SUPPORTING INFORMATION

UNEXPECTED FORMATION OF 4,7-DIHALOBENZO[*b*]THIOPHENES USING OHIRA-BESTMANN REAGENTS AND REACTIVITY OF THE HALOGEN-SUBSTITUTED BENZO[*b*]THIOPHENES IN SUZUKI-MIYAURA COUPLING WITH PHENYLBORONIC ACID

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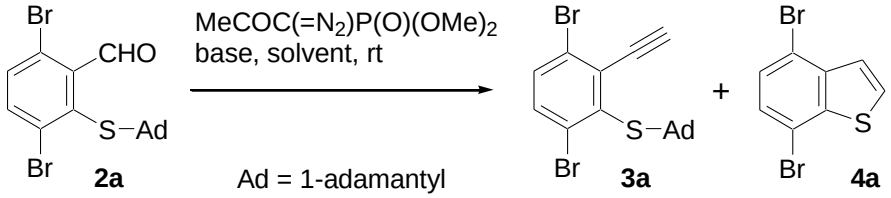
Experimental

Melting points were measured on a Yanagimoto MP-J3 micro melting point apparatus and are not corrected. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded either on a Bruker Avance III-400 or a Bruker Avance 400 spectrometer. ^{1}H (700 MHz) and ^{13}C (176 MHz) NMR spectra were measured on a Bruker Biospin Avance III-700 or a JEOL ECA 700 spectrometer. Mass spectra were taken on a Bruker solariX spectrometer or a JEOL JMS-T spectrometer.

General procedure for the reaction of compounds 2 with Ohira-Bestmann reagent

To a mixture of **2a** (500.0 mg, 1.162 mmol), K_2CO_3 (321.9 mg, 2.329 mmol), THF (3.5 mL) in MeOH (5 mL) was added a solution of dimethyl (1-diazo-2-oxopropyl)phosphonate (276.6 mg, 1.439 mmol) in MeOH (2 mL) at 0 °C.* The reaction mixture was stirred at 0 °C for 20 min then at room temperature for 19 h. The reaction mixture was poured into brine and extracted with EtOAc. The organic layer was dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was treated with silica gel column chromatography (hexane-$CHCl_3$, 4:1) to give 367.6 mg of **3a** (0.8625 mmol) and 26.5 mg of **4a** (0.09076 mmol). *Thus, total 7 mL of MeOH was used.

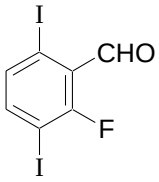
Table S1. Reaction of **2a** with Ohira-Bestmann reagent[a]



Entry	Base	Solvent	Yield of **3a** / %	Yield of **4a** / %
1	K_2CO_3	MeOH-THF (2:1)	74	8
2[b]			60	8
3[c]			59	9
4		MeOH	42	11
5		MeOH- trace H_2O	41	13
6		EtOH	65	8[d]
7		1-PrOH	trace	trace
8		2-PrOH	0[e]	0[e]
9	MeONa[f]	MeOH	55[g]	20[g]
10		DMF	0[e]	0[e]

a) The reaction was followed by TLC until no significant change was observed. b) Reaction at 0 °C. c) The reaction was conducted in the presence of 18-crown-6. d) 1-Adamantyl ethyl ether was obtained in a similar yield. e) The starting aldehyde was recovered. f) 6 equiv. of the alkoxide was used. g) Average value of 2 runs.

NMR spectra



1c

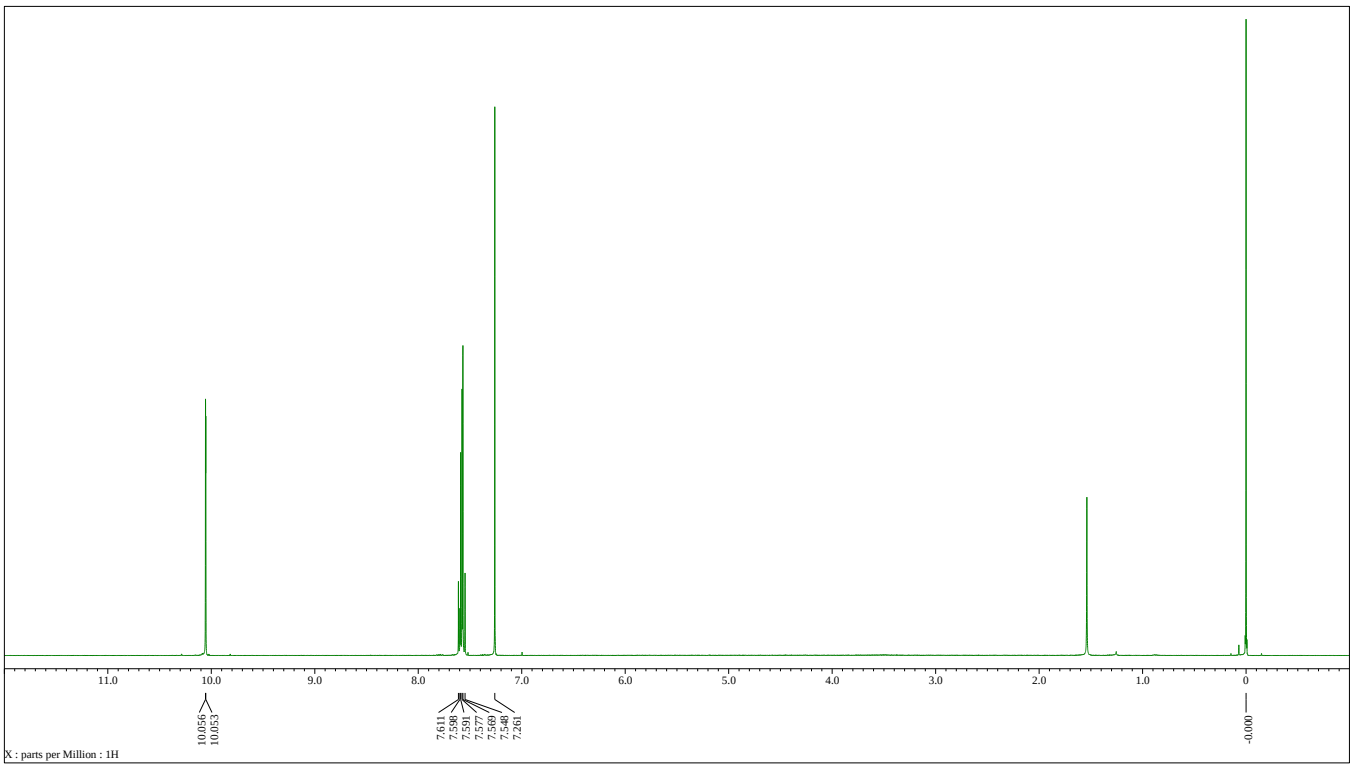


FIGURE S1 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1c**

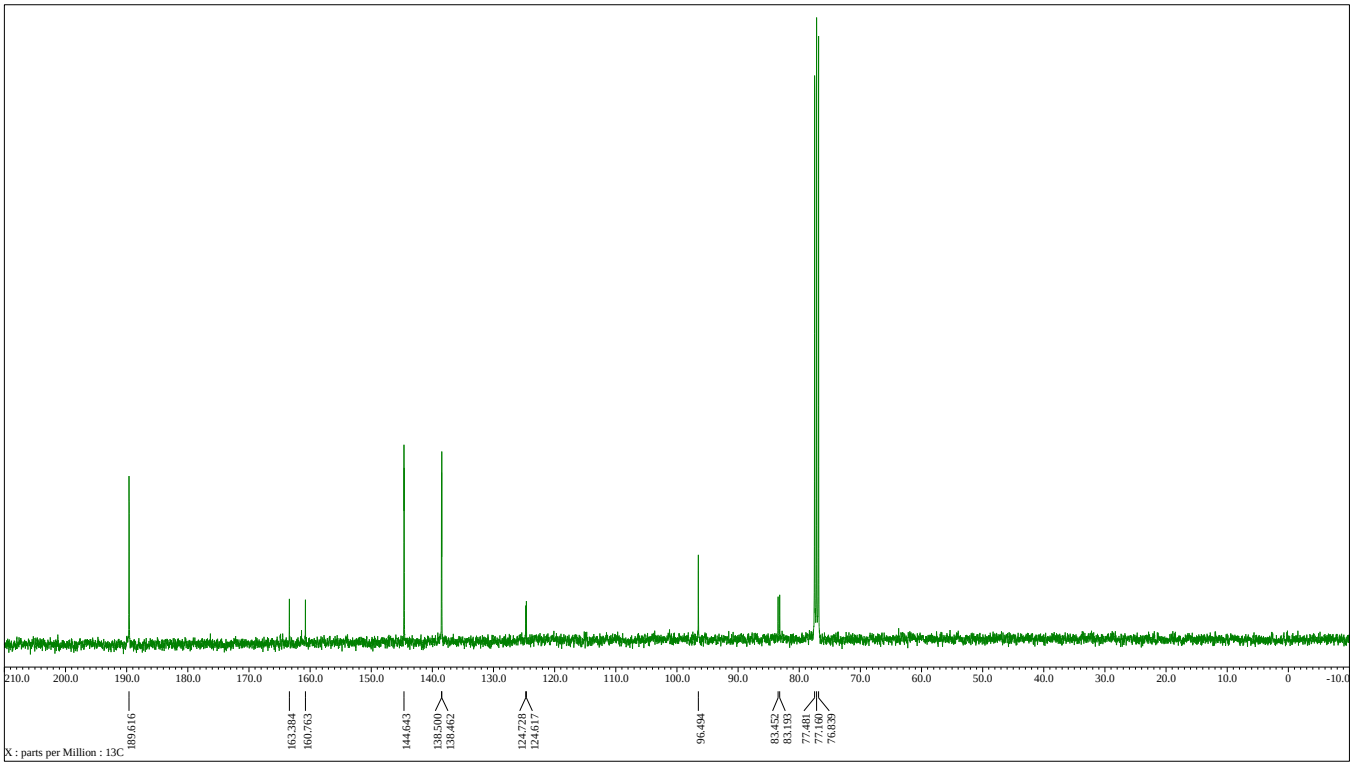
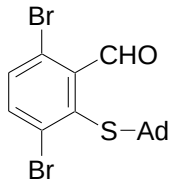


FIGURE S2 ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **1c**



2a

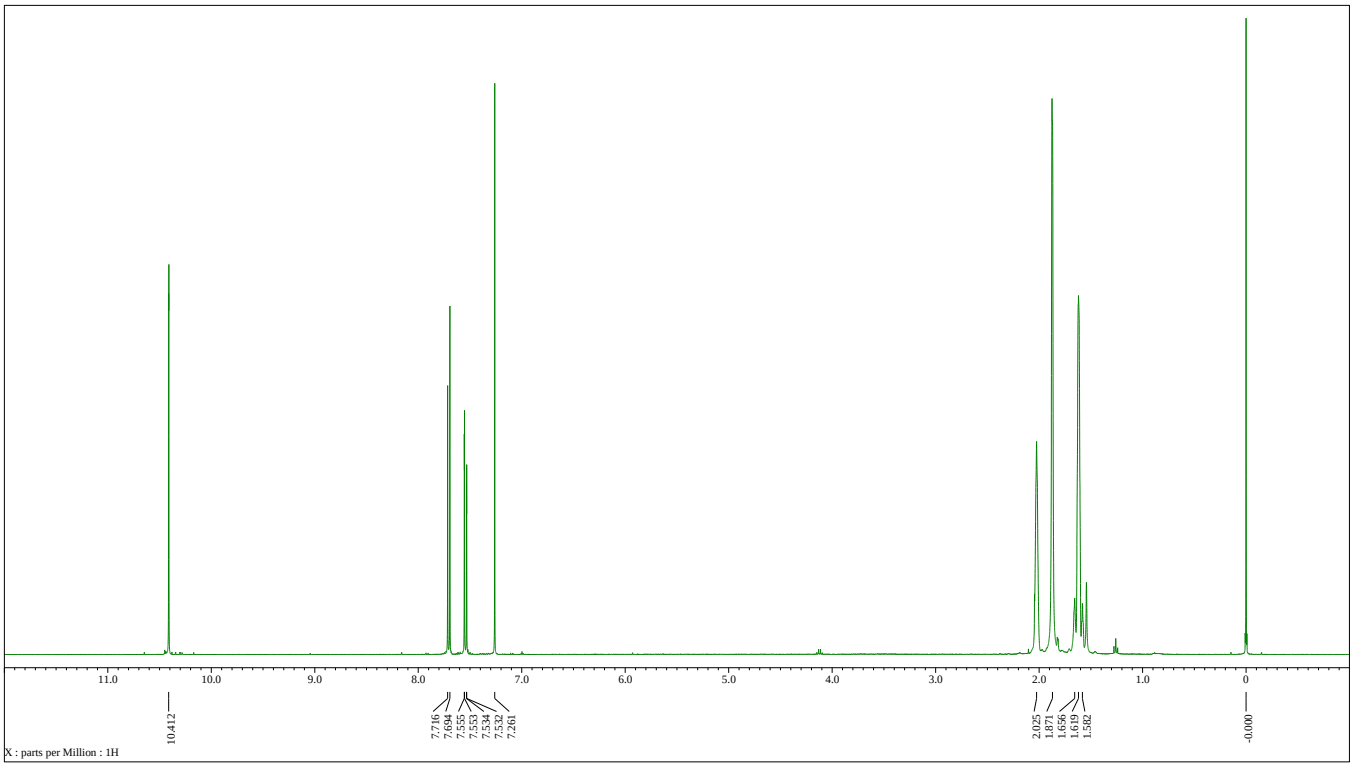


FIGURE S3 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2a**

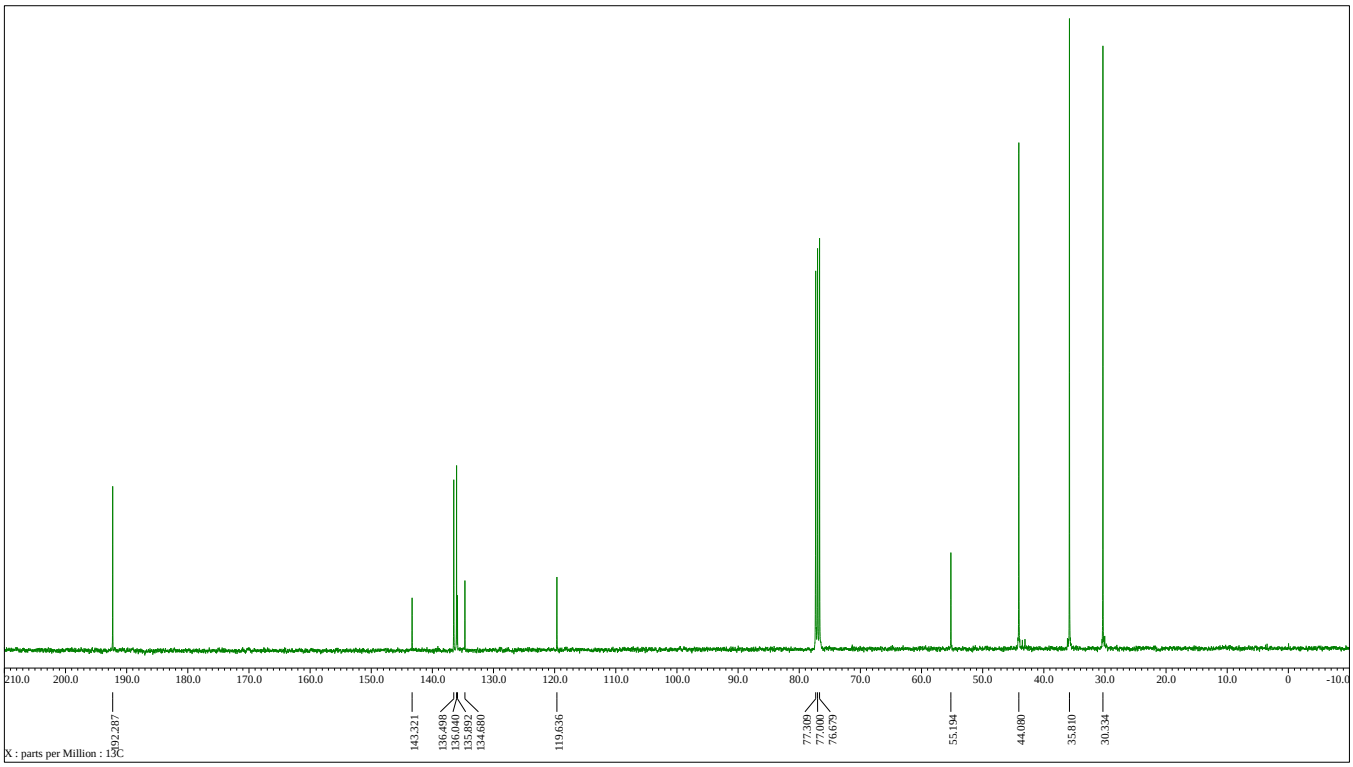
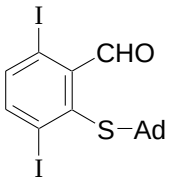


FIGURE S4 $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **2a**



2c

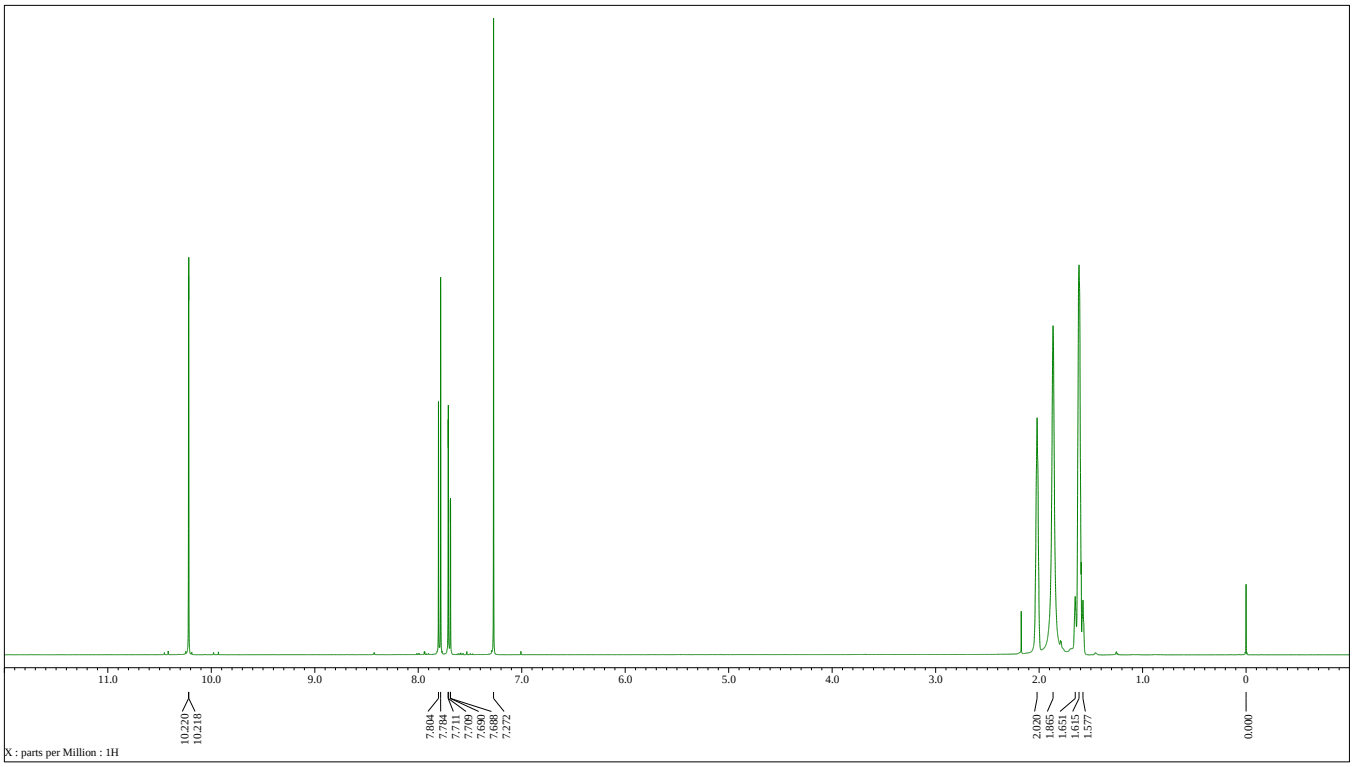


FIGURE S5 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2c**

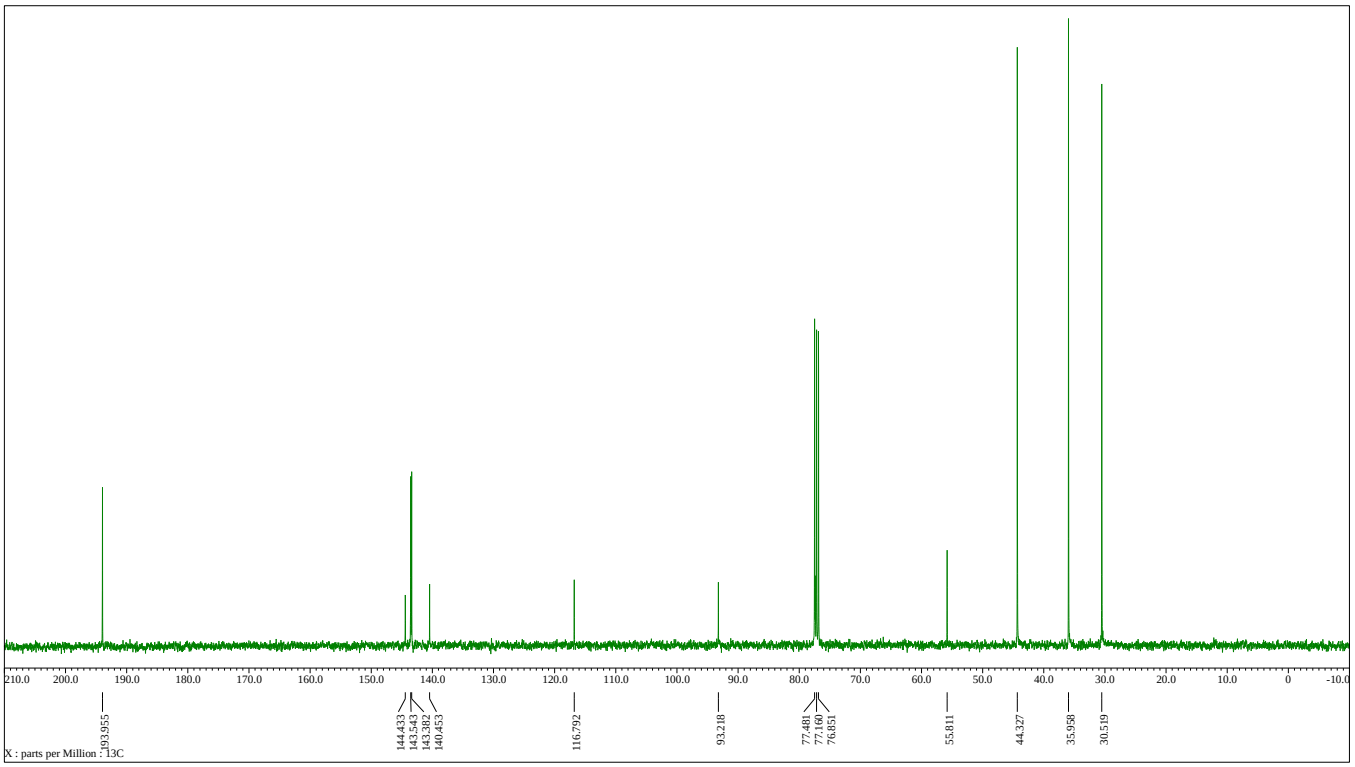
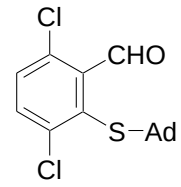


FIGURE S6 $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **2c**



2d

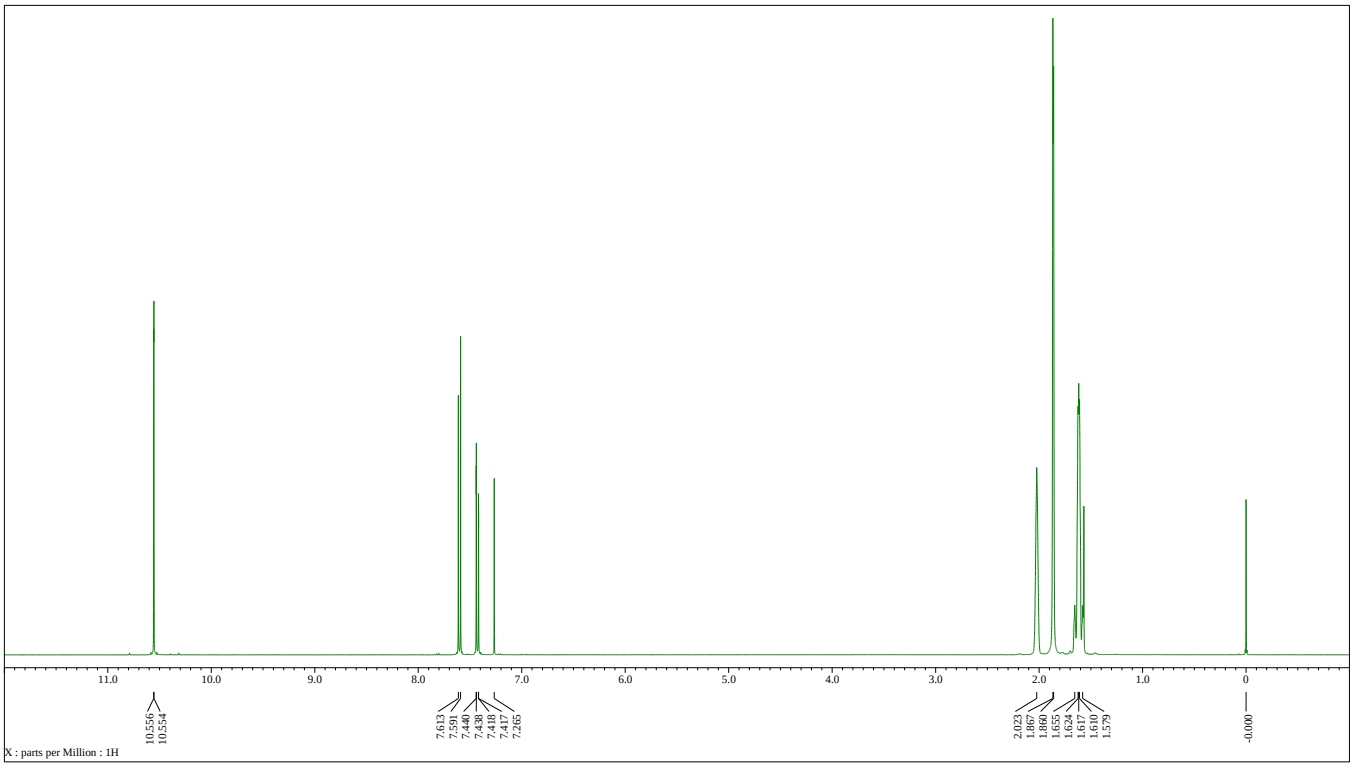


FIGURE S7 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2d**

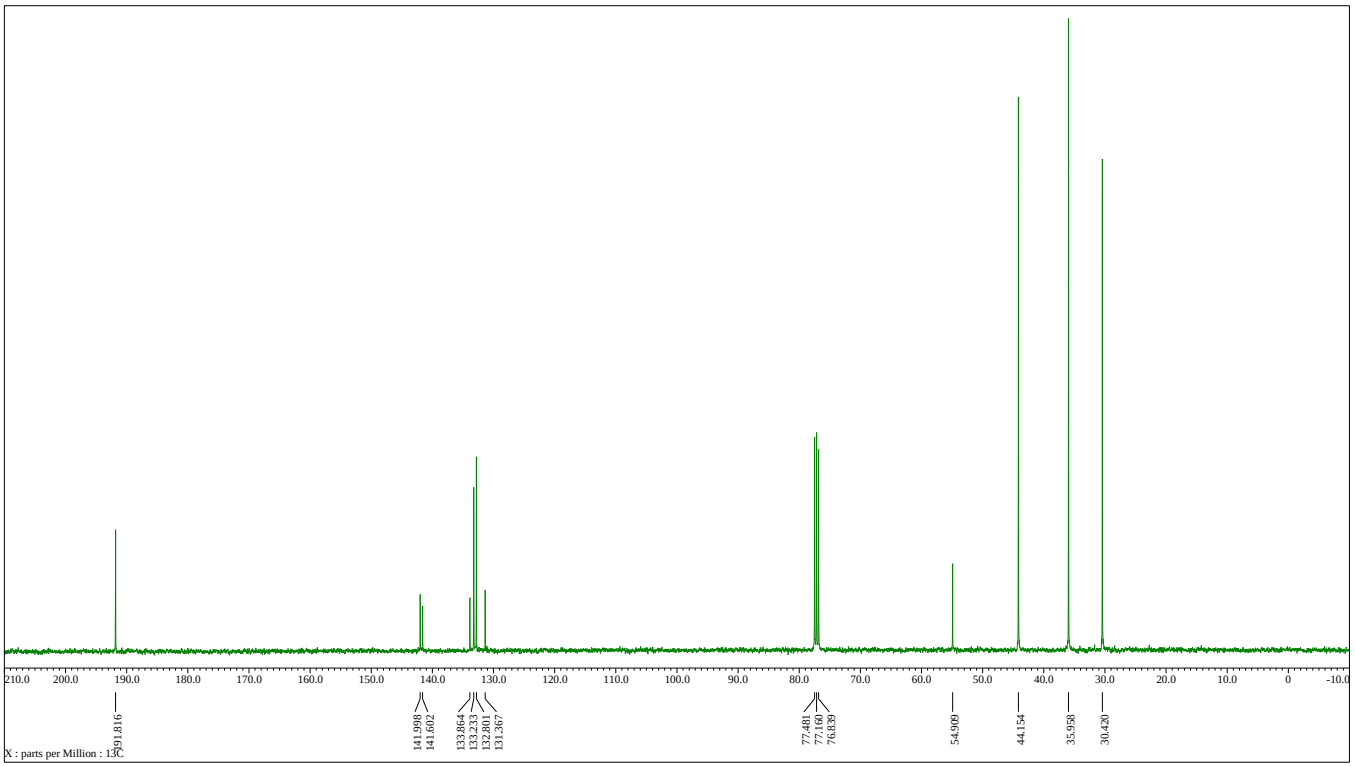
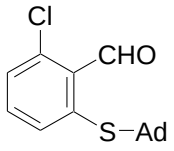


FIGURE S8 ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **2d**



2k

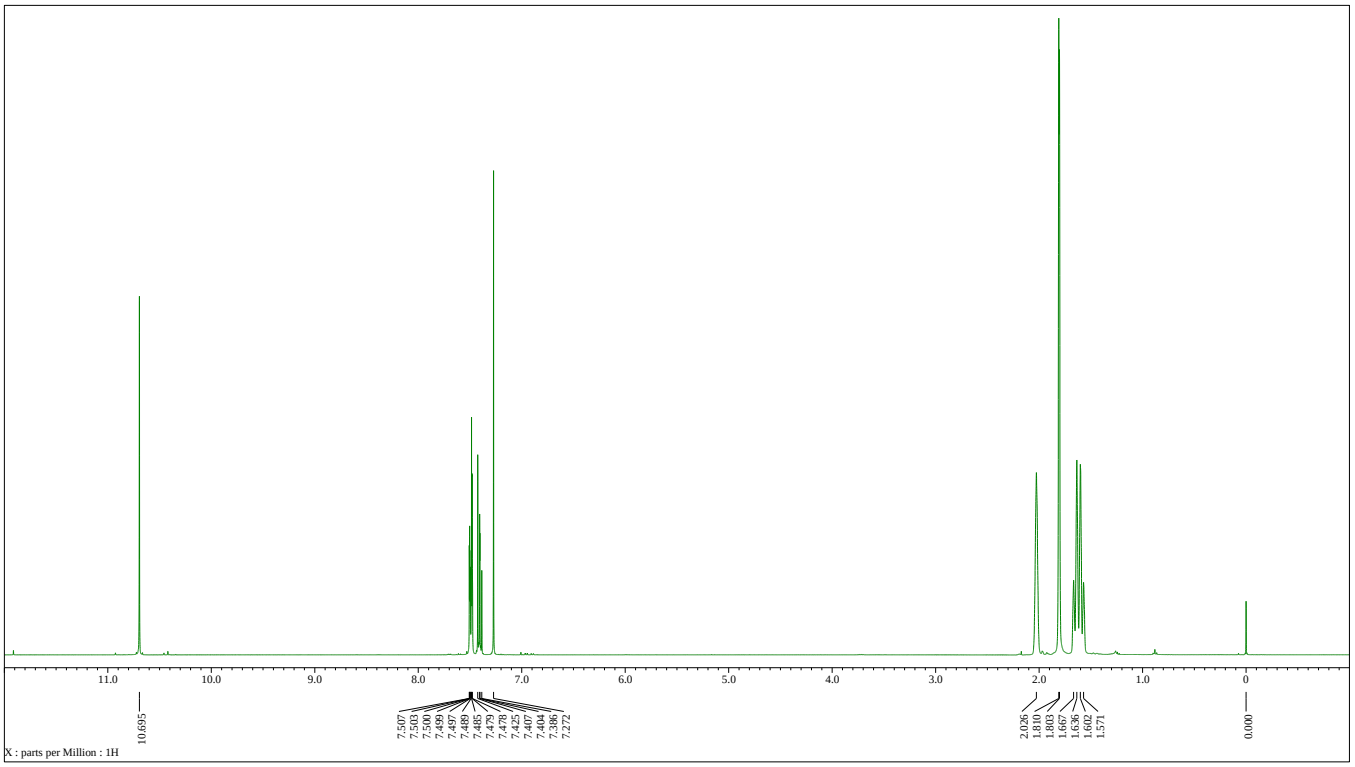


FIGURE S9 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2k**

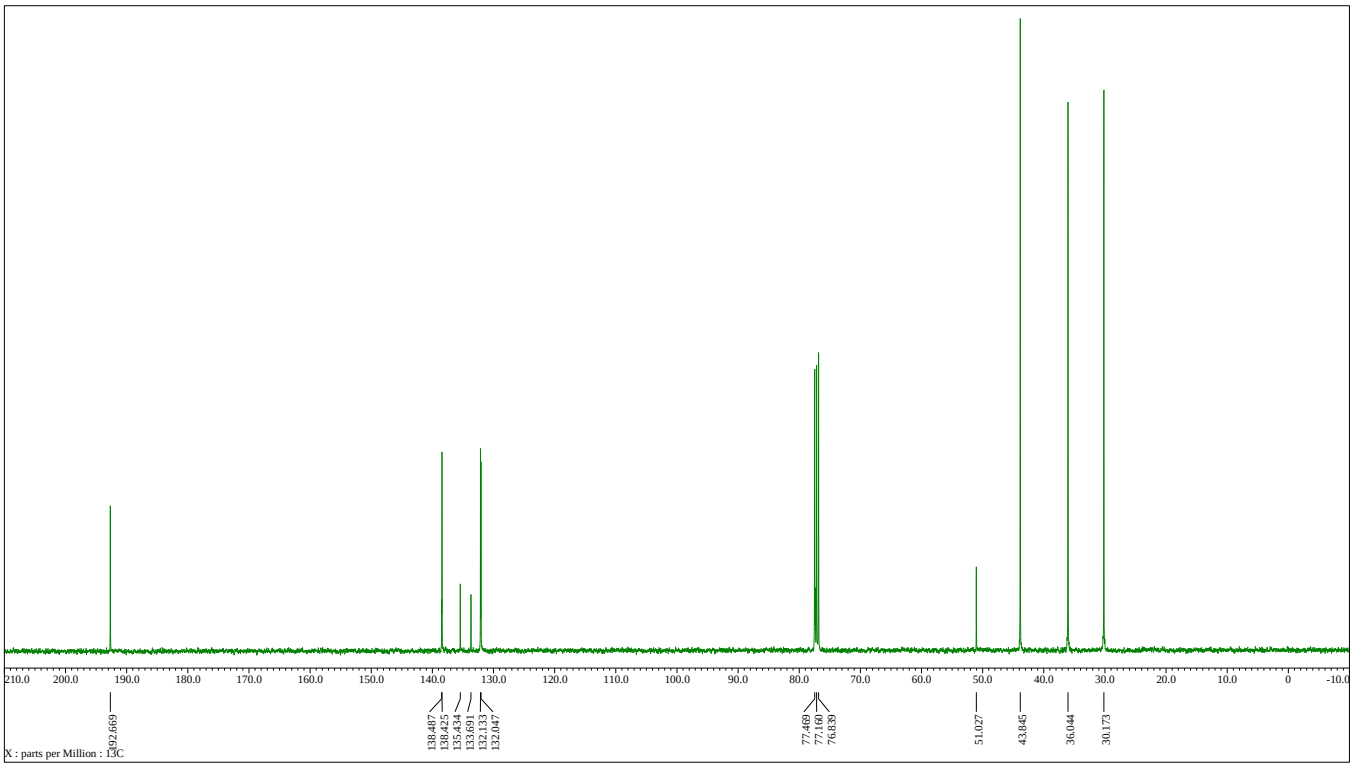
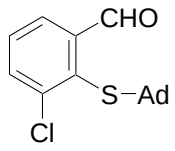


FIGURE S10 ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **2k**



2l

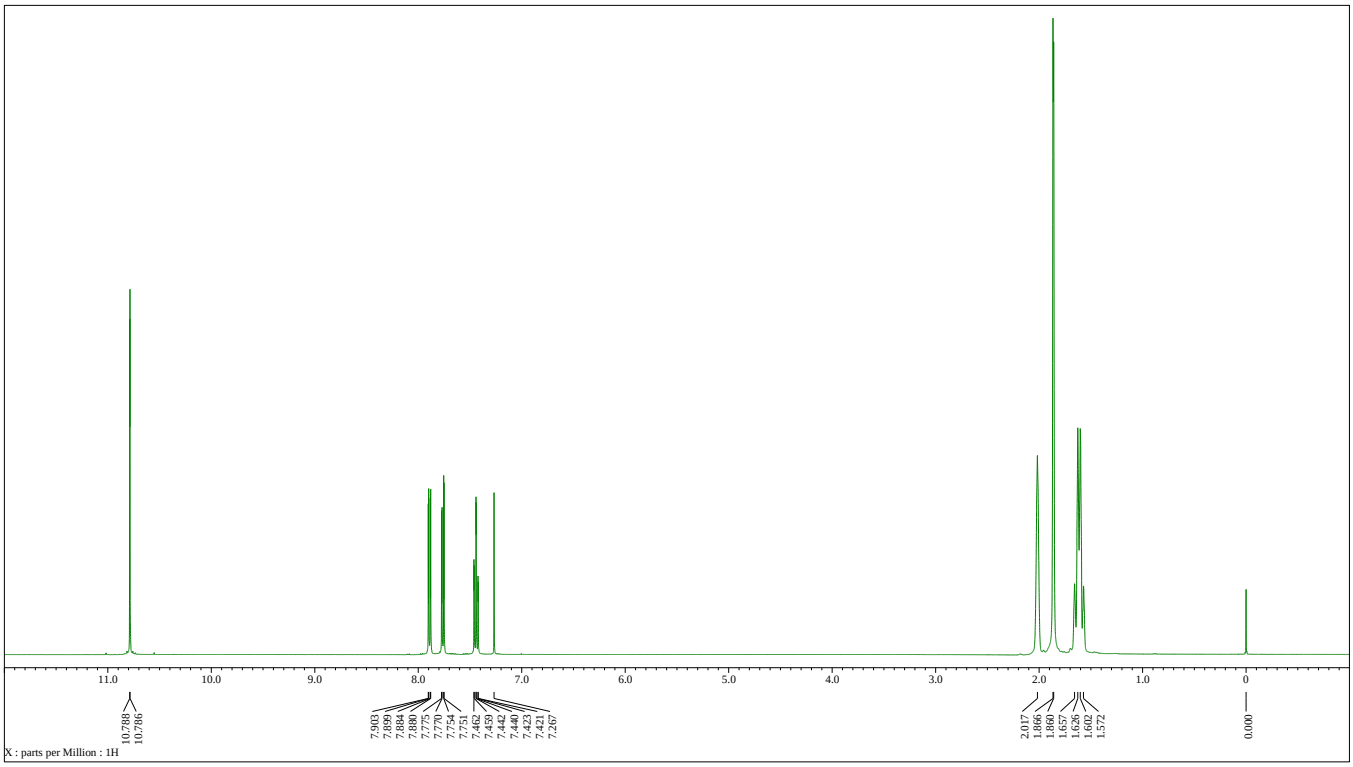


FIGURE S11 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2l**

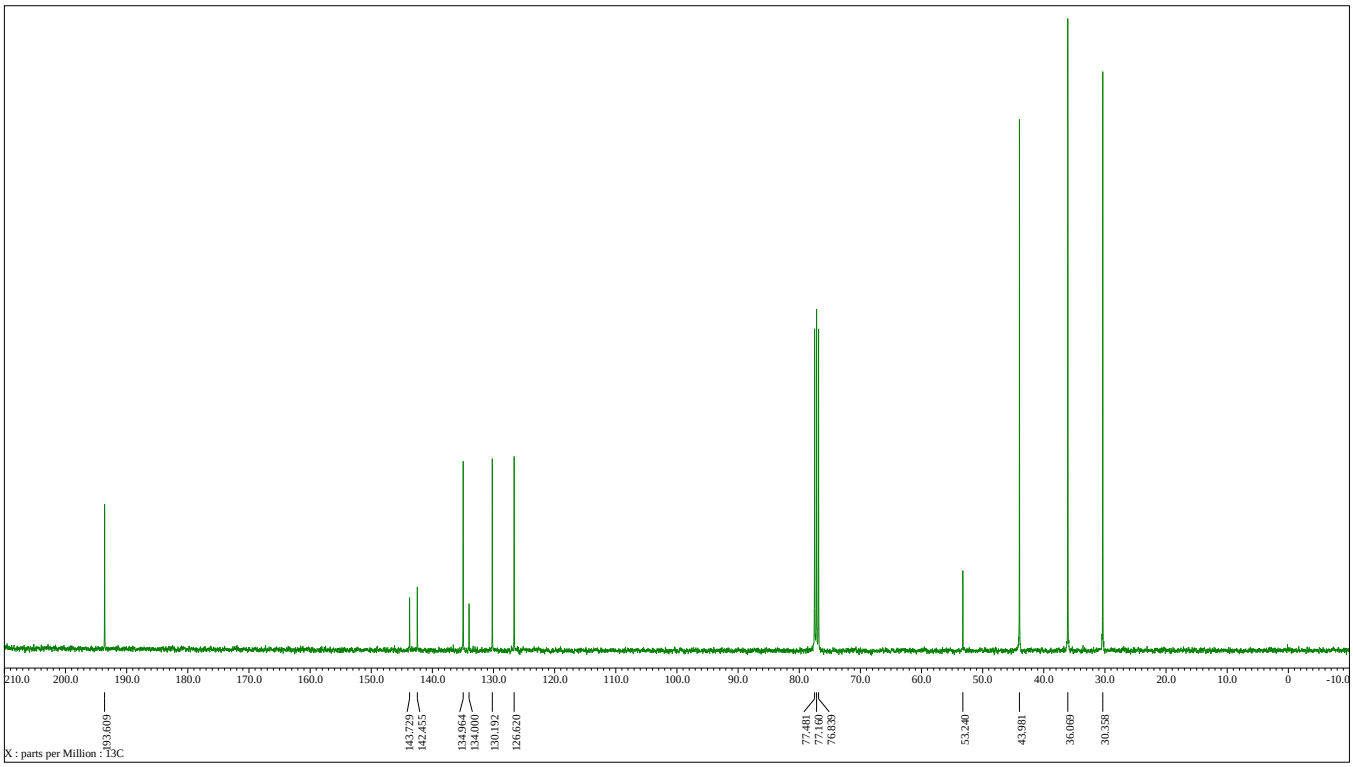
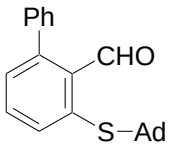


FIGURE S12 $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **2l**



2o

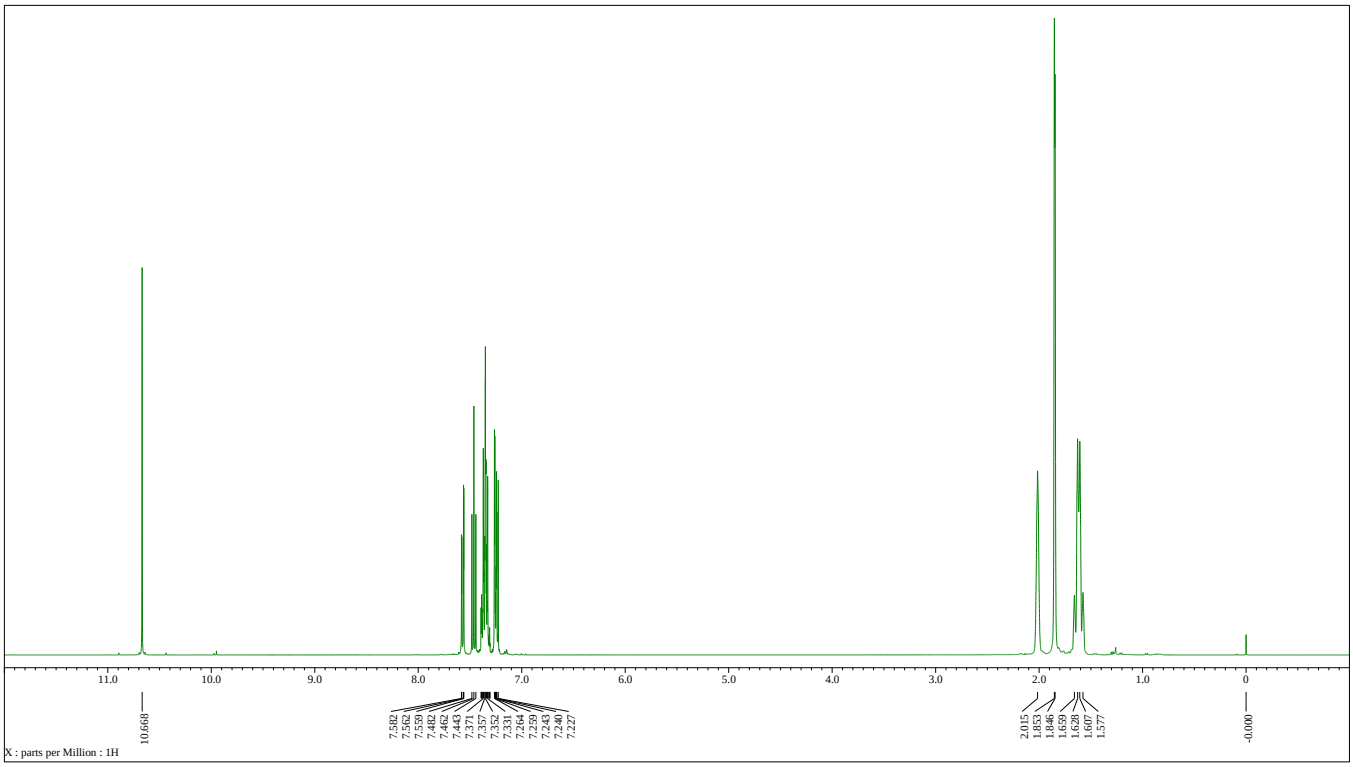


FIGURE S13 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2o**

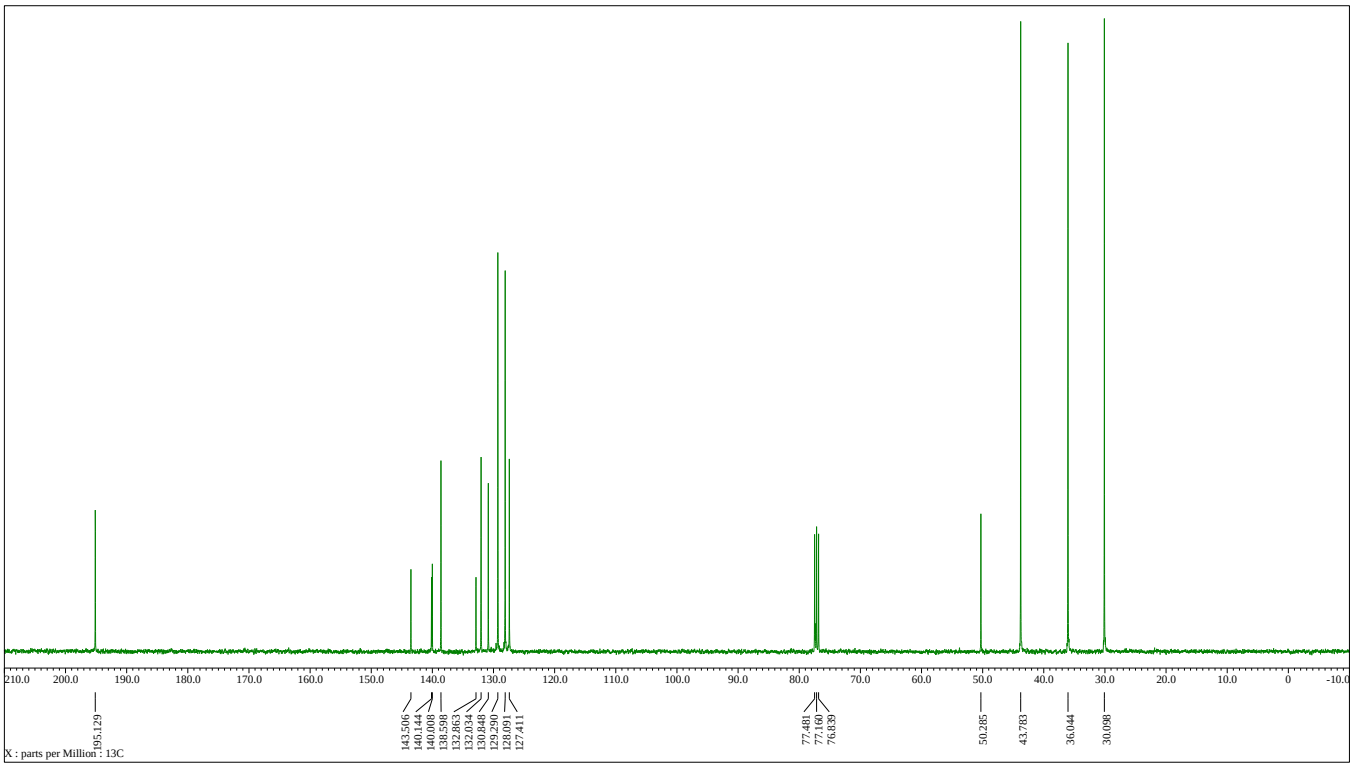
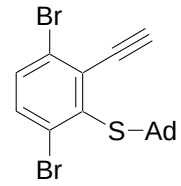


FIGURE S14 $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **2o**



3a

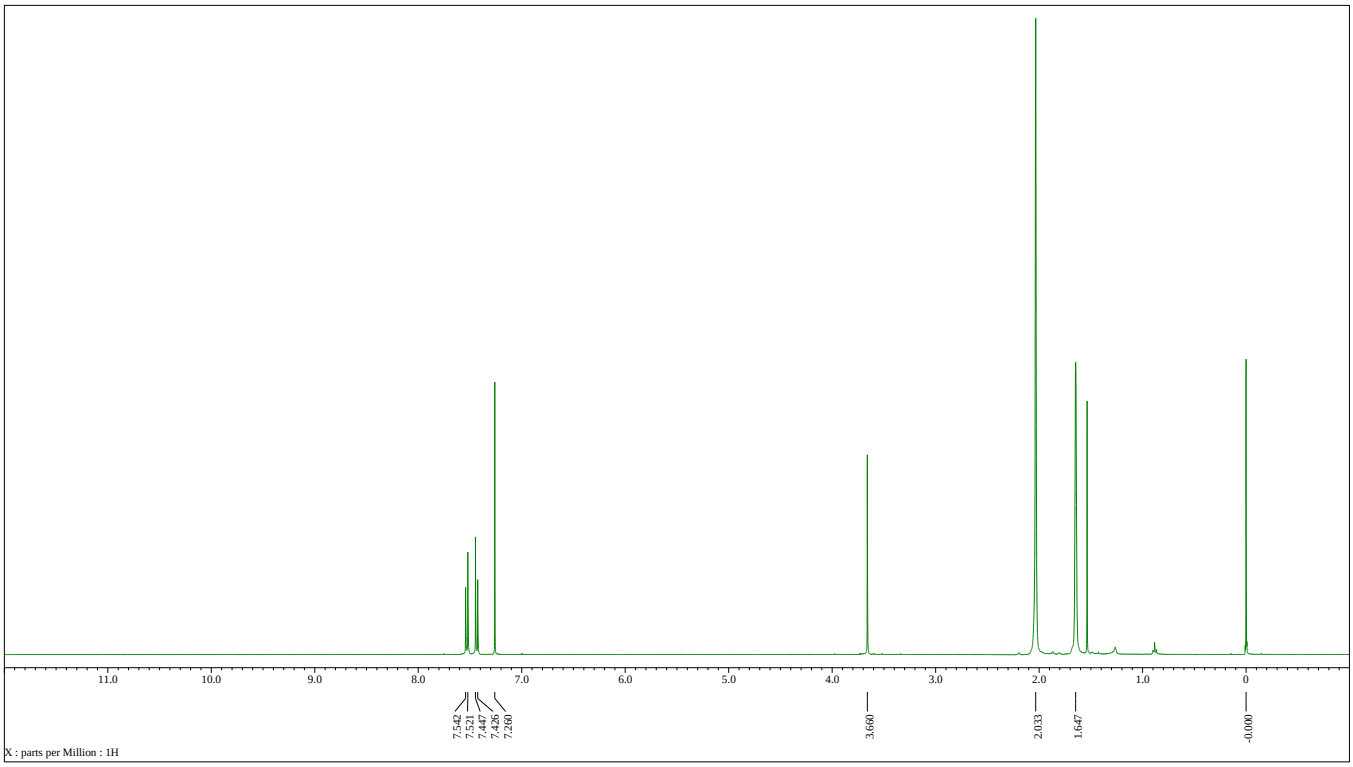


FIGURE S15 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3a**

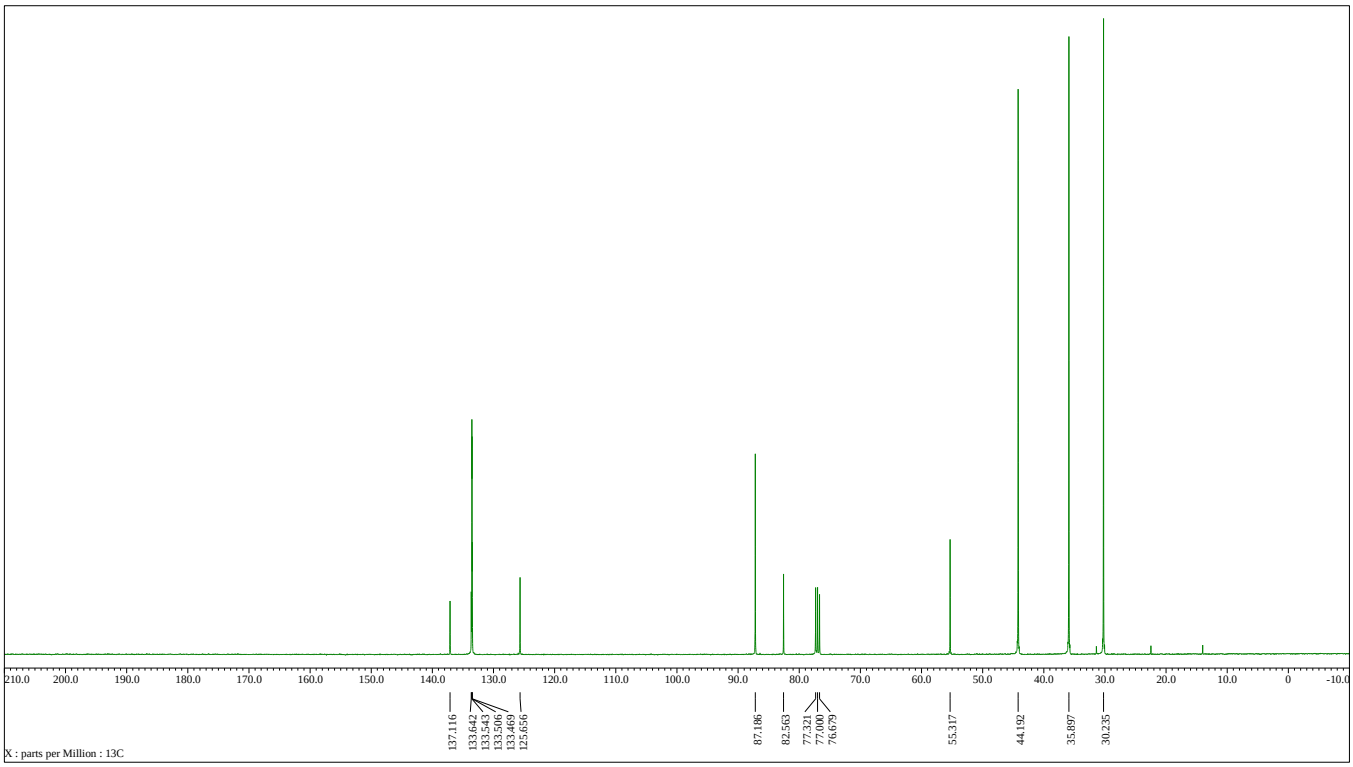
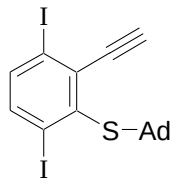


FIGURE S16 $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3a**



3c

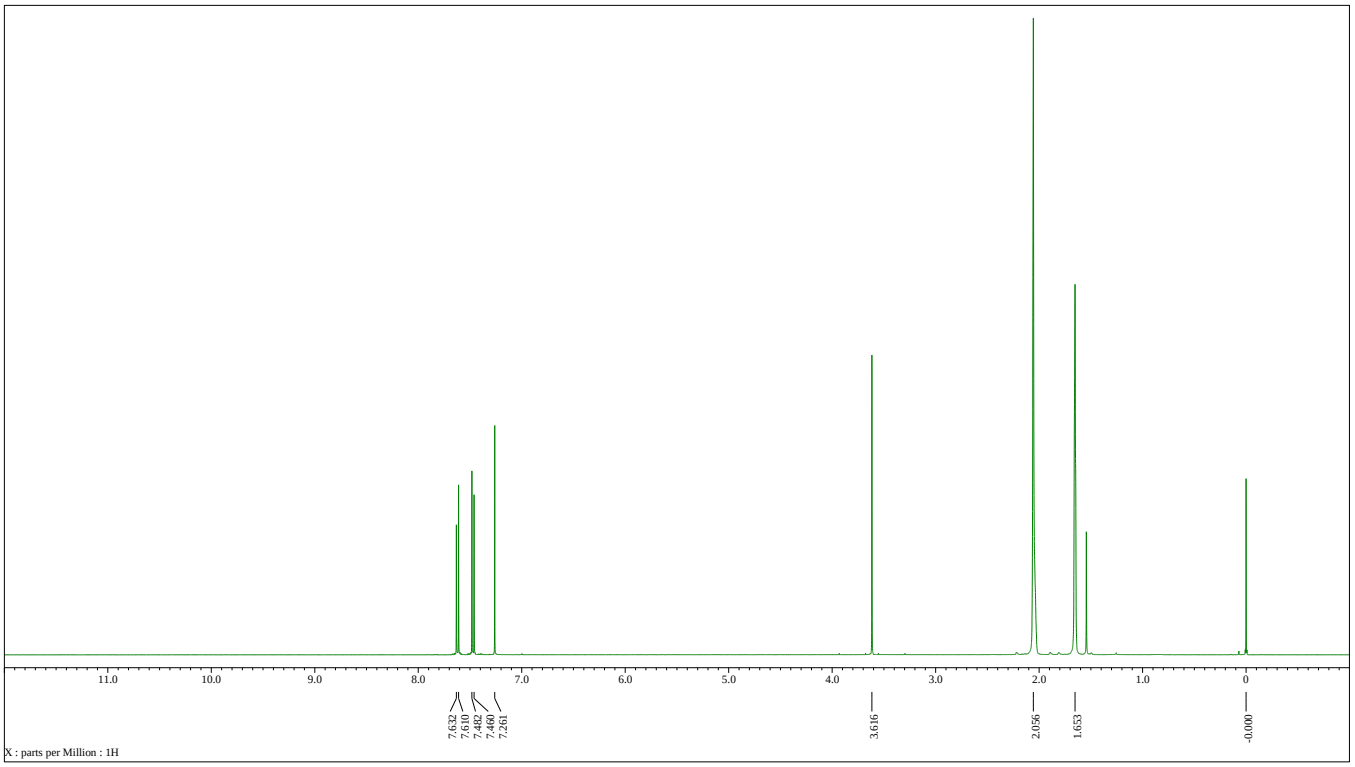


FIGURE S17 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3c**

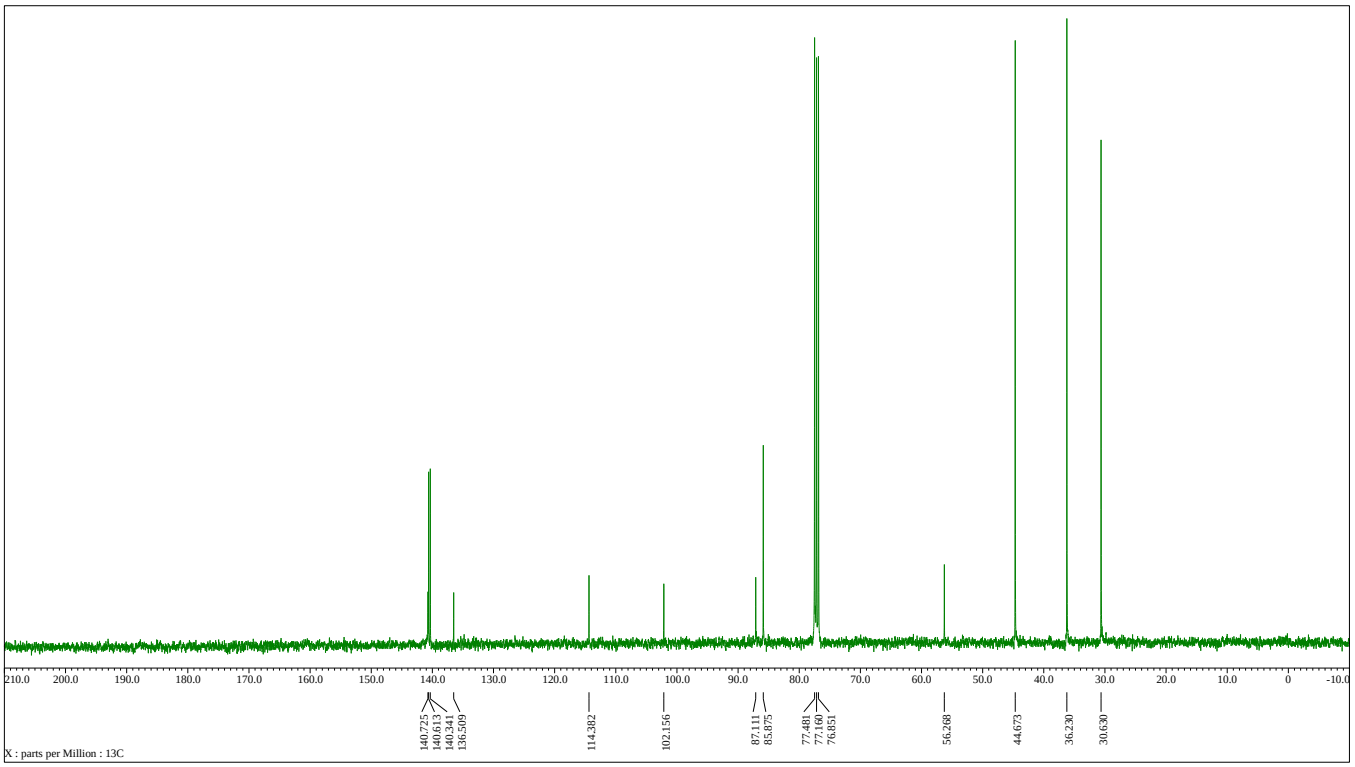
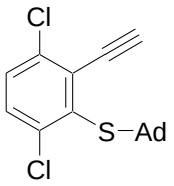


FIGURE S18 $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3c**



3d

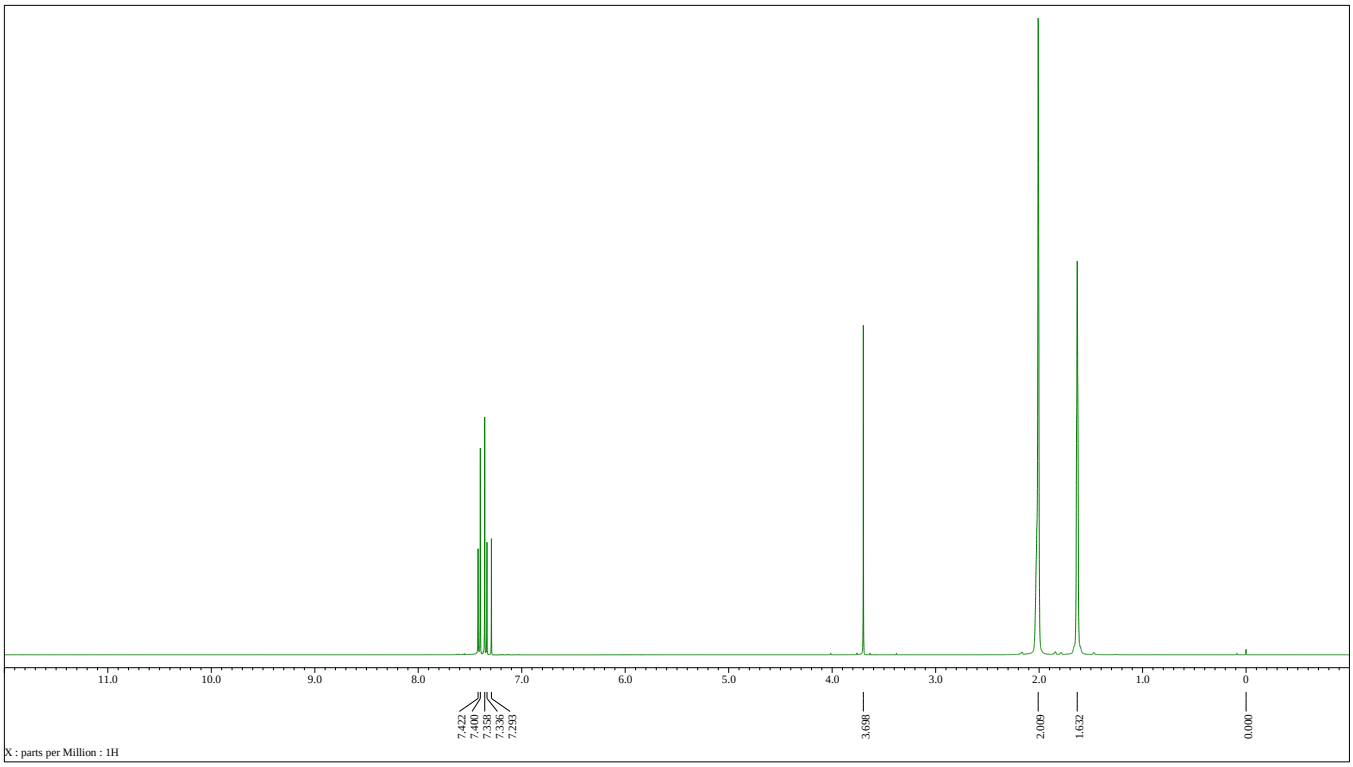


FIGURE S19 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3d**

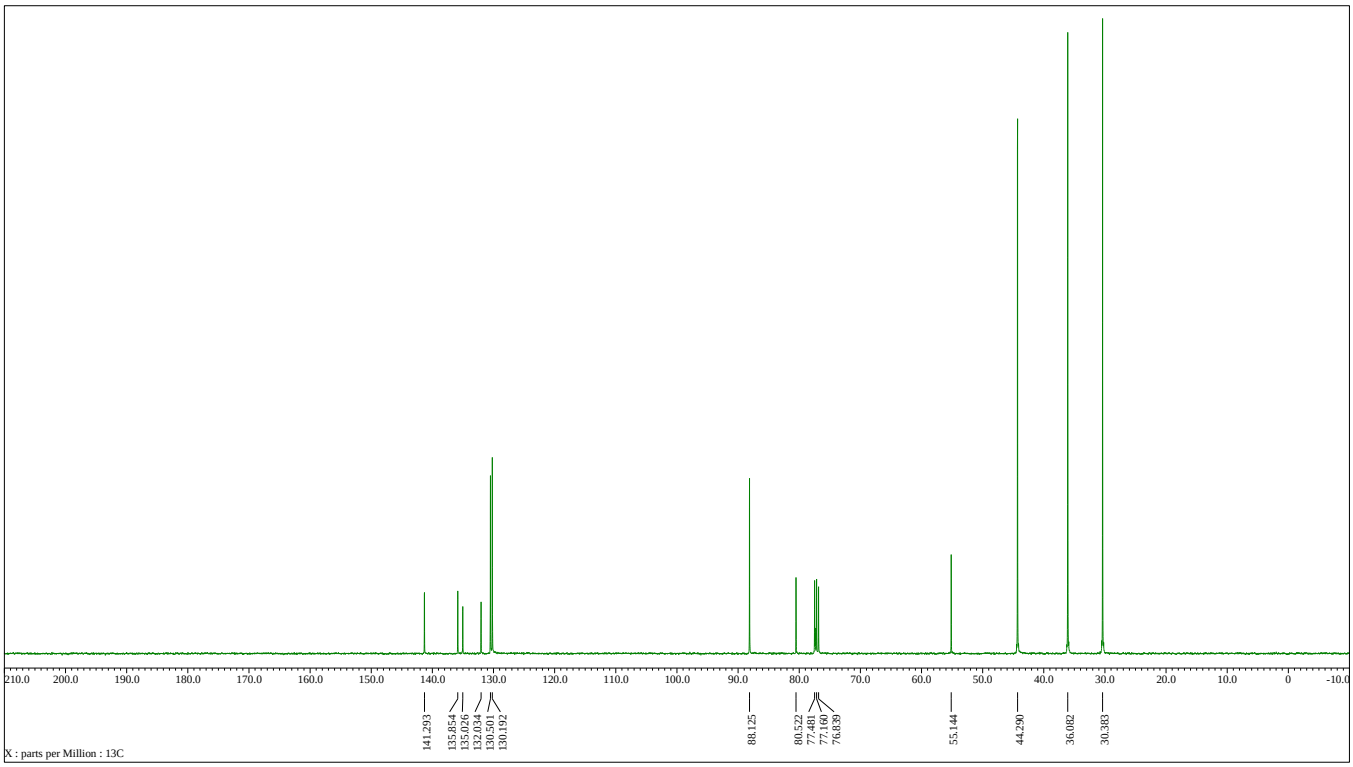
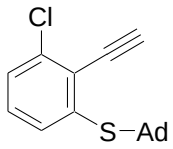


FIGURE S20 $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3d**



3k

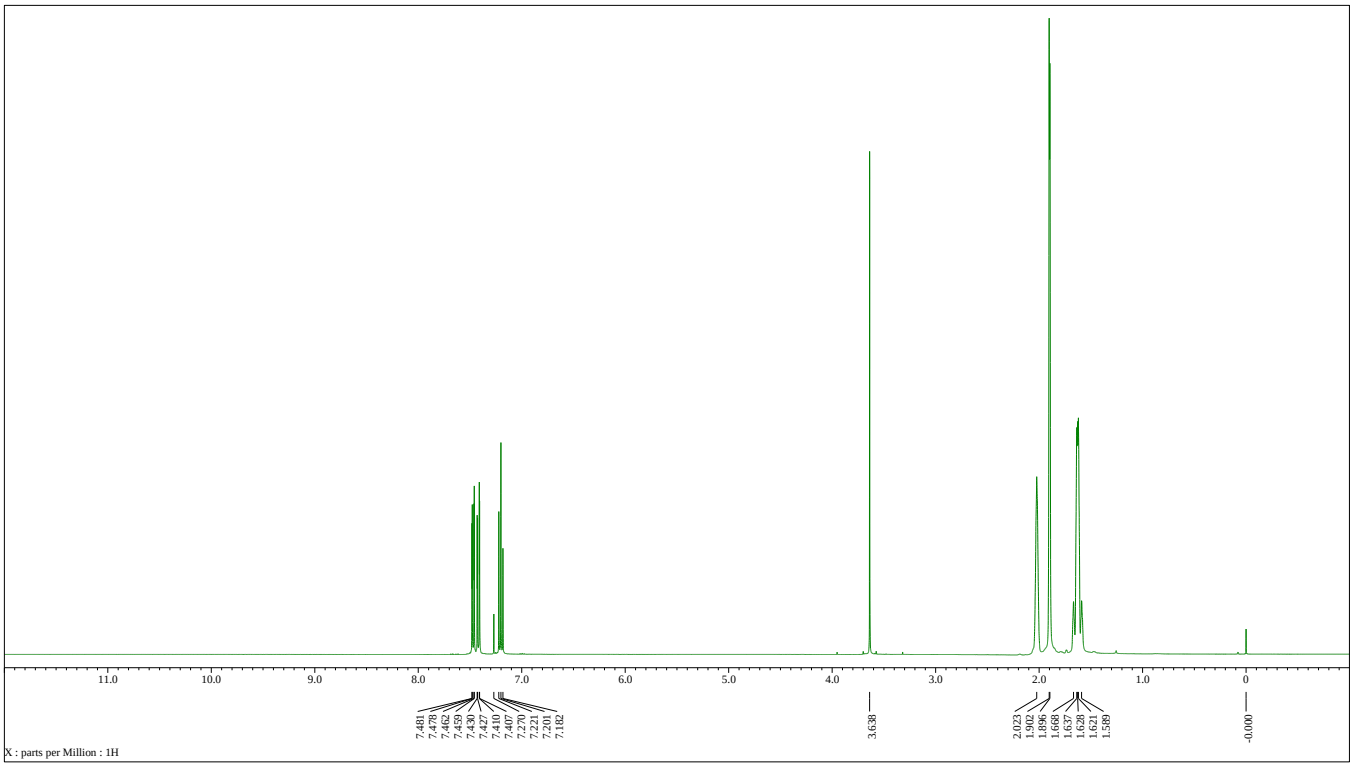


FIGURE S21 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3k**

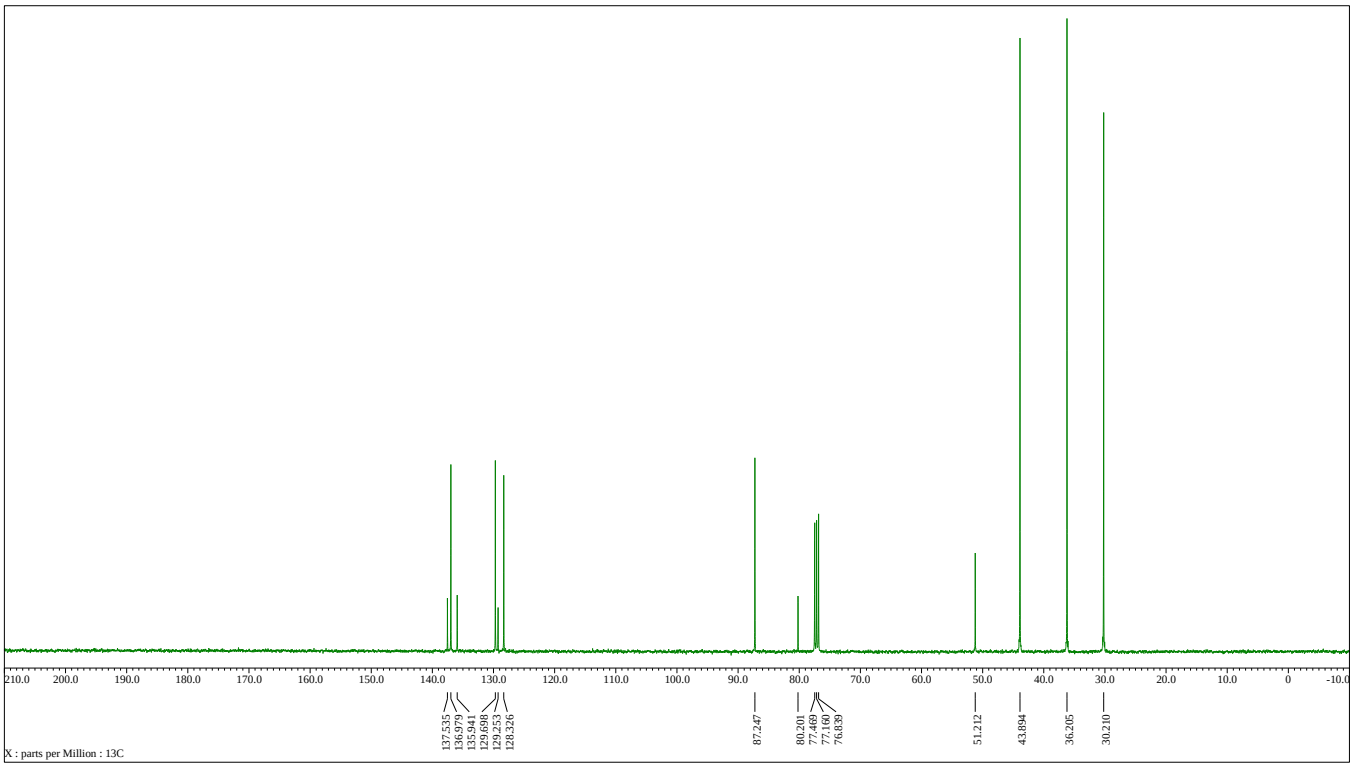
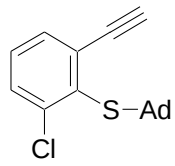


FIGURE S22 $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3k**



3l

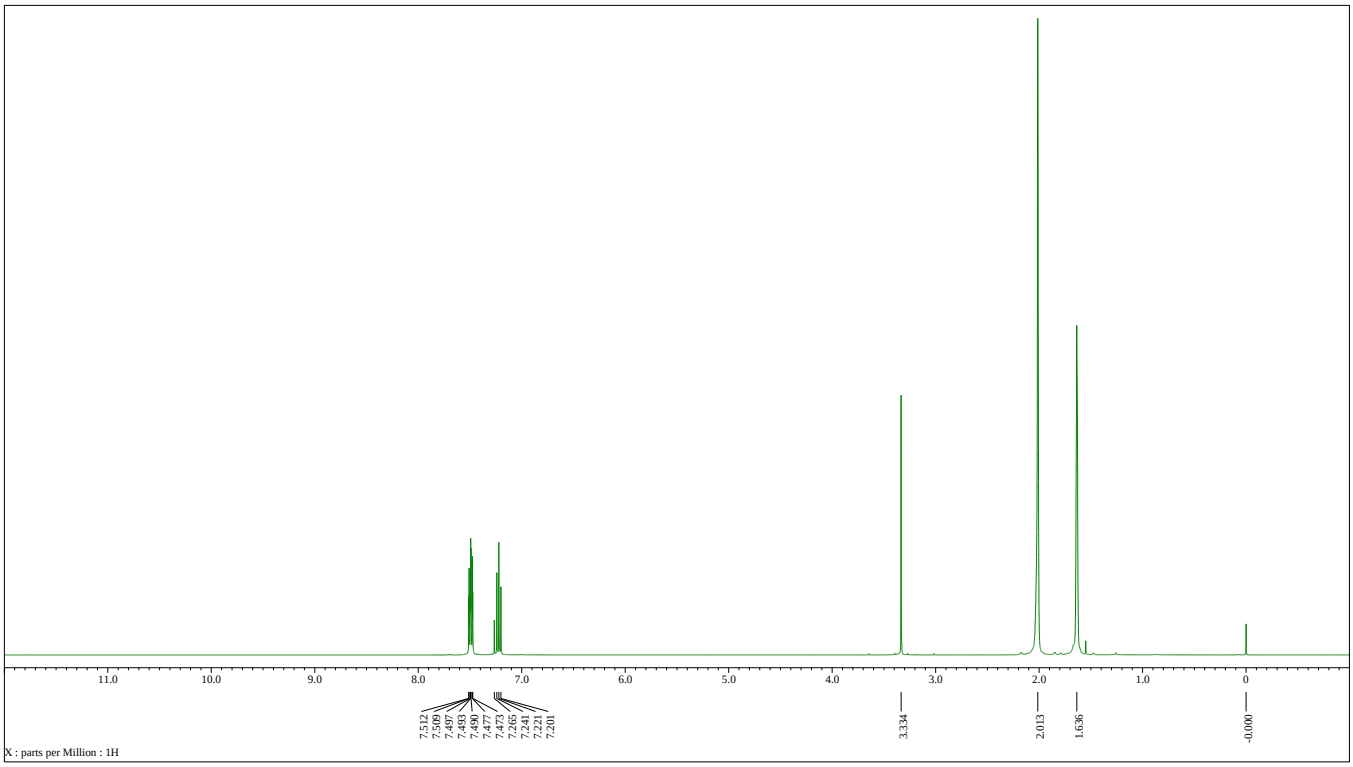


FIGURE S23 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3l**

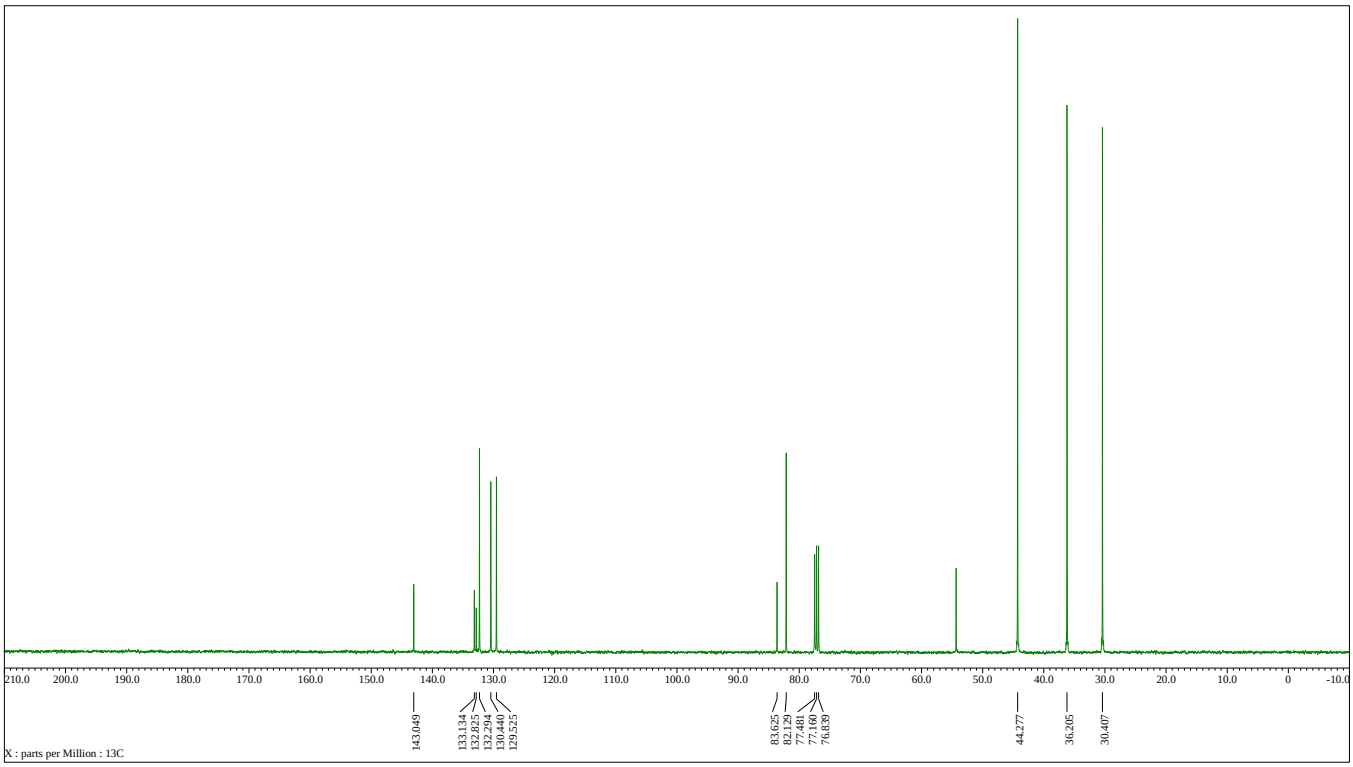
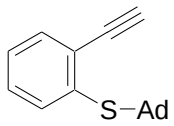


FIGURE S24 $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3l**



3m

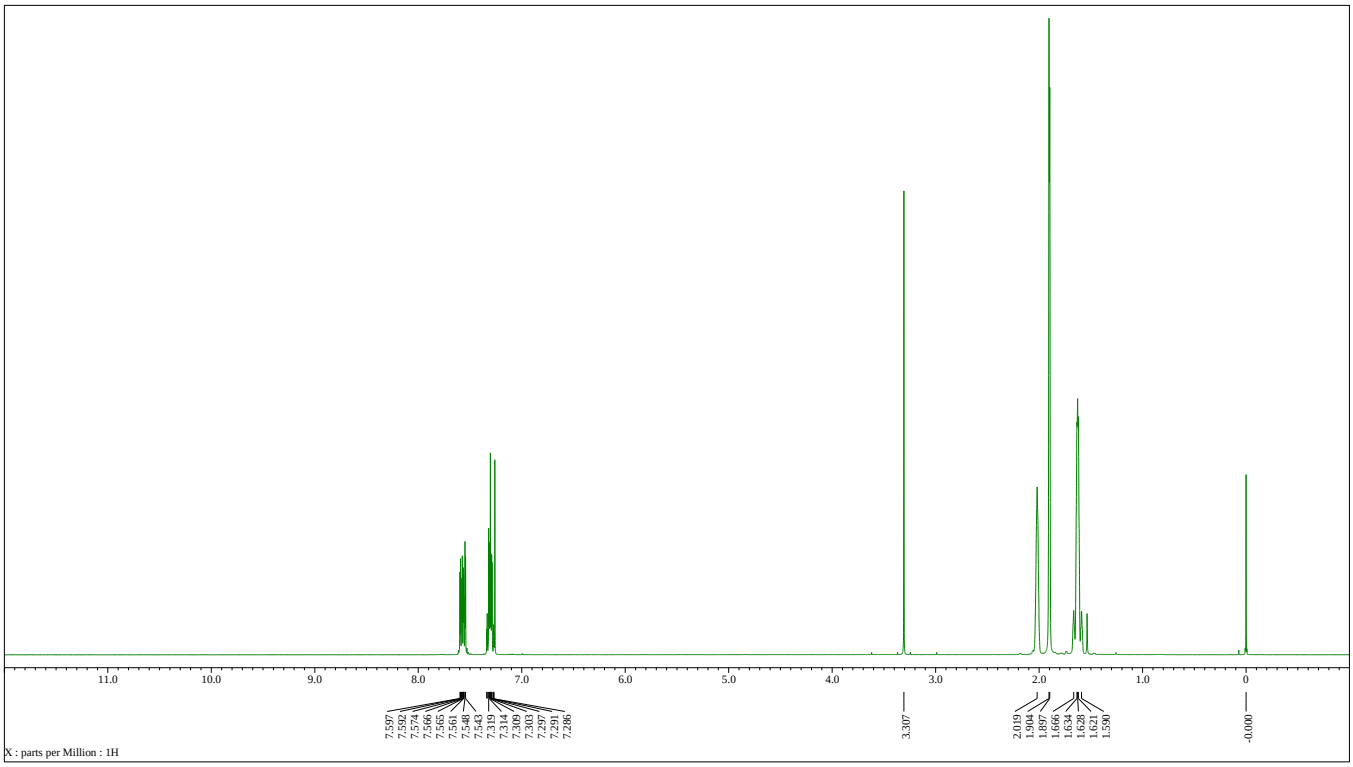


FIGURE S25 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3m**

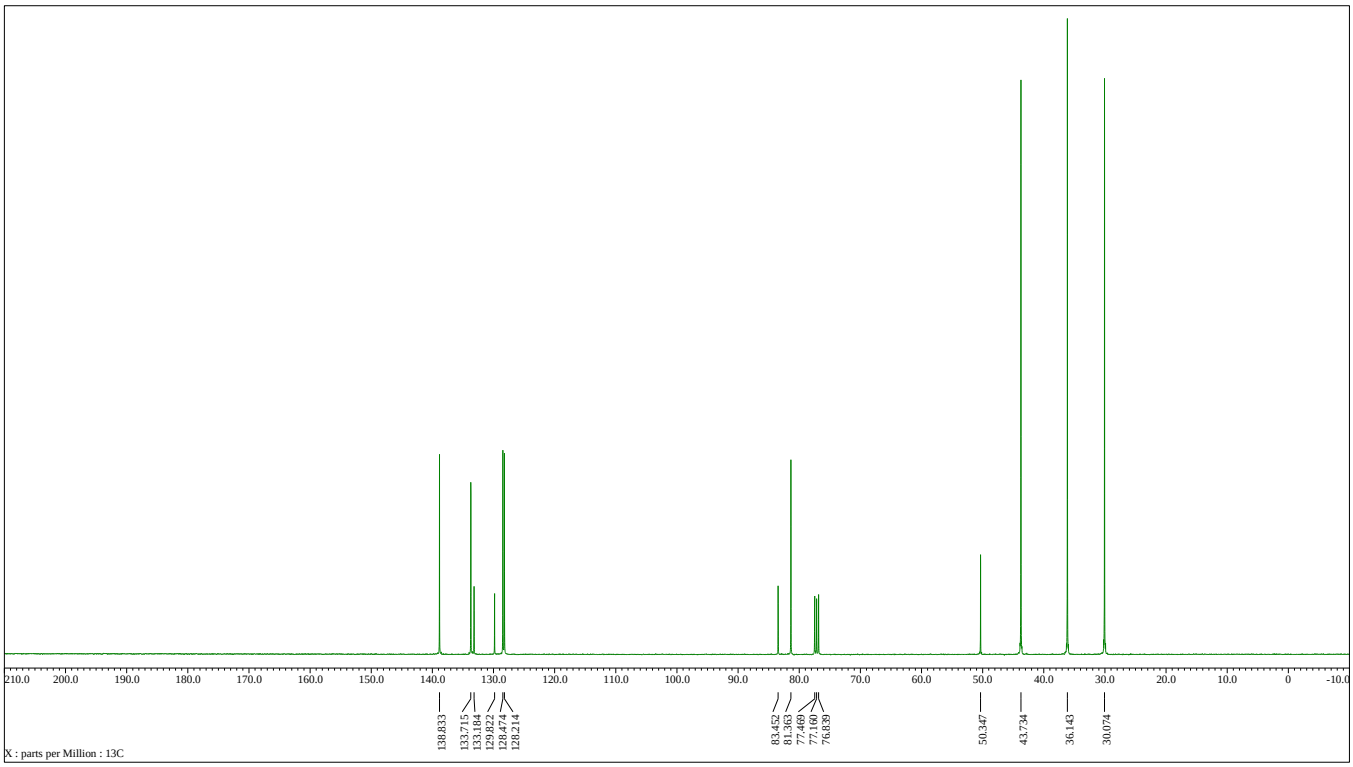
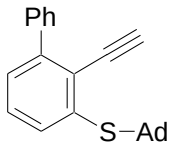


FIGURE S26 $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3m**



3o

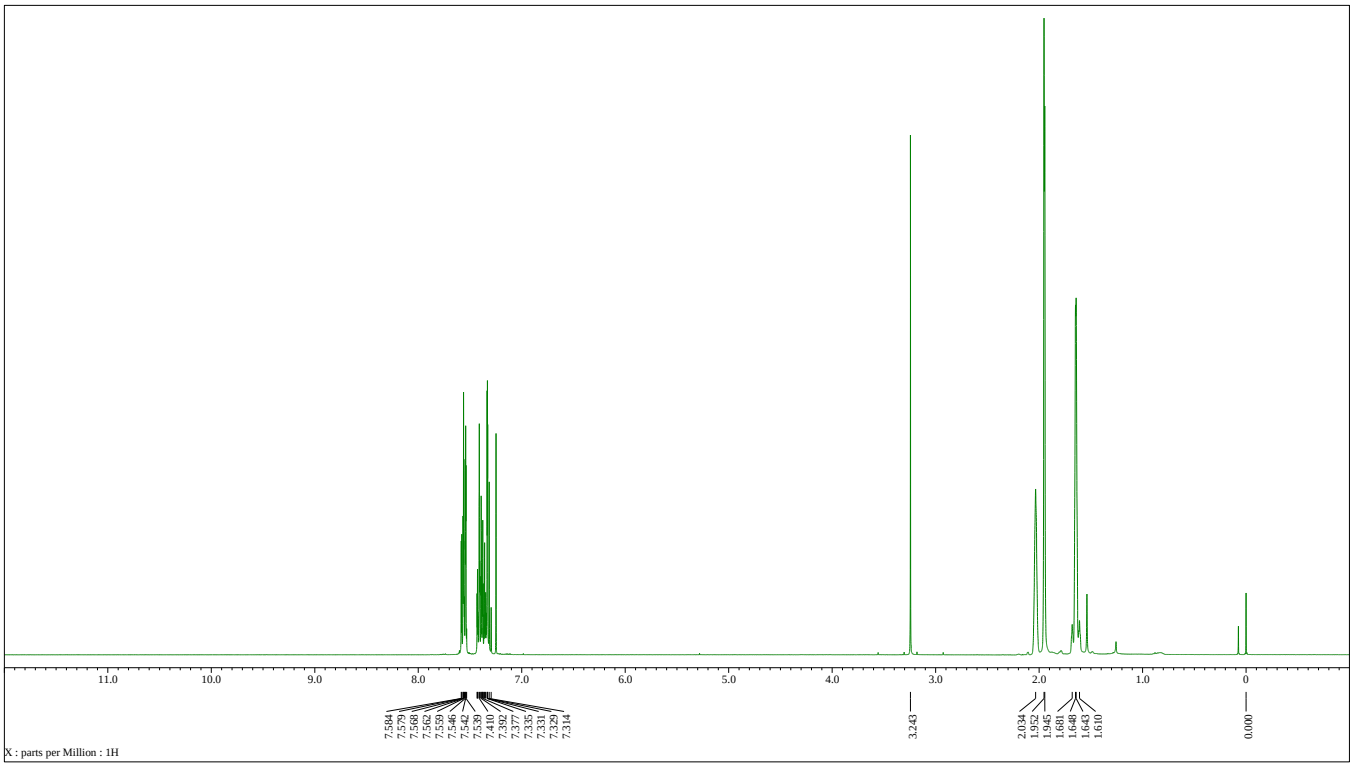


FIGURE S27 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3o**

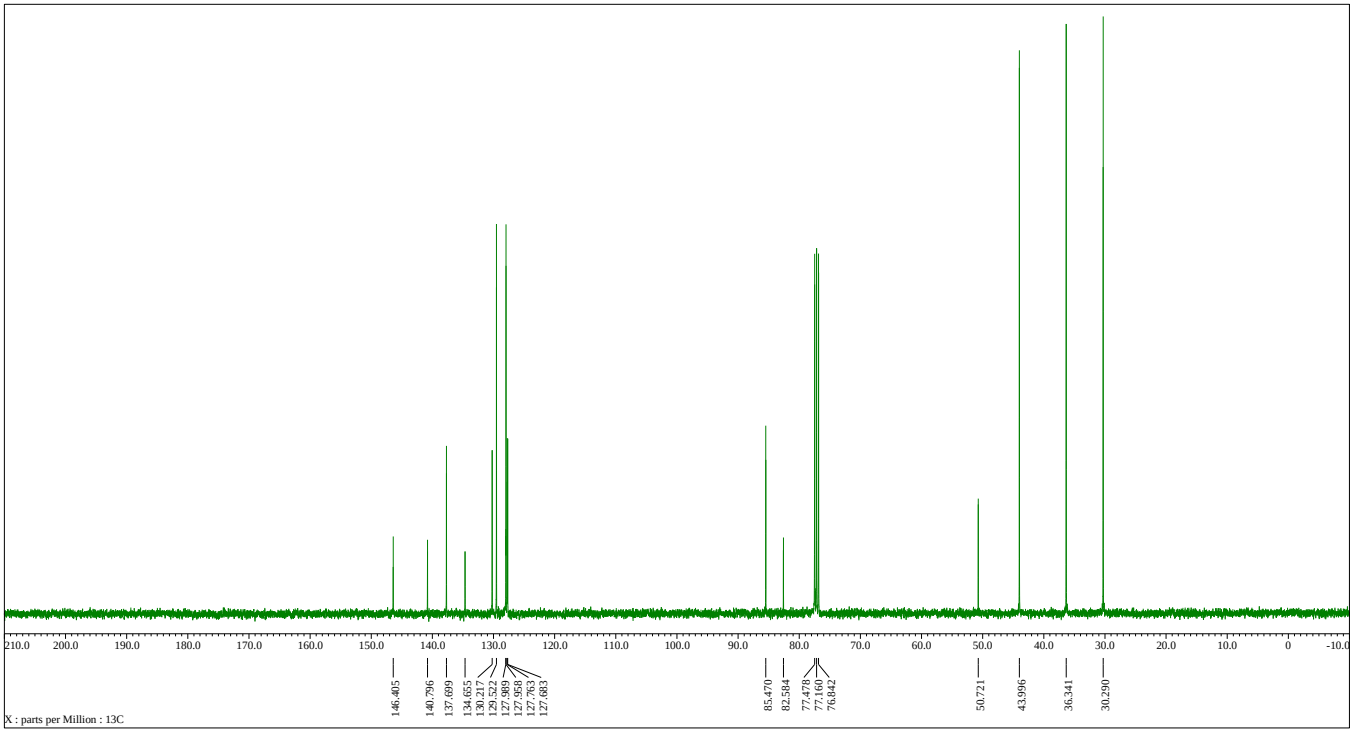
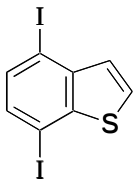


FIGURE S28 $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3o**



4c

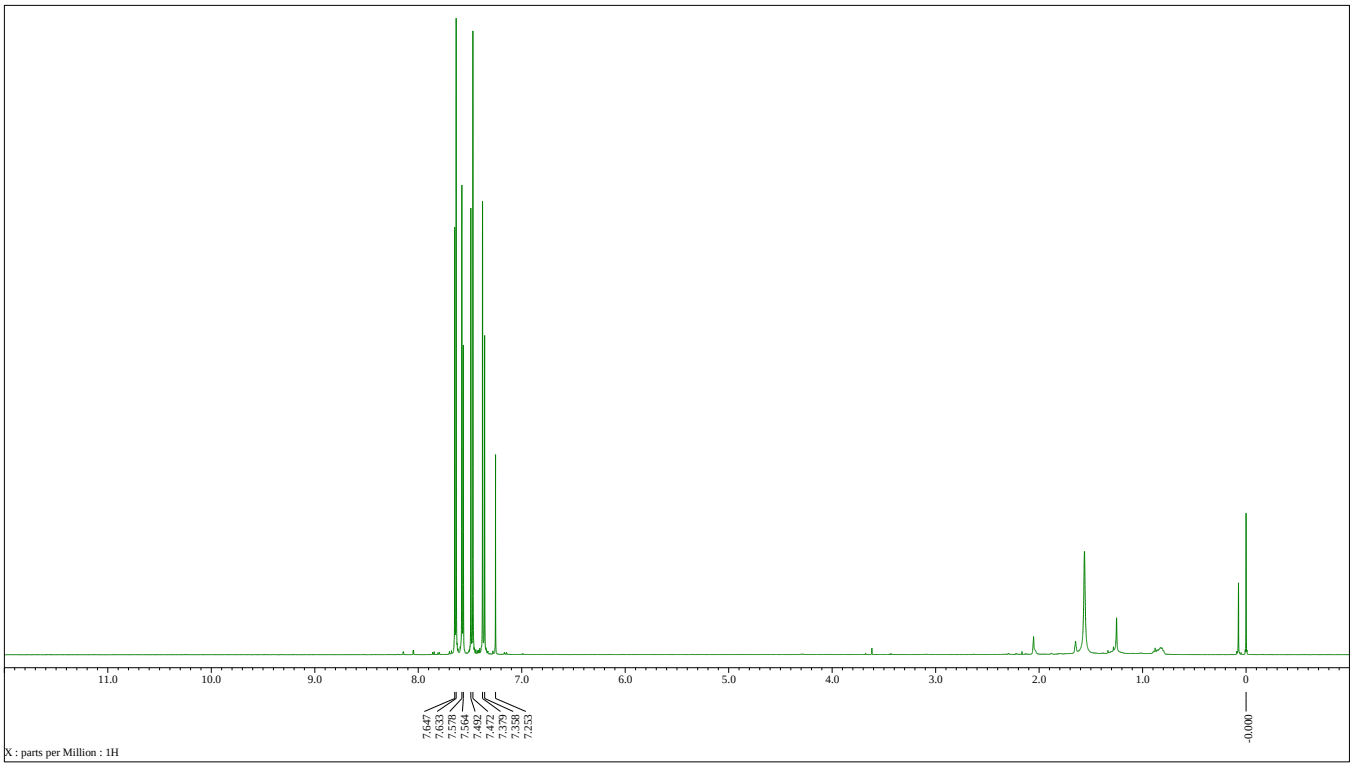


FIGURE S29 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4c**

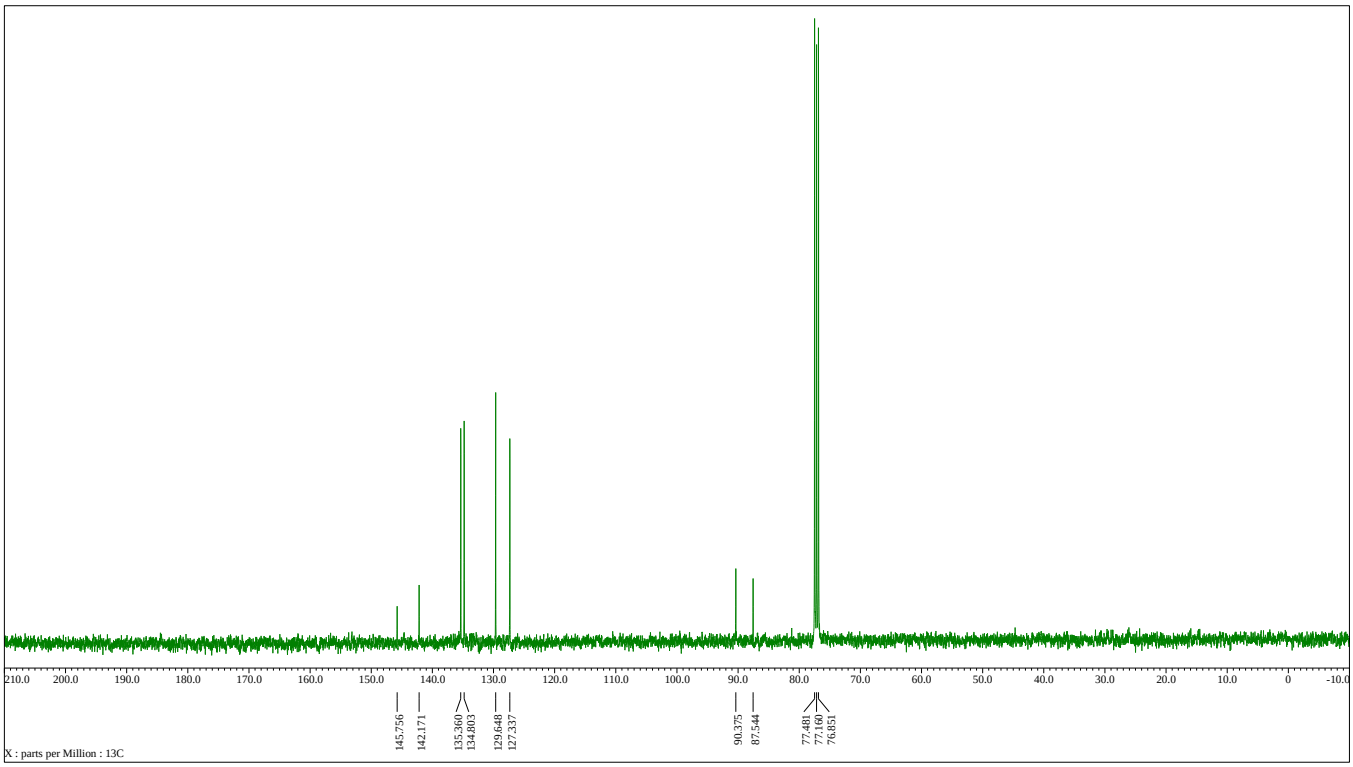
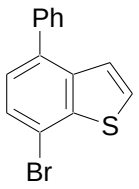


FIGURE S30 $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **4c**



4q

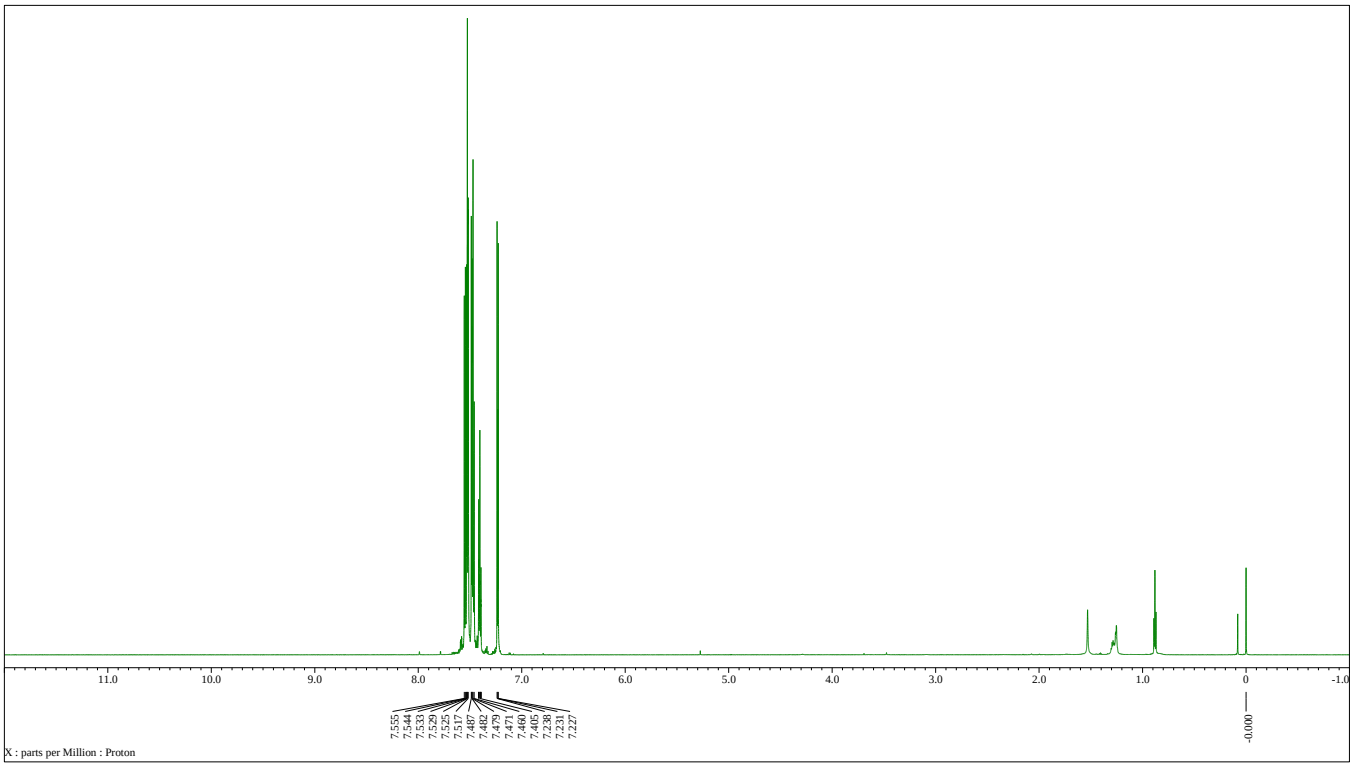


FIGURE S31 ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of **4q**

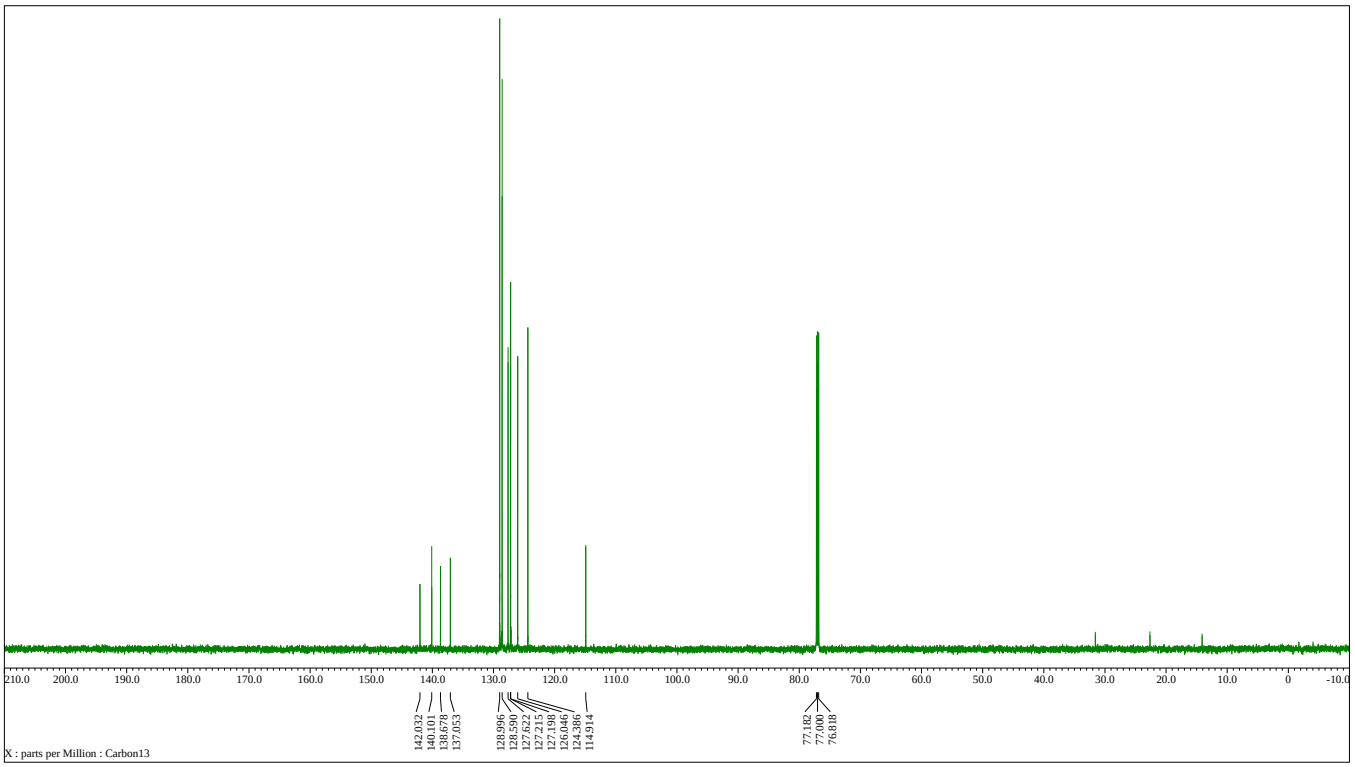
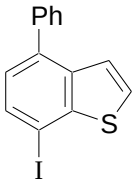


FIGURE S32 $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$) spectrum of **4q**



4r

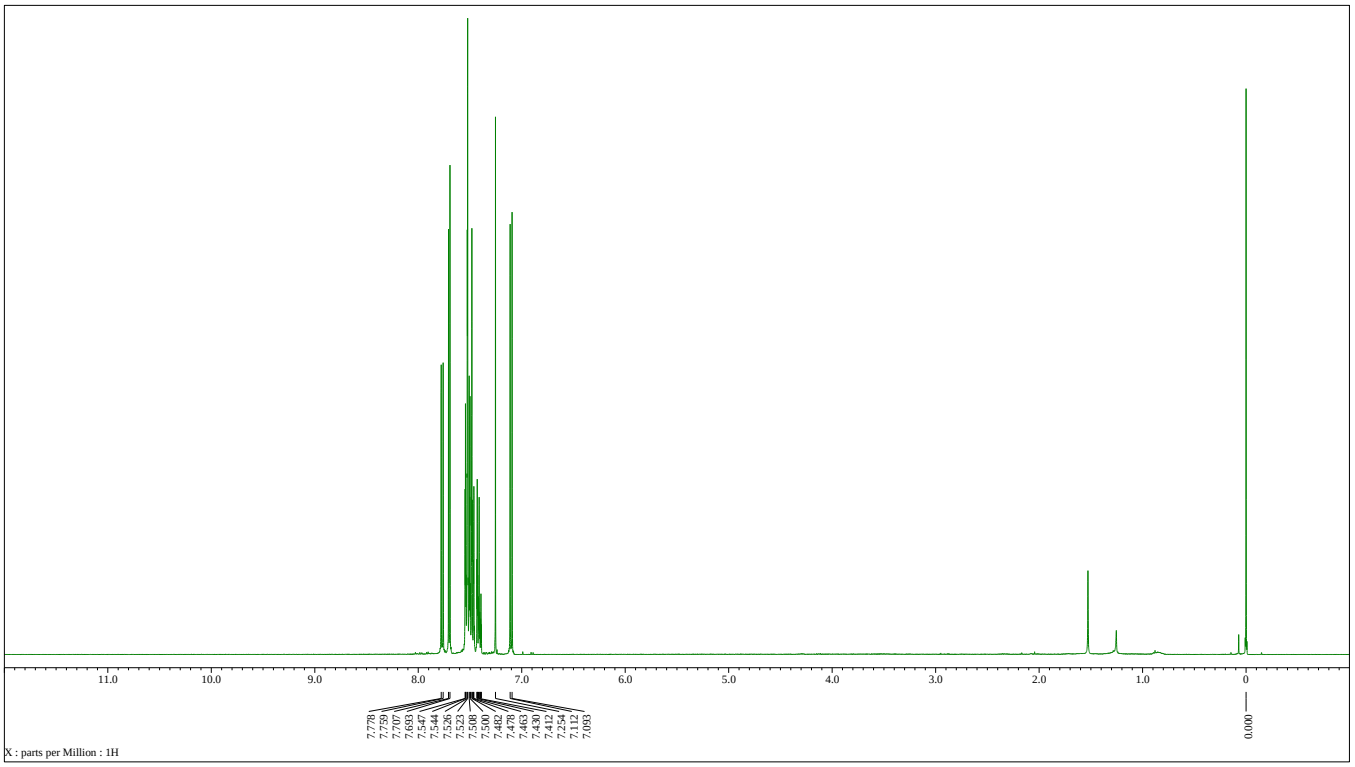


FIGURE S33 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4r**

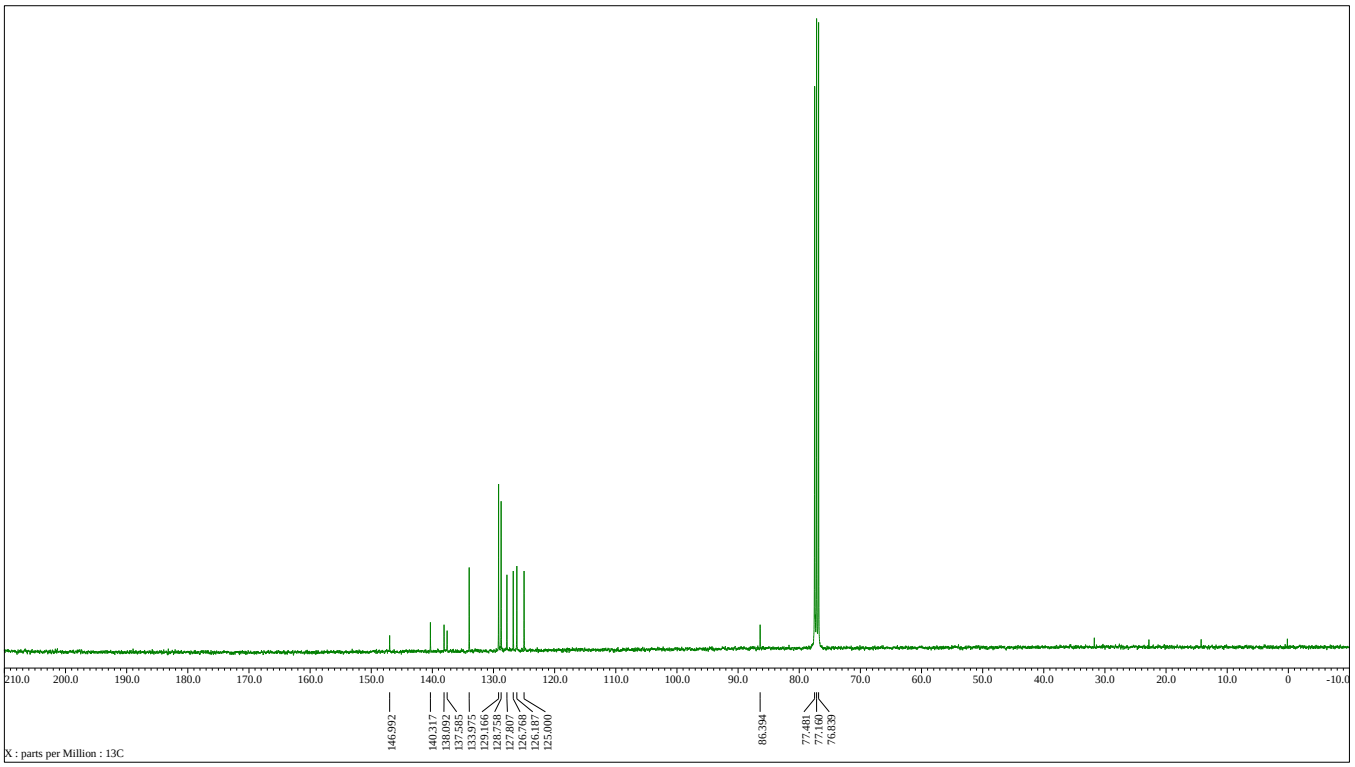
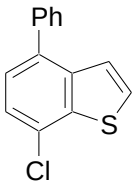


FIGURE S34 $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **4r**



4s

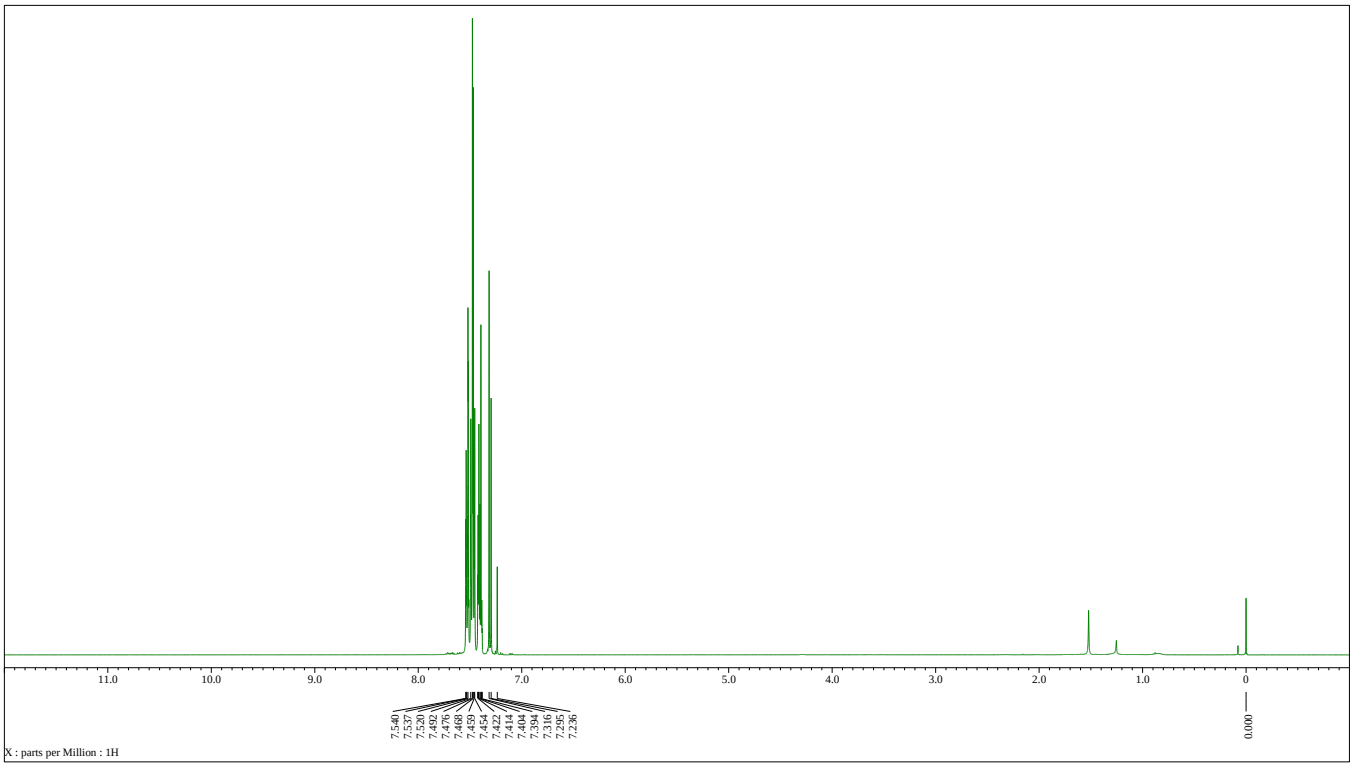


FIGURE S35 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4s**

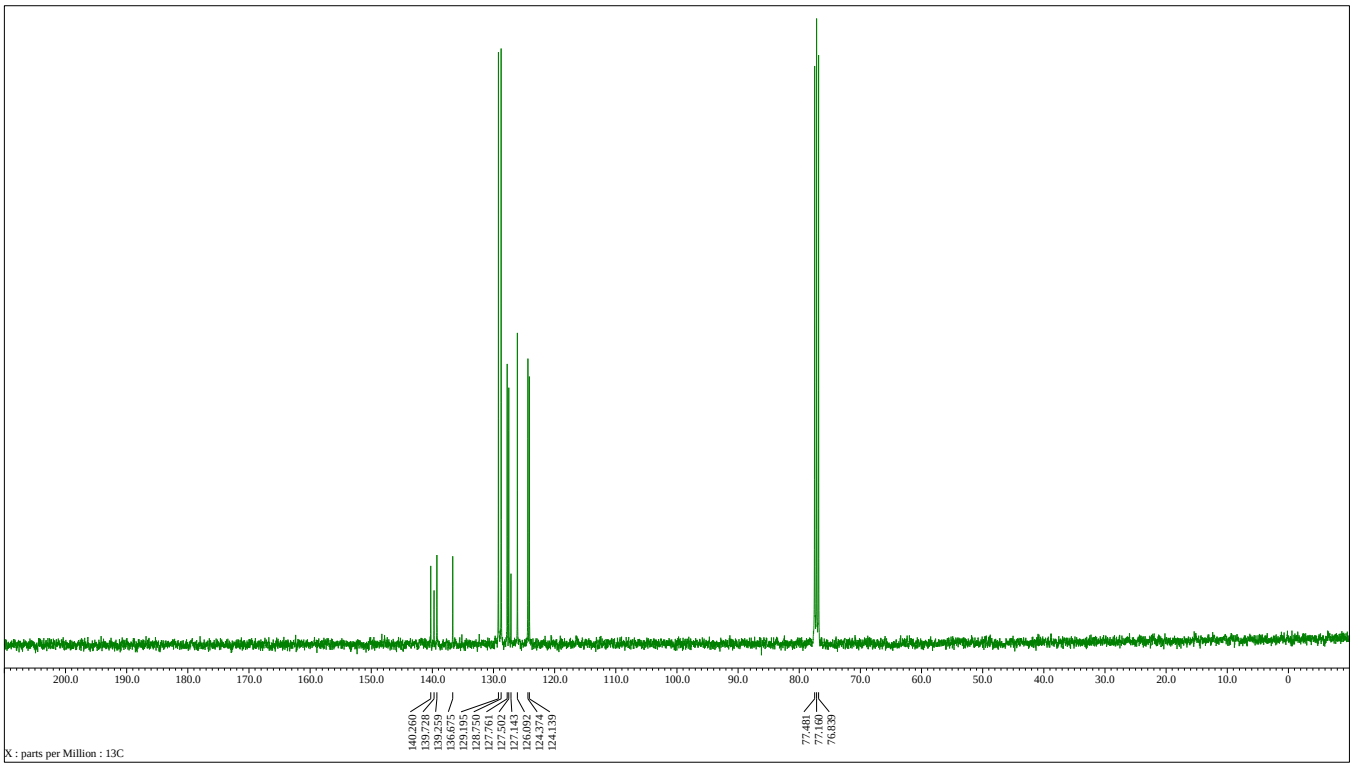
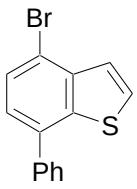


FIGURE S36 $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **4s**



4t

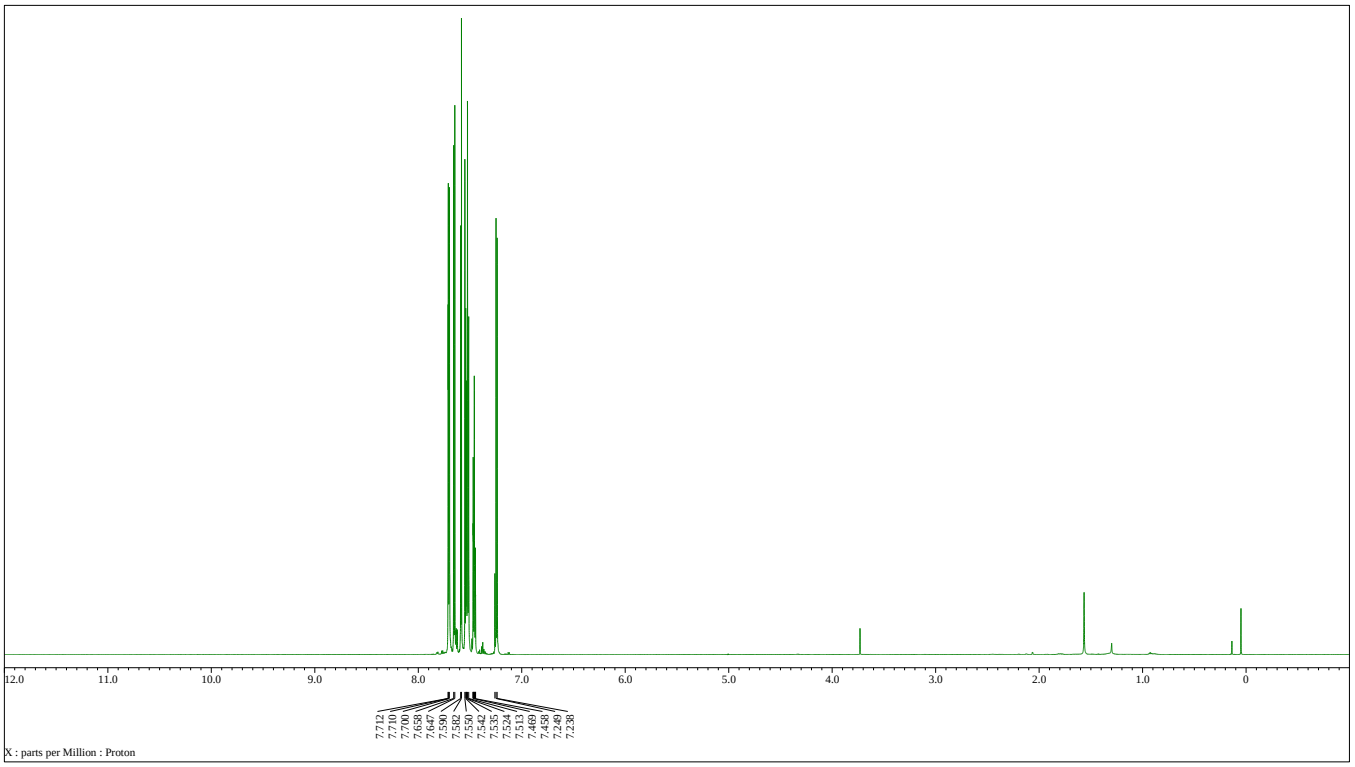


FIGURE S37 ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of **4t**

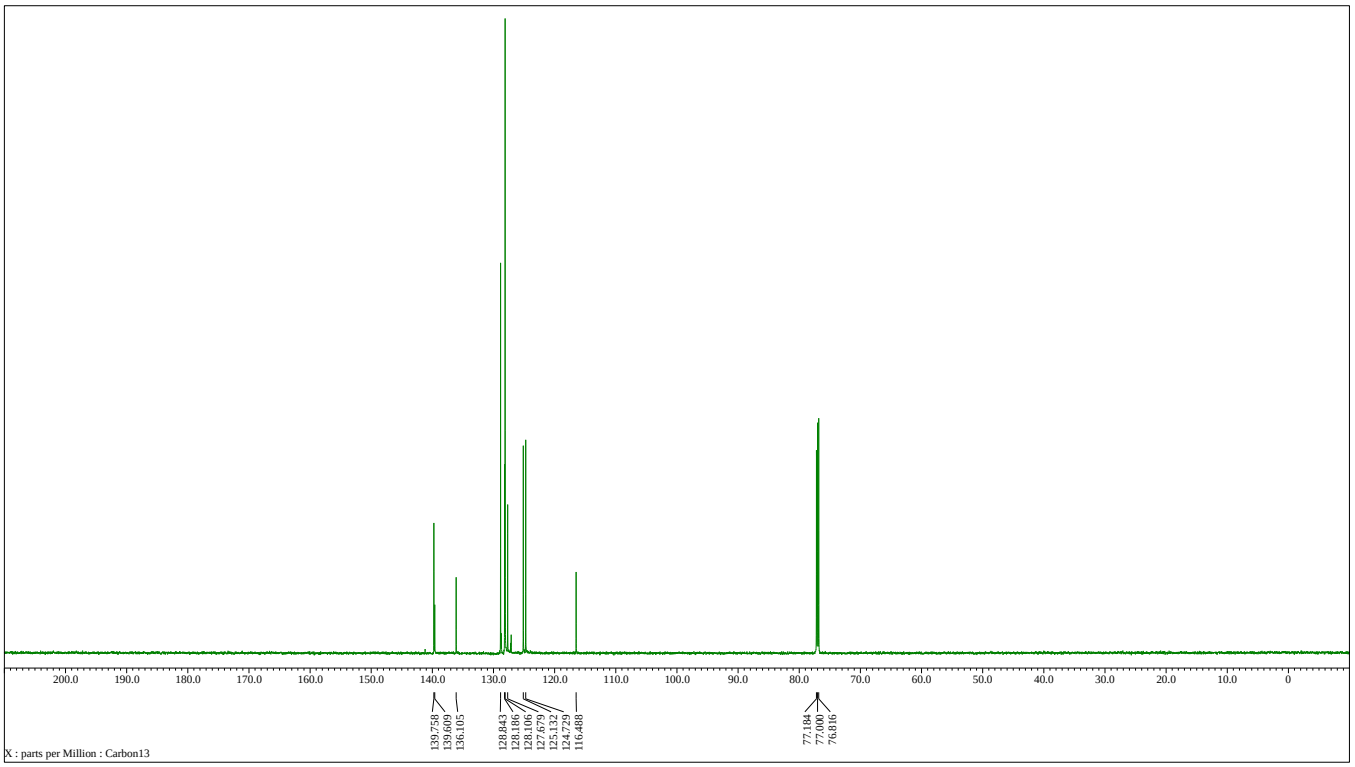
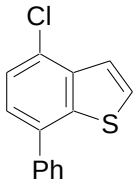


FIGURE S38 $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$) spectrum of **4t**



4v

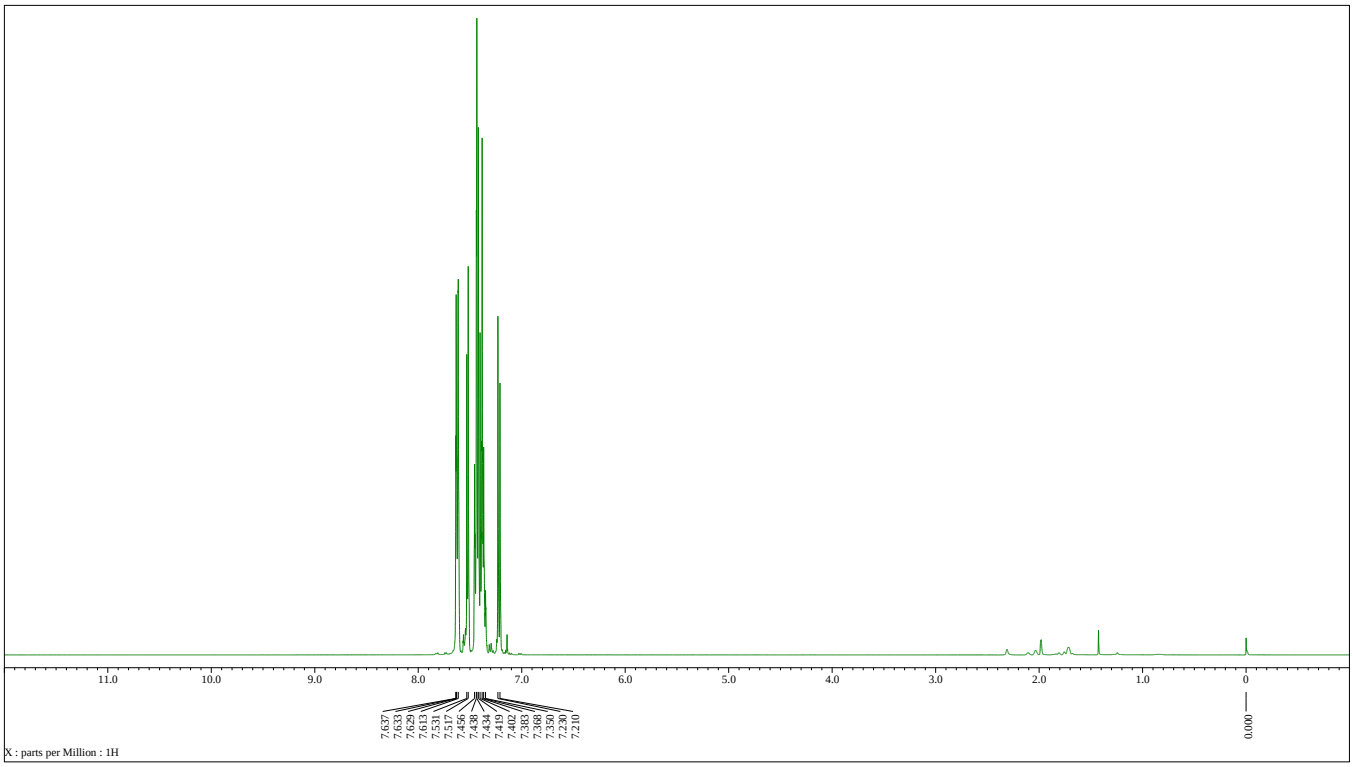


FIGURE S39 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4v**

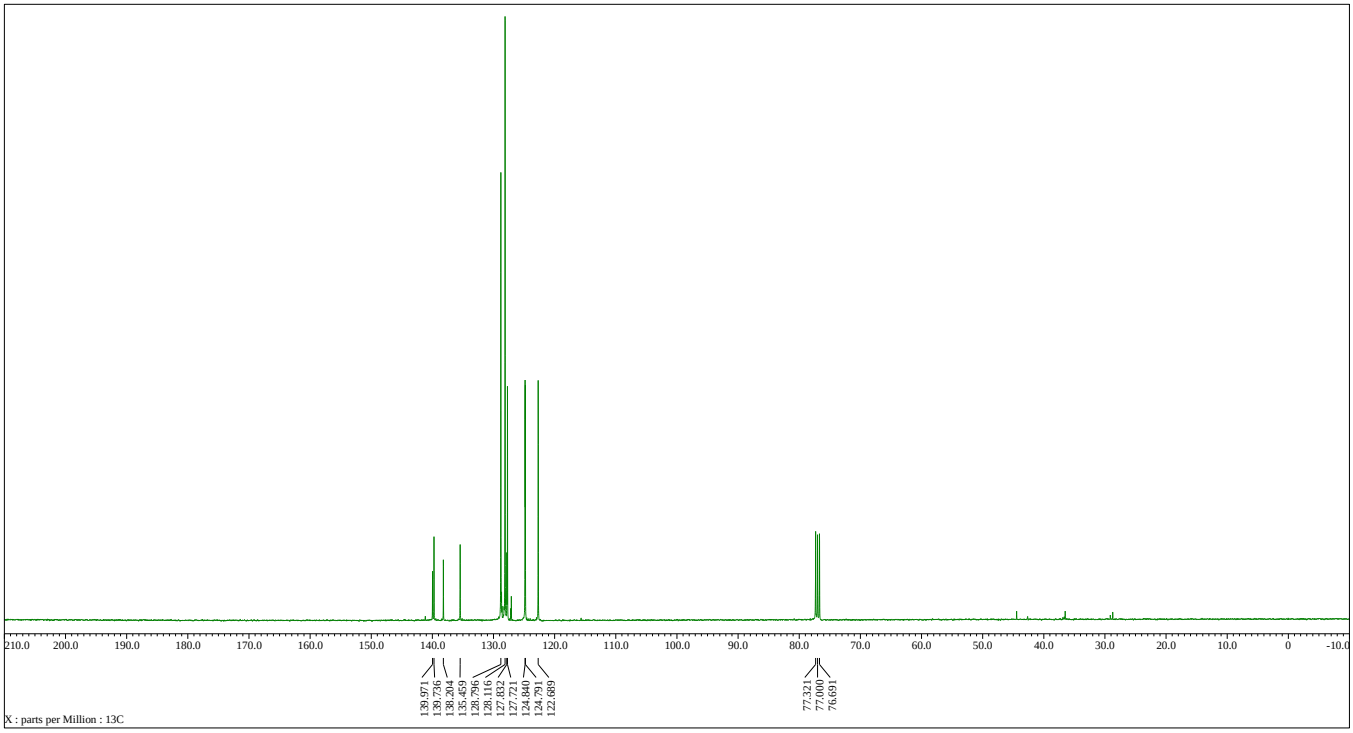
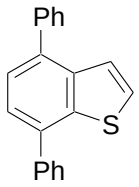


FIGURE S40 $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **4v**



4w

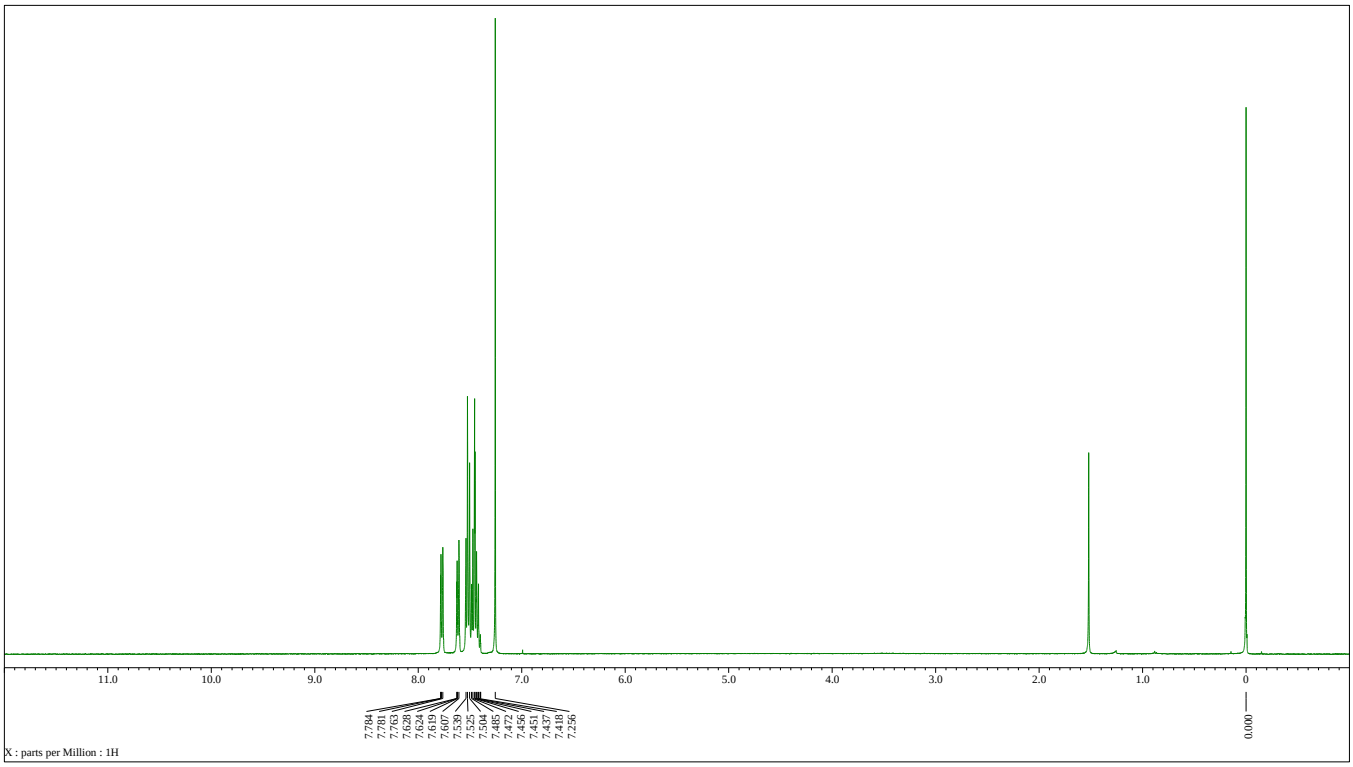


FIGURE S41 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4w**

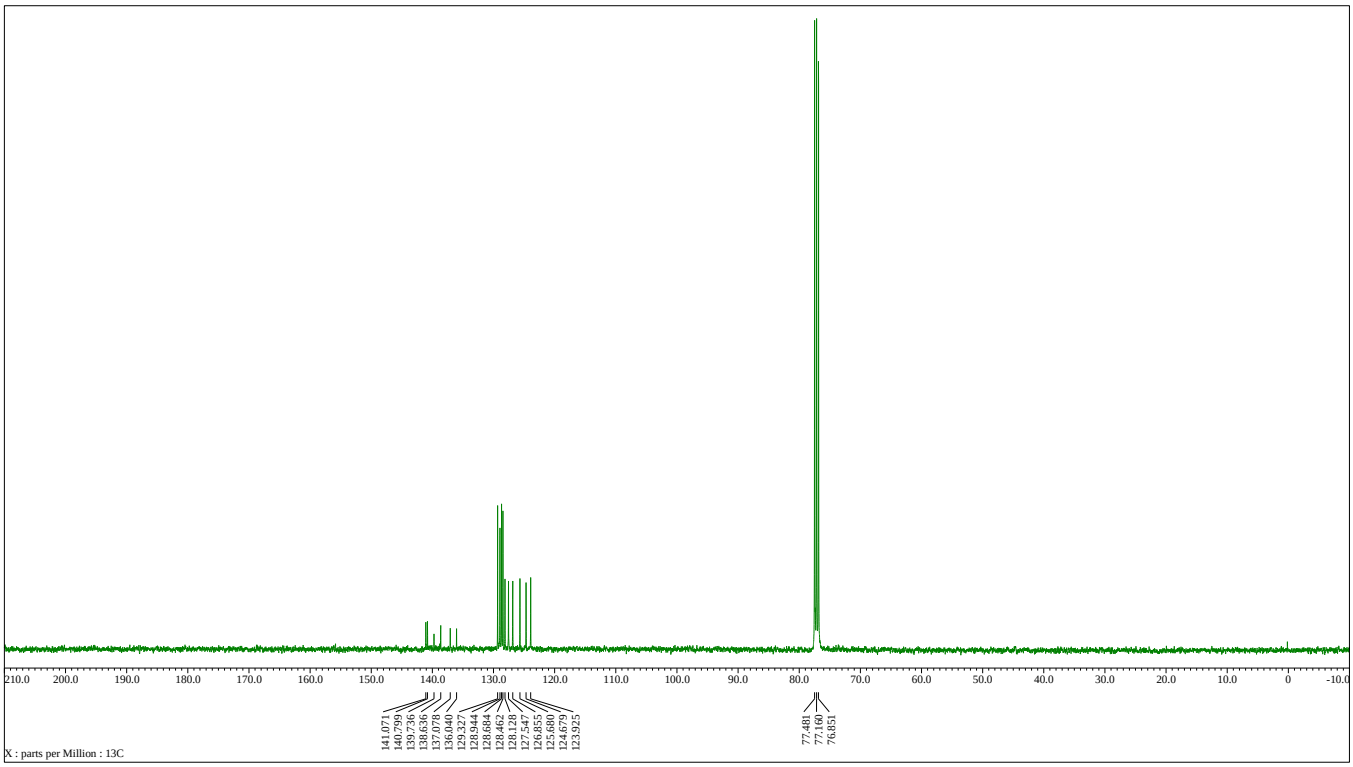
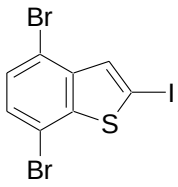


FIGURE S42 $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **4w**



11

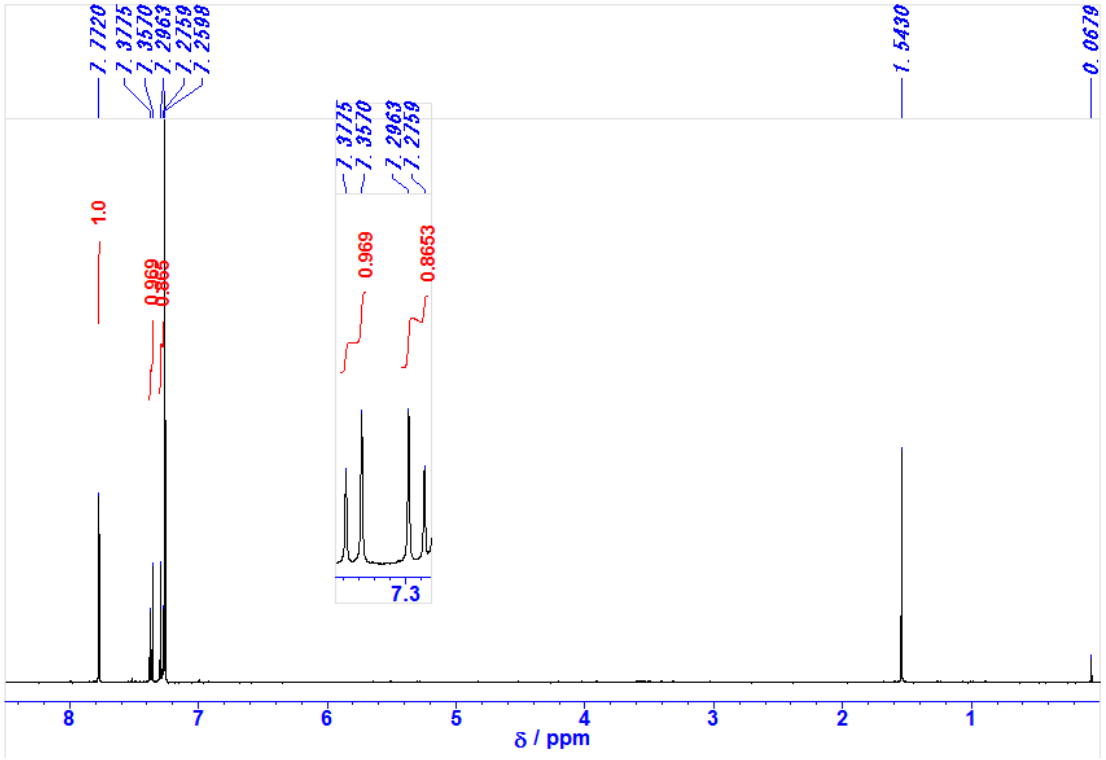


FIGURE S43 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11**

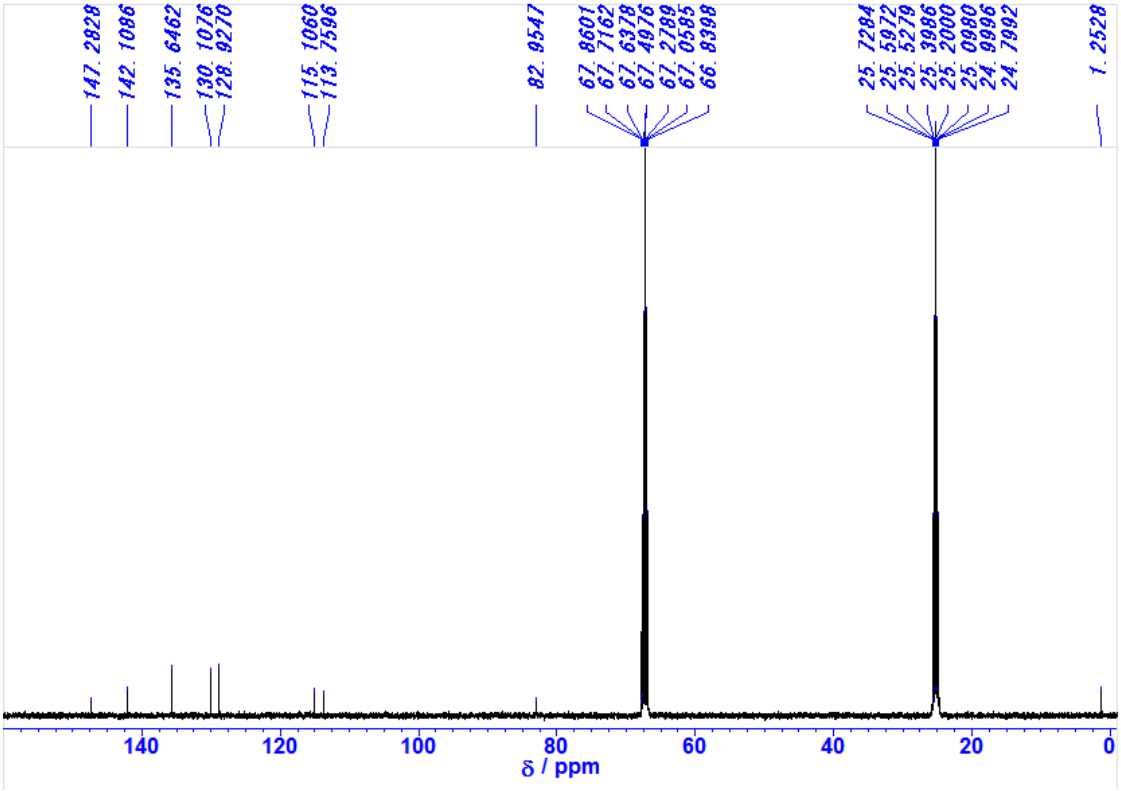
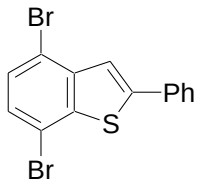


FIGURE S44 ^{13}C{^{1}H} NMR (100 MHz, THF-d_8) spectrum of **11**



13

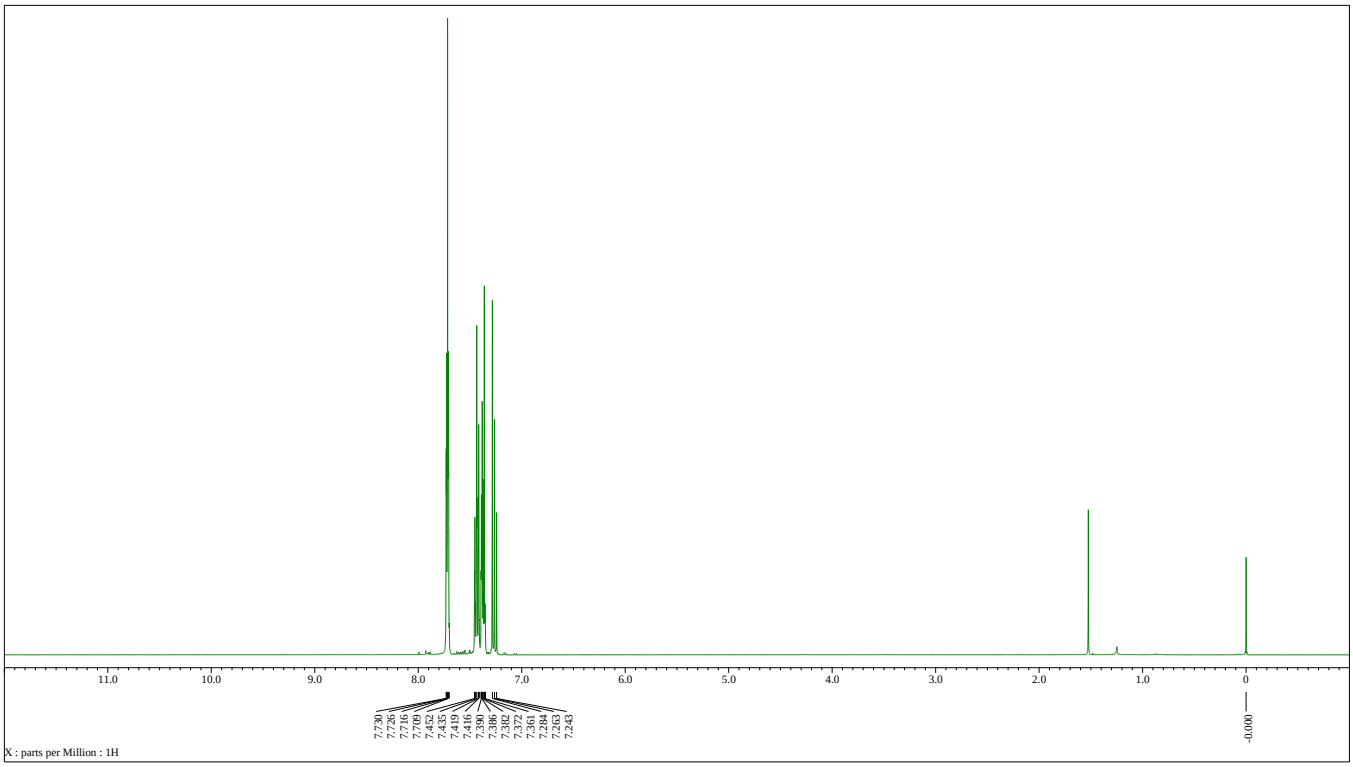


FIGURE S45 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **13**

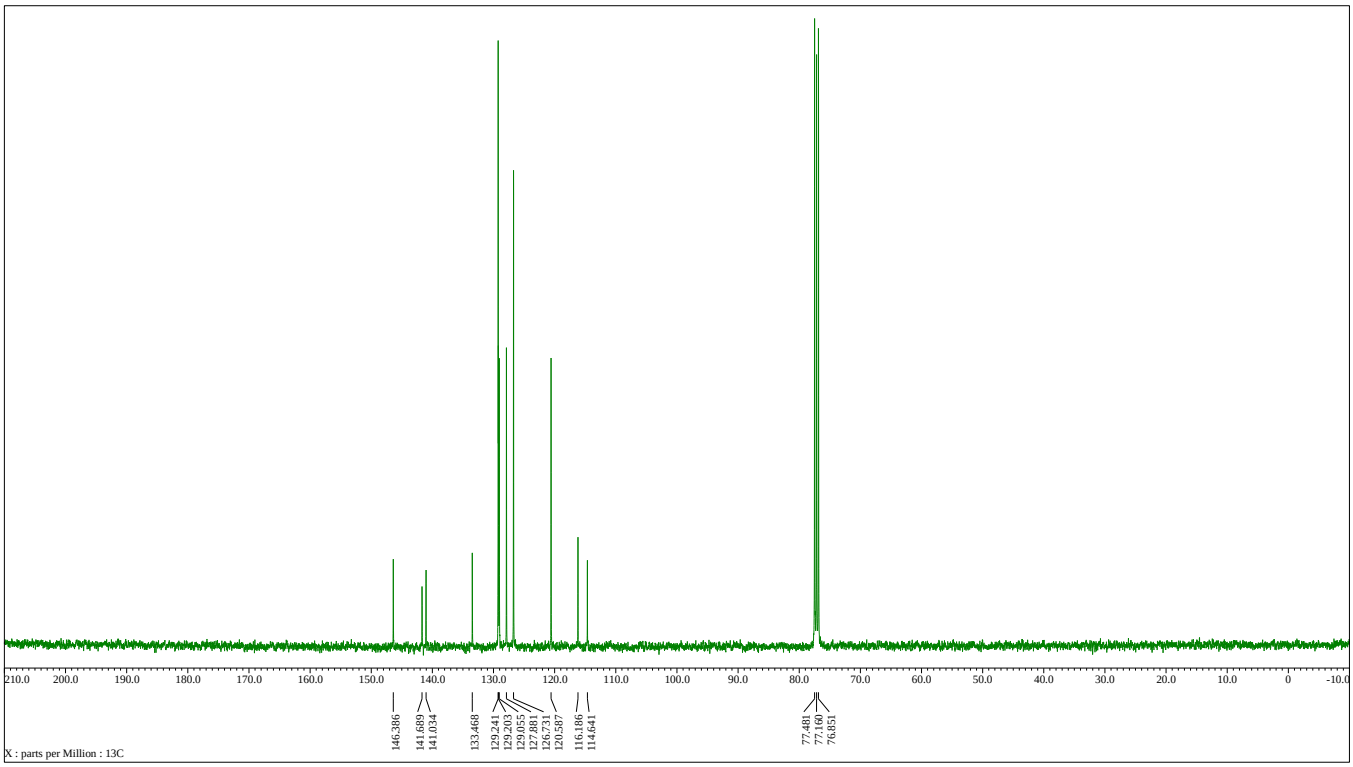
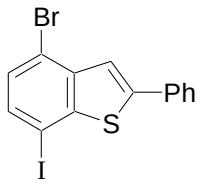


FIGURE S46 $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **13**



14

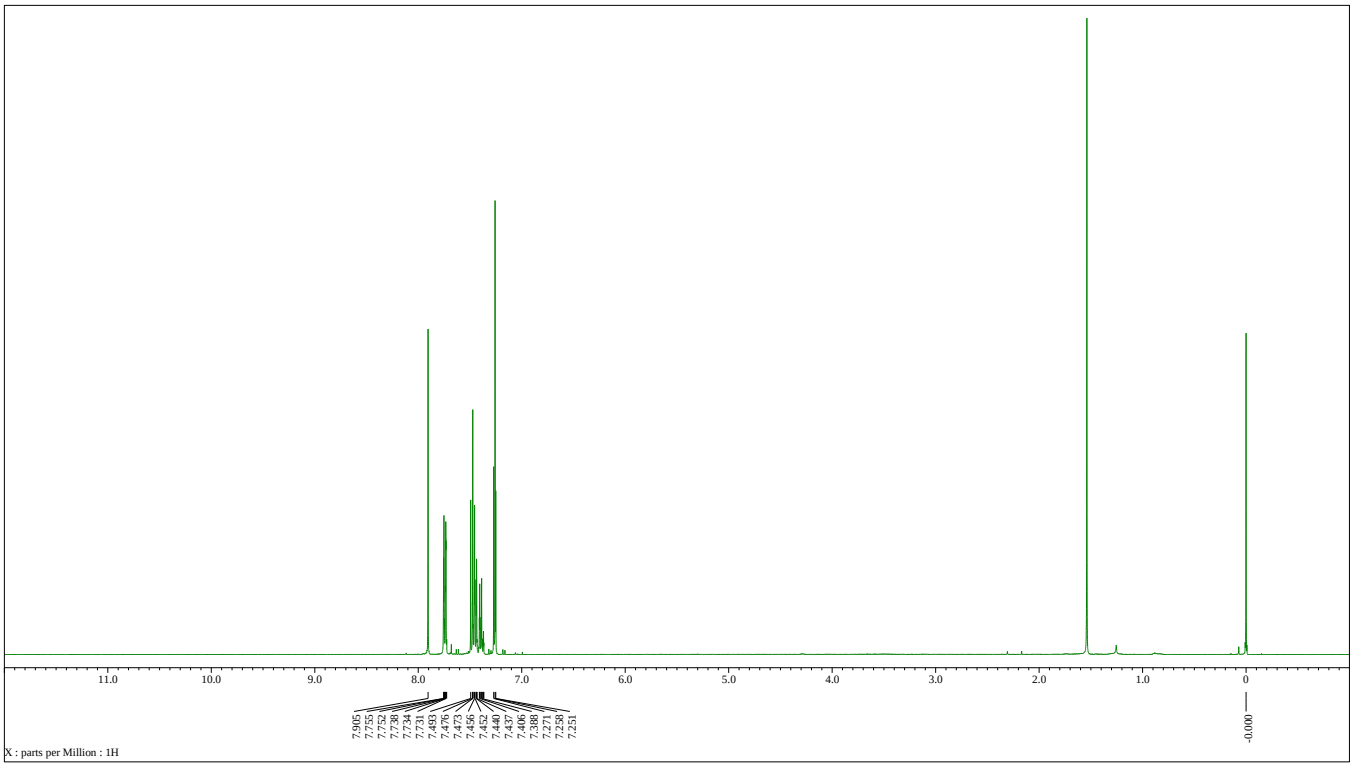


FIGURE S47 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **14**

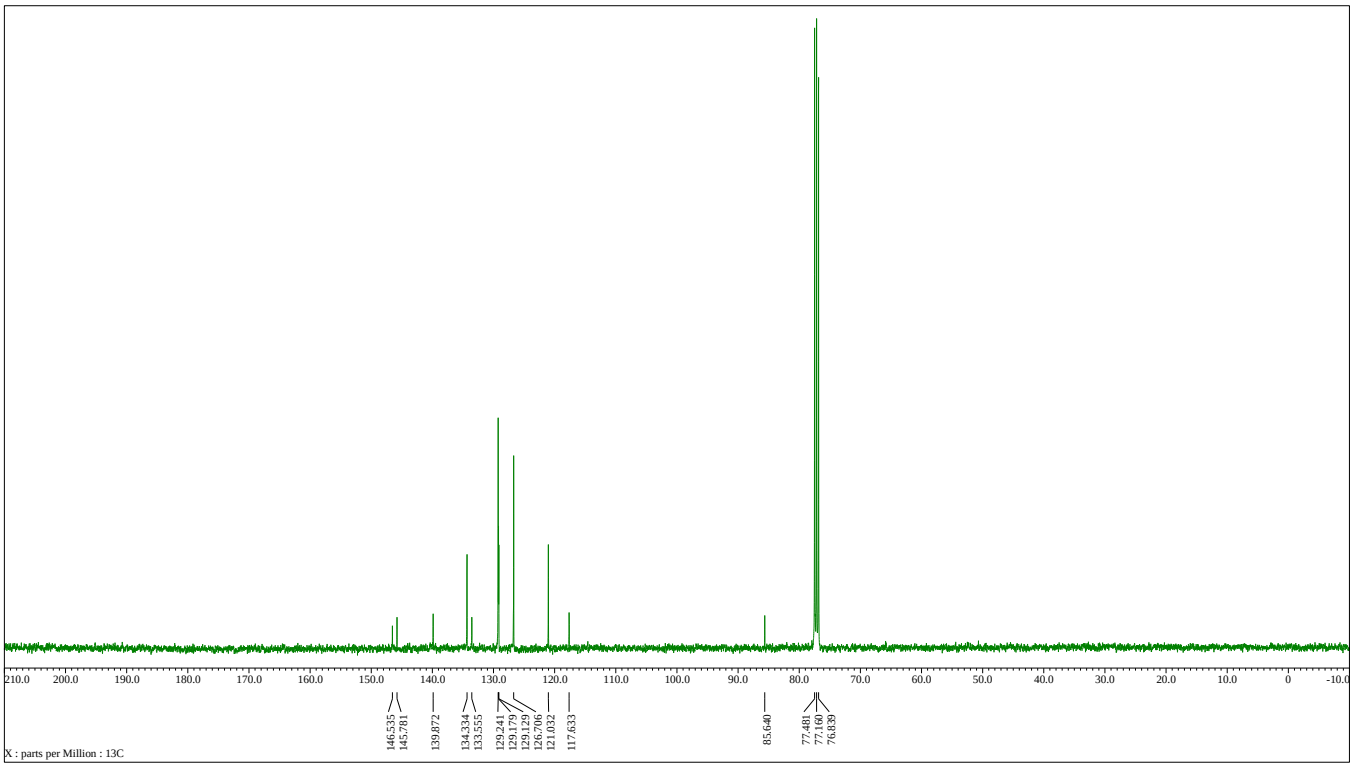


FIGURE S48 $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **14**