32}FN_2Si]^+$ $[M + H]^+$: 395.2319, Found: 395.2308; FTIR (NaCl): ν 3051, 2941, 2864, 2140, 1585, 1465, 1433, 1265, 1124, 696 cm^{-1}

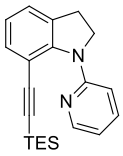
6-chloro-1-(pyridin-2-yl)-7-((triisopropylsilyl)ethynyl)indoline (6i)



Following the general reaction procedure C, **6i** was obtained as a yellow oil (28.7 mg, 0.07 mmol, Yield: 50%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 4.9, 1.3 Hz, 1H), 7.53 – 7.44 (m, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.81 (dd, *J* = 7.8, 4.9 Hz, 1H), 4.36

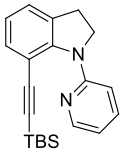
(t, *J* = 8.3 Hz, 2H), 3.04 (t, *J* = 8.3 Hz, 2H), 0.99 – 0.82 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.63, 147.83, 147.67, 136.06, 135.78, 133.08, 124.74, 122.02, 116.45, 113.25, 109.48, 106.20, 100.39, 54.57, 28.28, 18.46 × 6, 11.03 × 3; HRMS (ESI): m/z calculated for $[C_{24}H_{32}ClN_2Si]^+$ $[M + H]^+$: 411.2023, Found: 411.2017; FTIR (NaCl): ν 2954, 2891, 2148, 1699, 1587, 1469, 1427, 1309, 1232, 1062, 995, 883, 804 cm^{-1}

1-(pyridin-2-yl)-7-((triethylsilyl)ethynyl)indoline (6j)



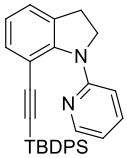
Following the general reaction procedure D, **6j** was obtained as a brown solid (33.7 mg, 0.10 mmol, Yield: 72%); m.p. = 60-62 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (ddd, *J* = 5.0, 2.0, 0.8 Hz, 1H), 7.49 (ddd, *J* = 8.4, 7.6, 2.0 Hz, 1H), 7.27 – 7.25 (m, 1H), 7.17 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.80 (ddd, *J* = 7.6, 5.0, 0.8 Hz, 1H), 4.33 (t, *J* = 8.4 Hz, 2H), 3.07 (t, *J* = 8.3 Hz, 2H), 0.82 (t, *J* = 7.9 Hz, 9H), 0.42 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.75, 147.51, 146.20, 135.74, 134.60, 132.23, 125.14, 121.29, 115.96, 113.22, 108.80, 103.58, 100.84, 53.69, 28.63, 7.28 × 3, 4.08 × 3; HRMS (ESI): m/z calculated for $[C_{21}H_{27}N_2Si]^+$ $[M + H]^+$:335.1944, Found: 335.1938; FTIR (NaCl): ν 3583, 2954, 2873, 2144, 1593, 1579, 1469, 1433, 1377, 1263, 1016 cm^{-1}

7-((tert-butyldimethylsilyl)ethynyl)-1-(pyridin-2-yl)indoline (6k)



Following the general reaction procedure D, **6k** was obtained as a brown solid (38.8 mg, 0.12 mmol, Yield: 83%); m.p. = 86-88 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 – 8.25 (m, 1H), 7.49 (ddd, *J* = 8.6, 7.6, 2.0 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.17 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.94 (d, *J* = 8.6 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.80 (ddd, *J* = 7.6, 5.0, 0.8 Hz, 1H), 4.33 (t, *J* = 8.3 Hz, 2H), 3.08 (t, *J* = 8.3 Hz, 2H), 0.79 (s, 9H), -0.09 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.81, 147.51, 146.25, 135.94, 134.58, 132.13, 125.18, 121.32, 116.03, 113.23, 108.76, 103.18, 101.51, 53.75, 28.65, 25.98 × 3, 16.42, -4.89 × 2; HRMS (ESI): m/z calculated for $[C_{21}H_{27}N_2Si]^+$ $[M + H]^+$: 335.1944, Found: 335.1936; FTIR (NaCl): ν 3053, 2954, 2854, 2304, 2146, 1593, 1581, 1469, 1433, 1265, 894, 704 cm^{-1}

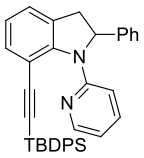
7-((tert-butyldiphenylsilyl)ethynyl)-1-(pyridin-2-yl)indoline (6l)



Following the general reaction procedure D, **6l** was obtained as a yellow oil (47.5 mg, 0.10 mmol, Yield: 74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 5.2 Hz, 1H), 7.57 (dd, *J* = 7.6, 1.4 Hz, 4H), 7.42 – 7.26 (m, 7H), 7.21 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.17 – 7.11 (m, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.89 (t, *J* = 7.6 Hz, 1H), 6.55 (dd, *J* = 7.6, 5.2 Hz, 1H), 4.33 (t, *J* = 8.3 Hz, 2H), 3.09 (t, *J* = 8.3 Hz, 2H), 0.96 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.67, 147.53, 146.17, 136.21 × 2, 135.52 × 4, 134.77,

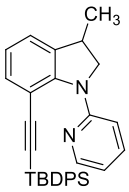
133.37, 132.71, 129.20 × 2, 127.54 × 4, 125.58, 121.38, 116.26, 112.76, 108.56, 106.49, 98.22, 53.79, 28.61, 27.02 × 3, 18.48; HRMS (ESI): m/z calculated for $[C_{31}H_{31}N_2Si]^+$ $[M + H]^+$: 459.2257, Found: 459.2254; FTIR (NaCl): ν 3444, 3068, 2956, 2927, 2854, 2146, 1699, 1593, 1581, 1469, 1433, 1323, 1111, 819, 700 cm^{-1}

7-((tert-butyldiphenylsilyl)ethynyl)-2-phenyl-1-(pyridin-2-yl)indoline (6m)



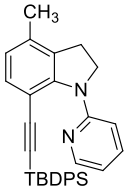
Following the general reaction procedure D, **6m** was obtained as a white solid (60.6 mg, 0.11 mmol, Yield: 81%); m.p. = 194-196 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.07 (m, 1H), 7.69 – 7.59 (m, 4H), 7.46 – 7.42 (m, 3H), 7.39 – 7.19 (m, 10H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.57 (dd, *J* = 7.6, 5.0 Hz, 1H), 5.62 (d, *J* = 8.7 Hz, 1H), 3.86 (dd, *J* = 15.5, 8.7 Hz, 1H), 2.96 (d, *J* = 15.7 Hz, 1H), 0.95 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.89, 147.92, 146.41, 143.91, 136.56, 135.60 × 4, 133.50, 133.33, 132.68, 132.44, 129.24 × 2, 128.61 × 2, 127.57 × 4, 127.05, 125.83, 125.69 × 2, 122.25, 116.64, 111.83, 110.14, 106.71, 97.58, 68.08, 38.75, 26.98 × 3, 18.58; HRMS (ESI): m/z calculated for $[C_{37}H_{35}N_2Si]^+$ $[M + H]^+$: 535.2570, Found: 535.2563; FTIR (NaCl): ν 3052, 2985, 2304, 2148, 1469, 1431, 1265, 894, 702 cm^{-1}

7-((tert-butyldiphenylsilyl)ethynyl)-3-methyl-1-(pyridin-2-yl)indoline (6n)



Following the general reaction procedure D, **6n** was obtained as a yellow oil (49.6 mg, 0.11 mmol, Yield: 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.08 (m, 1H), 7.59 – 7.56 (m, 4H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.25 (m, 6H), 7.21 – 7.09 (m, 2H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.54 (ddd, *J* = 7.6, 5.0, 0.8 Hz, 1H), 4.48 (dd, *J* = 10.7, 8.7 Hz, 1H), 3.91 (dd, *J* = 10.7, 7.1 Hz, 1H), 3.47 – 3.34 (m, 1H), 1.30 (d, *J* = 7.1 Hz, 3H), 0.96 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.81, 147.57, 145.78, 140.01, 136.29, 135.53 × 4, 133.41, 133.36, 132.83, 129.21 × 2, 127.55 × 4, 124.46, 121.57, 116.22, 112.58, 108.58, 106.51, 98.16, 61.74, 35.36, 27.03 × 3, 19.39, 18.48; HRMS (ESI): m/z calculated for $[C_{32}H_{33}N_2Si]^+$ $[M + H]^+$: 473.2413, Found: 473.2414; FTIR (NaCl): ν 3070, 2927, 2146, 1581, 1469, 1429, 1325, 1300, 1251, 1109, 908, 819 cm^{-1}

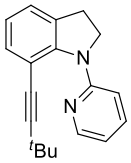
7-((tert-butyldiphenylsilyl)ethynyl)-4-methyl-1-(pyridin-2-yl)indoline (6o)



Following the general reaction procedure D, **6o** was obtained as a yellow oil (60.2 mg, 0.13 mmol, Yield: 91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 5.1 Hz, 1H), 7.58 – 7.58 (m, 4H), 7.41 – 7.21

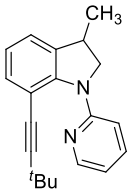
(m, 7H), 7.18 – 7.10 (m, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 6.54 (dd, *J* = 7.9, 5.1 Hz, 1H), 4.35 (t, *J* = 8.3 Hz, 2H), 2.99 (t, *J* = 8.3 Hz, 2H), 2.26 (s, 3H), 0.95 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.83, 147.52, 145.84, 136.16 × 2, 135.58, 135.53 × 4, 133.51, 133.14, 132.67, 129.15 × 2, 127.51 × 4, 122.90, 116.14, 112.79, 106.78, 106.04, 97.32, 53.58, 27.39, 27.02 × 3, 18.91, 18.48; HRMS (ESI): m/z calculated for $[C_{32}H_{33}N_2Si]^+$ $[M + H]^+$: 473.2413, Found: 473.2404; FTIR (NaCl): ν 3070, 2954, 2146, 1693, 1593, 1446, 1381, 1111, 908, 819 cm^{-1}

7-(3,3-dimethylbut-1-yn-1-yl)-1-(pyridin-2-yl)indoline (6p)



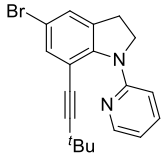
Following the general reaction procedure D, **6p** was obtained as a yellow solid (27.8 mg, 0.10 mmol, Yield: 72%); m.p. = 82-84 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.50 (ddd, *J* = 8.4, 7.8, 1.9 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.13 (dd, *J* = 7.8, 1.1 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.84 (t, *J* = 7.8 Hz, 1H), 6.79 (ddd, *J* = 7.8, 5.0, 1.1 Hz, 1H), 4.33 (t, *J* = 8.2 Hz, 2H), 3.07 (t, *J* = 8.2 Hz, 2H), 0.99 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.19, 147.53, 145.88, 135.85, 134.45, 131.49, 124.23, 121.48, 115.68, 113.33, 109.74, 107.17, 77.10, 53.74, 30.54 × 3, 28.87, 28.00; HRMS (ESI): m/z calculated for $[C_{19}H_{21}N_2]^+$ $[M + H]^+$: 277.1705, Found: 277.1702; FTIR (NaCl): ν 3419, 2966, 2922, 2108, 1635, 1593, 1581, 1469, 1433, 1327,1151, 987 cm^{-1}

7-(3,3-dimethylbut-1-yn-1-yl)-3-methyl-1-(pyridin-2-yl)indoline (6q)



Following the general reaction procedure D, **6q** was obtained as a yellow oil (30.1 mg, 0.10 mmol, Yield: 74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (ddd, *J* = 5.0, 1.9, 0.8 Hz, 1H), 7.50 (ddd, *J* = 8.5, 7.1, 1.9 Hz, 1H), 7.19 (d, *J* = 8.5 Hz, 1H), 7.10 (dt, *J* = 7.1, 0.8 Hz, 1H), 6.95 – 6.84 (m, 2H), 6.78 (ddd, *J* = 7.1, 5.0, 0.8 Hz, 1H), 4.46 (dd, *J* = 10.7, 8.7 Hz, 1H), 3.88 (dd, *J* = 10.7, 7.1 Hz, 1H), 3.44 – 3.35 (m, 1H), 1.28 (d, *J* = 6.9 Hz, 3H), 0.99 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.29, 147.57, 145.47, 139.66, 135.84, 131.53, 123.02, 121.59, 115.57, 113.04, 109.70, 107.08, 77.04, 61.64, 35.56, 30.51 × 3, 27.96, 19.36; HRMS (ESI): m/z calculated for $[C_{20}H_{23}N_2]^+$ $[M + H]^+$: 291.1961, Found: 291.1859; FTIR (NaCl): ν 2964, 2868, 2218, 1728, 1579, 1429, 1220, 1056, 910 cm^{-1}

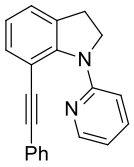
5-bromo-7-(3,3-dimethylbut-1-yn-1-yl)-1-(pyridin-2-yl)indoline (6r)



Following the general reaction procedure D, **6r** was obtained as a yellow oil (43.6 mg, 0.12 mmol, Yield: 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 – 8.18 (m, 1H), 7.52 (ddd, *J* = 8.4, 7.2, 1.9 Hz, 1H), 7.30 (d, *J* = 2.0 Hz, 1H), 7.22 (d, *J* = 2.0 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.82 (dd, *J* = 7.2, 5.0 Hz, 1H), 4.30 (t, *J* = 8.3 Hz, 2H), 3.07 (t, *J* = 8.3 Hz, 2H), 0.98 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ

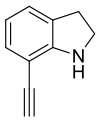
155.74, 147.60, 145.12, 136.48, 135.97, 133.62, 127.24, 116.14, 113.43, 112.87, 110.95, 108.31, 76.01, 53.87, 30.37 × 3, 28.60, 27.96; HRMS (ESI): m/z calculated for $[C_{19}H_{20}BrN_2]^+$ $[M + H]^+$: 355.0810, Found: 355.0811; FTIR (NaCl): ν 2968, 2899, 2222, 1593, 1469, 1359, 1321, 1213, 1153, 910, 862 cm^{-1}

7-(phenylethynyl)-1-(pyridin-2-yl)indoline (6s)

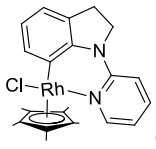


Following the general reaction procedure E, **6s** was obtained as a yellow solid (27.8 mg, 0.09mmol, Yield: 67%); m.p. = 97-99 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 – 8.30 (m, 1H), 7.46 (ddd, *J* = 8.4, 7.8, 1.9 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.24 – 7.15 (m, 4H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.98 – 6.92 (m, 2H), 6.89 (t, *J* = 7.6 Hz, 1H), 6.86 – 6.78 (m, 1H), 4.36 (t, *J* = 8.3 Hz, 2H), 3.13 (t, *J* = 8.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.54, 147.57, 145.98, 135.86, 134.48, 131.38, 130.98 × 2, 128.00 × 2, 127.80, 125.00, 123.36, 121.28, 116.08, 113.26, 108.12, 98.33, 87.81, 53.66, 28.67; HRMS (ESI): m/z calculated for $[C_{21}H_{17}N_2]^+$ $[M + H]^+$: 297.1392, Found: 297.1395; FTIR (NaCl): ν 3051, 2916, 2848, 2303, 1589, 1467, 1431, 1265, 1153, 1066, 894, 702 cm^{-1}

7-ethynylindoline (6a')

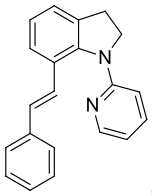


Following the reported method[3,4], **6a'** was obtained as a colorless oil (13.3 mg, 0.09 mmol, Yield: 62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.03 (m, 2H), 6.60 (t, *J* = 7.5 Hz, 1H), 4.21 (s, NH), 3.63 (t, *J* = 8.4 Hz, 2H), 3.25 (s, 1H), 3.07 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.32, 130.03, 128.85, 125.16, 117.88, 101.81, 80.84, 80.66, 46.98, 29.83; HRMS (ESI): m/z calculated for $[C_{10}H_{10}N]^+$ $[M + H]^+$: 144.0813, Found: 144.0815; FTIR (NaCl): ν 3390, 3288, 2916, 2848, 2096, 1595, 1469, 1334, 1055, 1028 cm^{-1}

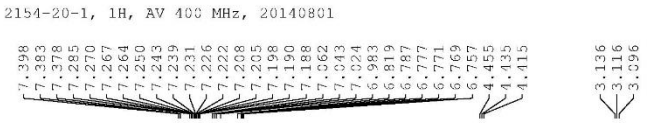


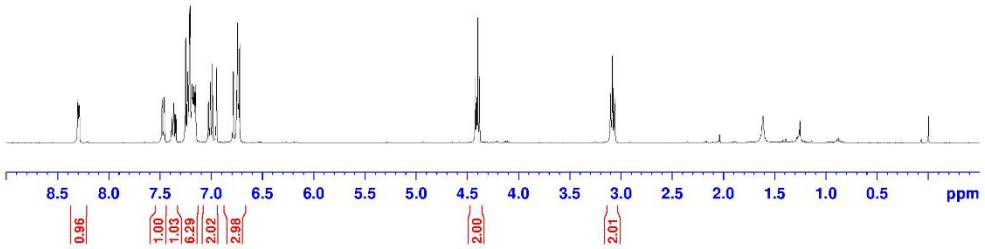
c1

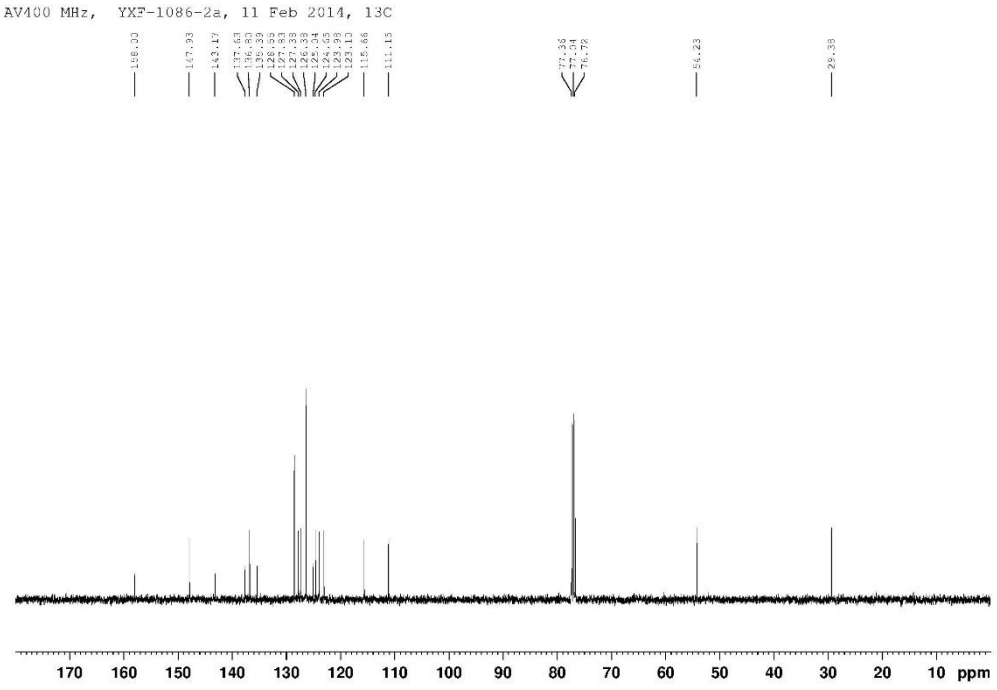
c1 was obtained as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (dd, *J* = 5.8, 1.8 Hz, 1H), 7.54 (ddd, *J* = 8.8, 7.3, 1.8 Hz, 1H), 7.37 (d, *J* = 7.3 Hz, 1H), 6.90 (t, *J* = 7.3 Hz, 1H), 6.77 (dd, *J* = 7.3, 1.8 Hz, 1H), 6.74 – 6.65 (m, 1H), 6.54 (d, *J* = 8.8 Hz, 1H), 3.98 (td, *J* = 9.8, 5.8 Hz, 1H), 3.70 (dd, *J* = 18.7, 9.8 Hz, 1H), 3.35 – 3.18 (m, 2H), 1.39 (s, 15H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.11, 153.25, 141.54, 140.04, 139.74, 137.62, 137.59, 124.64, 124.60, 118.90, 114.62, 107.87, 95.61 × 2, 95.55 × 2, 48.36, 28.55, 8.82 × 5; HRMS (ESI): m/z calculated for $[C_{23}H_{26}N_2Rh]^+$ $[M – Cl]^+$: 433.1151, Found: 433.1146; FTIR (NaCl): ν 3583, 3053, 2914, 1593, 1469, 1431, 1265, 894, 738 cm^{-1}

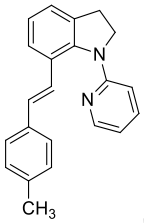


3a

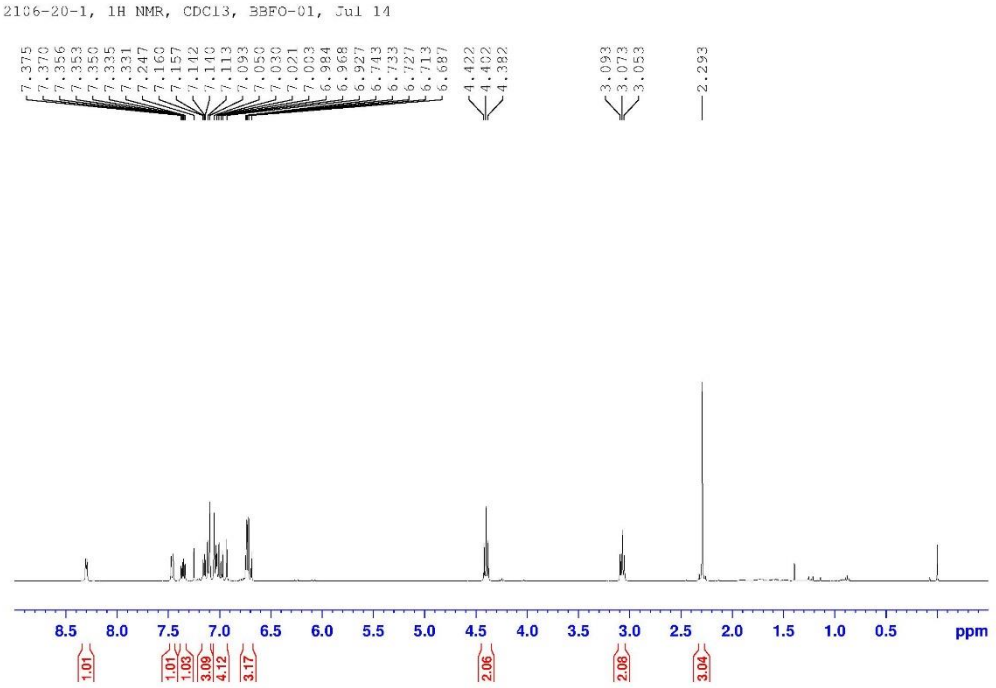

2154-20-1, 1H, AV 400 MHz, 20140801
7.398
7.383
7.378
7.285
7.270
7.267
7.264
7.250
7.243
7.239
7.231
7.226
7.222
7.208
7.205
7.198
7.190
7.188
7.062
7.043
7.024
6.983
6.819
6.787
6.777
6.771
6.769
6.757
4.455
4.435
4.415
3.136
3.116
3.096

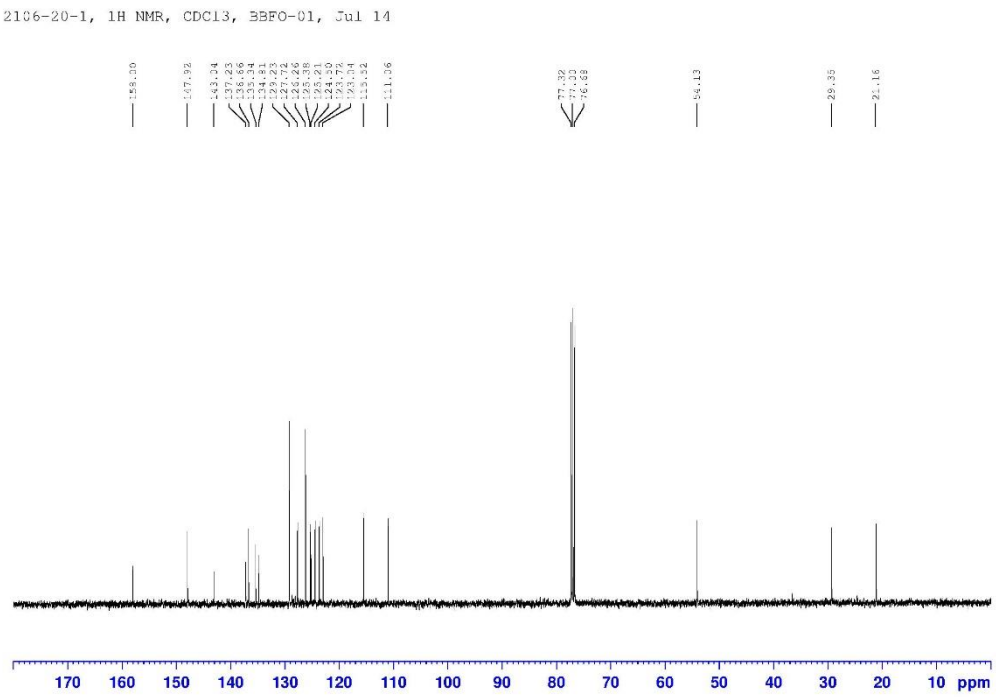

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.96
1.00
1.03
6.29
2.02
2.98
2.00
2.01

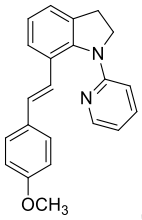

AV400 MHz, YXF-1086-2a, 11 Feb 2014, 13C
158.00
147.93
143.17
137.63
136.80
136.39
128.93
127.33
126.38
125.94
124.65
124.38
123.13
115.66
111.15
77.36
77.04
76.72
54.23
29.38
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



3b

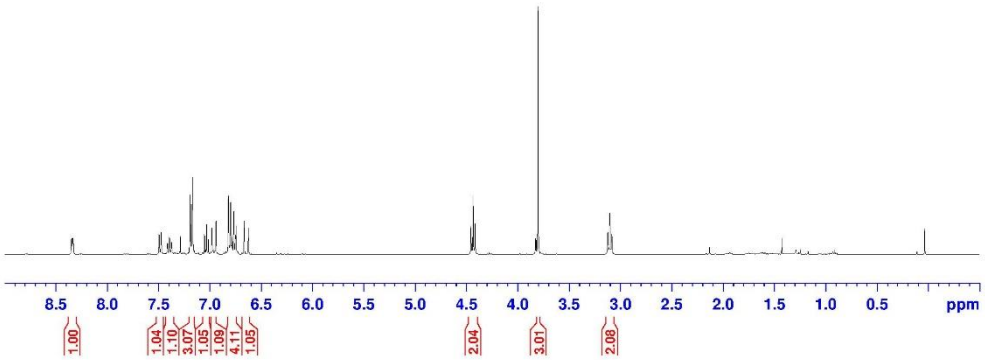

2106-20-1, 1H NMR, CDCl3, BBFO-01, Jul 14
7.375
7.370
7.356
7.353
7.350
7.335
7.331
7.247
7.160
7.157
7.142
7.140
7.113
7.093
7.050
7.030
7.021
7.003
6.984
6.968
6.927
6.743
6.733
6.727
6.713
6.687
4.422
4.402
4.382
3.093
3.073
3.053
2.293
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.01
1.01
1.03
3.09
4.12
3.17
2.06
2.08
3.04


2106-20-1, 1H NMR, CDCl3, BBFO-01, Jul 14
158.30
147.92
143.04
137.23
136.66
135.34
134.31
129.23
127.72
126.66
126.38
125.21
124.50
123.72
123.04
120.52
111.36
77.32
77.00
76.68
54.13
29.35
21.16
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

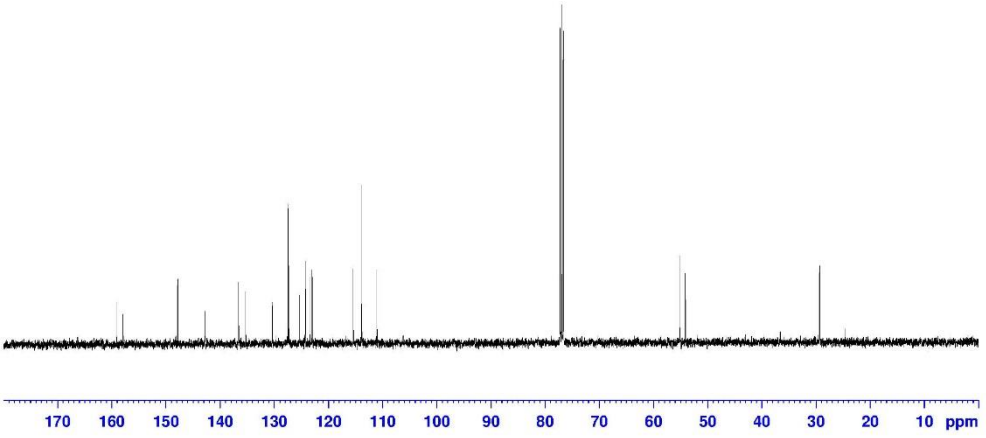


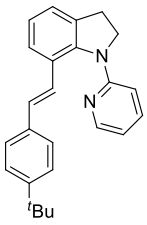
3c

2106-20-2, 1H NMR, CDCl3, BBFO-01, Jul 14

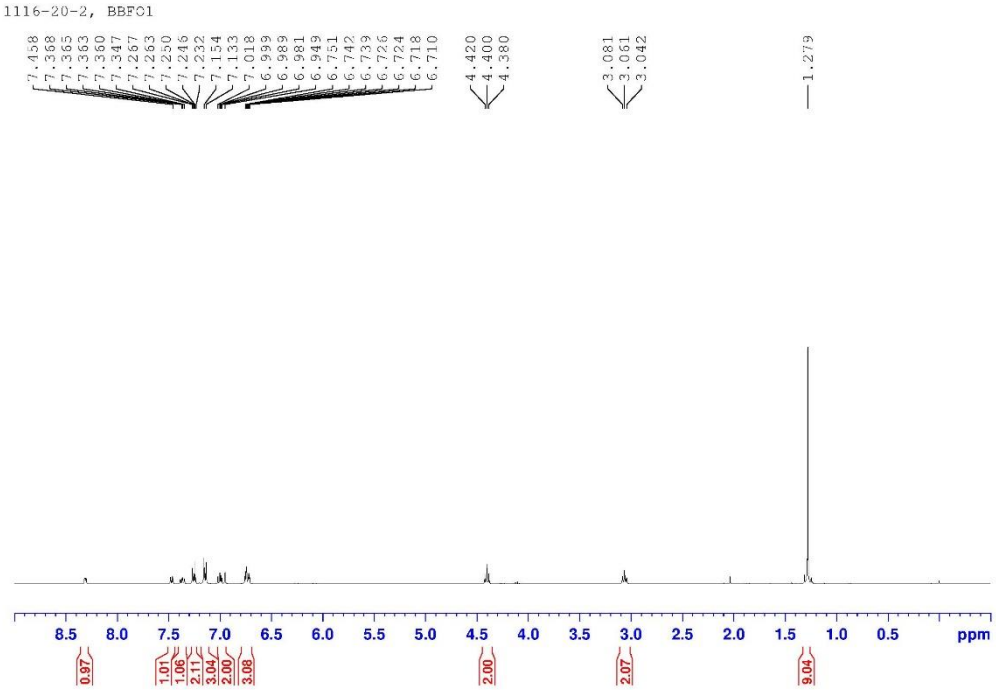


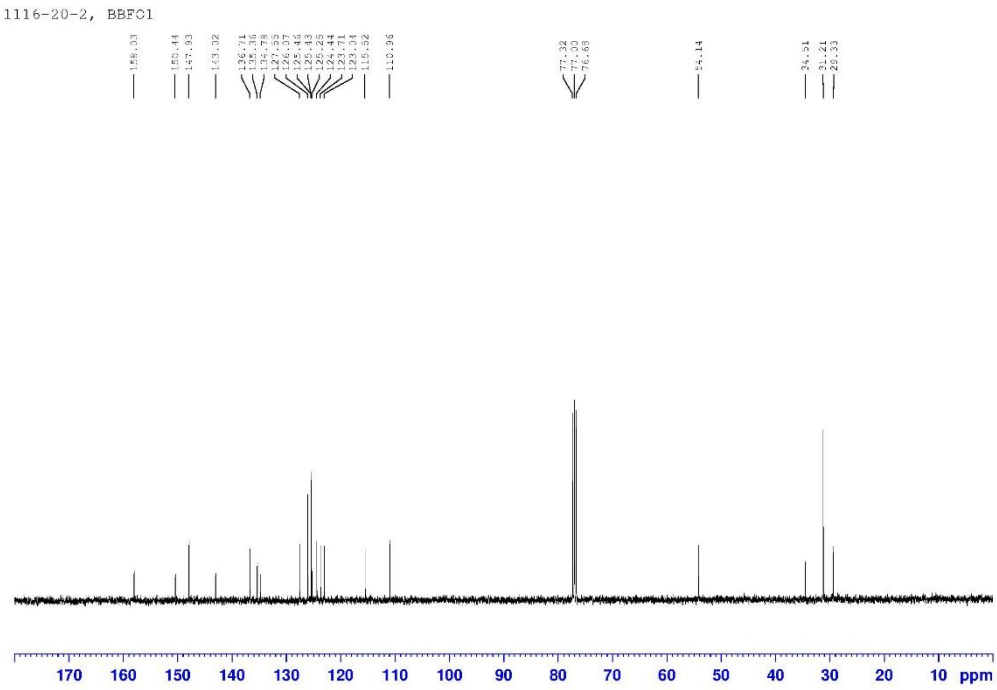
2106-20-2, 1H NMR, CDCl3, BBFO-01, Jul 14

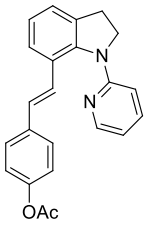



N
N
tBu

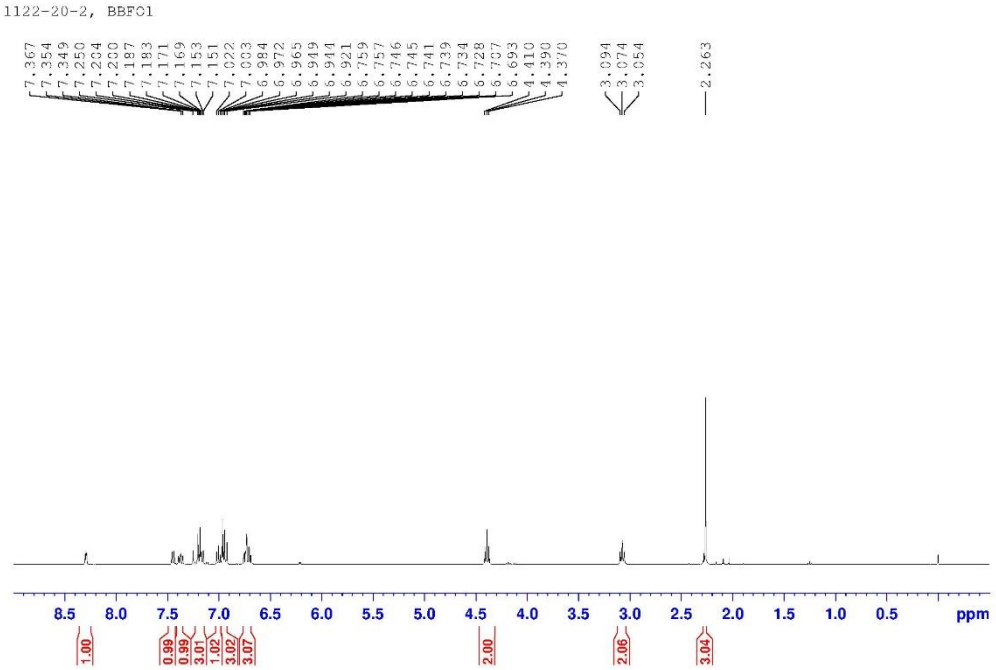
3d

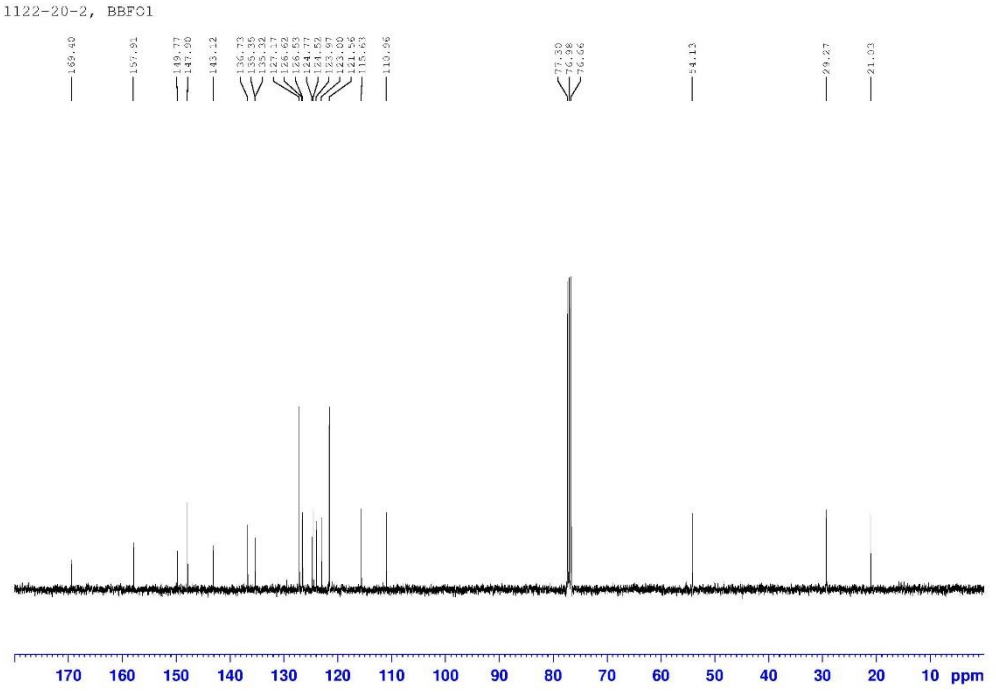

1116-20-2, BBFC1
7.458
7.368
7.365
7.363
7.360
7.347
7.267
7.263
7.250
7.246
7.232
7.154
7.133
7.018
6.999
6.989
6.981
6.949
6.751
6.742
6.739
6.726
6.724
6.718
6.710
4.420
4.400
4.380
3.081
3.061
3.042
1.279
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.97
1.01
1.06
2.11
3.04
2.00
3.08
2.00
2.07
9.04

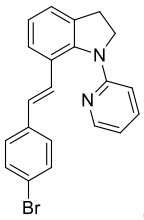

1116-20-2, BBFC1
158.03
150.44
147.93
143.02
136.71
135.36
134.78
127.55
126.97
125.44
125.03
125.26
124.44
123.71
123.04
115.52
110.96
77.32
77.00
76.68
54.14
34.51
31.21
28.33
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


N
N
OAc

3e

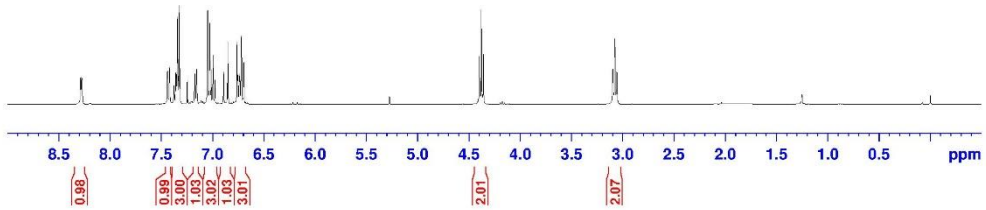

1122-20-2, BBFC1
7.367
7.354
7.349
7.250
7.204
7.200
7.187
7.183
7.171
7.169
7.153
7.151
7.022
7.003
6.984
6.972
6.965
6.949
6.941
6.921
6.759
6.757
6.746
6.745
6.741
6.739
6.734
6.728
6.707
6.693
4.410
4.390
4.370
3.094
3.074
3.054
2.263
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
0.99
0.99
3.01
1.02
3.02
3.07
2.00
2.06
3.04


1122-20-2, BBFC1
169.40
157.91
149.77
147.90
143.12
136.73
135.36
135.32
127.17
126.62
126.53
124.77
124.52
123.97
122.00
111.56
115.63
110.96
77.30
76.98
76.66
54.13
29.27
21.03
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

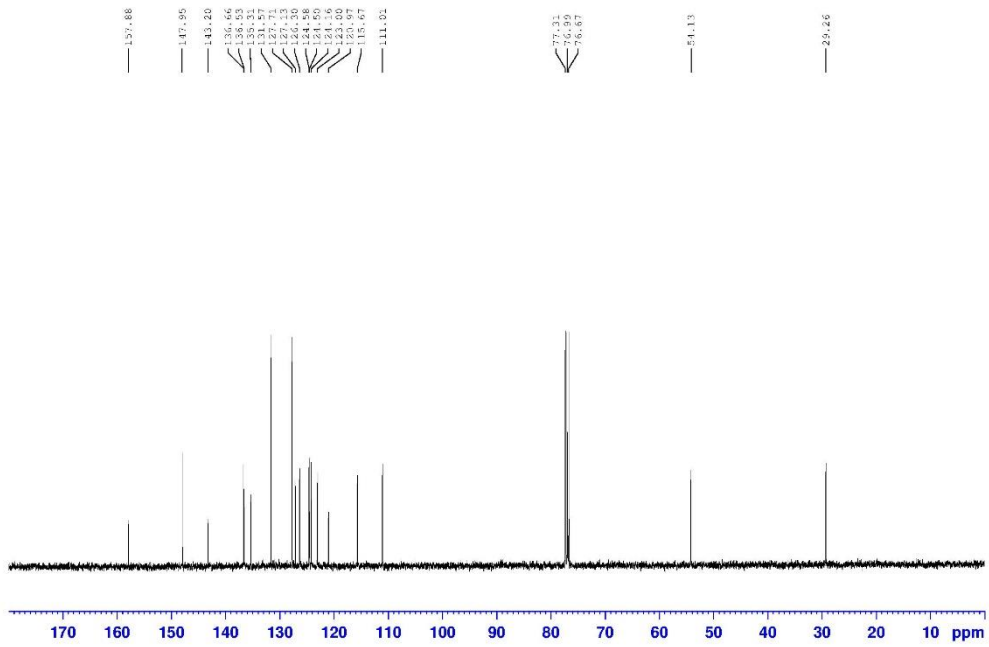


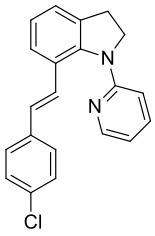
3f

1108-20-1, BBFC1, 1H-NMR,

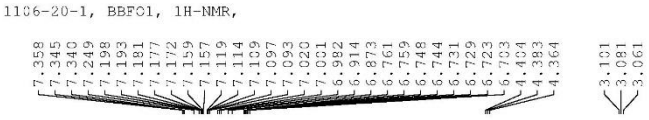


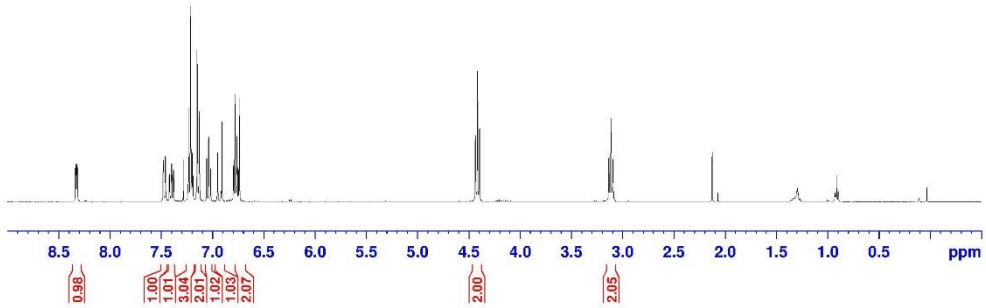
1108-20-1, BBFC1, 1H-NMR,

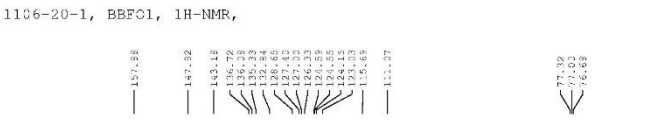


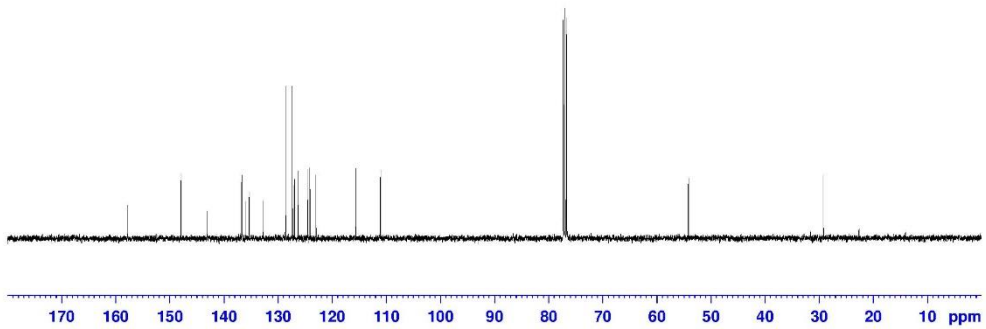

N
N
Cl

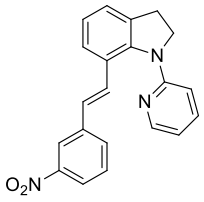
3g


1106-20-1, BBFC1, 1H-NMR,
7.358
7.345
7.340
7.249
7.198
7.193
7.181
7.177
7.172
7.159
7.157
7.119
7.114
7.109
7.097
7.093
7.020
7.001
6.982
6.914
6.873
6.761
6.759
6.748
6.744
6.731
6.729
6.723
6.703
4.404
4.383
4.364
3.101
3.081
3.061

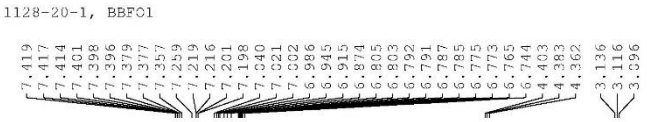

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.98
1.00
1.01
3.04
2.01
1.02
1.03
2.07
2.00
2.05

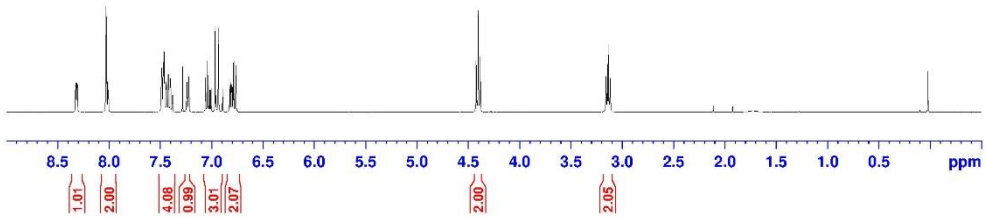

1106-20-1, BBFC1, 1H-NMR,
157.88
147.92
143.18
136.72
136.35
133.38
132.84
128.85
127.40
127.33
127.23
124.59
124.55
124.15
123.73
123.03
115.89
111.27
77.32
77.03
76.69
54.18
28.29

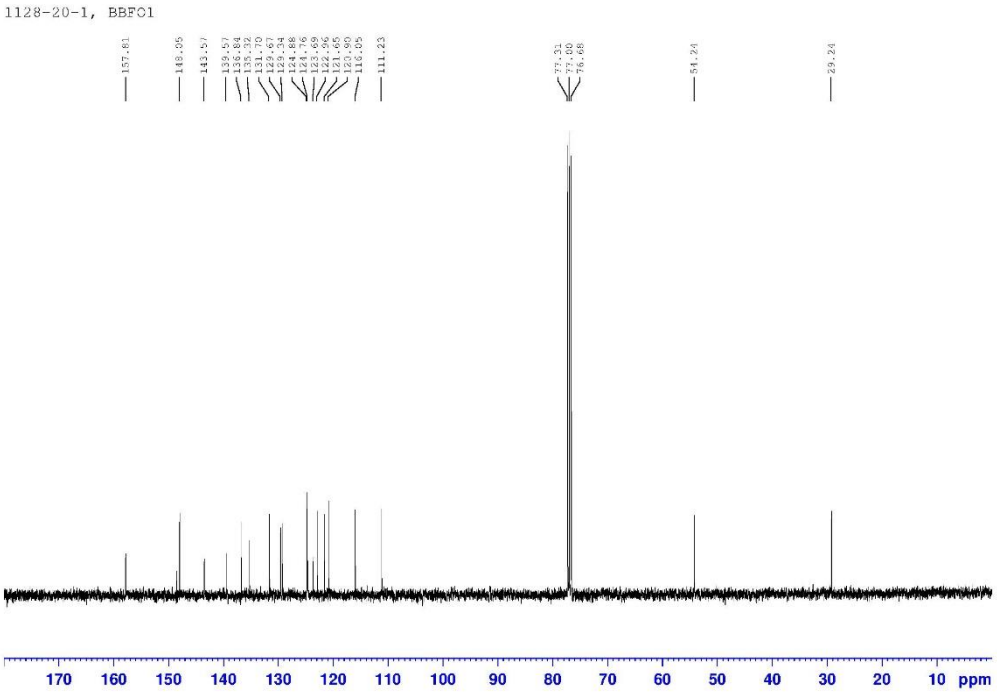

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

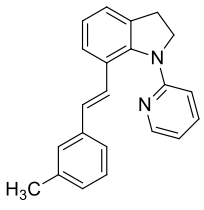


3h


1128-20-1, BBFC1
7.419
7.417
7.414
7.401
7.398
7.396
7.379
7.377
7.357
7.259
7.219
7.216
7.201
7.198
7.040
7.021
7.002
6.986
6.945
6.915
6.874
6.805
6.803
6.792
6.791
6.787
6.785
6.775
6.773
6.765
6.744
4.403
4.383
4.362
3.136
3.116
3.096

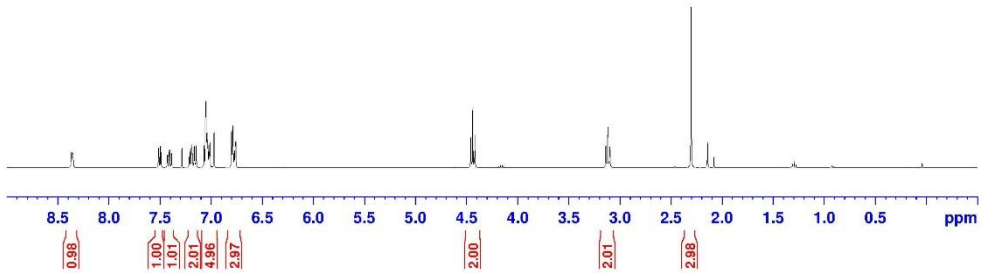

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.01
2.00
4.08
0.99
3.01
2.07
2.00
2.05


1128-20-1, BBFC1
157.81
148.05
143.57
139.57
136.84
135.32
131.70
129.67
129.34
124.88
124.76
123.69
122.96
121.65
120.90
116.05
111.23
77.31
77.00
76.68
54.24
29.24
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

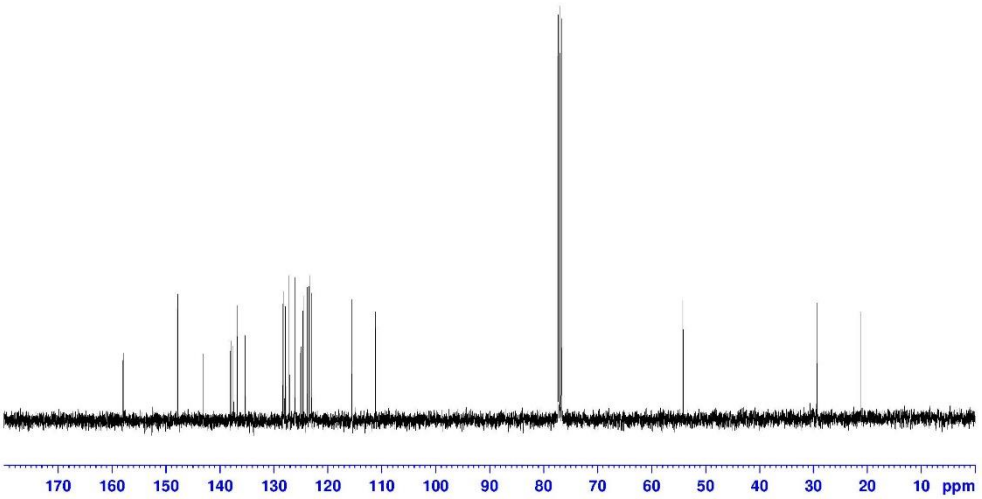


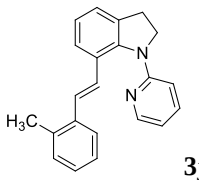
3i

1106-20-22, BBFO1, 1H-NMR,

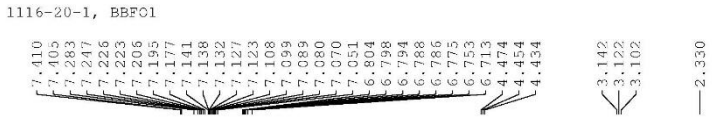


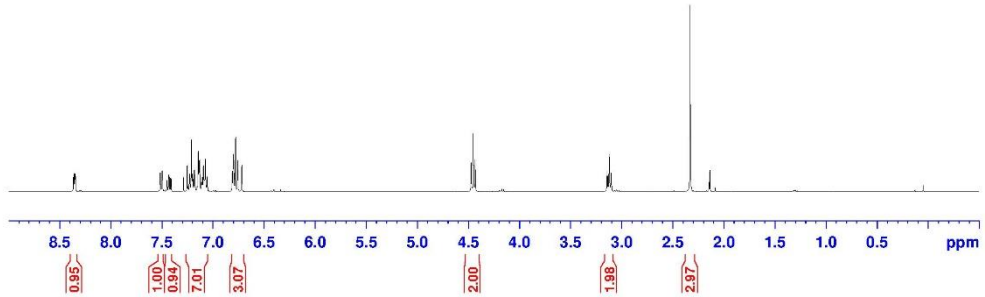
1106-20-2, BBFO1, 1H-NMR,

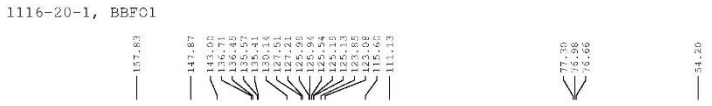


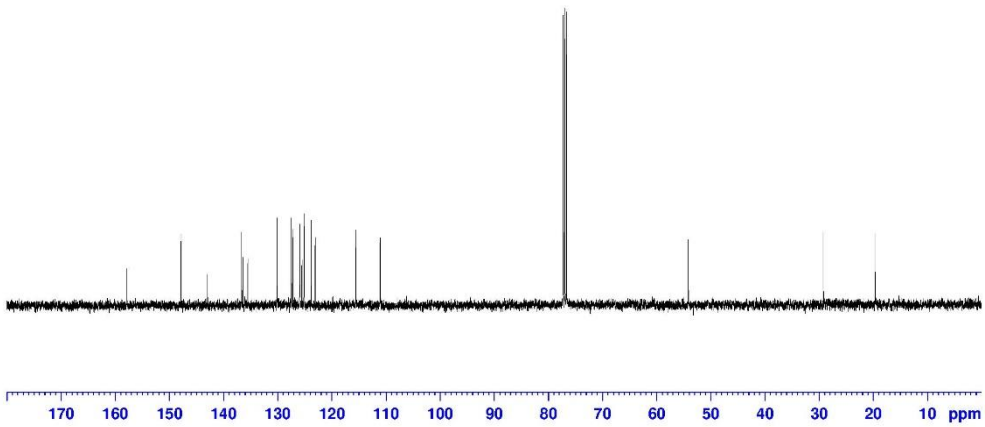

N
N
H3C

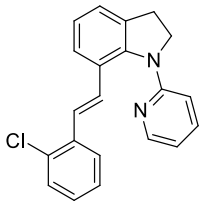
3j


1116-20-1, BBFC1
7.410
7.405
7.283
7.247
7.226
7.223
7.206
7.195
7.177
7.141
7.138
7.132
7.127
7.123
7.108
7.099
7.089
7.080
7.070
7.051
6.804
6.798
6.794
6.788
6.786
6.775
6.753
6.713
4.474
4.454
4.434
3.142
3.122
3.102
2.330

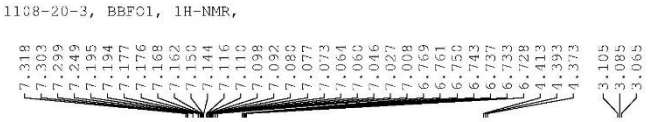

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.95
1.00
0.94
7.01
3.07
2.00
1.98
2.97

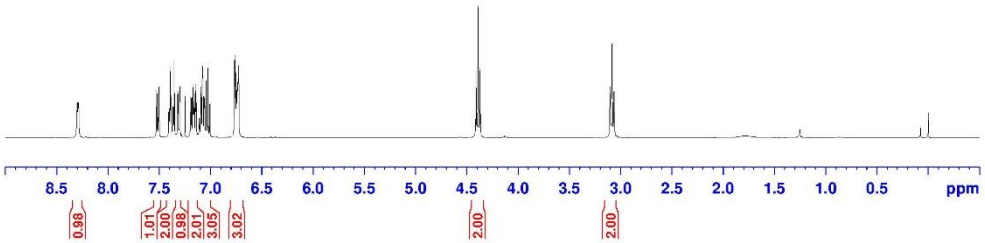

1116-20-1, BBFC1
157.82
147.87
143.08
136.71
136.45
135.57
135.41
130.14
127.51
127.21
125.96
125.84
125.54
125.19
124.13
123.68
120.80
115.66
111.13
77.30
76.98
76.66
54.20
29.29
19.70

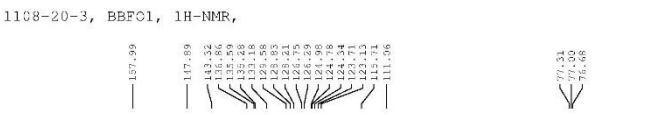

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

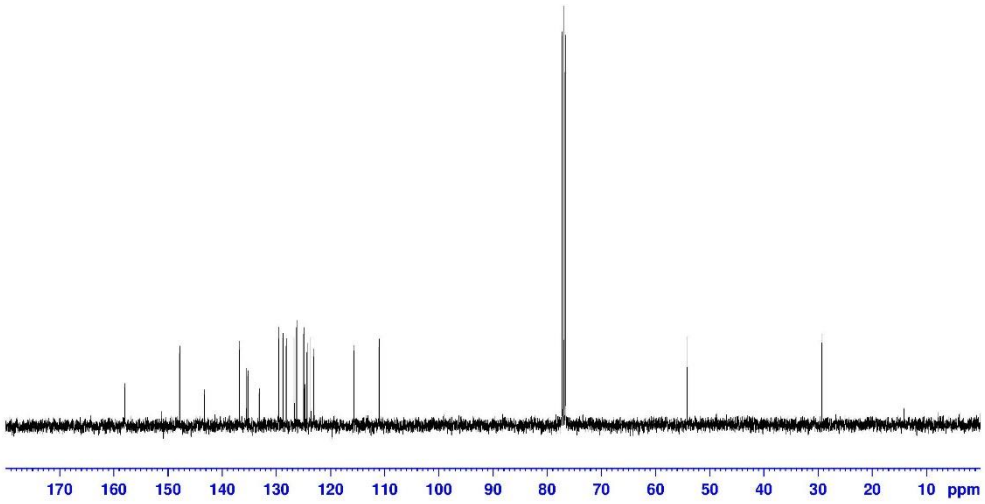

N
N
Cl

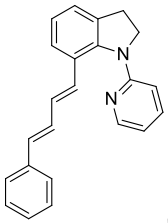
3k


1108-20-3, BBFC1, 1H-NMR,
7.318
7.303
7.299
7.249
7.195
7.194
7.177
7.176
7.168
7.162
7.150
7.144
7.116
7.110
7.098
7.092
7.080
7.077
7.073
7.064
7.060
7.046
7.027
7.008
6.769
6.761
6.750
6.743
6.737
6.733
6.728
4.413
4.393
4.373
3.105
3.085
3.065


8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.98
1.01
2.00
0.98
2.01
3.05
3.02
2.00
2.00

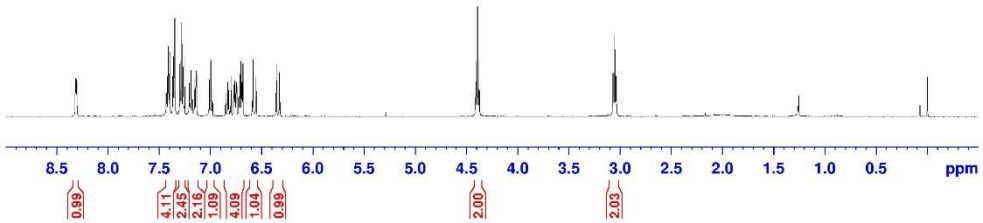

1108-20-3, BBFC1, 1H-NMR,
157.99
147.89
143.52
136.86
135.59
135.48
133.38
129.58
128.83
128.21
126.75
126.29
124.98
124.34
124.78
123.71
123.15
115.71
111.96
77.31
77.00
76.68
54.23
29.29


170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

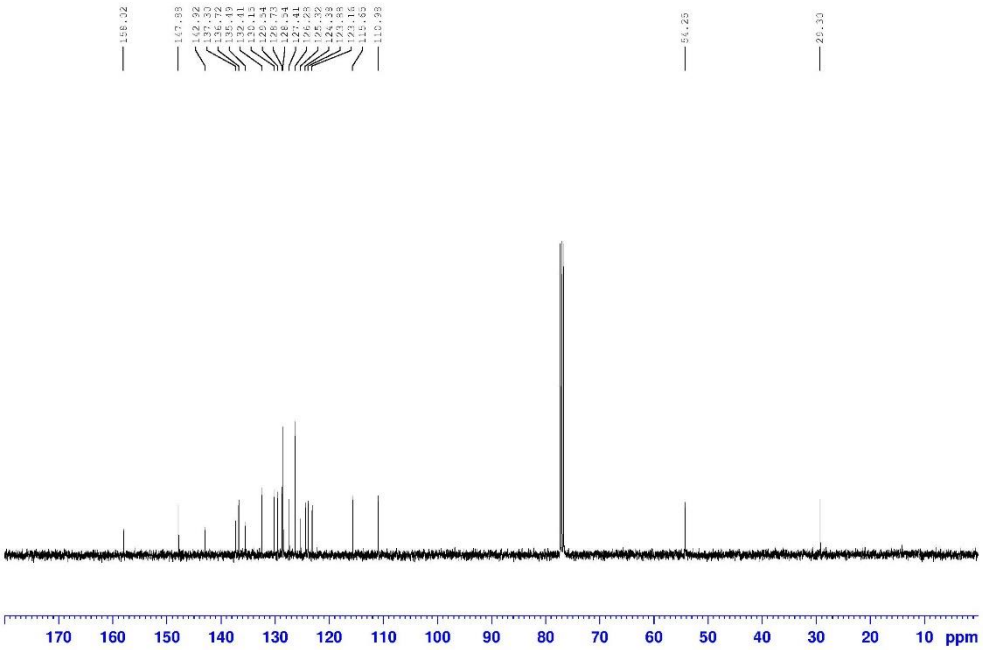


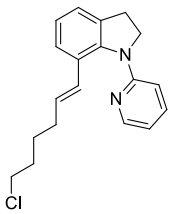
3l

1108--20-2, AV500



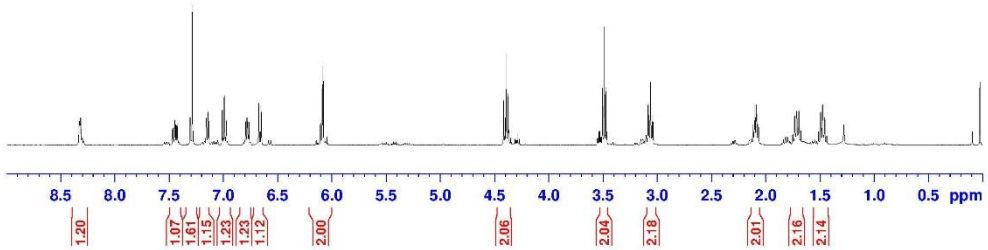
1108-20-2, BBFC1, 1H-NMR,



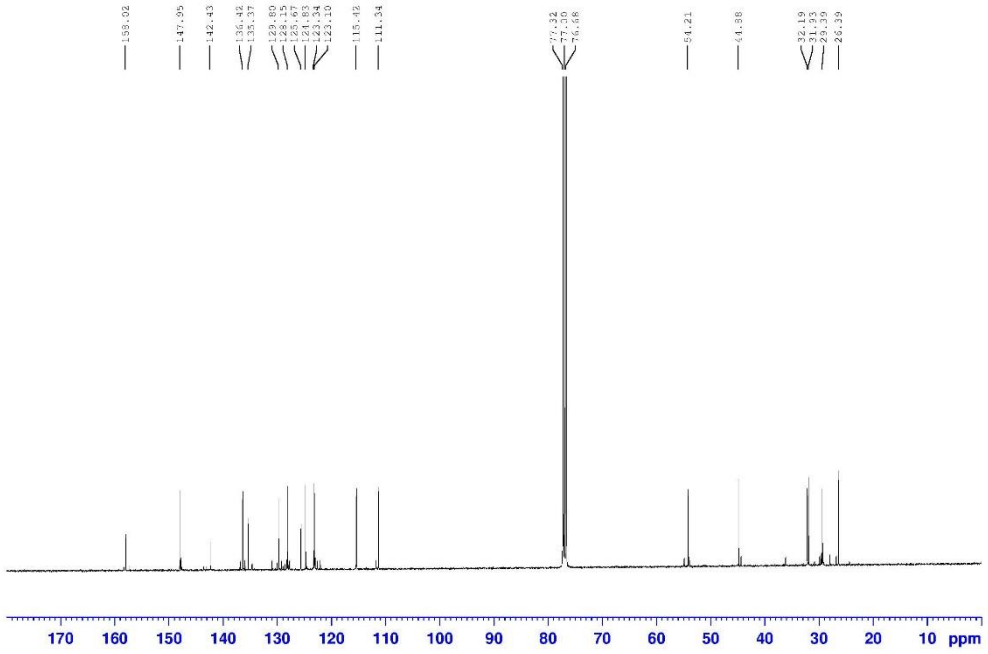


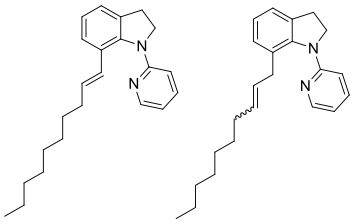
3m

2228-10-1A, BBFO1, Oct 14

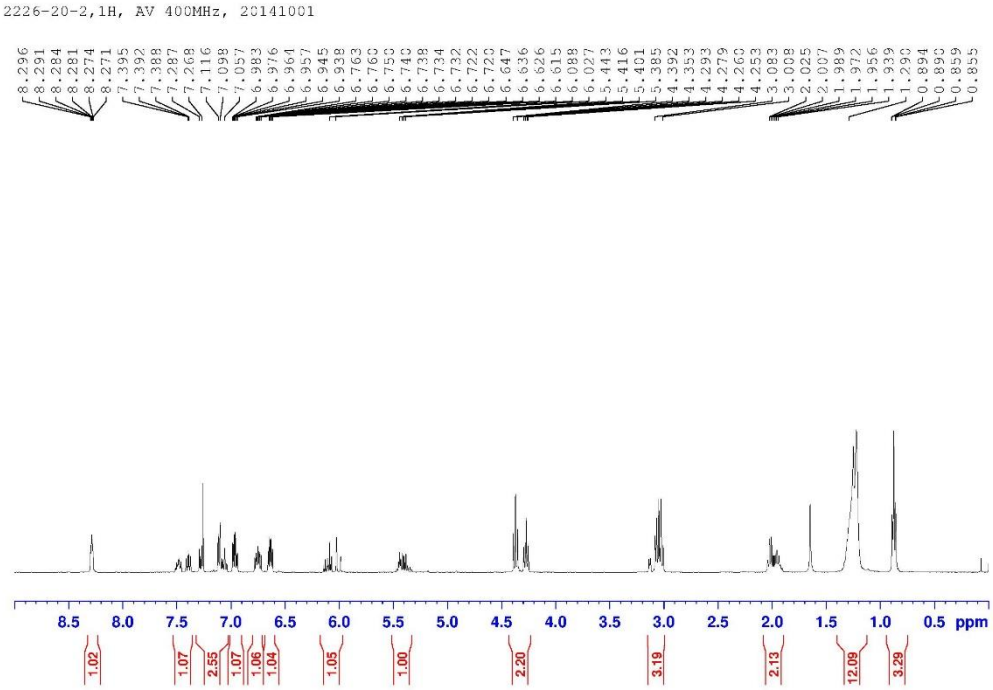


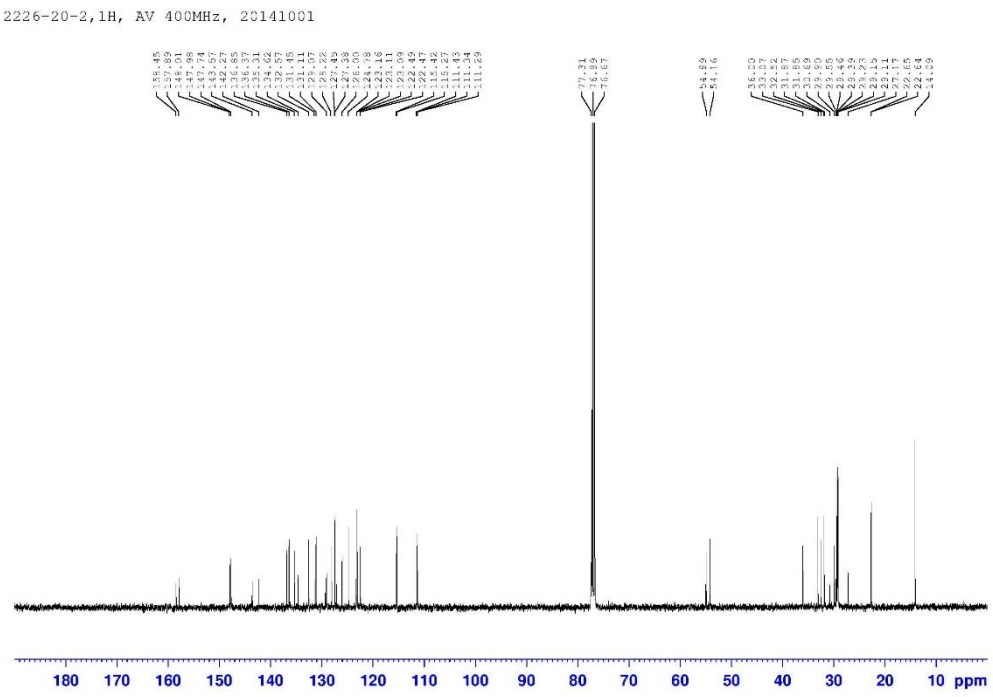
2228-10-1a, 1H CDCl3, oct2014, bbfc2

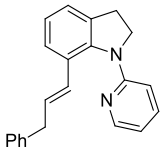




3n

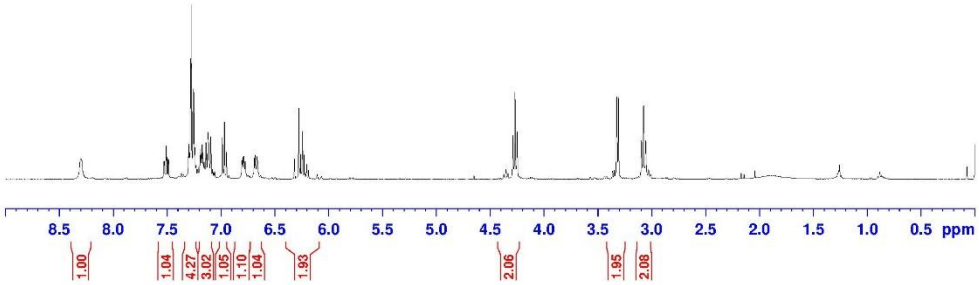

2226-20-2,1H, AV 400MHz, 20141001
8.296
8.291
8.284
8.281
8.274
8.271
7.395
7.392
7.388
7.287
7.268
7.116
7.098
7.057
6.983
6.976
6.961
6.957
6.945
6.938
6.763
6.762
6.753
6.740
6.738
6.734
6.732
6.722
6.720
6.647
6.636
6.626
6.615
6.088
6.027
5.443
5.416
5.401
5.385
4.392
4.353
4.293
4.279
4.260
4.253
3.083
3.008
2.025
2.007
1.989
1.972
1.956
1.939
1.290
0.894
0.890
0.859
0.855
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.02
1.07
1.07
2.55
1.07
1.06
1.04
1.05
1.00
2.20
3.19
2.13
12.09
3.29


2226-20-2,1H, AV 400MHz, 20141001
77.31
76.99
76.67
54.09
54.16
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

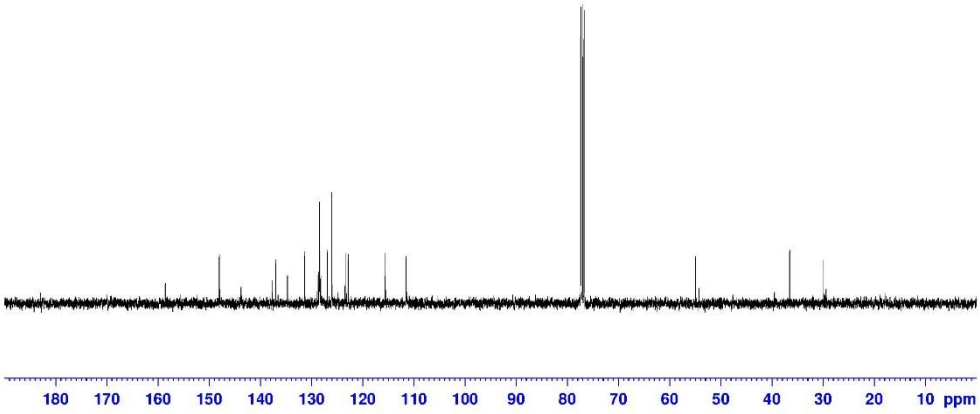


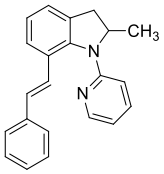
3o

2214-20, AV400, sep 14

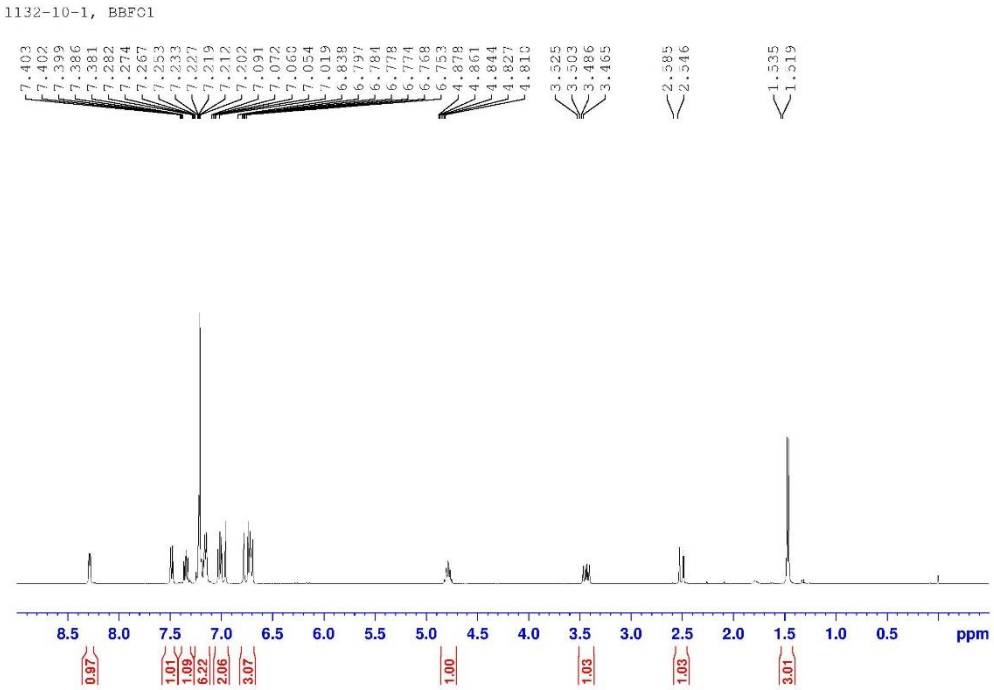


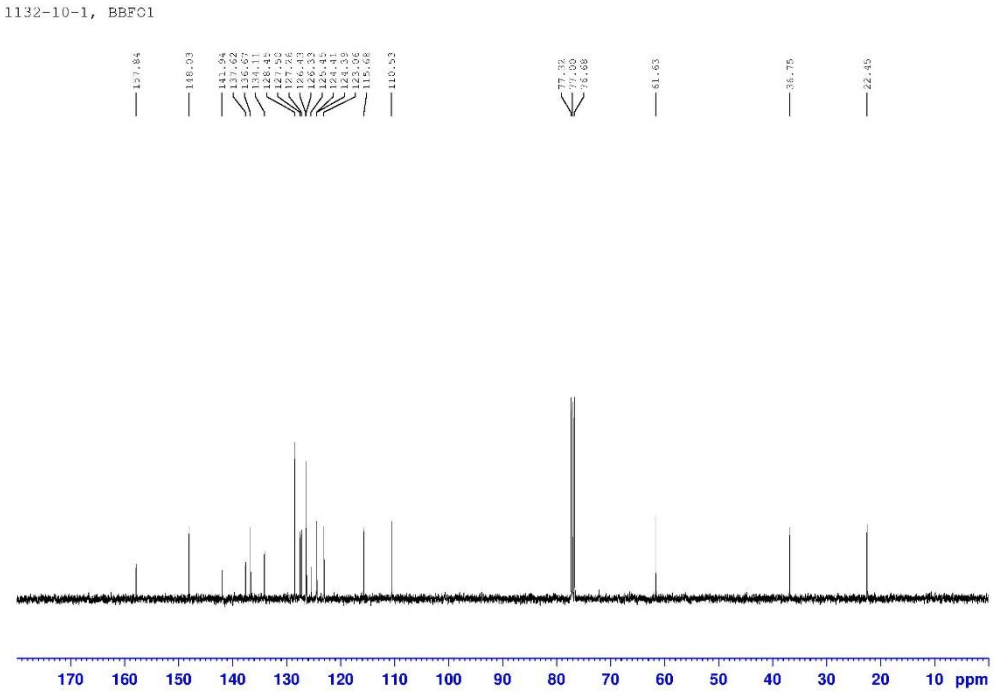
2196-1, AV400, sep 14

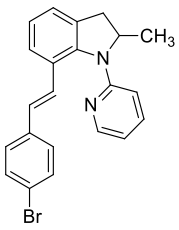



CH3
N
N

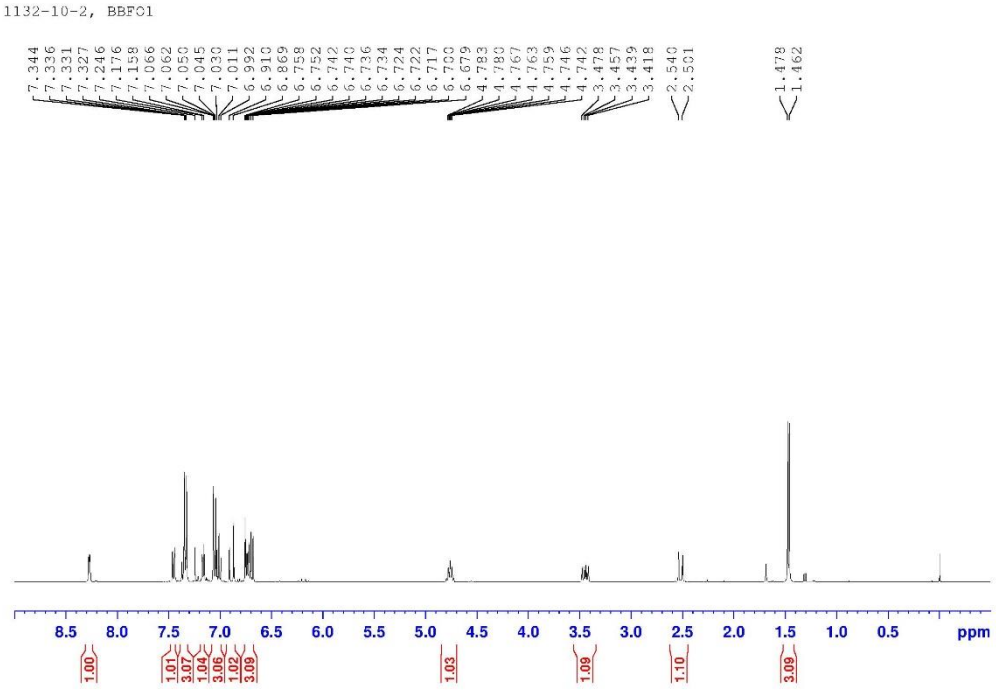
3p

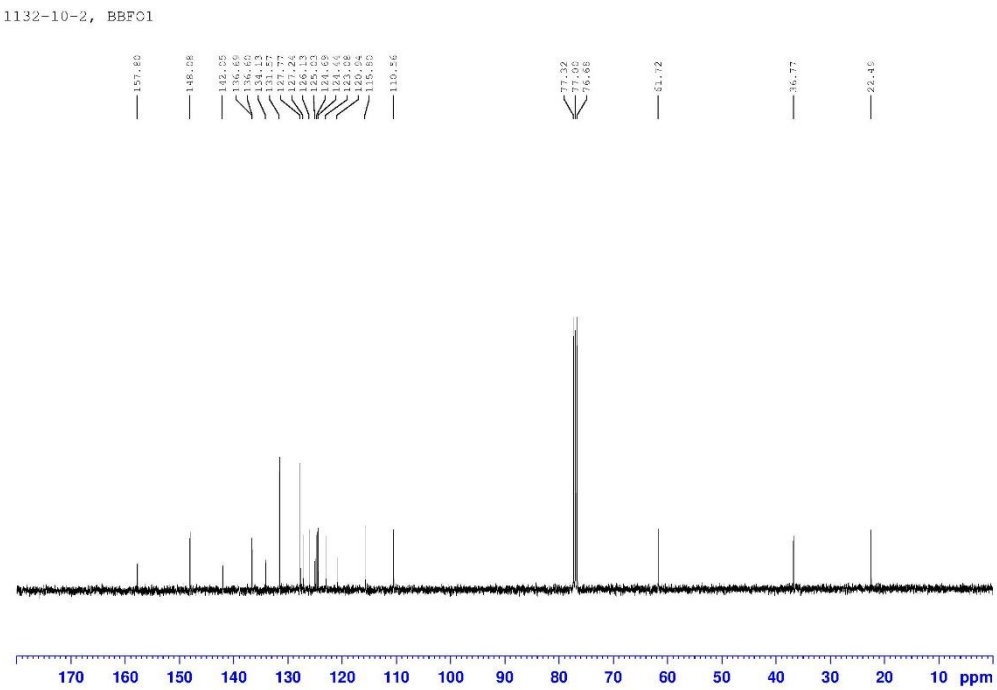

1132-10-1, BBFC1
7.403
7.402
7.399
7.386
7.381
7.282
7.274
7.267
7.253
7.233
7.227
7.219
7.212
7.202
7.091
7.072
7.060
7.054
7.019
6.838
6.797
6.784
6.778
6.774
6.768
6.753
4.878
4.861
4.844
4.827
4.810
3.525
3.503
3.486
3.465
2.585
2.546
1.535
1.519
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.97
1.01
1.09
6.22
2.06
3.07
1.00
1.03
1.03
3.01

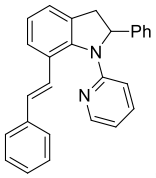

1132-10-1, BBFC1
157.84
148.03
141.94
137.62
136.67
134.11
128.45
127.50
127.26
126.43
126.32
124.45
124.41
124.39
123.06
115.68
110.53
77.32
77.00
76.68
61.63
36.75
22.45
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


CH3
N
N
Br

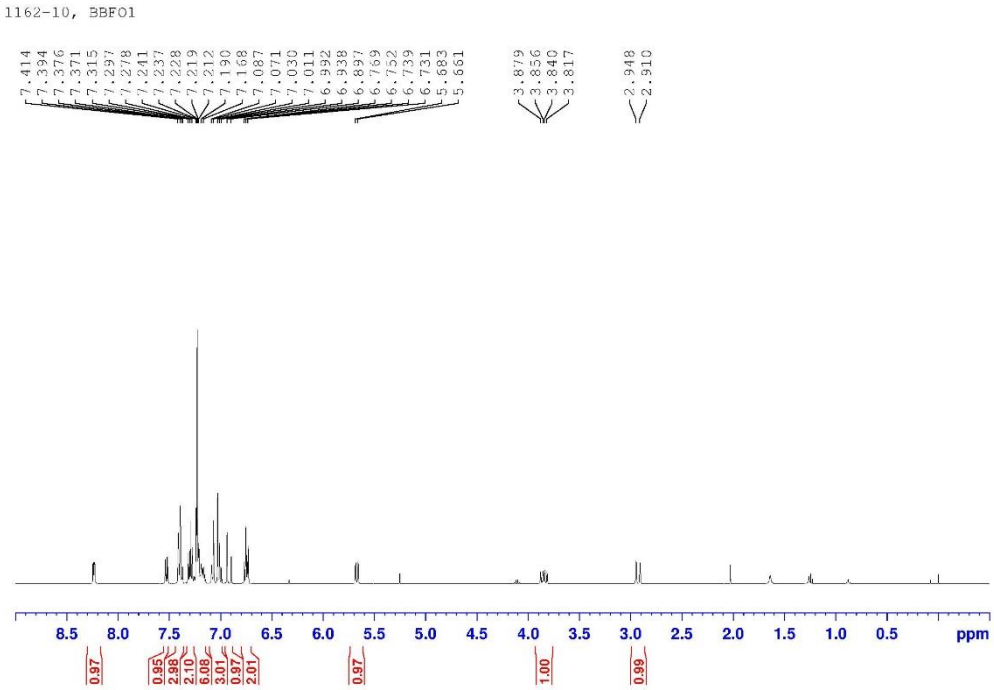
3q

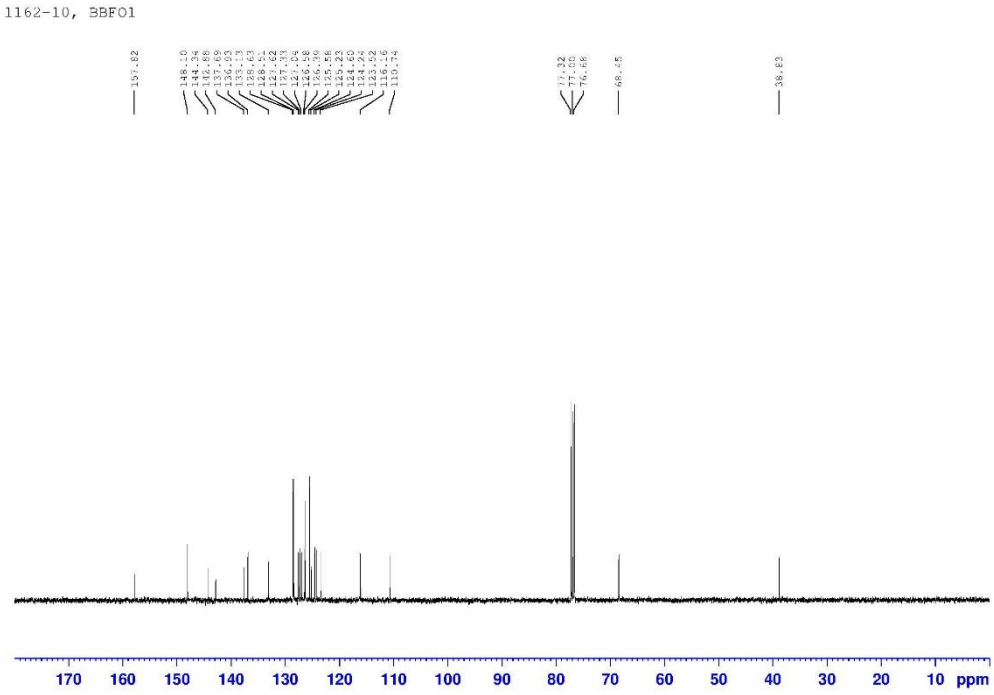

1132-10-2, BBFC1
7.344
7.336
7.331
7.327
7.246
7.176
7.158
7.066
7.062
7.053
7.045
7.030
7.011
6.992
6.910
6.869
6.758
6.752
6.742
6.740
6.736
6.734
6.724
6.722
6.717
6.700
6.679
4.783
4.780
4.767
4.763
4.759
4.746
4.742
3.478
3.457
3.439
3.418
2.540
2.501
1.478
1.462
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.01
3.07
1.04
3.06
1.02
3.09
1.03
1.09
1.10
3.09

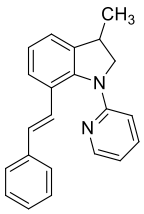

1132-10-2, BBFC1
157.80
148.08
142.05
136.69
136.60
134.13
131.57
127.77
127.24
126.13
125.03
124.69
124.66
123.08
120.04
115.80
110.56
77.32
77.00
76.68
61.72
36.77
22.46
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Ph
N
N

3r

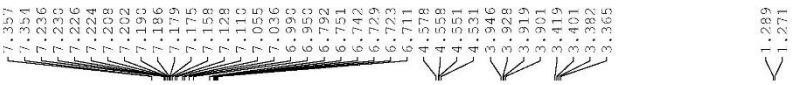

1162-10, BBFO1
7.414
7.394
7.376
7.371
7.315
7.297
7.278
7.241
7.237
7.228
7.219
7.212
7.190
7.168
7.087
7.071
7.030
7.011
6.992
6.938
6.897
6.769
6.752
6.739
6.731
5.683
5.661
3.879
3.856
3.840
3.817
2.948
2.910
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.97
0.95
2.98
2.10
6.08
3.01
0.97
2.01
0.97
1.00
0.99

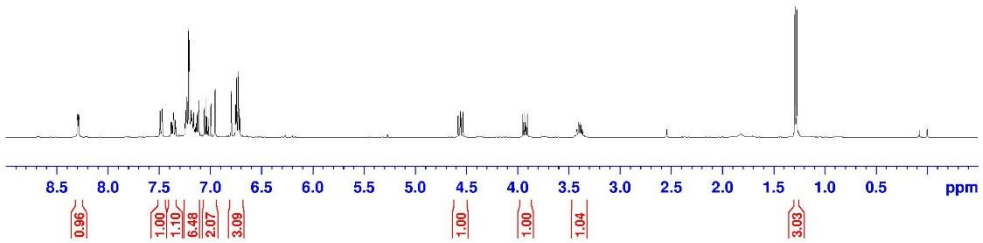

1162-10, BBFO1
159.82
148.10
144.34
142.88
137.69
136.93
133.13
128.63
128.51
127.62
127.33
126.98
126.38
125.86
125.23
124.60
124.24
123.52
116.16
110.74
77.32
77.00
76.68
68.45
38.83
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



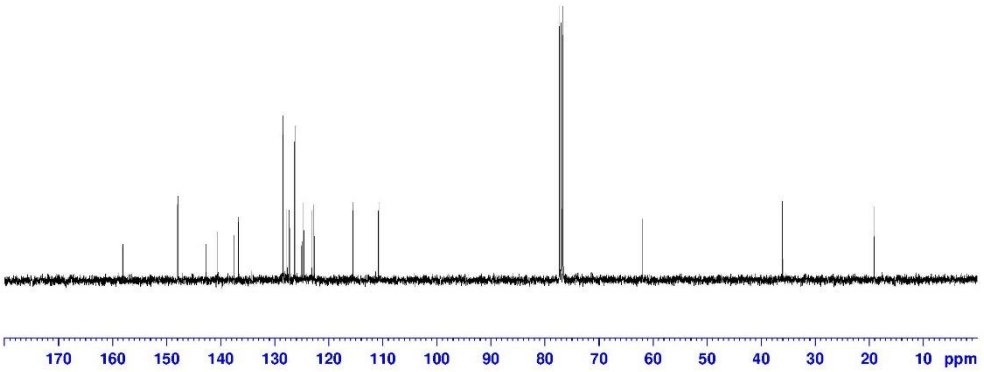
3s

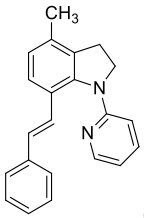
1158-10, BBFO1





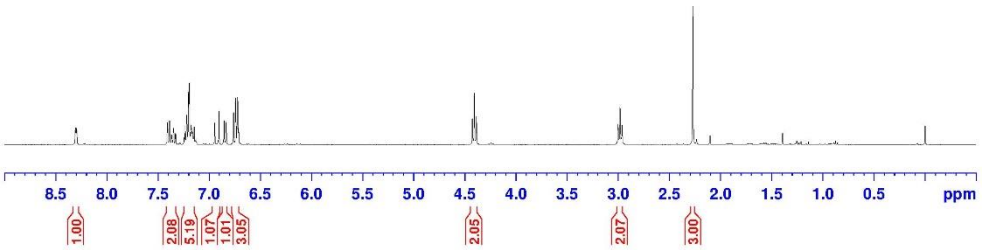
1158-10, BBFO1



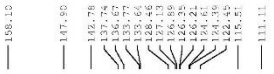


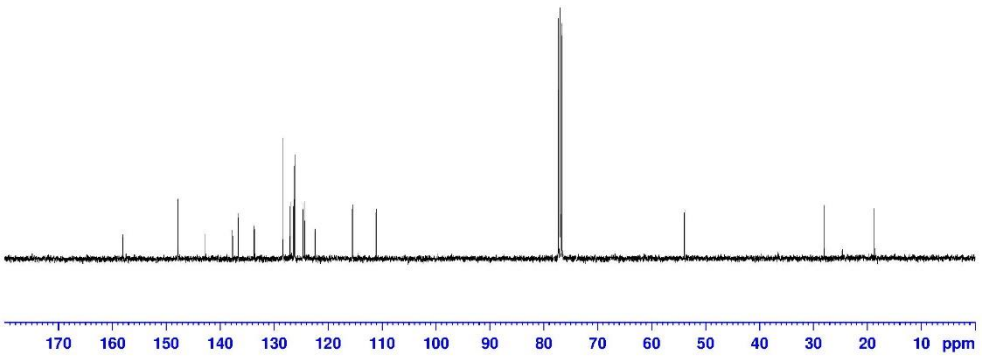
3t

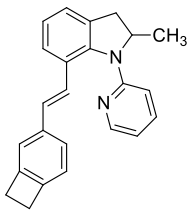
2104-10, 1H NMR, CDCl3, BBFO-01, Jul 14



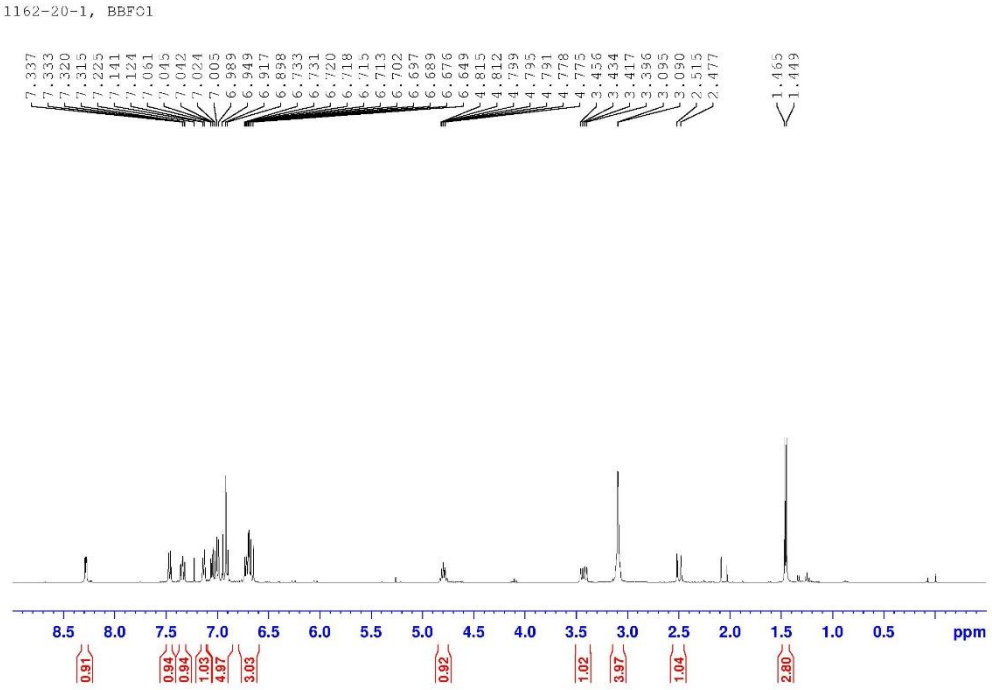
2104-10, 1H NMR, CDCl3, BBFO-01, Jul 14

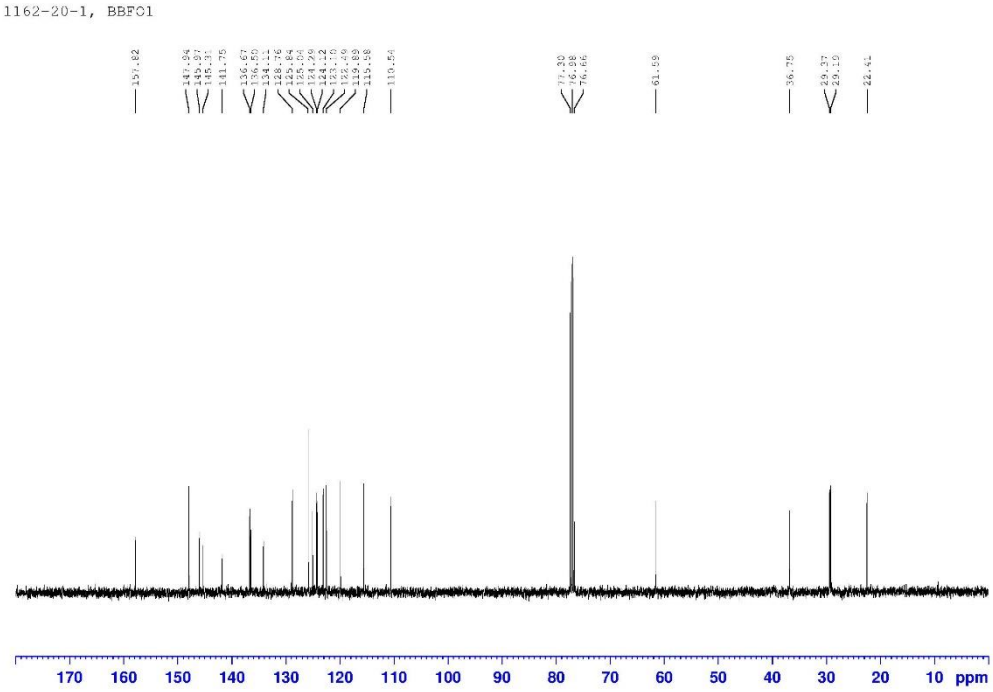


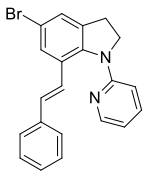




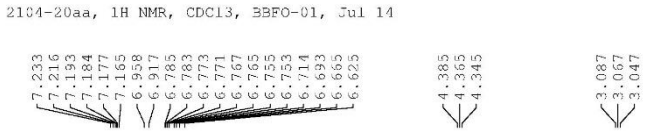
3u

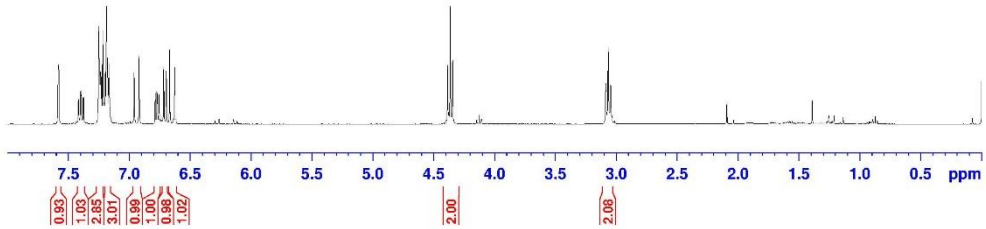

1162-20-1, BBFC1
7.337
7.333
7.320
7.315
7.225
7.141
7.124
7.061
7.045
7.042
7.024
7.005
6.989
6.949
6.917
6.898
6.733
6.731
6.720
6.718
6.715
6.713
6.702
6.697
6.689
6.676
6.649
4.815
4.812
4.799
4.795
4.791
4.778
4.775
3.456
3.434
3.417
3.396
3.095
3.090
2.515
2.477
1.465
1.449
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.91
0.94
0.94
1.03
4.97
3.03
0.92
1.02
3.97
1.04
2.80

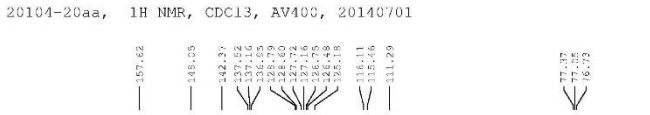

1162-20-1, BBFC1
157.82
147.94
145.07
141.75
136.67
128.76
125.84
125.04
124.29
123.72
122.49
119.89
110.54
77.30
76.98
76.66
61.59
36.75
29.37
29.10
22.61
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

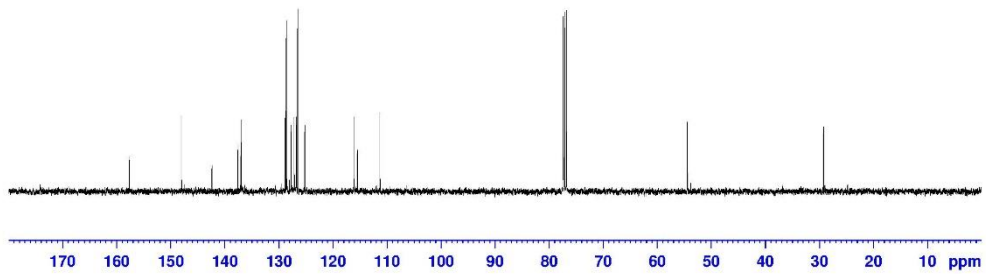

Br
N
N

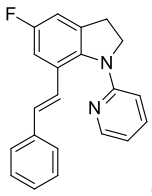
3v


2104-20aa, 1H NMR, CDCl3, BBFO-01, Jul 14
7.233
7.216
7.193
7.184
7.177
7.165
6.958
6.917
6.785
6.783
6.773
6.771
6.767
6.765
6.755
6.753
6.714
6.693
6.665
6.625
4.385
4.365
4.345
3.087
3.067
3.047

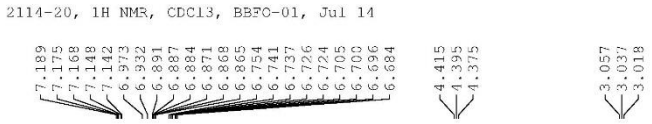

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.93
1.03
2.85
3.01
0.98
1.00
0.98
1.02
2.00
2.08

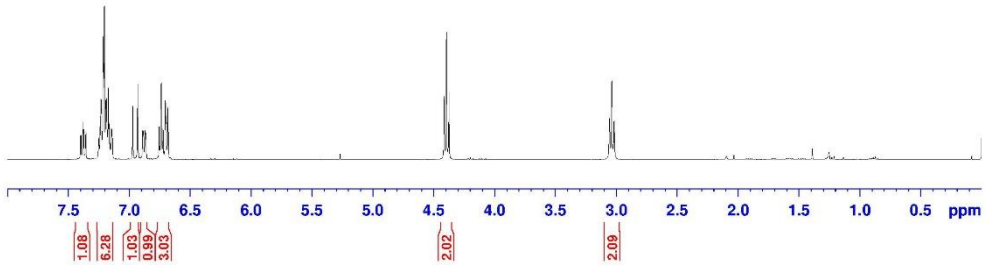

20104-20aa, 1H NMR, CDCl3, AV400, 20140701
157.62
148.05
142.37
137.62
137.16
136.55
128.89
128.60
127.72
127.16
126.75
126.18
125.18
116.11
115.46
111.29
77.37
77.05
76.73
54.37
29.16

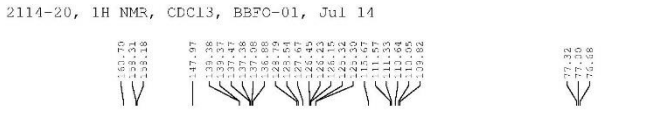

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

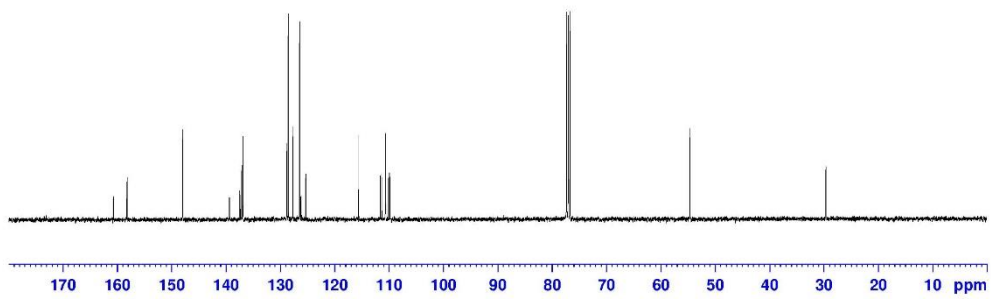


3w

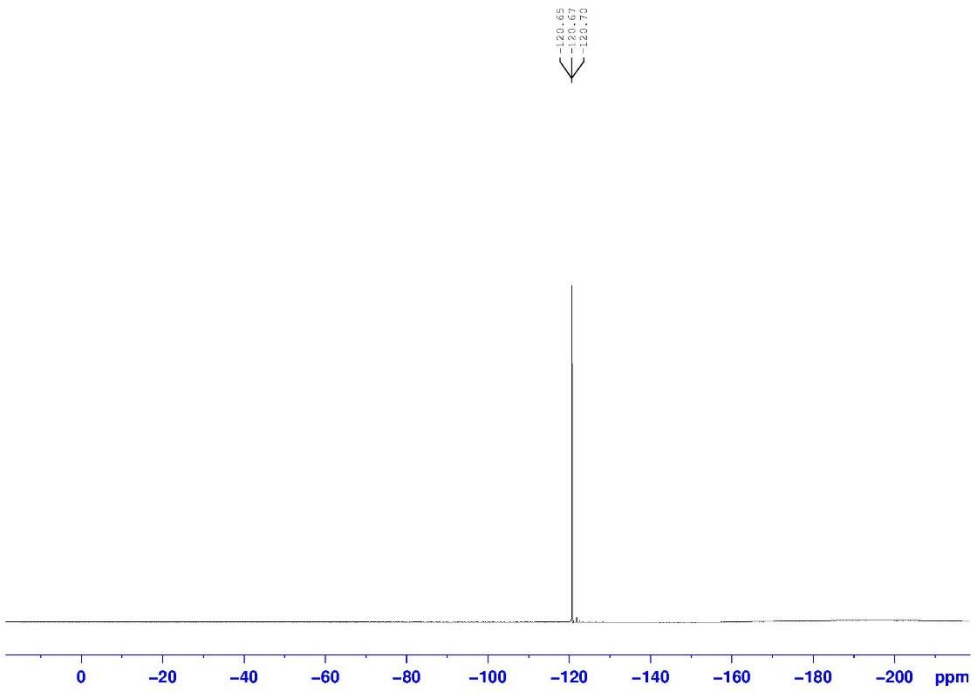

2114-20, 1H NMR, CDCl3, BBFO-01, Jul 14
7.189
7.175
7.168
7.148
7.142
6.973
6.932
6.891
6.887
6.884
6.871
6.868
6.865
6.754
6.741
6.737
6.726
6.724
6.705
6.703
6.696
6.684
4.415
4.395
4.375
3.057
3.037
3.018

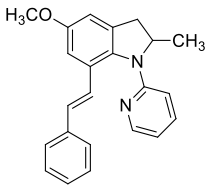

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.08
6.28
1.03
0.99
3.03
2.02
2.09


2114-20, 1H NMR, CDCl3, BBFO-01, Jul 14

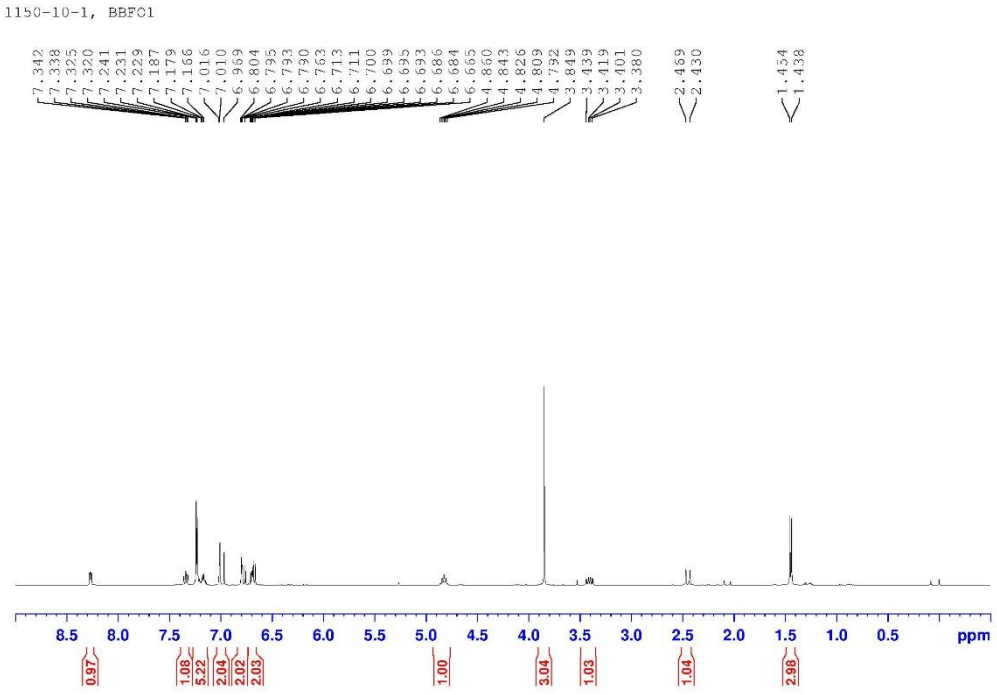

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

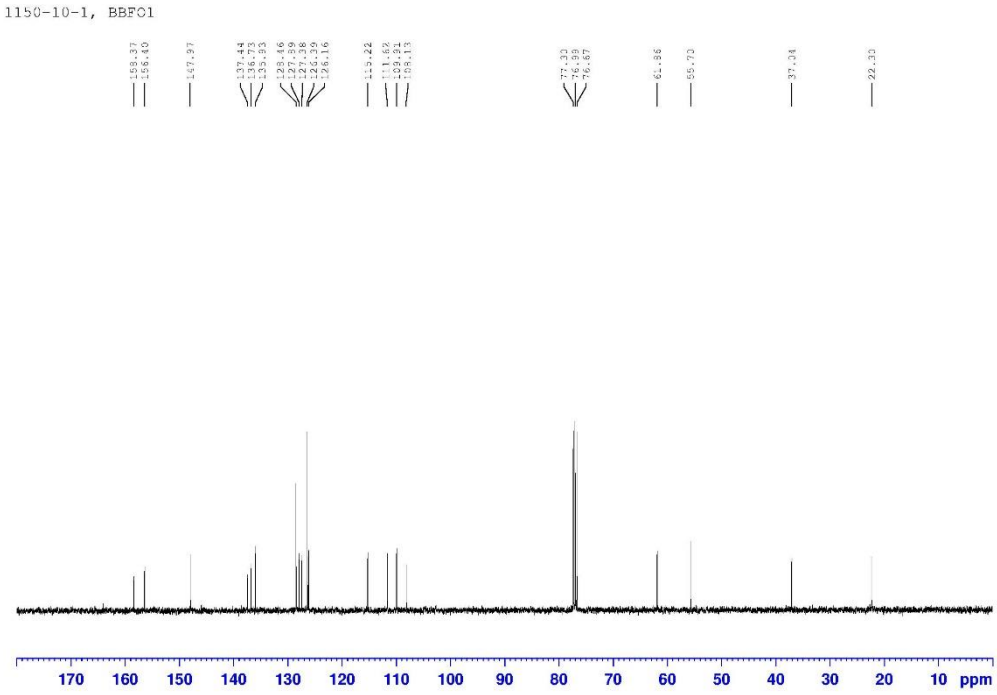
2114-20, 1H NMR, CDCl3, BBFO-01, Jul 14

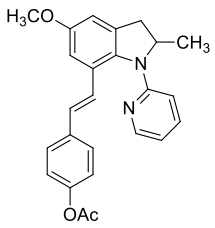




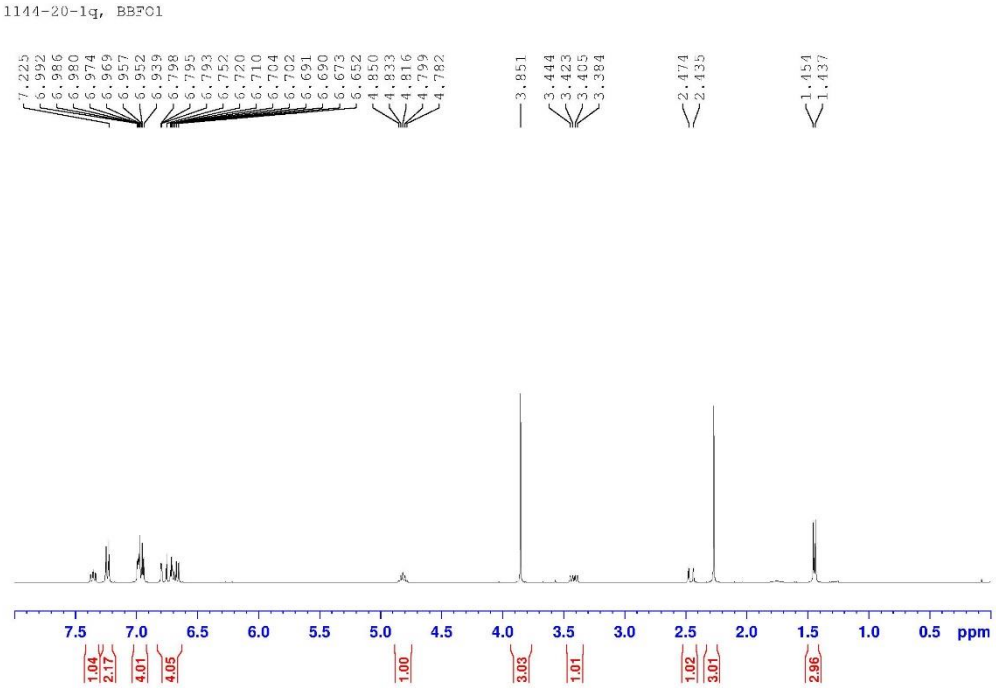
3x

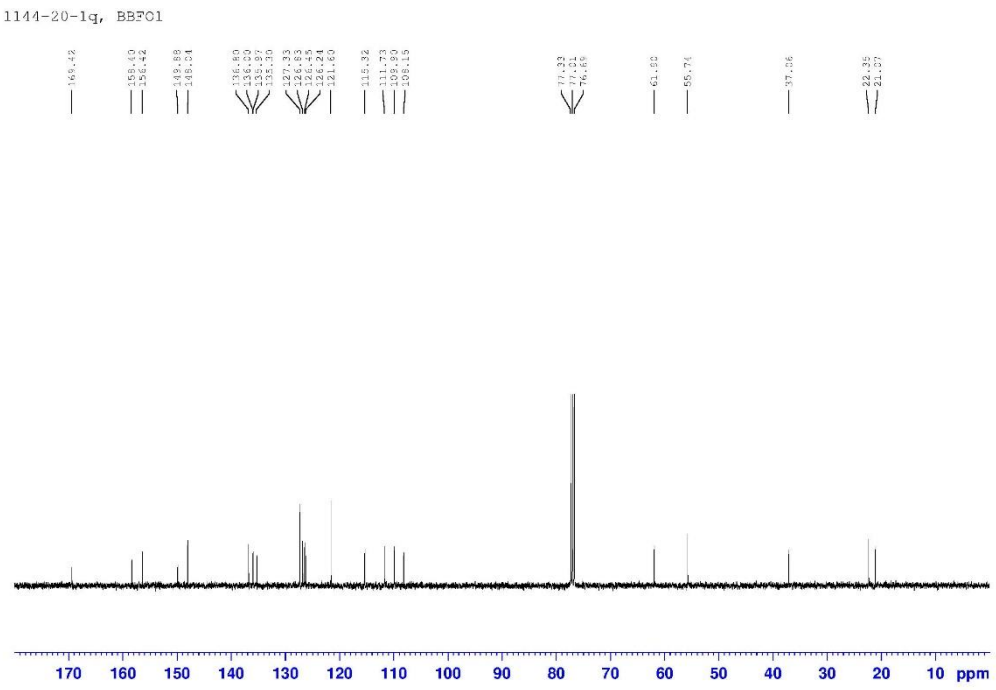

1150-10-1, BBFO1
7.342
7.338
7.325
7.320
7.241
7.231
7.229
7.187
7.179
7.166
7.016
7.010
6.969
6.804
6.795
6.793
6.730
6.763
6.713
6.711
6.700
6.699
6.695
6.693
6.686
6.684
6.665
4.860
4.843
4.826
4.809
4.792
3.849
3.439
3.419
3.401
3.380
2.469
2.430
1.454
1.438
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.97
1.08
5.22
2.04
2.02
2.03
1.00
3.04
1.03
1.04
2.98

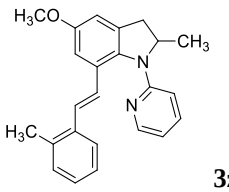

1150-10-1, BBFO1
159.37
156.40
147.97
137.44
136.73
135.93
128.46
127.39
127.38
126.39
126.16
115.22
111.62
109.91
105.13
77.30
77.04
76.67
61.86
56.70
37.04
22.30
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


H3CO
CH3
N
N
OAc

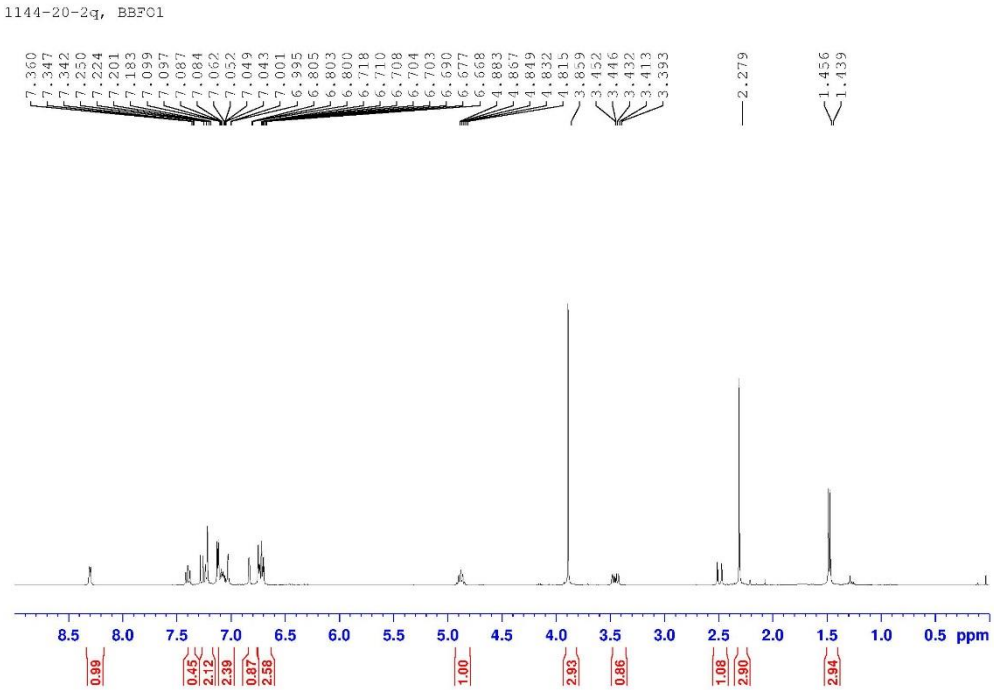
3y

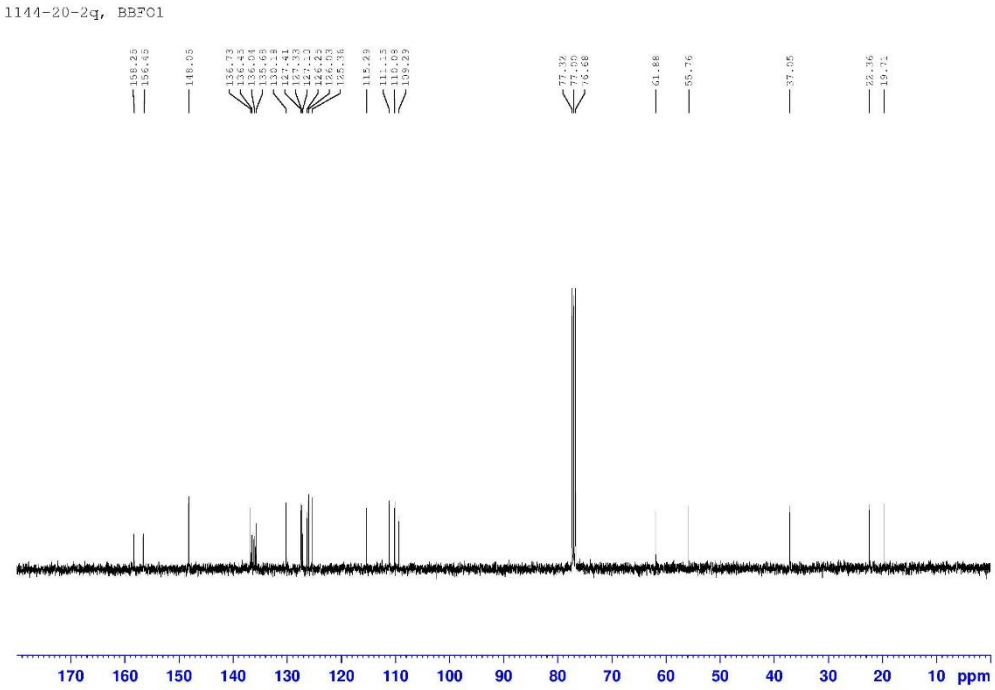

1144-20-1q, BBF01
7.225
6.992
6.986
6.980
6.974
6.969
6.957
6.952
6.939
6.798
6.795
6.793
6.752
6.720
6.710
6.704
6.702
6.691
6.690
6.673
6.652
4.850
4.833
4.816
4.799
4.782
3.851
3.444
3.423
3.405
3.384
2.474
2.435
1.454
1.437
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.04
2.17
4.01
4.05
1.00
3.03
1.01
1.02
3.01
2.96

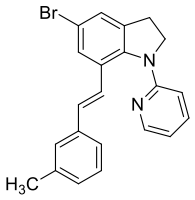

1144-20-1q, BBF01
168.42
158.40
156.42
149.88
148.84
136.80
136.09
135.87
135.36
127.33
126.83
126.55
126.24
121.60
115.32
111.73
109.80
108.15
77.32
77.01
76.69
61.80
55.74
37.86
22.35
21.07
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


H3CO
CH3
N
N
H3C

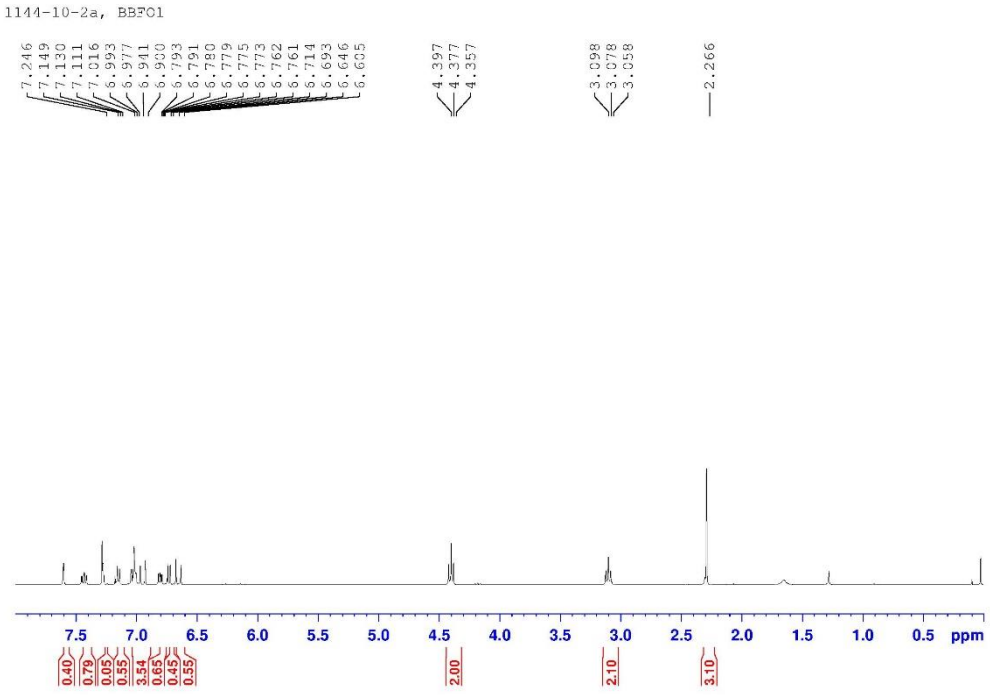
3z

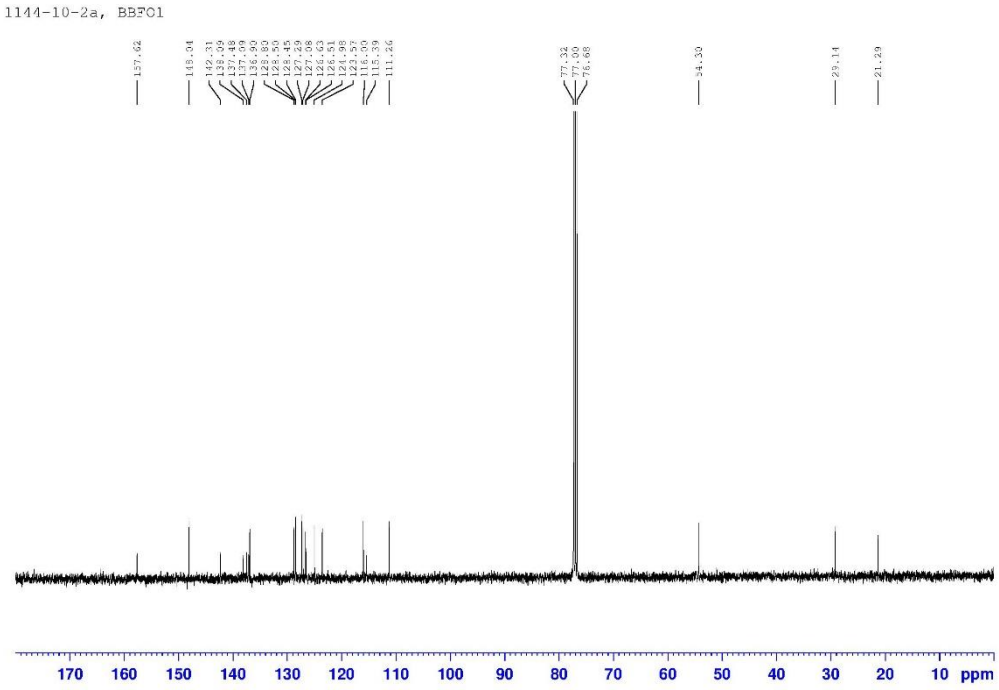

1144-20-2q, BBF01
7.360
7.347
7.342
7.250
7.224
7.201
7.183
7.099
7.097
7.087
7.084
7.062
7.052
7.049
7.043
7.001
6.995
6.805
6.803
6.800
6.718
6.710
6.708
6.704
6.703
6.690
6.677
6.668
4.883
4.867
4.849
4.832
4.815
3.859
3.452
3.446
3.432
3.413
3.393
2.279
1.456
1.439
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.99
0.45
2.12
2.39
0.87
2.58
1.00
2.93
0.86
1.08
2.90
2.94

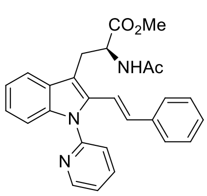

1144-20-2q, BBF01
156.25
156.45
148.05
136.73
136.45
136.04
135.68
133.18
127.41
127.33
127.13
126.23
126.03
125.36
115.29
111.15
110.68
109.29
77.32
77.00
76.68
61.88
55.76
37.05
22.36
19.71
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Br
N
N
H3C

3aa

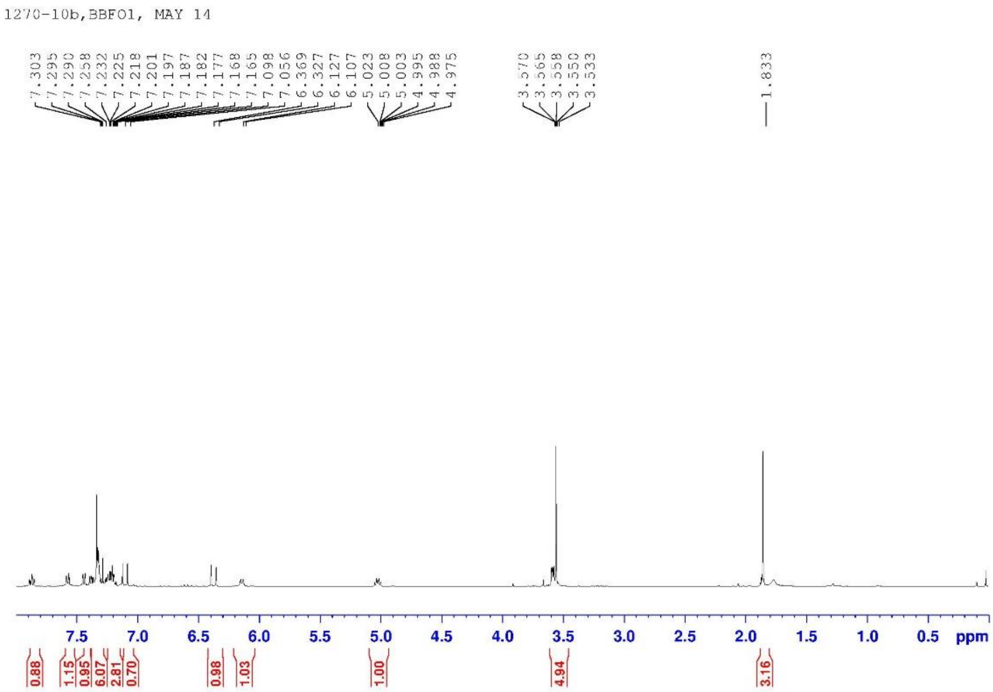

1144-10-2a, BBF01
7.246
7.149
7.130
7.111
7.016
6.993
6.977
6.941
6.930
6.793
6.791
6.780
6.779
6.775
6.773
6.762
6.761
6.714
6.693
6.646
6.605
4.397
4.377
4.357
3.098
3.078
3.058
2.266
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.40
0.79
0.05
0.55
3.54
0.65
0.45
0.55
2.00
2.10
3.10


1144-10-2a, BBF01
157.62
148.04
142.31
138.09
137.48
137.09
136.80
128.80
128.50
128.45
127.49
127.08
126.63
126.51
124.98
123.57
116.00
115.39
111.26
77.32
77.00
76.68
34.30
29.14
21.29
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

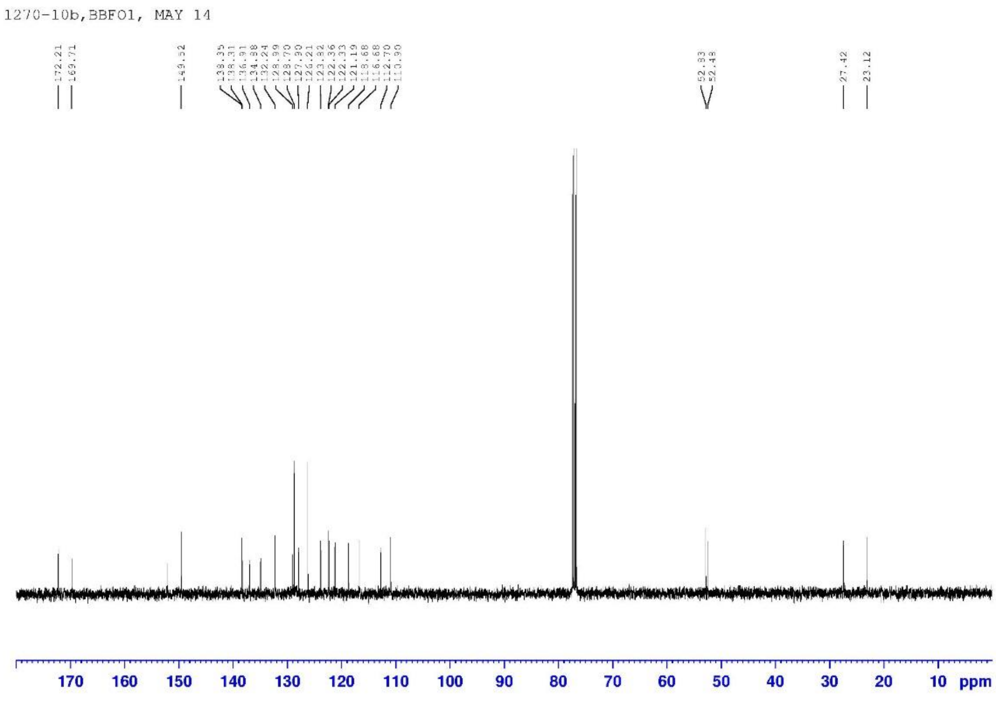


CO2Me
NHAc
N
N

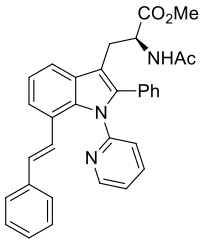
5a



1270-10b,BBFO1, MAY 14
7.303
7.295
7.290
7.258
7.232
7.225
7.218
7.201
7.197
7.187
7.182
7.177
7.168
7.165
7.098
7.056
6.369
6.327
6.127
6.107
5.023
5.008
5.003
4.995
4.988
4.975
3.570
3.565
3.558
3.550
3.533
1.833
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.88
1.15
0.95
6.07
2.81
0.70
0.98
1.03
1.00
4.94
3.16

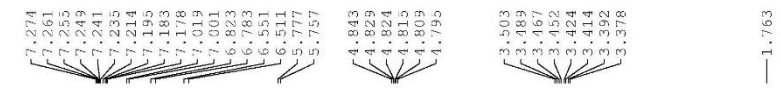


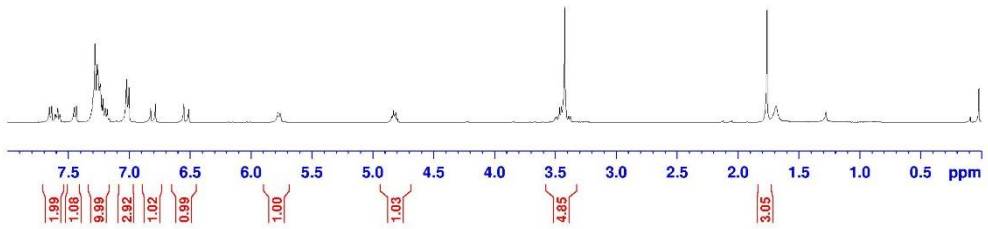
1270-10b,BBFO1, MAY 14
172.21
169.71
52.83
52.48
27.42
23.12
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



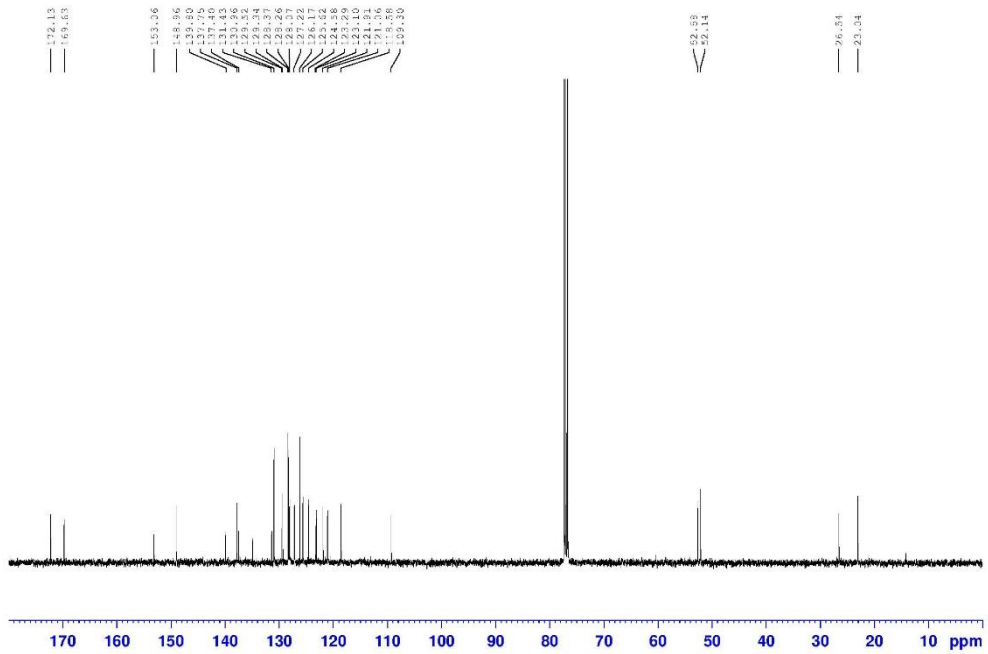
5b

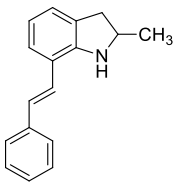
2070-10, 1H NMR, CDCl3, BBFO-01, Jul 14



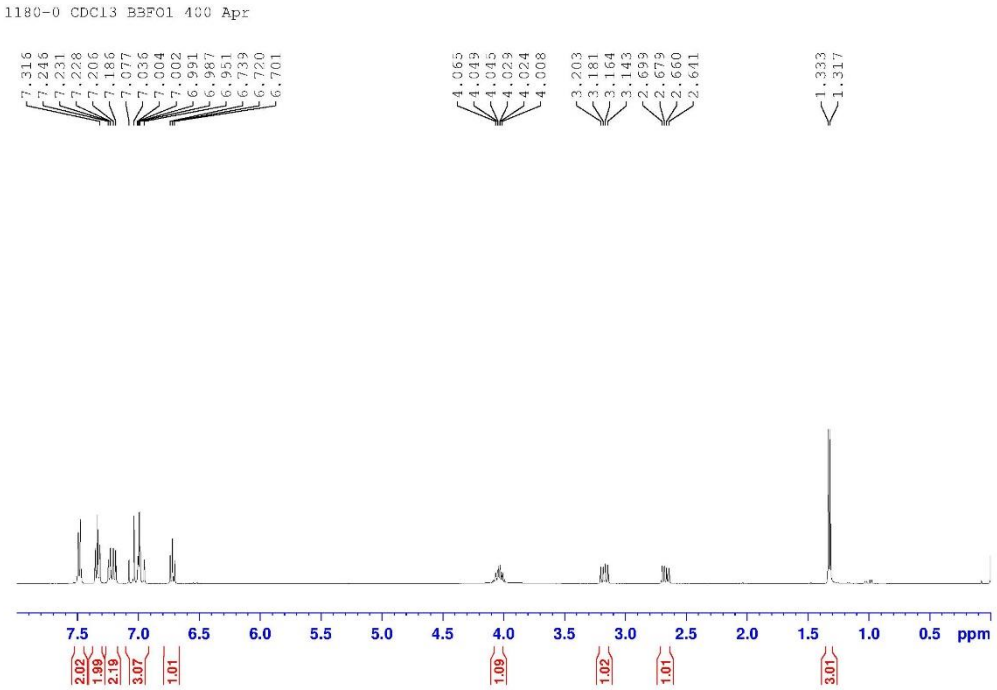


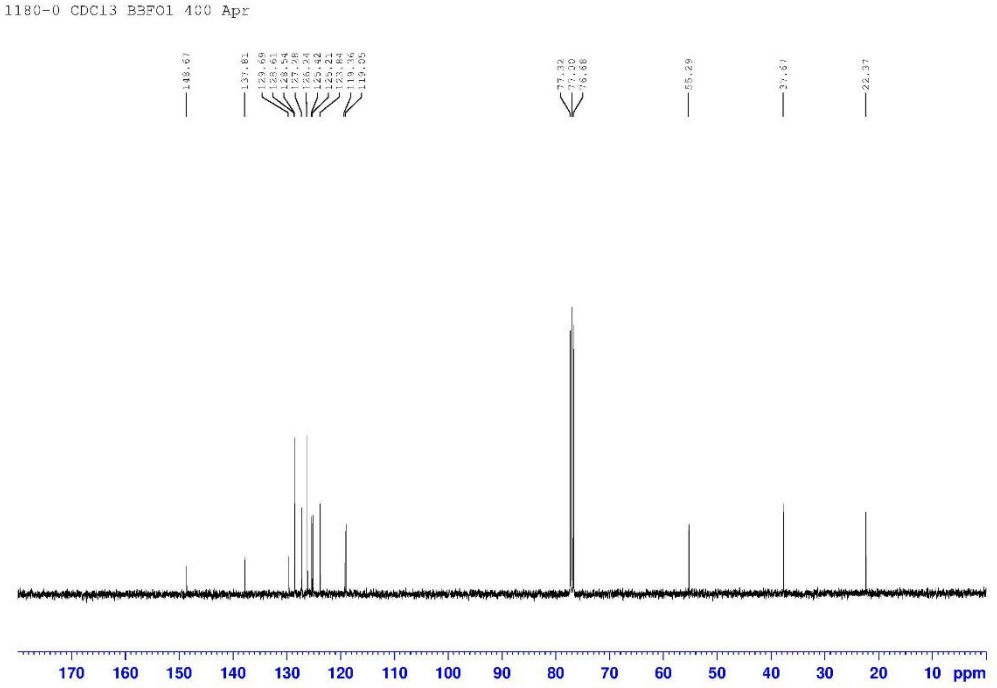
2070-20, 13C NMR, CDCl3, AV400, 20140703

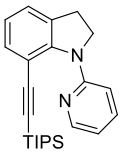




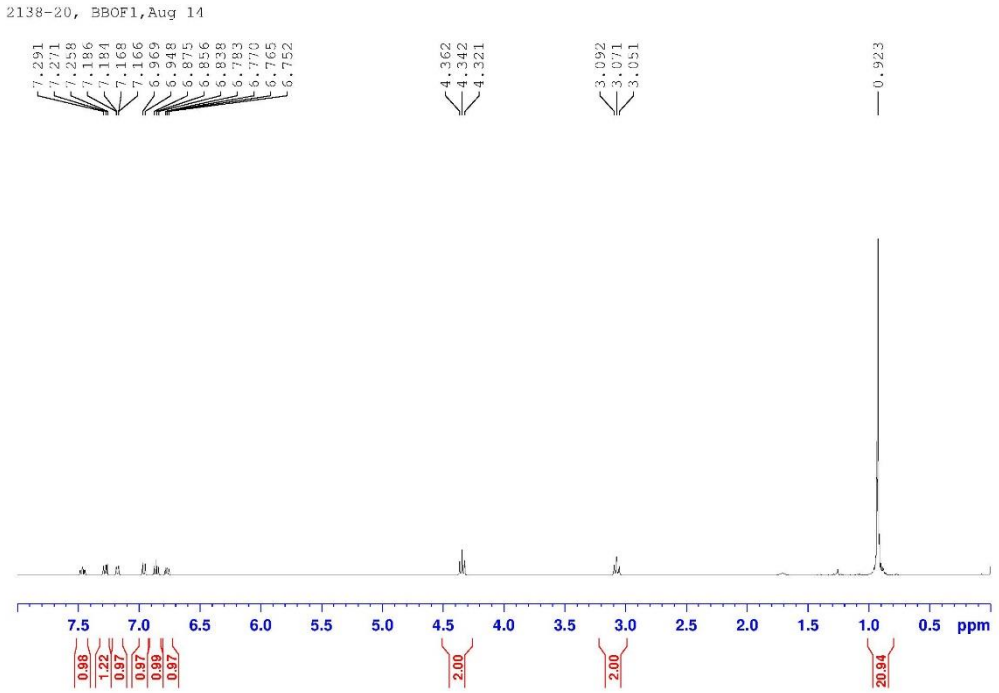
3p'

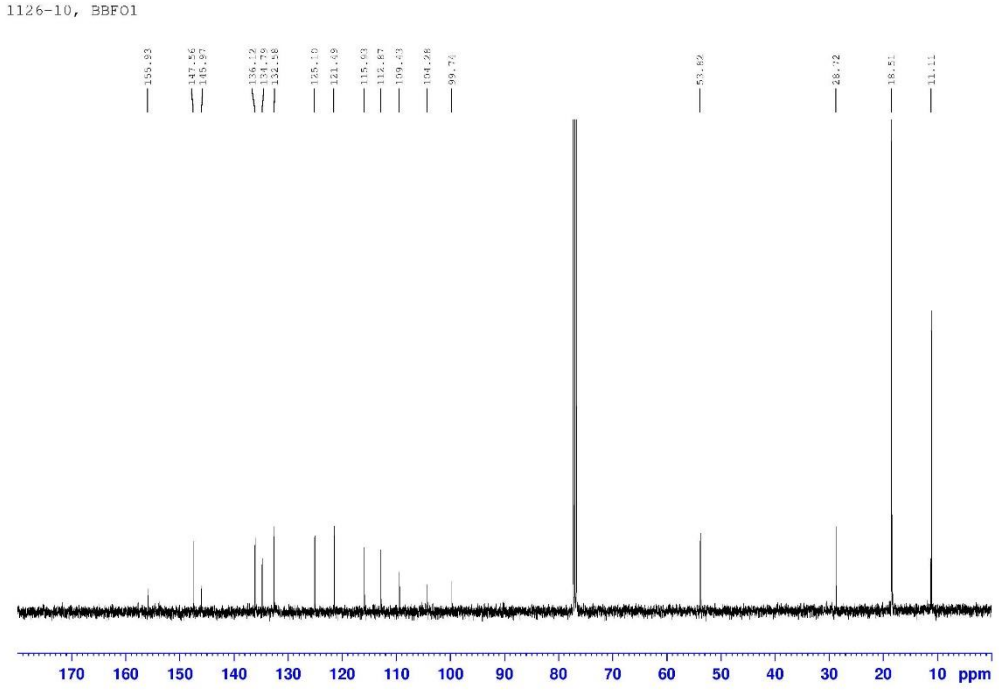

1180-0 CDCl3 BBFO1 400 Apr
7.316
7.246
7.231
7.228
7.206
7.186
7.077
7.036
7.004
7.002
6.991
6.987
6.951
6.739
6.720
6.701
4.065
4.049
4.045
4.029
4.024
4.008
3.203
3.181
3.164
3.143
2.699
2.679
2.660
2.641
1.333
1.317
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.02
1.99
2.19
3.07
1.01
1.09
1.02
1.01
3.01

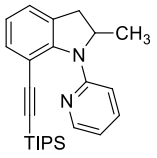

1180-0 CDCl3 BBFO1 400 Apr
148.67
137.82
129.69
128.61
128.54
127.38
126.24
125.42
125.21
123.84
119.76
119.05
77.32
77.00
76.68
55.29
37.67
22.37
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


N
N
TIPS

6a

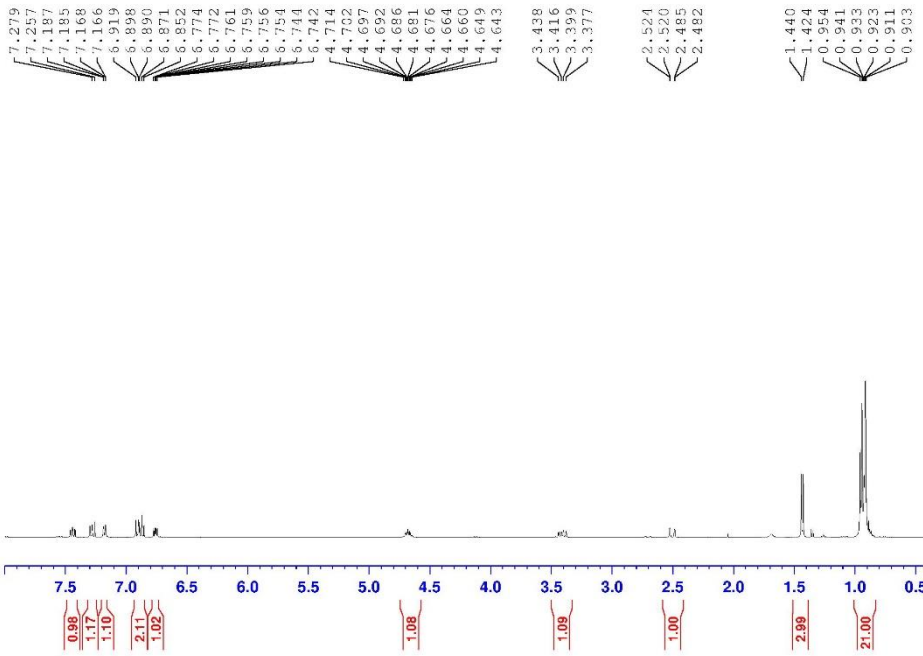

2138-20, BBOF1,Aug 14
7.291
7.271
7.258
7.186
7.184
7.168
7.166
6.969
6.948
6.875
6.856
6.838
6.783
6.770
6.765
6.752
4.362
4.342
4.321
3.092
3.071
3.051
0.923
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.98
1.22
0.97
0.97
0.99
0.97
2.00
2.00
20.94


1126-10, BBFO1
155.93
147.56
145.97
136.12
134.79
132.58
125.10
121.49
115.03
112.87
109.43
104.26
99.76
53.82
28.72
18.51
11.11
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

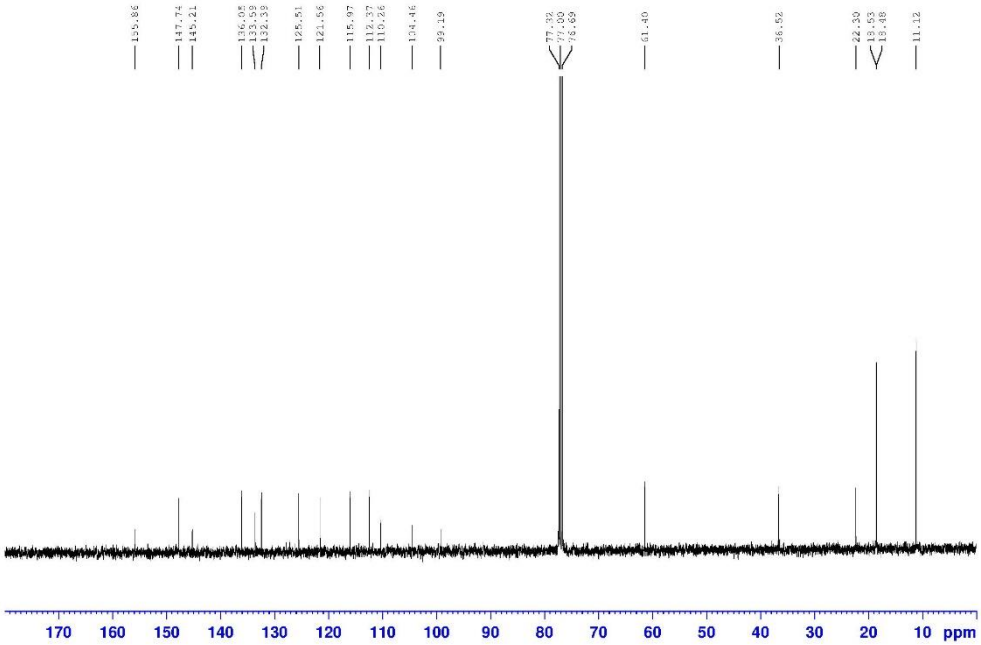


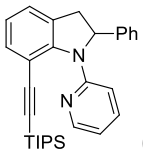
6b

1206-20-1b CDCl3 BBFO1 400 Apr

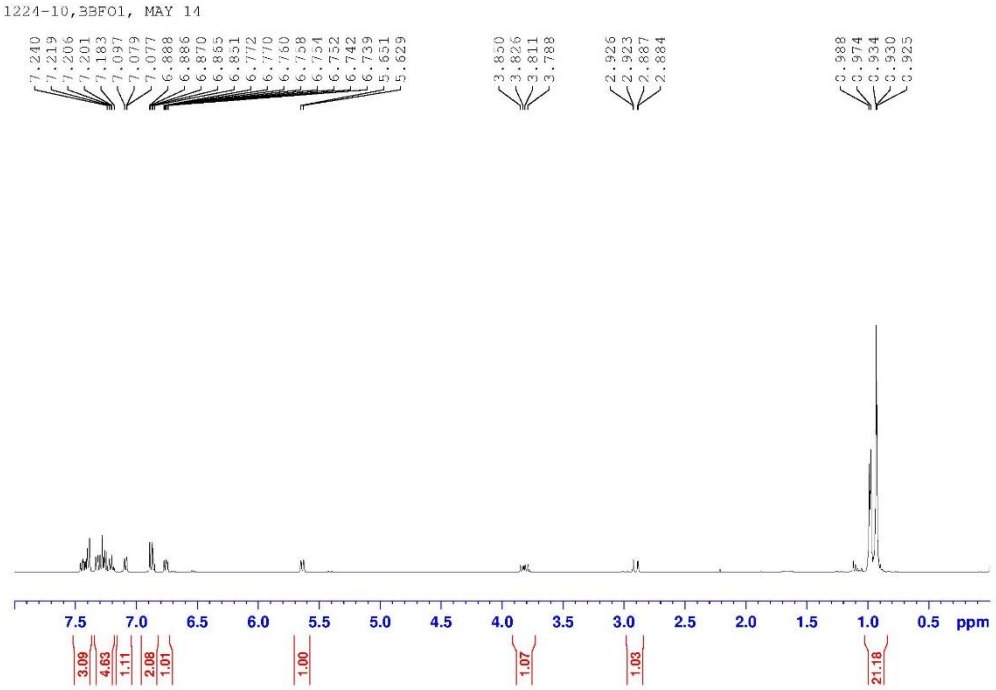


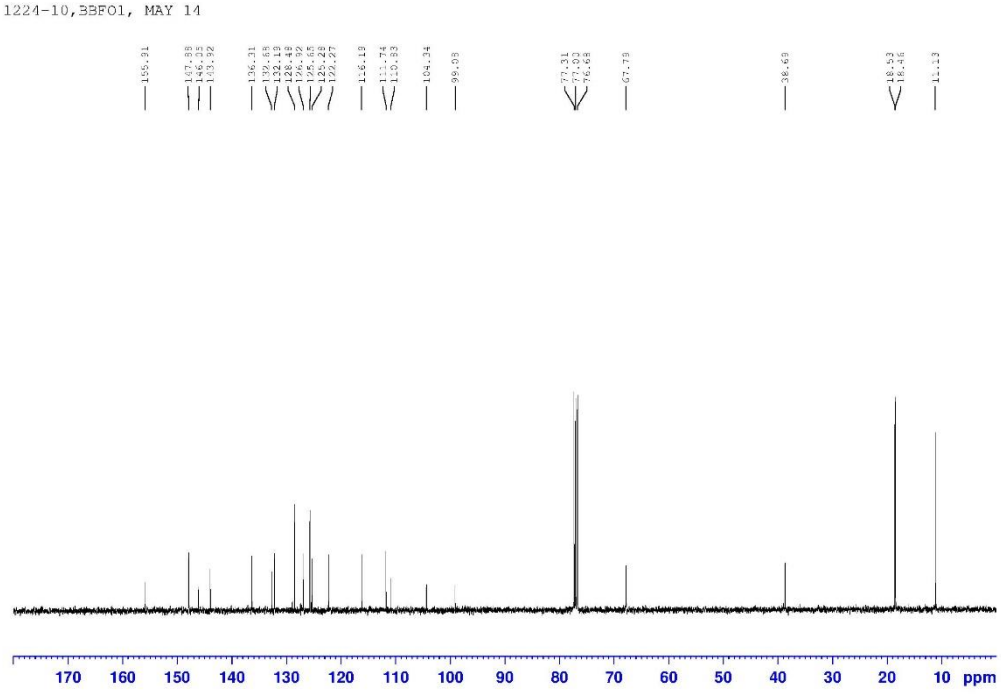
1206-20-1a CDCl3 BBFO1 400 Apr

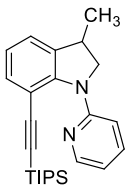



Ph
N
N
TIPS

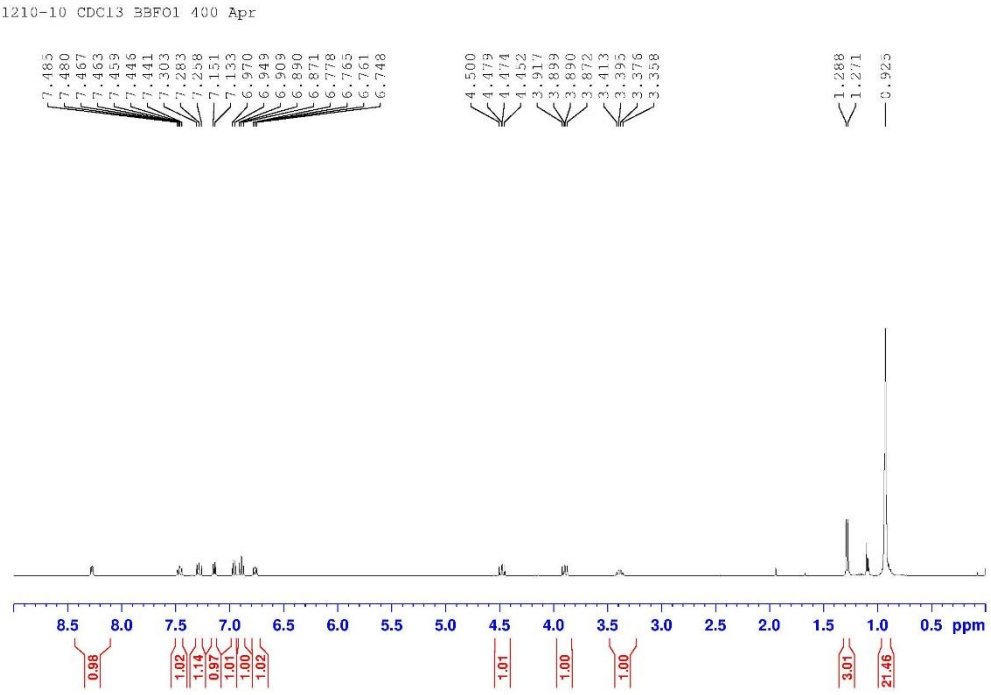
6c

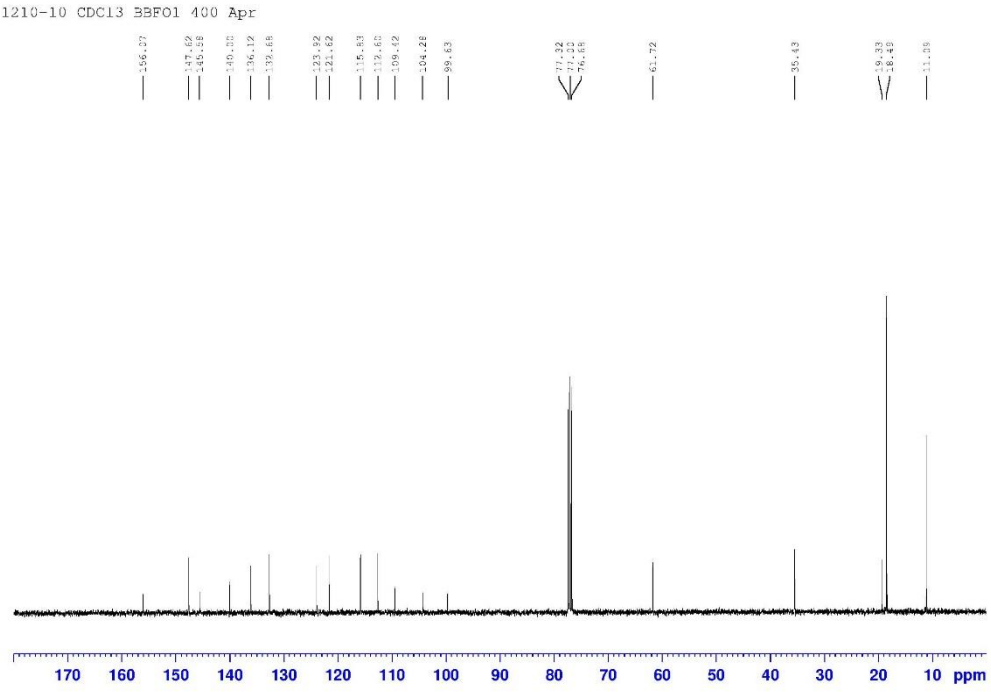

1224-10,3BFO1, MAY 14
7.240
7.219
7.206
7.201
7.183
7.097
7.079
7.077
6.888
6.886
6.870
6.865
6.851
6.772
6.770
6.760
6.758
6.754
6.752
6.742
6.739
5.651
5.629
3.850
3.826
3.811
3.788
2.926
2.923
2.887
2.884
3.988
3.974
3.934
3.930
3.925
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.09
4.63
1.11
2.08
1.01
1.00
1.07
1.03
21.18

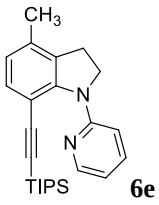

1224-10,3BFO1, MAY 14
156.91
147.38
146.25
138.92
136.31
132.68
132.19
128.49
126.92
125.65
122.88
122.27
116.19
111.74
110.83
104.34
99.03
77.31
77.00
76.68
67.79
38.69
18.93
18.46
11.13
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


CH3
N
N
TIPS

6d

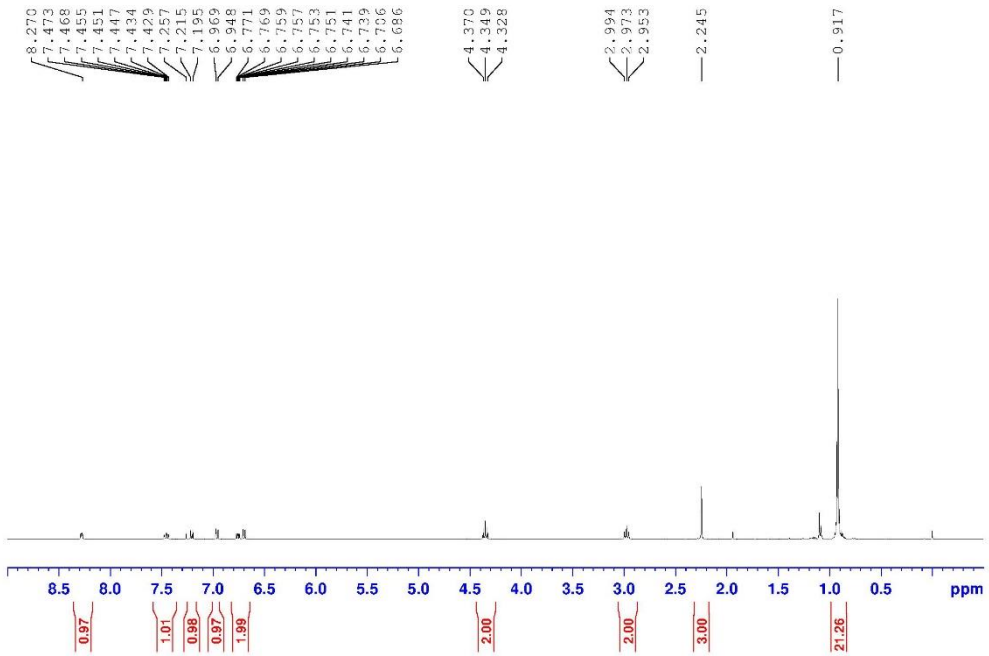

1210-10 CDCl3 BBF01 400 Apr
7.485
7.480
7.467
7.463
7.459
7.446
7.441
7.303
7.283
7.258
7.151
7.133
6.970
6.949
6.909
6.890
6.871
6.778
6.765
6.761
6.748
4.500
4.479
4.474
4.452
3.917
3.899
3.890
3.872
3.413
3.395
3.376
3.358
1.288
1.271
0.925
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5 ppm
0.98
1.02
1.14
0.97
1.01
1.00
1.02
1.01
1.00
1.00
3.01
21.46


1210-10 CDCl3 BBF01 400 Apr
156.07
147.62
145.68
136.12
123.92
121.62
115.83
112.63
109.42
104.28
99.63
77.32
77.00
76.68
61.72
35.43
19.33
18.49
11.58
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

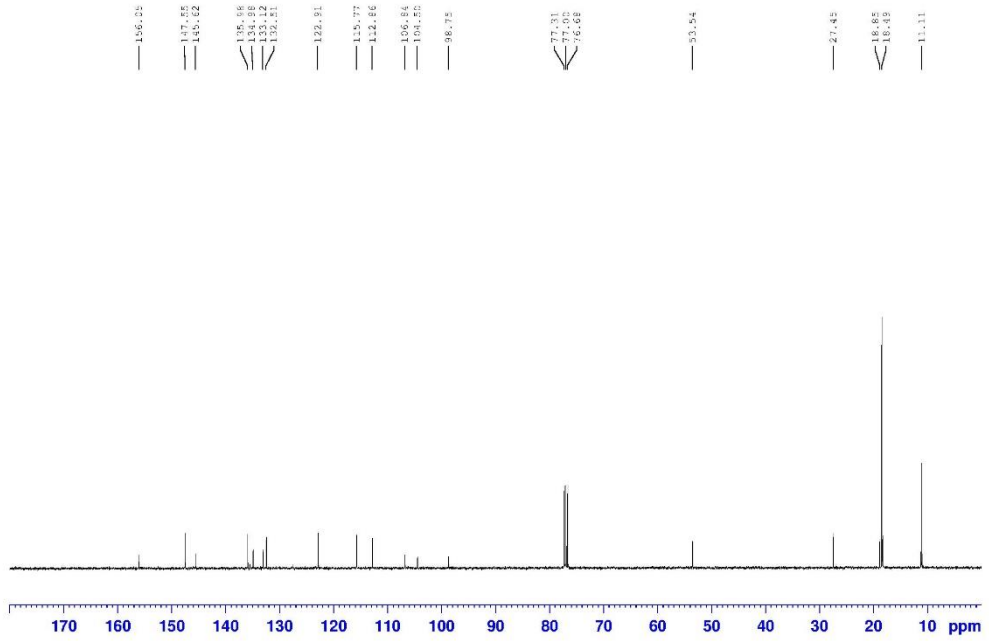


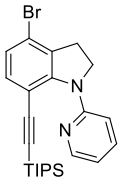
6e

2096-10, 1H NMR, CDCl3, BBFO-01, Jul 14

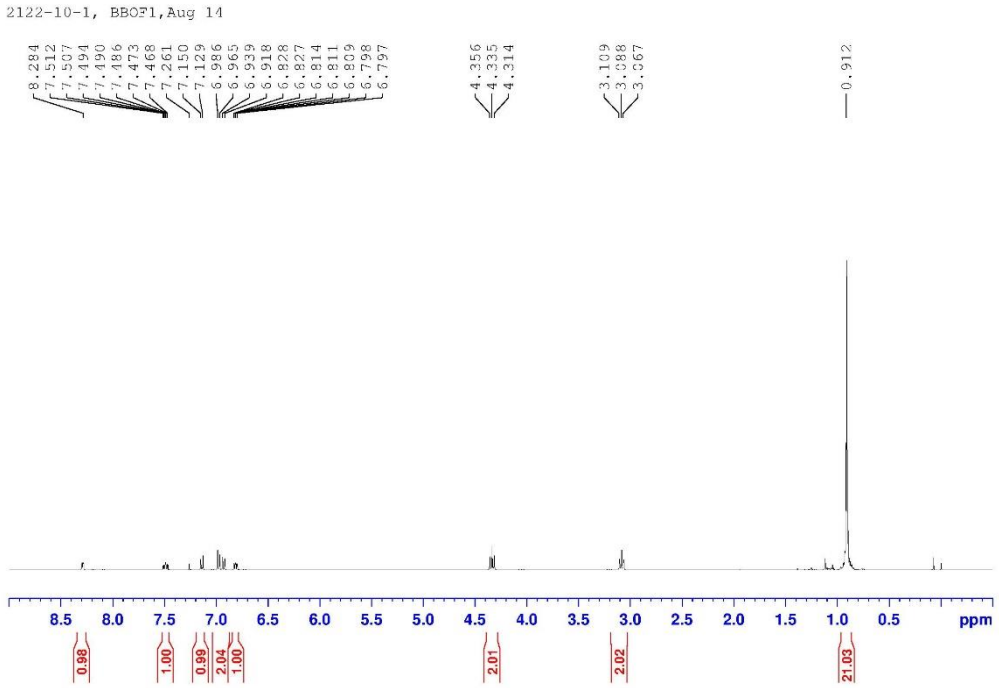


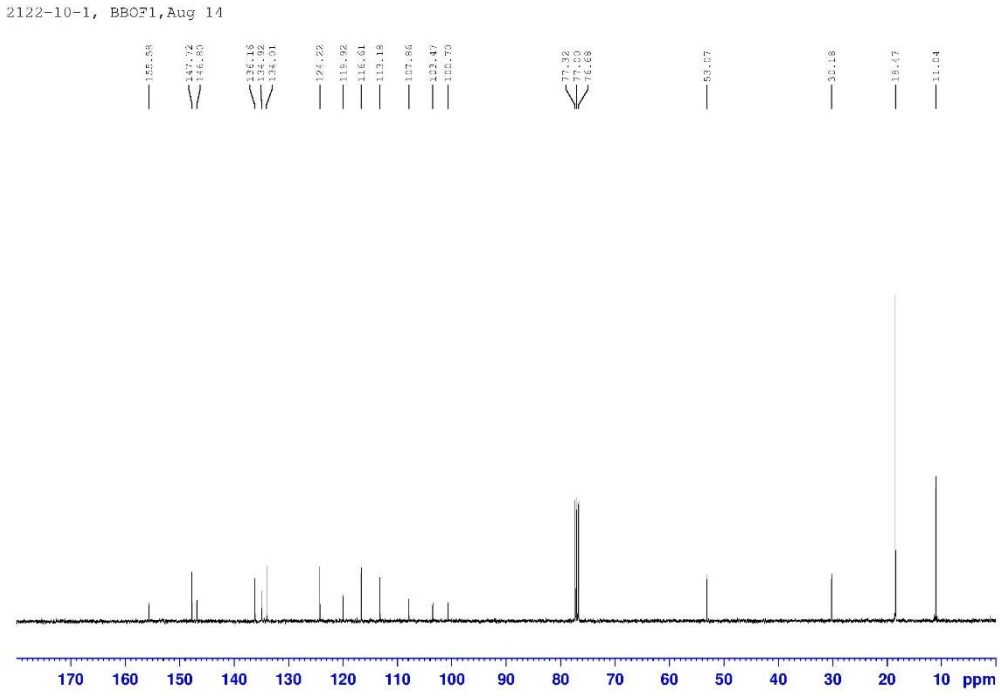
2096-10, 1H NMR, CDCl3, BBFO-01, Jul 14

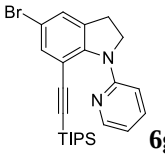



Br
N
N
TIPS

6f

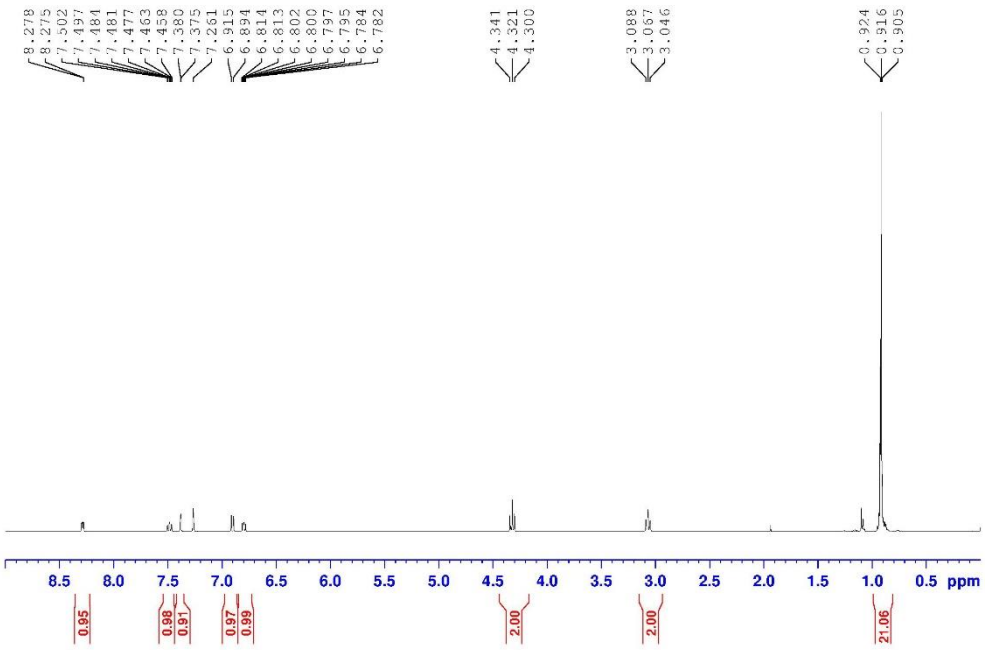

2122-10-1, BBOF1,Aug 14
8.284
7.512
7.507
7.494
7.490
7.486
7.473
7.468
7.261
7.150
7.129
6.986
6.965
6.939
6.918
6.828
6.827
6.814
6.811
6.809
6.798
6.797
4.356
4.335
4.314
3.109
3.088
3.067
0.912
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.98
1.00
0.99
2.04
1.00
2.01
2.02
21.03


2122-10-1, BBOF1,Aug 14
155.58
147.42
146.80
136.18
134.92
134.01
124.22
119.92
116.61
113.18
107.86
103.47
100.73
77.32
77.00
76.68
53.87
30.18
18.47
11.04
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

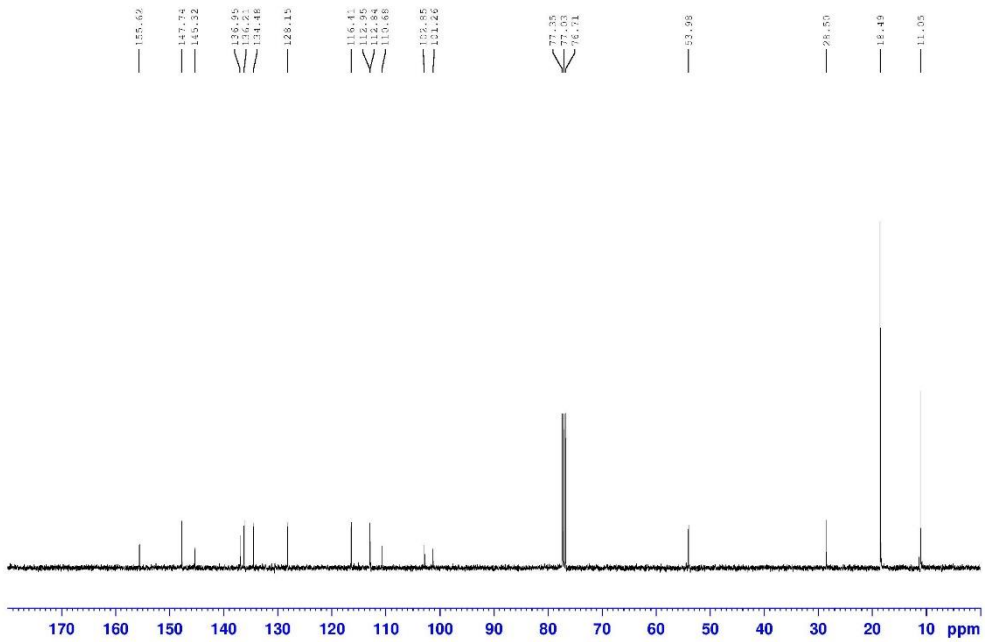


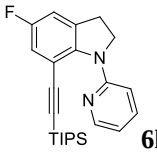
6g

1252-10,3BF01, MAY 14



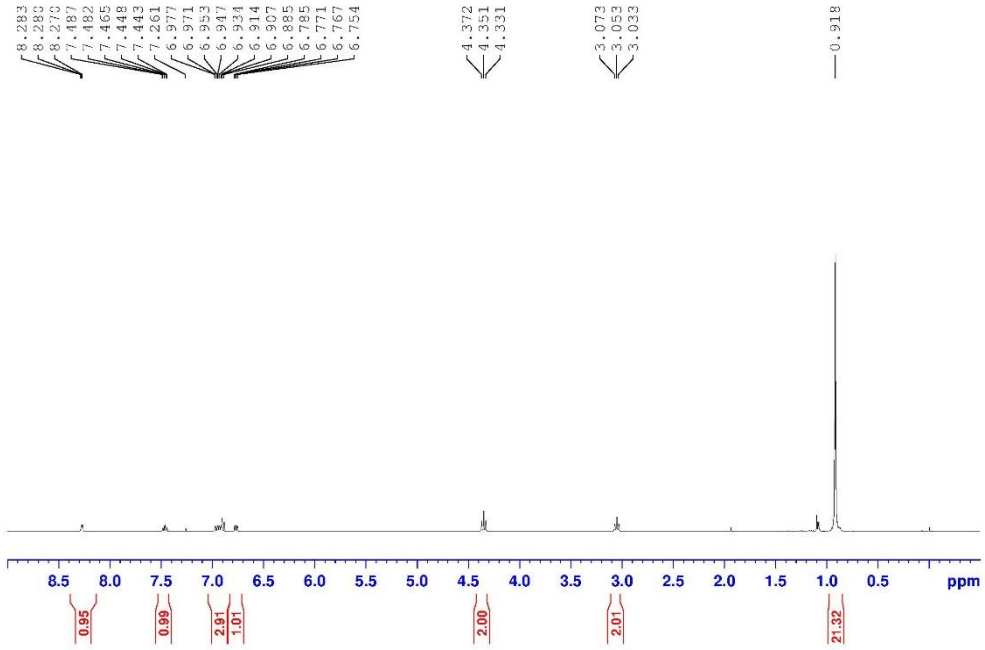
1252-10,3BF01, MAY 14



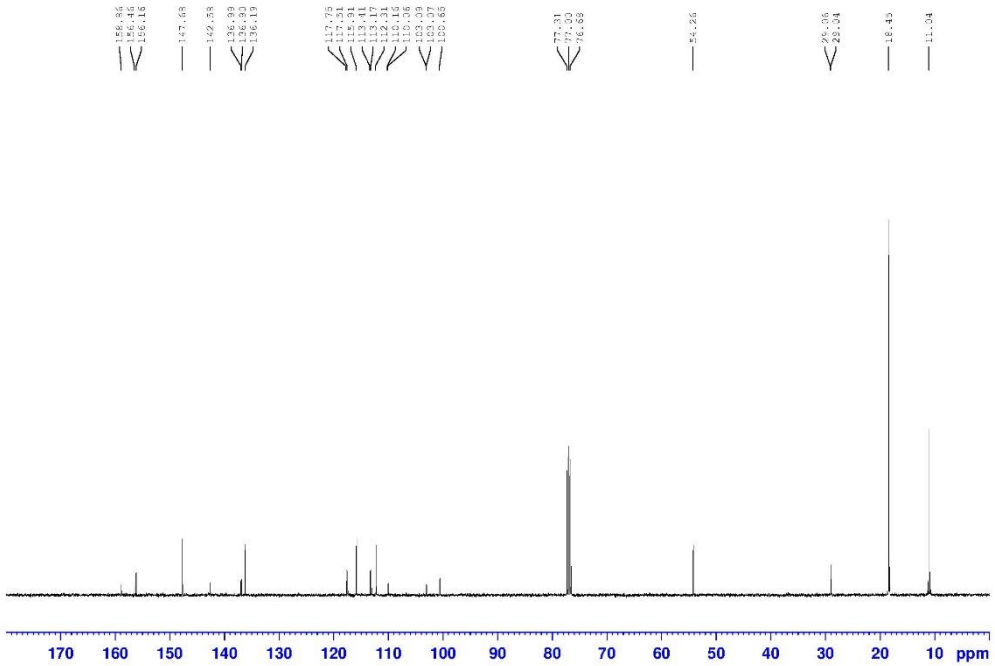


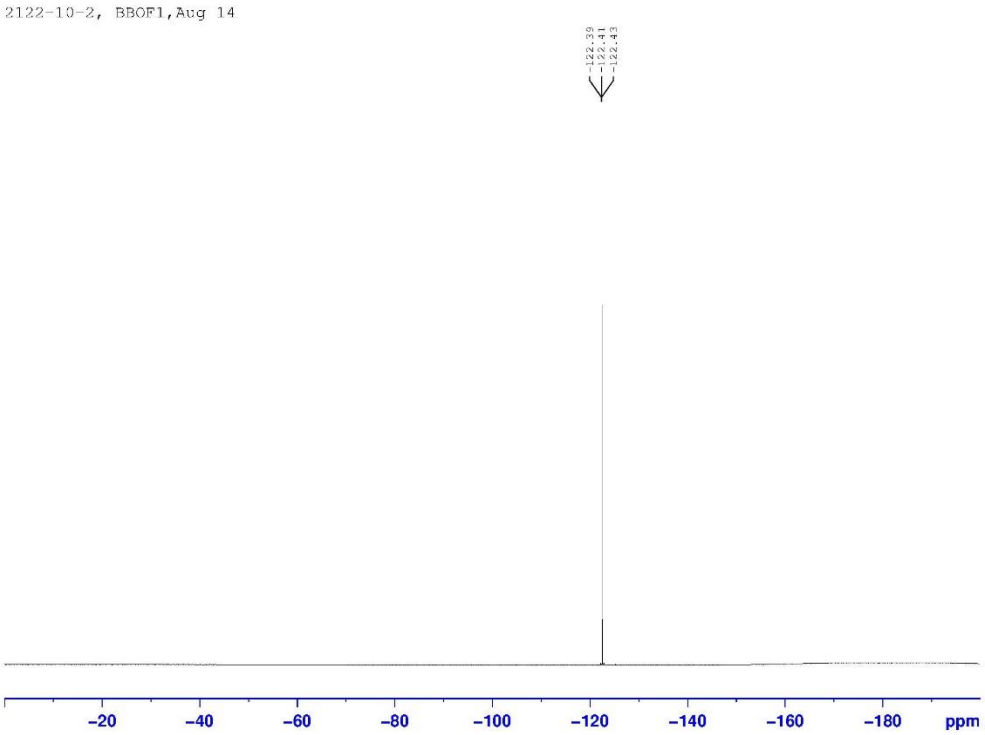
6h

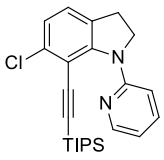
2122-10-2, BBOF1,Aug 14



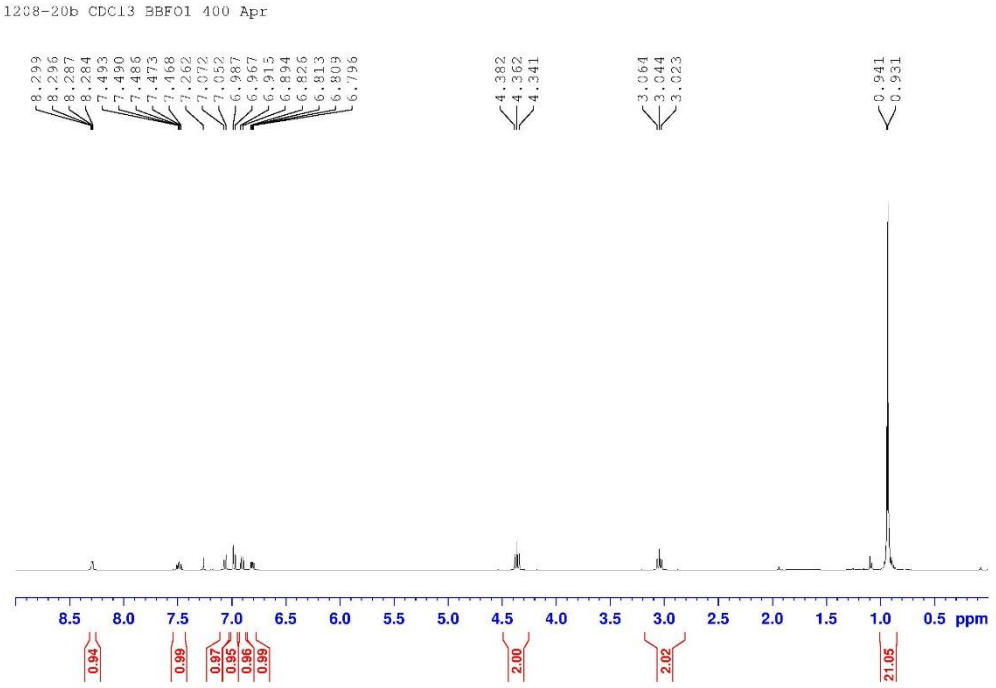
2122-10-2, BBOF1,Aug 14

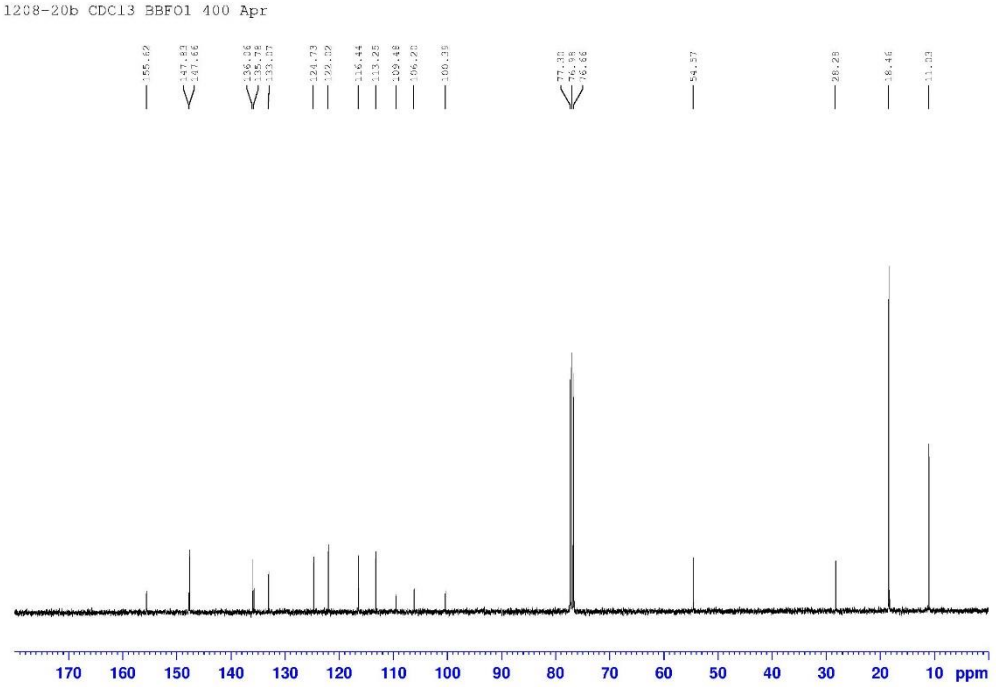


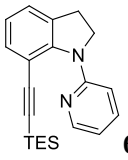

2122-10-2, BBOF1,Aug 14
-122.39
-122.41
-122.43
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm


Cl
N
N
TIPS

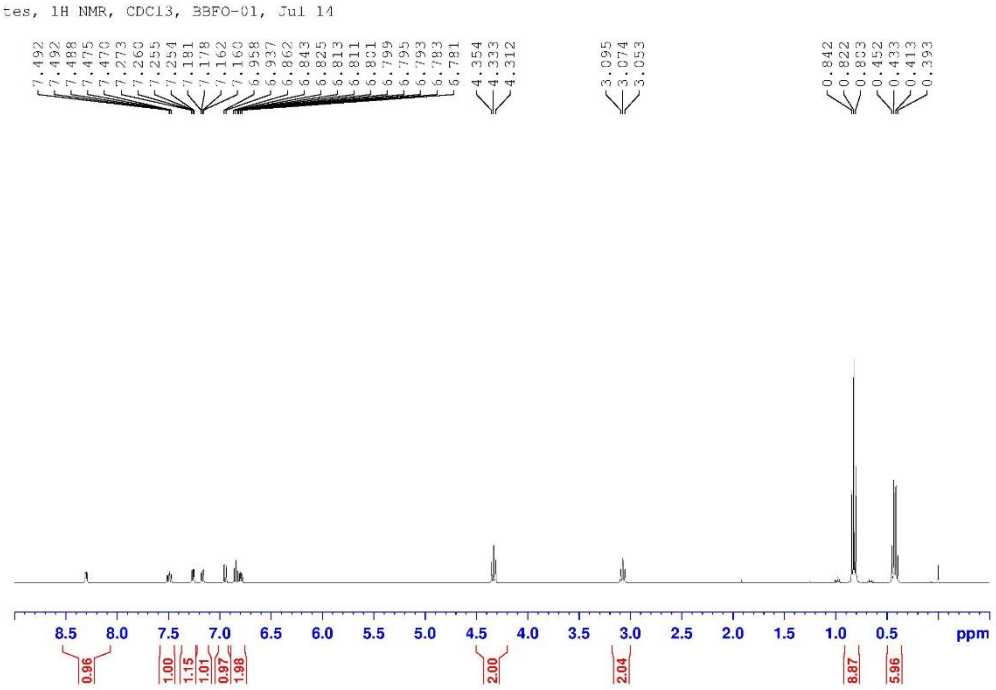
6i

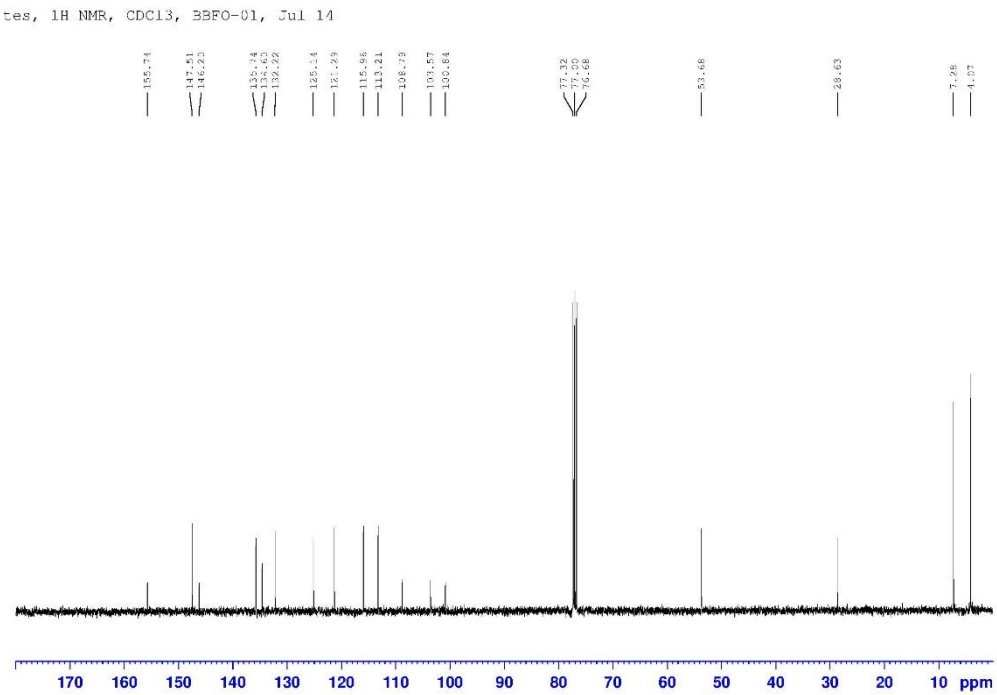

1208-20b CDCl3 BBF01 400 Apr
8.299
8.296
8.287
8.284
7.493
7.490
7.486
7.473
7.468
7.262
7.072
7.052
6.987
6.967
6.915
6.894
6.826
6.813
6.809
6.796
4.382
4.362
4.341
3.064
3.044
3.023
0.941
0.931
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.94
0.99
0.97
0.95
0.96
0.99
2.00
2.02
21.05

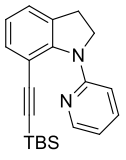

1208-20b CDCl3 BBF01 400 Apr
155.62
147.83
147.66
136.26
135.78
133.07
124.73
122.32
116.44
113.25
109.48
106.23
100.35
77.32
76.98
76.66
54.57
26.28
18.46
11.03
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


N
N
TES

6j

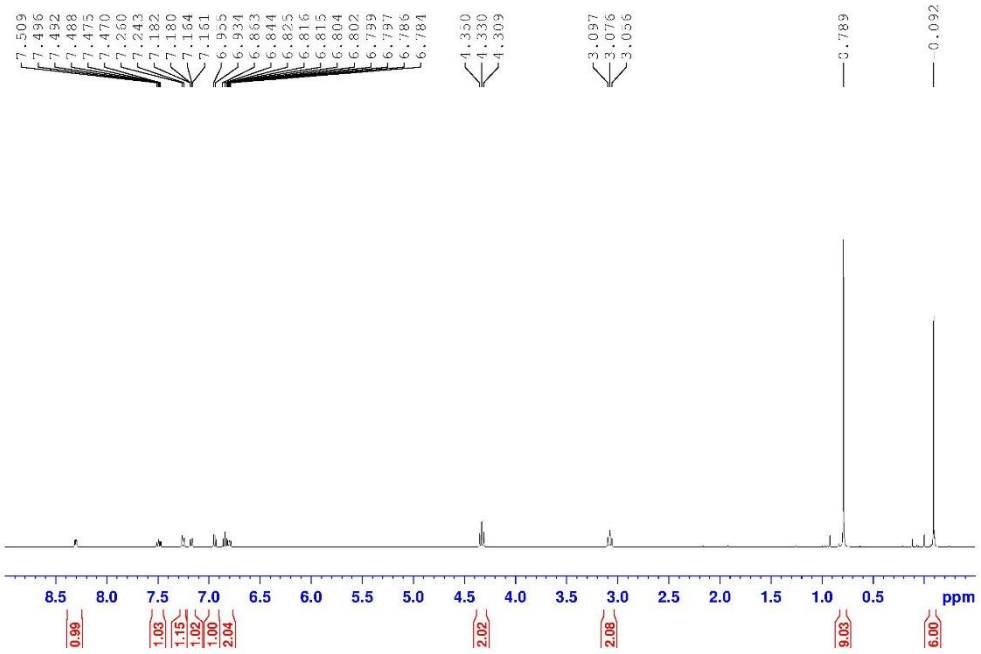

tes, 1H NMR, CDCl3, BBFO-01, Jul 14
7.492
7.492
7.488
7.475
7.470
7.273
7.260
7.255
7.254
7.181
7.178
7.162
7.160
6.958
6.937
6.862
6.843
6.825
6.813
6.811
6.801
6.799
6.795
6.793
6.783
6.781
4.354
4.333
4.312
3.095
3.074
3.053
0.842
0.822
0.803
0.452
0.433
0.413
0.393
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.96
1.00
1.15
1.01
0.97
1.98
2.00
2.04
8.87
5.96


tes, 1H NMR, CDCl3, BBFO-01, Jul 14
155.74
147.51
146.20
135.24
132.63
132.22
126.14
121.29
115.96
113.21
108.79
103.57
100.84
77.32
77.00
76.68
53.68
28.63
7.26
4.07
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

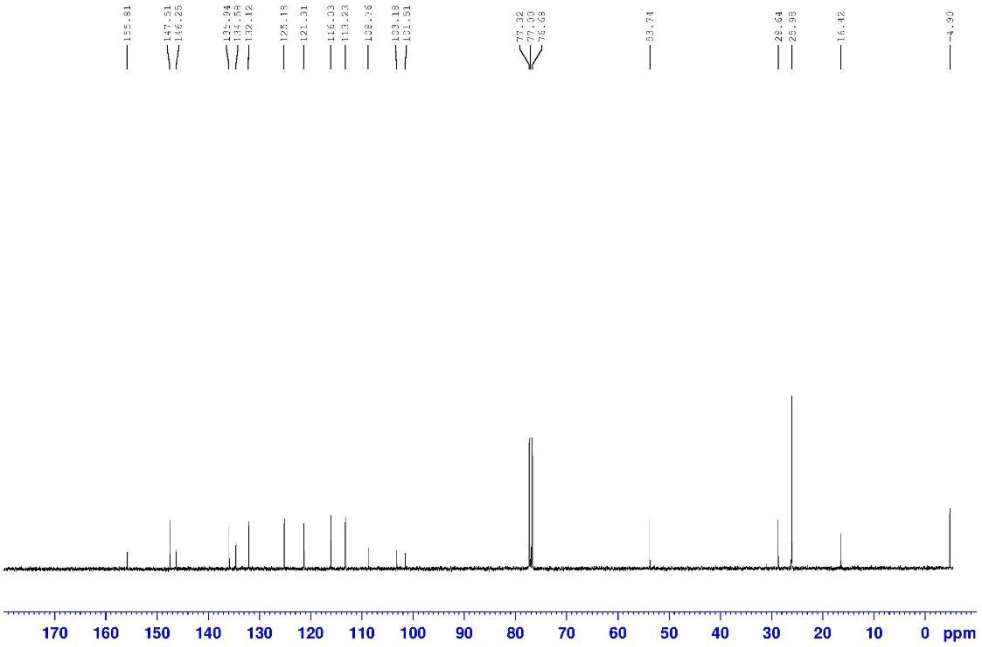


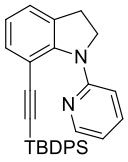
6k

tbs-2, 1H NMR, CDCl3, BBFO-01, Jul 14



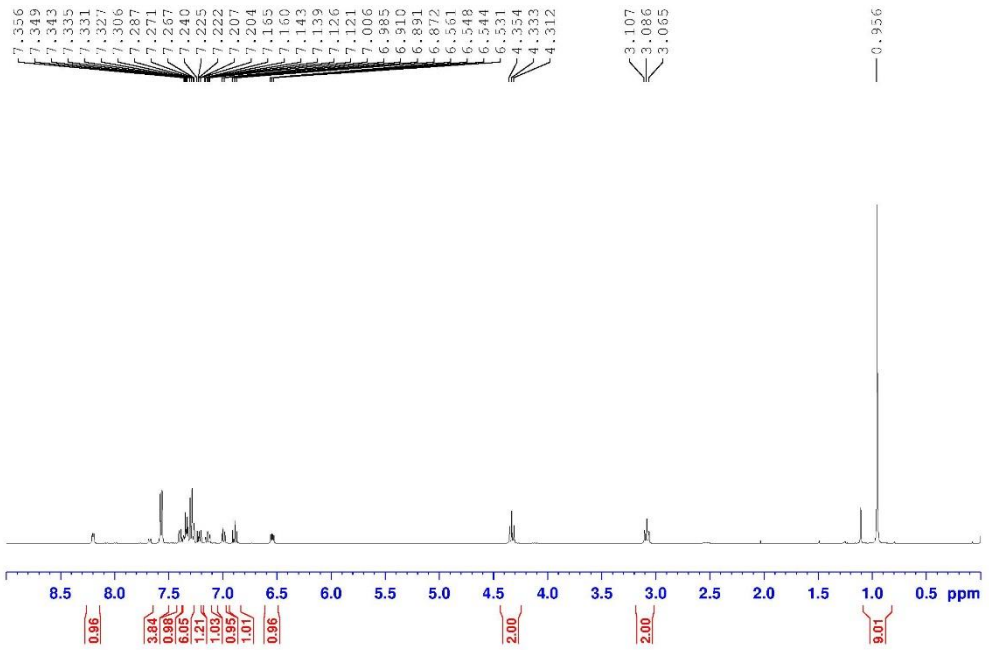
tls, 1H NMR, CDCl3, BBFO-01, Jul 14



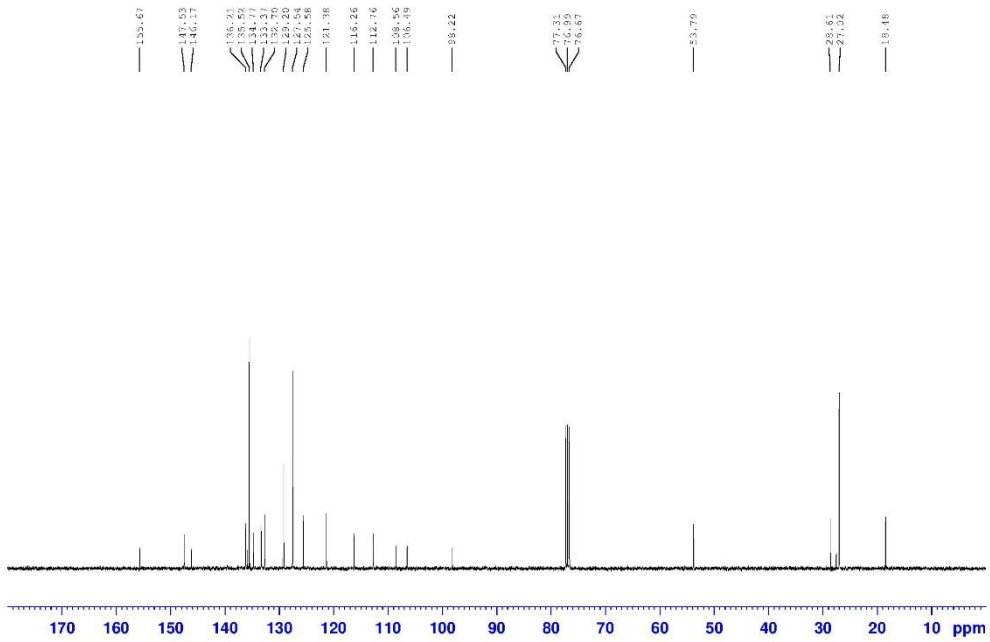


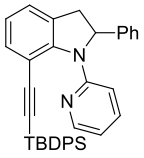
6l

1270-20, 1H, CDCl3, 400MHz, AV400



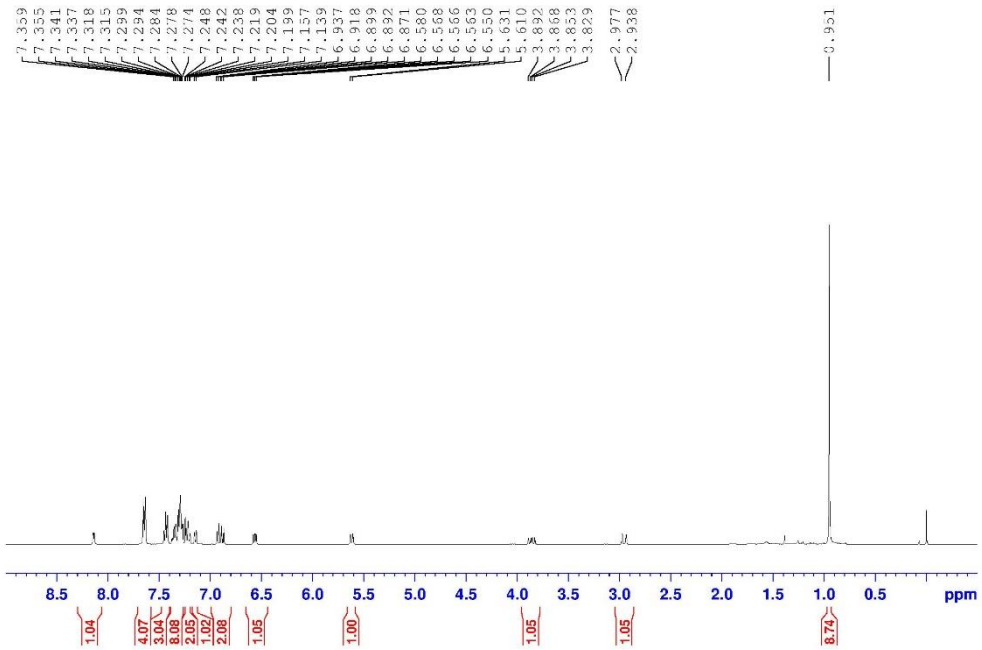
1270-20, 1H, CDCl3, 400MHz, AV400



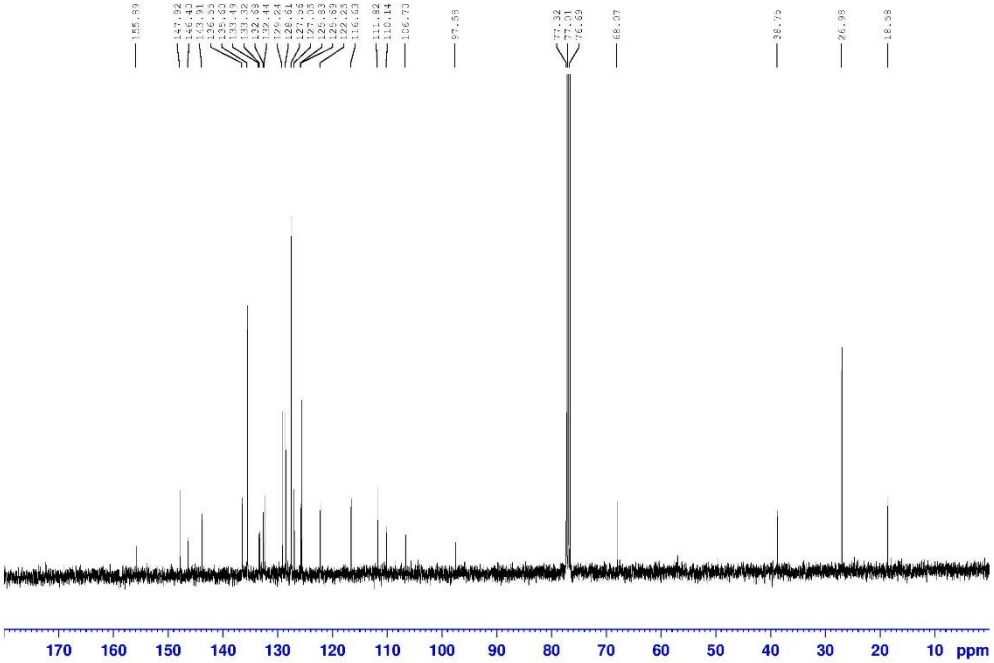


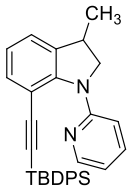
6m

2040-10a, BBFO 1

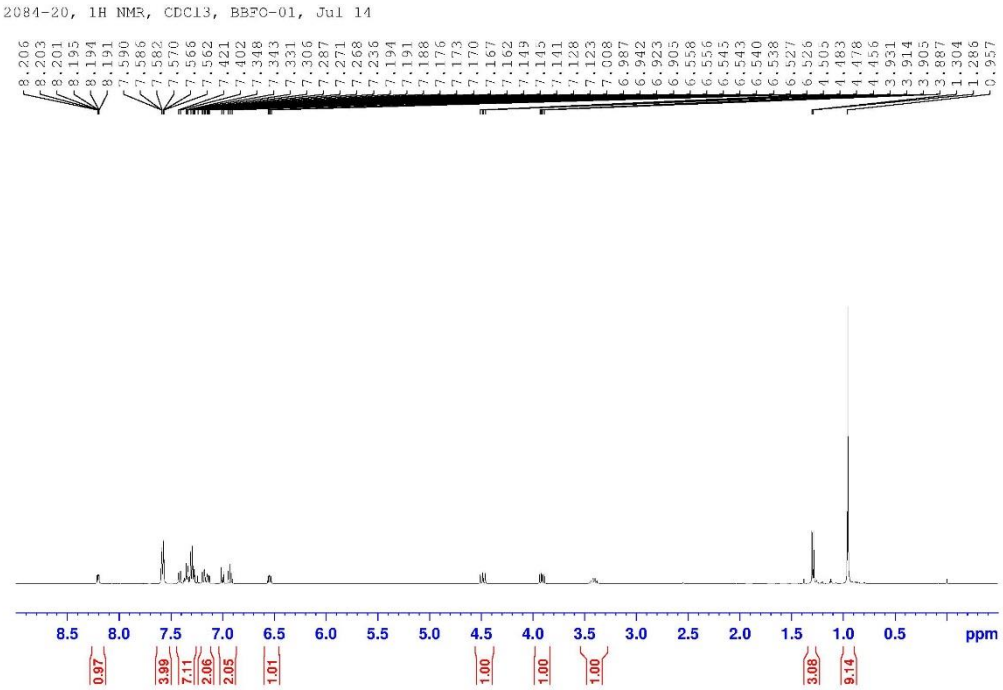


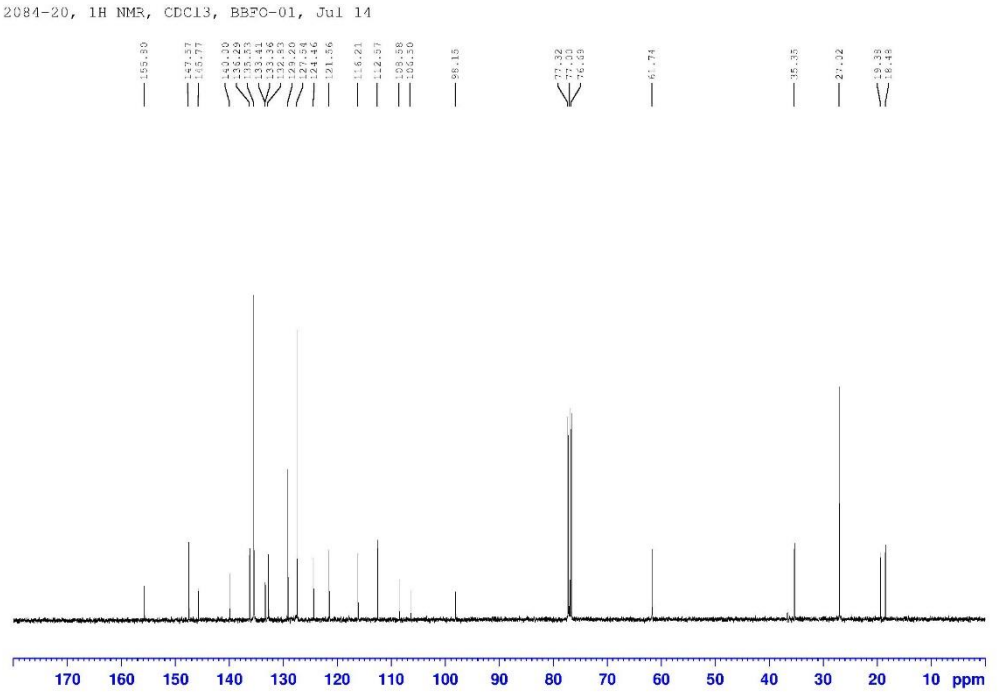
2040-10a, BBFO 1

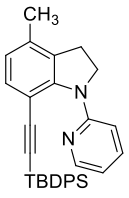



CH3
N
N
TBDPS

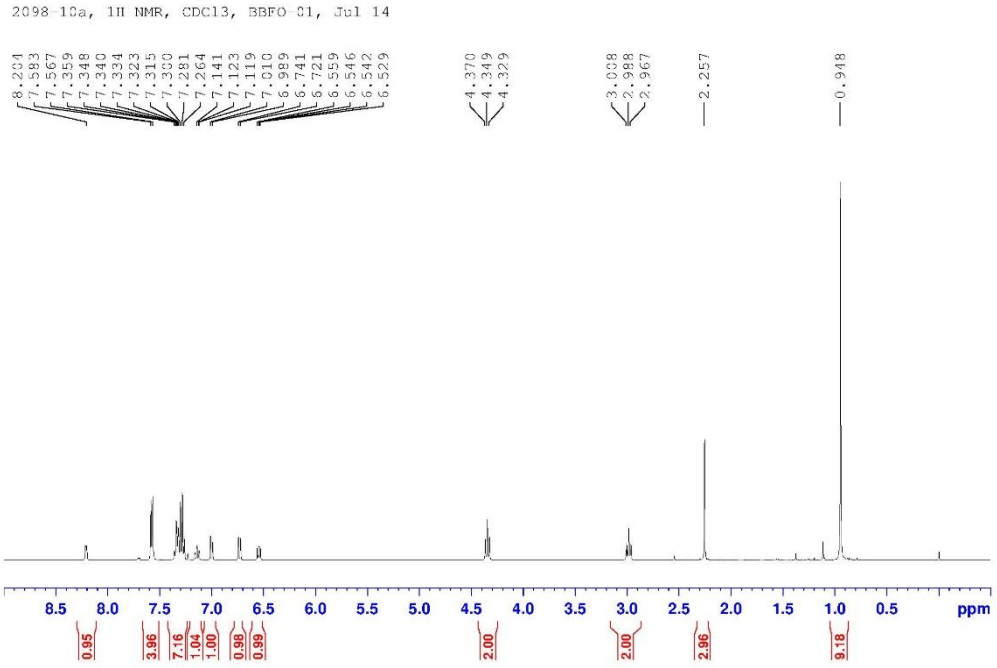
6n

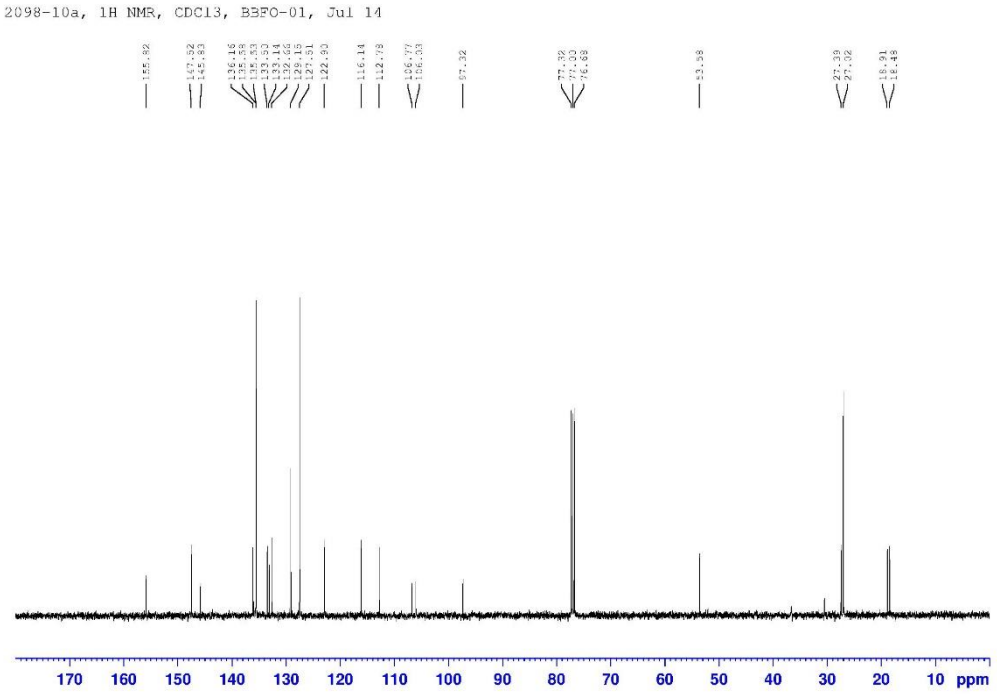

2084-20, 1H NMR, CDCl3, BBFO-01, Jul 14
8.206
8.203
8.201
8.195
8.194
8.191
7.590
7.586
7.582
7.570
7.566
7.562
7.421
7.402
7.348
7.343
7.331
7.306
7.287
7.271
7.268
7.236
7.194
7.191
7.188
7.176
7.173
7.170
7.167
7.162
7.149
7.145
7.141
7.128
7.123
7.008
6.987
6.942
6.923
6.905
6.558
6.556
6.545
6.543
6.540
6.538
6.527
6.526
4.505
4.483
4.478
4.456
3.931
3.914
3.905
3.887
1.304
1.286
0.957
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.97
3.99
7.11
2.06
2.05
1.01
1.00
1.00
1.00
3.08
9.14

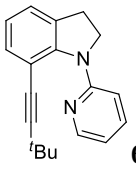

2084-20, 1H NMR, CDCl3, BBFO-01, Jul 14
155.90
147.37
145.77
140.30
136.29
135.53
133.41
133.36
132.33
129.20
127.54
124.46
121.56
116.21
112.97
108.98
106.30
98.15
77.32
77.00
76.69
61.74
35.35
21.02
19.38
18.48
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


CH3
N
N
TBDPS

6o

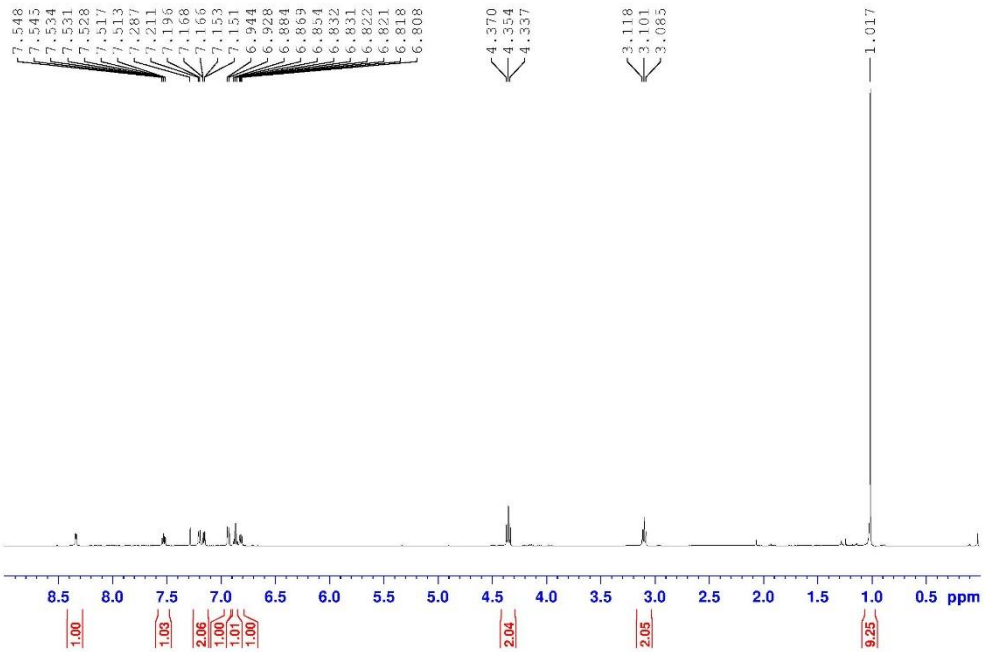

2098-10a, 1H NMR, CDCl3, BBFO-01, Jul 14
8.204
7.583
7.567
7.359
7.348
7.340
7.334
7.323
7.315
7.300
7.281
7.264
7.141
7.123
7.119
7.010
6.989
6.741
6.721
6.559
6.546
6.542
6.529
4.370
4.349
4.329
3.038
2.988
2.967
2.257
0.948
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.95
3.96
7.16
1.04
1.00
0.98
0.99
2.00
2.00
2.96
9.18


2098-10a, 1H NMR, CDCl3, BBFO-01, Jul 14
155.82
147.92
145.93
136.16
135.58
134.53
133.93
133.14
132.66
129.15
127.51
122.90
116.14
112.78
106.77
106.03
87.32
77.32
77.03
76.68
53.58
27.39
27.02
18.91
18.48
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

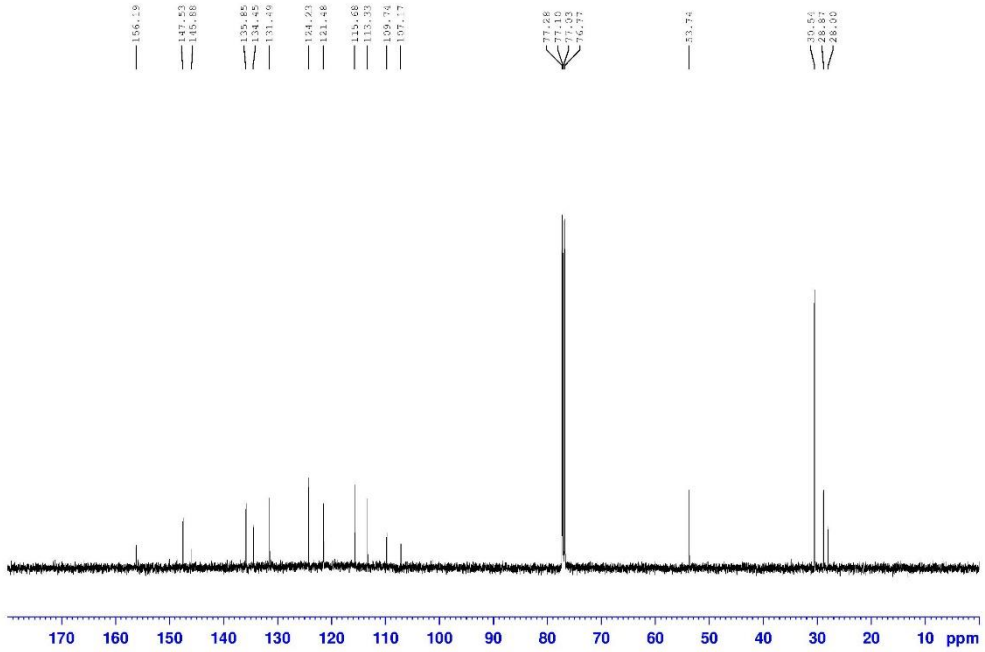


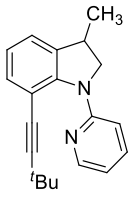
6p

1268-30, AV500, May 14

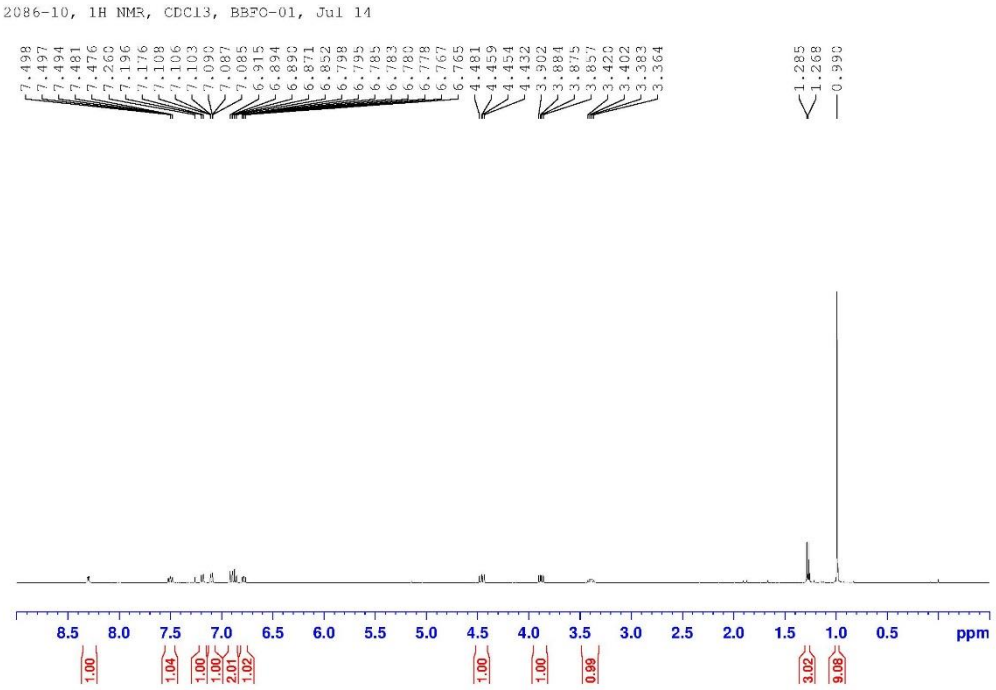


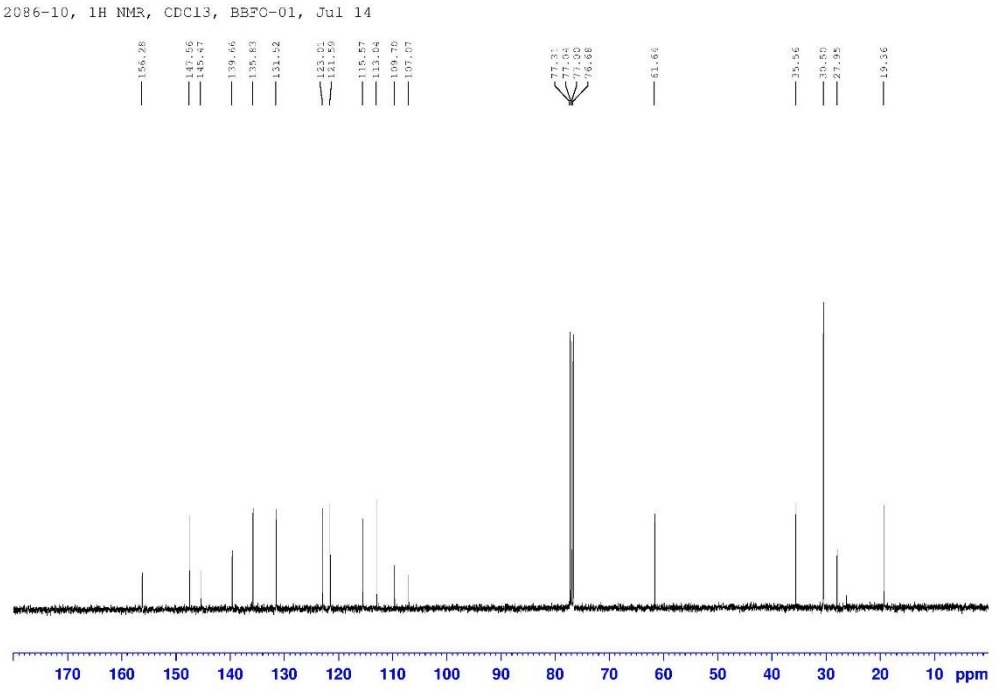
1268-30, AV500, May 14, 13C

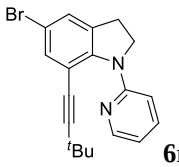



CH3
N
N
tBu

6q

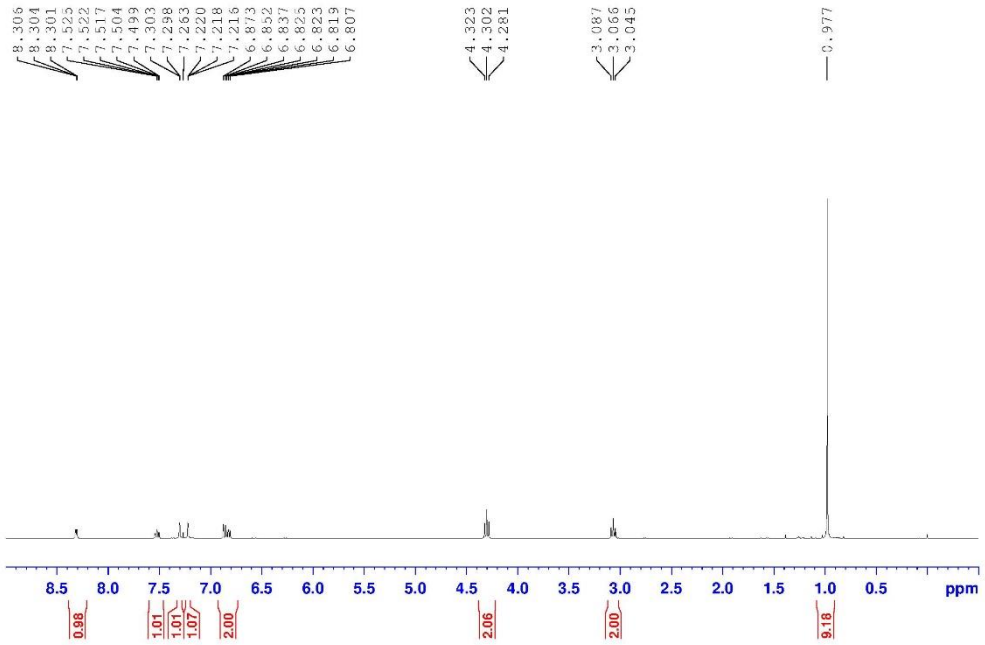

2086-10, 1H NMR, CDCl3, BBFO-01, Jul 14
7.498
7.497
7.494
7.481
7.476
7.260
7.196
7.176
7.108
7.106
7.103
7.090
7.087
7.085
6.915
6.894
6.890
6.871
6.852
6.798
6.795
6.785
6.783
6.780
6.778
6.767
6.765
4.481
4.459
4.454
4.432
3.902
3.884
3.875
3.857
3.420
3.402
3.383
3.364
1.285
1.268
0.990
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.04
1.00
1.00
2.01
1.02
1.00
1.00
0.99
3.02
9.08


2086-10, 1H NMR, CDCl3, BBFO-01, Jul 14
156.28
147.56
145.47
139.66
135.83
131.52
123.01
121.59
115.57
113.04
109.70
107.07
77.31
77.04
76.88
61.64
35.56
30.50
27.95
19.36
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

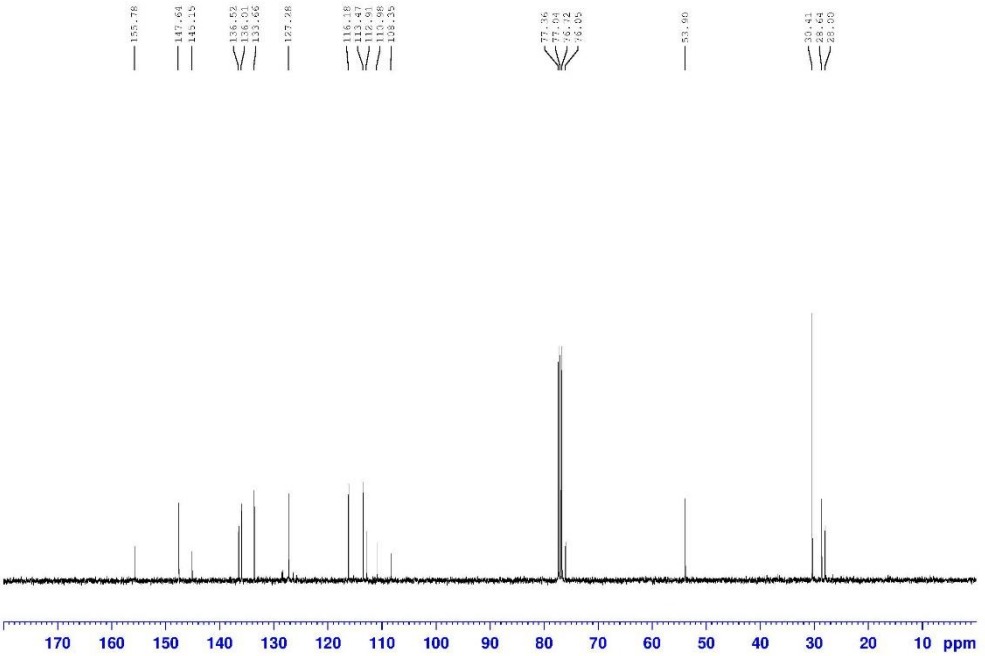


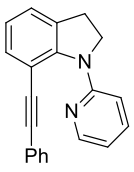
6r

2084-30, 1H NMR, CDCl3, BBFO-01, Jul 14

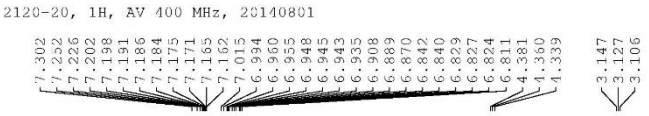


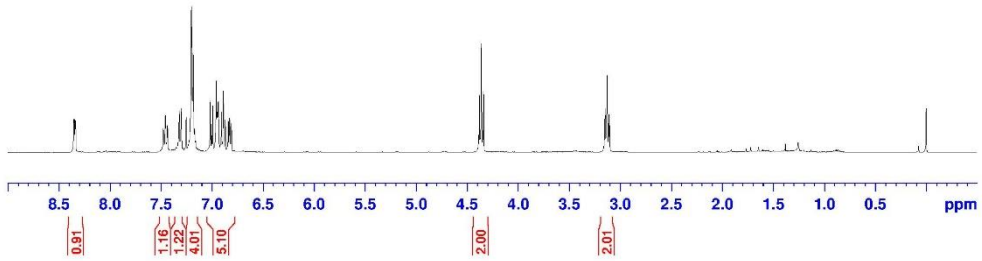
2084-30, 1H NMR, CDCl3, BBFO-01, Jul 14



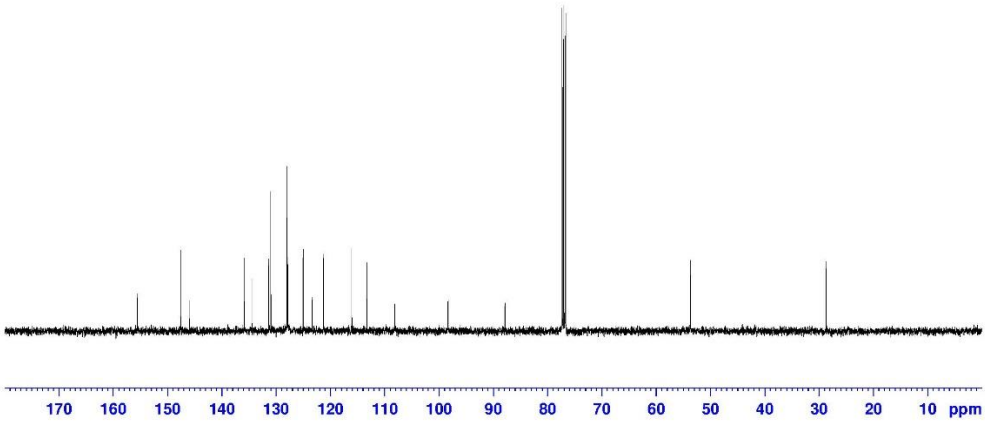

N
N
Ph

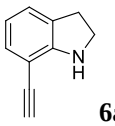
6s


2120-20, 1H, AV 400 MHz, 20140801
7.302
7.252
7.226
7.202
7.198
7.191
7.186
7.184
7.175
7.171
7.165
7.162
7.015
6.994
6.960
6.955
6.948
6.945
6.943
6.935
6.908
6.889
6.870
6.842
6.840
6.829
6.827
6.824
6.811
4.381
4.360
4.339
3.147
3.127
3.106


8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.91
1.16
1.22
4.01
5.10
2.00
2.01

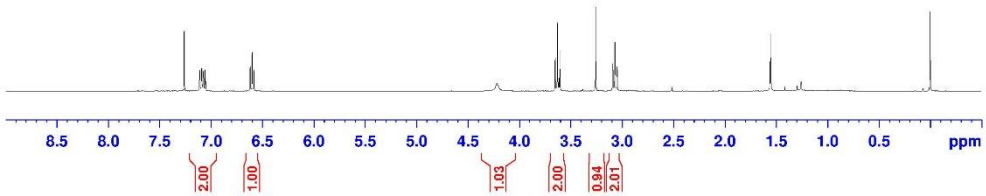

2120-20, 1H, AV 400 MHz, 20140801
155.55
147.57
145.68
139.86
134.48
131.38
130.08
129.80
127.80
125.00
123.36
121.28
116.09
113.26
108.11
98.33
87.81
77.31
77.00
76.68
53.66
28.67


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

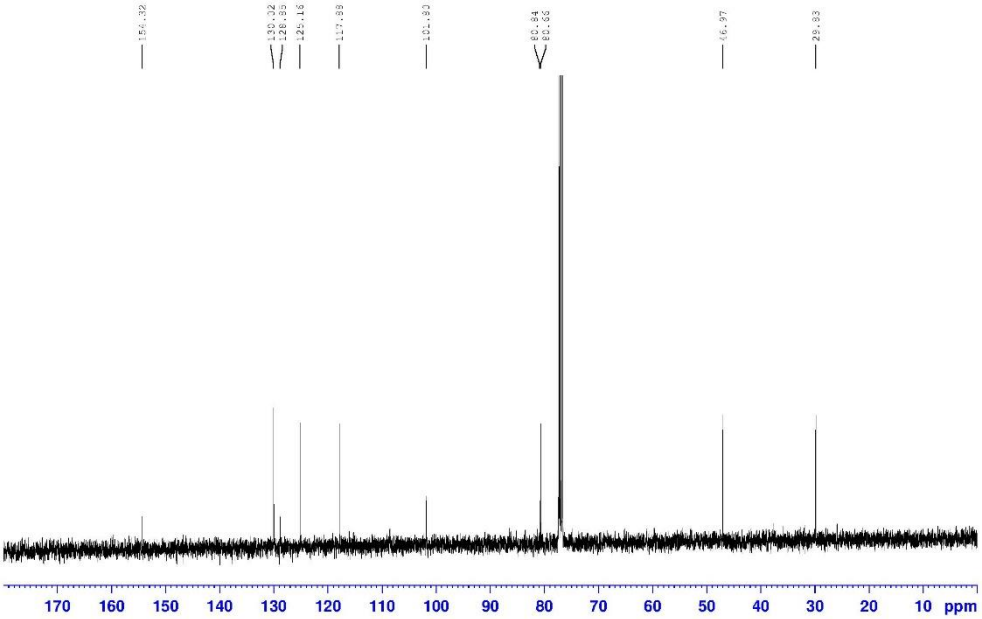


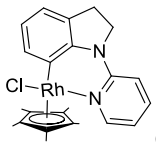
6a’

2144-10, BBOF1,Aug 14

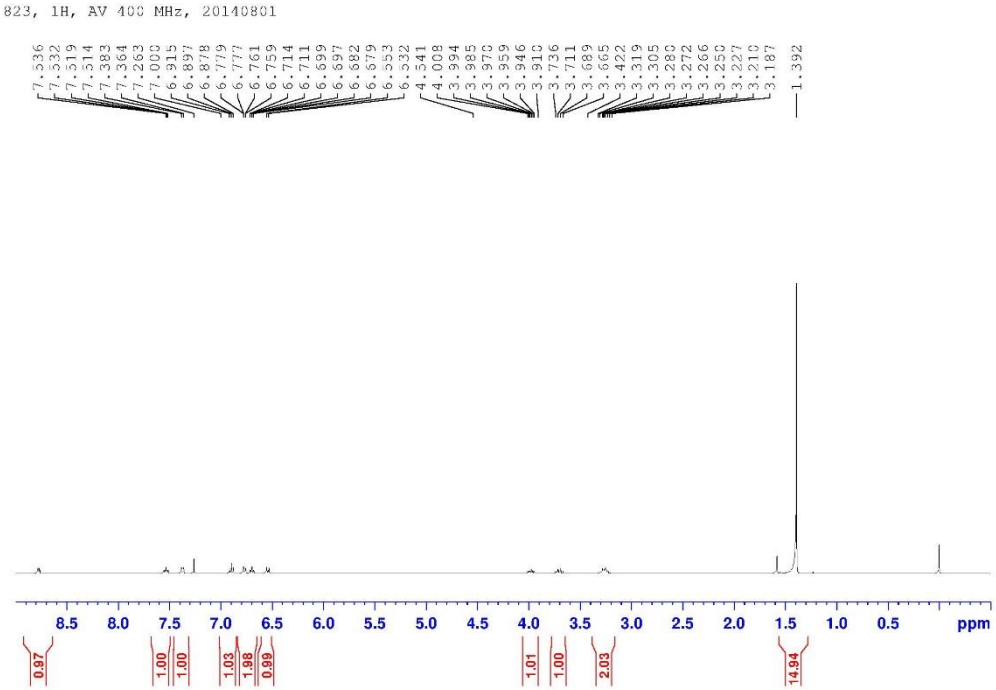


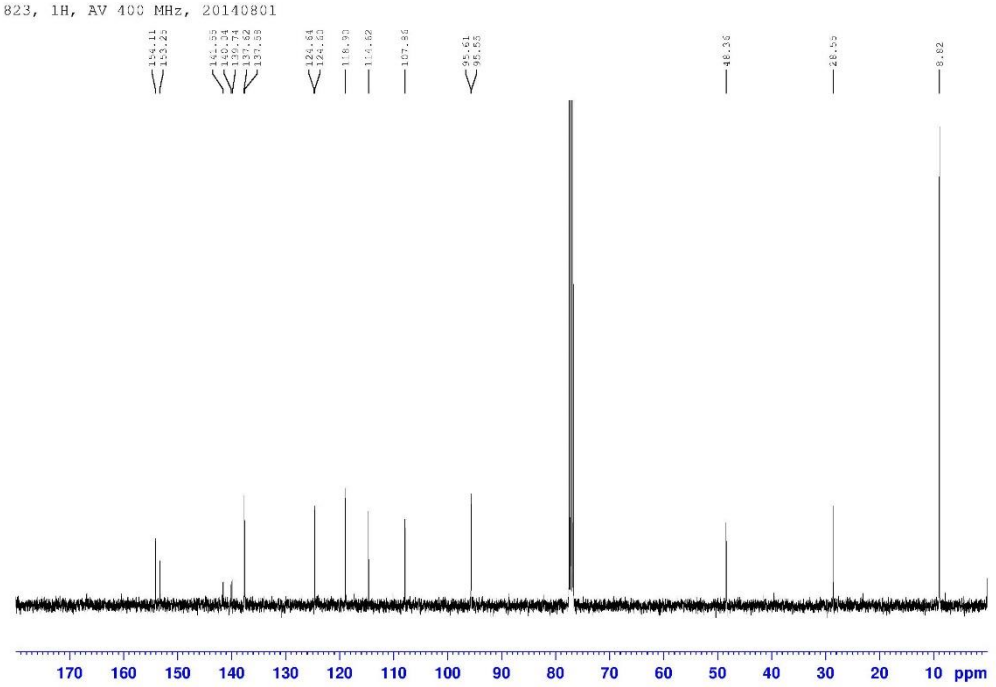
2144-10, BBOF1,Aug 14




Cl
Rh
N
N

c1

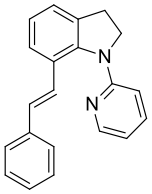

823, 1H, AV 400 MHz, 20140801
7.536
7.532
7.519
7.514
7.383
7.364
7.263
7.000
6.915
6.897
6.878
6.779
6.777
6.761
6.759
6.714
6.711
6.699
6.697
6.682
6.679
6.553
6.532
4.541
4.008
3.994
3.985
3.970
3.959
3.946
3.910
3.736
3.711
3.689
3.665
3.422
3.319
3.305
3.280
3.272
3.266
3.250
3.227
3.210
3.187
1.392
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.97
1.00
1.00
1.03
1.98
0.99
1.01
1.00
2.03
14.94

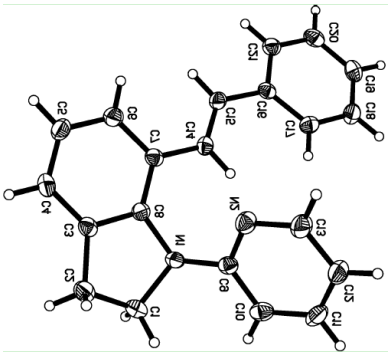

823, 1H, AV 400 MHz, 20140801
154.11
153.25
146.35
140.34
139.74
137.62
137.58
126.84
126.53
118.90
116.62
107.86
95.61
95.55
48.36
28.59
8.82
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

X-ray Data

X-Ray Structure for 3a

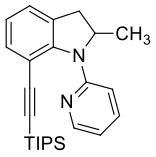
Cambridge Crystallographic Data Centre Deposition Number: 1029305

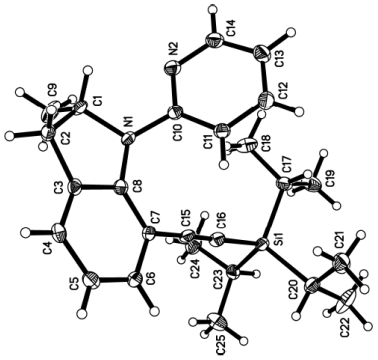




X-Ray Structure for 6b

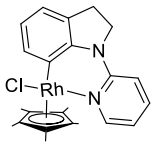
Cambridge Crystallographic Data Centre Deposition Number: 1029306

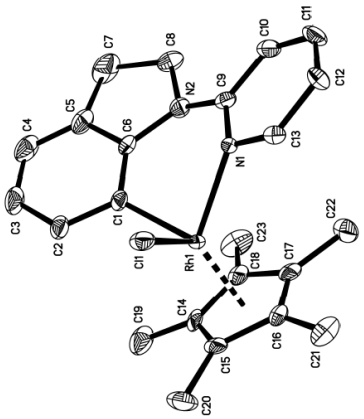




X-Ray Structure for c1

Cambridge Crystallographic Data Centre Deposition Number: 1029307





Reference:

[1] S. Wagaw, S. L. Buchwald, *J. Org. Chem*., **1996**, *61*, 7240.

[2] J. P. Brand, J. Waser, *Angew. Chem. Int. Ed.*, **2010**, *49*, 7304.

[3] V. Smout, A. Peschiulli, S. Verbeeck, E. A. Mitchell, W, Herrebout, P. Bultinck, C. M. L. V. Velde, D. Berthelot, L. Meerpoel, B. U. W. Maes, *J. Org. Chem*. **2013**, *78*, 9803.

[4] K. D. Collins, F. Lied, F. Glorius, *Chem. Commun*. **2014**, *50*, 4459.