Supporting Information

Pd/Cu Cooperative Catalysis: An Efficient Synthesis of (3-Isoindazolyl)allenes via Cross-coupling of 2-Alkynyl Azobenzenes and Terminal Alkynes

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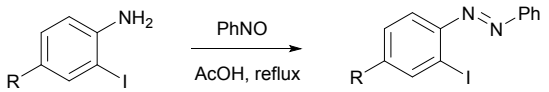
General Methods

NMR spectra were recorded in $CDCl_3$ with TMS for ^1H (400 MHz) and ^{13}C (100 MHz). Melting points were uncorrected and were recorded on a digital melting point apparatus. High resolution mass spectra were performed on an electrospray ionization mass spectrometer. Flash column chromatography was performed using silica gel of 230-400 mesh with distilled solvents. Commercially available reagents and solvents were used without further purification.

Synthesis of Starting Materials

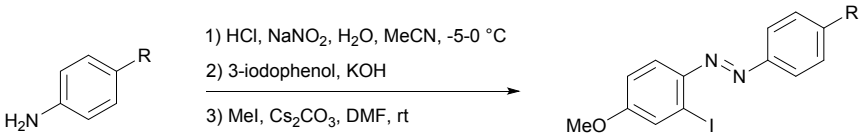
Preparation of 2-iodoazobenzenes **1a-e**



R = H **1a**
Me **1b**
^{t}Bu **1c**
F **1d**
Cl **1e**

Compounds **1a-e** were prepared by the literature method.[1]

Preparation of 2-iodoazobenzenes **1f** and **1g**



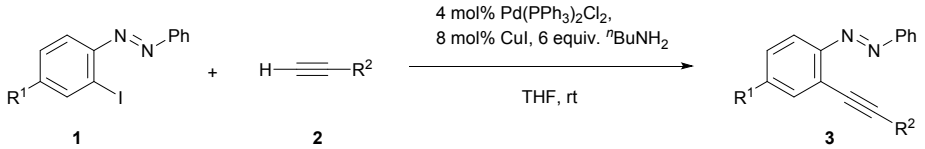
R = CN **1f**
COOEt **1g**

Compound **1f** was prepared by the literature method.[1]

Following the literature procedure,[1] compound **1g** was prepared. To a solution of ethyl 4-aminobenzoate (10 mmol, 1.0 equiv) in 4 mL of MeCN/H_2O (1/3) was added concentrated HCl (20 mmol, 2.0 equiv). The reaction mixture was then cooled to -5-0 °C. To the cooled solution a solution of $NaNO_2$ (12 mmol, 1.2 equiv) in MeCN/H_2O (1/1) was added at -5-0 °C. Then the reaction mixture was allowed to stir at -5-0 °C for 30 min. This diazonium salt solution was added to a solution of 3-iodophenol (11 mmol, 1.1 equiv) and KOH (20 mmol, 2.0 equiv) in 20 mL of MeCN/H_2O (9:1) at -5-0 °C. Then the reaction mixture was warm to room temperature over 3 h and stirred at room temperature for an additional 3 h. The reaction mixture was then diluted with EtOAc and the aqueous layer acidified. The organic layer was washed with 10 mL×2 10% HCl solution, 10 mL×2 brine and 10 mL H_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to give a red solid. The red solid was dissolved in 100 mL DMF and Cs_2CO_3 (21 mmol, 2.1 equiv) and MeI (12 mmol, 1.2 equiv) were added. The mixture was allowed to stir at 30 °C for 24 h and then diluted with 10% HCl solution, and extracted with 20 mL×3 EtOAc. The combined organics were washed with 20 mL H_2O, 20 mL×2 0.5 M NaOH solution and 20 mL H_2O. The organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The solids were then recrystallized from an EtOH/H_2O mixture, to yield 2.65 g of dark red solid in 65% yield; mp 183-185 °C; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.43 (t, 3H, J = 7.1 Hz), 3.89

(s, 3H), 4.42 (q, 2H, *J* = 7.1 Hz), 6.98 (dd, 1H, *J* = 2.4, 8.8 Hz), 7.56 (d, 1H, *J* = 2.4 Hz), 7.73 (d, 1H, *J* = 8.8 Hz), 7.98 (d, 2H, *J* = 8.8 Hz), 8.19 (d, 2H, *J* = 8.8 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ = 14.3, 55.9, 61.2, 106.2, 115.5, 118.0, 123.0, 124.0, 130.6, 132.0, 145.3, 154.8, 162.7, 166.0; ESI-HRMS: Found: m/z 411.0204. Calcd for $C_{16}H_{15}IN_2O_3$: $(M+H)^+$ 411.0206.

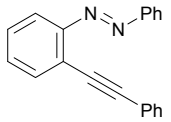
General procedure for preparation of 2-alkynyl azobenzenes **3a−h**.



1 **2** **3**

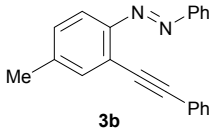
R^1 = H	R^2 = Ph	**3a**
Me	R^2 = Ph	**3b**
^{t}Bu	R^2 = Ph	**3c**
F	R^2 = Ph	**3d**
Cl	R^2 = Ph	**3e**
H	R^2 = $MeOC_6H_4$	**3f**
H	R^2 = ClC_6H_4	**3g**
H	R^2 = ^{n}Pr	**3h**

The 2-iodoazobenzene **1** (1.0 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (28.1 mg, 0.04 mmol, 0.04 equiv), CuI (15.2 mg, 0.08 mmol, 0.08 equiv) and ^{n}BuNH$_2$ (497 μL, 6.0 mmol, 6.0 equiv) were dissolved in 10 mL anhydrous THF under N_2. The mixture was immediately purged by N_2 three times. To resulting solution terminal alkyne **2** (1.2 mmol, 1.2 equiv) was added dropwise. The mixture was stirred at room temperature. After the reaction was completed according to TLC reaction control (2-7 h), NH_4Cl saturated aqueous solution (15 mL) was added. The organic layer was separated, and the aqueous layer was extracted twice with ethyl acetate (5 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The crude residue was purified by column chromatography on silica gel (hexane/ethyl acetate 100:1 to 50:1) to afford compounds **3a-h**.



3a

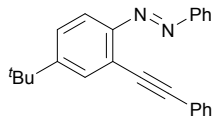
*1-phenyl-2-(2-(phenylethynyl)phenyl)diazene (**3a**)*. Yield 80% (226 mg); red solid; mp 53-55 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34-7.39 (m, 3H), 7.41-7.47 (m, 2H), 7.48-7.56 (m, 3H), 7.58-7.62 (m, 2H), 7.69-7.77 (m, 2H), 8.02 (d, 2H, *J* = 7.2 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ = 86.8, 95.6, 116.2, 123.3, 123.4, 123.7, 128.36, 128.43, 128.9, 129.1, 130.5, 131.3, 131.6, 133.3, 152.8, 153.0; ESI-HRMS: Found: m/z 283.1240. Calcd for $C_{20}H_{14}N_2$: $(M+H)^+$ 283.1235.



3b

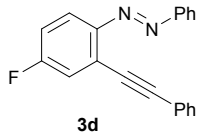
*1-(4-methyl-2-(phenylethynyl)phenyl)-2-phenyldiazene (**3b**)*. Yield 78% (231 mg); red solid; mp 83-85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.43 (s, 3H), 7.23 (dd, 1H, *J* = 1.2, 8.4 Hz), 7.35-7.39 (m, 3H), 7.45-7.55 (m, 4H), 7.56-7.62 (m, 2H), 7.69 (d, 1H, *J* = 8.4 Hz), 8.01 (d, 2H, *J* = 7.2 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ = 21.2, 87.0, 95.2, 115.9, 123.1, 123.5, 123.8, 128.3, 128.4, 129.1,

129.9, 131.0, 131.6, 133.6, 141.1, 151.1, 152.9; ESI-HRMS: Found: m/z 297.1399. Calcd for $C_{21}H_{16}N_2$: $(M+H)^+$ 297.1392.



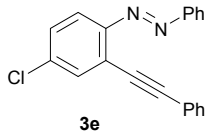
3c

*1-(4-(tert-butyl)-2-(phenylethynyl)phenyl)-2-phenyldiazene (**3c**)*. Yield 75% (254 mg); red solid; mp 83-85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.38 (s, 9H), 7.32-7.39 (m, 3H), 7.42-7.54 (m, 4H), 7.58-7.63 (m, 2H), 7.68-7.73 (m, 2H), 8.01 (d, 2H, *J* = 7.2 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ = 31.1, 35.0, 87.4, 94.9, 115.8, 122.8, 123.2, 123.4, 123.5, 126.4, 128.3, 129.0, 130.1, 131.0, 131.6, 151.0, 152.9, 154.1; ESI-HRMS: Found: m/z 339.1868. Calcd for $C_{24}H_{22}N_2$: $(M+H)^+$ 339.1861.



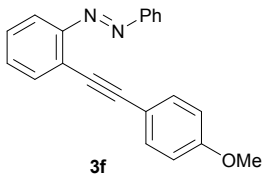
3d

*1-(4-fluoro-2-(phenylethynyl)phenyl)-2-phenyldiazene (**3d**)*. Yield 65% (195 mg); red solid; mp 79-81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.09-7.16 (m, 1H), 7.36-7.43 (m, 4H), 7.47-7.56 (m, 3H), 7.57-7.61 (m, 2H), 7.80 (dd, 1H, *J* = 3.4, 9.0 Hz), 7.99-8.02 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ = 85.7 (d, *J* = 3.1 Hz), 96.7, 116.4 (d, *J* = 23.0 Hz), 118.1 (d, *J* = 8.9 Hz), 119.4 (d, *J* = 23.7 Hz), 123.0, 123.2, 128.4, 128.8, 129.2 (d, *J* = 10.0 Hz), 131.3, 131.7, 149.6 (d, *J* = 3.1 Hz), 152.7, 162.4, 164.9; ESI-HRMS: Found: m/z 301.1151. Calcd for $C_{20}H_{13}FN_2$: $(M+H)^+$ 301.1141.



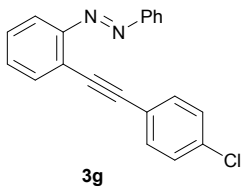
3e

*1-(4-chloro-2-(phenylethynyl)phenyl)-2-phenyldiazene (**3e**)*. Yield 69% (220 mg); red solid; mp 88-90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35-7.41 (m, 4H), 7.49-7.62 (m, 5H), 7.68-7.75 (m, 2H), 7.98-8.04 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ = 85.5, 96.8, 117.4, 123.0, 123.3, 125.3, 128.4, 128.8, 129.2 (overlapped), 131.5, 131.7, 132.8, 136.4, 151.3, 152.7; ESI-HRMS: Found: m/z 317.0847. Calcd for $C_{20}H_{13}ClN_2$: $(M+H)^+$ 317.0846.



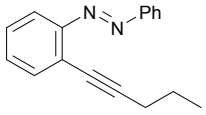
3f

*1-(2-((4-methoxyphenyl)ethynyl)phenyl)-2-phenyldiazene (**3f**)*. Yield 55% (172 mg); red solid; mp 73-75 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.84 (s, 3H), 6.88-6.93 (m, 2H), 7.37-7.56 (m, 7H), 7.67-7.76 (m, 2H), 8.00-8.05 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ = 55.3, 85.6, 95.8, 114.0, 115.6, 116.1, 123.2, 124.0, 128.5, 129.1, 130.5, 131.2, 133.1, 133.2, 152.89, 152.91, 159.8; ESI-HRMS: Found: m/z 313.1343. Calcd for $C_{21}H_{16}N_2O$: $(M+H)^+$ 313.1341.



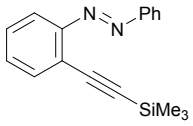
3g

*1-(2-((4-chlorophenyl)ethynyl)phenyl)-2-phenyldiazene (**3g**).* Yield 60% (190 mg); red solid; mp 80-82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31-7.37 (m, 2H), 7.41-7.47 (m, 2H), 7.47-7.58 (m, 5H), 7.67-7.72 (m, 1H), 7.73-7.77 (m, 1H), 7.97-8.04 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ = 87.8, 94.4, 116.2, 121.9, 123.2, 123.3, 128.7, 129.1 (overlapped), 130.5, 131.4, 132.8, 133.3, 134.4, 152.8, 153.1; ESI-HRMS: Found: m/z 317.0836. Calcd for $C_{20}H_{13}ClN_2$: $(M+H)^+$ 317.0846.



3h

*1-(2-(pent-1-yn-1-yl)phenyl)-2-phenyldiazene (**3h**).* Yield 50% (124 mg); red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.09 (t, 3H, *J* = 7.3 Hz), 1.61-1.76 (m, 2H), 2.50 (t, 2H, *J* = 6.8 Hz), 7.32-7.41 (m, 2H), 7.46-7.55 (m, 3H), 7.56-7.61 (m, 1H), 7.65-7.70 (m, 1H), 7.95-8.00 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ = 13.6, 21.8, 22.2, 77.9, 97.0, 115.9, 123.2, 124.6, 128.1, 129.0, 130.4, 131.1, 133.5, 152.9, 153.2; ESI-HRMS: Found: m/z 249.1387. Calcd for $C_{17}H_{16}N_2$: $(M+H)^+$ 249.1392.

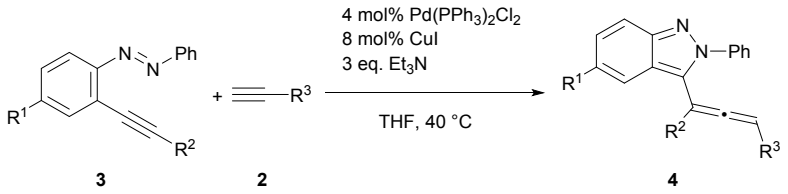


3i

Compound **3i** was prepared by the literature method.[1]

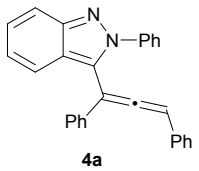
Synthesis of (3-Isoindazolyl)allenes

General procedure for preparation of (3-isoindazolyl)allene **4a−k** and **4o−s**



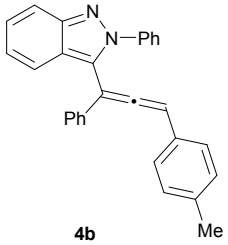
3 **2** **4**

Compound **3** (0.25 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (7.0 mg, 0.01 mmol, 0.04 equiv), CuI (3.8 mg, 0.02 mmol, 0.08 equiv) and Et_3N (108 μL, 0.75 mmol, 3.0 equiv) were dissolved in 2.5 mL anhydrous THF under N_2. The mixture was immediately purged by N_2 three times. To resulting solution terminal alkyne **2** (0.50 mmol) was added. The mixture was stirred at 40 °C. After the reaction was completed according to TLC reaction control (14-24 h). The solvent was removed in vacuo. The crude residue was purified by column chromatography on silica gel (hexane/ethyl acetate 50:1 to 20:1) to afford desire product.



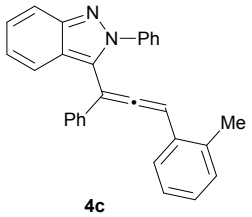
4a

*3-(1,3-diphenylpropa-1,2-dien-1-yl)-2-phenyl-2H-indazole (**4a**)*. Yield 40% (78 mg); pale yellow solid; mp 138-140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.41 (s, 1H), 7.03-7.10 (m, 3H), 7.16-7.23 (m, 3H), 7.24-7.31 (m, 3H), 7.31-7.41 (m, 6H), 7.48 (d, 1H, *J* = 8.8 Hz), 7.54-7.61 (m, 2H), 7.81 (d, 1H, *J* = 8.8 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ = 98.6, 103.0, 117.9, 120.6, 122.2, 122.6, 125.5, 126.82, 126.84, 127.2, 127.7, 127.9, 128.3, 128.72, 128.76, 129.0, 129.3, 132.4, 134.5, 140.2, 149.0, 209.5; ESI-HRMS: Found: m/z 385.1711. Calcd for $C_{28}H_{20}N_2$: $(M+H)^+$ 385.1705.



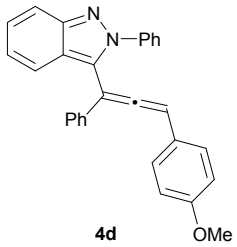
4b

*2-phenyl-3-(1-phenyl-3-(p-tolyl)propa-1,2-dien-1-yl)-2H-indazole (**4b**)*. Yield 82% (82 mg); pale yellow solid; mp 119-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.30 (s, 3H), 6.38 (s, 1H), 6.94 (d, 2H, *J* = 8.0 Hz), 7.02 (d, 2H, *J* = 8.0 Hz), 7.03-7.09 (m, 1H), 7.21-7.29 (m, 3H), 7.29-7.40 (m, 6H), 7.47 (d, 1H, *J* = 8.4 Hz), 7.55-7.61 (m, 2H), 7.80 (d, 1H, *J* = 8.8 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ = 21.2, 98.4, 102.8, 117.9, 120.6, 122.2, 122.5, 125.5, 126.79, 126.83, 127.2, 127.8, 128.3, 128.7, 128.9, 129.3, 129.4, 129.5, 134.7, 137.7, 140.3, 149.0, 209.4; ESI-HRMS: Found: m/z 399.1867. Calcd for $C_{29}H_{22}N_2$: $(M+H)^+$ 399.1861.



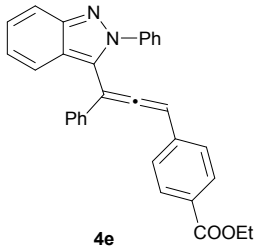
4c

*2-phenyl-3-(1-phenyl-3-(o-tolyl)propa-1,2-dien-1-yl)-2H-indazole (**4c**)*. Yield 62% (62 mg); pale yellow viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.22 (s, 3H), 6.52 (s, 1H), 6.95-7.12 (m, 5H), 7.20-7.39 (m, 9H), 7.42 (d, 1H, *J* = 8.4 Hz), 7.53-7.60 (m, 2H), 7.80 (d, 1H, *J* = 8.8 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ = 19.8, 96.0, 102.1, 117.9, 120.7, 122.1, 122.4, 125.5, 126.2, 126.8 (overlapped), 127.7, 127.8, 127.9, 128.2, 128.7, 128.9, 129.4, 130.6, 130.7, 134.6, 135.4, 140.2, 149.0, 210.0; ESI-HRMS: Found: m/z 399.1865. Calcd for $C_{29}H_{22}N_2$: $(M+H)^+$ 399.1861.



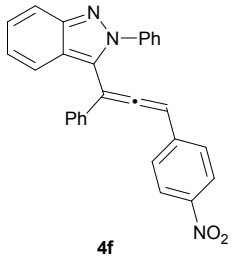
4d

*3-(3-(4-methoxyphenyl)-1-phenylpropa-1,2-dien-1-yl)-2-phenyl-2H-indazole (**4d**).* Yield 73% (76 mg); pale yellow viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.77 (s, 3H), 6.38 (s, 1H), 6.74 (d, 2H, *J* = 8.8 Hz), 6.97 (d, 2H, *J* = 8.8 Hz), 7.06 (dd, 1H, *J* = 6.8, 8.4 Hz), 7.20-7.29 (m, 3H), 7.29-7.35 (m, 3H), 7.35-7.41 (m, 3H), 7.46 (d, 1H, *J* = 8.4 Hz), 7.54-7.60 (m, 2H), 7.80 (d, 1H, *J* = 8.8 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ = 55.3, 98.1, 102.8, 114.2, 117.9, 120.7, 122.2, 122.5, 124.5, 125.5, 126.79, 126.84, 127.8, 128.3, 128.5, 128.7, 129.0, 129.7, 134.8, 140.3, 149.0, 159.3, 209.2; ESI-HRMS: Found: m/z 415.1816. Calcd for $C_{29}H_{22}N_2O$: $(M+H)^+$ 415.1810.



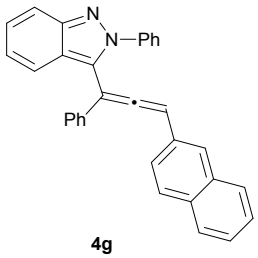
4e

*ethyl 3-(1,3-diphenylpropa-1,2-dien-1-yl)-2-phenyl-2H-indazole-5-carboxylate (**4e**).* Yield 66% (78 mg); pale yellow viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.38 (t, 3H, *J* = 7.2 Hz), 4.36 (q, 2H, *J* = 7.2 Hz), 6.45 (s, 1H), 7.05-7.09 (m, 3H), 7.24-7.36 (m, 6H), 7.36-7.41 (m, 3H), 7.44 (d, 1H, *J* = 8.5 Hz), 7.54-7.58 (m, 2H), 7.81 (d, 1H, *J* = 8.8 Hz), 7.88 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ = 14.3, 60.9, 98.1, 103.5, 118.0, 120.4, 122.4, 122.6, 125.5, 126.88, 126.91, 127.0, 128.2, 128.5, 128.7, 128.9, 129.0, 129.5, 130.0, 133.9, 137.2, 140.1, 149.0, 166.1, 210.2; ESI-HRMS: Found: m/z 457.1908. Calcd for $C_{31}H_{24}N_2O_2$: $(M+H)^+$ 457.1916.



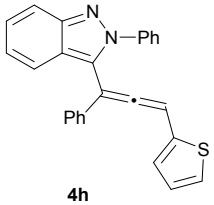
4f

*3-(3-(4-nitrophenyl)-1-phenylpropa-1,2-dien-1-yl)-2-phenyl-2H-indazole (**4f**).* Yield: 70% (75 mg); pale yellow solid; mp 179-181 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.46 (s, 1H), 7.06-7.13 (m, 3H), 7.30-7.38 (m, 6H), 7.38-7.45 (m, 4H), 7.51-7.58 (m, 2H), 7.82 (d, 1H, *J* = 8.8 Hz), 8.04 (d, 2H, *J* = 8.8 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ = 97.4, 104.2, 118.1, 120.3, 122.7, 124.1, 125.6, 126.99, 127.03, 127.7, 128.1, 128.5, 128.6, 128.7, 129.1, 129.2, 133.4, 139.6, 140.2, 146.9, 149.1, 210.7; ESI-HRMS: Found: m/z 430.1564. Calcd for $C_{28}H_{19}N_3O_2$: $(M+H)^+$ 430.1556.



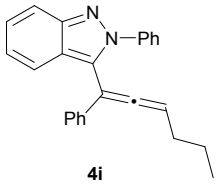
4g

*3-(3-(naphthalen-2-yl)-1-phenylpropa-1,2-dien-1-yl)-2-phenyl-2H-indazole (**4g**)*. Yield 82% (89 mg); pale yellow solid; mp 95-97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.63 (s, 1H), 7.08-7.21 (m, 2H), 7.26-7.38 (m, 3H), 7.38-7.52 (m, 8H), 7.53-7.60 (m, 2H), 7.61-7.72 (m, 3H), 7.72-7.83 (m, 2H), 7.87 (d, 1H, *J* = 8.8 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ = 99.0, 103.2, 117.9, 120.6, 122.3, 122.6, 124.7, 125.6 (overlapped), 126.1, 126.3, 126.5, 126.9 (overlapped), 127.7, 127.8, 128.0, 128.4, 128.8, 129.0, 129.3, 129.9, 132.9, 133.5, 134.5, 140.3, 149.0, 210.1; ESI-HRMS: Found: m/z 435.1858. Calcd for $C_{32}H_{22}N_2$: $(M+H)^+$ 435.1861.



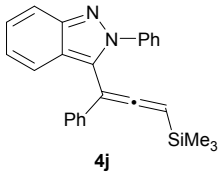
4h

*2-phenyl-3-(1-phenyl-3-(thiophen-2-yl)propa-1,2-dien-1-yl)-2H-indazole (**4h**)*. Yield 79% (77 mg); pale yellow viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.67 (s, 1H), 6.83-6.87 (m, 1H), 6. 92 (dd, 1H, *J* = 3.6, 5.2 Hz), 7.05-7.11 (m, 1H), 7.15-7.19 (m, 1H), 7.20-7.28 (m, 5H), 7.31-7.40 (m, 4H), 7.52 (d, 1H, *J* = 8.4 Hz), 7.58-7.63 (m, 2H), 7.80 (d, 1H, *J* = 8.8 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ = 92.6, 103.3, 117.9, 120.6, 122.3, 122.7, 125.4, 125.6, 126.3, 126.9, 127.1, 127.6, 128.0, 128.3, 128.7, 128.9, 129.0, 134.4, 136.0, 140.2, 149.0, 209.3; ESI-HRMS: Found: m/z 391.1272. Calcd for $C_{26}H_{18}N_2S$: $(M+H)^+$ 391.1269.



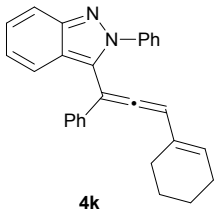
4i

*2-phenyl-3-(1-phenylhexa-1,2-dien-1-yl)-2H-indazole (**4i**)*. Yield 50% (44 mg); pale yellow viscous oil; 1H NMR (400 MHz, $CDCl_3$) δ = 0.80 (t, 3H, *J* = 7.2 Hz), 1.17-1.35 (m, 2H), 1.69-1.82 (m, 2H), 5.40 (t, 1H, *J* = 7.2 Hz), 6.99-7.06 (m, 1H), 7.17-7.25 (m, 2H), 7.26-7.30 (m, 3H), 7.30-7.42 (m, 5H), 7.55-7.61 (m, 2H), 7.80 (d, 1H, *J* = 8.8 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ = 13.7, 22.4, 30.0, 95.3, 98.8, 117.8, 120.8, 121.8, 122.3, 125.4, 126.6, 126.7, 127.2, 128.1, 128.5, 128.8, 130.4, 135.5, 140.3, 148.9, 206.9; ESI-HRMS: Found: m/z 351.1853. Calcd for $C_{25}H_{22}N_2$: $(M+H)^+$ 351.1861.



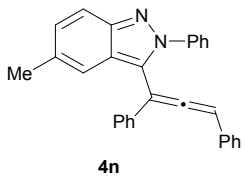
4j

*2-phenyl-3-(1-phenyl-3-(trimethylsilyl)propa-1,2-dien-1-yl)-2H-indazole (**4j**)*. Yield 80% (76 mg); pale yellow viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.15 (s, 9H), 5.36 (s, 1H), 7.09-7.15 (m, 1H), 7.20-7.28 (m, 3H), 7.28-7.35 (m, 2H), 7.37-7.47 (m, 4H), 7.52 (d, 1H, *J* = 8.4 Hz), 7.65-7.67 (m, 2H), 7.87 (d, 1H, *J* = 8.8 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ = -0.8, 87.0, 92.5, 117.8, 120.8, 121.8, 122.6, 125.2, 125.9, 126.6, 126.8, 128.1, 128.6, 128.8, 130.0, 135.2, 140.3, 149.0, 209.8; ESI-HRMS: Found: m/z 381.1795. Calcd for $C_{25}H_{24}N_2Si$: $(M+H)^+$ 381.1787.



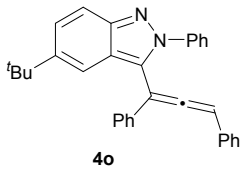
4k

*3-(3-(cyclohex-1-en-1-yl)-1-phenylpropa-1,2-dien-1-yl)-2-phenyl-2H-indazole (**4k**)*. Yield 65% (63 mg); pale yellow viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.40-1.70 (m, 5H), 1.83-1.98 (m, 1H), 2.00-2.12 (m, 2H), 5.67 (t, 1H, *J* = 4.0 Hz), 6.07 (s, 1H), 7.02-7.09 (m, 1H), 7.16-7.29 (m, 5H), 7.29-7.41 (m, 4H), 7.46 (d, 1H, *J* = 8.4 Hz), 7.54-7.60 (m, 2H), 7.80 (d, 1H, *J* = 8.8 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ = 22.1, 22.4, 25.8, 25.9, 101.76, 101.82, 117.8, 120.7, 122.0, 122.5, 125.3, 126.6, 126.8, 127.5, 128.2, 128.6, 128.7, 128.8, 130.1, 131.0, 135.4, 140.3, 148.9, 208.4. ESI-HRMS: Found: m/z 389.2024. Calcd for $C_{28}H_{24}N_2$: $(M+H)^+$ 389.2018.



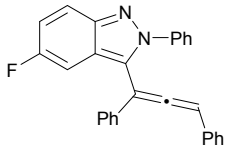
4n

*3-(1,3-diphenylpropa-1,2-dien-1-yl)-5-methyl-2-phenyl-2H-indazole (**4n**)*. Yield 85% (85 mg); pale yellow solid; mp 151-153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.35 (s, 3H), 6.40 (s, 1H), 7.03-7.07 (m, 2H), 7.17-7.29 (m, 8H), 7.29-7.39 (m, 5H), 7.52-7.59 (m, 2H), 7.70 (d, 1H, *J* = 8.8 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ = 21.8, 98.4, 103.0, 117.6, 118.5, 122.8, 125.4, 126.7, 127.2, 127.6, 127.8, 128.16, 128.21, 128.66, 128.74, 128.9, 129.8, 131.7, 132.4, 134.5, 140.3, 148.0, 209.4; ESI-HRMS: Found: m/z 399.1859. Calcd for $C_{29}H_{22}N_2$: $(M+H)^+$ 399.1861.



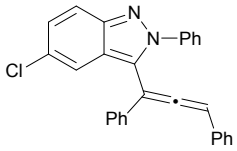
4o

*5-(tert-butyl)-3-(1,3-diphenylpropa-1,2-dien-1-yl)-2-phenyl-2H-indazole (**4o**).* Yield 85% (94 mg); pale yellow solid; mp 155-157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.26 (s, 9H), 6.51 (s, 1H), 7.13-7.16 (m, 2H), 7.17-7.27 (m, 6H), 7.27-7.37 (m, 6H), 7.46 (dd, 1H, *J* = 2.0, 9.2 Hz), 7.54-7.57 (m, 2H), 7.74 (d, 1H, *J* = 9.2 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ = 31.1, 34.8, 98.5, 103.2, 114.7, 117.4, 122.5, 125.4, 126.7, 126.9, 127.4, 127.7, 127.8, 128.1, 128.6, 128.75, 128.85, 129.0, 132.6, 134.4, 140.5, 144.9, 147.8, 209.4; ESI-HRMS: Found: m/z 441.2333. Calcd for $C_{32}H_{28}N_2$: $(M+H)^+$ 441.2331.



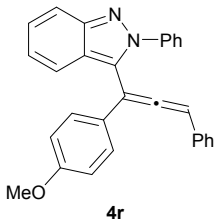
4p

*3-(1,3-diphenylpropa-1,2-dien-1-yl)-5-fluoro-2-phenyl-2H-indazole (**4p**).* Yield 74% (74 mg); pale yellow viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.40 (s, 1H), 6.99-7.08 (m, 3H), 7.09-7.34 (m, 9H), 7.34-7.41 (m, 3H), 7.52-7.59 (m, 2H), 7.77 (dd, 1H, *J* = 4.8, 5.6 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ = 98.7, 102.7, 103.0 (d, *J* = 24.3 Hz), 118.5 (d, *J* = 28.9 Hz), 120.1 (d, *J* = 9.6 Hz), 121.9 (d, *J* = 11.9 Hz), 125.4, 126.7, 127.2, 127.8, 128.0, 128.5, 128.75, 128.85, 129.0, 132.2, 134.2, 140.1, 146.4, 157.2, 159.6, 209.5; ESI-HRMS: Found: m/z 403.1618. Calcd for $C_{28}H_{19}FN_2$: $(M+H)^+$ 403.1611.



4q

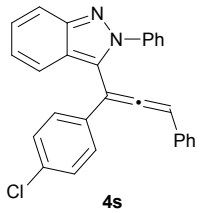
*5-chloro-3-(1,3-diphenylpropa-1,2-dien-1-yl)-2-phenyl-2H-indazole (**4q**).* Yield 75% (79 mg); pale yellow solid; mp 142-144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.42 (s, 1H), 7.00-7.08 (m, 2H), 7.13-7.24 (m, 3H), 7.24-7.34 (m, 6H), 7.34-7.42 (m, 3H), 7.45 (s, 1H), 7.52-7.61 (m, 2H), 7.73 (d, 1H, *J* = 9.2 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ = 98.8, 102.5, 119.2, 119.5, 122.9, 125.4, 126.7, 127.2, 127.83, 127.86, 128.1, 128.3, 128.6, 128.8, 128.9, 129.0, 129.2, 132.1, 134.1, 149.9, 147.3, 209.5; ESI-HRMS: Found: m/z 419.1310. Calcd for $C_{28}H_{19}ClN_2$: $(M+H)^+$ 419.1315.



4r

*3-(1-(4-methoxyphenyl)-3-phenylpropa-1,2-dien-1-yl)-2-phenyl-2H-indazole (**4r**).* Yield 72% (75 mg); pale yellow viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.78 (s, 3H), 6.36 (s, 1H), 6.78-6.85 (m, 2H), 6.99-7.10 (m, 3H), 7.14-7.22 (m, 3H), 7.22-7.28 (m, 2H), 7.30-7.42 (m, 4H), 7.48 (d, 1H , *J* = 8.4 Hz), 7.54-7.61 (m, 2H), 7.80 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ = 55.3, 98.6, 102.5, 114.2, 117.9, 120.7, 122.2, 122.5, 125.5, 126.6, 126.8, 127.2, 127.6, 128.1, 128.4,

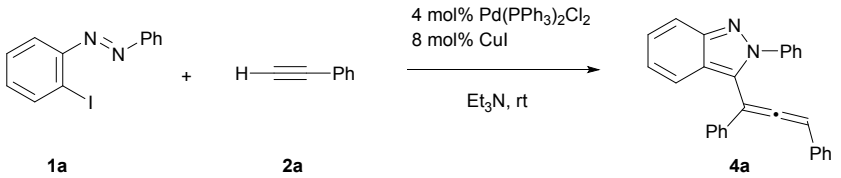
128.7, 129.0, 129.6, 132.7, 140.3, 149.0, 159.4, 208.9; ESI-HRMS: Found: m/z 415.1801. Calcd for $C_{29}H_{22}N_2O$: $(M+H)^+$ 415.1810.



4s

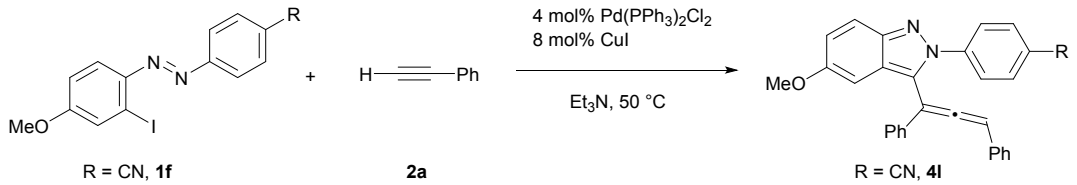
*3-(1-(4-chlorophenyl)-3-phenylpropa-1,2-dien-1-yl)-2-phenyl-2H-indazole (**4s**).* Yield 73% (76 mg); pale yellow viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.43 (s, 1H), 6.99-7.12 (m, 3H), 7.16-7.27 (m, 7H), 7.30-7.42 (m, 4H), 7.45 (d, 1H, *J* = 8.8 Hz), 7.51-7.59 (m, 2H), 7.80 (d, 1H, *J* = 8.8 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ = 99.0, 102.2, 118.0, 120.4, 122.4, 122.5, 125.5, 126.9, 127.3, 127.9, 128.0, 128.5, 128.76, 128.79, 128.97, 129.04, 132.0, 133.0, 133.8, 140.1, 149.0, 209.5; ESI-HRMS: Found: m/z 419.1313. Calcd for $C_{28}H_{19}ClN_2$: $(M+H)^+$ 419.1315.

<u>One-pot procedure for the preparation of (3-isoindazolyl)allene from substituted 2-iodoazobenzene and terminal alkyne</u>



1a **2a** **4a**

The 1-(2-iodophenyl)-2-phenyldiazene **1a** (1.0 mmol, 1 equiv), $Pd(PPh_3)_2Cl_2$ (28.1 mg, 0.04 mmol, 0.04 equiv), CuI (15.2 mg, 0.08 mmol, 0.08 equiv) were dissolved in 10 mL Et_3N under N_2. The mixture was immediately purged by N_2 three times. To resulting solution phenylacetylene **2a** (3.0 mmol, 3.0 equiv) was added dropwise. The mixture was stirred at room temperature for overnight. Then the reaction mixture was concentrated in vacuo. The crude residue was purified by column chromatography on silica gel (hexane/ethyl acetate 50:1 to 20:1) to afford compound **4a** in 40% yield (154 mg).

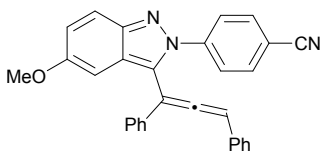


R = CN, **1f**
COOEt, **1g**

2a

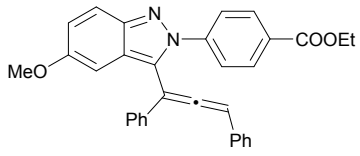
R = CN, **4l**
COOEt, **4m**

The substituted 2-iodoazobenzene **1f**/**1g** (0.25 mmol, 1 equiv), $Pd(PPh_3)_2Cl_2$ (7.0 mg, 0.01 mmol, 0.04 equiv), CuI (3.8 mg, 0.02 mmol, 0.08 equiv) were dissolved in 2.5 mL Et_3N under N_2. The mixture was immediately purged by N_2 three times. To resulting solution phenylacetylene **2a** (0.75 mmol, 3.0 equiv) was added dropwise. The mixture was stirred at 50 °C for overnight. Then the reaction mixture was concentrated in vacuo. The crude residue was purified by column chromatography on silica gel (hexane/ethyl acetate 50:1 to 20:1) to afford desired product.



4l

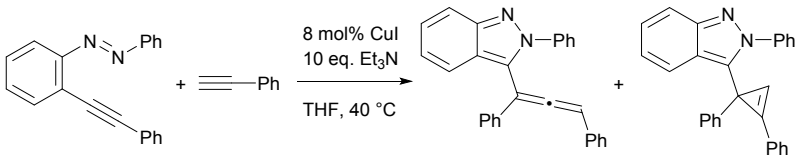
*4-(3-(1,3-diphenylpropa-1,2-dien-1-yl)-5-methoxy-2H-indazol-2-yl)benzonitrile (**4l**)*. Yield 49% (54 mg); pale yellow viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.57 (s, 3H), 6.56 (d, 1H, *J* = 2.1 Hz), 6.60 (s, 1H), 7.02-7.08 (m, 1H), 7.15-7.22 (m, 2H), 7.22-7.33 (m, 8H), 7.60 (d, 2H, *J* = 8.4 Hz), 7.66 (d, 1H, *J* = 9.6 Hz), 7.74 (d, 2H, *J* = 8.4 Hz) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 55.2, 96.3, 98.8, 103.0, 111.4, 118.1, 119.4, 123.2, 123.3, 125.3, 126.8, 127.4, 128.1, 128.20, 128.25, 128.86, 128.94, 132.4, 132.8, 133.7, 143.7, 146.5, 155.8, 209.3; ESI-HRMS: Found: m/z 440.1760. Calcd for $C_{30}H_{21}N_3O$: $(M+H)^+$ 440.1763.



4m

*ethyl 4-(3-(1,3-diphenylpropa-1,2-dien-1-yl)-5-methoxy-2H-indazol-2-yl)benzoate (**4m**)*. Yield 60% (73 mg); pale yellow viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.41 (t, 3H, *J* = 7.2 Hz), 3.60 (s, 3H), 4.39 (q, 2H, *J* = 7.1 Hz), 6.55 (s, 1H), 6.59 (d, 1H, *J* = 2.4 Hz), 7.05 (dd, 1H, *J* = 2.4, 9.6 Hz), 7.08-7.37 (m, 10H), 7.53-7.75 (m, 3H), 8.02 (d, 2H, *J* = 8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.3, 55.2, 61.2, 96.4, 98.6, 103.1, 119.4, 122.6, 123.1, 124.7, 126.8, 127.4, 127.8, 128.0, 128.1, 128.76, 128.84, 129.7, 130.3, 132.5, 134.0, 143.8, 146.2, 155.6, 165.8, 209.3; ESI-HRMS: Found: m/z 487.2021. Calcd for $C_{32}H_{26}N_2O_3$: $(M+H)^+$ 487.2022.

Control reactions



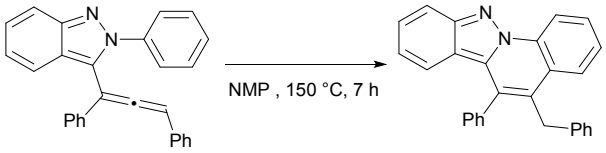
3a **2a** **4a** **4a'**

Compound **3a** (71 mg, 0.25 mmol), CuI (3.8 mg, 0.02 mmol) and Et_3N (360 µL, 2.5 mmol) were dissolved in 2.5 mL anhydrous THF under N_2. The mixture was immediately purged by N_2 three times. To resulting solution phenylacetylene **2a** (0.5 mmol) was added. The mixture was stirred at 40 °C for 24 h. The solvent was removed in vacuo. The crude residue was purified by column chromatography on silica gel (hexane/ethyl acetate 50:1 to 20:1) to afford **4a** and **4a'** in 49% and 30% yield respectively.

*3-(1,2-diphenylcycloprop-2-en-1-yl)-2-phenyl-2H-indazole (**4a'**)*. Yield 30% (29 mg); pale yellow viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.65 (s, 1H), 6.99-7.05 (m, 1H), 7.15-7.23 (m, 3H), 7.23-7.33 (m, 6H), 7.37-7.45 (m, 5H), 7.47-7.53 (m, 2H), 7.66 (d, 1H, *J* = 8.4 Hz), 7.75 (d, 1H, *J* = 8.8 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ = 27.7, 103.8, 117.8, 120.7, 121.1, 121.4, 121.9, 126.0,

126.1, 126.3, 126.4, 126.5, 128.4, 128.7, 128.75, 128.82, 129.3, 129.6, 139.0, 140.5, 145.4, 148.8; ESI-HRMS: Found: m/z 385.1712. Calcd for $C_{28}H_{20}N_2$: $(M+H)^+$ 385.1705.

Thermal Cyclization of Compound 4a



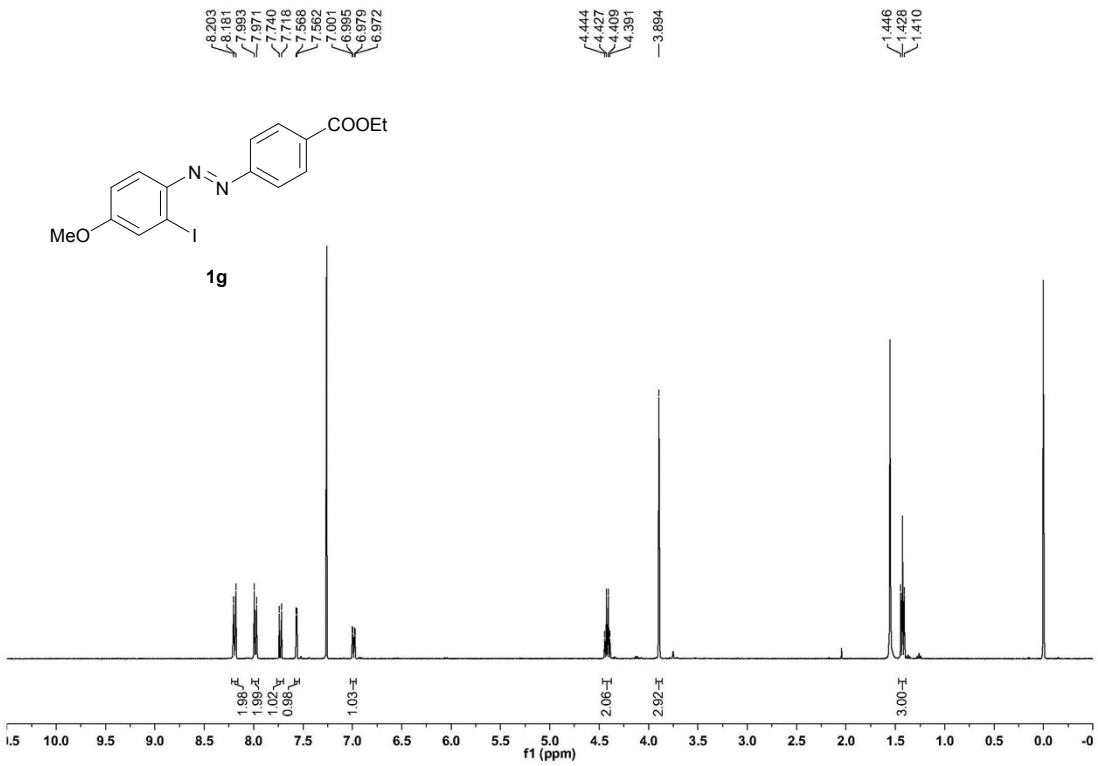
4a **5**

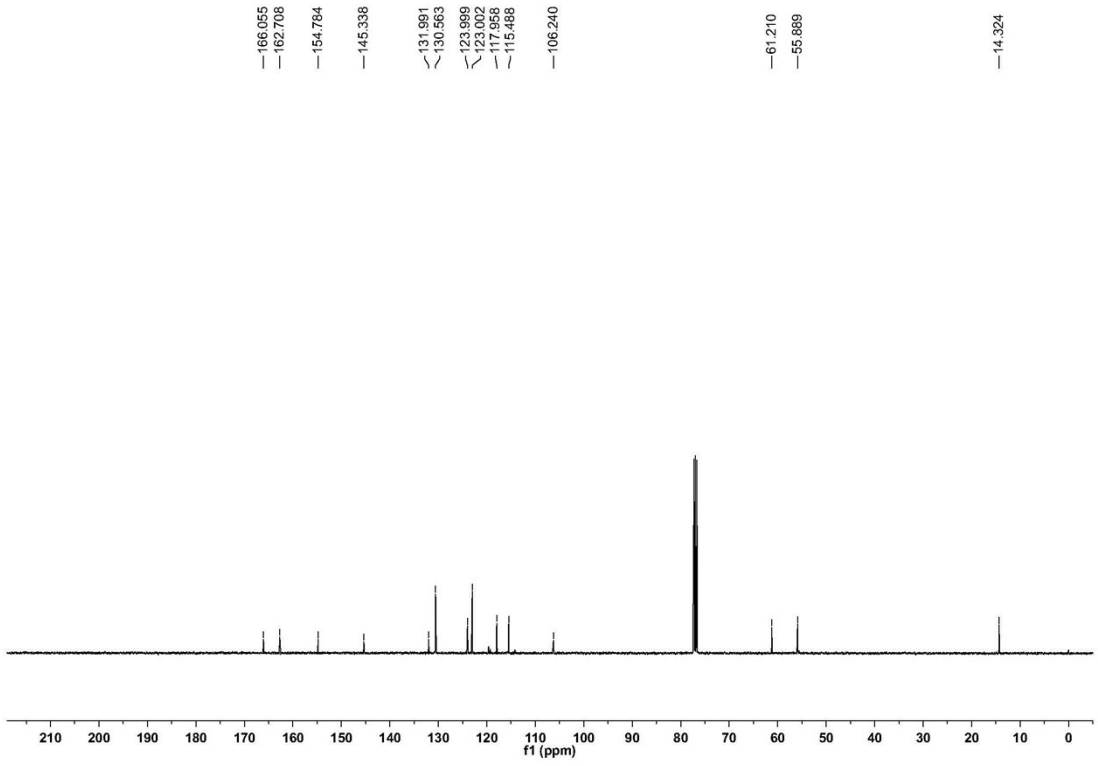
Compound **4a** (96 mg, 0.25 mmol) was dissolved in 2.5 mL anhydrous NMP in a 10 ml seal tube. The mixture was immediately purged by N_2 three times and then sitrred at 150 °C for 2 h. After the reaction was completed, the solvent was evaporated under vacuum. The crude residue was purified by column chromatography (hexane/ethyl acetate 20:1) on silica gel to afford 5-benzyl-6-phenylindazolo[2,3-*a*]quinolone **5** as a white solid; mp 197-199 °C; yield 53% (51 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.33 (s, 2H), 6.51 (d, 1H, *J* = 8.5 Hz), 6.81-6.93 (m, 1H), 7.07 (d, 2H, *J* = 6.8 Hz), 7.10-7.26 (m, 3H), 7.37-7.45 (m, 3H), 7.45-7.58 (m, 4H), 7.69-7.79 (m, 1H), 7.86-7.97 (m, 2H), 9.06 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ = 34.5, 116.3, 117.3, 117.6, 120.4, 121.5, 124.8, 126.0, 126.2, 126.5, 127.6, 128.0, 128.5, 128.6, 128.9, 129.0, 129.1, 129.4, 131.7, 131.9, 133.9, 136.6, 140.2, 149.4; ESI-HRMS: Found: m/z 385.1709. Calcd for $C_{28}H_{20}N_2$: $(M+H)^+$ 385.1705.

Reference

1. Shirtcliff, L. D.; Weakley, T. J. R.; Haley, M. M. *J. Org. Chem.* **2004**, *69*, 6979.

^{1}H and ^{13}C NMR spectra



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7.360


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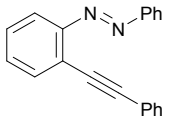
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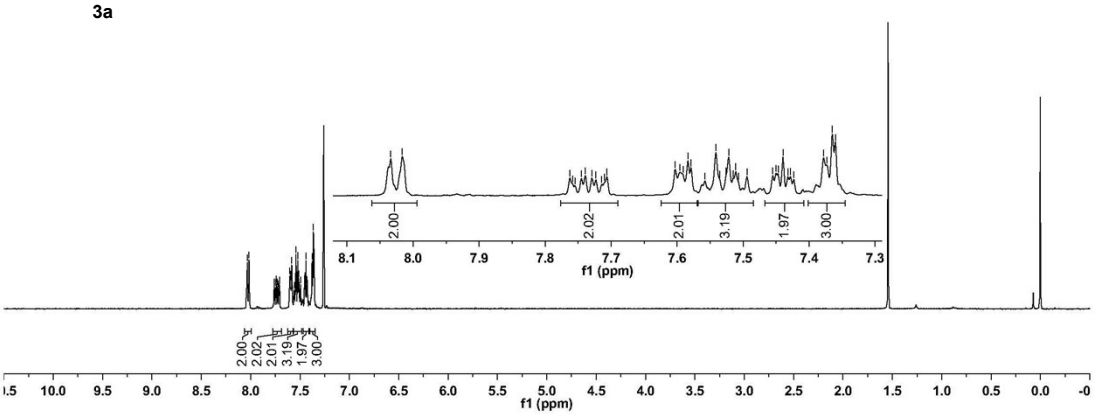
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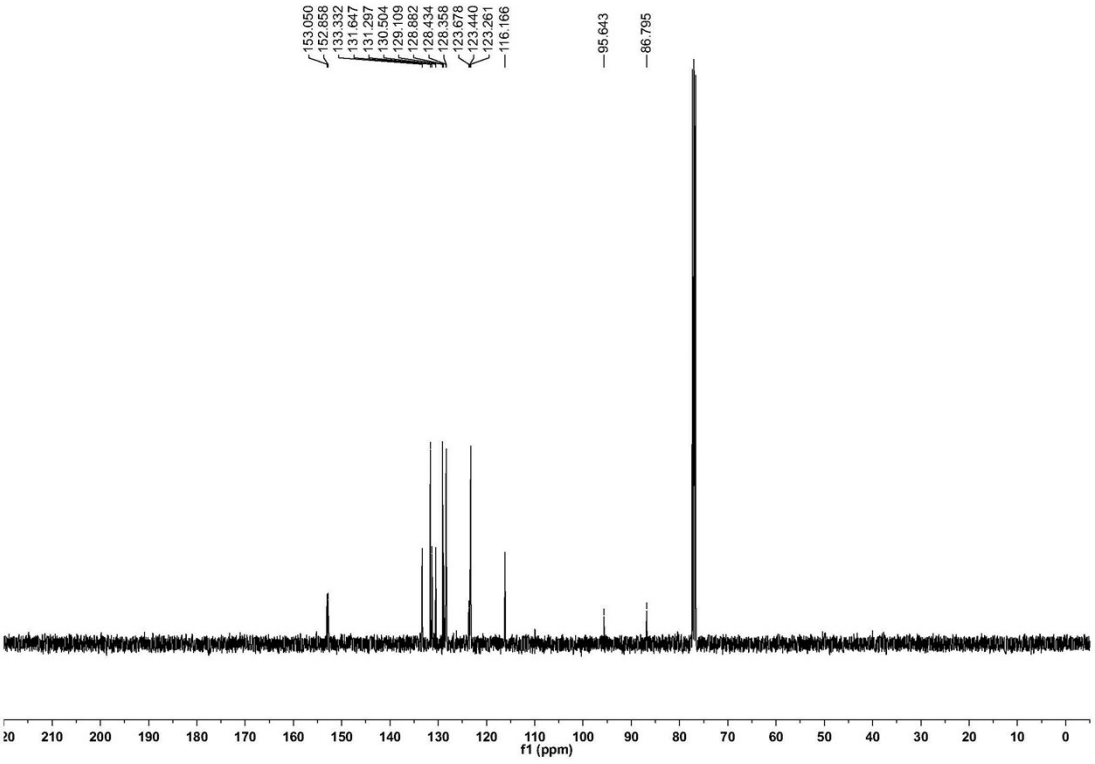
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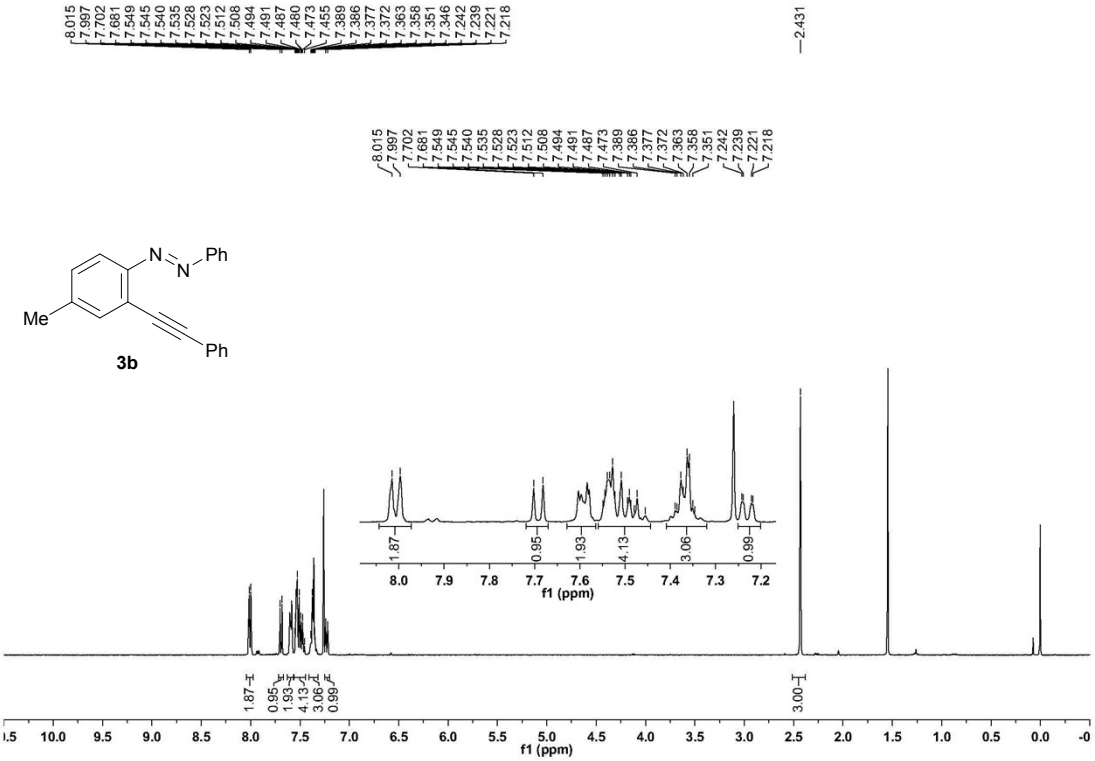
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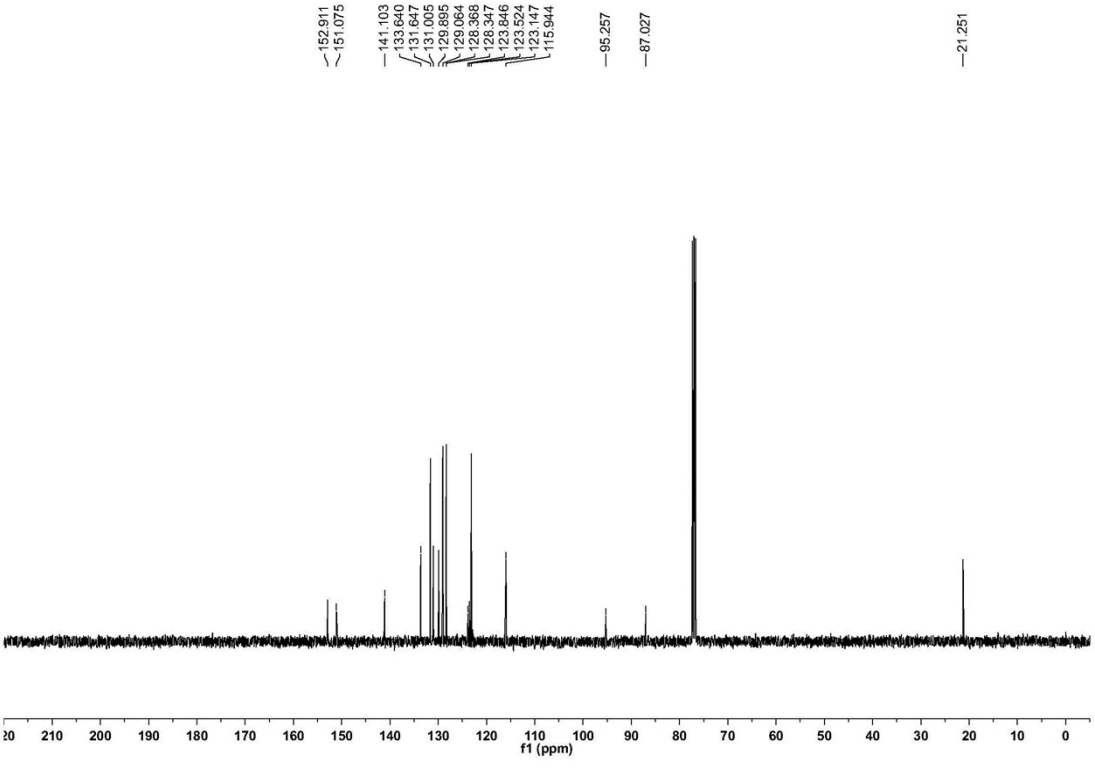
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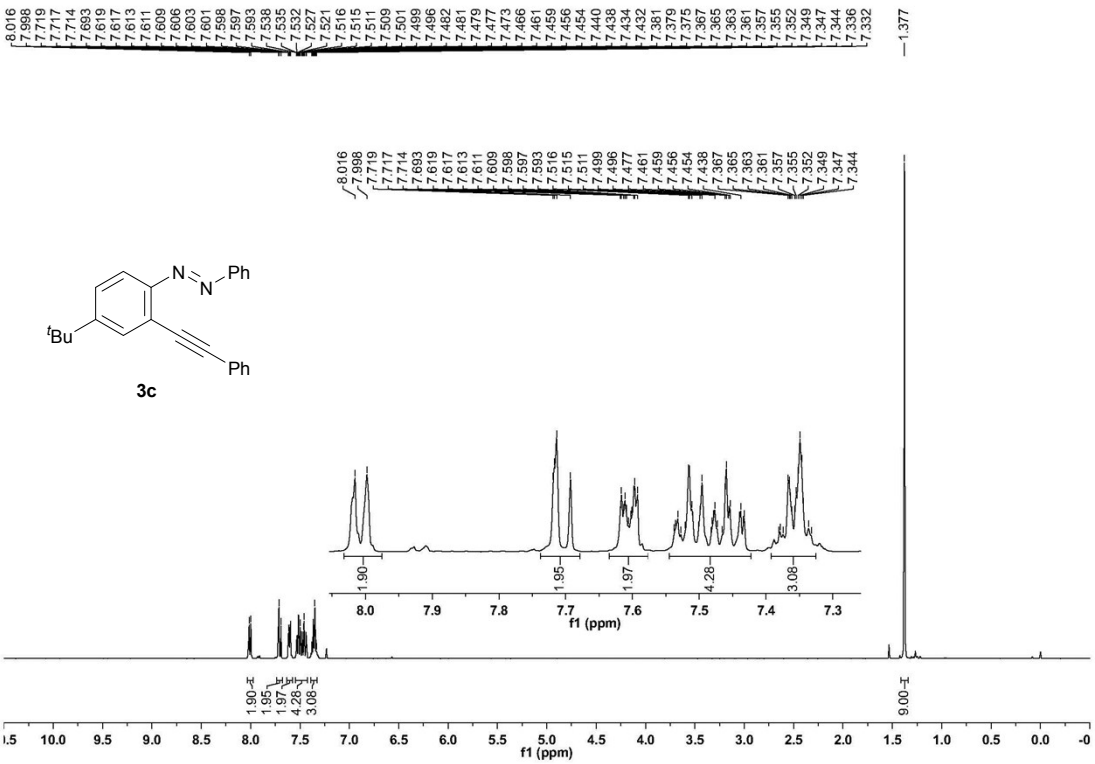
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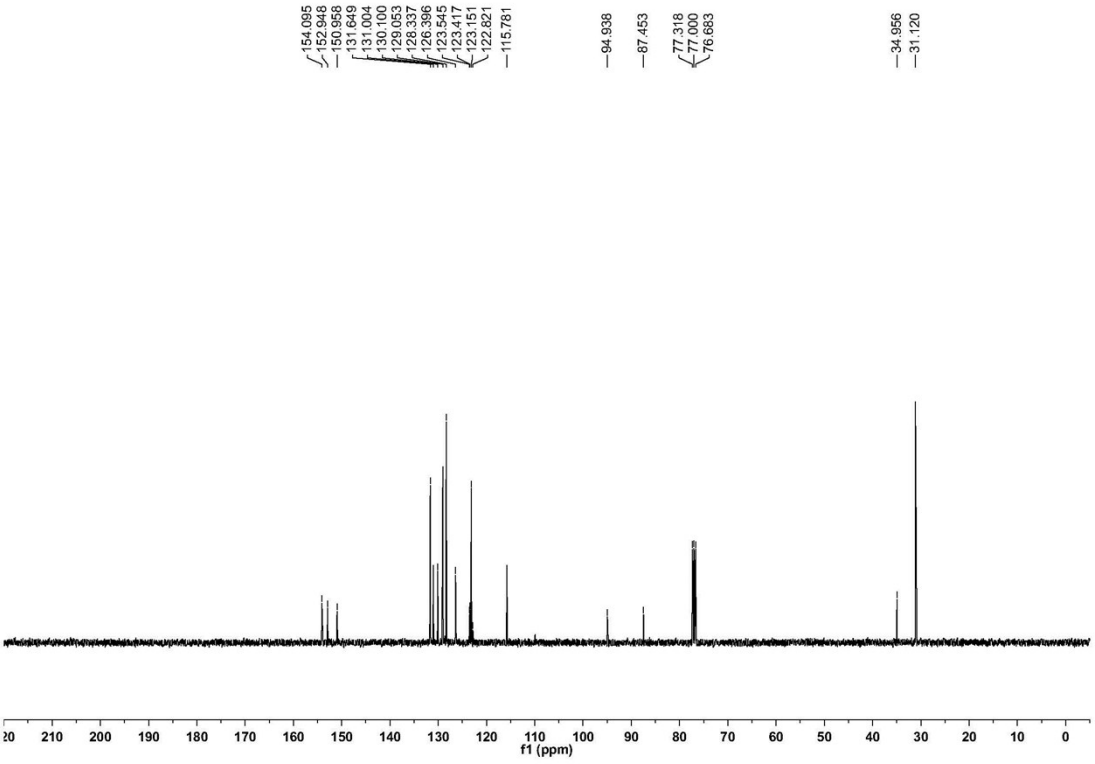
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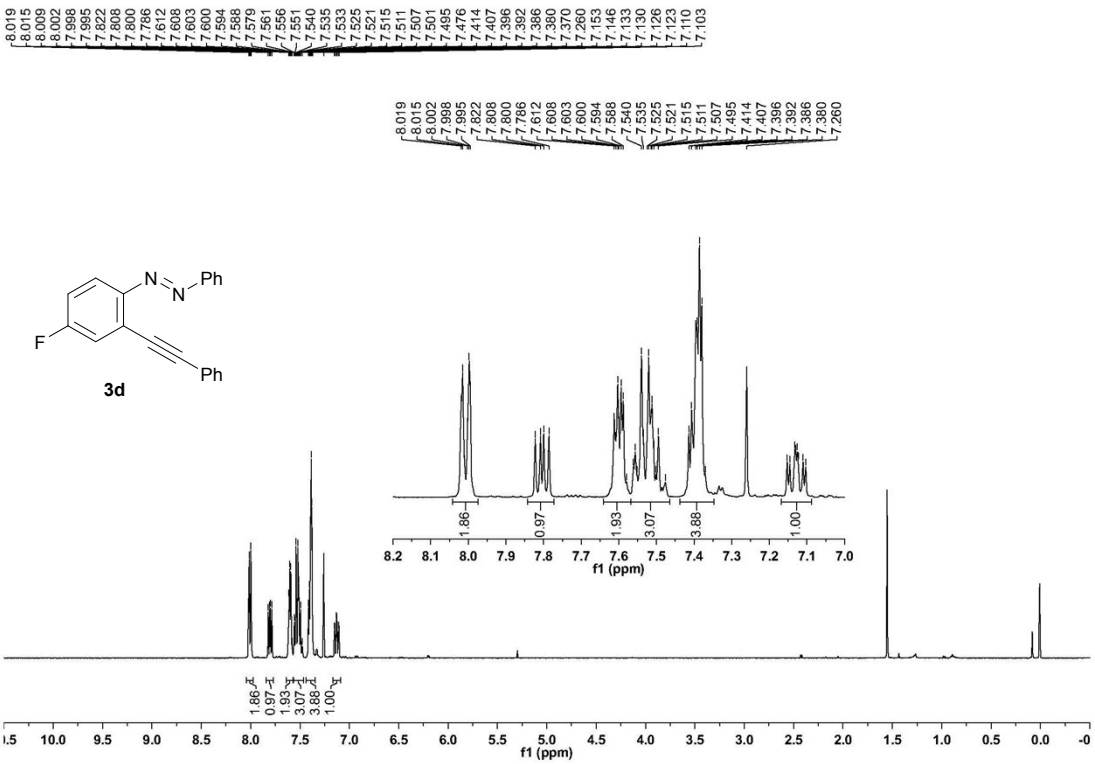
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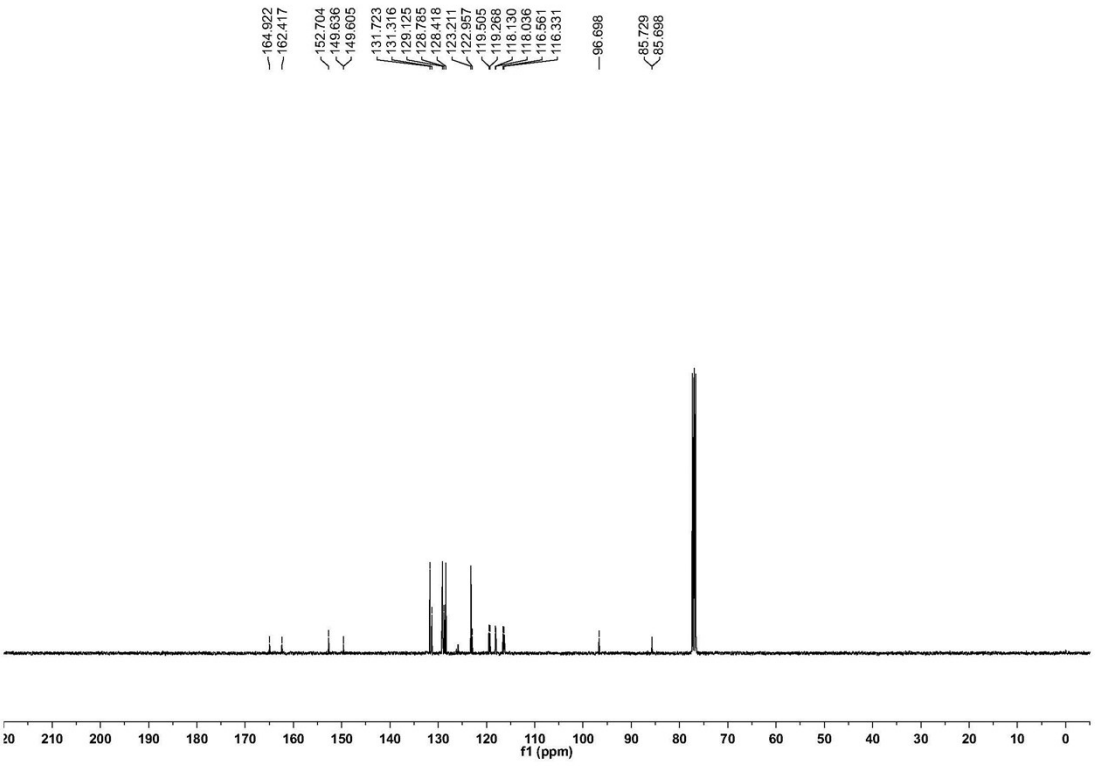
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85.698
f1 (ppm)


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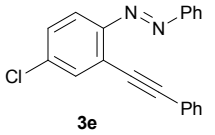
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Ph

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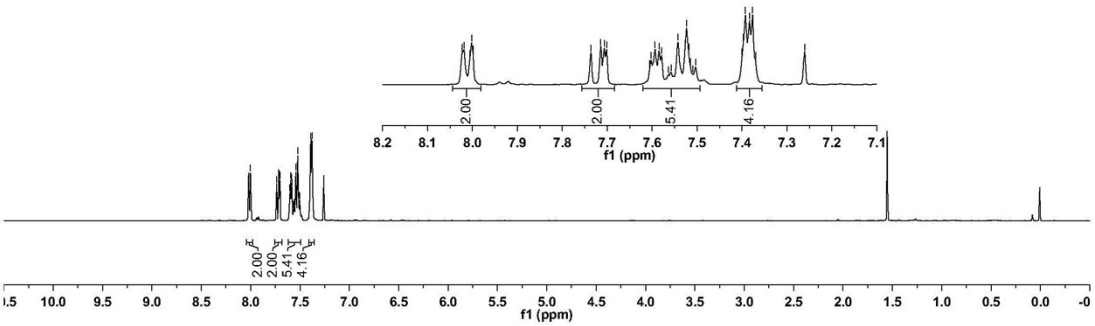
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f1 (ppm)


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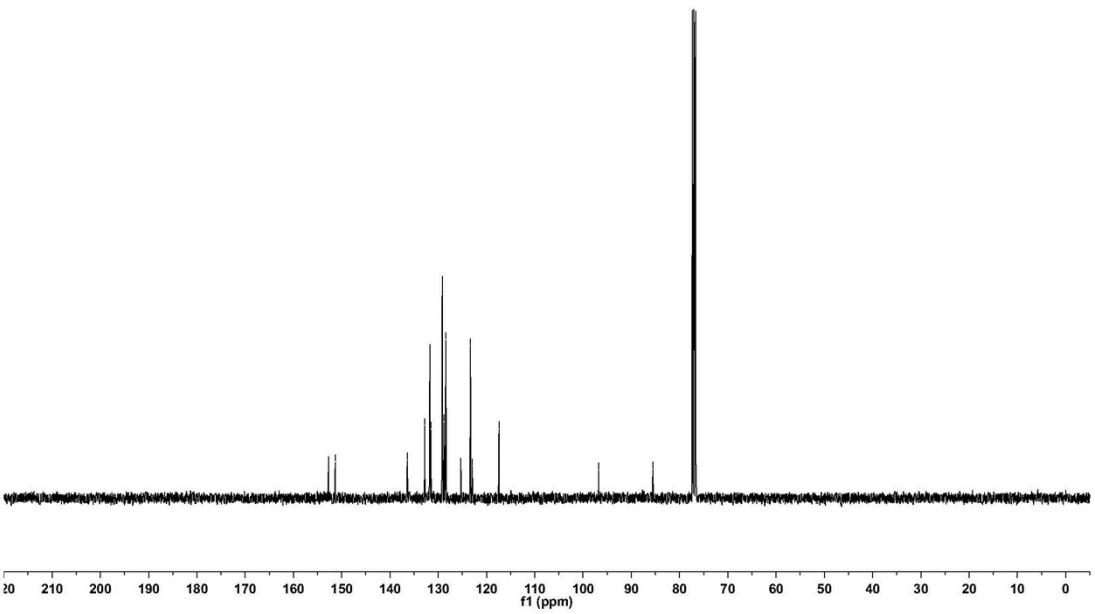
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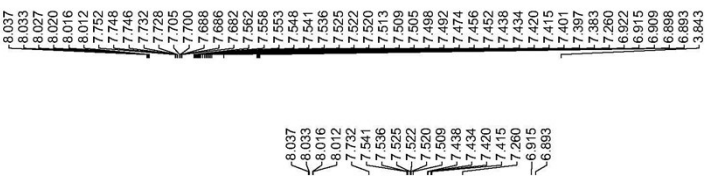
f1 (ppm)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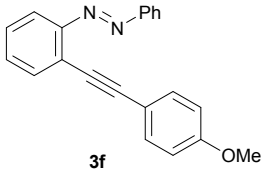
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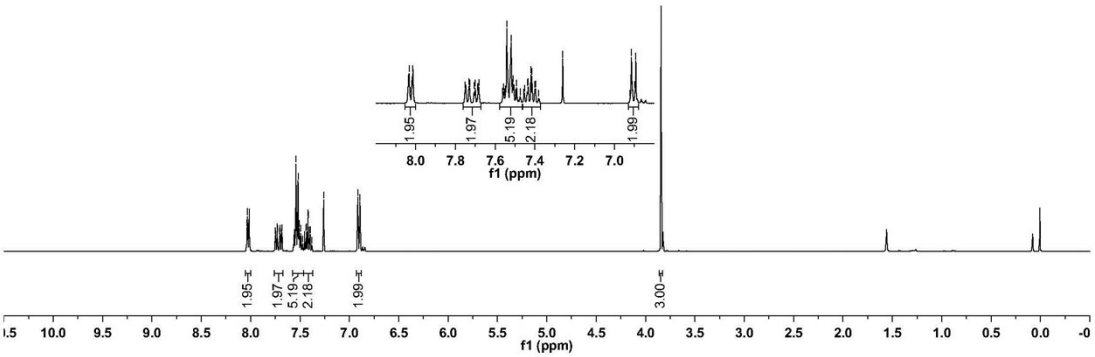
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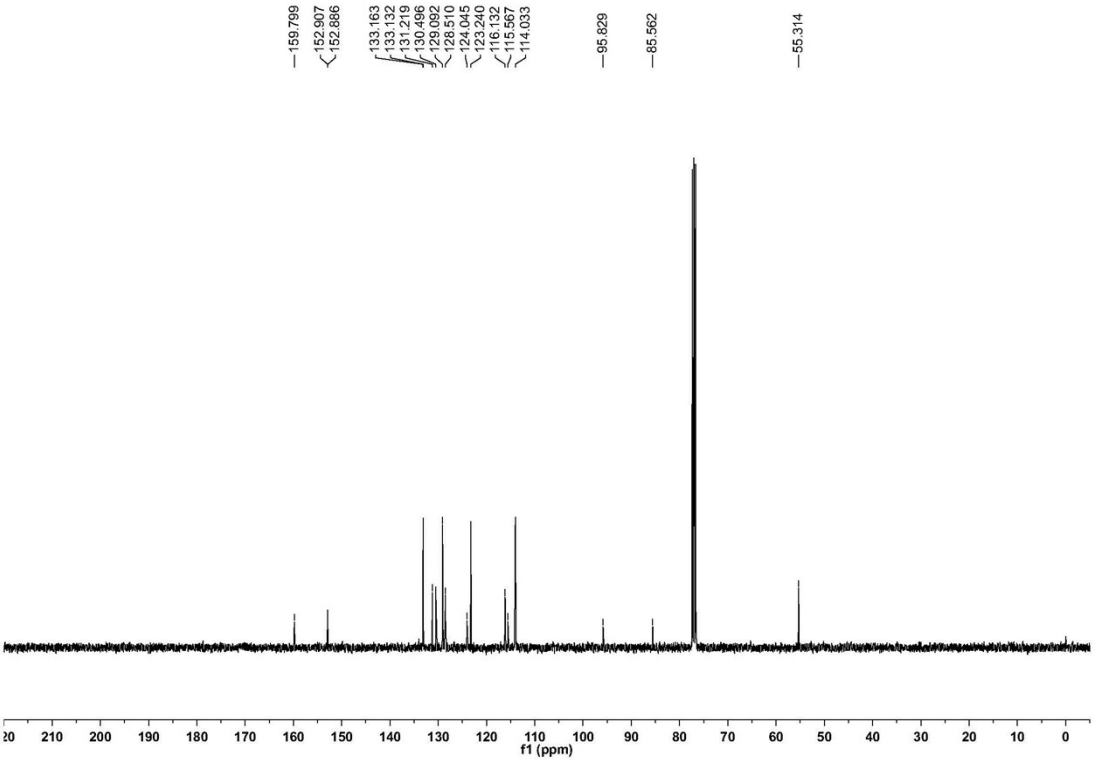
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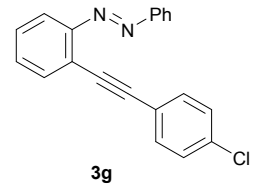

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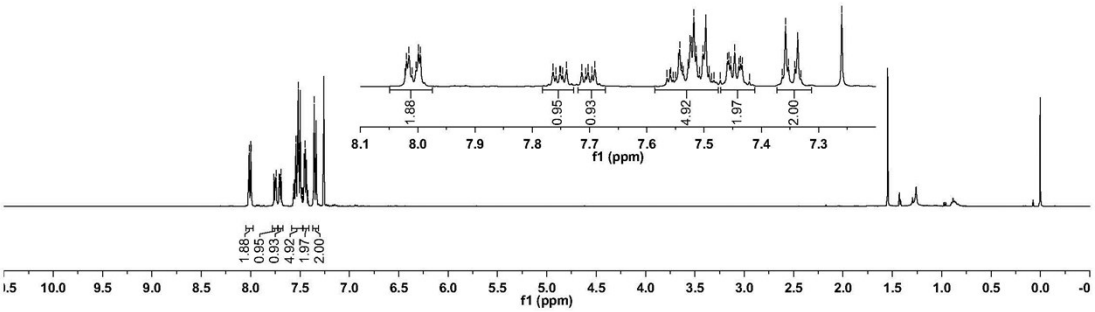
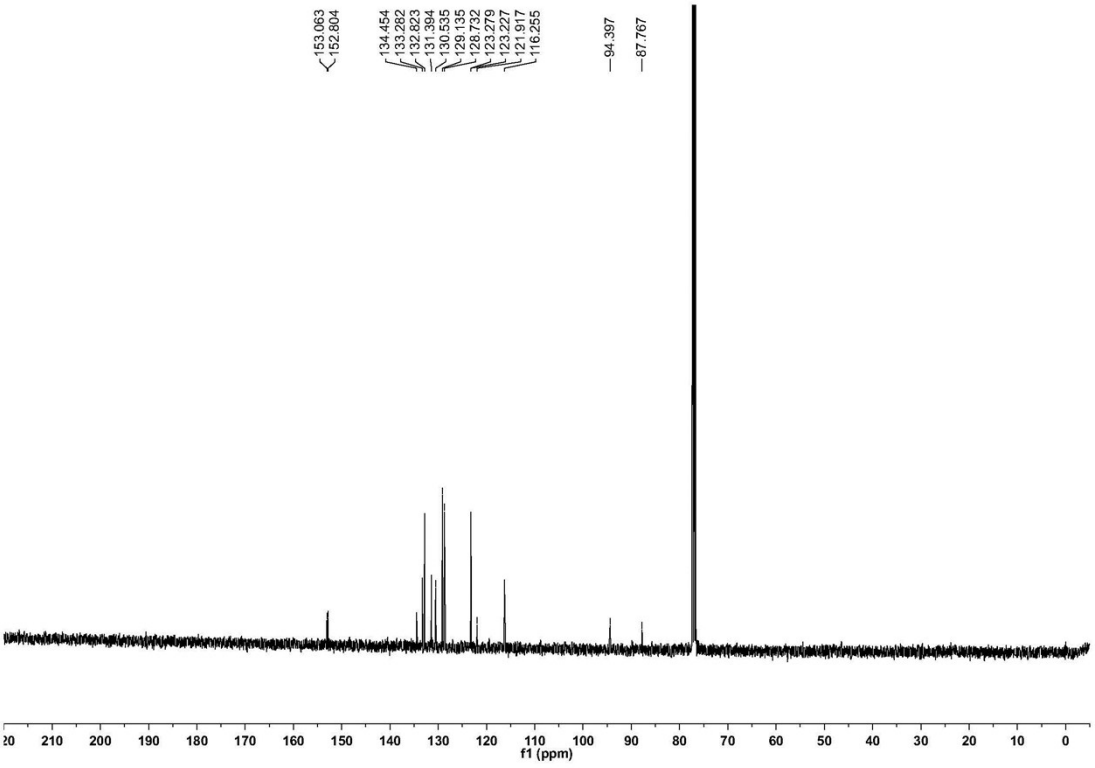
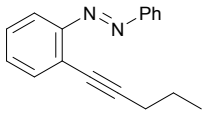
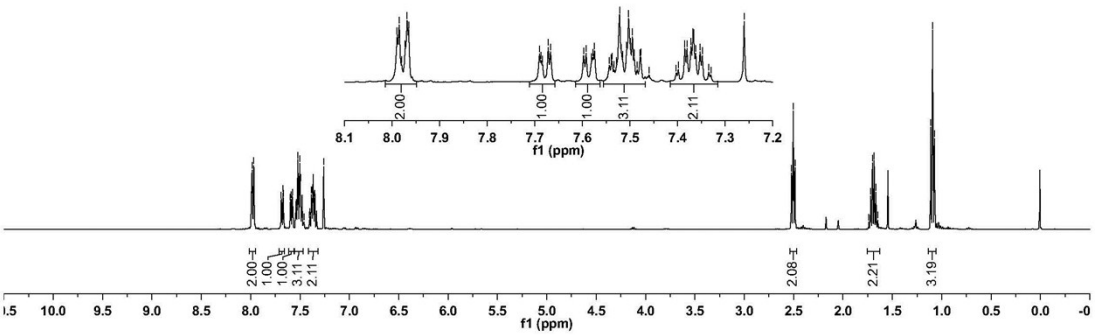
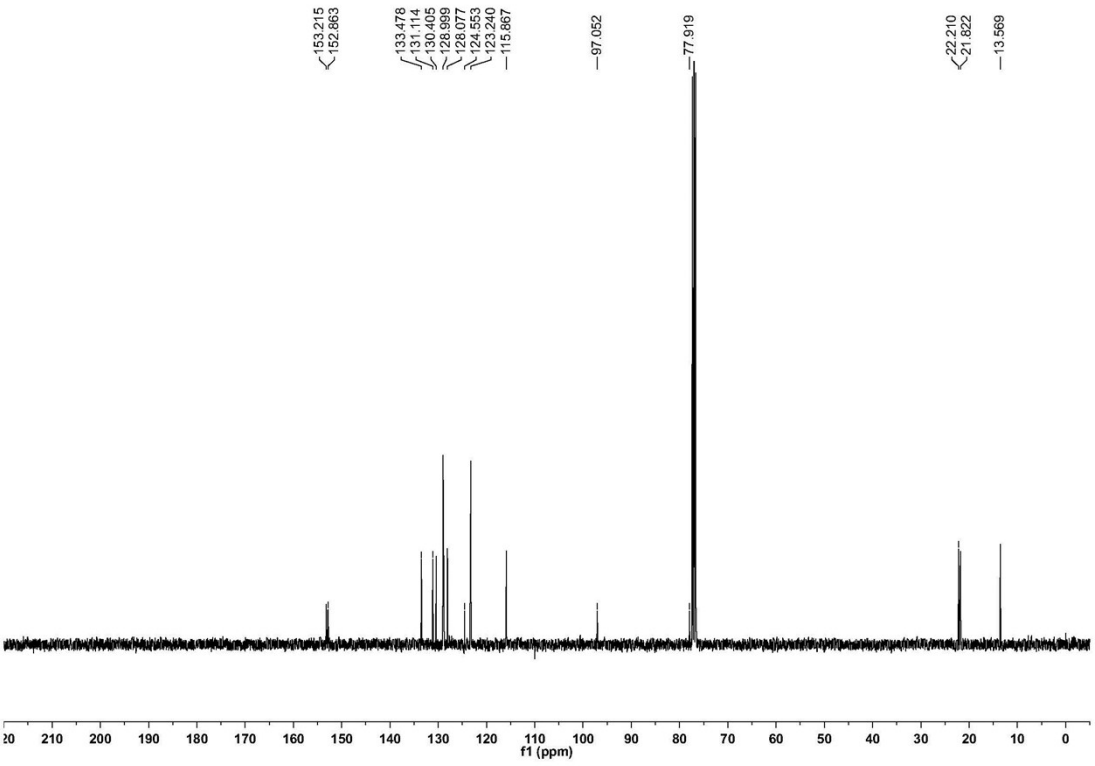


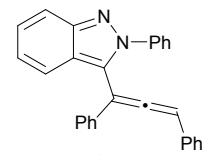




3h







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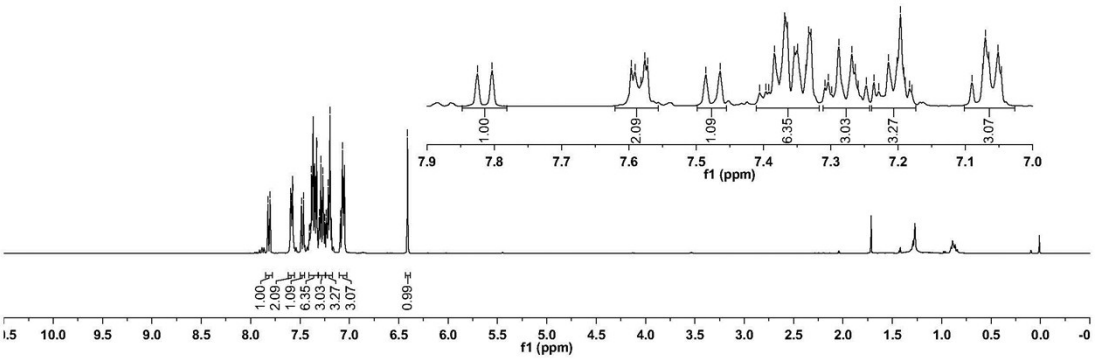
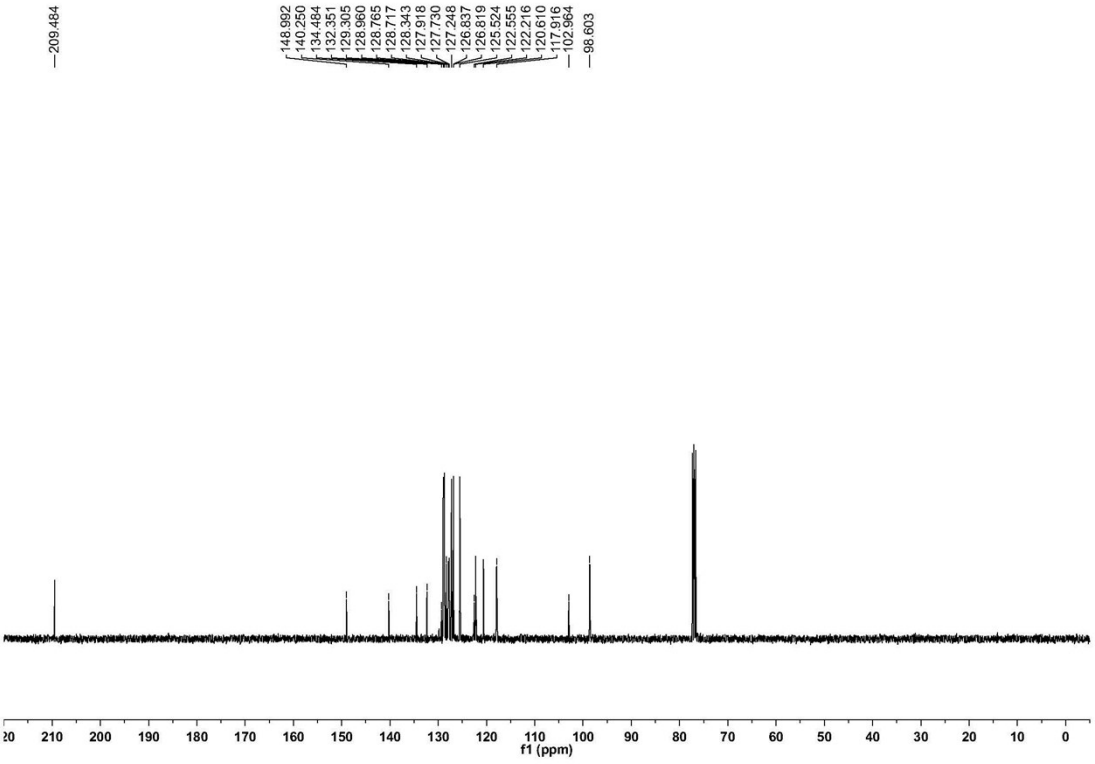
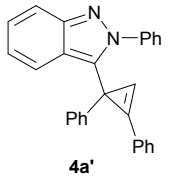
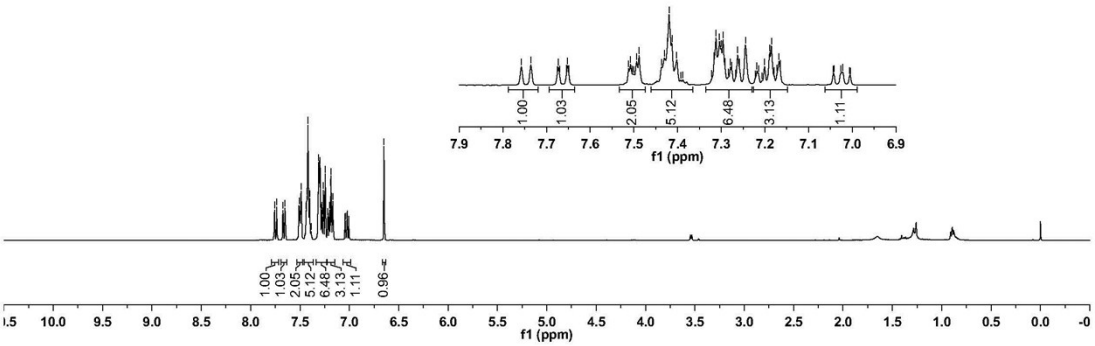
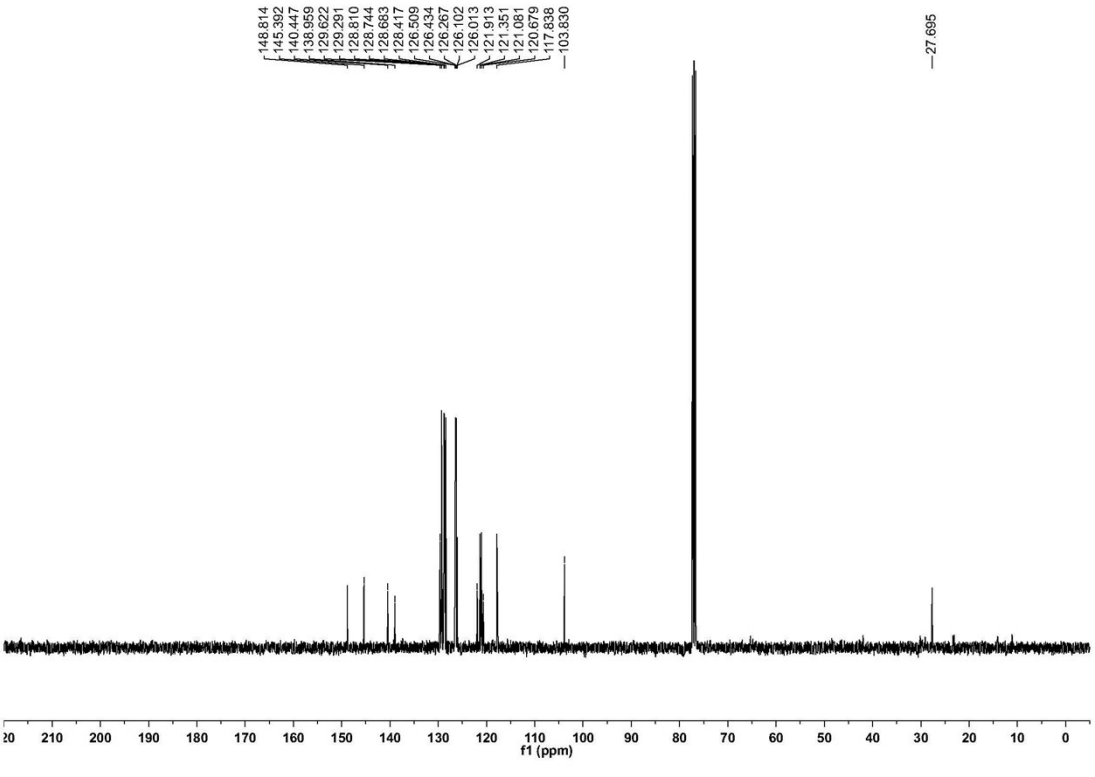


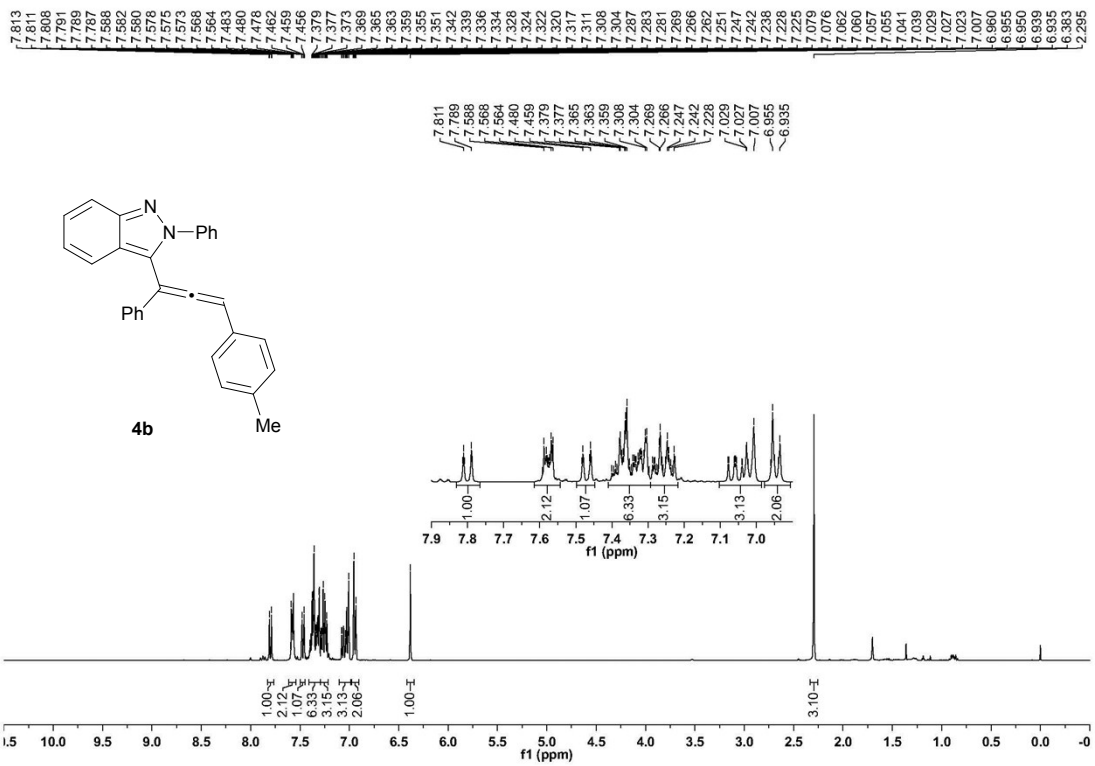




4a'



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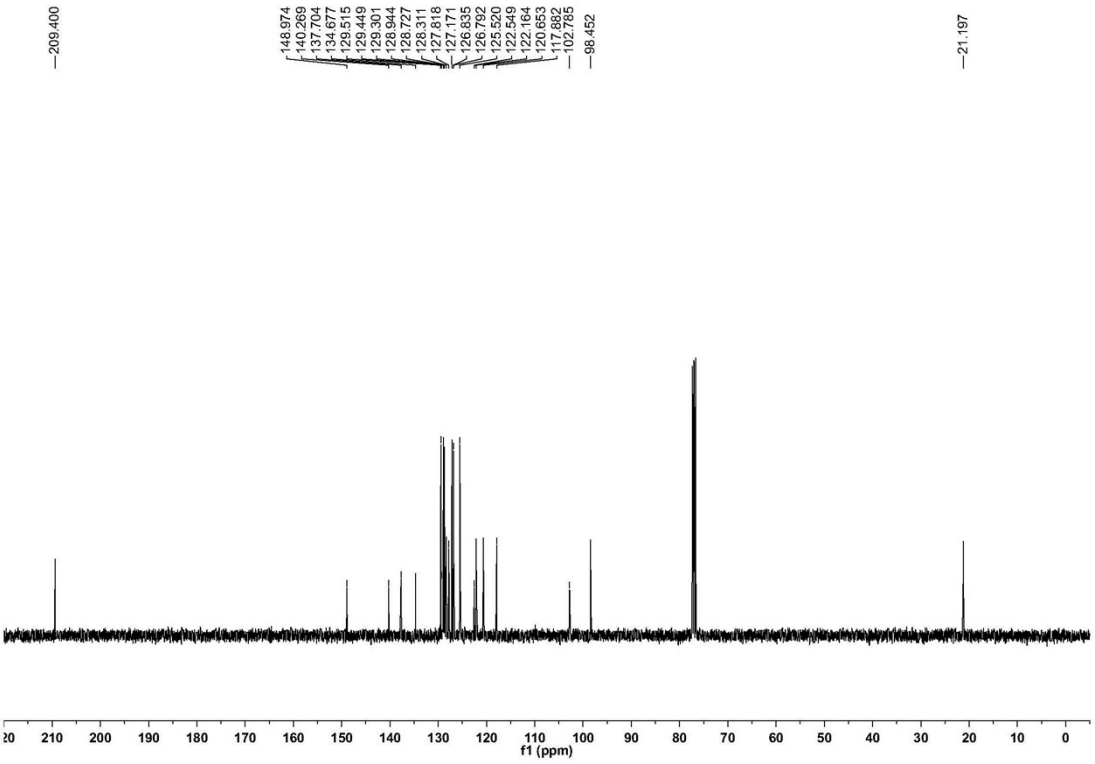
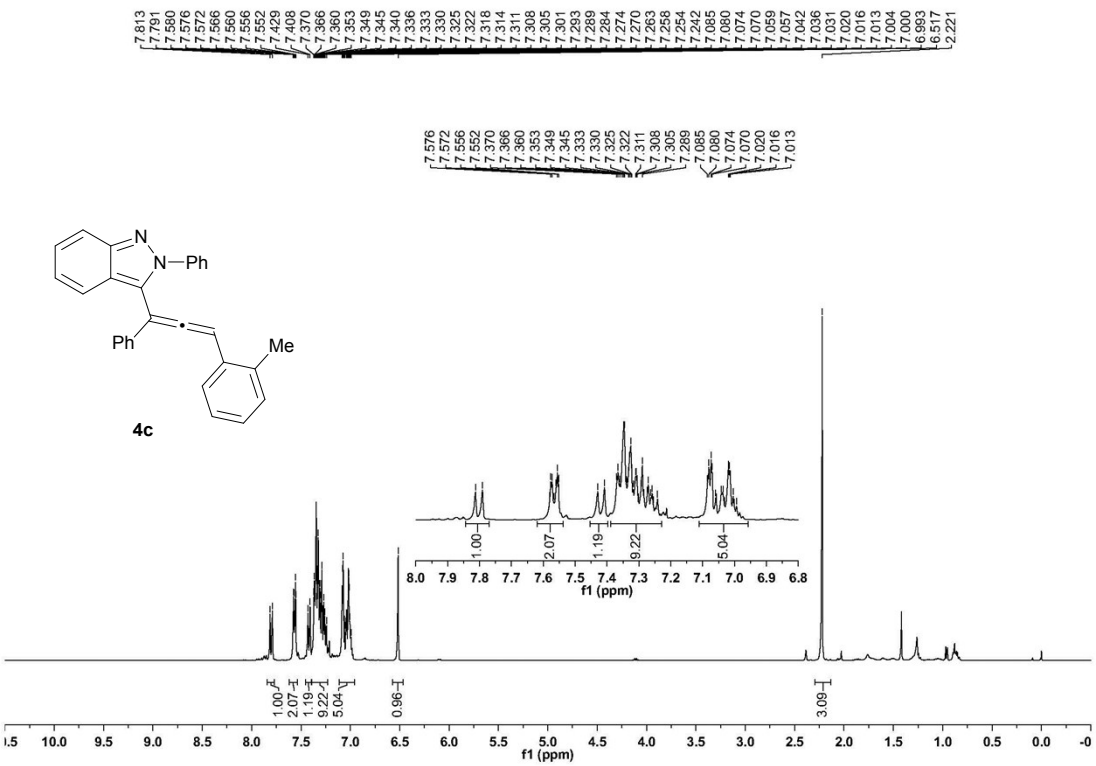
N—Ph
Ph
Me
4b
f1 (ppm)


f1 (ppm)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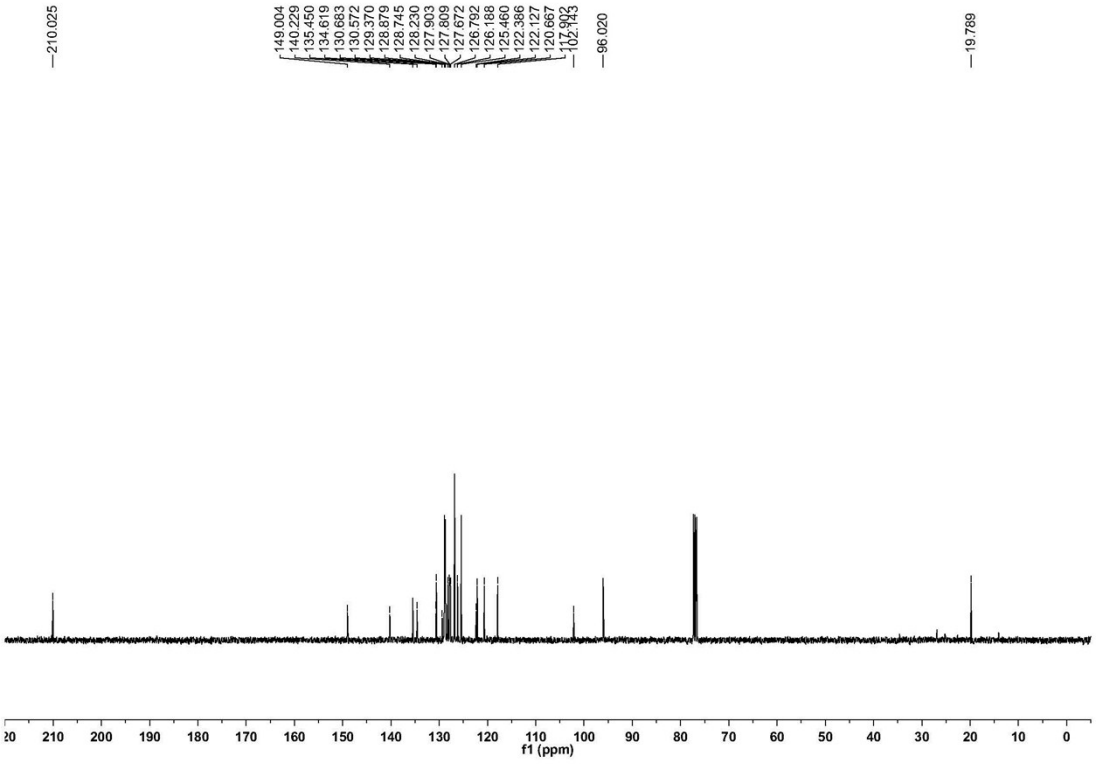
7.572
7.566
7.560
7.556
7.552
7.429
7.408
7.370
7.366
7.360
7.353
7.349
7.345
7.340
7.336
7.333
7.330
7.325
7.322
7.318
7.314
7.311
7.308
7.305
7.301
7.293
7.289
7.284
7.274
7.270
7.263
7.258
7.254
7.242
7.085
7.080
7.074
7.070
7.059
7.057
7.042
7.036
7.031
7.020
7.016
7.013
7.004
7.000
6.993
6.517
2.221
7.576
7.572
7.556
7.552
7.370
7.366
7.360
7.353
7.349
7.345
7.333
7.330
7.325
7.322
7.311
7.308
7.305
7.289
7.085
7.080
7.074
7.070
7.020
7.016
7.013
N
N—Ph
Ph
Me
4c
1.00
2.07
1.19
9.22
5.04
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
1.00
2.07
1.19
9.22
5.04
0.96
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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130.683
130.572
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128.879
128.745
128.230
127.903
127.809
127.672
126.792
126.188
125.460
122.386
122.127
120.667
117.902
102.143
96.020
19.789
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.810
7.788
7.584
7.578
7.570
7.564
7.560
7.472
7.451
7.391
7.387
7.378
7.374
7.369
7.363
7.359
7.351
7.345
7.342
7.339
7.334
7.329
7.322
7.316
7.312
7.309
7.296
7.292
7.286
7.276
7.261
7.256
7.250
7.246
7.242
7.233
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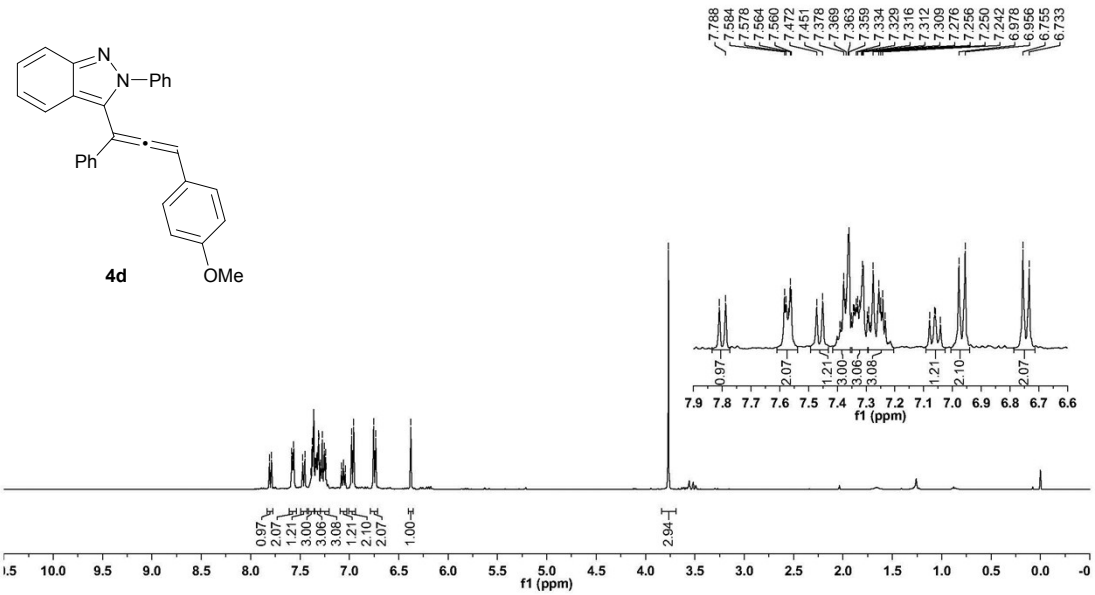
7.062
7.059
7.041
6.978
6.956
6.755
6.733
6.377
3.767


N
N—Ph
Ph
4d
OMe
7.788
7.584
7.578
7.564
7.560
7.472
7.451
7.378
7.369
7.363
7.359
7.334
7.329
7.316
7.312
7.309
7.276
7.256
7.250
7.242
6.978
6.956
6.755
6.733
0.97
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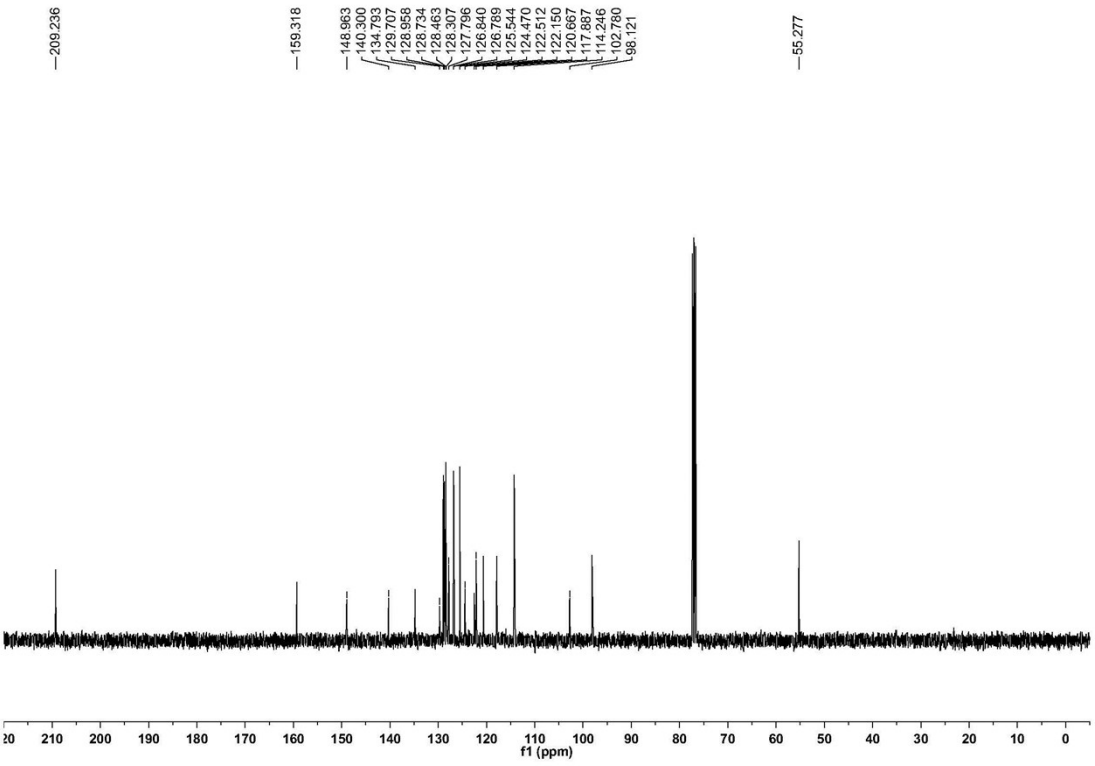
1.21
3.00
3.06
3.08
1.21
2.10
2.07
1.00
2.94
f1 (ppm)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140.300
134.793
129.707
128.958
128.734
128.463
128.307
127.796
126.840
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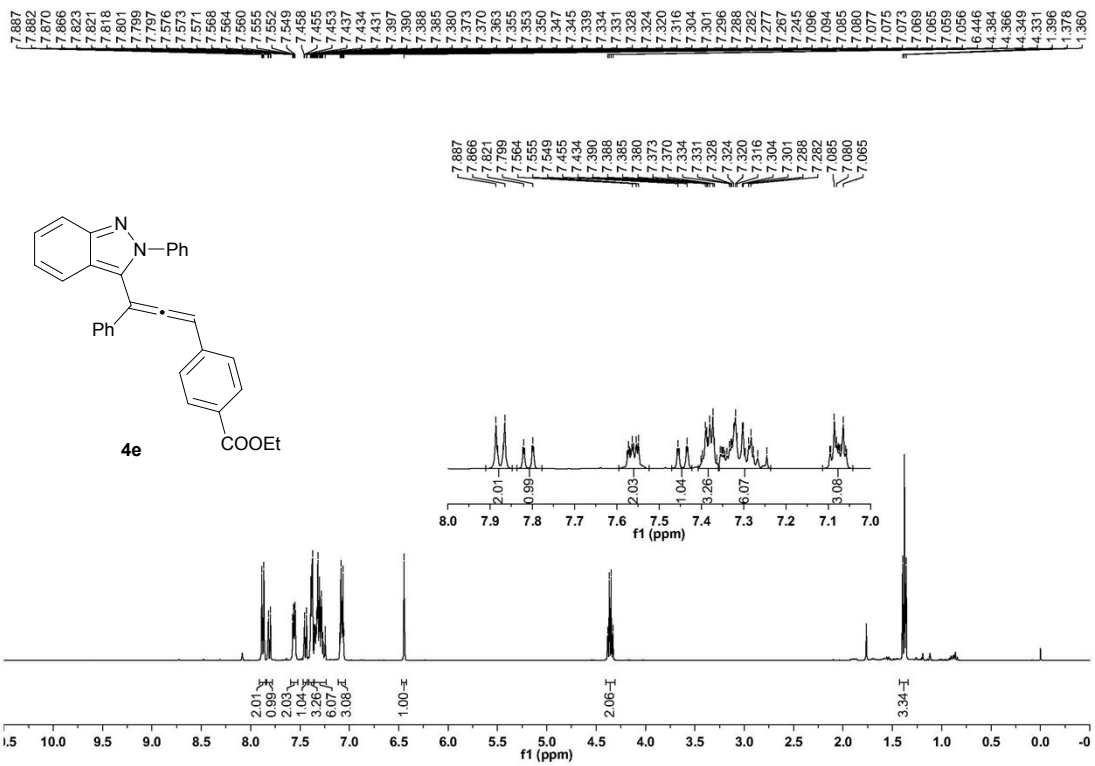
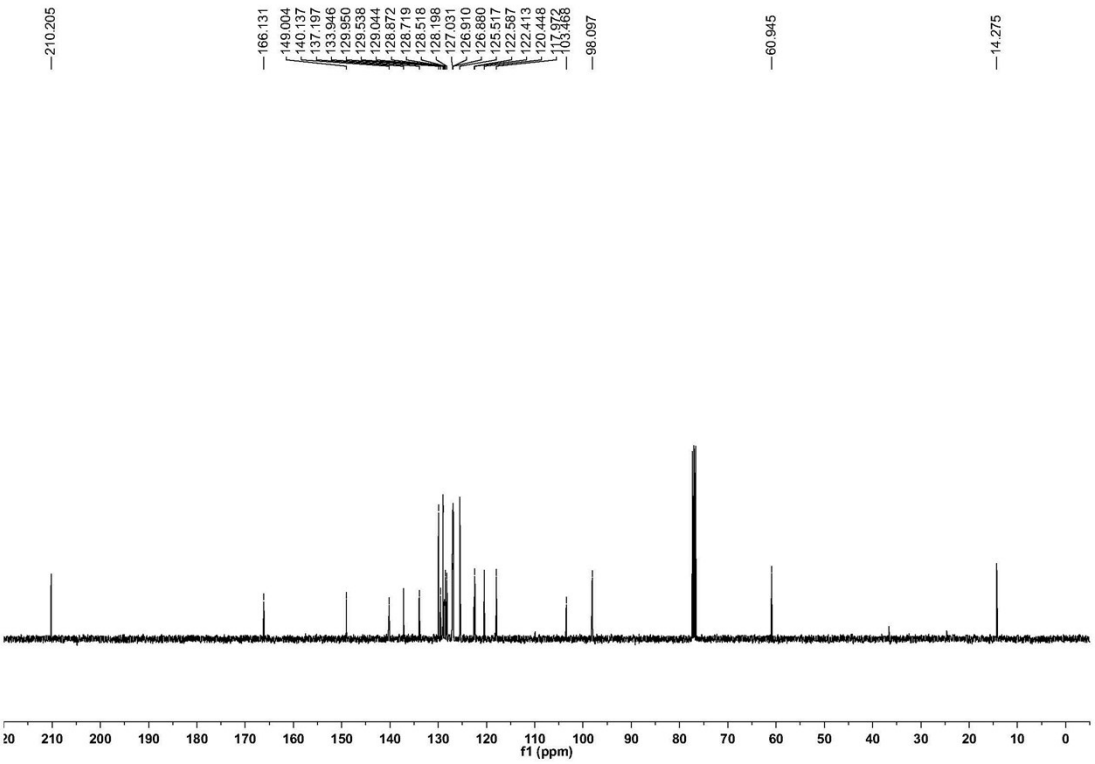
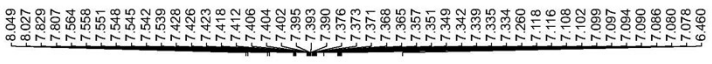
122.512
122.150
120.667
117.887
114.246
102.780
98.121
55.277
f1 (ppm)


N
N—Ph
Ph
COOEt
4e
f1 (ppm)


f1 (ppm)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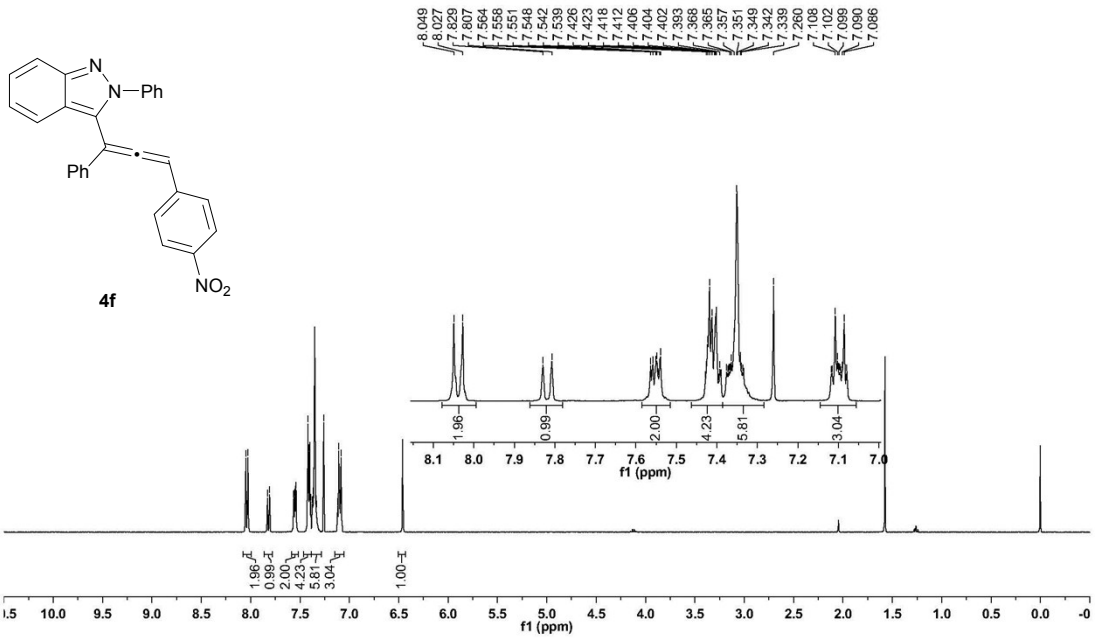
7.551
7.548
7.545
7.542
7.539
7.428
7.426
7.423
7.418
7.412
7.406
7.404
7.402
7.395
7.393
7.390
7.376
7.373
7.371
7.368
7.365
7.357
7.351
7.349
7.342
7.339
7.335
7.334
7.260
7.118
7.116
7.108
7.102
7.099
7.097
7.094
7.090
7.086
7.080
7.078
6.460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N—Ph
Ph
NO2
4f
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8.027
7.829
7.807
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7.556
7.551
7.548
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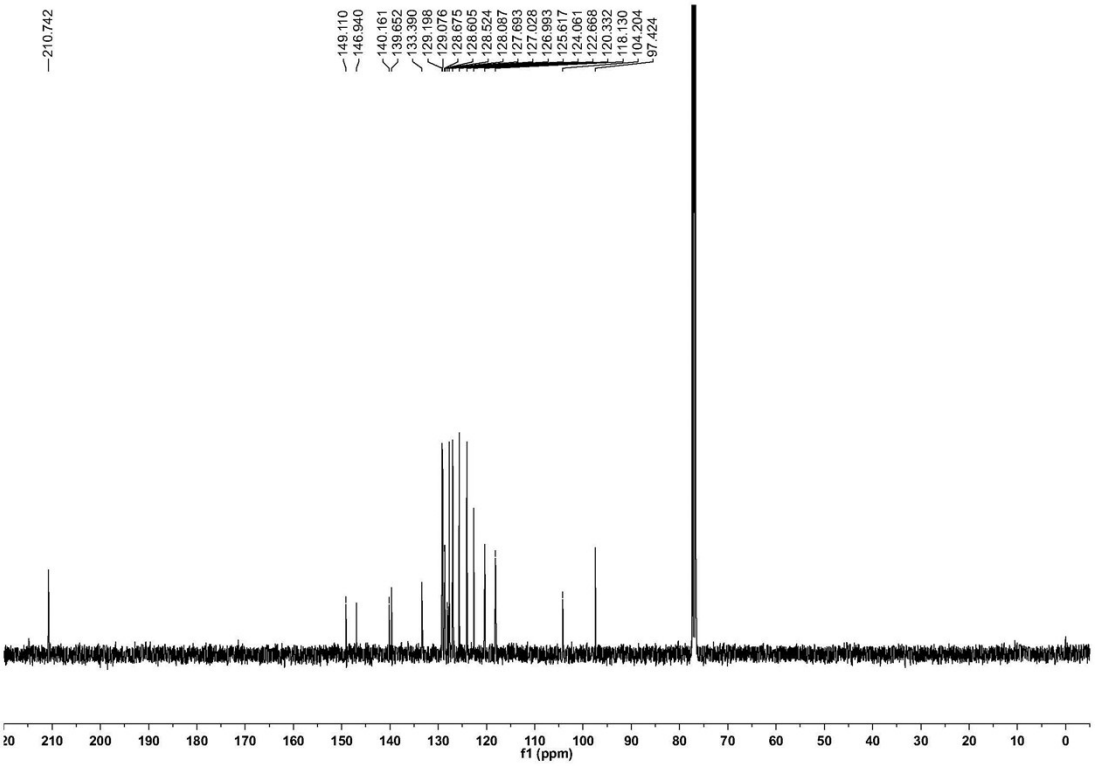
7.426
7.423
7.418
7.412
7.406
7.404
7.402
7.393
7.368
7.365
7.357
7.351
7.349
7.342
7.339
7.260
7.108
7.102
7.099
7.090
7.086
1.96
0.99
2.00
4.23
5.81
3.04
1.00
f1 (ppm)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128.524
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127.693
127.028
126.993
125.617
124.061
122.668
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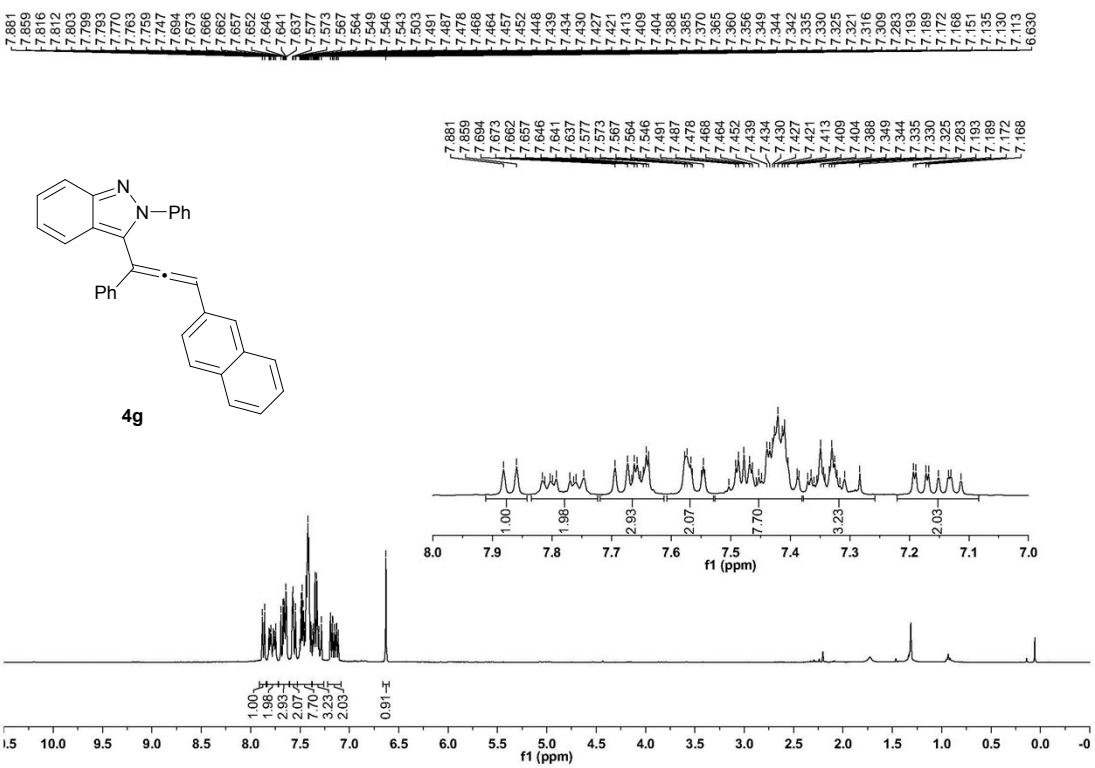
118.130
104.204
97.424
f1 (ppm)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7.673
7.666
7.662
7.657
7.652
7.646
7.641
7.637
7.577
7.573
7.567
7.564
7.549
7.546
7.543
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7.491
7.487
7.478
7.468
7.464
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7.452
7.448
7.439
7.434
7.430
7.427
7.421
7.413
7.409
7.404
7.388
7.385
7.370
7.365
7.360
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7.344
7.342
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7.330
7.325
7.321
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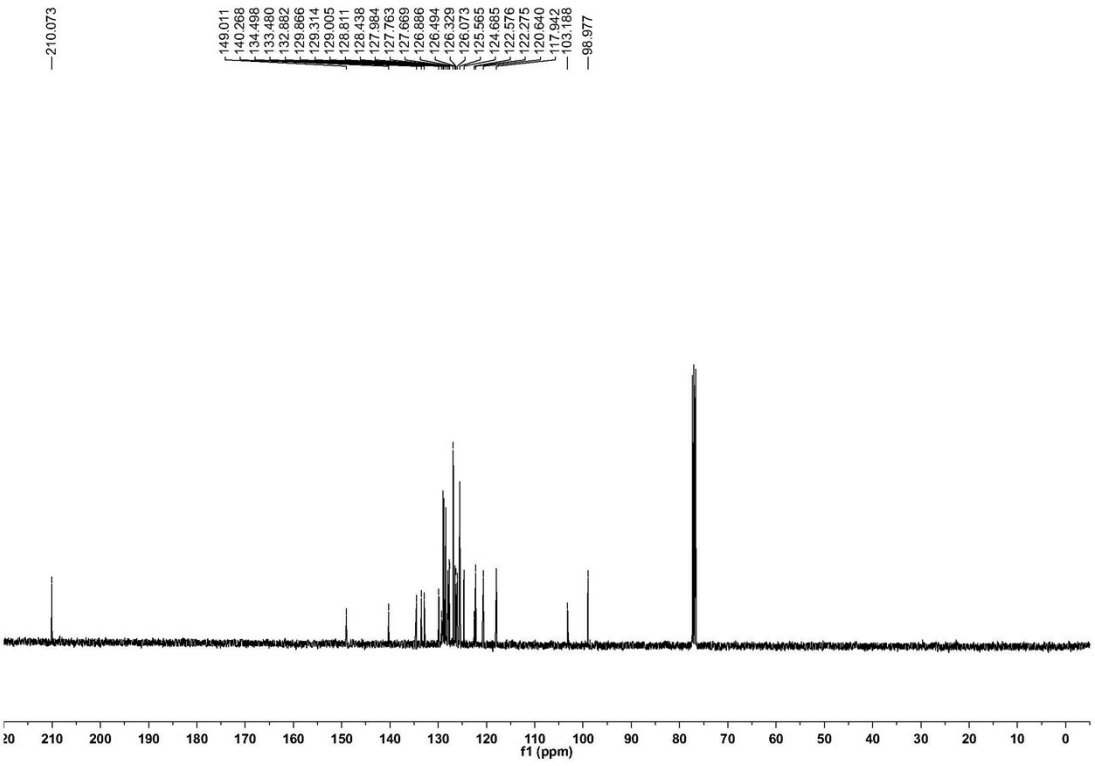
7.309
7.283
7.193
7.189
7.172
7.168
7.151
7.135
7.130
7.113
6.630
N
N—Ph
Ph
4g
1.00
1.98
2.93
2.07
7.70
3.23
2.03
0.91
f1 (ppm)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129.314
129.005
128.811
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127.984
127.763
127.669
126.886
126.494
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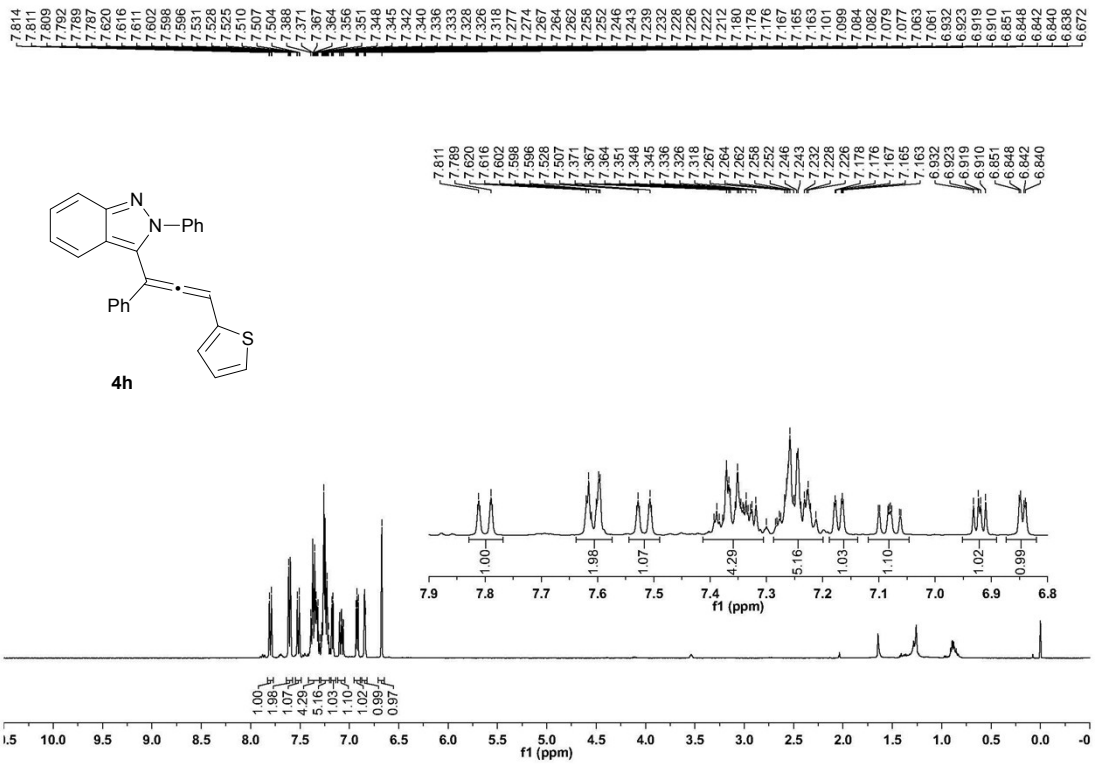
125.565
124.685
122.576
122.275
120.640
117.942
103.186
98.977
f1 (ppm)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7.611
7.602
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7.596
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7.525
7.510
7.507
7.504
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7.371
7.367
7.364
7.356
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7.267
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7.063
7.061
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6.923
6.919
6.910
6.851
6.848
6.842
6.840
6.838
6.672
N
N—Ph
Ph
S
4h
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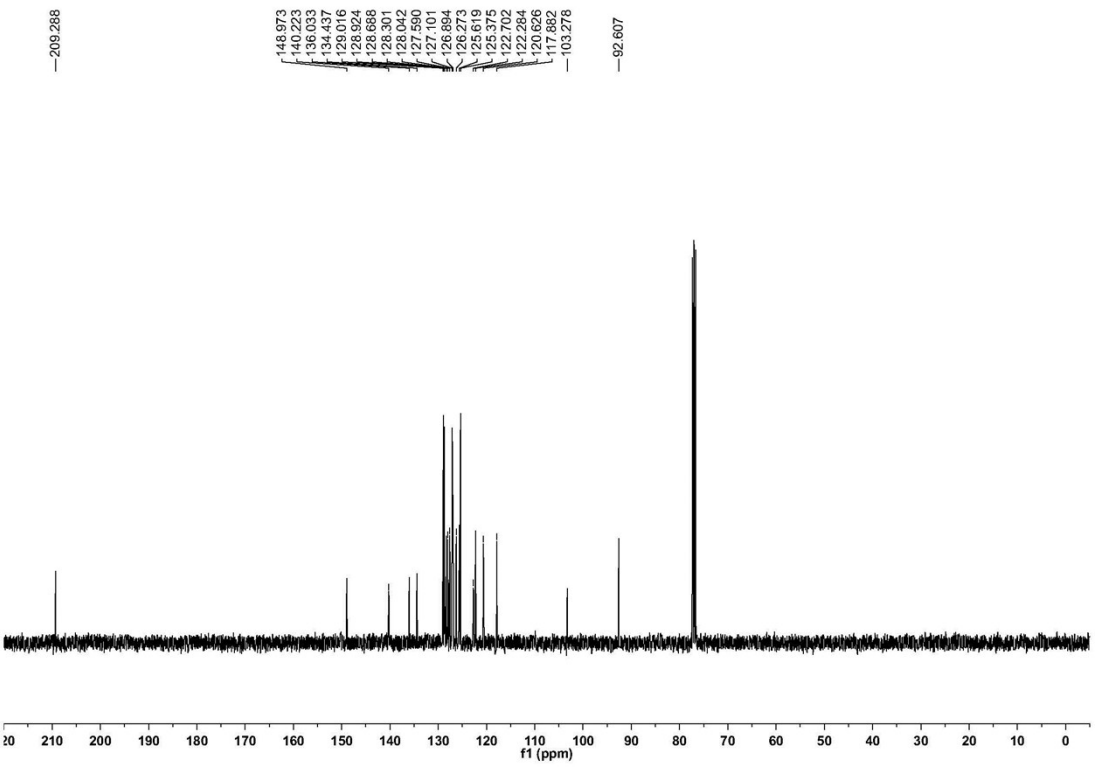
1.07
4.29
5.16
1.03
1.10
1.02
0.99
0.97
f1 (ppm)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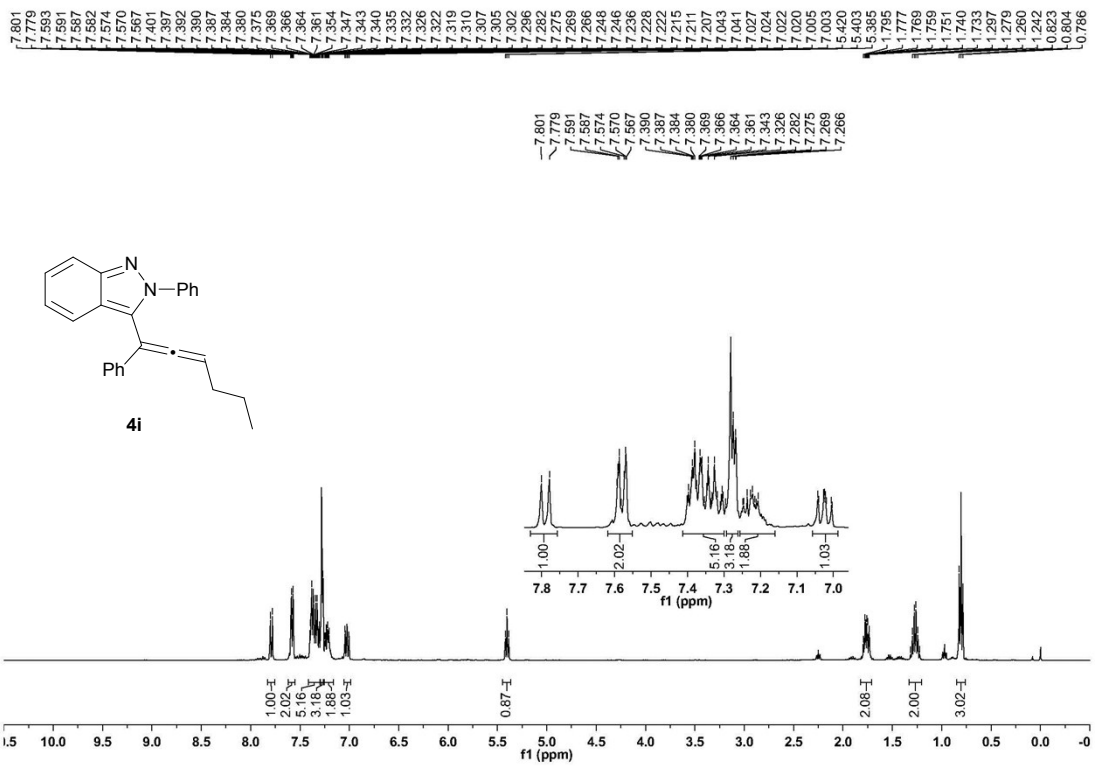
92.607
f1 (ppm)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7.390
7.387
7.384
7.380
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7.366
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7.322
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7.275
7.269
7.266
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7.041
7.027
7.024
7.022
7.020
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7.003
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5.403
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1.740
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1.297
1.279
1.260
1.242
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0.804
0.786
N
N—Ph
Ph
4i
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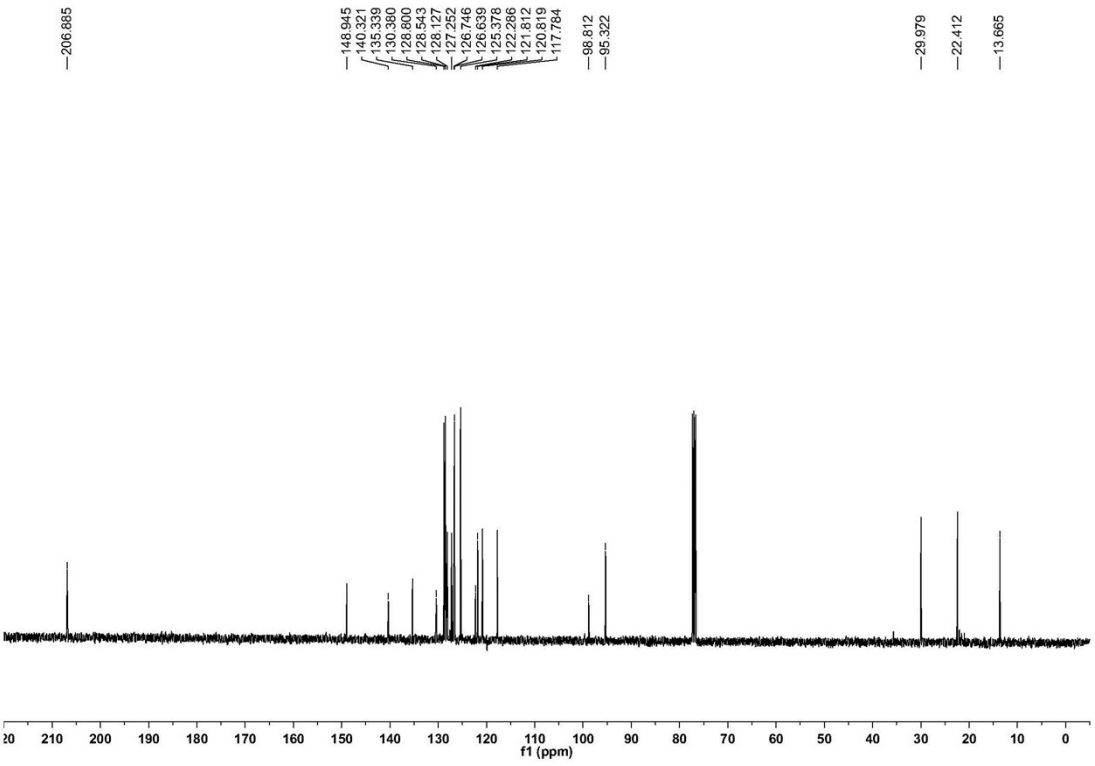
5.16
3.18
1.88
1.03
0.87
2.08
2.00
3.02
f1 (ppm)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120.819
117.784
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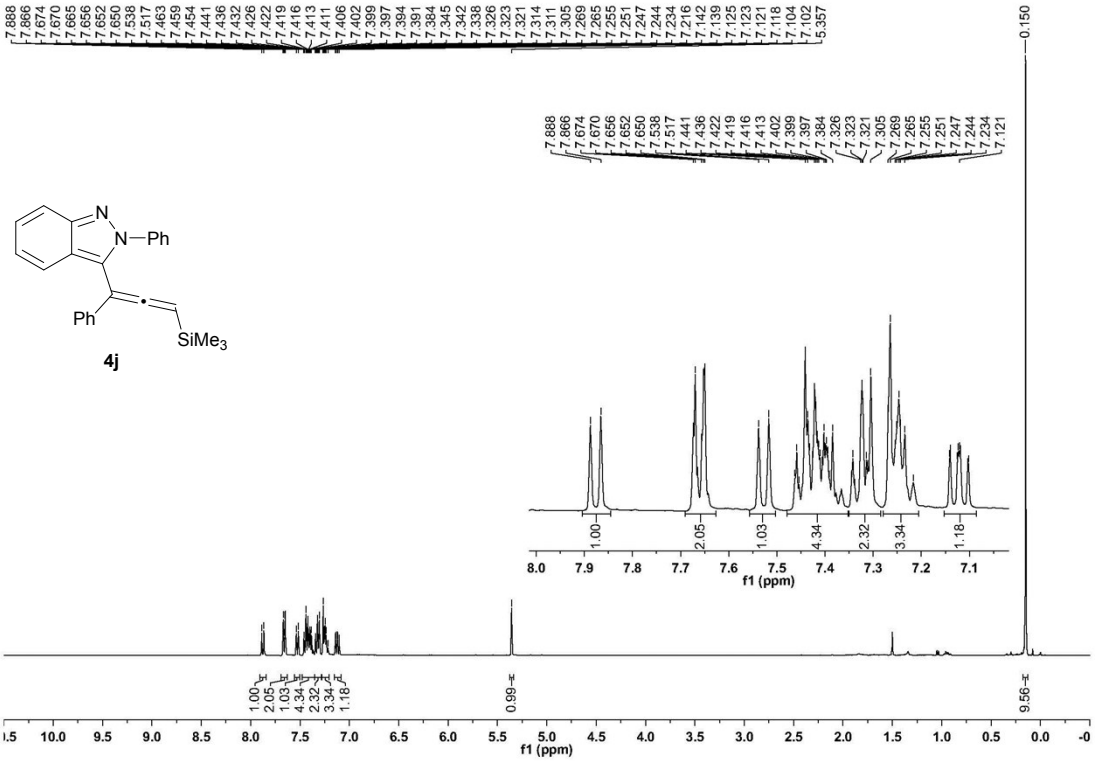
29.979
22.412
13.665
f1 (ppm)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7.454
7.441
7.436
7.432
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7.422
7.419
7.416
7.413
7.411
7.406
7.402
7.399
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7.391
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7.323
7.321
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7.311
7.305
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7.251
7.247
7.244
7.234
7.216
7.142
7.139
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7.123
7.121
7.118
7.104
7.102
5.357
0.150
N
N—Ph
Ph
SiMe3
4j
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2.05
1.03
4.34
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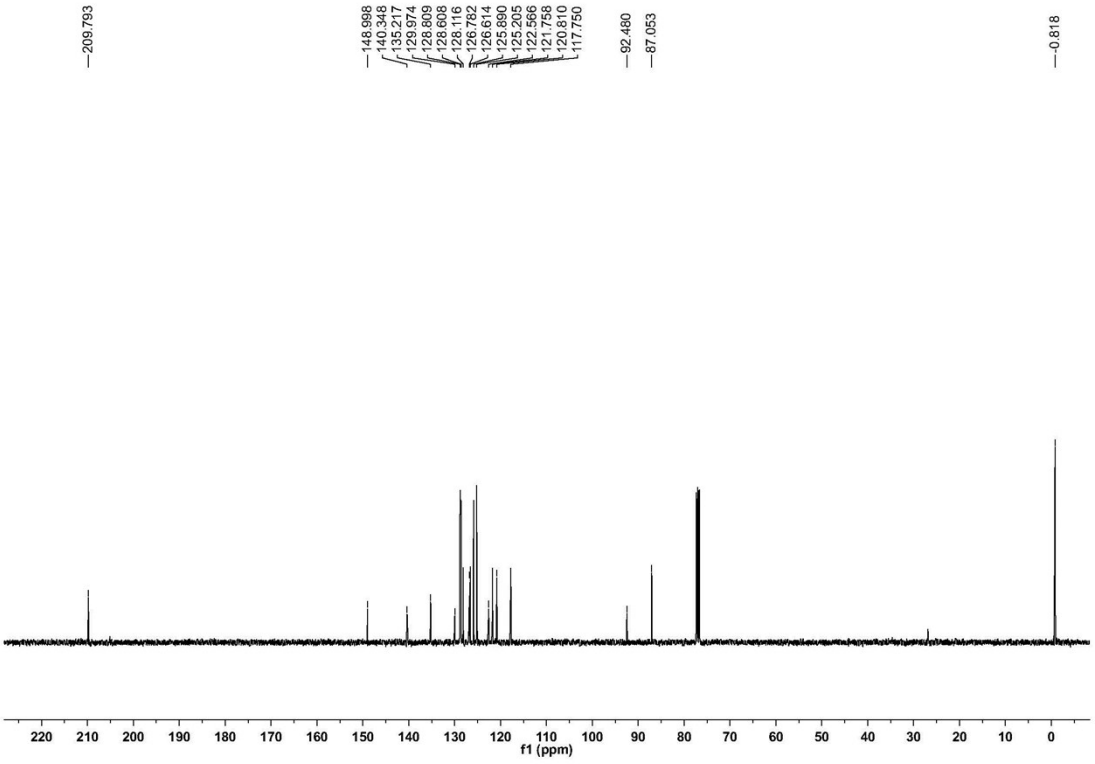
1.18
0.99
9.56
f1 (ppm)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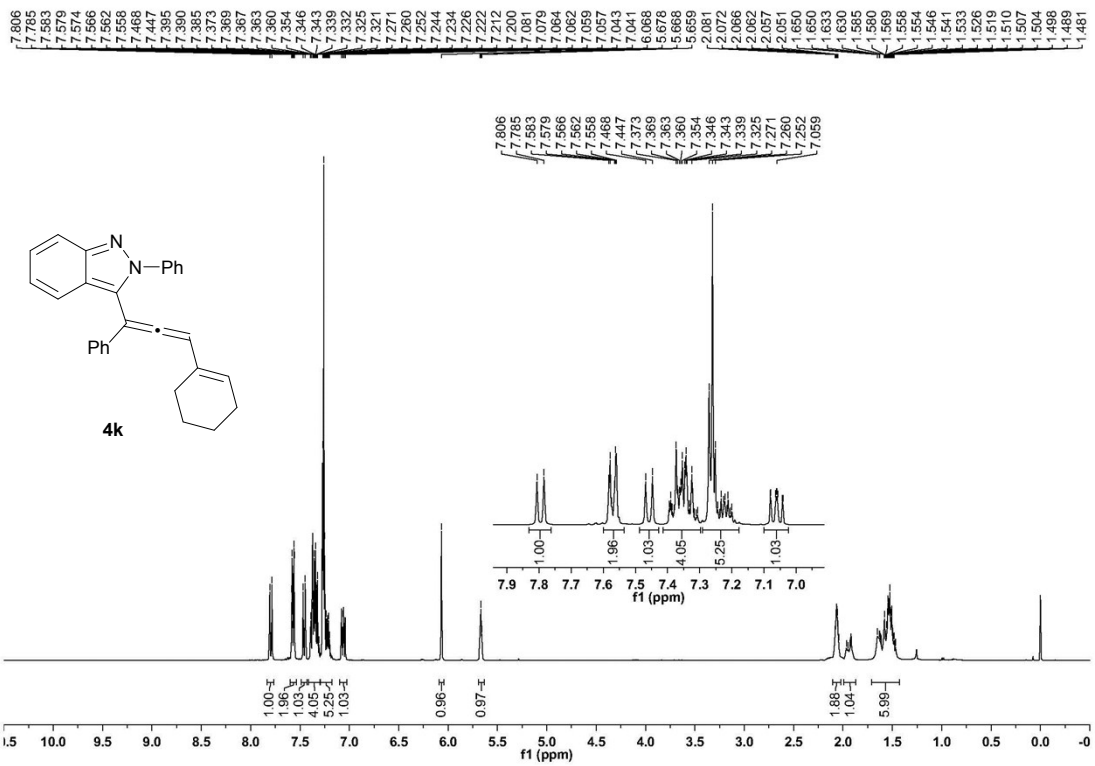
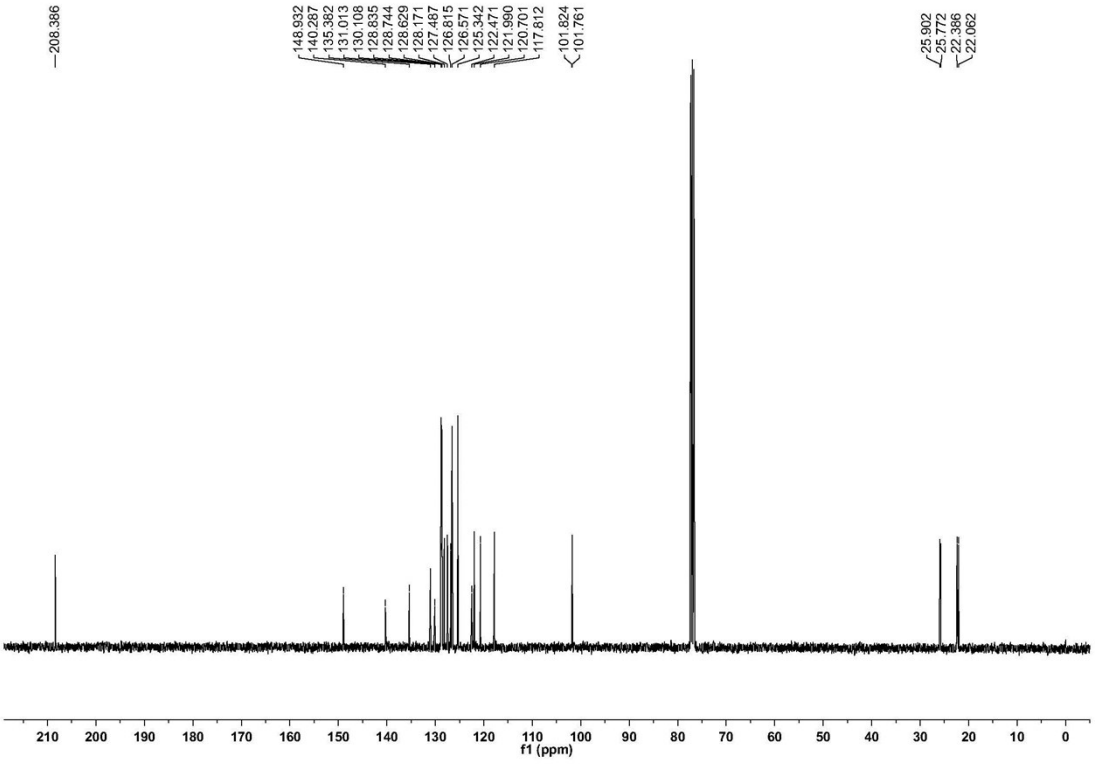
f1 (ppm)


4k
f1 (ppm)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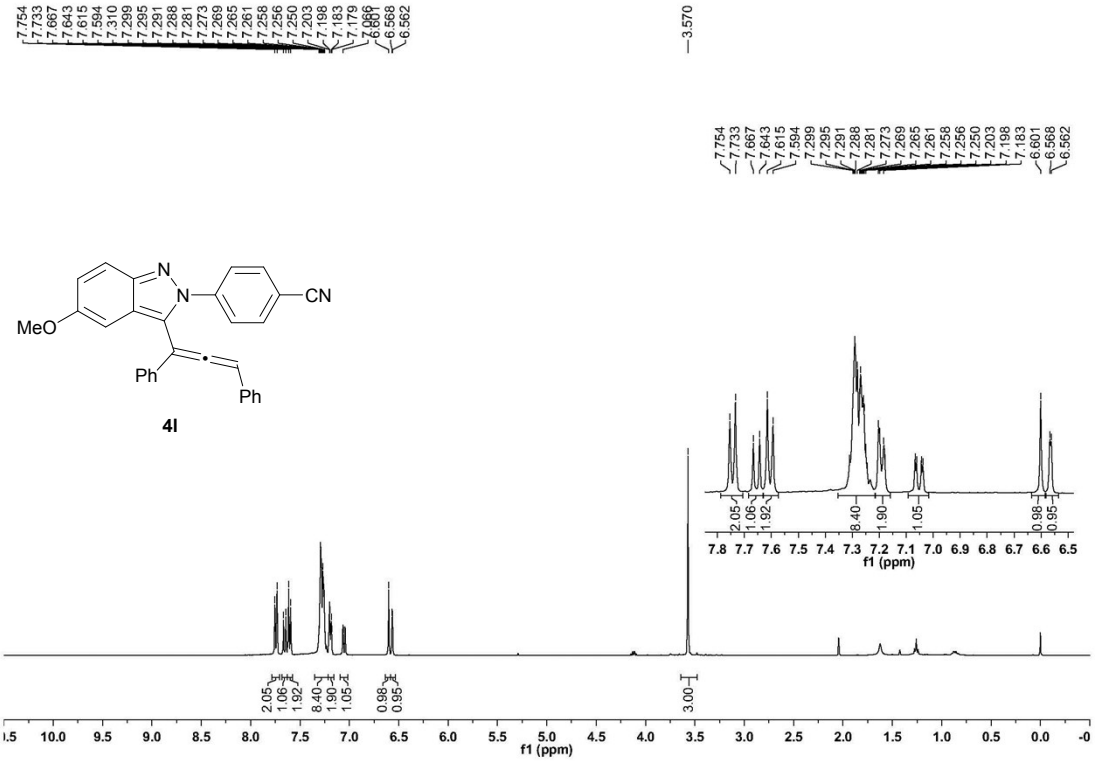
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7.265
7.261
7.258
7.256
7.250
7.203
7.198
7.183
7.179
6.601
6.568
6.562
3.570
MeO
N
N
CN
Ph
Ph
4l
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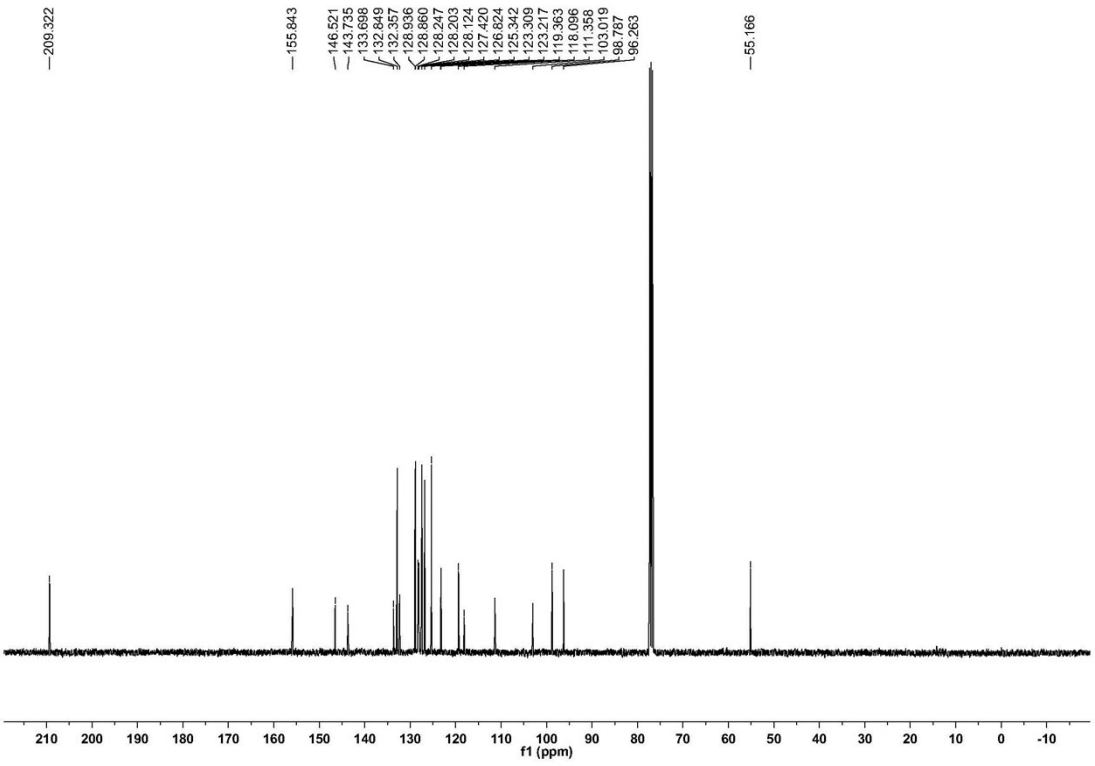
1.06
1.92
8.40
1.90
1.05
0.98
0.95
3.00
f1 (ppm)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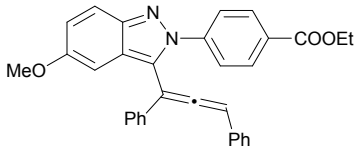
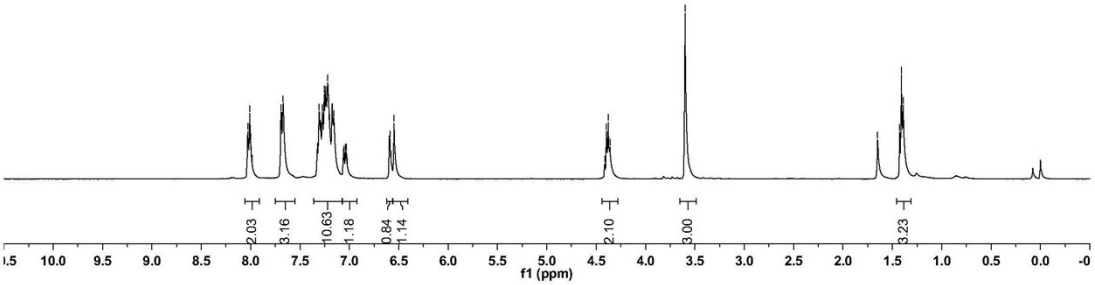
155.843
146.521
143.735
133.698
132.849
132.357
128.936
128.860
128.247
128.203
128.124
127.420
126.824
125.342
123.309
123.217
119.363
118.096
111.358
103.019
98.787
96.263
55.166
f1 (ppm)


8.030
8.023
8.013
8.008
8.001
7.994
7.987
7.694
7.688
7.677
7.673
7.666
7.657
7.329
7.325
7.306
7.293
7.289
7.273
7.255
7.247
7.243
7.238
7.225
7.220
7.214
7.209
7.199
7.177
7.172
7.157
7.062
7.056
7.048
7.043
7.038
7.032
7.025
7.019
6.595
6.589
6.579
6.547
4.414
4.396
4.378
4.360
3.600
1.650
1.641
1.426
1.408
1.390


N
N
COOEt
MeO
Ph
Ph

4m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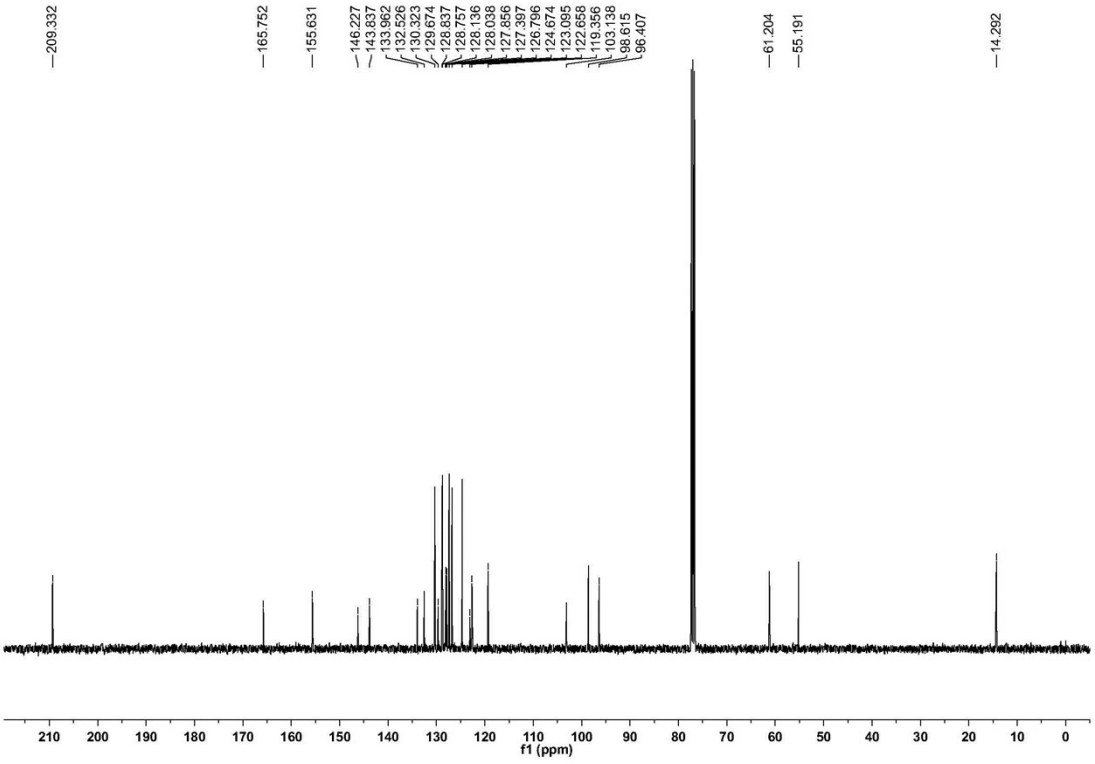
3.16
10.63
1.18
0.84
1.14
2.10
3.00
3.23
f1 (ppm)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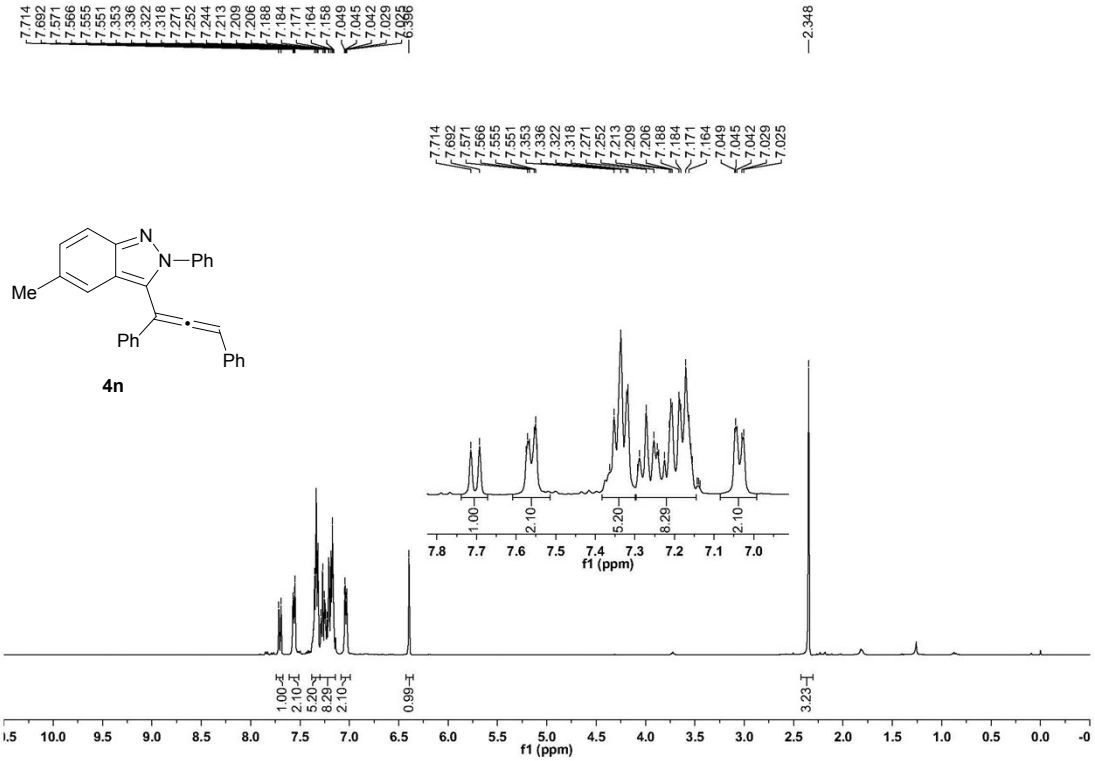
165.752
155.631
146.227
143.837
133.962
132.526
130.323
129.674
128.837
128.757
128.136
128.038
127.856
127.397
126.796
124.674
123.095
122.658
119.356
103.138
98.615
96.407
61.204
55.191
14.292
f1 (ppm)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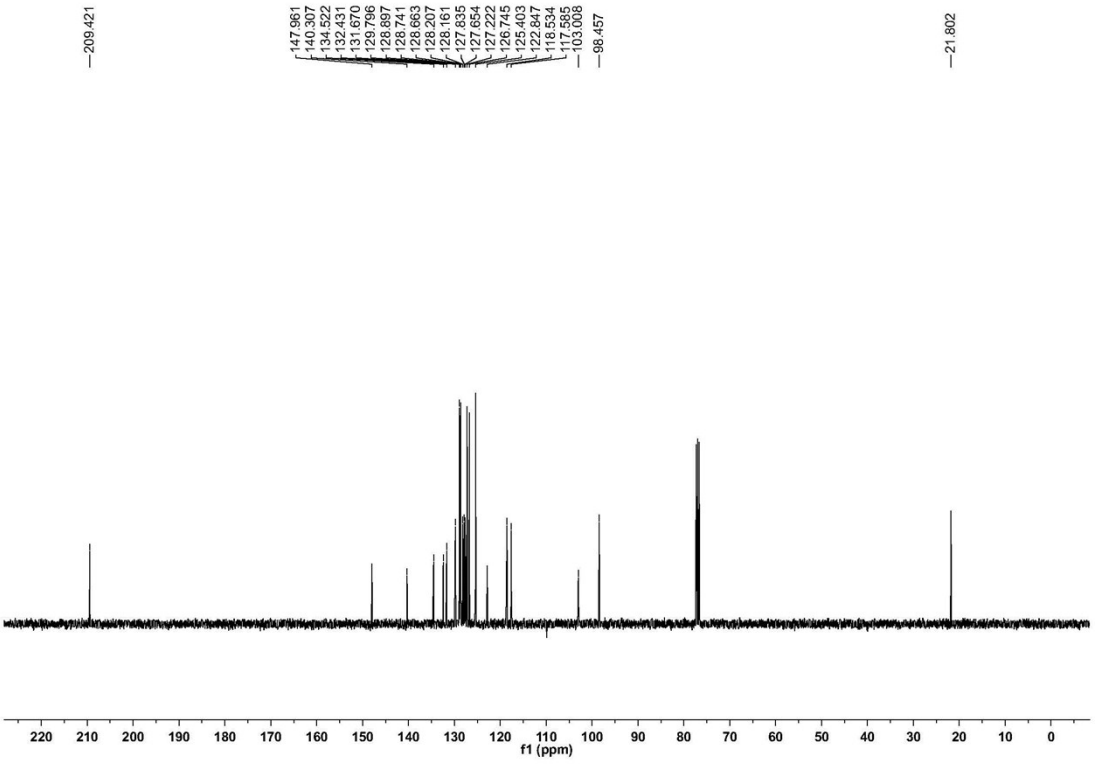
7.692
7.571
7.566
7.555
7.551
7.353
7.336
7.322
7.318
7.271
7.252
7.244
7.213
7.209
7.206
7.188
7.184
7.171
7.164
7.158
7.049
7.045
7.042
7.029
7.025
6.396
2.348
N
N—Ph
Me
Ph
Ph
4n
1.00
2.10
5.20
8.29
2.10
0.99
3.23
f1 (ppm)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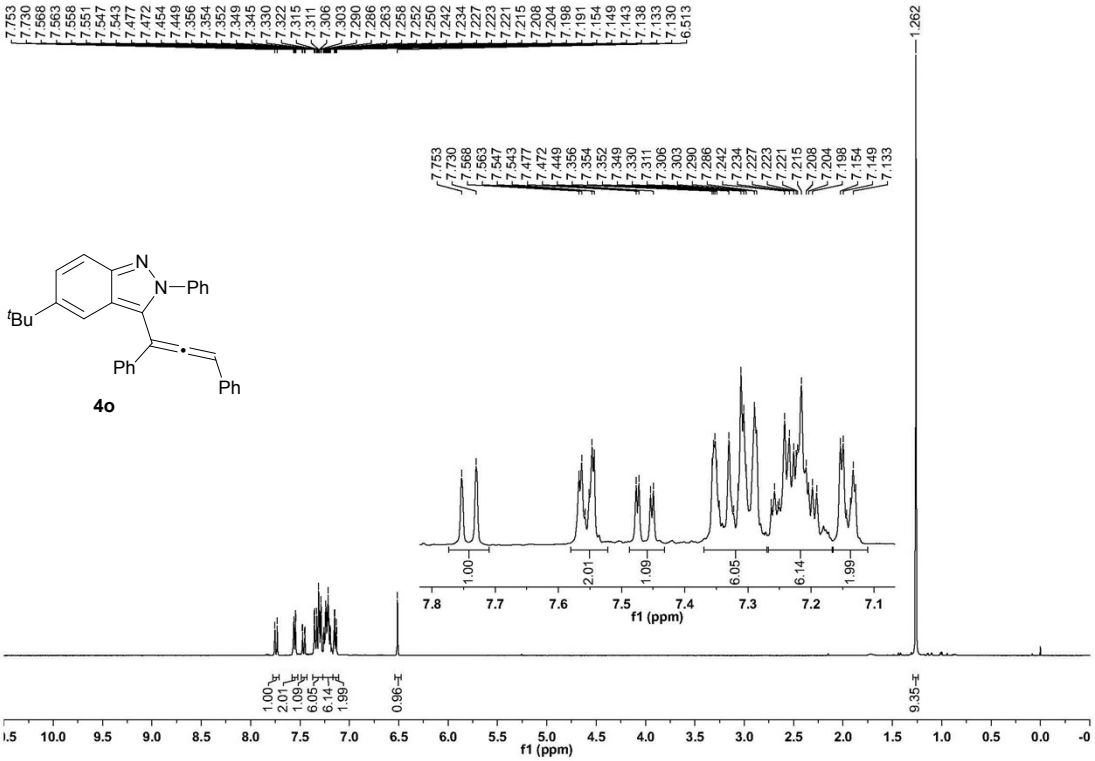
140.307
134.522
132.431
131.670
129.796
128.897
128.741
128.663
128.207
128.161
127.835
127.654
127.222
126.745
125.403
122.847
118.534
117.585
103.008
98.457
21.802
f1 (ppm)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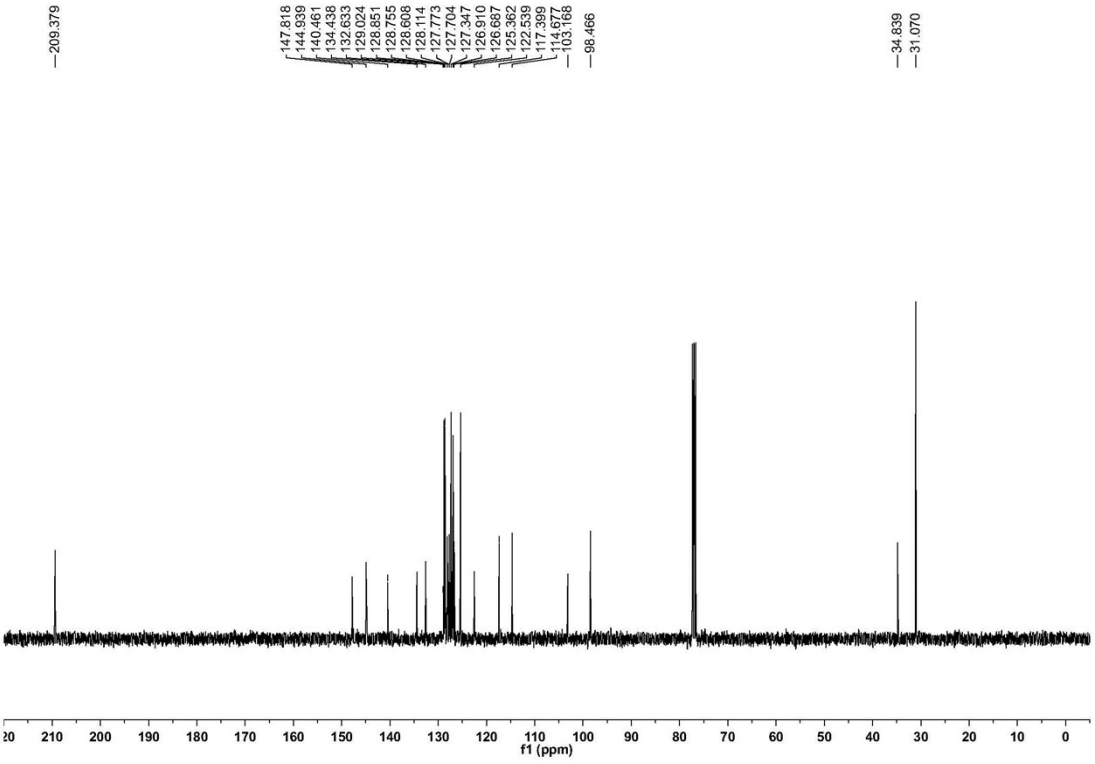
7.730
7.568
7.563
7.558
7.551
7.547
7.543
7.477
7.472
7.454
7.449
7.356
7.354
7.352
7.349
7.345
7.330
7.322
7.315
7.311
7.306
7.303
7.290
7.286
7.263
7.258
7.252
7.250
7.242
7.234
7.227
7.223
7.221
7.215
7.208
7.204
7.198
7.191
7.154
7.149
7.143
7.138
7.133
7.130
6.513
1.262
N
N—Ph
tBu
Ph
Ph
4o
1.00
2.01
1.09
6.05
6.14
1.99
0.96
9.35
f1 (ppm)


209.379
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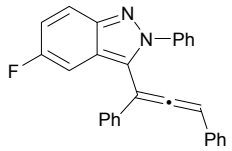
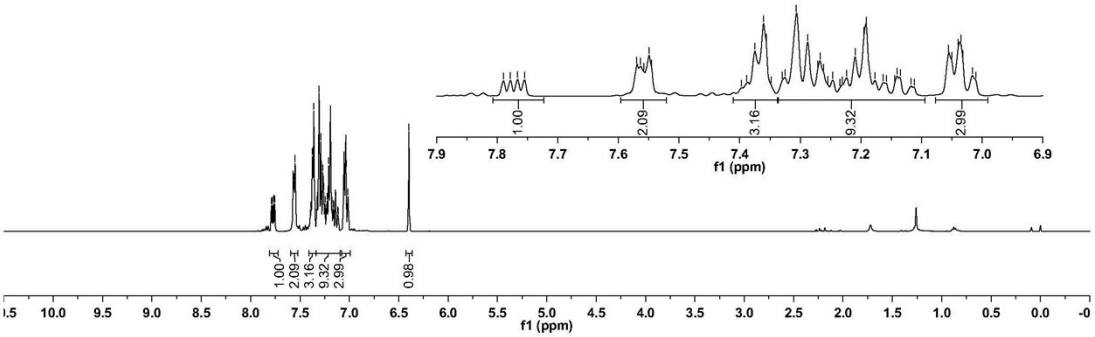
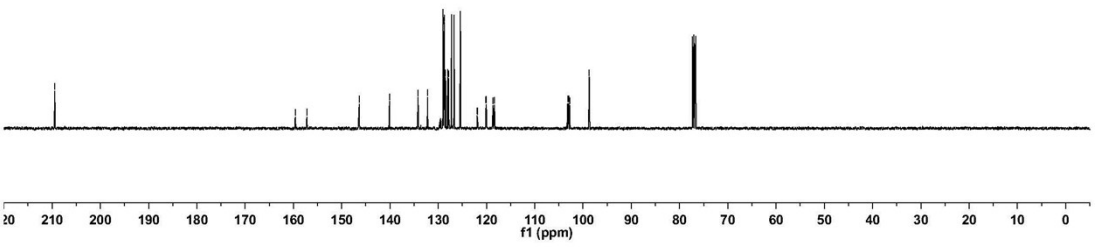
144.939
140.461
134.438
132.633
129.024
128.851
128.755
128.608
128.114
127.773
127.704
127.347
126.910
126.687
125.362
122.539
117.399
114.677
103.168
98.466
34.839
31.070
f1 (ppm)

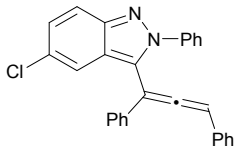


4p



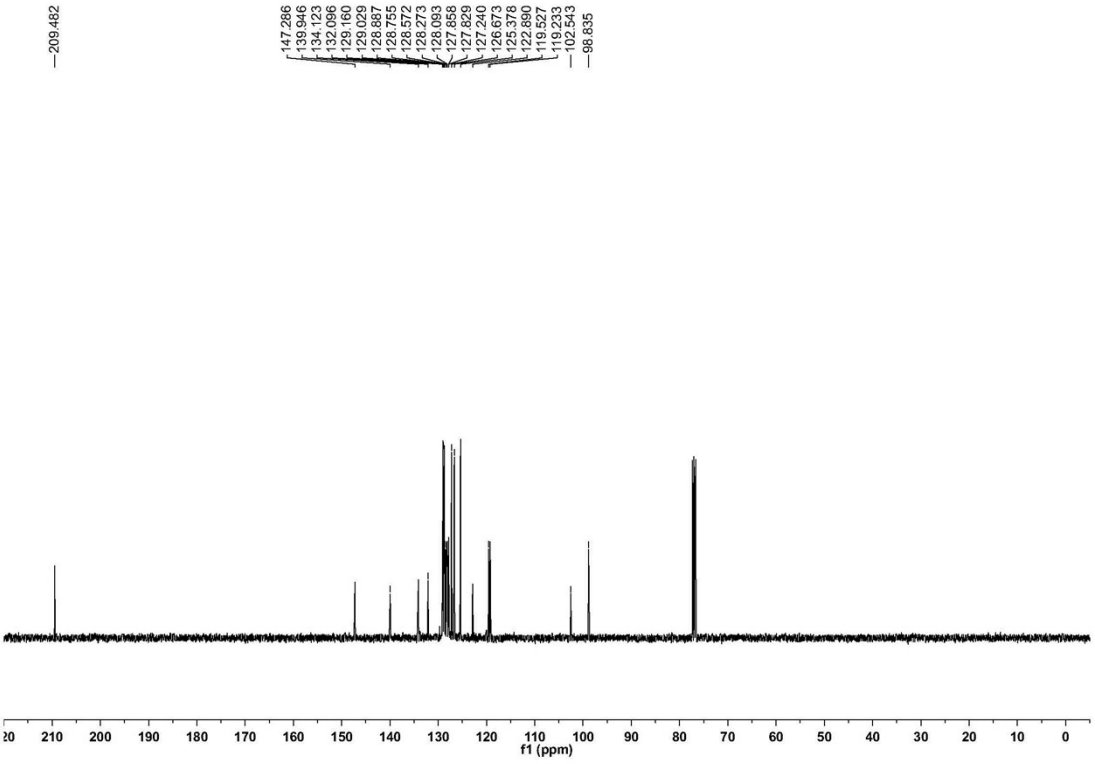



7.746
7.723
7.568
7.559
7.549
7.544
7.450
7.387
7.376
7.364
7.358
7.301
7.292
7.287
7.279
7.275
7.268
7.258
7.252
7.220
7.207
7.191
7.176
7.045
7.039
7.026
6.414


N
N—Ph
Cl
Ph
Ph

4q

7.746
7.723
7.568
7.559
7.549
7.544
7.450
7.387
7.376
7.364
7.358
7.301
7.292
7.287
7.279
7.275
7.268
7.258
7.252
7.220
7.207
7.191
7.176
7.045
7.039
7.026
1.00
2.11
1.13
3.35
6.21
3.25
2.11
0.99
f1 (ppm)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139.946
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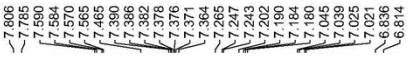
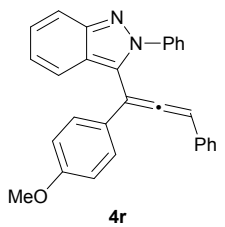
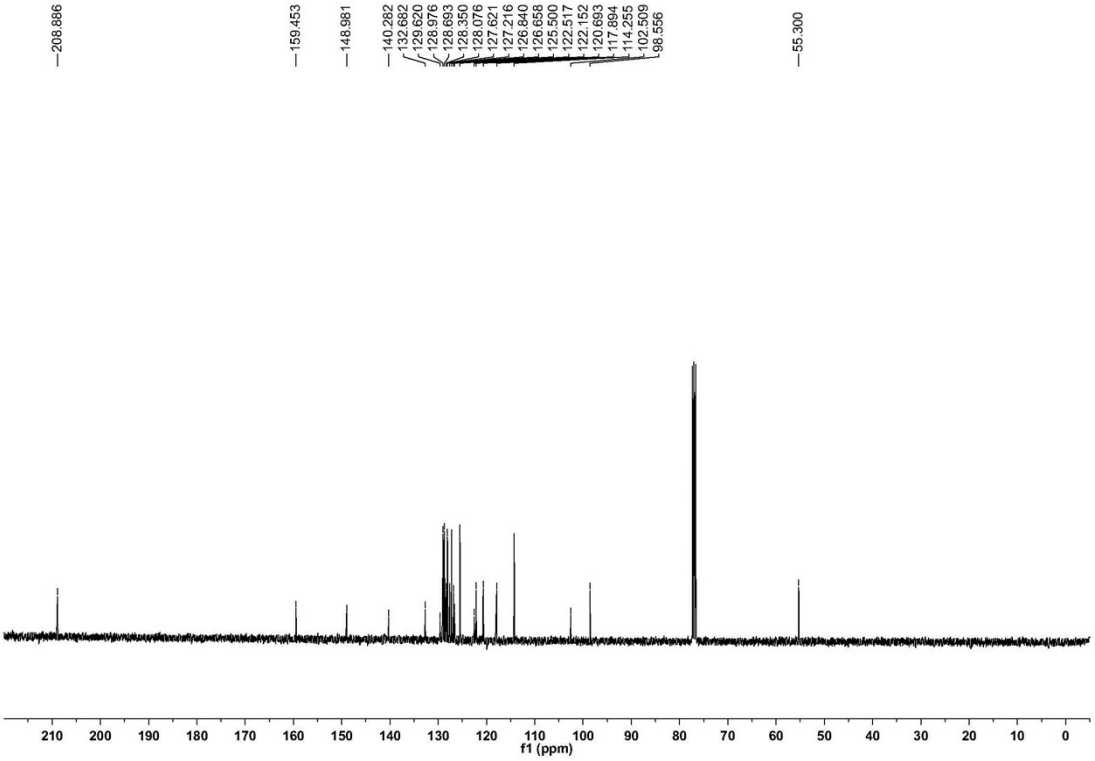
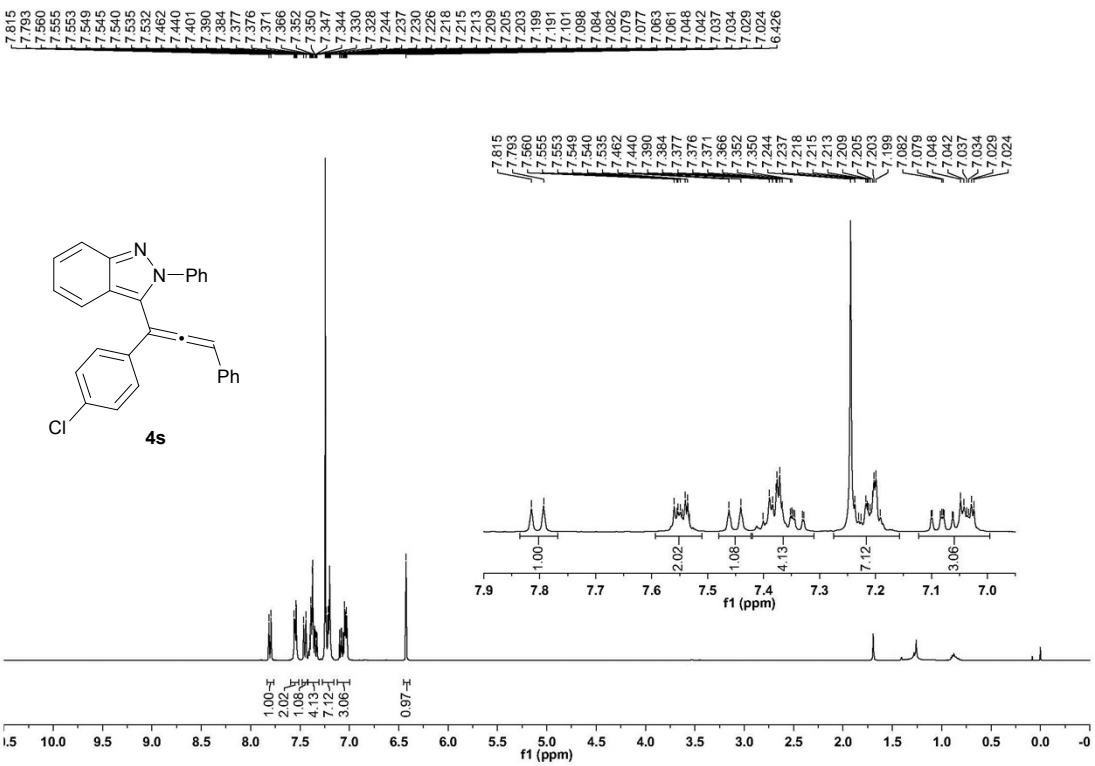
132.096
129.160
129.029
128.887
128.755
128.572
128.273
128.093
127.858
127.829
127.240
126.673
125.378
122.890
119.527
119.233
102.543
98.835
f1 (ppm)

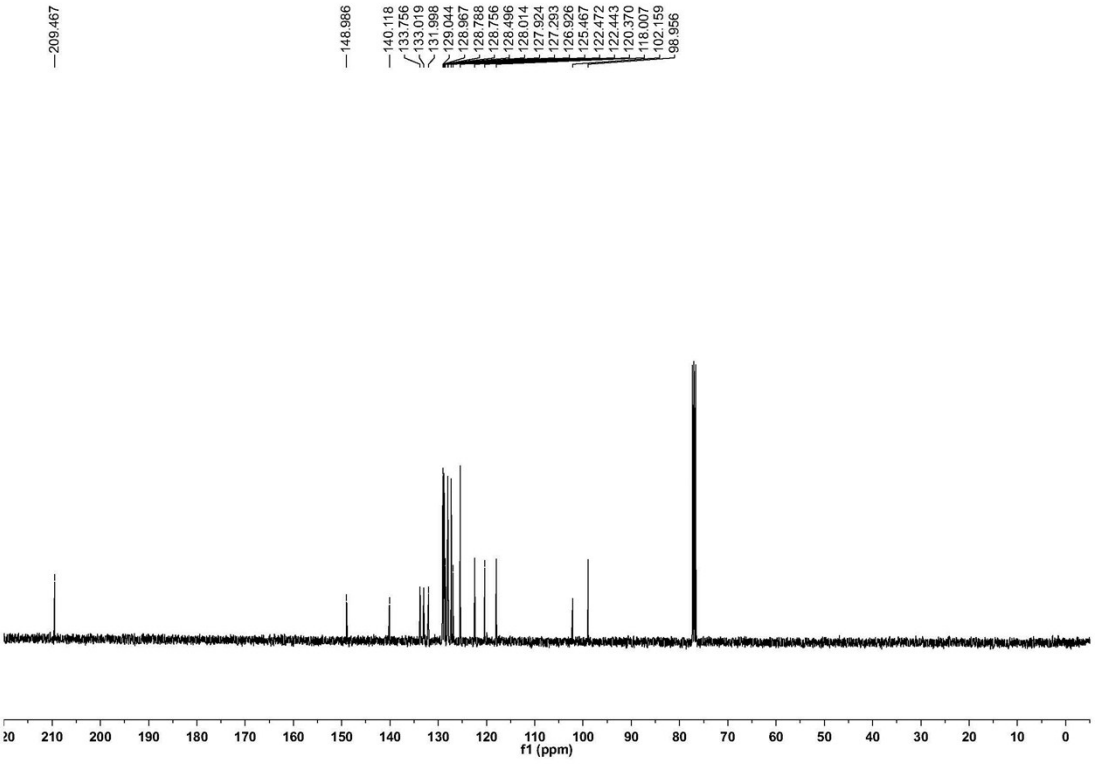




4r




4s
f1 (ppm)


f1 (ppm)


9.067
9.046
7.934
7.930
7.927
7.925
7.913
7.909
7.906
7.903
7.767
7.764
7.749
7.746
7.742
7.728
7.725
7.544
7.537
7.532
7.524
7.519
7.510
7.507
7.504
7.489
7.486
7.483
7.468
7.465
7.442
7.439
7.427
7.422
7.414
7.403
7.400
7.238
7.226
7.222
7.218
7.205
7.201
7.190
7.186
7.163
7.159
7.155
7.141
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6.898
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6.881
6.877
6.862
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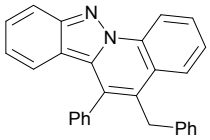
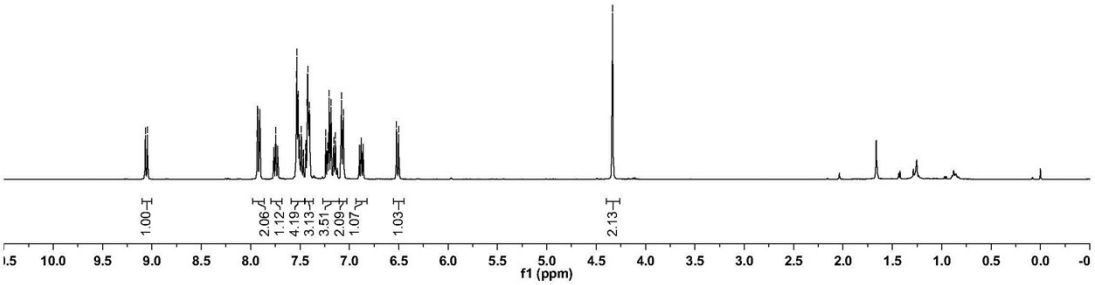
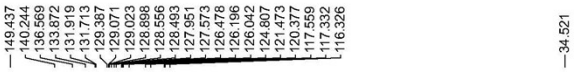
6.522
6.501
4.334


N
N
Ph
Ph

5


1.00
2.06
1.12
4.19
3.13
3.51
2.09
1.07
1.03
2.13
f1 (ppm)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133.872
131.919
131.713
129.387
129.071
129.023
128.898
128.556
128.493
127.951
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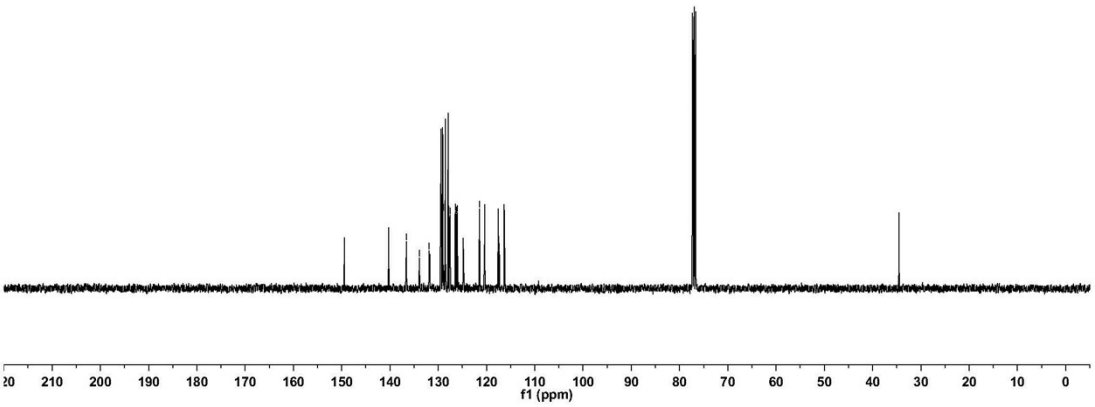
126.478
126.196
126.042
124.607
121.473
120.377
117.559
117.332
116.326
34.521


f1 (ppm)