

Supporting Information

Visible-Light Photoredox Catalyzed Decarboxylative Alkylation of Heteroarenes Using Carboxylic Acids with Hydrogen Release

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General Information

The cobalt complexes $\text{Co}(\text{dmgH})_2\text{PyCl}$,¹ $[\text{Co}(\text{dmgH})_2\text{Py}_2]\text{PF}_6$,¹ $\text{Co}(\text{dmgH})_2(4\text{-NMe}_2\text{Py})\text{Cl}$ ¹ and $\text{Co}(\text{dmgH})_2(4\text{-CONMe}_2\text{Py})\text{Cl}$ ² were prepared according to the reported procedures. EtOAc and CH_3CN were freshly distilled over CaH_2 . If no special indicated, other reagents and solvents were used as commercially available without further purification. All the reactions were carried out in reaction tubes on Wattecs Parral Reactor under argon atmosphere. Column chromatographic purification of products was accomplished using 200-300 mesh silica gel.

NMR spectra were measured on a Bruker Avance-400 spectrometer in the solvents indicated; chemical shifts are reported in units (ppm) by assigning TMS resonance in the ^1H spectrum as 0.00 ppm, CDCl_3 resonance in the ^{13}C spectrum as 77.0 ppm. ^{19}F spectrum was determined relative to CFC_3 as external standard. Coupling constants are reported in Hz with multiplicities denoted as br (broad), s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Infrared spectra were collected on a Thermo Fisher Nicolet 6700 FT-IR spectrometer using ATR (Attenuated Total Reflectance) method. Absorption maxima (ν_{max}) are reported in wavenumbers (cm^{-1}). HRMS were performed on Fourier Transform Ion Cyclotron Resonance Mass Spectrometer. Analytical gas chromatography (GC) for liquid phase was carried out on a Thermo Trace 1300 gas chromatograph, equipped with a flame ionization detector and a TR-V1 column ($0.32\text{ mm} \times 30\text{ m}$, Film: $1.8\text{ }\mu\text{m}$). Analytical gas chromatography (GC) for gas sample were carried out on a SHIMDZU GC-2014ATF/SPL (TDX-01 60/80 mesh, $2.0\text{ mm} \times 3.2\text{ mm} \times 2.1\text{ mm}$ -FID, TCD- permanent gases, N_2 carrier gas). The systems allow for the determination of H_2 , Ar, CO and CO_2 within the ranges: $\text{H}_2 \geq 0.5\text{ vol\%}$ -100 vol%, $\text{CO} \geq 2\text{ ppm}$, $\text{CO}_2 \geq 100\text{ ppm}$. UV-vis absorption spectrum, the quantum yield measurement and steady-state emission spectra were recorded using a PerkinElmer Lambda or a HITACHI F-4500 Fluorescence Spectrometer. Cyclic voltammetry experiments were studied On a CHI660E Electrochemical Workstation equipped with the conventional three electrode system under argon atmosphere. The measurements were performed in mixture solvent of $\text{CH}_3\text{CN}/\text{EtOAc}$ (1:1) containing 0.1 M $n\text{-Bu}_4\text{PF}_6$ using ferrocene/ferrocenium (Fc^+/Fc^0) as an internal reference. The working electrode was a glassy carbon disk electrode ($d = 0.3\text{ cm}$). The auxiliary and reference electrode consisted of a Pt tablets and an Ag/AgNO_3 (0.1 M in CH_3CN), respectively. Glassy carbon disk electrode was polished with the $d = 0.05\text{ micron}$ Alumina powder and a polishing cloth before each measurement.

General procedure for synthesis of **3**

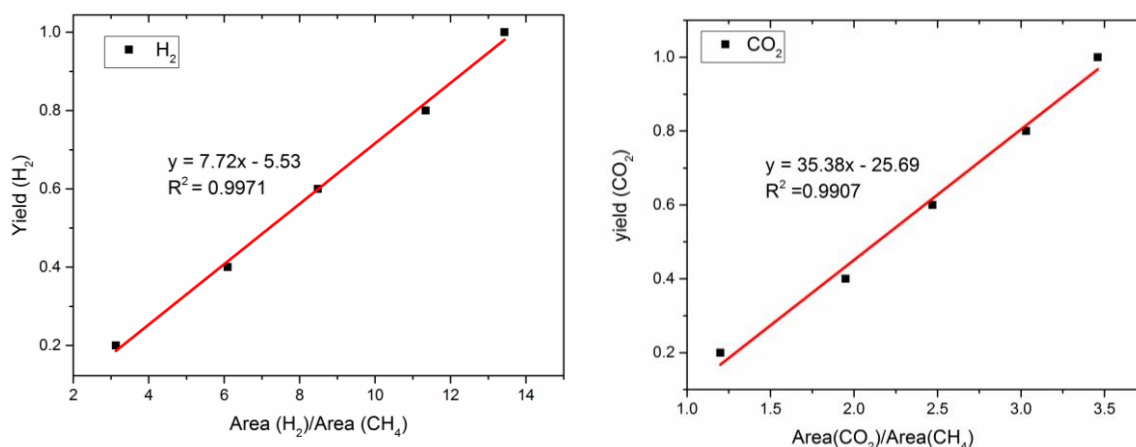
To a Schlenk tube containing a stirring bar was added Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (0.002 mmol, 1 mol%), [Co(dmgh)₂Py₂]PF₆ (0.006 mmol, 3 mol%), *n*-Bu₄NOAc (0.06 mmol, 30 mol%) heterocycles **1** (0.20 mmol, 1.0 equiv) and carboxylic acids **2** (0.40 mmol, 2.0 equiv). Then anhydrous EtOAc (1.0 mL) was added to the reaction tube via syringe in glove box. The reaction mixture was stirred for 30 h at Wattecs Parallel Light Reactor (Blue LED Light source, 10 W every position) at ambient temperature (the temperature range from 40 °C to 44 °C). The gas phase was detected for the H₂ and CO₂ yield using methane as an internal standard. It is worth noting that the inaccordance of product yield with H₂ and CO₂ evolution in **3ae–3ah**, **3an** synthesis should be attributed to the decarboxylative elimination of the carboxylic acid substrate.³ Finally, the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel to afford compounds **3**.



Wattecs Parallel Light Reactor (Blue LED Light source, 10 W every position)

Procedure for drawing the standard-curve for H₂ calculation

Five standard Schlenk tubes were filled with Ar. Then, CH₄ (0.5 mL) was injected to each tubes as internal standard. After that, H₂ (4.50 mL, 3.60 mL, 2.70 mL, 1.80 mL, 0.90 mL) was injected to each tube respectively. These amounts of H₂ were corresponding to H₂ yields (100%, 80%, 60%, 40% and 20%, respectively) in standard reaction. These tubes were kept for 3 h to make the gas mix uniformly. Afterwards, these samples were detected by GC. The standard-curve was made by the different values of Area (H₂)/Area (CH₄) with the corresponding H₂ yields. Meanwhile, the standard-curve for CO₂ calculation was made by the same method.



The standard-curve for the calculation of H₂ and CO₂ yield using CH₄ as an internal standard

Detecting the accuracy of the standard-curve:

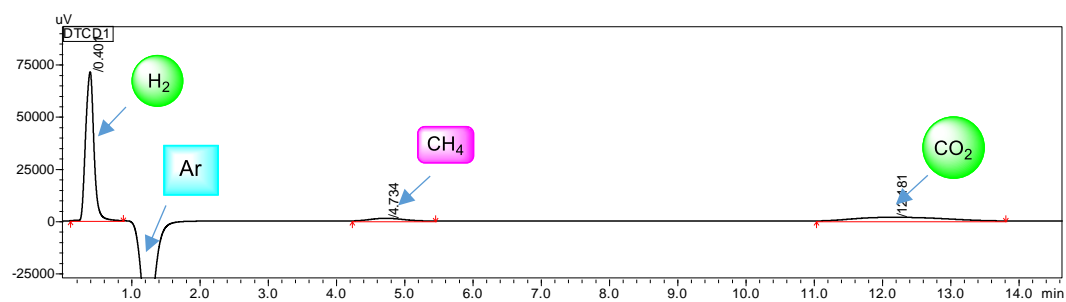
In order to detect the accuracy of the standard-curve for the calculation of H₂, three groups of parallel tests were conducted. One group of parallel test was conducted as below. Three standard Schlenk tubes were filled with Ar. Then, CH₄ (0.5 mL) was injected to each tubes as internal standard. After that, H₂ (1.35 mL) was injected to each tube respectively. These amounts of H₂ were corresponding to H₂ yields (30%) in standard reaction. These tubes were kept for 3 h to make the gas mix uniformly. Afterwards, these samples were detected by GC. Then put different values of Area (H₂)/Area (CH₄) to the standard-curve and different yields were obtained (results was shown in measurement 1, 2 and 3 in the below table). Other groups were detected using similar operations. The accuracy of CO₂ plot was demonstrated with similar strategy.

As shown in the below table, every parallel tests exhibited the similar results and the relative errors of every parallel tests are not greater than 2.3% and 3.3% for H₂ and CO₂, respectively. The ranges of parallel tests are not greater than 1% and 2% for the yields of H₂ and CO₂

H ₂ : $y = 7.72x - 5.53$, $R^2 = 0.9971$				CO ₂ : $y = 35.38x - 25.69$, $R^2 = 0.9907$			
standard yield	30%	60%	90%	standard yield	30%	60%	90%
measurement 1	31%	60%	91%	measurement 1	29%	58%	88%
measurement 2	30%	59%	91%	measurement 2	31%	60%	89%
measurement 3	31%	60%	90%	measurement 3	30%	59%	90%
mean	30.7%	59.7%	90.7%	mean	30%	59%	89%
range (max-min) yield	1%	1%	1%	range (max-min) yield	2%	2%	2%
relative error ^a	2.3%	1.2%	0.8%	relative error ^a	3.3%	1.7%	1.1%

^athe relative largest measurement - mean/mean.

GC spectrum of the H₂ and CO₂ yield under optimized conditions

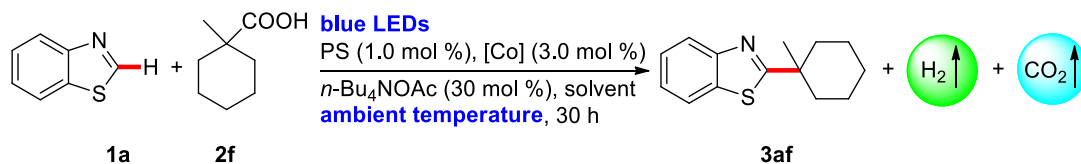


Area (H₂): 644594; Area (CO₂): 182018; Area (CH₄): 49927.

$$y = 7.72 * [\text{Area (H}_2\text{)}/\text{Area (CH}_4\text{)}] - 5.53 = 94\%$$

$$y = 35.38 * [\text{Area (CO}_2\text{)}/\text{Area (CH}_4\text{)}] - 25.69 = 103\%$$

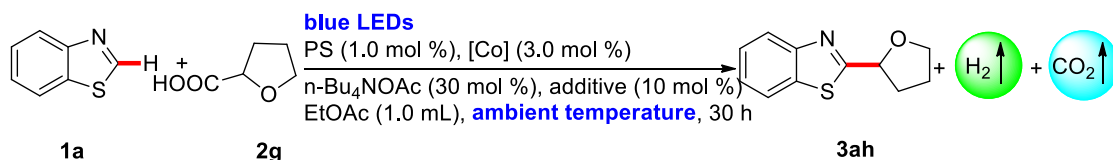
Table S1. Optimizing the reaction conditions of 3af.



entry ^a	photosensitizer (PS)	[Co]	solvent	H ₂ (%)	CO ₂ (%)	3af (%)
1	Ir[dF(CF ₃)ppy] ₂ dtbbpy	[Co(dmgh) ₂ Py ₂]PF ₆	EtOAc	106	118	22
2	Ir[dF(CF ₃)ppy] ₂ dtbbpy	Co(dmgh) ₂ (4-CO ₂ NMe ₂ Py)Cl	EtOAc	93	85	22
3	Ir[dF(CF ₃)ppy] ₂ dtbbpy	Co(dmgh) ₂ PyCl	EtOAc	122	105	28
4	Ir[dF(CF ₃)ppy] ₂ dtbbpy	Co(dmgh) ₂ (4-NMe ₂ Py)Cl	EtOAc	59	72	38
5	Ir[dF(CF ₃)ppy] ₂ dtbbpy	Co(dmgh) ₂ (4-NMe ₂ Py)Cl	MeOH	ND	ND	ND
6	Ir[dF(CF ₃)ppy] ₂ dtbbpy	Co(dmgh) ₂ (4-NMe ₂ Py)Cl	EtOH	ND	ND	ND
7	Ir[dF(CF ₃)ppy] ₂ dtbbpy	Co(dmgh) ₂ (4-NMe ₂ Py)Cl	<i>t</i> -AmOH	47	68	<5
8	Ir[dF(CF ₃)ppy] ₂ dtbbpy	Co(dmgh) ₂ (4-NMe ₂ Py)Cl	<i>i</i> -PrOH	102	112	42 (42)
9	Ir[dF(CF ₃)ppy] ₂ dtbbpy	Co(dmgh) ₂ (4-NMe ₂ Py)Cl	DME	72	95	<5

^a Reaction conditions: **1a** (0.20 mmol), **2f** (0.40 mmol), solvent (1.0 mL), PS (1.0 mol %), [Co] (3.0 mol %), irradiation with blue LEDs for 30 h. ND = no detected, ¹H NMR yield was reported using Cl₂CHCHCl₂ as internal standard.

Table S2. Optimizing the reaction conditions of 3ah.



entry ^a	photosensitizer (PS)	[Co]	additive	H ₂ (%)	CO ₂ (%)	3ah (%)
1	Ir[dF(CF ₃)ppy] ₂ dtbbpy	[Co(dmgh) ₂ Py ₂]PF ₆	—	60	73	34
2	Ir[dF(CF ₃)ppy] ₂ dtbbpy	Co(dmgh) ₂ (4-CO ₂ NMe ₂ Py)Cl	—	71	79	41
3	Ir[dF(CF ₃)ppy] ₂ dtbbpy	Co(dmgh) ₂ (4-NMe ₂ Py)Cl	—	75	85	50
4	Ir[dF(CF ₃)ppy] ₂ dtbbpy	Co(dmgh) ₂ (4-NMe ₂ Py)Cl	Pd(PPh ₃)Cl ₂	<5	<5	<5
5	Ir[dF(CF ₃)ppy] ₂ dtbbpy	Co(dmgh) ₂ (4-NMe ₂ Py)Cl	Cu(OAc) ₂	42	38	15
6	Ir[dF(CF ₃)ppy] ₂ dtbbpy	Co(dmgh) ₂ (4-NMe ₂ Py)Cl	CuCl	59	63	17
7	Ir[dF(CF ₃)ppy] ₂ dtbbpy	Co(dmgh) ₂ (4-NMe ₂ Py)Cl	CuI	48	57	23
8	Ir[dF(CF ₃)ppy] ₂ dtbbpy	Co(dmgh) ₂ (4-NMe ₂ Py)Cl	CuCl ₂ ·2H ₂ O	90	92	62 (61)
9	Ir[dF(CF ₃)ppy] ₂ dtbbpy	Co(dmgh) ₂ (4-NMe ₂ Py)Cl	Cu(OTf) ₂	48	39	32

^a Reaction conditions: **1a** (0.20 mmol), **2h** (0.40 mmol), solvent (1.0 mL), PS (1.0 mol %), [Co] (3.0 mol %), irradiation with blue LEDs for 30 h, ¹H NMR yield was reported using Cl₂CHCHCl₂ as internal standard.

GC-MS analysis of the crude products

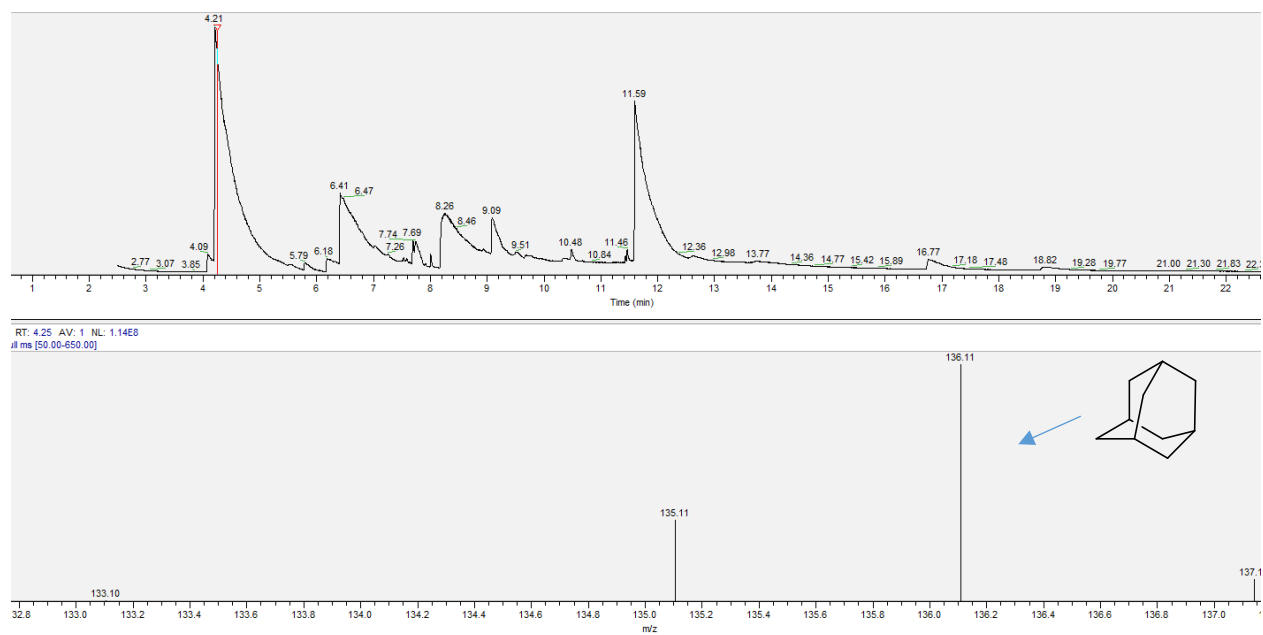


Figure S1. GC-MS spectrum of the crude products in **3aa** synthesis.

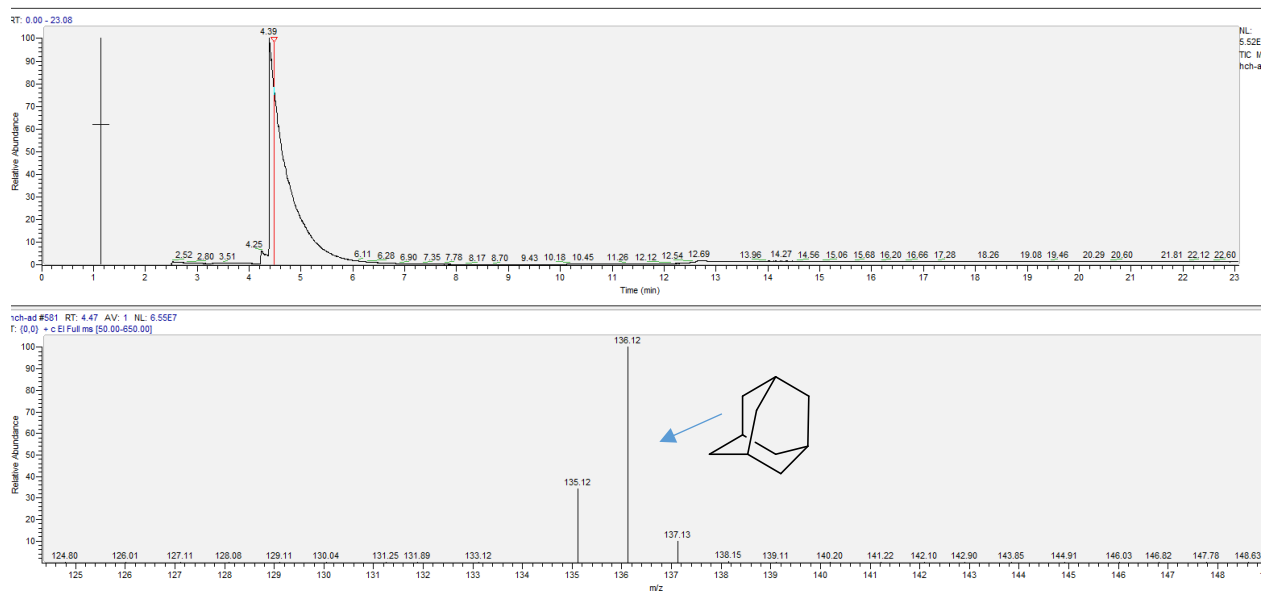


Figure S2. GC-MS spectrum of adamantane.

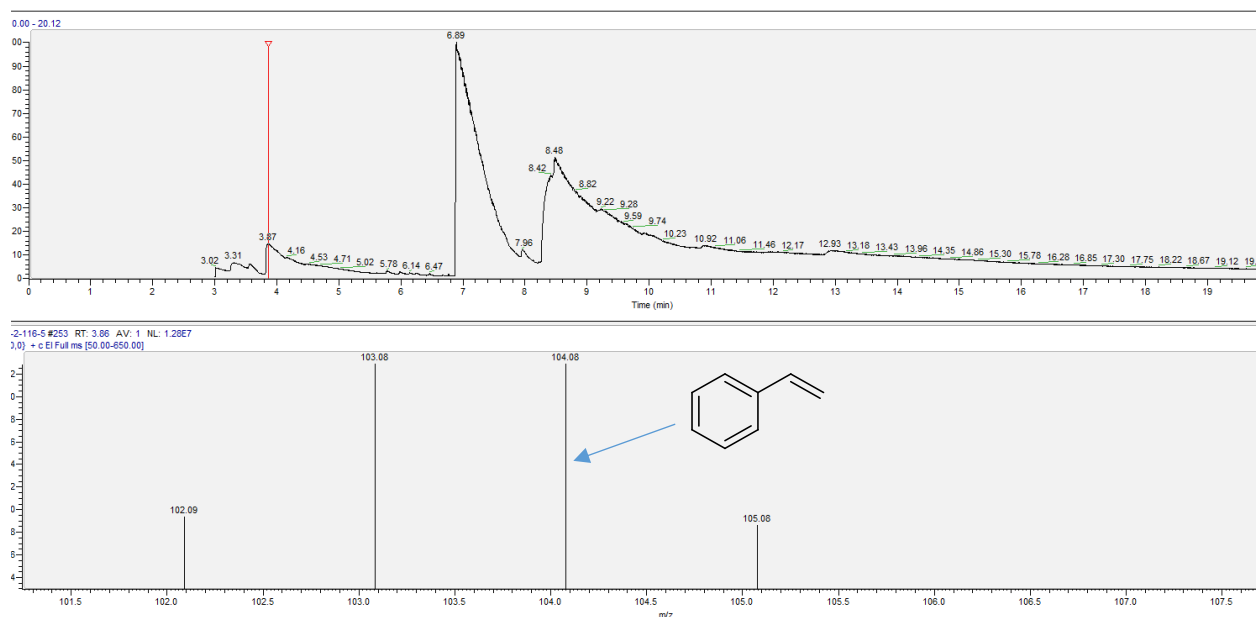
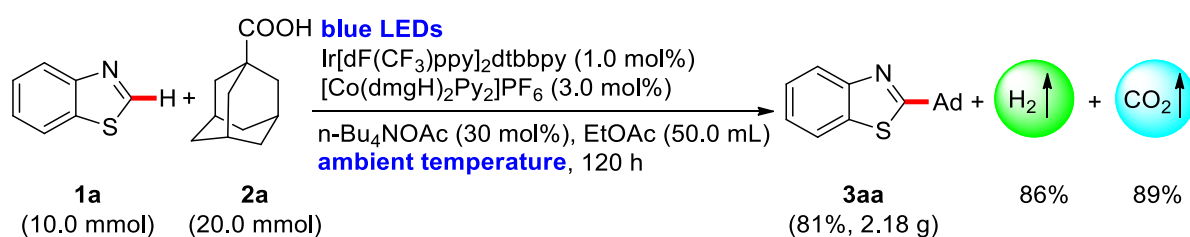


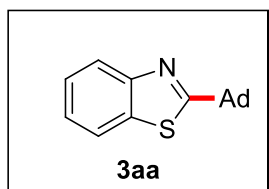
Figure S3. GC-MS spectrum of reaction mixture of **1a** with 3-phenylpropionic acid.



Scheme S1. Gram-scale reaction (Reaction conditions: 10.0 mmol of benzothiazole **1a**, 20.0 mmol of 1-adamantane carboxylic acid **2a**, 1 mol% Ir[dF(CF₃)ppy]₂dtbbpy, 3.0 mol% [Co(dmgH)₂Py₂]PF₆, 30 mol% *n*-Bu₄NOAc in 50 mL of EtOAc, blue LEDs, 120 h irradiation at ambient temperature).

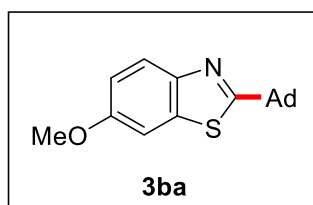
Characterization data for products

Compound **3aa**⁴



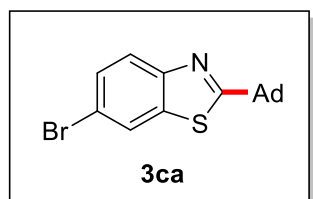
According to the general procedure, **3aa** (yellow solid, 49.5 mg) was obtained by column chromatography with the eluting (petroleum ether/Et₂O = 100/1) in 92% yield with 94% H₂ yield and 103% CO₂ yield. ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.45–7.41 (m, 1H), 7.33–7.29 (m, 1H), 2.15 (s, 9H), 1.81 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 182.1, 153.1, 134.3, 125.6, 124.3, 122.6, 121.5, 42.9 (3C), 40.1, 36.5 (3C), 28.5 (3C); MS: *m/z*: [M]⁺, 269.10.

Compound **3ba**⁴



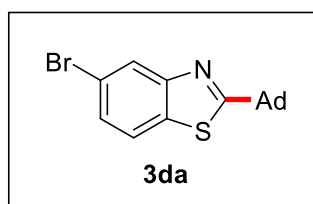
According to the general procedure, **3ba** (yellow solid, 50.9 mg) was obtained by column chromatography with the eluting (petroleum ether/Et₂O = 200/1) in 85% yield with 91% H₂ yield and 99% CO₂ yield. ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.8 Hz, 1H), 7.31 (d, *J* = 2.4 Hz, 1H), 7.03 (dd, *J* = 8.8, *J* = 2.4 Hz, 1H), 3.85 (s, 3H), 2.13 (s, 9H), 1.81 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 179.6, 157.1, 147.6, 135.5, 123.0, 114.8, 104.2, 55.7, 42.9 (3C), 40.0, 36.5 (3C), 28.5 (3C); MS: *m/z*: [M]⁺, 299.11.

Compound **3ca**



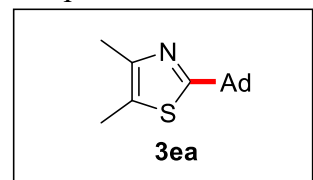
According to the general procedure, **3ca** (white solid, 60.5 mg) was obtained by column chromatography with the eluting (petroleum ether/Et₂O = 200/1) in 87% yield with 89% H₂ yield and 95% CO₂ yield. ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 2.0 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.52 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 1H), 2.13 (s, 9H), 1.81 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 184.0, 154.4, 133.2, 127.4, 125.6, 122.6, 119.2, 42.9 (3C), 40.3, 36.4 (3C), 28.5 (3C); IR (cm⁻¹): ν 3357, 3188, 2919, 2850, 1660, 1634, 1470, 1423, 1322, 1217, 876, 817, 732, 720; HRMS: *m/z*: [M + H]⁺ calculated for C₁₇H₁₈BrNS, 348.0416; found 348.0408.

Compound **3da**⁵



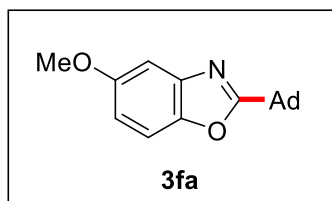
According to the general procedure, a prolonged reaction time of 42 h was applied, **3da** (white solid, 62.9 mg) was obtained by column chromatography with the eluting (petroleum ether/Et₂O = 200/1) in 90% yield with 99% H₂ yield and 100% CO₂ yield. ¹H NMR (400 MHz, CDCl₃): δ 8.14 (d, *J* = 2.0 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.42 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz, 1H), 2.13 (s, 9H), 1.81 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 184.0, 154.4, 133.2, 127.4, 125.6, 122.6, 119.2, 42.9 (3C), 40.3, 36.4 (3C), 28.5 (3C); MS: *m/z*: [M]⁺, 347.04.

Compound **3ea**



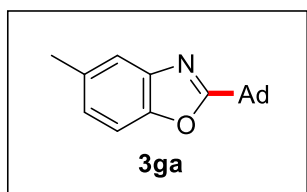
According to the general procedure, **3ea** (white solid, 26.0 mg) was obtained by column chromatography with the eluting (petroleum ether/Et₂O = 70/1) in 53% yield with 50% H₂ yield and 56% CO₂ yield. ¹H NMR (400 MHz, CDCl₃) δ 2.30–2.29 (m, 6H), 2.08 (s, 3H), 2.01 (s, 6H), 1.76 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 176.9, 147.0, 123.8, 43.16 (3C), 39.0, 36.5 (3C), 28.6 (3C), 14.7, 11.2; IR (cm⁻¹): ν 3356, 3193, 2919, 2849, 1659, 1633, 1470, 1425, 1343, 1317, 1137, 1013, 809, 721, 703; HRMS: *m/z*: [M + H]⁺ calculated for C₁₅H₂₂NS, 248.1467; found 248.1475.

Compound **3fa**



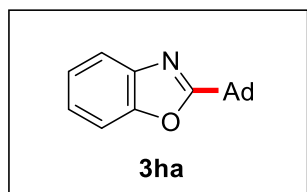
According to the general procedure, **3fa** (yellow solid, 49.6 mg) was obtained by column chromatography with the eluting (petroleum ether/Et₂O = 50/1) in 88% yield with 92% H₂ yield and 90% CO₂ yield. ¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, *J* = 8.8 Hz, 1H), 7.20 (d, *J* = 2.4 Hz, 1H), 6.88 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H), 3.83 (s, 3H), 2.14 (s, 9H), 1.81 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 173.9, 156.9, 145.1, 142.0, 112.6, 110.4, 102.9, 55.9, 40.2 (3C), 36.5 (3C), 36.1, 28.0 (3C); HRMS: *m/z*: [M + H]⁺ calculated for C₁₈H₂₂NO₂, 284.1645; found 284.1637.

Compound **3ga**⁶



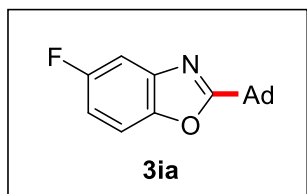
According to the general procedure, **3ga** (white solid, 50.1 mg) was obtained by column chromatography with eluting (petroleum ether/Et₂O = 200/1) in 94% yield with 97% H₂ yield and 94% CO₂ yield. ¹H NMR (400 MHz, CDCl₃) δ 7.47 (s, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.09 (d, *J* = 8.0 Hz), 2.45 (s, 3H), 2.14 (s, 9H), 1.81 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 173.0, 148.6, 141.4, 133.6, 125.2, 119.6, 109.6, 40.2 (3C), 36.4 (3C), 36.0, 27.9 (3C), 21.4; IR (cm⁻¹): ν 3361, 3179, 2920, 2851, 1660, 1632, 1506, 1423, 1378, 1263, 1133, 1046, 749, 725, 719; HRMS: *m/z*: [M + H]⁺ calculated for C₁₈H₂₂NO, 268.1696; found 268.1702.

Compound **3ha**⁴



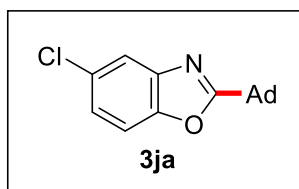
According to the general procedure, **3ha** (white solid, 46.8 mg) was obtained by column chromatography with the eluting (petroleum ether/Et₂O = 100/1) in 92% yield with 100% H₂ yield and 98% CO₂ yield. ¹H NMR (400 MHz, CDCl₃) δ 7.71–7.68 (m, 1H), 7.49–7.47 (m, 1H), 7.29–7.27 (m, 2H), 2.16–2.13 (m, 9H), 1.82 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 172.9, 150.4, 141.2, 124.2, 123.9, 119.6, 110.3, 40.2 (3C), 36.4 (3C), 36.0, 27.9 (3C); MS: *m/z*: [M]⁺, 253.13.

Compound **3ia**



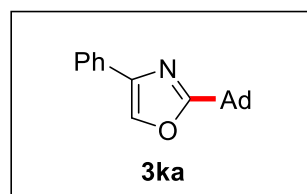
According to the general procedure, **3ia** (yellow solid, 46.6 mg) were obtained by column chromatography with the eluting (petroleum ether/Et₂O = 100/1) in 86% yield and 89% H₂ yield and 95% CO₂ yield. ¹H NMR (400 MHz, CDCl₃) δ 7.41–7.35 (m, 2H), 7.04–6.99 (m, 1H), 2.14 (s, 9H), 1.82 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 174.9, 159.8 (d, ¹*J*_{C-F} = 238.1 Hz), 146.8 (d, ⁴*J*_{C-F} = 0.9 Hz), 142.1 (d, ³*J*_{C-F} = 12.9 Hz), 111.8 (d, ²*J*_{C-F} = 26.1 Hz), 110.5 (d, ³*J*_{C-F} = 10.0 Hz), 106.2 (d, ²*J*_{C-F} = 25.4 Hz), 40.2 (3C), 36.4 (3C), 36.2, 27.9 (3C); ¹⁹F NMR (376 MHz, CDCl₃): -118.8; HRMS: *m/z*: [M + H]⁺ calculated for C₁₇H₁₉FNO, 272.1445; found 272.1449.

Compound **3ja**⁶



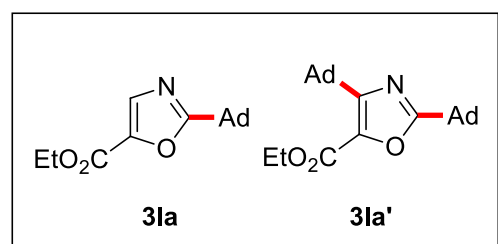
According to the general procedure, **3ja** (white solid, 52.1 mg) was obtained by column chromatography with the eluting (petroleum ether/Et₂O = 200/1) in 90% yield with 90% H₂ yield and 100% CO₂ yield. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 2.0 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 1H), 7.25 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz, 1H), 2.14 (s, 9H), 1.82 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 174.4, 149.1, 142.4, 129.3, 124.5, 119.7, 111.0, 40.1 (3C), 36.4 (3C), 36.2, 27.8 (3C); MS: *m/z*: [M]⁺, 287.07.

Compound **3ka**



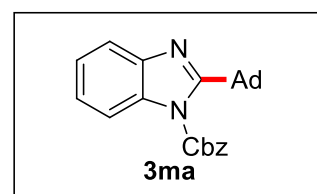
According to the general procedure, **3ka** (yellow solid, 45.4 mg) was obtained by column chromatography with the eluting (petroleum ether/Et₂O = 100/1) in 81% yield with 90% H₂ yield and 87% CO₂ yield. ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.30–7.26 (m, 1H), 7.22 (s, 1H), 2.10 (s, 9H), 1.80 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 170.4, 150.2, 128.7 (2C), 128.4, 127.9, 123.9 (2C), 121.4, 40.3 (3C), 36.4 (3C), 35.7, 28.0 (3C); IR (cm⁻¹): ν 2905, 2851, 1637, 1547, 1452, 1413, 1345, 1326, 1284, 1128, 1081, 944, 737, 691; HRMS: *m/z*: [M + H]⁺ calculated for C₁₉H₂₂NO, 280.1696; found 280.1697.

Compounds **3la** and **3la'**



According to the general procedure, **3la** (white solid, 35.1 mg, 64%) and **3la'** (white solid, 20.1 mg, 25%) were obtained by column chromatography with eluting (petroleum ether/Et₂O = 100/1) in 89% total yield with 95% H₂ yield and 92% CO₂ yield. **3la:3la'** = 2.6:1.0. **3la**: ¹H NMR (400 MHz, CDCl₃) δ 7.64 (s, 1H), 4.37 (q, *J* = 6.8 Hz, 2H), 2.08 (s, 9H), 1.79 (s, 6H), 1.38 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 174.0, 158.0, 141.8, 133.9, 61.2, 40.0 (3C), 36.3 (3C), 36.1, 27.8 (3C), 14.3; IR (cm⁻¹): ν 3363, 3187, 2919, 2851, 1742, 1660, 1525, 1470, 1314, 1212, 1144, 868, 832, 723; HRMS: *m/z*: [M + H]⁺ calculated for C₁₆H₂₂NO₃, 276.1594; found 276.1597. **3la'**: ¹H NMR (400 MHz, CDCl₃) δ 4.36 (q, *J* = 7.2 Hz, 2H), 2.12 (s, 6H), 2.08–2.05 (m, 12H), 1.81–1.72 (m, 12H), 1.40 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.3, 159.1, 157.3, 136.0, 60.8, 40.1 (3C), 39.9 (3C), 36.8 (3C), 36.4 (3C), 35.8, 34.7, 28.7 (3C), 28.0 (3C), 14.4; IR (cm⁻¹): ν 3362, 3177, 2908, 2851, 1632, 1478, 1452, 1345, 1322, 1132, 1047, 854, 812, 704; HRMS: *m/z*: [M + H]⁺ calculated for C₂₆H₃₆NO₃, 410.2690; found 410.2735.

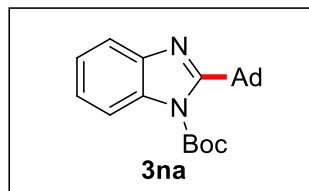
Compound **3ma**



According to the general procedure, **3ma** (white solid, 48.4 mg) was obtained by column chromatography with the eluting (petroleum ether/Et₂O = 50/1) in 63% yield with 66% H₂ yield and 79% CO₂ yield. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.53–7.50 (m, 2H), 7.46–7.39 (m, 3H), 7.29–7.20 (m, 2H), 5.53 (s, 2H), 2.31 (d, *J* = 2.8 Hz, 6H), 2.08 (s, 3H), 1.80–1.73 (m, 6H); ¹³C NMR (100 MHz,

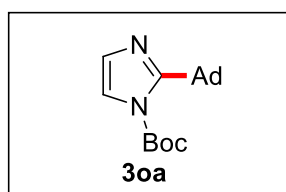
CDCl₃) δ 162.4, 151.0, 141.4, 134.1, 134.0, 129.1, 129.0 (2C), 128.9 (2C), 124.3, 124.0, 119.8, 114.6, 69.9, 39.5 (3C), 38.5, 36.5 (3C), 28.5 (3C); IR (cm⁻¹): ν 3359, 3035, 2905, 2849, 1754, 1658, 1456, 1382, 1307, 1189, 1050, 980, 762, 744; HRMS: m/z : [M + H]⁺ calculated for C₂₅H₂₇N₂O₂, 387.2067; found 387.2070.

Compound **3na**



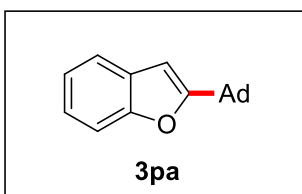
According to the general procedure, **3na** (white solid, 44.1 mg) was obtained by column chromatography with the eluting (petroleum ether/Et₂O = 40/1) in 63% yield with 64% H₂ yield and 70% CO₂ yield. ¹H NMR (400 MHz, CDCl₃) δ 7.74–7.67 (m, 2H), 7.29–7.26 (m, 2H), 2.33 (s, 6H), 2.11 (s, 3H), 1.88–1.76 (m, 6H), 1.72 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 162.2, 149.7, 141.3, 134.1, 123.9, 123.5, 119.7, 113.7, 85.3, 39.6 (3C), 38.2, 36.6 (3C), 28.5 (3C), 28.0 (3C); IR (cm⁻¹): ν 3357, 3189, 2918, 2849, 1751, 1659, 1632, 1470, 1454, 1322, 1132, 1151, 844, 763, 702; HRMS: m/z : [M + H]⁺ calculated for C₂₂H₂₉N₂O₂, 353.2224; found 353.2211.

Compound **3oa**



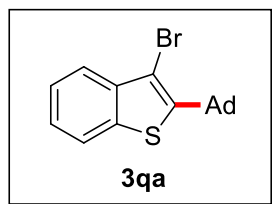
According to the general procedure, **3oa** (white solid, 25.0 mg) was obtained by column chromatography with eluting (petroleum ether/Et₂O = 30/1) in 41% yield with 49% H₂ yield and 51% CO₂ yield. ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, J = 1.6 Hz, 1H), 6.82 (d, J = 2.0 Hz, 1H), 2.21 (s, 6H), 2.06 (s, 3H), 1.82–1.73 (m, 6H), 1.61 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 157.7, 148.1, 126.0, 120.6, 84.6, 39.2 (3C), 37.4, 36.6 (3C), 28.5 (3C), 27.9 (3C); IR (cm⁻¹): ν 3360, 3186, 2919, 2851, 1752, 1658, 1634, 1485, 1470, 1345, 1314, 1132, 1157, 859, 815, 748; HRMS: m/z : [M + H]⁺ calculated for C₁₈H₂₇N₂O₂, 303.2067; found 303.2071.

Compound **3pa**



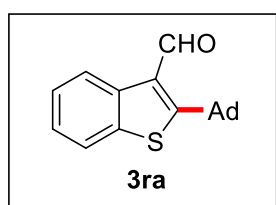
According to the general procedure, **3pa** (white solid, 31.5 mg) was obtained by column chromatography with eluting (petroleum ether/Et₂O = 100/1) in 62% yield with 66% H₂ yield and 70% CO₂ yield. ¹H NMR (400 MHz, CDCl₃) δ 7.50–7.47 (m, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.22–7.14 (m, 2H), 6.30 (s, 1H), 2.09 (s, 3H), 2.01 (s, 6H), 1.83–1.76 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 167.6, 154.3, 128.8, 122.9, 122.2, 120.3, 110.8, 98.5, 40.9 (3C), 36.8 (3C), 34.9, 28.2 (3C); IR (cm⁻¹): ν 3357, 3189, 2918, 2849, 1659, 1632, 1470, 1456, 1136, 738, 721, 706; HRMS: m/z : [M]⁺ calculated for C₁₈H₂₀O, 252.1509; found 252.1515.

Compound **3qa**



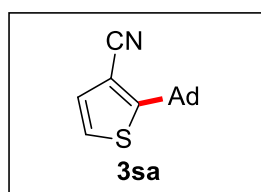
According to the general procedure, **3qa** (white solid, 53.2 mg) was obtained by column chromatography with the eluting (pure petroleum ether) in 77% yield with 75% H₂ yield and 82% CO₂ yield. ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.43–7.38 (m, 1H), 7.34–7.30 (m, 1H), 2.33 (d, *J* = 2.4 Hz, 6H), 2.12 (s, 3H), 1.84–1.77 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 149.1, 139.8, 135.6, 124.7, 124.5, 122.4, 121.9, 101.5, 40.9 (3C), 37.6, 36.5 (3C), 28.7 (3C); IR (cm⁻¹): ν 3357, 3188, 2919, 2850, 1659, 1632, 1470, 1424, 1299, 1137, 1019, 806, 724, 703; HRMS: *m/z*: [M]⁺ calculated for C₁₈H₁₉BrS, 346.0385; found 346.0396.

Compound **3ra**



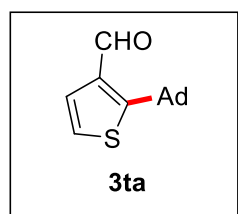
According to the general procedure, **3ra** (white solid, 33.3 mg) was obtained by column chromatography with the eluting (petroleum ether/Et₂O = 100/1) in 56% yield with 63% H₂ yield and 58% CO₂ yield. ¹H NMR (400 MHz, CDCl₃) δ 10.88 (s, 1H), 8.68 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 2.28 (s, 6H), 2.16 (s, 3H), 1.83 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 185.8, 173.1, 138.7, 136.1, 129.3, 125.8, 125.0, 124.8, 121.3, 44.9 (3C), 39.2, 36.3 (3C), 28.9 (3C); IR (cm⁻¹): ν 3361, 3195, 2920, 2850, 1660, 1633, 1470, 1458, 1347, 1132, 1159, 900, 810, 734; HRMS: *m/z*: [M]⁺ calculated for C₁₉H₂₀OS, 296.1229; found 296.1228.

Compound **3sa**⁷



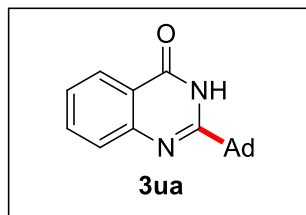
According to the general procedure, **3sa** (yellow solid, 44.5 mg) was obtained by column chromatography with eluting (petroleum ether/Et₂O = 100/1) in 91% yield with 91% H₂ yield and 100% CO₂ yield. ¹H NMR (400 MHz, CDCl₃) δ 7.17 (d, *J* = 5.6 Hz, 1H), 7.12 (d, *J* = 5.2 Hz, 1H), 2.17 (s, 6H), 2.12 (s, 3H), 1.79 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 167.5, 130.5, 122.3, 116.4, 104.3, 42.6 (3C), 37.5, 36.2 (3C), 28.6 (3C); MS: *m/z*: [M]⁺, 243.09.

Compound **3ta**⁷



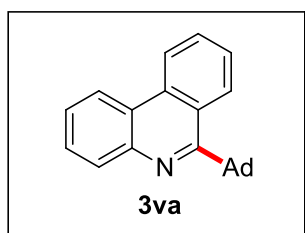
According to the general procedure, **3ta** (white solid, 36.3 mg) was obtained by column chromatography with eluting (petroleum ether/Et₂O = 100/1) in 74% yield with 74% H₂ yield and 74% CO₂ yield. White Solid. ¹H NMR (400 MHz, CDCl₃) δ 10.48 (s, 1H), 7.51 (d, *J* = 5.2 Hz, 1H), 7.04 (d, *J* = 5.6 Hz, 1H), 2.18 (s, 6H), 2.13 (s, 3H), 1.81 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 185.1, 168.0, 136.6, 128.9, 121.3, 44.8 (3C), 38.4, 36.3 (3C), 28.9 (3C); MS: *m/z*: [M]⁺, 246.09.

Compound **3ua**



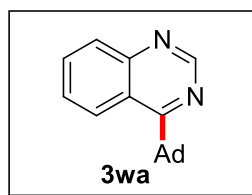
According to the general procedure, **3ua** (yellow solid, 40.0 mg) was obtained by column chromatography with eluting (petroleum ether/DCM/Et₂O = 10/2/1) in 71% yield with 73% H₂ yield and 85% CO₂ yield. ¹H NMR (400 MHz, CDCl₃) δ 11.04 (s, 1H), 8.27 (d, *J* = 7.6 Hz, 1H), 7.78–7.72 (m, 2H), 7.48–7.45 (m, 1H), 2.18 (s, 6H), 2.15 (s, 3H), 1.85 (s, 6H); Yellow solid. ¹³C NMR (100 MHz, CDCl₃) δ 163.7, 161.8, 149.4, 134.4, 127.7, 126.3, 126.1, 120.8, 39.7 (3C), 39.1, 36.5 (3C), 28.3 (3C); IR (cm⁻¹): ν 3395, 3175, 3404, 2920, 2849, 1633, 1607, 1469, 1420, 1344, 1254, 1104, 986, 868, 762, 722; HRMS: *m/z*: [M]⁺ calculated for C₁₈H₂₀N₂O, 280.1570; found 280.1579.

Compound **3va**



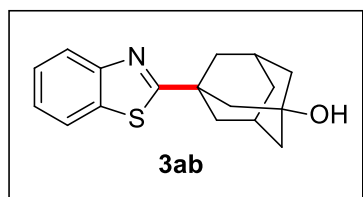
According to the general procedure, **3va** (white solid, 51.3 mg) was obtained by column chromatography with eluting (petroleum ether/Et₂O = 100/1) in 82% yield with 90% H₂ yield and 88% CO₂ yield. White solid. ¹H NMR (400 MHz, CDCl₃) δ 8.84 (d, *J* = 8.4 Hz, 1H), 8.66 (d, *J* = 8.4 Hz, 1H), 8.49 (dd, *J* = 8.4 Hz, *J* = 0.8 Hz, 1H), 8.11 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 1H), 7.75–7.71 (m, 1H), 7.69–7.65 (m, 1H), 7.62–7.55 (m, 2H), 2.48 (d, *J* = 2.4 Hz, 6H), 2.22 (s, 3H), 1.90 (q, *J* = 12.0 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 166.0, 143.1, 134.0, 130.2, 129.1, 128.3, 128.0, 126.4, 125.6, 124.4, 123.2, 123.0, 121.6, 42.9, 42.0 (3C), 37.2 (3C), 29.2 (3C); IR (cm⁻¹): ν 3359, 3187, 3072, 2902, 2849, 1659, 1632, 1485, 1453, 1345, 1252, 1167, 1049, 992, 758, 728; HRMS: *m/z*: [M + H]⁺ calculated for C₂₃H₂₄N, 314.1903; found 314.1909.

Compound **3wa**



According to the general procedure, **3wa** (pale red solid, 36.7 mg) was obtained by column chromatography with the eluting (petroleum ether/Et₂O = 50/1) in 69% yield with 76% H₂ yield and 81% CO₂ yield. ¹H NMR (400 MHz, CDCl₃) δ 9.25 (s, 1H), 8.67 (d, *J* = 8.8 Hz, 1H), 8.06 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 1H), 7.84–7.80 (m, 1H), 7.60–7.55 (m, 1H), 2.37 (d, *J* = 2.8 Hz, 6H), 2.21 (s, 3H), 1.89 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 176.1, 153.9, 151.0, 132.3, 130.2, 126.3, 125.9, 123.3, 42.8, 41.7 (3C), 36.8 (3C), 28.8 (3C); IR (cm⁻¹): ν 3358, 3199, 2920, 2849, 1633, 1470, 1450, 1373, 1360, 1137, 1100, 997, 824, 762; HRMS: *m/z*: [M + H]⁺ calculated for C₁₈H₂₁N₂, 265.1699; found 265.1694.

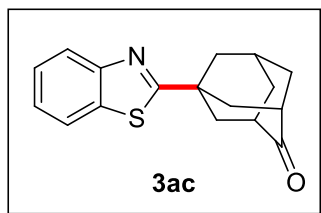
Compound **3ab**⁴



According to the general procedure, **3ab** (white solid, 50.2 mg) was obtained by column chromatography with eluting (petroleum ether/Et₂O = 1/1) in 88% yield with 98% H₂ yield and 93% CO₂ yield. ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.86–7.84 (m, 1H), 7.46–7.42 (m, 1H), 7.36–7.31 (m, 1H), 2.38–2.37 (m, 2H), 2.12 (s, 2H), 2.09–2.01 (m, 4H), 1.88 (br, 1H), 1.81 (s, 4H),

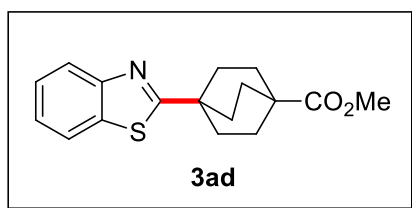
1.73–1.64 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 180.0, 153.0, 134.3, 125.8, 124.6, 122.7, 121.5, 68.6, 50.2, 44.3 (2C), 43.4, 41.7 (2C), 35.0, 30.7 (2C); IR (cm^{-1}): ν 3357, 3191, 2919, 2850, 1659, 1633, 1470, 1437, 1353, 1244, 1115, 1080, 929, 759, 729; MS: m/z : $[\text{M}]^+$, 285.11.

Compound **3ac**



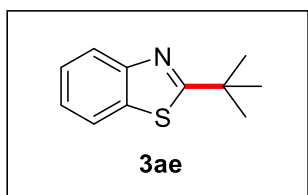
According to the general procedure, **3ac** (white solid, 39.2 mg) were obtained by column chromatography with eluting (petroleum ether/ Et_2O = 20/1) in 69% yield with 71% H_2 yield and 74% CO_2 yield. ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.49–7.45 (m, 1H), 7.39–7.35 (m, 1H), 2.73 (s, 2H), 2.50–2.43 (m, 4H), 2.38 (s, 2H), 2.34–2.32 (m, 1H), 2.20–2.08 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 216.3, 178.3, 153.0, 134.3, 126.0, 124.8, 122.8, 121.6, 46.2 (2C), 43.7 (2C), 41.8, 39.6, 38.3 (2C), 27.8; IR (cm^{-1}): ν 3354, 3195, 2920, 2851, 1724, 1633, 1470, 1436, 1268, 1241, 1135, 1060, 875, 762, 735; HRMS: m/z : $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{17}\text{H}_{18}\text{NOS}$, 284.1104; found 284.1108.

Compound **3ad**



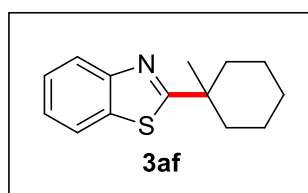
According to the general procedure, **3ad** (white solid, 52.9 mg) was obtained by column chromatography with eluting (petroleum ether/ Et_2O = 50/1) in 88% yield with 92% H_2 yield and 98% CO_2 yield. ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.43–7.46 (m, 1H), 7.36–7.32 (m, 1H), 3.69 (s, 3H), 2.12–2.08 (m, 6H), 1.99–1.95 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 180.0, 177.8, 153.2, 134.6, 125.8, 124.6, 122.7, 121.5, 51.8, 39.2, 38.3, 31.8 (3C), 28.4 (3C); IR (cm^{-1}): ν 3359, 3182, 2920, 2870, 1731, 1632, 1509, 1437, 1348, 1312, 1132, 1067, 1021, 897, 757, 732; HRMS: m/z : $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{17}\text{H}_{20}\text{NO}_2\text{S}$, 302.1209; found 302.1206.

Compound **3ae**⁴



According to the general procedure, **3ae** (yellow liquid, 14.0 mg) was obtained by column chromatography with eluting (petroleum ether/ Et_2O = 200/1) in 37% yield with 66% H_2 yield and 59% CO_2 yield. ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 1.52 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 181.8, 153.2, 134.9, 125.7, 124.5, 122.6, 121.4, 38.3, 30.7 (3C); MS: m/z : $[\text{M}]^+$, 191.07

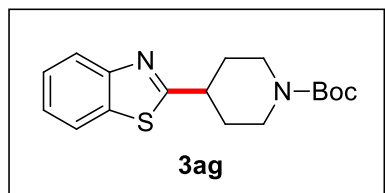
Compound **3af**



According to the general procedure, employing $\text{Co}(\text{dmgH})_2(\text{DMAP})\text{Cl}$ as cobalt catalyst and changing the solvent to *i*-PrOH, **3af** (yellow liquid, 19.4 mg) was obtained by column chromatography with eluting (petroleum ether/ Et_2O = 200/1) in 42% yield with 108% H_2 yield and 105% CO_2 yield.

^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.46–7.42 (m, 1H), 7.35–7.31 (m, 1H), 2.27–2.21 (m, 2H), 1.74–1.45 (m, 8H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 181.7, 153.3, 134.9, 125.6, 124.4, 122.7, 121.5, 42.0, 38.5 (2C), 29.7, 25.8, 22.6 (2C); IR (cm^{-1}): ν 3356, 3198, 2922, 2851, 1659, 1632, 1470, 1437, 1312, 1262, 1189, 1009, 959, 758, 729; HRMS: m/z : $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{14}\text{H}_{18}\text{NS}$, 232.1154; found 232.1159.

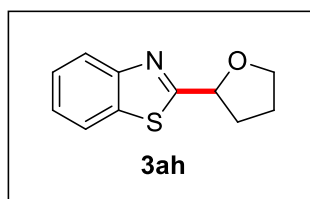
Compound **3ag**



According to the general procedure, **3ag** (white solid, 19.1 mg,) was obtained by column chromatography with eluting (petroleum ether/ Et_2O = 100/1) in 30% total yield with 57% H_2 yield and 86% CO_2 yield.

^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 4.24 (br, 2H), 3.30–3.22 (m, 1H), 2.92 (t, J = 11.6 Hz, 2H), 2.16 (d, J = 12.8 Hz, 2H), 1.90–1.80 (m, 2H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.1, 154.7, 153.1, 134.5, 126.0, 124.8, 122.7, 121.6, 79.7, 43.7 (2C), 41.5, 32.1 (2C), 28.5 (3C); IR (cm^{-1}): ν 3359, 3062, 2975, 2851, 1692, 1632, 1515, 1422, 1365, 1317, 1275, 1167, 1010, 889, 760, 731; HRMS: m/z : $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{17}\text{H}_{23}\text{N}_2\text{O}_2\text{S}$, 319.1475; found 319.1479.

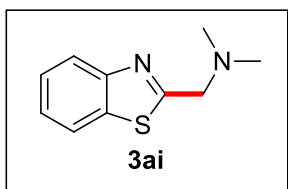
Compound **3ah**⁸



According to the general procedure, employing $\text{Co}(\text{dmgH})_2(\text{DMAP})\text{Cl}$ as cobalt catalyst and introducing 10 mol% of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ as additive, **3ah** (colorless oil, 24.9 mg) was obtained by column chromatography with eluting (petroleum ether/ Et_2O = 200/1) in 61% yield with 82% H_2 yield and 91% CO_2 yield.

^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 5.35 (dd, J = 7.8 Hz, J = 5.4 Hz, 1H), 4.19–4.13 (m, 1H), 4.04–3.98 (m, 1H), 2.57–2.48 (m, 1H), 2.31–2.23 (m, 1H), 2.07–2.00 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 176.4, 153.6, 134.7, 125.9, 124.7, 122.7, 121.7, 78.7, 69.4, 33.3, 25.7; MS: m/z : $[\text{M}]^+$, 205.05.

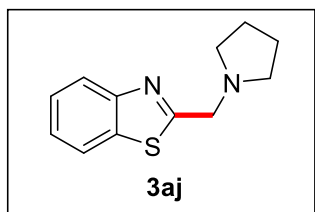
Compound **3ai**



According to the general procedure, employing $\text{Co}(\text{dmgH})_2(\text{DMAP})\text{Cl}$ as cobalt catalyst and increasing the amount of **2** to 0.6 mmol, **3ai** (yellow liquid, 23.2 mg) was obtained by column chromatography with eluting (petroleum ether/ Et_2O = 200/1) in 60% total yield with 72% H_2 yield and 75% CO_2 yield.

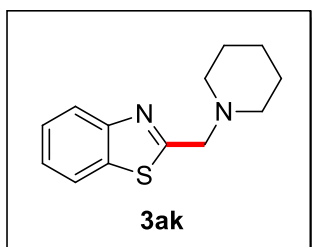
^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.48–7.44 (m, 1H), 7.39–7.35 (m, 1H), 3.90 (s, 2H), 2.42 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.2, 153.1, 135.4, 125.8, 124.8, 122.8, 121.7, 61.7, 45.8 (2C); IR (cm^{-1}) ν 3359, 3059, 2975, 2853, 1736, 1633, 1455, 1436, 1348, 1264, 1138, 1036, 843, 760, 731; HRMS: m/z : $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{10}\text{H}_{13}\text{N}_2\text{S}$, 193.0794; found 193.0798.

Compound **3aj**



According to the general procedure, employing $\text{Co}(\text{dmgH})_2(\text{DMAP})\text{Cl}$ as cobalt catalyst and increasing the amount of **2** to 0.6 mmol, **3aj** (yellow liquid, 26.9 mg) was obtained by column chromatography with eluting (petroleum ether/ Et_2O = 200/1) in 62% yield with 68% H_2 yield and 82% CO_2 yield. ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.47–7.43 (m, 1H), 7.38–7.34 (m, 1H), 4.09 (s, 2H), 2.74–2.70 (m, 4H), 1.89–1.82 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.6, 153.2, 135.4, 125.7, 124.7, 122.8, 121.7, 58.0, 54.4 (2C), 23.8 (2C); IR (cm^{-1}): ν 3359, 3193, 2919, 2849, 1659, 1633, 1470, 1429, 1349, 1320, 1164, 1121, 862, 760, 721; HRMS: m/z : $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{12}\text{H}_{15}\text{N}_2\text{S}$, 219.0950; found 219.0939.

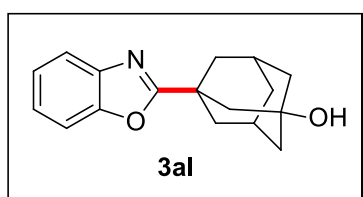
Compound **3ak**



According to the general procedure, employing $\text{Co}(\text{dmgH})_2(\text{DMAP})\text{Cl}$ as cobalt catalyst and increasing the amount of **2** to 0.6 mmol, **3ak** (white solid, 26.3 mg) was obtained by column chromatography with eluting (petroleum ether/ Et_2O = 200/1) in 57% total yield with 57% H_2 yield and 73% CO_2 yield.

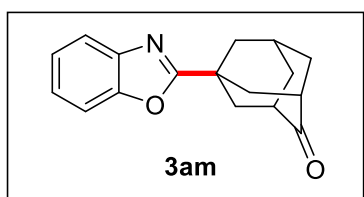
^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 3.90 (s, 2H), 2.57 (br s, 4H), 1.64 (q, J = 5.2 Hz, 4H), 1.49–1.47 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.4, 153.3, 135.5, 125.7, 124.7, 122.7, 121.7, 61.0, 54.9 (2C), 26.0, 24.0 (2C); IR (cm^{-1}): ν 3358, 3176, 2935, 2851, 1754, 1762, 1528, 1469, 1336, 1312, 1132, 1189, 855, 759, 730; HRMS: m/z : $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{13}\text{H}_{17}\text{N}_2\text{S}$, 233.1107; found 233.1103.

Compound **3al**



According to the general procedure, **3al** (white solid, 36.5 mg) was obtained by column chromatography with eluting (petroleum ether/ Et_2O = 250/1) in 68% yield with 74% H_2 yield and 77% CO_2 yield. ^1H NMR (400 MHz, CDCl_3) δ 7.72–7.68 (m, 1H), 7.51–7.47 (m, 1H), 7.32–7.28 (m, 2H), 2.38 (s, 2H), 2.13 (s, 2H), 2.10–2.02 (m, 4H), 1.82 (d, J = 2.8 Hz, 4H), 1.74–1.66 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.4, 150.5, 141.0, 124.5, 124.1, 119.7, 110.4, 68.2, 47.6, 44.2 (2C), 39.3, 39.0 (2C), 34.9, 30.3 (2C); HRMS: m/z : $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{17}\text{H}_{20}\text{NO}_2$, 270.1489; found 270.1466.

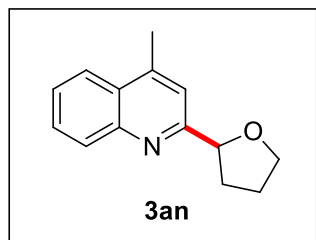
Compound **3am**



According to the general procedure, **3am** (white solid, 40.2 mg) was obtained by column chromatography with eluting (petroleum ether/ Et_2O = 250/1) in 75% yield with 76% H_2 yield and 72% CO_2 yield. ^1H NMR (400 MHz, CDCl_3) δ 7.72–7.68 (m, 1H), 7.52–7.48 (m, 1H), 7.35–7.30 (m, 2H), 2.72 (s, 2H), 2.48 (d, J = 2.4 Hz, 4H), 2.39 (s, 2H), 2.33–2.31 (m, 1H), 2.20–2.08 (m, 4H); ^{13}C

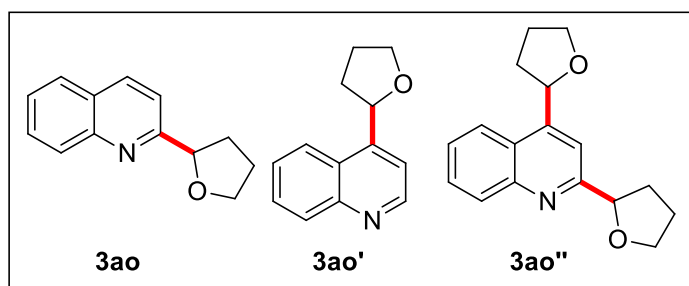
NMR (100 MHz, CDCl₃) δ 216.2, 170.3, 150.5, 140.9, 124.8, 124.3, 119.8, 110.5, 45.8 (2C), 41.3 (2C), 39.3, 38.3 (2C), 35.7, 27.3; IR (cm⁻¹): ν 3353, 3050, 2934, 2859, 1726, 1635, 1456, 1419, 1373, 1267, 1243, 1175, 1042, 930, 864, 747; HRMS: m/z : [M + H]⁺ calculated for C₁₇H₁₈NO₂, 268.1332; found 268.1337.

Compound **3an**⁹



According to the general procedure, an increased amount of **2** (0.8 mmol) and reduced reaction time (22 h) were applied, **3an** (colorless oil, 35.4 mg) was obtained by column chromatography with eluting (petroleum ether/Et₂O = 250/1) in 83% yield with 107% H₂ yield and 92% CO₂ yield. ¹H NMR (400 MHz, CDCl₃) δ 8.05 (dd, J = 8.4 Hz, J = 0.4 Hz, 1H), 7.94 (dd, J = 8.4 Hz, J = 0.8 Hz, 1H), 7.68–7.64 (m, 1H), 7.52–7.47 (m, 1H), 7.43 (s, 1H), 5.14 (t, J = 7.2 Hz, 1H), 4.19–4.14 (m, 1H), 4.05–4.00 (m, 1H), 2.68 (s, 3H), 2.53–2.46 (m, 1H), 2.11–1.97 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.1, 147.3, 144.9, 129.6, 129.1, 127.4, 125.8, 123.7, 118.6, 82.1, 69.2, 33.3, 25.9, 18.9; MS: m/z : [M]⁺, 213.08.

Compound **3ao**¹⁰, **3ao'**¹⁰, **3ao''**¹¹



According to the general procedure, an increased amount of **2** (0.8 mmol) and reduced reaction time (22 h) were applied, **3ao** (colorless oil, 4.1 mg, 10%), **3ao'** (colorless oil, 15.8 mg, 40%) and **3ao''** (colorless oil, 2.1 mg, 4%) were obtained by column chromatography with eluting (petroleum ether/Et₂O = 100/1) in 54% total yield with 70% H₂ yield and 90% CO₂ yield. **3ao**: ¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, J = 8.4 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.70 (t, J = 7.2 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.51 (t, J = 7.2 Hz, 1H), 5.21–5.17 (m, 1H), 4.21–4.15 (m, 1H), 4.08–4.02 (m, 1H), 2.56–2.48 (m, 1H), 2.13–2.00 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.6, 147.5, 136.7, 129.4, 129.0, 127.6, 127.4, 126.1, 118.0, 82.1, 69.3, 33.4, 25.9; MS: m/z : [M]⁺, 119.14; **3ao'**: ¹H NMR (400 MHz, CDCl₃) δ 8.89 (d, J = 4.4 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.71 (t, J = 7.2 Hz, 1H), 7.58–7.55 (m, 2H), 5.63 (t, J = 7.2 Hz, 1H), 4.26–4.21 (m, 1H), 4.09–4.03 (m, 1H), 2.67–2.59 (m, 1H), 2.13–1.97 (m, 2H), 1.91–1.83 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 150.5, 149.4, 148.2, 130.3, 128.9, 126.3, 125.6, 123.2, 116.5, 76.7, 69.0, 33.9, 26.0; MS: m/z : [M]⁺, 119.11; **3ao''**: ¹H NMR (400 MHz, CDCl₃) δ 8.09 (t, J = 7.2 Hz, 1H), 7.90 (t, J = 8.8 Hz, 1H), 7.74–7.66 (m, 2H), 7.51 (t, J = 7.6 Hz, 1H), 5.63–5.57 (m, 1H), 5.18–5.14 (m, 1H), 4.29–4.16 (m, 2H), 4.08–4.01 (m, 2H), 2.66–2.57 (m, 1H), 2.54–2.45 (m, 1H), 2.16–2.00 (m, 5H), 1.93–1.82 (m, 1H); MS: m/z : [M]⁺, 269.07.

Mechanistic studies

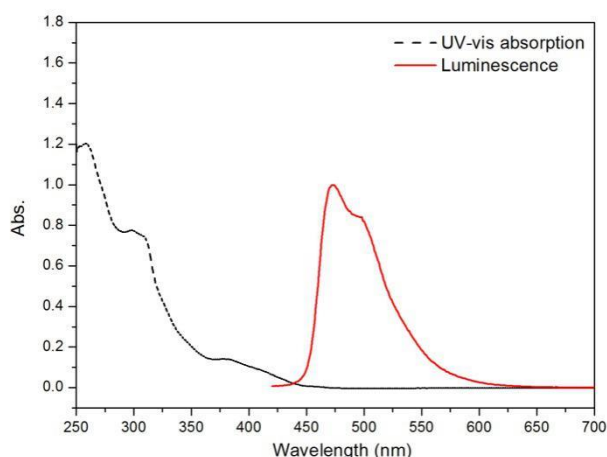
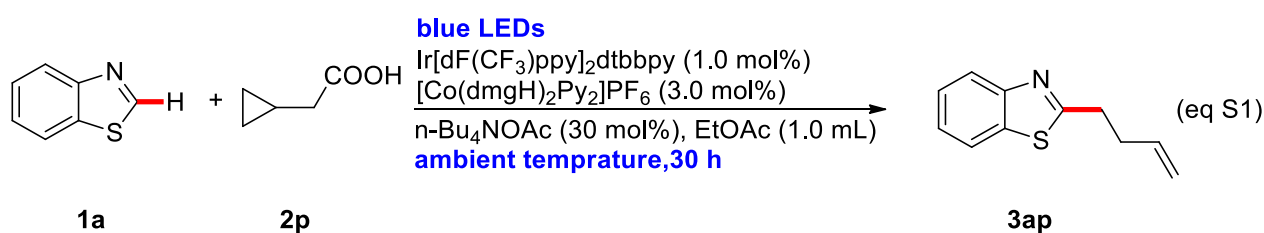


Figure S3. UV-vis absorption (left) and luminescence (right) spectra of Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ in degassed CH₃CN/EtOAc.

Radical Clock Experiments:



Substrate **1a** (0.20 mmol, 1.0 equiv), **2p** (0.2 mmol, 2.0 equiv), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (0.002 mmol, 1 mol%) and [Co(dmgh)₂Py₂](PF₆) (0.006 mmol, 3 mol%) and n-Bu₄NOAc (0.06 mmol, 30 mol%) were added into a 50 mL reaction tube. Then anhydrous EtOAc (1.0 mL) was added to the reaction tube via syringe in glove box. The reaction mixture was stirred for 30 h on Watecs Parallel Light Reactor at ambient temperature. **3ap**: yellow liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.48–7.44 (m, 1H), 7.38–7.33 (m, 1H), 5.95–5.88 (m, 1H), 5.14 (dd, *J* = 17.2 Hz, *J* = 1.6 Hz, 1H), 5.06 (dd, *J* = 10.0 Hz, *J* = 1.2 Hz, 1H), 3.22 (t, *J* = 8.0 Hz, 2H), 2.68–2.62 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 171.2, 153.2, 136.4, 135.2, 125.9, 124.7, 122.6, 121.5, 116.2, 33.7, 33.4; MS: *m/z*: [M]⁺, 189.10.

Quantum yield measurements:

Determination the light intensity at 402 nm:

According to the procedure of Yoon,¹² the photon flux of the spectrophotometer was determined by standard ferrioxalate actinometry.¹³ A 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (1.47 g) in H₂SO₄ (20 mL of a 0.05 M solution). A buffered solution of 1,

10-phenanthroline was prepared by dissolving phenanthroline (25 mg) and sodium acetate (5.63 g) in H₂SO₄ (25 mL of a 0.5 M solution). Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, the ferrioxalate solution (2.0 mL) was placed in a cuvette and irradiated for 90 seconds at $\lambda = 402$ nm. After irradiation, the phenanthroline solution (0.35 mL) was added to the cuvette and the mixture was allowed to rest in the dark for 1 hour to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured. Conversion was calculated using eq S2.

$$\text{mol Fe}^{2+} = \frac{V \cdot \Delta A}{l \cdot \epsilon} = \frac{0.00235 \text{ L} \cdot 1.884}{1.000 \text{ cm} \cdot 11,100 \text{ L} \cdot \text{mol}^{-1} \text{ cm}^{-1}} = 3.99 \times 10^{-7} \text{ mol} \quad (\text{eq S2})$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.000 cm), and ϵ is the molar absorptivity at 510 nm (11,100 L mol⁻¹cm⁻¹). The photon flux can be calculated using eq S3.

$$\text{Photon flux} = \frac{\text{mol Fe}^{2+}}{\Phi \cdot t \cdot f} = \frac{3.99 \times 10^{-7} \text{ mol}}{1.07 \cdot 90.0 \text{ s} \cdot 0.99356} = 4.17 \times 10^{-9} \text{ einstein s}^{-1} \quad (\text{eq S3})$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.07 for a 0.15 M solution at $\lambda = 402$ nm), t is the time (90.0 s), and f is the fraction of light absorbed at $\lambda = 402$ nm (eq S4).

Determination of fraction of light absorbed at 450 nm for the ferrioxalate solution:

The fraction of light absorbed (f) by this solution was calculated using eq S4, where A is the measured absorbance of the above ferrioxalate solution at 402 nm which was measured to be 2.1909 (Figure S4), indicating the fraction of light absorbed (f) is 0.99356. Finally, the photon flux was calculated to be 4.17×10^{-9} einstein s⁻¹.

$$f = 1 - 10^{-A} = 0.98280 \quad (\text{eq S4})$$

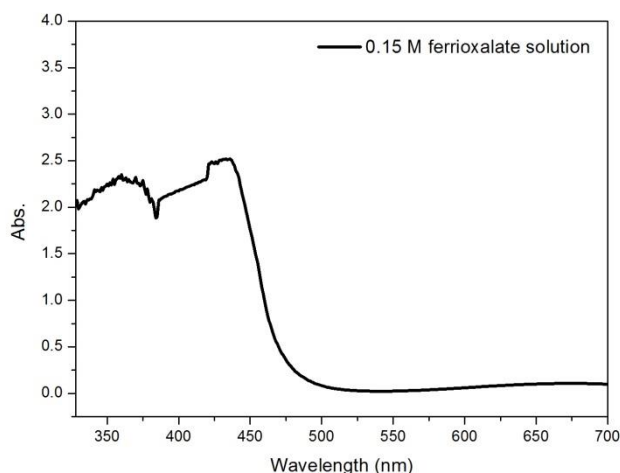


Figure S4. UV-vis spectrum of 0.15 M ferrioxalate solution.

Quantum yield calculation:

A cuvette was charged with **1a** (0.2 mmol), **2a** (0.4 mmol), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (0.002 mmol), [Co(dmgH)₂Py₂](PF₆) (0.006 mmol), n-Bu₄NOAc (0.06 mmol), and 1.0 mL degassed EtOAc in glovebox under Ar atmosphere. The cuvette was then capped with a PTFE stopper. The sample was irradiated (λ = 402 nm, slit width = 10.0 nm) for 27,000 s (7.5 h). After irradiation, the yield of product formed was determined by ¹H NMR to be 24% using 1,1,2,2-tetrachloroethane as an internal standard. The quantum yield was determined using eq S5.

$$\Phi = \frac{\text{mol prod}}{\text{flux} \cdot t \cdot f} = \frac{0.24 \times 0.2 \times 10^{-3} \text{ mol}}{4.17 \times 10^{-9} \text{ einstein s}^{-1} \cdot 27,000 \text{ s} \cdot 0.99404} = 0.43 \quad (\text{eq S5})$$

The quantum yield Φ for the reaction was calculated to be 0.43.

Absorbance of catalyst:

The absorbance of Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ in EtOAc was measured at the reaction concentration of 2×10^{-3} M (Figure S5). The absorbance at 402 nm is 2.2247, indicating the fraction of light absorbed (f) is 0.99404.

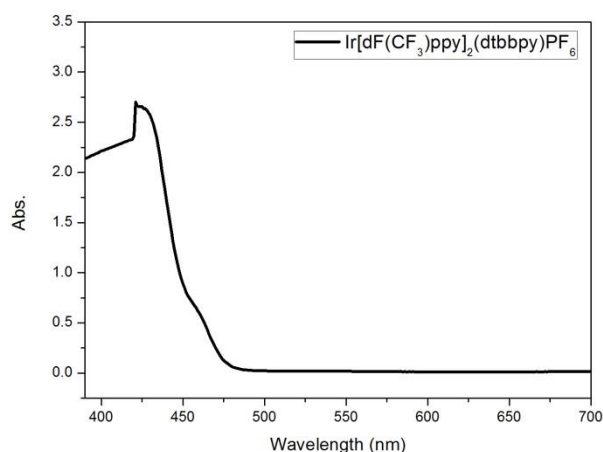
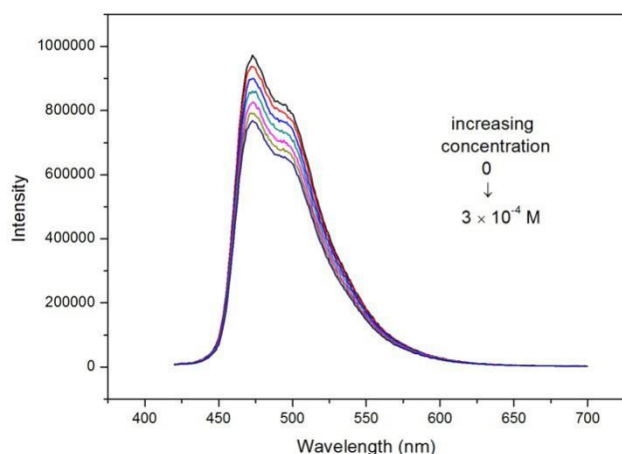


Figure S5. UV-vis absorption of 2×10^{-3} M $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$.

Emission Quenching Experiments:

Emission intensities were recorded using a spectrofluorimeter. All $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ solutions were excited at 402 nm and the emission intensity at 472 nm was observed. A mixture solvent of EtOAc/ CH_3CN (1:1) was selected as solvent, and the solvent was degassed with a stream of argon for 30 min. In a typical experiment, the emission spectrum of the sample was collected after the sample was degassed with a stream of argon for 15 minutes. First, the emission spectrum of a 2.5×10^{-5} M solution of $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ in EtOAc/ CH_3CN (1:1) was collected. Then, appropriate amount of quencher was added to the measured solution and the emission spectrum of the sample was collected.



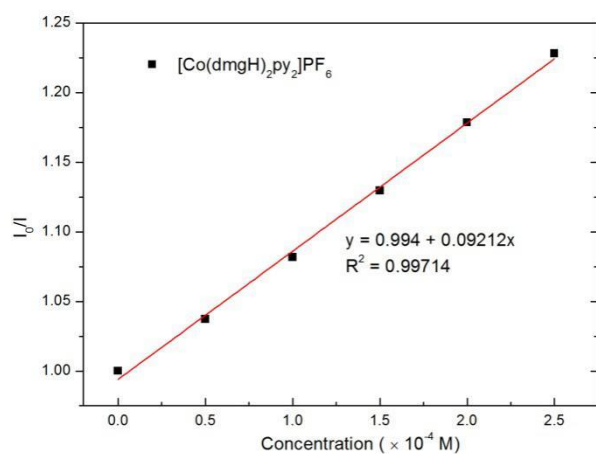


Figure S6. $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ emission quenching by $[\text{Co}(\text{dmgh})_2\text{Py}_2]\text{PF}_6$.

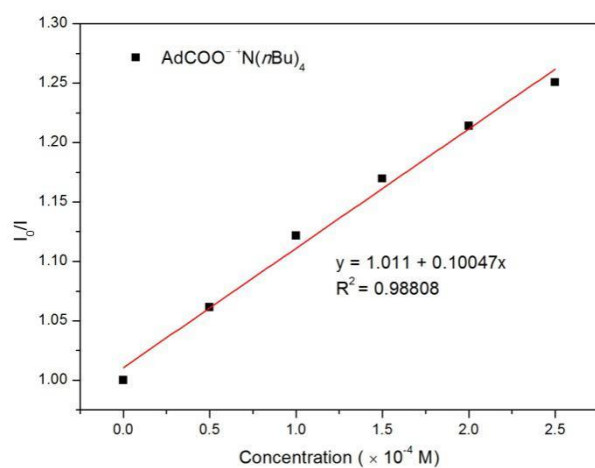
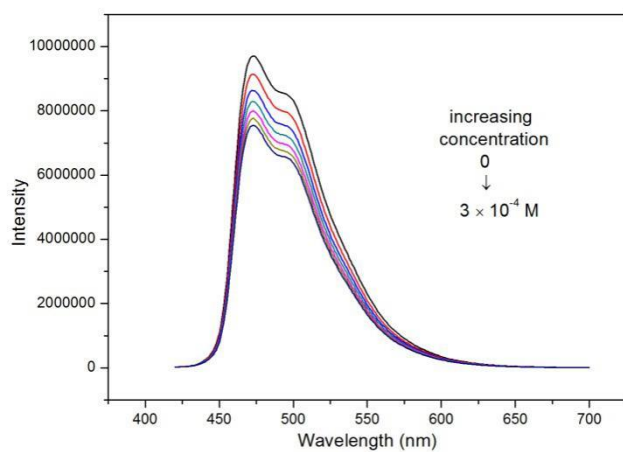


Figure S7. $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ emission quenching by $\text{AdCO}_2\text{N}(\text{n-Bu})_4$.

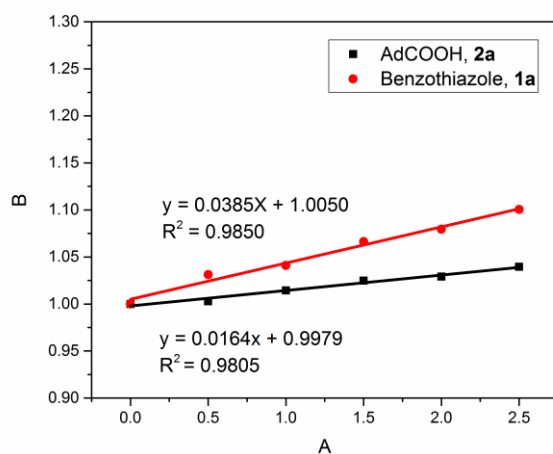
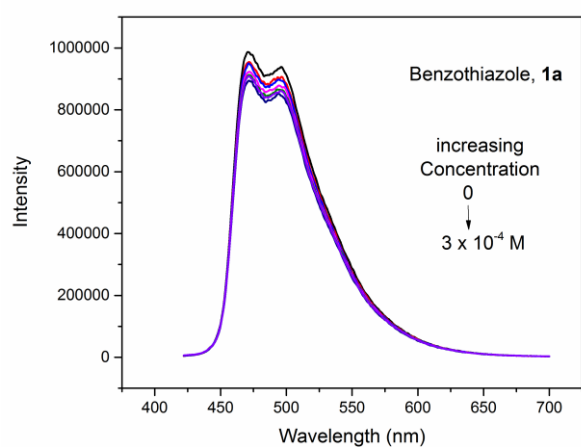
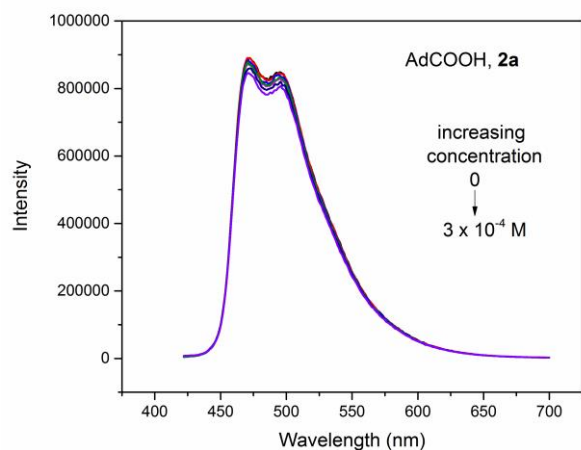


Figure S8. Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ emission quenching by **2a** and **1a**.

Cyclic Voltammetry (CV) Experiments:

As the solvent of EtOAc failed undergoing cyclic voltammetry experiments and considering that CH₃CN displays the widest detection window for the reduction oxidation potentials,¹⁴ and the most reported

electrochemical data were detected in CH₃CN.¹⁵ Meanwhile, 43% yield of product was obtained in the mixture solvent of EtOAc/CH₃CN (1:1) in our work (Table 1, entry 19). Thus the reduction oxidation potentials of **1a**, **2a**, AdCOON(n-Bu)₄, Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ and the cobalt were detected in the mixture solvent of EtOAc/CH₃CN (1:1).

For the electrochemical measurements a three-electrode system connected to an electrochemical station was used. The reference electrode, Ag/AgNO₃ in 0.1 M AgNO₃, was calibrated versus Fc⁺/Fc⁰ using the same experimental conditions as for the sample. A glassy carbon electrode was used as working electrode. And a Pt wire was used as counter electrode. All electrochemical measurements were performed in EtOAc/CH₃CN under dry argon atmosphere.

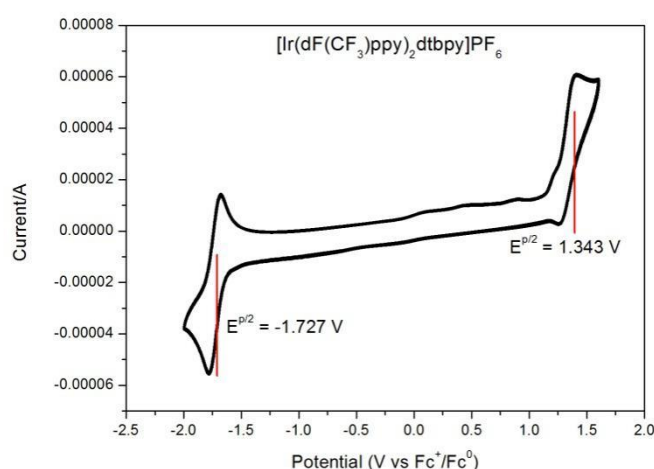


Figure S9. Cyclic voltammogram (CV) of 3 mM Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ in 0.1 M nBu₄PF₆ EtOAc/CH₃CN (1:1) solution under Ar. Conditions: working electrode: glassy carbon electrode; reference electrode: Ag⁺/Ag; scan rate = 100 mV/s. E_{p/2}^{Ir(III)/Ir(IV)} = + 1.74 V vs. SCE, E_{p/2}^{Ir(II)/Ir(III)} = - 1.33 V vs. SCE.

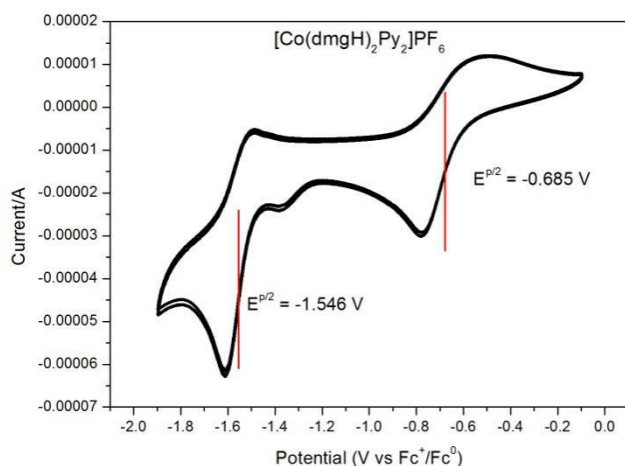


Figure S10. Cyclic voltammogram (CV) of 1 mM $[\text{Co}(\text{dmgh})_2\text{Py}_2]\text{PF}_6$ in 0.1 M nBu_4PF_6 EtOAc/ CH_3CN (1:1) solution under Ar. Conditions: working electrode: glassy carbon electrode; reference electrode: Ag^+/Ag ; scan rate = 100 mV/s. $E_{\text{p}/2}^{\text{Co(III)/Co(II)}} = -0.29$ V vs. SCE, $E_{\text{p}/2}^{\text{Co(II)/Co(I)}} = -1.15$ V vs. SCE.

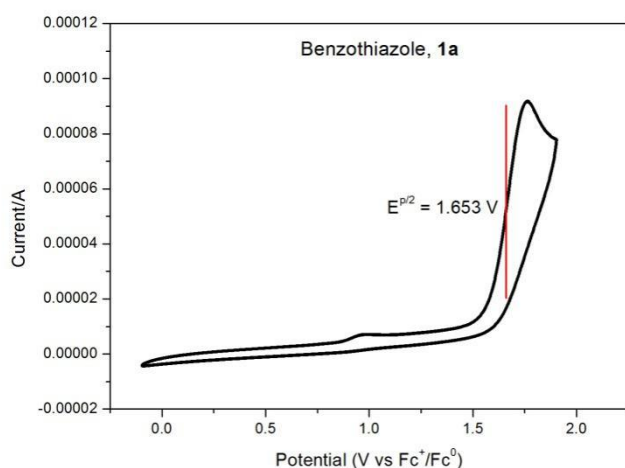


Figure S11. Cyclic voltammogram (CV) of 3 mM **1a** in 0.1 M nBu_4PF_6 EtOAc/ CH_3CN (1:1) solution under Ar. Conditions: working electrode: glassy carbon electrode; reference electrode: Ag^+/Ag ; scan rate = 100 mV/s. $E_{\text{p}/2}^{\text{1a}^+/\text{1a}} = +2.05$ V vs. SCE.

Preparation of $\text{AdCO}_2\text{nBu}_4\text{N}$

A mixture of AdCOOH (**2a**, 2 mmol, 1.0 equiv) and 40 wt% tetrabutylammonium hydroxide (TBA) MeOH solution (1.0 equiv) was stirred at room temperature for 4 h. The solvent was then evaporated in vacuo. The resulting product was dried under high vacuum and stored in glovebox. ^1H NMR (400 MHz, D_2O) δ 3.20–3.15 (m, 8H), 1.94 (s, 3H), 1.77 (d, $J = 2.4$ Hz, 6H), 1.71–1.59 (m, 14H), 1.38–1.29 (m, 8H), 0.93 (t, $J = 7.2$ Hz, 12H); ^{13}C NMR (100 MHz, D_2O) δ 58.1 (4C), 42.1, 39.5 (3C), 36.2 (3C), 28.1 (3C), 23.1 (4C), 19.1 (4C), 12.8 (4C).

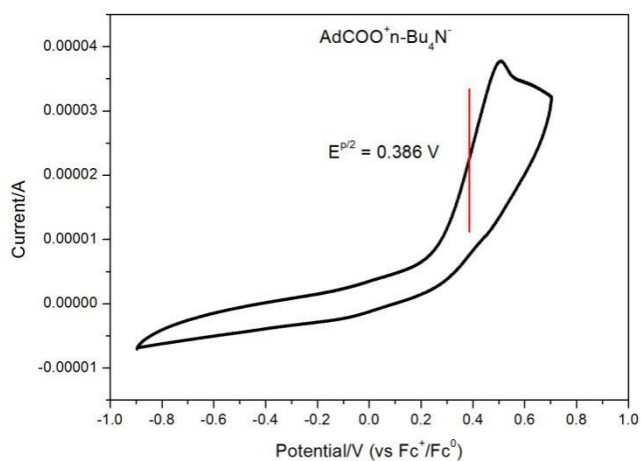


Figure S12. Cyclic voltammogram (CV) of 3 mM $\text{AdCO}_2n\text{-Bu}_4\text{N}$ in 0.1 M nBu_4PF_6 EtOAc/ CH_3CN (1:1) solution under Ar. Conditions: working electrode: glassy carbon electrode; reference electrode: Ag^+/Ag ; scan rate = 100 mV/s. $E_{\text{p}/2}^{\text{AdCOO}^\bullet/\text{AdCOO}^-} = +0.79$ V vs. SCE.

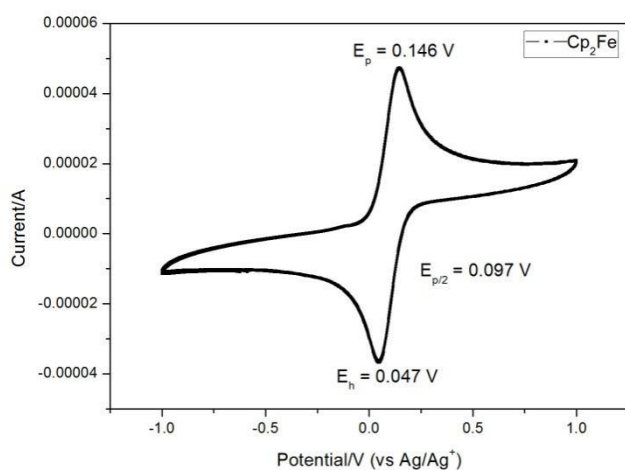
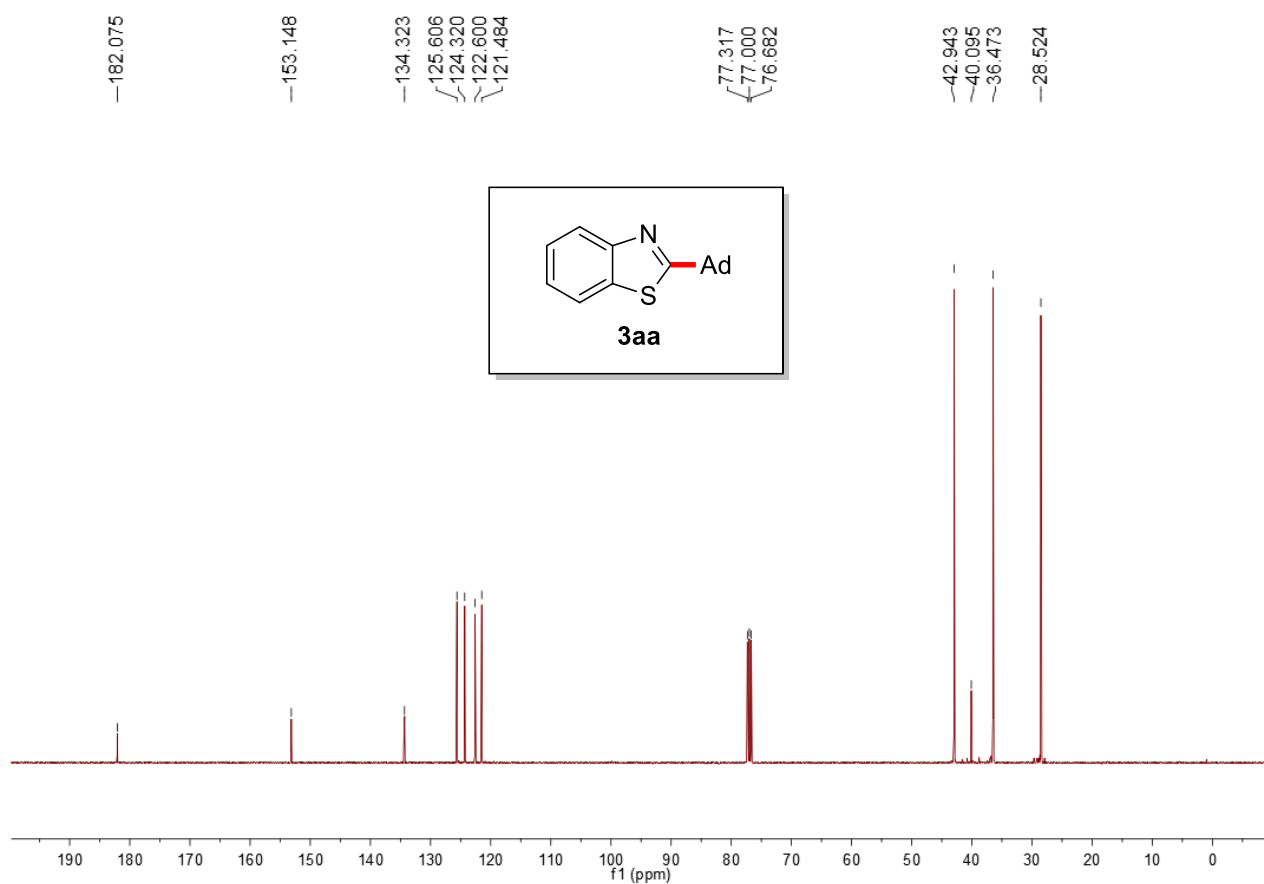
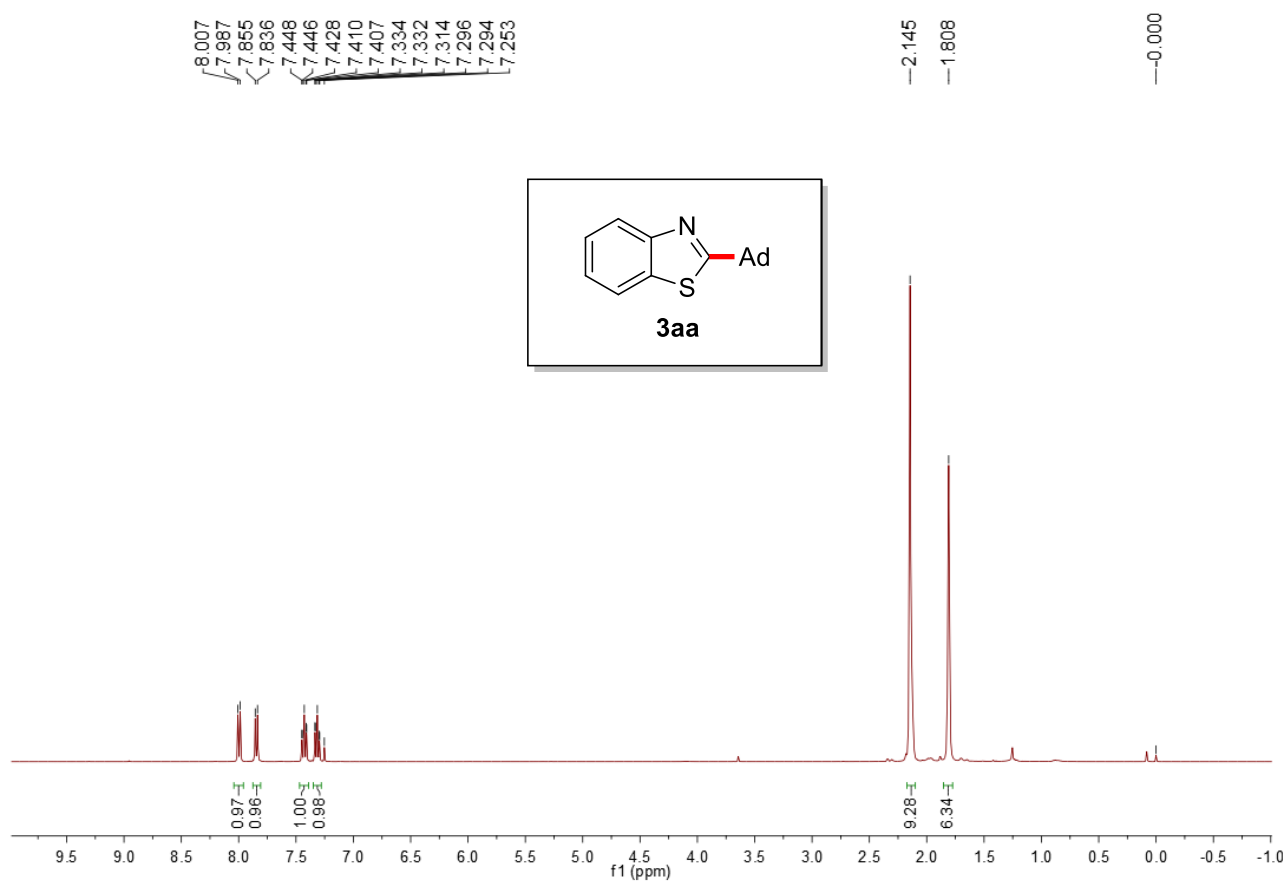


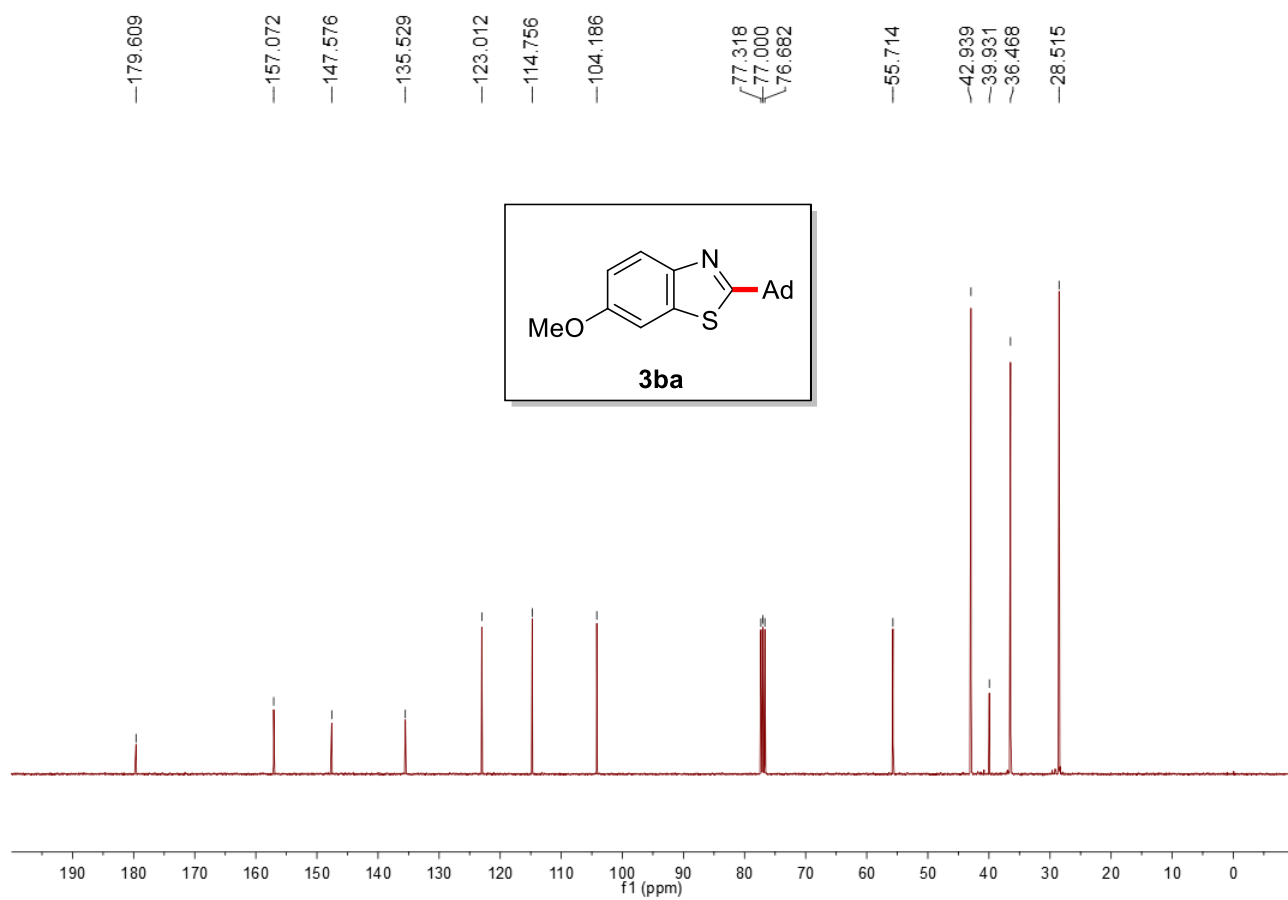
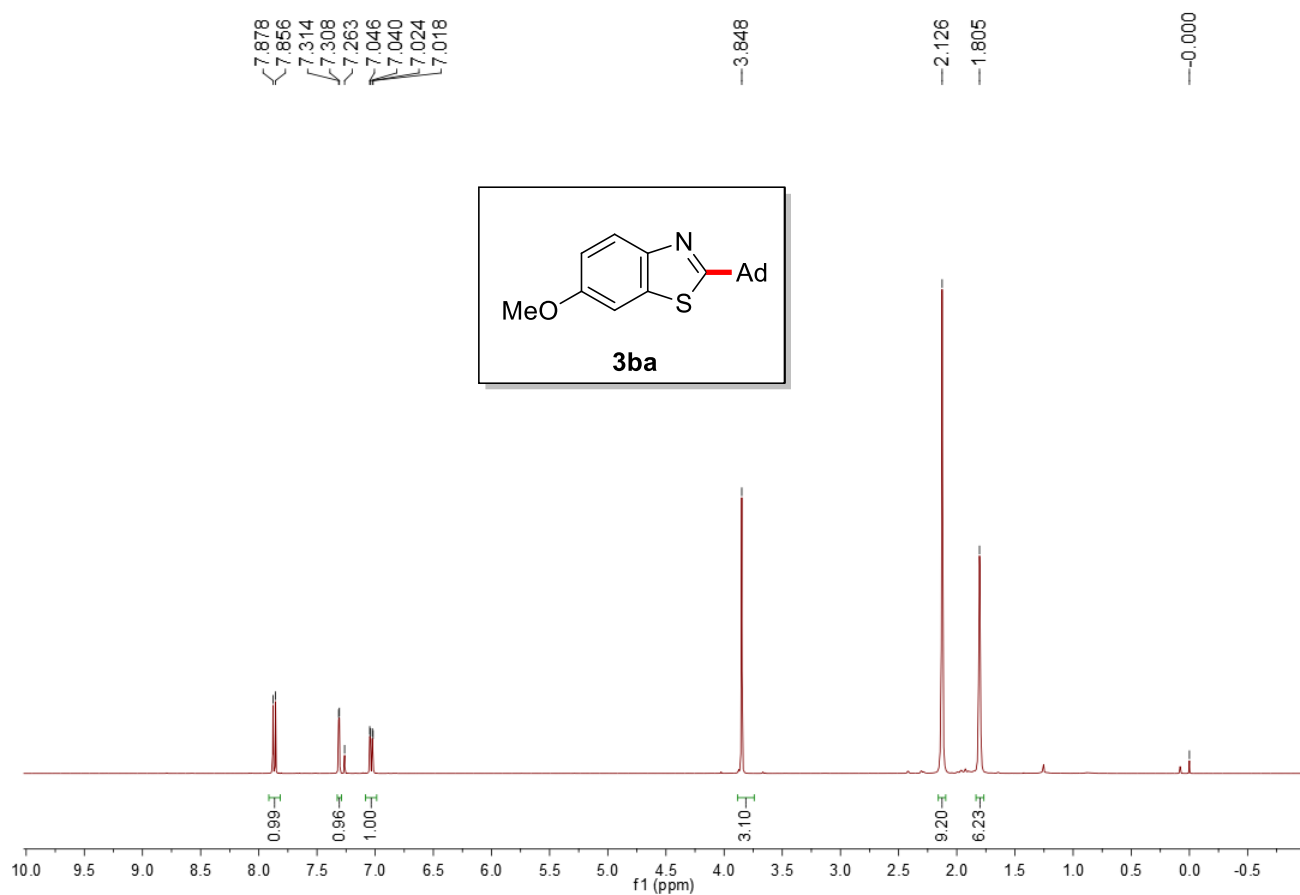
Figure S13. CV spectra of 3 mM Cp_2Fe in 0.1 M nBu_4PF_6 in degassed EtOAc/ CH_3CN with scan rate 100 mV/s.

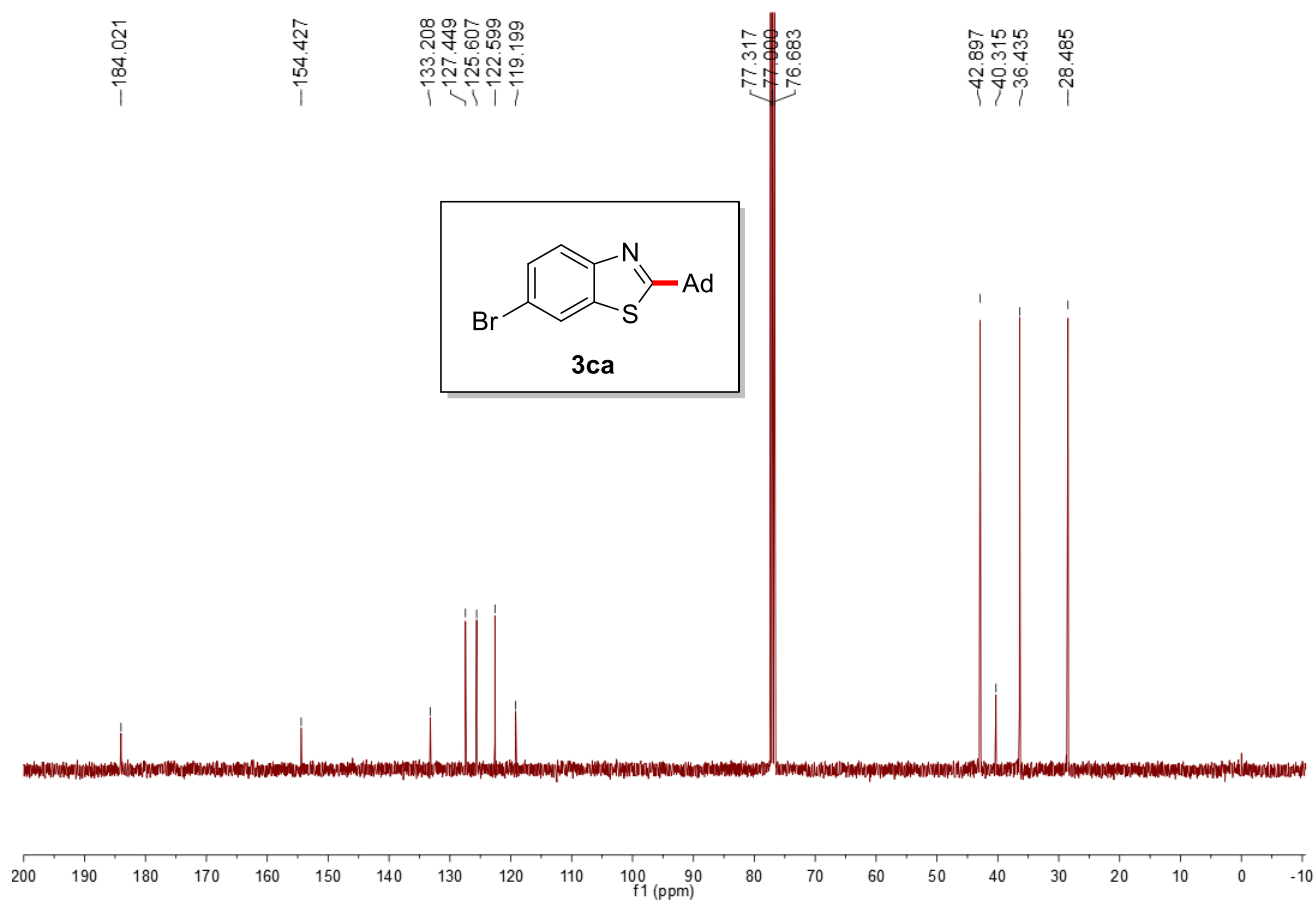
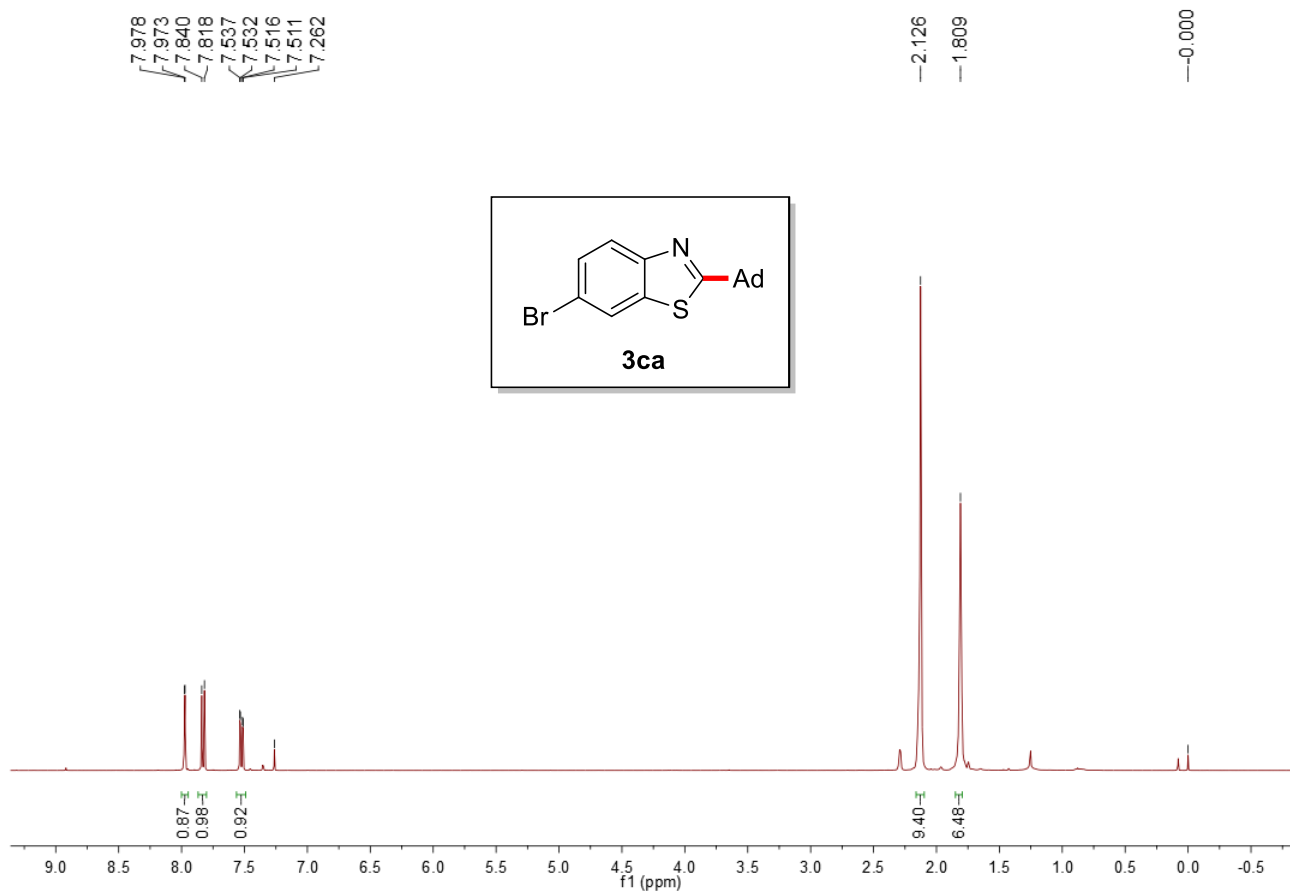
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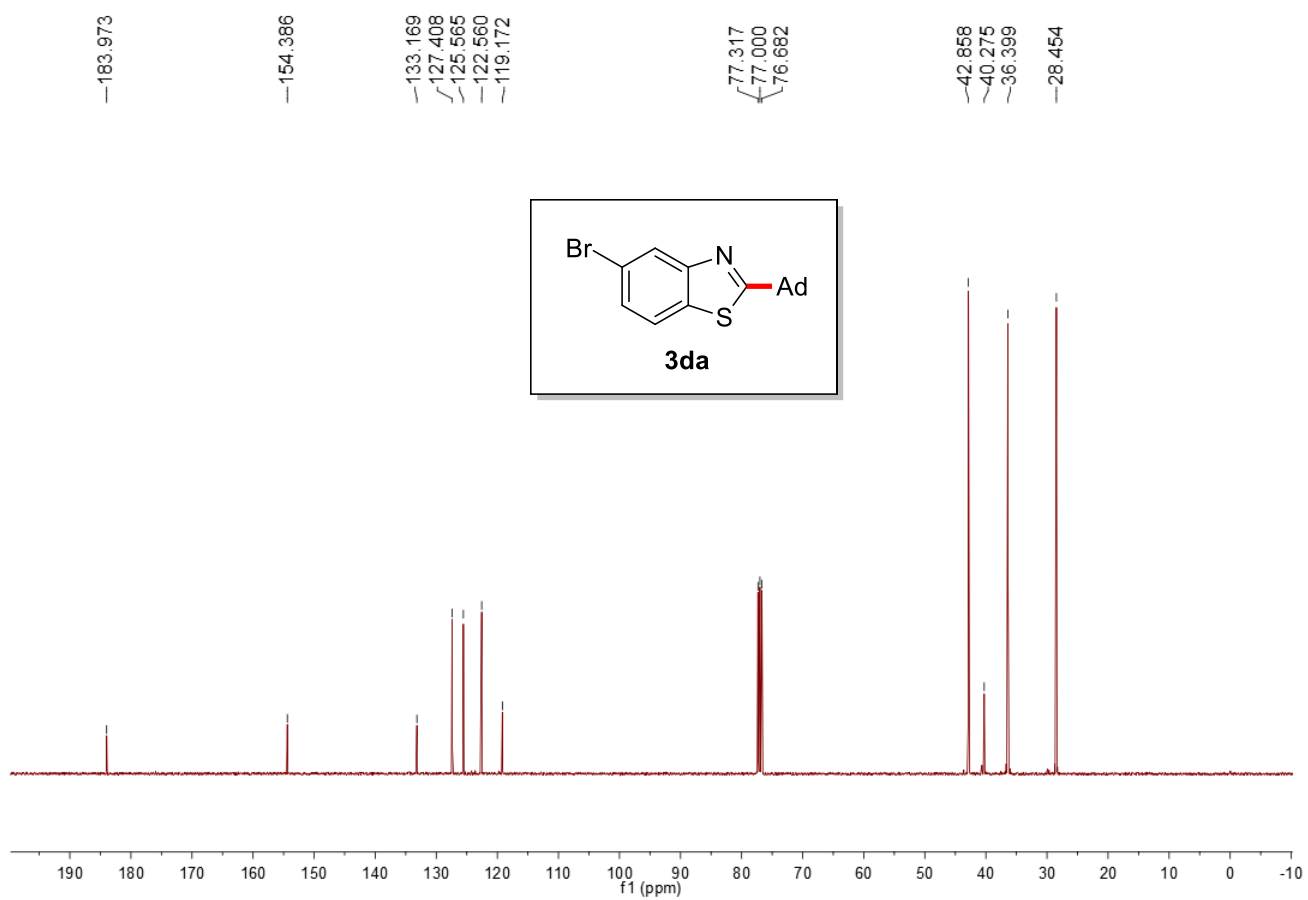
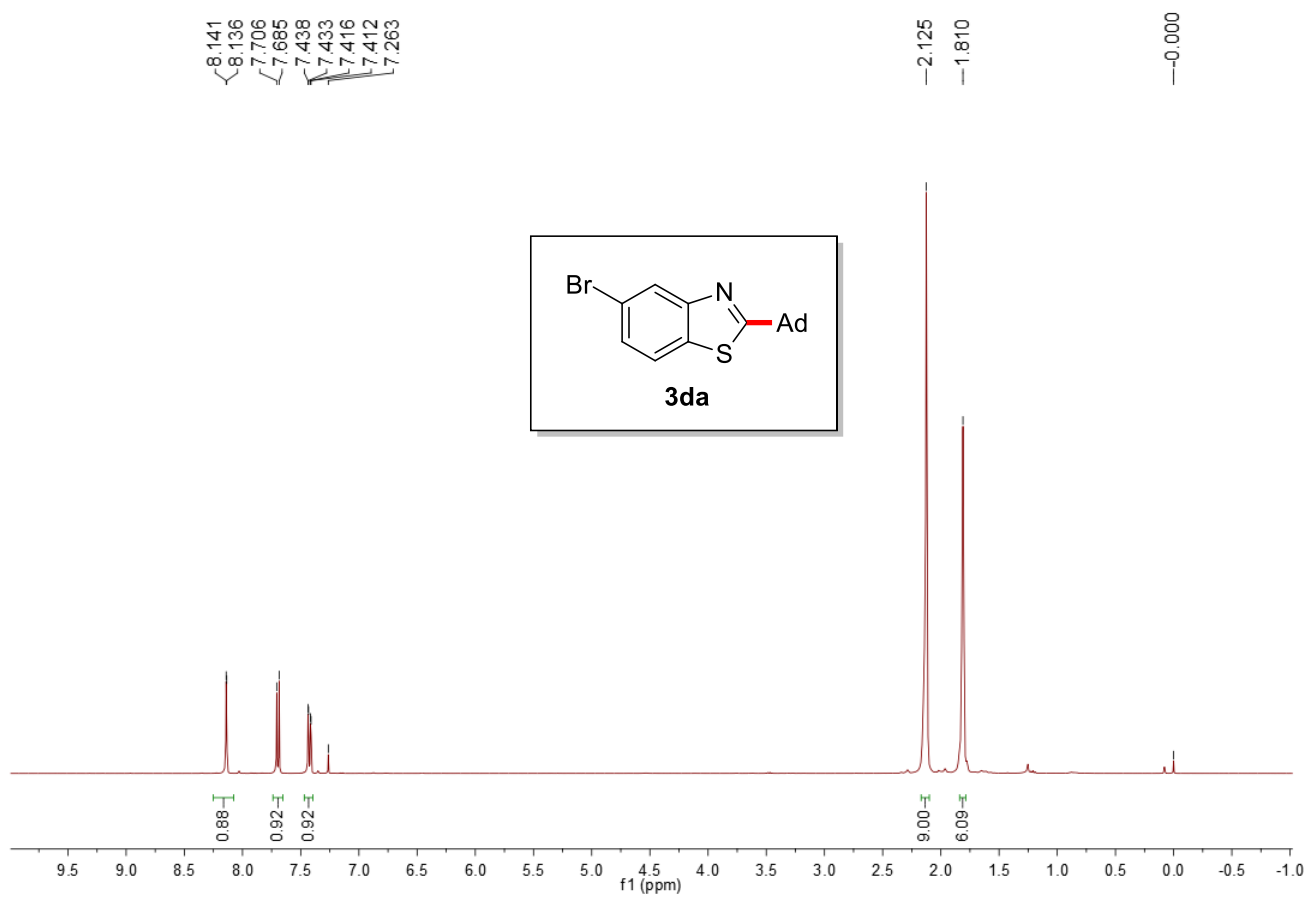
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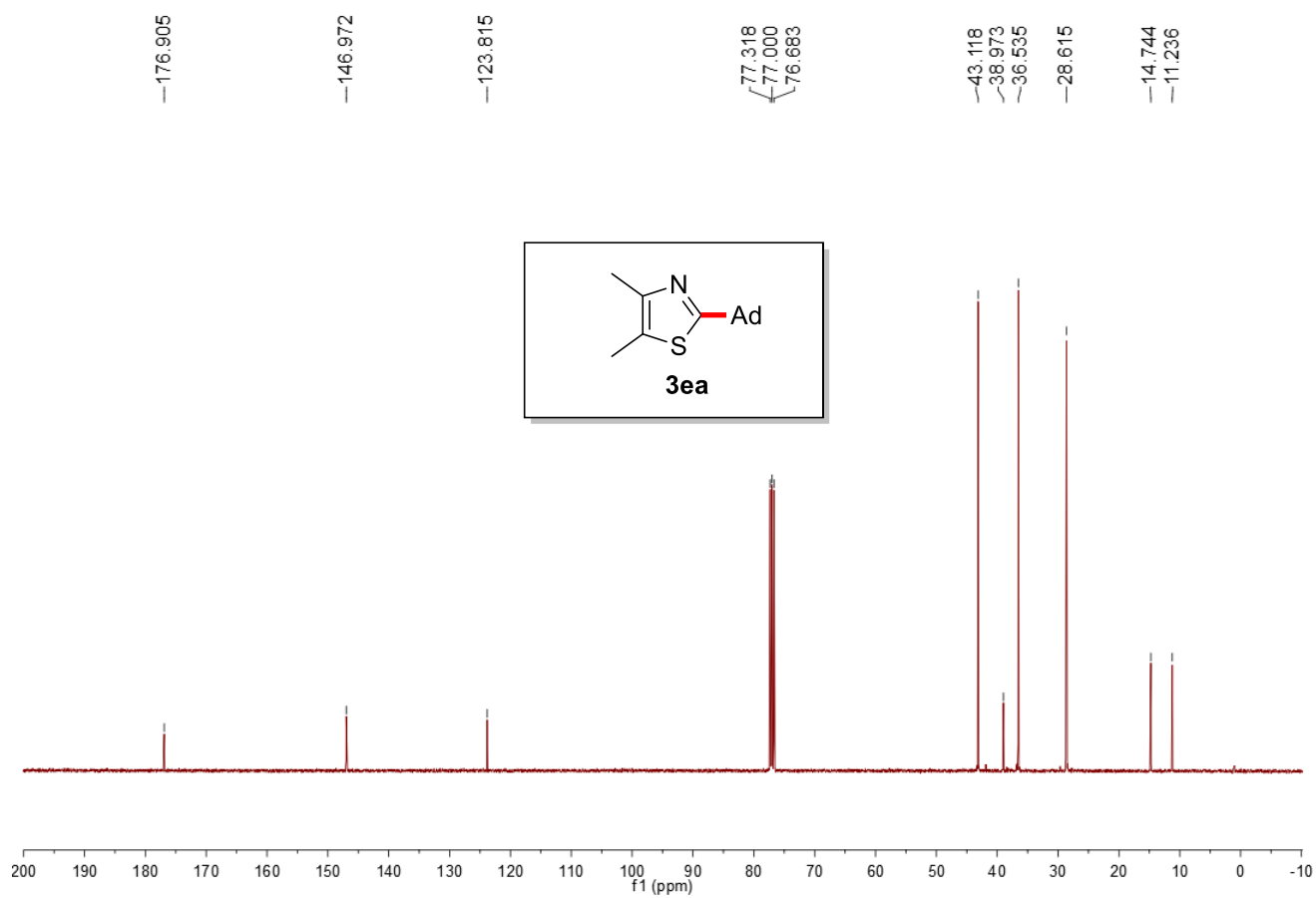
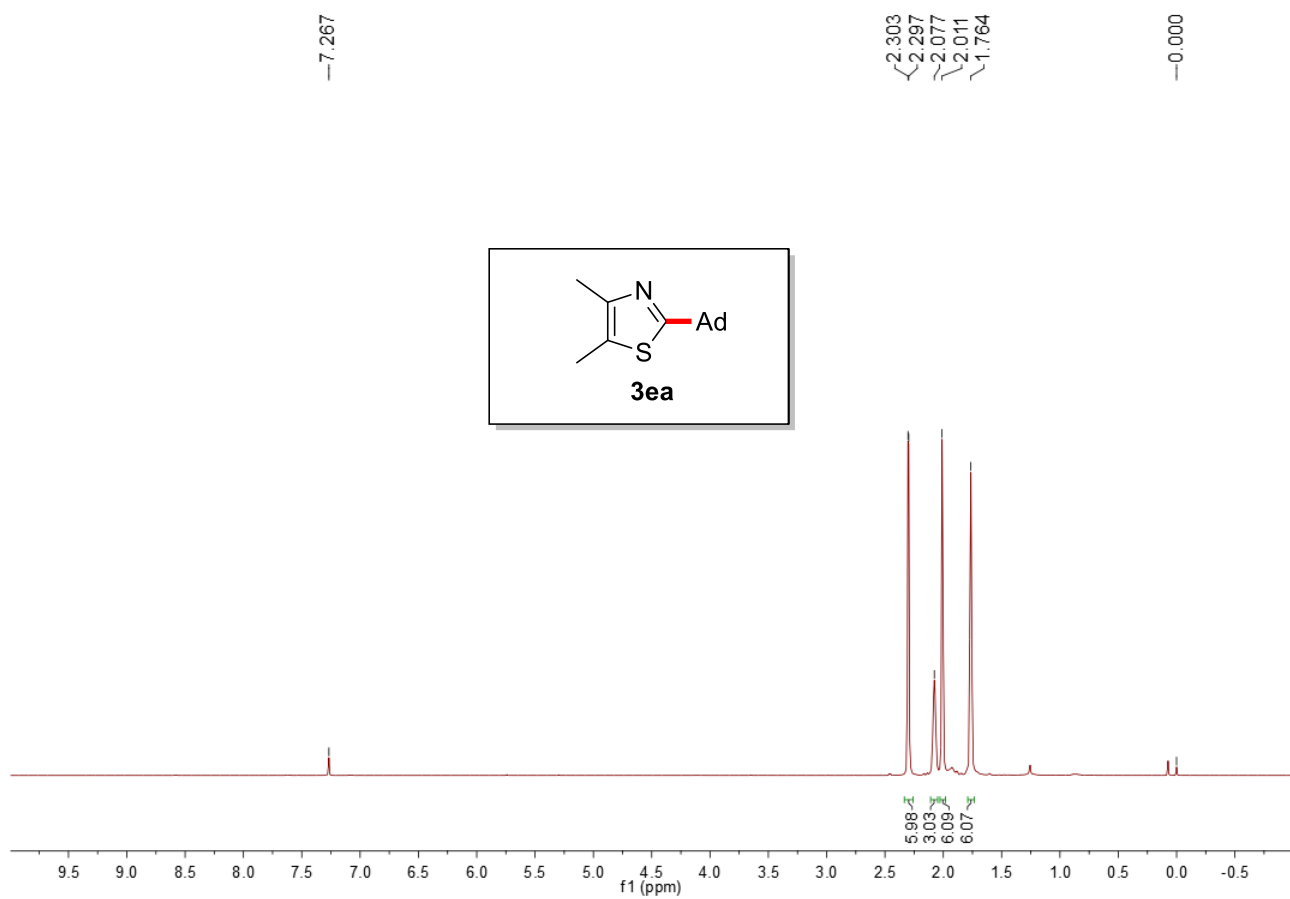
Spectrum

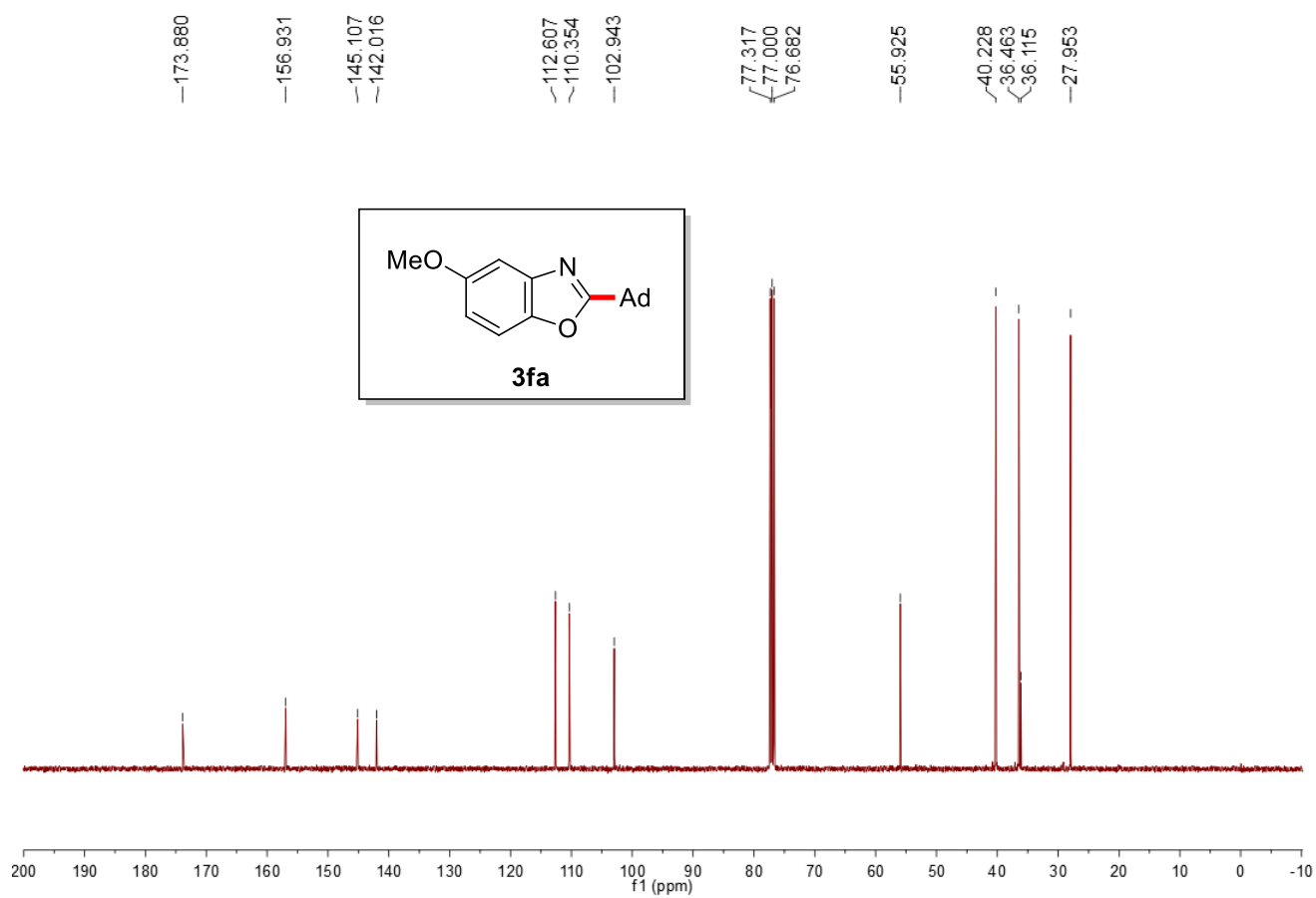
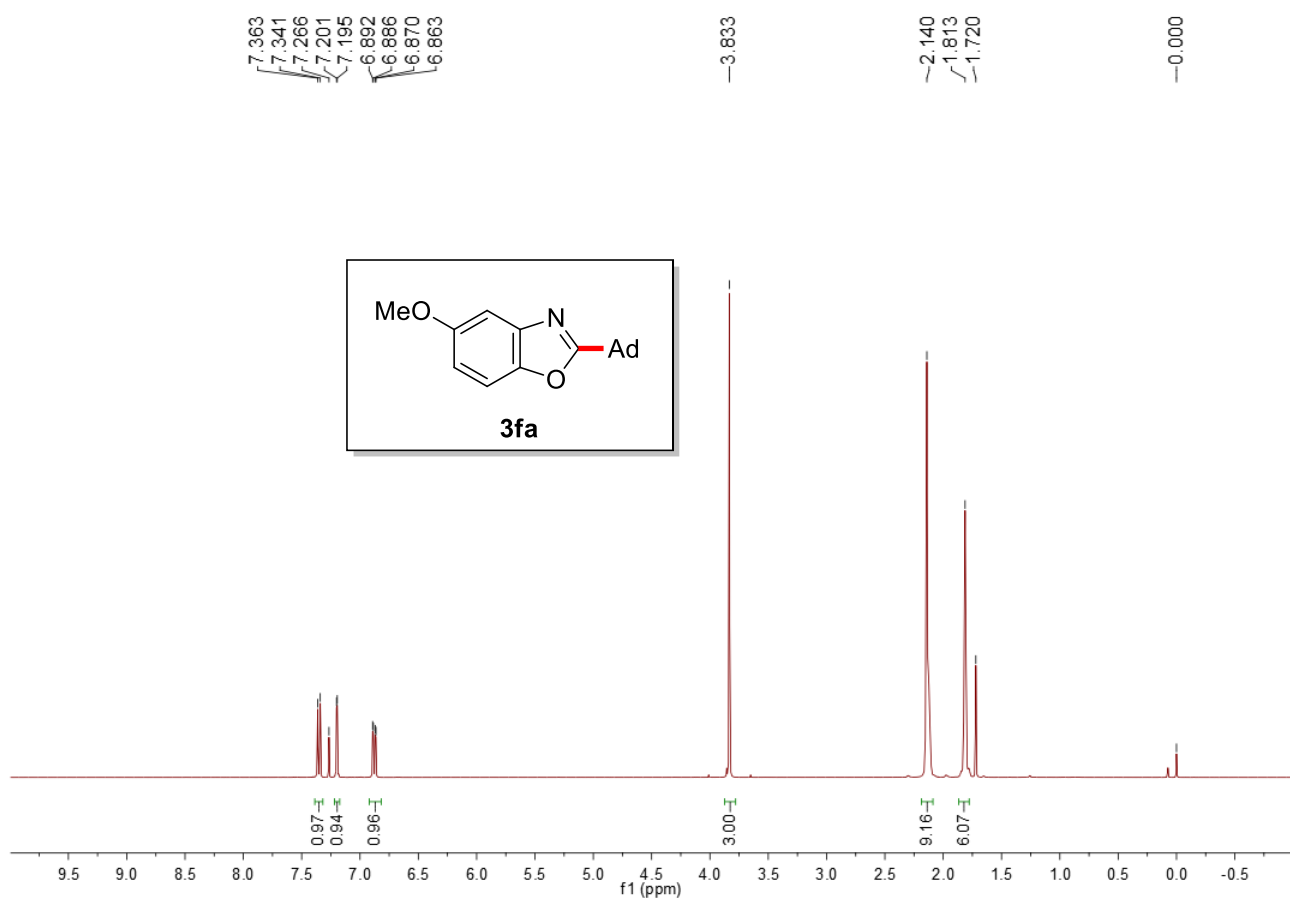


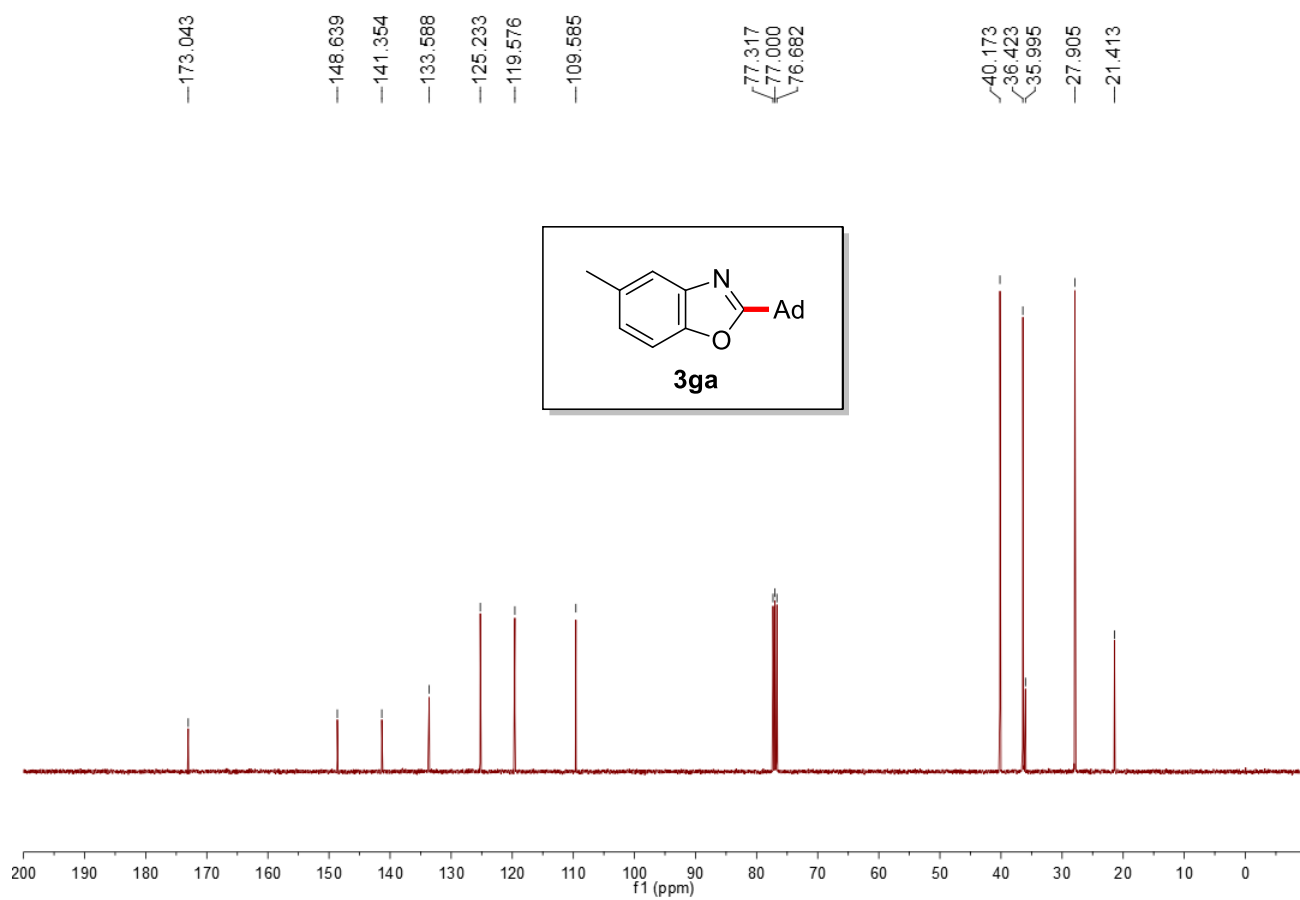
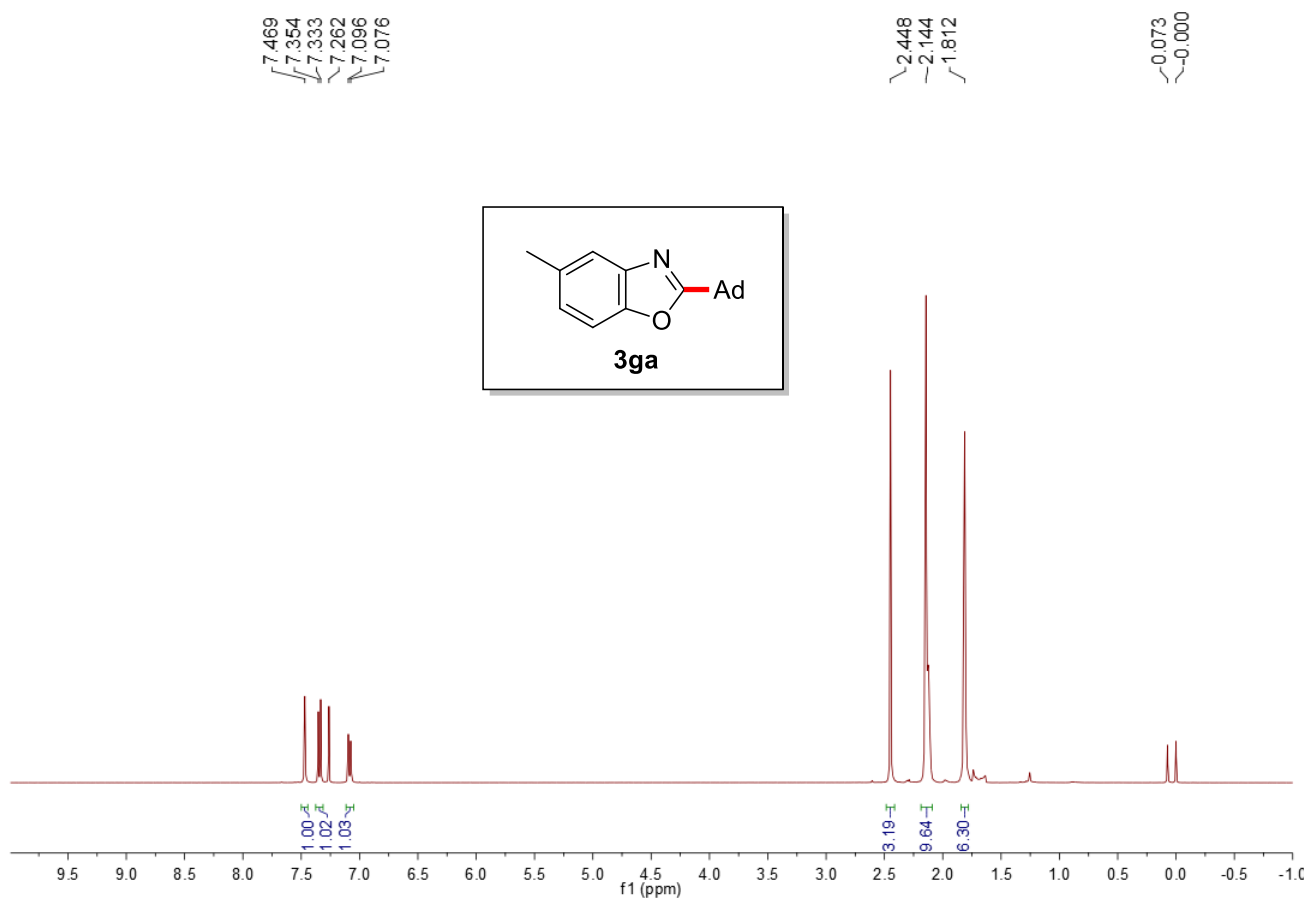


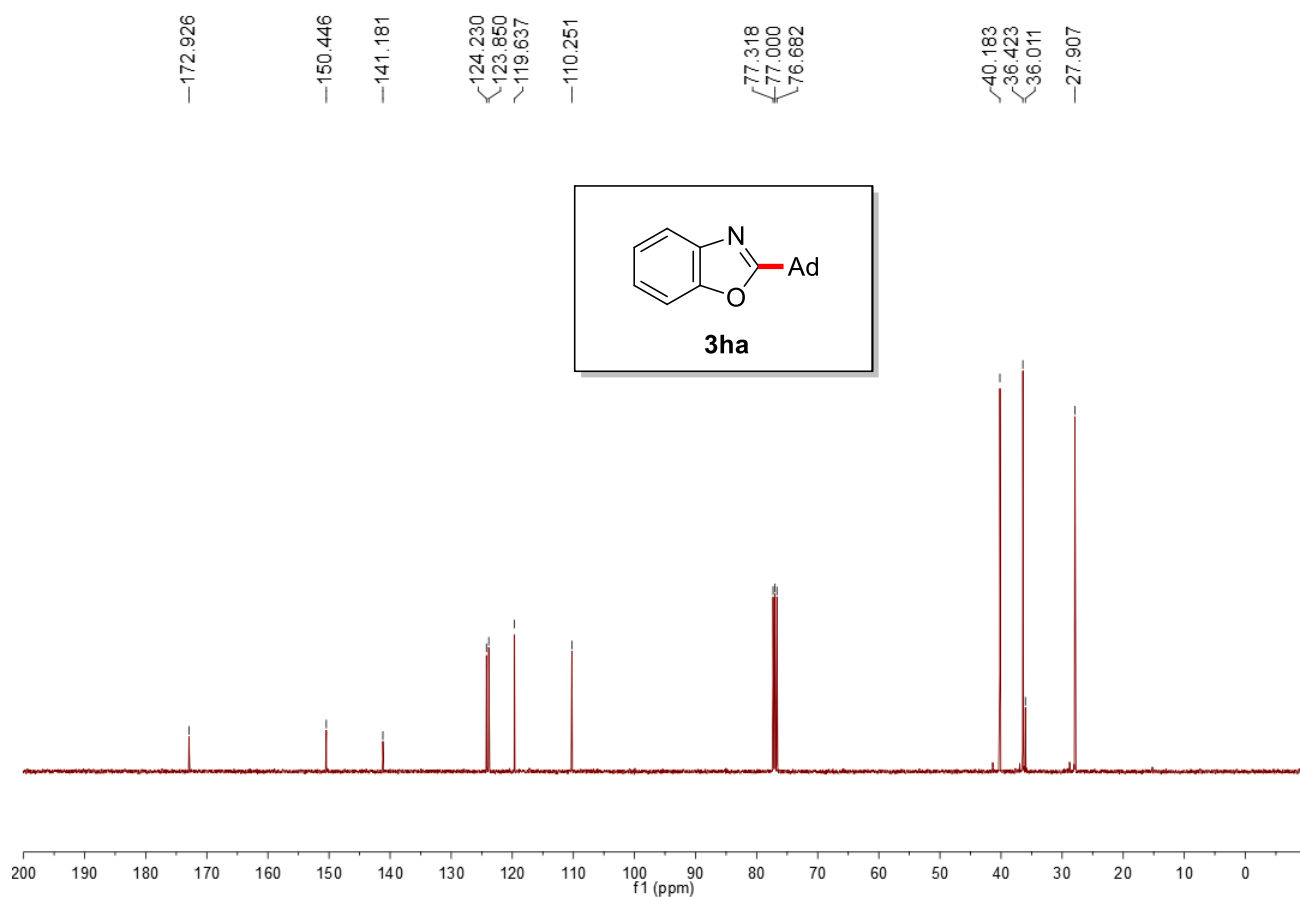
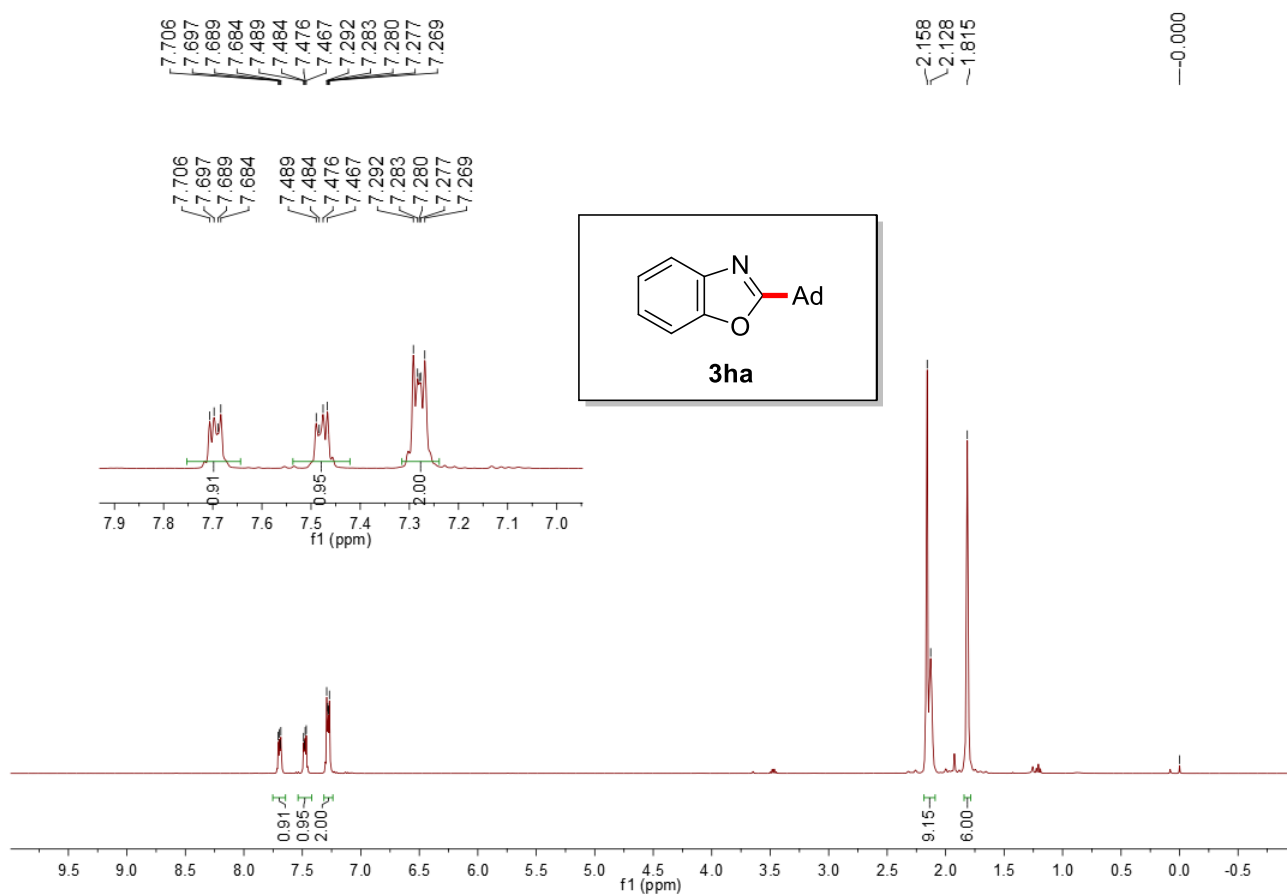


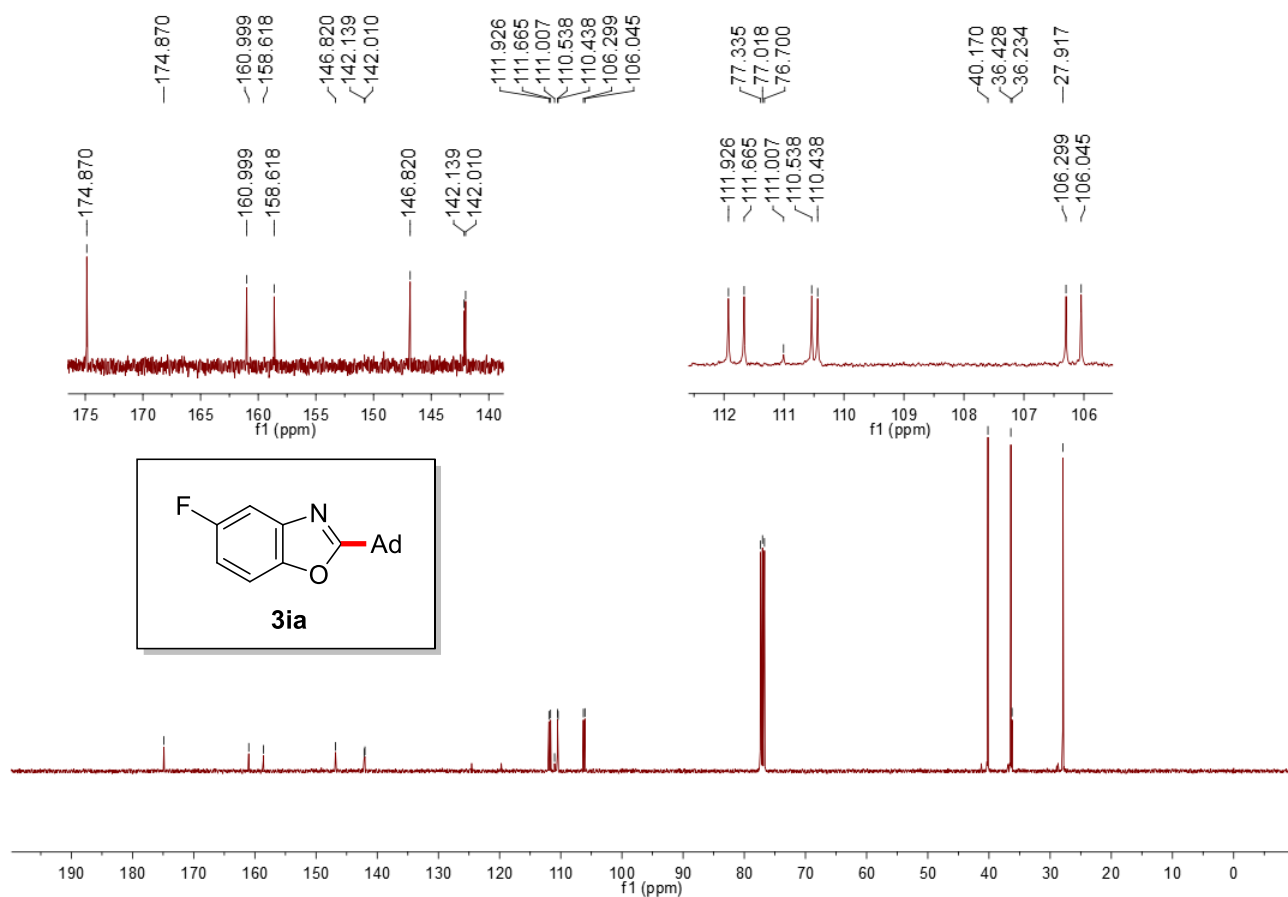
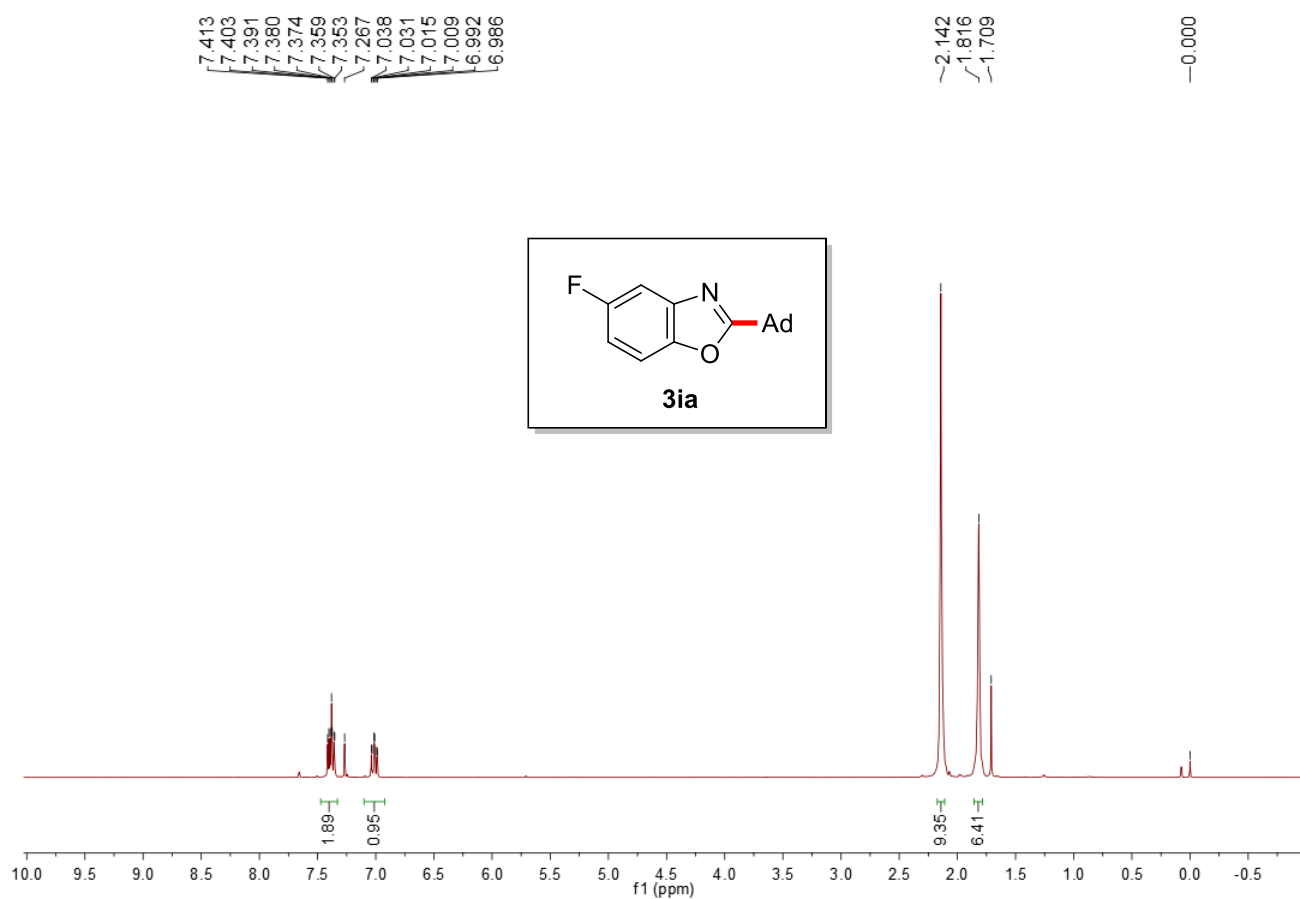


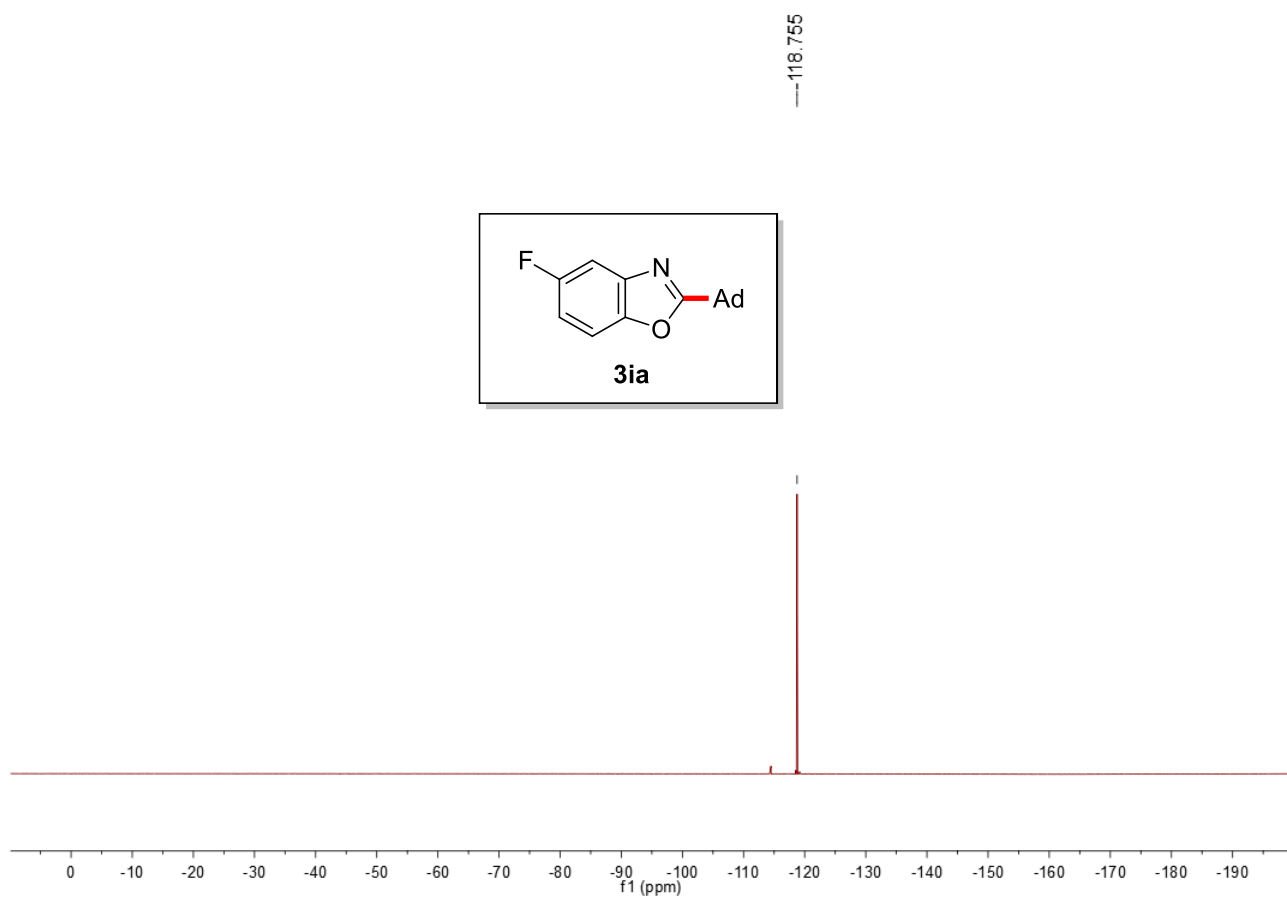


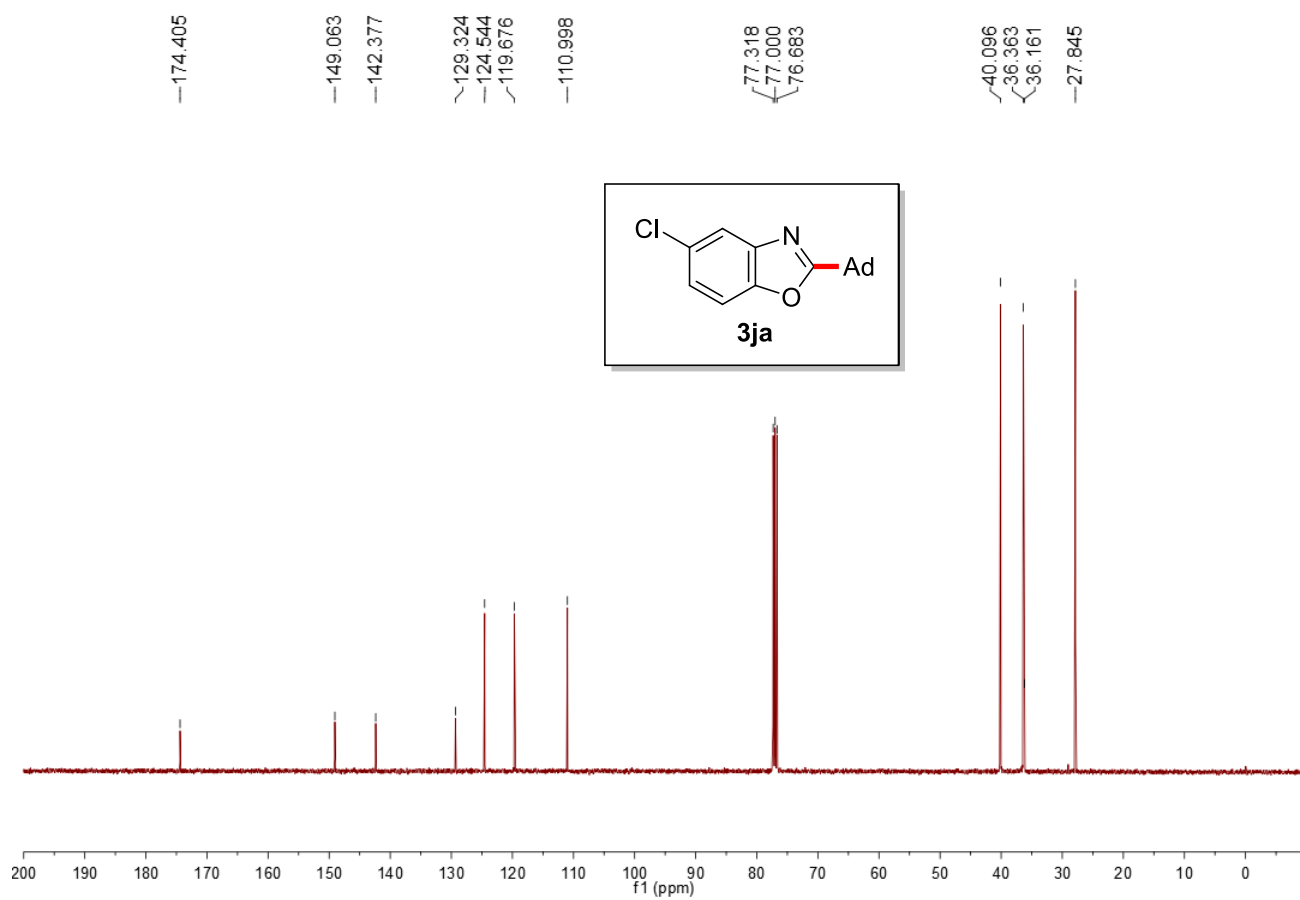
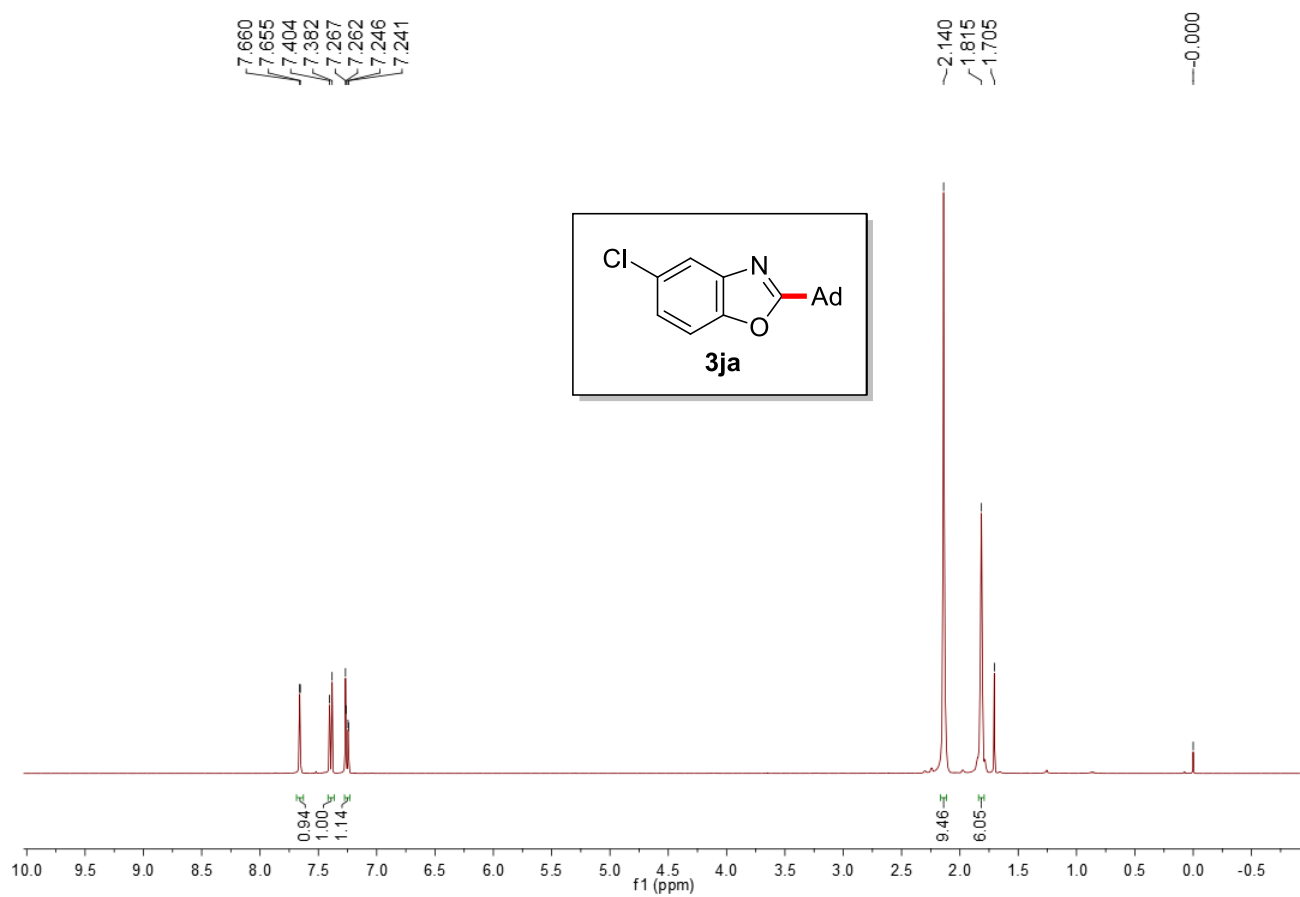


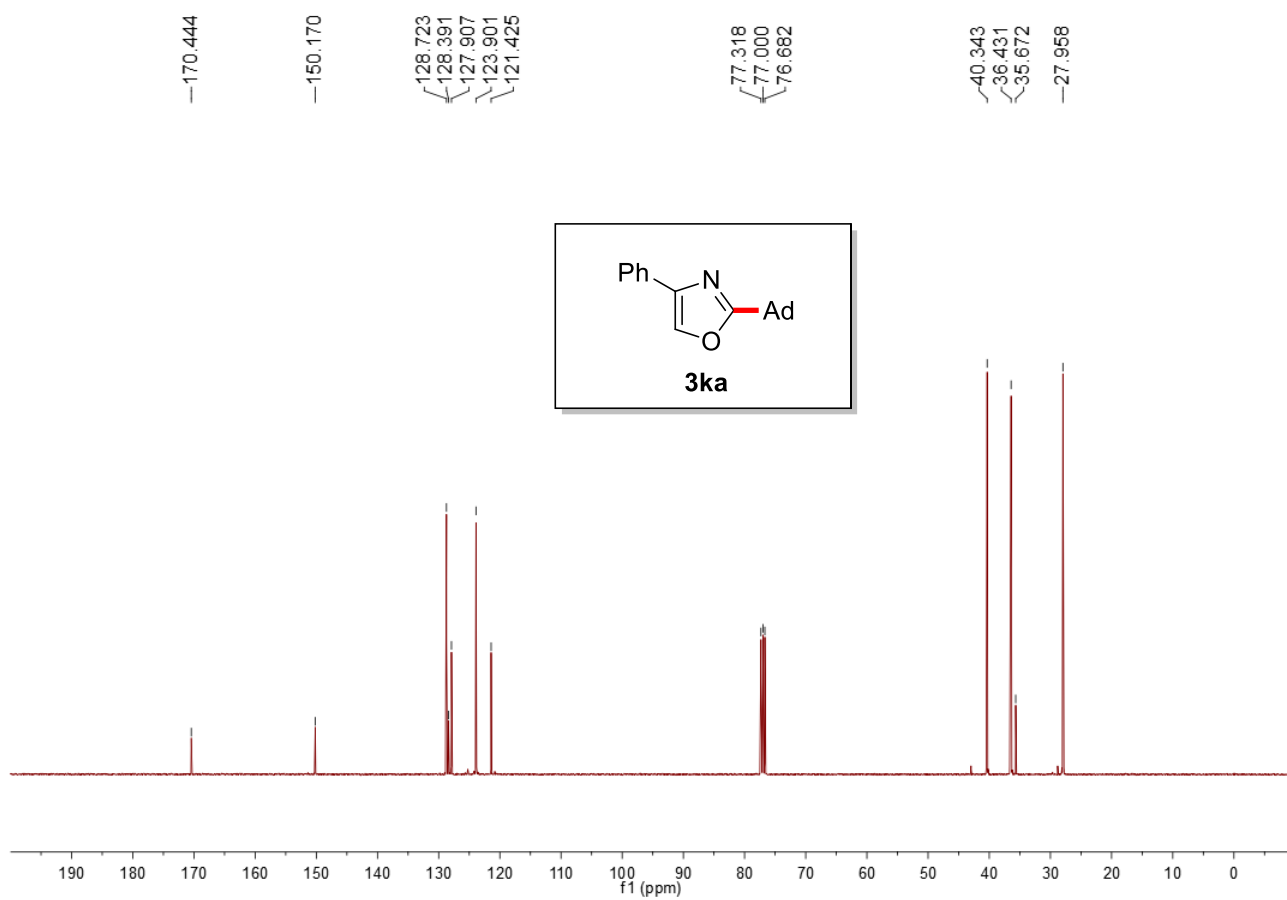
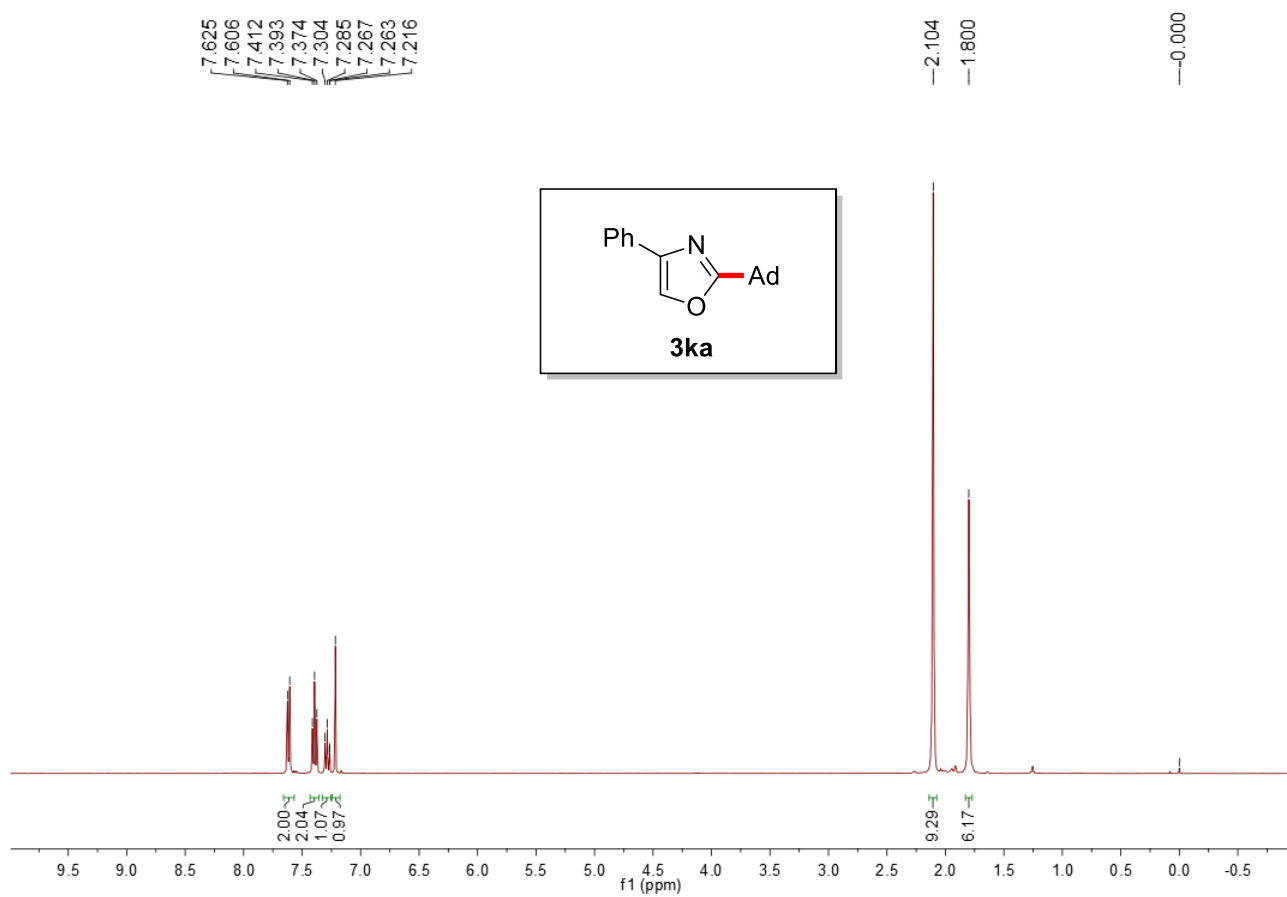


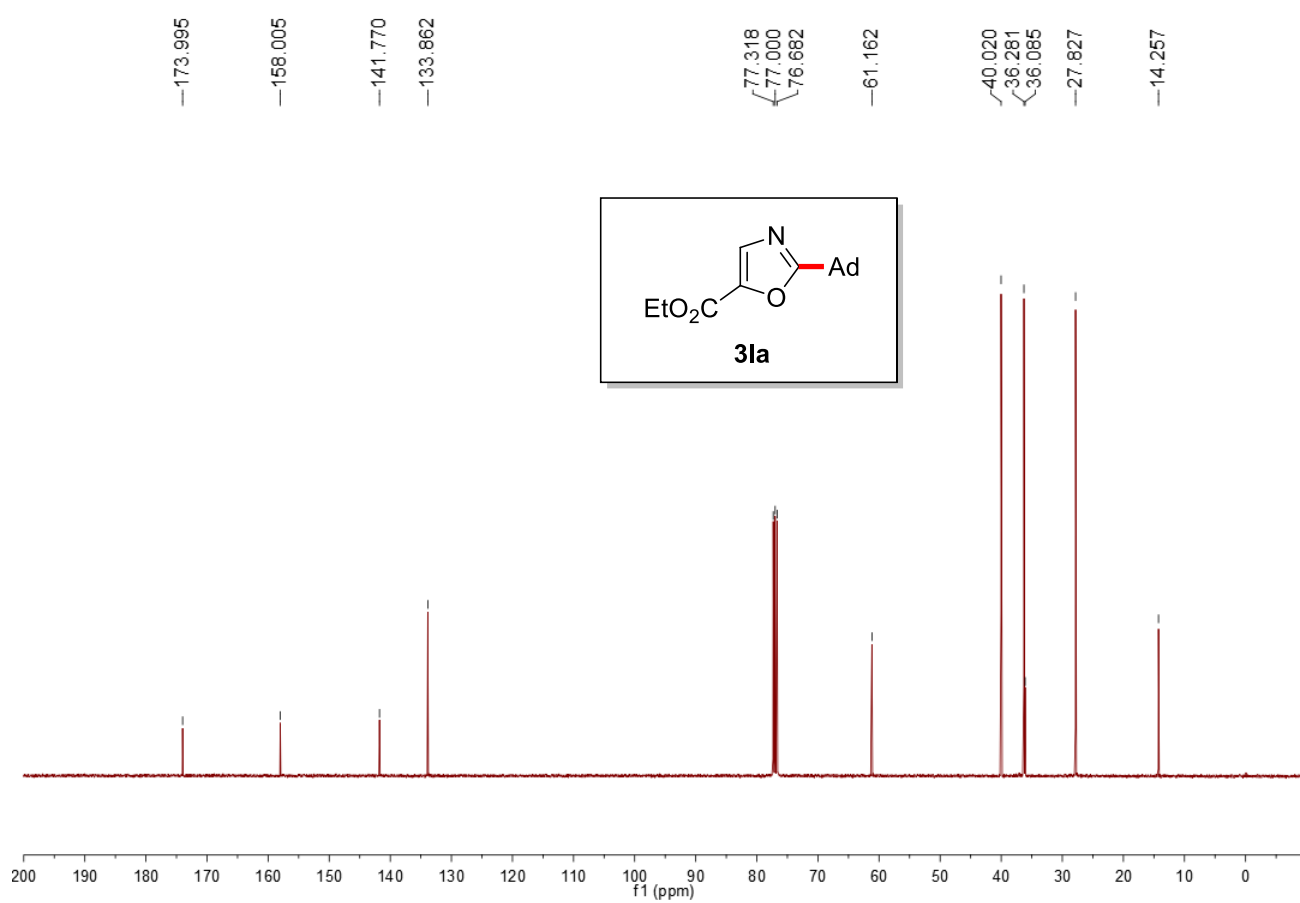
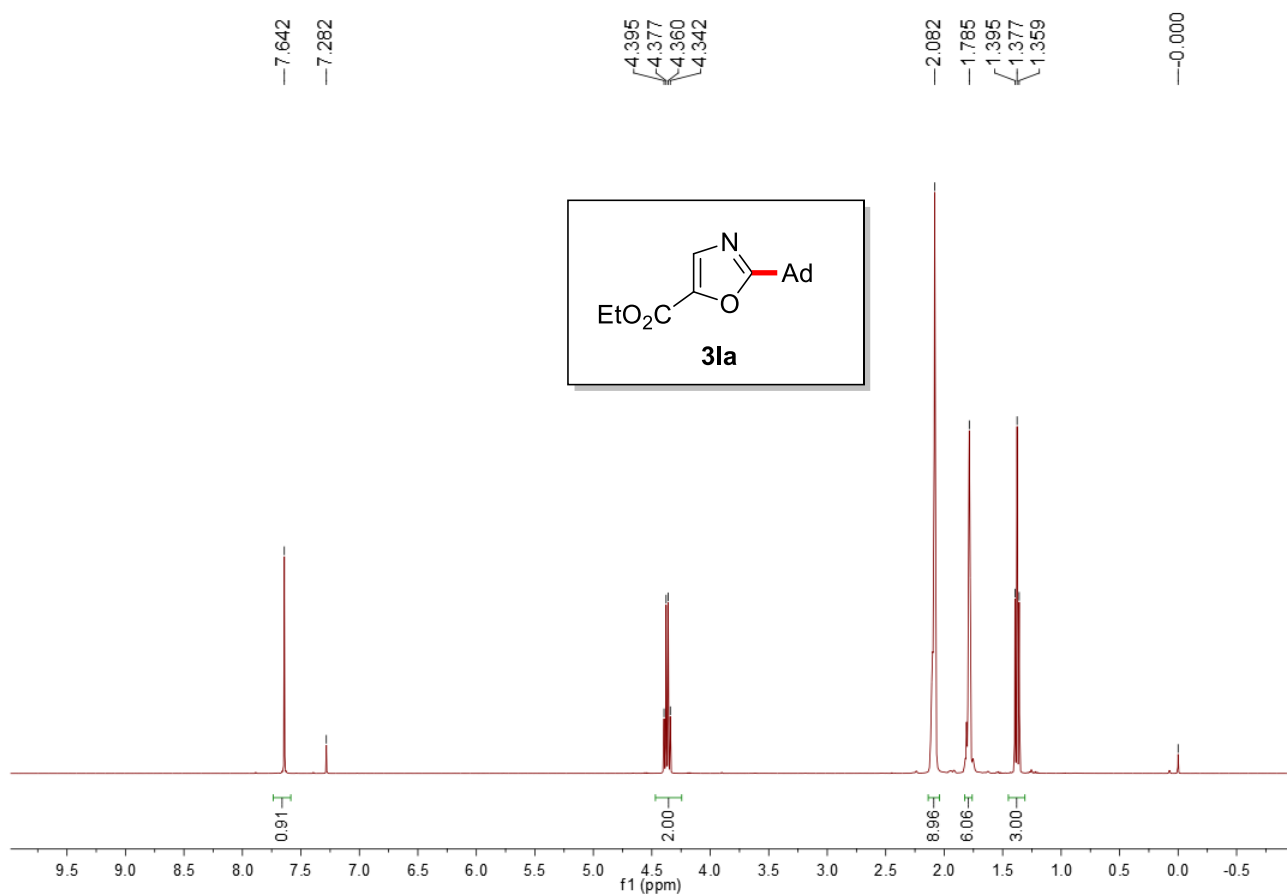


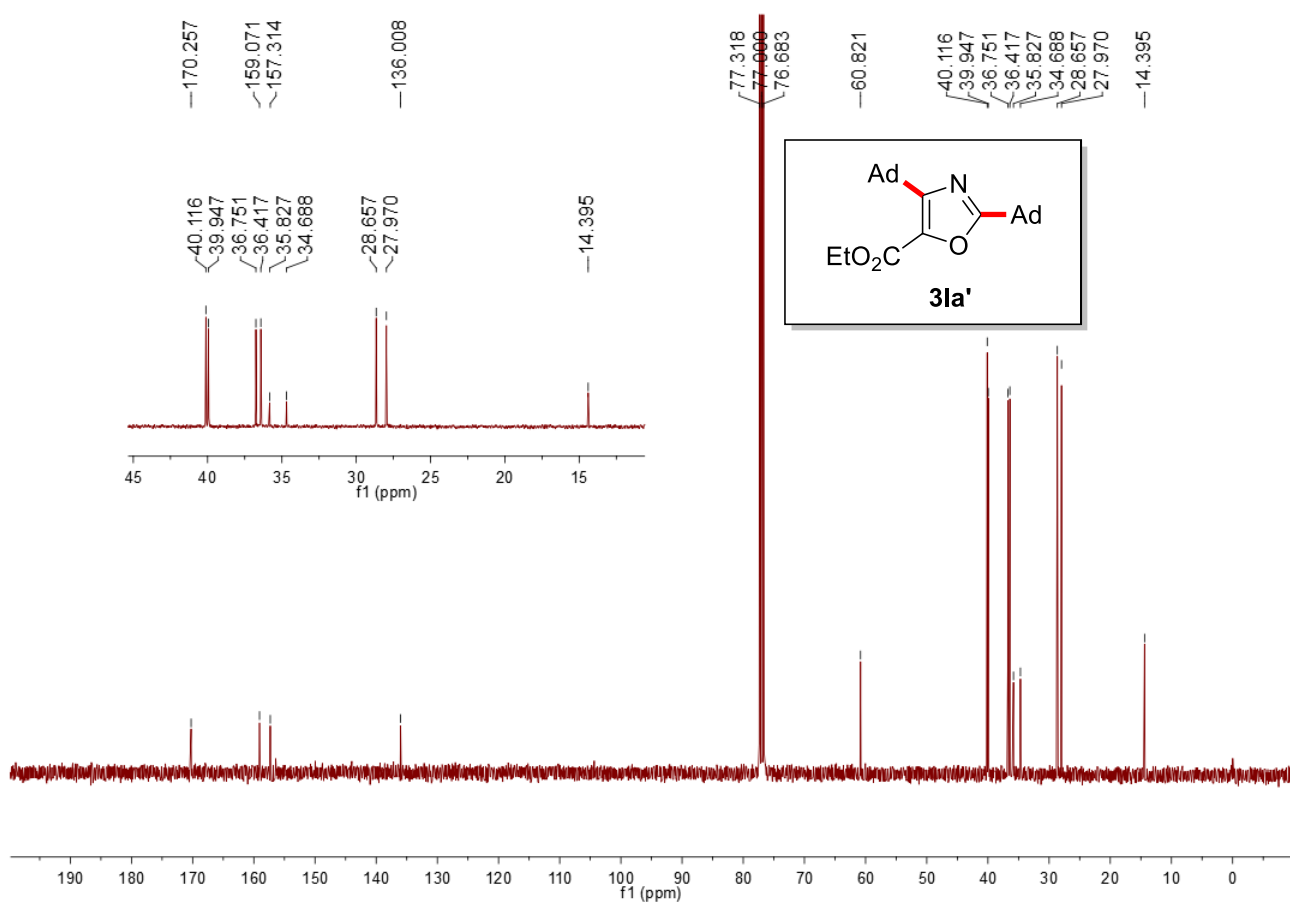
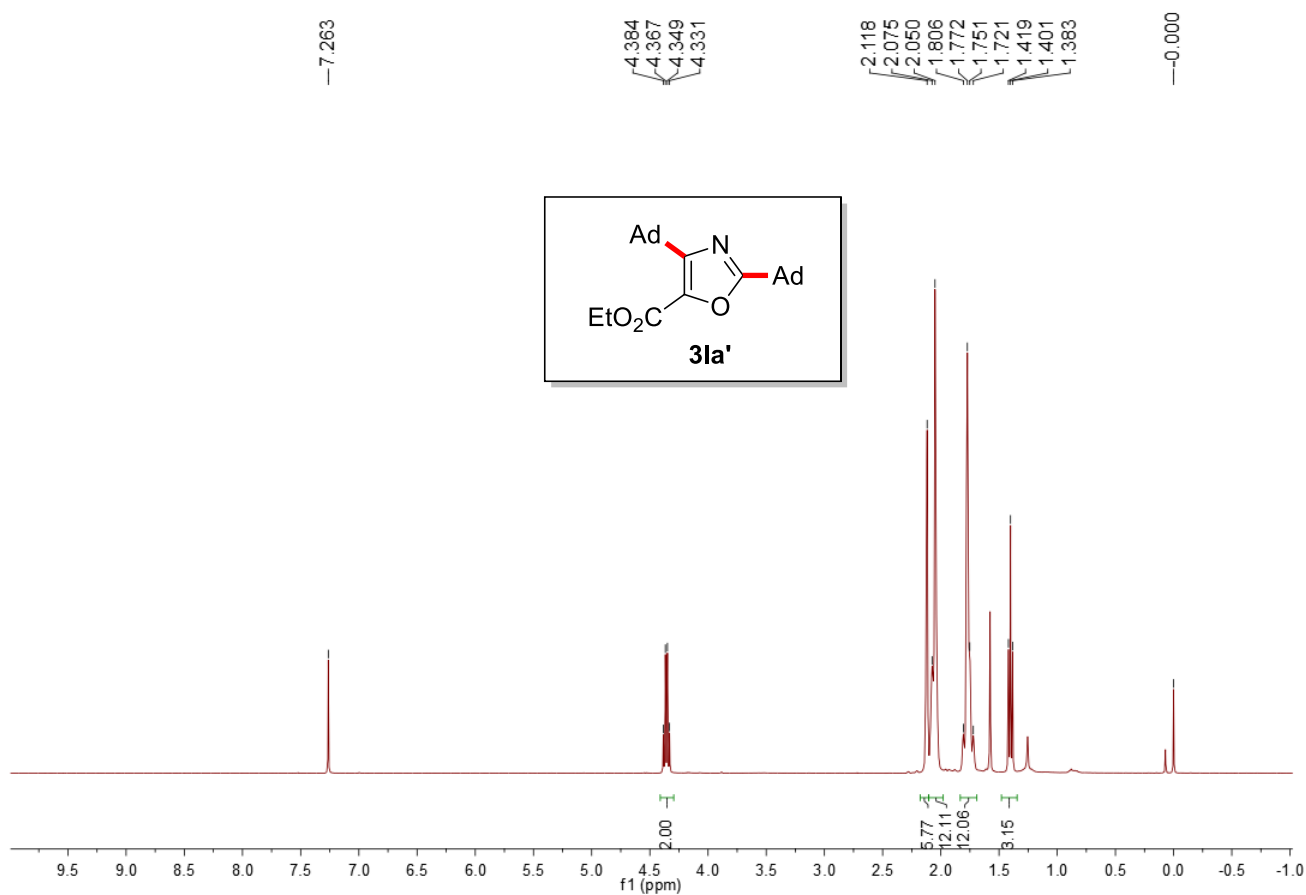


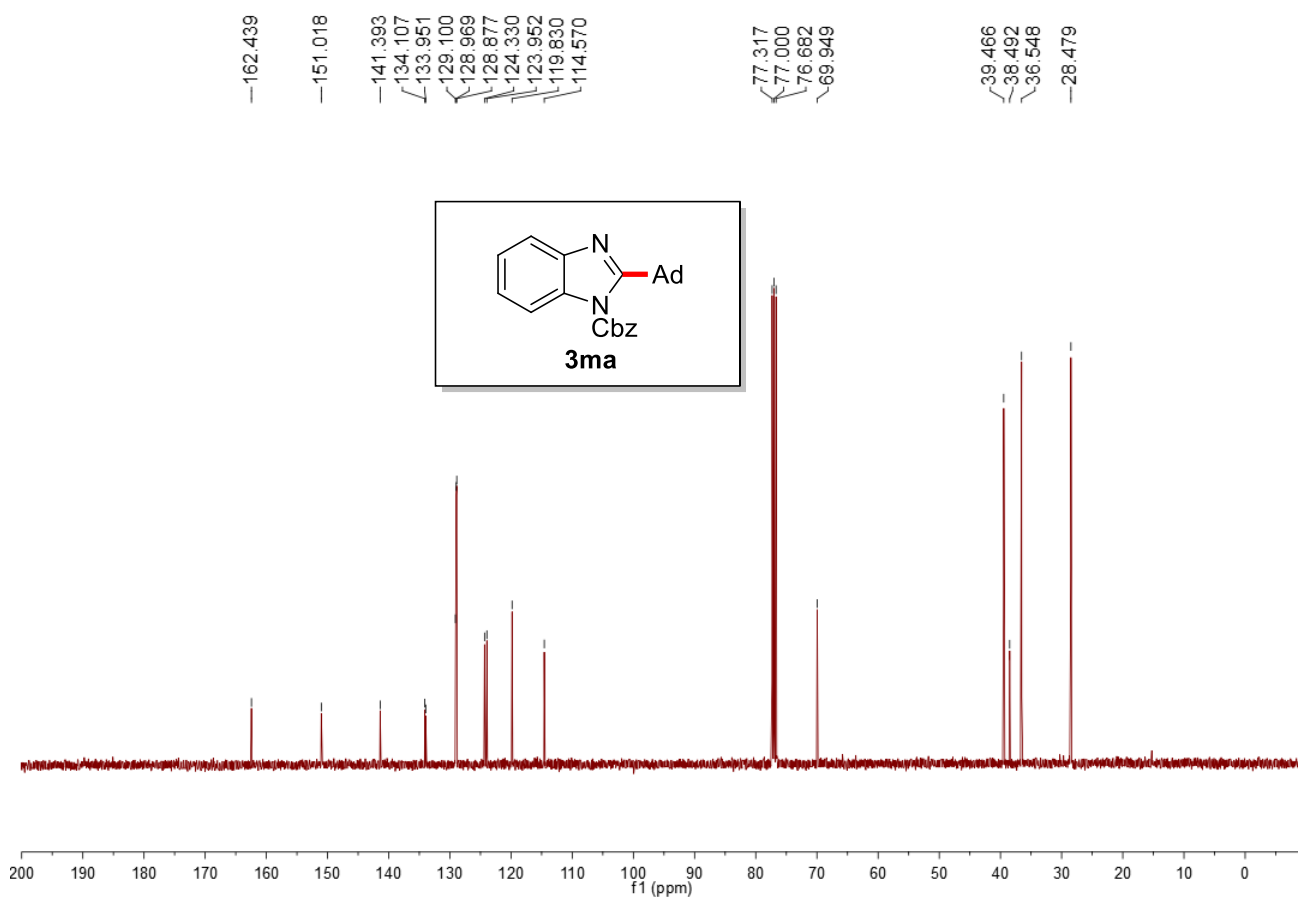
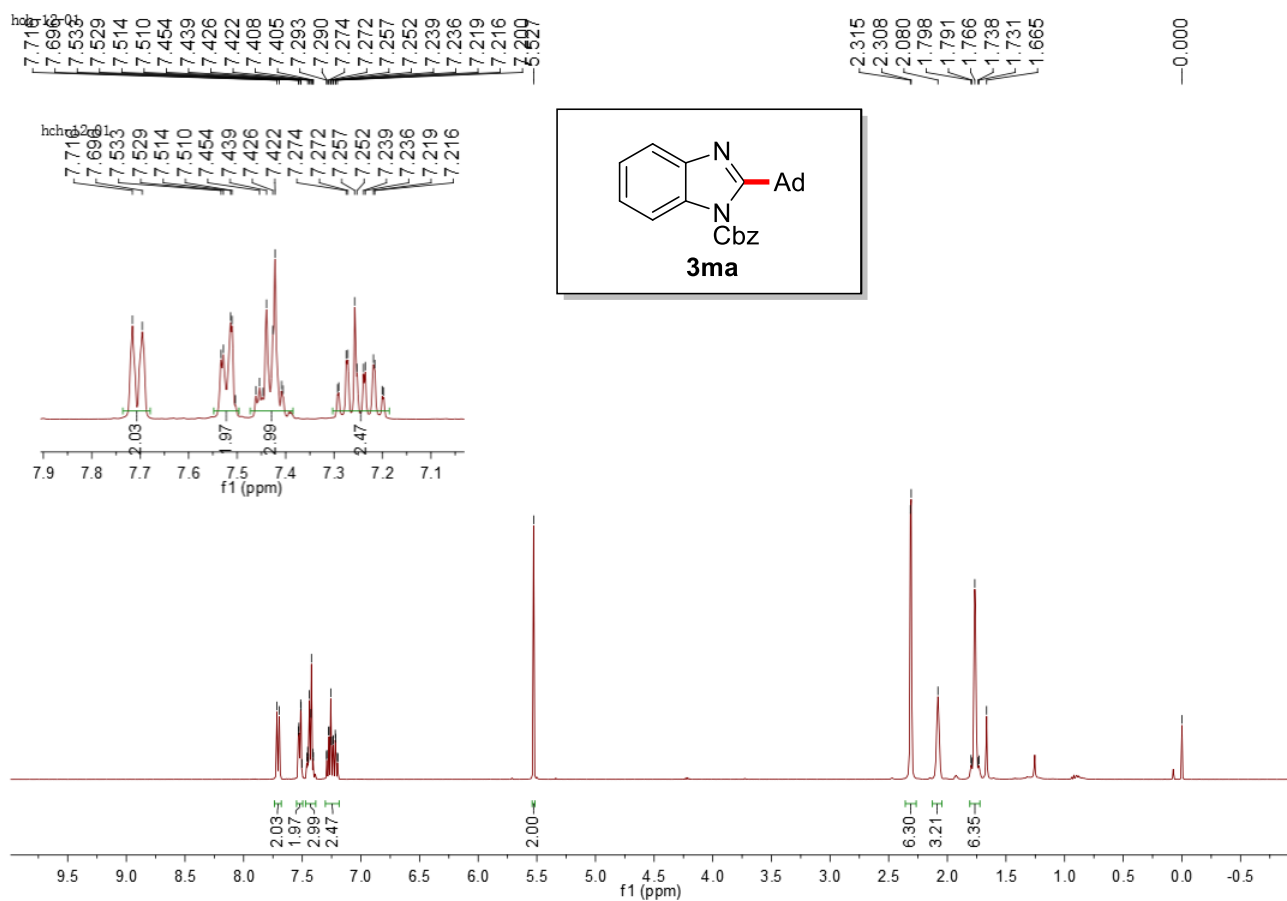


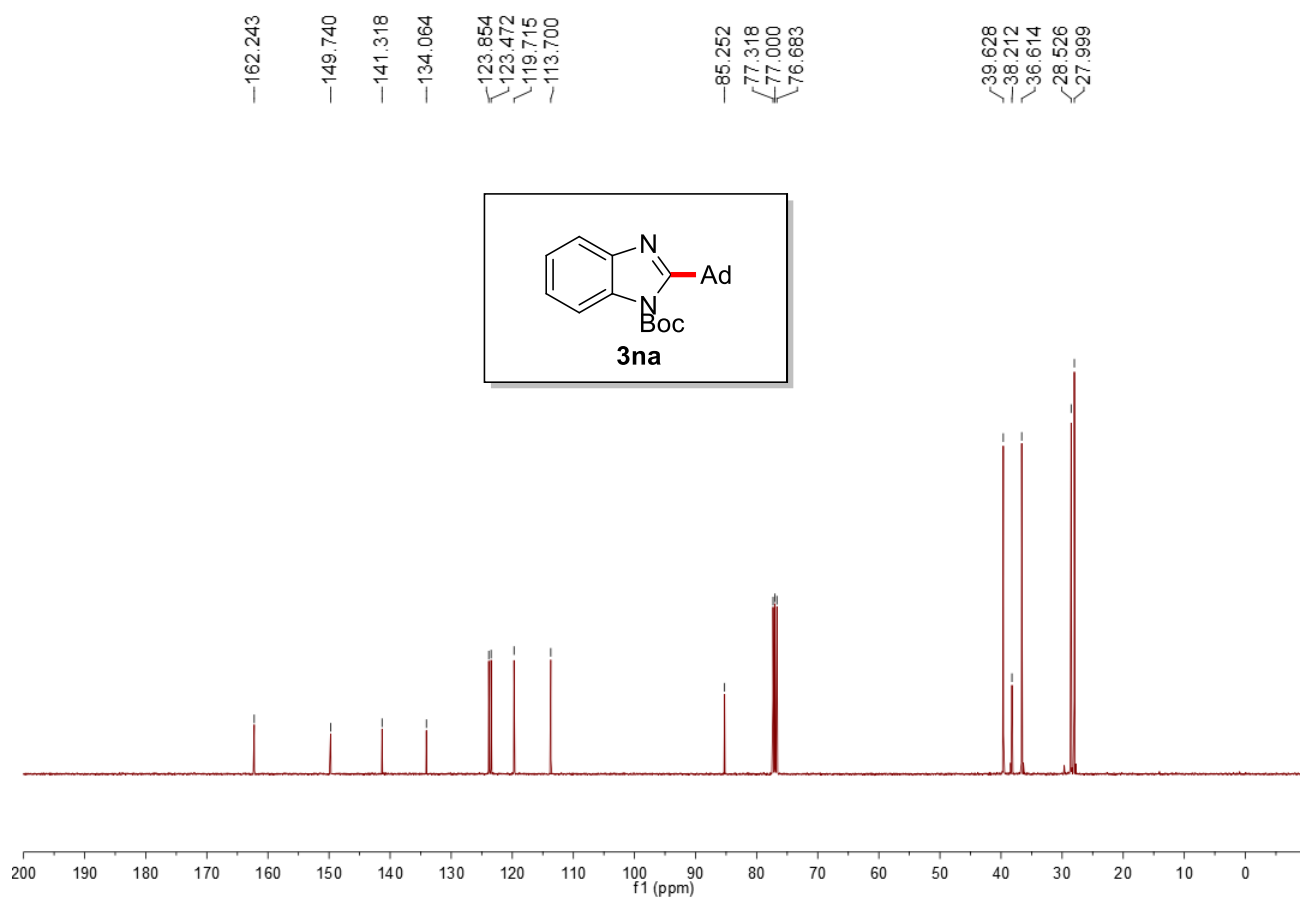
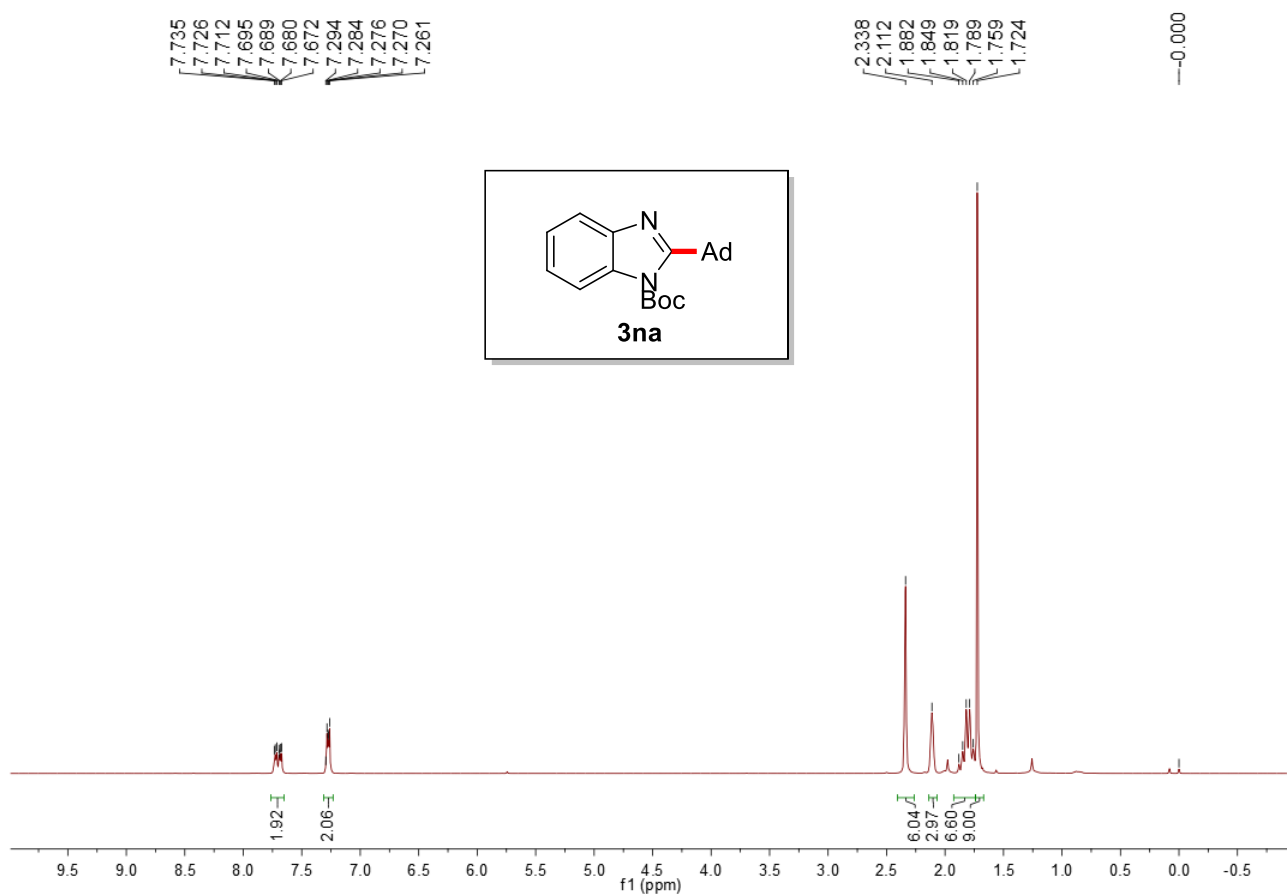


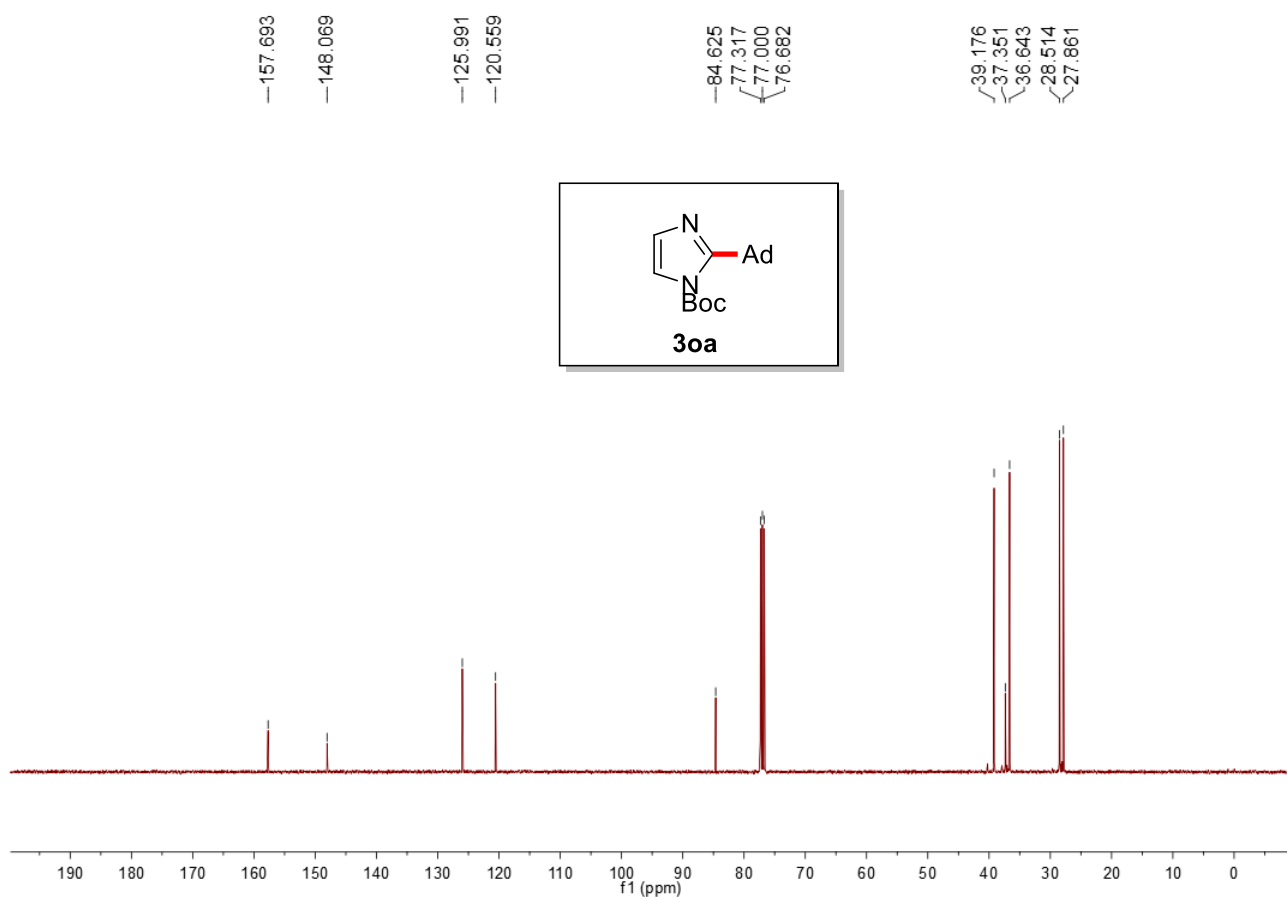
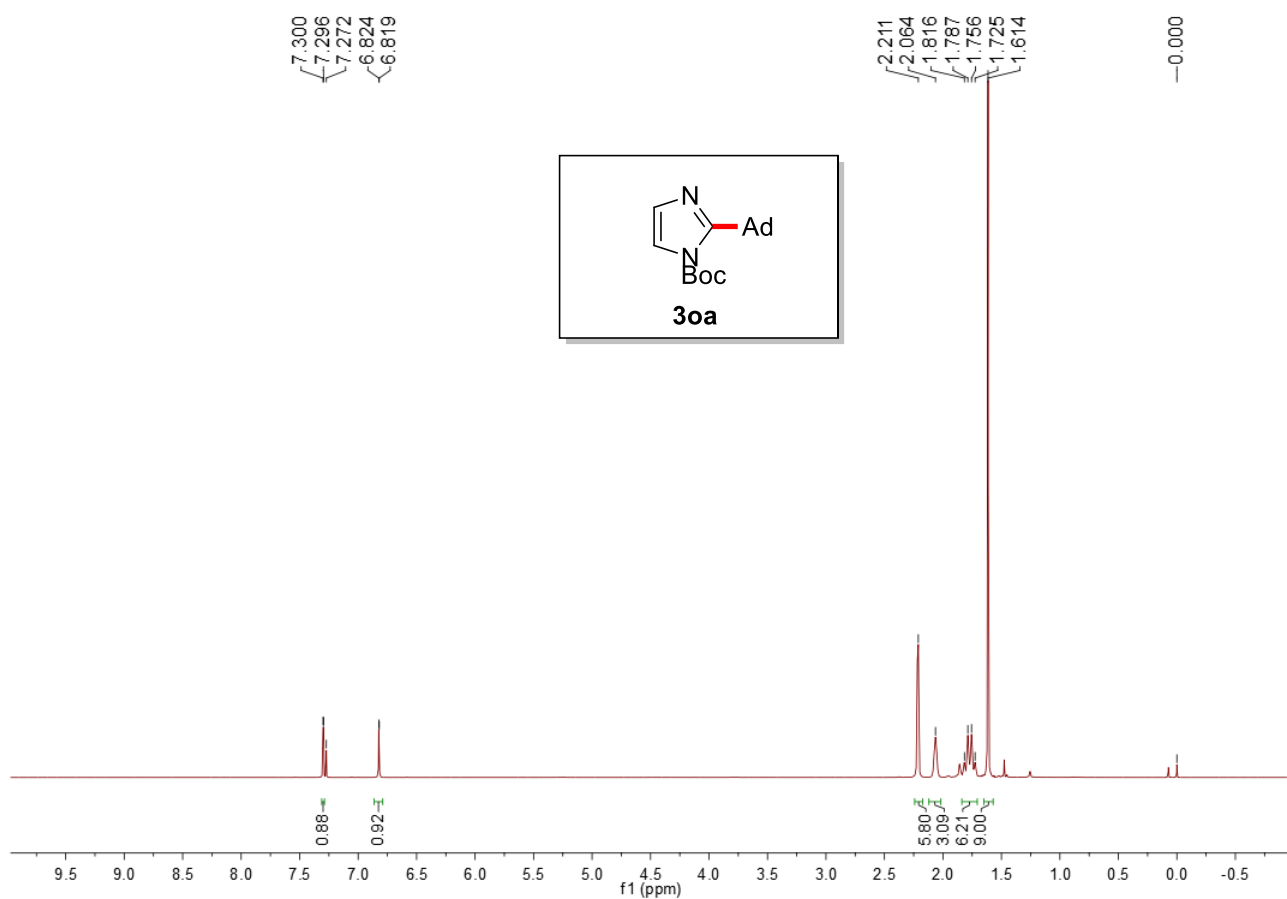


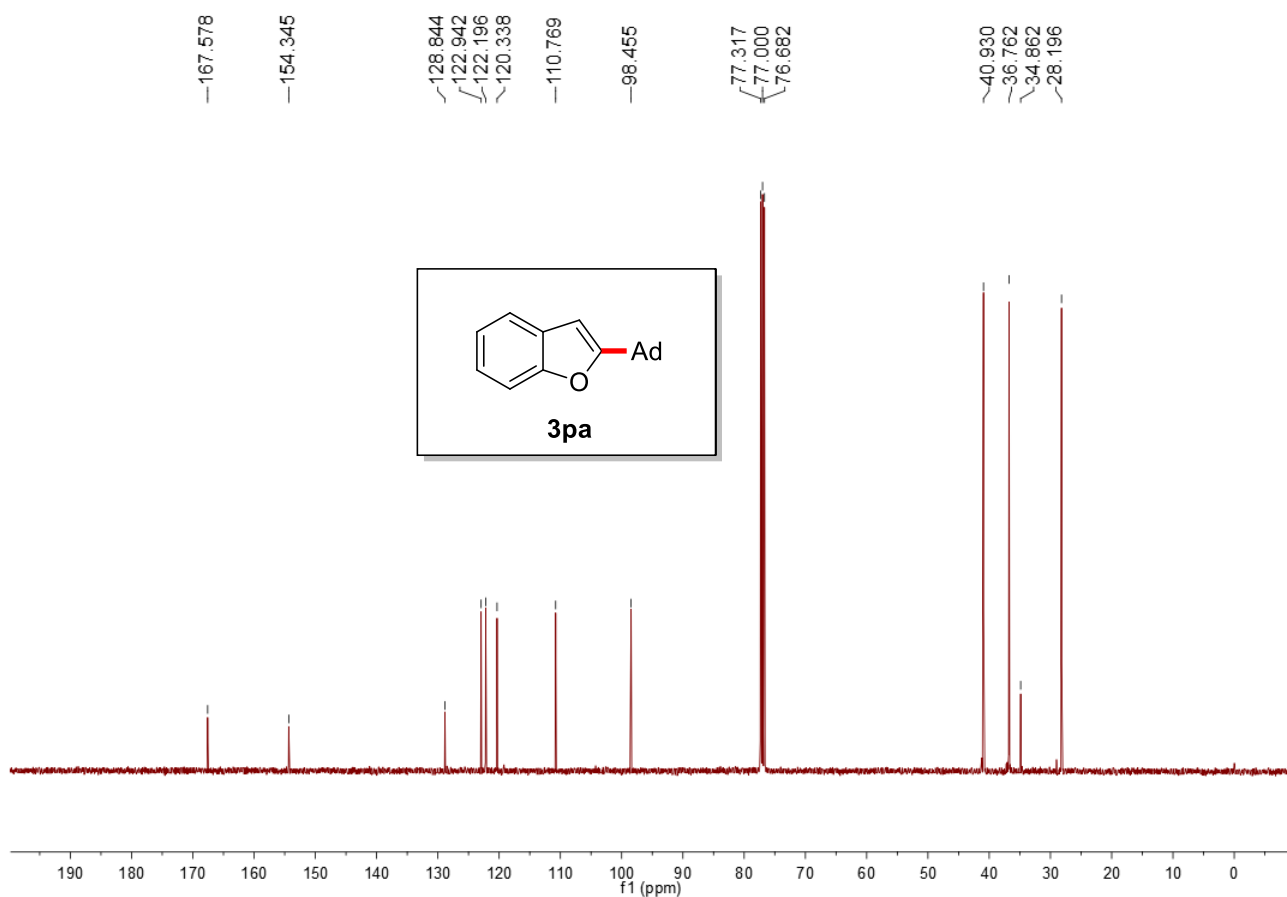
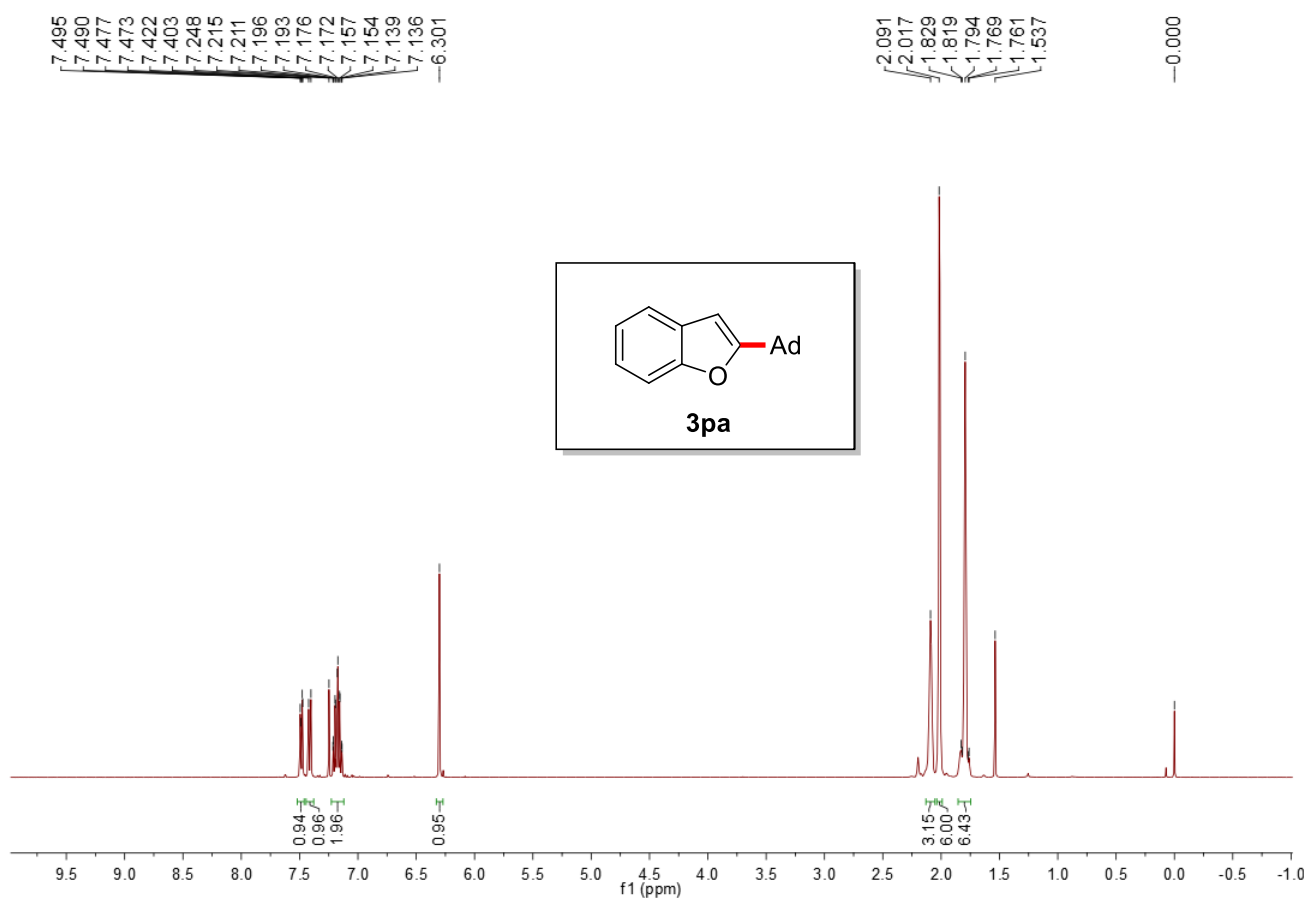


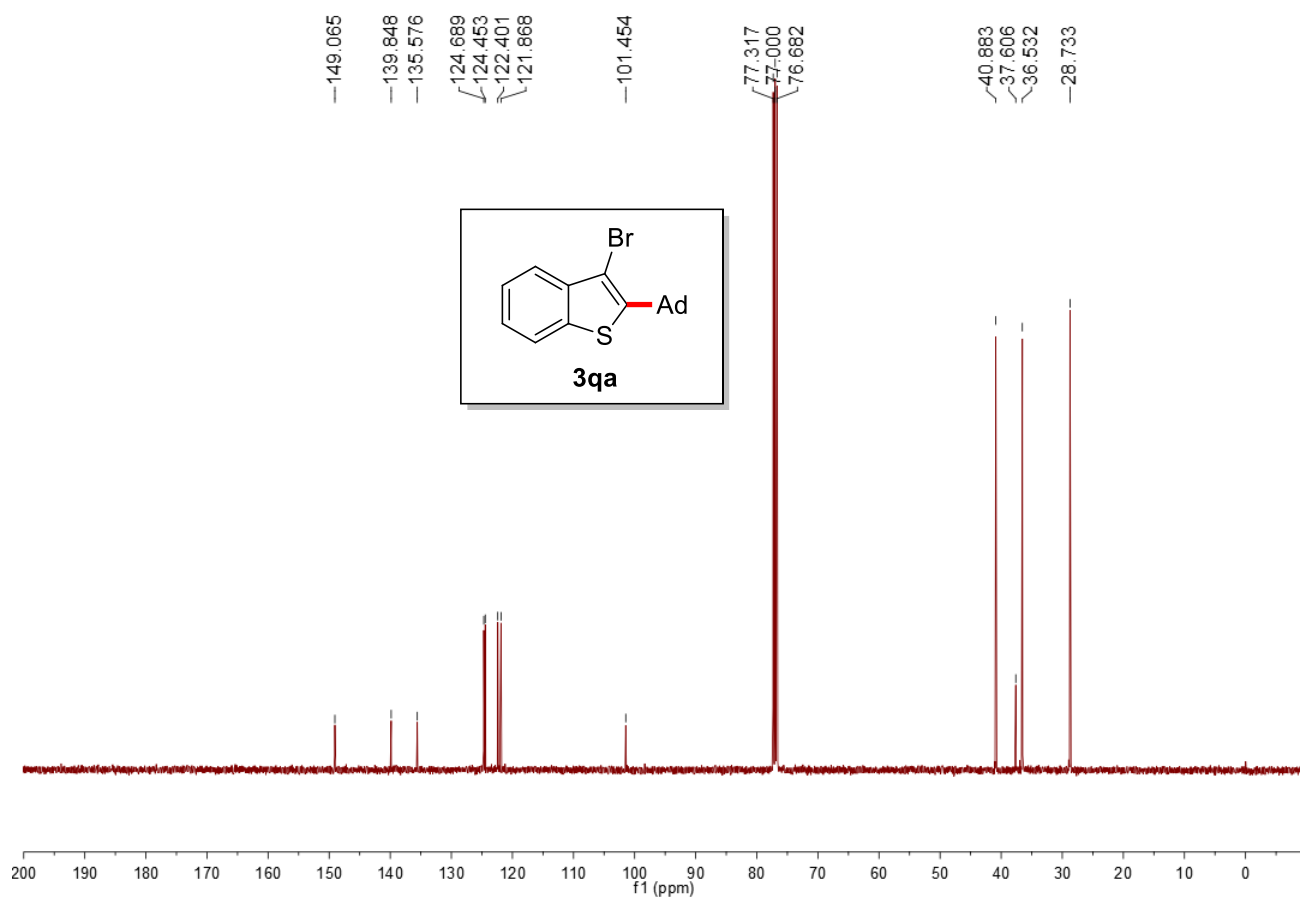
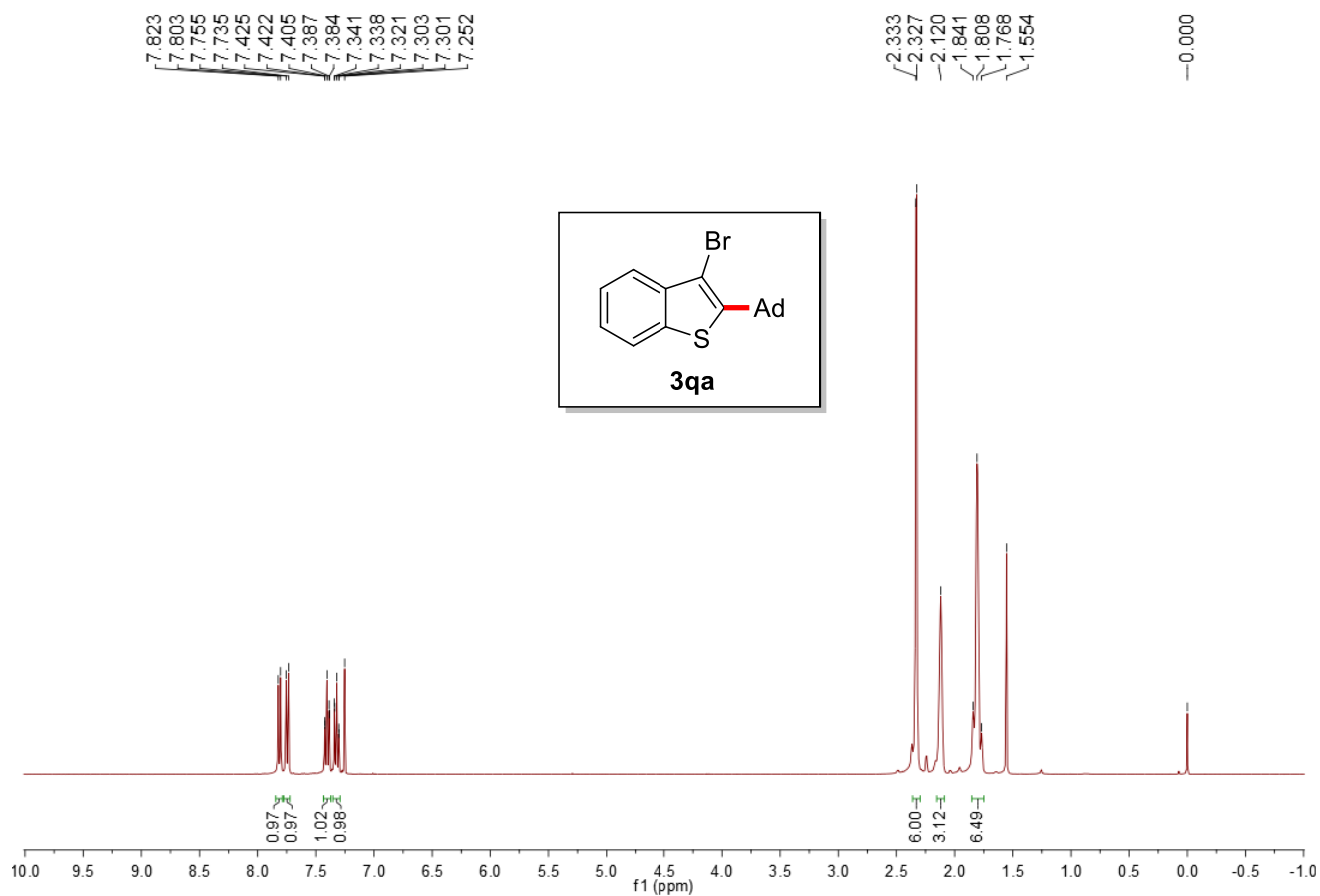


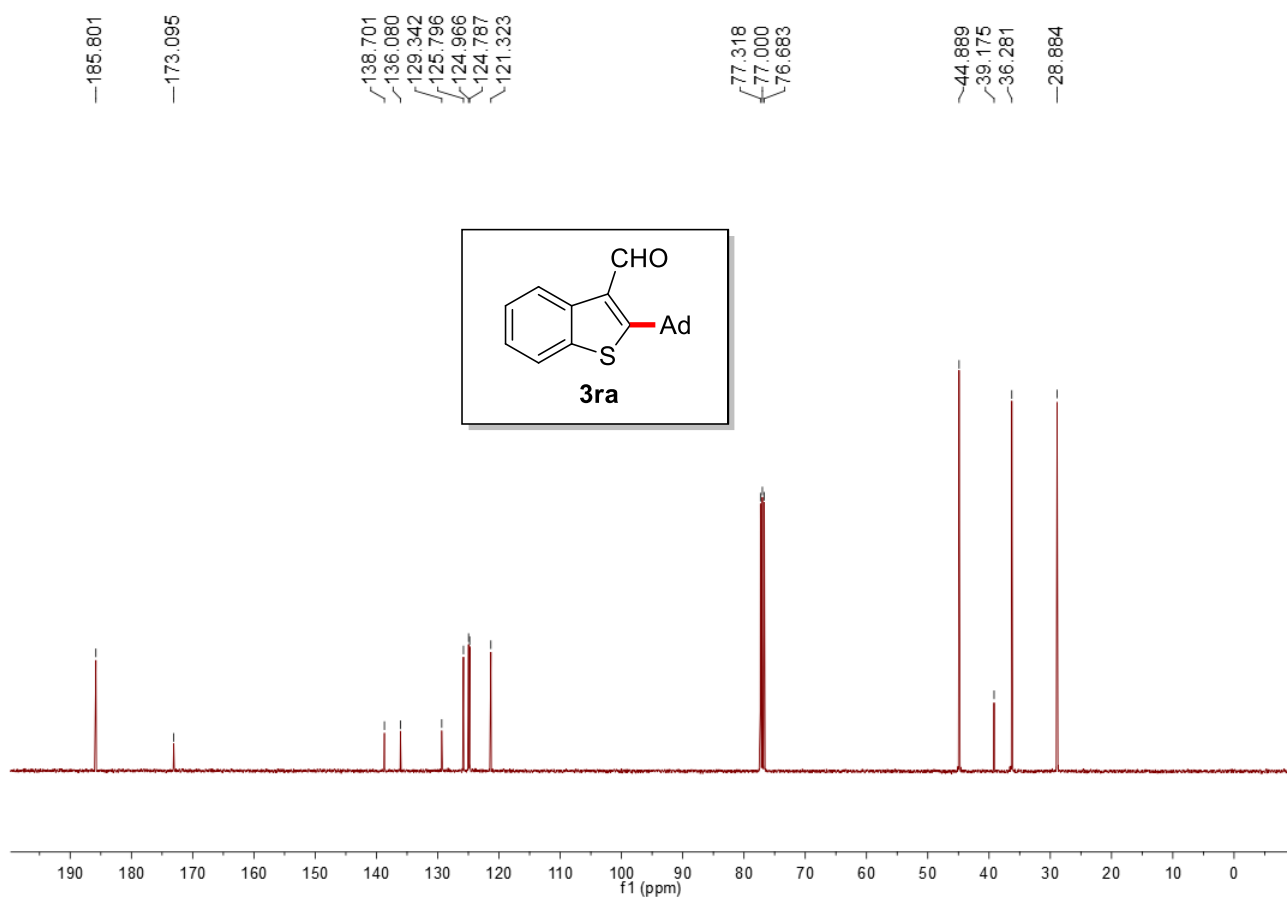
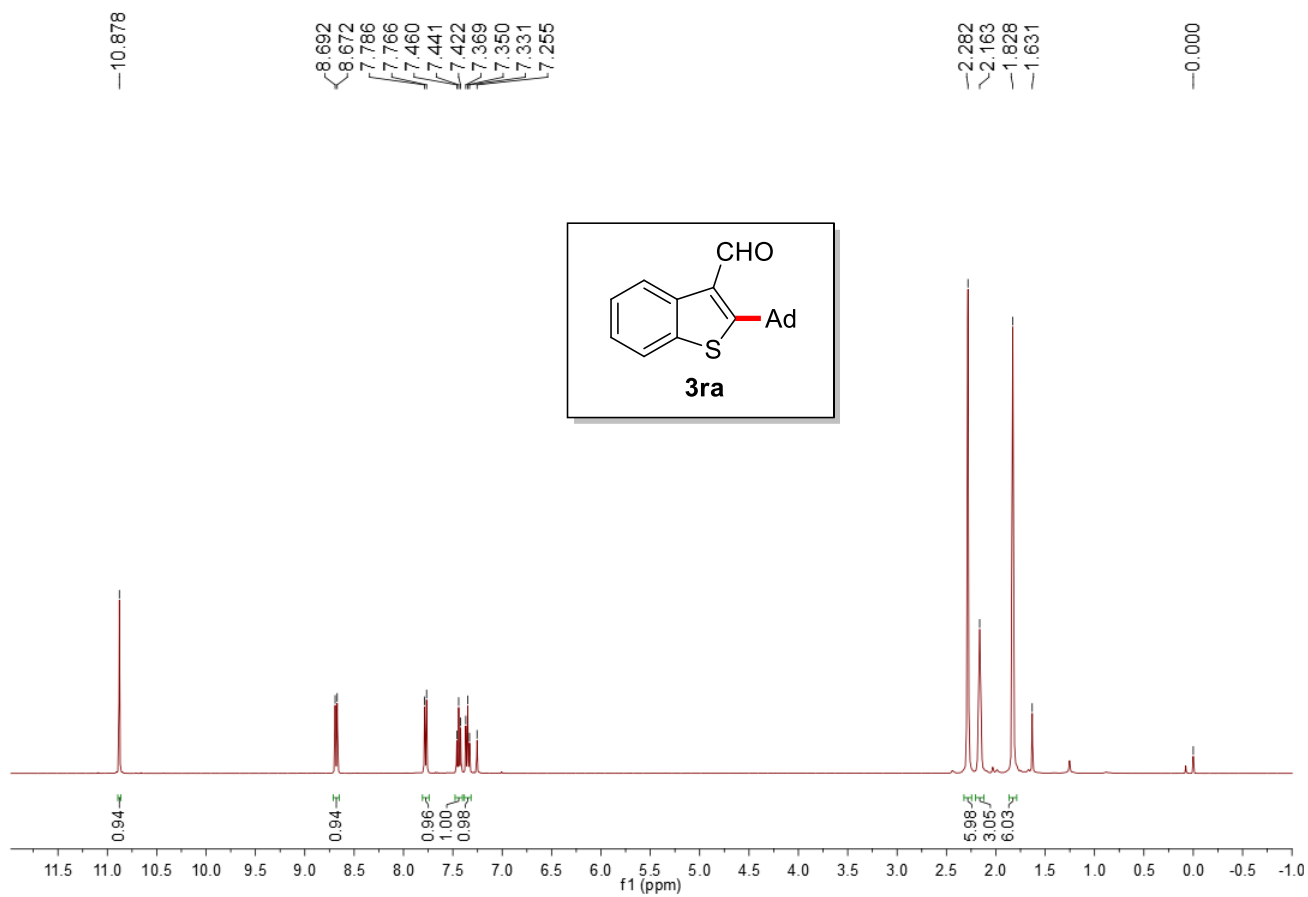


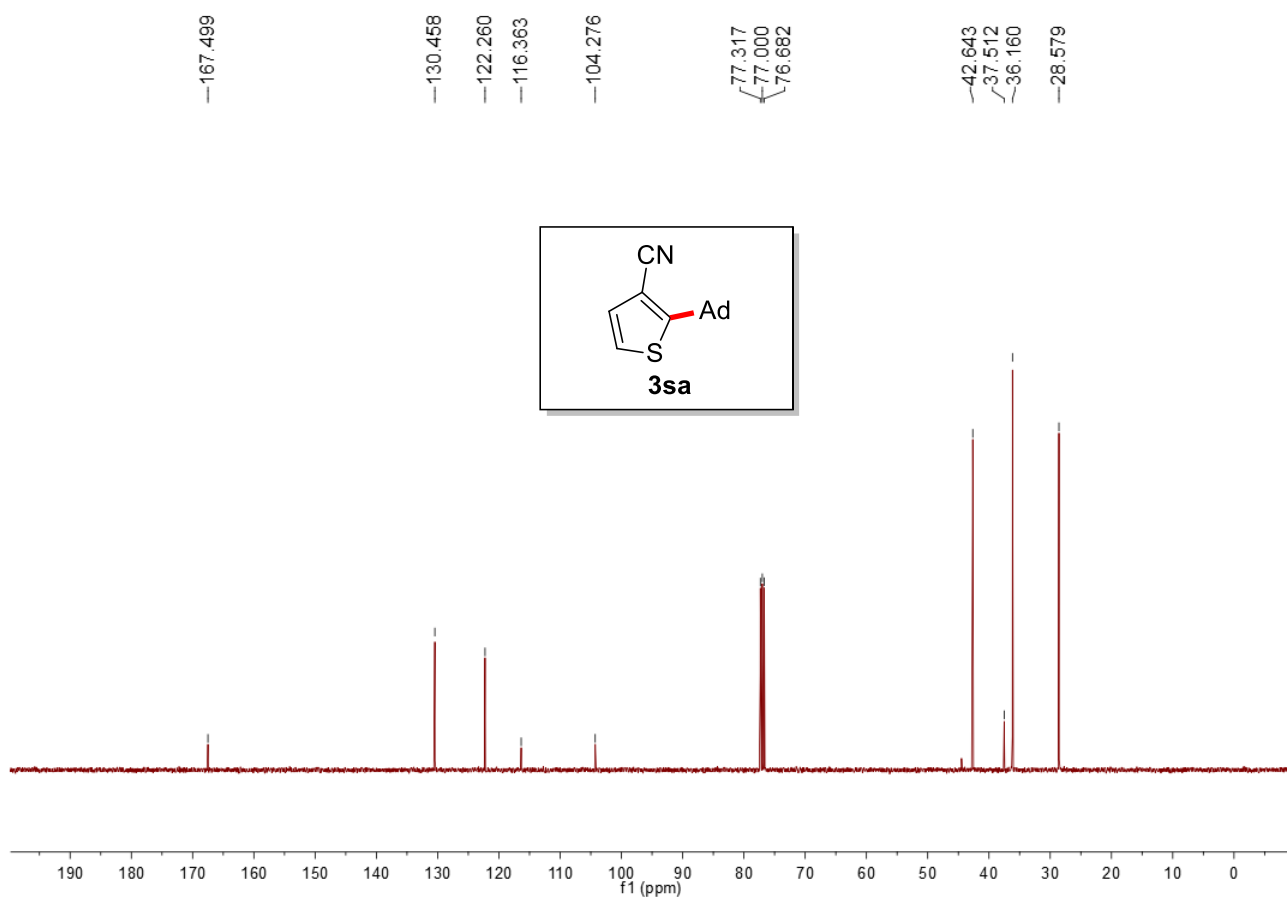
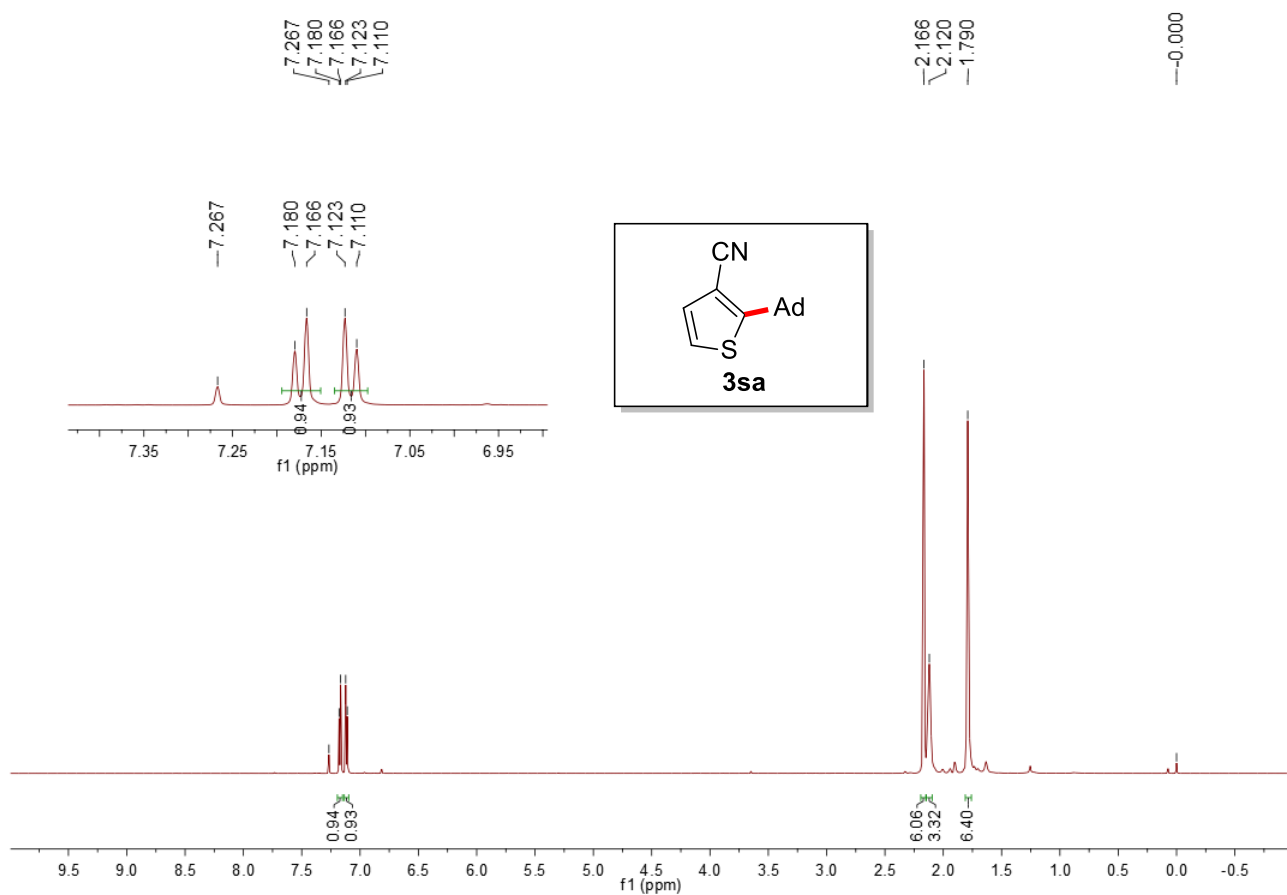


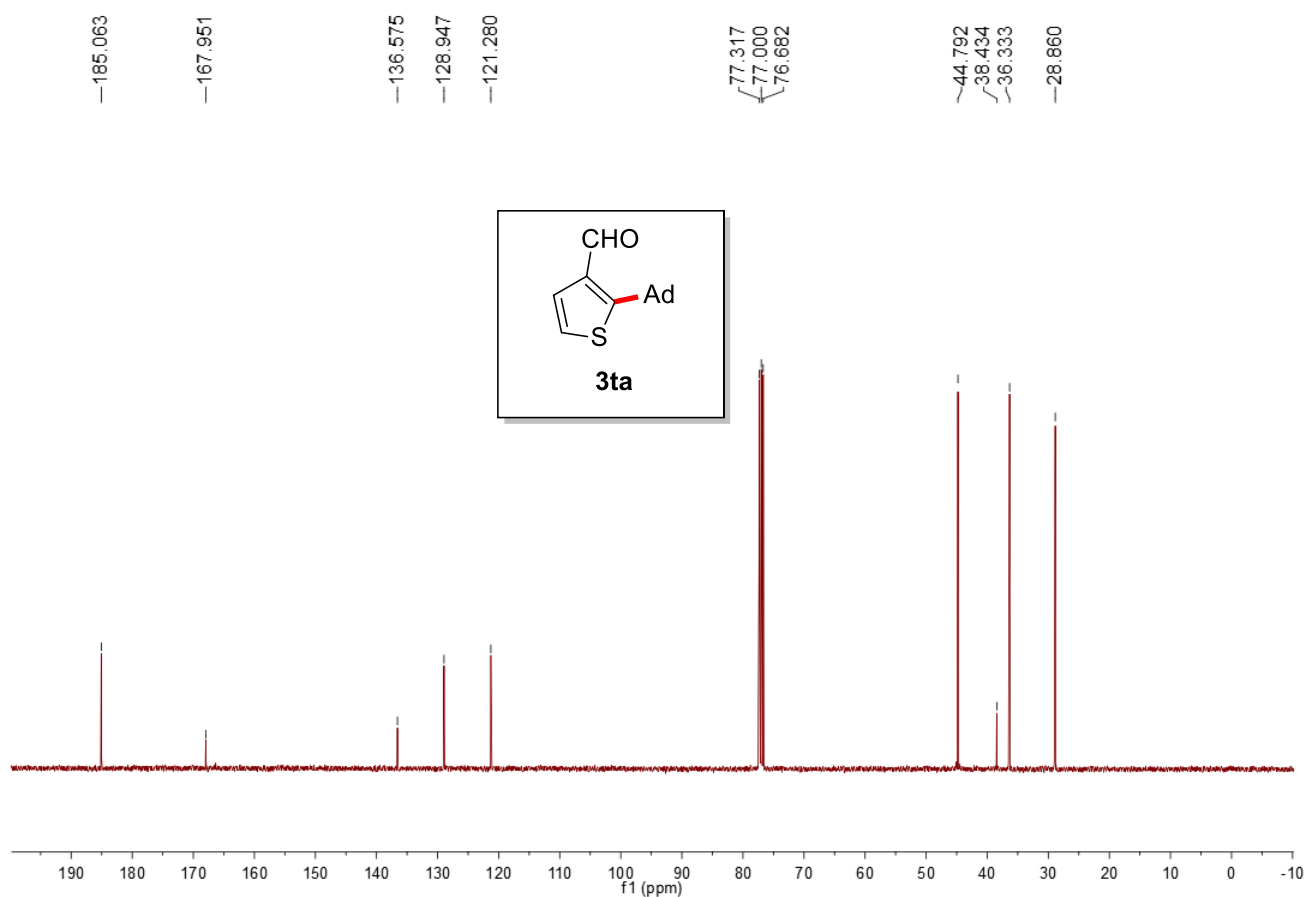
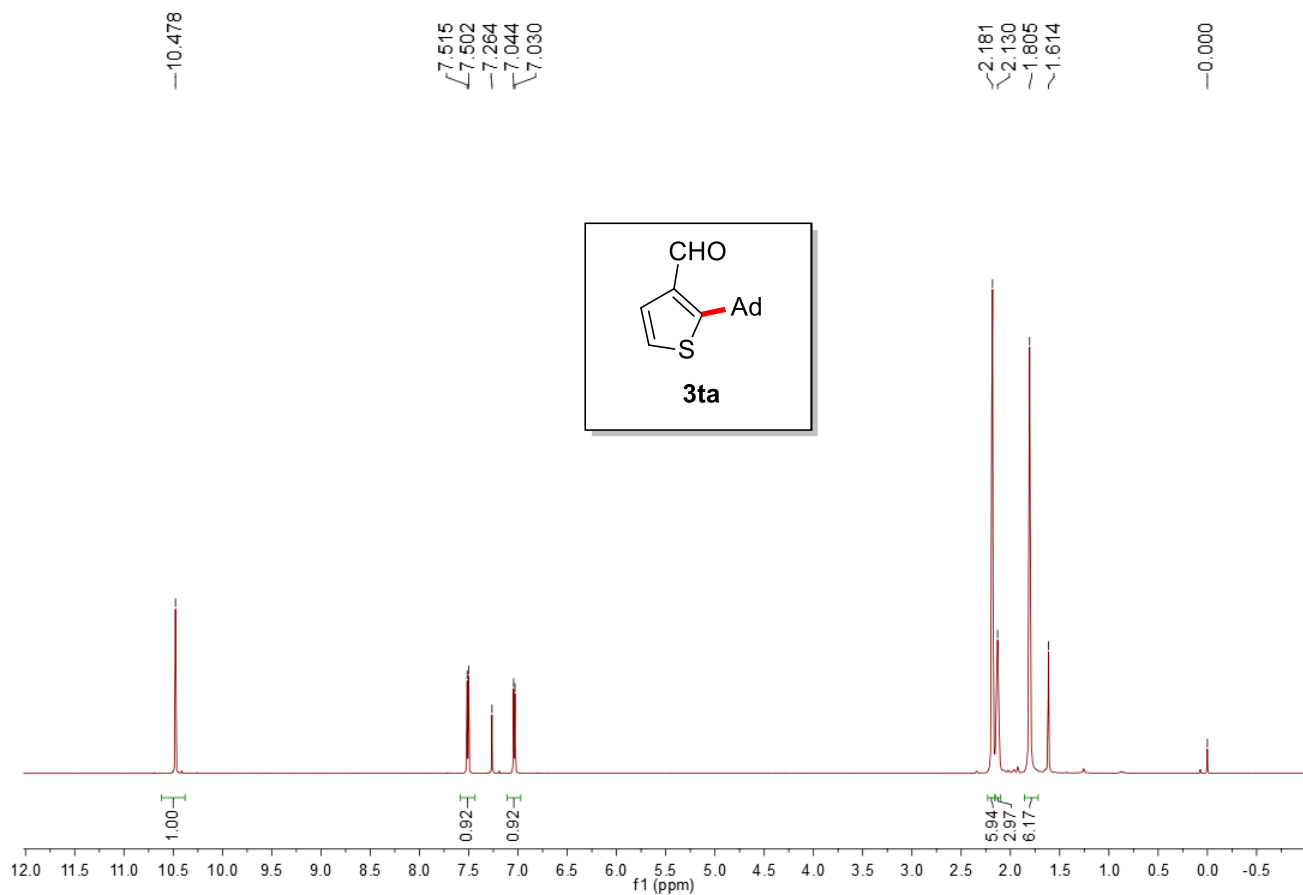


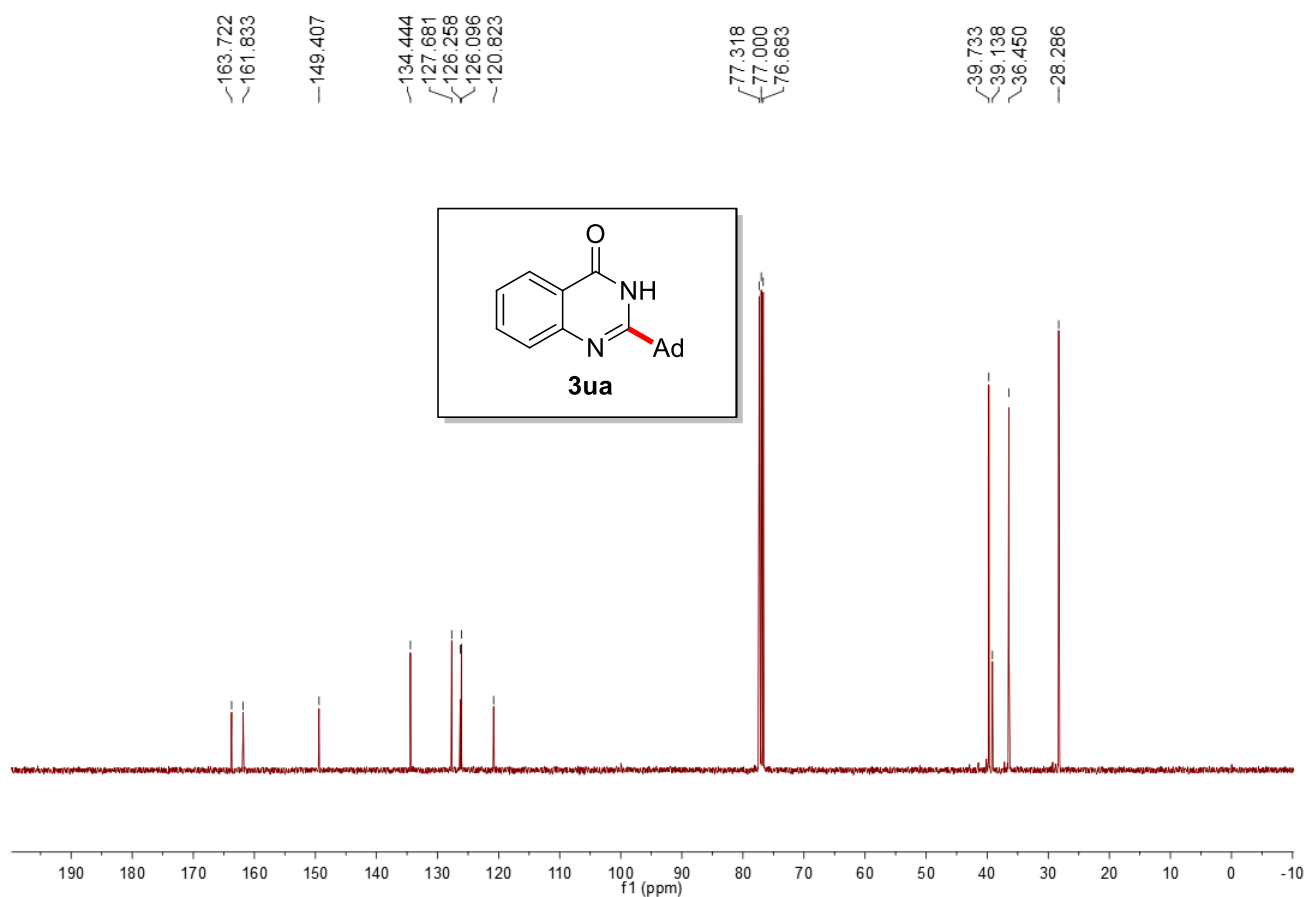
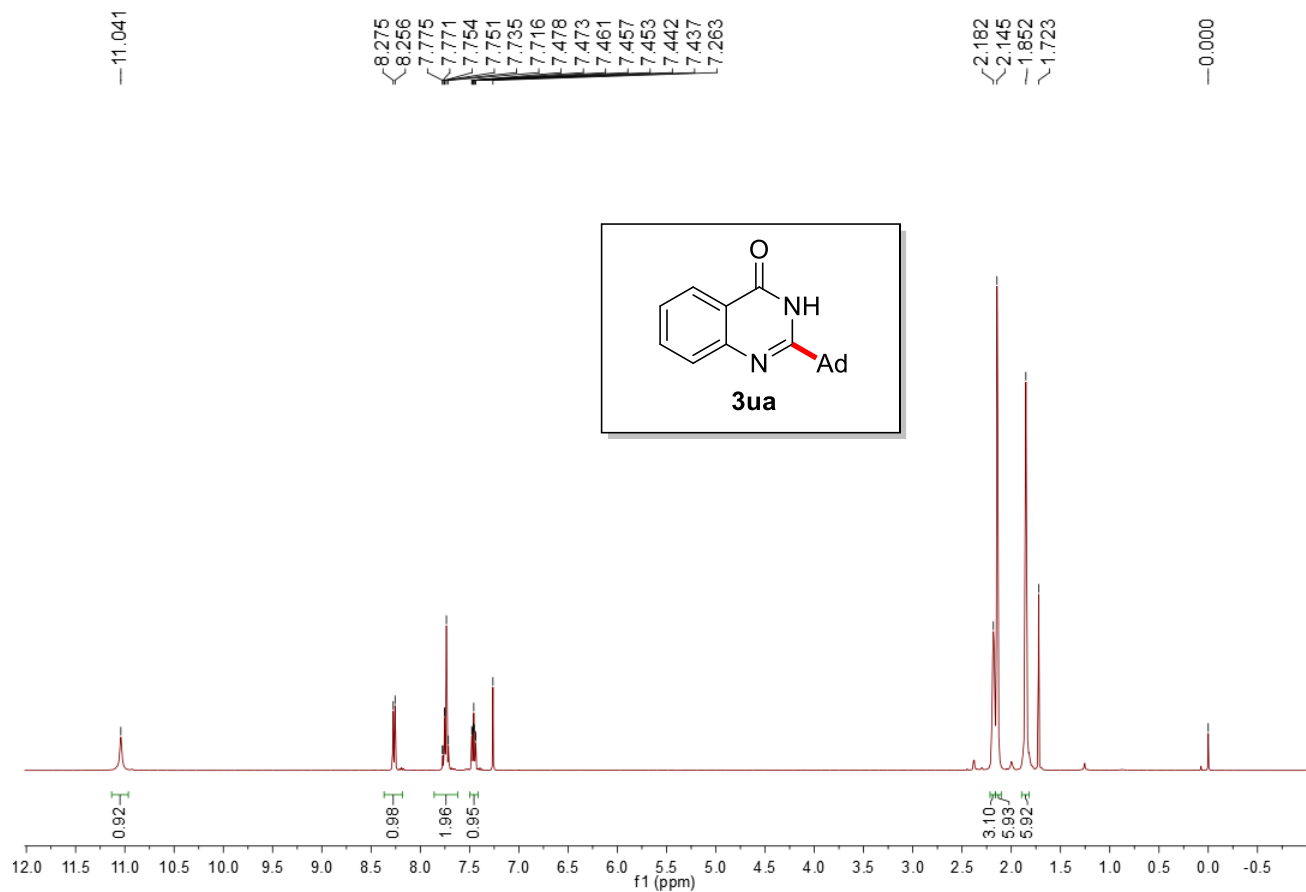


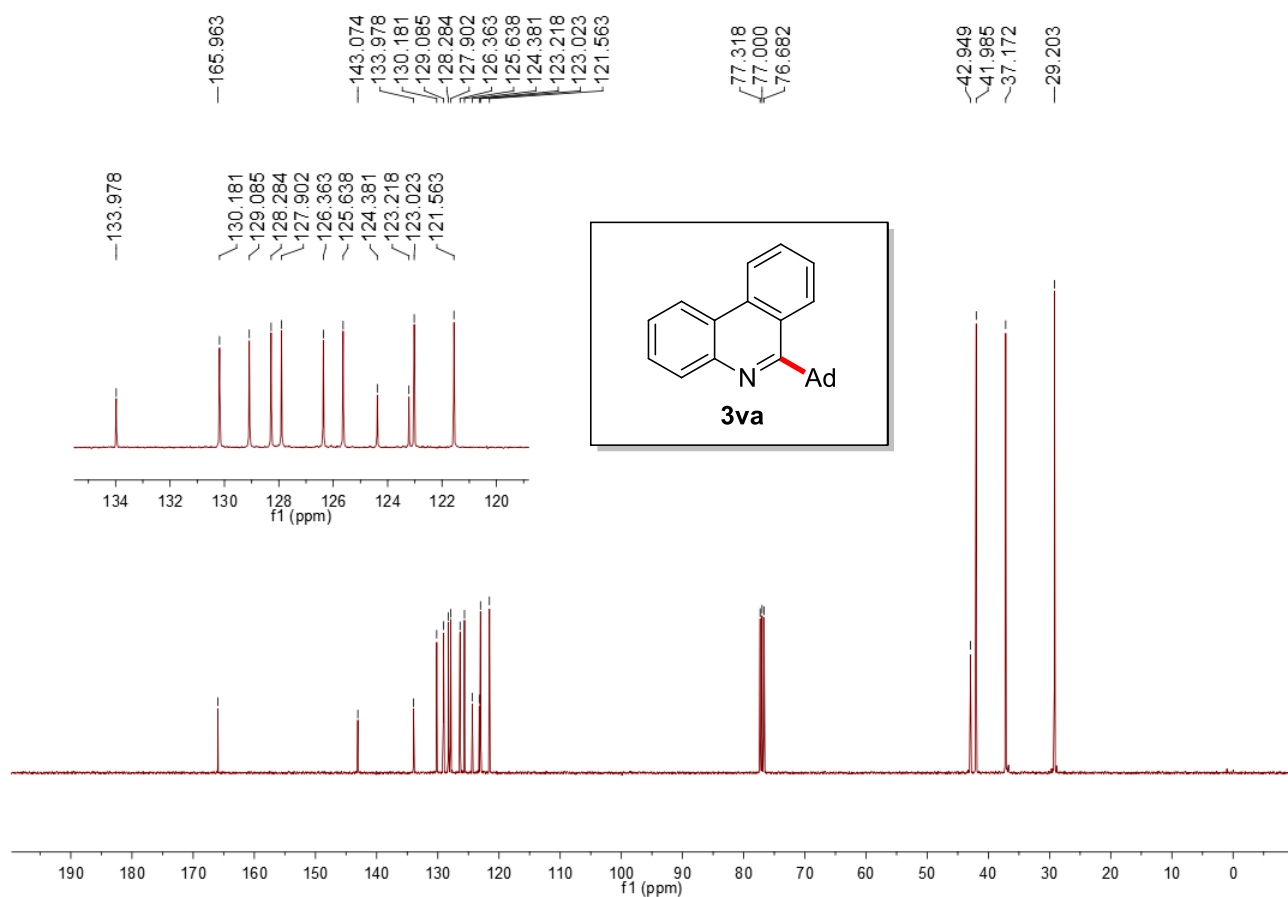
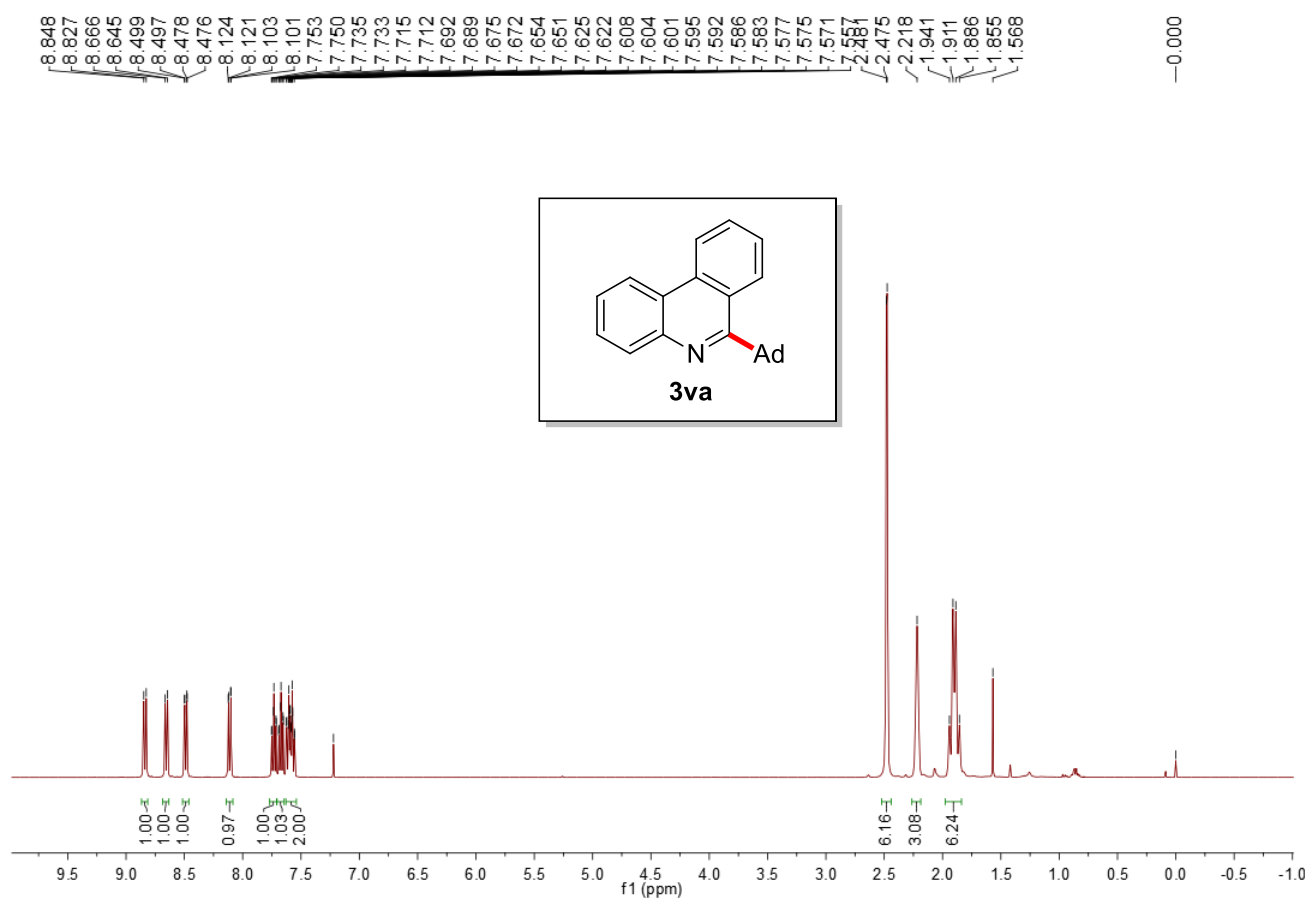


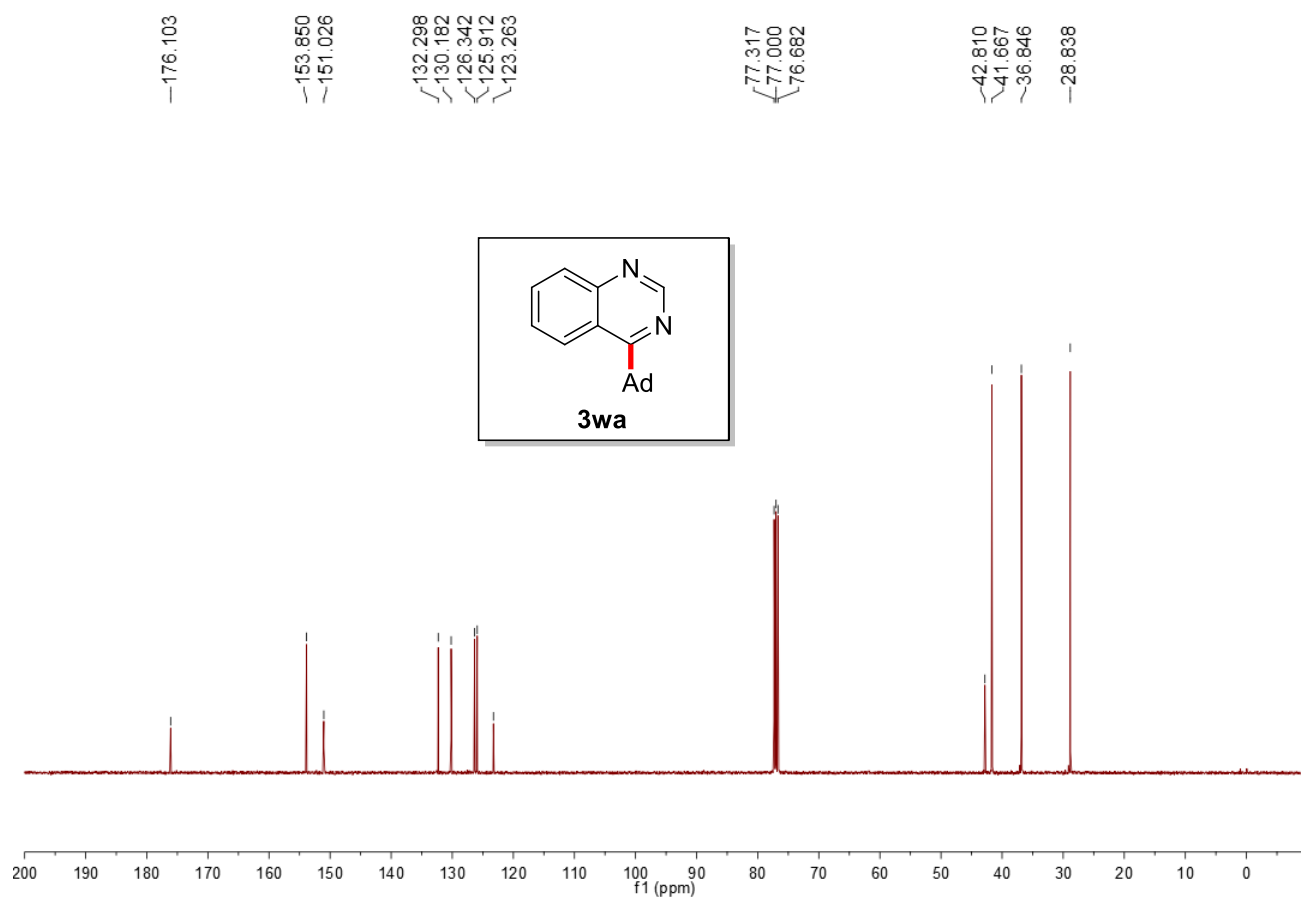
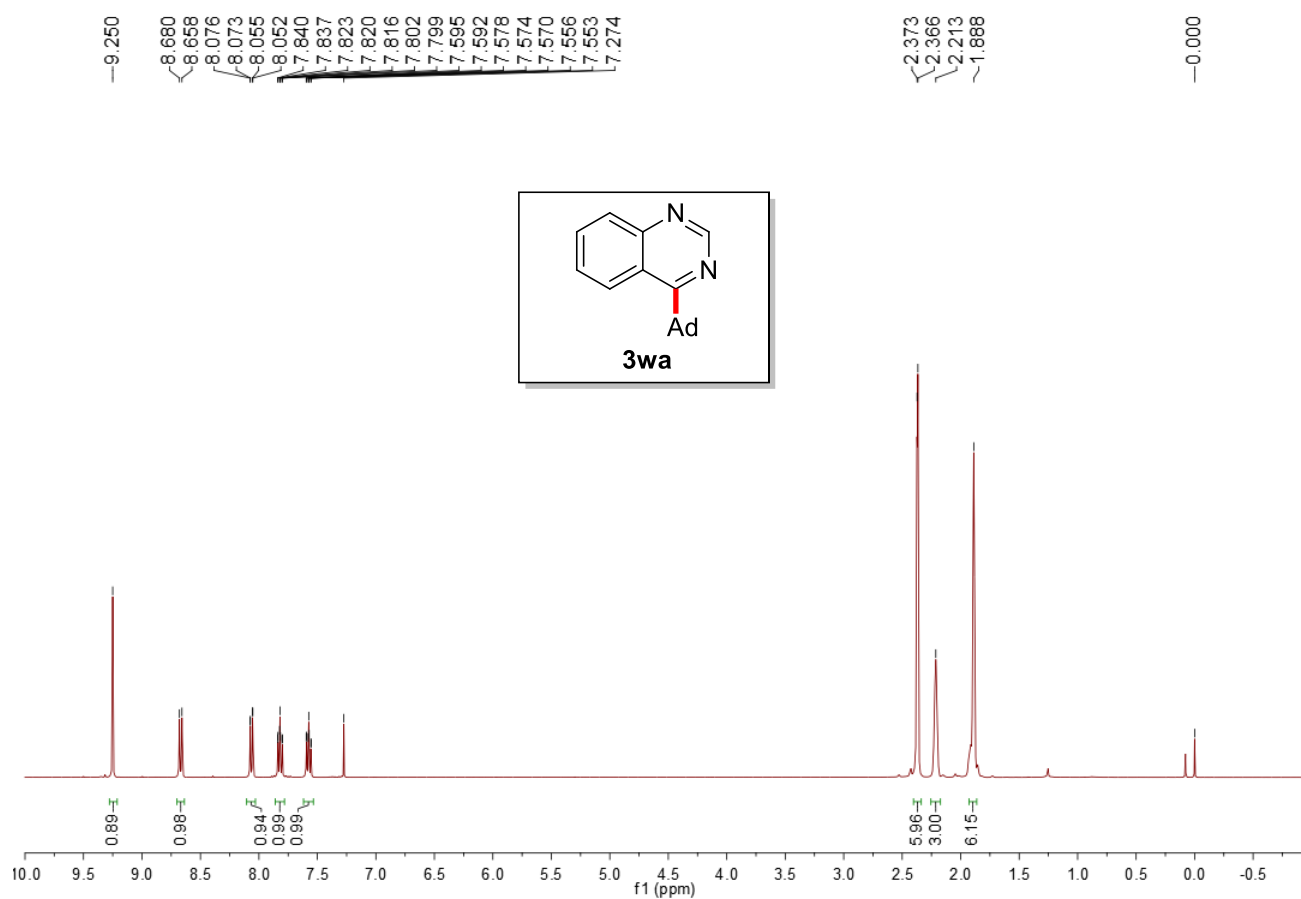




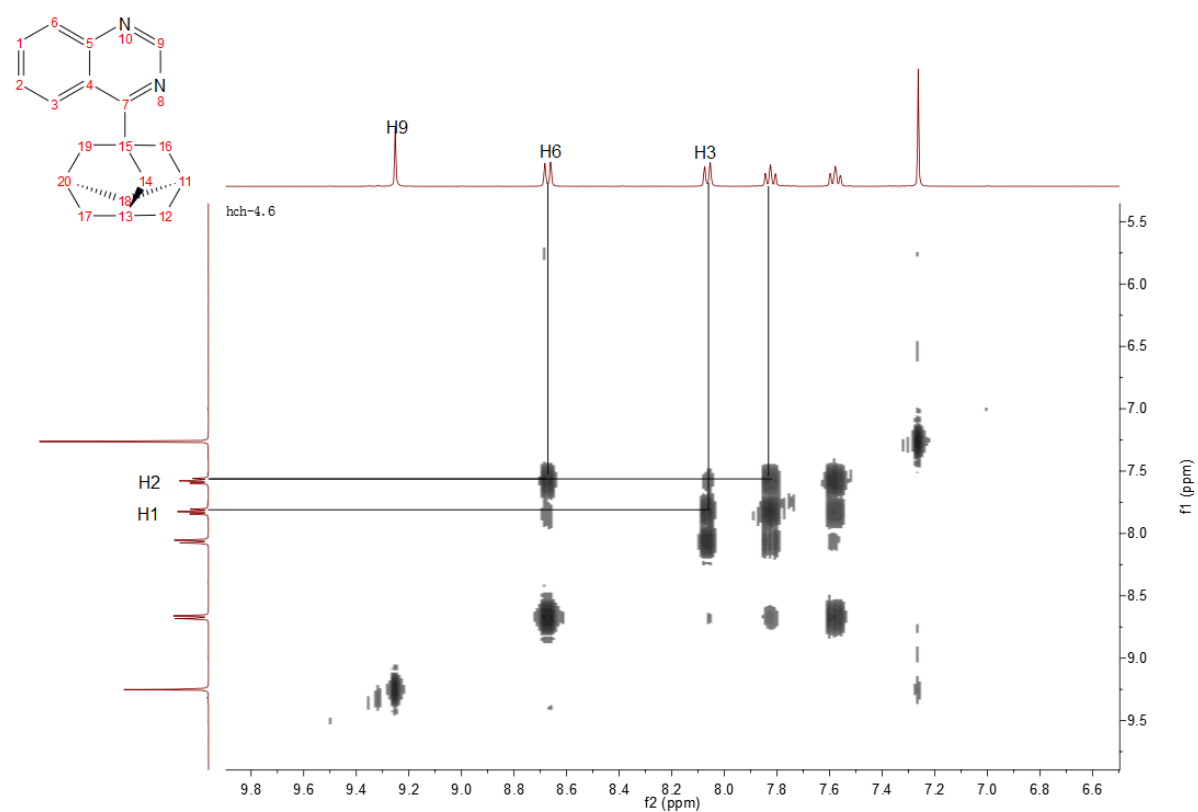




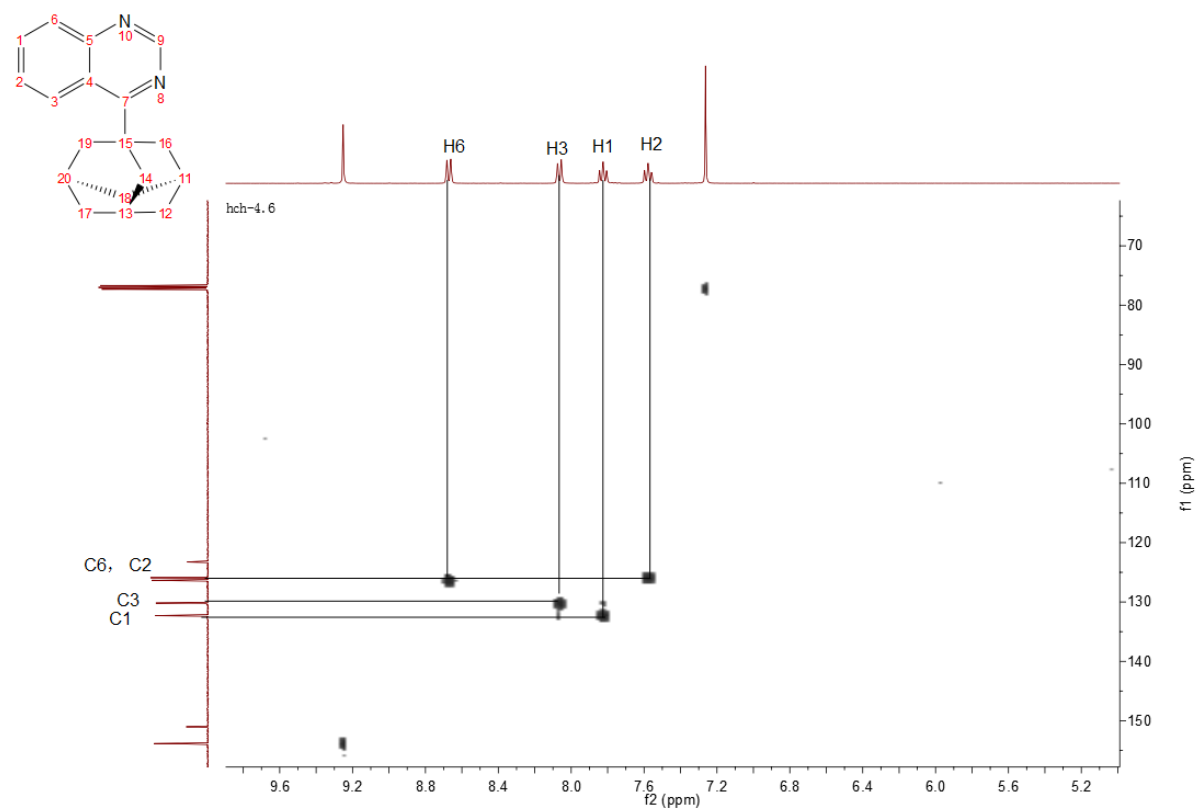




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