Supporting Information

Gold(I)- and Rhodium(III)- Catalyzed Formal Regiodivergent C−H Alkynylation of 1-arylpyrazolones

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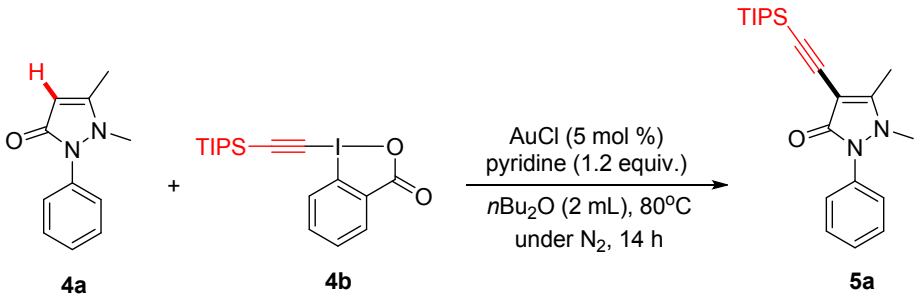
I. General Information.

Commercially available reagents were used as received without further purification, unless stated otherwise. Anhydrous solvents were purified and dried by standard procedures. 1-aryl-5-pyrazolones[1] and hypervalent iodine alkynes [2] were prepared by following literature reports. All reactions were carried out in a nitrogen-filled dry box. All unknown products were characterized by ^{1}H NMR, ^{13}C NMR spectroscopy, and high-resolution mass spectrometry (HRMS). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker NMR spectrometer (400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane in the NMR solvents indicated. Column chromatography was performed on silica gel (300-400 mesh) using ethyl acetate (EA)/petroleum ether (PE) or MeOH/CH_2Cl_2 as eluents.

II. Optimization Table



4a **4b** **5a**

Entry	cat. (mol %)	additive (mol %)	solvent	*T* (°C)	Yield[b] (%)
1	$Au(PPh_3)Cl$	-	MeCN	80	23
2	$AuCl_3$	-	MeCN	80	10
3	AuCl	TFA	MeCN	80	18
4[c]	AuCl	$Zn(OTf)_2$	MeCN	80	trace
5	AuCl	Pyridine	MeCN	80	60
6	AuCl	Na_2CO_3	MeCN	80	21
7	AuCl	Na_2CO_3	DCM	80	56
8	AuCl	Pyridine	$^{n}Bu_2O$	80	70

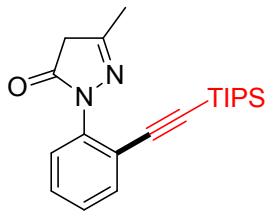
9	AuCl	Pyridine	THF	80	64
10[d]	**AuCl**	**Pyridine**	**$^{n}Bu_2O$**	**80**	**72**

[a]Reaction conditions: (1) 1a (0.20 mmol), 2a (0.24 mmol), catalyst (5 mol %), additives (1.2 equiv.) in a solvent (2.0 mL) under N_2 for 14 h. [b]Isolated yield after column chromatography. [c] $Zn(OTf)_2$（20 mmol %）was used as additive. [d]1.0 mL $^{n}Bu_2O$ was used as solvent.

III. Experimental Information and Characterization Data

1. Rh(III)-Catalyzed Alkynylation

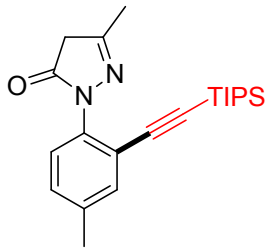
Representative Procedure for the Rh(III)-Catalyzed Alkynylation (Synthesis of 3). 3-Methyl-1-phenyl-1H-pyrazol-5-one (**1a**, 0.20 mmol), alkyne (**2a**, 0.24 mmol), $[RhCp^*Cl_2]_2$ (0.008 mmo), $AgSbF_6$ (0.032 mmol), and Na_2CO_3 (0.3 mmol) were added into a pressure tube, to which was then added DCE (2 mL). The mixture was stirred under N_2 atmosphere at 80 °C for 12 hours. After that, the solvent was removed under vacuum and the residue was purified by silica gel chromatography using ethyl acetate/petroleum ether (3:1) to afford product **3a** as a colorless oil liquid (51.3 mg, 73%).



3a, 73%

3-methyl-1-(2-((triisopropylsilyl)ethynyl)phenyl)-1*H*-pyrazol-5(4*H*)-one

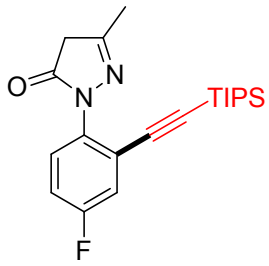
Isolation by column chromatography (EA/PE = 3:1) yielded **3a** (51.3 mg, 73%) as a colorless oil liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 – 7.57 (m, 1H), 7.38 – 7.35 (m, 2H), 7.31 – 7.27 (m, 1H), 4.33 (s, 2H), 2.13 (s, 3H), 1.09 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.1, 155.5, 138.0, 134.1, 129.0, 128.1, 126.9, 121.6, 103.0, 96.2, 41.6, 18.5, 17.0, 11.2. **HRMS**: $[M+H]^+$ calculated for $C_{21}H_{31}N_2OSi^+$: 355.2200, found 355.2198.



3b, 80%

3-methyl-1-(4-methyl-2-((triisopropylsilyl)ethynyl)phenyl)-1*H*-pyrazol-5(4*H*)-one

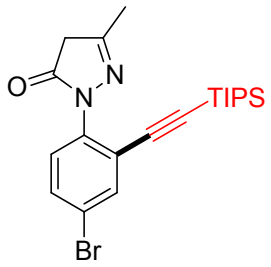
Isolation by column chromatography (EA/PE = 3:1) yielded **3b** (36.8 mg, 80%) as a red oil liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39 (d, J = 1.3 Hz, 1H), 7.23 (d, J = 8.1 Hz, 1H), 7.17 (dd, J = 8.1, 1.4 Hz, 1H), 3.32 (s, 2H), 2.33 (s, 3H), 2.12 (s, 3H), 1.01 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.2, 155.3, 138.3, 135.5, 134.4, 129.9, 126.9, 121.4, 103.1, 95.5, 41.5, 20.9, 18.5, 17.0, 11.2. **HRMS**: $[M+H]^+$ calculated for $C_{22}H_{33}N_2OSi^+$: 369.2357, found 359.2356.



3c, 87%

1-(4-fluoro-2-((triisopropylsilyl)ethynyl)phenyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one

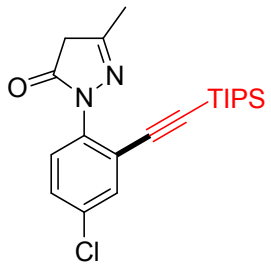
Isolation by column chromatography (EA/PE = 3:1) yielded **3c** (65 mg, 87%) as a red oil liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.27 (dd, J = 8.8, 5.2 Hz, 1H), 7.22 – 7.19 (m, 1H), 7.03 – 6.99 (m, 1H), 3.26 (s, 2H), 2.06 (s, 3H), 1.08 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.2, 161.6 (d, J_{C-F} = 249.0 Hz), 155.6, 134.4 (d, J_{C-F} = 3.1 Hz), 129.0 (d, J_{C-F} =9.4 Hz), 123.7 (d, J_{C-F} = 10.3 Hz), 120.5 (d, J_{C-F} = 24.1 Hz), 116.4 (d, J_{C-F} = 22.8 Hz), 101.8 (d, J_{C-F} = 2.5 Hz), 97.8, 41.5, 18.6, 17.1, 11.2. **19F NMR (376 MHz, CDCl3)**: δ -112.8. **HRMS**: $[M+H]^+$ calculated for $C_{21}H_{30}FN_2OSi^+$:373.2106, found 373.2103.



3d, 87%

1-(4-bromo-2-((triisopropylsilyl)ethynyl)phenyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one

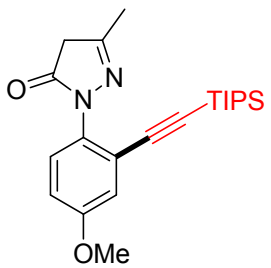
Isolation by column chromatography (EA/PE = 3:1) yielded **3d** (74.8 mg, 87%) as a brown oil liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 (d, J = 2.3 Hz, 1H), δ 7.42 (dd, J = 8.5, 2.3 Hz, 1H), 7.19 – 7.17 (m, 1H), 3.27 (s, 2H), 2.07 (s, 3H), 1.02 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.9, 155.7, 137.1, 136.6, 132.1, 128.1, 123.2, 121.4, 101.5, 98.2, 41.5, 18.5, 17.5, 11.2. **HRMS**: $[M+H]^+$ calculated for $C_{21}H_{30}BrN_2OSi^+$: 433.1305, found 433.1307.



3e, 80%

1-(4-chloro-2-((triisopropylsilyl)ethynyl)phenyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one

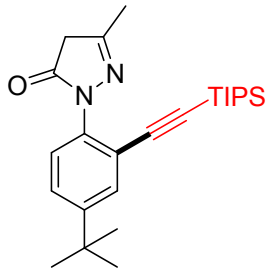
Isolation by column chromatography (EA/PE = 3:1) yielded **3e** (62 mg, 80%) as a red oil liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (d, J = 2.1 Hz, 1H), 7.33 – 7.29 (m, 1H), 3.33 (s, 2H), 2.13 (s, 3H), 1.08 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.9, 155.7, 136.7, 133.6, 133.5, 129.1 127.9, 122.9, 101.6, 98.0, 41.5, 18.5, 17.0, 11.1. **HRMS**: $[M+H]^+$ calculated for $C_{21}H_{30}ClN_2OSi^+$: 389.1810, found 389.1806.



3f, 65%

1-(4-methoxy-2-((triisopropylsilyl)ethynyl)phenyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one

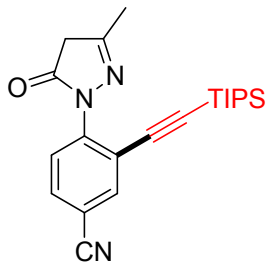
Isolation by column chromatography (EA/PE = 3:1) yielded **3f** (50 mg, 65%) as a light yellow solid. mp 138 − 140 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.20 – 7.18 (m, 1H), 7.00 (d, J = 2.9 Hz, 1H), 6.84 (dd, J = 8.8, 2.9 Hz, 1H), 3.74 (s, 3H), 3.25 (s, 2H), 2.05 (s, 3H), 1.01 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.4, 159.1, 155.3, 131.2, 128.6, 123.1, 118.2, 115.4, 102.8, 95.9, 55.6, 41.5, 18.5, 16.99, 11.2. **HRMS**: $[M+H]^+$ calculated for $C_{22}H_{33}N_2O_2Si^+$: 385.2306, found 385.2308.



3g, 71%

1-(4-(*tert*-butyl)-2-((triisopropylsilyl)ethynyl)phenyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one

Isolation by column chromatography (EA/PE = 3:1) yielded **3g** (58 mg, 71%) as a light yellow solid. mp 166 − 168 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 (d, J = 2.2 Hz, 1H), 7.33 (dd, J = 8.4, 2.2 Hz, 1H), 7.22 – 7.19 (m, 1H), 3.26 (s, 2H), 2.05 (s, 3H), 1.24 (s, 9H), 1.03 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.2, 155.3, 151.4, 135.6, 130.9, 126.7, 126.5, 121.1, 103.5, 95.2, 41.5, 34.6, 31.1, 18.5, 17.0, 11.2. **HRMS**: $[M+H]^+$ calculated for $C_{25}H_{39}N_2OSi^+$: 411.2826, found 411.2833.

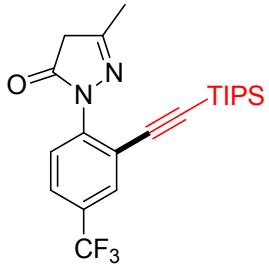


3h, 70%

4-(3-methyl-5-oxo-4,5-dihydro-1*H*-pyrazol-1-yl)-3-((triisopropylsilyl)ethynyl)benzonitrile

Isolation by column chromatography (EA/PE = 3:1) yielded **3h** (53 mg, 70%) as a red oil liquid.

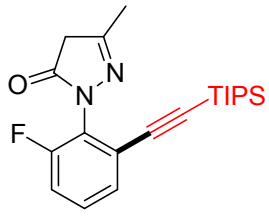
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 1.7 Hz, 1H), 7.61 (dd, J = 8.4, 1.9 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 3.37 (s, 2H), 2.15 (s, 3H), 1.09 – 1.08 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.6, 156.4, 141.5, 138.1, 131.9, 126.6, 121.6, 117.6, 111.4, 101.0, 100.0, 41.6, 18.6, 17.0, 11.2. **HRMS**: $[M+H]^+$ calculated for $C_{22}H_{30}N_3OSi^+$:380.2153, found 380.2152.



3i, 68%

3-methyl-1-(4-(trifluoromethyl)-2-((triisopropylsilyl)ethynyl)phenyl)-1*H*-pyrazol-5(4*H*)-one

Isolation by column chromatography (EA/PE = 3:1) yielded **3i** (60 mg, 68%) as a red oil liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82 (d, J = 1.5 Hz, 1H), 7.61 (dd, J = 8.4, 1.7 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 3.36 (s, 2H), 2.16 (s, 3H), 1.12 – 1.10 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.7, 156.0, 140.8, 131.2 (q, $J_{C\text{-}F}$ = 11.6 Hz), 130.0 (q, $J_{C\text{-}F}$ = 32.9Hz), 126.8, 125.6 (q, $J_{C\text{-}F}$ = 10.5 Hz), 123.4 (d, $J_{C\text{-}F}$ = 270.7 Hz), 121.6, 101.7, 98.7, 41.6, 18.5, 17.1, 11.2. **19F NMR (376 MHz, CDCl3)**: δ -62.8. **HRMS**: $[M+H]^+$ calculated for $C_{25}H_{39}N_2OSi^+$: 423.2074, found 423.2067.

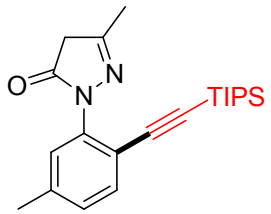


3j, 35%

1-(2-fluoro-6-((triisopropylsilyl)ethynyl)phenyl)-3-methyl-1H-pyrazol-5(4H)-one

Isolation by column chromatography (EA/PE = 3:1) yielded **3j** (26 mg, 35%) as a red oil liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 – 7.36 (m, 1H), 7.33 – 7.28 (m, 1H), 7.17 – 7.13 (m, 1H), 3.37 – 3.31 (m,2H), 2.14 (s, 3H), 1.09 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.2, 158.4 (d, $J_{C\text{-}F}$ = 253.0 Hz), 156.2, 130.1 (d, $J_{C\text{-}F}$ = 9.0 Hz), 129.2 (d, $J_{C\text{-}F}$ = 3.5 Hz), 126.17 (d, $J_{C\text{-}F}$ = 14.0

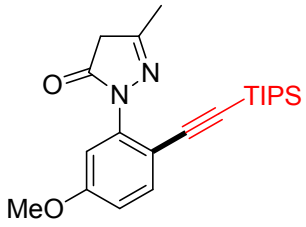
Hz), 125.0 (d, J_{C-F} = 1.5 Hz), 116.7 (d, J_{C-F} = 20.3 Hz), 101.6 (d, J_{C-F} = 4.1 Hz), 97.6, 41.0, 18.5, 17.1, 11.2. **19F NMR (376 MHz, CDCl3)**: δ -118.8. **HRMS**: $[M+H]^+$ calculated for $C_{21}H_{30}FN_2OSi^+$:373.2106, found 373.2109.



3k, 73%

3-methyl-1-(5-methyl-2-((triisopropylsilyl)ethynyl)phenyl)-1*H*-pyrazol-5(4*H*)-one

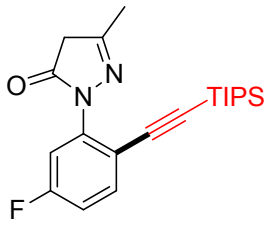
Isolation by column chromatography (EA/PE = 3:1) yielded **3k** (54 mg, 73%) as a red oil liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 (d, J = 7.9 Hz, 1H), 7.18 (s, 1H), 7.11 (d, J = 7.9 Hz, 1H), 3.34 (s, 2H), 2.35 (s, 3H), 2.13 (s, 3H), 1.08 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.1, 155.4, 139.6, 137.9, 133.8, 129.0, 127.5, 118.7, 103.1, 95.1, 41.6, 21.2, 18.5, 16.9, 11.2. **HRMS**: $[M+H]^+$ calculated for $C_{22}H_{30}N_3OSi^+$:369.2357, found 369.2355.



3l, 61%

1-(5-methoxy-2-((triisopropylsilyl)ethynyl)phenyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one

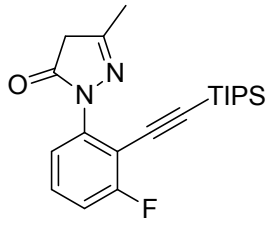
Isolation by column chromatography (EA/PE = 3:1) yielded **3l** (47 mg, 61%) as a light yellow oil liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 (d, J = 8.6 Hz, 1H), 6.90 (d, J = 2.6 Hz, 1H), 6.85 (dd, J = 8.6, 2.6 Hz, 1H), 3.81 (s, 3H), 3.33 (s, 2H), 2.14 (s, 3H), 1.10 –1.08 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.9, 160.0, 155.5, 139.3, 135.1, 114.7, 113.8, 112.1, 103.1, 94.1, 55.5, 41.6, 18.6, 17.0, 11.3. **HRMS**: $[M+H]^+$ calculated for $C_{21}H_{30}BrN_2OSi^+$:385.2306, found 385.2304.



3m (i), 65%

1-(5-fluoro-2-((triisopropylsilyl)ethynyl)phenyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one

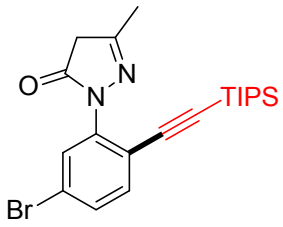
Isolation by column chromatography (EA/PE = 3:1) yielded **3m (i)** (48 mg, 65%) as a red oil liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.27 (dd, J = 8.8, 5.2 Hz, 1H), 7.13 (dd, J = 9.1, 2.6 Hz, 1H), 7.04 – 6.99 (m, 1H), 3.34 (s, 2H), 2.15 (s, 3H), 1.09 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.2, 161.6 (d, J_{C-F} = 249.0 Hz), 155.6, 134.4 (d, J_{C-F} = 3.1 Hz), 129.0 (d, J_{C-F} =9.4 Hz), 123.7 (d, J_{C-F} = 10.3 Hz), 120.5 (d, J_{C-F} = 24.1 Hz), 116.4 (d, J_{C-F} = 22.8 Hz), 101.75 (d, J_{C-F} = 2.5 Hz), 97.8, 41.5, 18.6, 17.1, 11.2. **19F NMR (376 MHz, CDCl3)**: δ -109.0. **HRMS**: $[M+H]^+$ calculated for $C_{21}H_{30}FN_2OSi^+$:373.2106, found 373.2107.



3m (ii), 27%

1-(3-fluoro-2-((triisopropylsilyl)ethynyl)phenyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one

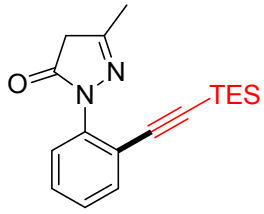
Isolation by column chromatography (EA/PE = 3:1) yielded **3m (ii)** (20 mg, 27%) as a red oil liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36 – 7.30 (m, 1H), 7.20 (d, J = 8.0 Hz, 1H), 7.10 – 7.06 (m, 1H), 3.35 (s, 2H), 2.15 (s, 3H), 1.10 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.1, 164.0 (d, J_{C-F} = 253.4 Hz), 155.7, 139.5 (d, J_{C-F} = 3.2 Hz, 1H), 129.4 (d, J_{C-F} = 9.4 Hz), 122.3 (d, J_{C-F} = 3.5 Hz), 115.1 (d, J_{C-F} = 21.3 Hz), 110.8 (d, J_{C-F} = 17.8 Hz), 102.8 (d, J_{C-F} = 4.0 Hz), 95.9, 41.6, 18.5, 17.1, 11.2.



3n, 68%

1-(5-bromo-2-((triisopropylsilyl)ethynyl)phenyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one

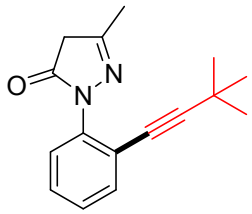
Isolation by column chromatography (EA/PE = 3:1) yielded **3n** (61 mg, 68%) as a red oil liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (d, J = 0.9 Hz, 1H), 7.45 – 7.40 (m, 2H), 3.33 (s, 2H), 2.13 (s, 3H), 1.08 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.7, 155.8, 139.0, 135.0, 131.1, 129.8, 122.2, 120.3, 102.1, 97.7, 41.5, 18.5, 17.0, 11.2. **HRMS**: $[M+H]^+$ calculated for $C_{21}H_{30}BrN_2OSi^+$:433.1305, found 433.1305.



3o, 48%

3-methyl-1-(2-((triethylsilyl)ethynyl)phenyl)-1*H*-pyrazol-5(4*H*)-one

Isolation by column chromatography (EA/PE = 3:1) yielded **3o** (26 mg, 48%) as a red oil liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 (d, J = 7.6 Hz, 1H), 7.38 (d, J = 3.8 Hz, 2H), 7.31 – 7.27 (m, 1H), 3.36 (s, 2H), 2.16 (s, 3H), 1.07 (t, J = 15.6 Hz, 9H), 0.63 (q, J = 7.9 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.0, 155.4, 138.2, 133.9, 129.1, 128.0, 126.8, 121.2, 103.3, 97.4, 41.6, 17.0, 7.4, 4.3. **HRMS**: $[M+H]^+$ calculated for $C_{21}H_{30}BrN_2OSi^+$:313.1731, found 313.1732.

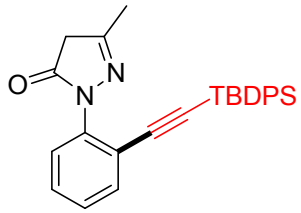


3p, 83%

1-(2-(3,3-dimethylbut-1-yn-1-yl)phenyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one

Isolation by column chromatography (EA/PE = 3:1) yielded **3p** (68 mg, 83%) as a light yellow

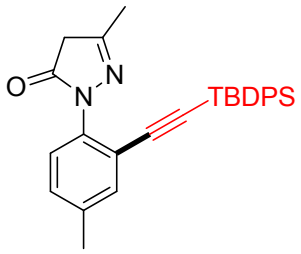
solid. mp 90 − 92 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 – 7.47 (m, 1H), 7.38 – 7.34 (m, 1H), 7.32 – 7.28 (m, 1H), 7.27 – 7.25 (m, 1H), 3.37 (s, 2H), 2.17 (s, 3H), 1.26 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.1, 155.3, 137.9, 133.1, 126.7, 121.8, 103.9, 95.7, 41.6, 30.8, 28.1, 17.0. **HRMS**: $[M+H]^+$ calculated for $C_{16}H_{19}N_2O^+$: 255.1492, found 255.1491.



3q, 78%

1-(2-((*tert*-butyldiphenylsilyl)ethynyl)phenyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one

Isolation by column chromatography (EA/PE = 3:1) yielded **3q** (68 mg, 78%) as a light yellow solid. mp 102 − 104 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85 – 7.82 (m, 4H), 7.71 (d, J = 7.5 Hz, 1H), 7.43 – 7.45 (m, 2H), 7.42 – 7.39 (m, 3H), 7.37 – 7.34 (m, 4H), 3.12 (s, 2H), 1.94 (s, 3H), 1.12 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.2, 155.7, 138.6, 135.6, 133.9, 133.2, 129.6, 129.5, 128.1, 127.7, 126.9, 121.0, 105.2, 95.1, 41.4, 27.0, 18.6, 16.8. **HRMS**: $[M+H]^+$ calculated for $C_{21}H_{30}BrN_2OSi^+$:437.2044, found 437.2038.

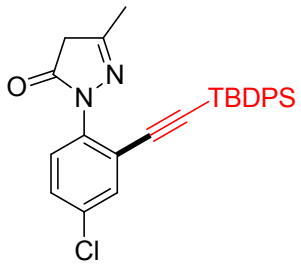


3r, 72%

1-(2-((*tert*-butyldiphenylsilyl)ethynyl)-4-methylphenyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one

Isolation by column chromatography (EA/PE = 3:1) yielded **3r** (65 mg, 72%) as a light yellow solid. mp 82 − 84 °C.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84 – 7.82 (m, 4H), 7.52 (s, 1H), 7.41 – 7.36 (m, 6H), 7.32 – 7.30 (m, 1H), 7.24 – 7.19 (m, 1H), 3.11 (s, 2H), 2.38 (s, 3H), 1.94 (s, 3H), 1.12 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.4, 155.6, 138.4, 135.7, 134.3, 133.3, 130.5,

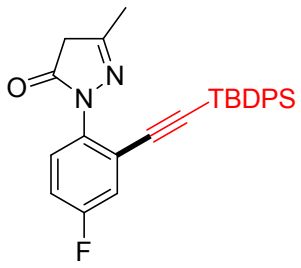
129.6, 127.8, 127.0, 120.9, 119.0, 105.4, 94.6, 41.4, 27.7, 21.1, 18.7, 16.9. **HRMS**: $[M+H]^+$ calculated for $C_{29}H_{31}N_2OSi^+$:451.2200, found 451.2200.



3s, 75%

1-(2-((*tert*-butyldiphenylsilyl)ethynyl)-4-chlorophenyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one

Isolation by column chromatography (EA/PE = 3:1) yielded **3s** (70 mg, 75%) as a light yellow solid. mp 96 − 98 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.82 – 7.80 (m, 4H), 7.68 (d, J = 2.0 Hz, 1H), 7.44 – 7.37 (m, 8H), 3.11 (s, 2H), 1.94 (s, 3H), 1.12 (s, 9H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 171.1, 156.1, 137.2, 135.6, 133.7, 133.5, 132.9, 129.7, 129.6, 128.0, 127.9, 122.4, 103.7, 97.0, 41.4, 27.0, 18.7, 16.9. **HRMS**: $[M+H]^+$ calculated for $C_{28}H_{28}ClN_2OSi^+$:471.1654, found 471.1651.



3t, 70%

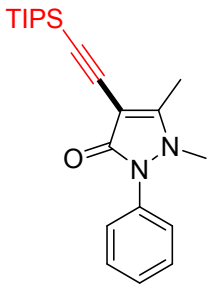
1-(2-((*tert*-butyldiphenylsilyl)ethynyl)-4-fluorophenyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one

Isolation by column chromatography (EA/PE = 3:1) yielded **3t** (63 mg, 70%) as a light yellow solid. mp 130 − 132 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.81 – 7.79 (m, 4H), 7.44 – 7.37(m, 8H), 7.17 – 7.12 (m, 1H), 3.09 (s, 2H), 1.93 (s, 3H), 1.11 (s, 9H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 171.3, 161.6 (d, J_{C-F} = 249.2 Hz), 155.9, 135.6, 135.0 (d, J_{C-F} = 3.1 Hz), 132.9, 129.7, 129.0 (d, J_{C-F} = 9.3 Hz), 127.8, 123.1 (d, J_{C-F} = 10.3 Hz), 120.4 (d, J_{C-F} = 24.3 Hz), 117.0 (d, J_{C-F} = 22.8 Hz), 103.8, 96.7, 41.3, 27.0, 18.6, 16.9. **19F NMR (376 MHz, CDCl3)**: δ -112.5. **HRMS**:

$[M+H]^+$ calculated for $C_{21}H_{30}BrN_2OSi^+$:455.1949, found 455.1945.

2. Au(I)-Catalyzed Alkynylation

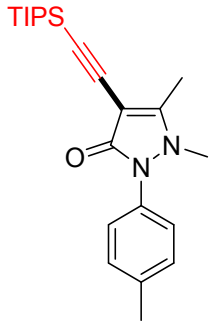
Representative procedures for the Au(I)-Catalyzed Alkynylation (Synthesis of Product 5). 2,3-Dimethyl-1-phenyl-1H-pyrazol-5-one (**4a**, 0.20 mmol), alkynes (**2a**, 0.24 mmol), AuCl (0.010 mmo), and pyridine (0.24 mmol) were added into a pressure tube, to which was added ^{n}Bu$_2$O (1 mL). The mixture was stirred under N_2 atmosphere at 80 ^{o}C for 14 hours. After that, the combined mixture was washed with saturated aqueous solution of Na_2CO_3 and was extracted with Ethyl acetate (3*40 mL). then dried over anhydrous Na_2SO_4, filtered and evaporated in vacuo. the residue was purified by silica gel chromatography using ethyl acetate/petroleum ether (2:1) to afford product **5a** as a white solid (52 mg, 71 %).



5a, 71%

1,5-dimethyl-2-phenyl-4-((triisopropylsilyl)ethynyl)-1*H*-pyrazol-3(2*H*)-one

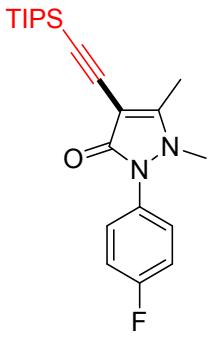
Isolation by column chromatography (EA/PE = 2:1) yielded **5a** (52 mg, 71%) as a white solid. mp 182 − 184 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.45 – 7.41 (m, 2H), 7.33 – 7.28 (m, 3H), 3.13 (s, 3H), 2.35 (s, 3H), 1.10 (m, 21H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 164.5, 157.5, 134.7, 129.1, 127.0, 124.4, 96.7, 95.6, 95.5, 35.4, 18.7, 12.3, 11.2. **HRMS**: $[M+H]^+$ calculated for $C_{22}H_{33}N_2OSi^+$: 369.2357, found 369.2355.



5b, 70%

1,5-dimethyl-2-(*p*-tolyl)-4-((triisopropylsilyl)ethynyl)-1*H*-pyrazol-3(2*H*)-one

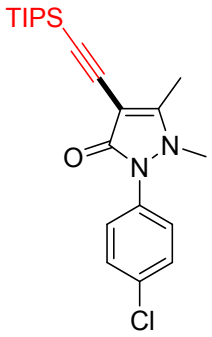
Isolation by column chromatography (EA/PE = 2:1) yielded **5b** (53 mg, 70%) as a white solid. mp 178 − 180 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.22 (d, J = 8.4 Hz, 2H), 7.19 – 7.17 (m, 2H), 3.11 (s, 3H), 2.35 (s, 3H), 2.34 (s, 3H), 1.10 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.5, 156.8, 137.2, 129.8, 124.9, 97.0, 95.4, 95.3, 35.2, 21.1, 18.7, 12.3, 11.3. **HRMS**: $[M+H]^+$ calculated for $C_{22}H_{33}N_2OSi^+$: 383.2313, found 383.2313.



5c, 72%

2-(4-fluorophenyl)-1,5-dimethyl-4-((triisopropylsilyl)ethynyl)-1H-pyrazol-3(2H)-one

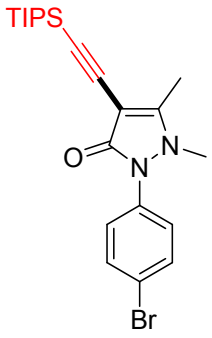
Isolation by column chromatography (EA/PE = 2:1) yielded **5c** (56 mg, 72%) as a white solid. mp 156 − 158 °C.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.31 – 7.27 (m, 2H), 7.14 – 7.09 (m, 2H), 3.11 (s, 3H), 2.35 (s, 3H), 1.10 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.8, 161.4 (d, J_{C-F} = 247.3 Hz), 157.7, 130.9 (d, J_{C-F} = 3.0 Hz), 126.5 (d, J_{C-F} = 8.6 Hz), 116.1 (d, J_{C-F} = 23.0 Hz), 96.6, 95.8, 95.6, 35.4, 18.7, 12.4, 11.3. **19F NMR (376 MHz, CDCl3)**: δ -114.2. **HRMS**: $[M+H]^+$ calculated for $C_{22}H_{32}FN_2OSi^+$:387.2262, found 387.2265.



5d, 70%

2-(4-chlorophenyl)-1,5-dimethyl-4-((triisopropylsilyl)ethynyl)-1H-pyrazol-3(2H)-one

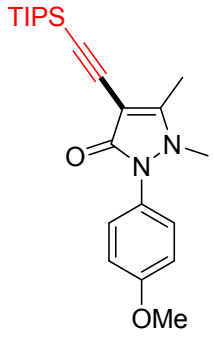
Isolation by column chromatography (EA/PE = 2:1) yielded **5d** (56 mg, 70%) as a white solid. mp 138 − 140 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 – 7.39 (m, 2H), 7.29 – 7.26 (m, 2H), 3.12 (s, 3H), 2.36 (s, 3H), 1.11 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.6, 158.6, 133.4, 132.4, 129.3, 125.2, 96.3, 96.2, 96.0, 35.7, 18.7, 12.4, 11.2. **HRMS**: $[M+H]^+$ calculated for $C_{22}H_{32}ClN_2OSi^+$: 403.1964, found 403.1964.



5e, 82%

2-(4-bromophenyl)-1,5-dimethyl-4-((triisopropylsilyl)ethynyl)-1H-pyrazol-3(2H)-one

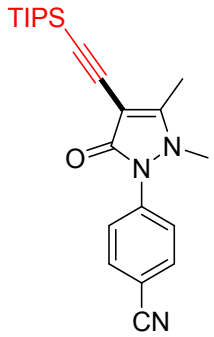
Isolation by column chromatography (EA/PE = 2:1) yielded **5e** (73 mg, 82%) as a white solid. mp 158 − 160 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.57 – 7.55 (m, 2H), 7.26 – 7.22 (m, 2H), 3.12 (s, 3H), 2.36 (s, 3H), 1.11 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.6, 158.8, 134.0, 132.3, 125.4, 120.3, 96.4, 96.3, 96.1, 35.9, 18.7, 12.5, 11.3. **HRMS**: $[M+H]^+$ calculated for $C_{22}H_{32}BrN_2OSi^+$: 447.1462, found 447.1461.



5f, 61%

2-(4-methoxyphenyl)-1,5-dimethyl-4-((triisopropylsilyl)ethynyl)-1*H*-pyrazol-3(2*H*)-one

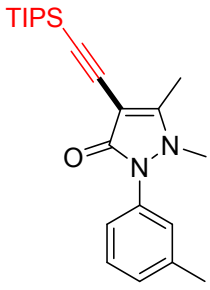
Isolation by column chromatography (EA/PE = 2:1) yielded **5f** (49 mg, 61%) as a white solid. mp 128 − 130 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.21 (d, J = 8.9 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 3.81 (s, 3H), 3.10 (s, 3H), 2.33 (s, 3H), 1.10 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.5, 158.9, 155.9, 127.3, 127.0, 114.5, 97.0, 95.1, 94.7, 55.5, 34.9, 18.7, 12.2, 11.2. **HRMS**: $[M+H]^+$ calculated for $C_{22}H_{32}BrN_2OSi^+$: 399.2462, found 399.2462.



5g, 65%

4-(2,3-dimethyl-5-oxo-4-((triisopropylsilyl)ethynyl)-2,5-dihydro-1H-pyrazol-1-yl)benzonitrile

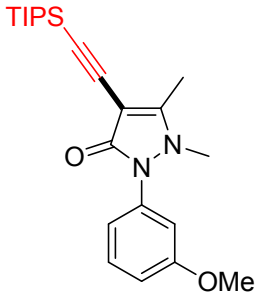
Isolation by column chromatography (EA/PE = 2:1) yielded **5g** (51 mg, 65%) as a white solid. mp 188 − 190 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (d, J = 8.7 Hz, 2H), 7.50 (d, J = 8.7 Hz, 1H), 3.14 (s, 3H), 2.38 (s, 3H), 1.10 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.6, 161.1, 139.0, 133.1, 122.9, 118.4, 109.4, 97.4, 96.9, 95.6, 36.7, 18.7, 12.7, 11.2. **HRMS**: $[M+H]^+$ calculated for $C_{23}H_{32}N_3OSi^+$: 394.2311, found 394.2311.



5h, 75%

1,5-dimethyl-2-(*m*-tolyl)-4-((triisopropylsilyl)ethynyl)-1*H*-pyrazol-3(2*H*)-one

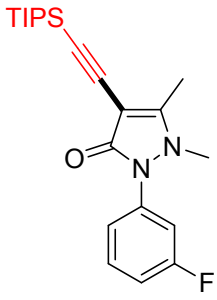
Isolation by column chromatography (EA/PE = 2:1) yielded **5h** (57.3 mg, 75%) as a white solid. mp 110 − 112 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28 (dd, J = 14.3, 6.5 Hz, 1H), 7.17 (s, 1H), 7.08 (t, J = 8.5 Hz, 2H), 3.12 (s, 3H), 2.36 (s, 3H), 2.34 (s, 3H), 1.11 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.5, 157.1, 139.1, 134.6, 128.9, 127.9, 125.4, 121.5, 96.8, 95.4, 95.3, 35.3, 21.3, 18.6, 12.2, 11.2. **HRMS**: $[M+H]^+$ calculated for $C_{23}H_{32}N_3OSi^+$: 383.2513, found 383.2513.



5i, 62%

2-(3-methoxyphenyl)-1,5-dimethyl-4-((triisopropylsilyl)ethynyl)-1H-pyrazol-3(2H)-one

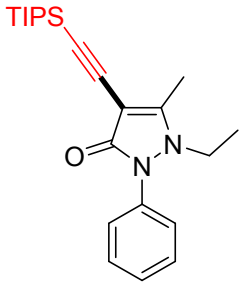
Isolation by column chromatography (EA/PE = 2:1) yielded **5i** (50 mg, 62%) as a white solid. mp 124 − 126 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.29 (dd, J = 17.2, 9.1 Hz, 1H), 6.93-6.92 (m, 1H), 6.87-6.81 (m, 2H), 3.80 (s, 3H), 3.13 (s, 3H), 2.35 (s, 3H), 1.11 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.6, 160.2, 157.8, 135.9, 129.8, 116.3, 113.1, 110.0, 96.8, 95.8, 95.6, 55.5, 35.6, 18.7, 12.4, 11.3. **HRMS**: $[M+H]^+$ calculated for $C_{23}H_{32}N_3OSi^+$: 399.2462, found 399.2465.



5j, 70%

2-(3-fluorophenyl)-1,5-dimethyl-4-((triisopropylsilyl)ethynyl)-1*H*-pyrazol-3(2*H*)-one

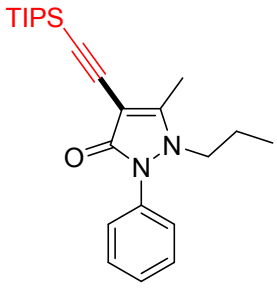
Isolation by column chromatography (EA/PE = 2:1) yielded **5j** (54 mg, 70%) as a white solid. mp 136 − 138 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 – 7.36 (m, 1H), 7.14 – 7.09 (m, 2H), 7.00 – 6.95 (m, 1H), 3.14 (s, 3H), 2.36 (s, 3H), 1.11 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.7, 162.9 (d, J_{C-F} = 247.1 Hz), 159.1, 136.4 (d, J_{C-F} = 10.2 Hz), 130.3 (d, J_{C-F} = 9.1 Hz), 119.3 (d, J_{C-F} = 3.2 Hz), 113.6(d, J_{C-F} = 21.1 Hz), 111.2 (d, J_{C-F} = 24.9 Hz), 96.4, 96.3, 96.1, 36.0, 18.7, 12.5, 11.3. **19F NMR (376 MHz, CDCl3)**: δ -111.2. **HRMS**: $[M+H]^+$ calculated for $C_{22}H_{32}FN_2OSi^+$:387.2262, found 387.2259.



5k, 71%

1-ethyl-5-methyl-2-phenyl-4-((triisopropylsilyl)ethynyl)-1*H*-pyrazol-3(2*H*)-one

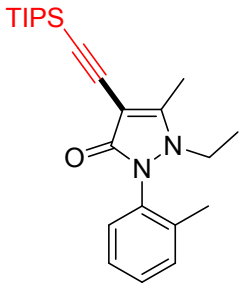
Isolation by column chromatography (EA/PE = 2:1) yielded **5k** (54 mg, 71%) as a white solid. mp 132 − 134 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 (t, J = 7.8 Hz, 2H), 7.34 (d, J = 7.5 Hz, 2H), 7.30 – 7.26 (m, 1H), 3.63 (q, J = 7.0 Hz, 2H), 2.36 (s, 3H), 1.10 (m, 21H), 0.92 (t, J = 7.0 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.2, 156.6, 134.7, 129.1, 126.9, 124.5, 96.9, 96.8, 95.6, 42.7, 18.7, 12.3, 11.4, 11.3. **HRMS**: $[M+H]^+$ calculated for $C_{23}H_{35}N_2OSi^+$: 383.2510, found 383.2510.



5l, 56%

5-methyl-2-phenyl-1-propyl-4-((triisopropylsilyl)ethynyl)-1*H*-pyrazol-3(2*H*)-one

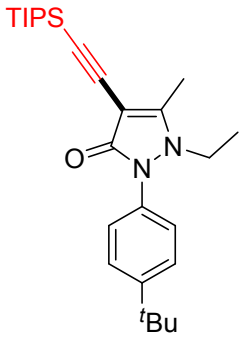
Isolation by column chromatography (EA/PE = 2:1) yielded **5l** (44 mg, 56%) as a white solid. mp 118 − 120 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 – 7.40 (m, 2H), 7.33 – 7.27 (m, 3H), 3.54 (t, J = 14.8 Hz, 2H), 2.36 (s, 3H), 1.40 – 1.32 (m, 2H), 1.13 – 1.08 (m, 21H), 0.74 (t, J = 7.5 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.2, 156.3, 134.7, 129.1, 127.1, 124.7, 96.9, 95.5, 95.3, 49.0, 20.6, 18.7, 12.3, 11.3, 10.9. **HRMS**: $[M+H]^+$ calculated for $C_{24}H_{37}N_2OSi^+$: 397.2670, found 383.2510.



5m, 53%

1-ethyl-5-methyl-2-(*o*-tolyl)-4-((triisopropylsilyl)ethynyl)-1*H*-pyrazol-3(2*H*)-one

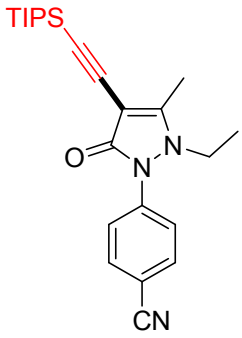
Isolation by column chromatography (EA/PE = 2:1) yielded **5m** (42 mg, 53%) as a white solid. mp 148 − 150 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.31 – 7.27 (m, 2H), 7.26 – 7.20 (m, 1H), 7.09 (d, J = 7.5 Hz, 1H), 3.53 – 3.48 (m, 2H), 2.36 (s, 3H), 2.30(s, 3H), 1.12 (m, 21H), 0.98 (t, J = 7.0 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.8, 154.6, 137.0, 133.6, 131.4, 128.8, 127.4, 126.6, 97.3, 94.9, 94.8, 41.8, 18.7, 18.0, 12.5, 11.9, 11.3. **HRMS**: $[M+H]^+$ calculated for $C_{24}H_{37}N_2OSi^+$: 397.2667, found 397.2667.



5n, 58%

2-(4-(*tert*-butyl)phenyl)-1-ethyl-5-methyl-4-((triisopropylsilyl)ethynyl)-1*H*-pyrazol-3(2*H*)-one

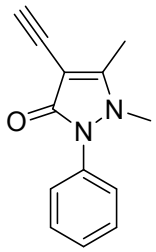
Isolation by column chromatography (EA/PE = 2:1) yielded **5n** (51 mg, 58%) as a white solid. mp 112 − 114 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 – 7.43 (m, 2H), 7.27 – 7.24 (m, 2H), 3.63 (q, J = 7.0 Hz, 2H), 2.36 (s, 3H), 1.32(s, 3H), 1.12 (m, 21H), 0.93 (t, J = 7.0 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.2, 156.0, 150.1, 132.0, 126.1, 124.3, 97.0, 96.6, 95.4, 42.5, 34.6, 31.3, 18.7, 12.1, 11.5, 11.3. **HRMS**: $[M+H]^+$ calculated for $C_{27}H_{43}N_2OSi^+$: 439.3139, found 439.3139.



5o, 61%

4-(2-ethyl-3-methyl-5-oxo-4-((triisopropylsilyl)ethynyl)-2,5-dihydro-1*H*-pyrazol-1-yl)benzonitrile

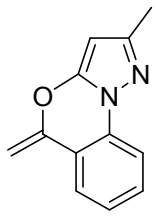
Isolation by column chromatography (EA/PE = 2:1) yielded **5o** (43 mg, 61%) as a white solid. mp 144 − 146 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72 (d, J = 8.7 Hz, 2H), 7.52 (d, J = 8.7 Hz, 2H), 3.14 (s, 3H), 2.38 (s, 3H), 1.10 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.1, 160.0, 138.9, 133.1, 123.1, 118.3, 109.5, 98.5, 96.8, 95.6, 43.5, 18.6, 12.4, 11.2, 10.7. **HRMS**: $[M+H]^+$ calculated for $C_{24}H_{34}N_3OSi^+$: 408.2466, found 408.2462.



6, 81%

4-ethynyl-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one

Compound **6** was obtained as a white solid (86.3 mg, 81%, 0.5 mmol) by following a reported procedure. mp 137 − 139 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.42 (m, 2H), 7.33 – 7.30 (m, 3H), 3.22 (s, 1H), 3.14 (s, 3H), 2.34 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.4, 157.1, 134.3, 129.1, 127.2, 124.9, 92.8, 81.9, 74.1, 35.0, 12.0. **HRMS**: $[M+H]^+$ calculated for $C_{12}H_{11}N_2O^+$:199.0866, found 199.0866.

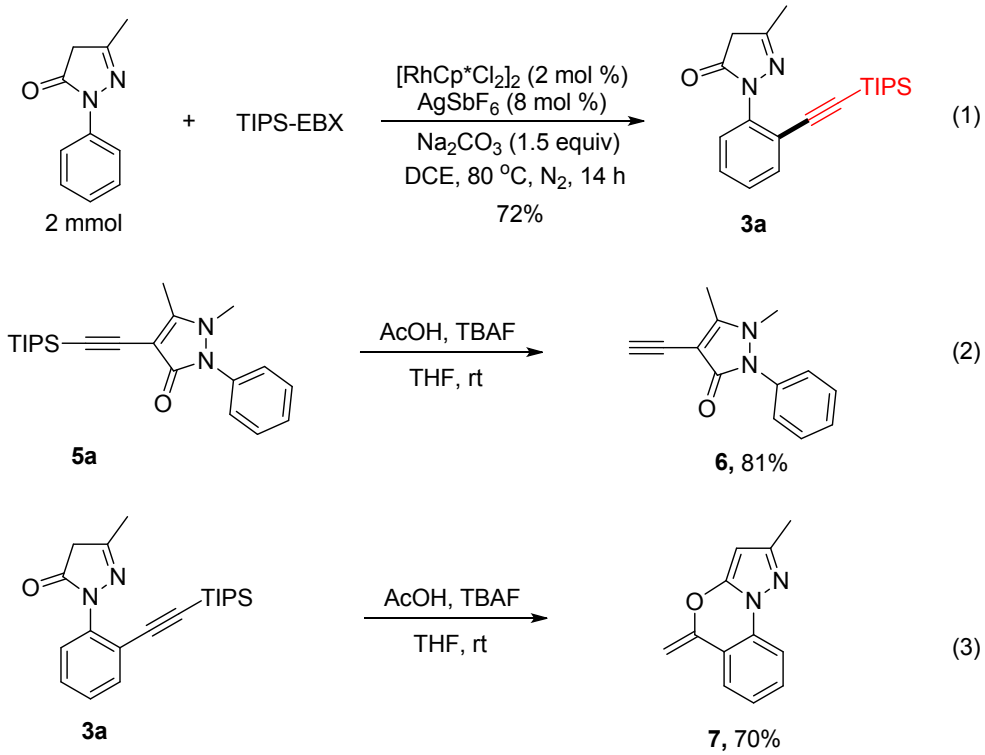


7, 75%

2-methyl-5-methylene-5*H*-benzo[*d*]pyrazolo[5,1-*b*][1,3]oxazine

Compound **7** was obtained as a white solid (225 mg, 75%, 1.42 mmol) by following a reported procedure. mp 122 − 124 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.10 – 7.06 (m, 1H), 5.47 (s, 1H), 4.95 (d, J = 2.9 Hz, 1H), 4.77 (d, J = 2.9 Hz, 1H), 2.27 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 150.9, 150.6, 148.4, 132.0, 130.9, 124.9, 124.1, 115.8, 113.7, 89.6, 87.4, 14.5. **HRMS**: $[M+H]^+$ calculated for $C_{12}H_{11}N_2O^+$:199.0866, found 199.0866.

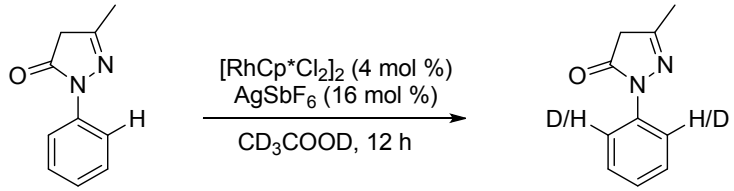
IV. Derivatization



Notably, this method is found to be scalable. Product **3a** could be obtained in 72% yield when the reaction is scaled up to 2 mmol under a reduced (2 mol %) loading of the Rh(III) catalyst. To further demonstrate the synthetic utility of the products, the derivatization of **3a** and **5a** was then carried out. Desilylation of **5a** by treatment with TBAF/AcOH at room temperature produces **6** in 81% yield. Interestingly, when **3a** was subjected to the same reaction condition, a cyclization of the desilylated intermediate occurred to afford **7** in 70% yield.

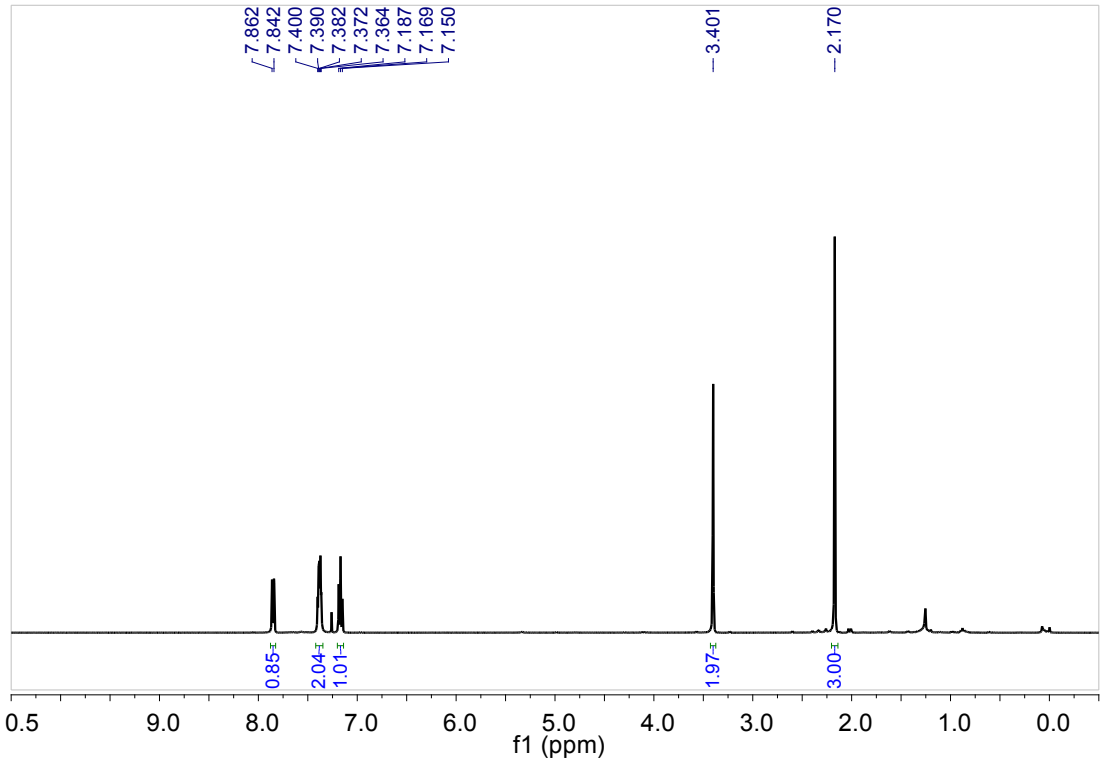
V. Mechanism Studies

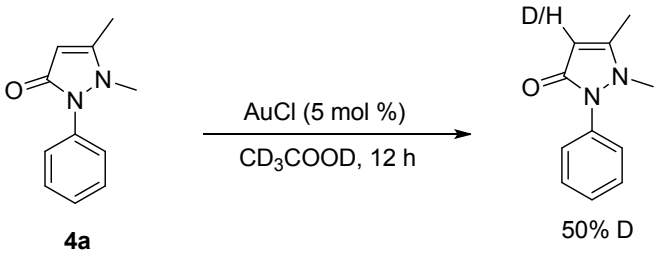
1. H/D exchange of the substrate



1a 58% D

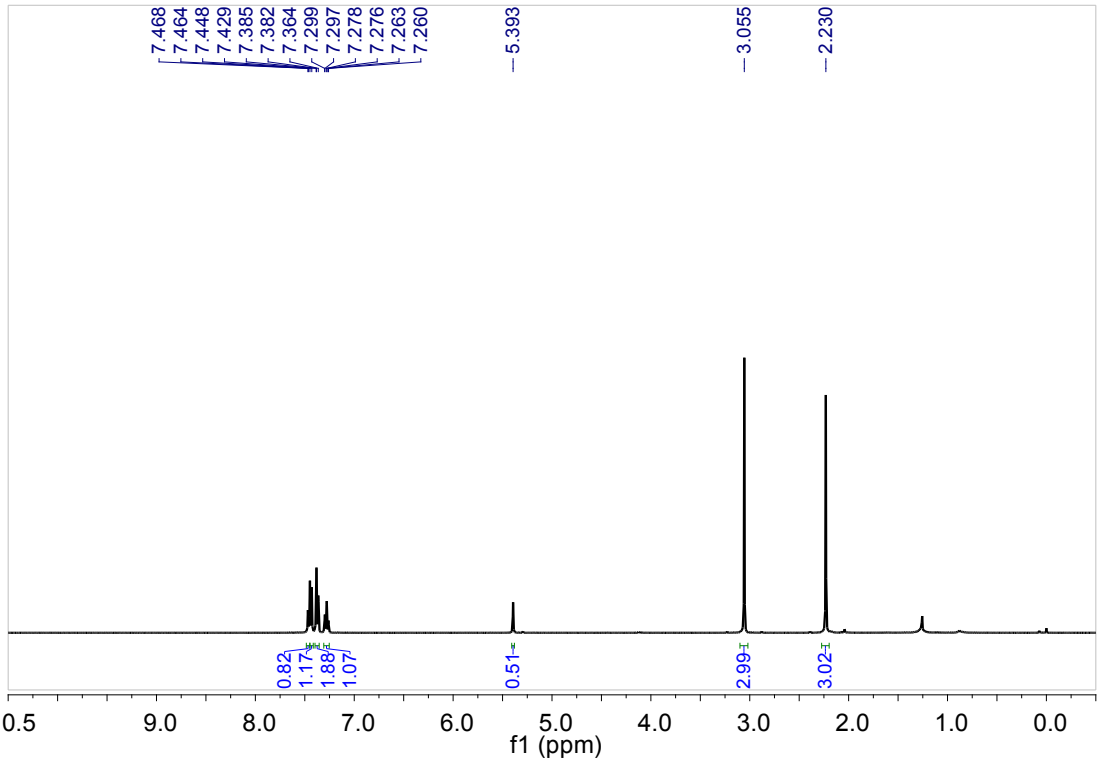
3-methyl-1-phenyl-1H-pyrazol-5-one (**1a**, 0.2 mmol), $[RhCp^*Cl_2]_2$ (0.008 mmol), $AgSbF_6$ (0.032 mmol) were added into a pressure tube. The resulting mixture was dissolved in DCE (2 mL) and was stirred for seconds under N_2 atmosphere, to which was added HOAc-d_4 (0.4 mmol). The mixture was stirred under N_2 atmosphere at 80 ^oC for 12 hours. After that, the solvent was removed under vacuum and the residue was purified by silica gel chromatography using ethyl acetate/petroleum ether (5:1) to afford residue starting material, which was characterized by ^1H NMR spectroscopy. The *ortho* C-H of nitrone was partially deuterated (58% D).



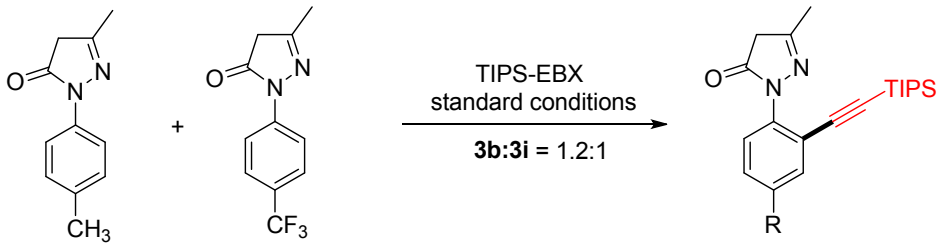


4a 50% D

2,3-dimethyl-1-phenyl-1H-pyrazol-5-one (**4a**, 0.2 mmol), AuCl (0.010mmol), were added into a pressure tube. The resulting mixture was dissolved in $^{n}Bu_2O$ (1 mL) and was stirred for seconds under N_2 atmosphere, to which was added HOAc-d_4 (0.4 mmol). The mixture was stirred under N_2 atmosphere at 80 ^{o}C for 14 hours. After that, the solvent was removed under vacuum and the residue was purified by silica gel chromatography using ethyl MeOH/CH_2Cl_2 (20:1) to afford residue starting material, which was characterized by ^{1}H NMR spectroscopy. The 4-site C-H of heterocyclic was partially deuterated (50% D).

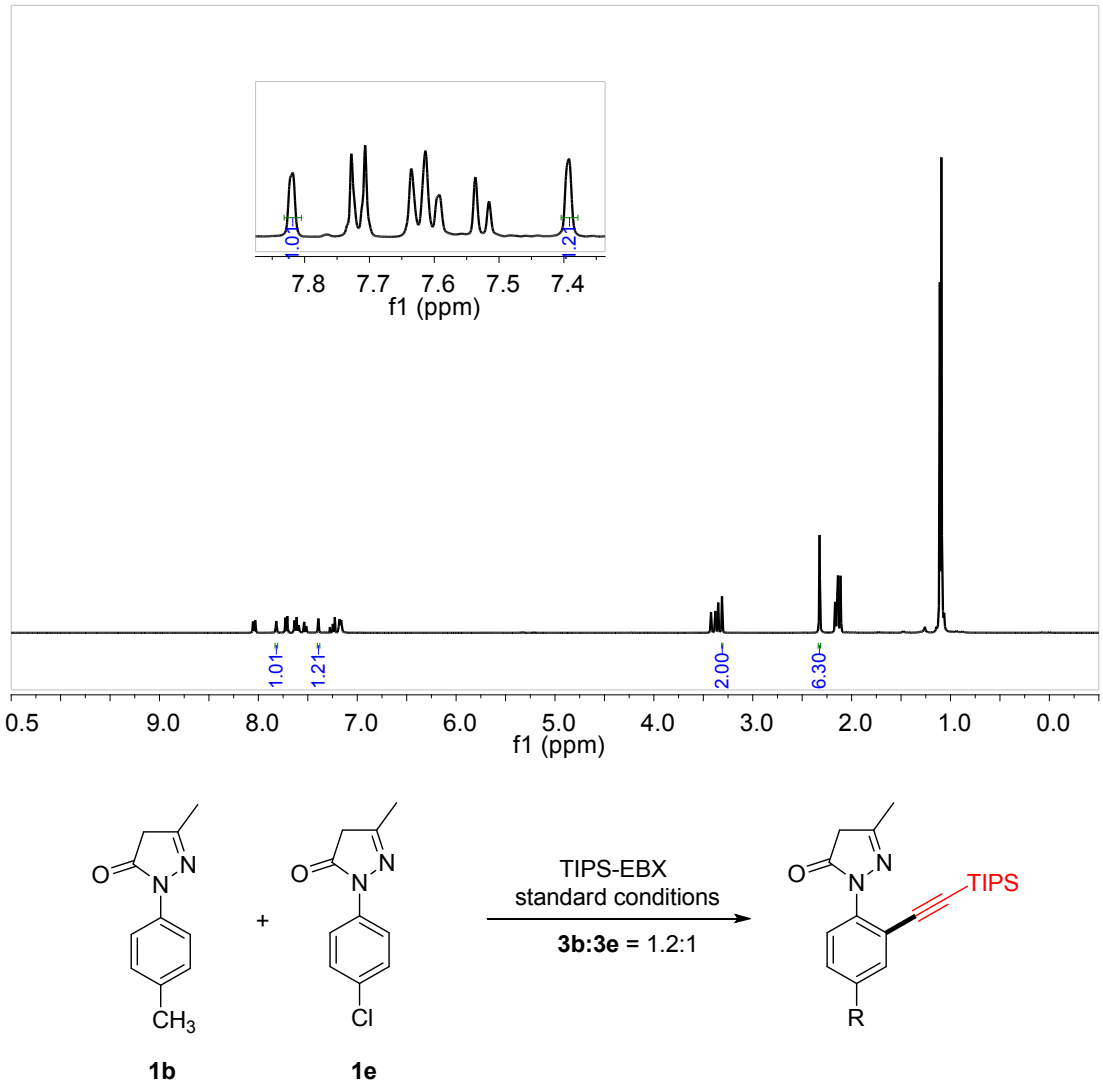


2. Competition Reactions

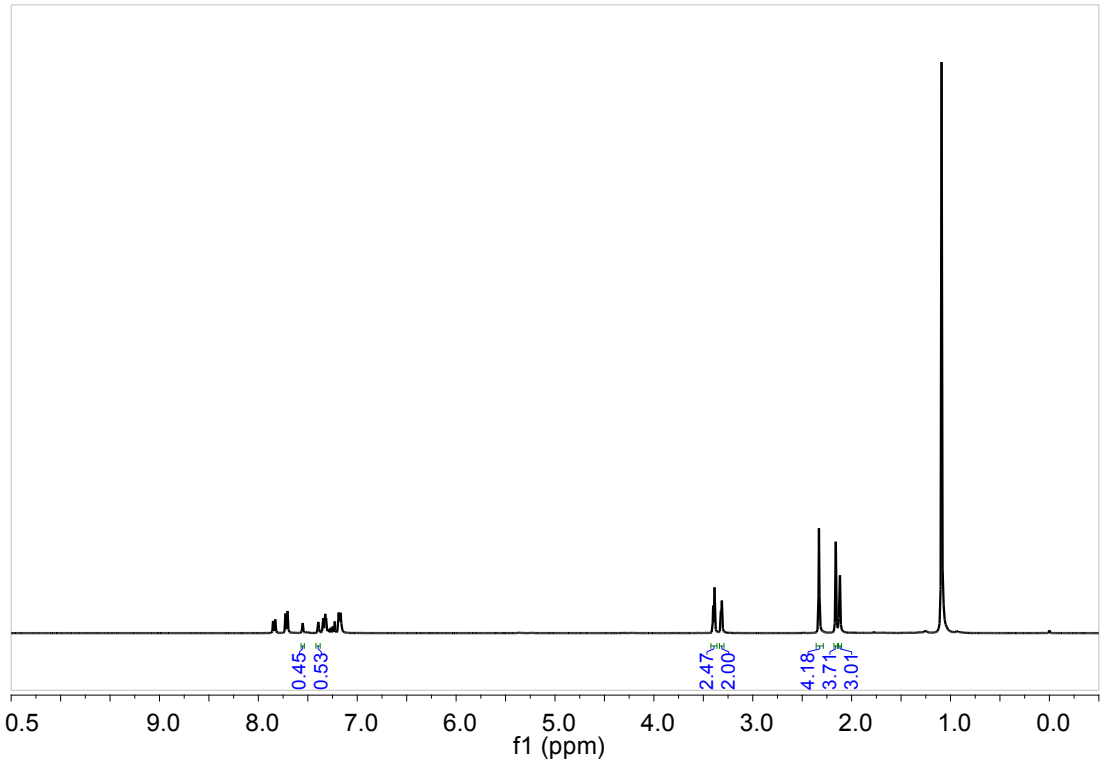


1b **1i**

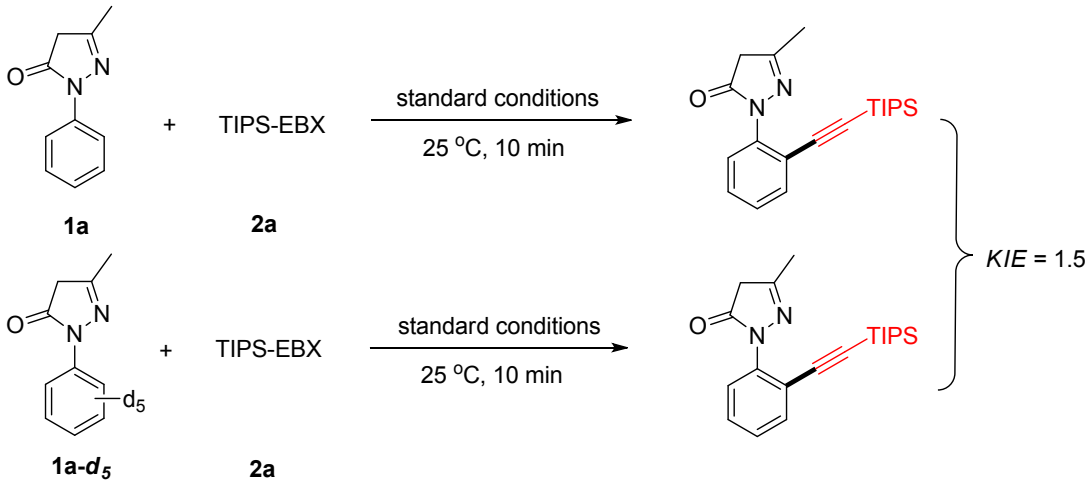
1b (0.2 mmol), **1i** (0.2 mmol), TIPS-EBX (0.24 mmol), $[RhCp^*Cl_2]_2$ (0.008 mmol), $AgSbF_6$ (0.032 mmol) were added into a pressure tube. The resulting mixture was dissolved in DCE (2 mL) and was stirred for seconds under N_2 atmosphere. The mixture was stirred under N_2 atmosphere at 80 °C for 14 hours. After that, the solvent was removed under vacuum and the residue was purified by silica gel chromatography using ethyl acetate/petroleum ether (3:1) to afford the mixture of **1b** and **1i**, which was characterized by ^1H NMR spectroscopy. **3b**:**3i** = 1.2:1.



1b (0.2 mmol), **1e** (0.2 mmol), TIPS-EBX (0.24 mmol), $[RhCp^*Cl_2]_2$ (0.008 mmol), $AgSbF_6$ (0.032 mmol) were added into a pressure tube. The resulting mixture was dissolved in DCE (2 mL) and was stirred for seconds under N_2 atmosphere. The mixture was stirred under N_2 atmosphere at 80 °C for 14 hours. After that, the solvent was removed under vacuum and the residue was purified by silica gel chromatography using ethyl acetate/petroleum ether (3:1) to afford the mixture of **1b** and **1e**, which was characterized by ^1H NMR spectroscopy. **3b**:**3e** = 1.2:1.

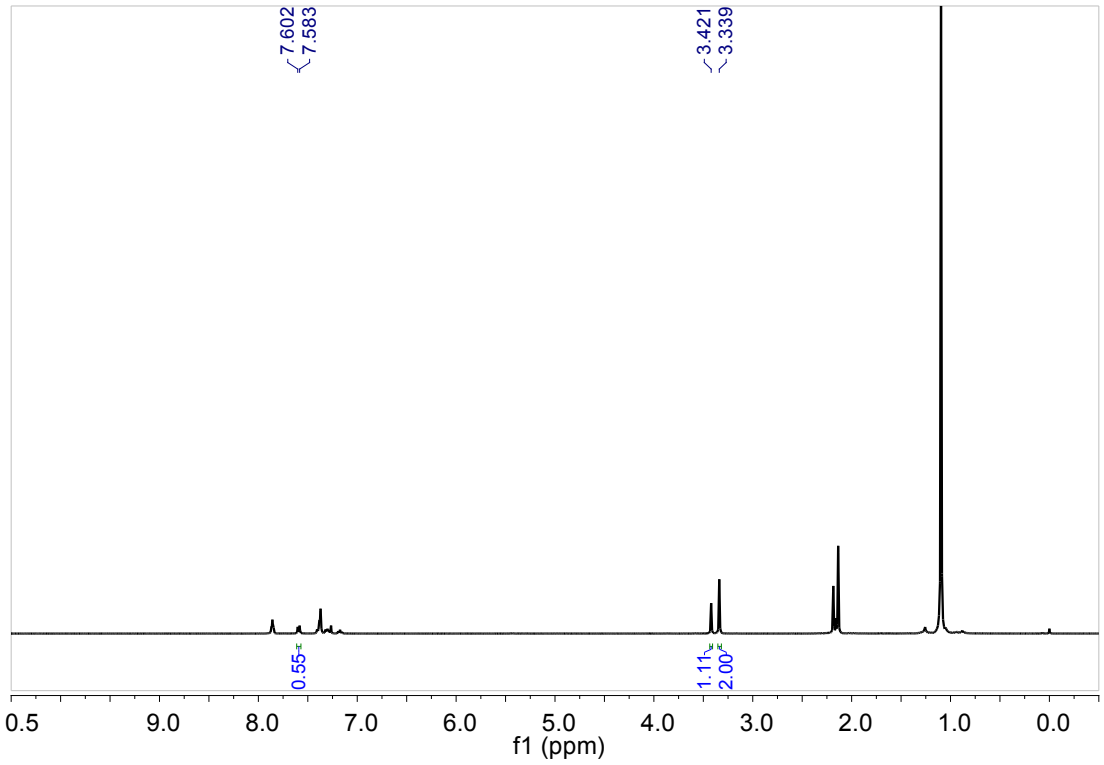


3. Kinetic effect experiment

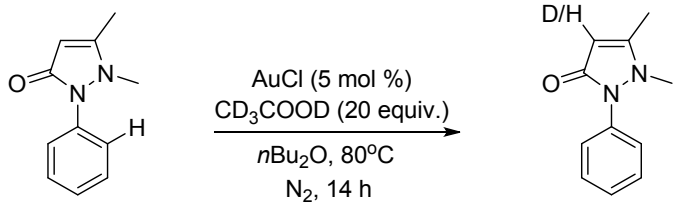


Two pressure tubes were separately charged with **1a** (0.2 mmol) and **1a**-d_5 (0.2 mmol), and to each tube was added, $[RhCp^*Cl_2]_2$ (0.008 mmol), $AgSbF_6$ (0.032 mmol), Na_2CO_3 (0.3 mmol). Each resulting mixture was dissolved in DCE (2 mL) and was stirred for seconds under N_2 atmosphere, to each of which was added TIPS-EBX (0.24 mmol). The two reaction mixtures were stirred side by side in an oil bath preheated at 25 °C for 10 min. After that, the reaction was

quenched in an ice bath and pentane was rapidly added to each tube. The two mixtures were combined and the solvent was removed under vacuum. The crude product **3a** and **3a**-d_5 for 64% (NMR yield). The KIE value was determined to be k_H/k_D = 1.5 on the basis of ^{1}H NMR analysis.



4. Mechanistic Consideration under Au-Catalyzed Conditions



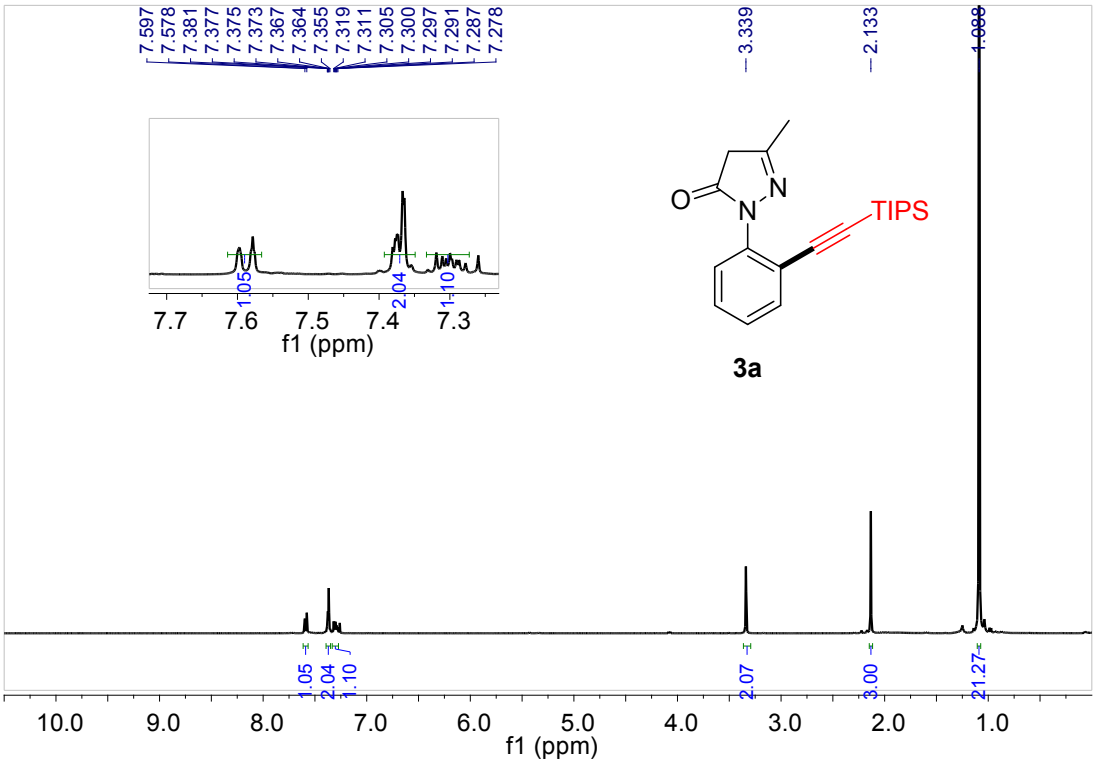
4a 50 % D

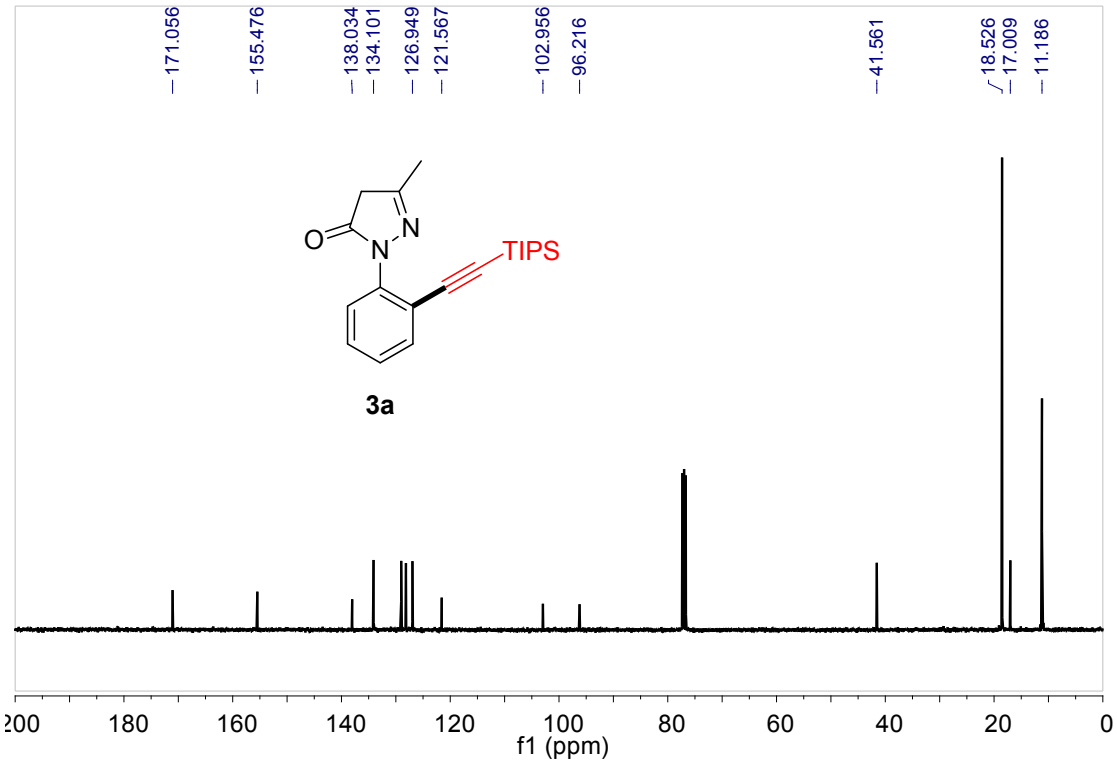
VI. References

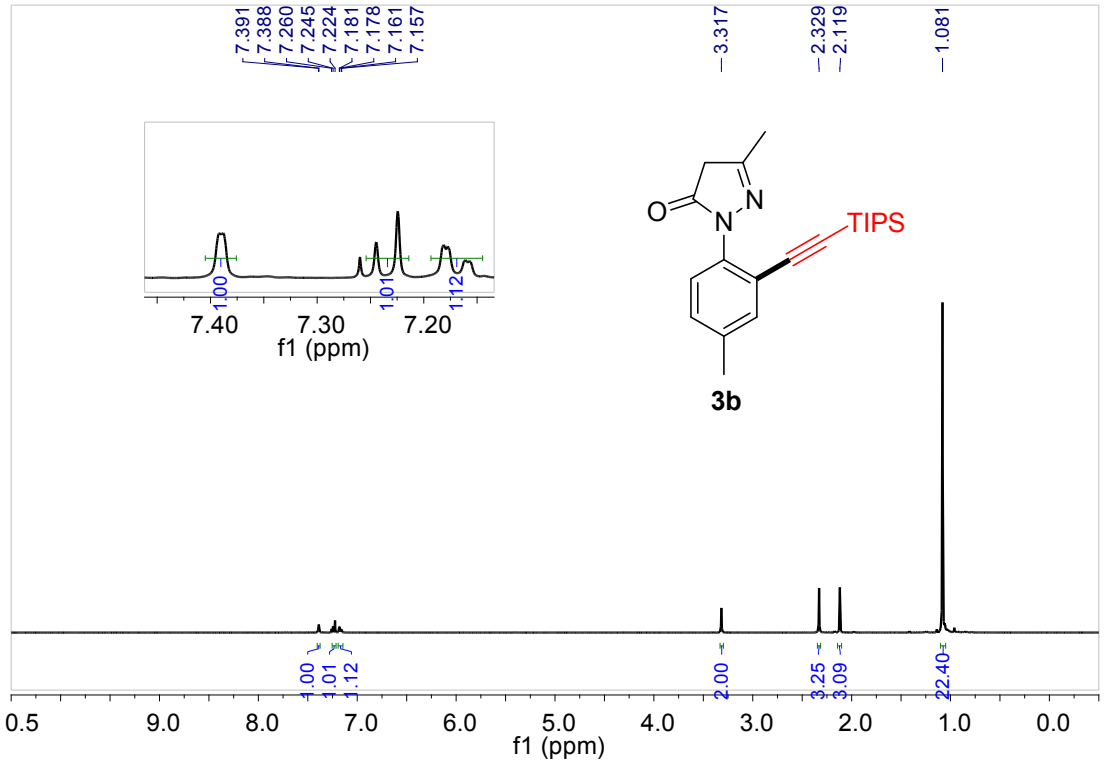
(1) K. Jay, C. Di and S. Samant, *RSC Adv*., 2014, **4**, 30712-30717.

(2) J. P. Brand, C. Chevalley, R. Scopelliti and J. Waser, *Chem.Eur. J.*, 2012, **18**, 5655.

VII. NMR Spectra



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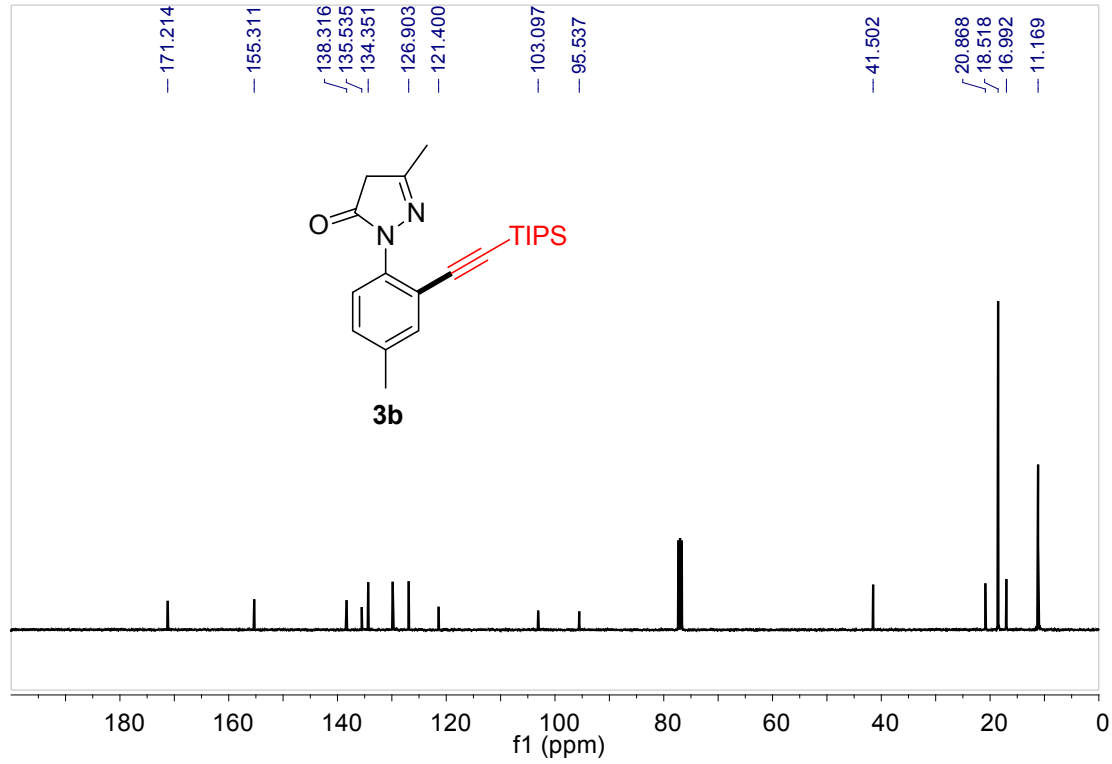
7.245
7.224
7.181
7.178
7.161
7.157
3.317
2.329
2.119
1.081
1.00
1.01
1.12
7.40
7.30
7.20
f1 (ppm)
O
N
N
TIPS
3b
1.00
1.01
1.12
2.00
3.25
3.09
22.40
0.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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135.535
134.351
126.903
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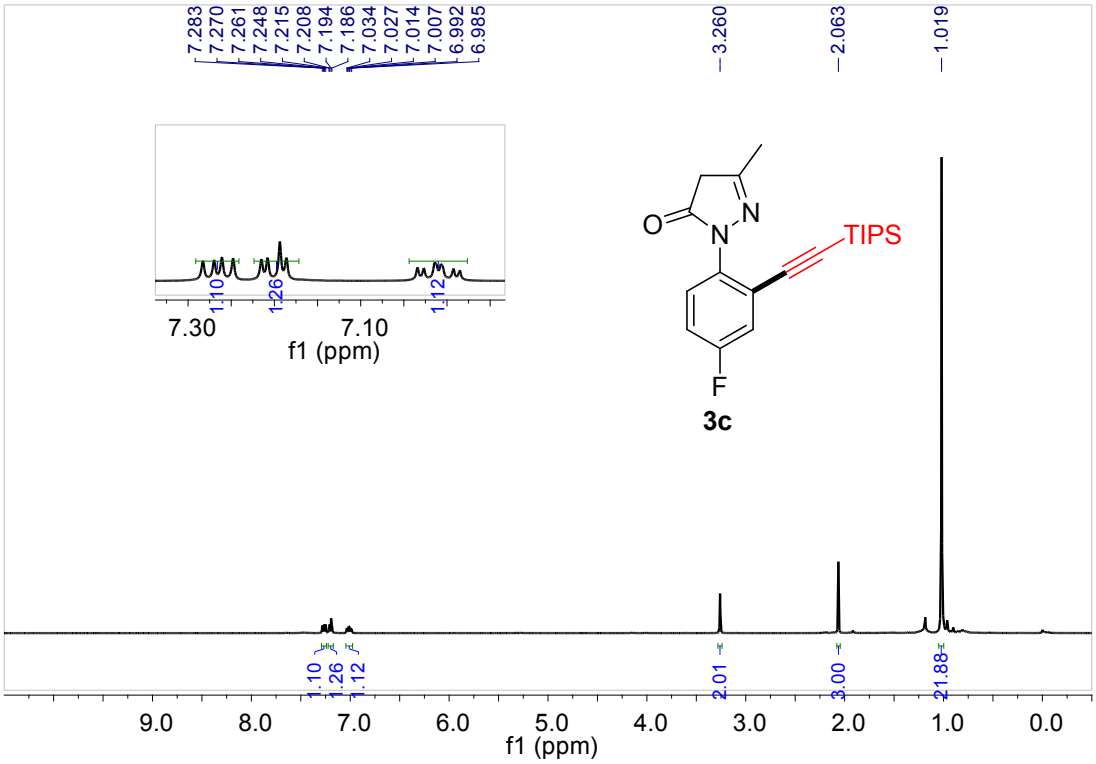
103.097
95.537
41.502
20.868
18.518
16.992
11.169
O
N
N
TIPS
3b
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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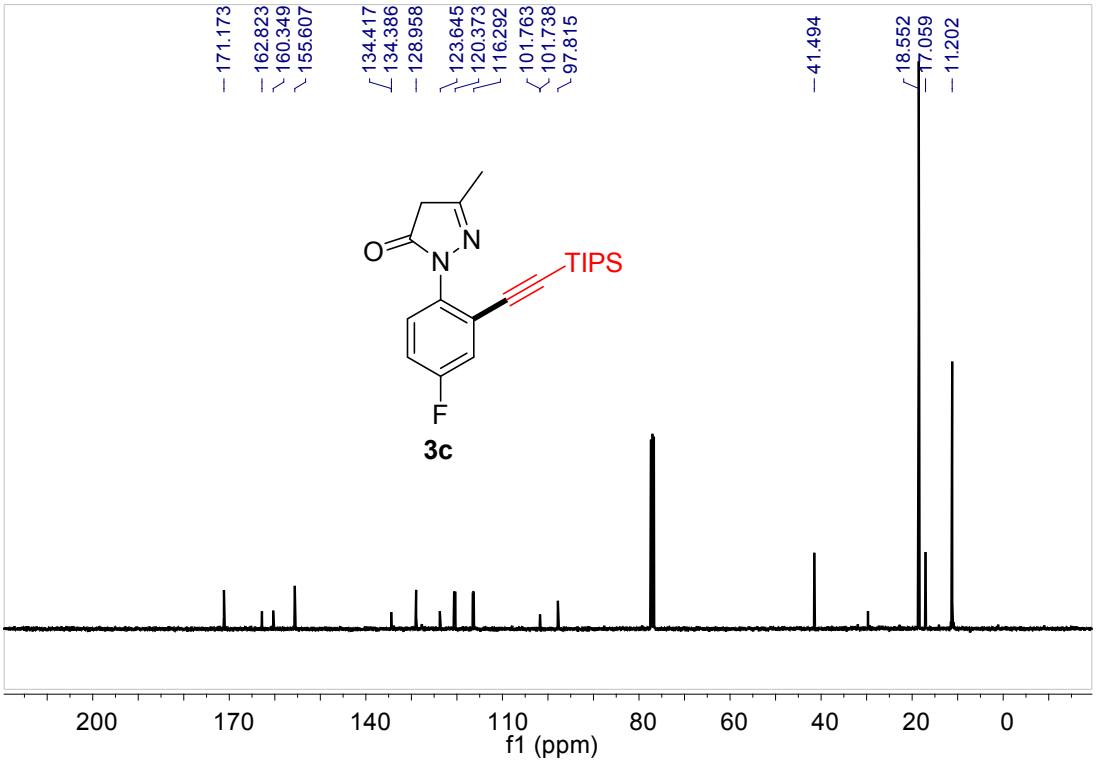
7.215
7.208
7.194
7.186
7.034
7.027
7.014
7.007
6.992
6.985
3.260
2.063
1.019
1.10
1.26
1.12
7.30
7.10
f1 (ppm)
O
N
N
TIPS
F
3c
1.10
1.26
1.12
2.01
3.00
21.88
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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134.386
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123.645
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116.292
101.763
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97.815
41.494
18.552
17.059
11.202
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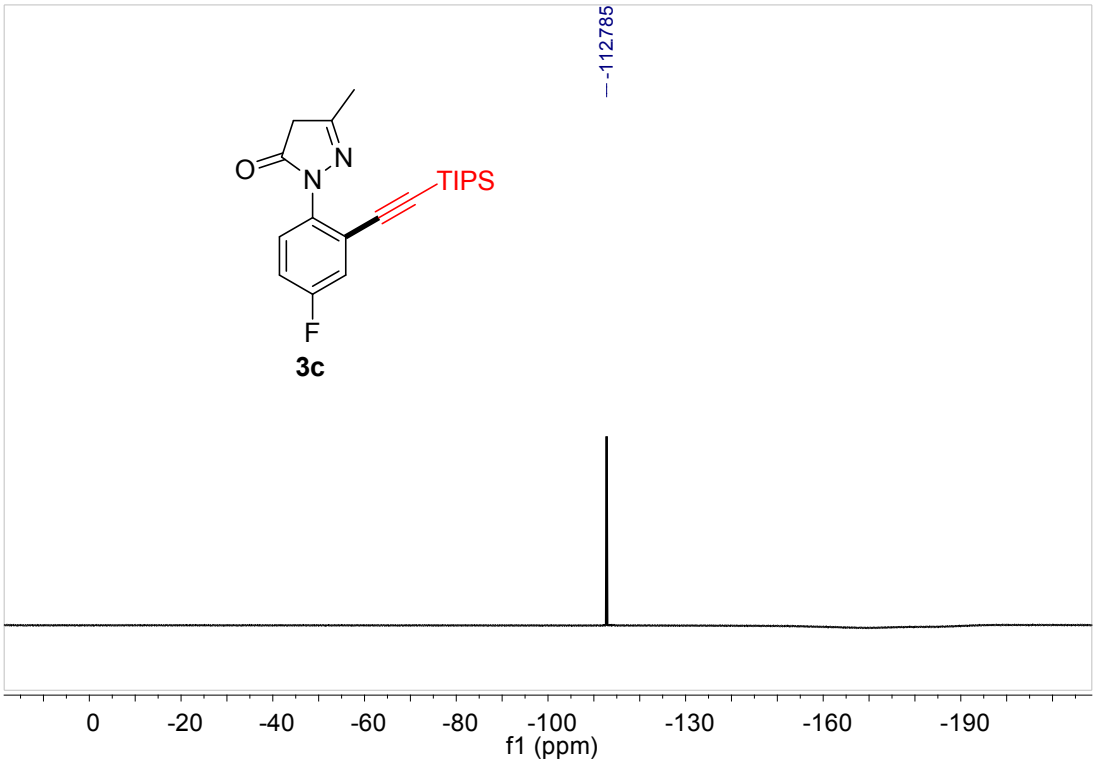
N
N
TIPS
F
3c
200
170
140
110
80
60
40
20
0
f1 (ppm)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N
N
TIPS
F
3c
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-20
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-60
-80
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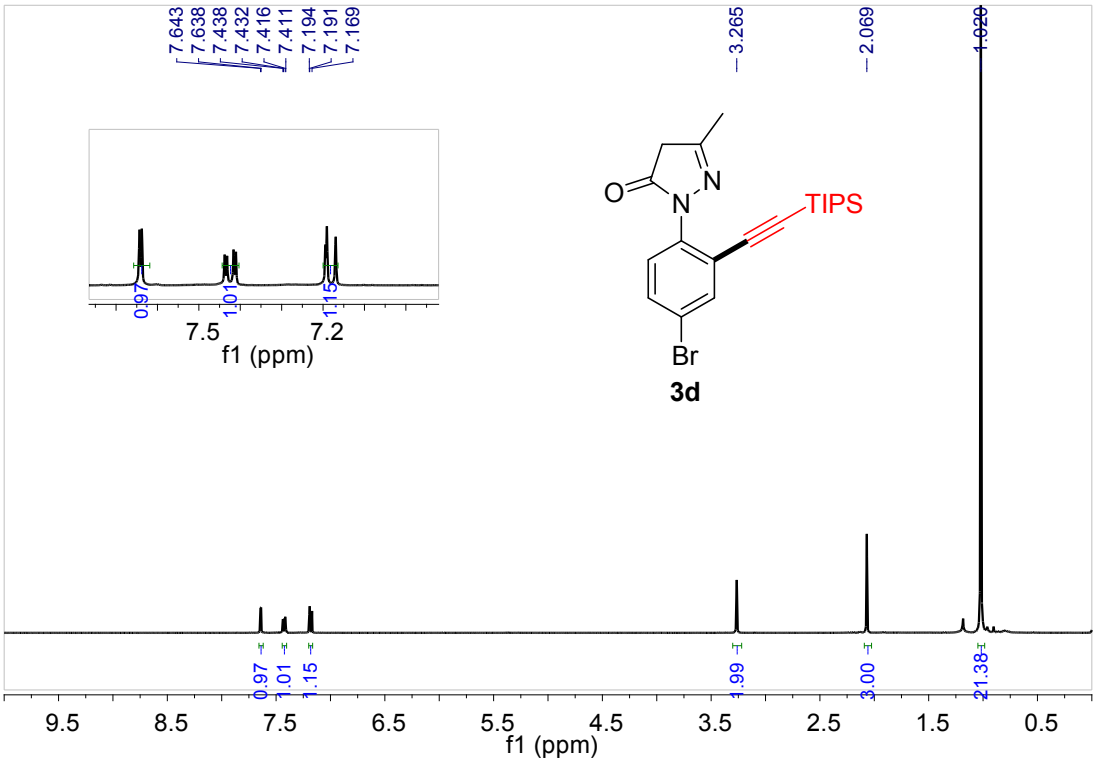
-160
-190
f1 (ppm)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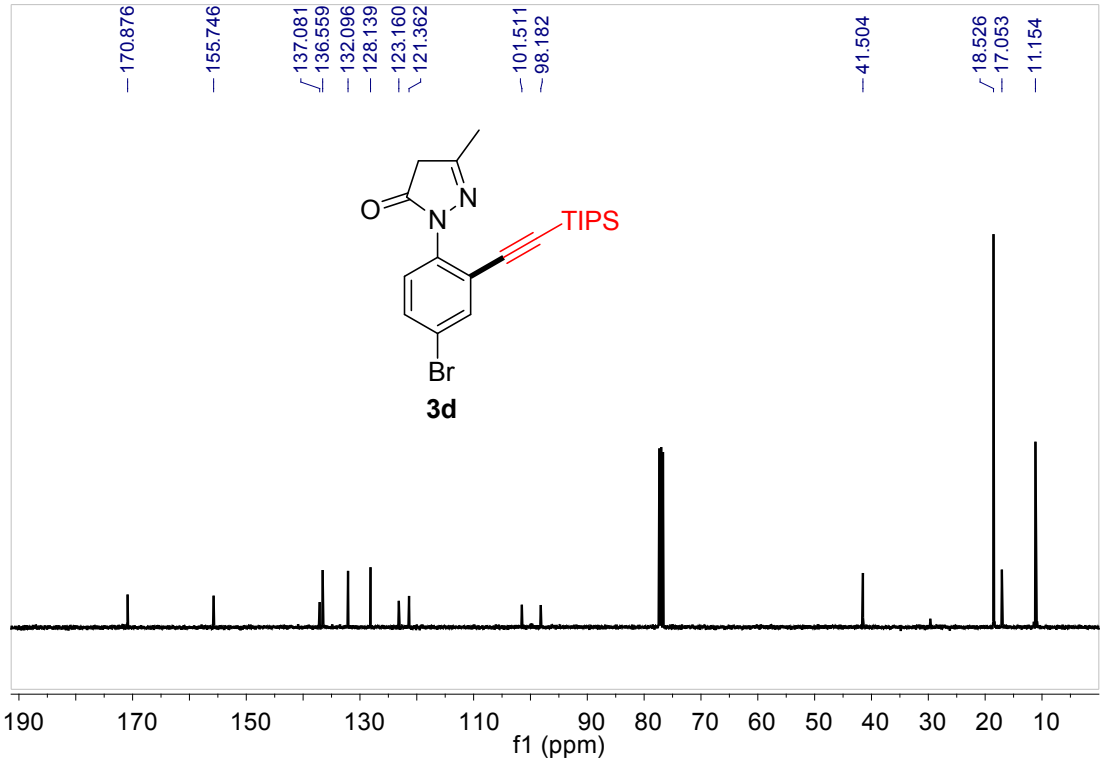
7.411
7.194
7.191
7.169
3.265
2.069
1.020
0.97
1.01
1.15
7.5
7.2
f1 (ppm)
O
N
N
TIPS
Br
3d
0.97
1.01
1.15
1.99
3.00
21.38
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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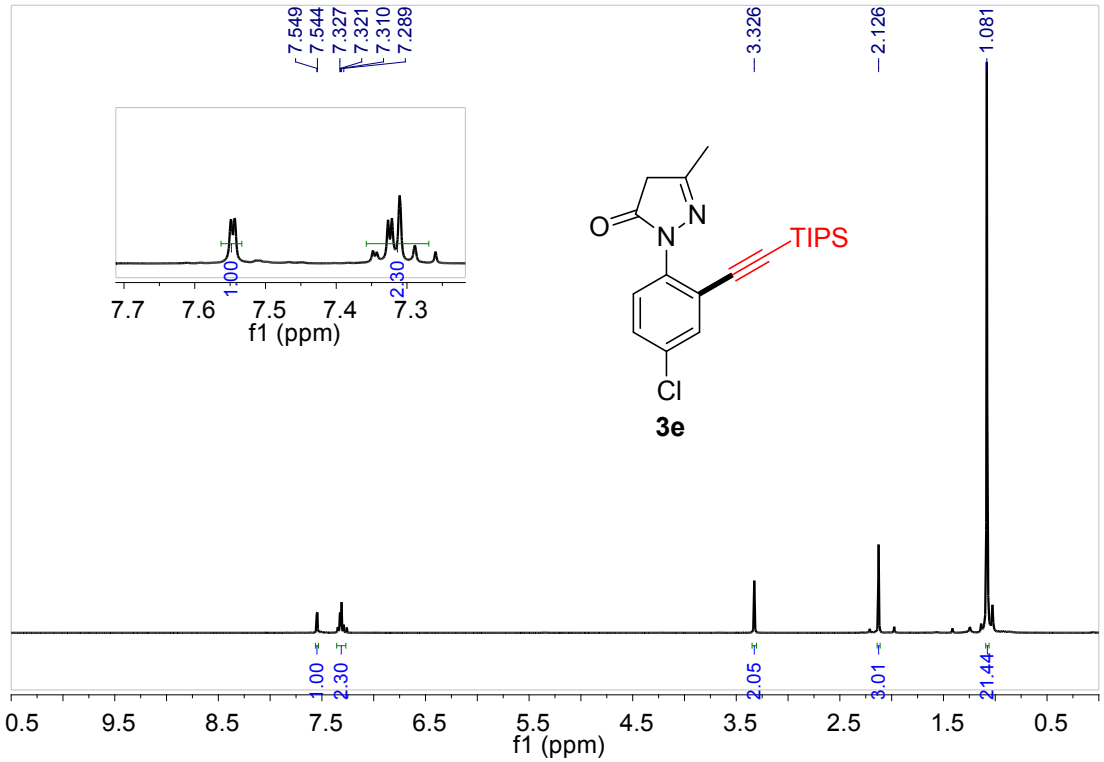
136.559
132.096
128.139
123.160
121.362
101.511
98.182
41.504
18.526
17.053
11.154
O
N
N
TIPS
Br
3d
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.289
3.326
2.126
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1.00
2.30
7.7
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7.4
7.3
f1 (ppm)
O
N
N
TIPS
Cl
3e
1.00
2.30
2.05
3.01
21.44
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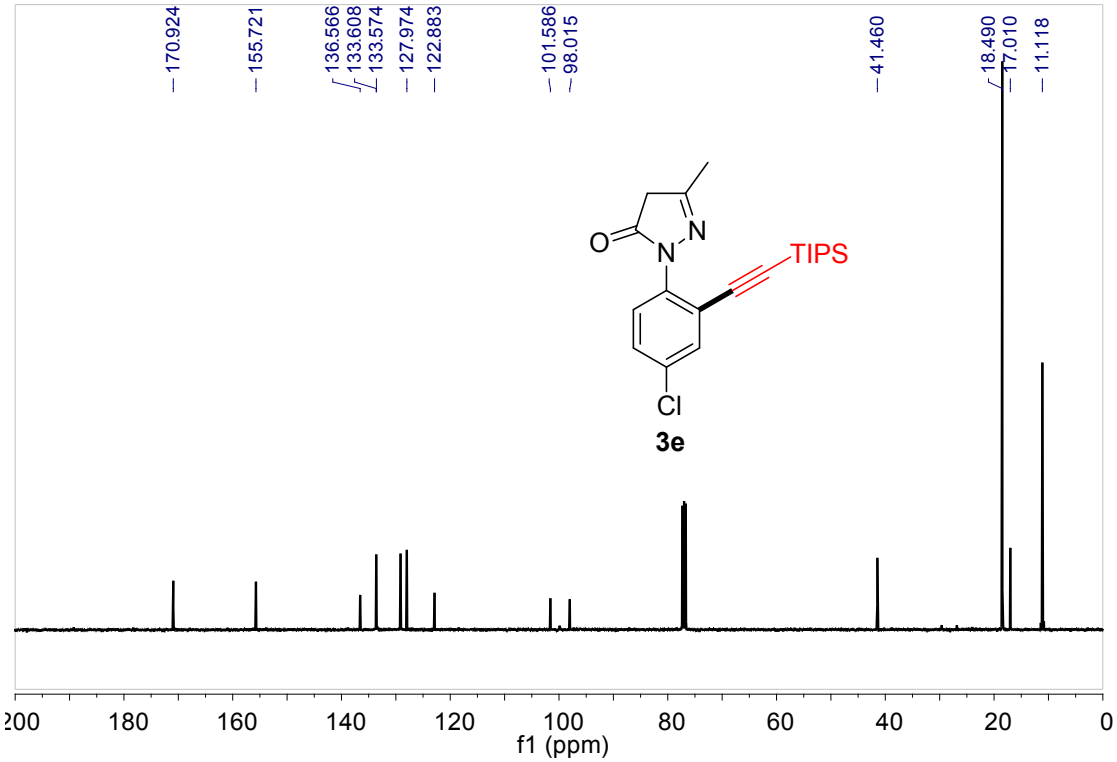
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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98.015
41.460
18.490
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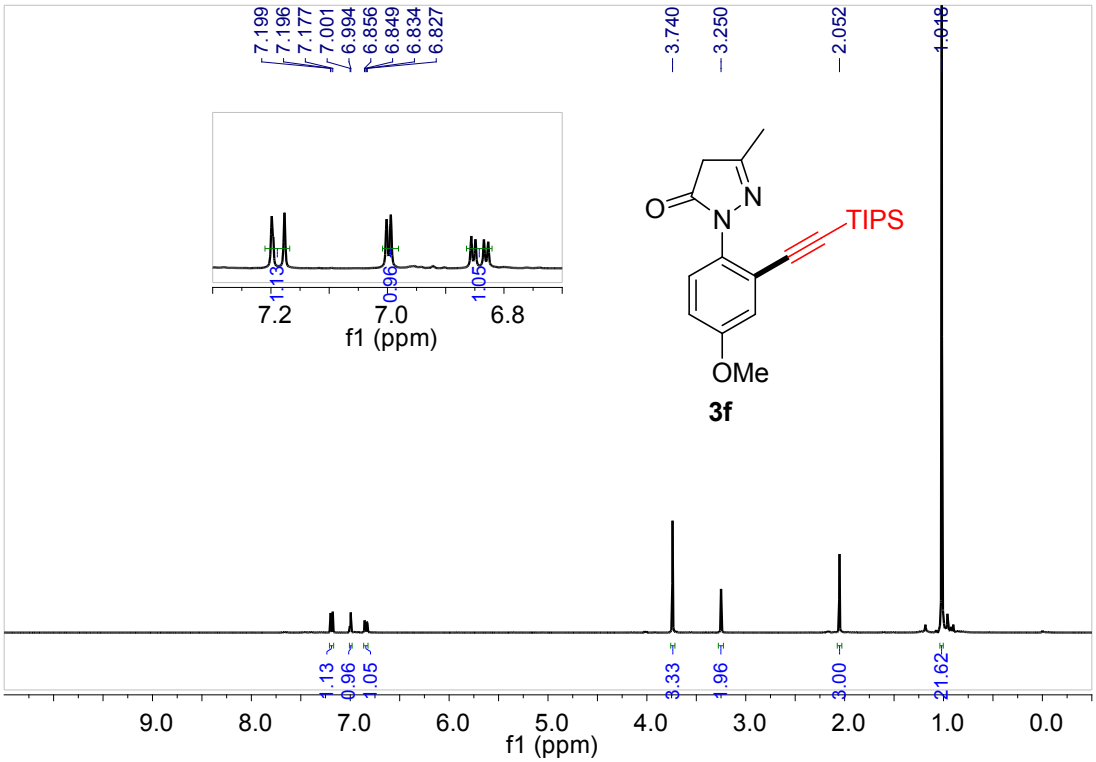
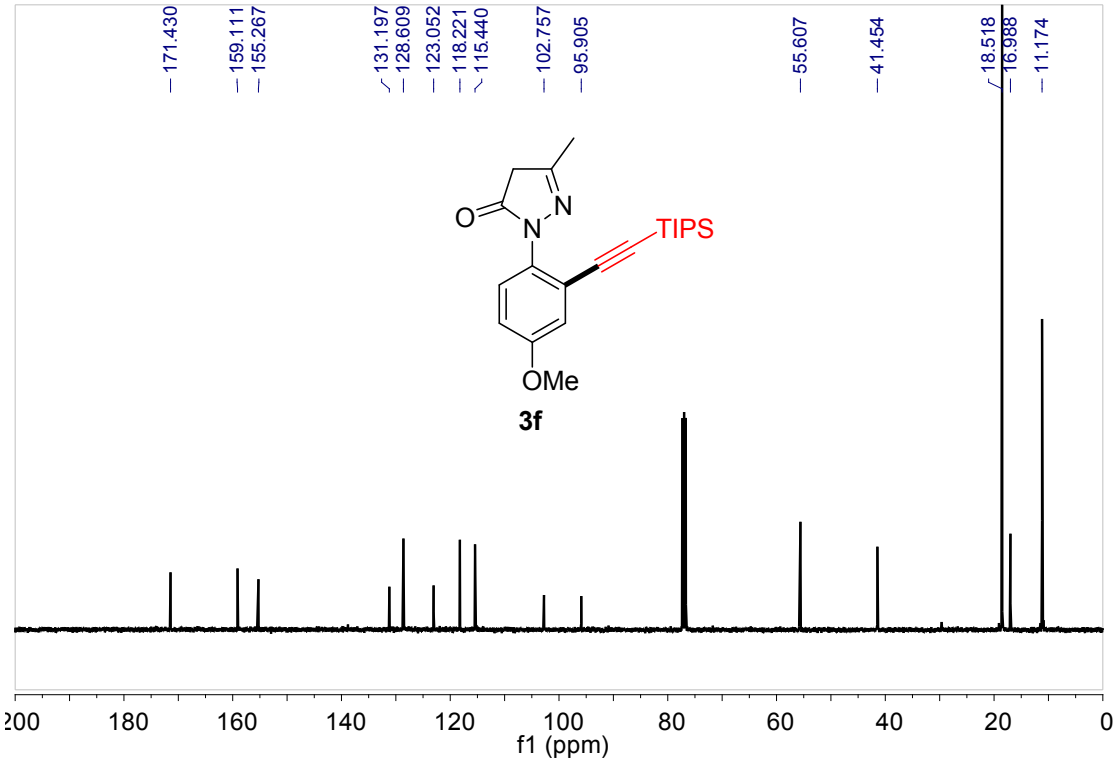
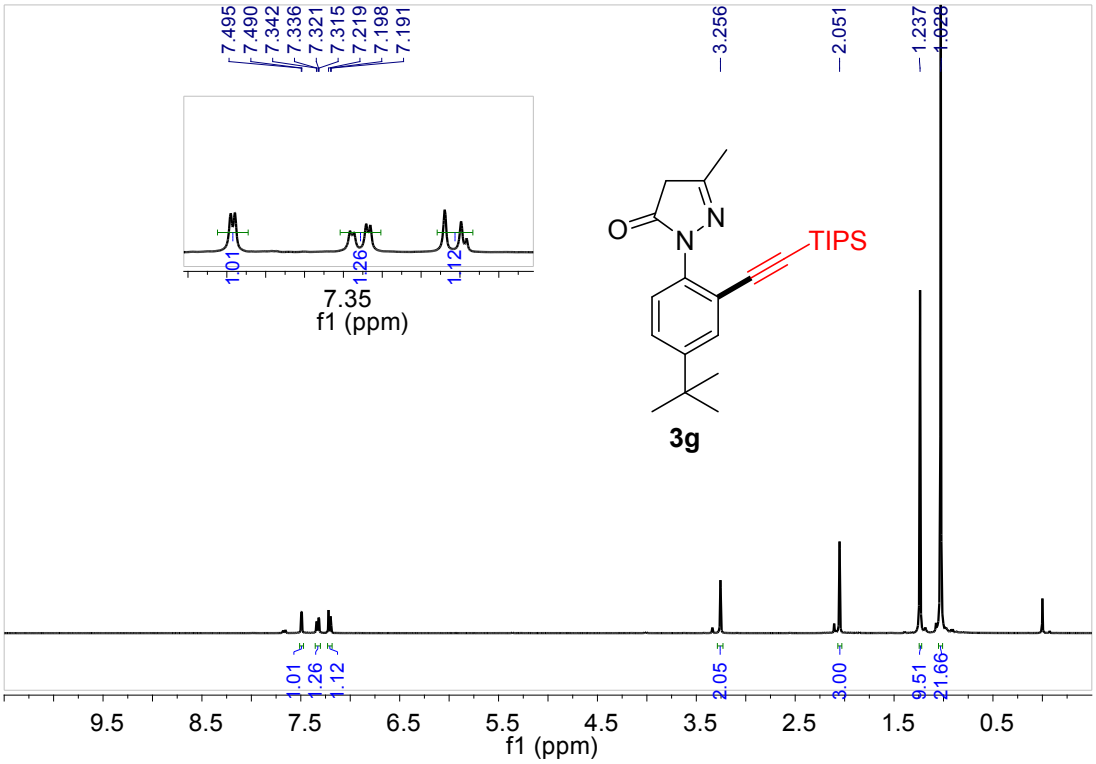
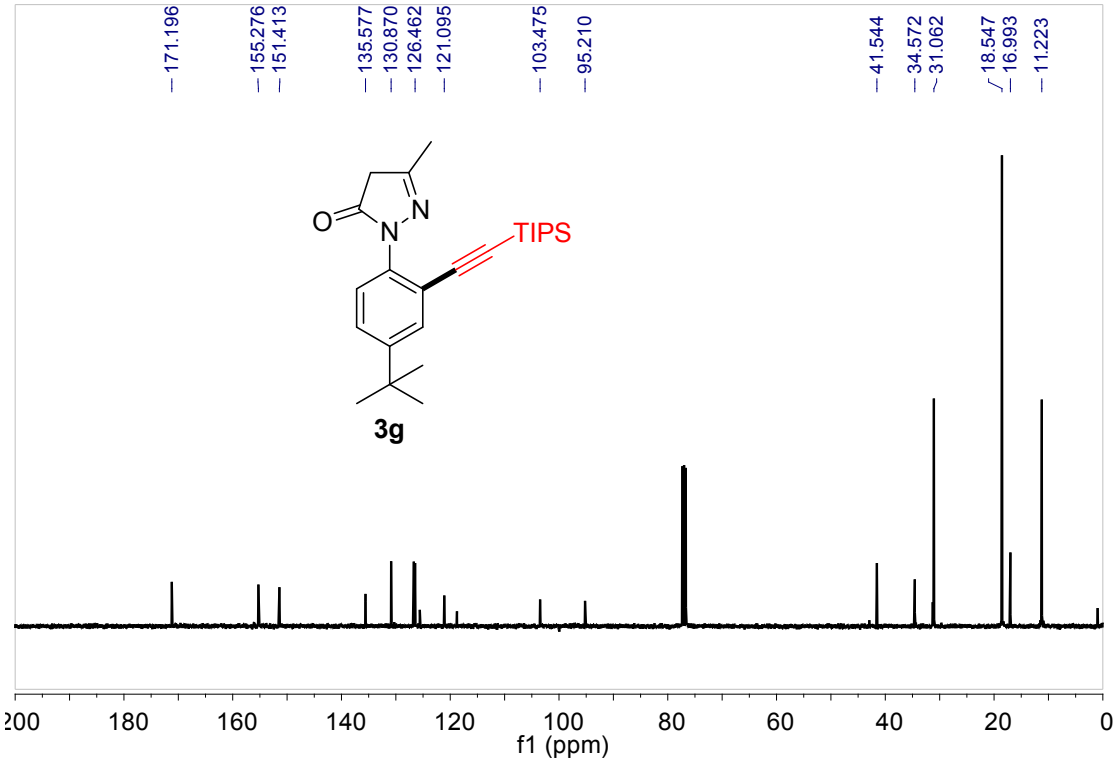
O
N
N
TIPS
Cl
3e
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.199
7.196
7.177
7.001
6.994
6.856
6.849
6.834
6.827
3.740
3.250
2.052
1.019
1.13
0.96
1.05
7.2
7.0
6.8
f1 (ppm)
O
N
N
TIPS
OMe
3f
1.13
0.96
1.05
3.33
1.96
3.00
21.62
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


171.430
159.111
155.267
131.197
128.609
123.052
118.221
115.440
102.757
95.905
55.607
41.454
18.518
16.988
11.174
O
N
N
TIPS
OMe
3f
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.495
7.490
7.342
7.336
7.321
7.315
7.219
7.198
7.191
3.256
2.051
1.237
1.020
1.01
1.26
1.12
7.35
f1 (ppm)
O
N
N
TIPS
3g
1.01
1.26
1.12
2.05
3.00
9.51
21.66
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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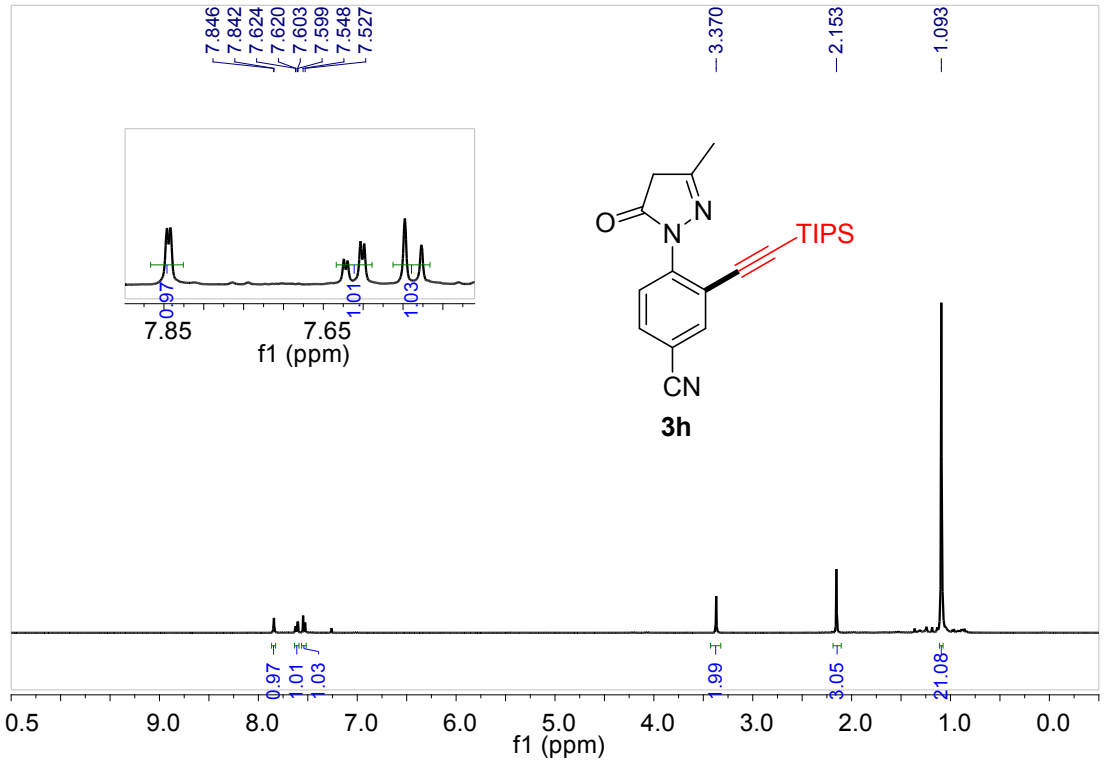
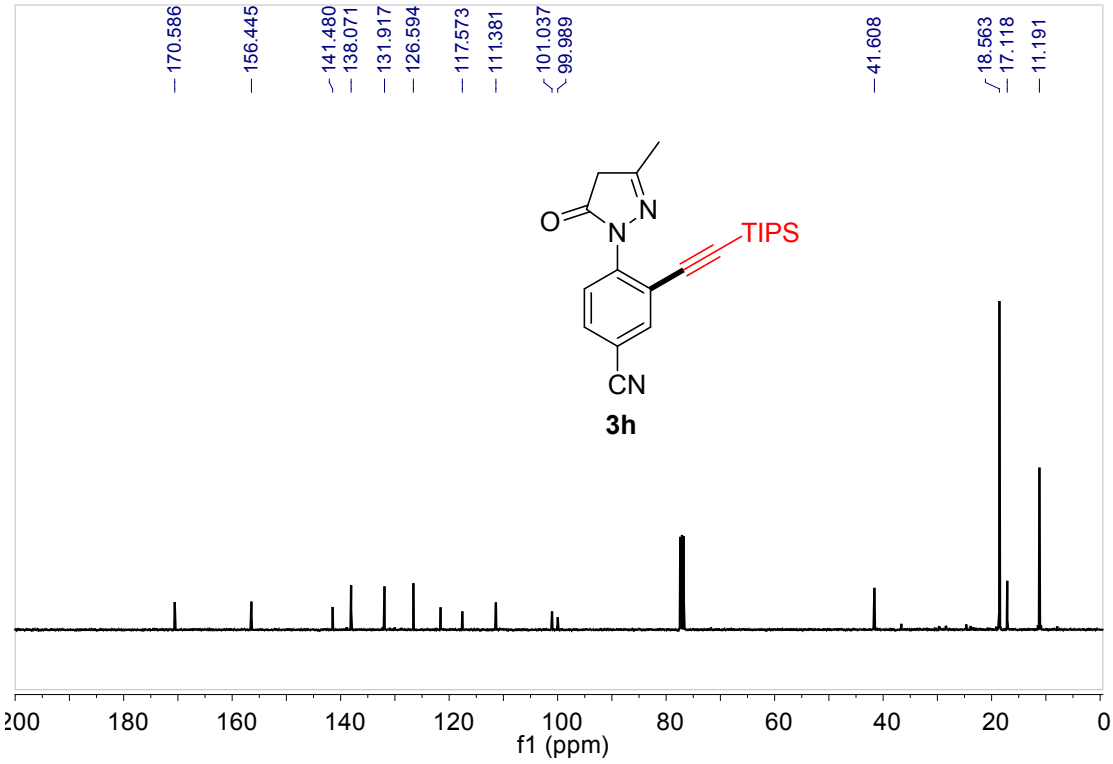
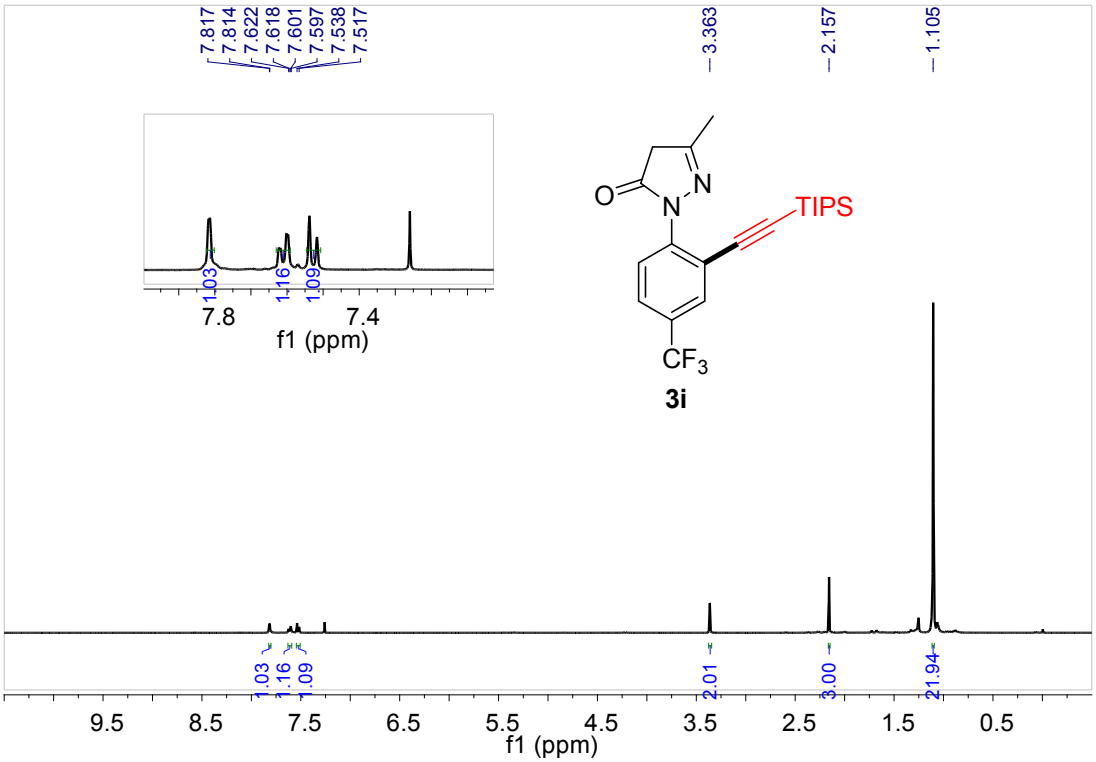
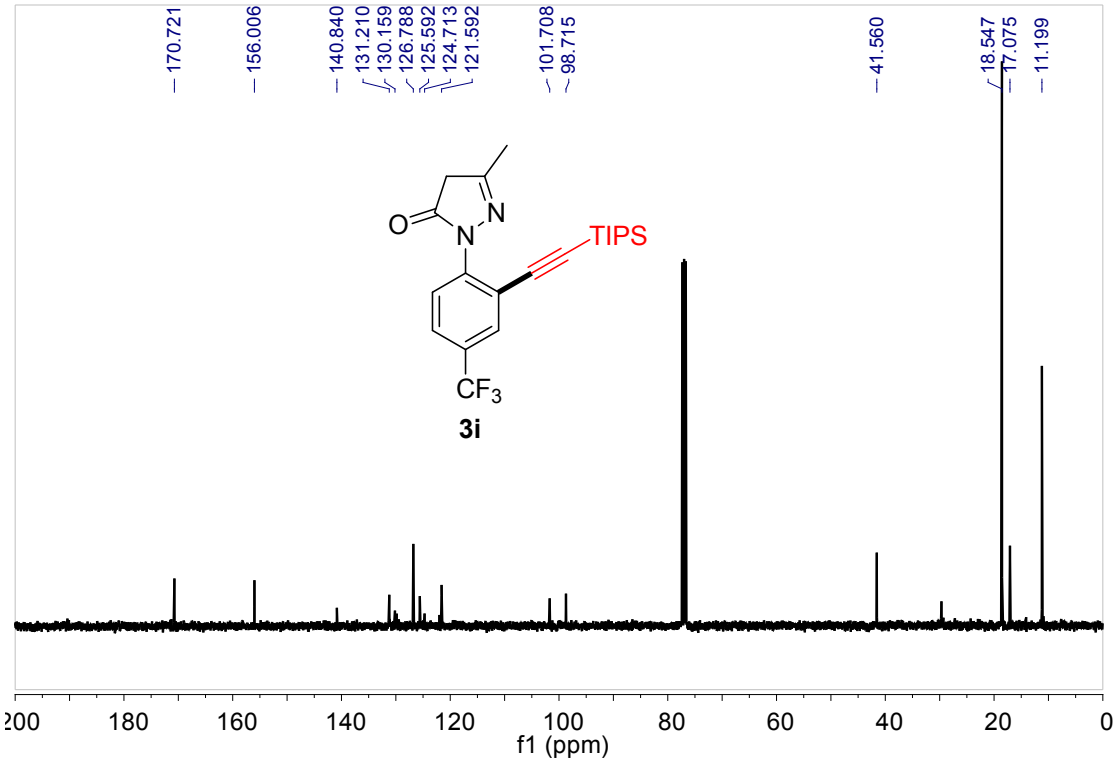
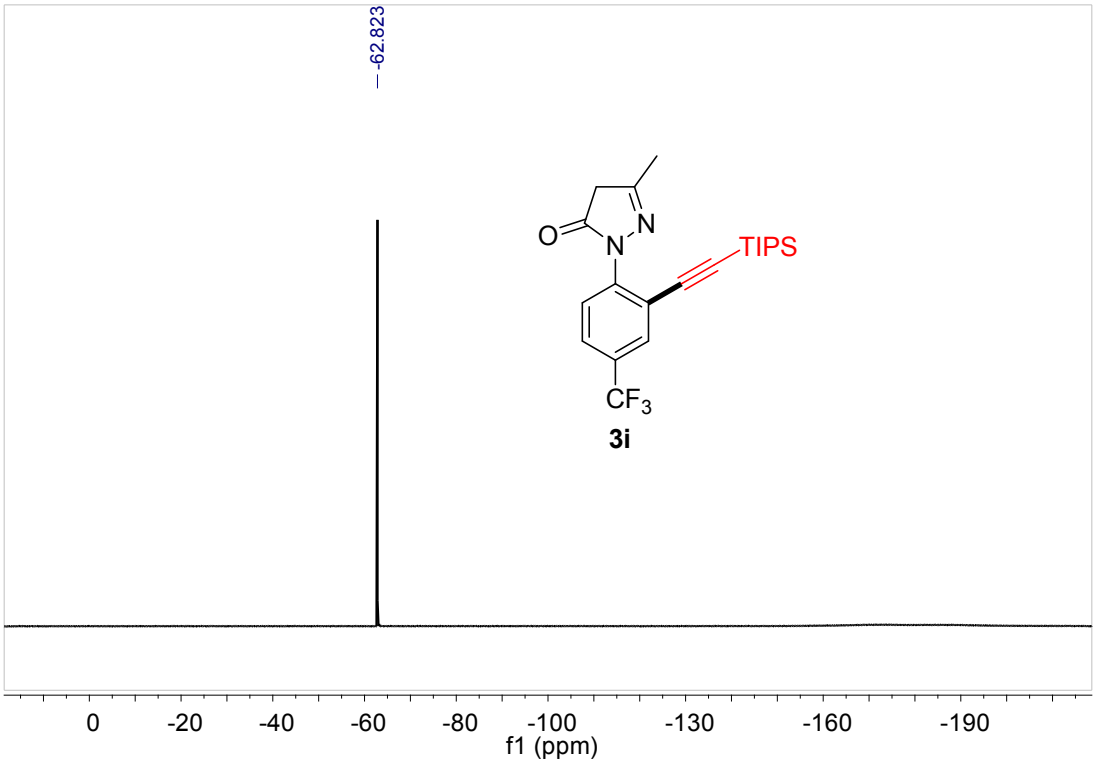
155.276
151.413
135.577
130.870
126.462
121.095
103.475
95.210
41.544
34.572
31.062
18.547
16.993
11.223
O
N
N
TIPS
3g
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

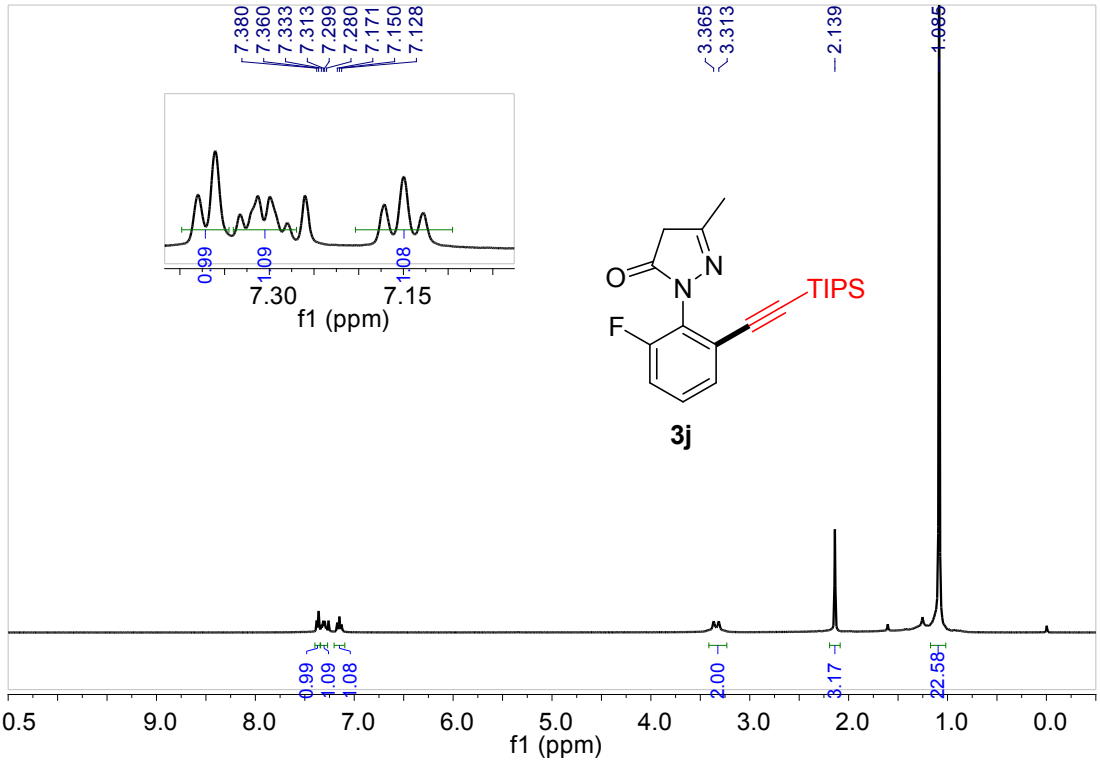

7.846
7.842
7.624
7.620
7.603
7.599
7.548
7.527
3.370
2.153
1.093
0.97
1.01
1.03
7.85
7.65
f1 (ppm)
O
N
N
TIPS
CN
3h
0.97
1.01
1.03
1.99
3.05
21.08
0.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

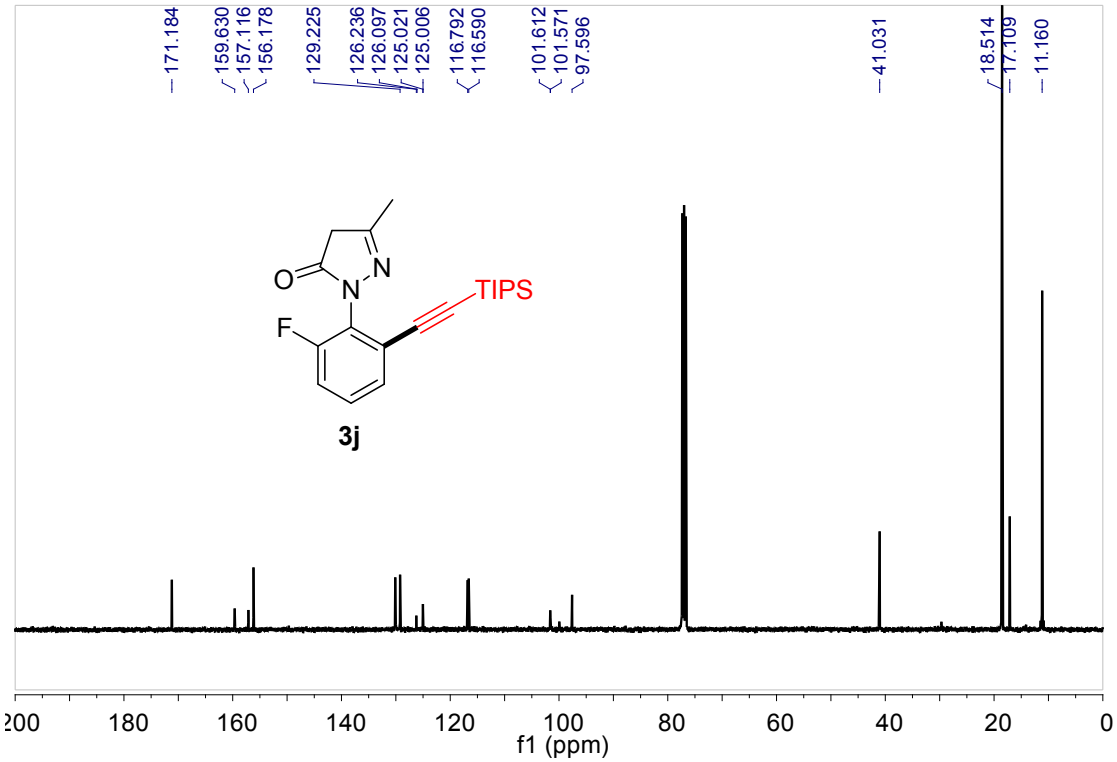

170.586
156.445
141.480
138.071
131.917
126.594
117.573
111.381
101.037
99.989
41.608
18.563
17.118
11.191
O
N
N
TIPS
CN
3h
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

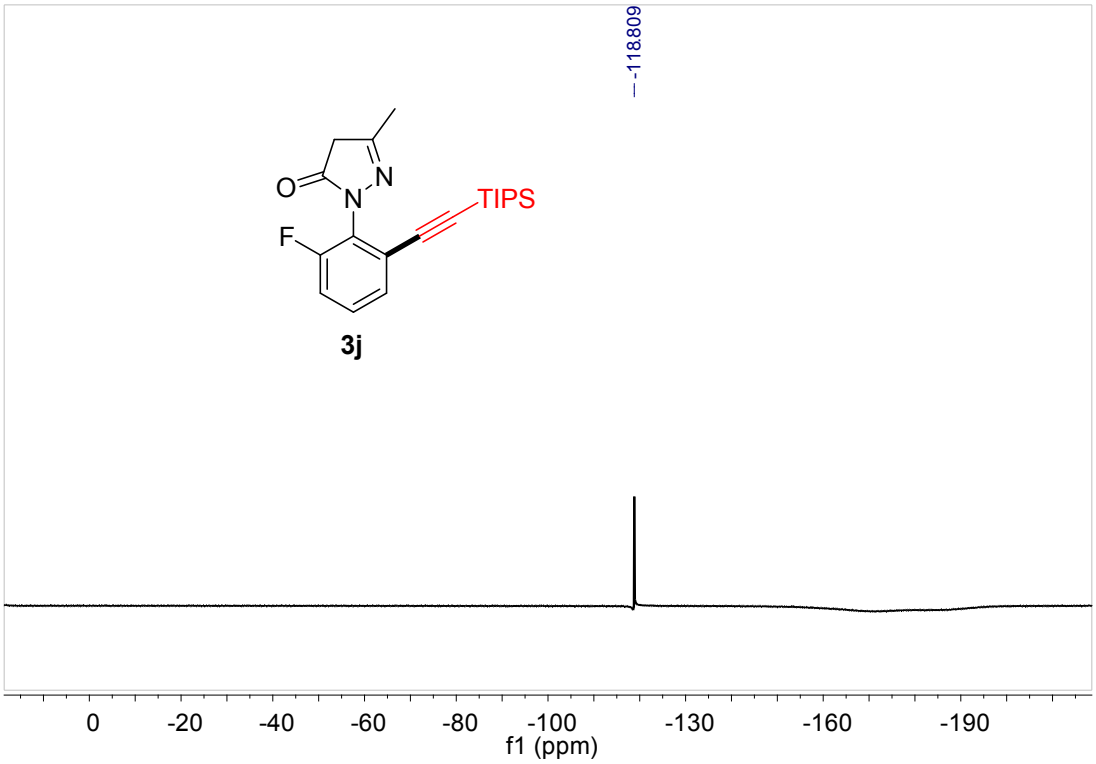

7.817
7.814
7.622
7.618
7.601
7.597
7.538
7.517
3.363
2.157
1.105
1.03
1.16
1.09
7.8
7.4
f1 (ppm)
O
N
N
TIPS
CF3
3i
1.03
1.16
1.09
2.01
3.00
21.94
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

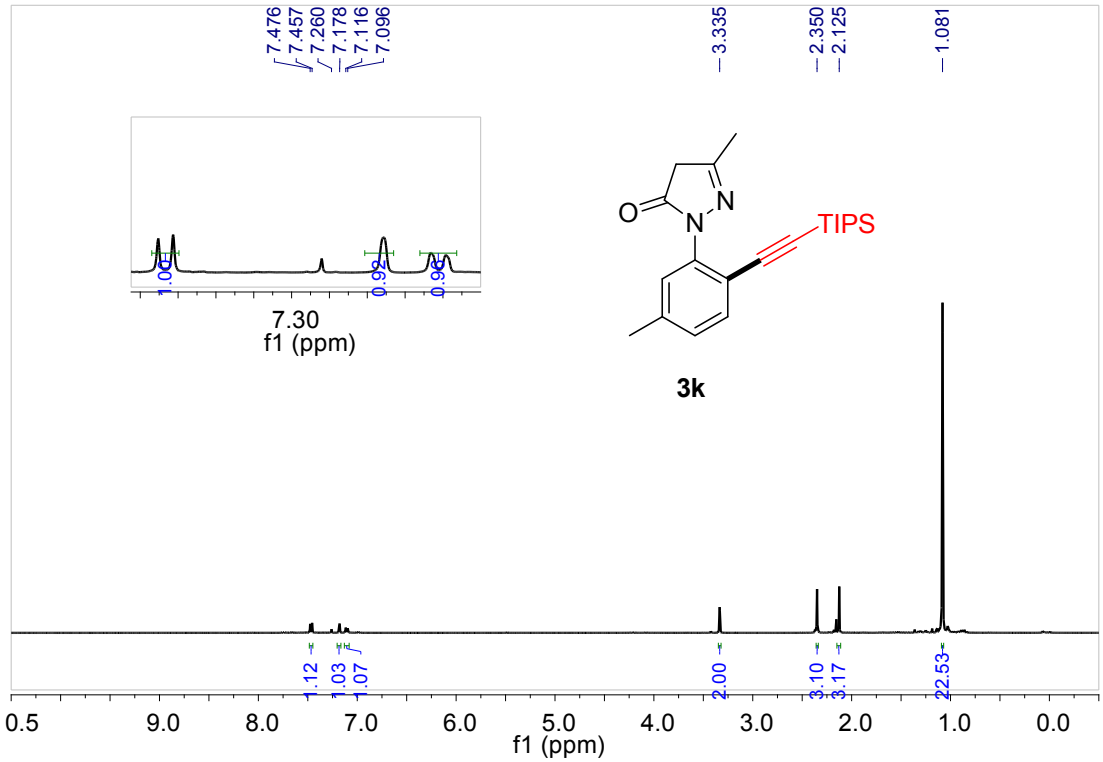

170.721
156.006
140.840
131.210
130.159
126.788
125.592
124.713
121.592
101.708
98.715
41.560
18.547
17.075
11.199
O
N
N
TIPS
CF3
3i
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

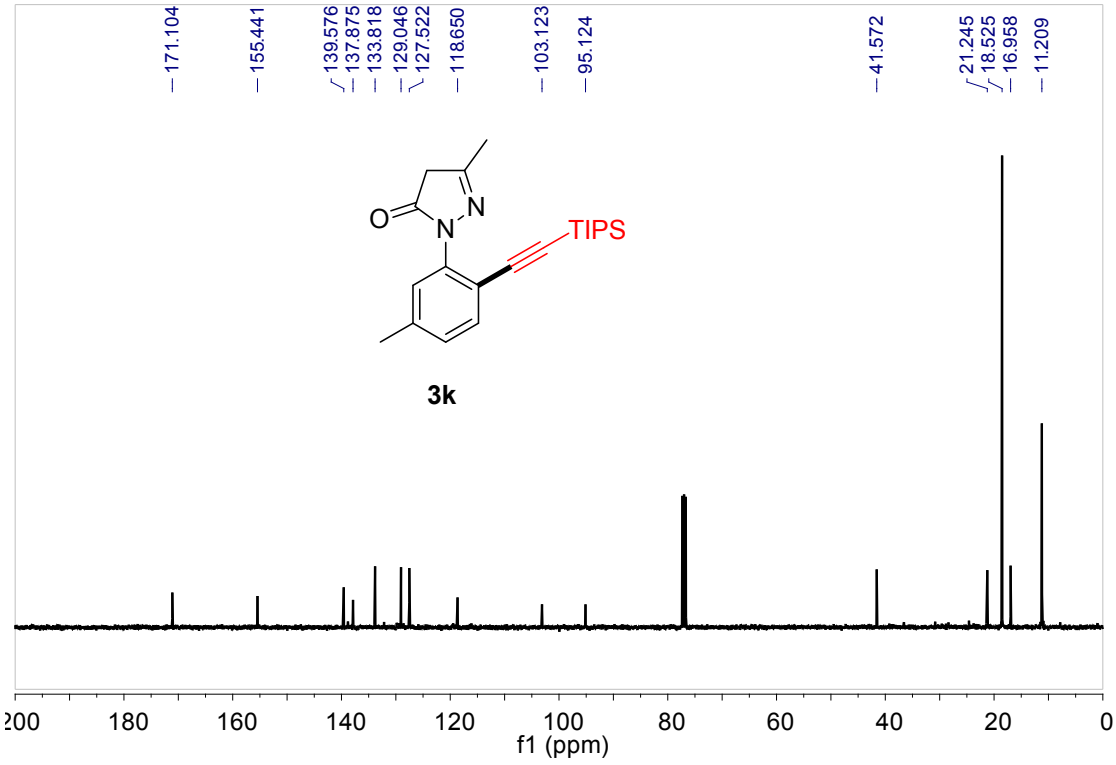

-62.823
TIPS
CF3
3i
0
-20
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)

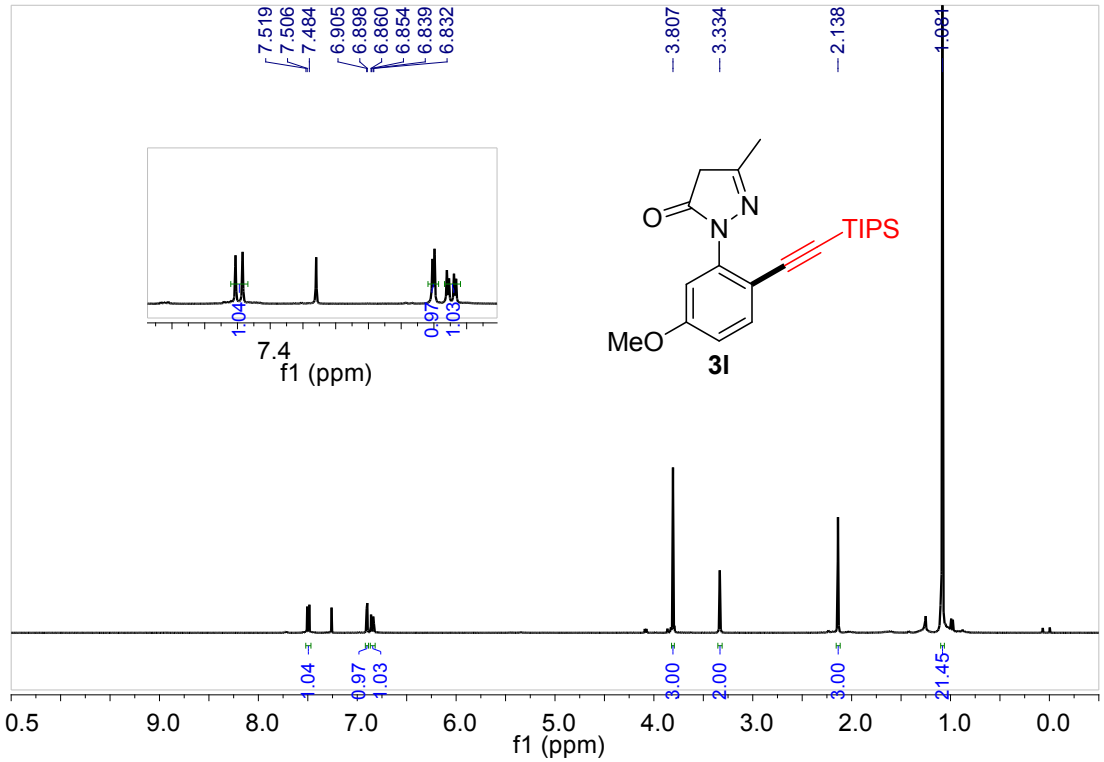

7.380
7.360
7.333
7.313
7.299
7.280
7.171
7.150
7.128
3.365
3.313
2.139
1.000
0.99
1.09
1.08
7.30
7.15
f1 (ppm)
TIPS
F
3j
0.99
1.09
1.08
2.00
3.17
22.58
0.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

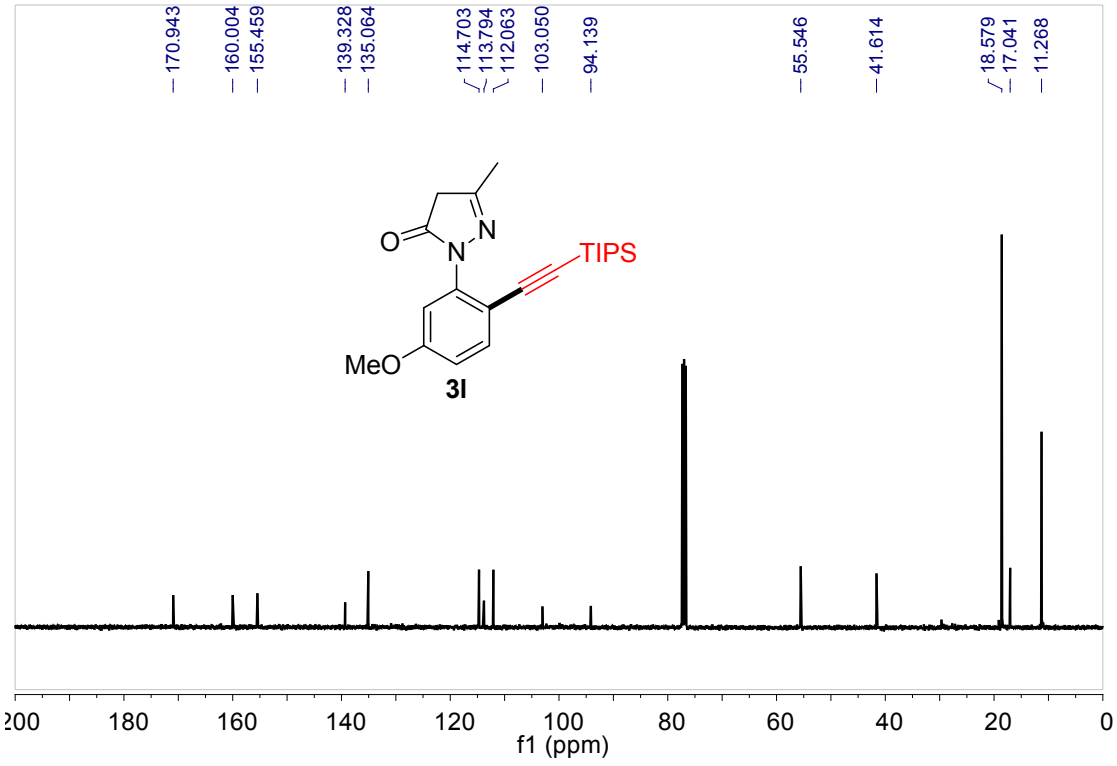

171.184
159.630
157.116
156.178
129.225
126.236
126.097
125.021
125.006
116.792
116.590
101.612
101.571
97.596
41.031
18.514
17.109
11.160
O
N
N
F
TIPS
3j
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

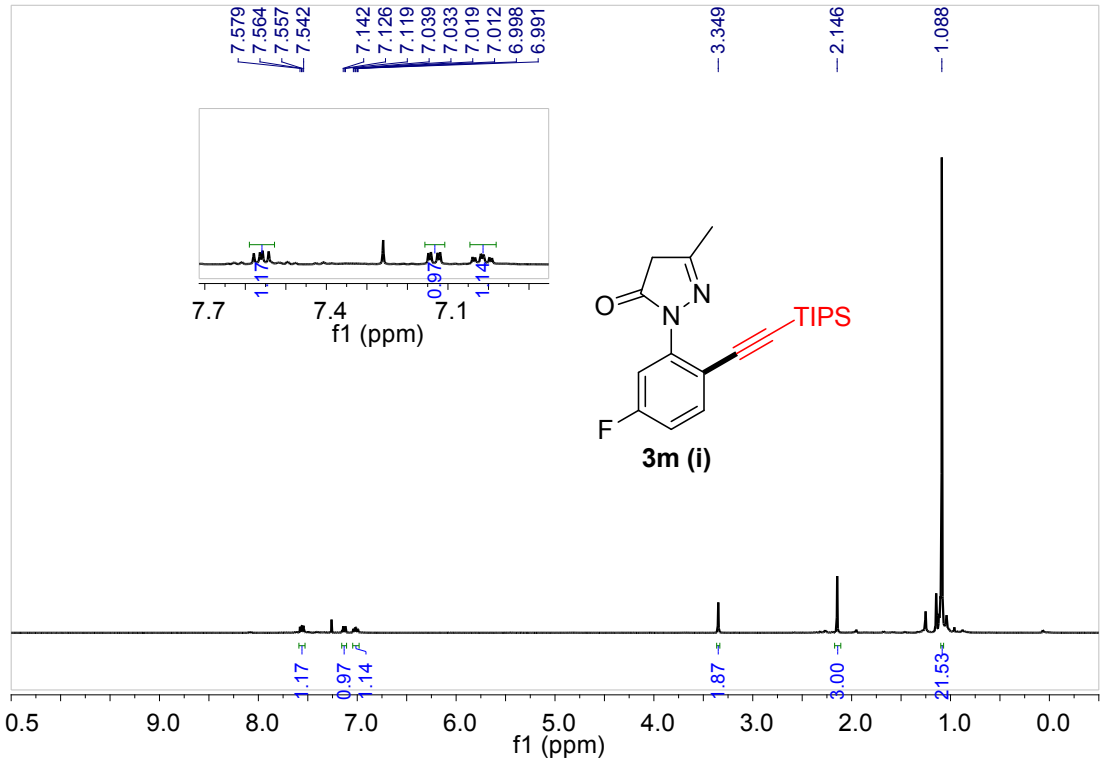

-118.809
O
N
N
F
TIPS
3j
0
-20
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)

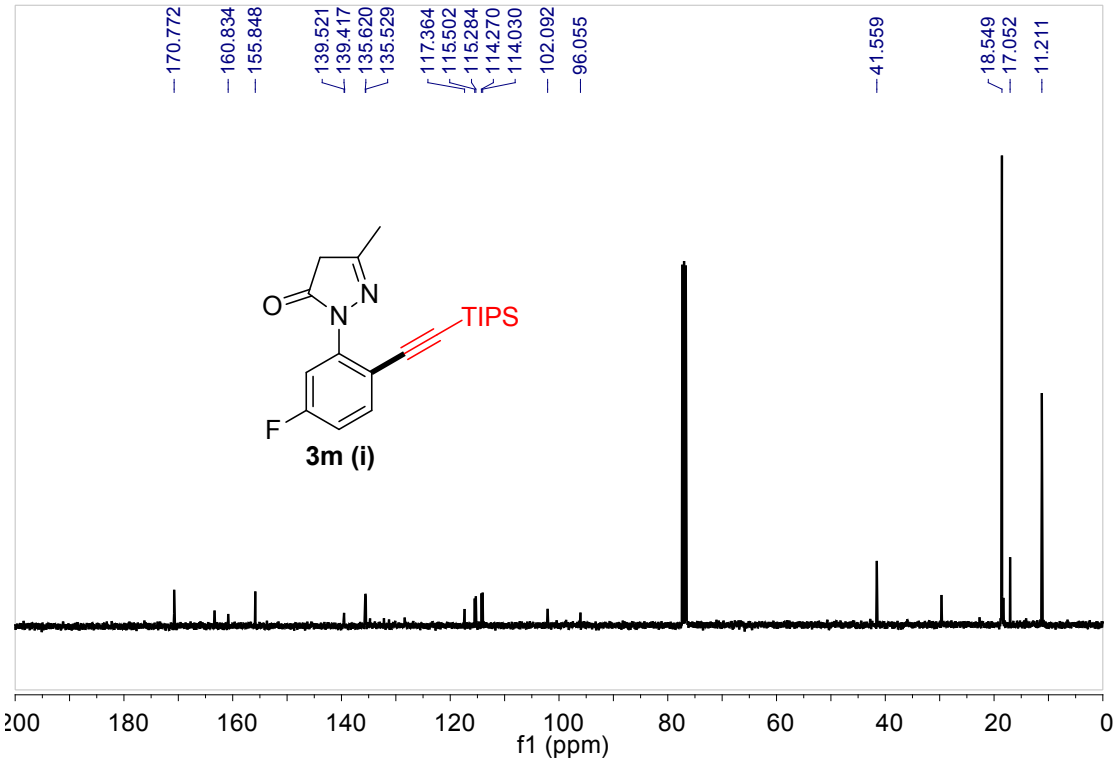

7.476
7.457
7.260
7.178
7.116
7.096
3.335
2.350
2.125
1.081
1.00
0.92
0.96
7.30
f1 (ppm)
O
N
N
TIPS
3k
1.12
1.03
1.07
2.00
3.10
3.17
22.53
0.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

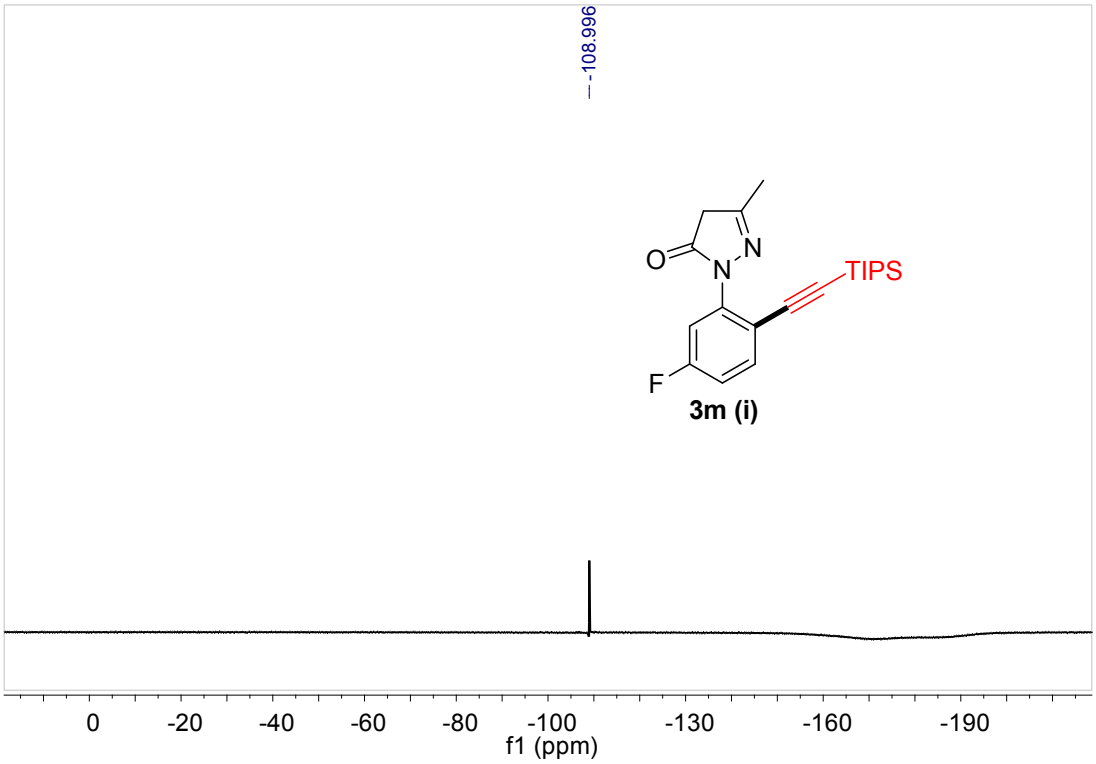

171.104
155.441
139.576
137.875
133.818
129.046
127.522
118.650
103.123
95.124
41.572
21.245
18.525
16.958
11.209
O
N
N
TIPS
3k
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

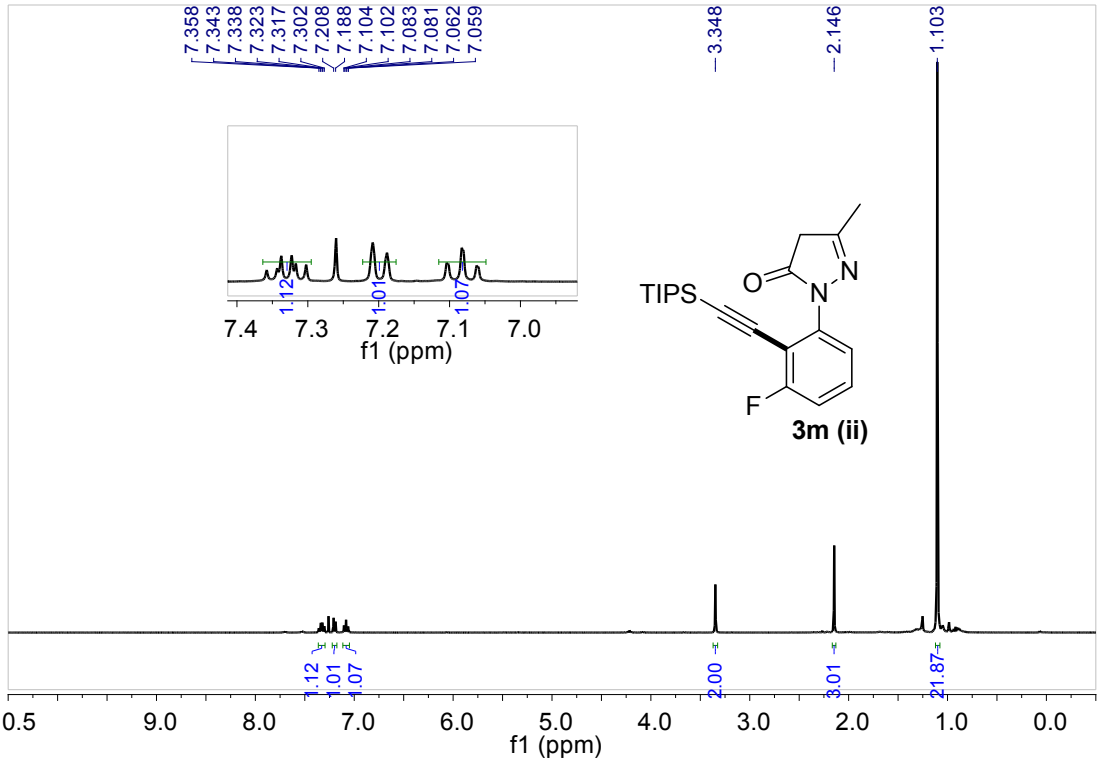

7.519
7.506
7.484
6.905
6.898
6.860
6.854
6.839
6.832
3.807
3.334
2.138
1.001
1.04
0.97
1.03
3.00
2.00
3.00
21.45
7.4
f1 (ppm)
O
N
N
TIPS
MeO
3l
0.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

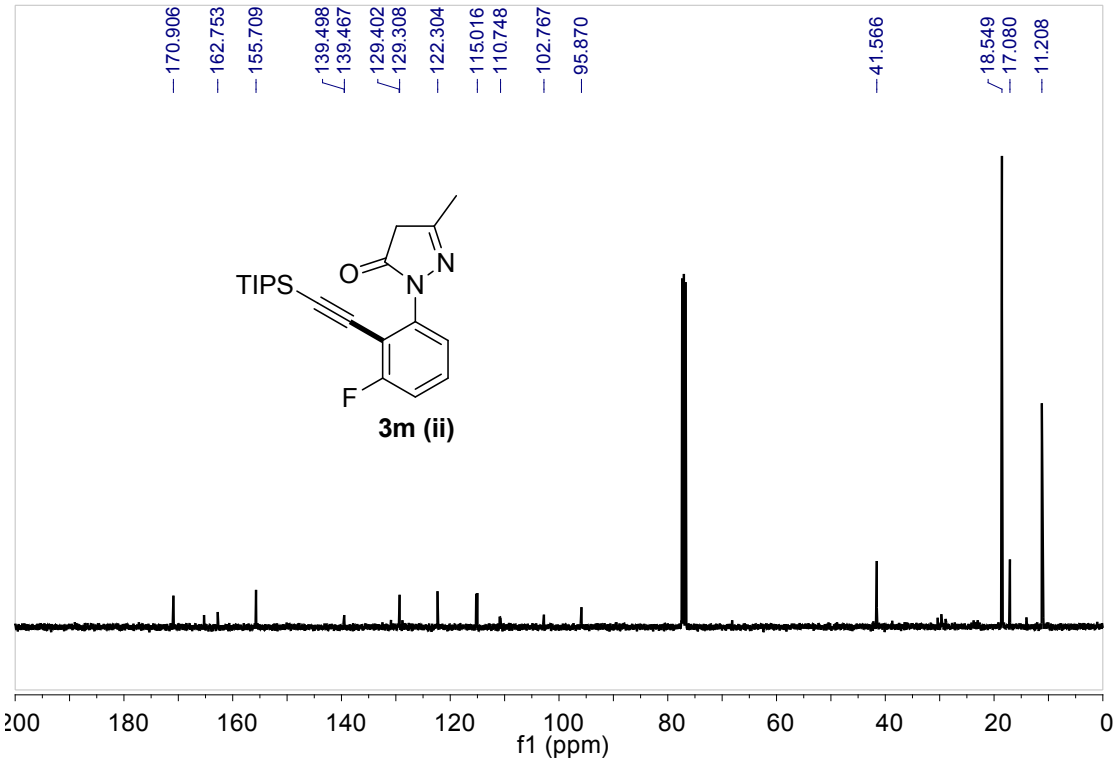

170.943
160.004
155.459
139.328
135.064
114.703
113.794
112.063
103.050
94.139
55.546
41.614
18.579
17.041
11.268
O
N
N
TIPS
MeO
3l
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

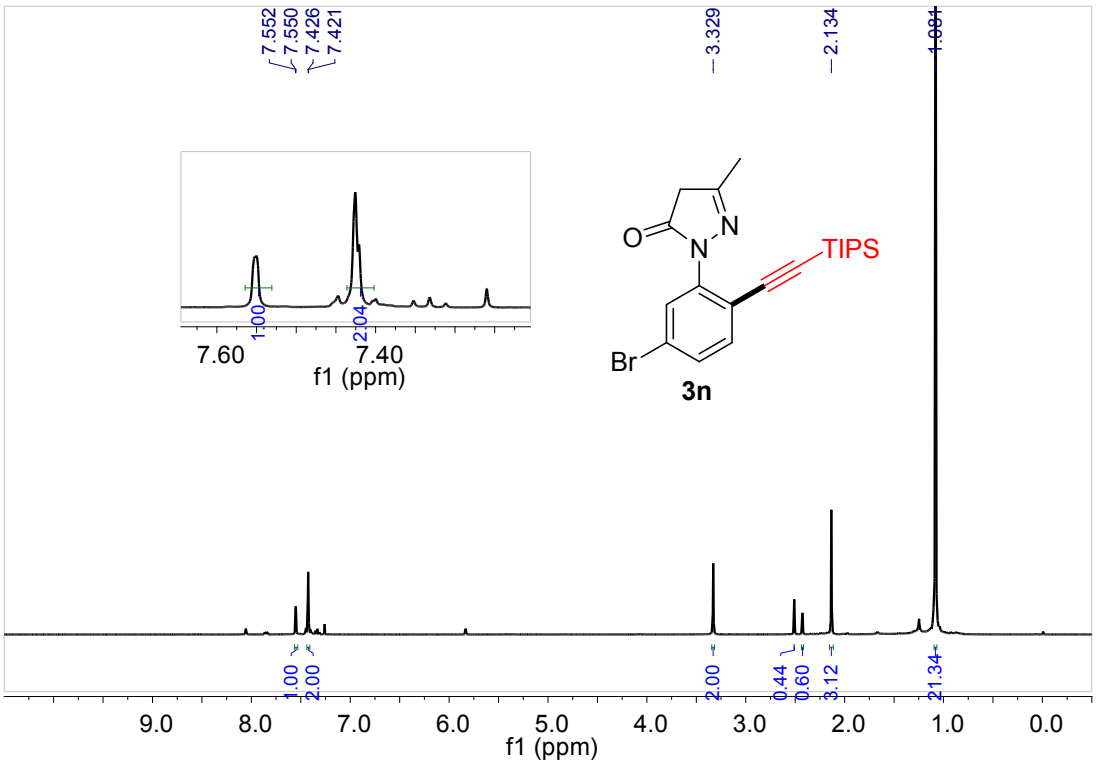

7.579
7.564
7.557
7.542
7.142
7.126
7.119
7.039
7.033
7.019
7.012
6.998
6.991
3.349
2.146
1.088
1.17
0.97
1.14
1.87
3.00
21.53
f1 (ppm)
O
N
N
TIPS
F
3m (i)

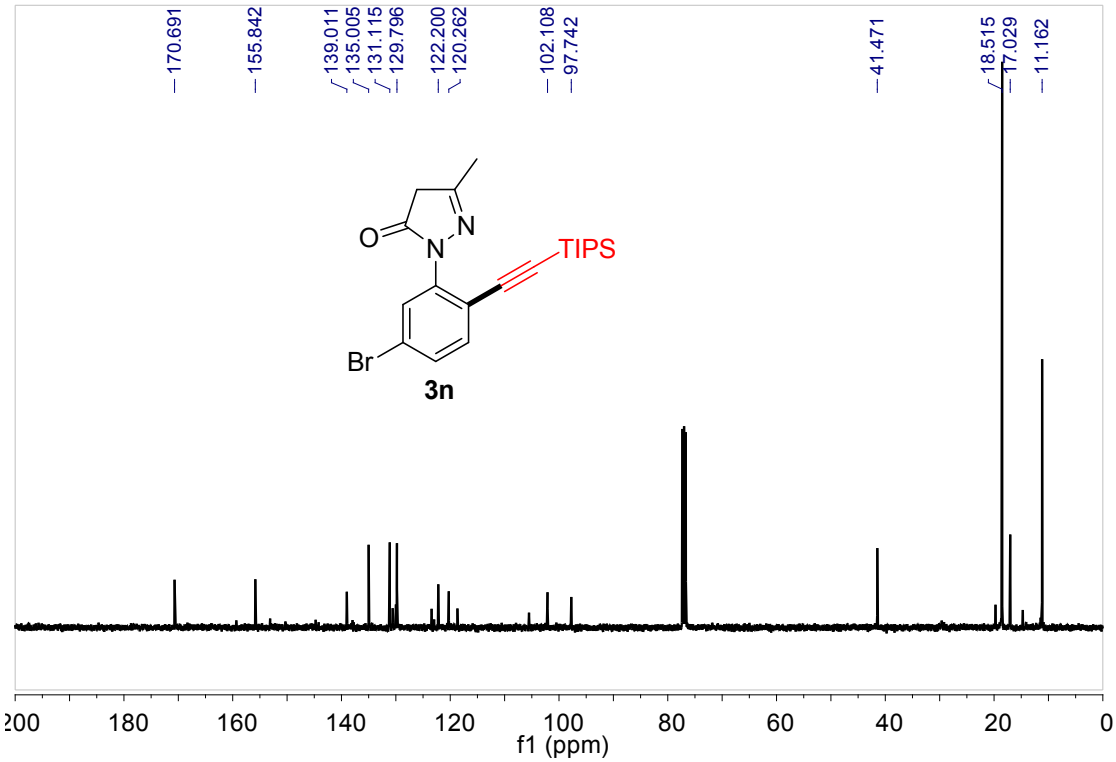

170.772
160.834
155.848
139.521
139.417
135.620
135.529
117.364
115.502
115.284
114.270
114.030
102.092
96.055
41.559
18.549
17.052
11.211
f1 (ppm)
O
N
N
TIPS
F
3m (i)

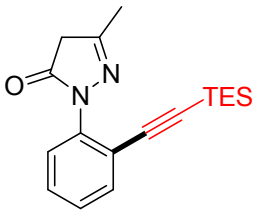

-108.996
O
N
N
TIPS
F
3m (i)
0
-20
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)


7.358
7.343
7.338
7.323
7.317
7.302
7.208
7.188
7.104
7.102
7.083
7.081
7.062
7.059
3.348
2.146
1.103
1.12
1.01
1.07
7.4
7.3
7.2
7.1
7.0
f1 (ppm)
TIPS
O
N
N
F
3m (ii)
1.12
1.01
1.07
2.00
3.01
21.87
0.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

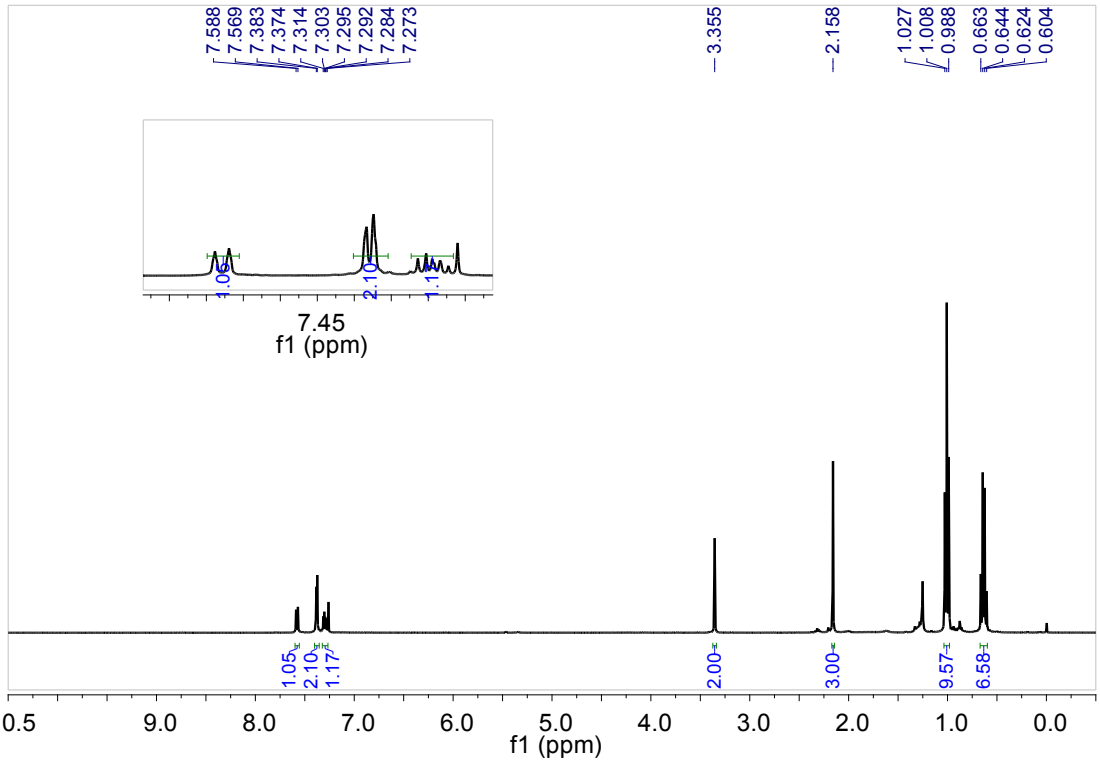

170.906
162.753
155.709
139.498
139.467
129.402
129.308
122.304
115.016
110.748
102.767
95.870
41.566
18.549
17.080
11.208
TIPS
O
N
N
F
3m (ii)
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

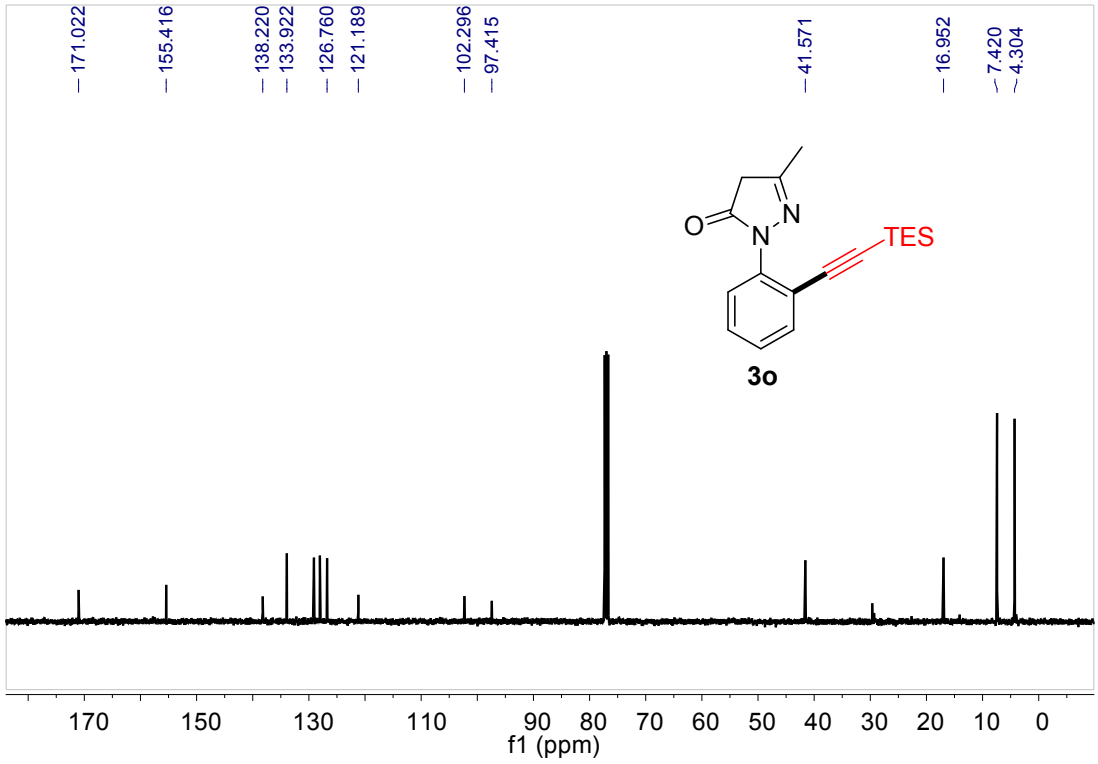

7.552
7.550
7.426
7.421
3.329
2.134
1.081
1.00
2.04
7.60
7.40
f1 (ppm)
O
N
N
TIPS
Br
3n
1.00
2.00
2.00
0.44
0.60
3.12
21.34
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

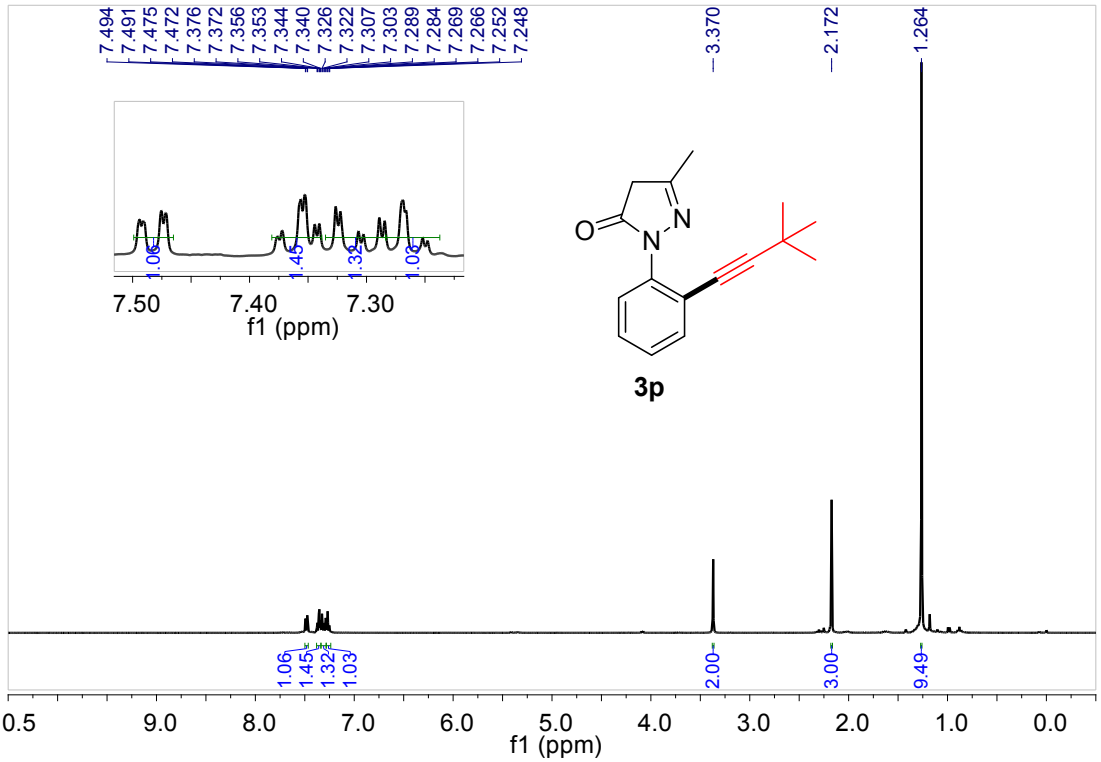

170.691
155.842
139.011
135.005
131.115
129.796
122.200
120.262
102.108
97.742
41.471
18.515
17.029
11.162
O
N
N
TIPS
Br
3n
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

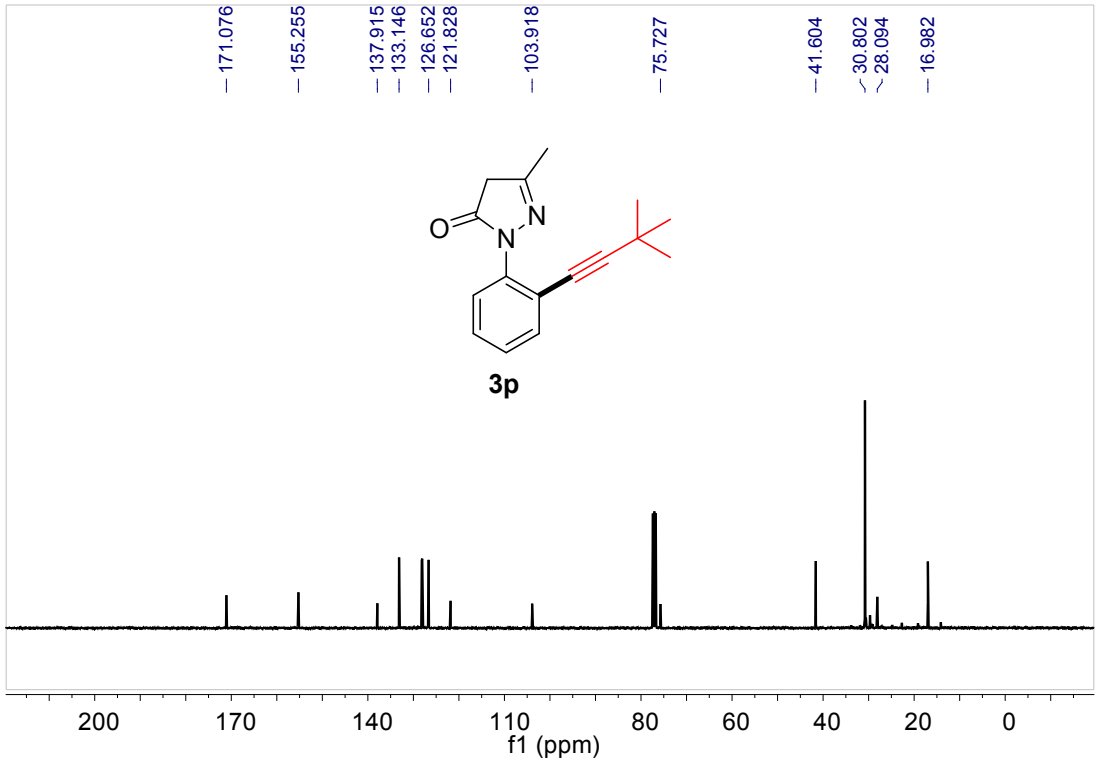

O
N
N
TES

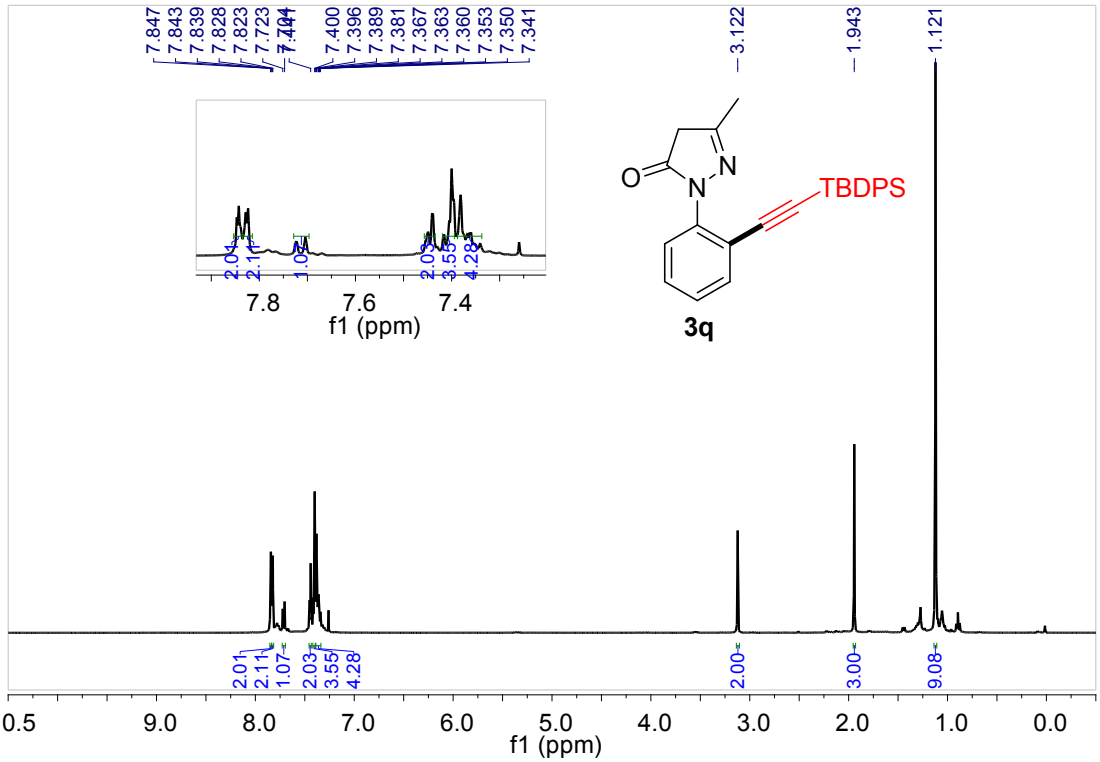
3o

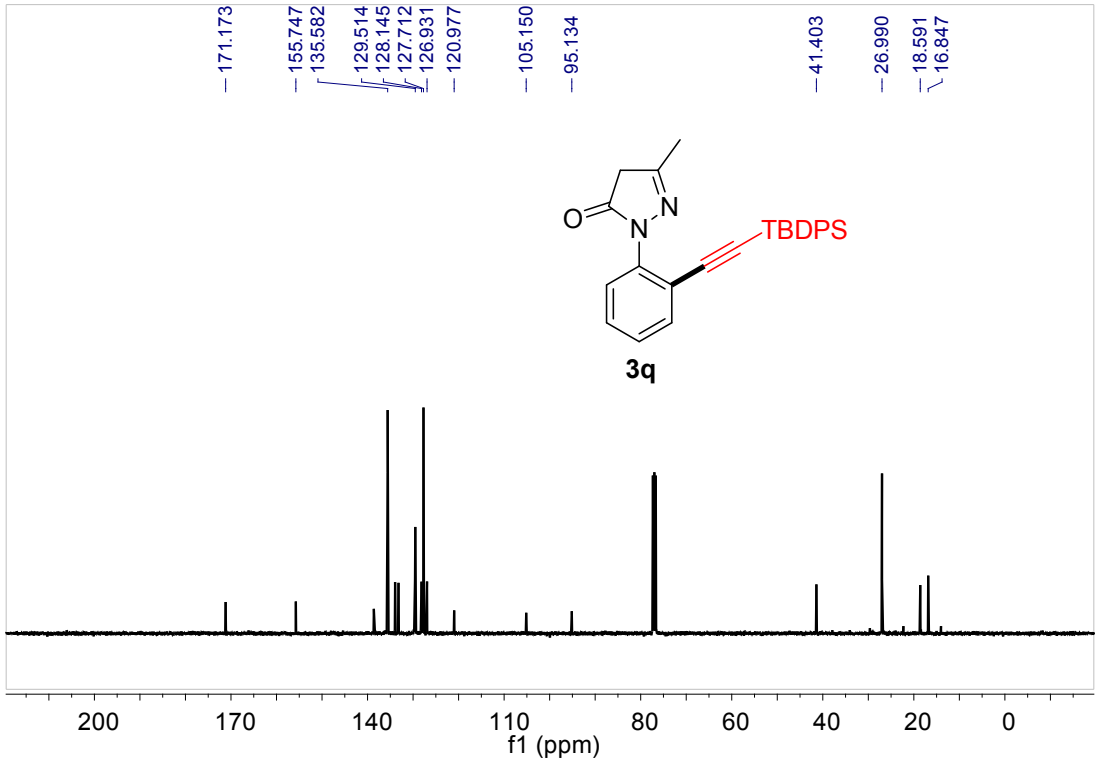

7.588
7.569
7.383
7.374
7.314
7.303
7.295
7.292
7.284
7.273
3.355
2.158
1.027
1.008
0.988
0.663
0.644
0.624
0.604
1.05
2.10
1.17
7.45
f1 (ppm)
1.05
2.10
1.17
2.00
3.00
9.57
6.58
0.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


171.022
155.416
138.220
133.922
126.760
121.189
102.296
97.415
41.571
16.952
7.420
4.304
O
N
N
TES
3o
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.494
7.491
7.475
7.472
7.376
7.372
7.356
7.353
7.344
7.340
7.326
7.322
7.307
7.303
7.289
7.284
7.269
7.266
7.252
7.248
3.370
2.172
1.264
1.06
1.45
1.32
1.03
7.50
7.40
7.30
f1 (ppm)
O
N
N
3p
1.06
1.45
1.32
1.03
2.00
3.00
9.49
0.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


171.076
155.255
137.915
133.146
126.652
121.828
103.918
75.727
41.604
30.802
28.094
16.982
O
N
N
3p
200
170
140
110
80
60
40
20
0
f1 (ppm)


7.847
7.843
7.839
7.828
7.823
7.723
7.400
7.396
7.389
7.381
7.367
7.363
7.360
7.353
7.350
7.341
3.122
1.943
1.121
2.04
2.11
1.07
2.03
3.55
4.28
7.8
7.6
7.4
f1 (ppm)
O
N
N
TBDPS
3q
2.01
2.11
1.07
2.03
3.55
4.28
2.00
3.00
9.08
0.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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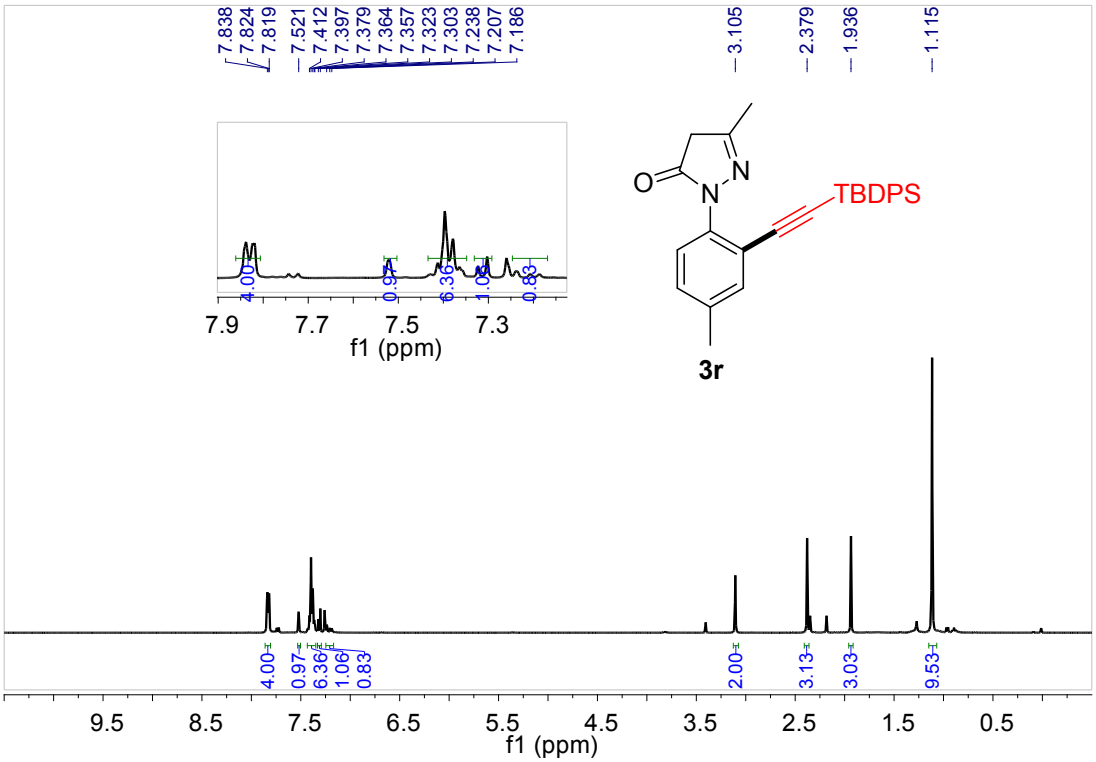
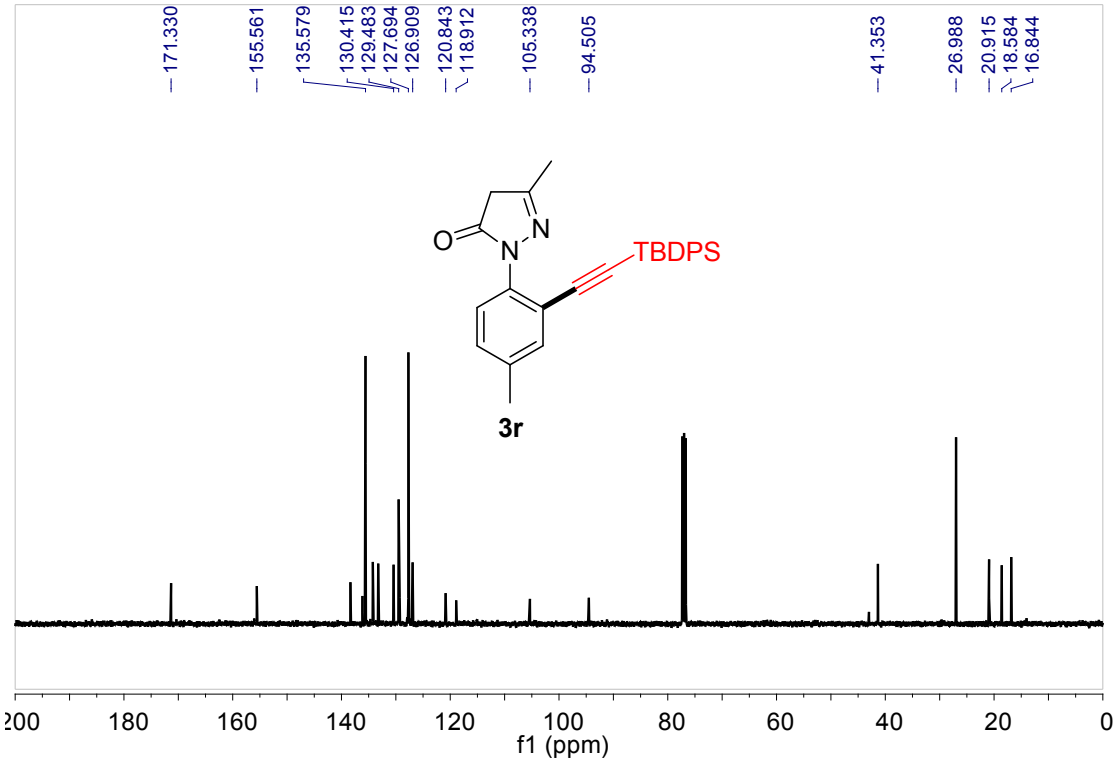
155.747
135.582
129.514
128.145
127.712
126.931
120.977
105.150
95.134
41.403
26.990
18.591
16.847
O
N
N
TBDPS
3q
200
170
140
110
80
60
40
20
0
f1 (ppm)


7.838
7.824
7.819
7.521
7.412
7.397
7.379
7.364
7.357
7.323
7.303
7.238
7.207
7.186
3.105
2.379
1.936
1.115
4.00
0.97
6.36
1.06
0.83
7.9
7.7
7.5
7.3
f1 (ppm)
O
N
N
TBDPS
3r
4.00
0.97
6.36
1.06
0.83
2.00
3.13
3.03
9.53
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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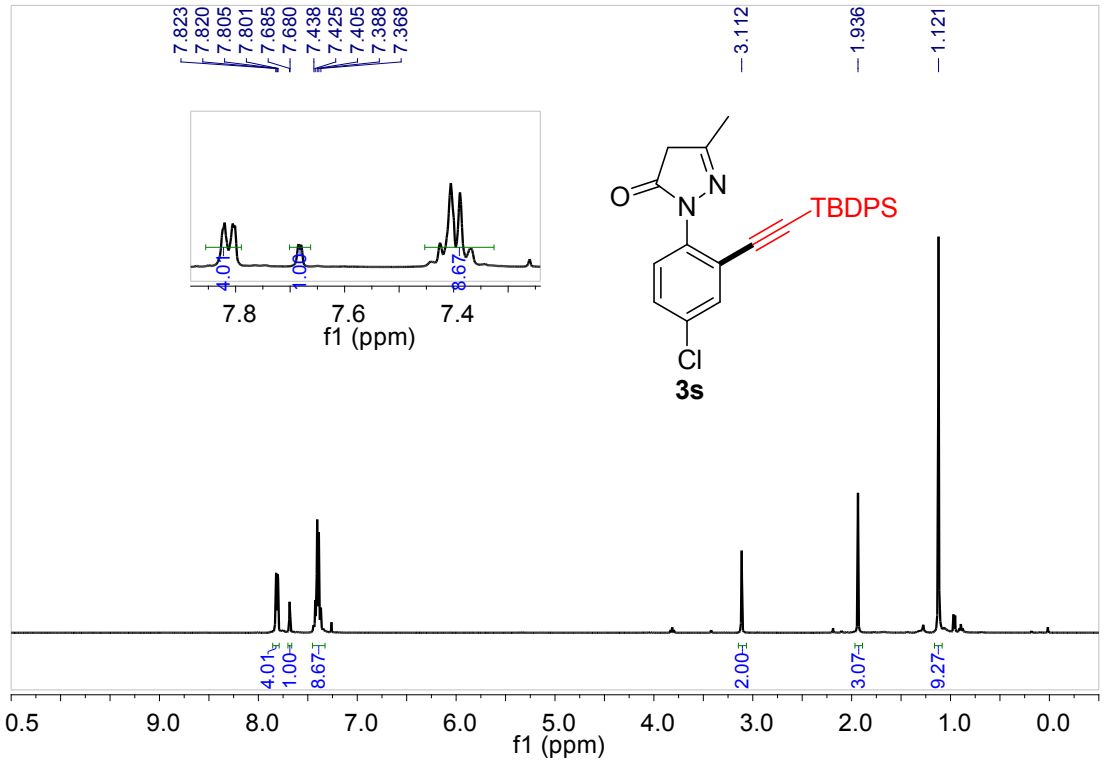
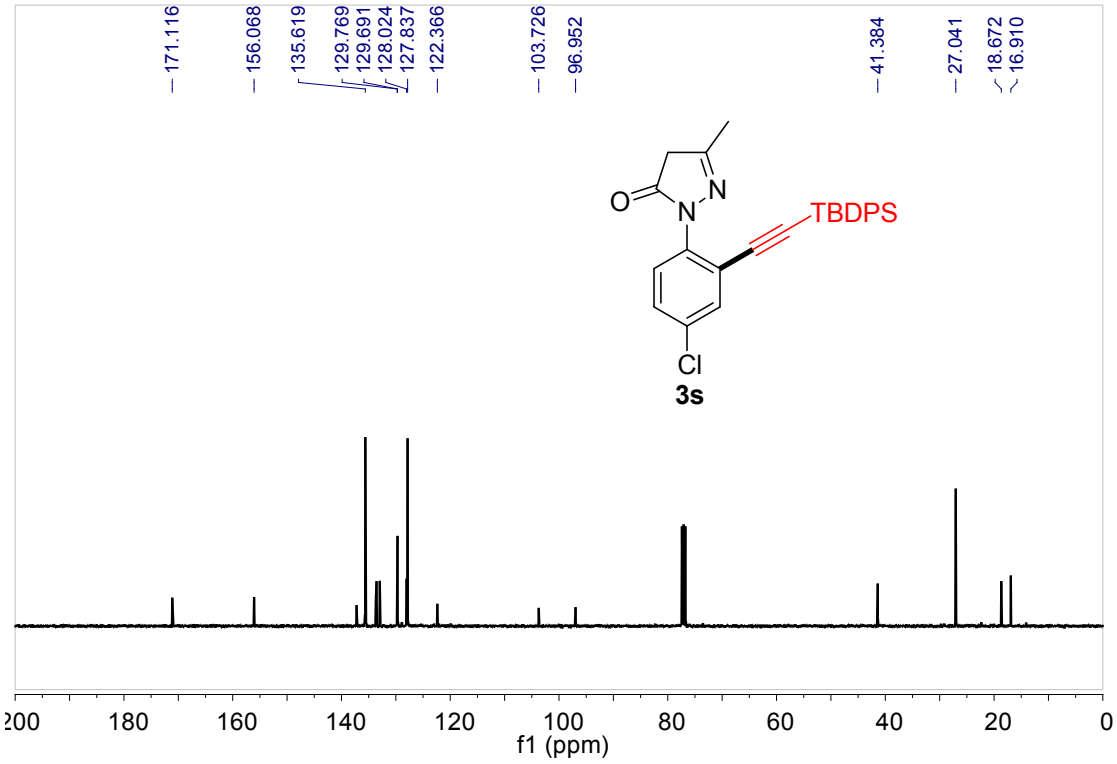
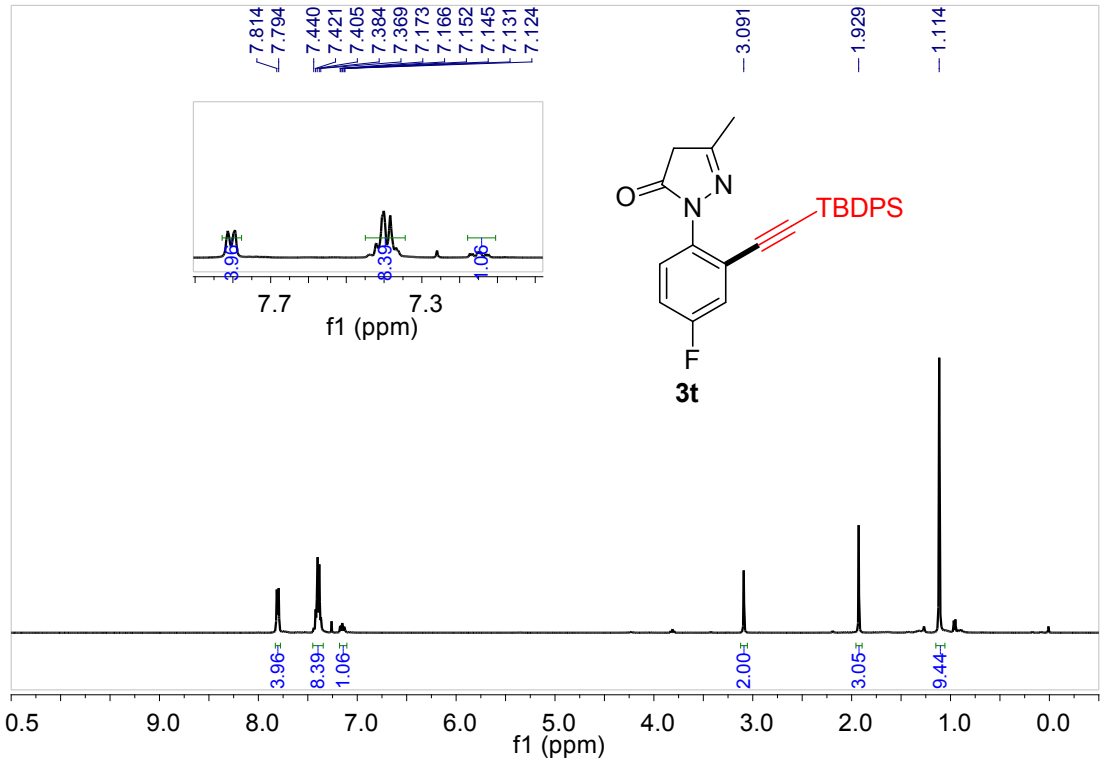
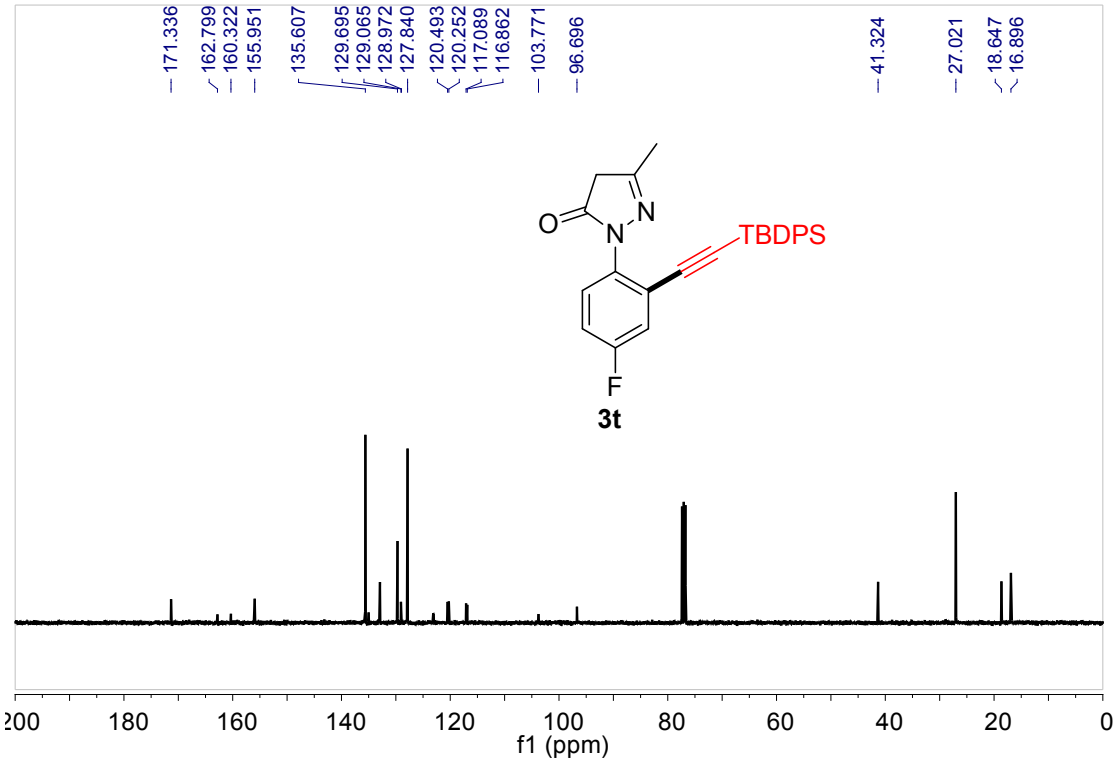
155.561
135.579
130.415
129.483
127.694
126.909
120.843
118.912
105.338
94.505
41.353
26.988
20.915
18.584
16.844
O
N
N
TBDPS
3r
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.823
7.820
7.805
7.801
7.685
7.680
7.438
7.425
7.405
7.388
7.368
3.112
1.936
1.121
4.01
1.00
8.67
7.8
7.6
7.4
f1 (ppm)
O
N
N
TBDPS
Cl
3s
4.01
1.00
8.67
2.00
3.07
9.27
0.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


171.116
156.068
135.619
129.769
129.691
128.024
127.837
122.366
103.726
96.952
41.384
27.041
18.672
16.910
O
N
N
TBDPS
Cl
3s
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.814
7.794
7.440
7.421
7.405
7.384
7.369
7.173
7.166
7.152
7.145
7.131
7.124
3.091
1.929
1.114
3.96
8.39
1.06
7.7
7.3
f1 (ppm)
O
N
N
TBDPS
F
3t
3.96
8.39
1.06
2.00
3.05
9.44
0.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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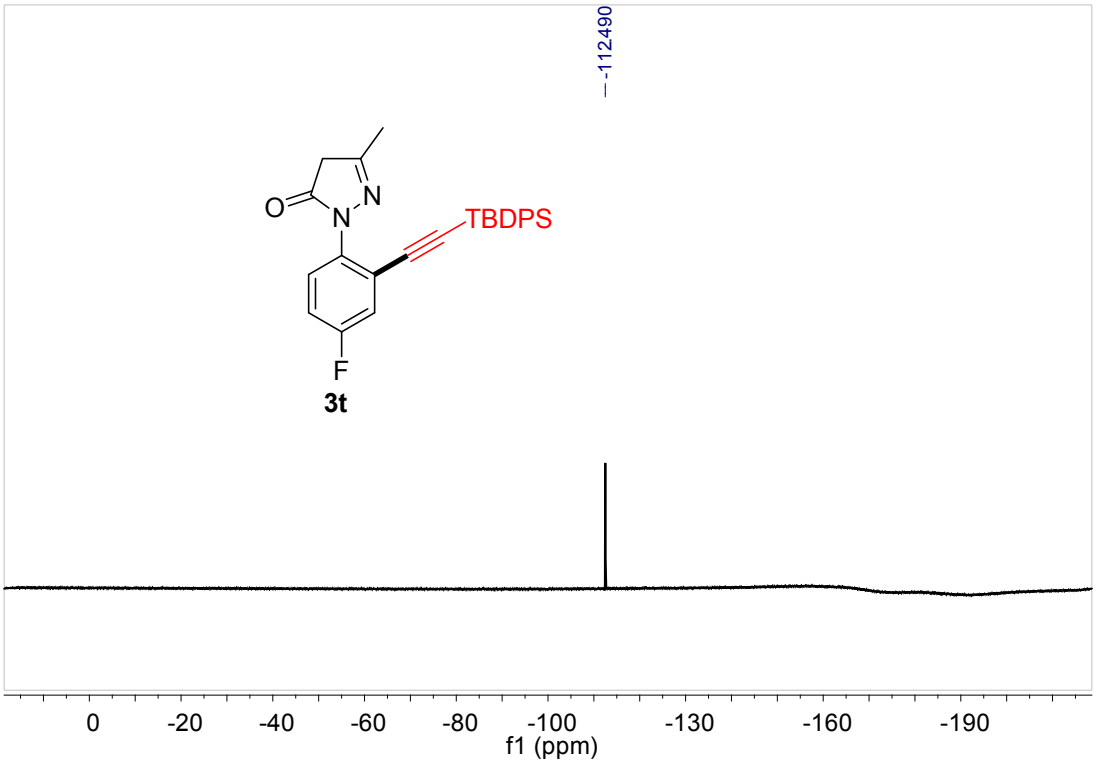
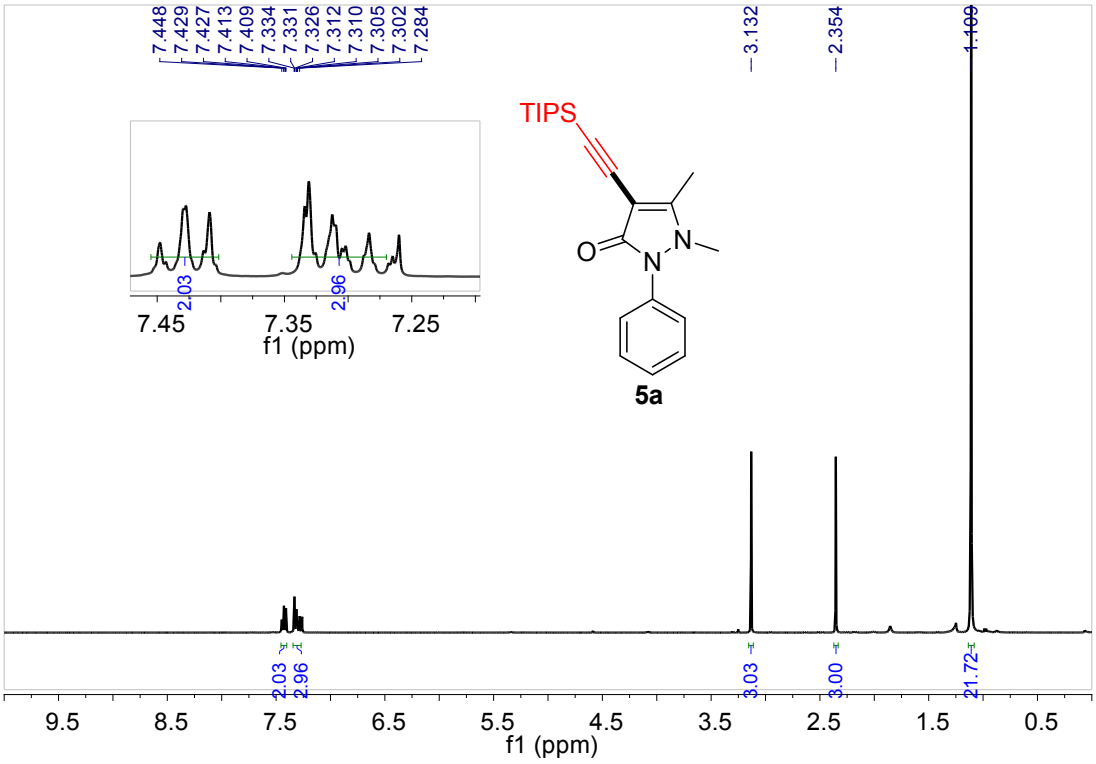
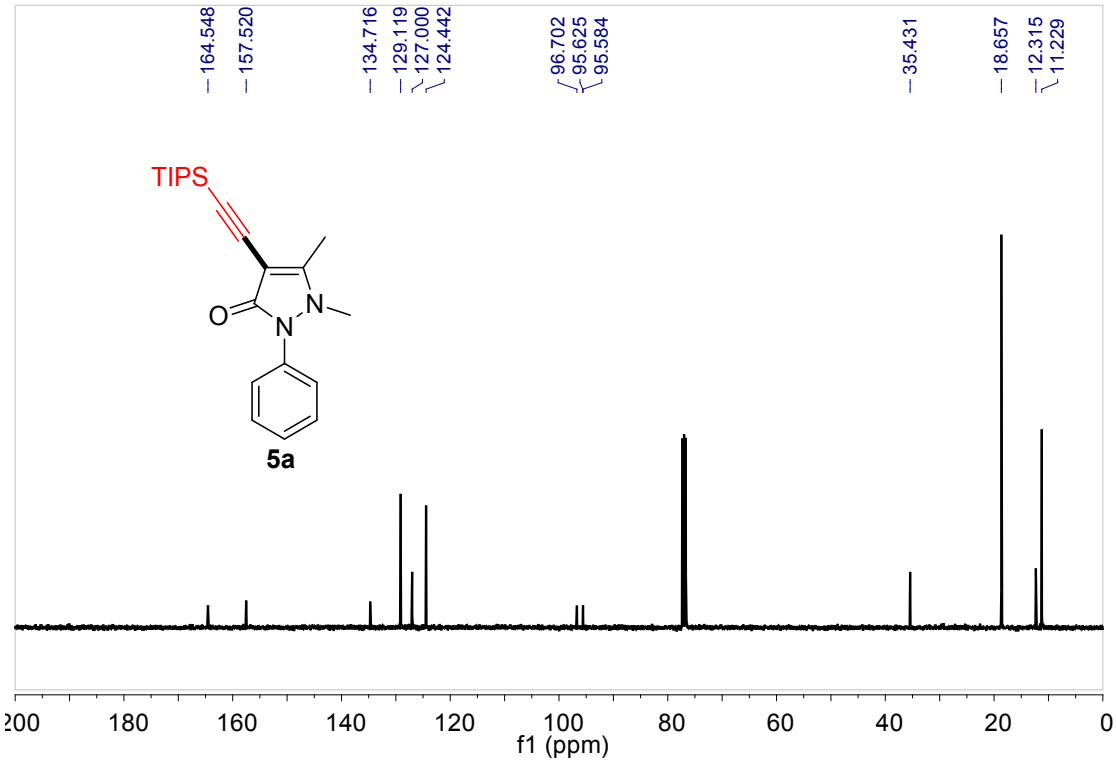
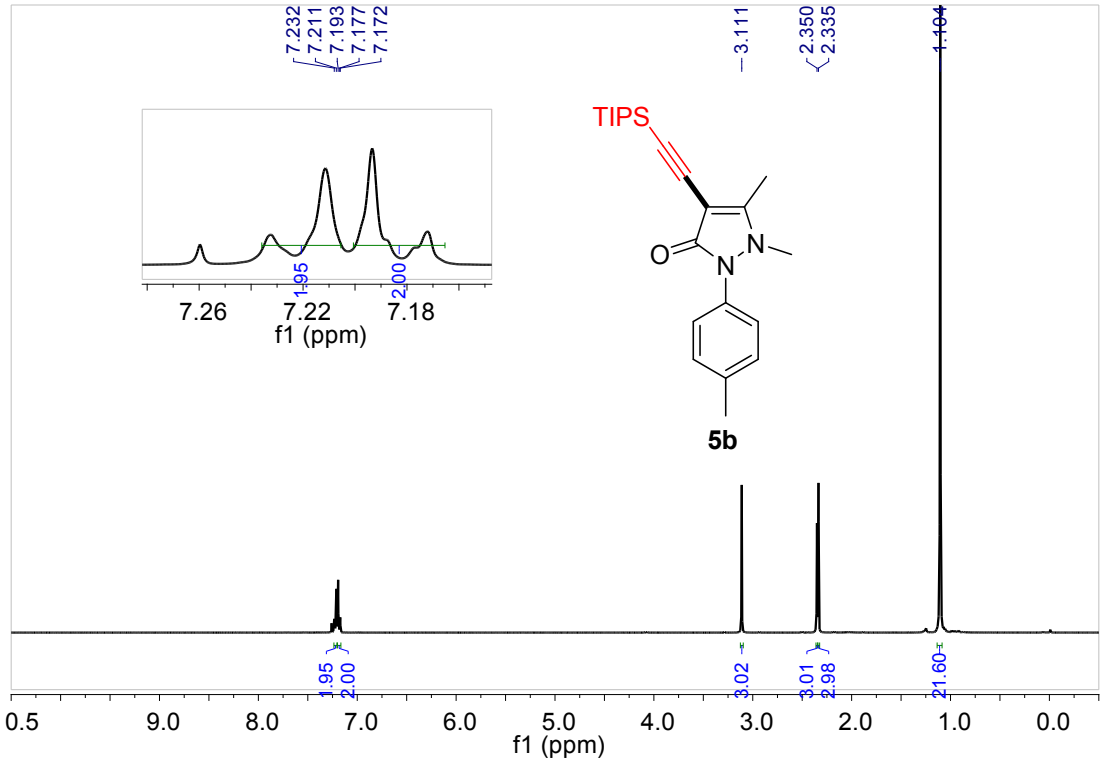
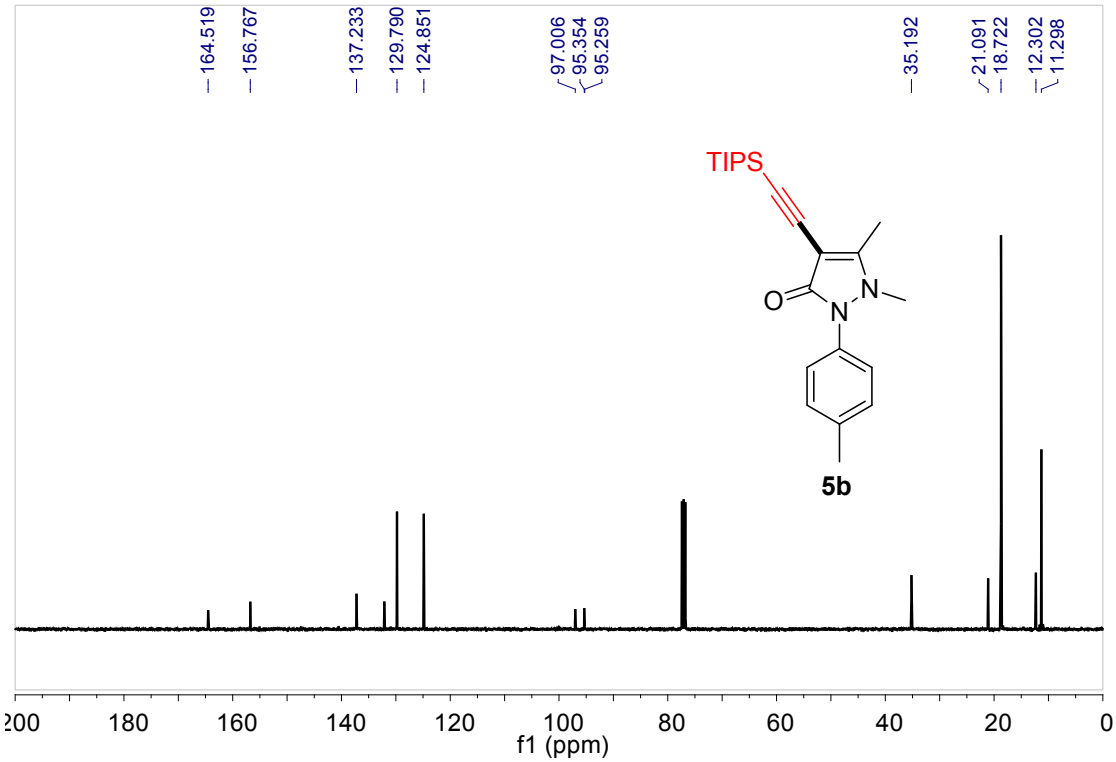
162.799
160.322
155.951
135.607
129.695
129.065
128.972
127.840
120.493
120.252
117.089
116.862
103.771
96.696
41.324
27.021
18.647
16.896
O
N
N
TBDPS
F
3t
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

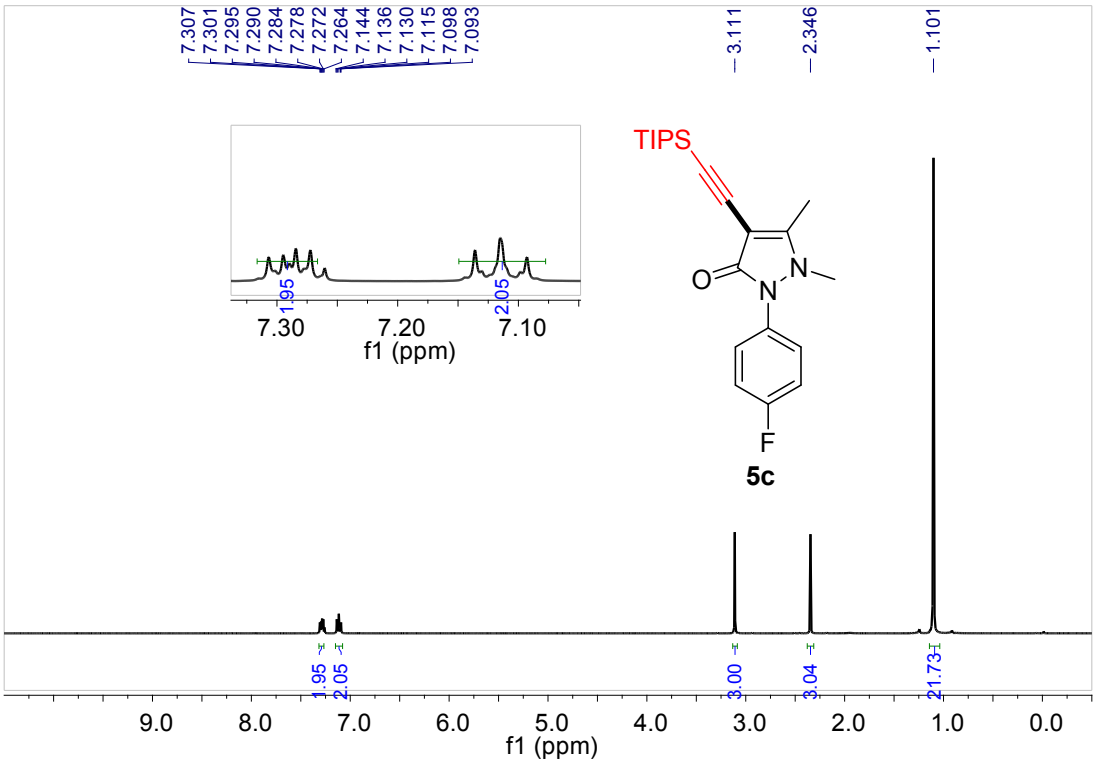

-112.490
TBDPS
F
3t
0
-20
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)

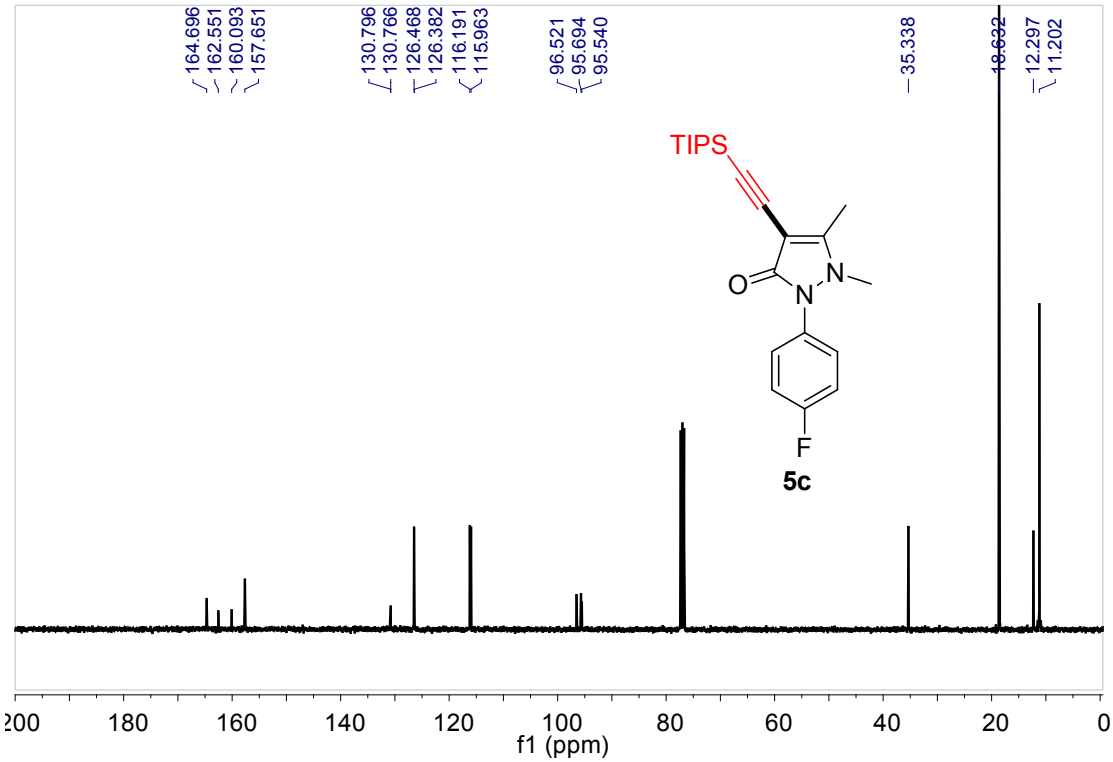

7.448
7.429
7.427
7.413
7.409
7.334
7.331
7.326
7.312
7.310
7.305
7.302
7.284
3.132
2.354
1.199
TIPS
2.03
2.96
7.45
7.35
7.25
f1 (ppm)
5a
2.03
2.96
3.03
3.00
21.72
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

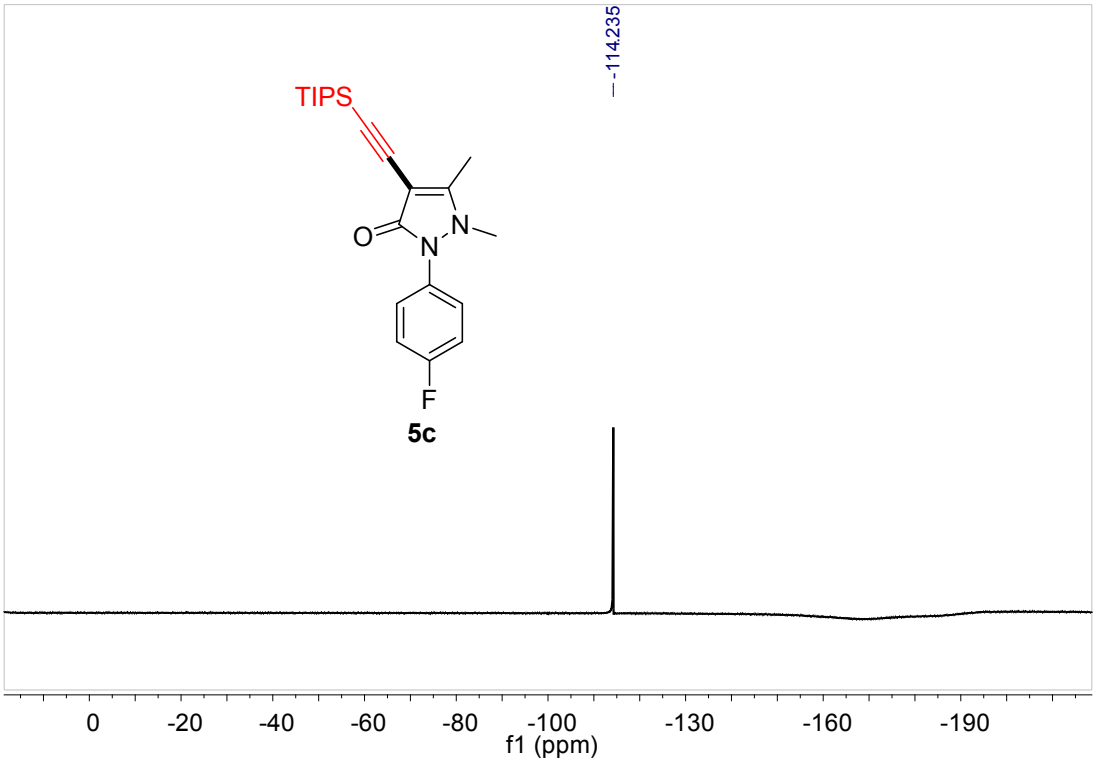

164.548
157.520
134.716
129.119
127.000
124.442
96.702
95.625
95.584
35.431
18.657
12.315
11.229
TIPS
O
N
N
5a
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

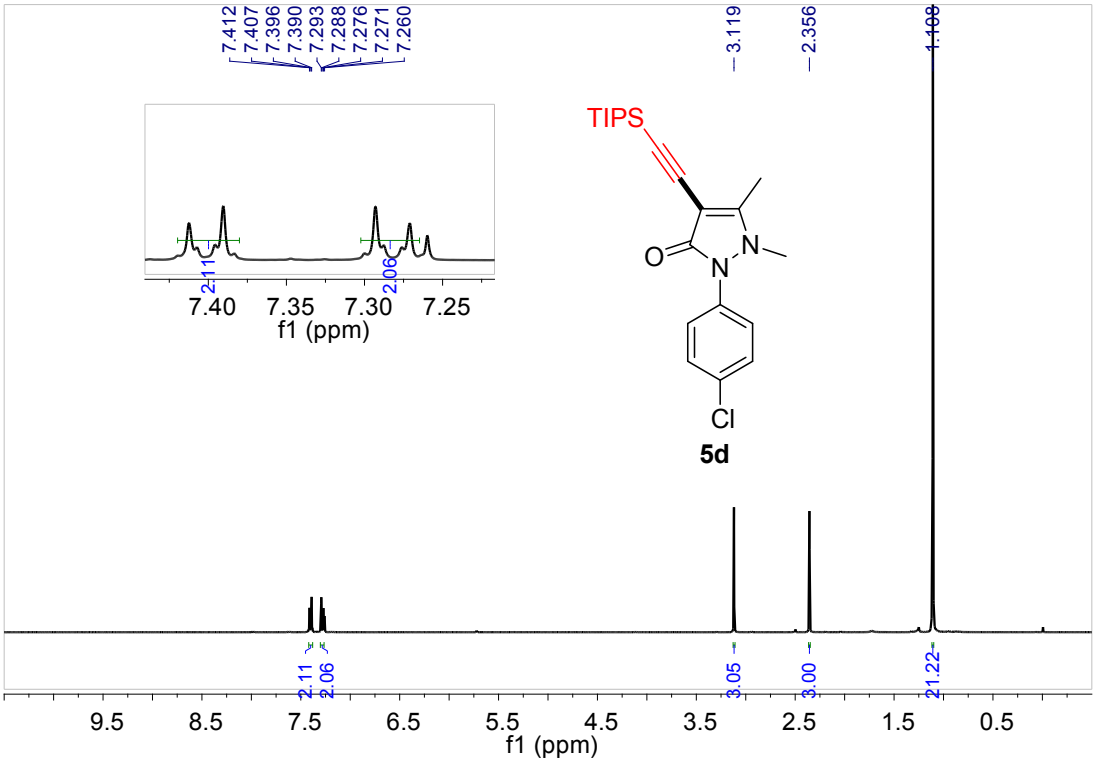

7.232
7.211
7.193
7.177
7.172
3.111
2.350
2.335
1.194
1.95
2.00
7.26
7.22
7.18
f1 (ppm)
TIPS
O
N
N
5b
1.95
2.00
3.02
3.01
2.98
21.60
0.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

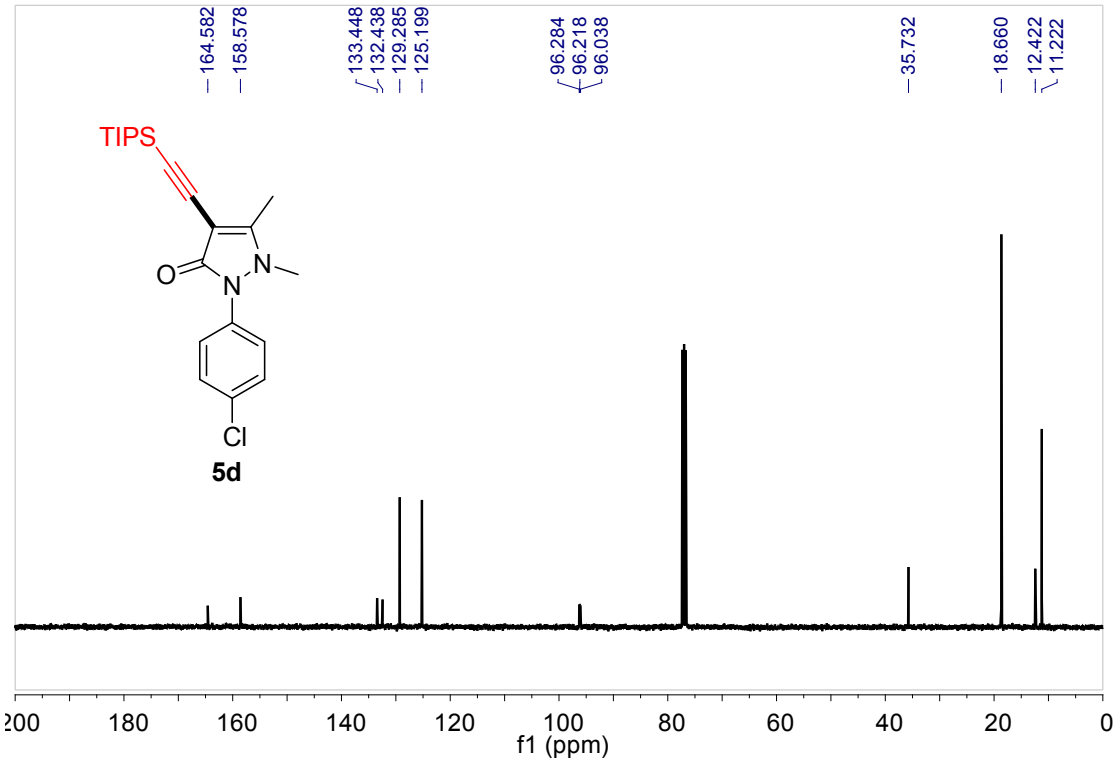

164.519
156.767
137.233
129.790
124.851
97.006
95.354
95.259
35.192
21.091
18.722
12.302
11.298
TIPS
O
N
N
5b
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

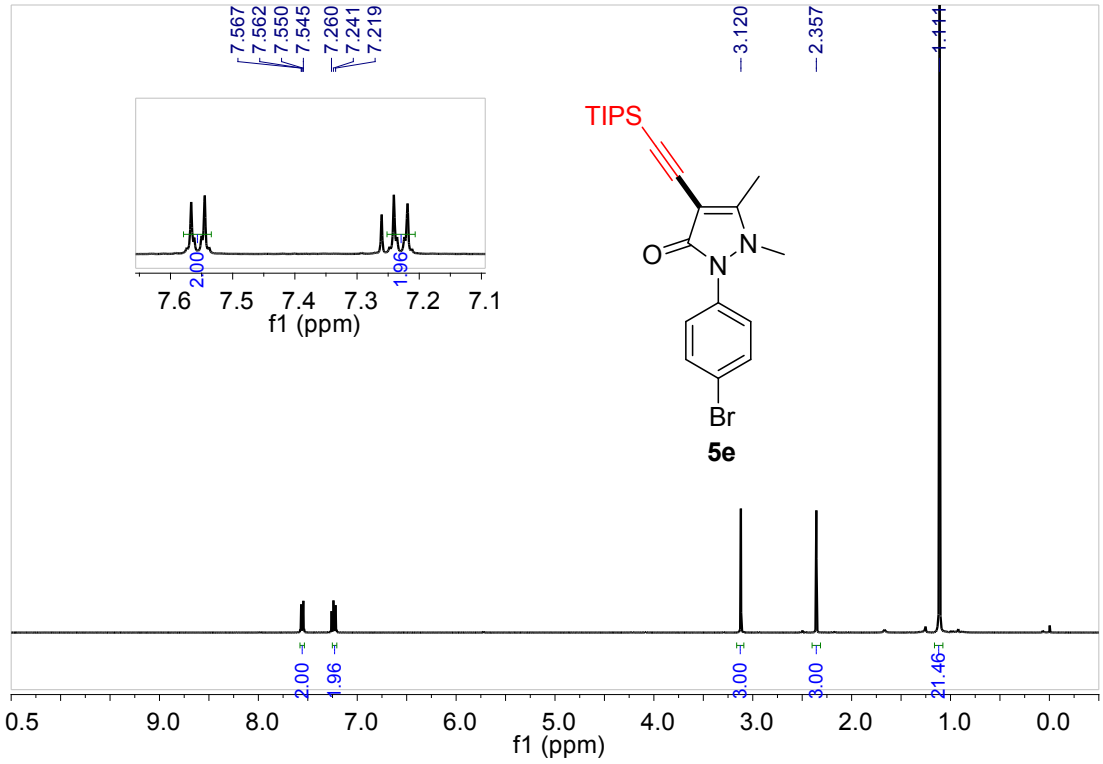

7.307
7.301
7.295
7.290
7.284
7.278
7.272
7.264
7.144
7.136
7.130
7.115
7.098
7.093
3.111
2.346
1.101
1.95
2.05
7.30
7.20
7.10
f1 (ppm)
TIPS
O
N
N
F
5c
1.95
2.05
3.00
3.04
21.73
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

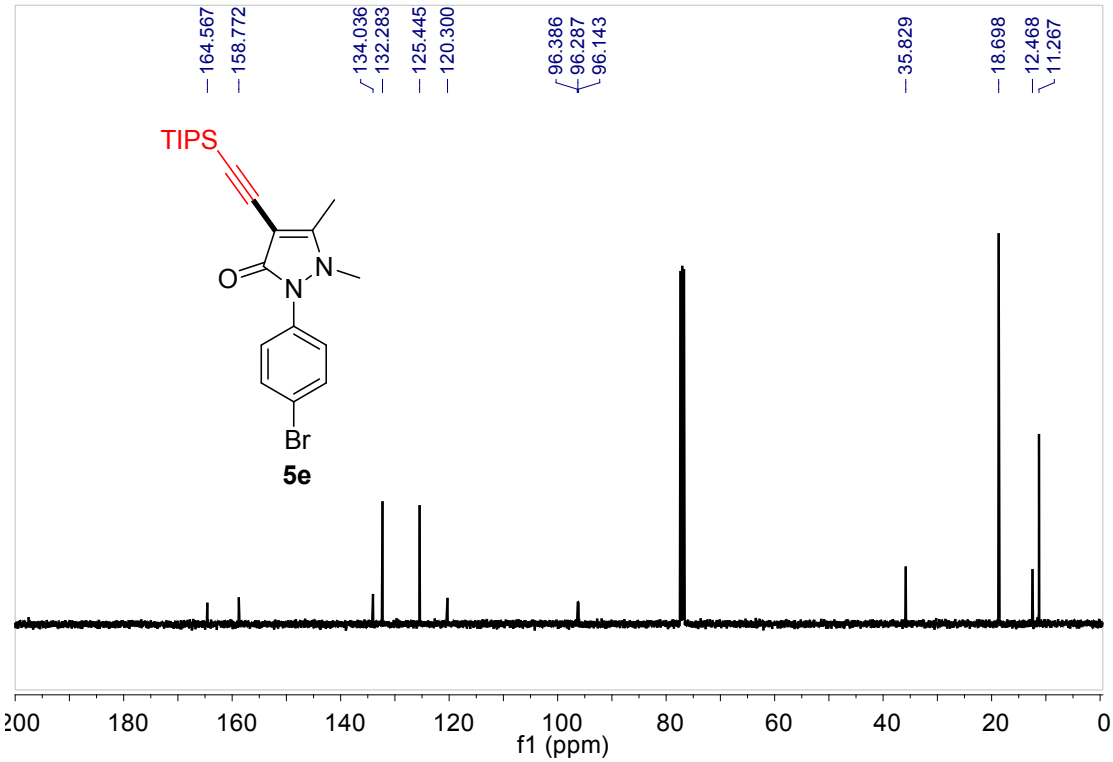

164.696
162.551
160.093
157.651
130.796
130.766
126.468
126.382
116.191
115.963
96.521
95.694
95.540
35.338
18.632
12.297
11.202
TIPS
O
N
N
F
5c
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

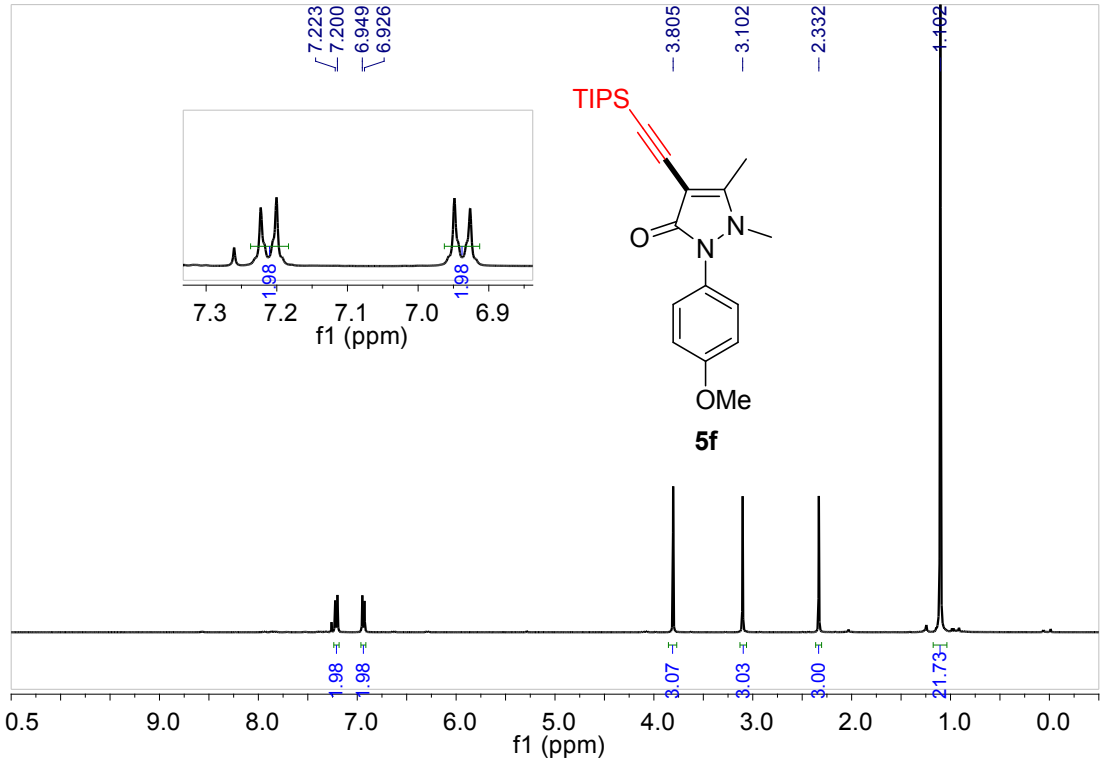

-114.235
TIPS
O
N
N
F
5c
0
-20
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)

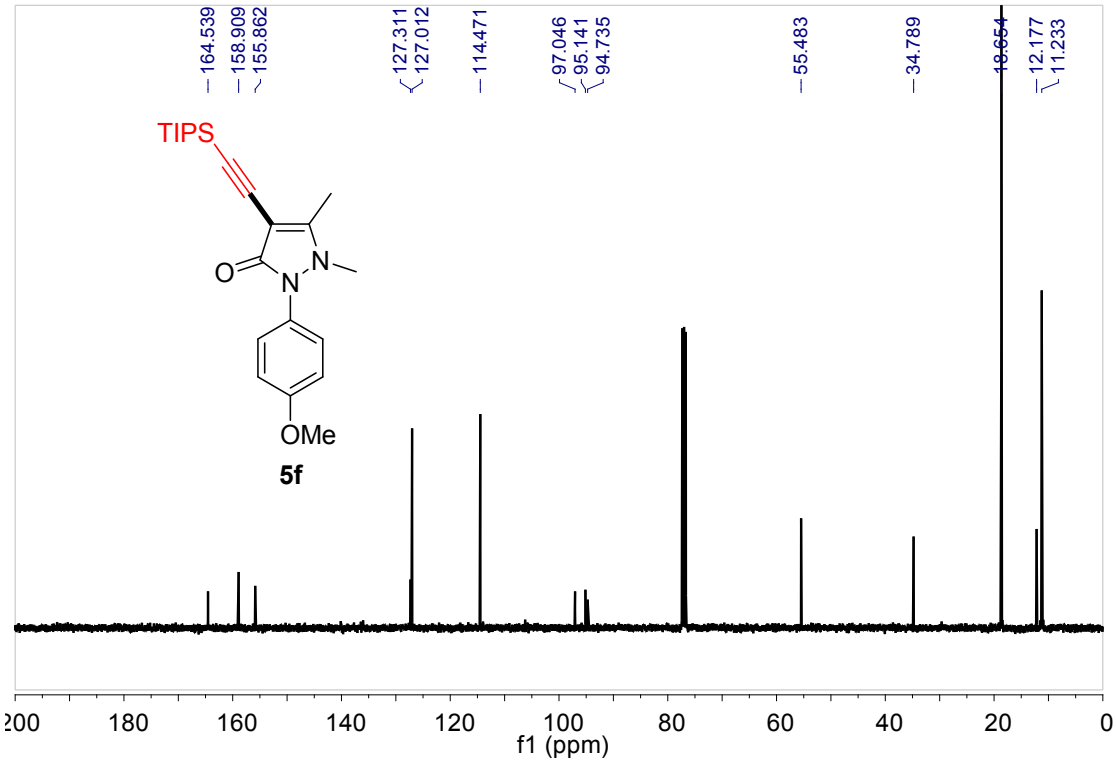

7.412
7.407
7.396
7.390
7.293
7.288
7.276
7.271
7.260
3.119
2.356
1.108
2.11
2.06
7.40
7.35
7.30
7.25
f1 (ppm)
TIPS
O
N
N
Cl
5d
2.11
2.06
3.05
3.00
21.22
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


164.582
158.578
133.448
132.438
129.285
125.199
96.284
96.218
96.038
35.732
18.660
12.422
11.222
TIPS
O
N
N
Cl
5d
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.567
7.562
7.550
7.545
7.260
7.241
7.219
3.120
2.357
1.414
TIPS
O
N
N
Br
5e
2.00
1.96
7.6
7.5
7.4
7.3
7.2
7.1
f1 (ppm)
2.00
1.96
3.00
3.00
21.46
0.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


164.567
158.772
134.036
132.283
125.445
120.300
96.386
96.287
96.143
35.829
18.698
12.468
11.267
TIPS
O
N
N
Br
5e
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.223
7.200
6.949
6.926
3.805
3.102
2.332
1.192
TIPS
1.98
1.98
1.98
7.3
7.2
7.1
7.0
6.9
f1 (ppm)
O
N
N
OMe
5f
1.98
1.98
3.07
3.03
3.00
21.73
0.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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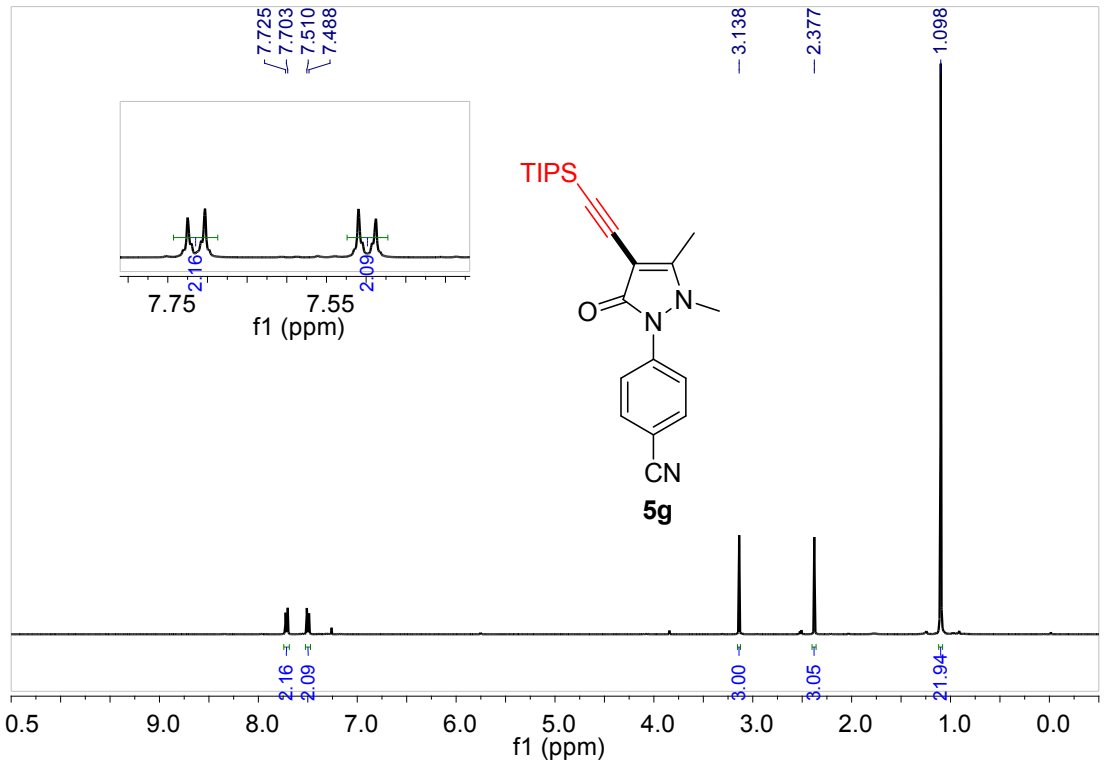
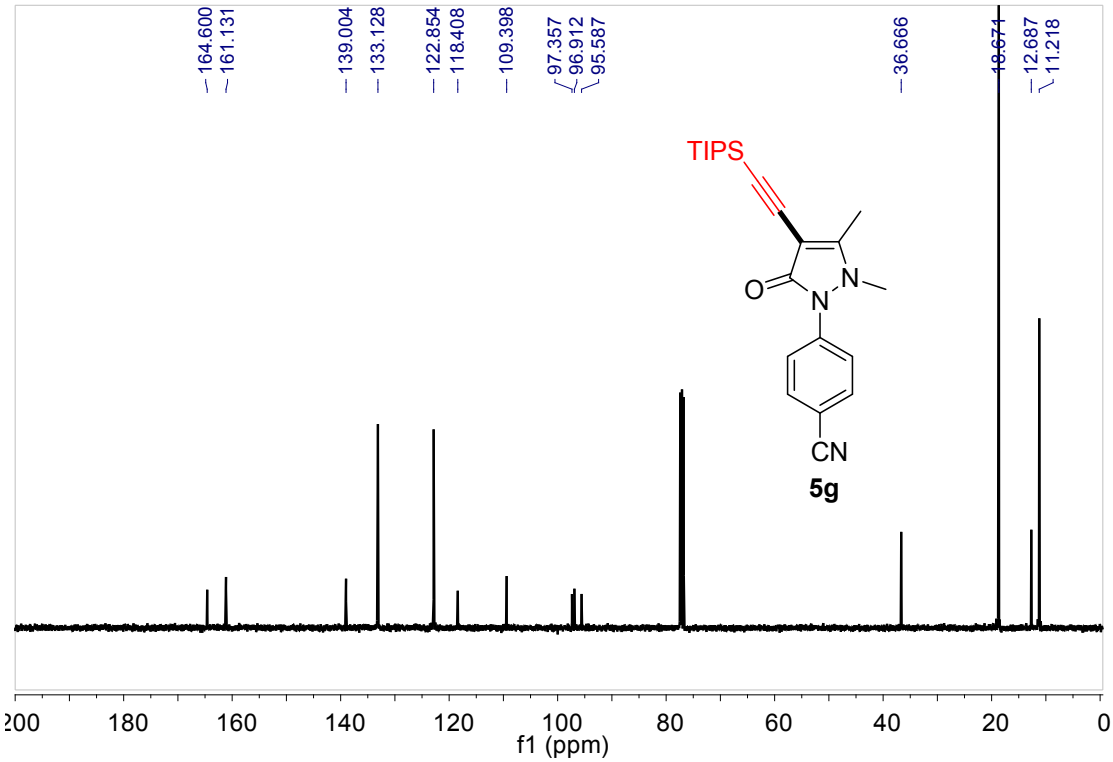
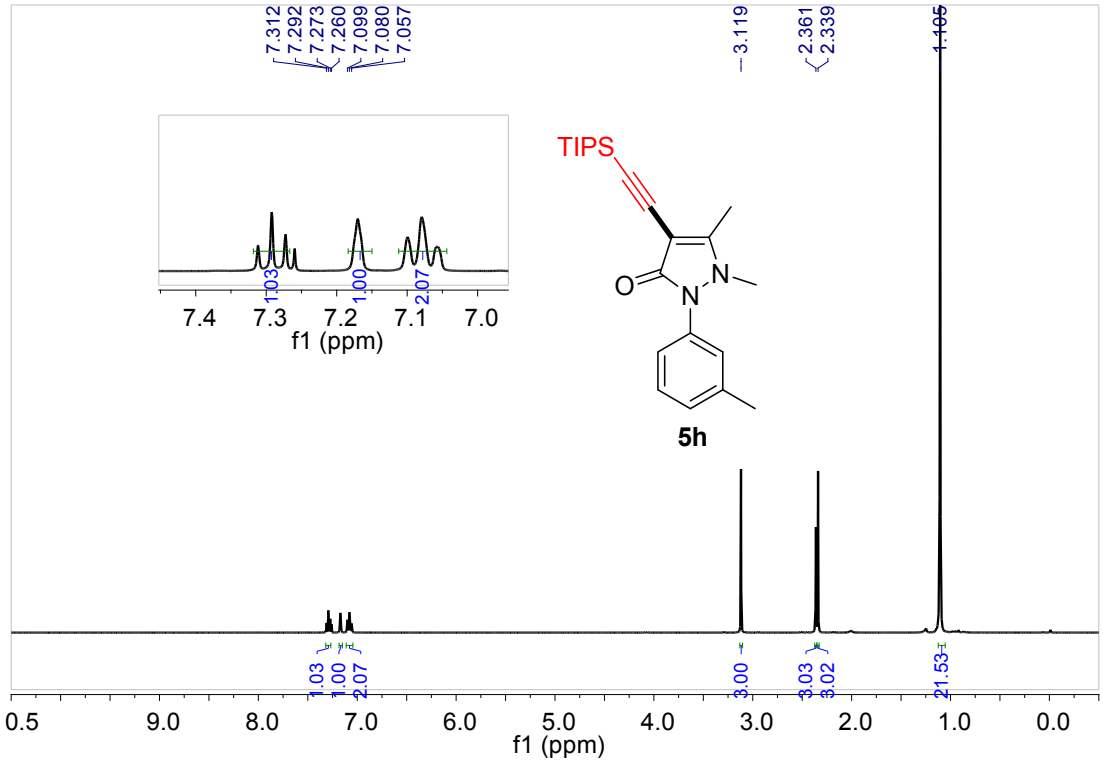
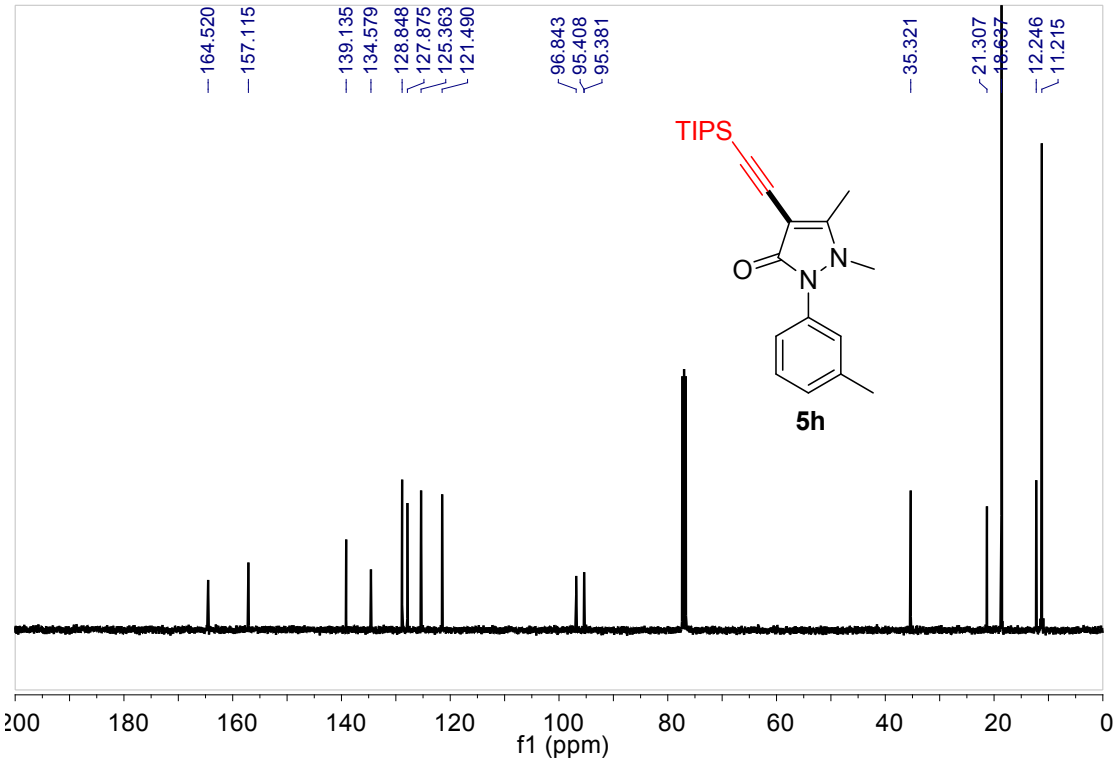
158.909
155.862
127.311
127.012
114.471
97.046
95.141
94.735
55.483
34.789
18.664
12.177
11.233
TIPS
O
N
N
OMe
5f
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.725
7.703
7.510
7.488
3.138
2.377
1.098
2.16
2.09
7.75
7.55
f1 (ppm)
TIPS
O
N
N
CN
5g
2.16
2.09
3.00
3.05
21.94
0.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


164.600
161.131
139.004
133.128
122.854
118.408
109.398
97.357
96.912
95.587
36.666
18.671
12.687
11.218
TIPS
O
N
N
CN
5g
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.312
7.292
7.273
7.260
7.099
7.080
7.057
3.119
2.361
2.339
1.195
1.03
1.00
2.07
7.4
7.3
7.2
7.1
7.0
f1 (ppm)
TIPS
O
N
N
5h
1.03
1.00
2.07
3.00
3.03
3.02
21.53
0.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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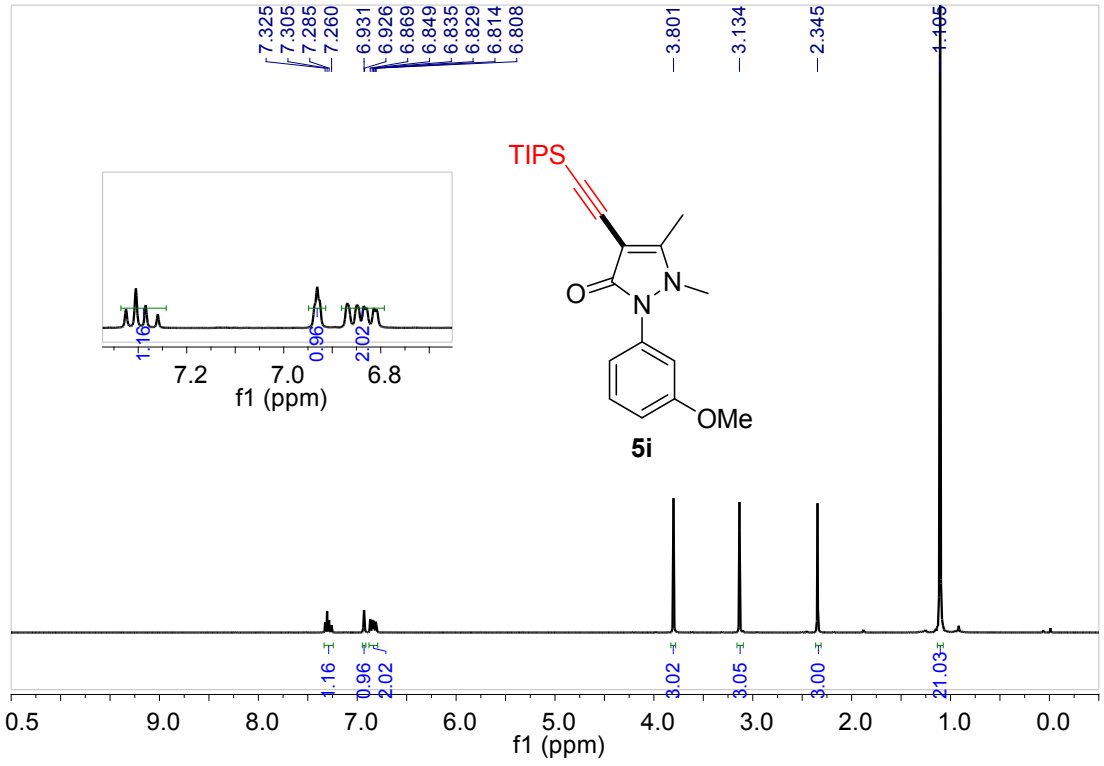
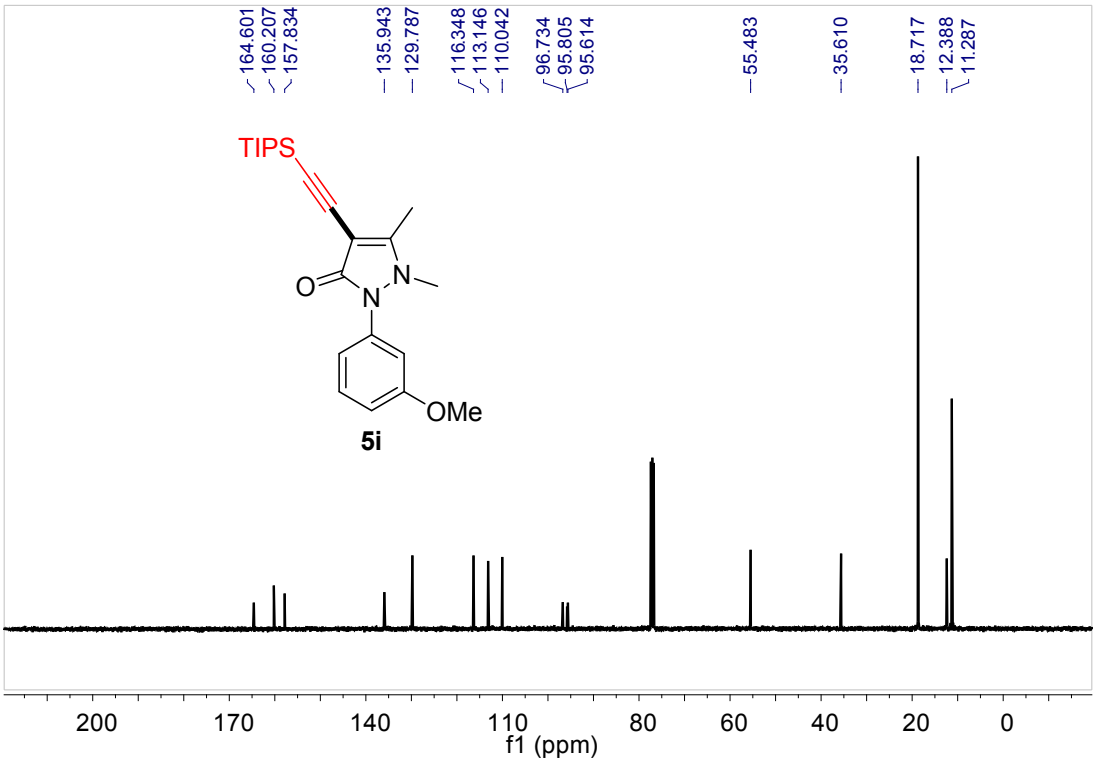
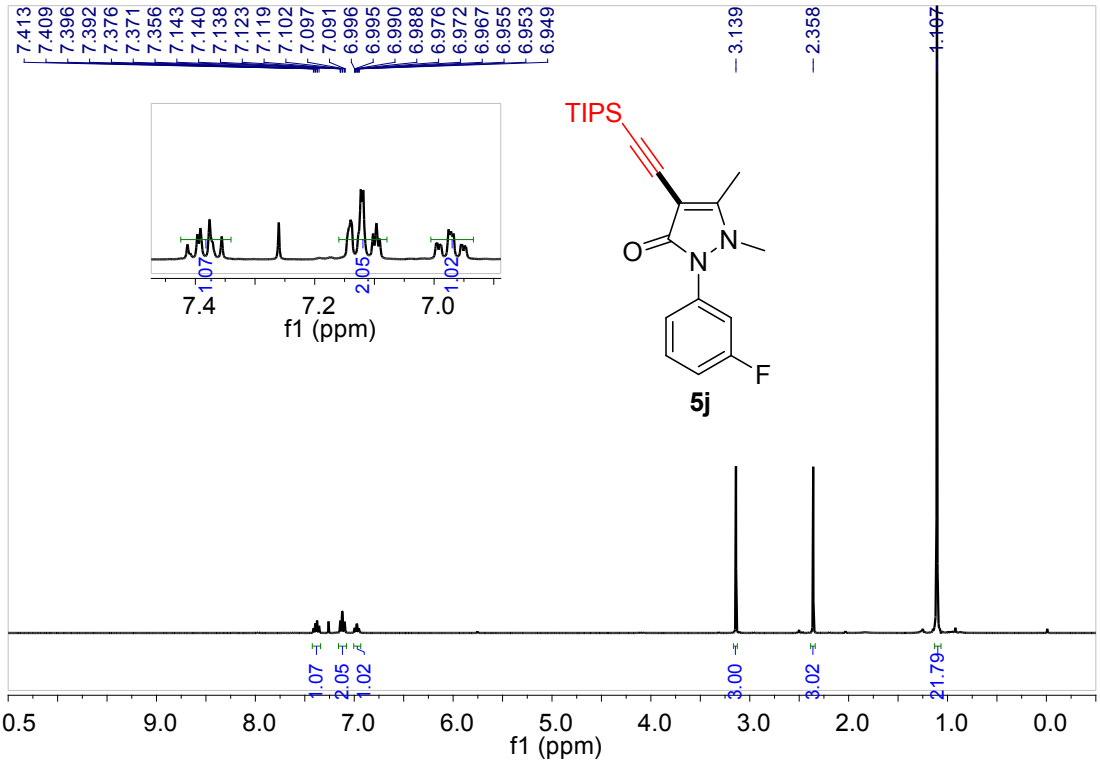
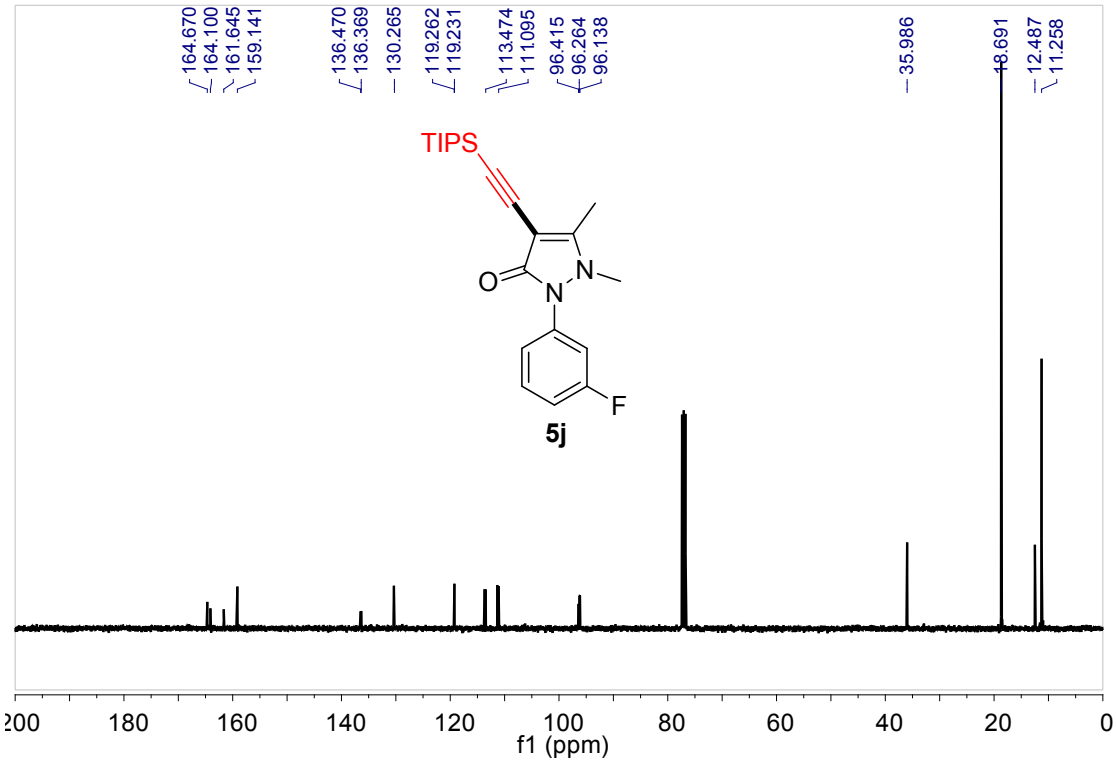
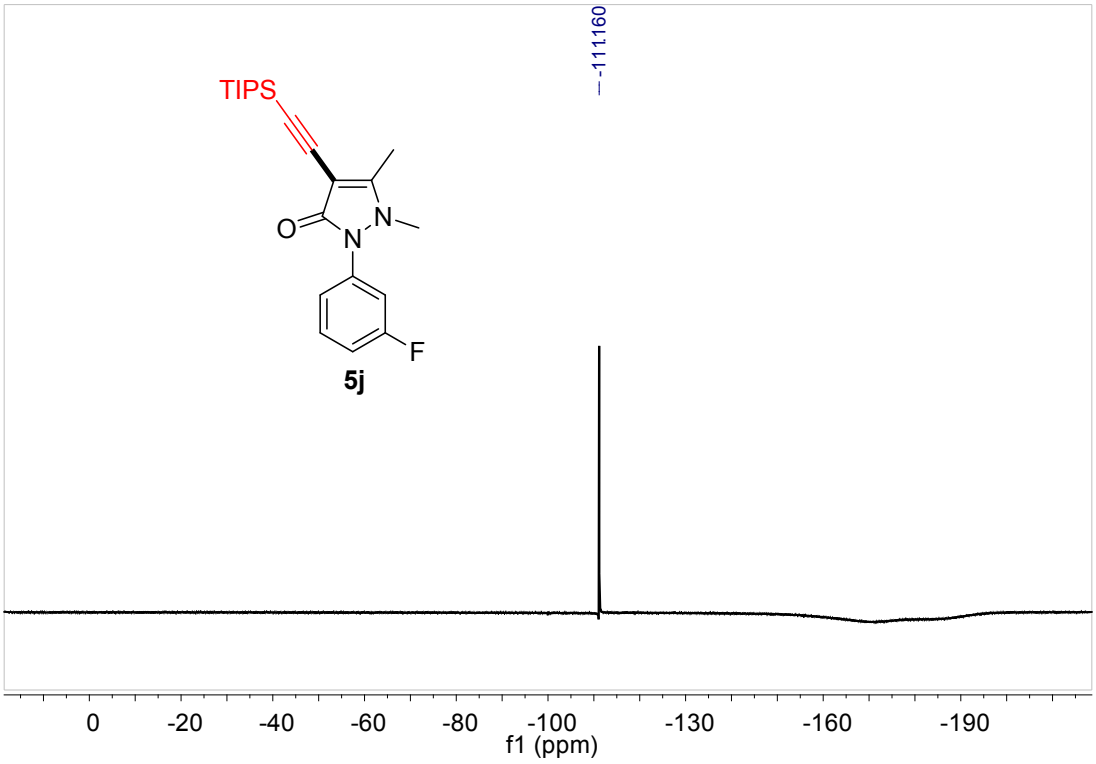
157.115
139.135
134.579
128.848
127.875
125.363
121.490
96.843
95.408
95.381
35.321
21.307
18.637
12.246
11.215
TIPS
O
N
N
5h
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.325
7.305
7.285
7.260
6.931
6.926
6.869
6.849
6.835
6.829
6.814
6.808
3.801
3.134
2.345
1.195
TIPS
O
N
N
OMe
5i
1.16
0.96
2.02
7.2
7.0
6.8
f1 (ppm)
1.16
0.96
2.02
3.02
3.05
3.00
21.03
0.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


164.601
160.207
157.834
135.943
129.787
116.348
113.146
110.042
96.734
95.805
95.614
55.483
35.610
18.717
12.388
11.287
TIPS
O
N
N
OMe
5i
200
170
140
110
80
60
40
20
0
f1 (ppm)


7.413
7.409
7.396
7.392
7.376
7.371
7.356
7.143
7.140
7.138
7.123
7.119
7.102
7.097
7.091
6.996
6.995
6.990
6.988
6.976
6.972
6.967
6.955
6.953
6.949
3.139
2.358
1.107
1.07
2.05
1.02
7.4
7.2
7.0
f1 (ppm)
TIPS
O
N
N
F
5j
3.00
3.02
21.79
0.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


164.670
164.100
161.645
159.141
136.470
136.369
130.265
119.262
119.231
113.474
111.095
96.415
96.264
96.138
35.986
18.691
12.487
11.258
TIPS
O
N
N
F
5j
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


-111.160
TIPS
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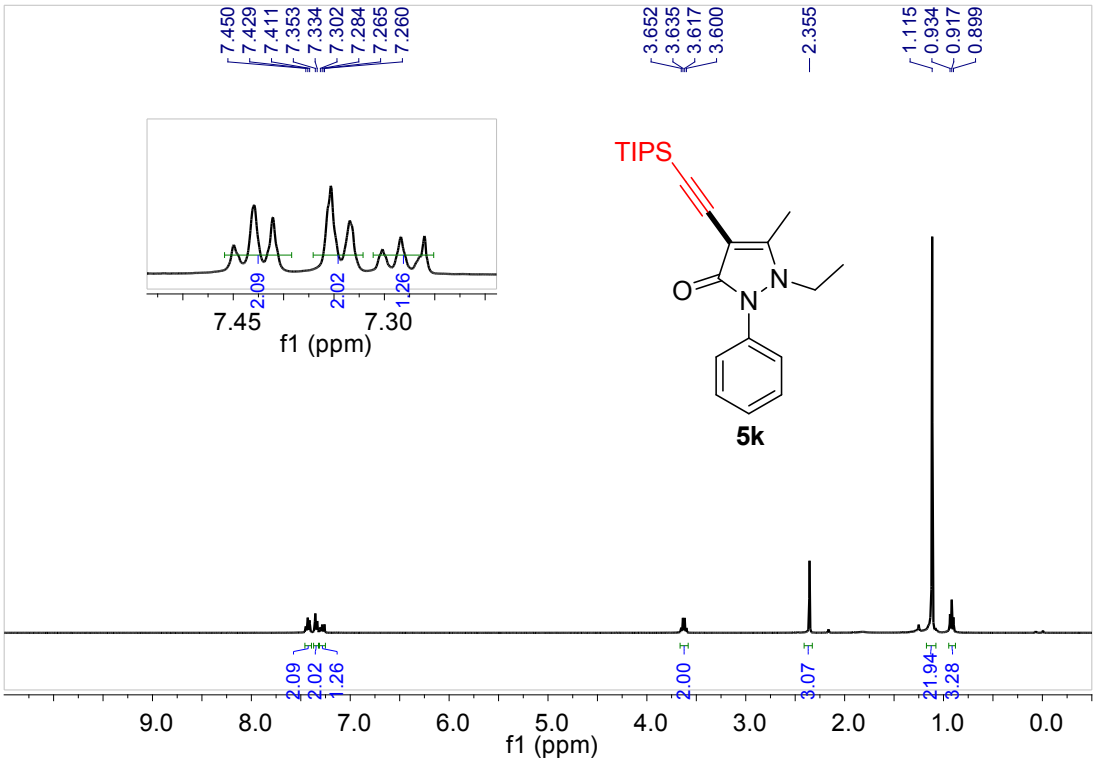
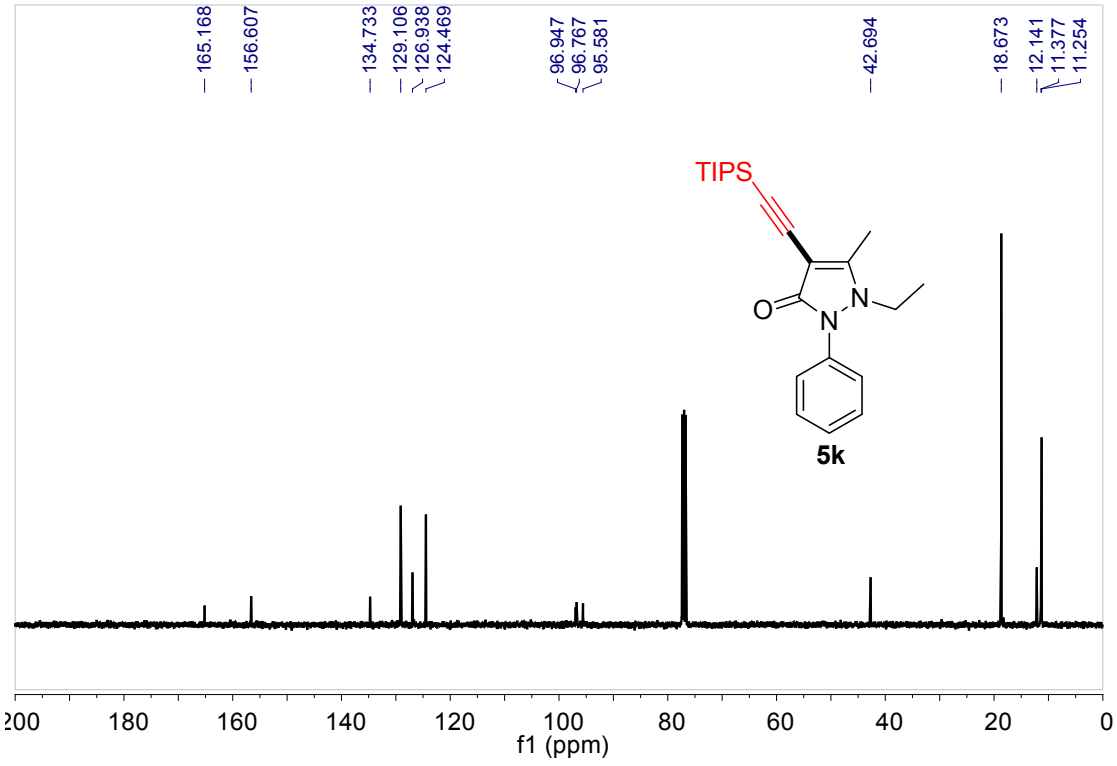
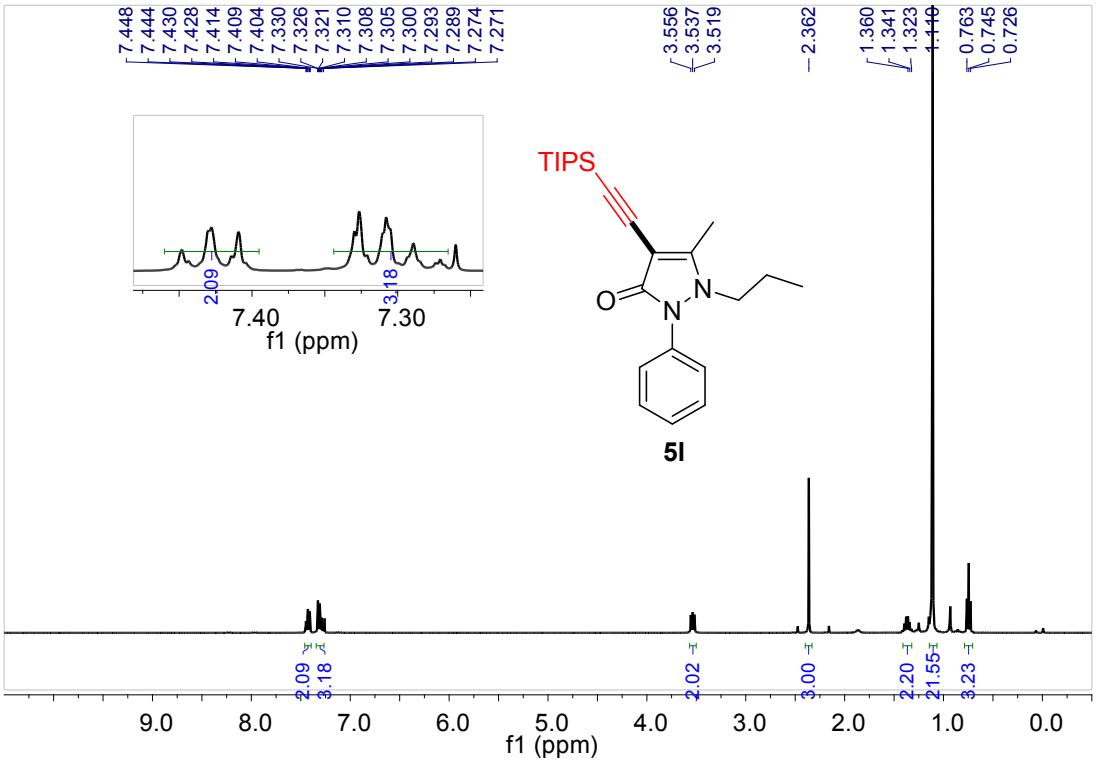
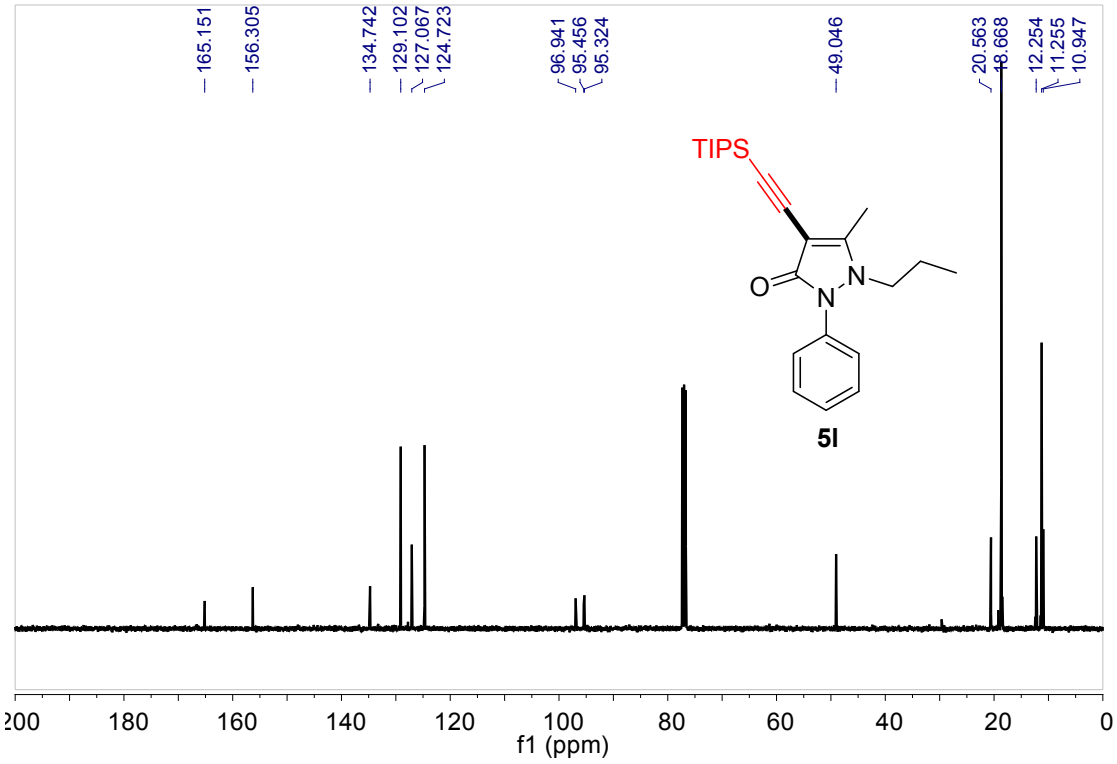
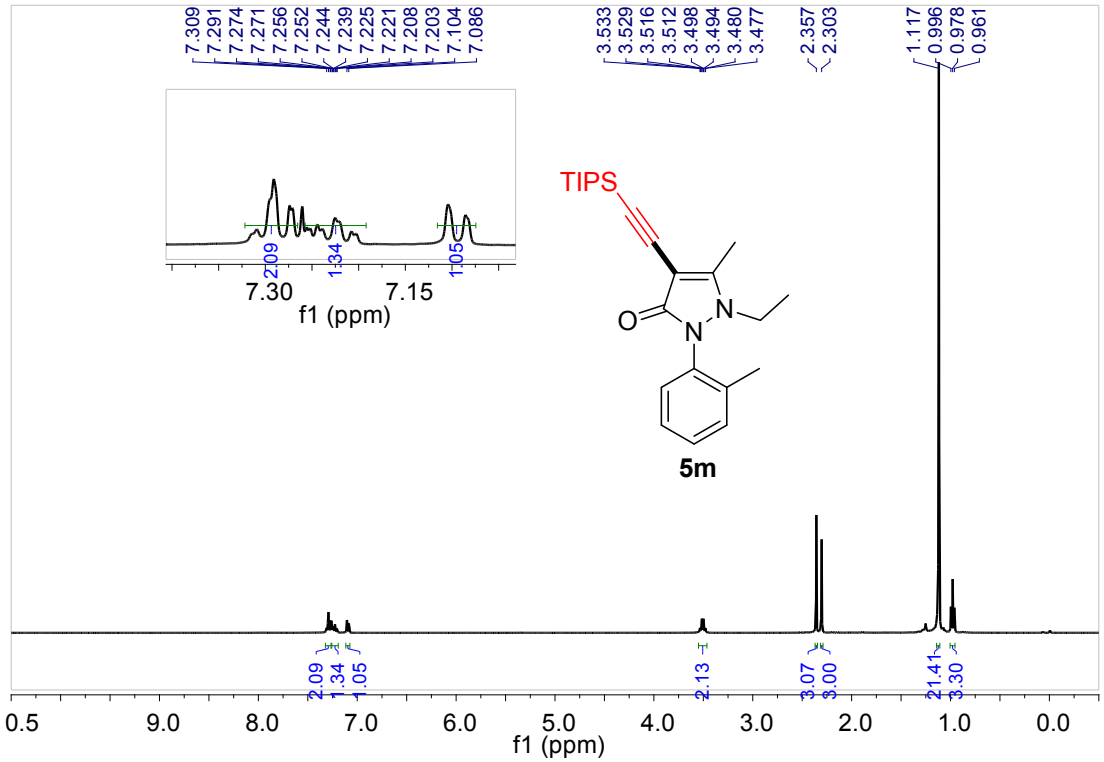
N
N
F
5j
0
-20
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)

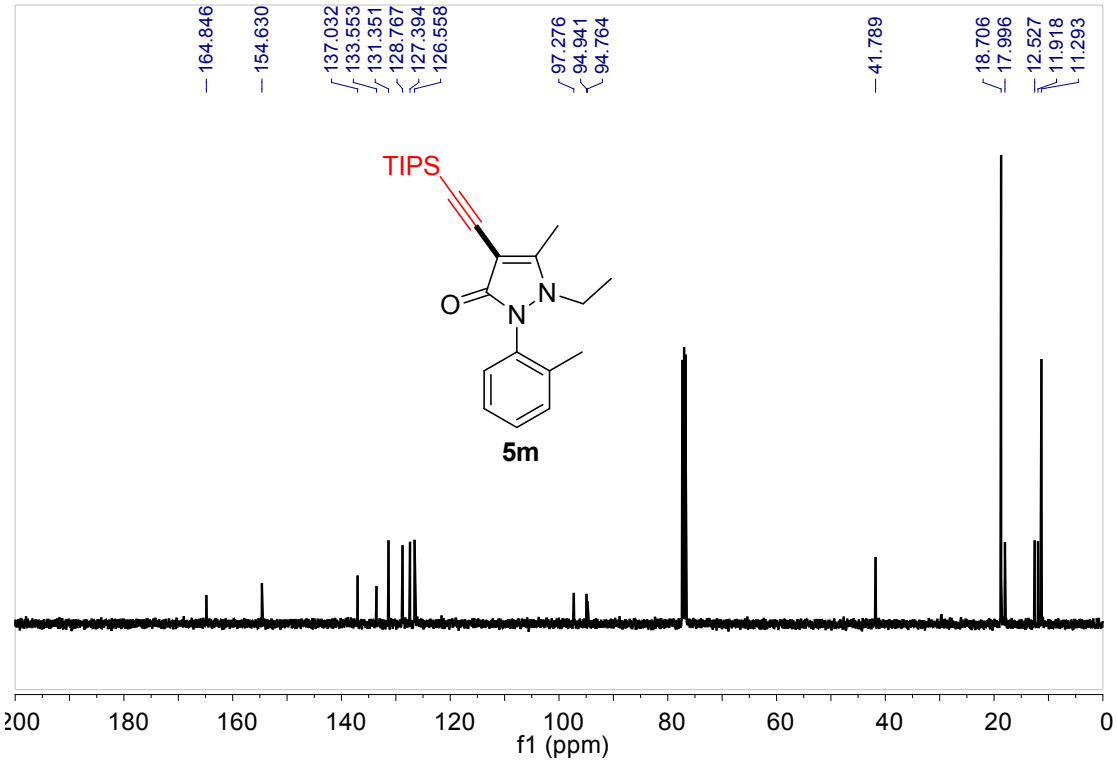

7.450
7.429
7.411
7.353
7.334
7.302
7.284
7.265
7.260
3.652
3.635
3.617
3.600
2.355
1.115
0.934
0.917
0.899
TIPS
O
N
N
5k
2.09
2.02
1.26
7.45
7.30
f1 (ppm)
2.09
2.02
1.26
2.00
3.07
21.94
3.28
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

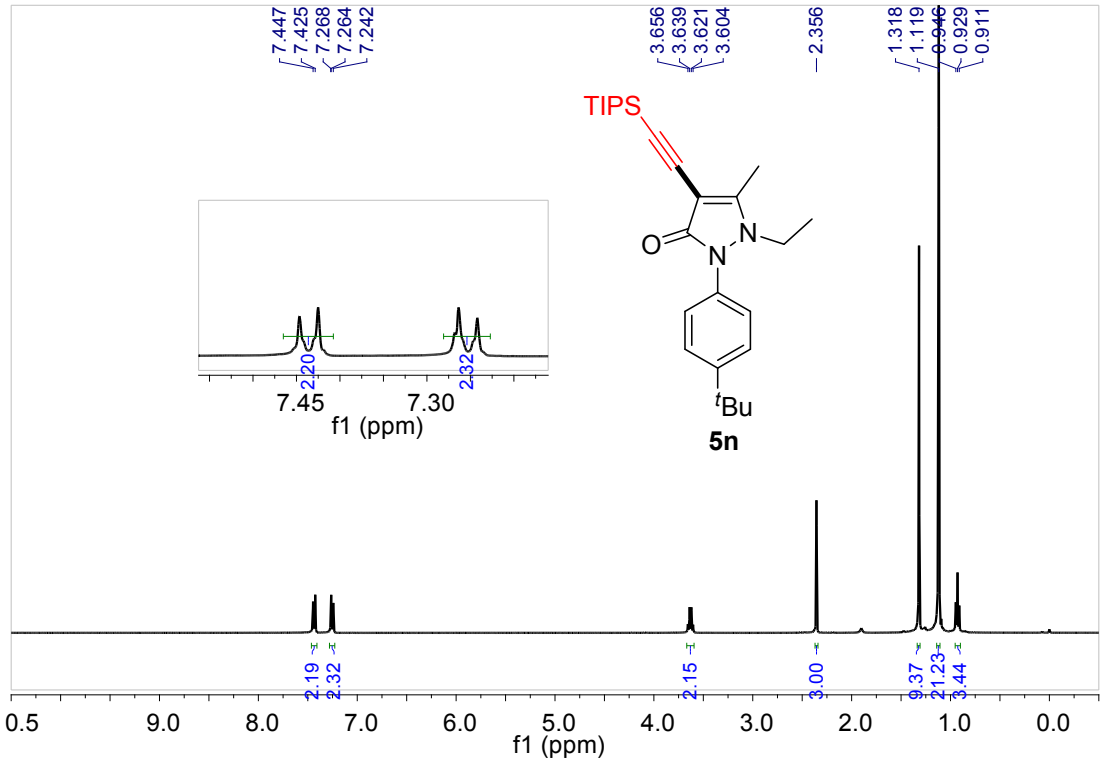

165.168
156.607
134.733
129.106
126.938
124.469
96.947
96.767
95.581
42.694
18.673
12.141
11.377
11.254
TIPS
O
N
N
5k
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

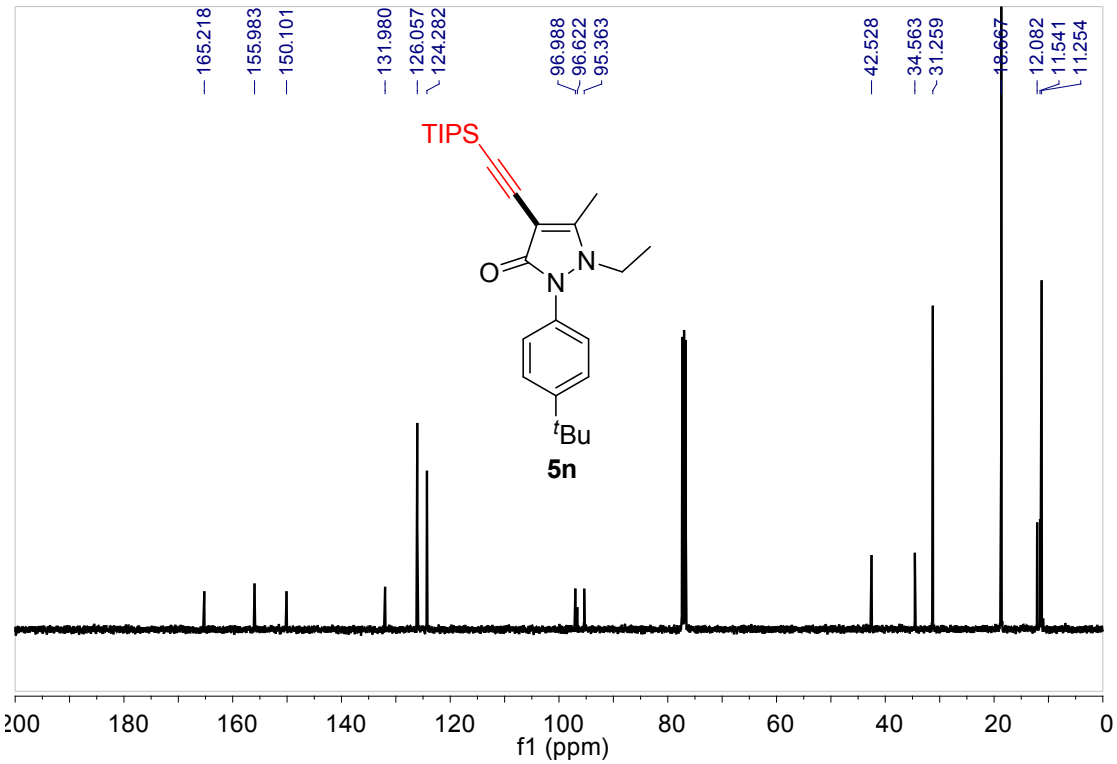

7.448
7.444
7.430
7.428
7.414
7.409
7.404
7.330
7.326
7.321
7.310
7.308
7.305
7.300
7.293
7.289
7.274
7.271
3.556
3.537
3.519
2.362
1.360
1.341
1.323
1.149
0.763
0.745
0.726
2.09
3.18
7.40
7.30
f1 (ppm)
TIPS
O
N
N
5l
2.09
3.18
2.02
3.00
2.20
21.55
3.23
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

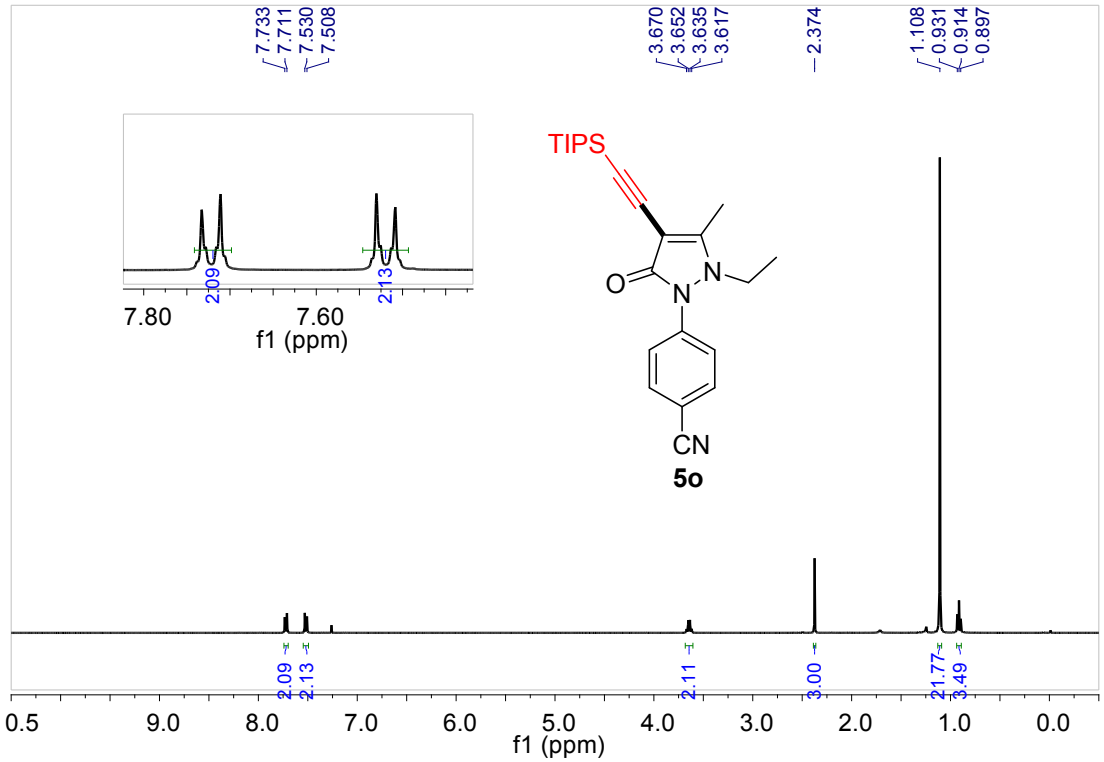

165.151
156.305
134.742
129.102
127.067
124.723
96.941
95.456
95.324
49.046
20.563
18.668
12.254
11.255
10.947
TIPS
O
N
N
5l
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

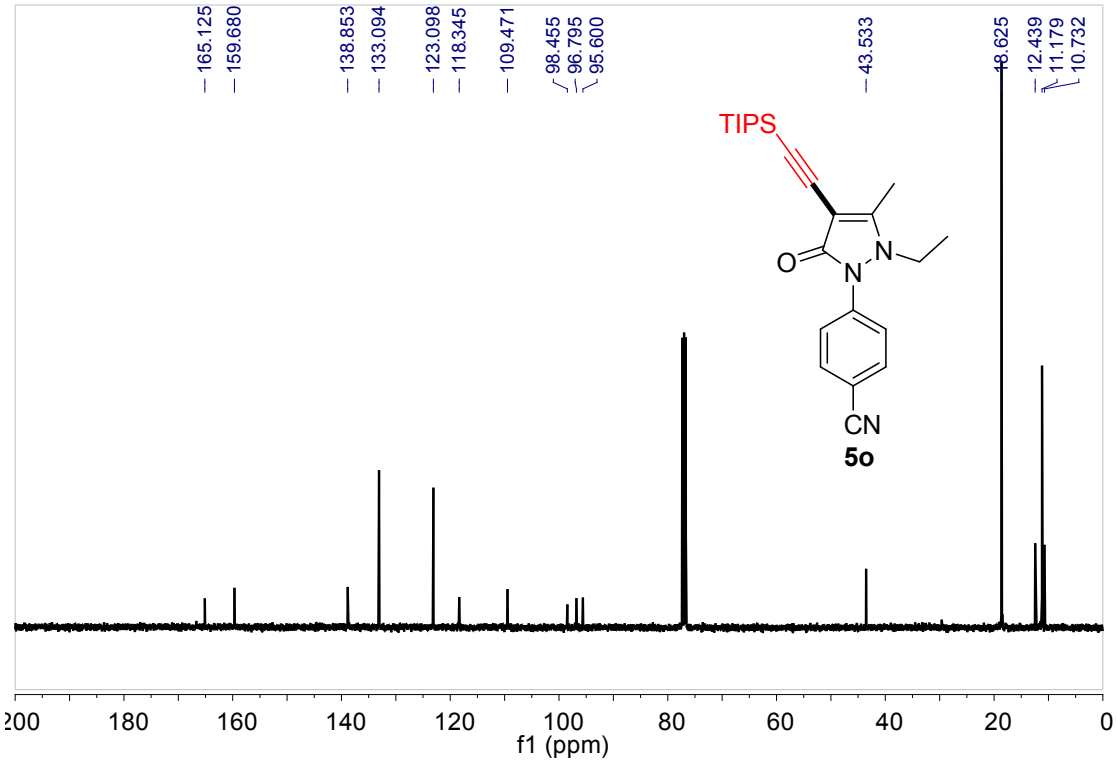

7.309
7.291
7.274
7.271
7.256
7.252
7.244
7.239
7.225
7.221
7.208
7.203
7.104
7.086
3.533
3.529
3.516
3.512
3.498
3.494
3.480
3.477
2.357
2.303
1.117
0.996
0.978
0.961
2.09
1.34
1.05
7.30
7.15
f1 (ppm)
TIPS
O
N
N
5m
2.09
1.34
1.05
2.13
3.07
3.00
21.41
3.30
0.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

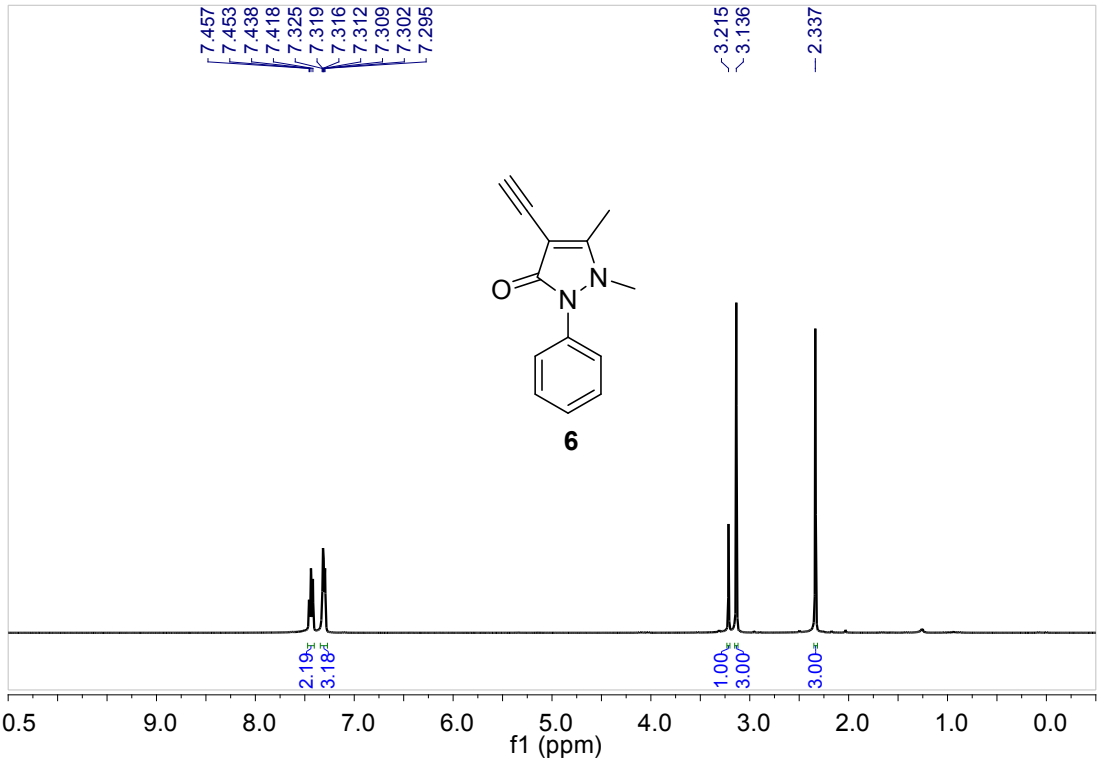

164.846
154.630
137.032
133.553
131.351
128.767
127.394
126.558
97.276
94.941
94.764
41.789
18.706
17.996
12.527
11.918
11.293
TIPS
O
N
N
5m
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

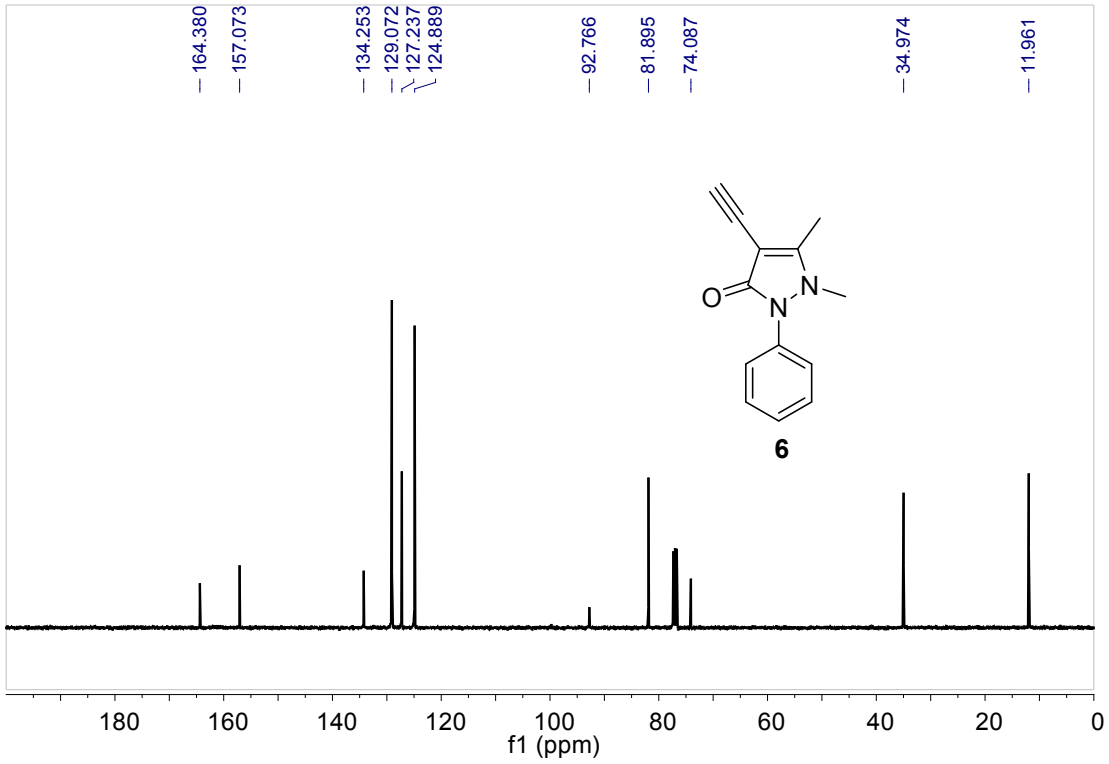

7.447
7.425
7.268
7.264
7.242
3.656
3.639
3.621
3.604
2.356
1.318
1.119
0.946
0.929
0.911
TIPS
O
N
N
tBu
5n
2.20
2.32
7.45
7.30
f1 (ppm)
2.19
2.32
2.15
3.00
9.37
21.23
3.44
0.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

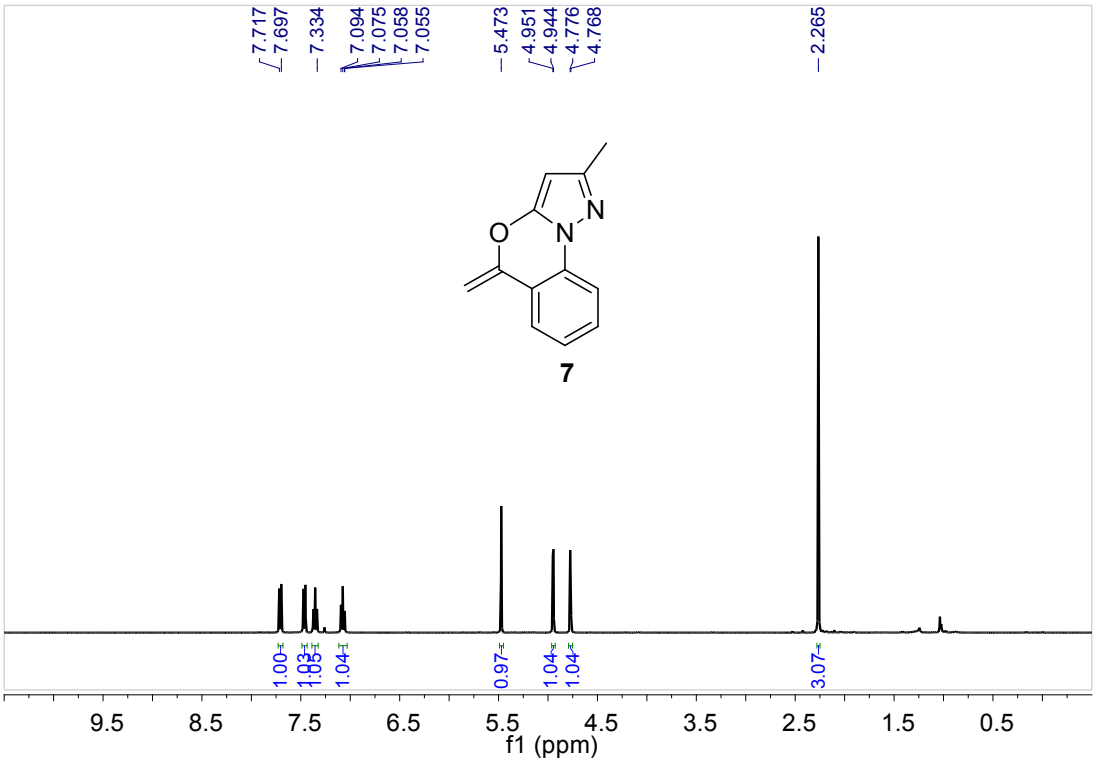

165.218
155.983
150.101
131.980
126.057
124.282
96.988
96.622
95.363
42.528
34.563
31.259
18.667
12.082
11.541
11.254
TIPS
O
N
N
tBu
5n
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

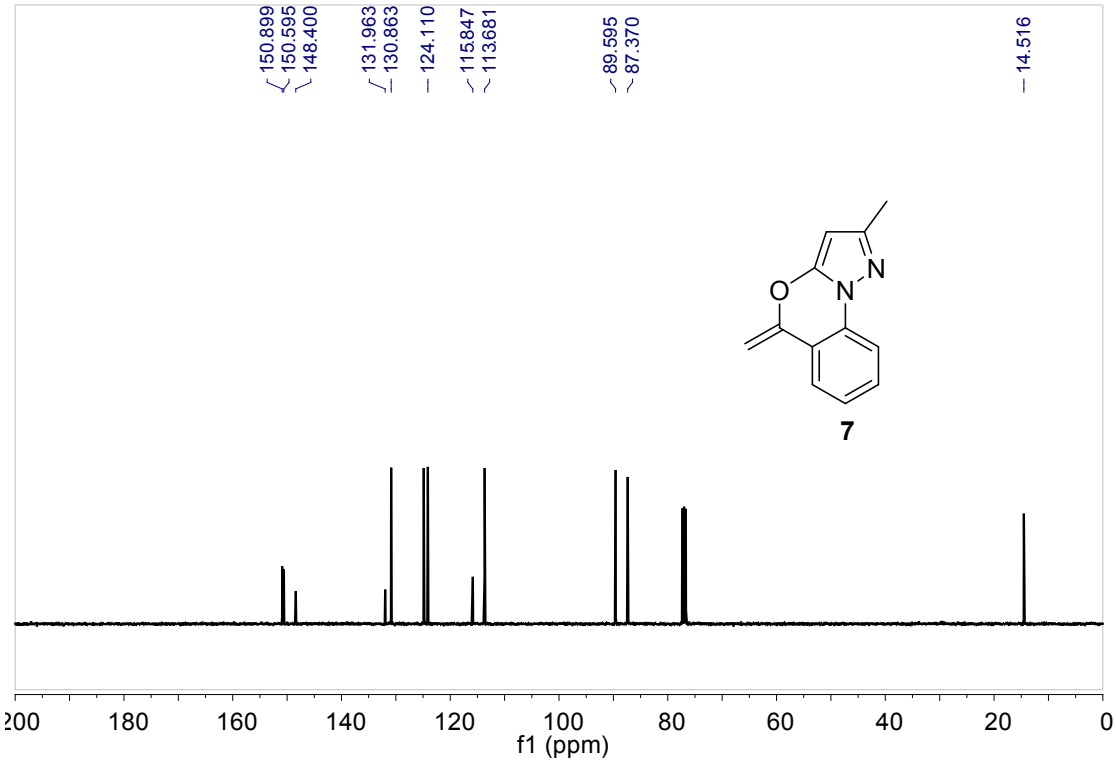

7.733
7.711
7.530
7.508
3.670
3.652
3.635
3.617
2.374
1.108
0.931
0.914
0.897
TIPS
O
N
N
CN
5o
2.09
2.13
7.80
7.60
f1 (ppm)
2.09
2.13
2.11
3.00
21.77
3.49
0.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


165.125
159.680
138.853
133.094
123.098
118.345
109.471
98.455
96.795
95.600
43.533
18.625
12.439
11.179
10.732
TIPS
O
N
N
CN
5o
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.457
7.453
7.438
7.418
7.325
7.319
7.316
7.312
7.309
7.302
7.295
3.215
3.136
2.337
O
N
N
6
2.19
3.18
1.00
3.00
3.00
0.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


164.380
157.073
134.253
129.072
127.237
124.889
92.766
81.895
74.087
34.974
11.961
O
N
N
6
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.717
7.697
7.334
7.094
7.075
7.058
7.055
5.473
4.951
4.944
4.776
4.768
2.265
O
N
N
7
1.00
1.03
1.05
1.04
0.97
1.04
1.04
3.07
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


150.899
150.595
148.400
131.963
130.863
124.110
115.847
113.681
89.595
87.370
14.516
O
N
N
7
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)