Electronic Supplementary Material (ESI) for Green Chemistry.

Substituent-Controlled Selective Synthesis of 1,2-Diketones and Internal Alkynes from Terminal Alkynes with Arylboronic Acids via α-Stilbene Radicals by Heteroleptic Cu(I) Complexes Under Visible-Light

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1. General considerations:

The ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ on Bruker spectrometers 300 MHz and 400 MHz NMR spectrometer with TMS as an internal standard. Mass spectra were recorded on Xevo G2S Q-TOF spectrometer. The light source for photochemical reactions was Kessil 456nm Blue LED (model number: KSPR160L-456-EU). Reaction tubes made of borosilicate glass were used as reaction vessels. The distance between the light source and the reaction vessel was 8 cm. TLC was performed on using Merck pre-coated TLC plates (Merck 60 F254) and detected under UV light. Column chromatographic separation was carried out with silica gel (100-200 mesh). Reagents and solvents were purified as per standard procedures and used.

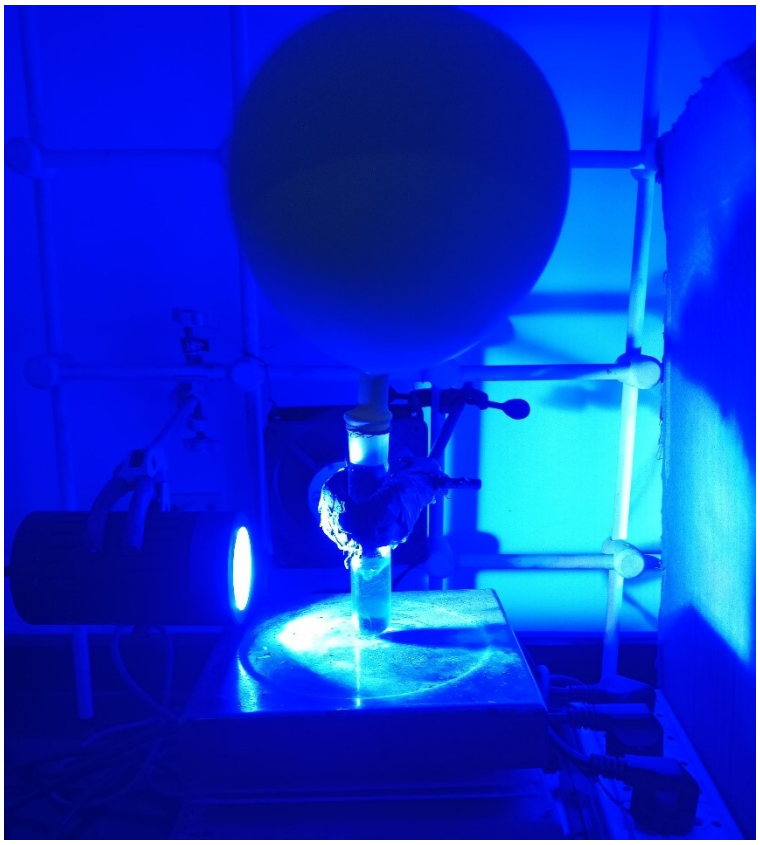


Figure S1: Reaction setup with Kessil PR160L-456nm Blue LED

2. Preparation of Substrates and Catalyst.

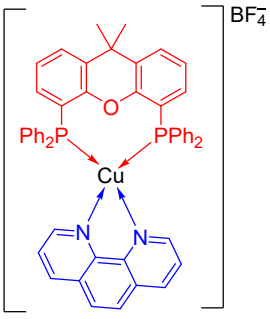
2.1 Procedure A for synthesis of 1,2-diketones.

Reaction tube was charged with alkynes **1** (0.78 mmol), boronic acid **2** (1.56 mmol), PC (5 mol%) and triethylamine (1.17 mmol) in MeOH (10 mL). The reaction mixture was irradiated with blue LED under O_2 atmosphere about 12h. After completion of the reaction mixture, solvent was evaporated under reduced pressure. The crude products was purified by column chromatography using EtOAc/Hexanes (1:9) as eluent to furnish the corresponding 1,2-diketones.

2.2 Procedure B for synthesis of copper (I) catalysts.

2.2.1 Synthesis of [Cu(phen)(Xantphos)]BF_4 *PC-1*[1]

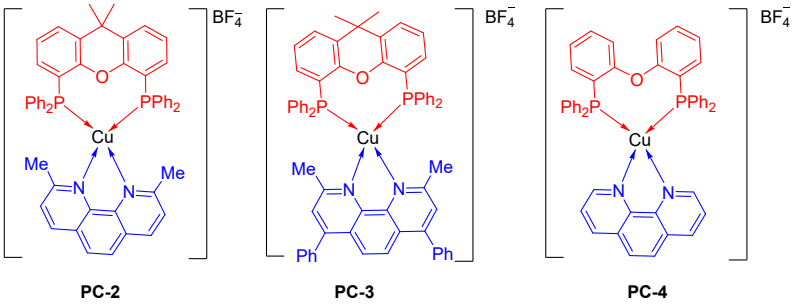
$[Cu(CH_3CN)_4]BF_4$ (500mg, 1.6 mmol) and Xantphos (0.920 mg, 1.6 mmol) were dissolved in 20 mL THF and allowed to stir at room temperature for 1h. A solution of 1,10-phenanthroline (286 mg, 1.6 mmol) in THF (10 mL) was added in one portion and stirred for 1h. The solvent was evaporator under reduced pressure. The crude complex was precipitated by dissolving DCM (5mL) solvent followed by addition of pentane. It was filtered, washed several times with water and dried under vacuum (1.15 g, 88% yield) and characterized by NMR and UV-visible spectra.



PC-1

2.2.2 Synthesis of Copper (I) catalysts *PC-2, PC-3and PC-4*[1]

PC-2, PC-3 and PC-4 catalysts were prepared following procedure B.



2.3. UV–visible absorption spectra of PC-1, PC-2, PC-3 and PC-4.

UV-Visible absorption studies were investigated for the PC-1-4 and shown figure S2. Absorption maximum for PC-1, PC-2, PC-3 and PC-4 shows at 378nm, 383nm, 380 nm, and 382 nm respectively.

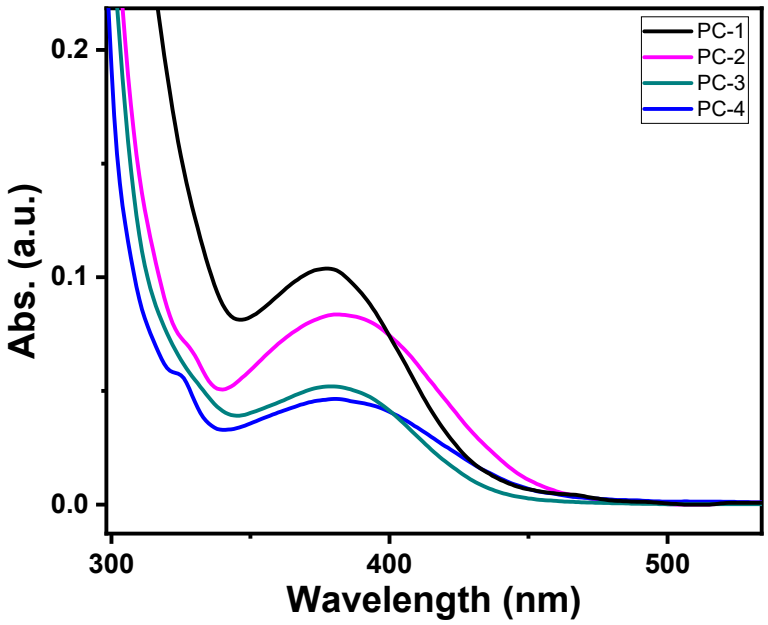
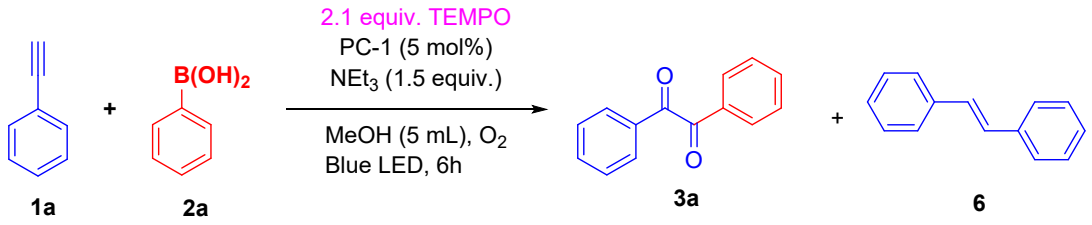


Figure S2: UV-Vis absorption spectra of PC-1-4

3. Preliminary mechanistic study

3.1 Intermediate-trapping experiments and by-products.

Reaction tube was charged with alkynes **1a** (0.78 mmol), boronic acid **2a** (1.56 mmol), PC-1 (5 mol%) and triethylamine (1.17 mmol). The reaction mixture was irradiated with blue LED under O_2 atmosphere about 6h. The formation of the product **3a** (Figure S3) and by-product stilbene **6** (Figure S4). Stilbene **6** was confirmed by HRMS.



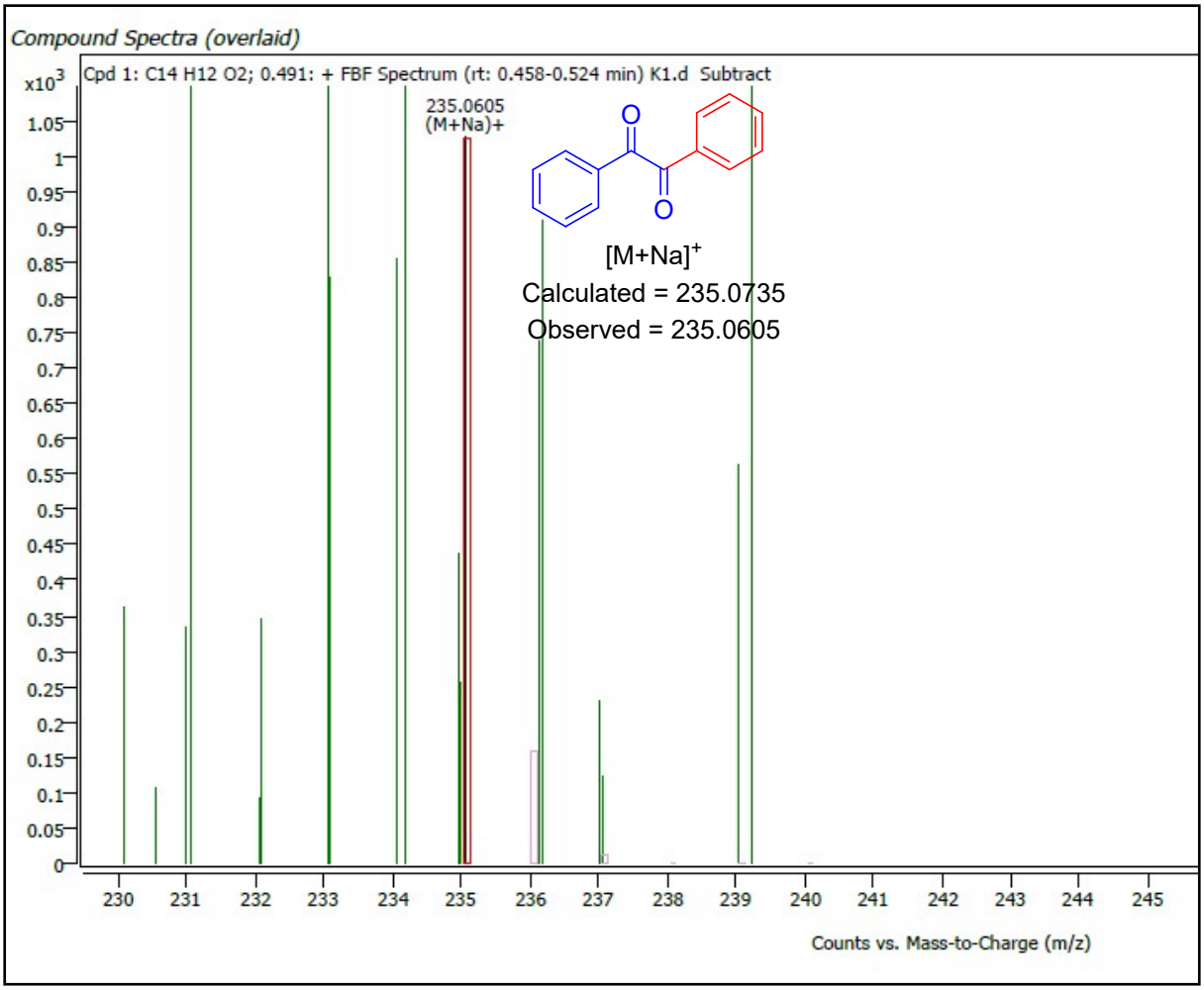


Figure S3: Analysis of reaction mixture by HRMS

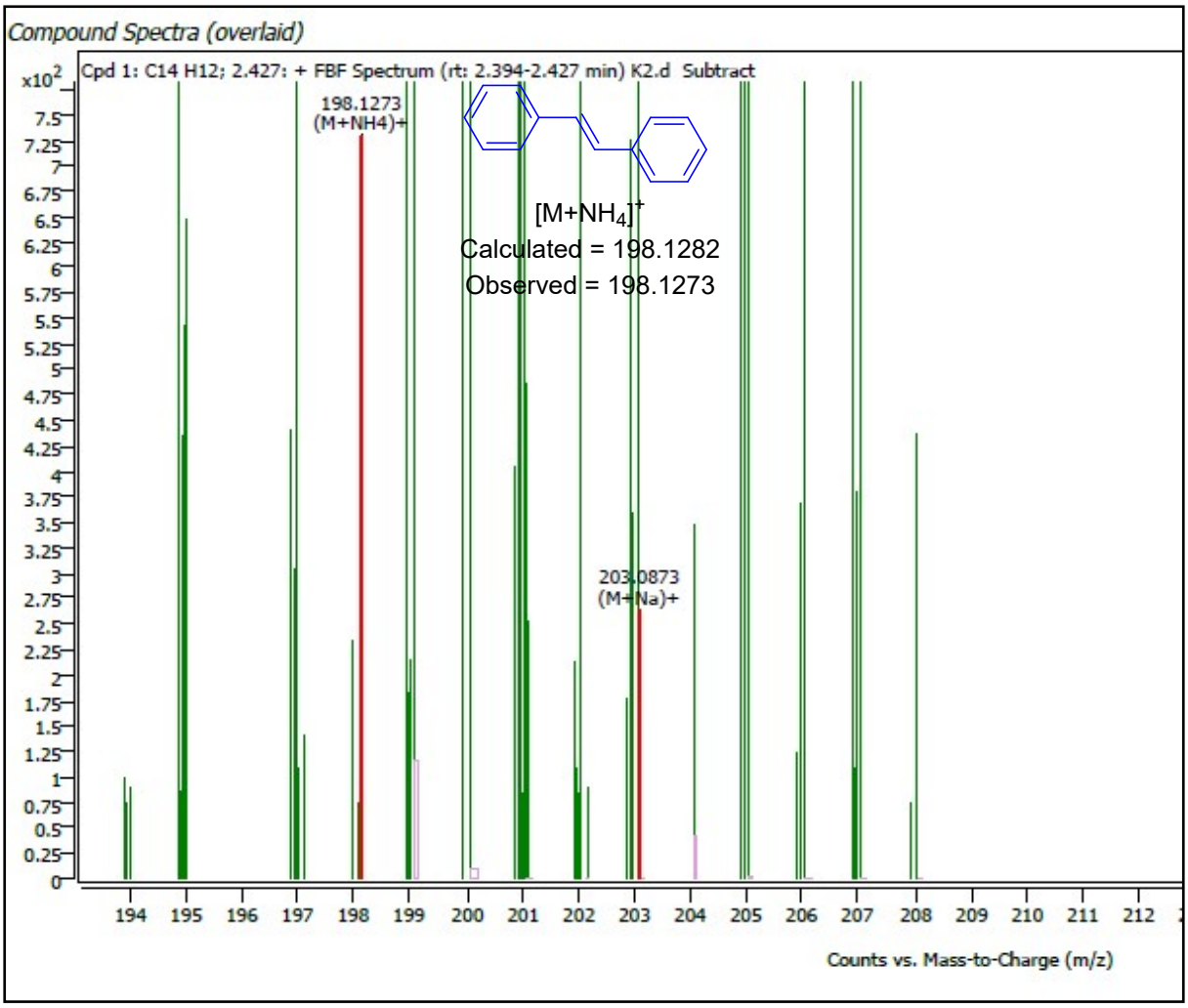
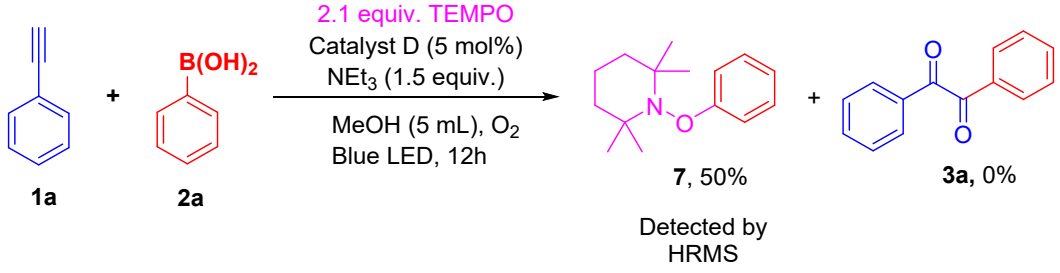


Figure S4: Analysis of reaction mixture by HRMS

3.2 Radical-trapping experiment.

Reaction tube was charged with alkynes **1a** (0.78 mmol), boronic acid **2a** (1.56 mmol), PC-1 (5 mol%) and triethylamine (1.17 mmol). To this reaction mixture, 2,2,6,6-tetramethylpiperidineoxy (TEMPO) (1.63 mmol) as radical scavenger were added. The reaction mixture was characterised with HRMS. The formation of phenyl radical-TEMPO **7** (Figure S5) adduct was confirmed by HRMS and isolated in 50% yield.



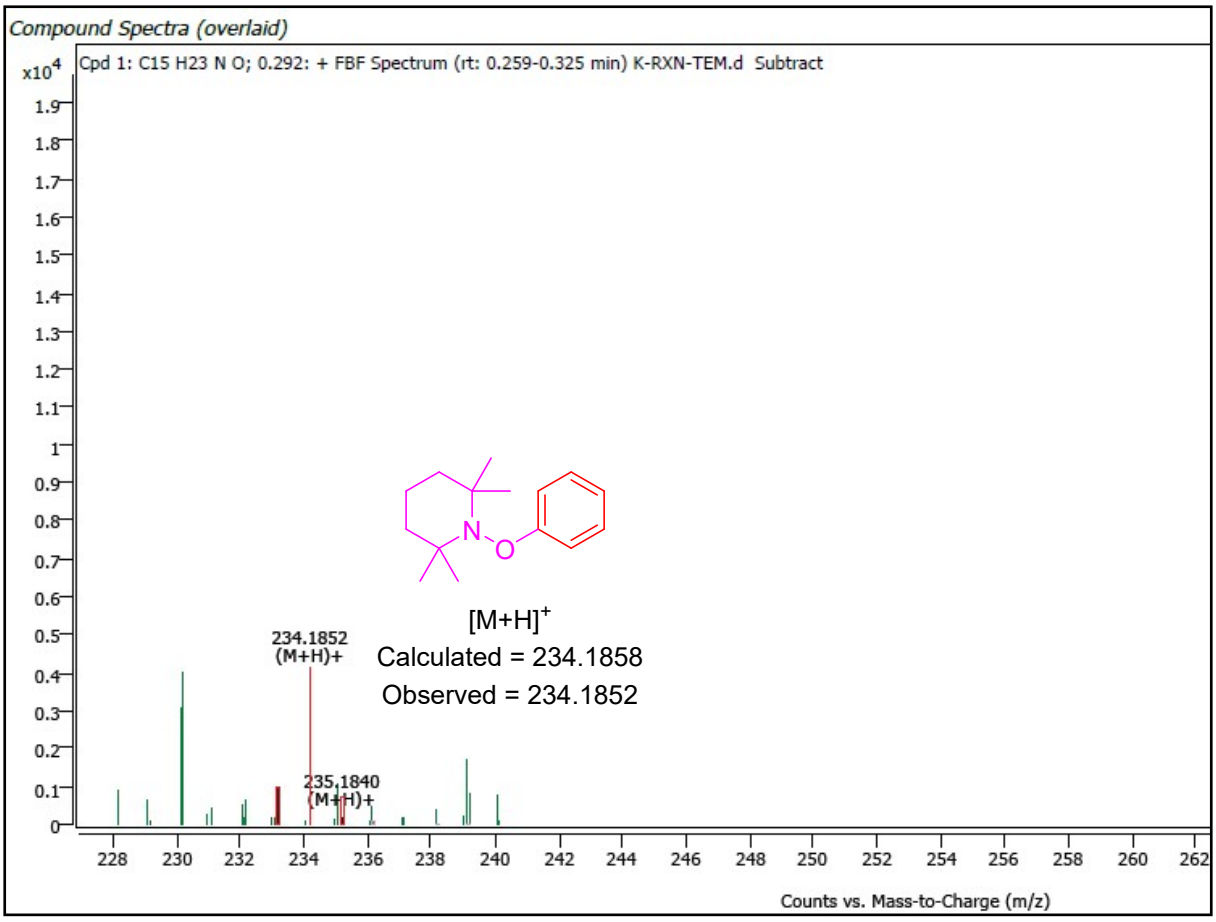


Figure S5: Analysis of reaction mixture by HRMS

3.3 Stern-Volmer experiments

Stern-Volmer quenching experiment were carried out with freshly prepared solution of 1×10^{-4} M PC-1 and quenched by phenylboronic acid **2a** in MeOH at room temperature. The solutions were excited at 378 nm and luminescence was measured at 450 nm.

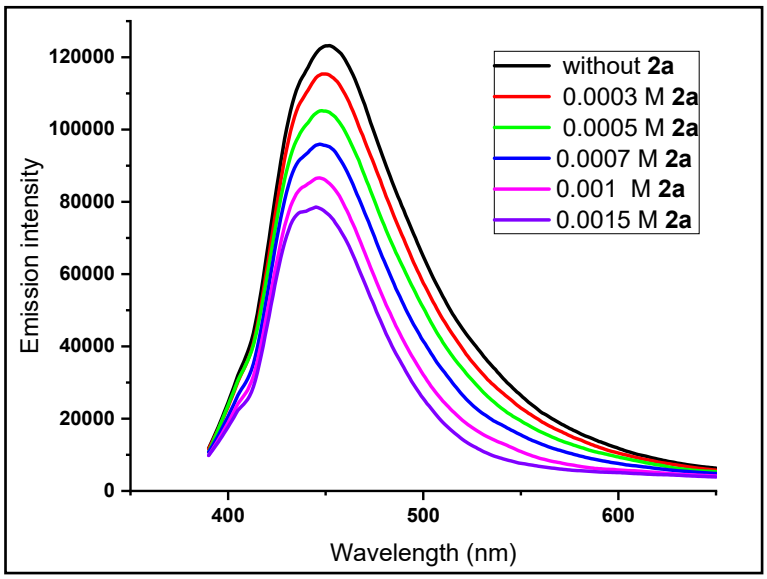


Figure S6: Emission spectra of PC-1 at different concentration of **2a**

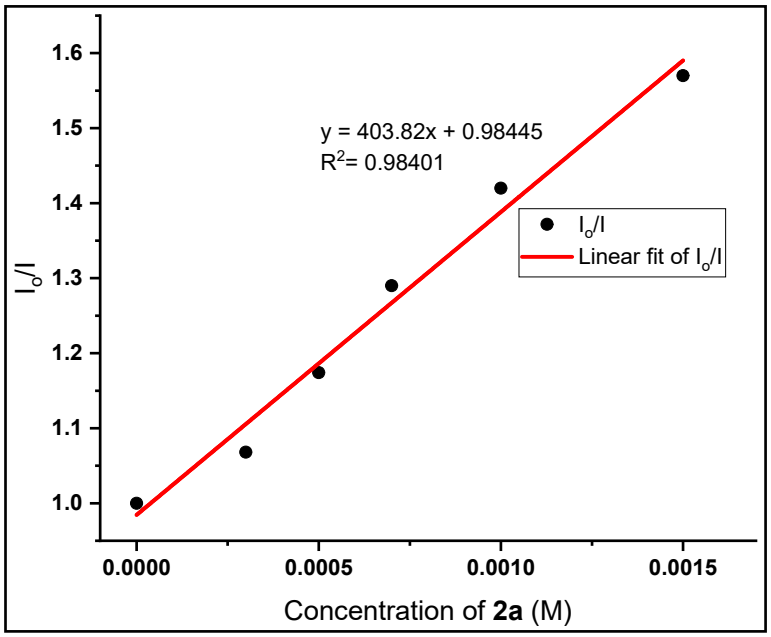
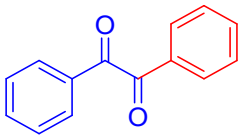


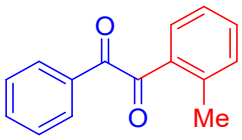
Figure S7: Stern–Volmer plot of PC-1 at different concentration of **2a**

4. Characterization data for the products



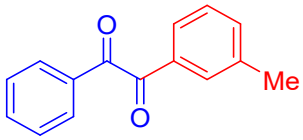
Benzil 3a[2]

3a (115 mg) was synthesized from procedure A; Yellow Oily liquid; 70% yield (eluent: EtOAc/Hexanes= 1:9);^{1}H NMR (300 MHz, $CDCl_3$):δ_H 7.98 (d, *J*= 7.5 Hz, 4H), 7.66 (t, *J*= 7.5 Hz, 2H), 7.52 (t, *J*= 7.8 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$):δ_C 194.4, 134.6, 133.2, 129.8, 128.9.



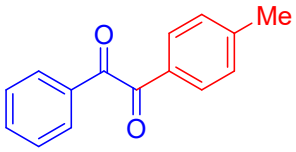
1-phenyl-2-(o-tolyl)ethane-1,2-dione 3b[3]

3b (113 mg) was synthesized from procedure A; Yellow Oily liquid; 65% yield (eluent: EtOAc/Hexanes= 1:9);^{1}H NMR (300 MHz, $CDCl_3$):δ_H 8.00 (d, *J*= 8.1 Hz, 2H), 7.67 (d, *J*= 7.5 Hz, 2H), 7.55-7.527 (m, 3H), 7.36 (d, *J*= 7.8 Hz, 1H), 7.30 (t, *J*= 7.5 Hz, 1H), 2.72 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$):δ_C 196.7, 194.7, 141.3, 134.6, 133.7, 133.2, 132.9, 132.5, 131.9, 129.9, 129.0, 126.0, 21.8.



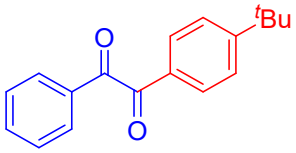
1-phenyl-2-(m-tolyl)ethane-1,2-dione 3c[3]

3c (106 mg) was synthesized from procedure A; Yellow Oily liquid; 61% yield (eluent: EtOAc/Hexanes= 1:9);^{1}H NMR (400 MHz, $CDCl_3$):δ_H 7.98 (t, *J*= 7.2 Hz, 2H), 7.69 (t, *J*= 4 Hz, 2H), 7.57-7.53 (m, 1H), 7.43-7.36 (m, 3H), 7.31 (t, *J*= 6.4 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$):δ_C 194.8, 194.7, 139.0, 135.7, 134.8, 133.07, 133.03, 130.2, 129.9, 129.0, 128.9, 127.2, 21.2.



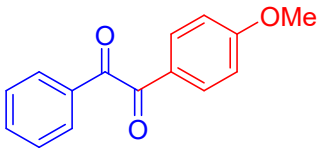
1-phenyl-2-(p-tolyl)ethane-1,2-dione 3d[4]

3d (119 mg) was synthesized from procedure A; Yellow Oily liquid; 68% yield (eluent: EtOAc/Hexanes= 1:9);^{1}H NMR (300 MHz, $CDCl_3$):δ_H 7.99 (d, *J*= 8.1 Hz, 2H), 7.89 (d, *J*= 7.8 Hz, 2H), 7.68-7.62 (m, 1H), 7.53 (t, *J*= 6.9 Hz, 2H), 7.33-7.27 (*J*= 7.8 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$):δ_C 194.6, 194.2, 146.1, 134.6, 133.3, 130.8, 130.0, 129.8, 129.7, 128.9, 21.8.



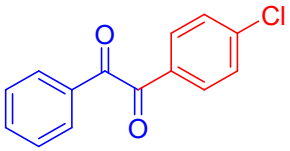
1-(4-(tert-butyl)phenyl)-2-phenylethane-1,2-dione 3e[2]

3e (155 mg) was synthesized from procedure A; Yellow Oily liquid; 75% yield (eluent: EtOAc/Hexanes= 1:9);^{1}H NMR (300 MHz, $CDCl_3$):δ_H 8.00 (d, *J*= 8.1 Hz, 2H), 7.94 (t, *J*= 6.9 Hz, 2H), 7.68 (t, *J*= 7.2 Hz, 1H), 7.55-7.49 (m, 4H), 1.35 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$):δ_C 194.7, 194.2, 159.0, 134.6, 133.2, 130.6, 129.9, 128.9, 128.2, 126.0, 35.4, 30.9.



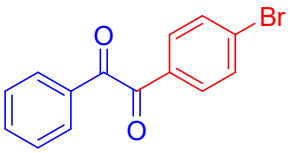
1-(4-methoxyphenyl)-2-phenylethane-1,2-dione 3f[2]

3f (112 mg) was synthesized from procedure A; Yellow Oily liquid; 60% yield (eluent: EtOAc/Hexanes= 1:9);^{1}H NMR (300 MHz, $CDCl_3$):δ_H 7.99 (t, *J*= 6 Hz, 4H), 7.67-7.59 (m, 1H), 7.53 (t, *J*= 7.8 Hz, 2H), 6.99 (d, *J*= 9 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$):δ_C 194.8, 193.1, 165.0, 134.6, 133.3, 132.3, 129.8, 128.9, 126.1, 114.3, 55.6.



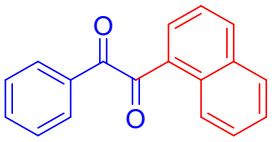
1-(4-chlorophenyl)-2-phenylethane-1,2-dione 3g[2]

3g (107 mg) was synthesized from procedure A; Yellow Oily liquid; 56% yield (eluent: EtOAc/Hexanes= 1:9);^{1}H NMR (400 MHz, $CDCl_3$):δ_H 7.90-7.83 (m, 4H), 7.69-7.57 (m, 1H), 7.46-7.39 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$):δ_C 193.8, 193.0, 141.6, 135.0, 132.8, 131.2, 129.9, 129.4, 129.0.



1-(4-bromophenyl)-2-phenylethane-1,2-dione 3h[2]

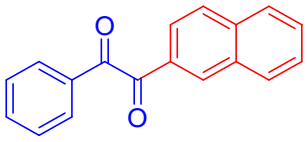
3h (117 mg) was synthesized from procedure A; Yellow Oily liquid; 52% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (300 MHz, $CDCl_3$):δ_H 7.98 (d, *J*= 10.4 Hz, 2H), 7.87 (d, *J*= 8.4 Hz, 2H), 7.68 (t, *J*= 6.9 Hz, 3H), 7.55 (t, *J*= 7.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$):δ_C 193.8, 193.3, 135.1, 132.7, 132.4, 131.7, 131.2, 130.5, 129.9, 129.1.



1-(naphthalen-1-yl)-2-phenylethane-1,2-dione 3i[2]

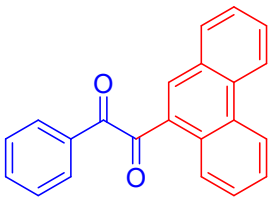
3i (131 mg) was synthesized from procedure A; Yellow Oily liquid; 65% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (300 MHz, $CDCl_3$):δ_H 9.23 (d, *J*= 8.7 Hz, 1H), 8.02 (d, *J*= 8.1 Hz, 1H), 7.94 (d, *J*= 7.8 Hz, 2H), 7.84 (t, *J*= 7.5 Hz, 2H), 7.67 (t, *J*= 6.9 Hz, 1H), 7.57-7.49

(q, *J*= 7.2 Hz, 2H), 7.43-7.34 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$):δ_C 197.2, 194.6, 136.0, 135.1, 134.7, 134.1, 133.9, 130.9, 130.0, 129.4, 129.0, 128.8, 128.6, 127.1, 125.9, 124.4.



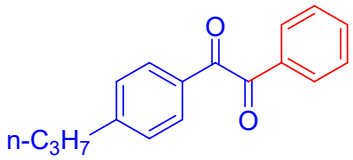
1-(naphthalen-2-yl)-2-phenylethane-1,2-dione 3j[4]

3j (125 mg) was synthesized from procedure A; Yellow Oily liquid; 62% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (300 MHz, $CDCl_3$):δ_H 8.33 (s, 1H), 8.04 (d, *J*= 8.4 Hz, 1H), 7.96 (t, *J*= 7.8 Hz, 3H), 7.90-7.80 (m, 2H), 7.61-7.54 (q, *J*= 7.5 Hz, 2H), 7.50-7.42 (q, *J*= 8.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$):δ_C 194.6, 136.4, 134.9, 133.5, 133.1, 132.3, 130.3, 130.0, 129.9, 129.5, 129.2, 129.0, 127.9, 127.9, 127.2, 123.6.



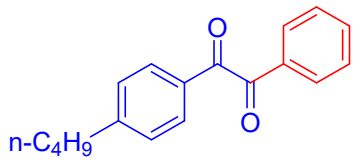
1-(phenanthren-9-yl)-2-phenylethane-1,2-dione 3k[5]

3k (178 mg) was synthesized from procedure A; Yellow solid; 74% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (300 MHz, $CDCl_3$):δ_H 9.35-9.31(m, 1H), 8.76-8.67 (m, 2H), 8.22 (s, 1H), 8.08 (d, *J*= 7.2 Hz, 2H), 7.88 (d, *J*= 8.1 Hz, 1H), 7.82-7.71 (m, 3H), 7.68-7.57(m, 2H), 7.55-7.50 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$):δ_C 196.2, 194.2, 138.3, 134.6, 133.6, 133.1, 131.0, 130.7, 130.4, 130.3, 129.6, 129.0, 128.5, 128.3, 127.9, 127.6, 127.2, 126.8, 122.8, 122.7.



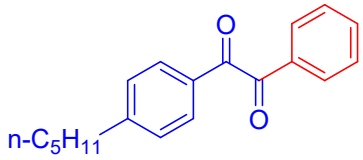
1-phenyl-2-(4-propylphenyl)ethane-1,2-dione 3l[6]

3l (135 mg) was synthesized from procedure A; Yellow Oily liquid; 69% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (400 MHz, $CDCl_3$):δ_H 7.98 (d, *J*= 8 Hz, 2H), 7.89 (d, *J*= 8 Hz, 2H), 7.66 (t, *J*= 7.6 Hz, 1H), 7.52 (t, *J*= 7.6 Hz, 2H), 7.32 (t, *J*= 8 Hz, 2H), 2.68 (t, *J*= 7.2 Hz, 2H), 1.71-1.62 (m, 2H), 0.96 (t, *J*= 7.6 Hz, 3Hz). ^{13}C NMR (101 MHz, $CDCl_3$):δ_C 194.7, 194.3, 150.8, 134.7, 133.1, 130.8, 130.0, 129.9, 129.1, 128.9, 38.2, 24.1, 13.7.



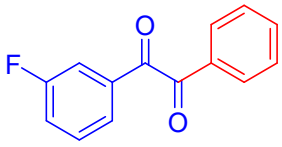
1-(4-butylphenyl)-2-phenylethane-1,2-dione 3m[7]

3m (131mg) was synthesized from procedure A; Yellow Oily liquid; 63% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (400 MHz, $CDCl_3$):δ_H 7.90 (d, *J*= 7.6 Hz, 2H), 7.82 (d, *J*= 8 Hz, 2H), 7.59 (t, *J*= 7.6 Hz, 1H), 7.44 (t, *J*= 7.6 Hz, 2H), 7.24 (t, *J*= 8 Hz, 2H), 2.62 (t, *J*= 7.6 Hz, 2H), 1.58-1.50 (m, 2H), 1.32-1.25 (m, 2H), 0.86 (d, *J*= 4.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$):δ_C 194.8, 194.3, 151.1, 134.7, 133.1, 130.7, 130.0, 129.9, 129.1, 128.9, 35.9, 33.1, 22.2, 13.8.



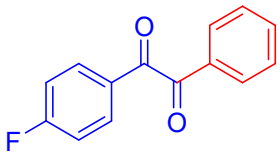
1-(4-pentylphenyl)-2-phenylethane-1,2-dione 3n

3n (152 mg) was synthesized from procedure A; Yellow Oily liquid; 70% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (300 MHz, $CDCl_3$):δ_H 8.01-7.89 (dd, *J*= 7.5 Hz, 8.1 Hz, 4H), 7.69 (t, *J*= 7.2 Hz, 1H), 7.54 (t, *J*= 7.5 Hz, 2H), 7.34-7.28 (t, *J*= 8.1 Hz, 2H), 2.73 (t, *J*= 7.2 Hz, 2H), 1.69 (d, *J*= 6.6 Hz, 2H), 1.36 (t, *J*= 3. Hz, 4H), 0.94 (t, *J*= 6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$):δ_C 194.7, 194.2, 151.1, 134.6, 133.5, 131.0, 130.1, 129.9, 129.1, 128.9, 36.2, 31.4, 30.6, 22.4, 13.9.



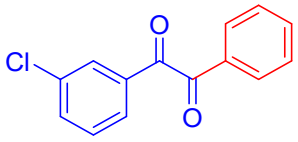
1-(3-fluorophenyl)-2-phenylethane-1,2-dione 3o[8]

3o (101 mg) was synthesized from procedure A; Yellow Oily liquid; 57% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (300 MHz, $CDCl_3$):δ_H 7.98 (d, 2H), 7.75-7.66 (q, *J*= 7.5 Hz, 3H), 7.55-7.46 (m, 3H), 7.39-7.33 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$):δ_C 193.7, 193.0, 164.5, 161.2, 135.1, 134.9, 132.7, 130.8 (d , *J*= 7.5 Hz), 129.9, 129.1, 128.2, 126.0 (d *J*= 3 Hz), 122.1 (d, *J*= 21.7 Hz), 116.2 (d, *J*= 18.7 Hz). ^{19}F NMR (471 MHz, $CDCl_3$): δ_F -110.5 (s, 1F).



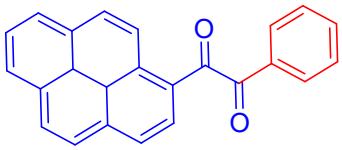
1-(4-fluorophenyl)-2-phenylethane-1,2-dione 3p[2]

3p (119 mg) was synthesized from procedure A; Yellow Oily liquid; 67% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (400 MHz, $CDCl_3$):δ_H 7.96-7.93 (m, 2H), 7.90 (d, *J*= 5.7 Hz, 2H), 7.61 (t, *J*= 5.7 Hz, 1H), 7.46 (t, *J*= 6 Hz, 2H), 7.13 (t, *J*= 6.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$):δ_C 194.0, 192.7, 168.0, 165.5, 135.0, 132.9 (t, *J*= 7.5 Hz), 129.9, 129.8, 129.5, 129.0, 116.5 (d, *J*= 22 Hz).



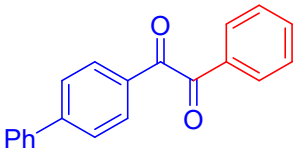
1-(3-chlorophenyl)-2-phenylethane-1,2-dione 3q[8]

3q (127 mg) was synthesized from procedure A; Yellow Oily liquid; 67% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (400 MHz, $CDCl_3$):δ_H 7.90 (d, *J*= 5.1 Hz, 3H), 7.77 (d, *J*= 6 Hz, 1H), 7.62-7.54 (m, 2H), 7.47 (t, *J*= 5.7, 2H), 7.40 (t, *J*= 12 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$):δ_C 193.6, 192.9, 135.4, 135.1, 134.8, 134.5, 132.6, 130.3, 129.9, 129.5, 129.1, 128.1.



1-(3a1,5a1-dihydropyren-1-yl)-2-phenylethane-1,2-dione 3r[9]

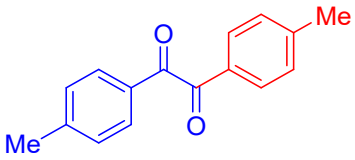
3r (215 mg) was synthesized from procedure A; Yellow Solid; 82% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (300 MHz, $CDCl_3$):δ_H 9.59 (d, *J*= 9.3 Hz, 1H), 8.35-8.26 (m, 4H), 8.21 (d, *J*= 8.7 Hz, 1H), 8.10-8.01(m, 5H), 7.67 (t, *J*= 14 Hz, 1H), 7.53 (t, *J*= 7.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$):δ_C 197.3, 194.8, 135.8, 134.5, 133.7, 131.6, 131.2, 131.1, 131.0, 130.9, 130.4, 130.0, 129.0, 127.2, 127.0, 126.6, 125.1, 124.9, 124.7, 124.0, 123.9.



1-([1,1'-biphenyl]-4-yl)-2-phenylethane-1,2-dione 3s[8]

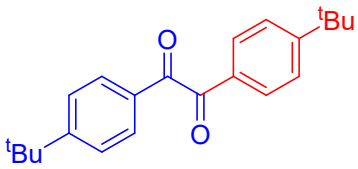
3s (122 mg) was synthesized from procedure A; Yellow solid; 55% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (400 MHz, $CDCl_3$):δ_H 8.06 (d, *J*= 8 Hz, 2H), 8.01 (d, *J*= 8 Hz, 2H), 7.74 (d, *J*= 8 Hz, 2H), 7.69-7.61 (m, 3H), 7.54 (t, *J*= 7.6 Hz, 2H), 7.49 (t, *J*= 7.6 Hz,

2H), 7.43 (d, *J*= 7.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$):δ_C 194.5, 194.1, 147.6, 139.5, 134.8, 133.0, 131.7, 130.5, 129.9, 129.0, 128.6, 127.6, 127.3.



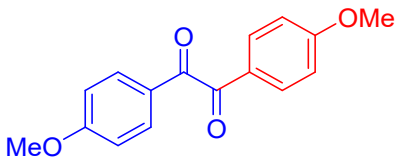
1,2-di-p-tolylethane-1,2-dione 3u[4]

3u (131 mg) was synthesized from procedure A; Yellow Oily liquid; 71% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (400 MHz, $CDCl_3$):δ_H 7.78 (d, *J*= 8 Hz, 4H), 7.30 (d, *J*= 8 Hz, 4H), 2.34 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$):δ_C 194.5, 146.0, 130.7, 130.0, 129.9, 21.9.



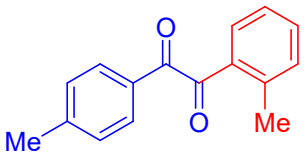
1,2-bis(4-(tert-butyl)phenyl)ethane-1,2-dione 3v[10]

3v (188 mg) was synthesized from procedure A; Yellow Solid; 75% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (400 MHz, $CDCl_3$):δ_H 7.83 (d, *J*= 8 Hz, 4H), 7.44 (d, *J*= 8.4 Hz, 4H), 1.25 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$):δ_C 194.5, 158.8, 130.6, 129.9, 126.0, 35.3, 30.9.



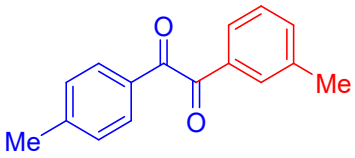
1,2-bis(4-methoxyphenyl)ethane-1,2-dione 3w[4]

3w (126 mg) was synthesized from procedure A; Yellow Oily liquid; 60% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (300 MHz, $CDCl_3$):δ_H 7.96 (d, *J*= 8.7 Hz, 4H), 6.98 (d, *J*= 8.7 Hz, 4H), 3.88 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 193.3, 164.8, 132.3, 126.4, 114.3, 55.5.



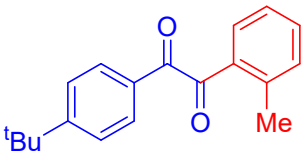
1-(o-tolyl)-2-(p-tolyl)ethane-1,2-dione 3x[3]

3x (129 mg) was synthesized from procedure A; Yellow Oily liquid; 70% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (400 MHz, $CDCl_3$):δ_H 7.79 (d, *J*= 6 Hz, 2H), 7.56 (d, *J*= 5.7 Hz, 1H), 7.41 (t, *J*= 5.7 Hz, 1H), 7.26 (t, *J*= 6.6 Hz, 3H), 7.17 (t, *J*= 5.4 Hz, 1H), 2.61 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$):δ_C 196.9, 194.6, 146.0, 141.3, 133.7, 133.0, 132.5, 131.9, 130.7, 130.0, 129.7, 126.0, 21.9.



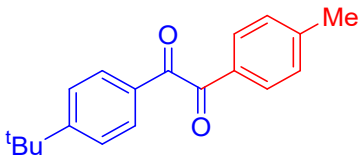
1-(m-tolyl)-2-(p-tolyl)ethane-1,2-dione 3y[3]

3y (134 mg) was synthesized from procedure A; Yellow Oily liquid; 72% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (400 MHz, $CDCl_3$):δ_H 7.87 (d, *J*= 6.3 Hz, 2H), 7.77 (d, *J*= 6.6 Hz, 2H), 7.46 (d, *J*= 5.7 Hz, 1H), 7.40 (d, *J*= 5.4 Hz, 1H), 7.31 (d, *J*= 6 Hz, 2H), 2.43 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$):δ_C 195.0, 194.4, 146.1, 138.9, 135.6, 133.1, 130.6, 130.2, 130.0, 129.7, 128.8, 127.2, 21.9, 21.2.



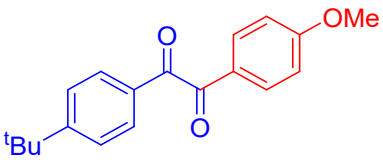
1-(4-(tert-butyl)phenyl)-2-(o-tolyl)ethane-1,2-dione 3z

3z (159 mg) was synthesized from procedure A; Yellow Oily liquid; 73% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (300 MHz, $CDCl_3$):δ_H 7.94-7.93 (m, 2H), 7.68 (d, *J*= 7.8 Hz, 1H), 7.56-7.46 (m, 3H), 7.35 (d, *J*= 7.5 Hz, 1H), 7.29 (t, *J*= 6.9 Hz, 1H), 2.71 (s, 3H), 1.38 (t, *J*= 3.3 Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$):δ_C 196.9, 194.4, 158.7, 141.1, 133.5, 132.8, 132.4, 132.2, 130.8, 129.9, 126.0, 125.9, 35.3, 31.0, 21.6.



1-(4-(tert-butyl)phenyl)-2-(p-tolyl)ethane-1,2-dione 3aa[6]

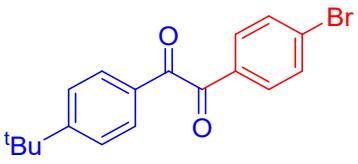
3aa (157 mg) was synthesized from procedure A; Yellow Oily liquid; 72% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (300 MHz, $CDCl_3$):δ_H 7.93 (t, *J*= 8.7 Hz, 4H), 7.54 (d, *J*= 8.4 Hz, 2H), 7.32 (t, *J*= 8.1 Hz, 2H), 2.44 (s, 3H), 1.36 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$):δ_C 194.3, 158.8, 145.8, 130.9, 130.7, 129.9, 129.8, 129.6, 125.9, 35.3, 30.9, 21.7.



1-(4-(tert-butyl)phenyl)-2-(4-methoxyphenyl)ethane-1,2-dione 3ab[2]

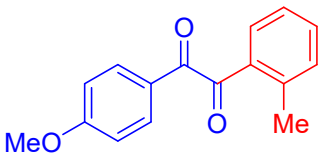
3ab (140 mg) was synthesized from procedure A; Yellow Oily liquid; 61% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (300 MHz, $CDCl_3$):δ_H 7.97-7.90(dd, *J*= 9 Hz, 8.4 Hz, 4H),

7.53 (d, *J*= 8.1 Hz, 2H), 6.99 (d, *J*= 8.7 Hz, 2H), 3.89 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$):δ_C 194.5, 193.3, 164.9, 158.8, 132.3, 130.8, 129.8, 126.4, 125.9, 114.3, 55.6, 35.3, 30.9.



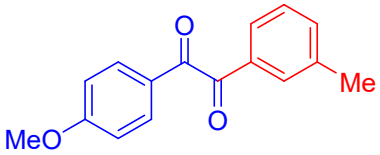
1-(4-bromophenyl)-2-(4-(tert-butyl)phenyl)ethane-1,2-dione 3ac

3ac (180 mg) was synthesized from procedure A; Yellow Oily liquid; 67% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (300 MHz, $CDCl_3$):δ_H 7.91-7.83 (dd, *J*= 8.4 Hz, 8.4 Hz, 4H), 7.67 (d, *J*= 7.8 Hz, 2H), 7.55 (d, *J*= 8.1 Hz, 2H), 1.35 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$):δ_C 193.3, 159.2, 132.3, 132.0, 131.7, 130.4, 130.2, 129.8, 126.0, 35.3, 30.9.



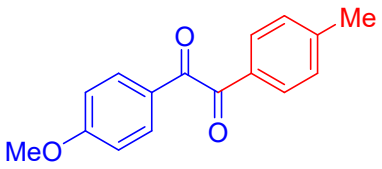
1-(4-methoxyphenyl)-2-(o-tolyl)ethane-1,2-dione 3ad[11]

3ad (152 mg) was synthesized from procedure A; Yellow Oily liquid; 77% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (300 MHz, $CDCl_3$):δ_H 7.97 (t, *J*= 7.2 Hz, 2H), 7.67 (d, *J*= 7.8 Hz, 1H), 7.50 (t, *J*= 7.5 Hz, 1H), 7.34-7.23 (m, 2H), 7.00 (d, *J*= 9 Hz, 2H), 3.88(s, 3H), 2.70 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$):δ_C 197.0, 193.4, 164.8, 141.1, 133.4, 132.8, 132.4, 132.3, 132.2, 126.3, 125.9, 114.3, 55.5, 21.6.



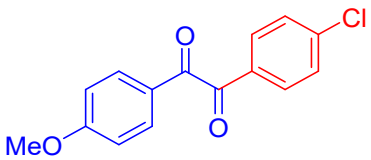
1-(4-methoxyphenyl)-2-(m-tolyl)ethane-1,2-dione 3ae[11]

3ae (148 mg) was synthesized from procedure A; Yellow Oily liquid; 75% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (300 MHz, $CDCl_3$):δ_H 7.87 (d, *J*= 6.6 Hz, 2H), 7.69 (d, *J*= 6.3 Hz, 2H), 7.38(d, *J*= 5.7 Hz, 1H), 7.32 (t, *J*= 5.4 Hz, 1H), 6.90 (d, *J*= 6.6 Hz, 2H), 3.80 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$):δ_C 195.1, 193.2, 164.9, 138.9, 135.6, 133.2, 132.4, 130.2, 128.8, 127.2, 126.1, 114.3, 55.6, 21.2.



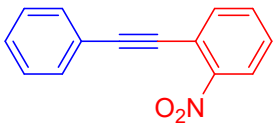
1-(4-methoxyphenyl)-2-(p-tolyl)ethane-1,2-dione 3af[8]

3af (136 mg) was synthesized from general procedure; Yellow Oily liquid; 69% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (300 MHz, $CDCl_3$):δ_H 7.94 (d, *J*= 8.7 Hz, 2H), 7.88 (d, *J*= 7.8 Hz, 2H), 7.31 (d, *J*= 7.8 Hz, 2H), 6.98 (d, *J*= 8.7 Hz, 2H), 3.88 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$):δ_C 194.5, 193.2, 164.9, 145.8, 132.3, 131.0, 130.0, 129.6, 126.4, 114.3, 55.6, 21.8.



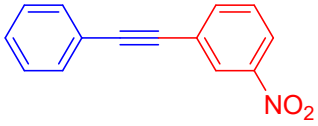
1-(4-chlorophenyl)-2-(4-methoxyphenyl)ethane-1,2-dione 3ag[2]

3ag (139 mg) was synthesized from procedure A; Yellow Oily liquid; 65% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (300 MHz, $CDCl_3$):δ_H 7.96-7.91 (m, 4H), 7.50 (d, *J*= 8.7 Hz, 2H), 7.00 (d, *J*= 9 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$):δ_C 193.2, 192.3, 165.1, 141.3, 132.4, 131.7, 131.2, 129.3, 126.0, 114.4, 55.6.



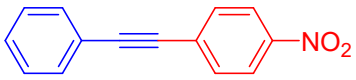
1-nitro-2-(phenylethynyl)benzene 4a[12]

4a (141 mg) was synthesized from procedure A; Yellow Solid; 76% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (400 MHz, $CDCl_3$):δ_H 8.06 (d, *J*= 8 Hz, 1H), 7.70 (d, *J*= 7.6 Hz, 1H), 7.59-7.55 (m, 3H), 7.45 (t, *J*= 8 Hz, 1H), 7.37 (d, *J*= 4.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$):δ_C 149.6, 134.5, 132.8, 132.0, 129.2, 128.5, 128.4, 124.7, 122.4, 118.7, 97.1, 84.8.



1-nitro-3-(phenylethynyl)benzene 4b[13]

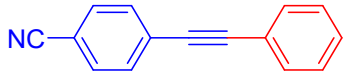
4b (115 mg) was synthesized from procedure A; Yellow Solid; 62% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (300 MHz, $CDCl_3$):δ_H 8.24 (s, 1H), 8.06 (d, *J*= 1.2 Hz, 1.2 Hz, 1H), 7.71 (d, *J*= 7.8 Hz, 1H), 7.46-7.340 (m, 3H), 7.28 (d, *J*= 2.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$):δ_C 147.3, 136.0, 130.7, 128.2, 128.0, 127.4, 125.3, 124.2, 121.7, 121.3, 91.0, 85.9.



1-nitro-4-(phenylethynyl)benzene 4c[12]

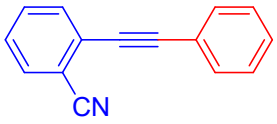
4c (131 mg) was synthesized from procedure A; Yellow Solid; 71% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (400 MHz, $CDCl_3$):δ_H 8.21 (d, *J*= 9 Hz, 2H), 7.66 (d, *J*= 8.7

Hz, 2H), 7.56 (t, *J*= 3.6 Hz, 2H), 7.39 (d, *J*= 5.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$):δ_C 147.0, 132.2, 131.8, 130.2, 129.2, 128.5, 123.6, 122.1, 94.7, 87.5.



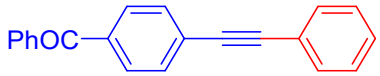
4-(phenylethynyl)benzonitrile 4d[14]

4d (102 mg) was synthesized from procedure A; White Solid; 60% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (300 MHz, $CDCl_3$):δ_H 7.53 (d, *J*= 11.4 Hz, 4H), 7.46 (d, *J*= 3.3 Hz, 2H), 7.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$):δ_C 132.0, 131.9, 131.7, 129.0, 128.4, 122.3, 118.3, 111.6, 93.8, 87.7.



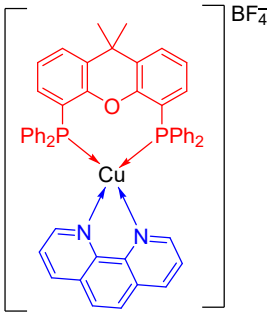
2-(phenylethynyl)benzonitrile 4e[12]

4e (120 mg) was synthesized from procedure A; White Solid; 68% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (400 MHz, $CDCl_3$):δ_H 7.62-7.59 (m, 3H), 7.57-7.56 (m, 3H), 7.47-7.43 (m, 2H), 7.39-7.35 (m, 1H).



phenyl(4-(phenylethynyl)phenyl)methanone 4f[14]

4f (180 mg) was synthesized from procedure A; White Solid; 80% yield (eluent: EtOAc/Hexanes= 1:9); ^{1}H NMR (300 MHz, $CDCl_3$):δ_H 7.72 (t, *J*= 7.8 Hz, 5H), 7.55-7.48 (m, 5H), 7.42 (d, *J*= 7.5 Hz, 2H), 7.28 (d, *J*= 3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$):δ_C 195.7, 137.5, 136.8, 131.9, 131.7, 131.3, 129.9, 129.8, 129.8, 128.3, 128.3, 128.3, 122.8, 92.4, 88.6.



PC-1

[Cu(phen)(Xantphos)]BF_4 ***PC-1***[1]

PC-1 was synthesised from Procedure B; Yellow Crystalline Solid; 88% yield; ^{1}H NMR (300 MHz, $CDCl_3$):δ_H 8.57 (d, *J*= 7.5 Hz, 2H), 8.45 (s, 2H), 8.05 (s, 2H), 7.70 (d, *J*= 13.5 Hz, 4H), 7.18 (t, *J*= 7.5 Hz, 6H), 7.03 (t, *J*= 6.6 Hz, 7H), 6.89 (s, 9H), 6.58 (s, 2H), 1.78 (s, 6H).

5. References

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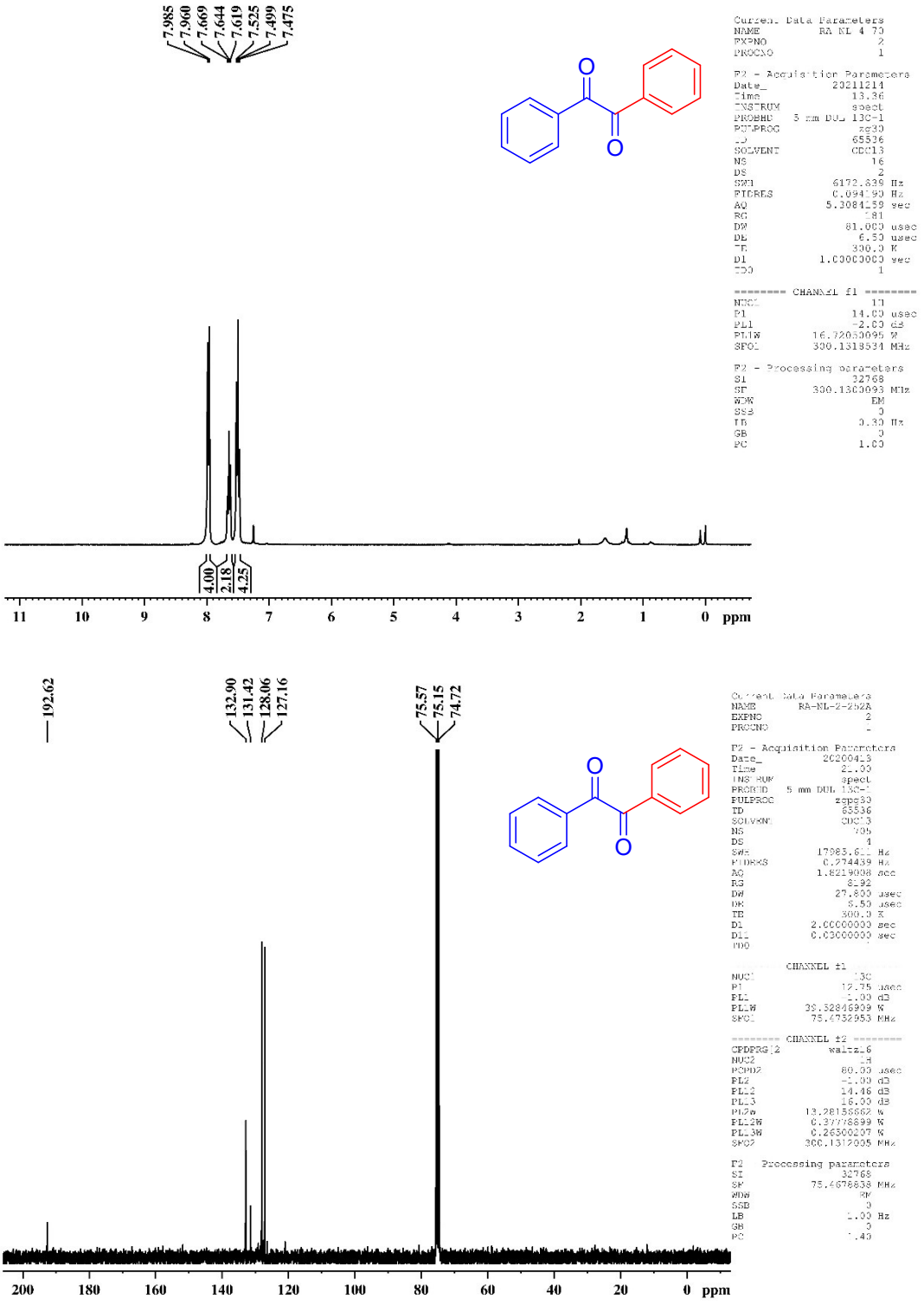
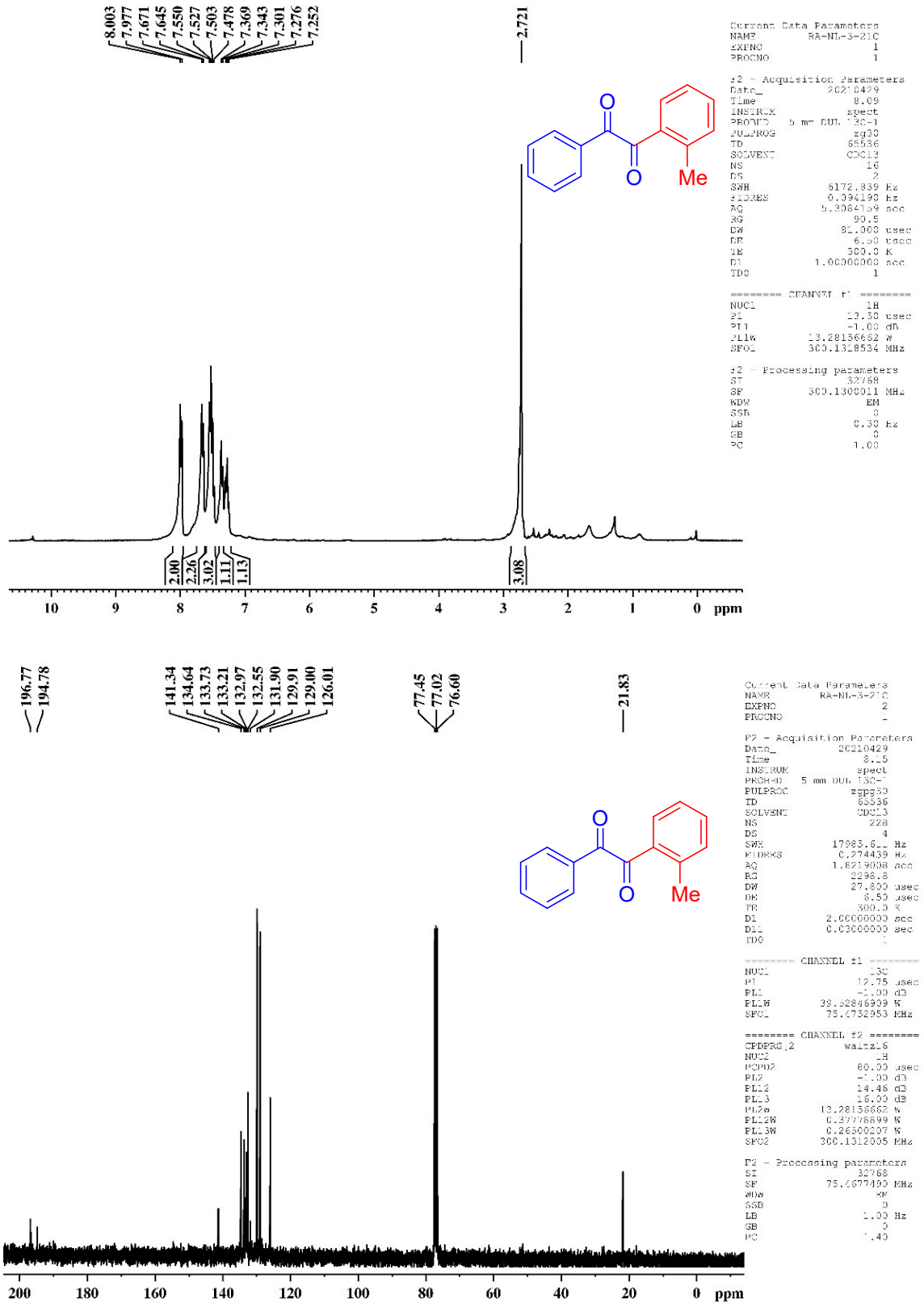
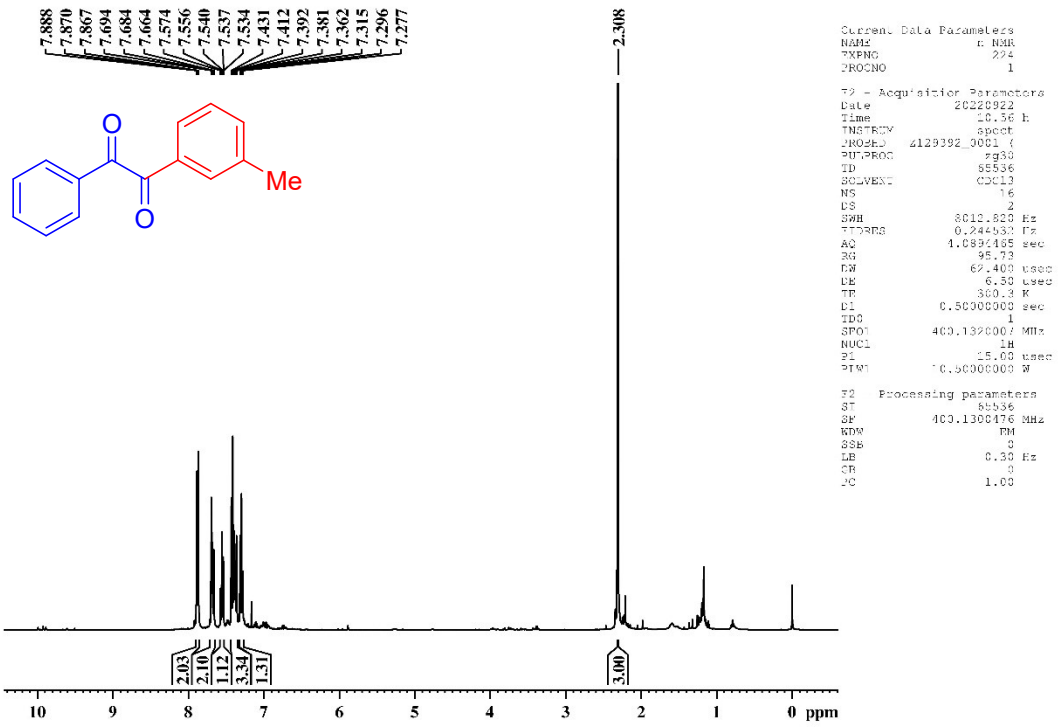
6. Copies of ^{1}H, ^{19}F and ^{13}C NMR spectra

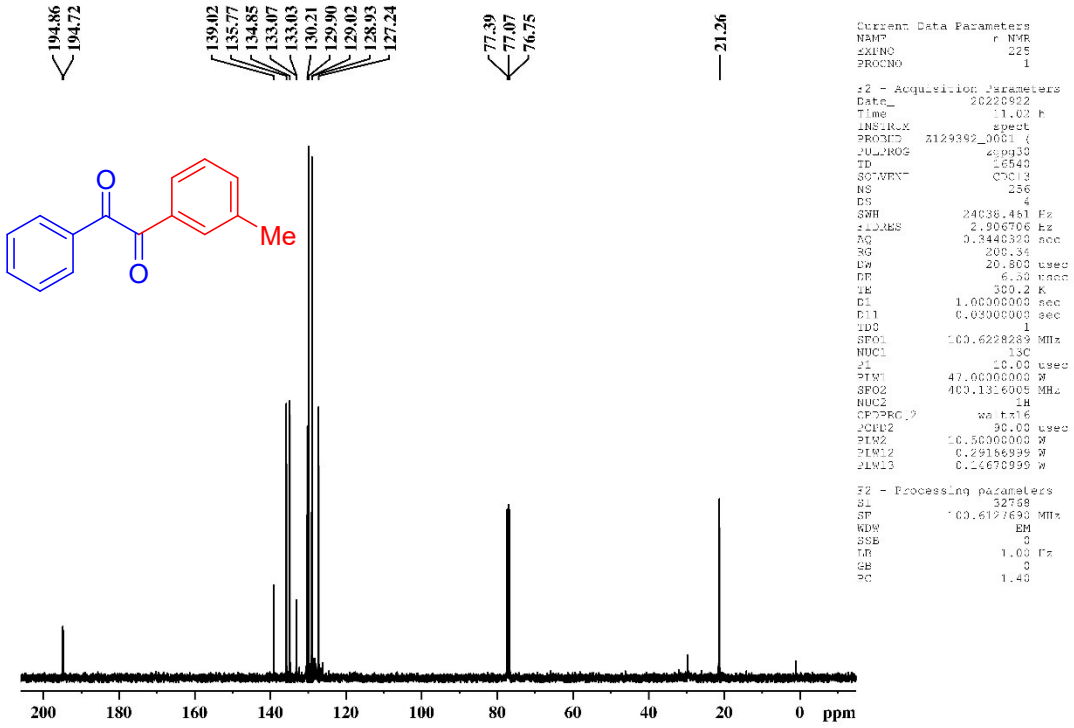


^{1}H & ^{13}C NMR spectra of compound **3a**

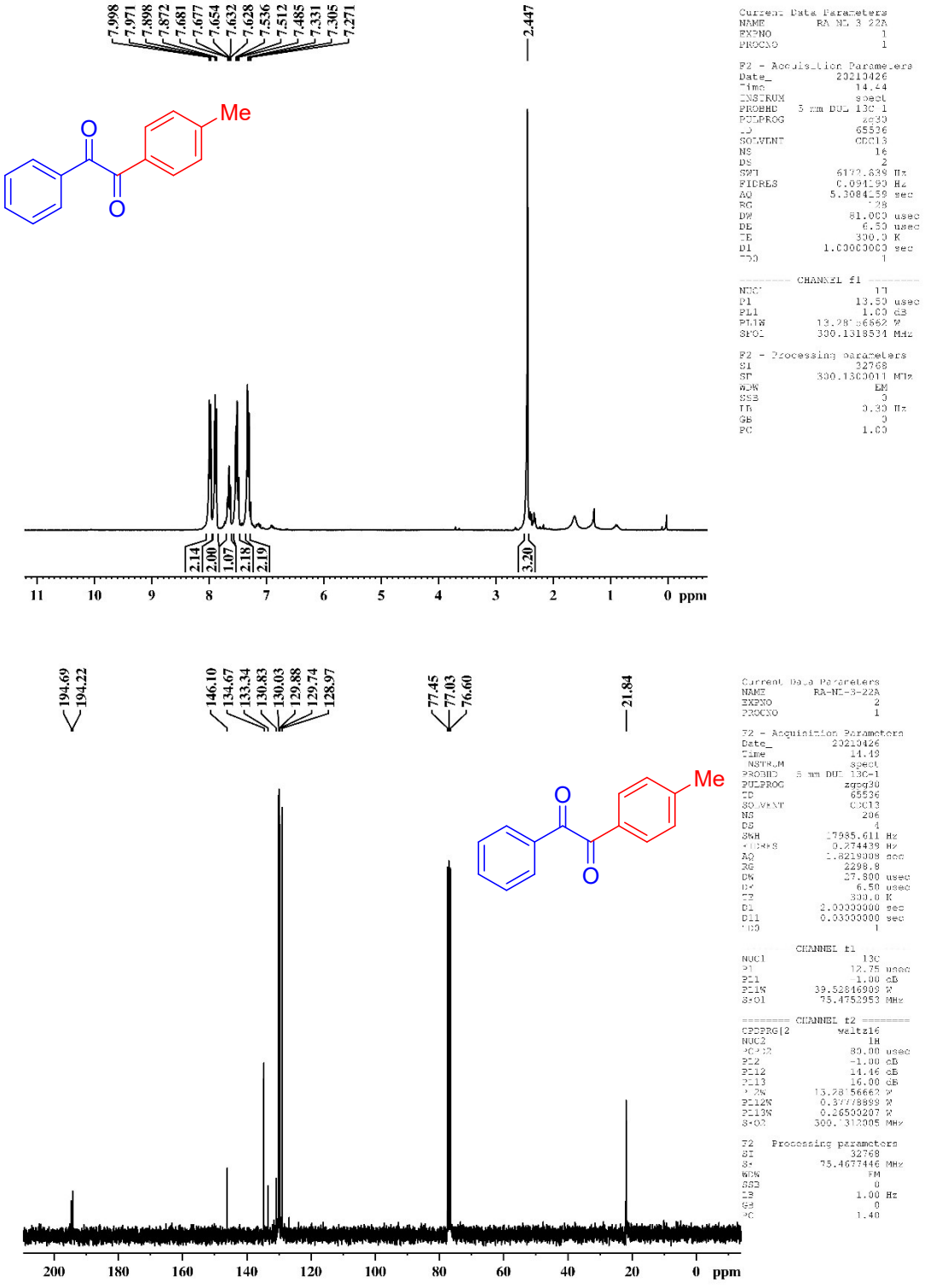


^{1}H & ^{13}C NMR spectra of compound **3b**

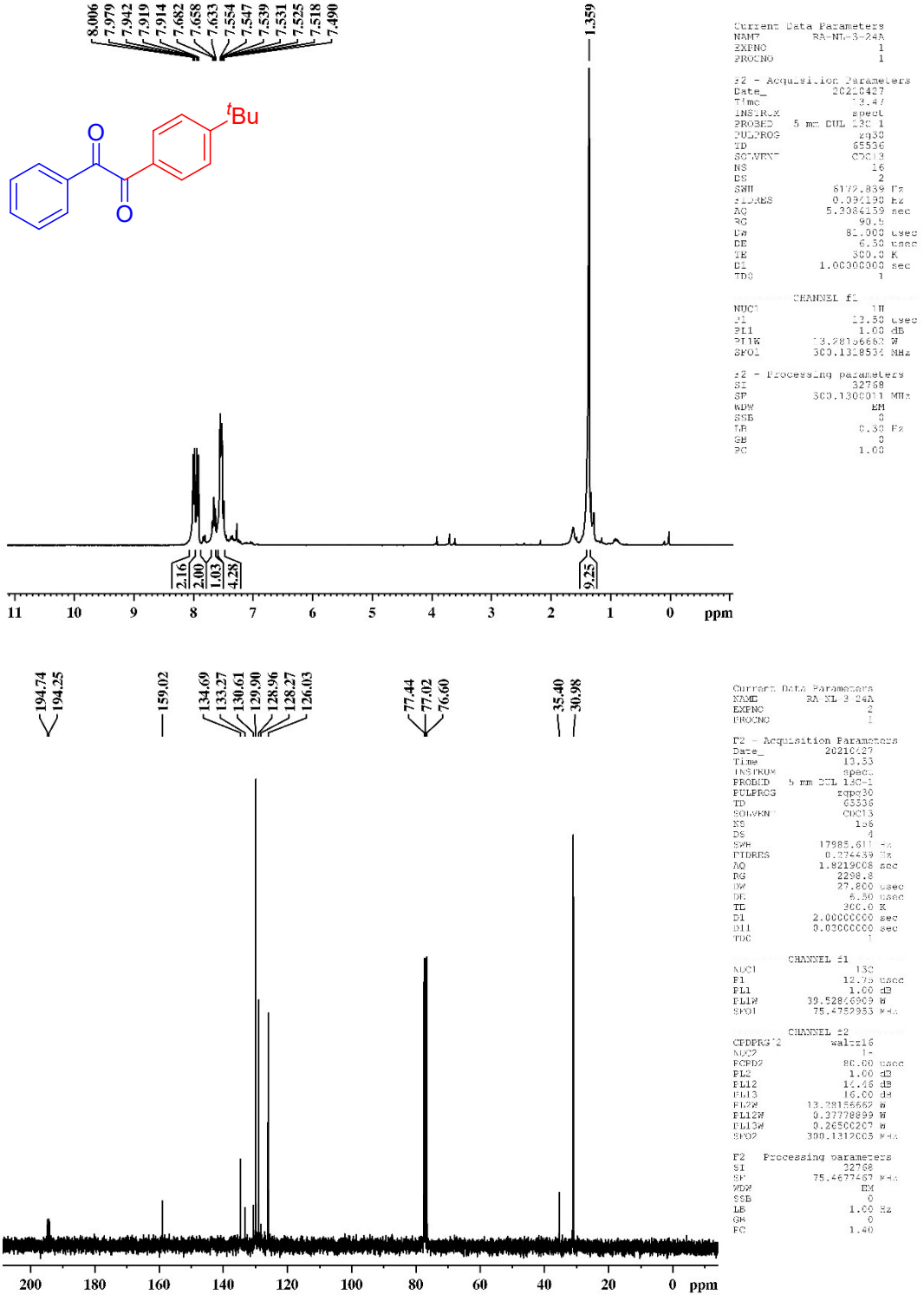




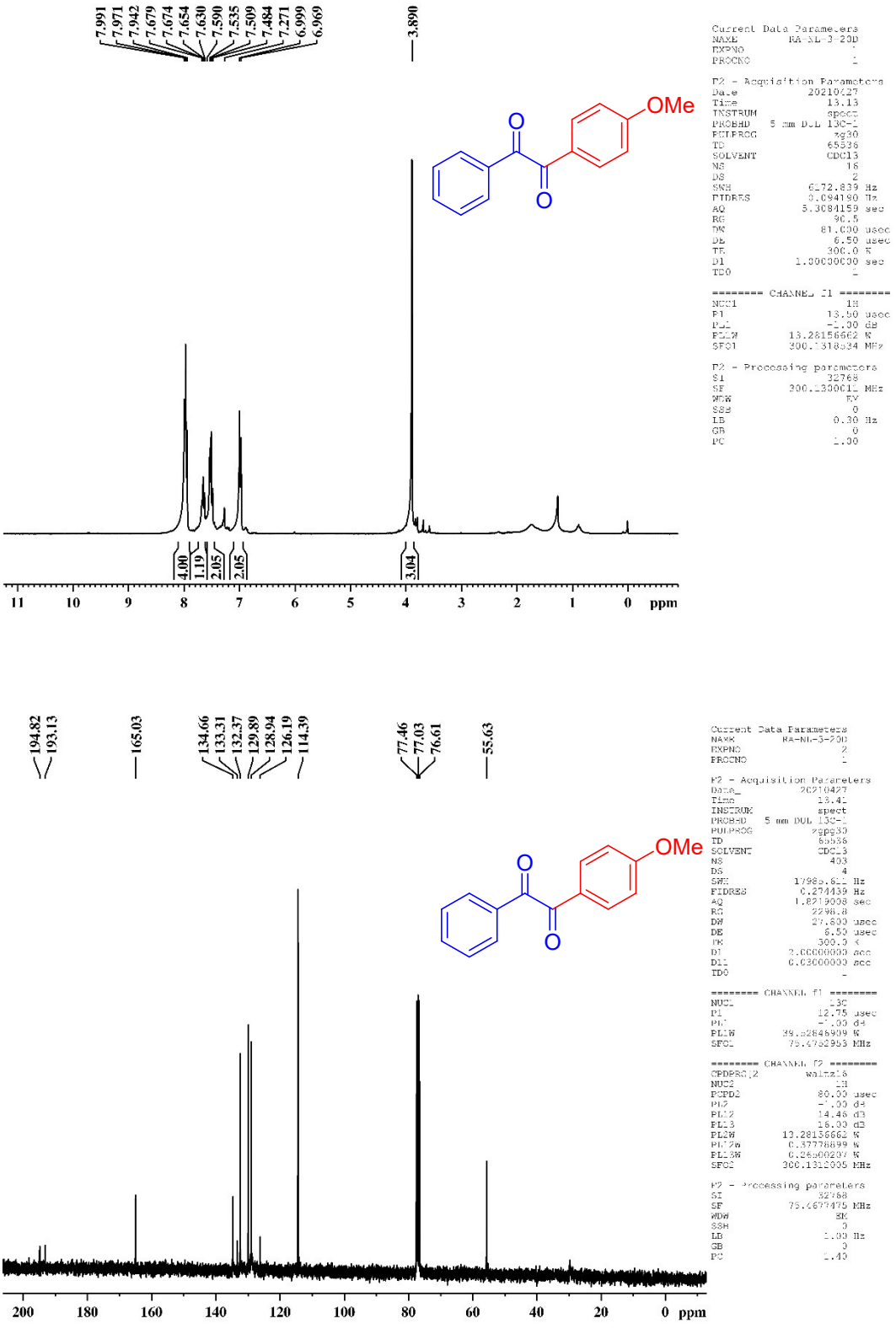
^{1}H & ^{13}C NMR spectra of compound **3c**



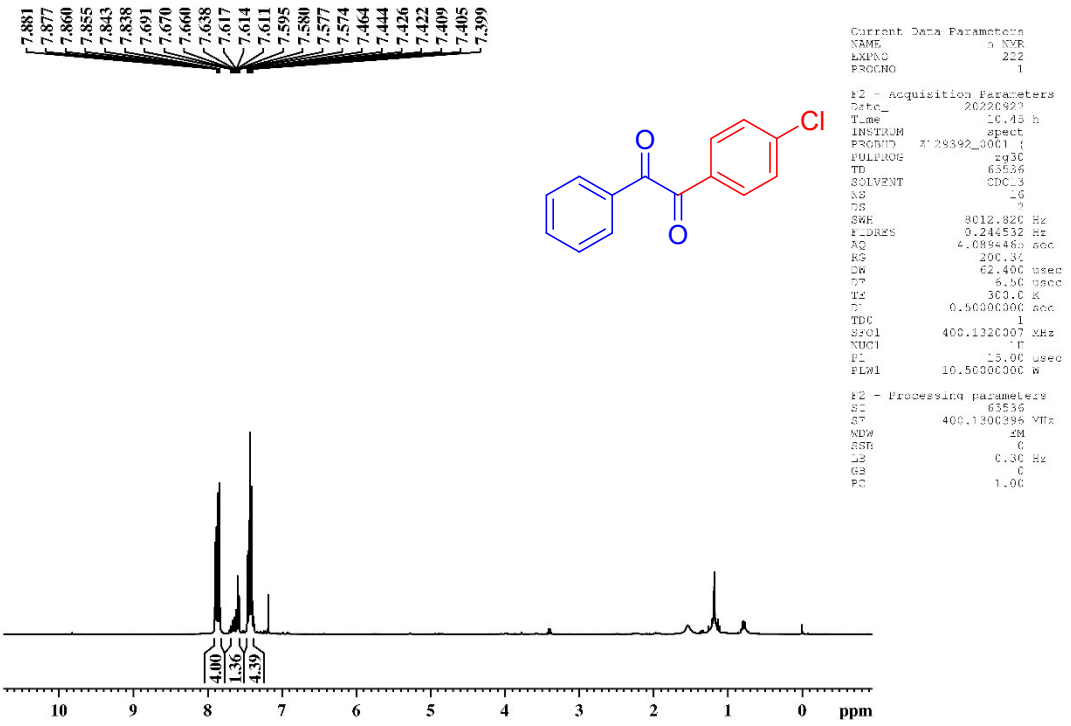
^{1}H & ^{13}C NMR spectra of compound **3d**

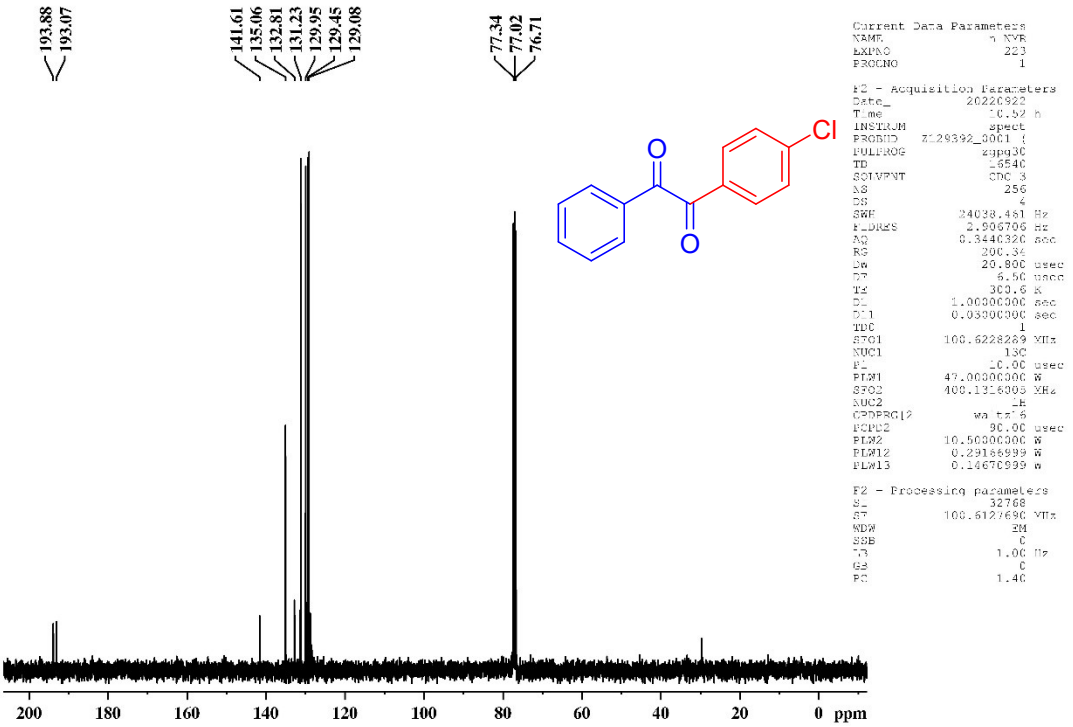


^{1}H & ^{13}C spectra of compound **3e**

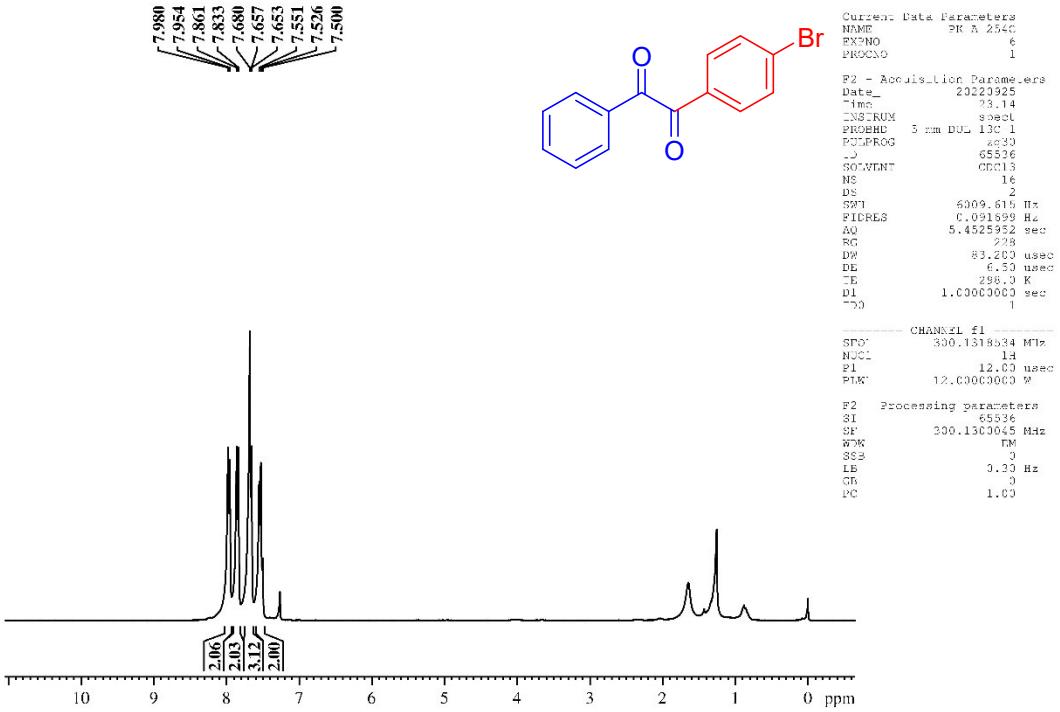


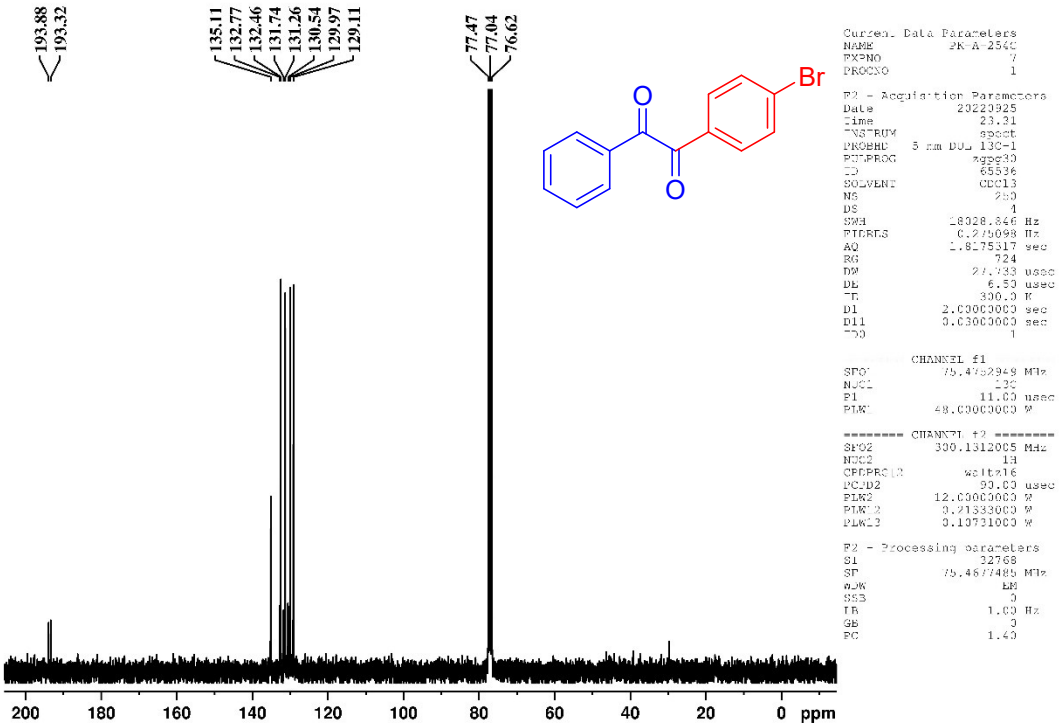
^{1}H & ^{13}C spectra of compound **3f**



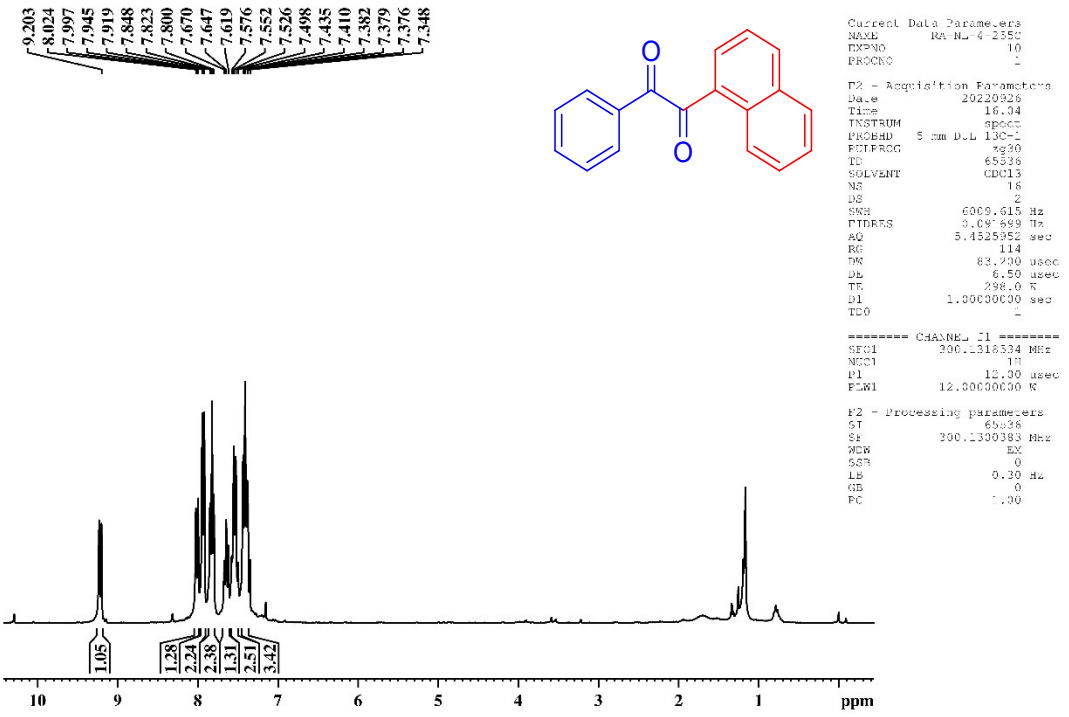


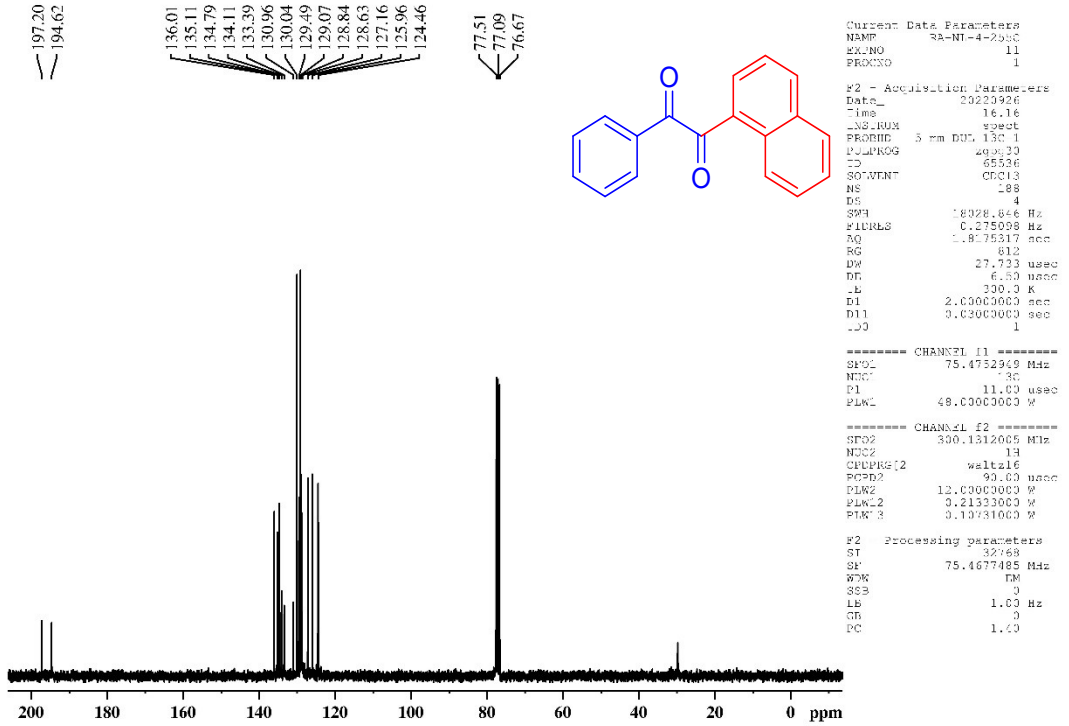
^{1}H & ^{13}C spectra of compound **3g**



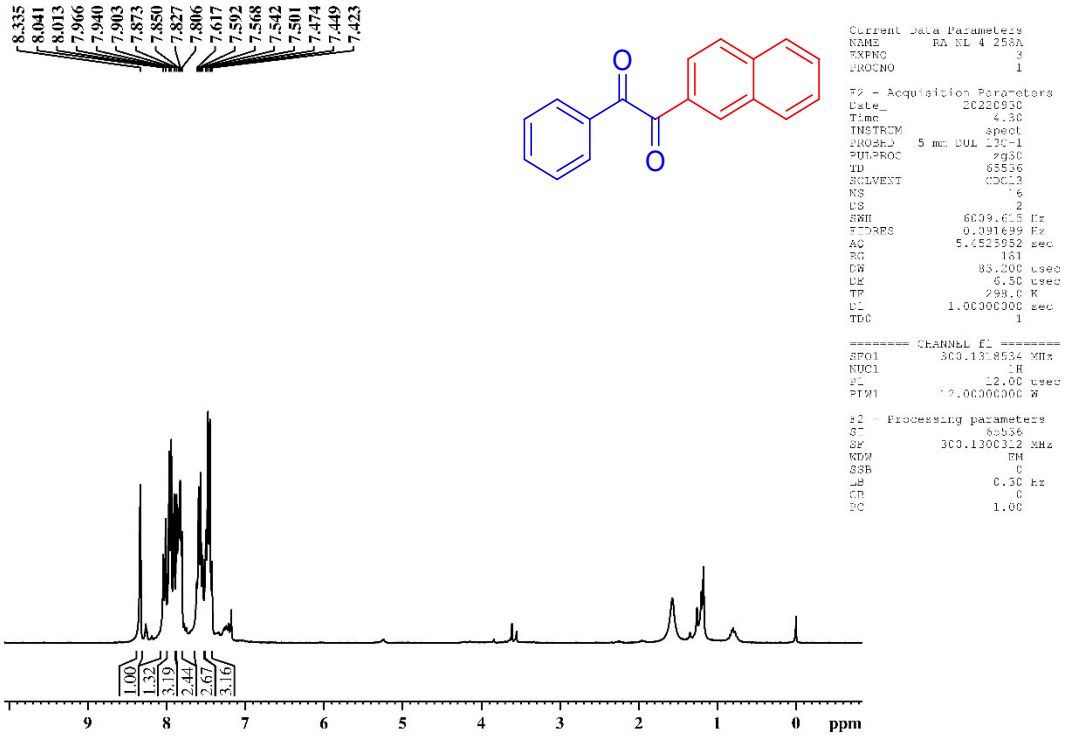


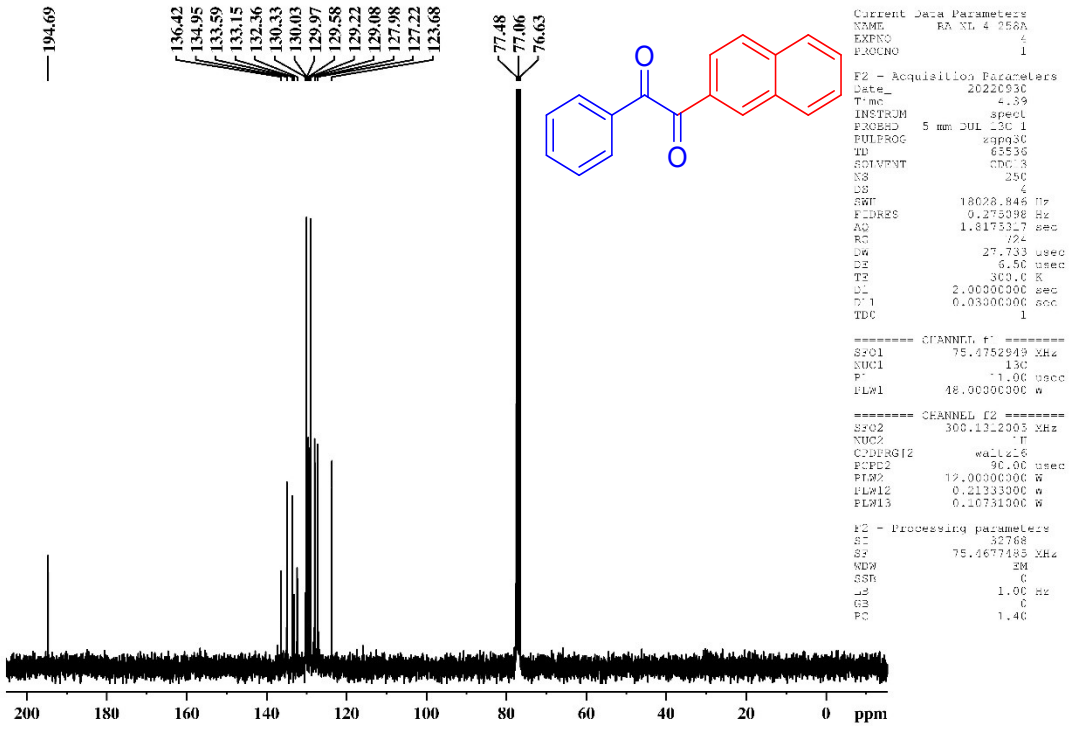
^{1}H & ^{13}C spectra of compound **3h**



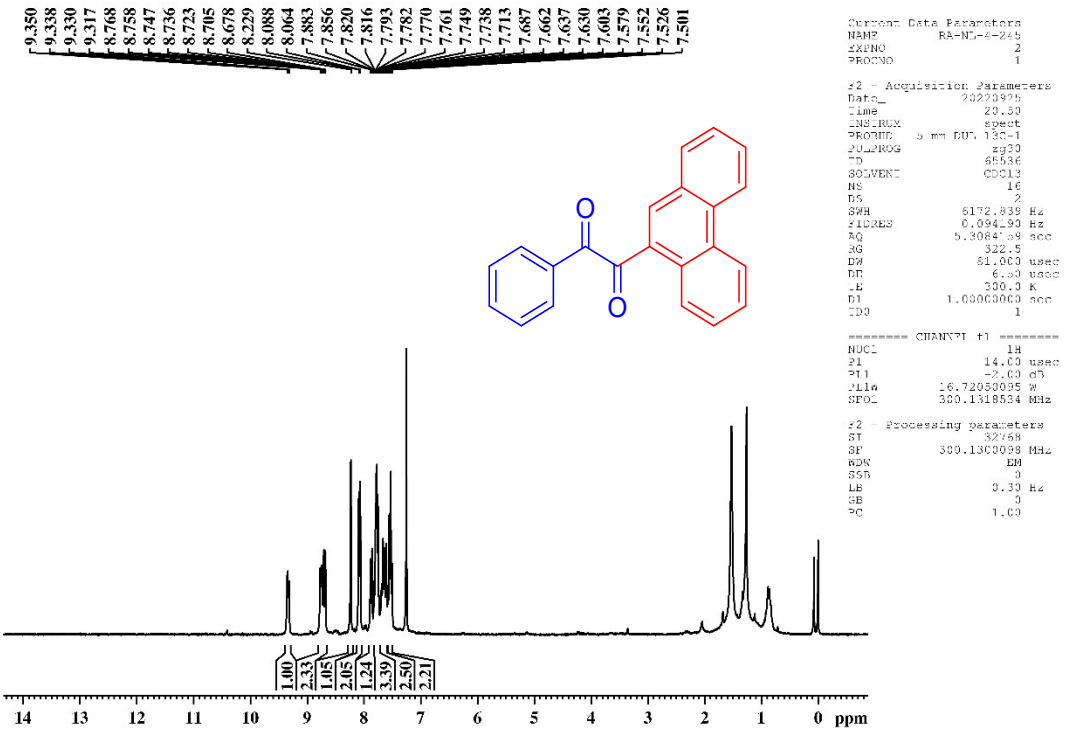


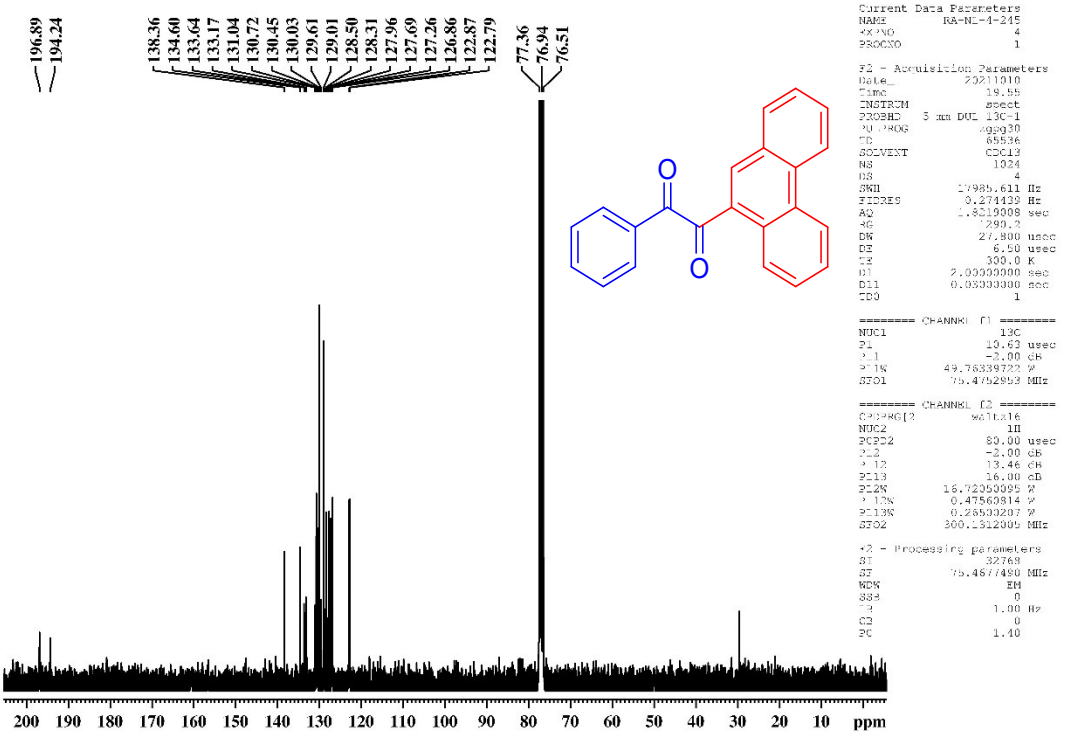
^{1}H & ^{13}C spectra of compound **3i**



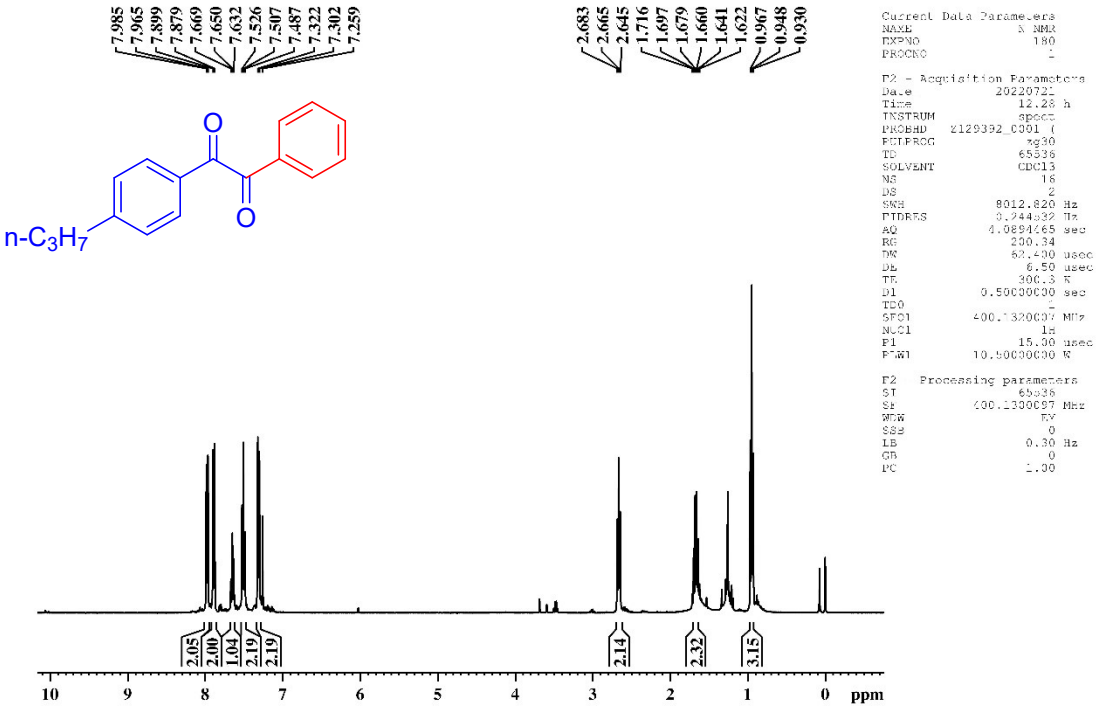


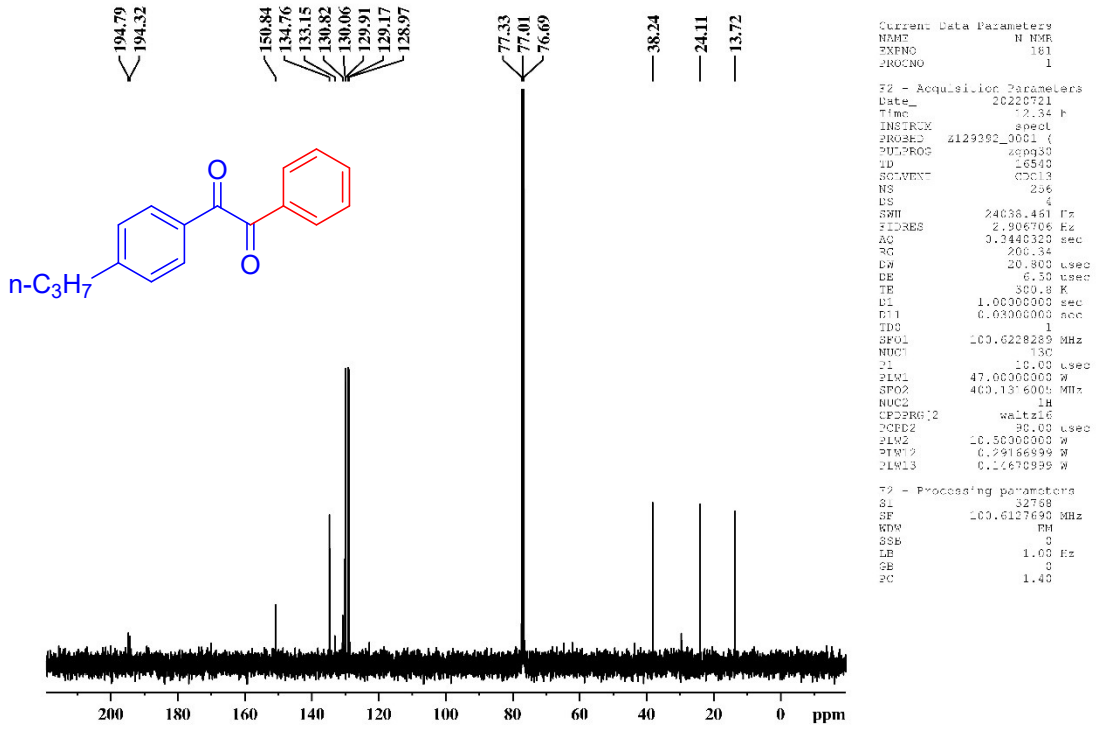
^{1}H & ^{13}C spectra of compound **3j**



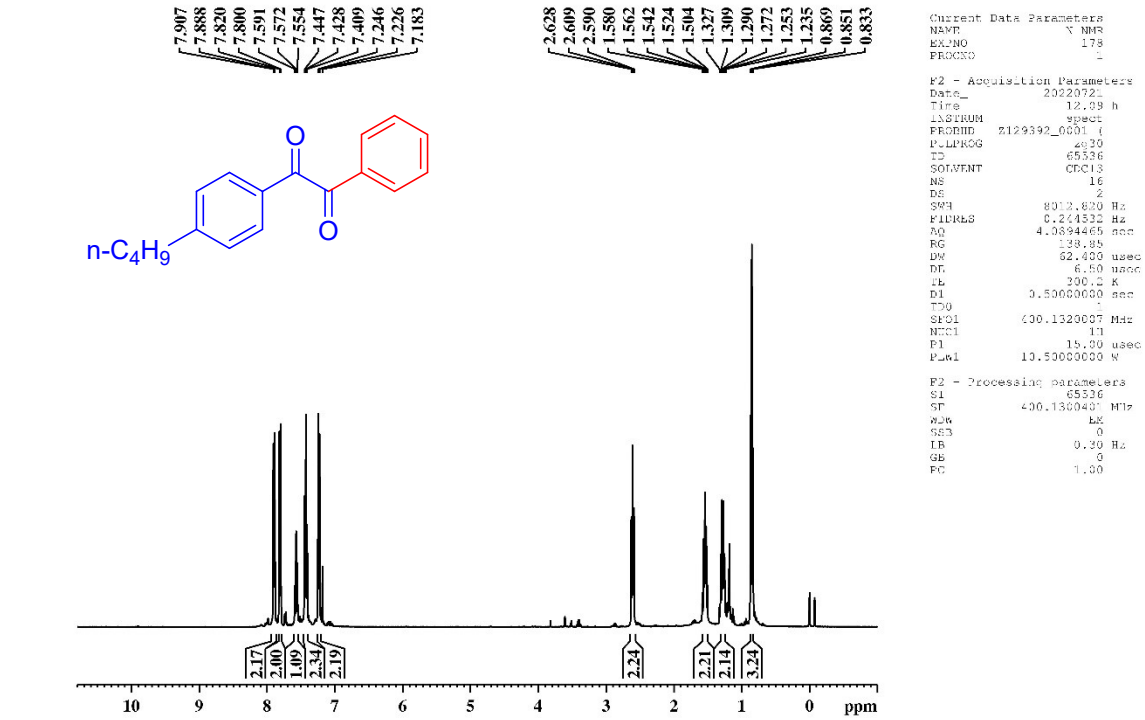


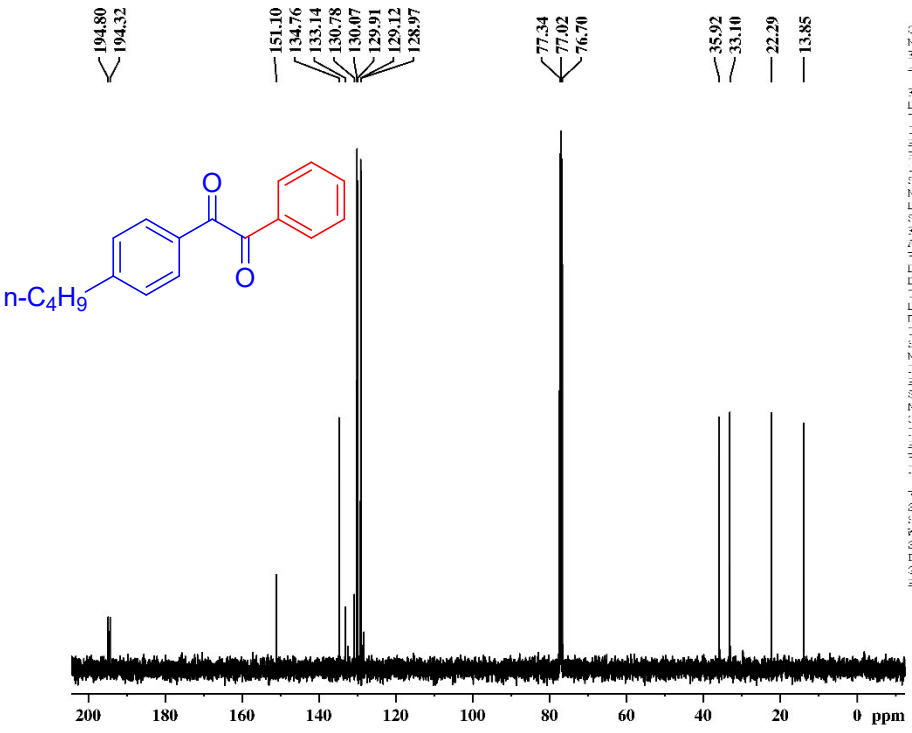
^{1}H & ^{13}C spectra of compound **3k**





^{1}H & ^{13}C spectra of compound **3l**





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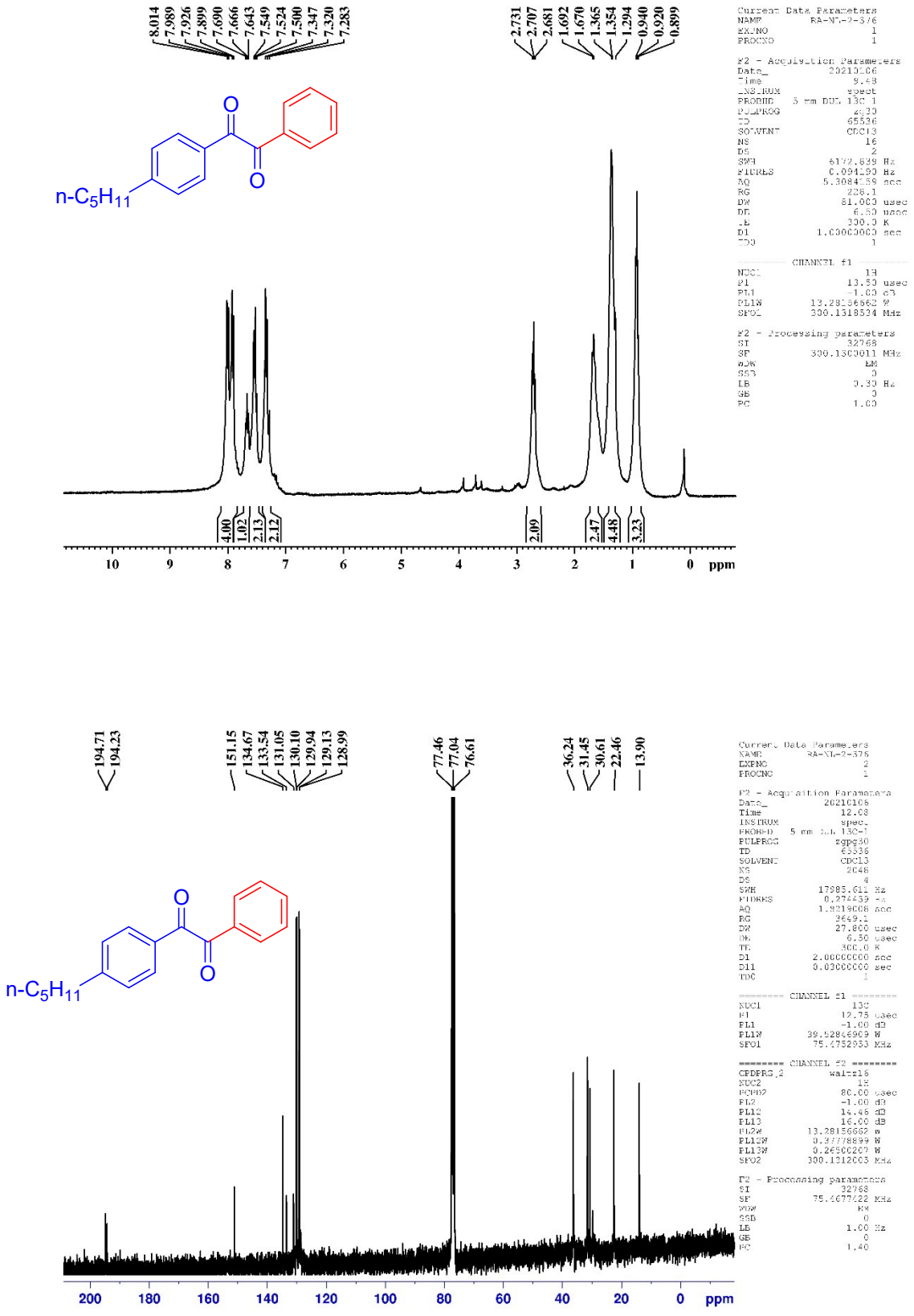
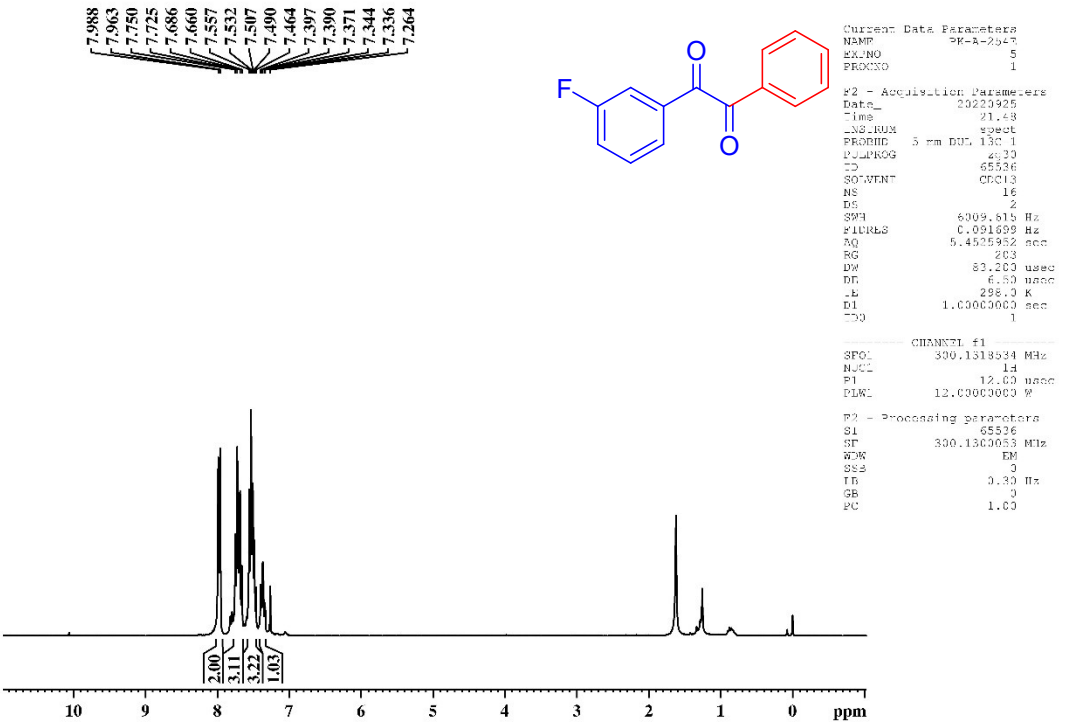
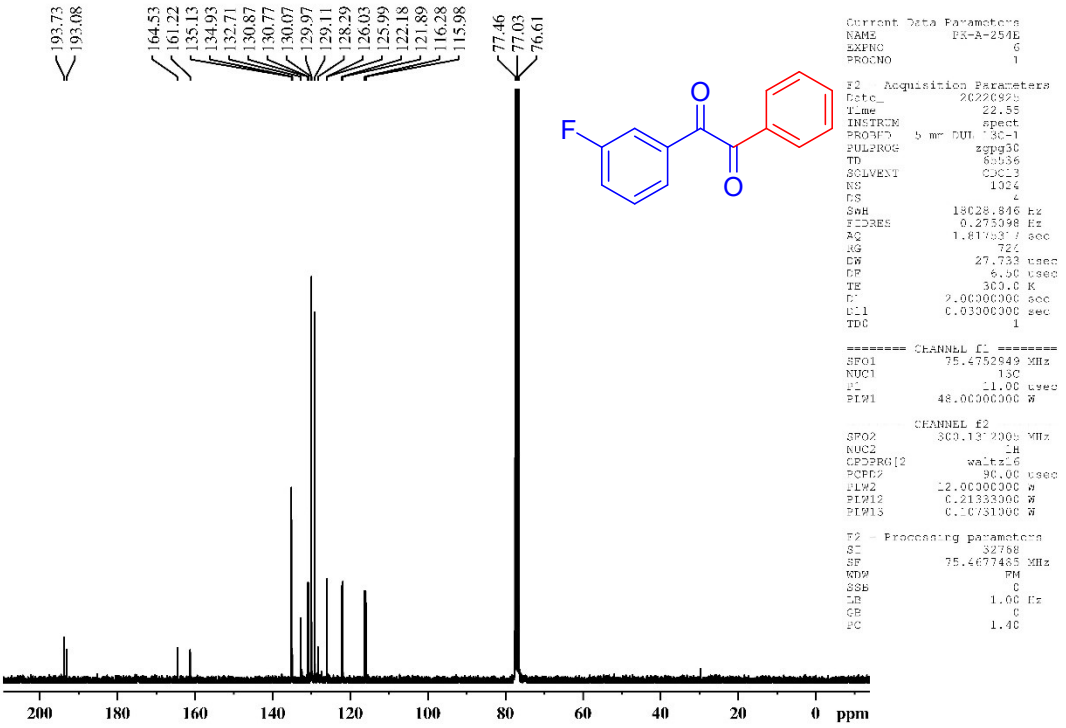
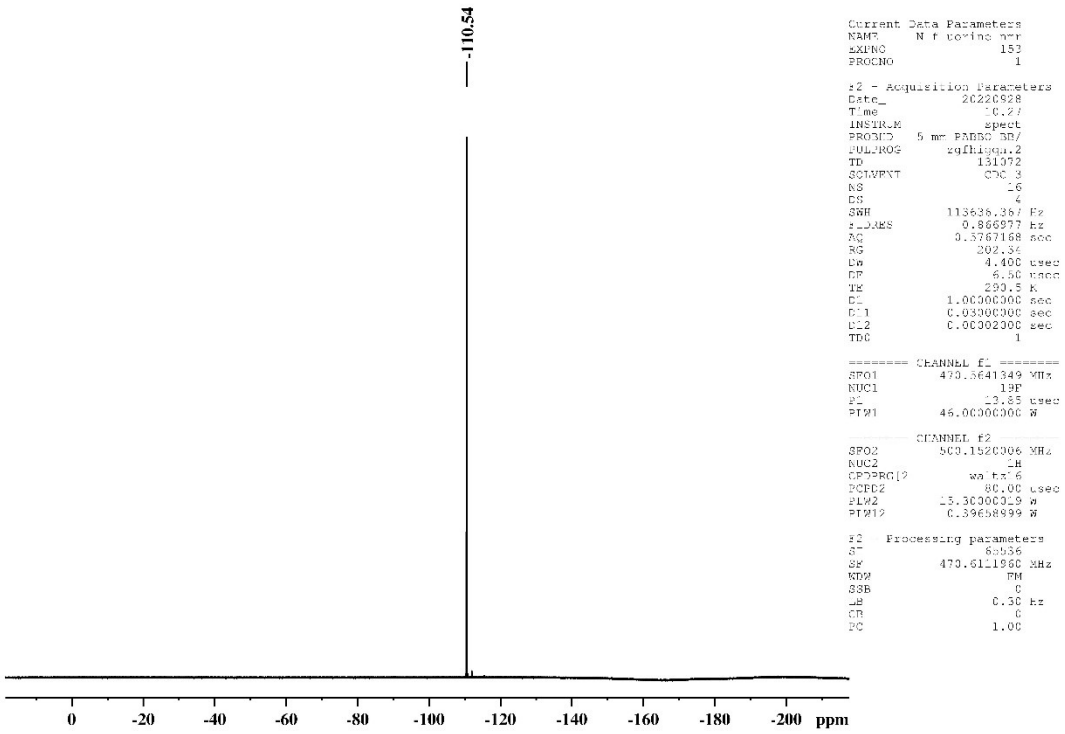


^{1}H & ^{13}C spectra of compound **3n**

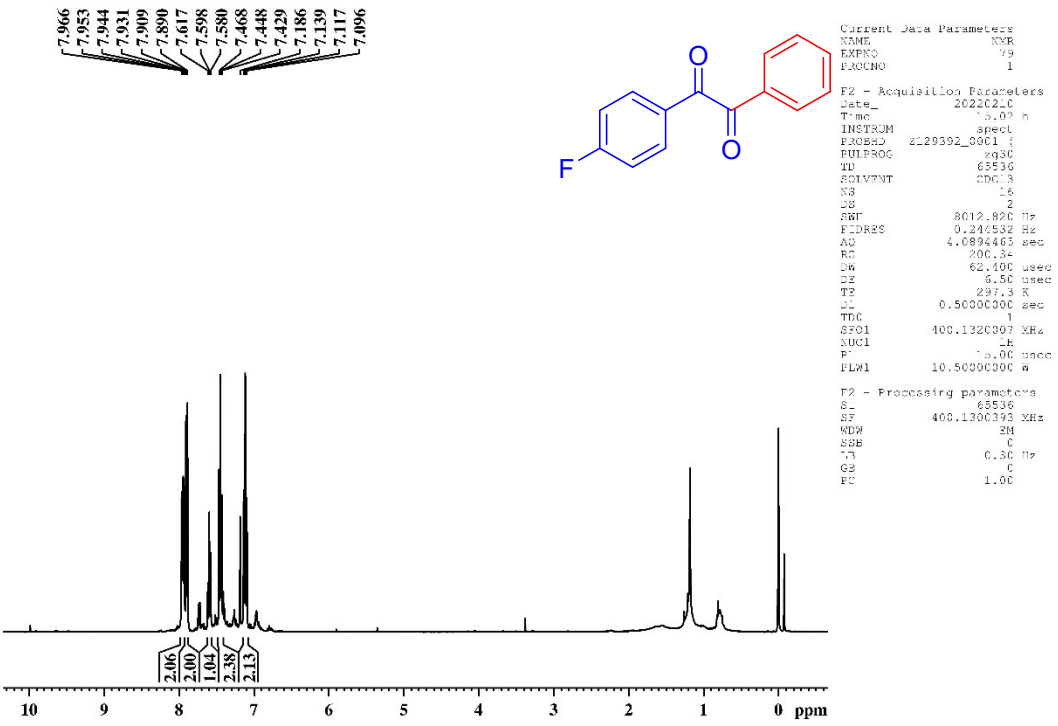


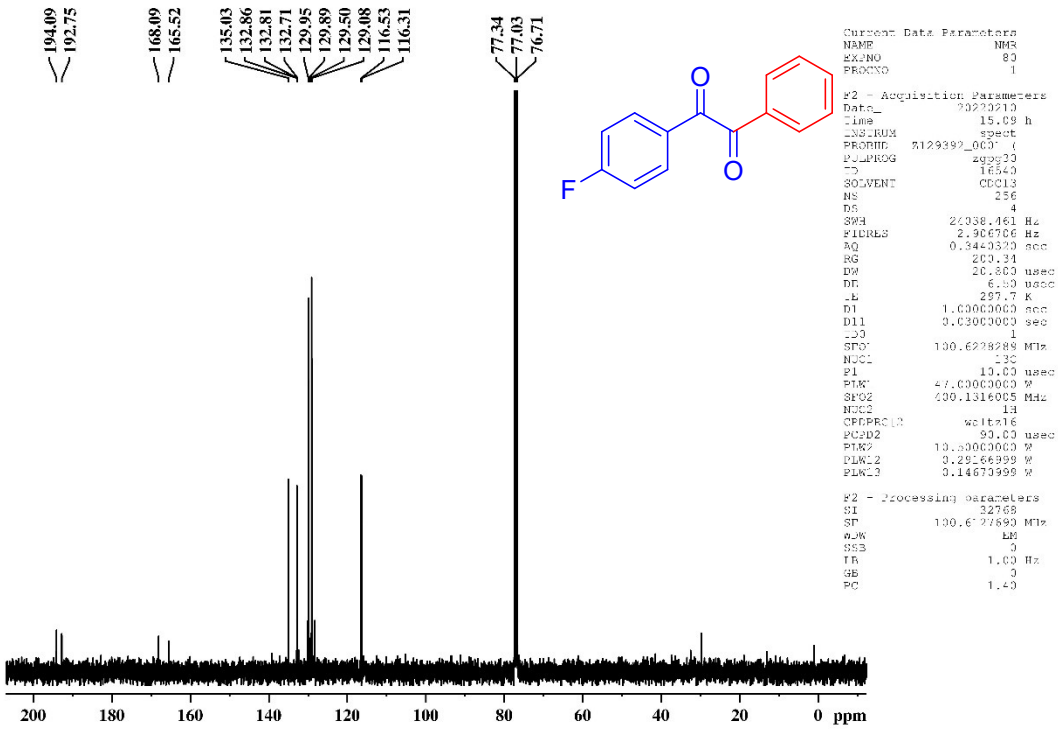


^{1}H & ^{13}C spectra of compound **3o**

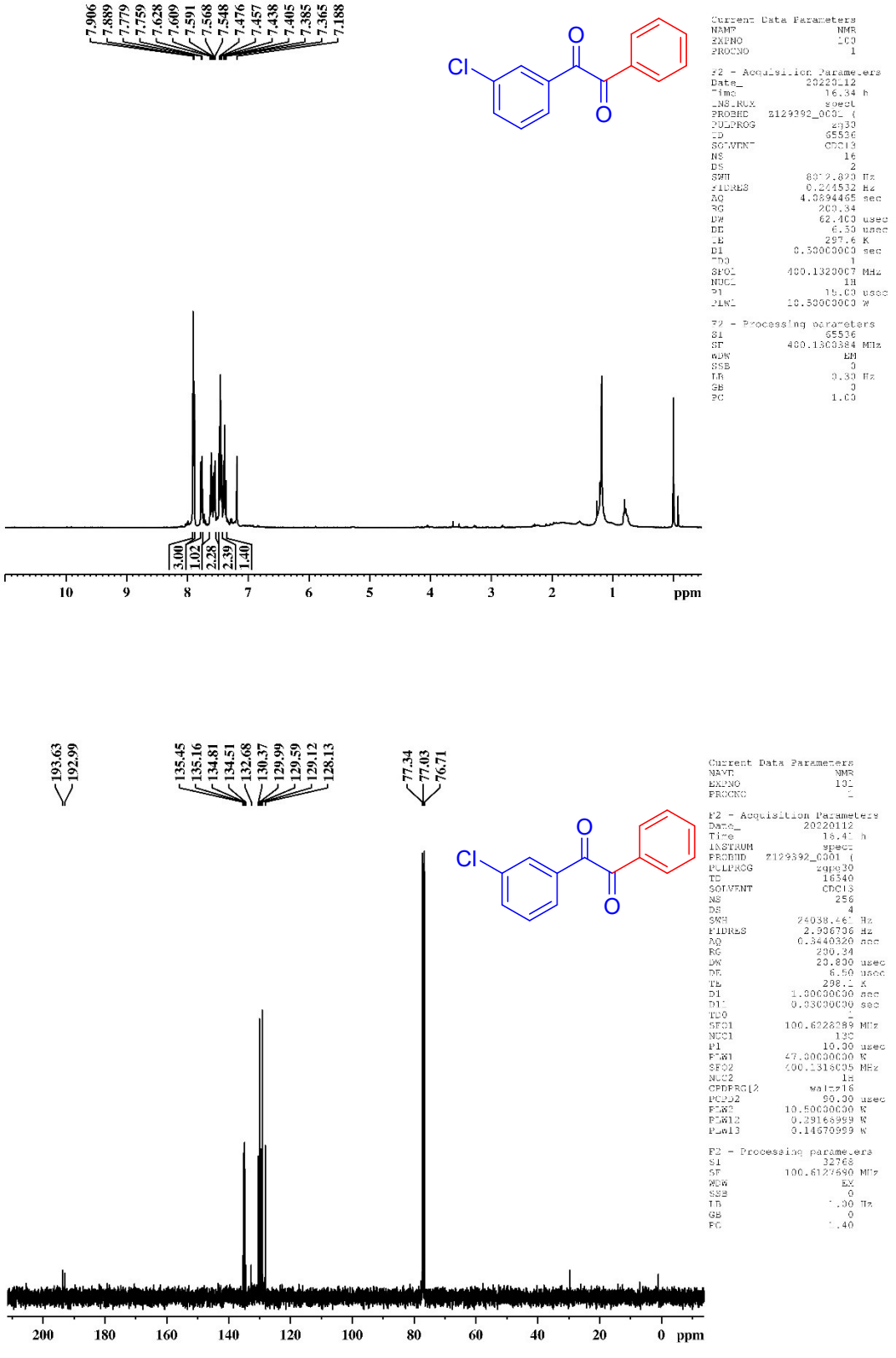


^{19}F spectrum of compound **3o**

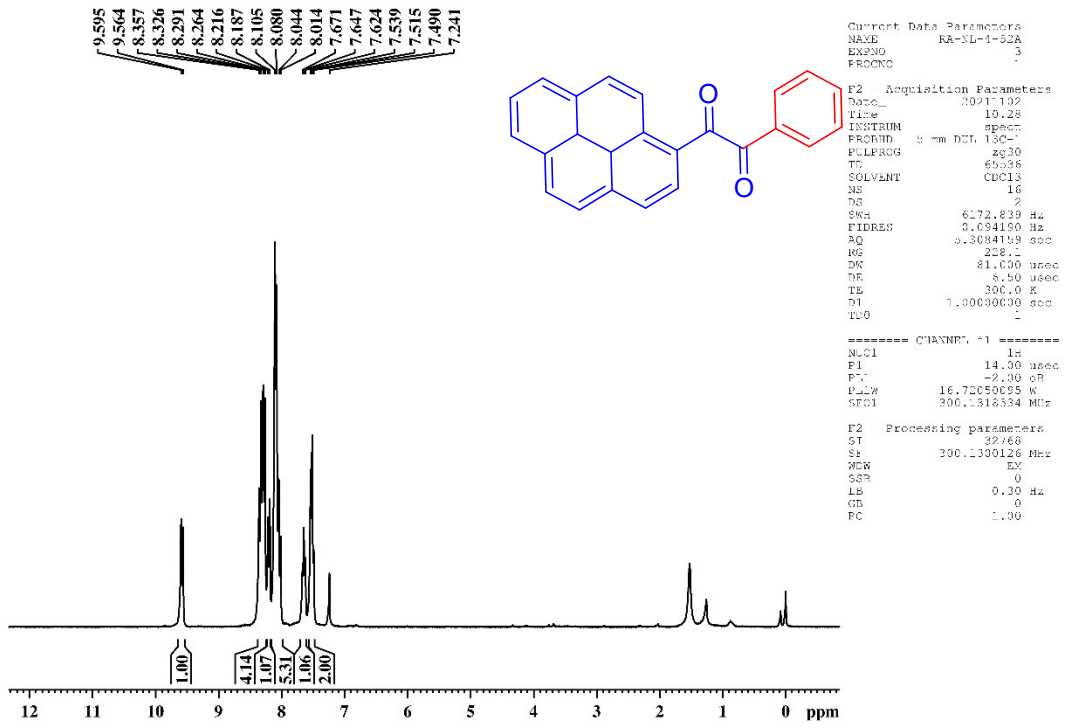


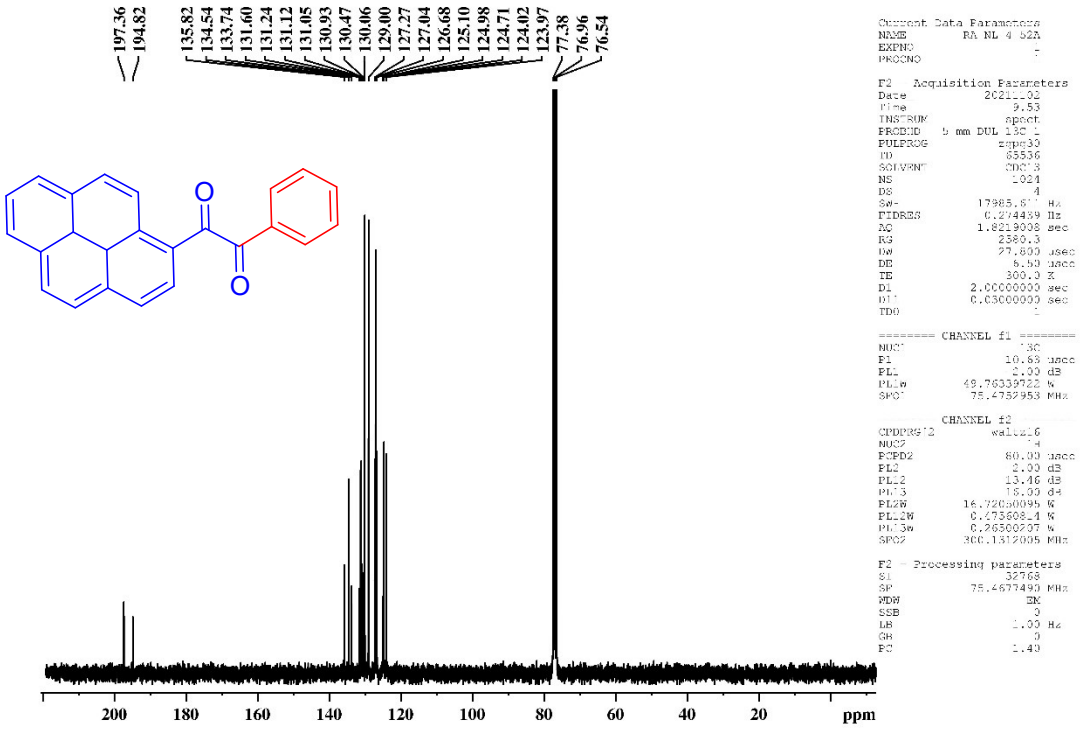


^{1}H & ^{13}C spectra of compound **3p**

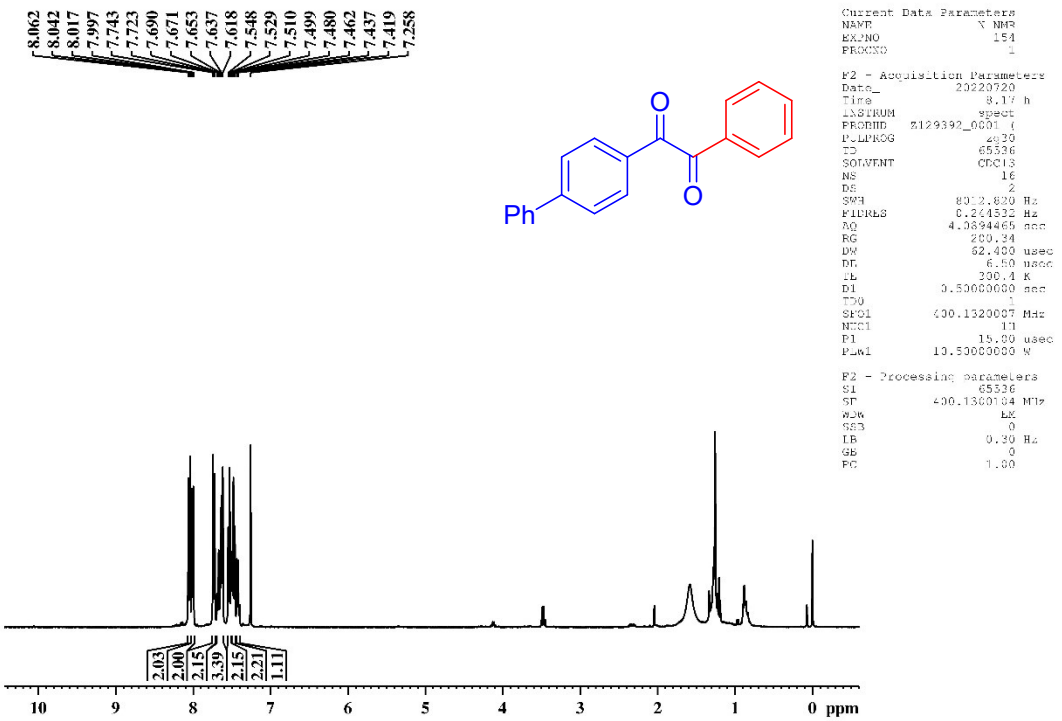


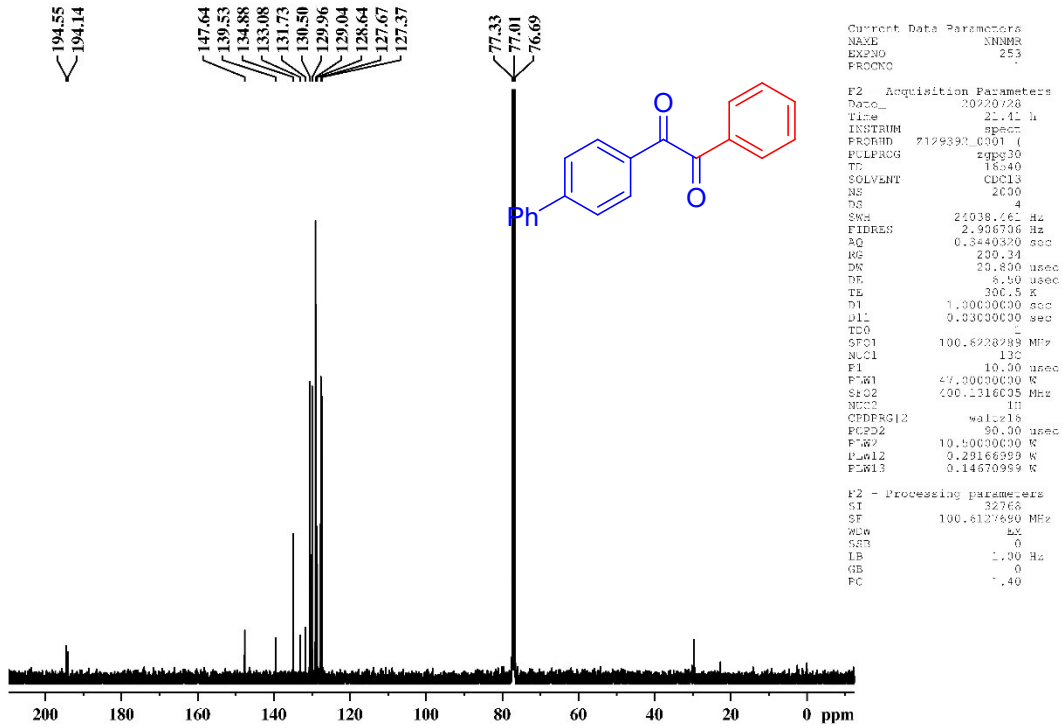
^{1}H & ^{13}C spectra of compound **3q**



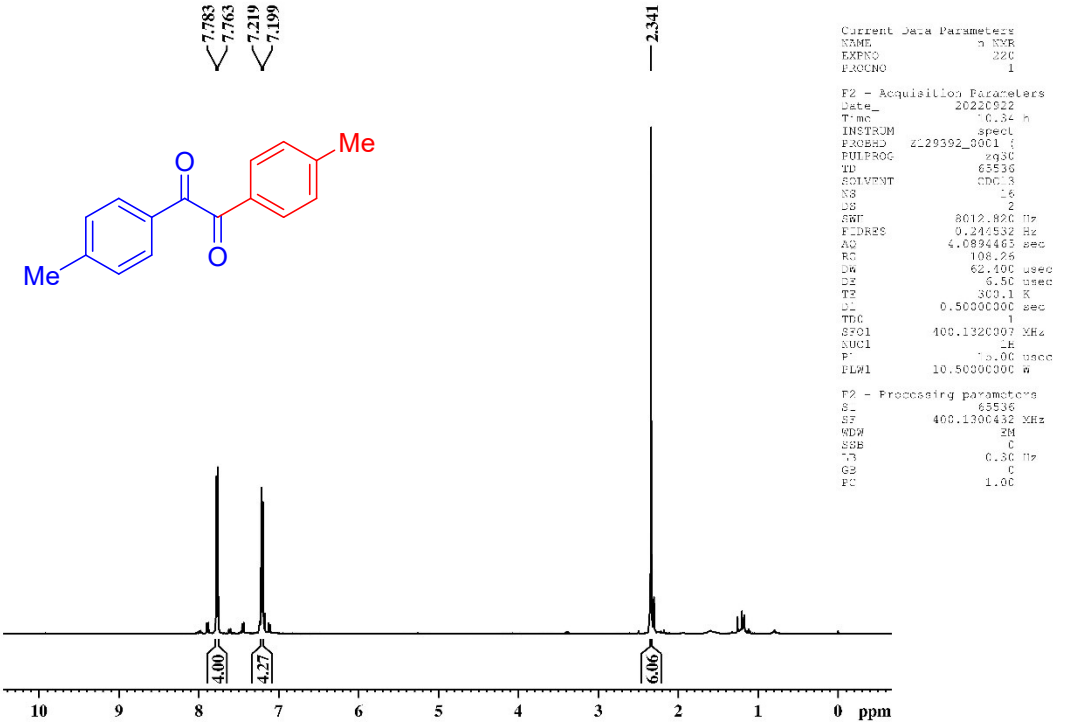


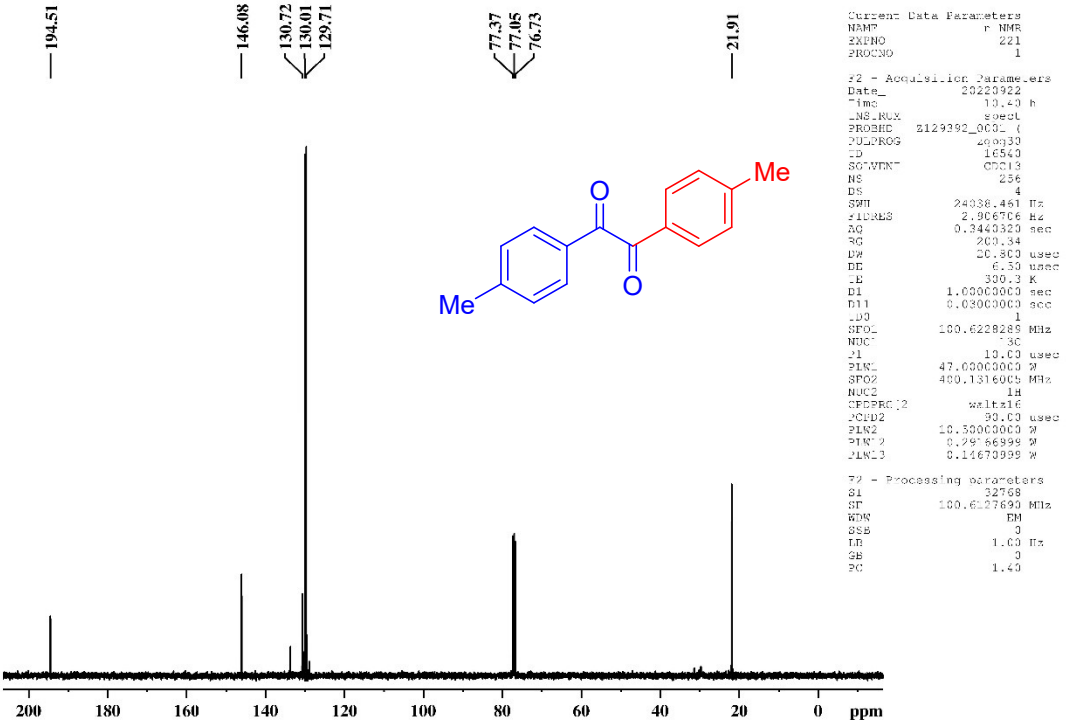
^{1}H & ^{13}C spectra of compound **3r**



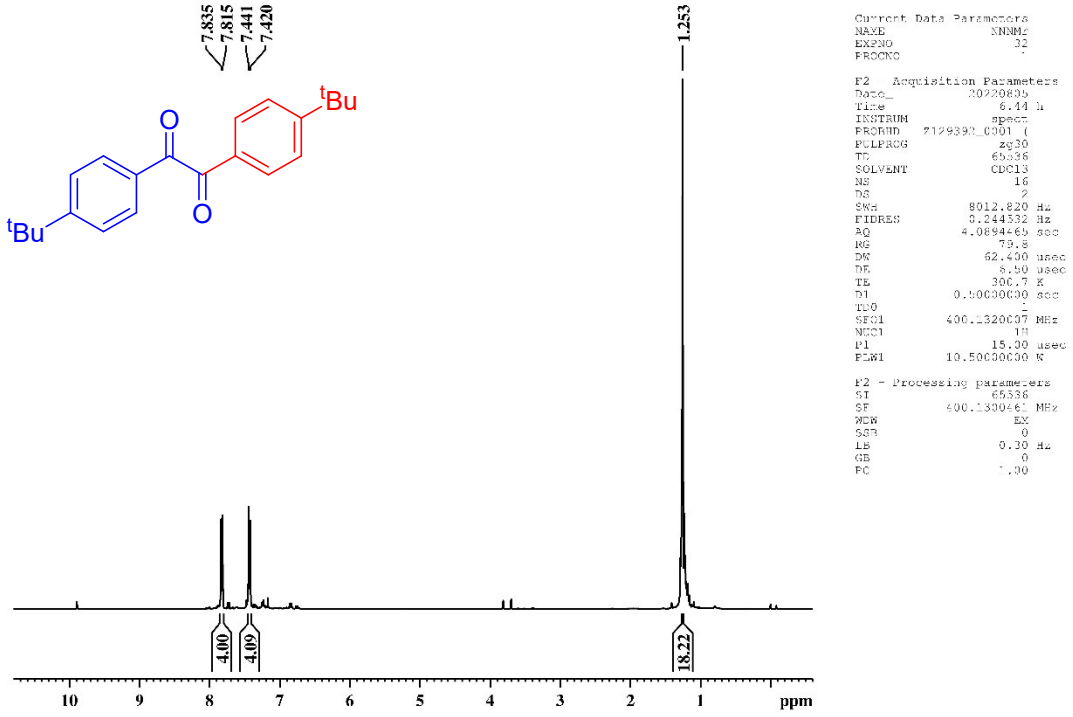


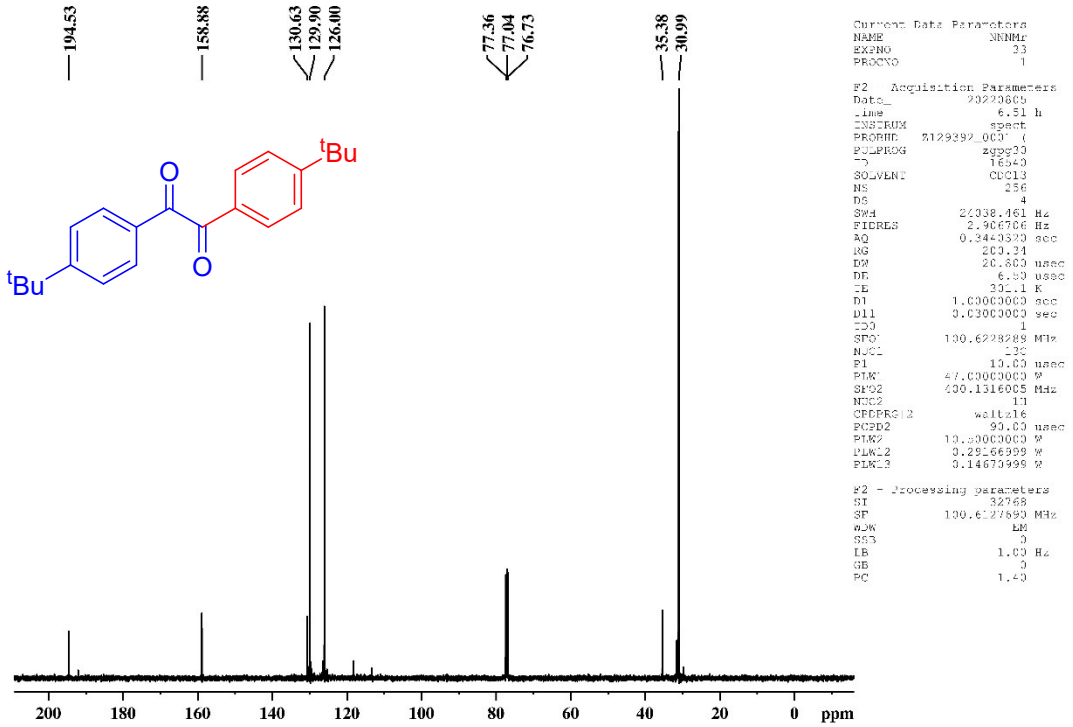
^{1}H & ^{13}C spectra of compound **3s**



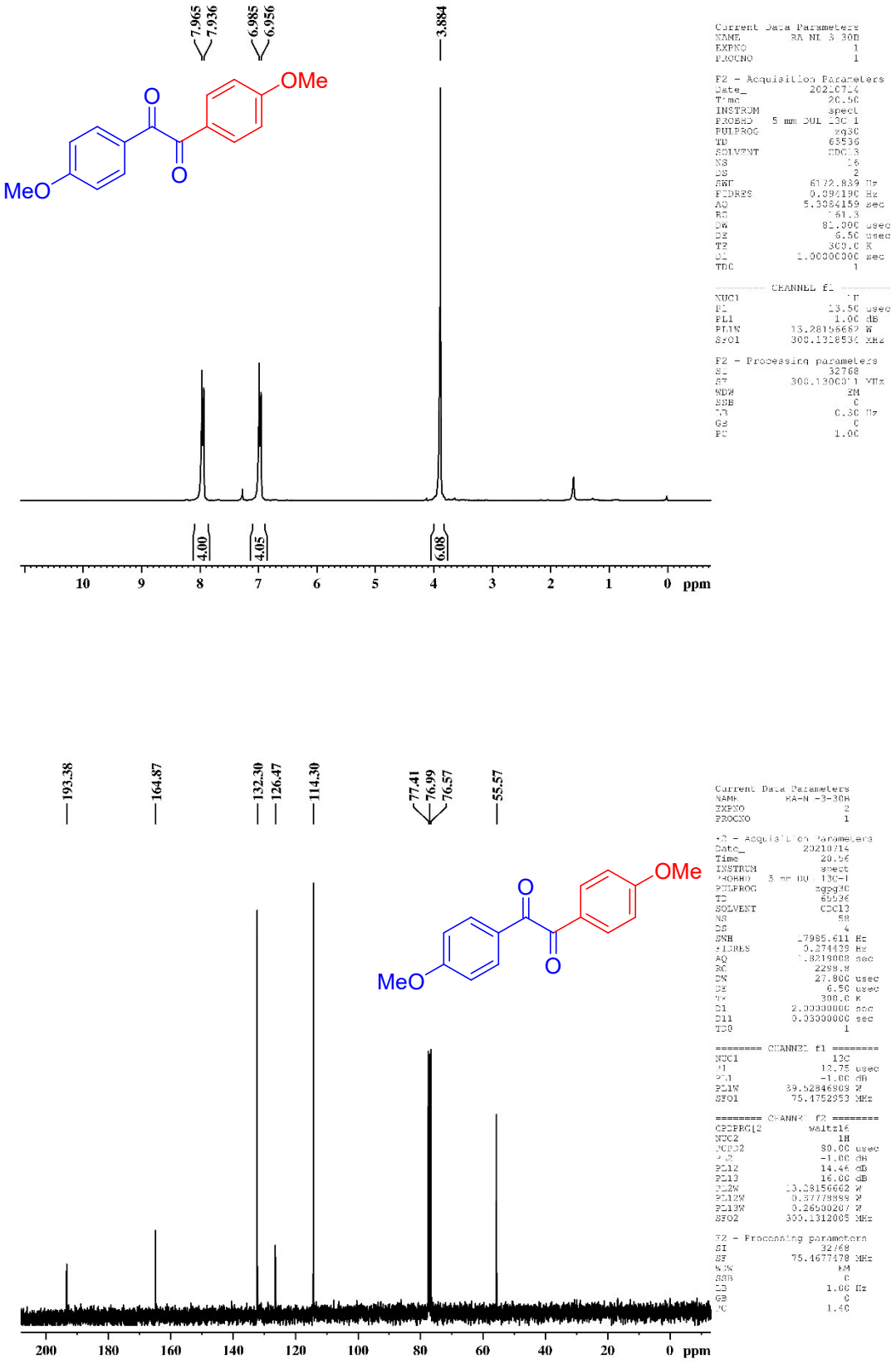


^{1}H & ^{13}C spectra of compound **3u**

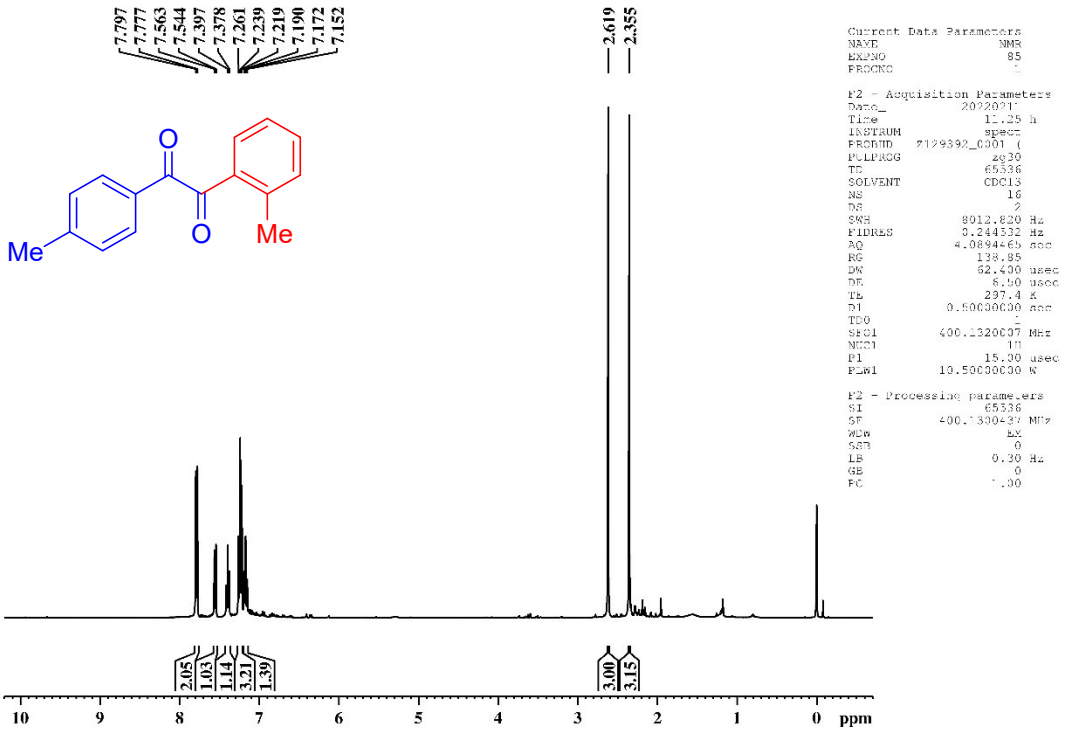


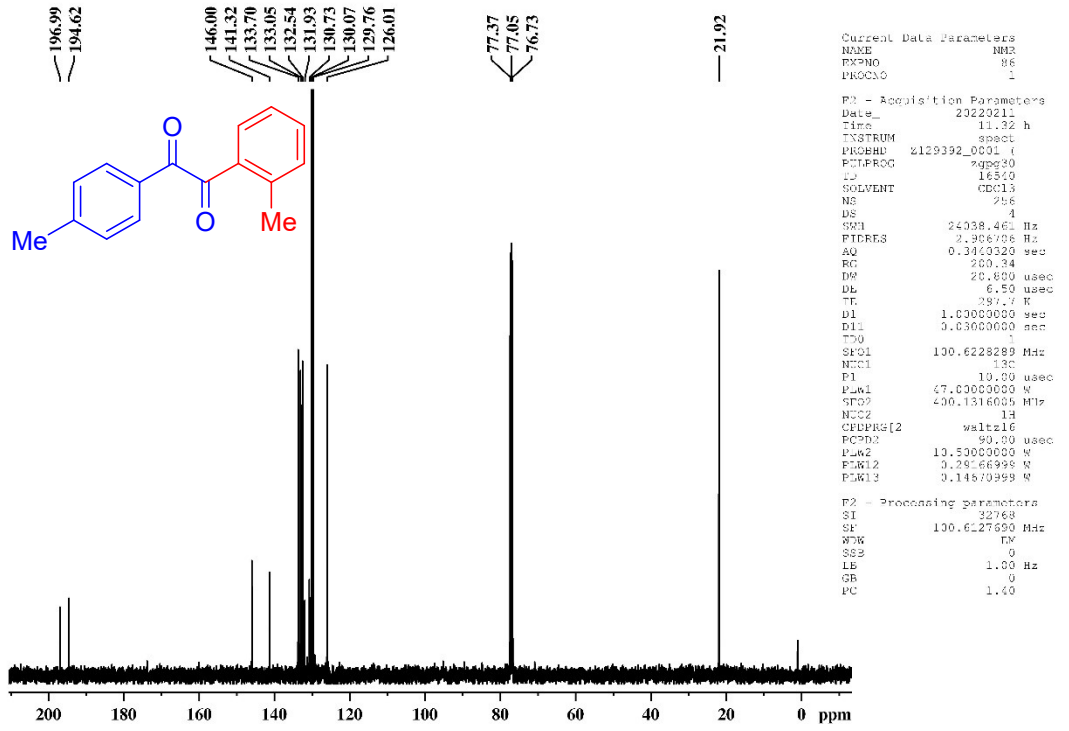


^{1}H & ^{13}C spectra of compound **3v**

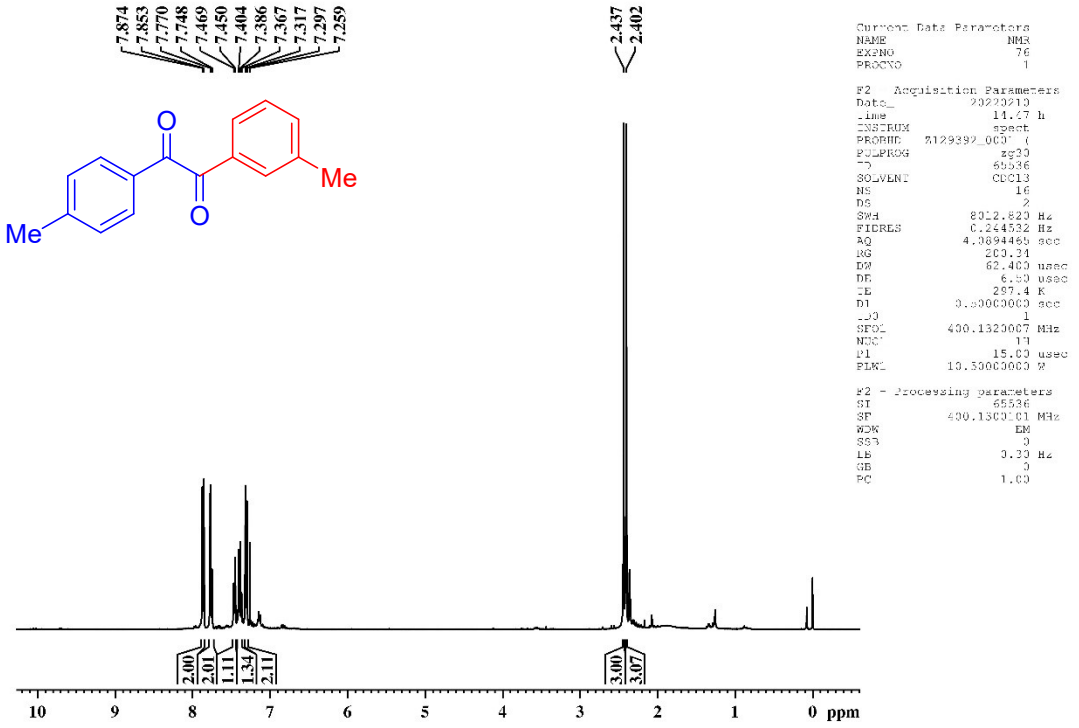


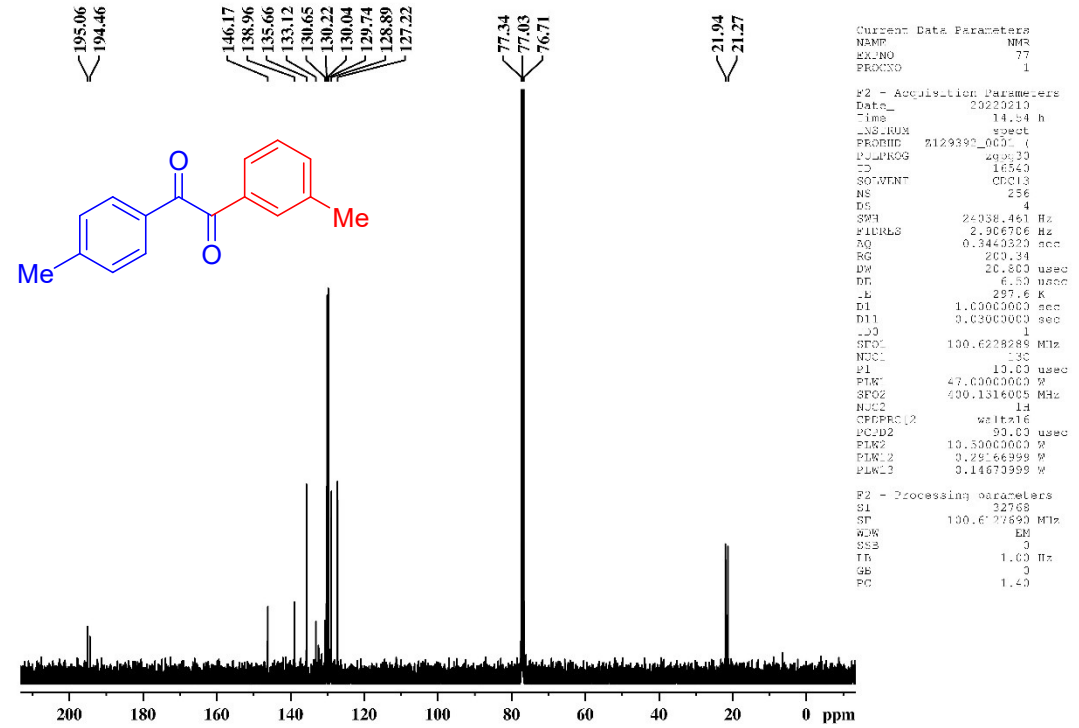
^{1}H & ^{13}C spectra of compound **3w**



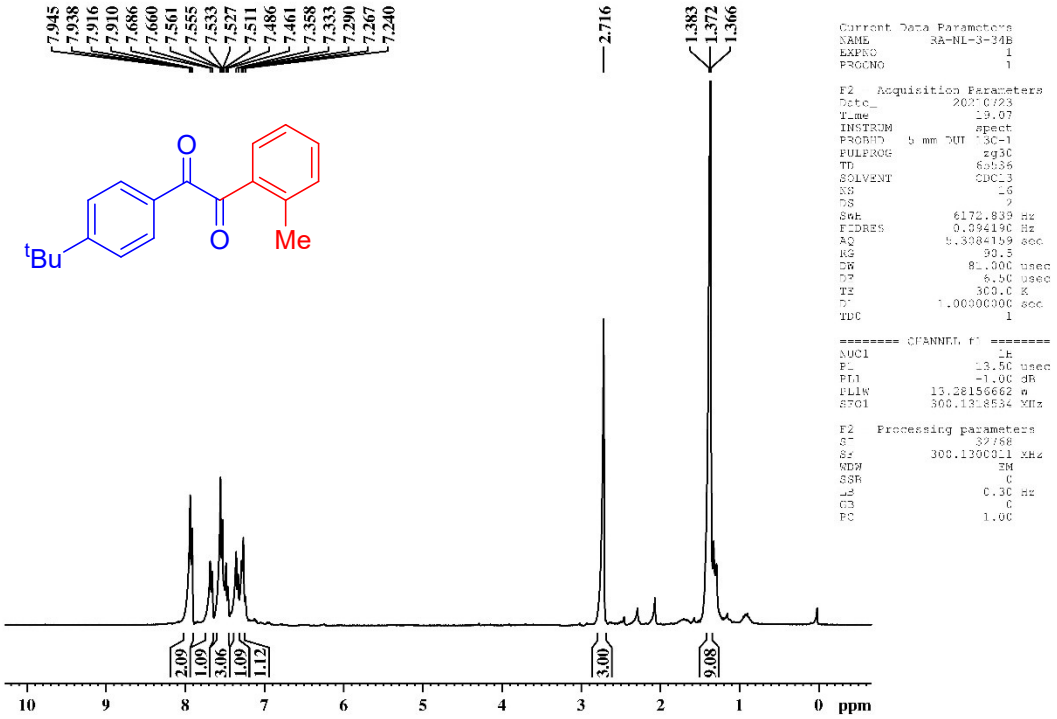


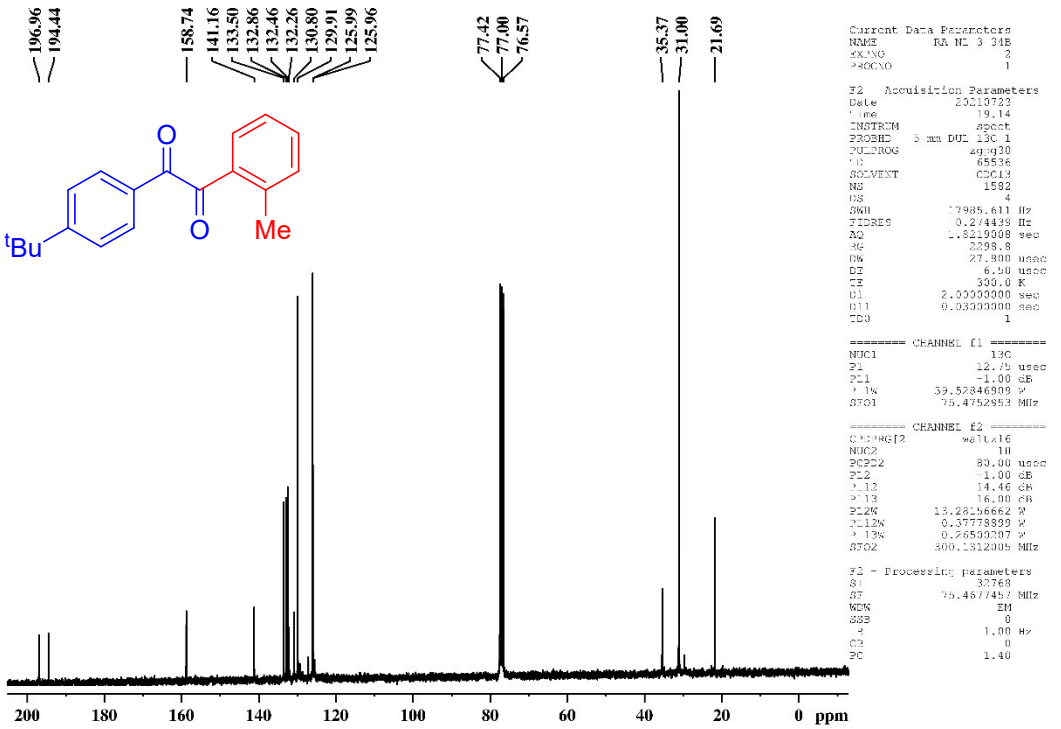
^{1}H & ^{13}C spectra of compound **3x**



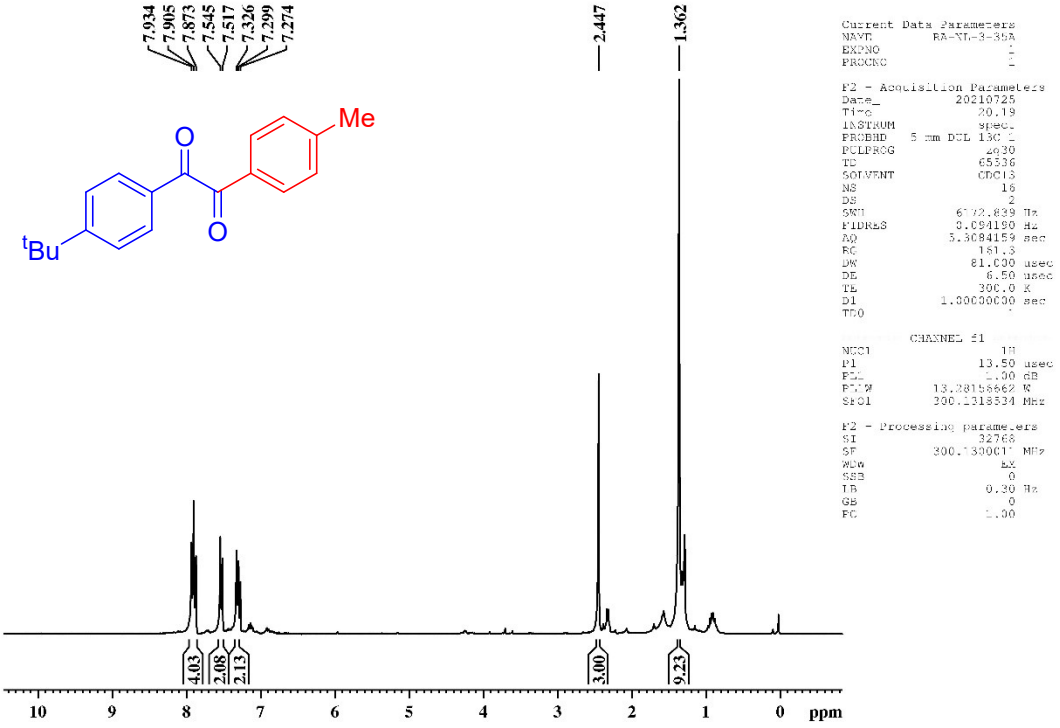


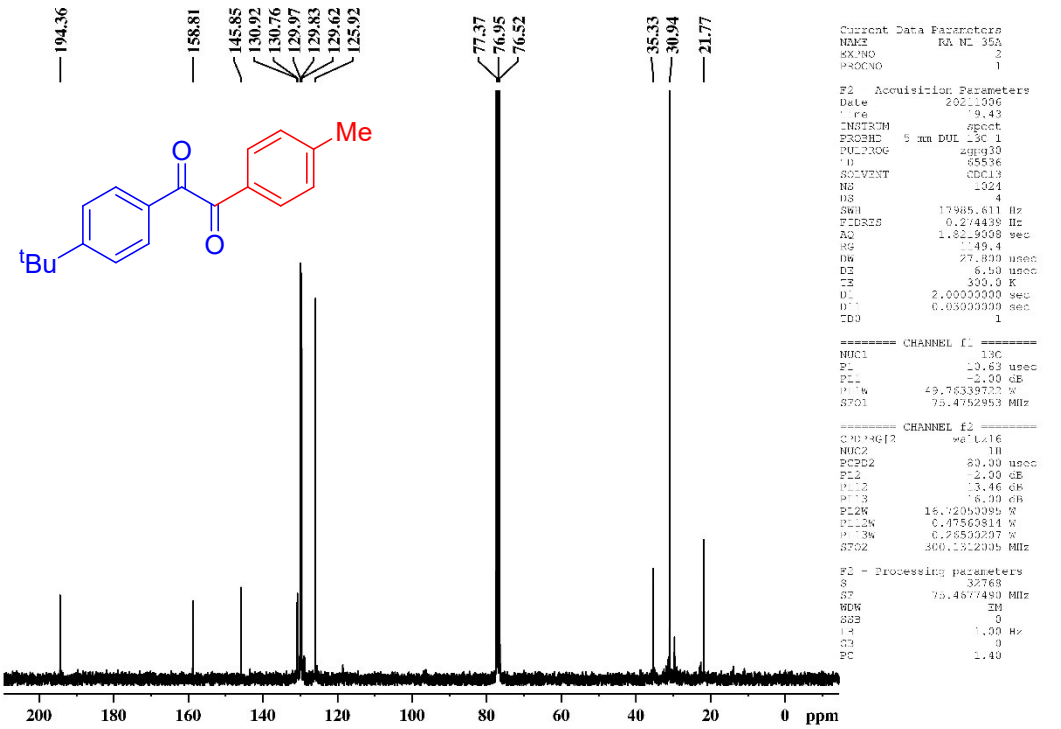
^{1}H & ^{13}C spectra of compound **3y**



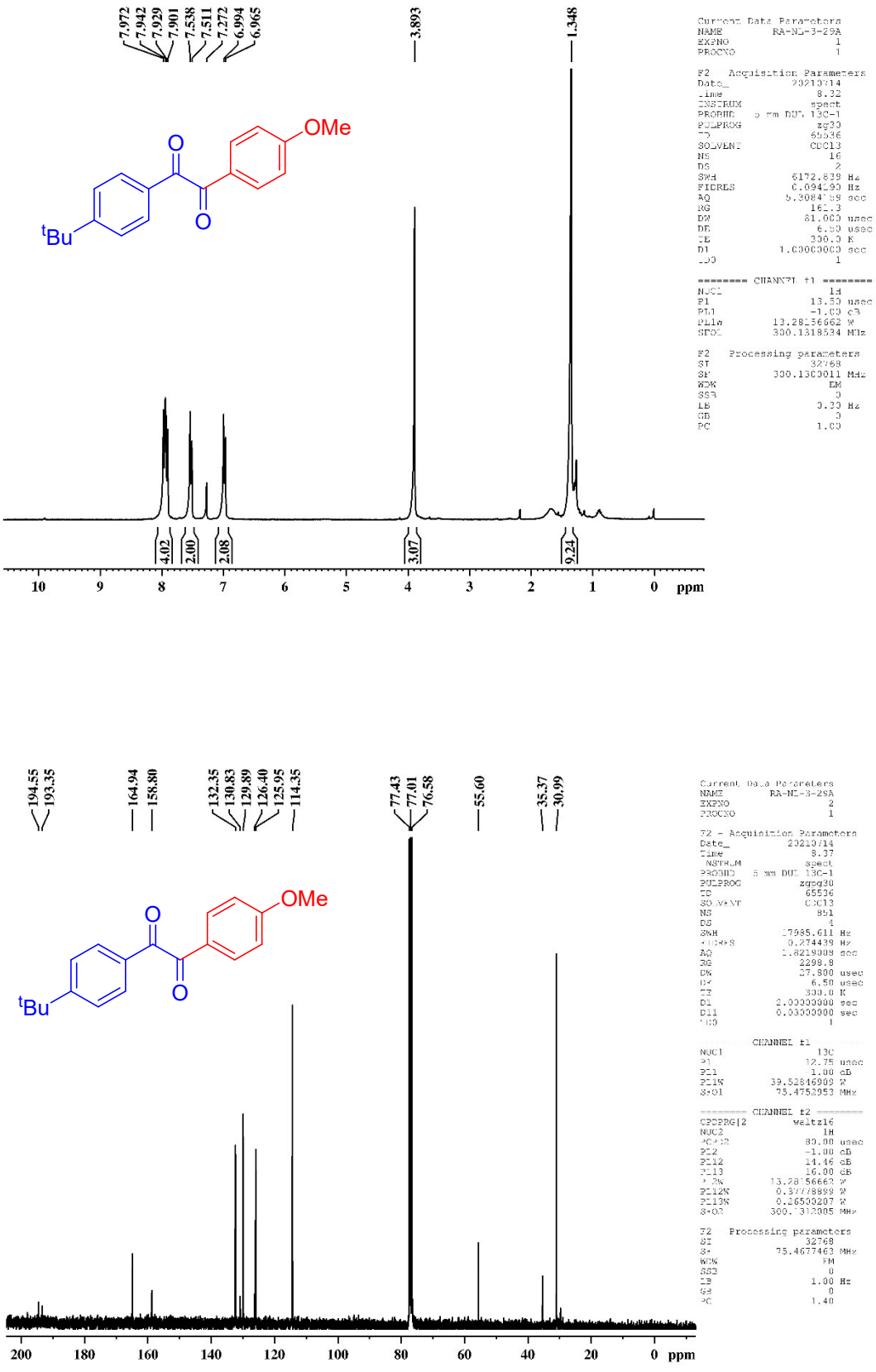


^{1}H & ^{13}C spectra of compound **3z**

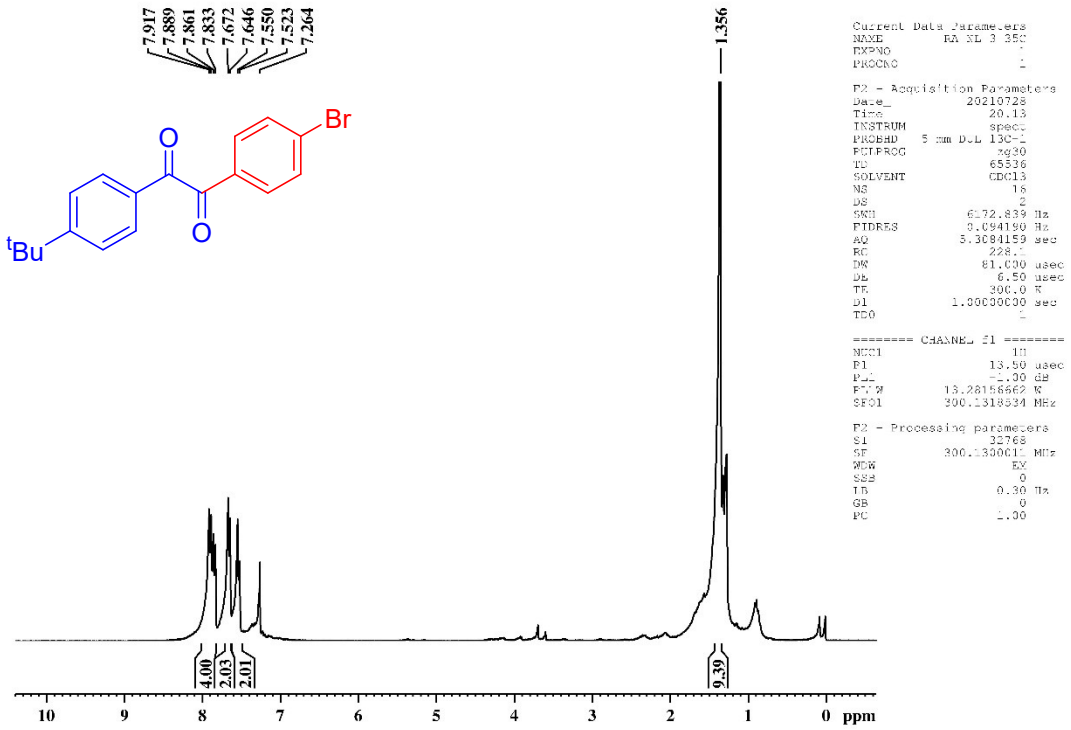


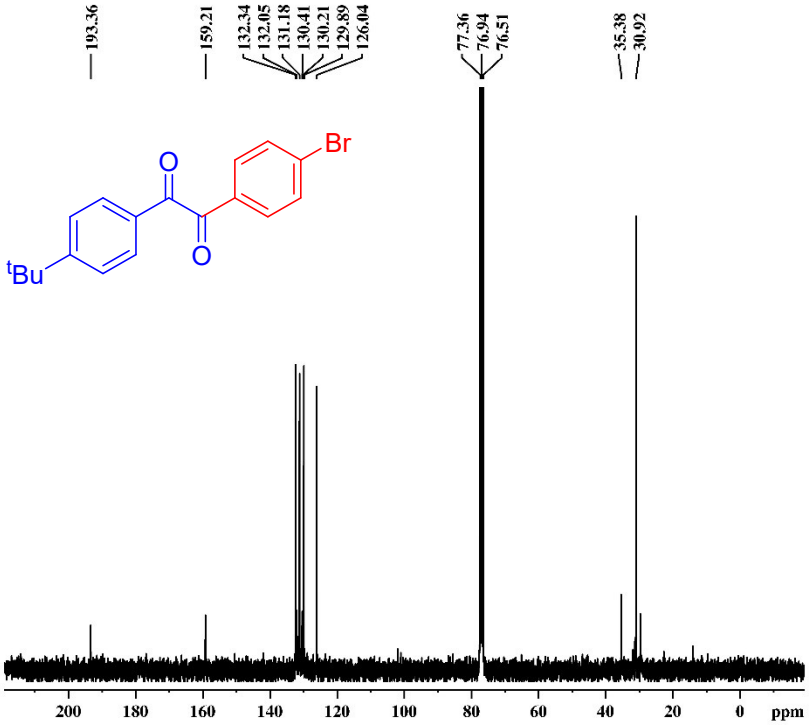


^{1}H & ^{13}C spectra of compound **3aa**

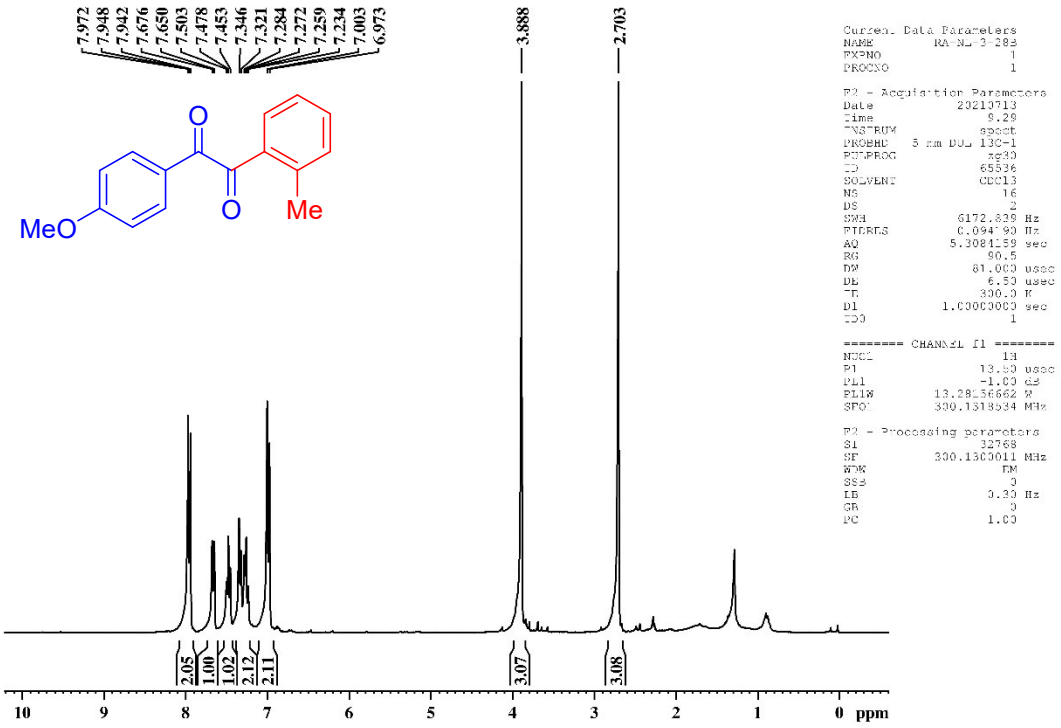


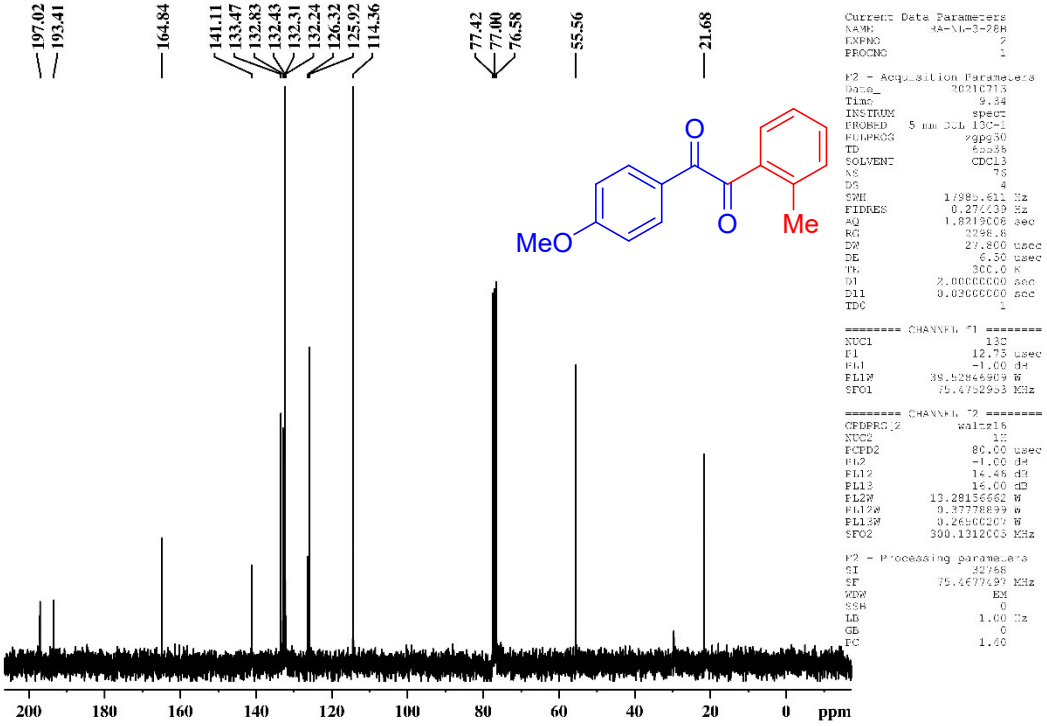
^{1}H & ^{13}C spectra of compound **3ab**



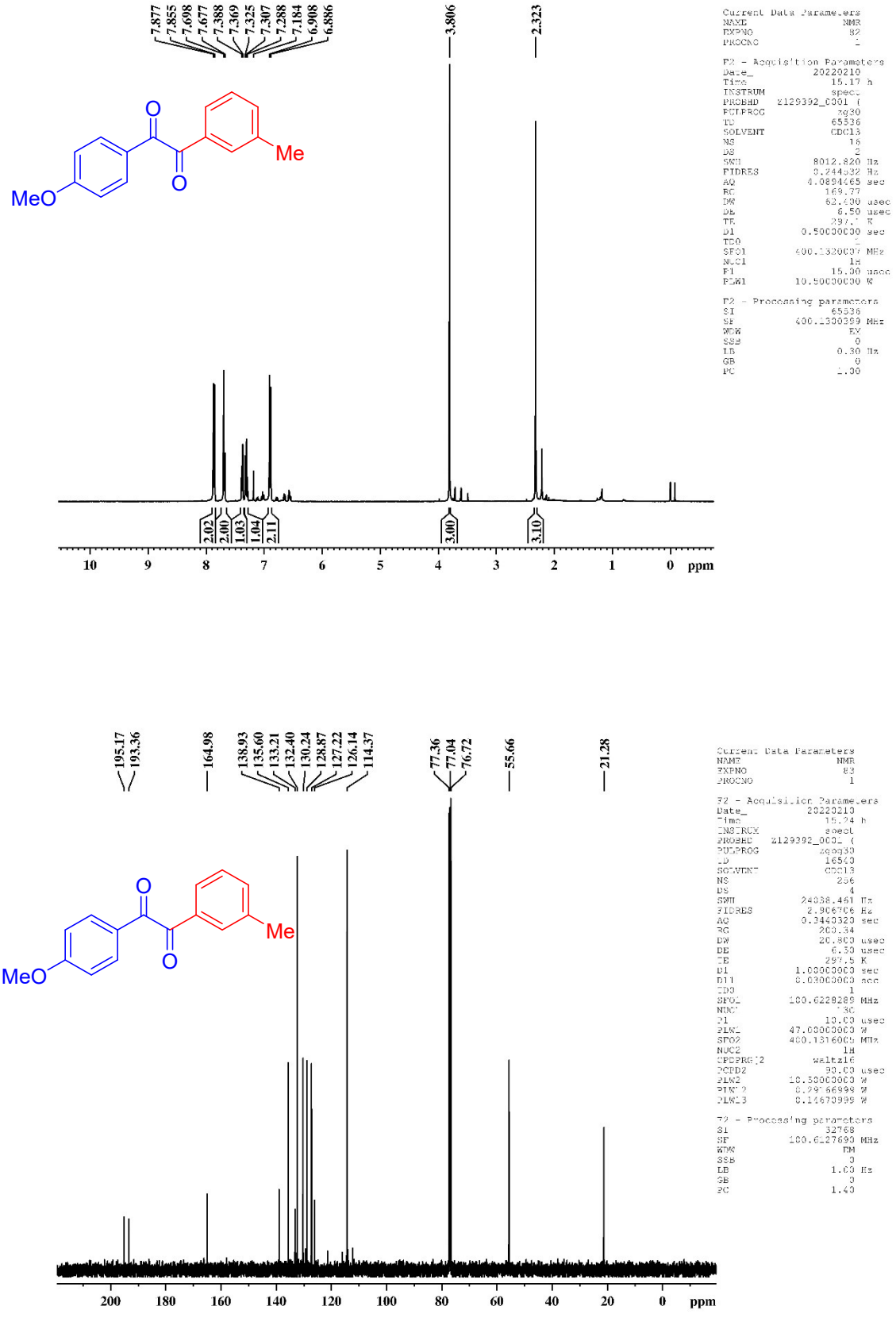


^{1}H & ^{13}C spectra of compound **3ac**

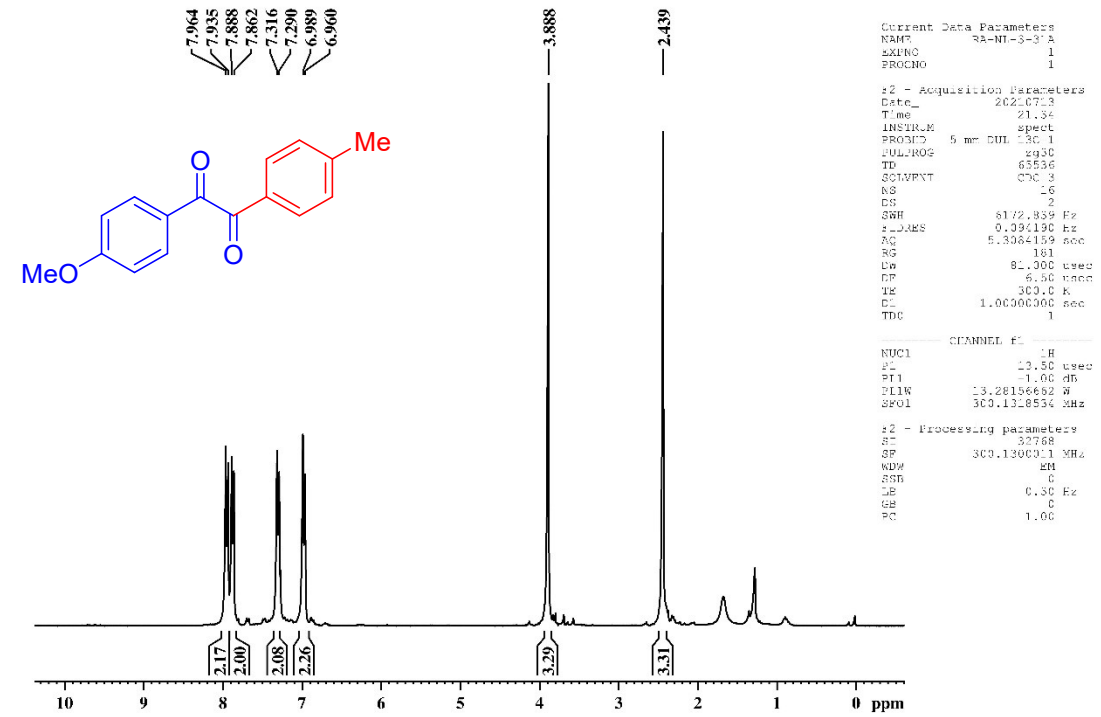


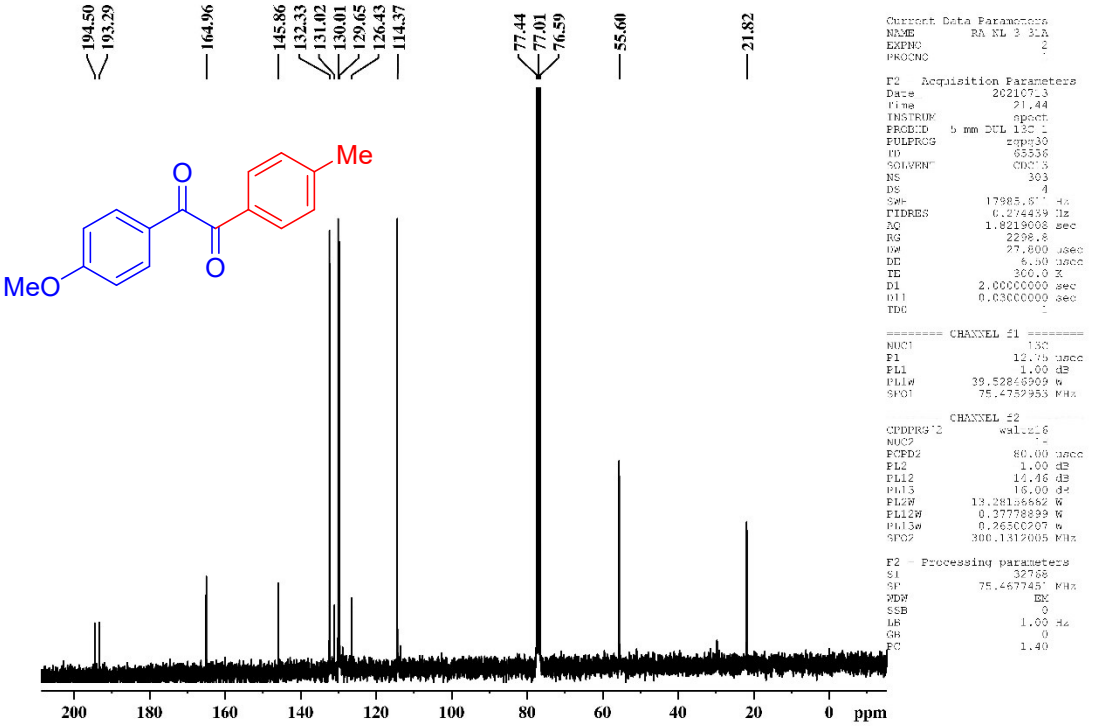


^{1}H & ^{13}C spectra of compound **3ad**

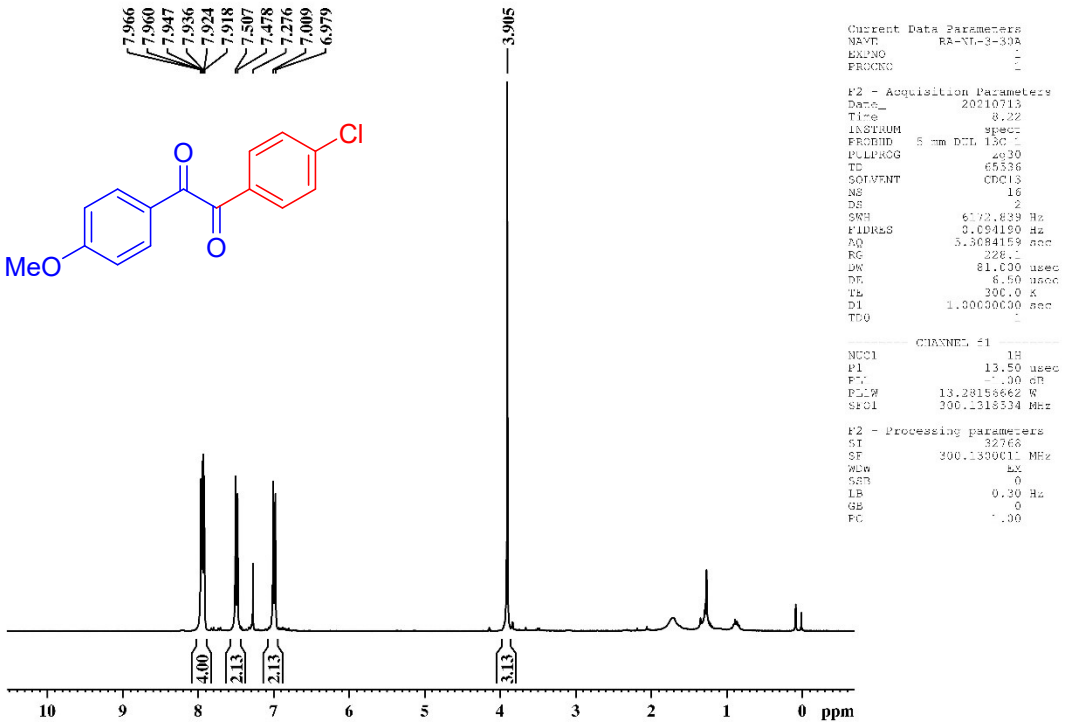


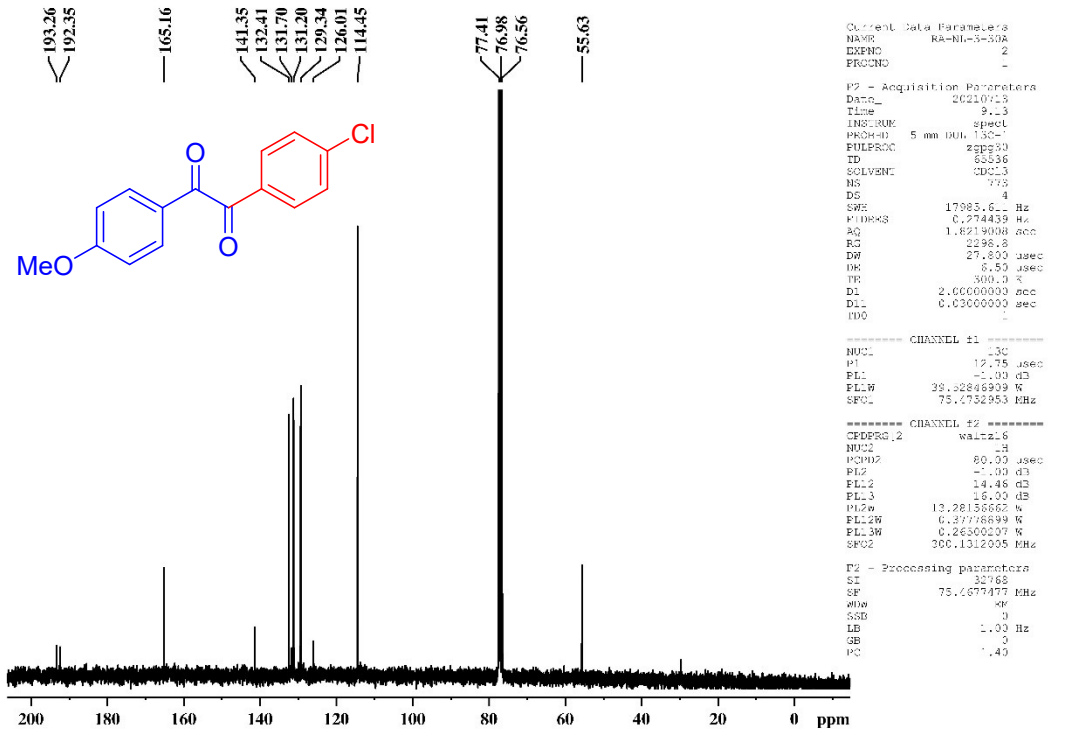
^{1}H & ^{13}C spectra of compound **3ae**



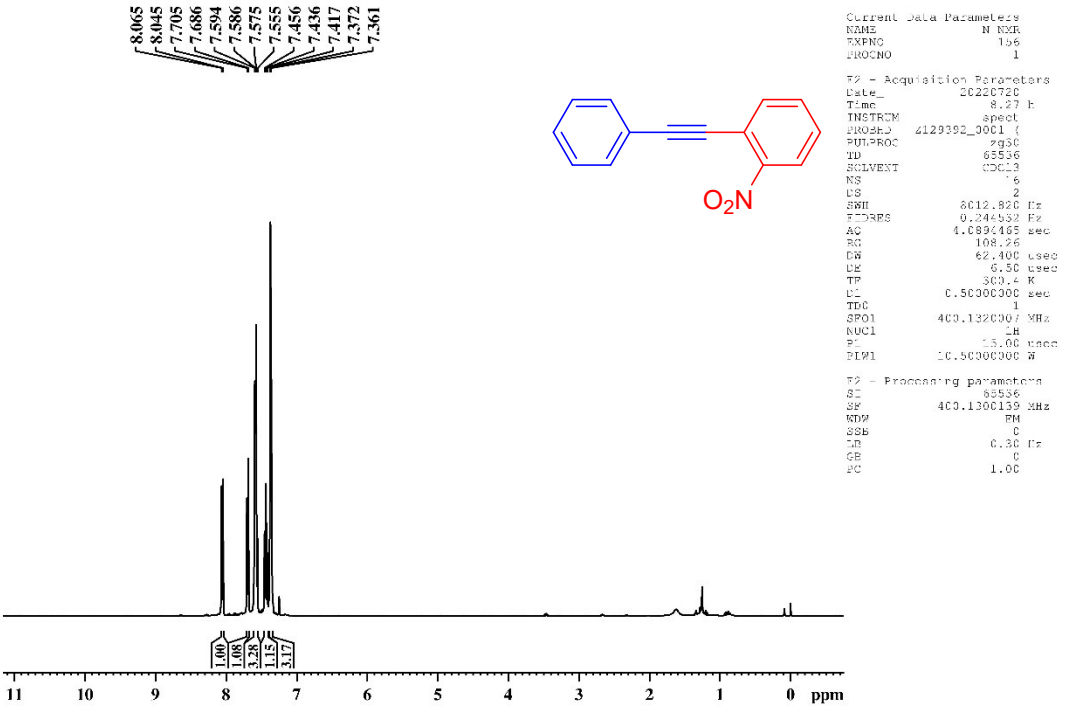


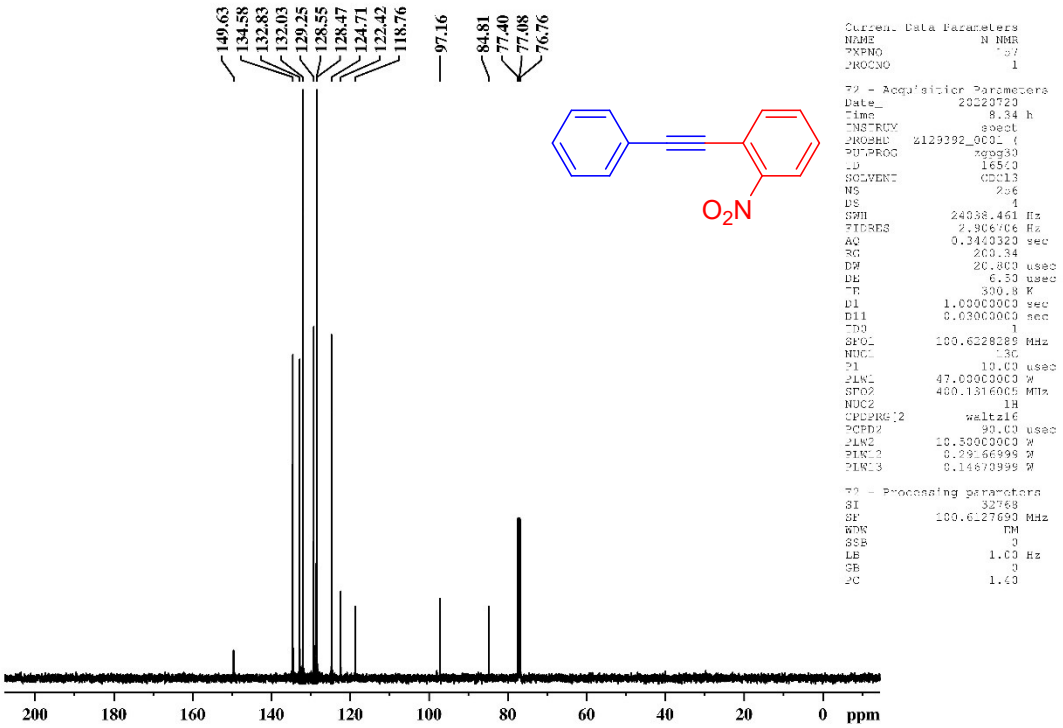
^{1}H & ^{13}C spectra of compound **3af**



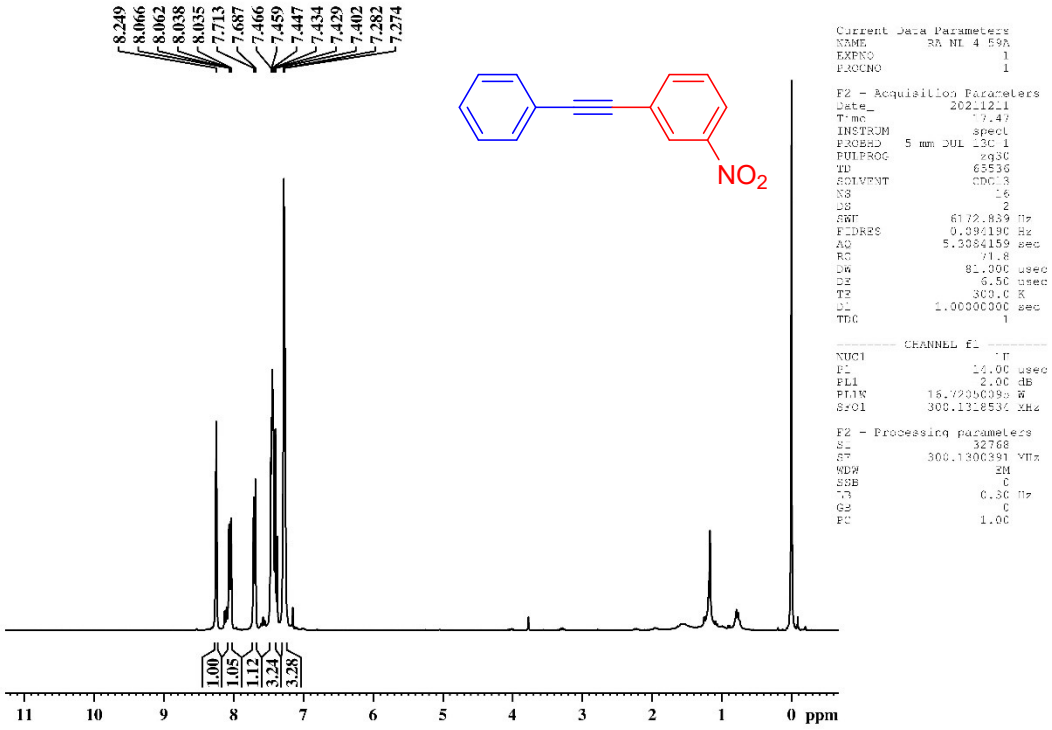


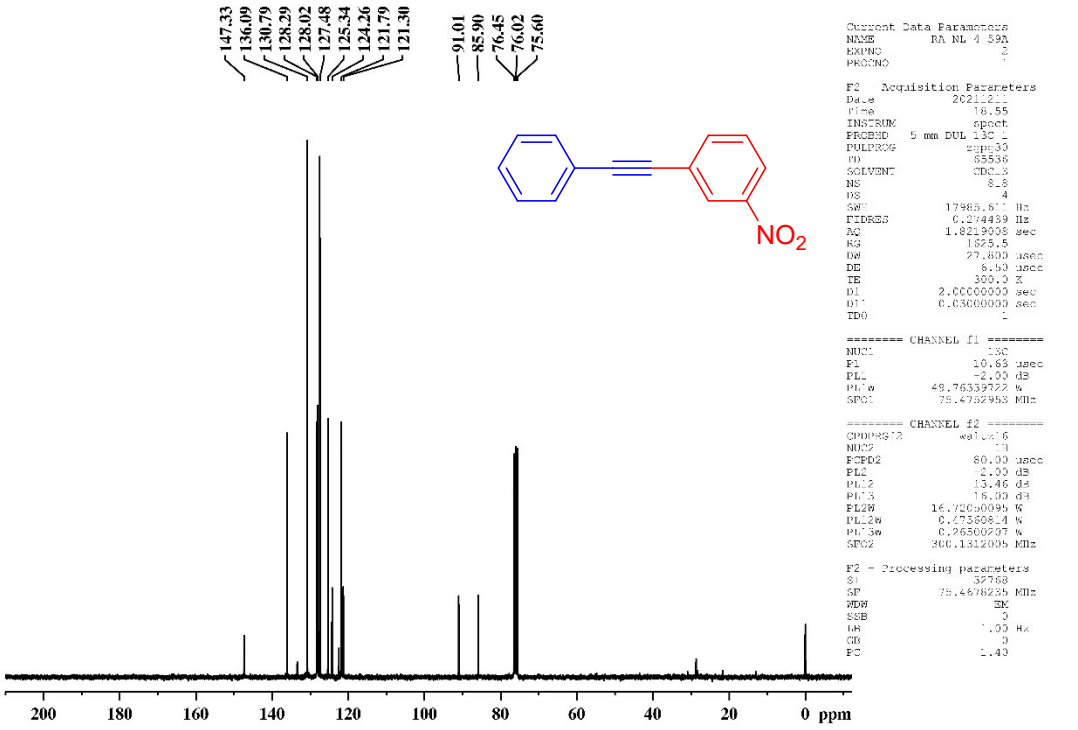
^{1}H & ^{13}C spectra of compound **3ag**



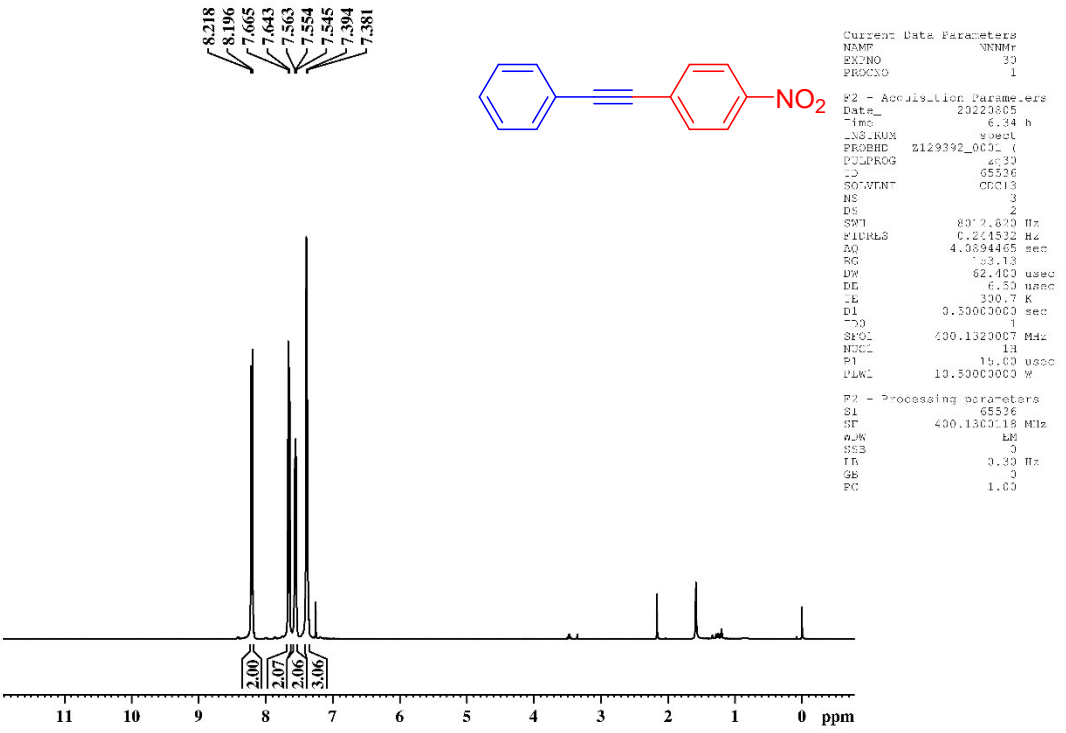


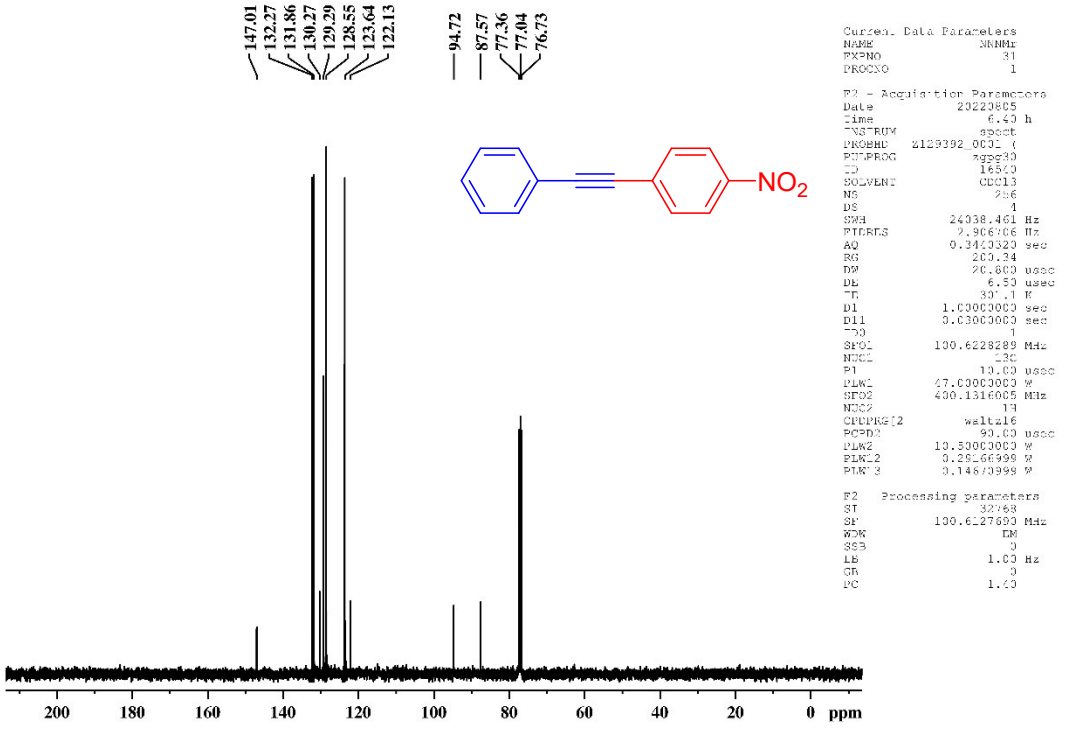
^{1}H & ^{13}C spectra of compound **4a**



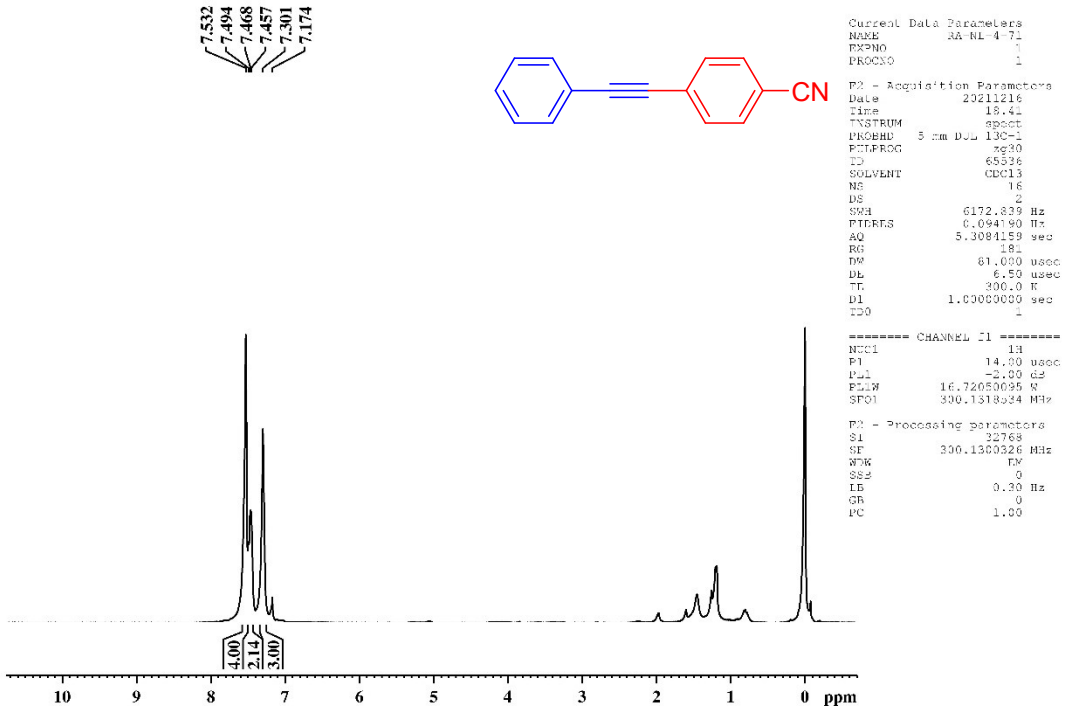


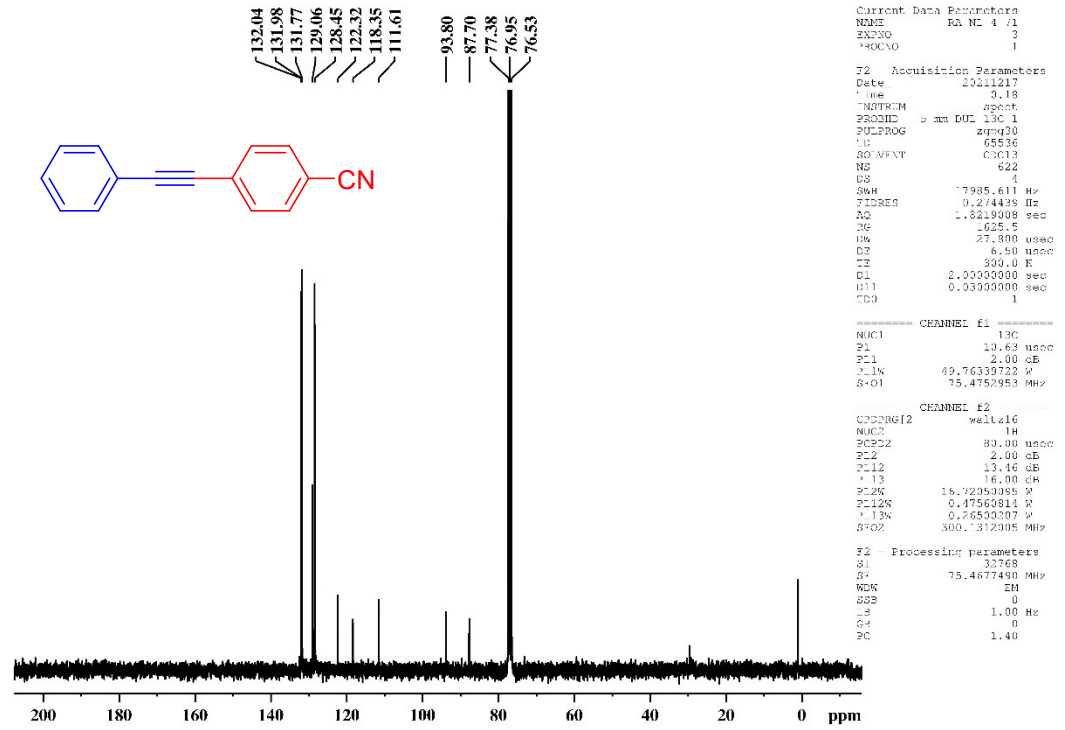
^{1}H & ^{13}C spectra of compound **4b**



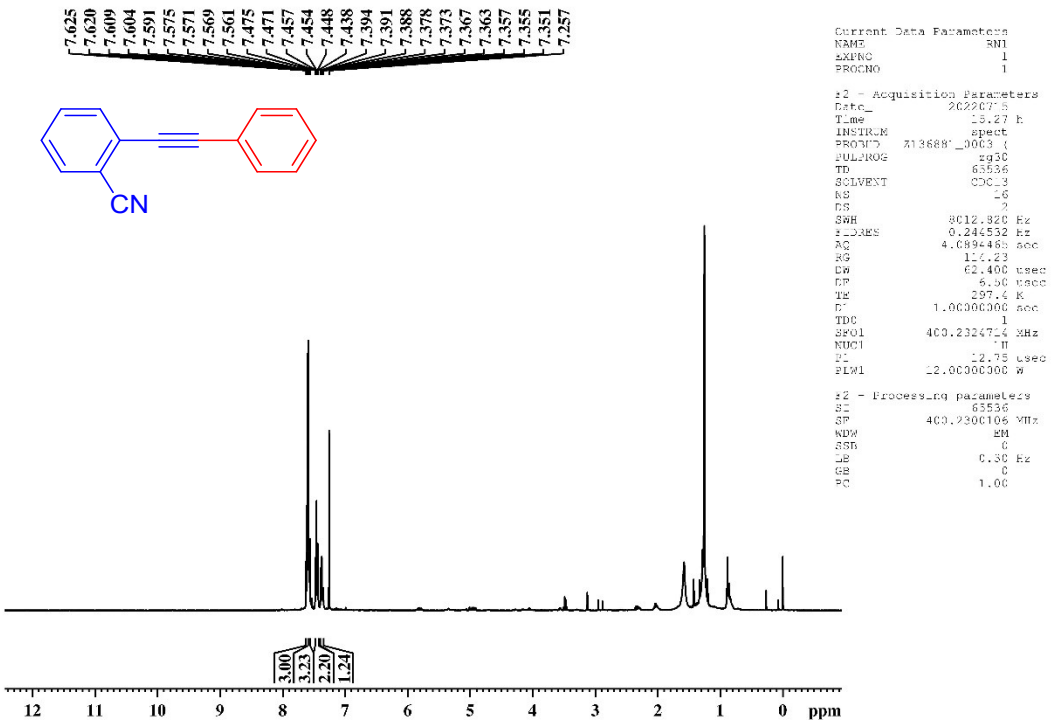


^{1}H & ^{13}C spectra of compound **4c**

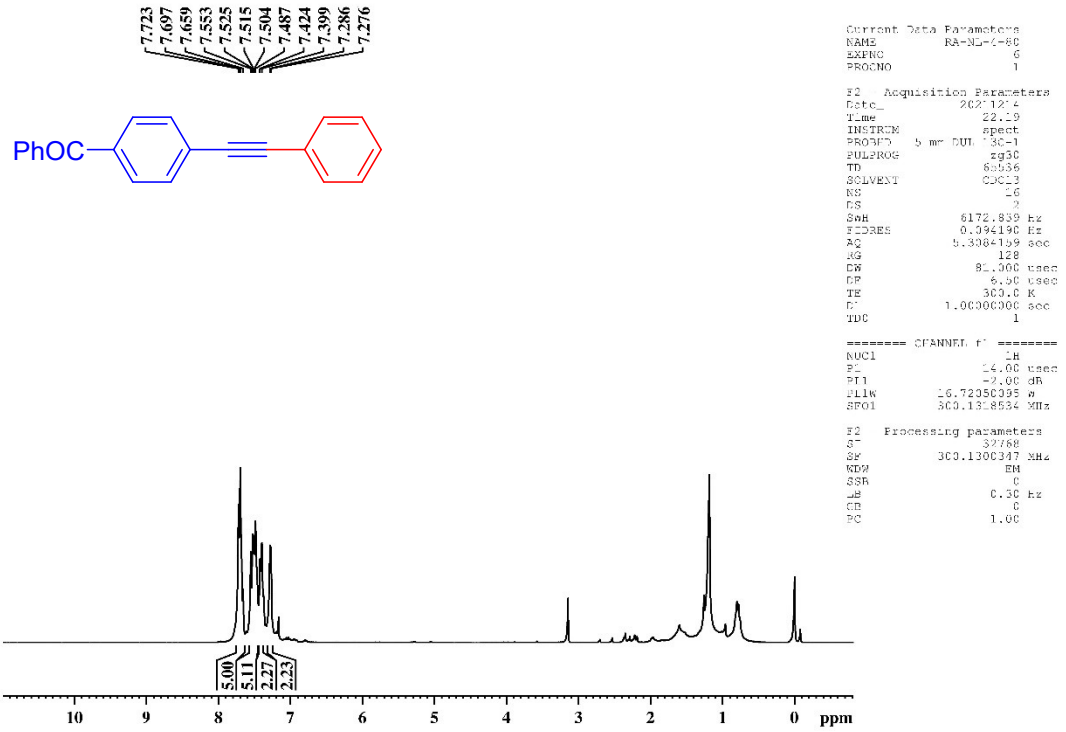


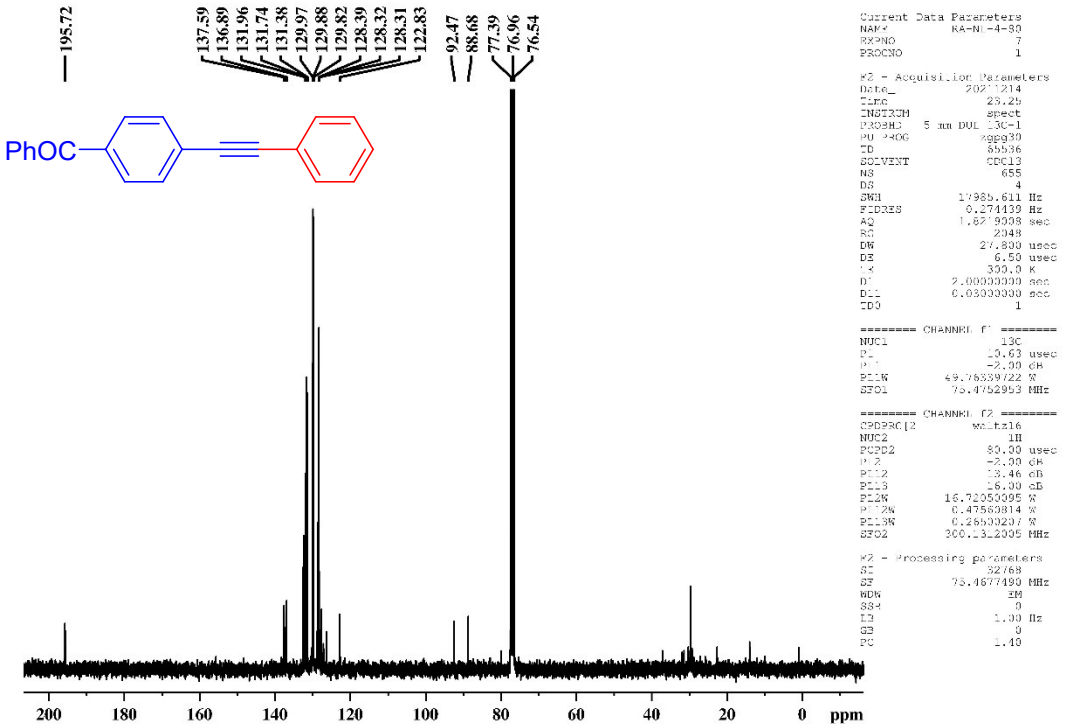


^{1}H & ^{13}C spectra of compound **4d**

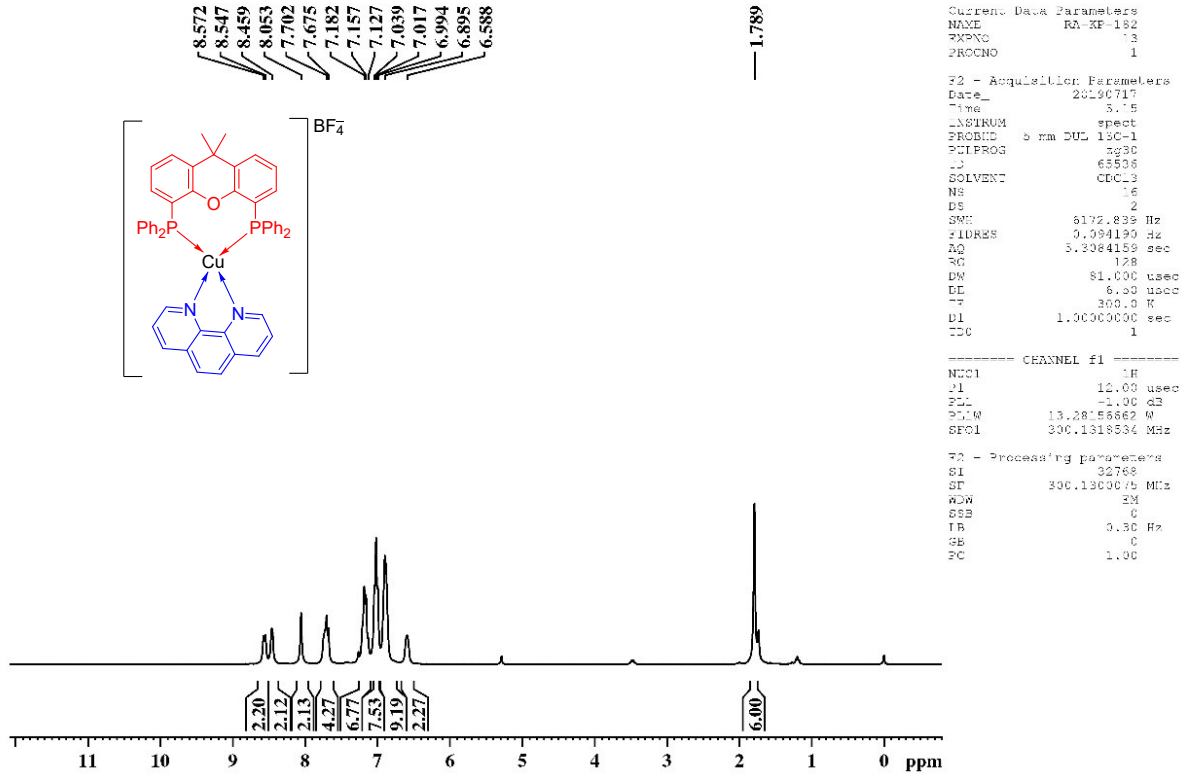


^{1}H NMR spectrum of compound **4e**





^{1}H & ^{13}C spectra of compound **4f**

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Current Data Parameters
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EXPNO                    13
PROCNO                    1

F2 - Acquisition Parameters
Date_              20190717
Time                   5.15
INSTRUM                spect
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PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               6172.839 Hz
FIDRES            0.094190 Hz
AQ                5.3084159 sec
RG                      128
DW                 81.000 usec
DE                  6.50 usec
TE                 300.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                    12.00 usec
PL1                  -1.00 dB
PL1W          13.28156662 W
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF            300.1300075 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
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^{1}H NMR spectrum of Photocatalyst **PC-1**