Supporting Information

Rh(III)-catalyzed [4 + 1] annulation of 1-arylindazolones with alkynyl cyclobutanols: access to indazolo[1,2-*a*]indazolones

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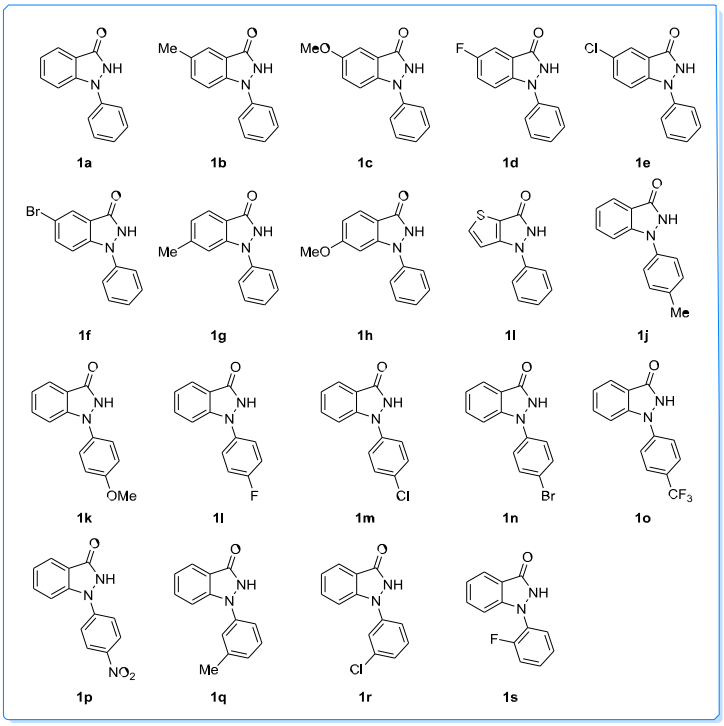
1. General information

The NMR spectra were recorded on the Bruker spectrometer in $CDCl_3$ at room temperature. ^1H NMR (500 MHz) chemical shifts (δ) were referenced to internal standard TMS (δ = 0.00 ppm), and $^{13}C\{^1H\}$ NMR (126 MHz) chemical shifts were referenced to internal solvent $CDCl_3$ (δ = 77.16 ppm) and chemical shifts are reported as parts per million (ppm). The high-resolution mass spectrometric data was recorded on Waters Synapt G2 Si tandem mass spectrometer with electron spray ionization (ESI) source. Products were purified by flash column chromatography on silica gel (200-300 mesh) with freshly distilled ethyl acetate (EA) and petroleum ether (PE). 1-Arylindazolones[1,2] and alkynyl cyclobutanols[3] were prepared according to the reported literatures. Other reagents and solvents were obtained from commercial suppliers and used without further purification unless otherwise noted.

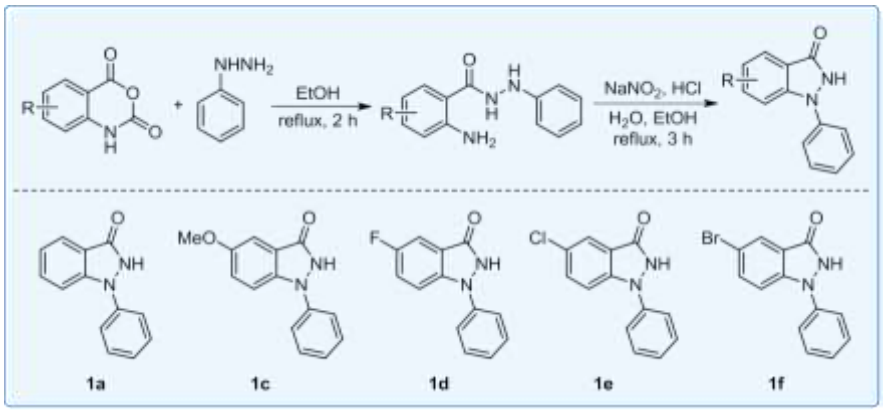
2. General procedure for the synthesis of 1-arylindazolones



Scheme S1. List of 1-arylindazolone substrates used in this study

Method A

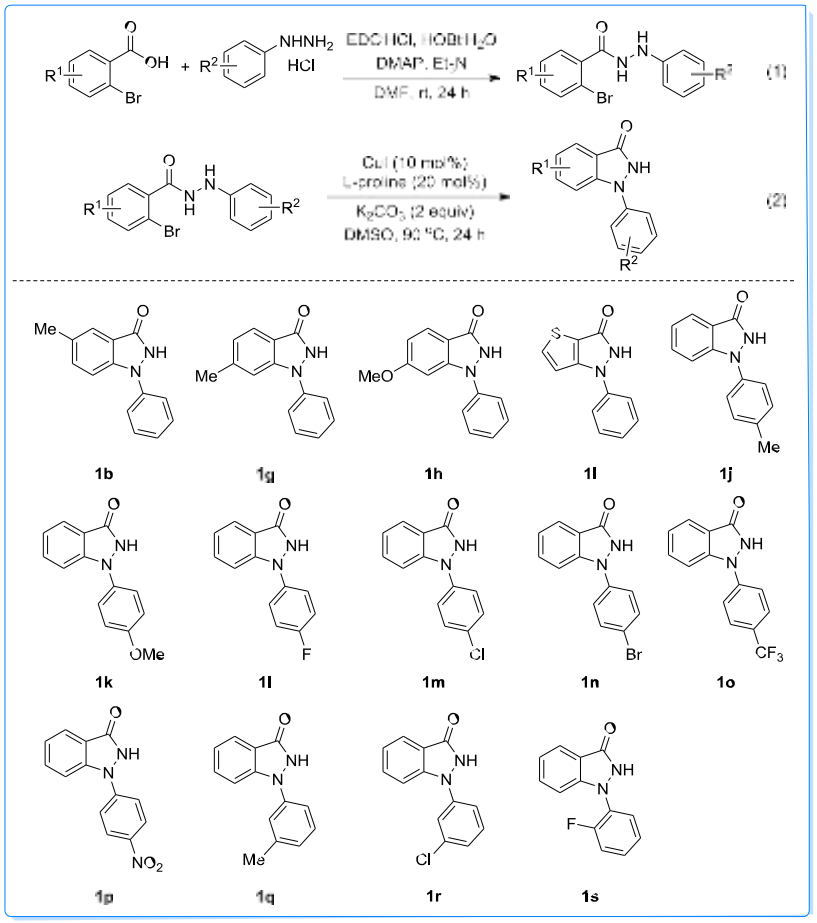
To a stirred solution of isatoic anhydride (12.0 mmol) in ethanol (20 mL), phenylhydrazine (12.0 mmol) was added. The reaction mixture was refluxed for 2 h and then it was allowed to cool to room temperature. The resulting precipitated hydrazide was filtered out and washed with ethanol. Then, 25 mL of 1.0 M HCl was added into this hydrazide. To this slurry, $NaNO_2$ (18.0 mmol, in 10 mL water) was added and the reaction mixture was refluxed for 3 h after adding 25 mL of ethanol. The reaction mixture was cooled to room temperature and the resulting precipitate was filtered out and washed with water and ethanol to provide the 1-arylindazolone as a light yellow solid. 1-Arylindazolones **1a** and **1c-1f** were known compounds and the spectra data are consistent with those reported in literature.[1]



Scheme S2. Preparation of 1-arylindazolones (**Method A**)

Method B

1-Arylindazolones **1b** and **1g-1s** was prepared according to the following procedure (**Scheme S3**).[2] (1) Et_3N (10 mmol, 1.0 equiv) was added to a solution of phenylhydrazine hydrochloride (10 mmol, 1.0 equiv) and 2-bromobenzoic acid (10 mmol, 1.0 equiv) in dry DMF (20 mL) and the mixture was stirred at room temperature for 10 min. Then to the mixture were added EDC·HCl (11 mmol, 1.1 equiv), HOBt·H_2O (11 mmol, 1.1 equiv), and DMAP (0.5 mmol, 5.0 mol %), and the mixture



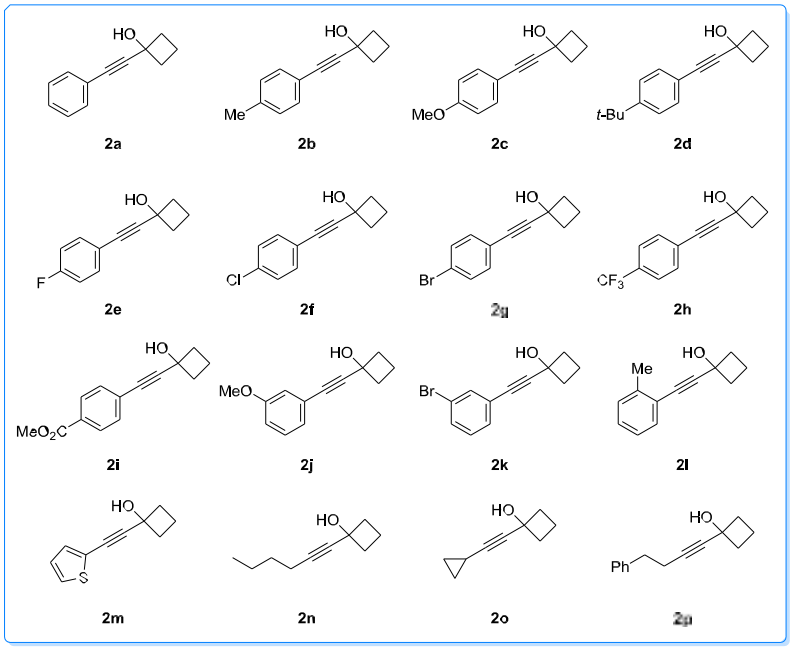
Scheme S3. Preparation of 1-arylindazolones (**Method B**)

was further stirred at room temperature for 24 h. Upon completion, the reaction was quenched with water, the resulting precipitate was filtered out and washed with water and ethyl acetate to provide the 2-bromobenzohydrazide as a white solid. The crude product was used in the next step without further purification.

(2) A mixture of 2-bromobenzohydrazide (10 mmol), CuI (190 mg, 1 mmol, 10 mol%), L-proline (230 mg, 2 mmol, 20 mol%), and K_2CO_3 (2.76 g, 20 mmol) in DMSO (20 mL) was stirred at 90 ^oC for 24 h under nitrogen atmosphere. Upon completion, the reaction mixture was quenched with saturated aqueous NH_4Cl (50 mL), and the resulting precipitate was filtered out and washed with water and ethyl acetate to provide the 1-arylindazolone as a light yellow solid. 1-Arylindazolones

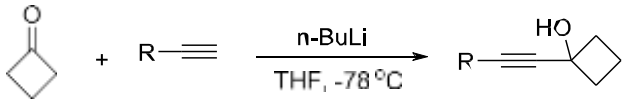
1b and **1g-1s** were known compounds and the spectra data are consistent with those reported in literature.[2]

3. General procedure for the synthesis of alkynyl cyclobutanols



Scheme S4. List of alkynyl cyclobutanol substrates used in this study

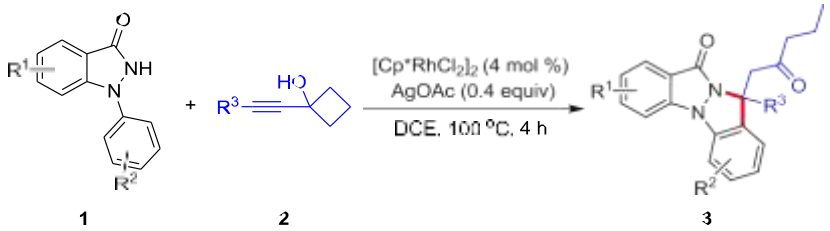
Alkynyl cyclobutanols **2a-2p** were synthesized following the reported procedure.[3] The spectra data are consistent with those reported in literature.



To a solution of the corresponding terminal alkyne (10 mmol, 1 equiv) in THF (25 mL), n-BuLi (1.6 M in hexane, 6.3 mL, 10 mmol, 1 equiv) was added dropwise by syringe at -78 °C. After stirring for 30 min, a solution of cyclobutanone (10 mmol, 1 equiv) in THF (10 mL) was added dropwise and the mixture was stirred at the same temperature for 1 h. The solution was then allowed to warm to room temperature, quenched with saturated aqueous NH_4Cl and extracted with EtOAc (30 mL x 3). The combined organic layer was then washed with brine (30 mL x 2), dried

over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (eluent: PE/EA = 15:1 to 8:1) to afford the pure alkynyl cyclobutanols.

4. General procedure for the synthesis of indazolo[1,2-*a*]indazolones

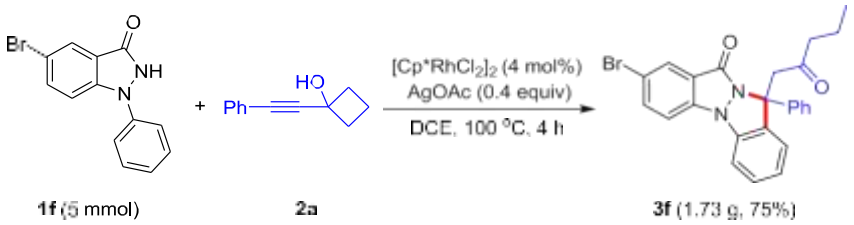


1 2 3

To an oven-dried sealed tube charged with 1-arylindazolones **1** (0.2 mmol), alkynyl cyclobutanols **2** (0.24 mmol), $[Cp^*RhCl_2]_2$ (5 mg, 4 mol%), and AgOAc (14 mg, 0.4 mmol) was added 1,2-dichloroethane (1 mL) at room temperature. The reaction mixture was allowed to stir at 100 °C under a N_2 atmosphere for 4 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with ethyl acetate (20 mL) and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (eluent: PE/EA = 4:1 to 3:1) to afford the products **3**.

5. Gram-scale synthesis and synthetic transformation

(a) Gram-scale synthesis

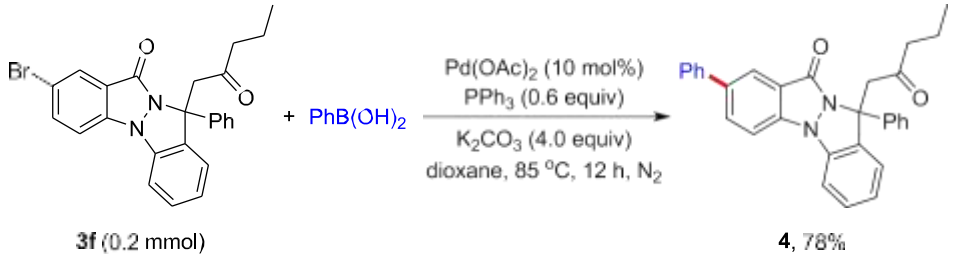


1f (5 mmol) **2a** **3f** (1.73 g, 75%)

To a 100 mL round-bottomed flask charged with 5-bromo-1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1f** (1.45 g, 5 mmol), 1-(phenylethynyl)cyclobutan-1-ol **2a** (1.04 g, 6 mmol), $[Cp^*RhCl_2]_2$ (124

mg, 4 mol%), and AgOAc (334 mg, 2 mmol) was added 1,2-dichloroethane (15 mL) at room temperature. The reaction mixture was allowed to stir at 100 °C under a N_2 atmosphere for 4 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with EtOAc (50 mL) and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (eluent: PE/EA = 4:1) to afford 1.73 g of **3f** in 75% yield as a white semisolid.

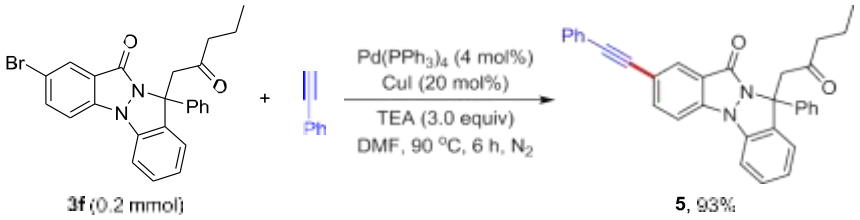
(b) Suzuki coupling reactions



3f (0.2 mmol) **4**, 78%

To an oven-dried sealed tube charged with 8-bromo-12-(2-oxopentyl)-12-phenyl-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one **3f** (92 mg, 0.2 mmol), phenylboronic acid (36.6 mg, 0.3 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), PPh_3 (31.5 mg, 0.12 mmol), and K_2CO_3 (110.6 mg, 0.8 mmol) was added 1,4-dioxane (2 mL) at room temperature. The reaction mixture was allowed to stir at 85 °C under a N_2 atmosphere for 12 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with EtOAc (10 mL) and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (eluent: PE/EA = 4/1) to afford 71.5 mg of **4** in 78% yield as a white semisolid.

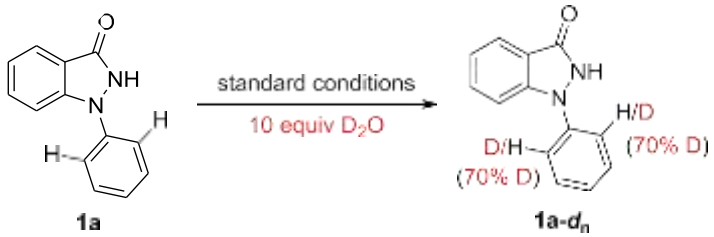
(c) Sonogashira coupling reactions



To an oven-dried sealed tube charged with 8-bromo-12-(2-oxopentyl)-12-phenyl-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one **3f** (92 mg, 0.2 mmol), phenylacetylene (31 mg, 0.3 mmol), $Pd(PPh_3)_4$ (10 mg, 0.008 mmol), CuI (8 mg, 0.04 mmol), and Et_3N (61.2 mg, 0.6 mmol) was added DMF (2 mL) at room temperature. The reaction mixture was allowed to stir at 90 °C under a N_2 atmosphere for 6 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with EtOAc (30 mL), washed with brine (20 mL x 2), dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (eluent: PE/EA = 4/1) to afford 89.7 mg of **5** in 93% yield as a white semisolid.

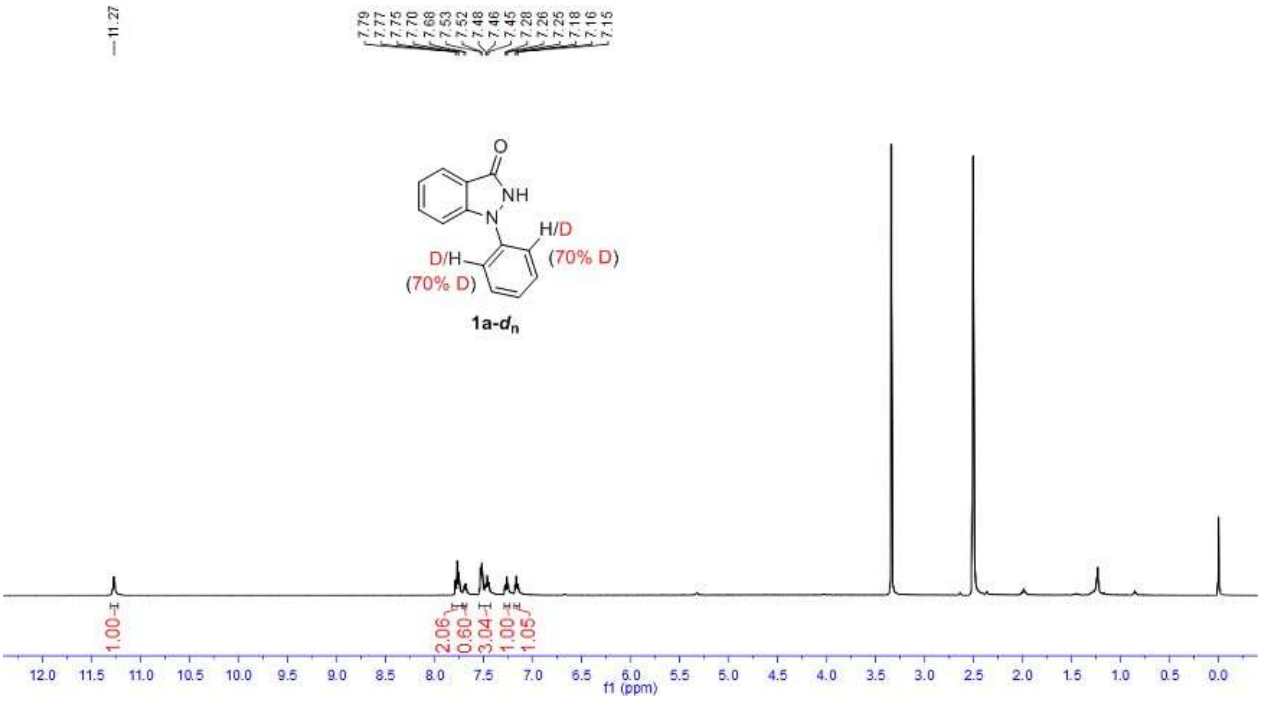
6. Mechanistic studies

(a)

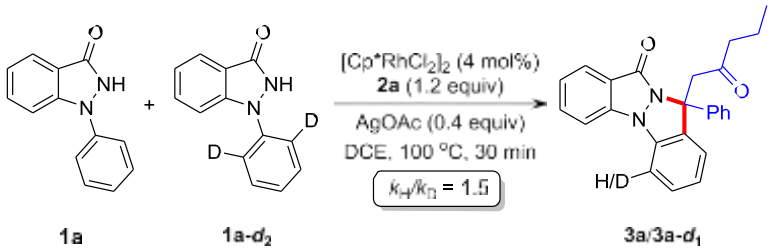


To an oven-dried sealed tube charged with 1-phenyl-1*H*-indazol-3(2*H*)-one **1a** (42 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (5 mg, 4 mol%), and AgOAc (14 mg, 0.4 mmol) were added D_2O (40 mg, 2 mmol) and dichloroethane (1 mL) at room temperature. The reaction mixture was allowed to stir at 100 °C under a N_2 atmosphere for 4 h. The reaction mixture was then cooled to room temperature, diluted

with EtOAc (20 mL) and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (eluent: PE/EA = 6:1) to afford the products. The deuterium incorporation was calculated from ^{1}H NMR spectroscopy.

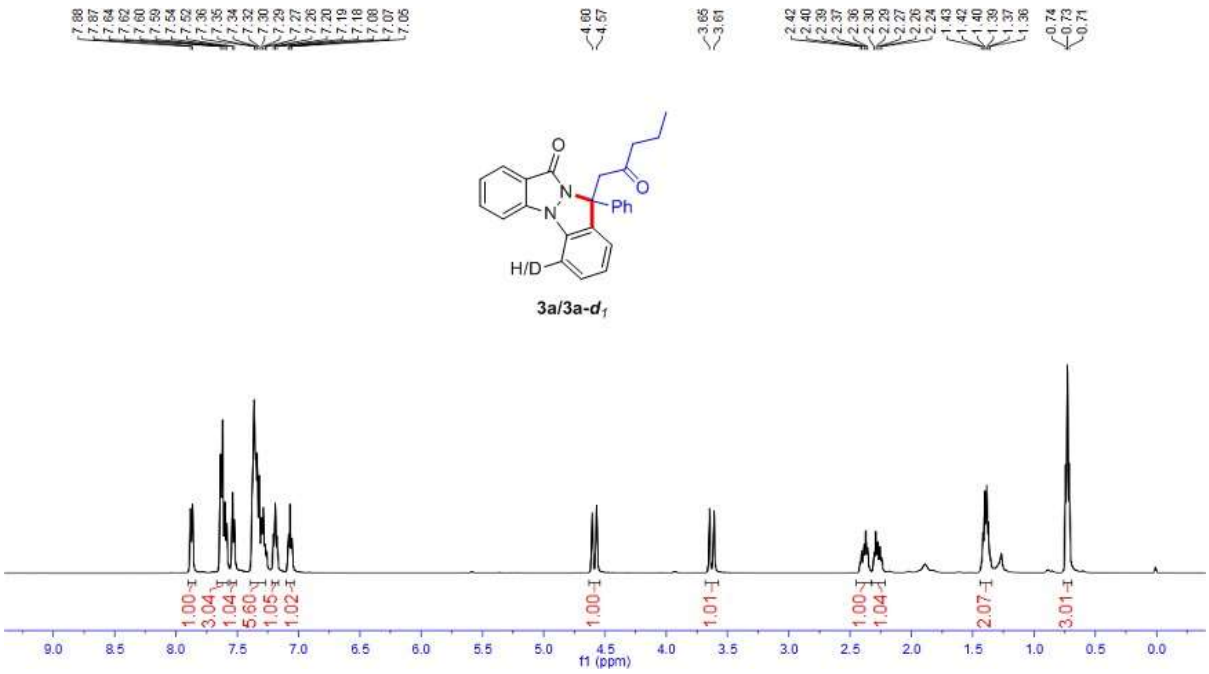


(b)

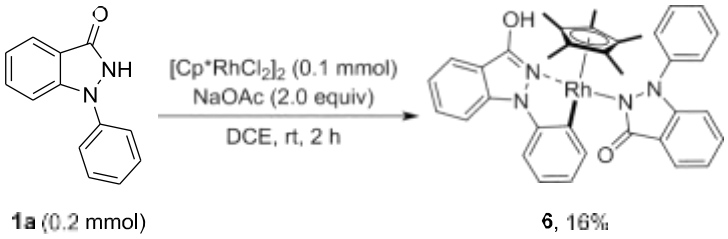


To an oven-dried sealed tube charged with the mixture of 1-phenyl-1*H*-indazol-3(2*H*)-one **1a** (21 mg, 0.1 mmol), **1a-*d*$_2$** (21.2 mg, 0.1 mmol), alkynyl cyclobutanols **2a** (42 mg, 0.24 mmol), $[Cp^*RhCl_2]_2$ (5 mg, 4 mol%), and AgOAc (14 mg, 0.4 mmol) was added 1,2-dichloroethane (1 mL) at room temperature. The reaction mixture was allowed to stir at 100 °C under a N_2 atmosphere for 30 min, and then was immediately quenched with EtOAc (10 mL). The reaction

mixture was cooled to room temperature and concentrated in vacuo. The residue was purified by flash column chromatography (PE/EA = 4:1) to afford **3a** and **3a-*d*$_1$**. A kinetic isotope effect value of k_H/k_D = 1.5 was calculated on the basis of ^{1}H NMR analysis.

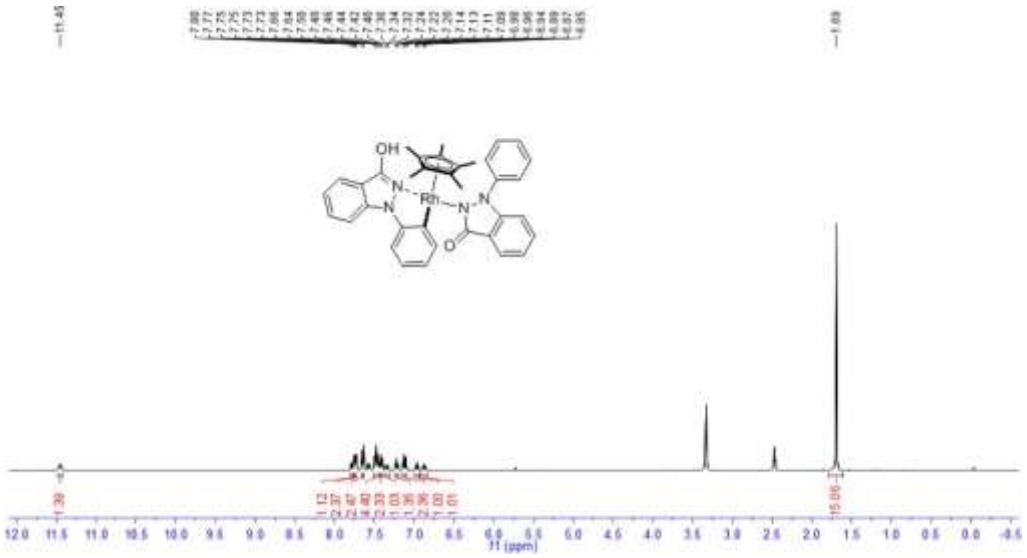


(c)

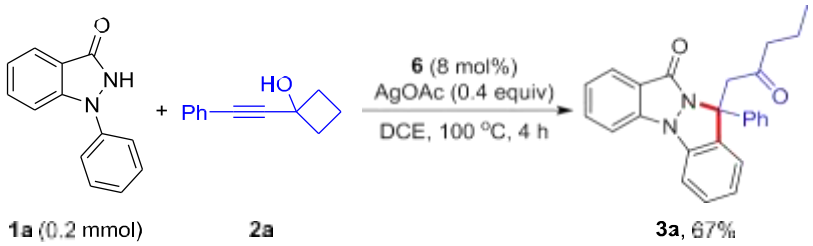


The preparation of cyclometalated Rh(III) complexe **6** was carried out according to the reported procedure.[4] To an oven-dried sealed tube charged with 1-phenyl-1*H*-indazol-3(2*H*)-one **1a** (42 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (61.8 mg, 0.1 mmol), and NaOAc (32.8 mg, 0.4 mmol) was added dichloroethane (3.5 mL) at room temperature. The reaction mixture was allowed to stir at room temperature under air for 2 h. The reaction mixture was then diluted with EtOAc (5 mL) and

concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (CH_2Cl_2/MeOH = 50:1) to afford 21.5 mg of the cyclometalated Rh(III) complexe **6** in 16% yield as a dark brown solid, which was further recrystallized by CH_2Cl_2/pentane (1:5) to give the Rh(III) complexe **6** as a red solid. **^{1}H NMR** (500 MHz, DMSO-d_6): δ 11.45 (br, 1H), 7.80-7.76 (m, 1H), 7.75-7.73 (m, 2H), 7.65 (d, J = 8.2 Hz, 2H), 7.50-7.45 (m, 4H), 7.44-7.40 (m, 2H), 7.36-7.32 (m, 1H), 7.24-7.20 (m, 1H), 7.15-7.10 (m, 2H), 6.98-6.94 (m, 1H), 6.90-6.85 (m, 1H), 1.69 (s, 15H). The Rh(III) complexe **6** was a known compound and the spectra data are consistent with those reported in literature.[4]



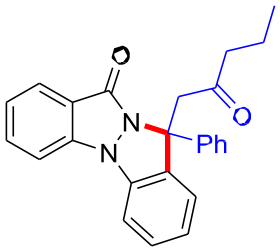
(d)



To an oven-dried sealed tube charged with 1-phenyl-1*H*-indazol-3(2*H*)-one **1a** (42 mg, 0.2 mmol), 1-(phenylethynyl)cyclobutan-1-ol **2a** (42 mg, 0.24 mmol), Rh(III) complexe **6** (10.7 mg, 8 mol%), and AgOAc (14 mg, 0.4 mmol) was added dichloroethane (1 mL) at room temperature. The reaction mixture was allowed to stir at 100 °C under a N_2 atmosphere for 4 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with EtOAc (20 mL) and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (eluent: PE/EA = 4:1) to afford 51.2 mg of **3a** in 67% yield as a white solid.

7. Characterization data of products

12-(2-oxopentyl)-12-phenyl-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3a)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white solid in 85% yield (65 mg);

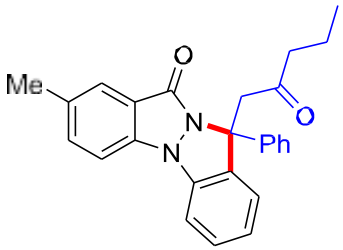
M.p. = 147-148 ºC;

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, J = 7.9 Hz, 1H), 7.65-7.58 (m, 3H), 7.54 (d, J = 8.3 Hz, 1H), 7.40-7.27 (m, 6H), 7.21-7.18 (m, 1H), 7.09-7.06 (m, 1H), 4.59 (d, J = 17.9 Hz, 1H), 3.63 (d, J = 17.9 Hz, 1H), 2.39 (dt, J = 16.7, 7.3 Hz, 1H), 2.28 (dt, J = 16.9, 7.2 Hz, 1H), 1.44-1.35 (m, 2H), 0.73 (t, J = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.0, 160.6, 142.0, 140.7, 137.8, 135.0, 132.3, 129.3, 129.0, 128.2, 126.0, 124.6, 123.5, 122.7, 121.9, 120.1, 110.7, 108.6, 68.8, 47.2, 45.1, 16.9, 13.5;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{23}N_2O_2$ 383.1755; Found 383.1759.

8-methyl-12-(2-oxopentyl)-12-phenyl-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3b)



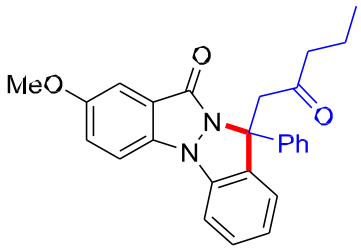
Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white semisolid in 76% yield (60.2 mg);

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68-7.57 (m, 3H), 7.45-7.39 (m, 2H), 7.38-7.25 (m, 6H), 7.05-7.01 (m, 1H), 4.57 (d, J = 17.9 Hz, 1H), 3.60 (d, J = 17.9 Hz, 1H), 2.43-2.33 (m, 4H), 2.30-2.21 (m, 1H), 1.45-1.33 (m, 2H), 0.72 (t, J = 7.1 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 205.9, 160.8, 142.2, 139.5, 138.2, 134.9, 133.8, 131.8, 129.2, 129.0, 128.2, 126.0, 124.1, 123.4, 122.5, 120.3, 110.6, 108.5, 68.9, 47.3, 45.1, 21.2, 17.0, 13.6;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}N_2O_2$ 397.1911; Found 397.1911.

8-methoxy-12-(2-oxopentyl)-12-phenyl-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3c)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 3/1) as a white semisolid in 90% yield (74.2 mg);

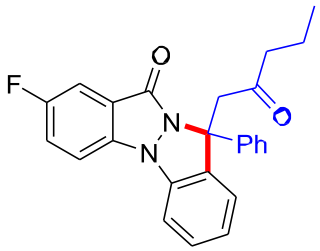
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, J = 7.5 Hz, 2H), 7.46 (d, J = 8.9 Hz, 1H), 7.39-7.33 (m, 3H), 7.32-7.24 (m, 5H), 7.06-7.03 (m, 1H), 4.59 (d, J = 17.9 Hz, 1H), 3.84 (s, 3H), 3.60 (d, J =

17.9 Hz, 1H), 2.39 (dt, *J* = 16.7, 7.3 Hz, 1H), 2.28 (dt, *J* = 16.8, 7.3 Hz, 1H), 1.45-1.36 (m, 2H), 0.73 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 205.9, 161.0, 155.7, 142.2, 138.4, 136.5, 134.8, 129.2, 129.0, 128.2, 126.0, 123.4, 122.9, 122.4, 120.5, 112.2, 108.3, 105.1, 68.9, 56.0, 47.3, 45.1, 17.0, 13.6;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}N_2O_3$ 413.1860; Found 413.1857.

8-fluoro-12-(2-oxopentyl)-12-phenyl-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3d)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white solid in 63% yield (50.4 mg);

M.p. = 142-143 ºC;

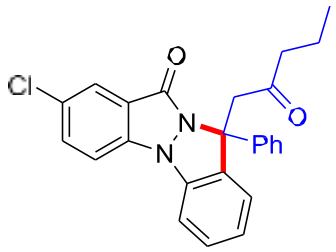
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7.6 Hz, 2H), 7.54-7.49 (m, 2H), 7.40-7.34 (m, 4H), 7.33-7.27 (m, 3H), 7.10-7.07 (m, 1H), 4.59 (d, *J* = 18.0 Hz, 1H), 3.60 (d, *J* = 18.0 Hz, 1H), 2.39 (dt, *J* = 16.7, 7.3 Hz, 1H), 2.27 (dt, *J* = 16.9, 7.2 Hz, 1H), 1.44-1.35 (m, 2H), 0.74 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.0, 160.2 (d, *J* = 4.0 Hz), 158.5 (d, *J* = 241.7 Hz), 141.8, 137.9, 137.8, 134.8, 129.3, 129.1, 128.3, 125.9, 123.5, 122.9, 120.9 (d, *J* = 26.2 Hz), 120.8 (d, *J* = 8.6 Hz), 112.1 (d, *J* = 8.3 Hz), 110.1 (d, *J* = 24.1 Hz), 108.4, 69.1, 47.1, 45.1, 16.9, 13.5;

^{19}F NMR (471 MHz, $CDCl_3$): δ -120.3 (s, 1F);

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}FN_2O_2$ 401.1660; Found 401.1659.

8-chloro-12-(2-oxopentyl)-12-phenyl-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3e)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white solid in 82% yield (68.3 mg);

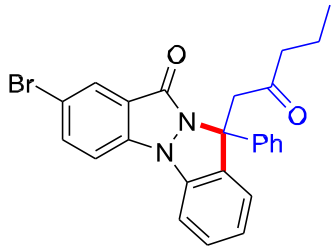
M.p. = 144-145 ºC;

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (s, 1H), 7.61 (d, J = 7.9 Hz, 2H), 7.54 (d, J = 8.7 Hz, 1H), 7.47 (d, J = 8.7 Hz, 1H), 7.38-7.35 (m, 3H), 7.33-7.26 (m, 3H), 7.10-7.07 (m, J = 7.5 Hz, 1H), 4.58 (d, J = 18.0 Hz, 1H), 3.60 (d, J = 18.0 Hz, 1H), 2.43-2.35 (m, 1H), 2.30-2.23 (m, 1H), 1.44-1.36 (m, 2H), 0.74 (t, J = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.0, 159.5, 141.7, 139.0, 137.5, 134.9, 132.7, 129.4, 129.1, 128.3, 127.4, 125.9, 124.2, 123.4, 123.0, 121.1, 111.9, 108.6, 69.0, 47.0, 45.1, 16.9, 13.5;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}ClN_2O_2$ 417.1365; Found 417.1367.

8-bromo-12-(2-oxopentyl)-12-phenyl-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3f)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white semisolid in 87% yield (80.1 mg);

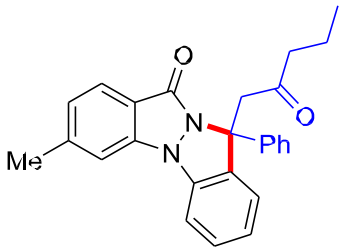
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, J = 1.6 Hz, 1H), 7.68 (dd, J = 8.7, 1.8 Hz, 1H), 7.60 (d, J = 7.6 Hz, 2H), 7.42 (d, J = 8.7 Hz, 1H), 7.39-7.35 (m, 3H), 7.32-7.27 (m, 3H), 7.11-7.08 (m, 1H),

4.57 (d, *J* = 18.0 Hz, 1H), 3.60 (d, *J* = 18.0 Hz, 1H), 2.38 (dt, *J* = 16.6, 7.3 Hz, 1H), 2.26 (dt, *J* = 16.8, 7.3 Hz, 1H), 1.40 (dq, *J* = 14.8, 7.5 Hz, 2H), 0.74 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.0, 159.3, 141.7, 139.2, 137.4, 135.2, 135.0, 129.4, 129.1, 128.4, 127.4, 125.9, 123.5, 123.1, 121.6, 114.6, 112.2, 108.6, 69.0, 47.1, 45.1, 17.0, 13.6;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}BrN_2O_2$ 461.0860; Found 461.0865.

7-methyl-12-(2-oxopentyl)-12-phenyl-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3g)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white solid in 66% yield (52.3 mg);

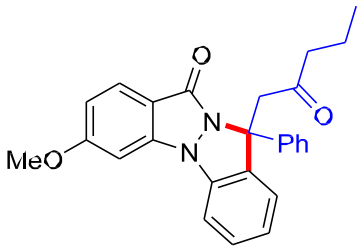
M.p. = 155-156 ºC;

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.65-7.60 (m, 2H), 7.38-7.27 (m, 7H), 7.09-7.03 (m, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 4.57 (d, *J* = 17.9 Hz, 1H), 3.61 (d, *J* = 17.9 Hz, 1H), 2.52 (s, 3H), 2.38 (dt, *J* = 16.9, 7.3 Hz, 1H), 2.27 (dt, *J* = 16.9, 7.2 Hz, 1H), 1.43-1.34 (m, 2H), 0.72 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.0, 160.8, 143.4, 142.1, 141.1, 137.9, 135.0, 129.2, 129.0, 128.2, 125.9, 124.2, 123.7, 123.4, 122.6, 117.7, 110.7, 108.6, 68.7, 47.3, 45.1, 22.5, 16.9, 13.5;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}N_2O_2$ 397.1911; Found 397.1909.

7-methoxy-12-(2-oxopentyl)-12-phenyl-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3h)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 3/1) as a white solid in 73% yield (60.2 mg);

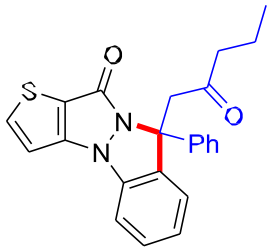
M.p. = 162-163 °C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, J = 8.7 Hz, 1H), 7.64-7.60 (m, 2H), 7.38-7.35 (m, 3H), 7.32-7.27 (m, 3H), 7.08-7.05 (m, 1H), 6.92 (d, J = 2.0 Hz, 1H), 6.78 (dd, J = 8.7, 2.0 Hz, 1H), 4.57 (d, J = 17.9 Hz, 1H), 3.94 (s, 3H), 3.59 (d, J = 17.9 Hz, 1H), 2.38 (dt, J = 16.9, 7.3 Hz, 1H), 2.27 (dt, J = 16.9, 7.2 Hz, 1H), 1.42-1.35 (m, 2H), 0.72 (t, J = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.1, 163.8, 160.9, 142.5, 142.2, 137.7, 135.2, 129.2, 129.0, 128.1, 125.9, 125.7, 123.5, 122.8, 113.3, 111.2, 108.6, 94.1, 68.7, 55.9, 47.3, 45.1, 16.9, 13.6;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}N_2O_3$ 413.1860; Found 413.1860.

9-(2-oxopentyl)-9-phenyl-9*H*,11*H*-thieno[2',3':4,5]pyrazolo[1,2-*a*]indazol-11-one (3i)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white semisolid in 57% yield (44.3 mg);

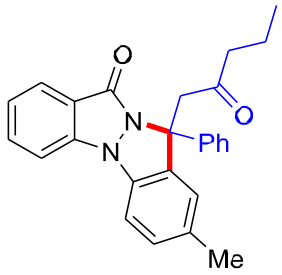
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, J = 5.2 Hz, 1H), 7.62 (d, J = 7.5 Hz, 2H), 7.39-7.27 (m, 5H), 7.15 (d, J = 7.9 Hz, 1H), 7.12 (d, J = 5.2 Hz, 1H), 7.07-7.04 (m, 1H), 4.56 (d, J = 17.9 Hz,

1H), 3.59 (d, *J* = 17.9 Hz, 1H), 2.41 (dt, *J* = 16.8, 7.3 Hz, 1H), 2.28 (dt, *J* = 16.9, 7.2 Hz, 1H), 1.46-1.36 (m, 2H), 0.75 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.0, 158.5, 148.2, 142.0, 137.4, 137.0, 135.2, 129.2, 129.0, 128.2, 125.9, 123.5, 123.0, 114.6, 111.0, 108.3, 69.7, 47.2, 45.0, 16.9, 13.5;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{21}N_2O_2S$ 389.1319; Found 389.1319.

2-methyl-12-(2-oxopentyl)-12-phenyl-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3j)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white solid in 74% yield (58.7 mg);

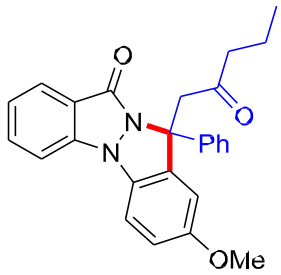
M.p. = 196-197 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.8 Hz, 1H), 7.63-7.57 (m, 3H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.39-7.34 (m, 2H), 7.31-7.27 (m, 1H), 7.20 (d, *J* = 8.1 Hz, 1H), 7.20-7.14 (m, 2H), 7.11 (s, 1H), 4.57 (d, *J* = 17.8 Hz, 1H), 3.62 (d, *J* = 17.8 Hz, 1H), 2.42-2.26 (m, 5H), 1.44-1.36 (m, 2H), 0.73 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.0, 160.5, 142.1, 140.7, 135.6, 135.3, 132.5, 132.2, 129.8, 129.0, 128.2, 125.9, 124.6, 124.1, 121.6, 119.8, 110.6, 108.3, 68.8, 47.2, 45.2, 21.3, 16.9, 13.5;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}N_2O_2$ 397.1911; Found 397.1914.

2-methoxy-12-(2-oxopentyl)-12-phenyl-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3k)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 3/1) as a white solid in 71% yield (58.6 mg);

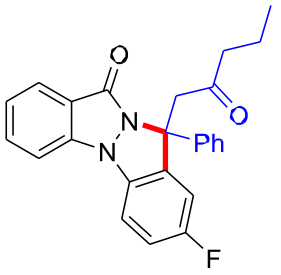
M.p. = 166-167 ºC;

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, J = 7.9 Hz, 1H), 7.63-7.55 (m, 3H), 7.48 (d, J = 8.3 Hz, 1H), 7.38-7.33 (m, 2H), 7.31-7.27 (m, 1H), 7.24 (d, J = 8.5 Hz, 1H), 7.18-7.13 (m, 1H), 6.92-6.86 (m, 2H), 4.58 (d, J = 17.9 Hz, 1H), 3.78 (s, 3H), 3.62 (d, J = 17.9 Hz, 1H), 2.40 (dt, J = 16.9, 7.3 Hz, 1H), 2.29 (dt, J = 16.9, 7.2 Hz, 1H), 1.45-1.36 (m, 2H), 0.74 (t, J = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 205.8, 160.7, 155.9, 141.8, 141.0, 136.6, 132.2, 132.0, 129.0, 128.2, 125.9, 124.6, 121.5, 119.6, 113.4, 110.7, 110.4, 109.0, 68.9, 55.9, 47.0, 45.0, 16.9, 13.5;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}N_2O_3$ 413.1860; Found 413.1859.

2-fluoro-12-(2-oxopentyl)-12-phenyl-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3l)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white solid in 52% yield (41.7 mg);

M.p. = 195-196 ºC;

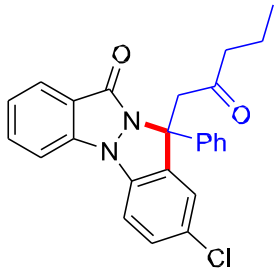
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, J = 7.9 Hz, 1H), 7.64-7.57 (m, 3H), 7.49 (d, J = 8.3 Hz, 1H), 7.40-7.36 (m, 2H), 7.33-7.28 (m, 1H), 7.26 (dd, J = 8.2, 4.3 Hz, 1H), 7.22-7.18 (m, 1H), 7.10-7.03 (m, 2H), 4.60 (d, J = 18.1 Hz, 1H), 3.59 (d, J = 18.1 Hz, 1H), 2.43 (dt, J = 16.9, 7.3 Hz, 1H), 2.30 (dt, J = 17.0, 7.2 Hz, 1H), 1.40 (dt, J = 14.7, 7.3 Hz, 2H), 0.75 (t, J = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 205.9, 161.0, 158.9 (d, J = 242.2 Hz), 141.5, 141.3, 137.0, 136.9, 134.4 (d, J = 1.8 Hz), 132.5, 129.2, 128.4, 125.8, 124.7, 122.2, 119.9, 115.9 (d, J = 24.1 Hz), 111.3 (d, J = 25.7 Hz), 109.2 (d, J = 8.5 Hz), 68.8 (d, J = 2.1 Hz), 47.1, 44.9, 16.9, 13.5;

^{19}F NMR (471 MHz, $CDCl_3$): δ -119.7 (s, 1F);

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}FN_2O_2$ 401.1660; Found 401.1659.

2-chloro-12-(2-oxopentyl)-12-phenyl-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3m)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white solid in 63% yield (52.5 mg);

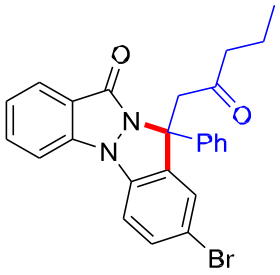
M.p. = 207-208 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, J = 7.9 Hz, 1H), 7.63-7.56 (m, 3H), 7.49 (d, J = 8.3 Hz, 1H), 7.41-7.36 (m, 2H), 7.35-7.28 (m, 2H), 7.28-7.26 (m, 1H), 7.25-7.20 (m, 2H), 4.59 (d, J = 18.1 Hz, 1H), 3.58 (d, J = 18.1 Hz, 1H), 2.43 (dt, J = 16.9, 7.3 Hz, 1H), 2.30 (dt, J = 16.9, 7.2 Hz, 1H), 1.46-1.37 (m, 2H), 0.76 (t, J = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 205.9, 160.7, 141.4, 140.8, 137.1, 136.5, 132.5, 129.2, 129.2, 128.4, 127.8, 125.7, 124.7, 123.6, 122.3, 120.0, 110.7, 109.3, 68.7, 47.1, 44.9, 16.9, 13.5;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}ClN_2O_2$ 417.1365; Found 417.1365.

2-bromo-12-(2-oxopentyl)-12-phenyl-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3n)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white solid in 49% yield (45.1 mg);

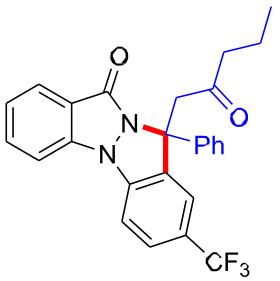
M.p. = 211-212 °C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, J = 7.9 Hz, 1H), 7.64-7.59 (m, 1H), 7.59-7.56 (m, 2H), 7.49 (d, J = 8.3 Hz, 1H), 7.46 (dd, J = 8.4, 1.8 Hz, 1H), 7.41-7.36 (m, 3H), 7.33-7.30 (m, 1H), 7.23-7.18 (m, 2H), 4.59 (d, J = 18.1 Hz, 1H), 3.57 (d, J = 18.1 Hz, 1H), 2.43 (dt, J = 16.9, 7.4 Hz, 1H), 2.30 (dt, J = 17.0, 7.2 Hz, 1H), 1.45-1.38 (m, 2H), 0.76 (t, J = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 205.9, 160.6, 141.4, 140.8, 137.4, 137.0, 132.6, 132.1, 129.2, 128.5, 126.4, 125.7, 124.7, 122.4, 120.1, 115.0, 110.8, 109.8, 68.6, 47.2, 45.0, 16.9, 13.5;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}BrN_2O_2$ 461.0860; Found 461.0867.

12-(2-oxopentyl)-12-phenyl-2-(trifluoromethyl)-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3o)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white solid in 67% yield (60.4 mg);

M.p. = 214-215 °C;

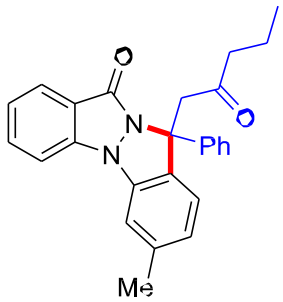
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, J = 7.9 Hz, 1H), 7.67-7.62 (m, 2H), 7.60-7.54 (m, 3H), 7.50 (s, 1H), 7.42-7.36 (m, 3H), 7.34-7.30 (m, 1H), 7.28-7.24 (m, 1H), 4.63 (d, J = 18.2 Hz, 1H), 3.62 (d, J = 18.2 Hz, 1H), 2.42 (dt, J = 16.7, 7.3 Hz, 1H), 2.31 (dt, J = 16.9, 7.2 Hz, 1H), 1.44-1.37 (m, 2H), 0.74 (t, J = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.1, 160.7, 141.3, 140.4, 140.2, 136.0, 132.7, 129.3, 128.6, 127.2 (q, J = 3.8 Hz), 125.7, 124.8, 124.7 (q, J = 33.1 Hz), 124.2 (q, J = 272.3 Hz), 122.9, 120.4, 120.3 (d, J = 3.7 Hz), 110.9, 108.2, 68.7, 47.3, 44.9, 17.0, 13.5;

^{19}F NMR (471 MHz, $CDCl_3$): δ -61.3 (s, 3F);

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{22}F_3N_2O_2$ 451.1628; Found 451.1631.

3-methyl-12-(2-oxopentyl)-12-phenyl-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3q)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white solid in 69% yield (54.7 mg);

M.p. = 172-173 °C;

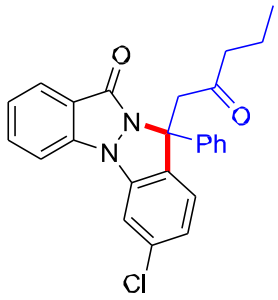
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, J = 7.9 Hz, 1H), 7.62 (d, J = 7.4 Hz, 2H), 7.59 (d, J = 7.2 Hz, 1H), 7.54 (d, J = 8.3 Hz, 1H), 7.37-7.33 (m, 2H), 7.29-7.25 (m, 1H), 7.21-7.16 (m, 2H), 7.15

(s, 1H), 6.87 (d, *J* = 7.7 Hz, 1H), 4.55 (d, *J* = 17.9 Hz, 1H), 3.60 (d, *J* = 17.9 Hz, 1H), 2.42-2.34 (m, 4H), 2.27 (dt, *J* = 16.9, 7.2 Hz, 1H), 1.39 (dt, *J* = 14.7, 7.3 Hz, 2H), 0.72 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.1, 160.4, 142.1, 140.5, 139.6, 137.8, 132.24, 132.18, 129.0, 128.1, 125.9, 124.6, 123.5, 123.2, 121.8, 120.0, 110.7, 109.3, 68.7, 47.2, 45.1, 21.8, 16.9, 13.5;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}N_2O_2$ 397.1911; Found 397.1910.

3-chloro-12-(2-oxopentyl)-12-phenyl-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3r)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white solid in 75% yield (62.5 mg);

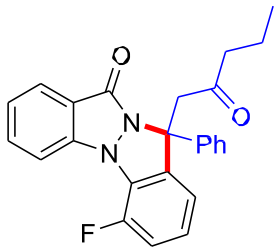
M.p. = 179-180 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.8 Hz, 1H), 7.64-7.57 (m, 3H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.38-7.35 (m, 2H), 7.32-7.28 (m, 2H), 7.24-7.20 (m, 2H), 7.03 (dd, *J* = 8.1, 1.7 Hz, 1H), 4.58 (d, *J* = 18.1 Hz, 1H), 3.58 (d, *J* = 18.1 Hz, 1H), 2.41 (dt, *J* = 16.9, 7.3 Hz, 1H), 2.28 (dt, *J* = 16.9, 7.2 Hz, 1H), 1.41 (dt, *J* = 14.7, 7.2 Hz, 2H), 0.75 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.0, 160.7, 141.6, 140.6, 138.7, 135.1, 133.7, 132.6, 129.1, 128.4, 125.8, 124.7, 124.1, 122.6, 122.5, 120.2, 110.9, 109.0, 68.6, 47.2, 45.0, 16.9, 13.5;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}ClN_2O_2$ 417.1365; Found 417.1363.

4-fluoro-12-(2-oxopentyl)-12-phenyl-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3s)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white semisolid in 66% yield (52.9 mg);

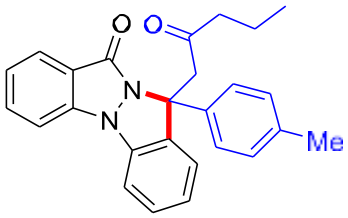
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86-7.80 (m, 2H), 7.61-7.55 (m, 3H), 7.39-7.34 (m, 2H), 7.31-7.28 (m, 1H), 7.21-7.18 (m, 1H), 7.14-7.10 (m, 1H), 7.08 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.02-6.98 (m, 1H), 4.65 (d, *J* = 18.0 Hz, 1H), 3.60 (d, *J* = 18.0 Hz, 1H), 2.43 (dt, *J* = 16.9, 7.3 Hz, 1H), 2.30 (dt, *J* = 17.0, 7.2 Hz, 1H), 1.45-1.37 (m, 2H), 0.75 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.0, 160.6, 147.0 (d, *J* = 245.0 Hz), 141.7, 141.1, 138.7 (d, *J* = 2.8 Hz), 132.6 (d, *J* = 2.4 Hz), 129.1, 128.4, 125.8, 125.5 (d, *J* = 13.0 Hz), 124.1, 123.8 (d, *J* = 6.4 Hz), 122.3, 119.9, 119.0 (d, *J* = 3.2 Hz), 116.8 (d, *J* = 19.5 Hz), 113.0 (d, *J* = 16.4 Hz), 68.5 (d, *J* = 1.2 Hz), 47.0, 45.0, 16.9, 13.5;

^{19}F NMR (471 MHz, $CDCl_3$): δ -126.0 (s, 1F);

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}FN_2O_2$ 401.1660; Found 401.1660.

12-(2-oxopentyl)-12-(*p*-tolyl)-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3t)



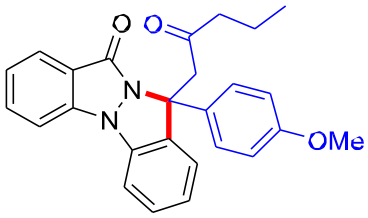
Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white semisolid in 73% yield (57.9 mg);

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, J = 7.9 Hz, 1H), 7.62-7.57 (m, 1H), 7.53 (d, J = 8.3 Hz, 1H), 7.49 (d, J = 8.2 Hz, 2H), 7.38-7.35 (m, 1H), 7.33-7.30 (m, 2H), 7.20-7.16 (m, 3H), 7.08-7.04 (m, 1H), 4.57 (d, J = 17.8 Hz, 1H), 3.62 (d, J = 17.8 Hz, 1H), 2.38 (dt, J = 16.7, 7.3 Hz, 1H), 2.33-2.24 (m, 4H), 1.43-1.35 (m, 2H), 0.73 (t, J = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.0, 160.3, 140.5, 139.0, 138.0, 137.6, 135.2, 132.3, 129.6, 129.2, 125.9, 124.6, 123.4, 122.7, 121.8, 120.0, 110.7, 108.5, 68.7, 47.2, 45.1, 21.1, 16.9, 13.5;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}N_2O_2$ 397.1911; Found 397.1912.

12-(4-methoxyphenyl)-12-(2-oxopentyl)-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3u)



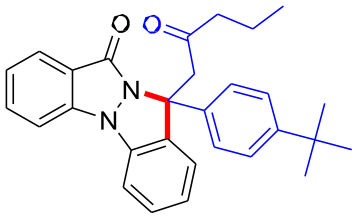
Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 3/1) as a white semisolid in 76% yield (62.7 mg);

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, J = 7.9 Hz, 1H), 7.61-7.58 (m, 1H), 7.56-7.50 (m, 3H), 7.37 (dd, J = 11.3, 3.9 Hz, 1H), 7.33 (d, J = 7.7 Hz, 1H), 7.29 (d, J = 7.6 Hz, 1H), 7.20-7.17 (m, 1H), 7.08-7.05 (m, 1H), 6.90-6.85 (m, 2H), 4.56 (d, J = 17.8 Hz, 1H), 3.77 (s, 3H), 3.61 (d, J = 17.8 Hz, 1H), 2.38 (dt, J = 16.8, 7.3 Hz, 1H), 2.27 (dt, J = 16.9, 7.2 Hz, 1H), 1.39 (dt, J = 14.7, 7.4 Hz, 2H), 0.72 (t, J = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.1, 160.2, 159.4, 140.4, 137.7, 135.1, 134.1, 132.3, 129.2, 127.4, 124.6, 123.5, 122.7, 121.8, 120.0, 114.2, 110.6, 108.5, 68.4, 55.4, 47.3, 45.1, 16.9, 13.5;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}N_2O_3$ 413.1860; Found 413.1858.

12-(4-(*tert*-butyl)phenyl)-12-(2-oxopentyl)-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3v)



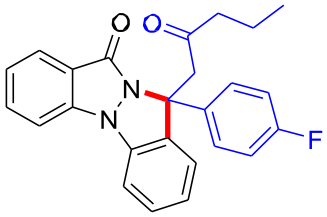
Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white semisolid in 75% yield (65.8 mg);

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, J = 7.7 Hz, 1H), 7.62-7.59 (m, 1H), 7.55-7.53 (m, 3H), 7.41-7.30 (m, 5H), 7.20-7.17 (m, 1H), 7.08-7.05 (m, 1H), 4.60 (d, J = 17.9 Hz, 1H), 3.61 (d, J = 17.9 Hz, 1H), 2.43-2.34 (m, 1H), 2.32-2.23 (m, 1H), 1.43-1.36 (m, 2H), 1.28 (s, 9H), 0.72 (t, J = 7.3 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.1, 160.3, 151.1, 140.4, 138.9, 137. 7, 135.2, 132.2, 129.2, 125.9, 125.6, 124.6, 123.4, 122.7, 121.8, 120.1, 110.7, 108.5, 68.6, 47.2, 45.1, 34.6, 31.3, 16.9, 13.5;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{31}N_2O_2$ 439.2381; Found 439.2378.

12-(4-fluorophenyl)-12-(2-oxopentyl)-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3w)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white semisolid in 72% yield (57.7 mg);

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, J = 7.9 Hz, 1H), 7.64-7.58 (m, 3H), 7.53 (d, J = 8.3 Hz, 1H), 7.40-7.37 (m, 1H), 7.34 (d, J = 7.8 Hz, 1H), 7.30 (d, J = 7.6 Hz, 1H), 7.21-7.18 (m, 1H), 7.10-

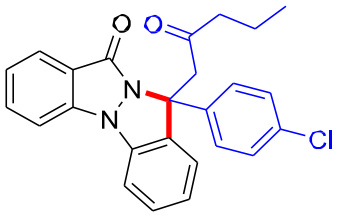
7.01 (m, 3H), 4.53 (d, *J* = 17.9 Hz, 1H), 3.62 (d, *J* = 17.9 Hz, 1H), 2.38 (dt, *J* = 16.7, 7.3 Hz, 1H), 2.27 (dt, *J* = 16.9, 7.2 Hz, 1H), 1.43-1.35 (m, 2H), 0.72 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 205.8, 162.4 (d, *J* = 247.7 Hz), 160.5, 140.7, 137.9 (d, *J* = 3.2 Hz), 137.8, 134.6, 132.4, 129.5, 128.1 (d, *J* = 8.3 Hz), 124.6, 123.5, 122.8, 122.0, 119.9, 115.8 (d, *J* = 21.6 Hz), 110.7, 108.6, 68.3, 47.3, 45.1, 16.9, 13.5;

^{19}F NMR (471 MHz, $CDCl_3$): δ -114.1 (s, 1F);

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}FN_2O_2$ 401.1660; Found 401.1657.

12-(4-chlorophenyl)-12-(2-oxopentyl)-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3x)



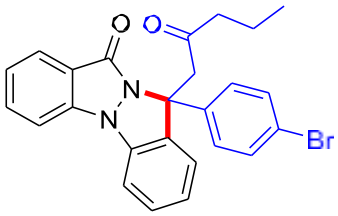
Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white semisolid in 52% yield (43.3 mg);

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.8 Hz, 1H), 7.63-7.60 (m, 1H), 7.58-7.53 (m, 3H), 7.40-7.37 (m, 1H), 7.35-7.29 (m, 4H), 7.22-7.19 (m, 1H), 7.09-7.06 (m, 1H), 4.51 (d, *J* = 17.9 Hz, 1H), 3.62 (d, *J* = 17.9 Hz, 1H), 2.42-2.34 (m, 1H), 2.31-2.23 (m, 1H), 1.43-1.35 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 205.7, 160.6, 140.8, 140.6, 137.8, 134.4, 134.2, 132.5, 129.5, 129.1, 127.6, 124.6, 123.5, 122.8, 122.1, 119.9, 110.8, 108.7, 68.4, 47.1, 45.1, 16.9, 13.5;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}ClN_2O_2$ 417.1365; Found 417.1364.

12-(4-bromophenyl)-12-(2-oxopentyl)-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3y)



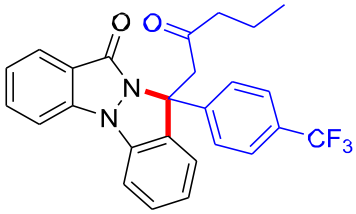
Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white semisolid in 63% yield (58 mg);

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, J = 7.9 Hz, 1H), 7.63-7.60 (m, 1H), 7.53 (d, J = 8.3 Hz, 1H), 7.52-7.46 (m, 4H), 7.40-7.37 (m, 1H), 7.34 (d, J = 7.7 Hz, 1H), 7.29 (d, J = 7.5 Hz, 1H), 7.22-7.19 (m, 1H), 7.09-7.06 (m, 1H), 4.51 (d, J = 17.9 Hz, 1H), 3.62 (d, J = 17.9 Hz, 1H), 2.38 (dt, J = 16.9, 7.3 Hz, 1H), 2.27 (dt, J = 16.9, 7.2 Hz, 1H), 1.42-1.35(m, 2H), 0.72 (t, J = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 205.7, 160.6, 141.1, 140.8, 137.8, 134.4, 132.5, 132.1, 129.5, 127.9, 124.6, 123.5, 122.8, 122.4, 122.1, 119.9, 110.8, 108.7, 68.4, 47.0, 45.1, 16.9, 13.5;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}BrN_2O_2$ 461.0860; Found 461.0860.

12-(2-oxopentyl)-12-(4-(trifluoromethyl)phenyl)-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3z)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white semisolid in 53% yield (47.8 mg);

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, J = 7.9 Hz, 1H), 7.77 (d, J = 8.3 Hz, 2H), 7.65-7.61 (m, 3H), 7.55 (d, J = 8.3 Hz, 1H), 7.42-7.39 (m, 1H), 7.36-7.33 (m, 2H), 7.23-7.20 (m, 1H), 7.11-7.08

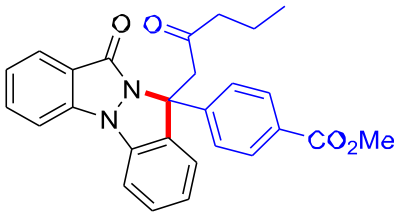
(m, 1H), 4.53 (d, *J* = 17.9 Hz, 1H), 3.67 (d, *J* = 17.9 Hz, 1H), 2.40 (dt, *J* = 16.8, 7.3 Hz, 1H), 2.32-2.25 (m, 1H), 1.44-1.36 (m, 2H), 0.73 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 205.6, 160.8, 145.8, 141.0, 137.9, 134.1, 132.6, 130.4 (q, *J* = 32.6 Hz), 129.7, 126.6, 126.0 (q, *J* = 3.7 Hz), 124.7, 124.0 (q, *J* = 272.7 Hz), 123.5, 122.9, 122.2, 119.9, 110.8, 108.8, 68.5, 46.9, 45.1, 16.9, 13.5;

^{19}F NMR (471 MHz, $CDCl_3$): δ -62.7 (s, 3F);

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{22}F_3N_2O_2$ 451.1628; Found 451.1630.

methyl 4-(12-oxo-10-(2-oxopentyl)-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-yl)benzoate (3aa)



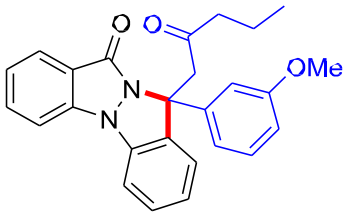
Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white semisolid in 68% yield (59.9 mg);

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 2H), 7.63-7.60 (m, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.40-7.37 (m, 1H), 7.36-7.31 (m, 2H), 7.22-7.19 (m, 1H), 7.09-7.06 (m, 1H), 4.54 (d, *J* = 17.9 Hz, 1H), 3.89 (s, 3H), 3.65 (d, *J* = 17.9 Hz, 1H), 2.44-2.35 (m, 1H), 2.32-2.24 (m, 1H), 1.43-1.35 (m, 2H), 0.72 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 205.6, 166.6, 160.8, 146.7, 141.0, 137.8, 134.4, 132.5, 130.3, 129.9, 129.6, 126.1, 124.6, 123.4, 122.9, 122.1, 119.9, 110.8, 108.7, 68.6, 52.3, 46.9, 45.0, 16.9, 13.5;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{25}N_2O_4$ 441.1809; Found 441.1809.

12-(3-methoxyphenyl)-12-(2-oxopentyl)-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3ab)



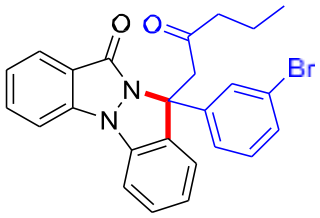
Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 3/1) as a white semisolid in 74% yield (61.1 mg);

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, J = 7.9 Hz, 1H), 7.62-7.59 (m, 1H), 7.53 (d, J = 8.3 Hz, 1H), 7.38-7.27 (m, 4H), 7.23-7.17 (m, 3H), 7.08-7.05 (m, 1H), 6.83 (dd, J = 8.1, 1.7 Hz, 1H), 4.59 (d, J = 17.9 Hz, 1H), 3.78 (s, 3H), 3.60 (d, J = 18.0 Hz, 1H), 2.39 (dt, J = 16.7, 7.3 Hz, 1H), 2.27 (dt, J = 16.9, 7.2 Hz, 1H), 1.42-1.34 (m, 2H), 0.72 (t, J = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 205.9, 160.5, 160.0, 143.6, 140.7, 137.7, 134.8, 132.3, 130.0, 129.3, 124.6, 123.4, 122.7, 121.9, 119.9, 118.1, 113.1, 112.4, 110.7, 108.6, 68.7, 55.4, 47.1, 45.0, 16.9, 13.5;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}N_2O_3$ 413.1860; Found 413.1860.

12-(3-bromophenyl)-12-(2-oxopentyl)-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3ac)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white semisolid in 66% yield (60.8 mg);

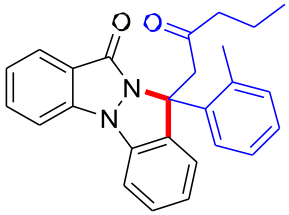
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, J = 7.9 Hz, 1H), 7.72 (s, 1H), 7.63-7.60 (m, 2H), 7.54 (d, J = 8.3 Hz, 1H), 7.42 (d, J = 7.9 Hz, 1H), 7.40-7.33 (m, 2H), 7.30 (d, J = 7.6 Hz, 1H), 7.25-7.19

(m, 2H), 7.09-7.06 (m, 1H), 4.54 (d, *J* = 18.0 Hz, 1H), 3.60 (d, *J* = 18.0 Hz, 1H), 2.42-2.35 (m, 1H), 2.31-2.24 (m, 1H), 1.43-1.33 (m, 2H), 0.72 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 205.6, 160.9, 144.3, 141.1, 137.9, 134.3, 132.5, 131.4, 130.6, 129.5, 128.9, 124.8, 124.6, 123.3, 123.1, 122.9, 122.1, 119.9, 110.9, 108.7, 68.2, 46.9, 45.0, 16.9, 13.5;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}BrN_2O_2$ 461.0860; Found 461.0859.

12-(2-oxopentyl)-12-(*o*-tolyl)-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3ad)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white solid in 71% yield (56.3 mg);

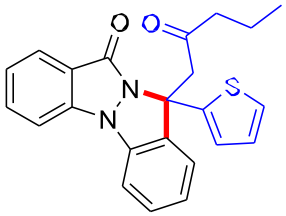
M.p. = 109-110 ºC;

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.9 Hz, 1H), 7.65-7.61 (m, 2H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.39-7.36 (m, 1H), 7.32-7.28 (m, 2H), 7.24-7.22 (m, 1H), 7.18-7.15 (m, 1H), 7.07 (d, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 7.00-6.97 (m, 1H), 4.42 (d, *J* = 15.7 Hz, 1H), 3.69 (d, *J* = 15.7 Hz, 1H), 2.35-2.28 (m, 1H), 2.27-2.19 (m, 1H), 1.77 (s, 3H), 1.37-1.30 (m, 2H), 0.65 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.4, 158.9, 138.6, 137.3, 137.3, 137.3, 134.8, 133.5, 132.4, 129.5, 128.8, 126.6, 126.3, 124.8, 123.6, 122.8, 121.4, 119.6, 110.0, 107.7, 67.6, 47.3, 46.2, 20.4, 16.9, 13.5;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}N_2O_2$ 397.1911; Found 397.1908.

12-(2-oxopentyl)-12-(thiophen-2-yl)-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3ae)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white solid in 58% yield (45.1 mg);

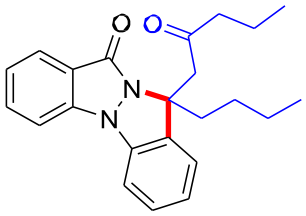
M.p. = 146-147 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, J = 7.9 Hz, 1H), 7.63-7.58 (m, 1H), 7.52 (d, J = 8.3 Hz, 1H), 7.41-7.37 (m, 1H), 7.33-7.31 (m, 2H), 7.24 (dd, J = 5.1, 1.1 Hz, 1H), 7.21 (dd, J = 3.6, 1.1 Hz, 1H), 7.18-7.15 (m, 1H), 7.08-7.05 (m, 1H), 6.96 (dd, J = 5.1, 3.7 Hz, 1H), 4.68 (d, J = 17.9 Hz, 1H), 3.64 (d, J = 17.9 Hz, 1H), 2.38 (dt, J = 16.9, 7.3 Hz, 1H), 2.27 (dt, J = 16.9, 7.2 Hz, 1H), 1.42-1.35 (m, 2H), 0.72 (t, J = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 205.6, 159.9, 146.0, 140.0, 137.2, 134.9, 132.5, 129.7, 127.3, 125.7, 125.3, 124.7, 123.2, 122.7, 121.7, 119.8, 110.4, 108.5, 65.8, 47.7, 45.1, 16.9, 13.5;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{21}N_2O_2S$ 389.1319; Found 389.1318.

12-butyl-12-(2-oxopentyl)-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3af)



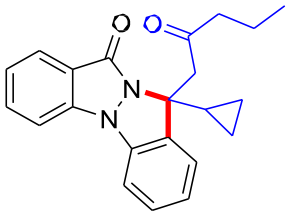
Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white semisolid in 77% yield (55.8 mg);

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, J = 7.9 Hz, 1H), 7.60-7.55 (m, 1H), 7.48 (d, J = 8.3 Hz, 1H), 7.37-7.31 (m, 1H), 7.28-7.24 (m, 1H), 7.18 (d, J = 7.5 Hz, 1H), 7.16-7.13 (m, 1H), 7.05-7.02 (m, 1H), 4.03 (d, J = 17.4 Hz, 1H), 3.23 (d, J = 17.4 Hz, 1H), 2.54 (td, J = 13.7, 3.9 Hz, 1H), 2.30-2.19 (m, 2H), 2.03-1.97 (m, 1H), 1.40-1.32 (m, 2H), 1.28-1.17 (m, 3H), 1.01-0.90 (m, 1H), 0.76 (t, J = 7.1 Hz, 3H), 0.69 (t, J = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.6, 159.2, 138.5, 136.9, 134.9, 132.0, 129.1, 124.5, 122.7, 122.3, 121.1, 119.7, 110.0, 108.1, 67.6, 47.6, 45.3, 38.8, 25.7, 22.5, 16.8, 14.0, 13.5;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{27}N_2O_2$ 363.2068; Found 363.2068.

12-cyclopropyl-12-(2-oxopentyl)-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3ag)



Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white solid in 76% yield (52.7 mg);

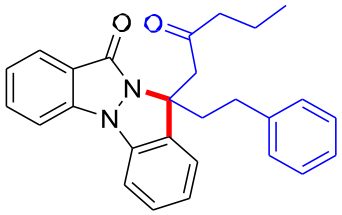
M.p. = 117-118 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, J = 7.9 Hz, 1H), 7.59-7.56 (m, 1H), 7.49 (d, J = 8.3 Hz, 1H), 7.35-7.32 (m, 1H), 7.27 (d, J = 7.9 Hz, 1H), 7.17-7.13 (m, 2H), 7.03-7.00 (m, 1H), 4.37 (d, J = 18.0 Hz, 1H), 3.34 (d, J = 18.0 Hz, 1H), 2.37-2.30 (m, 1H), 2.29-2.21 (m, 1H), 1.59-1.54 (m, 1H), 1.40-1.33 (m, 2H), 0.72-0.67 (m, 4H), 0.60-0.53 (m, 1H), 0.49-0.41 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.5, 161.1, 140.5, 137.5, 135.3, 132.2, 129.0, 124.5, 122.6, 122.1, 121.6, 119.9, 110.5, 108.4, 67.6, 46.6, 45.0, 21.0, 16.9, 13.5, 2.1, 1.2;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{23}N_2O_2$ 347.1755; Found 347.1752.

12-(2-oxopentyl)-12-phenethyl-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (3ah)



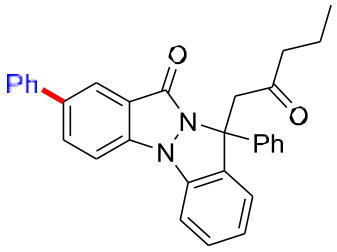
Following the general procedure, the title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white semisolid in 80% yield (65.7mg);

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, J = 7.9 Hz, 1H), 7.61-7.58 (m, 1H), 7.50 (d, J = 8.3 Hz, 1H), 7.40-7.36 (m, 1H), 7.29 (d, J = 7.9 Hz, 1H), 7.25 (d, J = 8.1 Hz, 1H), 7.19-7.15 (m, 3H), 7.11-7.03 (m, 4H), 4.04 (d, J = 17.4 Hz, 1H), 3.28 (d, J = 17.4 Hz, 1H), 2.97-2.89 (m, 1H), 2.60-2.49 (m, 1H), 2.36-2.21 (m, 4H), 1.42-1.34 (m, 2H), 0.71 (t, J = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.5, 159.5, 140.8, 138.8, 137.1, 134.5, 132.1, 129.4, 128.4, 128.4, 126.0, 124.6, 122.9, 122.5, 121.3, 119.7, 110.0, 108.3, 67.5, 47.6, 45.4, 40.7, 30.2, 16.9, 13.5;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{27}N_2O_2$ 411.2068; Found 411.2072.

12-(2-oxopentyl)-8,12-diphenyl-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (4)



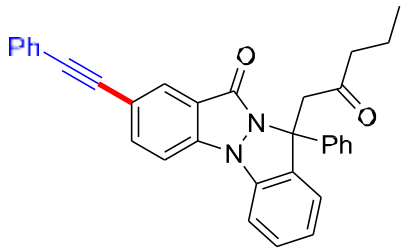
The title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white semisolid in 78% yield (71.5 mg);

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.87 (d, J = 8.5 Hz, 1H), 7.66-7.60 (m, 5H), 7.47-7.44 (m, 2H), 7.40-7.29 (m, 7H), 7.10-7.07 (m, 1H), 4.62 (d, J = 18.0 Hz, 1H), 3.64 (d, J = 18.0 Hz, 1H), 2.45-2.37 (m, 1H), 2.34-2.25 (m, 1H), 1.46-1.37 (m, 2H), 0.74 (t, J = 7.3 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.1, 160.7, 141.9, 140.5, 139.8, 137.7, 135.4, 135.0, 131.8, 129.3, 129.05, 129.01, 128.3, 127.3, 127.1, 125.9, 123.4, 122.8, 122.7, 120.6, 111.1, 108.6, 68.9, 47.2, 45.1, 16.9, 13.6;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{27}N_2O_2$ 459.2068; Found 459.2066.

12-(2-oxopentyl)-12-phenyl-8-(phenylethynyl)-10*H*,12*H*-indazolo[1,2-*a*]indazol-10-one (5)



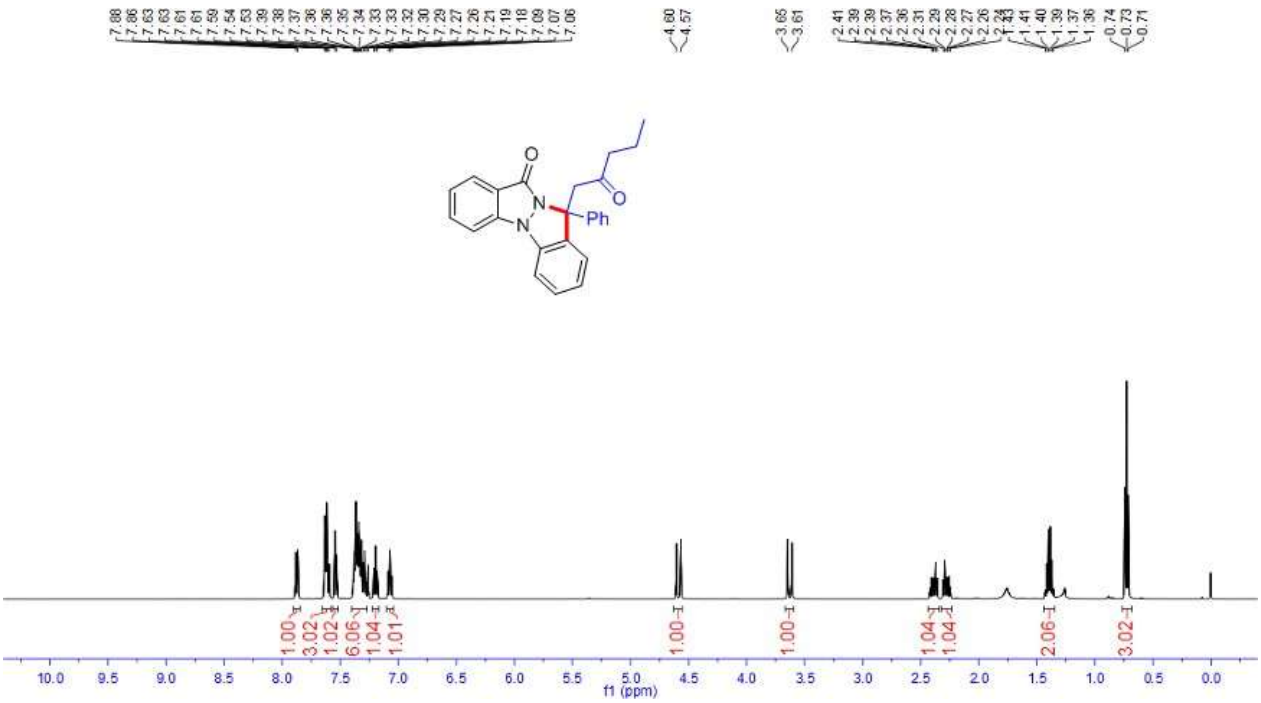
The title compound was isolated by flash chromatography (eluent: PE/EA = 4/1) as a white semisolid in 93% yield (89.7 mg);

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, J = 0.7 Hz, 1H), 7.75 (dd, J = 8.6, 1.4 Hz, 1H), 7.65-7.59 (m, 2H), 7.56-7.53 (m, 2H), 7.51 (d, J = 8.6 Hz, 1H), 7.41-7.28 (m, 9H), 7.13-7.06 (m, 1H), 4.58 (d, J = 18.0 Hz, 1H), 3.63 (d, J = 18.0 Hz, 1H), 2.40 (dt, J = 16.8, 7.3 Hz, 1H), 2.28 (dt, J = 16.9, 7.2 Hz, 1H), 1.45-1.36 (m, 2H), 0.74 (t, J = 7.4 Hz, 3H);

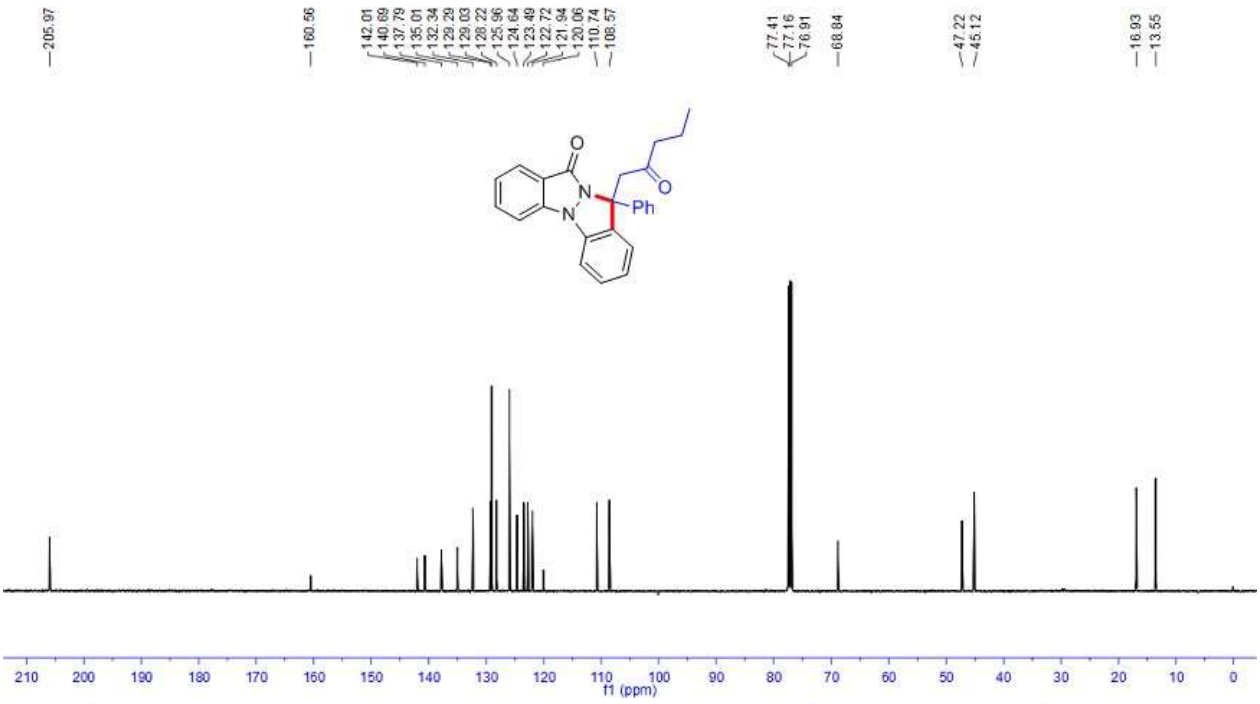
^{13}C NMR (126 MHz, $CDCl_3$): δ 206.1, 159.7, 141.7, 139.2, 137.2, 135.5, 135.1, 131.7, 129.4, 129.1, 128.5, 128.34, 128.33, 128.1, 125.9, 123.5, 123.4, 123.1, 120.1, 116.8, 110.6, 108.7, 89.2, 89.1, 68.9, 47.1, 45.1, 16.9, 13.6;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{33}H_{27}N_2O_2$ 483.2068; Found 483.2065.

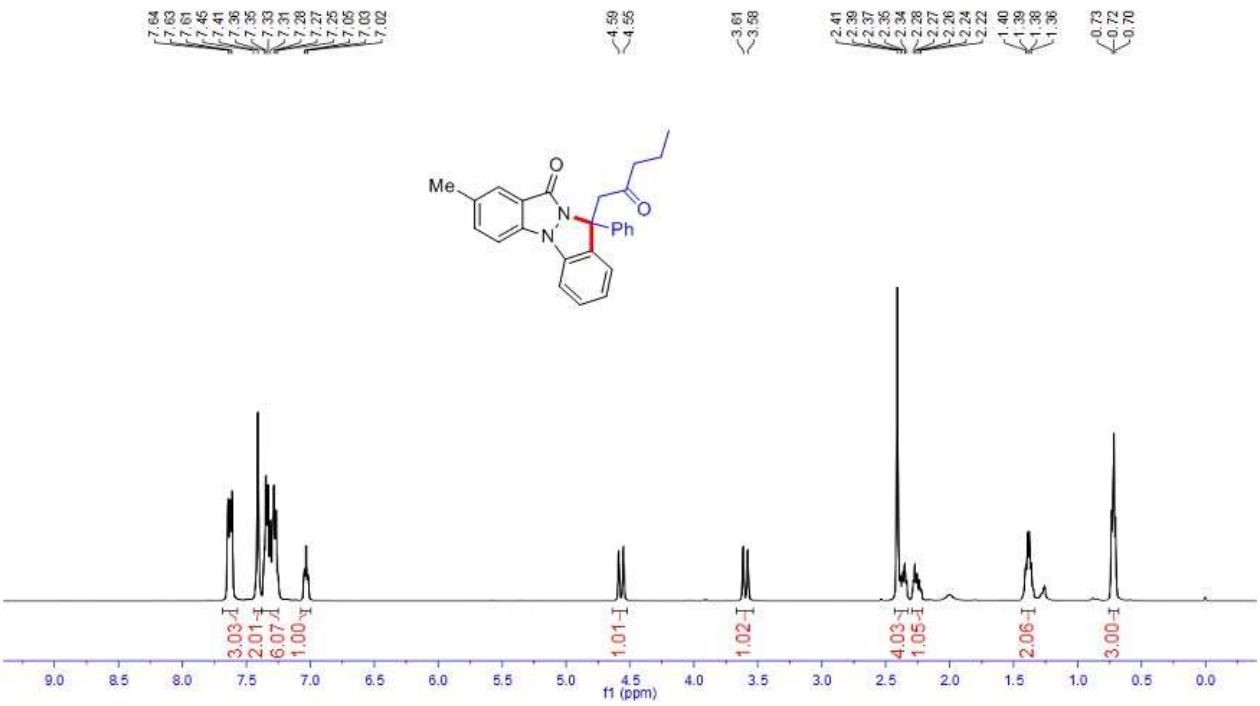
8. Copies of NMR spectra



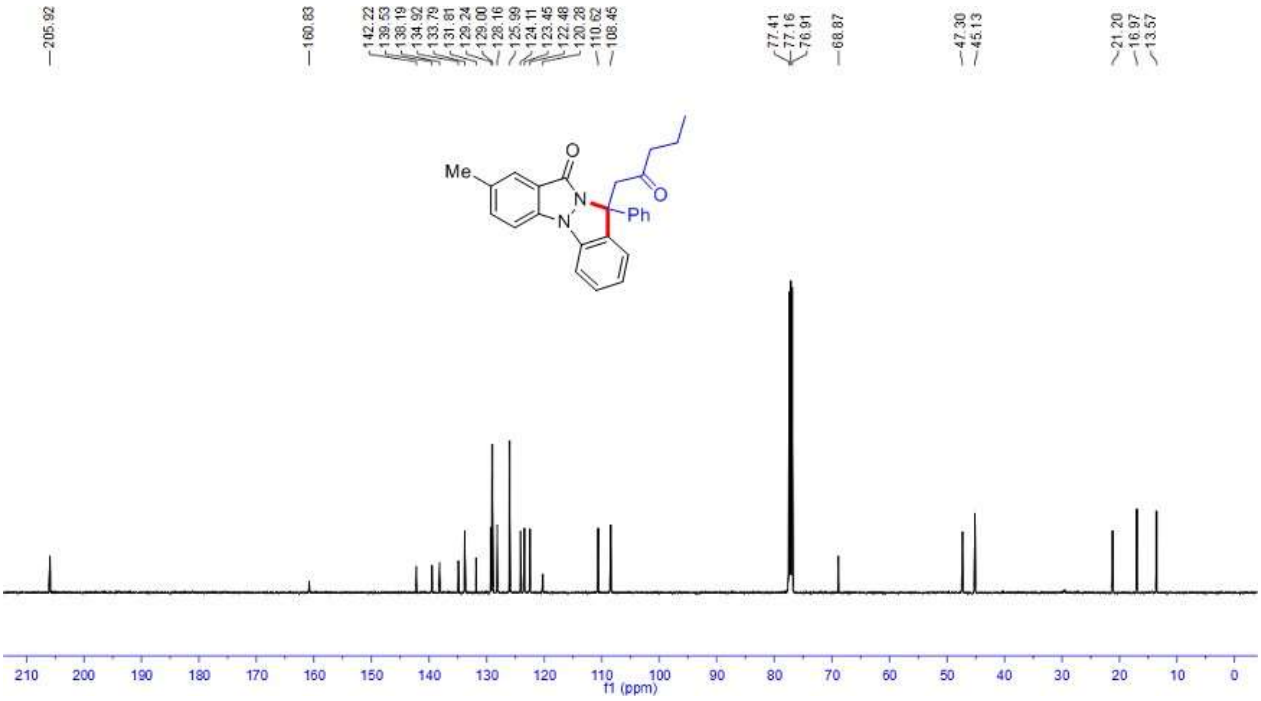
^{1}H NMR spectrum of **3a (**$CDCl_3$, 500 MHz**)**



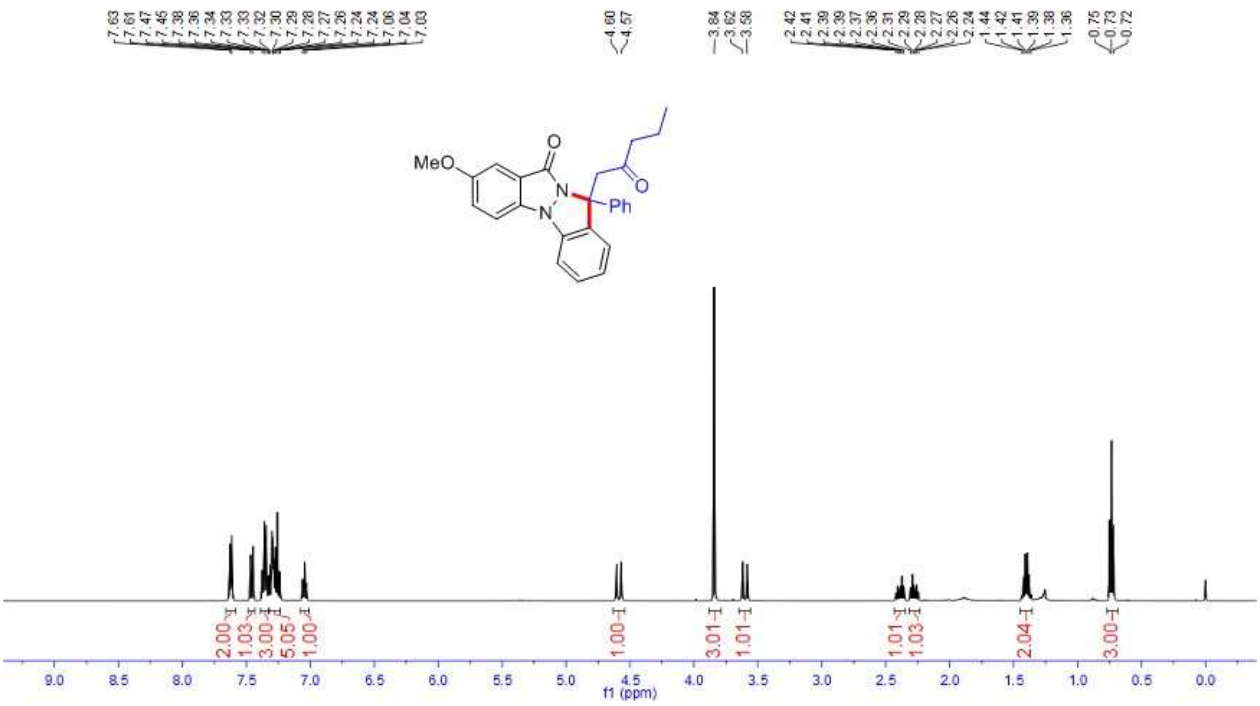
^{13}C NMR spectrum of **3a (**$CDCl_3$, 126 MHz**)**



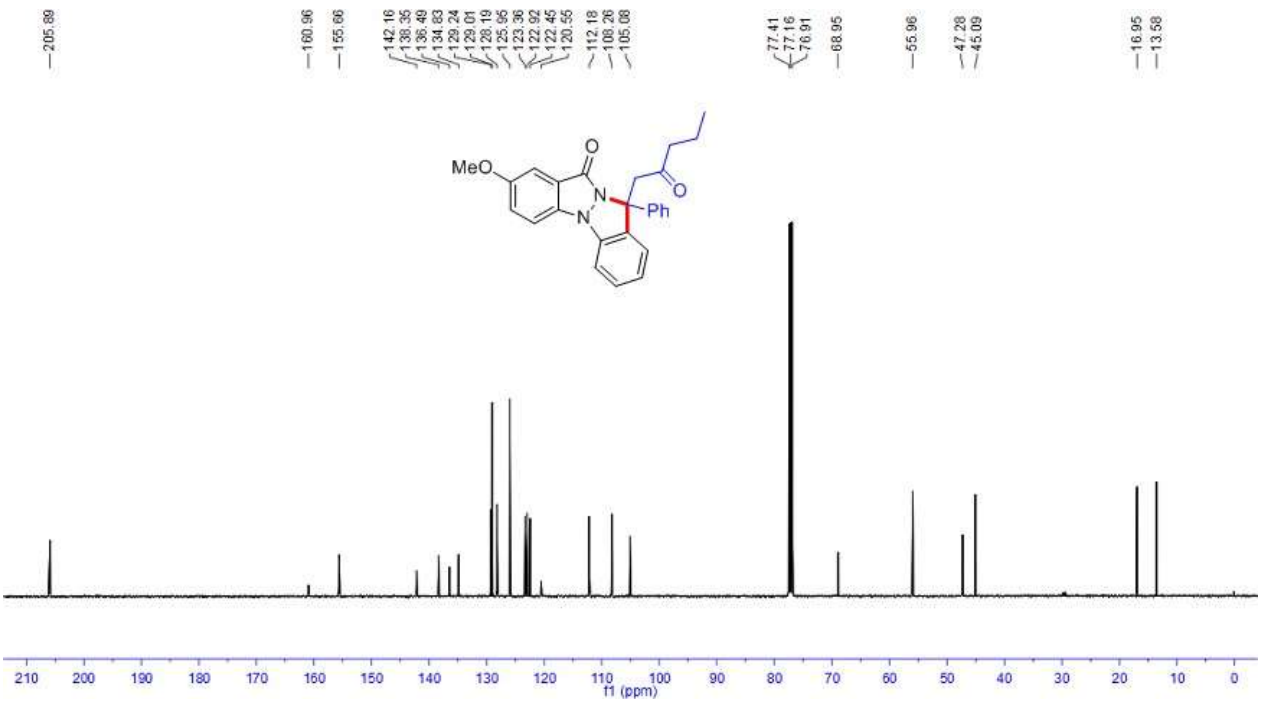
^{1}H NMR spectrum of **3b (**$CDCl_3$, 500 MHz**)**



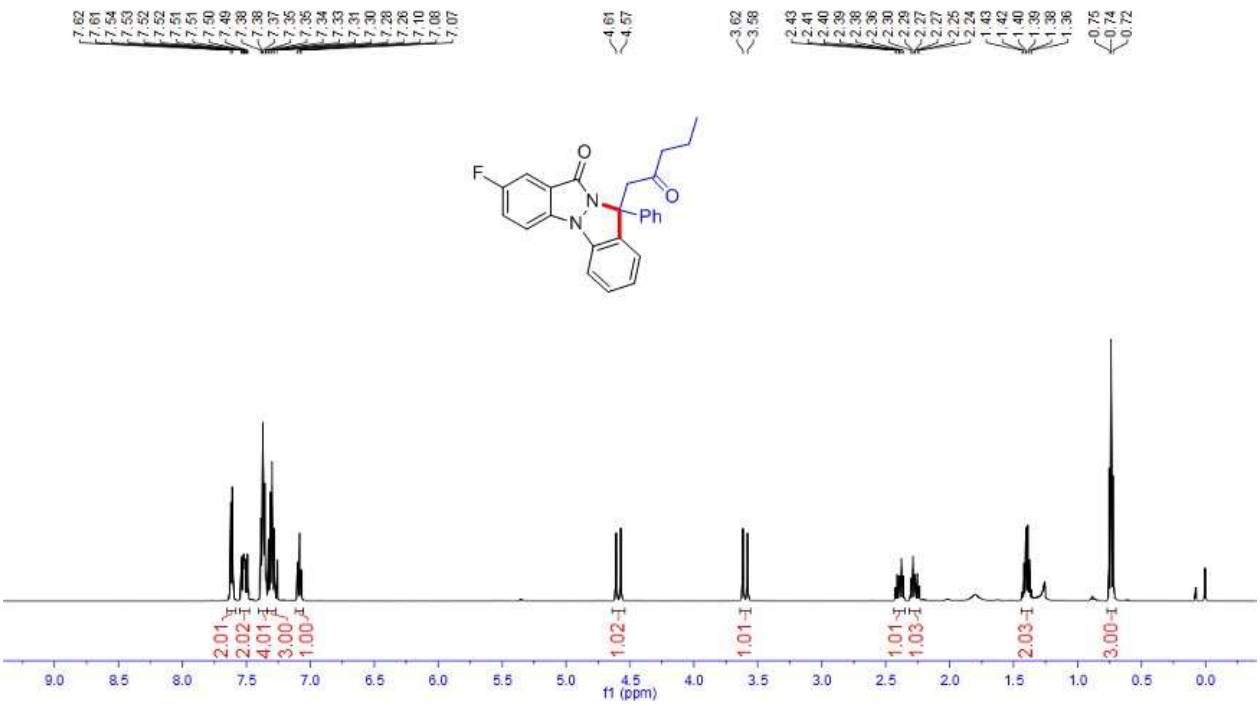
^{13}C NMR spectrum of **3b (**$CDCl_3$, 126 MHz**)**



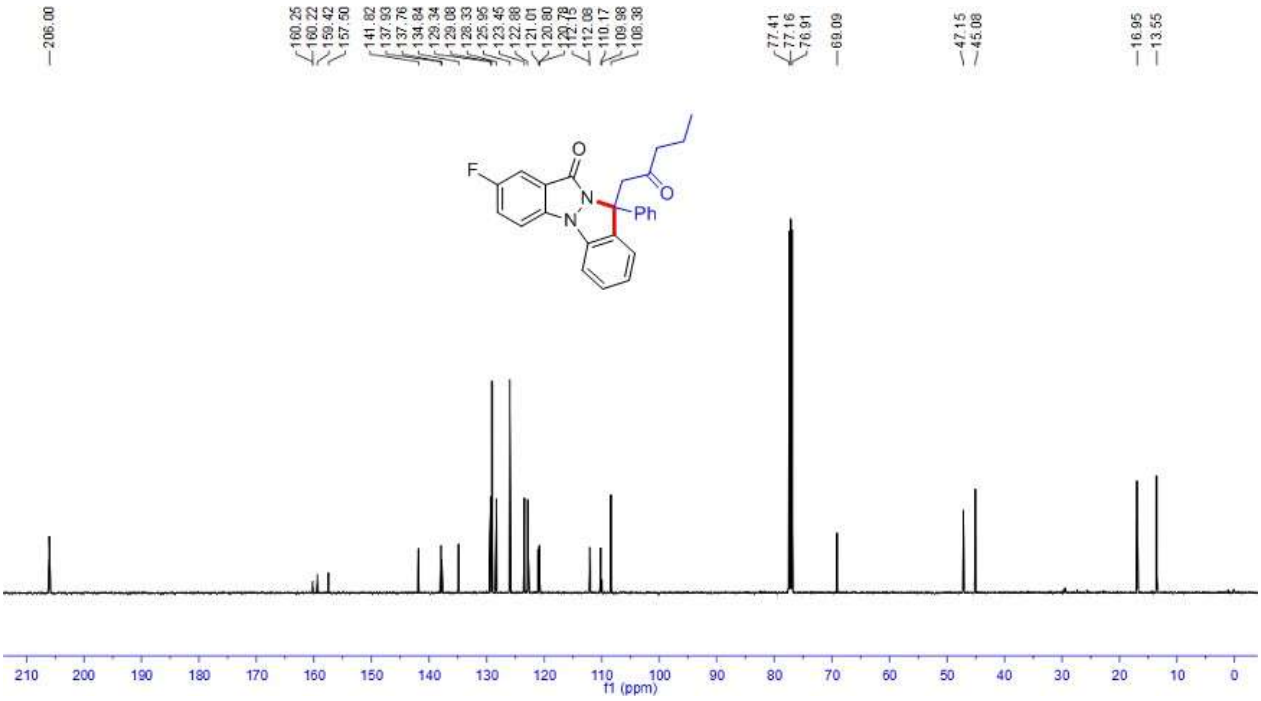
^{1}H NMR spectrum of **3c (**$CDCl_3$, 500 MHz**)**



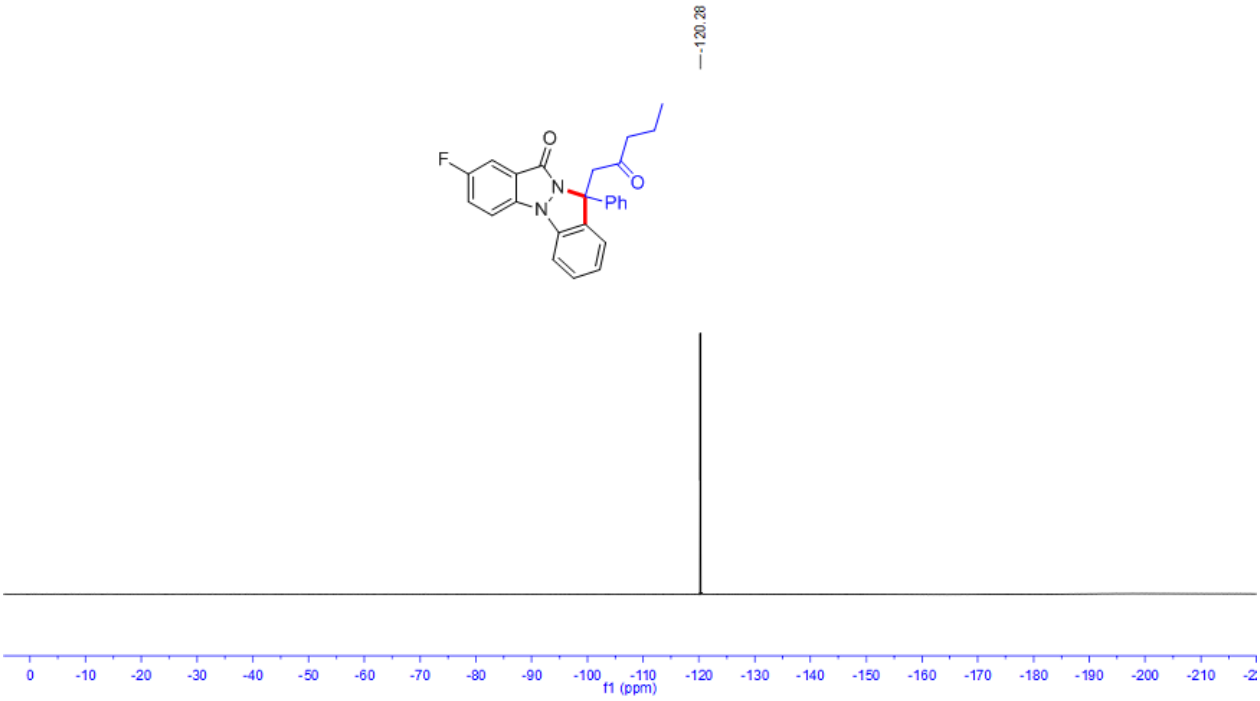
^{13}C NMR spectrum of **3c (**$CDCl_3$, 126 MHz**)**



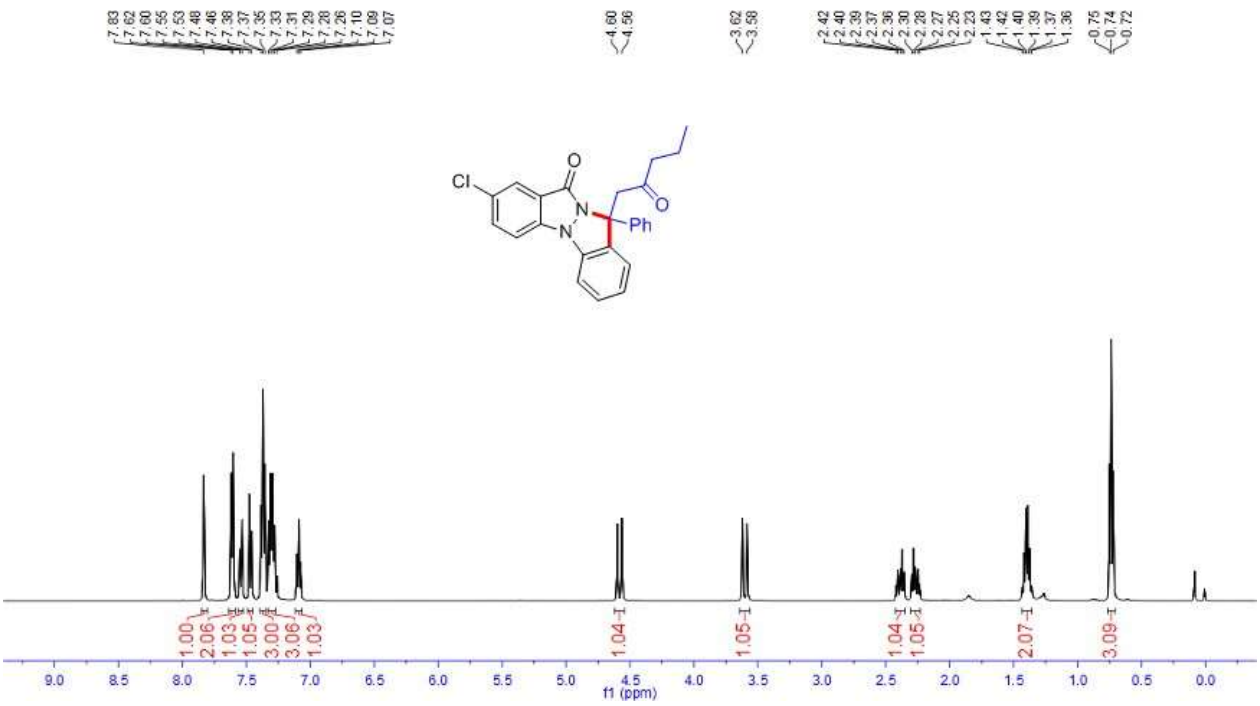
^{1}H NMR spectrum of **3d (**$CDCl_3$, 500 MHz**)**



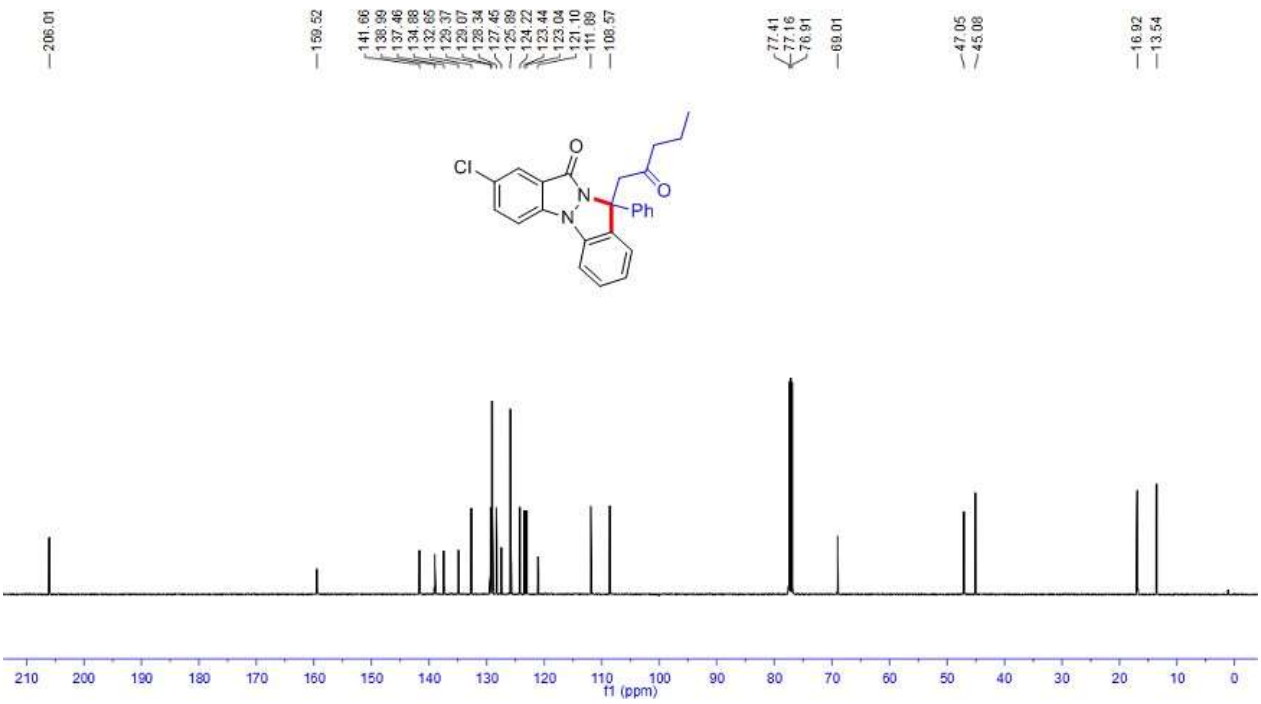
^{13}C NMR spectrum of **3d (**$CDCl_3$, 126 MHz**)**



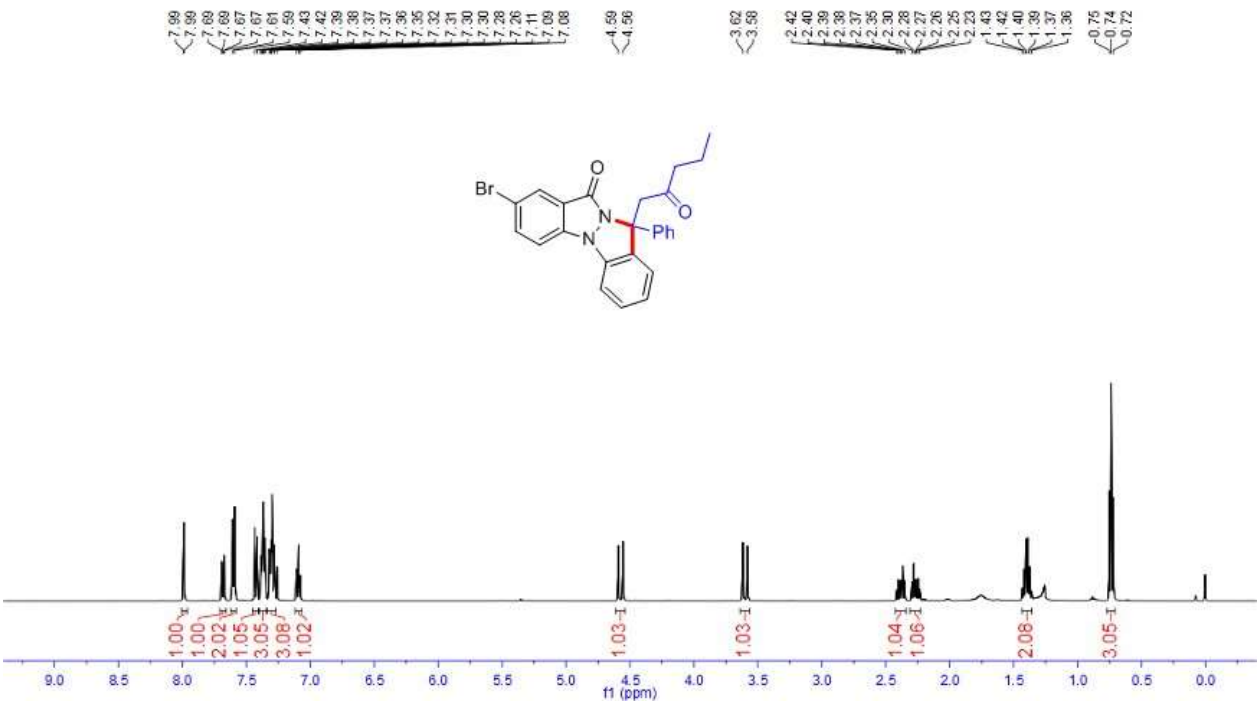
^{19}F NMR spectrum of **3d (**$CDCl_3$, 471 MHz**)**



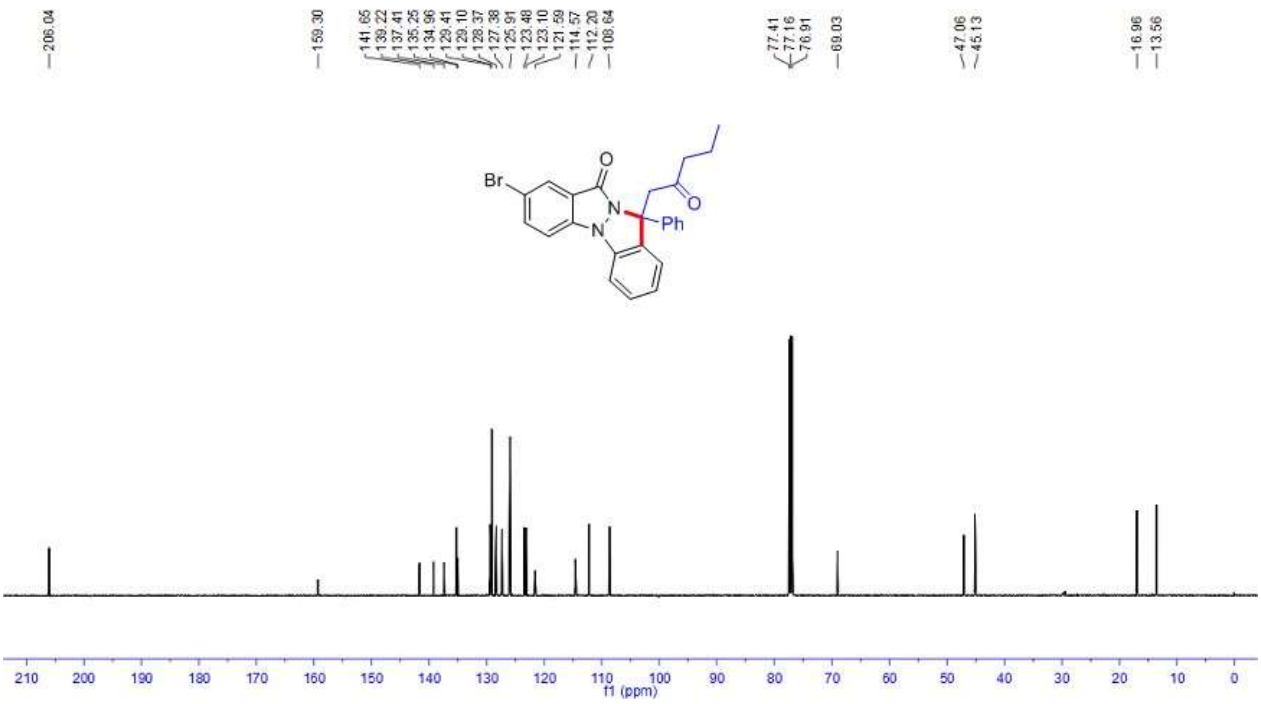
^{1}H NMR spectrum of **3e (**$CDCl_3$, 500 MHz**)**



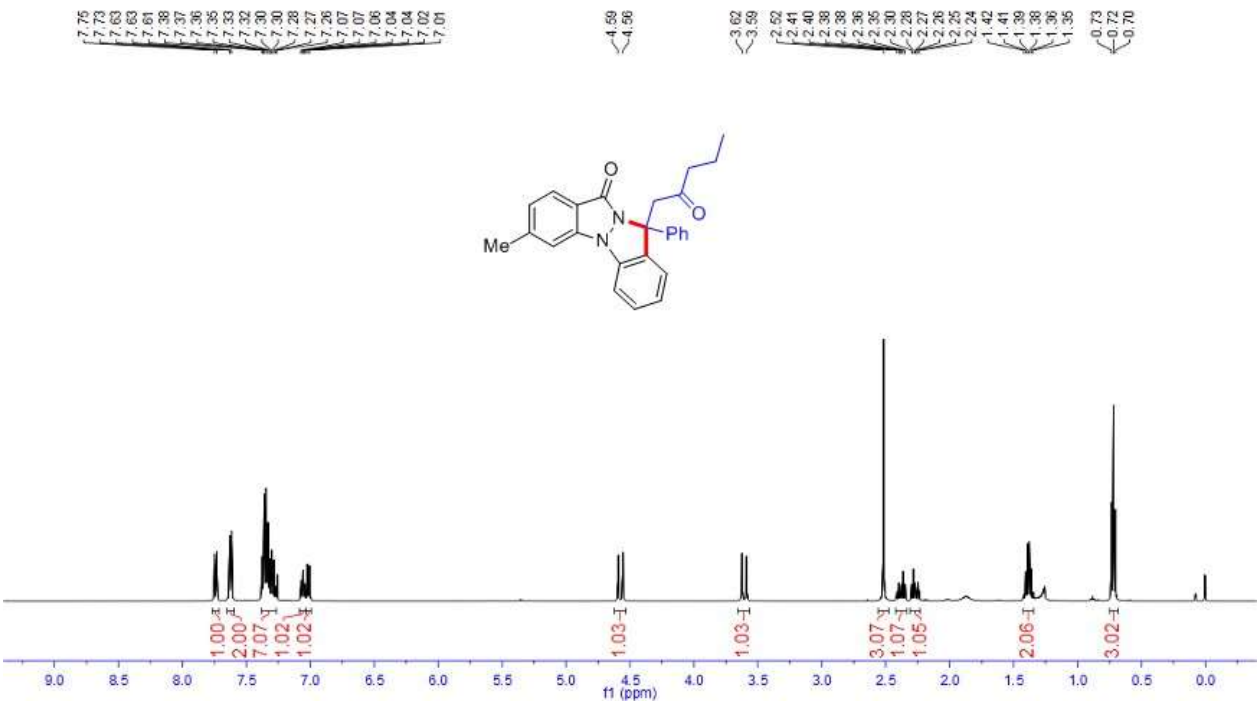
^{13}C NMR spectrum of **3e (**$CDCl_3$, 126 MHz**)**



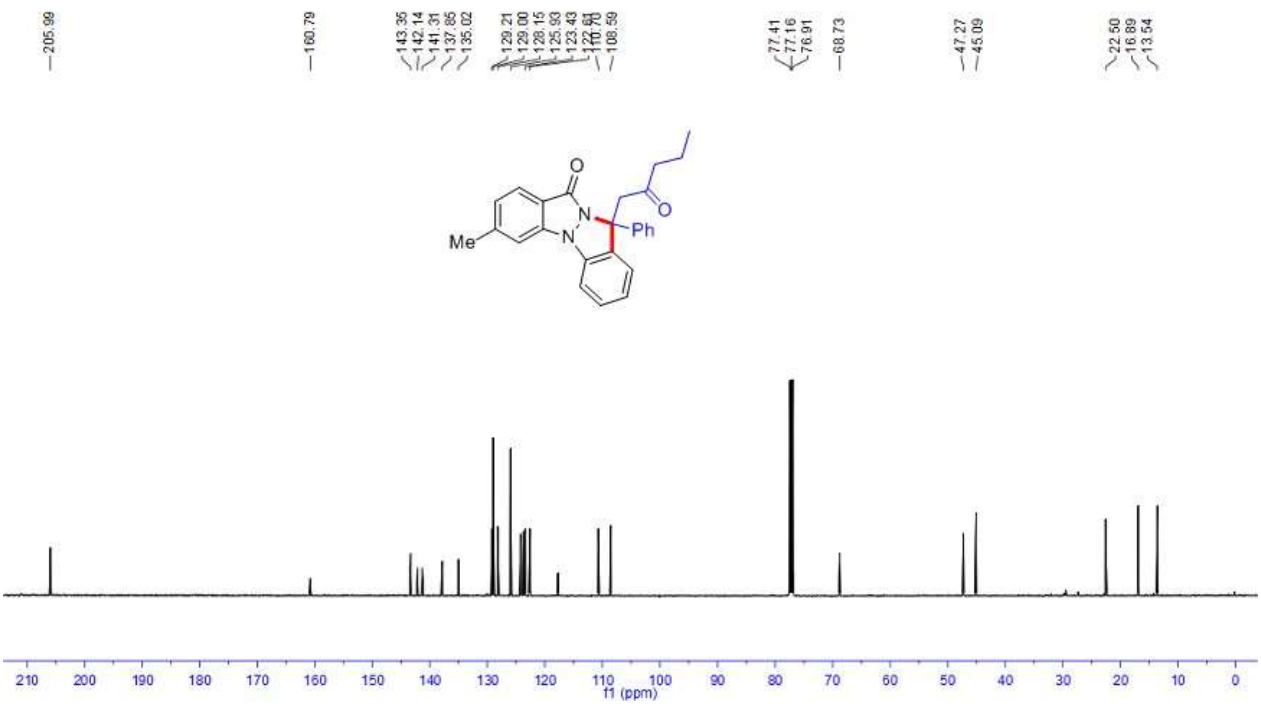
^{1}H NMR spectrum of **3f (**$CDCl_3$, 500 MHz**)**



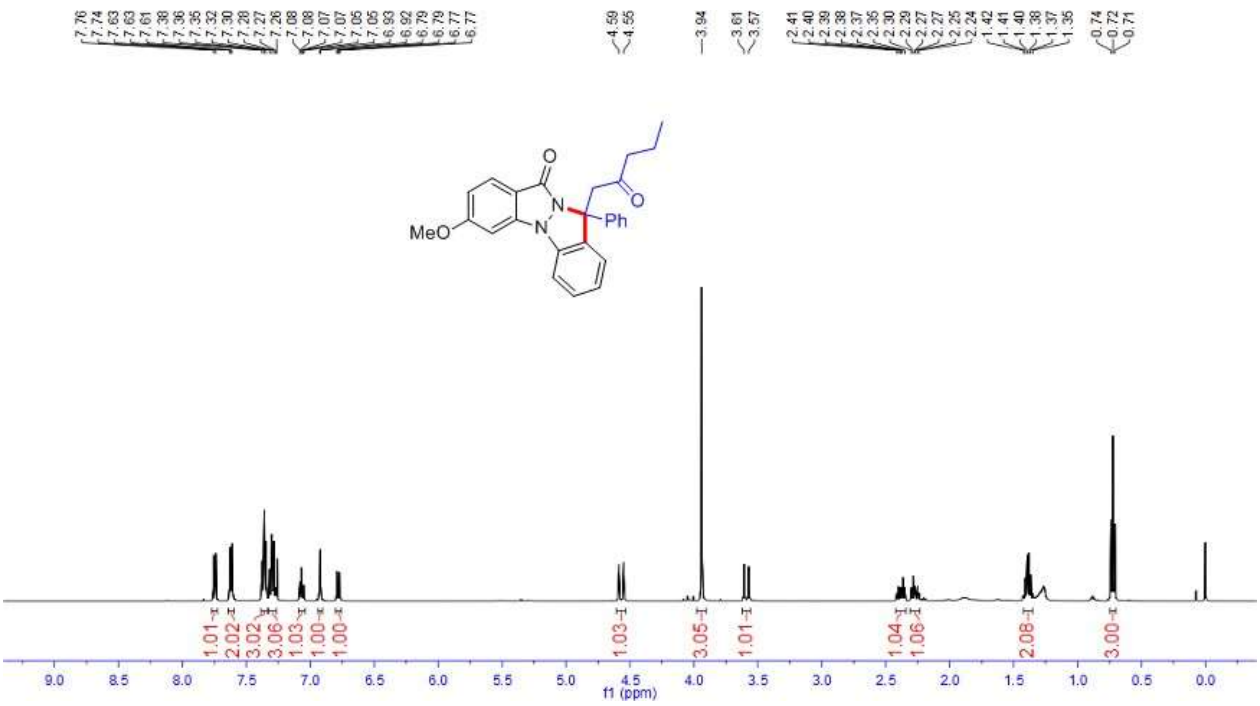
^{13}C NMR spectrum of **3f (**$CDCl_3$, 126 MHz**)**



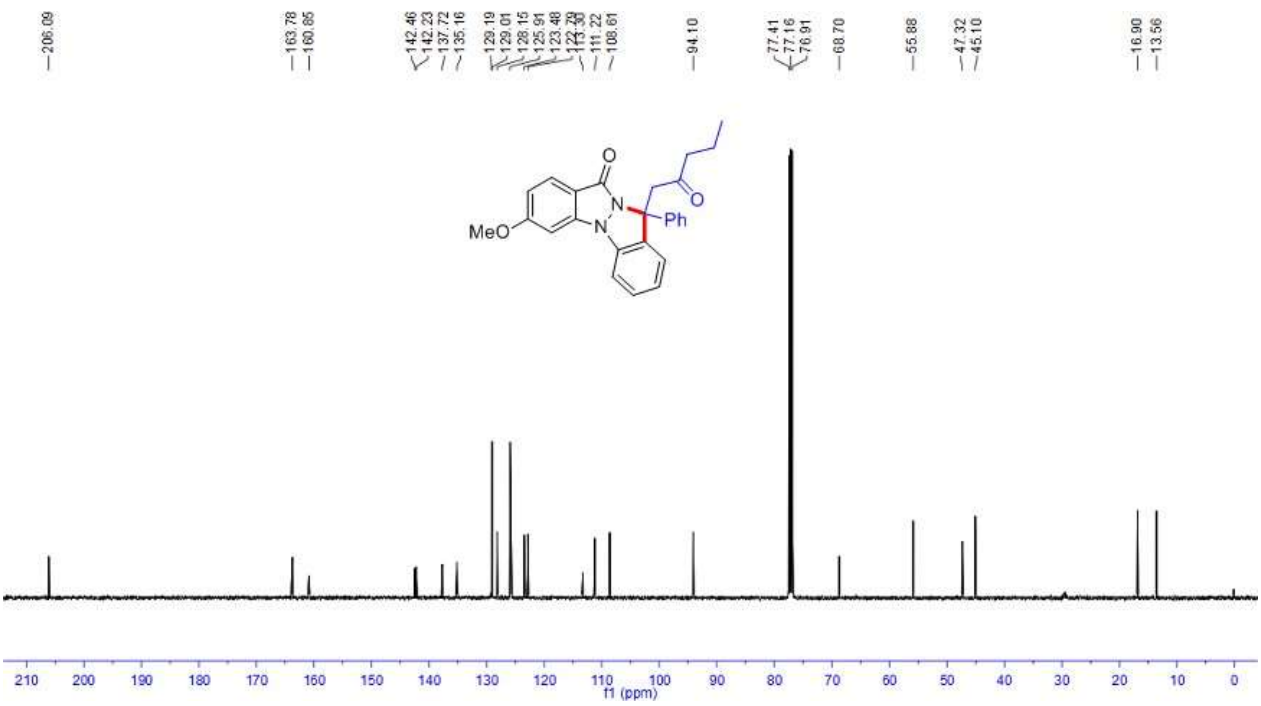
^{1}H NMR spectrum of **3g (**$CDCl_3$, 500 MHz**)**



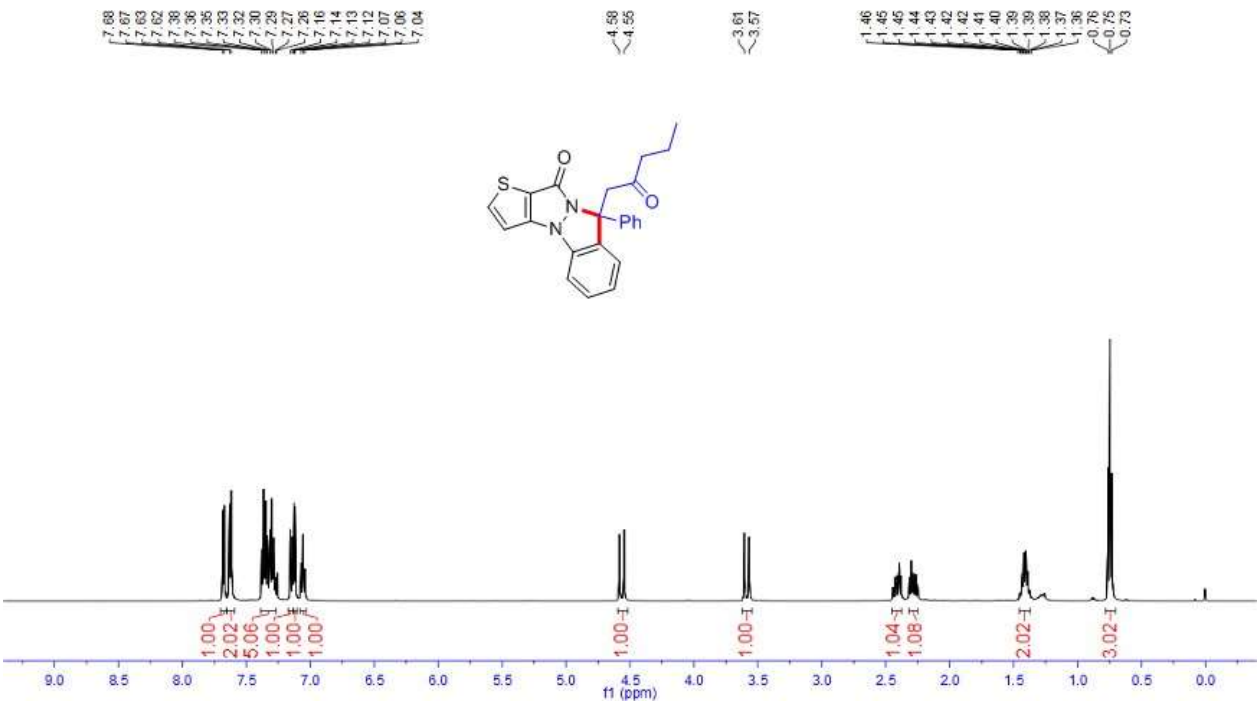
^{13}C NMR spectrum of **3g (**$CDCl_3$, 126 MHz**)**



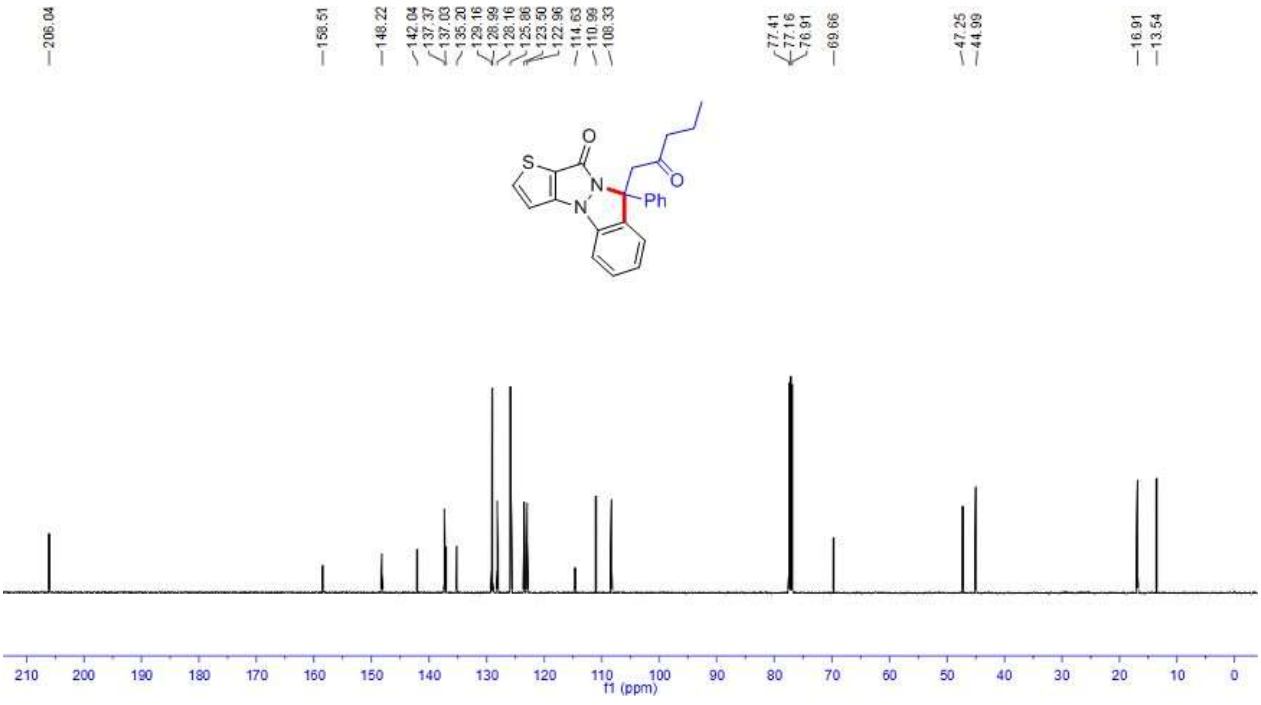
^{1}H NMR spectrum of **3h (**$CDCl_3$, 500 MHz**)**



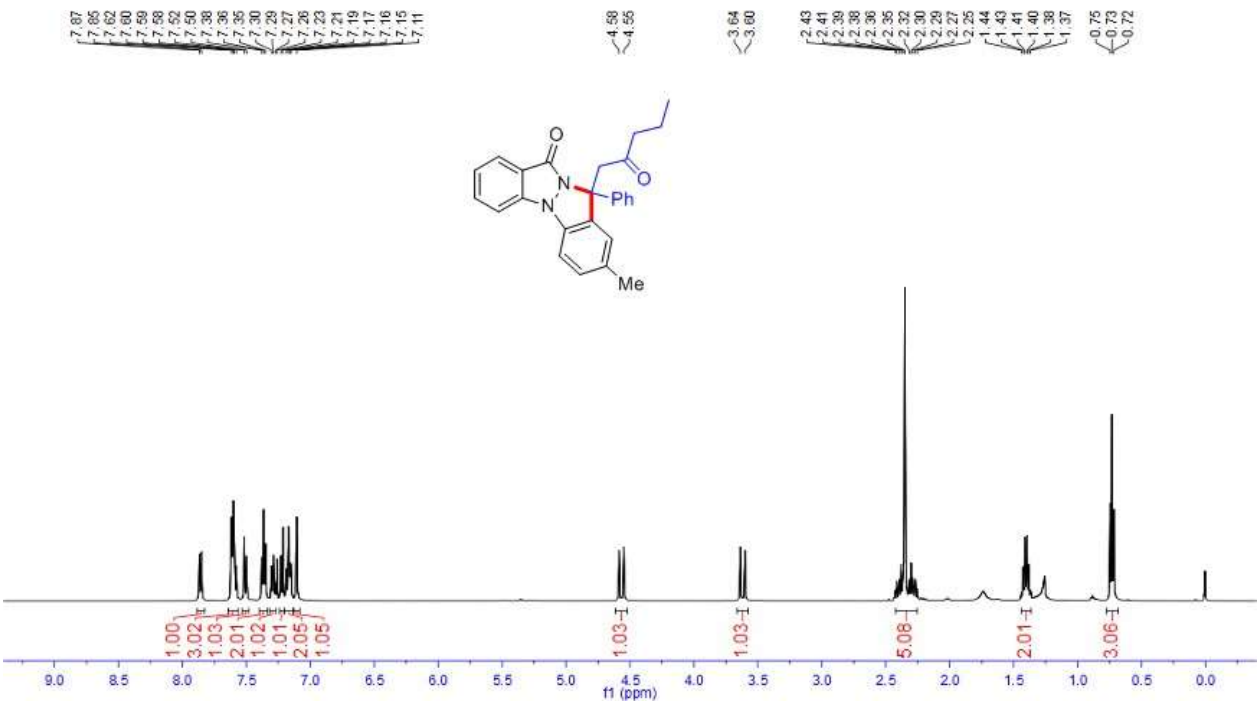
^{13}C NMR spectrum of **3h (**$CDCl_3$, 126 MHz**)**



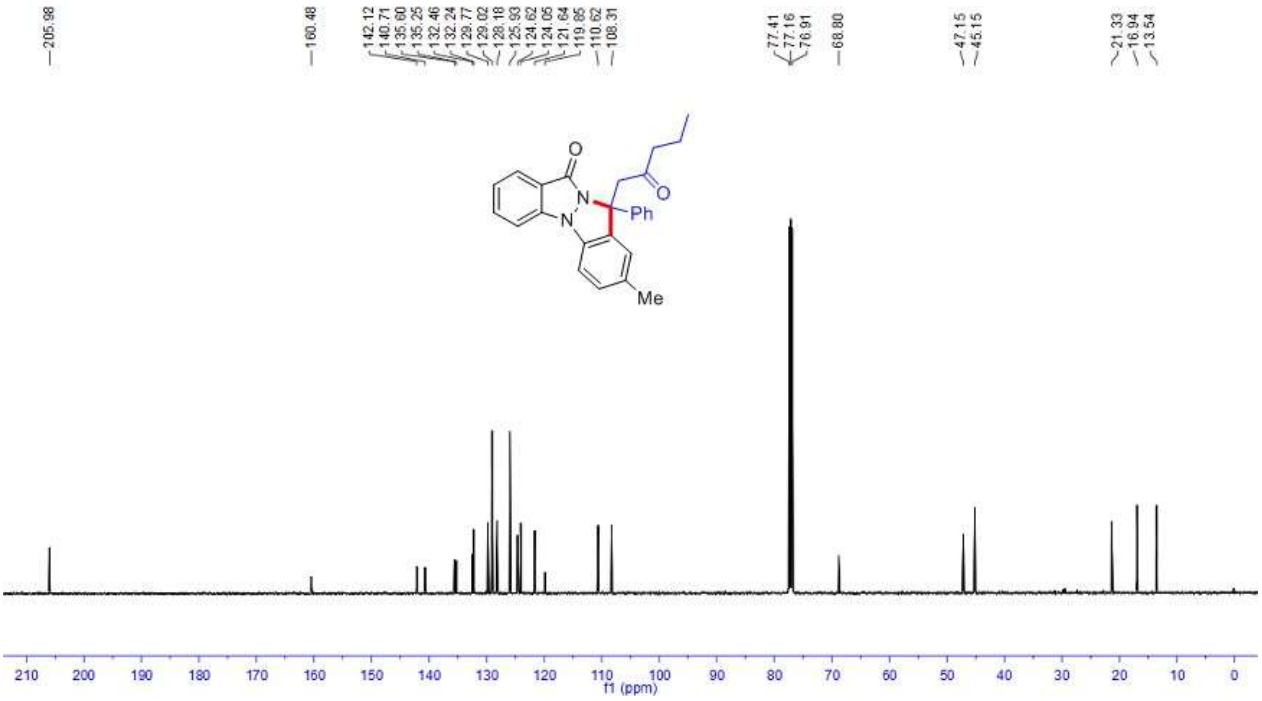
^{1}H NMR spectrum of **3i (**$CDCl_3$, 500 MHz**)**



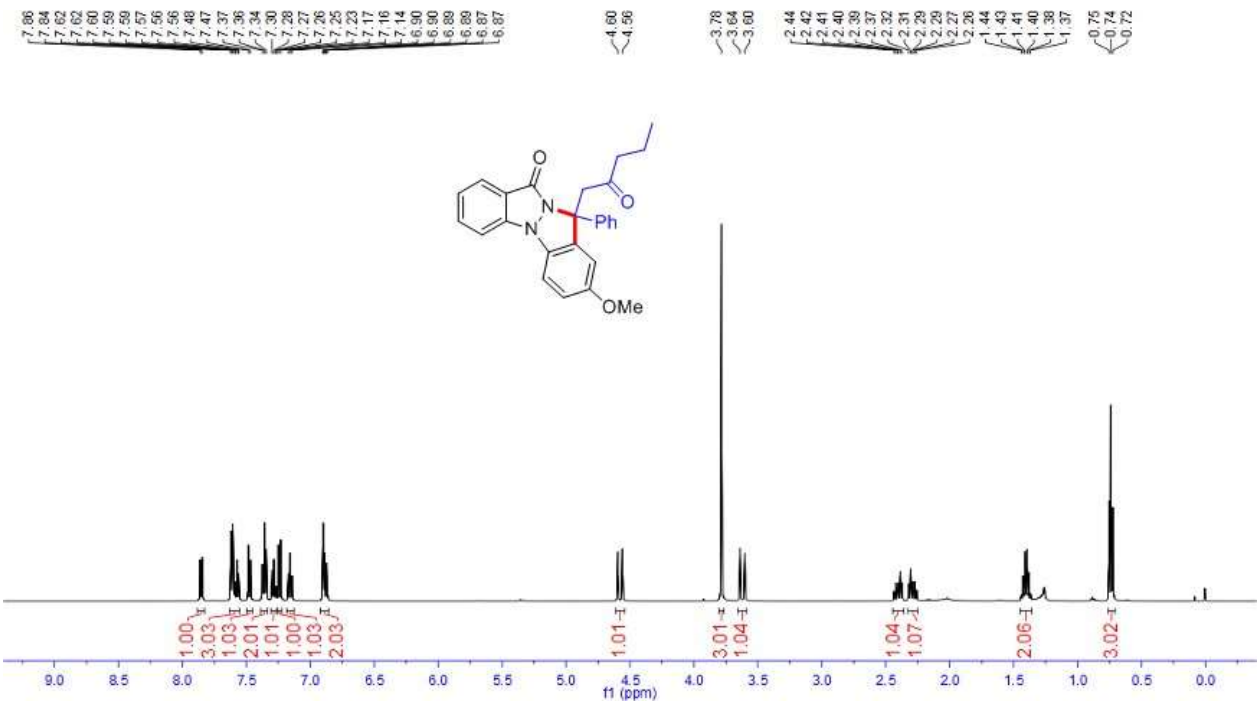
^{13}C NMR spectrum of **3i (**$CDCl_3$, 126 MHz**)**



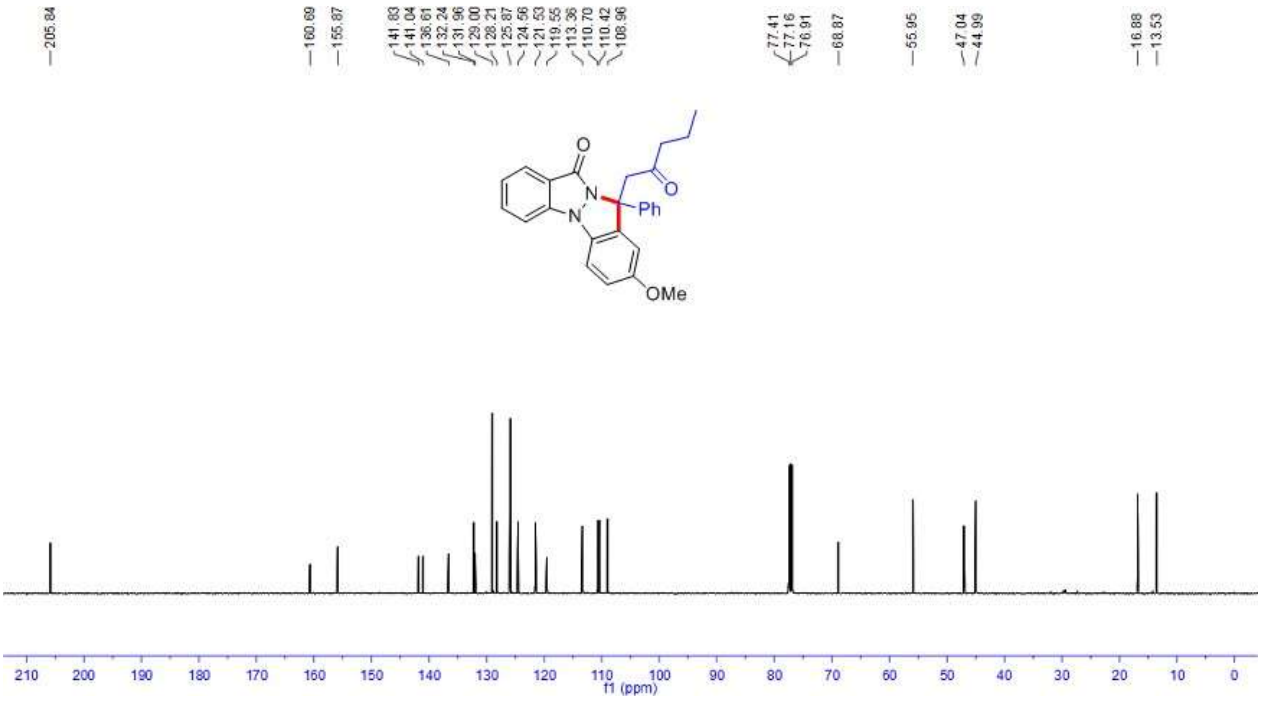
^{1}H NMR spectrum of **3j (**$CDCl_3$, 500 MHz**)**



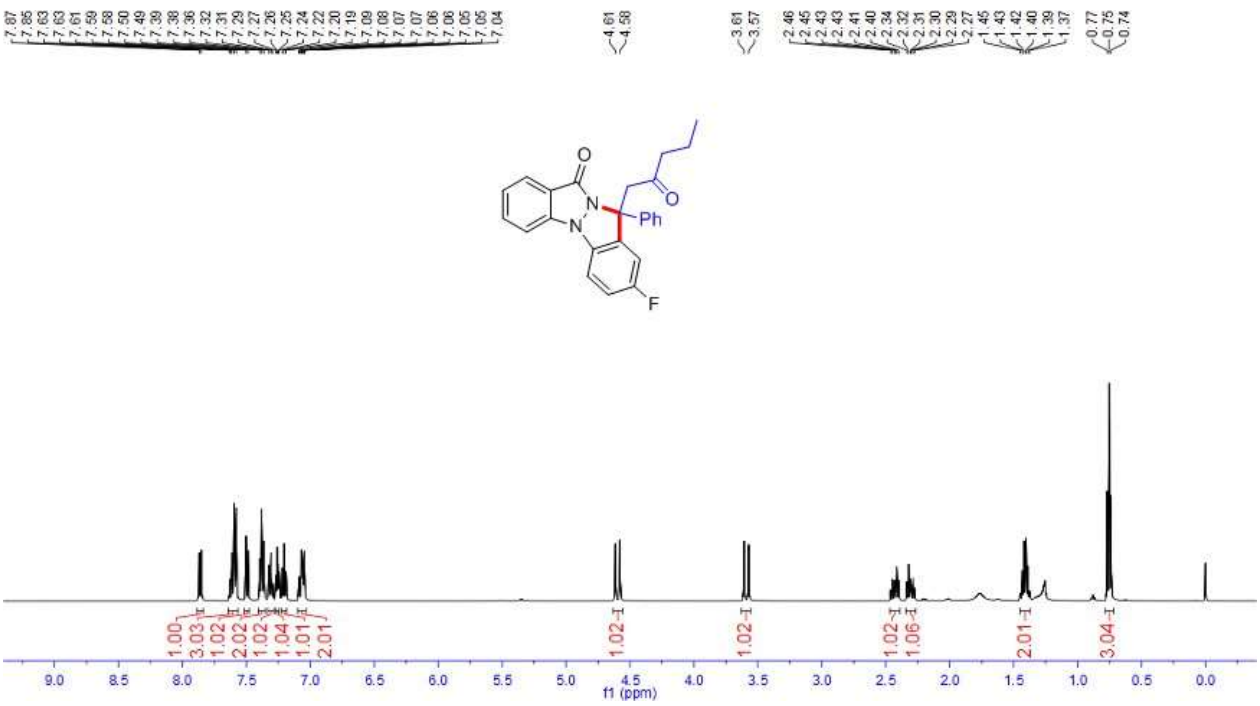
^{13}C NMR spectrum of **3j (**$CDCl_3$, 126 MHz**)**



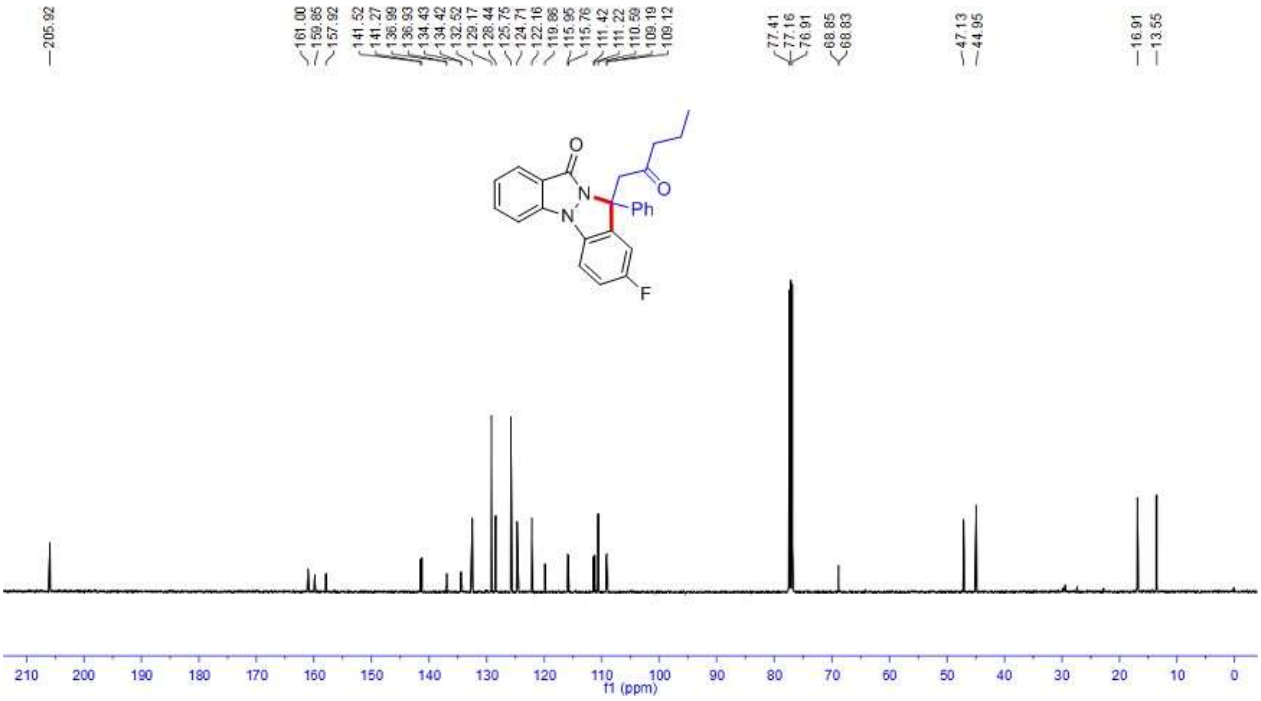
^{1}H NMR spectrum of **3k (**$CDCl_3$, 500 MHz**)**



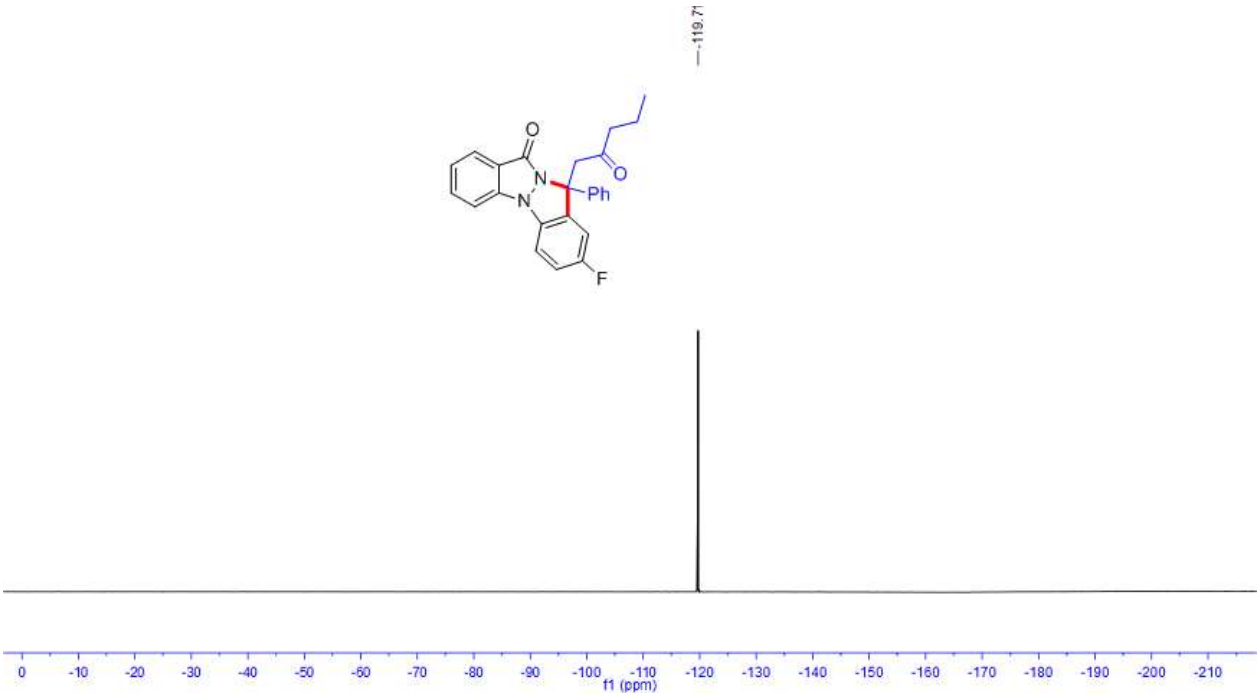
^{13}C NMR spectrum of **3k (**$CDCl_3$, 126 MHz**)**



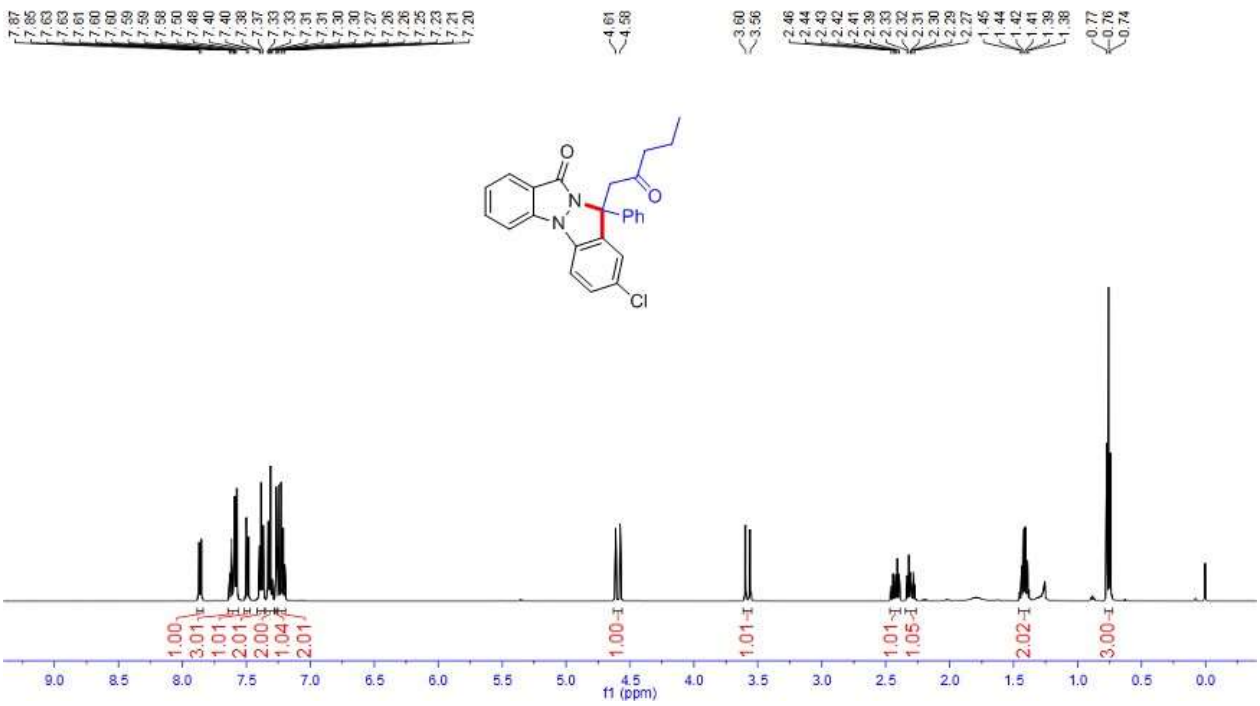
^{1}H NMR spectrum of **3l (**$CDCl_3$, 500 MHz**)**



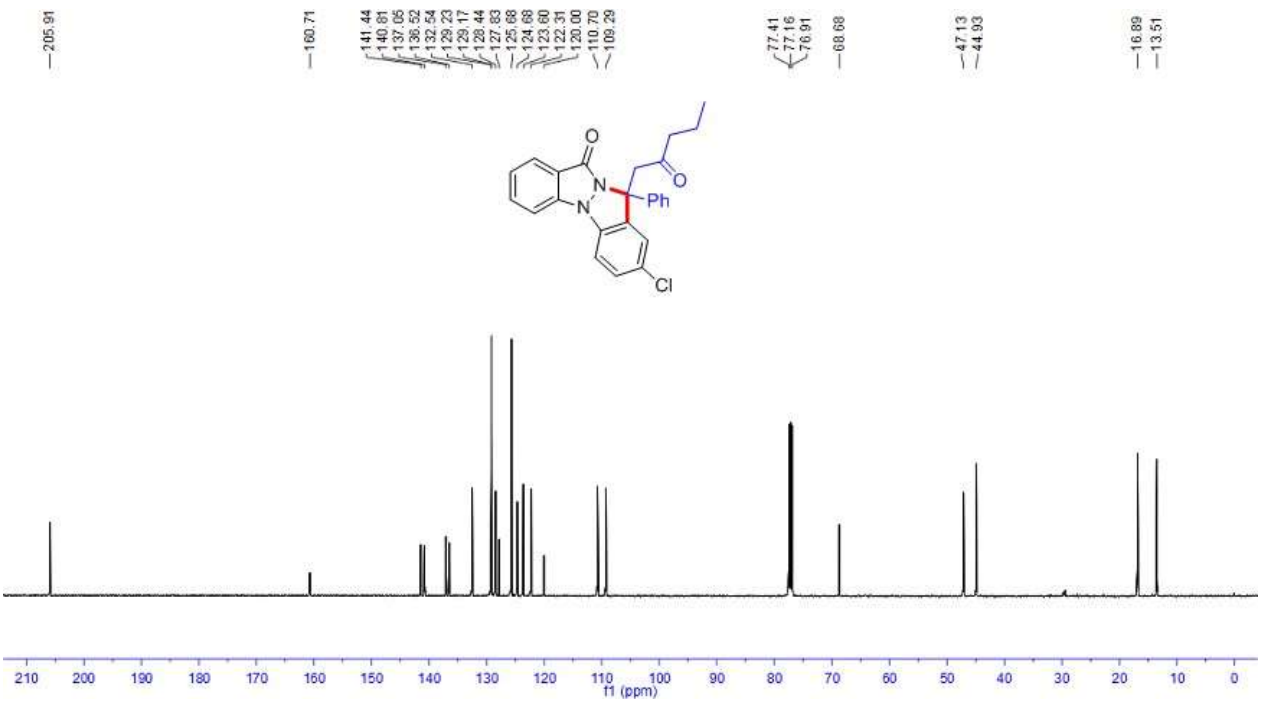
^{13}C NMR spectrum of **3l (**$CDCl_3$, 126 MHz**)**



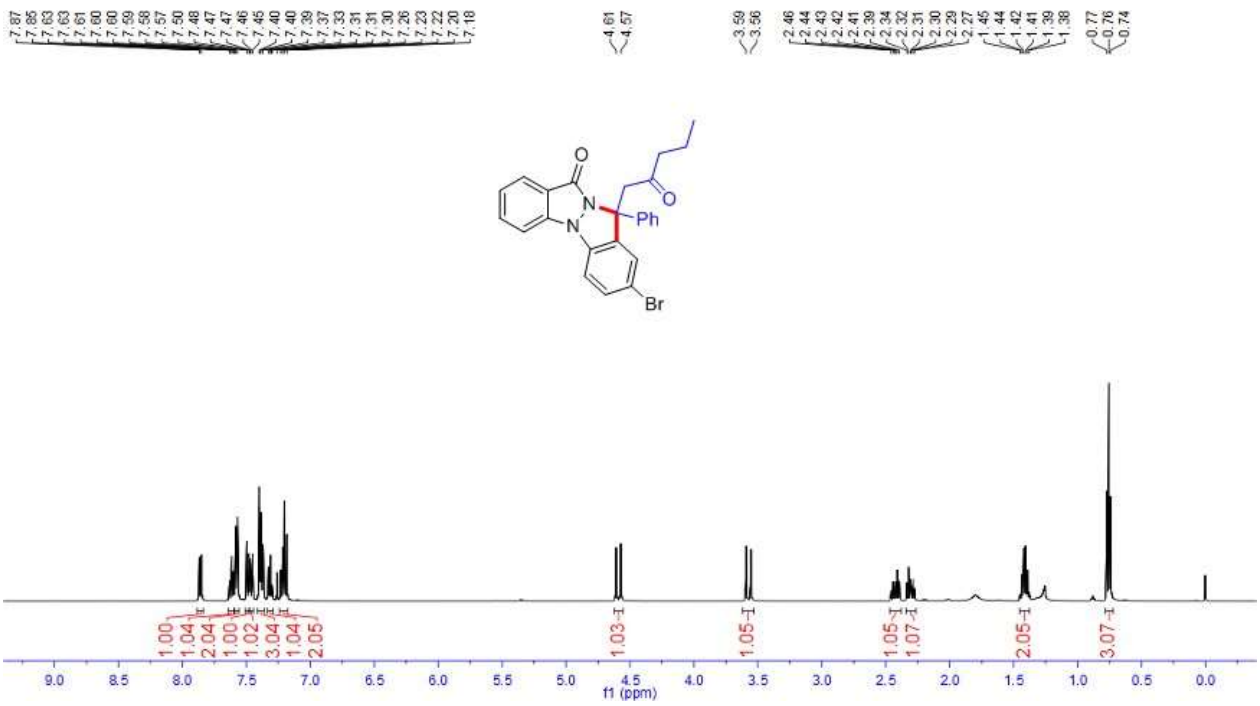
^{19}F NMR spectrum of **3l (**$CDCl_3$, 471 MHz**)**



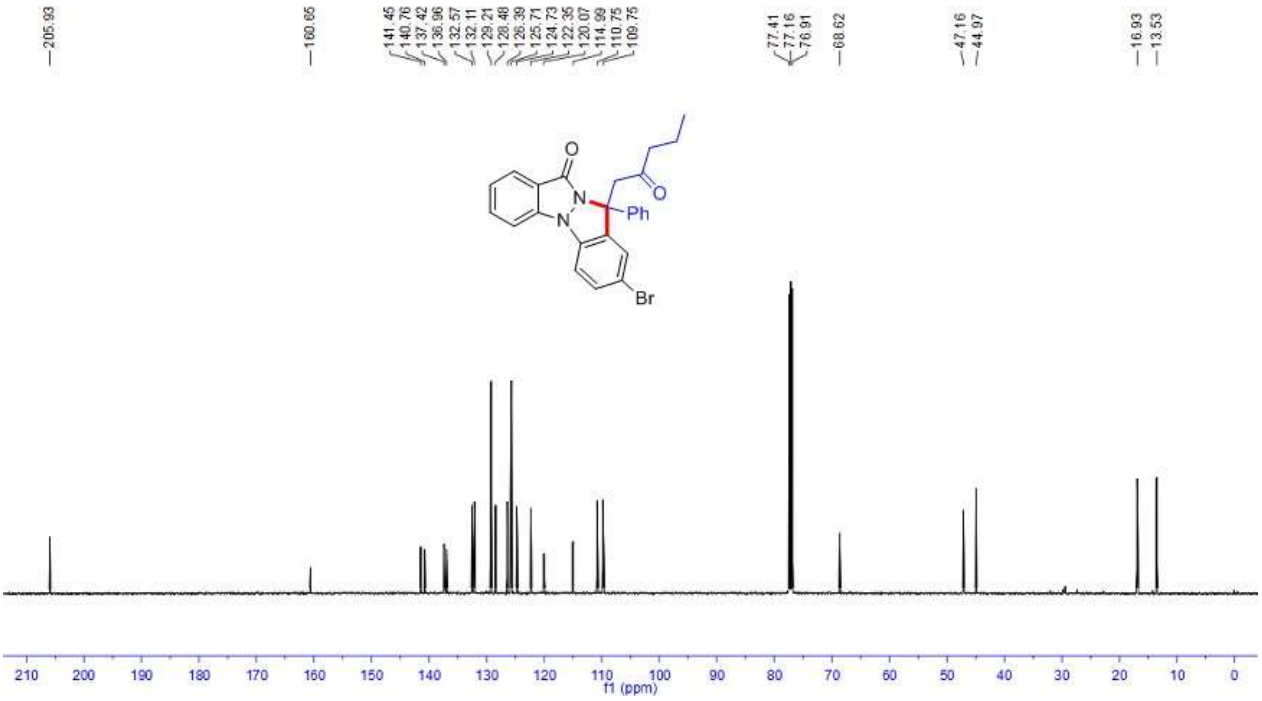
^{1}H NMR spectrum of **3m (**$CDCl_3$, 500 MHz**)**



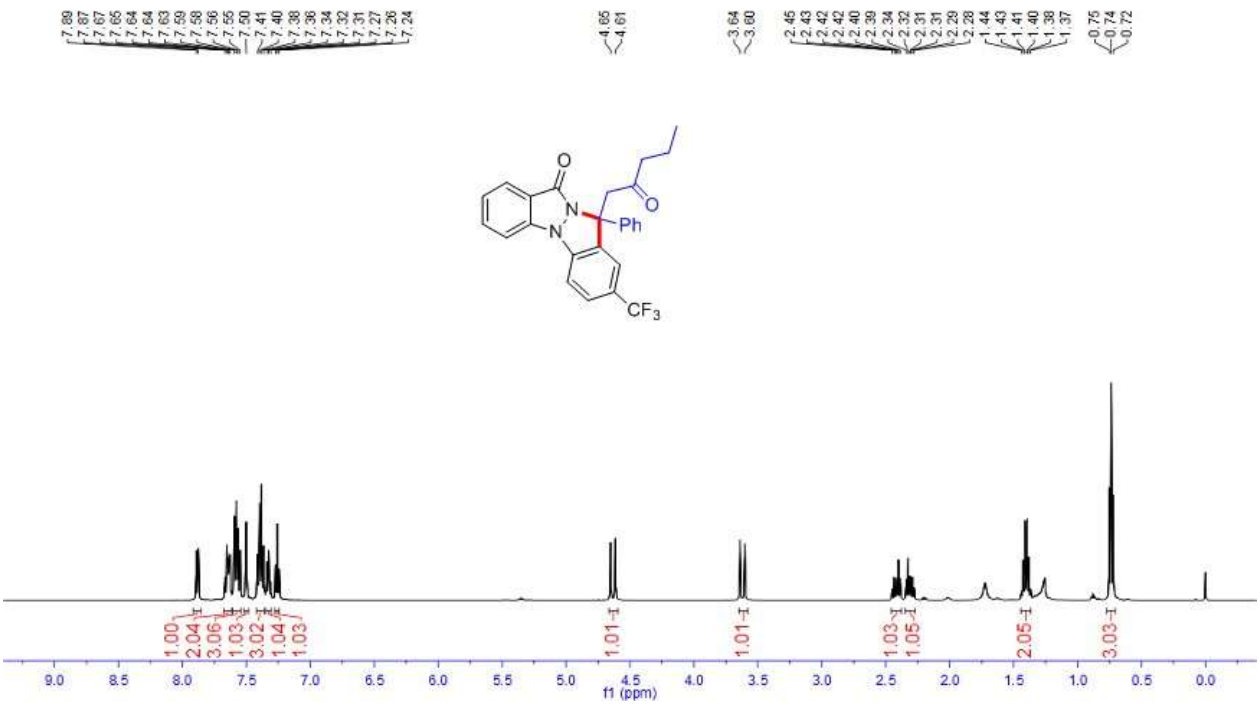
^{13}C NMR spectrum of **3m (**$CDCl_3$, 126 MHz**)**



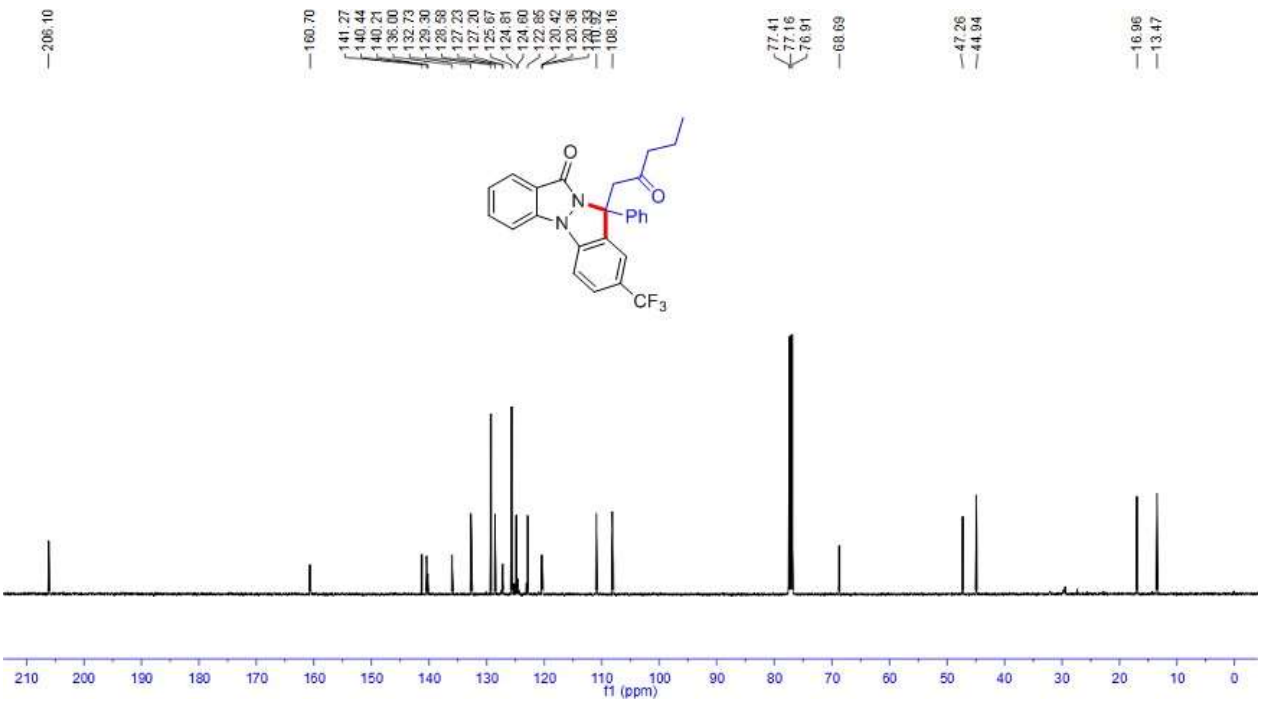
^{1}H NMR spectrum of **3n (**$CDCl_3$, 500 MHz**)**



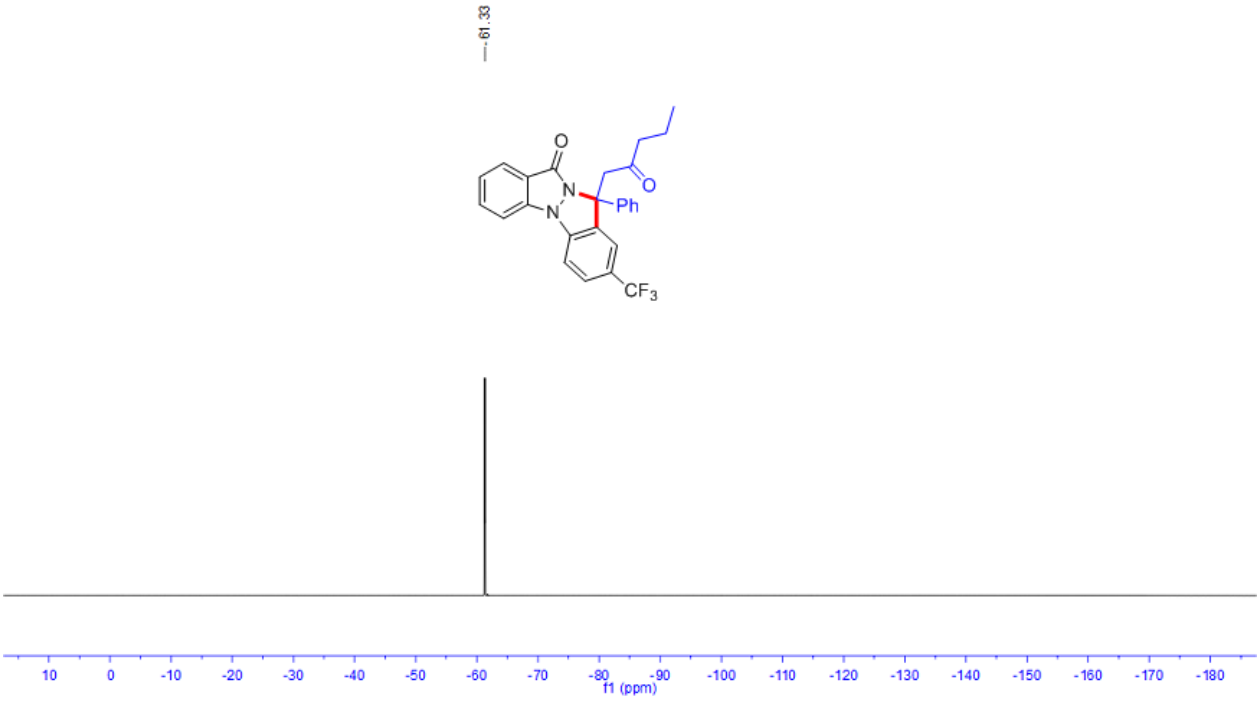
^{13}C NMR spectrum of **3n (**$CDCl_3$, 126 MHz**)**



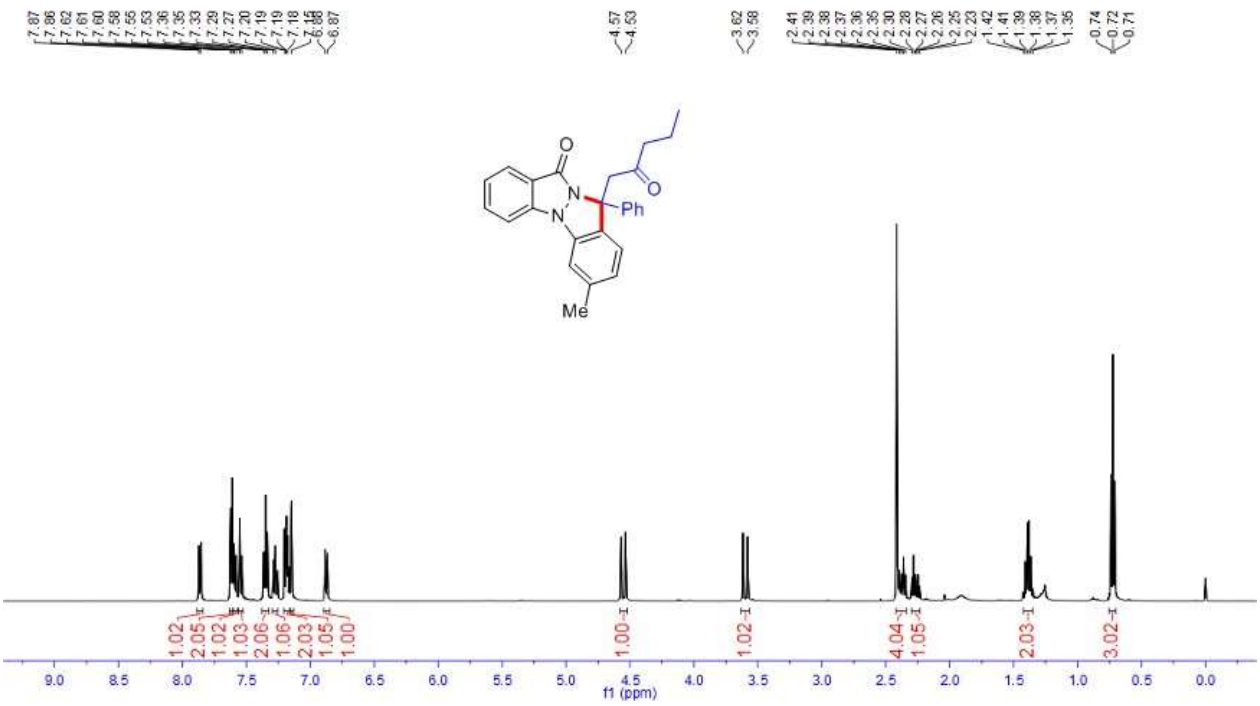
^{1}H NMR spectrum of **3o (**$CDCl_3$, 500 MHz**)**



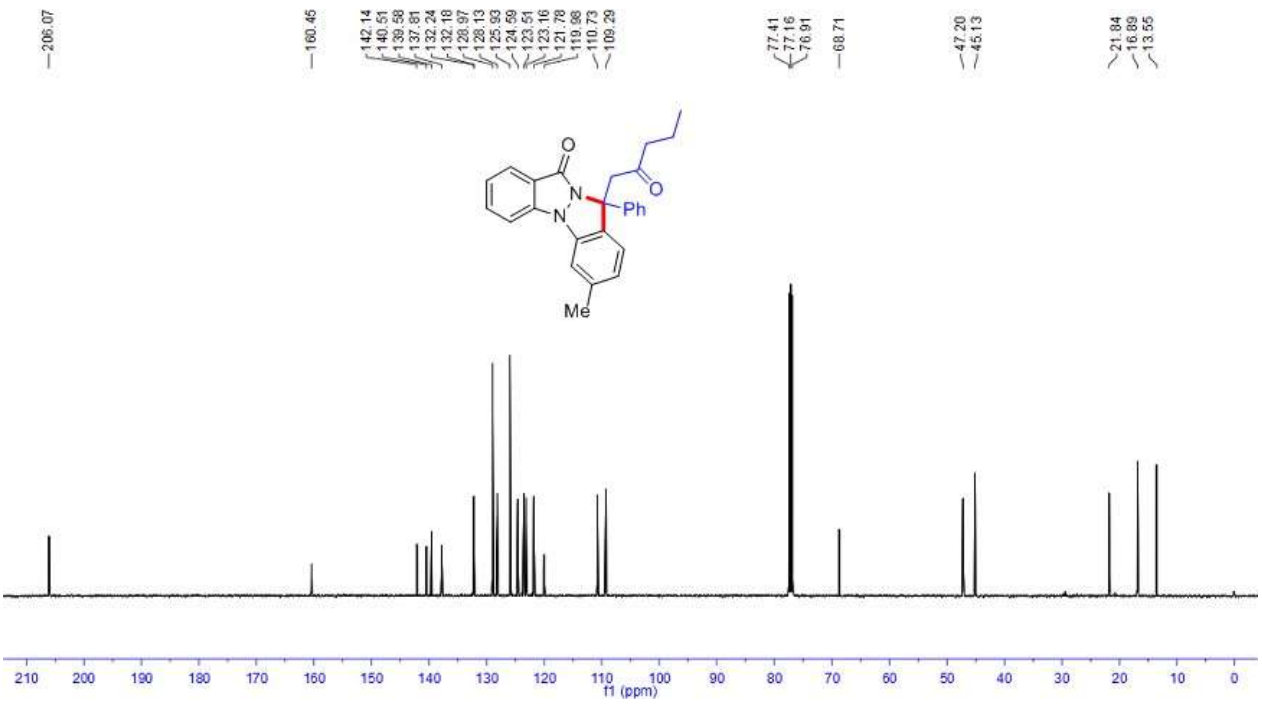
^{13}C NMR spectrum of **3o (**$CDCl_3$, 126 MHz**)**



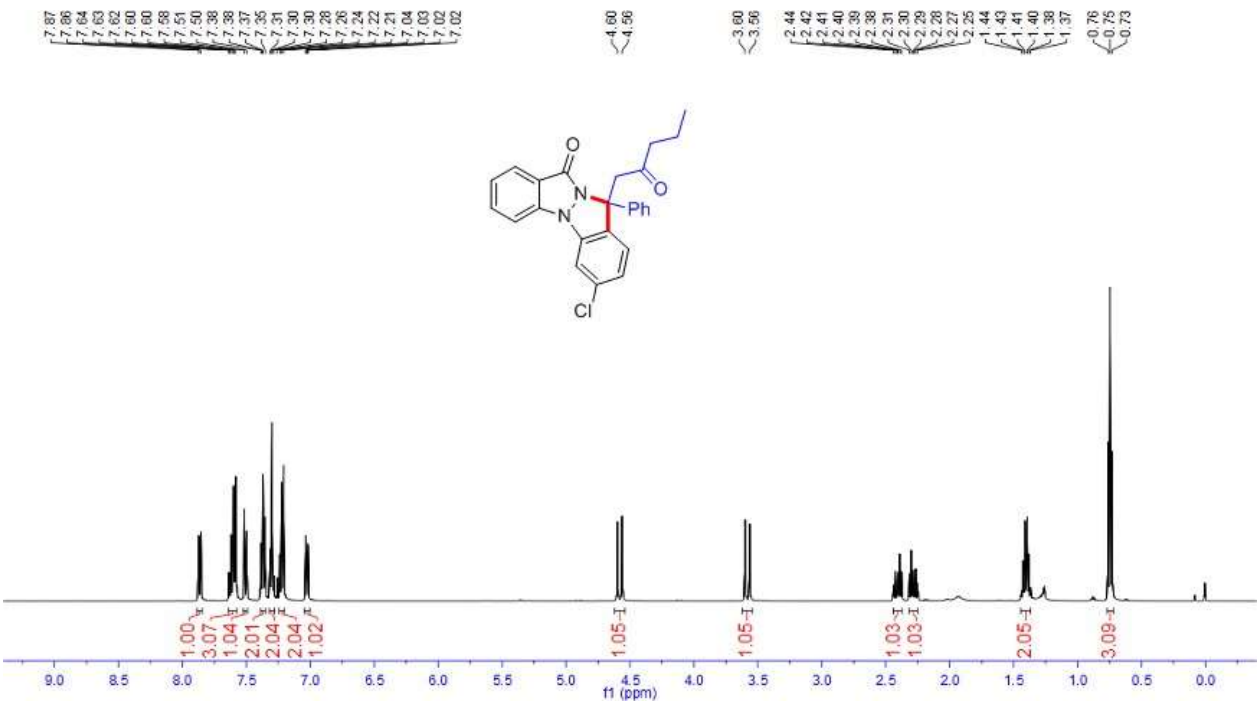
^{19}F NMR spectrum of **3o (**$CDCl_3$, 471 MHz**)**



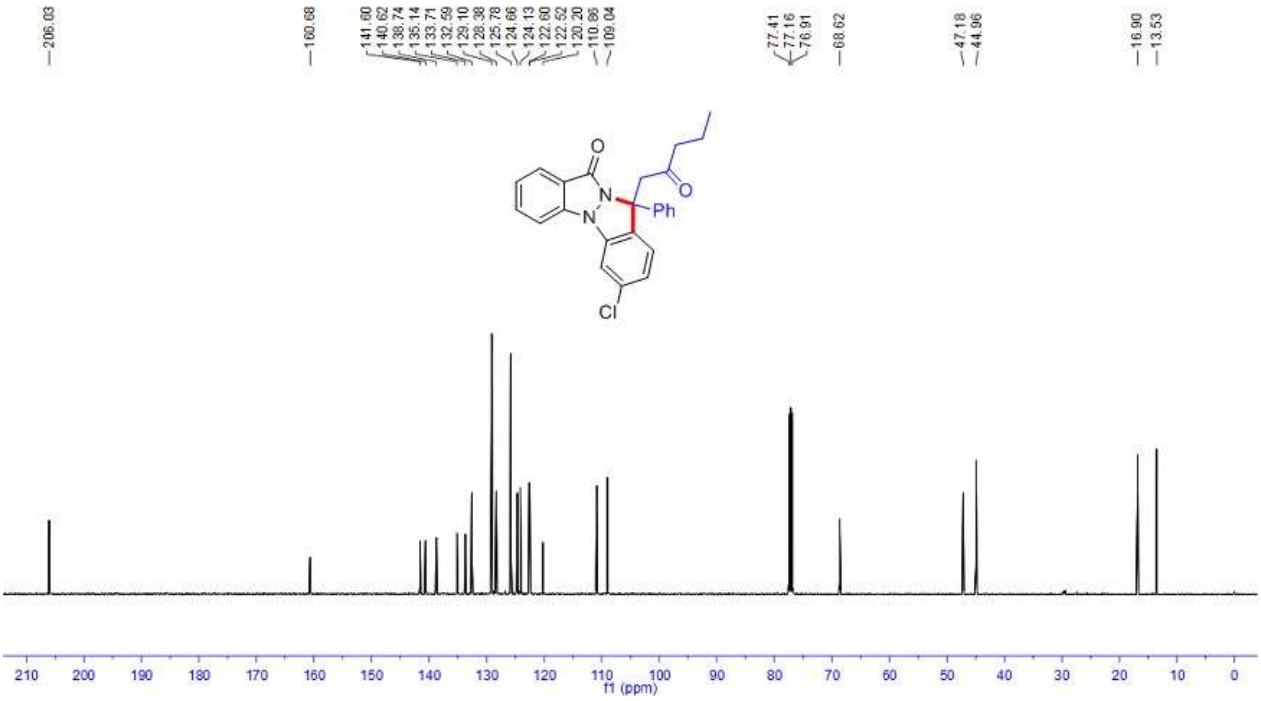
^{1}H NMR spectrum of **3q (**$CDCl_3$, 500 MHz**)**



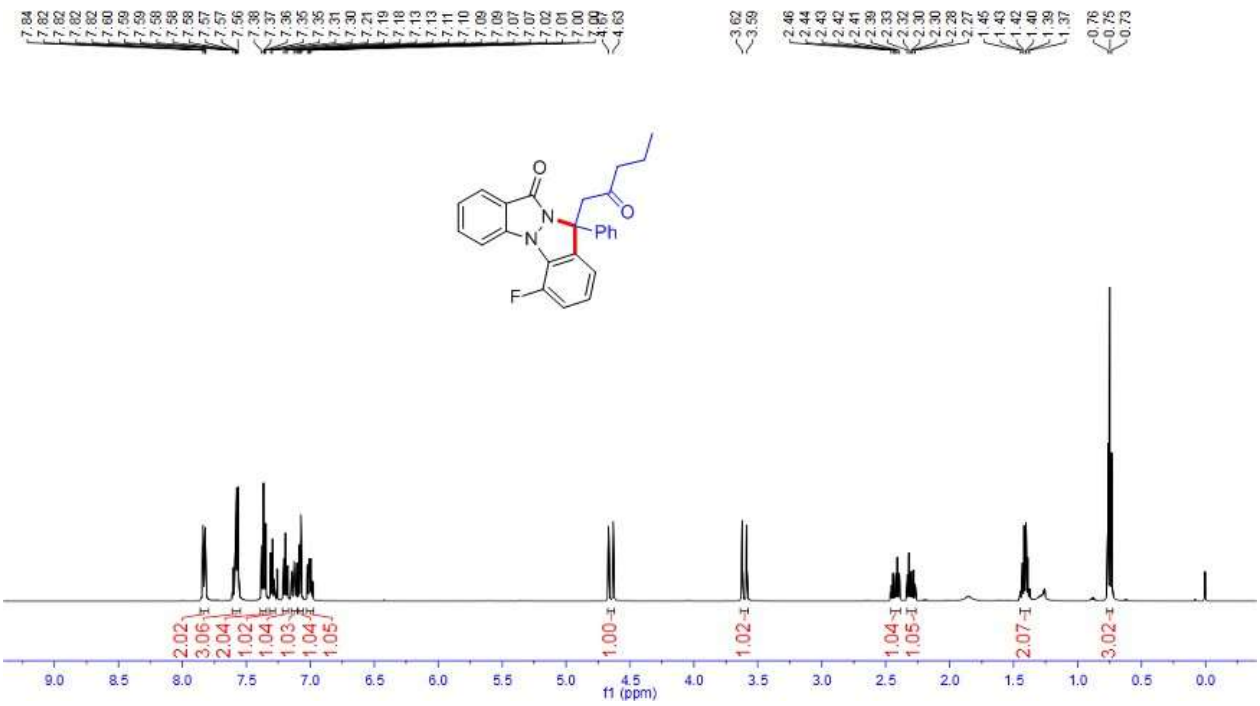
^{13}C NMR spectrum of **3q (**$CDCl_3$, 126 MHz**)**



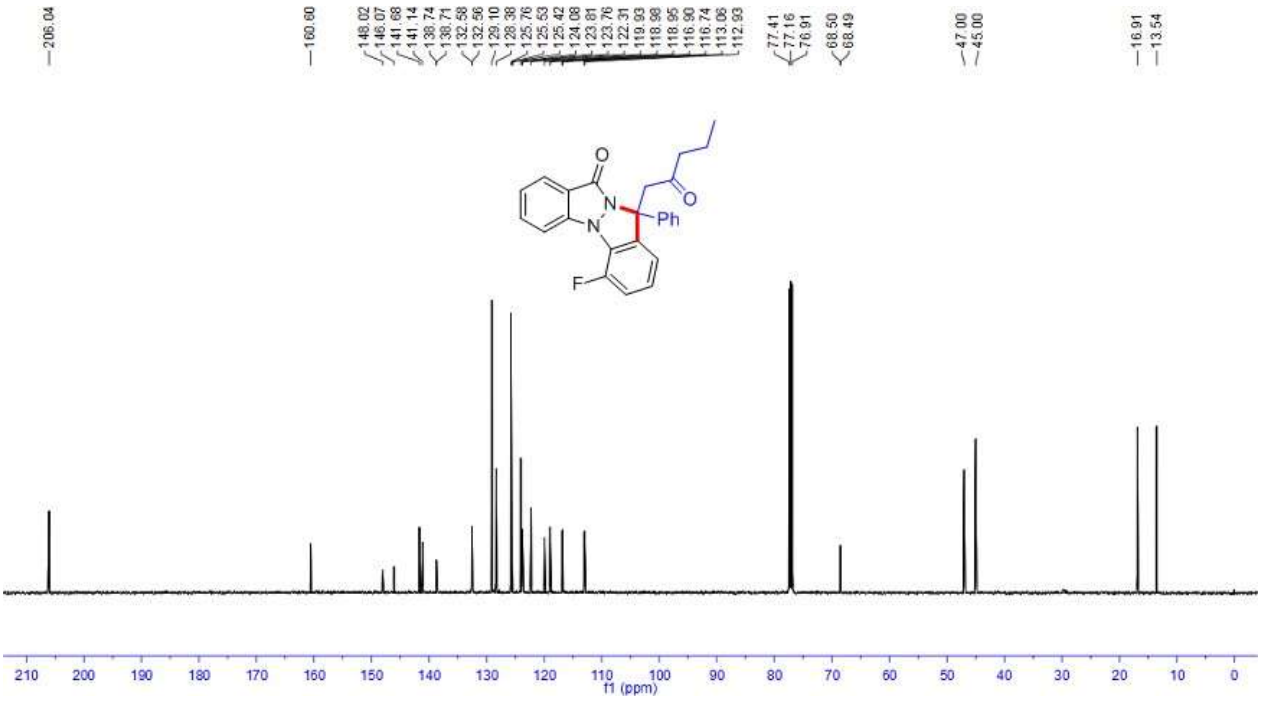
^{1}H NMR spectrum of **3r (**$CDCl_3$, 500 MHz**)**



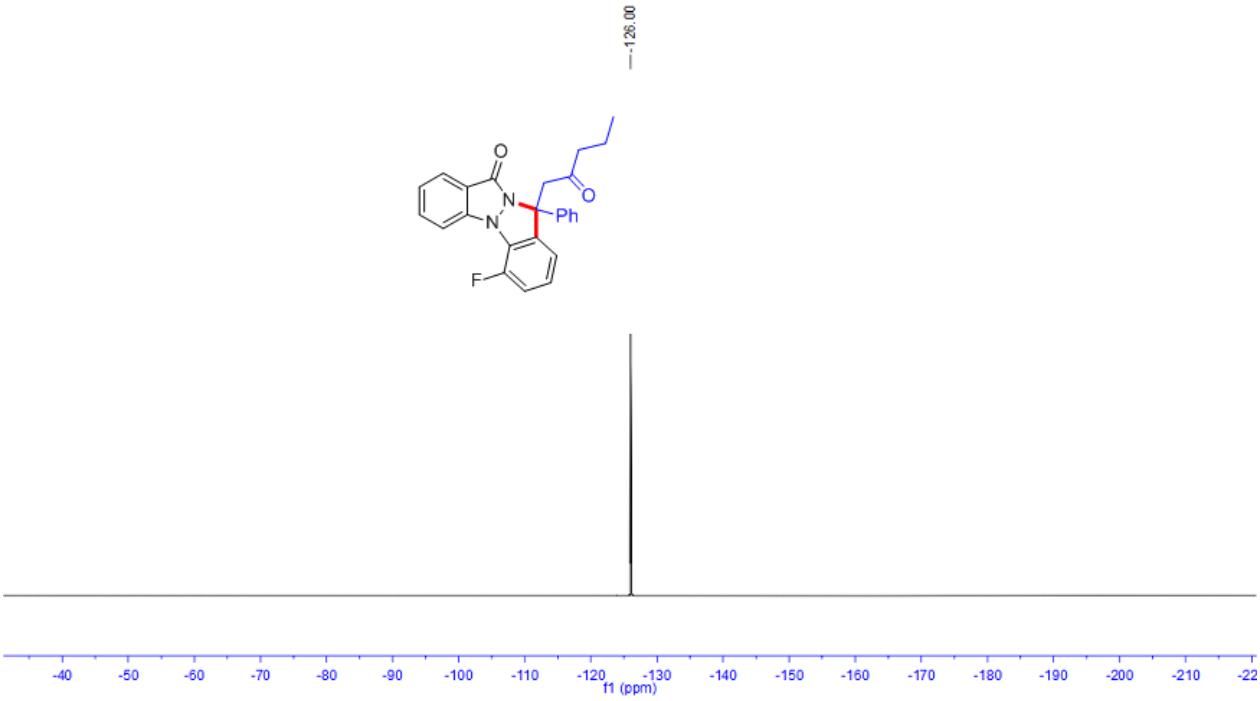
^{13}C NMR spectrum of **3r (**$CDCl_3$, 126 MHz**)**



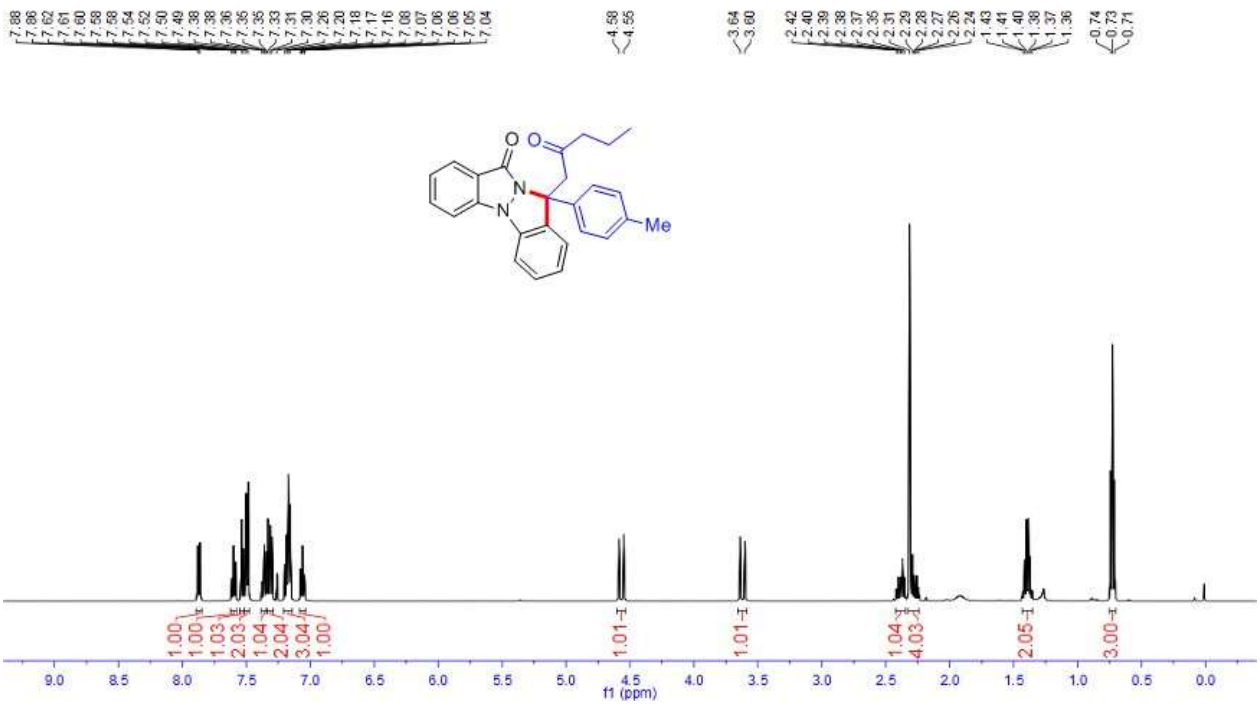
^{1}H NMR spectrum of **3s (**$CDCl_3$, 500 MHz**)**



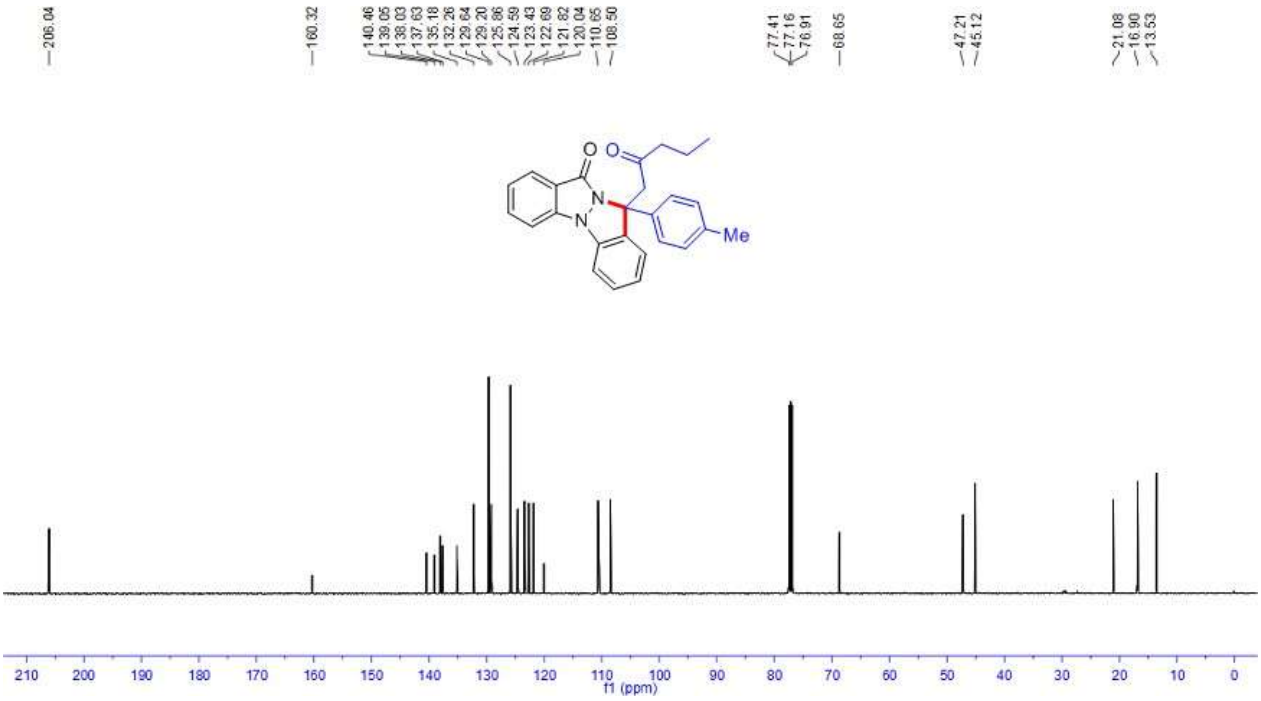
^{13}C NMR spectrum of **3s (**$CDCl_3$, 126 MHz**)**



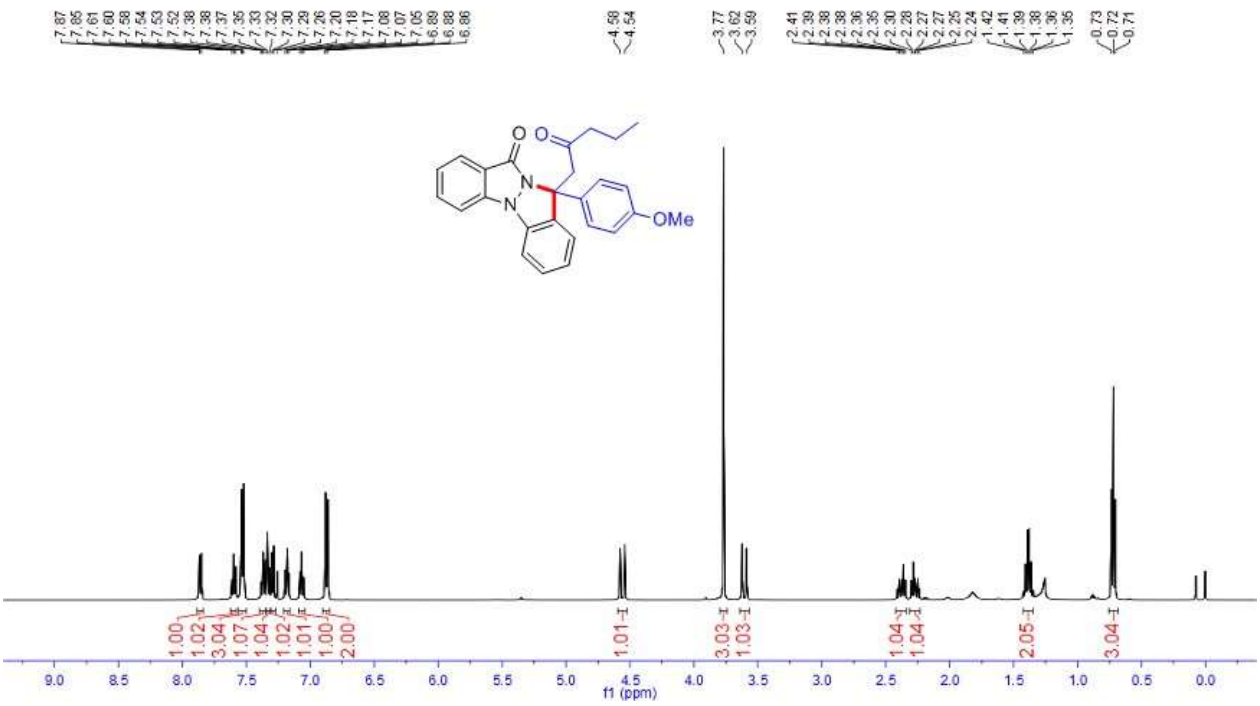
^{19}F NMR spectrum of **3s (**$CDCl_3$, 471 MHz**)**



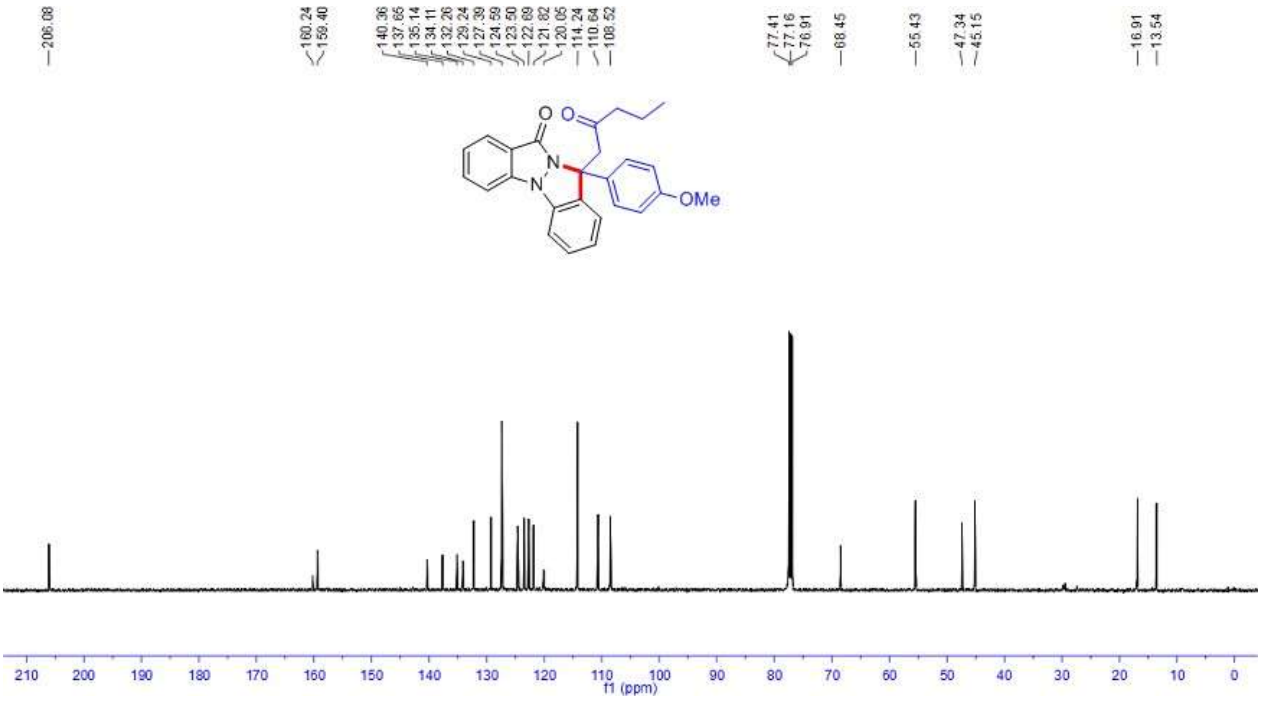
^{1}H NMR spectrum of **3t (**$CDCl_3$, 500 MHz**)**



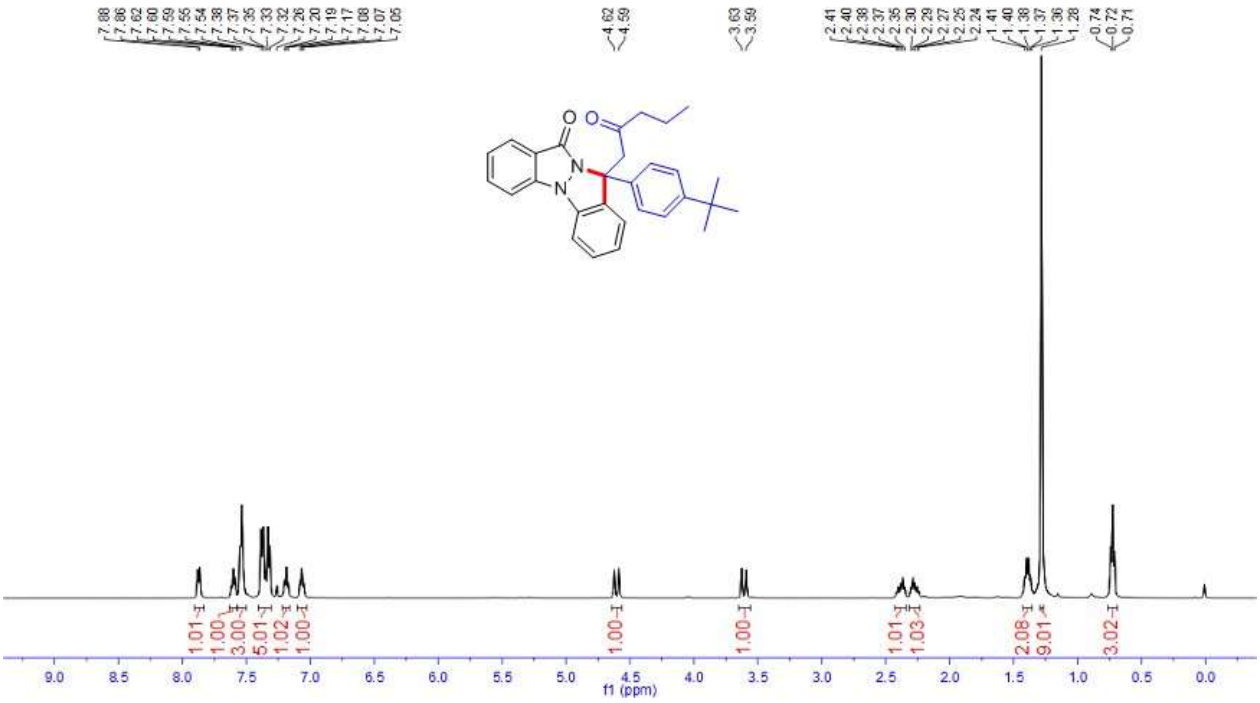
^{13}C NMR spectrum of **3t (**$CDCl_3$, 126 MHz**)**



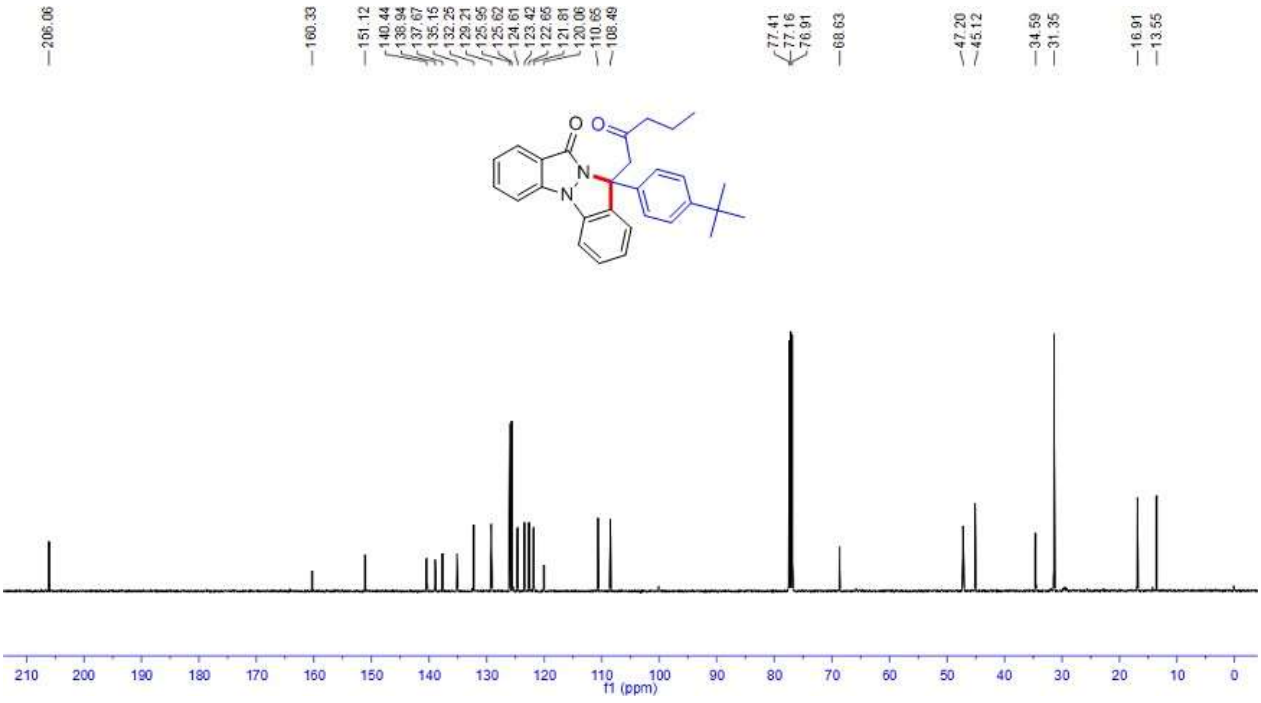
^{1}H NMR spectrum of **3u (**$CDCl_3$, 500 MHz**)**



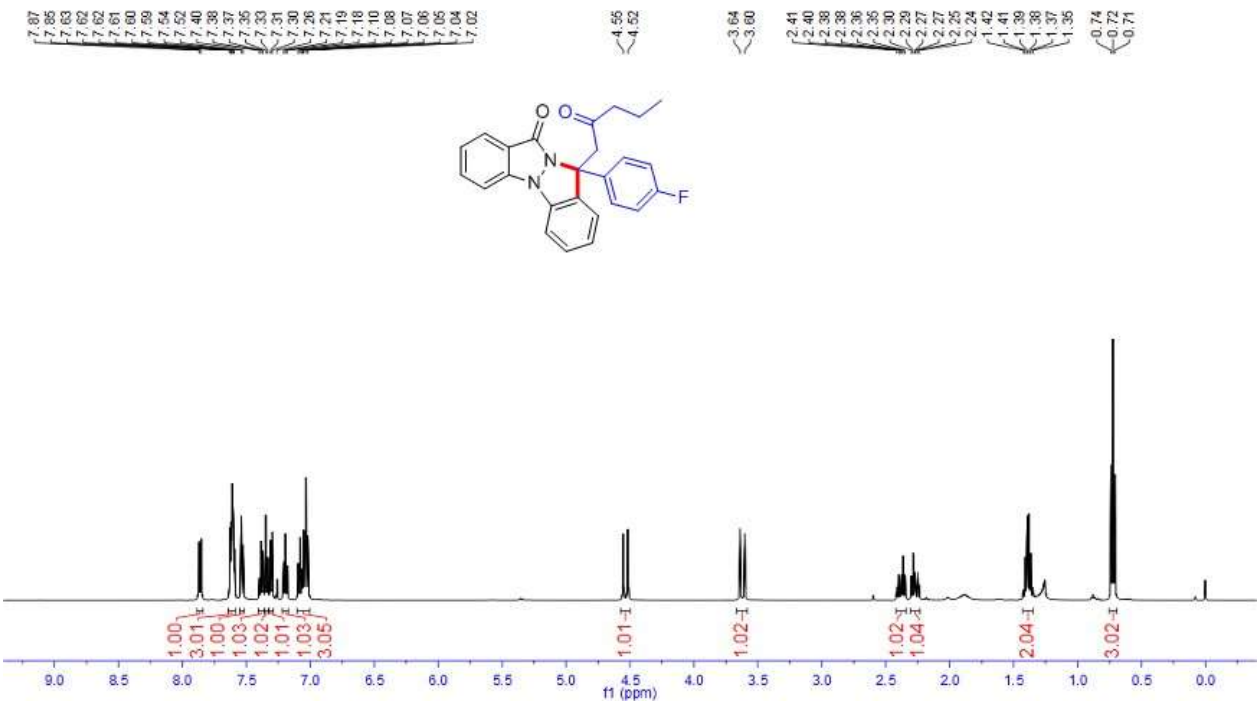
^{13}C NMR spectrum of **3u (**$CDCl_3$, 126 MHz**)**



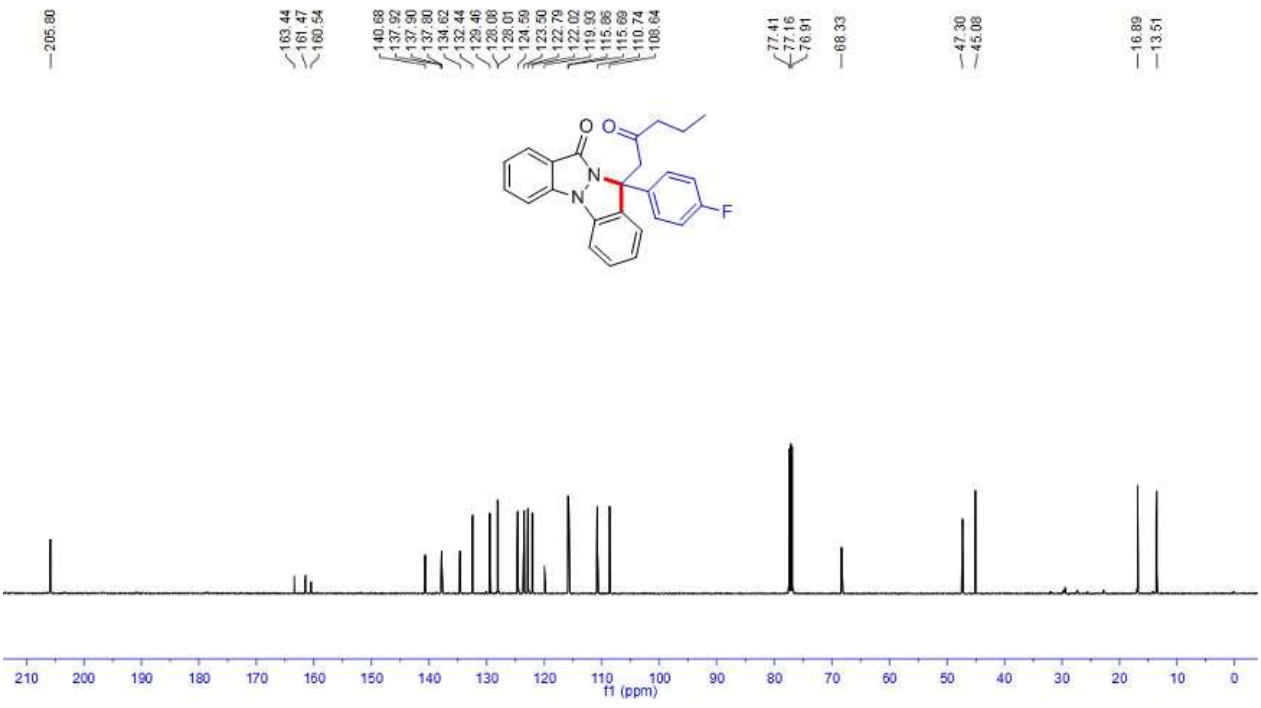
^{1}H NMR spectrum of **3v (**$CDCl_3$, 500 MHz**)**



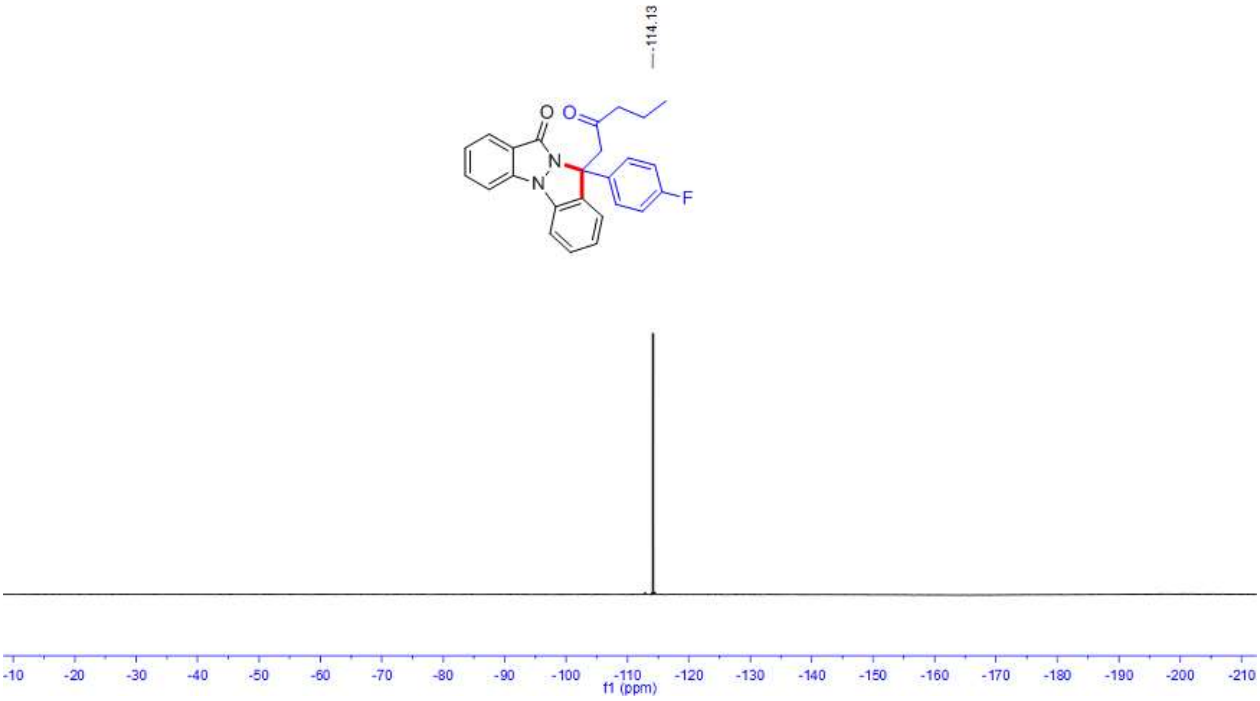
^{13}C NMR spectrum of **3v (**$CDCl_3$, 126 MHz**)**



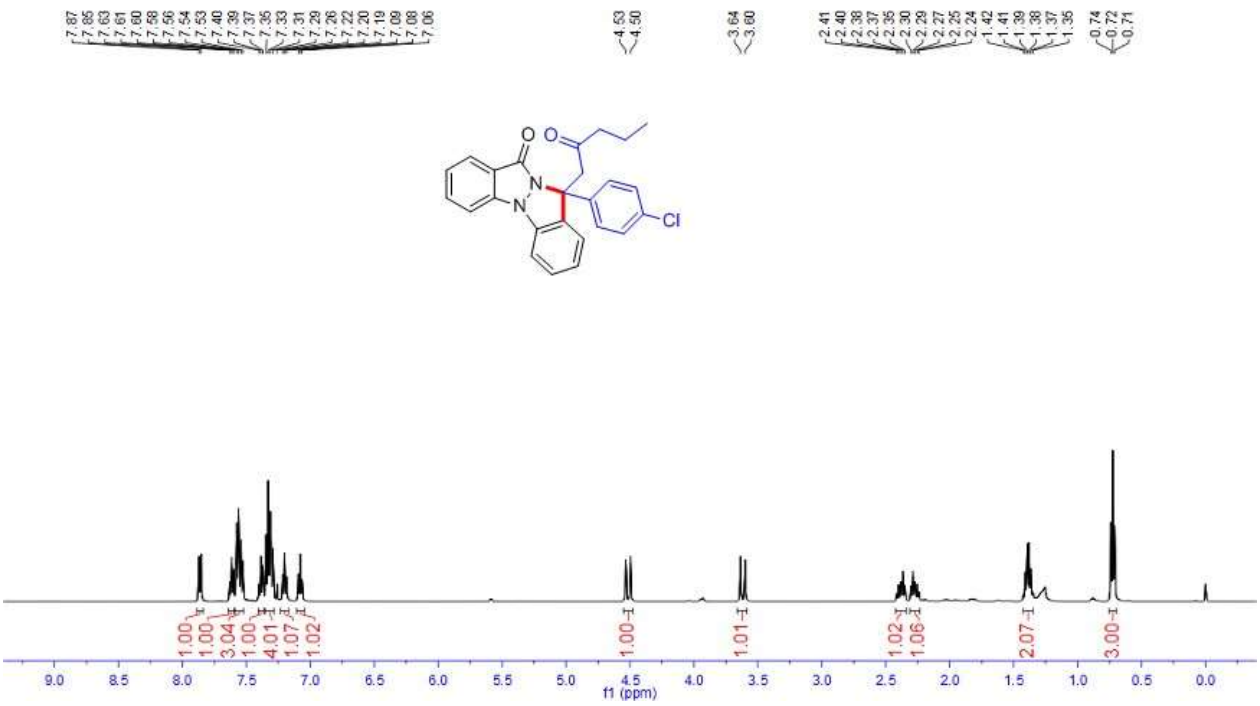
^{1}H NMR spectrum of **3w (**$CDCl_3$, 500 MHz**)**



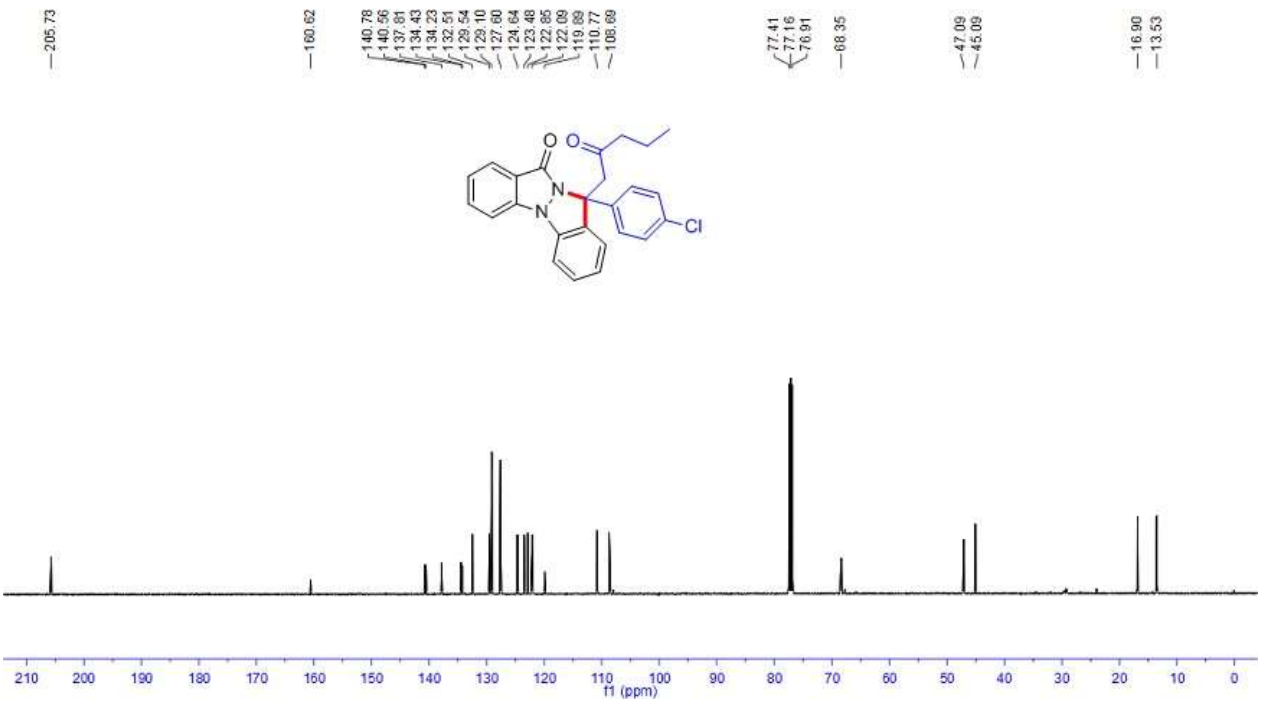
^{13}C NMR spectrum of **3w (**$CDCl_3$, 126 MHz**)**



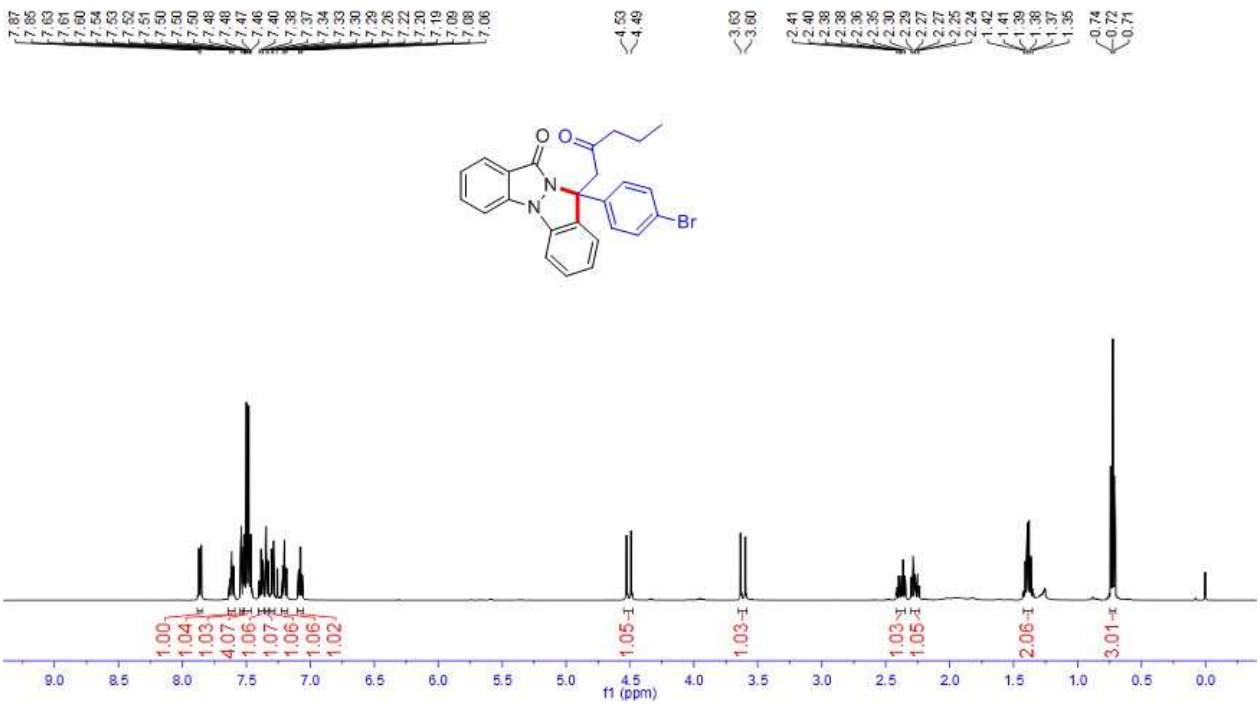
^{19}F NMR spectrum of **3w (**$CDCl_3$, 471 MHz**)**



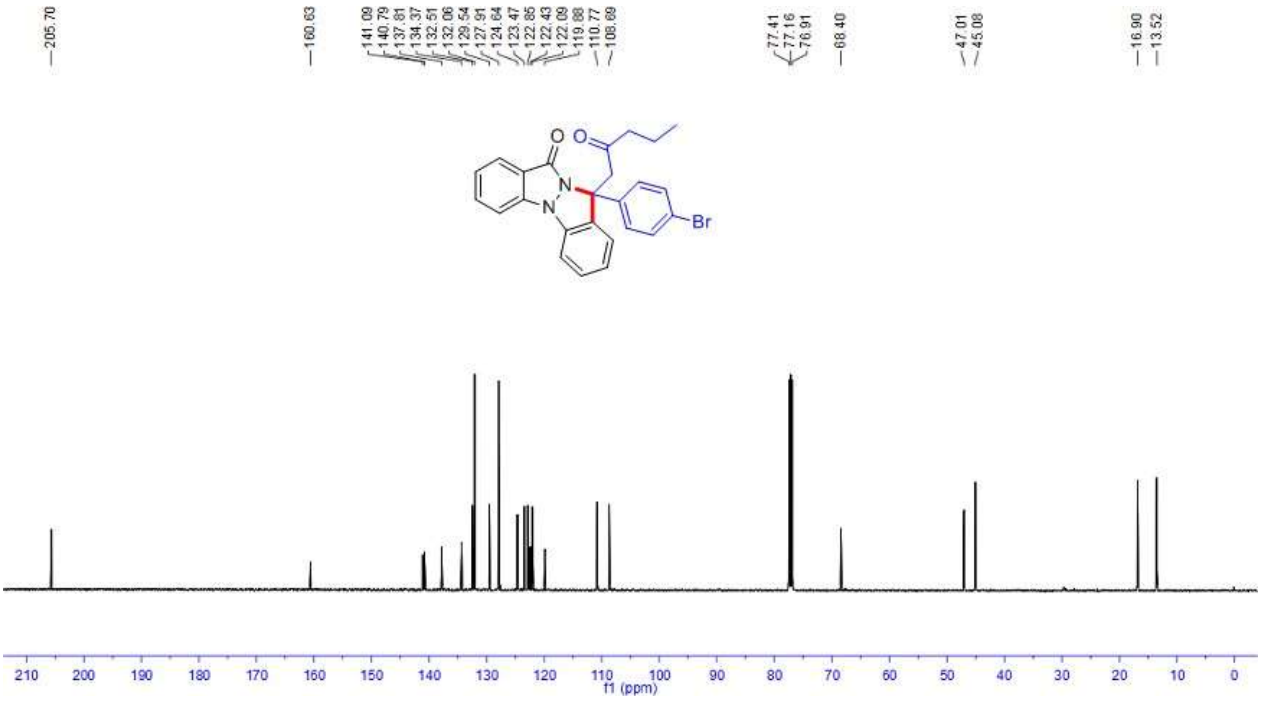
^{1}H NMR spectrum of **3x (**$CDCl_3$, 500 MHz**)**



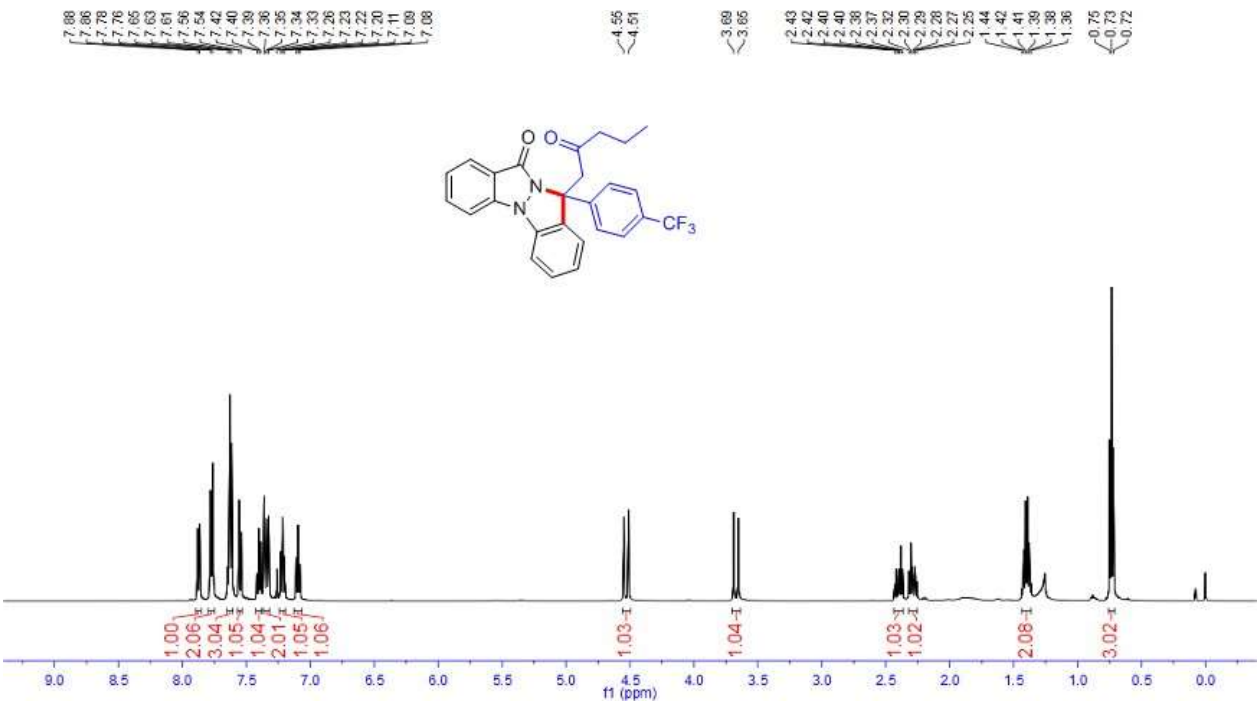
^{13}C NMR spectrum of **3x (**$CDCl_3$, 126 MHz**)**



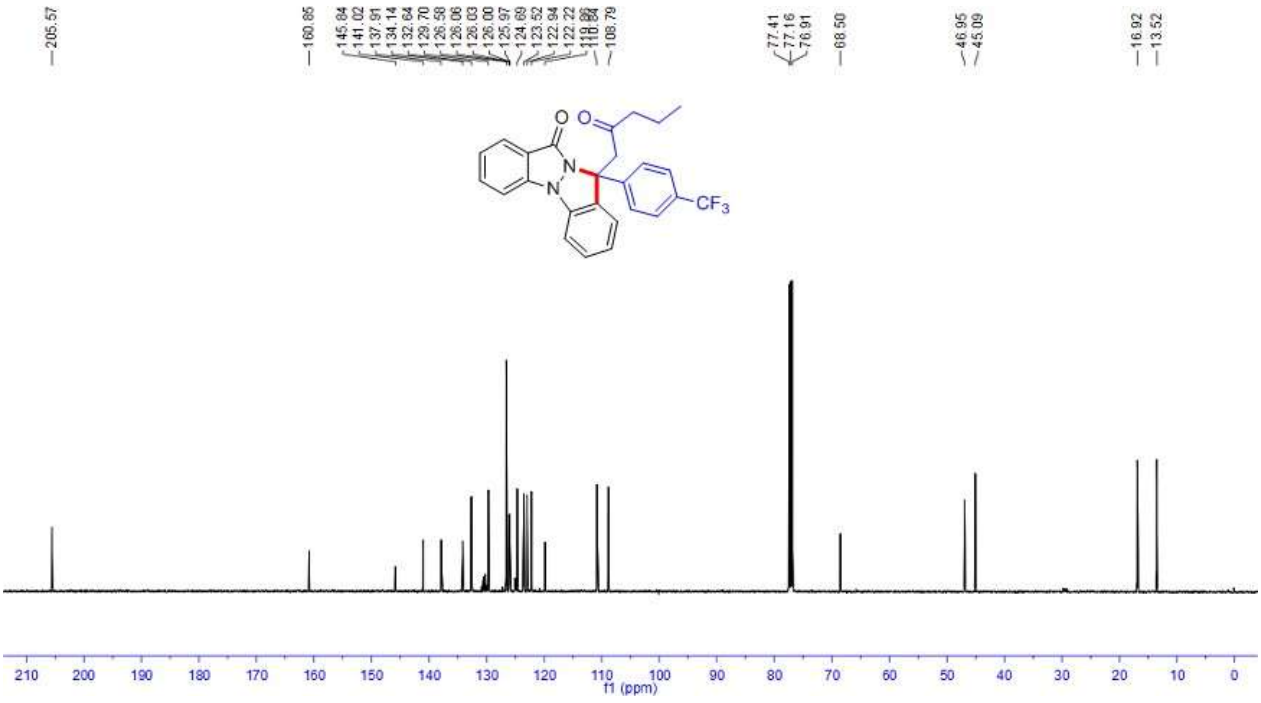
^{1}H NMR spectrum of **3y (**$CDCl_3$, 500 MHz**)**



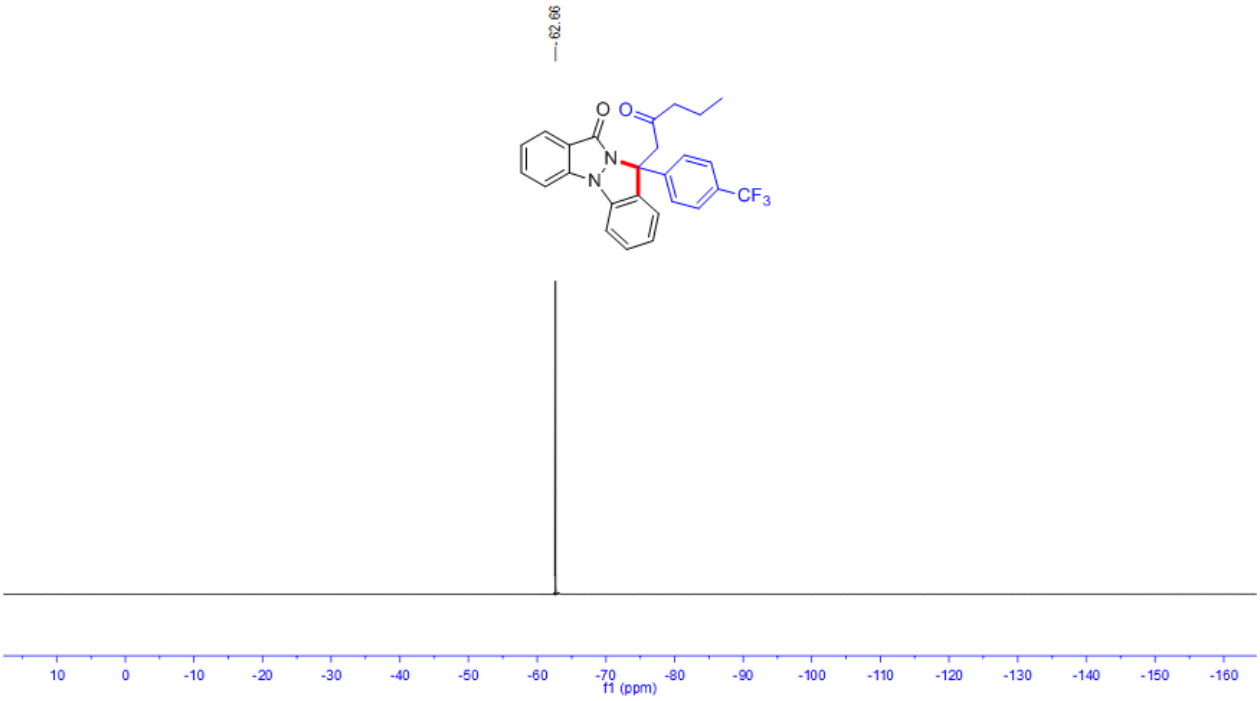
^{13}C NMR spectrum of **3y (**$CDCl_3$, 126 MHz**)**



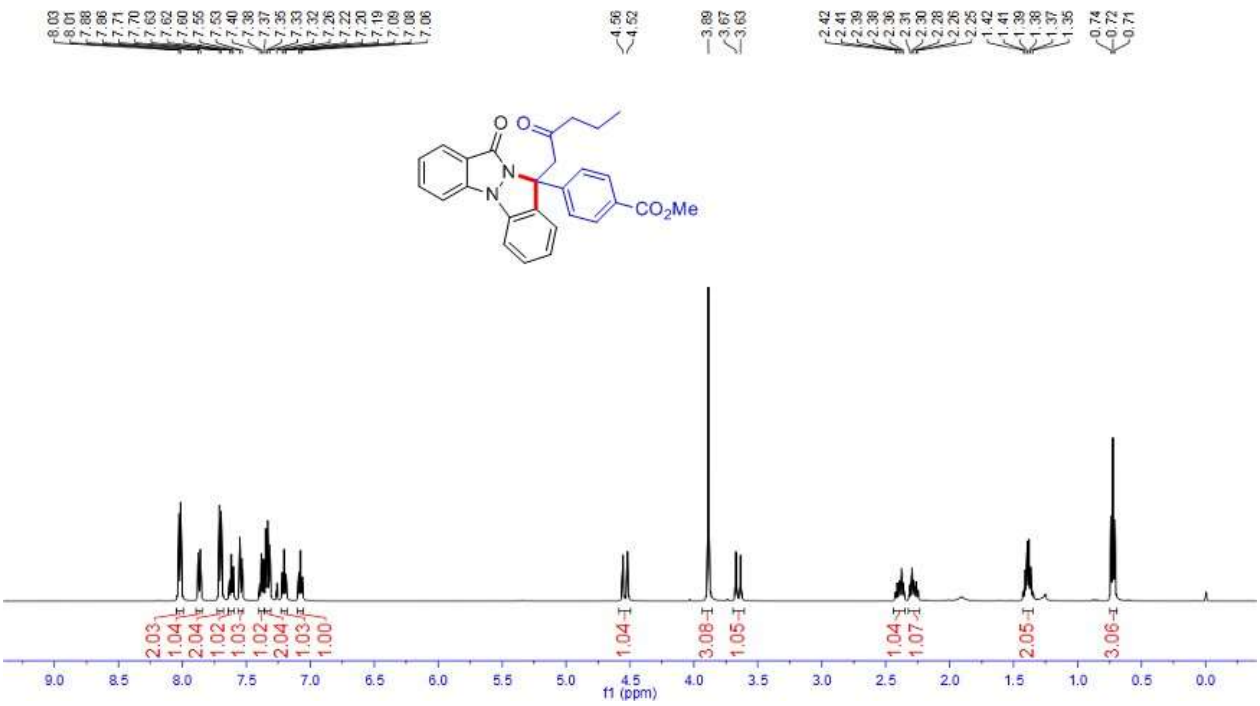
^{1}H NMR spectrum of **3z (**$CDCl_3$, 500 MHz**)**



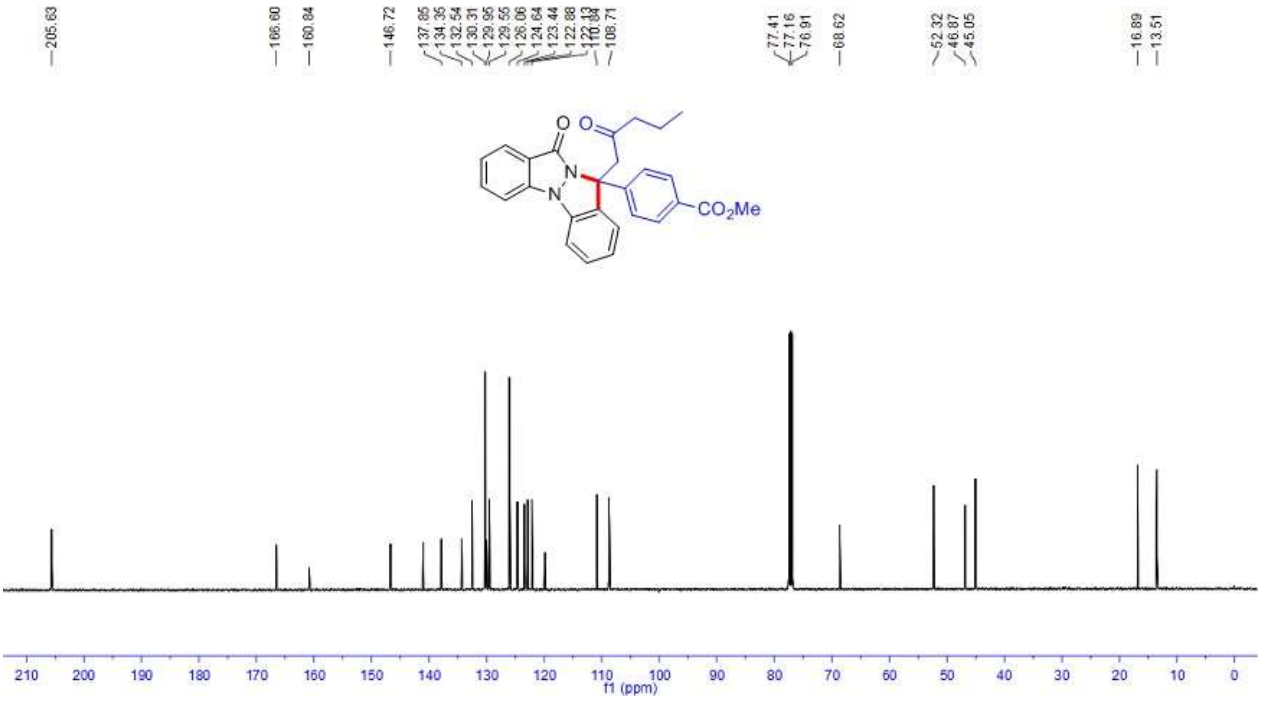
^{13}C NMR spectrum of **3z (**$CDCl_3$, 126 MHz**)**



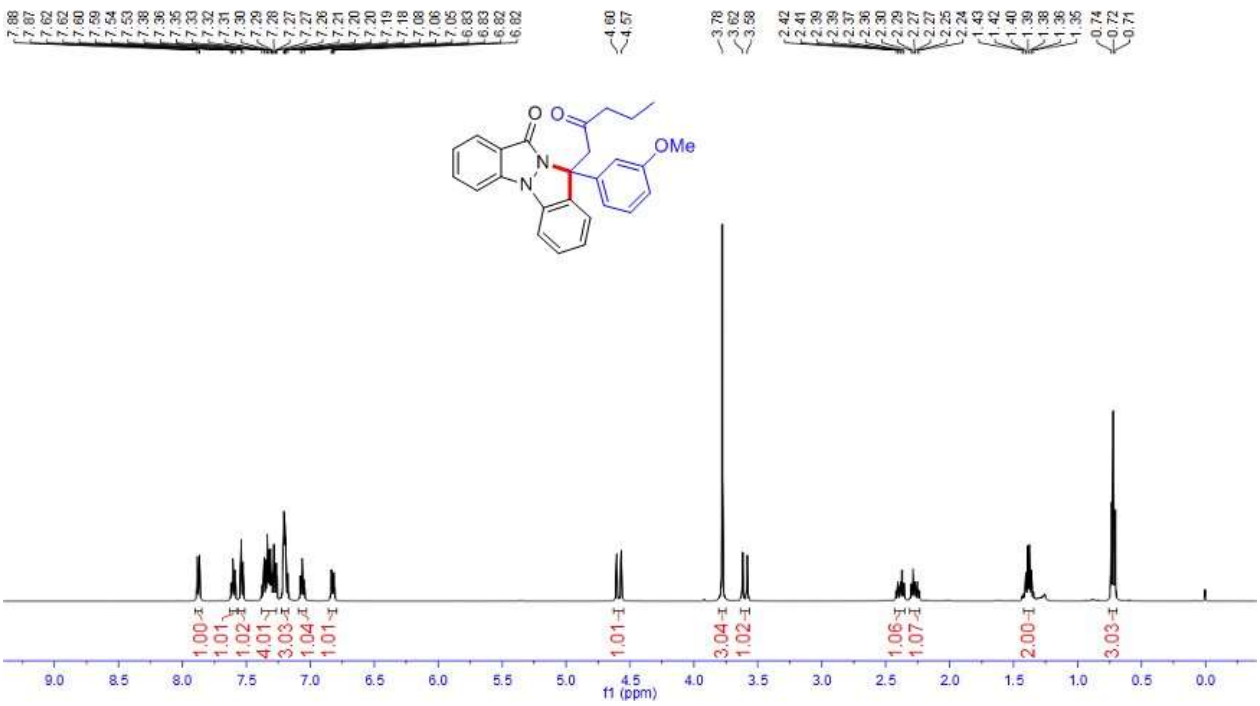
^{19}F NMR spectrum of **3z (**$CDCl_3$, 471 MHz**)**



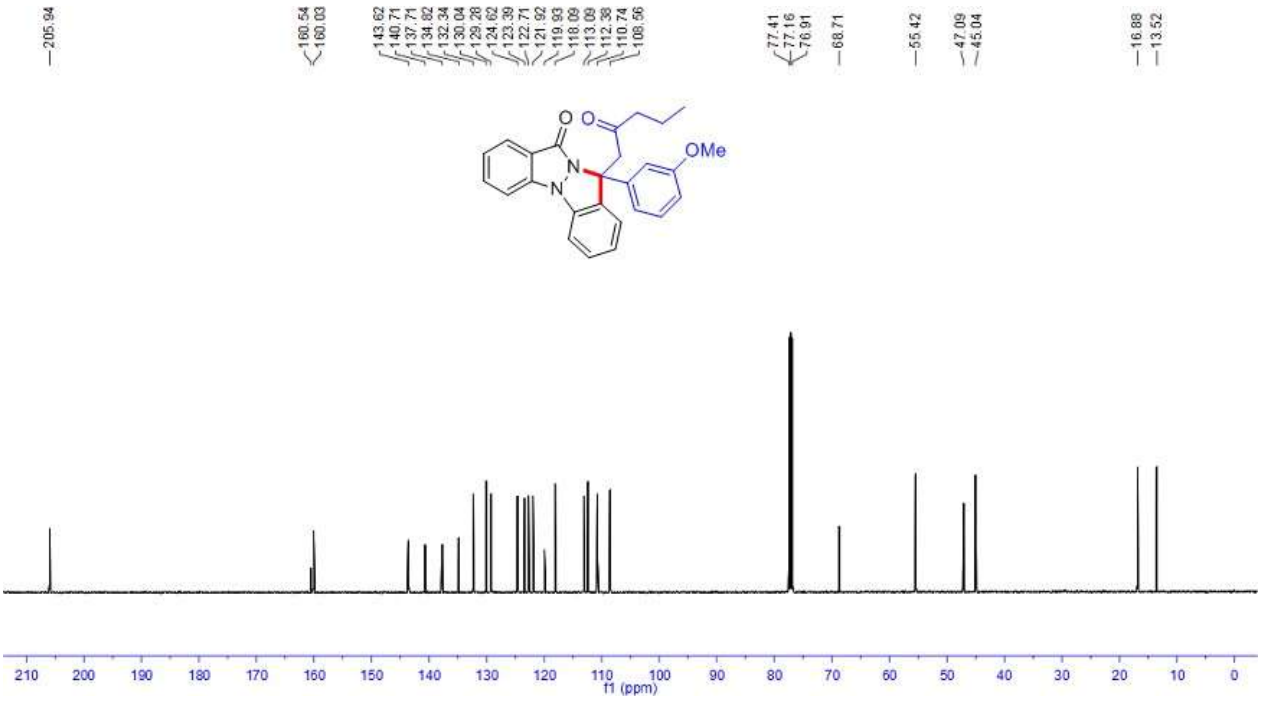
^{1}H NMR spectrum of **3aa (**$CDCl_3$, 500 MHz**)**



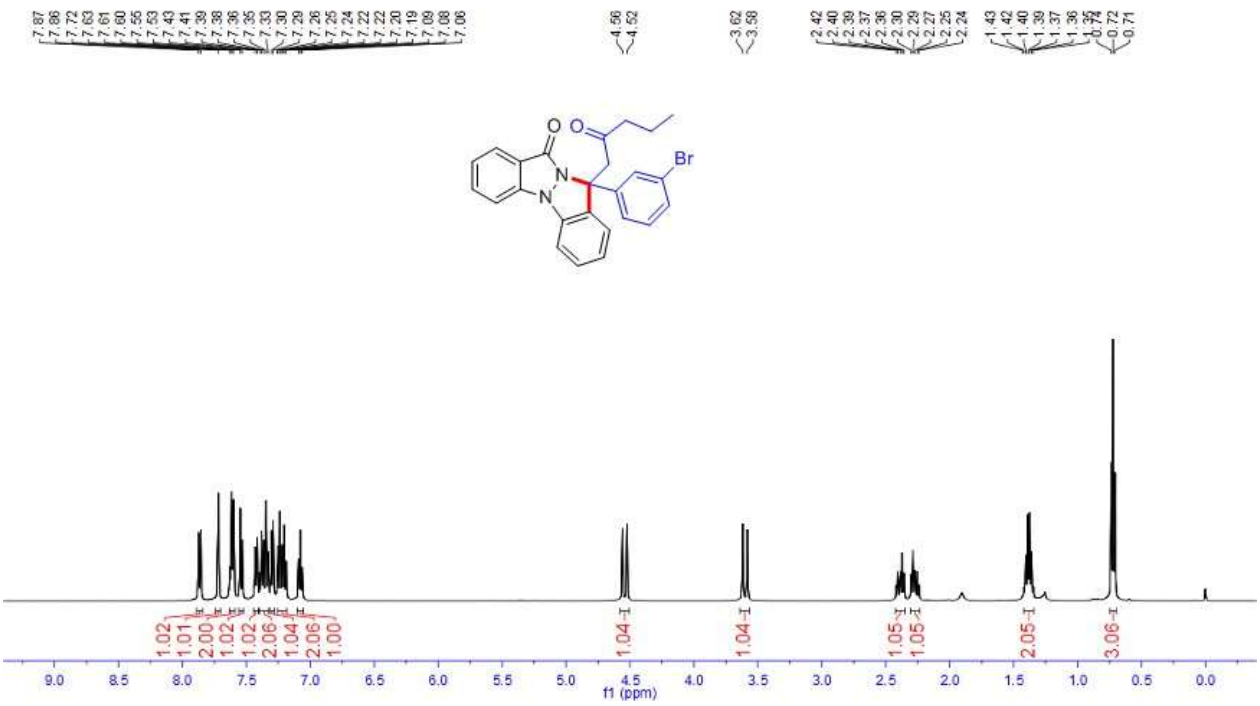
^{13}C NMR spectrum of **3aa (**$CDCl_3$, 126 MHz**)**



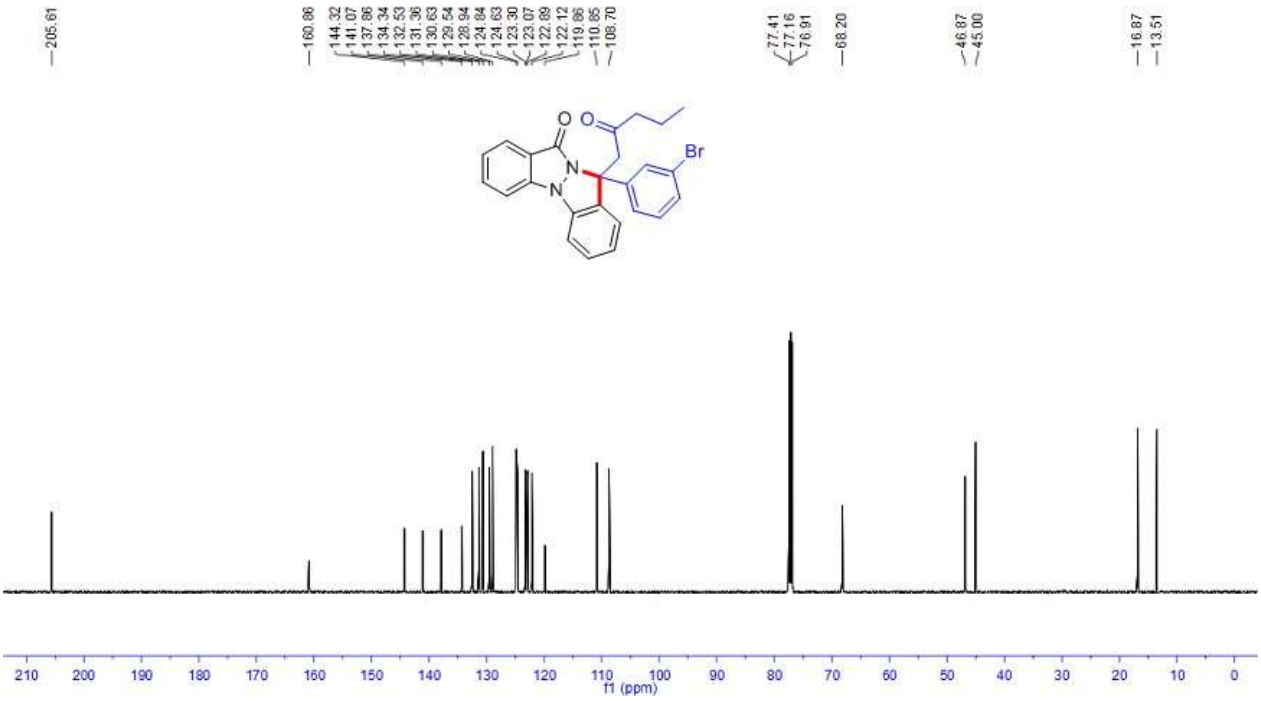
^{1}H NMR spectrum of **3ab (**$CDCl_3$, 500 MHz**)**



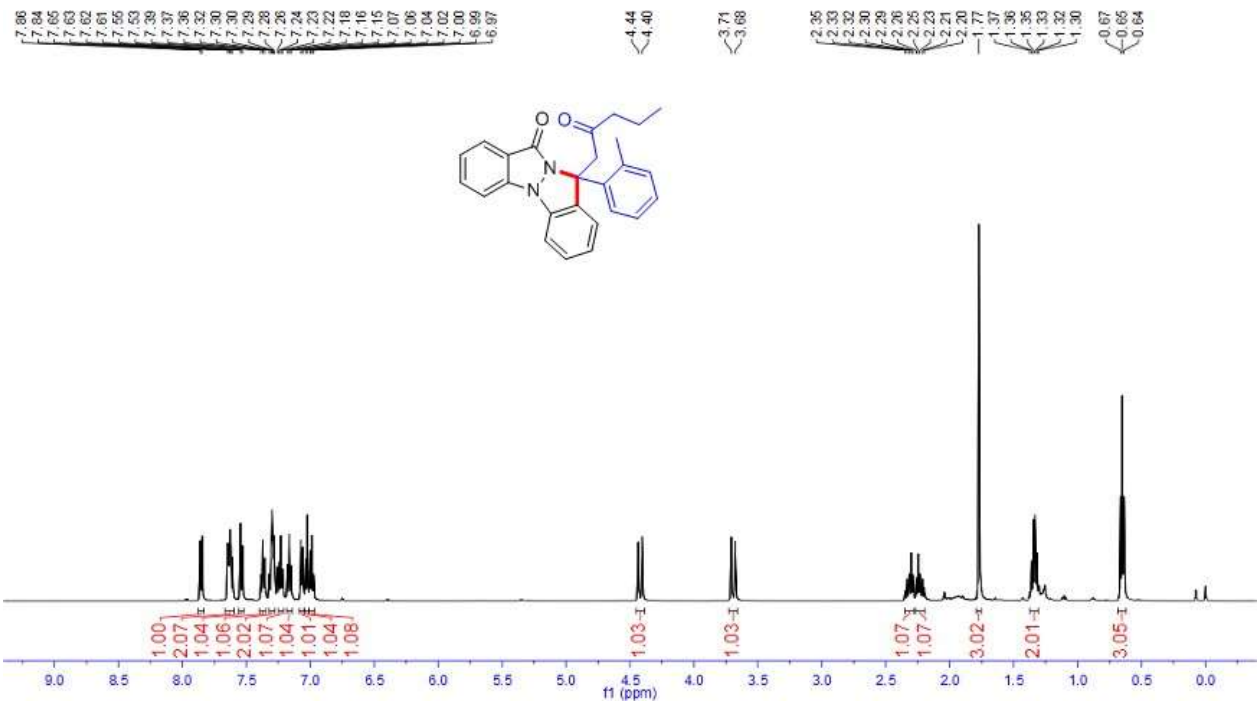
^{13}C NMR spectrum of **3ab (**$CDCl_3$, 126 MHz**)**



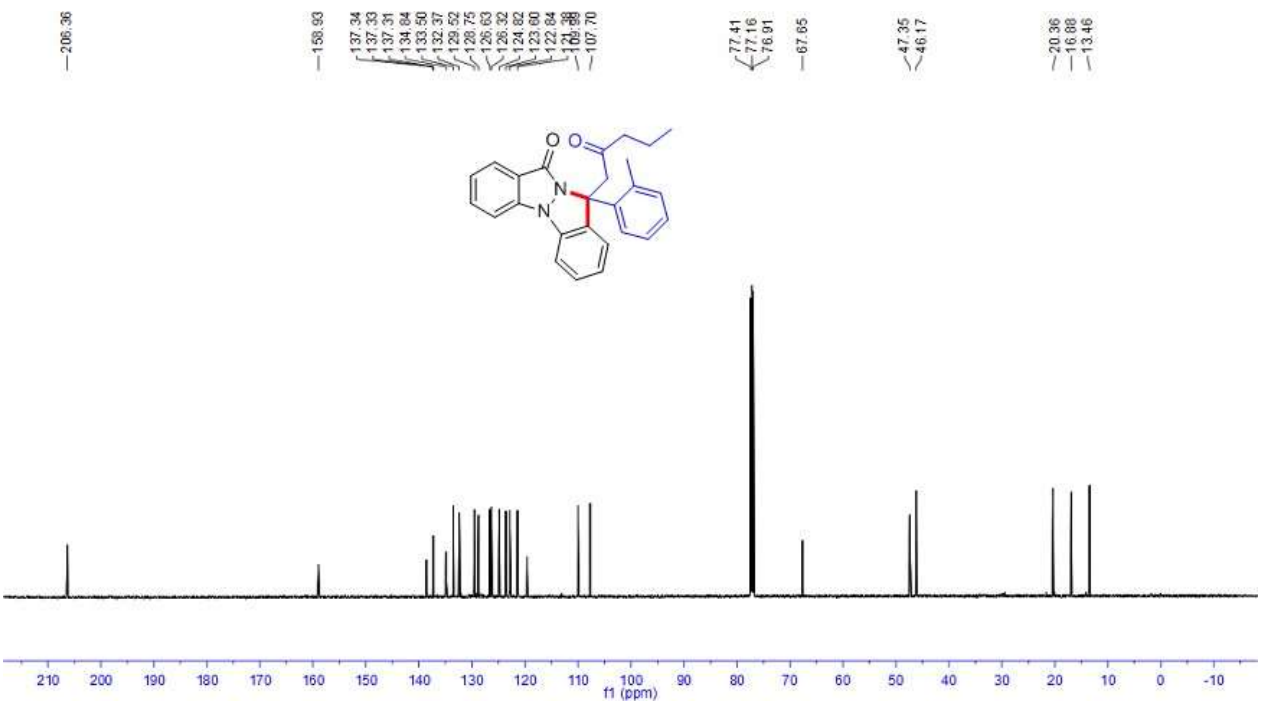
^{1}H NMR spectrum of **3ac (**$CDCl_3$, 500 MHz**)**



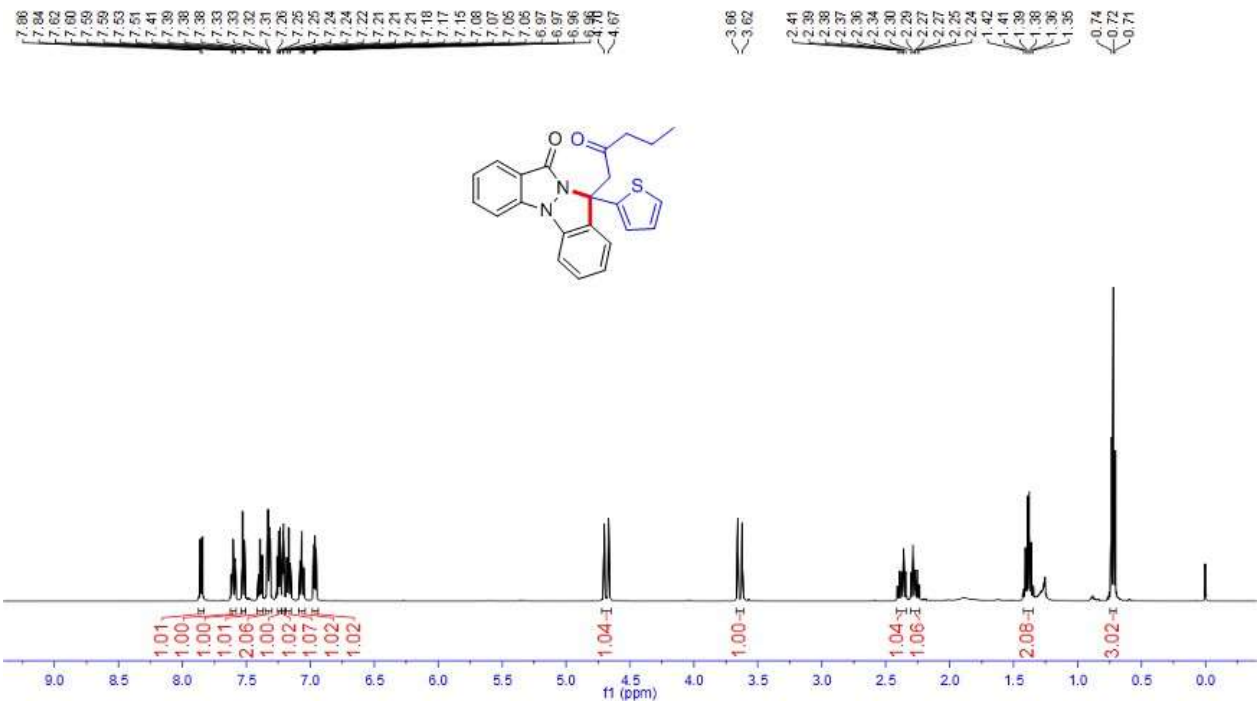
^{13}C NMR spectrum of **3ac (**$CDCl_3$, 126 MHz**)**



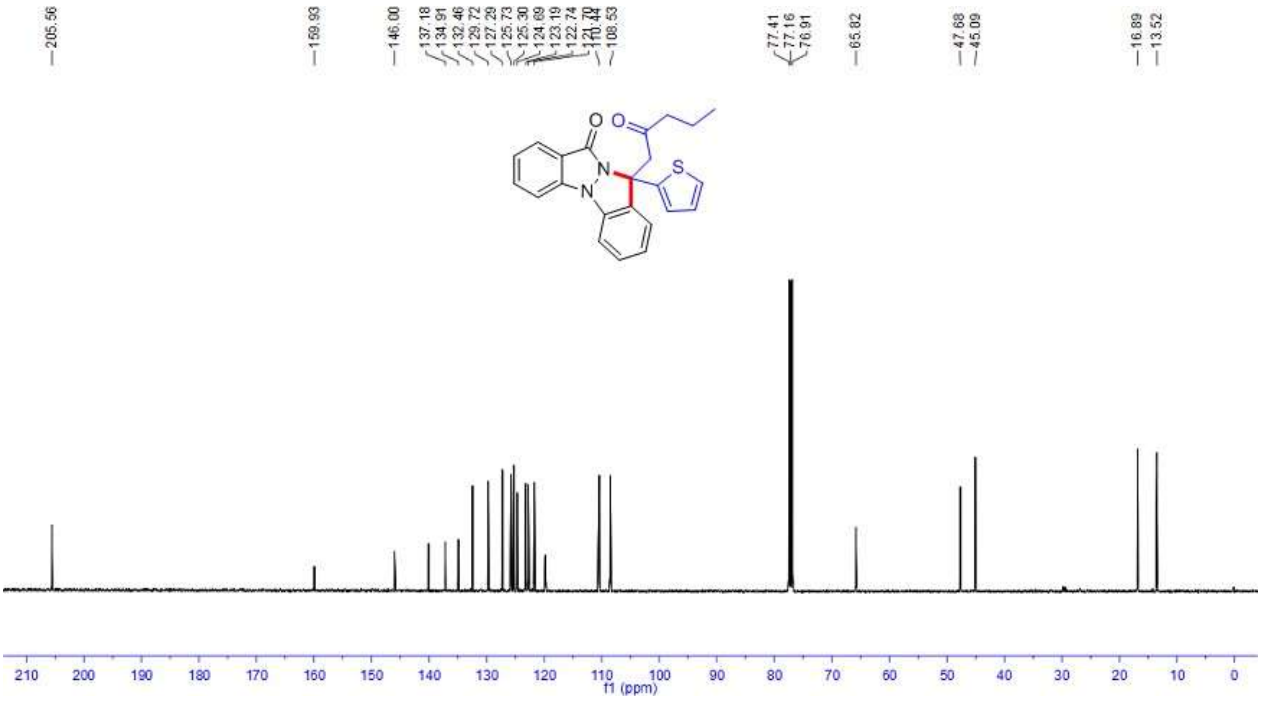
^{1}H NMR spectrum of **3ad (**$CDCl_3$, 500 MHz**)**



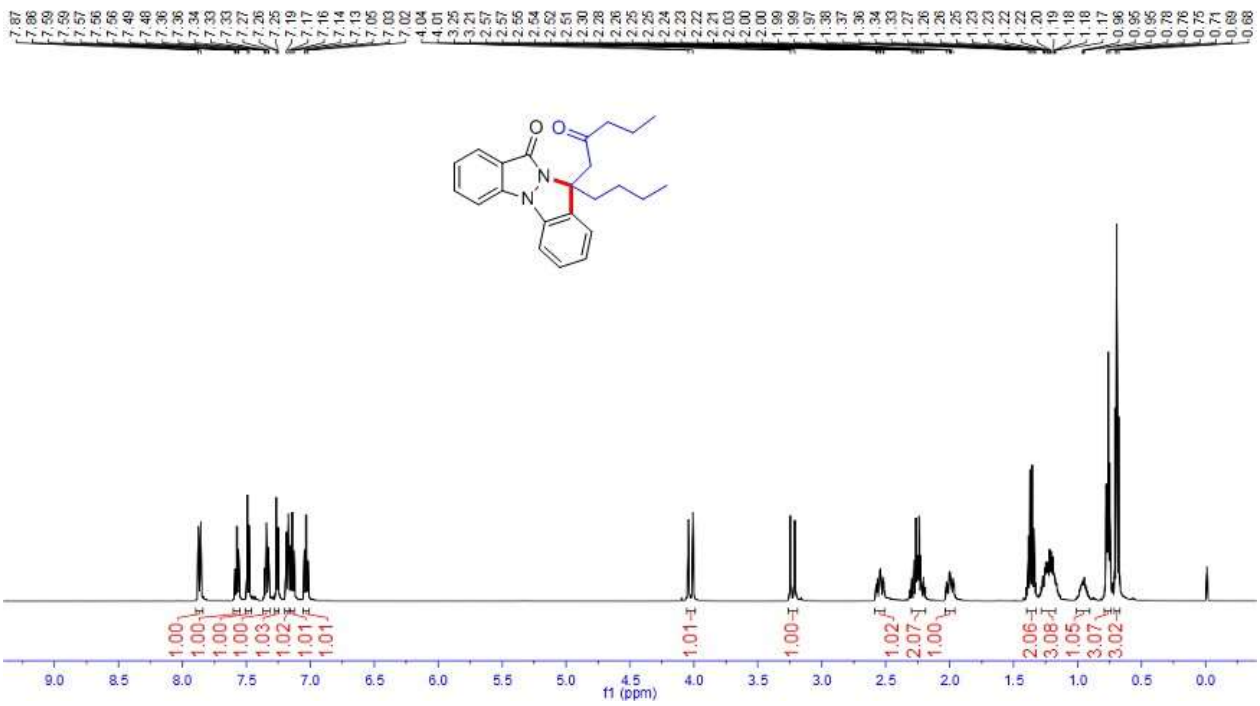
^{13}C NMR spectrum of **3ad (**$CDCl_3$, 126 MHz**)**



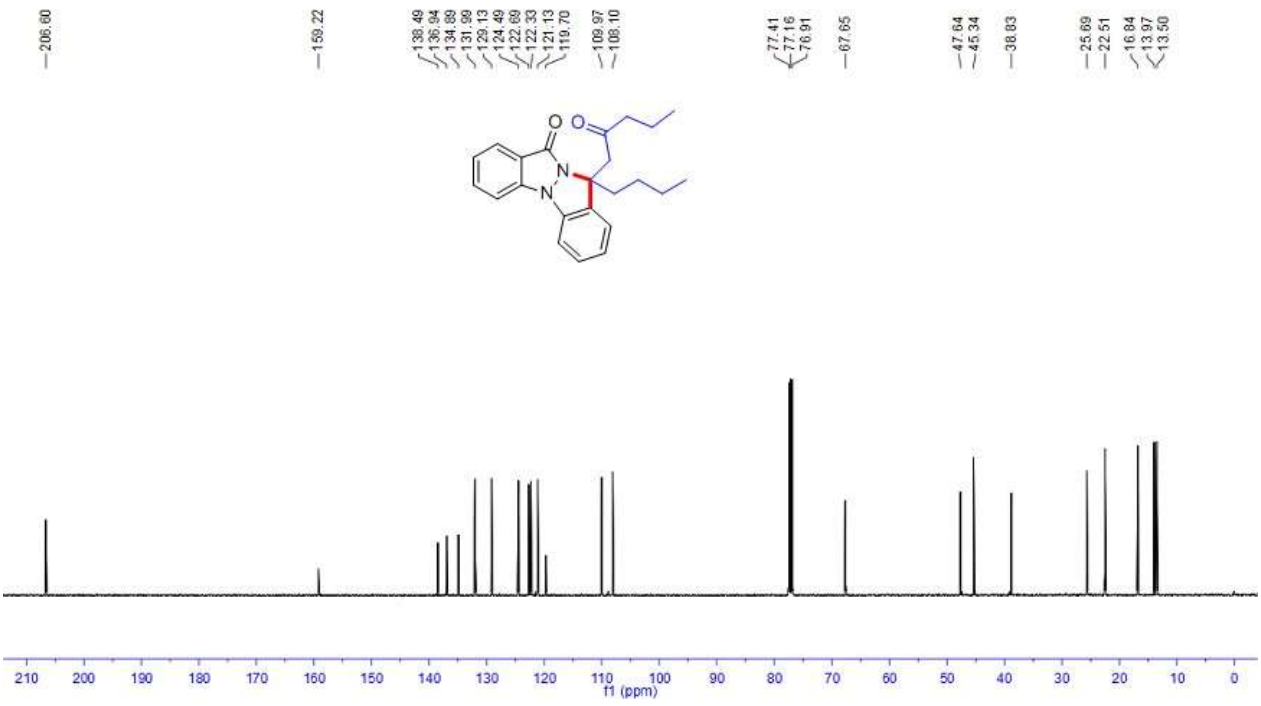
^{1}H NMR spectrum of **3ae (**$CDCl_3$, 500 MHz**)**



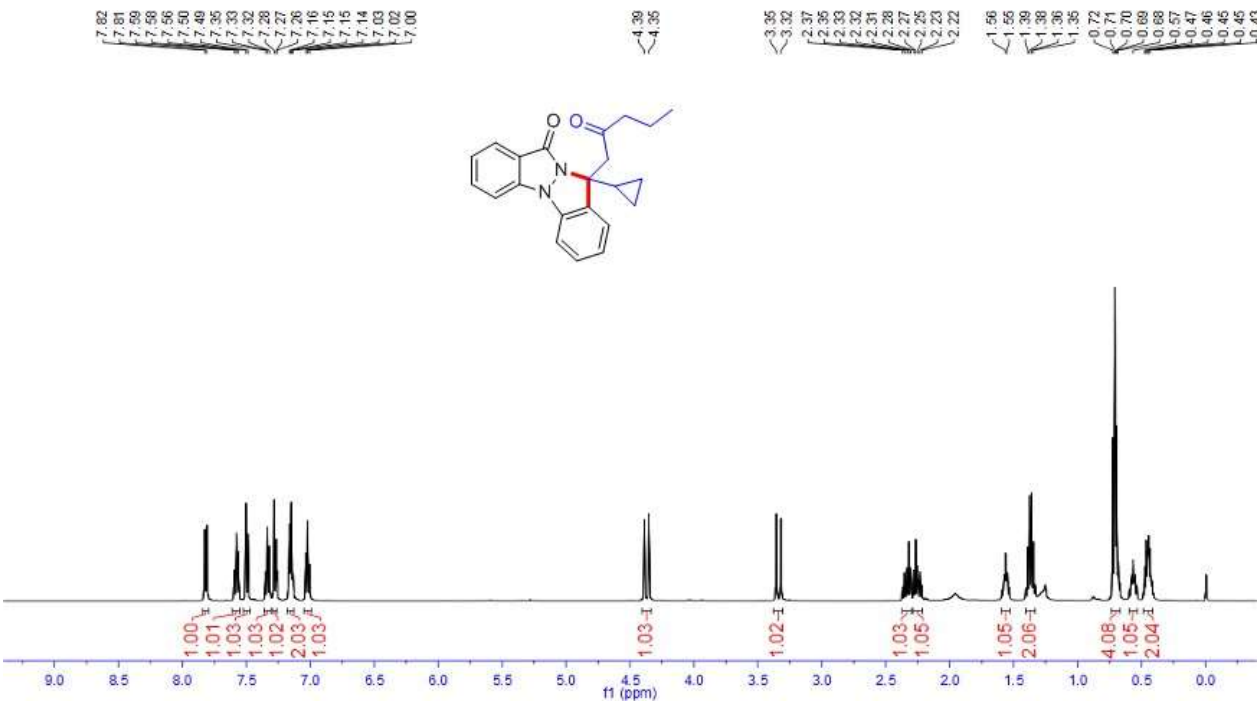
^{13}C NMR spectrum of **3ae (**$CDCl_3$, 126 MHz**)**



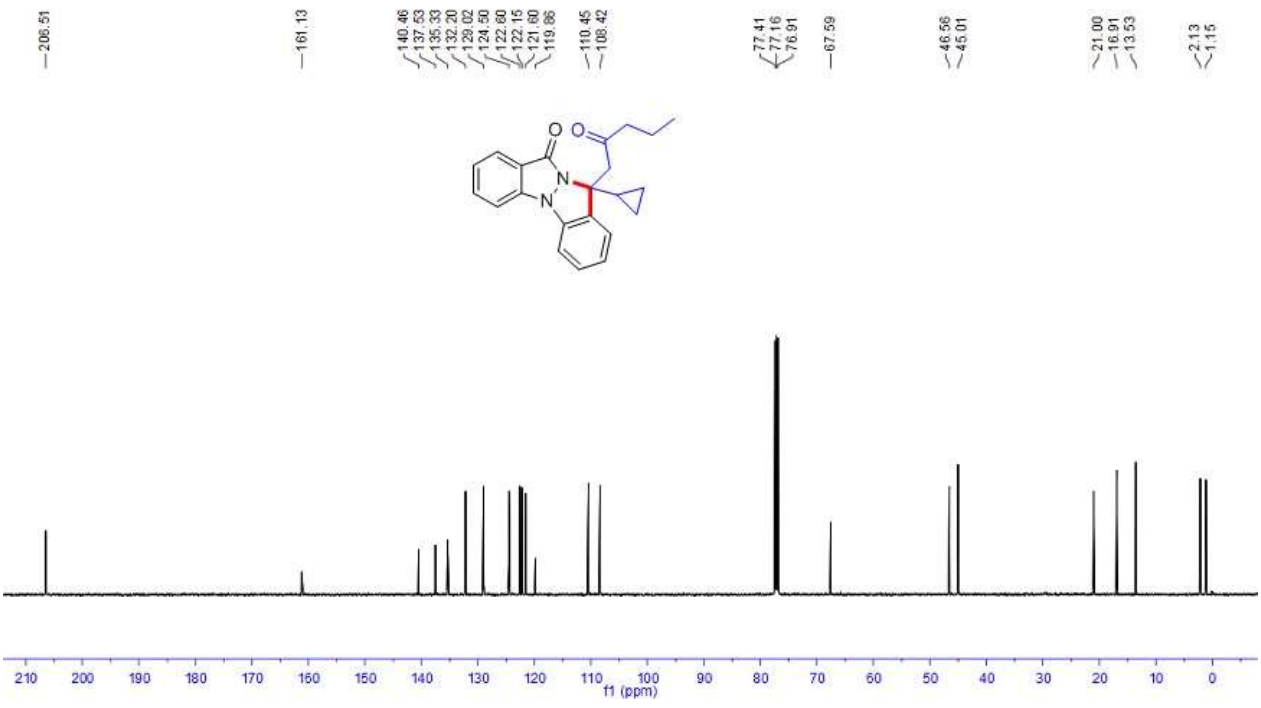
^{1}H NMR spectrum of **3af (**$CDCl_3$, 500 MHz**)**



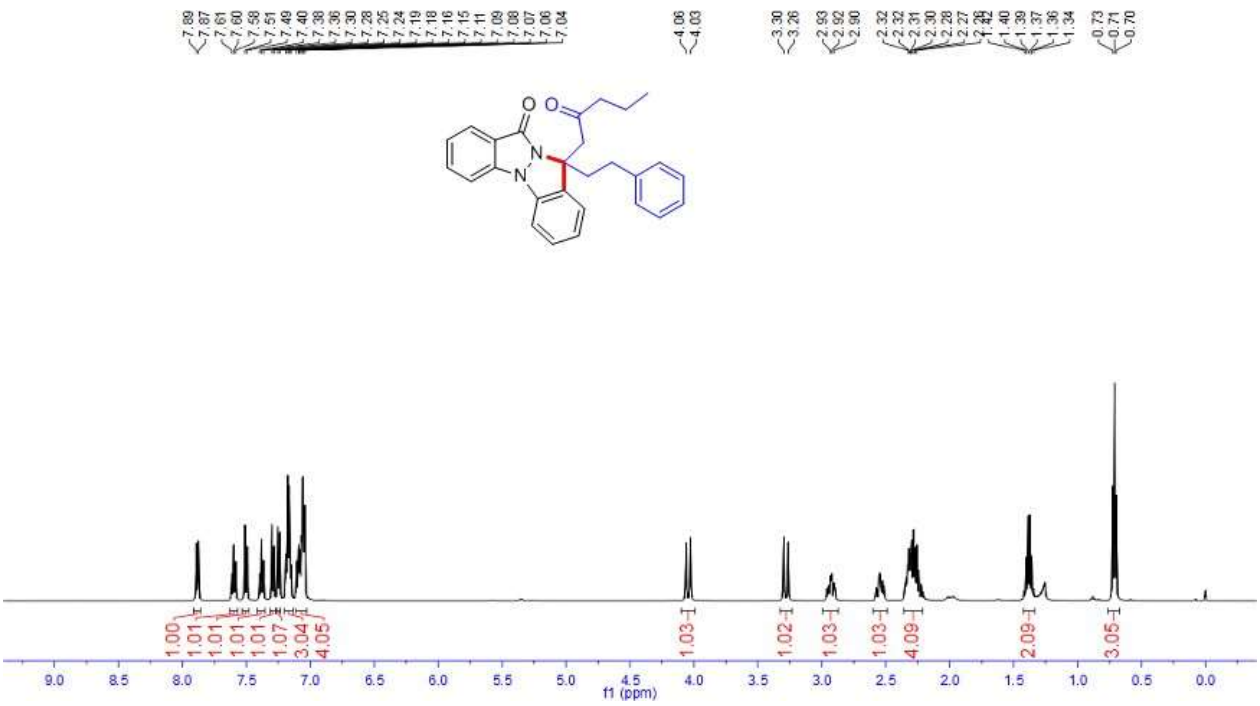
^{13}C NMR spectrum of **3af (**$CDCl_3$, 126 MHz**)**



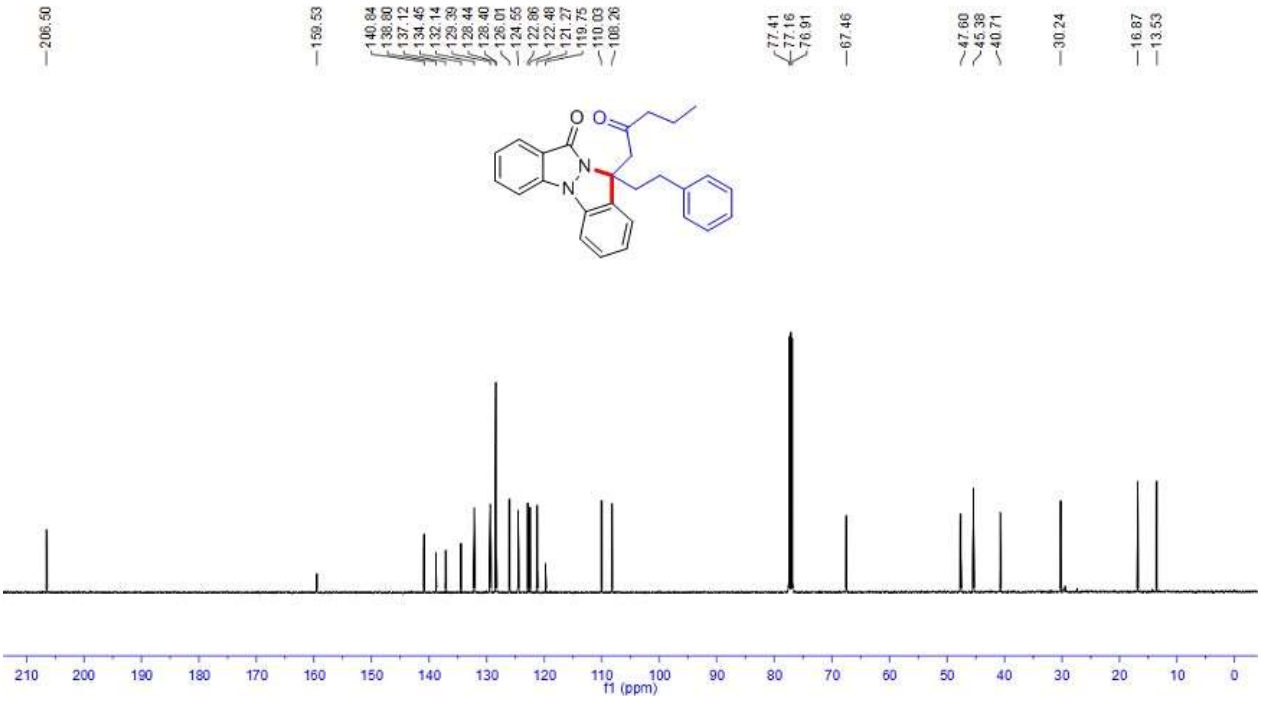
^{1}H NMR spectrum of **3ag (**$CDCl_3$, 500 MHz**)**



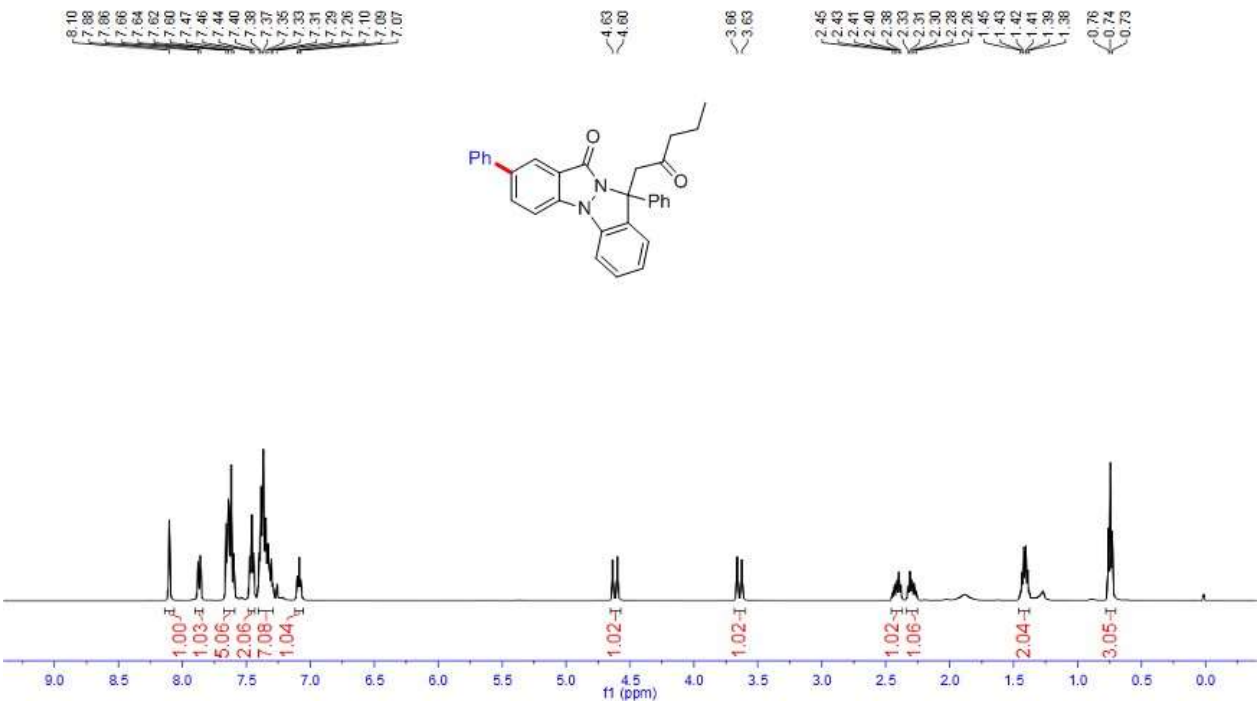
^{13}C NMR spectrum of **3ag (**$CDCl_3$, 126 MHz**)**



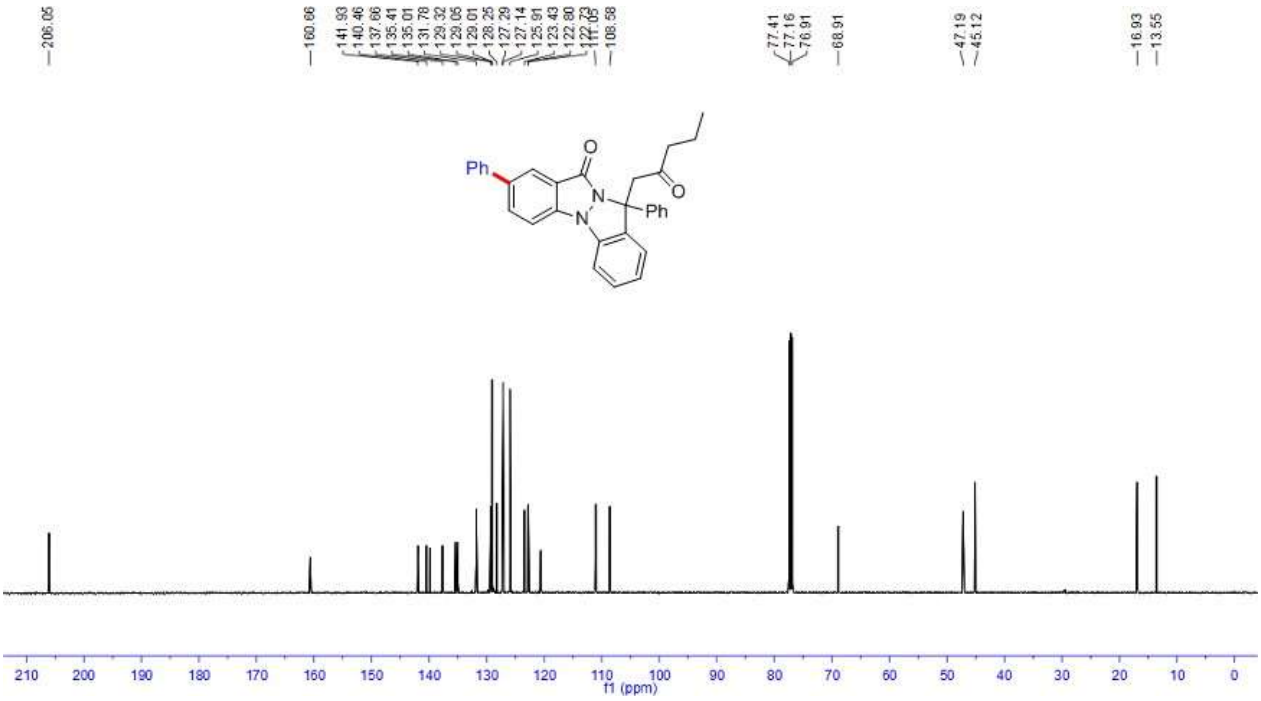
^{1}H NMR spectrum of **3ah (**$CDCl_3$, 500 MHz**)**



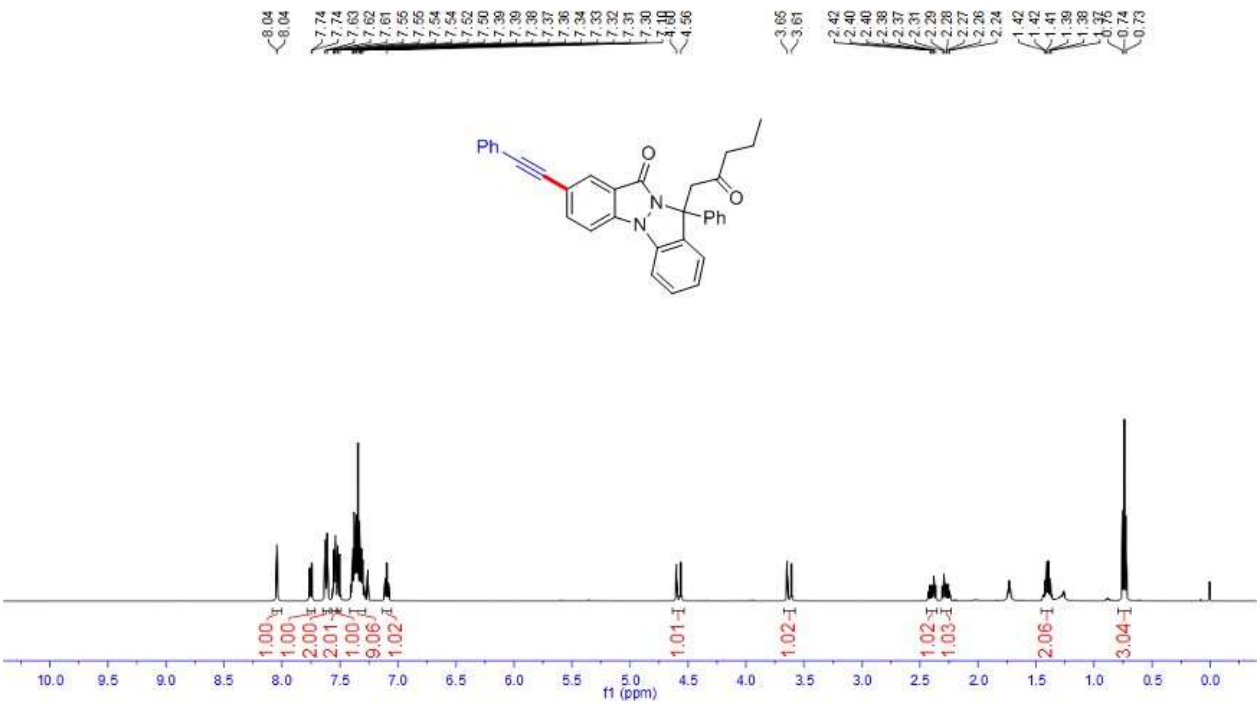
^{13}C NMR spectrum of **3ah (**$CDCl_3$, 126 MHz**)**



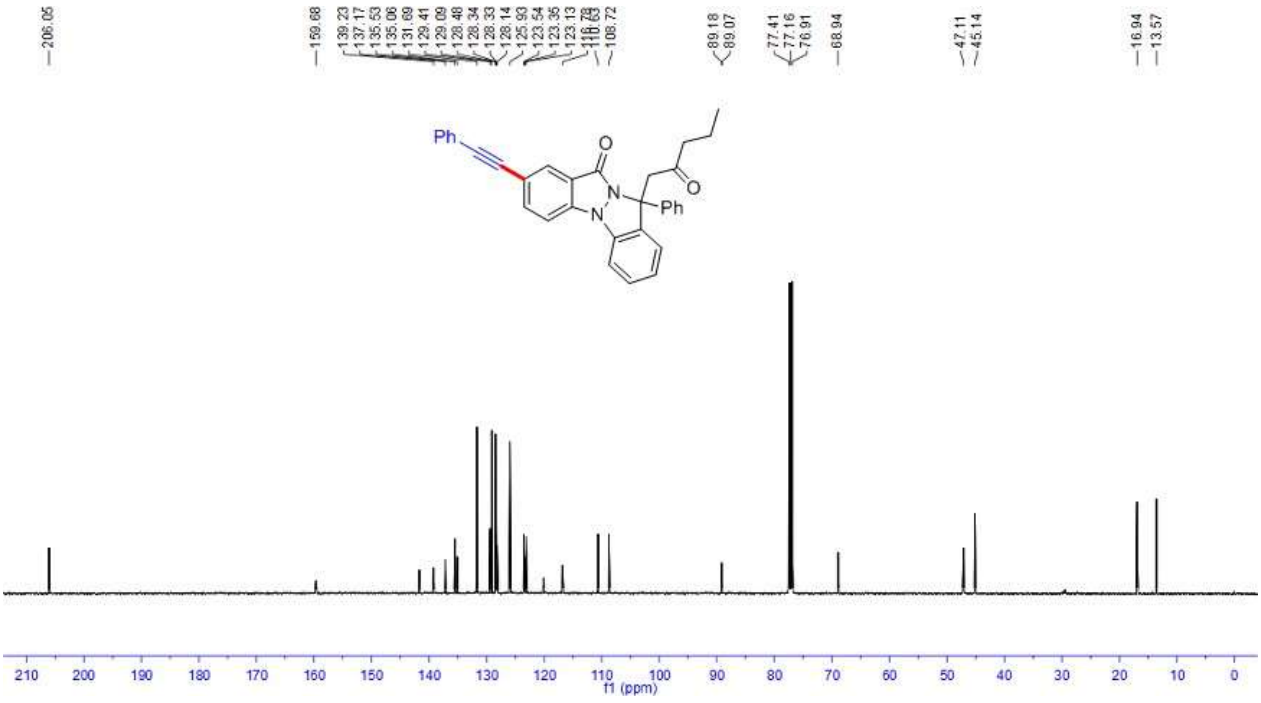
^{1}H NMR spectrum of **4 (**$CDCl_3$, 500 MHz**)**



^{13}C NMR spectrum of **4 (**$CDCl_3$, 126 MHz**)**



^{1}H NMR spectrum of **5 (**$CDCl_3$, 500 MHz**)**



^{13}C NMR spectrum of **5 (**$CDCl_3$, 126 MHz**)**

9. The crystallographic data of 3m

The single crystals of **3m** suitable for X-ray diffraction analysis were grown by slow evaporation of acetone solution of **3m**. ORTEP drawing of **3m** with 50% probability ellipsoids is shown in Figure S1. Its crystal parameters and refinement metrics are summarized in Table S1.

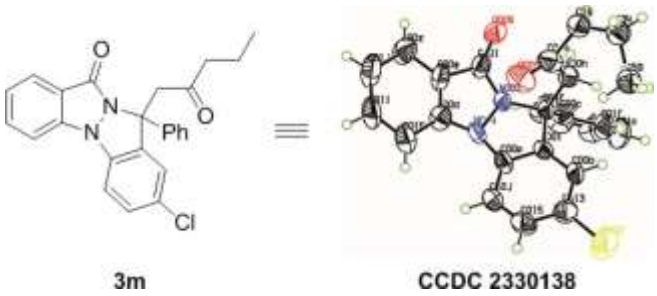


Figure S1. ORTEP drawing of **3m** with thermal ellipsoids at 50% probability.

Table S1Crystal data and structure refinement for 3m

Identification code	2_sq	
Empirical formula	C100 H84 Cl4 N8 O8	
Formula weight	1667.55	
Temperature	296.15 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 8.944(3) Å	α = 90°.
	b = 19.542(7) Å	β = 100.017(7)°.
	c = 12.592(4) Å	γ = 90°.
Volume	2167.4(13) Å^3	
Z	1	
Density (calculated)	1.278 Mg/m^3	
Absorption coefficient	0.200 mm^{-1}	
F(000)	872	
Crystal size	0.1 x 0.1 x 0.1 mm^3	

Theta range for data collection	2.084 to 26.020°.
Index ranges	-11<=h<=9, -24<=k<=21, -15<=l<=15
Reflections collected	11886
Independent reflections	7981 [R(int) = 0.0447]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5947
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7981 / 333 / 601
Goodness-of-fit on F^2	1.536
Final R indices [I>2sigma(I)]	R1 = 0.1545, wR2 = 0.4102
R indices (all data)	R1 = 0.2015, wR2 = 0.4383
Absolute structure parameter	0.20(6)
Extinction coefficient	n/a
Largest diff. peak and hole	1.707 and -0.518 e.$Å^{-3}$

10. References

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