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Regiodivergent C–H Alkynylation of 2-Arylthiazoles Switched by Ru^{II} and Pd^{II} Catalysis

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1. General information

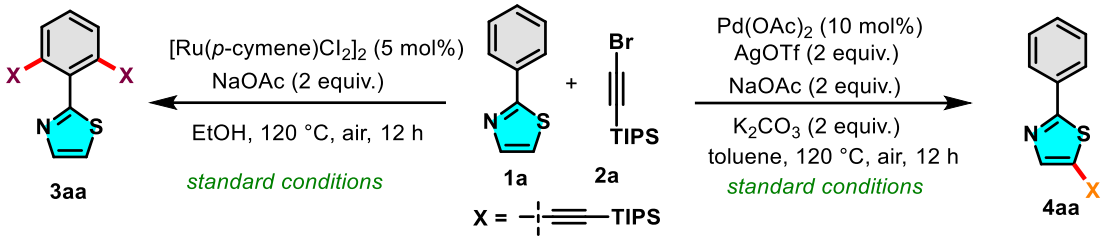
All the reagents were purchased from Bide Pharmatech Ltd. and Energy Chemical. All solvents were purchased from Greagent (Shanghai Titansci incorporated company) and used without further purification. Unless otherwise stated, all reactions were carried out in oven-dried glassware under air atmosphere. All heating reactions were heated by metal sand bath (WATTCAS, LAB-500).

^{1}H-NMR spectra were obtained on Bruker-600 NMR spectra for all the samples were recorded in deuterochloroform ($CDCl_3$). Chemical shifts (δ) were reported in parts per million relative to residual chloroform (7.28 ppm for ^{1}H; 77.23 ppm for ^{13}C), constants were reported in Hertz. ^{1}H NMR assignment abbreviations were the following: singlet (s), doublet (d), triplet (t), quartet (q), doublets of doublet (dd), doublets of triplet(dt) ,triplets of doublet(td), triplets of triplet (tt) and multiplet (m), integration and coupling constant(s) J in hertz (Hz). ^{13}C NMR spectra were recorded at 151 MHz on the same spectrometer and reported in ppm. All spectra were processed using the MestReNova program.

High-resolution mass spectra (HRMS) were recorded on a mass spectrometer (Thermo fisher Q Exactive HRMS) using electrospray ionization-time of flight (ESI-TOF) reflection experiments.

2. Optimization of the reaction conditions

Table S1. Optimization of the reaction conditions [a]

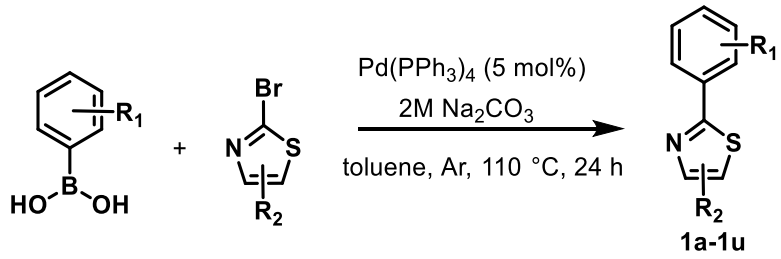


entry	variation from "standard conditions"	Yield [%][b] 3aa/4aa
1	none	81[c]/–
2	without [Ru(*p*-cymene)Cl_2]$_2$	0/–
3	without NaOAc	0/–
4	K_2CO_3 (2 equiv.) instead of NaOAc	61/–
5	carried out at 100 °C	63/–
6	carried out for 8 h	70/–
7	None	–/80
8	without $Pd(OAc)_2$	–/0
9	without AgOTf	–/50
10	without NaOAc	–/36
11	without K_2CO_3	–/22
12	AgOTf (1 equiv.)	–/71
13	Ag_2O (2 equiv.) instead of AgOTf	–/0
14	Ag_2CO_3 (2 equiv.) instead of AgOTf	–/0
15	AgOAc (2 equiv.) instead of AgOTf	–/trace
16	$Cu(OTf)_2$ (2 equiv.) instead of AgOTf	–/trace
17	NaOTf (2 equiv.) instead of AgOTf	–/55
18	carried out at 100 °C	–/68
19	carried out for 8 h	–/72

[a]Reaction conditions for **3aa**: **1a** (0.2 mmol), **2a** (entries 1–6, 0.44 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (5 mol%), NaOAc (0.4 mmol) and EtOH (1.5 mL). [a]Reaction conditions for **4aa**: 1a (0.2 mmol), **2a** (entries 7–17, 0.3 mmol), $Pd(OAc)_2$ (10 mol%), AgOTf (0.4 mmol), NaOAc (0.4 mmol), K_2CO_3 (0.4 mmol) and toluene (1.5 mL). [b]Isolated yield. [c]The reaction afforded trace *mono*-alkynylated product.

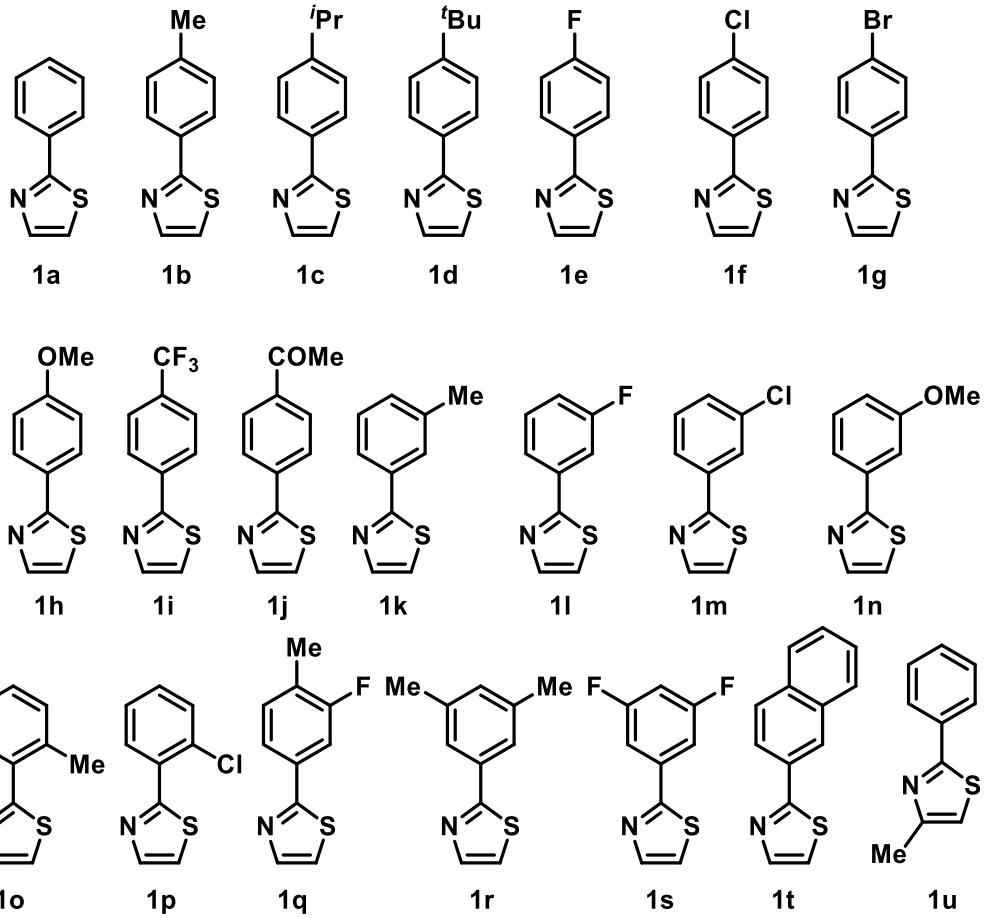
3. Experimental procedure

3.1 Procedure for the synthesis of starting materials



1a-1u

Synthesis of substrates 1a-1u[1]: To a 100 mL oven dried Schlenk tube, $Pd(PPh_3)_4$ (0.4 mmol, 5 mol%), phenylboronic acid derivatives (12 mmol, 1.5 equiv.), 2-bromothiazole derivatives (8 mmol, 1 equiv.), 2M Na_2CO_3 (15 ml) and toluene (15 ml) were successively added. The reaction mixture was stirred at 110 °C (metal sand bath temperature) for 24 hours under argon. Then the reaction mixture was quenched with water (10 mL) and extracted with EtOAc (3 x 20 mL). Combine organic phases and concentrate by drying under vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 30:1) to get the desired products.

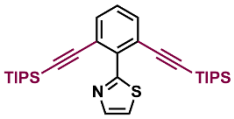


3.2 Ru(II)-catalyzed *ortho*-alkynylation: procedure and compound characterizations

General Procedure A: To a 15 mL oven dried Schlenk tube, 2-arylthiazole derivatives (0.2 mmol, 1 equiv.), $[Ru(p\text{-cymene})Cl_2]_2$ (6.1 mg, 0.01 mmol, 5 mol%), NaOAc (0.4 mmol, 2 equiv.), (bromoethynyl)triisopropylsilane (0.44 mmol, 2.2 equiv.) and EtOH (1.5 mL) were successively added. The reaction mixture was stirred at 120 °C (metal sand bath temperature) for 12 hours under the air. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography to afford the desired alkynylated products.

3.3 Pd(II)-catalyzed C5-alkynylation: procedure and compound characterizations

General Procedure B: To a 15 mL oven dried Schlenk tube, K_2CO_3 (0.4 mmol, 2 equiv.), 2-arylthiazole derivatives (0.2 mmol, 1 equiv.), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), NaOAc (0.4 mmol, 2 equiv.), AgOTf (0.4 mmol, 2 equiv.), (bromoethynyl)triisopropylsilane (0.3 mmol, 1.5 equiv.) and toluene (1.5 mL) were successively added. The reaction mixture was stirred at 120 °C (metal sand bath temperature) for 12 hours under the air. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography to afford the desired alkynylated products.

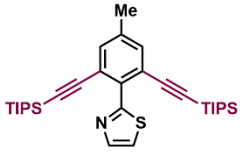


2-(2,6-Bis((triisopropylsilyl)ethynyl)phenyl)thiazole (3aa). Following the general procedure **A** using 2-phenylthiazole (32.2 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (114.8 mg, 0.44 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3aa** (84.4 mg, 81%) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, J = 3.3 Hz, 1H), 7.52 (d, J = 7.8 Hz, 2H), 7.41 (d, J = 3.3 Hz, 1H), 7.32 (t, J = 7.8 Hz, 1H), 0.97 (d, J = 1.6 Hz, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.2, 142.9, 138.9, 132.7, 129.0, 124.9, 120.4, 104.0, 96.3, 18.6, 11.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{48}NSSi_2$ 522.3040; Found 522.3028.

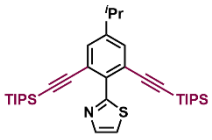


2-(4-Methyl-2,6-bis((triisopropylsilyl)ethynyl)phenyl)thiazole (3ba). Following the general procedure **A** using 2-(*p*-tolyl)thiazole (34.9 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (114.8 mg, 0.44 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3ba** (87.7 mg, 82%) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, J = 3.3 Hz, 1H), 7.39 (d, J = 3.3 Hz, 1H), 7.34 (s, 2H), 2.35 (s, 3H), 1.02 – 0.93 (m, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.3, 142.8, 139.1, 136.2, 133.4, 124.6, 120.3, 104.2, 95.7, 21.0, 18.7, 11.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{50}NSSi_2$ 536.3197; Found 536.3184.

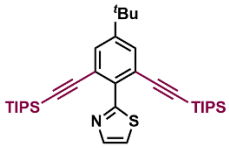


2-(4-Isopropyl-2,6-bis((triisopropylsilyl)ethynyl)phenyl)thiazole (3ca). Following the general procedure **A** using 2-(4-isopropylphenyl)thiazole (40.5 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (114.8 mg, 0.44 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3ca** (84.4 mg, 75%) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, J = 3.3 Hz, 1H), 7.38 (d, J = 3.3 Hz, 1H), 7.36 (s, 2H), 2.90 (p, J = 6.9 Hz, 1H), 1.27 (d, J = 6.9 Hz, 6H), 0.97 (d, J = 2.2 Hz, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.4, 150.0, 142.8, 136.6, 131.0, 124.7, 120.3, 104.4, 95.5, 33.9, 23.7, 18.7, 11.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{54}NSSi_2$ 564.3510; Found 564.3496.

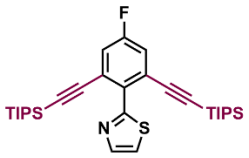


2-(4-(*tert*-Butyl)-2,6-bis((triisopropylsilyl)ethynyl)phenyl)thiazole (3da). Following the general procedure **A** using 2-(4-(*tert*-butyl)phenyl)thiazole (43.3 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (114.8 mg, 0.44 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3da** (90.0 mg, 78%) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, J = 3.3 Hz, 1H), 7.51 (s, 2H), 7.38 (d, J = 3.3 Hz, 1H), 1.35 (s, 9H), 0.97 (d, J = 1.8 Hz, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.4, 152.4, 142.8, 136.4, 129.9, 124.5, 120.3, 104.6, 95.4, 34.8, 31.1, 18.7, 11.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{35}H_{56}NSSi_2$ 578.3666; Found 578.3651.



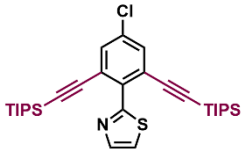
2-(4-Fluoro-2,6-bis((triisopropylsilyl)ethynyl)phenyl)thiazole (3ea). Following the general procedure **A** using 2-(4-fluorophenyl)thiazole (35.7 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (114.8 mg, 0.44 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3ea** (70.1 mg, 65%) as a brown liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, J = 3.3 Hz, 1H), 7.42 (d, J = 3.3 Hz, 1H), 7.22 (d, J = 8.7 Hz, 2H), 0.96 (s, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.4, 162.9, 161.3, 142.9, 135.3, 126.8, 126.7, 120.7, 119.8, 119.6, 102.87, 102.85, 97.9, 18.6, 11.2.

^{19}F NMR (565 MHz, $CDCl_3$) δ -112.00 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{47}FNSSi_2$ 540.2946; Found 540.2933.



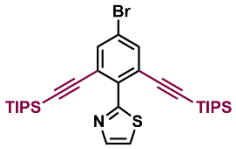
2-(4-Chloro-2,6-bis((triisopropylsilyl)ethynyl)phenyl)thiazole (3fa). Following the general procedure **A** using 2-(4-chlorophenyl)thiazole (38.9 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (114.8 mg, 0.44 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3fa** (78.8 mg, 71%) as a brown solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, J = 3.3 Hz, 1H), 7.49 (s, 2H), 7.42 (d, J = 3.3 Hz, 1H), 0.96 (s, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.1, 143.0, 137.3, 134.9, 132.4, 126.3, 120.7, 102.7, 98.1, 18.6,

11.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{47}ClNSSi_2$ 556.2650; Found 556.2637.

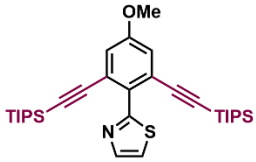


2-(4-Bromo-2,6-bis((triisopropylsilyl)ethynyl)phenyl)thiazole (3ga). Following the general procedure **A** using 2-(4-bromophenyl)thiazole (47.8 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (114.8 mg, 0.44 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3ga** (87.4 mg, 73%) as a yellowish solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, J = 3.2 Hz, 1H), 7.65 (s, 2H), 7.42 (d, J = 3.2 Hz, 1H), 0.96 (s, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.2, 143.0, 137.7, 135.2, 126.4, 122.7, 120.7, 102.5, 98.2, 18.6, 11.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{47}BrNSSi_2$ 600.2145; Found 600.2130.

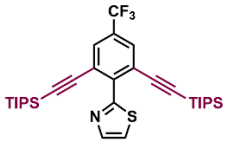


2-(4-Methoxy-2,6-bis((triisopropylsilyl)ethynyl)phenyl)thiazole (3ha). Following the general procedure **A** using 2-(4-methoxyphenyl)thiazole (38.2 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (114.8 mg, 0.44 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3ha** (83.7 mg, 76%) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, J = 3.3 Hz, 1H), 7.38 (d, J = 3.3 Hz, 1H), 7.04 (s, 2H), 3.85 (s, 3H), 0.96 (s, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.2, 159.5, 142.7, 131.7, 125.9, 120.4, 118.4, 104.0, 96.0, 55.8, 18.6, 11.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{50}NOSSi_2$ 552.3146; Found 552.3133.



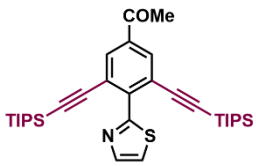
2-(4-(Trifluoromethyl)-2,6-bis((triisopropylsilyl)ethynyl)phenyl)thiazole (3ia). Following the general procedure **A** using 2-(4-(trifluoromethyl)phenyl)thiazole (45.7 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (114.8 mg, 0.44 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3ia** (82.5 mg, 70%) as a brown solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, J = 3.3 Hz, 1H), 7.72 (s, 2H), 7.46 (d, J = 3.3 Hz, 1H), 0.97 (d, J = 1.4 Hz, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.8, 143.2, 141.9, 131.9, 131.6, 129.0 (q, J = 3.4 Hz), 125.9, 124.1, 122.3, 120.9, 102.5, 98.8, 18.6, 11.2.

^{19}F NMR (565 MHz, $CDCl_3$) δ -63.22 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{47}F_3NSSi_2$ 590.2914; Found 590.2900.

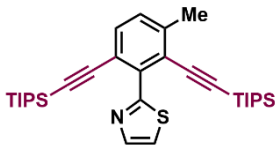


1-(4-(Thiazol-2-yl)-3,5-bis((triisopropylsilyl)ethynyl)phenyl)ethan-1-one (3ja). Following the general procedure **A** using 1-(4-(thiazol-2-yl)phenyl)ethan-1-one (40.5 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (114.8 mg, 0.44 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3ja** (69.8 mg, 62%) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (s, 2H), 7.89 (d, J = 3.3 Hz, 1H), 7.46 (d, J = 3.3 Hz, 1H), 2.65 (s, 3H), 0.97 (s, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.6, 163.2, 143.2, 142.6, 137.4, 132.0, 125.6, 120.8, 103.1, 97.9, 27.0, 18.6, 11.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{33}H_{50}NOSSi_2$ 564.3146; Found 564.3132.

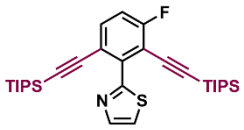


2-(3-Methyl-2,6-bis((triisopropylsilyl)ethynyl)phenyl)thiazole (3ka). Following the general procedure **A** using 2-(*m*-tolyl)thiazole (35.0 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (114.8 mg, 0.44 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3ka** (33.2 mg, 31%) as a yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, J = 3.3 Hz, 1H), 7.48 – 7.37 (m, 2H), 7.24 (d, J = 8.0 Hz, 1H), 2.49 (s, 3H), 0.99 – 0.92 (m, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.8, 142.8, 141.6, 139.1, 132.0, 130.3, 124.8, 122.2, 120.3, 104.2, 102.5, 101.0, 95.2, 21.5, 18.67, 18.65, 11.30, 11.27.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{50}NSSi_2$ 536.3197; Found 536.3192.



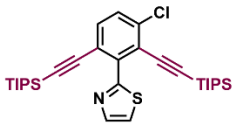
2-(3-Fluoro-2,6-bis((triisopropylsilyl)ethynyl)phenyl)thiazole (3la). Following the general procedure **A** using 2-(3-fluorophenyl)thiazole (35.7 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (114.8 mg, 0.44 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3la** (70.1 mg, 65%) as a brown solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, J = 3.3 Hz, 1H), 7.49 (dd, J = 8.7, 5.3 Hz, 1H), 7.44 (d, J = 3.3 Hz, 1H), 7.11 (t, J = 8.5 Hz, 1H), 0.97 (d, J = 10.1 Hz, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.7, 162.9, 162.0, 143.0, 140.8, 133.9, 133.8, 120.89, 120.87, 120.7, 116.6, 116.5, 114.1, 113.9, 103.1, 102.92, 102.89, 96.6, 95.9, 18.63, 18.59, 11.3, 11.2.

^{19}F NMR (565 MHz, $CDCl_3$) δ -106.22 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{47}FNSSi_2$ 540.2946; Found 540.2932.

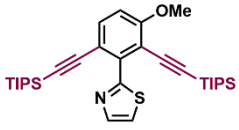


2-(3-Chloro-2,6-bis((triisopropylsilyl)ethynyl)phenyl)thiazole (3ma). Following the general procedure **A** using 2-(3-chlorophenyl)thiazole (38.9 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (114.8 mg, 0.44 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3ma** (76.6 mg, 69%) as a brown liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, J = 3.3 Hz, 1H), 7.49 – 7.39 (m, 3H), 0.97 (d, J = 14.7 Hz, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.6, 143.0, 140.6, 136.9, 132.7, 130.1, 124.8, 123.4, 120.7, 103.4, 103.1, 100.2, 97.4, 18.6, 11.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{47}ClNSSi_2$ 556.2650; Found 556.2635.



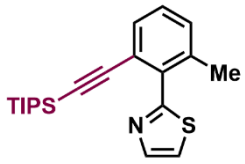
2-(3-Methoxy-2,6-bis((triisopropylsilyl)ethynyl)phenyl)thiazole (3na). Following the general procedure **A** using 2-(3-methoxyphenyl)thiazole (38.2 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (114.8 mg,

0.44 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3na** (84.8 mg, 77%) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, J = 3.3 Hz, 1H), 7.47 (d, J = 8.7 Hz, 1H), 7.39 (d, J = 3.3 Hz, 1H), 6.88 (d, J = 8.7 Hz, 1H), 3.89 (s, 3H), 0.96 (dd, J = 11.4, 3.0 Hz, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.1, 160.8, 142.8, 140.6, 133.7, 120.3, 116.9, 114.6, 111.6, 104.1, 101.2, 99.7, 93.7, 56.4, 18.6, 11.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{50}NOSSi_2$ 552.3146; Found 552.3132.

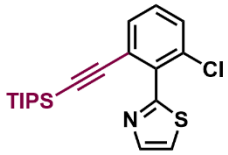


2-(2-Methyl-6-((triisopropylsilyl)ethynyl)phenyl)thiazole (3oa). Following the general procedure **A** using 2-(*o*-tolyl)thiazole (35.0 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (114.8 mg, 0.44 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3oa** (58.9 mg, 83%) as a green liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, J = 3.3 Hz, 1H), 7.44 (d, J = 3.3 Hz, 1H), 7.42 (d, J = 7.6 Hz, 1H), 7.27 (t, J = 7.7 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 2.17 (s, 3H), 0.97 (d, J = 2.5 Hz, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.5, 142.8, 138.3, 136.0, 130.6, 130.2, 129.1, 124.5, 120.3, 104.9, 95.5, 20.3, 18.6, 11.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{30}NSSi$ 356.1862; Found 356.1853.

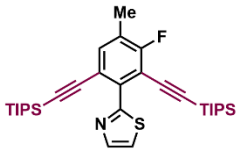


2-(2-Chloro-6-((triisopropylsilyl)ethynyl)phenyl)thiazole (3pa). Following the general procedure **A** using 2-(2-chlorophenyl)thiazole (39.0 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (114.8 mg, 0.44 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3pa** (60.0 mg, 80%) as a yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, J = 3.3 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.43 (dd, J = 8.2, 1.2 Hz, 1H), 7.32 (t, J = 7.9 Hz, 1H), 0.96 (s, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.9, 143.0, 135.4, 134.8, 131.4, 130.3, 129.7, 126.7, 121.0, 103.4, 97.4, 18.6, 11.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{27}ClNSSi$ 376.1316; Found 376.1313.



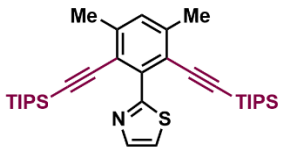
2-(3-Fluoro-4-methyl-2,6-bis((triisopropylsilyl)ethynyl)phenyl)thiazole (3qa). Following the general procedure **A** using 2-(3-fluoro-4-methylphenyl)thiazole (38.6 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (114.8 mg, 0.44 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3qa** (79.6 mg, 72%) as a brown solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, J = 3.3 Hz, 1H), 7.41 (d, J = 3.3 Hz, 1H), 7.38 – 7.30 (m, 1H), 2.29 (d, J = 2.0 Hz, 3H), 1.03 – 0.90 (m, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.12, 163.10, 162.3, 160.6, 142.91, 142.87, 138.2, 135.21, 135.17, 126.6, 126.4, 120.8, 120.6, 120.20, 120.18, 113.5, 113.3, 103.4, 102.2, 102.1, 97.1, 95.2, 19.1, 18.63, 18.59, 11.3, 11.2.

^{19}F NMR (565 MHz, $CDCl_3$) δ -110.15 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{49}FNSSi_2$ 554.3102; Found 554.3091.



2-(3,5-Dimethyl-2,6-bis((triisopropylsilyl)ethynyl)phenyl)thiazole (3ra). Following the general procedure **A** using 2-(3,5-dimethylphenyl)thiazole (37.8 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (114.8 mg, 0.44 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3ra** (69.2 mg, 63%) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, J = 3.3 Hz, 1H), 7.38 (d, J = 3.3 Hz, 1H), 7.17 (s, 1H), 2.46 (s, 6H), 0.96 (d, J = 2.5 Hz, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.3, 142.7, 140.9, 139.3, 131.6, 122.2, 120.2, 102.7, 99.8, 21.4, 18.7, 11.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{33}H_{52}NSSi_2$ 550.3353; Found 550.3344.

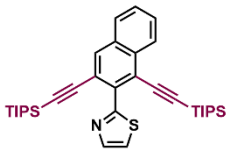
2-(3,5-Difluoro-2,6-bis((triisopropylsilyl)ethynyl)phenyl)thiazole (3sa). Following the general procedure **A** using 2-(3,5-difluorophenyl)thiazole (39.4 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (114.8 mg, 0.44 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3sa** (77.9 mg, 70%) as a brown solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, J = 3.3 Hz, 1H), 7.47 (d, J = 3.3 Hz, 1H), 6.96 (t, J = 8.6 Hz, 1H), 1.01 – 0.87 (m, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.6, 163.5, 161.9, 161.8, 161.7, 143.2, 121.0, 110.51, 110.46, 110.40, 110.36, 105.5, 105.3, 105.1, 102.4, 95.8, 18.6, 11.2.

^{19}F NMR (565 MHz, $CDCl_3$) δ -102.25 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{46}F_2NSSi_2$ 558.2779; Found 558.2786.

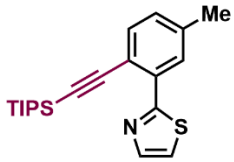


2-(1,3-Bis((triisopropylsilyl)ethynyl)naphthalen-2-yl)thiazole (3ta). Following the general procedure **A** using 2-(naphthalen-2-yl)thiazole (42.2 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (114.8 mg, 0.44 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3ta** (73.1 mg, 64%) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (d, J = 8.3 Hz, 1H), 8.06 (s, 1H), 7.91 (d, J = 3.3 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.59 – 7.54 (m, 1H), 7.45 (d, J = 3.3 Hz, 1H), 1.03 (d, J = 2.5 Hz, 21H), 1.00 (d, J = 2.4 Hz, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.8, 142.9, 136.8, 133.0, 132.93, 132.89, 128.3, 128.0, 127.9, 127.0, 123.0, 121.5, 120.5, 104.3, 102.5, 101.9, 95.7, 18.8, 18.7, 11.4, 11.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{35}H_{50}NSSi_2$ 572.3197; Found 572.3182.



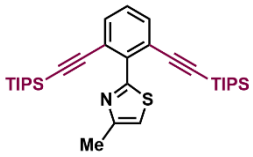
2-(5-Methyl-2-((triisopropylsilyl)ethynyl)phenyl)thiazole ($3ka_1$). Following the general procedure **A** using 2-(*m*-tolyl)thiazole (35.0 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (114.8 mg, 0.44 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **$3ka_1$** (39.1 mg, 55%) as a yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.90 (d, J = 3.2 Hz, 1H), 7.52 (d, J = 7.9 Hz, 1H), 7.41 (d, J = 3.2 Hz, 1H), 7.16 (dd, J = 8.1, 1.8 Hz, 1H), 2.41 (s, 3H), 1.20 – 1.12 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.6, 142.3, 139.1, 135.1, 134.8, 130.0, 128.9, 120.0, 118.3,

106.1, 99.3, 21.5, 18.9, 11.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{30}NSSi$ 356.1862; Found 356.1853.

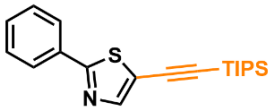


2-(2,6-Bis((triisopropylsilyl)ethynyl)phenyl)-4-methylthiazole (3ua). Following the general procedure **A** using 4-methyl-2-phenylthiazole (35.0 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (114.8 mg, 0.44 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3ua** (53.5 mg, 50%) as a yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, J = 7.8 Hz, 2H), 7.30 (t, J = 7.8 Hz, 1H), 6.95 (s, 1H), 2.46 (s, 3H), 0.97 (d, J = 1.6 Hz, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.7, 152.7, 139.4, 132.5, 128.9, 124.9, 115.0, 104.0, 96.1, 18.9, 18.6, 11.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{50}NSSi_2$ 536.3197; Found 536.3193.

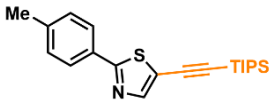


2-Phenyl-5-((triisopropylsilyl)ethynyl)thiazole (4aa). Following the general procedure **B** using 2-phenylthiazole (32.2 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (78.3 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4aa** (54.5 mg, 80%) as a yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 – 7.83 (m, 3H), 7.51 – 7.40 (m, 3H), 1.18 – 1.11 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.3, 148.2, 133.3, 130.6, 129.2, 126.7, 119.1, 100.3, 95.8, 18.8, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{28}NSSi$ 342.1706; Found 342.1697.

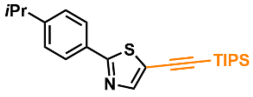


2-(*p*-Tolyl)-5-((triisopropylsilyl)ethynyl)thiazole (4ba). Following the general procedure **B** using 2-(*p*-tolyl)thiazole (35.0 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (78.3 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ba** (54.7 mg, 77%) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.80 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H), 1.17 – 1.11 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.5, 148.1, 141.0, 130.7, 129.9, 126.6, 118.6, 100.0, 95.9, 21.6, 18.8, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{30}NSSi$ 356.1862; Found 356.1853.

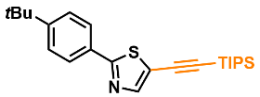


2-(4-Isopropylphenyl)-5-((triisopropylsilyl)ethynyl)thiazole (4ca). Following the general procedure **B** using 2-(4-isopropylphenyl)thiazole (40.7 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (78.3 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ca** (50.5 mg, 66%) as a yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.84 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 2.95 (hept, J = 6.9 Hz, 1H), 1.28 (d, J = 6.9 Hz, 6H), 1.18 – 1.10 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.5, 151.9, 148.1, 131.1, 127.3, 126.8, 118.6, 100.0, 96.0, 34.3, 23.9, 18.8, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{34}NSSi$ 384.2175; Found 384.2171.

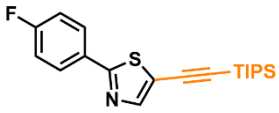


2-(4-(*tert*-Butyl)phenyl)-5-((triisopropylsilyl)ethynyl)thiazole (4da). Following the general procedure **B** using 2-(4-(tert-butyl)phenyl)thiazole (43.5 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (78.3 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4da** (50.8 mg, 64%) as a yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 1.35 (s, 9H), 1.18 – 1.10 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.4, 154.1, 148.2, 130.7, 126.5, 126.2, 118.6, 100.0, 96.0, 35.1, 31.3, 18.8, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{36}NSSi$ 398.2332; Found 398.2321.



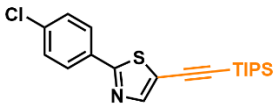
2-(4-Fluorophenyl)-5-((triisopropylsilyl)ethynyl)thiazole (4ea). Following the general procedure **B** using 2-(4-fluorophenyl)thiazole (35.8 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (78.3 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ea** (50.9 mg, 71%) as a yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 – 7.88 (m, 2H), 7.88 (s, 1H), 7.13 (t, J = 8.6 Hz, 2H), 1.20 – 1.08 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.0, 165.1, 163.4, 148.1, 129.72, 129.70, 128.7, 128.6, 119.2, 116.4, 116.2, 100.5, 95.6, 18.8, 11.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -109.58 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{27}FNSSi$ 360.1539; Found 360.1545.

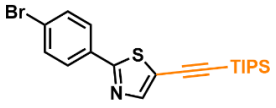


2-(4-Chlorophenyl)-5-((triisopropylsilyl)ethynyl)thiazole (4fa). Following the general procedure **B** using 2-(4-chlorophenyl)thiazole (39.1 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (78.3 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4fa** (54.0 mg, 72%) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.84 (d, J = 8.6 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 1.17 – 1.11 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 148.2, 136.6, 131.8, 129.4, 127.9, 119.5, 100.8, 95.5, 18.8, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{27}ClNSSi$ 376.1243; Found 376.1250.

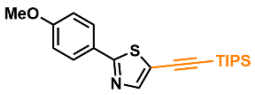


2-(4-Bromophenyl)-5-((triisopropylsilyl)ethynyl)thiazole (4ga). Following the general procedure **B** using 2-(4-bromophenyl)thiazole (48.0 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (78.3 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ga** (52.8 mg, 63%) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.78 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 1.16 – 1.11 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 148.3, 132.4, 132.2, 128.1, 124.9, 119.6, 100.8, 95.5, 18.8, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{27}BrNSSi$ 420.0811; Found 420.0798.

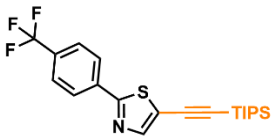


2-(4-Methoxyphenyl)-5-((triisopropylsilyl)ethynyl)thiazole (4ha). Following the general procedure **B** using 2-(4-methoxyphenyl)thiazole (38.2 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (78.3 mg, 0.3 mmol), thle residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ha** (55.6 mg, 75%) as an orange solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 – 7.68 (m, 3H), 6.95 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H), 1.19 – 1.07 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.3, 161.6, 148.0, 128.3, 126.3, 118.1, 114.5, 99.8, 96.0, 55.6, 18.8, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{30}NOSSi$ 372.1811; Found 372.1801.



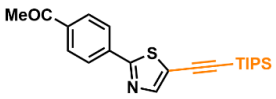
2-(4-(Trifluoromethyl)phenyl)-5-((triisopropylsilyl)ethynyl)thiazole (4ia). Following the general procedure **B** using 2-(4-(trifluoromethyl)phenyl)thiazole (45.8 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (78.3 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ia** (57.3 mg, 70%) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, J = 8.2 Hz, 2H), 7.95 (s, 1H), 7.70 (d, J = 8.2 Hz, 2H), 1.20 – 1.08 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.1, 148.4, 136.4, 132.20, 131.99, 126.9, 126.2 (q, J = 3.9 Hz), 120.4, 101.4, 95.3, 18.8, 11.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.88 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{27}F3NSSi$ 410.1507; Found 410.1512.

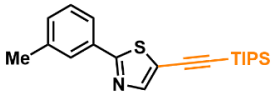


1-(4-(5-((Triisopropylsilyl)ethynyl)thiazol-2-yl)phenyl)ethan-1-one (4ja). Following the general procedure **B** using 1-(4-(thiazol-2-yl)phenyl)ethan-1-one (40.6 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (78.3 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ja** (49.8 mg, 65%) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.98 (m, 4H), 7.95 (s, 1H), 2.63 (s, 3H), 1.17 – 1.10 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.3, 166.5, 148.5, 138.2, 137.1, 129.2, 126.8, 120.5, 101.4, 95.4, 26.9, 18.8, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{30}NOSSi$ 384.1739; Found 384.1744.

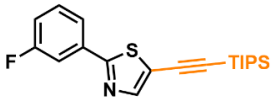


2-(*m*-Tolyl)-5-((triisopropylsilyl)ethynyl)thiazole (4ka). Following the general procedure **B** using 2-(*m*-tolyl)thiazole (35.0 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (78.3 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ka** (41.2 mg, 58%) as a yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.76 (s, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.32 (t, J = 7.7 Hz, 1H), 7.25 (d, J = 7.6 Hz, 1H), 2.41 (s, 3H), 1.14 (d, J = 4.1 Hz, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.5, 148.1, 139.0, 133.2, 131.4, 129.1, 127.3, 124.0, 118.9, 100.2, 95.8, 21.5, 18.8, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{30}NSSi$ 356.1862; Found 356.1852.



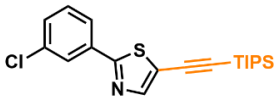
2-(3-Fluorophenyl)-5-((triisopropylsilyl)ethynyl)thiazole (4la). Following the general procedure **B** using 2-(3-fluorophenyl)thiazole (35.8 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (78.3 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4la** (40.2 mg, 56%) as a light yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.76 – 7.58 (m, 2H), 7.50 – 7.33 (m, 1H), 7.19 – 7.06 (m, 1H), 1.19 – 1.08 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 164.0, 162.4, 148.2, 135.34, 135.29, 130.82, 130.77, 122.44, 122.42, 119.8, 117.5, 117.4, 113.7, 113.5, 100.9, 95.5, 18.8, 11.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -111.94 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{27}FNSSi$ 360.1612; Found 360.1601.

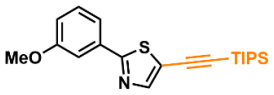


2-(3-Chlorophenyl)-5-((triisopropylsilyl)ethynyl)thiazole (4ma). Following the general procedure **B** using 2-(3-chlorophenyl)thiazole (39.1 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (78.3 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ma** (57.0 mg, 76%) as a yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.91 (s, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.40 (dt, J = 8.1, 1.6 Hz, 1H), 7.36 (t, J = 7.8 Hz, 1H), 1.21 – 1.09 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.3, 148.2, 135.3, 134.9, 130.45, 130.40, 126.7, 124.8, 119.9, 101.0, 95.5, 18.8, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{27}ClNSSi$ 376.1243; Found 376.1250.

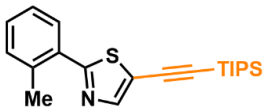


2-(3-Methoxyphenyl)-5-((triisopropylsilyl)ethynyl)thiazole (4na). Following the general procedure **B** using 2-(3-methoxyphenyl)thiazole (38.2 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (78.3 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4na** (51.9 mg, 70%) as a yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.71 (d, J = 7.7 Hz, 1H), 7.34 (td, J = 7.4, 1.4 Hz, 1H), 7.31 – 7.26 (m, 2H), 2.59 (s, 3H), 1.17 – 1.11 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.0, 147.5, 136.8, 132.6, 131.7, 130.1, 129.9, 126.3, 119.7, 100.1, 95.7, 21.6, 18.8, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{30}NOSSi$ 372.1811; Found 372.1801.



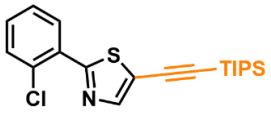
2-(*o*-Tolyl)-5-((triisopropylsilyl)ethynyl)thiazole (4oa). Following the general procedure **B** using 2-(*o*-tolyl)thiazole (35.1 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (78.3 mg, 0.3 mmol), the residue

was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4oa** (55.4 mg, 78%) as a yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.52 – 7.48 (m, 1H), 7.48 – 7.43 (m, 1H), 7.34 (t, J = 7.9 Hz, 1H), 7.01 – 6.94 (m, 1H), 3.87 (s, 3H), 1.20 – 1.08 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.1, 160.2, 148.1, 134.6, 130.2, 119.3, 119.2, 117.0, 111.2, 100.4, 95.7, 55.6, 18.8, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{30}NSSi$ 356.1862; Found 356.1852.

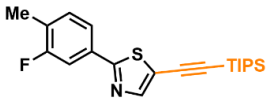


2-(2-Chlorophenyl)-5-((triisopropylsilyl)ethynyl)thiazole (4pa). Following the general procedure **B** using 2-(2-chlorophenyl)thiazole (39.1 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (78.3 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4pa** (53.2 mg, 71%) as a yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 – 8.20 (m, 1H), 7.99 (s, 1H), 7.49 (dd, J = 7.7, 1.6 Hz, 1H), 7.42 – 7.30 (m, 2H), 1.20 – 1.10 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.2, 146.8, 131.9, 131.7, 131.0, 130.9, 130.7, 127.3, 120.9, 100.8, 95.5, 18.8, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{27}ClNSSi$ 376.1316; Found 376.1307.



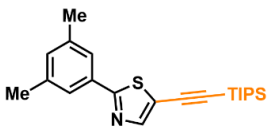
2-(3-Fluoro-4-methylphenyl)-5-((triisopropylsilyl)ethynyl)thiazole (4qa). Following the general procedure **B** using 2-(3-fluoro-4-methylphenyl)thiazole (38.6 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (78.3 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4qa** (38.0 mg, 51%) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.63 – 7.53 (m, 2H), 7.24 (t, J = 7.8 Hz, 1H), 2.31 (d, J = 1.8 Hz, 3H), 1.17 – 1.09 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9, 162.4, 160.8, 148.1, 132.9, 132.8, 132.2, 132.1, 127.8, 127.7, 122.14, 122.11, 119.3, 113.2, 113.1, 100.6, 95.6, 18.8, 14.81, 14.78, 11.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -116.28 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{29}FNSSi$ 374.1768; Found 374.1758.

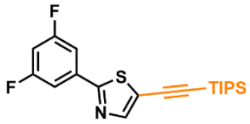


2-(3,5-Dimethylphenyl)-5-((triisopropylsilyl)ethynyl)thiazole (4ra). Following the general procedure **B** using 2-(3,5-dimethylphenyl)thiazole (37.8 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (78.3 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ra** (29.5 mg, 40%) as a light yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.53 (s, 2H), 7.07 (s, 1H), 2.37 (s, 6H), 1.21 – 1.05 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.8, 148.0, 138.9, 133.1, 132.4, 124.6, 118.8, 100.1, 95.9, 21.4, 18.8, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{32}NSSi$ 370.2019; Found 370.2009.



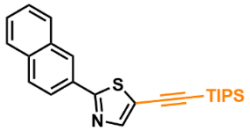
2-(3,5-Difluorophenyl)-5-((triisopropylsilyl)ethynyl)thiazole (4sa). Following the general procedure **B** using 2-(3,5-difluorophenyl)thiazole (39.4 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (78.3 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4sa** (33.2 mg, 44%) as a yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.58 – 7.32 (m, 2H), 6.88 (t, J = 8.6 Hz, 1H), 1.13 (d, J = 5.0 Hz, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.1, 164.3, 164.2, 162.64, 162.56, 148.3, 136.1, 120.5, 109.74, 109.70, 109.59, 109.55, 105.9, 105.7, 105.5, 101.6, 95.2, 18.8, 11.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -108.33 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{26}F_2NSSi$ 378.1445; Found 378.1449.

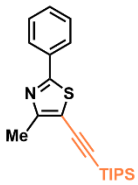


2-(Naphthalen-2-yl)-5-((triisopropylsilyl)ethynyl)thiazole (4ta). Following the general procedure **B** using 2-(naphthalen-2-yl)thiazole (42.3 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (78.3 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ta** (53.2 mg, 68%) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.01 (dd, J = 8.5, 1.8 Hz, 1H), 7.96 (s, 1H), 7.93 – 7.88 (m, 2H), 7.87 – 7.83 (m, 1H), 7.56 – 7.49 (m, 2H), 1.19 – 1.11 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.3, 148.3, 134.4, 133.3, 130.7, 129.0, 128.8, 128.0, 127.4, 127.1, 126.4, 123.9, 119.2, 100.5, 95.8, 18.8, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{30}NSSi$ 392.1789; Found 392.1797.



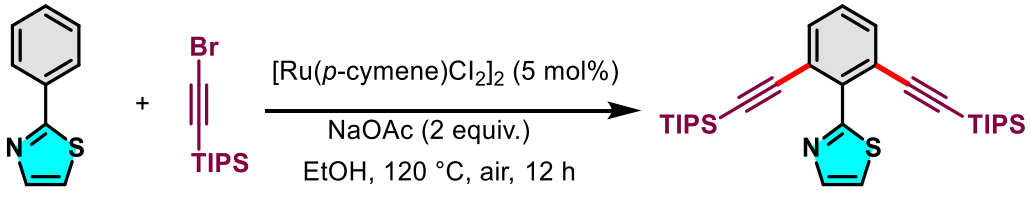
4-Methyl-2-phenyl-5-((triisopropylsilyl)ethynyl)thiazole (4ua). Following the general procedure **B** using 4-methyl-2-phenylthiazole (35.0 mg, 0.2 mmol) and (bromoethynyl)triisopropylsilane (78.3 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ua** (51.8 mg, 73%) as a yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 – 7.71 (m, 2H), 7.53 – 7.32 (m, 3H), 2.56 (s, 3H), 1.14 (d, J = 3.4 Hz, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 159.1, 133.4, 130.4, 129.1, 126.6, 113.9, 101.0, 96.8, 18.8, 16.6, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{30}NSSi$ 356.1862; Found 356.1853.

3.4 Ru(II)-catalyzed *ortho*-alkynylation: reaction on 3 mmol scale

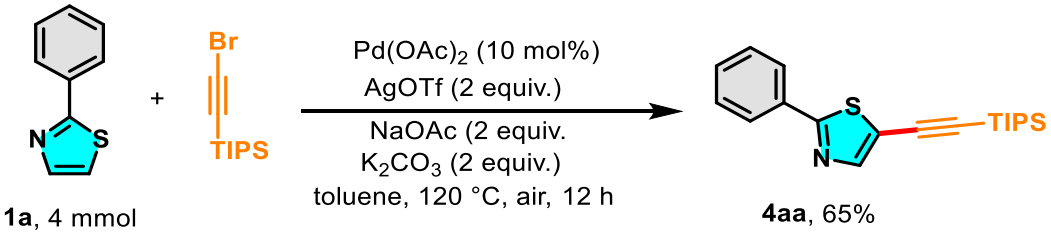


1a, 3 mmol **3aa**, 61%

To a 100 mL oven dried Schlenk tube, 2-phenylthiazole (483.6 mg, 3 mmol, 1 equiv.), [Ru(*p*-

cymene)$Cl_2]_2$ (91.8 mg, 0.15 mmol, 5 mol%), NaOAc (492.2 mg, 6 mmol, 2 equiv.), (bromoethynyl)triisopropylsilane (1.72 g, 6.6 mmol, 2.2 equiv.) and EtOH (30 mL) were successively added. The reaction mixture was stirred at 120 °C (metal sand bath temperature) for 12 hours under the air. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography (petroleum ether/ethyl acetate = 30:1) to afford the desired alkynylated product **3aa** (0.95 g, 61%).

3.5 Pd(II)-catalyzed C5-alkynylation: reaction on 4 mmol scale

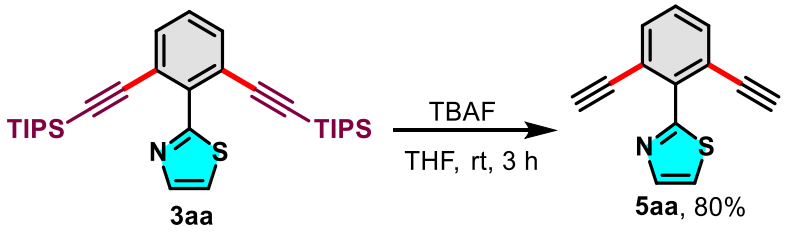


1a, 4 mmol

4aa, 65%

To a 100 mL oven dried Schlenk tube, K_2CO_3 (1.1 g, 8 mmol, 2 equiv.), 2-phenylthiazole (644.9 mg, 4 mmol, 1 equiv.), $Pd(OAc)_2$ (90.6 mg, 0.4 mmol, 10 mol%), AgOTf (2.0 g, 8 mmol, 2 equiv.), NaOAc (656.2 mg, 8 mmol, 2 equiv.), (bromoethynyl)triisopropylsilane (1.56 g, 6 mmol, 1.5 equiv.) and toluene (30 mL) were successively added. The reaction mixture was stirred at 120 °C (metal sand bath temperature) for 12 hours under the air. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography (petroleum ether/ethyl acetate = 30:1) to afford the desired alkynylated product **4aa** (0.89 g, 65%).

3.6 Preparation and characterization of products 5aa, 6aa, 7aa, 8aa, 9aa, 10aa



3aa

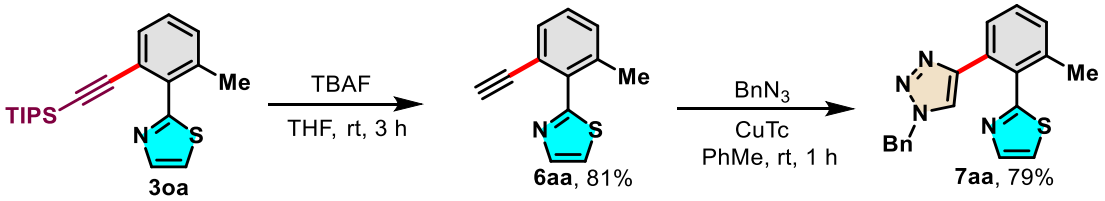
5aa, 80%

2-(2,6-Diethynylphenyl)thiazole (5aa). To a 15 mL oven dried Schlenk tube, **3aa** (104.4 mg, 0.2 mmol), TBAF (1 M in THF, 0.4 ml), and THF (1 ml) were successively added. The reaction mixture was stirred at room temperature for 3 hours under argon. After concentration of reaction mixture, the crude mixture was purified by silica column chromatography (petroleum ether/ethyl acetate = 30:1) to afford the desired product **5aa** (33.4 mg, 80%) as a black solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, J = 3.3 Hz, 1H), 7.60 (d, J = 7.8 Hz, 2H), 7.53 (d, J = 3.3 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 3.07 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.3, 143.0, 139.0, 133.7, 129.2, 123.4, 121.0, 82.3, 81.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_8NS$ 210.0365; Found 210.0372.



2-(2-Ethynyl-6-methylphenyl)thiazole (6aa). To a 15 mL oven dried Schlenk tube, **3oa** (71.1 mg, 0.2 mmol), TBAF (1 M in THF, 0.4 ml), and THF (1 ml) were successively added. The reaction mixture was stirred at room temperature for 3 hours under argon. After concentration of reaction mixture, the crude mixture was purified by silica column chromatography (petroleum ether/ethyl acetate = 30:1) to afford the desired product **6aa** (32.2 mg, 81%) as a green liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, J = 3.3 Hz, 1H), 7.49 (d, J = 3.3 Hz, 1H), 7.44 (dd, J = 7.3, 1.7 Hz, 1H), 7.32 – 7.26 (m, 2H), 2.99 (s, 1H), 2.20 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.1, 142.9, 138.4, 136.3, 130.9, 130.8, 129.2, 123.0, 120.6, 81.9, 81.4, 20.4.

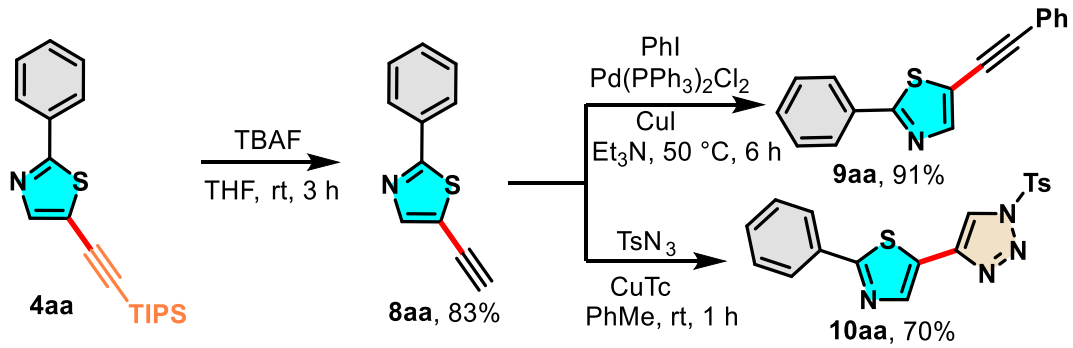
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{10}NS$ 200.0528; Found 200.0524.

2-(2-(1-Benzyl-1H-1,2,3-triazol-4-yl)-6-methylphenyl)thiazole (7aa). To a 15 mL oven dried Schlenk tube, **6aa** (39.8 mg, 0.2 mmol), BnN_3 (79.9 mg, 0.6 mmol, 2 equiv.), CuTc (19.2 mg, 0.1 mmol, 50 mol%), and toluene (1.5 ml) were successively added. The reaction mixture was stirred at room temperature for 1 hour under the air. After concentration of reaction mixture, the crude mixture was purified by silica column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the desired product **7aa** (52.4 mg, 79%) as a Yellowish solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 3.4 Hz, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.33 (dd, J = 5.1, 2.0 Hz, 3H), 7.31 (d, J = 3.3 Hz, 1H), 7.28 (d, J = 7.6 Hz, 1H), 7.13 – 7.03 (m, 2H), 6.37 (s, 1H), 5.36 (s, 2H), 2.15 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 146.2, 142.6, 138.4, 134.6, 131.5, 131.3, 130.0, 129.9, 129.1, 128.7, 128.1, 126.2, 121.8, 121.4, 54.0, 20.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{17}N_4S$ 333.1168; Found 333.1163.



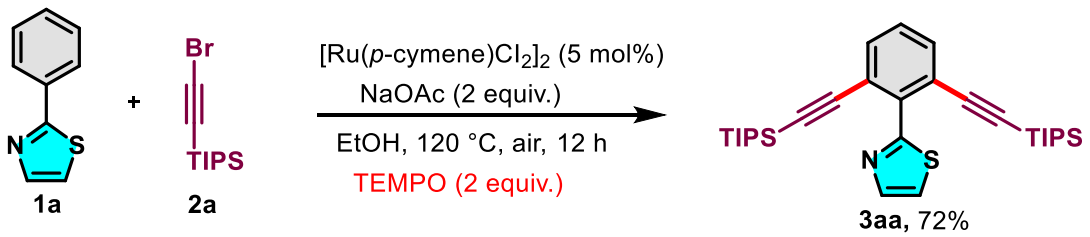
5-Ethynyl-2-phenylthiazole (8aa). To a 15 mL oven dried Schlenk tube, **4aa** (68 mg, 0.2 mmol), TBAF (1 M in THF, 0.4 ml), and THF (1 ml) were successively added. The reaction mixture was stirred at room temperature for 3 hours under argon. After concentration of reaction mixture, the crude mixture was purified by silica column chromatography (petroleum ether/ethyl

acetate = 30:1) to afford the desired product **8aa** (30.7 mg, 83%) as a yellow solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.94 – 7.90 (m, 2H), 7.47 – 7.41 (m, 3H), 3.51 (s, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 148.9, 133.1, 130.8, 129.2, 126.8, 117.6, 85.1, 73.8.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_8NS$ 186.0371; Found 186.0366.

2-Phenyl-5-(phenylethynyl)thiazole (9aa). To a 15 mL oven dried Schlenk tube, **8aa** (37 mg, 0.2 mmol), PhI (81.6 mg, 0.4 mmol, 2 equiv.), $Pd(PPh_3)_2Cl_2$ (7.0 mg, 0.01 mmol, 5 mol%), CuI (0.95 mg, 0.005 mmol, 2.5mol%), and Et_3N (1.5 ml) were successively added. The reaction mixture was stirred at 50 °C for 6 hour under argon. After concentration of reaction mixture, the crude mixture was purified by silica column chromatography (petroleum ether/ethyl acetate = 30:1) to afford the desired product **9aa** (47.5 mg, 91%) as a yellow solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.97 – 7.93 (m, 2H), 7.57 – 7.52 (m, 2H), 7.45 (dd, J = 5.1, 2.0 Hz, 3H), 7.40 – 7.34 (m, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 168.6, 147.6, 133.3, 131.6, 130.6, 129.2, 129.0, 128.6, 126.7, 122.5, 118.9, 96.8, 79.4.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{12}NS$ 262.0684; Found 262.0681.

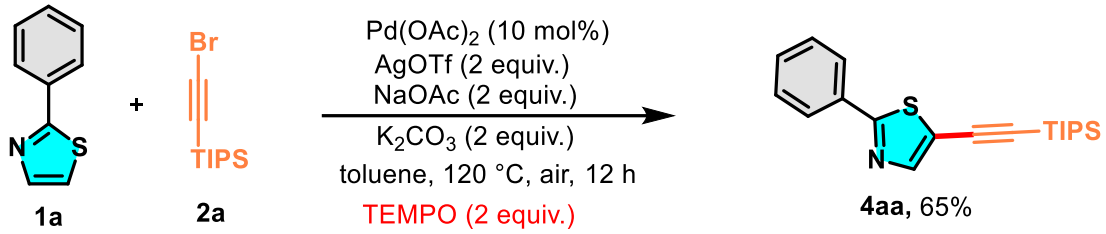
2-Phenyl-5-(1-tosyl-1H-1,2,3-triazol-4-yl)thiazole (10aa). To a 15 mL oven dried Schlenk tube, **8aa** (37 mg, 0.2 mmol), TsN_3 (118.3 mg, 0.6 mmol, 3 equiv.), CuTc (19.2 mg, 0.1 mmol, 50 mol%), and toluene (1.5 ml) were successively added. The reaction mixture was stirred at room temperature for 1 hour under the air. After concentration of reaction mixture, the crude mixture was purified by silica column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the desired product **10aa** (53.5 mg, 70%) as a white solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.14 (s, 1H), 8.04 (d, J = 8.5 Hz, 2H), 7.99 – 7.89 (m, 2H), 7.45 (dd, J = 5.2, 2.0 Hz, 3H), 7.41 (d, J = 8.2 Hz, 2H), 2.46 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 168.9, 147.9, 141.6, 139.7, 133.2, 132.8, 130.72, 130.69, 129.2, 129.0, 126.7, 126.2, 119.3, 22.0.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{15}N_4O_2S_2$ 383.0630; Found 383.0620.

3.7 TEMPO-trapping experiment



To a 15 mL oven dried Schlenk tube, 2-phenylthiazole (0.2 mmol, 1 equiv.), $[Ru(p\text{-cymene})Cl_2]_2$ (6.1 mg, 0.01 mmol, 5 mol%), NaOAc (0.4 mmol, 2 equiv.), (bromoethynyl)triisopropylsilane (0.44 mmol, 2.2 equiv.), TEMPO (0.4 mmol, 2 equiv.) and EtOH (1.5 mL) were successively added. The reaction mixture was stirred at 120 °C (metal sand bath temperature) for 12 hours under the air. After cooling the reaction at room temperature and concentration, the crude

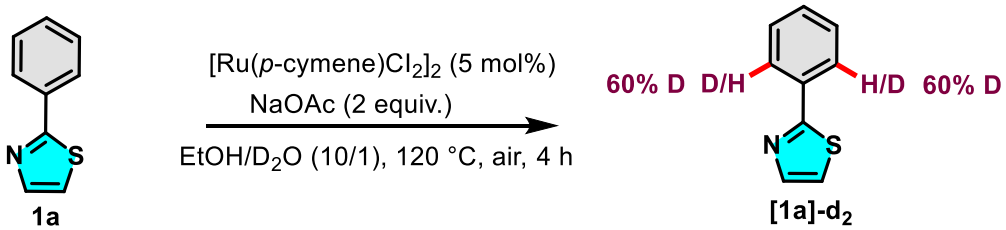
mixture was purified by silica column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the desired alkynylated product **3aa** (72%, 75.0 mg). This observation suggests the non-involvement of any radical pathway.



1a **2a** **4aa**, 65%

To a 15 mL oven dried Schlenk tube, K_2CO_3 (0.4 mmol, 2 equiv.), 2-phenylthiazole (0.2 mmol, 1 equiv.), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), NaOAc (0.4 mmol, 2 equiv.), AgOTf (0.4 mmol, 2 equiv.), (bromoethynyl)triisopropylsilane (0.3 mmol, 1.5 equiv.), TEMPO (0.4 mmol, 2 equiv.) and toluene (1.5 mL) were successively added. The reaction mixture was stirred at 120 °C (metal sand bath temperature) for 12 hours under the air. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the desired alkynylated product **4aa** (65%, 44.3 mg). This observation suggests the non-involvement of any radical pathway.

3.8 H/D exchange experiment



1a **[1a]-d_2**

2-Phenylthiazole **1a** (48.3 mg, 0.3 mmol, 1 equiv.), $[Ru(p\text{-cymene})Cl_2]_2$ (9.2 mg, 0.015 mmol, 5 mol%), NaOAc (49.2 mg, 0.6 mmol, 2 equiv.), D_2O (0.2 mL) and EtOH (2 mL) were charged into a Schlenk tube. The mixture was then stirred at 120 °C under the air for 4 h. Then, the reaction mixture was cooled to room temperature and filtered through a plug of celite. The organic phase was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 15:1) to afford **[1a]-d_2** as light yellow liquid in 82% isolated yield. Upon analyzing the ^1H NMR spectra as shown in **Figure S1**, the estimated deuterium incorporation at the *ortho*-position of the 2-phenyl ring was 60%.

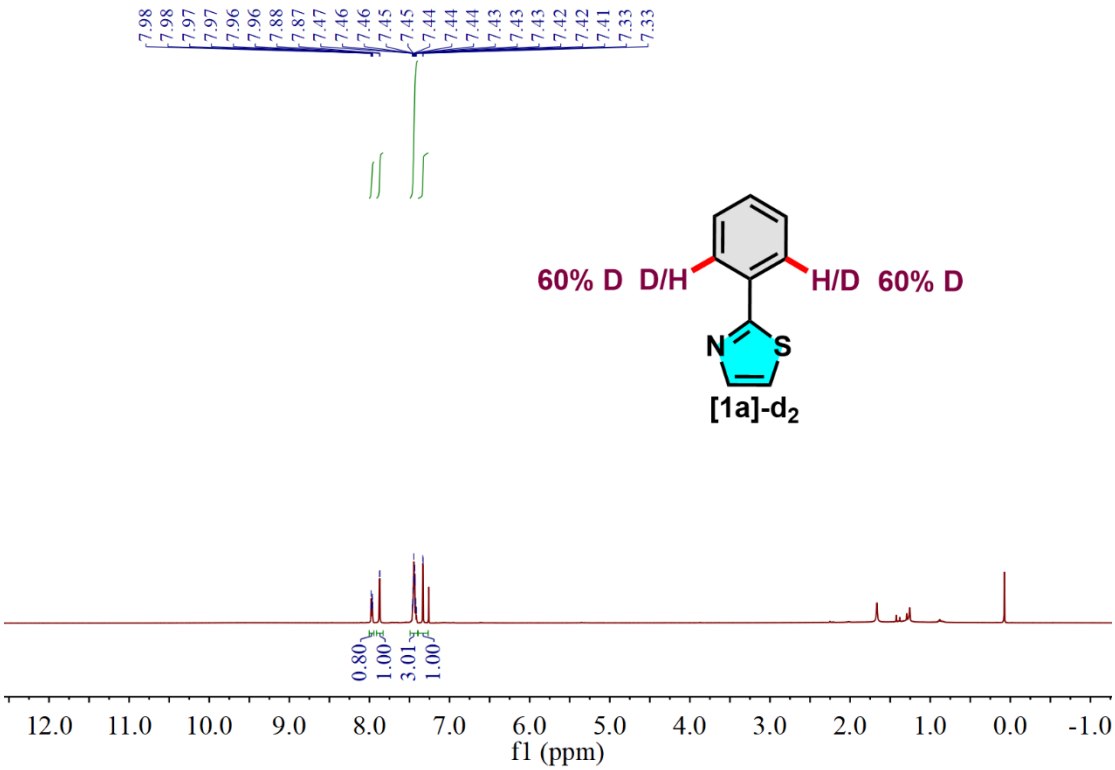
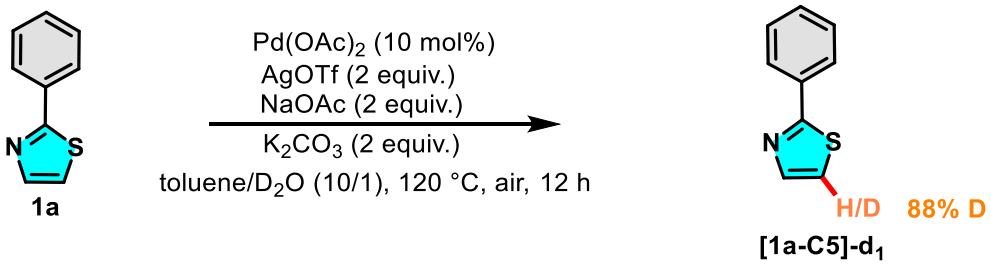


Figure S1. The ^{1}H NMR spectra of [**1a**]-d_2



2-Phenylthiazole **1a** (48.3 mg, 0.3 mmol, 1 equiv.), K_2CO_3 (82.9 mg, 0.6 mmol, 2 equiv.), $Pd(OAc)_2$ (6.8 mg, 0.03 mmol, 10 mol%), AgOTf (0.6 mmol, 2 equiv.), NaOAc (0.6 mmol, 2 equiv.), D_2O (0.2 mL) and toluene (2 mL) were charged into a Schlenk tube. The reaction mixture was stirred at 120 °C (metal sand bath temperature) for 12 hours under the air. The organic phase was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 15:1) to afford **[1a-C5]-d_1** as light yellow liquid in 78% isolated yield. Upon analyzing the ^{1}H NMR spectra as shown in **Figure S2**, the estimated deuterium incorporation at the C5-position of the thiazole ring was 88%.

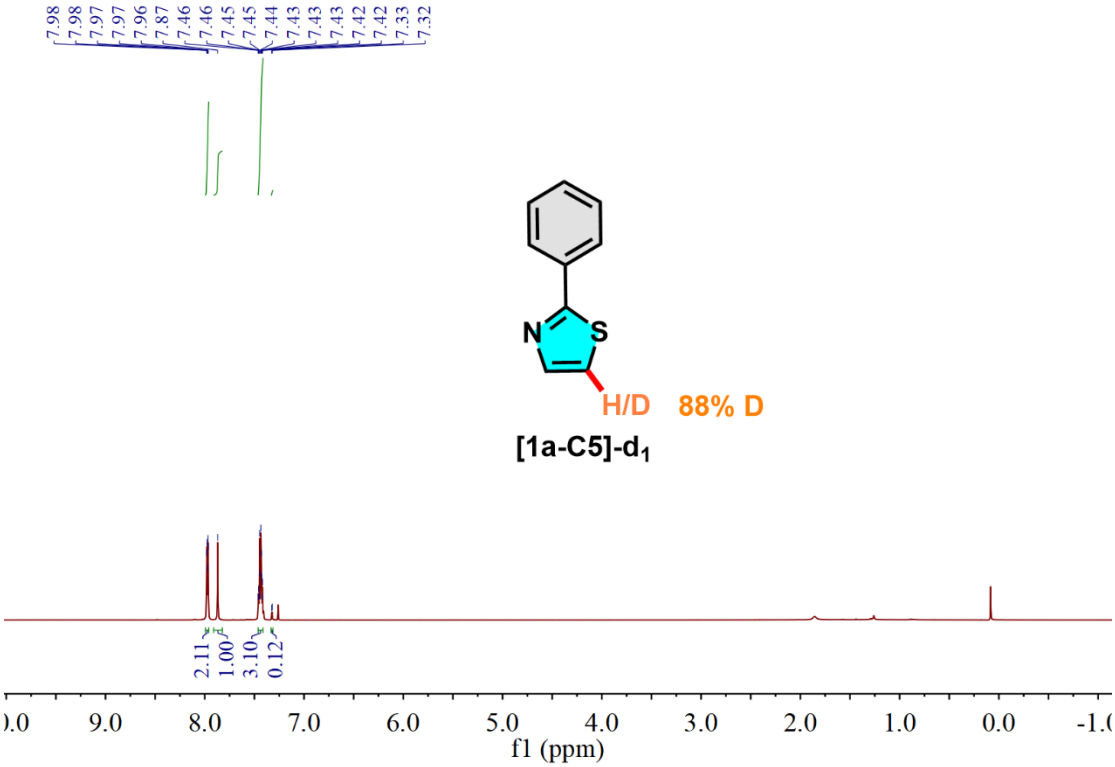
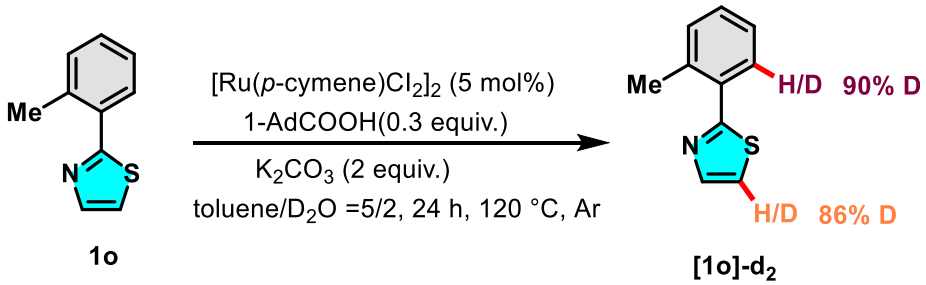


Figure S2. The ^{1}H NMR spectra of **[1a-C5]-d$_1$**

3.9 KIE determination



Synthesis of [1o]-d$_2$[2]: To a 15 mL oven dried Schlenk tube, 2-(*o*-tolyl)thiazole (52.5 mg, 0.3 mmol, 1 equiv.), K_2CO_3 (82.9mg, 0.6 mmol, 2 equiv.), [Ru(*p*-cymene)Cl_2]$_2$ (9.2 mg, 0.015 mmol, 5 mol%), 1-AdCOOH (16.2 mg, 0.09 mmol, 0.3 equiv.), D_2O (0.4 mL) and toluene (1 mL) were successively added. The reaction mixture was stirred at 120 °C (metal sand bath temperature) for 24 hours under argon. Then, the reaction mixture was cooled to room temperature and filtered through a plug of celite. The organic phase was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 15:1) to afford **[1o]-d$_2$** as white liquid in 85% isolated yield. Upon analyzing the ^{1}H NMR spectra

as shown in **Figure S3**, the estimated deuterium incorporation at the *ortho*-position of the 2-(*o*-tolyl) ring was 90% and at the C5-position of the thiazole ring was 86%.

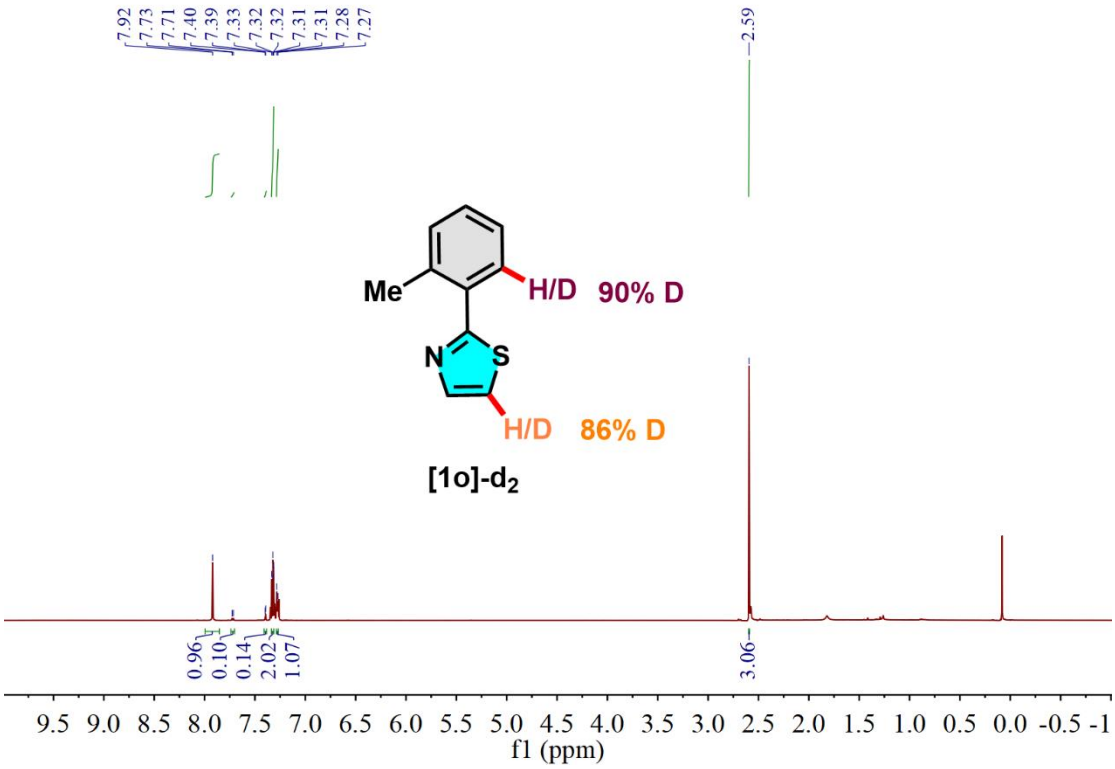
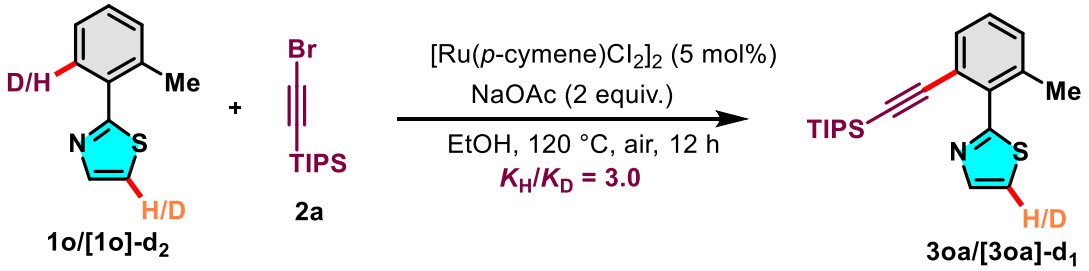


Figure S3. The ^{1}H NMR spectra of **[1o]-d$_2$**



To a 15 mL oven dried Schlenk tube, **1o** (26.3 mg, 0.15 mmol, 1 equiv.), **[1o]-d$_2$** (26.4 mg, 0.15 mmol, 1 equiv.), [Ru(*p*-cymene)Cl$_2$]$_2$ (4.5 mg, 0.0075 mmol, 5 mol%), NaOAc (24.6 mg, 0.3 mmol, 2 equiv.), (bromoethynyl)triisopropylsilane **2a** (58.7 mg, 0.225 mmol, 1.5 equiv.) and EtOH (1.5 mL) were successively added. The mixture was then stirred at 120 °C under the air for 12 h. Then, the reaction mixture was cooled to room temperature and filtered through a plug of celite. The organic phase was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1) to afford the mixture of products **3oa** and **[3oa]-d$_1$** as light yellow liquid. By analyzing the 1H NMR of the mixture **3oa** and **[3oa]-d$_1$** as shown in **Figure S4**, the ratio of **3oa** and **[3oa]-d$_1$** was determined

to be 0.75:0.25. Accordingly, the intermolecular KIE (k_H/k_D)= 0.75/1-0.75 = 3.0.

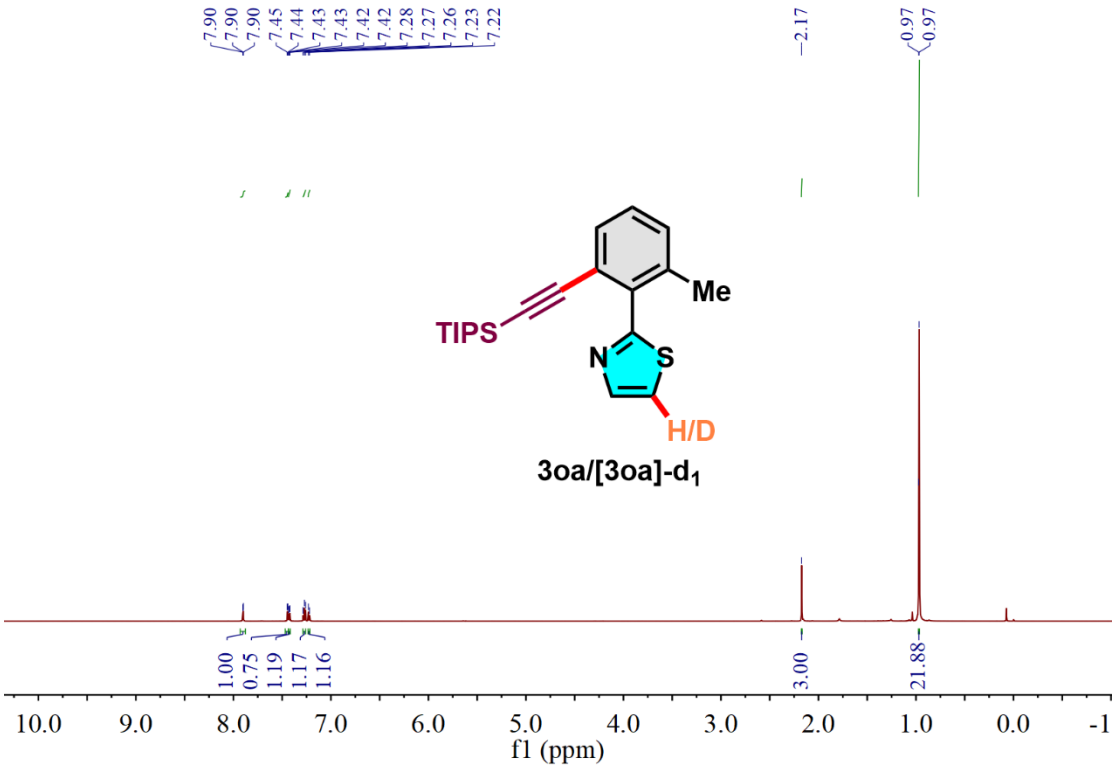
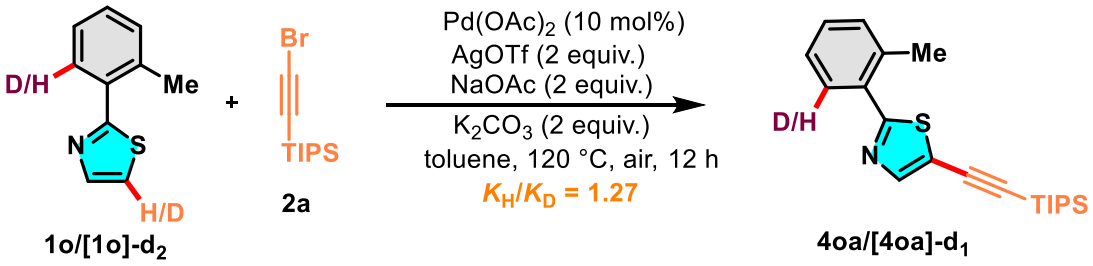


Figure S4. The ^{1}H NMR spectra of mixture **3oa** and **[3oa]-d$_1$**.



To a 15 mL oven dried Schlenk tube, **1o** (26.3 mg, 0.15 mmol, 1 equiv.), **[1o]-d$_2$** (26.4 mg, 0.15 mmol, 1 equiv.), K_2CO_3 (0.3 mmol, 2 equiv.), $Pd(OAc)_2$ (3.5 mg, 0.015 mmol, 10 mol%), NaOAc (0.3 mmol, 2 equiv.), AgOTf (0.3 mmol, 2 equiv.), (bromoethynyl)triisopropylsilane **2a** (58.7 mg, 0.225 mmol, 1.5 equiv.) and toluene (1.5 mL) were successively added. The mixture was then stirred at 120 °C under the air for 12 h. Then, the reaction mixture was cooled to room temperature and filtered through a plug of celite. The organic phase was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1) to afford the mixture of products **4oa** and **[4oa]-d$_1$** as light yellow liquid. By analyzing the 1H NMR of the mixture **4oa** and **[4oa]-d$_1$** as shown in **Figure S5**, the ratio of **4oa** and **[4oa]-d$_1$** was determined to be 0.56:0.44. Accordingly, the intermolecular KIE

(k_H/k_D)= 0.56/1-0.56 = 1.27.

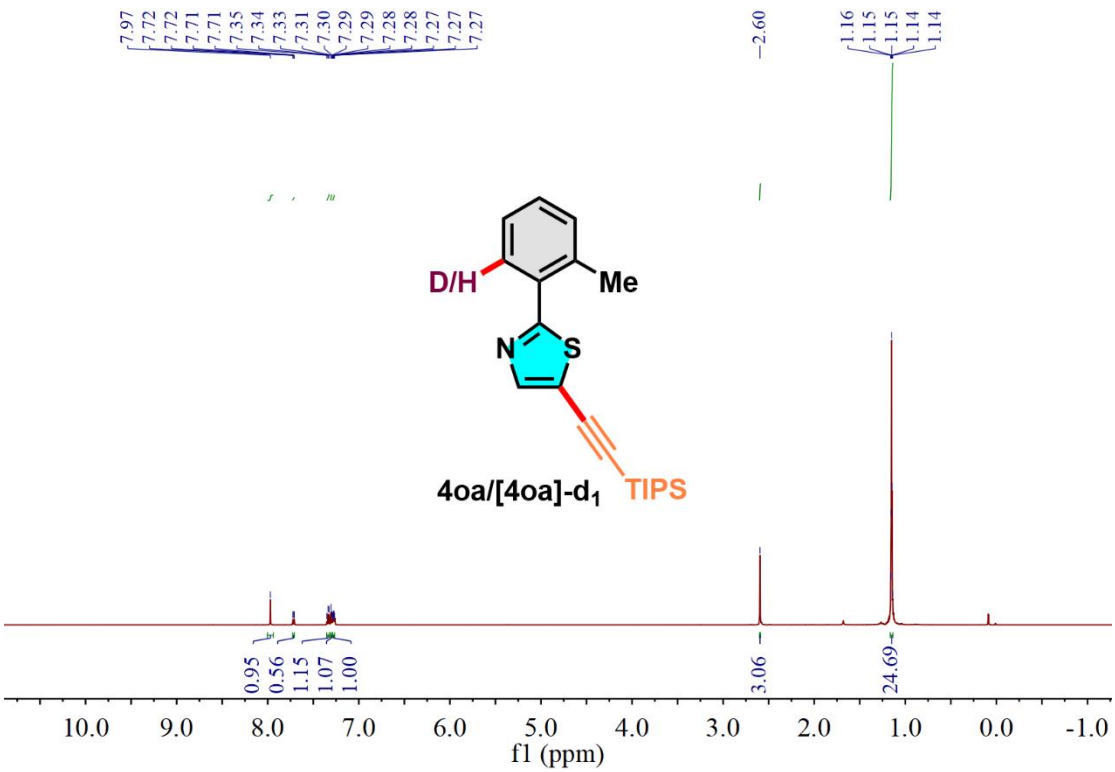


Figure S5. The ^{1}H NMR spectra of mixture **4oa** and **[4oa]-d$_1$**.

4. Crystallographic description

Colorless transparent block-like single crystals of **3la** were grown by layering a dichlormethane solution with hexane at ambient temperature. X-Ray diffraction data of one these crystals were collected on a R-AXIS SPIDER diffractometer. The measurements were performed with Mo-Kα radiation (λ = 0.71073 Å). Data were collected at 298(2) K, using the *ω*- and *φ*- scans to a maximum θ value of 28.327°. The data were refined by full-matrix least-squares techniques on F^2 with SHELXL-2018/3. And the structures were solved by direct methods SHELXL-2018/3. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at geometrically idealized positions. And an ORTEP representation of the structure is shown below.

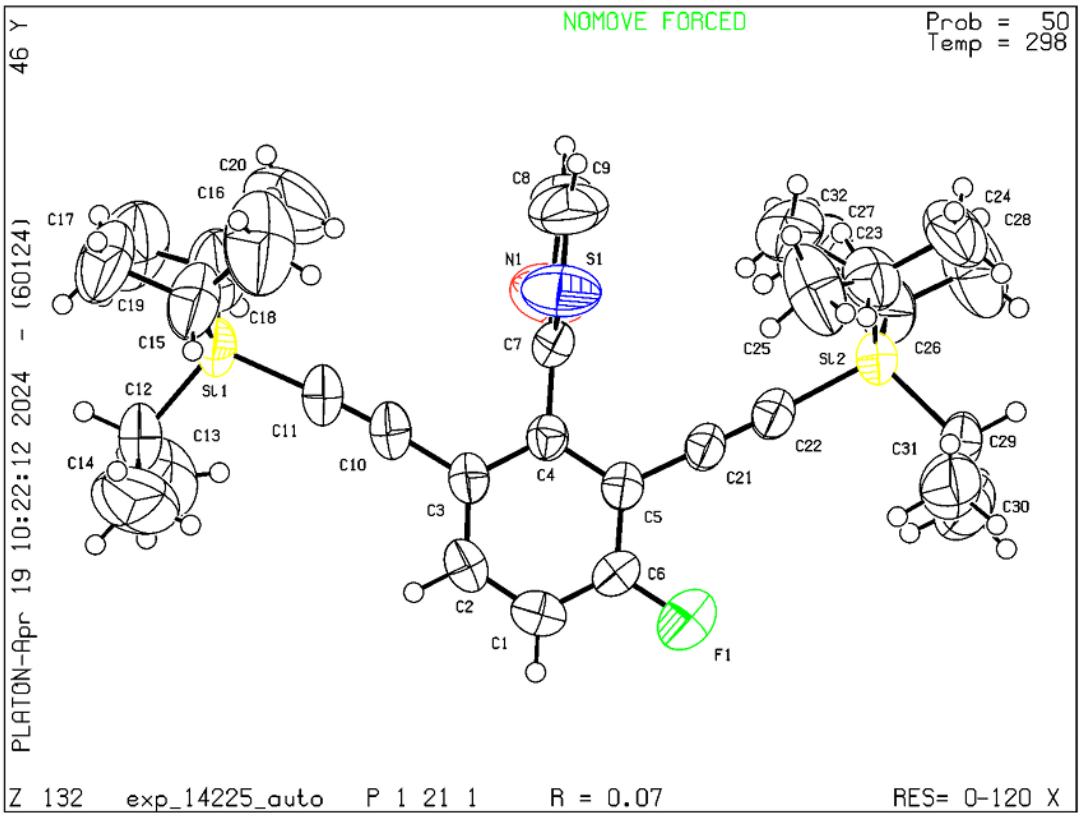


Figure S6. ORTEP diagram of **3la** with the thermal ellipsoids set at 50% probability.

Table S2 Crystal data and structure refinement for **3la**.

Identification code	exp_14225_auto
Empirical formula	$C_{31}H_{46}FNSSi_2$
Formula weight	539.93
Temperature/K	298.15
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.1462(4)
b/Å	13.1951(5)
c/Å	15.8775(7)
α/°	90
β/°	96.946(4)
γ/°	90
Volume/Å^3	1694.15(13)
Z	2
ρ_{calc}g/cm^3	1.058
μ/mm^{-1}	0.190
F(000)	584.0
Crystal size/mm^3	0.2 × 0.2 × 0.1
Radiation	Mo Kα (λ = 0.71073)

2Θ range for data collection/°	5.038 to 58.41
Index ranges	-10 ≤ h ≤ 11, -17 ≤ k ≤ 17, -21 ≤ l ≤ 21
Reflections collected	15050
Independent reflections	6943 [R_{int} = 0.0250, R_{sigma} = 0.0425]
Data/restraints/parameters	6943/13/348
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0659, wR_2 = 0.1685
Final R indexes [all data]	R_1 = 0.0993, wR_2 = 0.1946
Largest diff. peak/hole / e $Å^{-3}$	0.71/-0.19
Flack parameter	0.65(4)

Table S3 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for **3la**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
$Si^{(2)}$	8571.8(16)	203.1(10)	2955.6(8)	58.2(4)
$Si^{(1)}$	15967.6(18)	9.9(13)	8750.2(8)	69.4(5)
$S^{(1)}$	10348(3)	-55.4(18)	6359.2(15)	119.5(8)
$C^{(7)}$	12025(6)	145(4)	5847(3)	55.2(10)
$C^{(4)}$	13047(6)	-688(3)	5576(3)	49.3(10)
$C^{(3)}$	14415(6)	-1055(4)	6106(3)	57.2(11)
$C^{(21)}$	11307(6)	-726(3)	4180(3)	52.0(10)
$C^{(10)}$	14857(7)	-644(5)	6943(3)	68.5(13)
$C^{(1)}$	14986(9)	-2235(5)	5038(5)	80.0(16)
$C^{(26)}$	6583(7)	-97(6)	3386(4)	89.8(19)
$C^{(5)}$	12662(6)	-1104(4)	4761(3)	52.5(10)
$N^{(1)}$	12264(8)	1093(4)	5733(5)	108(2)
$C^{(22)}$	10219(6)	-390(4)	3694(3)	60.0(12)
$C^{(11)}$	15301(7)	-343(5)	7649(3)	75.4(15)
$F^{(1)}$	13303(6)	-2257(4)	3739(3)	115.1(14)
$C^{(2)}$	15356(7)	-1823(5)	5826(4)	74.2(16)
$C^{(6)}$	13642(7)	-1874(4)	4512(3)	62.5(13)
$C^{(18)}$	14078(10)	105(11)	9296(4)	139(4)
$C^{(29)}$	8668(7)	-382(5)	1882(3)	76.1(15)
$C^{(23)}$	9081(10)	1588(5)	2952(5)	94(2)
$C^{(28)}$	5041(8)	238(12)	2808(7)	162(5)
$C^{(31)}$	10319(9)	-202(8)	1541(5)	114(3)
$C^{(12)}$	17345(9)	-1046(6)	9214(4)	100(2)
$C^{(9)}$	9986(13)	1206(7)	6382(5)	109(3)
$C^{(24)}$	7989(11)	2206(6)	2287(6)	121(3)
$C^{(15)}$	17210(12)	1195(6)	8729(4)	112(3)

$C^{(27)}$	6564(10)	250(8)	4287(5)	125(3)
$C^{(8)}$	11058(15)	1666(6)	6028(7)	133(4)
$C^{(30)}$	8279(13)	-1509(6)	1893(5)	123(3)
$C^{(20)}$	12764(13)	783(11)	8879(9)	185(6)
$C^{(19)}$	14308(13)	20(14)	10248(5)	171(5)
$C^{(14)}$	18949(12)	-1122(11)	8804(8)	172(5)
$C^{(16)}$	16464(16)	2058(8)	8200(7)	181(6)
$C^{(13)}$	16395(16)	-2036(7)	9200(8)	168(5)
$C^{(17)}$	17954(14)	1577(7)	9604(5)	137(4)
$C^{(32)}$	9640(30)	2054(9)	3791(12)	102(7)
$C^{(25)}$	10690(20)	1932(15)	3176(17)	132(11)

Table S4 Anisotropic Displacement Parameters ($Å^2×10^3$) for **3la**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$Si^{(2)}$	55.9(7)	65.2(8)	50.9(6)	5.0(6)	-4.4(5)	-3.1(7)
$Si^{(1)}$	70.3(9)	90.7(11)	43.7(6)	3.8(7)	-6.8(5)	-0.7(8)
$S^{(1)}$	109.7(14)	120.1(16)	141.4(17)	19.5(14)	66.7(13)	22.4(13)
$C^{(7)}$	61(3)	58(3)	45(2)	-7(2)	0.4(17)	-1(2)
$C^{(4)}$	53(3)	49(2)	45(2)	3.1(19)	2.6(18)	-3(2)
$C^{(3)}$	58(3)	64(3)	47(2)	5(2)	-4(2)	1(2)
$C^{(21)}$	61(3)	51(2)	43(2)	-2.6(19)	-1(2)	-5(2)
$C^{(10)}$	69(3)	83(3)	50(3)	10(3)	-7(2)	1(3)
$C^{(1)}$	81(4)	70(3)	87(4)	-8(3)	3(3)	24(3)
$C^{(26)}$	64(3)	116(5)	89(4)	7(4)	8(3)	-20(4)
$C^{(5)}$	55(3)	54(2)	47(2)	1(2)	1.0(19)	-4(2)
$N^{(1)}$	120(5)	48(3)	160(6)	-7(3)	37(4)	-2(3)
$C^{(22)}$	68(3)	62(3)	48(2)	-5(2)	0(2)	-6(2)
$C^{(11)}$	73(3)	94(4)	54(3)	3(3)	-14(2)	-2(3)
$F^{(1)}$	129(3)	123(3)	89(3)	-35(2)	-4(2)	14(3)
$C^{(2)}$	64(3)	82(4)	70(3)	2(3)	-15(3)	17(3)
$C^{(6)}$	72(3)	64(3)	52(3)	-13(2)	8(2)	4(3)
$C^{(18)}$	97(5)	240(12)	82(4)	14(7)	19(4)	18(8)
$C^{(29)}$	82(4)	89(4)	52(3)	-1(3)	-11(2)	0(3)
$C^{(23)}$	100(5)	72(4)	104(5)	14(4)	-7(4)	-8(4)
$C^{(28)}$	62(4)	263(14)	157(8)	63(10)	-5(4)	-7(7)
$C^{(31)}$	93(5)	169(8)	84(4)	-8(5)	23(4)	19(5)
$C^{(12)}$	106(5)	123(6)	62(4)	4(4)	-23(3)	9(5)
$C^{(9)}$	121(7)	119(6)	91(5)	-21(5)	25(5)	47(6)

$C^{(24)}$	132(7)	84(5)	138(7)	30(5)	-19(6)	23(5)
$C^{(15)}$	145(7)	106(5)	77(4)	3(4)	-18(4)	-34(5)
$C^{(27)}$	112(6)	162(8)	110(6)	-21(6)	53(5)	-38(6)
$C^{(8)}$	187(11)	74(5)	141(8)	-21(5)	34(8)	30(6)
$C^{(30)}$	184(9)	95(5)	85(5)	-13(4)	-4(5)	-2(6)
$C^{(20)}$	92(7)	234(15)	229(13)	3(12)	21(7)	58(8)
$C^{(19)}$	154(8)	272(15)	97(6)	-3(8)	50(6)	-1(11)
$C^{(14)}$	116(8)	187(12)	216(13)	-15(10)	35(8)	50(8)
$C^{(16)}$	239(13)	137(9)	153(9)	60(8)	-34(9)	-76(9)
$C^{(13)}$	224(13)	98(6)	169(11)	38(7)	-22(9)	-9(7)
$C^{(17)}$	180(10)	127(7)	95(6)	-22(5)	-25(6)	-43(7)
$C^{(32)}$	136(15)	52(7)	118(13)	-14(7)	7(11)	-27(8)
$C^{(25)}$	94(13)	116(13)	170(20)	63(14)	-40(13)	-48(11)

Table S5 Bond Lengths for **3la**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
$Si^{(2)}$	$C^{(26)}$	1.875(6)	$C^{(1)}$	$C^{(2)}$	1.364(9)
$Si^{(2)}$	$C^{(22)}$	1.846(5)	$C^{(1)}$	$C^{(6)}$	1.379(9)
$Si^{(2)}$	$C^{(29)}$	1.881(6)	$C^{(26)}$	$C^{(28)}$	1.529(8)
$Si^{(2)}$	$C^{(23)}$	1.874(7)	$C^{(26)}$	$C^{(27)}$	1.505(8)
$Si^{(1)}$	$C^{(11)}$	1.827(5)	$C^{(5)}$	$C^{(6)}$	1.379(7)
$Si^{(1)}$	$C^{(18)}$	1.859(7)	$N^{(1)}$	$C^{(8)}$	1.367(11)
$Si^{(1)}$	$C^{(12)}$	1.882(8)	$F^{(1)}$	$C^{(6)}$	1.325(6)
$Si^{(1)}$	$C^{(15)}$	1.865(8)	$C^{(18)}$	$C^{(20)}$	1.488(10)
$S^{(1)}$	$C^{(7)}$	1.693(5)	$C^{(18)}$	$C^{(19)}$	1.505(9)
$S^{(1)}$	$C^{(9)}$	1.691(10)	$C^{(29)}$	$C^{(31)}$	1.529(8)
$C^{(7)}$	$C^{(4)}$	1.474(7)	$C^{(29)}$	$C^{(30)}$	1.520(8)
$C^{(7)}$	$N^{(1)}$	1.282(8)	$C^{(23)}$	$C^{(24)}$	1.531(8)
$C^{(4)}$	$C^{(3)}$	1.399(6)	$C^{(23)}$	$C^{(32)}$	1.488(17)
$C^{(4)}$	$C^{(5)}$	1.405(6)	$C^{(23)}$	$C^{(25)}$	1.390(17)
$C^{(3)}$	$C^{(10)}$	1.439(7)	$C^{(12)}$	$C^{(14)}$	1.532(9)
$C^{(3)}$	$C^{(2)}$	1.377(8)	$C^{(12)}$	$C^{(13)}$	1.518(9)
$C^{(21)}$	$C^{(5)}$	1.440(6)	$C^{(9)}$	$C^{(8)}$	1.251(12)
$C^{(21)}$	$C^{(22)}$	1.187(6)	$C^{(15)}$	$C^{(16)}$	1.500(10)
$C^{(10)}$	$C^{(11)}$	1.204(7)	$C^{(15)}$	$C^{(17)}$	1.533(8)

Table S6 Bond Angles for **3la**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
$C^{(26)}$	$Si^{(2)}$	$C^{(29)}$	112.1(3)	$C^{(6)}$	$C^{(5)}$	$C^{(4)}$	118.6(4)
$C^{(22)}$	$Si^{(2)}$	$C^{(26)}$	105.8(3)	$C^{(6)}$	$C^{(5)}$	$C^{(21)}$	119.8(4)
$C^{(22)}$	$Si^{(2)}$	$C^{(29)}$	107.1(2)	$C^{(7)}$	$N^{(1)}$	$C^{(8)}$	111.4(7)
$C^{(22)}$	$Si^{(2)}$	$C^{(23)}$	105.8(3)	$C^{(21)}$	$C^{(22)}$	$Si^{(2)}$	176.8(4)
$C^{(23)}$	$Si^{(2)}$	$C^{(26)}$	114.1(4)	$C^{(10)}$	$C^{(11)}$	$Si^{(1)}$	175.5(6)
$C^{(23)}$	$Si^{(2)}$	$C^{(29)}$	111.3(3)	$C^{(1)}$	$C^{(2)}$	$C^{(3)}$	121.3(5)
$C^{(11)}$	$Si^{(1)}$	$C^{(18)}$	107.2(3)	$C^{(1)}$	$C^{(6)}$	$C^{(5)}$	121.7(5)
$C^{(11)}$	$Si^{(1)}$	$C^{(12)}$	106.2(3)	$F^{(1)}$	$C^{(6)}$	$C^{(1)}$	119.4(5)
$C^{(11)}$	$Si^{(1)}$	$C^{(15)}$	107.2(3)	$F^{(1)}$	$C^{(6)}$	$C^{(5)}$	118.9(5)
$C^{(18)}$	$Si^{(1)}$	$C^{(12)}$	110.8(4)	$C^{(20)}$	$C^{(18)}$	$Si^{(1)}$	115.1(7)
$C^{(18)}$	$Si^{(1)}$	$C^{(15)}$	115.7(5)	$C^{(20)}$	$C^{(18)}$	$C^{(19)}$	119.1(10)
$C^{(15)}$	$Si^{(1)}$	$C^{(12)}$	109.2(4)	$C^{(19)}$	$C^{(18)}$	$Si^{(1)}$	117.0(6)
$C^{(9)}$	$S^{(1)}$	$C^{(7)}$	90.5(4)	$C^{(31)}$	$C^{(29)}$	$Si^{(2)}$	113.1(4)
$C^{(4)}$	$C^{(7)}$	$S^{(1)}$	122.7(4)	$C^{(30)}$	$C^{(29)}$	$Si^{(2)}$	111.1(5)
$N^{(1)}$	$C^{(7)}$	$S^{(1)}$	111.4(4)	$C^{(30)}$	$C^{(29)}$	$C^{(31)}$	110.4(7)
$N^{(1)}$	$C^{(7)}$	$C^{(4)}$	125.9(5)	$C^{(24)}$	$C^{(23)}$	$Si^{(2)}$	114.3(5)
$C^{(3)}$	$C^{(4)}$	$C^{(7)}$	121.3(4)	$C^{(32)}$	$C^{(23)}$	$Si^{(2)}$	116.3(7)
$C^{(3)}$	$C^{(4)}$	$C^{(5)}$	119.5(4)	$C^{(32)}$	$C^{(23)}$	$C^{(24)}$	119.0(9)
$C^{(5)}$	$C^{(4)}$	$C^{(7)}$	119.2(4)	$C^{(25)}$	$C^{(23)}$	$Si^{(2)}$	121.3(9)
$C^{(4)}$	$C^{(3)}$	$C^{(10)}$	121.1(5)	$C^{(25)}$	$C^{(23)}$	$C^{(24)}$	116.9(9)
$C^{(2)}$	$C^{(3)}$	$C^{(4)}$	119.6(5)	$C^{(14)}$	$C^{(12)}$	$Si^{(1)}$	112.4(6)
$C^{(2)}$	$C^{(3)}$	$C^{(10)}$	119.3(4)	$C^{(13)}$	$C^{(12)}$	$Si^{(1)}$	110.7(6)
$C^{(22)}$	$C^{(21)}$	$C^{(5)}$	178.0(5)	$C^{(13)}$	$C^{(12)}$	$C^{(14)}$	113.4(9)
$C^{(11)}$	$C^{(10)}$	$C^{(3)}$	176.1(6)	$C^{(8)}$	$C^{(9)}$	$S^{(1)}$	109.6(6)
$C^{(2)}$	$C^{(1)}$	$C^{(6)}$	119.3(5)	$C^{(16)}$	$C^{(15)}$	$Si^{(1)}$	117.6(6)
$C^{(28)}$	$C^{(26)}$	$Si^{(2)}$	113.8(5)	$C^{(16)}$	$C^{(15)}$	$C^{(17)}$	110.3(8)
$C^{(27)}$	$C^{(26)}$	$Si^{(2)}$	113.0(4)	$C^{(17)}$	$C^{(15)}$	$Si^{(1)}$	114.5(6)
$C^{(27)}$	$C^{(26)}$	$C^{(28)}$	112.3(8)	$C^{(9)}$	$C^{(8)}$	$N^{(1)}$	117.0(8)
$C^{(4)}$	$C^{(5)}$	$C^{(21)}$	121.6(4)				

Table S7 Torsion Angles **3la**.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
$S^{(1)}$	$C^{(7)}$	$C^{(4)}$	$C^{(3)}$	-90.5(5)	$C^{(22)}$	$Si^{(2)}$	$C^{(23)}$	$C^{(25)}$	23.4(16)
$S^{(1)}$	$C^{(7)}$	$C^{(4)}$	$C^{(5)}$	91.1(5)	$C^{(11)}$	$Si^{(1)}$	$C^{(18)}$	$C^{(20)}$	-53.6(11)
$S^{(1)}$	$C^{(7)}$	$N^{(1)}$	$C^{(8)}$	-2.5(8)	$C^{(11)}$	$Si^{(1)}$	$C^{(18)}$	$C^{(19)}$	159.0(10)
$S^{(1)}$	$C^{(9)}$	$C^{(8)}$	$N^{(1)}$	-1.8(12)	$C^{(11)}$	$Si^{(1)}$	$C^{(12)}$	$C^{(14)}$	66.1(7)
$C^{(7)}$	$S^{(1)}$	$C^{(9)}$	$C^{(8)}$	0.3(8)	$C^{(11)}$	$Si^{(1)}$	$C^{(12)}$	$C^{(13)}$	-61.8(7)
$C^{(7)}$	$C^{(4)}$	$C^{(3)}$	$C^{(10)}$	1.2(7)	$C^{(11)}$	$Si^{(1)}$	$C^{(15)}$	$C^{(16)}$	51.1(9)

C(7) C(4) C(3) C(2)	-178.9(5)	C(11) Si(1) C(15) C(17)	-177.0(7)
C(7) C(4) C(5) C(21)	0.9(7)	C(2) C(1) C(6) C(5)	0.2(10)
C(7) C(4) C(5) C(6)	179.2(5)	C(2) C(1) C(6) F(1)	178.4(6)
C(7) N(1) C(8) C(9)	2.9(13)	C(6) C(1) C(2) C(3)	0.0(10)
C(4) C(7) N(1) C(8)	177.5(6)	C(18) Si(1) C(12) C(14)	-177.8(7)
C(4) C(3) C(2) C(1)	0.2(9)	C(18) Si(1) C(12) C(13)	54.3(8)
C(4) C(5) C(6) C(1)	-0.6(8)	C(18) Si(1) C(15) C(16)	-68.4(9)
C(4) C(5) C(6) F(1)	-178.8(5)	C(18) Si(1) C(15) C(17)	63.5(8)
C(3) C(4) C(5) C(21)	-177.5(4)	C(29) Si(2) C(26) C(28)	-57.5(9)
C(3) C(4) C(5) C(6)	0.7(7)	C(29) Si(2) C(26) C(27)	172.8(6)
C(21) C(5) C(6) C(1)	177.7(6)	C(29) Si(2) C(23) C(24)	56.3(7)
C(21) C(5) C(6) F(1)	-0.5(8)	C(29) Si(2) C(23) C(32)	-158.9(11)
C(10) C(3) C(2) C(1)	-179.9(6)	C(29) Si(2) C(23) C(25)	-92.6(16)
C(26) Si(2) C(29) C(31)	-176.5(6)	C(23) Si(2) C(26) C(28)	70.2(9)
C(26) Si(2) C(29) C(30)	-51.7(6)	C(23) Si(2) C(26) C(27)	-59.6(7)
C(26) Si(2) C(23) C(24)	-71.7(7)	C(23) Si(2) C(29) C(31)	54.3(6)
C(26) Si(2) C(23) C(32)	73.1(11)	C(23) Si(2) C(29) C(30)	179.1(6)
C(26) Si(2) C(23) C(25)	139.3(16)	C(12) Si(1) C(18) C(20)	-169.2(9)
C(5) C(4) C(3) C(10)	179.5(5)	C(12) Si(1) C(18) C(19)	43.4(12)
C(5) C(4) C(3) C(2)	-0.6(7)	C(12) Si(1) C(15) C(16)	165.8(8)
N(1) C(7) C(4) C(3)	89.5(7)	C(12) Si(1) C(15) C(17)	-62.3(9)
N(1) C(7) C(4) C(5)	-88.9(7)	C(9) S(1) C(7) C(4)	-178.7(5)
C(22) Si(2) C(26) C(28)	-174.0(8)	C(9) S(1) C(7) N(1)	1.3(5)
C(22) Si(2) C(26) C(27)	56.3(7)	C(15) Si(1) C(18) C(20)	65.8(10)
C(22) Si(2) C(29) C(31)	-60.9(6)	C(15) Si(1) C(18) C(19)	-81.6(11)
C(22) Si(2) C(29) C(30)	64.0(6)	C(15) Si(1) C(12) C(14)	-49.2(8)
C(22) Si(2) C(23) C(24)	172.3(6)	C(15) Si(1) C(12) C(13)	-177.1(7)
C(22) Si(2) C(23) C(32)	-42.8(12)		

Table S8 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3la**.

Atom	***x***	***y***	***z***	**U(eq)**
H(1)	15634.12	-2752.69	4857.03	96
H(26)	6525.75	-838.43	3404.62	108
H(2)	16262.54	-2065.93	6180.79	89
H(18)	13577.24	-556.77	9147.58	167
H(29)	7806.82	-59.99	1486.73	91
H(23A)	10122	1575.4	2700.43	113
H(23)	8594.99	1795.89	3459.85	113

$H^{(28A)}$	4980.93	964.91	2800.61	243
$H^{(28B)}$	4074.29	-32.35	3017.81	243
$H^{(28C)}$	5098.21	-7.02	2243.2	243
$H^{(31A)}$	10530.6	512.44	1520.92	172
$H^{(31B)}$	10274.83	-481.55	980.14	172
$H^{(31C)}$	11189.04	-525.03	1906.79	172
$H^{(12)}$	17664.68	-875.92	9812.07	120
$H^{(9)}$	9123.34	1510.89	6620.94	131
$H^{(24A)}$	7763.98	1817.18	1775.6	182
$H^{(24B)}$	8550.26	2820.55	2169.62	182
$H^{(24C)}$	6966.85	2369.48	2500.33	182
$H^{(15)}$	18171.71	993.78	8451.95	135
$H^{(27A)}$	7396.17	-108.46	4650.41	187
$H^{(27B)}$	5497.66	116.73	4462.39	187
$H^{(27C)}$	6786.37	964.54	4324.05	187
$H^{(8)}$	11034.44	2367.41	5967.73	159
$H^{(30A)}$	9044.52	-1839.29	2311.97	185
$H^{(30B)}$	8375.47	-1793.76	1344.53	185
$H^{(30C)}$	7172.85	-1604.45	2028.18	185
$H^{(20A)}$	12893.45	1448.53	9122.13	277
$H^{(20B)}$	11698.49	518.55	8963.34	277
$H^{(20C)}$	12852.83	819.59	8282.2	277
$H^{(19A)}$	14865.06	-603.46	10412.06	257
$H^{(19B)}$	13247.12	28.32	10453.76	257
$H^{(19C)}$	14957.55	580.43	10485.86	257
$H^{(14A)}$	18690.07	-1253.28	8208.16	257
$H^{(14B)}$	19614.09	-1664.82	9063.26	257
$H^{(14C)}$	19548.39	-496.23	8884.27	257
$H^{(16A)}$	16325.89	1864.91	7612.93	271
$H^{(16B)}$	17181.79	2636.73	8277.12	271
$H^{(16C)}$	15407.23	2226.68	8371.76	271
$H^{(13A)}$	17127.03	-2589.45	9120.83	251
$H^{(13B)}$	15510	-2025.91	8742.49	251
$H^{(13C)}$	15948.93	-2120.62	9728.21	251
$H^{(17A)}$	17079.38	1739.75	9936.38	206
$H^{(17B)}$	18604.42	2172.3	9538.68	206
$H^{(17C)}$	18642.6	1059.62	9886.62	206
$H^{(32A)}$	8879.38	1873.63	4186.03	154
$H^{(32B)}$	9662.2	2777.82	3733.33	154
$H^{(32C)}$	10721.16	1811.42	3996.46	154

$H^{(25A)}$	11311.98	1424.67	3508.49	198
$H^{(25B)}$	10663.02	2543.45	3502.06	198
$H^{(25C)}$	11193.85	2066.05	2672.23	198

Table S9 Atomic Occupancy for **3la**.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
$H^{(23A)}$	0.50(2)	$H^{(23)}$	0.50(2)	$C^{(32)}$	0.50(2)
$H^{(32A)}$	0.50(2)	$H^{(32B)}$	0.50(2)	$H^{(32C)}$	0.50(2)
$C^{(25)}$	0.50(2)	$H^{(25A)}$	0.50(2)	$H^{(25B)}$	0.50(2)
$H^{(25C)}$	0.50(2)				

Colorless transparent block-like single crystals of **4ja** were grown by layering a dichlormethane solution with hexane at ambient temperature. X-Ray diffraction data of one these crystals were collected on a R-AXIS SPIDER diffractometer. The measurements were performed with Mo-Kα radiation (λ = 0.71073 Å). Data were collected at 298(2) K, using the *ω*- and *φ*- scans to a maximum θ value of 28.327°. The data were refined by full-matrix least-squares techniques on F^2 with SHELXL-2018/3. And the structures were solved by direct methods SHELXL-2018/3. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at geometrically idealized positions. And an ORTEP representation of the structure is shown below.

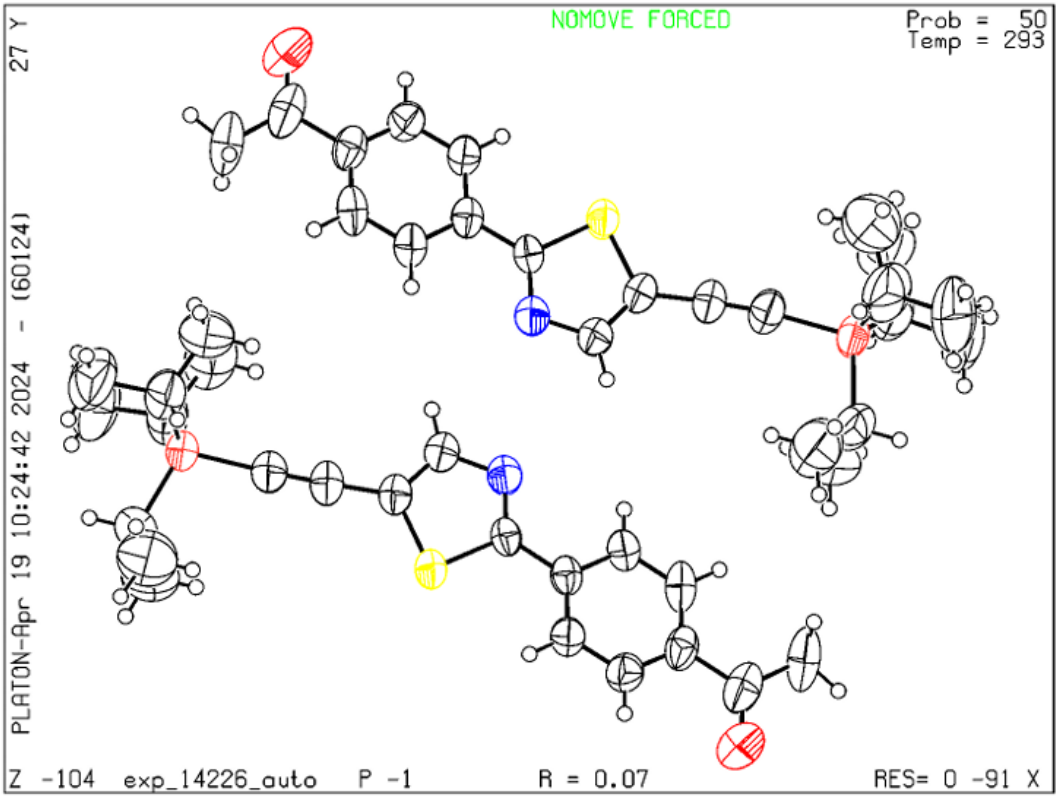


Figure S7. ORTEP diagram of **4ja** with the thermal ellipsoids set at 50% probability.

Table S10 Crystal data and structure refinement for **4ja**.

Identification code	exp_14226_auto
Empirical formula	$C_{22}H_{29}NOSSi$
Formula weight	383.61
Temperature/K	293.15
Crystal system	triclinic
Space group	P-1
a/Å	8.7980(7)
b/Å	12.4654(13)
c/Å	21.0908(14)
α/°	104.490(7)
β/°	90.974(6)
γ/°	91.921(7)
Volume/Å^3	2237.4(3)
Z	4
ρ_{calc}g/cm^3	1.139
μ/mm^{-1}	0.208
F(000)	824.0
Crystal size/mm^3	0.03 × 0.02 × 0.01
Radiation	Mo Kα (λ = 0.71073)

2Θ range for data collection/°	4.536 to 52.746
Index ranges	-10 ≤ h ≤ 10, -15 ≤ k ≤ 15, -26 ≤ l ≤ 26
Reflections collected	17857
Independent reflections	9131 [R_{int} = 0.0452, R_{sigma} = 0.0814]
Data/restraints/parameters	9131/4/483
Goodness-of-fit on F^2	1.019
Final R indexes [I>=2σ (I)]	R_1 = 0.0671, wR_2 = 0.1786
Final R indexes [all data]	R_1 = 0.1493, wR_2 = 0.2381
Largest diff. peak/hole / e $Å^{-3}$	0.30/-0.28

Table S11 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for **4ja**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
$S^{(2)}$	4532.7(9)	8161.6(8)	3730.8(3)	62.1(3)
$Si^{(2)}$	7810.3(11)	5728.0(9)	1608.7(4)	70.3(3)
$O^{(1)}$	-91(4)	11436(3)	6303.6(14)	129.4(13)
$N^{(2)}$	5686(3)	7514(2)	4685.7(12)	65.1(7)
$C^{(30)}$	3662(3)	8818(3)	5036.1(13)	51.9(8)
$C^{(31)}$	4646(3)	8152(3)	4547.1(12)	50.5(7)
$C^{(35)}$	7045(4)	6424(3)	2402.4(15)	72.8(10)
$C^{(33)}$	5989(3)	7253(3)	3573.8(14)	59.2(8)
$C^{(29)}$	3638(4)	8643(3)	5660.4(13)	60.7(8)
$C^{(32)}$	6430(4)	7009(3)	4133.1(15)	68.6(9)
$C^{(28)}$	2716(4)	9286(3)	6123.3(15)	72.1(10)
$C^{(25)}$	1807(4)	10086(3)	5976.4(15)	65.2(10)
$C^{(27)}$	2758(3)	9621(3)	4892.9(14)	63.2(9)
$C^{(34)}$	6561(4)	6828(3)	2933.3(15)	67.6(10)
$C^{(26)}$	1841(3)	10246(3)	5359.5(15)	69.6(10)
$C^{(24)}$	795(5)	10760(4)	6473.6(19)	86.9(12)
$C^{(39)}$	9802(4)	6313(4)	1568.6(17)	105.3(14)
$C^{(40)}$	10866(5)	6250(5)	2120(2)	143(2)
$C^{(42)}$	7640(6)	4205(4)	1564.9(19)	118.7(16)
$C^{(23)}$	871(5)	10644(4)	7139.8(17)	111.6(15)
$C^{(36)}$	6568(5)	6064(5)	963.9(18)	120.8(18)
$C^{(41)}$	10514(5)	5900(5)	899(2)	150(2)
$C^{(43)}$	8402(7)	3860(5)	2131(2)	153(2)
$C^{(44)}$	7938(7)	3430(4)	902(2)	160(2)
$C^{(37)}$	6686(8)	7296(6)	990(3)	185(3)
$C^{(38)}$	4922(5)	5631(7)	996(3)	201(4)

$S^{(1)}$	10552.3(9)	6786.5(7)	6267.2(3)	62.4(3)
$N^{(1)}$	9321(3)	7461(2)	5336.2(12)	67.7(8)
$C^{(6)}$	11342(3)	6180(3)	4950.8(13)	52.8(8)
$C^{(9)}$	10386(3)	6822(3)	5458.2(12)	49.9(7)
$C^{(13)}$	8098(4)	8477(3)	7632.5(16)	76.7(11)
$C^{(11)}$	9086(3)	7684(3)	6445.5(14)	58.6(8)
$C^{(5)}$	11300(4)	6348(3)	4326.6(14)	65.1(9)
$O^{(2)}$	15086(4)	3628(3)	3618.0(16)	140.5(14)
$C^{(4)}$	12200(4)	5724(3)	3847.2(14)	70.8(10)
$C^{(7)}$	12297(4)	5387(3)	5080.3(14)	65.6(9)
$C^{(12)}$	8566(4)	8092(3)	7098.7(15)	68.1(10)
$C^{(10)}$	8609(4)	7944(3)	5898.8(15)	68.1(9)
$C^{(3)}$	13156(4)	4940(3)	3981.3(15)	64.1(9)
$C^{(8)}$	13192(4)	4783(3)	4600.6(16)	71.6(10)
$C^{(2)}$	14130(5)	4275(4)	3461(2)	92.3(13)
$C^{(1)}$	13951(5)	4386(4)	2796.5(17)	106.6(15)
$C^{(20)}$	5606(6)	9953(4)	8192(2)	122.9(18)
$C^{(22)}$	4311(6)	9109(7)	7888(3)	179(3)
$C^{(21)}$	6023(7)	10727(5)	7763(3)	181(3)
$C^{(17)}$	6654(5)	8168(4)	8861.7(19)	118.2(16)
$C^{(18)}$	7754(7)	7402(5)	8968(3)	158(2)
$C^{(19)}$	5800(6)	8677(5)	9486.3(19)	156(2)
$C^{(14)}$	8845(6)	10242(5)	8831(2)	144(2)
$C^{(15)}$	10374(6)	9847(6)	8850(3)	166(2)
$C^{(16)}$	8370(7)	11109(5)	9424(2)	177(3)
$Si^{(1)}$	7302.4(12)	9228.1(10)	8410.8(4)	77.7(4)

Table S12 Anisotropic Displacement Parameters ($Å^2×10^3$) for **4ja**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$S^{(2)}$	70.5(5)	71.4(6)	44.1(4)	13.1(4)	7.6(4)	7.1(4)
$Si^{(2)}$	74.8(6)	85.3(8)	47.9(5)	8.5(5)	9.2(5)	18.6(6)
$O^{(1)}$	113(2)	155(4)	109(2)	7(2)	14.2(19)	55(2)
$N^{(2)}$	74.3(17)	69(2)	51.7(15)	12.7(14)	3.3(13)	9.1(15)
$C^{(30)}$	56.1(17)	51(2)	44.3(16)	6.0(14)	1.8(14)	-11.9(16)
$C^{(31)}$	57.1(17)	52(2)	39.5(15)	7.2(14)	0.2(13)	-9.4(16)
$C^{(35)}$	81(2)	77(3)	57.5(19)	10.1(18)	5.5(17)	11(2)
$C^{(33)}$	65.8(19)	58(2)	50.3(17)	6.5(16)	6.2(15)	-2.6(17)
$C^{(29)}$	77(2)	57(2)	46.6(17)	11.6(15)	3.8(15)	0.0(17)

$C^{(32)}$	74(2)	74(3)	56.1(19)	11.0(18)	7.7(17)	14.0(19)
$C^{(28)}$	94(3)	70(3)	45.4(17)	2.2(17)	17.3(17)	-15(2)
$C^{(25)}$	60.4(19)	66(2)	55.8(19)	-9.0(18)	8.9(16)	-13.1(18)
$C^{(27)}$	66(2)	69(2)	53.0(18)	11.6(17)	5.6(16)	4.1(18)
$C^{(34)}$	76(2)	71(3)	51.3(18)	7.1(17)	9.7(17)	-5.8(19)
$C^{(26)}$	58.4(19)	80(3)	64(2)	5.2(18)	1.2(16)	2.8(18)
$C^{(24)}$	82(3)	81(3)	82(2)	-9(2)	24(2)	-8(2)
$C^{(39)}$	97(3)	134(4)	79(3)	14(3)	19(2)	14(3)
$C^{(40)}$	84(3)	205(7)	128(4)	19(4)	-18(3)	14(3)
$C^{(42)}$	162(4)	109(4)	80(3)	11(3)	20(3)	25(3)
$C^{(23)}$	164(4)	97(3)	65(2)	1(2)	48(2)	-3(3)
$C^{(36)}$	118(4)	173(6)	74(3)	29(3)	-2(2)	53(4)
$C^{(41)}$	118(4)	199(6)	123(4)	14(4)	51(3)	6(4)
$C^{(43)}$	230(6)	115(5)	133(4)	54(4)	44(4)	69(4)
$C^{(44)}$	215(6)	111(4)	130(4)	-22(3)	42(4)	24(4)
$C^{(37)}$	247(7)	185(7)	154(5)	86(5)	17(5)	109(6)
$C^{(38)}$	75(3)	372(11)	143(5)	35(5)	-13(3)	43(5)
$S^{(1)}$	71.2(5)	68.7(6)	47.1(4)	13.0(4)	10.4(4)	8.7(4)
$N^{(1)}$	76.2(18)	72(2)	52.9(15)	10.9(14)	4.2(13)	12.9(16)
$C^{(6)}$	56.7(18)	49(2)	47.4(16)	3.3(14)	6.0(14)	-13.6(16)
$C^{(9)}$	62.0(18)	46.7(19)	39.0(15)	7.7(13)	2.1(13)	-3.9(15)
$C^{(13)}$	84(2)	80(3)	66(2)	13.5(19)	21.6(19)	13(2)
$C^{(11)}$	62.9(19)	52(2)	56.9(18)	5.4(16)	12.8(16)	3.6(16)
$C^{(5)}$	83(2)	60(2)	50.5(18)	10.4(16)	12.1(16)	-0.2(18)
$O^{(2)}$	109(2)	173(4)	124(3)	1(2)	25(2)	58(3)
$C^{(4)}$	96(3)	69(3)	43.3(17)	8.5(17)	13.8(17)	-15(2)
$C^{(7)}$	68(2)	74(3)	50.3(18)	6.2(17)	7.3(16)	6.5(19)
$C^{(12)}$	73(2)	71(3)	55.5(19)	6.1(17)	14.2(17)	2.5(19)
$C^{(10)}$	76(2)	70(3)	55.6(19)	9.3(18)	4.1(17)	19.8(19)
$C^{(3)}$	65(2)	55(2)	61(2)	-5.0(17)	13.0(17)	-12.7(18)
$C^{(8)}$	61.2(19)	84(3)	65(2)	9.8(19)	7.5(17)	7.9(19)
$C^{(2)}$	87(3)	91(3)	81(2)	-14(2)	34(2)	-13(2)
$C^{(1)}$	145(4)	95(3)	67(2)	-4(2)	45(2)	-10(3)
$C^{(20)}$	152(4)	134(5)	92(3)	34(3)	36(3)	85(4)
$C^{(22)}$	117(4)	266(9)	155(5)	51(5)	-19(4)	56(5)
$C^{(21)}$	241(7)	207(7)	136(4)	100(5)	72(4)	123(6)
$C^{(17)}$	144(4)	133(4)	89(3)	38(3)	44(3)	59(3)
$C^{(18)}$	191(6)	153(6)	159(5)	80(4)	57(4)	84(5)
$C^{(19)}$	212(6)	173(6)	99(3)	52(3)	78(4)	60(4)
$C^{(14)}$	151(5)	127(5)	123(4)	-31(3)	10(4)	23(4)

$C^{(15)}$	134(4)	186(7)	152(5)	-1(4)	-22(4)	-3(5)
$C^{(16)}$	249(7)	148(6)	99(3)	-33(3)	17(4)	-1(5)
$Si^{(1)}$	94.1(8)	84.7(9)	52.1(5)	8.8(5)	18.5(5)	29.3(6)

Table S13 Bond Lengths for **4ja**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
$S^{(2)}$	$C^{(31)}$	1.726(3)	$S^{(1)}$	$C^{(9)}$	1.722(3)
$S^{(2)}$	$C^{(33)}$	1.720(3)	$S^{(1)}$	$C^{(11)}$	1.721(3)
$Si^{(2)}$	$C^{(35)}$	1.832(3)	$N^{(1)}$	$C^{(9)}$	1.313(4)
$Si^{(2)}$	$C^{(39)}$	1.887(4)	$N^{(1)}$	$C^{(10)}$	1.362(4)
$Si^{(2)}$	$C^{(42)}$	1.879(5)	$C^{(6)}$	$C^{(9)}$	1.463(4)
$Si^{(2)}$	$C^{(36)}$	1.867(4)	$C^{(6)}$	$C^{(5)}$	1.384(4)
$O^{(1)}$	$C^{(24)}$	1.278(5)	$C^{(6)}$	$C^{(7)}$	1.393(4)
$N^{(2)}$	$C^{(31)}$	1.308(4)	$C^{(13)}$	$C^{(12)}$	1.194(4)
$N^{(2)}$	$C^{(32)}$	1.368(4)	$C^{(13)}$	$Si^{(1)}$	1.837(3)
$C^{(30)}$	$C^{(31)}$	1.467(4)	$C^{(11)}$	$C^{(12)}$	1.432(4)
$C^{(30)}$	$C^{(29)}$	1.388(4)	$C^{(11)}$	$C^{(10)}$	1.338(4)
$C^{(30)}$	$C^{(27)}$	1.387(4)	$C^{(5)}$	$C^{(4)}$	1.389(4)
$C^{(35)}$	$C^{(34)}$	1.199(4)	$O^{(2)}$	$C^{(2)}$	1.279(6)
$C^{(33)}$	$C^{(32)}$	1.344(4)	$C^{(4)}$	$C^{(3)}$	1.388(5)
$C^{(33)}$	$C^{(34)}$	1.429(4)	$C^{(7)}$	$C^{(8)}$	1.377(4)
$C^{(29)}$	$C^{(28)}$	1.390(4)	$C^{(3)}$	$C^{(8)}$	1.368(4)
$C^{(28)}$	$C^{(25)}$	1.390(5)	$C^{(3)}$	$C^{(2)}$	1.500(5)
$C^{(25)}$	$C^{(26)}$	1.365(4)	$C^{(2)}$	$C^{(1)}$	1.449(6)
$C^{(25)}$	$C^{(24)}$	1.497(5)	$C^{(20)}$	$C^{(22)}$	1.541(7)
$C^{(27)}$	$C^{(26)}$	1.382(4)	$C^{(20)}$	$C^{(21)}$	1.520(7)
$C^{(24)}$	$C^{(23)}$	1.449(5)	$C^{(20)}$	$Si^{(1)}$	1.879(5)
$C^{(39)}$	$C^{(40)}$	1.500(5)	$C^{(17)}$	$C^{(18)}$	1.435(6)
$C^{(39)}$	$C^{(41)}$	1.529(4)	$C^{(17)}$	$C^{(19)}$	1.533(4)
$C^{(42)}$	$C^{(43)}$	1.519(6)	$C^{(17)}$	$Si^{(1)}$	1.890(5)
$C^{(42)}$	$C^{(44)}$	1.520(5)	$C^{(14)}$	$C^{(15)}$	1.451(6)
$C^{(36)}$	$C^{(37)}$	1.523(8)	$C^{(14)}$	$C^{(16)}$	1.511(5)
$C^{(36)}$	$C^{(38)}$	1.537(7)	$C^{(14)}$	$Si^{(1)}$	1.873(5)

Table S14 Bond Angles for **4ja**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
$C^{(33)}$	$S^{(2)}$	$C^{(31)}$	89.51(15)	$C^{(11)}$	$S^{(1)}$	$C^{(9)}$	89.20(15)

C(35)	Si(2)	C(39)	107.87(16)	C(9)	N(1)	C(10)	110.1(3)
C(35)	Si(2)	C(42)	105.50(17)	C(5)	C(6)	C(9)	120.0(3)
C(35)	Si(2)	C(36)	107.03(18)	C(5)	C(6)	C(7)	118.7(3)
C(42)	Si(2)	C(39)	115.9(2)	C(7)	C(6)	C(9)	121.3(3)
C(36)	Si(2)	C(39)	109.9(2)	N(1)	C(9)	S(1)	114.4(2)
C(36)	Si(2)	C(42)	110.3(2)	N(1)	C(9)	C(6)	123.1(3)
C(31)	N(2)	C(32)	110.5(3)	C(6)	C(9)	S(1)	122.5(2)
C(29)	C(30)	C(31)	119.1(3)	C(12)	C(13)	Si(1)	172.2(4)
C(27)	C(30)	C(31)	121.8(3)	C(12)	C(11)	S(1)	122.3(3)
C(27)	C(30)	C(29)	119.0(3)	C(10)	C(11)	S(1)	109.5(2)
N(2)	C(31)	S(2)	114.1(2)	C(10)	C(11)	C(12)	128.2(3)
N(2)	C(31)	C(30)	123.8(3)	C(6)	C(5)	C(4)	119.5(3)
C(30)	C(31)	S(2)	122.1(2)	C(3)	C(4)	C(5)	121.5(3)
C(34)	C(35)	Si(2)	176.4(4)	C(8)	C(7)	C(6)	121.0(3)
C(32)	C(33)	S(2)	109.3(2)	C(13)	C(12)	C(11)	176.5(4)
C(32)	C(33)	C(34)	127.6(3)	C(11)	C(10)	N(1)	116.8(3)
C(34)	C(33)	S(2)	123.0(3)	C(4)	C(3)	C(2)	121.0(4)
C(30)	C(29)	C(28)	118.8(3)	C(8)	C(3)	C(4)	118.6(3)
C(33)	C(32)	N(2)	116.6(3)	C(8)	C(3)	C(2)	120.4(4)
C(25)	C(28)	C(29)	122.0(3)	C(3)	C(8)	C(7)	120.7(4)
C(28)	C(25)	C(24)	121.7(4)	O(2)	C(2)	C(3)	119.0(4)
C(26)	C(25)	C(28)	118.5(3)	O(2)	C(2)	C(1)	122.2(4)
C(26)	C(25)	C(24)	119.9(4)	C(1)	C(2)	C(3)	118.8(5)
C(26)	C(27)	C(30)	121.2(3)	C(22)	C(20)	Si(1)	110.8(4)
C(35)	C(34)	C(33)	176.9(4)	C(21)	C(20)	C(22)	112.5(5)
C(25)	C(26)	C(27)	120.6(4)	C(21)	C(20)	Si(1)	112.1(4)
O(1)	C(24)	C(25)	119.3(4)	C(18)	C(17)	C(19)	111.9(4)
O(1)	C(24)	C(23)	121.8(4)	C(18)	C(17)	Si(1)	117.1(4)
C(23)	C(24)	C(25)	118.9(4)	C(19)	C(17)	Si(1)	113.0(3)
C(40)	C(39)	Si(2)	115.5(3)	C(15)	C(14)	C(16)	116.6(5)
C(40)	C(39)	C(41)	112.1(4)	C(15)	C(14)	Si(1)	118.1(4)
C(41)	C(39)	Si(2)	113.4(3)	C(16)	C(14)	Si(1)	115.5(4)
C(43)	C(42)	Si(2)	115.0(3)	C(13)	Si(1)	C(20)	106.43(18)
C(43)	C(42)	C(44)	113.0(4)	C(13)	Si(1)	C(17)	107.71(18)
C(44)	C(42)	Si(2)	115.9(3)	C(13)	Si(1)	C(14)	105.51(19)
C(37)	C(36)	Si(2)	111.2(4)	C(20)	Si(1)	C(17)	109.4(2)
C(37)	C(36)	C(38)	113.0(5)	C(14)	Si(1)	C(20)	111.5(3)
C(38)	C(36)	Si(2)	111.3(4)	C(14)	Si(1)	C(17)	115.8(3)

Table S15 Torsion Angles for **4ja**.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
$S^{(2)}$	$C^{(33)}$	$C^{(32)}$	$N^{(2)}$	-0.7(4)	$S^{(1)}$	$C^{(11)}$	$C^{(10)}$	$N^{(1)}$	0.9(4)
$C^{(30)}$	$C^{(29)}$	$C^{(28)}$	$C^{(25)}$	0.9(5)	$C^{(6)}$	$C^{(5)}$	$C^{(4)}$	$C^{(3)}$	-0.6(5)
$C^{(30)}$	$C^{(27)}$	$C^{(26)}$	$C^{(25)}$	0.1(5)	$C^{(6)}$	$C^{(7)}$	$C^{(8)}$	$C^{(3)}$	-0.6(5)
$C^{(31)}$	$S^{(2)}$	$C^{(33)}$	$C^{(32)}$	0.5(3)	$C^{(9)}$	$S^{(1)}$	$C^{(11)}$	$C^{(12)}$	-178.2(3)
$C^{(31)}$	$S^{(2)}$	$C^{(33)}$	$C^{(34)}$	178.9(3)	$C^{(9)}$	$S^{(1)}$	$C^{(11)}$	$C^{(10)}$	-0.7(3)
$C^{(31)}$	$N^{(2)}$	$C^{(32)}$	$C^{(33)}$	0.4(4)	$C^{(9)}$	$N^{(1)}$	$C^{(10)}$	$C^{(11)}$	-0.7(4)
$C^{(31)}$	$C^{(30)}$	$C^{(29)}$	$C^{(28)}$	179.2(3)	$C^{(9)}$	$C^{(6)}$	$C^{(5)}$	$C^{(4)}$	-179.3(3)
$C^{(31)}$	$C^{(30)}$	$C^{(27)}$	$C^{(26)}$	-179.7(3)	$C^{(9)}$	$C^{(6)}$	$C^{(7)}$	$C^{(8)}$	179.8(3)
$C^{(35)}$	$Si^{(2)}$	$C^{(39)}$	$C^{(40)}$	55.1(4)	$C^{(11)}$	$S^{(1)}$	$C^{(9)}$	$N^{(1)}$	0.4(3)
$C^{(35)}$	$Si^{(2)}$	$C^{(39)}$	$C^{(41)}$	-173.5(4)	$C^{(11)}$	$S^{(1)}$	$C^{(9)}$	$C^{(6)}$	-178.9(2)
$C^{(35)}$	$Si^{(2)}$	$C^{(42)}$	$C^{(43)}$	-55.5(4)	$C^{(5)}$	$C^{(6)}$	$C^{(9)}$	$S^{(1)}$	-171.5(2)
$C^{(35)}$	$Si^{(2)}$	$C^{(42)}$	$C^{(44)}$	169.5(4)	$C^{(5)}$	$C^{(6)}$	$C^{(9)}$	$N^{(1)}$	9.3(4)
$C^{(35)}$	$Si^{(2)}$	$C^{(36)}$	$C^{(37)}$	65.7(4)	$C^{(5)}$	$C^{(6)}$	$C^{(7)}$	$C^{(8)}$	0.4(5)
$C^{(35)}$	$Si^{(2)}$	$C^{(36)}$	$C^{(38)}$	-61.3(5)	$C^{(5)}$	$C^{(4)}$	$C^{(3)}$	$C^{(8)}$	0.4(5)
$C^{(33)}$	$S^{(2)}$	$C^{(31)}$	$N^{(2)}$	-0.3(2)	$C^{(5)}$	$C^{(4)}$	$C^{(3)}$	$C^{(2)}$	-179.6(3)
$C^{(33)}$	$S^{(2)}$	$C^{(31)}$	$C^{(30)}$	179.1(2)	$C^{(4)}$	$C^{(3)}$	$C^{(8)}$	$C^{(7)}$	0.2(5)
$C^{(29)}$	$C^{(30)}$	$C^{(31)}$	$S^{(2)}$	169.8(2)	$C^{(4)}$	$C^{(3)}$	$C^{(2)}$	$O^{(2)}$	174.2(4)
$C^{(29)}$	$C^{(30)}$	$C^{(31)}$	$N^{(2)}$	-10.8(4)	$C^{(4)}$	$C^{(3)}$	$C^{(2)}$	$C^{(1)}$	-5.9(5)
$C^{(29)}$	$C^{(30)}$	$C^{(27)}$	$C^{(26)}$	0.0(5)	$C^{(7)}$	$C^{(6)}$	$C^{(9)}$	$S^{(1)}$	9.0(4)
$C^{(29)}$	$C^{(28)}$	$C^{(25)}$	$C^{(26)}$	-0.7(5)	$C^{(7)}$	$C^{(6)}$	$C^{(9)}$	$N^{(1)}$	-170.2(3)
$C^{(29)}$	$C^{(28)}$	$C^{(25)}$	$C^{(24)}$	178.8(3)	$C^{(7)}$	$C^{(6)}$	$C^{(5)}$	$C^{(4)}$	0.2(4)
$C^{(32)}$	$N^{(2)}$	$C^{(31)}$	$S^{(2)}$	0.0(4)	$C^{(12)}$	$C^{(11)}$	$C^{(10)}$	$N^{(1)}$	178.2(3)
$C^{(32)}$	$N^{(2)}$	$C^{(31)}$	$C^{(30)}$	-179.4(3)	$C^{(10)}$	$N^{(1)}$	$C^{(9)}$	$S^{(1)}$	0.1(4)
$C^{(28)}$	$C^{(25)}$	$C^{(26)}$	$C^{(27)}$	0.2(5)	$C^{(10)}$	$N^{(1)}$	$C^{(9)}$	$C^{(6)}$	179.4(3)
$C^{(28)}$	$C^{(25)}$	$C^{(24)}$	$O^{(1)}$	-175.6(4)	$C^{(8)}$	$C^{(3)}$	$C^{(2)}$	$O^{(2)}$	-5.8(5)
$C^{(28)}$	$C^{(25)}$	$C^{(24)}$	$C^{(23)}$	5.7(5)	$C^{(8)}$	$C^{(3)}$	$C^{(2)}$	$C^{(1)}$	174.0(3)
$C^{(27)}$	$C^{(30)}$	$C^{(31)}$	$S^{(2)}$	-10.4(4)	$C^{(2)}$	$C^{(3)}$	$C^{(8)}$	$C^{(7)}$	-179.8(3)
$C^{(27)}$	$C^{(30)}$	$C^{(31)}$	$N^{(2)}$	168.9(3)	$C^{(22)}$	$C^{(20)}$	$Si^{(1)}$	$C^{(13)}$	69.0(4)
$C^{(27)}$	$C^{(30)}$	$C^{(29)}$	$C^{(28)}$	-0.5(4)	$C^{(22)}$	$C^{(20)}$	$Si^{(1)}$	$C^{(17)}$	-47.1(4)
$C^{(34)}$	$C^{(33)}$	$C^{(32)}$	$N^{(2)}$	-179.0(3)	$C^{(22)}$	$C^{(20)}$	$Si^{(1)}$	$C^{(14)}$	-176.4(3)
$C^{(26)}$	$C^{(25)}$	$C^{(24)}$	$O^{(1)}$	3.9(5)	$C^{(21)}$	$C^{(20)}$	$Si^{(1)}$	$C^{(13)}$	-57.6(5)
$C^{(26)}$	$C^{(25)}$	$C^{(24)}$	$C^{(23)}$	-174.8(3)	$C^{(21)}$	$C^{(20)}$	$Si^{(1)}$	$C^{(17)}$	-173.7(4)
$C^{(24)}$	$C^{(25)}$	$C^{(26)}$	$C^{(27)}$	-179.3(3)	$C^{(21)}$	$C^{(20)}$	$Si^{(1)}$	$C^{(14)}$	57.0(5)
$C^{(39)}$	$Si^{(2)}$	$C^{(42)}$	$C^{(43)}$	63.7(4)	$C^{(18)}$	$C^{(17)}$	$Si^{(1)}$	$C^{(13)}$	54.2(5)
$C^{(39)}$	$Si^{(2)}$	$C^{(42)}$	$C^{(44)}$	-71.2(4)	$C^{(18)}$	$C^{(17)}$	$Si^{(1)}$	$C^{(20)}$	169.5(4)
$C^{(39)}$	$Si^{(2)}$	$C^{(36)}$	$C^{(37)}$	-51.2(4)	$C^{(18)}$	$C^{(17)}$	$Si^{(1)}$	$C^{(14)}$	-63.5(5)
$C^{(39)}$	$Si^{(2)}$	$C^{(36)}$	$C^{(38)}$	-178.2(4)	$C^{(19)}$	$C^{(17)}$	$Si^{(1)}$	$C^{(13)}$	-173.5(3)
$C^{(42)}$	$Si^{(2)}$	$C^{(39)}$	$C^{(40)}$	-62.8(4)	$C^{(19)}$	$C^{(17)}$	$Si^{(1)}$	$C^{(20)}$	-58.2(4)

$C^{(42)}$ $Si^{(2)}$ $C^{(39)}$ $C^{(41)}$	68.6(4)	$C^{(19)}$ $C^{(17)}$ $Si^{(1)}$ $C^{(14)}$	68.8(4)
$C^{(42)}$ $Si^{(2)}$ $C^{(36)}$ $C^{(37)}$	180.0(4)	$C^{(15)}$ $C^{(14)}$ $Si^{(1)}$ $C^{(13)}$	-46.2(5)
$C^{(42)}$ $Si^{(2)}$ $C^{(36)}$ $C^{(38)}$	52.9(5)	$C^{(15)}$ $C^{(14)}$ $Si^{(1)}$ $C^{(20)}$	-161.3(5)
$C^{(36)}$ $Si^{(2)}$ $C^{(39)}$ $C^{(40)}$	171.4(4)	$C^{(15)}$ $C^{(14)}$ $Si^{(1)}$ $C^{(17)}$	72.8(5)
$C^{(36)}$ $Si^{(2)}$ $C^{(39)}$ $C^{(41)}$	-57.1(4)	$C^{(16)}$ $C^{(14)}$ $Si^{(1)}$ $C^{(13)}$	168.9(4)
$C^{(36)}$ $Si^{(2)}$ $C^{(42)}$ $C^{(43)}$	-170.8(3)	$C^{(16)}$ $C^{(14)}$ $Si^{(1)}$ $C^{(20)}$	53.8(5)
$C^{(36)}$ $Si^{(2)}$ $C^{(42)}$ $C^{(44)}$	54.3(4)	$C^{(16)}$ $C^{(14)}$ $Si^{(1)}$ $C^{(17)}$	-72.1(5)

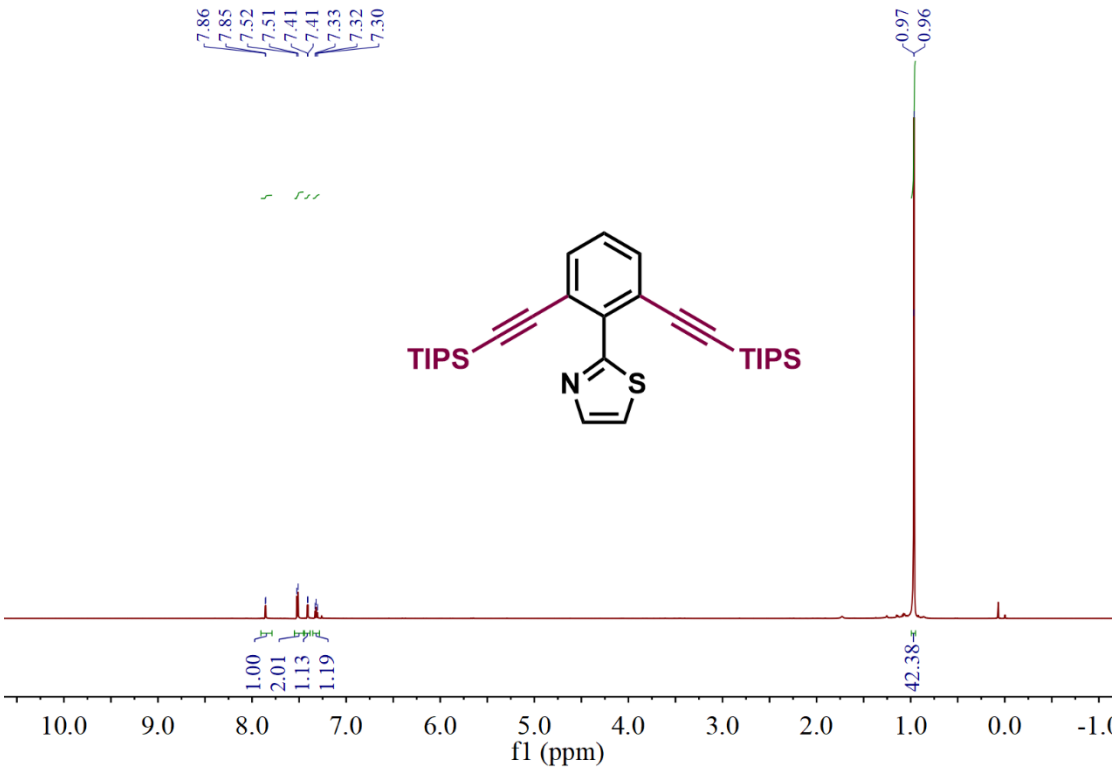
Table S16 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **4ja**.

Atom	***x***	***y***	***z***	**U(eq)**
$H^{(29)}$	4228.28	8104.55	5767.08	73
$H^{(32)}$	7202.12	6521.47	4143.83	82
$H^{(28)}$	2708.49	9177.55	6543.83	87
$H^{(27)}$	2768.28	9741.87	4475.33	76
$H^{(26)}$	1243.16	10779.02	5252.3	84
$H^{(39)}$	9682.11	7108.31	1616.66	126
$H^{(40A)}$	10388.55	6537.81	2530.35	215
$H^{(40B)}$	11782.26	6680.78	2101.37	215
$H^{(40C)}$	11109.15	5491.81	2081.03	215
$H^{(42)}$	6553.11	4074.7	1625.04	142
$H^{(23A)}$	1870.68	10870.1	7324.74	167
$H^{(23B)}$	659.56	9883.64	7139.81	167
$H^{(23C)}$	133.6	11101.92	7396.42	167
$H^{(36)}$	6953.91	5667.81	539.5	145
$H^{(41A)}$	10701.29	5124.55	825.37	226
$H^{(41B)}$	11456.38	6305.11	888.99	226
$H^{(41C)}$	9830.41	6010.09	563.62	226
$H^{(43A)}$	9474.56	4034.05	2138.91	230
$H^{(43B)}$	8236.05	3076.71	2075.83	230
$H^{(43C)}$	7977.17	4251.89	2535.76	230
$H^{(44A)}$	7385	3661.09	566.14	241
$H^{(44B)}$	7611.42	2687.08	902.05	241
$H^{(44C)}$	9006.88	3450.98	818.75	241
$H^{(37A)}$	6312.61	7713.15	1399.74	278
$H^{(37B)}$	6090.98	7437.11	636.15	278
$H^{(37C)}$	7730.7	7513.51	950.94	278
$H^{(38A)}$	4904.44	4841.2	934.54	302
$H^{(38B)}$	4311.92	5810.81	657.97	302

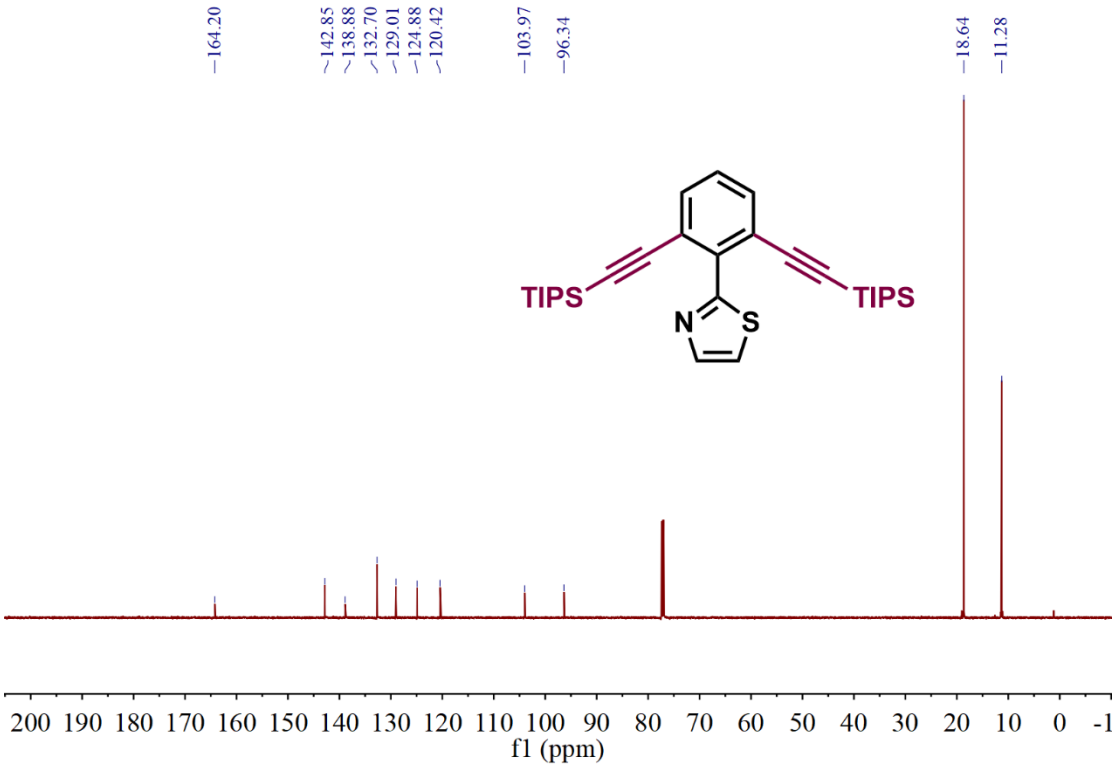
$H^{(38C)}$	4520.25	5971.24	1416.06	302
$H^{(5)}$	10674.16	6874.44	4228.91	78
$H^{(4)}$	12162.01	5833.91	3427.18	85
$H^{(7)}$	12330.6	5263.14	5497.23	79
$H^{(10)}$	7828.43	8430.36	5902.55	82
$H^{(8)}$	13829	4262.17	4698.64	86
$H^{(1A)}$	14593.62	3878.16	2513.99	160
$H^{(1B)}$	14232.14	5130.76	2783.54	160
$H^{(1C)}$	12909.71	4221.86	2651.59	160
$H^{(20)}$	5232.8	10413.47	8602.86	147
$H^{(22A)}$	3471.87	9492.55	7763.66	268
$H^{(22B)}$	3984.03	8716.1	8202.04	268
$H^{(22C)}$	4669.63	8592.12	7507.32	268
$H^{(21A)}$	6416.41	10306.39	7358.72	272
$H^{(21B)}$	6781.43	11267.99	7986.28	272
$H^{(21C)}$	5133.59	11096.16	7674.01	272
$H^{(17)}$	5881.06	7703.9	8568.5	142
$H^{(18A)}$	8511.68	7787.92	9283.42	238
$H^{(18B)}$	8229.62	7075.74	8562.66	238
$H^{(18C)}$	7255.28	6830.31	9129.43	238
$H^{(19A)}$	5393.25	8096.47	9666.62	234
$H^{(19B)}$	4983.34	9101.9	9382.79	234
$H^{(19C)}$	6487.01	9152.23	9800.57	234
$H^{(14)}$	8965.53	10693.74	8514.36	173
$H^{(15A)}$	11082.63	10469.17	8984.92	248
$H^{(15B)}$	10623.77	9417.45	8422.84	248
$H^{(15C)}$	10427.21	9394.21	9156.71	248
$H^{(16A)}$	8069.38	10756.17	9760.81	266
$H^{(16B)}$	7530.4	11497.94	9306.03	266
$H^{(16C)}$	9208.93	11624.2	9583.75	266

5. NMR charts

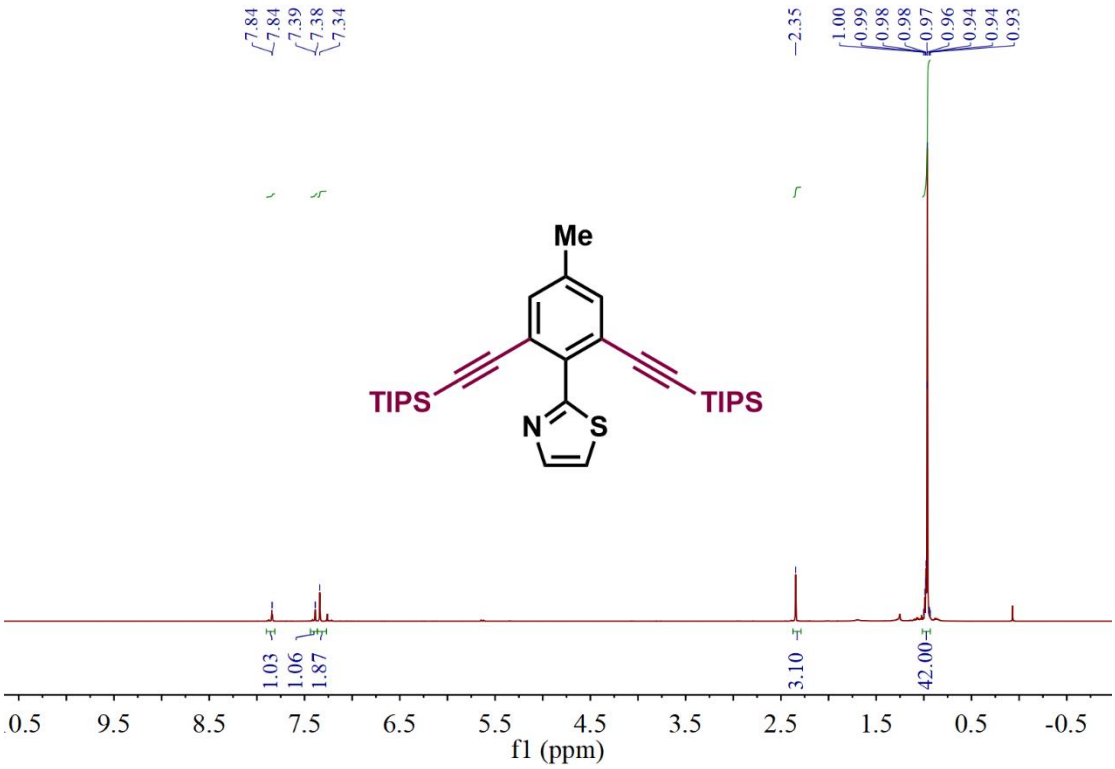
3aa | ^{1}H NMR ($CDCl_3$, 600 MHz)



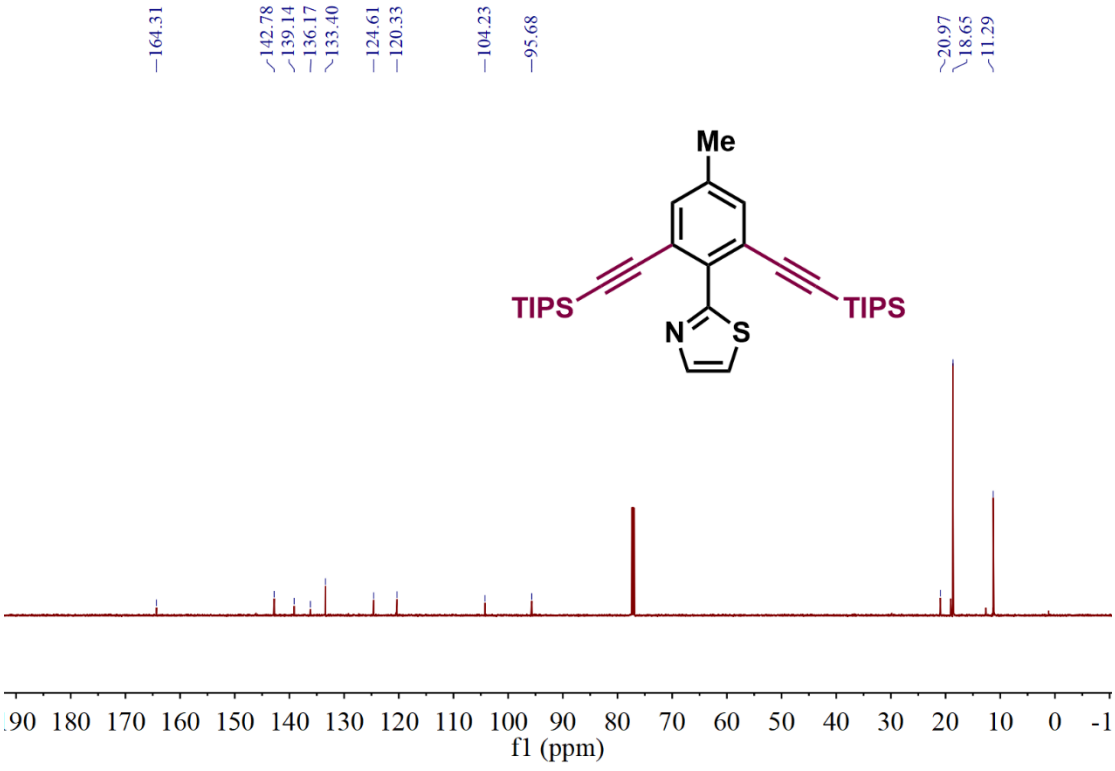
3aa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



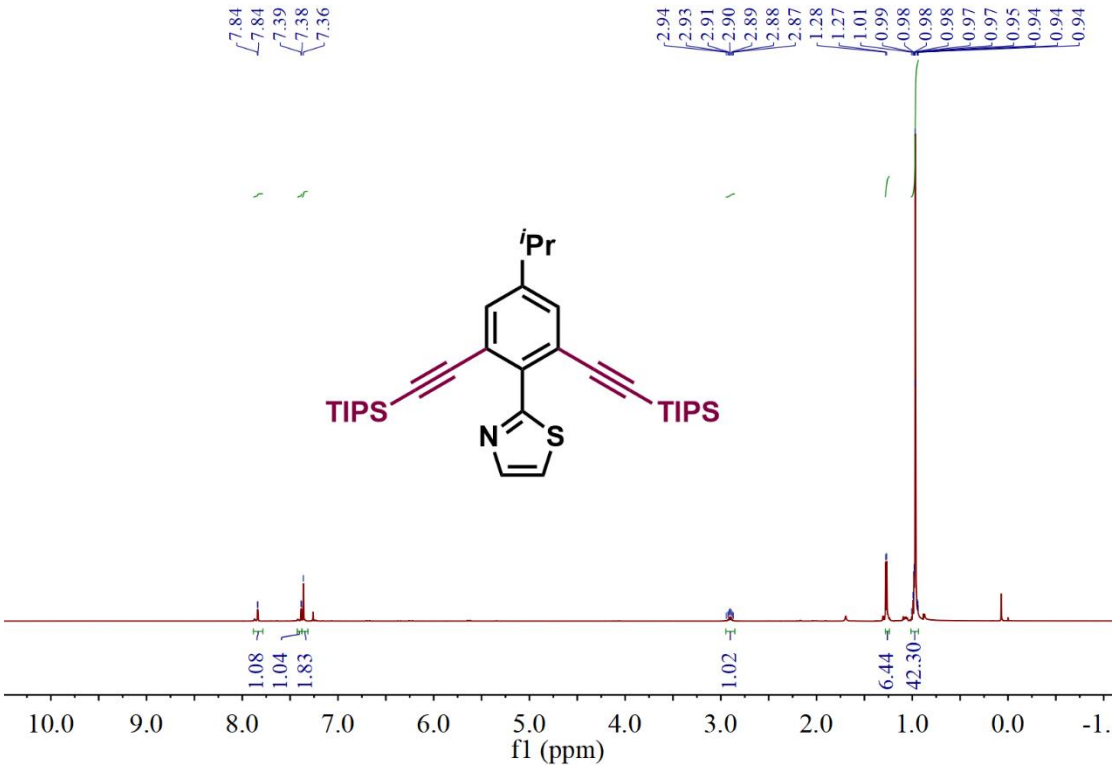
3ba | ^{1}H NMR ($CDCl_3$, 600 MHz)



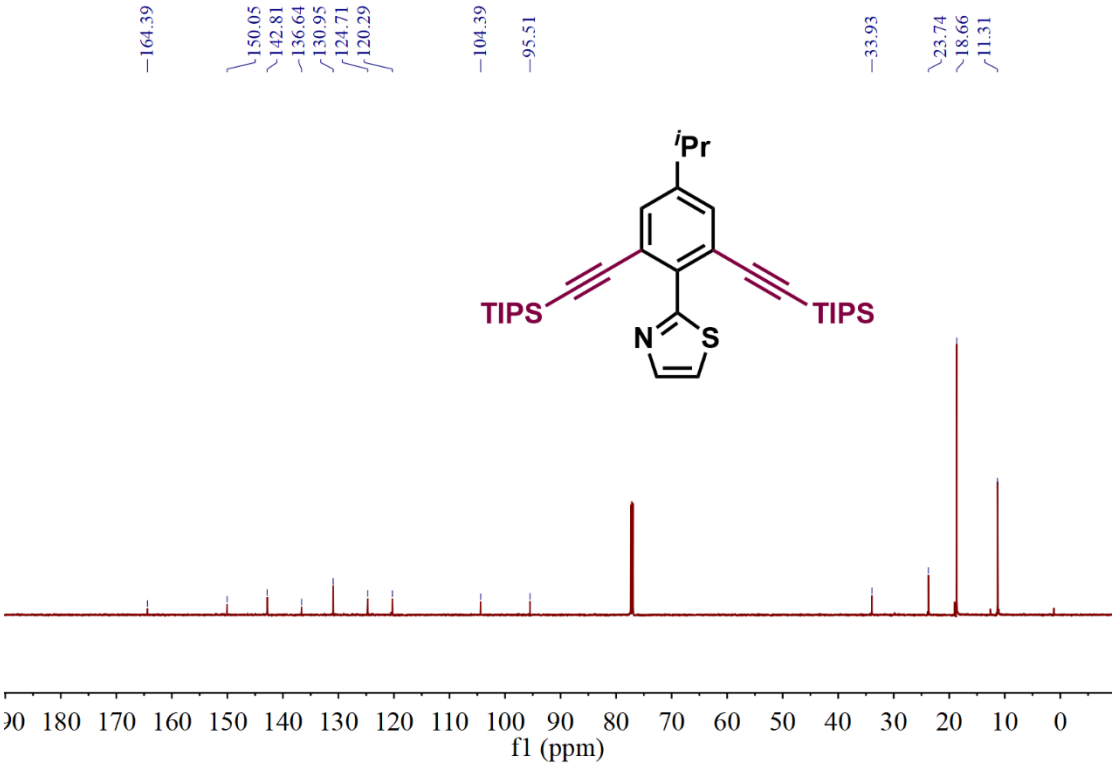
3ba | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



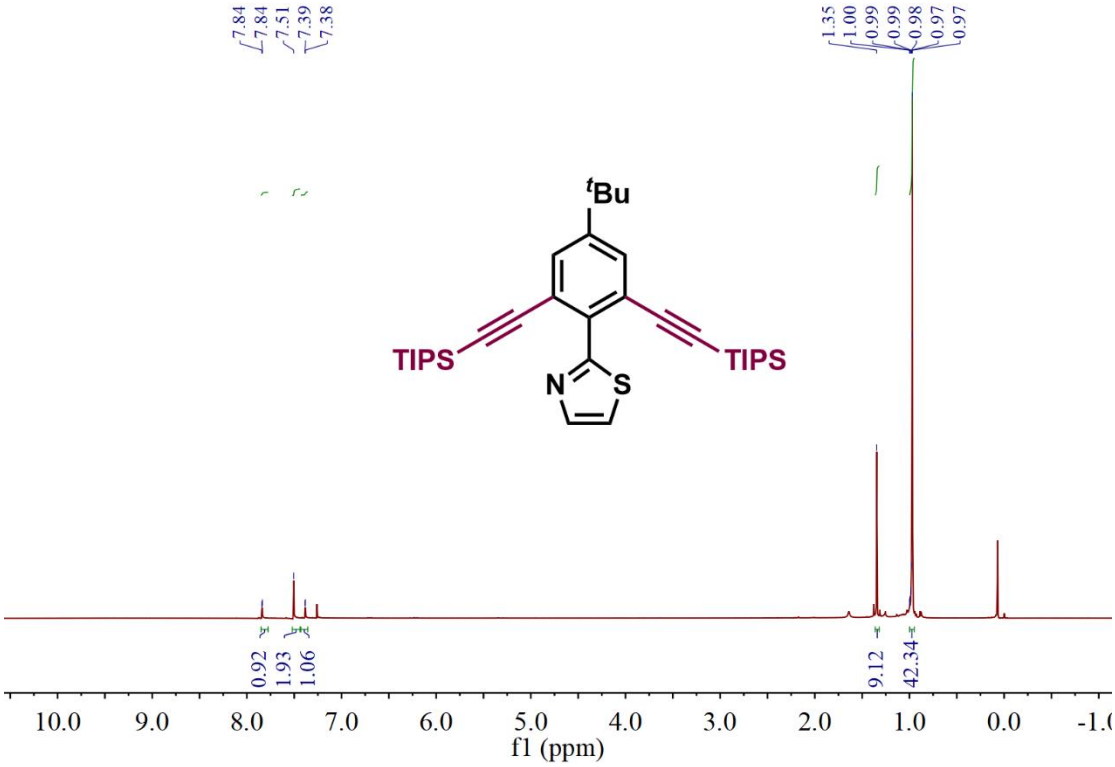
3ca | ^{1}H NMR ($CDCl_3$, 600 MHz)



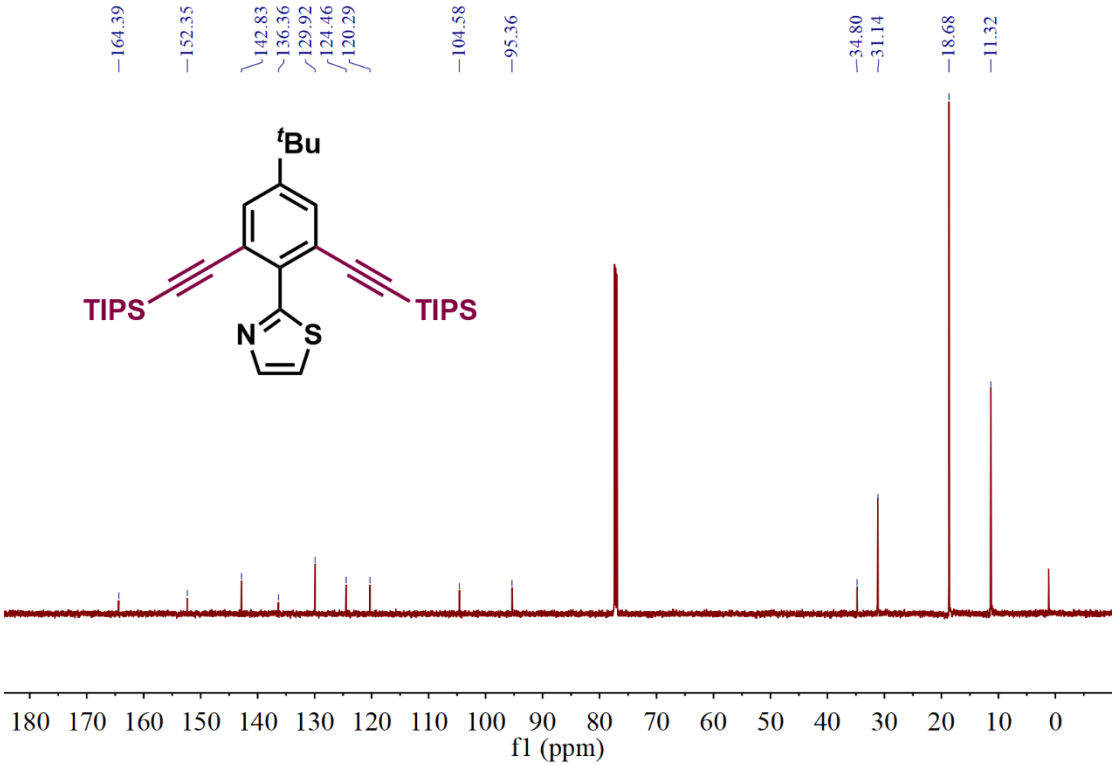
3ca | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



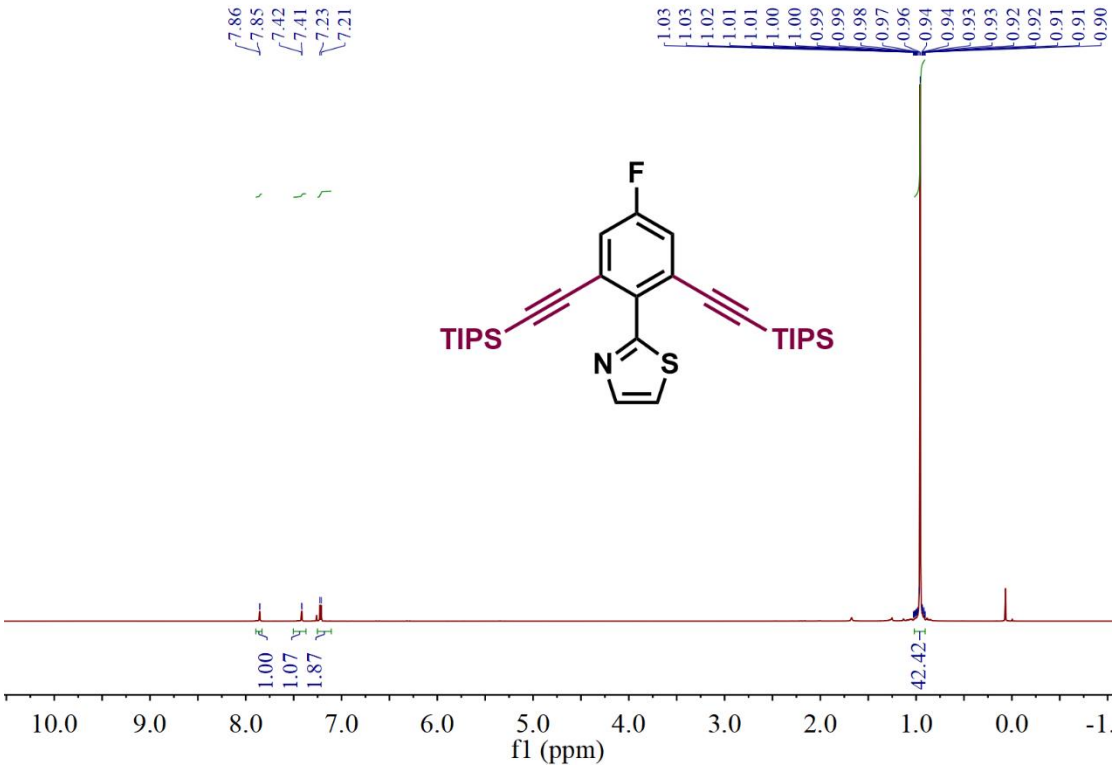
3da | ^{1}H NMR ($CDCl_3$, 600 MHz)



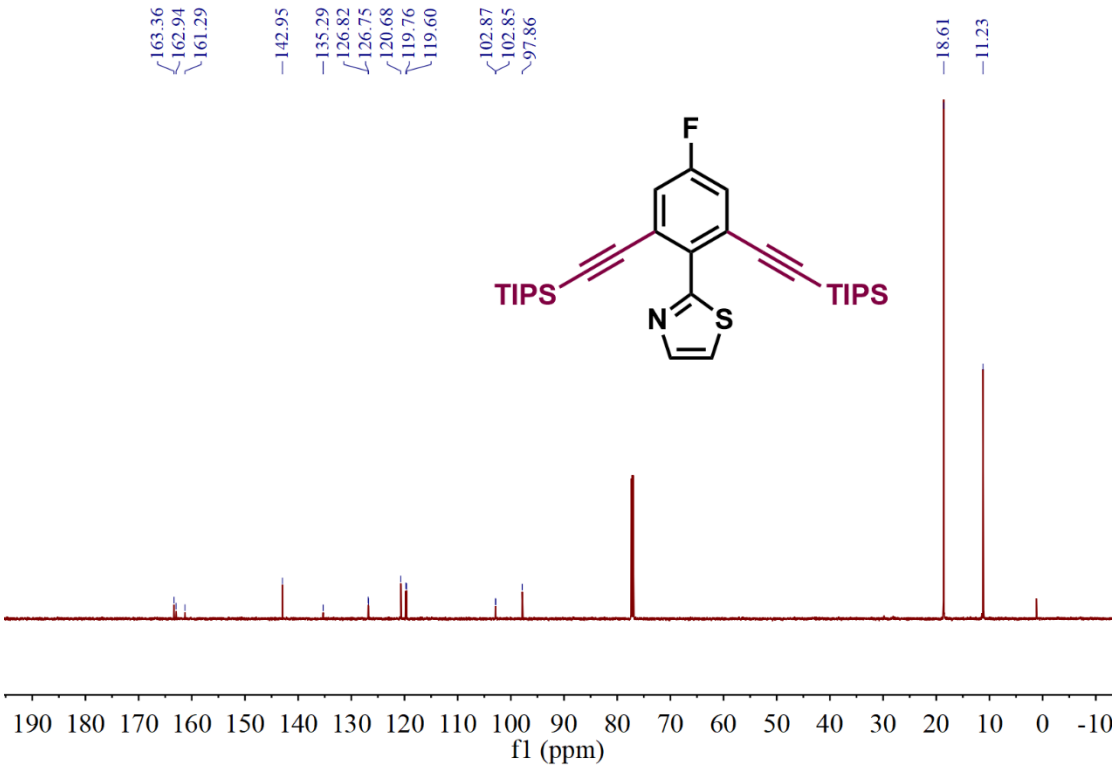
3da | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



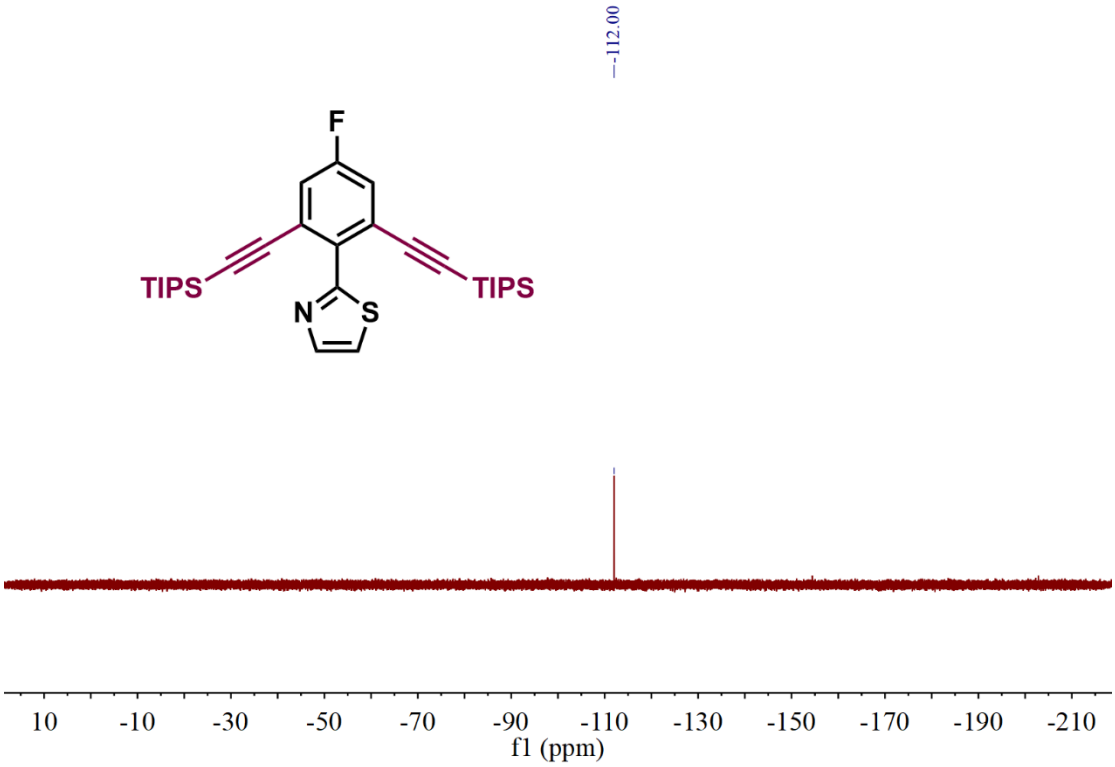
3ea | ^{1}H NMR ($CDCl_3$, 600 MHz)



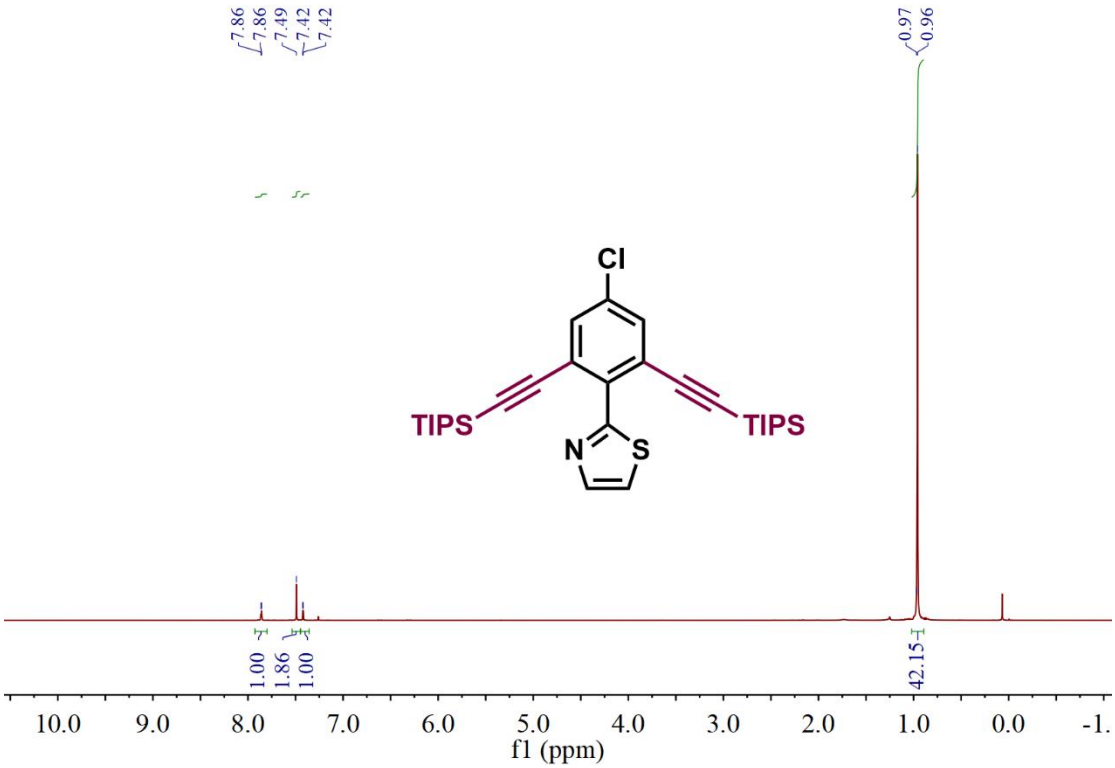
3ea | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



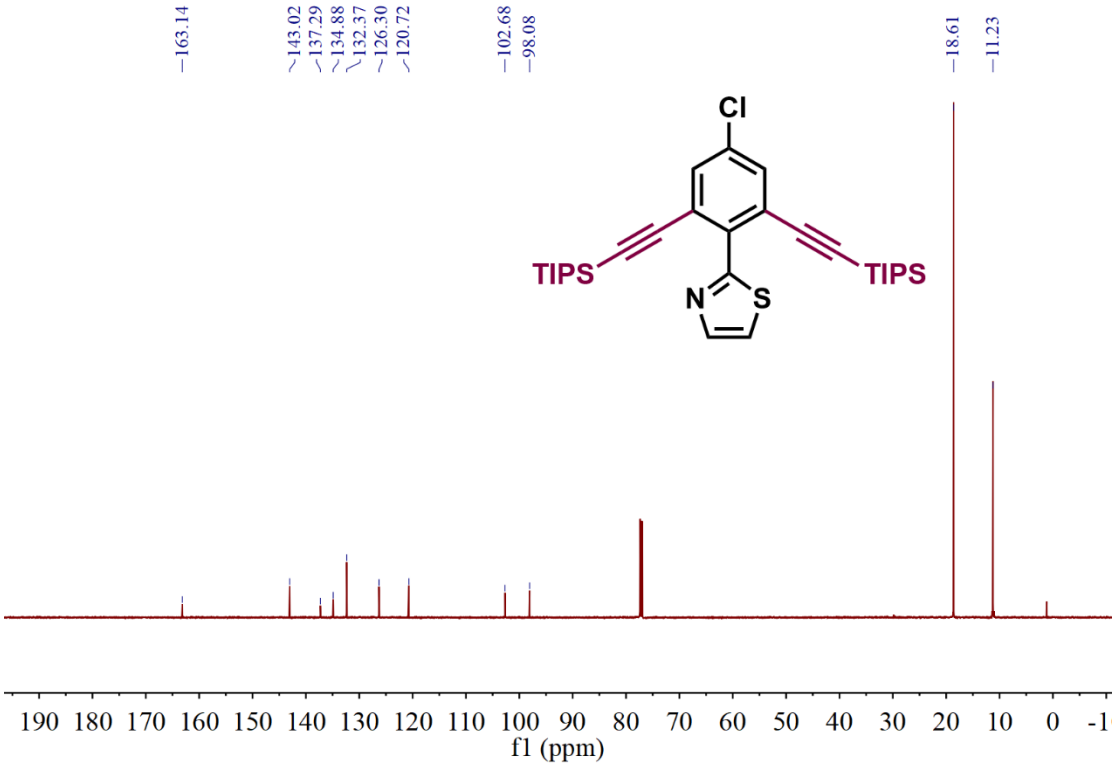
3ea | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



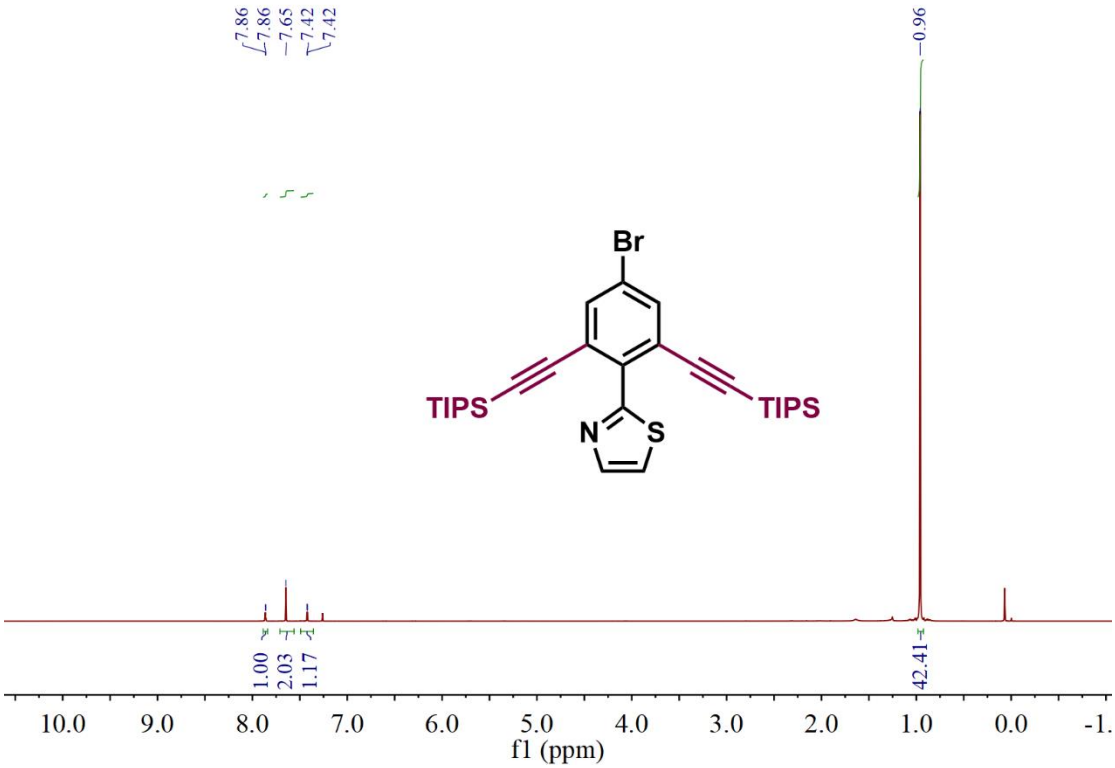
3fa | ^{1}H NMR ($CDCl_3$, 600 MHz)



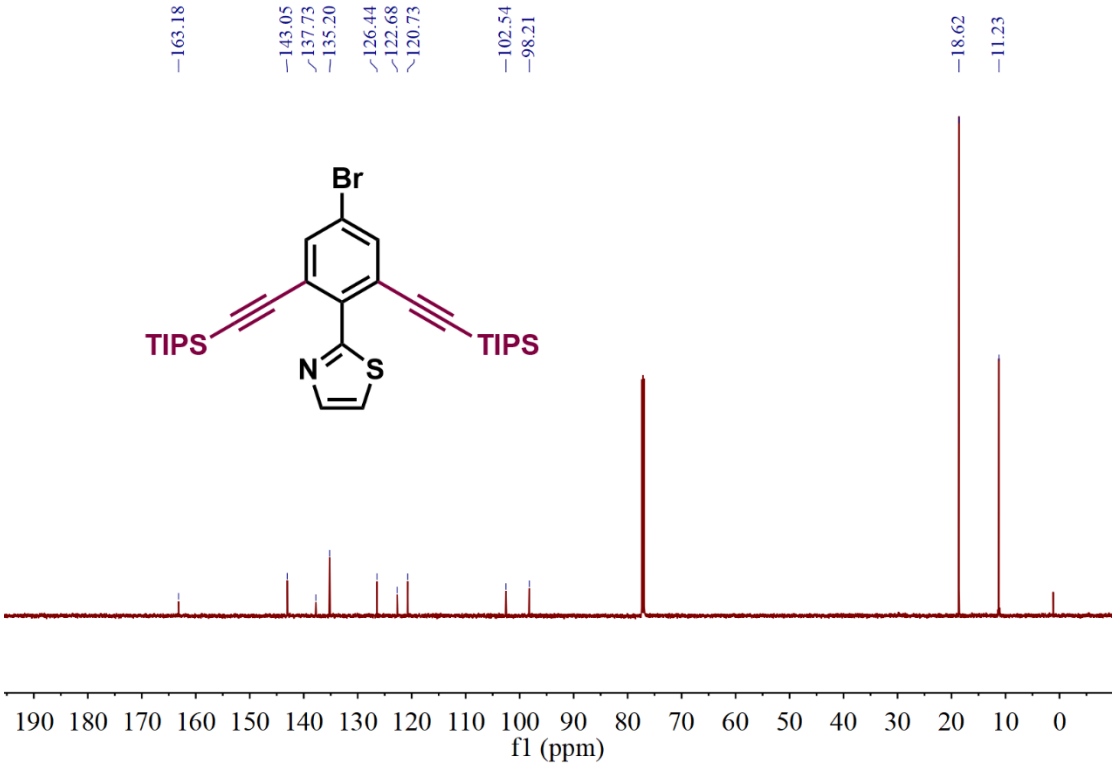
3fa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



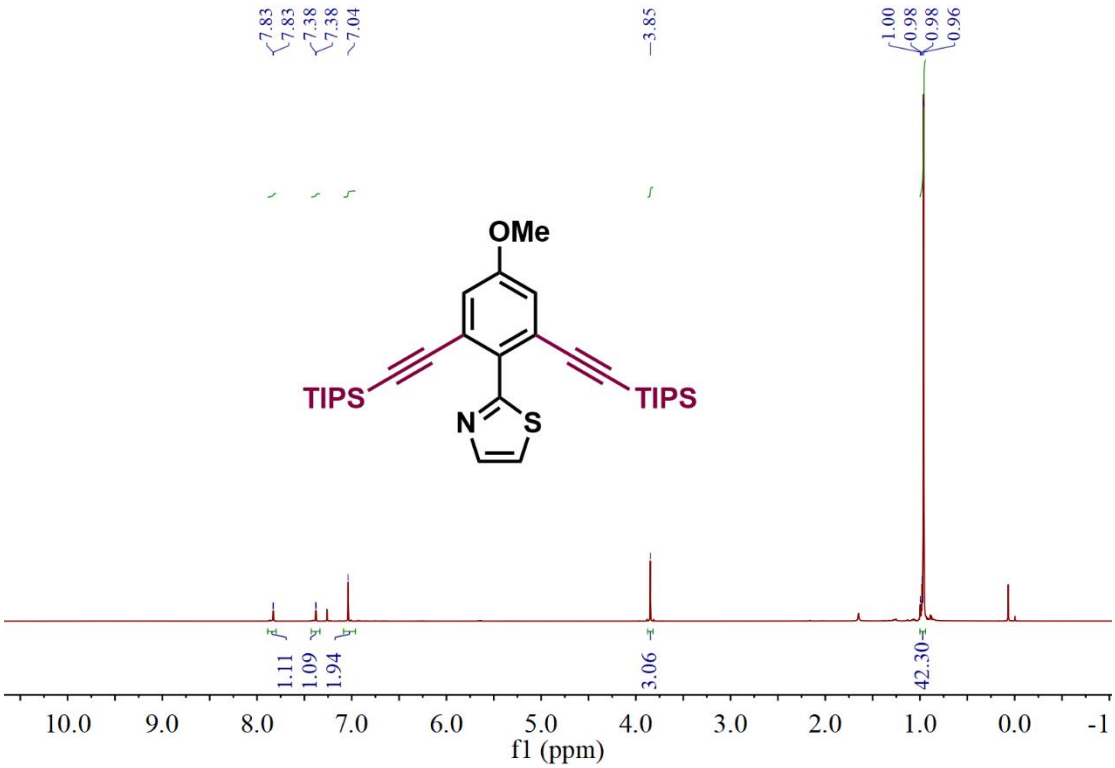
3ga | ^{1}H NMR ($CDCl_3$, 600 MHz)



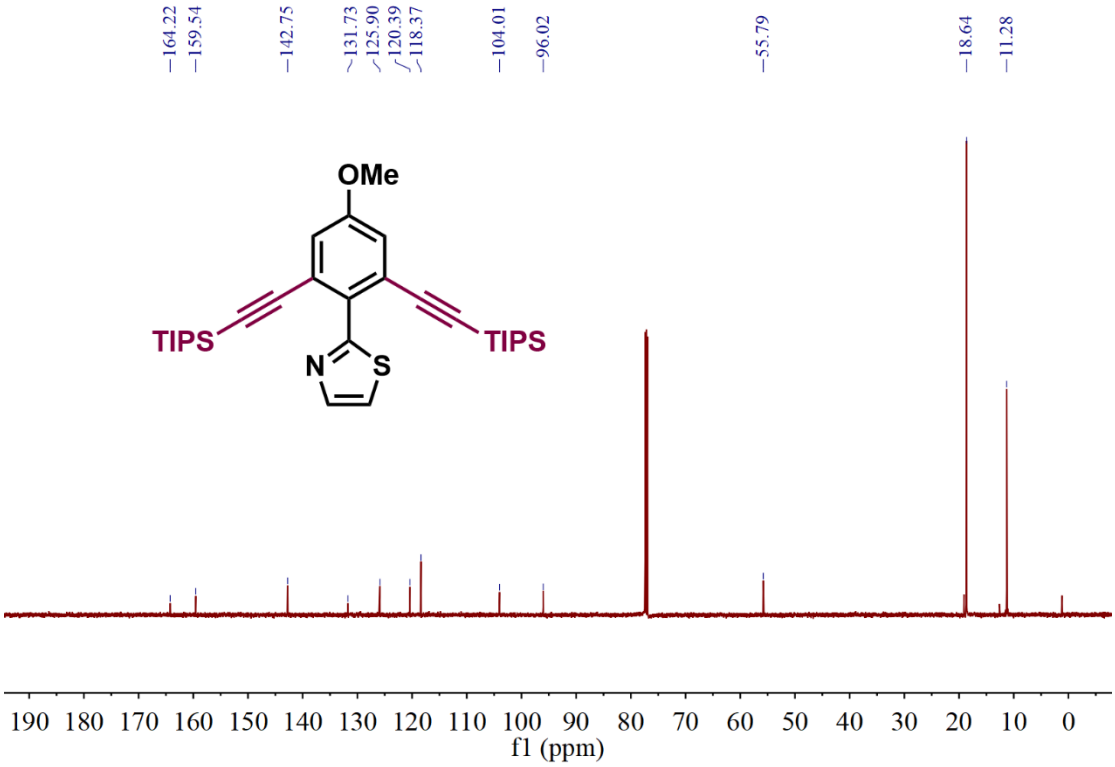
3ga | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



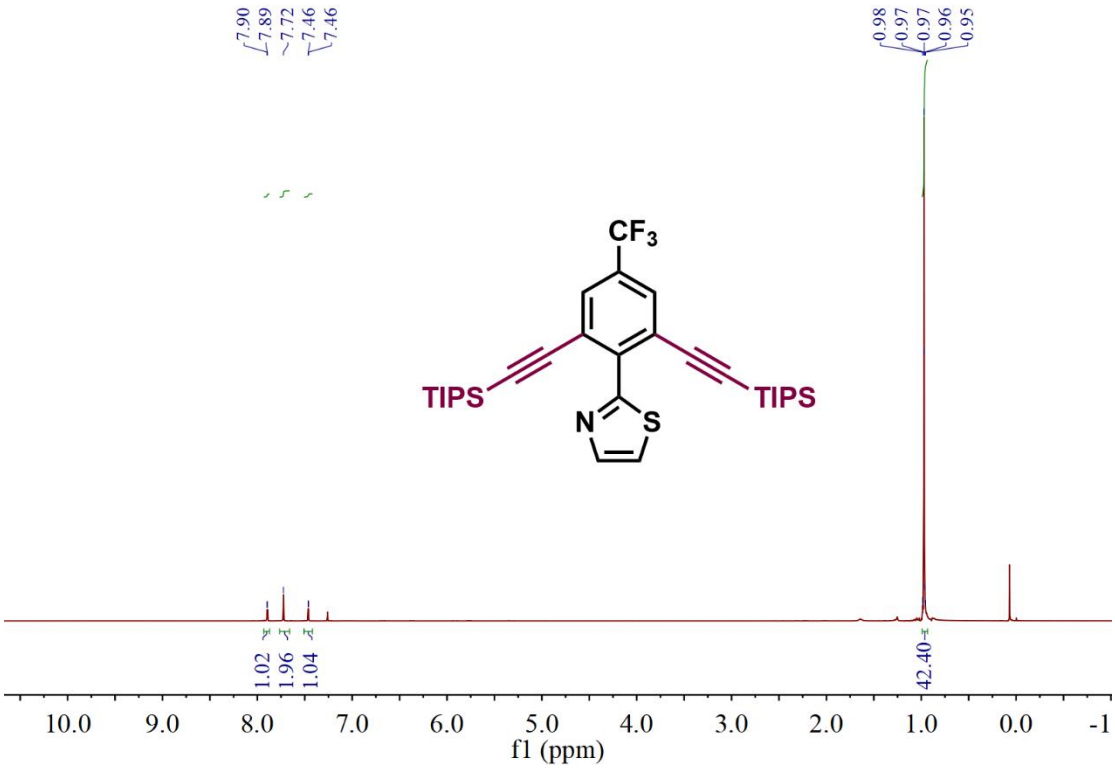
3ha | ^{1}H NMR ($CDCl_3$, 600 MHz)



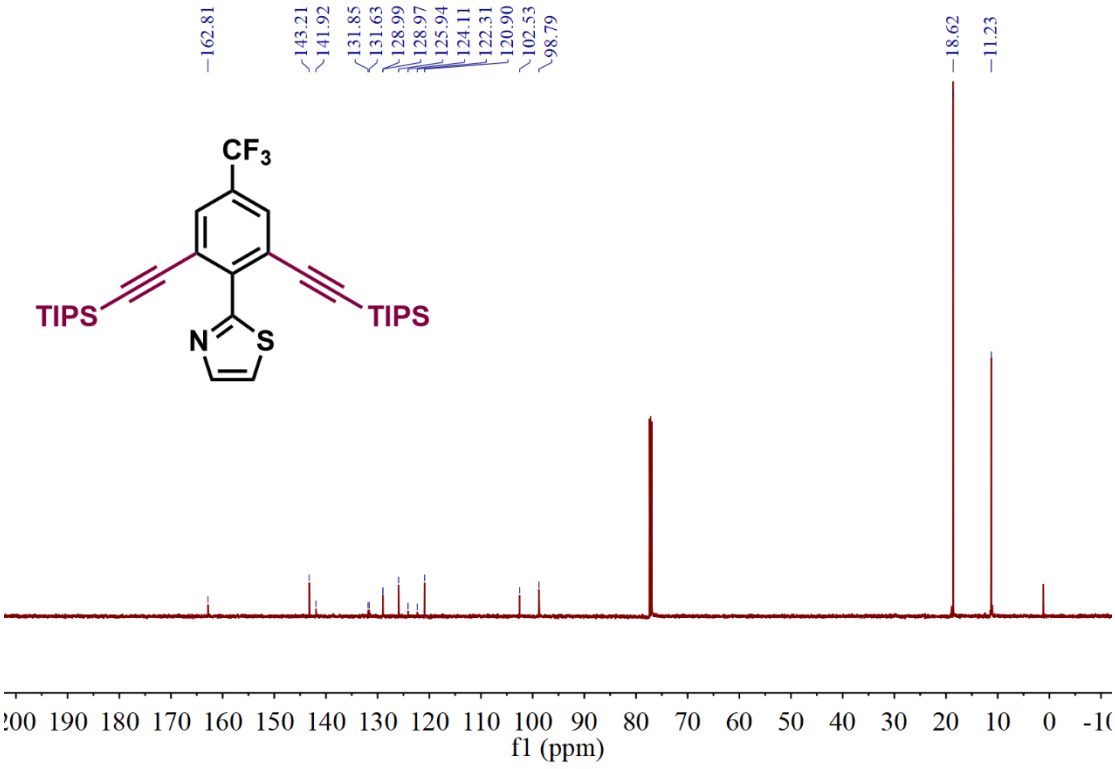
3ha | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



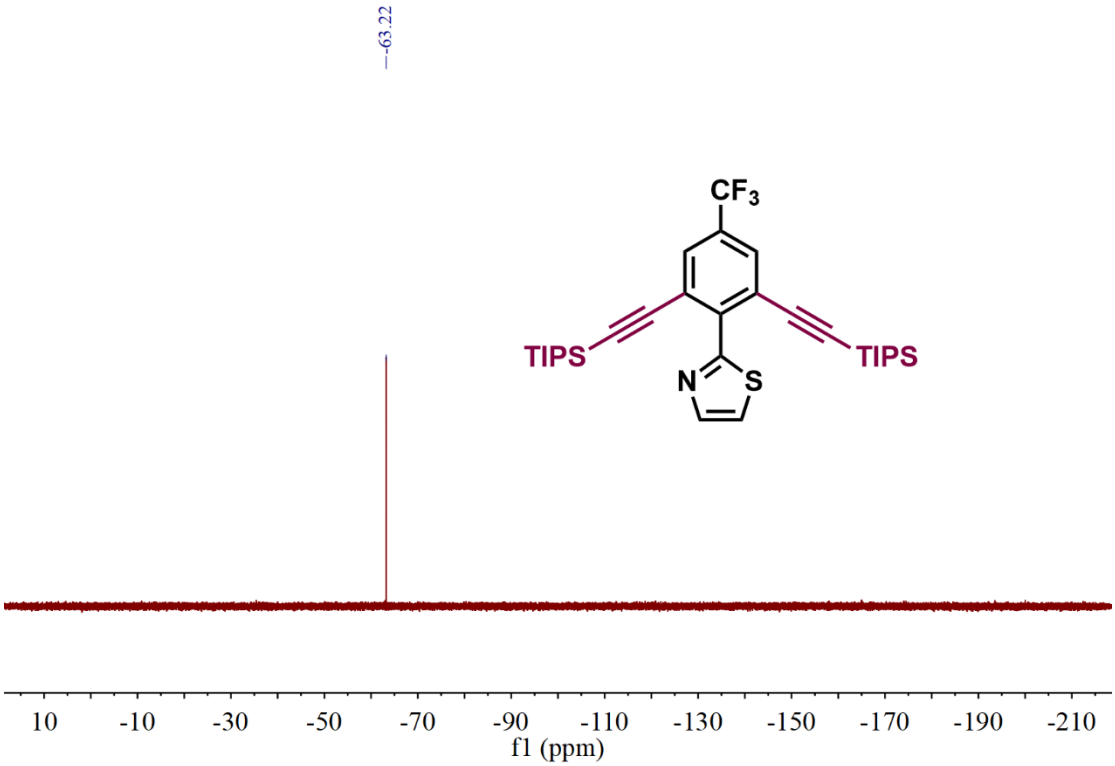
3ia | ^{1}H NMR ($CDCl_3$, 600 MHz)



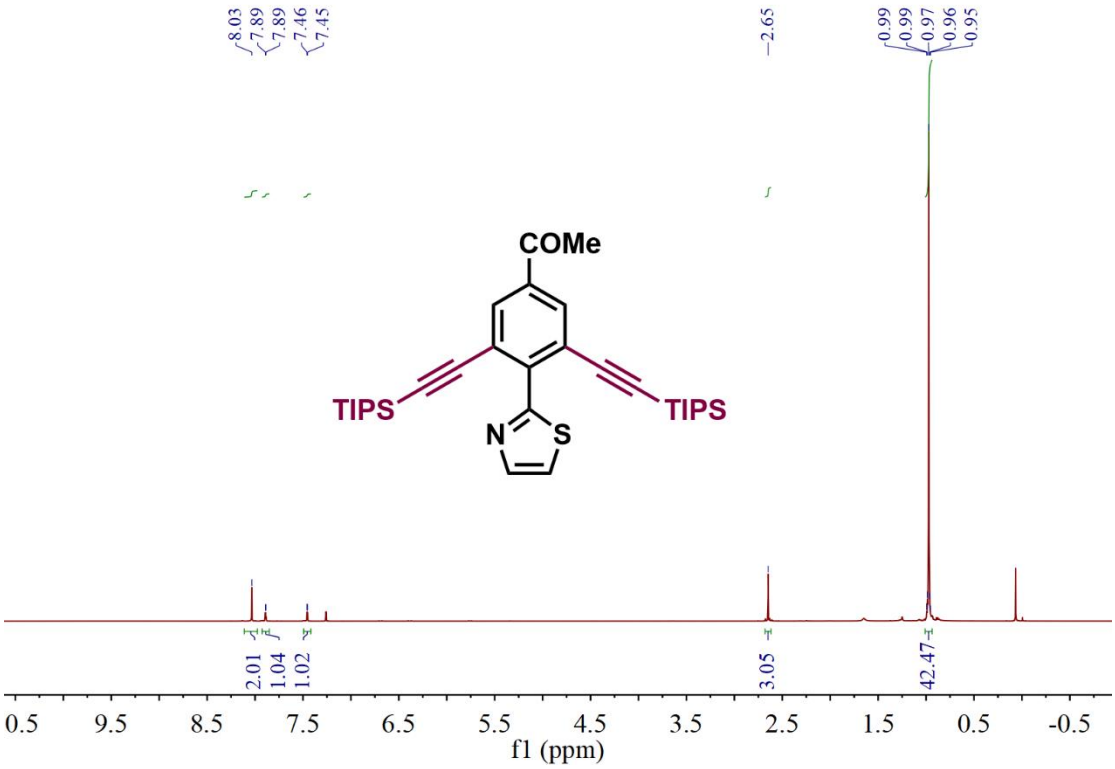
3ia | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



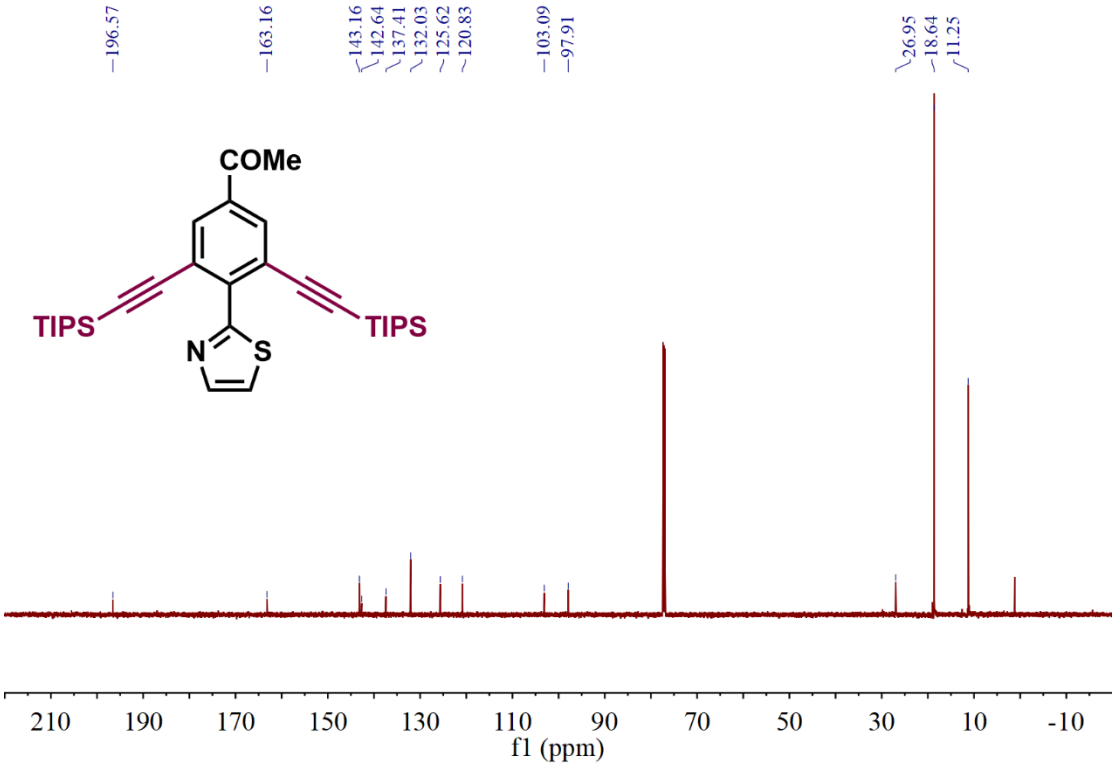
3ia | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



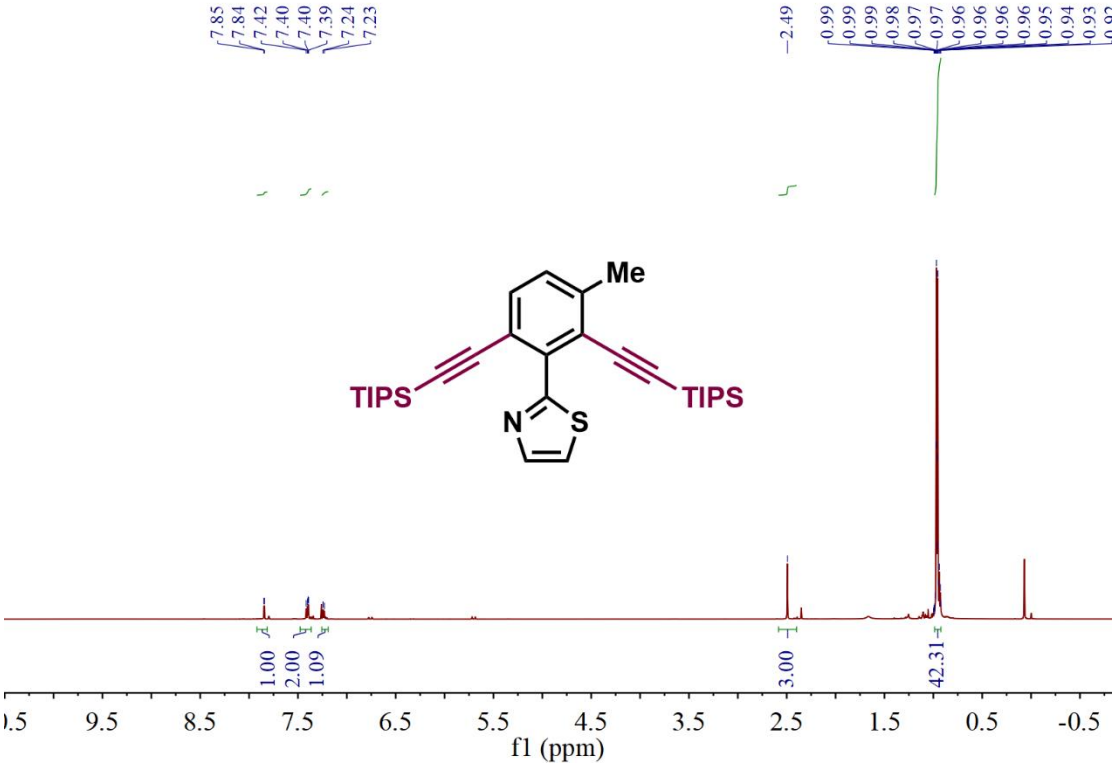
3ja | ^{1}H NMR ($CDCl_3$, 600 MHz)



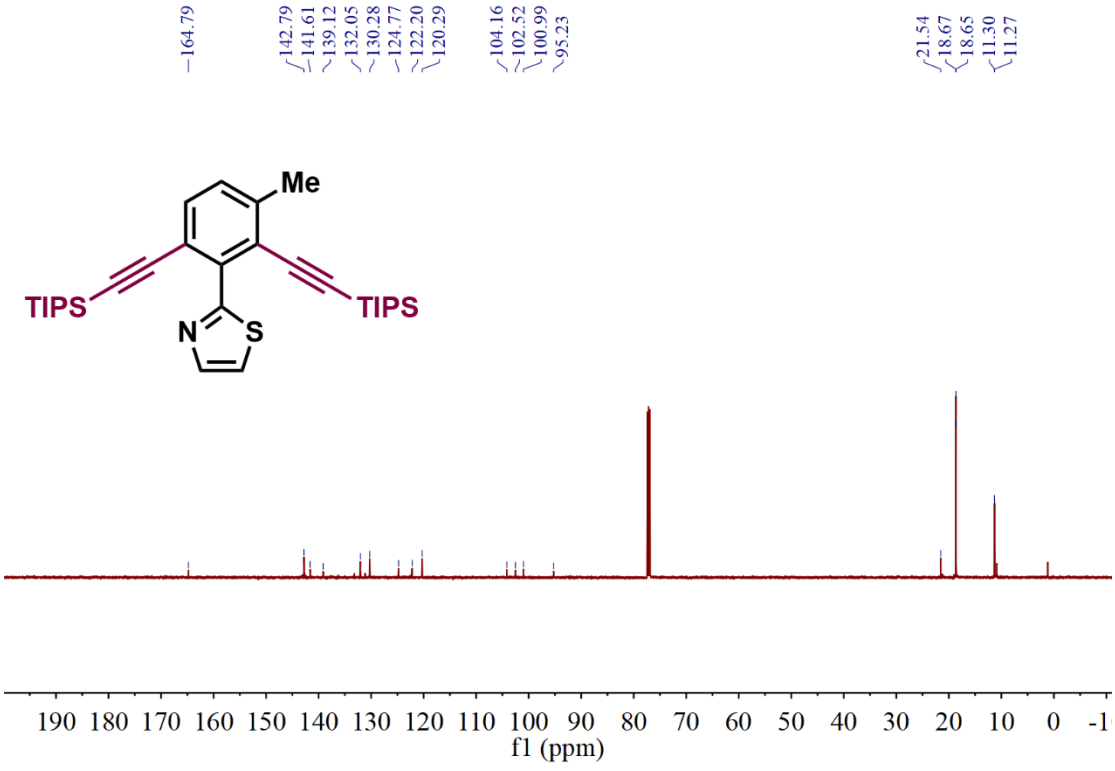
3ja | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



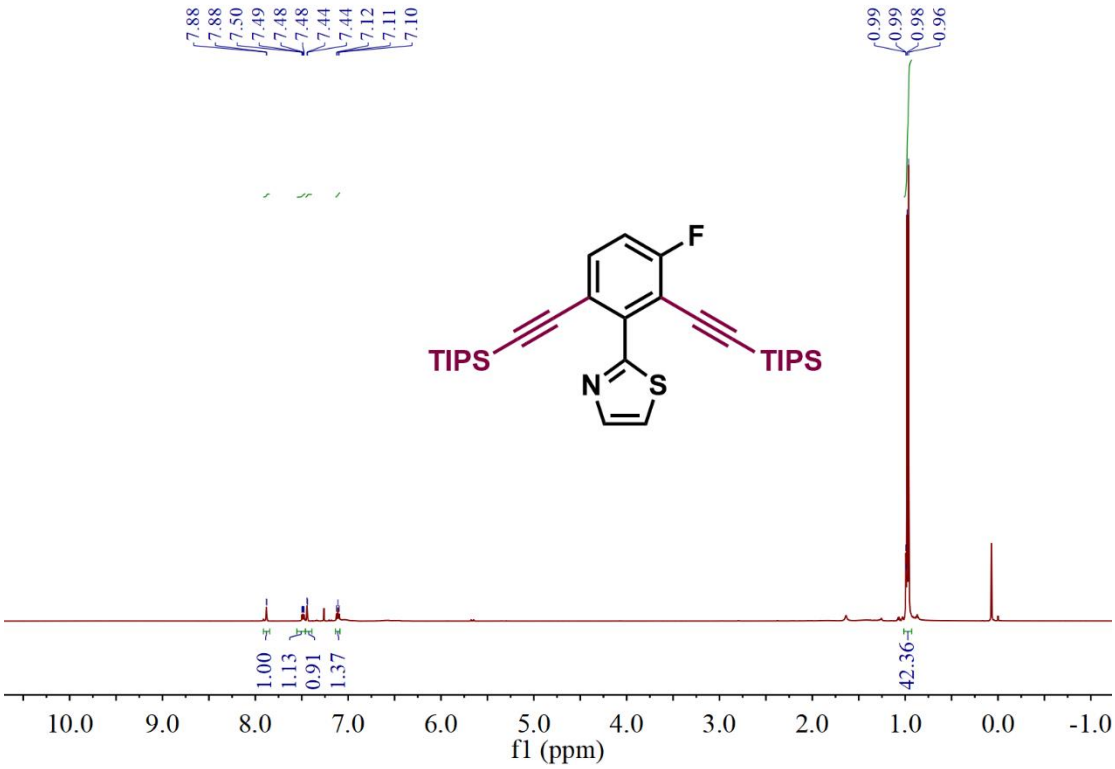
3ka | ^{1}H NMR ($CDCl_3$, 600 MHz)



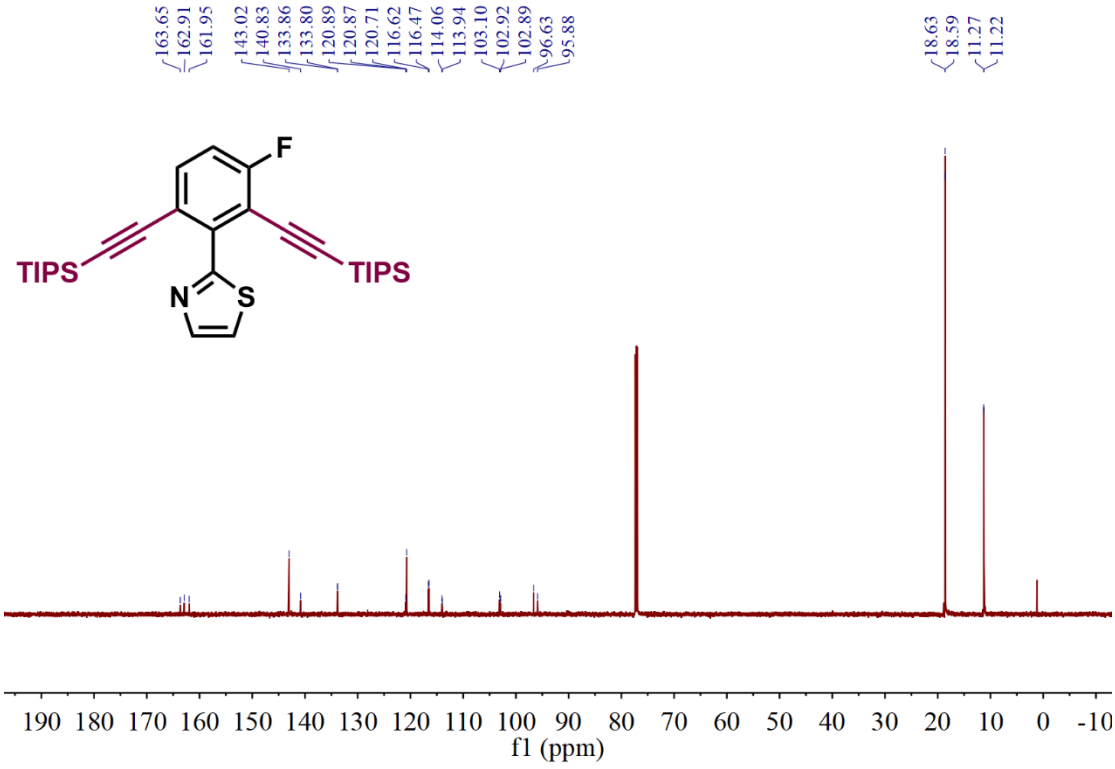
3ka | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



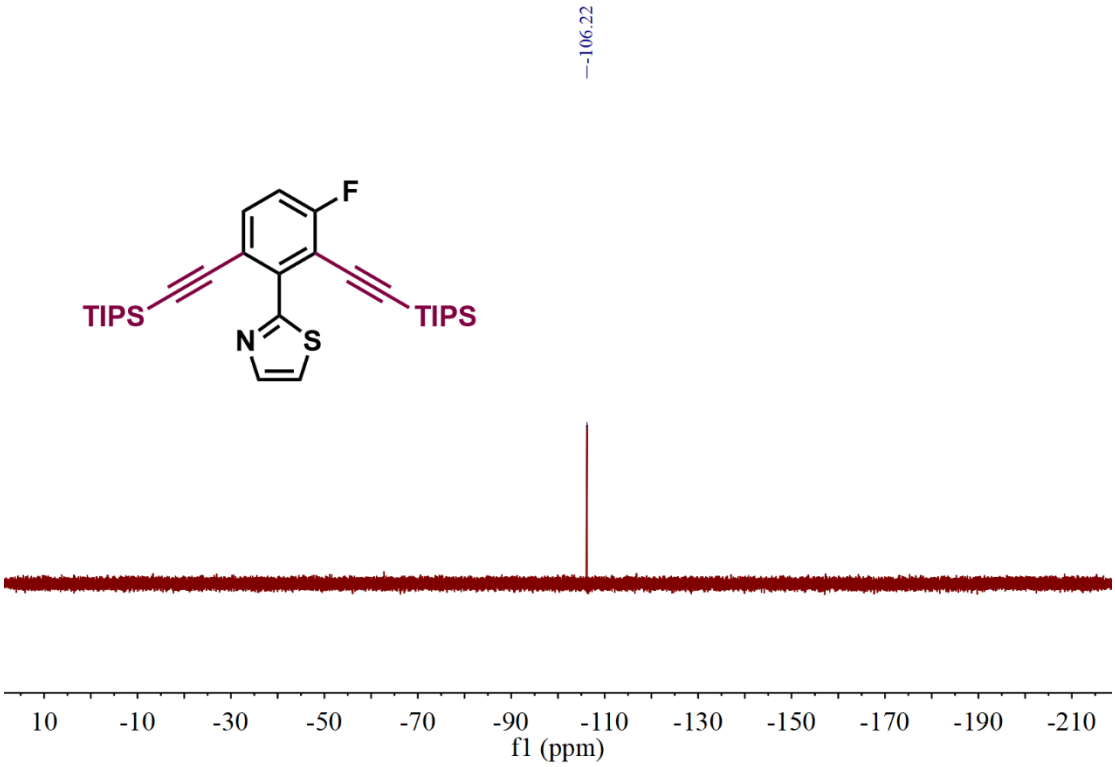
3la | ^{1}H NMR ($CDCl_3$, 600 MHz)



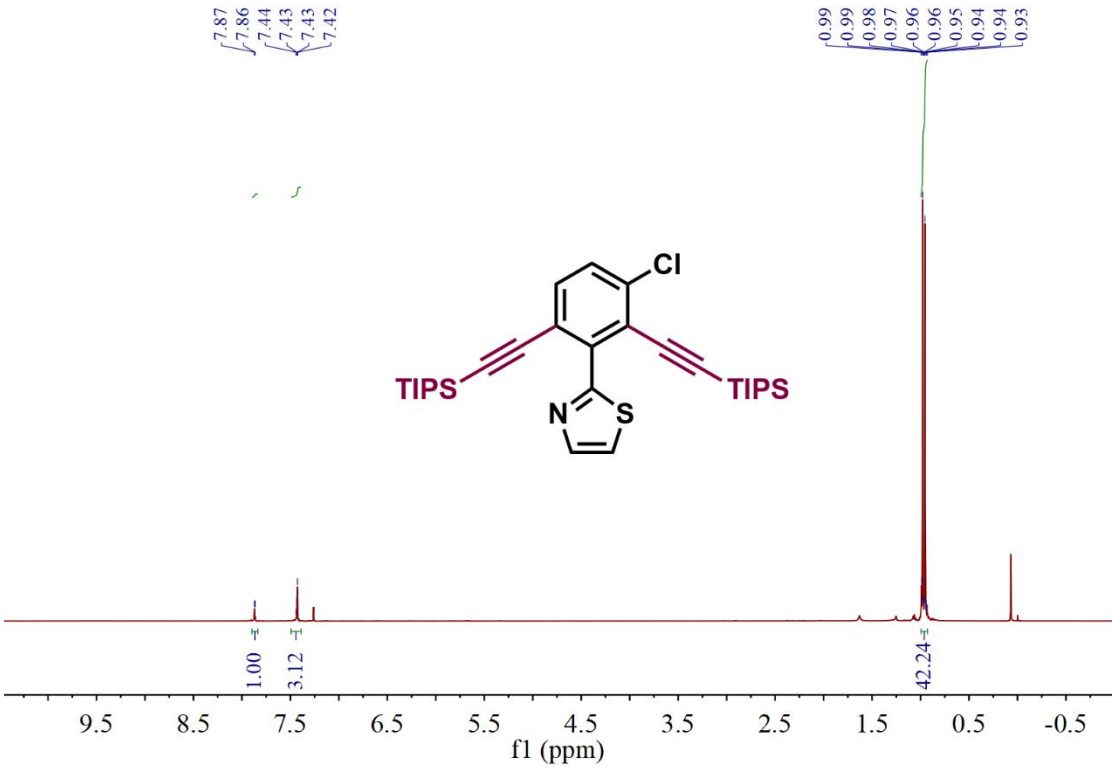
3la | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



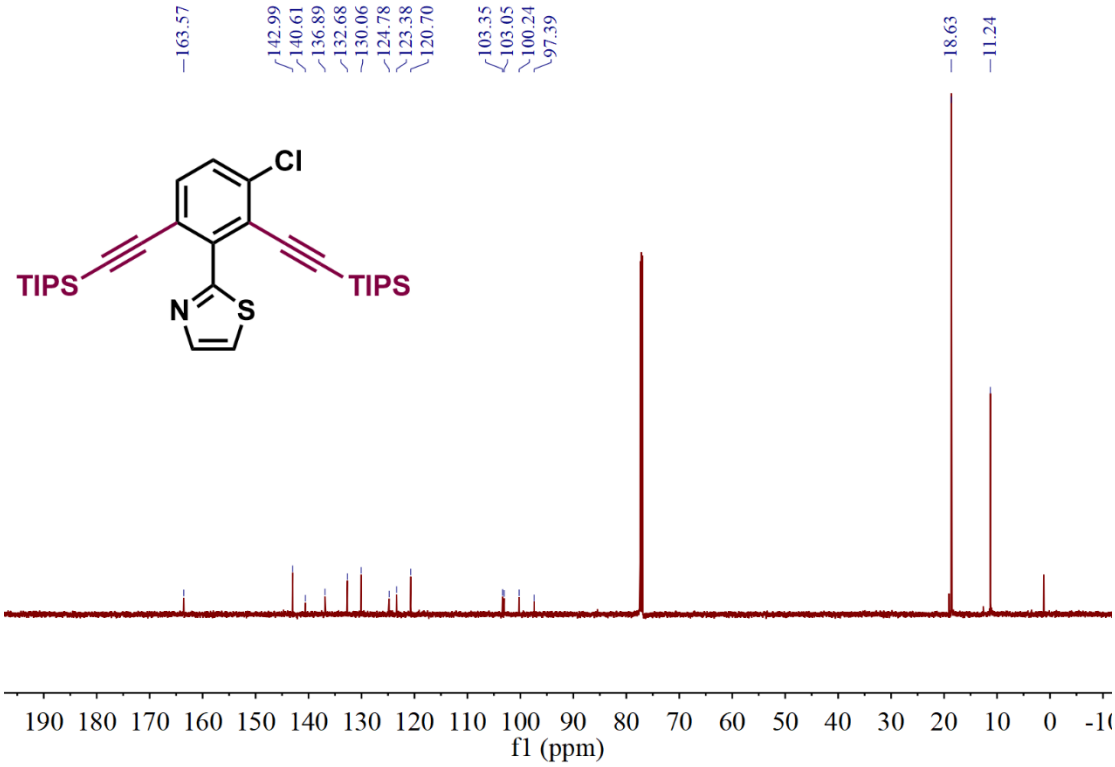
3la | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



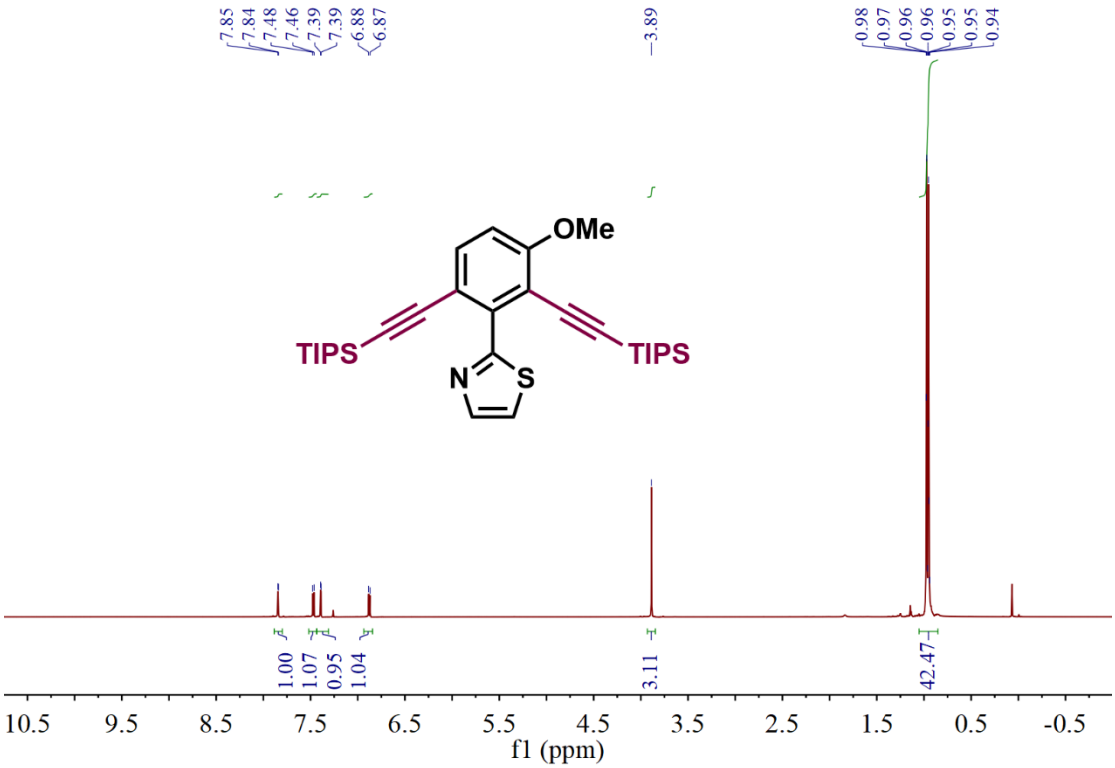
3ma | ^{1}H NMR ($CDCl_3$, 600 MHz)



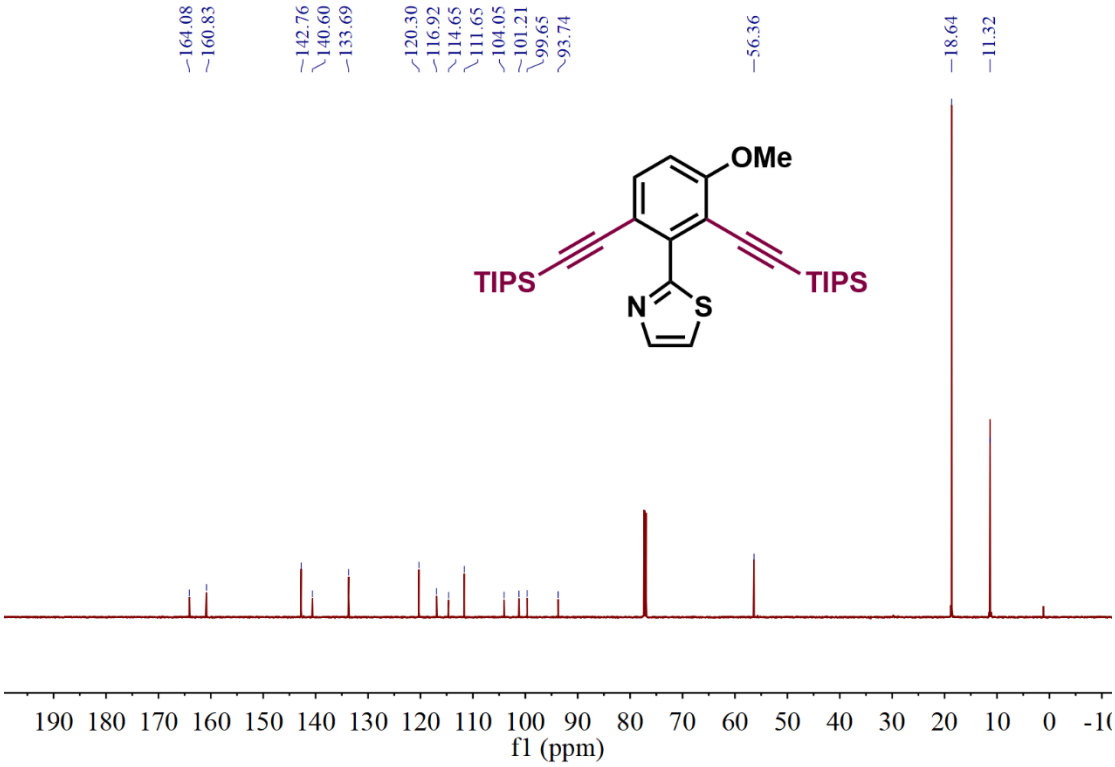
3ma | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



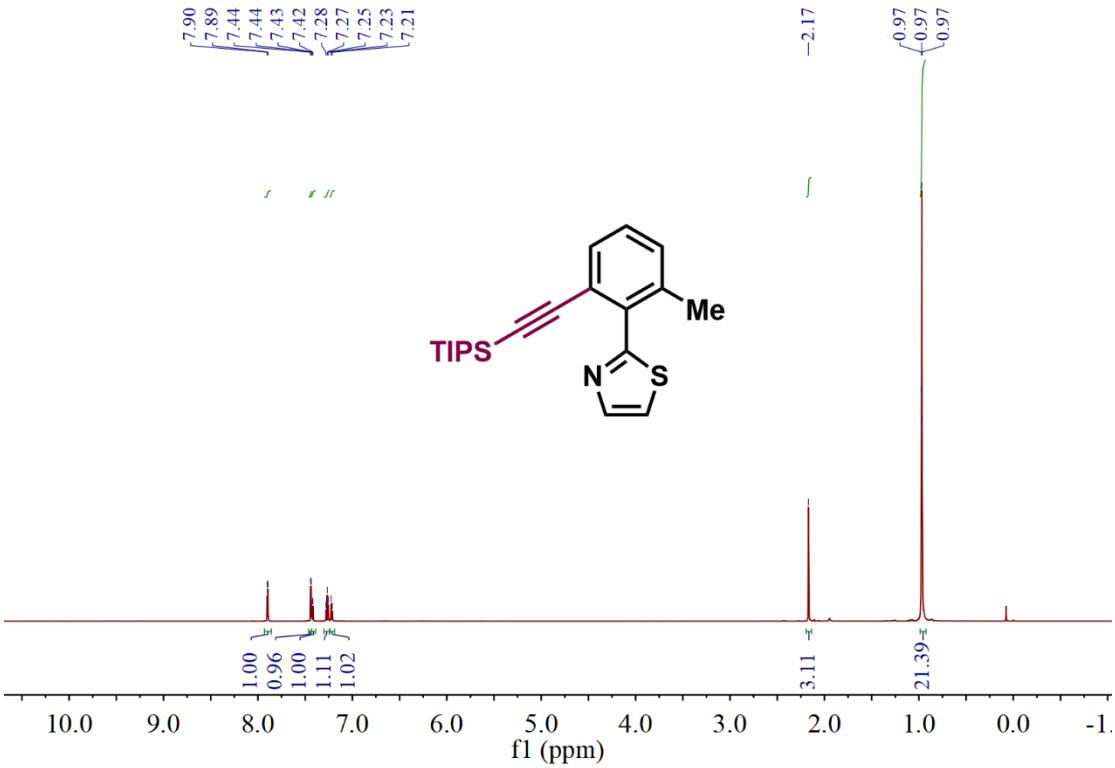
3na | ^{1}H NMR ($CDCl_3$, 600 MHz)



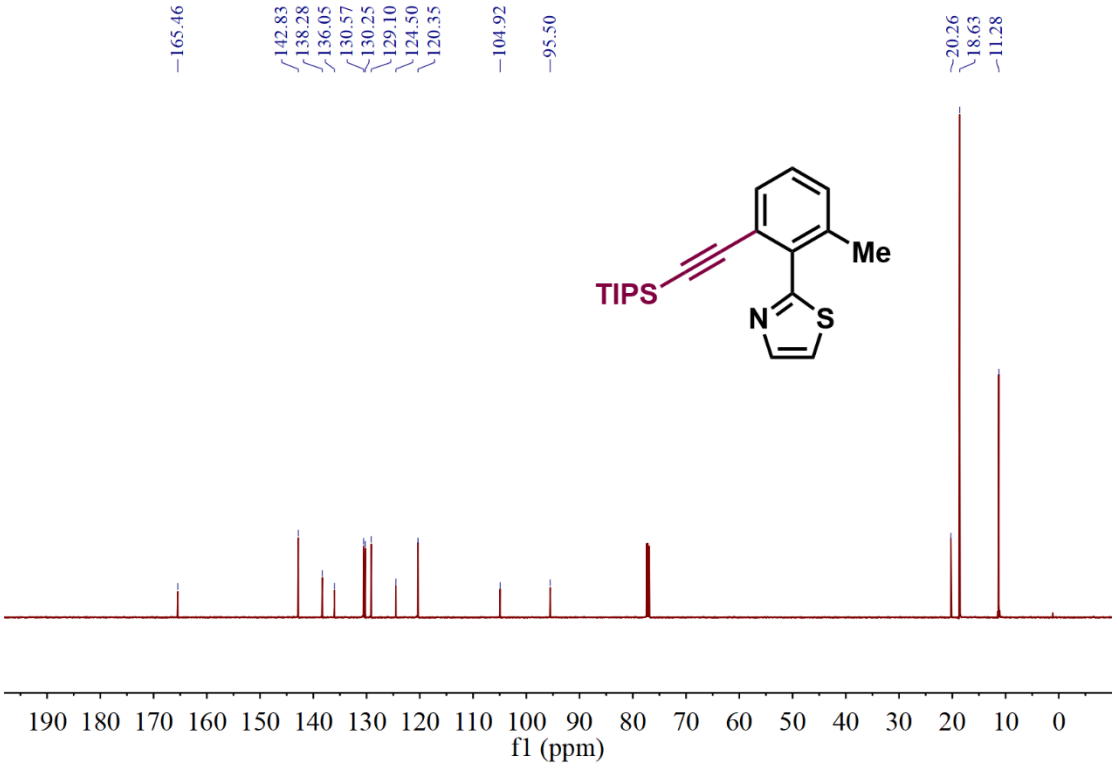
3na | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



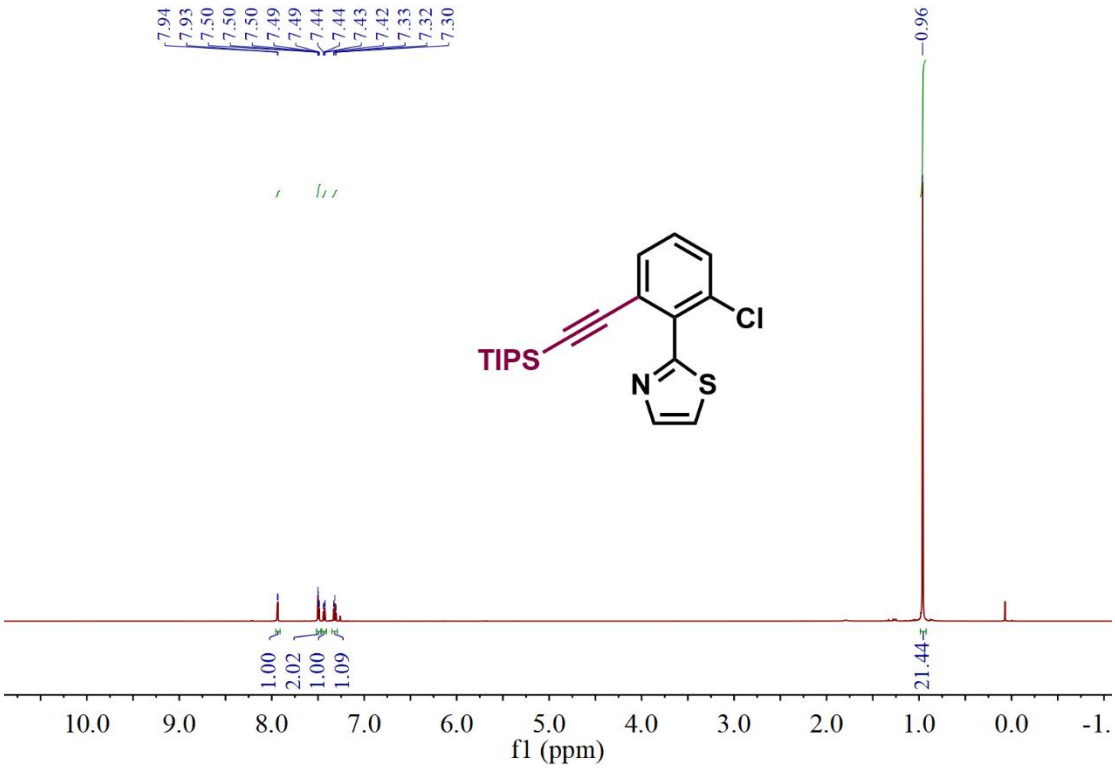
3oa | ^{1}H NMR ($CDCl_3$, 600 MHz)



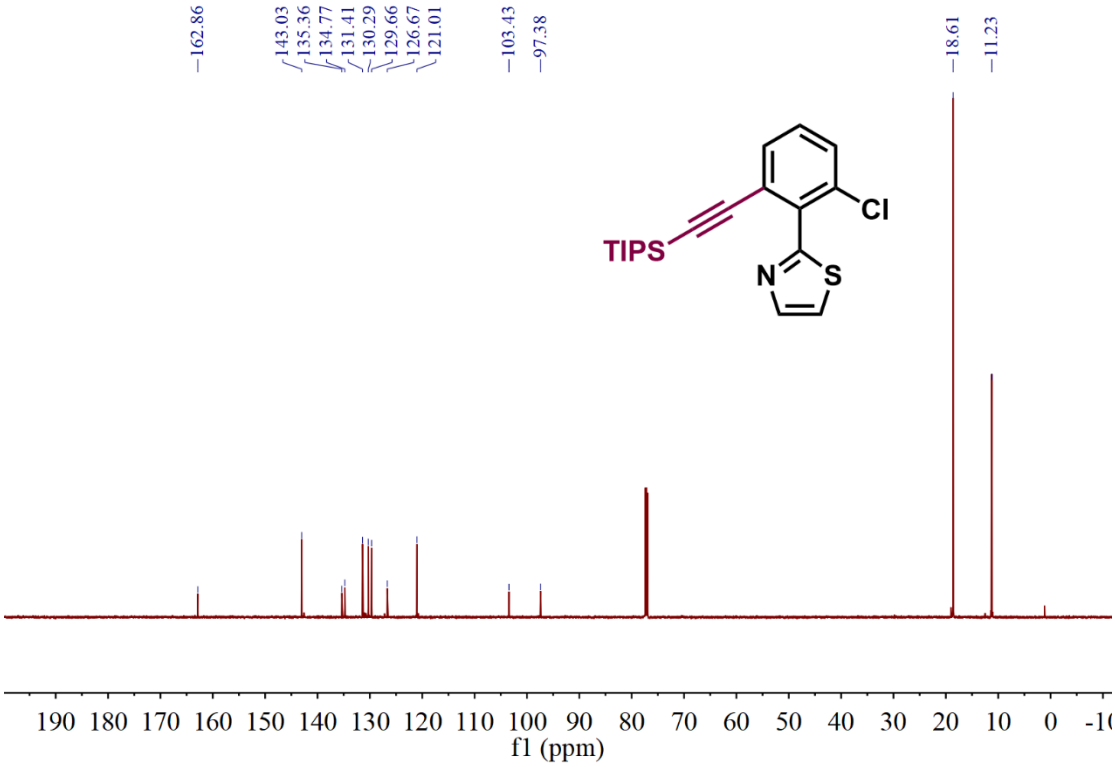
3oa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



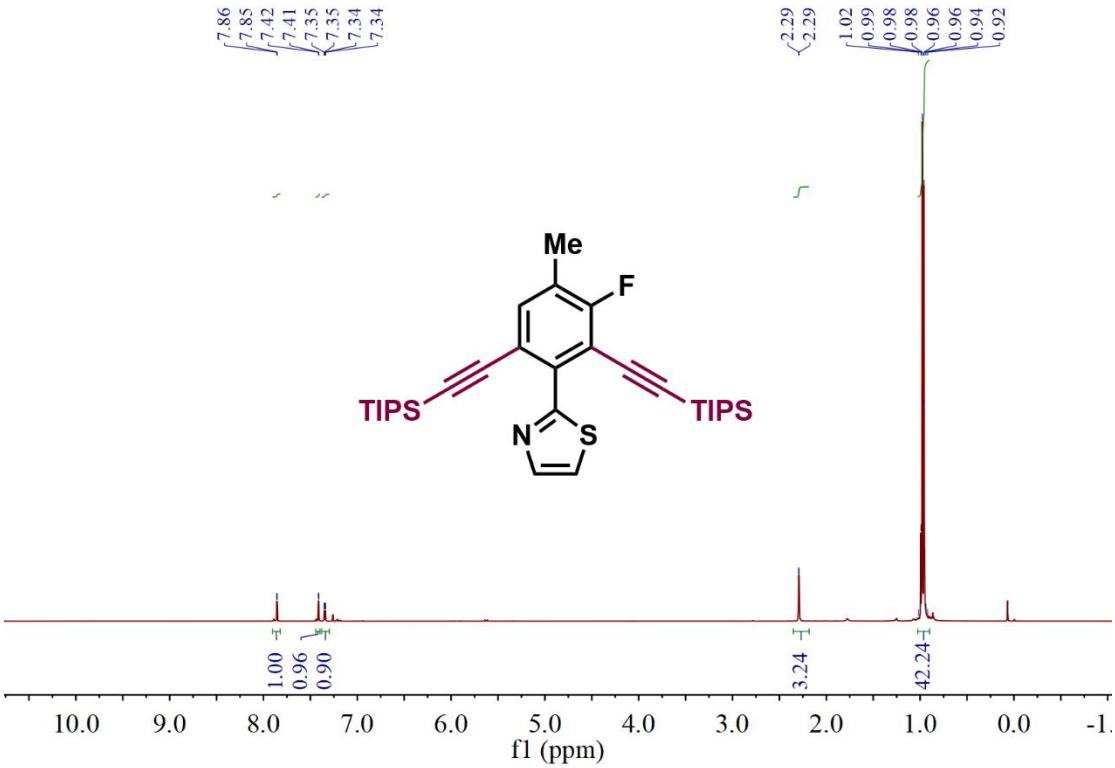
3pa | ^{1}H NMR ($CDCl_3$, 600 MHz)



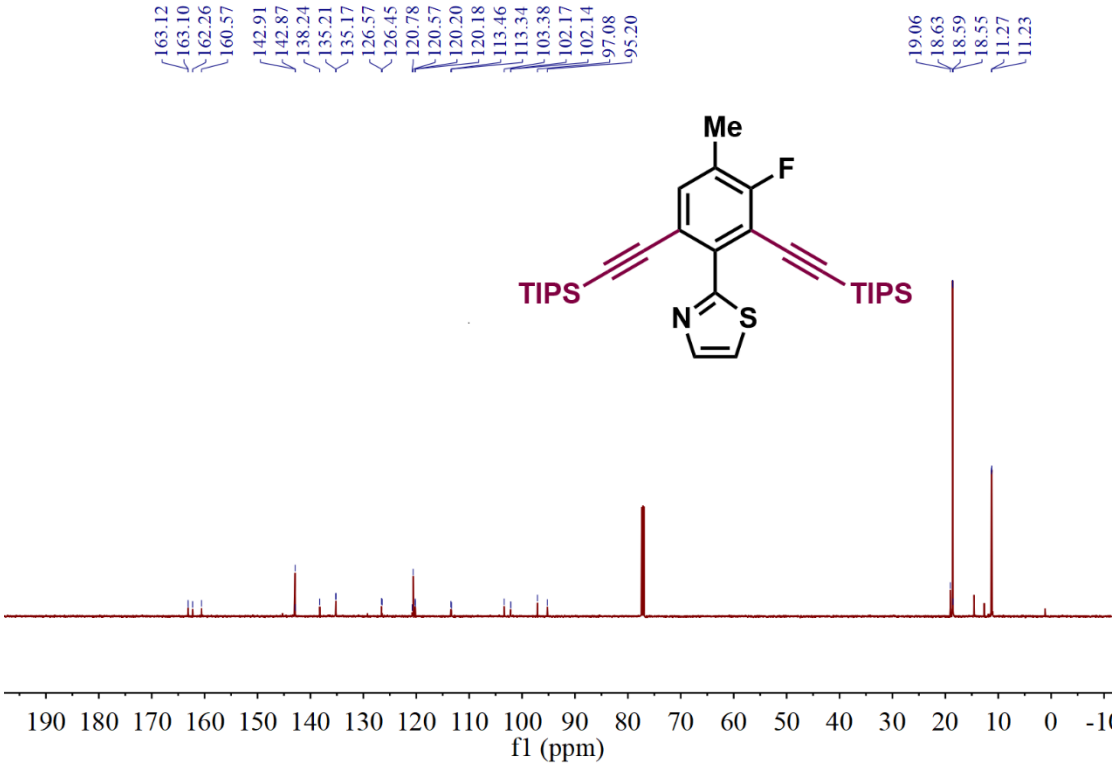
3pa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



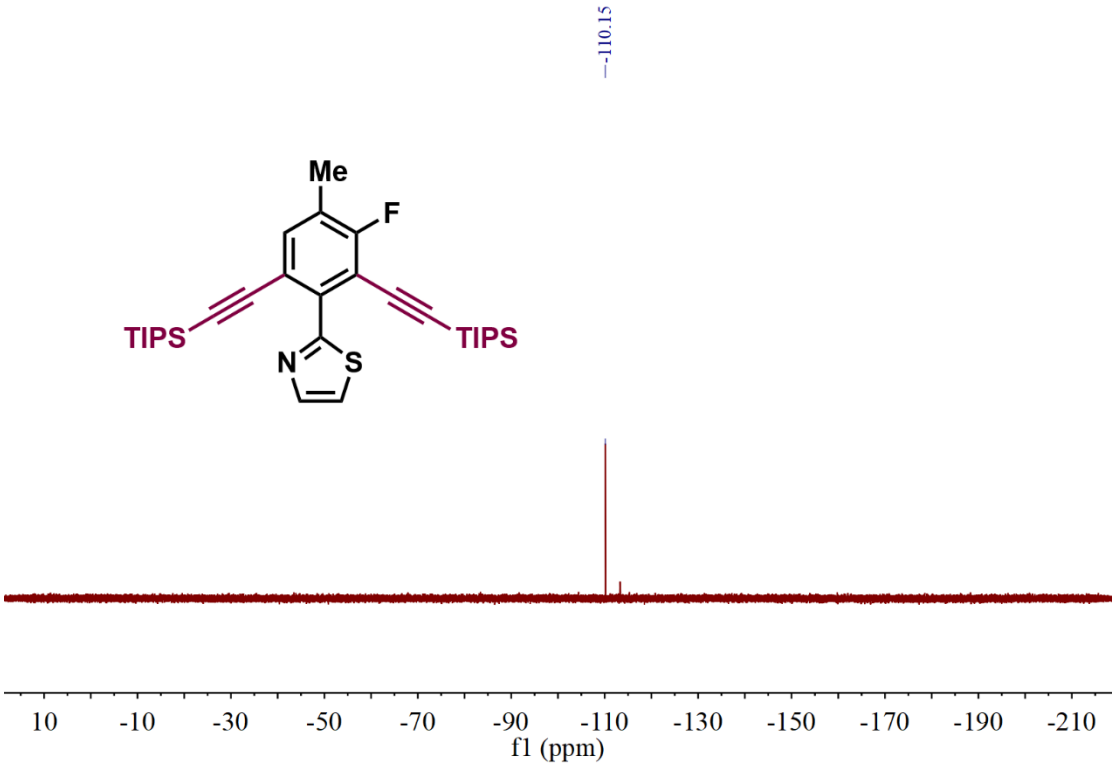
3qa | ^{1}H NMR ($CDCl_3$, 600 MHz)



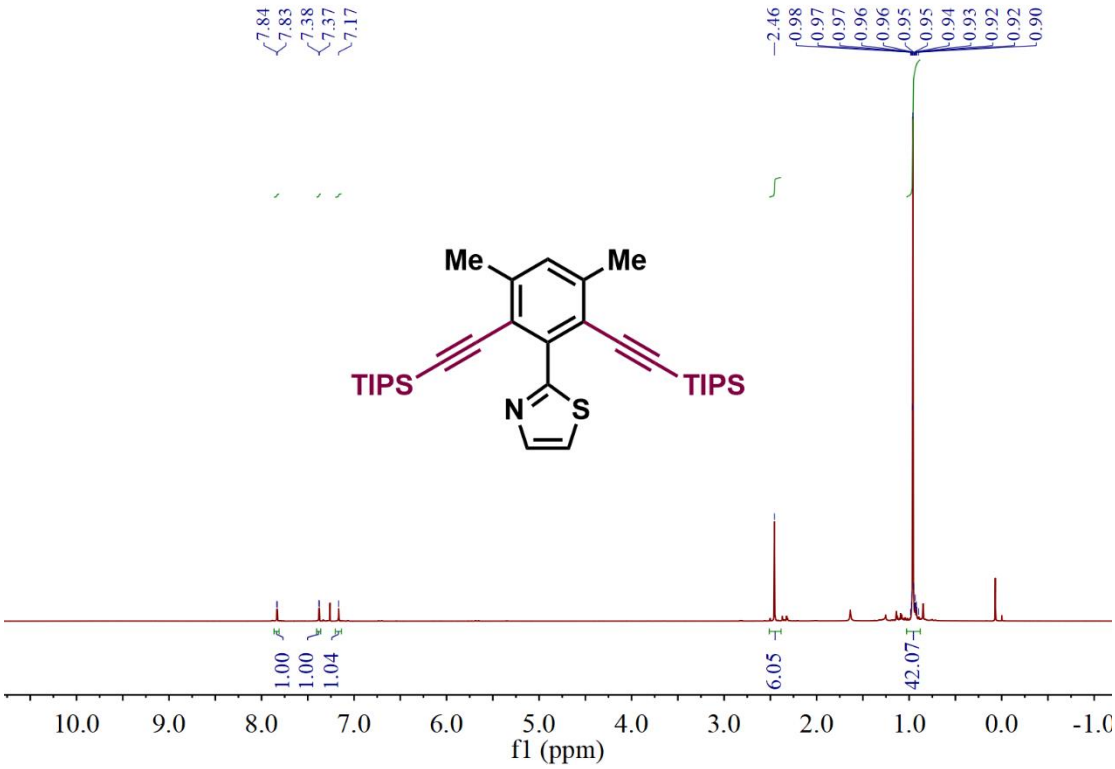
3qa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



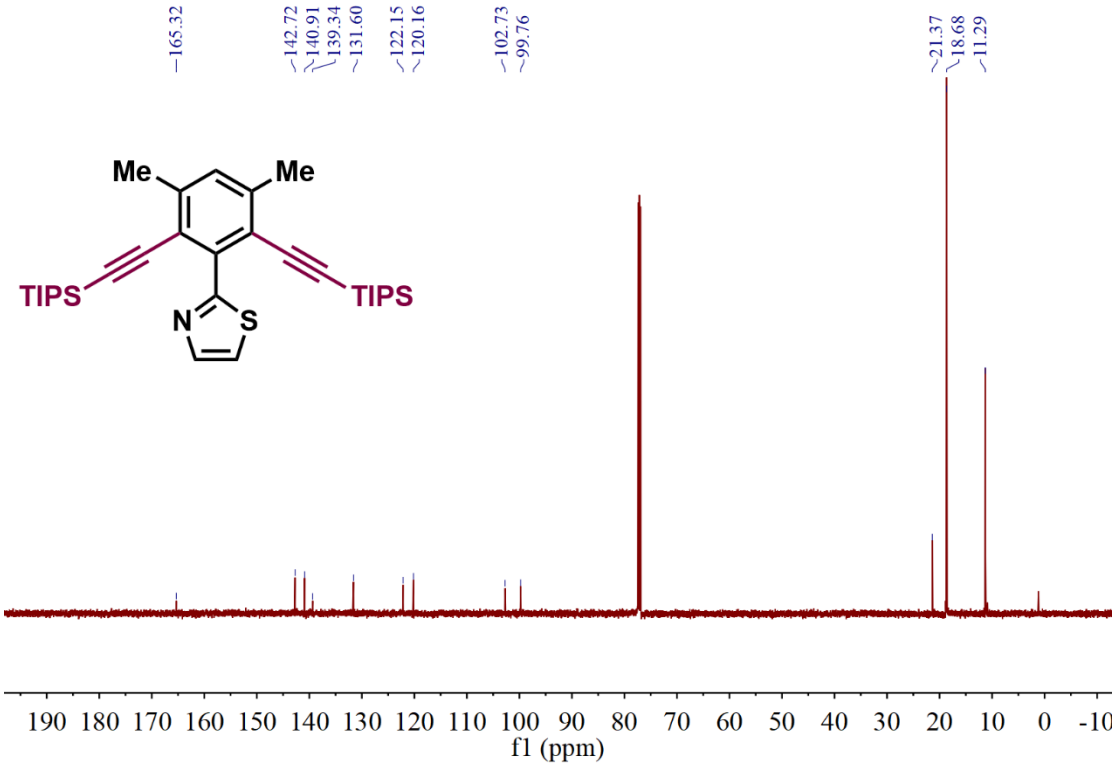
3qa | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



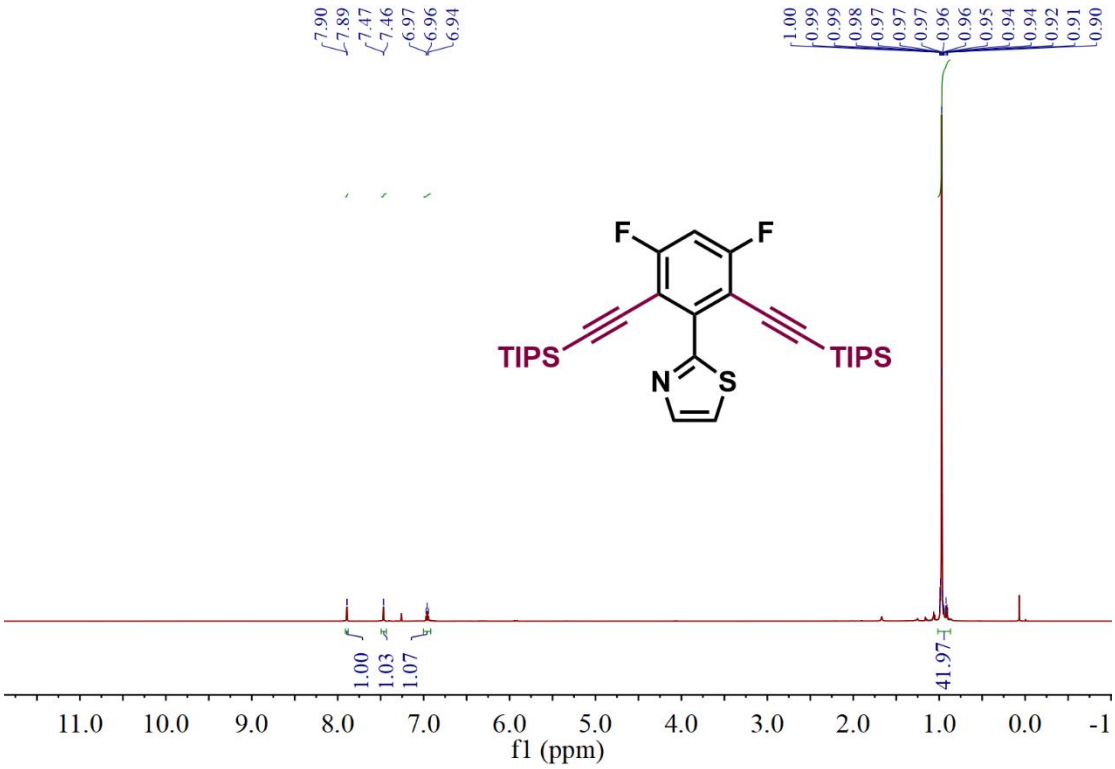
3ra | ^{1}H NMR ($CDCl_3$, 600 MHz)



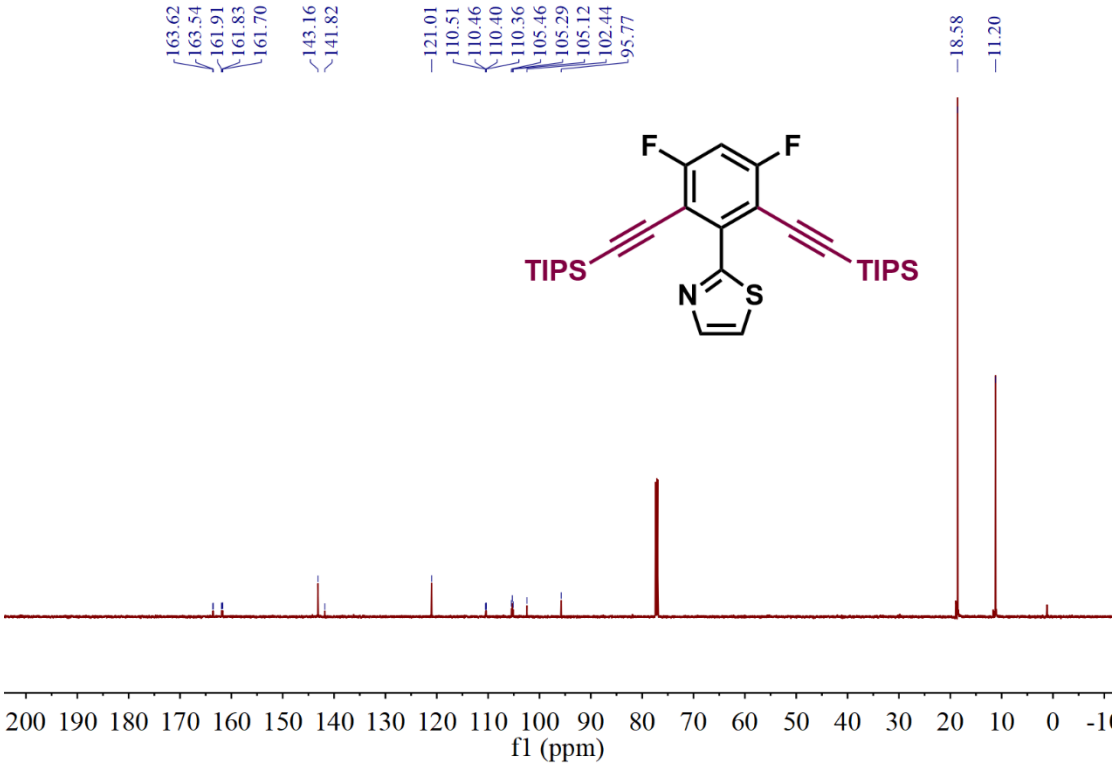
3ra | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



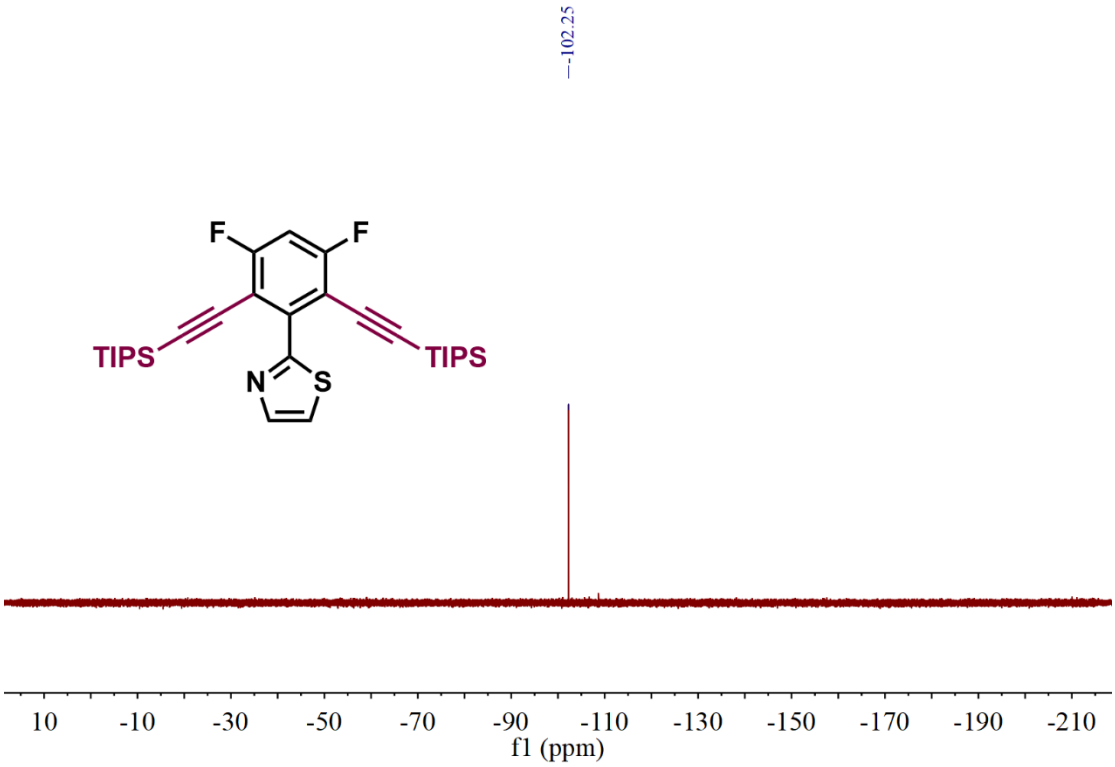
3sa | ^{1}H NMR ($CDCl_3$, 600 MHz)



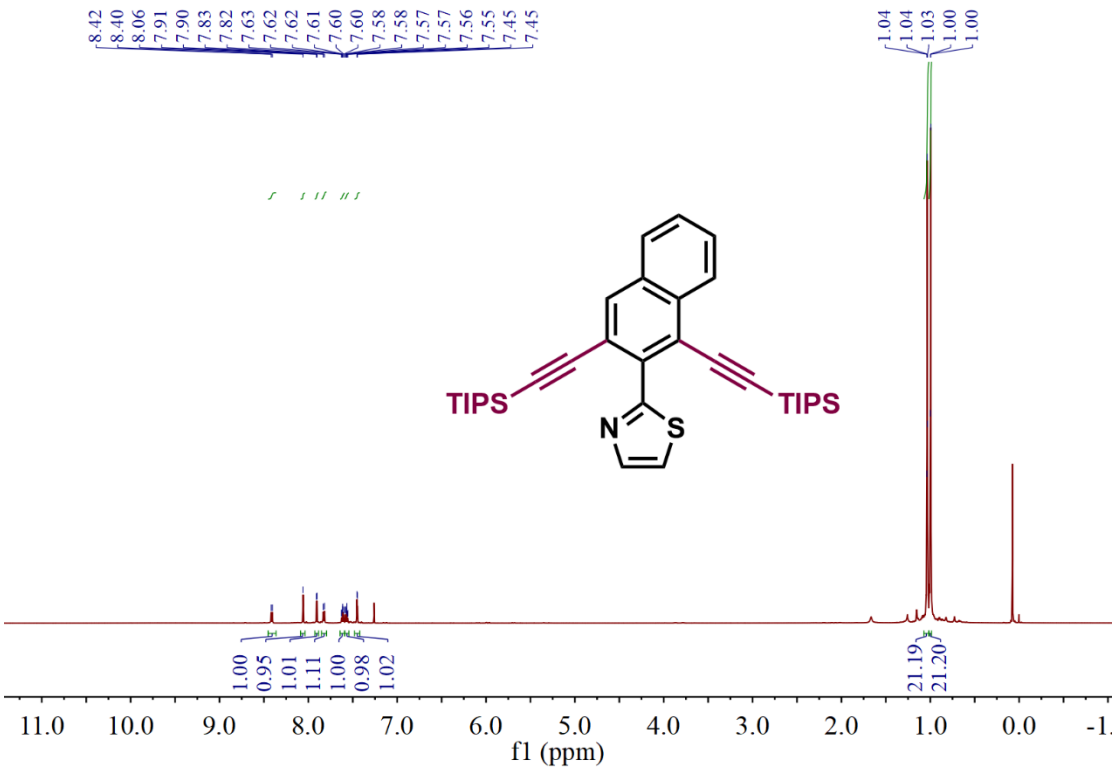
3sa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



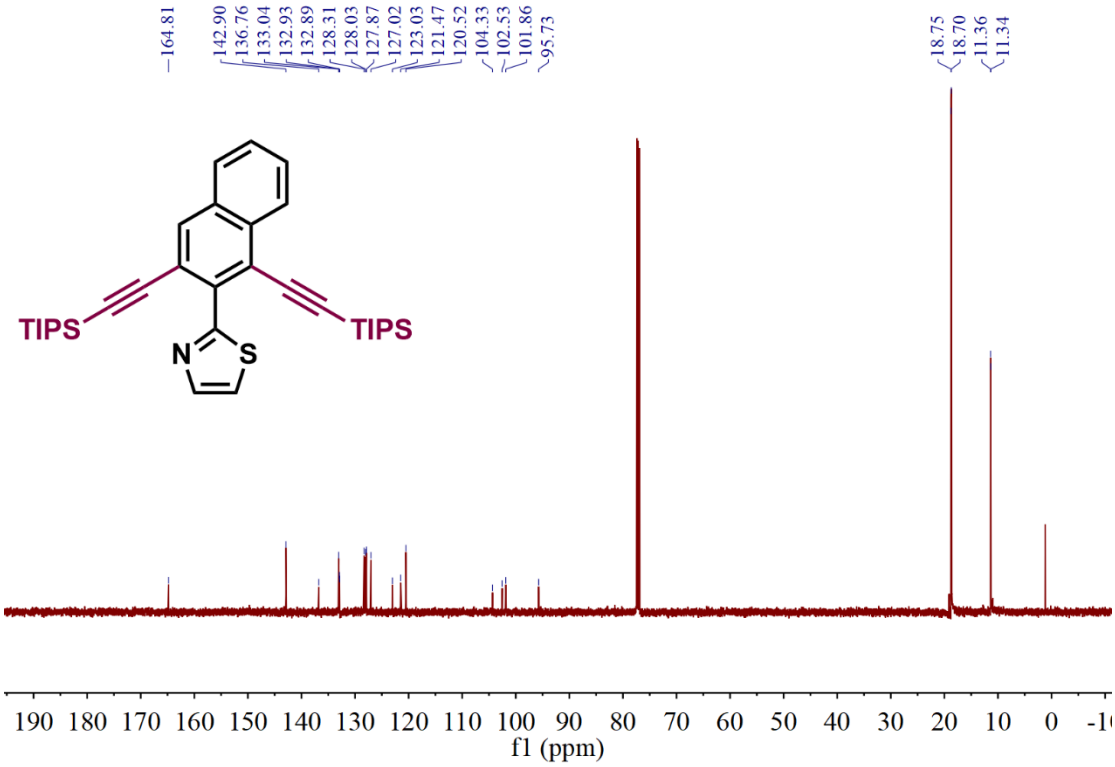
3sa | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



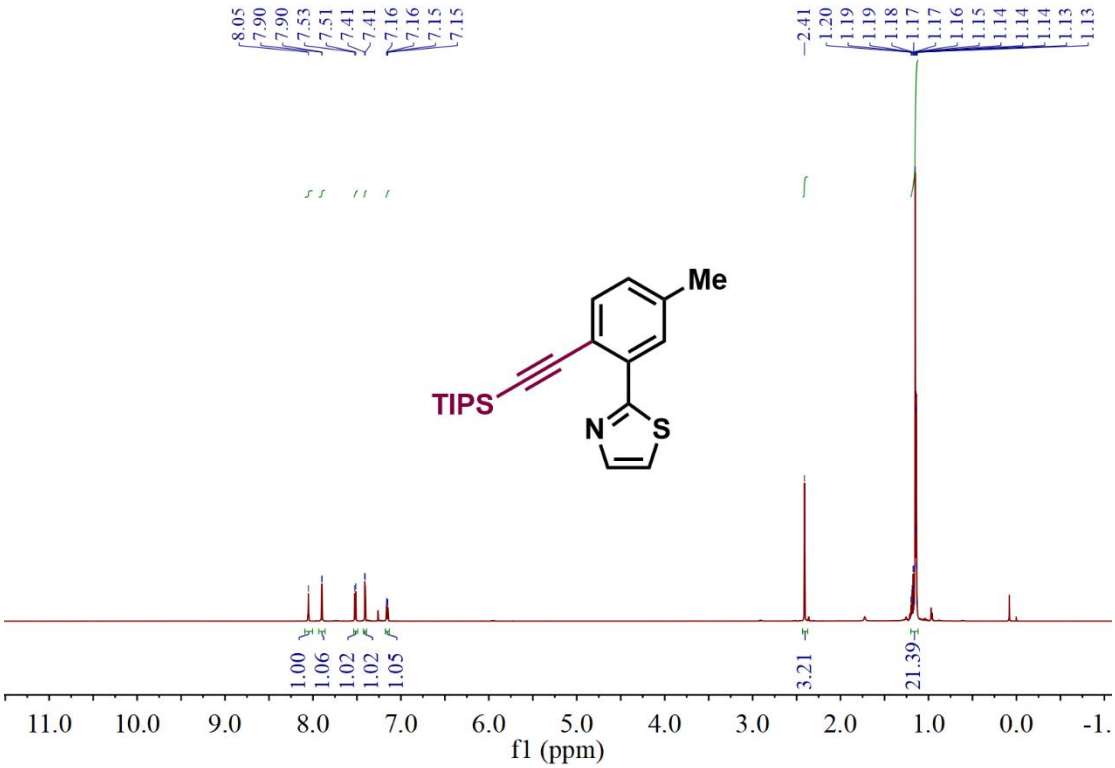
3ta | ^{1}H NMR ($CDCl_3$, 600 MHz)



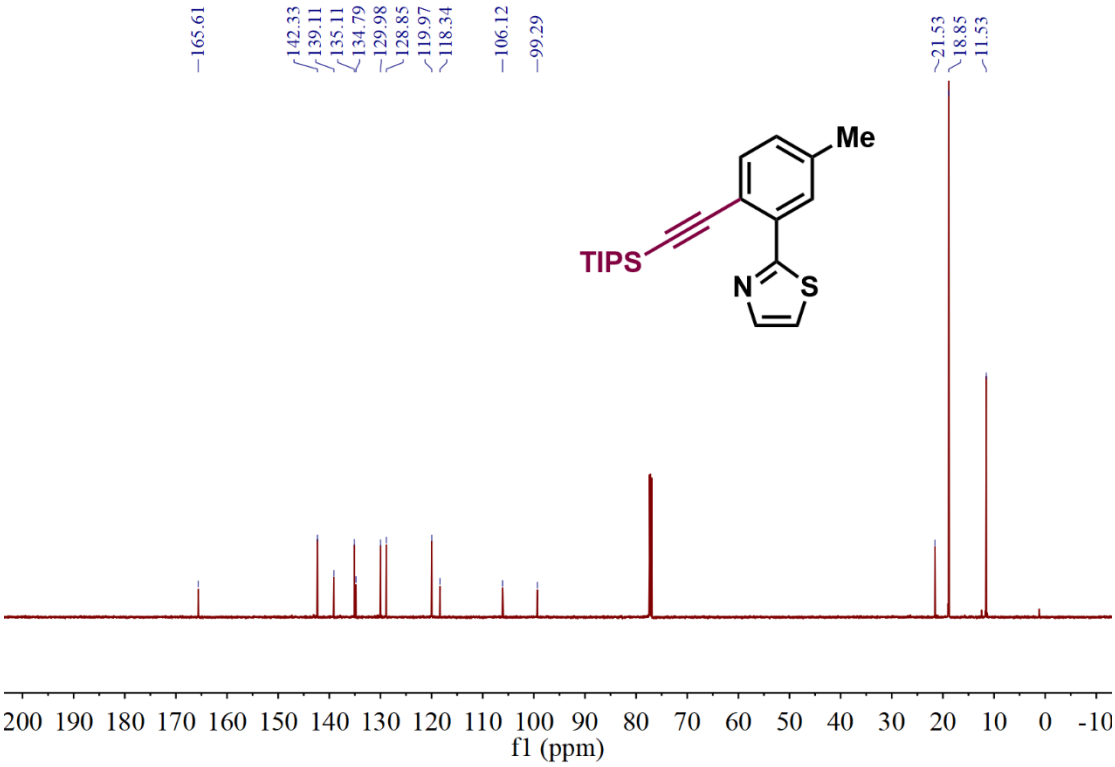
3ta | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



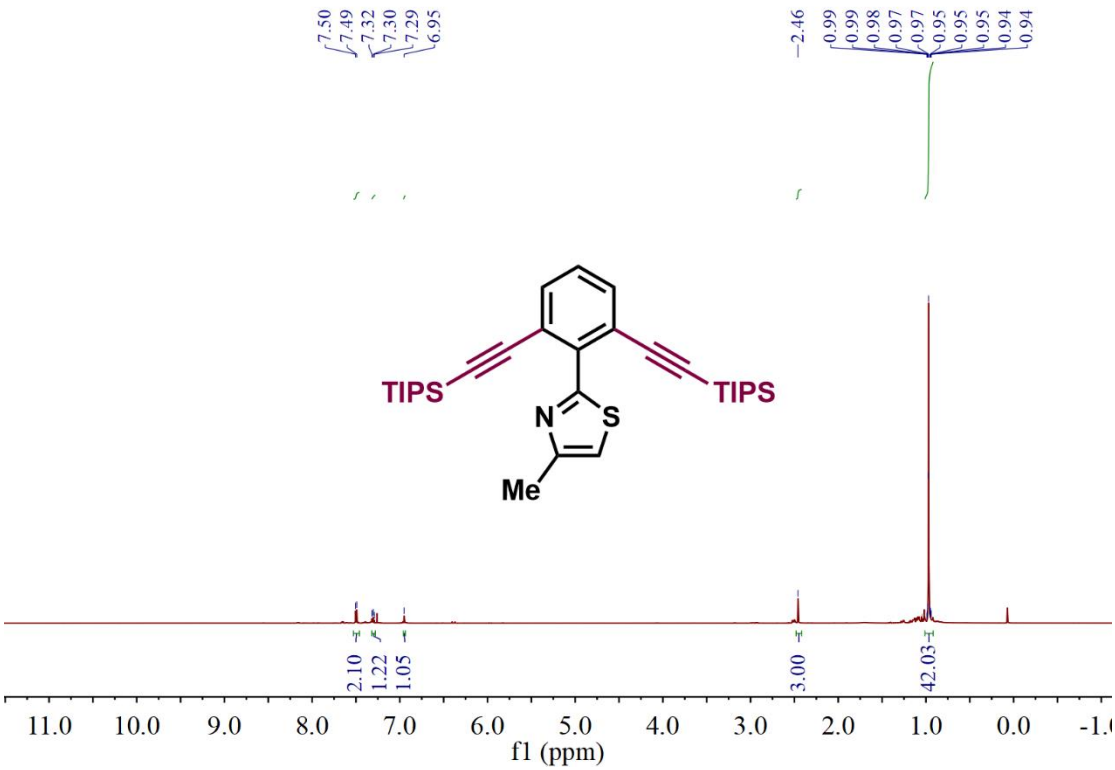
3ka$_1$ | ^{1}H NMR ($CDCl_3$, 600 MHz)



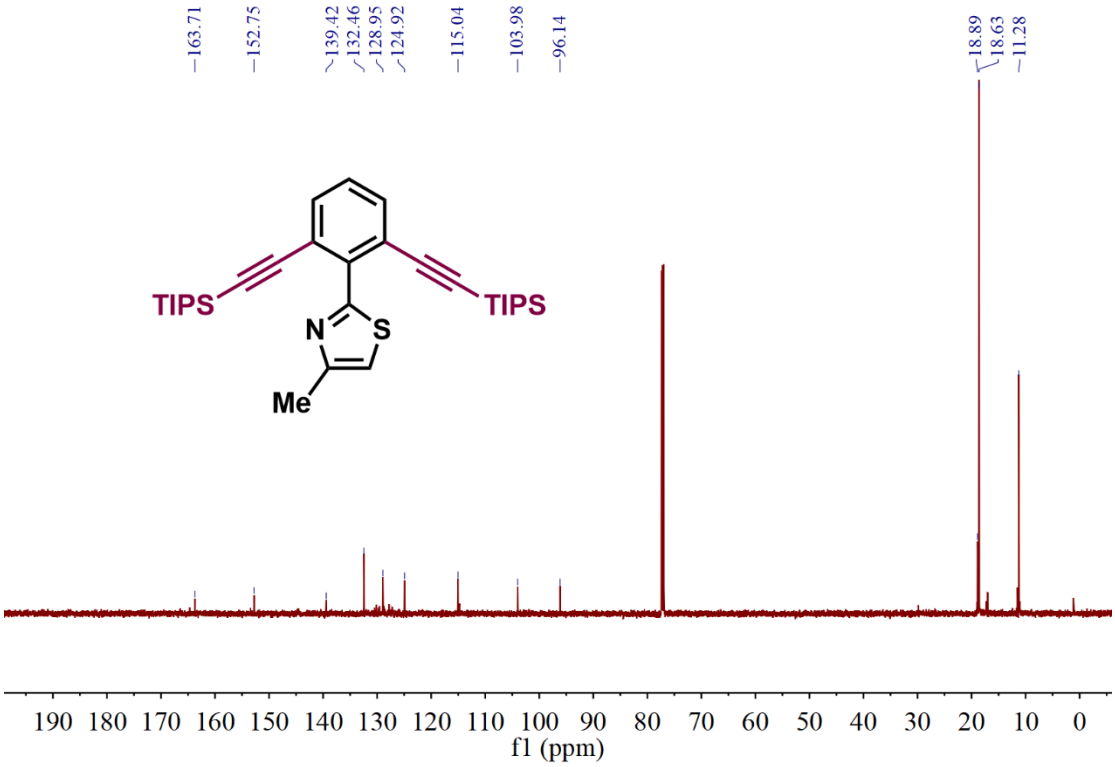
3ka$_1$ | $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz)



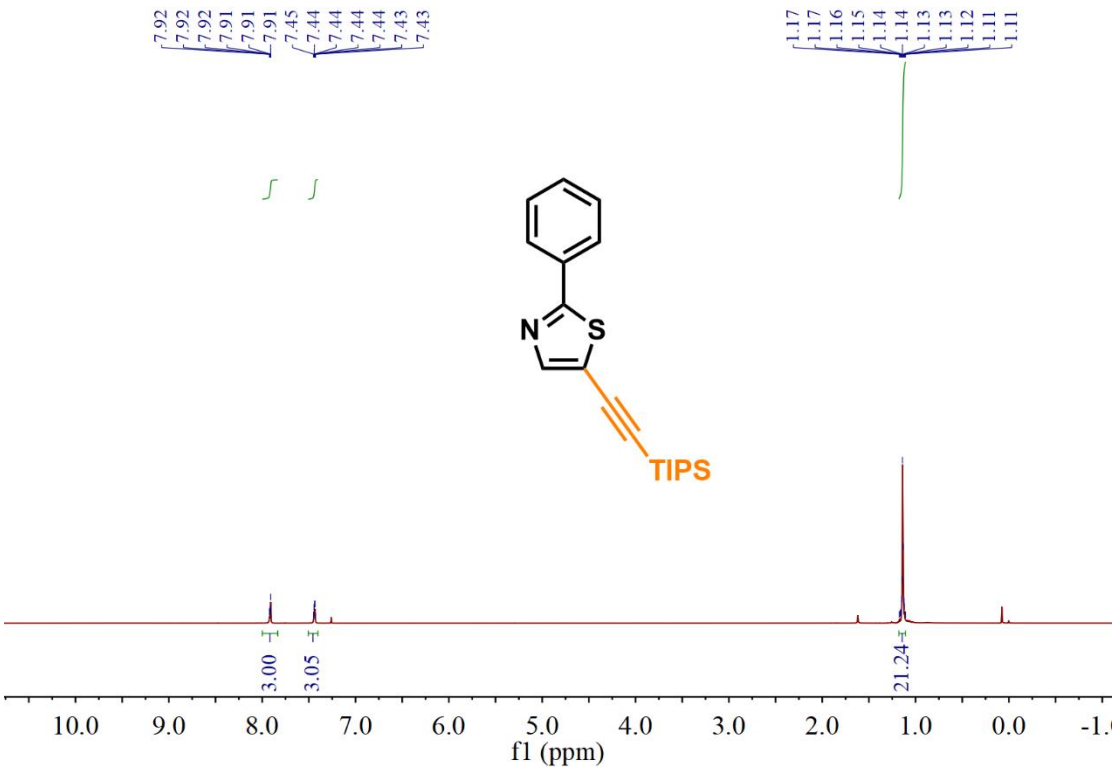
3ua | ^1H NMR ($CDCl_3$, 600 MHz)



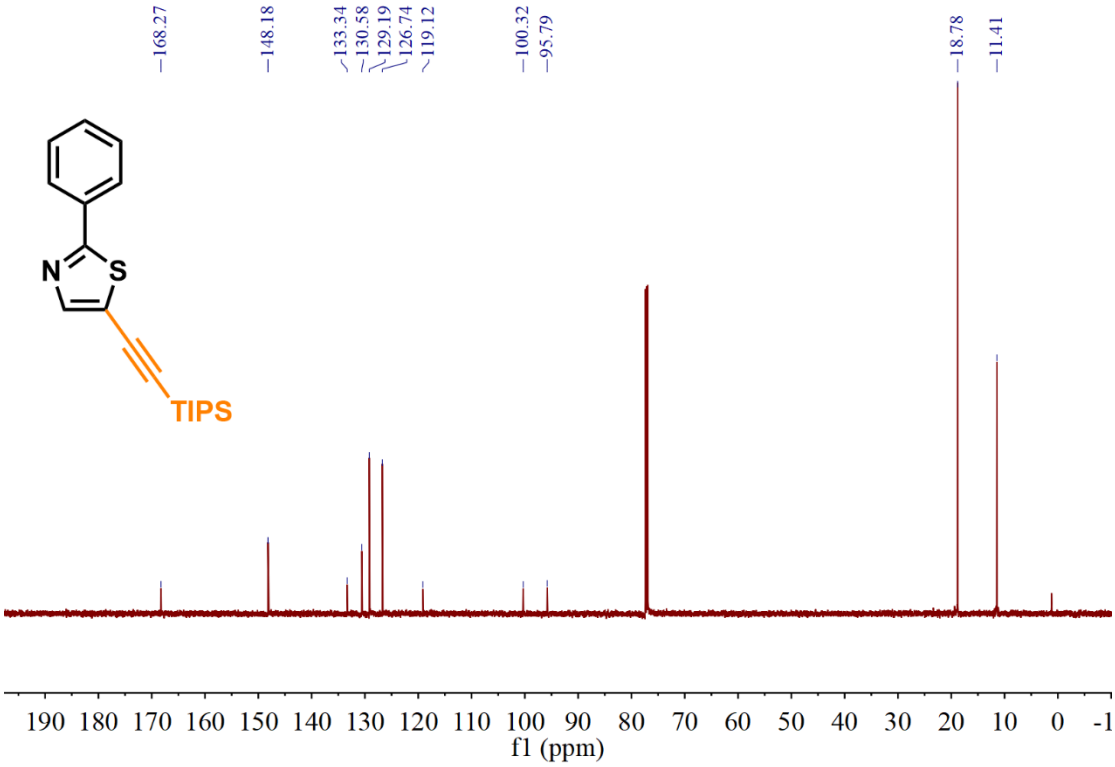
3ua | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



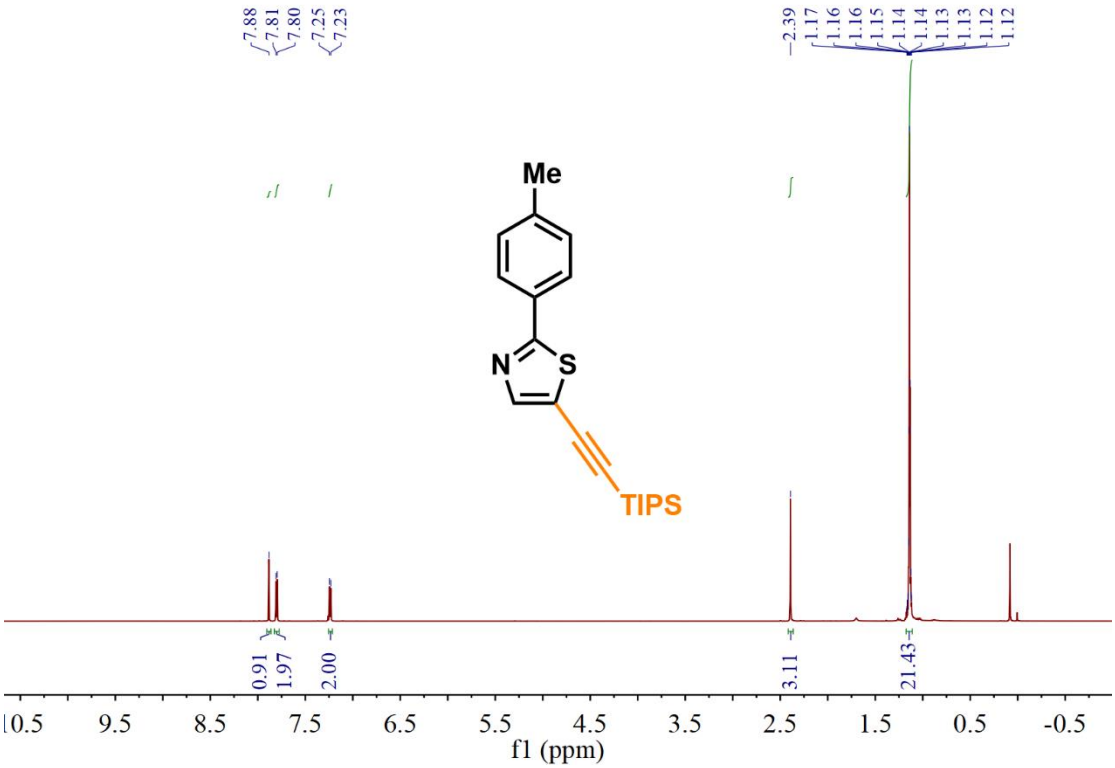
4aa | ^{1}H NMR ($CDCl_3$, 600 MHz)



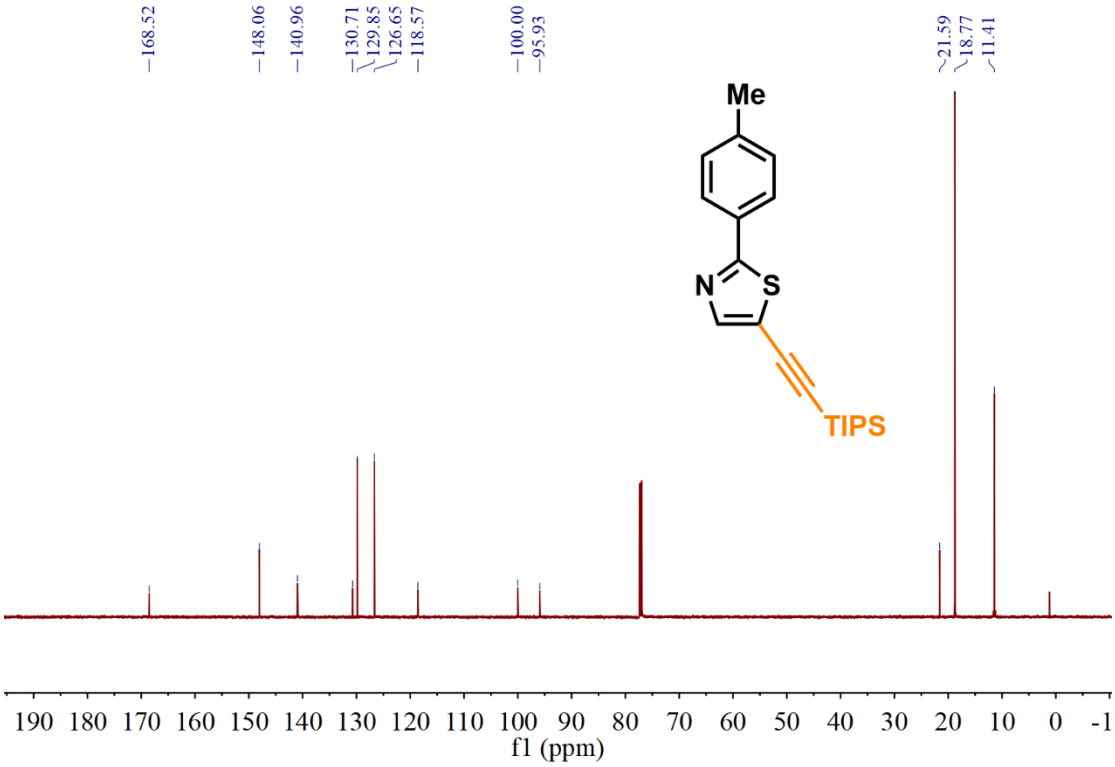
4aa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



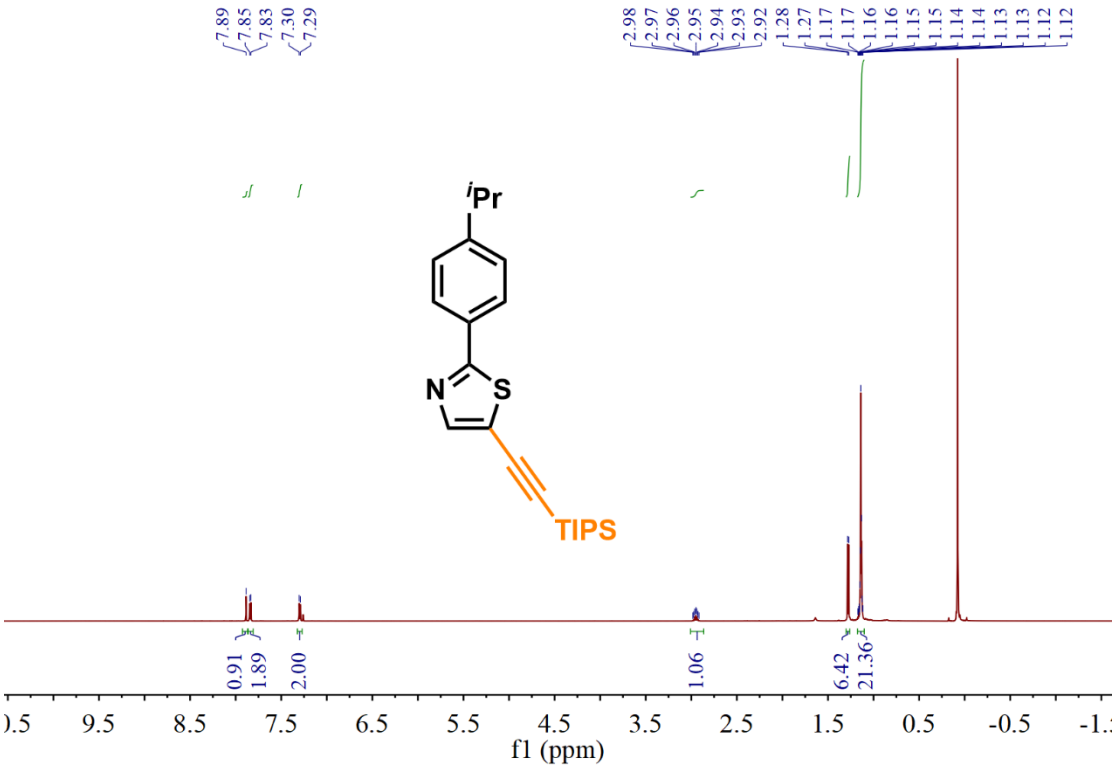
4ba | ^{1}H NMR ($CDCl_3$, 600 MHz)



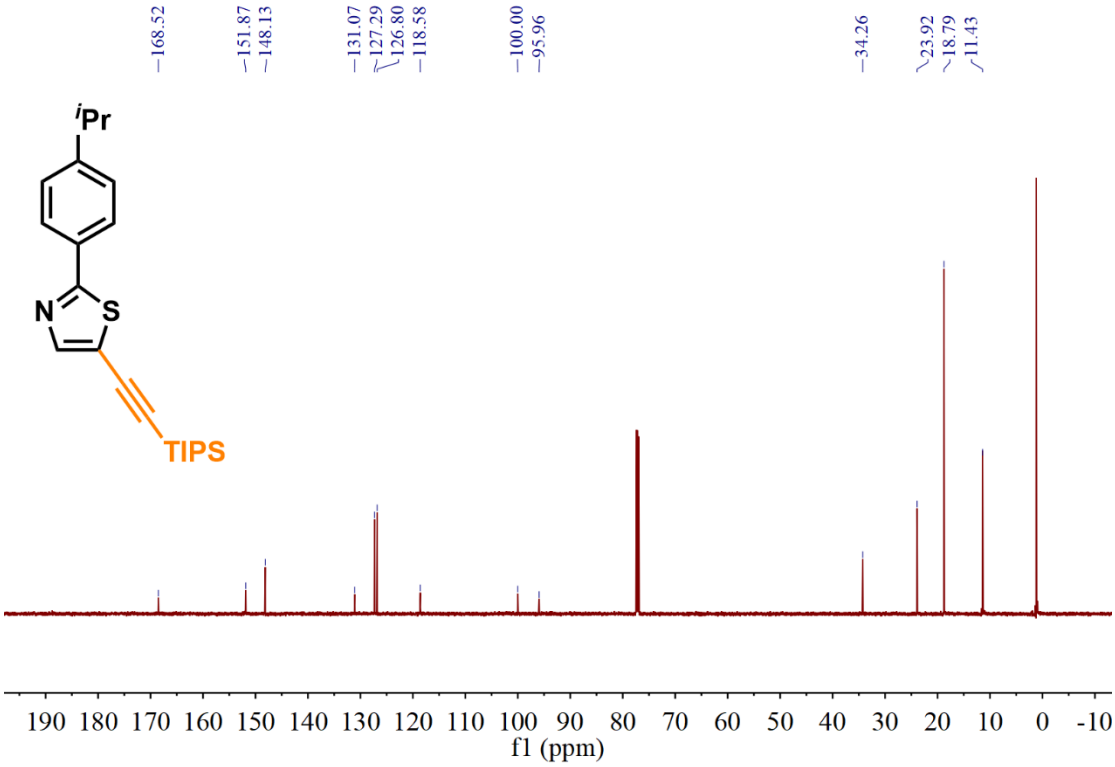
4ba | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



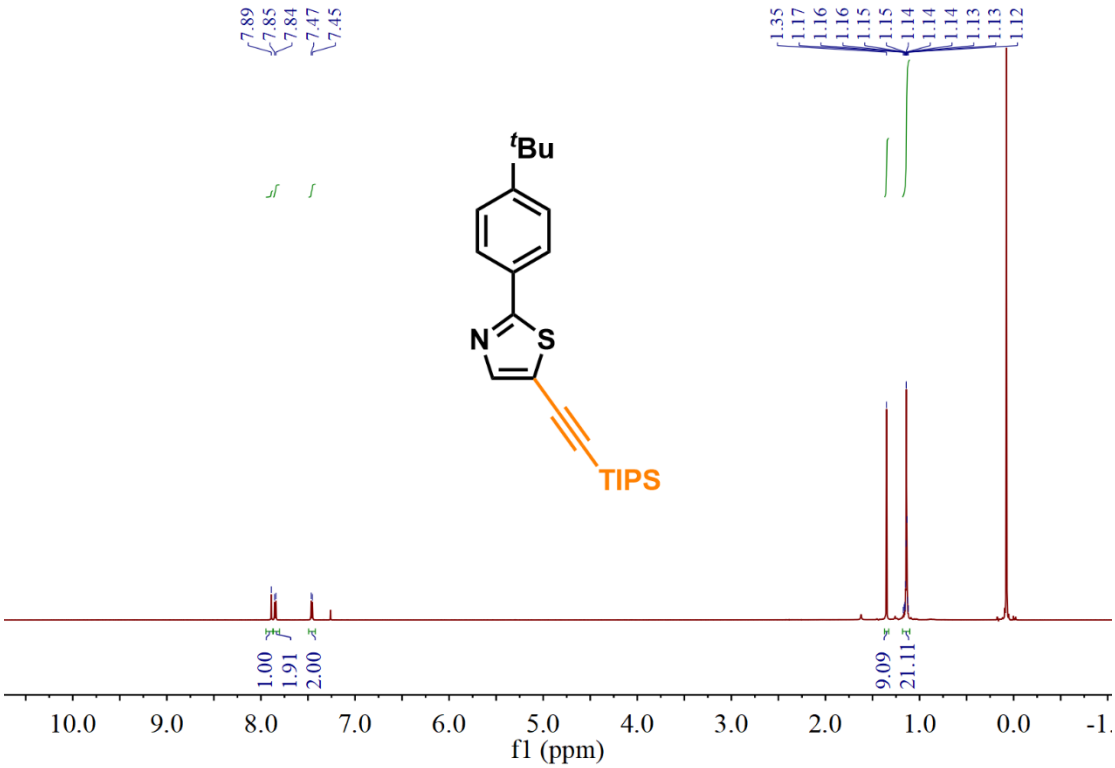
4ca | ^{1}H NMR ($CDCl_3$, 600 MHz)



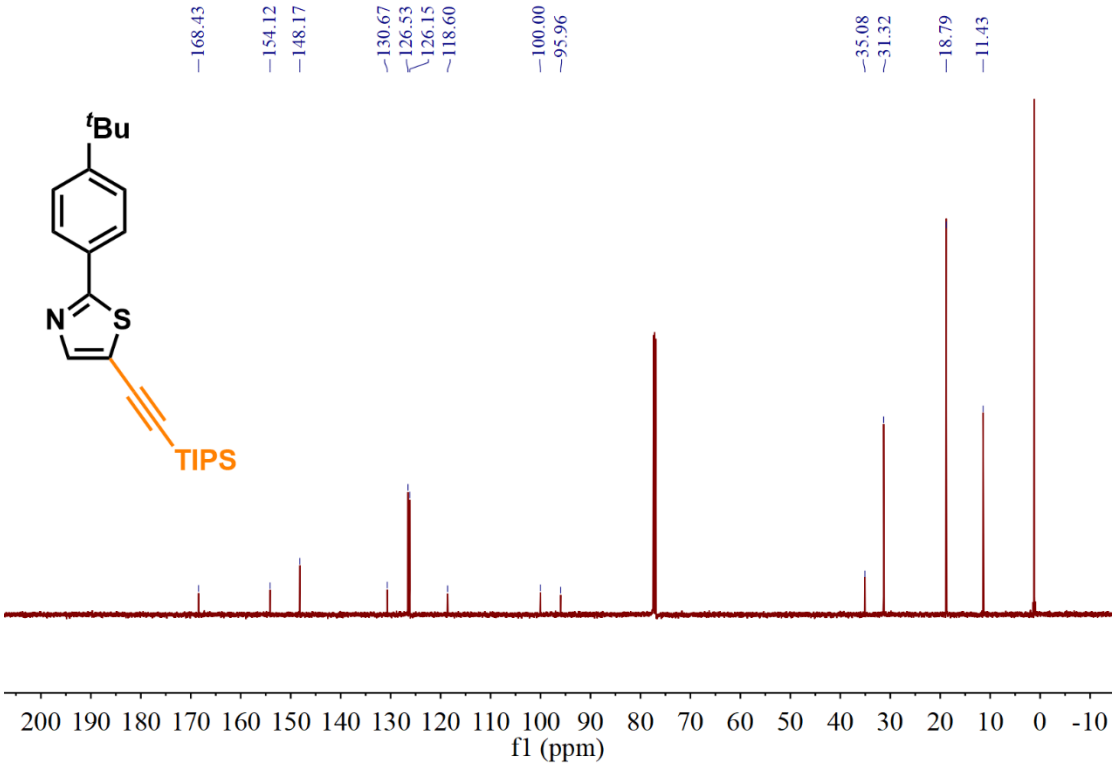
4ca | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



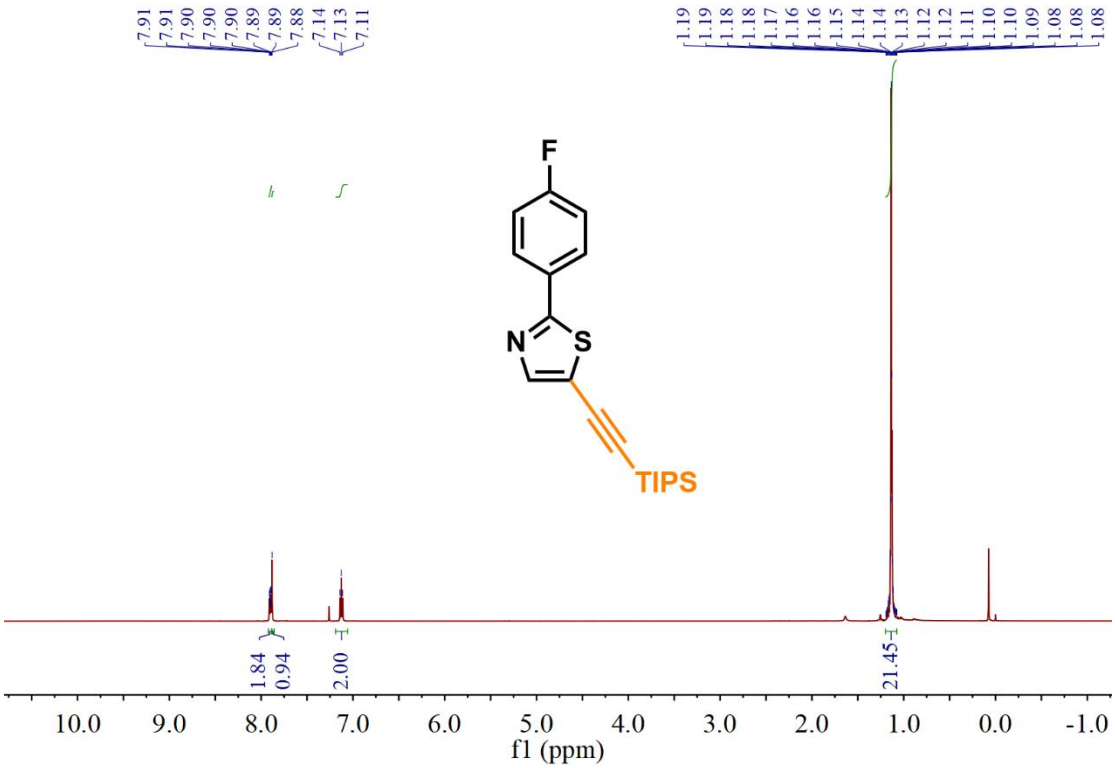
4da | ^{1}H NMR ($CDCl_3$, 600 MHz)



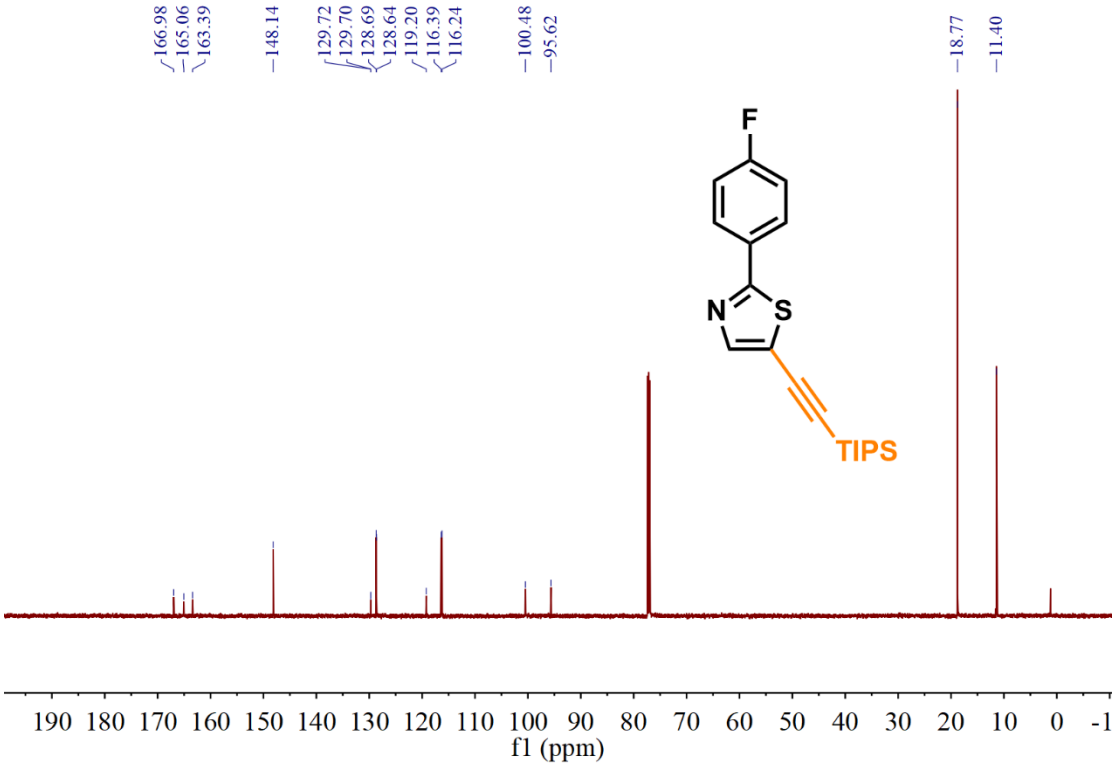
4da | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



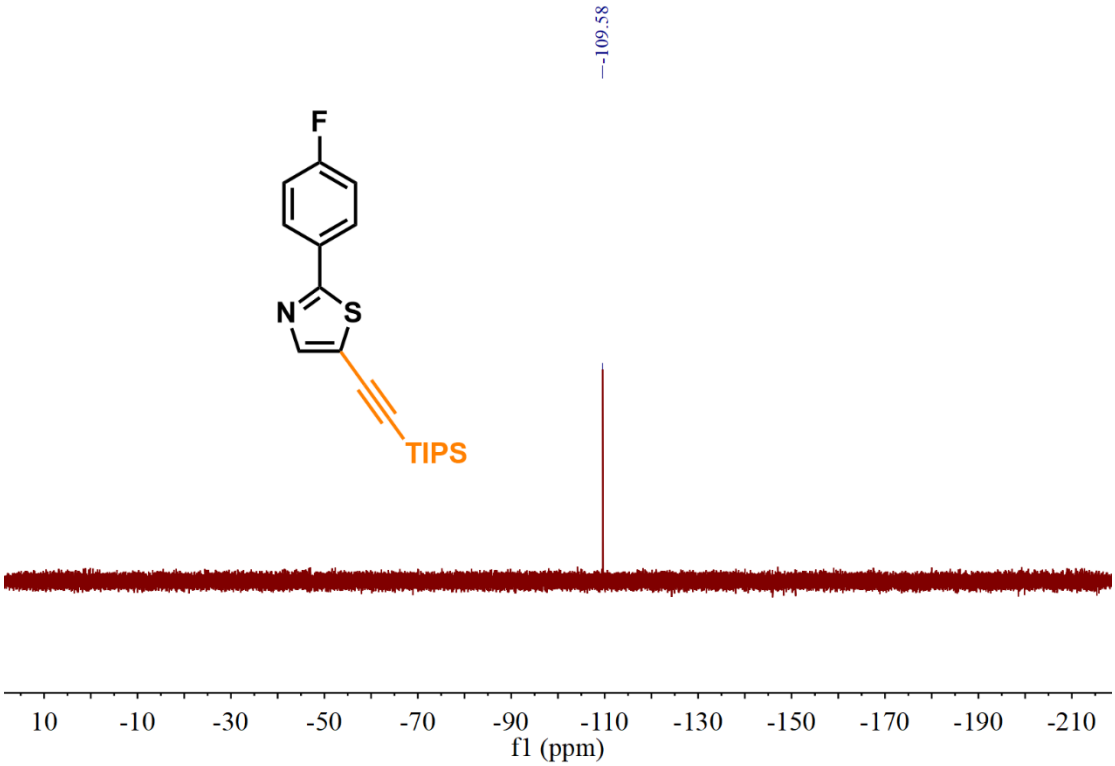
4ea | ^{1}H NMR ($CDCl_3$, 600 MHz)



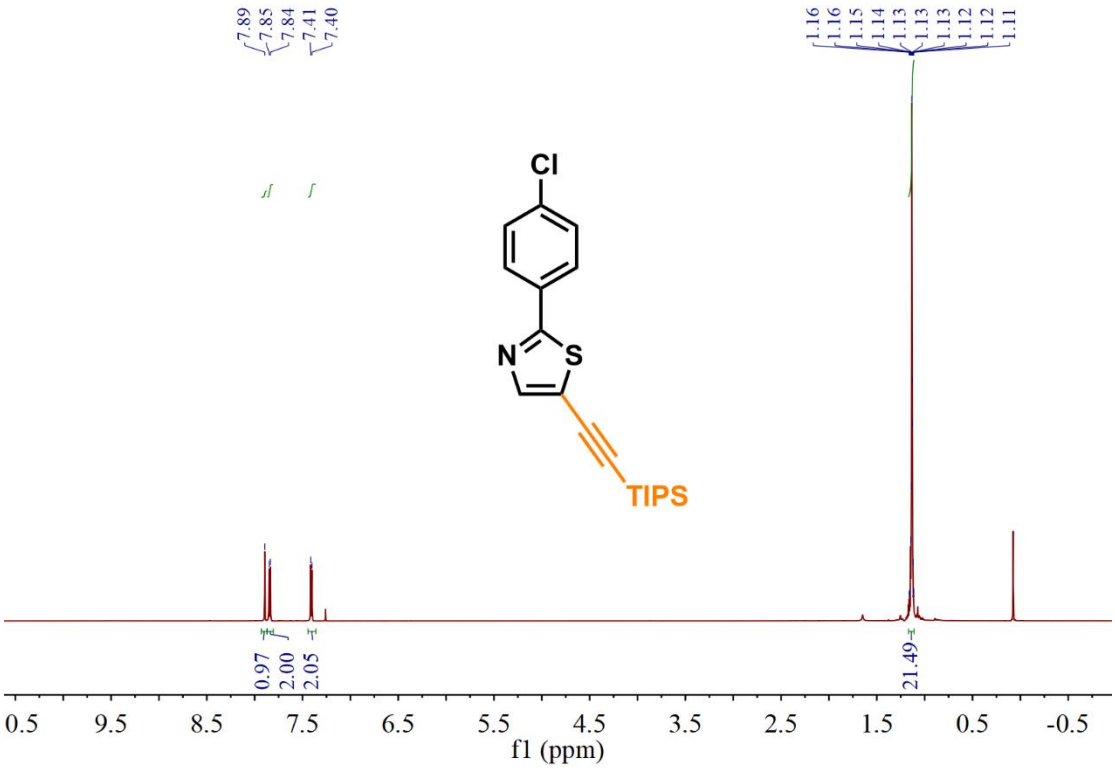
4ea | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



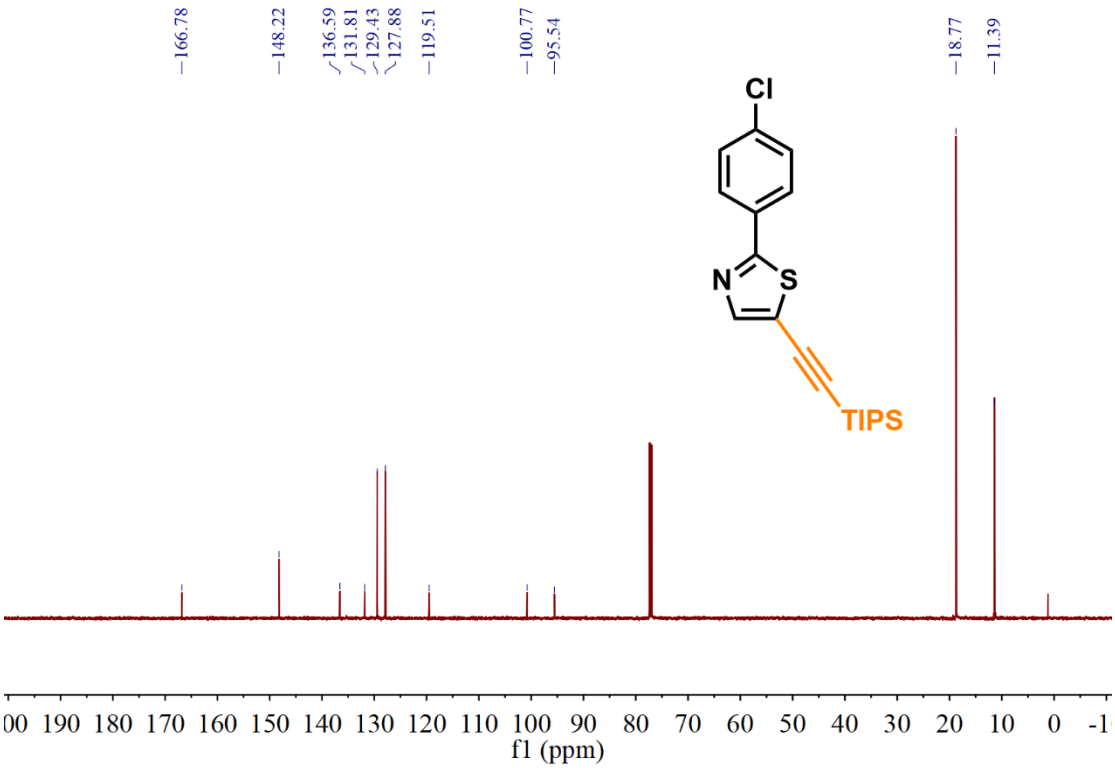
4ea | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



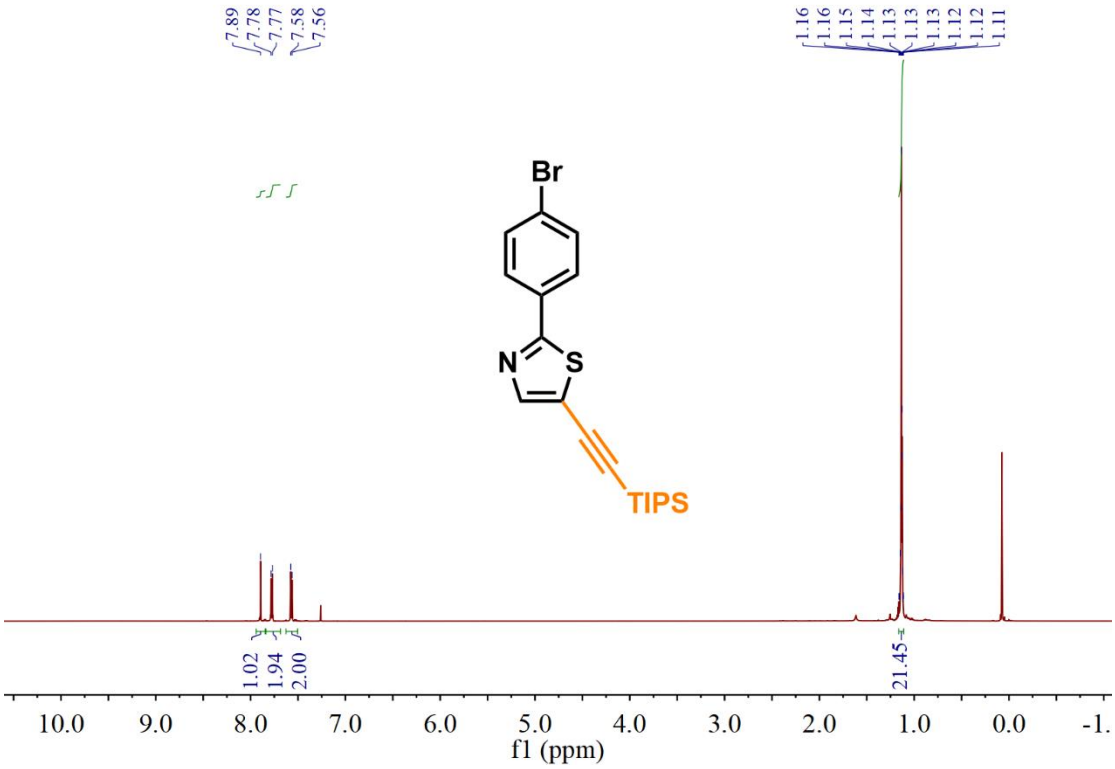
4fa | ^{1}H NMR ($CDCl_3$, 600 MHz)



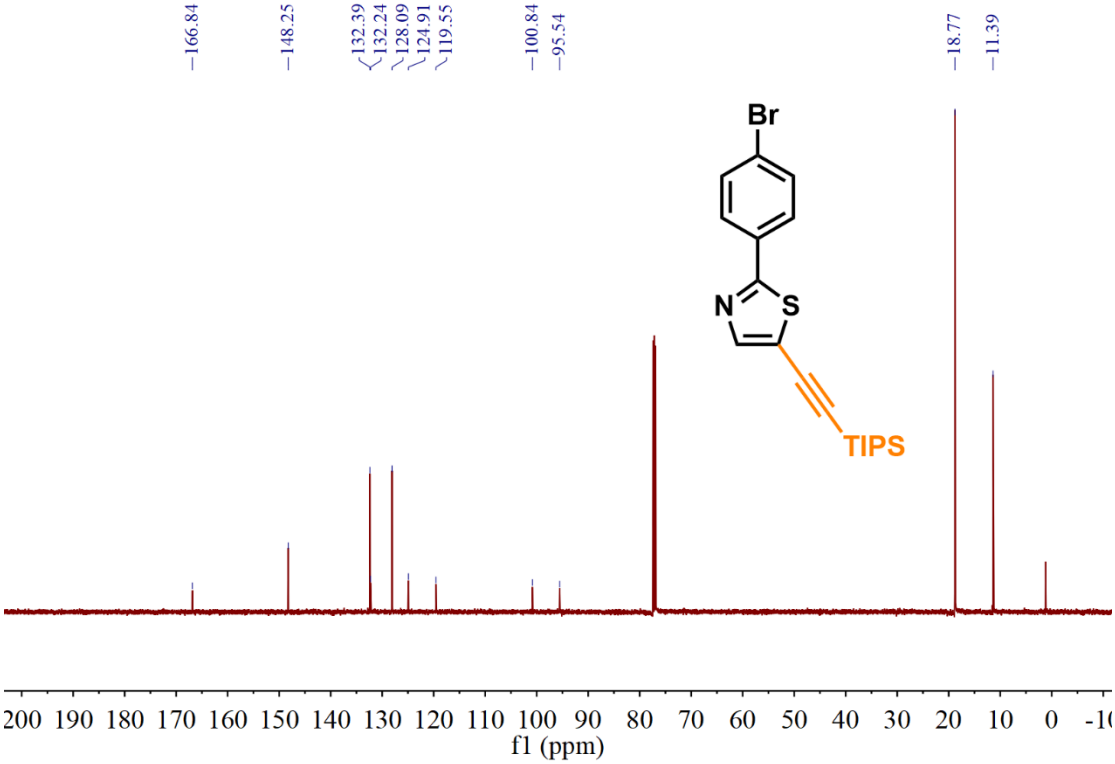
4fa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



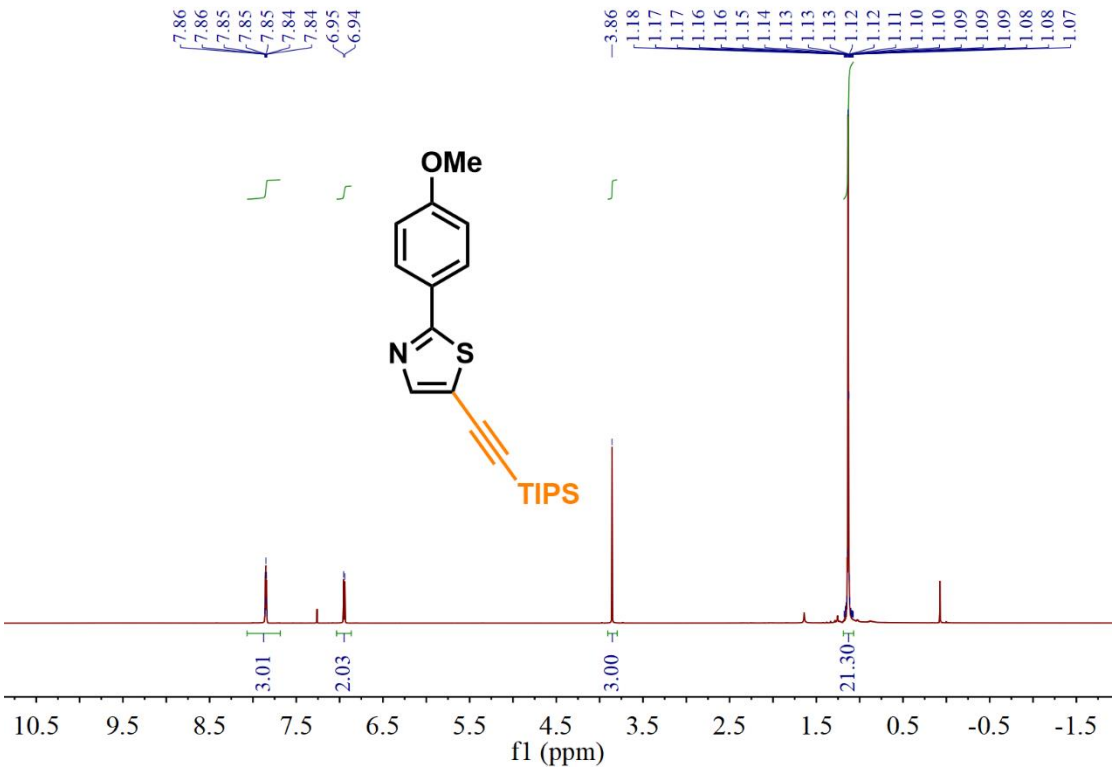
4ga | ^{1}H NMR ($CDCl_3$, 600 MHz)



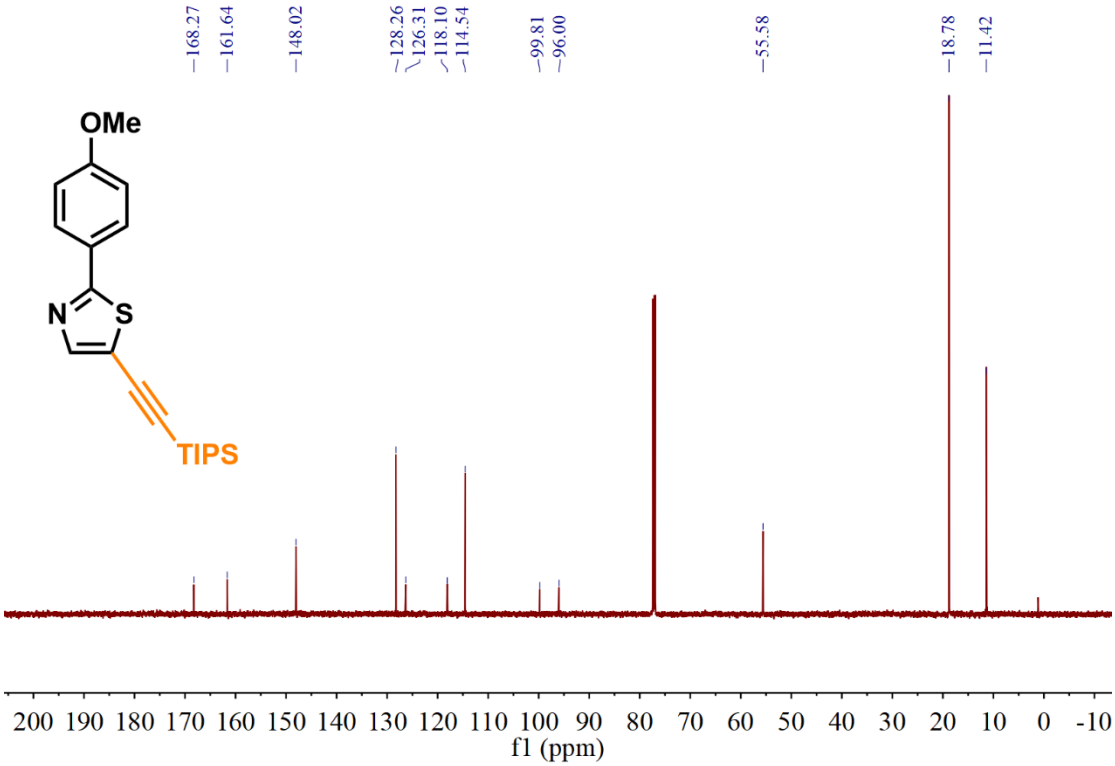
4ga | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



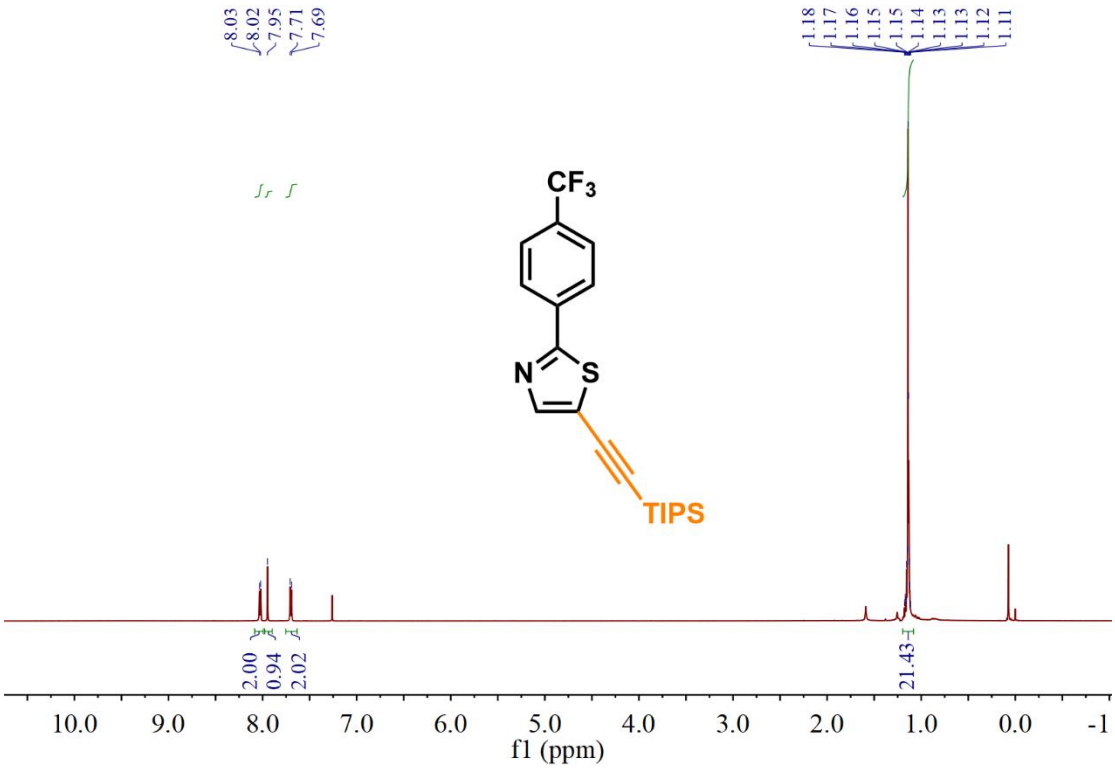
4ha | ^{1}H NMR ($CDCl_3$, 600 MHz)



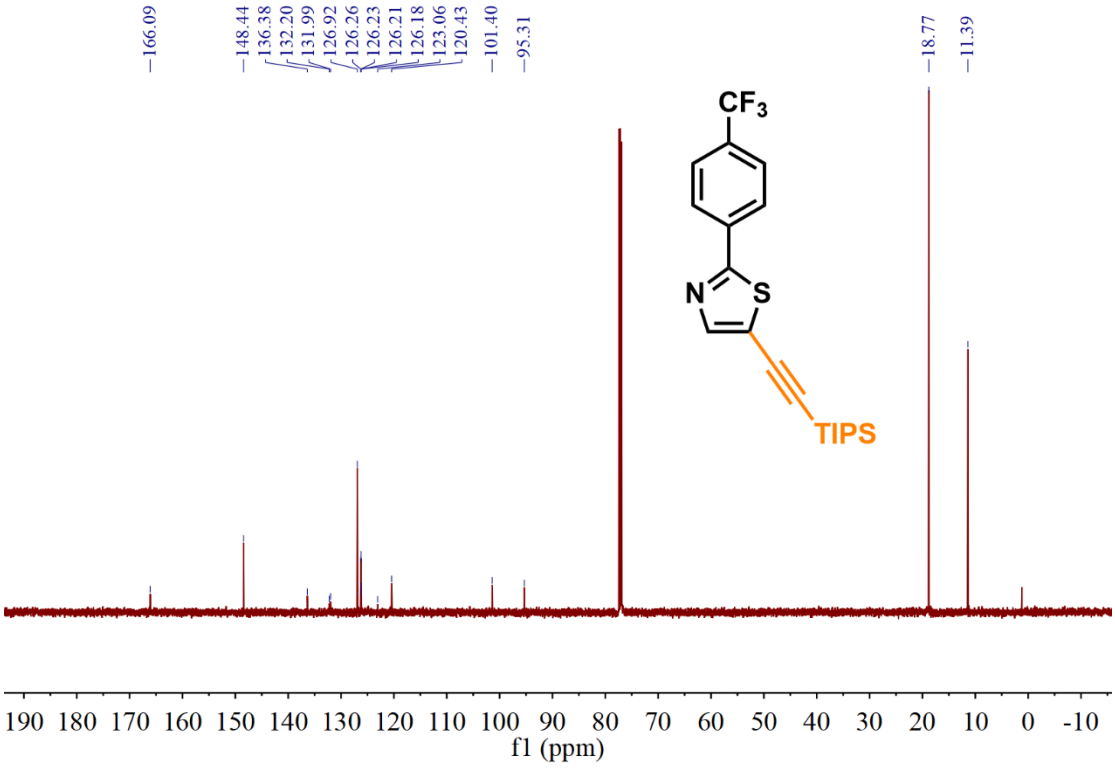
4ha | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



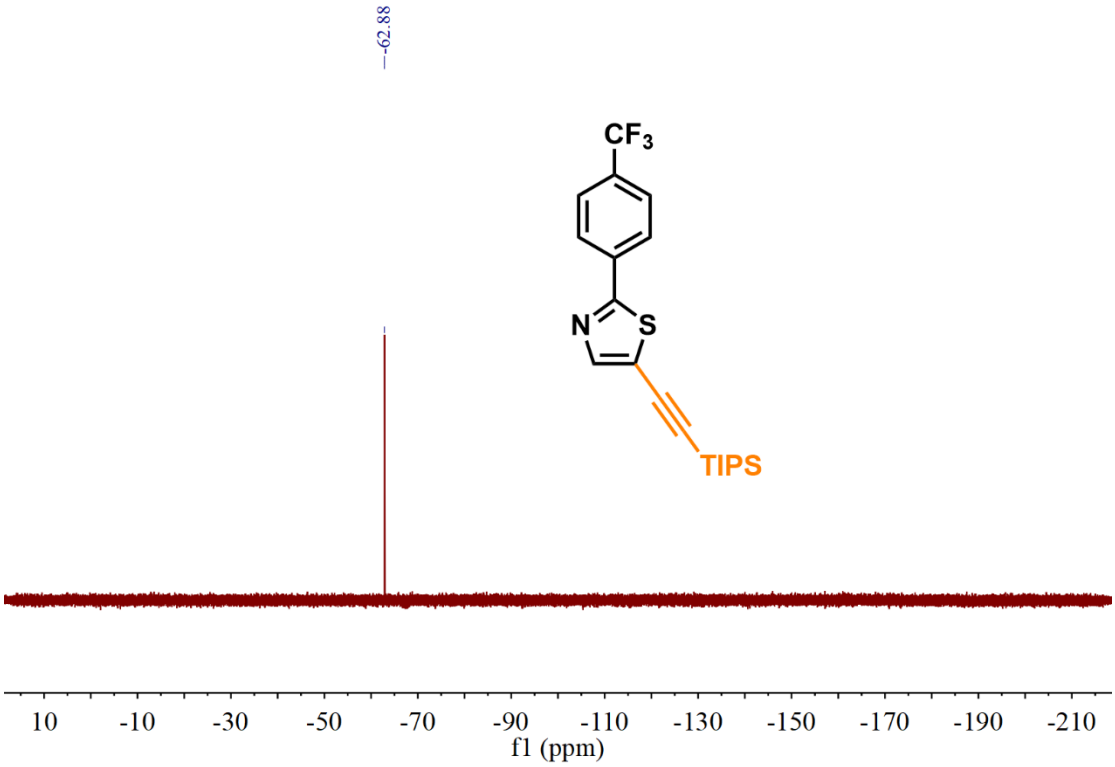
4ia | ^{1}H NMR ($CDCl_3$, 600 MHz)



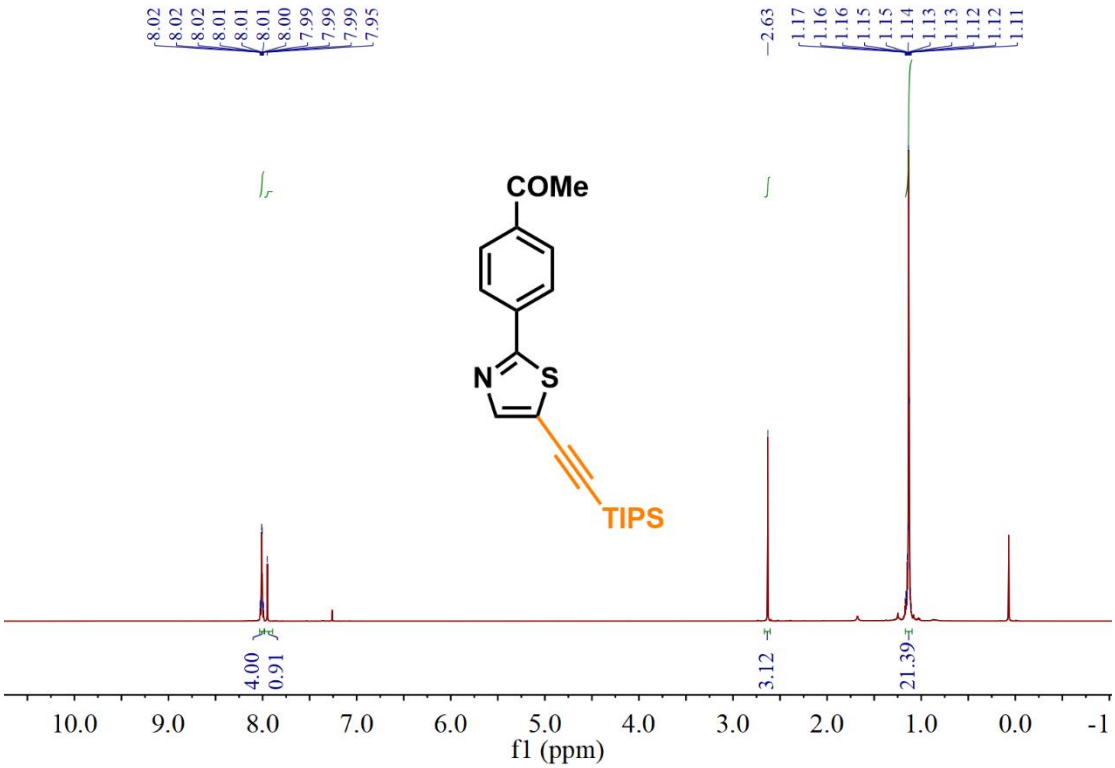
4ia | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



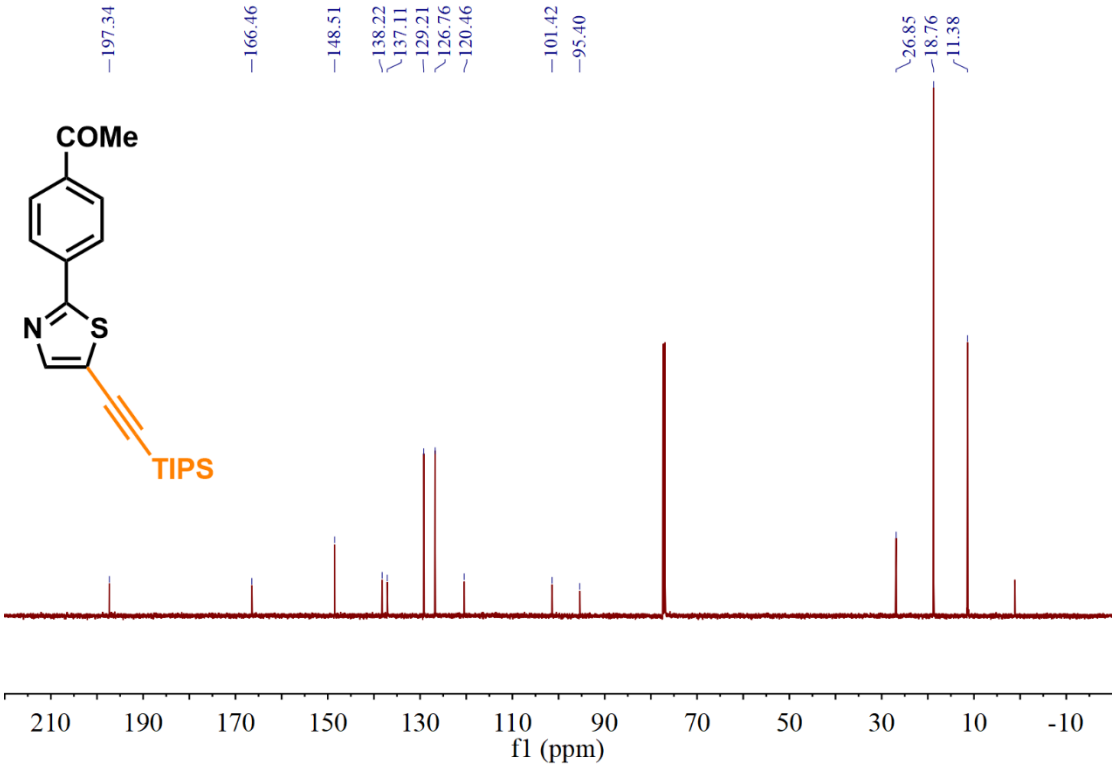
4ia | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



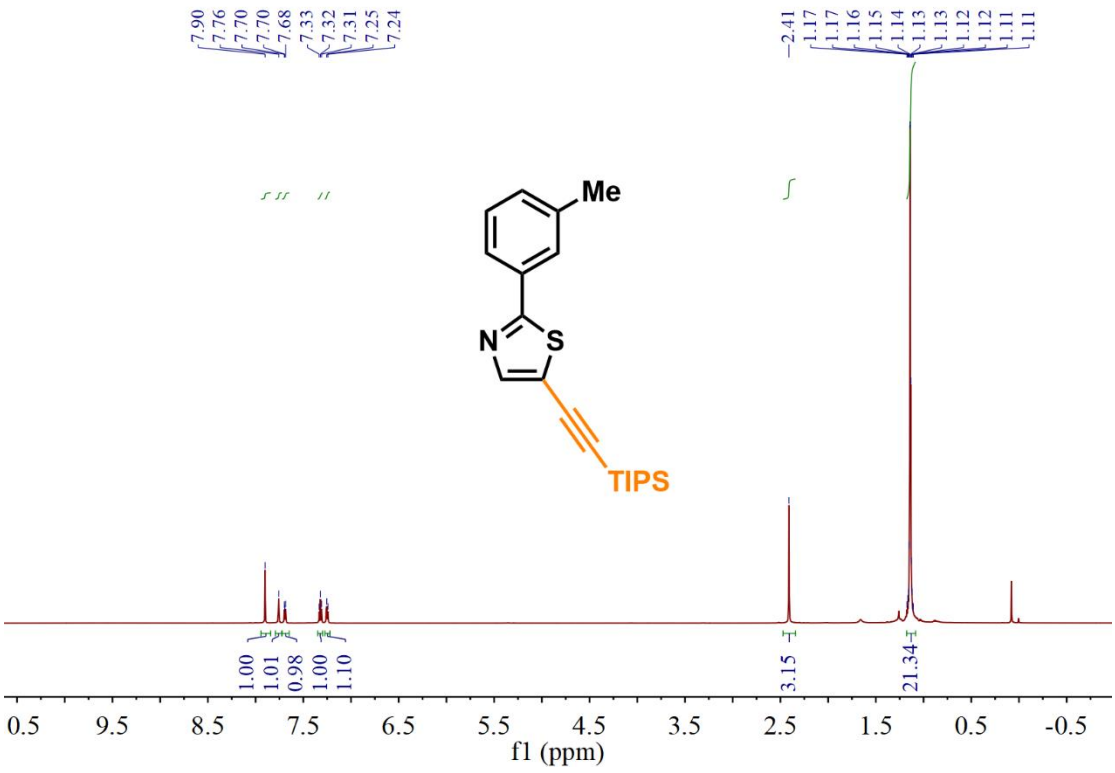
4ja | ^{1}H NMR ($CDCl_3$, 600 MHz)



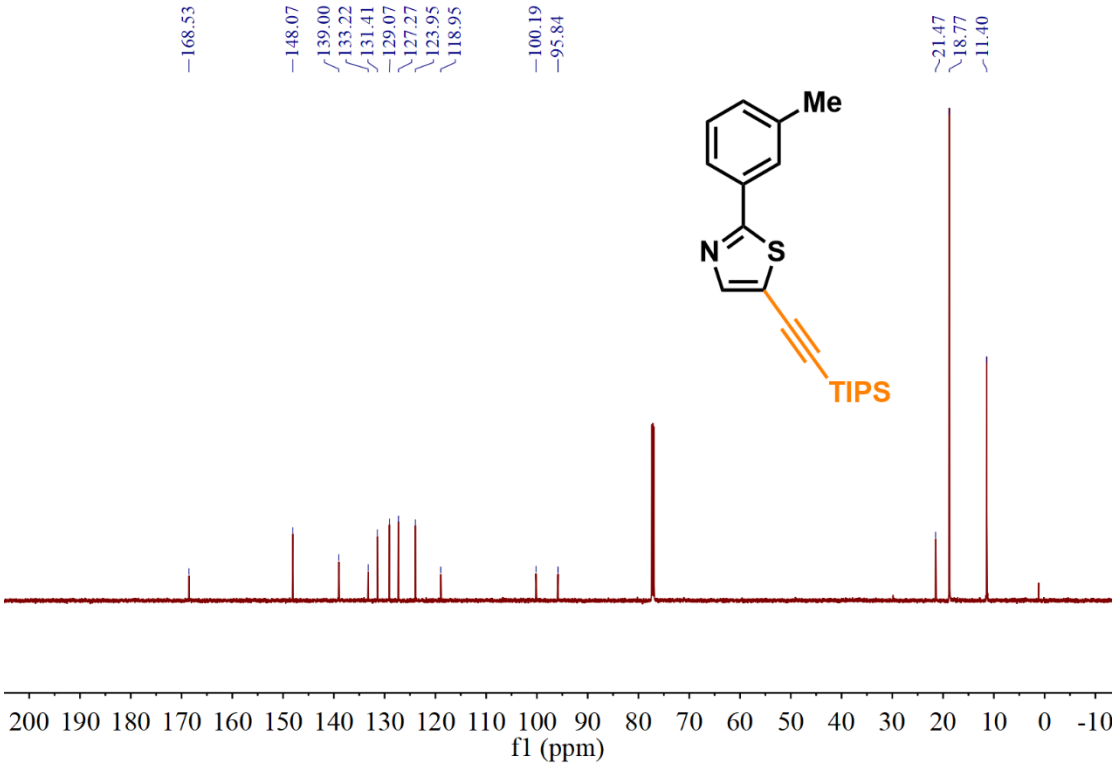
4ja | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



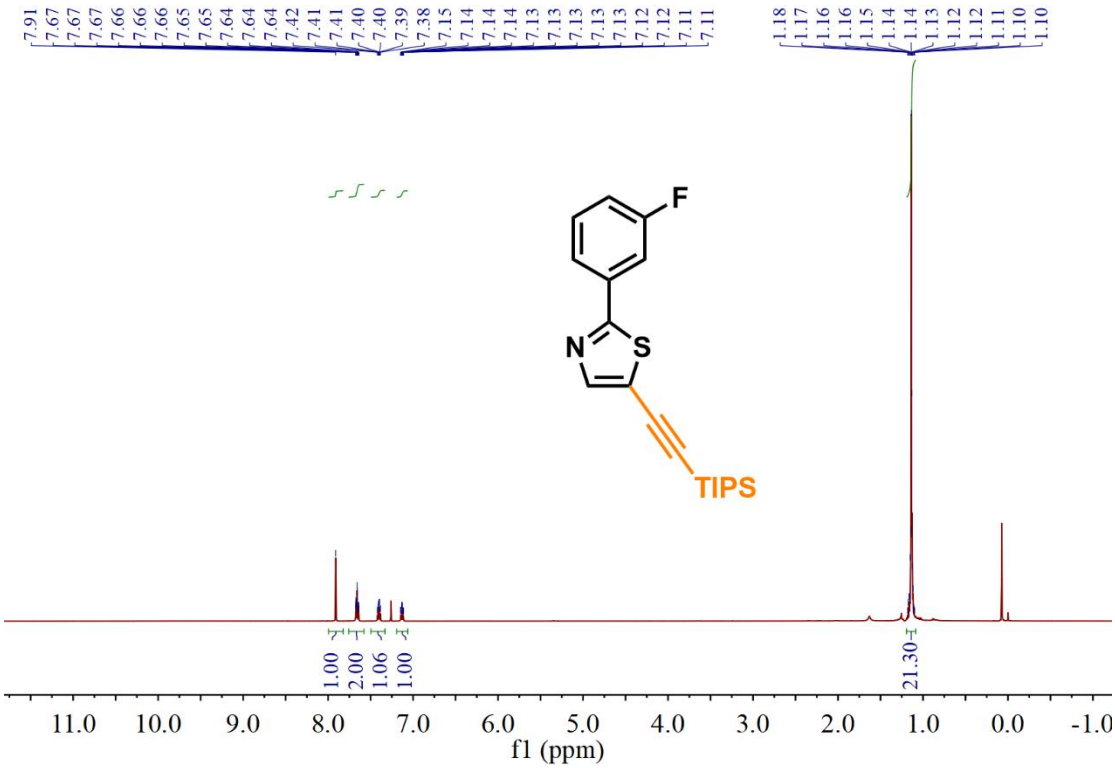
4ka | ^{1}H NMR ($CDCl_3$, 600 MHz)



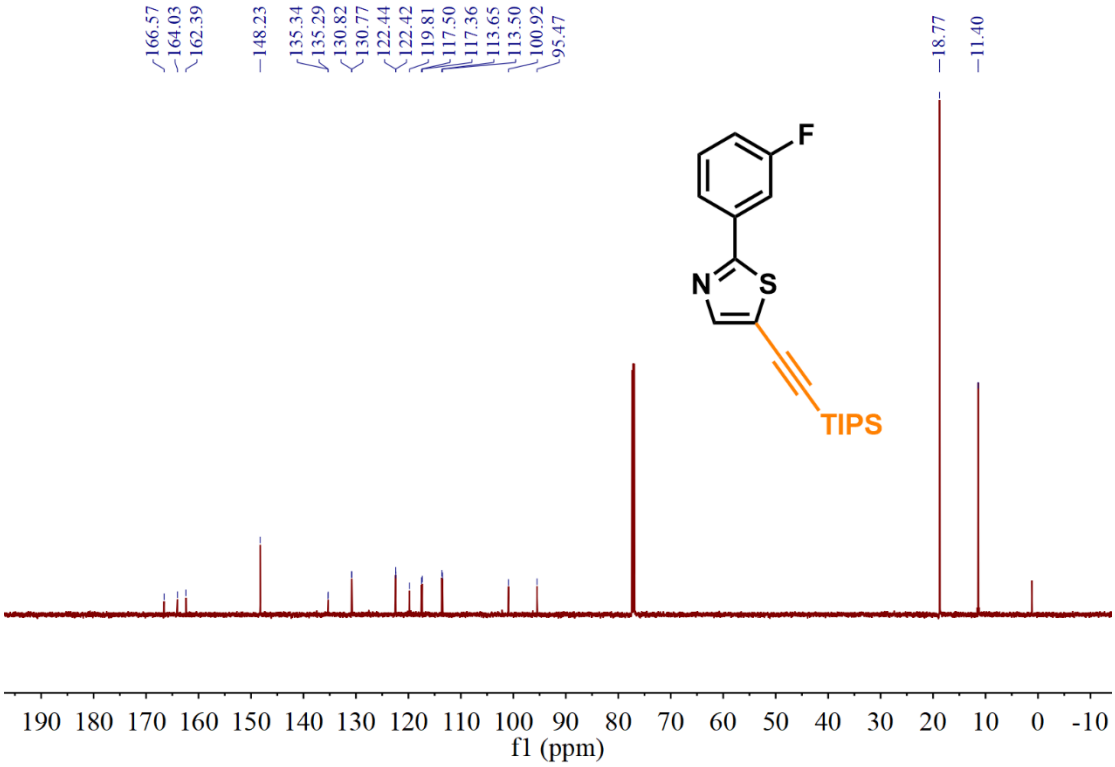
4ka | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



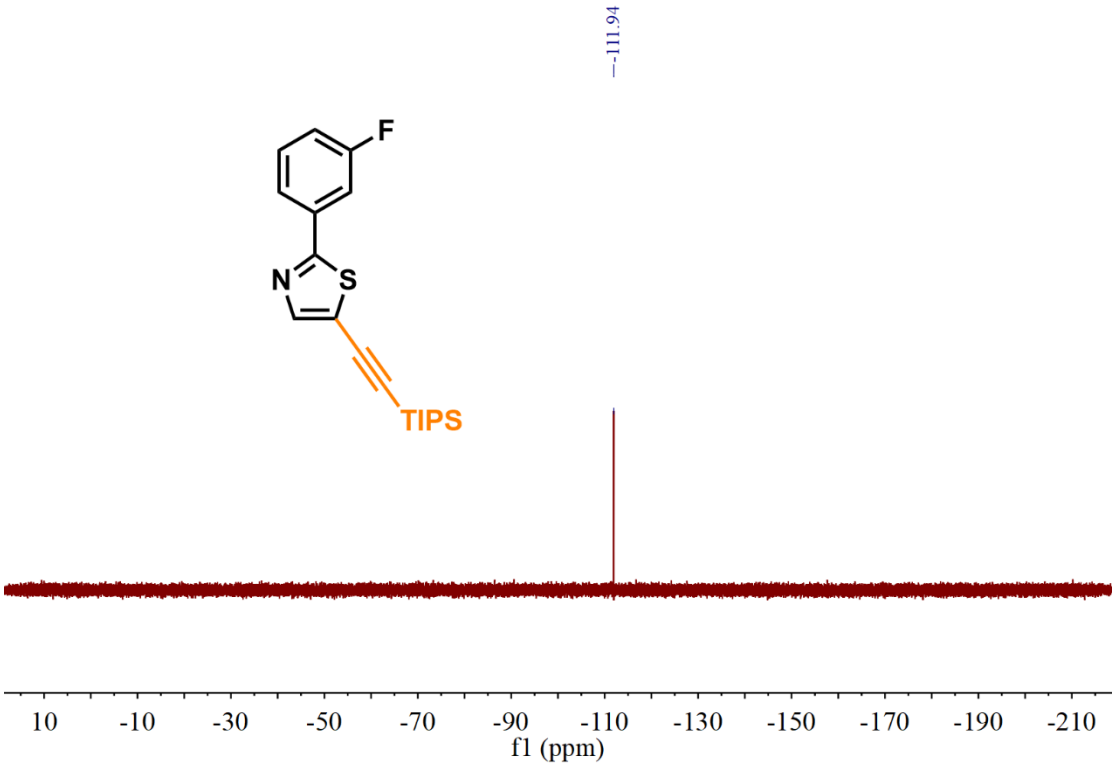
4la | ^{1}H NMR ($CDCl_3$, 600 MHz)



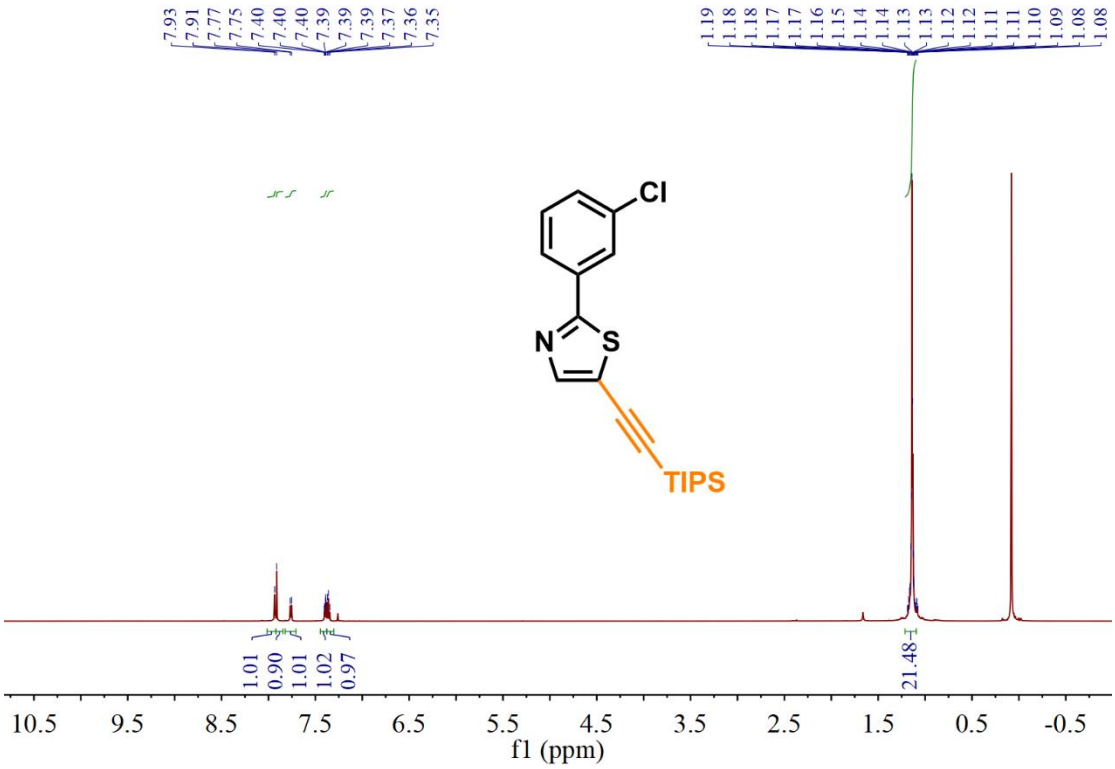
4la | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



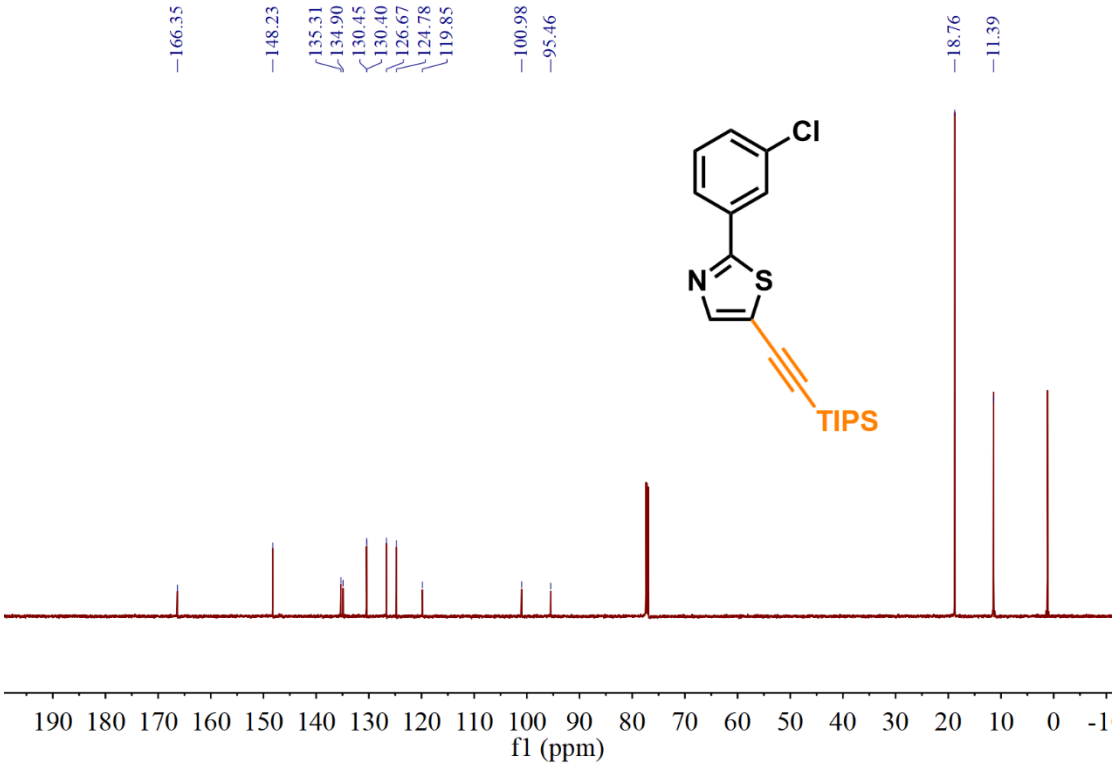
4la | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



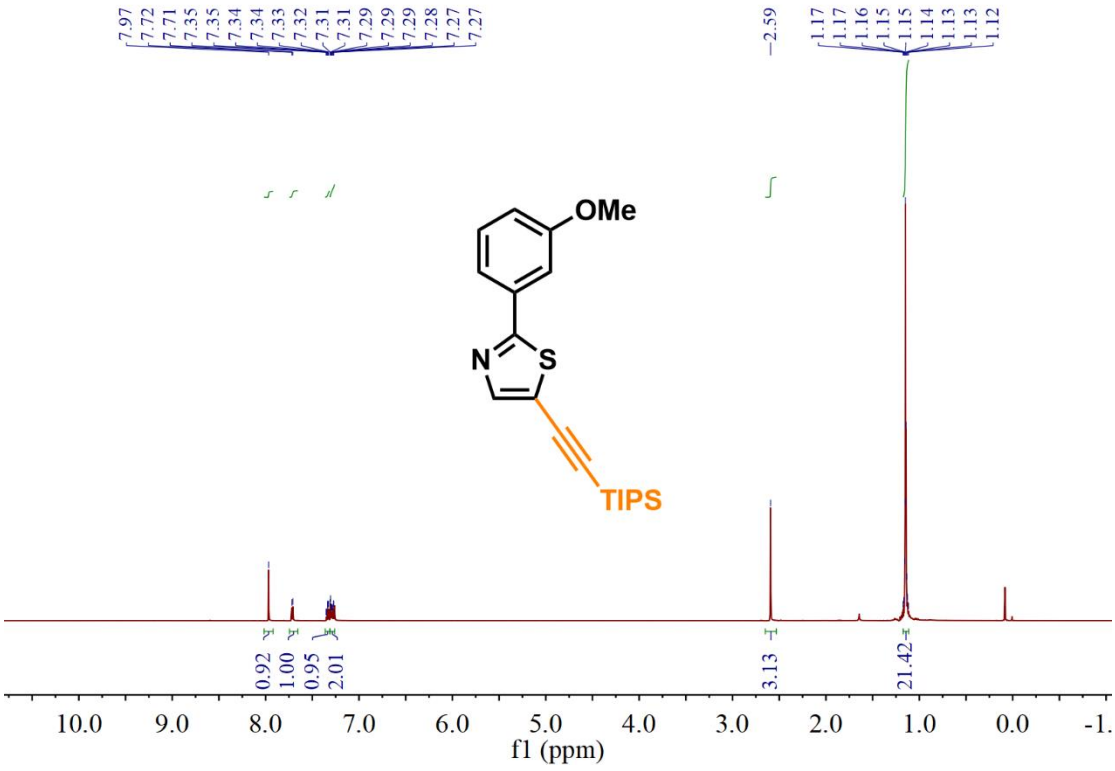
4ma | ^{1}H NMR ($CDCl_3$, 600 MHz)



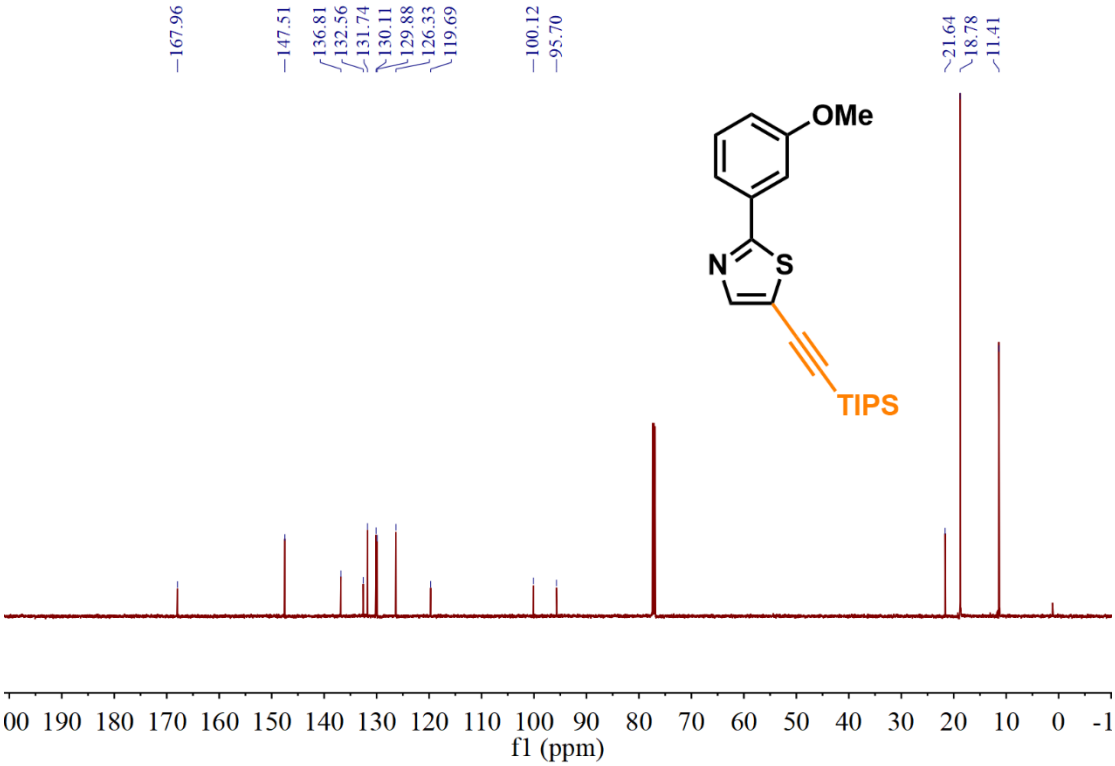
4ma | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



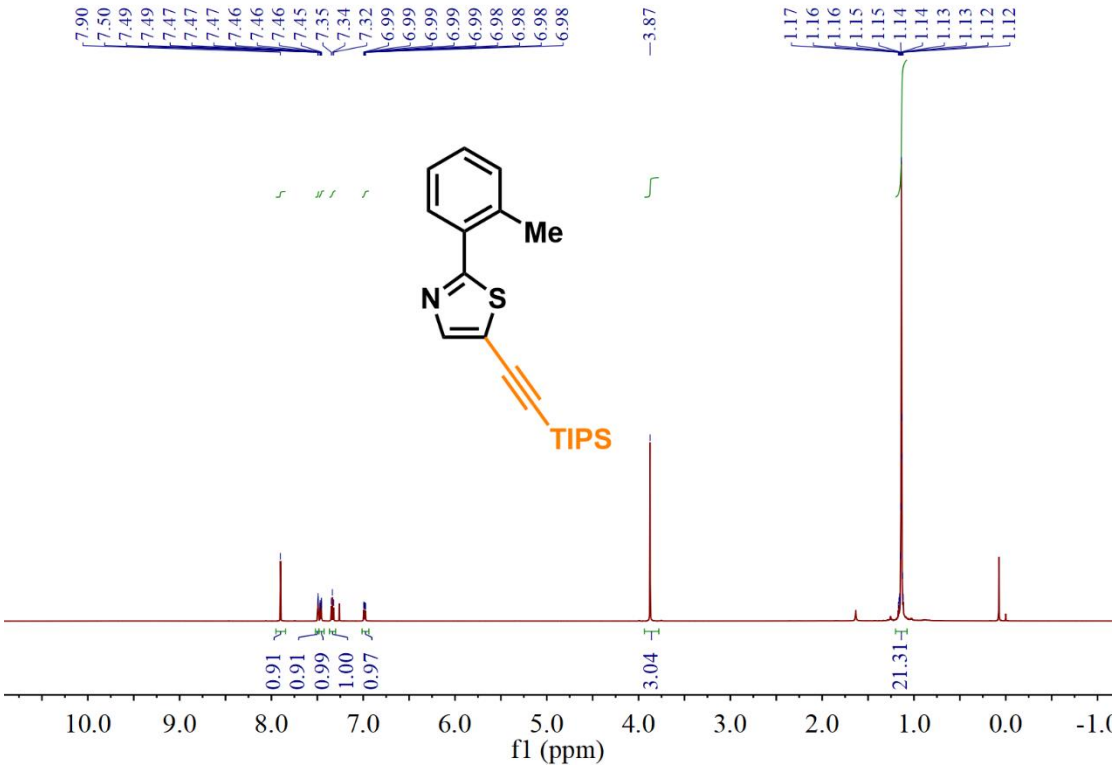
4na | ^{1}H NMR ($CDCl_3$, 600 MHz)



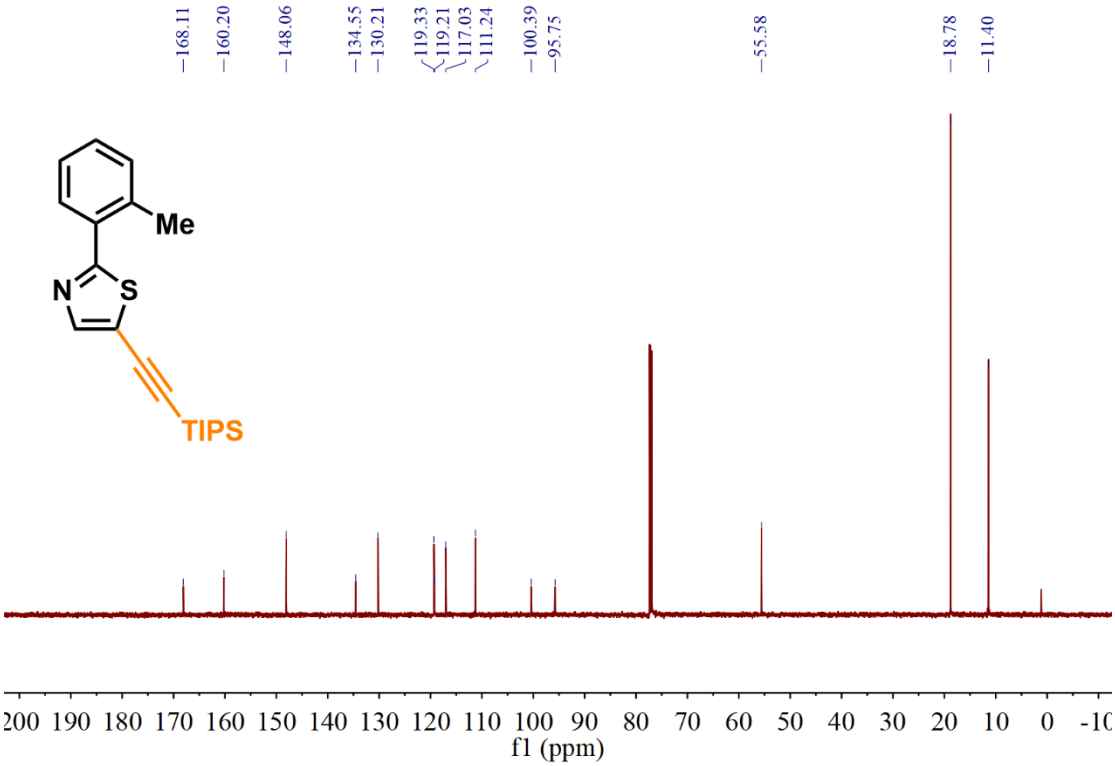
4na | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



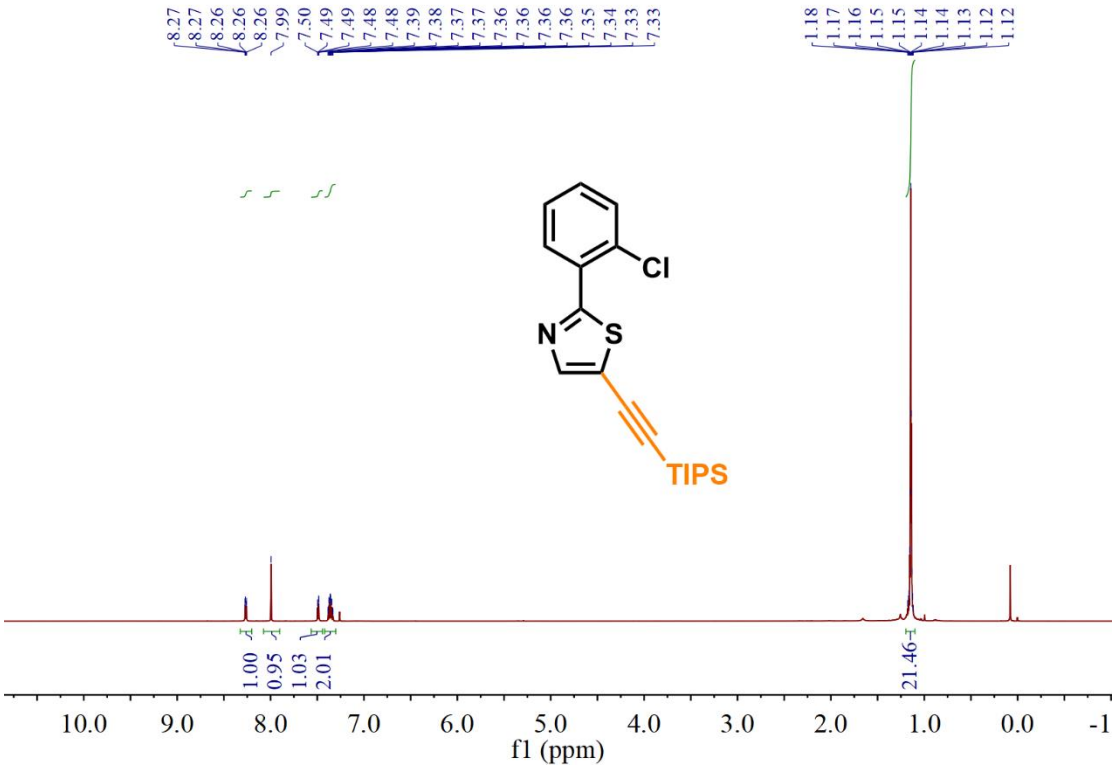
4oa | ^{1}H NMR ($CDCl_3$, 600 MHz)



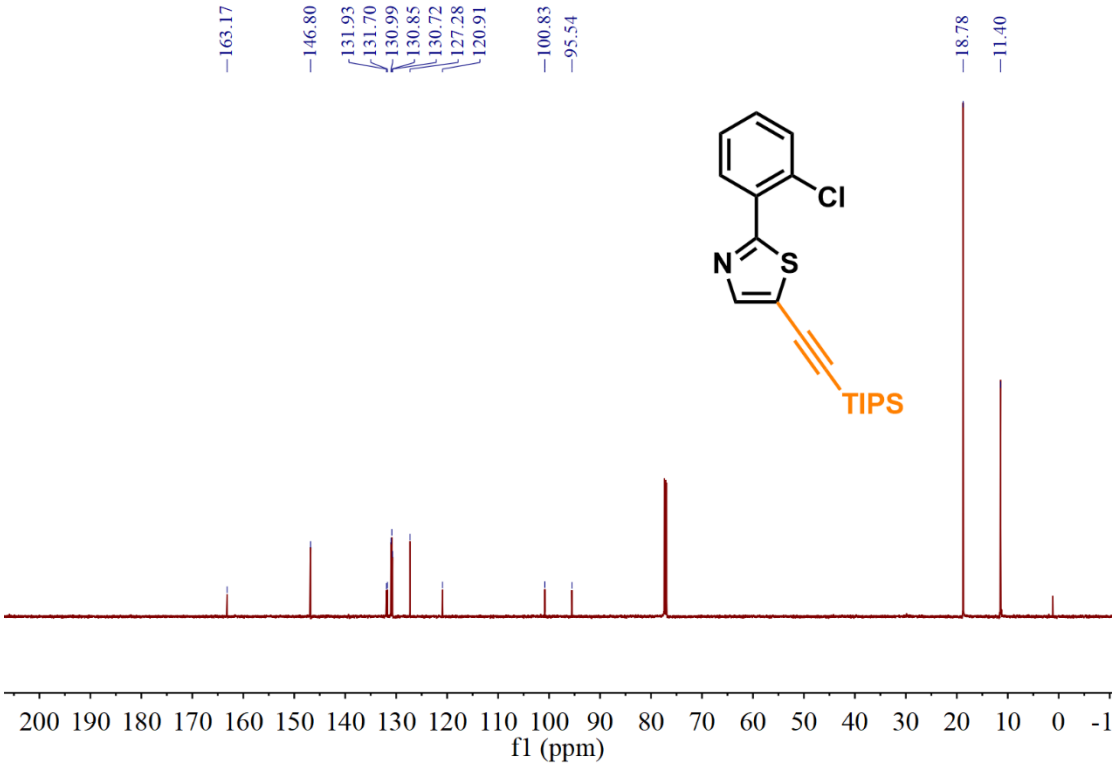
4oa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



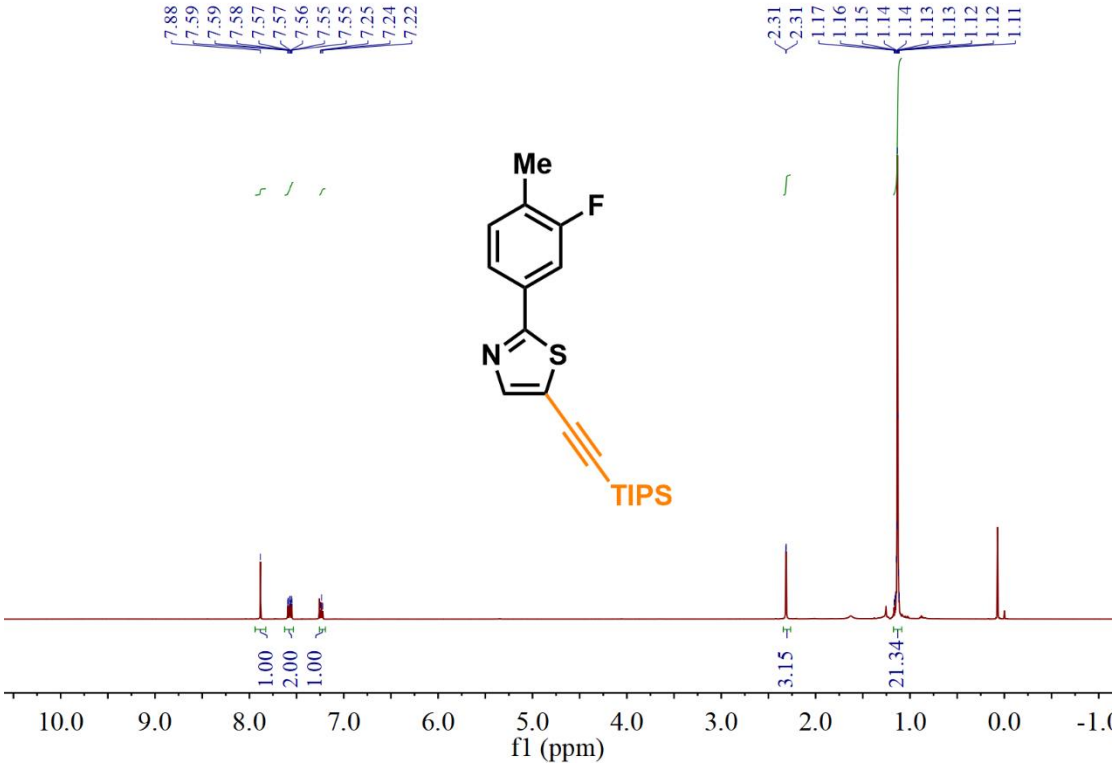
4pa | ^{1}H NMR ($CDCl_3$, 600 MHz)



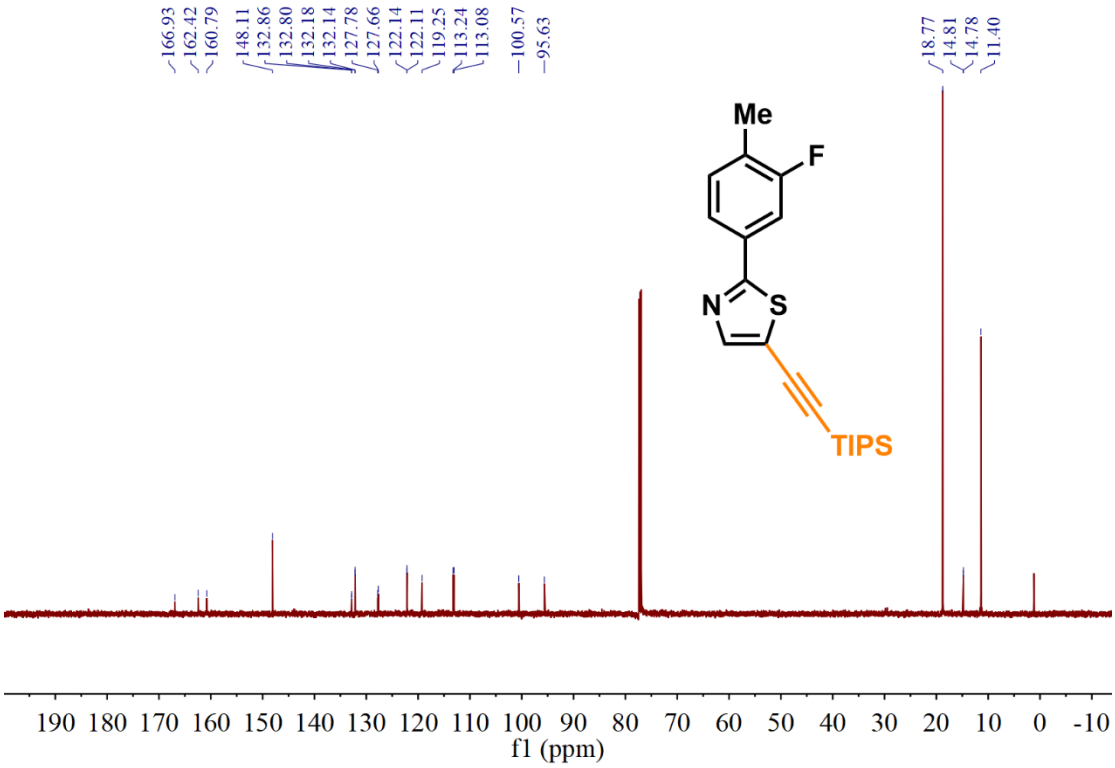
4pa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



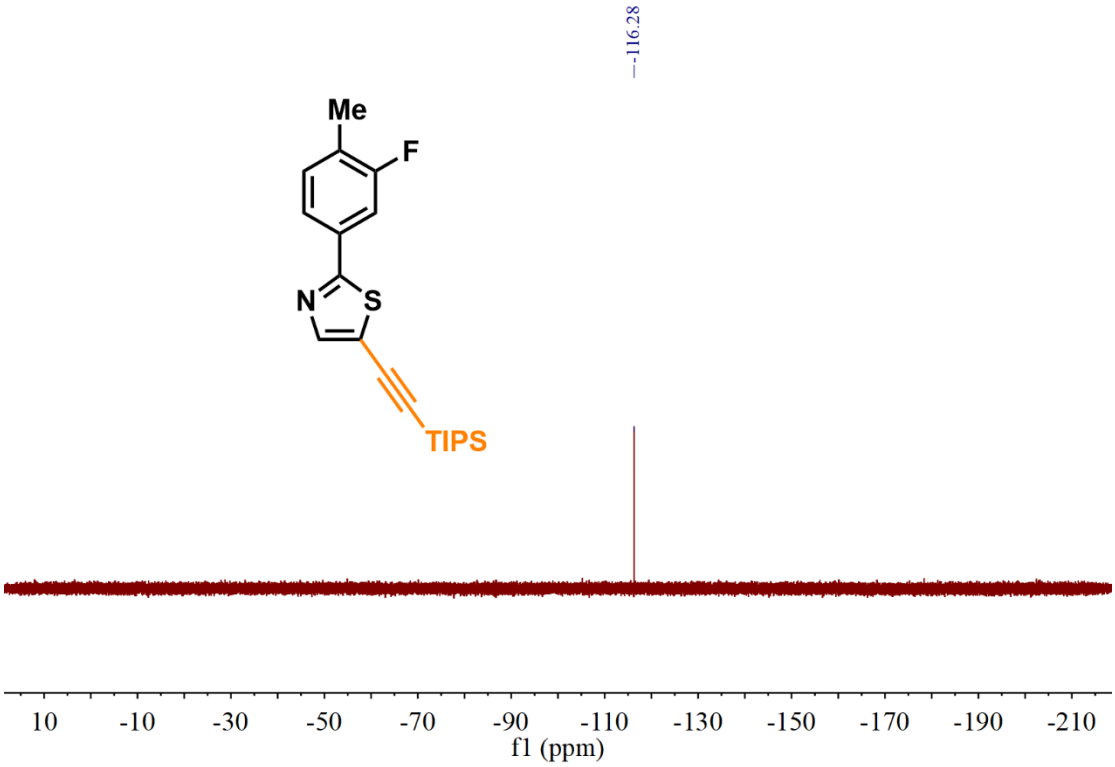
4qa | ^{1}H NMR ($CDCl_3$, 600 MHz)



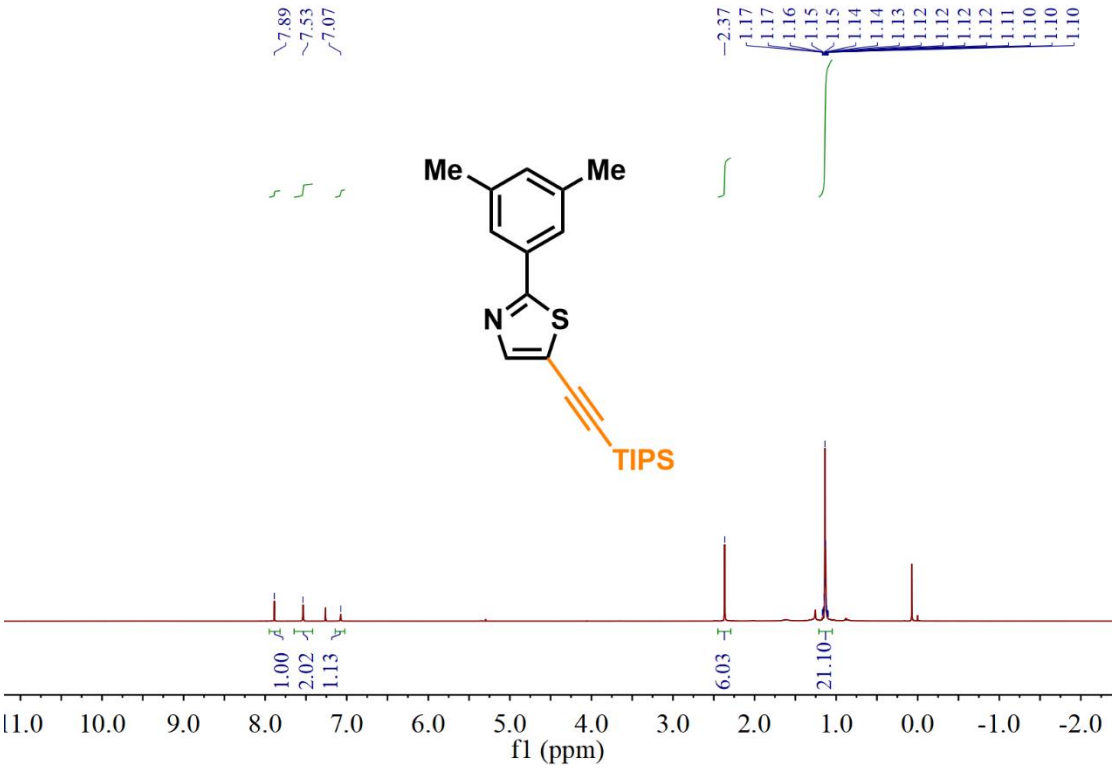
4qa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



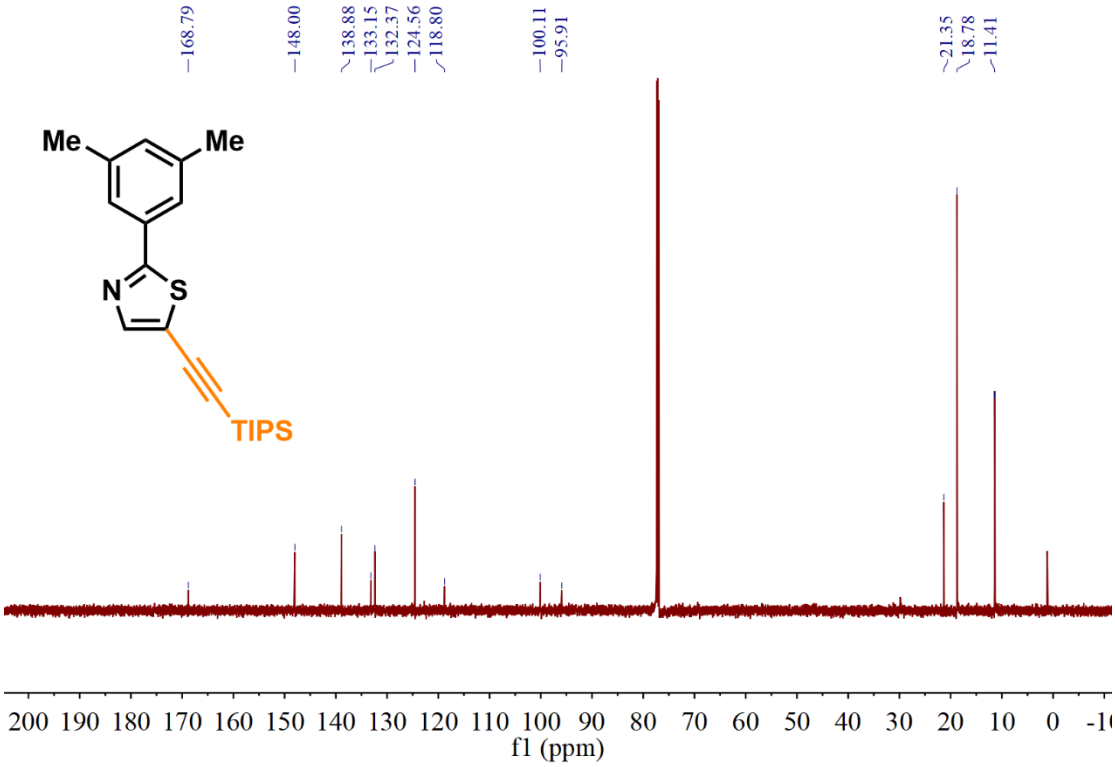
4qa | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



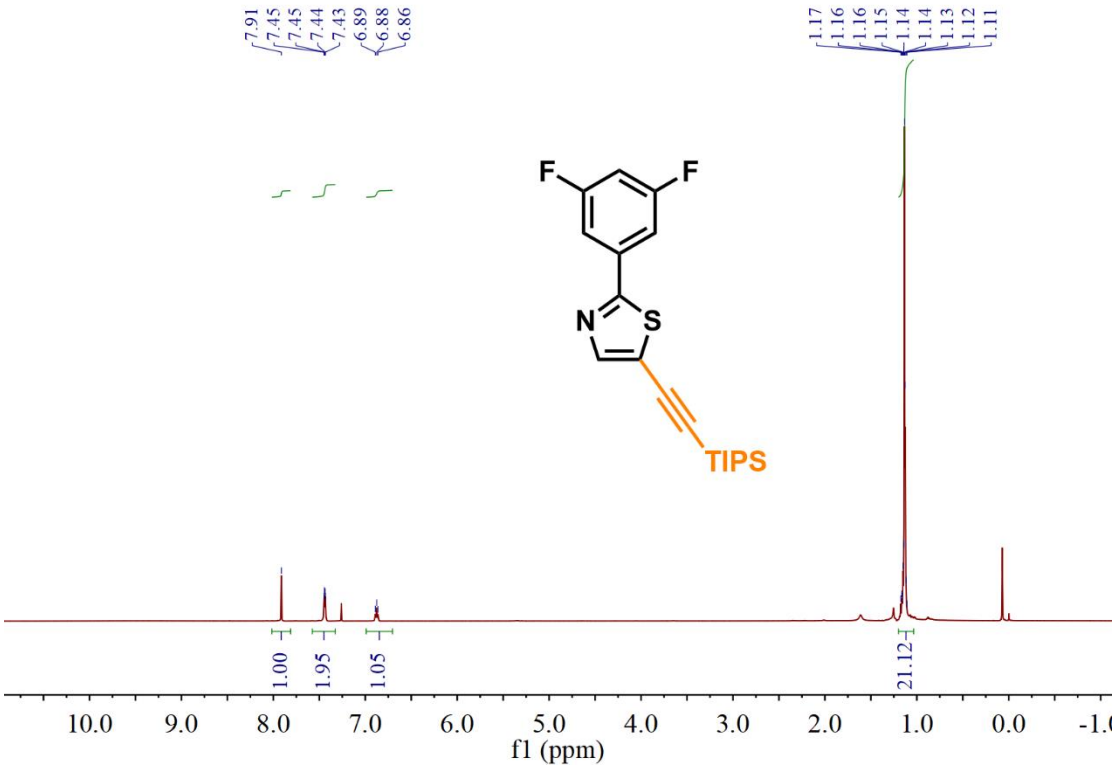
4ra | ^{1}H NMR ($CDCl_3$, 600 MHz)



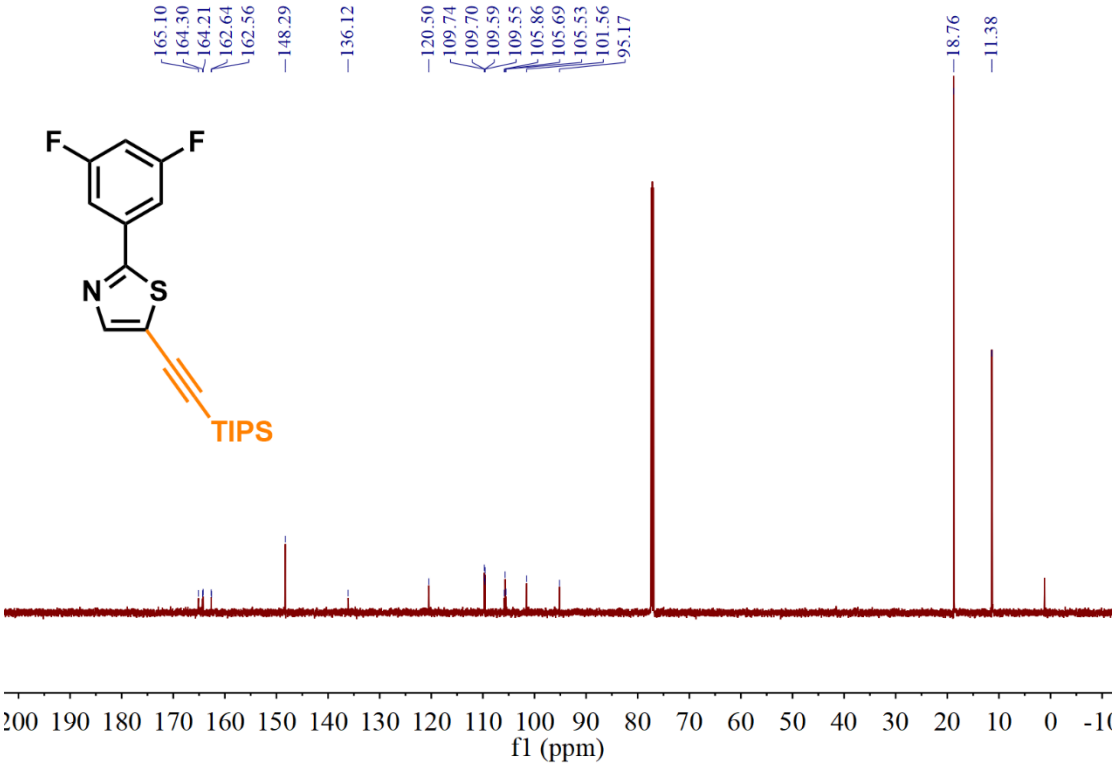
4ra | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



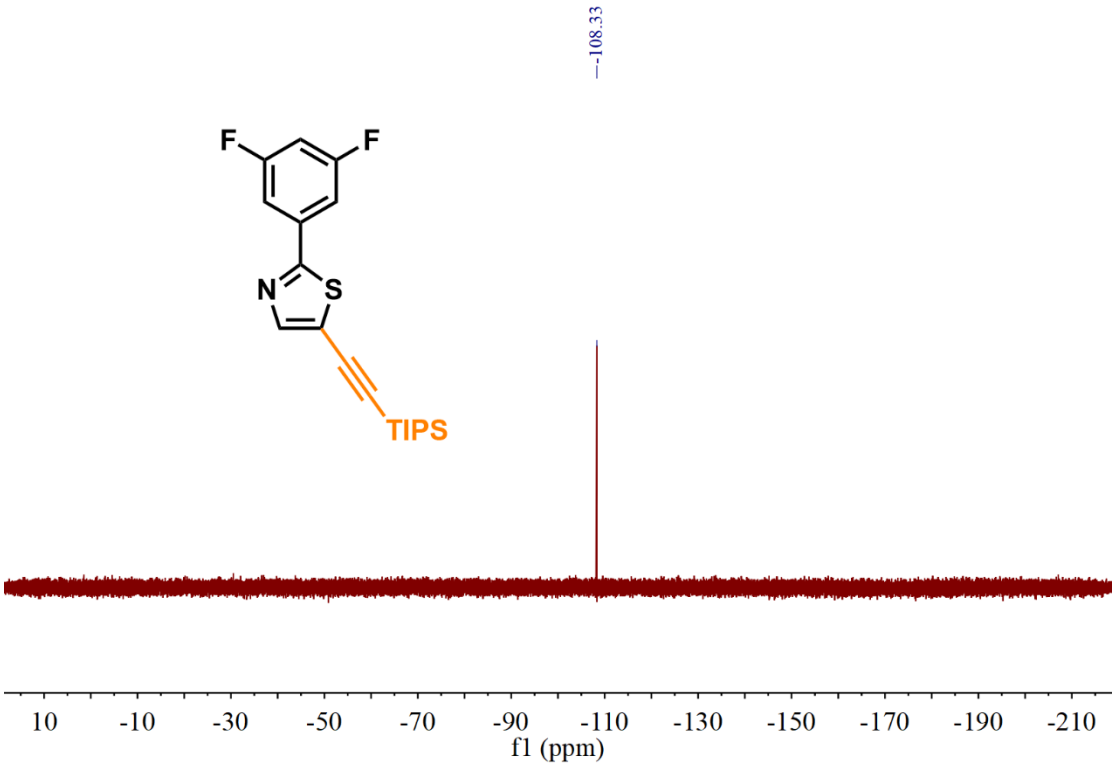
4sa | ^{1}H NMR ($CDCl_3$, 600 MHz)



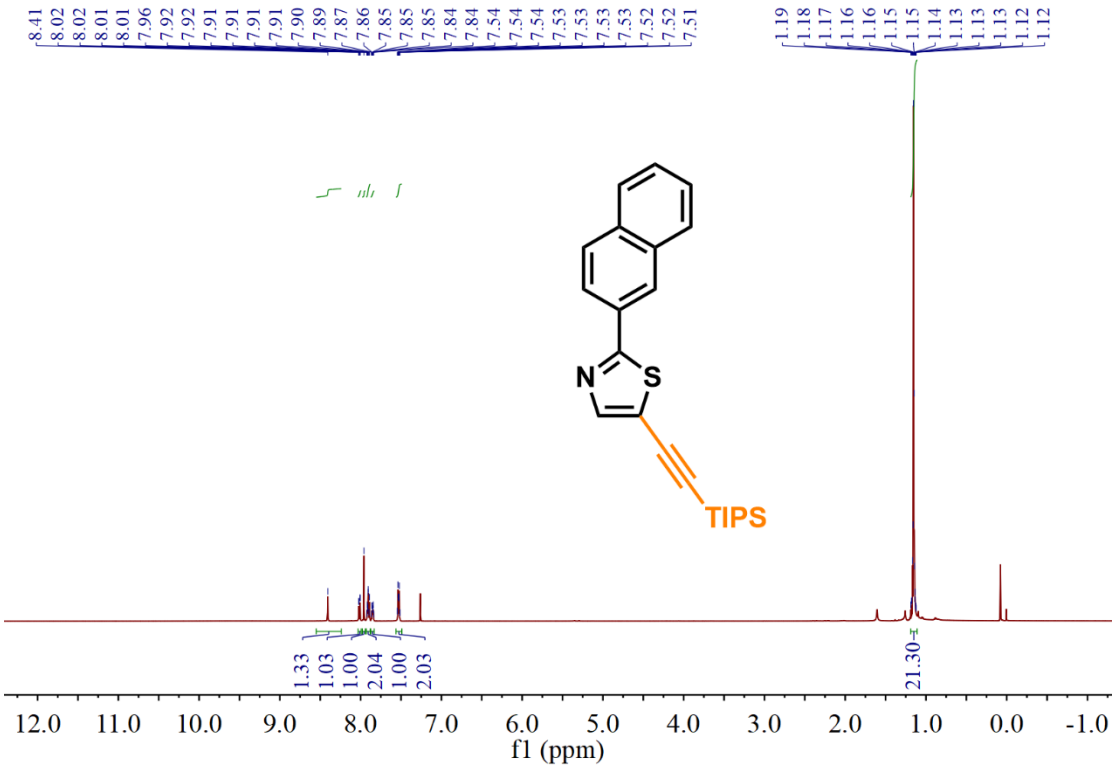
4sa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



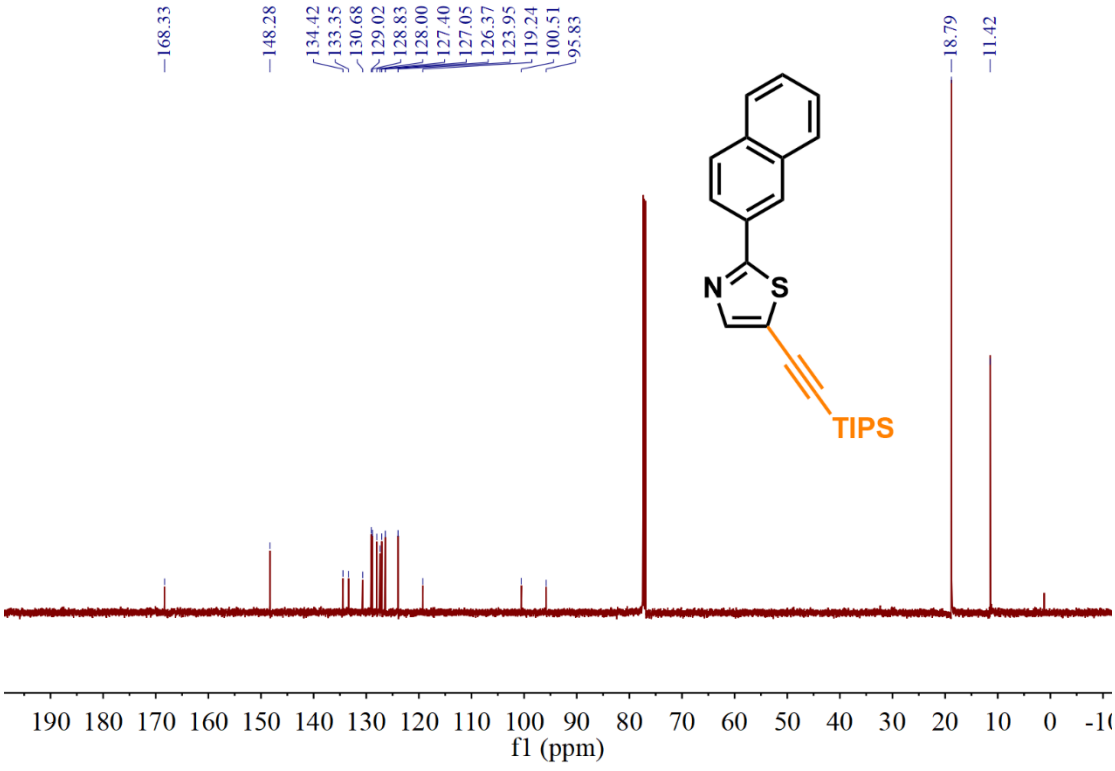
4sa | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



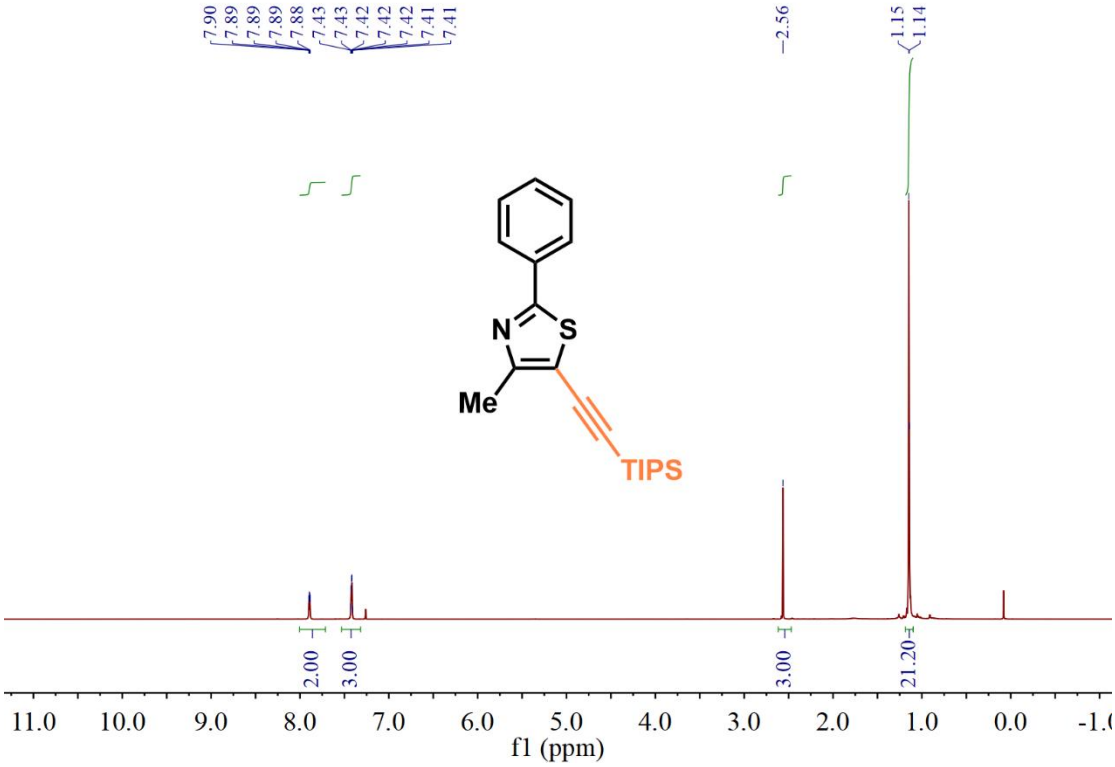
4ta | ^{1}H NMR ($CDCl_3$, 600 MHz)



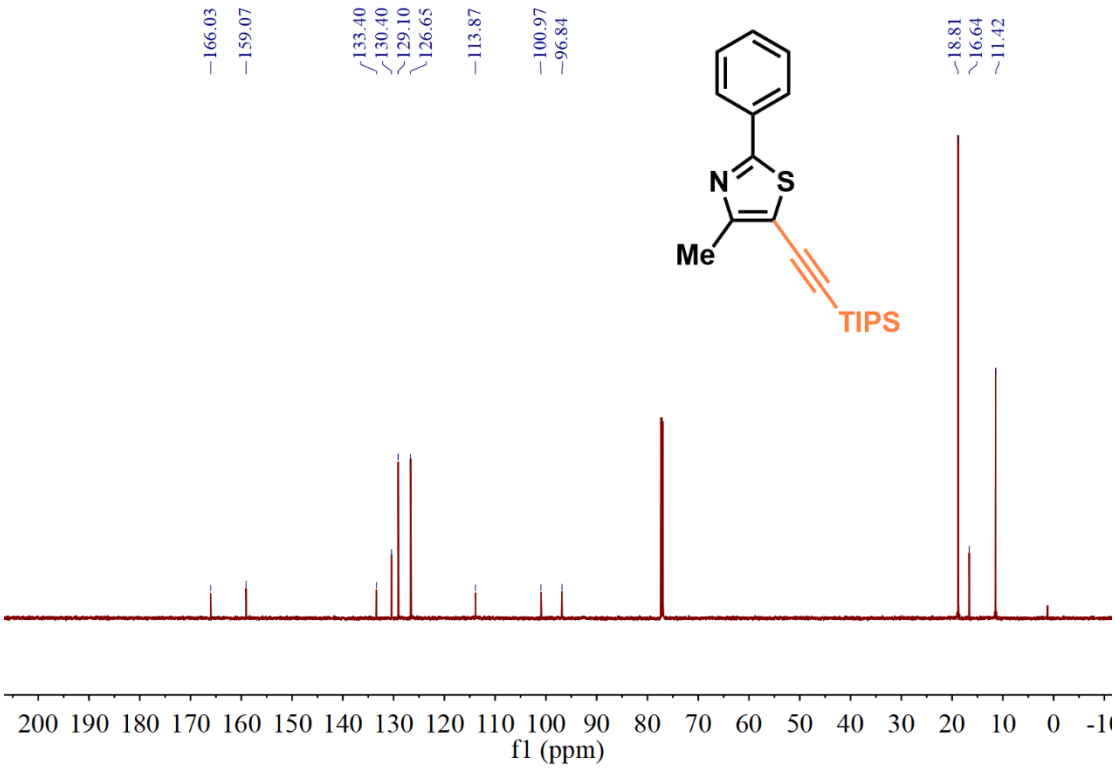
4ta | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



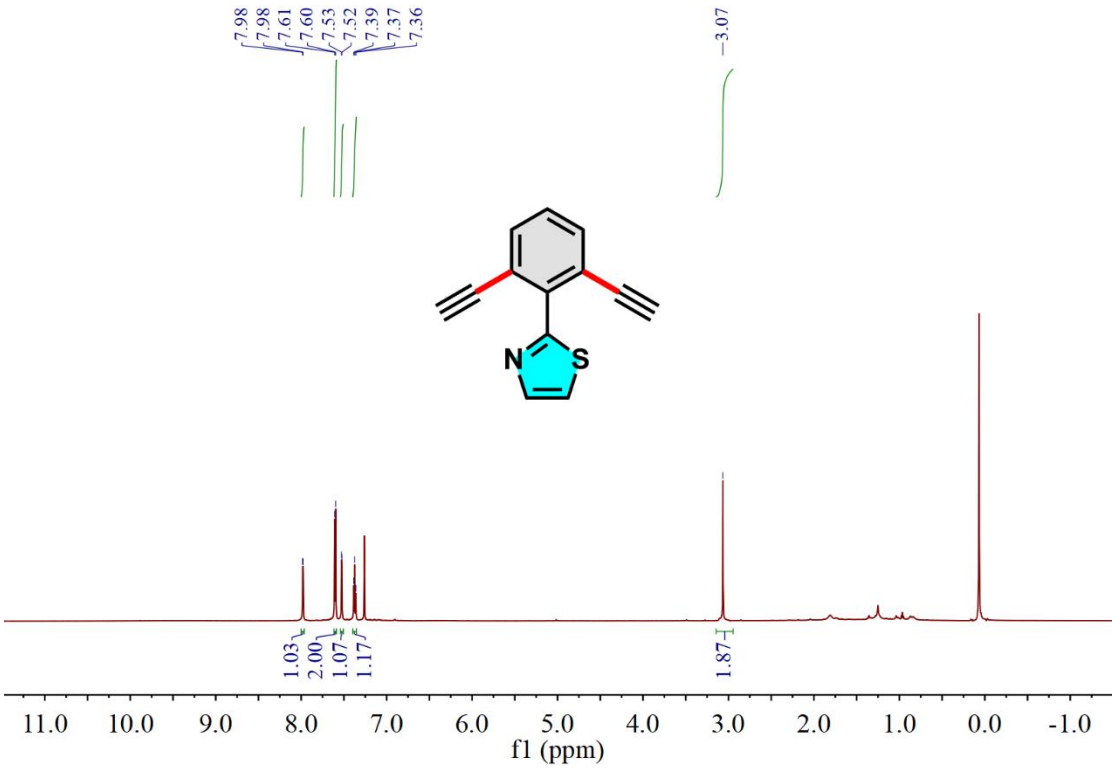
4ua | ^{1}H NMR ($CDCl_3$, 600 MHz)



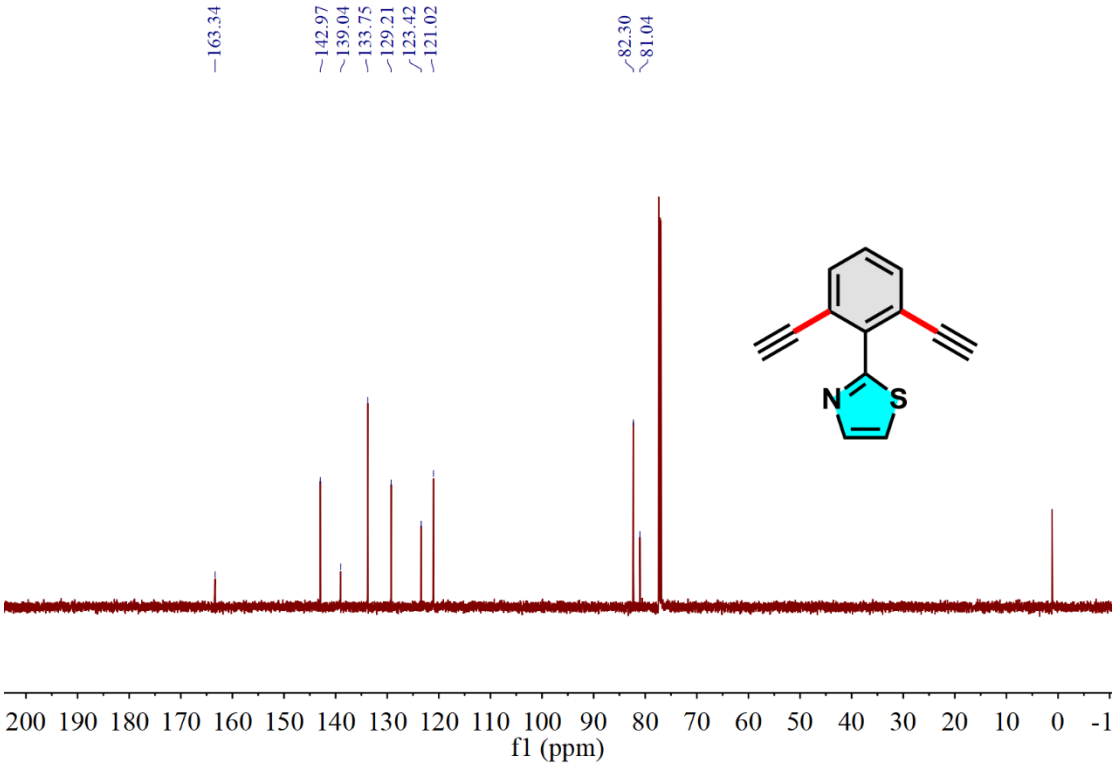
4ua | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



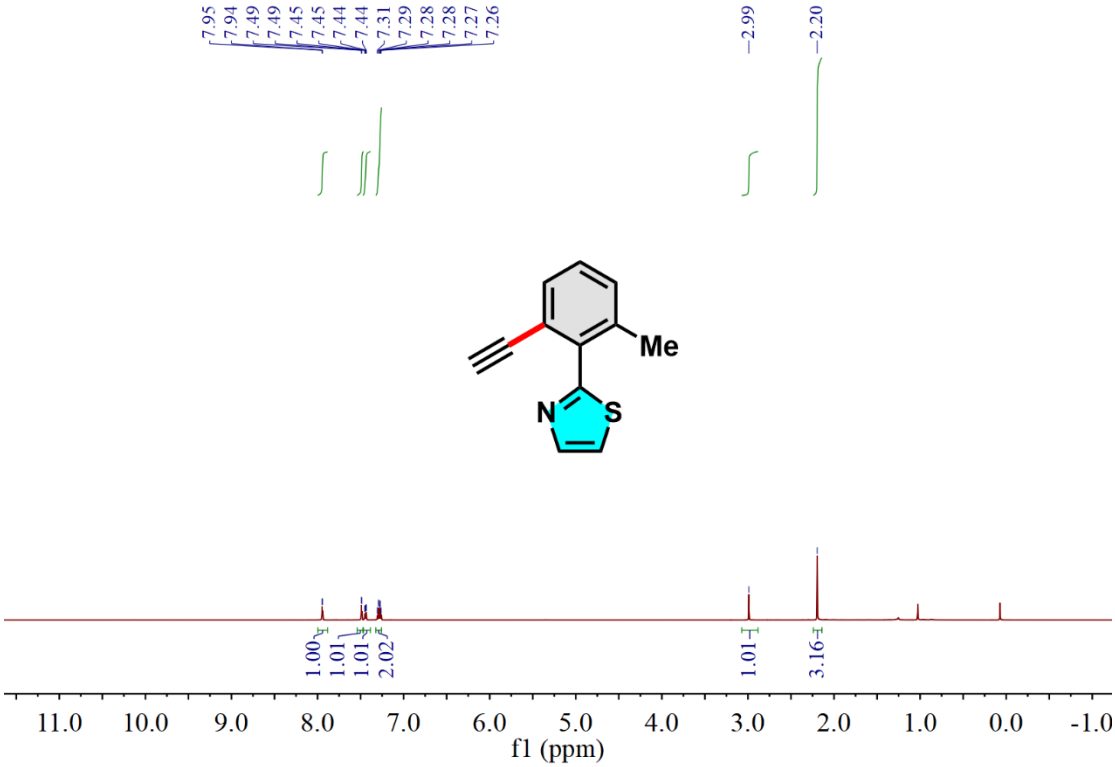
5aa | ^{1}H NMR ($CDCl_3$, 600 MHz)



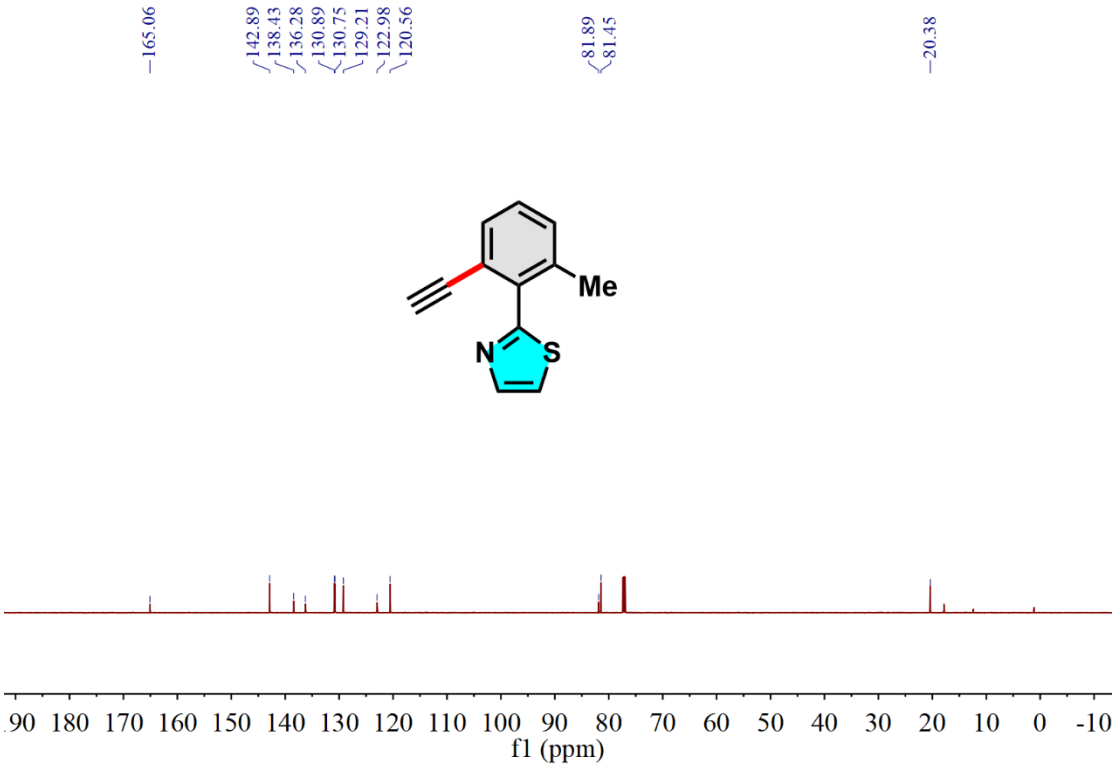
5aa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



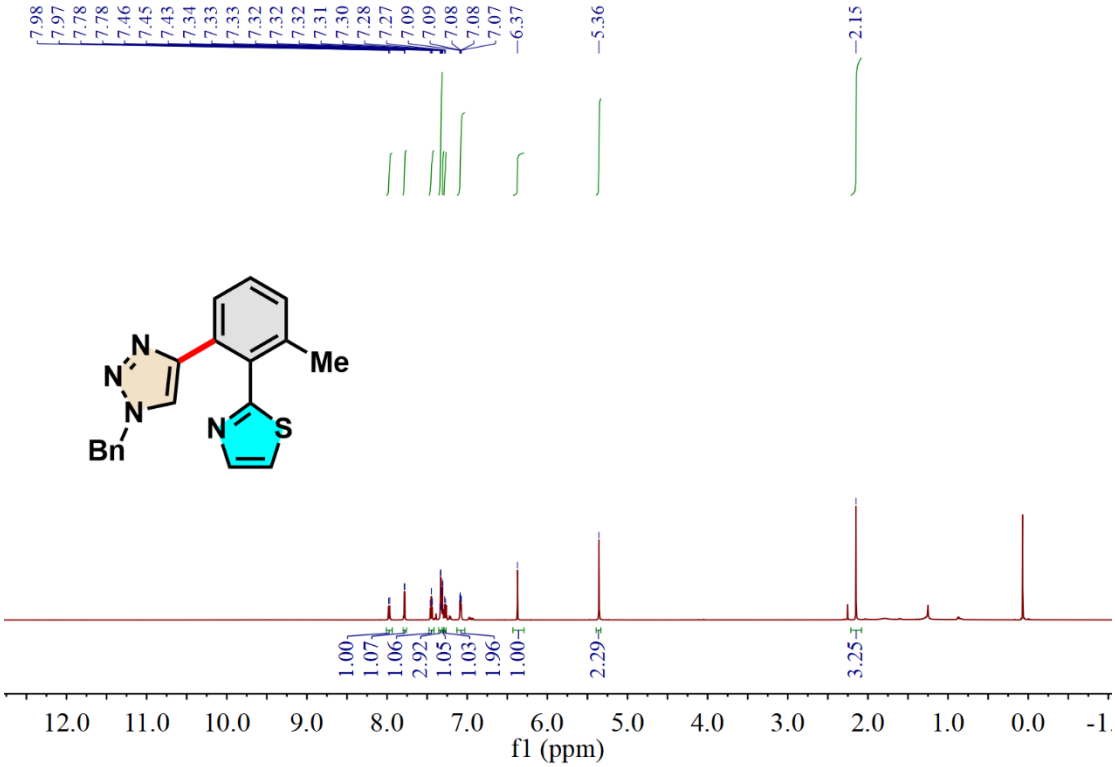
6aa | ^{1}H NMR ($CDCl_3$, 600 MHz)



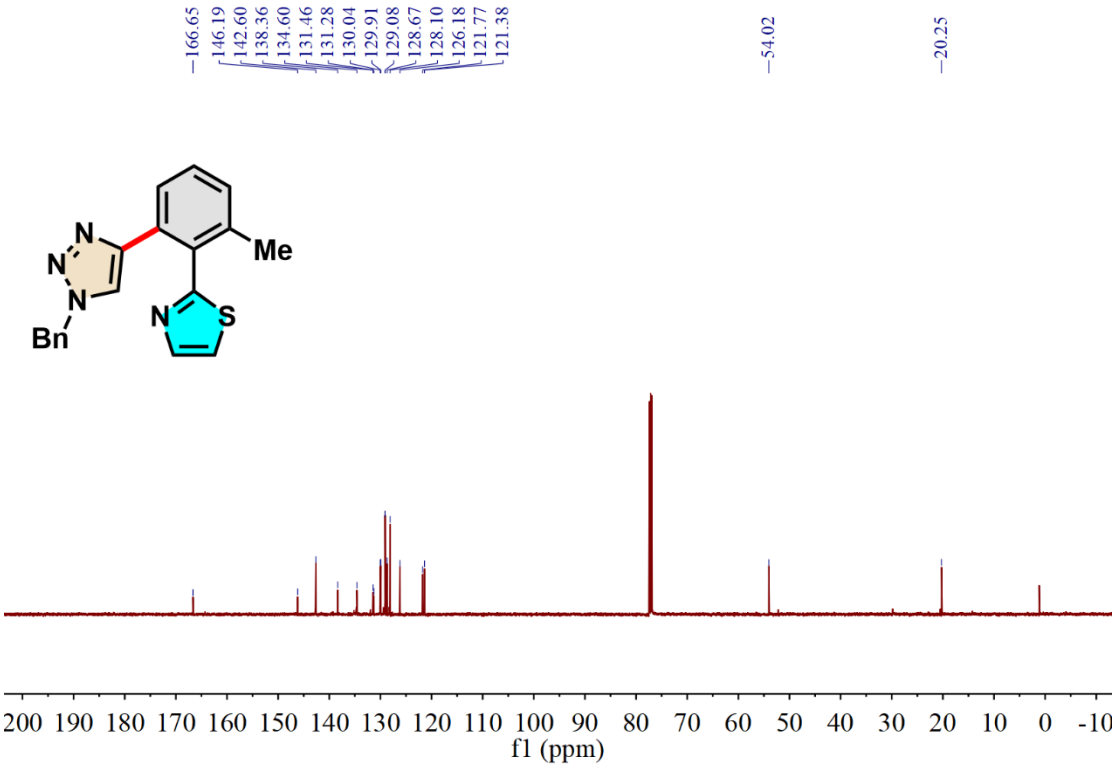
6aa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



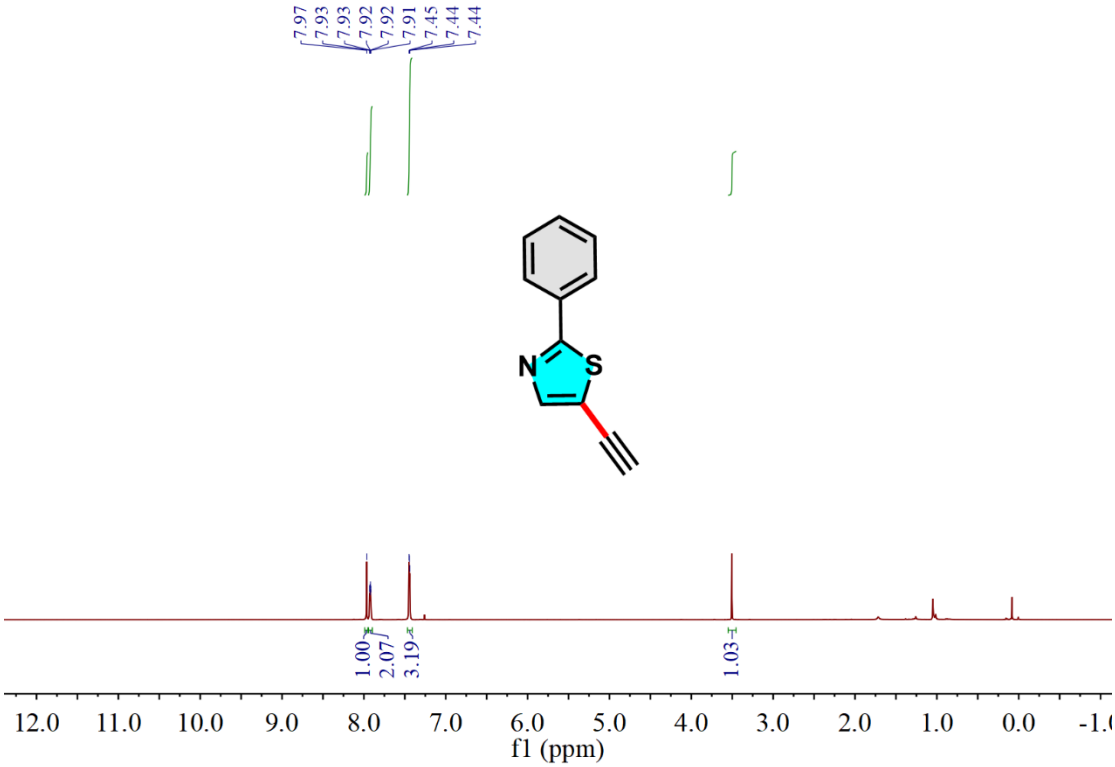
7aa | ^{1}H NMR ($CDCl_3$, 600 MHz)



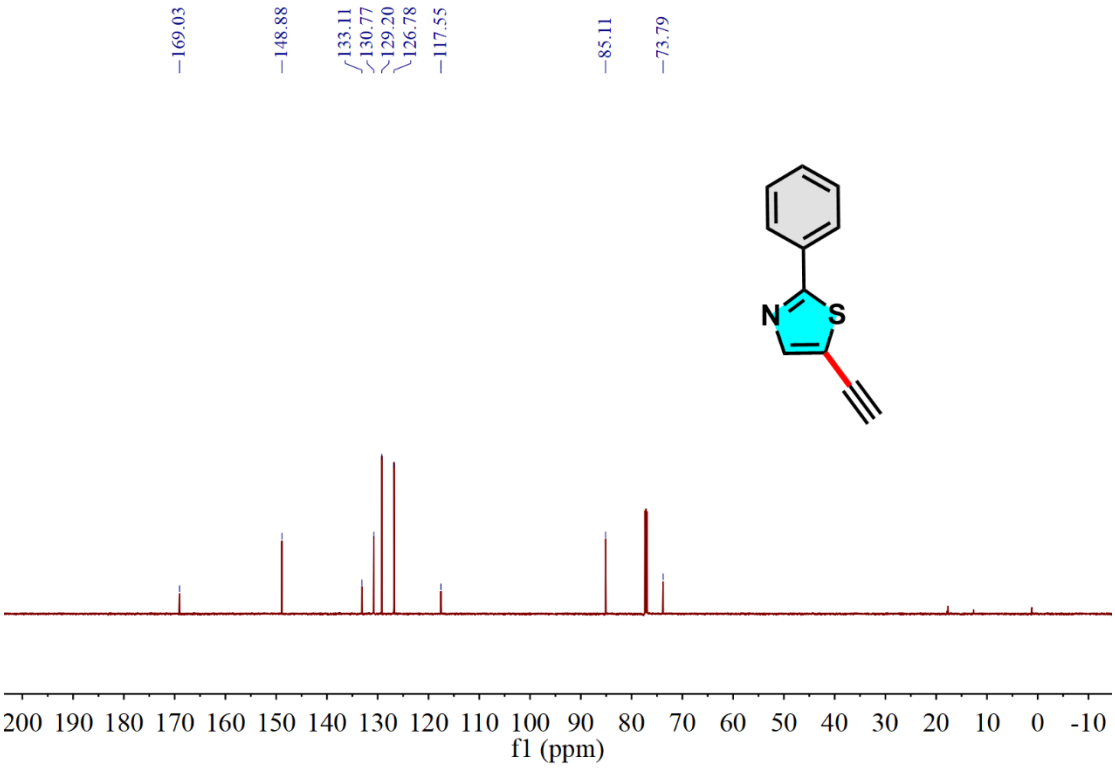
7aa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



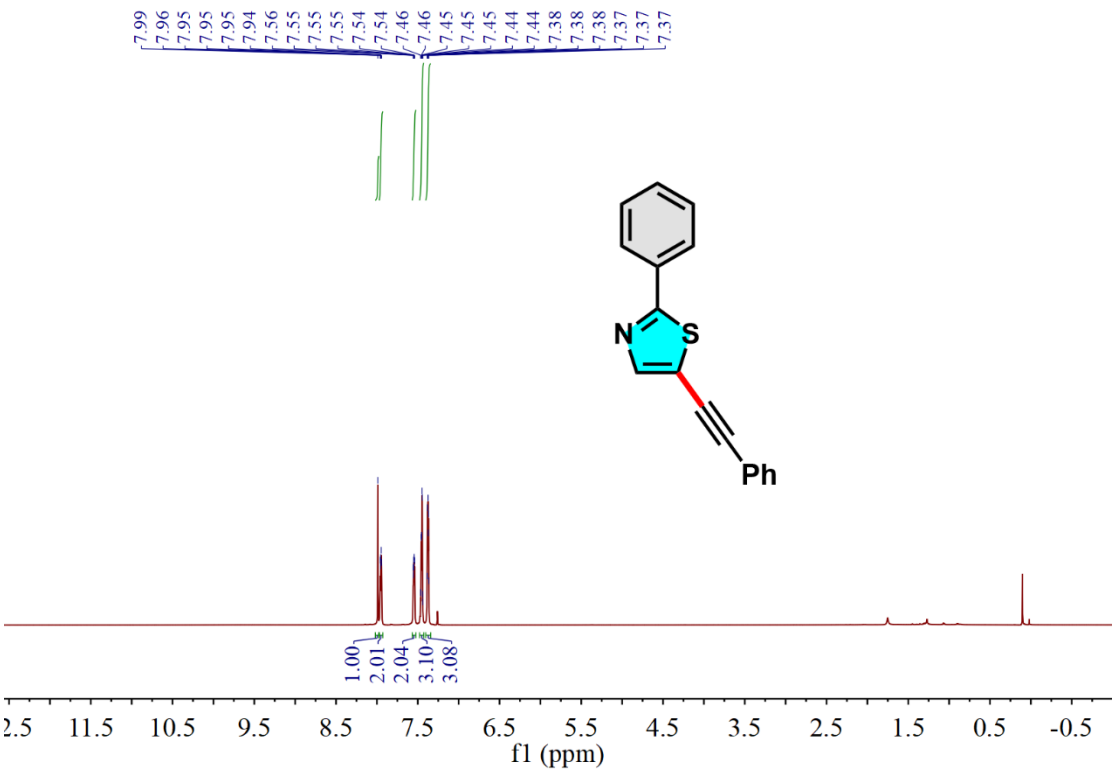
8aa | ^{1}H NMR ($CDCl_3$, 600 MHz)



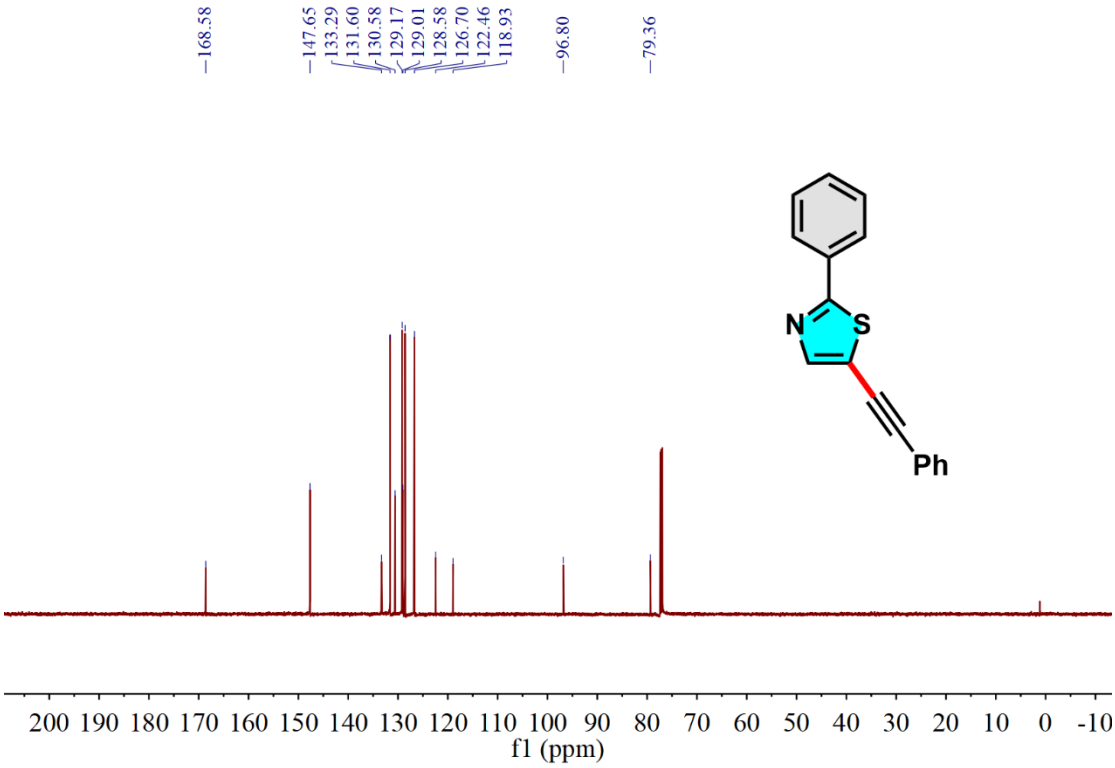
8aa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



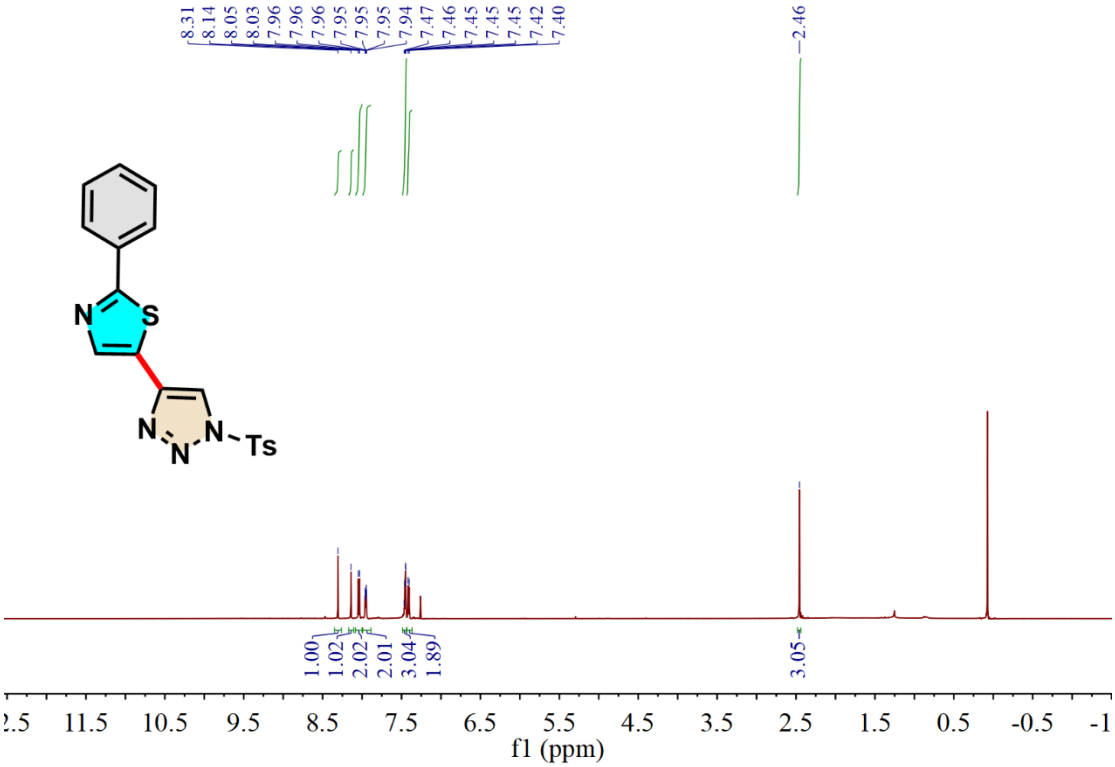
9aa | ^{1}H NMR ($CDCl_3$, 600 MHz)



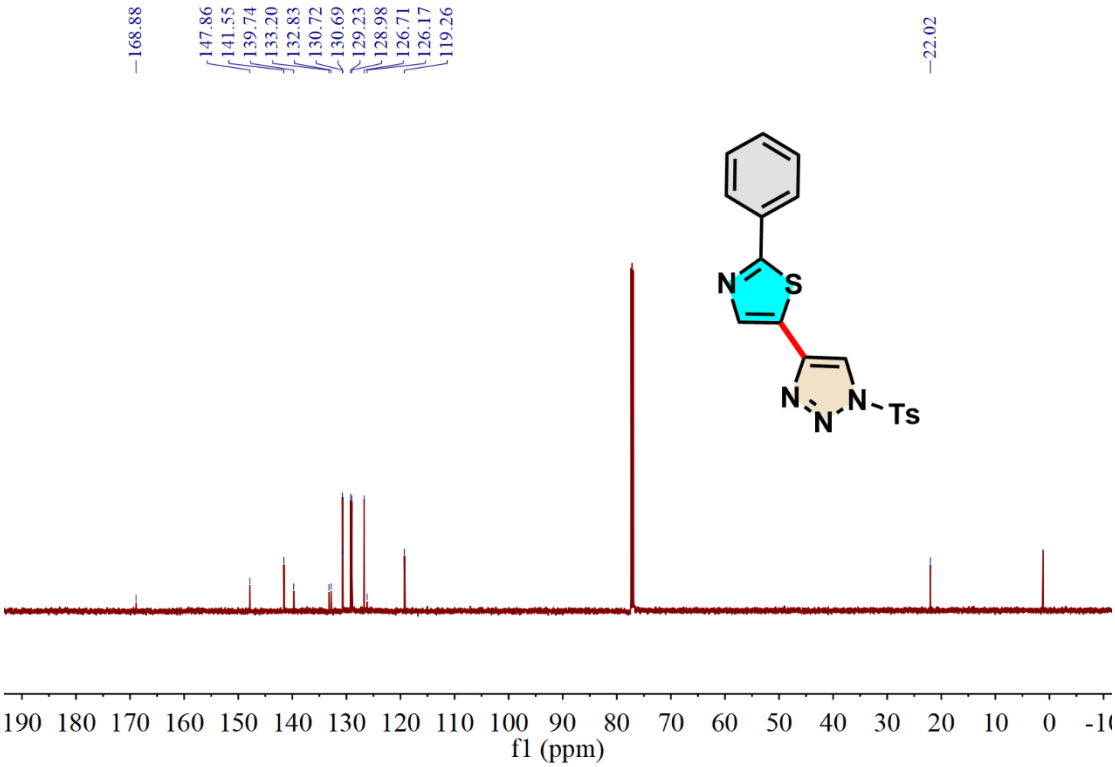
9aa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



10aa | ^{1}H NMR ($CDCl_3$, 600 MHz)



10aa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



6. References

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2 X. Huang, P. Zhou, X. Yang, R. Wang, G. Huang, T. Liang and Z. Zhang, *Adv. Synth. Catal.*, 2023, **365**, 3674-3679.