Electronic Supplementary Information

Consecutive π-Lewis Acidic Metal-Catalysed Cyclisation/Photochemical Radical Addition Promoted by *in situ* Generated 2-Benzopyrylium as the Photoredox Catalyst

Masahiro Terada,* Ryohei Yazaki, Ren Obayashi, Zen Iwasaki, Shigenobu Umemiya, Jun Kikuchi

e-mail: mterada@tohoku.ac.jp

Department of Chemistry, Graduate School of Science, Tohoku University,
Aoba-ku, Sendai 980-8578, Japan.

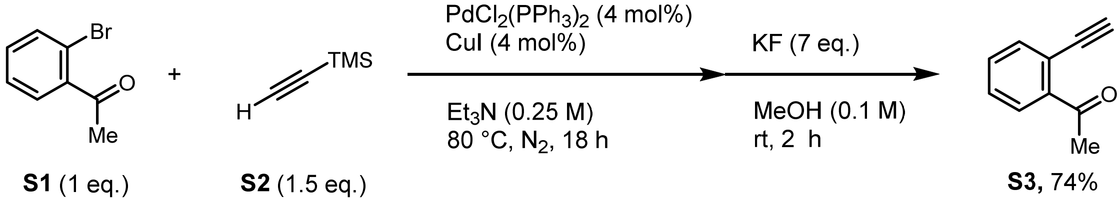
Contents

1. General Information.

Unless otherwise noted, all reactions were carried out under nitrogen or argon atmosphere in flame-dried glassware. Anhydrous 1,2-dichloroethane ($C_2H_4Cl_2$) was purchased from Aldrich. Other solvents and reagents were purchased from commercial suppliers and used without further purification. Techno Sigma-PER-AMPs were used as the λ_{max} = 405 and 448 nm light sources. Purification of products was carried out by flash column chromatography using silica gel 60 N (spherical, neutral, 40-50 μm; Kanto Chemical Co., Inc.). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF 254, 0.25 mm). ^{1}H NMR spectra were recorded on a JEOL ECA-600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane or solvent resonance as the internal standard ($CHCl_3$: 7.26 ppm, TMS: 0.00 ppm). $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL ECA-600 (151 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm). NMR yields were determined using $C_2H_2Br_4$ as the internal standard. Infrared spectra were recorded on a Jasco FT/IR-4100 spectrometer. Mass spectra analysis using the APCI ionization method was performed on a Bruker Daltonics SolariX 12T spectrometer and the FD method was performed using a JEOL JMS-T100GC spectrometer at the Macromolecule Research Center, Graduate School of Science, Tohoku University. UV-Vis absorption spectra were recorded on a JASCO V650DS spectrometer. Fluorescence spectra were recorded on a HITACHI F-4500.

2. Preparation of *ortho*-Carbonyl Alkynylbenzene Derivatives **1**

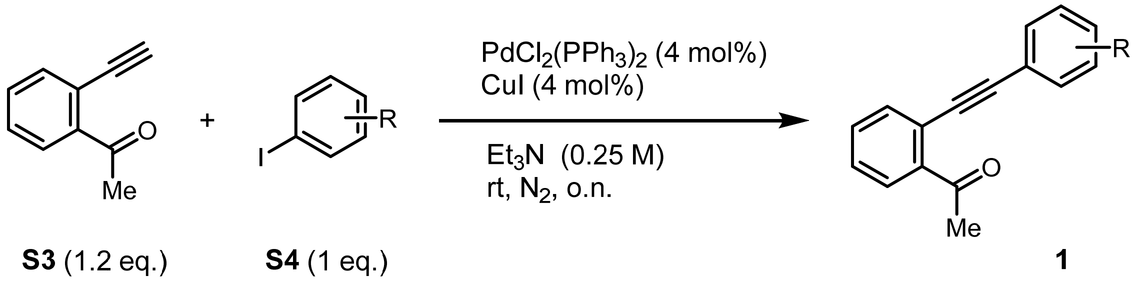
Preparation of **S3**



To an oven-dried three-neck flask with a magnetic stirrer bar were added $PdCl_2(PPh_3)_2$ (276.4 mg, 4 mol%), CuI (75.7 mg, 4 mol%). The atmosphere was replaced with nitrogen, then 2-bromoacetophenone **S1** (1.85 g, 1.16 mL, 10 mmol), trimethylsilylacetylene **S2** (1.5 g, 2.1 mL, 15 mmol) and triethylamine (40 mL) were added to the mixture, and the reaction mixture was stirred for 18 hours at 80 °C (oil bath). The reaction was quenched with aq. NH_4Cl. The resulting mixture was extracted with EtOAc, and the combined extracts were washed with H_2O and brine, dried over Na_2SO_4 and concentrated under reduced pressure after filtration.

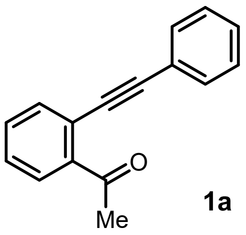
The crude product was used to the next reaction without further purification. To the crude product was added KF (4.1g, 70 mmol) and MeOH (100 mL), and stirred for 2 h at room temperature. The reaction was quenched with water. The resulting mixture was extracted with EtOAc, and the combined extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The residual crude product was purified by column chromatography on silica gel (hexane/EtOAc = 30:1 to 20:1) to give the product **S3** as red oil (959.1 mg, 74% yield).

Preparation of *ortho*-alkynylmethylketone **1**



General Procedure: To an oven-dried two-neck flask with a magnetic stirrer bar were added $PdCl_2(PPh_3)_2$ (4 mol%) and CuI (4 mol%). The atmosphere was replaced with nitrogen, then 2-ethynylacetophenone **S3** (1.5 mmol), iodobenzene derivative **S4** (1.25 mmol) and triethylamine (5 mL) were added to the mixture, and the reaction mixture was stirred overnight at room temperature. The reaction was quenched with aq. NH_4Cl. The resulting mixture was extracted with EtOAc, and the combined extracts were washed with aq. NH_4Cl, H_2O and brine, dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The residual crude product was purified by column chromatography on silica gel (hexane/EtOAc) to give product **1**.

1-(2-(Phenylethynyl)phenyl)ethan-1-one (**1a**)

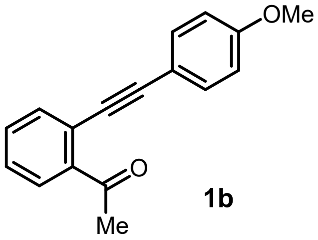


1a

98% yield; orange oil; hexane/EtOAc = 50:1 to 20:1

All spectroscopic data for **1a** (^{1}H NMR, ^{13}C{^{1}H} NMR, IR, and HRMS) were identical to the known compound.[1]

1-(2-((4-Methoxyphenyl)ethynyl)phenyl)ethan-1-one (**1b**)

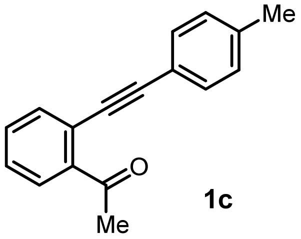


1b

96% yield; orange oil; hexane/EtOAc = 30:1 to 5:1

All spectroscopic data for **1b** (^{1}H NMR, ^{13}C{^{1}H} NMR, IR, and HRMS) were identical to the known compound.[1]

1-(2-(*p*-Tolylethynyl)phenyl)ethan-1-one (**1c**)

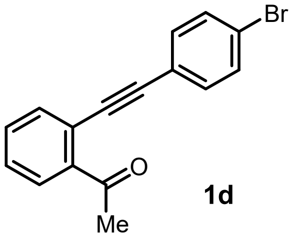


1c

82% yield; orange solid; hexane/EtOAc = 30:1 to 5:1

All spectroscopic data for **1c** (^{1}H NMR, ^{13}C{^{1}H} NMR, IR, and HRMS) were identical to the known compound.[1]

1-(2-((4-Bromophenyl)ethynyl)phenyl)ethan-1-one (**1d**)

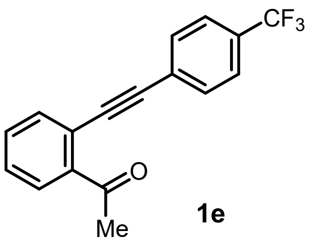


1d

86% yield; yellow solid; hexane/EtOAc = 30:1 to 10:1

All spectroscopic data for **1d** (^{1}H NMR, ^{13}C{^{1}H} NMR, IR, and HRMS) were identical to the known compound.[2]

1-(2-((4-(Trifluoromethyl)phenyl)ethynyl)phenyl)ethan-1-one (**1e**)

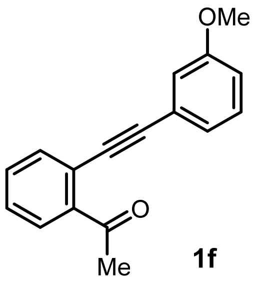


1e

89% yield; orange oil; hexane/EtOAc = 25:1 to 10:1

All spectroscopic data for **1e** (^{1}H NMR, ^{13}C{^{1}H} NMR, IR, and HRMS) were identical to the known compound.[1]

1-(2-((3-Methoxyphenyl)ethynyl)phenyl)ethan-1-one (**1f**)

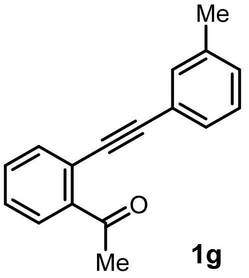


1f

90% yield; orange oil; hexane/EtOAc = 25:1 to 10:1

All spectroscopic data for **1f** (^{1}H NMR, ^{13}C{^{1}H} NMR, IR, and HRMS) were identical to the known compound.[3]

1-(2-(*m*-Tolylethynyl)phenyl)ethan-1-one (**1g**)

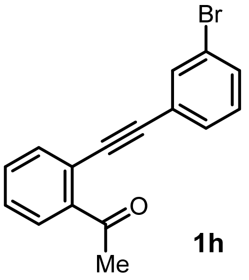


1g

95% yield; yellow oil; hexane/EtOAc = 30:1 to 5:1

All spectroscopic data for **1g** (^{1}H NMR, ^{13}C{^{1}H} NMR, IR, and HRMS) were identical to the known compound.[2]

1-(2-((3-Bromophenyl)ethynyl)phenyl)ethan-1-one (**1h**)

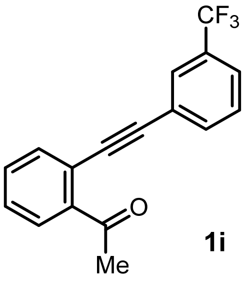


1h

88% yield; orange oil; hexane/EtOAc = 25:1 to 10:1

All spectroscopic data for **1h** (^{1}H NMR, ^{13}C{^{1}H} NMR, IR, and HRMS) were identical to the known compound.[2]

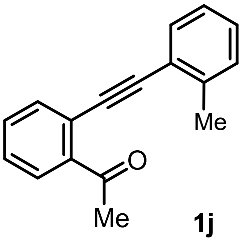
1-(2-((3-(Trifluoromethyl)phenyl)ethynyl)phenyl)ethan-1-one (**1i**)



1i

92% yield; orange oil; hexane/EtOAc = 25:1 to 5:1; R_f = 0.4 (Hexane/EtOAc = 5/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.78 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.73 (dd, *J* = 7.6 Hz, 1H), 7.65 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.52-7.48 (m, 2H), 7.44 (td, *J* = 7.6, 1.4 Hz, 1H), 2.76 (s, 3H); ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 199.8, 140.6, 134.7, 134.1, 131.4, 131.0 (q, J_{C-F} = 31.8 Hz), 129.0, 128.9, 128.7, 128.2 (q, J_{C-F} = 3.9 Hz), 125.2 (q, J_{C-F} = 4.3 Hz), 123.9, 123.6 (q, J_{C-F} = 271.7 Hz), 121.0, 92.9, 89.9, 29.6; IR (neat): 3065, 2981, 2916, 1688, 1489, 1430, 1336, 1165, 1122, 1091, 1071, 892, 803, 759, 695 cm^{-1}; HRMS (FD) *m*/*z*: [M]$^+$ Calcd for $C_{17}H_{11}F_3O$ 288.0757; Found 288.0761.

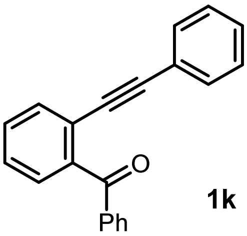
1-(2-(*o*-Tolylethynyl)phenyl)ethan-1-one (**1j**)



1j

89% yield; yellow oil; hexane/EtOAc = 25:1 to 5:1; R_f = 0.27 (hexane/EtOAc = 15/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.31-7.27 (m, 2H) 7.20-7.17 (m, 1H), 2.78 (s, 3H), 2.54 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 200.3, 140.4, 140.3, 134.0, 131.9, 131.2, 129.6, 128.8, 128.6, 128.1, 125.6, 122.6, 121.9, 94.0, 92.1, 29.9, 20.7; IR (neat): 3060, 3021, 2921, 2861, 2209, 1922, 1830, 1686, 1591, 1561, 1488, 1356, 1278, 1244, 955, 795 cm^{-1}; HRMS (APCI) *m*/*z*: [M + H]$^+$ Calcd for $C_{17}H_{15}O$ 235.1117; Found 235.1118.

Phenyl(2-(phenylethynyl)phenyl)methanone (**1k**)

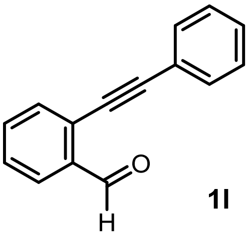


1k

92% yield; yellow oil; hexane/EtOAc = 30:1 to 5:1

All spectroscopic data for **1k** (^{1}H NMR, ^{13}C{^{1}H} NMR, IR, and HRMS) were identical to the known compound.[4]

2-(Phenylethynyl)benzaldehyde (**1l**)

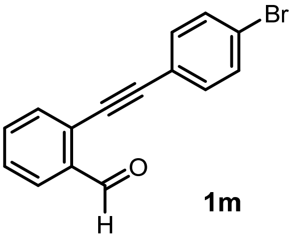


1l

58% yield; yellow oil; hexane/EtOAc = 30:1 to 5:1

All spectroscopic data for **1l** (^{1}H NMR, ^{13}C{^{1}H} NMR, IR, and HRMS) were identical to the known compound.[5]

2-((4-Bromophenyl)ethynyl)benzaldehyde (**1m**)



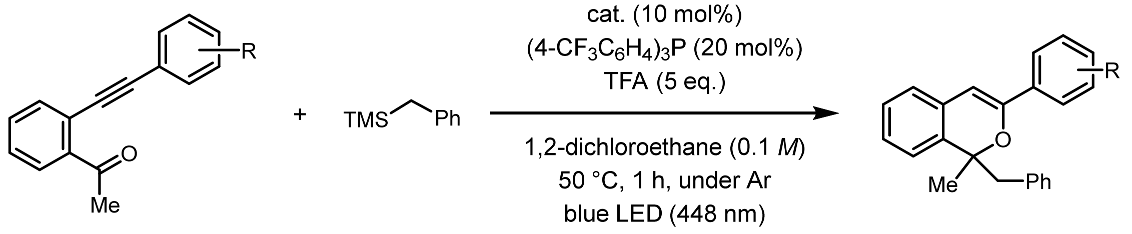
1m

82% yield; white solid; hexane/EtOAc = 25:1 to 10:1

All spectroscopic data for **1m** (^{1}H NMR, ^{13}C{^{1}H} NMR, IR, and HRMS) were identical to the known compound.[6]

3. Typical Procedures for The Intended Consecutive Transformation

General Procedure



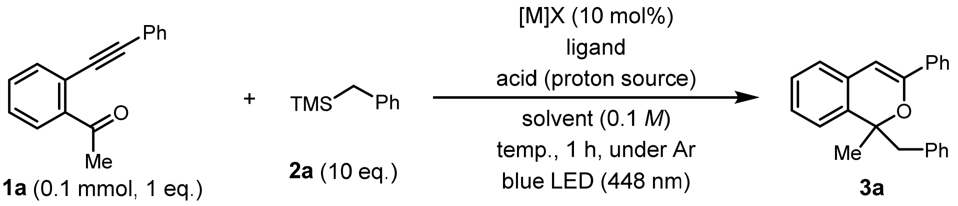
1 (0.1 mmol, 1 eq.) **2a** (10 eq.) **3**

To a dried two-neck flask were added 10 mol % (10 µmol) of metal catalyst ($AgNTf_2$: 3.9 mg or $Cu(NTf_2)_2$: 6.2 mg) and 20 mol% (20 µmol) of $(4\text{-}CF_3C_6H_4)_3P$ (9.3 mg). After insertion the light source (blue LED, λ_{max} = 448 nm), the atmosphere was replaced with argon. 1,2-dichloroethane (0.5 mL) was added to the flask. After 15 minutes, the mixture of benzyltrimethylsilane (**2a**) (189 µL, 1.0 mmol), TFA (38 µL, 0.5 mmol) in 1,2-dichloroethane (0.1 mL) were added to the mixture. The solution of *ortho*-alkynylmethylketone **1** (0.1 mmol) in 1,2-dichloroethane (0.3 mL) was successively added to the solution. The reaction was performed under the light irradiation at 50 °C (internal temperature) for 1 h. After completion of the reaction, the reaction mixture was concentrated under reduced pressure. The residual crude product was purified by column chromatography on silica gel (hexane only to hexane/EtOAc = 30:1) to give product **3**.

4. Screening of Reaction Conditions, Scope of Substrates, and Control Experiments

4.1. Screening of reaction conditions

Table S1. Initial screening of reaction conditions

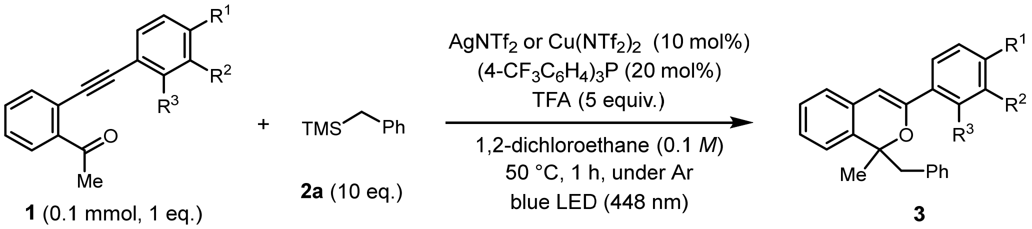


entry	[M]X	ligand (mol%)	acid (equiv.)	equiv. of **2a**	solvent	temp. (°C)	yield (%)	Table 1 entry
1	$AgNTf_2$	-	CF_3COOH (2.5)	2.5	CH_2Cl_2	0	28	entry 1
2	$AgNTf_2$	$P(OPh)_3$ (20)	CF_3COOH (2.5)	2.5		0	22	
3	$AgNTf_2$	PPh_3 (20)	CF_3COOH (2.5)	2.5		0	37	entry 2
4	$AgNTf_2$	$P(C_6F_5)_3$ (20)	CF_3COOH (2.5)	2.5		0	23	entry 3
5	$AgNTf_2$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	CF_3COOH (2.5)	2.5		0	43	entry 4
6	$AgNTf_2$	$P(4\text{-}CF_3C_6H_4)_3$ (10)	CF_3COOH (2.5)	2.5		0	27	
7	$AgNTf_2$	$P(4\text{-}CF_3C_6H_4)_3$ (15)	CF_3COOH (2.5)	2.5		0	36	
8	$AgNTf_2$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	CF_3COOH (2.5)	2.5	$ClCH_2CH_2Cl$	50	50	entry 5
9	$AgNTf_2$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	CF_3COOH (2.5)	5		50	46	
10	$AgNTf_2$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	CF_3COOH (2.5)	10		50	65	entry 6
11	**$AgNTf_2$**	**$P(4\text{-}CF_3C_6H_4)_3$ (20)**	**CF_3COOH (5)**	**10**		**50**	**76**	**entry 7**
12	$AgNTf_2$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	CF_3COOH (10)	10		50	64	entry 8
13	AgOTf	$P(4\text{-}CF_3C_6H_4)_3$ (20)	CF_3COOH (5)	10		50	71	entry 9
14	**$Cu(NTf_2)_2$**	**$P(4\text{-}CF_3C_6H_4)_3$ (20)**	**CF_3COOH (5)**	**10**		**50**	**78**	**entry 10**
15	$Cu(OTf)_2$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	CF_3COOH (5)	10		50	31	entry 11
16	$CuOTf\bullet C_6H_6$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	CF_3COOH (5)	10		50	34	entry 12
17	$AuNTf_2$	$P(4\text{-}CF_3C_6H_4)_3$ (10)	CF_3COOH (2.5)	10		50	38	entry 13
18	$Cu(NTf_2)_2$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	CF_3COOH (5)	10	THF	50	<6	
19	$Cu(NTf_2)_2$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	CF_3COOH (5)	10	MTBE	50	<6	
20	$Cu(NTf_2)_2$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	CF_3COOH (5)	10	CH_3CN	50	<5	
21	$Cu(NTf_2)_2$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	CF_3COOH (5)	10	PhCl	50	42	
22	$Cu(NTf_2)_2$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	CH_3COOH (5)	10	$ClCH_2CH_2Cl$	50	29	
23	$Cu(NTf_2)_2$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	CCl_3COOH (5)	10		50	56	
24	$Cu(NTf_2)_2$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	CF_3COOH (2.5)	10		50	51	
25	$Cu(NTf_2)_2$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	CF_3COOH (1)	10		50	33	
26	$Cu(NTf_2)_2$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	CF_3COOH (5)	5		50	47	
27	$Cu(NTf_2)_2$	$P(4\text{-}CF_3C_6H_4)_3$ (10)	CF_3COOH (5)	10		50	63	
28	$Cu(NTf_2)_2$	$P(4\text{-}CF_3C_6H_4)_3$ (50)	CF_3COOH (5)	10		50	15	
29	$Cu(NTf_2)_2$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	CF_3COOH (5)	10		0 (6 h)	37	
30[a]	$AgNTf_2$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	CF_3COOH (5)	10		50	17	entry 14

[a] purple LED: λ_{max} = 405 nm (standard blue LED: λ_{max} = 448 nm)

4.2. Scope of substrates

Table S2. Scope of substrates[a]

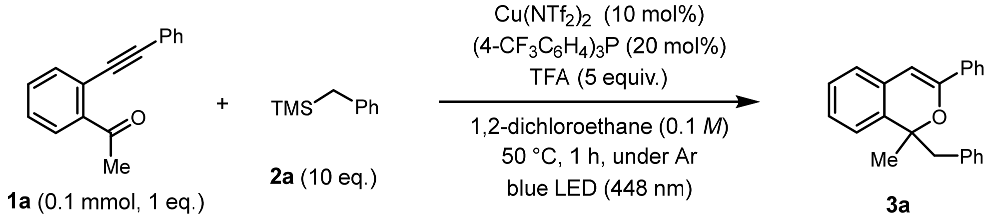


entry	**1**	R^1	R^2	R^3	**3**	$AgNTf_2$ Yield of **3** (%)[b]	$Cu(NTf_2)_2$ Yield of **3** (%)[b]
1[c]	**1b**	MeO	H	H	**3b**	48	54 (44)
2	**1c**	Me	H	H	**3c**	21	56 (47)
3	**1d**	Br	H	H	**3d**	10	65 (77)
4	**1e**	CF_3	H	H	**3e**	65 (72)	38
5	**1f**	H	MeO	H	**3f**	40 (39)	23
6	**1g**	H	Me	H	**3g**	50	52 (58)
7	**1h**	H	Br	H	**3h**	63 (59)	36
8	**1i**	H	CF_3	H	**3i**	42	53 (63)
9	**1j**	H	H	Me	**3j**	72 (74)	63

[a] Unless otherwise specified, all reactions were carried out using blue LED (λ_{max} = 448 nm), 0.1 mmol of **1**, 1.0 mmol (10 equiv.) of **2a**, 10 μmol (10 mol%) of $AgNTf_2$ or $Cu(NTf_2)_2$, 20 μmol (20 mol%) of $(4\text{-}CF_3C_6H_4)_3P$, and 5 equiv. of TFA in 1,2-dichloroethane (1 mL: 0.1 *M* of **1a**) at 50 °C for 1 h. [b] Yield was calculated from NMR analysis using 1,1,2,2-tetrabromoethane as an internal standard. Isolated yield is shown in parentheses. [c] At 0 °C for 6 h.

4.3. Control experiments

Table S3. Control experiments[a]

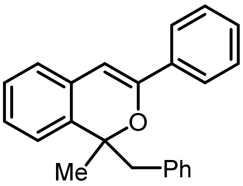


entry	condition	yield of **3a** (%)	recovery of **1a** (%)
1	without $Cu(NTf_2)_2$	0	75
2	no light irradiation	0	64
3	without TFA	13	0

[a] Unless otherwise specified, all reactions were carried out using blue LED (λ_{max} = 448 nm), 0.1 mmol of **1a**, 1.0 mmol (10 equiv.) of **2a**, 10 μmol (10 mol%) of $Cu(NTf_2)_2$, 20 μmol (20 mol%) of $(4\text{-}CF_3C_6H_4)_3P$, and 5 equiv. of TFA in 1,2-dichloroethane (1 mL: 0.1 *M* of **1a**) at 50 °C for 1 h.

5. Analytical Data of Products **3**

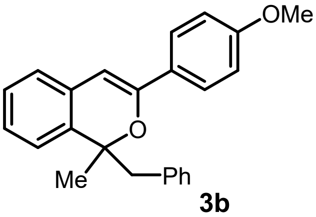
1-Benzyl-1-methyl-3-phenyl-1*H*-isochromene (**3a**)



3a

The metal catalyst at optimal conditions: $AgNTf_2$; 81% yield; White foam; R_f = 0.59 (Hexane/EtOAc = 10/1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.39-7.32 (m, 3H), 7.22 (td, *J* = 7.6, 1.4 Hz, 1H), 7.19-7.15 (m, 3H), 7.12-7.09 (m, 2H), 6.96 (dd, *J* = 7.9, 1.4 Hz, 2H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.47 (s, 1H), 3.22 (d, *J* = 13.8 Hz, 1H), 3.11 (d, *J* = 13.8 Hz, 1H), 1.71 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 150.5, 136.5, 134.6_3, 134.5_9, 131.1, 130.6, 128.6, 128.2, 127.7, 127.5, 126.3_1, 126.2_6, 125.0, 124.1, 123.7, 100.1, 80.8, 44.9, 24.4; IR (neat): 3061, 3028, 2980, 2922, 1723, 1698, 1495, 1452, 1272, 1235, 1089, 761, 700 cm^{-1}; HRMS (FD) *m*/*z*: $[M]^+$ Calcd for $C_{23}H_{20}O$ 312.1509; Found 312.1513.

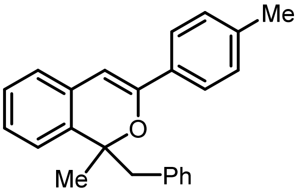
1-Benzyl-3-(4-methoxyphenyl)-1-methyl-1*H*-isochromene (**3b**)



3b

The reaction was performed at 0 °C for 6 h; The metal catalyst at optimal conditions: $Cu(NTf_2)_2$; 44% yield; White foam; R_f = 0.57 (Hexane/EtOAc = 10/1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 6.9, 2.1 Hz, 2H), 7.21-7.18 (m, 4H), 7.10-7.07 (m, 2H), 6.96 (dd, *J* = 7.6, 1.7 Hz, 2H), 6.92-6.90 (m, 3H), 6.36 (s, 1H), 3.85 (s, 3H), 3.22 (d, *J* = 13.4 Hz, 1H), 3.08 (d, *J* = 13.4 Hz, 1H), 1.70 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 160.1, 150.4, 136.6, 134.4, 131.1, 130.9, 127.6, 127.5, 127.2, 126.5, 126.2, 125.9, 123.8, 123.6, 113.6, 98.5, 80.7, 55.3, 44.7, 24.3; IR (neat): 3061, 3026, 2934, 2835, 1509, 1248, 1173, 1055, 1028, 932, 833, 700 cm^{-1}; HRMS (FD) *m*/*z*: $[M]^+$ Calcd for $C_{24}H_{22}O_2$ 342.1614; Found 342.1619.

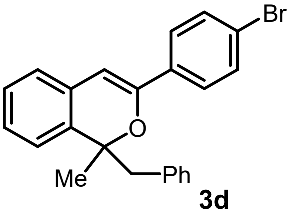
1-Benzyl-1-methyl-3-(*p*-tolyl)-1*H*-isochromene (**3c**)



3c

The metal catalyst at optimal conditions: $Cu(NTf_2)_2$; 47% yield; Colorless oil; R_f = 0.53 (Hexane/EtOAc = 10/1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.23-7.16 (m, 6H), 7.10-7.07 (m, 2H), 6.96 (d, *J* = 6.9 Hz, 2H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.42 (s, 1H), 3.22 (d, *J* = 13.8 Hz, 1H), 3.10 (d, *J* = 13.8 Hz, 1H), 2.38 (s, 3H), 1.70 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 150.7, 138.6, 136.6, 134.6, 131.8, 131.1, 130.8, 128.9, 127.6, 127.5, 126.2, 126.1, 125.0, 124.0, 123.7, 99.3, 80.7, 44.8, 24.4, 21.3; IR (neat): 3061, 3027, 2981, 2919, 1452, 1273, 1082, 1057, 803, 748, 699 cm^{-1}; HRMS (FD) *m*/*z*: $[M]^+$ Calcd for $C_{24}H_{22}O$ 326.1665; Found 326.1670.

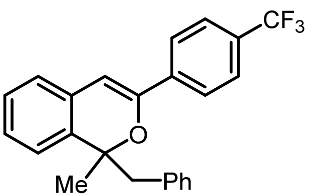
1-Benzyl-3-(4-bromophenyl)-1-methyl-1*H*-isochromene (**3d**)



3d

The metal catalyst at optimal condition: Cu(NTf$_2$)$_2$; 77% yield; White foam; R$_f$ = 0.63 (Hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.56 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.6 Hz, 2H), 7.24-7.16 (m, 4H), 7.15-7.10 (m, 2H), 6.95-6.93 (m, 3H), 6.45 (s, 1H), 3.21 (d, J = 13.7 Hz, 1H), 3.05 (d, J = 13.4 Hz, 1H), 1.70 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) δ 149.5, 136.3, 134.7, 133.5, 131.3, 131.0, 130.3, 127.8, 127.6, 126.7, 126.5, 126.3, 124.3, 123.7, 122.6, 100.5, 80.9, 45.0, 24.4; IR (neat): 3062, 3026¸ 2983, 1629, 1486, 1451, 1398, 1054, 1005, 805, 746, 700 cm^{-1}; HRMS (FD) *m/z*: [M]$^+$ Calcd for C$_{23}$H$_{19}$BrO 390.0614; Found 390.0618.

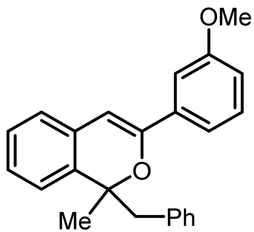
1-Benzyl-1-methyl-3-(4-(trifluoromethyl)phenyl)-1*H*-isochromene (**3e**)



3e

The metal catalyst at optimal condition: AgNTf$_2$; 72% yield; Colorless oil; R$_f$ = 0.57 (Hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.79 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.6 Hz, 2H), 7.24 (td, J = 7.7, 1.4 Hz, 1H), 7.22-7.12 (m, 5H), 6.96 (d, J = 7.6 Hz, 1H), 6.94 (d, J = 6.9 Hz, 2H), 6.53 (s, 1H), 3.22 (d, J = 13.8 Hz, 1H), 3.08 (d, J = 13.8 Hz, 1H), 1.72 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) δ 149.0, 138.0, 136.3, 134.9, 131.0, 130.1 (q, $J_{\text{C-F}}$ = 31.8 Hz), 130.0, 127.8, 127.6, 127.1, 126.4, 125.2 (q, $J_{\text{C-F}}$ = 4.3 Hz), 125.1 (q, $J_{\text{C-F}}$ = 271.5 Hz) 125.0, 124.6, 123.7, 101.9, 81.1, 45.1, 24.5; IR (neat): 3063, 3028, 2983, 1733, 1615, 1453, 1411, 1321, 1164, 1110, 1014, 851, 807, 750, 700 cm^{-1}; HRMS (FD) *m/z*: [M]$^+$ Calcd for C$_{24}$H$_{19}$F$_3$O 380.1383; Found 380.1387.

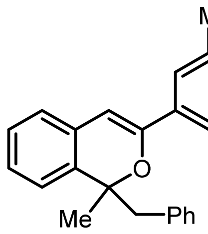
1-Benzyl-3-(3-methoxyphenyl)-1-methyl-1*H*-isochromene (**3f**)



3f

The metal catalyst at optimal conditions: AgNTf$_2$; 39% yield; Colorless oil; R$_f$ = 0.57 (Hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.33 (dt, J = 7.8, 1.3 Hz, 1H), 7.29 (t, J = 7.9 Hz, 1H), 7.24-7.17 (m, 5H), 7.12-7.10 (m, 2H), 6.99-6.97 (m, 2H), 6.92 (d, J = 7.9 Hz, 1H), 6.89 (m, 1H), 6.46 (s, 1H), 3.82 (s, 3H), 3.23 (d, J = 13.4 Hz, 1H), 3.11 (d, J = 13.4 Hz, 1H), 1.69 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) δ 159.6, 150.3, 136.5, 136.1, 134.8, 131.1, 130.6, 129.1, 127.7, 127.6, 126.4, 126.3, 124.2, 123.6, 117.5, 114.4, 110.3, 100.4, 80.8, 55.3, 44.8, 24.4; IR (neat): 3064,3030, 2937, 2834, 1748,1670,1647, 1630, 1604, 1542, 1508, 1489, 1452, 1429, 1322, 1229, 1171, 1061, 784, 719, 671, 658 cm^{-1}; HRMS (APCI) *m/z*: [M + H]$^+$ Calcd for C$_{24}$H$_{23}$O 343.1693; Found 343.1693.

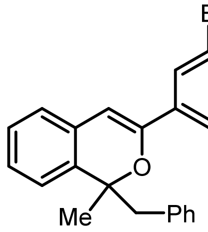
1-Benzyl-1-methyl-3-(*m*-tolyl)-1*H*-isochromene (**3g**)



3g

The metal catalyst at optimal conditions: Cu(NTf$_2$)$_2$; 58% yield; Colorless oil; R$_f$ = 0.49 (Hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.53 (d, *J* = 7.6 Hz, 1H), 7.52 (s, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.23-7.15 (m, 5H), 7.12-7.09 (m, 2H), 6.97 (d, *J* = 6.5 Hz, 2H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.46 (s, 1H), 3.22 (d, *J* = 13.8 Hz, 1H), 3.11 (d, *J* = 13.8 Hz, 1H), 2.38 (s, 3H), 1.71 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) δ 150.6, 137.8, 136.6, 134.7, 134.5, 131.1, 130.7, 129.4, 128.1, 127.7, 127.5, 126.3, 126.2, 125.7, 124.1, 123.7, 122.2, 100.0, 80.7, 44.8, 24.4, 21.5; IR (neat): 3058, 3026, 2998, 2988, 2938, 2910, 1600, 1485, 1454, 1080, 1061, 1032, 808, 782, 767, 748, 716, 700, 691 cm^{-1}; HRMS (FD) *m*/*z*: [M]$^+$ Calcd for $C_{24}H_{22}O$ 326.1665; Found 326.1670.

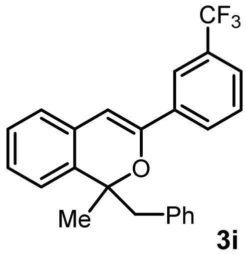
1-Benzyl-3-(3-bromophenyl)-1-methyl-1*H*-isochromene (**3h**)



3h

The metal catalyst at optimal conditions: AgNTf$_2$; 59% yield; Yellow oil; R$_f$ = 0.57 (Hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.83 (t, *J* = 1.9 Hz, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.45 (m, 1H), 7.25-7.17 (m, 5H), 7.15-7.11 (m, 2H), 6.96-6.93 (m, 3H), 6.46 (s, 1H), 3.21 (d, *J* = 13.7 Hz, 1H), 3.08 (d, *J* = 13.7 Hz, 1H), 1.71 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) δ 149.0, 136.7, 136.3, 134.8, 131.4, 131.0, 130.2, 129.7, 128.0, 127.8, 127.6, 126.8, 126.4, 124.4, 123.7, 123.4, 122.6, 101.1, 81.0, 45.0, 24.4; IR (neat): 3062, 3027, 2981, 2917, 1557, 1485, 1474, 1452, 1240, 1079, 1058, 1031, 781, 746, 700, 685 cm^{-1}; HRMS (FD) *m*/*z*: [M]$^+$ Calcd for $C_{23}H_{19}BrO$ 390.0614; Found 390.0618.

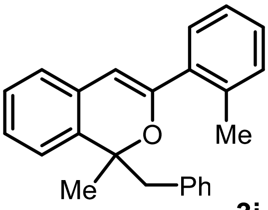
1-Benzyl-1-methyl-3-(3-(trifluoromethyl)phenyl)-1*H*-isochromene (**3i**)



3i

The metal catalyst at optimal conditions: Cu(NTf$_2$)$_2$; 63% yield; Colorless oil; Rf = 0.56 (Hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.92 (s, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.25-7.14 (m, 6H), 6.98-6.96 (m, 3H), 6.53 (s, 1H), 3.25 (d, *J* = 13.7 Hz, 1H), 3.07 (d, *J* = 13.7 Hz, 1H), 1.72 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) δ 149.0, 136.2, 135.4, 135.0, 131.0, 130.7 (q, $J_{C\text{-}F}$ = 31.8 Hz), 130.0, 128.6, 127.9, 127.8, 127.6, 127.0, 126.4, 125.0 (q, $J_{C\text{-}F}$ = 4.3 Hz), 124.5, 124.1 (q, $J_{C\text{-}F}$ = 271.7 Hz), 123.7, 121.8 (q, $J_{C\text{-}F}$ = 4.3 Hz), 101.2, 81.1, 45.1, 24.4; IR (neat): 3064, 3028, 2984, 1487, 1450, 1333, 1164, 1121, 1072, 748, 722, 694 cm^{-1}; HRMS (FD) *m*/*z*: [M]$^+$ Calcd for $C_{24}H_{19}F_3O$ 380.1384; Found 380.1387.

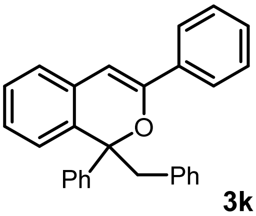
1-Benzyl-1-methyl-3-(*o*-tolyl)-1*H*-isochromene (**3j**)



3j

The metal catalyst at optimal conditions: AgNTf$_2$; 74% yield; Colorless oil; R$_f$ = 0.53 (Hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.47-7.45 (m, 1H), 7.25-7.19 (m, 4H), 7.17-7.11 (m, 3H), 7.06-7.03 (m, 2H), 6.88-6.86 (m, 2H), 6.76 (d, *J* = 7.6 Hz, 1H), 5.95 (s, 1H), 3.40 (d, *J* = 13.4 Hz, 1H), 3.15 (d, *J* = 13.4 Hz, 1H), 2.46 (s, 3H), 1.71 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) δ 152.8, 136.7, 136.4, 135.5, 133.2, 130.9, 130.8, 130.8, 128.7, 128.4, 127.7, 127.5, 126.2, 126.0, 125.6, 124.1, 123.7, 103.8, 81.5, 45.1, 25.0, 21.1; IR (neat): 3060, 3023, 2979, 2926, 1720, 1701,1633,1601, 1486, 1453, 1341, 1249, 1158, 1118, 1056, 1034, 759, 723 cm^{-1}; HRMS (APCI) *m*/*z*: [M + H]$^+$ Calcd for C$_{24}$H$_{23}$O 327.1743; Found 327.1743.

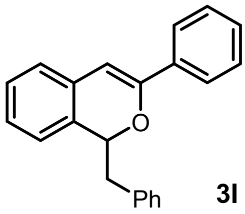
1-Benzyl-1,3-diphenyl-1*H*-isochromene (**3k**)



3k

The metal catalyst at optimal conditions: AgNTf$_2$; 30% yield; White solid; R$_f$ = 0.63 (Hexane/EtOAc = 15/1); Mp: 155.4-156.8 °C; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.72 (dt, *J* = 6.8, 1.5 Hz, 2H), 7.50 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.38-7.35 (m, 2H), 7.34-7.26 (m, 4H), 7.19-7.11 (m, 6H), 7.10-7.06 (m, 4H), 6.37 (s, 1H), 3.76 (d, *J* = 14.1 Hz, 1H), 3.69 (d, *J* = 14.1 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) δ 151.0, 143.0, 136.2, 134.2, 133.1, 131.5, 131.3, 128.6, 128.3, 128.0, 127.5, 127.4, 127.2, 126.3, 126.2, 126.2, 124.8, 124.6, 101.1, 83.9, 46.6; IR (neat): 3061, 3029, 2923, 2851, 1735, 1653, 1633, 1066, 1495, 1454, 1346, 1065, 1027, 794, 764 cm^{-1}; HRMS (APCI) *m*/*z*: [M + H]$^+$ Calcd for C$_{28}$H$_{23}$O 375.1743; Found 375.1744.

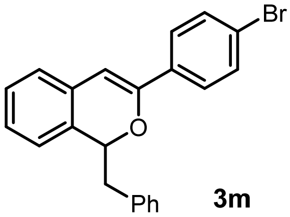
1-Benzyl-3-phenyl-1*H*-isochromene (**3l**)



3l

The metal catalyst at optimal conditions: AgNTf$_2$; 65% yield; White solid; R$_f$ = 0.63 (Hexane/EtOAc = 15/1); Mp: 103.9-104.8 °C; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.60-7.58 (m, 2H), 7.34-7.27 (m, 6H), 7.24 (m, 2H), 7.17-7.11 (m, 4H), 6.91-6.89 (m, 1H), 6.49 (s, 1H), 5.52 (dd, *J* = 9.0, 5.2 Hz, 1H), 3.31 (dd, *J* = 13.8, 9.0 Hz, 1H), 3.05 (dd, *J* = 13.8, 5.2 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) δ151.0, 137.5, 134.3, 130.8, 130.8, 129.8, 128.7, 128.2, 128.1, 126.4, 126.2, 125.1, 124.3, 124.0, 100.2, 79.1, 40.5; IR (neat): 3062, 3028, 2922, 2850, 1630, 1604, 1569, 1495, 1454, 1375, 1280, 1064, 1030, 795, 765 cm^{-1}; HRMS (APCI) *m*/*z*: [M + H]$^+$ Calcd for C$_{22}$H$_{19}$O 299.1430; Found 299.1430.

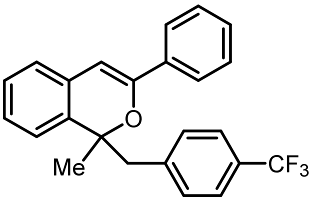
1-Benzyl-3-(4-bromophenyl)-1*H*-isochromene (**3m**)



3m

The metal catalyst at optimal conditions: $AgNTf_2$; 34% yield; White solid; $R_f = 0.67$ (Hexane/EtOAc = 15/1); Mp: 92.4-93.8 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.45-7.39 (m, 4H), 7.29-7.23 (m, 4H), 7.18-7.12 (m, 4H), 6.93 (t, $J = 7.9$ Hz, 1H), 6.46 (s, 1H), 5.50 (dd, $J = 9.3$, 5.2 Hz, 1H), 3.27 (dd, $J = 14.1$, 9.3 Hz, 1H), 3.01 (dd, $J = 14.1$, 5.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 149.9, 137.3, 133.2, 131.3, 130.9, 130.4, 129.7, 128.2, 128.1, 126.6, 126.6, 126.5, 124.2, 124.1, 122.7, 100.6, 79.1, 40.5; IR (neat): 3060, 3028, 2945, 2916, 1726, 1627, 1602, 1587, 1560, 1488, 1454, 1401, 1270, 1179, 1070, 1008, 795, 752 cm^{-1}; HRMS (APCI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{18}BrO$ 377.0536; Found 377.0536.

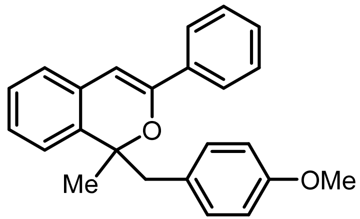
1-Methyl-3-phenyl-1-(4-(trifluoromethyl)benzyl)-1*H*-isochromene (**3n**)



3n

The metal catalyst at optimal conditions: $AgNTf_2$; 12% yield; White foam; $R_f = 0.66$ (Hexane/EtOAc = 5/1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.70-7.68 (m, 2H), 7.42-7.34 (m, 5H), 7.25-7.23 (m, 1H), 7.14-7.11 (m, 2H), 7.06 (d, $J = 7.9$ Hz, 2H), 6.93 (d, $J = 7.2$ Hz, 1H), 6.46 (s, 1H), 3.29 (d, $J = 13.4$ Hz, 1H), 3.16 (d, $J = 13.4$ Hz, 1H), 1.71 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 150.4, 140.7, 134.4, 134.1, 131.3, 130.6, 128.8, 128.6 (q, $J_{C\text{-}F} = 30.0$ Hz), 128.3, 128.0, 126.5, 124.9, 124.5 (q, $J_{C\text{-}F} = 4.4$ Hz), 124.3_4 (q, $J_{C\text{-}F} = 270.0$ Hz), 124.3_3, 123.6, 100.2, 80.6, 44.8, 24.6; IR (neat): 3069, 3032, 2925, 2854, 1712, 1613, 1493, 1442, 1325, 1274, 1164, 1122, 1066, 1019, 849,793 cm^{-1}; HRMS (APCI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{20}F_3O$ 381.1461; Found 381.1461.

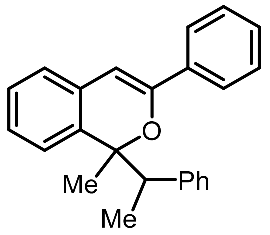
1-(4-Methoxybenzyl)-1-methyl-3-phenyl-1*H*-isochromene (**3o**)



3o

The metal catalyst at optimal conditions: $AgNTf_2$; 56% yield; White foam; $R_f = 0.60$ (Hexane/EtOAc = 5/1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.9 Hz, 2H), 7.39-7.34 (m, 3H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 7.2 Hz, 2H), 6.88 (m, 3H), 6.71 (d, *J* = 8.2 Hz, 2H), 6.46 (s, 1H), 3.77 (s, 3H), 3.15 (d, *J* = 13.7 Hz, 1H), 3.06 (d, *J* = 13.7 Hz, 1H), 1.69 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 158.1, 150.5, 134.7, 134.6, 132.0, 130.6, 128.6, 128.6, 128.2, 127.6, 126.3, 125.0, 124.1, 123.8, 113.0, 100.0, 80.9, 55.2, 43.9, 24.4; IR (neat): 3064, 3032, 2953, 2834, 1730, 1716, 1699, 1685, 1651, 1631, 1558, 1541, 1508, 1457, 1247, 795, 669, 656 cm^{-1}; HRMS (APCI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{23}O$ 343.1693; Found 343.1693.

1-methyl-3-phenyl-1-(1-phenylethyl)-1*H*-isochromene (**3p**)



3p

The metal catalyst at optimal conditions: $AgNTf_2$; 62% yield, dr = 65/35 ; Colorless oil; $R_f = 0.52$ (Hexane/EtOAc = 15/1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.78-7.77 (m, 1.30H), 7.58 (dd, *J* = 7.7, 1.9 Hz, 0.70H), 7.40 (t, *J* = 7.4 Hz, 1.30H), 7.35-7.31 (m, 1.65H), 7.24-7.08 (m, 7.40H), 7.05 (d, *J* = 7.7 Hz, 0.35H), 7.01-6.99 (m, 0.65H), 6.70 (d, *J* = 7.9 Hz, 0.65H), 6.41 (s, 0.65H), 6.39 (s, 0.35H), 3.57-3.51 (m, 1H), 1.75 (s, 1.05H), 1.54 (s, 1.95H), 1.41 (d, *J* = 7.2 Hz, 1.95H), 1.24 (d, *J* = 7.2 Hz, 1.05H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 150.4_0, 150.3_7, 142.2_4, 142.2_1, 134.8, 134.5, 134.3, 134.1, 130.8, 130.6, 129.7 (2C), 128.6, 128.5, 128.3, 128.0, 127.6, 127.5 (2C), 127.4, 126.4, 126.2, 126.0, 125.9, 125.0, 124.9 (2C), 124.2, 124.1, 124.0, 99.8, 99.4, 83.3, 83.2, 45.9, 45.0, 23.2, 22.4, 16.3, 15.6; IR (neat): 3064, 3030, 2979, 2935, 1716, 1689, 1602, 1491, 1452, 1375, 1339, 1272, 1057, 1027, 795, 765, 671, 651 cm^{-1}; HRMS (APCI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{23}O$ 343.1693; Found 343.1693.

6. UV-Vis Absorption Spectroscopy

To a solution of **1a** in CH_2Cl_2 (5.0×10^{-4} *M*) was added 1.0 equiv. of TFA and/or $AgNTf_2$, and then UV/Vis spectra were recorded (Fig. S1). The spectroscopic data indicates that the treatment of both $AgNTf_2$ and TFA enables the effective formation of 2-benzopyrylium cation intermediate **A**.

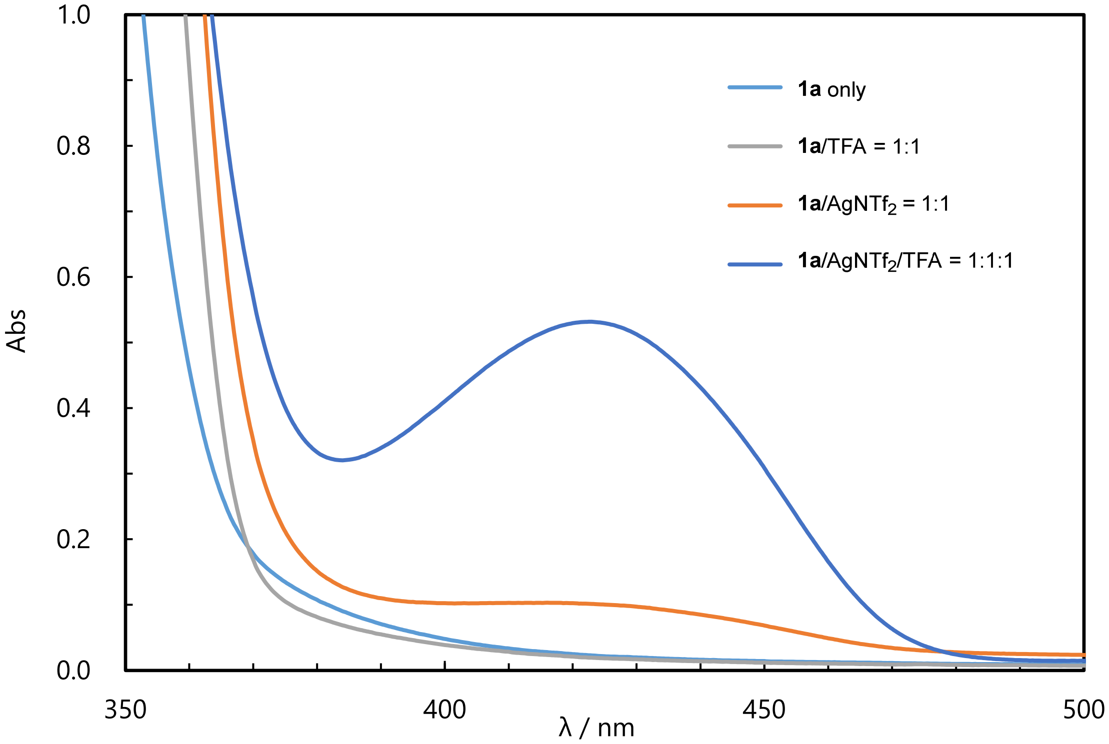
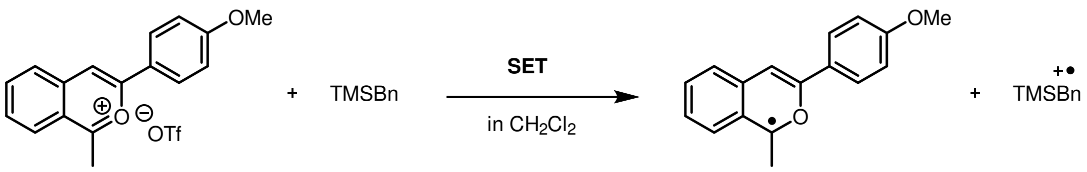


Fig. S1 UV-Vis Spectra of Related Species in CH_2Cl_2 (5.0×10^{-4} *M*).

7. Stern-Volmer Luminescence Quenching Experiments

Emission intensities were recorded on a HITACHI F-4500. The solutions were excited at 360 nm and the luminescence was measured at 565 nm. 2-benzopyrylium cation **1'b**$^+$ was prepared from **1b** and TMSOTf in accordance with the literature method.[7] This preparation method for 2-benzopyrylium cation is only useful for the electron rich substrate, such as **1b**. Stern-Volmer luminescence quenching experiments were run with prepared mixture of **1'b**$^+$OTf$^-$ (1.0×10^{-4} *M*) and TMSBn (indicated concentration) in CH_2Cl_2 solutions (**Fig. S2**). The data shows that TMSBn is competent at quenching the excited state of the **1'b**$^+$OTf$^-$.



1'b$^+$OTf$^-$

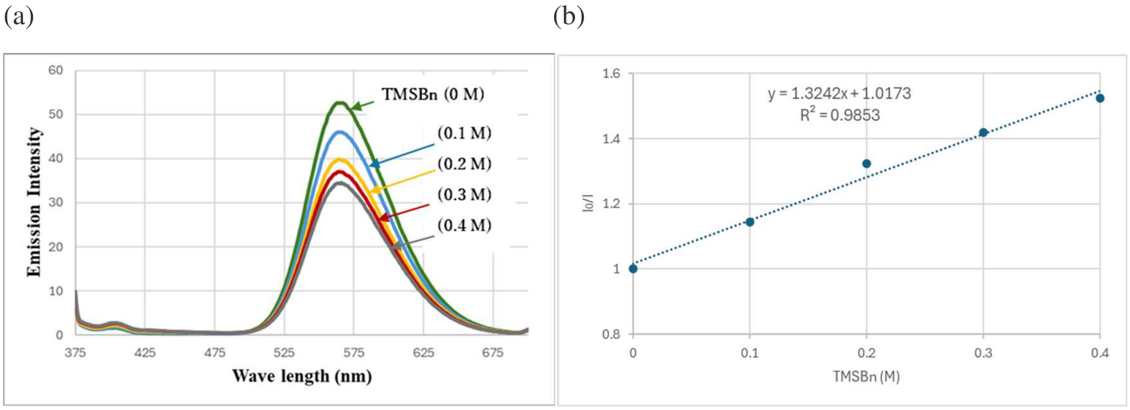


Fig. S2 (a) Fluorescence spectra of **1'b**$^+$OTf$^-$ in DCM with increasing amount of TMSBn. (b) The Stern-Volmer plots.

8. References

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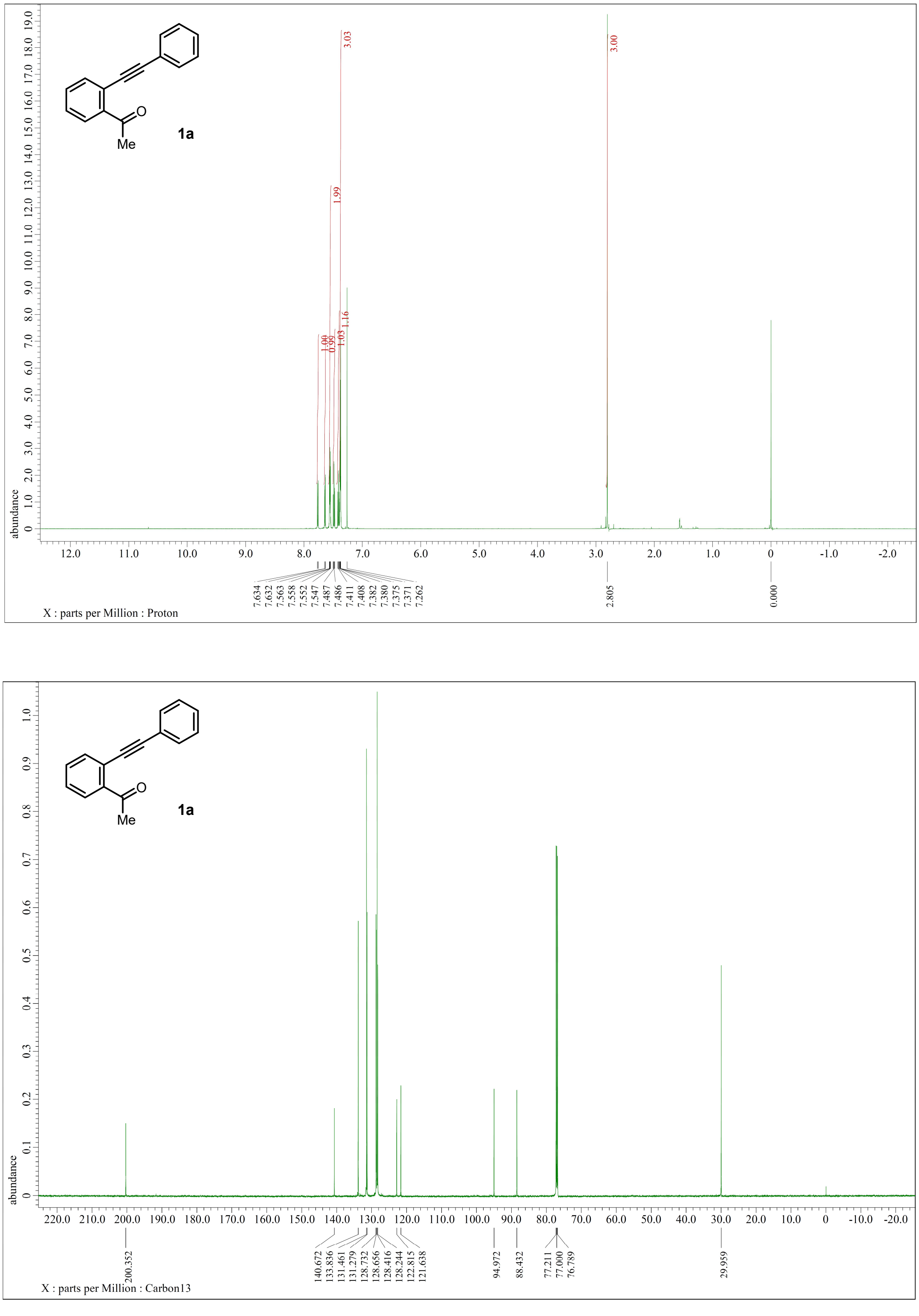
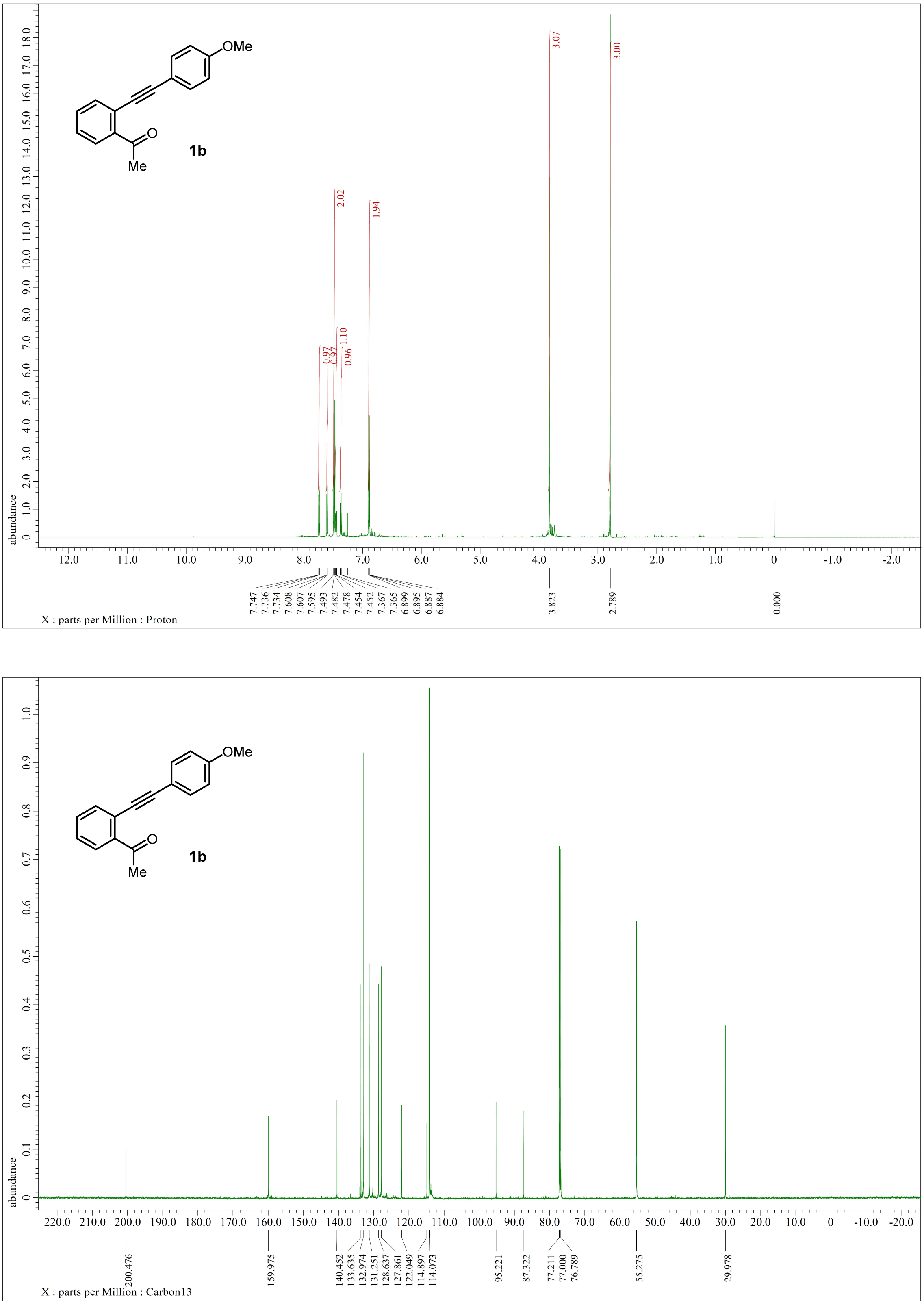
9. NMR Spectra

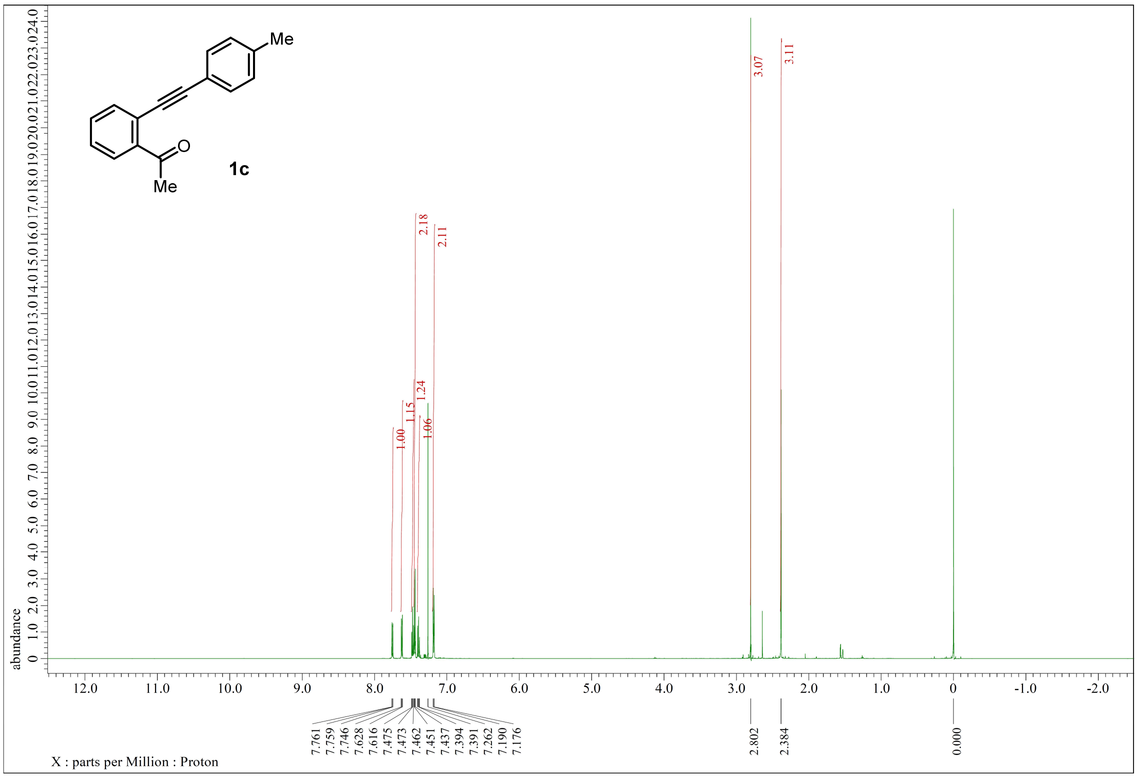
^{1}H NMR (600 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) spectra of **1a**.

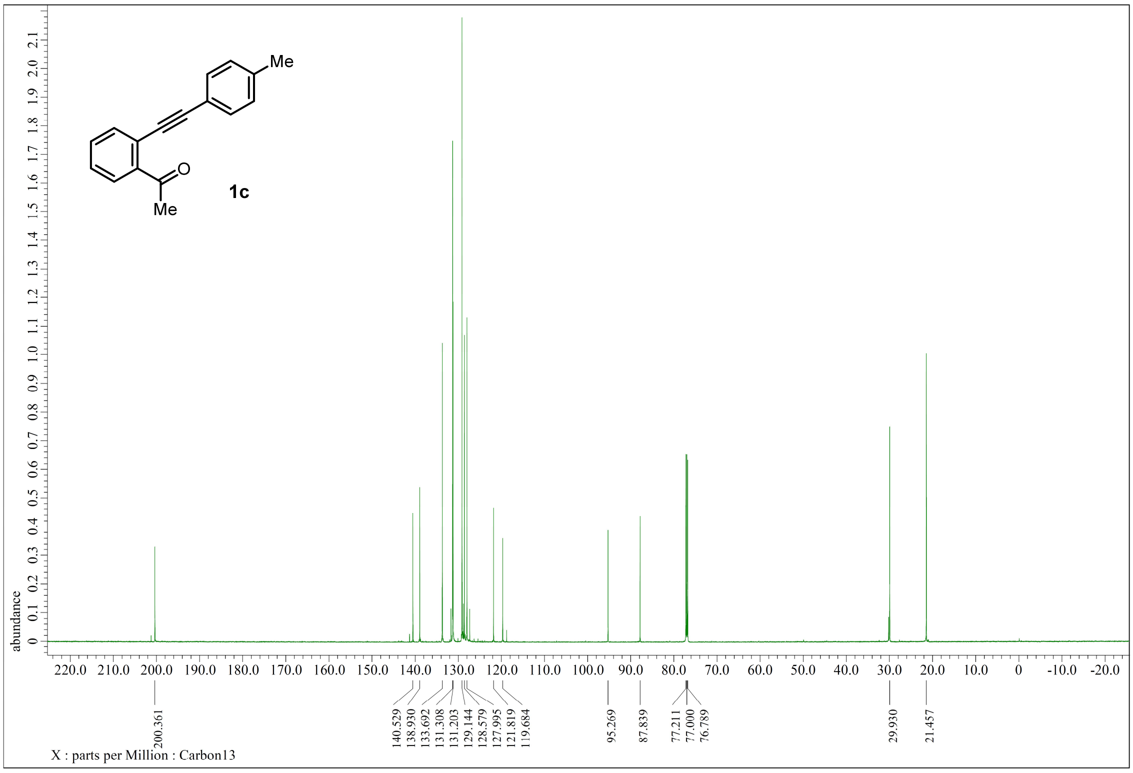


^{1}H NMR (600 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) spectra of **1b**.

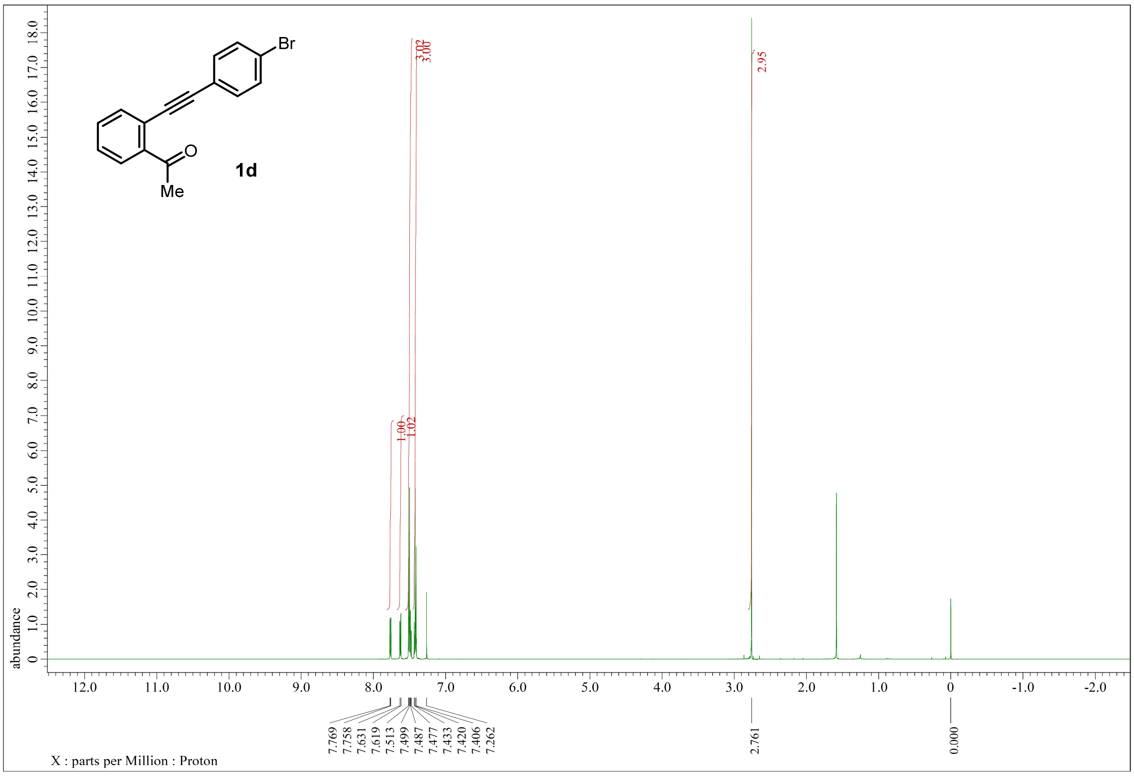


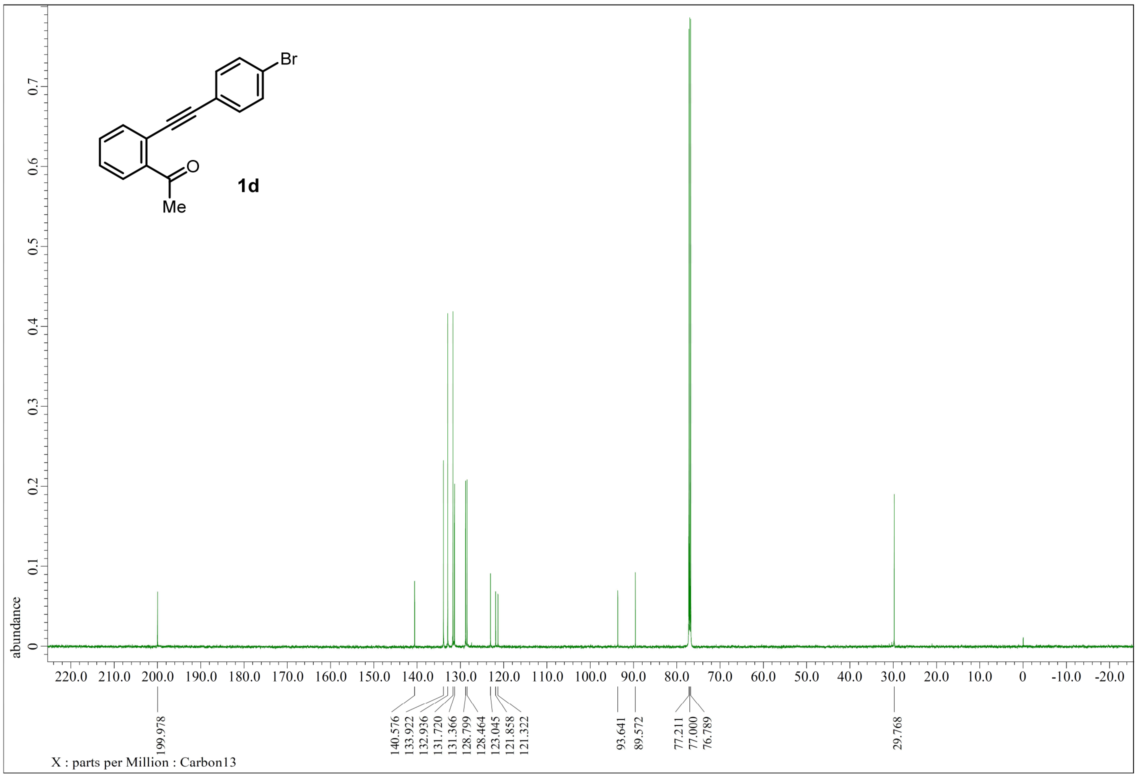
^{1}H NMR (600 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) spectra of **1c**.



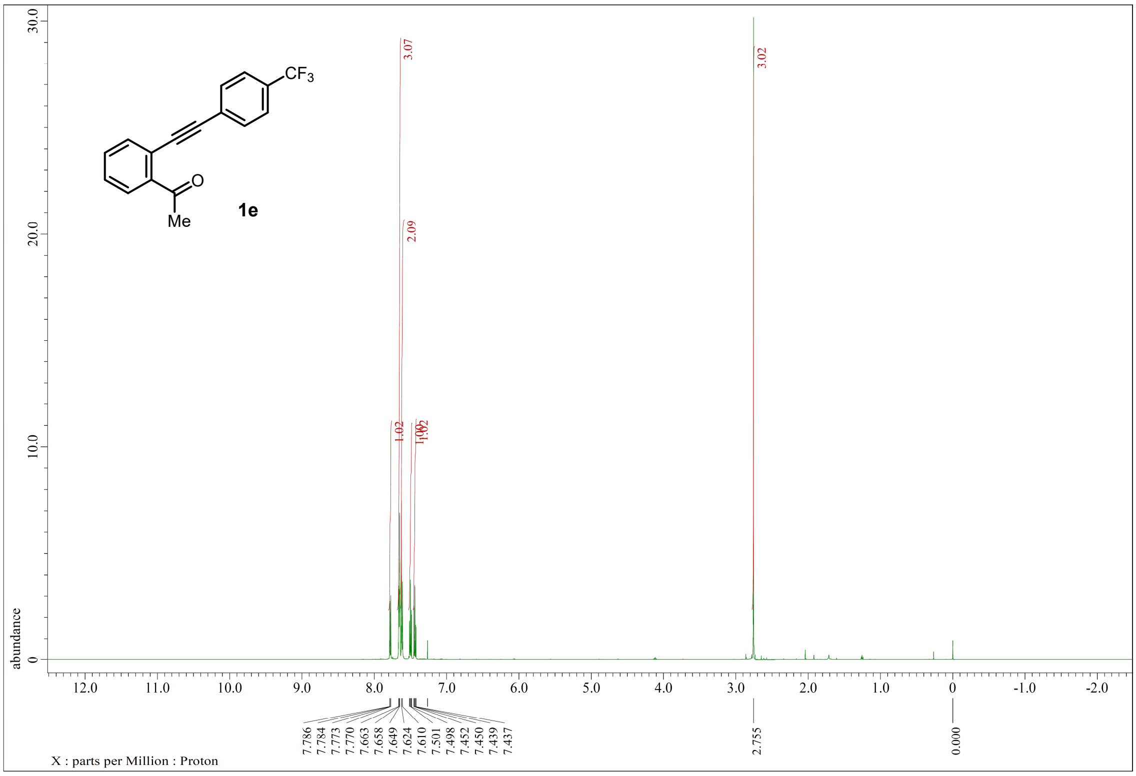


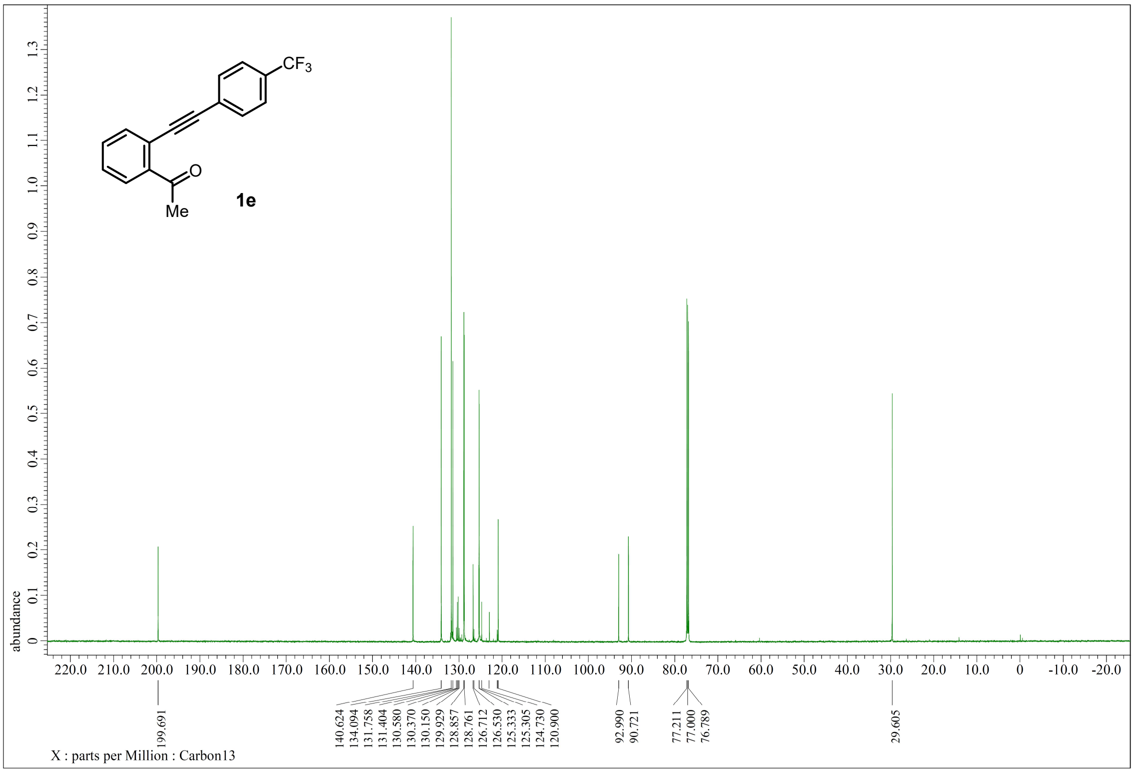
^{1}H NMR (600 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) spectra of **1d**.



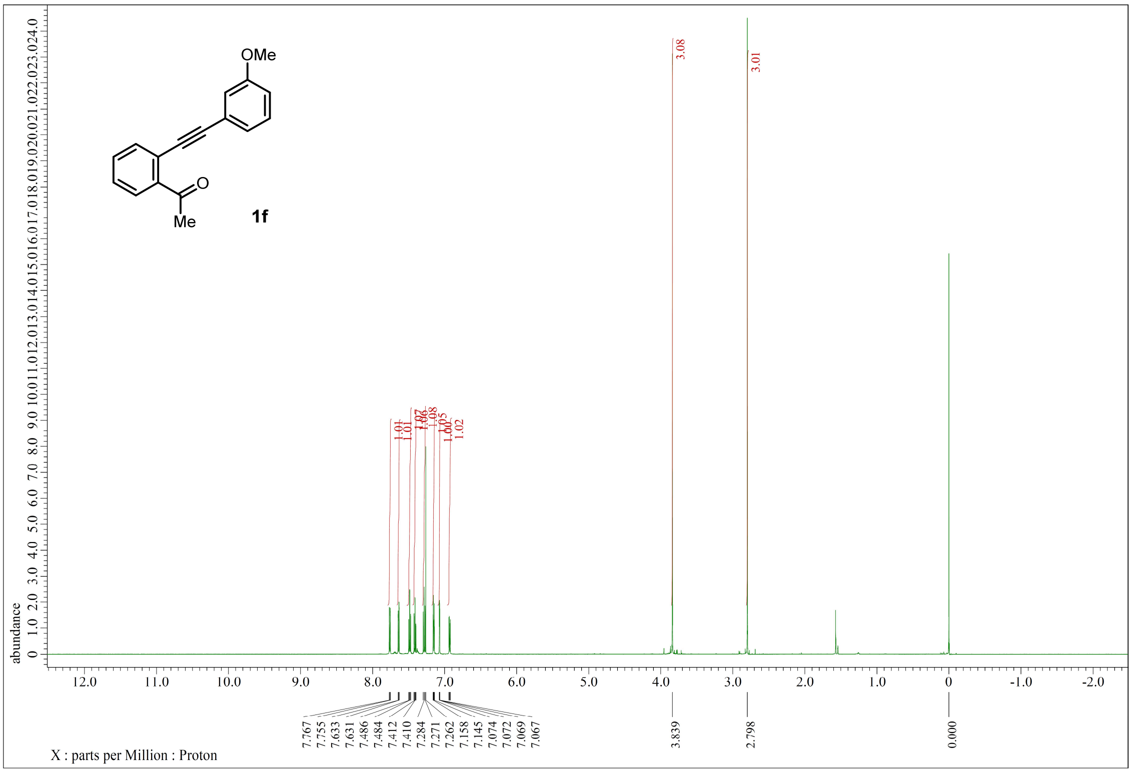


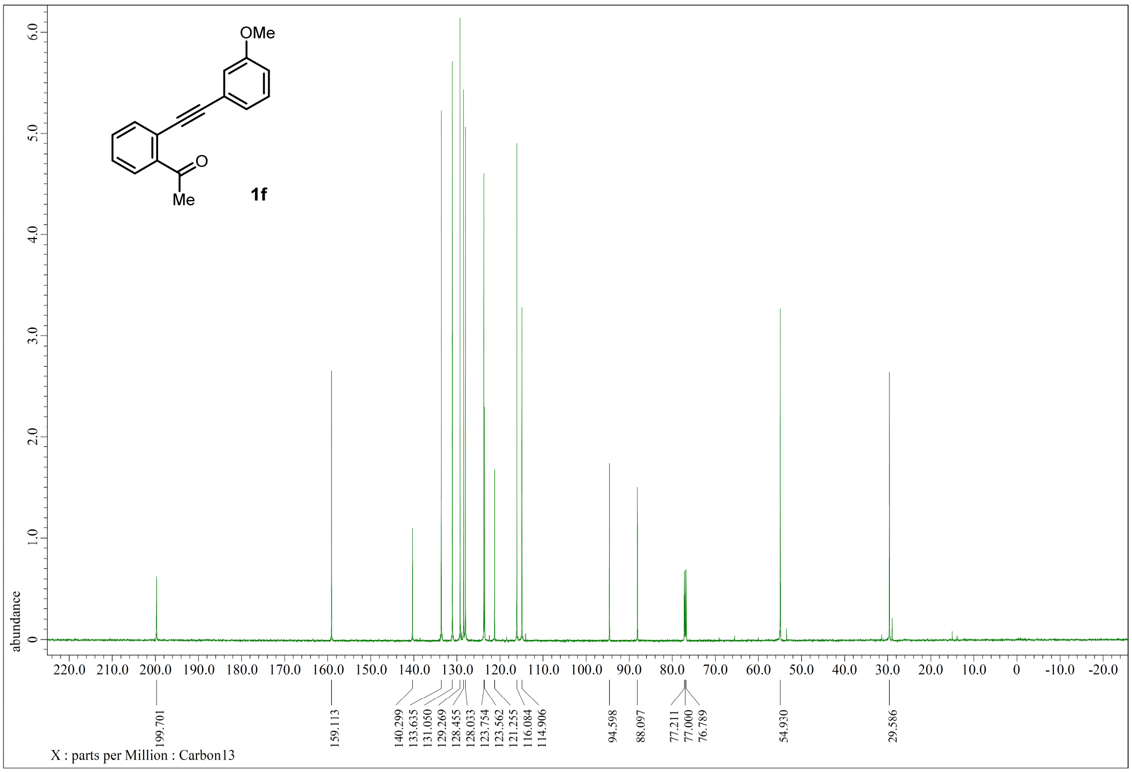
^{1}H NMR (600 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) spectra of **1e**.



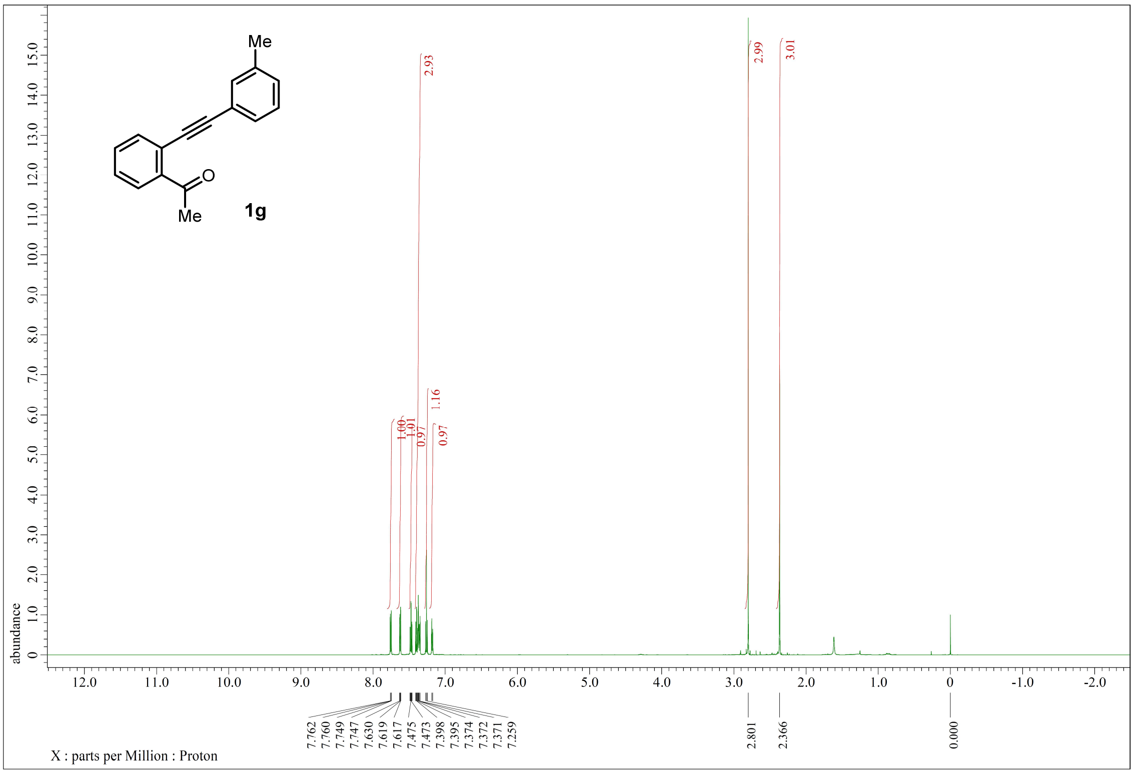


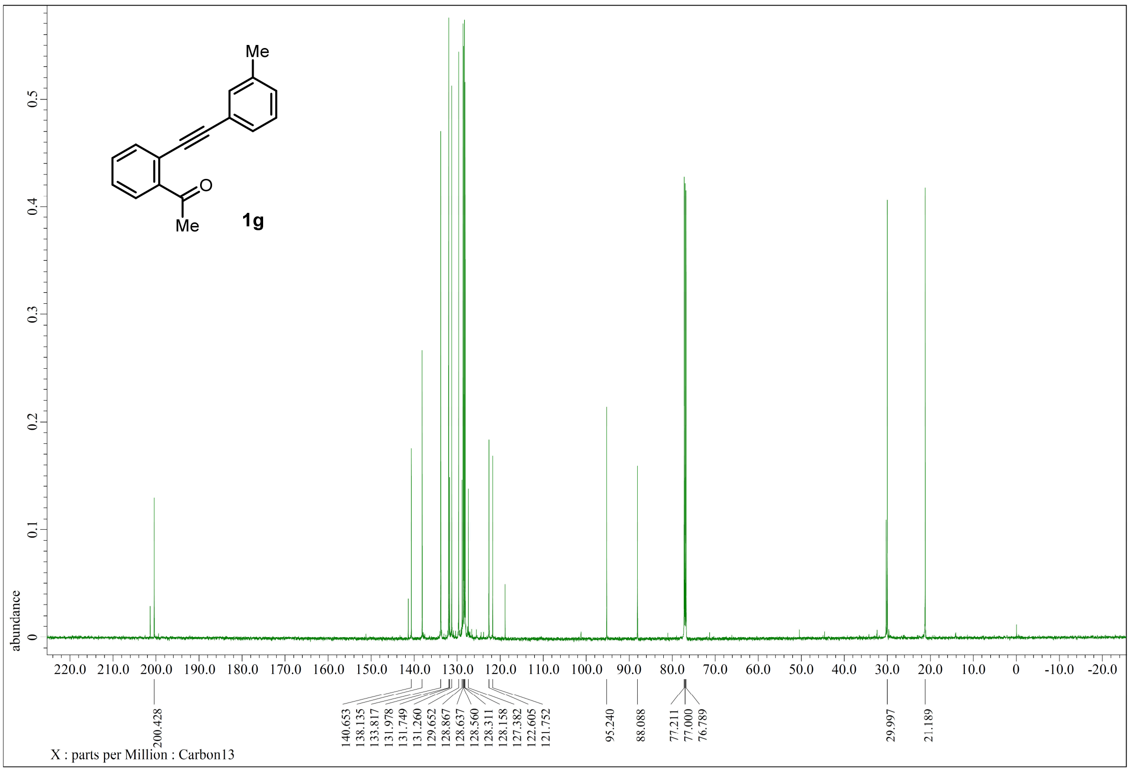
^{1}H NMR (600 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) spectra of **1f**.





^{1}H NMR (600 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) spectra of **1g**.





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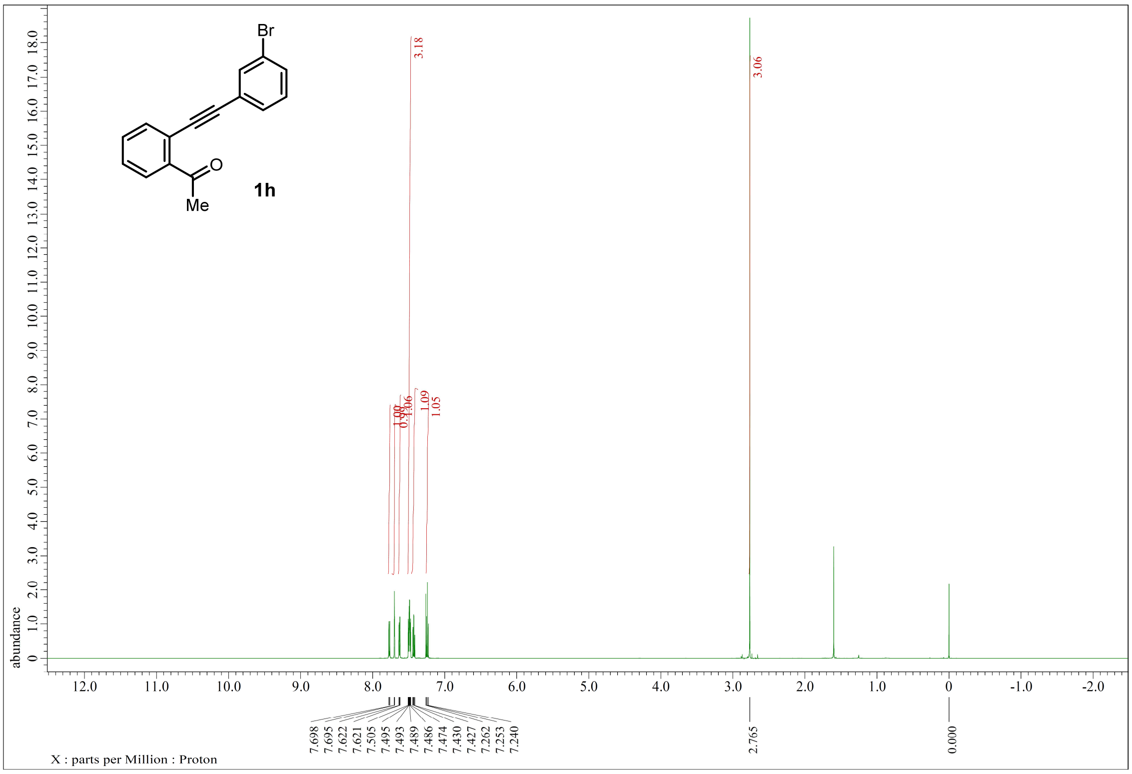

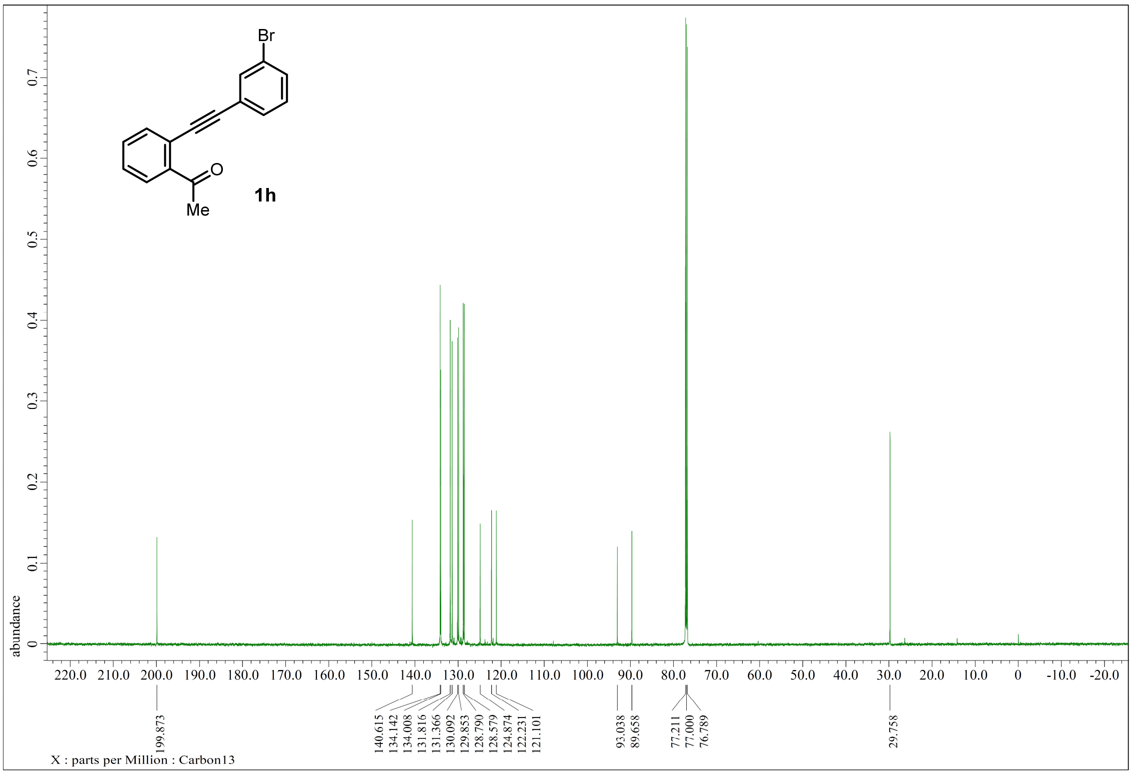

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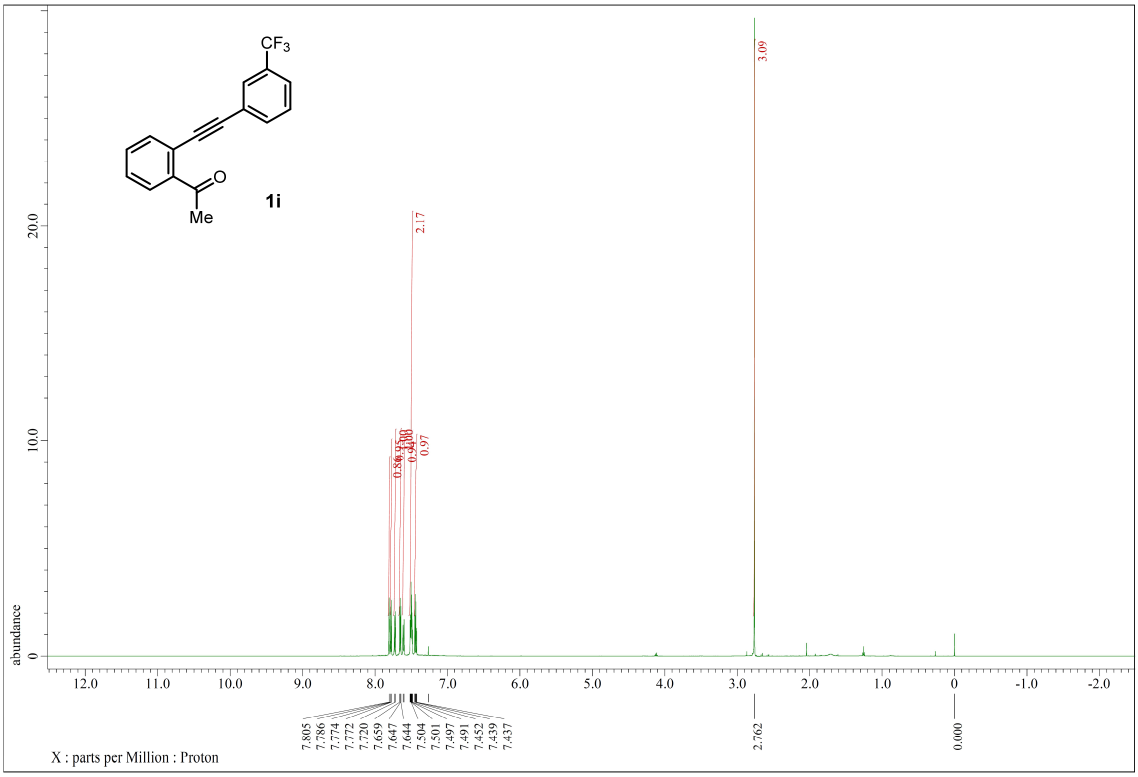
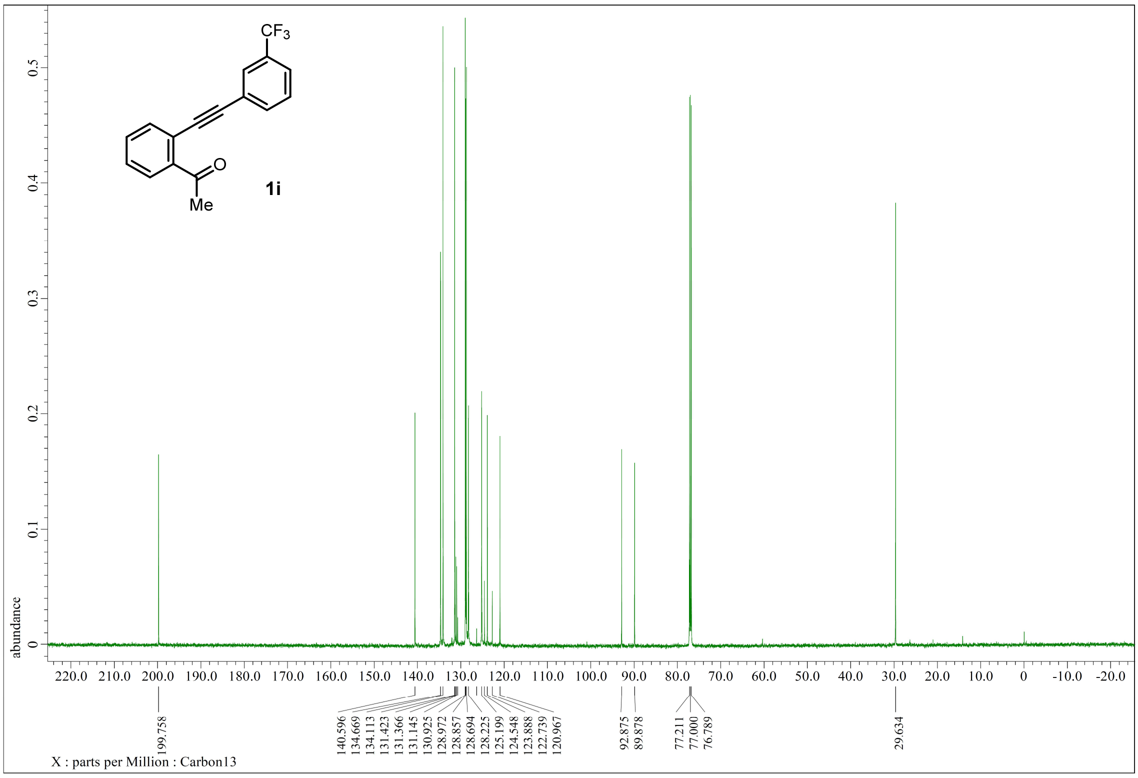
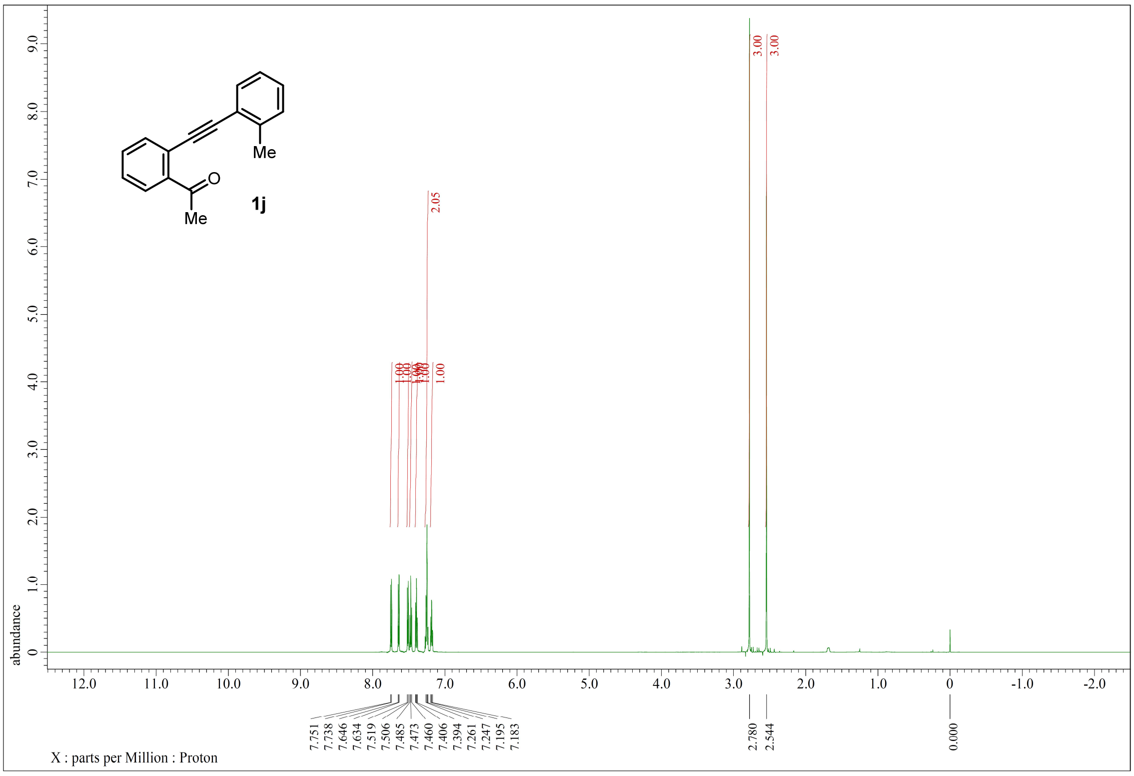
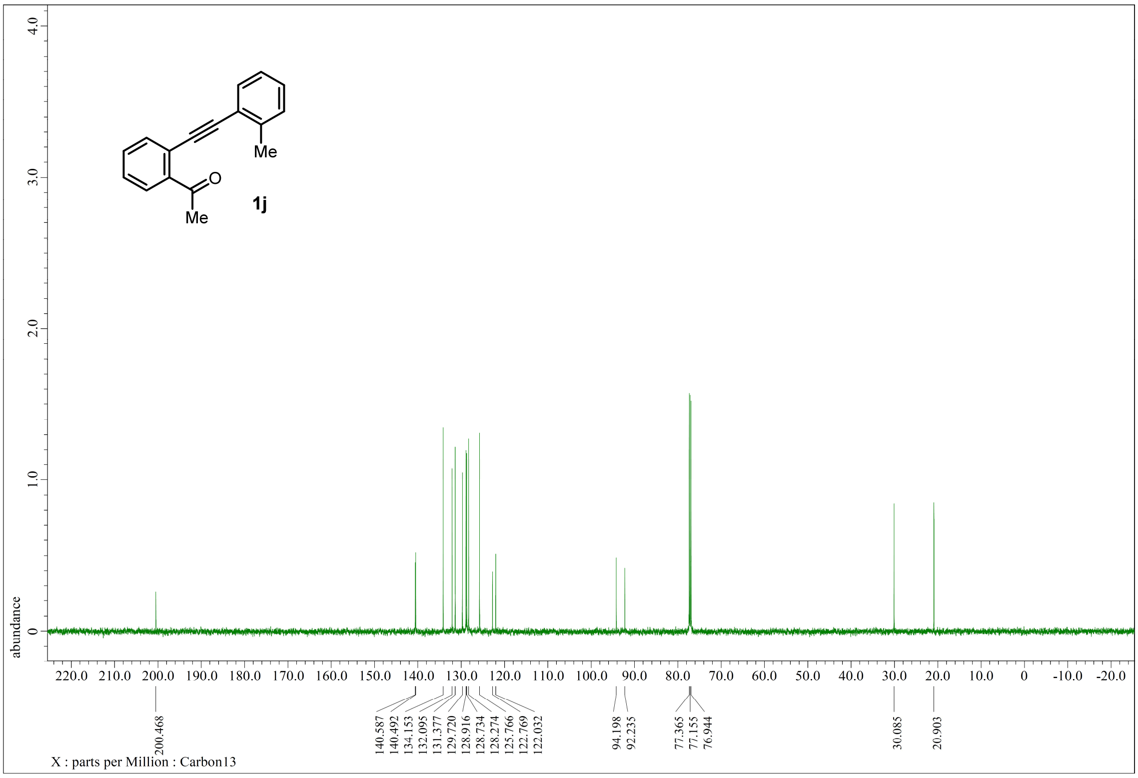


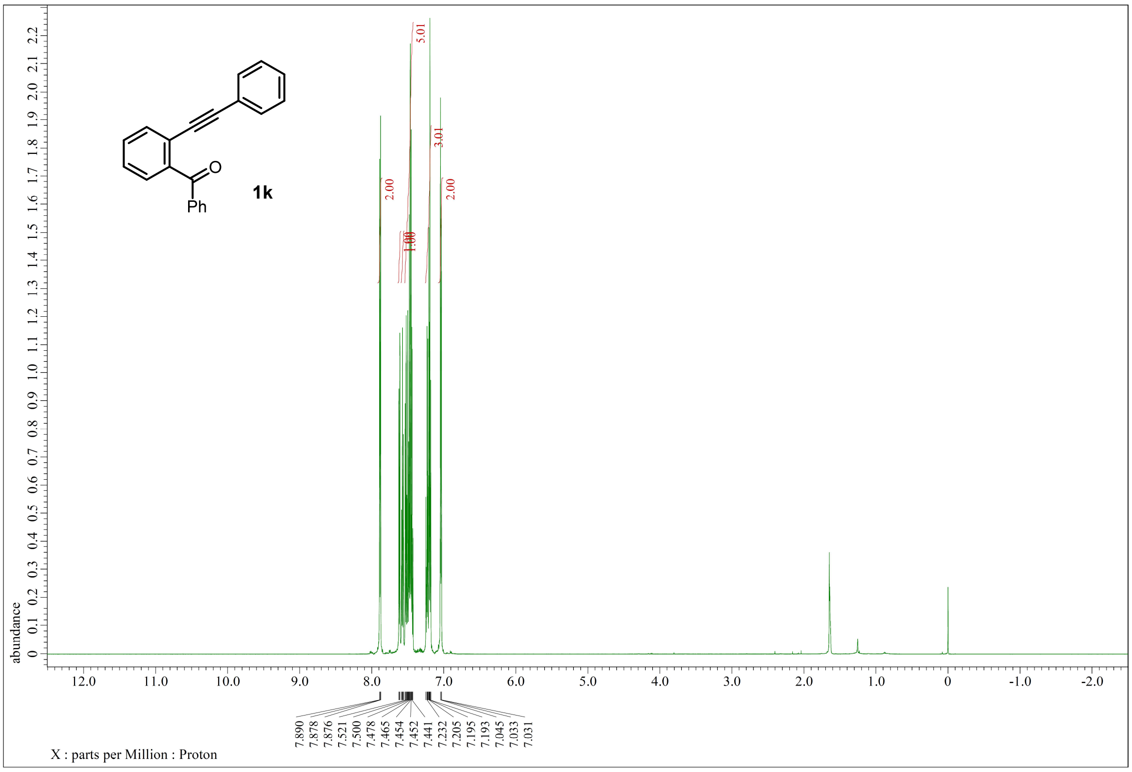


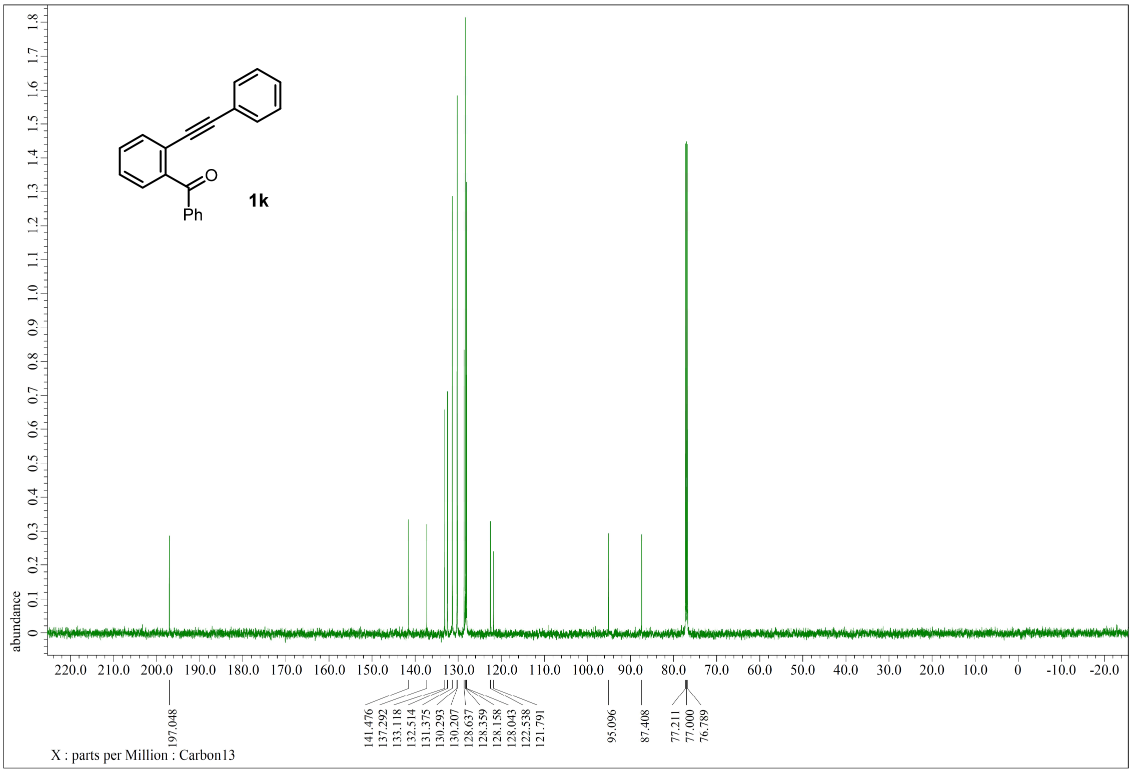
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectra of **1j**.





^{1}H NMR (600 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) spectra of **1k**.





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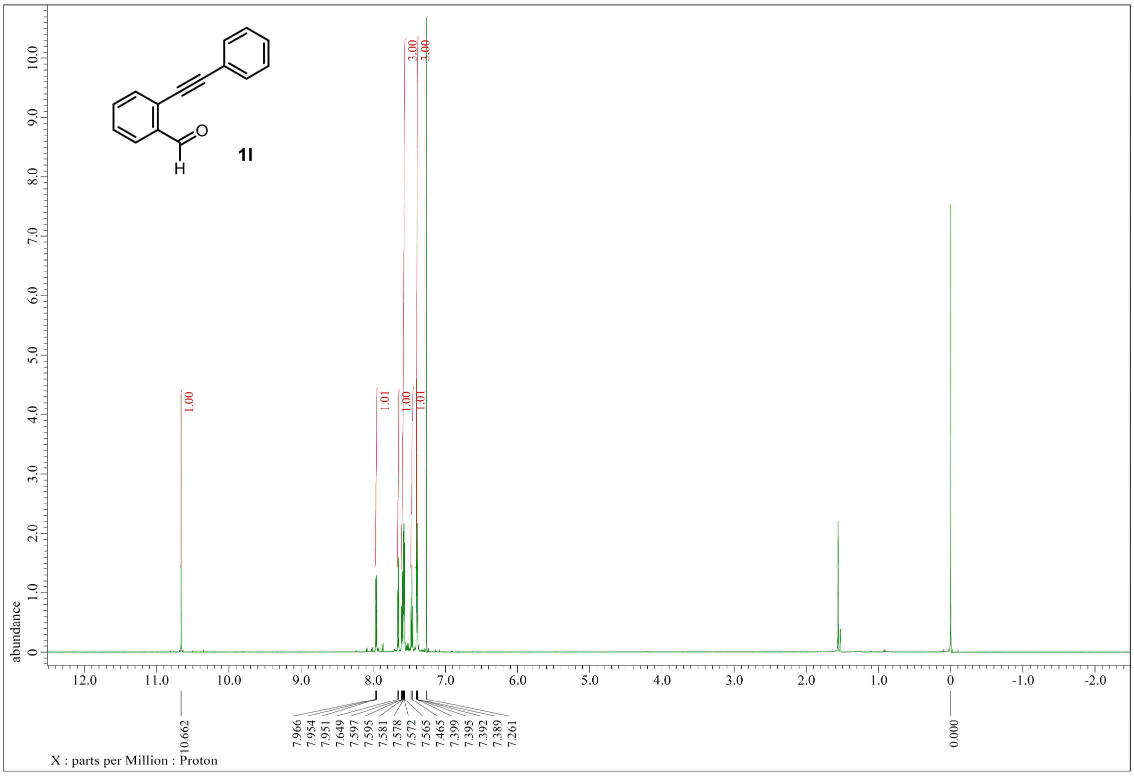

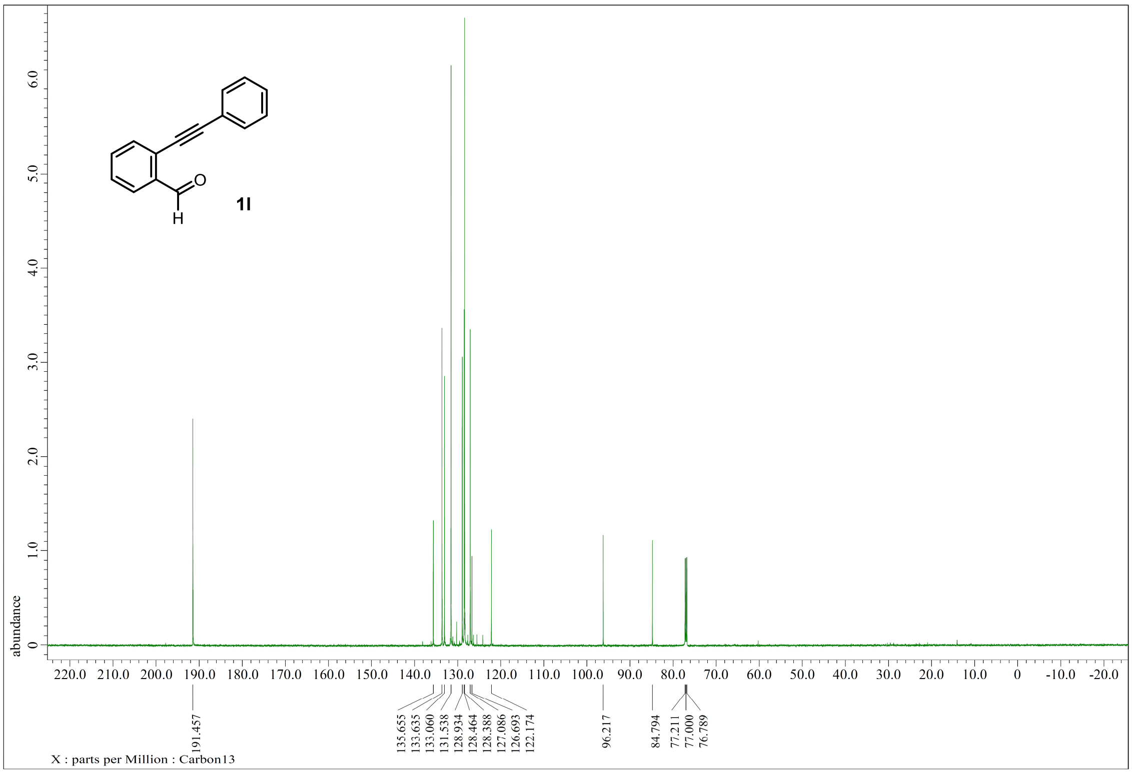

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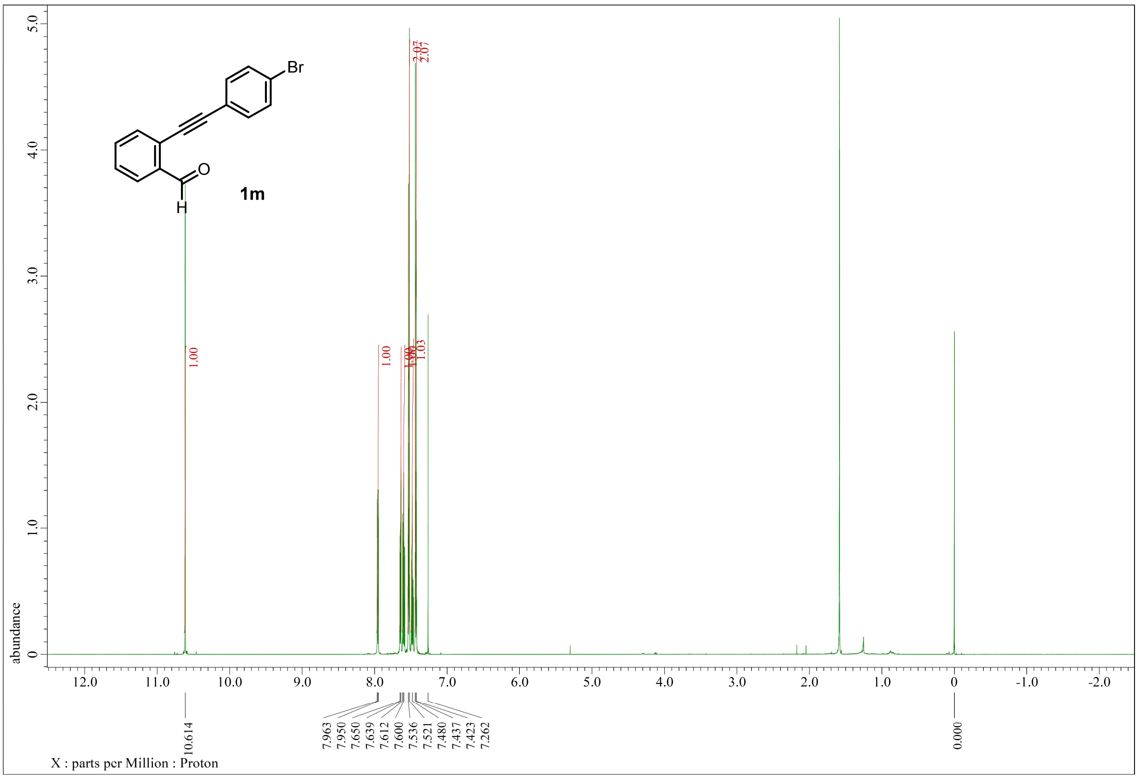

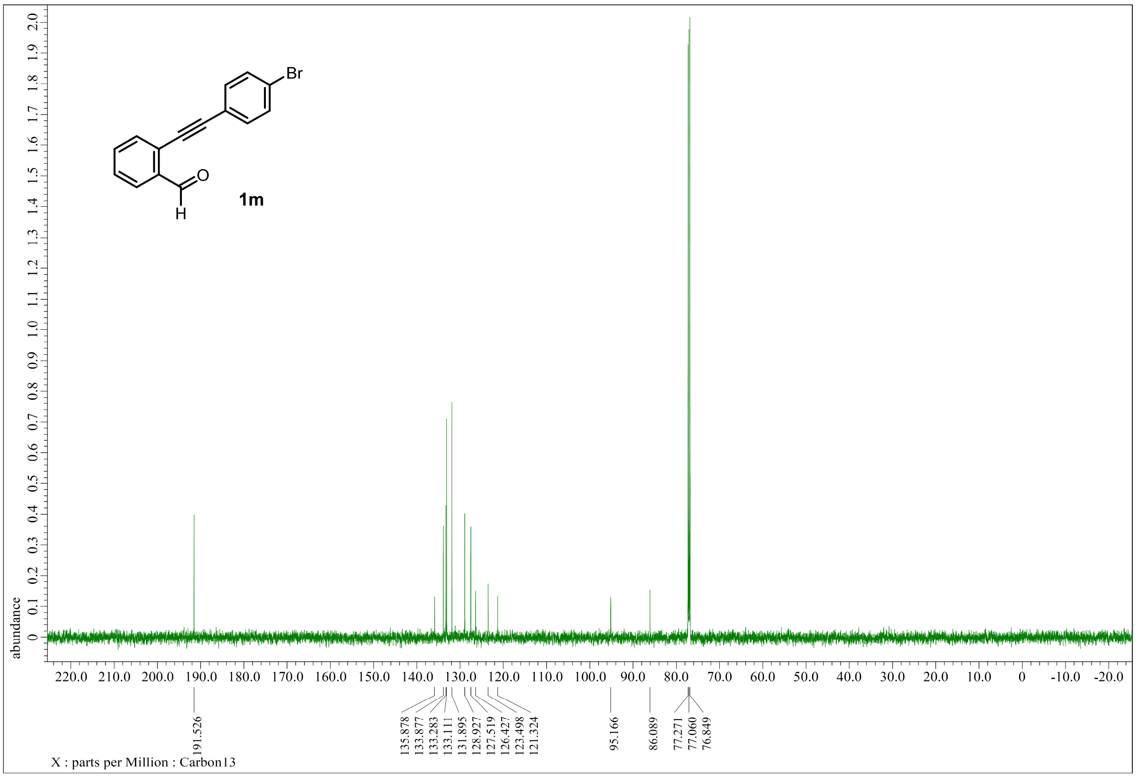

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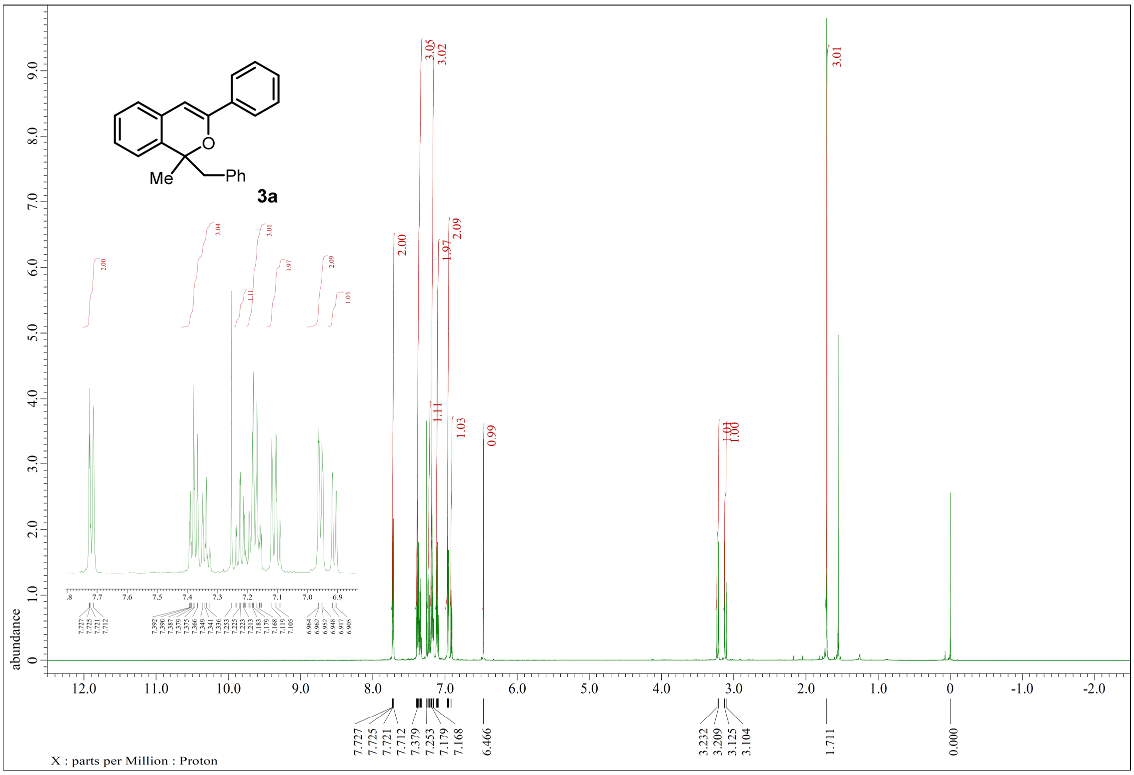

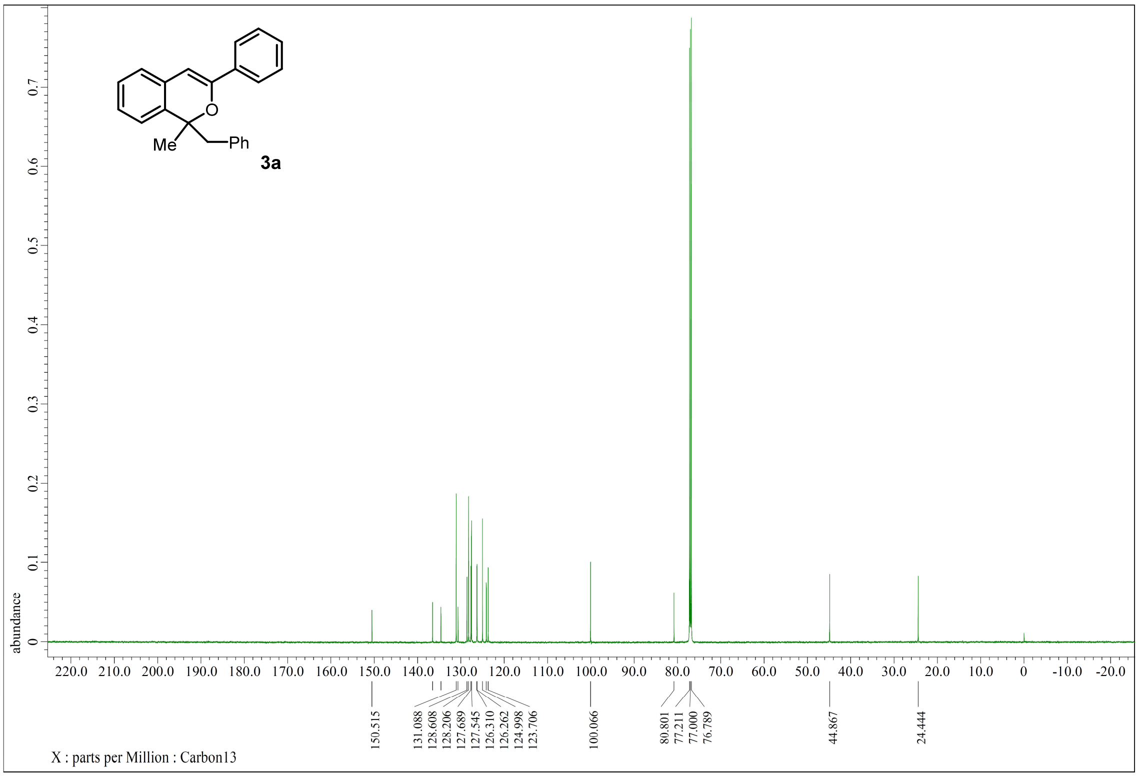

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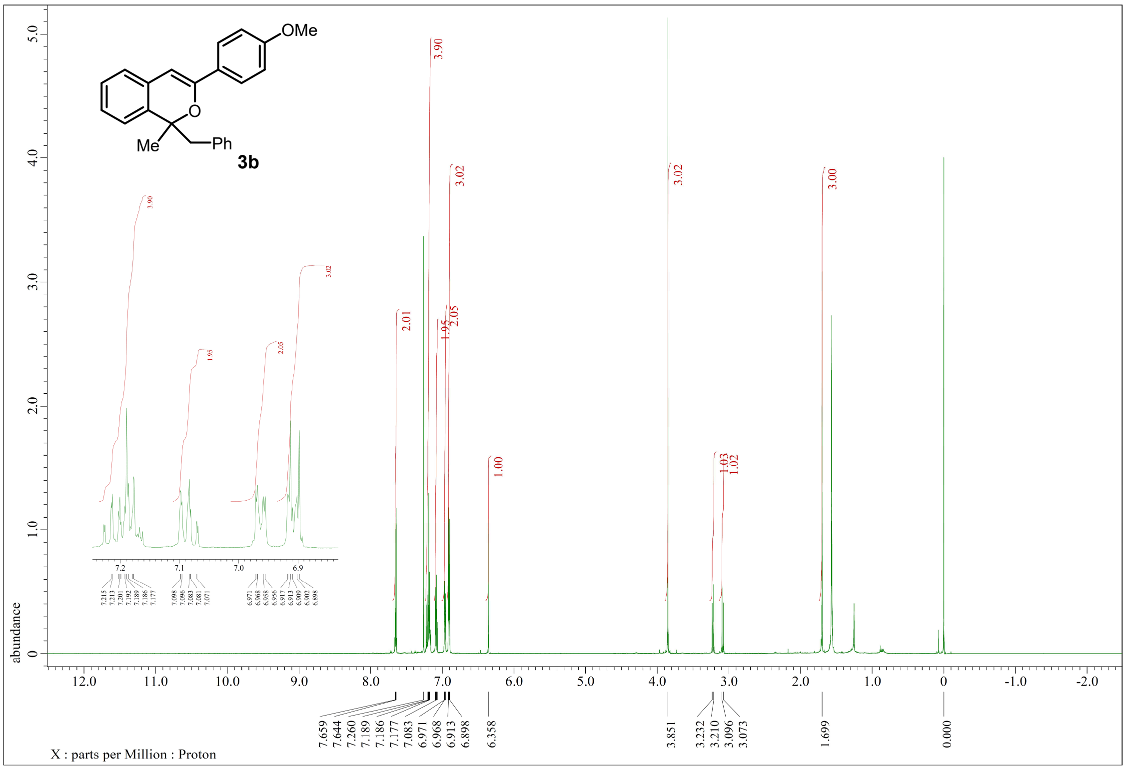

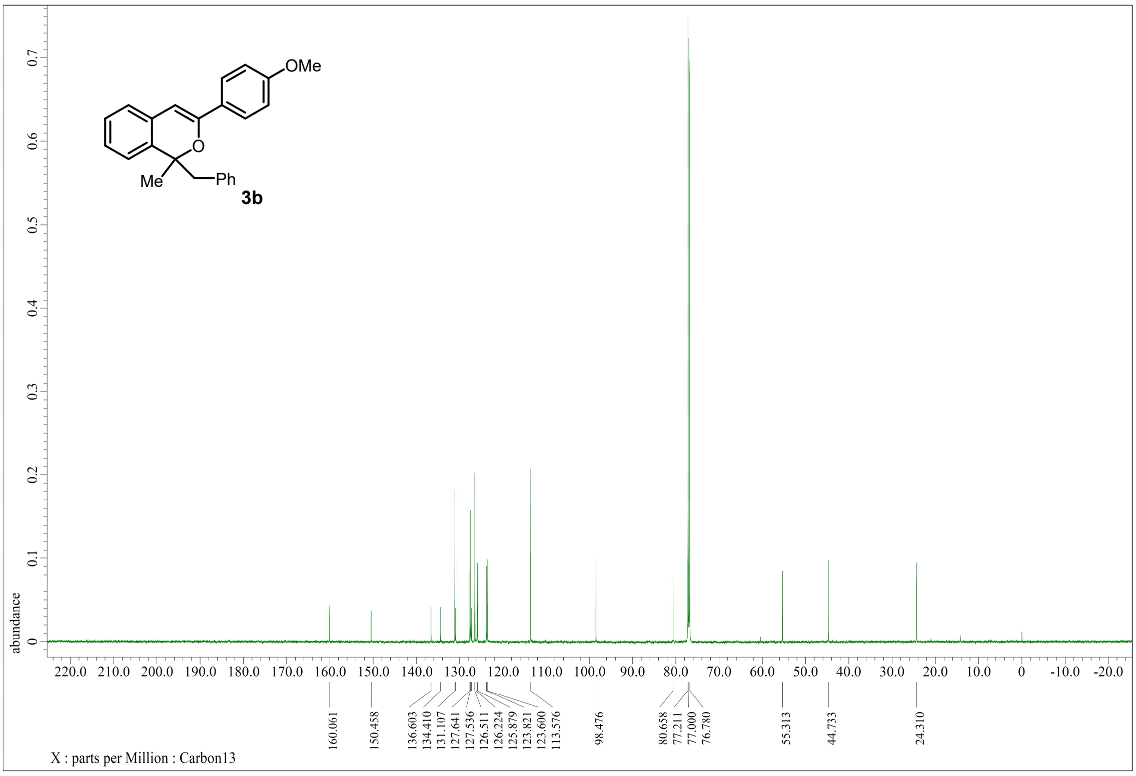

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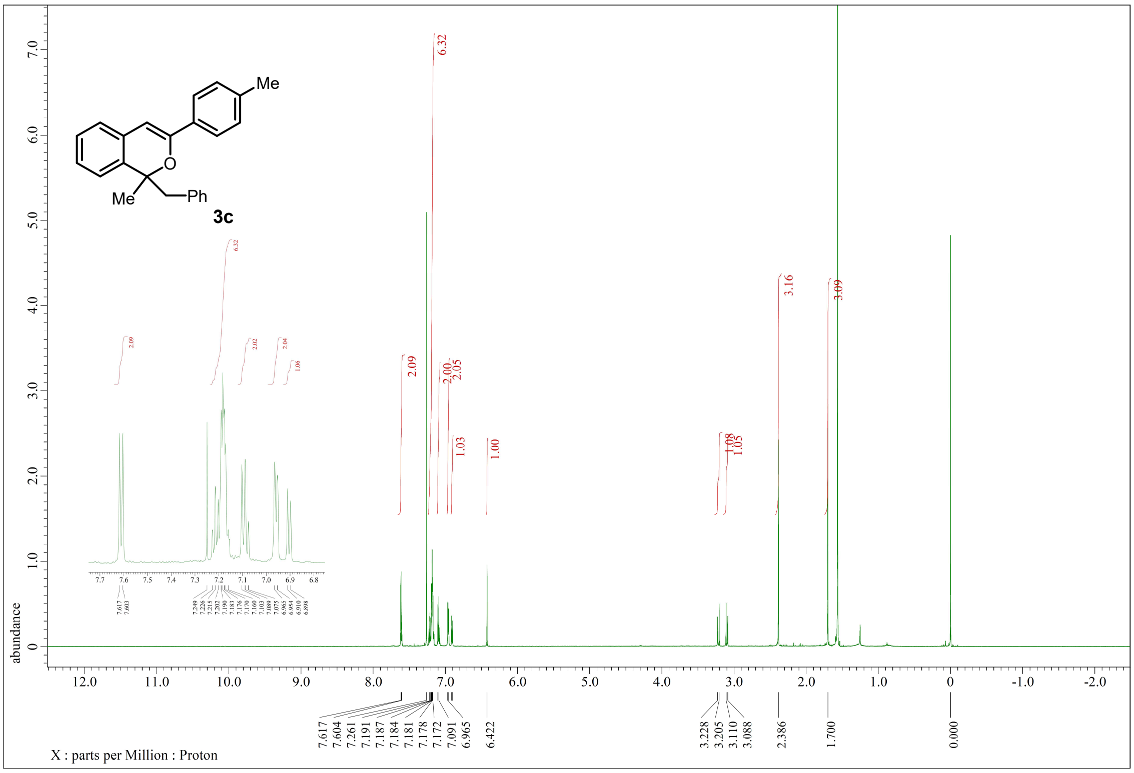

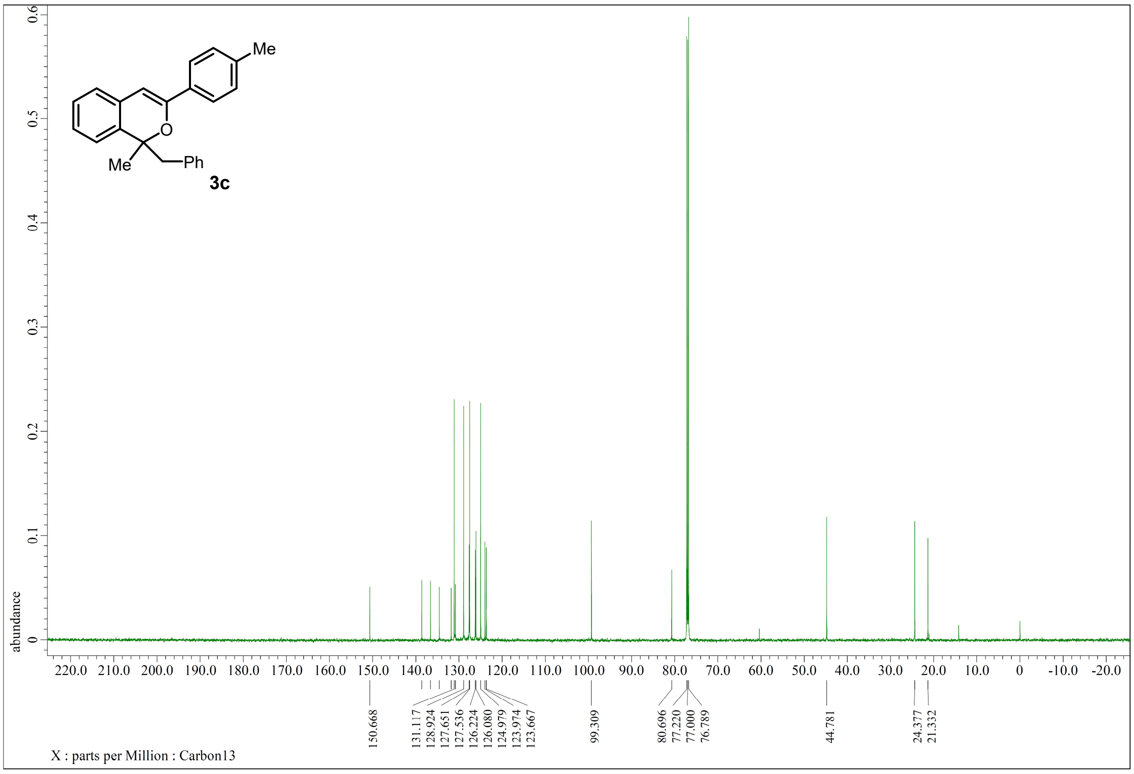

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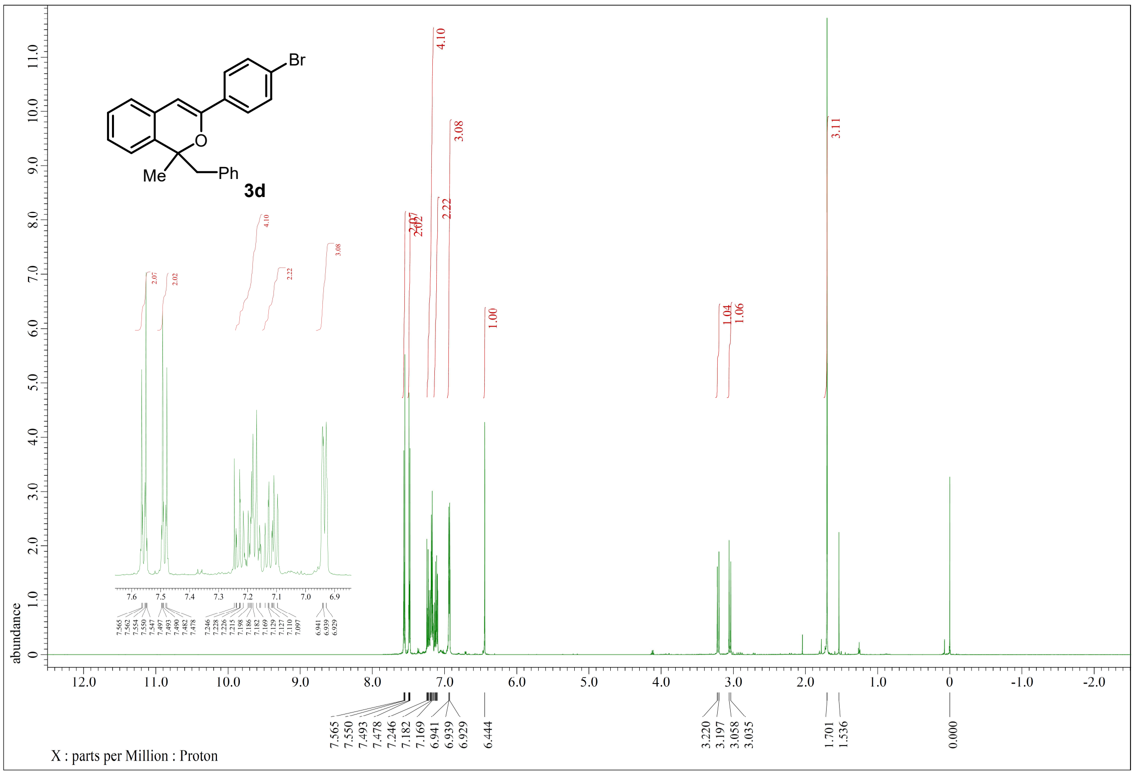

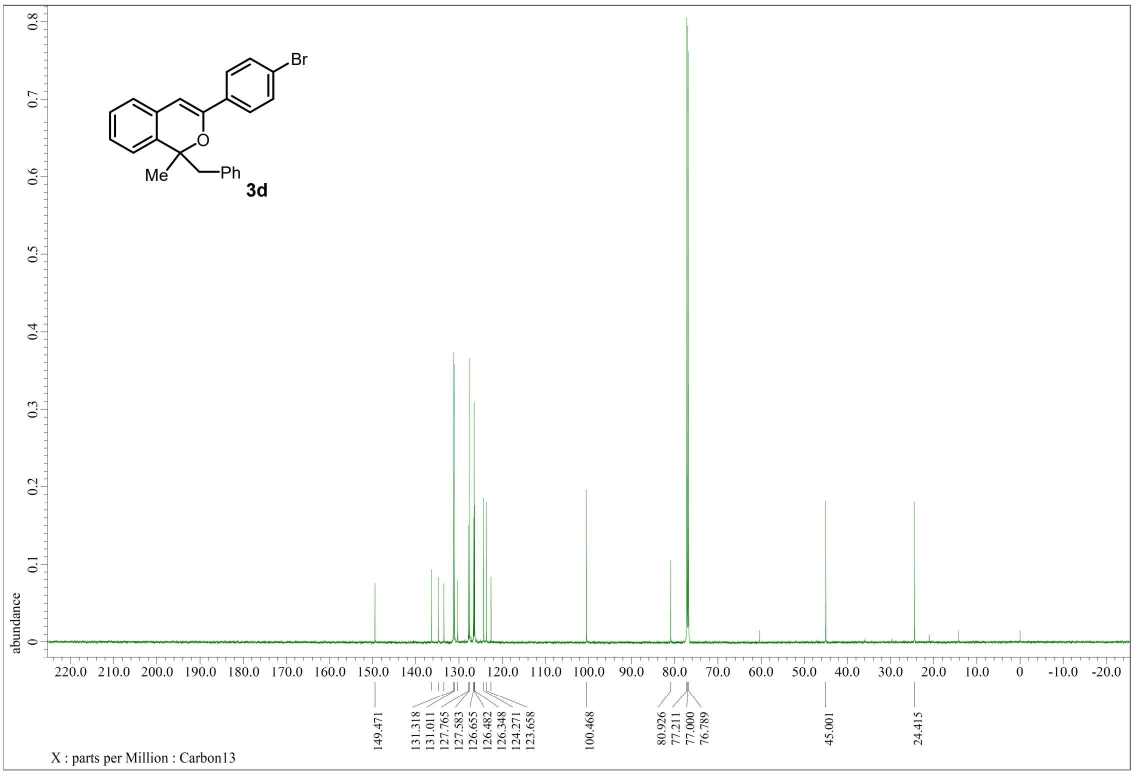

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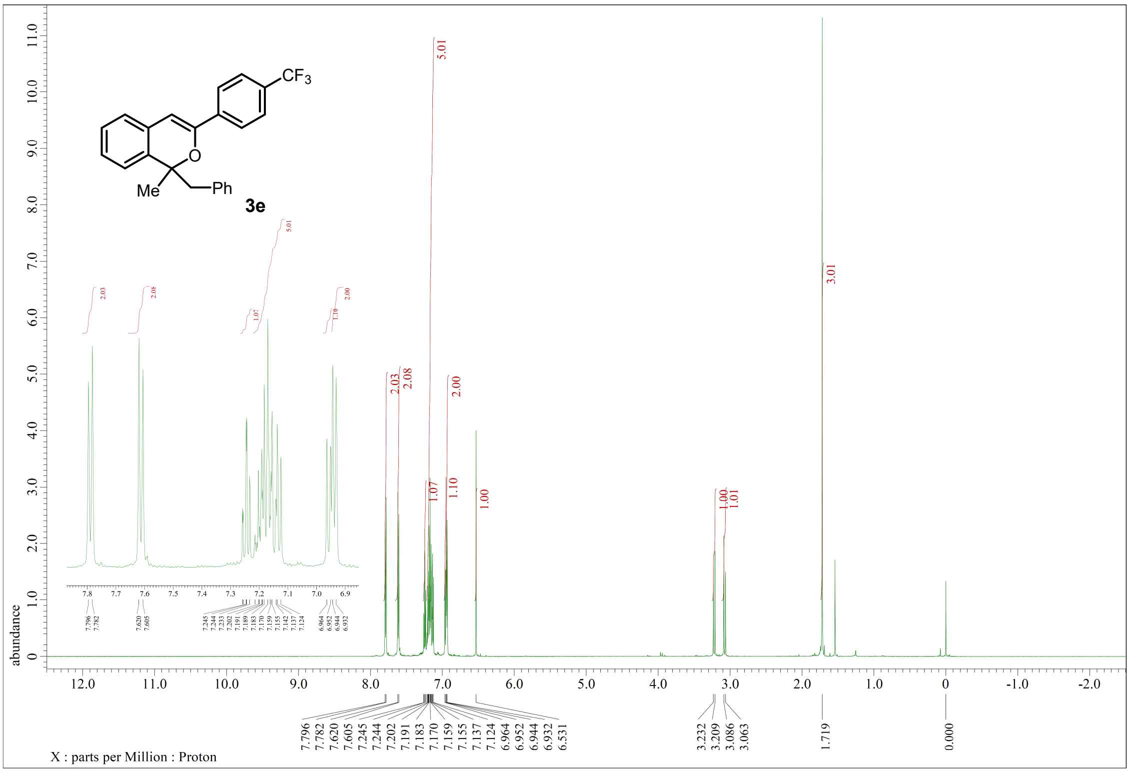

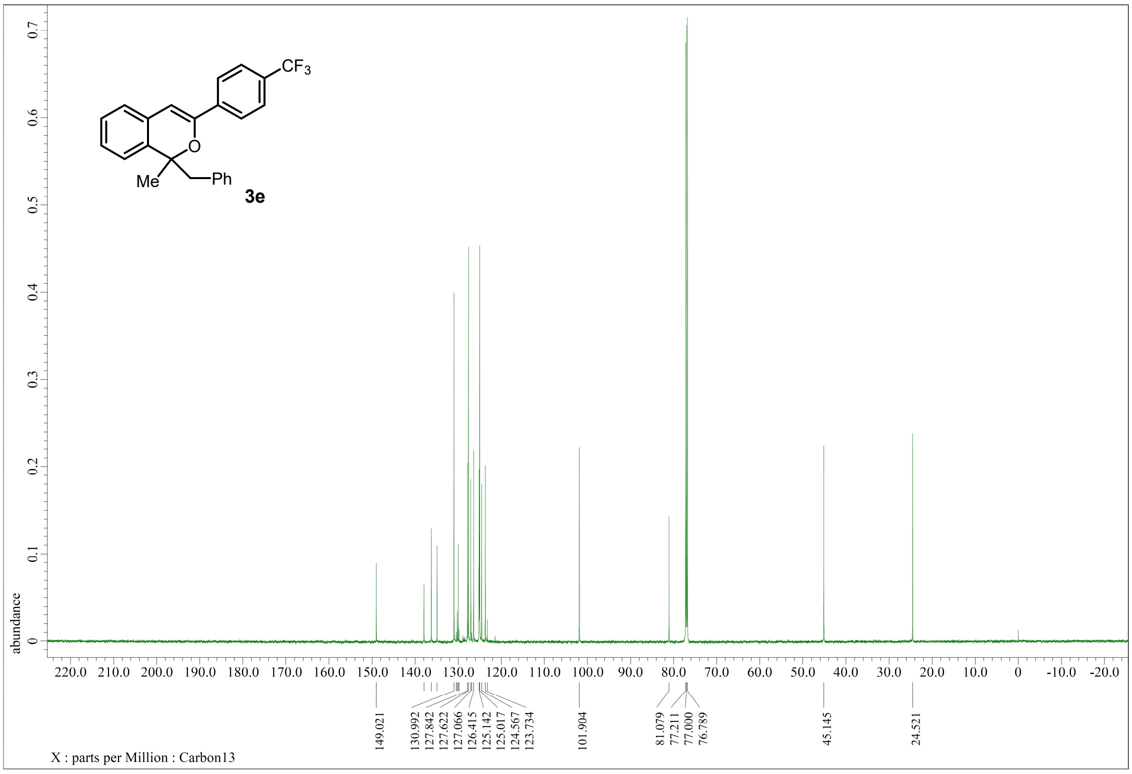

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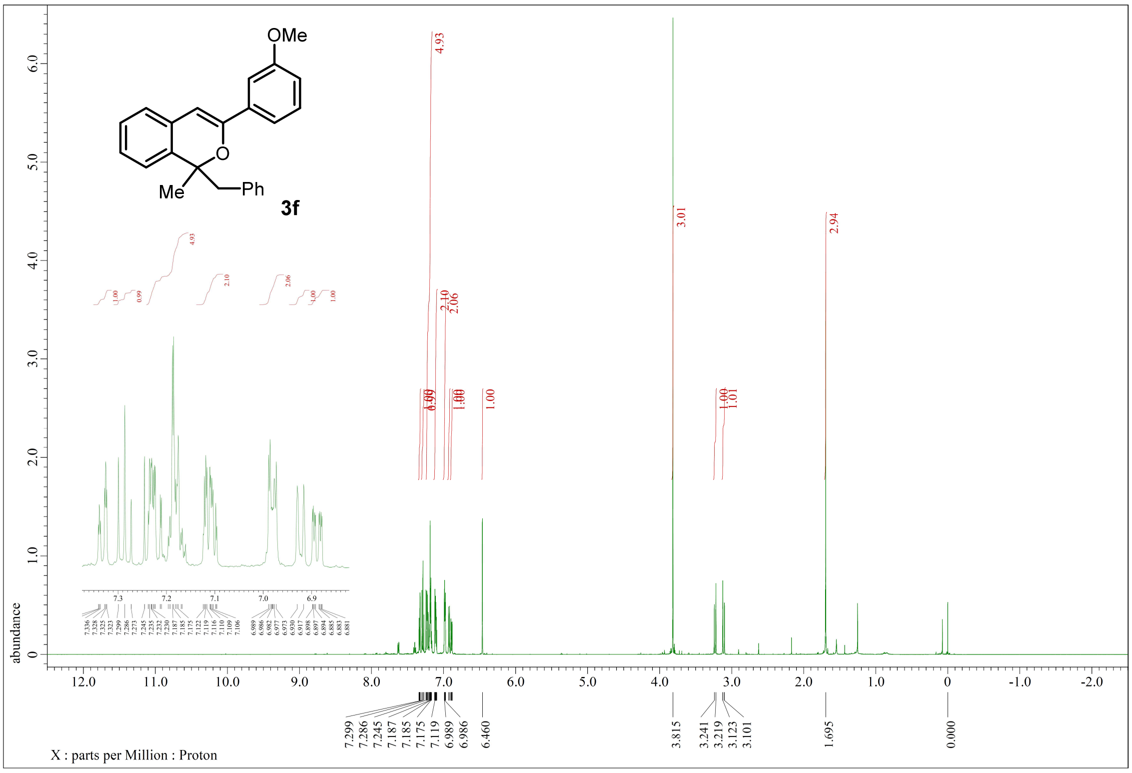

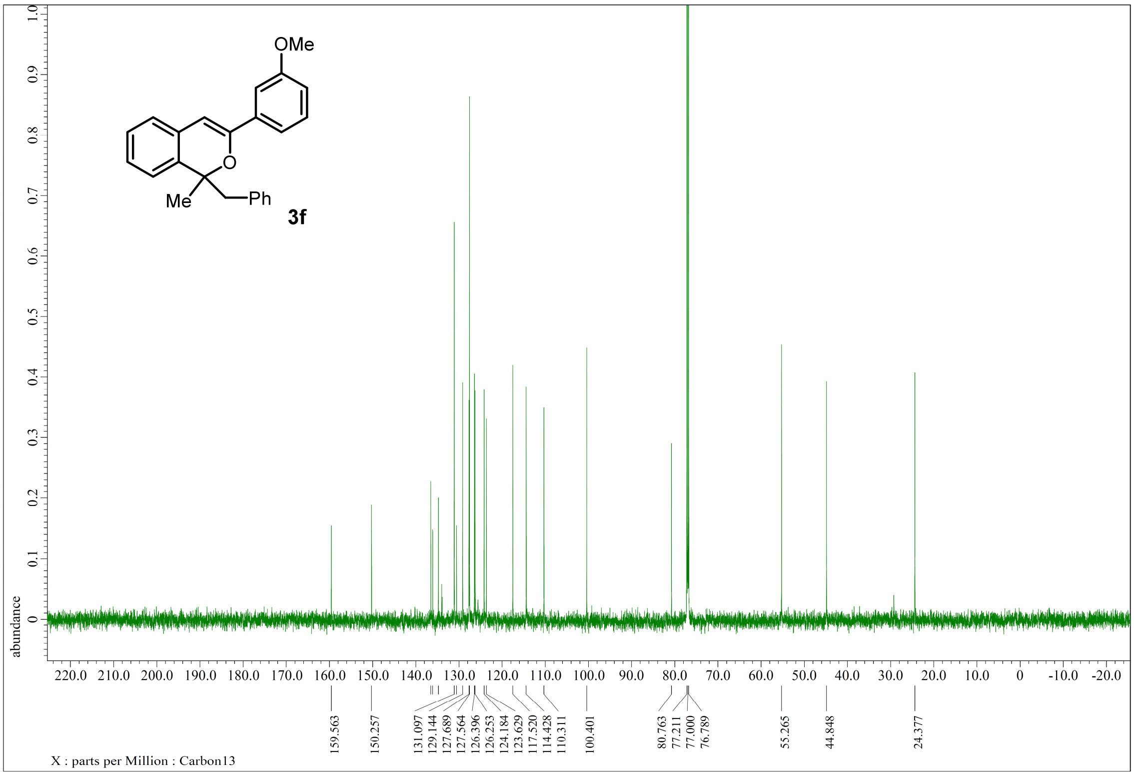

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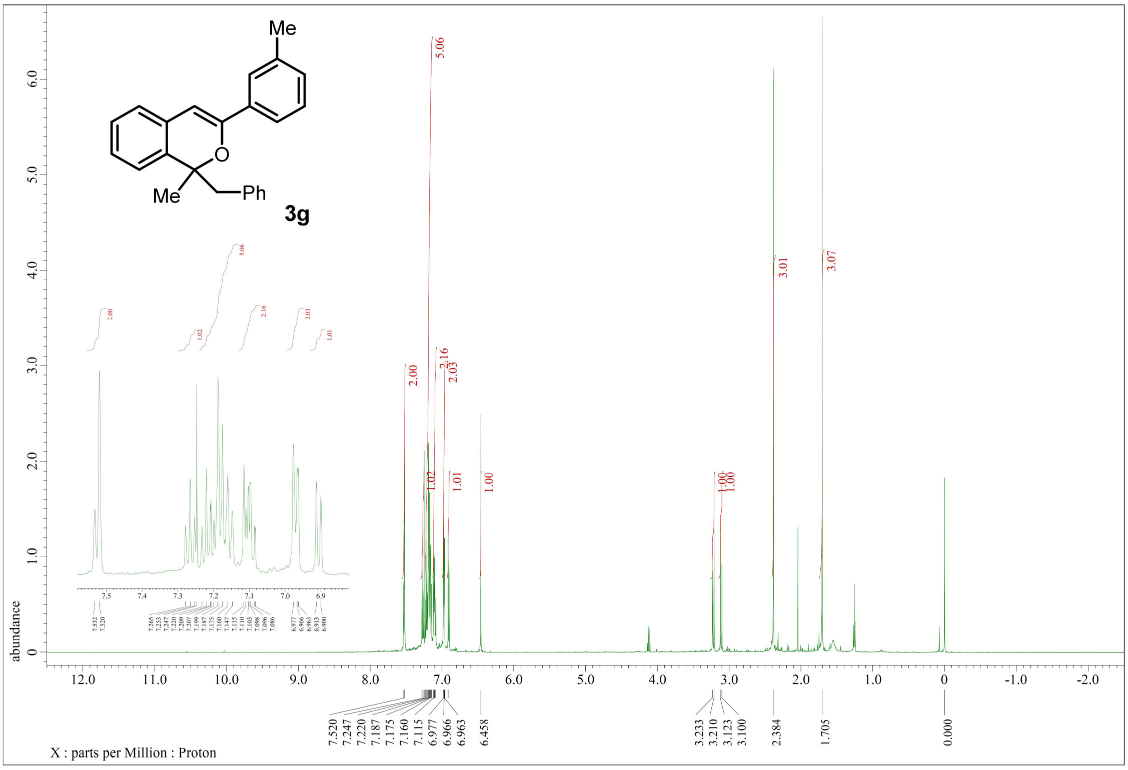

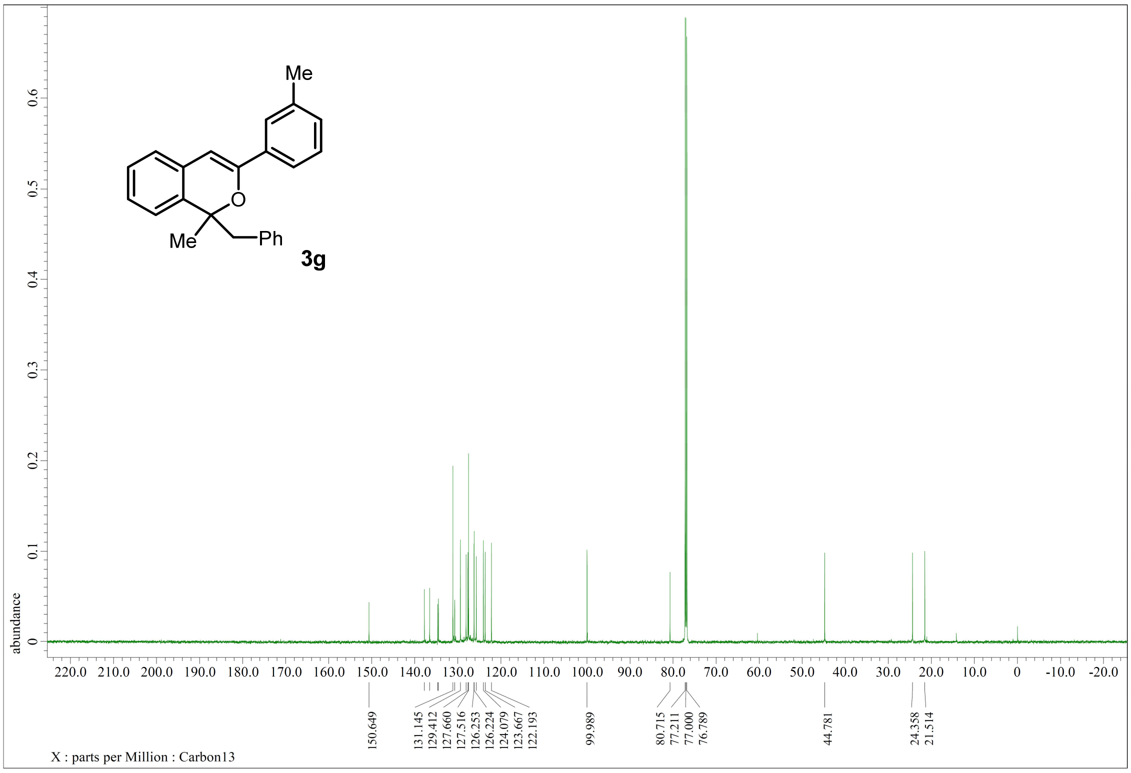

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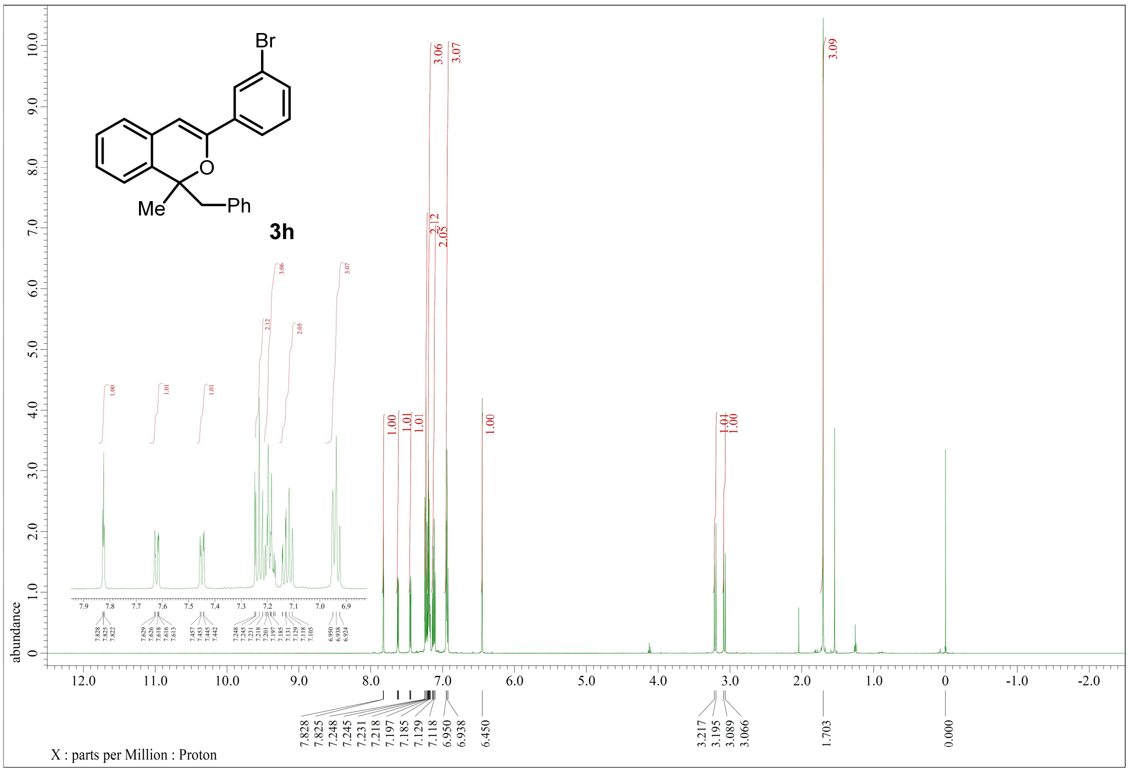

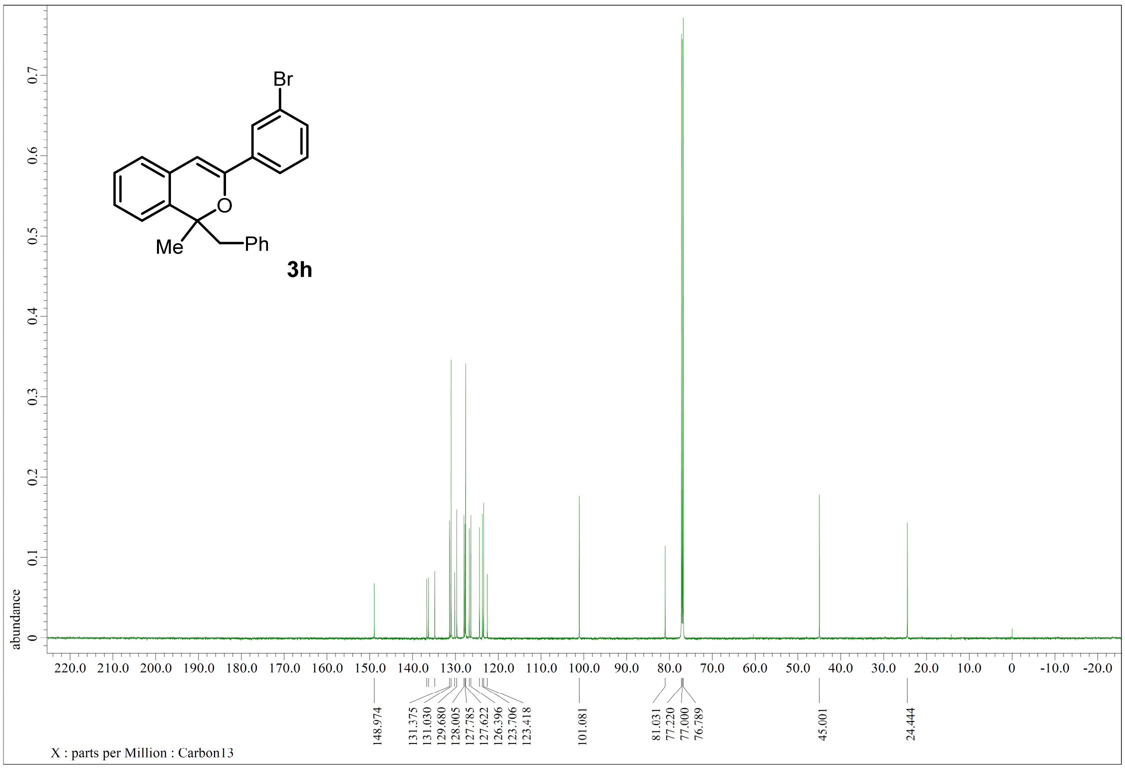

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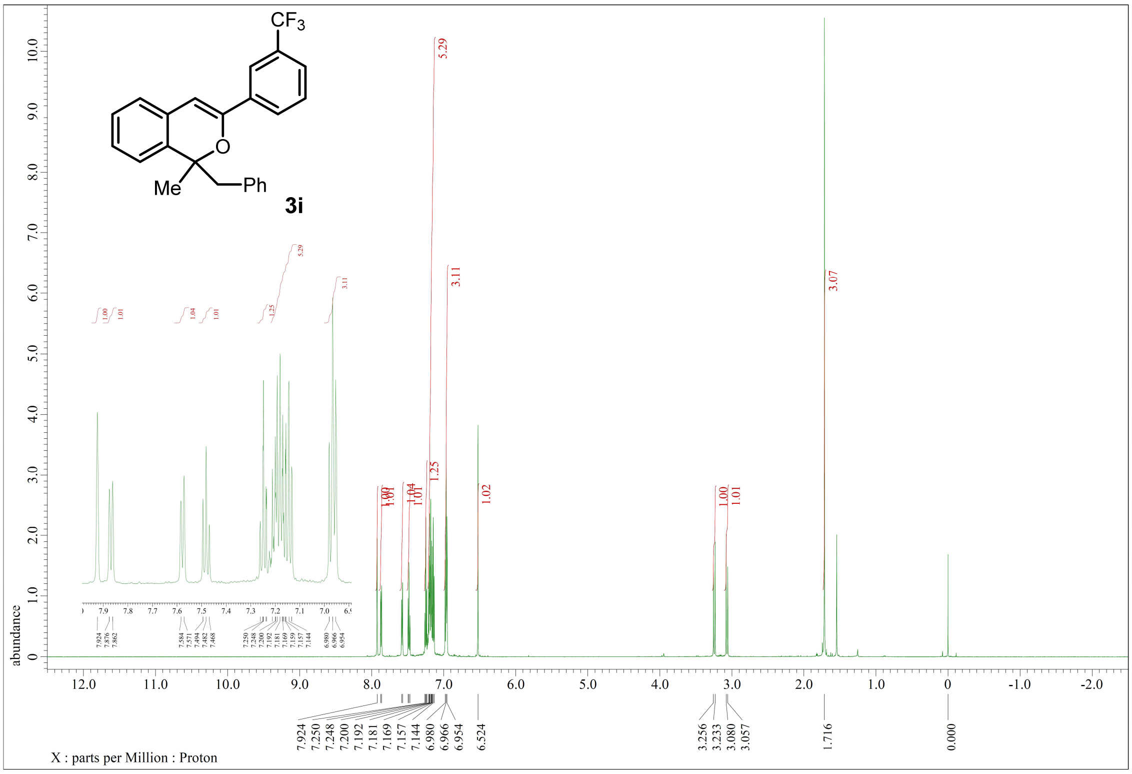

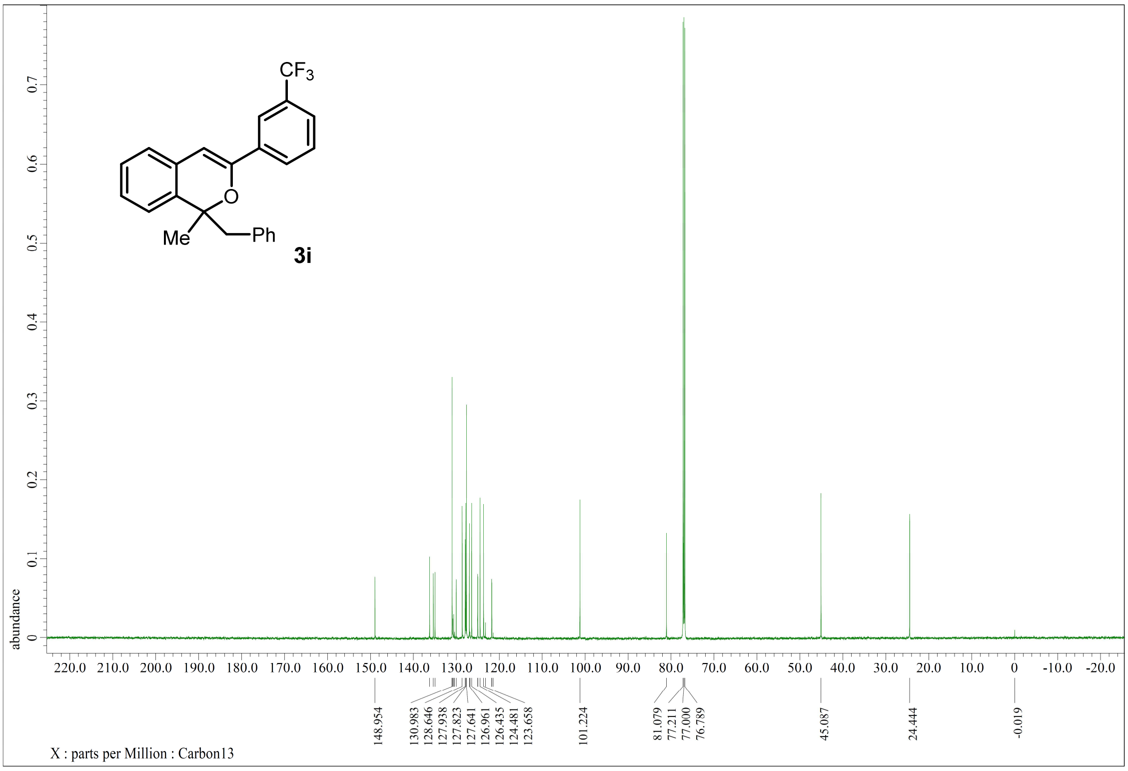

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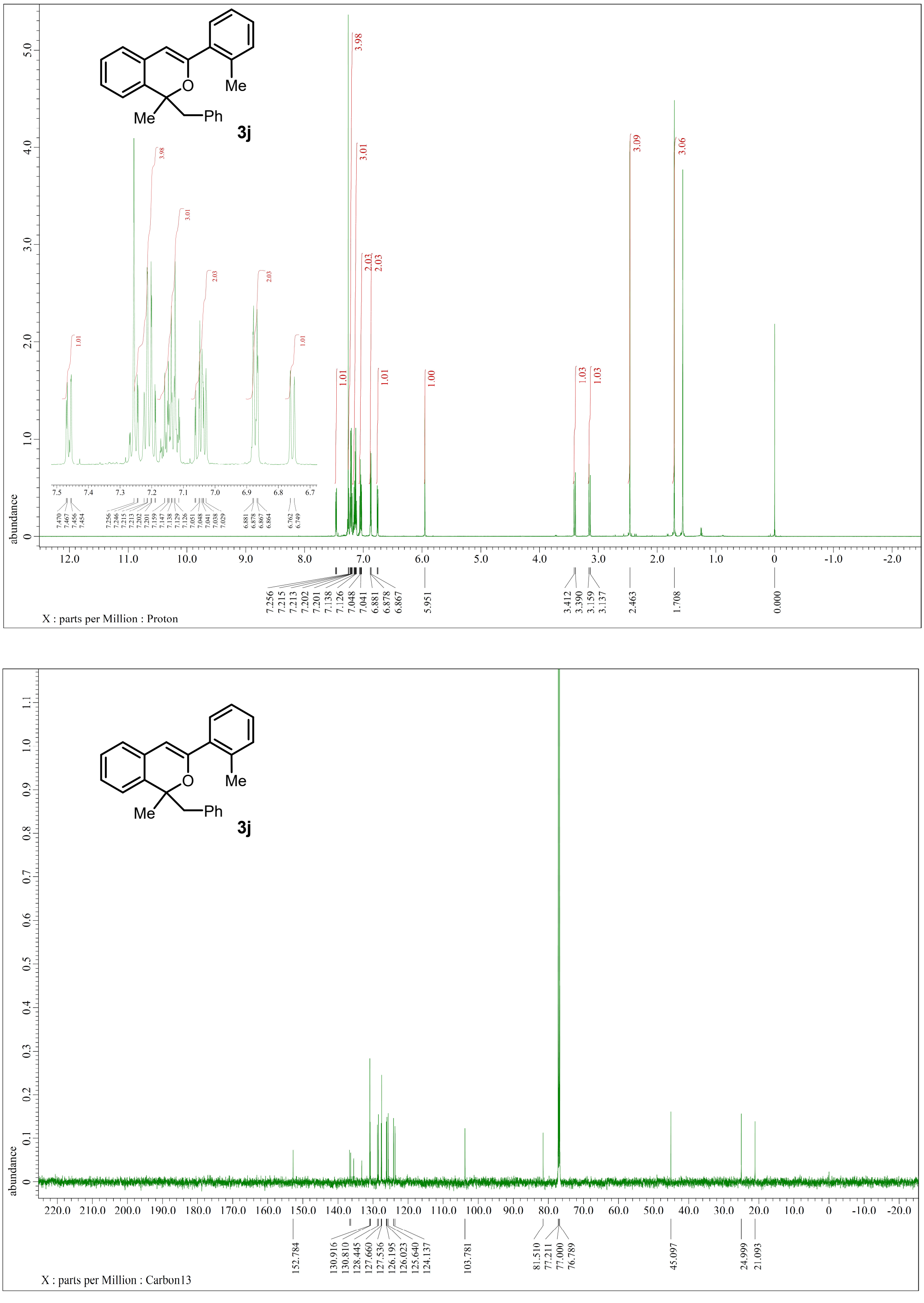

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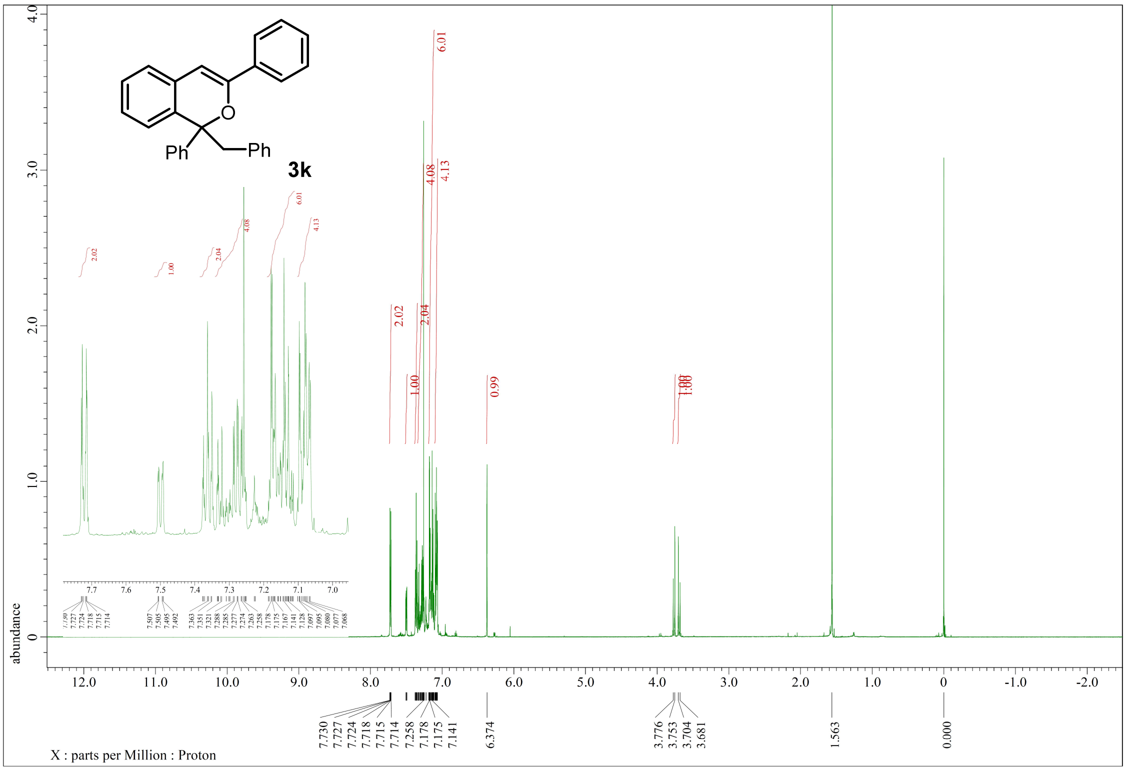
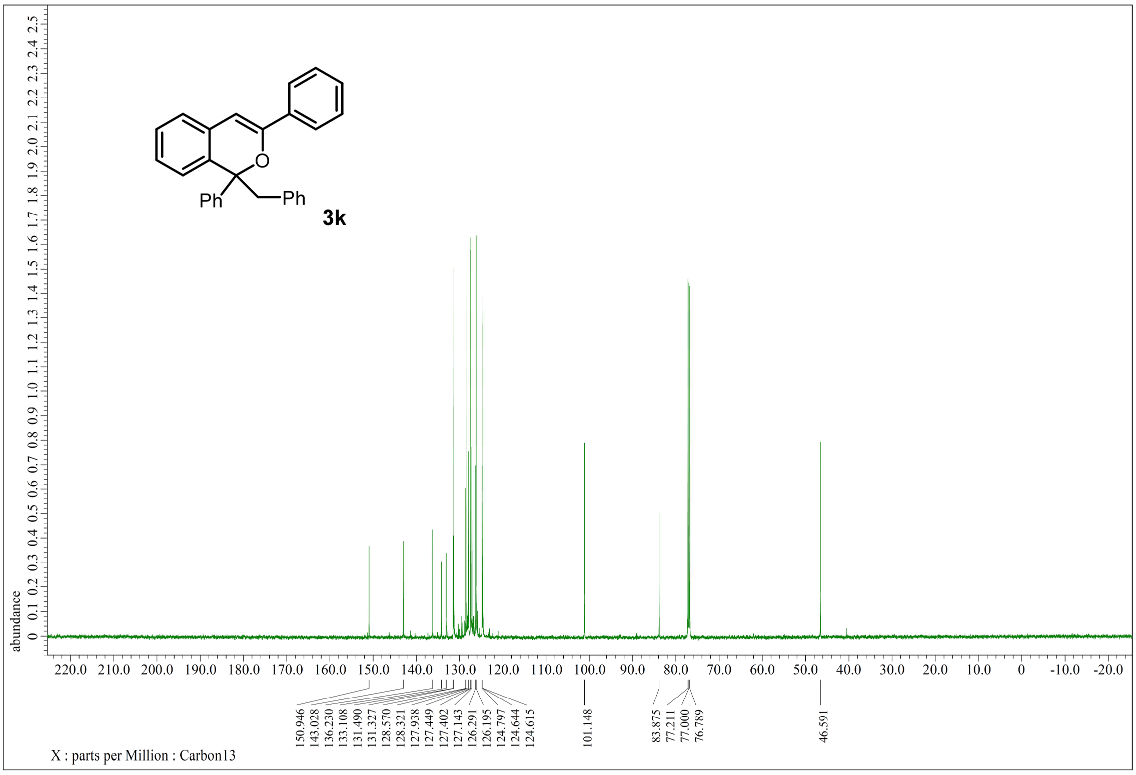
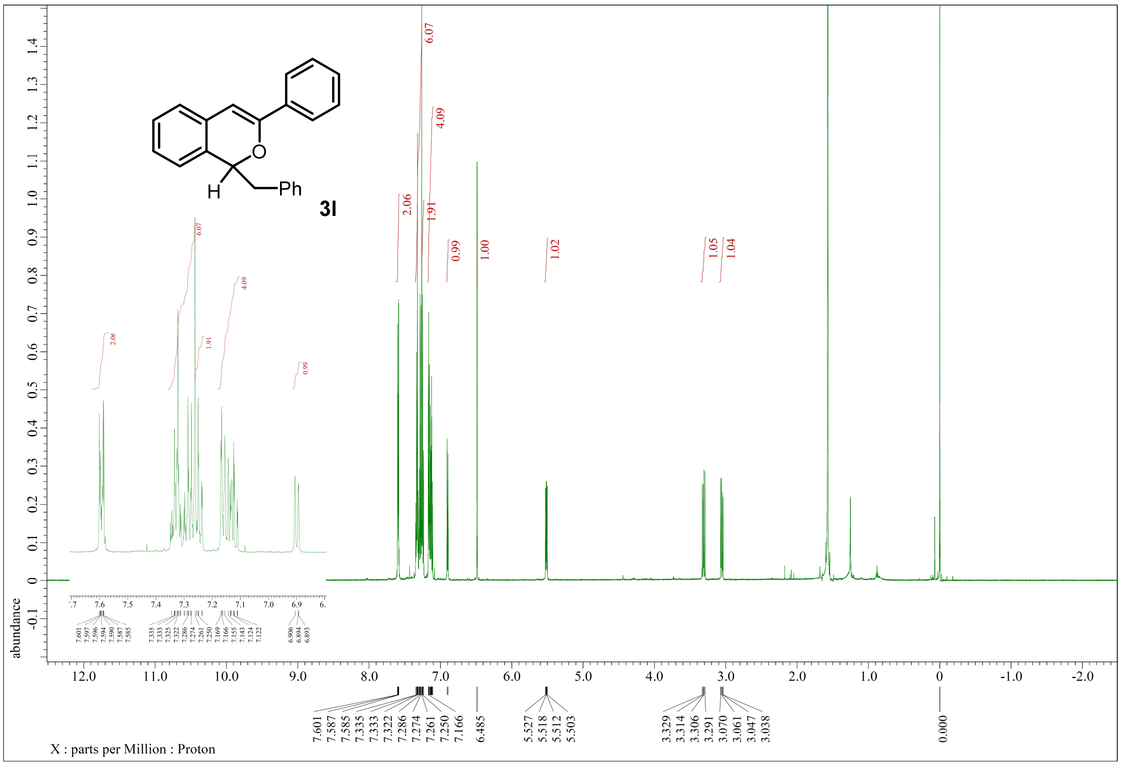
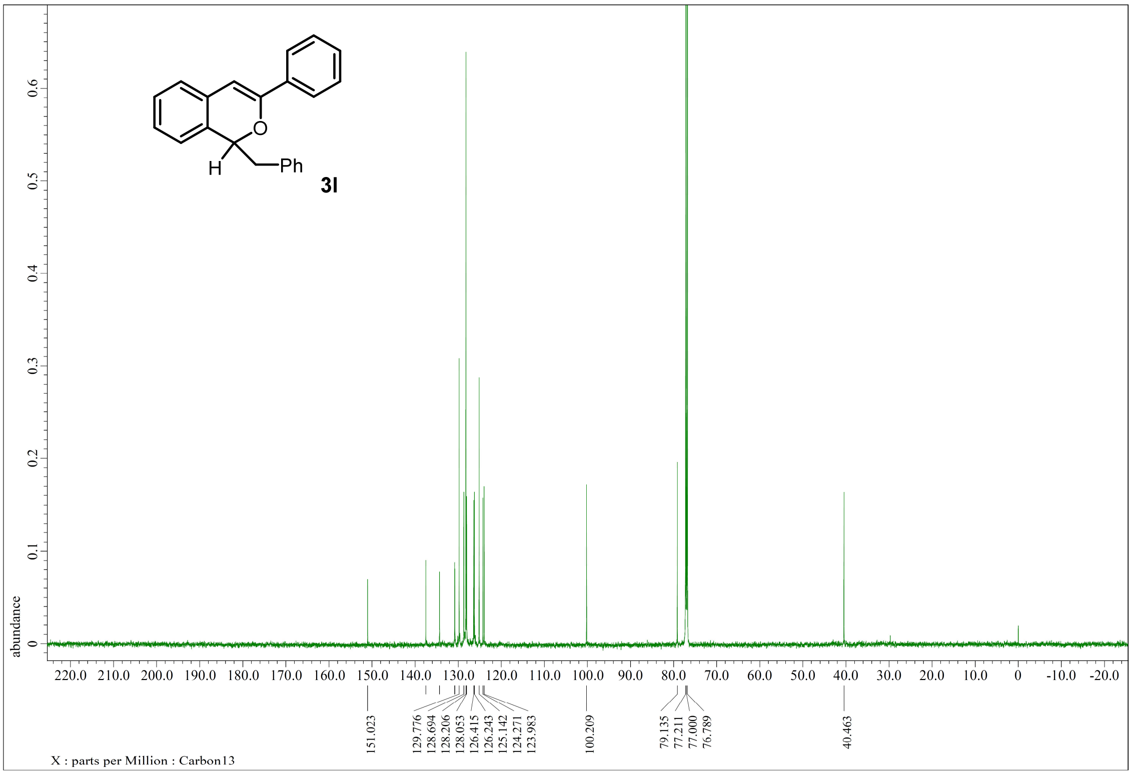


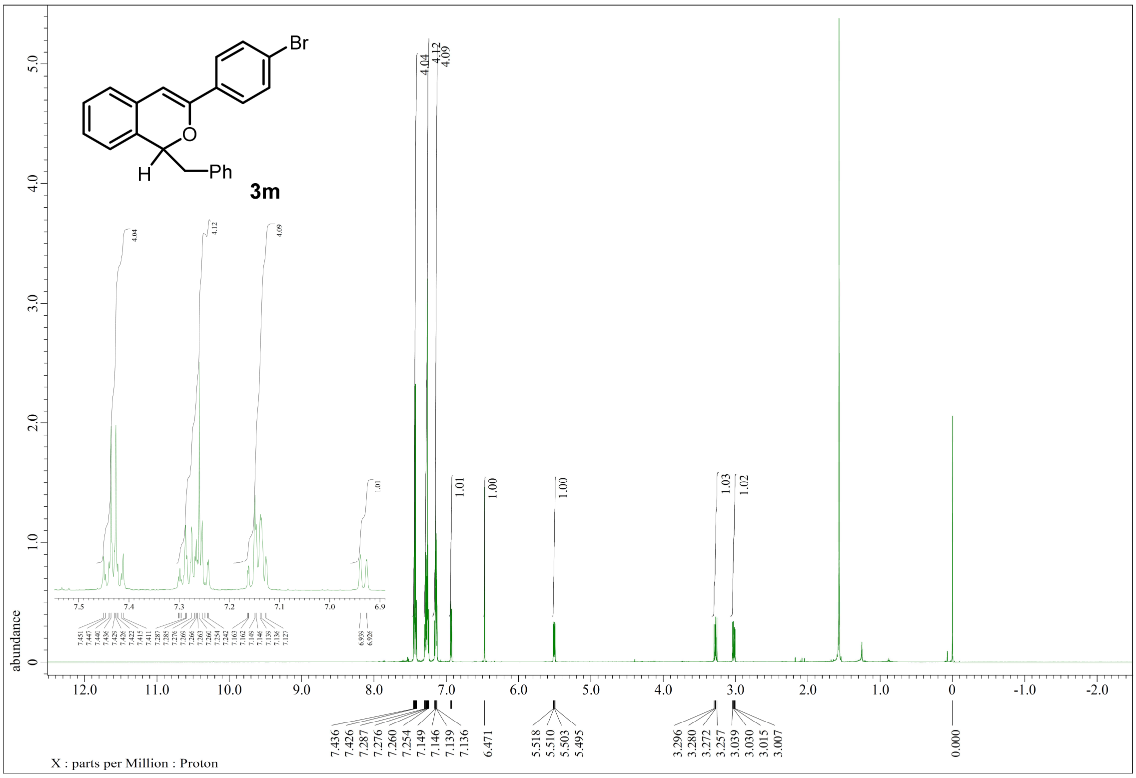


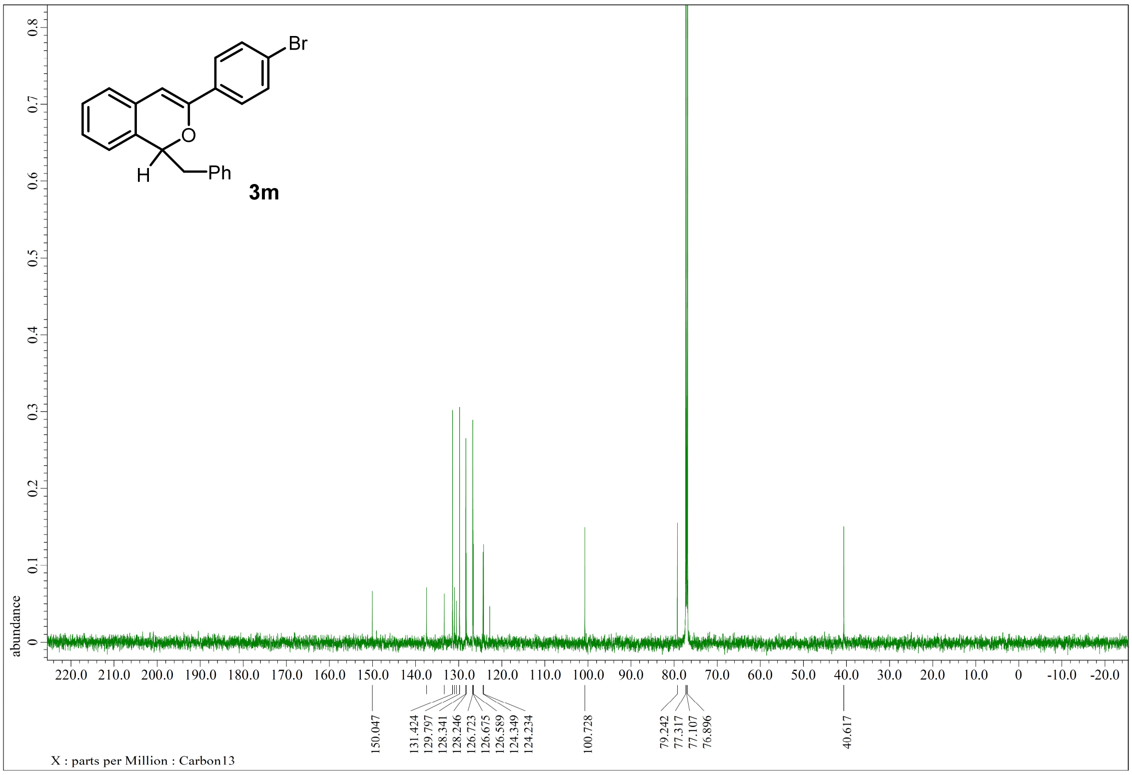
^{1}H NMR (600 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) spectra of **3l**.



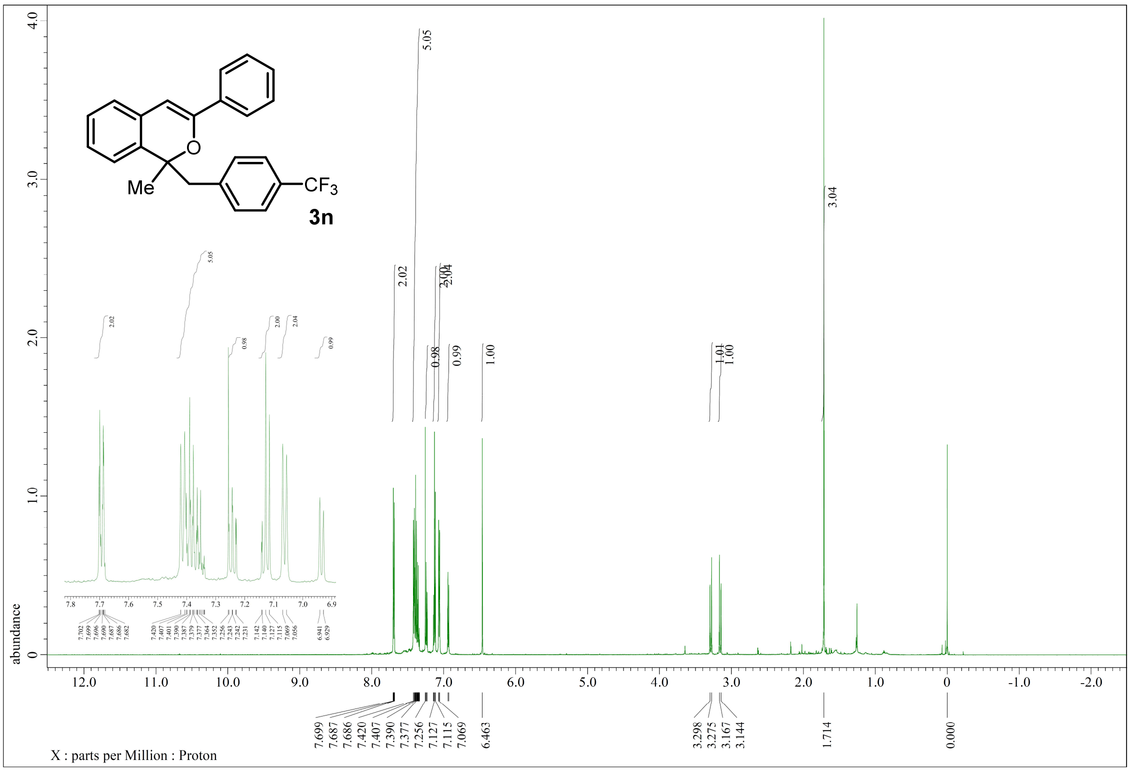


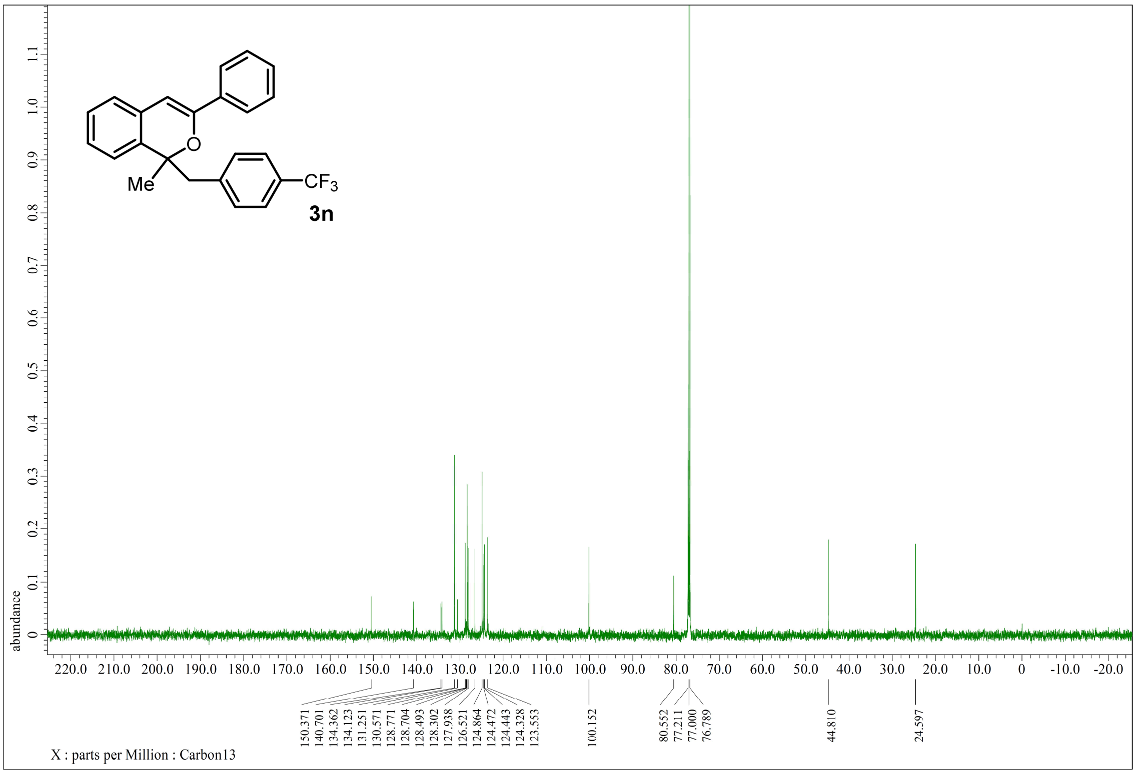
^{1}H NMR (600 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) spectra of **3m**.



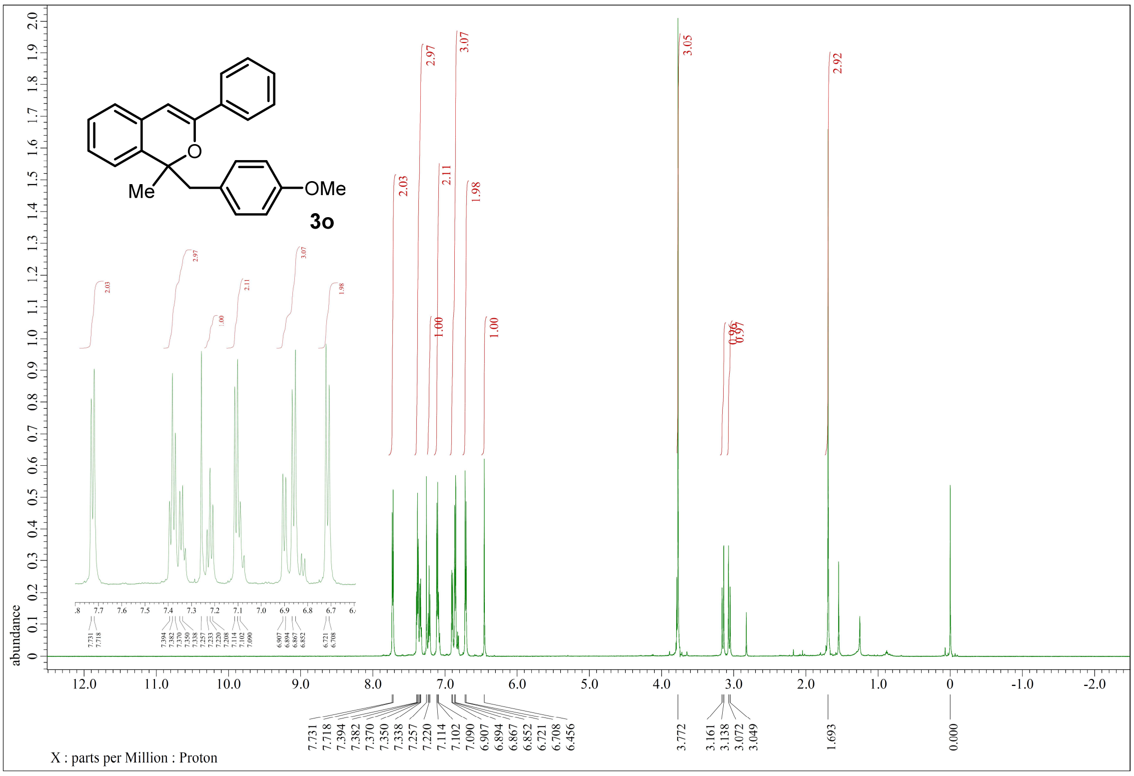


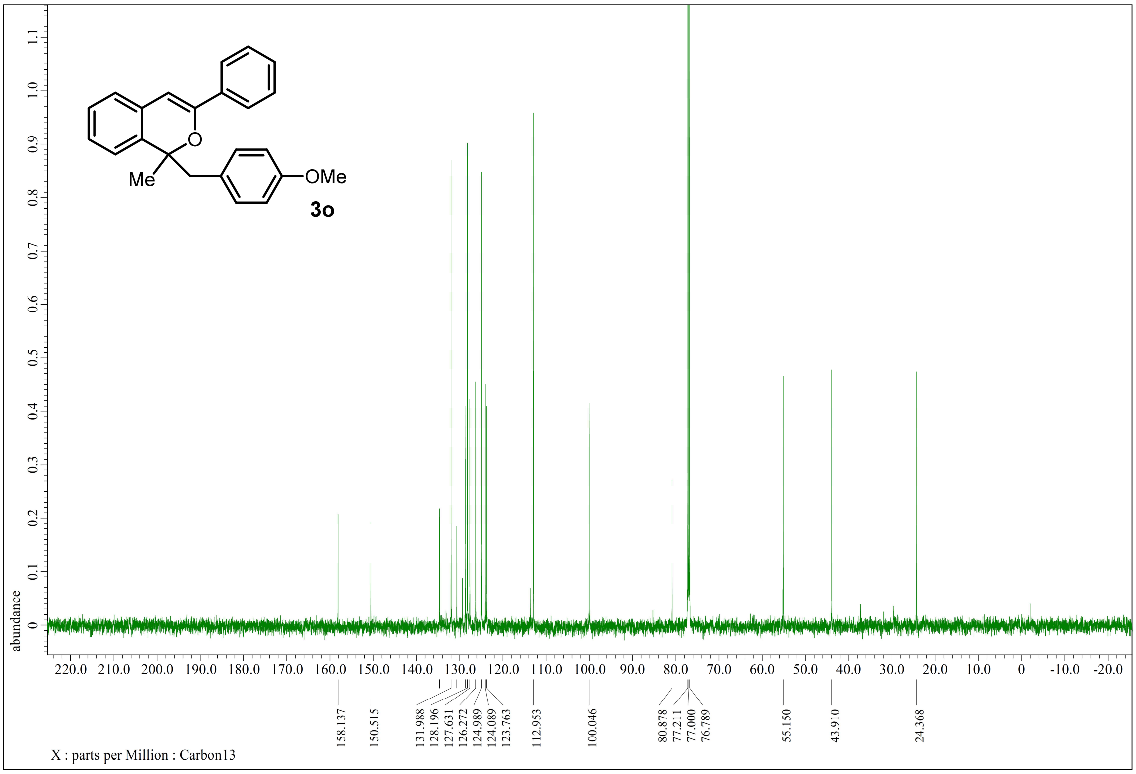
^{1}H NMR (600 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) spectra of **3n**.





^{1}H NMR (600 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) spectra of **3o**.





^{1}H NMR (600 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) spectra of **3p**.