Supplementary Information

3-Thiolated pyrroles/pyrrolines: controllable synthesis and usage for the construction of thiolated fluorophores

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General information

NMR

^{1}H and ^{13}C spectra were collected on 400 M NMR spectrometers (Bruker AVANCE). Chemical shifts for protons are reported in parts per million (ppm) downfield and are referenced to residual protium in the NMR solvent. ($CDCl_3$ = δ 7.26, DMSO-d_6 = δ 2.50). Chemical shifts for carbon are reported in parts per million downfield and are referenced to the carbon resonances of solvent ($CDCl_3$ = δ 77.0, DMSO-d_6 = δ 39.52). Date are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = double, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration.

MS

High-resolution mass spectra (HRMS) were performed on a micrOTOF-Q II instrument with an ESI or EI source.

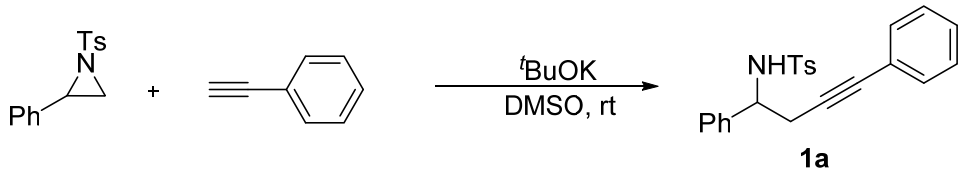
Chromatography

All solvents were obtained from commercial sources and were purified according to standard procedures. Petroleum ether (PE), where used, has the boiling point range 60-90 ºC. Column chromatography was performed with silica gel (300-400 mesh).

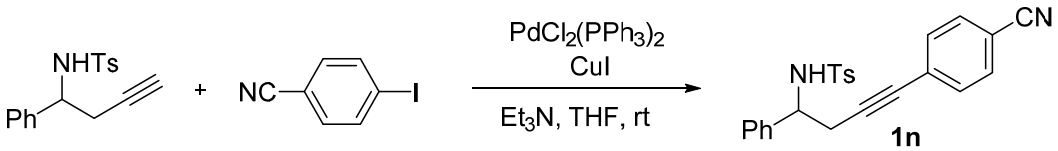
Experimental procedure

General procedure I: synthetic procedures of homopropargyl amine, sulfur reagents

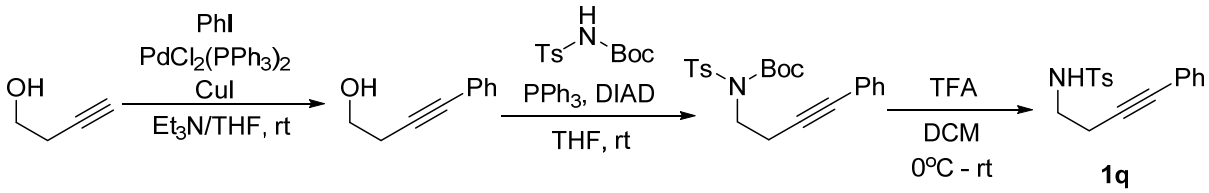
Compounds **1a**, **1l, 1m, 1o,** and **1p** are prepared following **general procedure A**. Compound **1n** is prepared following **general procedure B**. Preparation of **1q** and **1r** is according to the **general procedure C.**



General procedure A:[S1] Phenylacetylene (1.5 equiv.) was added to a stirred solution of ^{t}BuOK (1.5 equiv.) in DMSO (1 mL) for 10 min, and then aziridine (1.0 mmol) was added under nitrogen. The reaction mixture was stirred at room temperature until complete consumption of substrates (monitored by TLC). Then reaction mixture was quenched carefully with 1 N HCl aqueous solution. The resulting mixture was poured into EtOAc, and washed with H_2O and saturated aqueous $NaHCO_3$ solution. The organic layer was dried over anhydrous $MgSO_4$. The solvent was removed in vacuum and the crude product was purified by flash column chromatography to provide **1a** as a yellow solid.



General procedure B:[S2] Bis(triphenylphosphine)palladiu (II) dichloride (1 mol%), copper (I) iodide (2 mol%), 4-iodobenzonitrile (1.2 equiv.), homopropargyl tosylamide (1.0 mmol) and triethyl amine (1 mL) were added to dry THF (1 mL). The reaction mixture was stirred at room temperature until complete consumption of substrates (monitored by TLC). The solvent was removed in vacuum and the crude product was purified by flash column chromatography to provide **1n** as a white solid.

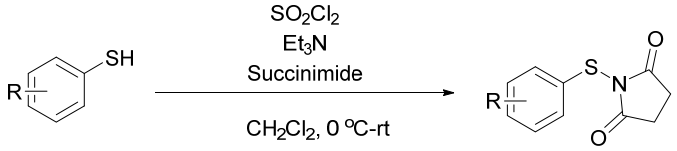


General procedure C:[S3] Bis(triphenylphosphine)palladiu(II)dichloride (1 mol%), copper(I)

iodide (2 mol%), iodobenzene (1.2 equiv.), 3-butyn-1-ol (1.0 mmol) and triethyl amine were added to dry THF. The reaction mixture was stirred at room temperature until complete consumption of substrates (monitored by TLC). The solvent was removed in vacuum and the crude product was purified by flash column chromatography to provide an orange oil.

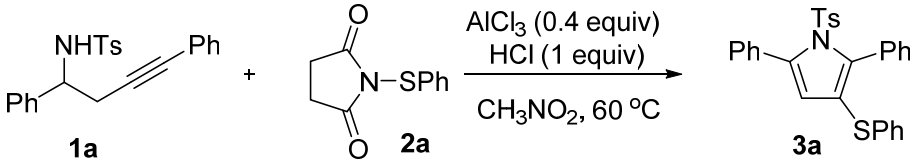
N-Boc *p*-toluenesulfonamide (1.2 equiv.) was dissolved in dry THF (3 mL) and triphenylphosphine (1.5 equiv.) was added. Then 4-phenyl but-3-yn-1-ol (1.0 mmol) was added followed by the addition of diethylazodicarboxylate (1.5 equiv.). The mixture was stirred at room temperature for 3 h. The solvent was removed in vacuum and the crude product was purified by flash column chromatography to provide *tert*-butyl (4-phenylbut-3-yn-1-yl)(tosyl)carbamate.

To a solution of *tert*-butyl (4-phenylbut-3-yn-1-yl)(tosyl)carbamate (1.0 mmol) in DCM (5 mL) was added trifluoroacetic acid (20 equiv.) at 0 ºC, and the mixture was stirred at room temperature for 3 h. The resulting mixture was poured into EtOAc, and washed with saturated aqueous $NaHCO_3$ solution. The organic layer was dried over anhydrous $MgSO_4$. The solvent was removed in vacuum and the crude product was purified by flash column chromatography on silica gel to provide **1q** as yellow solid.



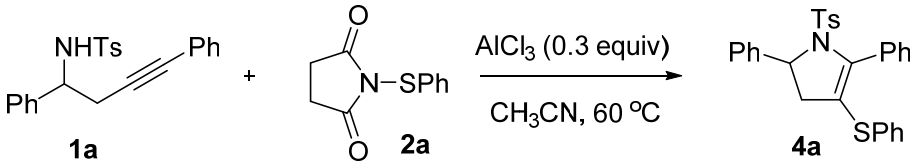
Sulfur reagents **2a-2k** were prepared as reported previously.[S4] To a solution of thiol (5.0 mmol, 1.0 equiv) and Et_3N (0.5 mmol, 0.1 equiv) in CH_2Cl_2 (10 mL) was added sulfuryl chloride (5.0 mmol, 1.0 equiv) dropwise at 0 °C. After stirring for 30 min, the reaction mixture was stirred for another 2 h at room temperature and then cooled to 0 °C. The resulting solution was transferred dropwise via cannula to a solution of succinimide (5.0 mmol, 1.0 equiv) and Et_3N (6.5 mmol, 1.3 equiv) in CH_2Cl_2 (8 mL) at 0 °C, and the reaction mixture was allowed to warm to room temperature and stirred for 2 h. The solution was diluted with H_2O (20 mL), extracted with CH_2Cl_2 (3 × 20 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography.

General procedure for the synthesis of 3-thiolated pyrroles



To a mixture of **1a** (0.15 mmol) and **2a** (1.2 equiv.) in 1.5 mL of CH_3NO_2 was added $AlCl_3$ (0.4 equiv.) and HCl (1.0 equiv.). The reaction was stirred at 60 °C until starting materials were completely consumed (monitored by TLC). The solvent was removed in vacuum and the crude product was purified by flash column chromatography to provide **3a** as a yellow solid (58 mg, 80%).

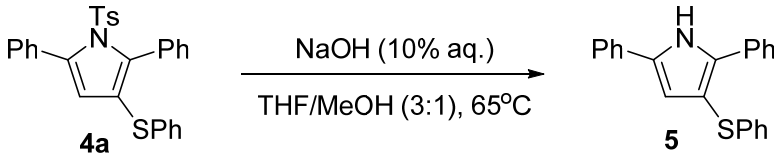
General procedure for the synthesis of 3-thiolated pyrrolines



To a mixture of **1a** (0.15 mmol) and **2a** (1.2 equiv.) in 1.5 mL of CH_3CN was added $AlCl_3$ (0.3 equiv.). The reaction was stirred at 60 °C until starting materials were completely consumed (TLC monitoring). The solvent was removed in vacuum and the crude product was purified by flash column chromatography to provide **4a** as a light yellow solid (54.1 mg, 75%).

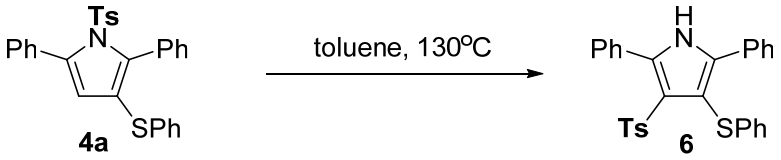
Further derivation of 4a

Desulfonation of 4a



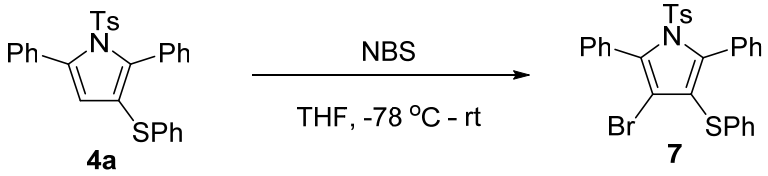
To a 10 mL tube was added **4a** (0.15 mmol), and 10% NaOH aqueous solution (0.6 mL) in the mixed solvent of THF (1.5 mL) and MeOH (0.5 mL). The reaction mixture was stirred at 65°C for 6 h. The reaction mixture was cooled, diluted with CH_2Cl_2 and washed with aq. NH_4Cl. The organic layer was separated and removed in vacuum, and then the crude product was purified by flash column chromatography to provide **5** as light yellow oil (36.3mg, 74%).

Sulfonyl migration of 4a



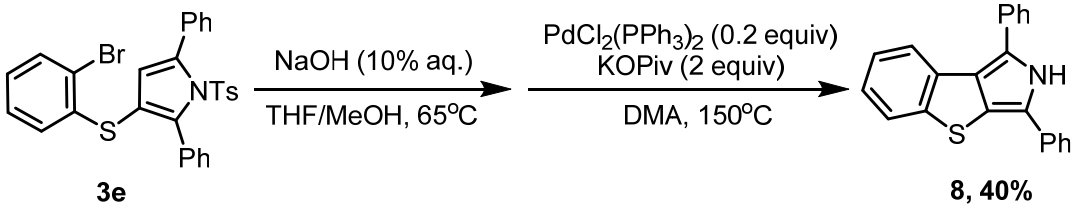
To a 10 mL tube was added **4a** (0.15 mmol) in toluene (1.5 mL), and the reaction mixture was stirred at 130 °C for 3h. The solvent was removed in vacuum and the crude product was purified by flash column chromatography to provide **6** as yellow solid (52.2 mg, 72%).

Bromination of 4a



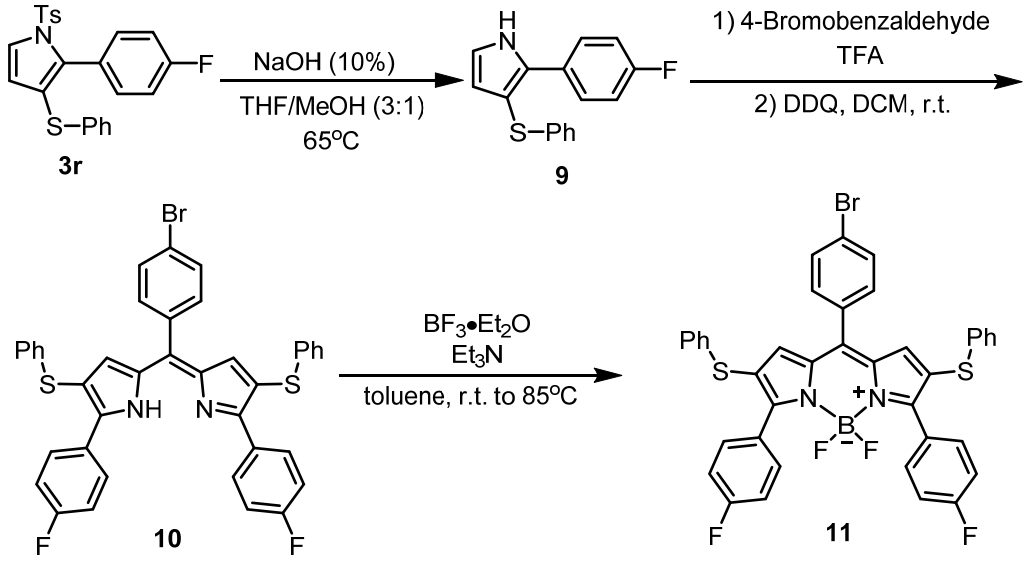
To a 10 mL tube was added **4a** (0.15 mmol) in THF (1mL) in -78 °C. Then NBS (2.0 equiv.) was dissolved in THF (1.5 mL) and added to the mixture dropwise. The reaction mixture was stirred at room temperature for 6 h. The solvent was removed in vacuum and the crude product was purified by flash column chromatography to provide **7** as a yellow solid (50.3 mg, 60%).

Synthesis of thienopyrrole



Detosylation of **3e** (0.15 mmol) is according to the synthetic procedure of **5**, and the product was used directly without purification. To a mixture of detosylation product in 1.5 mL of DMA was added bis(triphenylphosphine)palladiu(II)dichloride (0.2 equiv.) and pivalic acid potassium (2.0 equiv.). The reaction mixture was stirred at 150 °C for 24 h. The reaction mixture was cooled, diluted with EtOAc and washed with H_2O. The organic layer was separated and removed in vacuum, and then the crude product was purified by flash column chromatography to provide **8** as white solid (19.5 mg, 40% for two steps).

Synthesis of S-BODIPY



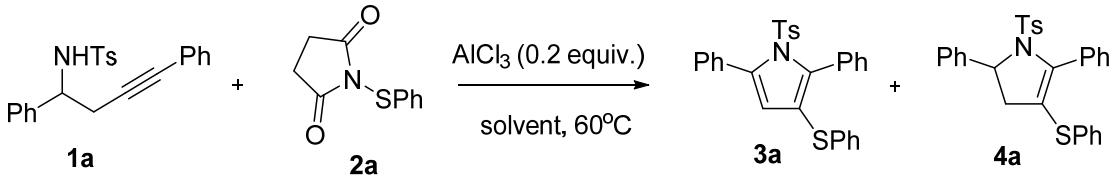
Compounds **9** is prepared according to the desulfonation of **4a**.

A mixture of 4-bromobenzaldehyde (0.15 mmol) and **9** (2.0 equiv.) in DCM (1.6 mL) was stirred for 5 min at room temperature. TFA (0.4 equiv.) was then added. The condensation reaction was stirred at room temperature for 3 h until **9** was consumed completely. The solvent was removed in vacuum and the condensation product was used directly in the next step. This crude product was then dissolved in DCM (3 mL), followed by the addition of DDQ (1.1 equiv.) and the resulting mixture was stirred for 1 h. The solvent was removed in vacuum and the crude product was purified by flash column chromatography on silica gel to provide **10** as red solid (70.6 mg, 67%).

$BF_3 \cdot Et_2O$ (30 equiv.) was added to a solution of **10** (0.15 mmol) in toluene (3mL) in a flask under nitrogen atmosphere. Et_3N (15 equiv.) was added dropwise. The resulting mixture was stirred under nitrogen atmosphere for 1 h, and then heated to 85 °C for 3 h. The reaction mixture was cooled, diluted with CH_2Cl_2 and washed with $NaHCO_3$ (sat, aq.), followed by washing with water and brine. The organic layer was separated and removed in vacuum, then the crude product was purified by flash column chromatography to provide **11** as dark blue solid (68.6 mg, 61%).

Optimization of reaction conditions

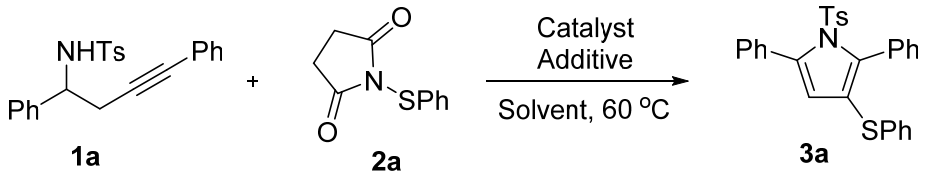
Table S1. Solvent screening[a]



Entry	Solvent	Product	Yield(%)[b]
1	CH_3NO_2	**3a**	47
2	THF	**4a**	58
3	CH_3CN	**4a**	62
4	DMF	0	0
5	DMSO	0	0
6	Toluene	**4a**	46
7	DCE	**4a**	40

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), $AlCl_3$ (0.02 mmol), in solvent (1.5 mL) at 60 °C for 2-12 h. [b] Isolated yield.

Table S2. Condition optimization for the synthesis of 3-thiolated pyrroles[a]

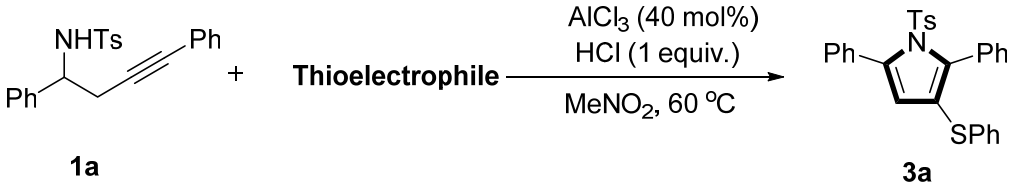


Entry	Solvent	Cat(equiv.)	Additive(equiv.)	Temp(℃)	Yield (%)[b]
1	CH_3NO_2	CuCl(0.2)	-	60	0
2	CH_3NO_2	$Cu(OAc)_2$(0.2)	-	60	0
3	CH_3NO_2	$AlCl_3$(0.2)	-	60	47
4	CH_3NO_2	$AlCl_3$(0.4)	-	60	67

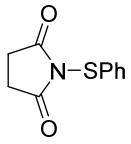
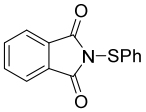
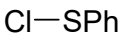
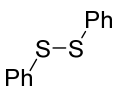
5	CH_3NO_2	$AlCl_3$(0.6)	-	60	67
6	CH_3NO_2	$AlCl_3$(0.8)	-	60	50
7	CH_3NO_2	$AlCl_3$(1.0)	-	60	45
8	CH_3NO_2	$AlCl_3$(0.4)	-	80	61
9	CH_3NO_2	$AlCl_3$(0.4)	-	100	29
10[b]	CH_3NO_2	$AlCl_3$(0.4)	TfOH(0.4)	60	21
11	CH_3NO_2	$AlCl_3$(0.4)	TFA(0.4)	60	64
12	CH_3NO_2	$AlCl_3$(0.4)	HCl(0.4)	60	70
13	**CH_3NO_2**	**$AlCl_3$(0.4)**	**HCl(1.0)**	**60**	**75**
14	CH_3NO_2	$AlCl_3$(0.4)	TEMPO(1.0)	60	35
15	CH_3NO_2	$AlCl_3$(0.4)	NH_4Cl(1.0)	60	53
16	CH_3NO_2	$AlCl_3$(0.4)	*p*-TsOH(1.0)	60	61
17	CH_3NO_2	$AlCl_3$(0.4)	TMSCl(1.0)	60	67

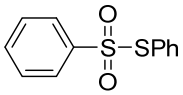
[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), catalyst, in CH_3NO_2 (1.5 mL) at 60 °C for 1 - 6 h. [b] Isolated yield.

Table S3. Screening of different thioelectrophiles[a]



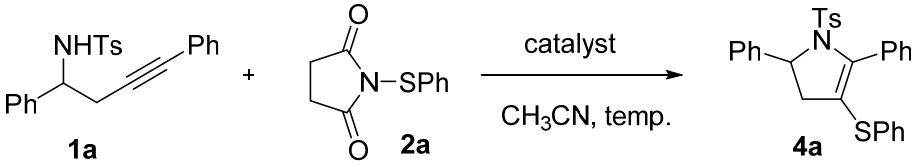
1a **3a**

Entry	Thioelectrophiles	Yield (%)[b]
1		75
2		< 10
3		72
4		54

5		58

[a]Reaction conditions: **1a** (0.1 mmol), **thioelectrophile** (0.15 mmol), $AlCl_3$ (40 mol%), HCl (0.1 mmol) in CH_3NO_2 (1.5 mL) at 60 °C for 1 - 6 h. [b] Isolated yield.

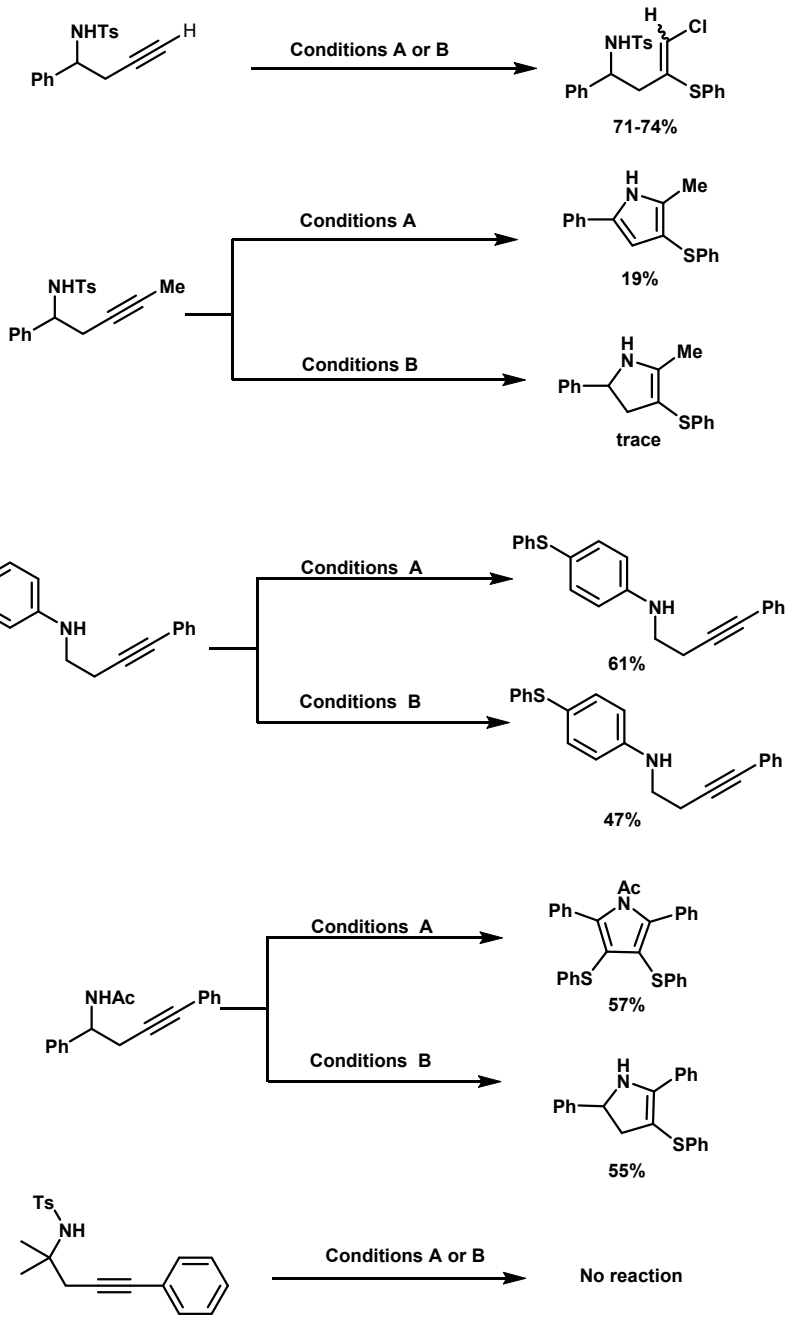
Table S4. Condition optimization for the synthesis of 3-thiolated pyrrolines[a]



Entry	Solvent	Cat. (equiv.)	Temp (℃)	Product	Yield(%)[b]
1	CH_3CN	TfOH(0.2)	60	4a	55
2	CH_3CN	TfA(0.2)	60	-	0
3	CH_3CN	BF_3Et_2O(0.2)	60	4a	25
4	CH_3CN	$Sc(OTf)_3$(0.2)	60	4a	47
5	CH_3CN	$CuCl_2$(0.2)	60	3a,4a	27:62
6	CH_3CN	$CuSO_4$(0.2)	60	-	0
7	CH_3CN	$Cu(OAc)_2$(0.2)	60	3a	25
8	CH_3CN	$ZnCl_2$(0.2)	60	-	0
9	CH_3CN	$FeCl_3$(0.2)	60	-	0
10	CH_3CN	$MgCl_2$(0.2)	60	-	0
11	CH_3CN	$(CF_3SO_2)_2NH$(0.2)	60	4a	51
12	CH_3CN	$AlCl_3$(0.2)	60	4a	62
13	**CH_3CN**	**$AlCl_3$(0.3)**	**60**	**4a**	**80**
14	CH_3CN	$AlCl_3$(0.4)	60	3a,4a	14:74
15	CH_3CN	$AlCl_3$(0.6)	60	3a,4a	16:69

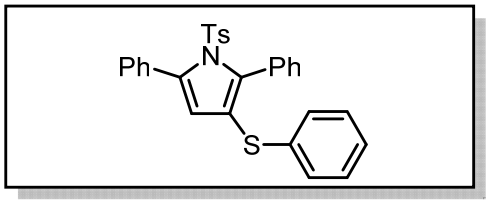
[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), catalyst, in CH_3CN (1.5 mL) at 60 °C for 1 - 12 h. [b] Isolated yield.

Examination of other homopropargylic amides/amines



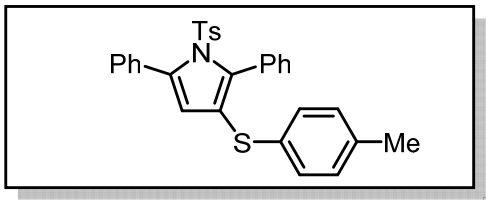
Characterization of products

2,5-Diphenyl-3-(phenylthio)-1-tosyl-1*H*-pyrrole (3a)



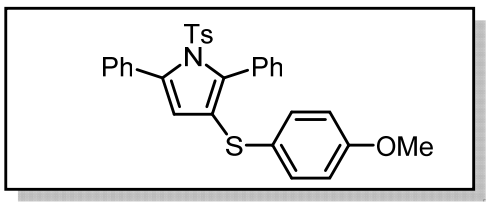
Yield: 54.1 mg (75%); yellow solid; m.p. 114-116 ℃; R_f = 0.40 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc = 24:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55-7.52 (m, 2H), 7.43-7.40 (m, 8H), 7.17-7.10 (m, 7H), 6.95-6.93 (m, 2H), 6.23 (s, 1H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 144.7, 141.3, 140.9, 136.9, 134.6, 132.7, 131.1, 131.0, 129.6, 129.0, 128.8, 128.6, 128.3, 127.9, 127.6, 127.23, 127.17, 125.8, 121.2, 119.5, 21.7. HRMS (ESI) m/z calcd. for $C_{29}H_{23}NO_2S_2$ $[M+H]^+$: 482.1243, found: 482.1243.

2,5-Diphenyl-3-(p-tolylthio)-1-tosyl-1*H*-pyrrole (3b)



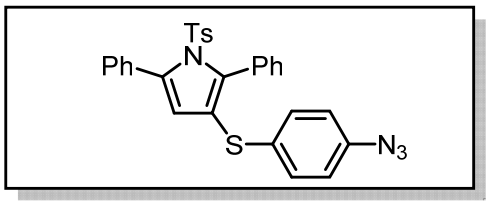
Yield: 54.2 mg (73%); yellow solid; m.p. 120-122 ℃; R_f = 0.40 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc = 24:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54-7.51 (m, 2H), 7.46-7.40 (m, 8H), 7.15-7.10 (m, 4H), 6.98 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 8.0 Hz, 2H), 6.17 (s, 1H), 2.42 (s, 3H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.6, 140.8, 140.1, 136.2, 134.6, 132.7, 132.6, 131.2, 131.1, 129.64, 129.56, 128.99, 128.95, 128.5, 128.2, 127.6, 127.2, 127.1, 120.8, 21.6, 20.9. HRMS (ESI) m/z calcd. for $C_{30}H_{25}NO_2S_2$ $[M+H]^+$: 496.1399, found: 496.1398.

3-((4-Methoxyphenyl)thio)-2,5-diphenyl-1-tosyl-1*H*-pyrrole (3c)



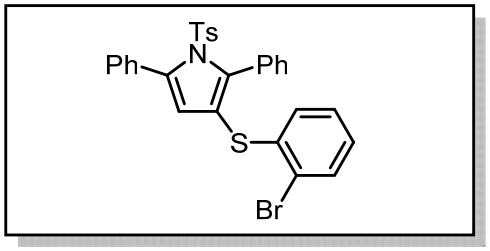
Yield: 53.7 mg (70%); yellow solid; m.p. 243-245 ℃; R_f = 0.4 (PE:EtOAc = 9:1); purification: flash chromatography (PE:EtOAc = 11:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50-7.47 (m, 2H), 7.46-7.42 (m, 5H), 7.40-7.38 (m, 3H), 7.10 (q, J = 8.4 Hz, 4H), 7.03 (dt, J = 9.6, 3.2 Hz, 2H), 6.72 (dt, J = 10.0, 3.2 Hz, 2H), 6.05 (s, 1H), 3.75 (s, 3H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.9, 144.6, 140.6, 138.3, 134.6, 132.8, 132.3, 131.4, 131.1, 129.6, 129.0, 128.4, 128.2, 127.5, 127.3, 127.1, 125.9, 122.6, 120.0, 114.6, 55.3, 21.7. HRMS (ESI) m/z calcd. for $C_{30}H_{25}NO_3S_2$ $[M+H]^+$: 512.1349, found: 512.1347.

3-((4-Azidophenyl)thio)-2,5-diphenyl-1-tosyl-1*H*-pyrrole (3d)



Yield: 37.6 mg (48%); yellow solid; m.p. 134-136 ℃; R_f = 0.4 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc = 24:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53-7.51 (m, 2H), 7.43-7.40 (m, 8H), 7.12 (q, J = 8.4 Hz, 4H), 6.94 (dt, J = 9.2, 2.4 Hz, 2H), 6.81 (dt, J = 9.2, 2.4 Hz, 2H), 6.17 (s, 1H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.8, 140.9, 140.8, 138.1, 134.7, 132.9, 132.7, 131.1, 131.0, 130.0, 129.6, 129.1, 128.7, 128.4, 127.7, 127.3, 127.2, 120.7, 119.7, 119.6, 21.7. HRMS (ESI) m/z calcd. for $C_{29}H_{22}N_4O_2S_2$ $[M+H]^+$: 523.1257, found: 523.1267.

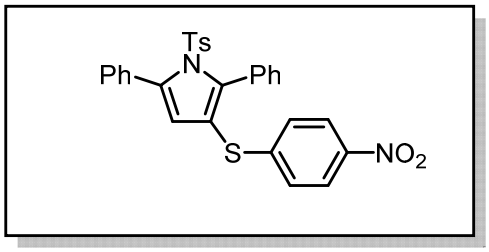
3-((2-Bromophenyl)thio)-2,5-diphenyl-1-tosyl-1*H*-pyrrole (3e)



Yield: 38.6 mg (46%); yellow solid; m.p. 140-142 ℃; R_f = 0.35 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc = 19:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56-7.53 (m, 2H), 7.45-7.37 (m, 9H), 7.12 (q, J = 8.4 Hz, 4H), 7.00 - 6.92 (m, 2H), 6.50 (dd, J = 7.6, 2.0 Hz, 1H), 6.26 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 143.0,

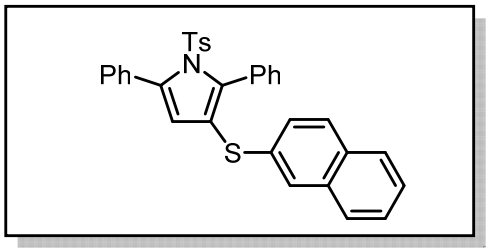
141.2, 138.8, 134.7, 132.8, 132.6, 131.1, 130.6, 129.6, 129.1, 128.8, 128.4, 127.7, 127.6, 127.5, 127.3, 127.2, 126.5, 121.4, 121.3, 117.7, 21.7. HRMS (ESI) m/z calcd. for $C_{29}H_{22}BrNO_2S_2$ $[M+H]^+$: 562.0328, 560.0348 , found: 562.0338, 560.0357.

3-((4-Nitrophenyl)thio)-2,5-diphenyl-1-tosyl-1*H*-pyrrole (3f)



Yield: 24.5 mg (41%); yellow solid; m.p. 238-240 ℃; R_f = 0.4 (PE:EtOAc = 9:1); purification: flash chromatography (PE:EtOAc = 11:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96 (dt, J = 9.6, 2.4 Hz, 2H), 7.58-7.56 (m, 2H), 7.46-7.36 (m, 6H), 7.30 (dt, J = 5.6, 1.2 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 6.87 (dt, J = 9.6, 2.8 Hz, 2H), 6.33 (s, 1H), 2.47 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.2, 145.3, 145.1, 143.7, 141.4, 134.8, 132.4, 131.0, 130.3, 129.7, 129.3, 129.1, 128.7, 127.8, 127.4, 127.3, 125.6, 123.9, 121.2, 115.1, 21.8. HRMS (ESI) m/z calcd. for $C_{29}H_{22}N_2O_4S_2$ $[M+H]^+$: 527.1094, found: 527.1093.

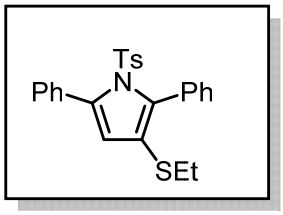
3-(Naphthalen-2-ylthio)-2,5-diphenyl-1-tosyl-1*H*-pyrrole (3g)



Yield: 52.6 mg (66%); yellow solid; m.p. 246-248 ℃; R_f = 0.35 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc = 19:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 8.8 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.55-7.53 (m, 2H), 7.47-7.40 (m, 11H), 7.18-7.13 (m, 4H), 7.09 (dd, J = 8.8, 2.0 Hz, 1H), 6.25 (s, 1H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.78, 140.0, 139.8, 133.8, 133.3, 132.5, 131.7, 130.6, 130.1, 130.0, 128.6, 128.1, 127.6, 127.5, 127.3, 126.7, 126.6, 126.3, 126.2, 126.0, 125.5,

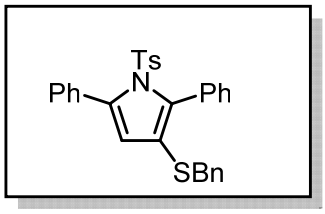
125.3, 125.1, 124.7, 120.1, 118.40, 20.7. HRMS (ESI) m/z calcd. for $C_{33}H_{25}NO_2S_2$ $[M+H]^+$: 532.1399, found: 532.1398.

3-(Ethylthio)-2,5-diphenyl-1-tosyl-1*H*-pyrrole (3h)



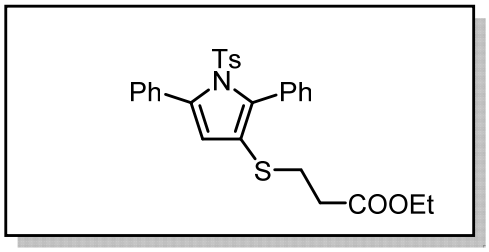
Yield: 33.8 mg (52%); yellow liquid; R_f = 0.4 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc = 24:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54-7.51 (m, 2H), 7.44-7.40 (m, 8H), 7.10-7.04 (m, 4H), 6.31 (s, 1H), 2.62 (q, J = 7.2 Hz, 2H), 2.36 (s, 3H), 1.06 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.5, 140.3, 137.7, 134.6, 132.8, 131.7, 131.2, 129.6, 128.9, 128.2, 128.1, 127.6, 127.2, 127.0, 122.1, 118.9, 28.4, 21.6, 14.5. HRMS (ESI) m/z calcd. for $C_{25}H_{23}NO_2S_2$ $[M+H]^+$: 434.1243, found: 434.1241.

3-(Benzylthio)-2,5-diphenyl-1-tosyl-1*H*-pyrrole (3i)



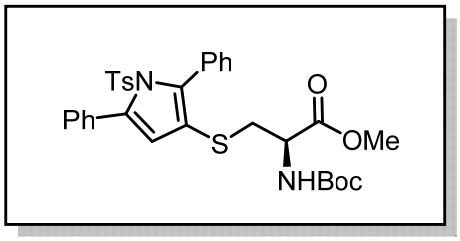
Yield: 40.1 mg (54%); yellow liquid; R_f = 0.4 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc = 24:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46-7.36 (m, 9H), 7.24 (d, J = 3.6 Hz, 1H), 7.19-7.15 (m, 3H), 7.08(d, J = 8.4 Hz, 2H), 7.03-6.99 (m, 4H), 6.18 (s, 1H), 3.75 (s, 2H), 2.3 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.5, 139.7, 139.1, 137.3, 134.9, 132.8, 131.3, 131.3, 129.7, 129.0, 128.8, 128.3, 128.17, 128.15, 127.5, 127.1, 127.0, 120.9, 119.8, 39.6, 21.6. HRMS (ESI) m/z calcd. for $C_{30}H_{25}NO_2S_2$ $[M+H]^+$: 496.1399, found: 496.1397.

Ethyl 3-((2,5-diphenyl-1-tosyl-1*H*-pyrrol-3-yl)thio)propanoate (3j)



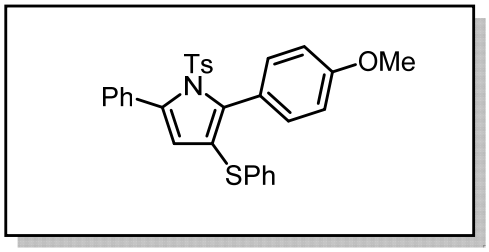
Yield: 53.8 mg (71%); yellow liquid; R_f = 0.4 (PE:EtOAc = 6:1); purification: flash chromatography (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53-7.51 (m, 2H), 7.44-7.40 (m, 8H), 7.26 (q, J = 8.4 Hz, 4H), 6.32 (s, 1H), 4.04 (q, J = 7.2 Hz, 2H), 2.82 (t, 7.2 Hz, 2H), 2.36-2.33 (m, 5H), 1.19 (t, J = 6.8 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.4, 144.6, 140.3, 134.6, 132.6, 131.34, 131.25, 129.7, 128.9, 128.2, 127.6, 127.2, 127.0, 120.6, 119.0, 60.6, 34.4, 29.4, 21.6, 14.1. HRMS (ESI) m/z calcd. for $C_{28}H_{27}NO_4S_2$ $[M+H]^+$: 506.1454, found: 504.1452.

Methyl *N*-(tert-butoxycarbonyl)-*S*-(2,5-diphenyl-1-tosyl-1*H*-pyrrol-3-yl)-*L*-cysteinate (3k)



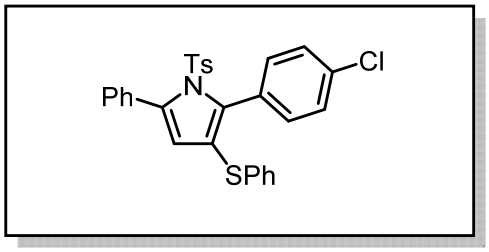
Yield: 21.8 mg (24%); yellow liquid; R_f = 0.35 (PE:EtOAc = 6:1); purification: flash chromatography (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48-7.38 (m, 10H), 7.07 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 6.30 (s, 1H), 4.95 (d, J = 8.0 Hz, 1H), 4.39-4.32 (m, 1H), 3.51 (s, 3H), 3.05 (dd, J = 14.0, 4.8 Hz, 1H), 2.95 (dd, J = 10.0, 4.8 Hz, 1H), 2.36(s, 3H), 1.39 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.7, 144.8, 140.1, 139.3, 134.9, 132.6, 131.4, 131.2, 129.8, 129.1, 128.5, 128.3, 127.6, 127.3, 127.1, 119.6, 119.3, 80.1, 53.1, 52.4, 36.9, 28.3, 21.6. HRMS (ESI) m/z calcd. for $C_{32}H_{34}N_2O_6S_2$ $[M+H]^+$: 607.1931, found: 607.1930.

2-(4-Methoxyphenyl)-5-phenyl-3-(phenylthio)-1-tosyl-1*H*-pyrrole (3l)



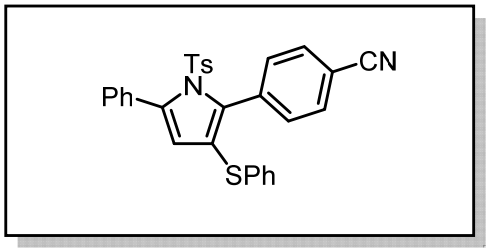
Yield: 56.7 mg (74%); yellow solid; m.p. 131-133℃; R_f = 0.2 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc = 19:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (dd, J = 8.0, 2.0 Hz, 2H), 7.44-7.39 (m, 3H), 7.32 (dt, J = 9.6 , 2.8 Hz, 2H), 7.16-7.11(m, 7H), 6.94-6.89(m, 4H), 6.24 (s, 1H), 3.87 (s, 3H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.9, 144.7, 141.7, 140.6, 137.2, 134.7, 133.0, 129.5, 129.1, 128.8, 128.2, 127.7, 127.6, 127.2, 125.7, 123.3, 121.6, 118.4, 112.9, 55.3, 21.7. HRMS (ESI) m/z calcd. for $C_{30}H_{25}NO_3S_2$ $[M+H]^+$: 512.1349, found: 512.1344.

2-(4-Chlorophenyl)-5-phenyl-3-(phenylthio)-1-tosyl-1*H*-pyrrole (3m)



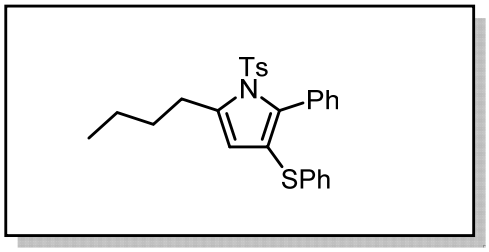
Yield: 51.8 mg (67%); yellow solid; m.p. 210-212 ℃; R_f = 0.3 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc = 19:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53-7.50 (m, 2H), 7.44-7.39 (m, 4H), 7.37-7.33 (m, 4H), 7.16-7.09 (m, 7H), 6.93-6.91 (m, 2H), 6.22 (s, 1H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.0, 141.3, 139.9, 136.6, 136.5, 134.7, 134.5, 132.5, 132.3, 129.6, 129.2, 128.9, 128.5, 128.0, 127.7, 127.6, 127.1, 126.1, 121.3, 120.1, 21.7. HRMS (ESI) m/z calcd. for $C_{29}H_{22}ClNO_2S_2$ $[M+H]^+$: 516.0853, found: 516.0862.

4-(5-Phenyl-3-(phenylthio)-1-tosyl-1*H*-pyrrol-2-yl)benzonitrile (3n)



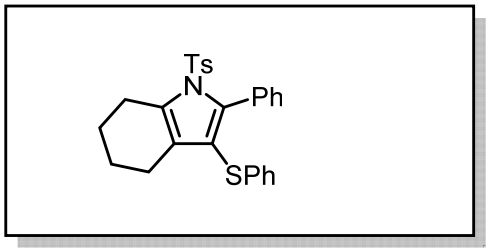
Yield: 57.7 mg (76%); white solid; m.p. 210-212 ℃; R_f = 0.4 (PE:EtOAc = 4:1); purification: flash chromatography (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (dt, J = 8.0, 1.6 Hz, 2H), 7.57 (dt, J = 8.4, 2.0 Hz, 2H), 7.49-7.47 (m, 2H), 7.43-7.39 (m, 3H), 7.19-7.14 (m, 5H), 7.06 (dt, J = 8.4, 2.0 Hz, 2H), 6.97-6.94 (m, 2H), 6.19 (s, 1H), 2.43 (s, 3H) ; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.3, 142.3, 138.3, 135.9, 135.6, 134.2, 131.9, 131.4, 131.1, 129.8, 129.3, 129.1, 128.8, 128.6, 127.8, 127.1, 126.6, 122.3, 121.1, 118.9, 111.7, 21.7. HRMS (ESI) m/z calcd. for $C_{30}H_{22}N_2O_2S_2$ $[M+H]^+$: 507.1195, found: 507.1195.

5-Butyl-2-phenyl-3-(phenylthio)-1-tosyl-1*H*-pyrrole (3o)



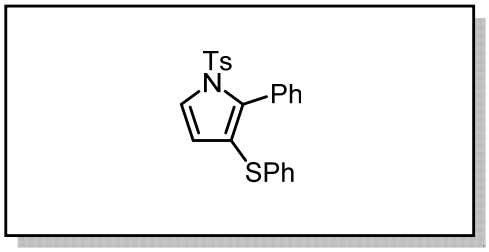
Yield: 29.1 mg (42%); yellow liquid; R_f = 0.4 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc = 24:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35-7.27 (m, 5H), 7.19-7.14 (m, 6H), 7.09 (tt, J = 7.2, 1.2 Hz, 1H), 6.97-6.95 (m, 2H), 2.96 (t, J = 7.2 Hz, 2H), 2.41 (s, 3H), 1.73-1.65 (m, 2H), 1.48-1.38 (m , 2H), 0.96 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.7, 139.9, 139.5, 137.8, 136.3, 131.6, 130.9, 129.5, 128.7, 128.4, 127.2, 127.1, 126.7, 125.4, 116.7, 116.6, 31.4, 29.2, 22.5, 21.7, 14.0. HRMS (ESI) m/z calcd. for $C_{27}H_{27}NO_2S_2$ $[M+H]^+$: 462.1556, found: 462.1561.

2-Phenyl-3-(phenylthio)-1-tosyl-4,5,6,7-tetrahydro-1*H*-indole (3p)



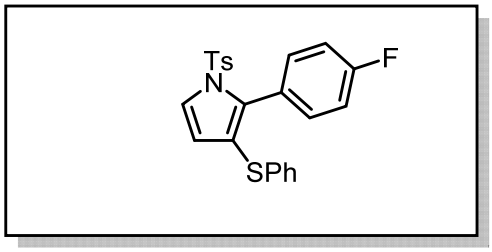
Yield: 36.5 mg (53%); yellow liquid; R_f = 0.35 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc = 24:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35-7.26 (m, 5H), 7.21 7.11 (m, 6H), 7.05 (tt, J = 7.2, 1.2 Hz, 1H), 6.86-6.84 (m, 2H), 3.01 (t, J = 6.0 Hz, 2H), 2.42 (s, 3H), 2.20 (t, J = 6.0 Hz, 2H), 1.84-1.78 (m, 2H), 1.68-1.62 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.6, 139.7, 137.9, 136.2, 132.9, 131.7, 130.7, 129.5, 128.7, 128.5, 127.0, 126.8, 126.5, 126.0, 124.9, 116.2, 25.4, 23.5, 22.3, 22.0, 21.7. HRMS (ESI) m/z calcd. for $C_{27}H_{25}NO_2S_2$ $[M+H]^+$: 460.1399, found: 460.1398.

2-Phenyl-3-(phenylthio)-1-tosyl-1*H*-pyrrole (3q)



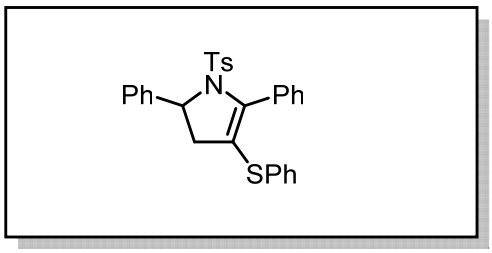
Yield: 46.8 mg (77%); grey solid; m.p. 81-83 °C; R_f = 0.35 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc = 24:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, J = 7.2 Hz, 1H), 7.37 (tt, J = 7.2, 1.2 Hz, 1H), 7.28 (d, J = 7.8 Hz, 2H), 7.23 (d, J = 8.8 Hz, 2H), 7.18-7.06 (m , 7H), 7.00-6.98 (m, 2H), 6.36 (d, J = 3.2 Hz, 1H), 2.39 (s, 3H) ; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.1, 127.29, 127.26, 135.2, 131.9, 129.5, 129.1, 128.9, 128.8, 127.4, 127.3, 127.3, 125.5, 123.5, 117.1, 116.4, 21.7. HRMS (ESI) m/z calcd. for $C_{23}H_{19}NO_2S_2$ $[M+H]^+$: 406.0930, found: 406.0931.

2-(4-Fluorophenyl)-3-(phenylthio)-1-tosyl-1*H*-pyrrole (3r)



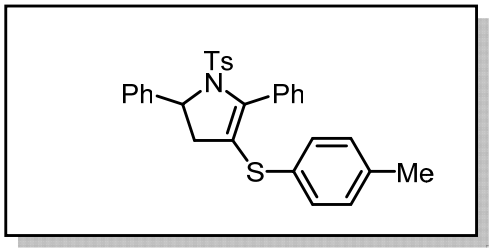
Yield: 45.7 mg (72%); grey liquid; R_f = 0.35 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc = 24:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, J = 3.2 Hz, 1H), 7.25-2.23 (m, 2H), 7.18-7.14 (m, 4H), 7.09 (tt, J = 7.6, 1.2 Hz, 1H), 7.06 (m, 2H), 6.98-6.94 (m, 4H), 6.37 (d, J = 3.6 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.1 (J = 248.0 Hz), 145.3, 137.4, 136.5, 135.2, 133.8 (J = 8.0 Hz), 129.6, 128.8, 127.3 (J = 8.0 Hz), 125.6, 125.0 (J = 4 Hz), 123., 117.5, 116.4, 114.4 (J = 22.0 Hz), 21.7; ^{19}F NMR ($CDCl_3$, 376.3 MHz): δ -112.00. HRMS (ESI) m/z calcd. for $C_{23}H_{18}FNO_2S_2$ $[M+H]^+$: 424.0836, found: 424.0842.

2,5-Diphenyl-4-(phenylthio)-1-tosyl-2,3-dihydro-1*H*-pyrrole (4a)



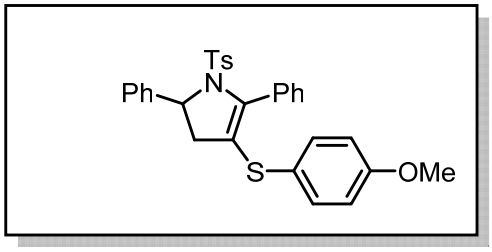
Yield: 58.0 mg (80%); yellow solid; m.p. 131-133 ℃; R_f = 0.3 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc = 19:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66-7.60(m, 4H), 7.47-7.33 (m, 10H), 7.10 (tt, J = 7.2, 1.2 Hz, 1H), 7.05-7.02 (m, 2H), 6.77-6.75 (m, 2H), 6.86-6.84 (m, 2H), 5.37 (d, J = 8.0 Hz, 1H), 2.67 (dd, J = 16.0, 9.2 Hz, 1H), 2.50 (s, 3H), 2.28 (dd, J = 16.4, 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.1, 142.9, 142.1, 134.9, 133.6, 131.5, 129.8, 129.7, 129.2, 128.8, 128.7, 127.71, 127.66, 127.6, 126.8, 125.8, 119.6, 63.0, 41.4, 21.7. HRMS (ESI) m/z calcd. for $C_{29}H_{25}NO_2S_2$ $[M+H]^+$: 484.1399, found: 484.1399.

2,5-Diphenyl-4-(p-tolylthio)-1-tosyl-2,3-dihydro-1*H*-pyrrole (4b)



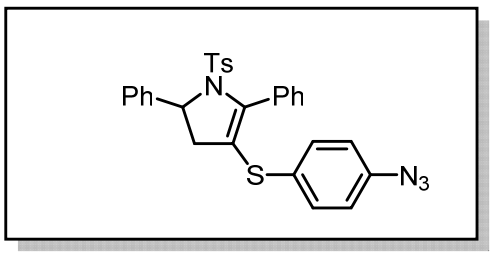
Yield: 60.4 mg (81%); yellow solid; m.p. 144-146 ℃; R_f = 0.3 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc = 19:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67 (dd, J = 8.4, 1.6 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.48-7.33 (m, 10 H), 6.87 (d, J = 8.0 Hz, 2H), 6.79 (d, J = 8.0 Hz, 2H), 5.34 (d, J = 8.1 Hz, 1H), 2.60 (dd, J = 16.0, 8.8 Hz, 1H), 2.50 (s, 3H), 2.27-2.23 (m , 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.0, 142.0, 141.4, 137.1, 134.7, 131.7, 130.5, 129.62, 129.56, 129.5, 129.00, 128.6, 127.7, 127.6, 127.6, 125.8, 120.8, 62.9, 41.2, 21.7, 21.0. HRMS (ESI) m/z calcd. for $C_{30}H_{27}NO_2S_2$ $[M+H]^+$: 498.1556, found: 498.1554.

4-((4-Methoxyphenyl)thio)-2,5-diphenyl-1-tosyl-2,3-dihydro-1*H*-pyrrole (4c)



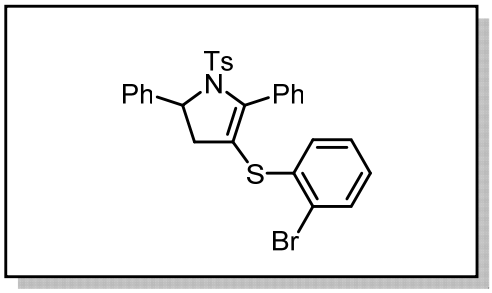
Yield: 51.6 mg (67%); yellow liquid; R_f = 0.2 (PE:EtOAc = 9:1); purification: flash chromatography (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61-7.58 (m, 4H), 7.44 (d, J = 7.8 Hz, 2H), 7.40-7.31 (m, 5H), 7.07 (tt, J = 7.6, 1.2 Hz, 1H), 7.03-6.94 (m, 4H), 5.36 (d, J = 8.4 Hz, 1H), 3.85 (s, 3H), 2.64 (dd, J = 16.0, 9.2 Hz, 1H), 2.49 (s, 3H), 2.24 (dd, J = 16.0, 1.6 Hz, 1H) ; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.3, 144.1, 143.3, 142.2, 135.0, 134.0, 131.2, 129.7, 129.4, 128.8, 128.7, 127.71, 127.65, 126.6, 125.8, 123.8, 117.5, 113.1, 62.9, 55.3, 41.3, 21.8. HRMS (ESI) m/z calcd. for $C_{30}H_{27}NO_3S_2$ $[M+H]^+$: 514.1505, found: 514.1500.

4-((4-Azidophenyl)thio)-2,5-diphenyl-1-tosyl-2,3-dihydro-1*H*-pyrrole (4d)



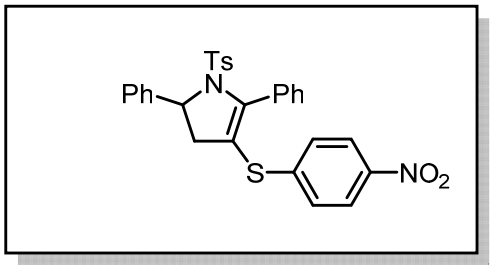
Yield: 43.2 mg (55%); yellow liquid; R_f = 0.2 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc = 19:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64-7.59 (m, 4H), 7.45-7.32 (m, 10H), 6.81 (dt, J = 9.2, 2.8 Hz, 2H), 6.67 (dt, J = 9.6, 2.8 Hz, 2H), 5.36 (d, J = 8.0 Hz, 1H), 2.63 (dd, J = 16.0, 8.8 Hz, 1H), 2.49 (s, 3H), 2.21 (dd, J = 16.0, 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.2, 142.9, 142.0, 139.1, 134.9, 131.7, 131.5, 129.73, 129.71, 129.3, 128.8, 127.8, 127.72, 127.70, 125.7, 119.6, 119.4, 62.9, 41.5, 21.7. HRMS (ESI) m/z calcd. for $C_{29}H_{24}N_4O_2S_2$ $[M+H]^+$: 525.1413, found: 525.1410.

4-((2-Bromophenyl)thio)-2,5-diphenyl-1-tosyl-2,3-dihydro-1*H*-pyrrole (4e)



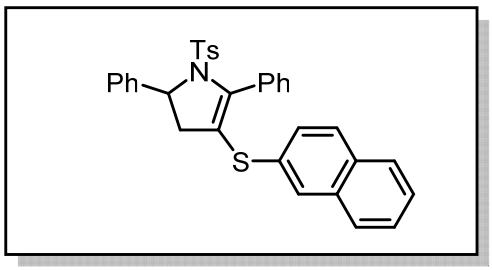
Yield: 72.4 mg (86%); yellow solid; m.p. 155-156 ℃; R_f = 0.2 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc = 19:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65-7.60 (m, 4H), 7.52 (d, J = 7.8 Hz, 2H), 7.45-7.34 (m, 9 H), 6.91 (t, J = 7.8 Hz, 1H), 6.77 (t, J = 7.8 Hz, 1H), 6.41 (d, J = 8.0 Hz, 1H), 5.45 (d, J = 9.2 Hz, 1H), 2.82 (dd, J = 16.0, 9.2 Hz, 1H), 2.50 (s, 3H), 2.33 (d, J = 16.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.9, 143.2, 141.1, 134.6, 133.9, 131.9, 130.0, 128.8, 128.7, 128.5, 128.4, 127.8, 126.73, 126.67, 126.6, 126.4, 124.7, 122.0, 116.1, 62.0, 40.4, 20.7. HRMS (ESI) m/z calcd. for $C_{29}H_{24}BrNO_2S_2$ $[M+H]^+$: 564.0485, 562.0505, found: 564.0486, 562.0503.

4-((4-Nitrophenyl)thio)-2,5-diphenyl-1-tosyl-2,3-dihydro-1*H*-pyrrole (4f)



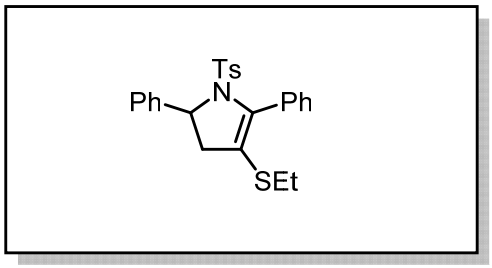
Yield: 52.3 mg (66%); yellow solid; m.p. 195-197 ℃; R_f = 0.2 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc = 19:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82 (dt, J = 8.8, 1.6 Hz, 2H), 7.60-7.52 (m, 6H), 7.48-7.40 (m, 6H), 7.36 (d, J = 8.0 Hz, 2H), 6.77 (dt, J = 8.8 Hz, 2.0 Hz, 2H), 5.54 (d, J = 8.0 Hz, 1H), 2.91 (dd, J = 16.4, 9.6 Hz, 1H), 2.53 (s, 3H), 2.37 (dd, J = 8.8, 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.3, 145.56, 144.8, 144.5, 141.9, 135.1, 130.5, 129.9, 129.8, 129.7, 129.0, 128.0, 127.8, 127.7, 127.1, 125.5, 123.8, 114.2, 63.1, 41.7, 21.7. HRMS (ESI) m/z calcd. for $C_{29}H_{24}N_2O_4S_2$ $[M+H]^+$: 529.1250, found: 529.1245.

4-(Naphthalen-2-ylthio)-2,5-diphenyl-1-tosyl-2,3-dihydro-1*H*-pyrrole (4g)



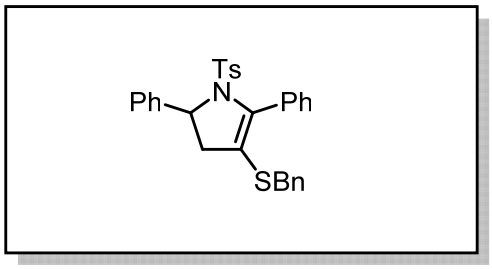
Yield: 42.4 mg (53%); yellow solid; m.p. 132-134 ℃; R_f = 0.2 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc = 19:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72-7.68 (m , 3H), 7.63 (d, 8.4 Hz, 2H), 7.50-7.31 (m, 14H), 7.23 (d, J = 1.6 Hz, 1H), 6.93 (dd, J = 8.8, 2.0 Hz, 1H), 5.38 (d, J = 8.8 Hz, 1H), 2.66 (dd, J = 16.0, 8.8 Hz, 1H), 2.51 (s, 3H), 2.38-2.34 (m , 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.2, 143.2, 142.1, 134.9, 133.4, 131.9, 131.6, 131.1, 129.81, 129.76, 129.3, 128.8, 128.4, 128.3, 127.74, 127.70, 127.69, 127.6, 127.2, 126.5, 126.1, 119. 4, 63.0, 41.5, 21.8. HRMS (ESI) m/z calcd. for $C_{33}H_{27}NO_2S_2$ $[M+H]^+$: 534.1556, found: 534.1547.

4-(Ethylthio)-2,5-diphenyl-1-tosyl-2,3-dihydro-1*H*-pyrrole (4h)



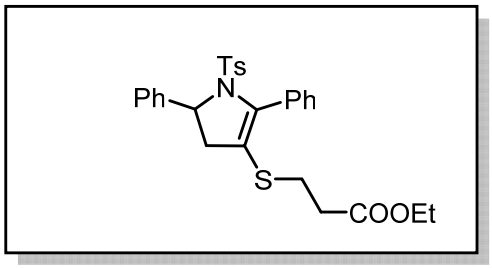
Yield: 26.1 mg (40%); yellow liquid; R_f = 0.3 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc = 19:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60-7.57 (m, 4H), 7.48 (d, J = 7.2 Hz, 2H), 7.44-7.36 (m, 5H), 7.31-7.29 (m, 3H), 5.30 (d, J = 7.8 Hz, 1H), 2.67 (dd, J = 16.4, 9.2 Hz, 1H), 2.53-2.39 (m, 6H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.0, 142.6, 138.3, 134.5, 132.3, 129.6, 129.5, 128.8, 128.6, 127.74, 127.72, 127.6, 125.7, 122.1, 62.6, 41.2, 26.48, 21.7, 14.9. HRMS (ESI) m/z calcd. for $C_{25}H_{25}NO_2S_2$ $[M+H]^+$: 436.1399, found: 436.1399.

4-(Benzylthio)-2,5-diphenyl-1-tosyl-2,3-dihydro-1*H*-pyrrole (4i)



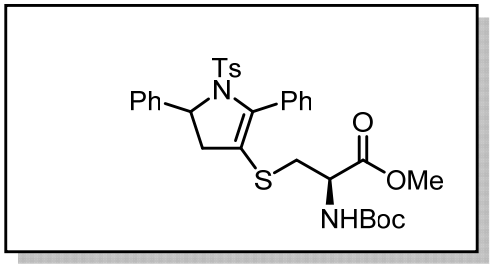
Yield: 53.7 mg (72%); yellow solid; m.p. 137-139 ℃; R_f = 0.4 (PE:EtOAc = 9:1); purification: flash chromatography (PE:EtOAc = 11:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (d, J = 8.0 Hz, 2H), 7.46-7.44(m, 2H), 7.39-7.36 (m, 3H), 7.31-7.26 (m, 7H), 7.18-7.09 (m, 3H), 6.94 (d, J = 7.6 Hz, 2H), 5.25 (dd, J = 9.2, 2.0 Hz, 1H), 3.65 (q, J = 9.6 Hz, 2H), 2.73 (dd, J = 16.0, 9.6 Hz, 1H), 2.54 (dd, J = 16.4, 2.4 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.9, 142.6, 140.1, 136.9, 134.7, 132.0, 129.64, 129.57, 128.8, 128.6, 128.52, 128.47, 127.7, 127.6, 127.4, 127.1, 125.8, 120.6, 62.6, 41.6, 37.1, 21.7. HRMS (ESI) m/z calcd. for $C_{30}H_{27}NO_2S_2$ $[M+H]^+$: 498.1556, found: 498.1560.

Ethyl 3-((2,5-diphenyl-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)thio)propanoate (4j)



Yield: 36.5 mg (48%); yellow liquid; R_f = 0.25 (PE:EtOAc = 6:1); purification: flash chromatography (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59-7.56 (m, 4H), 7.49 (d, J = 8.0 Hz, 2H), 7.44-7.37 (m, 5H), 7.32-7.30 (m, 3H), 5.33 (d, J = 8.0 Hz, 1H), 4.06-3.93 (m, 2H), 2.73-2.59 (m, 3H), 2.50 (dd, J = 16.4, 2.0 Hz, 1H), 2.46 (s, 3H), 2.13 (td, J = 7.6, 2.0 Hz, 2H), 1.16 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.1, 144.0, 142.3, 140.2, 134.5, 131.9, 129.6, 129.5, 128.8, 128.7, 127.7, 127.6, 127.5, 125.6, 120.3, 62.6, 60.6, 41.2, 34.4, 27.1, 21.6, 14. HRMS (ESI) m/z calcd. for $C_{28}H_{29}NO_4S_2$ $[M+H]^+$: 508.1611, found: 508.1617.

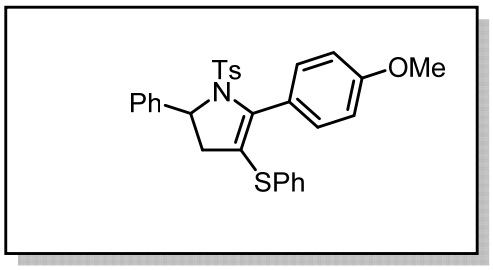
Methyl *N*-(*tert*-butoxycarbonyl)-S-(2,5-diphenyl-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)-L-cysteinate (4k)



Yield: 47.3 mg (52%); yellow liquid; R_f = 0.3 (PE:EtOAc = 4:1); purification: flash chromatography (PE:EtOAc = 5:1); the product was isolated as two diasteroisomer (3:2): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55-7.47 (m, 6H), 7.41-7.37 (m, 5H), 7.33-7.28 (m, 3H), 5.35-5.29 (m, 1H), 5.05 (d, J = 7.2 Hz, 0.6H), 4.89 (d, J = 8.0 Hz, 0.4H), 4.23-4.18 (m, 0.6H), 4.14-4.09 (m, 0.4H), 3.63 (s, 1.2H), 3.44 (s, 1.8H), 2.91-2.72 (m, 3H), 2.60 (d, J = 2.0 Hz, 0.6H), 2.56 (d, J = 2.0 Hz, 0.4H), 2.46 (s, 1.8H), 2.44 (s, 1.2H), 1.42 (s, 5.4H), 1.37 (s, 3.6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.86 (170.77), 154.86 (154.82), 144.13 (144.07), 142.50 (142.35), 140.09, 134.74, 134.48, 131.89, 129.69 (129.66), 129.62, 128.93 (128.88), 128.80, 127.84, 127.68 (127.63), 127.56, 125.84 (125.80), 119.78, 80.30 (80.24), 62.70 (62.61), 53.37,

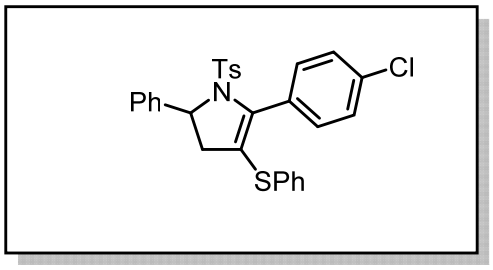
52.54 (52.44), 41.44 (41.35), 34.65 (34.45), 28.28 (28.23), 21.70 (21.67). HRMS (ESI) m/z calcd. for $C_{32}H_{36}N_2O_6S_2$ $[M+Na]^+$:631.1907, found: 631.1906.

5-(4-Methoxyphenyl)-2-phenyl-4-(phenylthio)-1-tosyl-2,3-dihydro-1*H*-pyrrole (4l)



Yield: 55.4 mg (72%); yellow liquid; R_f = 0.3 (PE:EtOAc = 9:1); purification: flash chromatography (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62-7.58 (m, 4H), 7.45 (d, J = 7.6 Hz, 2H), 7.40-7.32 (m, 5H), 7.07 (tt, J = 7.2, 1.2 Hz, 1H), 7.03-6.95 (m, 4H), 6.82-6.79 (m, 2H), 5.36 (d, J = 8.4Hz, 1H), 3.86 (s, 3H), 2.65 (dd, J = 16.0, 9.2 Hz, 1H), 2.50 (s, 3H), 2.24 (dd, J = 16.0, 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.3, 144.1, 143.3, 142.2, 135.0, 134.0, 131.2, 129.7, 129.4, 128.8, 128.7, 127.1, 127.7, 126.6, 125.8, 123.8, 117.5, 113.1, 62.9, 55.3, 41.3, 21.7. HRMS (ESI) m/z calcd. for $C_{30}H_{27}NO_3S_2$ $[M+H]^+$:514.1505, found: 514.1515.

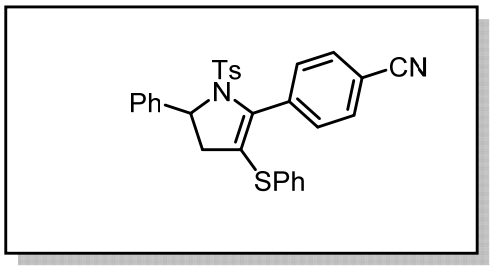
5-(4-Chlorophenyl)-2-phenyl-4-(phenylthio)-1-tosyl-2,3-dihydro-1*H*-pyrrole (4m)



Yield: 48.1 mg (62%); yellow liquid; R_f = 0.4 (PE:EtOAc = 9:1); purification: flash chromatography (PE:EtOAc = 11:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61-7.57 (m, 4H), 7.42-7.32 (m, 9H), 7.11 (tt, J = 7.2, 1.2 Hz, 1H), 7.07-7.02 (m, 2H), 6.86-6.83 (m, 2H), 5.33 (dd, J = 8.8, 1.2 Hz, 1H), 2.63 (dd, J = 16.4, 9.2 Hz, 1H), 2.51 (s, 3H), 2.81-2.24 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.3, 141.8, 141.5, 135.0, 134.7, 133.2, 130.9, 130.1, 129.8,

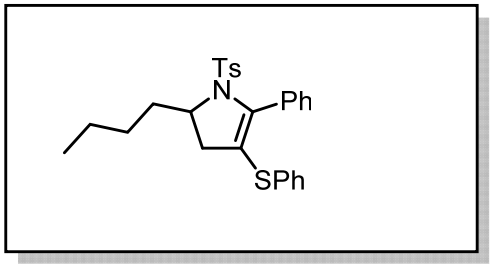
128.9, 128.8, 128.0, 127.8, 127.7, 127.1, 125.7, 120.7, 63.0, 41.4, 21.8. HRMS (ESI) m/z calcd. for $C_{29}H_{24}ClNO_2S_2$ $[M+H]^+$: 518.1010, found: 518.1012.

4-(5-Phenyl-3-(phenylthio)-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)benzonitrile (4n)



Yield: 54.9 mg (72%); white solid; m.p. 180-182 ℃; R_f = 0.25 (PE:EtOAc = 4:1); purification: flash chromatography (PE:EtOAc = 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.77-7.71 (m, 4H), 7.60-7.58 (d, J = 8.4 Hz, 2H), 7.37 (t, J = 4.0 Hz, 6H), 7.16 (tt, J = 7.2, 1.2 Hz, 1H), 7.10-7.06 (m, 2H), 6.90-6.88 (m, 2H), 5.28 (dd, J = 9.2, 2.0 Hz, 1H), 2.58 (dd, J = 16.4, 8.8 Hz, 1H), 2.51 (s, 3H), 2.27 (dd, J = 16.8, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 141.4, 139.5, 136.4, 134.2, 132.2, 131.5, 130.0, 129.9, 129.0, 128.8, 128.0, 127.72, 127.67, 125.7, 124.7, 118.7, 112.2, 63.0, 41.5, 13.8. HRMS (ESI) m/z calcd. For $C_{30}H_{24}N_2O_2S_2$ $[M+H]^+$:509.1352, found: 509.1368.

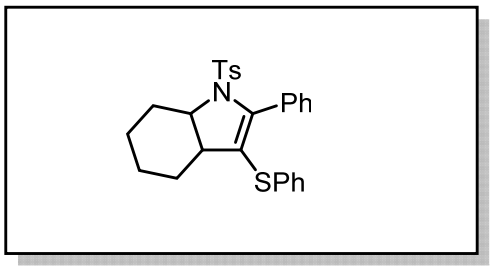
2-Butyl-5-phenyl-4-(phenylthio)-1-tosyl-2,3-dihydro-1*H*-pyrrole (4o)



Yield: 35.4 mg (51%); yellow liquid; R_f = 0.25 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc = 19:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59-7.57 (m, 4H), 7.45-7.39 (m, 3H), 7.32 (d, J = 8.0 Hz, 2H), 7.20-7.17 (m, 3H), 7.04-7.02 (m, 2H), 4.23-4.18 (m, 1H), 2.49 (s, 3H), 2.22 (dd, J = 16.4, 8.8 Hz, 1H), 1.81-1.75 (m, 2H), 1.54-1.47 (m, 2H), 1.43-1.38 (m, 3H), 0.95 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.8, 141.9, 134.8, 133.9, 132.2, 130.3, 129.6, 129.5, 129.0, 128.9, 127.7, 127.6, 127.0, 121.0, 61.2, 38.8,

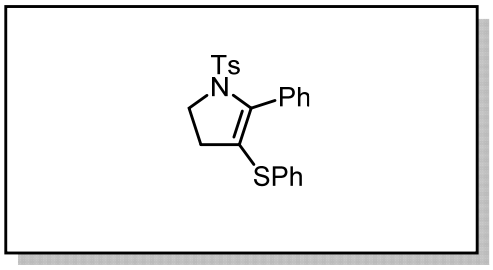
35.7, 27.2, 22.6, 21.7, 14.1. HRMS (ESI) m/z calcd. for $C_{27}H_{29}NO_2S_2$ $[M+H]^+$:464.1712, found: 464.1728

2-Phenyl-3-(phenylthio)-1-tosyl-3a,4,5,6,7,7a-hexahydro-1*H*-indole (4p)



Yield: 45.0 mg (65%); yellow liquid; R_f = 0.2 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc = 19:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 (d, J = 8.4 Hz, 2H), 7.35-7.25 (m, 7H), 7.18-7.09 (m, 3H), 7.01 (dt, J = 6.8, 2.0 Hz, 2H), 3.21-3.14 (m, 1H), 2.87-2.83 (m, 1H), 2.46 (s, 3H), 2.44-2.37 (m, 1H), 1.91-1.57 (m, 5H), 1.11 (tt, J = 12.8, 3.6 Hz, 1H), 0.96 (td, J = 12.4, 3.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.9, 144.0, 135.6, 134.3, 131.4, 130.1, 129.4, 128.8, 128.3, 127.9, 127.1, 125.8, 120.0, 71.2, 50.6, 31.9, 29.0, 25.6, 25.5, 21.7. HRMS (ESI) m/z calcd. for $C_{27}H_{27}NO_2S_2$ $[M+H]^+$: 462.1556, found: 462.1567.

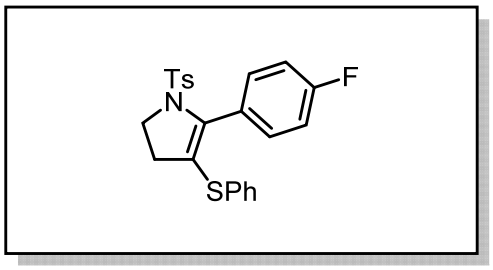
5-Phenyl-4-(phenylthio)-1-tosyl-2,3-dihydro-1*H*-pyrrole (4q)



Yield: 36.3 mg (60%); white solid; white solid; m.p. 106-108 ℃; R_f = 0.3 (PE:EtOAc = 9:1); purification: flash chromatography (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58-7.55 (m, 4H), 7.45-7.39 (m, 3H), 7.32 (d, J = 8.4 Hz, 2H), 7.23-7.17 (m, 3H), 7.08-7.06 (m, 2H), 7.02 (t, J = 8.0 Hz, 2H), 2.48 (s, 3H), 2.14 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.0, 143.2, 134.3, 133.8, 131.5, 130.0, 129.7, 129.6, 129.0, 128.9, 127.7, 127.5,

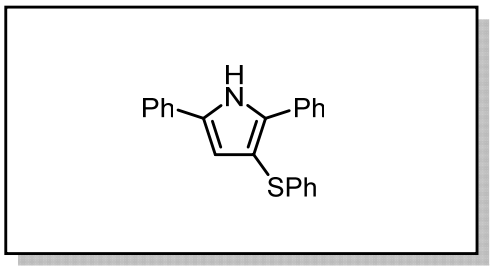
126.9, 121.4, 49.9, 33.2, 21.6. HRMS (ESI) m/z calcd. for $C_{23}H_{21}NO_2S_2$ $[M+H]^+$: 408.1086, found: 408.1087.

5-(4-Fluorophenyl)-4-(phenylthio)-1-tosyl-2,3-dihydro-1*H*-pyrrole (4r)



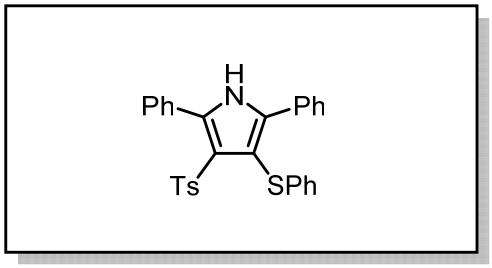
Yield: 45.9 mg (72%); white solid; white solid; m.p. 100-102 ℃; R_f = 0.3 (PE:EtOAc = 9:1); purification: flash chromatography (PE:EtOAc = 9:1); ^{1}H NMR (DMSO-d_6, 400 MHz): δ 7.57 (d, J = 8.8 Hz, 2H), 7.52-7.48 (m, 4H), 7.29-7.22 (m, 5H), 7.02-6.99 (m, 2H), 4.02 (t, J = 8.0 Hz, 2H), 2.47 (s, 3H), 2.02 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.6 (J = 244.0 Hz), 144.9, 142.8, 134.0, 133.3, 132.0 (J = 8.0 Hz), 130.5, 129.8, 129.5, 128.5 (J = 3.0 Hz), 128.0, 127.5, 121.7, 115.1 (J = 22.0 Hz), 50.2, 33.3, 21.6; ^{19}F NMR ($CDCl_3$, 376.3 MHz): δ -111.42. HRMS (ESI) m/z calcd. for $C_{23}H_{20}FNO_2S_2$ $[M+H]^+$: 426.0992, found: 426.0998.

2,5-Diphenyl-3-(phenylthio)-1*H*-pyrrole (5)



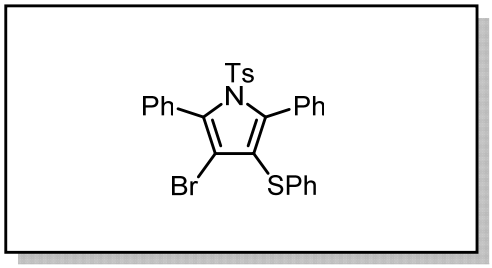
Yield: 36.3 mg (74%); yellow liquid; R_f = 0.4 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc = 24:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.73 (s, 1H), 7.67-7.65 (m, 2H), 7.55-7.52 (m, 2H), 7.41 (q, J = 8.0 Hz, 4H), 7.33-7.21 (m, 6H), 7.11-7.17 (m, 1H), 6.71 (d, J = 2.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.0, 136.4, 132.6, 131.6, 131.5, 129.1, 128.83, 128.75, 127.6, 127.0, 126.9, 125.9, 124.7, 123.8, 114.4, 108.1. HRMS (ESI) m/z calcd. for $C_{22}H_{17}NS$ $[M]^+$: 327.1076, found: 327.1077.

2,5-Diphenyl-3-(phenylthio)-4-tosyl-1H-pyrrole (6)



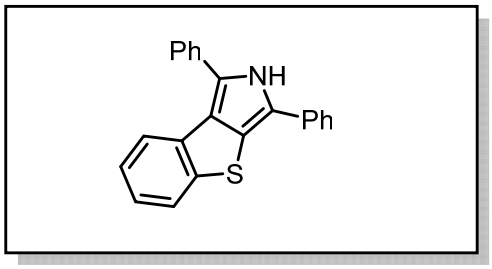
Yield: 52.2 mg (72%); yellow solid; white solid; m.p. 188-189 ℃; R_f = 0.3 (PE:EtOAc = 4:1); purification: flash chromatography (PE:EtOAc = 4:1); ^{1}H NMR (DMSO-*d*$_6$, 400 MHz): δ 12.65(s, 1H), 7.66-7.63 (m, 2H), 7.58-7.55 (m, 4H), 7.35-7.27 (m, 3H), 7.50-7.49 (m, 3H), 7.11-7.08 (m, 4H), 7.01 (t, J = 6.8 Hz, 1H), 6.79 (d, J = 8.0 Hz, 2H), 2.22 (s, 3H); ^{13}C NMR (DMSO-*d*$_6$, 100 MHz): δ 142.81, 139.8, 138.8, 138.6, 137.9, 130.9, 130.8, 130.0, 129.1, 128.8, 128.6, 128.22, 128.15, 127.5, 126.9, 124.5, 124.3, 122.9, 103.6, 20.94. HRMS (ESI) m/z calcd. for $C_{29}H_{23}NO_2S_2$ $[M+H]^+$: 482.1243, found: 482.1236.

3-Bromo-2,5-diphenyl-4-(phenylthio)-1-tosyl-1*H*-pyrrole (7)



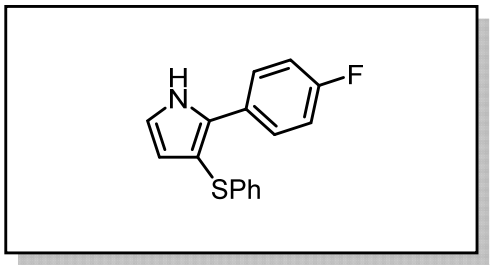
Yield: 50.3 mg (60%); yellow solid; m.p. 174-176 ℃; R_f = 0.25 (PE:EtOAc = 49:1); purification: flash chromatography (PE:EtOAc = 49:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54-7.52 (m, 2H), 7.48-7.45 (m, .3H), 7.43-7.36 (m, 5H), 7.19-7.10 (m, 7H), 6.83 (dt, J = 6.8, 2.0 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.3, 143.3, 137.1, 136.2, 134.8, 131.3, 131.2, 131.1, 130.6, 129.4, 129.2, 128.9, 128.8, 127.6, 127.3, 126.3, 125.4, 118.9, 113.2, 21.8. HRMS (ESI) m/z calcd. for $C_{29}H_{22}BrNO_2S_2$ $[M+H]^+$:562.0328, 560.0348, found: 562.0335, 560.0355.

1,3-Diphenyl-2*H*-benzo[4,5]thieno[2,3-*c*]pyrrole (8)



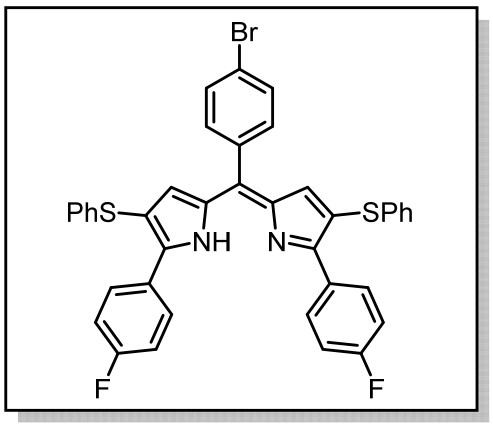
Yield: 19.5 mg (40%); white solid; m.p. 222-224 ℃; R_f = 0.3 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc =19:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.80 (s, 1H), 8.04 (dd, J = 6.8, 2.0 Hz, 1H), 7.77-7.74 (m, 3H), 7.58-7.54 (m, 4H), 7.48 (t, J = 7.6 Hz, 2H), 7.44-7.40 (m, 1H), 7.30 (qd, J = 7.2, 1.2 Hz, 2H), 7.23 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.2, 132.8, 131.5, 131.4, 129.2, 128.84, 128.75, 127.7, 127.2, 126.9, 125.9, 125.7, 125.0, 124.2, 123.8, 123.6, 123.3, 121.3. HRMS (ESI) m/z calcd. for $C_{22}H_{15}NS$ $[M]^+$:325.0920, found: 325.0918.

2-(4-Fluorophenyl)-3-(phenylthio)-1*H*-pyrrole (9)



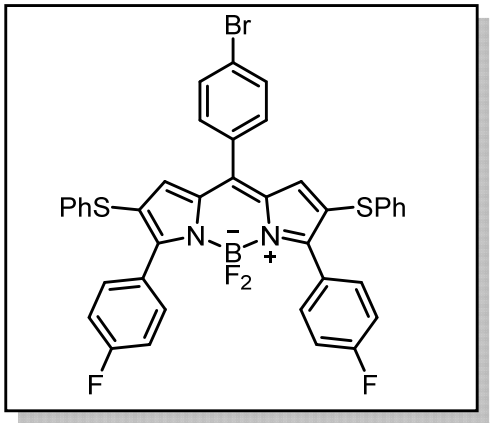
Yield: 37.9 mg (94%); yellow liquid; R_f = 0.3 (PE:EtOAc = 19:1); purification: flash chromatography (PE:EtOAc = 19:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.52 (s, 1H), 7.55-7.52 (m, 2H), 7.23-7.19 (m, 2H), 7.13-7.03 (m, 5H), 6.92 (t, J = 2.8 Hz, 1H), 6.41 (t, J = 2.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.2 (J = 245.0 Hz), 140.2, 134.8, 128.8 (J = 7.0 Hz), 127.9 (J = 3.0 Hz), 125.6, 124.6, 118.6, 117.2, 115.7 (J = 21.0 Hz), 105.9; ^{19}F NMR ($CDCl_3$, 376.3 MHz): δ -114.19. HRMS (ESI) m/z calcd. for $C_{16}H_{12}FNS$ $[M]^+$:269.0669, found: 269.0676.

(*Z*)-5-((4-Bromophenyl)(5-(4-fluorophenyl)-4-(phenylthio)-2*H*-pyrrol-2-ylidene)methyl)-2-(4-fluorophenyl)-3-(phenylthio)-1H-pyrrole (10)



Yield: 70.6 mg (67%); red solid; m.p. 208-210 ℃; R_f = 0.4 (PE:CH_2Cl_2 = 4:1); purification: flash chromatography (PE:CH_2Cl_2 = 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 13.77 (s, 1H), 8.02-7.98 (m, 4H), 7.58 (dt, J = 8.4, 2.4 Hz, 2H), 7.39 (dt, J = 8.4, 2.4 Hz, 2H), 7.23-7.19 (m, 4H), 7.17-7.08 (m, 10H), 6.08 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): 163.4 (J = 250.0 Hz), 154.0, 139.9, 137.4, 135.6, 132.3, 131.3, 129.80 (J = 8.0 Hz), 129.1, 128.7 (J = 3.0 Hz), 127.2, 125.9, 124.0, 119.7, 115.8 (J = 22.0 Hz); ^{19}F NMR ($CDCl_3$, 376.3 MHz): δ -110.66. HRMS (ESI) m/z calcd. for $C_{39}H_{26}BrF_2N_2S_2$ $[M+H]^+$: 705.0665, 703.0683, found: 705.0690, 703.0675.

10-(4-Bromophenyl)-5,5-difluoro-3,7-bis(4-fluorophenyl)-2,8-bis(phenylthio)-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (11)

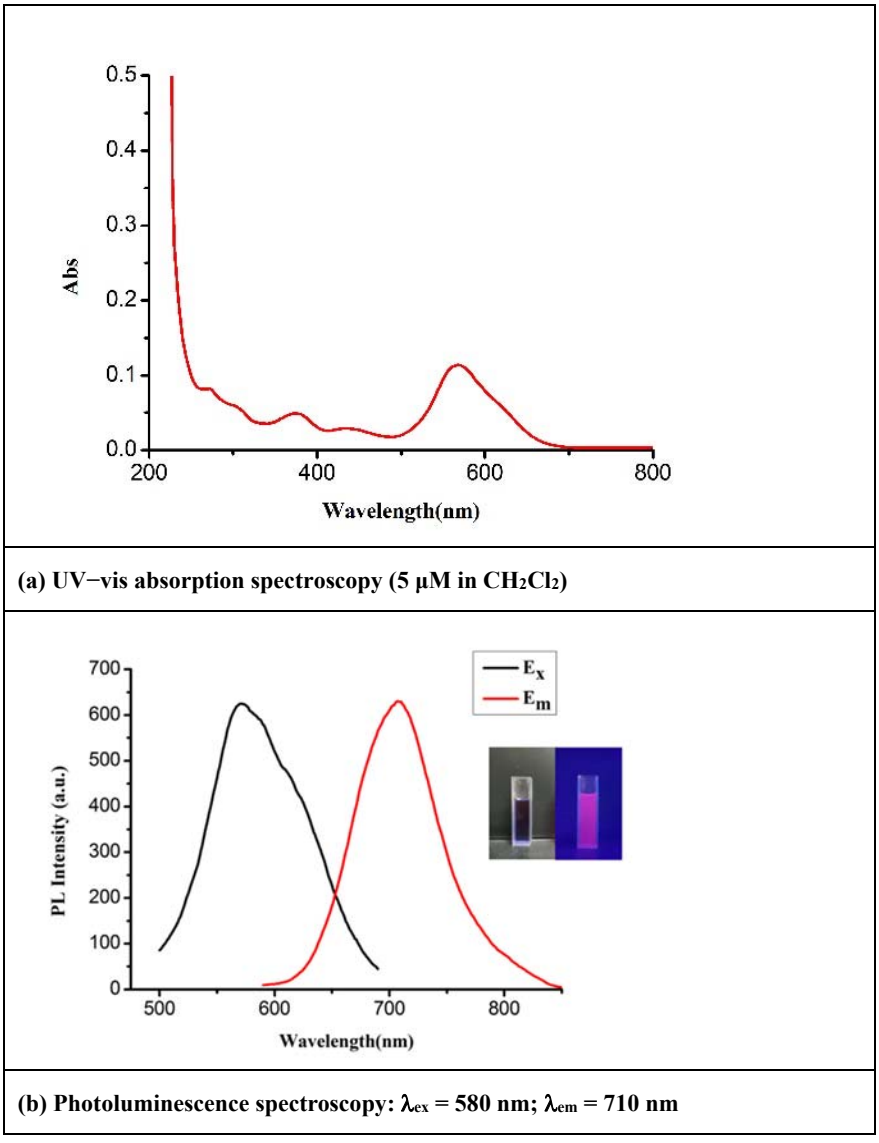


Yield: 68.6 mg (61%); dark blue solid; m.p. 201-203℃; R_f = 0.3 (PE:CH_2Cl_2 = 2:1); purification: flash chromatography (PE:CH_2Cl_2 = 3:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67 (dt, J = 8.4, 1.6 Hz, 2H), 7.52-7.19(m, 4H), 7.45 (dt, J = 8.4, 1.6 Hz, 2H), 7.21-7.17 (m, 4H), 7.13 (tt, J = 6.8, 1.2 Hz, 2H), 7.7 (dt, J = 6.8, 1.2 Hz, 4H), 7.04-6.99 (m, 6H); ^{13}C NMR

($CDCl_3$, 100 MHz): δ 163.5 (J = 249.0 Hz), 159.8, 142.4, 136.3, 135.2, 134.2, 132.3, 132.1, 132.0 (J = 8.0 Hz), 129.1, 128.4, 126.5, 126.1 (J = 3.0 Hz), 125.7, 115.0 (J = 21.0 Hz); ^{19}F NMR ($CDCl_3$, 376.3 MHz): δ -110.35, -130.02 (q, J = 30.0 Hz); ^{11}B NMR ($CDCl_3$, 128 MHz): δ 0.69 (t, J = 35.8 Hz). HRMS (ESI) m/z calcd. for $C_{39}H_{24}BBrF_4N_2S_2$ $[M]^+$: 752.057, 750.059, found: 752.061, 750.059.

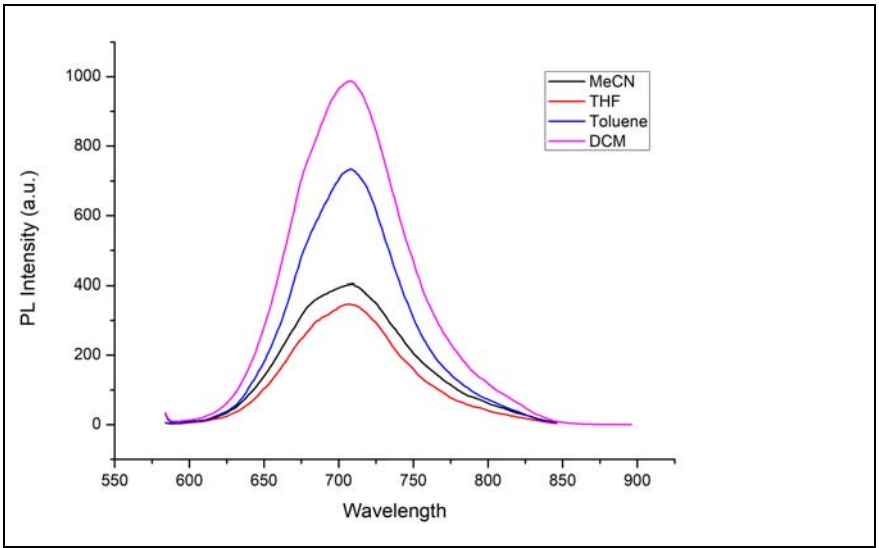
Spectral properties of Bisthiolated BODIPY

Figure S1. Absorption and Fluorescence spectra of S-BODIPY



(a) UV−vis absorption spectroscopy (5 µM in CH_2Cl_2)

(b) Photoluminescence spectroscopy: λ_{ex} = 580 nm; λ_{em} = 710 nm



(c) Photoluminescence in 4 kinds of solvents (MeCN, THF, Toluene, and CH_2Cl_2)

Figure S2. Molecular absorptivity in different solvents

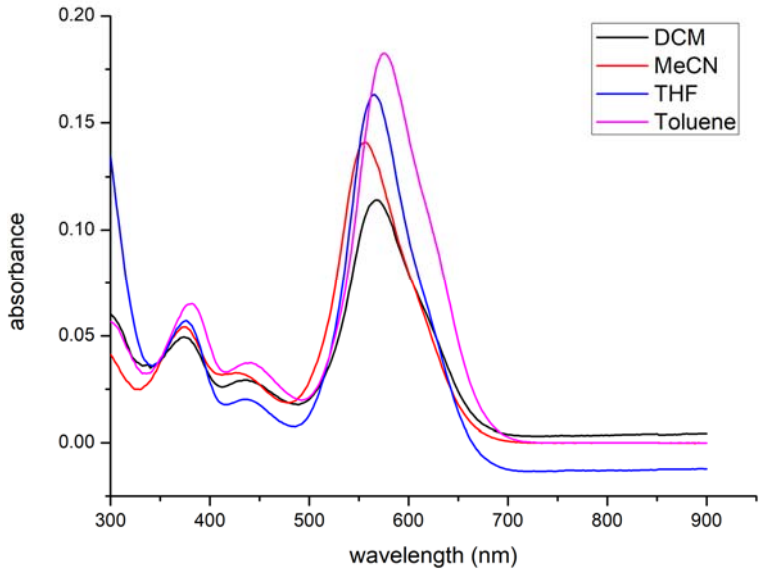
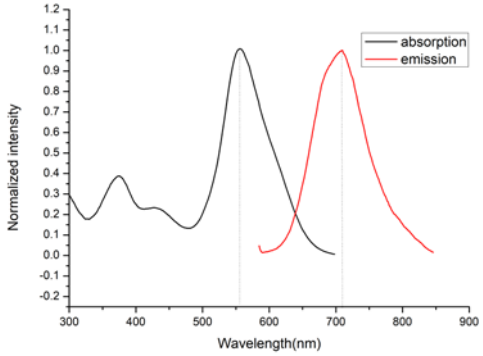
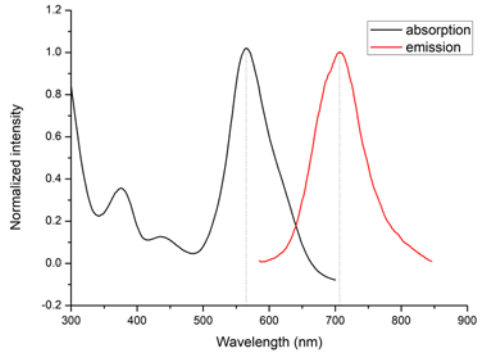


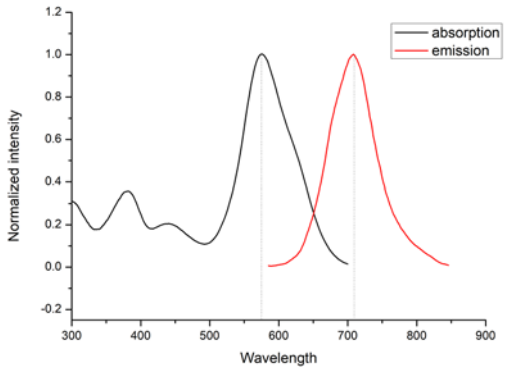
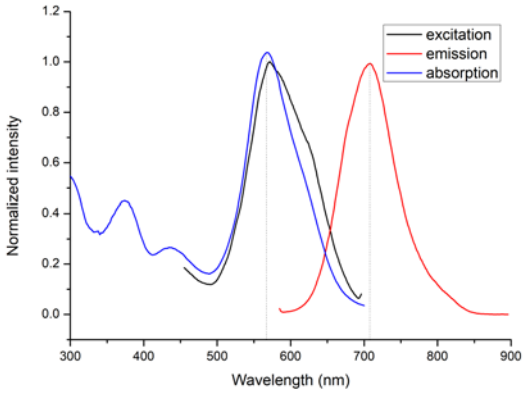
Figure S3. Stokes shifts in different solvents



MeCN: λ_{abs} = 558 nm, λ_{em} = 709 nm;



THF: λ_{abs} = 564 nm, λ_{em} = 707 nm;

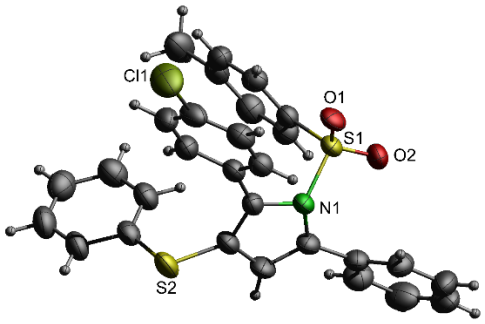
Δλ = 151 nm	**Δλ = 143 nm**
	
Toluene: λ_{abs} = 576 nm, λ_{em} = 708 nm; **Δλ = 132 nm**	**DCM: λ_{abs} = 568 nm, λ_{em} = 710 nm;** **Δλ = 140 nm**

The quantum yield of fluorescence of bisthiolated BODIPY was determined by using Rhodamine 6G ($\Phi_{F\ ref}$ = 95%) as a reference in methanol following the known procedure (Dyes and Pigments, 2020, 178, 108322), and the average quantum yield (ΦF) of bisthiolated BODIPY is **7.5%.**

$$\varphi_F = \varphi_{F\ ref.} \frac{F_{sample}}{F_{ref.}} \frac{A_{ref.}}{A_{sample}} \frac{\eta^2_{sample}}{\eta^2_{ref.}}$$

X-ray crystal data

Figure S4. Crystal data of 3m (CCDC 2036448)

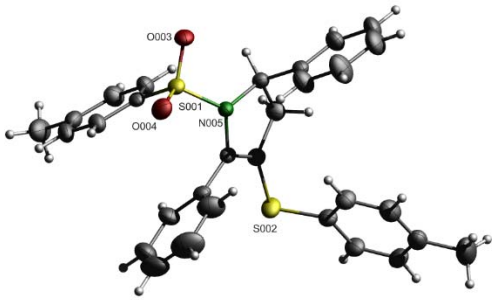


Crystal data	
Chemical formula	$C_{29}H_{22}ClNO_2S_2$
M_r	516.05
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	293
a, b, c (Å)	8.0048 (3), 11.7155 (5), 13.6559 (5)
β (°)	92.414 (3)
V (Å^3)	1279.52 (9)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	3.06
Crystal size (mm)	0.21 × 0.14 × 0.06

Data collection	
Diffractometer	SuperNova, Dual, Cu at home/near, Eos diffractometer
Absorption correction	Multi-scan *CrysAlis PRO* 1.171.40.53 (Rigaku Oxford Diffraction, 2019) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.524, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4814, 3484, 3365
R_{int}	0.016
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.597
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.090, 1.03
No. of reflections	3484
No. of parameters	318
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.23, −0.20
Absolute structure	Flack H D (1983), Acta Cryst. A39, 876-881
Absolute structure parameter	0.001 (13)

Computer programs: CrysAlis PRO 1.171.40.53 (Rigaku OD, 2019), XS, G.M. Sheldrick, Acta Cryst. (2008). A64, 112-122, XL, O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339-341.

Figure S5. Crystal data of 4b (CCDC 2036449)



Crystal data	
Chemical formula	$C_{30}H_{27}NO_2S_2$
M_r	497.64
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	298
a, b, c (Å)	9.9298 (7), 11.0745 (7), 13.1127 (9)
α, β, γ (°)	70.550 (2), 77.681 (2), 76.720 (2)
V (Å^3)	1308.52 (15)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.23

Crystal size (mm)	× ×
Data collection	
Diffractometer	Bruker *APEX*-II CCD diffractometer
Absorption correction	Multi-scan *SADABS2016*/2 (Bruker,2016/2) was used for absorption correction. wR2(int) was 0.0941 before and 0.0690 after correction. The Ratio of minimum to maximum transmission is 0.7966. The λ/2 correction factor is Not present.
T_{min}, T_{max}	0.594, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16878, 4539, 3728
R_{int}	0.037
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.065, 0.149, 1.10
No. of reflections	4539
No. of parameters	318
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.35, −0.42

Computer programs: SAINT v8.37A (Bruker, 2015), XL (Sheldrick, 2008), Olex2 (Dolomanov et al., 2009).

References:

[S1] C. H. Ding, L. X. Dai, X. L. Hou, *Tetrahedron* **2005**, *61*, 9586−9593.

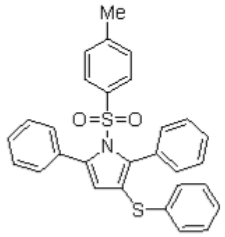
[S2] S. J. Gharpure, D. S. Vishwakarma, R. K. Patel, *Chem. Commun*. **2019**, *55*, 6858–6861.

[S3] R. Pi, M. B. Zhou,Y. Yang, C. Gao, R. J. Song, J. H. Li, *Chem. Commun.* **2015**, *51*, 13550−13553.

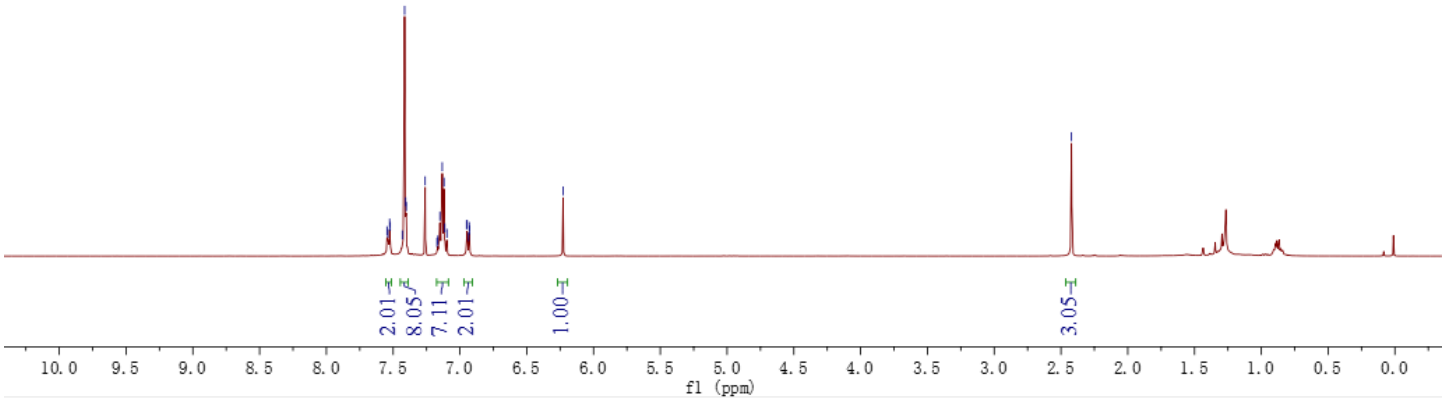
[S4] (a)W. C. Gao, T. Liu, B. Zhang, X. Li, W. L. Wei, Q. Liu, J. Tian, H. H. Chang, *J. Org. Chem.* **2016**, *81*, 11297−11304. (b) W. C. Gao, Y. F. Cheng, H. H. Chang, X. Li, W. L. Wei, P. Yang, *J. Org. Chem.* **2019**, *84*, 4312−4317.

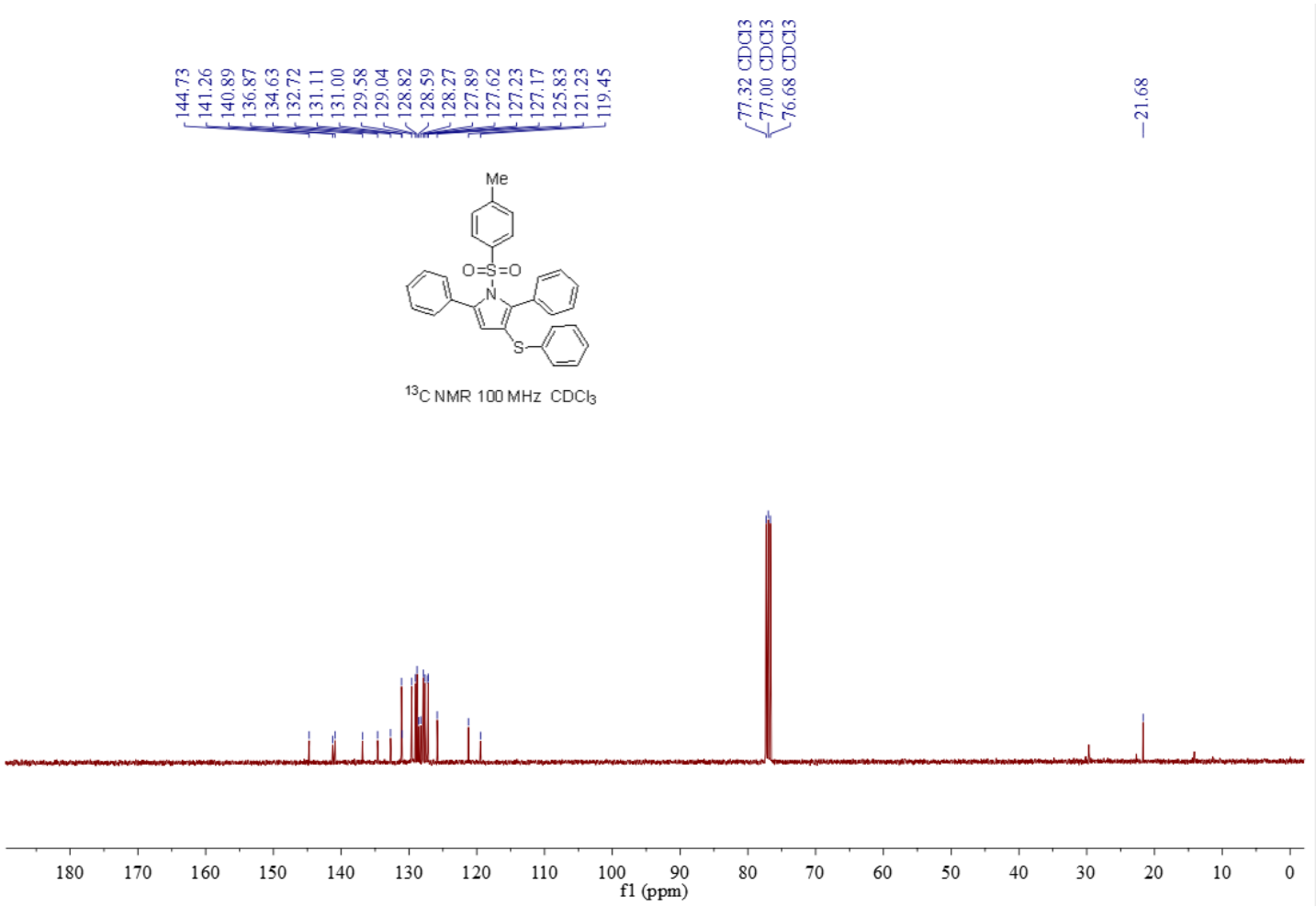
Copies of NMR spectra

3a



^{1}H NMR 400 MHz $CDCl_3$

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140.89
136.87
134.63
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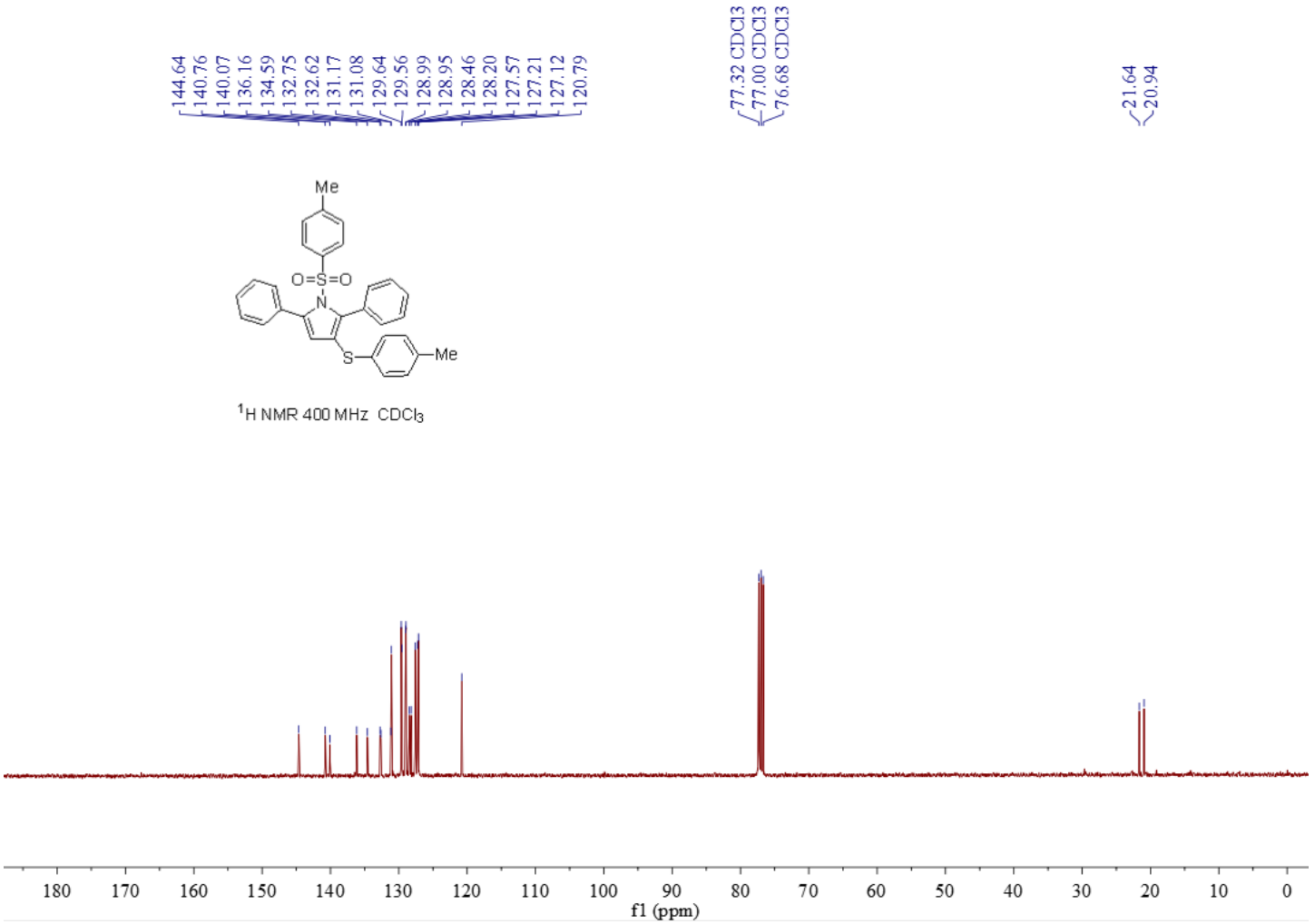
131.11
131.00
129.58
129.04
128.82
128.59
128.27
127.89
127.62
127.23
127.17
125.83
121.23
119.45
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
21.68
Me
O=S=O
N
S
13C NMR 100 MHz CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

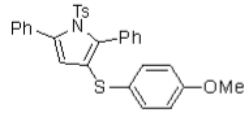
3b

^{1}H NMR 400 MHz $CDCl_3$

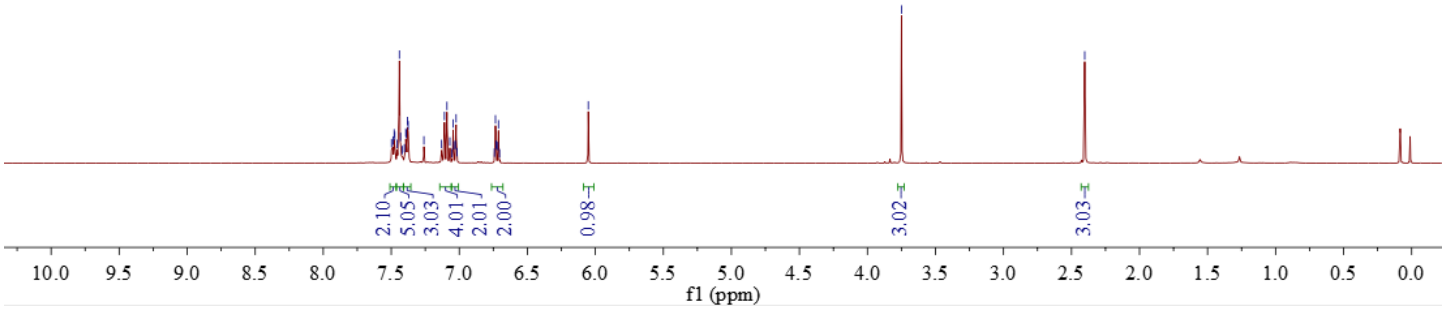


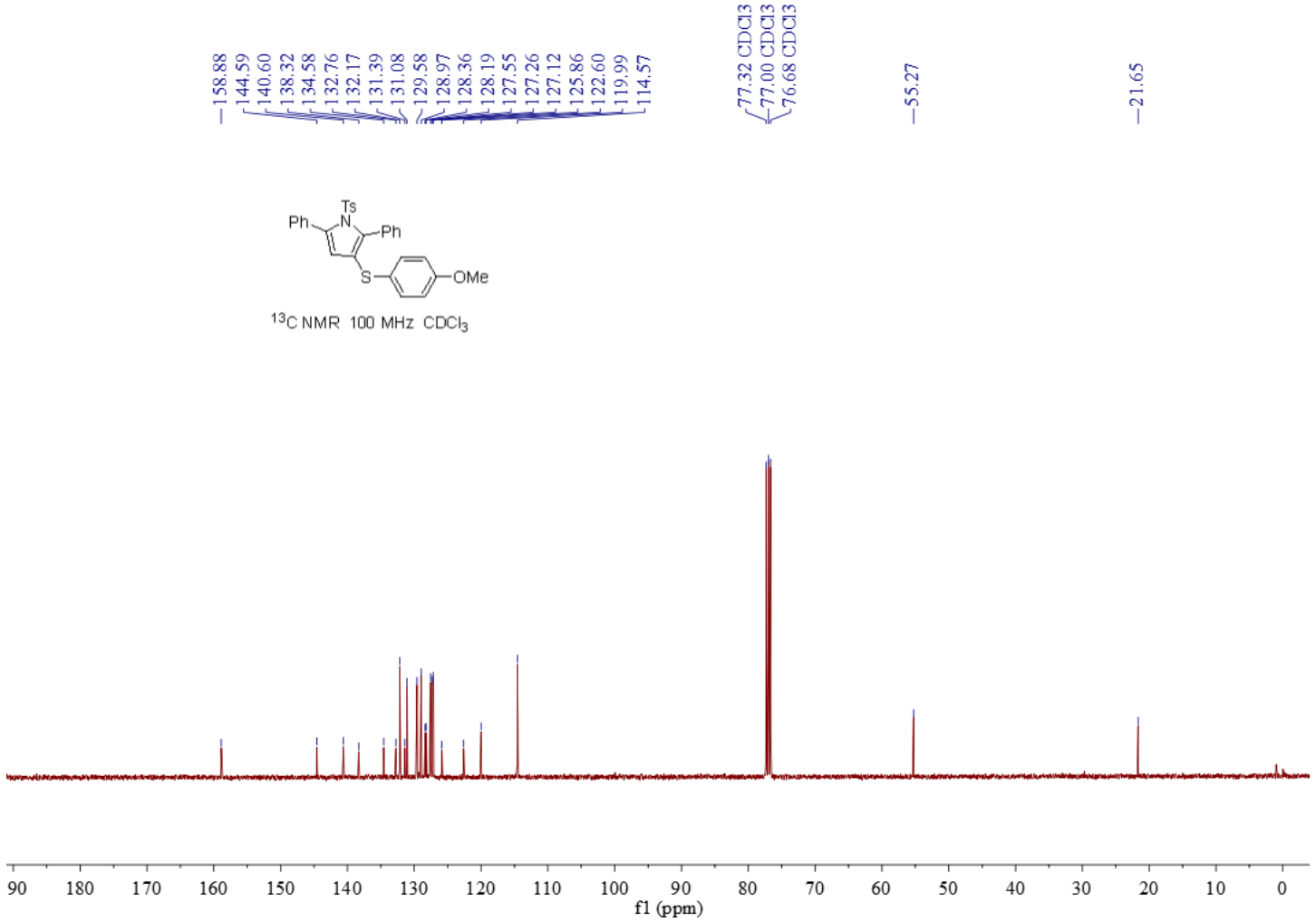
^{1}H NMR 400 MHz $CDCl_3$

3c



^{1}H NMR 400 MHz $CDCl_3$

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138.32
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131.39
131.08
129.58
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128.36
128.19
127.55
127.26
127.12
125.86
122.60
119.99
114.57
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
55.27
21.65
Ts
N
Ph
Ph
S
OMe
13C NMR 100 MHz CDCl3
90
180
170
160
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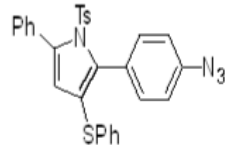
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3d



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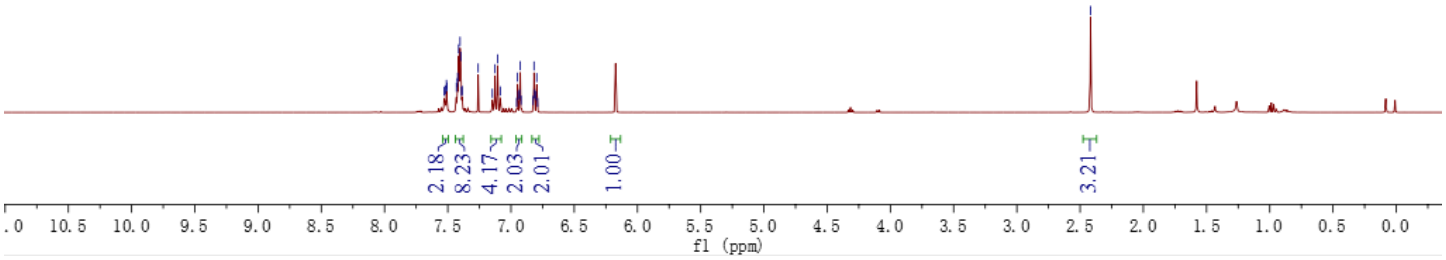

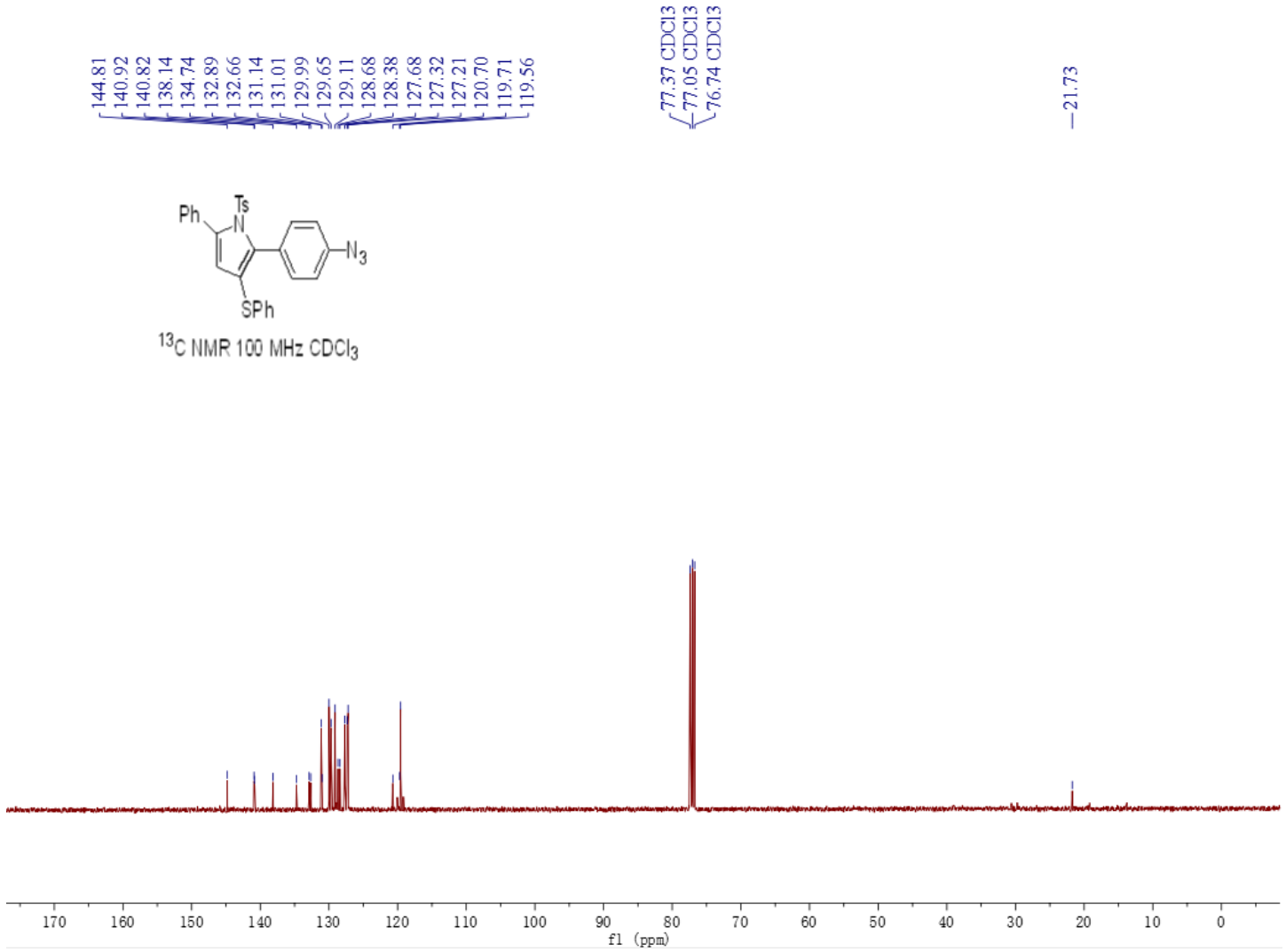
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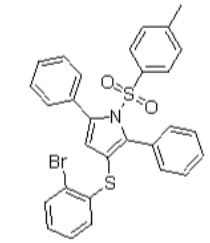
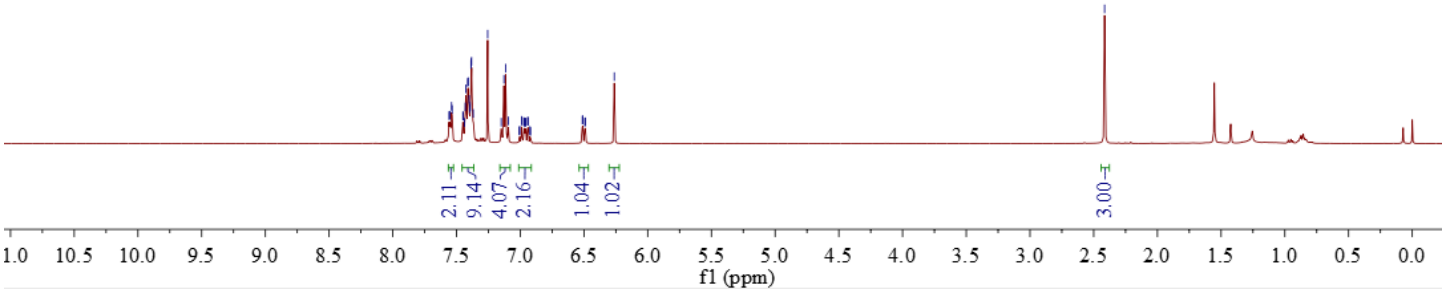
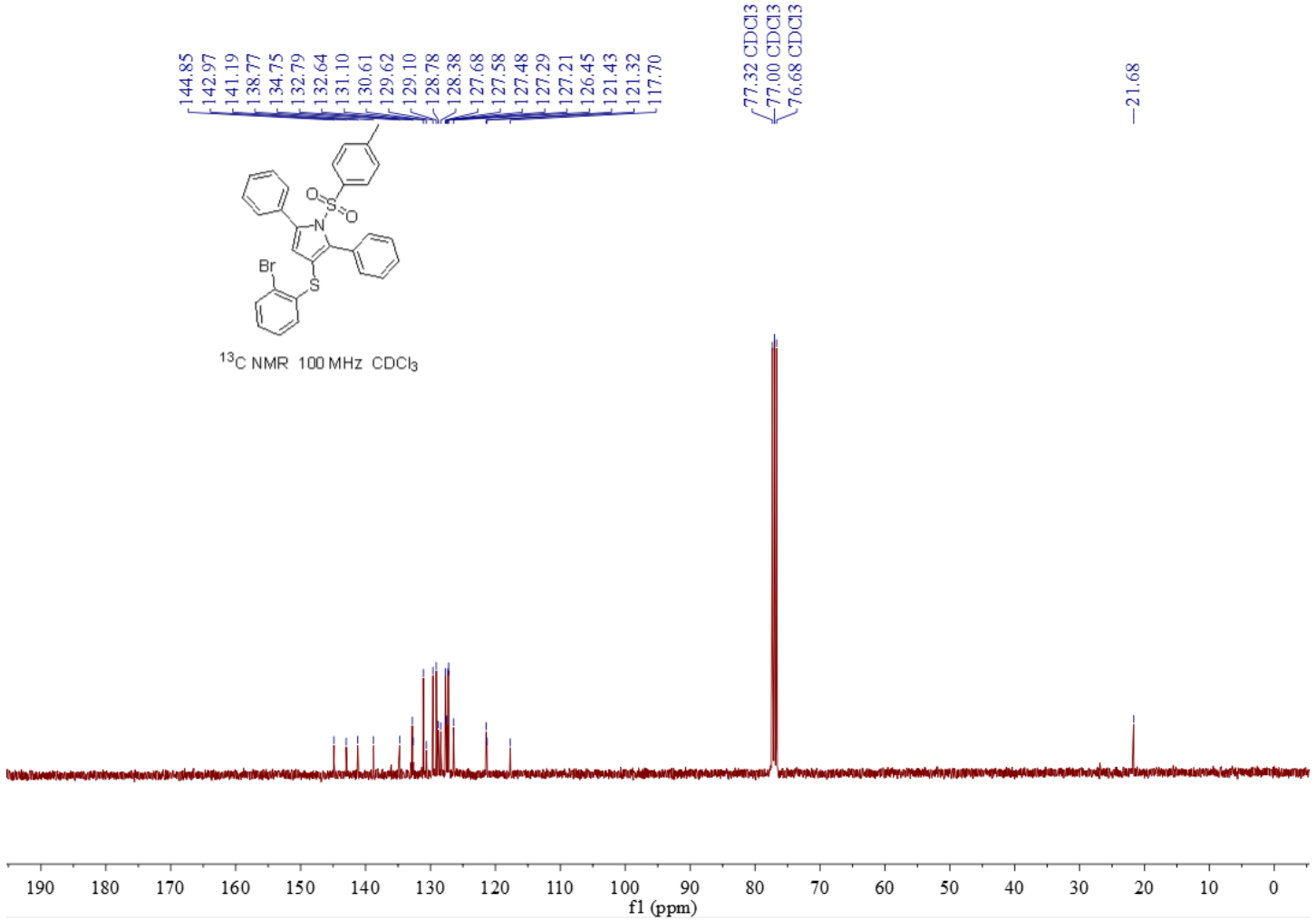
132.89
132.66
131.14
131.01
129.99
129.65
129.11
128.68
128.38
127.68
127.32
127.21
120.70
119.71
119.56
77.37 CDCl3
77.05 CDCl3
76.74 CDCl3
21.73
Ph
Ts
N
N3
SPh
13C NMR 100 MHz CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3e



^{1}H NMR 400 MHz $CDCl_3$

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128.38
127.68
127.58
127.48
127.29
127.21
126.45
121.43
121.32
117.70
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
21.68
Br
S
N
O
O
S
13C NMR 100 MHz CDCl3
190
180
170
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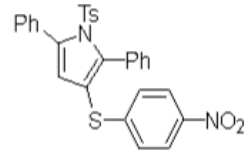
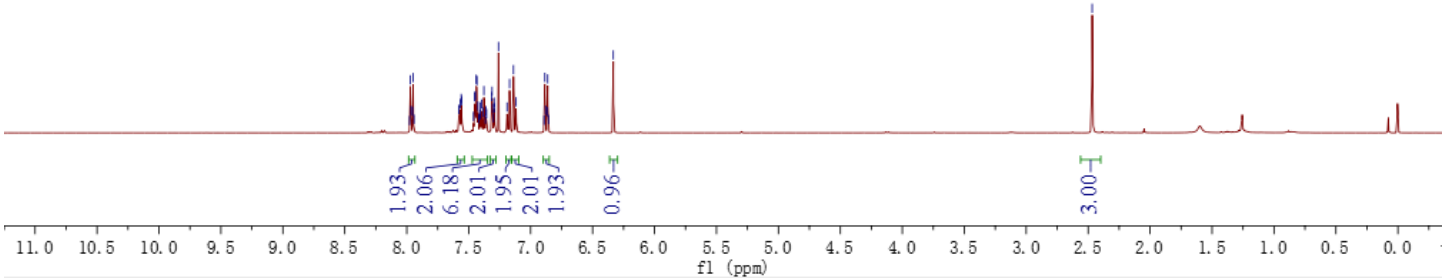
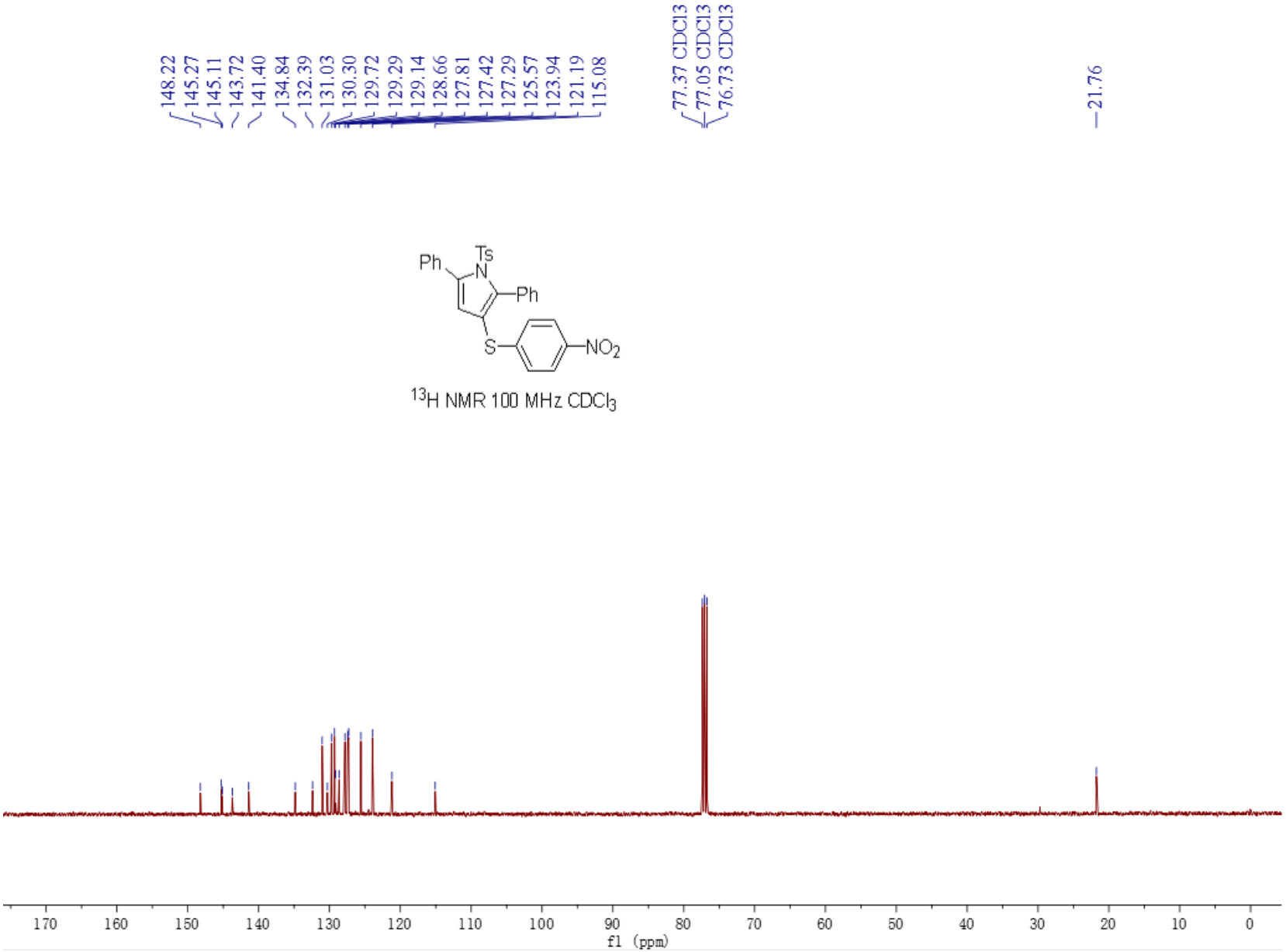
30
20
10
0
f1 (ppm)

3f



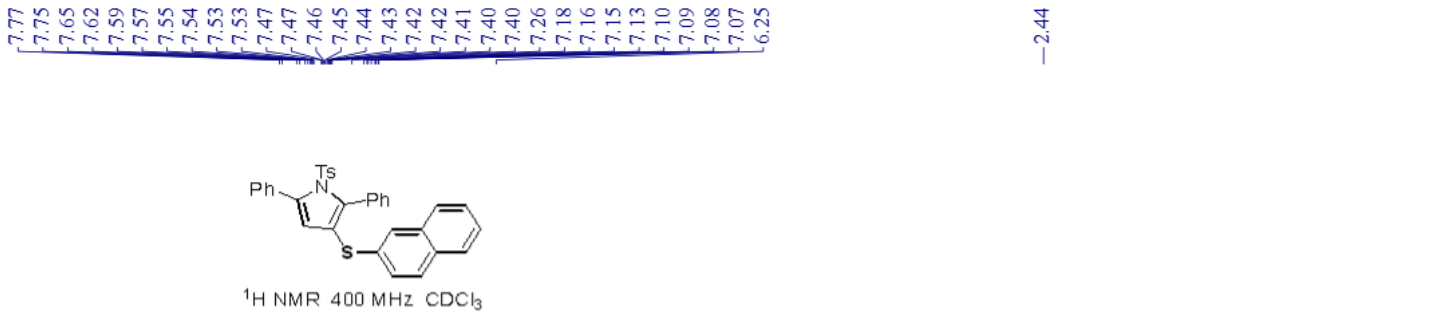
^{1}H NMR 400 MHz $CDCl_3$





^{13}H NMR 100 MHz $CDCl_3$

3g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7.54
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7.47
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7.45
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7.43
7.42
7.42
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7.26
7.18
7.16
7.15
7.13
7.10
7.09
7.08
7.07
6.25
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Ts
N
Ph
Ph
S
1H NMR 400 MHz CDCl3
1.23
1.28
1.30
2.10
11.00
4.17
1.04
0.99
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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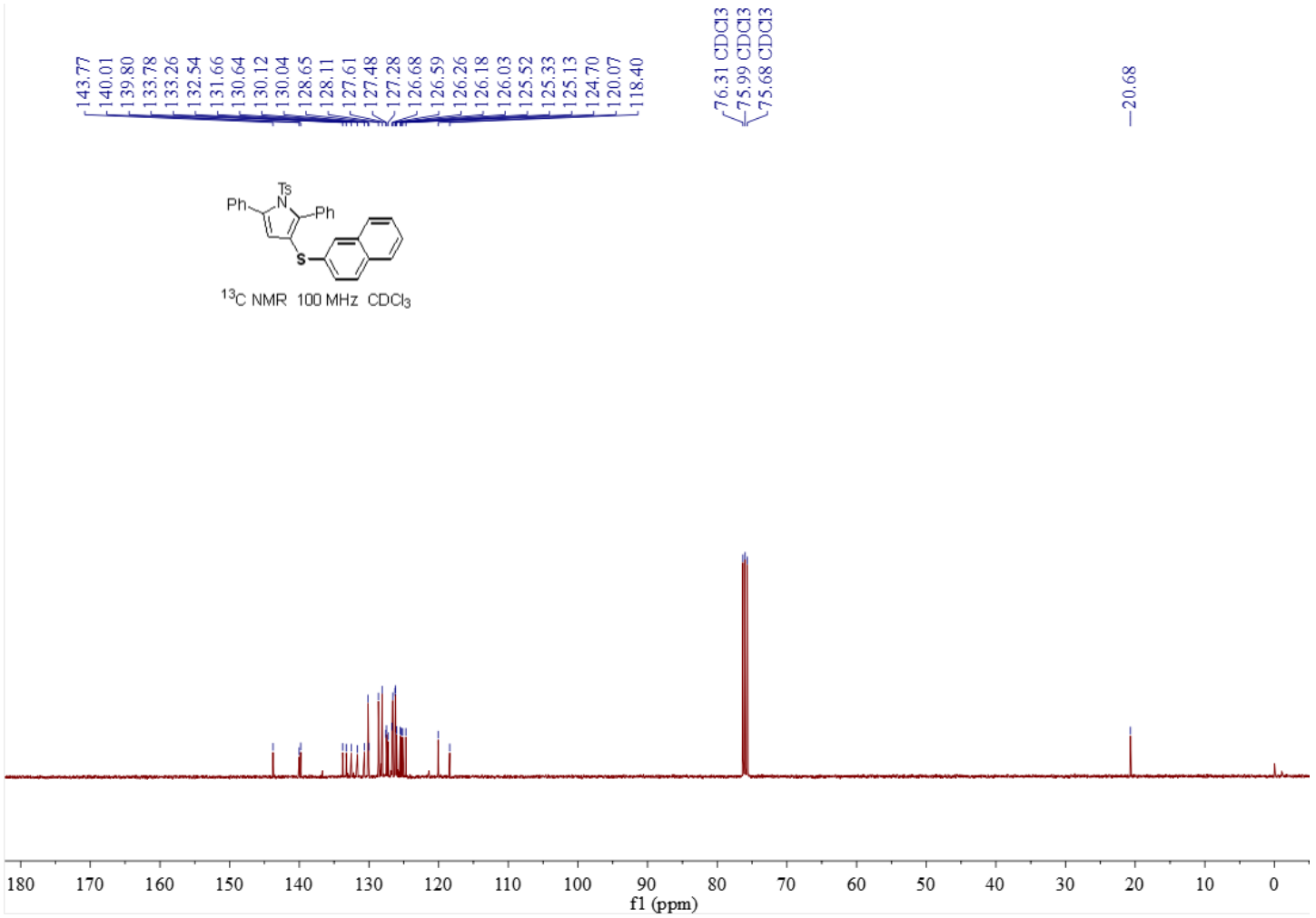
f1 (ppm)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127.28
126.68
126.59
126.26
126.18
126.03
125.52
125.33
125.13
124.70
120.07
118.40
76.31 CDCl3
75.99 CDCl3
75.68 CDCl3
20.68
Ts
N
Ph
Ph
S
13C NMR 100 MHz CDCl3
180
170
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30
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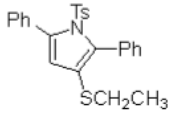
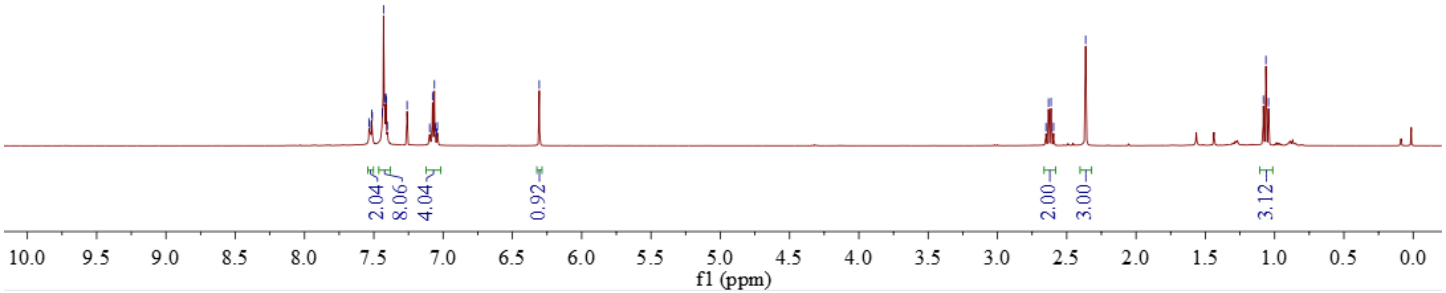
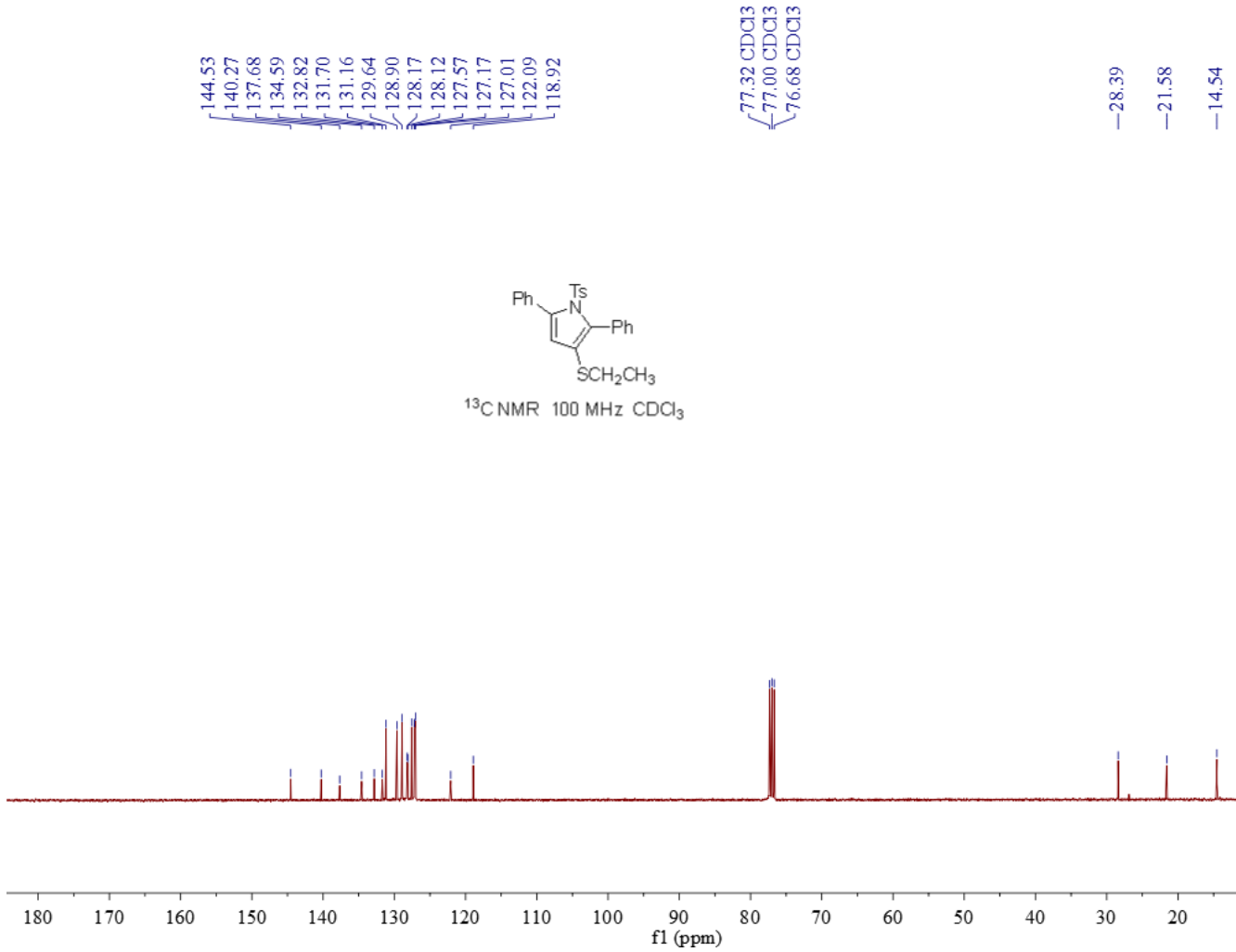
f1 (ppm)

3h



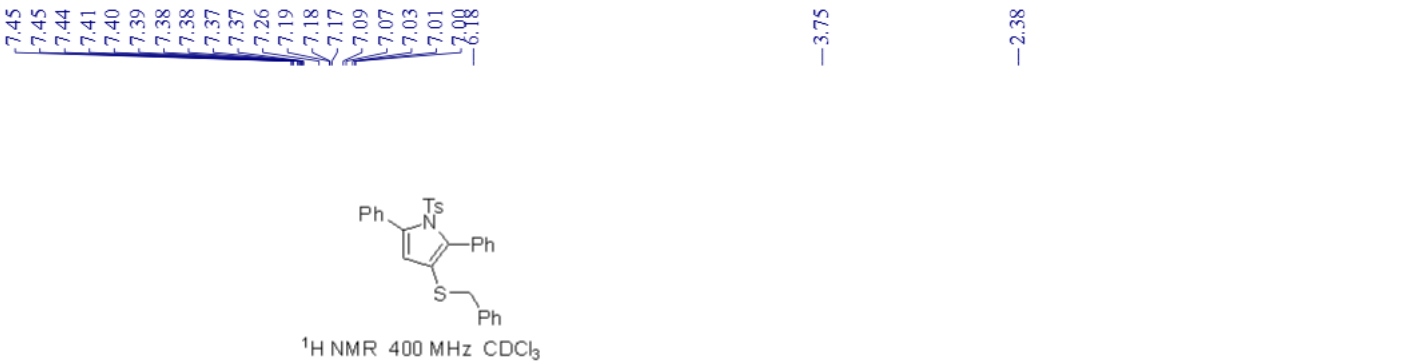
^{1}H NMR 400 MHz $CDCl_3$





^{13}C NMR 100 MHz $CDCl_3$

3i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7.17
7.09
7.07
7.03
7.01
7.00
6.18
3.75
2.38
Ph
Ts
N
Ph
S
Ph
1H NMR 400 MHz CDCl3
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3.05
2.10
4.02
1.00
2.01
3.14
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
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2.5
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1.0
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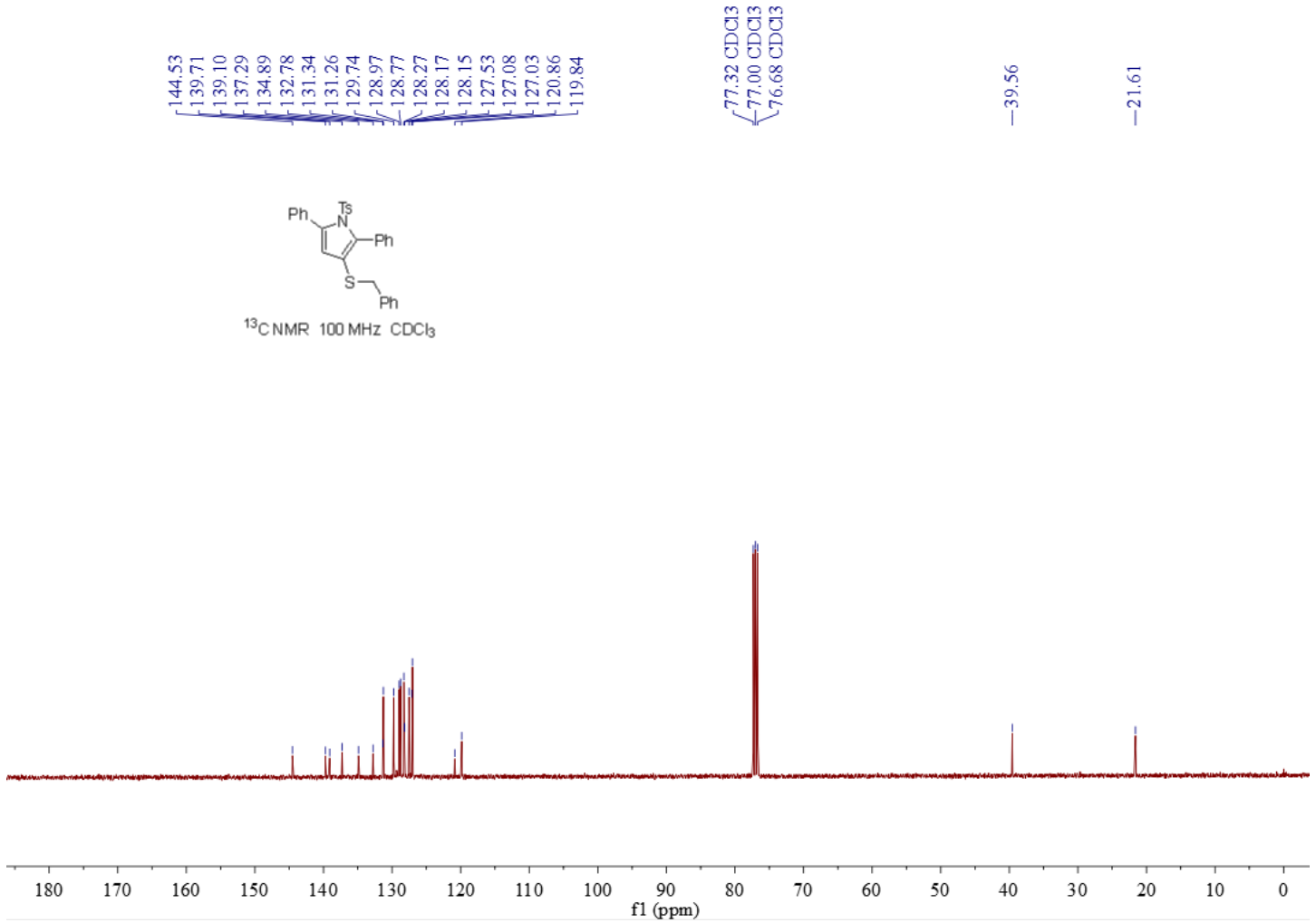
0.0
f1 (ppm)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131.26
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128.17
128.15
127.53
127.08
127.03
120.86
119.84
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
39.56
21.61
Ph
Ts
N
Ph
S
Ph
13C NMR 100 MHz CDCl3
180
170
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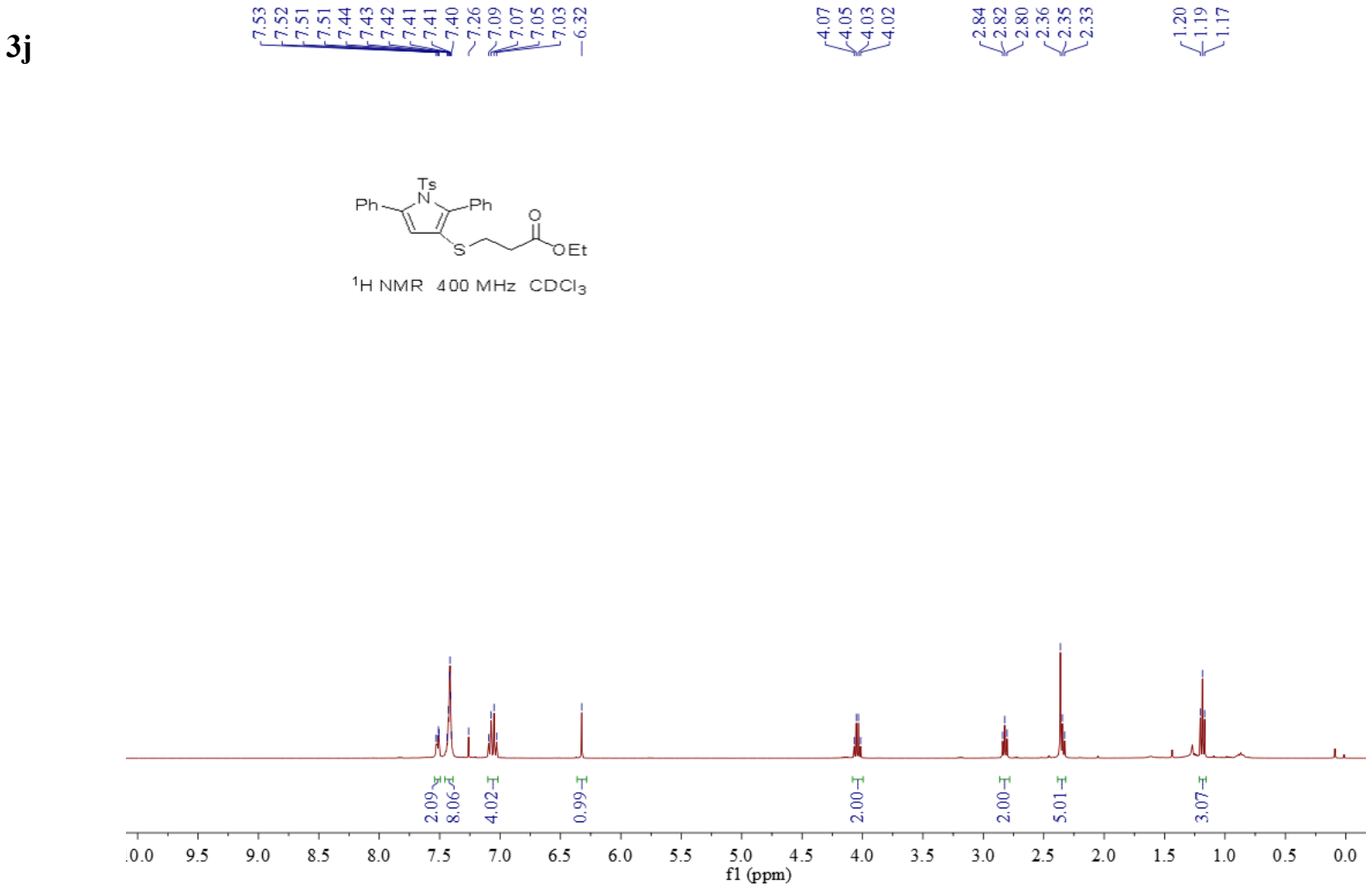
f1 (ppm)

3j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7.05
7.03
6.32
4.07
4.05
4.03
4.02
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1.19
1.17
Ts
N
Ph
Ph
O
S
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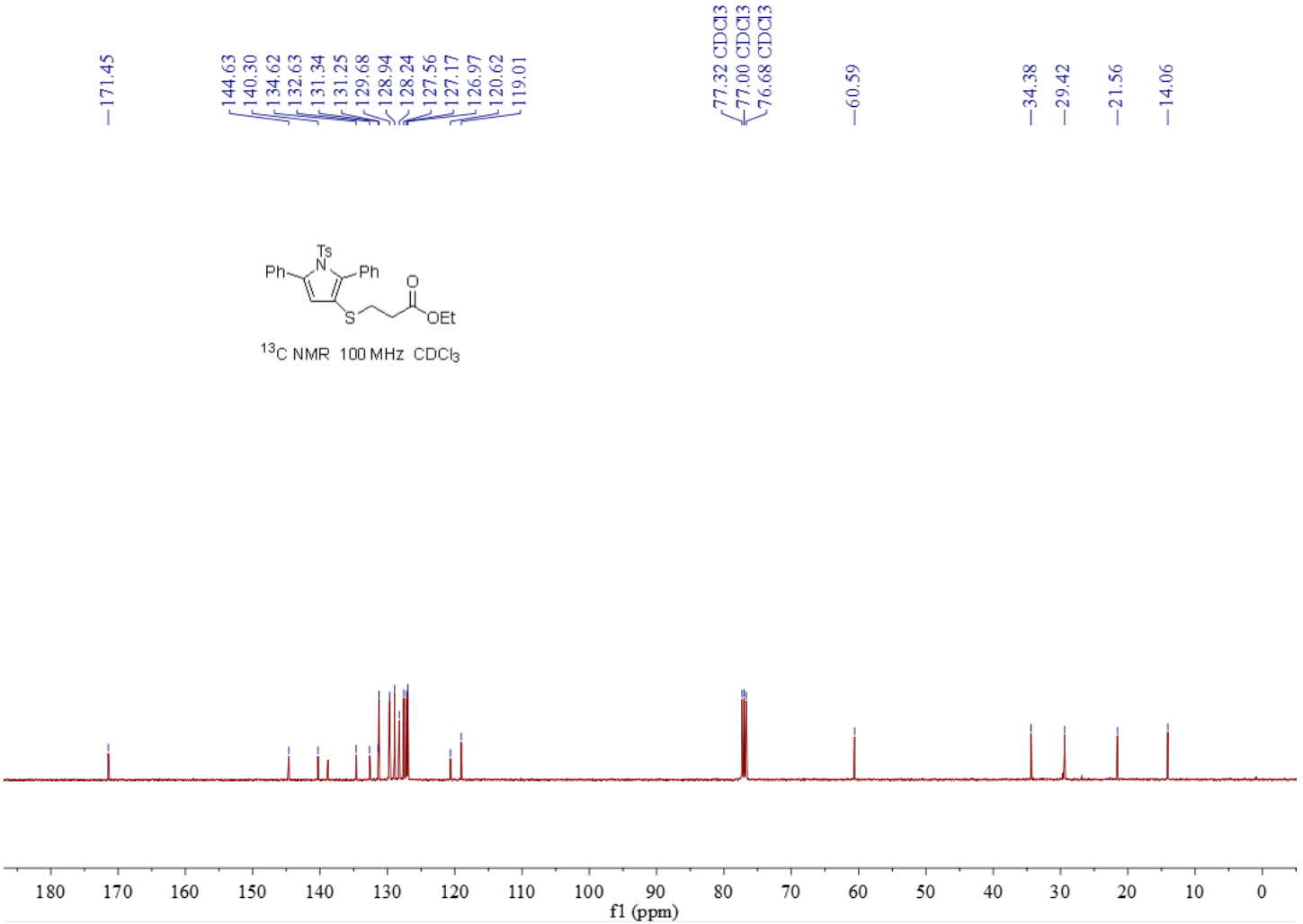
3.07
f1 (ppm)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126.97
120.62
119.01
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
60.59
34.38
29.42
21.56
14.06
Ts
N
Ph
Ph
O
S
OEt
13C NMR 100 MHz CDCl3
180
170
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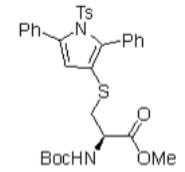
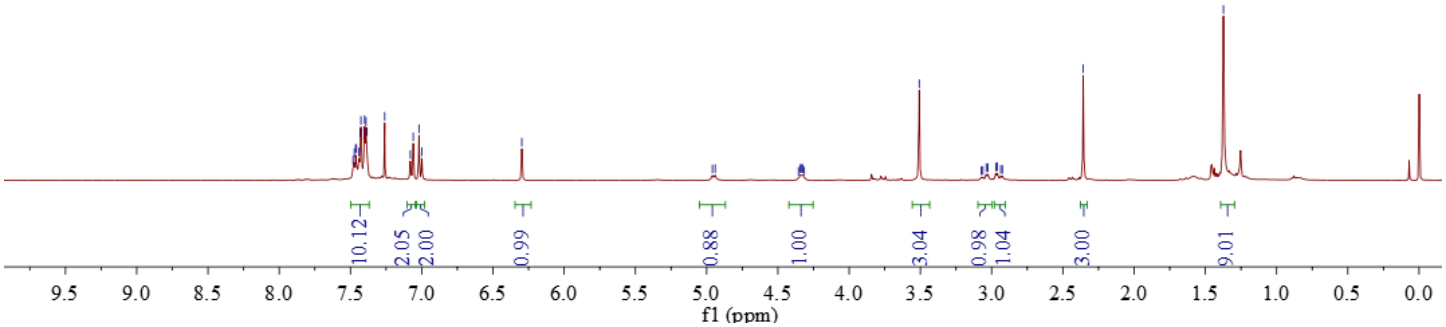
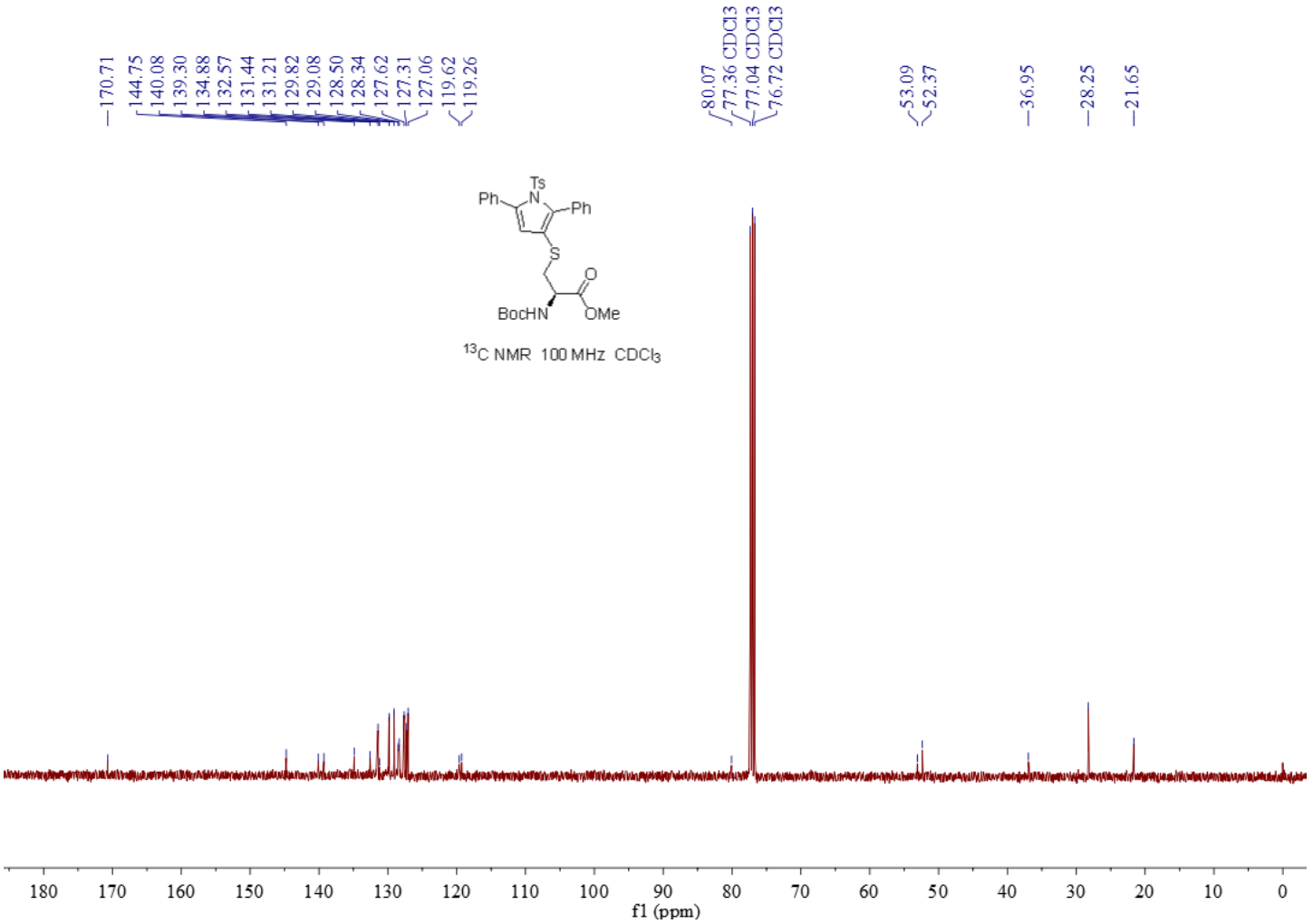
f1 (ppm)

3k



^{1}H NMR 400 MHz $CDCl_3$

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144.75
140.08
139.30
134.88
132.57
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131.21
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129.08
128.50
128.34
127.62
127.31
127.06
119.62
119.26
80.07
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
53.09
52.37
36.95
28.25
21.65
Ts
N
Ph
Ph
S
O
BocHN
OMe
13C NMR 100 MHz CDCl3
180
170
160
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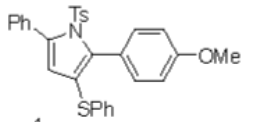
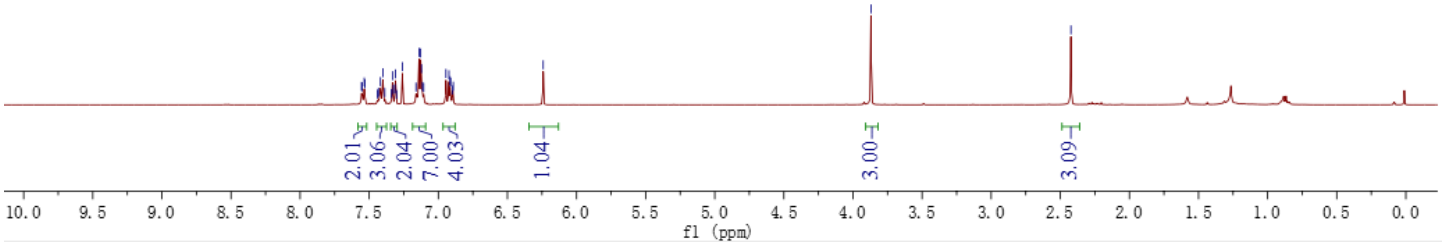
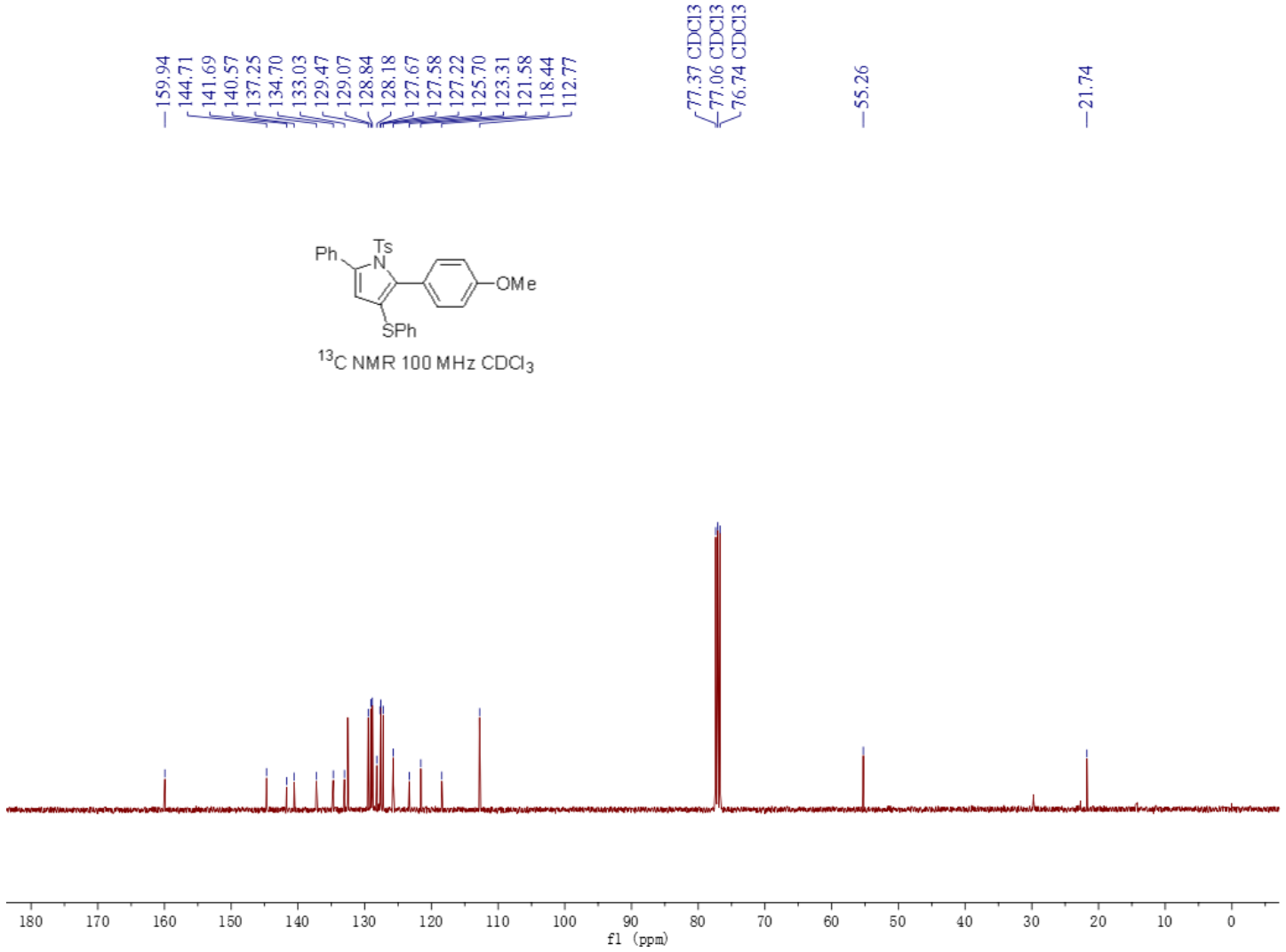
f1 (ppm)

3l



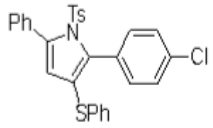
^{1}H NMR 400 MHz $CDCl_3$



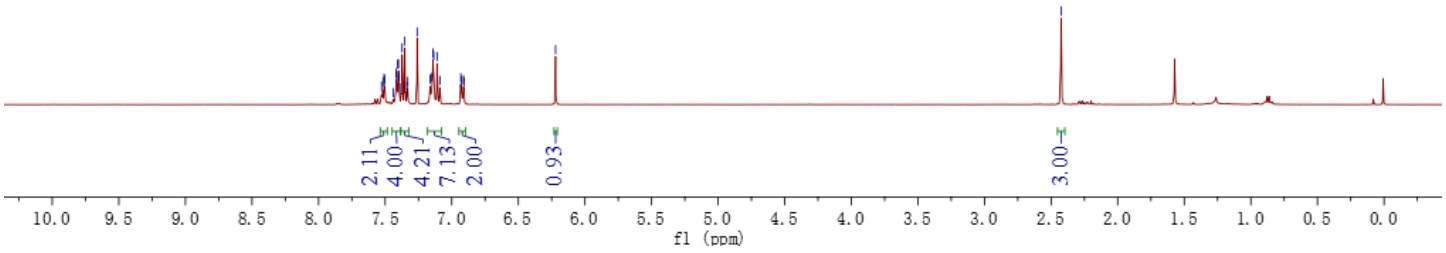


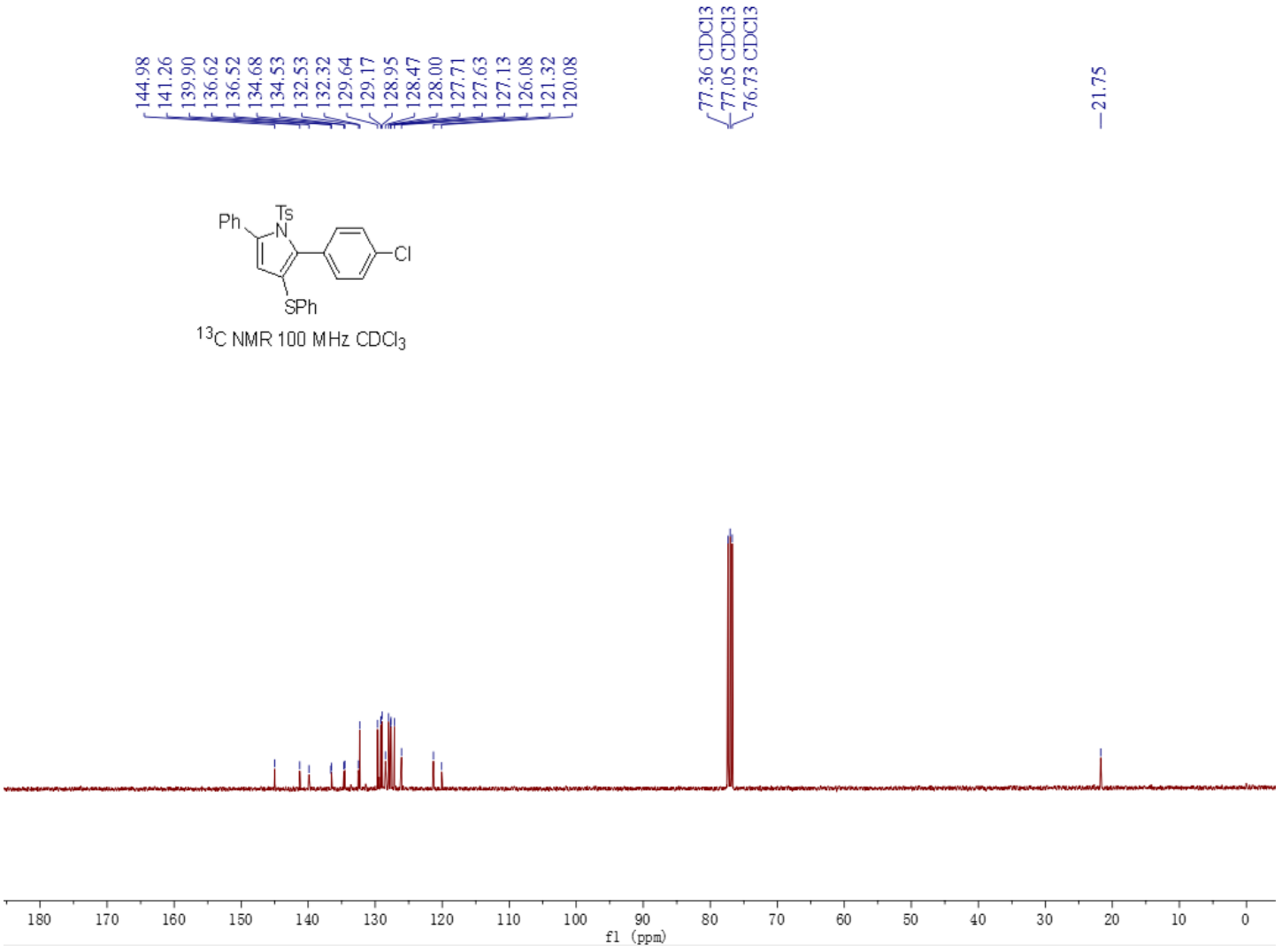
^{13}C NMR 100 MHz $CDCl_3$

3m



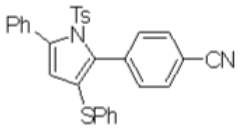
^{1}H NMR 400 MHz $CDCl_3$



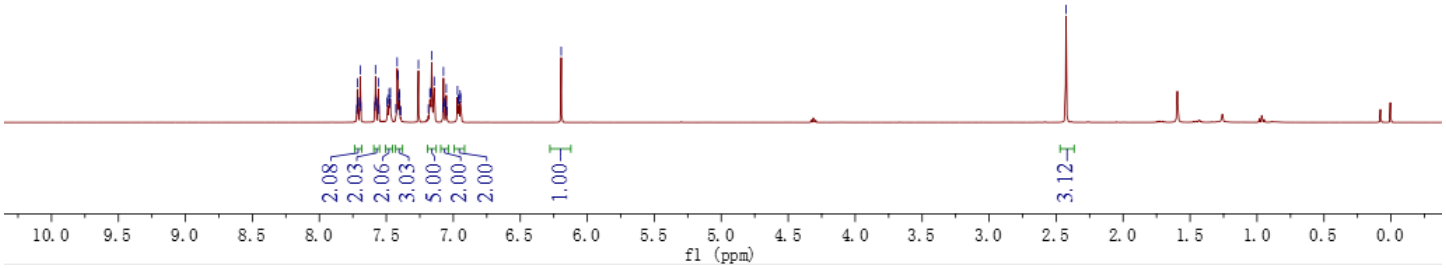


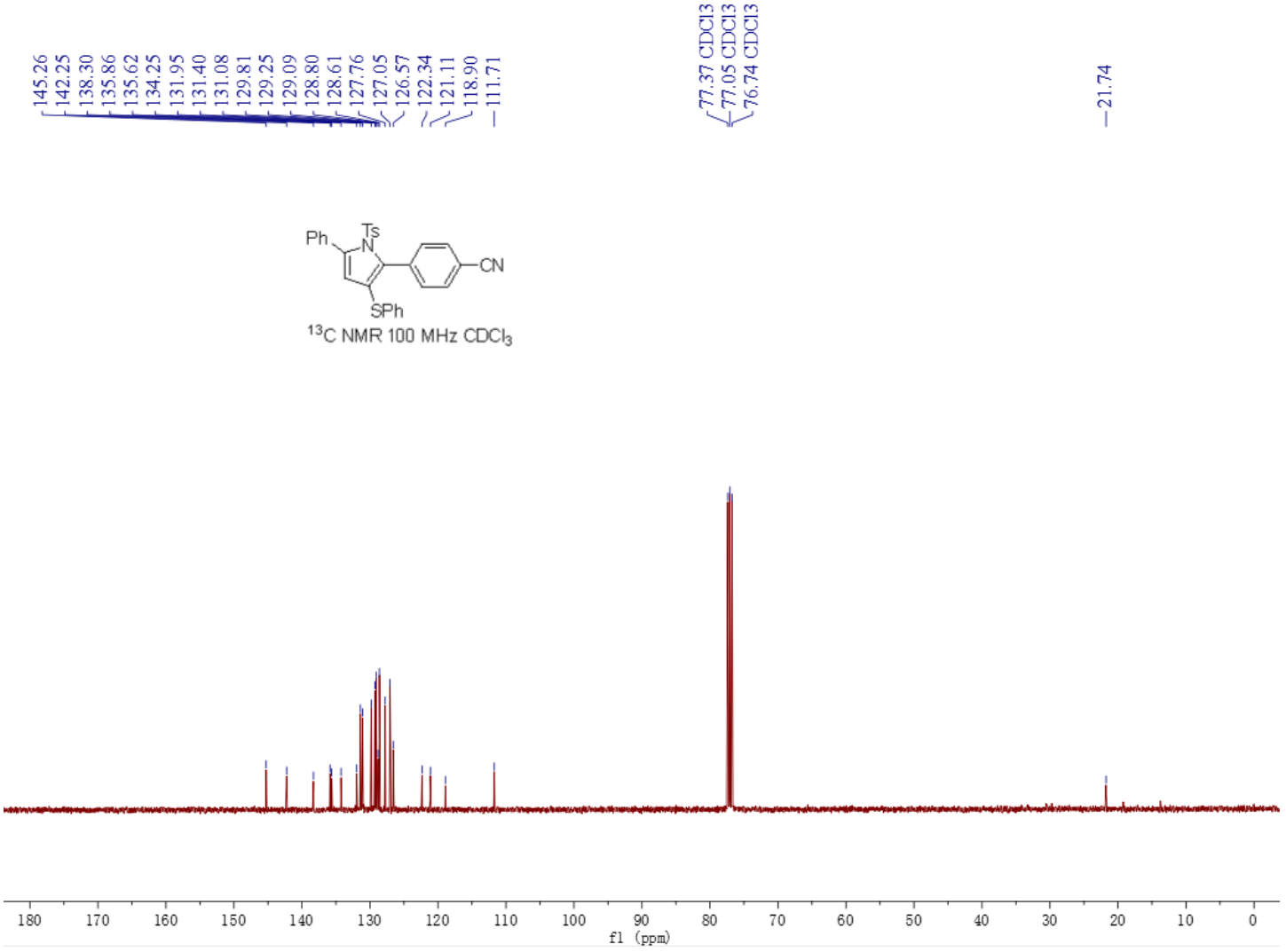
^{13}C NMR 100 MHz $CDCl_3$

3n



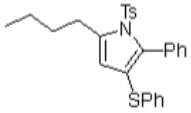
^{1}H NMR 400 MHz $CDCl_3$



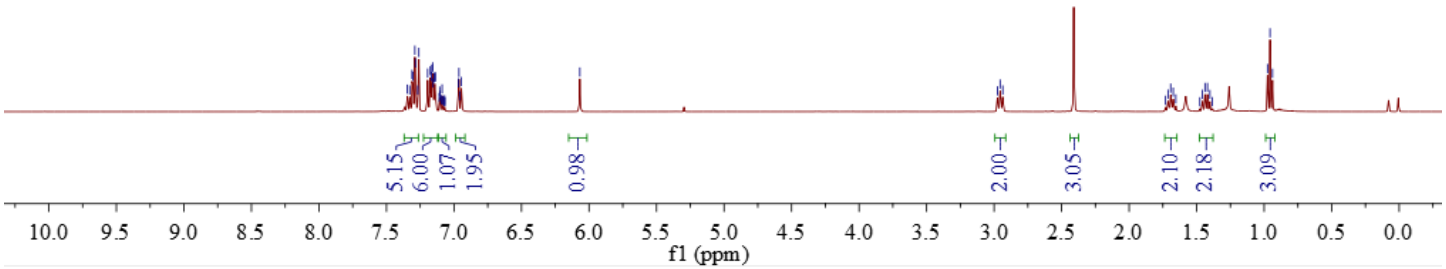


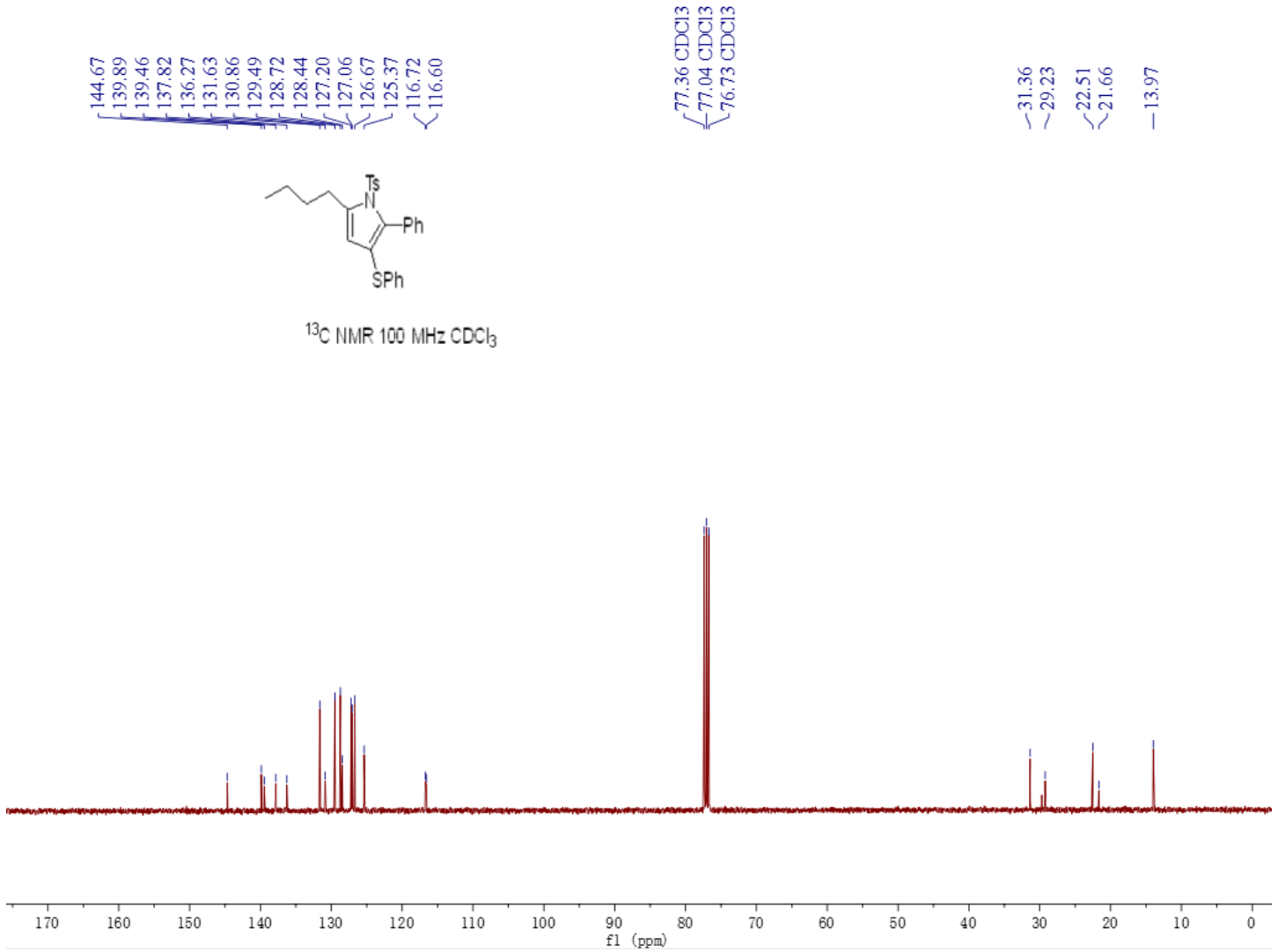
^{13}C NMR 100 MHz $CDCl_3$

3o



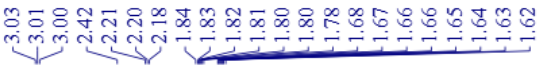
^{1}H NMR 400 MHz $CDCl_3$

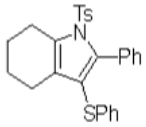




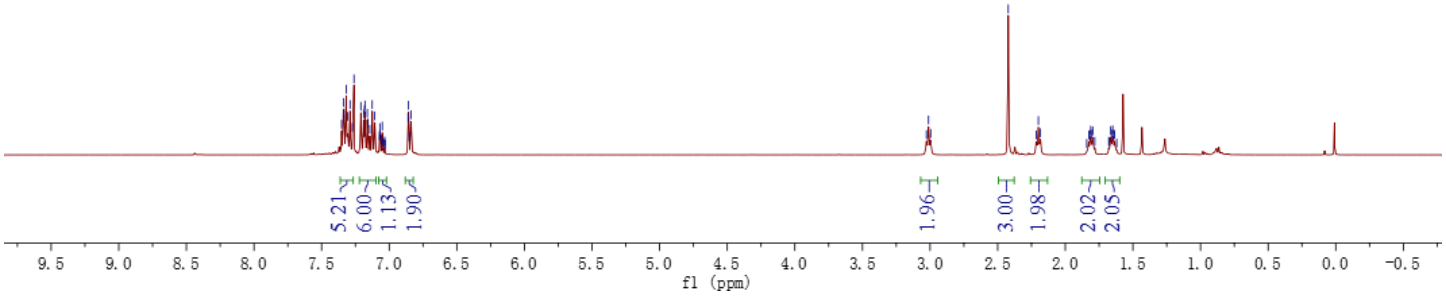
^{13}C NMR 100 MHz $CDCl_3$

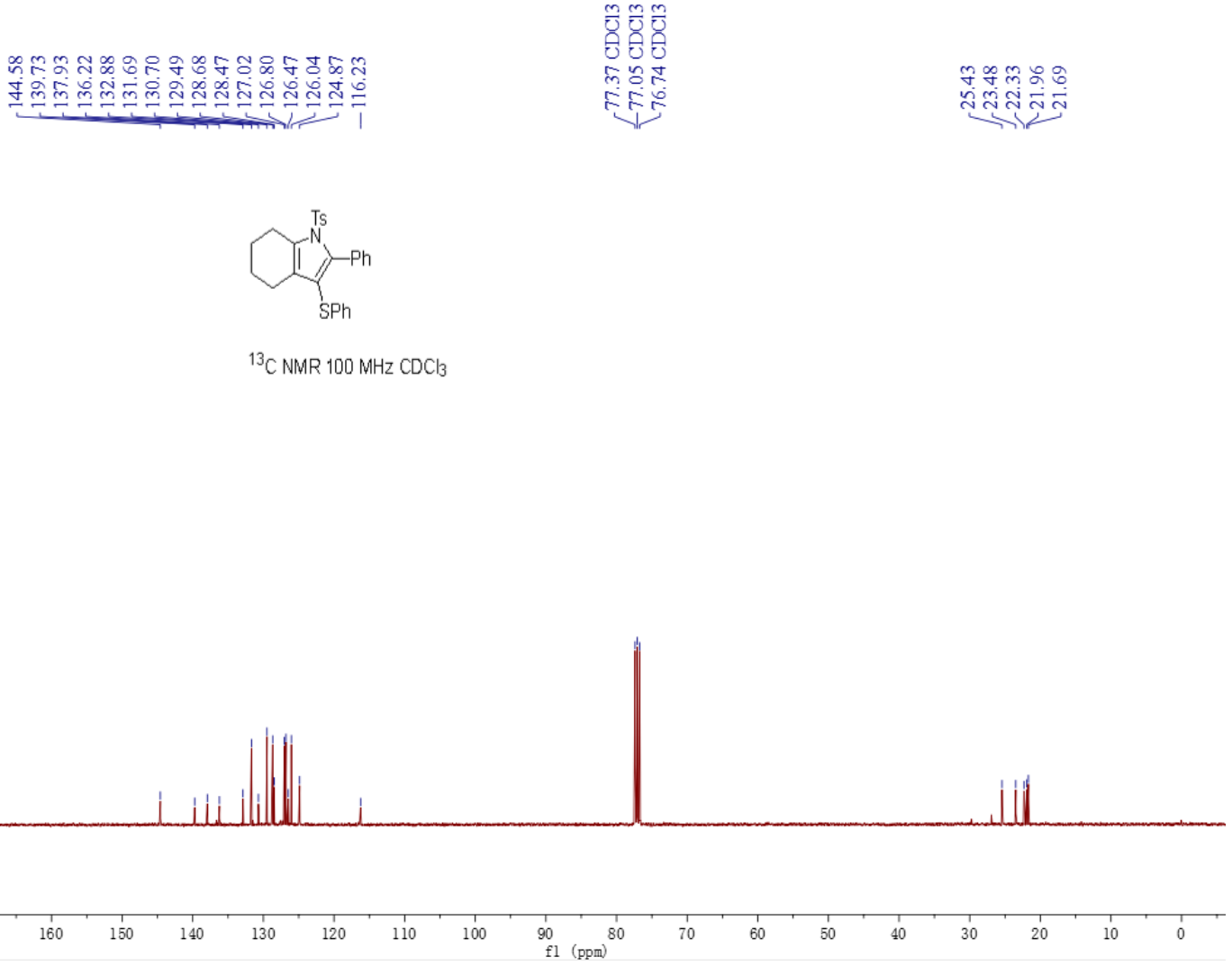
3p





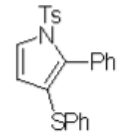
^{1}H NMR 400 MHz $CDCl_3$



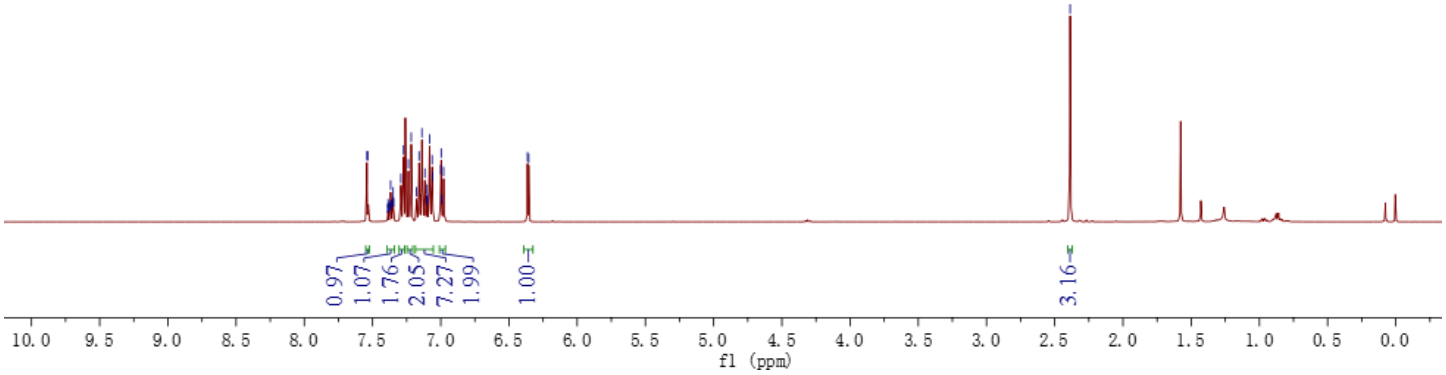


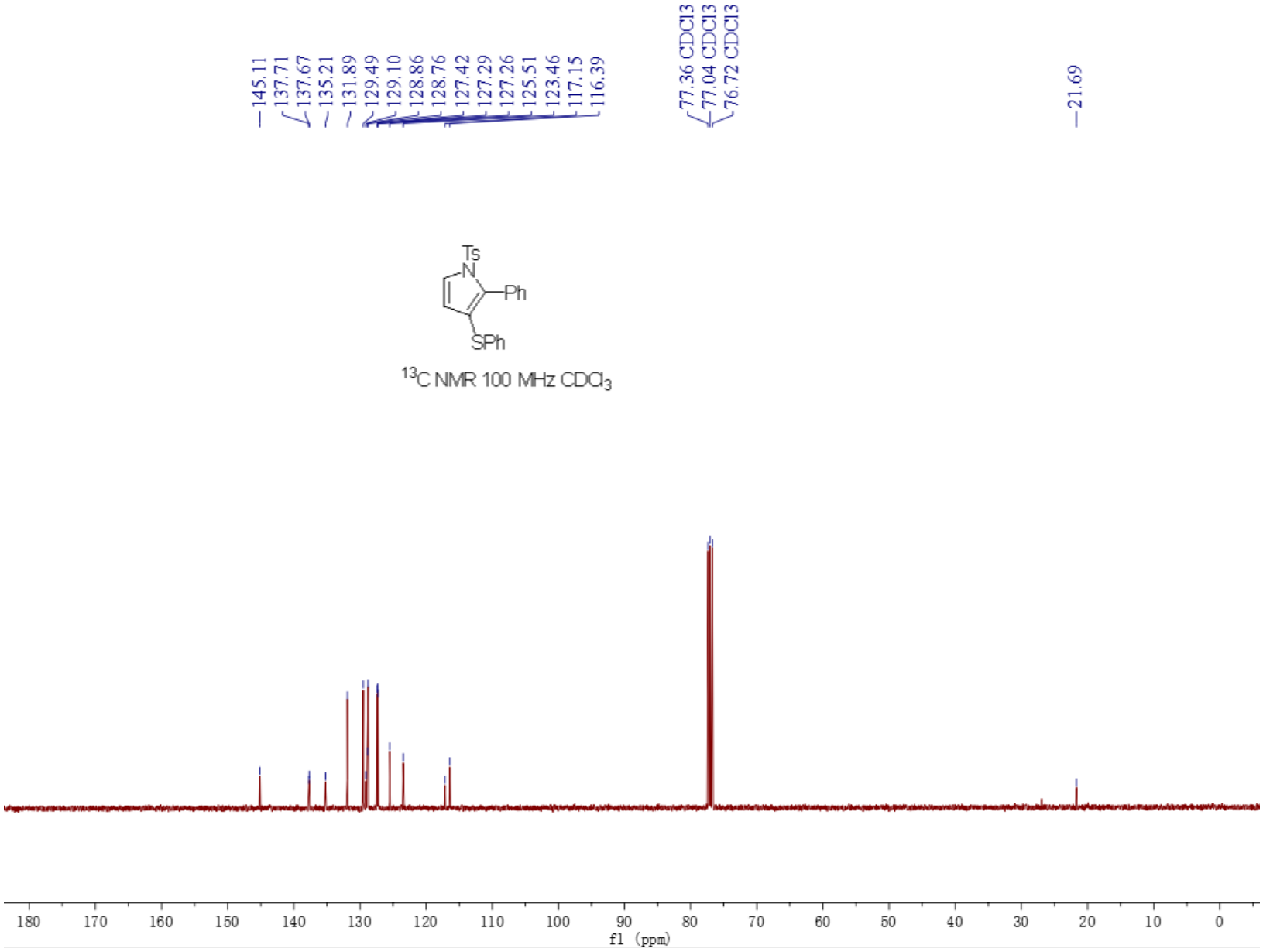
^{13}C NMR 100 MHz $CDCl_3$

3q

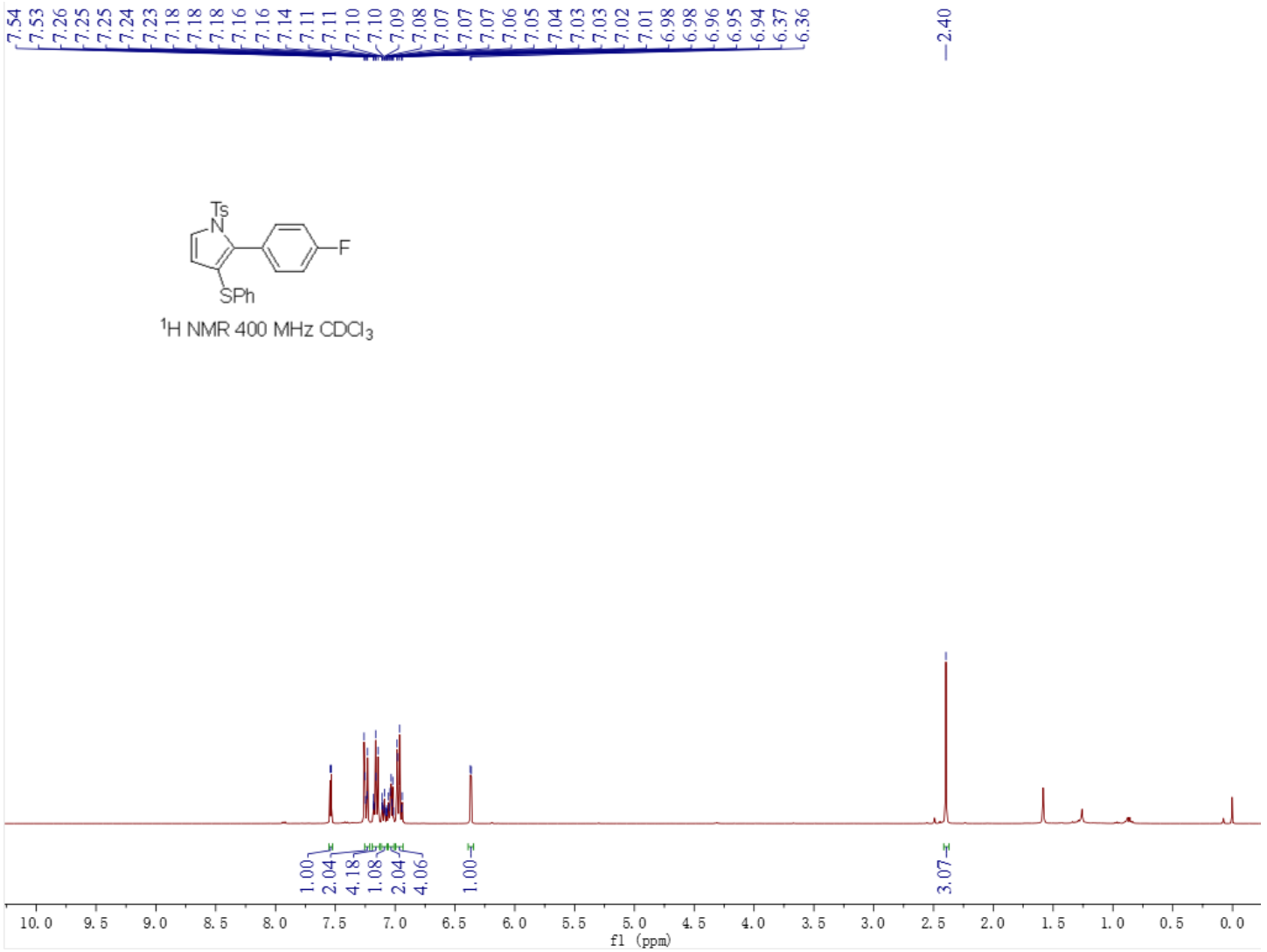


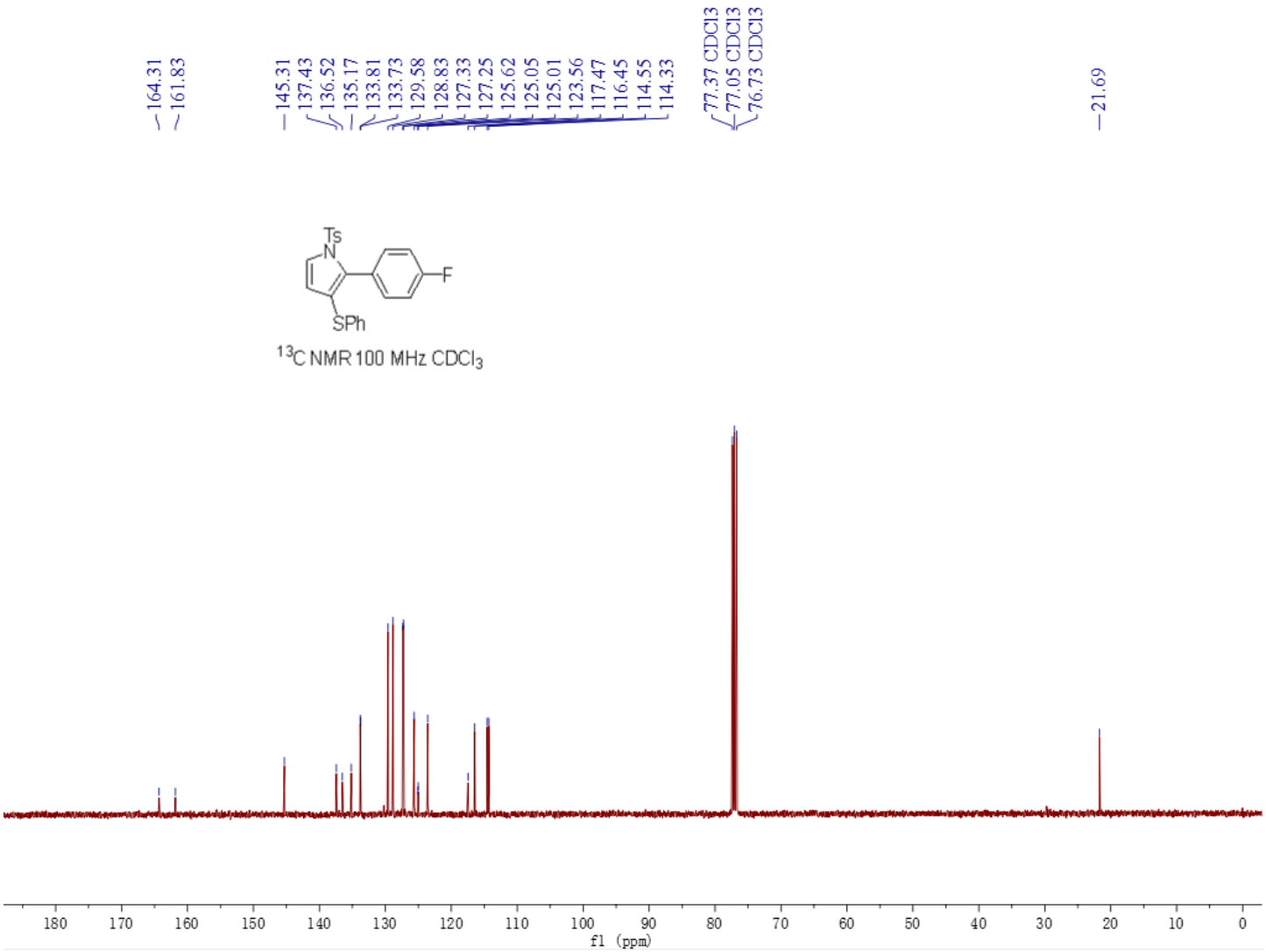
^{1}H NMR 400 MHz $CDCl_3$

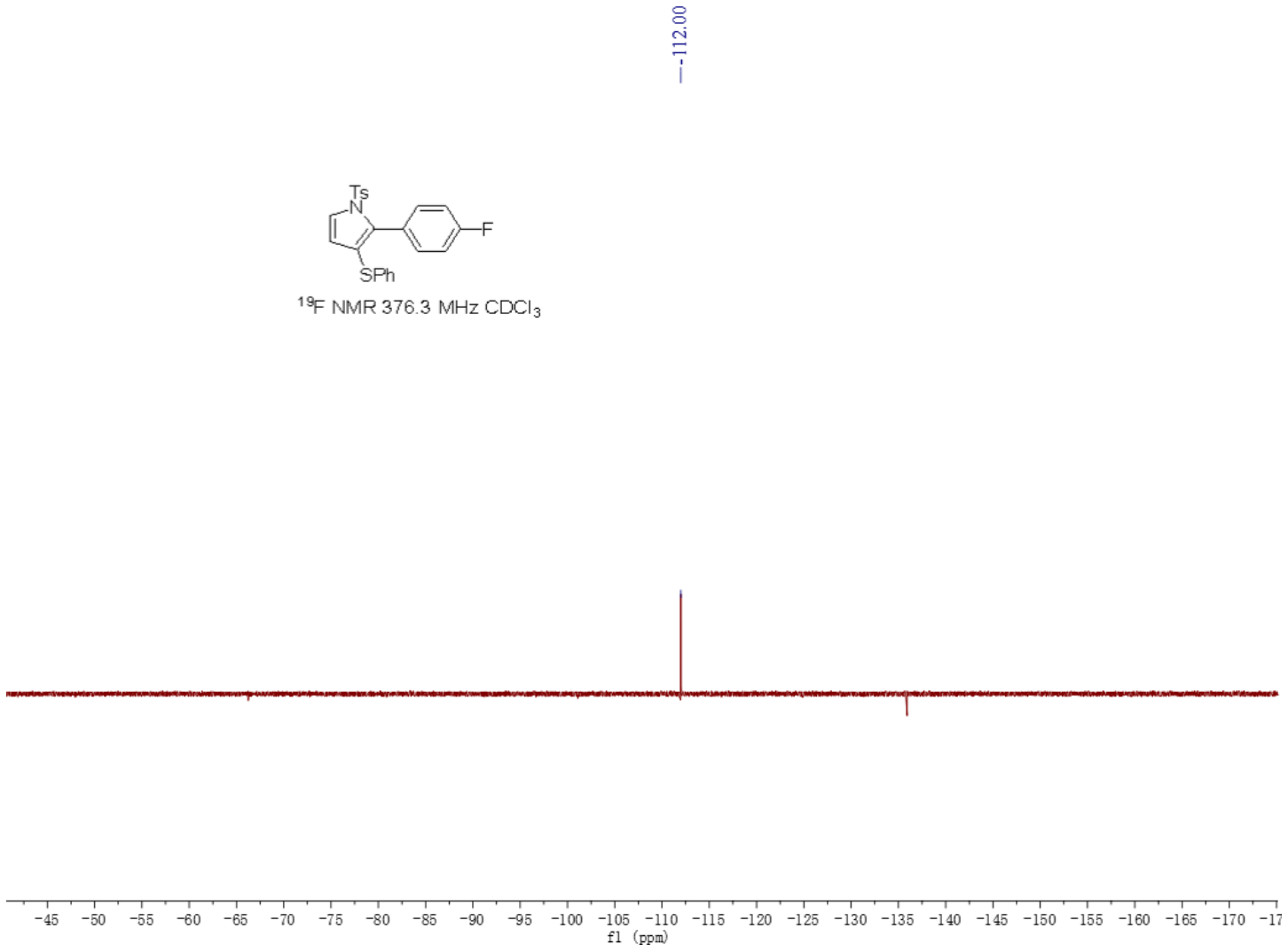



145.11
137.71
137.67
135.21
131.89
129.49
129.10
128.86
128.76
127.42
127.29
127.26
125.51
123.46
117.15
116.39
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
21.69
Ts
N
Ph
SPh
13C NMR 100 MHz CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3r

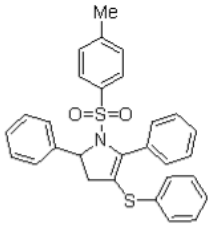

7.54
7.53
7.26
7.25
7.25
7.24
7.23
7.18
7.18
7.18
7.16
7.16
7.14
7.11
7.11
7.10
7.10
7.09
7.08
7.07
7.07
7.07
7.06
7.05
7.04
7.03
7.03
7.02
7.01
6.98
6.98
6.96
6.95
6.94
6.37
6.36
2.40
Ts
N
F
SPh
1H NMR 400 MHz CDCl3
1.00
2.04
4.18
1.08
2.04
4.06
1.00
3.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


164.31
161.83
145.31
137.43
136.52
135.17
133.81
133.73
129.58
128.83
127.33
127.25
125.62
125.05
125.01
123.56
117.47
116.45
114.55
114.33
77.37 CDCl3
77.05 CDCl3
76.73 CDCl3
21.69
Ts
N
F
SPh
13C NMR 100 MHz CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

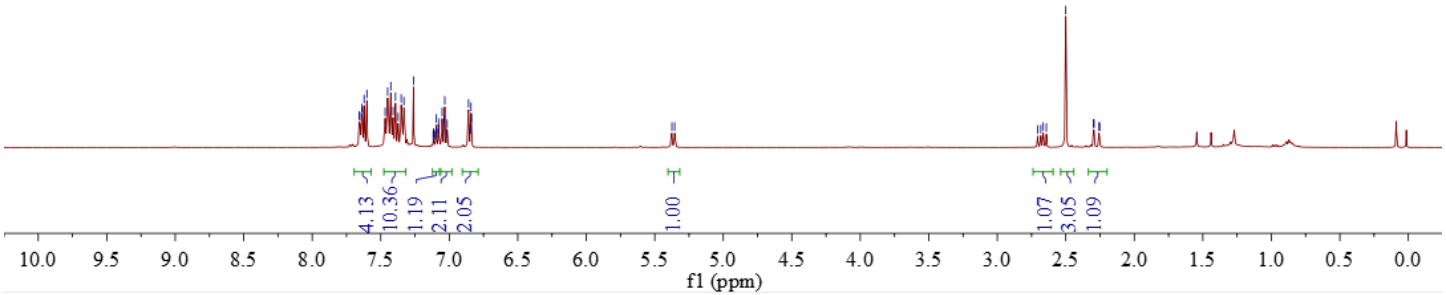


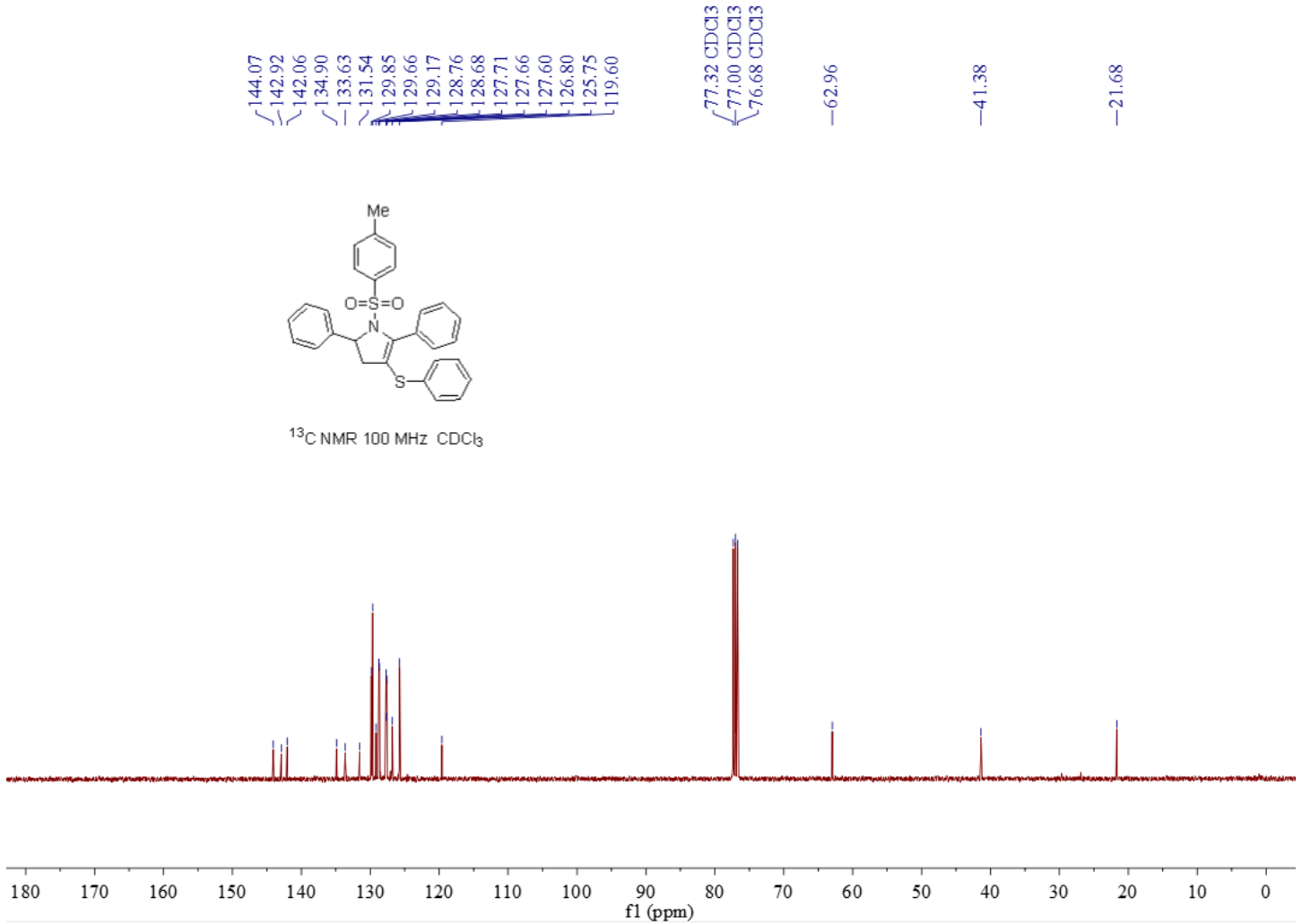
^{19}F NMR 376.3 MHz $CDCl_3$

4a



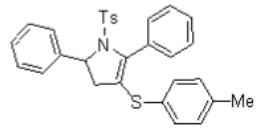
^{1}H NMR 400 MHz $CDCl_3$



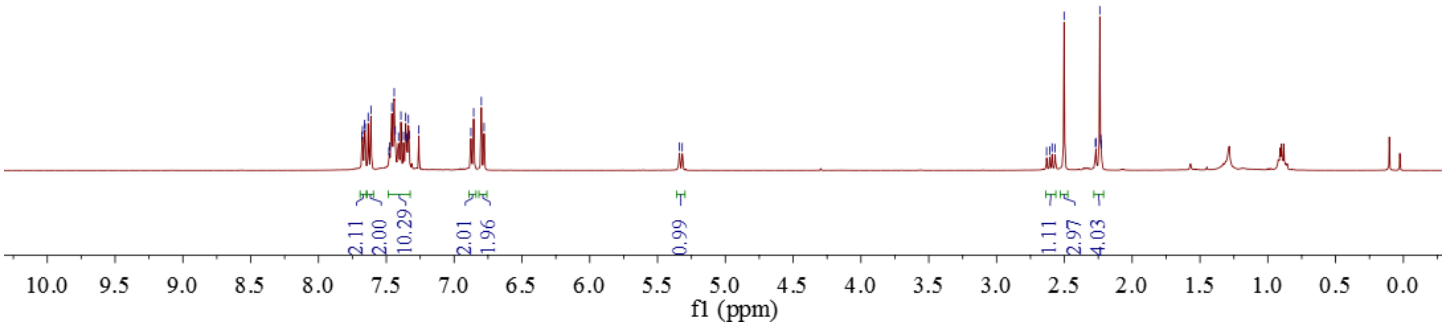


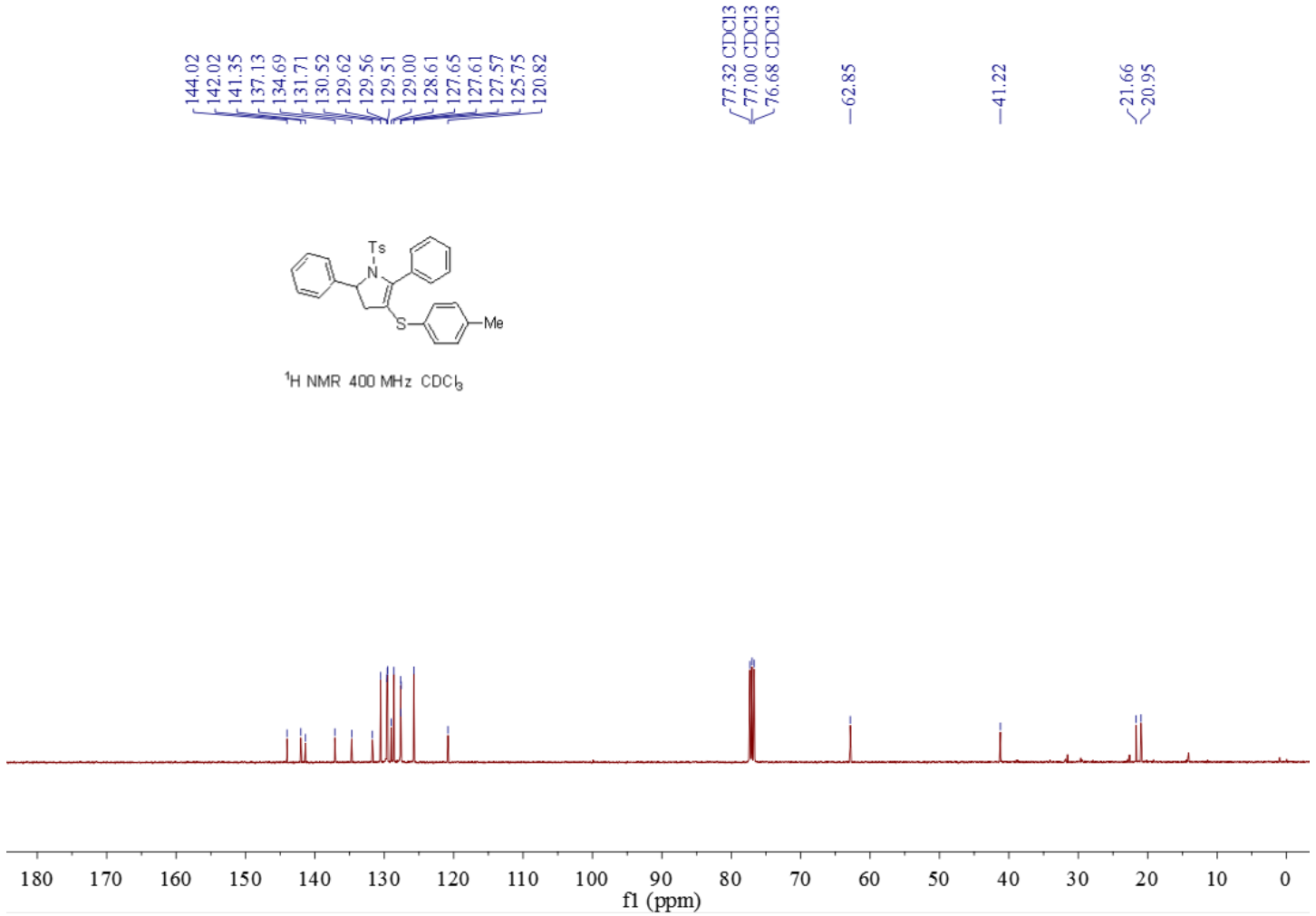
^{13}C NMR 100 MHz $CDCl_3$

4b

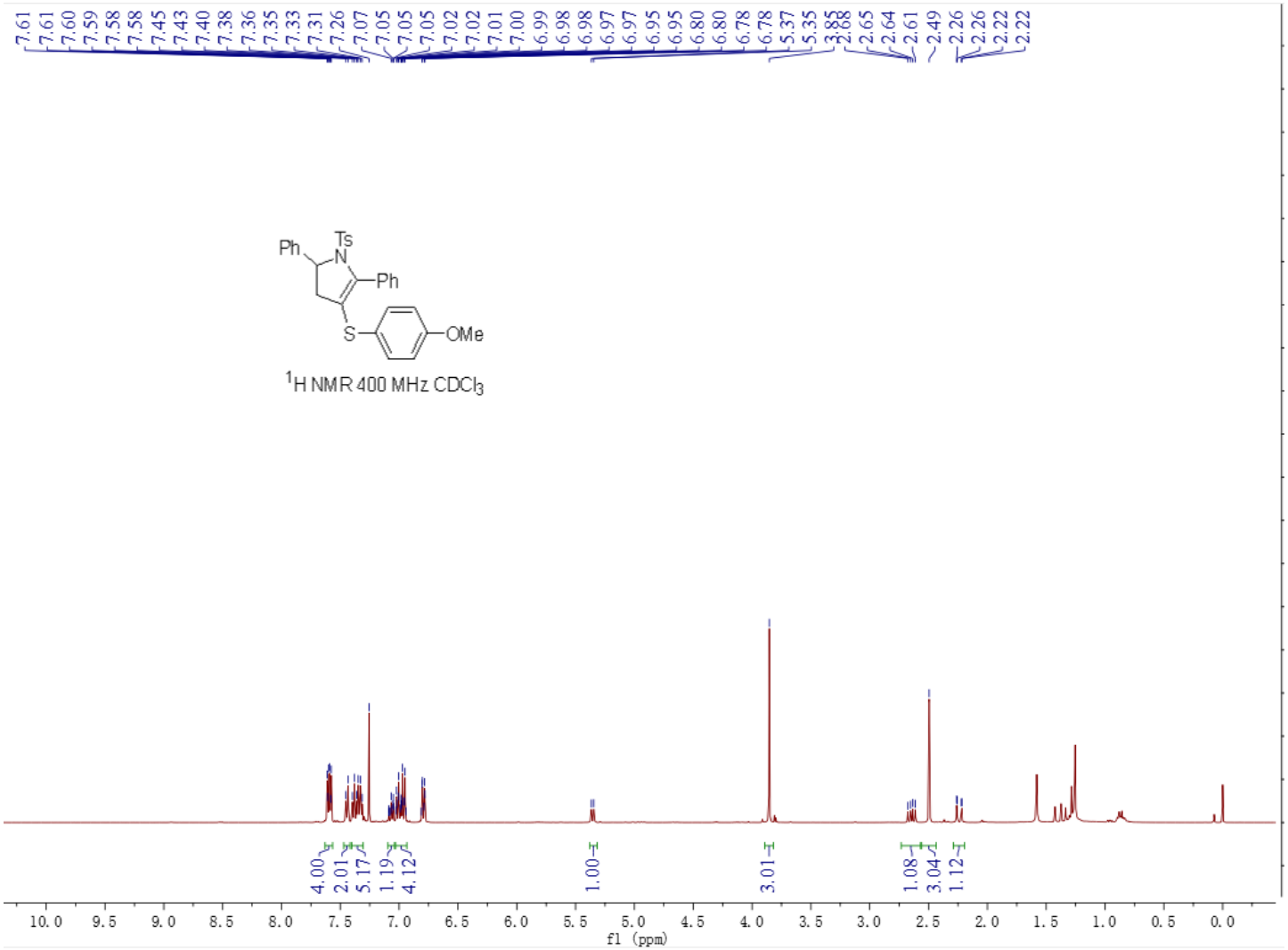


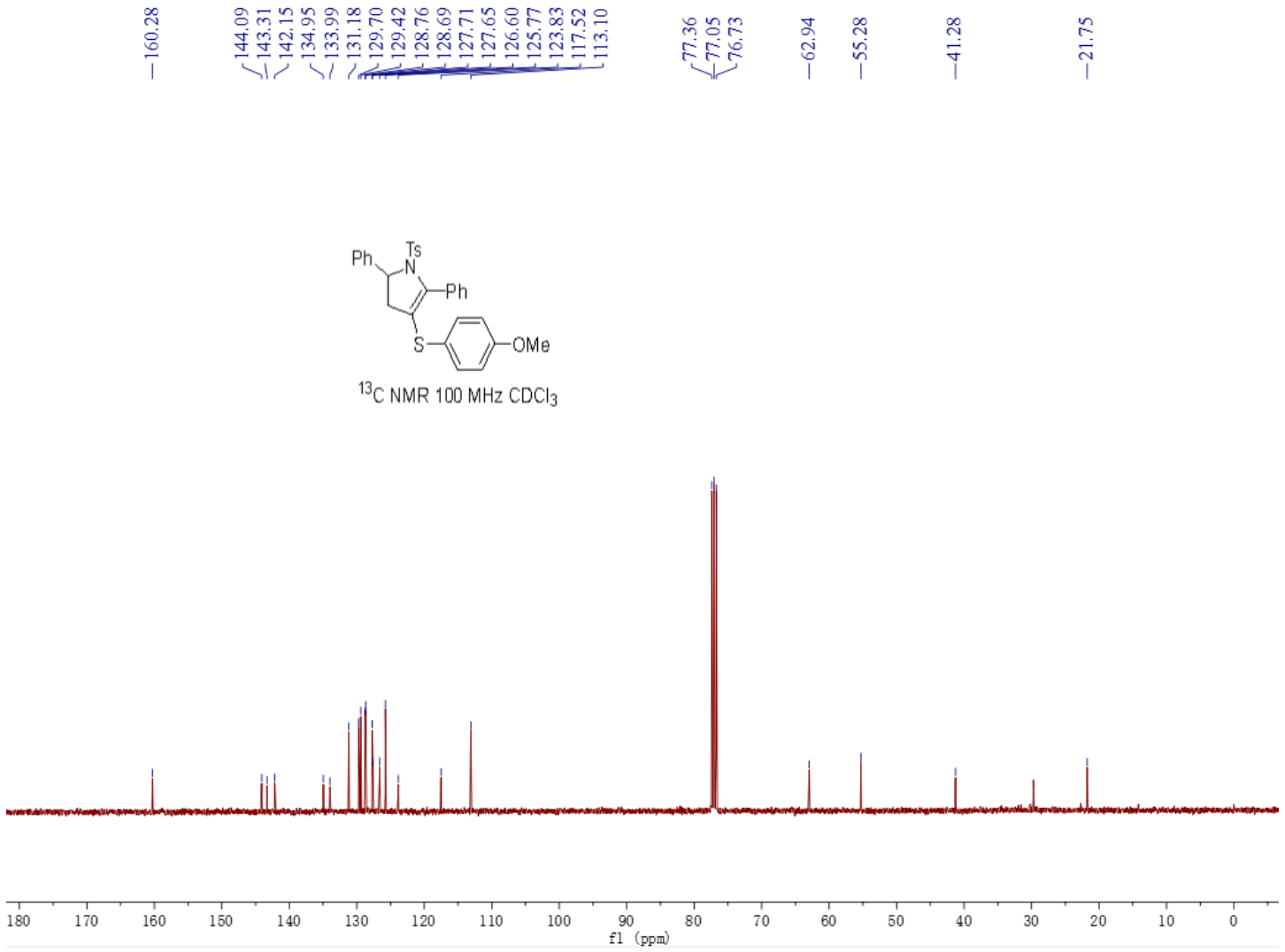
^{1}H NMR 400 MHz $CDCl_3$



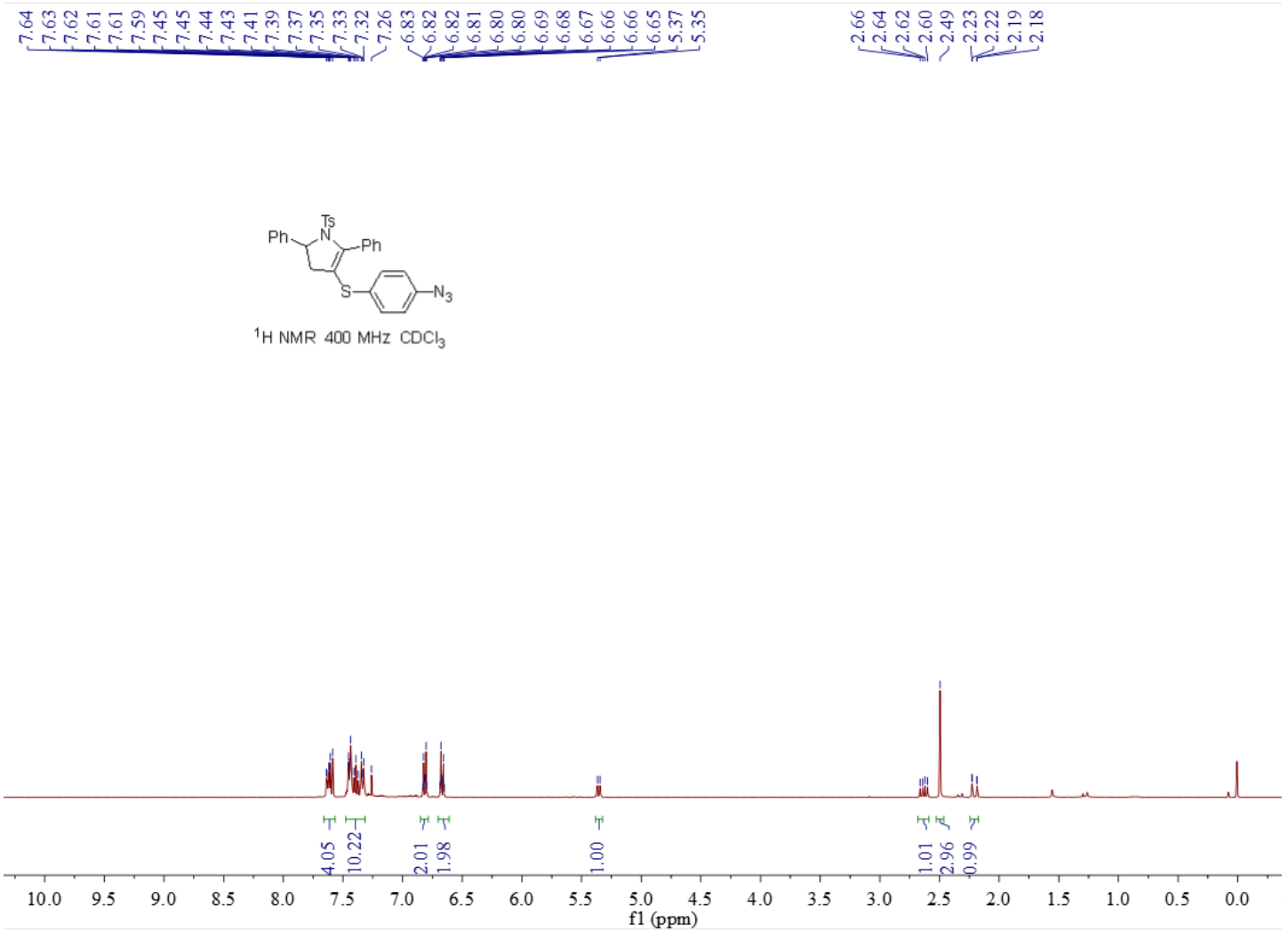

144.02
142.02
141.35
137.13
134.69
131.71
130.52
129.62
129.56
129.51
129.00
128.61
127.65
127.61
127.57
125.75
120.82
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
62.85
41.22
21.66
20.95
Ts
N
S
Me
1H NMR 400 MHz CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

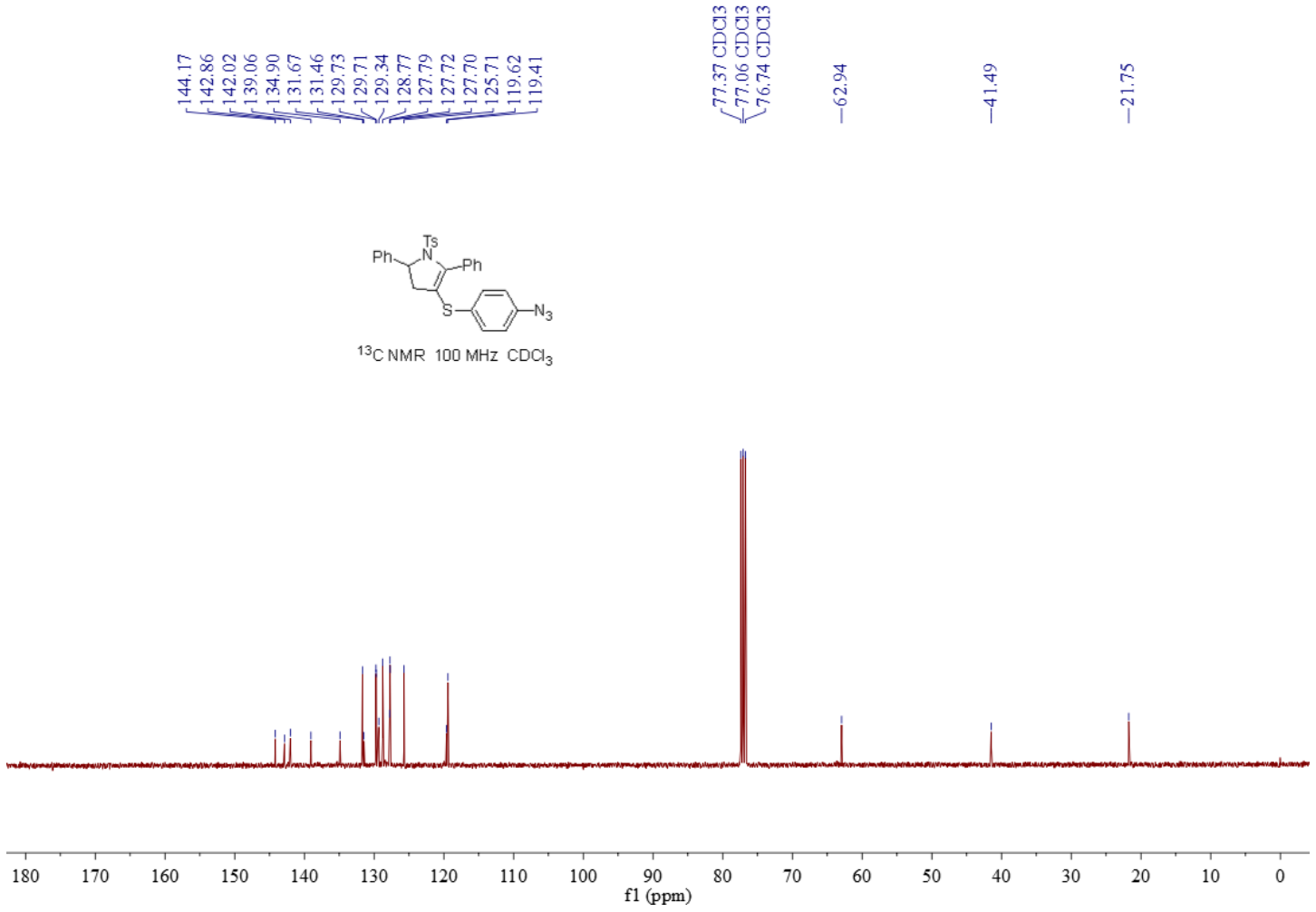
4c


7.61 7.61 7.60 7.59 7.58 7.58 7.45 7.43 7.40 7.38 7.36 7.35 7.33 7.31 7.26 7.07 7.05 7.05 7.05 7.02 7.02 7.01 7.00 6.99 6.98 6.98 6.97 6.97 6.95 6.95 6.80 6.80 6.78 6.78 5.37 5.35 3.85 3.84 2.65 2.64 2.61 2.49 2.26 2.26 2.22 2.22
Ph
Ts
N
Ph
S
OMe
1H NMR 400 MHz CDCl3
4.00 2.01 5.17 1.19 4.12 1.00 3.01 1.08 3.04 1.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

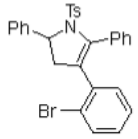

160.28
144.09
143.31
142.15
134.95
133.99
131.18
129.70
129.42
128.76
128.69
127.71
127.65
126.60
125.77
123.83
117.52
113.10
77.36
77.05
76.73
62.94
55.28
41.28
21.75
Ph
Ts
N
Ph
S
OMe
13C NMR 100 MHz CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4d

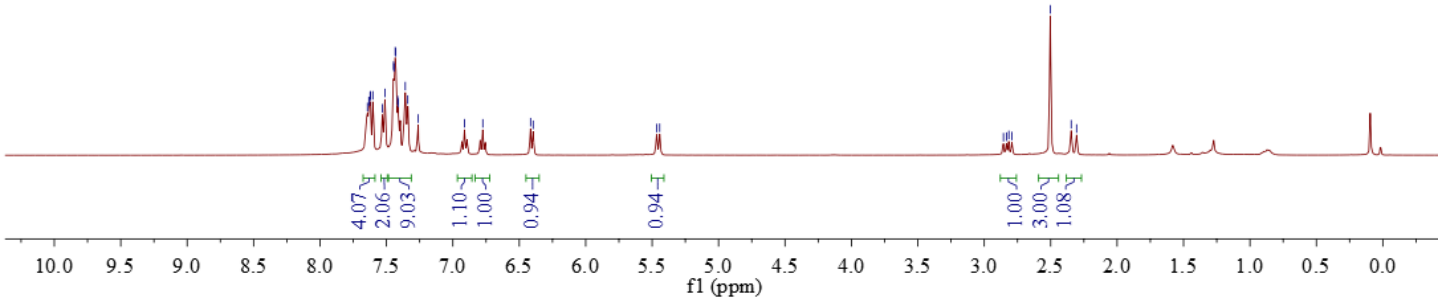

7.64
7.63
7.62
7.61
7.61
7.59
7.45
7.45
7.44
7.43
7.41
7.39
7.37
7.35
7.33
7.32
7.26
6.83
6.82
6.82
6.81
6.80
6.80
6.69
6.68
6.67
6.66
6.66
6.65
5.37
5.35
2.66
2.64
2.62
2.60
2.49
2.23
2.22
2.19
2.18
Ts
N
Ph
Ph
S
N3
1H NMR 400 MHz CDCl3
4.05
10.22
2.01
1.98
1.00
1.01
2.96
0.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

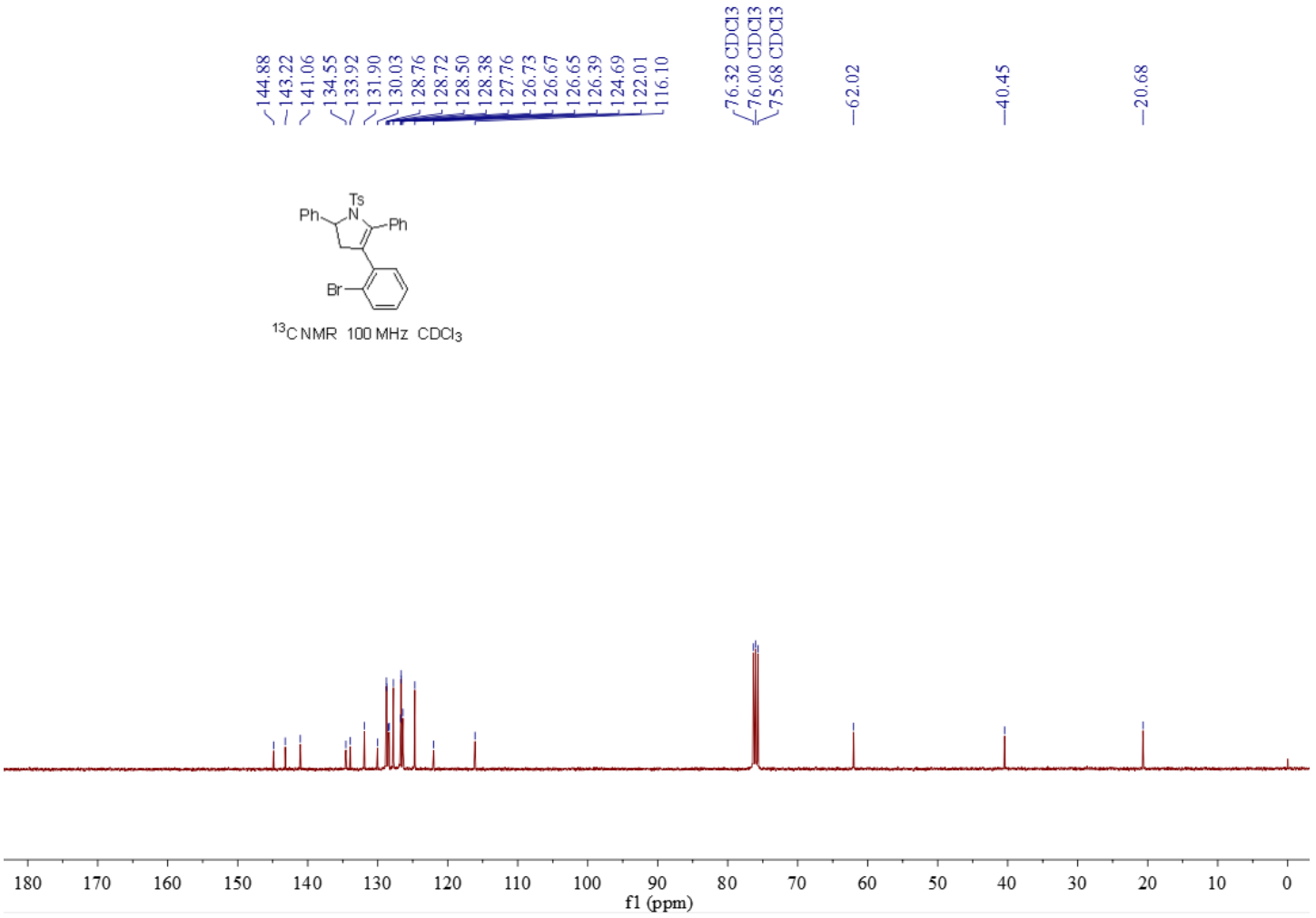

144.17
142.86
142.02
139.06
134.90
131.67
131.46
129.73
129.71
129.34
128.77
127.79
127.72
127.70
125.71
119.62
119.41
77.37 CDCl3
77.06 CDCl3
76.74 CDCl3
62.94
41.49
21.75
Ts
N
Ph
Ph
S
N3
13C NMR 100 MHz CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4e

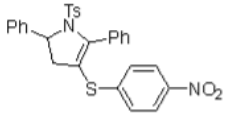


^{1}H NMR 400 MHz $CDCl_3$

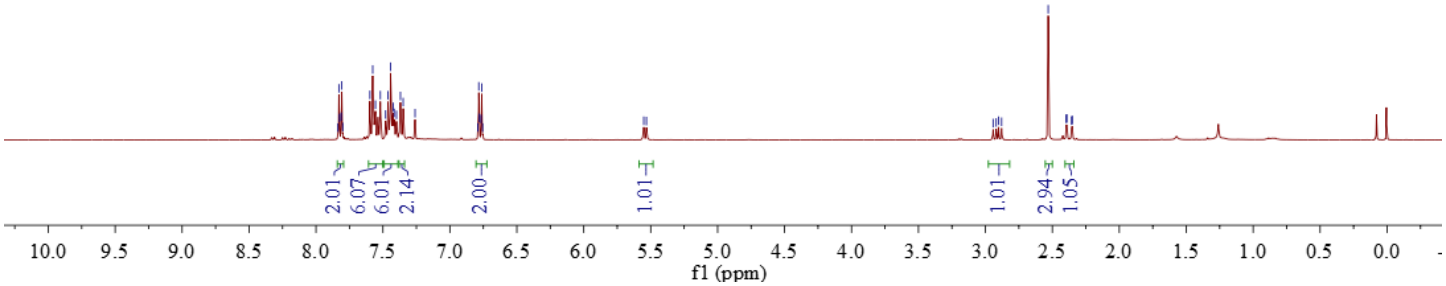


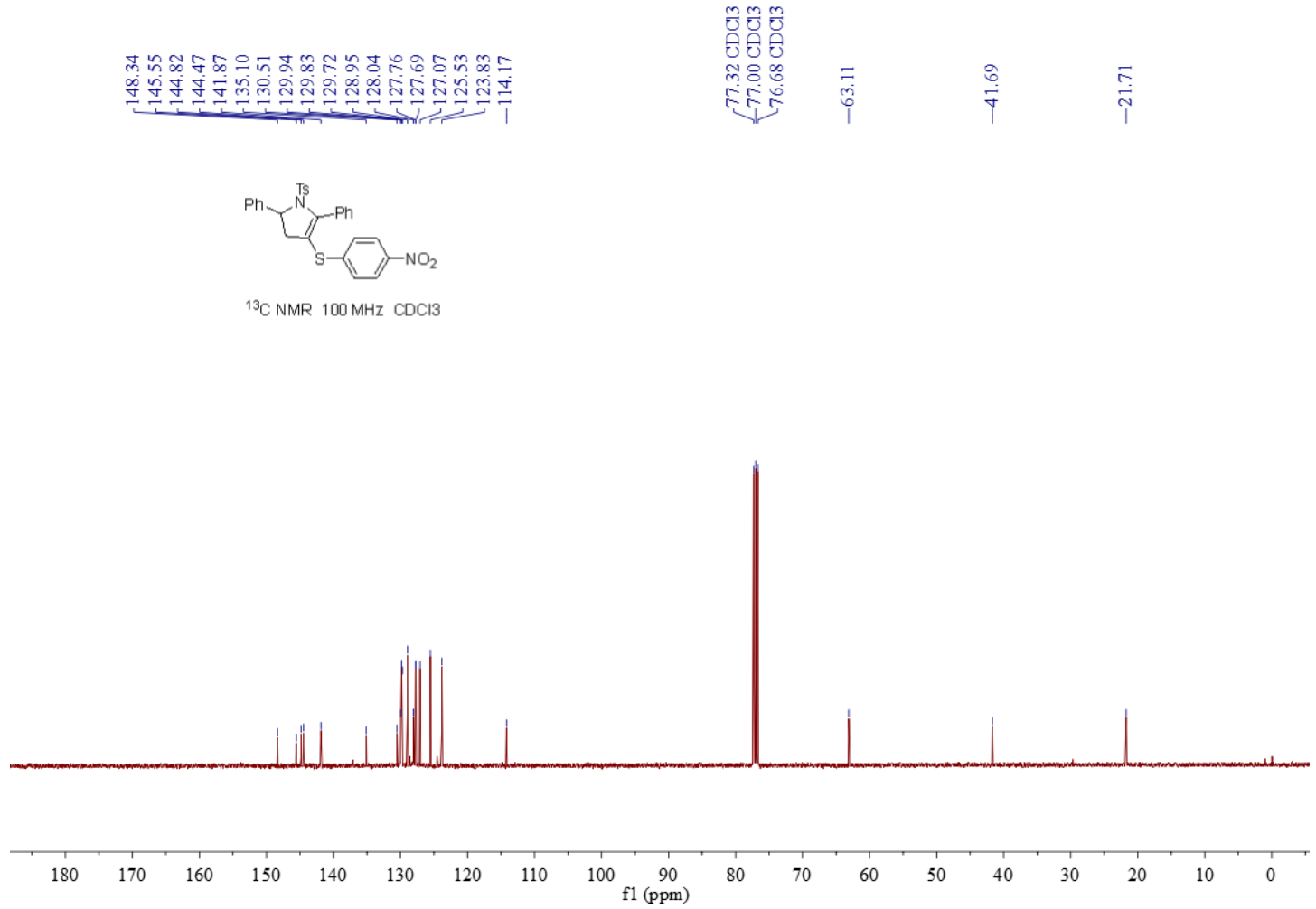

144.88
143.22
141.06
134.55
133.92
131.90
130.03
128.76
128.72
128.50
128.38
127.76
126.73
126.67
126.65
126.39
124.69
122.01
116.10
76.32 CDCl3
76.00 CDCl3
75.68 CDCl3
62.02
40.45
20.68
Ts
N
Ph
Ph
Br
13C NMR 100 MHz CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4f



^{1}H NMR 400 MHz CDCl3




148.34
145.55
144.82
144.47
141.87
135.10
130.51
129.94
129.83
129.72
128.95
128.04
127.76
127.69
127.07
125.53
123.83
114.17
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
63.11
41.69
21.71
Ts
N
Ph
Ph
S
NO2
13C NMR 100 MHz CDCl3
180
170
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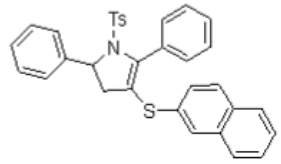
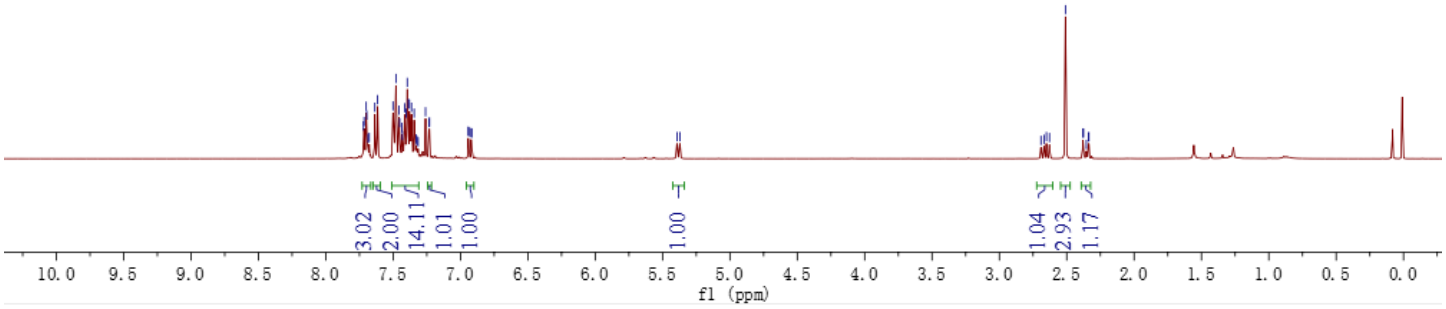
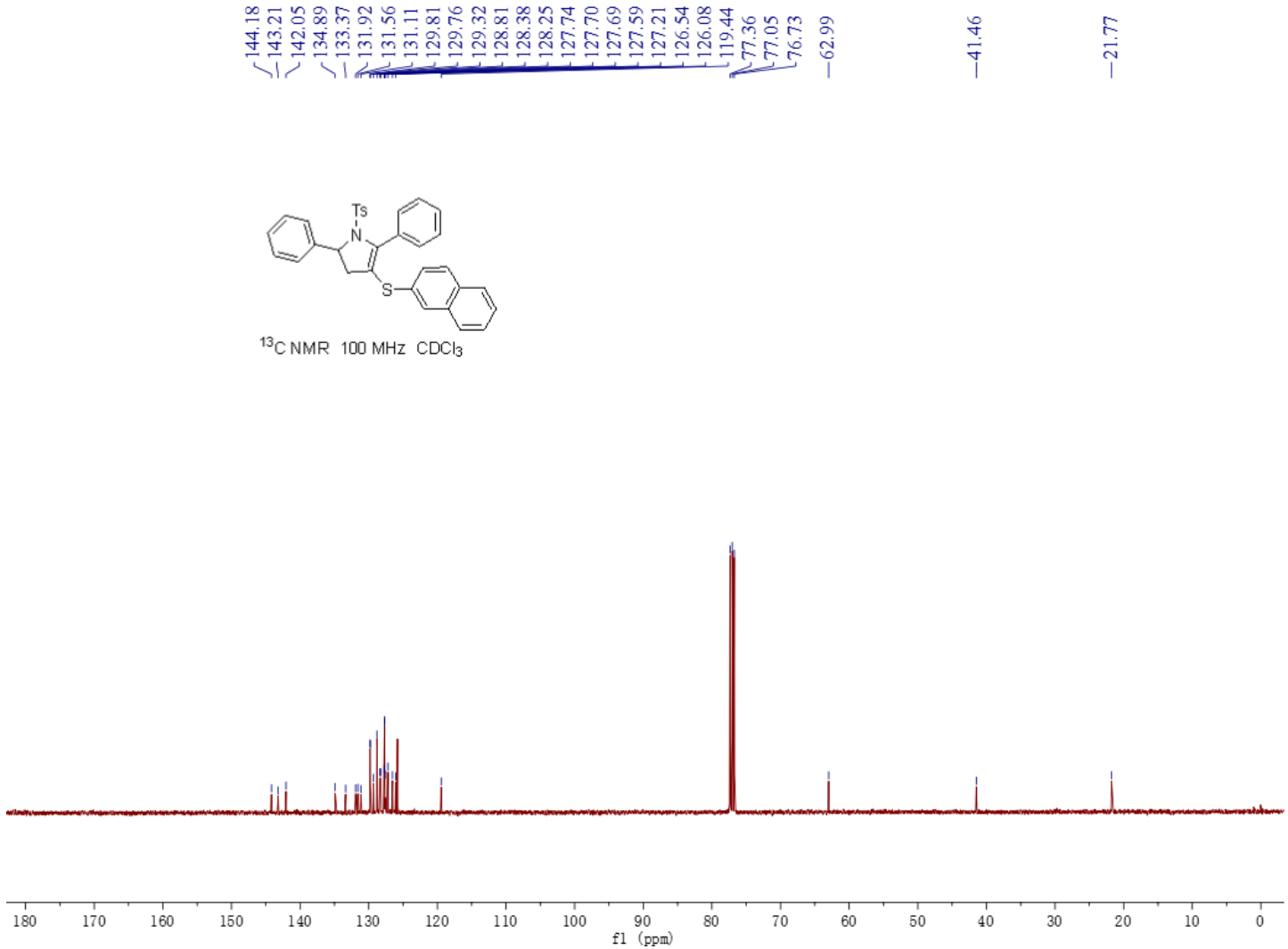
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4g

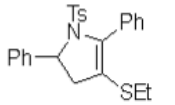


^{1}H NMR 400 MHz $CDCl_3$

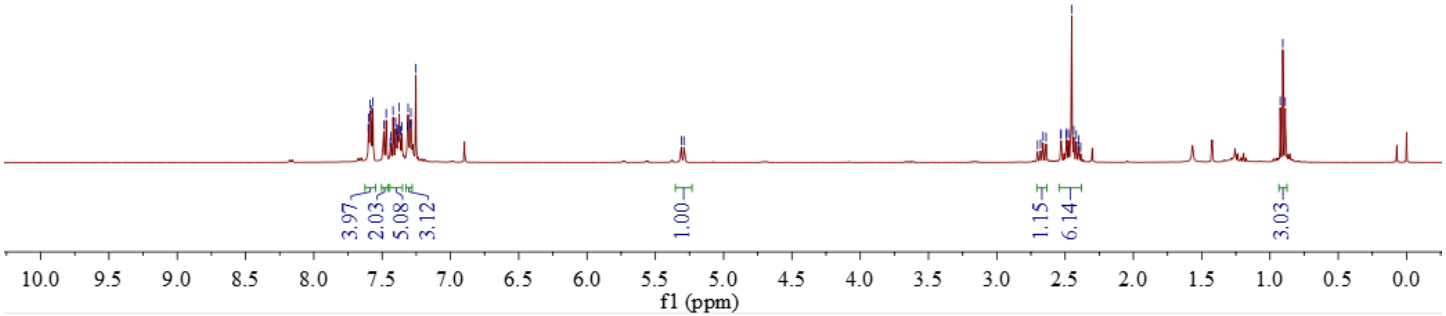


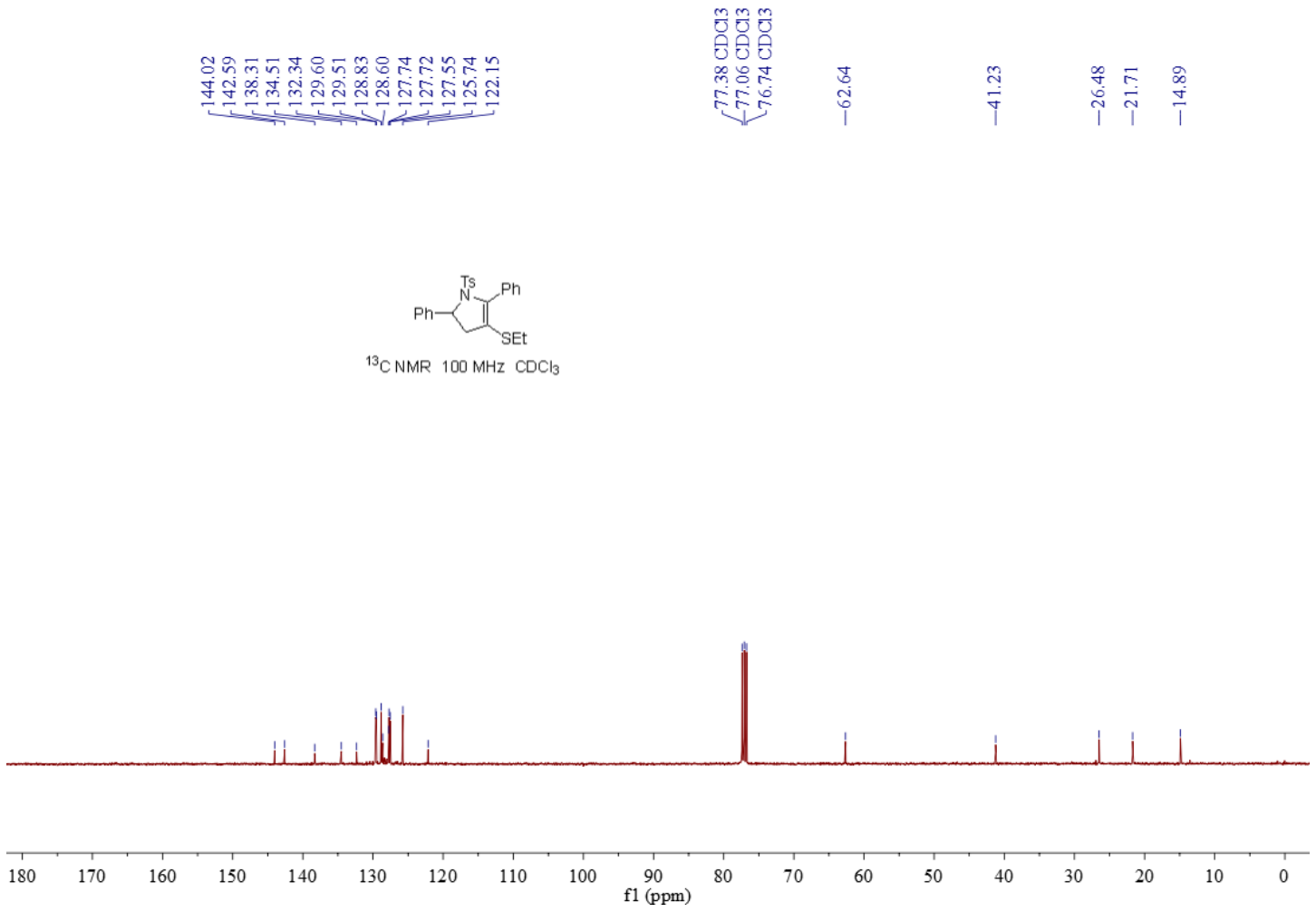

144.18
143.21
142.05
134.89
133.37
131.92
131.56
131.11
129.81
129.76
129.32
128.81
128.38
128.25
127.74
127.70
127.69
127.59
127.21
126.54
126.08
119.44
77.36
77.05
76.73
62.99
41.46
21.77
Ts
N
S
13C NMR 100 MHz CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4h



^{1}H NMR 400 MHz

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142.59
138.31
134.51
132.34
129.60
129.51
128.83
128.60
127.74
127.72
127.55
125.74
122.15
77.38 CDCl3
77.06 CDCl3
76.74 CDCl3
62.64
41.23
26.48
21.71
14.89
Ts
N
Ph
Ph
SEt
13C NMR 100 MHz CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
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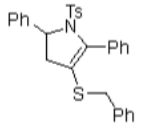
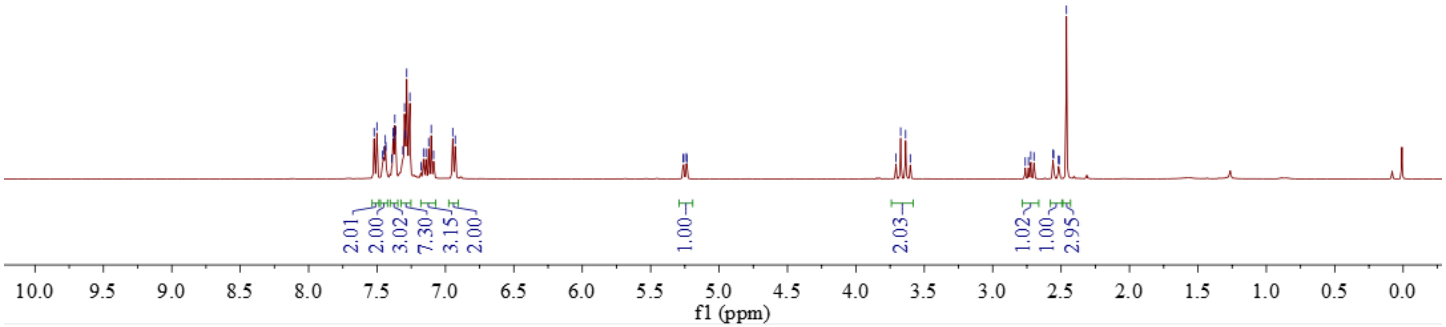
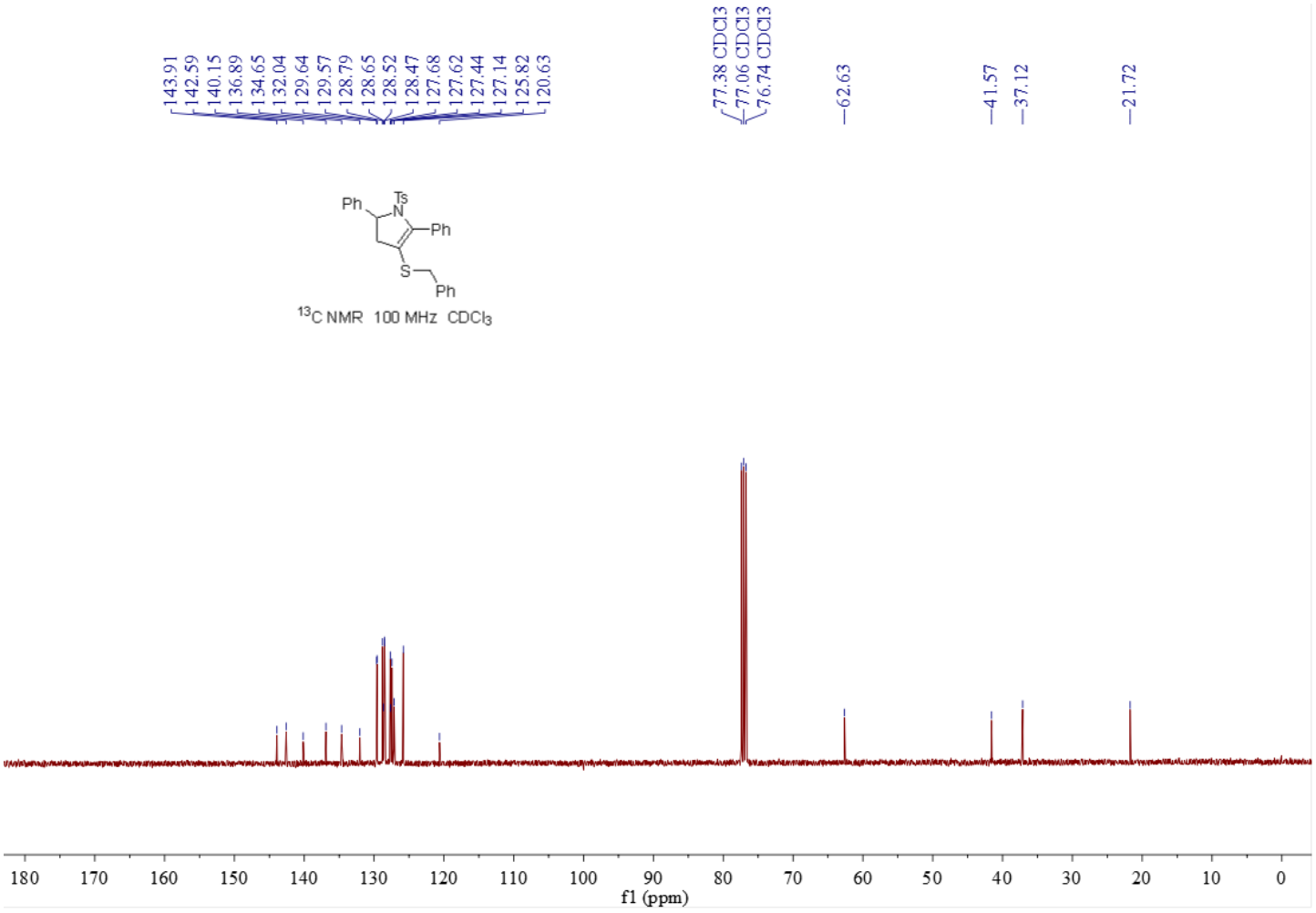
50
40
30
20
10
0
f1 (ppm)

4i



^{1}H NMR 400 MHz $CDCl_3$

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128.47
127.68
127.62
127.44
127.14
125.82
120.63
77.38 CDCl3
77.06 CDCl3
76.74 CDCl3
62.63
41.57
37.12
21.72
Ph
Ts
N
Ph
S
Ph
13C NMR 100 MHz CDCl3
180
170
160
150
140
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110
100
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70
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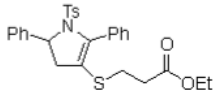
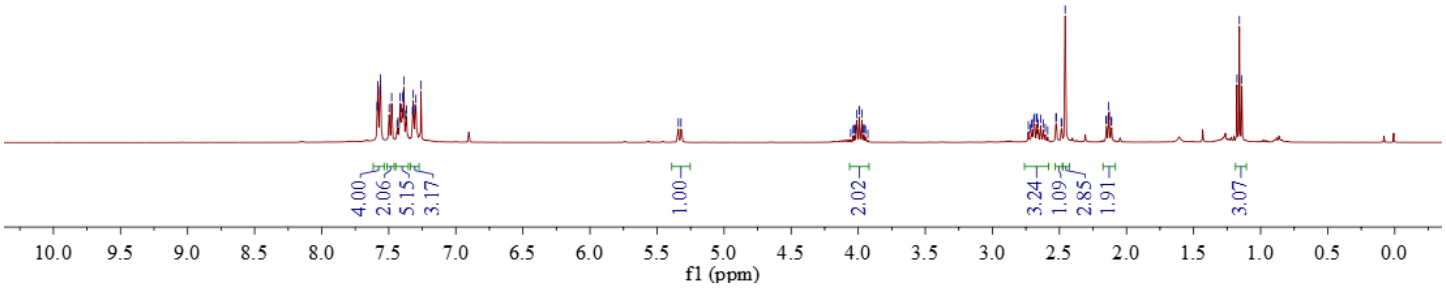
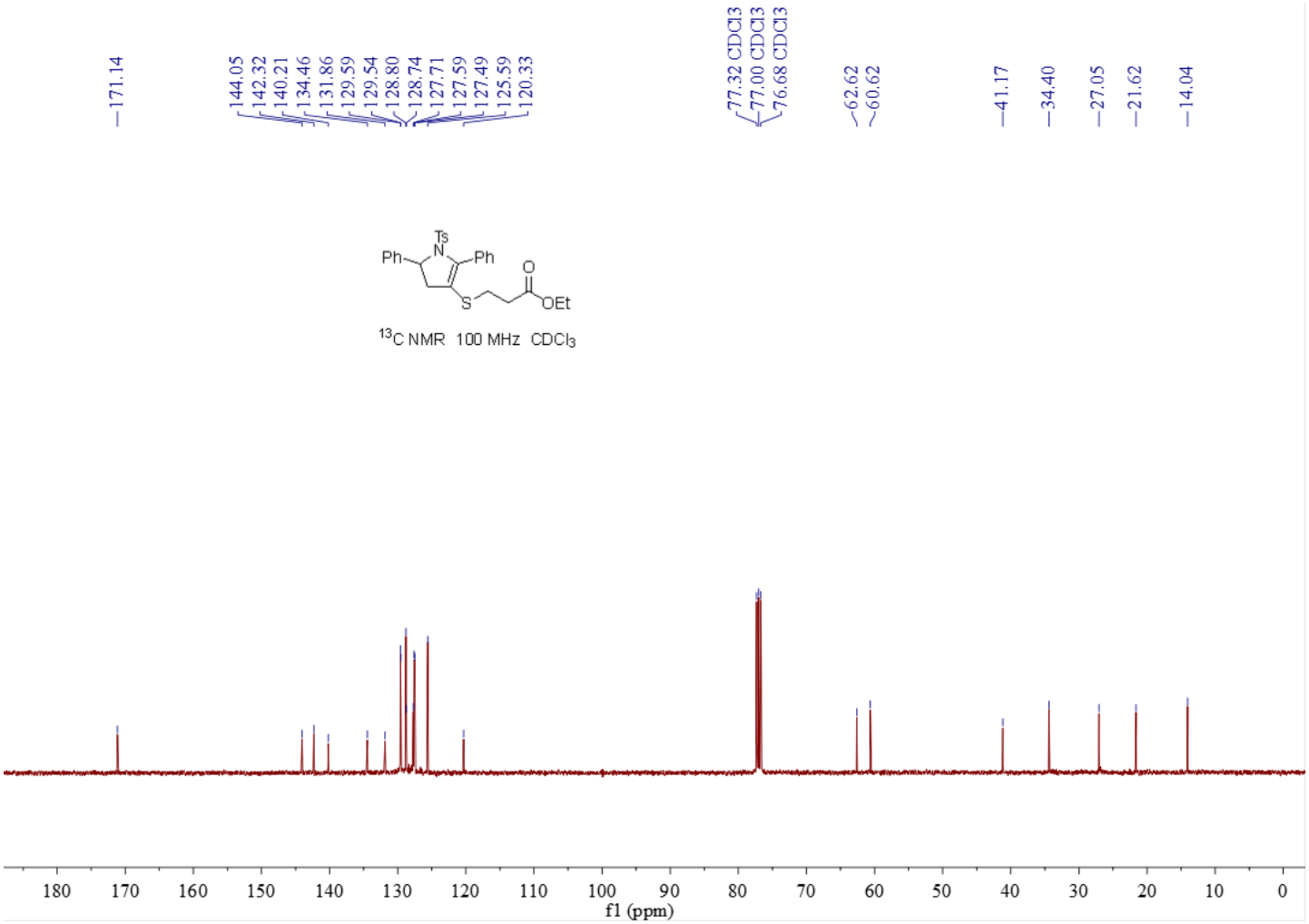
50
40
30
20
10
0
f1 (ppm)

4j



^{1}H NMR 400 MHz $CDCl_3$

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134.46
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129.59
129.54
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128.74
127.71
127.59
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125.59
120.33
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
62.62
60.62
41.17
34.40
27.05
21.62
14.04
Ts
N
Ph
Ph
O
S
OEt
13C NMR 100 MHz CDCl3
180
170
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130
120
110
100
90
80
70
60
50
40
30
20
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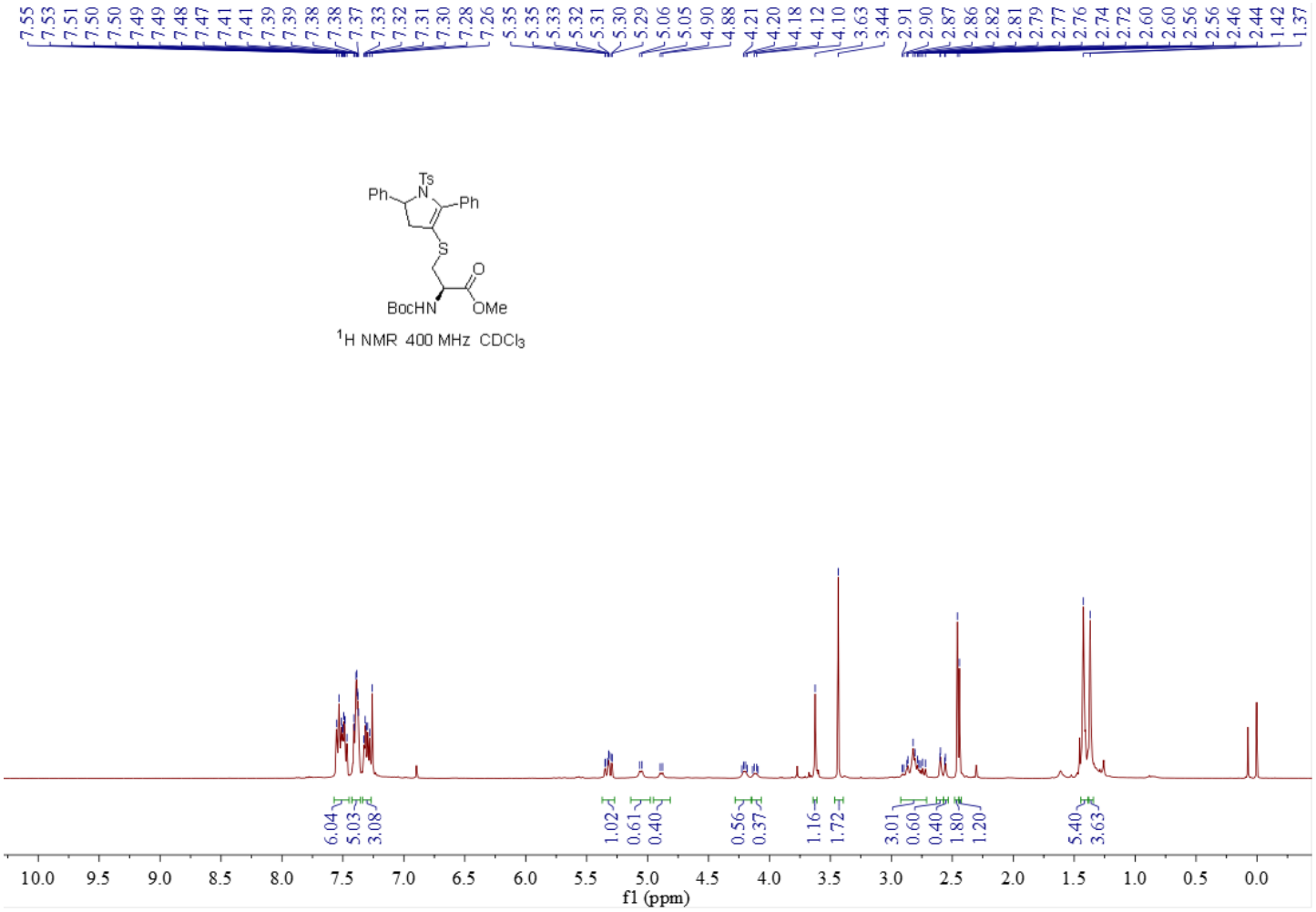
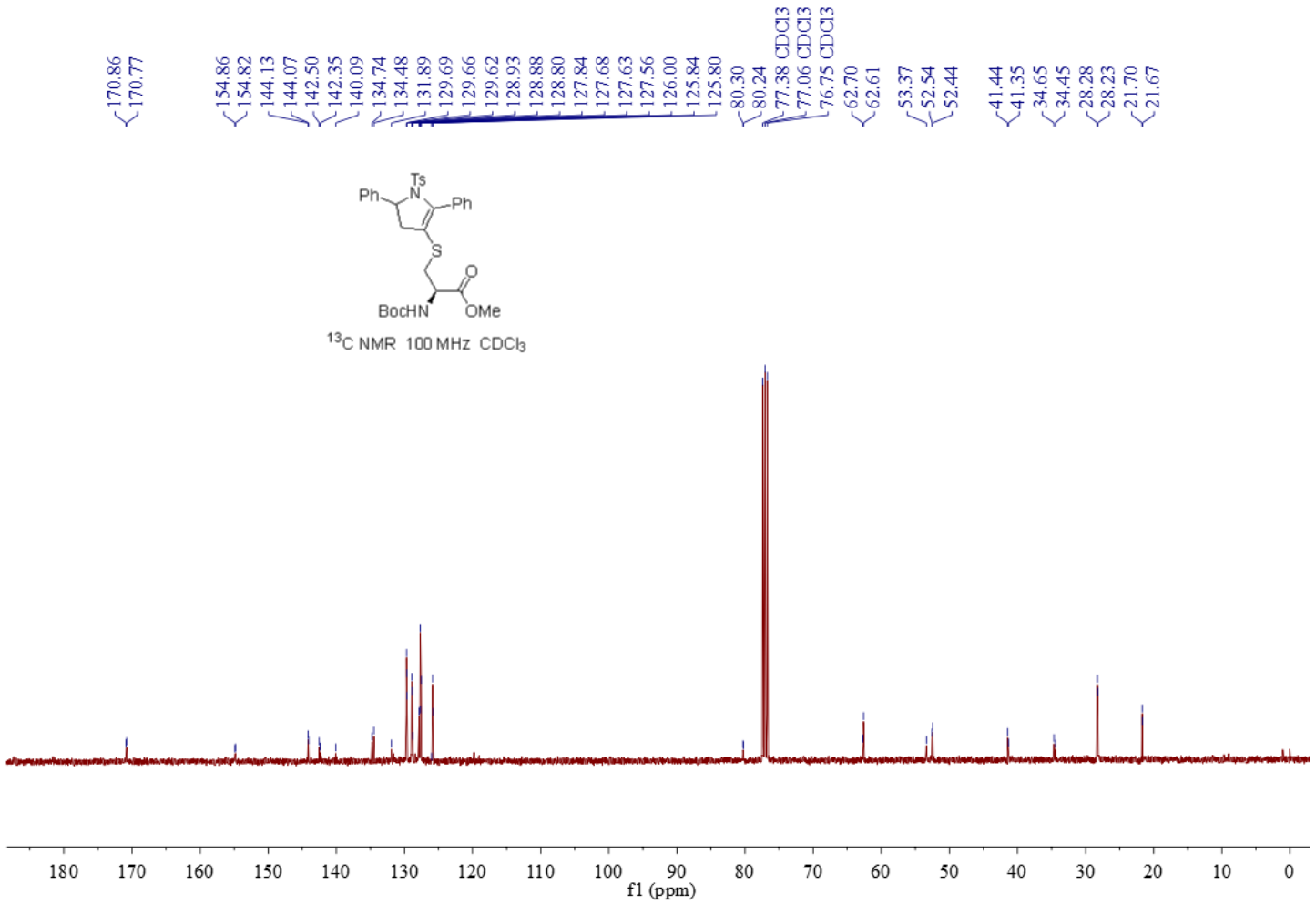
0
f1 (ppm)

4k


7.55 7.53 7.51 7.50 7.50 7.49 7.49 7.48 7.47 7.41 7.41 7.39 7.39 7.38 7.38 7.37 7.33 7.32 7.31 7.30 7.28 7.26
5.35 5.35 5.33 5.32 5.31 5.30 5.29 5.06 5.05 4.90 4.88
4.21 4.20 4.18 4.12 4.10 3.63 3.44
2.91 2.90 2.87 2.86 2.82 2.81 2.79 2.77 2.76 2.74 2.72 2.60 2.60 2.56 2.56 2.46 2.44 1.42 1.37
Ts
N
Ph
Ph
S
O
BocHN
OMe
1H NMR 400 MHz CDCl3
6.04 5.03 3.08 1.02 0.61 0.40 0.56 0.37 1.16 1.72 3.01 0.60 0.40 1.80 1.20 5.40 3.63
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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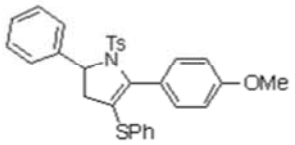
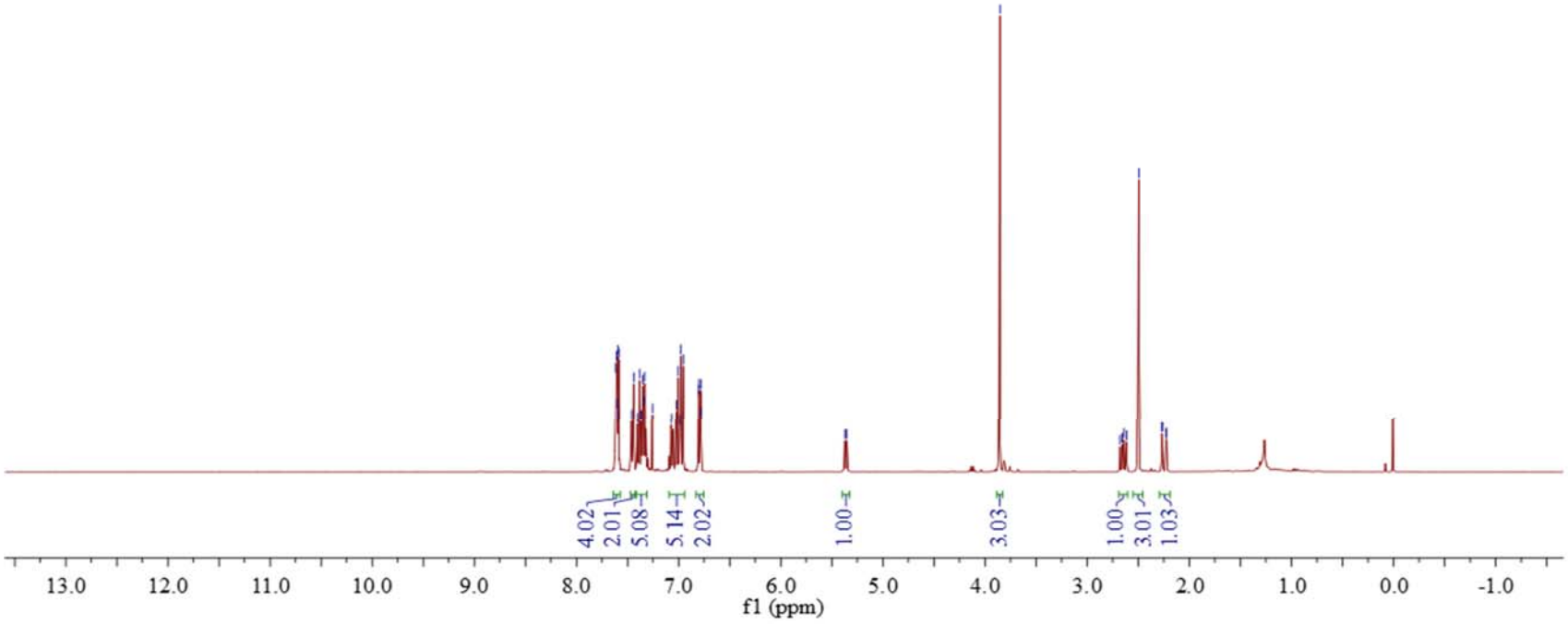
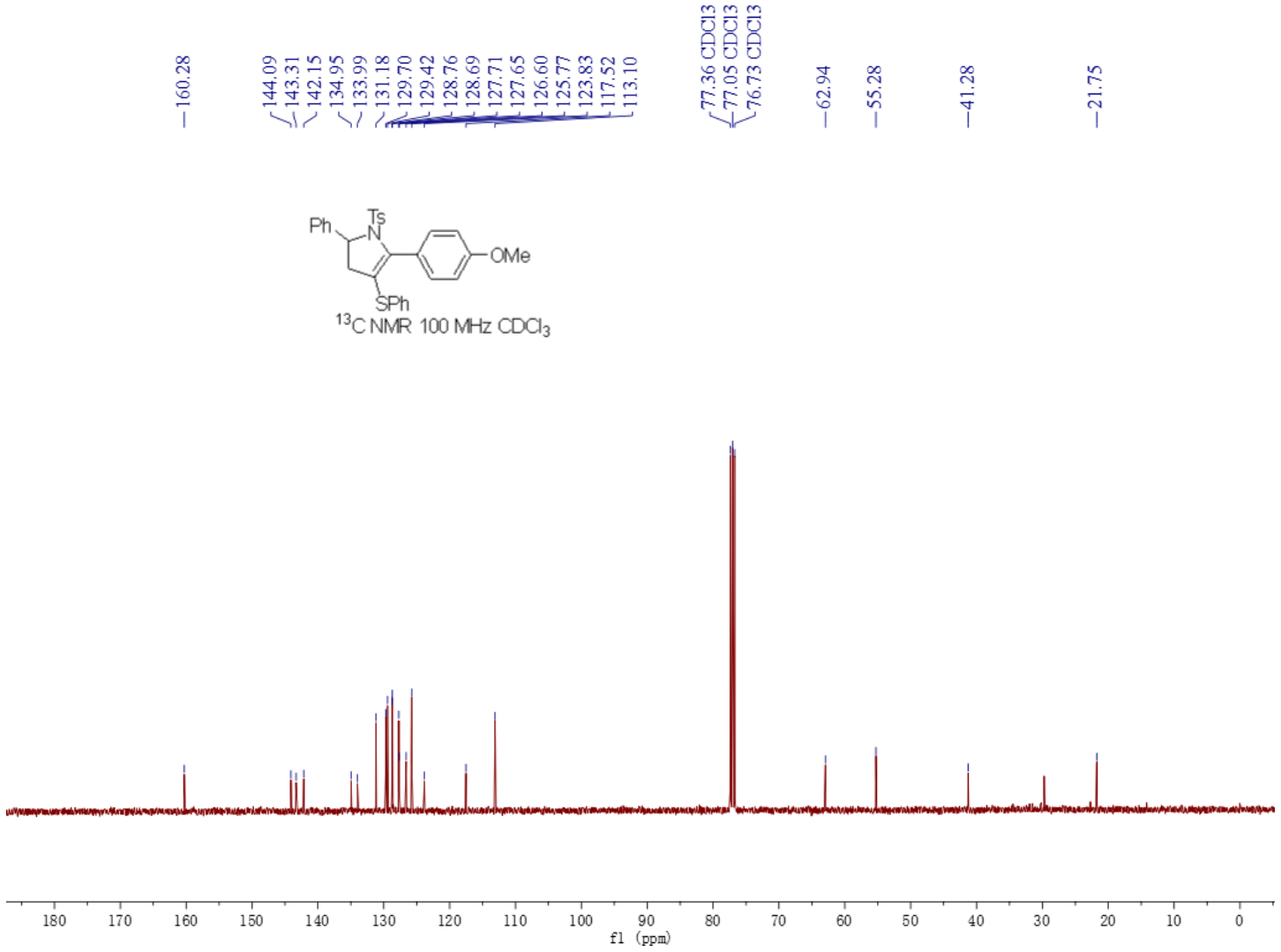
170.77
154.86
154.82
144.13
144.07
142.50
142.35
140.09
134.74
134.48
131.89
129.69
129.66
129.62
128.93
128.88
128.80
127.84
127.68
127.63
127.56
126.00
125.84
125.80
80.30
80.24
77.38 CDCl3
77.06 CDCl3
76.75 CDCl3
62.70
62.61
53.37
52.54
52.44
41.44
41.35
34.65
34.45
28.28
28.23
21.70
21.67
Ts
N
Ph
Ph
S
O
BocHN
OMe
13C NMR 100 MHz CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4l



^{1}H NMR 400 MHz $CDCl_3$

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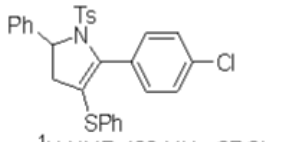
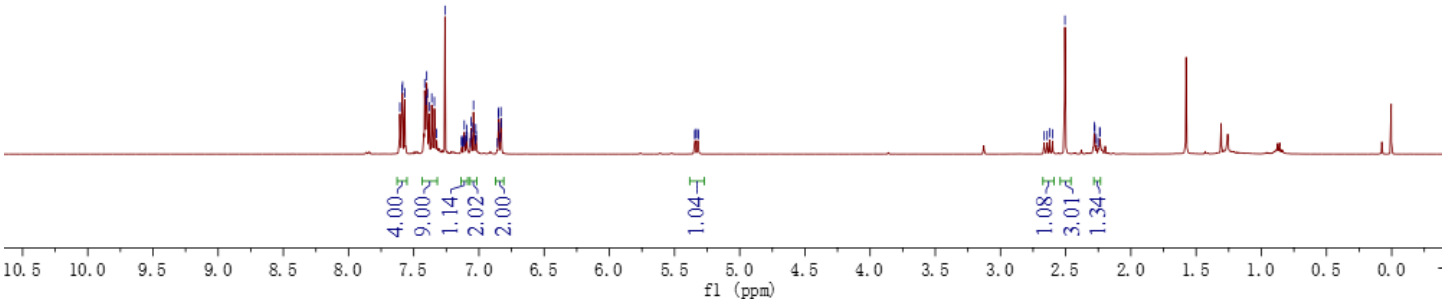
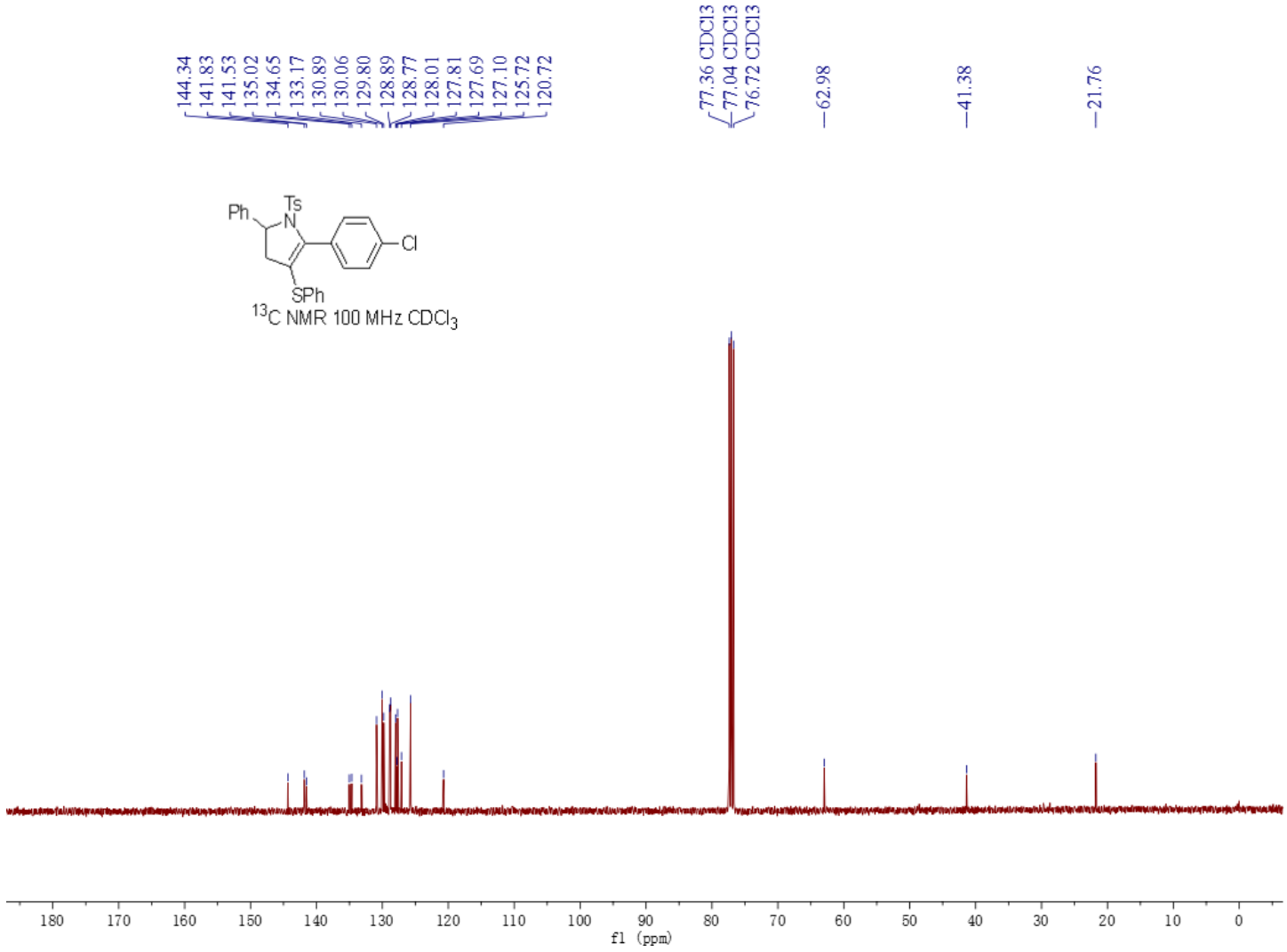
142.15
134.95
133.99
131.18
129.70
129.42
128.76
128.69
127.71
127.65
126.60
125.77
123.83
117.52
113.10
77.36 CDCl3
77.05 CDCl3
76.73 CDCl3
62.94
55.28
41.28
21.75
Ph
Ts
N
OMe
SPh
13C NMR 100 MHz CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4m



^{1}H NMR 400 MHz $CDCl_3$

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141.83
141.53
135.02
134.65
133.17
130.89
130.06
129.80
128.89
128.77
128.01
127.81
127.69
127.10
125.72
120.72
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
62.98
41.38
21.76
Ph
Ts
N
Cl
SPh
13C NMR 100 MHz CDCl3
180
170
160
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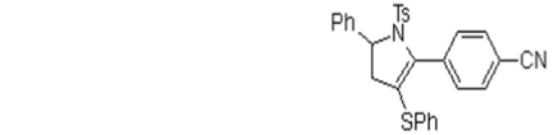
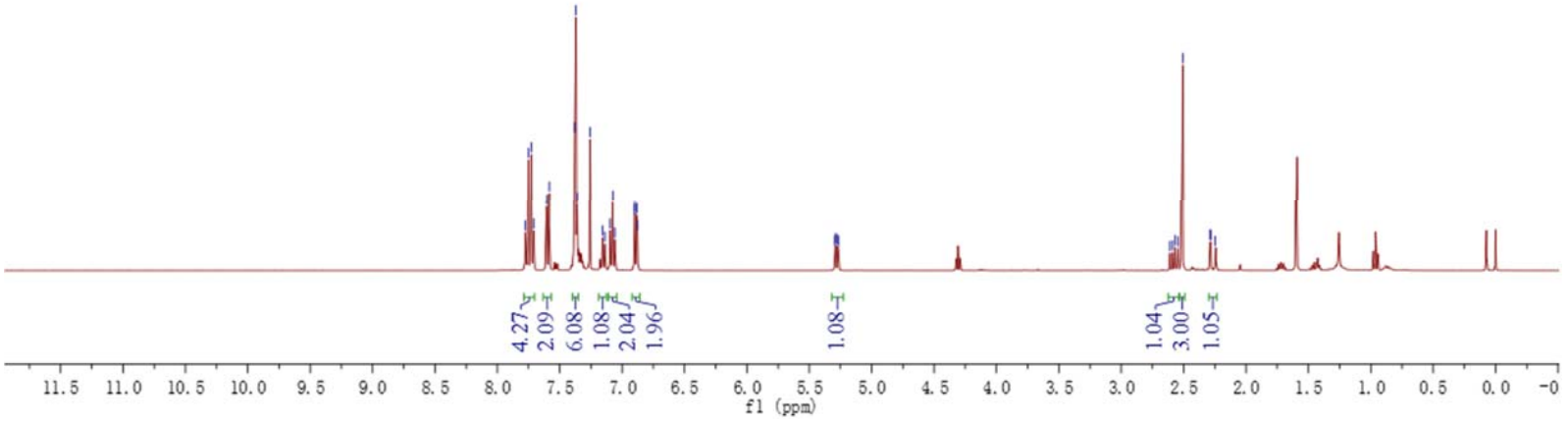
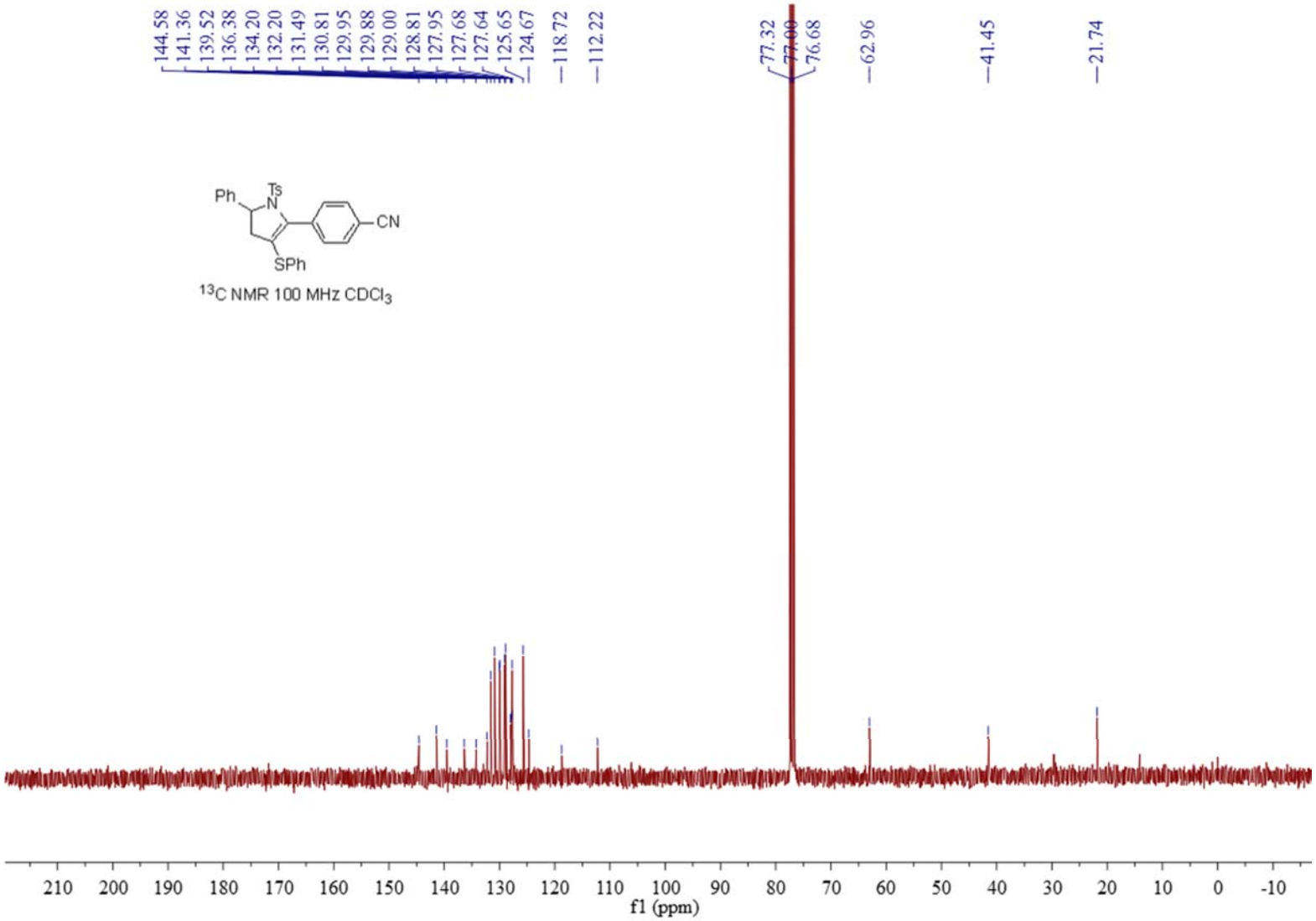
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4n



^{1}H NMR 400 MHz $CDCl_3$

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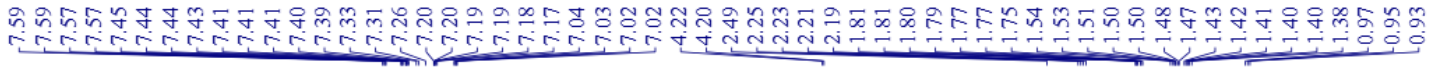
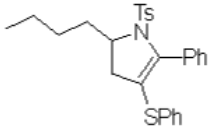
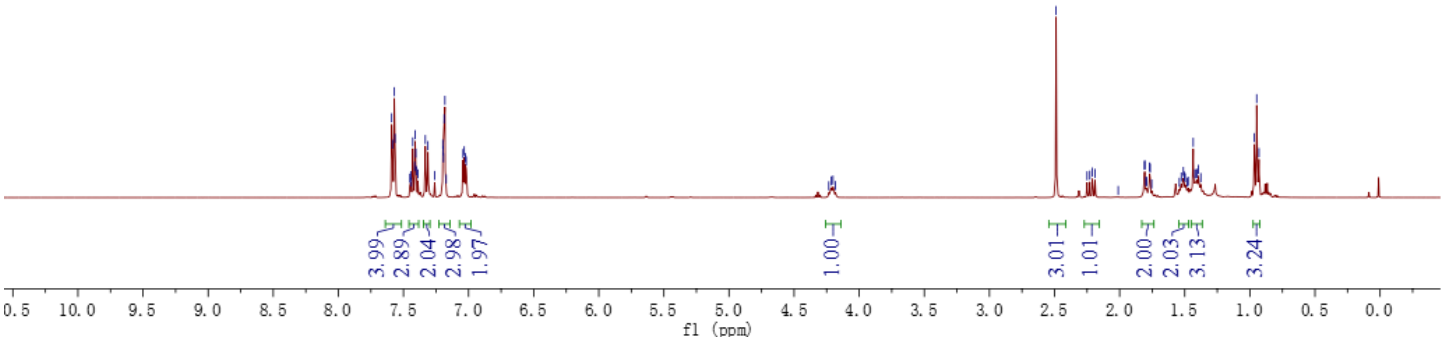
134.20
132.20
131.49
130.81
129.95
129.88
129.00
128.81
127.95
127.68
127.64
125.65
124.67
118.72
112.22
77.32
77.00
76.68
62.96
41.45
21.74
Ph
Ts
N
CN
SPh
13C NMR 100 MHz CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

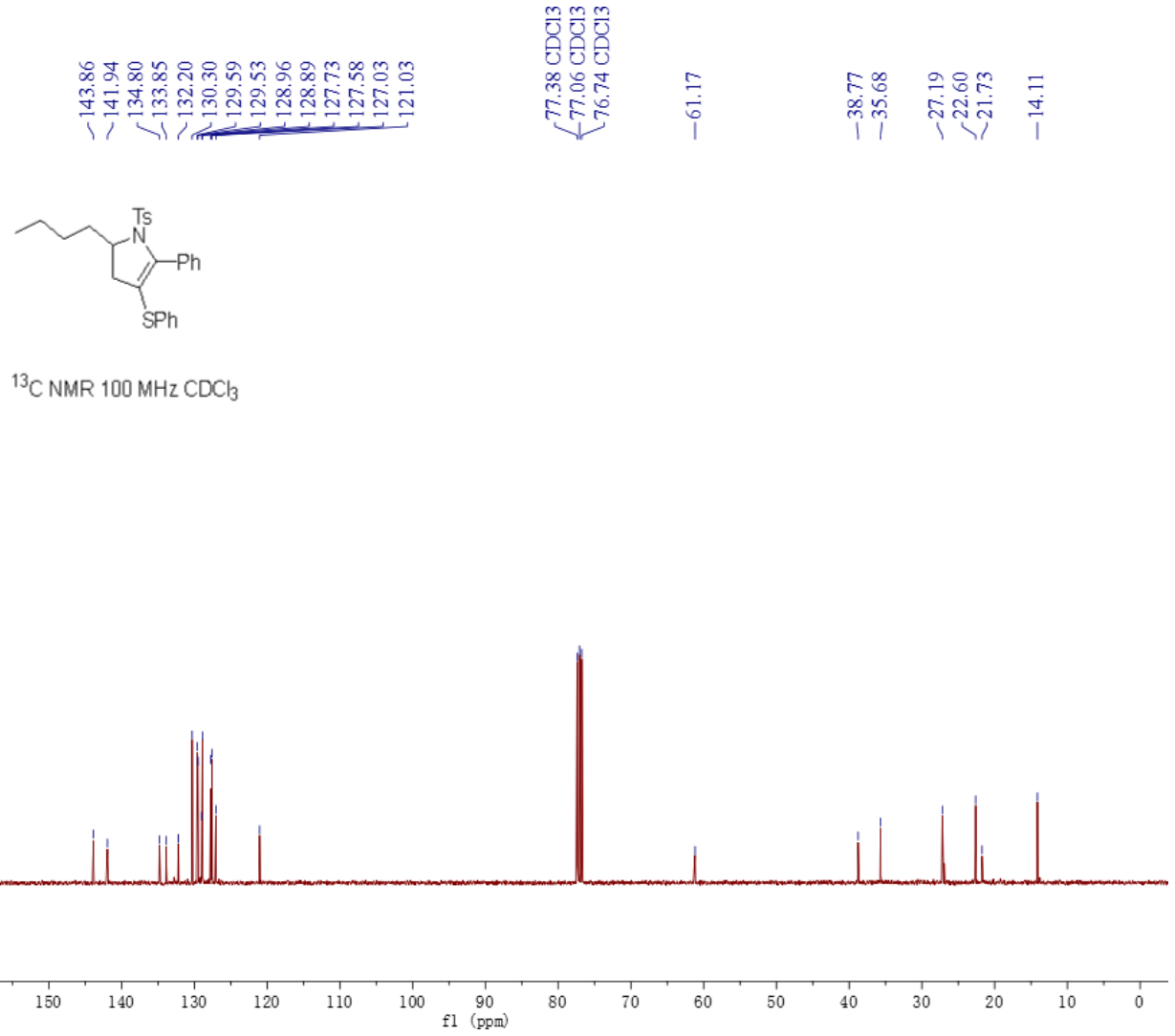
4o





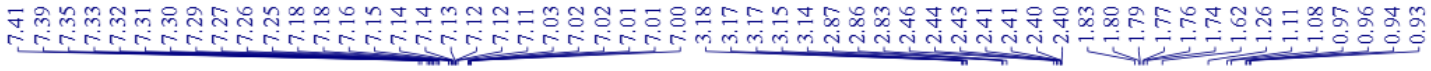
^{1}H NMR 400 MHz $CDCl_3$

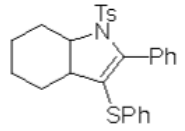




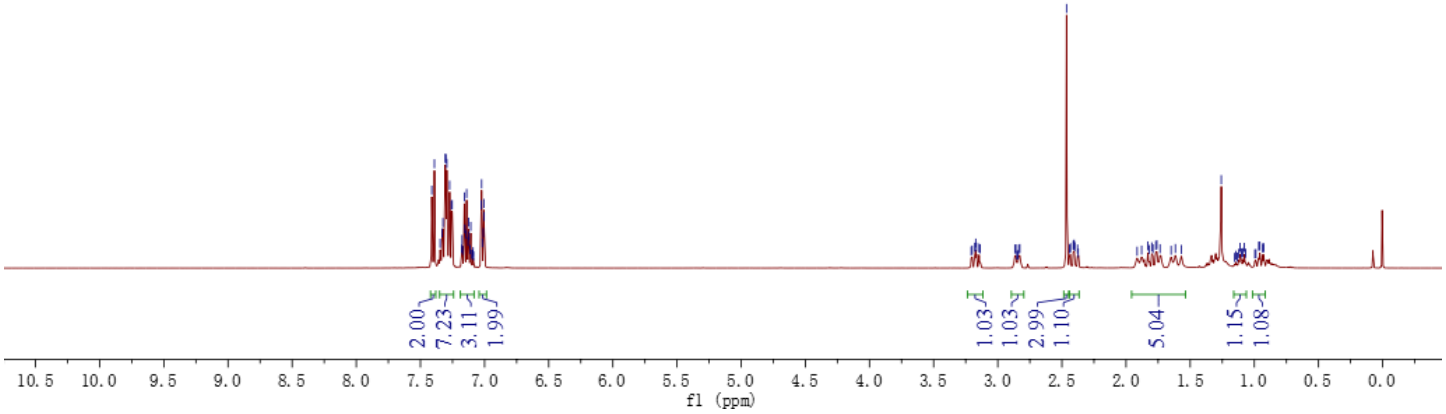
^{13}C NMR 100 MHz $CDCl_3$

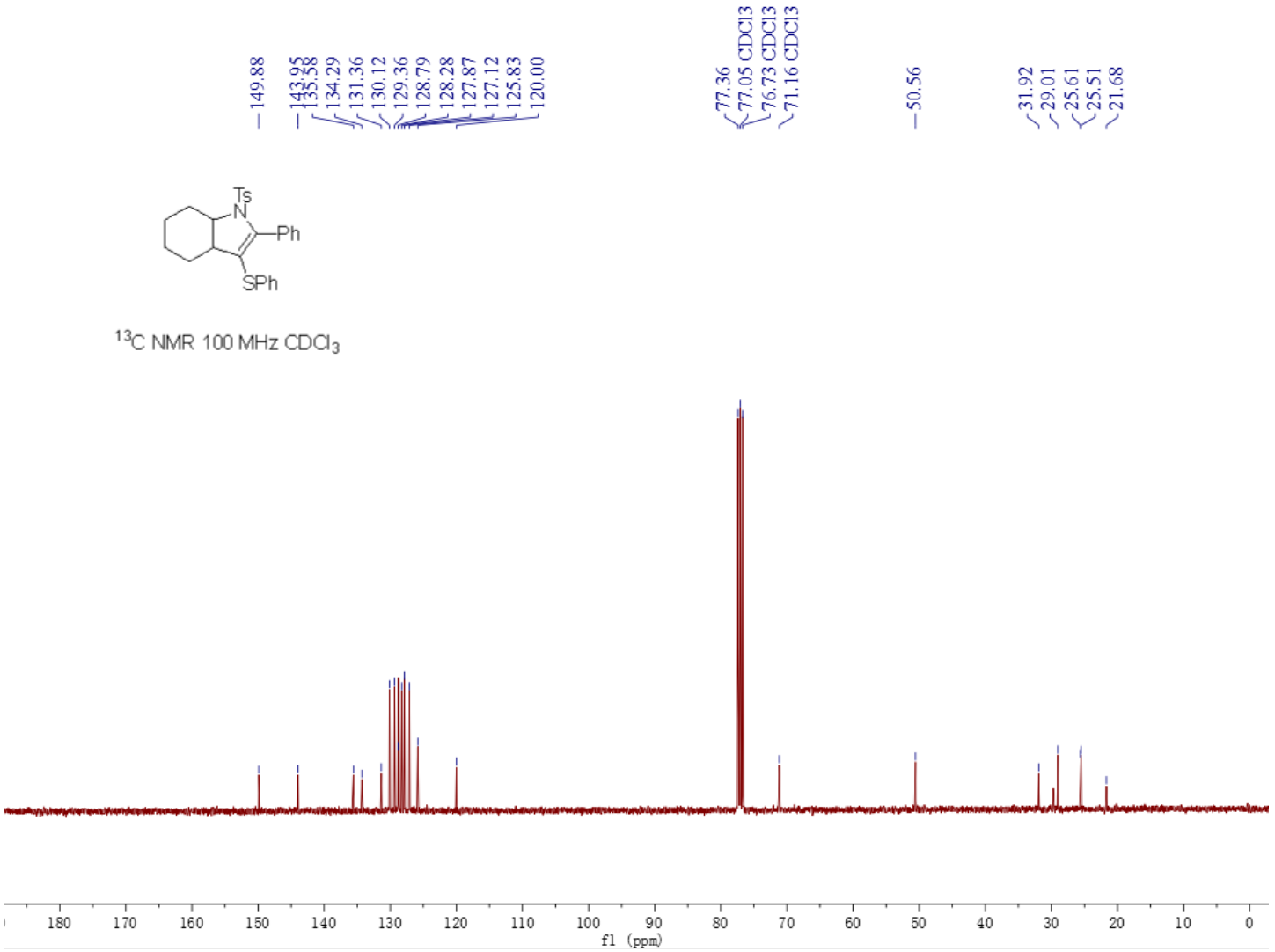
4p





^{1}H NMR 400 MHz $CDCl_3$

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134.29
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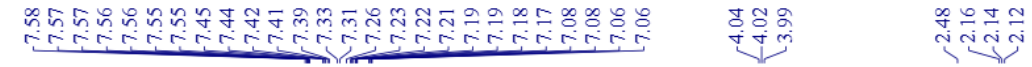
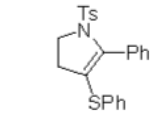
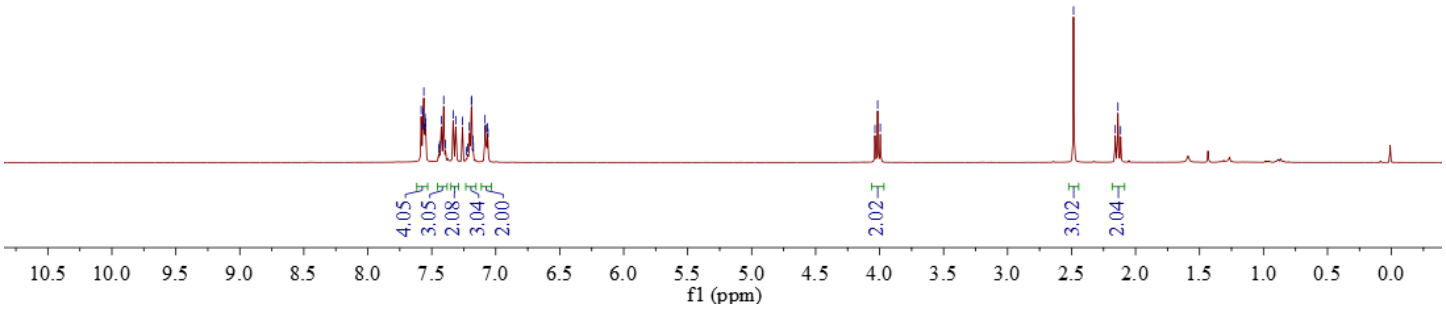
130.12
129.36
128.79
128.28
127.87
127.12
125.83
120.00
77.36
77.05 CDCl3
76.73 CDCl3
71.16 CDCl3
50.56
31.92
29.01
25.61
25.51
21.68
Ts
N
Ph
SPh
13C NMR 100 MHz CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

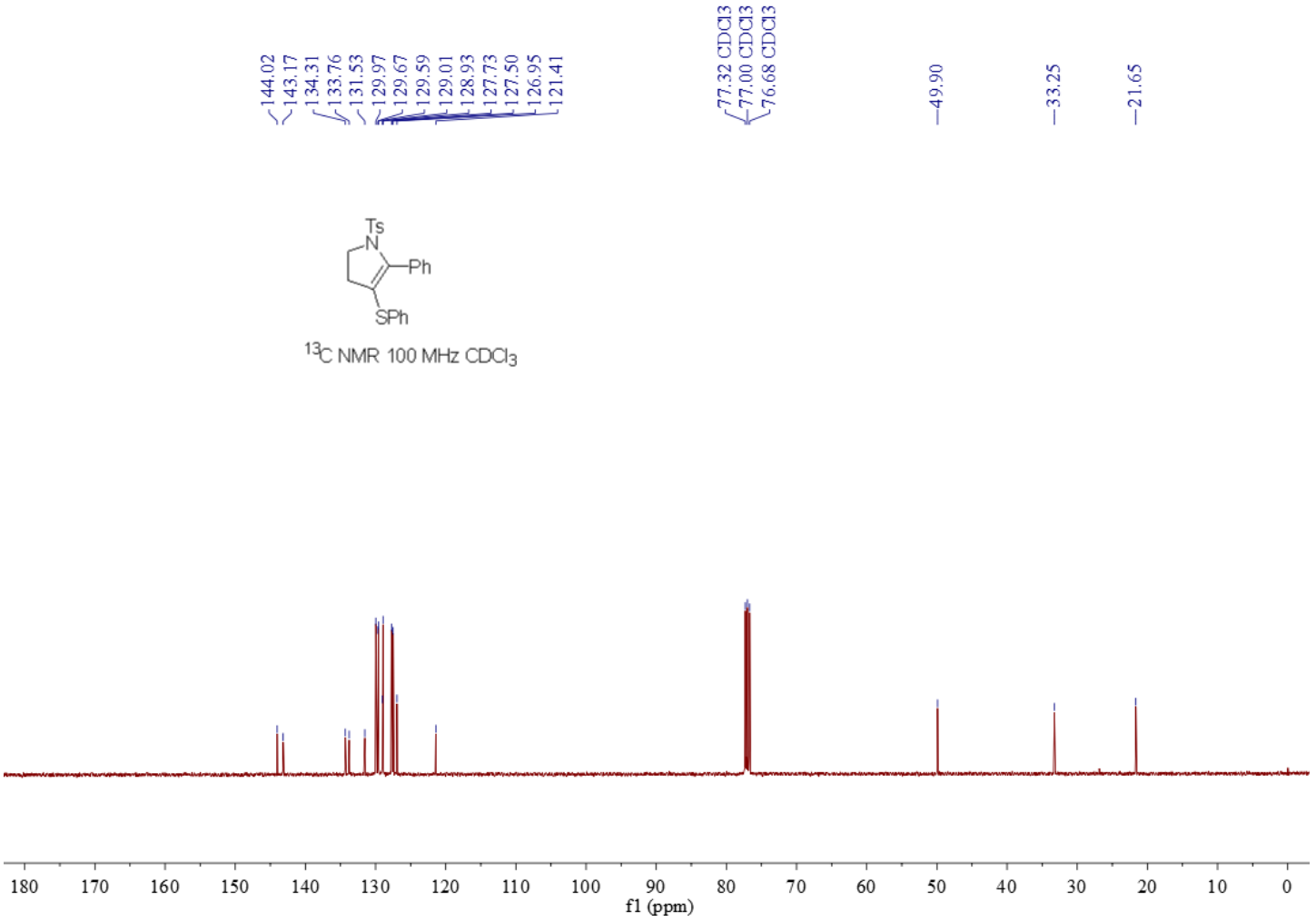
4q





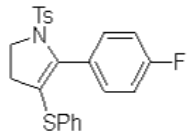
^{1}H NMR 400 MHz $CDCl_3$



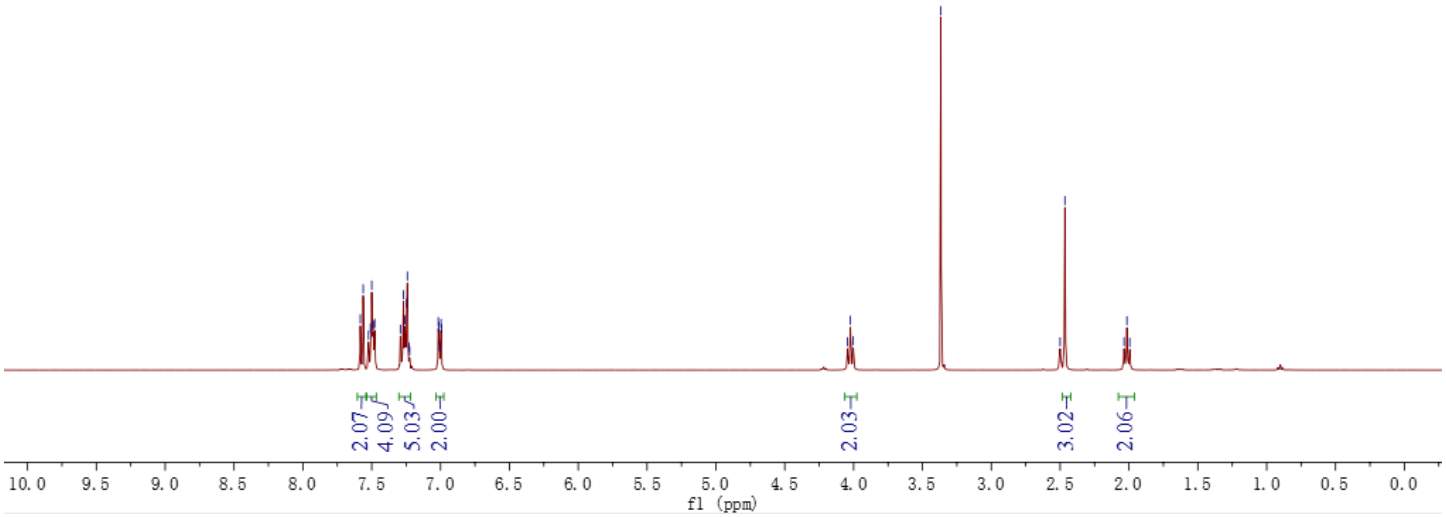


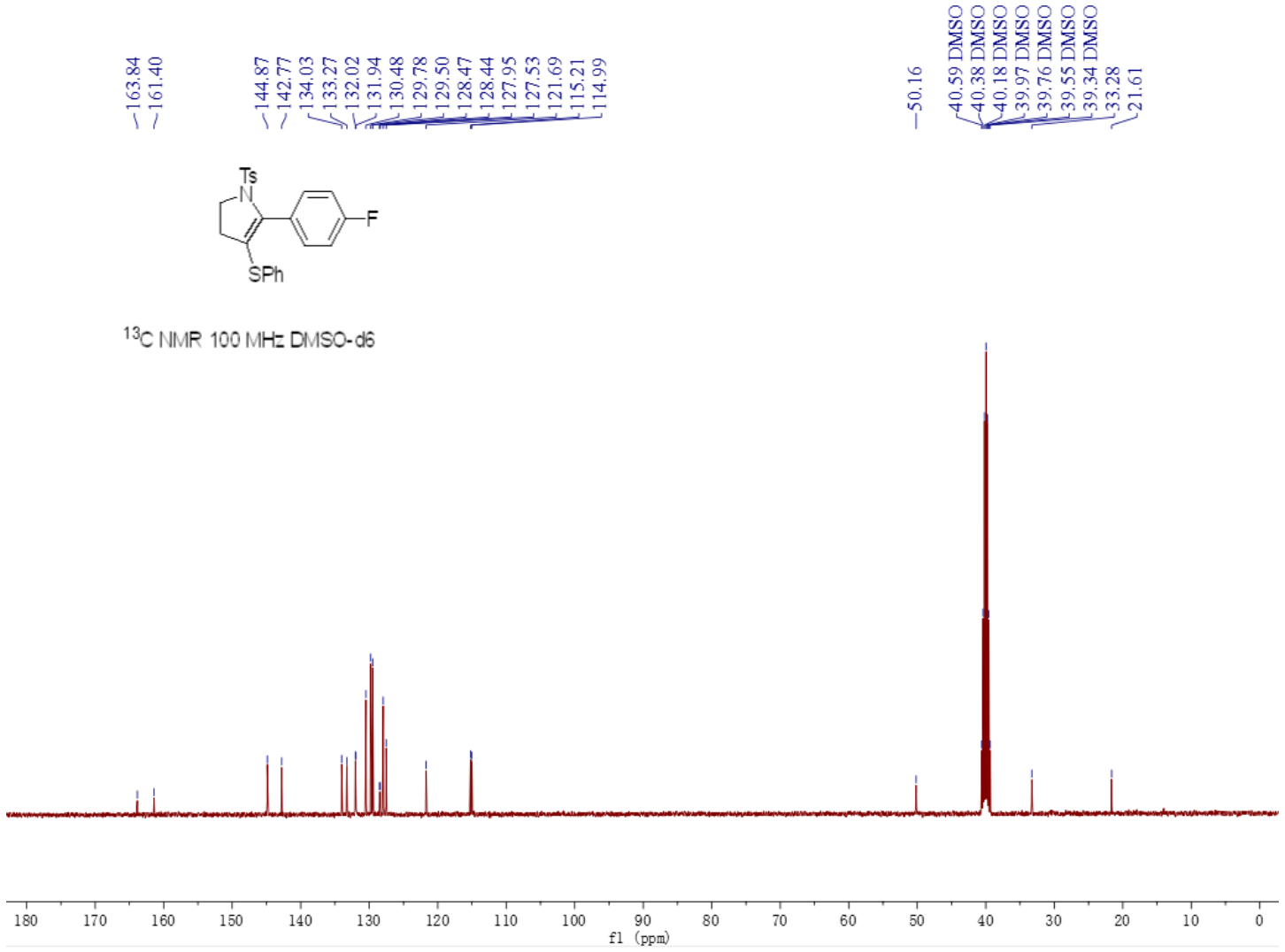
^{13}C NMR 100 MHz $CDCl_3$

4r



^{1}H NMR 400 MHz DMSO-d6




163.84
161.40
144.87
142.77
134.03
133.27
132.02
131.94
130.48
129.78
129.50
128.47
128.44
127.95
127.53
121.69
115.21
114.99
50.16
40.59 DMSO
40.38 DMSO
40.18 DMSO
39.97 DMSO
39.76 DMSO
39.55 DMSO
39.34 DMSO
33.28
21.61
Ts
N
F
SPh
13C NMR 100 MHz DMSO-d6
180
170
160
150
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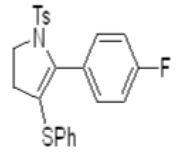
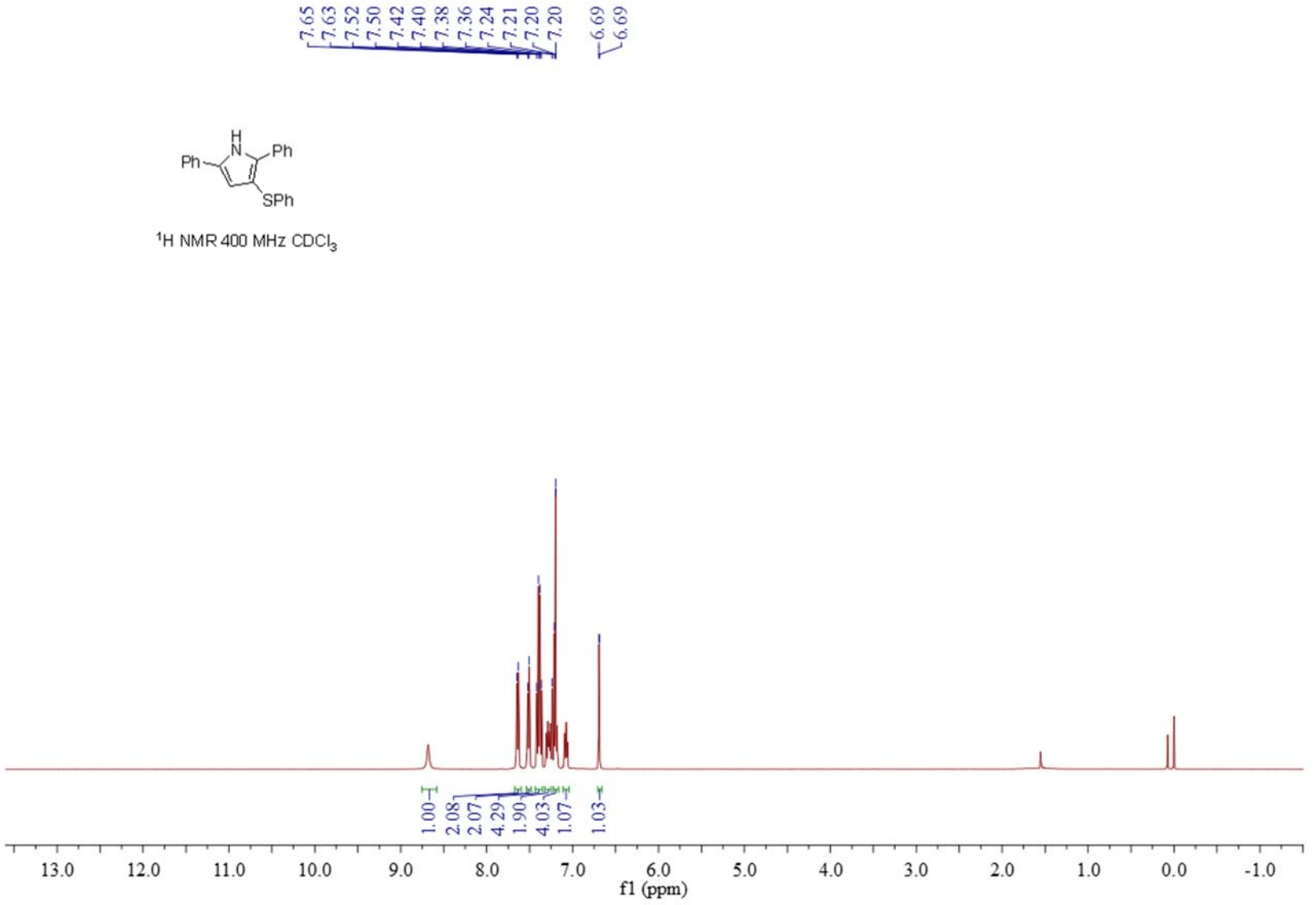
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

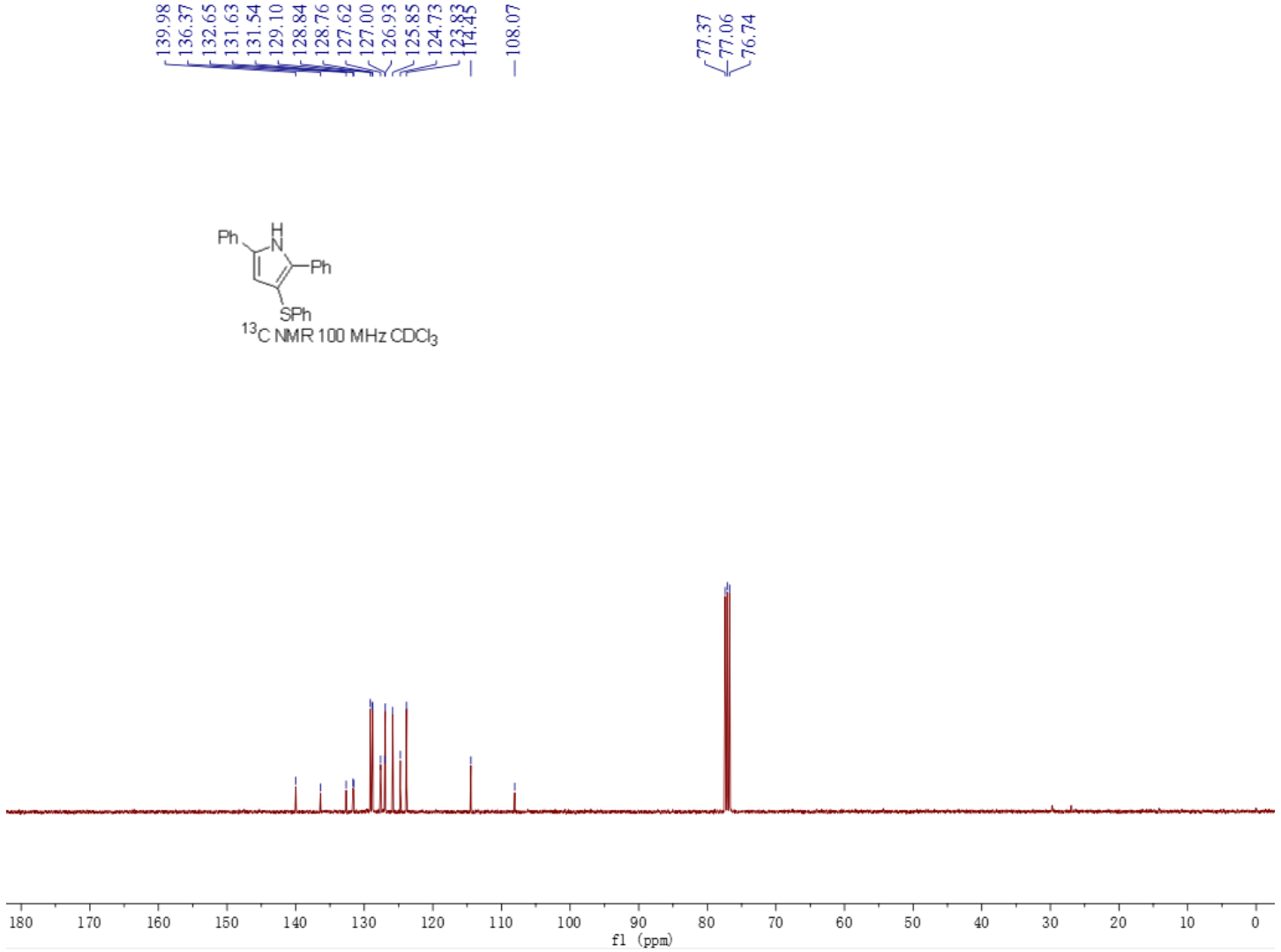


^{19}F NMR 376.3 MHz $CDCl_3$

5



^{1}H NMR 400 MHz $CDCl_3$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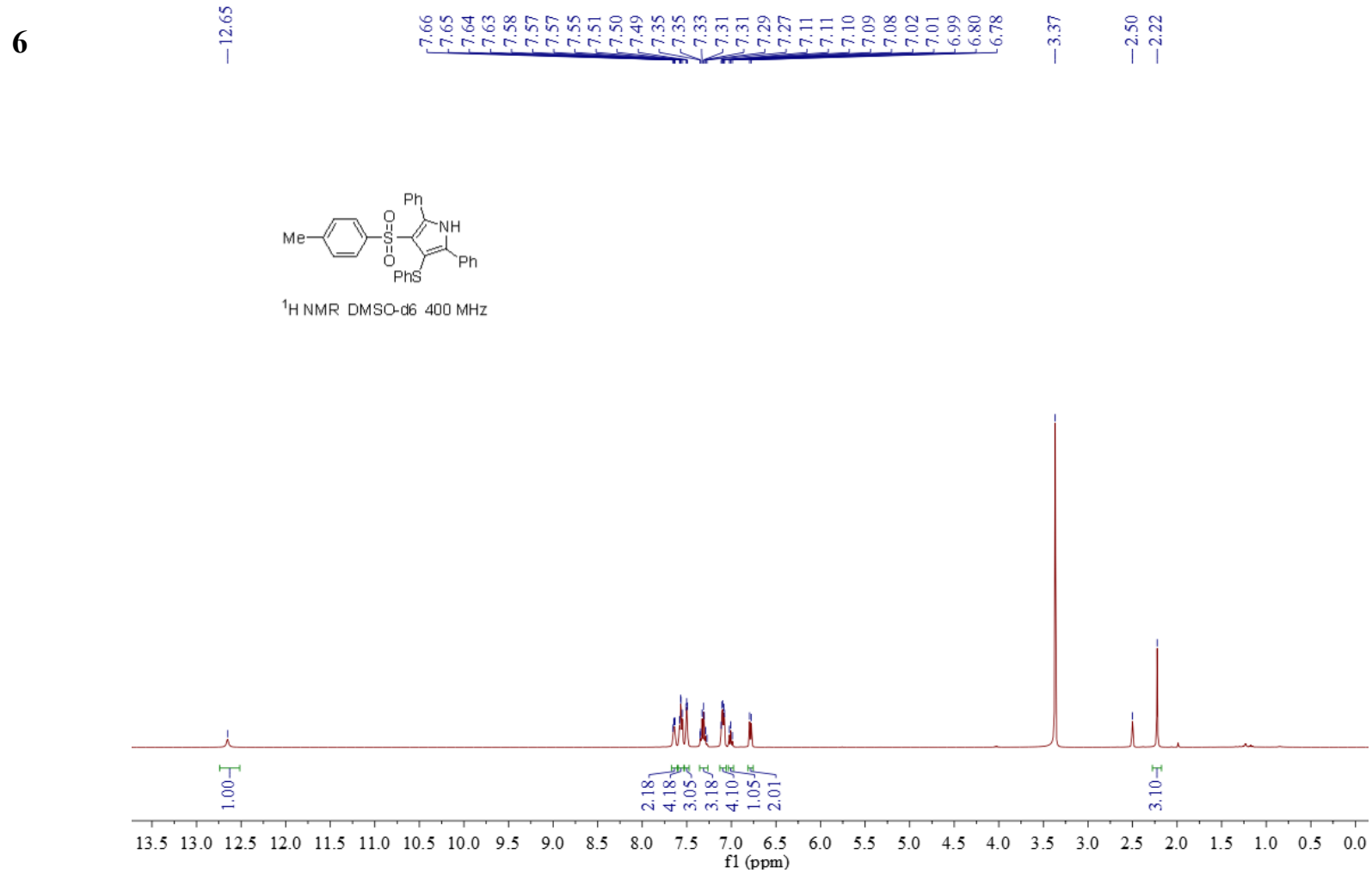
132.65
131.63
131.54
129.10
128.84
128.76
127.62
127.00
126.93
125.85
124.73
123.83
114.45
108.07
77.37
77.06
76.74
Ph
N
H
Ph
SPh
13C NMR 100 MHz CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

6


12.65
7.66
7.65
7.64
7.63
7.58
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7.57
7.55
7.51
7.50
7.49
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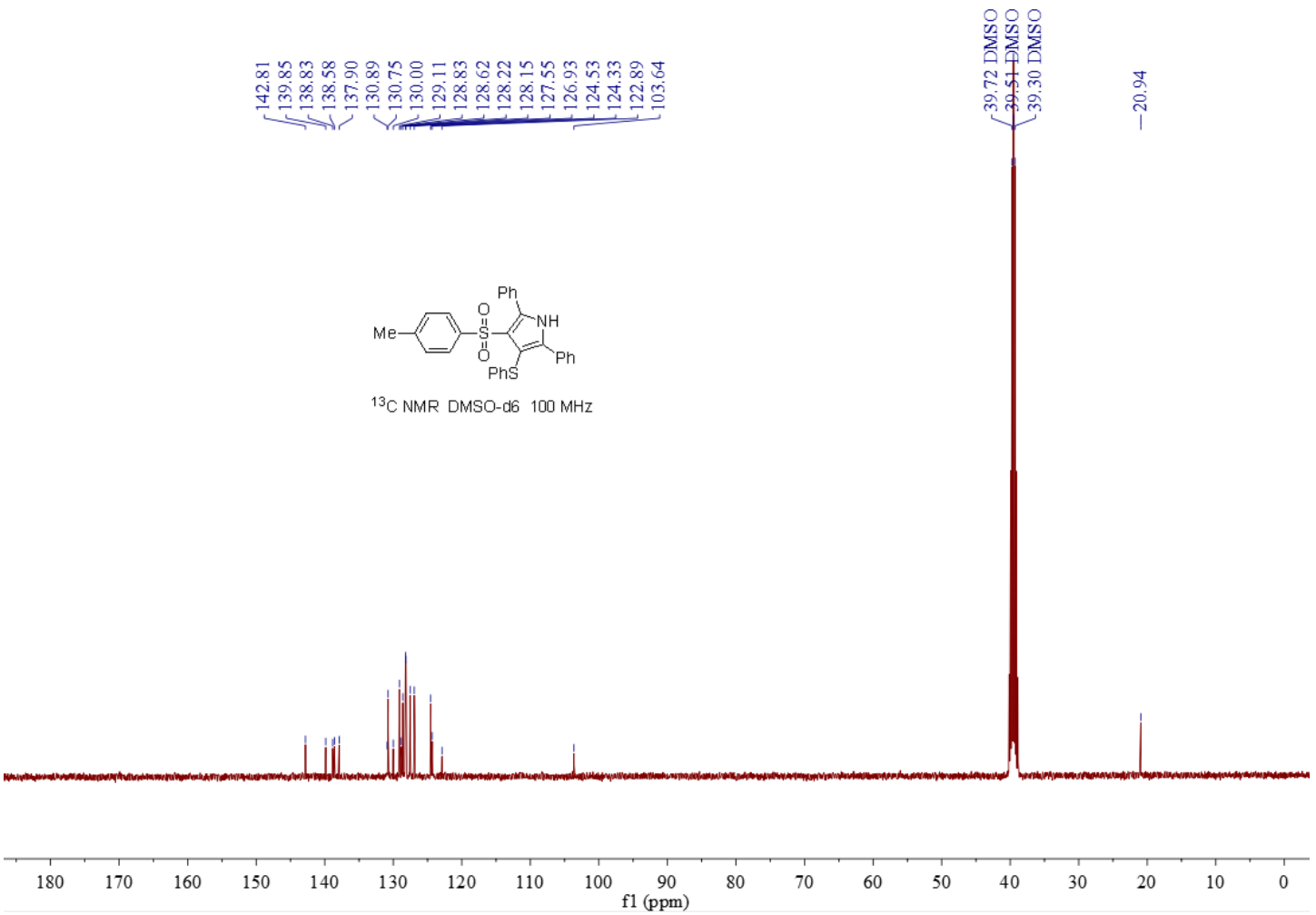
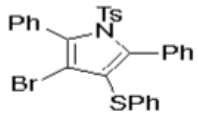
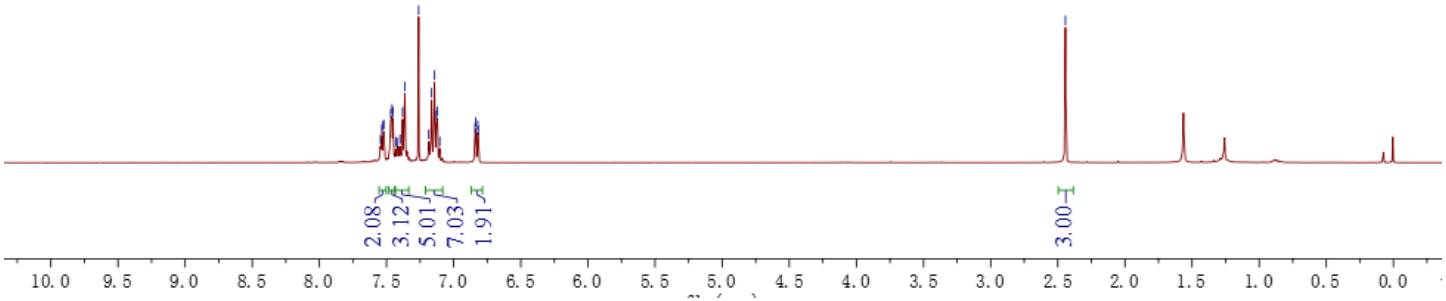
7.35
7.33
7.31
7.31
7.29
7.27
7.11
7.11
7.10
7.09
7.08
7.02
7.01
6.99
6.80
6.78
3.37
2.50
2.22
Me
Ph
NH
Ph
PhS
O=S=O
1H NMR DMSO-d6 400 MHz
1.00
2.18
4.18
3.05
3.18
4.10
1.05
2.01
3.10
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

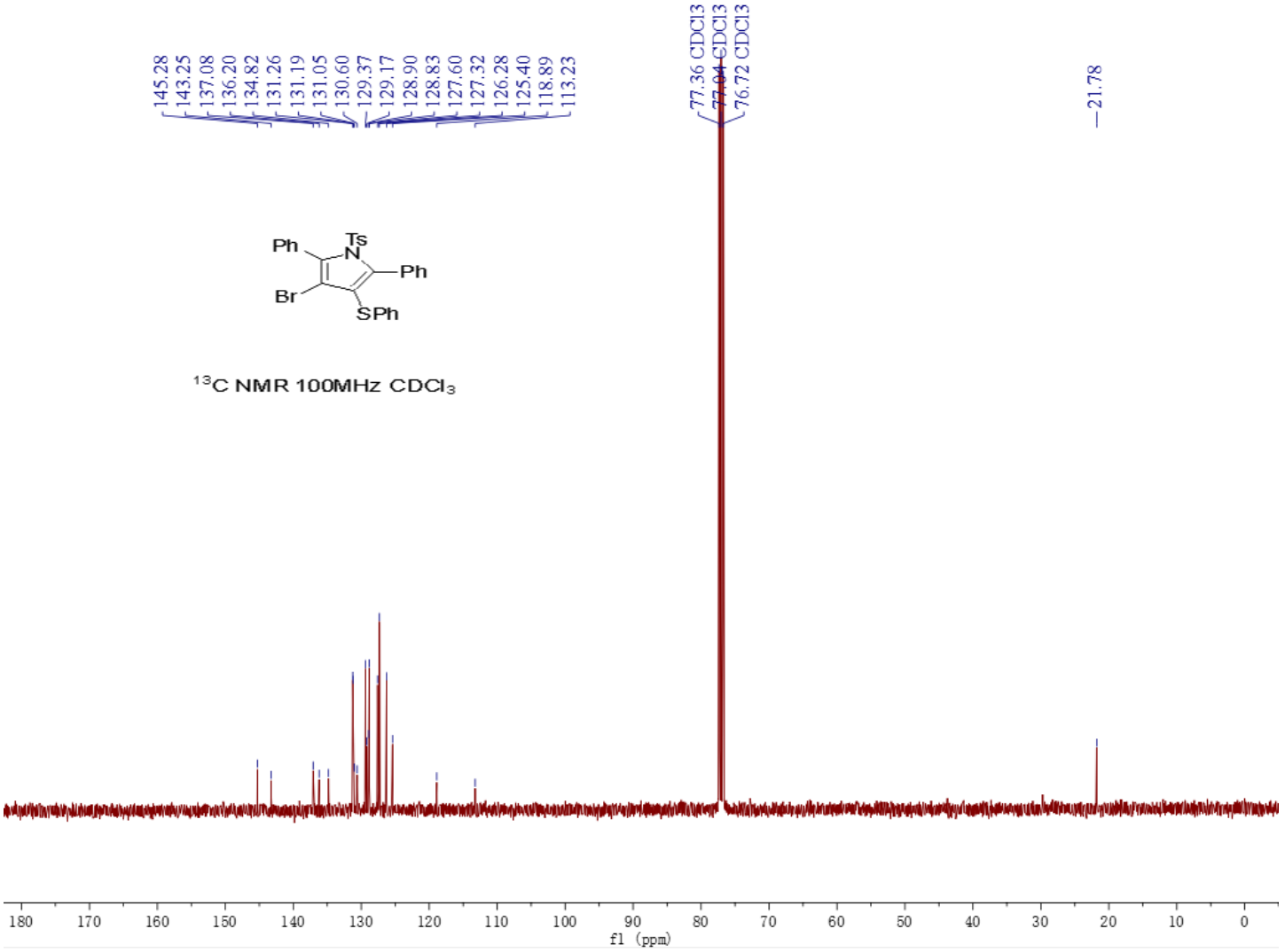

142.81
139.85
138.83
138.58
137.90
130.89
130.75
130.00
129.11
128.83
128.62
128.22
128.15
127.55
126.93
124.53
124.33
122.89
103.64
39.72 DMSO
39.51 DMSO
39.30 DMSO
20.94
Ph
NH
Me
S
O
O
Ph
PhS
13C NMR DMSO-d6 100 MHz
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

7

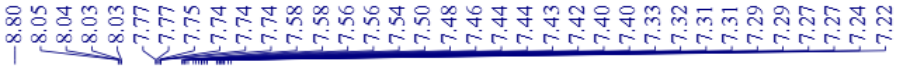


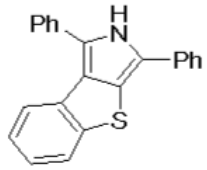
^{1}H NMR 400MHz $CDCl_3$



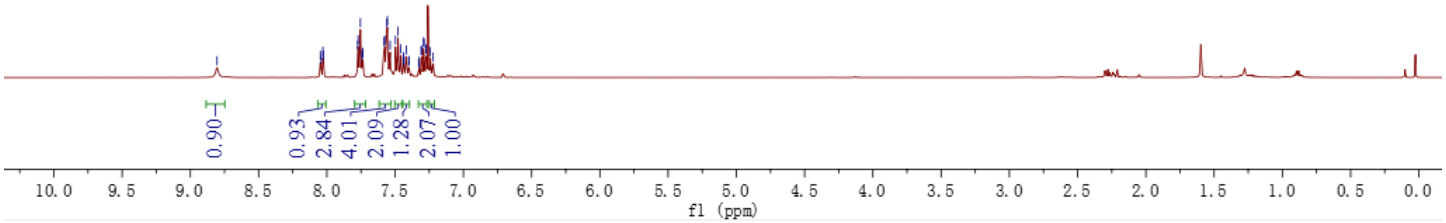

145.28
143.25
137.08
136.20
134.82
131.26
131.19
131.05
130.60
129.37
129.17
128.90
128.83
127.60
127.32
126.28
125.40
118.89
113.23
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
21.78
Ph
Ts
N
Ph
Br
SPh
^{13}C NMR 100MHz CDCl$_3$
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

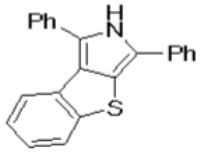
8



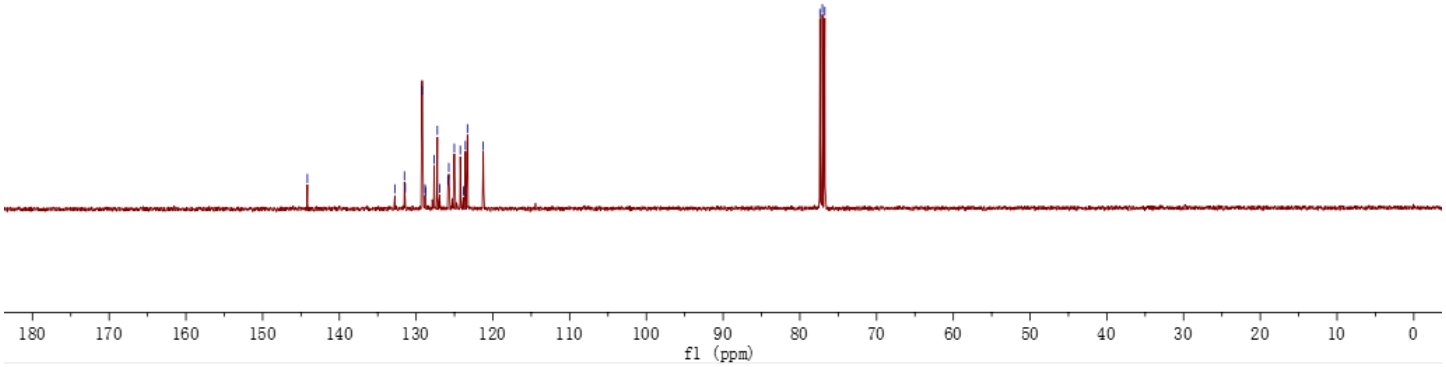


^{1}H NMR 400 MHz $CDCl_3$

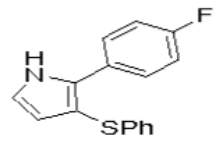




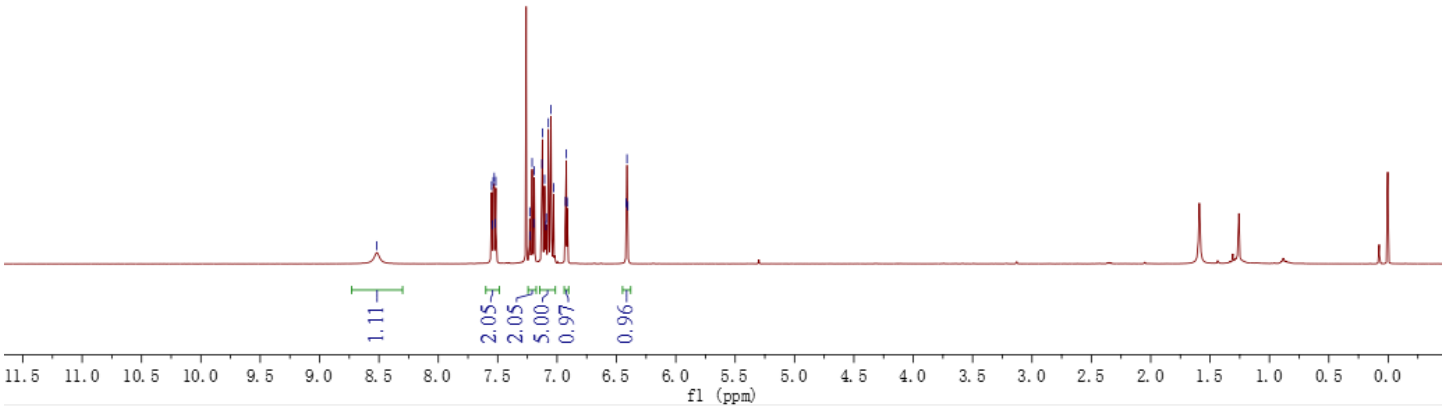
^{13}C NMR 100 MHz $CDCl_3$

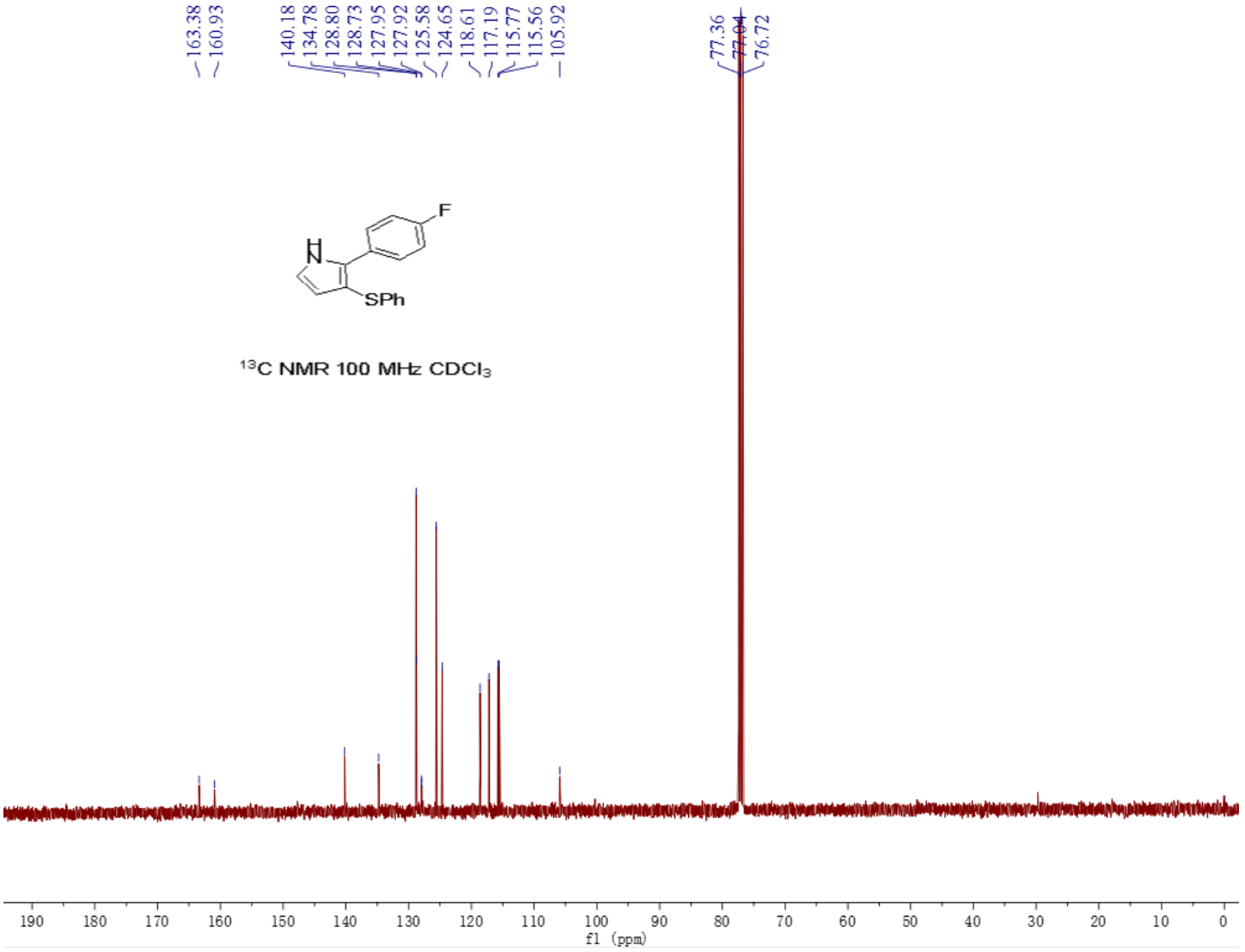


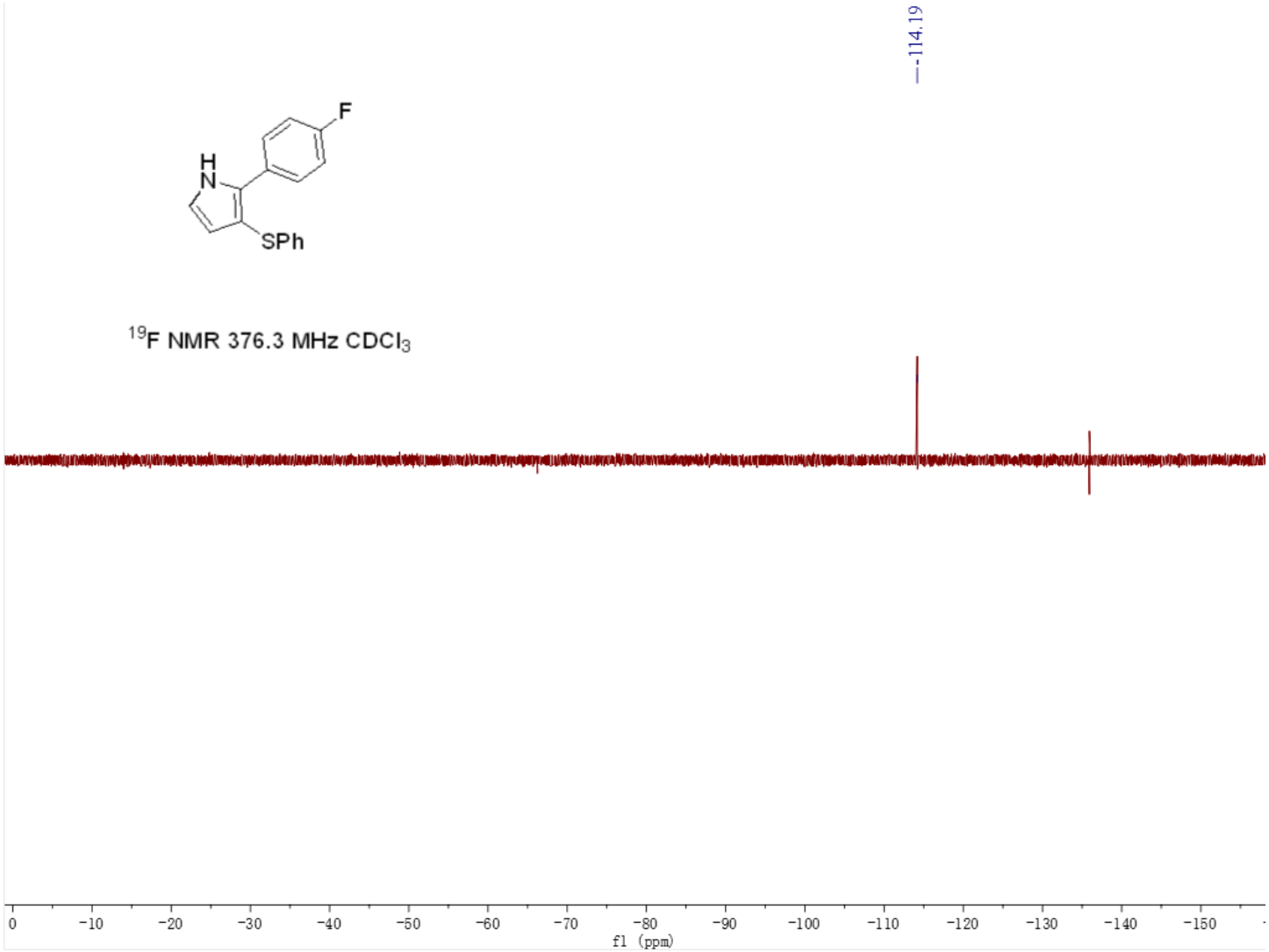
9



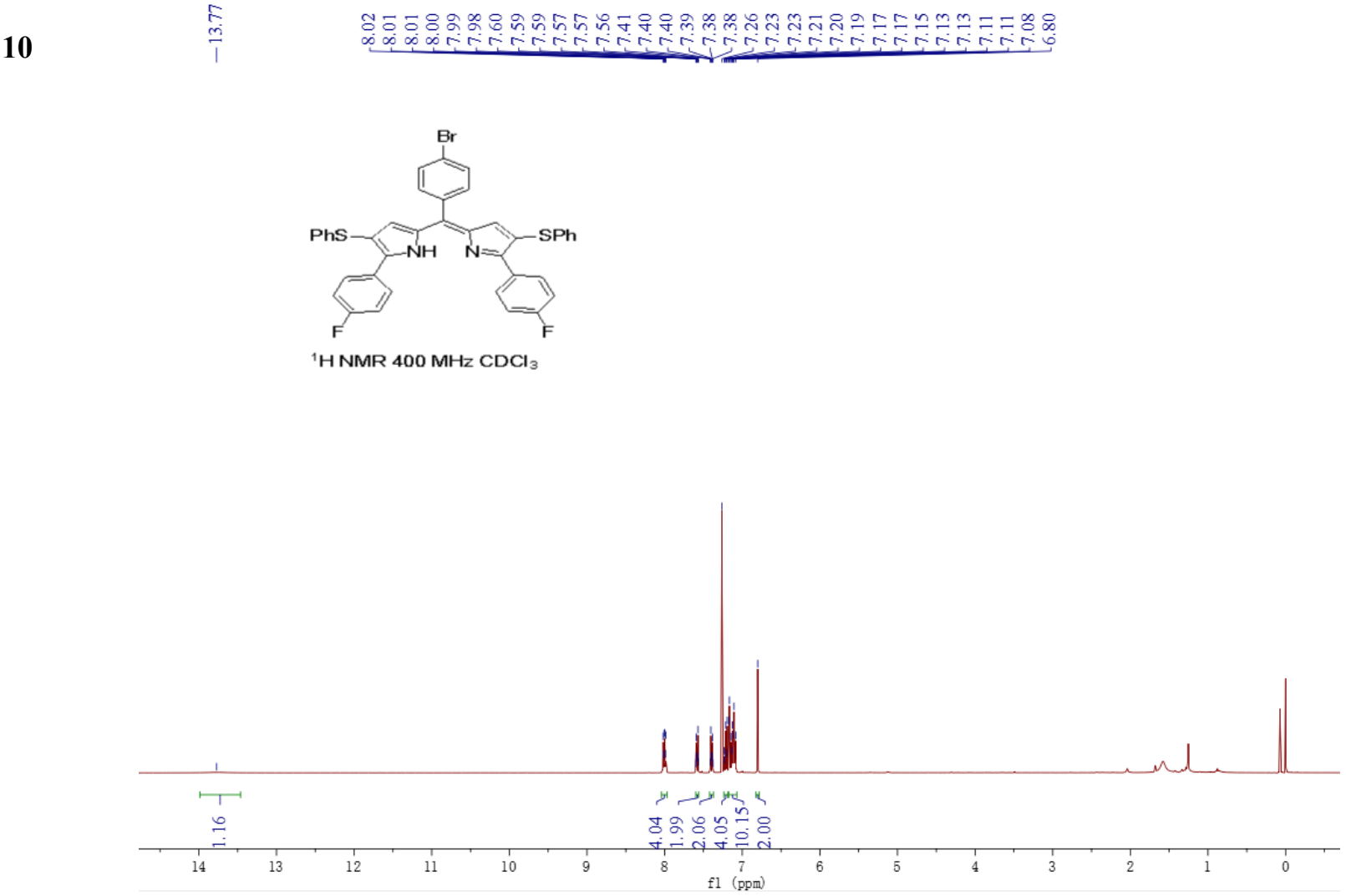
^{1}H NMR 400 MHz $CDCl_3$



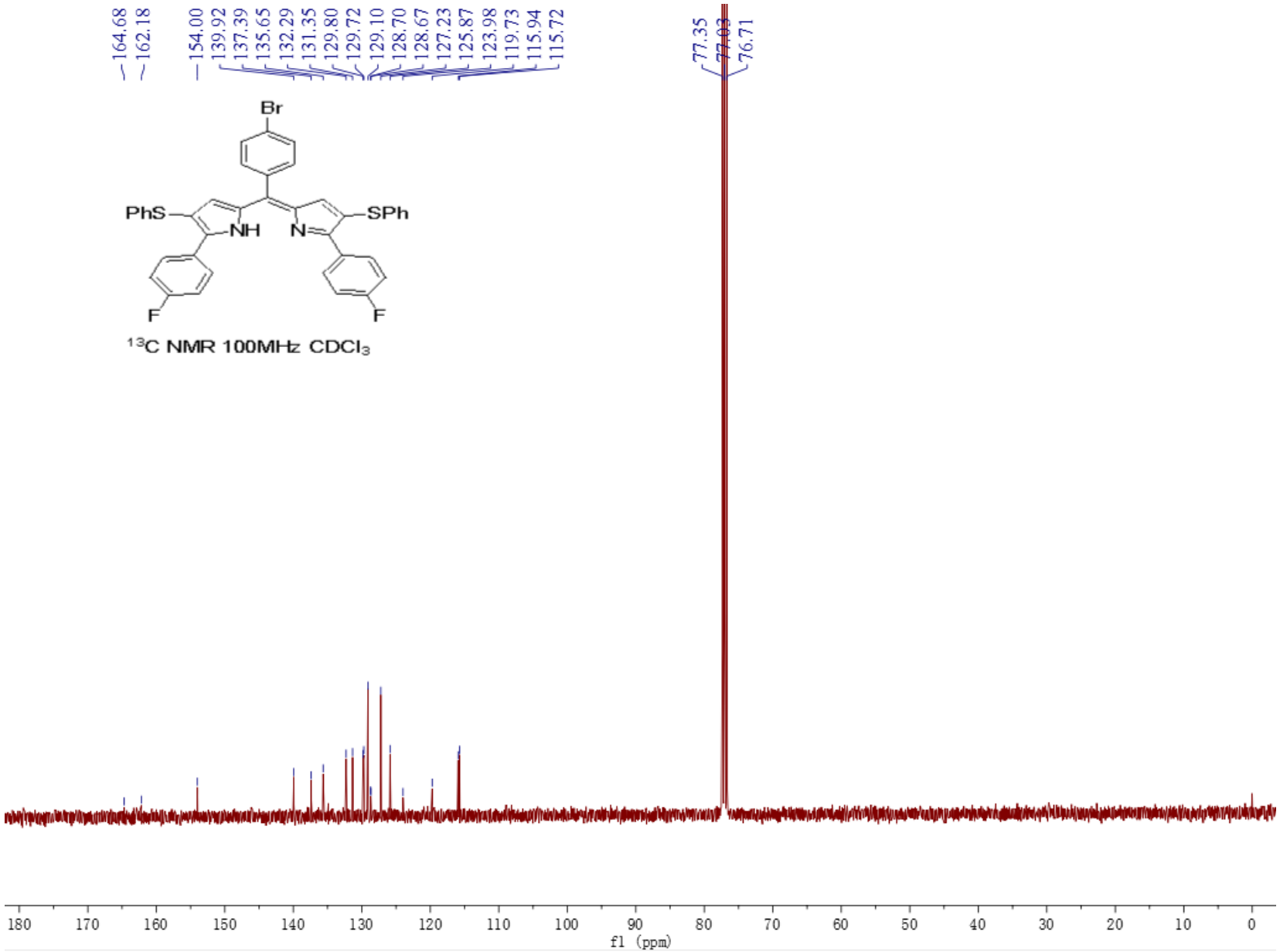

163.38
160.93
140.18
134.78
128.80
128.73
127.95
127.92
125.58
124.65
118.61
117.19
115.77
115.56
105.92
77.36
77.04
76.72
F
H
N
SPh
13C NMR 100 MHz CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

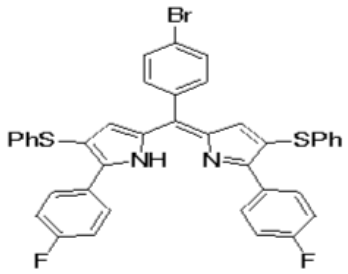

F
H
N
SPh
^{19}F NMR 376.3 MHz $CDCl_3$
-114.19
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)

10



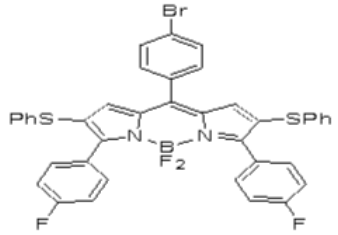
^{1}H NMR 400 MHz $CDCl_3$


164.68
162.18
154.00
139.92
137.39
135.65
132.29
131.35
129.80
129.72
129.10
128.70
128.67
127.23
125.87
123.98
119.73
115.94
115.72
77.35
77.03
76.71
Br
PhS
NH
N
SPh
F
F
13C NMR 100MHz CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

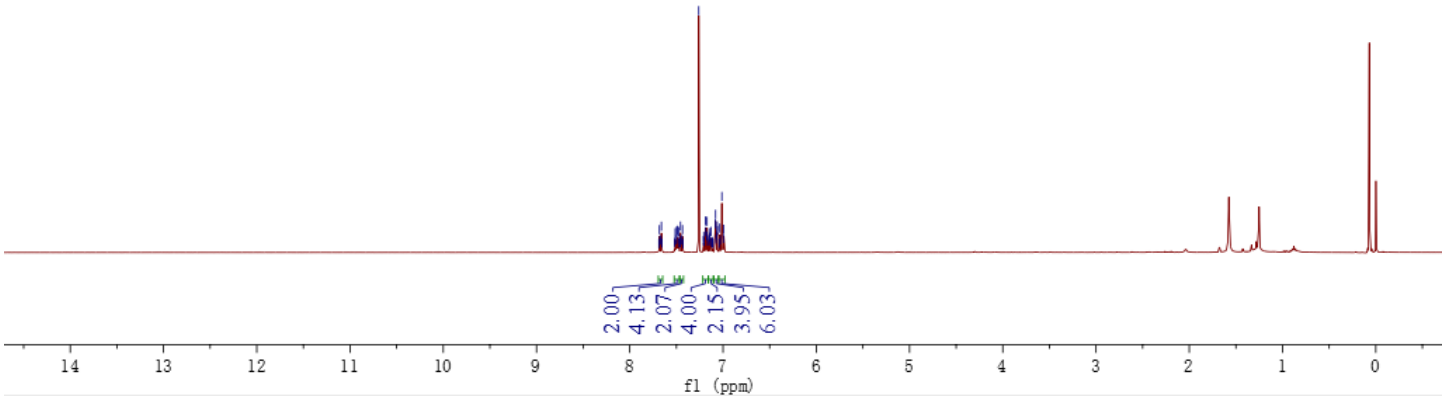


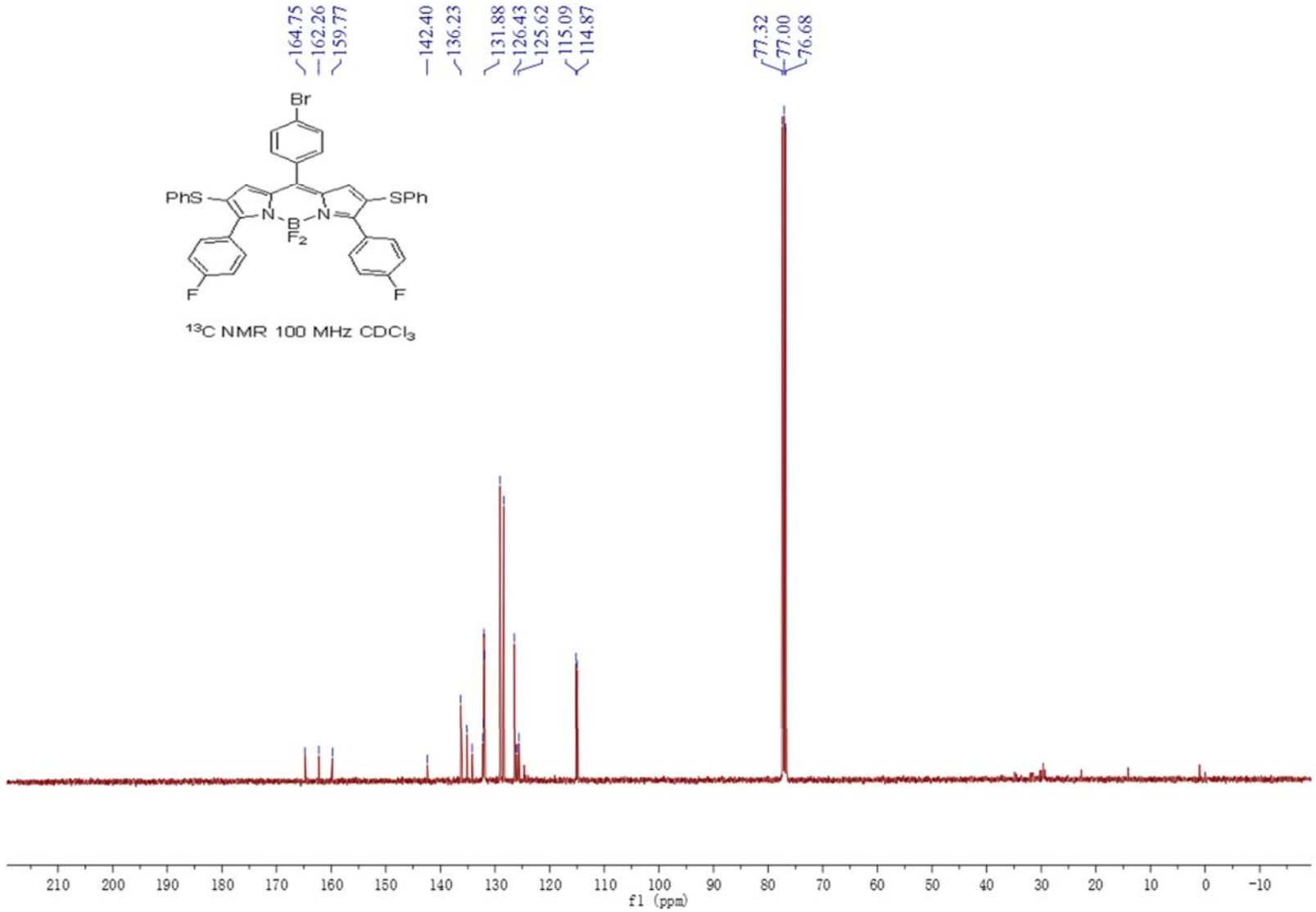
^{19}F NMR 376.3 MHz $CDCl_3$

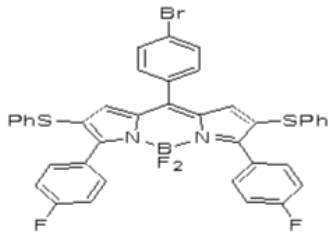
11



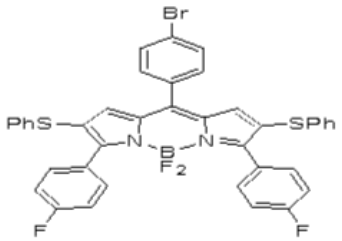
^{1}H NMR 400 MHz $CDCl_3$



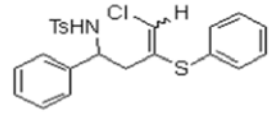

164.75
162.26
159.77
142.40
136.23
131.88
126.43
125.62
115.09
114.87
77.32
77.00
76.68
Br
PhS
SPh
N
B
N
F2
F
F
13C NMR 100 MHz CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



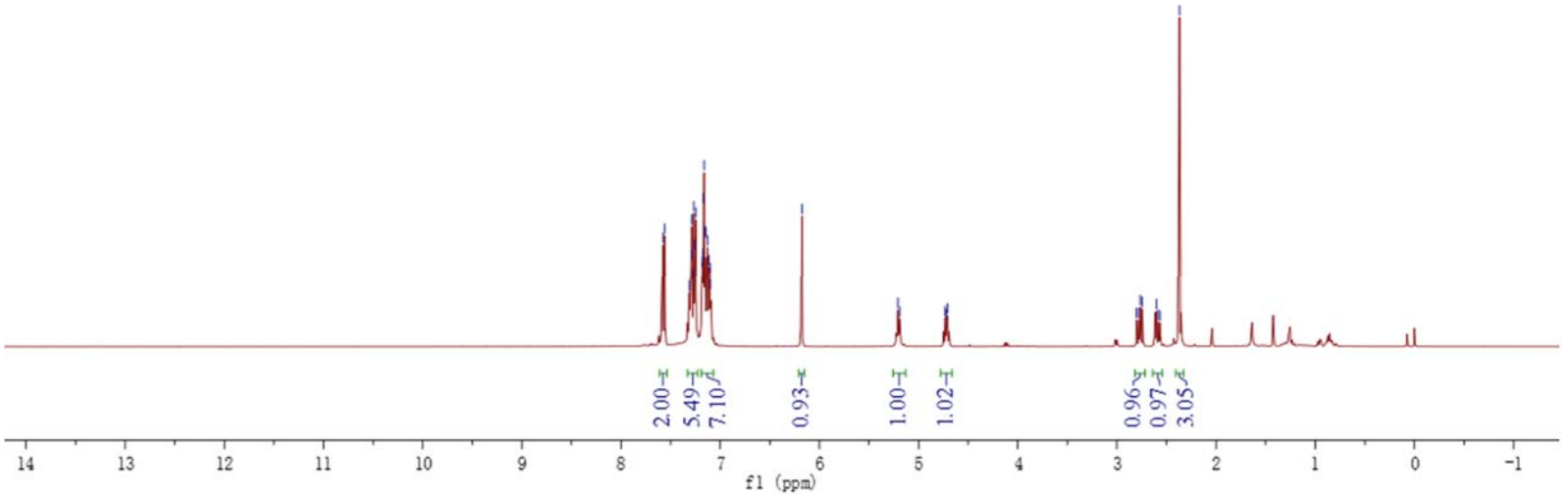
^{19}F NMR 376.3 MHz $CDCl_3$

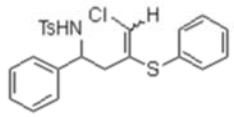


^{11}B NMR 128 MHz $CDCl_3$

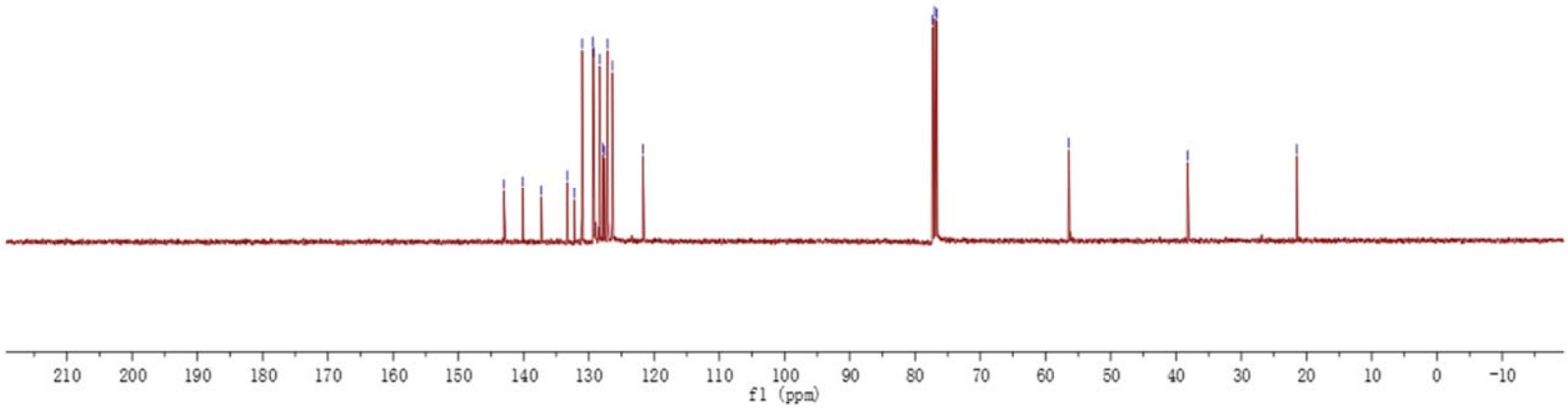


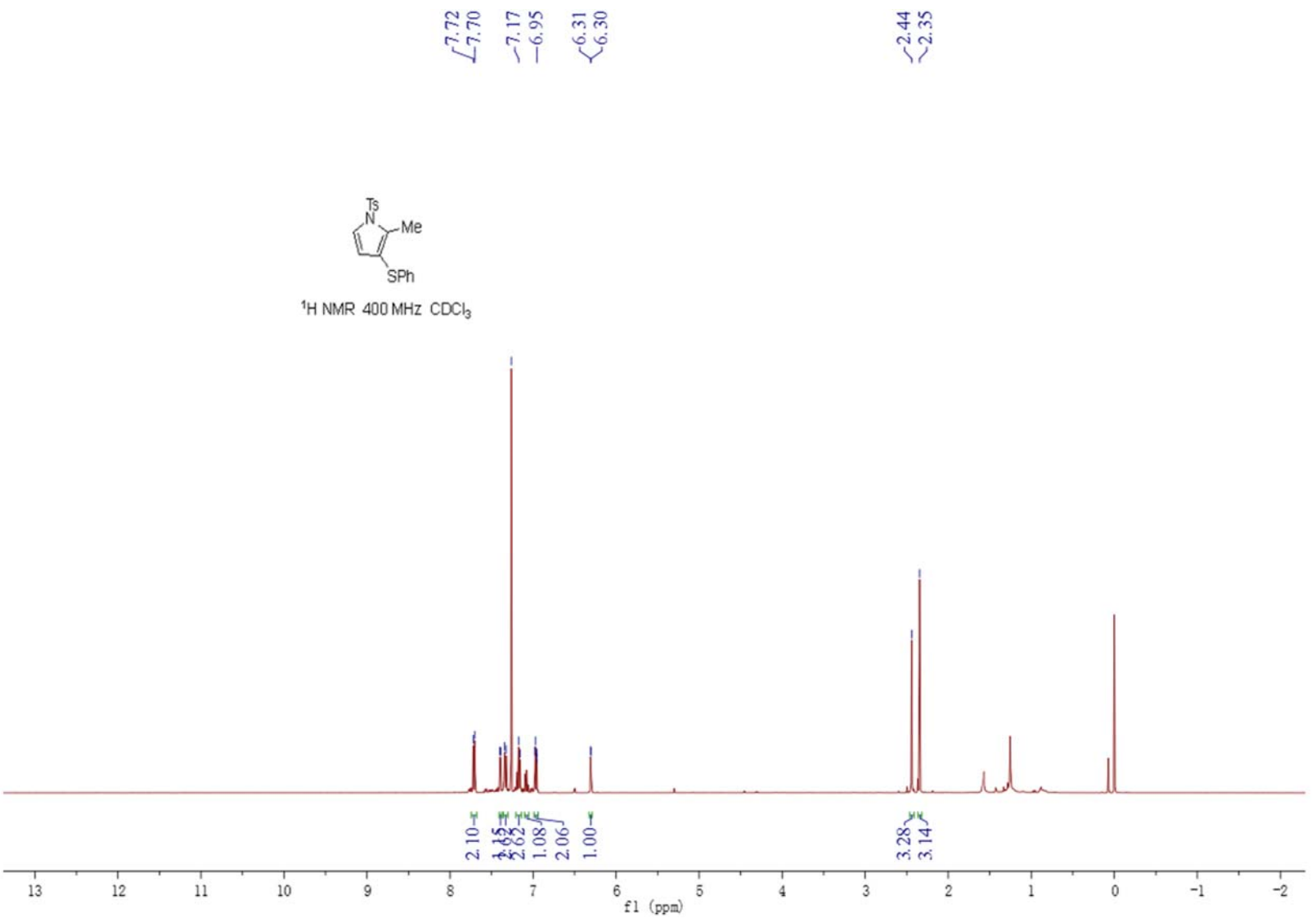
^{1}H NMR 400 MHz $CDCl_3$

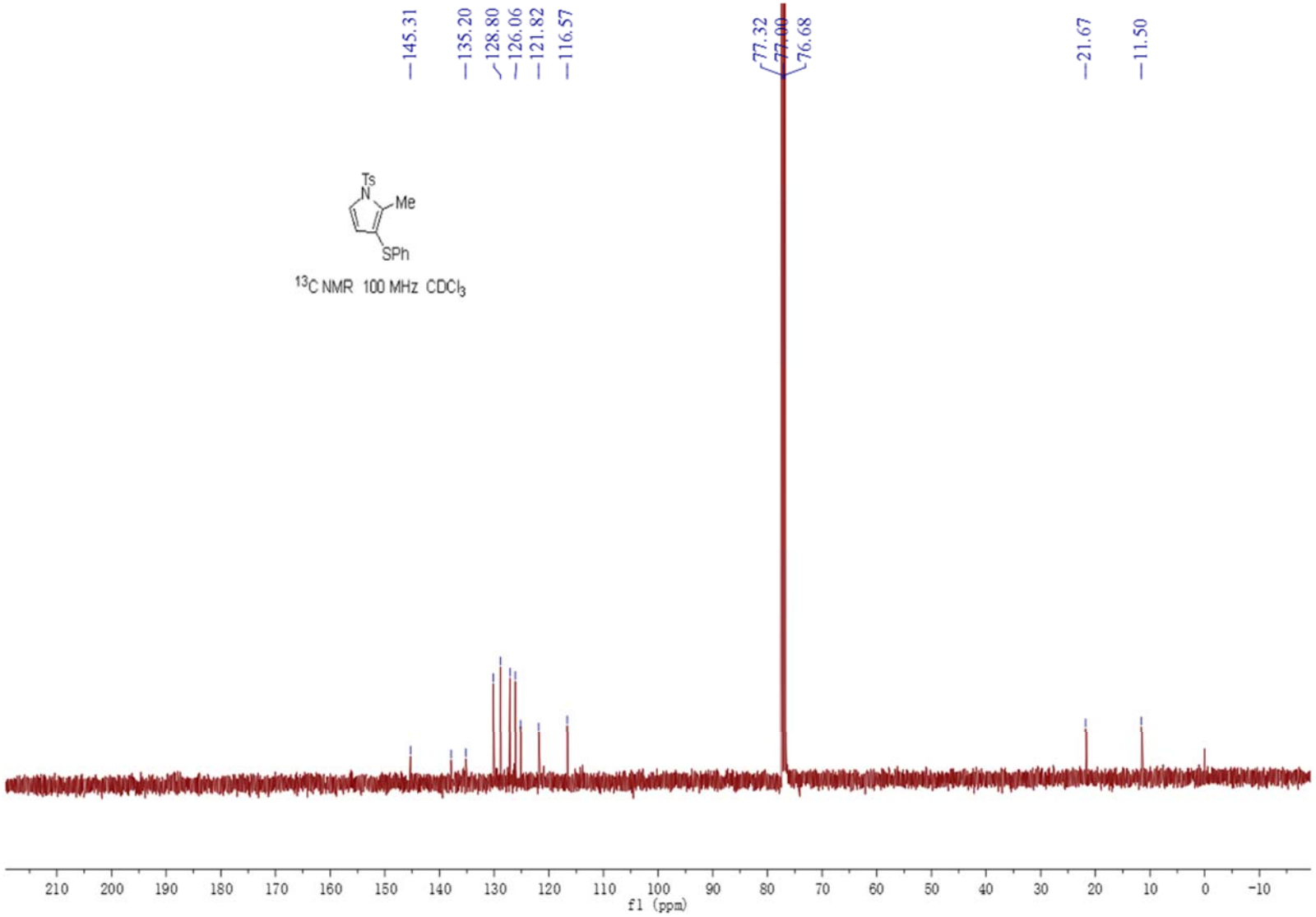


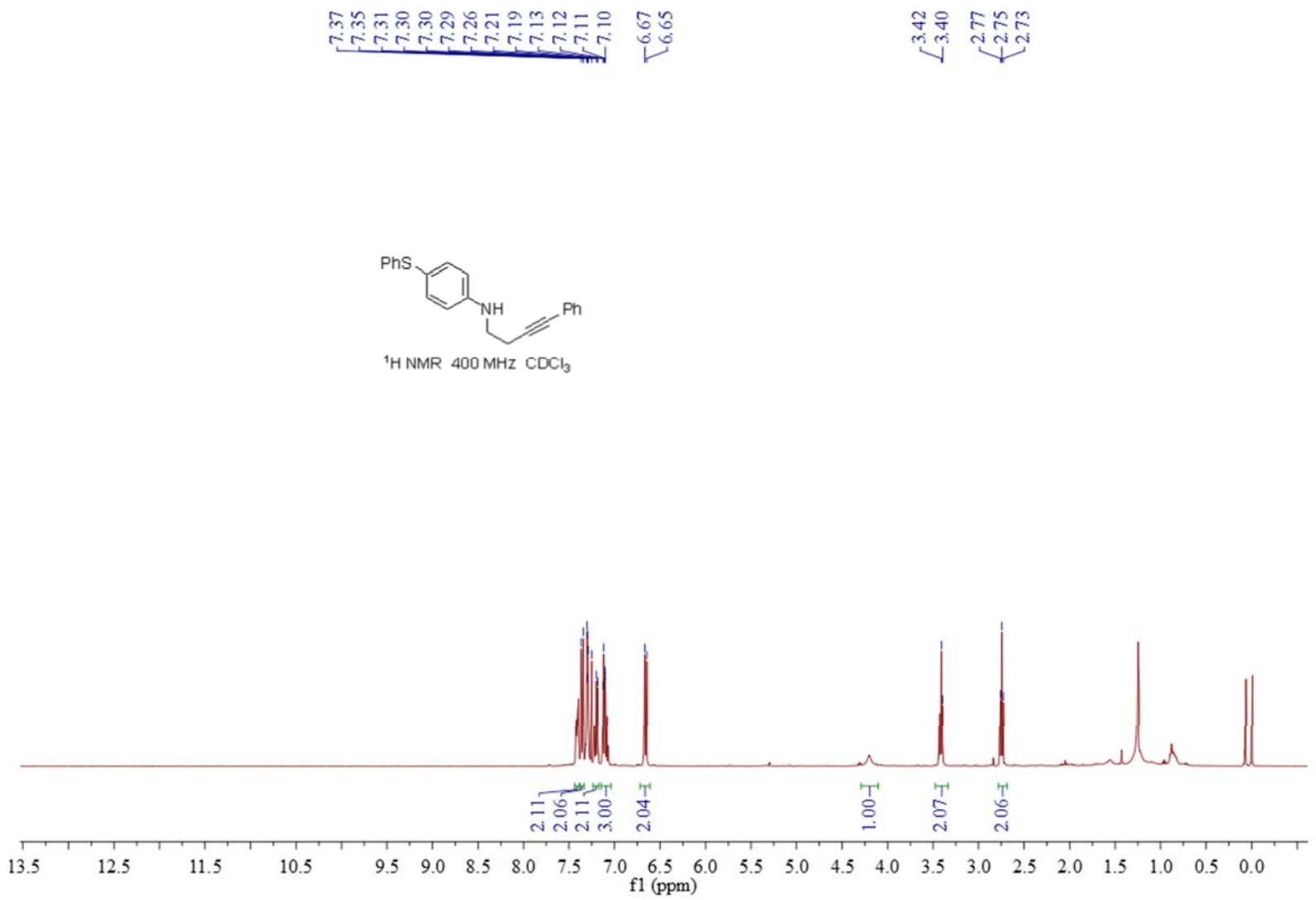


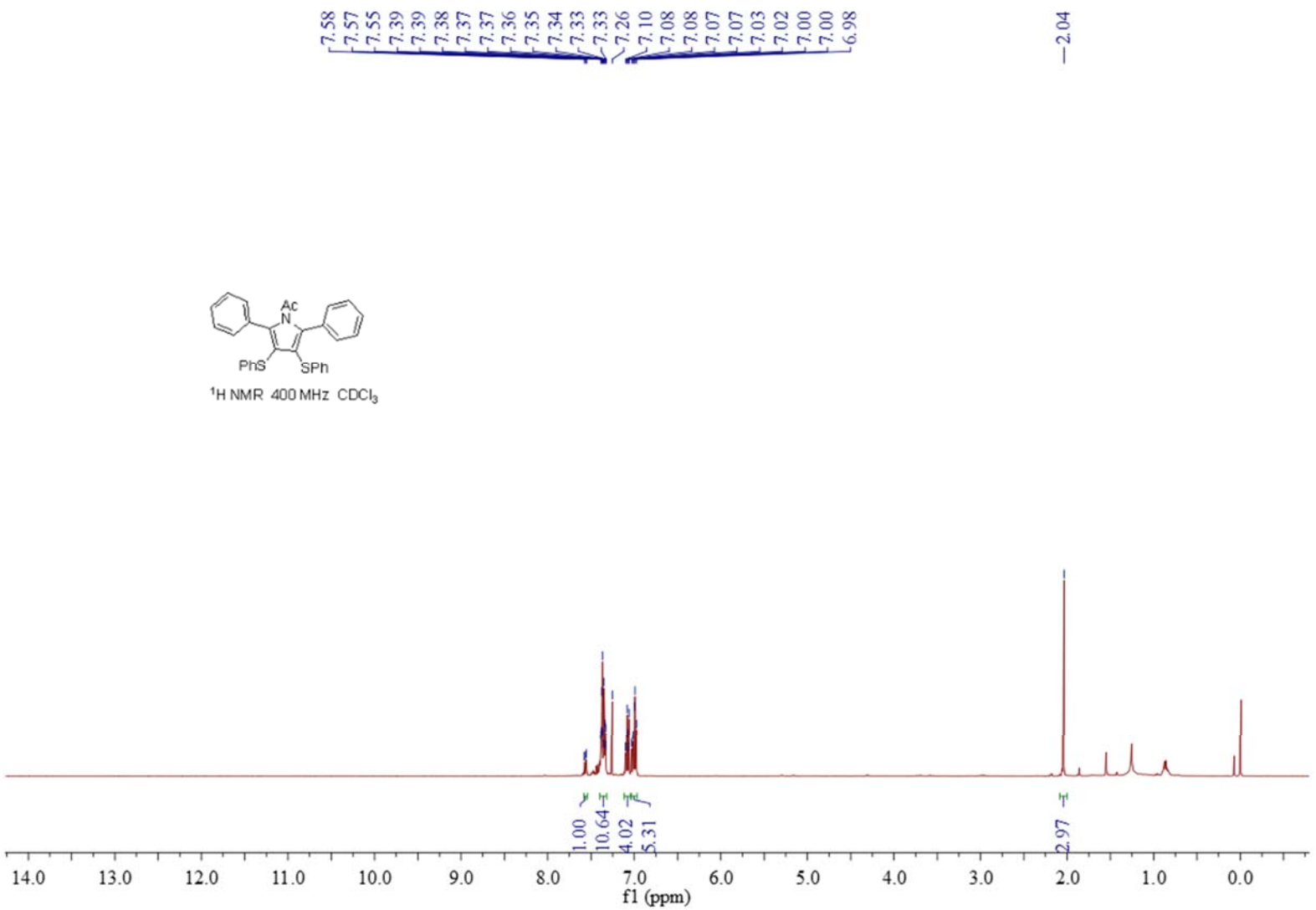
^{13}C NMR 100 MHz $CDCl_3$

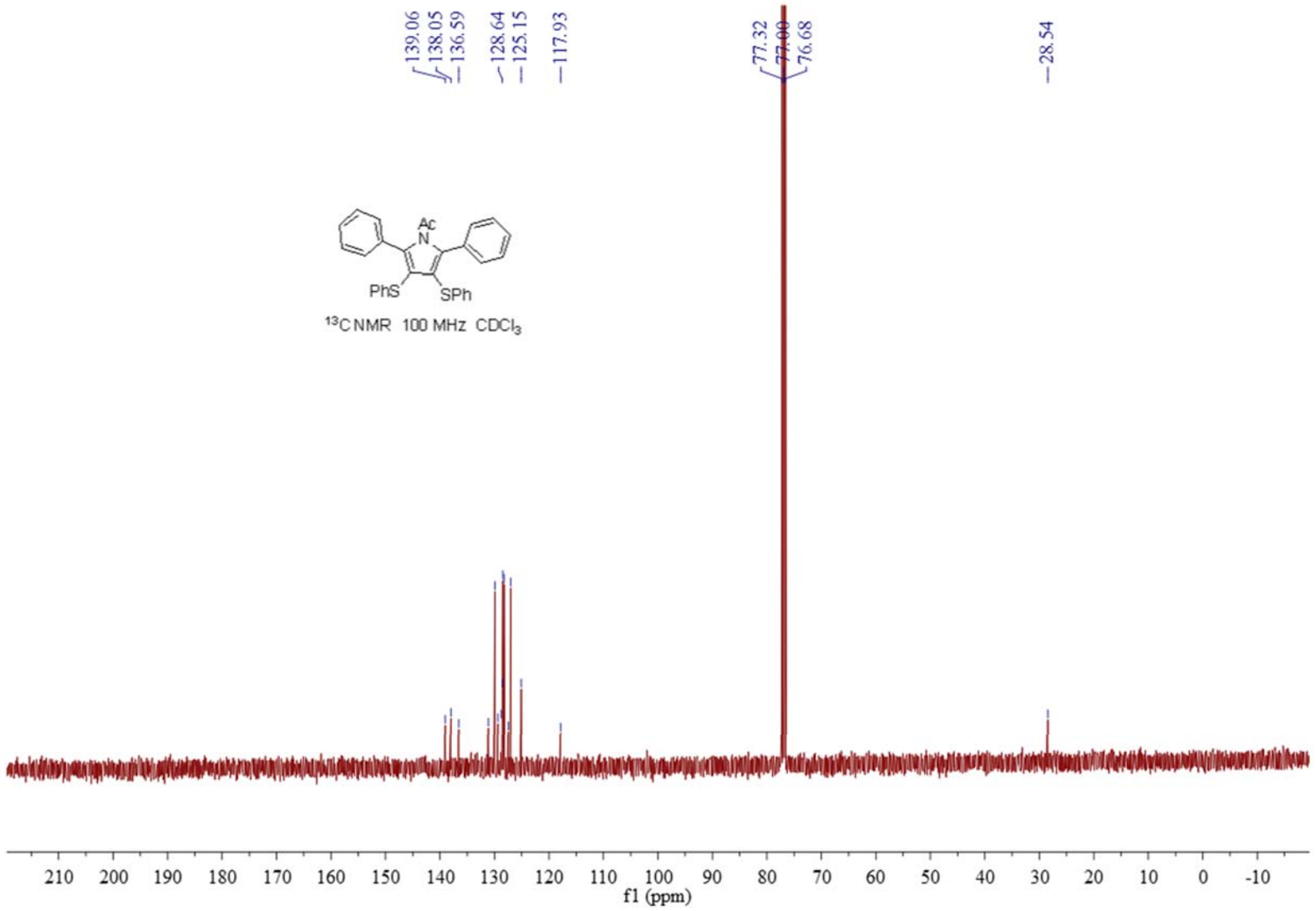


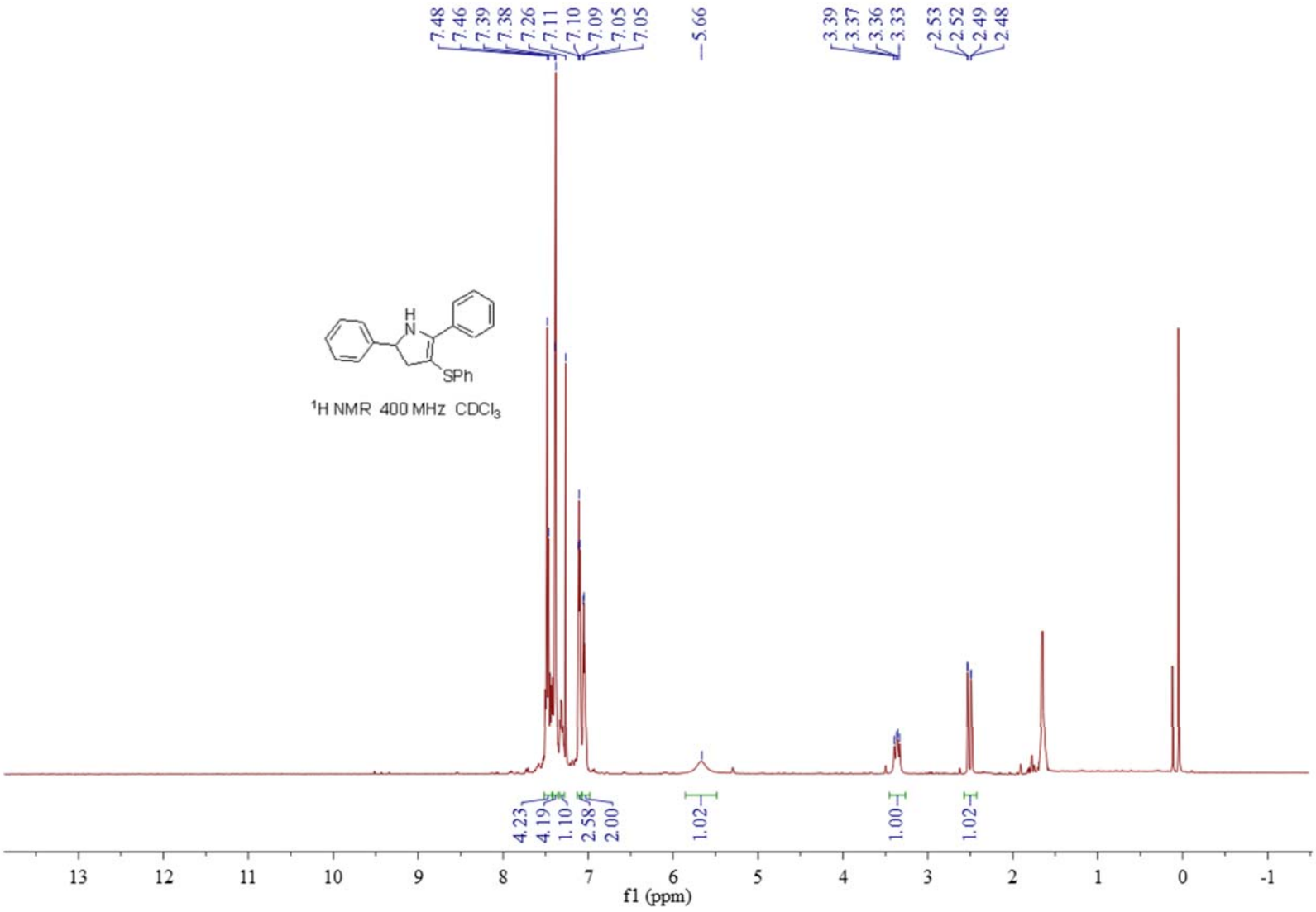

7.72
7.70
7.17
6.95
6.31
6.30
2.44
2.35
Ts
N
Me
SPh
1H NMR 400 MHz CDCl3
2.10
1.15
2.02
1.08
2.06
1.00
3.28
3.14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
f1 (ppm)

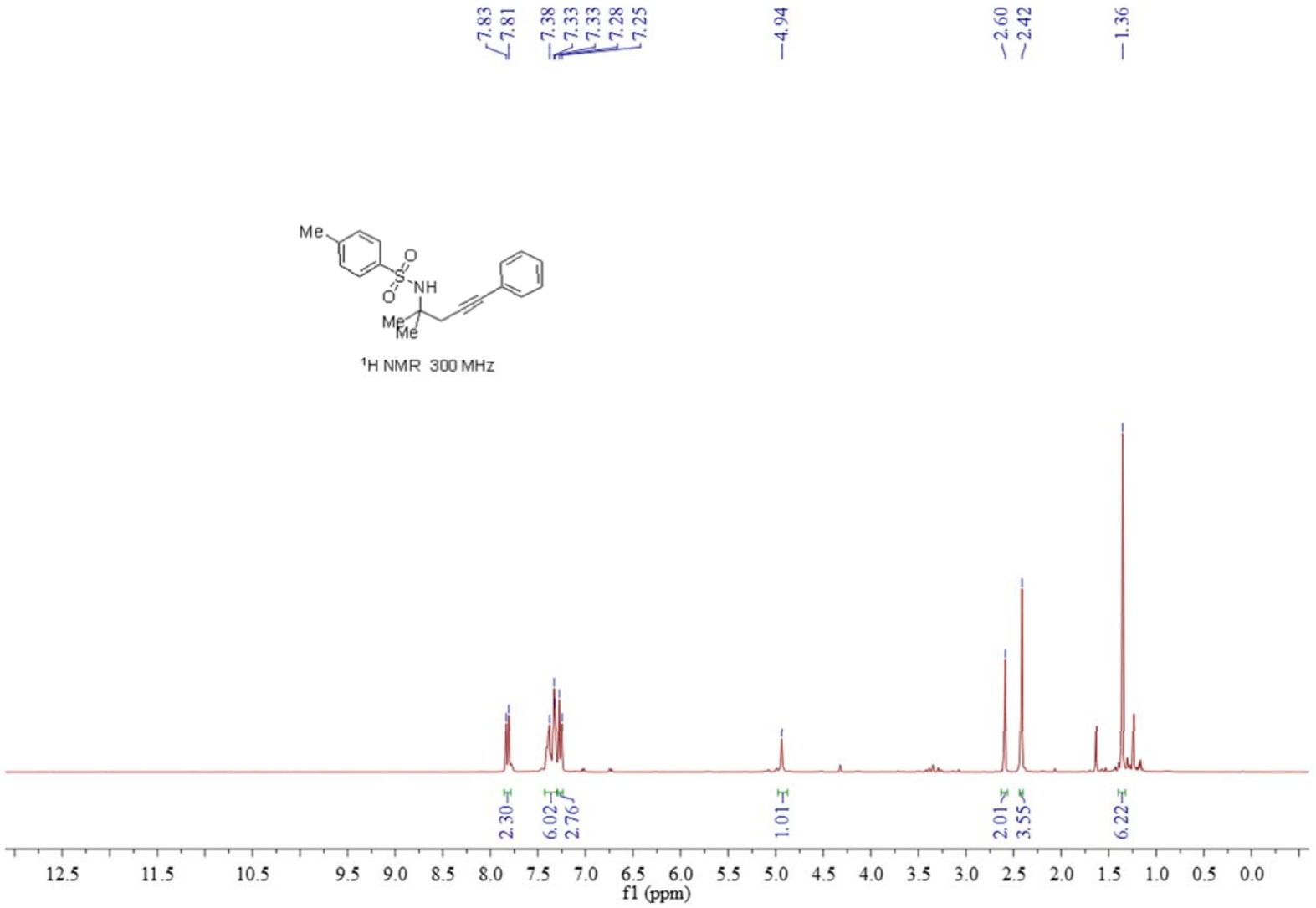

145.31
135.20
128.80
126.06
121.82
116.57
77.32
77.00
76.68
21.67
11.50
Ts
N
Me
SPh
13C NMR 100 MHz CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.37
7.35
7.31
7.30
7.30
7.29
7.26
7.21
7.19
7.13
7.12
7.11
7.10
6.67
6.65
3.42
3.40
2.77
2.75
2.73
PhS
NH
Ph
1H NMR 400 MHz CDCl3
2.11
2.06
2.11
3.00
2.04
1.00
2.07
2.06
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


7.58
7.57
7.55
7.39
7.39
7.38
7.37
7.37
7.36
7.35
7.34
7.33
7.33
7.26
7.10
7.08
7.08
7.07
7.07
7.03
7.02
7.00
7.00
6.98
2.04
Ac
N
PhS
SPh
1H NMR 400 MHz CDCl3
1.00
10.64
4.02
5.31
2.97
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


139.06
138.05
136.59
128.64
125.15
117.93
77.32
77.00
76.68
28.54
Ac
N
PhS
SPh
13C NMR 100 MHz CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.48
7.46
7.39
7.38
7.26
7.11
7.10
7.09
7.05
7.05
5.66
3.39
3.37
3.36
3.33
2.53
2.52
2.49
2.48
H
N
SPh
1H NMR 400 MHz CDCl3
4.23
4.19
1.10
2.58
2.00
1.02
1.00
1.02
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


7.83
7.81
7.38
7.33
7.33
7.28
7.25
4.94
2.60
2.42
1.36
Me
O
O
NH
Me
Me
¹H NMR 300 MHz
2.30
6.02
2.76
1.01
2.01
3.55
6.22
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)