Supporting Information

Copper-catalyzed cascade cyclization of 1,5-enynes via consecutive trifluoromethylazidation/diazidation and click reaction: self-assembly of triazole fused isoindolines

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Contents

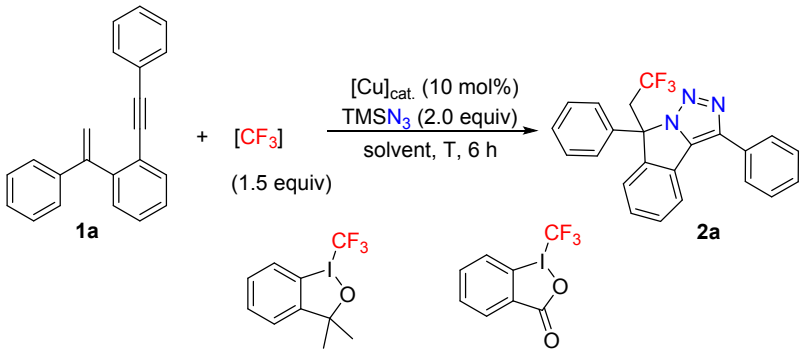
General remarks

Unless otherwise indicated, all glassware was oven dried by a heat gun before use and all reactions were performed under an atmosphere of argon. THF was distilled from sodium (Na) under argon (Ar) atmosphere. MeCN was purified and dried according to standard methods prior to use. All other solvents were purchased from Adamas and used as received. Isatoic anhydride and other materials obtained from commercial suppliers were used without further purification. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. All NMR spectra were recorded on a AM-300 or AM-400 spectrophotometers in $CDCl_3$, NMR chemical shifts are reported in ppm referenced to the solvent peaks of $CDCl_3$ (7.26 ppm for ^1H and 77.0 ppm for ^{13}C, respectively). Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Flash column chromatography was performed using 300-400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. Mass spectra were recorded by ESI, and HRMS were measured on a HP-5989 instrument.

Optimizization of reaction conditions for the synthesis of 2a

Our studies commended with 1-(phenylethynyl)-2-(1-phenylvinyl)benzene **1a** (1.0 equiv) as the pilot substrate, Togni reagent II (1.5 equiv) as trifluoromethyl source, and $TMSN_3$ (2.0 equiv) as azide source using CuI (0.01 equiv) as catalyst and MeCN (1.0 mL) as solvent at 50 ^oC under argon atmosphere. To our delight, the corresponding CF_3-containing triazole fused isoindoline **2a** was isolated in 75% yield (Table S1, entry 1). Next, we examined the catalytic efficiency of various copper (I) salts, and found that CuTc was the best one, leading to the highest yield (86%) (Table S1, entries 2-4). While copper (II) salt $Cu(OTf)_2$ was detrimental to the reaction efficiency (Table S1, entry 5). Using Togni reagent I as trifluoromethyl source also afforded an acceptable, but lower yield (76%) (Table S1, entry 6). Solvent effect was also investigated, and it was identified that MeCN was better than other solvents such as MeOH, DCE (1,2-dichloroethane), and 1,4-dioxane (Table S1, entries 7-9). Changing the reaction temperature to 60 ^oC or 40 ^oC, no better results could be realized (Table S1, entries 10-11). Decreasing the reaction temperature to 30 ^oC made the reaction sluggish, revealing that the reaction temperature was critical to the reaction efficiency (Table S1, entry 12). When the catalyst loading was increased to 20 mol%, the desired product was only isolated in 83% yield. Gratifyingly, the yield could be improved to 92% with adding only 5 mol% of catalyst probably because the lower catalyst loading might help the tandem reaction occur more smoothly (Table S1, entries 13-14). No reaction occurred in the absence of the copper catalyst (Table S1, entry 15).

Table S1 Optimizization of reaction conditions for the synthesis of 2a

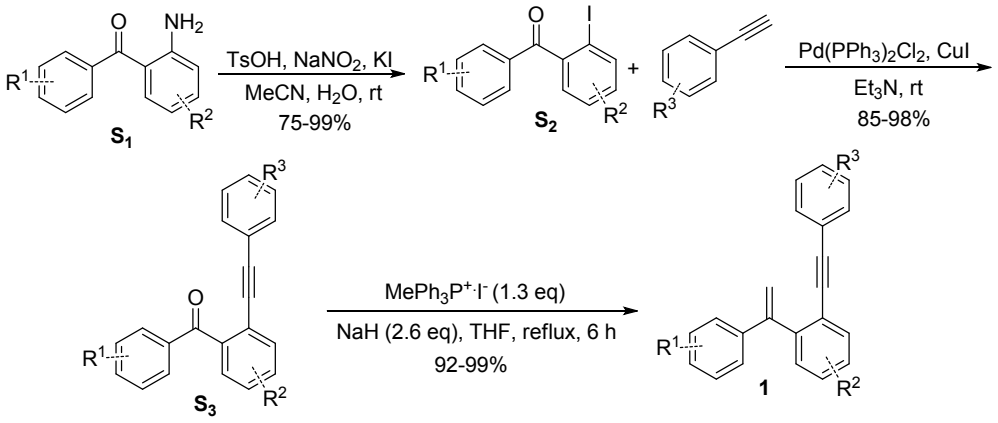


Entry[a]	[CF_3]	[$Cu]_{cat.}$ (mol%)	Solvent	T (^oC)	Yield (%)[b]
1	Togni reagent II	CuI	MeCN	50	75
2	Togni reagent II	CuBr	MeCN	50	70
3	Togni reagent II	CuTc	MeCN	50	86
4	Togni reagent II	$Cu(MeCN)_4PF_6$	MeCN	50	58
5	Togni reagent II	$Cu(OTf)_2$	MeCN	50	N R[c]
6	Togni reagent I	CuTc	MeCN	50	72
7	Togni reagent II	CuTc	MeOH	50	15
8	Togni reagent II	CuTc	DCE	50	78
9	Togni reagent II	CuTc	1,4-dioxane	50	64
10	Togni reagent II	CuTc	MeCN	60	83
11	Togni reagent II	CuTc	MeCN	40	66
12	Togni reagent II	CuTc	MeCN	30	Trace
13[d]	Togni reagent II	CuTc	MeCN	50	83
14[e]	***Togni reagent II***	***CuTc***	***MeCN***	***50***	***92***
15[f]	Togni reagent II	-	MeCN	50	N R[c]

[a] Reaction conditions unless specified otherwise: $[Cu]_{cat.}$ (0.01 mmol, 0.10 equiv), [CF_3] (0.15 mmol, 1.5 equiv), $TMSN_3$ (0.20 mmol, 2.0 equiv), **1a** (0.10 mmol, 1.0 equiv), solvent (1.0 mL), arogen atmosphere for 6 h. [b] Isolated yield. [c] N R = No Reaction. [d] 20 mol% catalyst was used. [e] 5 mol% catalyst was used. [f] No copper catalyst was used.

General procedure for the synthesis of substrate 1

Compounds 1 were partially prepared according to previously reported work and the corresponding spectroscopic data was consistent with those in reported literature.[1] 2-Aminobenzophenones $\mathbf{S_1}$ were prepared from isatoic anhydride according to related literature.[2]



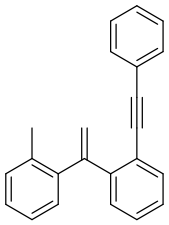
The synthesis of $\mathbf{S_2}$: To a 150 mL flask charged with $\mathbf{S_1}$ (10 mmol, 1.0 equiv) and TsOH (30 mmol, 3.0 equiv) in MeCN (50 mL) was added $NaNO_2$ (20 mmol, 2.0 equiv) and KI (25 mmol, 2.5 equiv) dissolved in H_2O (30 mL) dropwise at room temperature and the resulting solution was stirred at room temperature for another 2 h. Upon completion, saturated aqueous sodium sulfite was added to the solution to quench the reaction. After removal of the most of MeCN solvent under reduced pressure, the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by silica gel flash chromatography (petroleum ether / ethyl acetate = 50 / 1) to afford $\mathbf{S_2}$ in good yields ranging from 75% to 99%.

The synthesis of $\mathbf{S_3}$: To a stirred solution of $\mathbf{S_2}$ (1.0 equiv) and terminal aromatic alkynes (1.2 equiv) in Et_3N (30 mL) was added $PdCl_2(PPh_3)_2$ (2 mol%) and CuI (2 mol%). The resulted mixture was stirred at room temperature for 8 h. After the separation of ammonium salt by filtration and the removal of solvent under reduced pressure, the residue was purified by column chromatography on silica gel to afford the corresponding $\mathbf{S_3}$ in good yields ranging from 85% to 98%.

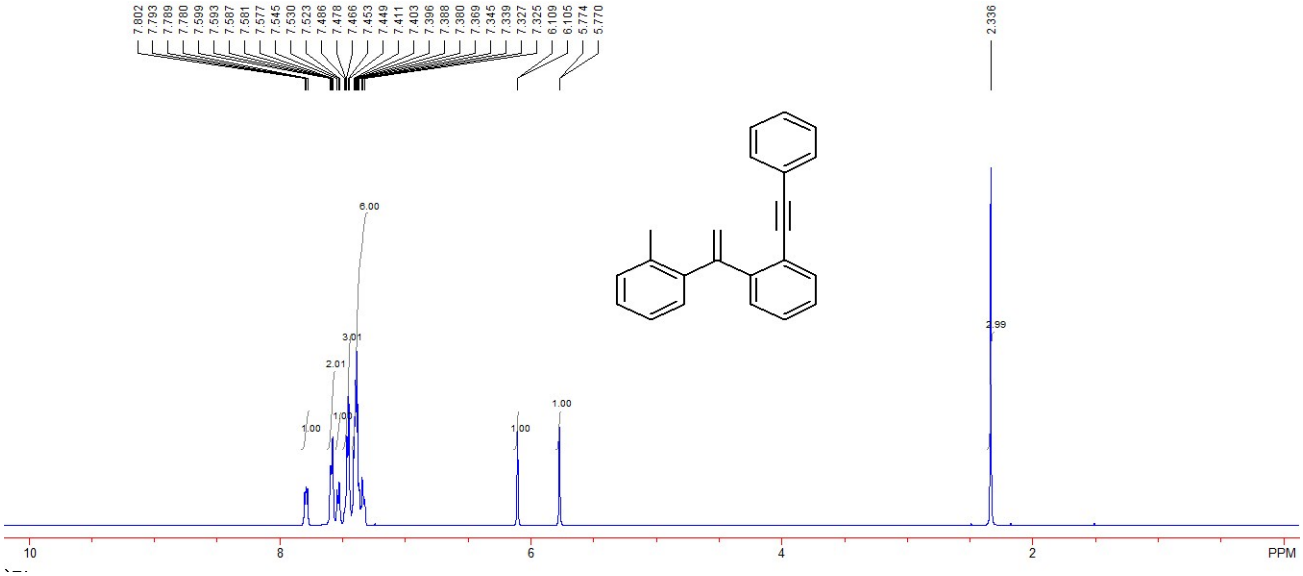
The synthesis of **1**: A solution of methyltriphenylphosphonium bromide (1.3 equiv) and NaH (2.6 equiv) in THF (5.0 mL) was stirred at 70 °C under N_2 for 2 h. Afterwards compound $\mathbf{S_3}$ (1.0 equiv) in THF (5.0 mL) was added and the reaction solution was stirred at 70 °C for another 4 h. Upon completion, the reaction was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica

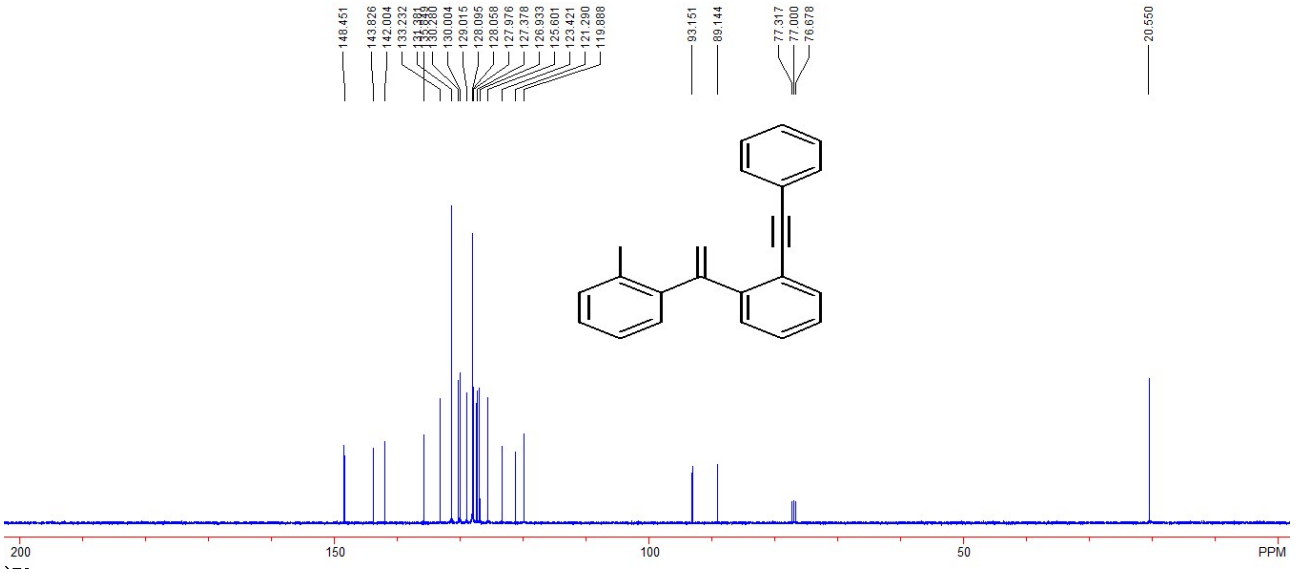
gel flash chromatography (eluent: petroleum ether) to afford the products **1** in excellent yields ranging from 92% to 99%.

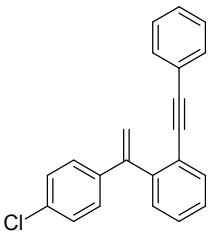
Spectroscopic data for substrates 1



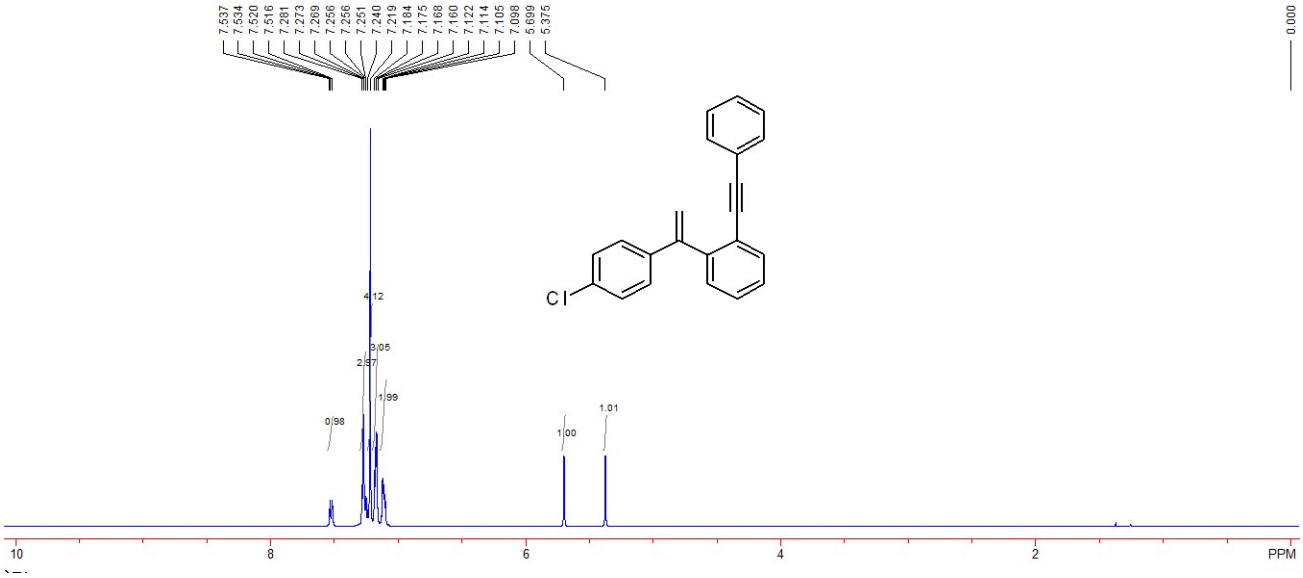
Compound 1b: 2.36 g, 80%, A colorless oil; IR (CH_2Cl_2): ν 3054, 3020, 2925, 1602, 1492, 1442, 912, 778, 754, 731, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 2.34 (s, 3H), 5.77 (d, 1H, J = 1.6 Hz), 6.11 (d, 1H, J = 1.6 Hz), 7.33-7.41 (m, 6H), 7.45-7.49 (m, 3H), 7.52-7.55 (m, 1H), 7.58-7.60 (m, 2H), 7.79 (dd, 1H, J_1 = 7.6 Hz, J_2 = 3.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 20.6, 89.1, 93.2, 119.9, 121.3, 123.4, 125.6, 126.9, 127.4, 127.98, 128.06, 128.10, 129.0, 130.0, 130.3, 131.4, 133.2, 135.8, 142.0, 143.8, 148.5; MS (ESI) *m/z*: 295.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{23}H_{19}^+$ requires: 295.1481, Found: 295.1469.

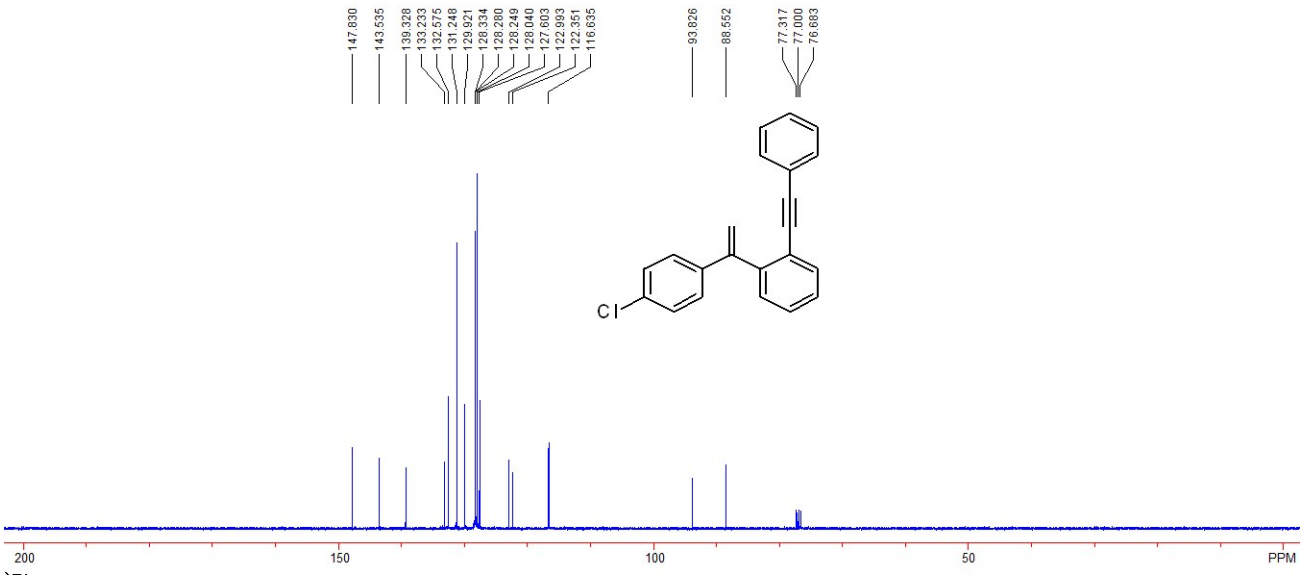


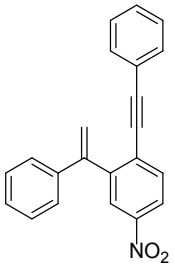




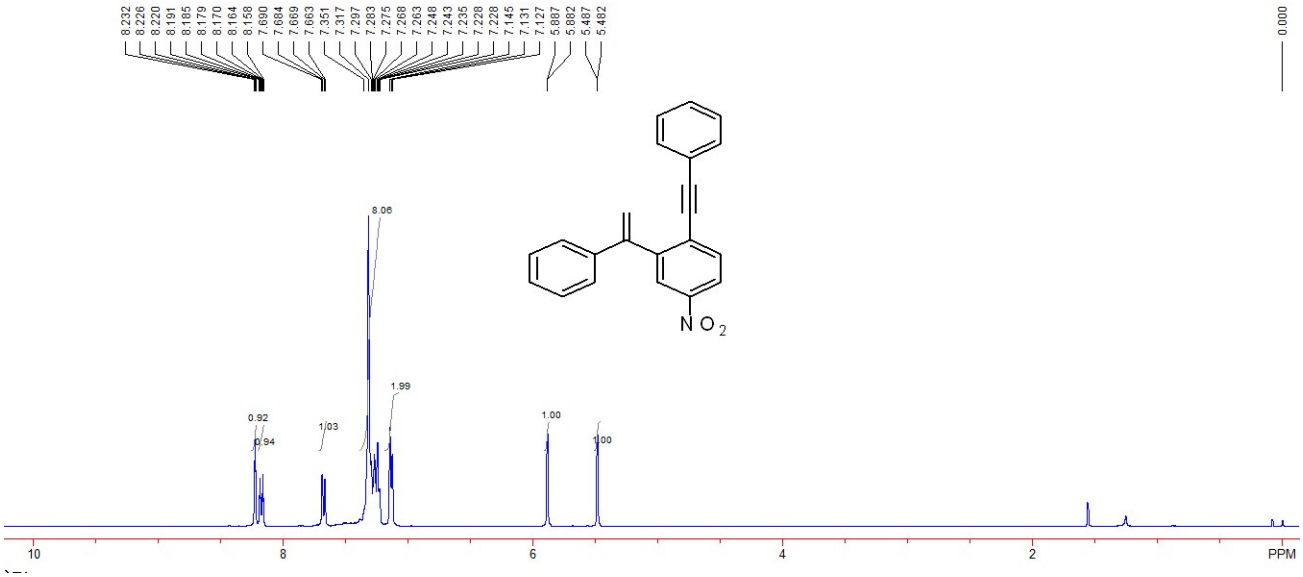
Compound 1c: 2.46 g, 78%, A colorless oil; IR (CH_2Cl_2): ν 3078, 3065, 3026, 1598, 1491, 1442, 1259, 1113, 1091, 1013, 909, 836, 771, 755, 732, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 5.38 (s, 1H), 5.70 (s, 1H), 7.10-7.12 (m, 2H), 7.16-7.18 (m, 3H), 7.22 (brs, 4H), 7.24-7.28 (m, 3H), 7.53 (dd, 1H, J_1 = 7.2 Hz, J_2 = 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 88.6, 93.8, 116.6, 122.4, 123.0, 127.6, 128.0, 128.2, 128.28, 128.33, 129.9, 131.2, 132.6, 133.2, 139.3, 143.5, 147.8; MS (ESI) *m/z*: 315.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{22}H_{16}Cl^+$ requires: 315.0935, Found: 315.0927.

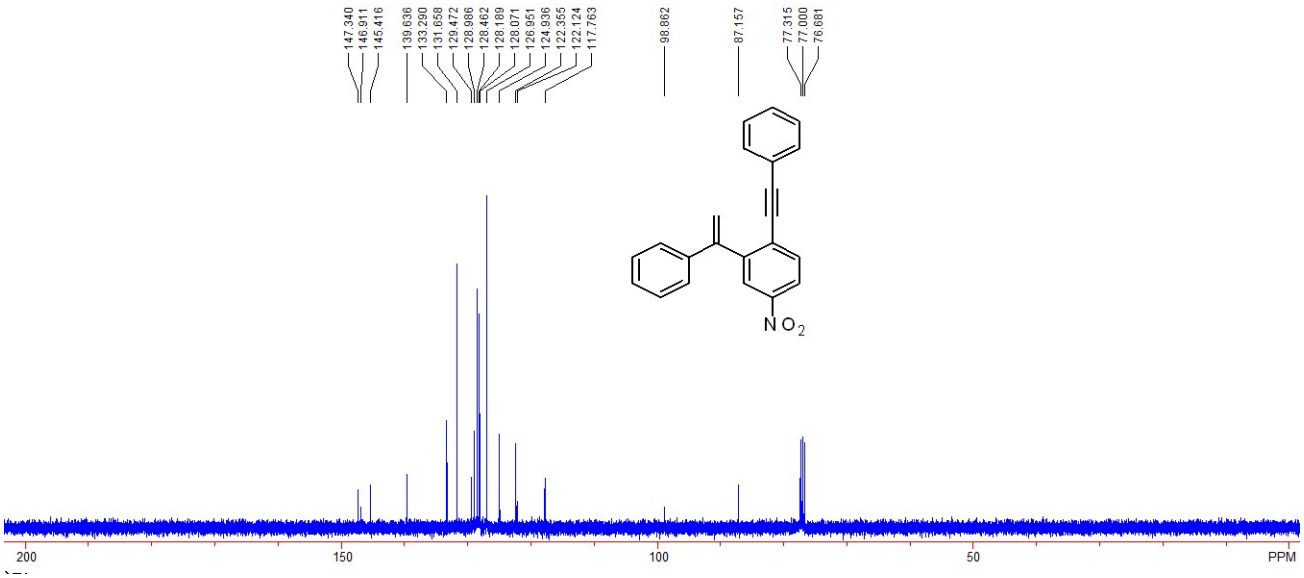


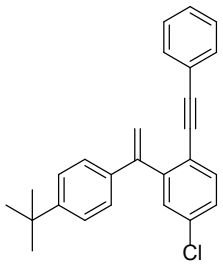




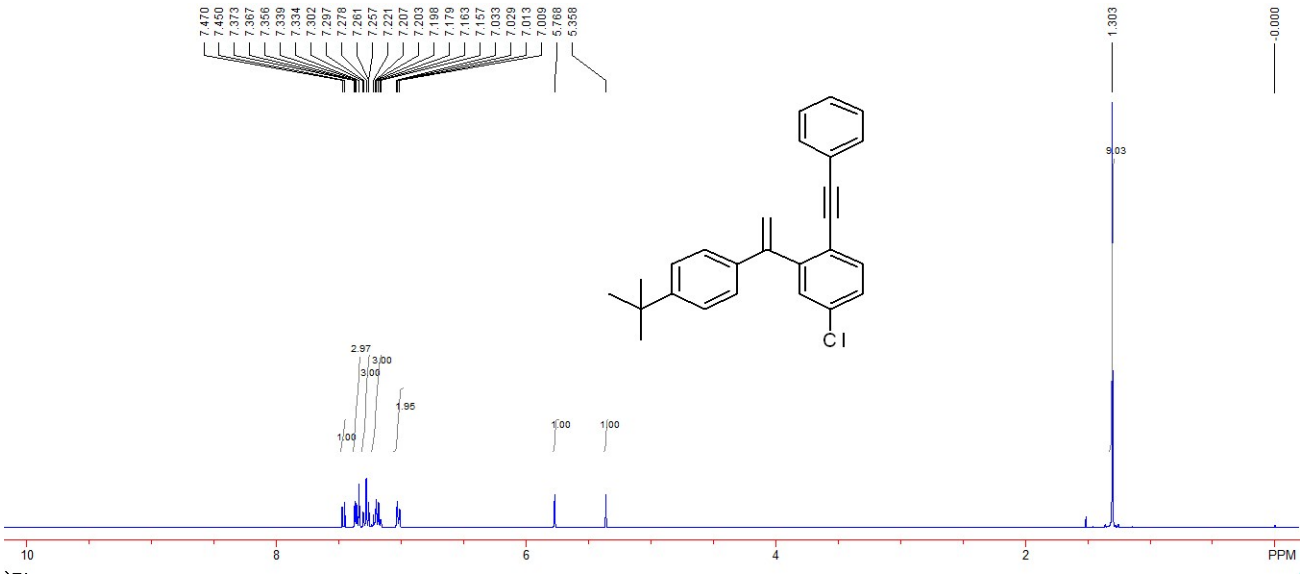
Compound 1d: 2.12 g, 65%, A colorless oil; IR (CH_2Cl_2): ν 3081, 3056, 3031, 2917, 2212, 1600, 1574, 1515, 1493, 1442, 1332, 1287, 1076, 907, 837, 823, 779, 755, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 5.48 (d, 1H, J = 2.0 Hz), 5.88 (d, 1H, J = 2.0 Hz), 7.14 (dd, 2H, J_1 = 7.2 Hz, J_2 = 1.6 Hz), 7.23-7.35 (m, 8H), 7.68 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2.4 Hz), 8.16-8.19 (m, 1H), 8.23 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 87.2, 98.9, 117.8, 122.1, 122.4, 124.9, 127.0, 128.1, 128.2, 128.5, 129.0, 129.5, 131.7, 133.3, 139.6, 145.4, 146.9, 147.3; MS (ESI) *m/z*: 326.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{22}H_{16}NO_2^+$ requires: 326.1176, Found: 326.1183.

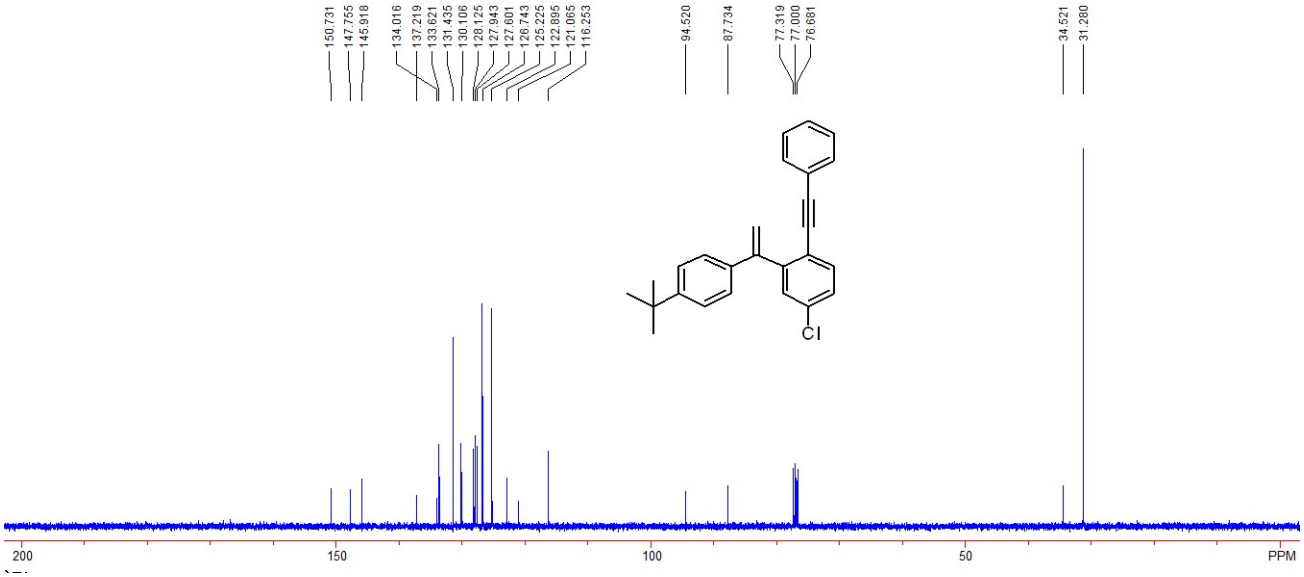


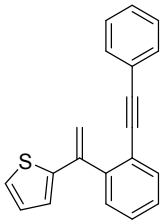




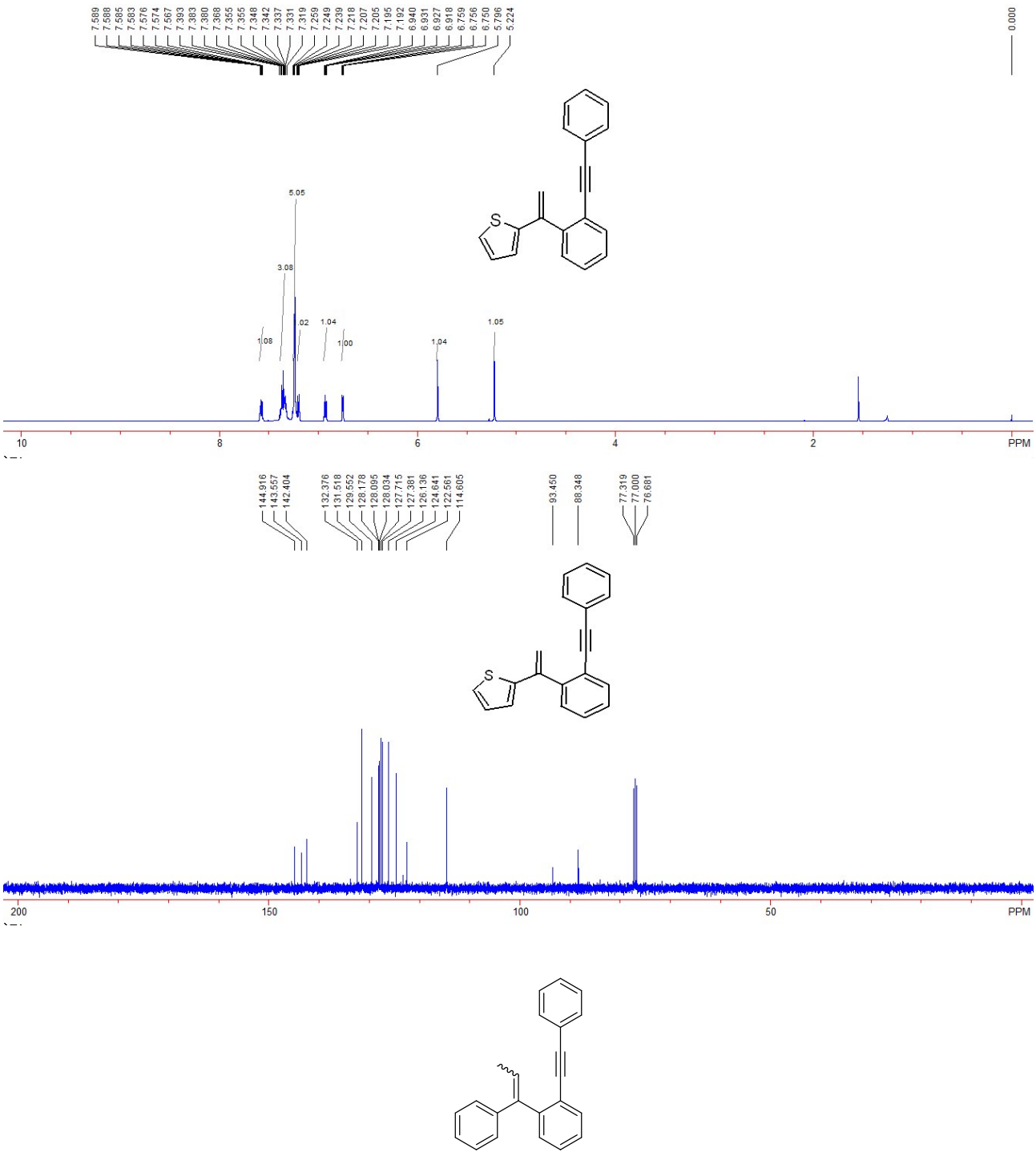
Compound 1e: 2.04 g, 55%, A colorless oil; IR (CH_2Cl_2): ν 3062, 2961, 2900, 2867, 1672, 1585, 1513, 1492, 1469, 1399, 1363, 1269, 1105, 1086, 908, 887, 840, 821, 754, 689 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.30 (s, 9H), 5.36 (s, 1H), 5.77 (s, 1H), 7.02 (dd, 2H, J_1 = 8.0 Hz, J_2 = 1.6 Hz), 7.16-7.22 (m, 3H), 7.26-7.30 (m, 3H), 7.33-7.37 (m, 3H), 7.46 (d, 1H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 31.3, 34.5, 87.7, 94.5, 116.3, 121.1, 122.9, 125.2, 126.7, 127.6, 127.9, 128.1, 130.1, 131.4, 133.6, 134.0, 137.2, 145.9, 147.8, 150.7; MS (ESI) *m/z*: 371.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{26}H_{24}Cl^+$ requires: 371.1561, Found: 371.1552.





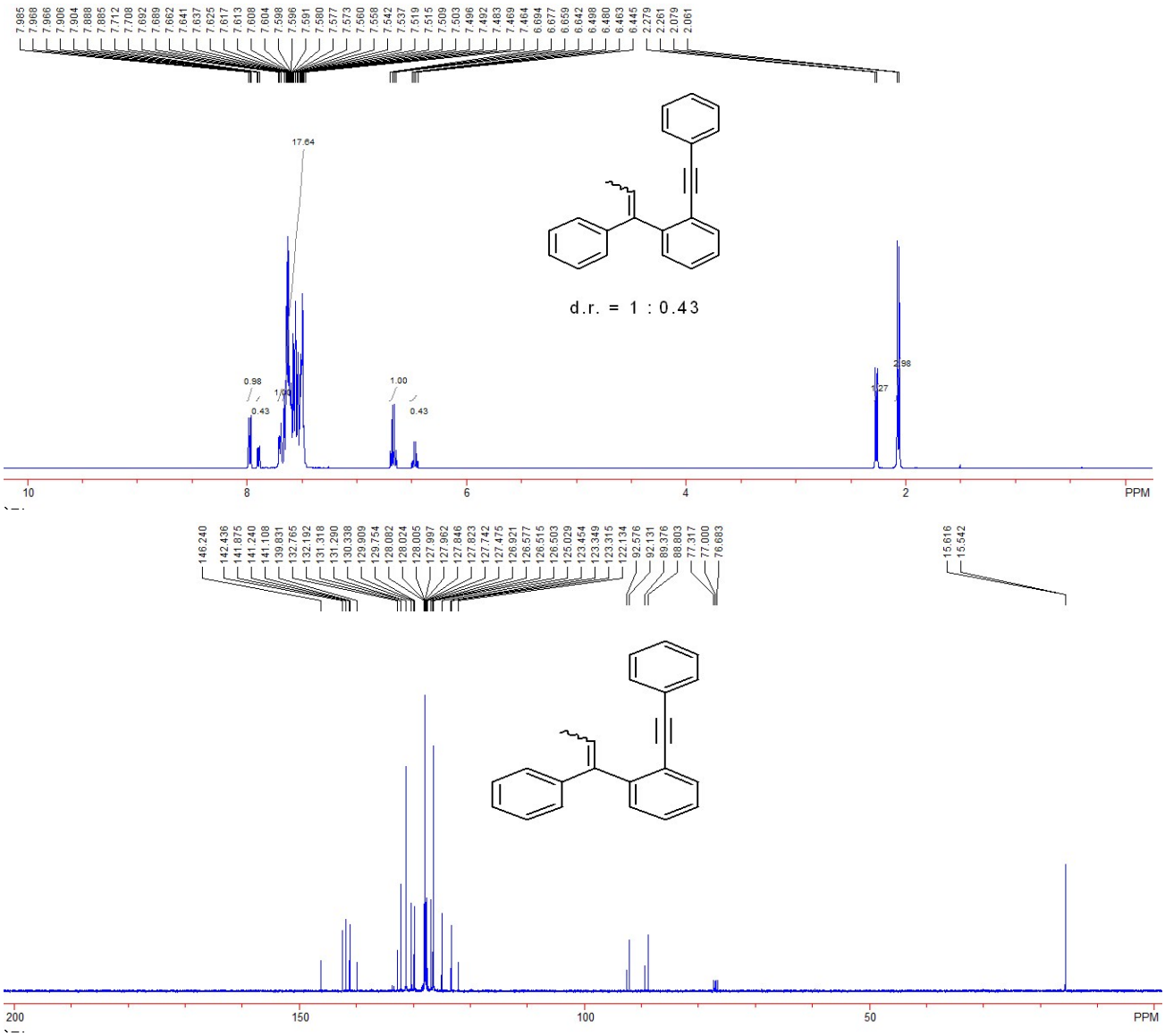


Compound 1g: 1.49 g, 52%, A colorless oil; IR (CH_2Cl_2): ν 3060, 3020, 2923, 1598, 1492, 1442, 1227, 1069, 892, 851, 755, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 5.22 (s, 1H), 5.80 (s, 1H), 6.75-6.76 (m, 1H), 6.92-6.94 (m, 1H), 7.19-7.22 (m, 1H), 7.24-7.26 (m, 5H), 7.32-7.39 (m, 3H), 7.57-7.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 88.3, 93.5, 114.6, 122.6, 124.6, 126.1, 127.4, 127.7, 128.0, 128.1, 128.2, 129.6, 131.5, 132.4, 142.4, 143.6, 144.9; MS (ESI) *m/z*: 287.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{20}H_{15}S^+$ requires: 287.0889, Found: 287.0903.



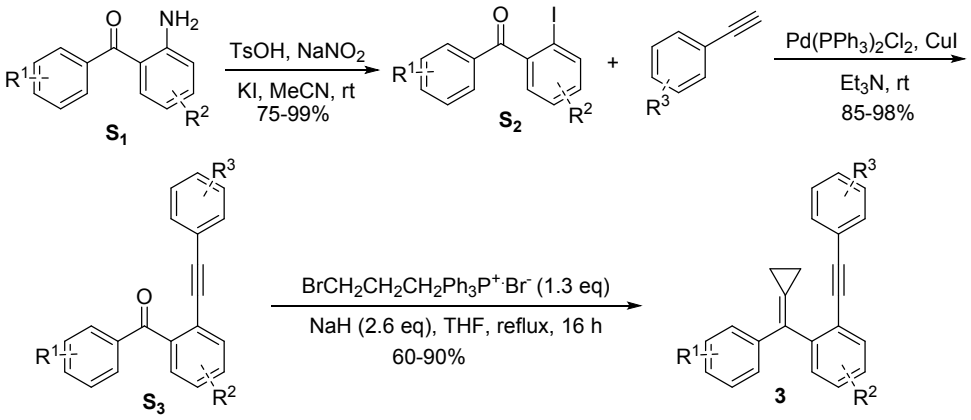
Compound 1h: 2.06 g, 70%, A colorless oil, obtained as a 1:0.43 mixture of isomers; IR (CH_2Cl_2): ν 3078, 3056, 3023, 2906, 1598, 1491, 1441, 1070, 1028, 965, 948, 900, 846, 752, 689 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 2.07 (d, 3H, J = 7.2 Hz), 2.27 (d, 1.29 H, J = 7.2 Hz), 6.47 (q, 0.43 H, J = 7.2 Hz), 6.67 (q, 1H, J = 7.2 Hz), 7.48-7.66 (m, 17.59H), 7.70 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.90 (dd, 0.43H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.97 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.5, 15.6, 88.8, 89.4, 92.1, 92.6, 122.1, 123.32, 123.35, 123.5, 125.0, 126.50, 126.52, 126.6, 126.9, 127.5, 127.7, 127.82, 127.85, 127.96, 128.00, 128.01, 128.02,

128.1, 129.8, 129.9, 130.3, 131.29, 131.32, 132.2, 132.8, 139.8, 141.1, 141.2, 141.9, 142.4, 146.2; MS (ESI) *m/z*: 295.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{23}H_{19}^+$ requires: 295.1481, Found: 295.1485.



General procedure for the synthesis of substrates 3

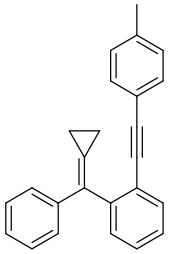
Compounds 3 were partially prepared according to previously reported work[3] and the corresponding spectroscopic data was consistent with those in the reported literature.



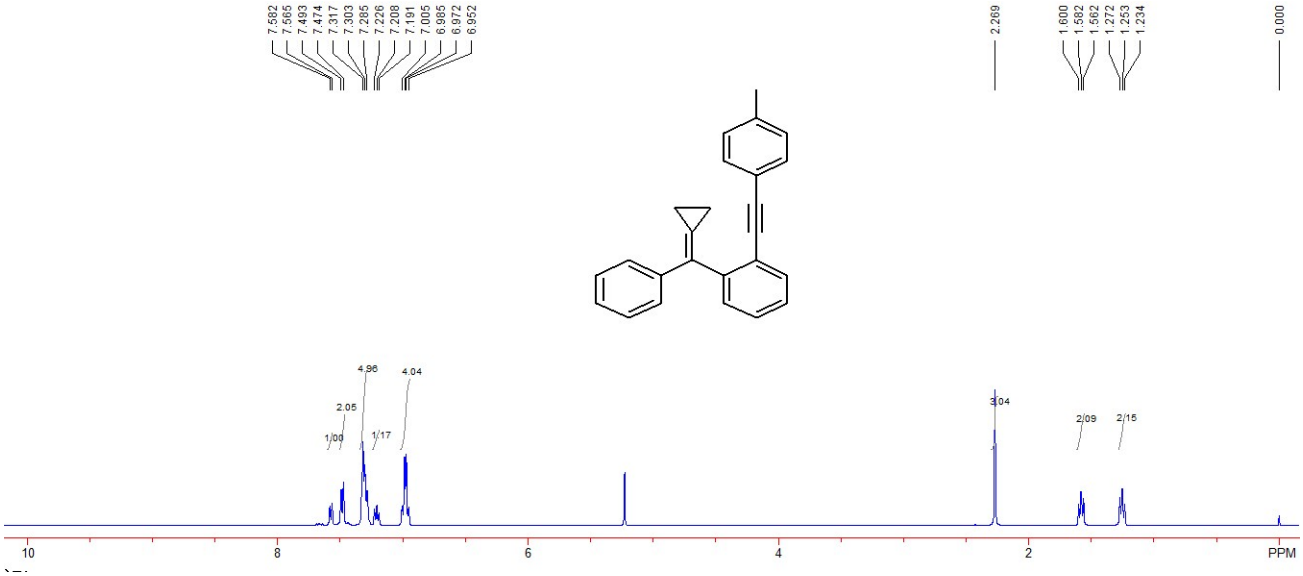
The procedures for the preparation of substrates $\mathbf{S_2}$ and $\mathbf{S_3}$ were shown as above.

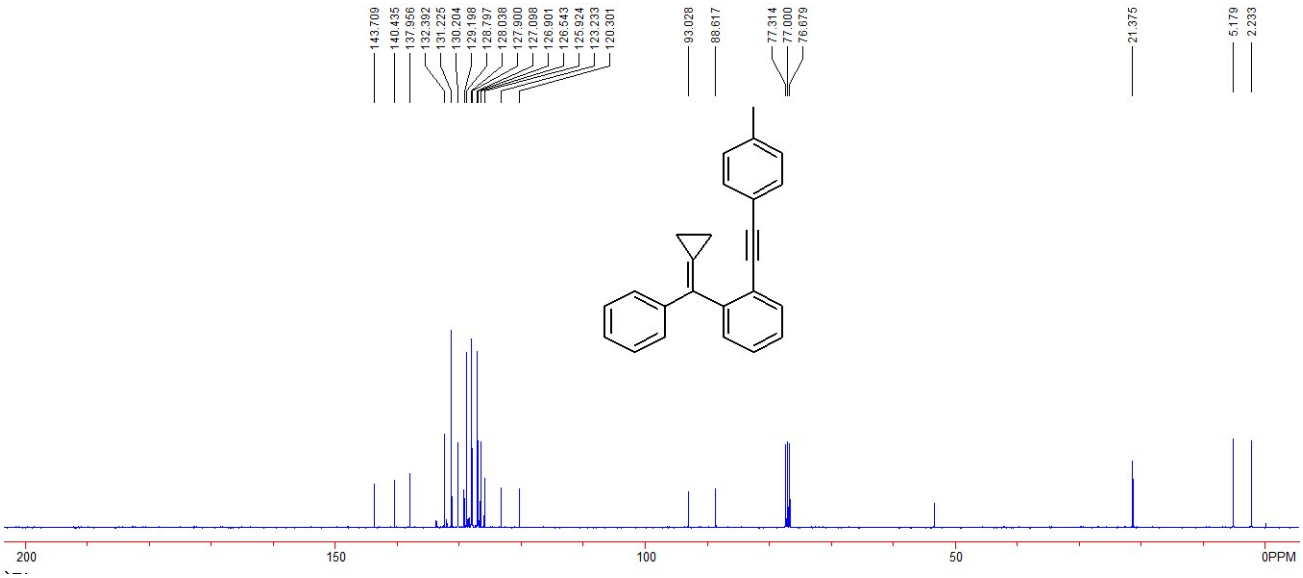
The synthesis of **3**: A solution of 3-bromopropyltriphenylphosphonium bromide (1.3 equiv) and NaH (2.6 equiv) in THF (5.0 mL) was stirred at 70 ^{o}C under N_2 for 8 h. Afterwards compound $\mathbf{S_3}$ (1.0 equiv) in THF (5.0 mL) was added and the reaction solution was stirred at 70 ^{o}C for another 8 h. Upon completion, the reaction was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether) to afford the products **3** in excellent yields ranging from 60% to 90%.

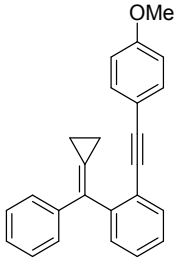
Spectroscopic data for substrates 3



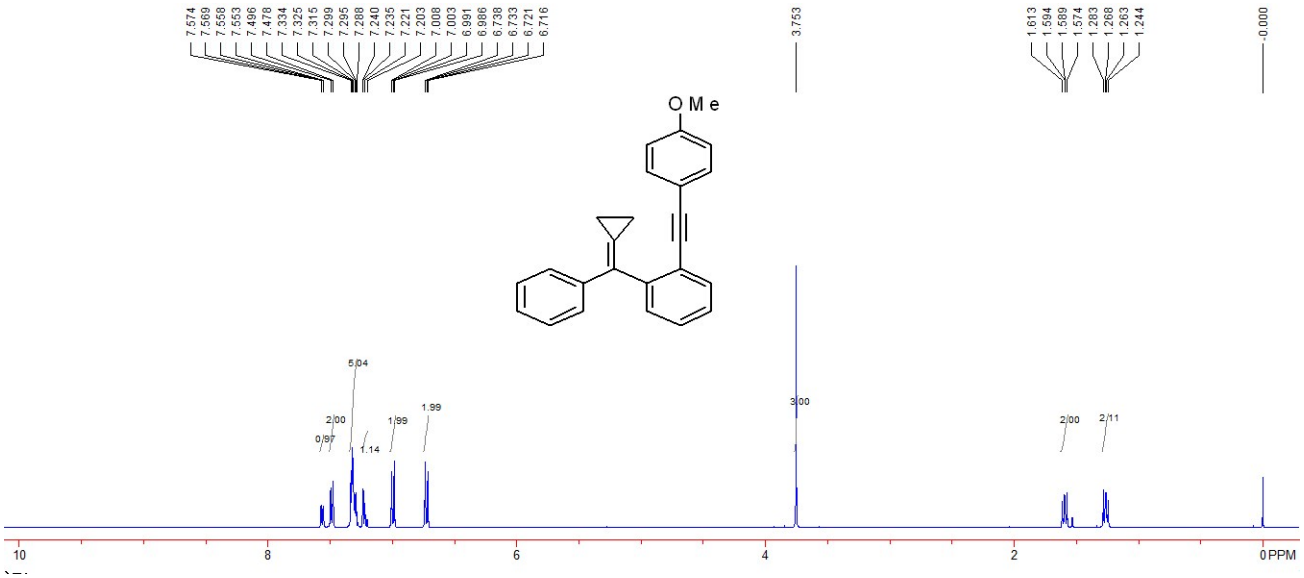
Compound 3b: 1.45 g, 45%, A colorless oil; IR (CH_2Cl_2): ν 3053, 3023, 2967, 2917, 2864, 1592, 1509, 1493, 1438, 1181, 1118, 1028, 904, 815, 755, 721, 693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.25 (t, 2H, *J* = 7.6 Hz), 1.58 (t, 2H, *J* = 7.6 Hz), 2.27 (s, 3H), 6.95-7.01 (m, 4H), 7.21 (t, 1H, *J* = 7.2 Hz), 7.29-7.32 (m, 5H), 7.48 (d, 2H, *J* = 7.6 Hz), 7.57 (d, 1H, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 2.2, 5.2, 21.4, 88.6, 93.0, 120.3, 123.2, 125.9, 126.5, 126.9, 127.1, 127.9, 128.0, 128.8, 129.2, 130.2, 131.2, 132.4, 138.0, 140.4, 143.7; MS (ESI) *m/z*: 321.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{25}H_{21}^+$ requires: 321.1638, Found: 321.1645.

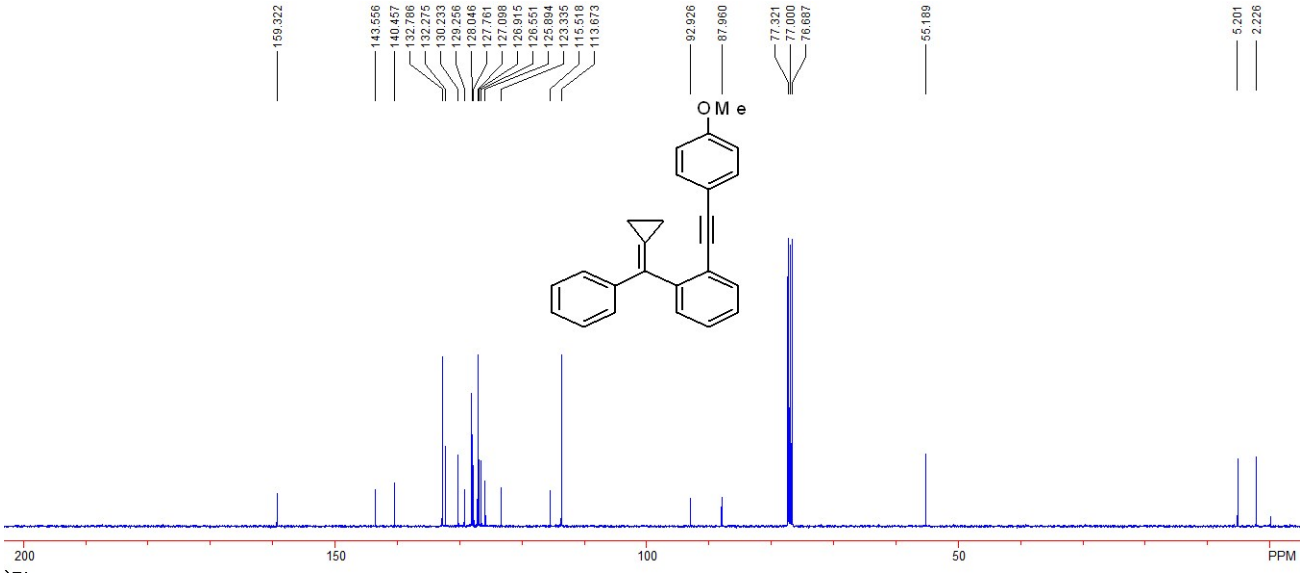


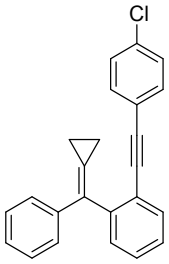




Compound 3c: 1.68 g, 50%, A colorless oil; IR (CH_2Cl_2): ν 3053, 2963, 2836, 1776, 1604, 1509, 1493, 1439, 1286, 1247, 1173, 1077, 1026, 830, 800, 756, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.24-1.28 (m, 2H), 1.57-1.61 (m, 2H), 3.75 (s, 3H), 6.73 (dd, 2H, J_1 = 6.8 Hz, J_2 = 2.0 Hz), 7.00 (dd, 2H, J_1 = 6.8 Hz, J_2 = 2.0 Hz), 7.20-7.24 (m, 1H), 7.29-7.33 (m, 5H), 7.49 (d, 2H, J = 7.2 Hz), 7.56 (dd, 1H, J_1 = 6.4 Hz, J_2 = 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 2.2, 5.2, 55.2, 88.0, 92.9, 113.7, 115.5, 123.3, 125.9, 126.6, 126.9, 127.1, 127.8, 128.0, 129.3, 130.2, 132.3, 132.8, 140.5, 143.6, 159.3; MS (ESI) *m/z*: 337.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{25}H_{21}O^+$ requires: 337.1587, Found: 337.1594.

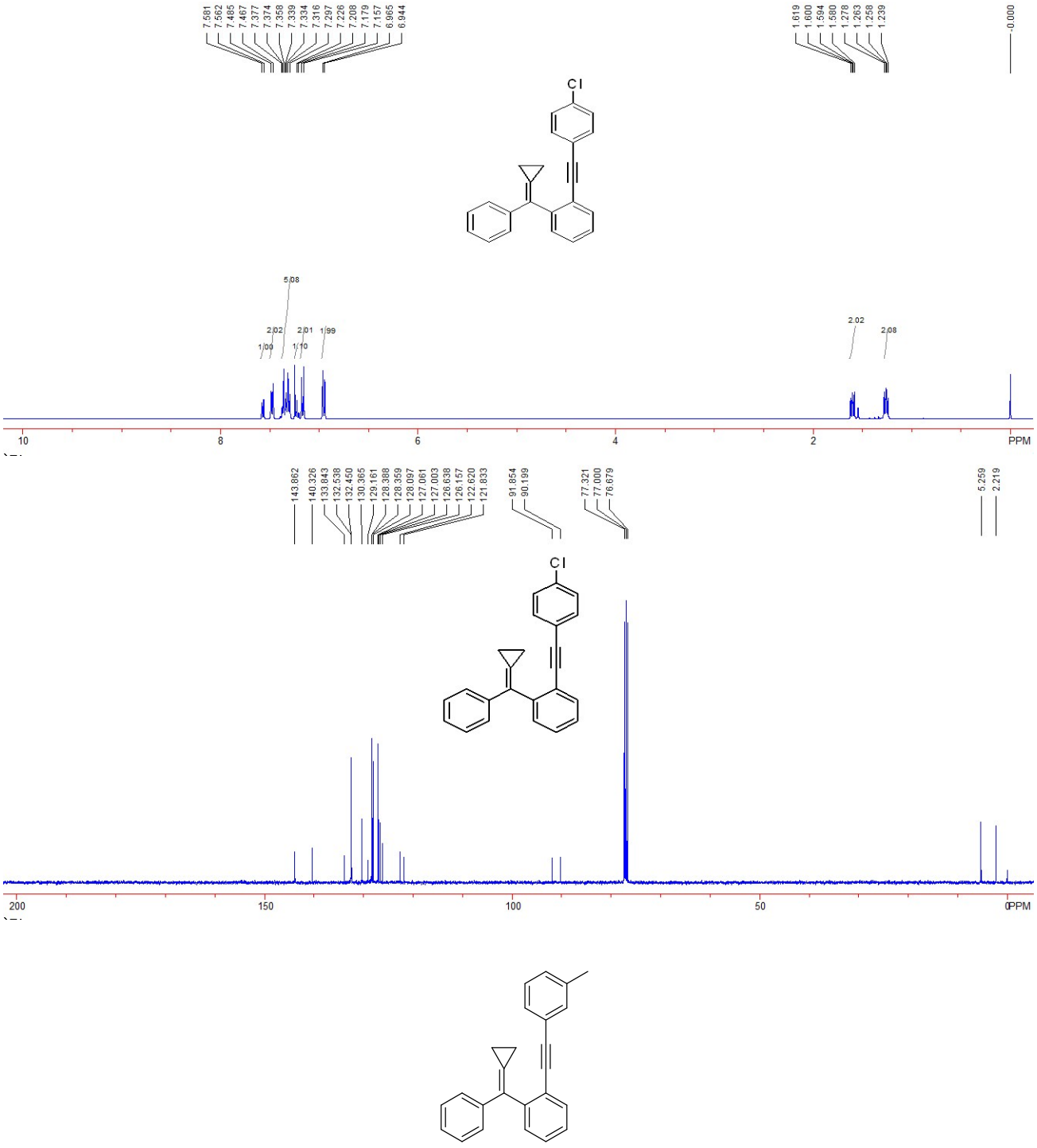






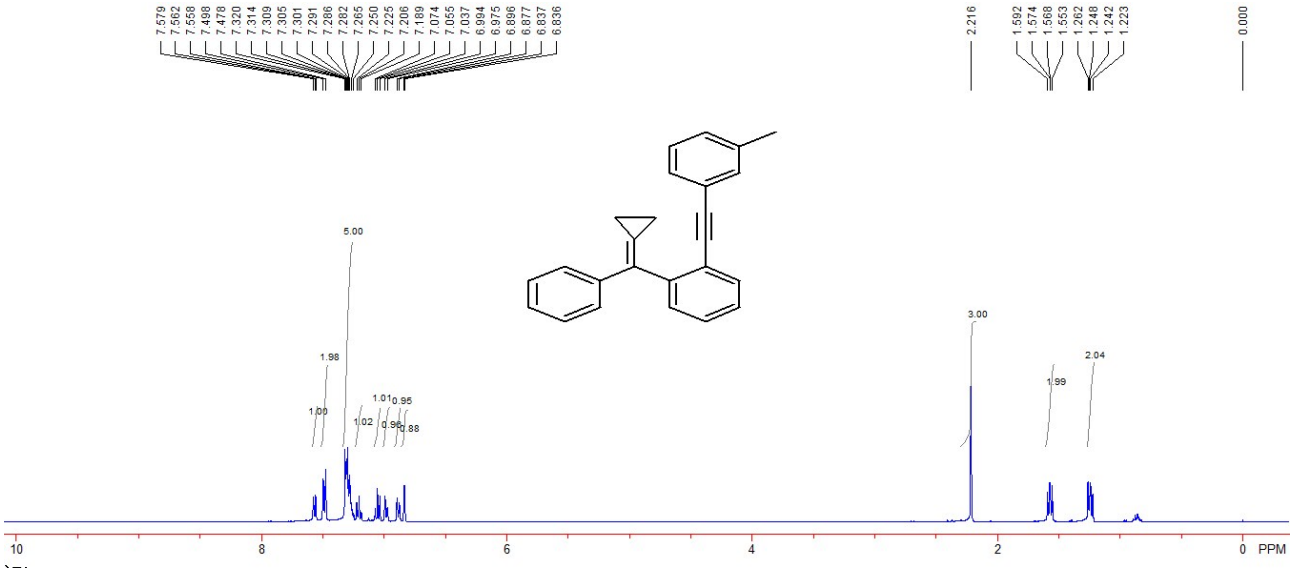
Compound 3d: 1.81 g, 53%, A colorless oil; IR (CH_2Cl_2): ν 3056, 3023, 2970, 1778, 1671, 1592, 1491, 1445, 1263, 1089, 1013, 827, 756, 734, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.24-1.28 (m, 2H), 1.58-1.62 (m, 2H), 6.95 (d, 2H, J = 8.4 Hz), 7.17 (d, 2H, J = 8.8 Hz), 7.22 (d, 1H, J = 7.2 Hz), 7.30-7.38 (m, 5H), 7.48 (d, 2H, J = 7.2 Hz), 7.57 (d, 1H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 2.2, 5.3, 90.2, 91.9, 121.8, 122.6, 126.2, 126.6, 127.0, 127.1, 128.1, 128.36, 128.39,

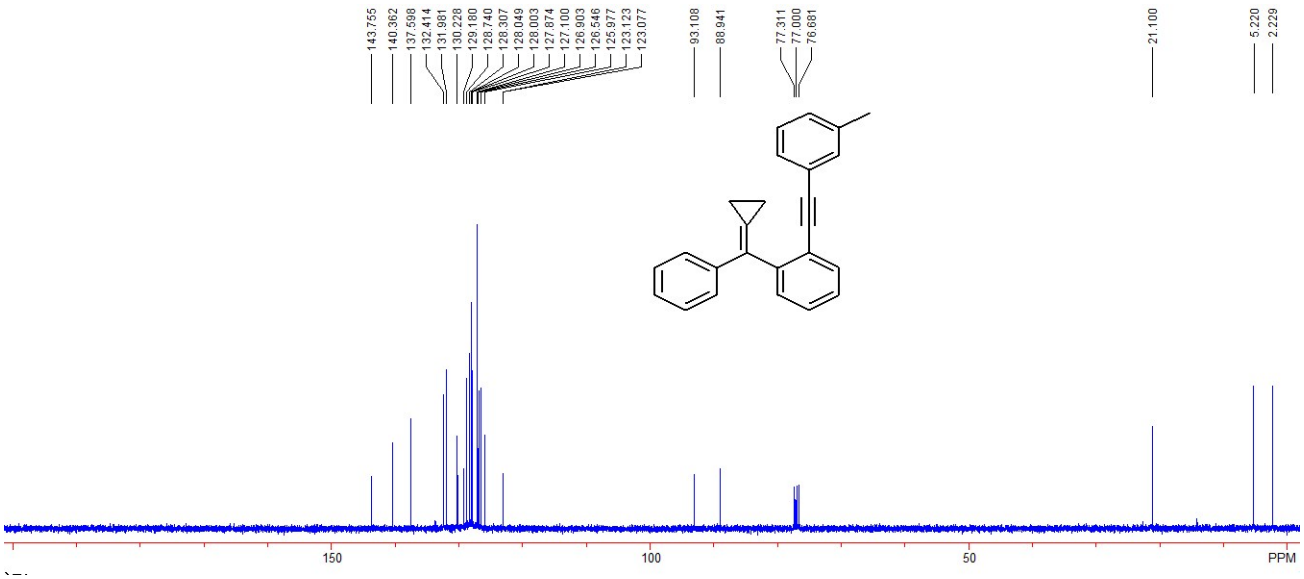
129.2, 130.4, 132.45, 132.54, 133.8, 140.3, 143.9; MS (ESI) *m/z*: 341.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{24}H_{18}Cl^+$ requires: 341.1092, Found: 341.1094.

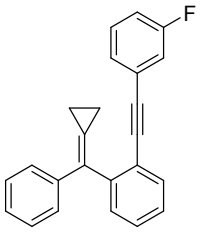


Compound 3e: 1.86 g, 58%, A colorless oil; IR (CH_2Cl_2): ν 3056, 3023, 2970, 2914, 1781, 1599, 1575, 1489, 1444, 1157, 900, 783, 756, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.22-1.26 (m, 2H), 1.55-1.59 (m, 2H), 2.22 (s, 3H), 6.84 (d, 1H, J = 0.4 Hz), 6.89 (d, 1H, J = 7.6 Hz), 6.98 (d, 1H, J = 7.6 Hz), 7.06 (t, 1H, J = 7.6 Hz), 7.21 (t, 1H, J = 7.6 Hz), 7.25-7.32 (m, 5H), 7.49 (d, 2H, J = 8.0 Hz), 7.57 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 2.2, 5.2,

21.1, 88.9, 93.1, 123.07, 123.12, 126.0, 126.5, 126.9, 127.1, 127.9, 128.00, 128.05, 128.3, 128.7, 129.2, 130.2, 132.0, 132.4, 137.6, 140.4, 143.8; MS (ESI) *m/z*: 321.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{25}H_{21}^+$ requires: 321.1638, Found: 321.1647.

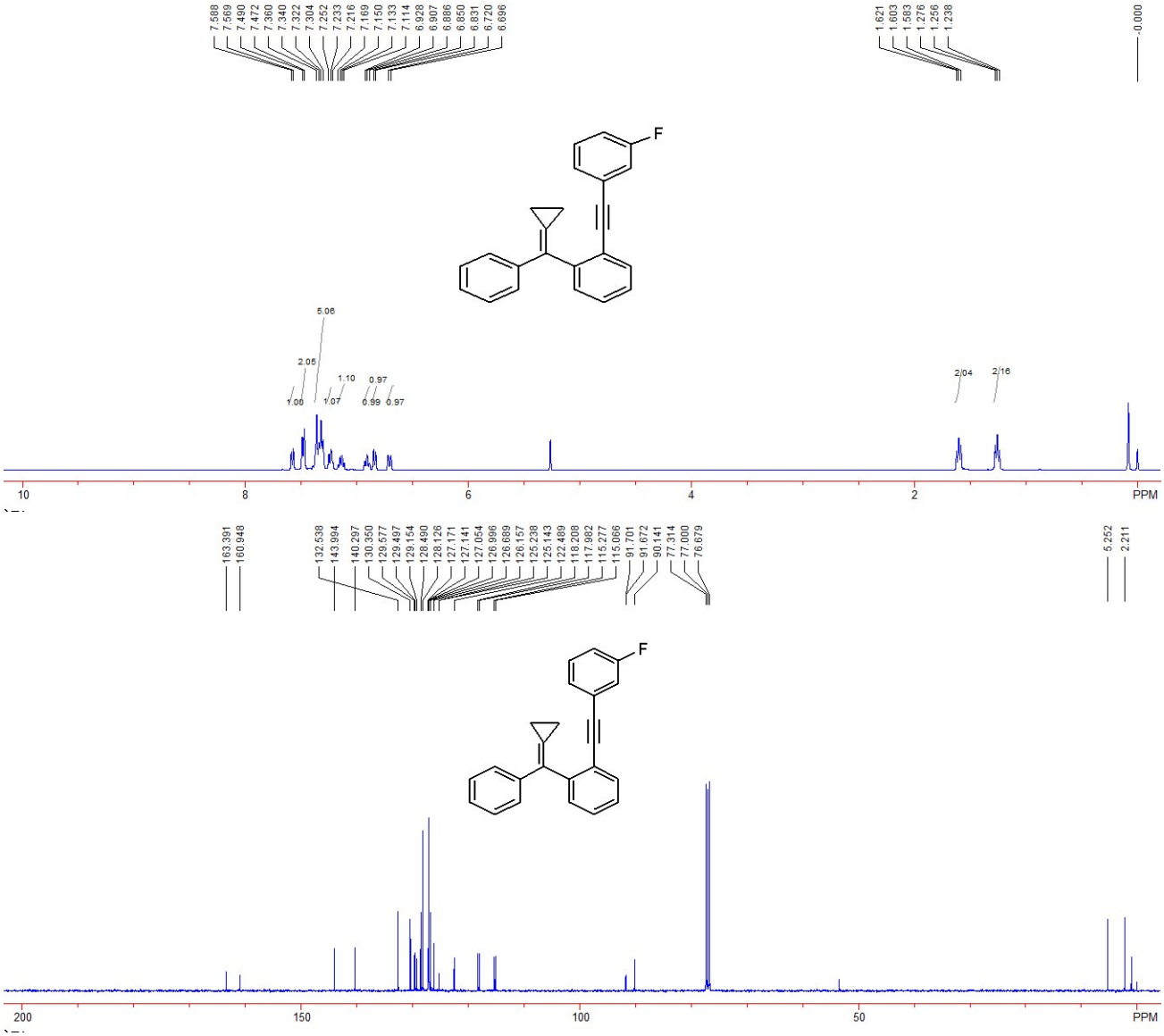


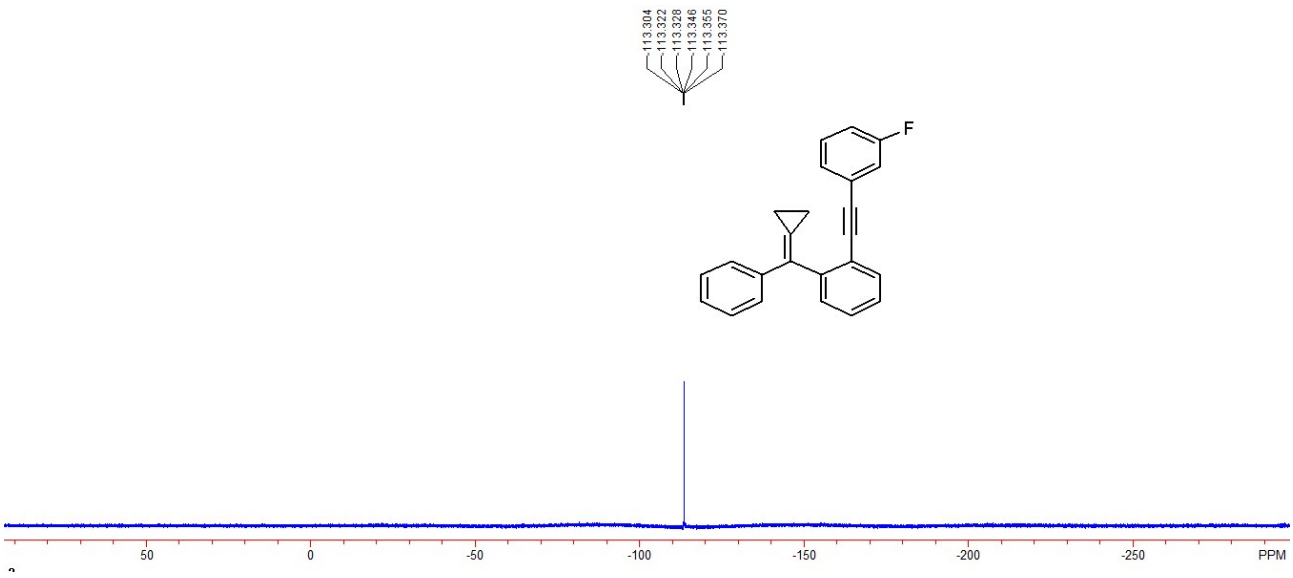


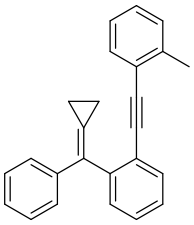


Compound 3f: 1.40 g, 43%, A colorless oil; IR (CH_2Cl_2): ν 3065, 2964, 2903, 1775, 1607, 1575, 1490, 1442, 1260, 1078, 1014, 942, 867, 790, 774, 755, 695, 673 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.26 (t, 2H, *J* = 7.6 Hz), 1.60 (t, 2H, *J* = 7.6 Hz), 6.71 (d, 1H, *J* = 9.6 Hz), 6.84 (d, 1H, *J* = 7.6 Hz), 6.91 (t, 1H, *J* = 8.4 Hz), 7.11-7.17 (m, 1H), 7.23 (t, 1H, *J* = 7.6 Hz), 7.30-7.36 (m, 5H),

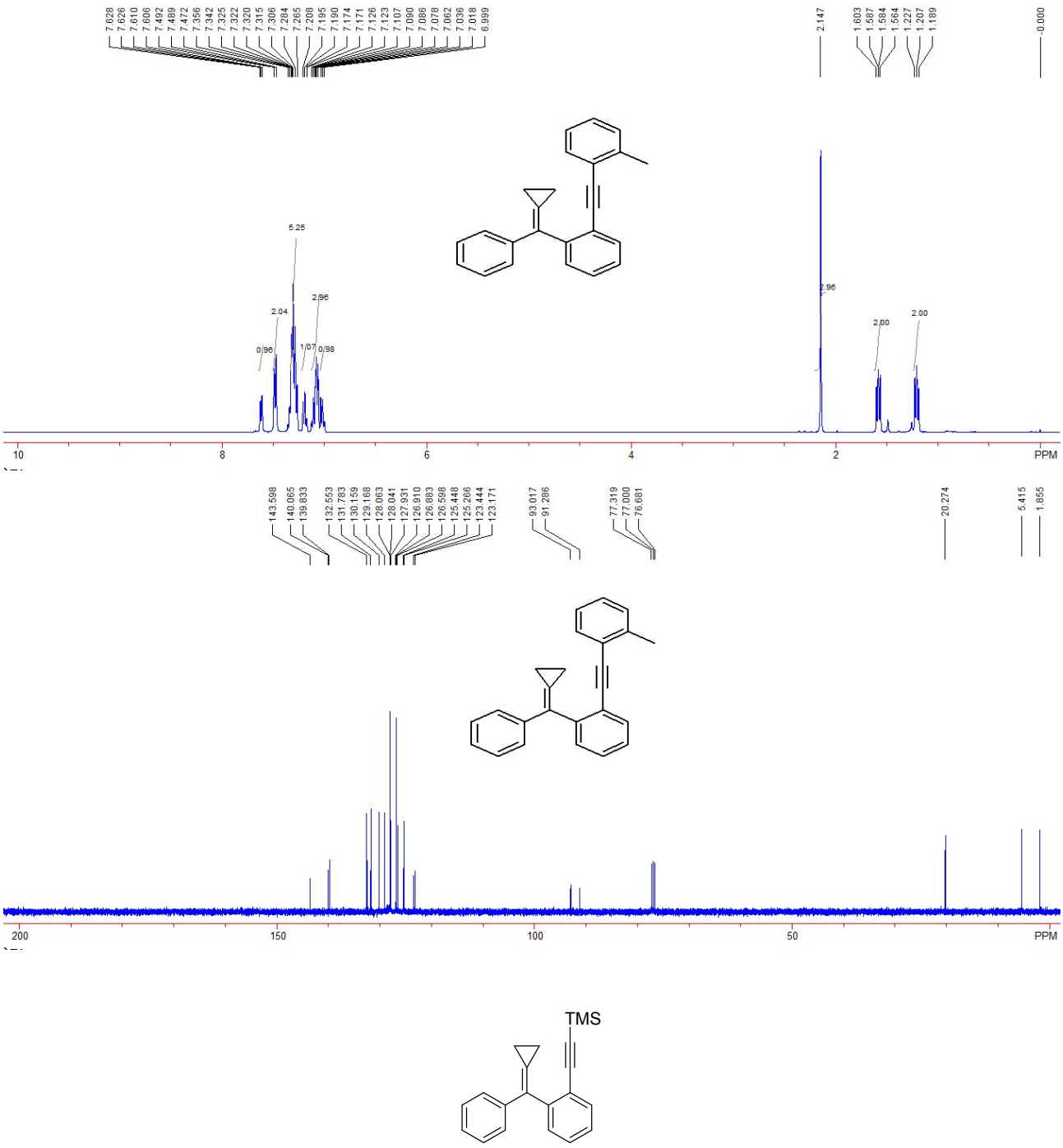
7.48 (d, 2H, J = 7.2 Hz), 7.58 (d, 1H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 2.2, 5.3, 90.1, 91.7 (d, $J_{C\text{-}F}$ = 2.9 Hz), 115.2 (d, $J_{C\text{-}F}$ = 21.1 Hz), 118.1 (d, $J_{C\text{-}F}$ = 22.6 Hz), 122.5, 125.2 (d, $J_{C\text{-}F}$ = 19.5 Hz), 126.2, 126.7, 127.0, 127.1, 127.2 (d, $J_{C\text{-}F}$ = 3.0 Hz), 128.1, 128.5, 129.2, 129.5 (d, $J_{C\text{-}F}$ = 8.0 Hz), 130.4, 132.5, 140.3, 144.0, 162.2 (d, $J_{C\text{-}F}$ = 244.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -113.3 (td, 1F, J_1 = 9.0 Hz, J_2 = 6.8 Hz); (ESI) *m/z*: 325.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{24}H_{18}F^+$ requires: 325.1387, Found: 325.1392.



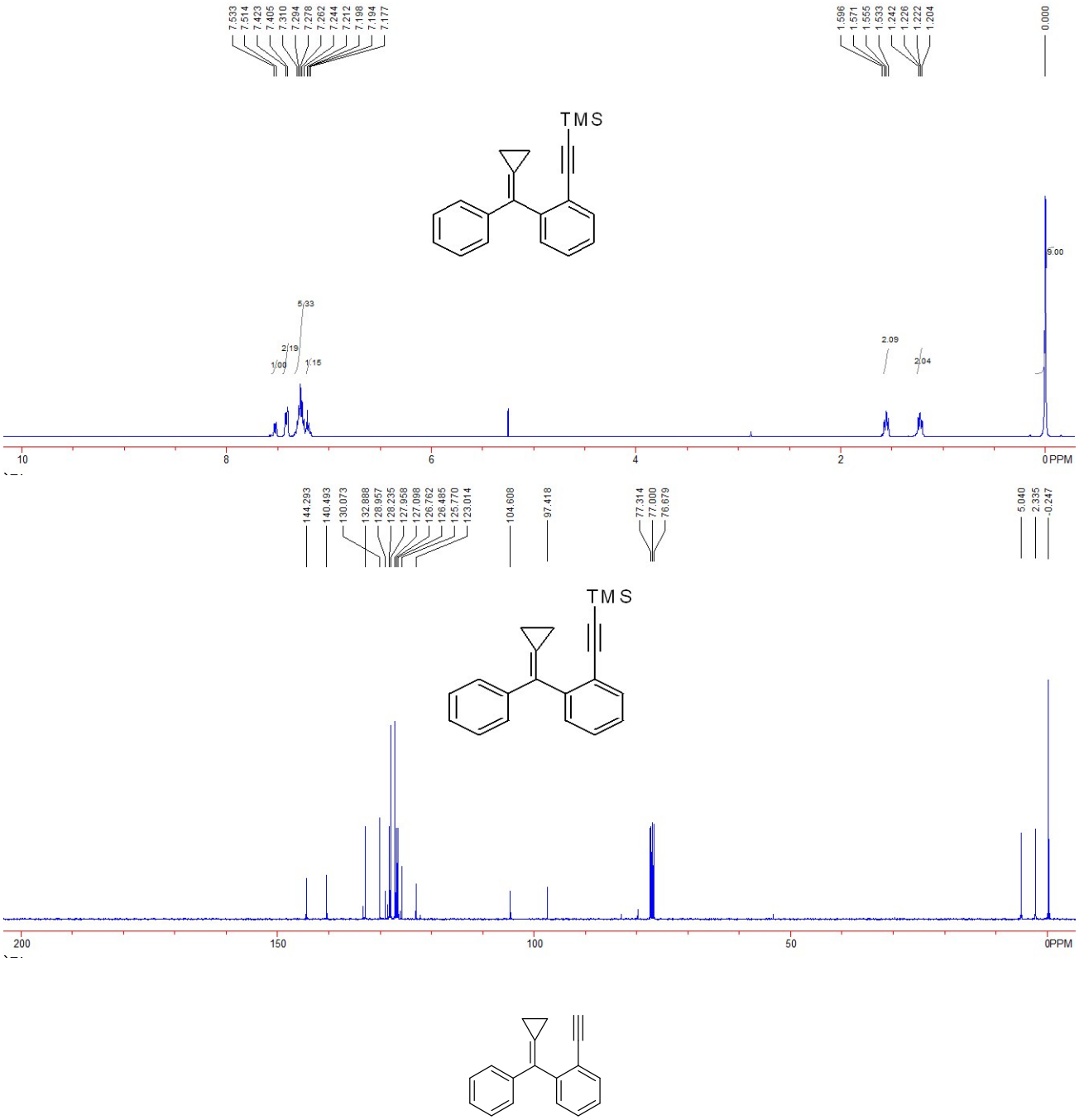




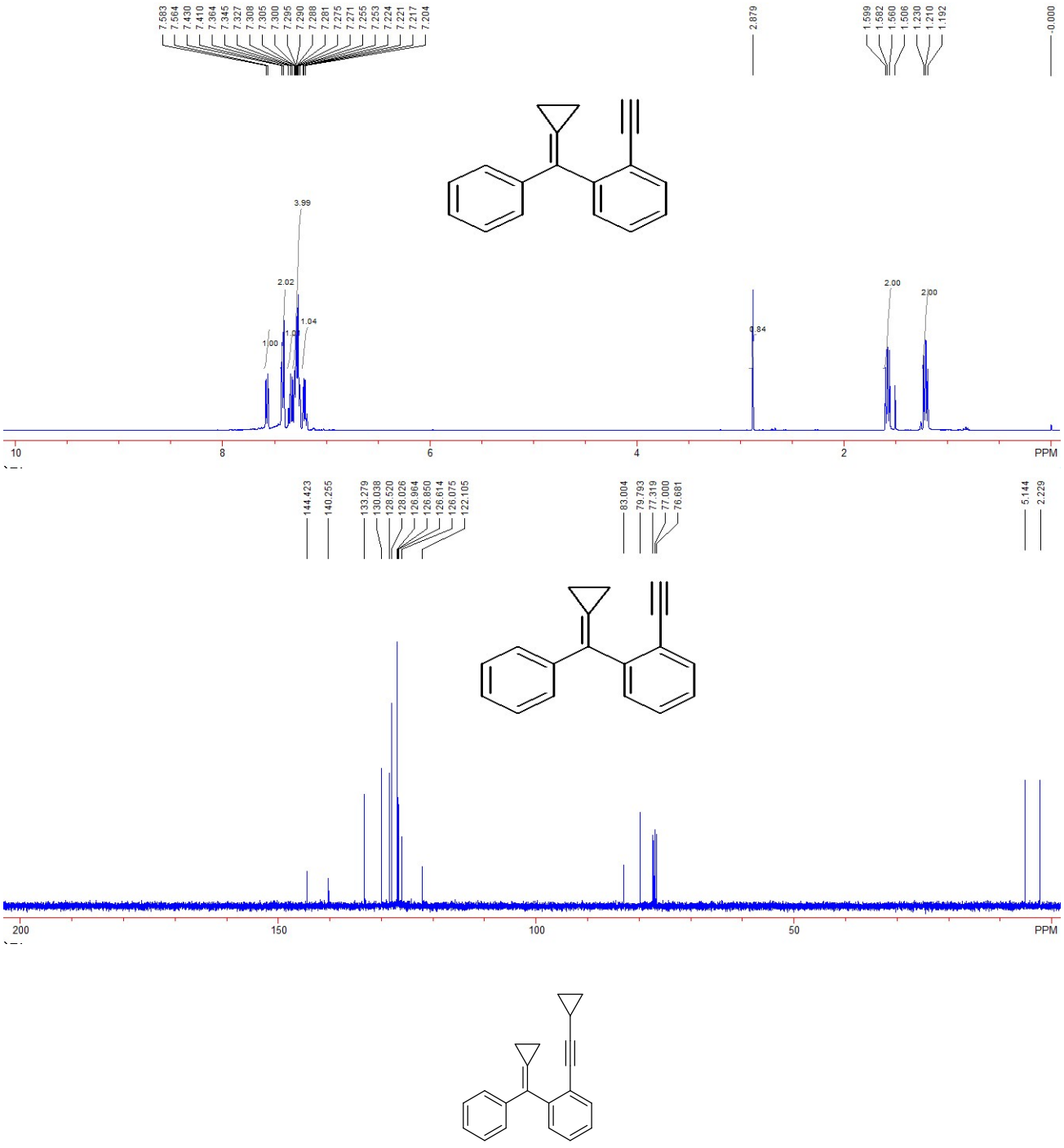
Compound 3g: 867 mg, 27%, A colorless oil; IR (CH_2Cl_2): ν 3055, 3020, 2970, 2917, 1597, 1492, 1437, 1183, 1119, 1028, 897, 755, 721, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.19-1.23 (m, 2H), 1.56-1.60 (m, 2H), 2.15 (s, 3H), 7.02 (t, 1H, J = 7.6 Hz), 7.06-7.13 (m, 3H), 7.17-7.21 (m, 1H), 7.27-7.36 (m, 5H), 7.48 (dd, 2H, J_1 = 8.0 Hz, J_2 = 1.2 Hz), 7.62 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 1.9, 5.4, 20.3, 91.3, 93.0, 123.2, 123.4, 125.3, 125.4, 126.6, 126.88, 126.91, 127.9, 128.0, 128.1, 129.2, 130.2, 131.8, 132.6, 139.8, 140.1, 143.6; MS (ESI) *m/z*: 321.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{25}H_{21}^+$ requires: 321.1638, Found: 321.1644.



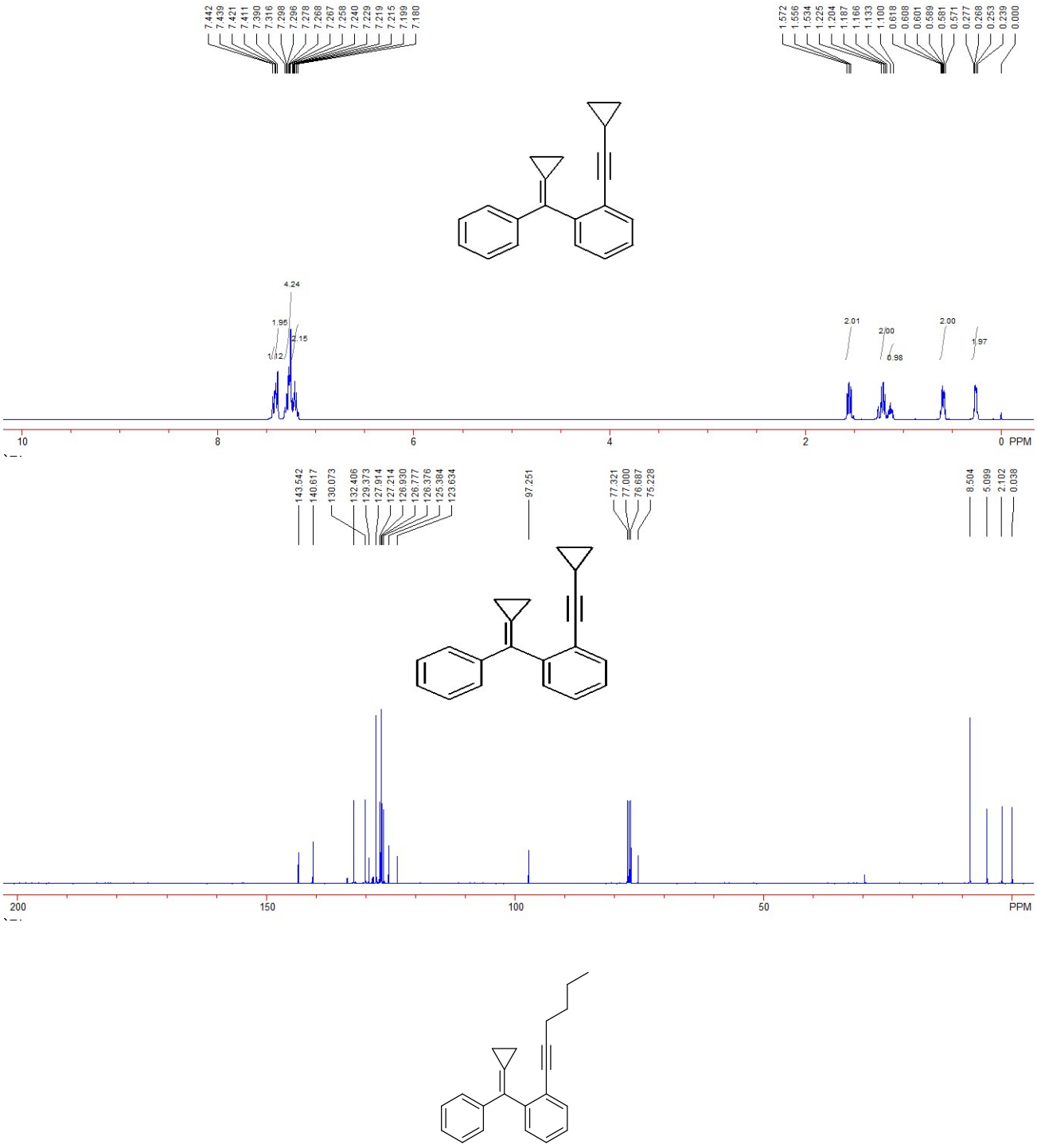
Compound 3h: 728 mg, 24%, A colorless oil; IR (CH_2Cl_2): ν 3062, 3026, 2959, 2897, 2155, 1778, 1494, 1446, 1248, 1077, 906, 860, 839, 757, 693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.00 (s, 9H), 1.20-1.24 (m, 2H), 1.53-1.60 (m, 2H), 7.18-7.21 (m, 1H), 7.24-7.31 (m, 5H), 7.41 (d, 2H, *J* = 7.2 Hz), 7.52 (d, 1H, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ -0.2, 2.3, 5.0, 97.4, 104.6, 123.0, 125.8, 126.5, 126.8, 127.1, 128.0, 128.2, 129.0, 130.1, 132.9, 140.5, 144.3; MS (ESI) *m/z*: 303.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{21}H_{23}Si^+$ requires: 303.1564, Found: 303.1568.



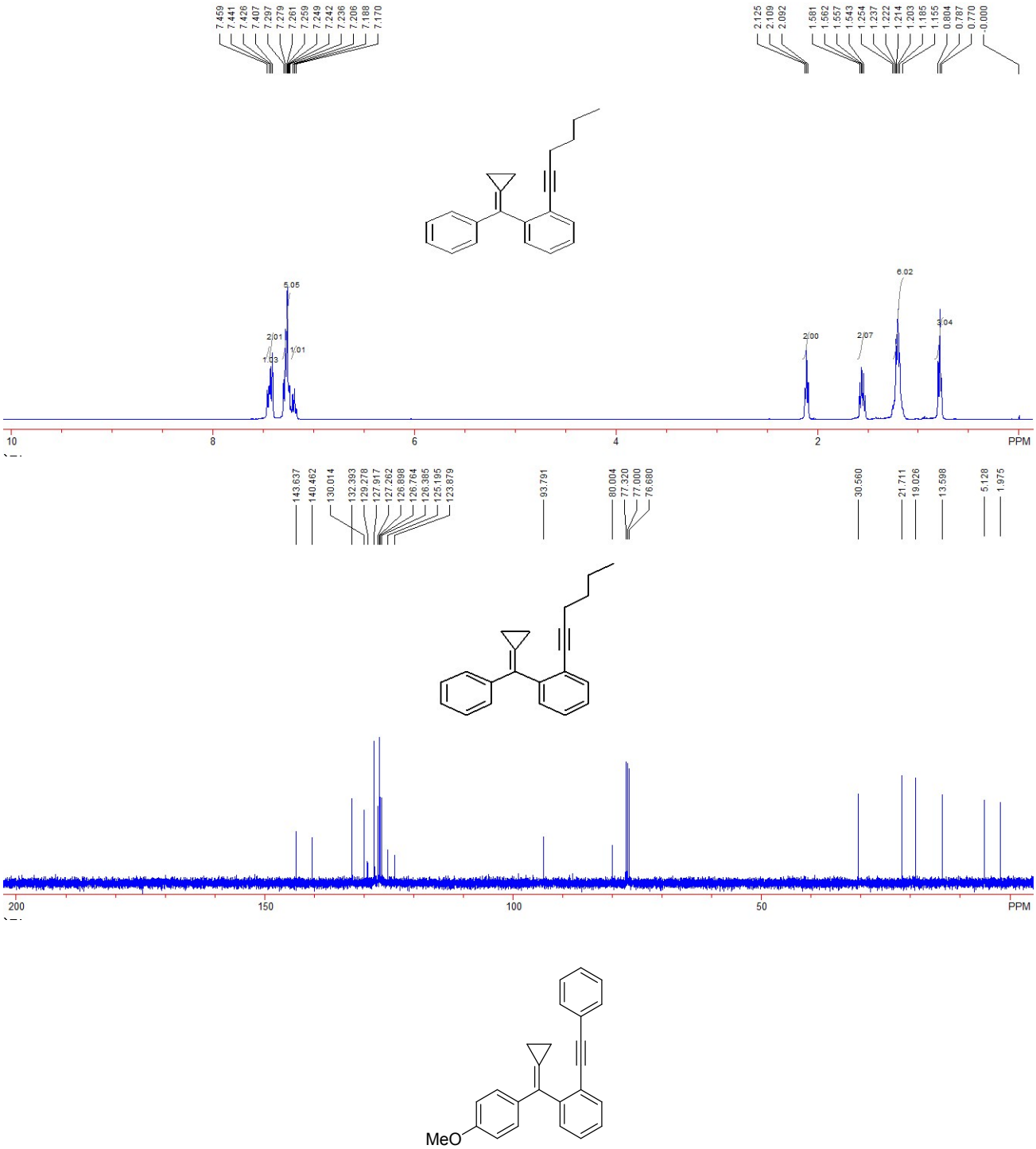
Compound 3h': 462 mg, 20%, A colorless oil; IR (CH_2Cl_2): ν 3059, 3023, 2917, 2845, 1776, 1723, 1596, 1493, 1478, 1446, 1157, 1076, 898, 758, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.19-1.23 (m, 2H), 1.51-1.60 (m, 2H), 2.88 (s, 1H), 7.20-7.22 (m, 1H), 7.25-7.31 (m, 4H), 7.35 (t, 1H, J = 7.6 Hz), 7.42 (d, 2H, J = 8.0 Hz), 7.57 (d, 1H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 2.2, 5.1, 79.8, 83.0, 122.1, 126.1, 126.6, 126.9, 127.0, 128.0, 128.5, 130.0, 133.3, 140.3, 144.4; MS (ESI) *m/z*: 231.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{18}H_{15}^+$ requires: 231.1169, Found: 231.1178.



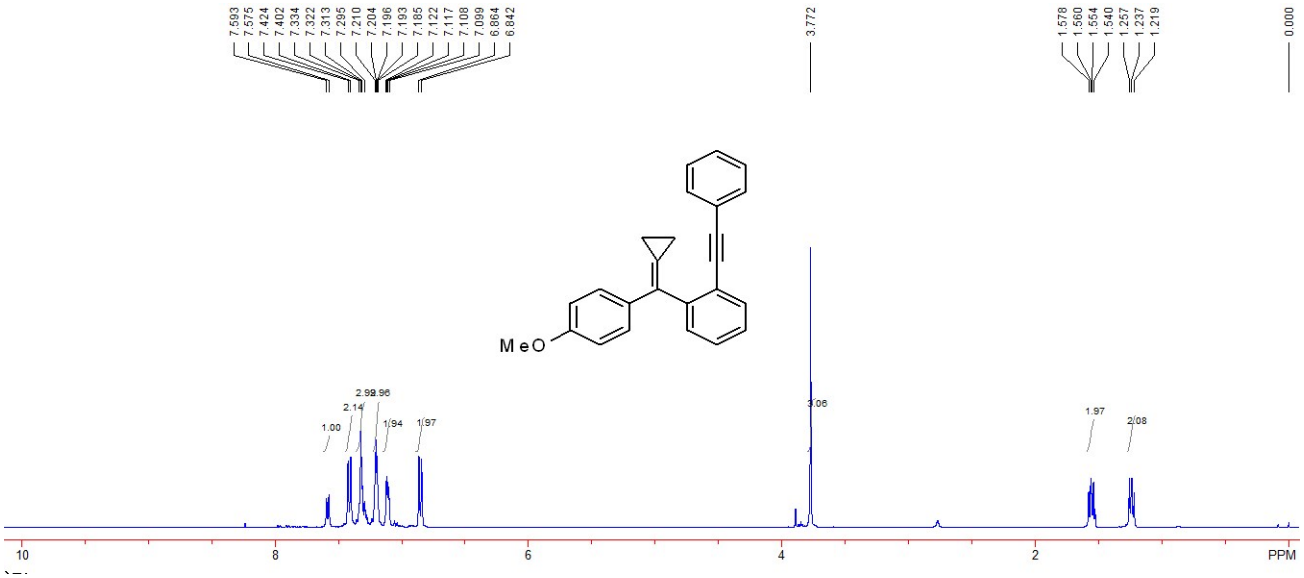
Compound 3i: 1.33 g, 49%, A colorless oil; IR (CH_2Cl_2): ν 3081, 3053, 3009, 2970, 1778, 1494, 1479, 1441, 1051, 1043, 1031, 954, 903, 843, 825, 811, 768, 755, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.24-0.28 (m, 2H), 0.57-0.62 (m, 2H), 1.10-1.13 (m, 1H), 1.17-1.23 (m, 2H), 1.53-1.57 (m, 2H), 7.18-7.23 (m, 2H), 7.24-7.32 (m, 4H), 7.39-7.44 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 0.0, 2.1, 5.1, 8.5, 75.2, 97.3, 123.6, 125.4, 126.4, 126.8, 126.9, 127.2, 127.9, 129.4, 130.1, 132.4, 140.6, 143.5; MS (ESI) *m/z*: 271.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{21}H_{19}^+$ requires: 271.1481, Found: 271.1494.

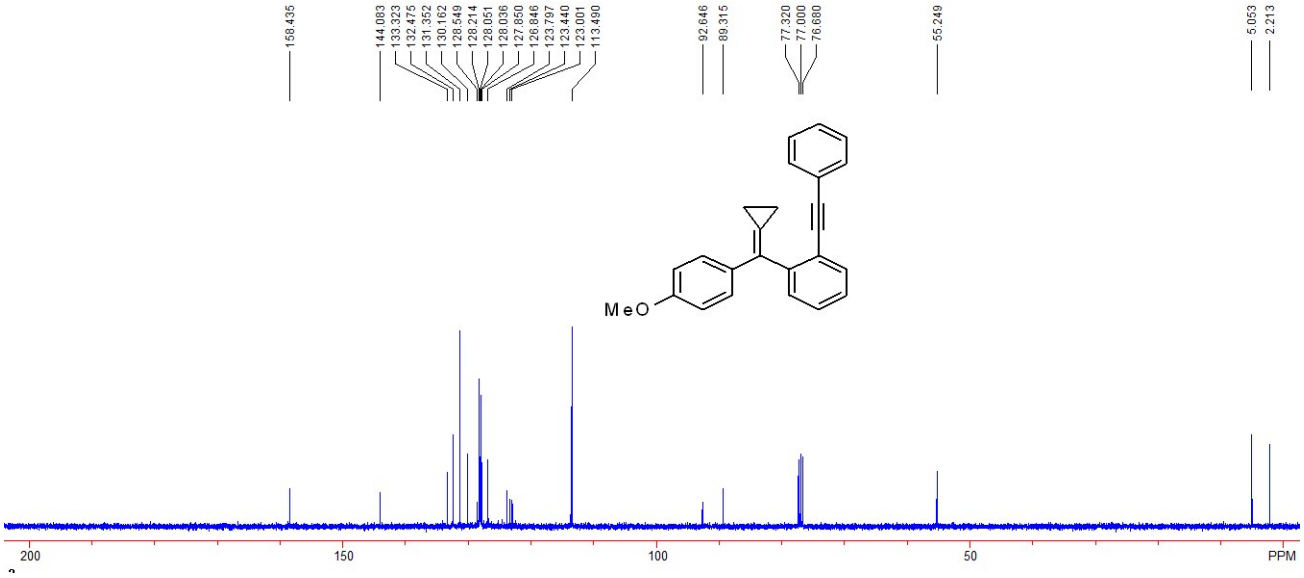


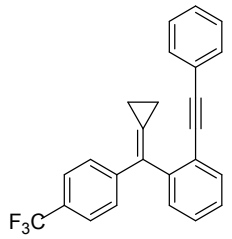
Compound 3j: 948 mg, 33%, A colorless oil; IR (CH_2Cl_2): ν 3062, 2957, 2930, 2871, 1778, 1597, 1481, 1465, 1446, 1286, 1076, 1054, 1026, 757, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.79 (t, 3H, *J* = 6.8 Hz), 1.16-1.25 (m, 6H), 1.54-1.58 (m, 2H), 2.11 (t, 2H, *J* = 6.8 Hz), 7.19 (t, 1H, *J* = 7.2 Hz), 7.24-7.30 (m, 5H), 7.42 (d, 2H, *J* = 7.6 Hz), 7.45 (d, 1H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 2.0, 5.1, 13.6, 19.0, 21.7, 30.6, 80.0, 93.8, 123.9, 125.2, 126.4, 126.8, 126.9, 127.3, 127.9, 129.3, 130.0, 132.4, 140.5, 143.6; MS (ESI) *m/z*: 287.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{22}H_{23}^+$ requires: 287.1795, Found: 287.1805.



Compound 3l: 2.02 g, 60%, A colorless oil; IR (CH_2Cl_2): ν 3053, 2967, 2925, 2833, 1775, 1664, 1599, 1508, 1493, 1463, 1441, 1300, 1246, 1175, 1030, 827, 755, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.22-1.26 (m, 2H), 1.54-1.58 (m, 2H), 3.77 (s, 3H), 6.85 (d, 2H, J = 8.0 Hz), 7.10-7.12 (m, 2H), 7.19-7.21 (m, 3H), 7.30-7.33 (m, 3H), 7.41 (d, 2H, J = 8.8 Hz), 7.58 (d, 1H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 2.2, 5.1, 55.2, 89.3, 92.6, 113.5, 123.0, 123.4, 123.8, 126.8, 127.9, 128.0, 128.1, 128.2, 128.5, 130.2, 131.4, 132.5, 133.3, 144.1, 158.4; MS (ESI) *m/z*: 337.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{25}H_{21}O^+$ requires: 337.1587, Found: 337.1584.

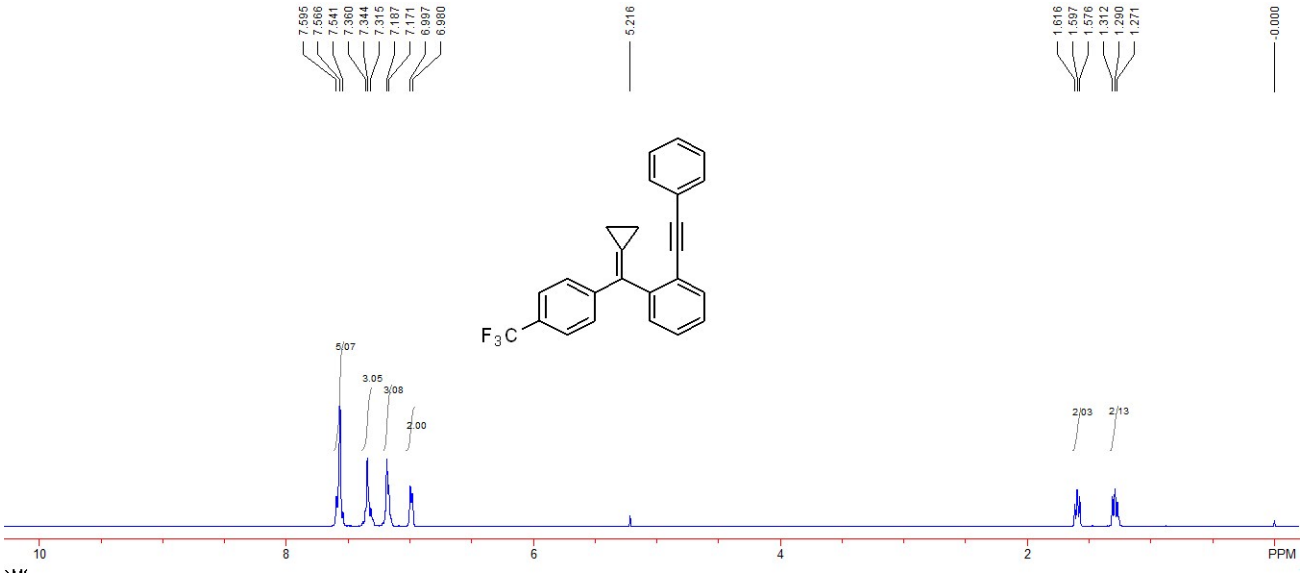


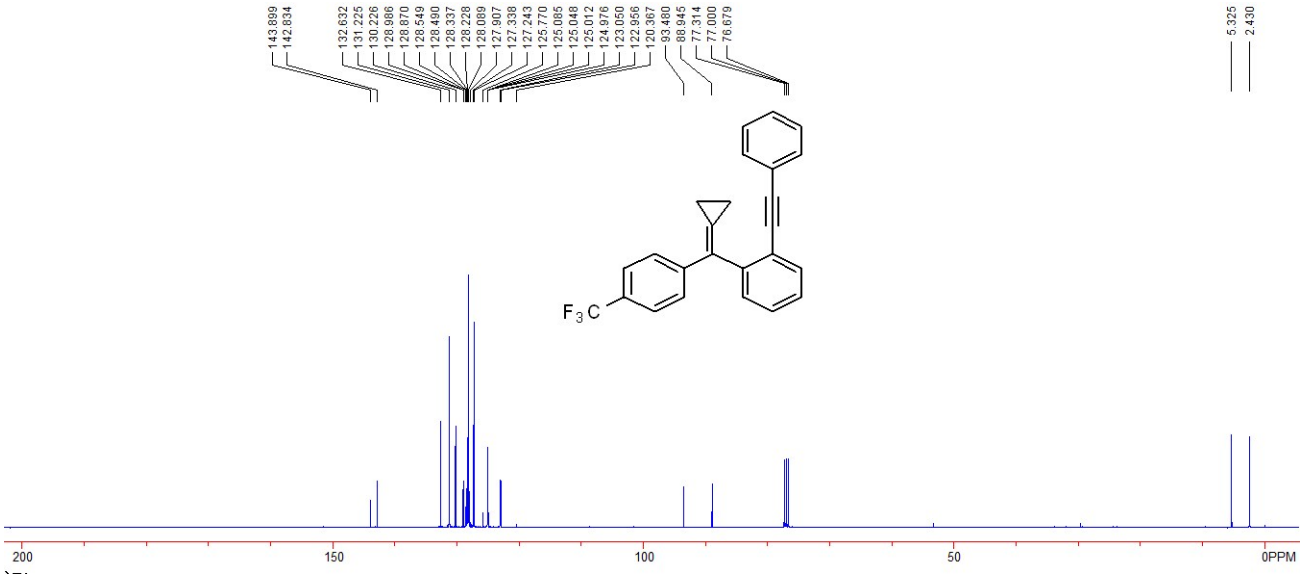


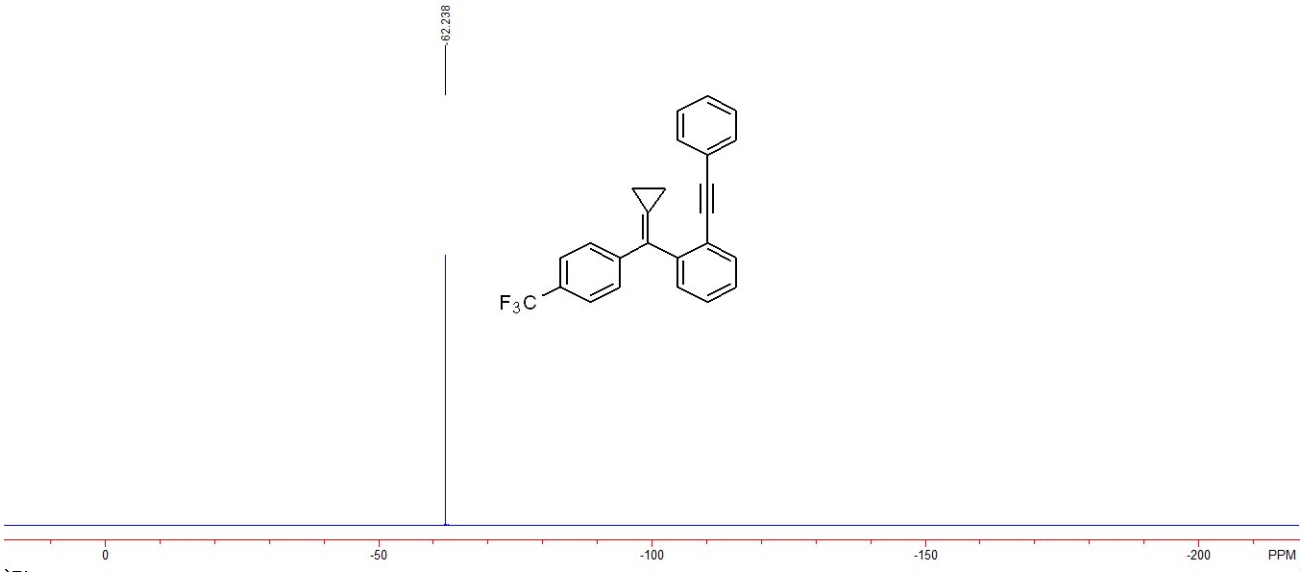


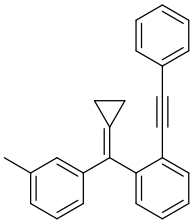
Compound 3n: 1.31 g, 35%, A colorless oil; IR (CH_2Cl_2): ν 3062, 3023, 2970, 1612, 1492, 1407, 1321, 1166, 1157, 1110, 1066, 1016, 858, 752, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.29 (t, 2H, J = 7.6 Hz), 1.60 (t, 2H, J = 7.6 Hz), 6.99 (d, 2H, J = 6.8 Hz), 7.17-7.19 (m, 3H), 7.32-7.36 (m, 3H), 7.54-7.60 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 2.4, 5.3, 88.9, 93.5, 123.0, 123.1, 125.0 (q, $J_{C\text{-}F}$ = 3.6 Hz), 127.16 (q, $J_{C\text{-}F}$ = 277.9 Hz), 127.24, 127.3, 128.1, 128.3, 128.4 (q, $J_{C\text{-}F}$ = 32.1 Hz), 128.5, 129.0, 130.2, 131.2, 132.6, 142.8, 143.9; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -

62.2 (s, 3F); MS (ESI) *m/z*: 375.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{25}H_{18}F_3^+$ requires: 375.1355, Found: 375.1374.

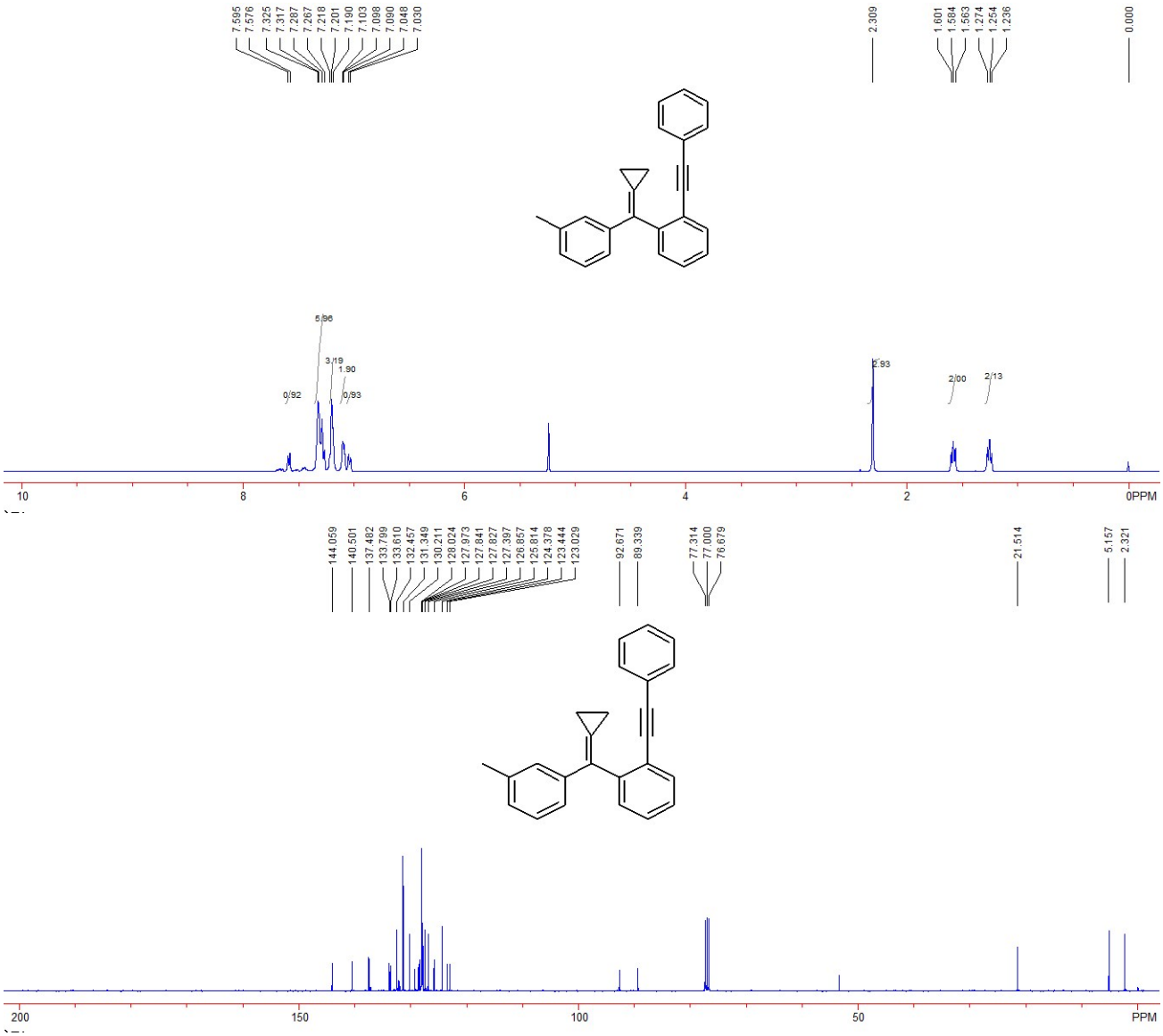


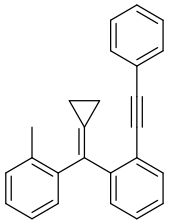




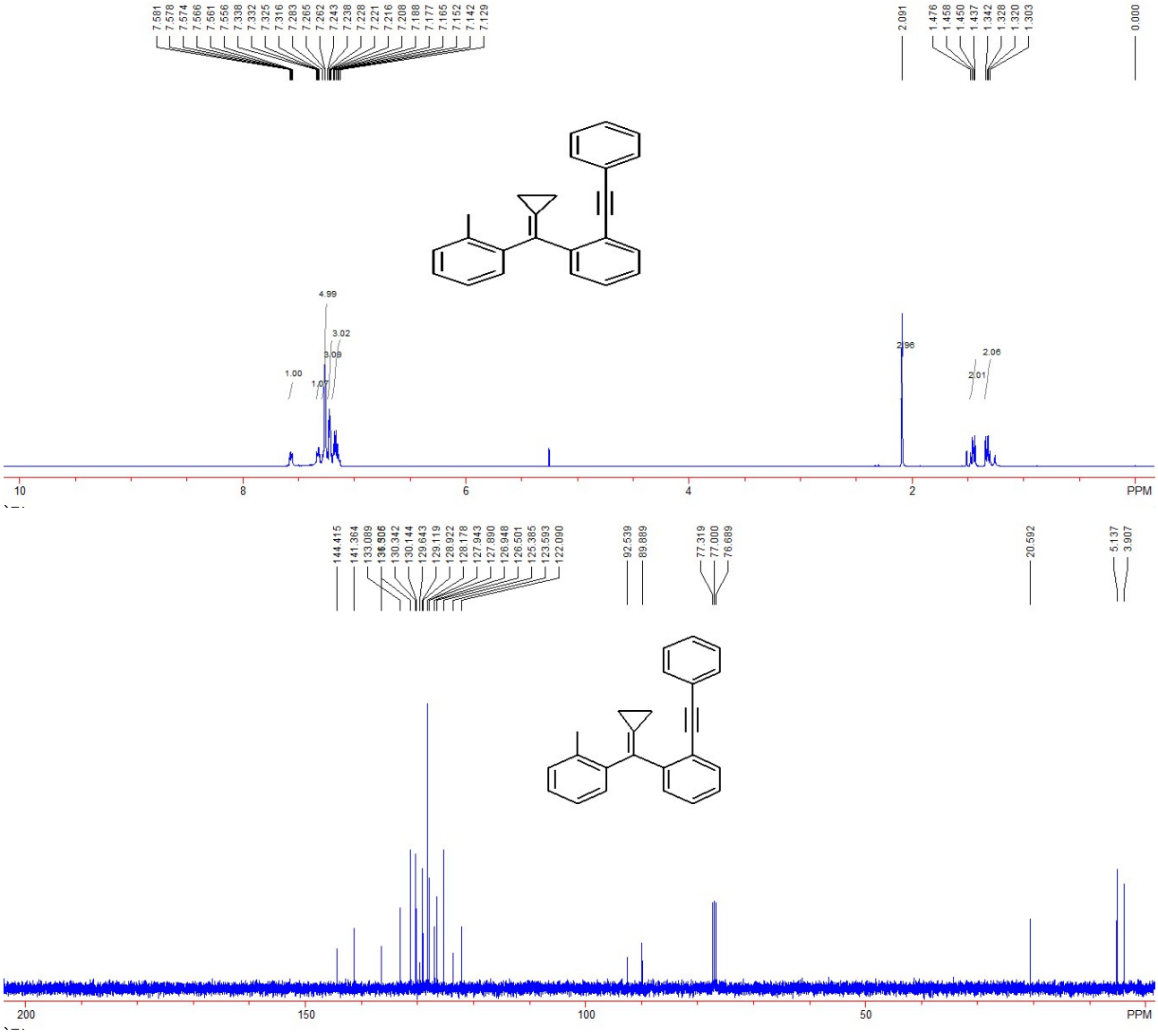


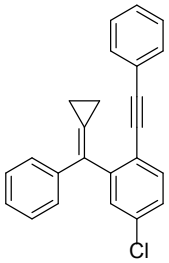
Compound 3o: 1.83 g, 57%, A colorless oil; IR (CH_2Cl_2): ν 3053, 2970, 2914, 2861, 1774, 1710, 1599, 1492, 1438, 1258, 1160, 1119, 785, 755, 721, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.25 (t, 2H, *J* = 7.6 Hz), 1.58 (t, 2H, *J* = 7.6 Hz), 2.31 (s, 3H), 7.04 (d, 1H, *J* = 7.2 Hz), 7.09-7.10 (m, 2H), 7.19-7.22 (m, 3H), 7.27-7.33 (m, 6H), 7.59 (d, 1H, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 2.3, 5.2, 21.5, 89.3, 92.7, 123.0, 123.4, 124.4, 125.8, 126.9, 127.4, 127.83, 127.84, 127.97, 128.02, 130.2, 131.3, 132.5, 133.6, 133.8, 137.5, 140.5, 144.1; MS (ESI) *m/z*: 321.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{25}H_{21}^+$ requires: 321.1638, Found: 321.1646.



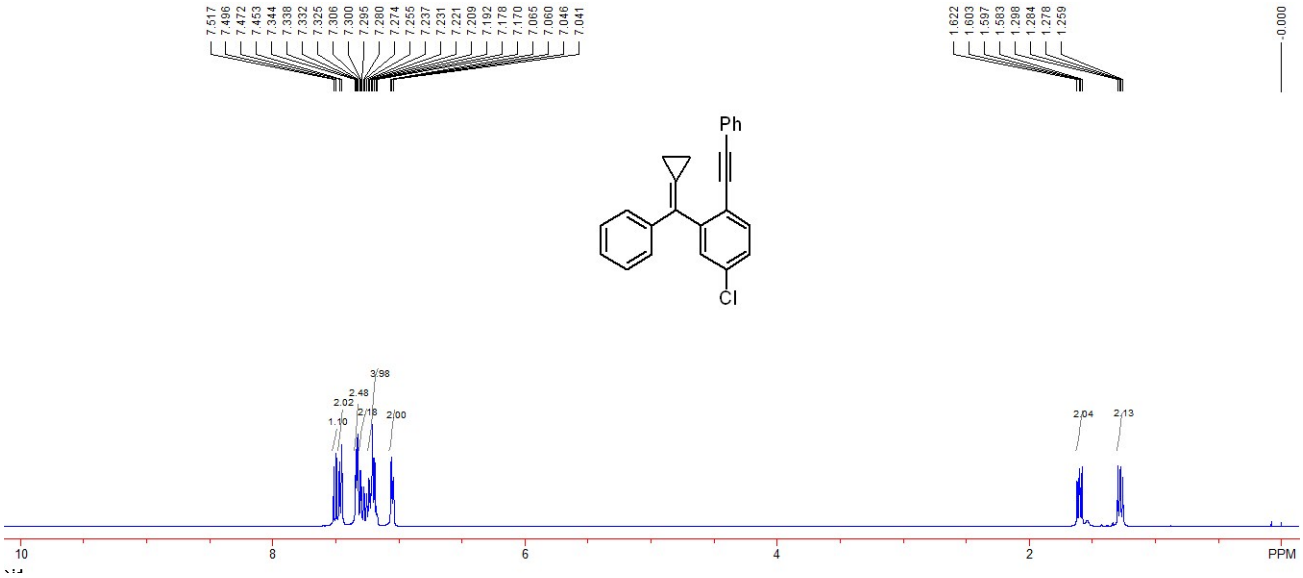


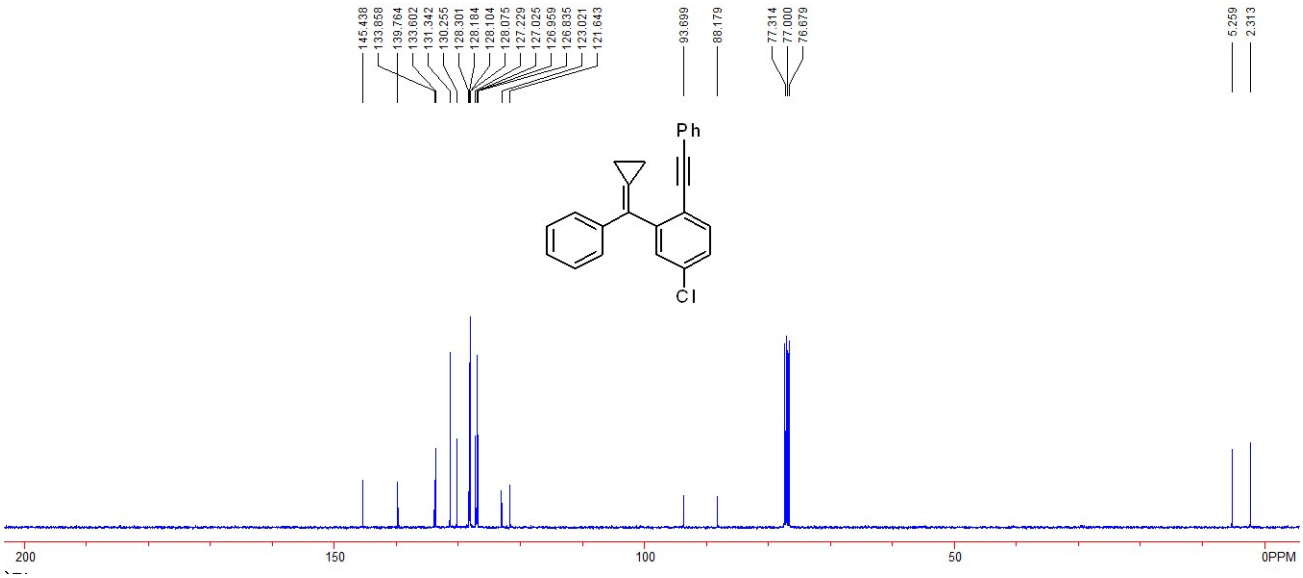
Compound 3p: 161 mg, 5%, A colorless oil; IR (CH_2Cl_2): ν 3022, 2989, 2920, 2875, 1772, 1708, 1598, 1492, 1438, 1256, 1162, 1121, 785, 755, 723, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.30-1.34 (m, 2H), 1.44-1.48 (m, 2H), 2.09 (s, 3H), 7.13-7.19 (m, 3H), 7.21-7.24 (m, 3H), 7.26-7.28 (m, 5H), 7.32-7.34 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 3.9, 5.1, 20.6, 89.9, 92.5, 122.1, 123.6, 125.4, 126.5, 126.9, 127.89, 127.94, 128.2, 128.9, 129.1, 129.6, 130.1, 130.3, 131.3, 133.1, 136.5, 141.4, 144.4; MS (ESI) *m/z*: 321.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{25}H_{21}^+$ requires: 321.1638, Found: 321.1642.

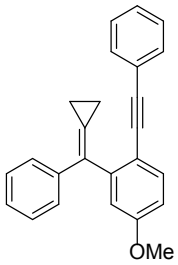




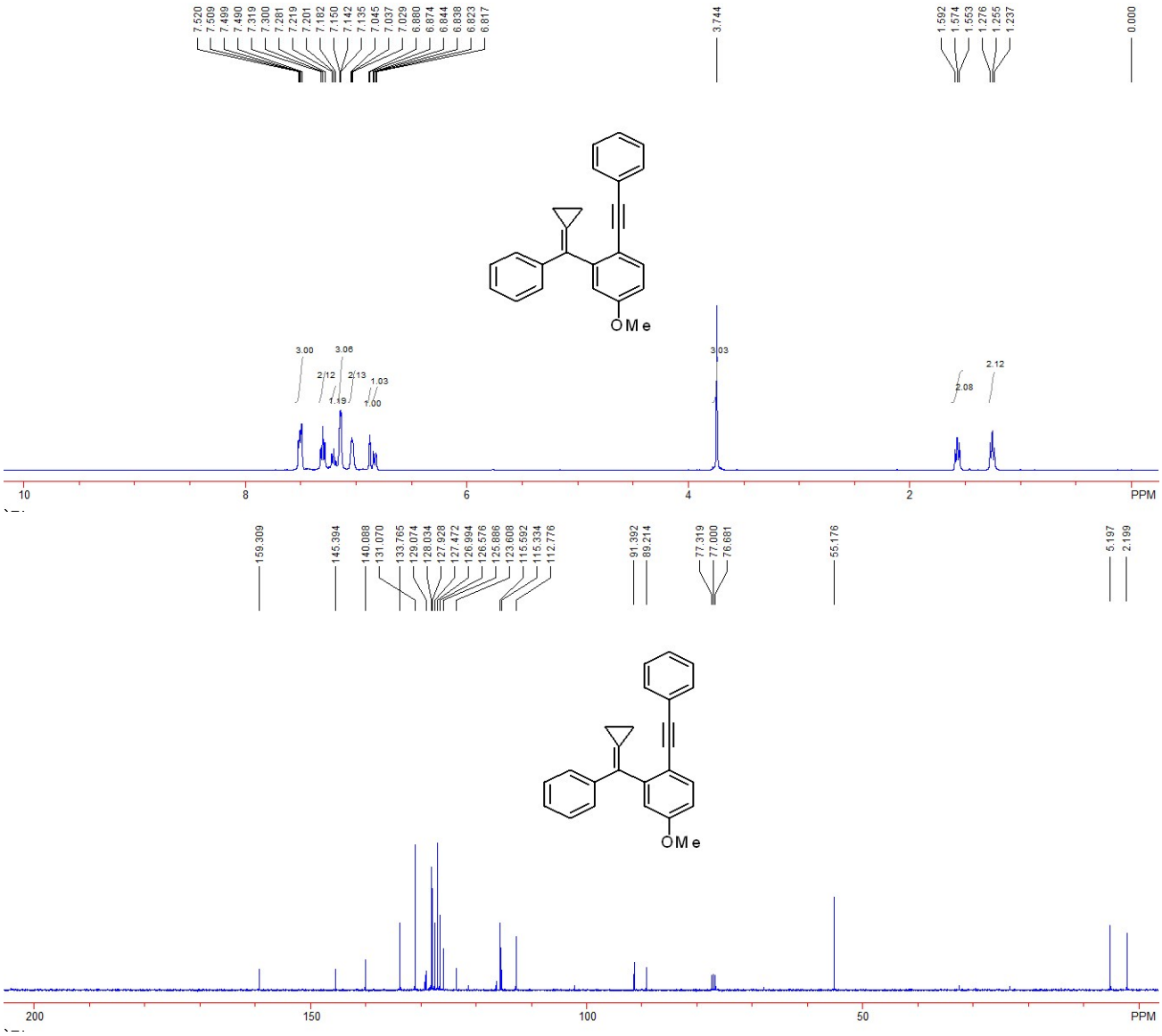
Compound 3q: 1.91 g, 56%, A colorless oil; IR (CH_2Cl_2): ν 3087, 3056, 2973, 2923, 1781, 1670, 1596, 1584, 1493, 1472, 1395, 1288, 1091, 1076, 821, 756, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.26-1.30 (m, 2H), 1.58-1.62 (m, 2H), 7.05 (dd, 2H, J_1 = 7.6 Hz, J_2 = 2.0 Hz), 7.17-7.24 (m, 4H), 7.26-7.31 (m, 2H), 7.33-7.34 (m, 2H), 7.46 (d, 2H, J = 7.6 Hz), 7.51 (d, 1H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 2.3, 5.3, 88.2, 93.7, 121.6, 123.0, 126.8, 126.96, 127.03, 127.2, 128.08, 128.10, 128.2, 128.3, 130.3, 131.3, 133.6, 133.9, 139.8, 145.4; MS (ESI) *m/z*: 341.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{24}H_{18}Cl^+$ requires: 341.1092, Found: 341.1089.

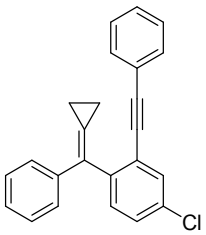




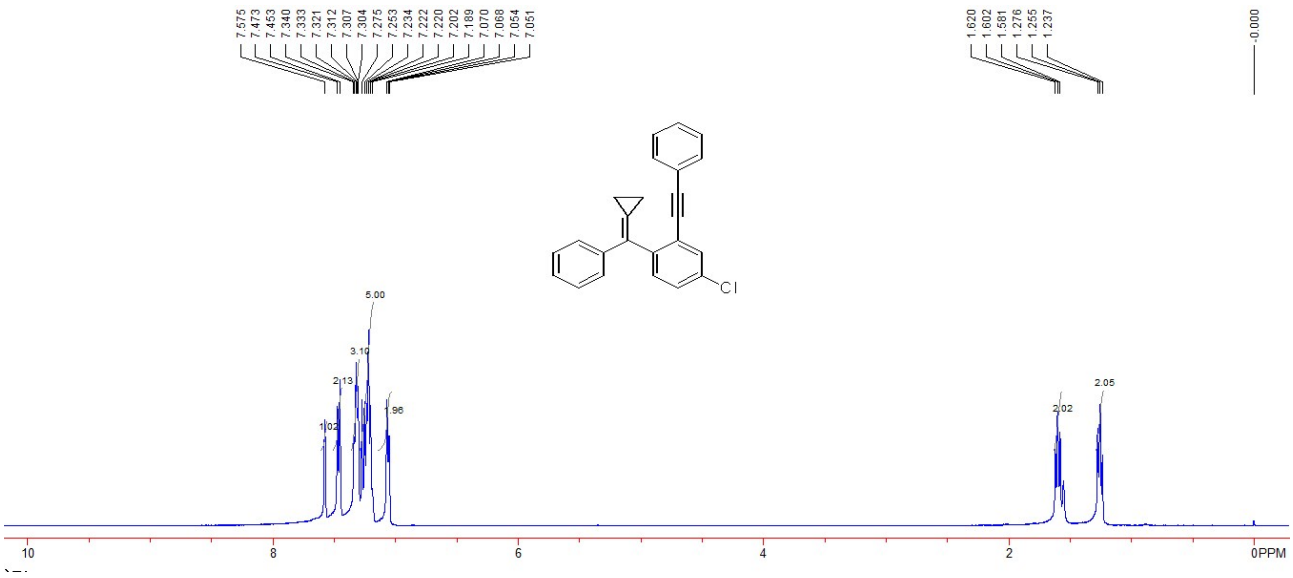


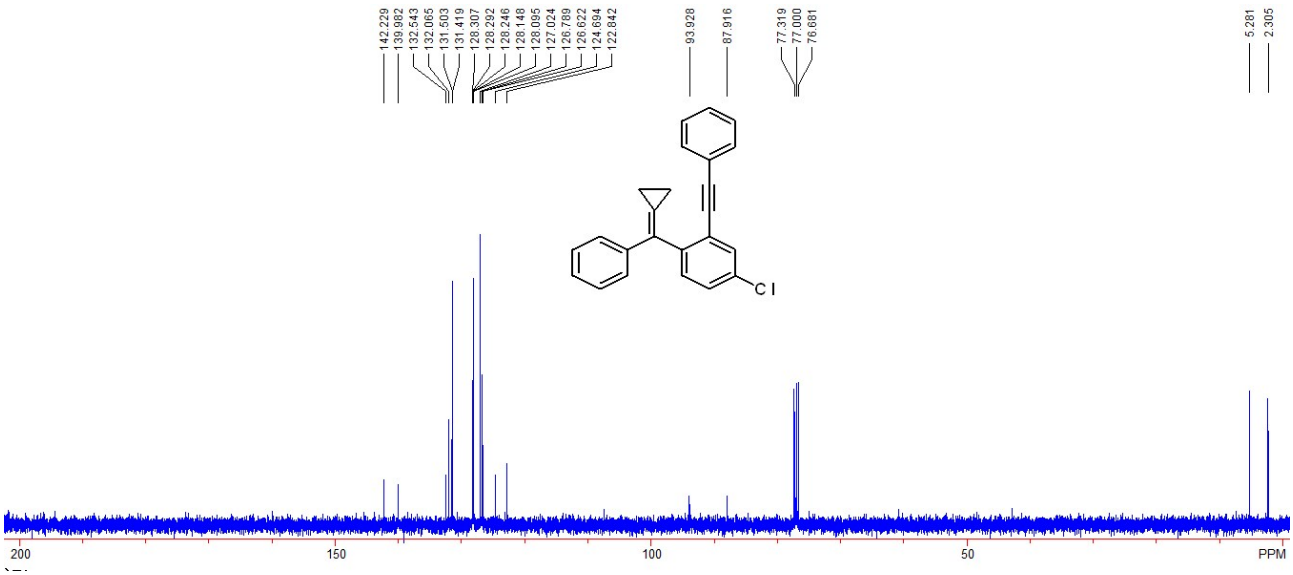
Compound 3r: 2.16 g, 64%, A white solid, m.p. 122-124 ^{o}C; IR (CH_2Cl_2): ν 3056, 3028, 2961, 2931, 2831, 1603, 1594, 1493, 1444, 1286, 1219, 1170, 1038, 879, 807, 754, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.26 (t, 2H, J = 7.6 Hz), 1.57 (t, 2H, J = 7.6 Hz), 3.74 (s, 3H), 6.83 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2.4 Hz), 6.88 (d, 1H, J = 2.4 Hz), 7.04 (t, 2H, J = 3.2 Hz), 7.14 (t, 3H, J = 3.2 Hz), 7.20 (t, 1H, J = 7.6 Hz), 7.30 (t, 2H, J = 7.6 Hz), 7.49-7.52 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 2.2, 5.2, 55.2, 89.2, 91.4, 112.8, 115.3, 115.6, 123.6, 125.9, 126.6, 127.0, 127.5, 127.9, 128.0, 129.1, 131.1, 133.8, 140.1, 145.4, 159.3; MS (ESI) *m/z*: 337.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{25}H_{21}O^+$ requires: 337.1587, Found: 337.1603.

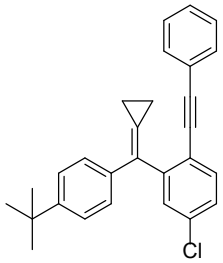




Compound 3s: 1.33 g, 39%, A colorless oil; IR (CH_2Cl_2): ν 3084, 3053, 2978, 1597, 1491, 1475, 1442, 1091, 910, 879, 840, 817, 768, 756, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.26 (t, 2H, J = 7.6 Hz), 1.60 (t, 2H, J = 7.6 Hz), 7.06 (dd, 2H, J_1 = 6.8 Hz, J_2 = 1.2 Hz), 7.19-7.28 (m, 5H), 7.30-7.34 (m, 3H), 7.46 (d, 2H, J = 8.0 Hz), 7.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 2.3, 5.3, 87.9, 93.9, 122.8, 124.7, 126.6, 126.8, 127.0, 128.10, 128.15, 128.2, 128.29, 128.31, 131.4, 131.5, 132.1, 132.5, 140.0, 142.2; MS (ESI) *m/z*: 341.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{24}H_{18}Cl^+$ requires: 341.1092, Found: 341.1105.

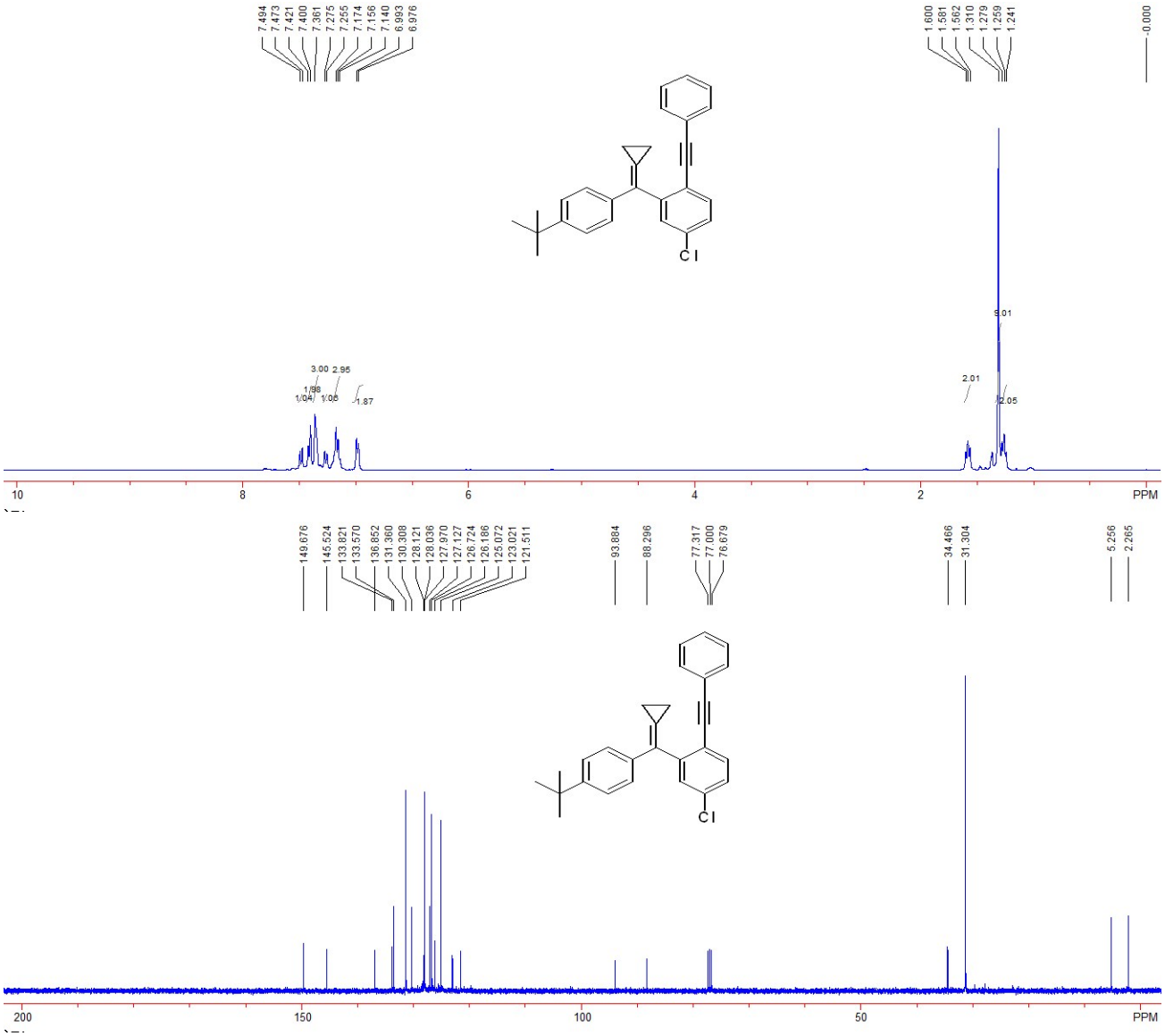




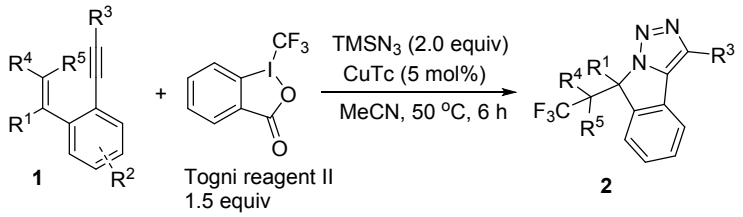


Compound 3t: 1.07 g, 27%, A colorless oil; IR (CH_2Cl_2): ν 3056, 2961, 2900, 2872, 1782, 1700, 1585, 1494, 1466, 1267, 1203, 1112, 1088, 1023, 820, 755, 689 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.26 (t, 2H, *J* = 7.6 Hz), 1.31 (s, 9H), 1.58 (t, 2H, *J* = 7.6 Hz), 6.98 (d, 2H, *J* = 6.8 Hz), 7.14-7.17 (m, 3H), 7.27 (d, 1H, *J* = 8.0 Hz), 7.36 (brs, 3H), 7.41 (d, 2H, *J* = 8.4 Hz), 7.48 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 2.3, 5.3, 31.3, 34.5, 88.3, 93.9, 121.5, 123.0, 125.1, 126.2, 126.7, 127.1, 127.97, 128.04, 128.1, 130.3, 131.4, 133.6, 133.8, 136.9, 145.5, 150.0; MS

(ESI) *m/z*: 397.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{28}H_{26}Cl^+$ requires: 397.1718, Found: 397.1704.

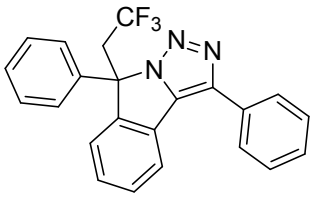


General procedure for the synthesis of products 2

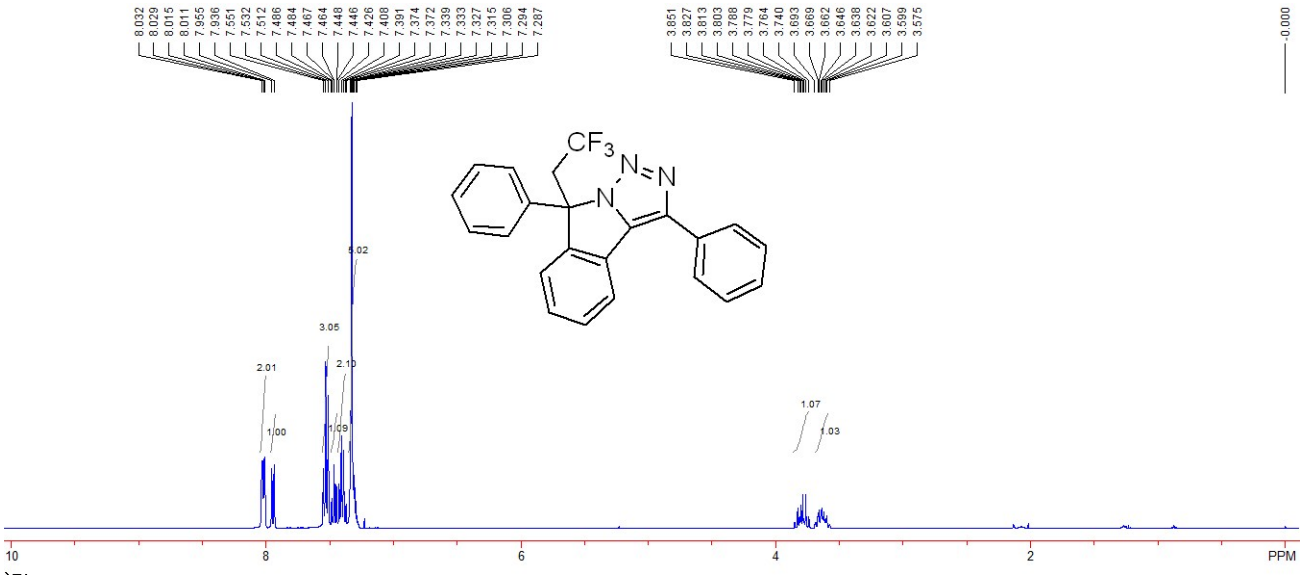


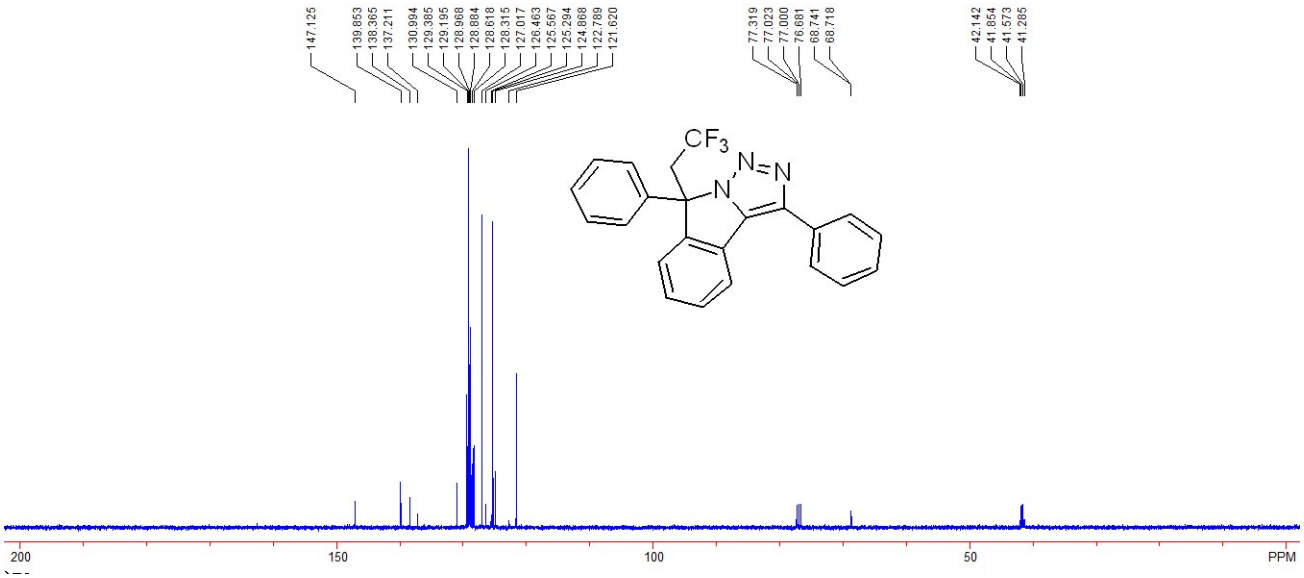
1 (0.2 mmol, 1.0 equiv), Togni reagent II (0.30 mmol, 1.5 equiv), CuTc (0.010 mmol, 0.05 equiv) were dissolved in MeCN (2.0 mL), then $TMSN_3$ (0.40 mmol, 2.0 equiv) was added dropwise and the reaction tube was placed in a pre-heated 50 ^oC oil bath. The reaction was stopped after 6 h and the reaction mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the products **2** in good yield.

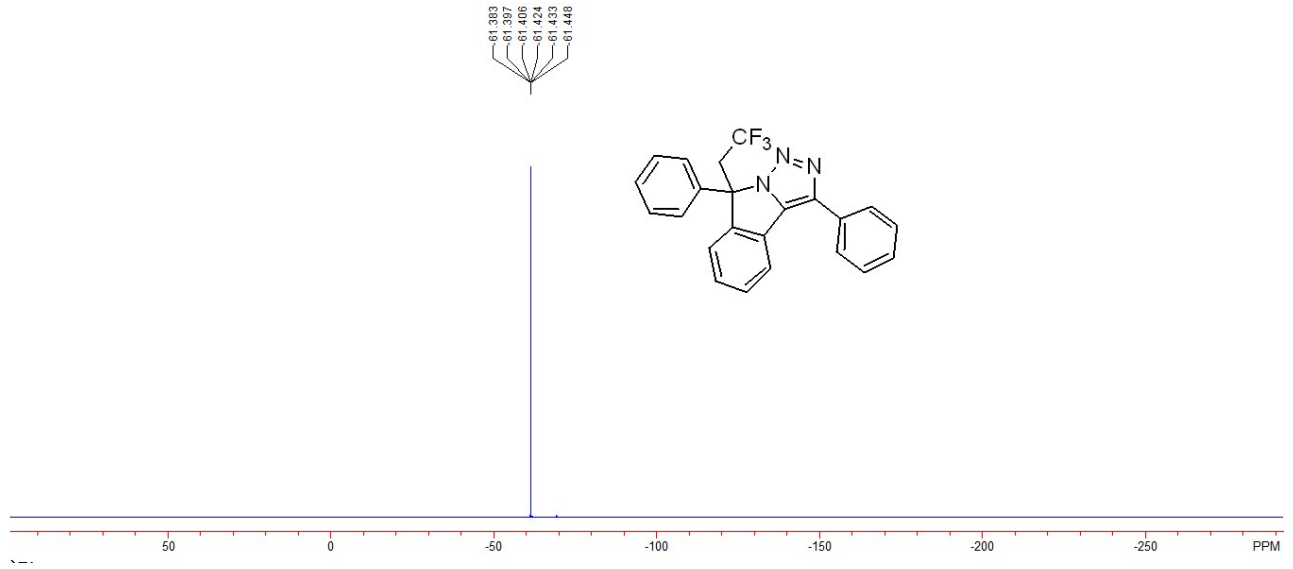
Spectroscopic data for products 2

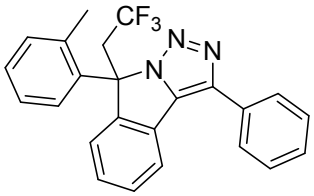


Compound 2a: 72 mg, 92%, A white solid, m.p. 180-182 °C; IR (CH_2Cl_2): ν 3065, 2923, 2856, 1733, 1498, 1448, 1375, 1356, 1312, 1258, 1134, 1124, 1113, 1039, 984, 760, 728, 694, 674 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 3.58-3.69 (m, 1H), 3.74-3.85 (m, 1H), 7.29-7.34 (m, 5H), 7.37-7.43 (m, 2H), 7.47 (td, 1H, J_1 = 8.0 Hz, J_2 = 0.8 Hz), 7.53 (t, 3H, J = 8.0 Hz), 7.95 (d, 1H, J = 7.6 Hz), 8.02 (dd, 2H, J_1 = 7.2 Hz, J_2 = 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 41.7 (q, $J_{C\text{-}F}$ = 28.8 Hz), 68.7, 121.6, 124.2 (q, $J_{C\text{-}F}$ = 277.8 Hz), 124.9, 125.3, 126.5, 127.0, 128.3, 128.6, 128.9, 129.0, 129.2, 129.4, 131.0, 137.2, 138.4, 139.9, 147.1; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -61.4 (td, 3F, J_1 = 9.0 Hz, J_2 = 5.6 Hz); MS (ESI) *m/z*: 392.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{23}H_{17}F_3N_3^+$ requires: 392.1369, Found: 392.1368.



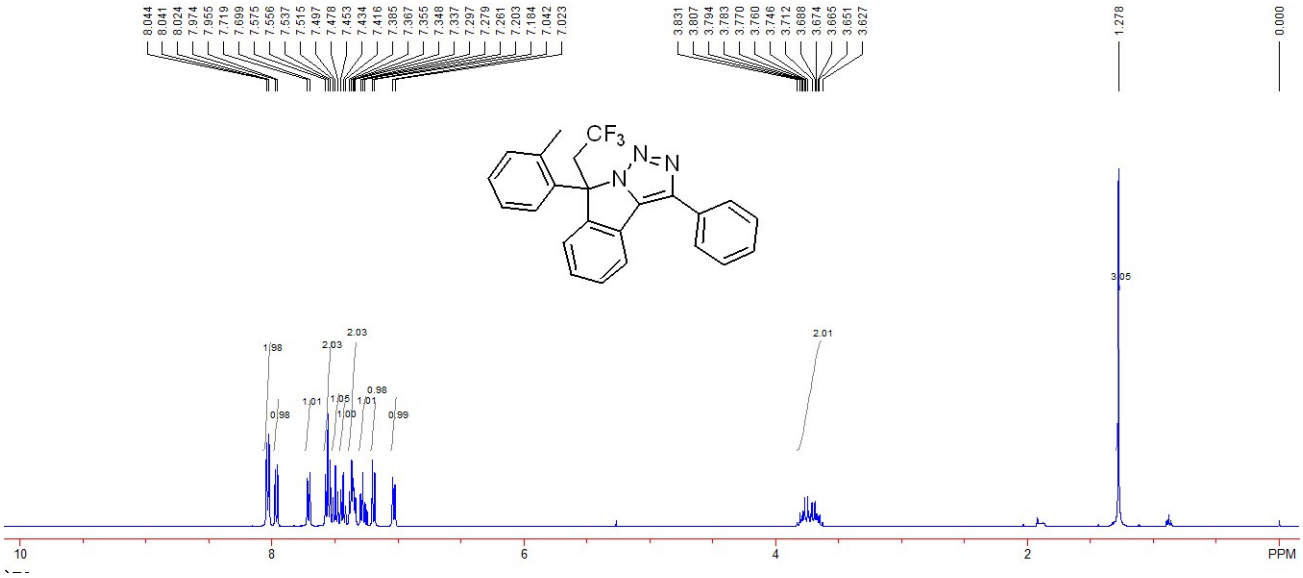


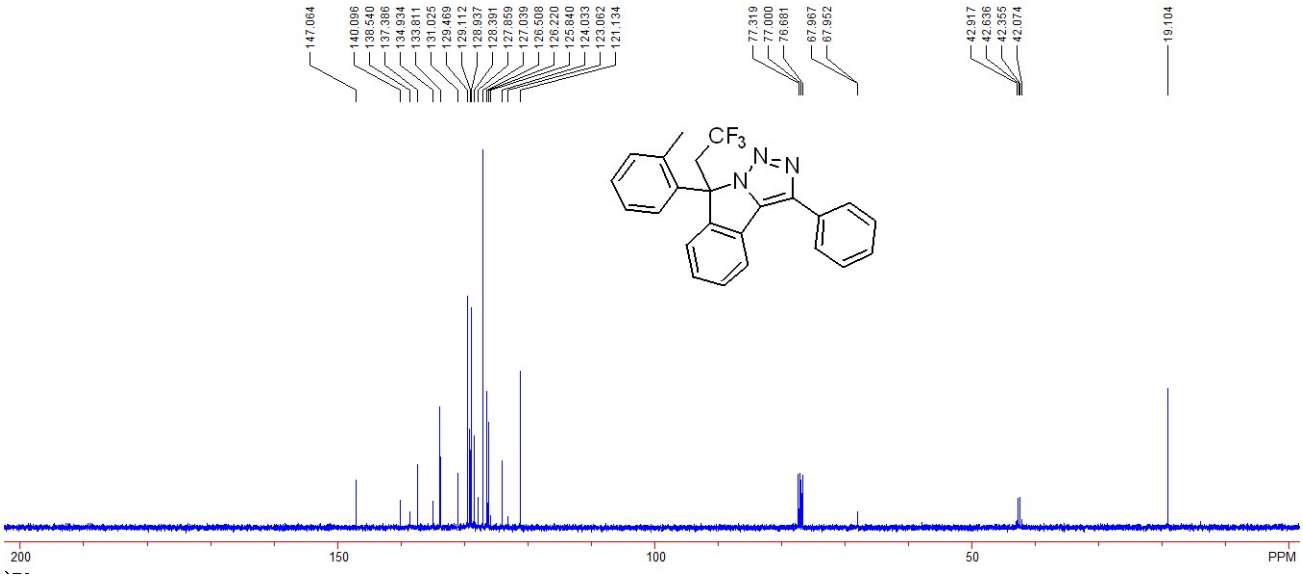


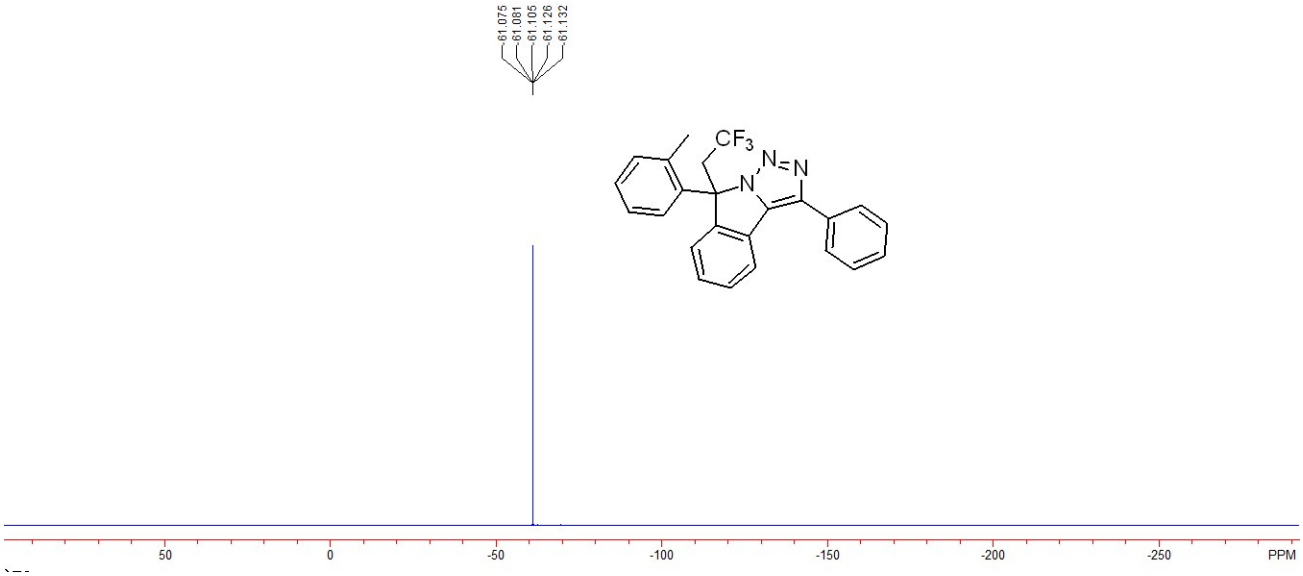


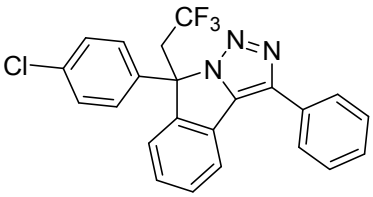
Compound 2b: 72 mg, 89%, A white solid, m.p. 176-178 ^{o}C; IR (CH_2Cl_2): ν 3062, 2984, 1494, 1446, 1381, 1356, 1320, 1256, 1138, 1114, 840, 758, 748, 730, 718, 695 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.28 (s, 3H), 3.63-3.83 (m, 2H), 7.03 (d, 1H, J = 7.6 Hz), 7.19 (d, 1H, J = 7.6 Hz), 7.28 (t, 1H, J = 7.2 Hz), 7.34-7.39 (m, 2H), 7.43 (t, 1H, J = 7.6 Hz), 7.50 (t, 1H, J = 7.2 Hz), 7.56 (t, 2H, J = 7.6 Hz), 7.71 (d, 1H, J = 8.0 Hz), 7.96 (d, 1H, J = 7.6 Hz), 8.03 (dd, 2H, J_1 = 8.0 Hz, J_2 = 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.1, 42.5 (q, J_{C-F} = 28.1 Hz), 68.0 (q, J_{C-F} = 1.5 Hz), 121.1, 124.0, 124.5 (q, J_{C-F} = 277.8 Hz), 126.2, 126.5, 127.0, 127.9, 128.4, 128.9, 129.1, 129.5, 131.0, 133.8, 134.9, 137.4, 138.5, 140.1, 147.1; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -61.1 (td,

3F, J_1 = 10.2 Hz, J_2 = 2.3 Hz); MS (ESI) *m/z*: 406.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{24}H_{19}F_3N_3^+$ requires: 406.1526, Found: 406.1526.

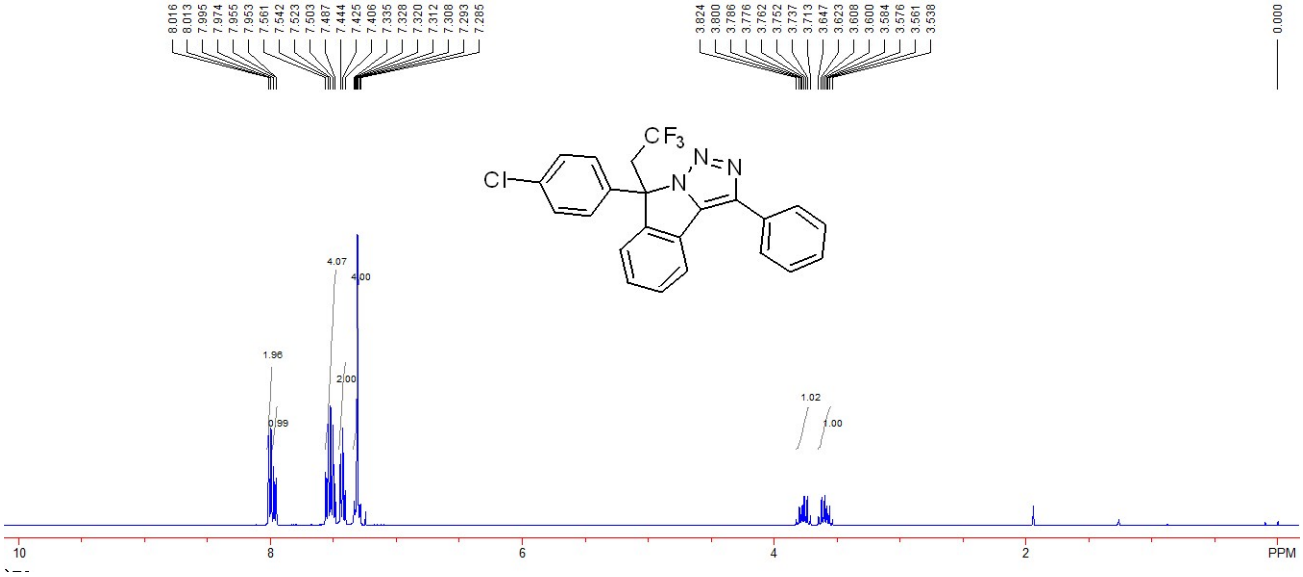


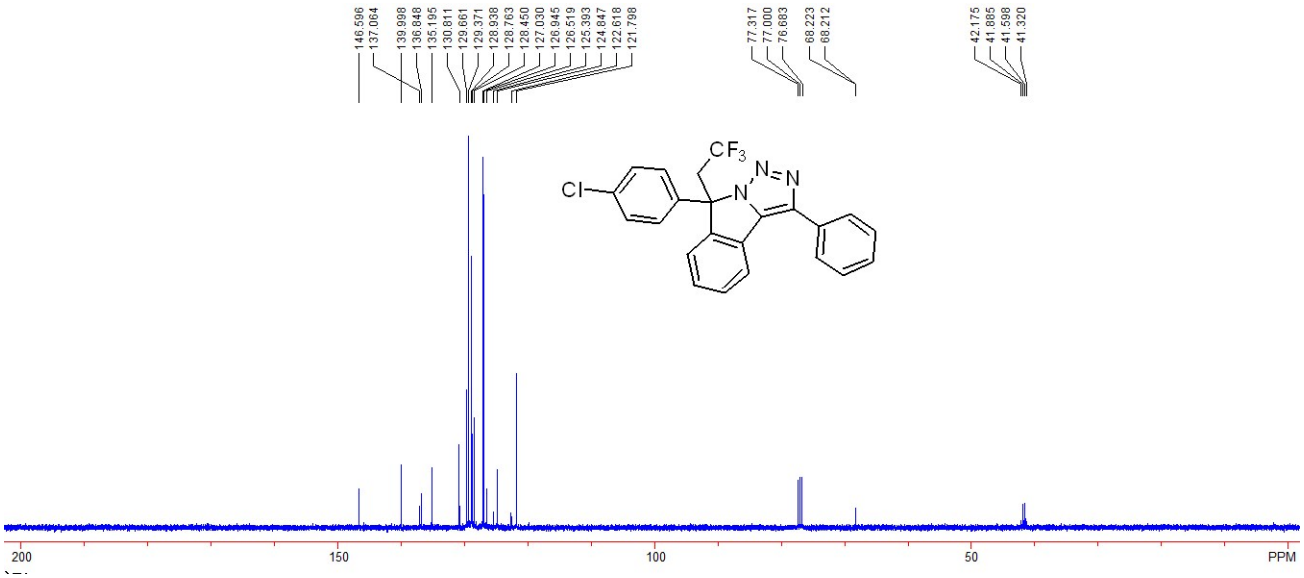


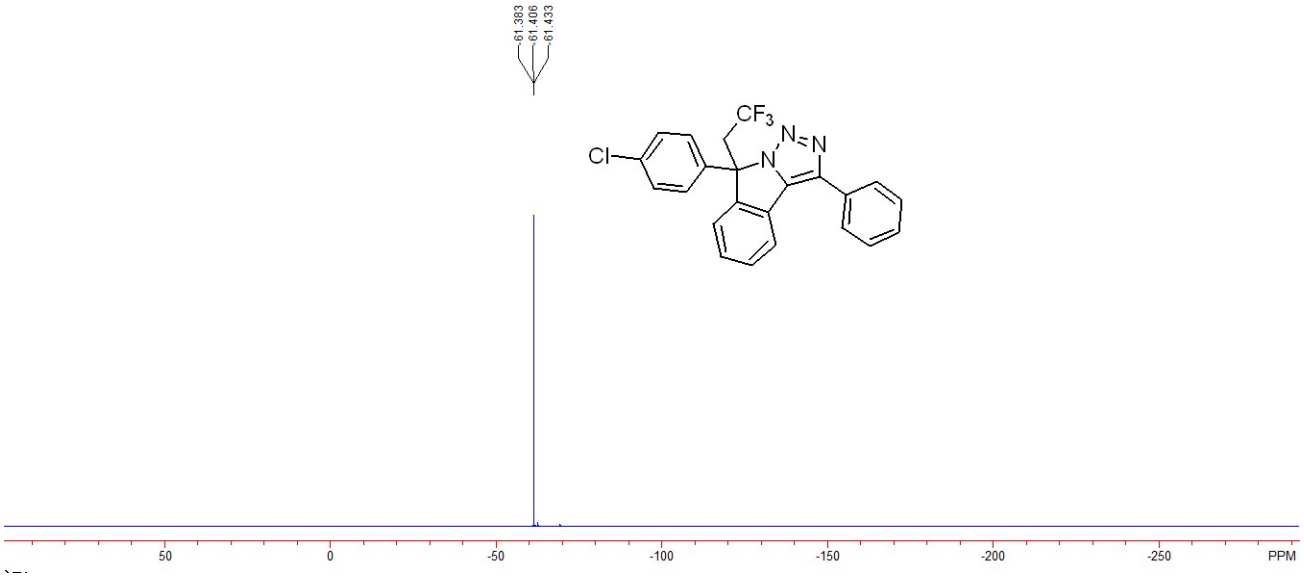


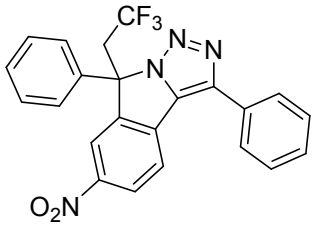


Compound 2c: 80 mg, 94%, A white solid, m.p. 193-195 ^{o}C; IR (CH_2Cl_2): ν 3065, 2918, 2845, 1495, 1377, 1356, 1259, 1136, 1115, 1097, 1014, 761, 731, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.54-3.65 (m, 1H), 3.71-3.82 (m, 1H), 7.29-7.34 (m, 4H), 7.43 (t, 2H, J = 7.6 Hz), 7.49-7.56 (m, 4H), 7.96 (dd, 1H, J_1 = 7.6 Hz, J_2 = 0.8 Hz), 8.00 (dd, 2H, J_1 = 7.6 Hz, J_2 = 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 41.7 (q, J_{C-F} = 28.7 Hz), 68.2 (q, J_{C-F} = 1.1 Hz), 121.8, 124.0 (q, J_{C-F} = 277.5 Hz), 124.8, 126.5, 126.9, 127.0, 128.5, 128.8, 128.9, 129.4, 129.7, 130.8, 135.2, 136.8, 137.1, 140.0, 146.6; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -61.4 (t, 3F, J = 10.1 Hz); MS (ESI) *m/z*: 426.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{23}H_{16}ClF_3N_3^+$ requires: 426.0979, Found: 426.0980.



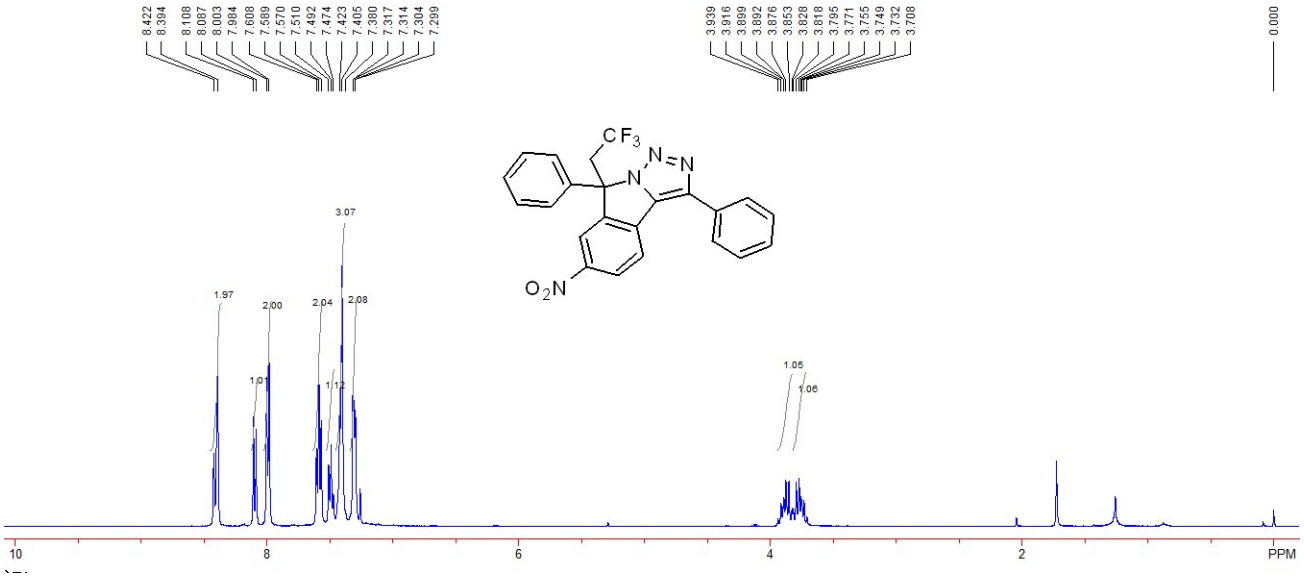


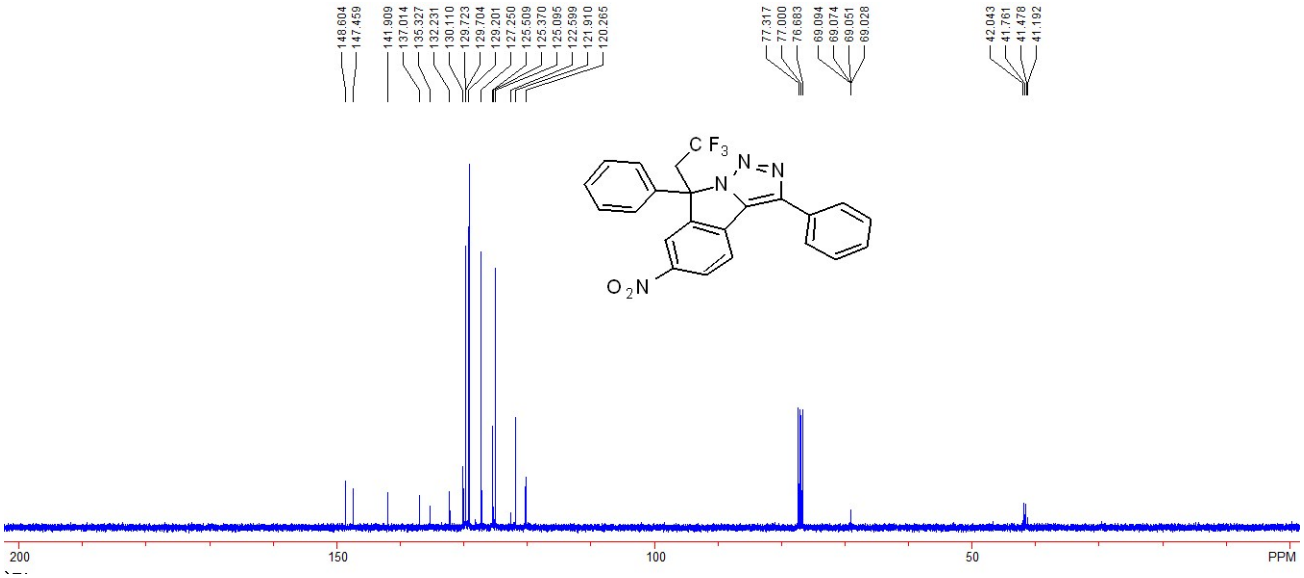


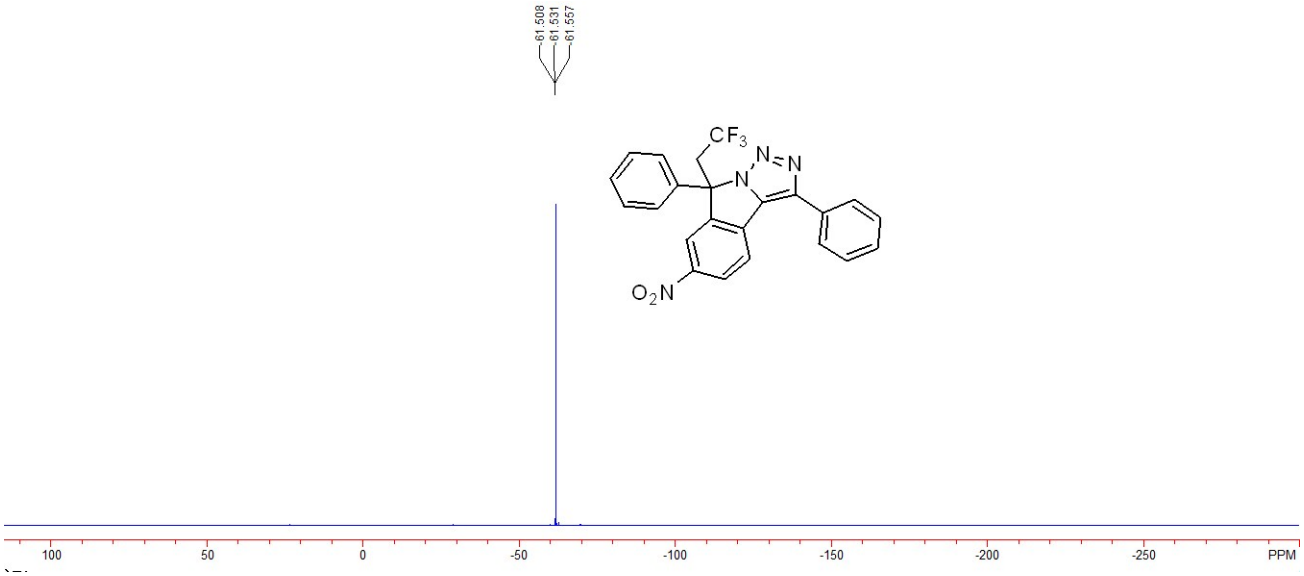


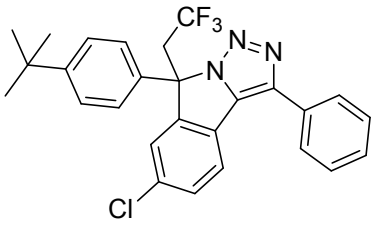
Compound 2d: 74 mg, 85%, A white solid, m.p. 174-176 ^{o}C; IR (CH_2Cl_2): ν 2923, 1530, 1449, 1377, 1342, 1258, 1132, 1121, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.71-3.82 (m, 1H), 3.83-3.94 (m, 1H), 7.30-7.32 (m, 2H), 7.38-7.42 (m, 3H), 7.49 (t, 1H, J = 7.2 Hz), 7.59 (t, 2H, J = 7.6 Hz), 7.99 (d, 2H, J = 7.6 Hz), 8.10 (d, 1H, J = 8.4 Hz), 8.39-8.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 41.6 (q, $J_{C\text{-}F}$ = 28.3 Hz), 69.1 (q, $J_{C\text{-}F}$ = 2.3 Hz), 120.3, 121.9, 124.0 (q, $J_{C\text{-}F}$ = 277.1 Hz), 125.1, 125.5, 127.3, 129.2, 129.70, 129.72, 130.1, 132.2, 135.3, 137.0, 141.9, 147.5,

148.6; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -61.5 (t, 3F, J = 9.8 Hz); MS (ESI) *m/z*: 437.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{23}H_{16}F_3N_4O_2^+$ requires: 437.1220, Found: 437.1219.

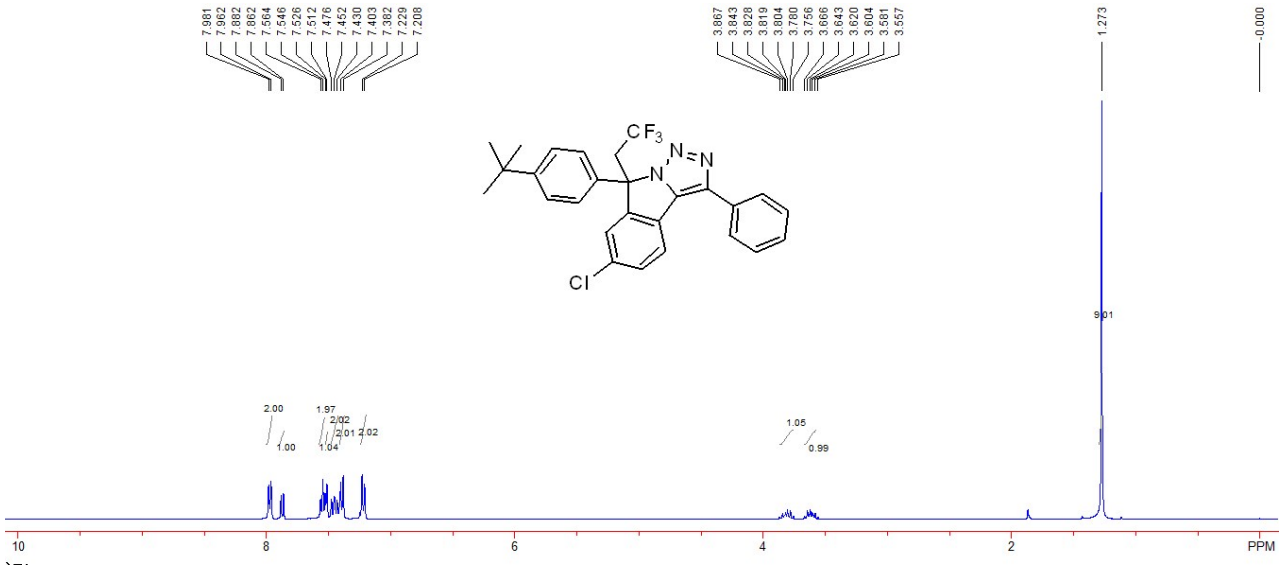


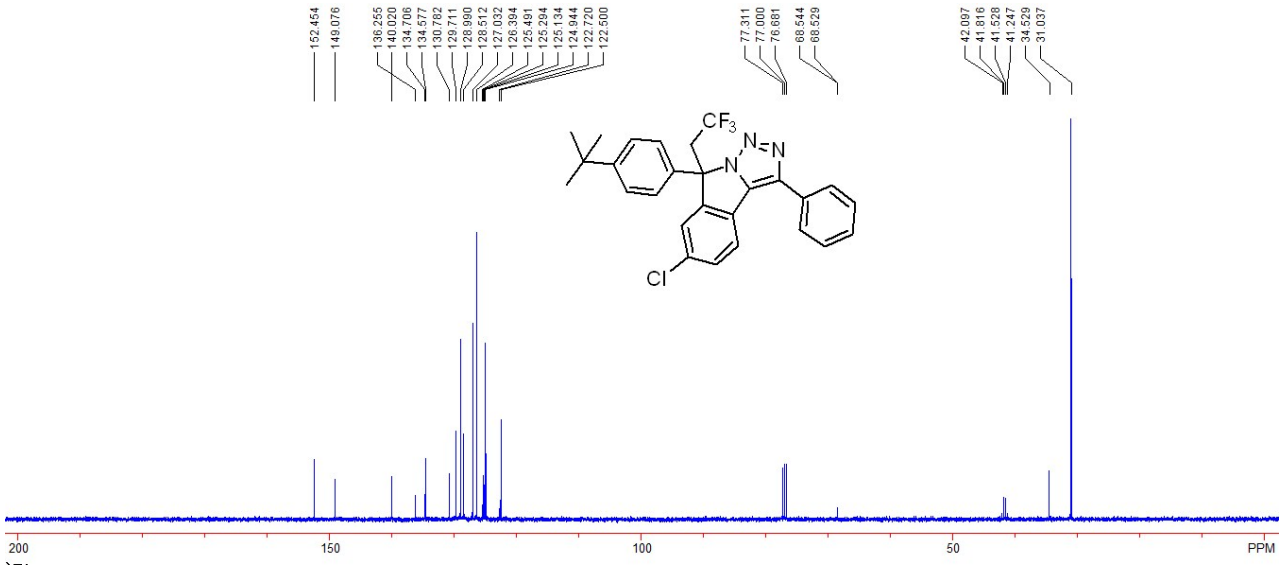


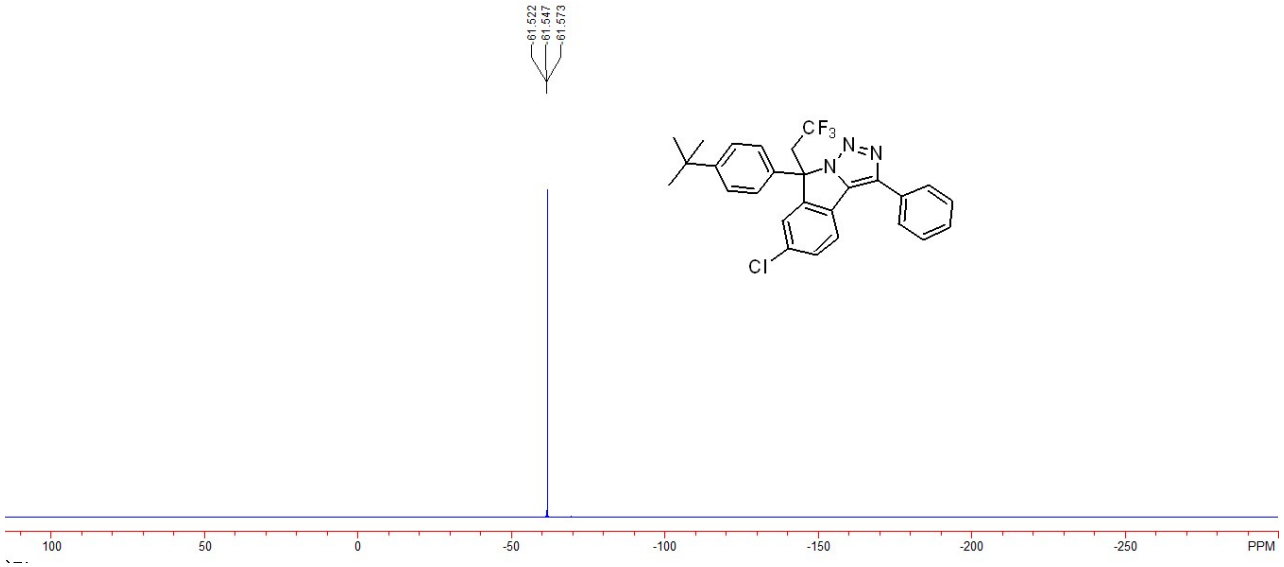


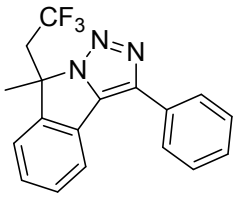


Compound 2e: 84 mg, 87%, A white solid, m.p. 201-203 °C; IR (CH_2Cl_2): ν 2964, 2868, 1451, 1374, 1353, 1259, 1172, 1139, 985, 965, 847, 823, 774, 760, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.27 (s, 9H), 3.56-3.67 (m, 1H), 3.76-3.87 (m, 1H), 7.22 (d, 2H, J = 8.4 Hz), 7.39 (d, 2H, J = 8.4 Hz), 7.43-7.48 (m, 2H), 7.51-7.53 (m, 1H), 7.56 (d, 2H, J = 7.2 Hz), 7.87 (d, 1H, J = 8.0 Hz), 7.97 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 31.0, 34.5, 41.7 (q, $J_{C\text{-}F}$ = 28.8 Hz), 68.5 (q, $J_{C\text{-}F}$ = 1.5 Hz), 122.5, 124.1 (q, $J_{C\text{-}F}$ = 277.1 Hz), 124.9, 125.1, 125.3, 126.4, 127.0, 128.5, 129.0, 129.7, 130.8, 134.6, 134.7, 136.3, 140.0, 149.1, 152.5; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -61.5 (t, 3F, J = 9.8 Hz); MS (ESI) *m/z*: 482.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{27}H_{24}ClF_3N_3^+$ requires: 482.1605, Found: 482.1605.



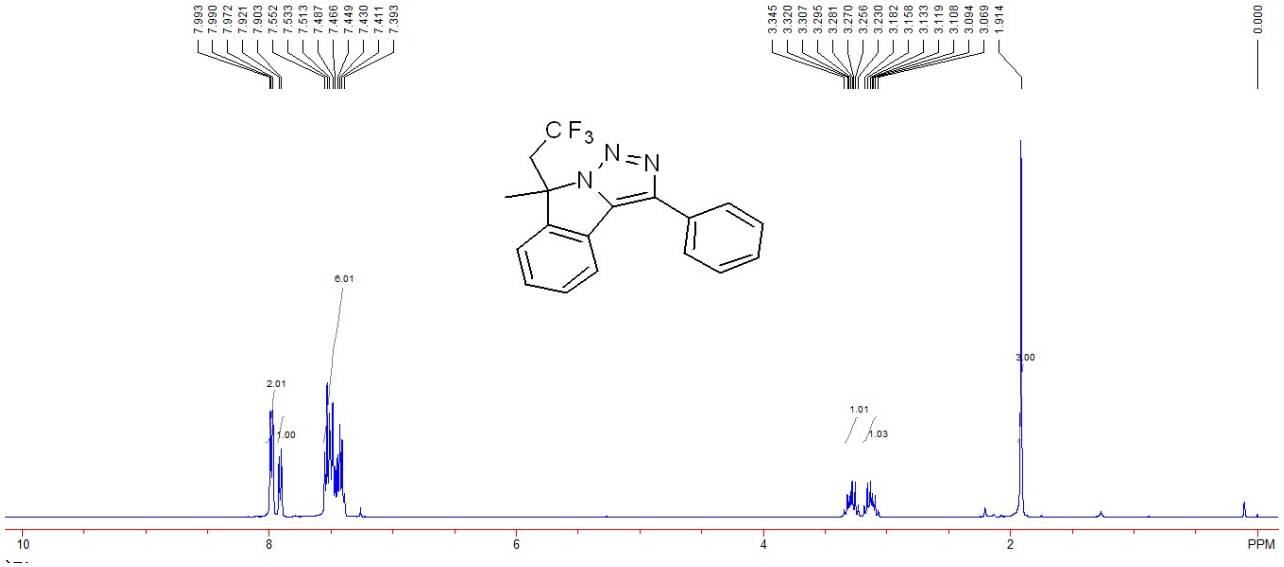


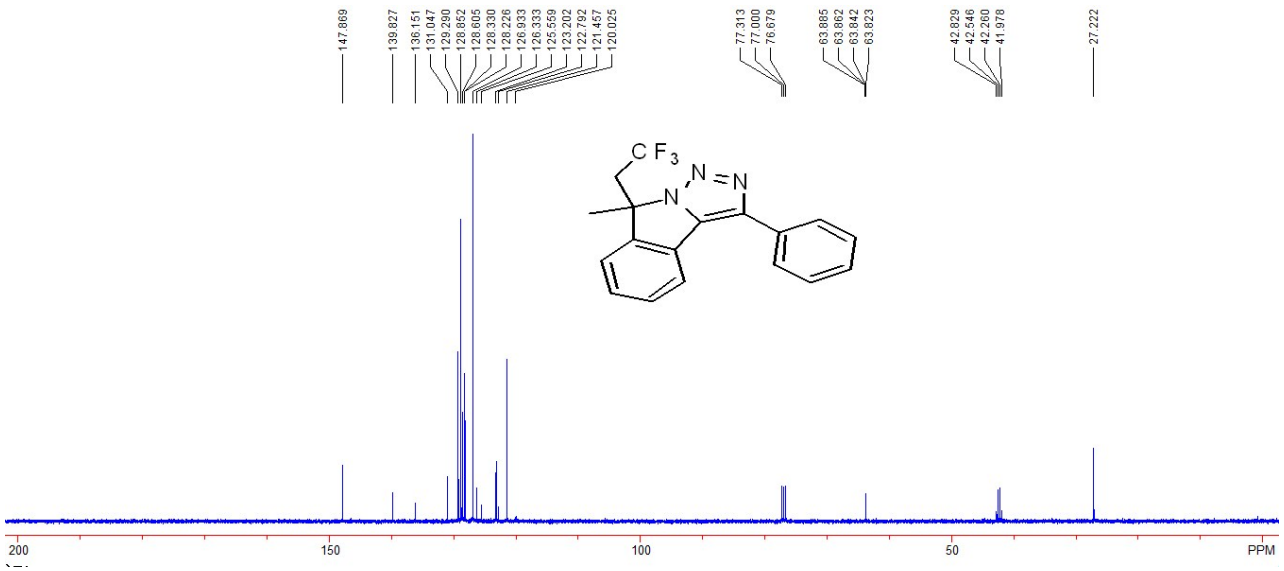


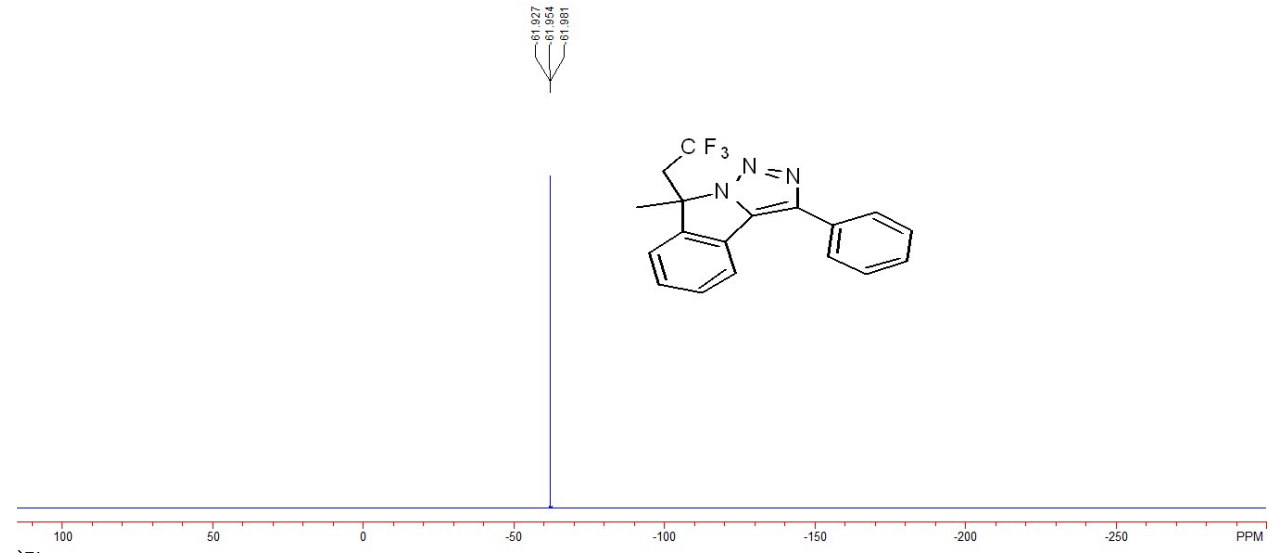


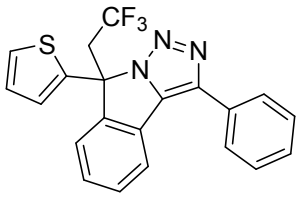
Compound 2f: 60 mg, 91%, A white solid, m.p. 155-157 ^{o}C; IR (CH_2Cl_2): ν 3065, 2981, 2931, 1494, 1450, 1374, 1358, 1260, 1161, 1121, 1096, 1066, 1052, 985, 760, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.91 (s, 3H), 3.07-3.18 (m, 1H), 3.23-3.35 (m, 1H), 7.39-7.55 (m, 6H), 7.91 (d, 1H, J = 8.4 Hz), 7.98 (dd, 2H, J_1 = 8.4 Hz, J_2 = 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 27.2, 42.4 (q, $J_{C\text{-}F}$ = 28.6 Hz), 63.9 (q, $J_{C\text{-}F}$ = 2.0 Hz), 121.5, 123.2, 124.2 (q, $J_{C\text{-}F}$ = 276.7 Hz), 126.3, 126.9, 128.2, 128.6, 128.9, 129.3, 131.0, 136.2, 139.8, 147.9; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$):

δ -62.0 (t, 3F, J = 10.2 Hz); MS (ESI) m/z: 330.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{18}H_{15}F_3N_3^+$ requires: 330.1213, Found: 330.1212.

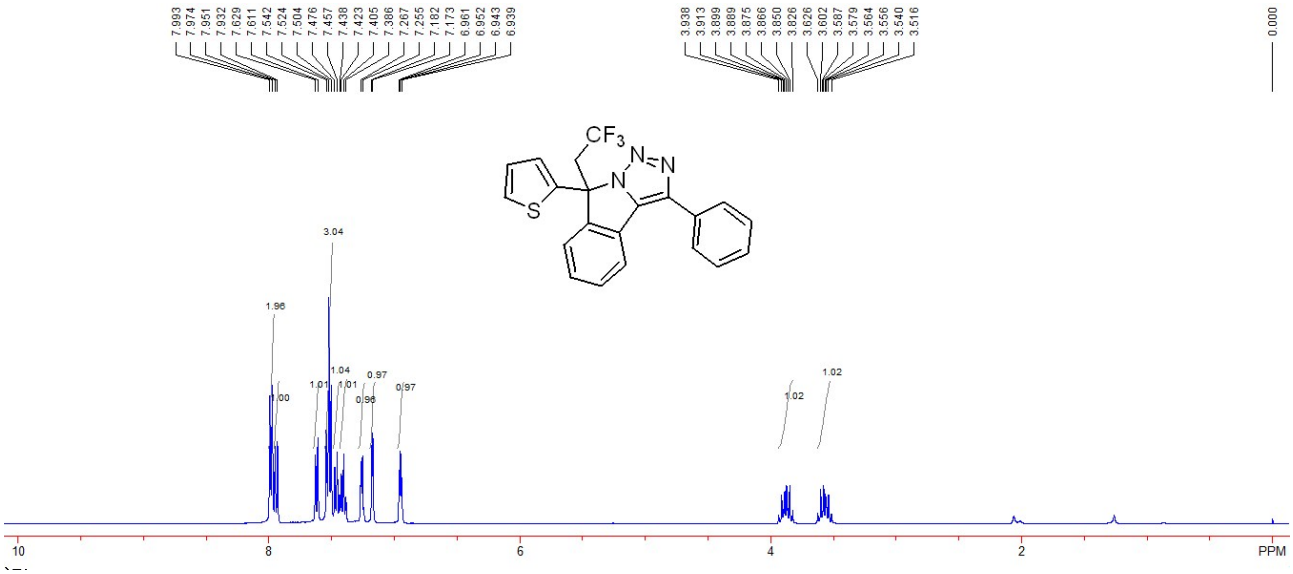


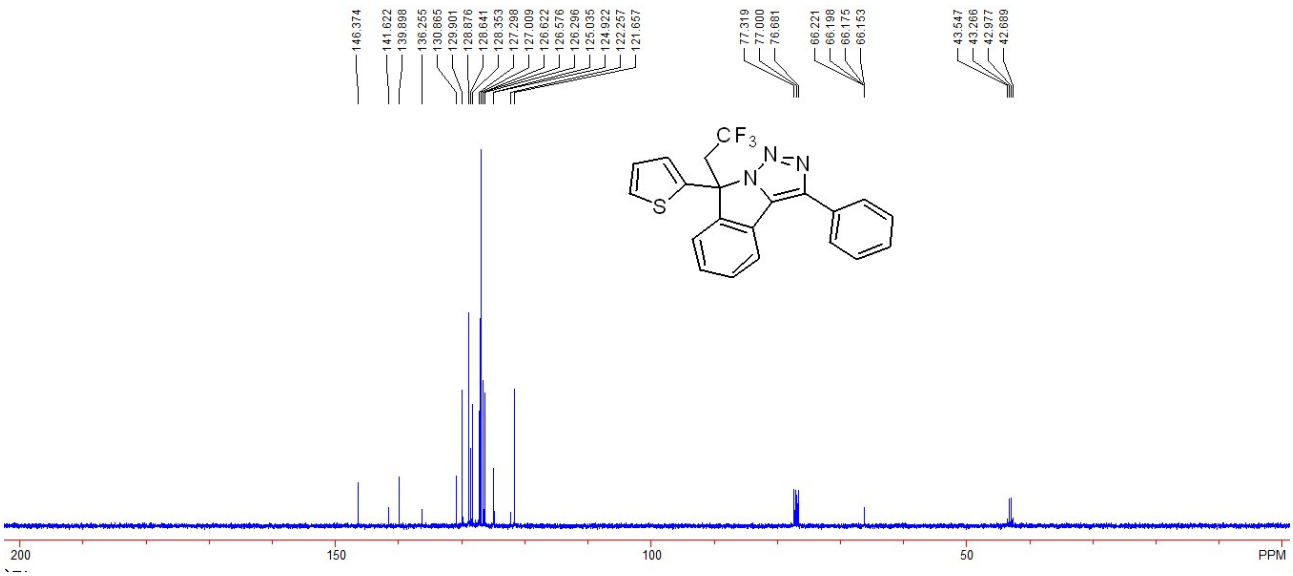


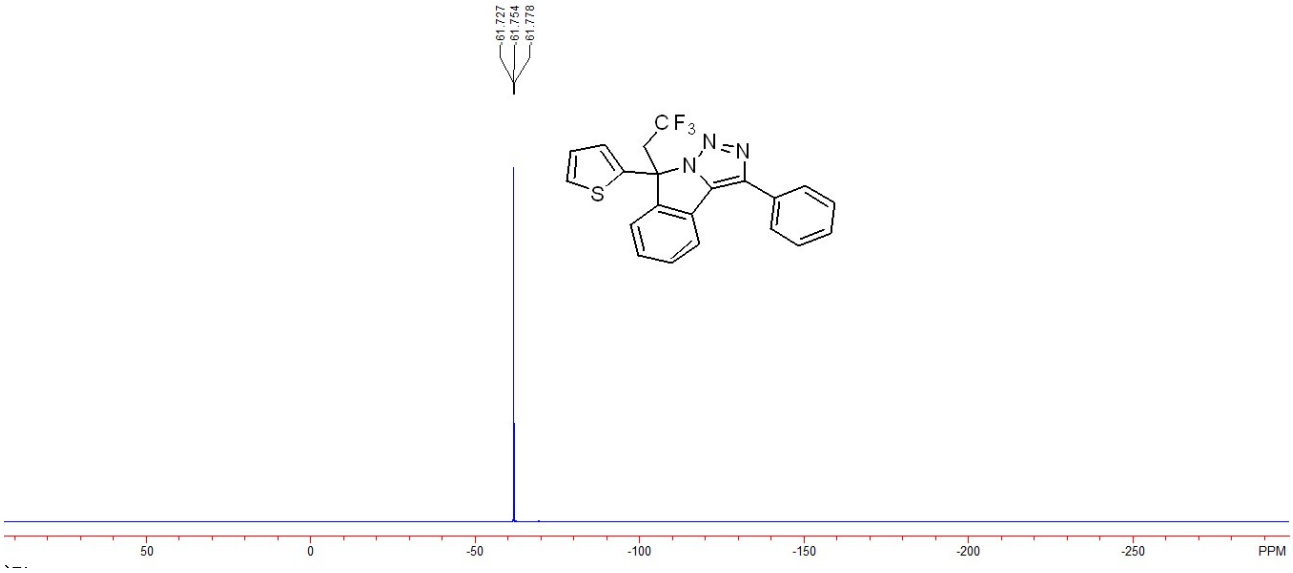


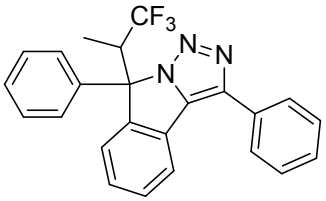


Compound 2g: 72 mg, 90%, A white solid, m.p. 177-179 ^{o}C; IR (CH_2Cl_2): ν 3081, 3065, 2976, 1610, 1496, 1448, 1376, 1356, 1309, 1259, 1237, 1170, 1122, 1111, 1049, 984, 761, 728, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.52-3.63 (m, 1H), 3.83-3.94 (m, 1H), 6.94-6.96 (m, 1H), 7.18 (d, 1H, J = 3.6 Hz), 7.26 (d, 1H, J = 4.8 Hz), 7.39-7.44 (m, 1H), 7.47 (d, 1H, J = 7.6 Hz), 7.50-7.54 (m, 3H), 7.62 (d, 1H, J = 7.6 Hz), 7.94 (d, 1H, J = 7.6 Hz), 7.98 (d, 2H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 43.1 (q, $J_{C\text{-}F}$ = 28.9 Hz), 66.2 (q, $J_{C\text{-}F}$ = 2.3 Hz), 121.7, 123.6 (q, $J_{C\text{-}F}$ = 277.8 Hz), 124.9, 126.3, 126.58, 126.62, 127.0, 127.3, 128.4, 128.6, 128.9, 129.9, 130.9, 136.3, 139.9, 141.6, 146.4; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -61.8 (t, 3F, J = 10.2 Hz); MS (ESI) *m/z*: 398.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{21}H_{15}F_3N_3S^+$ requires: 398.0933, Found: 398.0939.



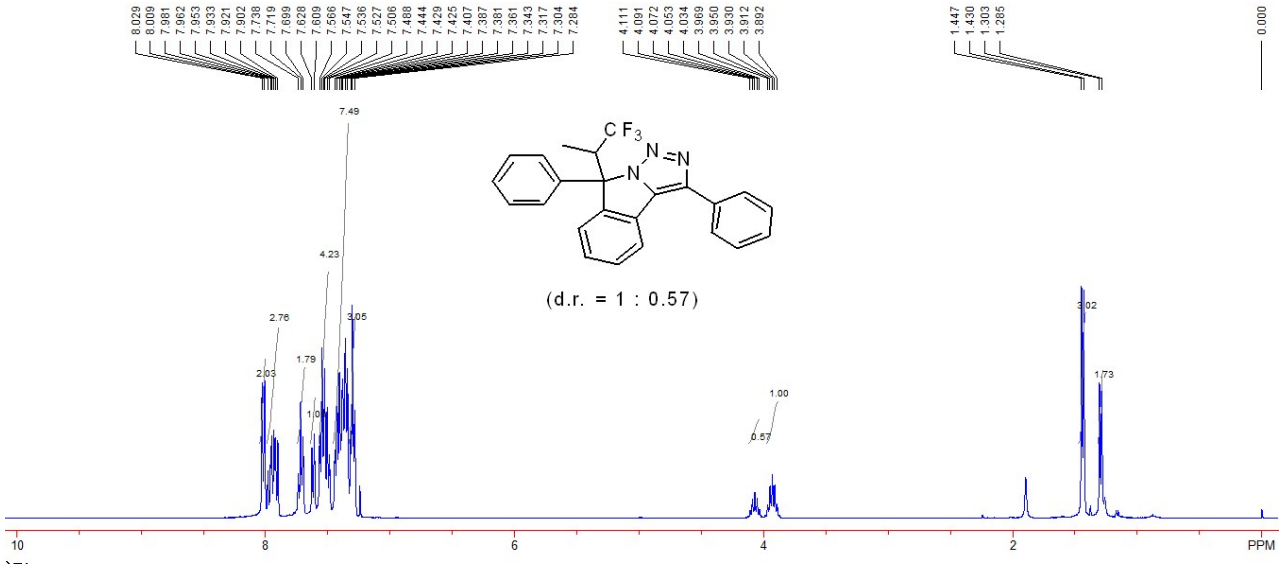


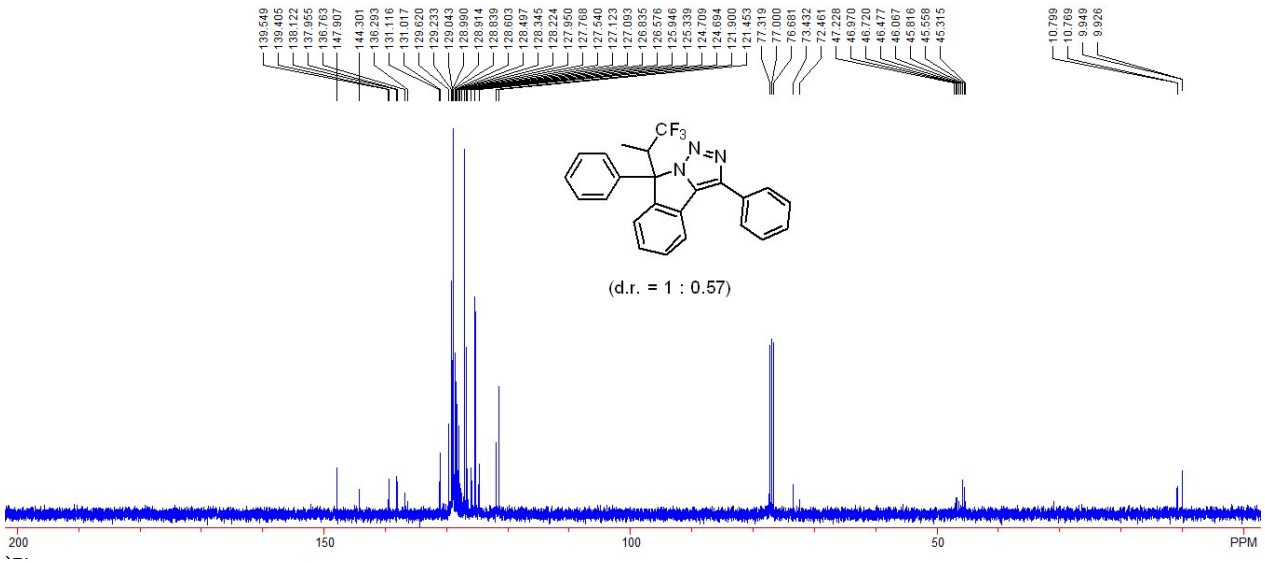


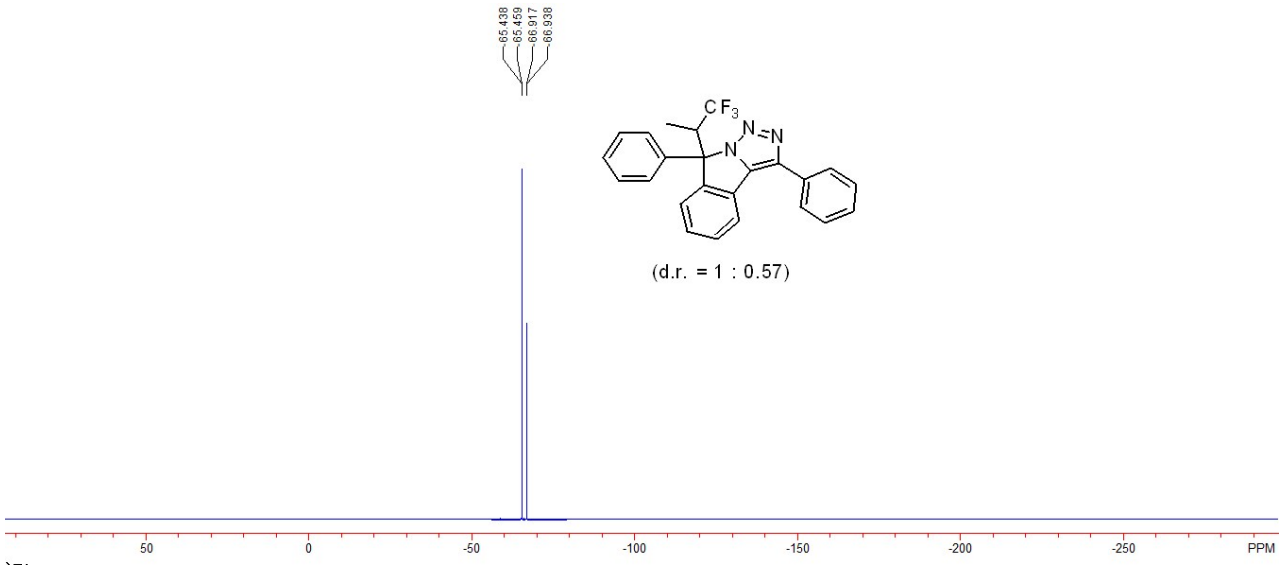


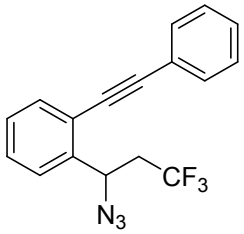
Compound 2h: 65 mg, 80%, A white solid, m.p. 184-186 ^{o}C, obtained as a 1:0.57 mixture of diastereoisomers; IR (CH_2Cl_2): ν 2954, 2923, 2852, 1497, 1458, 1448, 1354, 1264, 1175, 1125, 1074, 1044, 985, 759, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.29 (d, 1.71H, J = 7.2 Hz), 1.44 (d, 3H, J = 6.8 Hz), 3.89-3.97 (m, 1H), 4.03-4.11 (m, 0.57H), 7.28-7.32 (m, 3H), 7.34-7.44 (m, 7.56H), 7.49-7.57 (m, 4H), 7.62 (d, 1H, J = 7.6 Hz), 7.72 (t, 1.71H, J = 7.6 Hz), 7.90-7.98 (m, 2.71H), 8.02 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 9.9 (q, $J_{C\text{-}F}$ = 2.2 Hz), 10.8 (q, $J_{C\text{-}F}$ = 3.0 Hz), 45.7 (q, $J_{C\text{-}F}$ = 25.8 Hz), 46.8 (q, $J_{C\text{-}F}$ = 25.0 Hz), 72.5, 73.4, 121.5, 121.9, 124.6

(q, $J_{C\text{-}F}$ = 2.3 Hz), 124.7 (q, $J_{C\text{-}F}$ = 1.5 Hz), 125.1 (q, $J_{C\text{-}F}$ = 277.1 Hz), 125.3, 125.9, 126.2 (q, $J_{C\text{-}F}$ = 277.8 Hz), 126.6, 126.8, 127.09, 127.12, 127.8, 128.0, 128.2, 128.3, 128.5, 128.6, 128.8, 128.9, 128.99, 129.04, 129.2, 129.6, 131.0, 131.1, 136.3, 136.8, 138.0, 138.1, 139.4, 139.5, 144.3, 147.9; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -66.9 (d, 1.71F, J = 7.9 Hz), -65.4 (d, 3F, J = 7.9 Hz); MS (ESI) *m/z*: 406.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{24}H_{19}F_3N_3^+$ requires: 406.1526, Found: 406.1544.

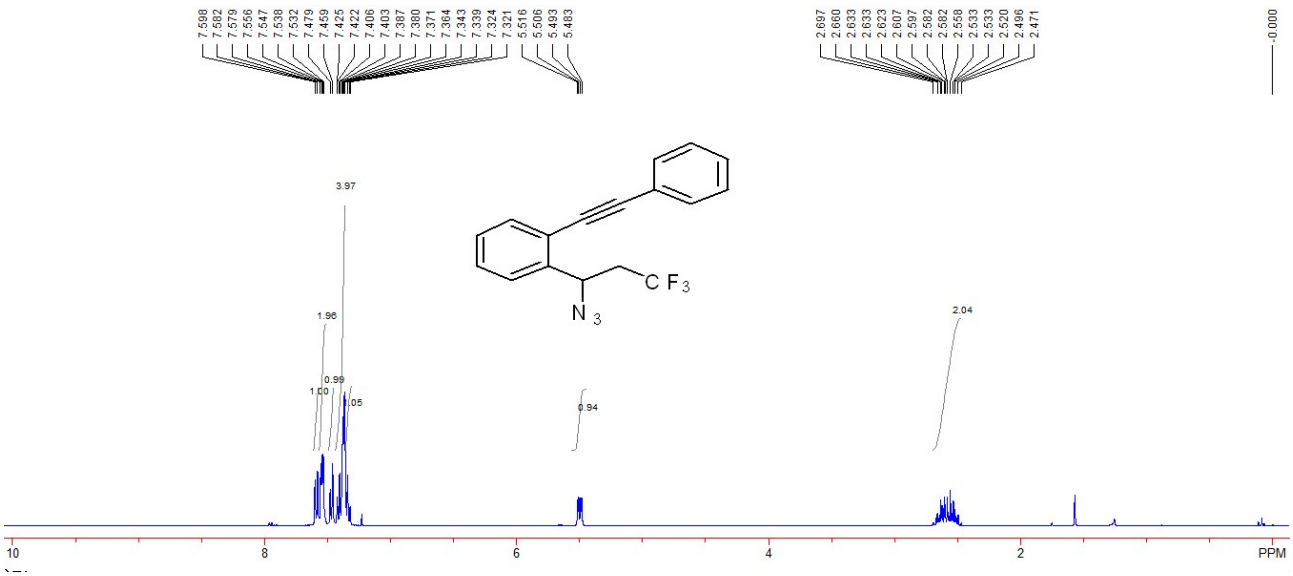








Compound 2i: 57 mg, 90%, A colorless liquid; IR (CH_2Cl_2): ν 3062, 3031, 2926, 2115, 1602, 1495, 1383, 1278, 1245, 1137, 1086, 755, 689 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 2.47-2.70 (m, 2H), 5.50 (dd, 1H, J_1 = 9.2 Hz, J_2 = 4.0 Hz), 7.33 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.36-7.43 (m, 4H), 7.47 (d, 1H, J = 8.0 Hz), 7.53-7.56 (m, 2H), 7.59 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 39.9 (q, $J_{C\text{-}F}$ = 28.1 Hz), 57.9 (q, $J_{C\text{-}F}$ = 3.1 Hz), 85.6, 95.7, 121.7, 122.4, 125.4 (q, $J_{C\text{-}F}$ = 276.1 Hz), 125.9, 128.49, 128.52, 128.9, 129.1, 131.5, 132.8, 139.5; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -64.2 (t, 3F, J = 10.2 Hz); MS (ESI) *m/z*: 316.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{17}H_{13}F_3N_3^+$ requires: 316.1056, Found: 316.1064.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7.579
7.556
7.547
7.538
7.532
7.479
7.459
7.425
7.422
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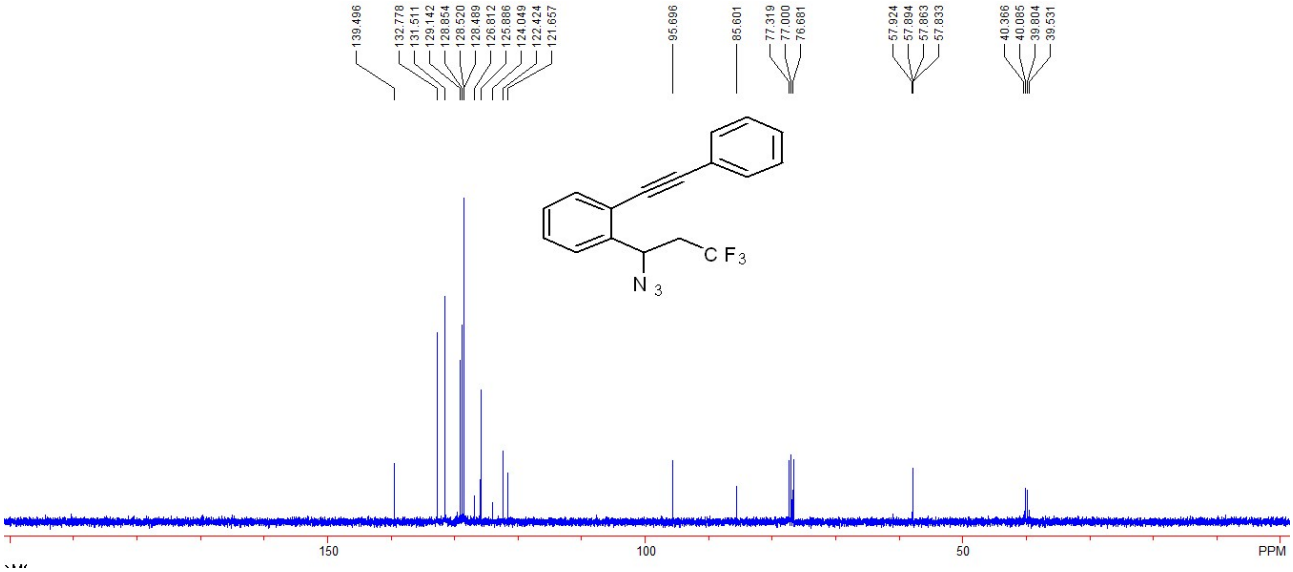
7.403
7.387
7.380
7.371
7.364
7.343
7.339
7.324
7.321
5.516
5.506
5.493
5.483
2.697
2.660
2.633
2.633
2.623
2.607
2.597
2.582
2.582
2.558
2.533
2.533
2.520
2.496
2.471
-0.000
3.97
1.96
1.00
0.99
1.05
0.94
2.04
C F3
N 3
10
8
6
4
2
PPM


139.496
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131.511
129.142
128.854
128.520
128.489
126.812
125.886
124.049
122.424
121.657
95.696
85.601
77.319
77.000
76.681
57.924
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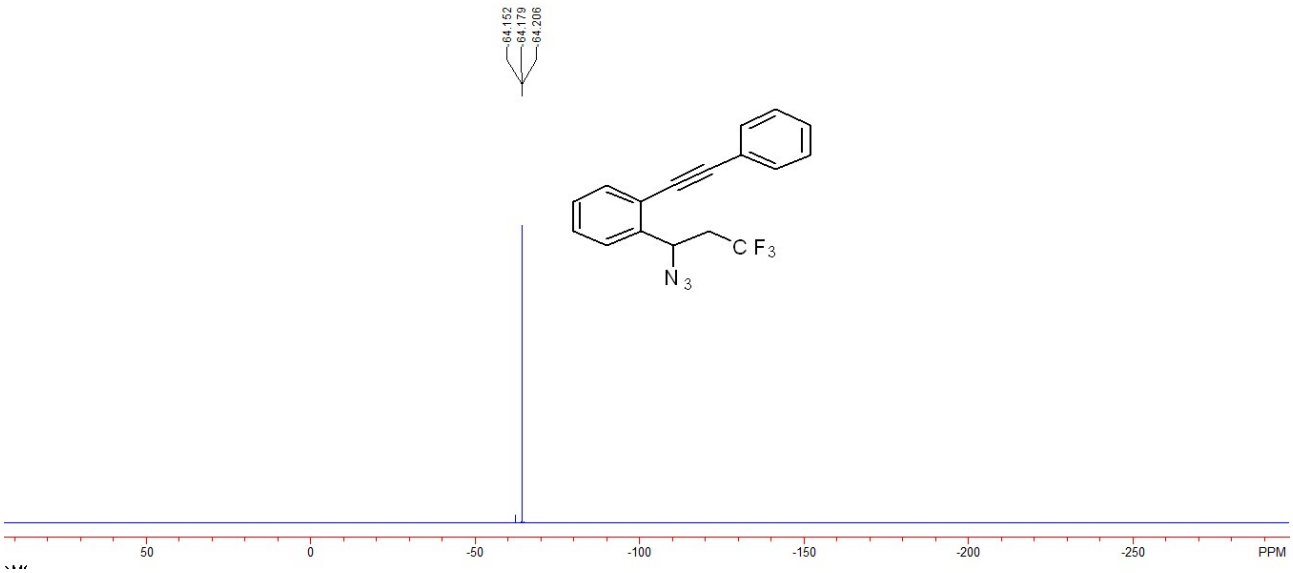
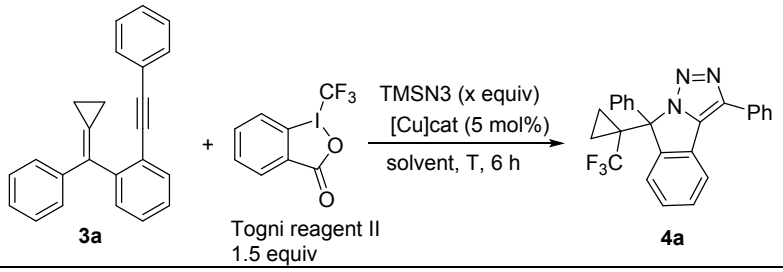
40.085
39.804
39.531
C F3
N 3
150
100
50
PPM


64.152
64.179
64.206
C F3
N 3
50
0
-50
-100
-150
-200
-250
PPM

Optimization of reaction conditions for the synthesis of 4a

Table S2 Optimization of reaction conditions for the synthesis of **4a**[a,b]

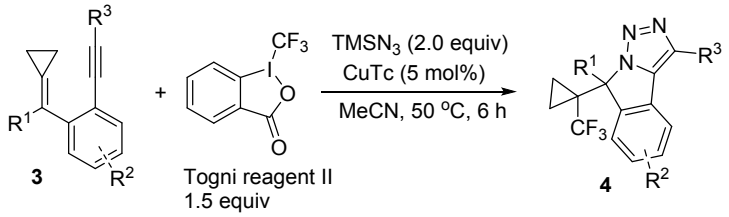


3a Togni reagent II 1.5 equiv **4a**

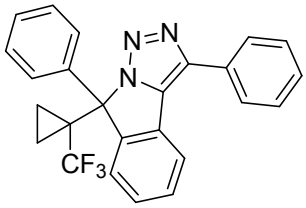
Entry	x (equiv)	$[Cu]_{cat.}$ (mol%)	Solvent	T (^{o}C)	Yield (%)
1	***2.0***	***CuTc***	***MeCN***	***50***	***82***
2	2.0	CuI	MeCN	50	70
3	2.0	CuBr	MeCN	50	73
4	2.0	$Cu(MeCN)_4PF_6$	MeCN	50	56
5	2.5	CuTc	MeCN	50	80
6	1.5	CuTc	MeCN	50	76
7[c]	2.0	CuTc	MeCN	50	59
8	2.0	CuTc	MeCN	60	77
9	2.0	CuTc	MeCN	40	71
10	2.0	CuTc	MeCN	30	N R[f]
11	2.0	CuTc	MeOH	50	23
12	2.0	CuTc	DCE	50	65
13	2.0	CuTc	1,4-dioxane	50	45
14[d]	2.0	CuTc	MeCN	50	81
15[e]	2.0	-	MeCN	50	N R[f]

[a] Reaction conditions unless specified otherwise: [Cu]cat. (0.005 mmol, 0.05 equiv), $[CF_3]$ (0.15 mmol, 1.5 equiv), $TMSN_3$ (x equiv), **3a** (0.10 mmol, 1.0 equiv), solvent (1.0 mL), T, arogen atmosphere for 6 h. [b] isolated yield. [c] Togni reagent I was used as trifluoromethyl source. [d] 10 mol% catalyst was used. [e] No catalyst was used. [f] N R = NO Reaction.

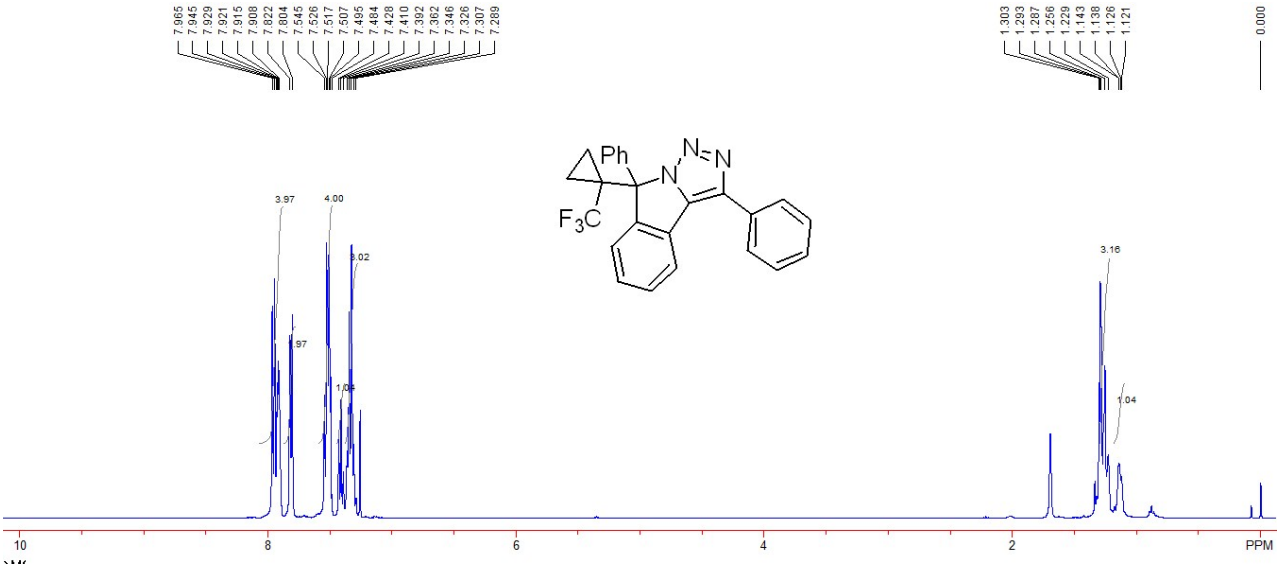
General procedure for the synthesis of products 4

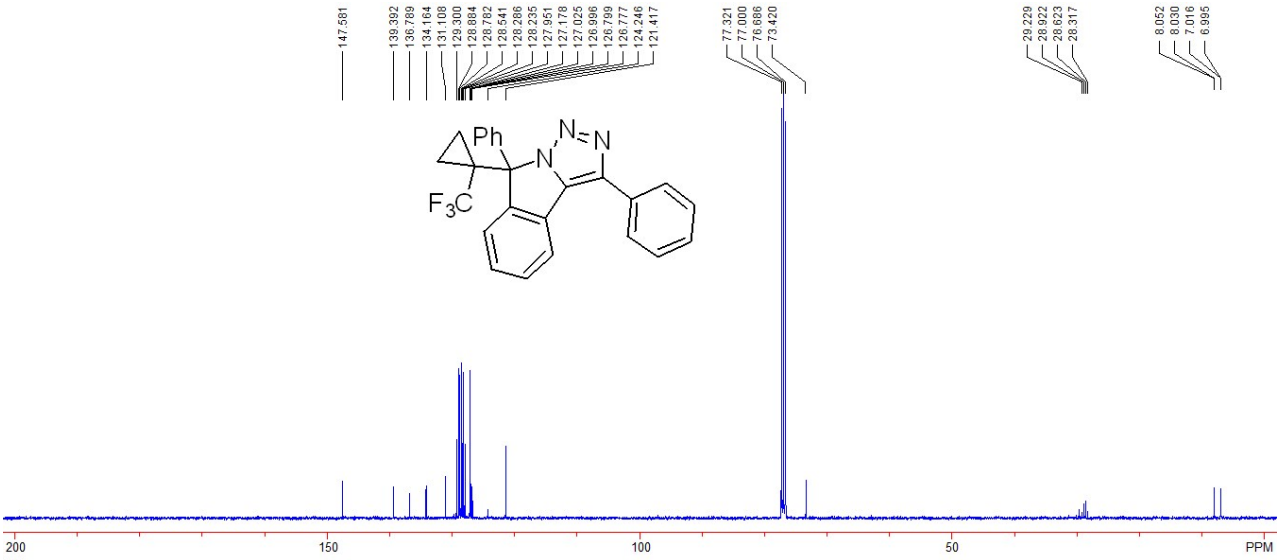


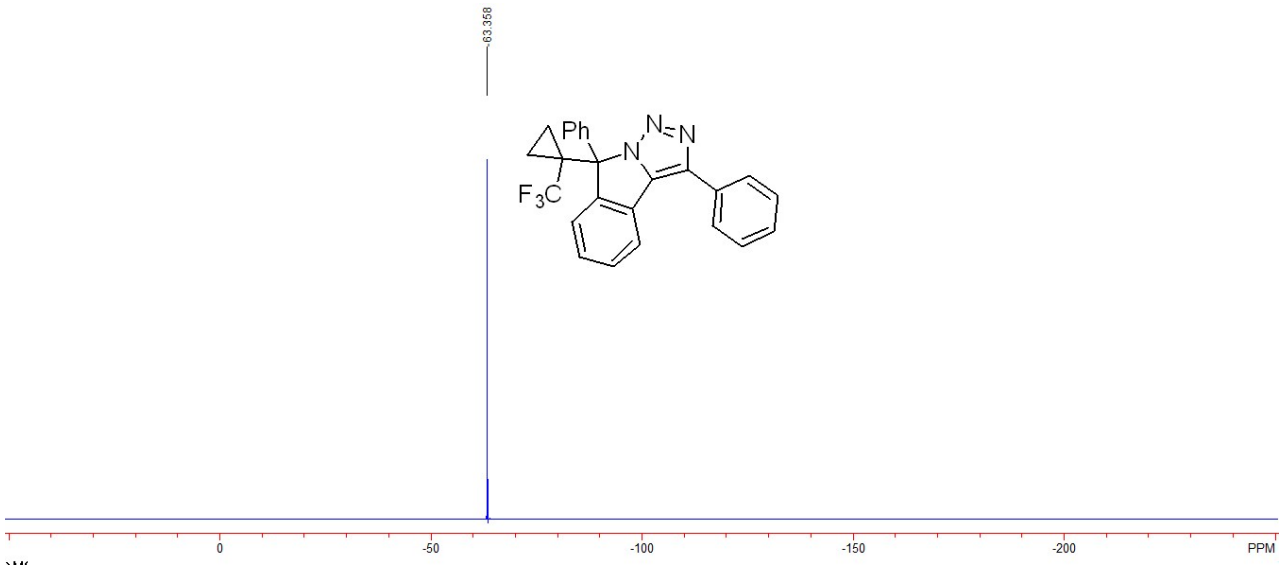
3 (0.2 mmol, 1.0 equiv), Togni reagent (0.30 mmol, 1.5 equiv), CuTc (0.010 mmol, 0.05 equiv) were dissolved in MeCN (2.0 mL), then $TMSN_3$ (0.40 mmol, 2.0 equiv) was added dropwise and the reaction tube was placed in a pre-heated 50 ^oC oil bath. The reaction was stopped after 6 h and the reaction mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the products **4** in good yield.

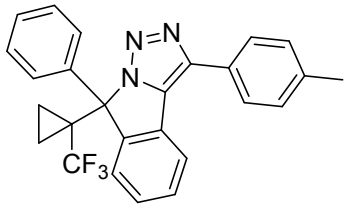


Compound 4a: 69 mg, 82%, A white solid, m.p. 165-167 ºC; IR (CH_2Cl_2): ν 3056, 3034, 1498, 1447, 1350, 1175, 1151, 1129, 1043, 985, 761, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.12-1.14 (m, 1H), 1.23-1.30 (m, 3H), 7.29-7.36 (m, 3H), 7.39-7.43 (m, 1H), 7.48-7.55 (m, 4H), 7.81 (d, 2H, J = 7.2 Hz), 7.91-7.97 (m, 4H),; ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 7.0 (q, $J_{C\text{-}F}$ = 2.1 Hz), 8.0 (q, $J_{C\text{-}F}$ = 2.2 Hz), 28.8 (q, $J_{C\text{-}F}$ = 30.1 Hz), 73.4, 121.4, 125.6 (q, $J_{C\text{-}F}$ = 275.0 Hz), 126.8 (q, $J_{C\text{-}F}$ = 2.2 Hz), 127.0, 127.2, 128.0, 128.2, 128.3, 128.5, 128.8, 128.9, 129.3, 131.1, 134.2, 136.8, 139.4, 147.6; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -63.4 (s, 3F); MS (ESI) *m/z*: 418.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{25}H_{19}F_3N_3^+$ requires: 418.1526, Found: 418.1526.

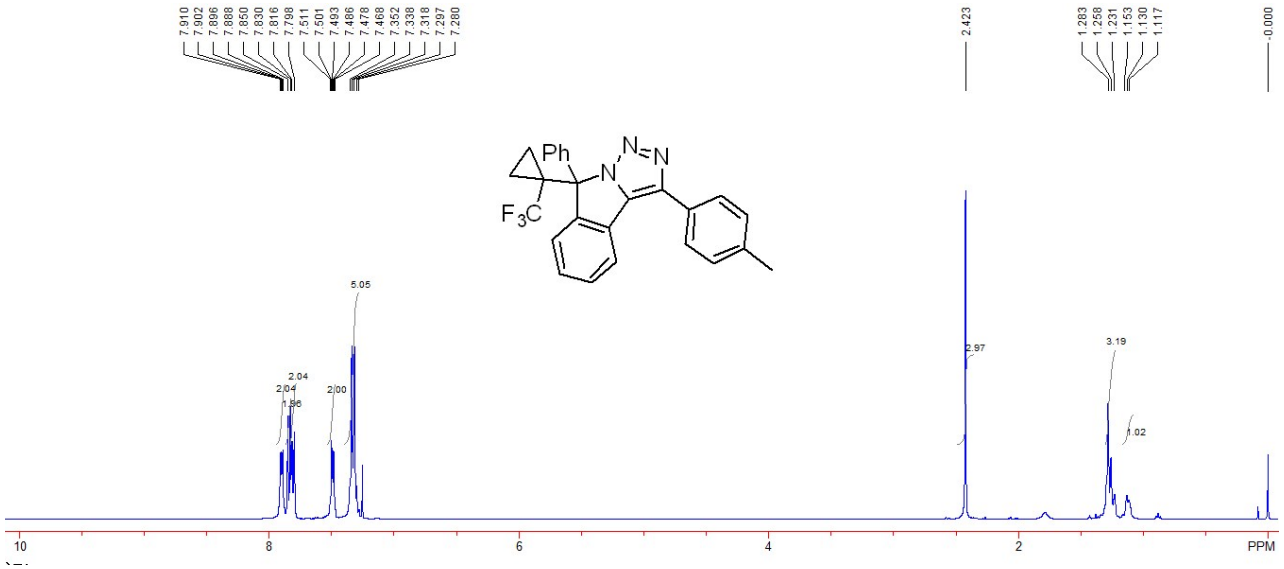








Compound 4b: 70 mg, 81%, A white solid, m.p. 167-168 ^{o}C; IR (CH_2Cl_2): ν 3059, 3034, 1512, 1356, 1170, 1152, 1138, 1130, 825, 773, 753, 730, 703 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.12-1.15 (m, 1H), 1.23-1.28 (m, 3H), 2.42 (s, 3H), 7.28-7.35 (m, 5H), 7.47-7.51 (m, 2H), 7.80-7.85 (m, 4H), 7.89-7.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 7.0 (q, J_{C-F} = 2.9 Hz), 8.0 (q, J_{C-F} = 2.2 Hz), 21.3, 28.8 (q, J_{C-F} = 29.9 Hz), 73.4, 121.3, 125.6 (q, J_{C-F} = 275.7 Hz), 126.8 (q, J_{C-F} = 1.4 Hz), 127.06, 127.13, 127.8, 128.2, 128.5, 128.7, 129.3, 129.5, 129.8, 134.2, 136.5, 138.2, 139.5, 147.5; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -63.3 (s, 3F); MS (ESI) *m/z*: 432.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{26}H_{21}F_3N_3^+$ requires: 432.1682, Found: 432.1684.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7.830
7.816
7.798
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7.501
7.493
7.486
7.478
7.468
7.352
7.338
7.318
7.297
7.280
2.423
1.283
1.258
1.231
1.153
1.130
1.117
0.000
Ph
N
N
N
F3C
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2.04
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2.00
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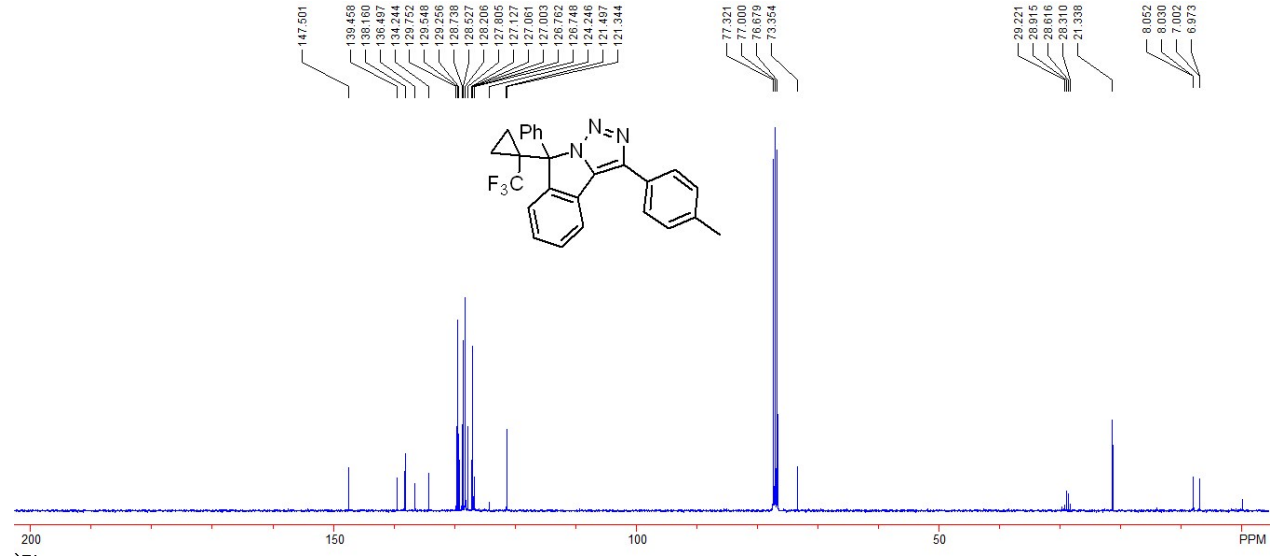
3.19
1.02
10
8
6
4
2
PPM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136.497
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129.752
129.548
129.256
128.738
128.527
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127.805
127.127
127.061
127.003
126.762
126.748
124.246
121.497
121.344
77.321
77.000
76.679
73.354
29.221
28.915
28.616
28.310
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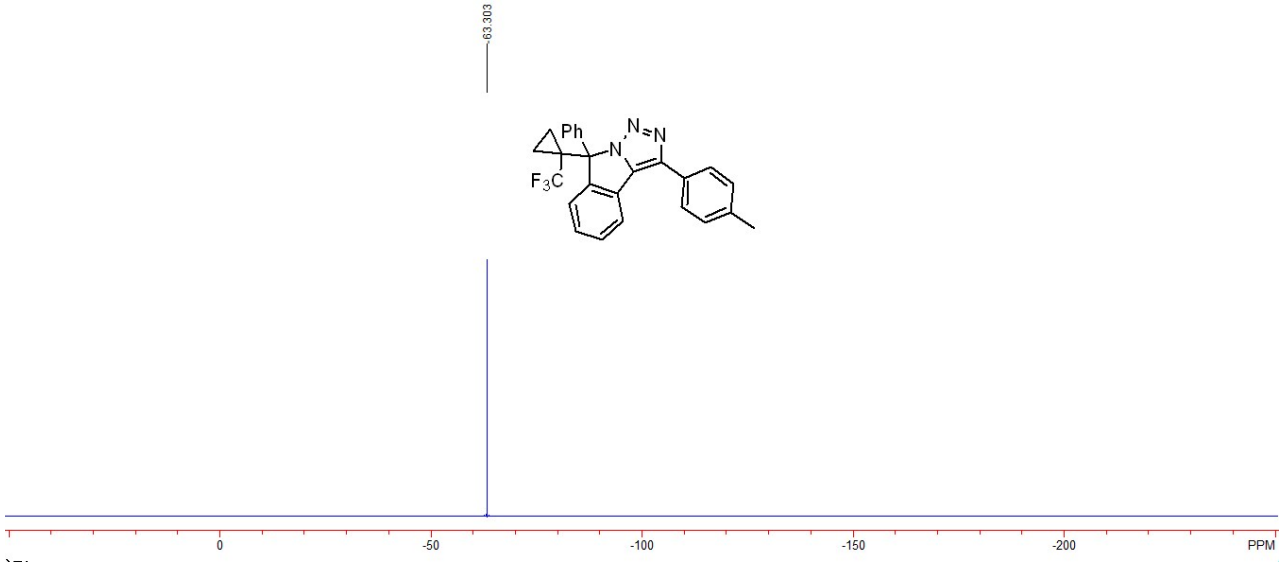
N
F3C
200
150
100
50
PPM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-100
-150
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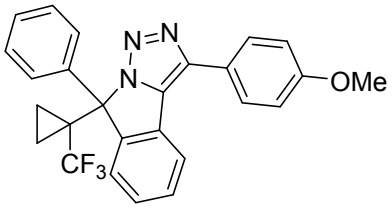
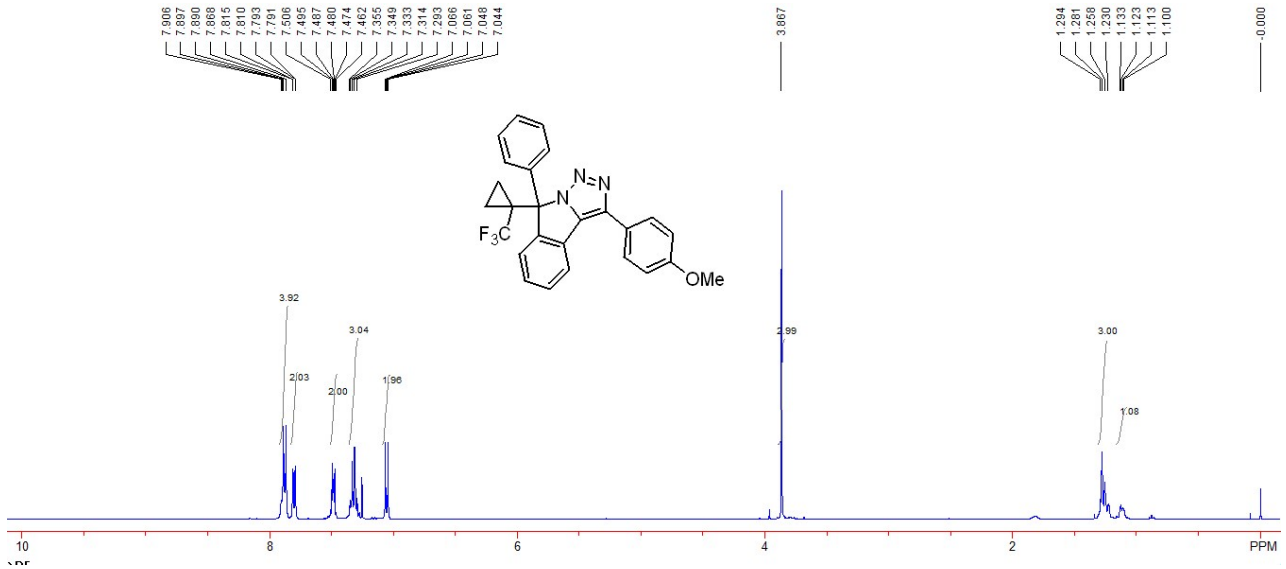
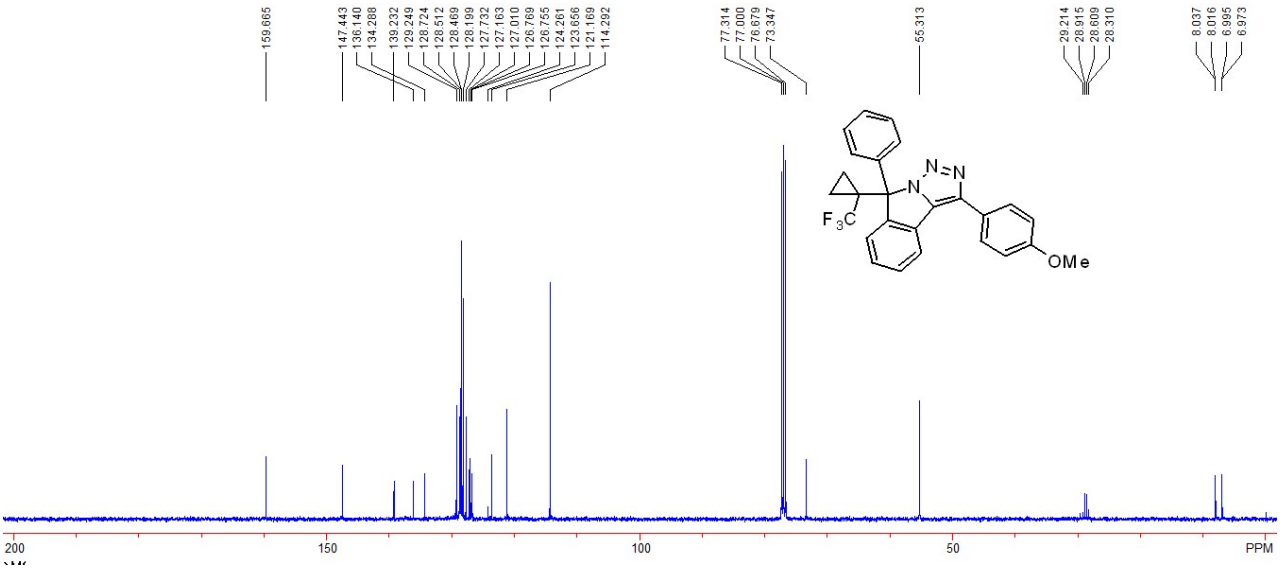
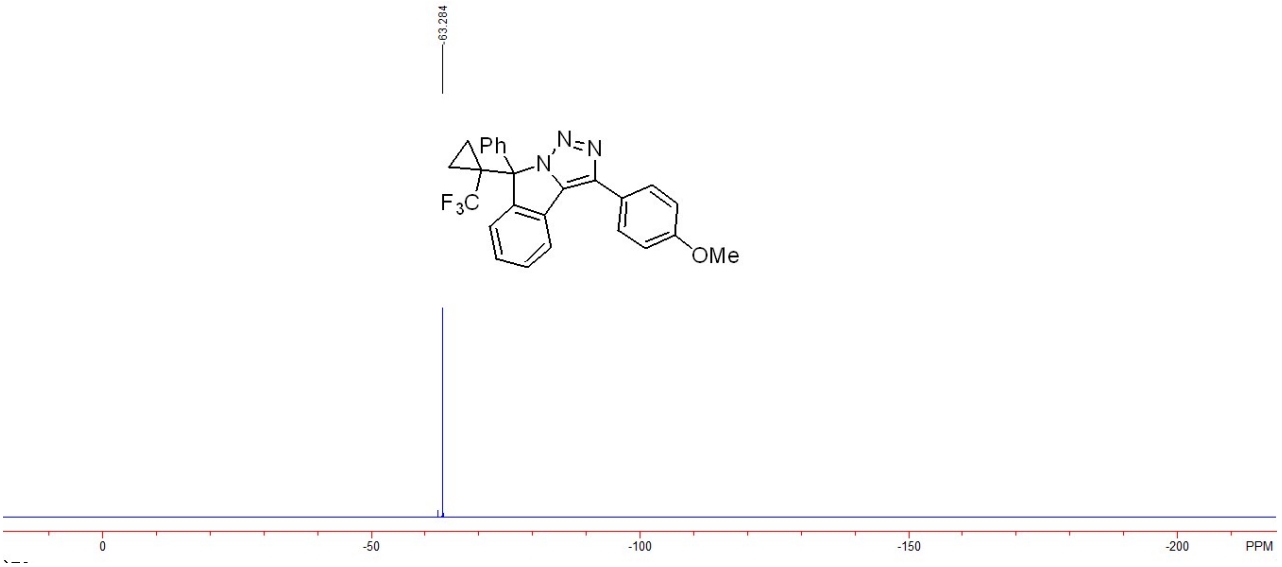
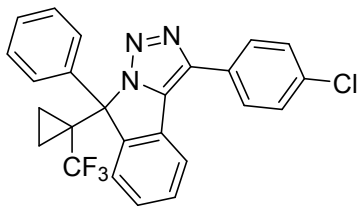


Compound 4c: 77 mg, 86%, A white solid, m.p. 159-161 ^{o}C; IR (CH_2Cl_2): ν 3065, 2923, 2831, 1614, 1509, 1454, 1350, 1247, 1177, 1153, 1139, 1128, 1108, 1037, 833, 770, 758, 741, 710 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.10-1.13 (m, 1H), 1.23-1.29 (m, 3H), 3.87 (s, 3H), 7.25 (dd, 2H, J_1 = 7.2 Hz, J_2 = 1.6 Hz), 7.29-7.36 (m, 3H), 7.46-7.51 (m, 2H), 7.79-7.82 (m, 2H), 7.87-7.91 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 7.0 (q, J_{C-F} = 2.2 Hz), 8.0 (q, J_{C-F} = 2.1 Hz), 28.8 (q, J_{C-F} = 30.6 Hz), 55.3, 73.3, 114.3, 121.2, 123.7, 125.6 (q, J_{C-F} = 274.9 Hz), 126.8 (q, J_{C-F} = 1.4 Hz), 127.2, 127.7, 128.2, 128.47, 128.51, 128.7, 129.2, 134.3, 136.1, 139.2, 147.4, 159.7; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -63.3 (s, 3F); MS (ESI) *m/z*: 448.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{26}H_{21}F_3N_3O^+$ requires: 448.1631, Found: 448.1633.



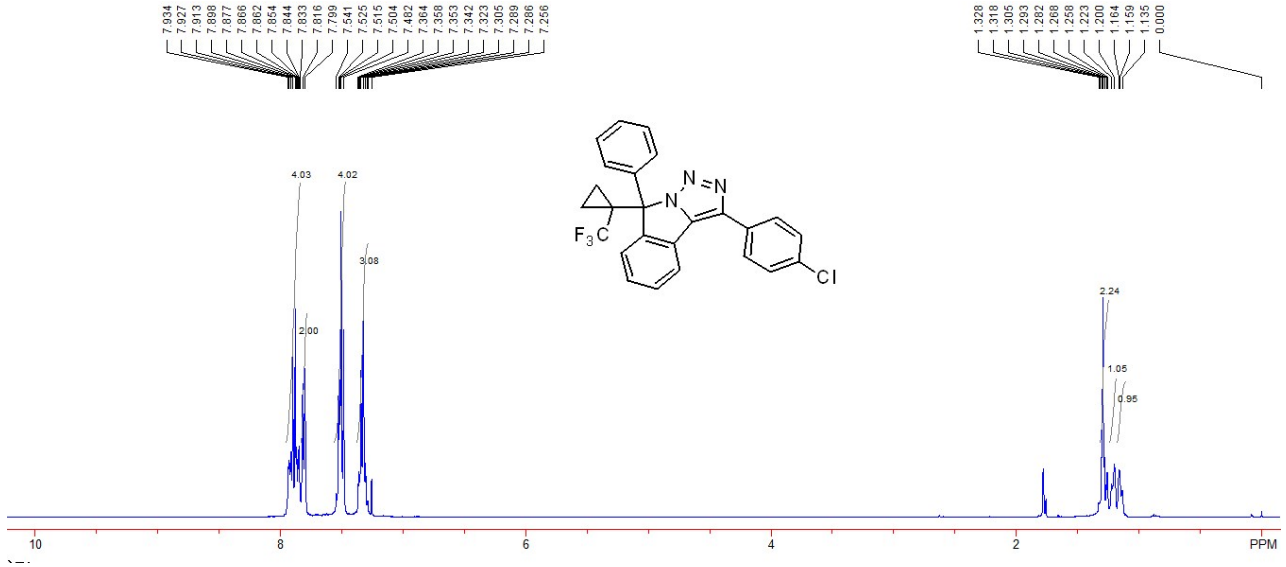


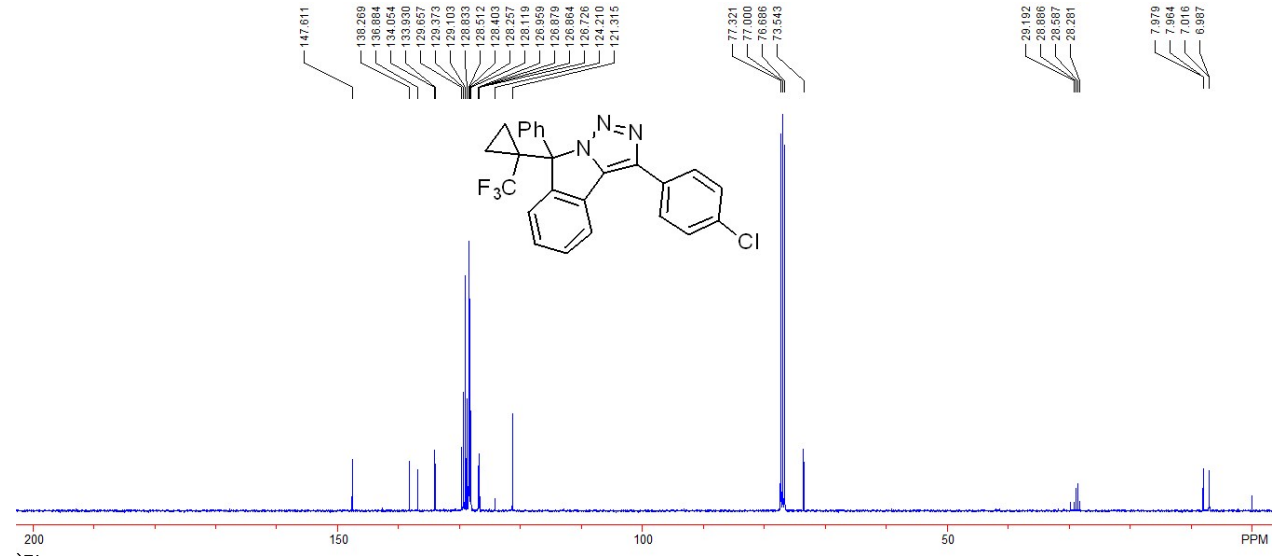


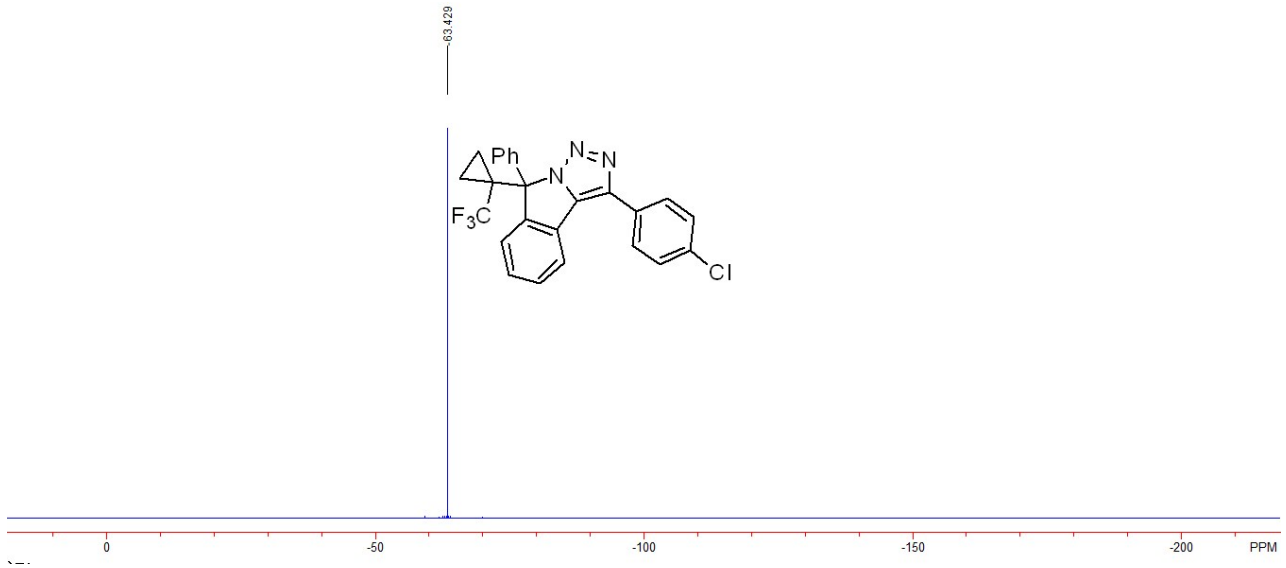


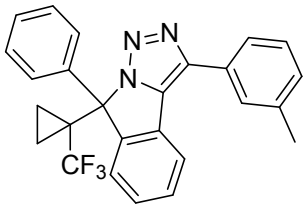
Compound 4d: 69 mg, 76%, A white solid, m.p. 185-187 ^{o}C; IR (CH_2Cl_2): ν 3115, 3062, 1490, 1455, 1351, 1184, 1169, 1151, 1131, 1090, 984, 835, 771, 746, 739, 703 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.13-1.22 (m, 1H), 1.26-1.33 (m, 3H), 7.26-7.36 (m, 3H), 7.48-7.54 (m, 4H), 7.80-7.84 (m, 2H), 7.85-7.93 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 7.0 (q, J_{C-F} = 2.9 Hz), 8.0 (q, J_{C-F} = 1.5 Hz), 28.7 (q, J_{C-F} = 30.6 Hz), 73.5, 121.3, 125.6 (q, J_{C-F} = 274.9 Hz), 126.7, 126.9 (q, J_{C-F} = 1.5 Hz), 128.1, 128.3, 128.4, 128.5, 128.8, 129.1, 129.4, 129.7, 133.9, 134.1, 136.9, 138.3,

147.6; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -63.4 (s, 3F); MS (ESI) *m/z*: 452.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{25}H_{18}ClF_3N_3^+$ requires: 452.1136, Found: 452.1136.

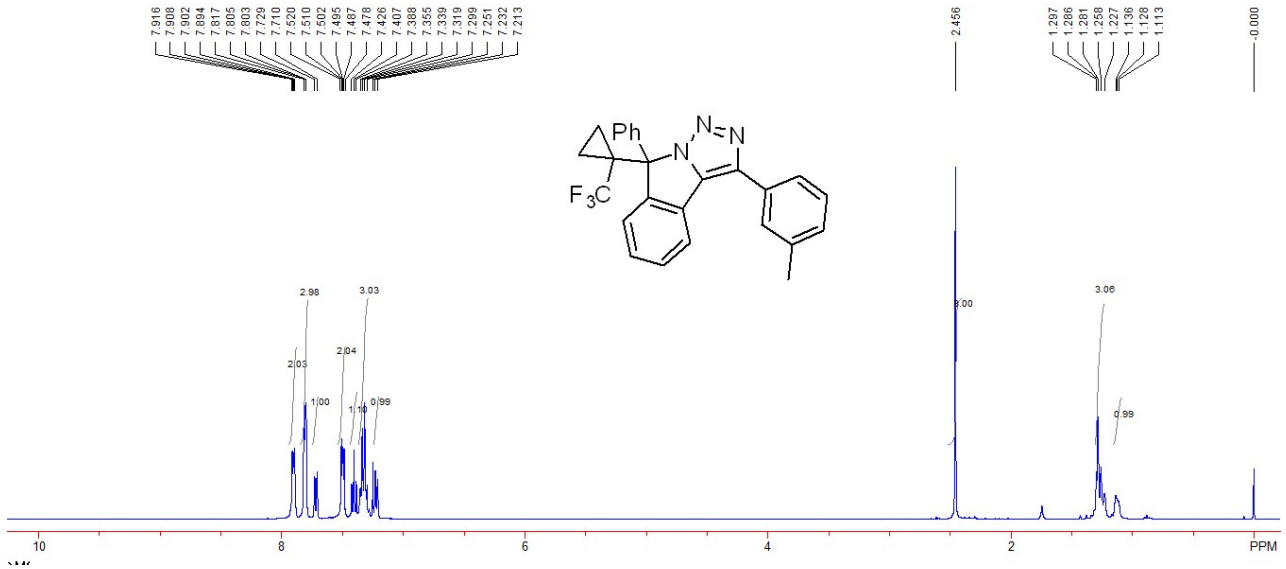


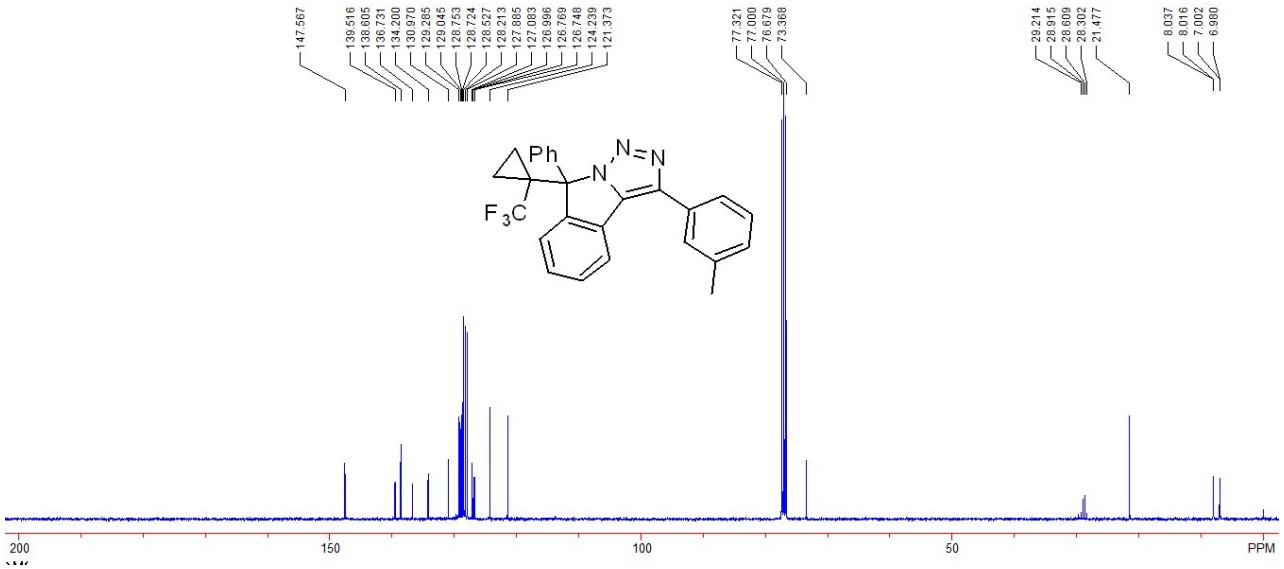


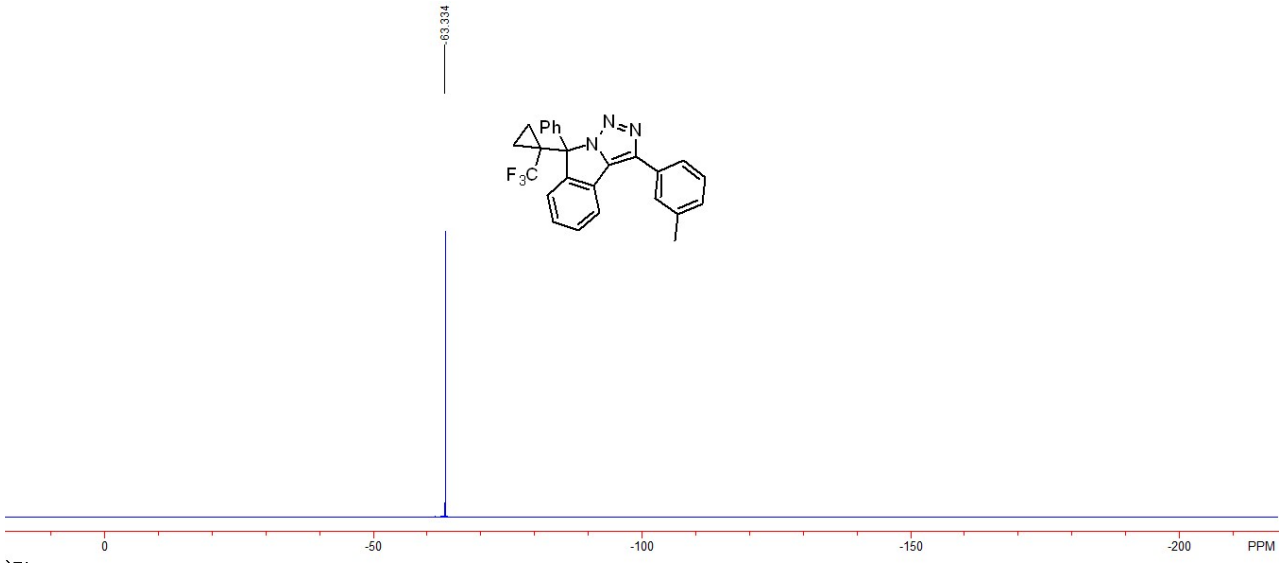


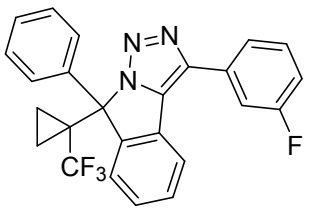


Compound 4e: 61 mg, 70%, A white solid, m.p. 177-179 °C; IR (CH_2Cl_2): ν 2962, 2917, 2851, 1449, 1350, 1313, 1249, 1153, 1130, 1035, 791, 770, 748, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.11-1.14 (m, 1H), 1.23-1.30 (m, 3H), 2.46 (s, 3H), 7.23 (t, 1H, J = 7.6 Hz), 7.30-7.36 (m, 3H), 7.41 (t, 1H, J = 7.6 Hz), 7.49-7.52 (m, 2H), 7.72 (d, 1H, J = 7.6 Hz), 7.80-7.82 (m, 3H), 7.89-7.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 7.0 (q, J_{C-F} = 2.2 Hz), 8.0 (q, J_{C-F} = 2.1 Hz), 21.5, 28.8 (q, J_{C-F} = 30.6 Hz), 73.4, 121.4, 124.2, 125.6 (q, J_{C-F} = 275.7 Hz), 126.8 (q, J_{C-F} = 2.1 Hz), 127.1, 127.9, 128.2, 128.5, 128.7, 128.8, 129.0, 129.3, 131.0, 134.2, 136.7, 138.6, 139.5, 147.6; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -63.3 (s, 3F); MS (ESI) *m/z*: 432.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{26}H_{21}F_3N_3^+$ requires: 432.1682, Found: 432.1684.



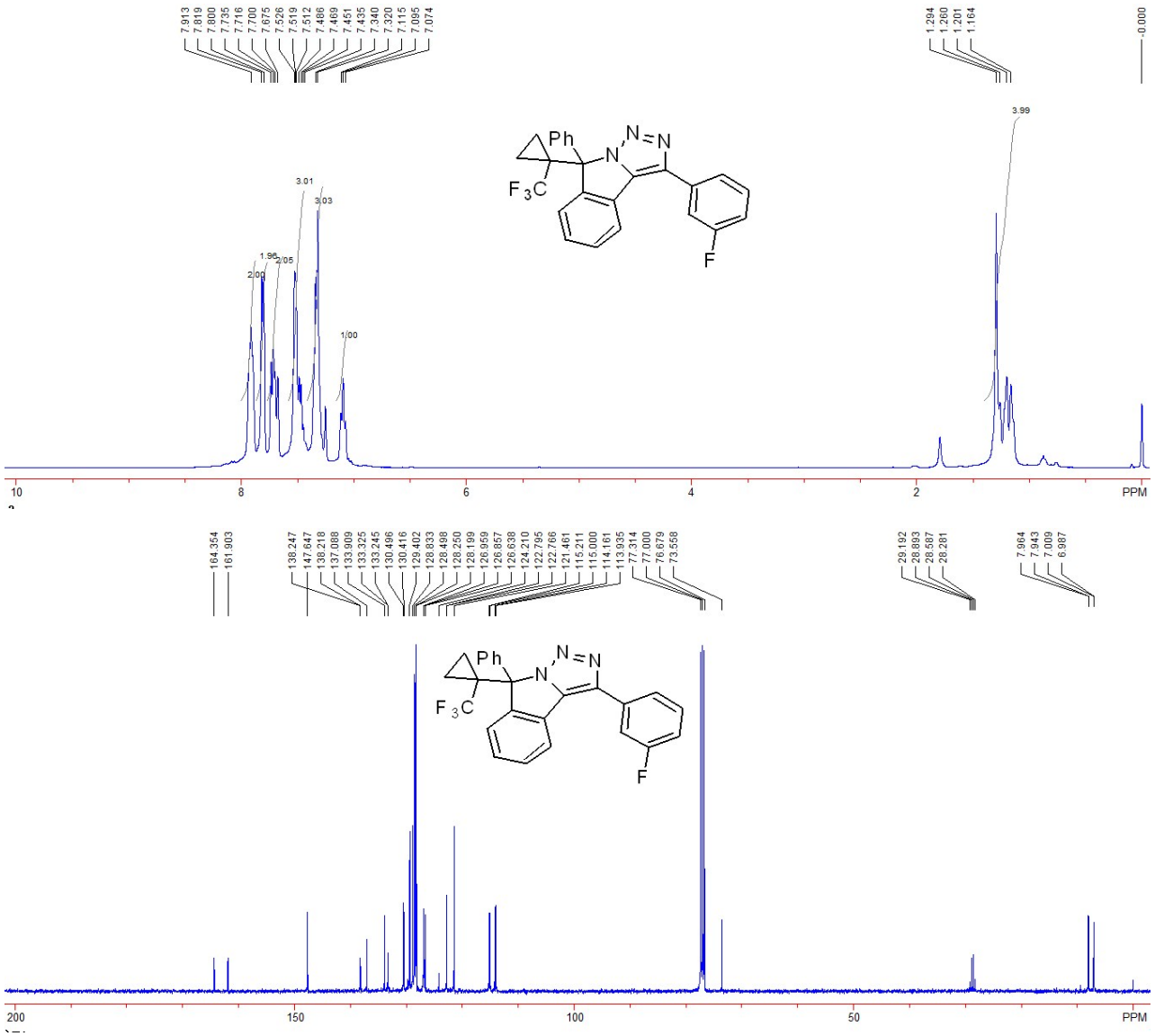


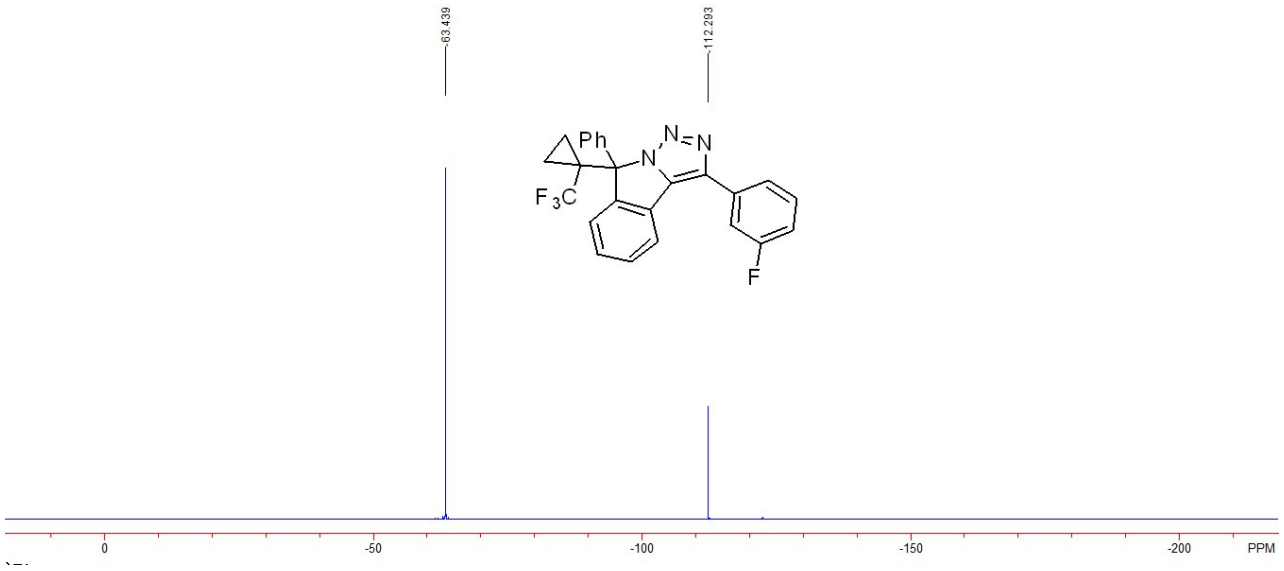


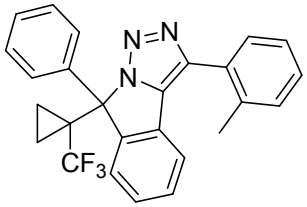


Compound 4f: 73 mg, 84%, A white solid, m.p. 188-190 ^{o}C; IR (CH_2Cl_2): ν 3065, 3023, 1616, 1584, 1493, 1349, 1266, 1167, 1152, 1130, 873, 790, 770, 746, 703, 685 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.16-1.29 (m, 4H), 7.10 (t, 1H, J = 8.0 Hz), 7.32-7.34 (m, 3H), 7.44-7.53 (m, 3H), 7.68-7.74 (m, 2H), 7.81 (d, 2H, J = 7.6 Hz), 7.91 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 7.0 (q, J_{C-F} = 2.2 Hz), 8.0 (q, J_{C-F} = 2.1 Hz), 28.7 (q, J_{C-F} = 30.6 Hz), 73.6, 114.0 (d, J_{C-F} = 22.6 Hz), 115.1 (d, J_{C-F} = 21.1 Hz), 121.5, 122.8 (d, J_{C-F} = 3.1 Hz), 125.6 (q, J_{C-F} = 274.9 Hz), 126.6, 126.8 (q, J_{C-F} = 1.5 Hz), 128.2, 128.3, 128.5, 128.8, 129.4, 130.5 (d, J_{C-F} = 8.0 Hz), 133.3 (d, J_{C-F} = 8.0 Hz),

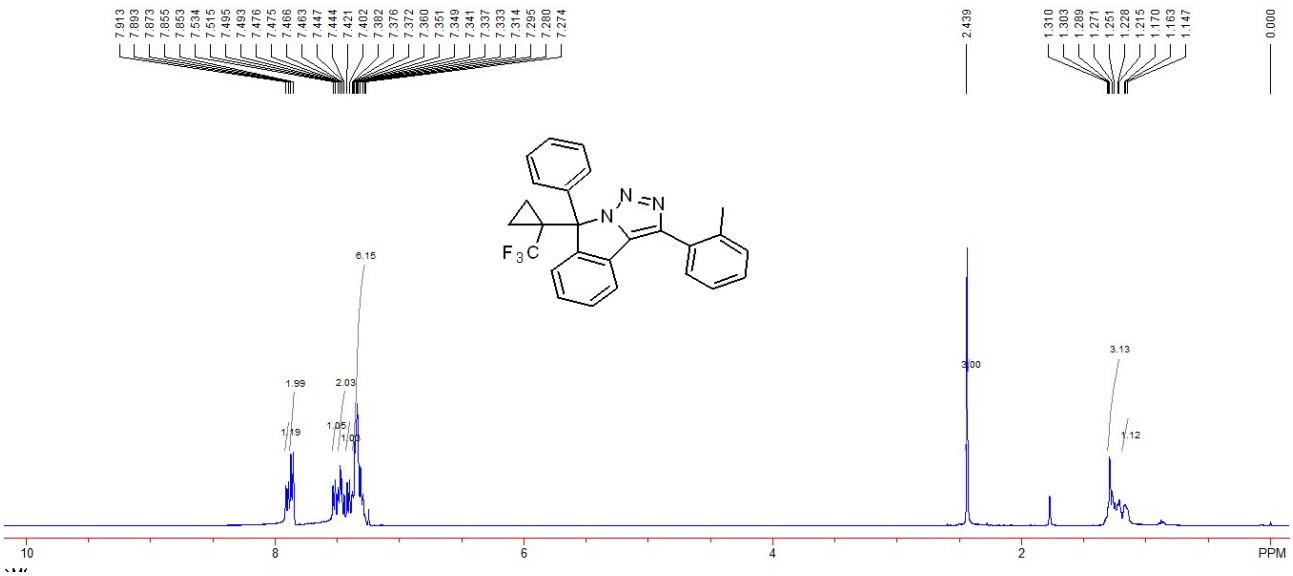
133.9, 137.1, 138.2 (d, $J_{C\text{-}F}$ = 2.9 Hz), 147.6, 163.1 (d, $J_{C\text{-}F}$ = 245.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -63.4 (s, 3F), -112.3 (s, 1F); MS (ESI) *m/z*: 436.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{25}H_{18}F_4N_3^+$ requires: 436.1431, Found: 436.1433.







Compound 4g: 70 mg, 81%, A white solid, m.p. 174-176 ^{o}C; IR (CH_2Cl_2): ν 3062, 3020, 1493, 1449, 1352, 1283, 1153, 1132, 784, 768, 754, 705 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.15-1.17 (m, 1H), 1.22-1.31 (m, 3H), 2.44 (s, 3H), 7.27-7.38 (m, 6H), 7.41 (d, 1H, J = 7.6 Hz), 7.44-7.50 (m, 2H), 7.52 (d, 1H, J = 7.6 Hz), 7.86 (dd, 2H, J_1 = 8.0 Hz, J_2 = 0.8 Hz), 7.90 (d, 1H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 7.0 (q, J_{C-F} = 2.3 Hz), 8.0 (q, J_{C-F} = 2.3 Hz), 20.3, 29.0 (q, J_{C-F} = 30.4 Hz), 73.6, 121.4, 125.6 (q, J_{C-F} = 275.2 Hz), 125.8, 126.7 (q, J_{C-F} = 1.9 Hz), 127.0, 127.8, 128.2, 128.56, 128.61, 128.8, 129.2, 129.8, 130.0, 130.8, 134.0, 137.3, 137.8, 138.7, 147.5; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -63.7 (s, 3F); MS (ESI) *m/z*: 432.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{26}H_{21}F_3N_3^+$ requires: 432.1682, Found: 432.1686.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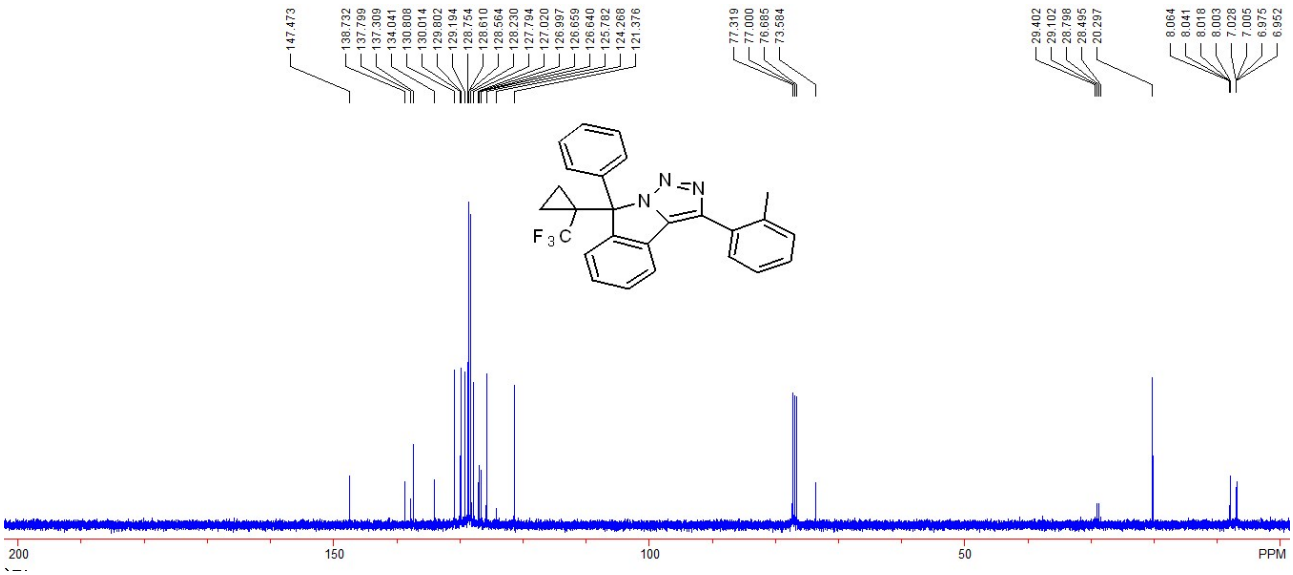
2
PPM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127.020
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126.659
126.640
125.782
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77.000
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73.584
29.402
29.102
28.798
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20.297
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8.003
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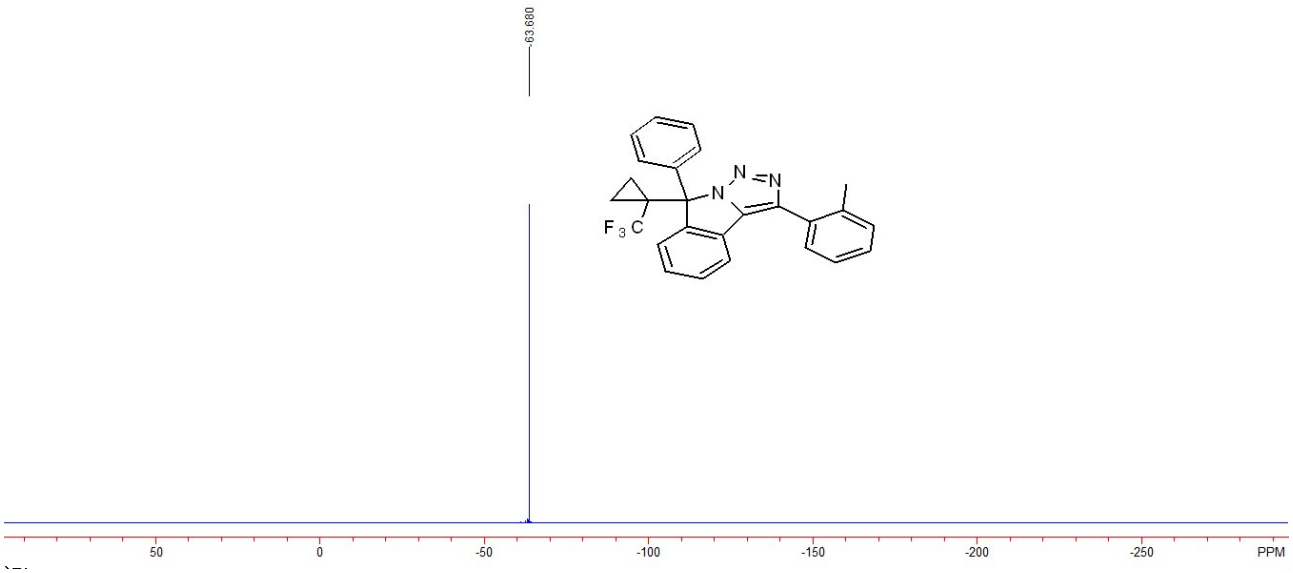
100
50
PPM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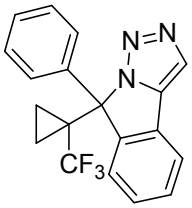
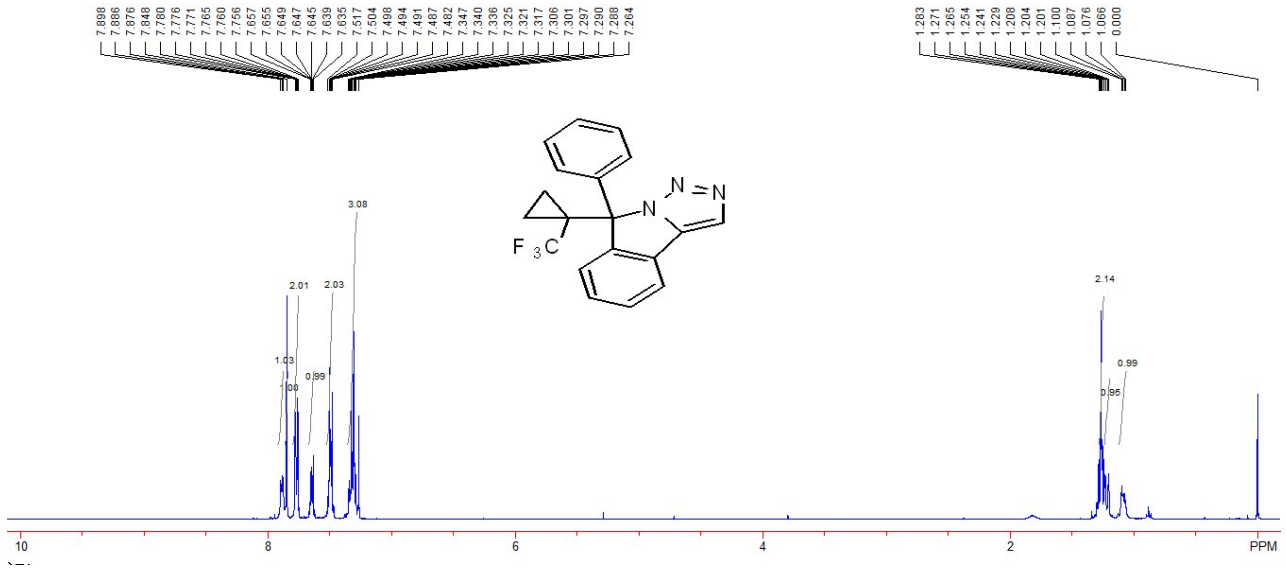
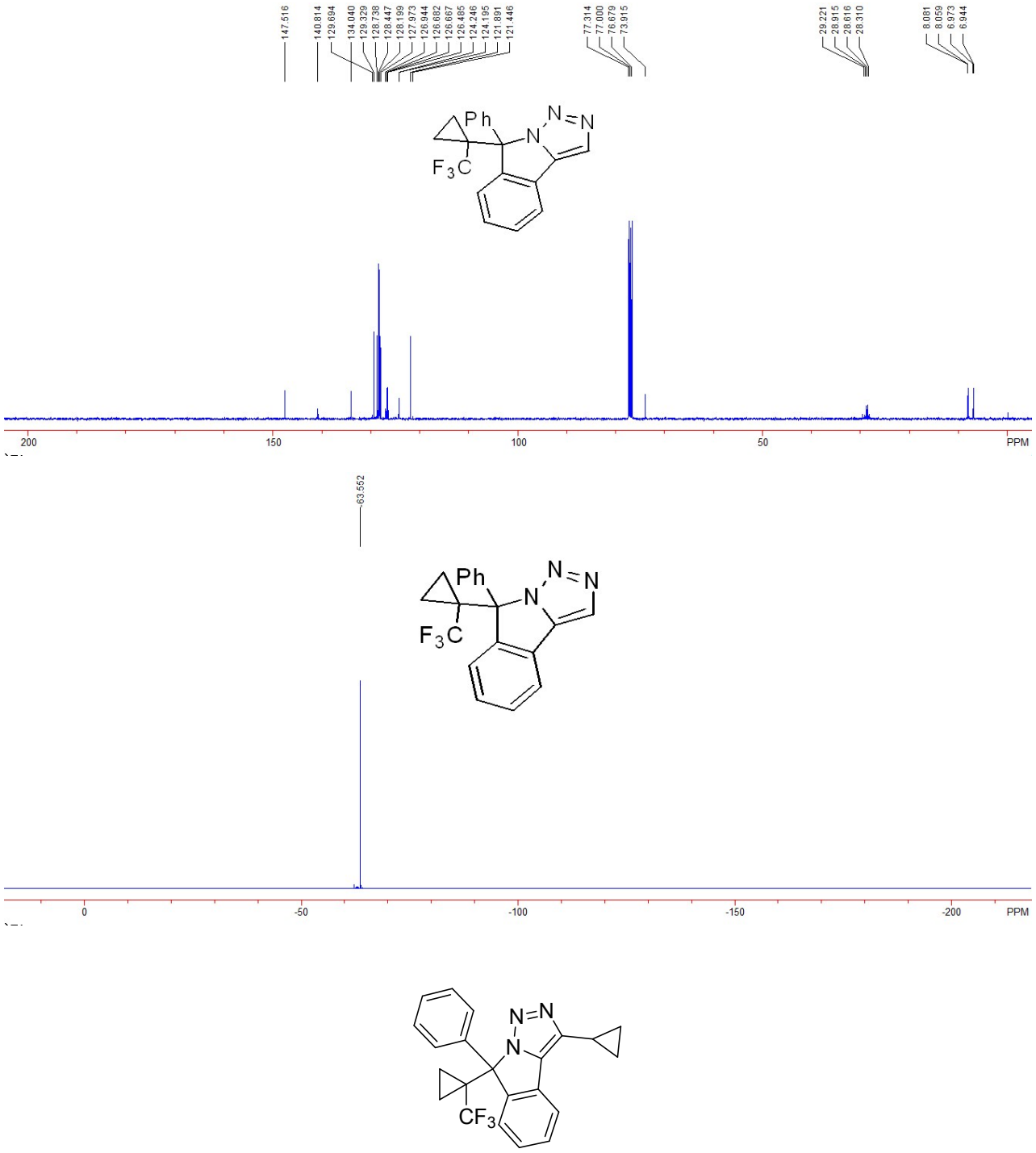


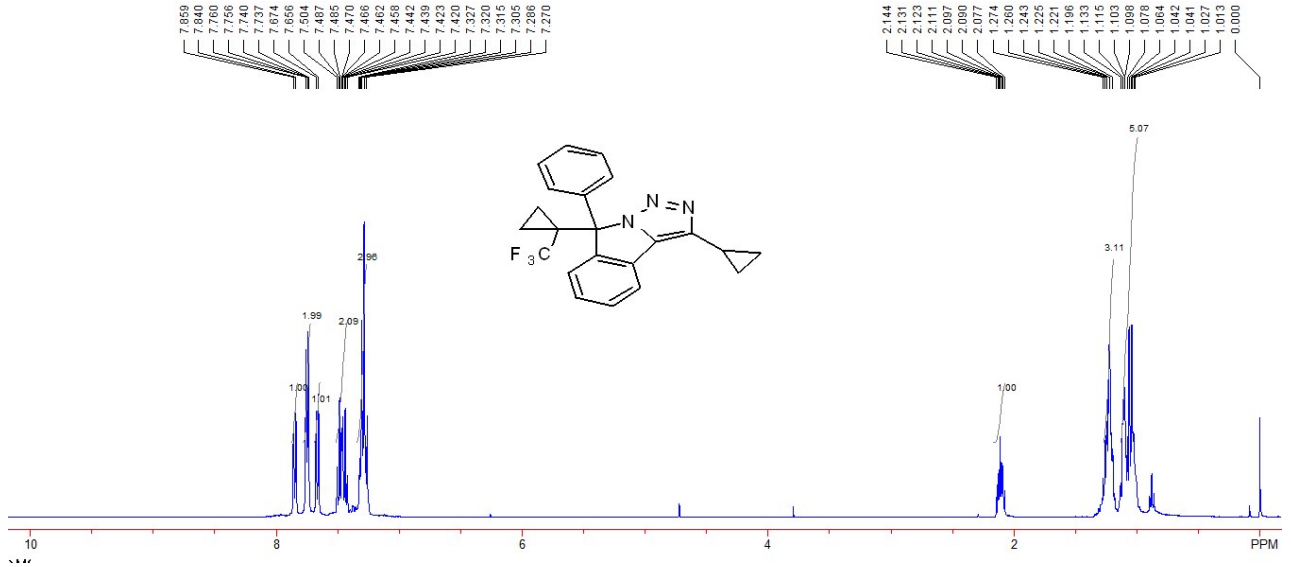
Compound 4h: 53 mg or 26 mg, 77% or 38%, A white solid, m.p. 157-159 ^{o}C; IR (CH_2Cl_2): ν 3065, 3026, 1491, 1453, 1350, 1282, 1176, 1157, 1165, 1127, 1041, 824, 771, 756, 747, 707, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.07-1.10 (m, 1H), 1.20-1.28 (m, 3H), 7.26-7.35 (m, 3H), 7.48-7.52 (m, 2H), 7.64-7.66 (m, 1H), 7.76-7.78 (m, 2H), 7.85 (s, 1H), 7.88-7.90 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 7.0 (q, $J_{C\text{-}F}$ = 2.9 Hz), 8.0 (q, $J_{C\text{-}F}$ = 2.2 Hz), 28.8 (q, $J_{C\text{-}F}$ = 29.9 Hz), 73.9, 121.9, 124.2, 125.6 (q, $J_{C\text{-}F}$ = 274.9 Hz), 126.5, 126.7 (q, $J_{C\text{-}F}$ = 2.5 Hz), 128.0, 128.2, 128.4, 128.7, 129.3, 134.0, 140.8, 147.5; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -63.6 (s, 3F); MS (ESI) *m/z*: 342.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{19}H_{15}F_3N_3^+$ requires: 342.1213, Found: 342.1215.

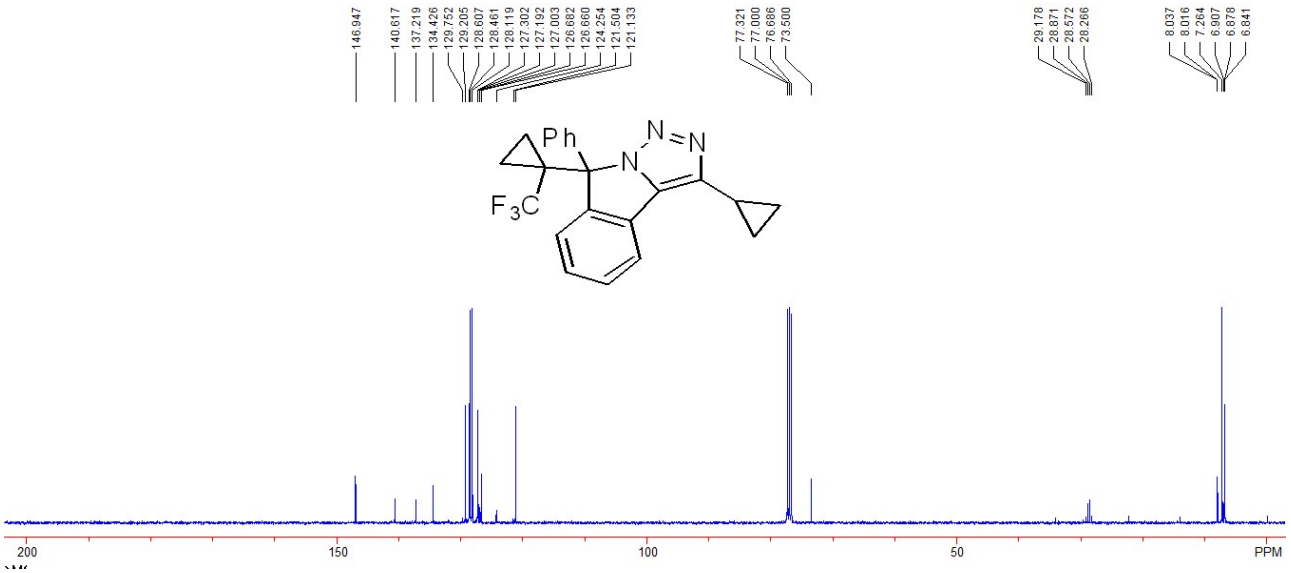


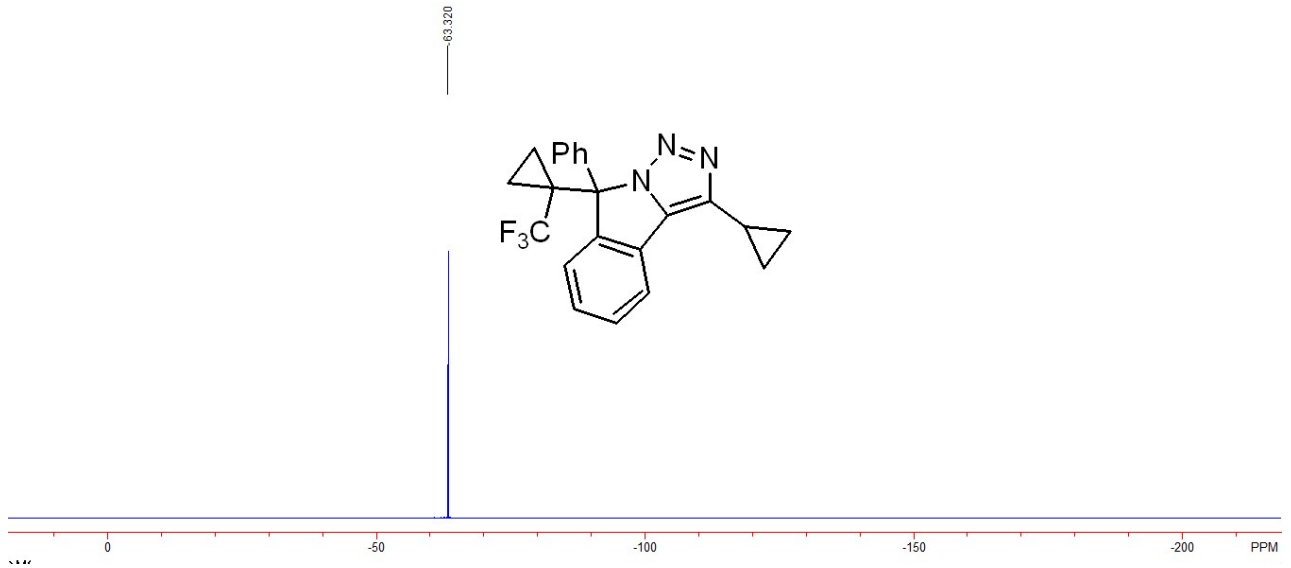


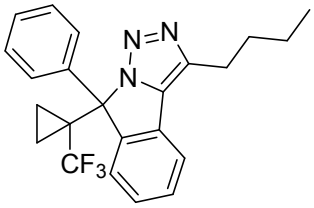
Compound 4i: 68 mg, 89%, A white solid, m.p. 139-141 ^{o}C; IR (CH_2Cl_2): ν 2979, 2920, 1444, 1355, 1176, 1153, 1140, 1127, 1046, 771, 757, 748, 705 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.01-1.13 (m, 5H), 1.20-1.27 (m, 3H), 2.08-2.14 (m, 1H), 7.27-7.33 (m, 3H), 7.42-7.50 (m, 2H), 7.66 (d, 1H, J = 7.2 Hz), 7.75 (dd, 2H, J_1 = 7.6 Hz, J_2 = 1.6 Hz), 7.86 (d, 1H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 6.8, 6.9 (q, $J_{C\text{-}F}$ = 1.9 Hz), 7.3, 8.0 (q, $J_{C\text{-}F}$ = 2.1 Hz), 28.7 (q, $J_{C\text{-}F}$ = 29.9 Hz), 73.5, 121.1, 125.6 (q, $J_{C\text{-}F}$ = 274.9 Hz), 126.7 (q, $J_{C\text{-}F}$ = 2.2 Hz), 127.2, 127.3, 128.1, 128.5, 128.6, 129.2, 129.8, 134.4, 137.2, 140.6, 146.9; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -63.3

(s, 3F); MS (ESI) *m/z*: 382.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{22}H_{19}F_3N_3^+$ requires: 382.1526, Found: 382.1527.

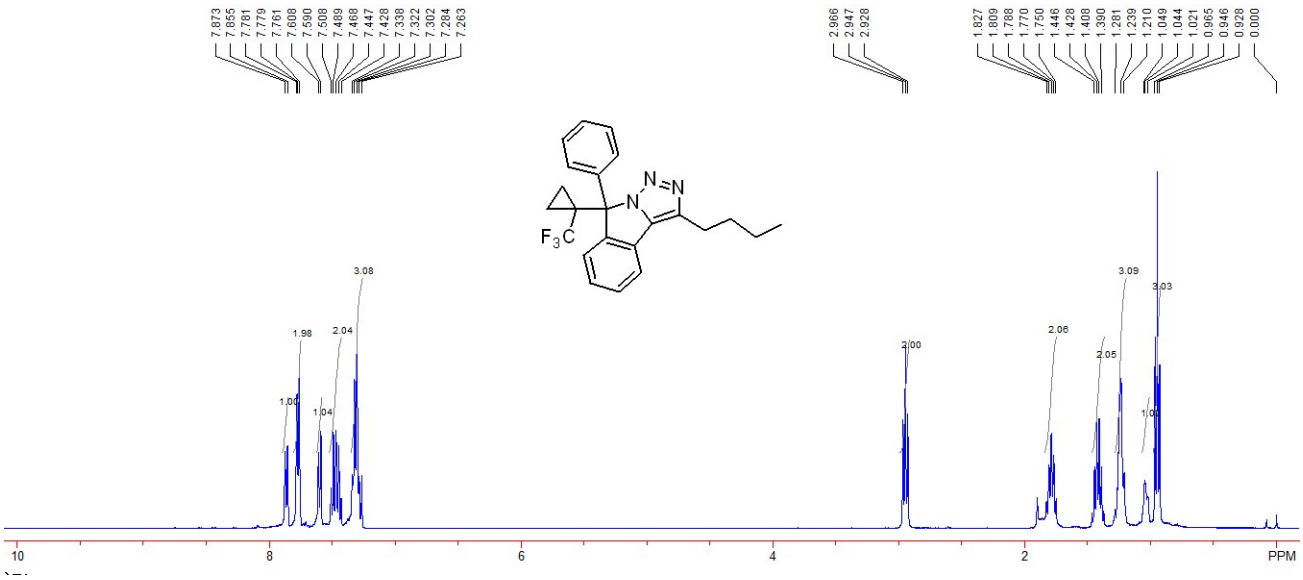


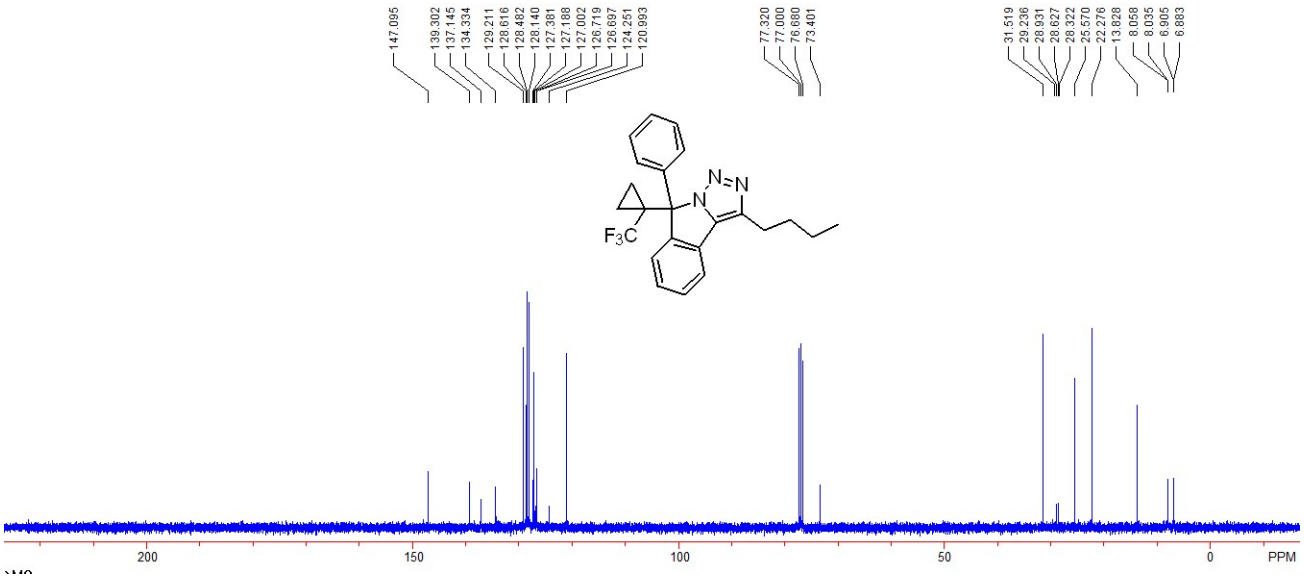


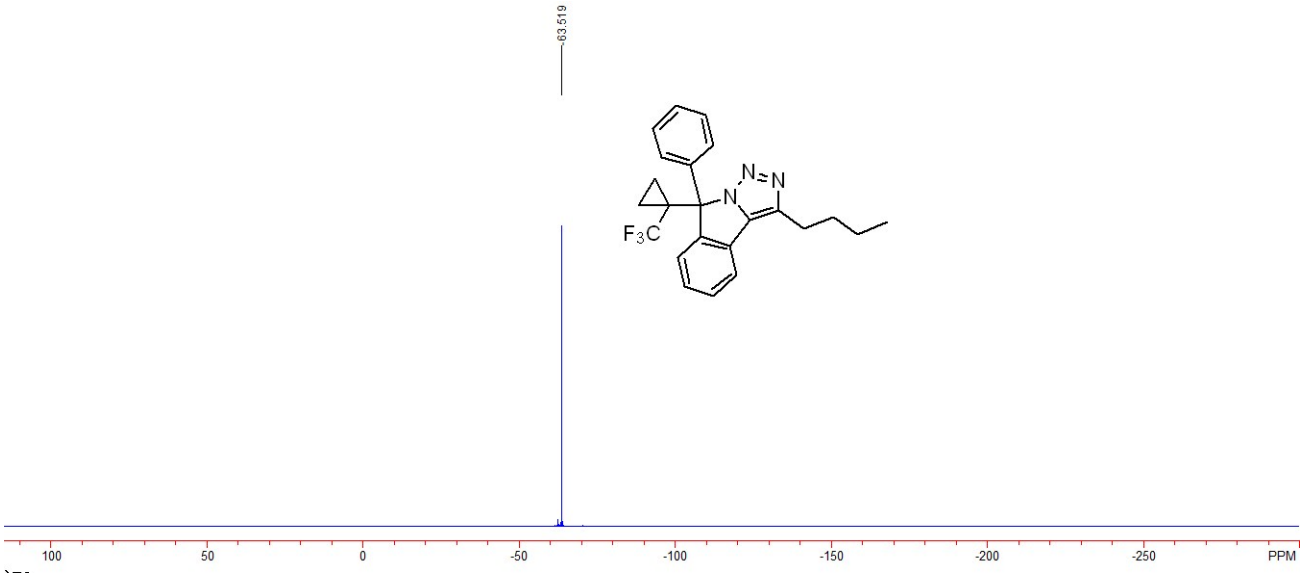


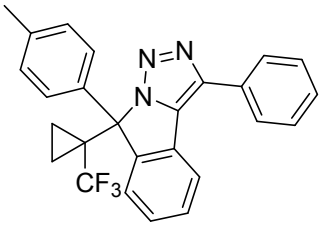


Compound 4j: 64 mg, 80%, A white solid, m.p. 144-146 ^{o}C; IR (CH_2Cl_2): ν 3062, 2931, 2859, 1459, 1349, 1173, 1151, 1129, 1040, 775, 758, 754, 705 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.95 (t, 3H, J = 7.6 Hz), 1.02-1.05 (m, 1H), 1.21-1.28 (m, 3H), 1.39-1.45 (m, 2H), 1.75-1.83 (m, 2H), 2.95 (t, 2H, J = 7.6 Hz), 7.26-7.34 (m, 3H), 7.43-7.51 (m, 2H), 7.60 (d, 1H, J = 7.2 Hz), 7.76-7.78 (m, 2H), 7.86 (d, 1H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 6.9 (q, J_{C-F} = 2.2 Hz), 8.0 (q, J_{C-F} = 2.3 Hz), 13.8, 22.3, 25.6, 28.8 (q, J_{C-F} = 30.4 Hz), 31.5, 73.4, 121.0, 125.6 (q, J_{C-F} = 275.1 Hz), 126.7 (q, J_{C-F} = 2.2 Hz), 127.2, 127.4, 128.1, 128.5, 128.6, 129.2, 134.3, 137.1, 139.3, 147.1; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -63.5 (s, 3F); MS (ESI) *m/z*: 398.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{23}H_{23}F_3N_3^+$ requires: 398.1839, Found: 398.1840.



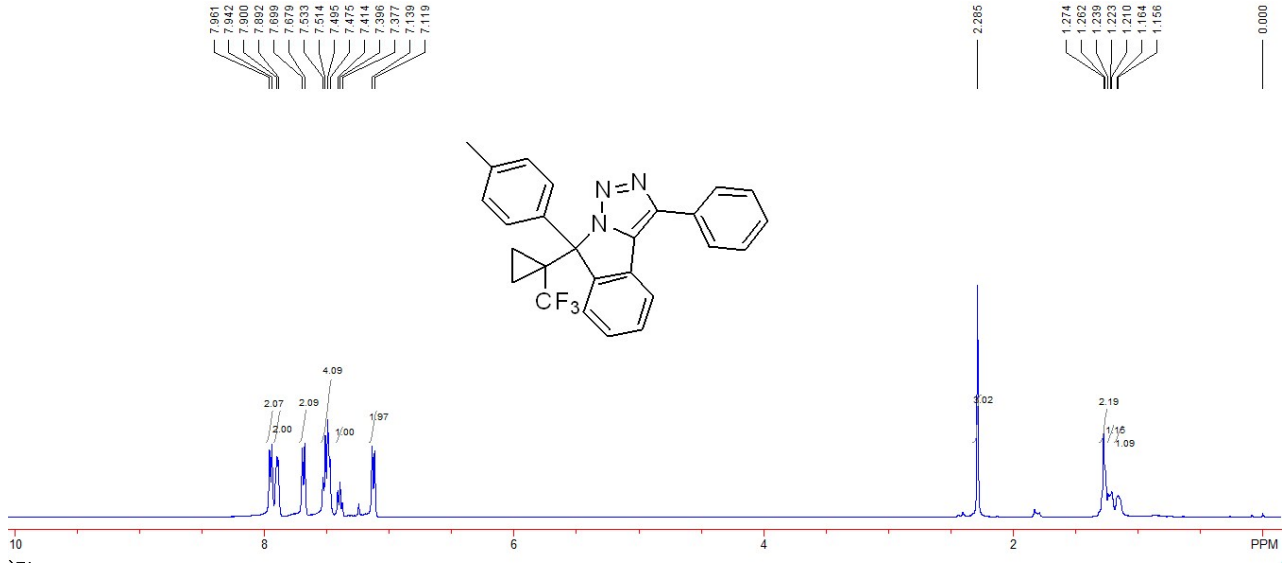


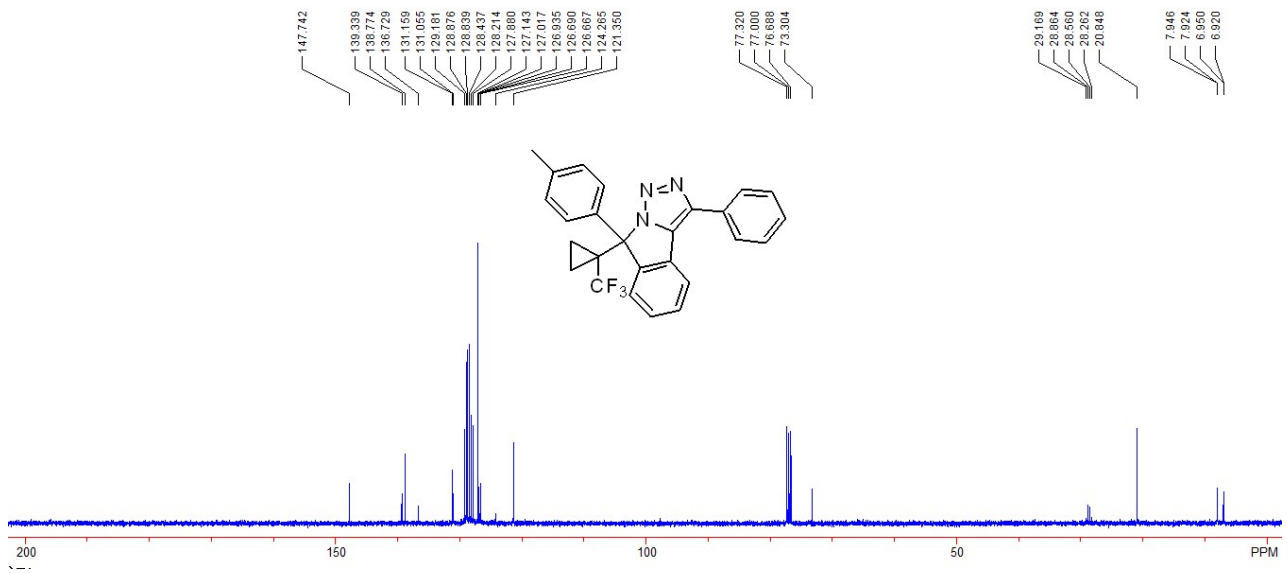


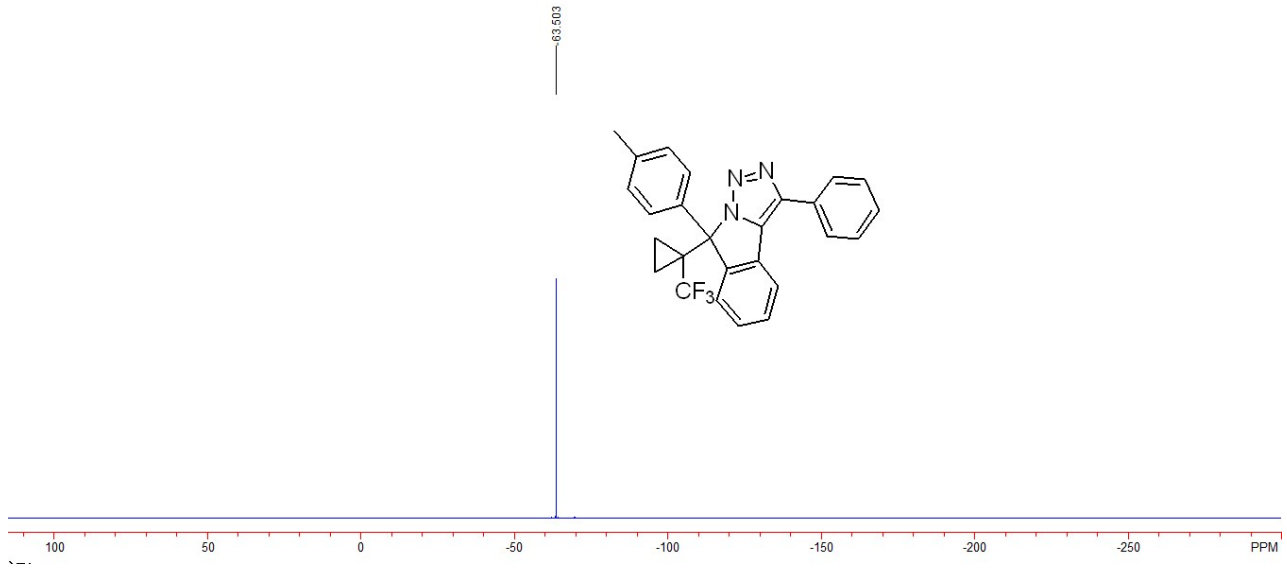


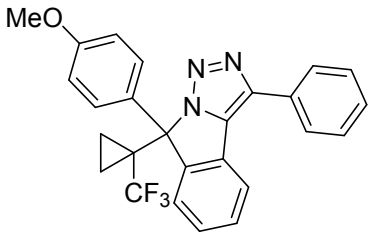
Compound 4k: 73 mg, 84%, A white solid, m.p. 173-175 ^{o}C; IR (CH_2Cl_2): ν 3062, 2912, 2843, 1607, 1511, 1446, 1351, 1184, 1152, 1127, 1049, 984, 822, 803, 761, 748, 697, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.15-1.16 (m, 1H), 1.21-1.27 (m, 3H), 2.29 (s, 3H), 7.13 (d, 2H, J = 8.0 Hz), 7.40 (t, 1H, J = 7.6 Hz), 7.48-7.53 (m, 4H), 7.69 (d, 2H, J = 8.0 Hz), 7.89-7.90 (m, 2H), 7.95 (d, 2H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 6.9 (q, J_{C-F} = 3.0 Hz), 7.9 (q, J_{C-F} = 2.2 Hz), 20.8, 28.7 (q, J_{C-F} = 30.4 Hz), 73.3, 121.4, 125.6 (q, J_{C-F} = 275.2 Hz), 126.7 (q, J_{C-F} = 2.3 Hz), 126.9, 127.1, 127.9, 128.2, 128.4, 128.8, 128.9, 129.2, 131.1, 131.2, 136.7, 138.8, 139.3, 147.7; ^{19}F

NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -63.5 (s, 3F); MS (ESI) *m/z*: 432.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{26}H_{21}F_3N_3^+$ requires: 432.1682, Found: 432.1682.

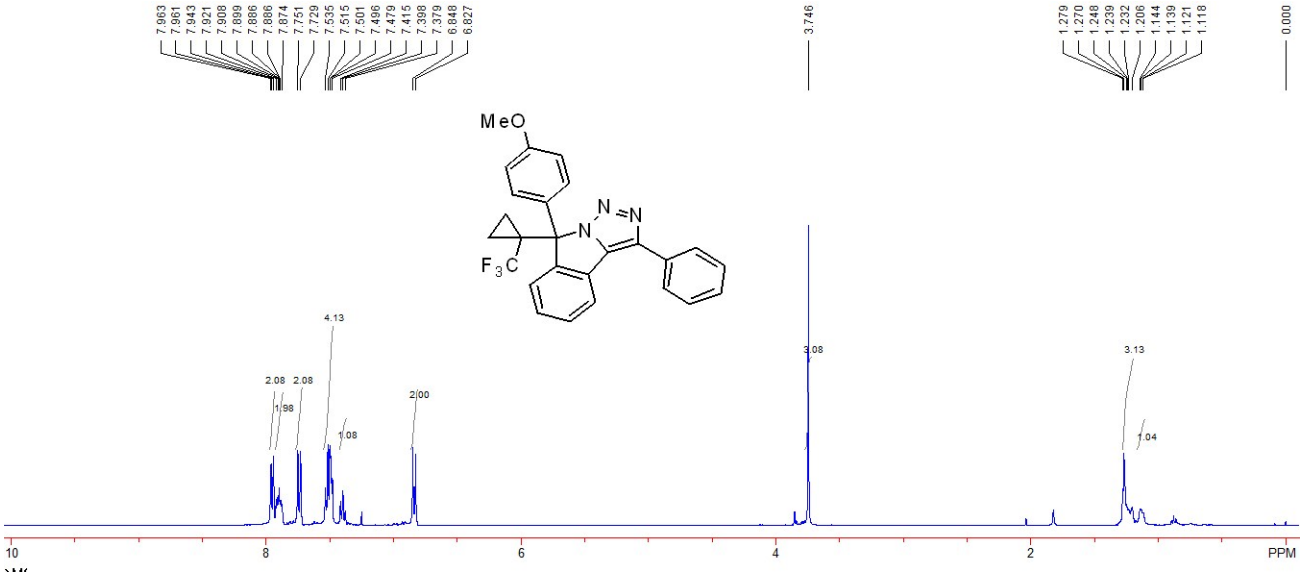


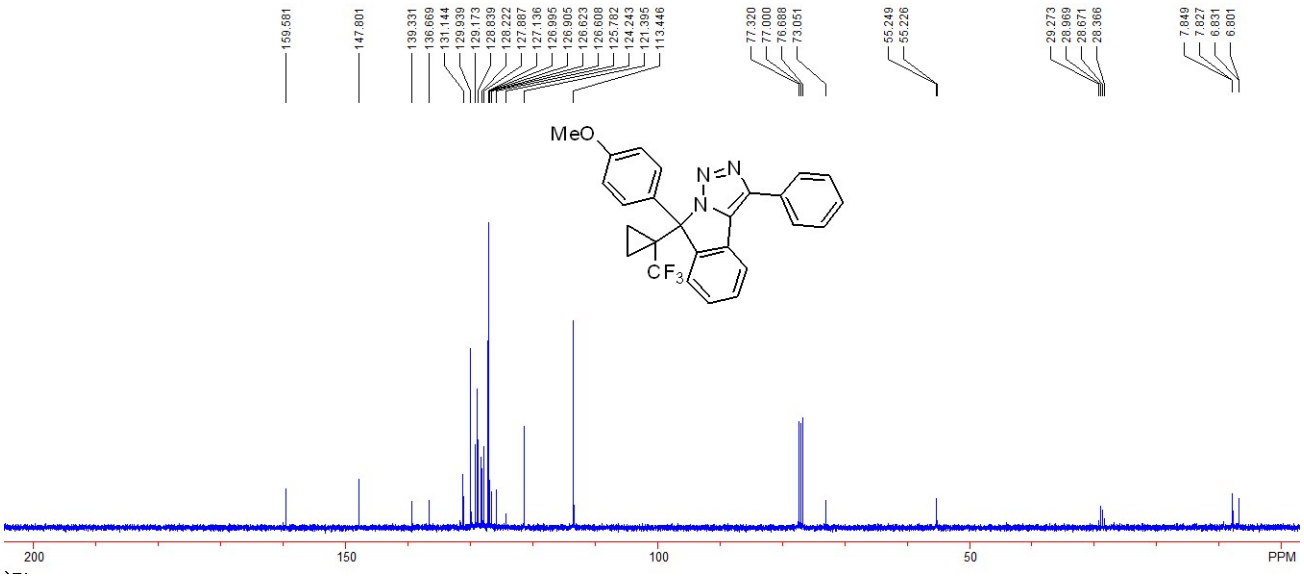


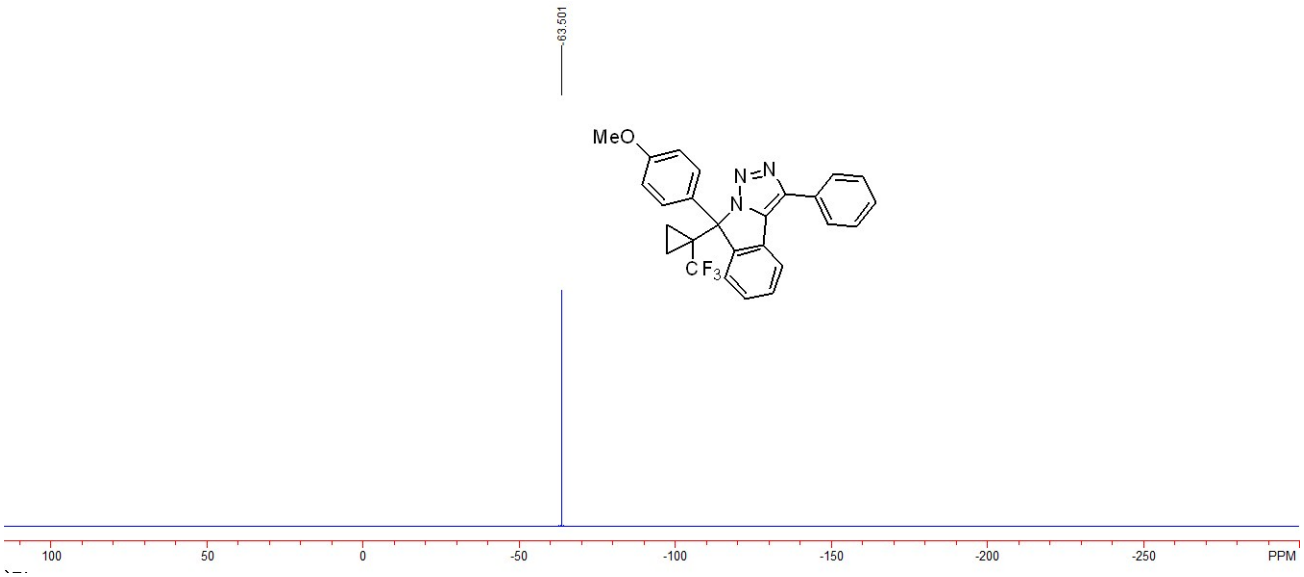


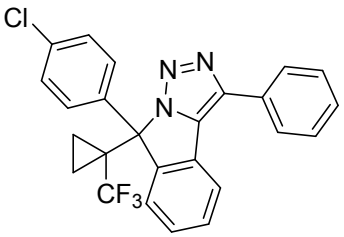


Compound 4l: 72 mg, 80%, A white solid, m.p. 188-190 °C; IR (CH_2Cl_2): ν 3056, 2970, 2837, 1608, 1513, 1447, 1352, 1259, 1187, 1153, 1129, 1033, 834, 795, 764, 749, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.12-1.14 (m, 1H), 1.21-1.28 (m, 3H), 3.75 (s, 3H), 6.84 (d, 2H, J = 8.4 Hz), 7.40 (t, 1H, J = 7.6 Hz), 7.48-7.54 (m, 4H), 7.74 (d, 2H, J = 8.8 Hz), 7.87-7.92 (m, 2H), 7.95 (dd, 2H, J_1 = 8.0 Hz, J_2 = 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 6.8 (q, $J_{C\text{-}F}$ = 2.0 Hz), 7.8 (q, $J_{C\text{-}F}$ = 2.2 Hz), 28.8 (q, $J_{C\text{-}F}$ = 29.8 Hz), 55.2, 73.1, 113.4, 121.4, 125.6 (q, $J_{C\text{-}F}$ = 275.2 Hz), 125.8, 126.6 (q, $J_{C\text{-}F}$ = 1.5 Hz), 126.9, 127.1, 127.9, 128.2, 128.8, 129.2, 129.9, 131.1, 136.7, 139.3, 147.8, 159.6; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -63.5 (s, 3F); MS (ESI) *m/z*: 448.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{26}H_{21}F_3N_3O^+$ requires: 448.1631, Found: 448.1633.



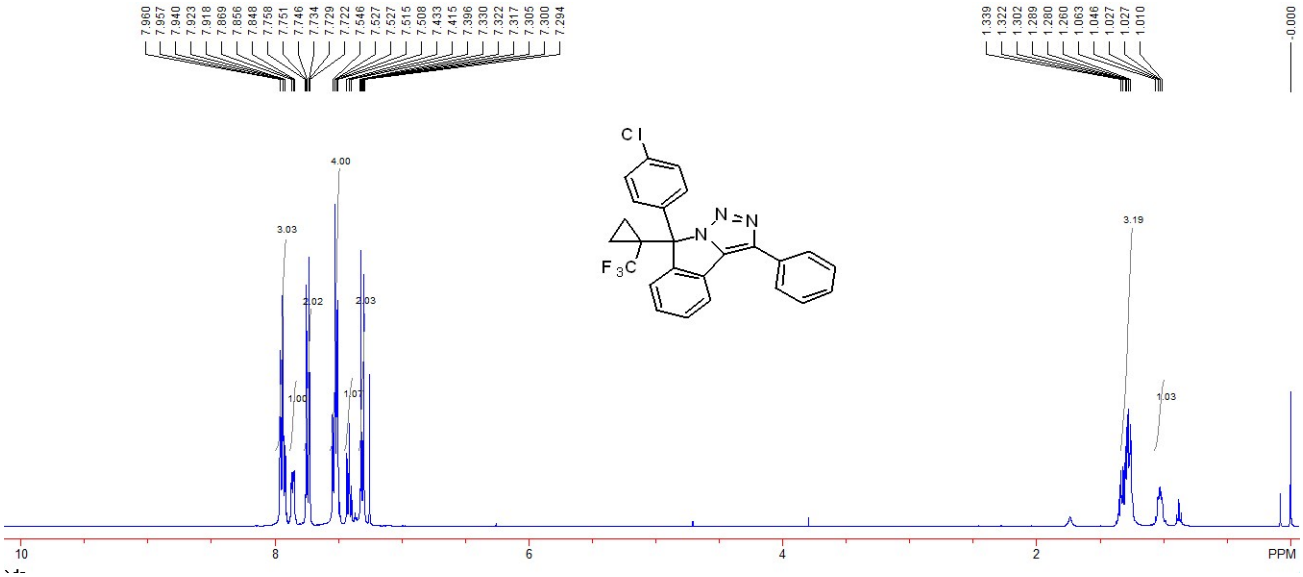


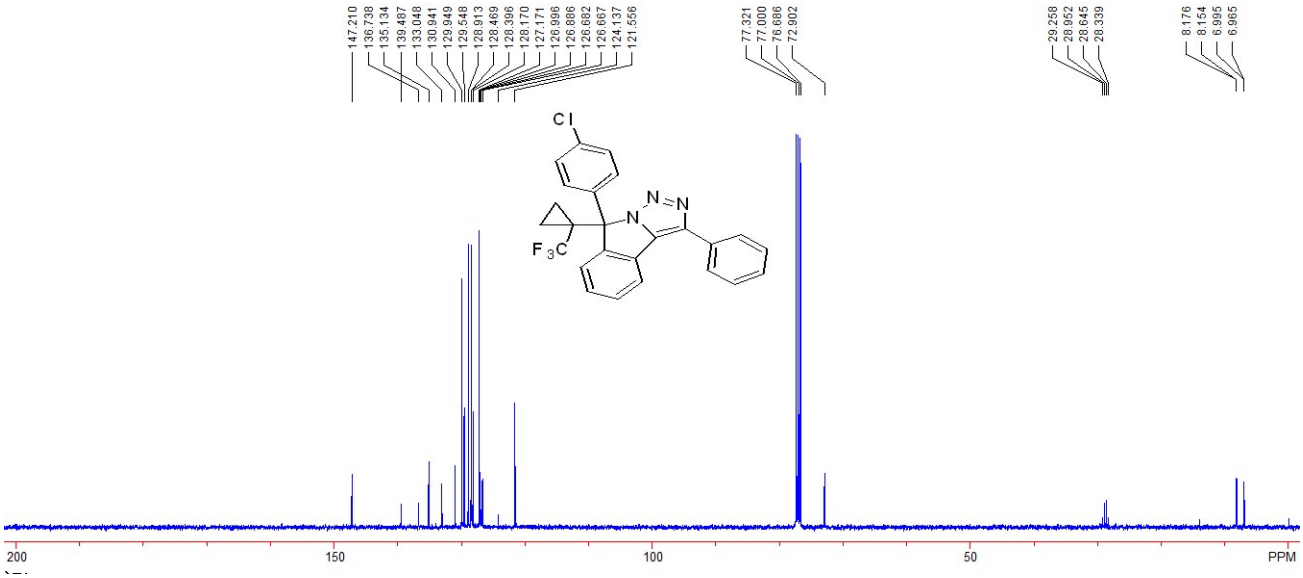


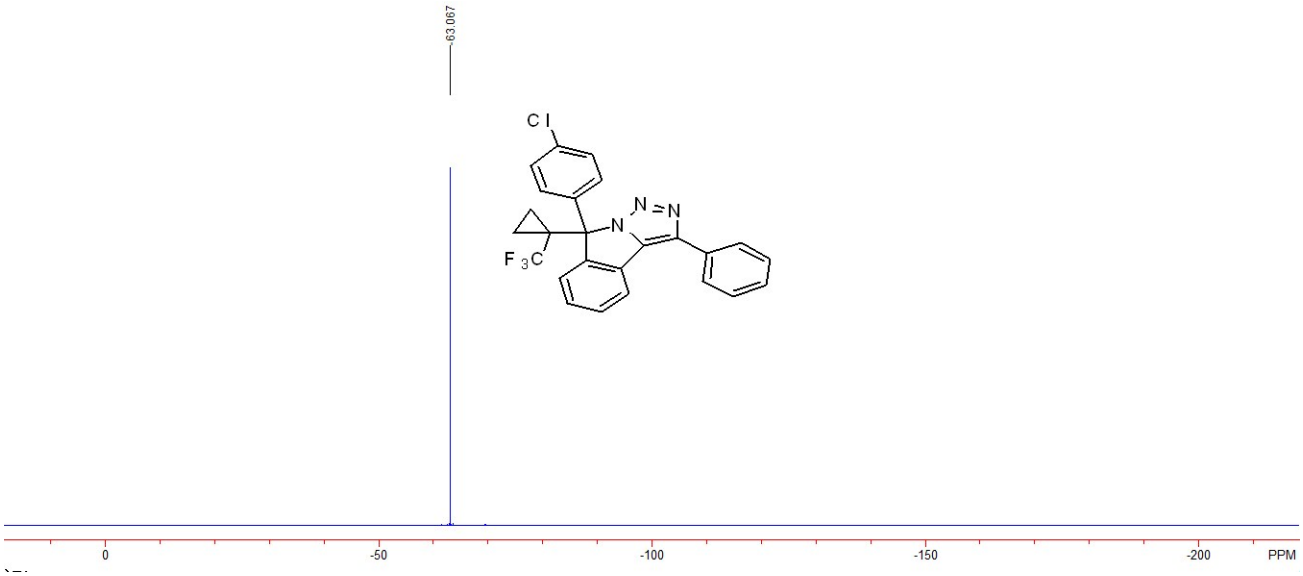


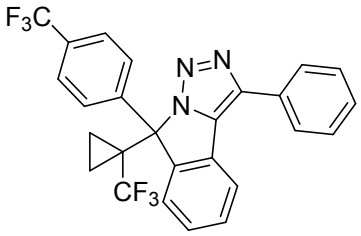
Compound 4m: 69 mg, 76%, A white solid, m.p. 185-187 ^{o}C; IR (CH_2Cl_2): ν 3048, 2923, 1492, 1351, 1184, 1164, 1153, 1133, 1095, 1015, 985, 829, 803, 762, 751, 723, 698, 689 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.01-1.06 (m, 1H), 1.26-1.34 (m, 3H), 7.29-7.33 (m, 2H), 7.42 (t, 1H, J = 7.6 Hz), 7.51-7.55 (m, 4H), 7.72-7.76 (m, 2H), 7.85-7.87 (m, 1H), 7.92-7.96 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 7.0 (q, $J_{C\text{-}F}$ = 3.0 Hz), 8.2 (q, $J_{C\text{-}F}$ = 2.2 Hz), 28.8 (q, $J_{C\text{-}F}$ = 30.7 Hz), 72.9, 121.6, 125.5 (q, $J_{C\text{-}F}$ = 274.9 Hz), 126.7 (q, $J_{C\text{-}F}$ = 1.5 Hz), 127.0, 127.2, 128.2, 128.4, 128.5, 128.9, 129.5, 129.9, 130.9, 133.0, 135.1, 136.7, 139.5, 147.2; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$):

δ -63.1 (s, 3F); MS (ESI) *m/z*: 452.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{25}H_{18}ClF_3N_3^+$ requires: 452.1136, Found: 452.1136.

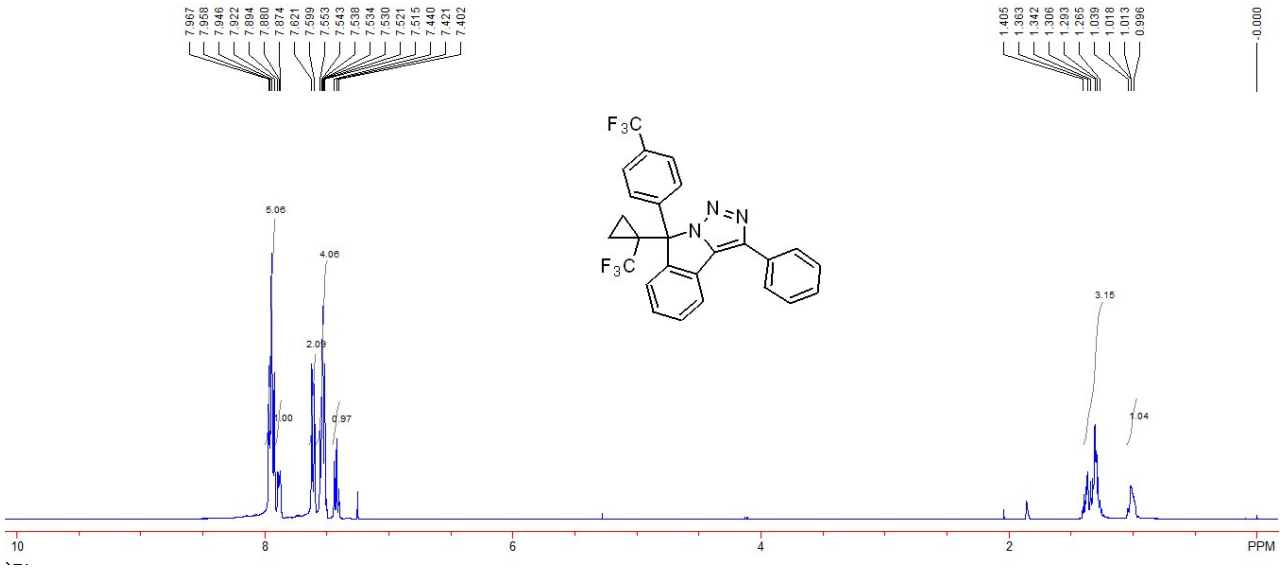


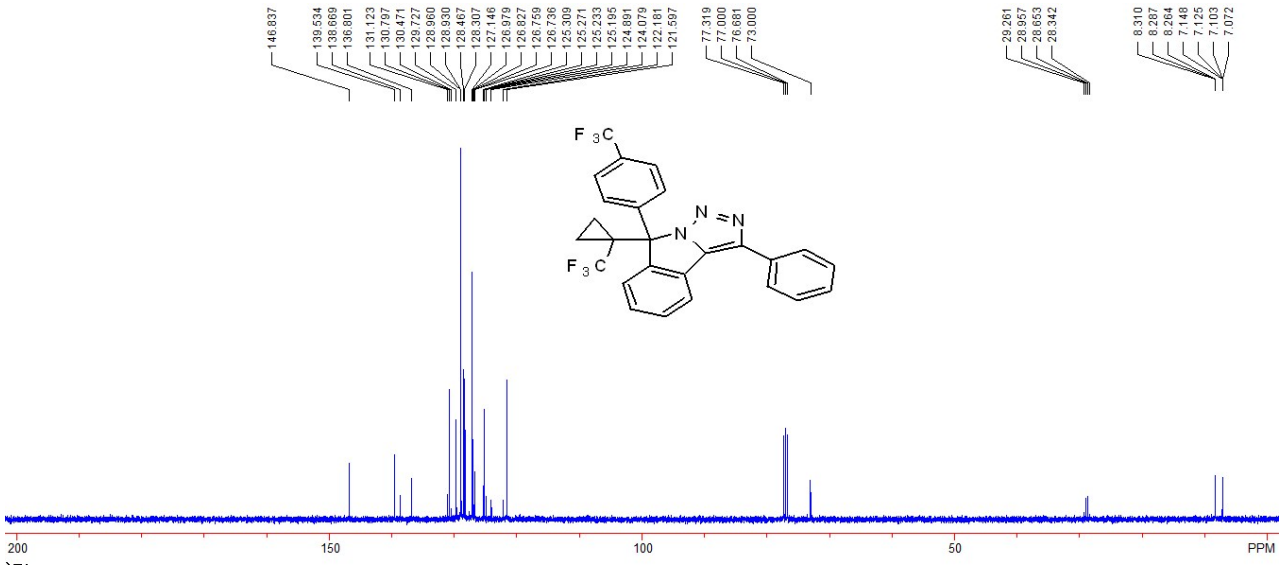


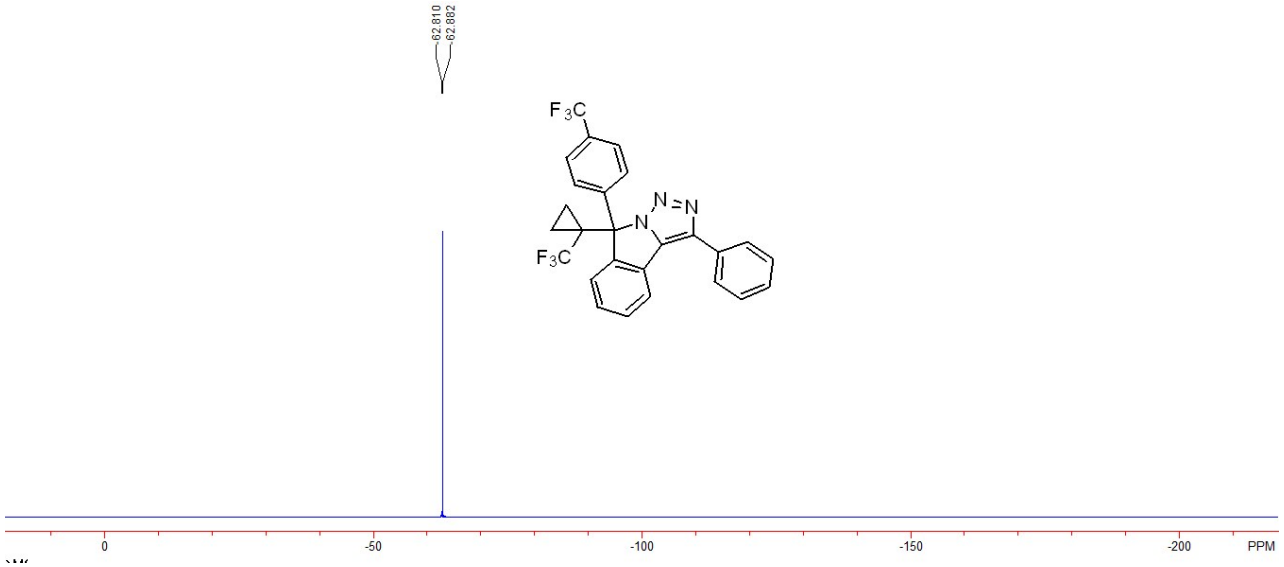


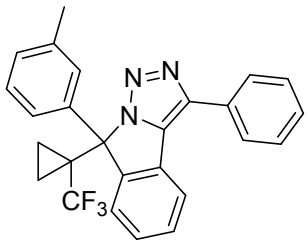


Compound 4n: 63 mg, 65%, A white solid, m.p. 178-180 ^{o}C; IR (CH_2Cl_2): ν 3112, 3056, 1613, 1433, 1350, 1326, 1165, 1155, 1131, 1122, 1072, 1017, 854, 840, 764, 749, 696, 689 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.00-1.04 (m, 1H), 1.27-1.41 (m, 3H), 7.42 (t, 1H, J = 7.6 Hz), 7.52-7.55 (m, 4H), 7.61 (d, 2H, J = 8.8 Hz), 7.87-7.89 (m, 1H), 7.92-7.97 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 7.1 (q, J_{C-F} = 2.2 Hz), 8.3 (q, J_{C-F} = 2.3 Hz), 28.8 (q, J_{C-F} = 30.4 Hz), 73.0, 121.6, 123.5 (q, J_{C-F} = 271.0 Hz), 125.3 (q, J_{C-F} = 3.8 Hz), 125.9 (q, J_{C-F} = 274.8 Hz), 126.7 (q, J_{C-F} = 2.3 Hz), 127.0, 127.1, 128.3, 128.5, 128.9, 129.0, 129.7, 130.8, 131.0 (q, J_{C-F} = 32.6 Hz), 136.8, 138.7, 139.5, 146.8; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -62.8 (s, 3F), -62.9 (s, 3F); MS (ESI) *m/z*: 486.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{26}H_{18}F_6N_3^+$ requires: 486.1399, Found: 486.1402.



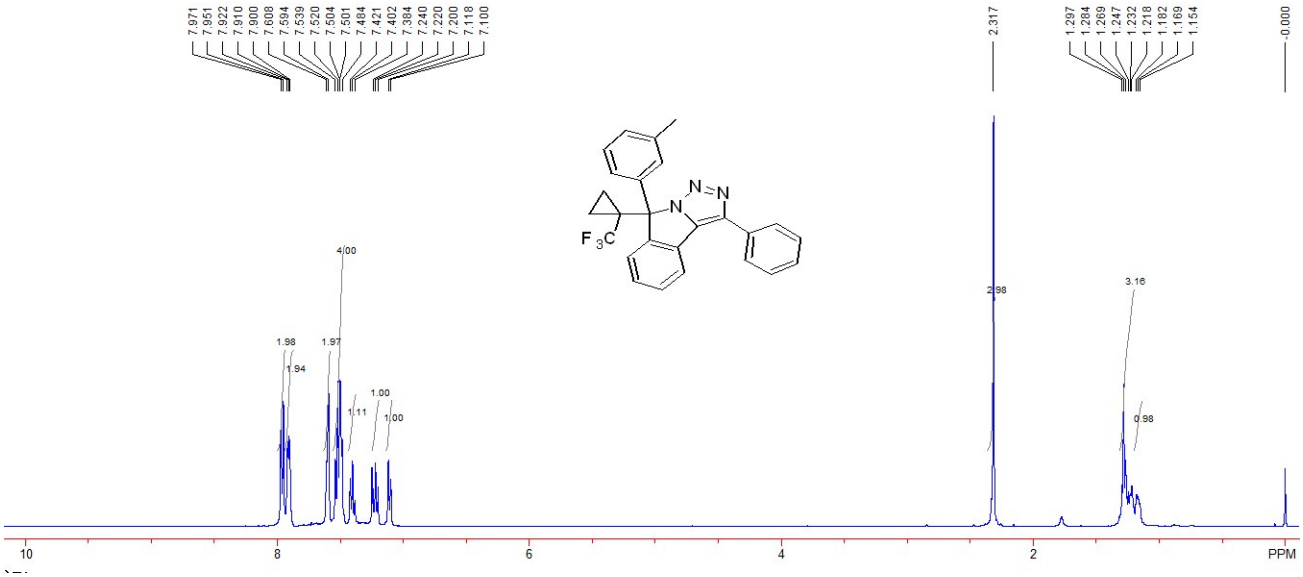


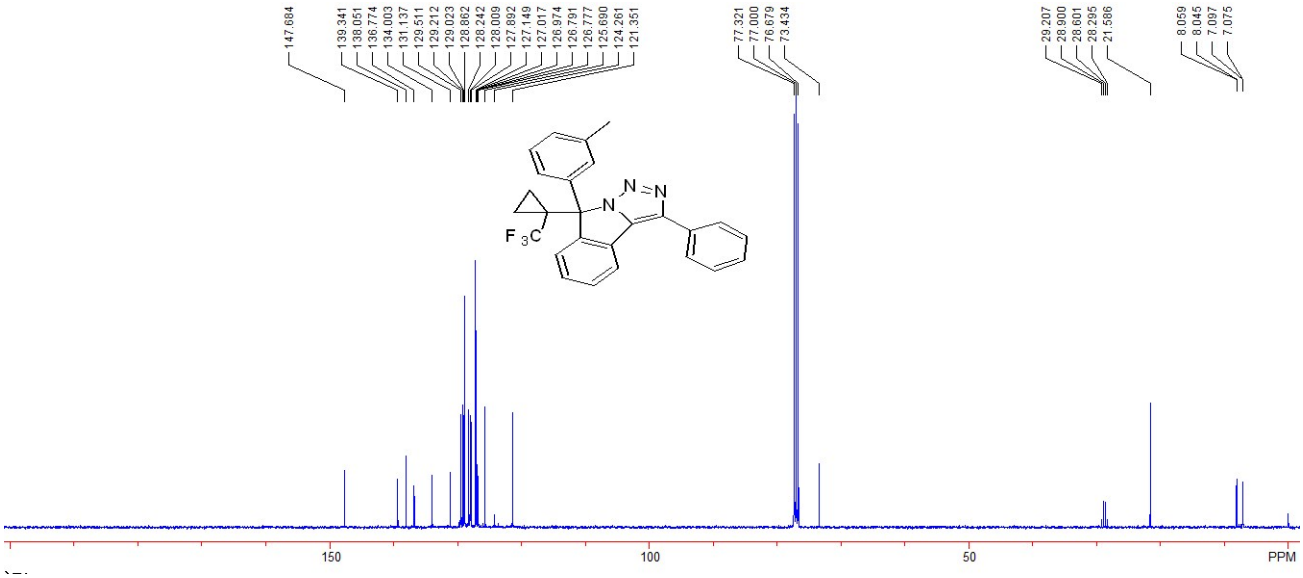


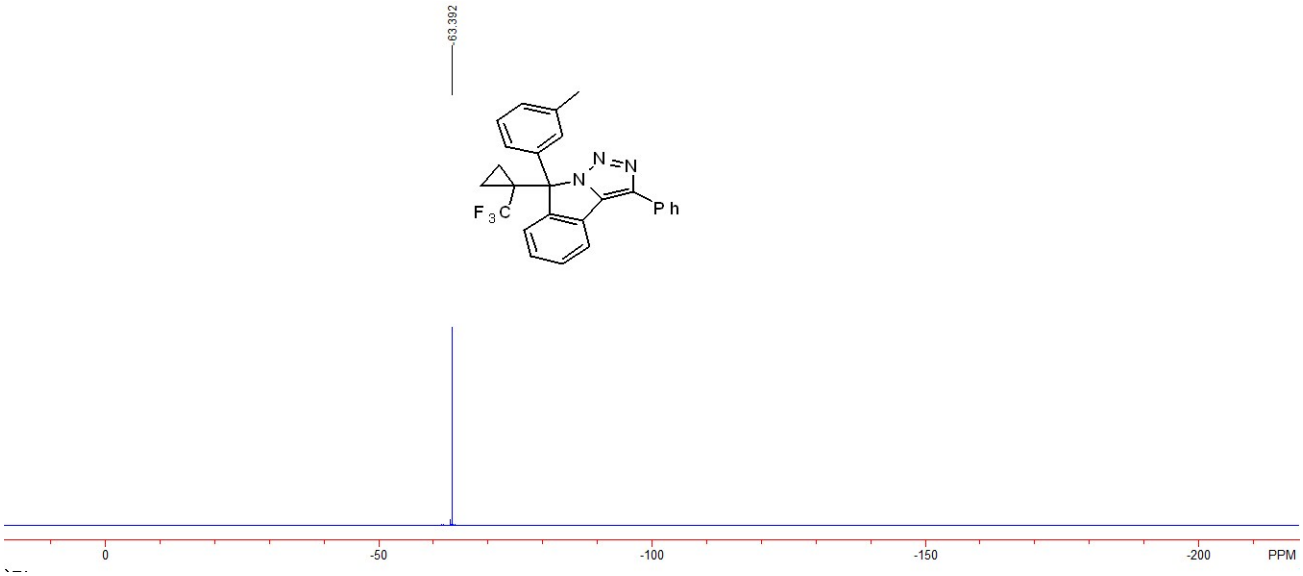


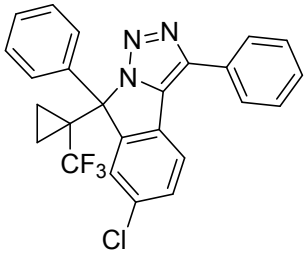
Compound 4o: 73 mg, 85%, A white solid, m.p. 158-160 ^{o}C; IR (CH_2Cl_2): ν 3062, 3031, 1605, 1489, 1354, 1170, 1160, 1146, 1126, 785, 765, 750, 709, 694 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.15-1.18 (m, 1H), 1.22-1.30 (m, 3H), 2.32 (s, 3H), 7.11 (d, 1H, J = 7.2 Hz), 7.22 (t, 1H, J = 8.0 Hz), 7.40 (t, 1H, J = 7.2 Hz), 7.48-7.54 (m, 4H), 7.59-7.61 (m, 2H), 7.90-7.92 (m, 2H), 7.96 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 7.1 (q, J_{C-F} = 2.2 Hz), 8.0 (q, J_{C-F} = 1.4 Hz), 21.6, 28.8 (q, J_{C-F} = 29.9 Hz), 73.4, 121.4, 125.6 (q, J_{C-F} = 275.6 Hz), 125.7, 126.8 (q, J_{C-F} = 1.4 Hz), 127.0, 127.1, 127.9, 128.0, 128.2, 128.9, 129.0, 129.2, 129.5, 131.1, 134.0, 136.8, 138.1,

139.3, 147.7; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -63.4 (s, 3F); MS (ESI) *m/z*: 432.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{26}H_{21}F_3N_3^+$ requires: 432.1682, Found: 432.1684.

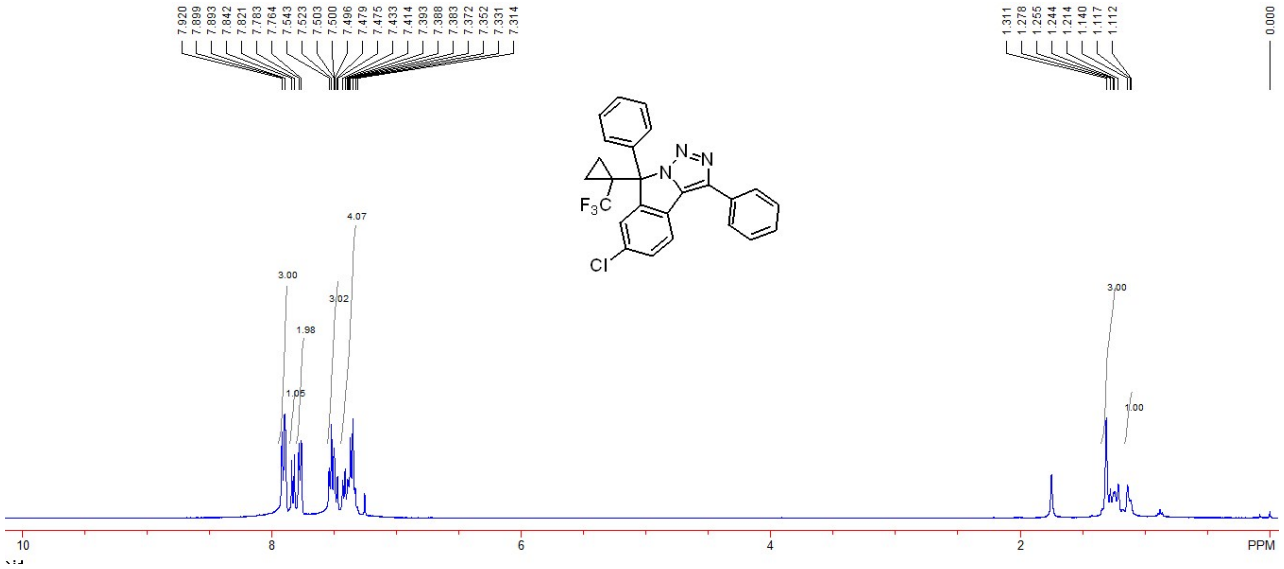


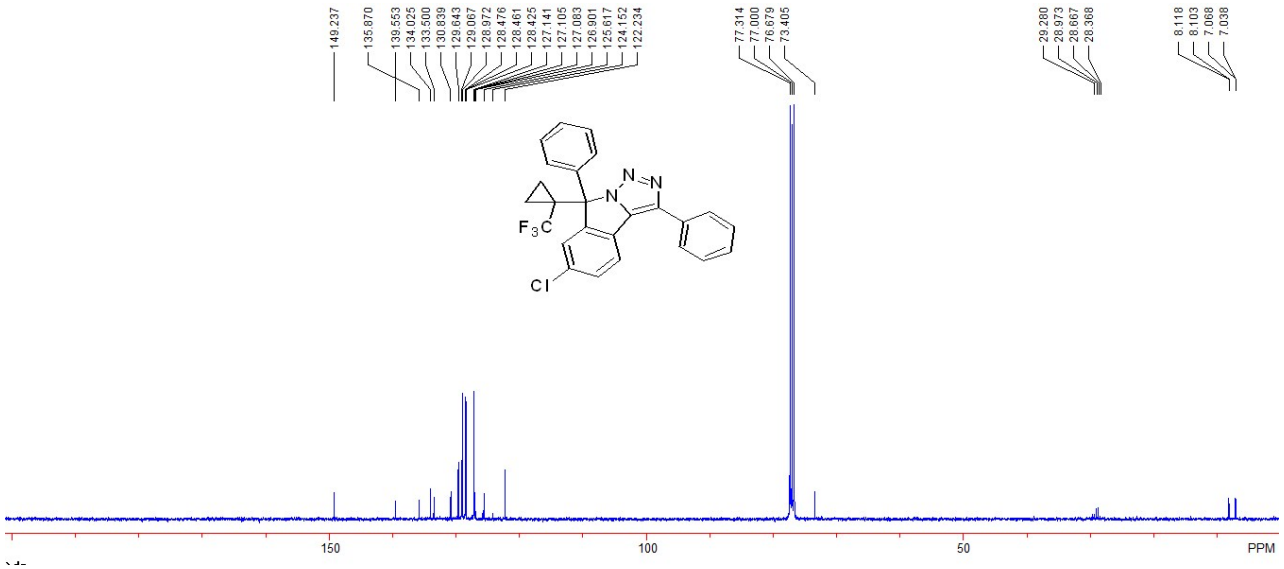


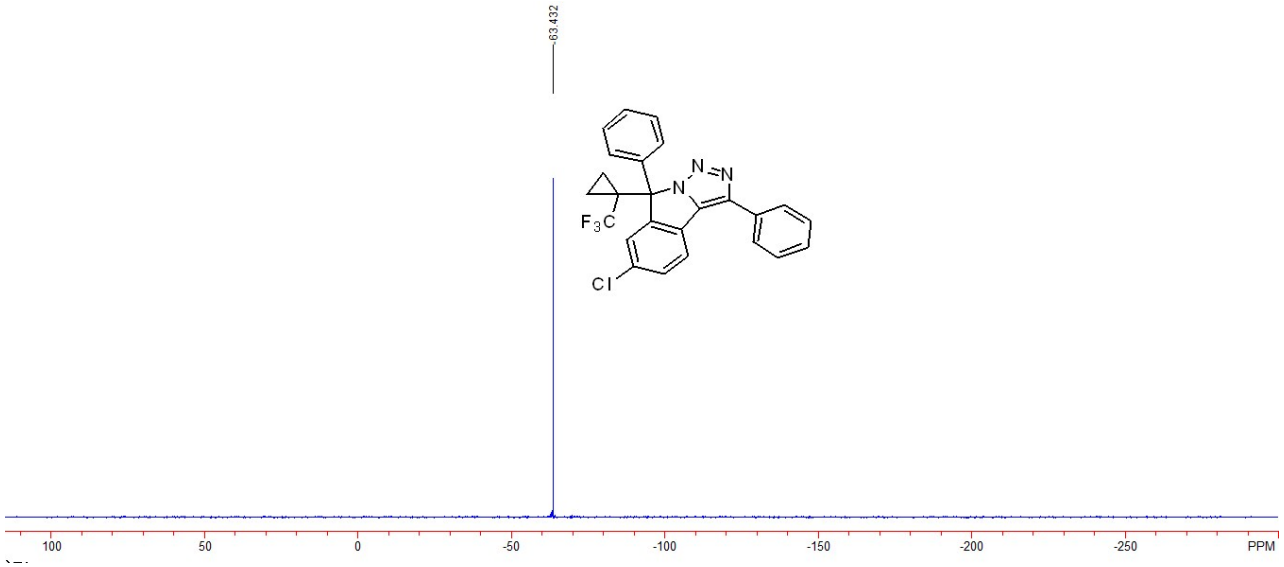


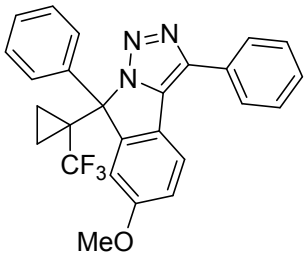


Compound 4q: 61 mg, 67%, A white solid, m.p. 174-176 ^{o}C; IR (CH_2Cl_2): ν 3065, 2920, 2848, 1492, 1449, 1349, 1151, 1129, 1081, 985, 826, 773, 754, 741, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.11-1.14 (m, 1H), 1.21-1.31 (m, 3H), 7.31-7.43 (m, 4H), 7.48-7.54 (m, 3H), 7.77 (d, 2H, J = 7.6 Hz), 7.83 (d, 1H, J = 8.4 Hz), 7.89-7.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 7.1 (q, J_{C-F} = 3.0 Hz), 8.1 (q, J_{C-F} = 1.5 Hz), 28.8 (q, J_{C-F} = 30.6 Hz), 73.4, 122.2, 125.6 (q, J_{C-F} = 274.9 Hz), 125.6, 127.09 (q, J_{C-F} = 2.2 Hz), 127.14, 128.4, 128.46, 128.48, 129.0, 129.1, 129.6, 130.8, 133.5, 134.0, 135.9, 139.6, 149.2; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -63.4 (s, 3F); MS (ESI) *m/z*: 452.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{25}H_{18}ClF_3N_3^+$ requires: 452.1136, Found: 452.1136.



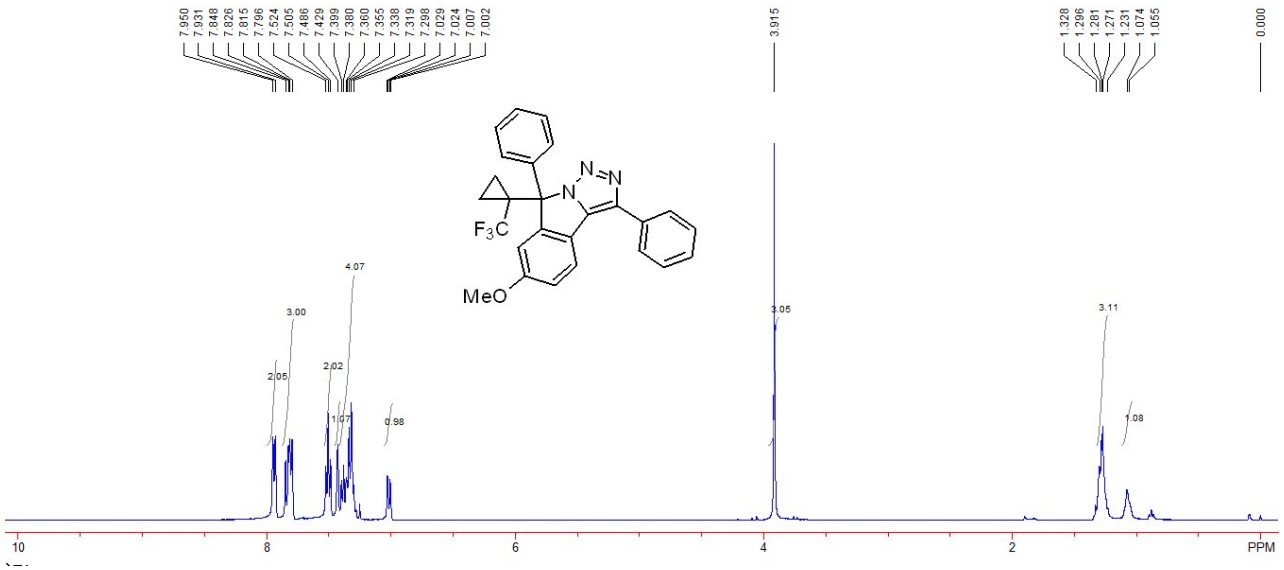


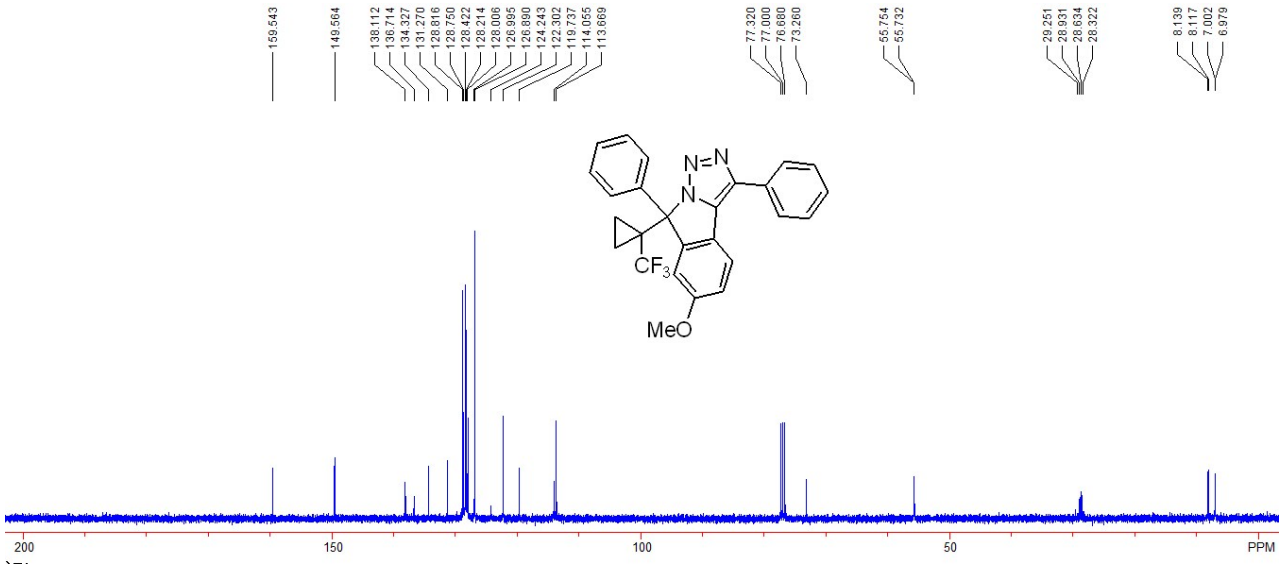


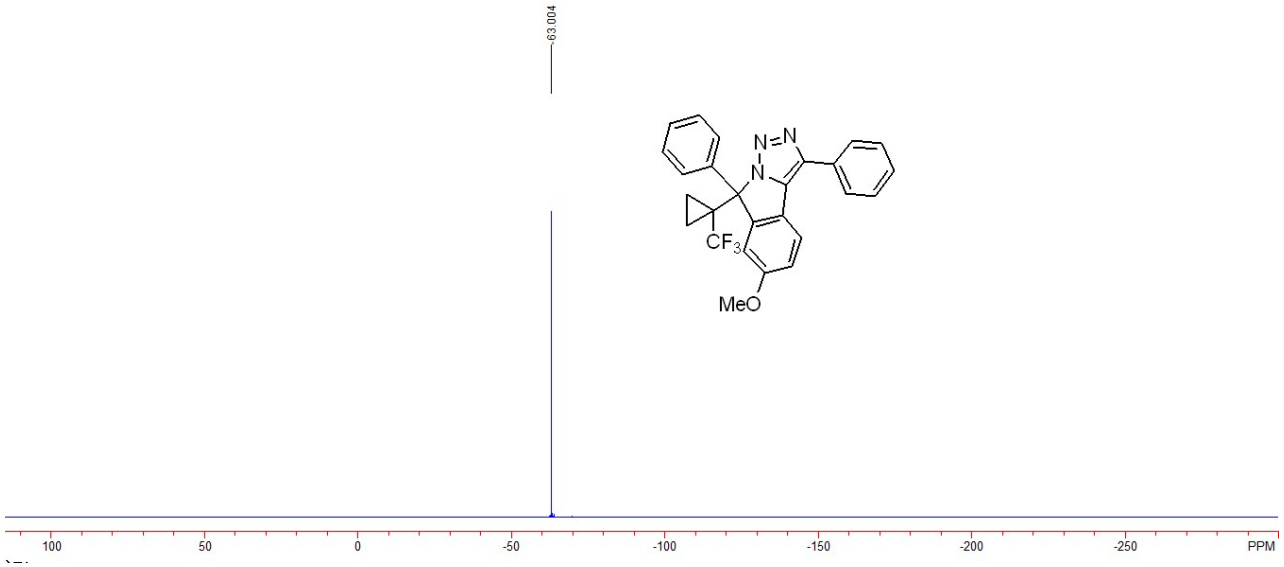


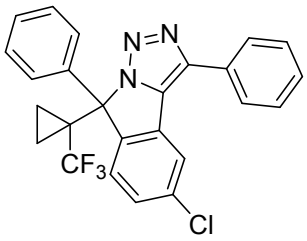
Compound 4r: 78 mg, 87%, A white solid, m.p. 166-168 ^{o}C; IR (CH_2Cl_2): ν 3062, 3031, 1592, 1497, 1472, 1446, 1351, 1289, 1236, 1150, 1129, 1048, 1034, 984, 774, 754, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.06-1.07 (m, 1H), 1.23-1.33 (m, 3H), 3.92 (s, 3H), 7.01 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.0 Hz), 7.30-7.40 (m, 4H), 7.43 (s, 1H), 7.51 (t, 2H, J = 7.6 Hz), 7.80-7.85 (m, 3H), 7.94 (d, 2H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 7.0 (q, $J_{C\text{-}F}$ = 2.3 Hz), 8.1 (q, $J_{C\text{-}F}$ = 2.2 Hz), 28.8 (q, $J_{C\text{-}F}$ = 29.7 Hz), 55.7, 73.3, 113.7, 114.1, 119.7, 122.3, 125.6 (q, $J_{C\text{-}F}$ = 275.2 Hz),

126.9, 127.0, 128.0, 128.2, 128.4, 128.75, 128.82, 131.3, 134.3, 136.7, 138.1, 149.6, 159.5; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -63.0 (s, 3F); MS (ESI) *m/z*: 448.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{26}H_{21}F_3N_3O^+$ requires: 448.1631, Found: 448.1633.

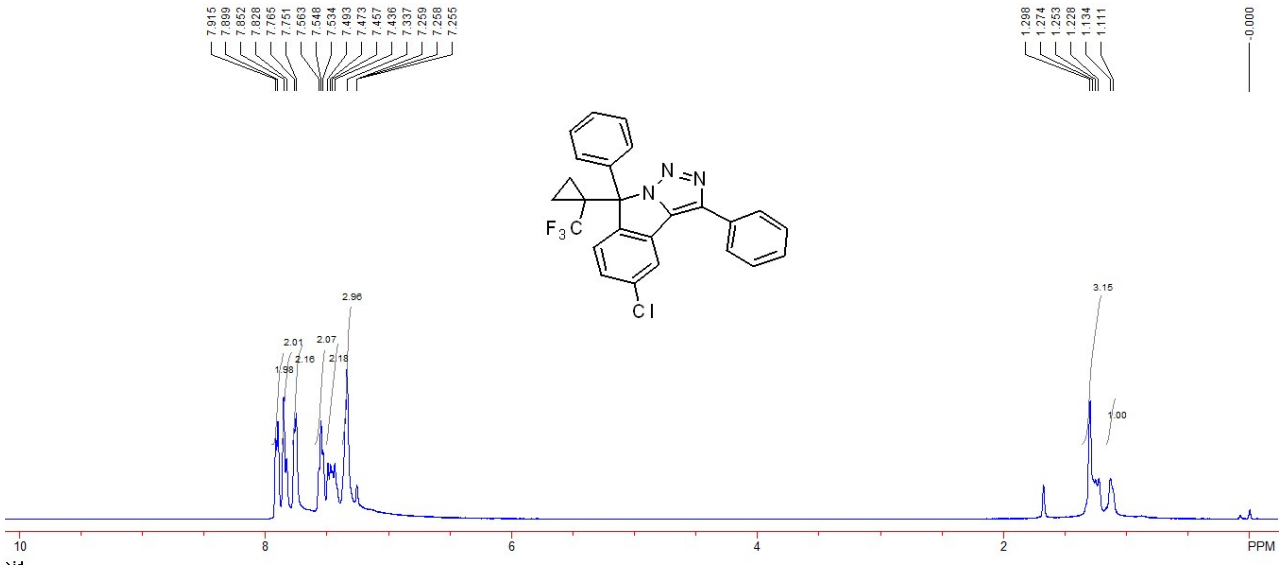


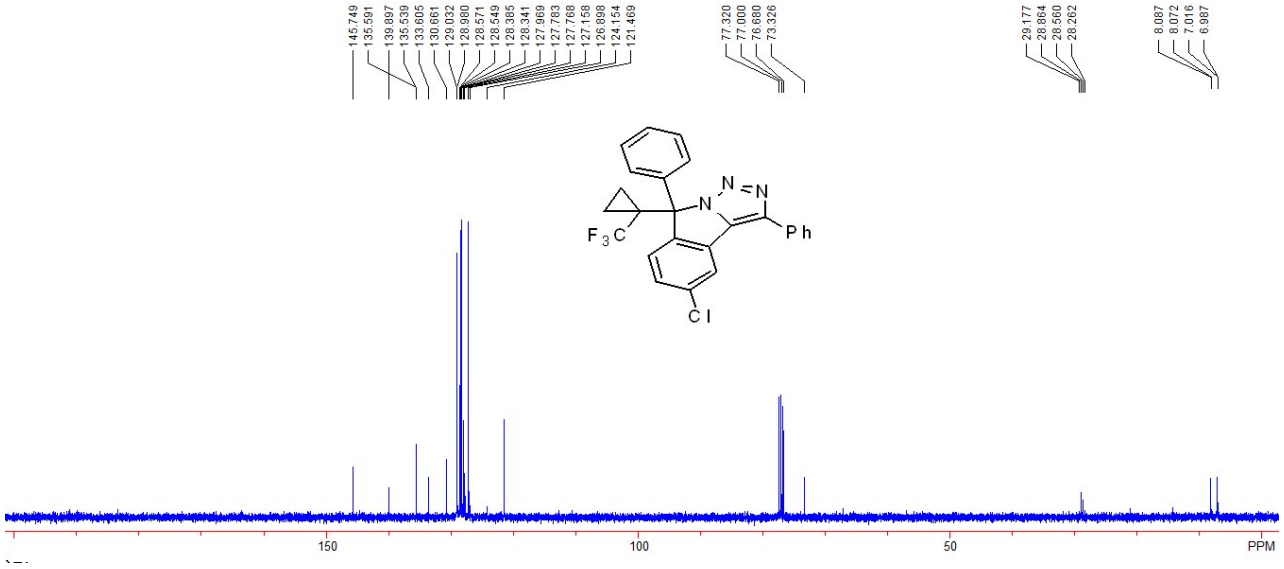






Compound 4s: 64 mg, 71%, A white solid, m.p. 172-174 ^{o}C; IR (CH_2Cl_2): ν 3073, 3026, 1496, 1447, 1349, 1172, 1156, 1130, 1082, 992, 831, 769, 752, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.11-1.13 (m, 1H), 1.23-1.30 (m, 3H), 7.26-7.34 (m, 3H), 7.44-7.49 (m, 2H), 7.53-7.56 (m, 2H), 7.75-7.77 (m, 2H), 7.83-7.85 (m, 2H), 7.90-7.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 7.0 (q, $J_{C\text{-}F}$ = 2.9 Hz), 8.1 (q, $J_{C\text{-}F}$ = 1.5 Hz), 28.7 (q, $J_{C\text{-}F}$ = 30.4 Hz), 73.3, 121.5, 125.5 (q, $J_{C\text{-}F}$ = 274.4 Hz), 127.2, 127.8 (q, $J_{C\text{-}F}$ = 1.5 Hz), 128.0, 128.3, 128.4, 128.5, 128.6, 128.98, 129.03, 130.7, 133.6, 135.5, 135.6, 139.9, 145.7; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -63.4 (s, 3F); MS (ESI) *m/z*: 452.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{25}H_{18}ClF_3N_3^+$ requires: 452.1136, Found: 452.1136.


7.915
7.899
7.852
7.828
7.765
7.751
7.563
7.548
7.534
7.493
7.473
7.457
7.436
7.337
7.259
7.258
7.255
1.298
1.274
1.253
1.228
1.134
1.111
0.000
2.96
2.01
2.07
2.16
2.18
1.98
3.15
1.00
F3C
Cl
10
8
6
4
2
PPM


145.749
135.591
139.897
135.539
133.605
130.661
129.032
128.980
128.571
128.549
128.385
128.341
127.969
127.783
127.768
127.158
126.898
124.154
121.469
77.320
77.000
76.680
73.326
29.177
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28.262
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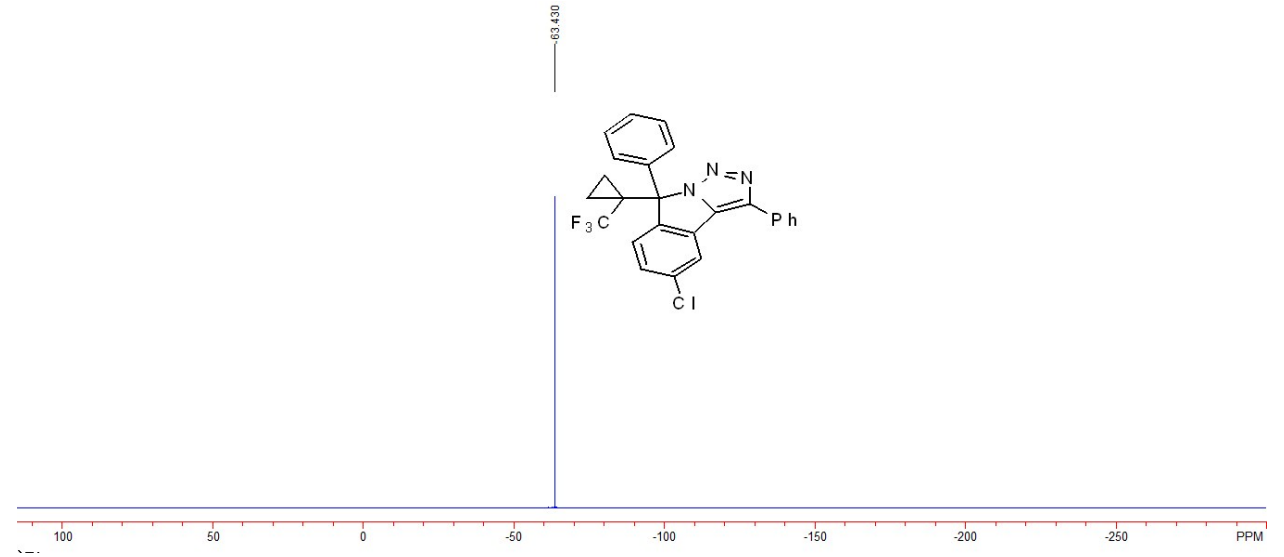
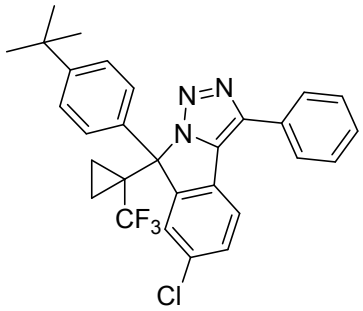
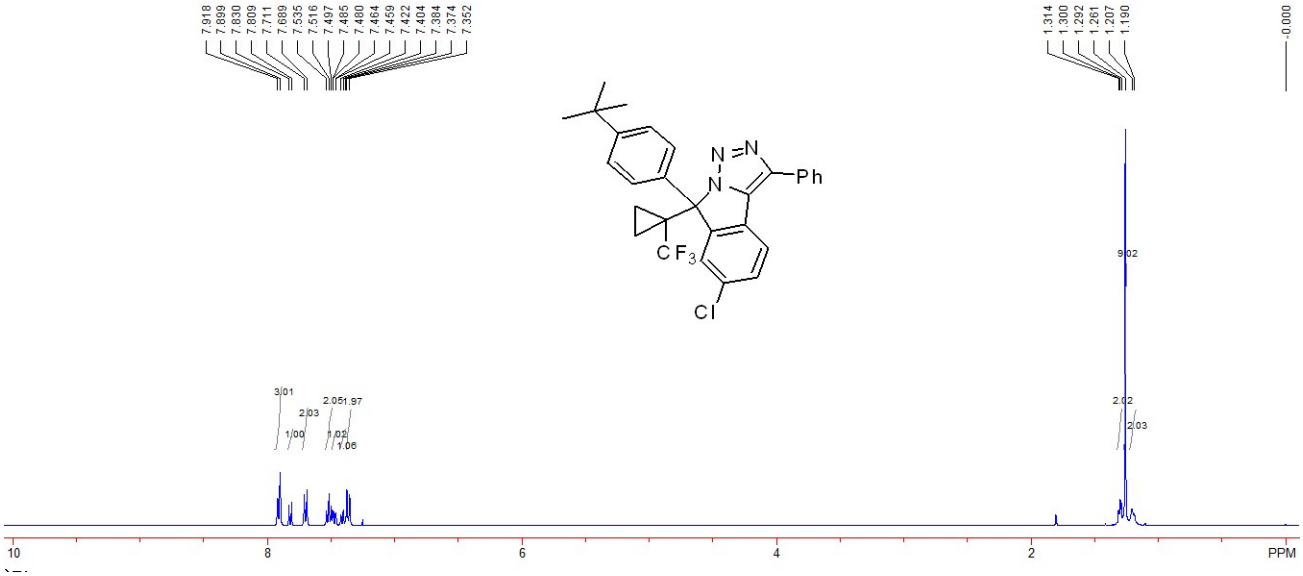
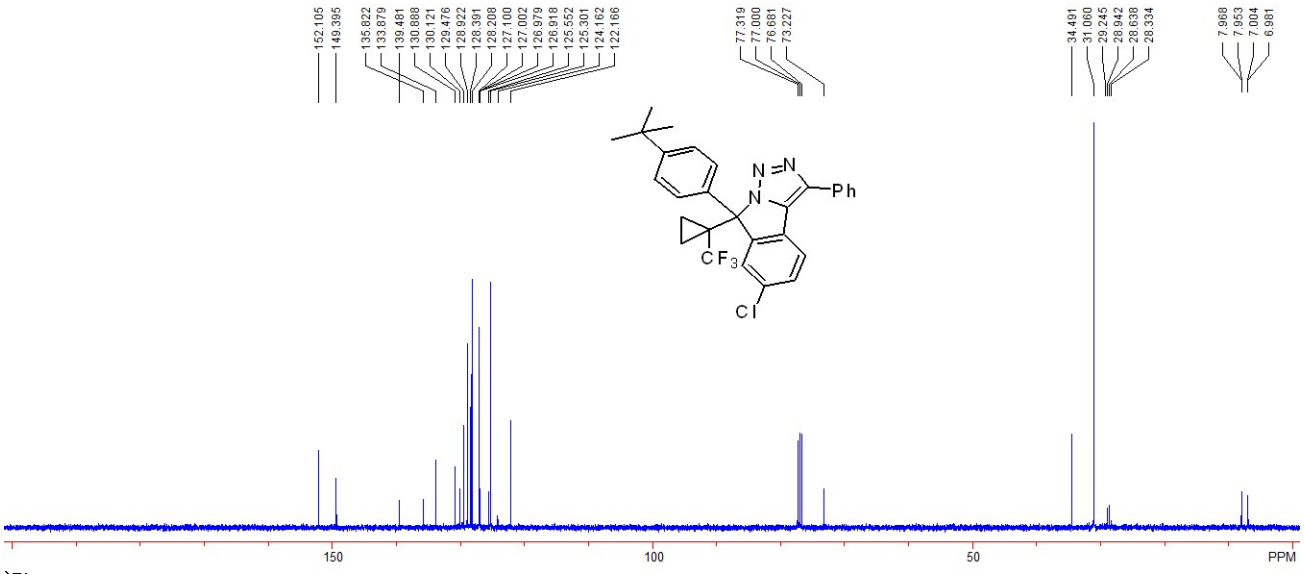
8.072
7.016
6.987
F3C
Ph
Cl
150
100
50
PPM

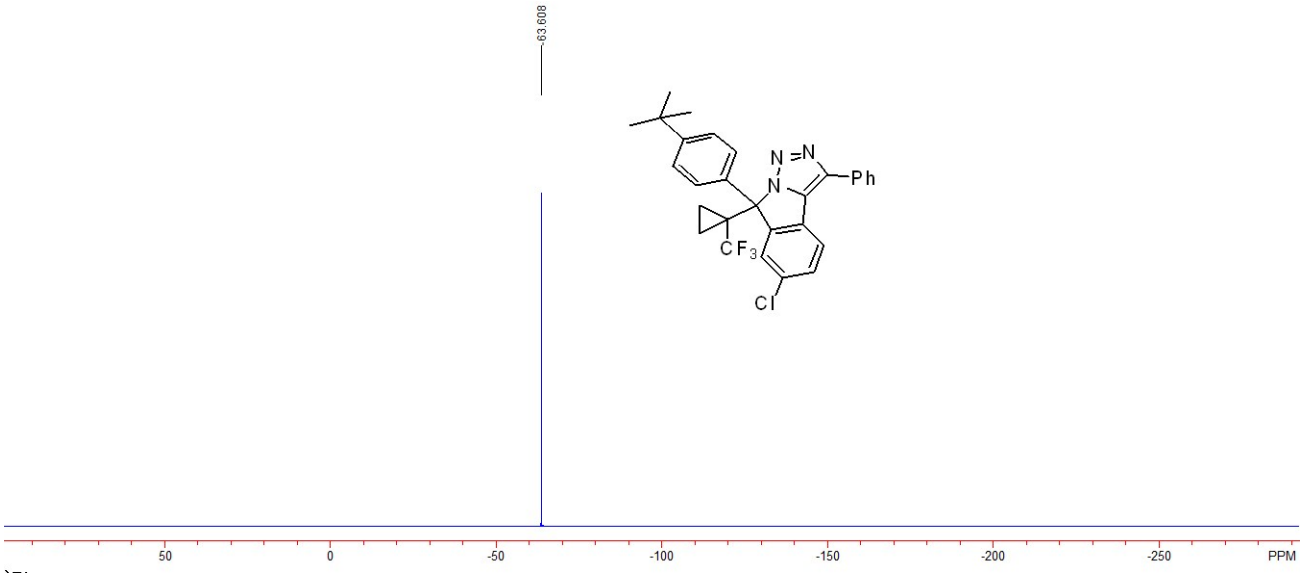

63.430
F3C
Ph
Cl
100
50
0
-50
-100
-150
-200
-250
PPM

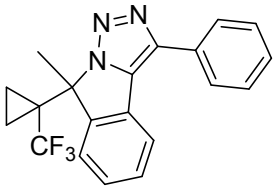


Compound 4t: 81 mg, 80%, A white solid, m.p. 191-193 ^{o}C; IR (CH_2Cl_2): ν 2959, 2868, 1448, 1349, 1151, 1142, 1132, 1104, 984, 823, 808, 776, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.19-1.21 (m, 2H), 1.26 (s, 9H), 1.29-1.31 (m, 2H), 7.35-7.38 (m, 2H), 7.41 (d, 1H, J = 7.2 Hz), 7.47 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2.0 Hz), 7.50-7.54 (m, 2H), 7.70 (d, 2H, J = 8.8 Hz), 7.82 (d, 1H, J = 8.4 Hz), 7.90-7.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 7.0 (q, J_{C-F} = 2.3 Hz), 8.0 (q, J_{C-F} = 1.5 Hz), 28.8 (q, J_{C-F} = 30.5 Hz), 31.1, 34.5, 73.2, 122.2, 125.3, 125.5 (q, J_{C-F} = 275.6 Hz), 125.6, 127.0 (q, J_{C-F} = 2.3 Hz), 127.1, 128.2, 128.4, 128.9, 129.5, 130.1, 130.9, 133.9, 135.8, 139.5, 149.4, 152.1; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -63.6 (s, 3F); MS (ESI) *m/z*: 508.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{29}H_{26}ClF_3N_3^+$ requires: 508.1762, Found: 508.1761.



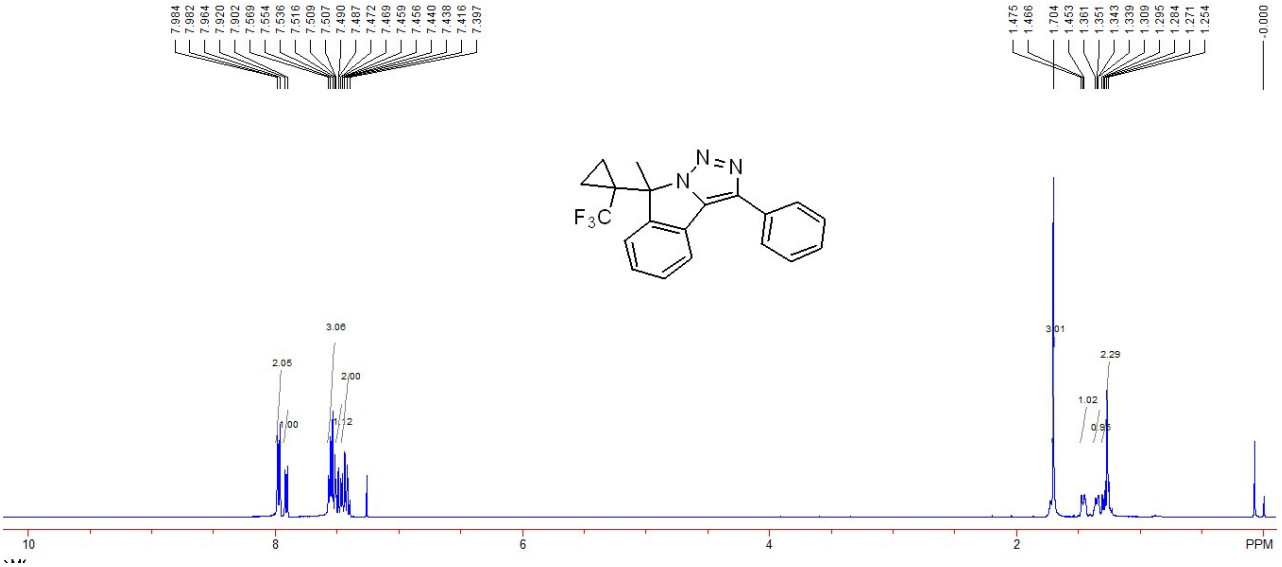


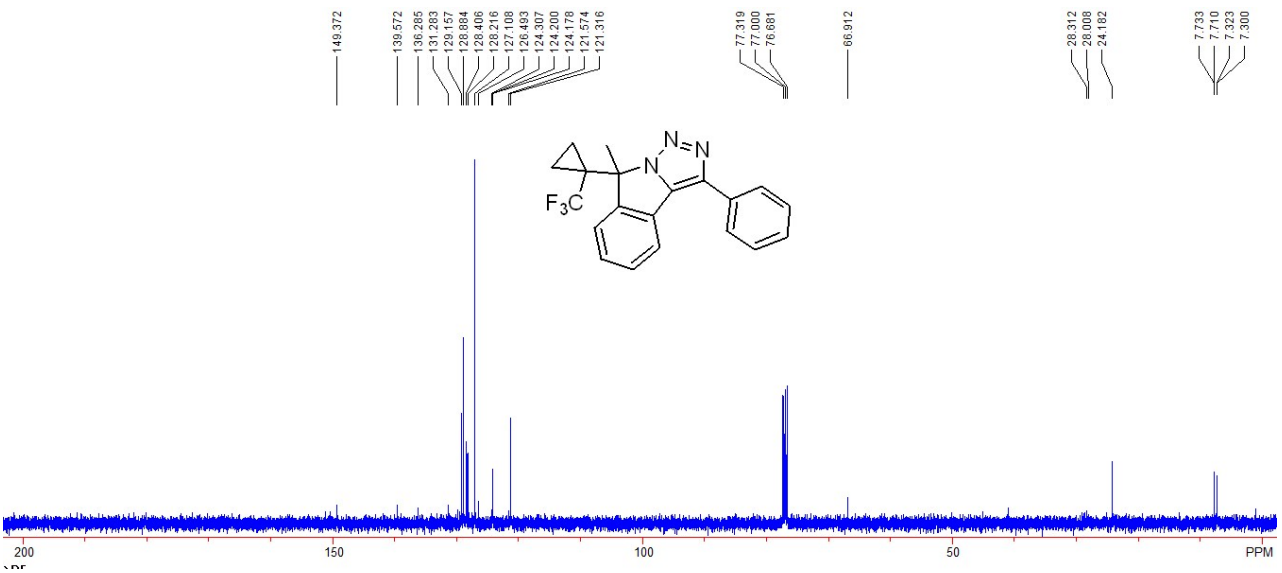


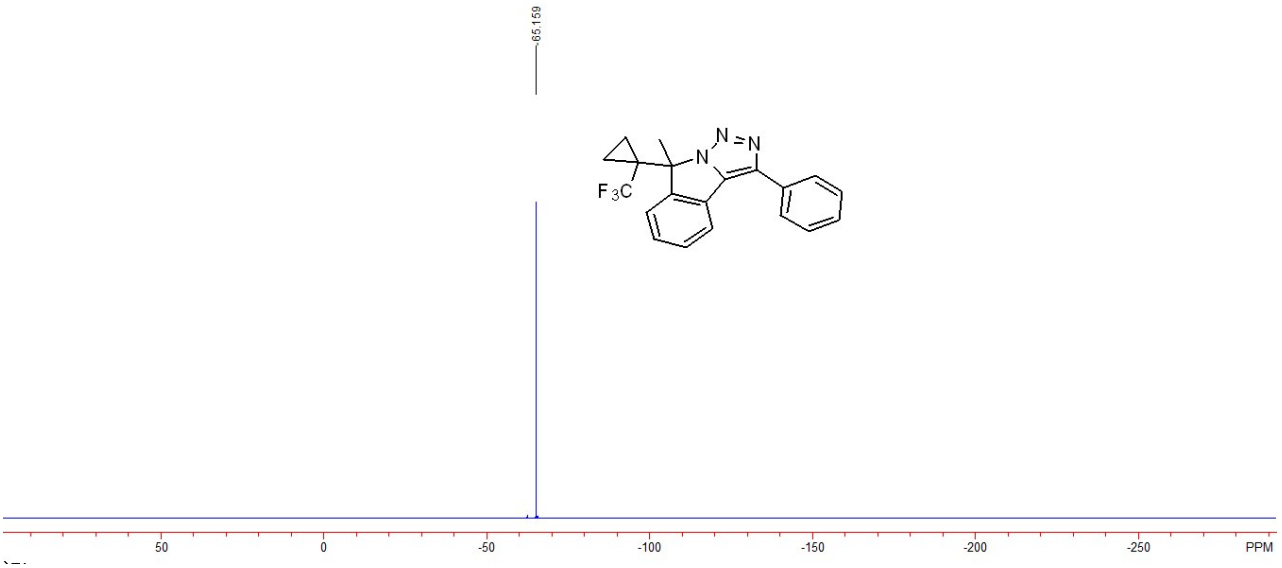


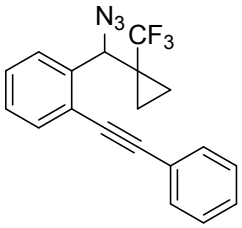
Compound 4u: 46 mg, 64%, A white solid, m.p. 133-135 ^{o}C; IR (CH_2Cl_2): ν 3062, 3034, 1610, 1496, 1459, 1448, 1355, 1139, 1085, 984, 762, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.25-1.31 (m, 2H), 1.34-1.36 (m, 1H), 1.45-1.48 (m, 1H), 1.70 (s, 3H), 7.40-7.49 (m, 3H), 7.51-7.57 (m, 3H), 7.91 (d, 1H, J = 7.2 Hz), 7.97 (dd, 2H, J_1 = 8.0 Hz, J_1 = 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 7.3 (q, $J_{C\text{-}F}$ = 2.3 Hz), 7.7 (q, $J_{C\text{-}F}$ = 2.3 Hz), 24.2, 28.2 (q, $J_{C\text{-}F}$ = 30.4 Hz), 66.9, 121.3, 124.2 (q, $J_{C\text{-}F}$ = 1.5 Hz), 125.6 (q, $J_{C\text{-}F}$ = 275.2 Hz), 127.1, 128.2, 128.4, 128.9, 129.2, 131.3,

136.3, 139.6, 149.4; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -65.2 (s, 3F); MS (ESI) *m/z*: 356.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{20}H_{17}F_3N_3^+$ requires: 356.1369, Found: 356.1369.

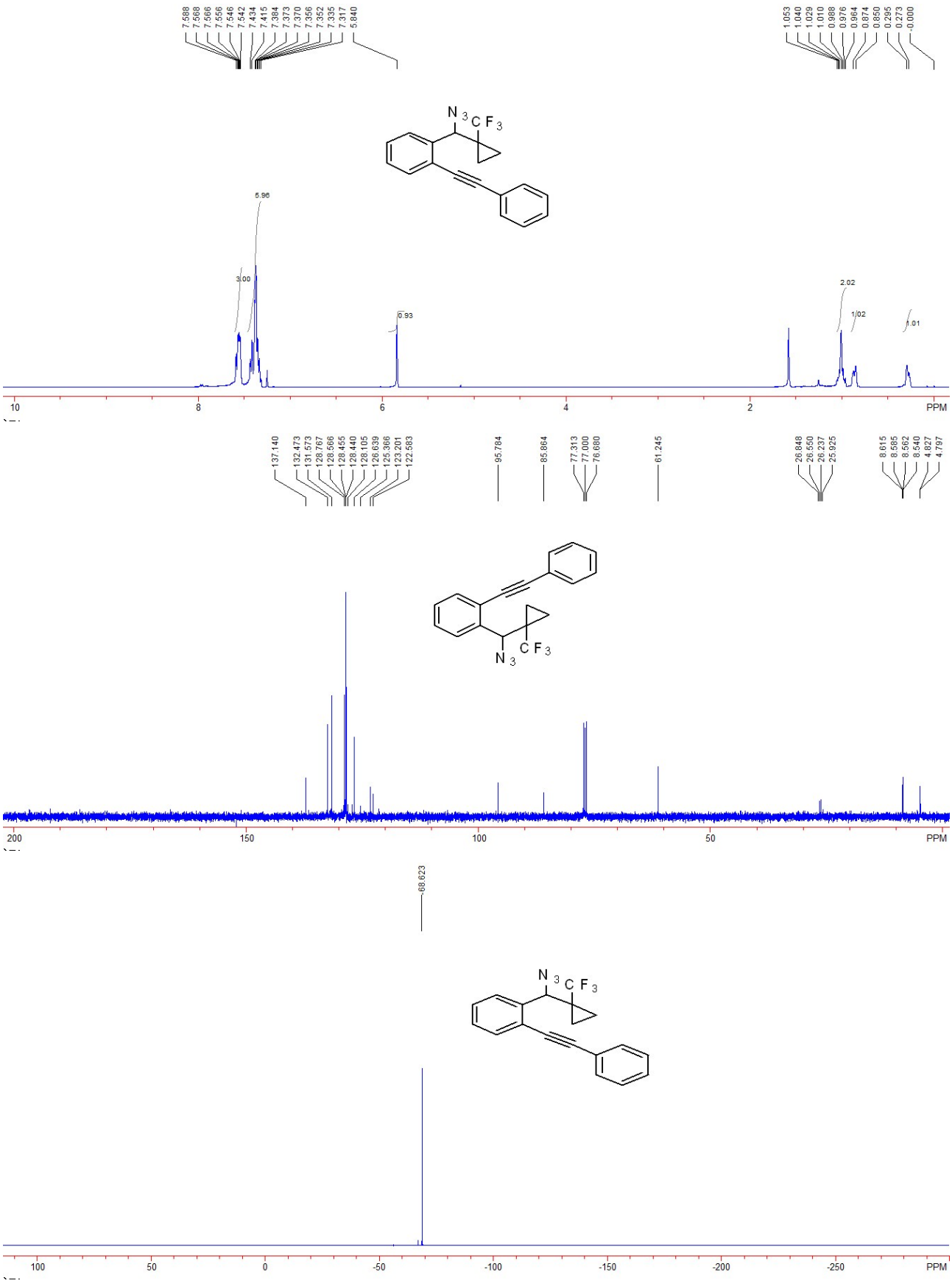




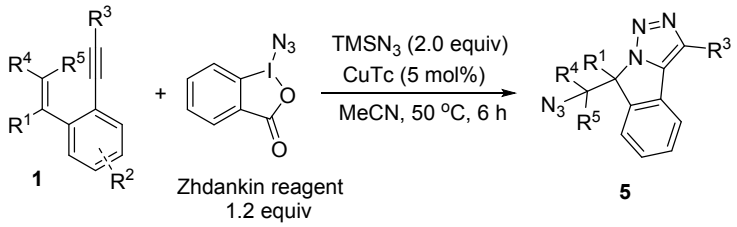




Compound 4v: 36 mg, 52%, A colorless liquid; IR (CH_2Cl_2): □ 3045, 3029, 2924, 2109, 1612, 1497, 1377, 1289, 1245, 1139, 1086, 760, 696; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.27-0.30 (m, 1H), 0.85-0.87 (m, 1H), 0.96-1.05 (m, 2H), 5.84 (s, 1H), 7.31-7.43 (m, 6H), 7.54-7.59 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 4.8 (q, J_{C-F} = 3.0 Hz), 8.6 (q, J_{C-F} = 1.3 Hz), 26.4 (q, J_{C-F} = 31.3 Hz), 61.2, 85.9, 95.8, 122.6, 123.2, 126.6, 126.7 (q, J_{C-F} = 273.9 Hz), 128.4, 128.5, 128.6, 128.8, 131.6, 132.5, 137.1; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -68.6 (s, 3F); MS (ESI) *m/z*: 342.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{19}H_{15}F_3N_3^+$ requires: 342.1213, Found: 342.1214.

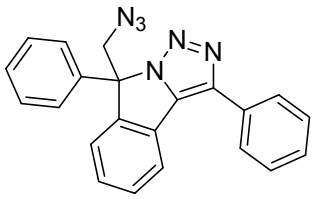

7.588
7.568
7.566
7.556
7.546
7.542
7.434
7.415
7.384
7.373
7.370
7.356
7.352
7.335
7.317
5.840
1.053
1.040
1.029
1.010
0.988
0.976
0.964
0.874
0.850
0.295
0.273
0.000
N3 CF3
5.96
3.00
0.93
2.02
1.02
1.01
10
8
6
4
2
PPM
137.140
132.473
131.573
128.767
128.566
128.455
128.440
128.105
126.639
125.366
123.201
122.583
95.784
85.864
77.313
77.000
76.680
61.245
26.848
26.550
26.237
25.925
8.615
8.585
8.562
8.540
4.827
4.797
N3 CF3
200
150
100
50
PPM
68.623
N3 CF3
100
50
0
-50
-100
-150
-200
-250
PPM

General procedure for the synthesis of products 5

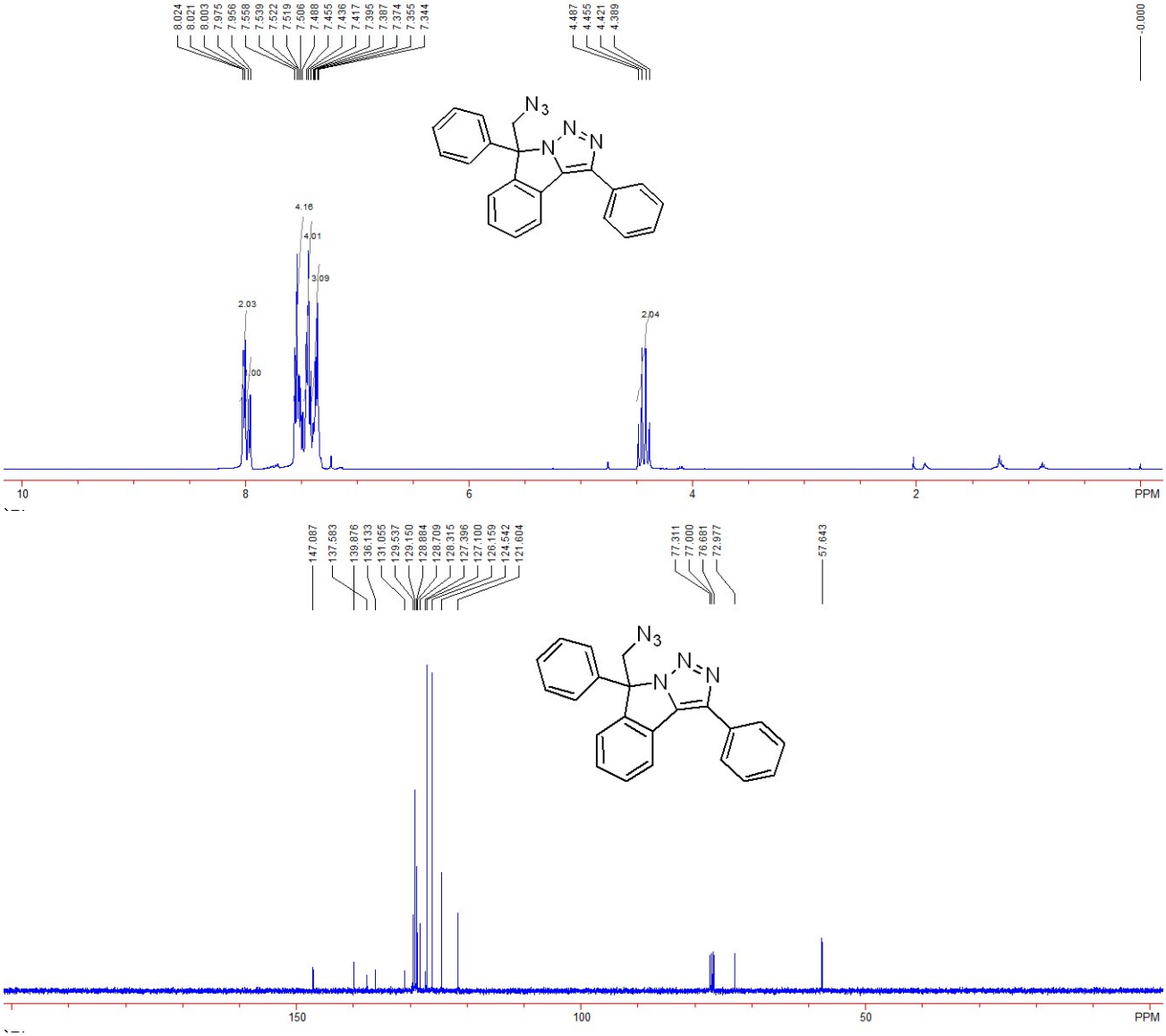


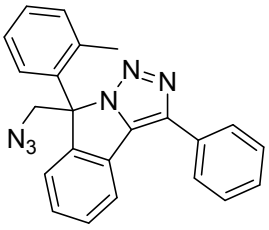
1 (0.2 mmol, 1.0 equiv), Zhdankin reagent (0.24 mmol, 1.2 equiv), CuTc (0.010 mmol, 0.05 equiv) were dissolved in MeCN (2.0 mL), then $TMSN_3$ (0.40 mmol, 2.0 equiv) was added dropwise and the reaction tube was placed in a pre-heated 50 ^oC oil bath. The reaction was stopped after 6 h and the reaction mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the products **5** in good yield.

Spectroscopic data for products 3

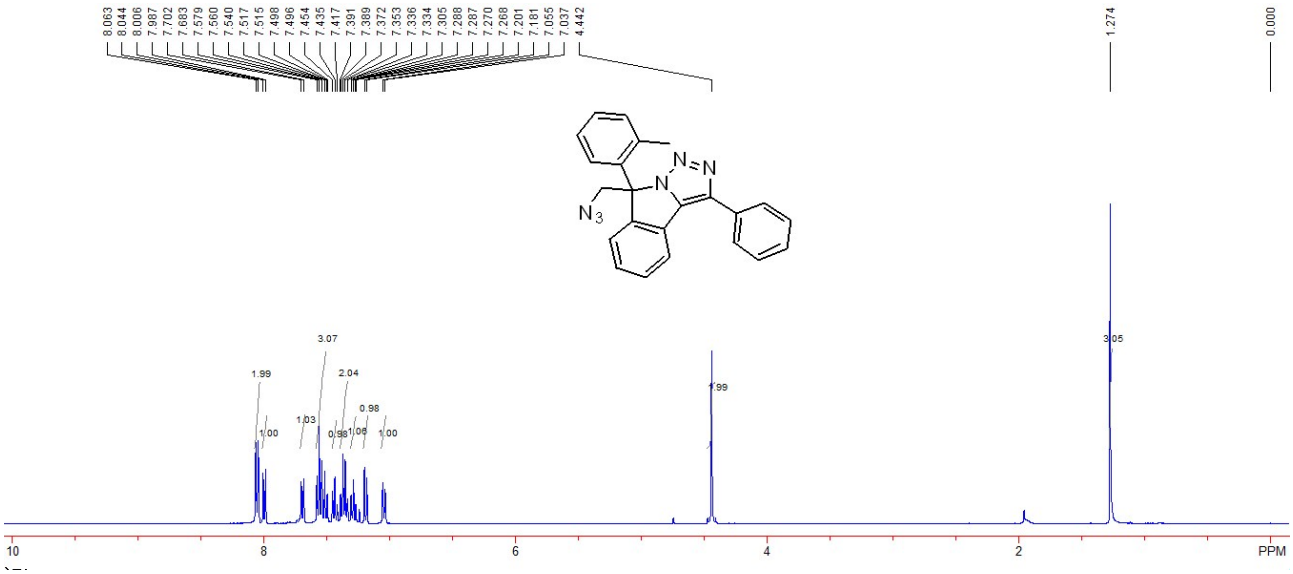


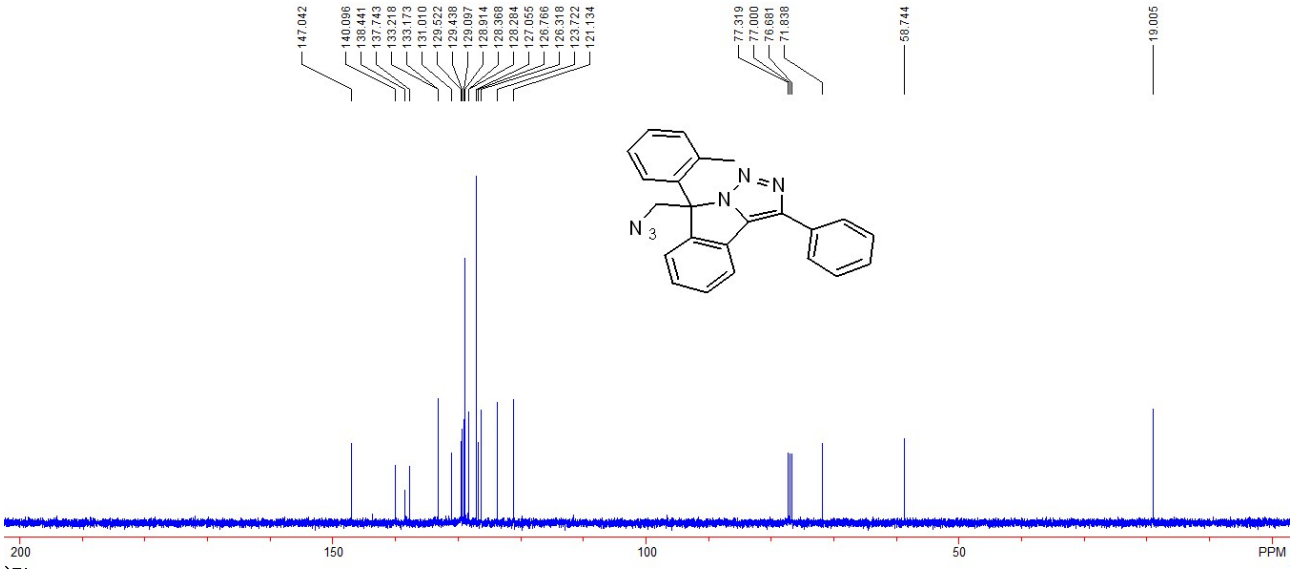
Compound 5a: 64 mg, 87%, A white solid, m.p. 183-185 °C; IR (CH_2Cl_2): ν 3059, 2954, 2921, 2851, 2106, 1735, 1660, 1497, 1470, 1447, 1253, 984, 762, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 4.41 (d, 1H, J = 12.8 Hz), 4.47 (d, 1H, J = 12.8 Hz), 7.34-7.40 (m, 3H), 7.40-7.46 (m, 4H), 7.49-7.56 (m, 4H), 7.97 (d, 1H, J = 7.6 Hz), 8.01 (dd, 2H, J_1 = 7.2 Hz, J_2 = 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 57.6, 73.0, 121.6, 124.5, 126.2, 127.1, 127.4, 128.3, 128.7, 128.9, 129.2, 129.5, 131.1, 136.1, 137.6, 139.9, 147.1; MS (ESI) *m/z*: 365.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{22}H_{17}N_6^+$ requires: 365.1509, Found: 365.1508.

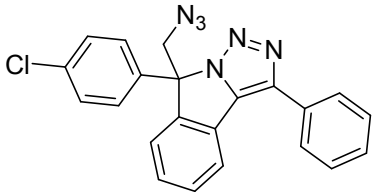




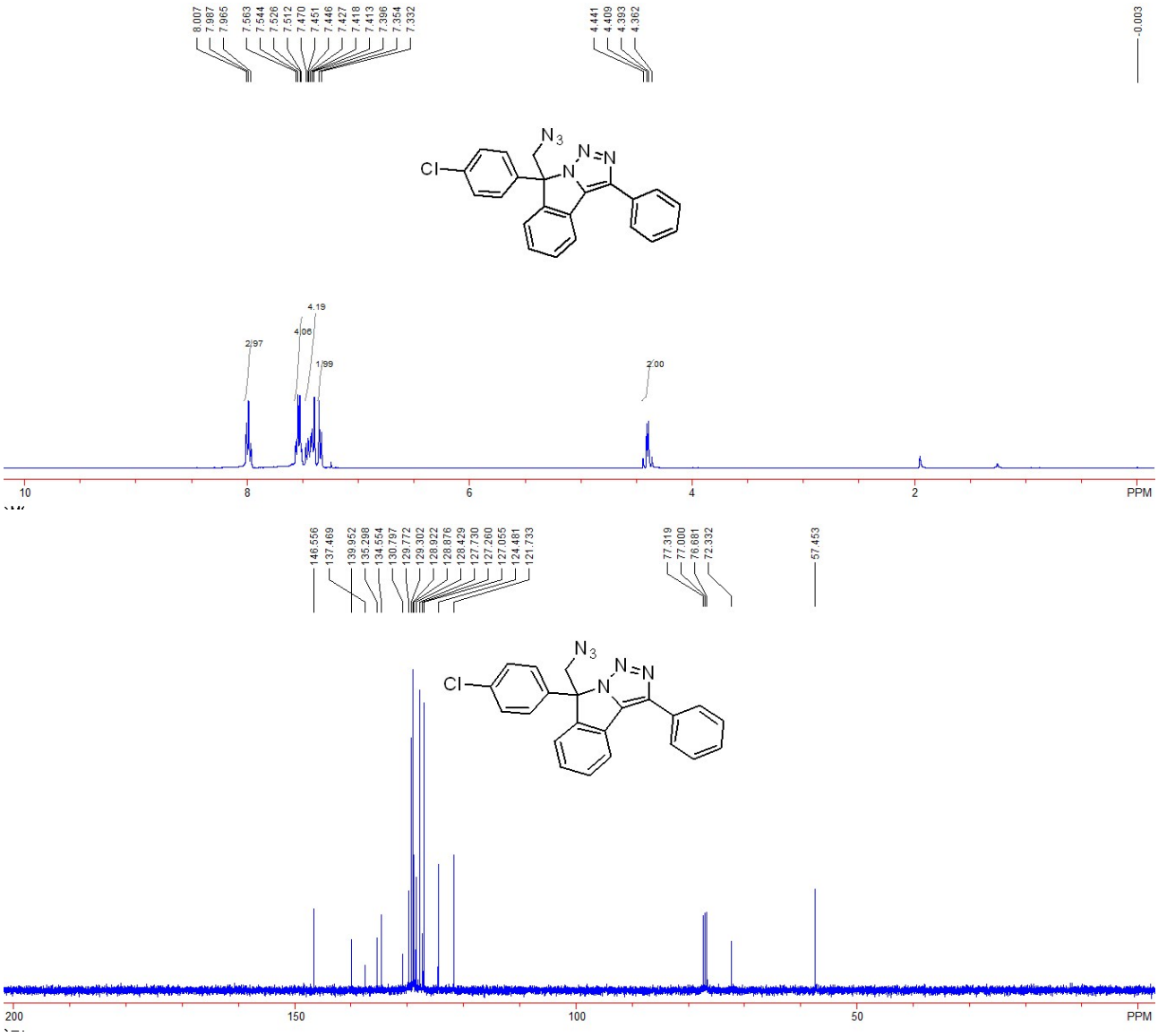
Compound 5b: 61 mg, 81%, A white solid, m.p. 168-170 ºC; IR (CH_2Cl_2): ν 3062, 2937, 2831, 2103, 1495, 1446, 1356, 1281, 1024, 984, 903, 761, 721, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.27 (s, 3H), 4.44 (s, 2H), 7.05 (d, 1H, J = 7.2 Hz), 7.19 (d, 1H, J = 8.0 Hz), 7.29 (td, 1H, J_1 = 7.2 Hz, J_2 = 0.8 Hz), 7.34-7.39 (m, 2H), 7.44 (t, 1H, J = 7.2 Hz), 7.50-7.58 (m, 3H), 7.69 (d, 1H, J = 7.6 Hz), 8.00 (d, 1H, J = 7.6 Hz), 8.05 (d, 2H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.0, 58.7, 71.8, 121.1, 123.7, 126.3, 126.8, 127.1, 128.3, 128.4, 128.9, 129.1, 129.4, 129.5, 131.0, 133.17, 133.22, 137.7, 138.4, 140.1, 147.0; MS (ESI) *m/z*: 379.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{23}H_{19}N_6^+$ requires: 379.1666, Found: 379.1678.

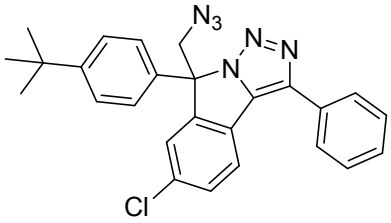




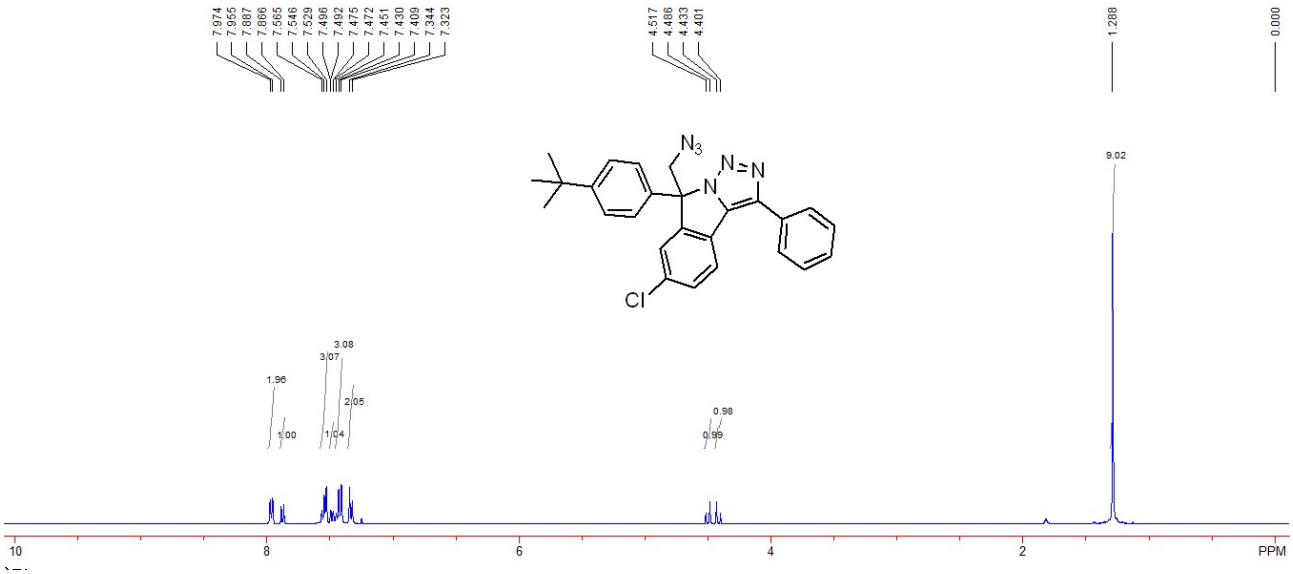


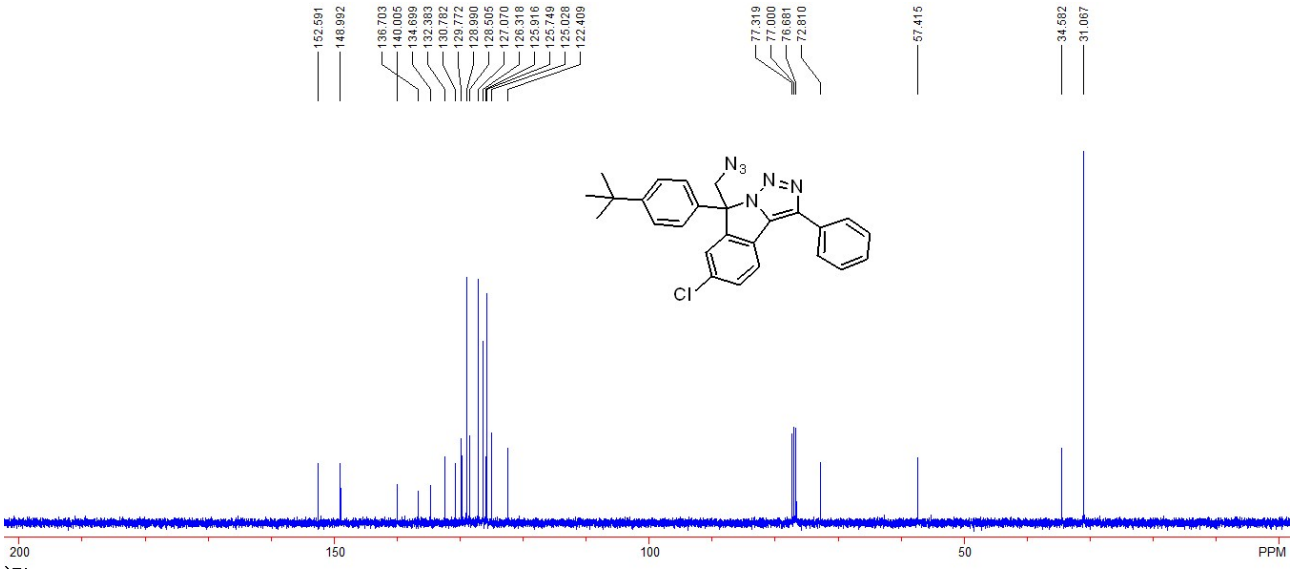
Compound 5c: 61 mg, 76%, A white solid, m.p. 193-195 ^{o}C; IR (CH_2Cl_2): ν 3059, 3001, 2931, 2089, 1493, 1448, 1362, 1301, 1278, 1094, 1012, 899, 836, 804, 763, 755, 702, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 4.38 (d, 1H, *J* = 12.8 Hz), 4.42 (d, 1H, *J* = 12.8 Hz), 7.34 (d, 2H, *J* = 8.0 Hz), 7.40-7.47 (m, 4H), 7.51-7.56 (m, 4H), 7.97-8.01 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 57.5, 72.3, 121.7, 124.5, 127.1, 127.3, 127.7, 128.4, 128.88, 128.92, 129.3, 129.8, 130.8, 134.6, 135.3, 137.5, 140.0, 146.6; MS (ESI) *m/z*: 399.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{22}H_{16}ClN_6^+$ requires: 399.1119, Found: 399.1133.

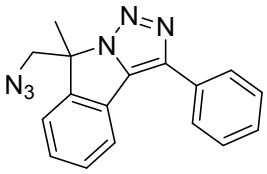




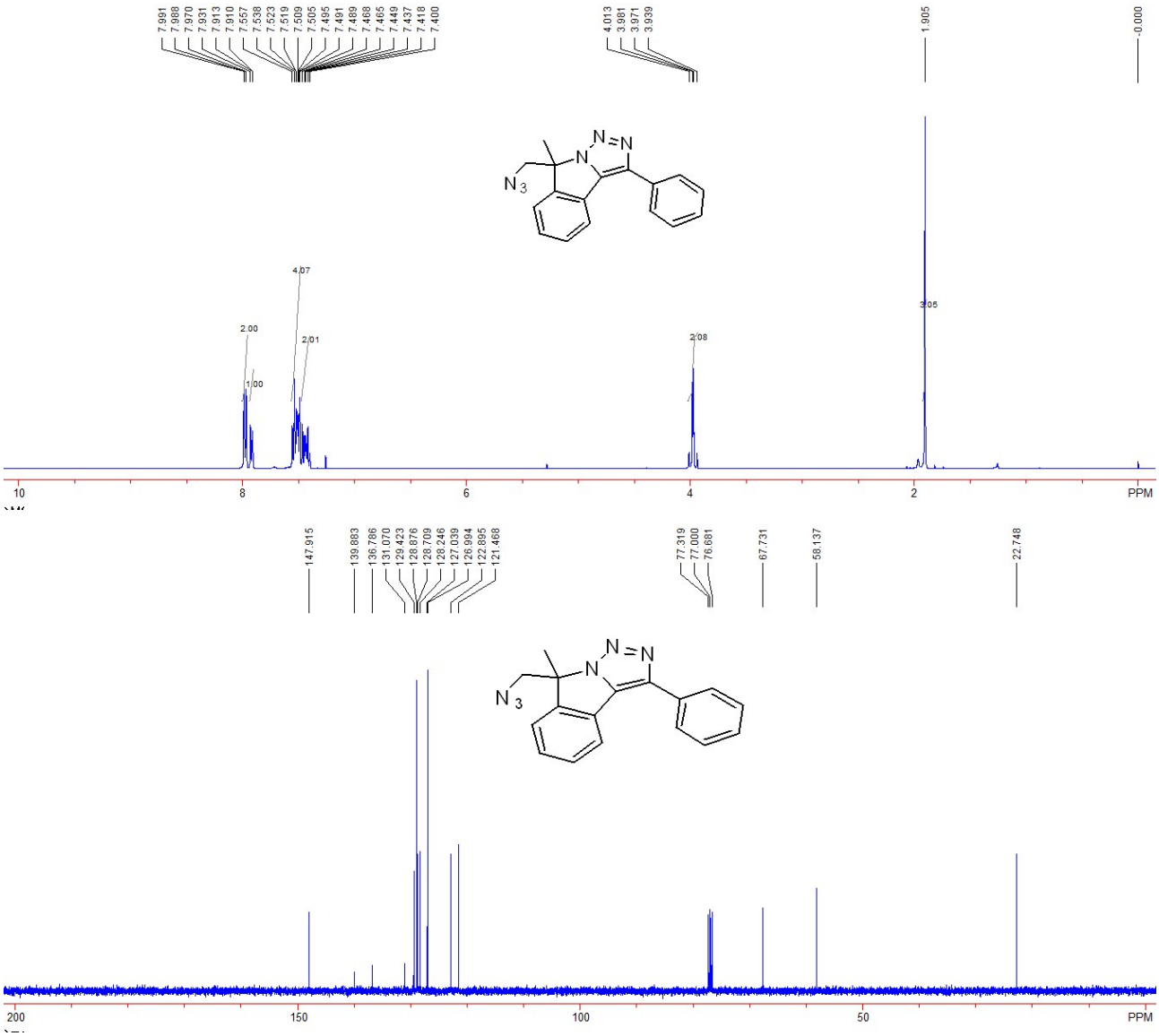
Compound 5d: 76 mg, 83%, A white solid, m.p. 205-207 ^{o}C; IR (CH_2Cl_2): ν 3067, 2964, 2868, 2105, 1451, 1356, 1269, 1087, 984, 826, 774, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.29 (s, 9H), 4.42 (d, 1H, J = 12.8 Hz), 4.50 (d, 1H, J = 12.8 Hz), 7.33 (d, 2H, J = 8.4 Hz), 7.41-7.45 (m, 3H), 7.48 (dd, 1H, J_1 = 8.4 Hz, J_2 = 1.2 Hz), 7.53-7.57 (m, 3H), 7.88 (d, 1H, J = 7.6 Hz), 7.96 (d, 2H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 31.1, 34.6, 57.4, 72.8, 122.4, 125.0, 125.7, 125.9, 126.3, 127.1, 128.5, 129.0, 129.8, 130.8, 132.4, 134.7, 136.7, 140.0, 149.0, 152.6; MS (ESI) *m/z*: 455.2 (M+H^{+}, 100); HRMS (ESI) Calcd. for $C_{26}H_{24}ClN_6^{+}$ requires: 455.1745, Found: 455.1761.

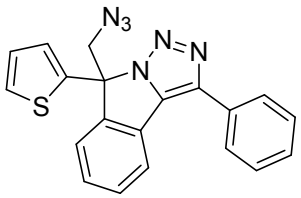




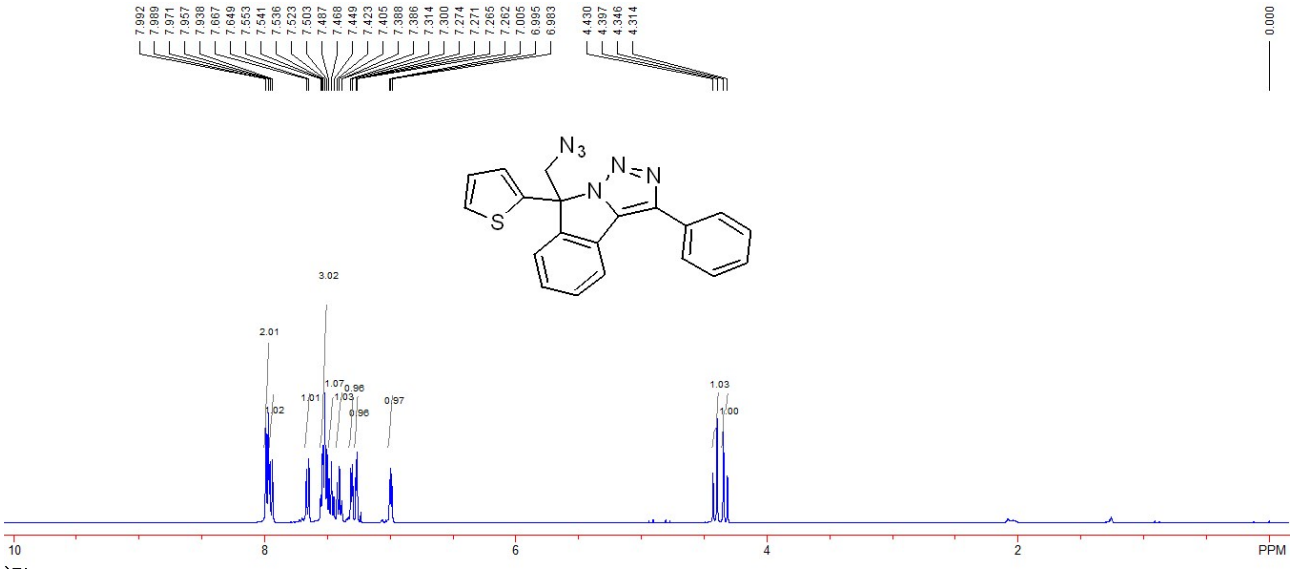


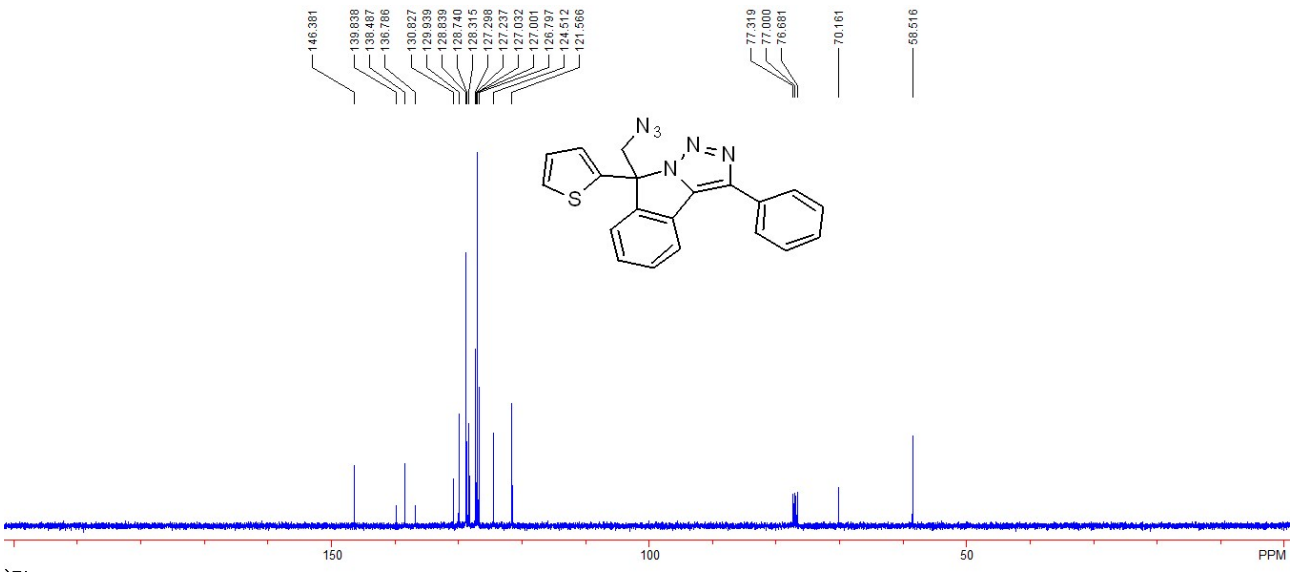
Compound 5e: 56 mg, 93%, A white solid, m.p. 174-176 ^{o}C; IR (CH_2Cl_2): ν 3056, 2981, 2929, 2103, 1496, 1449, 1359, 1309, 1280, 1019, 984, 779, 761, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.91 (s, 3H), 3.96 (d, 1H, J = 12.8 Hz), 4.00 (d, 1H, J = 12.8 Hz), 7.40-7.47 (m, 2H), 7.49-7.56 (m, 4H), 7.92 (dd, 1H, J_1 = 8.4 Hz, J_2 = 1.2 Hz), 7.98 (dd, 2H, J_1 = 8.4 Hz, J_2 = 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 22.7, 58.1, 67.7, 121.5, 122.9, 126.99, 127.04, 128.2, 128.7, 128.9, 129.4, 131.1, 136.8, 139.9, 147.9; MS (ESI) *m/z*: 303.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{17}H_{15}N_6^+$ requires: 303.1353, Found: 303.1357.

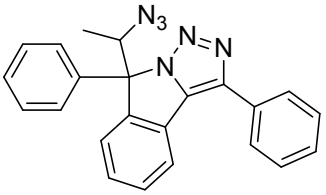




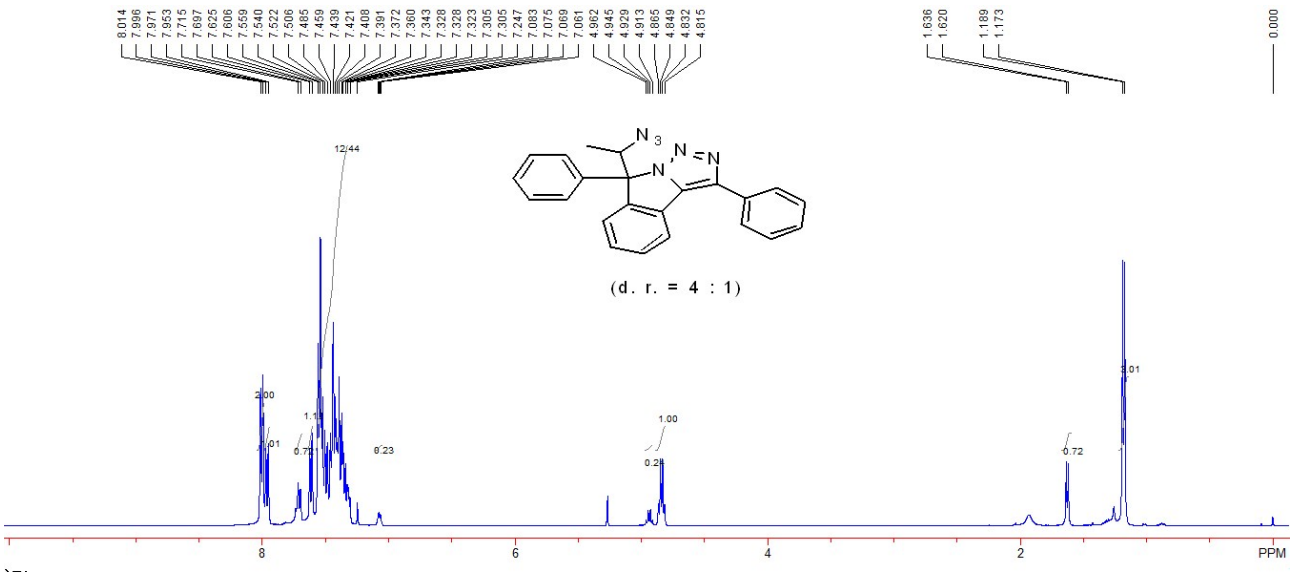
Compound 5f: 71 mg, 96%, A white solid, m.p. 187-189 ^{o}C; IR (CH_2Cl_2): ν 2940, 2829, 2104, 1497, 1471, 1447, 1358, 1279, 1238, 1022, 984, 761, 695 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 4.33 (d, 1H, J = 12.8 Hz), 4.41 (d, 1H, J = 12.8 Hz), 6.98-7.01 (m, 1H), 7.27 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.31 (d, 1H, J = 5.6 Hz), 7.40 (td, 1H, J_1 = 7.6 Hz, J_2 = 0.8 Hz), 7.45-7.50 (m, 1H), 7.52-7.55 (m, 3H), 7.66 (d, 1H, J = 7.2 Hz), 7.95 (d, 1H, J = 7.6 Hz), 7.98 (dd, 2H, J_1 = 7.6 Hz, J_2 = 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 58.5, 70.2, 121.6, 124.5, 126.8, 127.00, 127.03, 127.2, 127.3, 128.3, 128.7, 128.8, 129.9, 130.8, 136.8, 138.5, 139.8, 146.4; MS (ESI) *m/z*: 371.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{20}H_{15}N_6S^+$ requires: 371.1073, Found: 371.1080.

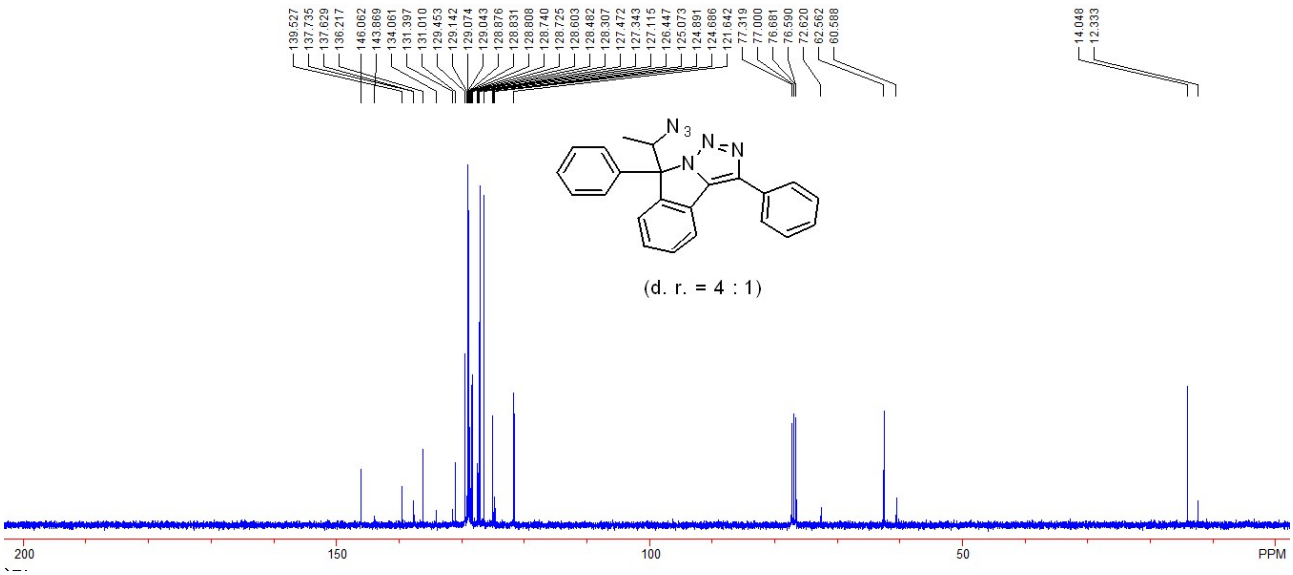


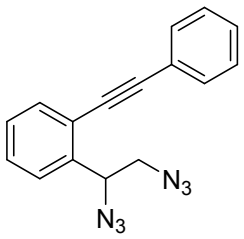




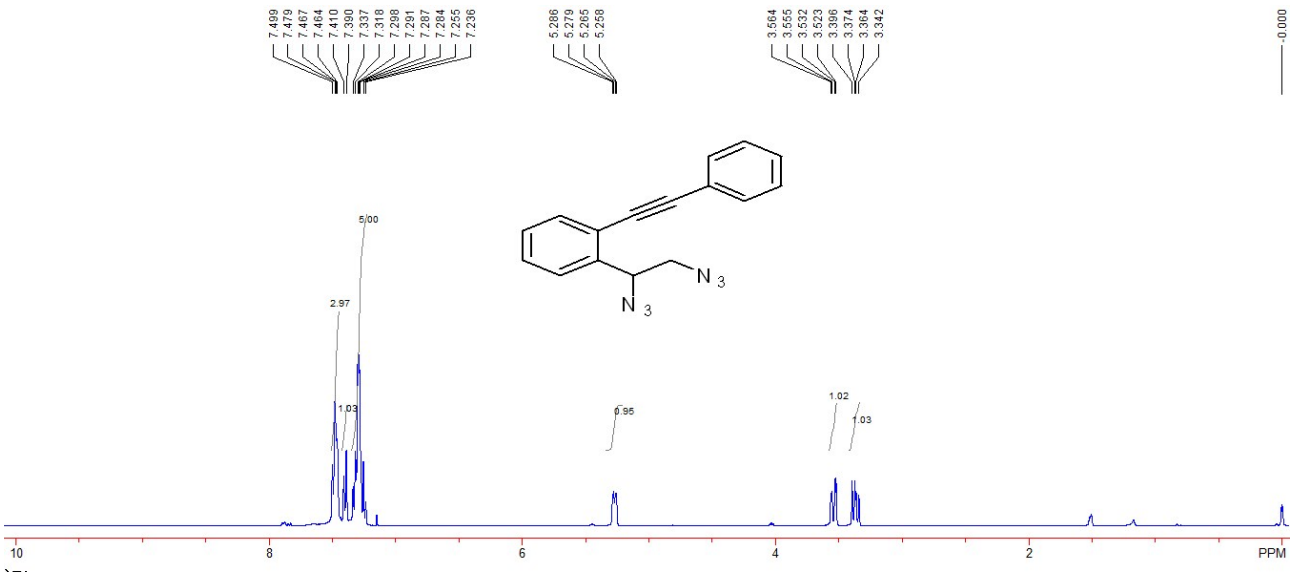
Compound 5h: 49 mg, 65%, A white solid, m.p. 190-192 ^{o}C, obtained as a 4:1 mixture of diastereoisomers; IR (CH_2Cl_2): ν 2956, 2921, 2852, 2113, 1496, 1447, 1356, 1256, 985, 763, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.18 (d, 3H, *J* = 6.4 Hz), 1.63 (d, 0.72H, *J* = 6.4 Hz), 4.84 (q, 1H, *J* = 6.4 Hz), 4.94 (q, 0.24H, *J* = 6.4 Hz), 7.06-7.08 (m, 0.24H), 7.25-7.56 (m, 12.4H), 7.62 (d, 1H, *J* = 7.6 Hz), 7.70-7.72 (m, 0.72H), 7.96 (d, 1H, *J* = 7.2 Hz), 8.00 (d, 2H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 12.3, 14.0, 60.6, 62.6, 72.6, 76.6, 121.6, 124.7, 124.9, 125.1, 126.4, 127.1, 127.3, 127.5, 128.3, 128.5, 128.6, 128.73, 128.74, 128.81, 128.83, 128.9, 129.0, 129.07, 129.14, 129.5, 131.0, 131.4, 134.1, 136.2, 137.6, 137.7, 139.5, 143.9, 146.1; MS (ESI) *m/z*: 379.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{23}H_{19}N_6^+$ requires: 379.1666, Found: 379.1683.







Compound 5i: 50 mg, 86%, A colorlss liquid; IR (CH_2Cl_2): ν 3062, 3031, 2920, 2096, 1596, 1493, 1258, 756, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 3.37 (dd, 1H, J_1 = 12.8 Hz, J_2 = 8.8 Hz), 3.54 (dd, 1H, J_1 = 12.8 Hz, J_2 = 3.6 Hz), 5.27 (dd, 1H, J_1 = 8.8 Hz, J_2 = 3.6 Hz), 7.24-7.34 (m, 5H), 7.40 (d, 1H, J = 8.0 Hz), 7.46-7.50 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 55.4, 63.6, 85.8, 95.4, 121.9, 122.4, 126.2, 128.5, 128.8, 129.0, 131.5, 132.6, 137.8; MS (ESI) *m/z*: 289.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{16}H_{13}N_6^+$ requires: 289.1196, Found: 289.1203.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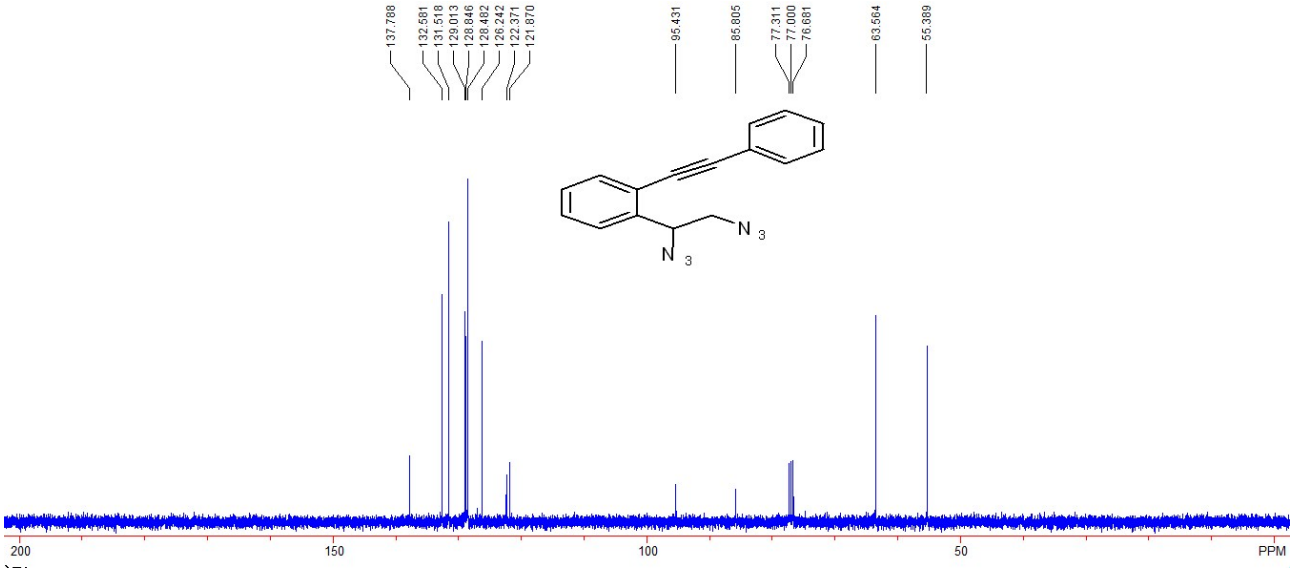
7.236
5.286
5.279
5.265
5.258
3.564
3.555
3.532
3.523
3.396
3.374
3.364
3.342
0.000
5.00
2.97
1.03
0.95
1.02
1.03
N 3
N 3
10
8
6
4
2
PPM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122.371
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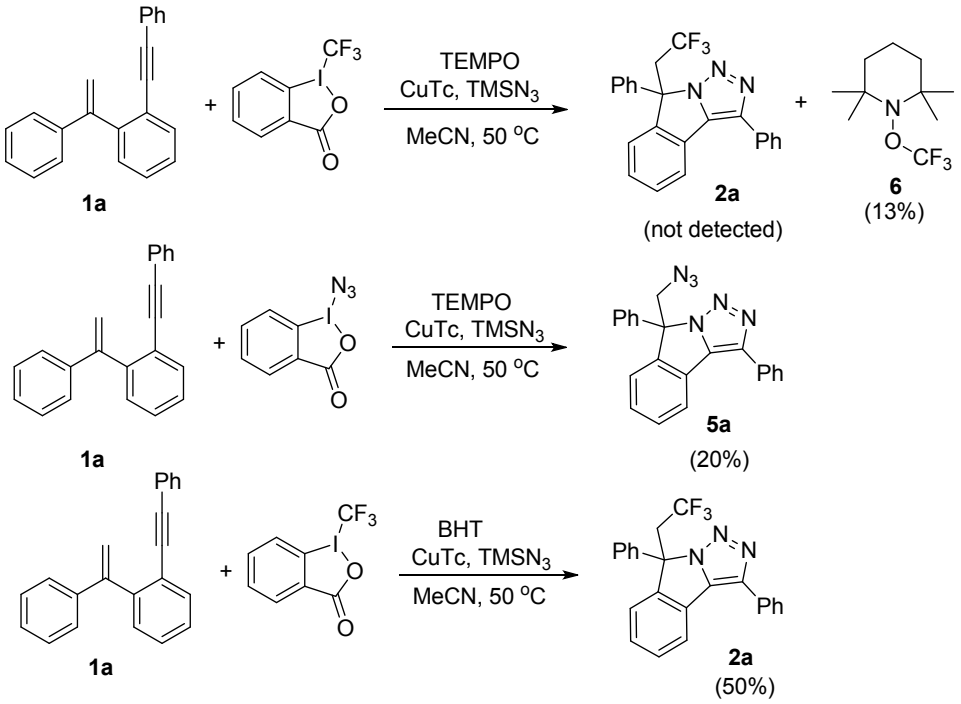
85.805
77.311
77.000
76.681
63.564
55.389
N 3
N 3
200
150
100
50
PPM

Control experiments

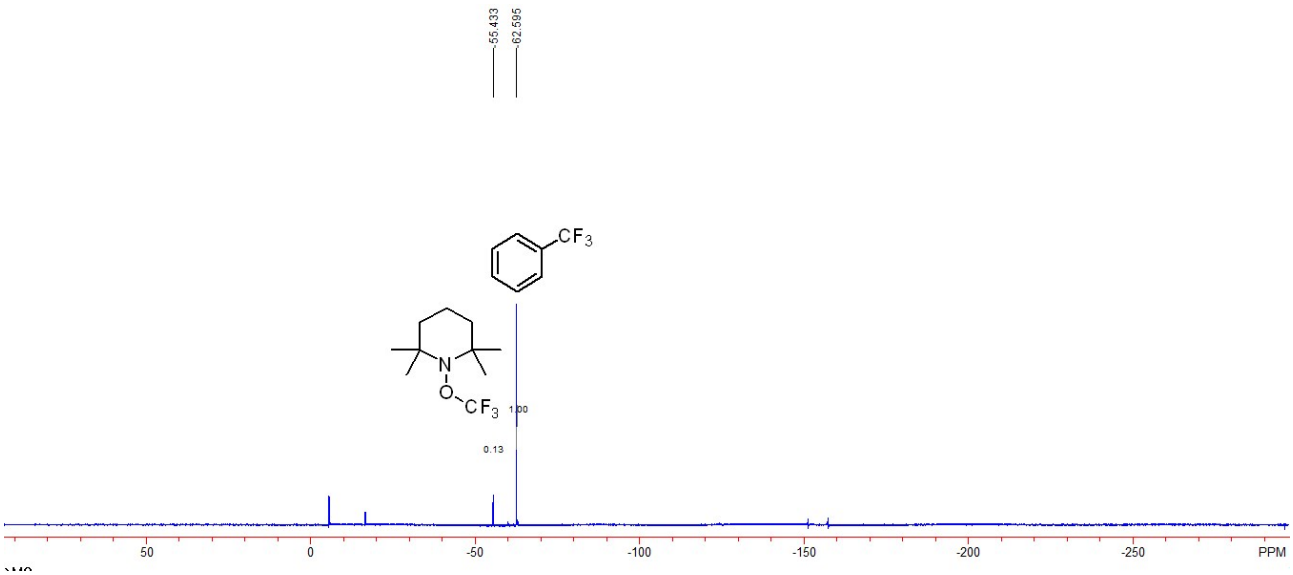
To gain the mechanistic insights of this cascade trifluoromethylazidation/diazidation and click reaction, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), a well-known radical scavenger, was used to react with **1a** and hypervalent reagents in the presence of catalytic amount of CuTc (5 mol%), respectively. The desired product **2a** was not detected and the TEMPO-trapping compound **6** was obtained in 13% yield on the basis of ^{19}F NMR spectroscopic analysis. N_3-containing triazole fused isoindoline **5a** was also isolated in 20% yield. The other conventional radical scavenger, 2,6-di-tert-butyl-4-methylphenol (BHT), also inhibited the formation of **2a** (only 50% isolated yield). These radical trapping experiments indicated that radical species existed in the reaction system.



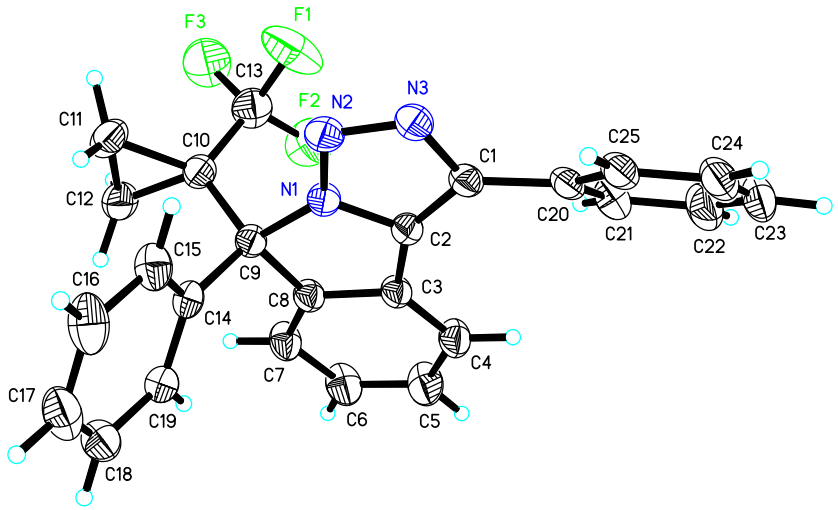
Scheme S1. Control experiments.

TEMPO experiments: **1a** (0.10 mmol), TEMPO (0.20 mmol), CuTc (0.0050 mmol) and Togni reagent II (0.15 mmol) or Zhdankin reagent (0.12 mmol) were added to a Schlenk tube with a magnetic bar. Then acetonitrile (1.0 mL) and $TMSN_3$ (0.20 mmol) were successively added and the reaction tube was heated to 50 °C for 12 h. Upon completion, the expected product **2a** was not obtained and the TEMPO-trapped complex **5** was detected in 13% yield on the basis of ^{19}F NMR spectroscopic analysis using (trifluoromethyl)benzene (0.10 mmol) as an internal standard. However, N_3-containing triazole fused isoindoline **5a** was isolated in 20% yield.

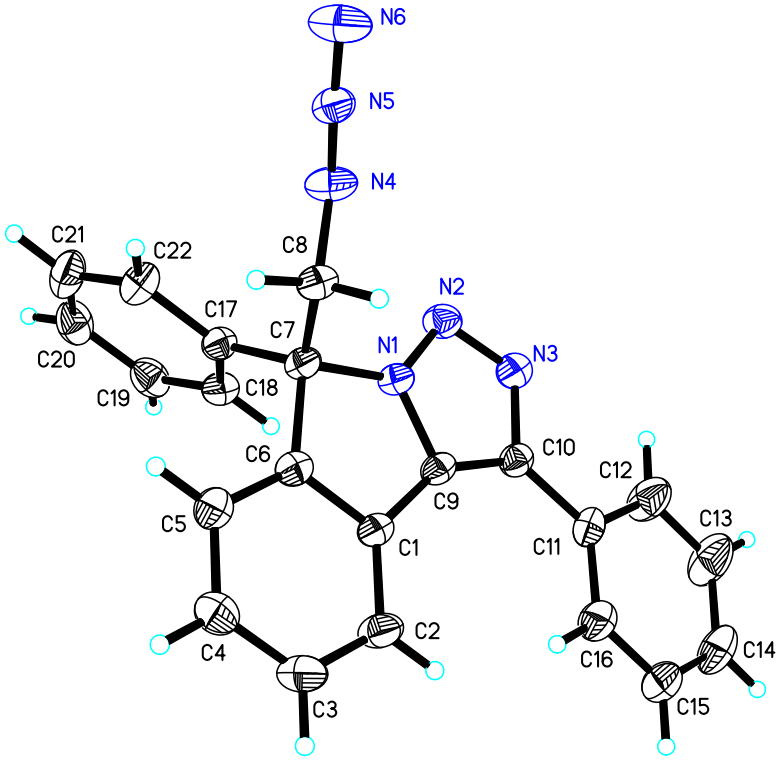
BHT experiment: **1a** (0.10 mmol), BHT (0.20 mmol), CuTc (0.005 mmol) and Togni reagent II (0.15 mmol) were added to Schlenk tube with a magnetic bar. Then acetonitrile (1.0 mL) and $TMSN_3$ (0.20 mmol) were successively added and the reaction tube was heated to 50 °C for 12 h. Upon completion, the expected product **2a** was isolated only in 50% yield.



The crystal data of 4a and 5a



The crystal data of **4a** have been deposited in CCDC with number 1440522. Empirical Formula: $C_{25}H_{18}F_3N_3$; Formula Weight: 417.42; Crystal Color, Habit: colorless, Crystal Dimensions: 0.210 x 0.160 x 0.130 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 21.381(8)Å, b = 12.571(4)Å, c = 16.690(6)Å, $\alpha = 90^o$, $\beta = 117.251(8)^o$, $\gamma = 90^o$, V = 3988(2)$Å^3$; Space group: C 2/c; Z = 8; D_{calc}= 1.390 g/cm^3; F_{000} = 1728; Final R indices [I>2sigma(I)] R1 = 0.0516, wR2 = 0.1250.



The crystal data of **5a** have been deposited in CCDC with number 1482939. Empirical Formula: $C_{44}H_{32}N_{12}$; Formula Weight: 728.81; Crystal Color, Habit: colorless, Crystal Dimensions: 0.200 x 0.160 x 0.130 mm^3; Crystal System: Triclinic; Lattice Parameters: a = 8.1858(10)Å, b = 10.1508(13)Å, c = 22.150(3)Å, α = 89.880(3)°, β = 83.440(3)°, γ = 78.898(3)°, V = 1793.9(4)^3; Space group: P -1; Z = 2; D_{calc}= 1.349 g/cm^3; F_{000} = 760; Final R indices [I>2sigma(I)] R1 = 0.0622, wR2 = 0.1446.

Reference

1 (a) J. Aziz, G. Frison, P. L. Menez, J.-D. Brion, A. Hamze, and M. Alami, *Adv. Synth. Catal.*, 2013, **355**, 3425-3436; (b) A. M. Sanjuán, M. A. Rashid, P. García-García, A. Martínez-Cuezva, M. A. Fernández-Rodríguez, F. Rodríguez, and R. Sanz, *Chem. - Eur. J.*, 2015, **21**, 3042-3052.

2 (a) S. V. Frye, M. C. Johnson, and N. L. Valvano, *J. Org. Chem.*, 1991, **56**, 3750-3752; (b) T. M. Acker, A. Khatri, K. M. Vance, C. Slabber, J. Bacsa, J. P. Snyder, S. F. Traynelis, and D. C. Liotta, *J. Med. Chem.*, 2013, **56**, 6434-6456.

3 B. Yao, Y. Li, Z. Liang, and Y. Zhang, *Org. Lett.*, 2011, **13**, 640-643.