SUPPORTING INFORMATION

Chemo-Orthogonal Biaryl Formation via Pd/Cu-Catalyzed Decarboxylative Coupling of Arylthianthrenium Salts

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General Methods

All reagents were purchased from commercial suppliers without further purification, and solvents were degassed with argon prior to use. Reactions were performed in oven-dried glassware under an argon atmosphere containing a Teflon-coated stirring bar and dry septum. All reactions were monitored by GC using tetradecane as an internal standard. Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. Flash column chromatography as performed over silica gel (200-300 mesh). NMR spectra were recorded on an Agilent DD2 400 MHz spectrometers using $CDCl_3$ or DMSO-d_6 as solvent with proton (400) and carbon (101) resonances. Chemical shifts (δ values) were reported in ppm relative to internal TMS (^{1}H NMR) or $CDCl_3$ (^{13}C NMR), respectively, and spin-spin coupling constants (*J*) were given in Hz. Melting points were measured on a Yanaco Micro Melting Point Apparatus. The High-resolution mass spectral (HRMS) data were obtained on Bruker Daltonics maXis Q-TOF (APCI and ESI).

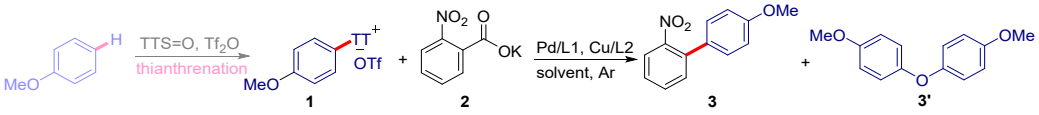
Preparation of the Starting Materials

All the potassium carboxylates were were prepared according to known literatures from carboxylic acids with potassium *t*-butoxide in EtOH.[1]

All the arylthianthrenium salts were prepared according to known literatures from arenes or arylboronic acids with thianthrene S-oxide in DCM or MeCN.[2] The arylthianthrenium salts were precipitated and washed with diethyl ether without further purification for the direct use.''

Optimization of the Reaction Conditions

Table S1: Optimization of the reaction conditions using potassium 2-nitrobenzoate (**1**) and *p*-methoxyphenylthianthrenium salt (**2**).[a]



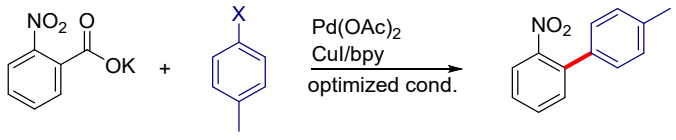
entry	Pd	L1	Cu	L2	Solvent	T	yield (%)	
							3	**3'**
1	$Pd(OAc)_2$	PPh_3	CuI	Phen	NMP/pyridine	110	30	15
2	''	''	''	''	DMSO	110	43	10
3	''	''	''	''	DMAc	''	35	11
4	''	''	''	''	NMP	''	36	8
5	''	''	''	''	DMF	''	30	6
6	''	''	''	''	Anisole	''	0	<1
7	''	''	''	''	*p*-xylene	''	2	<1
8	$Pd(OAc)_2$	PPh_3	''	Phen	DMSO	120	79	<1
9	''	''	CuCl	''	''	''	77	<1
10	''	''	CuBr	''	''	''	75	<1
11	''	''	Cu_2O	''	''	''	72	<1
12	''	''	$CuCl_2$	''	''	''	15	<1
13	''	''	-	''	''	''	0	8
14	$Pd(OAc)_2$	PPh_3	CuI	dtbpy	DMSO	120	87	<1

15	”	”	”	bpy	”	”	89	<1
16	”	”	”	TEMED	”	”	88	<1
17	”	”	”	None	”	”	40	13
18	$PdCl_2$	PPh_3	CuI	bpy	DMSO	120	85	<1
19	$Pd(acac)_2$	”	”	”	”	”	88	<1
20	$Pd(TFA)_2$	”	”	”	”	”	89	<1
21[b]	$Pd(OAc)_2$	PPh_3	CuI	bpy	DMSO	120	78	<1
22	$Pd(OAc)_2$	$P(Cy)_3$	CuI	bpy	DMSO	120	81	<1
23	”	$P(5F\text{-}Ph)_3$	”	”	”	”	76	<1
24	”	$P(2\text{-}Furyl)_3$	”	”	”	”	81	<1
25	$Pd(OAc)_2$	None	CuI	bpy	DMSO	120	99	<1
26	None	$P(Cy)_3$	”	”	”	”	0	<1
27[c]	$Pd(OAc)_2$	None	”	”	”	”	18	6
28[d]	”	”	”	”	”	”	0	<1
29[e]	”	”	”	”	”	”	0	12
30[f]	”	”	”	”	”	”	99	<1
31[g]	”	”	”	”	”	”	5	8

[a] Conditions: 0.2 mmol of **1**, 0.24 mmol of **2**, 2.5 mol% of [Pd] catalyst, 5 mol% of L1, 5 mol% of [Cu] catalyst, 5 mol% of L2, in 1 mL of solvent, under an argon atmosphere for 16 h; Yields determined by GC using *n*-tetradecane as the internal standard. [b] with 2 mol% of $Pd(OAc)_2$. [c] with 2.5 mol% of CuI and 2.5 mol% of bpy. [d] under air. [e] with 0.2 mmol of H_2O. [f] with 0.1 mmol of thianthrene. [g] 0.24 mmol of 2-nitrobenzoic acid and 0.36 mol of K_2CO_3 instead of **2**.

Selectivity on Arylthianthrenium Salts vs Arylhalides and Aryl triflates

Control Experiment with Arylhalides and Aryl triflates



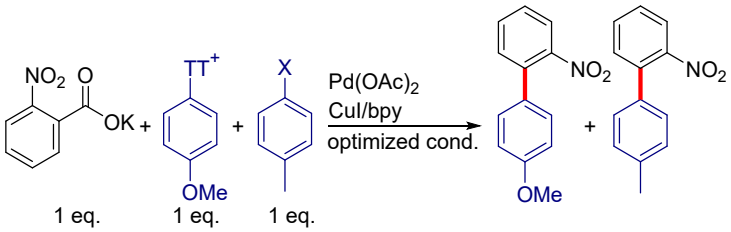
1.0 eq. 1 eq.

	X = OTf, Cl	X = Br	X = I
	n.d.	35%	56%
with TT	n.d.	35%	55%

Reaction Conditions: 0.2 mmol aryl halides or aryl triflates, 0.2 mmol 2-nitrobenzoate, with or without 0.1 mol thianthrene, 2.5 mol% $Pd(OAc)_2$, 5 mol% CuI, 5 mol% bpy, in 1 mL DMSO, at 120 °C, under an argon atmosphere for 16 h.

Procedure: An oven-dried vessel was charged with arylhalides or aryl triflates (0.20 mmol, 1 equiv.), and 2-nitrobenzoate (0.20 mmol, 1.2 equiv.), $Pd(OAc)_2$ (1.2 mg, 5.00 μmol, 0.025 equiv.), CuI (1.9 mg, 0.01 mmol, 0.05 equiv.), bpy (1.6 mg, 0.01 mmol, 0.05 equiv.), with or without thianthrene (21.6 mg, 0.1 mmol, 0.5 equiv.). Under argon atmosphere conditions, DMSO (1 mL) was added via syringe. The resulting reaction mixture was stirred at 120 °C for 16 h. Brine (10 mL) was added and the resulting mixture was extracted with ethyl acetate (3×20 mL). The combined organic layers were dried over $MgSO_4$, filtered, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography (SiO_2, ethyl acetate/cyclohexane gradient), affording the corresponding products.

Competing Experiment using Arylthianthrenium Salts with Arylhalides or Aryl triflates



1 eq. 1 eq. 1 eq.

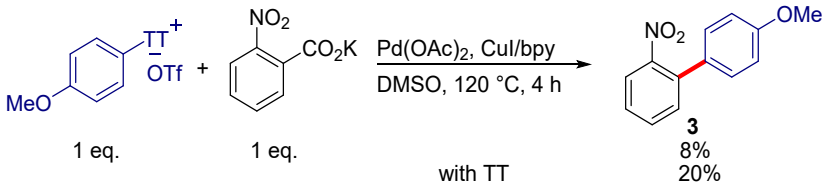
X = Cl	TT^+ vs. Cl		86%	n.d.
		with TT	87%	n.d.
X = OTf	TT^+ vs. OTf		87%	n.d.
		with TT	87%	n.d.
X = Br	TT^+ vs. Br		80%	9%
		with TT	83%	6%
X = I	TT^+ vs. I		62%	21%
		with TT	70%	12%

Reaction Conditions: 0.2 mmol 2-nitrobenzoate, 0.2 mmol aryl halides, 0.2 mmol arylthianthrenium salt, with or without 0.1 mol thianthrene, 2.5 mol% $Pd(OAc)_2$, 5 mol% CuI, 5 mol% bpy, in 1 mL DMSO, at 120 °C, under an argon atmosphere for 16 h.

Procedure: An oven-dried vessel was charged with arylhalides or aryl triflates (0.20 mmol, 1 equiv.), rylthianthrenium salt (0.20 mmol, 1 equiv.), and 2-nitrobenzoate (0.20 mmol, 1.2 equiv.), $Pd(OAc)_2$ (1.2 mg, 5.00 μmol, 0.025 equiv.), CuI (1.9 mg, 0.01 mmol, 0.05 equiv.), bpy (1.6 mg, 0.01 mmol, 0.05 equiv.), with or without thianthrene (21.6 mg, 0.1 mmol, 0.5 equiv.). Under argon atmosphere conditions, DMSO (1 mL) was added via syringe. The resulting reaction mixture was stirred at 120 °C for 16 h. Brine (10 mL) was added and the resulting mixture was extracted with ethyl acetate (3×20 mL). The combined organic layers were dried over $MgSO_4$, filtered, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography (SiO_2, ethyl acetate/cyclohexane gradient), affording the corresponding products.

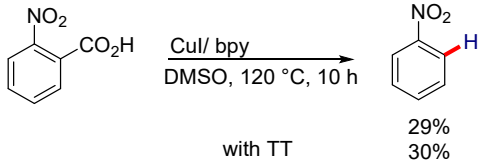
Mechanistic Studies

Effect of thianthrene addition on the transformation



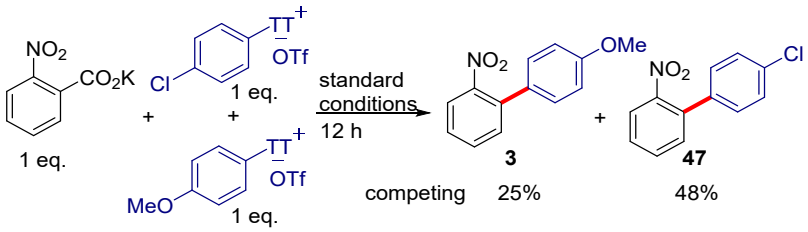
Reaction Conditions: 0.2 mmol 2-nitrobenzoate, 0.2 mmol 5-(4-methoxyphenyl)-5H-thianthren-5-ium trifluoromethanesulfonate, with or without 0.1 mol thianthrene, 2.5 mol% $Pd(OAc)_2$, 5 mol% CuI, 5 mol% bpy, in 1 mL DMSO, at 120 °C, under an argon atmosphere for 4 h; isolated yields.

Effect of thianthrene addition on the decarboxylation



Reaction Conditions: 0.2 mmol 2-nitro benzoic acid, with or without 0.1 mol thianthrene, 5 mol% CuI, 5 mol% bpy, in 1 mL DMSO, at 120 °C, under an argon atmosphere for 10 h; the yields were determined by GC.

Competing expriments with electronically different arylthianthrenium salts

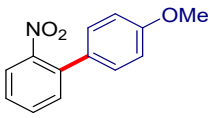


Reaction Conditions: 0.2 mmol 2-nitrobenzoate, 0.2 mmol 5-(4-methoxyphenyl)-5H-thianthren-5-ium trifluoromethanesulfonate, 0.2 mmol 5-(4-chlorophenyl)-5H-thianthren-5-ium trifluoromethanesulfonate, 2.5 mol% $Pd(OAc)_2$, 5 mol% CuI, 5 mol% bpy, in 1 mL DMSO, at 120 °C, under an argon atmosphere for 12 h; isolated yields.

Synthesis and Characterization of the Corresponding Products

General Procedure A: An oven-dried vessel was charged with arylthianthrenium salts (0.20 mmol, 1 equiv.), and potassium carboxylate (0.24 mmol, 1.2 equiv.), $Pd(OAc)_2$ (1.2 mg, 5.00 μmol, 0.025 equiv.), CuI (1.9 mg, 0.01 mmol, 0.05 equiv.), bpy (1.6 mg, 0.01 mmol, 0.05 equiv.). Under argon atmosphere conditions, DMSO (1 mL) was added via syringe. The resulting reaction mixture was stirred at 120 °C for 16 h. Brine (10 mL) was added and the resulting mixture was extracted with ethyl acetate (3×20 mL). The combined organic layers were dried over $MgSO_4$, filtered, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography (SiO_2, ethyl acetate/cyclohexane gradient), affording the corresponding products.

4'-methoxy-2-nitro-1,1'-biphenyl (3)



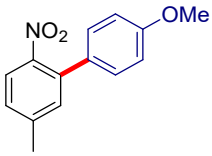
Compound **3** was prepared following the procedure **A**, starting from 5-(4-methoxyphenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (94.5 mg,0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol) After column chromatography on silica (Petroleum Ether: EtOAc = 15:1), **3** was afforded as yellowish-green oil liquid (44.0 mg, 96%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 – 7.77 (m, 1H), 7.63 – 7.54 (m, 1H), 7.49 – 7.39 (m, 2H), 7.28 – 7.24 (m, 2H), 7.01 – 6.92 (m, 2H), 3.85 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.7, 149.4, 135.8, 132.1, 131.9, 129.5, 129.1, 127.7, 124.0, 114.2, 55.3 ppm.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{11}NO_3Na^+$ 252.0631; found 252.0626.

4'-methoxy-5-methyl-2-nitro-1,1'-biphenyl (4)



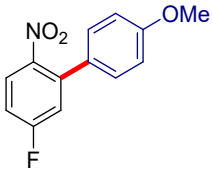
Compound **4** was prepared following the procedure **A**, starting from 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (94.5 mg, 0.2 mmol) and potassium 5-methyl-2-nitrobenzoate (52.6 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15:1), **4** was afforded as yellowish-green oil liquid (44.8 mg, 92%)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 – 7.69 (m, 1H), 7.28 – 7.17 (m, 4H), 6.99 – 6.91 (m, 2H), 3.83 (s, 3H), 2.44 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5, 147.0, 143.1, 136.0, 132.5, 129.9, 129.1, 128.2, 124.3, 114.1, 55.3, 21.3 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}NO_3^+$ 244.0968; found 244.0966.

5-fluoro-4'-methoxy-2-nitro-1,1'-biphenyl (5)



Compound **5** was prepared following the procedure **A**, starting from 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (94.5 mg, 0.2 mmol) and potassium 5-fluoro-2-nitrobenzoate (53.4 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15:1), **5** was afforded as yellow solid (44.5 mg, 90%)

M.P.: 94 – 95 °C.

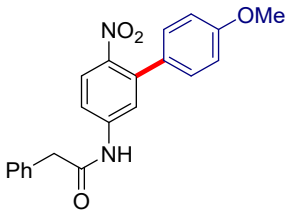
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 – 7.84 (m, 1H), 7.27 – 7.21 (m, 2H), 7.15 – 7.07 (m, 2H), 6.99 – 6.93 (m, 2H), 3.85 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) : δ 163.8 (d, *J* = 256.9 Hz), 160.0, 139.1 (d, *J* = 9.3 Hz), 129.0, 128.5 (d, *J* = 1.9 Hz), 126.8 (d, *J* = 10.0 Hz), 118.7 (d, *J* = 23.4 Hz), 114.6 (d, *J* = 23.5 Hz), 114.3, 55.3 ppm.

^{19}F NMR (377 MHz, $CDCl_3$): δ – 105.2 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{11}FNO_3^+$ 248.0717; found 248.0711.

N-(4'-methoxy-6-nitro-[1,1'-biphenyl]-3-yl)-2-phenylacetamide (6)



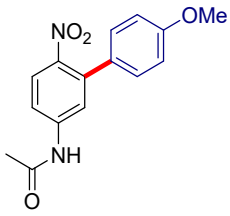
Compound **6** was prepared following the procedure **A**, starting from 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (94.5 mg, 0.2 mmol) and potassium 2-nitro-5-(2-phenylacetamido)benzoate (81.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 3:1), **6** was afforded as yellow waxy liquid (54.4 mg, 75%)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 – 7.72 (m, 2H), 7.59 – 7.51 (m, 1H), 7.47 (s, 1H), 7.39 – 7.31 (m, 3H), 7.28 (d, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.88 (d, *J* = 8.2 Hz, 2H), 3.79 (s, 3H), 3.70 (s, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.8, 159.6, 144.3, 141.3, 137.8, 133.7, 129.5, 129.3, 129.2, 129.0, 127.8, 125.8, 122.0, 117.8, 114.0, 55.2, 44.6 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{19}N_2O_4^+$ 363.1339; found 363.1330.

N-(4'-methoxy-6-nitro-[1,1'-biphenyl]-3-yl)acetamide (7)



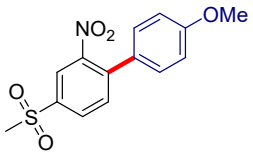
Compound **7** was prepared following the procedure **A**, starting from 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (94.5 mg, 0.2 mmol) and potassium 5-acetamido-2-nitrobenzoate (63.0 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 3:1), **7** was afforded as brown waxy liquid (49.1 mg, 83%)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 – 8.10 (m, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.67 – 7.52 (m, 2H), 7.21 – 7.11 (m, 2H), 6.94 – 6.82 (m, 2H), 3.80 (s, 3H), 2.16 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.0 159.6, 141.6, 137.8, 129.6, 129.0, 125.9, 125.0, 121.9, 117.8, 114.1, 55.3, 24.6 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{15}N_2O_4^+$ 287.1026; found 287.1018.

4'-methoxy-4-(methylsulfonyl)-2-nitro-1,1'-biphenyl (8)



Compound **8** was prepared following the procedure **A**, starting from 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (94.5 mg, 0.2 mmol) and potassium 4-(methylsulfonyl)-2-nitrobenzoate (68.0 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **8** was afforded as yellow solid (59.0 mg, 96%).

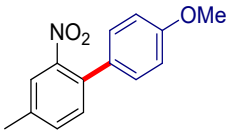
M.P.: 129 – 130 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 1.9 Hz, 1H), 8.16 – 8.09 (m, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.00 – 6.95 (m, 2H), 3.84 (s, 3H), 3.14 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.6, 149.3, 140.9, 140.1, 133.2, 130.4, 129.1, 127.4, 123.4, 114.6, 55.4, 44.4 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}NO_5S^+$ 308.0587; found 308.0581.

4'-methoxy-4-methyl-2-nitro-1,1'-biphenyl (9)



Compound **9** was prepared following the procedure **A**, starting from 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (94.5 mg, 0.2 mmol) and potassium 4-methyl-2-nitrobenzoate (52.6 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15:1), **9** was afforded as yellowish-green solid (38.4 mg, 79%).

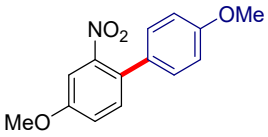
M.P.: 84 – 85 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 1H), 7.39 (d, *J* = 9.8 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.00 – 6.89 (m, 2H), 3.84 (s, 3H), 2.45 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5, 149.2, 138.2, 132.9, 132.9, 131.6, 129.5, 129.1, 124.2, 114.1, 55.3, 20.8 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}NO_3$ 244.0968; found 244.0968.

4,4'-dimethoxy-2-nitro-1,1'-biphenyl (10)



Compound **10** was prepared following the procedure **A**, starting from 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (94.5 mg, 0.2 mmol) and potassium 4-methoxy-2-nitrobenzoate (56.5 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 12:1), **10** was afforded as yellowish-green solid (38.4 mg, 74%).

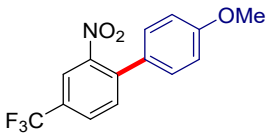
M.P.: 127 – 128 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.28 (m, 2H), 7.24 – 7.18 (m, 2H), 7.15 – 7.10 (m, 1H), 6.96 – 6.91 (m, 2H), 3.88 (s, 3H), 3.83 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5, 158.9, 149.8, 132.9, 129.6, 129.3, 128.3, 118.7, 114.2, 109.0, 56.0, 55.4 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}NO_4^+$ 260.0917; found 260.0908.

4'-methoxy-2-nitro-4-(trifluoromethyl)-1,1'-biphenyl (11)



Compound **11** was prepared following the procedure **A**, starting from 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (94.5 mg, 0.2 mmol) and potassium 2-nitro-4-(trifluoromethyl)benzoate (65.6 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 20:1), **11** was afforded as yellow solid (54.1 mg, 91%).

M.P.: 87 – 89 °C.

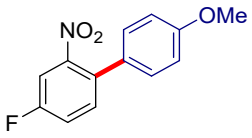
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.90 – 7.78 (m, 1H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.28 – 7.22 (m, 2H), 7.04 – 6.91 (m, 2H), 3.85 (s, 3H)ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.3, 149.2, 139.3, 132.7, 130.2 (q, *J* = 34.3 Hz), 129.1, 128.6 (q, *J* = 3.6 Hz), 127.9, 122.9 (q, *J* = 272.9 Hz), 121.3 (q, *J* = 2.0 Hz), 114.5, 55.3 ppm.

^{19}F NMR (377 MHz, $CDCl_3$): δ – 62.7 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{11}F_3NO_3^+$ 298.0686; found 298.0671.

4-fluoro-4'-methoxy-2-nitro-1,1'-biphenyl (12)



Compound **12** was prepared following the procedure **A**, starting from 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (94.5 mg, 0.2 mmol) and potassium 4-fluoro-2-nitrobenzoate (53.6 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 20:1), **12** was afforded as yellow solid (29.7 mg, 60%).

M.P.: 83 – 85 °C.

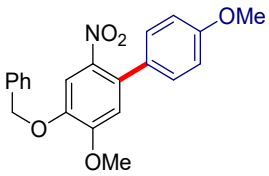
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 – 7.52 (m, 1H), 7.44 – 7.40 (m, 1H), 7.36 – 7.27 (m, 1H), 7.24 – 7.19 (m, 2H), 6.98 – 6.93 (m, 2H), 3.84 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.9 (d, *J* = 252.4 Hz), 159.7, 133.4 (d, *J* = 7.7 Hz) , 132.1 (d, *J* = 3.8 Hz), 129.2, 128.5, 119.4 (d, *J* = 21.1 Hz), 114.2, 111.6 (d, *J* = 26.6 Hz), 55.3 ppm.

^{19}F NMR (377 MHz, $CDCl_3$): δ – 112.0 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{11}FNO_3^+$ 248.0717; found 248.0708.

4-(benzyloxy)-4',5-dimethoxy-2-nitro-1,1'-biphenyl (13)



Compound **13** was prepared following the procedure **A**, starting from 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (94.5 mg, 0.2 mmol) and potassium 4-(benzyloxy)-5-methoxy-2-nitrobenzoate (81.9 mg, 0.24 mmol).After column chromatography on silica (Petroleum Ether: EtOAc = 15:1), **13** was afforded as brown solid (70.2 mg, 96%).

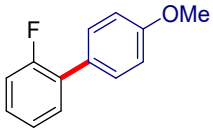
M.P.: 130 – 132 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (s, 1H), 7.52 – 7.45 (m, 2H), 7.44 – 7.39 (m, 2H), 7.38 – 7.33 (m, 1H), 7.25 – 7.19 (m, 2H), 6.99 – 6.91 (m, 2H), 6.79 (s, 1H), 5.21 (s, 2H), 3.94 (s, 3H), 3.84 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.3, 152.7, 146.7, 140.9, 135.7, 131.2, 130.3, 129.1, 128.7, 128.7, 128.3, 127.5, 113.9, 109.9, 71.3, 56.3, 55.2 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{20}NO_5^+$ 366.1336; found 366.1332.

2-fluoro-4'-methoxy-1,1'-biphenyl (14)



Compound **14** was prepared following the procedure **A**, starting from 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (94.5 mg, 0.2 mmol) and potassium 2-fluorobenzoate (42.8 mg, 0.24 mmol) with 0.1 mmol thianthrene, 10 mol% CuI and 10 mol% bpy at 160 ºC. After column chromatography on silica (Petroleum Ether: EtOAc = 20:1), **14** was afforded as yellow oil liquid (25.1 mg, 62%).

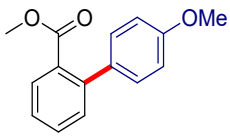
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 – 7.48 (m, 2H), 7.45 – 7.39 (m, 1H), 7.32 – 7.26 (m, 1H), 7.22 – 7.11 (m, 2H), 7.04 – 6.94 (m, 2H), 3.86 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.7 (d, *J* = 248.3 Hz), 159.2, 130.5 (d, *J* = 3.6 Hz), 130.1 (d, *J* = 3.1 Hz), 128.7 (d, *J* = 13.3 Hz), 128.3 (d, *J* = 8.2 Hz), 128.2, 124.3 (d, *J* = 3.9 Hz), 116.0 (d, *J* = 23.2 Hz), 113.9, 55.3 ppm.

^{19}F NMR (377 MHz, $CDCl_3$): δ – 117.1 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{12}FO^+$ 203.0867; found 203.0858.

methyl 4'-methoxy-[1,1'-biphenyl]-2-carboxylate (15)



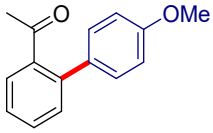
Compound **15** were prepared following the procedure **A**, starting from 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (94.5 mg, 0.2 mmol) and potassium 2-(methoxycarbonyl)benzoate (52.4 mg, 0.24 mmol) with 0.1 mmol thianthrene, 0.10 mmol CuCl, 10 mol% bpy at 160 ºC. After column chromatography on silica (Petroleum Ether: EtOAc = 15:1), **15** was afforded as colorless oil liquid (25.1 mg, 52%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 – 7.75 (m, 1H), 7.53 – 7.48 (m, 1H), 7.40 – 7.35 (m, 2H), 7.27 – 7.23 (m, 2H), 6.96 – 6.92 (m, 2H), 3.84 (s, 3H), 3.67 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.3, 158.9, 142.0, 133.6, 131.1, 130.8, 130.7, 129.7, 129.4, 126.7, 113.5, 55.2, 51.9 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{15}O_3^+$ 243.1016; found 243.1015.

1-(4'-methoxy-[1,1'-biphenyl]-2-yl)ethan-1-one (16)



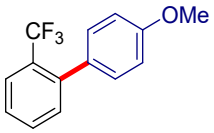
Compound **16** were prepared following the procedure **A**, starting from 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (94.5 mg, 0.2 mmol) and potassium 2-acetylbenzoate (48.6 mg, 0.24 mmol) with 0.1 mmol thianthrene, 0.10 mmol CuCl, 10 mol% bpy at 160 ºC. After column chromatography on silica (Petroleum Ether: EtOAc = 15:1), **16** was afforded as yellow oil liquid (26.3 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.47 (m, 2H), 7.42 – 7.35 (m, 2H), 7.29 – 7.25 (m, 2H), 7.01 – 6.91 (m, 2H), 3.86 (s, 3H), 2.02 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 205.3, 159.5, 140.9, 140.1, 133.0, 130.6, 130.1, 130.0, 127.8, 127.0, 114.1, 55.3, 30.4 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{15}O_2^+$ 227.1067; found 227.1061.

4'-methoxy-2-(trifluoromethyl)-1,1'-biphenyl (17)



Compound **17** was prepared following the procedure **A**, starting from 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (94.5 mg, 0.2 mmol) and potassium 2-(trifluoromethyl)benzoate (54.8 mg, 0.24 mmol) with 5 mol% $Pd(OAc)_2$, 0.10 mmol CuCl, 10 mol% bpy at 160 ºC. After column chromatography on silica (Petroleum Ether: EtOAc = 15:1), **17** was afforded as yellow oil liquid (15.2 mg, 30%).

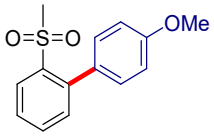
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.9 Hz, 1H), 7.59 – 7.51 (m, 1H), 7.49 -7.40 (m, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.00 – 6.89 (m, 2H), 3.86 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.1, 141.2, 132.3, 132.2, 131.2, 130.1 (q, *J* = 1.5 Hz), 128.6 (q, *J* = 29.3 Hz), 127.1, 126.0 (q, *J* = 6.1 Hz), 124.2 (q, *J* =275.5 Hz), 113.2, 55.2 ppm.

^{19}F NMR (377 MHz, $CDCl_3$): δ – 56.9 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{12}F_3O^+$ 253.0835; found 253.0833.

4'-methoxy-2-(methylsulfonyl)-1,1'-biphenyl (18)



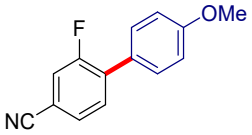
Compound **18** was prepared following the procedure **E**, starting from 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (94.5 mg, 0.2 mmol) and potassium 2-(methylsulfonyl)benzoate (57.2 mg, 0.24 mmol) with 5 mol% $Pd(OAc)_2$, 0.10 mmol CuCl, 10 mol% bpy at 160 ºC. After column chromatography on silica (Petroleum Ether: EtOAc = 7:1), **18** was afforded as yellow waxy liquid (27.3 mg, 52%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 – 8.16 (m, 1H), 7.65 – 7.60 (m, 1H), 7.56 – 7.50 (m, 1H), 7.44 – 7.38 (m, 2H), 7.38 – 7.34 (m, 1H), 7.00 – 6.95 (m, 2H), 3.86 (s, 3H), 2.62 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.7, 141.2, 139.4, 133.0, 132.9, 131.4, 130.5, 128.2, 127.6, 113.4, 55.3, 43.1 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{15}O_3S^+$ 263.0736; found 263.0724.

2-fluoro-4'-methoxy-[1,1'-biphenyl]-4-carbonitrile (19)



Compound **19** was prepared following the procedure **A**, starting from 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (94.5 mg, 0.2 mmol) and potassium 4-cyano-2-fluorobenzoate (48.8 mg, 0.24 mmol)) with 0.1 mmol thianthrene, 10 mol% CuI and 10 mol% bpy at 160 ºC. After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **19** was afforded as white solid (29.9 mg, 66%).

M.P.: 79 – 81 °C.

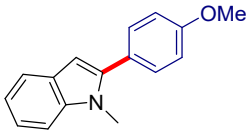
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 – 7.46 (m, 4H), 7.45 – 7.38 (m, 1H), 7.05 – 6.95 (m, 2H), 3.85 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.2, 159.0 (d, *J* = 251.9 Hz), 133.9 (d, *J* = 13.1 Hz), 131.2 (d, *J* = 5.1 Hz), 130.2 (d, *J* = 3.9 Hz), 128.3 (d, *J* = 3.9 Hz), 126.0, 119.8 (d, *J* = 26.6 Hz), 117.7 (d, *J* = 3.1 Hz), 114.2, 111.4 (d, *J* = 9.9 Hz), 55.3 ppm.

^{19}F NMR (377 MHz, $CDCl_3$): δ – 114.9 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{11}FNO^+$ 228.0819; found 228.0817.

2-(4-methoxyphenyl)-1-methyl-1H-indole (20)



Compound **20** was prepared following the procedure **A**, starting from 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (94.5 mg, 0.2 mmol) and potassium 1-methyl-1H-indole-2-carboxylate (51.2mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **20** was afforded as brown solid (24.2mg, 51%).

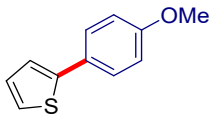
M.P.: 96 – 100 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 – 7.60 (m, 1H), 7.50 – 7.42 (m, 2H), 7.40 – 7.35 (m, 1H), 7.28 – 7.24 (m, 1H), 7.20 – 7.14 (m, 1H), 7.07 – 7.00 (m, 2H), 6.59 – 6.48 (m, 1H), 3.89 (s, 3H), 3.75 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.4, 141.4, 138.1, 130.6, 128.0, 125.2, 121.4, 120.2, 119.7, 113.9, 109.5, 101.0, 55.3, 31.0 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{16}NO^+$ 238.1226; found 238.1220.

2-(4-methoxyphenyl)thiophene (21)



Compound **21** was prepared following the procedure **A**, starting from 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (94.5 mg, 0.2 mmol) and potassium thiophene-2-carboxylate (39.9 mg, 0.24 mmol)) with 0.1 mmol thianthrene, 10 mol% CuI and 10 mol% bpy at 160 ºC. After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **21** was afforded as white solid (26.7mg, 70%).

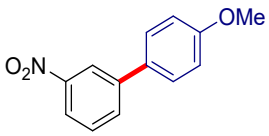
M.P.: 99 – 102 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 – 7.49 (m, 2H), 7.25 – 7.18 (m, 2H), 7.09 – 7.03 (m, 1H), 6.97 – 6.89 (m, 2H), 3.84 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.2, 144.3, 127.9, 127.3, 127.2, 123.8, 122.1, 114.2, 55.3 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{11}OS^+$ 191.0525; found 191.0519.

4'-methoxy-3-nitro-1,1'-biphenyl (22)

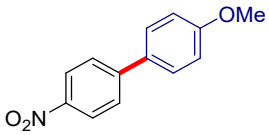


Compound **22** was prepared following the procedure **A**, starting from 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (94.5 mg, 0.2 mmol) and potassium 3-nitrobenzoate (49.2 mg, 0.24 mmol) with 5 mol% $Pd(OAc)_2$, 5 mol% Cu_2O, and 10 mol% Me_4Phen, and 10 mol% XPhos in NMP/quinoline (1:1) at 180 ºC. After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **22** was afforded as light yellow crystal (14.3mg, 31%).

M.P.: 79-81 °C

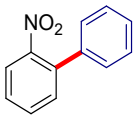
^{1}H NMR (400 MHz, $CDCl_3$): δ 1H NMR (400 MHz, Chloroform-d) δ 8.38 (t, *J* = 2.1 Hz, 1H), 8.18 – 8.08 (m, 1H), 7.88 – 7.84 (m, 1H), 7.58 – 7.53 (m, 3H), 7.03 – 6.99 (m, 2H), 3.86 (s, 3H) ppm.
Spectra data are consistent with the reported literature.[3]

4-methoxy-4'-nitro-1,1'-biphenyl (23)



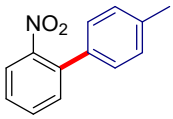
Compound **23** was prepared following the procedure **A**, starting from 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (94.5 mg, 0.2 mmol) and potassium 4-nitrobenzoate (49.2 mg, 0.24 mmol) with 5 mol% $Pd(OAc)_2$, 5 mol% Cu_2O, and 10 mol% Me_4Phen, and 10 mol% XPhos in NMP/quinoline (1:1) at 180 ºC. After column chromatography on silica (Petroleum Ether: EtOAc = 15:1), **23** was afforded as light yellow crystal (11.9 mg, 26%).
M.P.: 105-107 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 – 8.19 (m, 2H), 7.72 – 7.64 (m, 2H), 7.61 – 7.55 (m, 2H), 7.06 – 6.98 (m, 2H), 3.90 – 3.84 (m, 3H) ppm.
^{13}C NMR (101 MHz, $CDCl_3$): δ 160.3, 147.1, 146.4, 130.9, 128.5, 126.9, 124.0, 114.5, 55.3 ppm.
HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{11}NO_3Na^+$ 252.0631; found 252.0628.

2-nitro-1,1'-biphenyl (24)



Compound **24** was prepared following the procedure **A**, starting from 5-phenyl-5H-thianthren-5-ium trifluoromethanesulfonate (88.5 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 12:1), **24** was afforded as yellow oil liquid (33.9 mg, 85%).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 – 7.81 (m, 1H), 7.64 – 7.59 (m, 1H), 7.50 – 7.40 (m, 5H), 7.35 – 7.31 (m, 2H) ppm.
^{13}C NMR (101 MHz, $CDCl_3$): δ 149.2, 137.3, 136.3, 132.2, 131.9, 128.6, 128.2, 128.1, 127.8, 124.0 ppm.
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{10}NO_2^+$ 200.0706; found 200.0706.

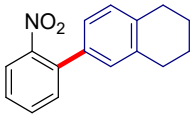
4'-methyl-2-nitro-1,1'-biphenyl (25)



Compound **25** was prepared following the procedure **A**, starting from 5-(p-tolyl)-5H-thianthren-5-ium trifluoromethanesulfonate (91.3 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15:1), **25** was afforded as yellow oil liquid (40.5 mg, 95%).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 – 7.80 (m, 1H), 7.63 – 7.57 (m, 1H), 7.49 – 7.42 (m,2H), 7.28 – 7.21 (m, 4H), 2.41 (s, 3H) ppm.
^{13}C NMR (101 MHz, $CDCl_3$): δ 149.3, 138.1, 136.2, 134.3, 132.1, 131.9, 129.4, 127.8, 127.7, 123.9, 21.2 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{12}NO_2^+$ 214.0863; found 214.0857.

6-(2-nitrophenyl)-1,2,3,4-tetrahydronaphthalene (26)



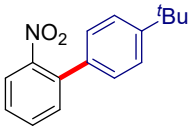
Compound **26** was prepared following the procedure **A**, starting from 5-(5,6,7,8-tetrahydronaphthalen-2-yl)-5H-thianthren-5-ium trifluoromethanesulfonate (99.3 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15:1), **26** was afforded as yellow oil liquid (38.5 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 – 7.77 (m, 1H), 7.63 – 7.55 (m, 1H), 7.49 – 7.40 (m, 2H), 7.16 – 7.09 (m, 1H), 7.09 – 7.00 (m, 2H), 2.85 – 2.77 (m, 4H), 1.87 – 1.80 (m, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 149.4, 137.6, 137.4, 136.4, 134.3, 132.1, 131.9, 129.4, 128.4, 127.7, 124.9, 123.9, 29.3, 29.1, 23.0 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{16}NO_2^+$ 254.1176; found 254.1174.

4'-(*tert*-butyl)-2-nitro-1,1'-biphenyl (27)



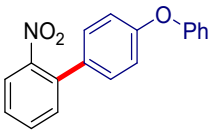
Compound **27** was prepared following the procedure **A**, starting from 5-(4-(tert-butyl)phenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (99.7 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15:1), **27** was afforded as yellow oil liquid (43.9 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 – 7.76 (m, 1H), 7.64 – 7.55 (m, 1H), 7.51 – 7.39 (m, 4H), 7.31 – 7.25 (m, 2H), 1.41 – 1.32 (m, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 151.2, 149.4, 136.1, 134.2, 132.1, 131.9, 127.8, 127.5, 125.6, 123.9, 34.6, 31.3 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{18}NO_2^+$ 256.1332; found 256.1332.

2-nitro-4'-phenoxy-1,1'-biphenyl (28)



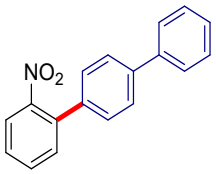
Compound **28** was prepared following the procedure **A**, starting from 5-(4-phenoxyphenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (106.9 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **28** was afforded as yellow oil liquid (40.8 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 – 7.79 (m, 1H), 7.64 – 7.58 (m, 1H), 7.51 – 7.43 (m, 2H), 7.41 – 7.33 (m, 2H), 7.31 – 7.24 (m, 2H), 7.18 – 7.12 (m, 1H), 7.11 – 6.99 (m, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.7, 156.5, 149.3, 135.6, 132.2, 131.9, 131.9, 129.8, 129.3, 128.0, 124.0, 123.8, 119.4, 118.5 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{14}NO_3^+$ 292.0968; found 292.0964.

2-nitro-1,1':4',1''-terphenyl (29)



Compound **29** was prepared following the procedure **A**, starting from 5-([1,1'-biphenyl]-4-yl)-5H-thianthren-5-ium trifluoromethanesulfonate (103.7 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **29** was afforded as yellow solid (49.6 mg, 90%).

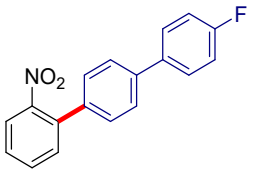
M.P.: 120 – 123 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 – 7.86 (m, 1H), 7.69 – 7.62 (m, 5H), 7.53 – 7.45 (m, 4H), 7.45 – 7.35 (m, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 149.3, 141.1, 140.3, 136.2, 135.9, 132.3, 131.9, 128.8, 128.3, 128.2, 127.6, 127.4, 127.1, 124.1 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{14}NO_2^+$ 276.1019; found 276.1015.

4''-fluoro-2-nitro-1,1':4',1''-terphenyl (30)



Compound **30** was prepared following the procedure **A**, starting from 5-(4'-fluoro-[1,1'-biphenyl]-4-yl)-5H-thianthren-5-ium trifluoromethanesulfonate (107.3 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15:1), **30** was afforded as yellow solid (49.3 mg, 84%).

M.P.: 96 - 98 °C.

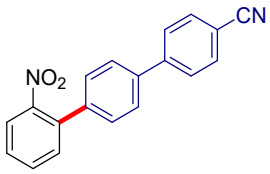
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 – 7.84 (m, 1H), 7.66 – 7.56 (m, 5H), 7.52 – 7.46 (m, 2H), 7.42 – 7.37 (m, 2H), 7.18 – 7.11 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.6 (d, *J* = 247.5 Hz), 149.2, 140.0, 136.4 (d, *J* = 3.9 Hz), 136.3, 135.8, 132.3, 131.9, 128.7 (d, *J* = 8.2 Hz), 128.4, 128.2, 127.2, 124.1, 115.7 (d, *J* = 21.6 Hz) ppm.

^{19}F NMR (377 MHz, $CDCl_3$): δ – 115.2 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{13}FNO_2^+$ 294.0925; found 294.0919.

2''-nitro-[1,1':4',1''-terphenyl]-4-carbonitrile (31)



Compound **31** was prepared following the procedure **A**, starting from 5-(4'-cyano-[1,1'-biphenyl]-4-yl)-5H-thianthren-5-ium trifluoromethanesulfonate (108.7 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 7:1), **31** was afforded as yellow solid (31.2 mg, 52%).

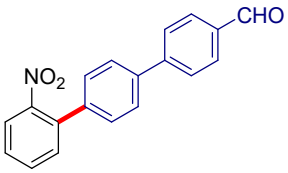
M.P.: 125 – 128 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 – 7.87 (m, 1H), 7.76 – 7.69 (m, 4H), 7.69 – 7.61 (m, 3H), 7.57 – 7.40 (m, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 149.0, 144.7, 138.8, 137.8, 135.5, 132.6, 132.5, 131.8, 128.6, 128.5, 127.6, 127.4, 124.2, 118.8, 111.1 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{13}N_2O_2^+$301.0972; found 301.0968.

2''-nitro-[1,1':4',1''-terphenyl]-4-carbaldehyde (32)



Compound **32** was prepared following the procedure **A**, starting from 5-(4'-formyl-[1,1'-biphenyl]-4-yl)-5H-thianthren-5-ium trifluoromethanesulfonate (109.3 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **32** was afforded as yellow solid (51.6 mg, 85%).

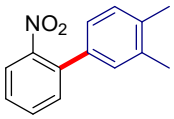
M.P.: 113 – 116 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.08 – 10.02 (m, 1H), 8.01 – 7.85 (m, 3H), 7.81 – 7.74 (m, 2H), 7.72 – 7.66 (m, 2H), 7.66 – 7.61 (m, 1H), 7.55 – 7.46 (m, 2H), 7.46 – 7.40 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 191.8, 149.1, 146.2, 139.4, 137.6, 135.6, 135.3, 132.4, 131.8, 130.3, 128.5, 128.4, 127.6, 127.6, 124.2 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{14}NO_3^+$ 304.0968; found 304.0966.

3',4'-dimethyl-2-nitro-1,1'-biphenyl (33)



Compound **33** was prepared following the procedure **A**, starting from 5-(3,4-dimethylphenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (94.1 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15:1), **33** was afforded as yellow solid (31.4 mg, 69%).

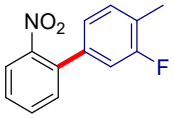
M.P.: 40 – 43 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 – 7. 78 (m, 1H), 7.63 – 7.57 (m, 1H), 7.49 – 7.42 (m, 2H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.16 – 7.11 (m, 1H), 7.11 – 7.06 (m, 1H), 2.32 (d, *J* = 3.3 Hz, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 149.3, 136.9, 136.8, 136.2, 134.7, 132.1, 131.9, 129.9, 128.9, 127.7, 125.2, 123.9, 19.8, 19.5 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}NO_2^+$ 228.1019; found 228.1015.

3'-fluoro-4'-methyl-2-nitro-1,1'-biphenyl (34)



Compound **34** was prepared following the procedure **A**, starting from 5-(3-fluoro-4-methylphenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (94.9 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15:1), **34** was afforded as yellow oil liquid (30.1 mg, 65%).

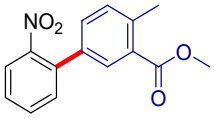
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 – 7.78 (m, 1H), 7.63 – 7.58 (m, 1H), 7.50 – 7.45 (m, 1H), 7.43 – 7.39 (m, 1H), 7.17 – 7.02 (m, 3H), 2.32 – 2.29 (m, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 161.3 (d, *J* = 247.5 Hz), 149.2, 135.4, 133.0 (d, *J* = 4.0 Hz), 132.2, 131.9, 131.0 (d, *J* = 6.6 Hz), 128.1, 126.8 (d, *J* = 8.2 Hz), 125.3 (d, *J* = 17.9 Hz), 124.0, 115.4 (d, *J* = 23.3 Hz), 14.5 (d, *J* = 3.1 Hz) ppm.

^{19}F NMR (377 MHz, $CDCl_3$): δ – 134.5 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{11}FNO_2^+$ 232.0768; found 232.0762.

methyl 4-methyl-2'-nitro-[1,1'-biphenyl]-3-carboxylate (35)



Compound **35** was prepared following the procedure **A**, starting from 5-(3-(methoxycarbonyl)-4-methylphenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (103.0 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **35** was afforded as colorless solid (33.6 mg, 62%).

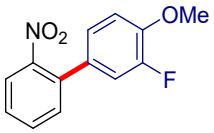
M.P.: 70 – 72 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 – 7.85 (m, 2H), 7.65 – 7.59 (m, 1H), 7.52 – 7.46 (m, 1H), 7.45 – 7.41 (m, 1H), 7.35 – 7.28 (m, 2H), 3.88 (s, 3H), 2.64 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.40 149.0 140.4, 135.4, 135.0, 132.5, 132.1, 132.0, 131.2, 130.1, 129.8, 128.4, 124.2, 51.9, 21.5 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{14}NO_4^+$ 272.0917; found 272.0917.

3'-fluoro-4'-methoxy-2-nitro-1,1'-biphenyl (36)



Compound **36** was prepared following the procedure **A**, starting from 5-(3-fluoro-4-methoxyphenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (98.1mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15:1), **36** was afforded as yellow solid (24.7 mg, 50%).

M.P.: 94 – 96 °C.

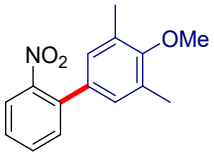
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 – 7.80 (m, 1H), 7.63 – 7.58 (m, 1H), 7.50 – 7.45 (m, 1H), 7.43 – 7.39 (m, 1H), 7.11 – 7.06 (m, 1H), 7.04 – 6.97 (m, 2H), 3.92 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 152.1 (d, *J* = 248.5 Hz), 149.2, 147.7 (d, *J* = 10.1 Hz), 134.7, 132.3, 131.8, 130.0 (d, *J* = 8.2 Hz), 128.2, 124.1, 123.9 (d, *J* = 3.9 Hz), 115.9 (d, *J* = 19.2 Hz), 113.4 (d, *J* = 3.0 Hz), 56.2 ppm.

^{19}F NMR (377 MHz, $CDCl_3$): δ – 134.1 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{11}FNO_3^+$ 248.0717; found 248.0713.

4'-methoxy-3',5'-dimethyl-2-nitro-1,1'-biphenyl (37)



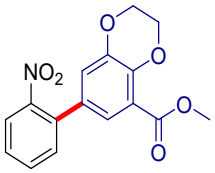
Compound **37** was prepared following the procedure **A**, starting from 5-(4-methoxy-3,5-dimethylphenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (100.1 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **37** was afforded as yellow oil liquid (42.7mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 9.2 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.46 – 7.40 (m, 2H), 6.97 (s, 2H), 3.76 (s, 3H), 2.31 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.1, 149.3, 136.0, 132.6, 132.0, 131.9, 131.2, 128.2, 127.7, 123.8, 59.7, 16.1 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{16}NO_3^+$ 258.1225; found 258.1225.

methyl 7-(2-nitrophenyl)-2,3-dihydrobenzo[*b*][1,4]dioxine-5-carboxylate (38)



Compound **38** was prepared following the procedure **A**, starting from 5-(8-(methoxycarbonyl)-2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-5H-thianthren-5-ium trifluoromethanesulfonate (111.7 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **38** was afforded as yellow solid (32.8 mg, 52%).

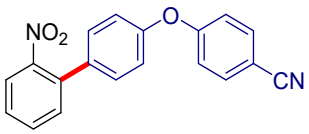
M.P.: 126 – 129 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.1 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.48 – 7.43 (m, 1H), 7.41 – 7.38 (m, 1H), 7.38 – 7.34 (m, 1H), 6.99 – 6.93 (m, 1H), 4.40 – 4.37 (m, 2H), 4.32 – 4.28 (m, 2H), 3.86 (s, 3H)ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.4, 148.9, 144.2, 144.1, 134.7, 132.3, 131.8, 129.6, 128.3, 124.1, 123.2, 120.6, 120.0, 64.6, 63.8, 52.1 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}NO_6^+$ 316.0816; found 316.0812.

4-((2'-nitro-[1,1'-biphenyl]-4-yl)oxy)benzonitrile (39)



Compound **39** was prepared following the procedure **A**, starting from 5-(4-(4-cyanophenoxy)phenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (111.9 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **39** was afforded as white solid (52.5 mg, 83%).

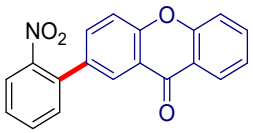
M.P.: 146 – 150 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 – 7.86 (m, 1H), 7.67 – 7.61 (m, 3H), 7.55 – 7.49 (m, 1H), 7.48 – 7.43 (m, 1H), 7.39 – 7.33 (m, 2H), 7.15 – 7.04 (m, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 161.0, 155.0, 149.2, 135.3, 134.2, 133.4, 132.4, 131.8, 129.8, 128.4, 124.2, 120.3, 118.7, 118.3, 106.3 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{13}N_2O_3^+$ 317.0921; found317.0917.

2-(2-nitrophenyl)-9*H*-xanthen-9-one (40)



Compound **40** was prepared following the procedure **A**, starting from 5-(9-oxo-9H-xanthen-2-yl)-5H-thianthren-5-ium trifluoromethanesulfonate (112.1 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 7:1), **40** was afforded as white solid (58.4 mg, 92%).

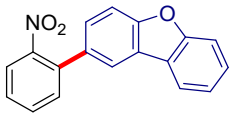
M.P.: 195 – 198 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 – 8.27 (m, 2H), 7.98 – 7.93 (m, 1H), 7.76 – 7.71 (m, 1H), 7.69 – 7.61 (m, 2H), 7.57 – 7.47 (m, 4H), 7.42 – 7.36 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 176.8, 156.1, 155.8, 148.8, 135.0, 135.0, 134.4, 133.5, 132.7, 132.3, 128.7, 126.7, 126.0, 124.5, 124.1, 121.8, 121.7, 118.4, 118.0 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{12}NO_4^+$ 318.0761; found 318.0761.

2-(2-nitrophenyl)dibenzo[*b,d*]furan (41)



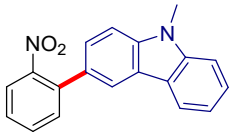
Compound **41** was prepared following the procedure **A**, starting from 5-(dibenzo[b,d]furan-2-yl)-5H-thianthren-5-ium trifluoromethanesulfonate (106.5 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **41** was afforded as yellow oil liquid (53.8 mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 – 7.86 (m, 3H), 7.65 – 7.55 (m, 3H), 7.54 – 7.45 (m, 3H), 7.45 – 7.31 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.6, 155.9, 149.4, 136.2, 132.3, 132.1, 128.3, 128.1, 127.5, 127.0, 124.7, 124.1, 124.1, 122.9, 120.8, 120.1, 111.8, 111.7 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{12}NO_3^+$ 290.0812; found 290.0808.

9-methyl-3-(2-nitrophenyl)-9*H*-carbazole (42)



Compound **42** was prepared following the procedure **A**, starting from 5-(9-methyl-9H-carbazol-3-yl)-5H-thianthren-5-ium trifluoromethanesulfonate (109.1 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **42** was afforded as yellow solid (33.9 mg, 56%).

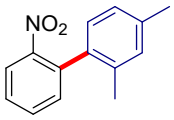
M.P.: 109 – 112 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 – 8.06 (m, 2H), 7.90 – 7.82 (m, 1H), 7.65 – 7.57 (m, 2H), 7.55 – 7.45 (m, 2H), 7.44 – 7.40 (m, 3H), 7.30 – 7.25 (m, 1H), 3.83 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 149.7, 141.3, 140.6, 137.0, 132.4, 132.0, 127.8, 127.4, 126.1, 125.5, 123.9, 123.0, 122.5, 120.4, 119.7, 119.2, 108.7, 108.6, 29.0 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{15}N_2O_2^+$ 303.1128; found 303.1124.

2,4-dimethyl-2'-nitro-1,1'-biphenyl (43)



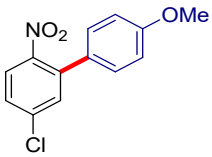
Compound **43** was prepared following the procedure **A**, starting from 5-(2,4-dimethylphenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (94.1mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15:1), **43** was afforded as yellow oil liquid (23.2 mg, 51%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 – 7.91 (m, 1H), 7.66 – 7.60 (m, 1H), 7.53 – 7.48 (m, 1H), 7.36 – 7.31 (m, 1H), 7.10 (s, 1H), 7.07 – 6.99 (m, 2H), 2.37 (s, 3H), 2.08 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 149.3, 137.9, 136.5, 135.4, 134.5, 132.4, 132.3, 130.8, 128.2, 128.1, 126.4, 124.0, 21.1, 19.7 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}NO_2^+$ 228.1019; found 228.1017.

5-chloro-4'-methoxy-2-nitro-1,1'-biphenyl (44)



Compound **44** was prepared following the procedure **A**, starting from 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (94.5 mg, 0.2 mmol) and potassium 5-chloro-2-nitrobenzoate (57.3 mg, 0.24 mmol) After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **44** was afforded as yellowish-green solid (50.6 mg, 96%)

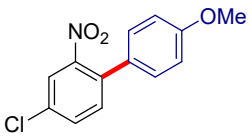
M.P.: 78 – 79 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 9.0 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.27 – 7.19 (m, 2H), 6.99 – 6.92 (m, 2H), 3.84 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.0, 147.5, 138.2, 137.7, 131.8, 129.0, 128.2, 127.7, 125.5, 114.3, 55.3 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{11}ClNO_3^+$ 264.0422; found 264.0418.

4-chloro-4'-methoxy-2-nitro-1,1'-biphenyl (45)



Compound **45** was prepared following the procedure **A**, starting from 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (94.5 mg, 0.2 mmol) and potassium 4-chloro-2-nitrobenzoate (57.5 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 12:1), **45** was afforded as yellow solid (42.7 mg, 81%).

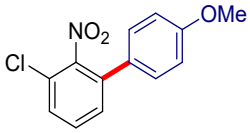
M.P.: 115 – 116 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 2.2 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.25 – 7.19 (m, 2H), 6.99 – 6.92 (m, 2H), 3.84 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.9, 149.5, 134.3, 133.4, 133.0, 132.2, 129.1, 128.3, 124.1, 114.3, 55.3 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{11}ClNO_3^+$ 264.0422; found 264.0416.

3-chloro-4'-methoxy-2-nitro-1,1'-biphenyl (46)



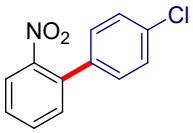
Compound **46** was prepared following the procedure **A**, starting from 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (94.5 mg, 0.2 mmol) and potassium 3-chloro-2-nitrobenzoate (57.5 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15:1), **46** was afforded as yellow oily liquid (20.6 mg, 39%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.41 (m, 2H), 7.36 – 7.31 (m, 1H), 7.31 – 7.26 (m, 2H), 6.97 – 6.92 (m, 2H), 3.83 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.2, 135.8, 130.6, 129.5, 129.2, 128.8, 127.6, 125.2, 114.4, 55.3 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{11}ClNO_3^+$ 264.0422; found 264.0420.

4'-chloro-2-nitro-1,1'-biphenyl (47)



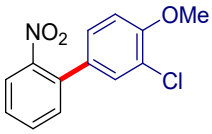
Compound **47** was prepared following the procedure **A**, starting from 5-(4-chlorophenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (95.4 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15:1), **47** was afforded as yellow oil liquid (39.7 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 – 7.83 (m, 1H), 7.65 – 7.60 (m, 1H), 7.53 – 7.47 (m, 1H), 7.43 – 7.37 (m, 3H), 7.27 – 7.23 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 149.0, 135.9, 135.1, 134.4, 132.5, 131.8, 129.2, 128.9, 128.5, 124.2 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_9ClNO_2^+$ 234.0316; found 234.0308.

3'-chloro-4'-methoxy-2-nitro-1,1'-biphenyl (48)



Compound **48** was prepared following the procedure **A**, starting from 5-(3-chloro-4-methoxyphenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (101.4 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **48** was afforded as yellow solid (39.6 mg, 75%).

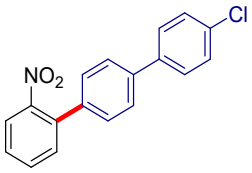
M.P.: 88 – 91 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 – 7.81 (m, 1H), 7.63 – 7.58 (m, 1H), 7.51 – 7.44 (m, 1H), 7.43 – 7.39 (m, 1H), 7.36 (d, *J* = 2.2 Hz, 1H), 7.20 – 7.13 (m, 1H), 6.96 (d, *J* = 8.5 Hz, 1H), 3.94 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 155.0, 149.1, 134.6, 132.3, 131.9, 130.4, 129.7, 128.3, 127.4, 124.2, 122.7, 112.0, 56.2 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{11}ClNO_3^+$ 264.0422; found 264.0422.

4''-chloro-2-nitro-1,1':4',1''-terphenyl (49)



Compound **49** was prepared following the procedure **A**, starting from 5-(4'-chloro-[1,1'-biphenyl]-4-yl)-5H-thianthren-5-ium trifluoromethanesulfonate (110.6 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **49** was afforded as yellow solid (40.9 mg, 66%).

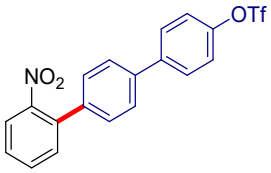
M.P.: 98 - 100 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 – 7.85 (m, 1H), 7.68 – 7.60 (m, 3H), 7.59 – 7.54 (m, 2H), 7.54 – 7.37 (m, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 149.2, 139.8, 138.7, 136.6, 135.8, 133.7, 132.4, 131.9, 129.0, 128.4, 128.3, 128.3, 127.2, 124.2 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{13}ClNO_2^+$ 310.0629; found 310.0620.

2''-nitro-[1,1':4',1''-terphenyl]-4-yl trifluoromethanesulfonate (50)



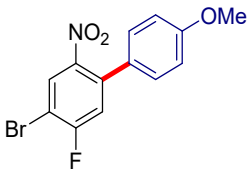
Compound **50** was prepared following the procedure **A**, starting from 5-(4'-(((trifluoromethyl)sulfonyl)oxy)-[1,1'-biphenyl]-4-yl)-5H-thianthren-5-ium trifluoromethanesulfonate (133.3 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **50** was afforded as yellow oil liquid (59.3 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 – 7.87 (m, 1H), 7.70 – 7.59 (m, 5H), 7.55 – 7.47 (m, 2H), 7.45 – 7.34 (m, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 149.2, 149.1, 140.8, 139.0, 137.2, 135.6, 132.4, 131.9, 128.9, 128.5, 128.4, 127.4, 124.2, 121.7, 118.7 (q, *J* = 322.2 Hz) ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{13}F_3NO_5S^+$424.0461; found424.0452.

4-bromo-5-fluoro-4'-methoxy-2-nitro-1,1'-biphenyl (51)



Compound **51** was prepared following the procedure **B**, starting from 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (141.8mg, 0.3 mmol) and potassium 4-bromo-5-fluoro-2-nitrobenzoate (60.4 mg, 0.20 mmol) with 0.1 mmol thianthrene and 5 mol% $Pd(OAc)_2$. After column chromatography on silica (Petroleum Ether: EtOAc = 20:1), **51** was afforded as yellow solid (32.5 mg, 50%).

M.P.: 92 – 94 °C.

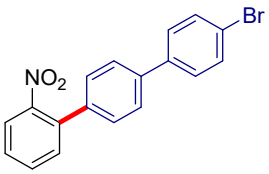
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 6.2 Hz, 1H), 7.23 – 7.20 (m, 2H), 7.18 (d, *J* = 8.6 Hz, 1H), 6.97 – 6.94 (m, 2H), 3.85 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.6 (d, *J* = 257.6 Hz), 160.2, 138.0 (d, *J* = 8.2 Hz), 135.8, 129.8 (d, *J* = 2.2 Hz), 128.9, 127.7 (d, *J* = 1.1 Hz), 119.2 (d, *J* = 24.2 Hz), 114.4, 107.8 (d, *J* = 23.6 Hz), 55.4 ppm.

^{19}F NMR (377 MHz, $CDCl_3$): δ – 99.8 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{10}BrFNO_3^+$325.9823; found325.9817.

4''-bromo-2-nitro-1,1':4',1''-terphenyl (52)



Compound **52** was prepared following the procedure **A**, starting from 5-(4'-bromo-[1,1'-biphenyl]-4-yl)-5H-thianthren-5-ium trifluoromethanesulfonate (119.5 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol) with 0.1 mmol thianthrene. After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **52** was afforded as yellow solid (51.0 mg, 72%).

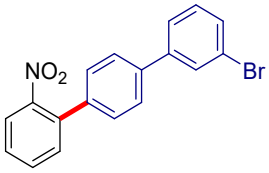
M.P.: 105 - 107 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.66 – 7.56 (m, 5H), 7.53 – 7.46 (m, 4H), 7.43 – 7.37 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 149.2, 139.8, 139.2, 136.7, 135.7, 132.4, 131.9, 131.8, 128.7, 128.4, 128.3, 127.1, 124.2, 121.9 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{13}BrNO_2^+$ 354.0124; found 354.0122.

3''-bromo-2-nitro-1,1':4',1''-terphenyl (53)



Compound **53** was prepared following the procedure **A**, starting from 5-(3'-bromo-[1,1'-biphenyl]-4-yl)-5H-thianthren-5-ium trifluoromethanesulfonate (119.5 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol) with 0.1 mmol thianthrene. After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **53** was afforded as yellow solid (58.6 mg, 83%).

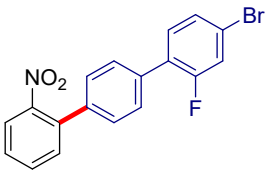
M.P.: 105 - 108 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 – 7.86 (m, 1H), 7.80 – 7.74 (m, 1H), 7.65 – 7.59 (m, 3H), 7.56 – 7.47 (m, 4H), 7.42 – 7.39 (m, 2H), 7.32 (t, *J* = 7.9 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 149.2, 142.4, 139.5, 136.9, 135.7, 132.4, 131.9, 130.5, 130.3, 130.1, 128.4, 128.3, 127.3, 125.7, 124.2, 122.9 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{13}BrNO_2^+$ 354.0124; found 354.0118.

4-bromo-2-fluoro-2''-nitro-1,1':4',1''-terphenyl (54)



Compound **54** was prepared following the procedure **A**, starting from 5-(4'-bromo-2'-fluoro-[1,1'-biphenyl]-4-yl)-5H-thianthren-5-ium trifluoromethanesulfonate (123.1 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol) 0.1 mmol thianthrene. After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **54** was afforded as yellow solid (65.3 mg, 88%).

M.P.: 102 - 105 °C.

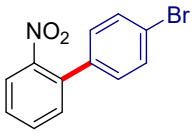
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 – 7.86 (m, 1H), 7.66 – 7.62 (m, 1H), 7.61 -7.56 (m, 2H), 7.53 – 7.47 (m, 2H), 7.44 – 7.32 (m, 5H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.4 (d, *J* = 253.5 Hz), 149.1, 137.0, 135.7, 134.6 (d, *J* = 1.0 Hz), 132.4, 131.9, 131.6 (d, *J* = 4.0 Hz), 129.0 (d, *J* = 3.2 Hz), 128.3, 128.1, 127.8 (d, *J* = 3.9 Hz), 127.3 (d, *J* = 13.3 Hz), 124.2, 121.6 (d, *J* = 9.6 Hz), 119.7 (d, *J* = 26.2 Hz) ppm.

^{19}F NMR (377 MHz, $CDCl_3$): δ – 114.8 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{12}BrFNO_2^+$ 372.0030; found 372.0030.

4'-bromo-2-nitro-1,1'-biphenyl (55)



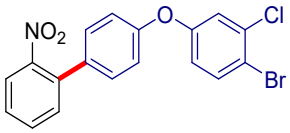
Compound **55** was prepared following the procedure **A**, starting from 5-(4-bromophenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (156.5 mg, 0.2 mmol) and potassium 2-nitrobenzoate (41.0 mg, 0.20 mmol) with 0.1 mmol thianthrene and 5 mol% $Pd(OAc)_2$. After column chromatography on silica (Petroleum Ether: EtOAc = 15:1), **55** was afforded as yellow oil liquid (22.7 mg, 41%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 – 7.85 (m, 1H), 7.65 – 7.60 (m, 1H), 7.58 – 7.48 (m, 3H), 7.43 – 7.38 (m, 1H), 7.23 – 7.15 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 148.9, 136.4, 135.2, 132.5, 131.8, 131.8, 129.5, 128.6, 124.3, 122.6 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_9BrNO_2^+$ 277.9811; found 277.9801.

4'-(4-bromo-3-chlorophenoxy)-2-nitro-1,1'-biphenyl (56)



Compound **56** was prepared following the procedure **A**, starting from 5-(4-(4-bromo-3-chlorophenoxy)phenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (129.2 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol) 0.1 mmol thianthrene. After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **56** was afforded as yellow solid (72.6 mg, 90%).

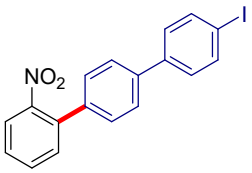
M.P.: 102 - 105 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 – 7.86 (m, 1H), 7.64 – 7.60 (m, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.33 – 7.29 (m, 2H), 7.17 (d, *J* = 2.7 Hz, 1H), 7.07 – 7.03 (m, 2H), 6.86 – 6.82 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.7, 156.3, 149.2, 135.4, 135.3, 134.3, 133.2, 132.3, 131.9, 129.6, 128.3, 124.1, 120.8, 119.1, 118.6, 116.2 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{12}BrClNO_3^+$403.9684; found 403.9682.

4''-iodo-2-nitro-1,1':4',1''-terphenyl (57)



Compound **57** was prepared following the procedure **A**, starting from 5-(4'-iodo-[1,1'-biphenyl]-4-yl)-5H-thianthren-5-ium trifluoromethanesulfonate (128.9 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol) with 0.1 mmol thianthrene. After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **57** was afforded as yellow solid (32.1 mg, 40%).

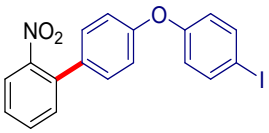
M.P.: 113 - 117 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 – 7.86 (m, 1H), 7.81 – 7.76 (m, 2H), 7.65 – 7.59 (m, 3H), 7.53 – 7.47 (m, 2H), 7.42 – 7.40 (m, 1H), 7.40 – 7.37 (m, 2H), 7.36 – 7.35 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 149.2, 139.9, 139.8, 137.9, 136.7, 135.8, 132.3, 131.9, 128.9, 128.5, 128.3, 127.1, 124.2, 93.4 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{13}INO_2^+$ 401.9985; found401.9976.

4'-(4-iodophenoxy)-2-nitro-1,1'-biphenyl (58)



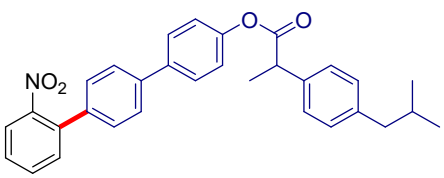
Compound **58** was prepared following the procedure **A**, starting from 5-(4-(4-iodophenoxy)phenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (132.1 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol) with 0.1 mmol thianthrene. After column chromatography on silica (Petroleum Ether: EtOAc = 15:1), **58** was afforded as yellow oil liquid (46.7 mg, 56%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.59 (m, 3H), 7.51 – 7.43 (m, 2H), 7.31 – 7.27 (m, 2H), 7.06 – 7.02 (m, 2H), 6.87 – 6.80 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.9, 156.7, 149.3, 138.8, 135.5, 132.5, 132.3, 131.9, 129.5, 128.2, 124.1, 121.4, 118.8, 86.6 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{13}INO_3^+$ 417.9935; found 417.9929.

2''-nitro-[1,1':4',1''-terphenyl]-4-yl 2-(4-isobutylphenyl)propanoate (59)



Compound **59** was prepared following the procedure **H**, 5-(4'-((2-(4-isobutylphenyl)propanoyl)oxy)-[1,1'-biphenyl]-4-yl)-5H-thianthren-5-ium trifluoromethanesulfonate (144.6 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol) with 0.1 mmol thianthrene and 5 mol% $Pd(OAc)_2$. After column

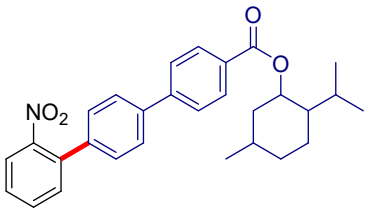
chromatography on silica (Petroleum Ether: EtOAc = 10:1), **59** was afforded as yellow waxy liquid (48.8 mg, 51%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.6 Hz, 1H), 7.65 – 7.57 (m, 5H), 7.52 – 7.46 (m, 2H), 7.41 – 7.37 (m, 2H), 7.36 – 7.31 (m, 2H), 7.20 – 7.15 (m, 2H), 7.14 – 7.07 (m, 2H), 4.02 – 3.93 (m, 1H), 2.53 – 2.47 (m, 2H), 1.95 – 1.85 (m, 1H), 1.68 – 1.61 (m, 3H), 0.96 – 0.91 (m, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.2, 150.5, 149.2, 140.8, 140.2, 138.0, 137.2, 136.3, 135.9, 132.3, 131.9, 129.5, 128.3, 128.2, 128.0, 127.3, 127.2, 124.1, 121.8, 45.3, 45.0, 30.2, 22.4, 18.5 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{31}H_{30}NO_4^+$ 480.2169; found 480.2162.

2-isopropyl-5-methylcyclohexyl 2''-nitro-[1,1':4',1''-terphenyl]-4-carboxylate (60)



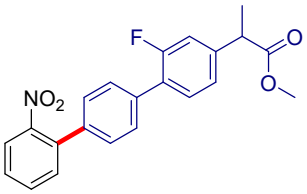
Compound **60** was prepared following the procedure **A**, 5-(4'-(((2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)-[1,1'-biphenyl]-4-yl)-5H-thianthren-5-ium trifluoromethanesulfonate (140.2 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **60** was afforded as yellow oil liquid (69.6 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 – 8.07 (m, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.72 – 7.65 (m, 4H), 7.64 – 7.59 (m, 1H), 7.51 – 7.45 (m, 2H), 7.44 – 7.38 (m, 2H), 5.07 – 4.91 (m, 1H), 2.18 (d, *J* = 12.6 Hz, 1H), 2.09 – 1.97 (m,1H), 1.80 – 1.71 (m, 2H), 1.66 – 1.54 (m, 2H), 1.21 – 1.10 (m, 2H), 1.00 – 0.92 (m, 7H), 0.87 – 0.82 (m, 3H)ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 149.2, 144.6, 139.9, 137.2, 135.7, 132.4, 131.9, 130.2, 129.9, 128.5, 128.4, 127.5, 127.0, 124.2, 74.9, 47.3, 41.0, 34.3, 31.5, 26.6, 23.7, 22.1, 20.8, 16.6 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{32}NO_4^+$ 458.2326; found 458.2324.

methyl 2-(2-fluoro-2''-nitro-[1,1':4',1''-terphenyl]-4-yl)propanoate (61)



Compound **61** was prepared following the procedure **A**, starting from 5-(2'-fluoro-4'-(1-methoxy-1-oxopropan-2-yl)-[1,1'-biphenyl]-4-yl)-5H-thianthren-5-ium trifluoromethanesulfonate (124.5 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.0 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **61** was afforded as yellow solid (51.6 mg, 68%).

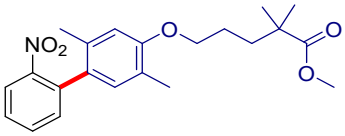
M.P.: 78 – 82 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.8 Hz, 1H), 7.65 – 7.58 (m, 3H), 7.51 – 7.37 (m, 5H), 7.20 – 7.13 (m, 2H), 3.82 – 3.75 (m, 1H), 3.71 (s, 3H), 1.55 (d, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.3, 159.7 (d, *J* = 249.5 Hz), 149.2, 142.2 (d, *J* = 8.2 Hz), 136.6, 135.8, 135.3, 132.3, 131.9, 130.7 (d, *J* = 3.9 Hz), 129.1 (d, *J* = 3.1 Hz), 128.2, 128.0, 126.9 (d, *J* = 13.1 Hz), 124.1, 123.6 (d, *J* = 3.1 Hz), 115.2 (d, *J* = 23.2 Hz), 52.1, 44.8, 18.3 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{19}FNO_4^+$ 380.1293; found 380.1286.

methyl 5-((2,5-dimethyl-2'-nitro-[1,1'-biphenyl]-4-yl)oxy)-2,2-dimethylpentanoate (62)



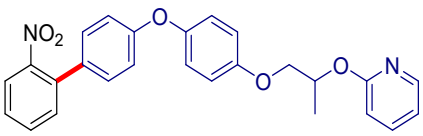
Compound **62** was prepared following the procedure **A**, starting from 5-(4-((5-methoxy-4,4-dimethyl-5-oxopentyl)oxy)-2,5-dimethylphenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (125.7 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol) with 0.1 mmol thianthrene and 5 mol% $Pd(OAc)_2$. After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **62** was afforded as green oil liquid (43.2 mg, 56%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.1 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.50 – 7.44 (m, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 6.87 (s, 1H), 6.67 (s, 1H), 3.99 – 3.94 (m, 2H), 3.68 (s, 3H), 2.19 (s, 3H), 2.06 (s, 3H), 1.79 – 1.73 (m, 4H), 1.24 (s, 6H)ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 178.2, 156.8, 149.6, 136.4, 134.0, 132.6, 132.2, 130.5, 128.8, 127.8, 123.9, 123.8, 112.3, 67.9, 51.7, 42.1, 37.1, 25.2, 25.1, 19.8, 15.6 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{28}NO_5^+$ 386.1962; found 386.1958.

2-((1-(4-((2'-nitro-[1,1'-biphenyl]-4-yl)oxy)phenoxy)propan-2-yl)oxy)pyridine (63)



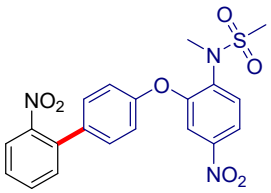
Compound **63** was prepared following the procedure **A**, starting from 5-(4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)phenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (137.1 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol) with 0.1 mmol thianthrene and 5 mol% Pd(OAc). After column chromatography on silica (Petroleum Ether: EtOAc = 5:1), **63** was afforded as green oil liquid (44.3 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 – 8.09 (m, 1H), 7.92 – 7.77 (m, 1H), 7.70 – 7.53 (m, 2H), 7.53 – 7.38 (m, 2H), 7.32 – 7.22 (m, 2H), 7.09 – 6.85 (m, 7H), 6.82 – 6.72 (m, 1H), 5.80 – 5.48 (m, 1H), 4.28 – 4.04 (m, 2H), 1.58 – 1.45 (m, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.1, 158.8, 155.5, 149.5, 149.3, 146.7, 138.7, 135.7, 132.2, 131.9, 131.1, 129.2, 127.9, 124.0, 121.2, 117.3, 116.8, 115.8, 111.7, 71.0, 69.2, 17.0 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{23}N_2O_5^+$ 443.1601; found 443.1596.

N-methyl-N-(4-nitro-2-((2'-nitro-[1,1'-biphenyl]-4-yl)oxy)phenyl)methanesulfonamide (64)



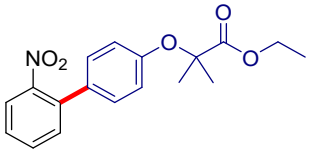
Compound **64** was prepared following the procedure **A**, starting from 5-(4-(2-(N-methylmethylsulfonamido)-5-nitrophenoxy)phenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (137.3 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **64** was afforded as green oil liquid (53.2 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 - 7.94 (m, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.79 – 7.73 (m, 1H), 7.69 – 7.63 (m, 2H), 7.55 – 7.47 (m, 2H), 7.41 – 7.37 (m, 2H), 7.16 – 7.12 (m, 2H), 3.36 (s, 3H), 3.01 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 154.8, 154.3, 149.1, 147.8, 137.3, 135.1, 134.9, 132.7, 132.0, 130.4, 128.7, 124.4, 119.6, 118.7, 113.6, 38.7, 37.9, 37.8 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}N_3O_7S^+$444.0860; found444.0854.

ethyl 2-methyl-2-((2'-nitro-[1,1'-biphenyl]-4-yl)oxy)propanoate (65)



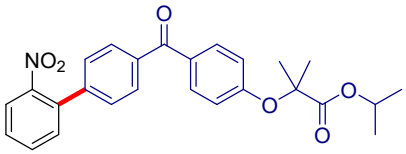
Compound **65** was prepared following the procedure **A**, starting from 5-(4-((1-ethoxy-2-methyl-1-oxopropan-2-yl)oxy)phenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (114.5 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **65** was afforded as green oil liquid (34.2 mg, 52%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 – 7.75 (m, 1H), 7.60 – 7.55 (m, 1H), 7.46 – 7.38 (m, 2H), 7.21 – 7.16 (m, 2H), 6.90 – 6.84 (m, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.63 (s, 6H), 1.26 – 1.22 (m, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.1, 155.7, 149.3, 135.7, 132.1, 131.9, 130.6, 128.8, 127.8, 123.9, 118.7, 79.2, 61.5, 25.4, 14.0 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{20}NO_5^+$ 330.1336; found 330.1334.

isopropyl 2-methyl-2-(4-(2'-nitro-[1,1'-biphenyl]-4-carbonyl)phenoxy)propanoate (66)



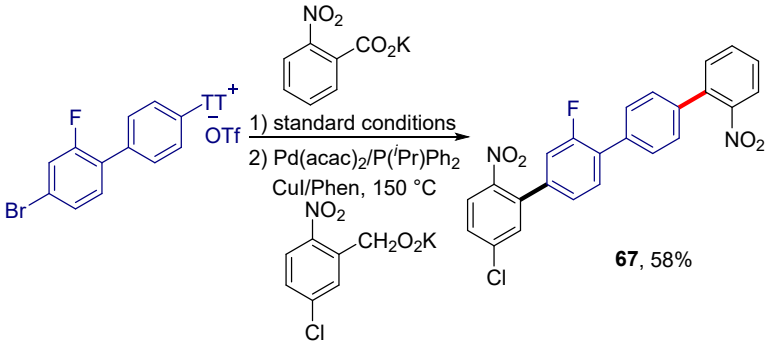
Compound **66** was prepared following the procedure **A**, starting from 5-(4-(4-((1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)benzoyl)phenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (138.1 mg, 0.2 mmol) and potassium 2-nitrobenzoate (49.2 mg, 0.24 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 10:1), **66** was afforded as green oil liquid (44.7 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 – 7.90 (m, 1H), 7.83 – 7.77 (m, 4H), 7.68 – 7.63 (m, 1H), 7.56 – 7.50 (m, 1H), 7.47 – 7.44 (m, 1H), 7.44 – 7.39 (m, 2H), 6.90 – 6.85 (m, 2H), 5.16 – 5.04 (m, 1H), 1.66 (s, 6H), 1.21 (d, *J* = 6.4 Hz, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 194.8, 173.1, 159.7, 148.9, 141.1, 137.7, 135.5, 132.6, 132.0, 131.8, 130.3, 130.0, 128.8, 127.8, 124.3, 117.2, 79.4, 69.3, 25.3, 21.5 ppm.

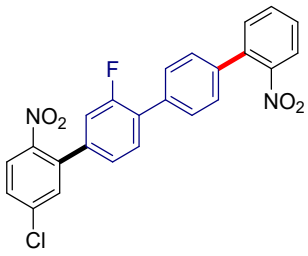
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{26}NO_6^+$ 448.1755; found 448.1755.

One-pot Subsequent Decarboxylative Arylation



Procedure B: An oven-dried vessel was charged with arylthianthrenium salts (0.20 mmol, 1.0 equiv.), potassium carboxylate (0.24 mmol, 1.2 equiv.), $Pd(OAc)_2$ (1.2 mg, 5.00 μmol, 0.025 equiv.), CuI (1.9 mg, 0.01 mmol, 0.05 equiv.), and bpy (1.6 mg, 0.01 mmol, 0.05 equiv.). Under an argon atmosphere, DMSO (1 mL) was added via syringe, and the resulting mixture was stirred at 120 °C for 16 h. Subsequently, potassium 5-chloro-2-nitrobenzoate (71.0 mg, 0.30 mmol, 1.5 equiv.), $Pd(acac)_2$ (3.0 mg, 10.0 μmol, 0.05 equiv.), $P(^iPr)Ph_2$ (2.5 mg, 10.0 μmol, 0.05 equiv.), CuI (3.8 mg, 0.02 mmol, 0.10 equiv.), and Phen (3.6 mg, 0.02 mmol, 0.10 equiv.) were added under argon. The reaction mixture was then stirred at 150 °C for an additional 16 h. After cooling, the mixture was diluted with brine (10 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified to afford the corresponding product. Compound **67**, selected as an example, was obtained as a green oil (52.0 mg, 58%).

5'''-chloro-2''-fluoro-2,2'''-dinitro-1,1':4',1'':4'',1'''-quaterphenyl (67)



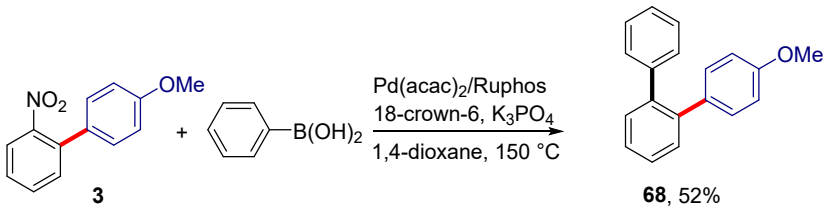
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 – 7.87 (m, 2H), 7.68 – 7.63 (m, 3H), 7.59 – 7.51 (m, 3H), 7.51 – 7.48 (m, 2H), 7.45 – 7.42 (m, 2H), 7.20 – 7.12 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$):) δ 159.6 (d, *J* = 251.5 Hz), 149.2, 147.1, 138.8, 137.4 (d, *J* = 8.2 Hz), 137.1, 136.6 (d, *J* = 2.0 Hz), 135.8, 134.8, 132.4, 132.0, 131.8, 131.0 (d, *J* = 3.9 Hz), 129.3 (d, *J* = 3.0 Hz), 128.8, 128.7, 128.4, 128.1, 125.9, 124.2, 124.0 (d, *J* = 3.0 Hz), 115.9 (d, *J* = 25.2 Hz) ppm.

^{19}F NMR (377 MHz, $CDCl_3$): δ – 116.5 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{15}ClFN_2O_4^+$ 449.0699; Found 449.0692.

NO_2 as a Leaving Group in Suzuki-Miyaura Coupling

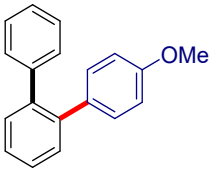


3

68, 52%

Procedure C:[4] An oven-dried vessel was charged with compound **3** (46 mg, 0.20 mmol, 1.0 equiv.), phenylboronic acid (61.0 mg, 0.50 mmol, 2.5 equiv.), $Pd(acac)_2$ (6.2 mg, 0.02 mmol, 0.1 equiv.), Ruphos (19.2 mg, 0.04 mmol, 0.2 equiv.), 18-crown-6 (5.3 mg, 0.02 mmol, 0.1 equiv.), and K_3PO_4 (127 mg, 0.6 mmol, 3.0 equiv.). Under an inert atmosphere, 1,4-dioxane (2 mL) was added via syringe. The resulting mixture was stirred at 150 °C for 24 h. Upon completion, the reaction was quenched with brine (10 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, ethyl acetate/cyclohexane gradient) to afford the corresponding product **68** as an oil liquid (27.0 mg, 52%).

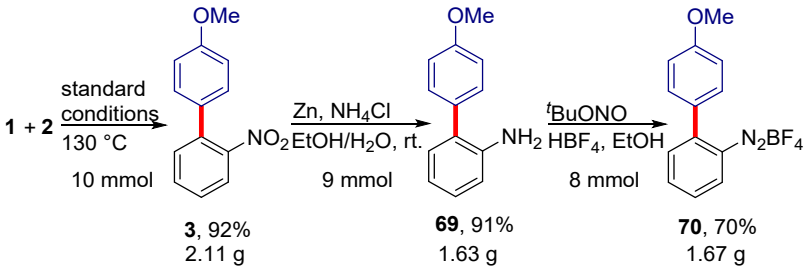
4-methoxy-1,1':2',1''-terphenyl (68)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 – 7.49 (m, 4H), 7.47 – 7.39 (m,3H), 7.34 - 7.29 (m, 1H), 7.28 – 7.04 (m, 3H), 7.01 – 6.98 (m, 2H), 3.86 (s, 3H) ppm.

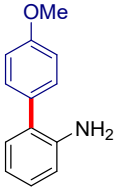
Spectra data are consistent with the reported literature.[4]

Gram-scale diazonium salt synthesis



Procedure D:[5] An oven-dried vessel was charged with arylthianthrenium salts (10.0 mmol, 1.0 equiv.), potassium carboxylate (12.0 mmol, 1.2 equiv.), $Pd(OAc)_2$ (56 mg, 0.25 mmol, 0.025 equiv.), CuI (95.0 mg, 0.5 mmol, 0.05 equiv.), and bpy (80.0 mg, 0.5 mmol, 0.05 equiv.). Under an argon atmosphere, DMSO (50 mL) was added via syringe. The resulting reaction mixture was stirred at 130 °C for 16 h to afford compound **3** as a yellow solid (2.11 g, 92%). A separate oven-dried vessel was charged with Zn (3.00 g, 46.25 mmol, 5.0 equiv.), NH_4Cl (5.00 g, 92.5 mmol, 10.0 equiv.), and compound **3**. Then, 40 mL of a mixed solvent (MeOH:H_2O = 2:1) was added, and the mixture was stirred at room temperature for one hour to afford compound **69** as a brown oily liquid (1.63 g, 92%). Aniline was dissolved in absolute ethanol (4 mL), followed by the addition of HBF_4 (16 mmol, 2.0 equiv.). The mixture was cooled to 0 °C, and t-BuONO (16 mmol, 2.0 equiv.) was added. After stirring at room temperature for two hours, compound **70** was obtained as a bright orange solid (1.67 g, 67%).

4'-methoxy-[1,1'-biphenyl]-2-amine (69)

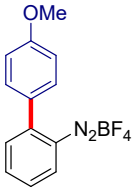


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 – 7.37 (m, 2H), 7.22 – 7.13 (m, 2H), 7.07 – 6.97 (m, 2H), 6.90 – 6.83 (m, 1H), 6.83. – 6.74 (m, 1H), 3.88 (s, 3H), 3.79 (s, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.6, 143.5, 131.6, 130.4, 130.1, 128.1, 127.3, 118.6, 115.5, 114.1, 55.2 ppm.

Spectra data are consistent with the reported literature.[5]

4'-methoxy-[1,1'-biphenyl]-2-diazonium tetrafluoroborate (70)



^{1}H NMR (400 MHz, D_2O): δ 8.63 – 8.61 (m, 1H), 8.33 – 8.28 (m, 1H), 8.01 – 7.99 (m, 1H), 7.92 – 7.89 (m, 1H), 7.72 – 7.69 (m, 2H), 7.29 – 7.27 (m, 2H), 3.96 (s, 3H) ppm.

Spectra data are consistent with the reported literature.[6]

Further Derivatization from Diazonium Salts

4-methoxy-1,1'-biphenyl (71)

70 **71**, 68%

Procedure E:[7] A solution of arenediazonium tetrafluoroborate (0.25 mmol) and eosin B, disodium salt (3.2 mg, 5 µmol, 2 mol%) in DMF (2 mL) was prepared in the dark. The solution was degassed by bubbling nitrogen through it under vigorous stirring, and the vessel was sealed. The mixture was then irradiated with green LEDs for 30 min at ambient temperature. After dilution with diethyl ether (5 mL), the mixture was washed with water (5 mL). The aqueous layer was back-extracted with diethyl ether (2 × 5 mL), and the combined organic extracts were washed with brine (5 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by column chromatography (SiO_2, ethyl acetate/cyclohexane gradient) afforded compound **71** as a yellow solid (31.0 mg, 68%).

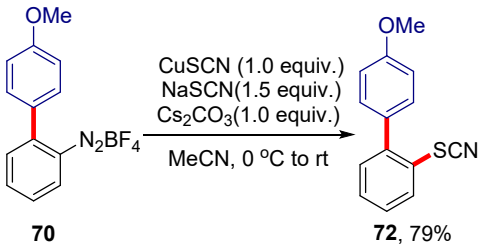
M.P.: 70 – 75 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 – 7.53 (m, 4H), 7.48 – 7.41 (m, 2H), 7.36 – 7.31 (m, 1H), 7.03 – 6.99 (m, 2H), 3.87 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.1, 140.8, 133.7, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3 ppm.

Spectra data are consistent with the reported literature.[7]

4'-methoxy-2-thiocyanato-1,1'-biphenyl (72)



70 **72**, 79%

Procedure F:[8] Cesium carbonate (65.2 mg, 0.2 mmol), NaSCN (24.3 mg, 0.3 mmol), and CuSCN (24.5 mg, 0.2 mmol) were suspended in acetonitrile (0.67 M) and the mixture was cooled to 0 °C. A solution of arenediazonium tetrafluoroborate (0.2 mmol) in acetonitrile (0.40 M) was added to the suspension. The resulting mixture was stirred at 0 °C for 1 h and then at room temperature overnight. The reaction was quenched with diethyl ether (10 mL), and the mixture was filtered. The filtrate was washed with water (2 × 10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, ethyl acetate/cyclohexane gradient) to afford compound **72** as a white solid (38.1 mg, 79%).

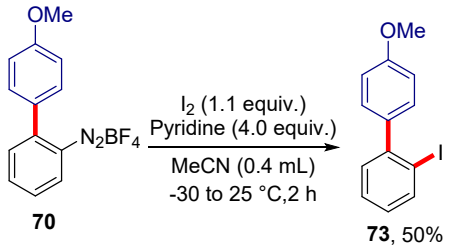
M.P.: 58 – 63 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 – 7.72 (m, 1H), 7.45 – 7.39 (m, 2H), 7.35 – 7.30 (m, 1H), 7.27 – 7.23 (m, 2H), 7.01 – 6.97 (m, 2H), 3.87 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.8, 141.9, 131.1, 130.8, 130.2, 129.2, 128.9, 128.8, 124.3, 114.1, 110.8, 55.3 ppm.

Spectra data are consistent with the reported literature.[8]

2-iodo-4'-methoxy-1,1'-biphenyl (73)



70 **73**, 50%

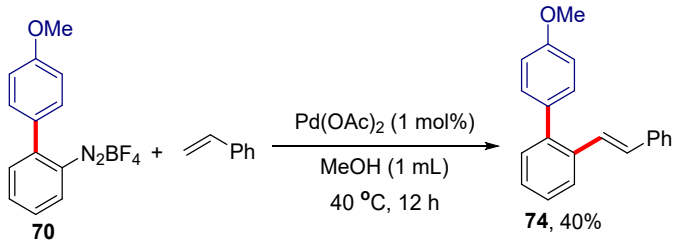
Procedure G[9] Pyridine (63 mg, 0.8 mmol, 4.0 equiv) was added dropwise over 30 seconds to a cooled (−30 °C) mixture of arenediazonium tetrafluoroborate (0.2 mmol), I_2 (56 mg, 0.22 mmol, 1.1 equiv) in MeCN (0.4 mL). After warming to room temperature over 2 h, the mixture was concentrated. The residue was diluted with Et_2O (5 mL) and the organic phase was washed with $Na_2S_2O_3$ (1 M, 5 mL) and brine (5 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated. Purification by flash chromatography (ethyl acetate/cyclohexane gradient) yielded compound **73** as a brown oil (31.0 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.9 Hz, 1H), 7.42 – 7.35 (m, 1H), 7.31 – 7.25 (m, 3H), 7.03 – 6.93 (m, 3H), 3.86 (s, 3H)ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.1, 146.3, 139.5, 136.7, 130.4, 130.2, 128.5, 128.1, 113.3, 99.2, 55.3 ppm.

Spectra data are consistent with the reported literature.[10]

(E)-4'-methoxy-2-styryl-1,1'-biphenyl (74)



70 **74**, 40%

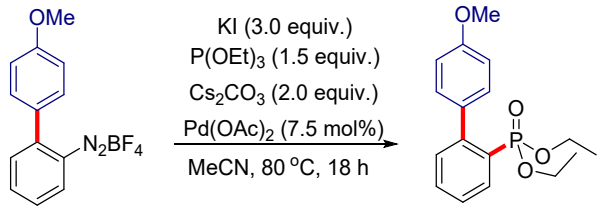
Procedure H:[11] A mixture of styrene (21 mg, 0.2 mmol, 1.0 equiv) and arenediazonium tetrafluoroborate (71 mg, 0.24 mmol, 1.2 equiv) in MeOH (1 mL) with $Pd(OAc)_2$ (0.5 mg, 1 mol%) was stirred at 40 °C for 12 h. The reaction was then quenched with brine (5 mL) and extracted with ethyl acetate (3 × 6 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by column chromatography (SiO_2, petroleum ether/EtOAc = 10:1) afforded compound **74** as a yellow oil (22.9 mg, 40%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 – 7.71 (m, 1H), 7.44 – 7.30 (m, 9H), 7.26 – 7.20 (m, 1H), 7.18 – 7.13 (m, 1H), 7.09 – 7.02 (m, 1H), 7.02 – 6.95 (m, 2H), 3.88 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.8, 140.8, 137.7, 135.4, 133.2, 131.0, 130.2, 129.2, 128.6, 128.0, 127.5, 127.4, 127.2, 126.5, 125.9, 113.6, 55.3 ppm.

Spectra data are consistent with the reported literature.[11]

diethyl (4'-methoxy-[1,1'-biphenyl]-2-yl)phosphonate (75)



70 **75**, 51%

Procedure I:[12] A mixture of aryl diazonium salt (0.2 mmol, 59.6 mg) and KI (0.6 mmol, 100.0 mg) in anhydrous MeCN (0.4 mL) was stirred under an argon atmosphere. To this mixture were added $Pd(OAc)_2$ (0.015 mmol, 3.5 mg), $P(OEt)_3$ (0.3 mmol, 50.0 mg), and Cs_2CO_3 (0.4 mmol, 131.0 mg), followed by additional MeCN (0.8 mL). The reactor was protected from light with aluminum foil and the reaction mixture was stirred at 80 °C for 18 h under argon. After cooling to room temperature, the mixture was diluted with EtOAc, washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, ethyl acetate/cyclohexane gradient) to afford compound **75** as a brown solid (32.7 mg, 51%).

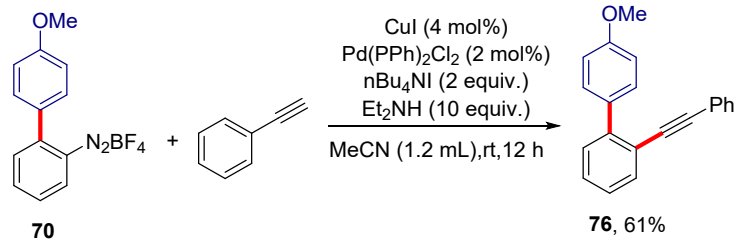
M.P.: 93 – 97 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.30 (m, 2H), 7.29 – 7.26 (m, 2H), 7.10 (d, J = 7.5 Hz, 1H), 7.01 – 6.95 (m, 2H), 6.94 – 6.88 (m, 1H), 4.17 – 4.01 (m, 4H), 3.85 (s, 3H), 1.27 – 1.22 (m, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.1, 145.2, 130.4, 130.3, 130.2, 128.2, 127.3, 120.2, 114.2, 112.9, 63.4, 63.3, 55.3, 16.1, 16.1 ppm.

Spectra data are consistent with the reported literature.[12]

4'-methoxy-2-(phenylethynyl)-1,1'-biphenyl (76)



70 **76**, 61%

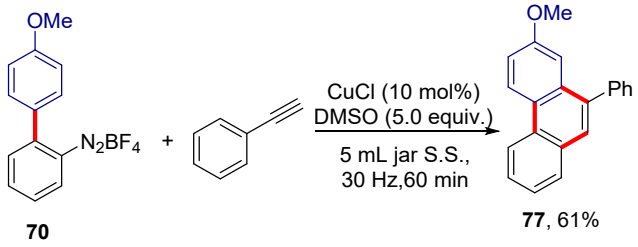
Procedure J:[9] An oven-dried Schlenk tube was charged under an argon atmosphere with arenediazonium salt (0.2 mmol), n-Bu_4NI (0.4 mmol), $PdCl_2(PPh_3)_2$ (0.004 mmol), CuI (0.008 mmol), diethylamine (2.0 mmol), phenylacetylene (0.4 mmol), and anhydrous MeCN (1.2 mL). The tube was sealed and the mixture was stirred at room temperature for 12 h. Upon completion, the reaction mixture was diluted with Et_2O, washed sequentially with HCl (1 M, twice) and a saturated NaCl solution. The organic phase was separated, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (eluent: n-hexane/AcOEt) to afford compound **76** as a yellow waxy liquid (34.7 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 – 7.60 (m, 3H), 7.44 – 7.36 (m, 4H), 7.34 – 7.27 (m, 4H), 7.01 (d, J = 8.9 Hz, 2H), 3.88 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.1, 143.4, 133.0, 132.9, 131.3, 130.5, 129.3, 128.5, 128.2, 128.0, 126.6, 123.5, 121.4, 113.3, 92.1, 89.6, 55.3 ppm.

Spectra data are consistent with the reported literature.[9]

2-methoxy-10-phenylphenanthrene (77)



70 **77**, 61%

Procedure K:[5] A 5.0 mL Retsch stainless steel milling jar was charged with arenediazonium tetrafluoroborate (0.2 mmol, 1.0 equiv.), phenylacetylene (0.6 mmol, 3.0 equiv.), cuprous chloride (0.02 mmol, 10 mol%), and DMSO (1.0 mmol, 5.0 equiv.) under air. A stainless-steel ball (2.8 g) was then introduced, and the mixture was milled at 30 Hz for 1 hour. Upon completion, the reaction mixture was quenched with dichloromethane. The organic layer was concentrated under reduced pressure and purified by silica gel chromatography (eluent: EtOAc/hexane) to afford the desired product. Compound **77** was obtained as a light yellow oil (34.7 mg, 61%).

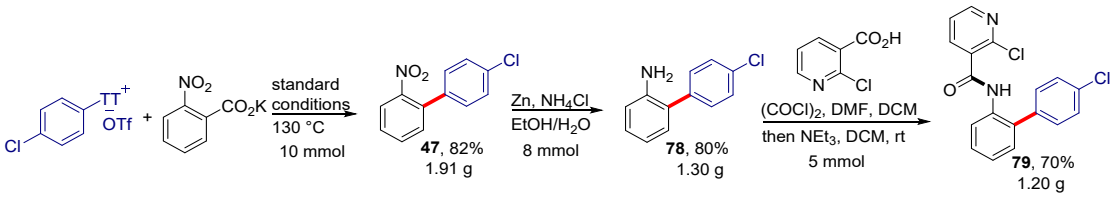
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, *J* = 8.9 Hz, 1H), 8.63 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.72 – 7.63 (m, 2H), 7.60 – 7.51 (m, 5H), 7.50 – 7.45 (m, 1H), 7.35 – 7.30 (m, 2H), 3.81 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.2, 140.9, 138.2, 132.5, 130.6, 130.1, 129.9, 128.6, 128.4, 128.1, 127.4, 126.7, 125.9, 125.0, 124.5, 122.0, 116.3, 107.9, 55.3 ppm.

Spectra data are consistent with the reported literature.[5]

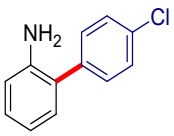
Synthesis of Fungicides

Synthsis of Boscalid



Procedure L: An oven-dried vessel was charged with arylthianthrenium salts (10.0 mmol, 1 equiv.), potassium carboxylate (12.0 mmol, 1.2 equiv.), $Pd(OAc)_2$ (56 mg, 0.25 mmol, 0.025 equiv.), CuI (95.0 mg, 0.5 mmol, 0.05 equiv.), and bpy (80.0 mg, 0.5 mmol, 0.05 equiv.). Under an argon atmosphere, DMSO (50 mL) was added via syringe. The resulting reaction mixture was stirred at 130 °C for 16 h. Compound **47** was obtained as a yellow solid (1.91 g, 82%).A separate oven-dried vessel was charged with Zn (40.0 mmol, 5.0 equiv.), NH_4Cl (80 mmol, 10.0 equiv.), and compound **47** (8 mmol, 1.0 equiv.). Then, 40 mL of a mixed solvent ($MeOH:H_2O$ = 2:1) was added. The mixture was stirred at room temperature for one hour. Compound **78** was obtained as a brown oily liquid (1.30 g, 80%). 2-Chloronicotinic acid (6.0 mmol, 1.0 equiv.) was suspended in DCM (0.2 M), followed by the addition of two drops of DMF. Oxalyl chloride (9 mmol, 1.5 equiv.) was added dropwise to the mixture at 0 °C. The reaction was allowed to proceed at room temperature for 3.5 hours, after which the volatiles were removed under reduced pressure. The resulting acyl chloride (6 mmol, 1.2 equiv.) and aniline (5 mmol, 1.0 equiv.) were dissolved in a mixture of ethyl acetate and water ($EA:H_2O$ = 2:1), followed by the addition of K_2CO_3 (11.0 mmol, 2.2 equiv.). The reaction was stirred at room temperature for 20 hours. Compound **79** was obtained as a white solid (1.20 g, 70%).

4'-chloro-[1,1'-biphenyl]-2-amine (78)

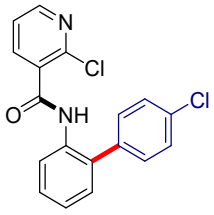


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 – 7.36 (m, 4H), 7.23 – 7.17 (m, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.91 – 6.83 (m, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 3.81 (s, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 143.1, 137.8, 133.0, 130.4, 130.3, 128.9, 128.8, 126.3, 118.8, 115.8 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{11}ClN^+$ 204.0575; found 204.0573.

2-chloro-N-(4'-chloro-[1,1'-biphenyl]-2-yl)nicotinamide (79)



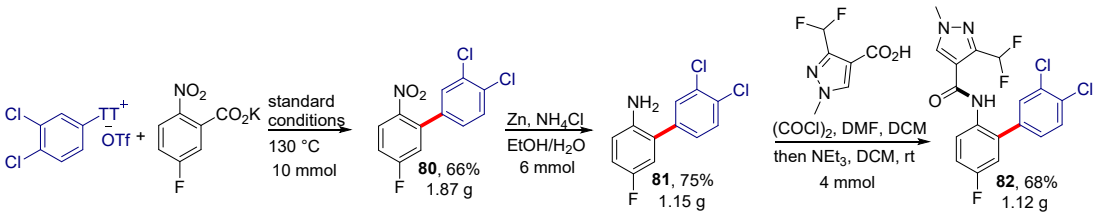
M.P.: 142 – 145 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 – 8.34 (m, 2H), 8.19 – 8.06 (m, 2H), 7.48 – 7.39 (m, 3H), 7.36 – 7.30 (m, 3H), 7.26 (d, J = 5.2 Hz, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.5, 151.3, 146.7, 140.1, 136.2, 134.4, 134.3, 132.2, 131.0, 130.8, 130.2, 129.3, 128.9, 125.3, 122.9, 122.1 ppm.

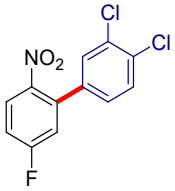
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{13}Cl_2N_2O^+$ 343.0399; found 343.0392.

Synthsis of Bixafen



Procedure M: An oven-dried vessel was charged with arylthianthrenium salts (10.0 mmol, 1.0 equiv.), potassium carboxylate (12.0 mmol, 1.2 equiv.), $Pd(OAc)_2$ (56 mg, 0.25 mmol, 0.025 equiv.), CuI (95.0 mg, 0.5 mmol, 0.05 equiv.), and bpy (80.0 mg, 0.5 mmol, 0.05 equiv.). Under an argon atmosphere, DMSO (50 mL) was added via syringe. The resulting reaction mixture was stirred at 130 °C for 16 h to afford compound **80** as a yellow solid (1.87 g, 66%). A separate oven-dried vessel was charged with Zn (30.0 mmol, 5.0 equiv.), NH_4Cl (60 mmol, 10.0 equiv.), and compound **80** (6 mmol, 1.0 equiv.). Then, 35 mL of a mixed solvent (MeOH:H_2O = 2:1) was added. The mixture was stirred at room temperature for one hour to afford compound **81** as a brown waxy liquid (1.51 g, 75%). 3-(Difluoromethyl)-1-methyl-1H-pyrazole-4-carboxylic acid (6.0 mmol, 1.0 equiv.) was suspended in DCM (0.2 M). Two drops of DMF were added, followed by the dropwise addition of oxalyl chloride (9 mmol, 1.5 equiv.) at 0 °C. The reaction mixture was stirred at room temperature for 3.5 hours, after which the volatiles were removed under reduced pressure. The resulting acyl chloride (4.8 mmol, 1.2 equiv.) and aniline (4 mmol, 1.0 equiv.) were dissolved in a mixture of ethyl acetate and water (EA:H_2O = 2:1), and K_2CO_3 (8.8 mmol, 2.2 equiv.) was added. The reaction was stirred at room temperature for 20 hours to afford compound **82** as a brown solid (1.12 g, 68%).

3',4'-dichloro-5-fluoro-2-nitro-1,1'-biphenyl (80)



M.P.: 83 – 87 °C.

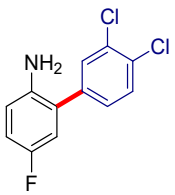
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (dd, *J* = 9.0, 5.0 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.41 (d, *J* = 2.1 Hz, 1H), 7.25 – 7.19 (m, 1H), 7.15 – 7.07 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.0 (d, *J* = 259.0 Hz), 144.7, 137.2 (d, *J* = 9.3 Hz), 136.5 (d, *J* = 1.5 Hz), 133.0 (d, *J* = 18.1 Hz), 130.6, 129.6, 127.4 (d, *J* = 9.3 Hz), 127.1, 118.8 (d, *J* = 23.6 Hz), 116.1, 115.9 (d, *J* =23.2 Hz) ppm.

^{19}F NMR (377 MHz, $CDCl_3$): δ – 103.6 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_7Cl_2FNO_2^+$ 285.9832; found 285.9832.

3',4'-dichloro-5-fluoro-[1,1'-biphenyl]-2-amine (81)



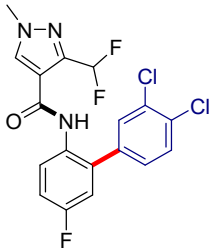
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 – 7.46 (m, 2H), 7.33 – 7.27 (m, 1H), 6.94 – 6.86 (m, 1H), 6.85 – 6.78 (m, 1H), 6.77 – 6.66 (m, 1H), 3.79 (s, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.3 (d, *J* = 238.8 Hz), 139.0 (d, *J* = 2.1 Hz), 138.3 (d, *J* = 2.1 Hz), 132.9, 131.8, 130.81, 130.79, 128.3, 126.1 (d, *J* = 7.4 Hz), 117.1 (d, *J* = 7.8 Hz), 116.4 (d, *J* = 22.9 Hz), 115.7 (d, *J* = 22.3 Hz) ppm.

^{19}F NMR (377 MHz, $CDCl_3$): δ – 126.5 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_9Cl_2FN^+$ 256.0091; found 256.0087.

N-(3',4'-dichloro-5-fluoro-[1,1'-biphenyl]-2-yl)-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide (82)



M.P.: 138 – 142 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 – 7.98 (m, 1H), 7.84 (s, 1H), 7.77 (s, 1H), 7.50 – 7.43 (m, 2H), 7.19 – 7.15 (m, 1H), 7.11 – 7.06 (m, 1H), 6.98 – 6.93 (m, 1H), 6.85 – 6.55 (m, 1H), 3.88 (s, 3H) ppm.

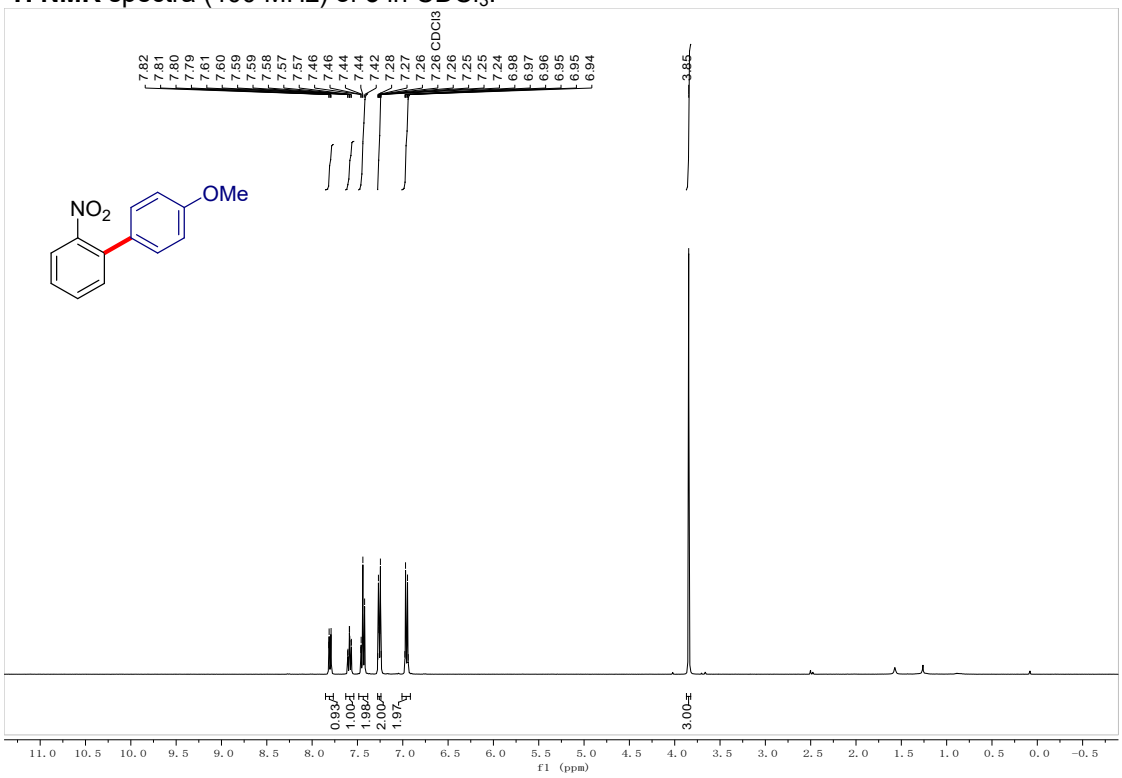
^{13}C NMR (101 MHz, $CDCl_3$): δ 159.63 (d, *J* = 247.5 Hz), 159.57, 142.7 (t, *J* =28.6 Hz), 137.1, 135.5, 134.0 (d, *J* = 9.2 Hz), 133.0, 132.5, 130.9, 130.8, 130.3 (d, *J* = 2.8 Hz), 128.4, 125.8 (d, *J* = 8.2 Hz), 116.7 (d, *J* = 23.2 Hz), 116.2, 115.5 (d, *J* = 22.2 Hz), 111.3 (t, *J* = 235.8 Hz), 39.5 ppm.

^{19}F NMR (377 MHz, $CDCl_3$): δ – 109.4, 116.3 ppm.

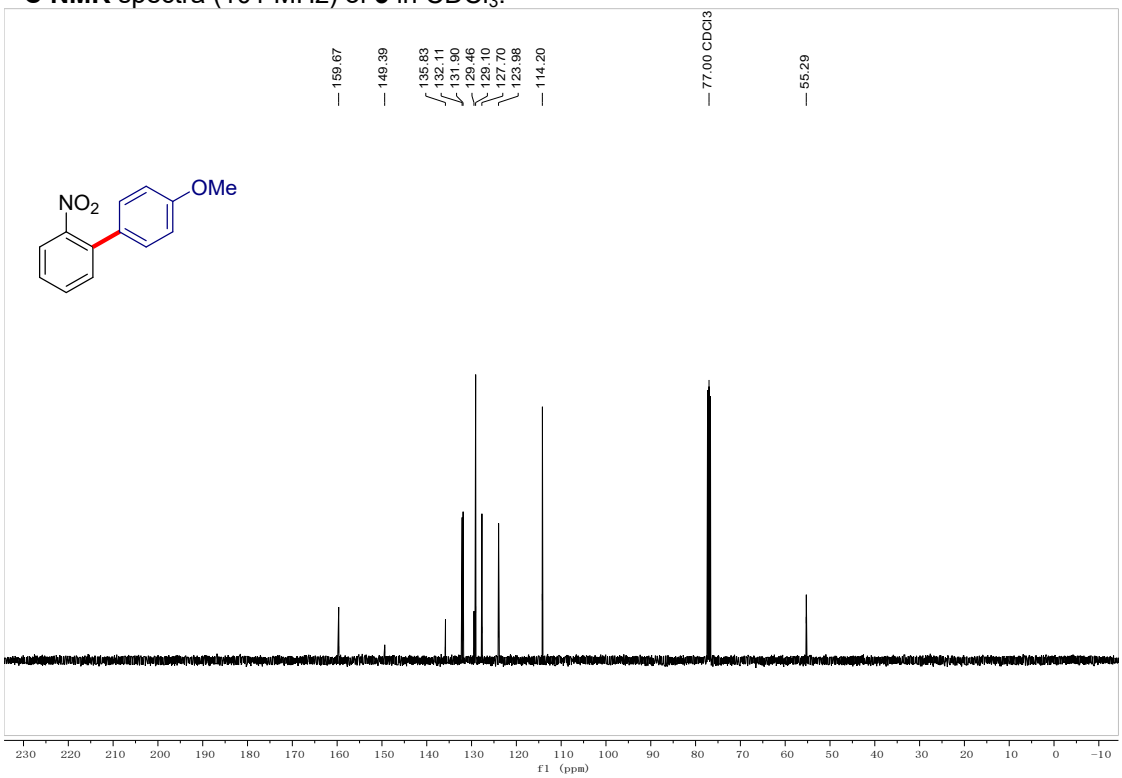
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{13}Cl_2F_3N_3O_2^+$ 414.0382; found 414.0378.

Copies of ^{1}H and ^{13}C NMR Spectra

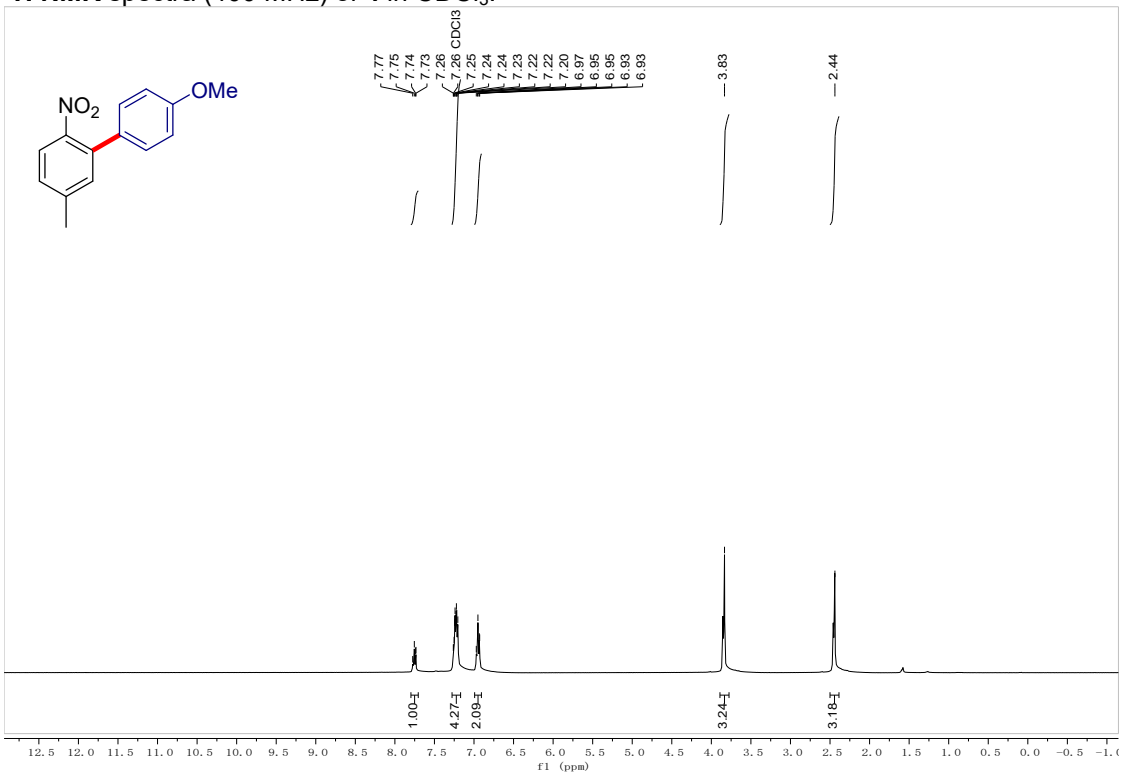
^{1}H NMR spectra (400 MHz) of **3** in $CDCl_3$.



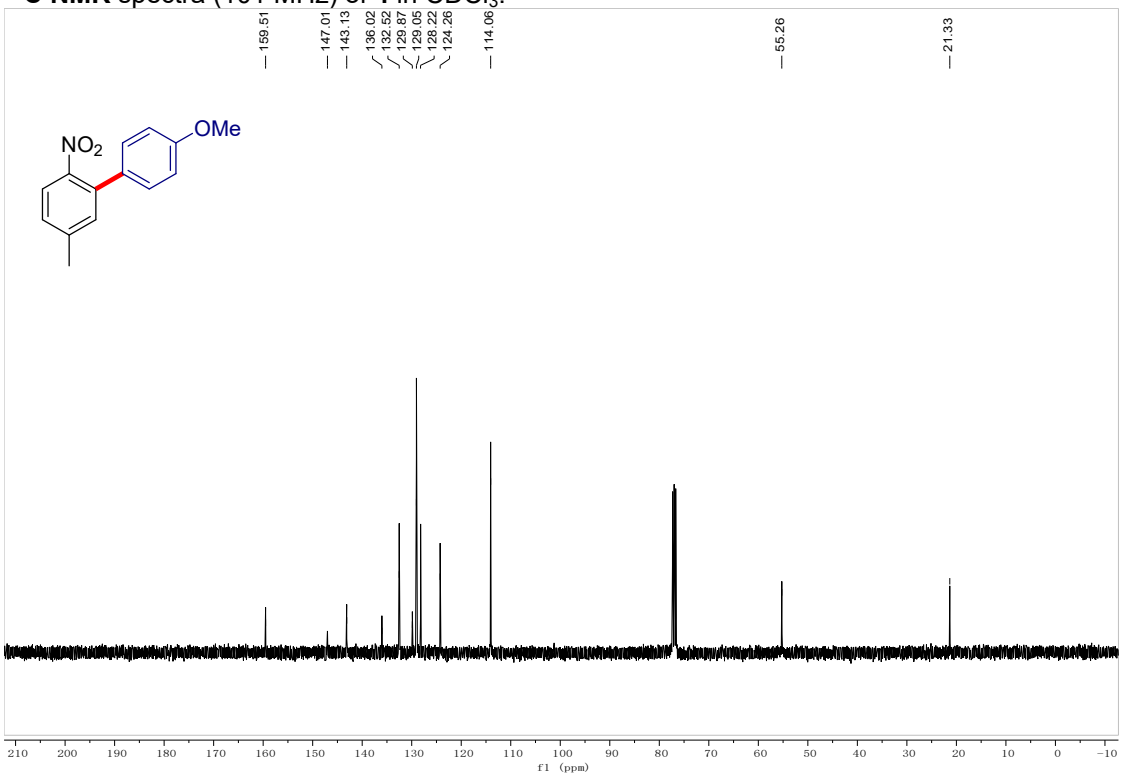
^{13}C NMR spectra (101 MHz) of **3** in $CDCl_3$.



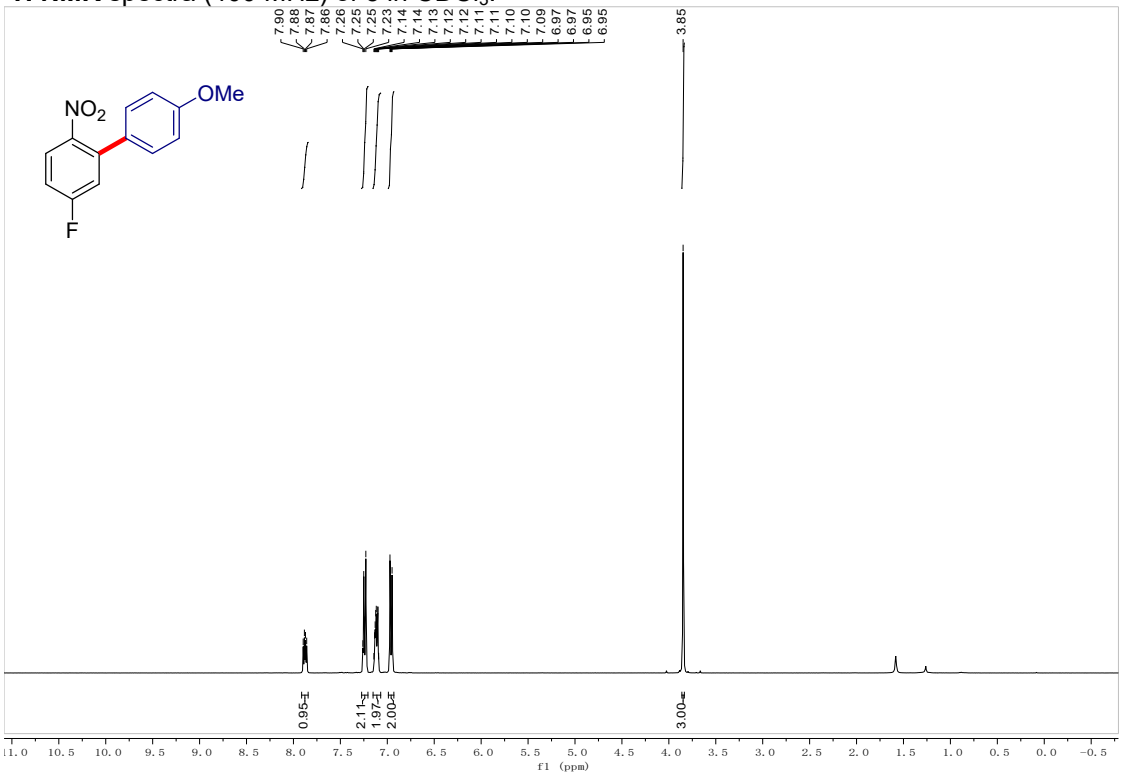
^{1}H NMR spectra (400 MHz) of **4** in $CDCl_3$.



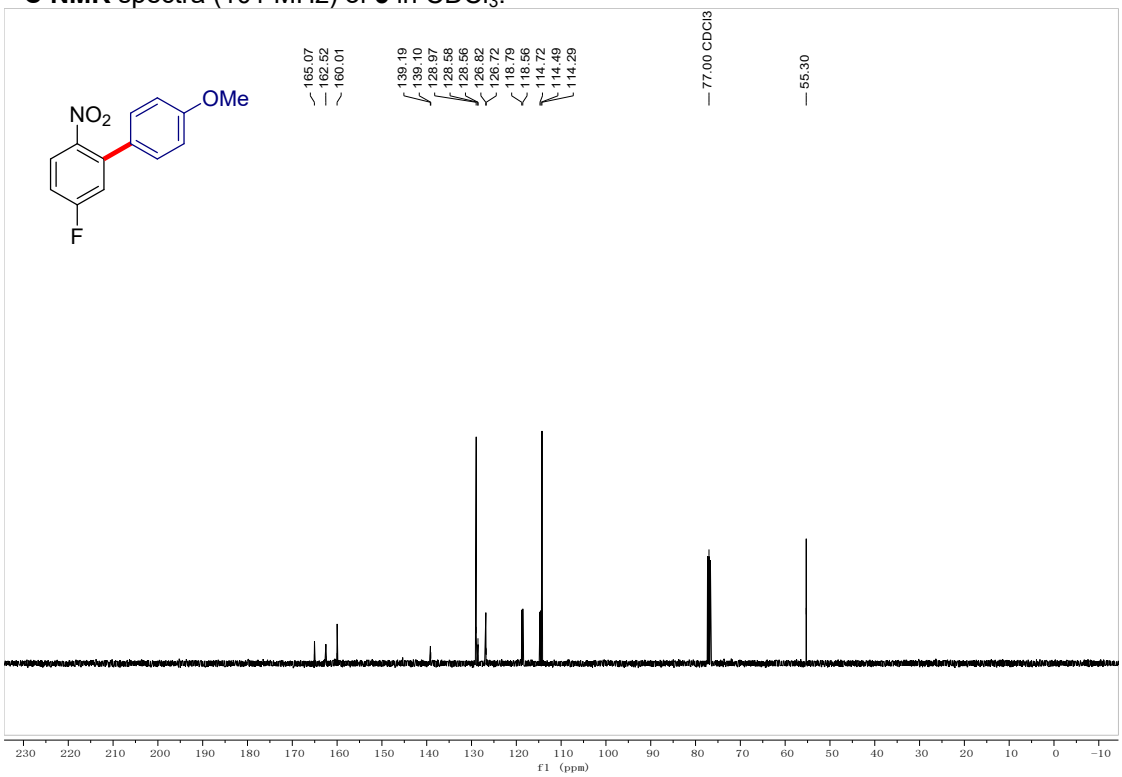
^{13}C NMR spectra (101 MHz) of **4** in $CDCl_3$.



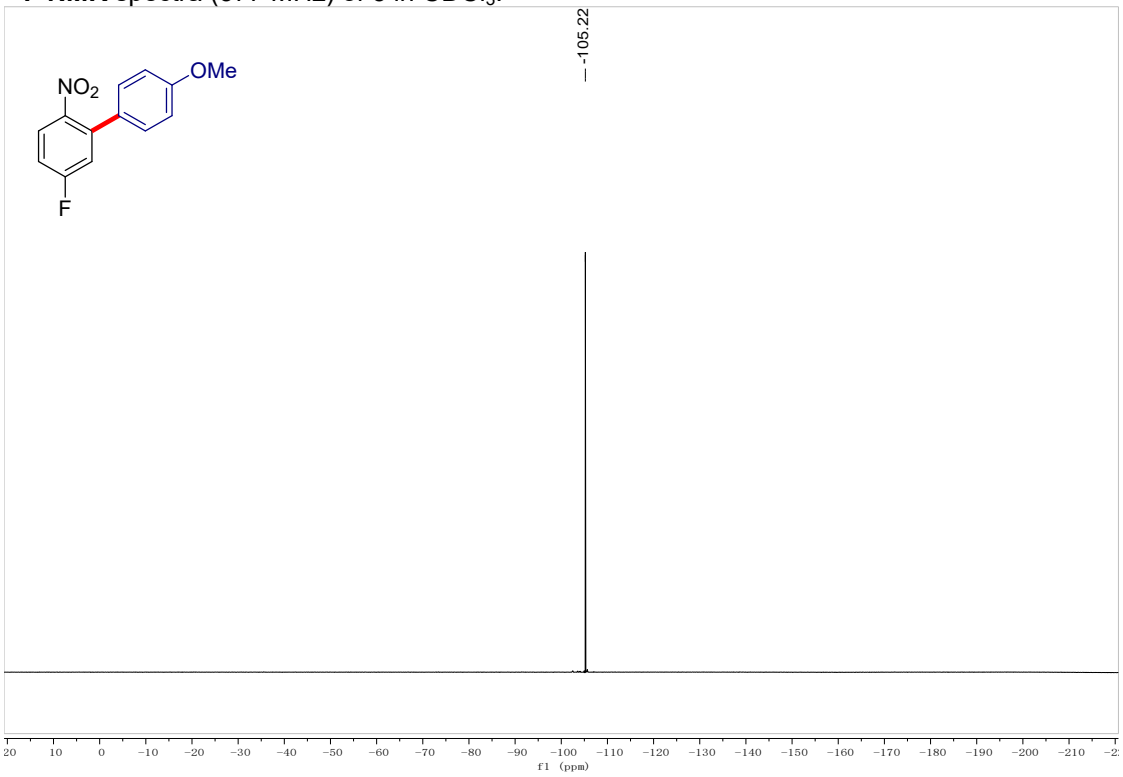
^{1}H NMR spectra (400 MHz) of **5** in $CDCl_3$.



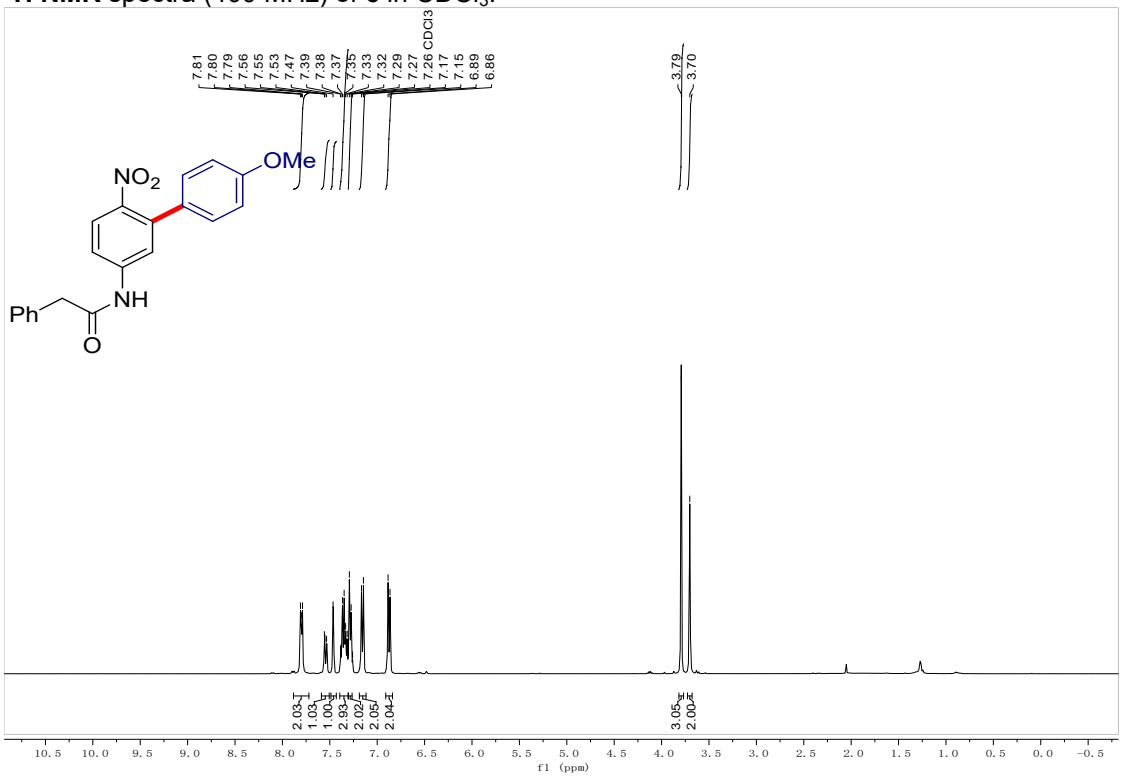
^{13}C NMR spectra (101 MHz) of **5** in $CDCl_3$.



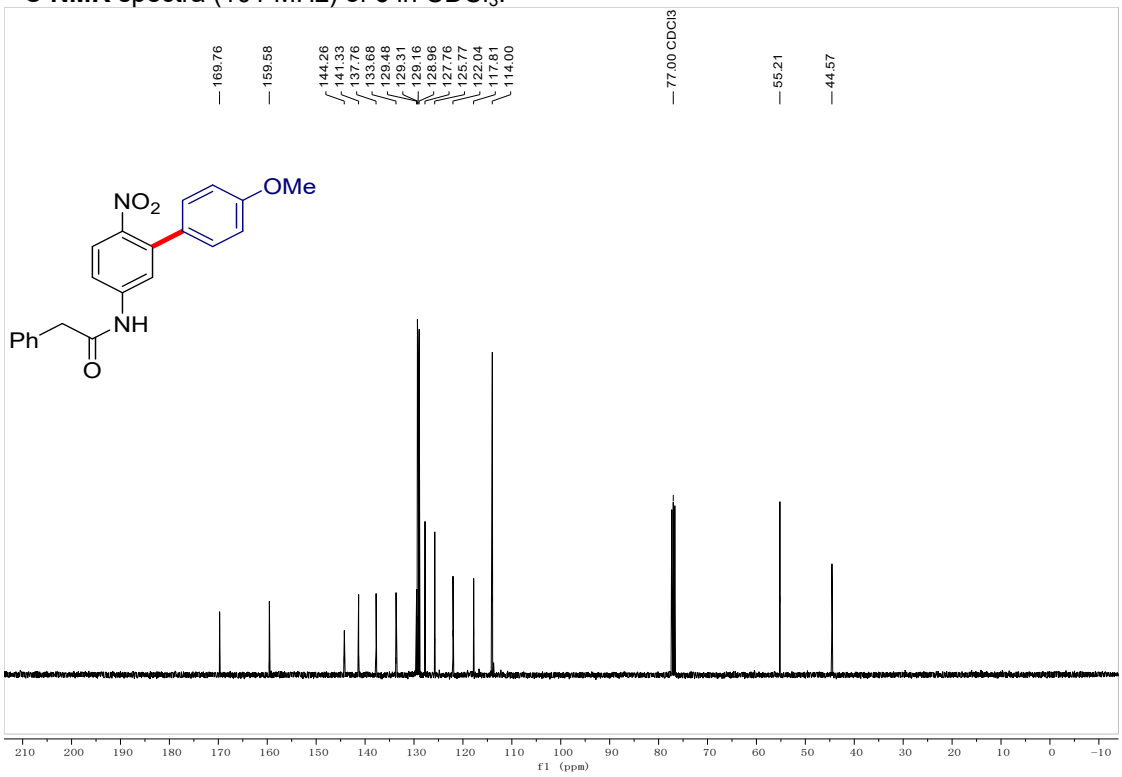
^{19}F NMR spectra (377 MHz) of **5** in $CDCl_3$.



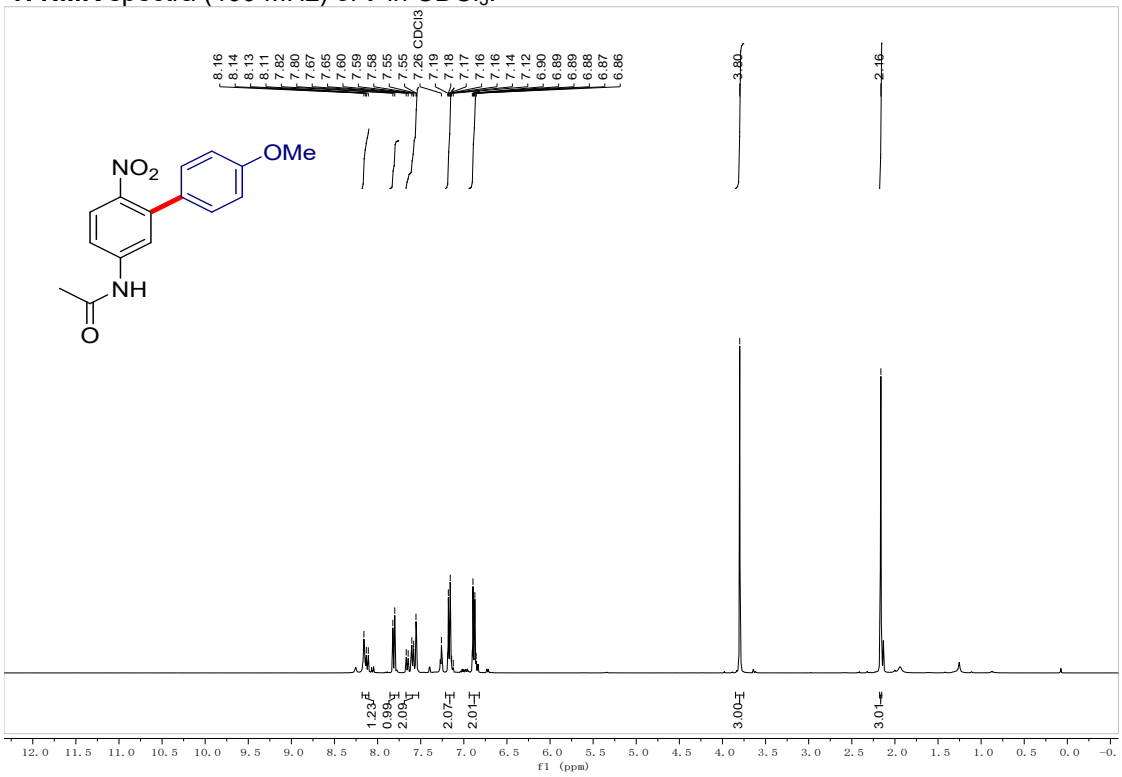
^{1}H NMR spectra (400 MHz) of **6** in $CDCl_3$.



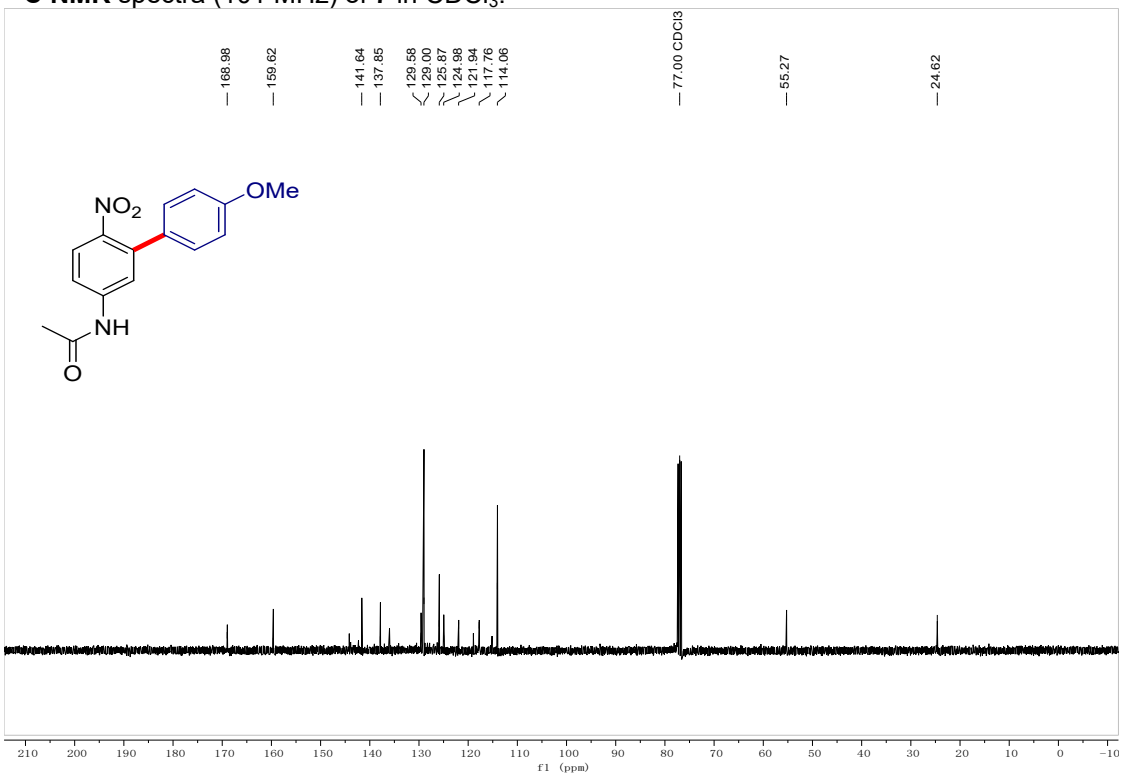
^{13}C NMR spectra (101 MHz) of **6** in $CDCl_3$.



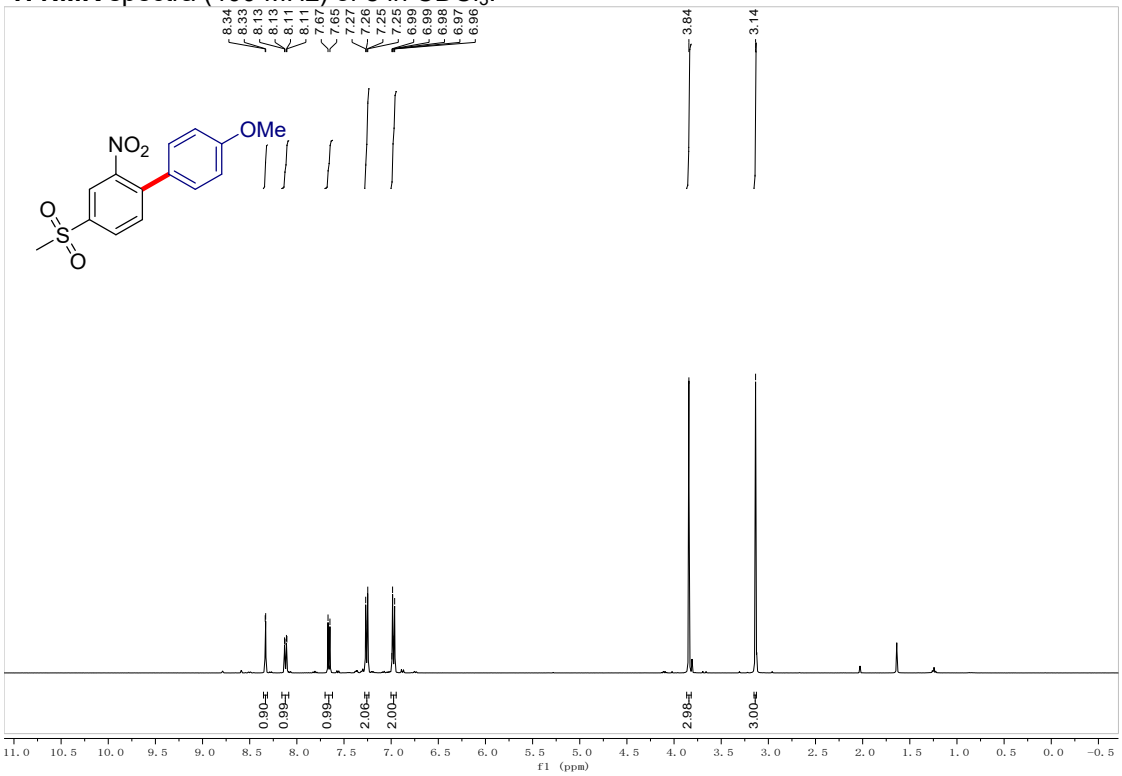
^{1}H NMR spectra (400 MHz) of **7** in $CDCl_3$.



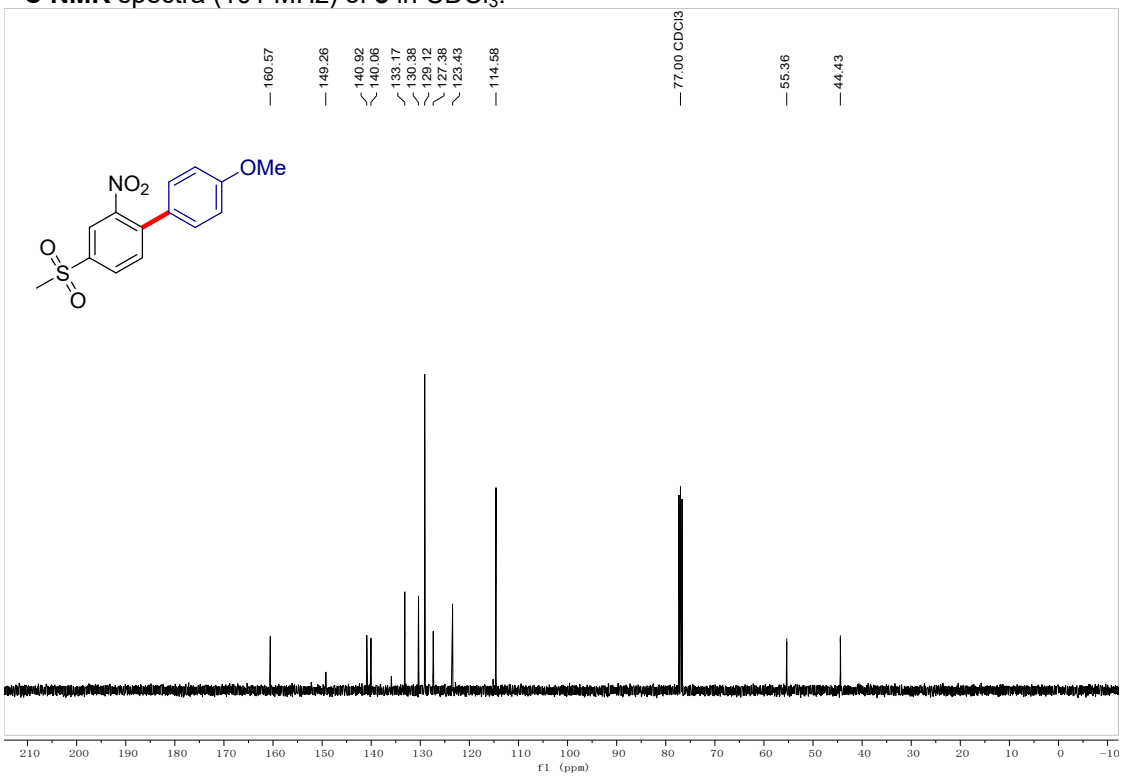
^{13}C NMR spectra (101 MHz) of **7** in $CDCl_3$.



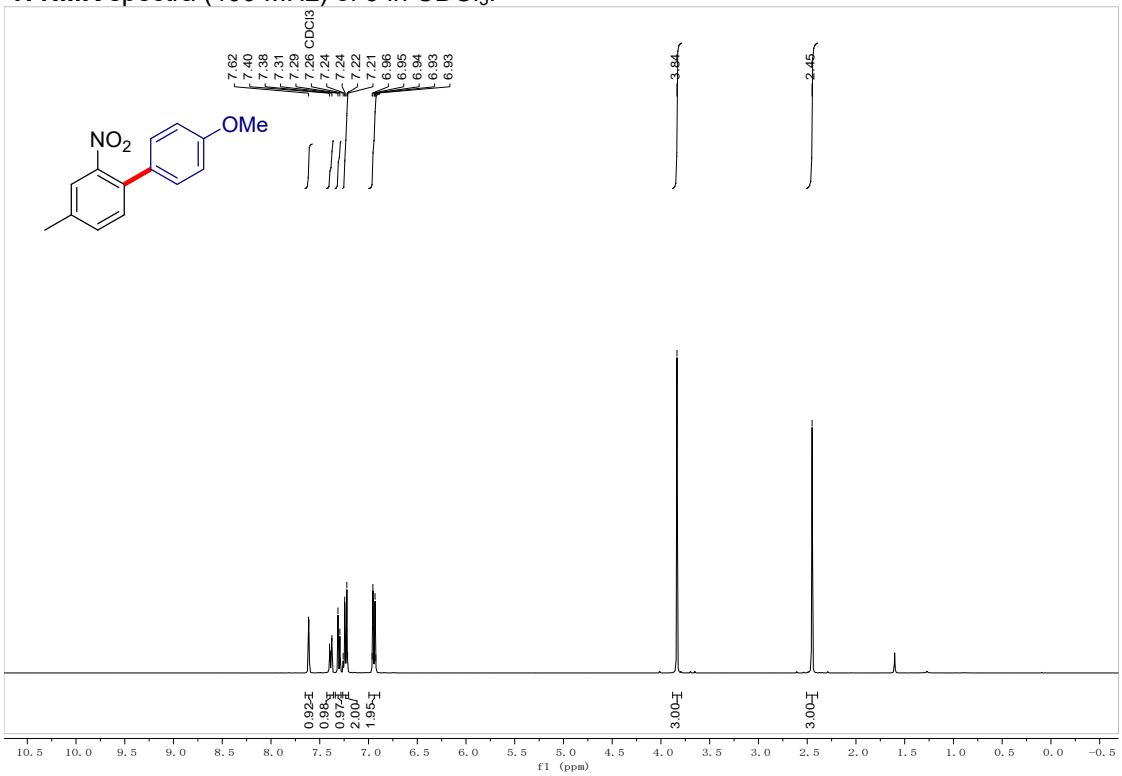
^{1}H NMR spectra (400 MHz) of **8** in $CDCl_3$.



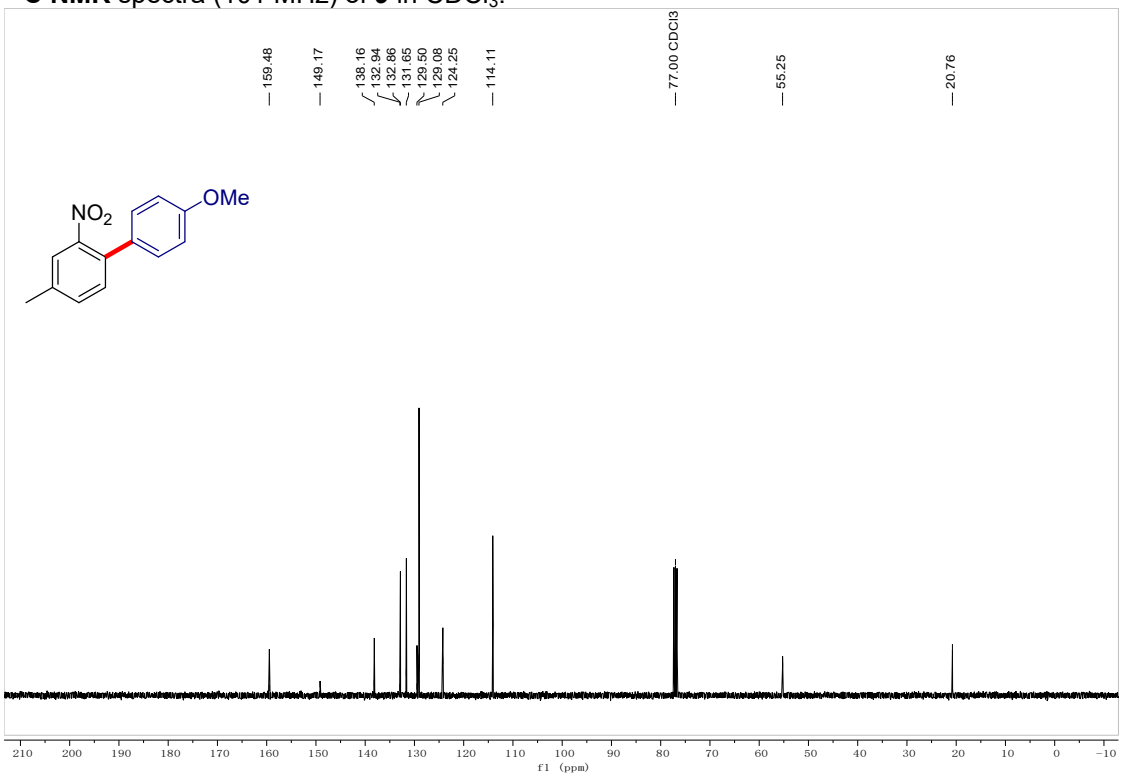
^{13}C NMR spectra (101 MHz) of **8** in $CDCl_3$.



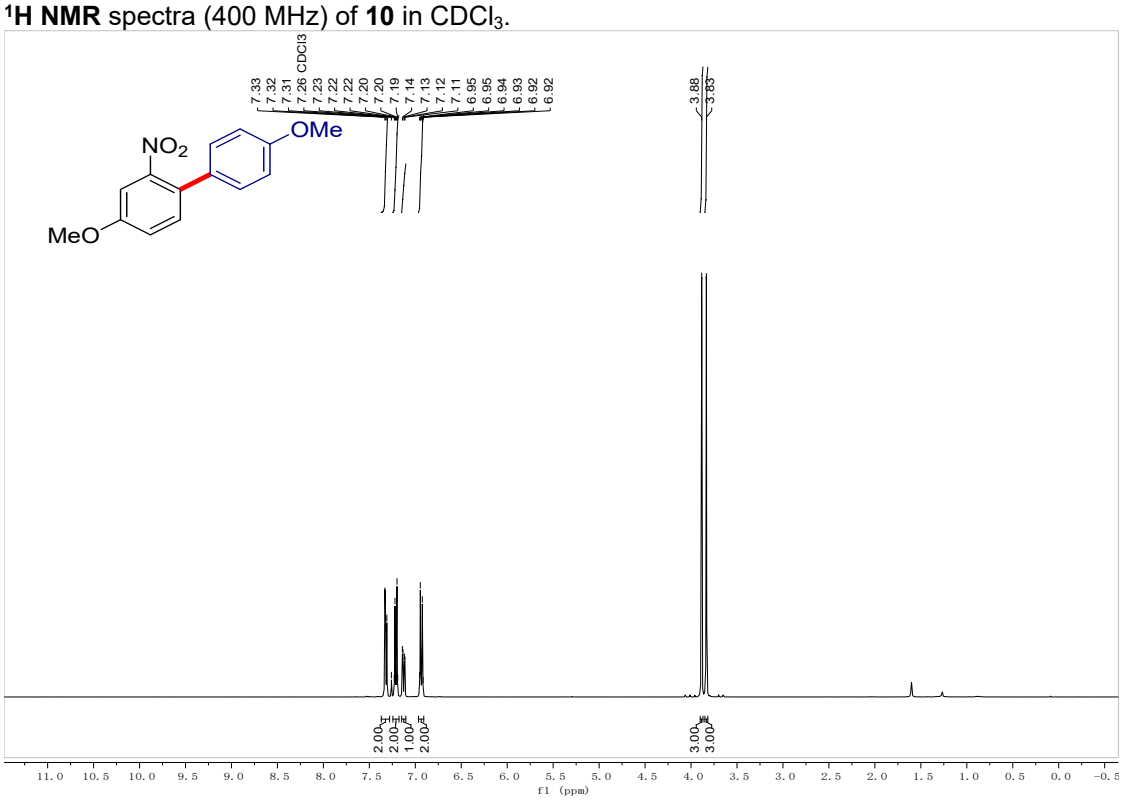
^{1}H NMR spectra (400 MHz) of **9** in $CDCl_3$.



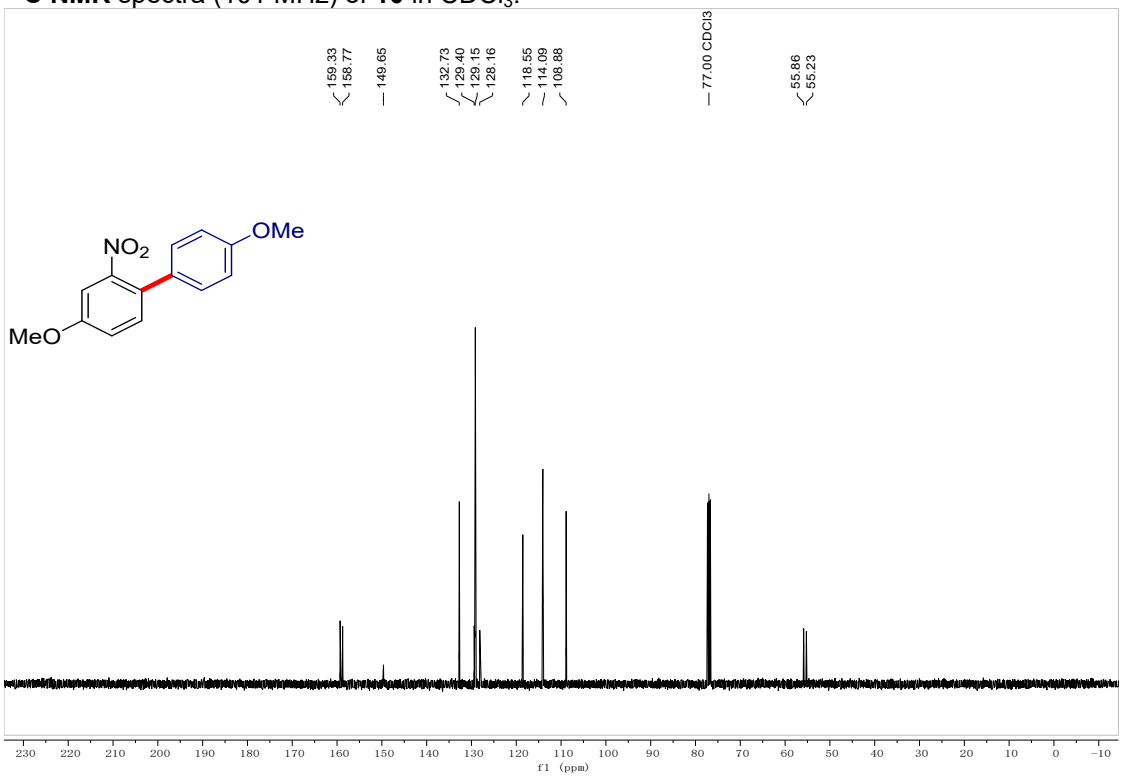
^{13}C NMR spectra (101 MHz) of **9** in $CDCl_3$.



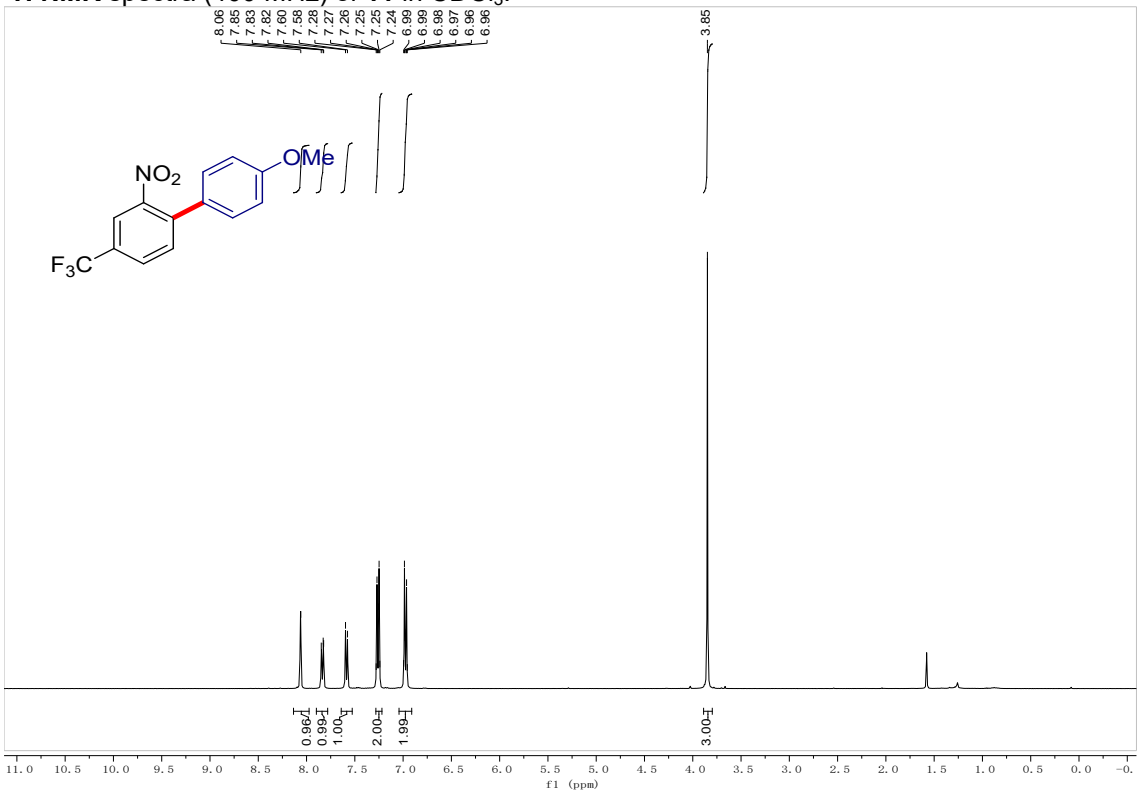
^{1}H NMR spectra (400 MHz) of **10** in $CDCl_3$.



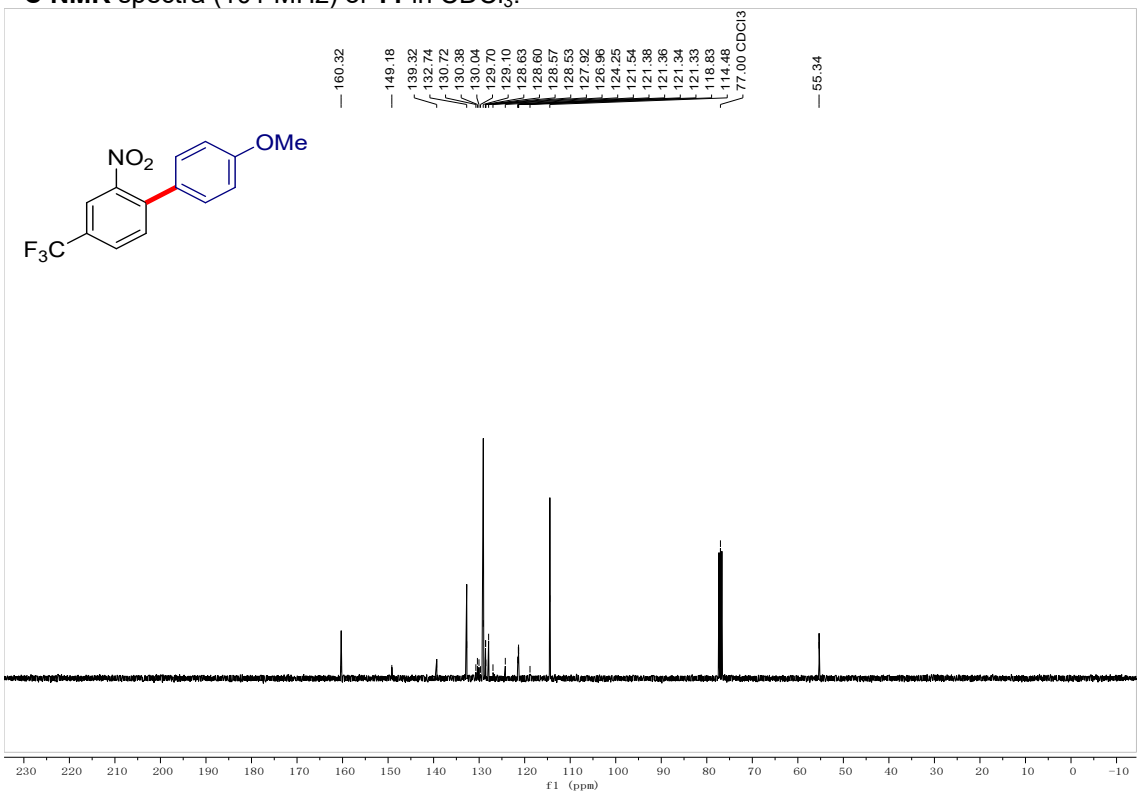
^{13}C NMR spectra (101 MHz) of **10** in $CDCl_3$.



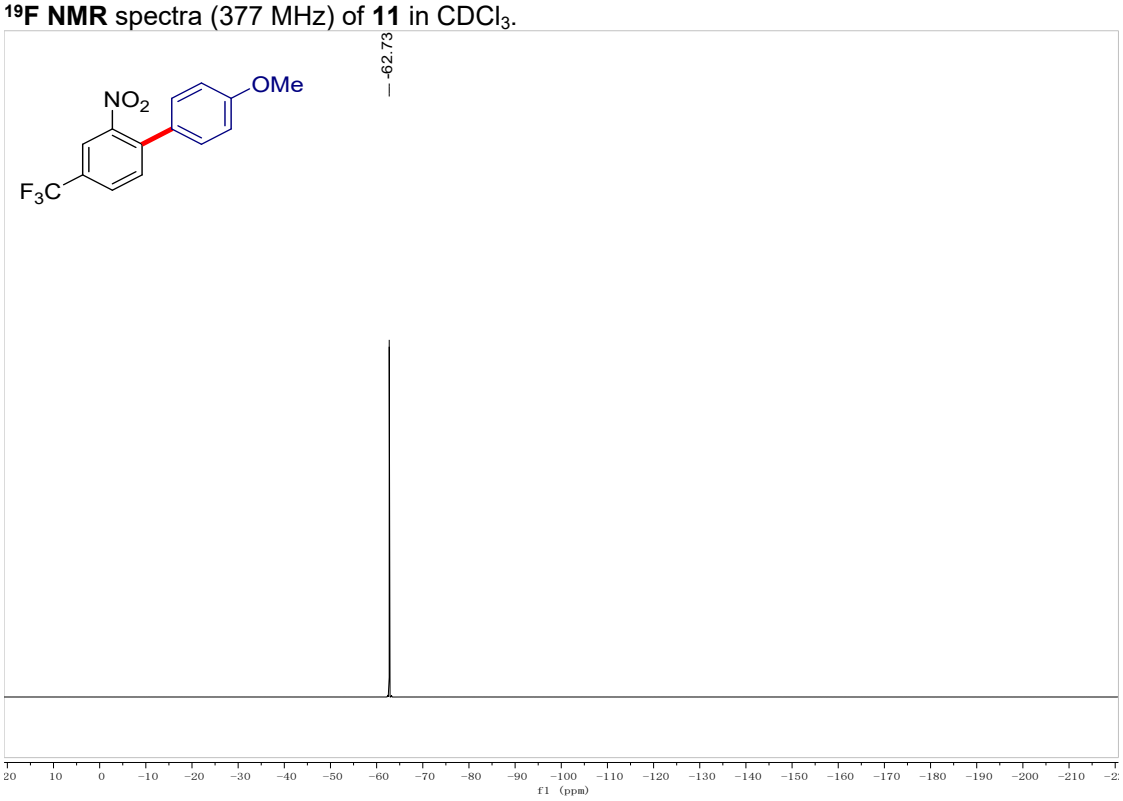
^{1}H NMR spectra (400 MHz) of **11** in $CDCl_3$.



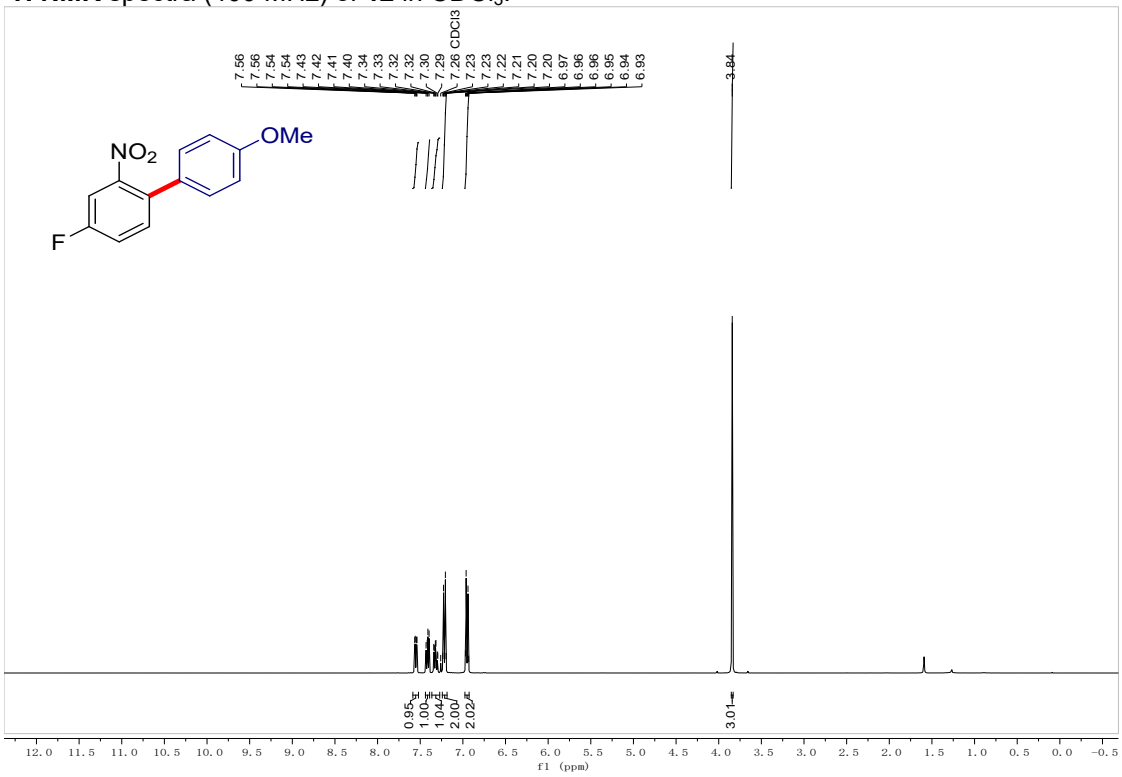
^{13}C NMR spectra (101 MHz) of **11** in $CDCl_3$.



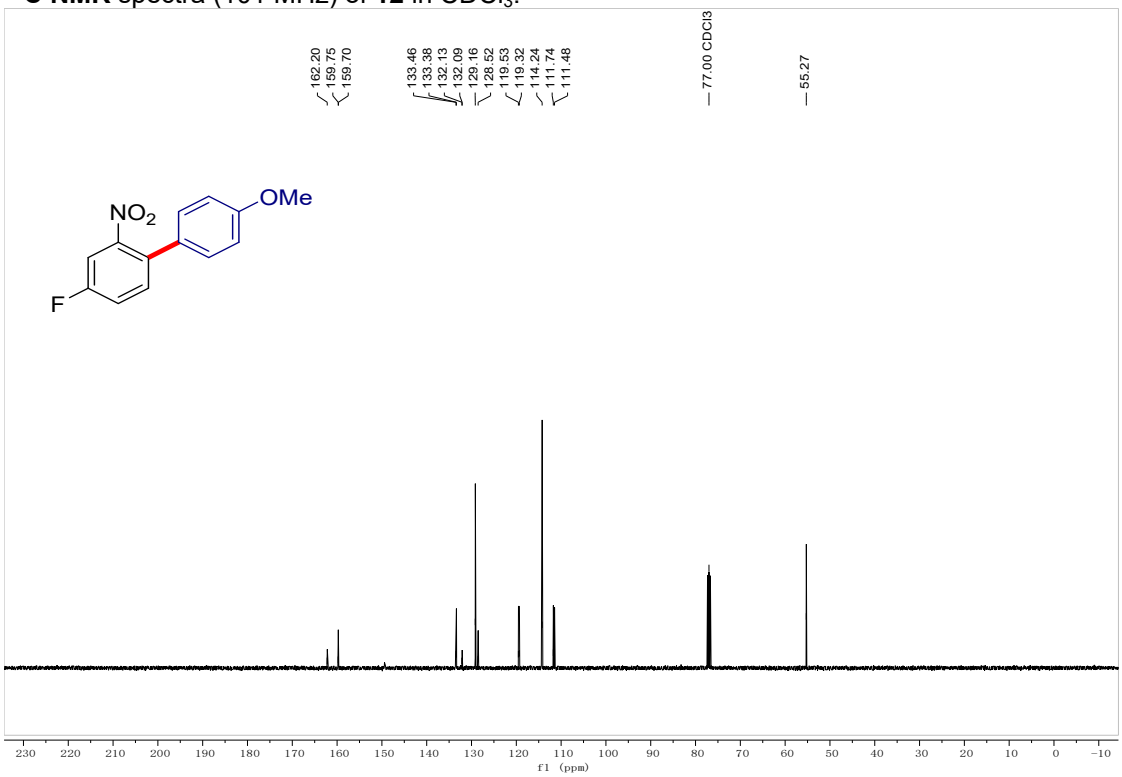
^{19}F NMR spectra (377 MHz) of **11** in $CDCl_3$.



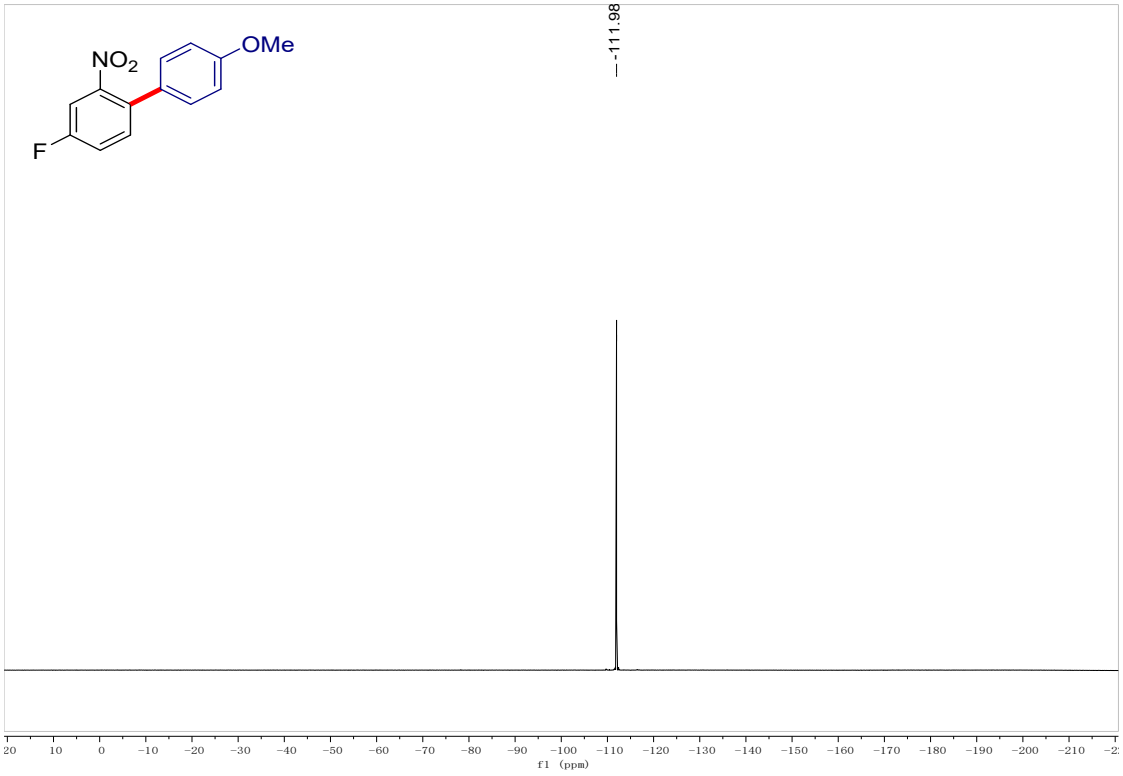
^{1}H NMR spectra (400 MHz) of **12** in $CDCl_3$.



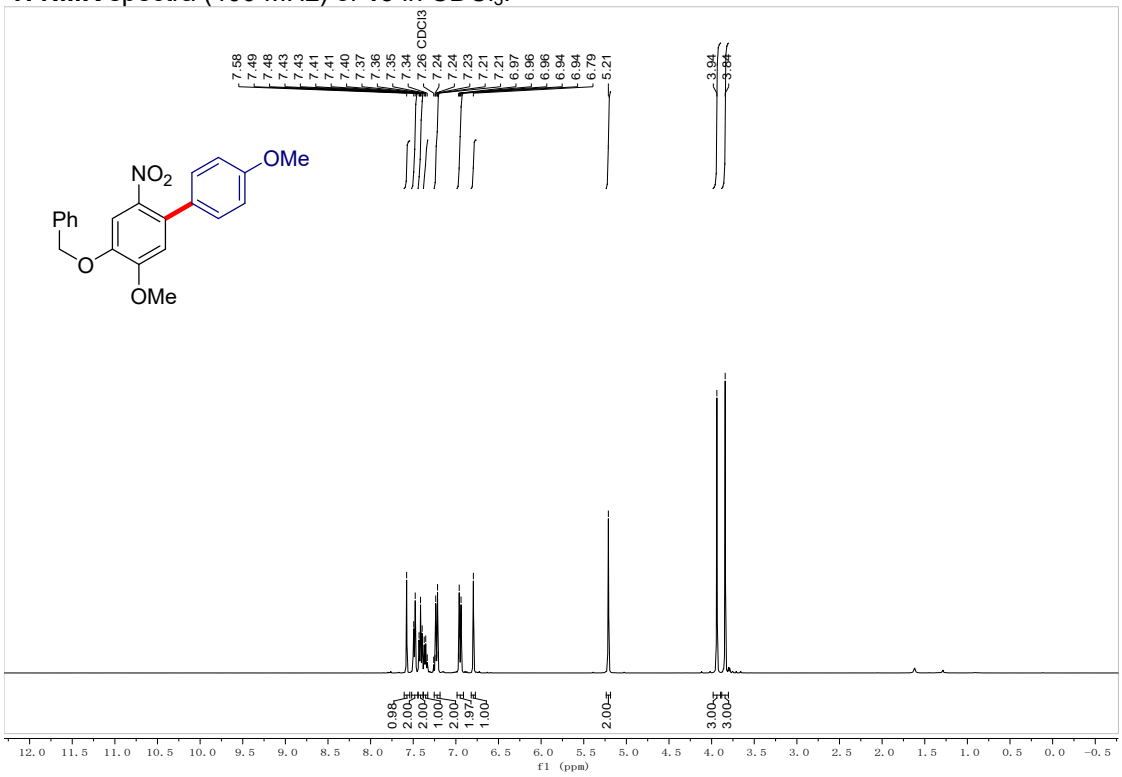
^{13}C NMR spectra (101 MHz) of **12** in $CDCl_3$.



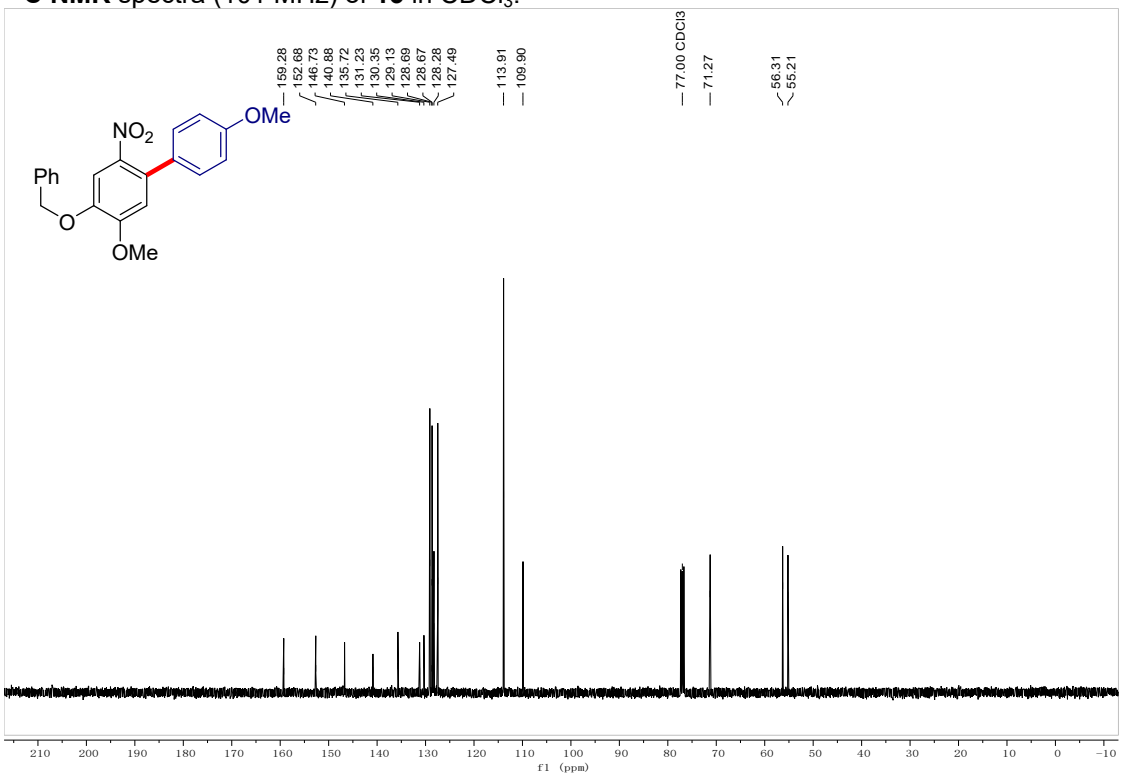
^{19}F NMR spectra (377 MHz) of **12** in $CDCl_3$.



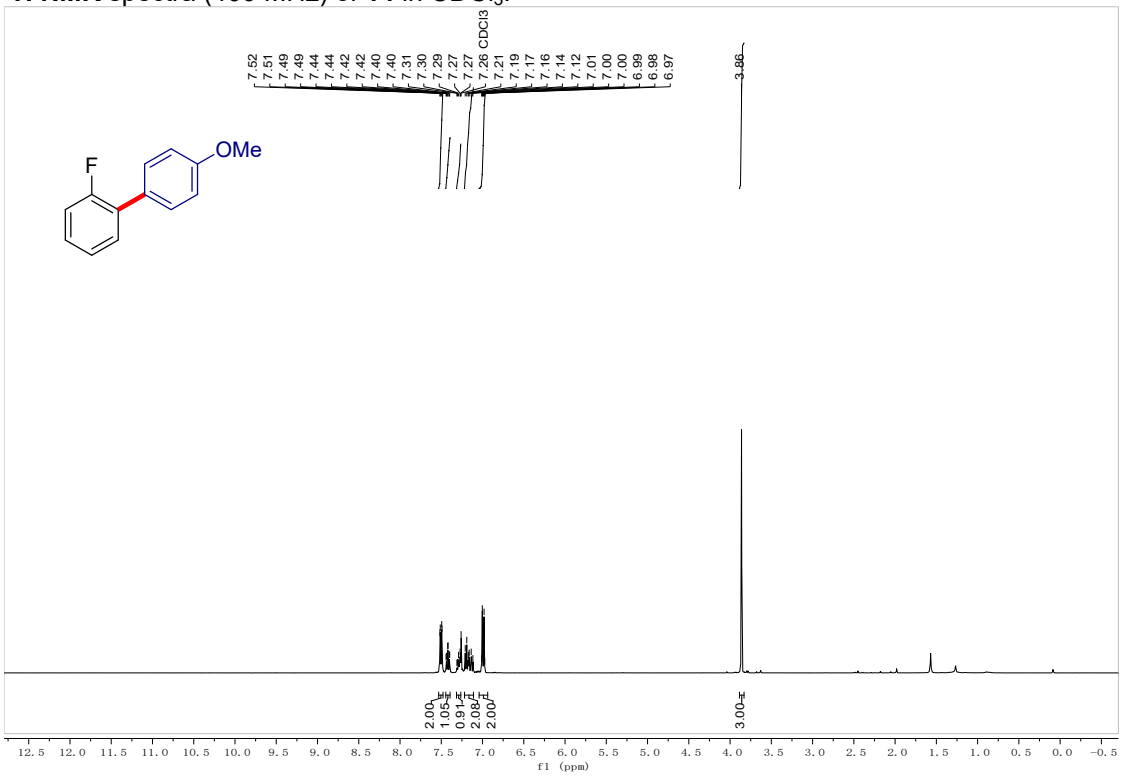
^{1}H NMR spectra (400 MHz) of **13** in $CDCl_3$.



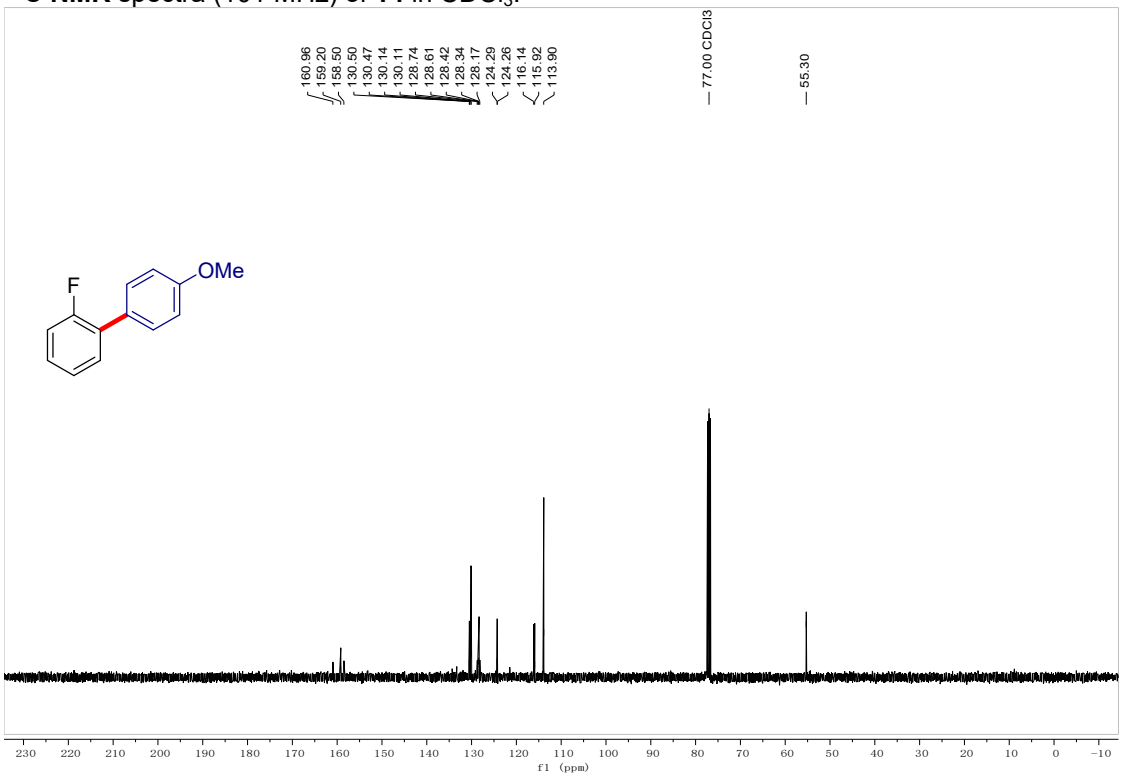
^{13}C NMR spectra (101 MHz) of **13** in $CDCl_3$.



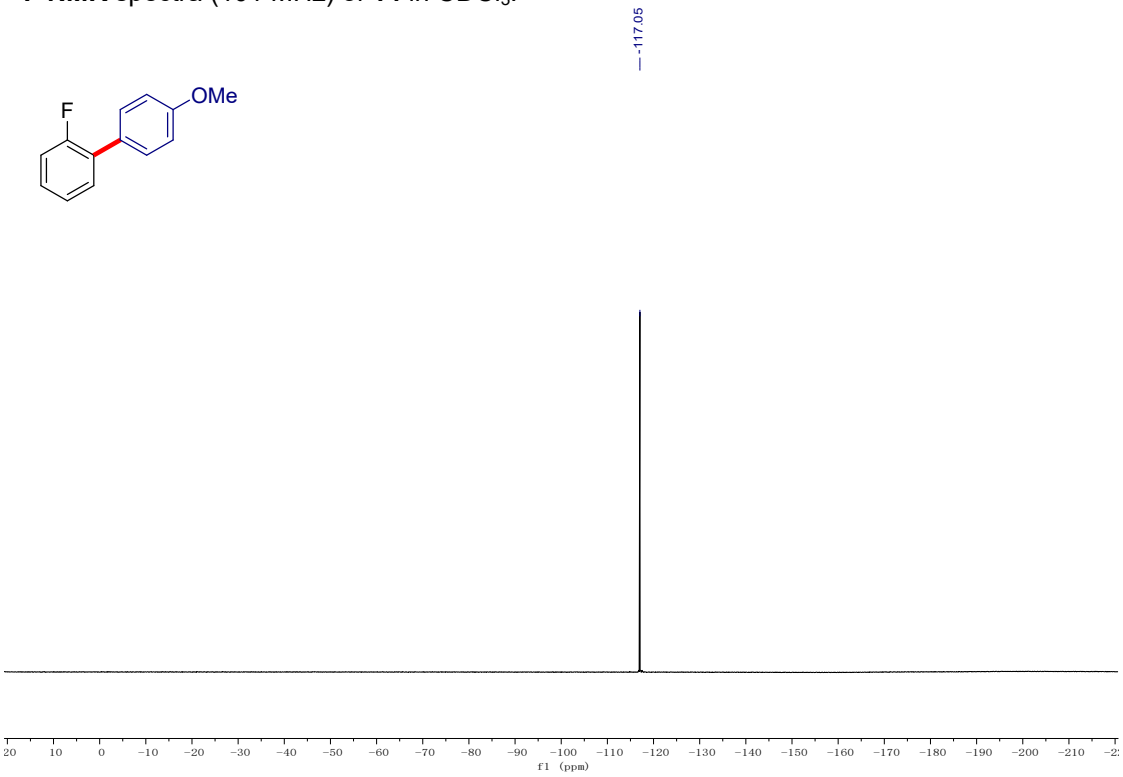
^{1}H NMR spectra (400 MHz) of **14** in $CDCl_3$.



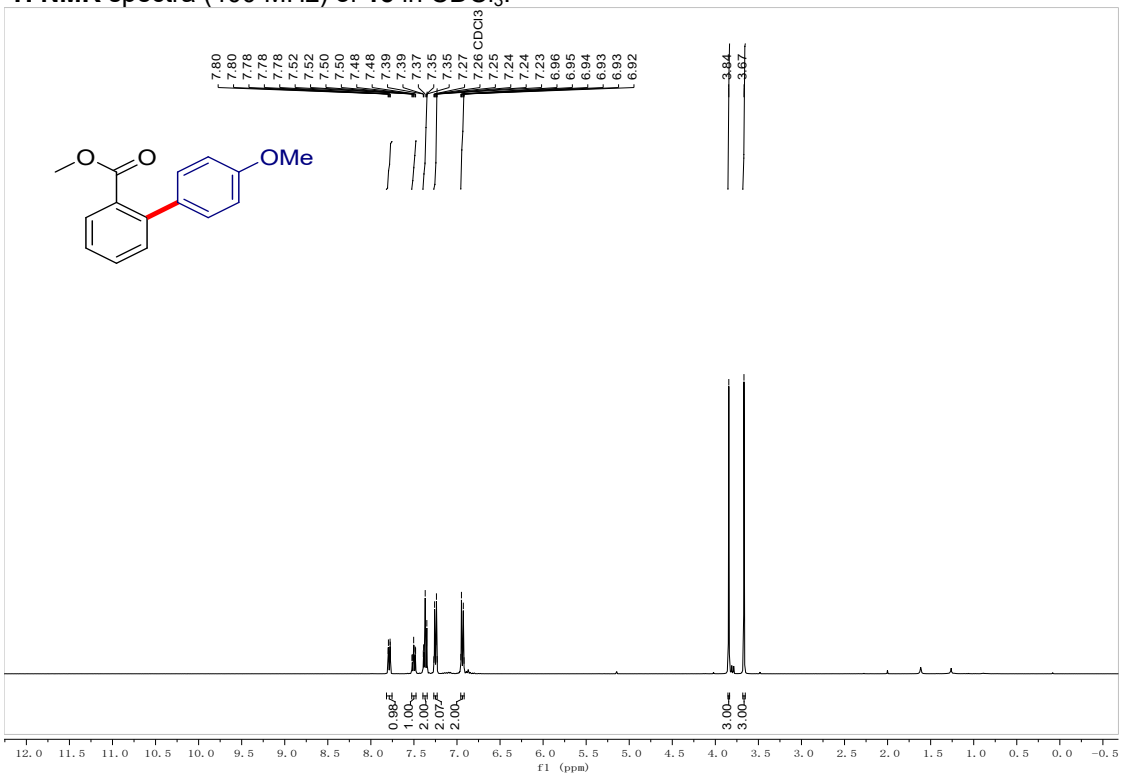
^{13}C NMR spectra (101 MHz) of **14** in $CDCl_3$.



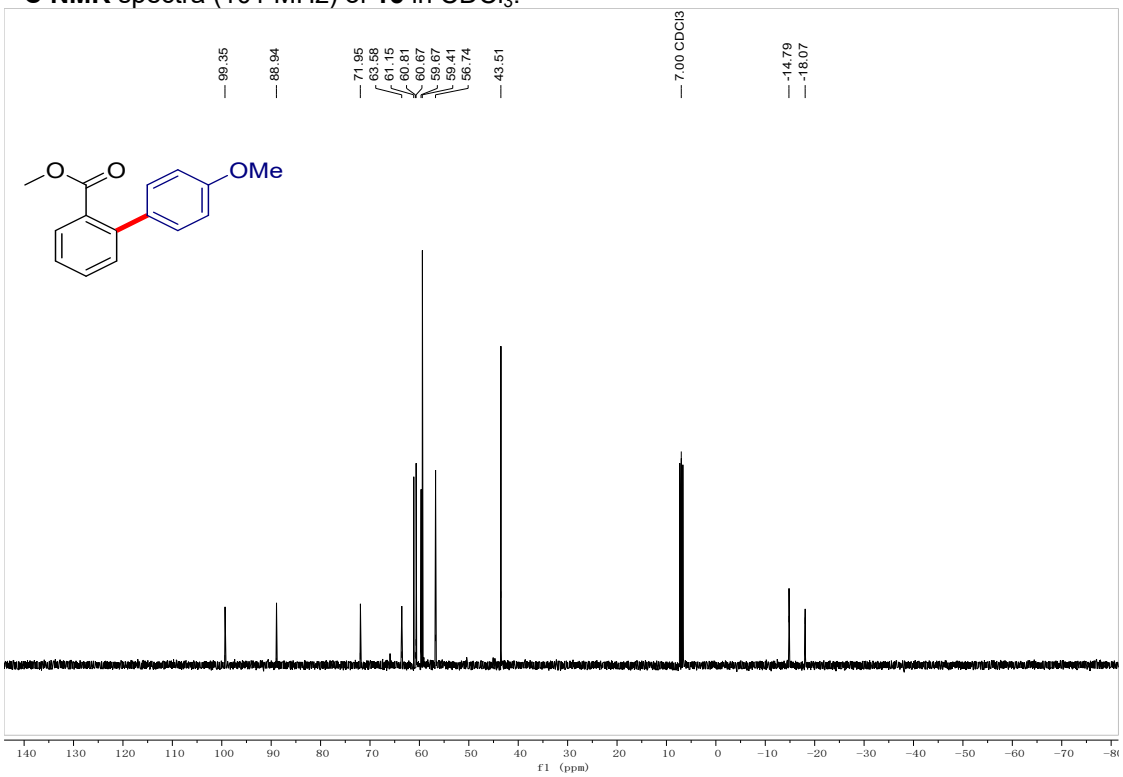
^{19}F NMR spectra (101 MHz) of **14** in $CDCl_3$.



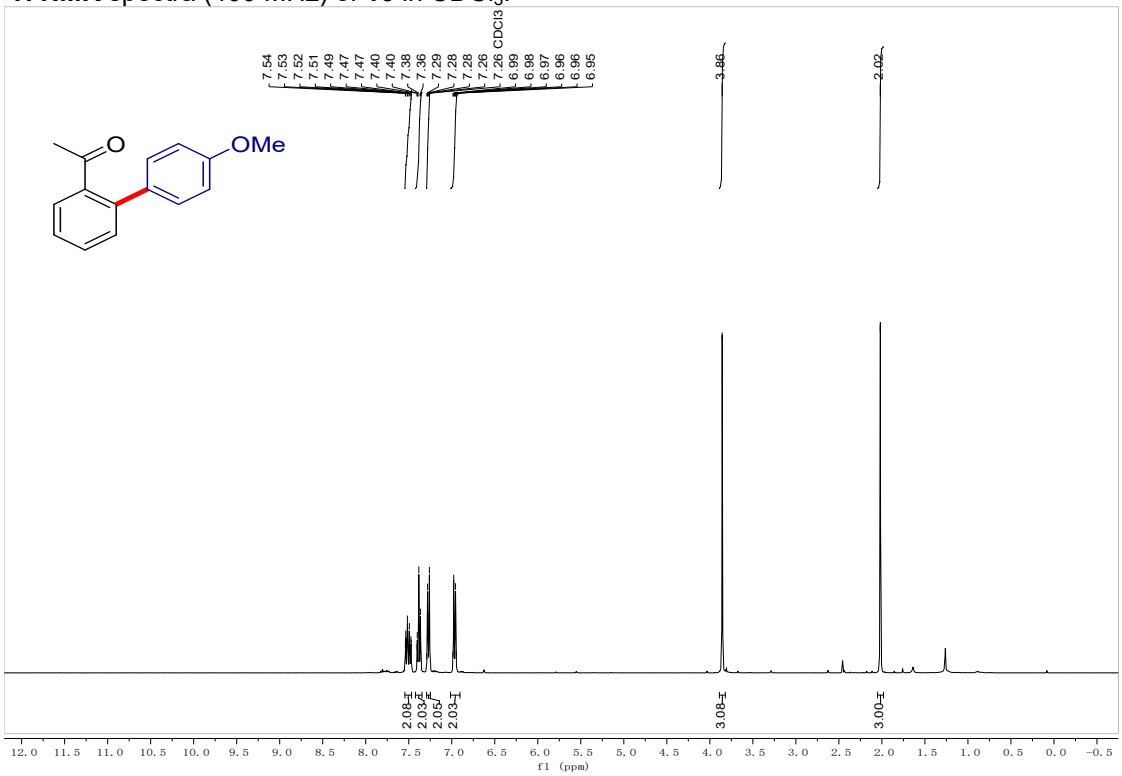
^{1}H NMR spectra (400 MHz) of **15** in $CDCl_3$.



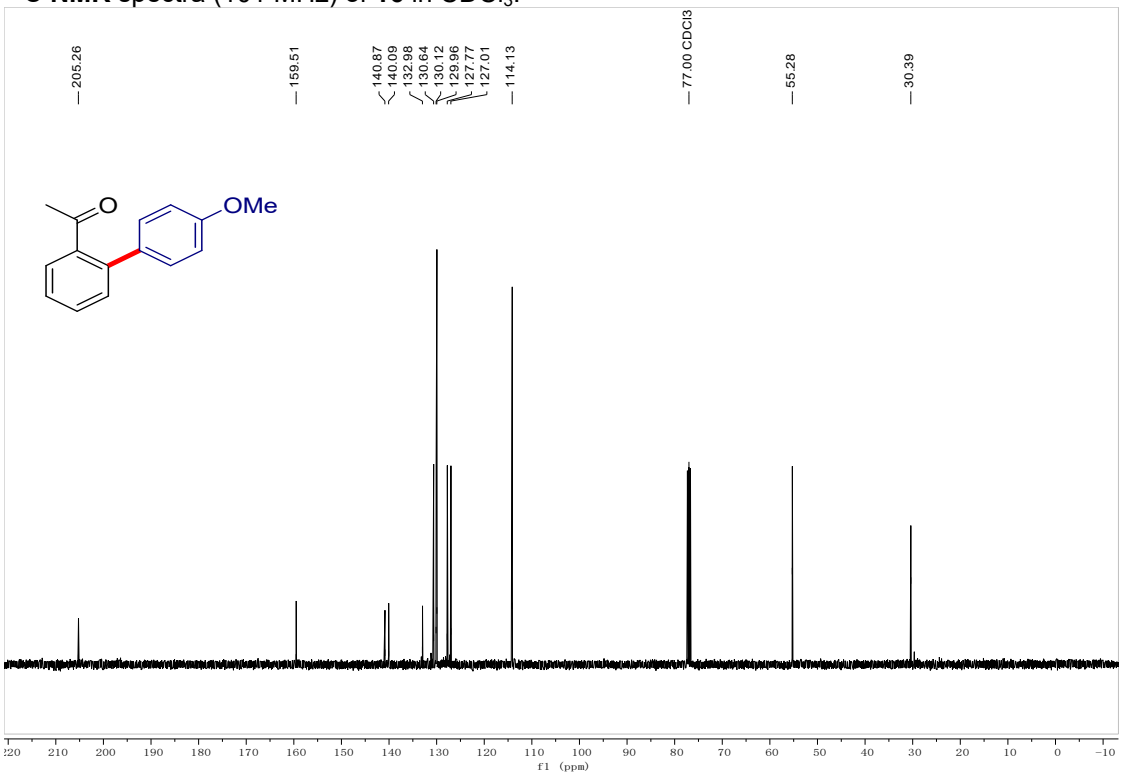
^{13}C NMR spectra (101 MHz) of **15** in $CDCl_3$.



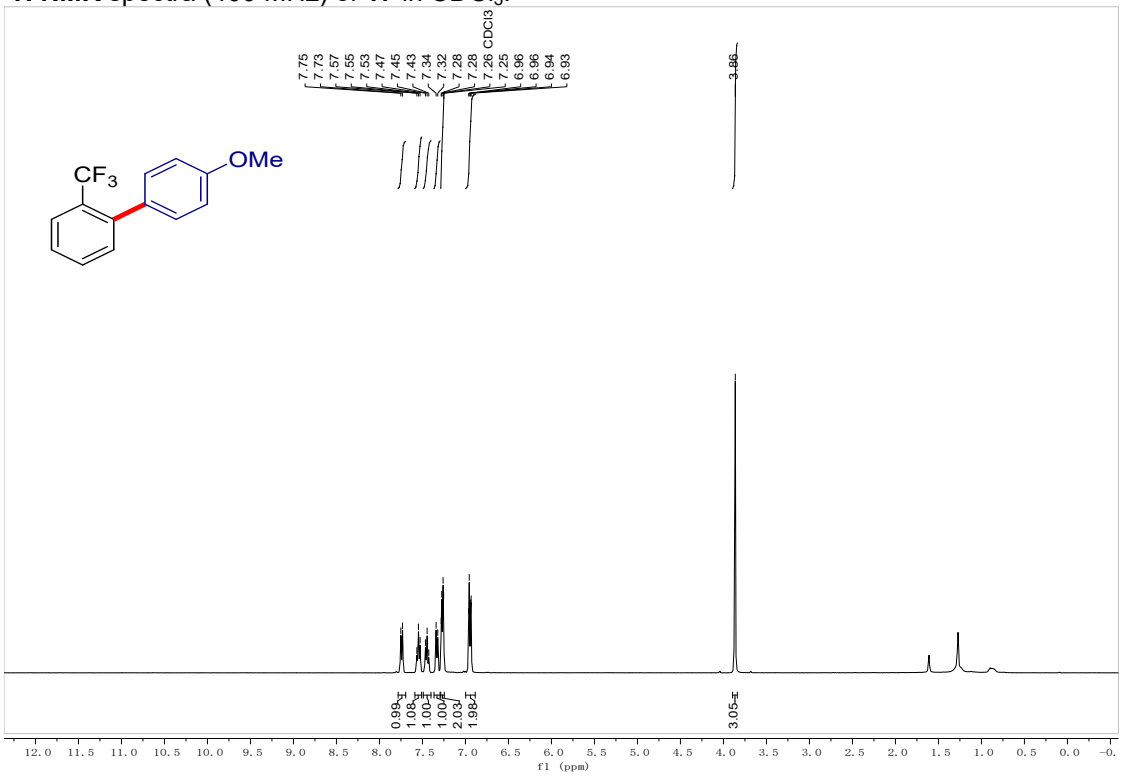
^{1}H NMR spectra (400 MHz) of **16** in $CDCl_3$.



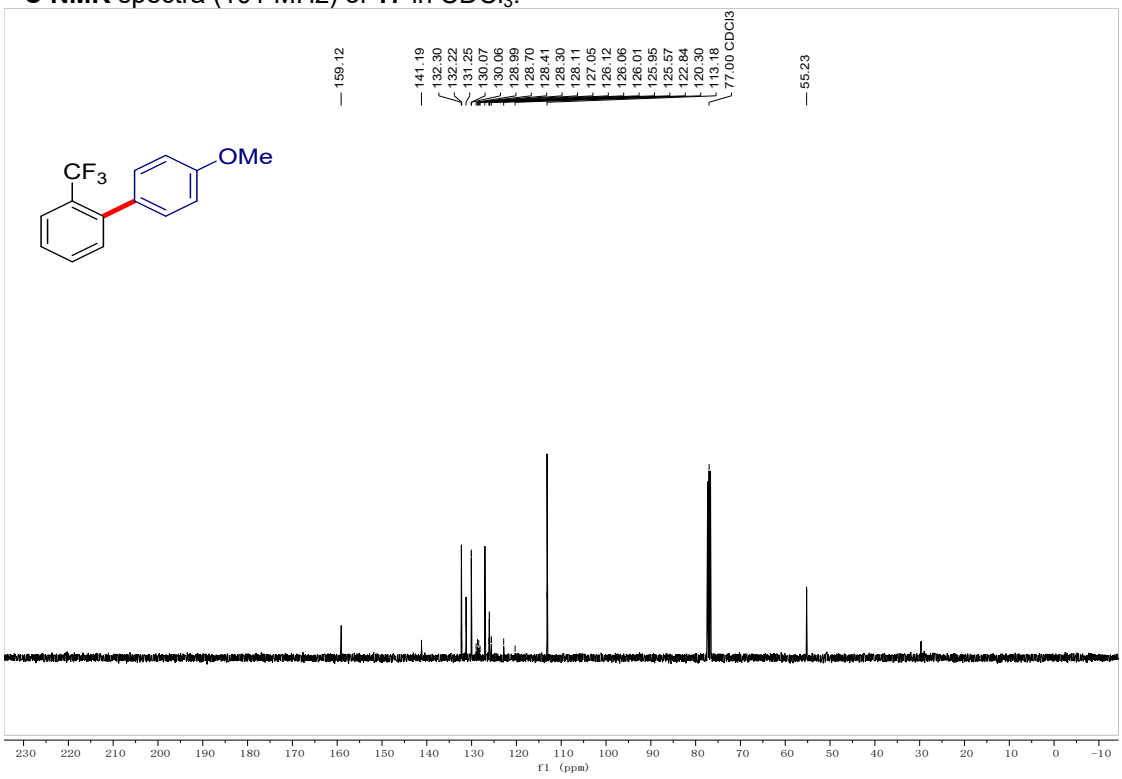
^{13}C NMR spectra (101 MHz) of **16** in $CDCl_3$.



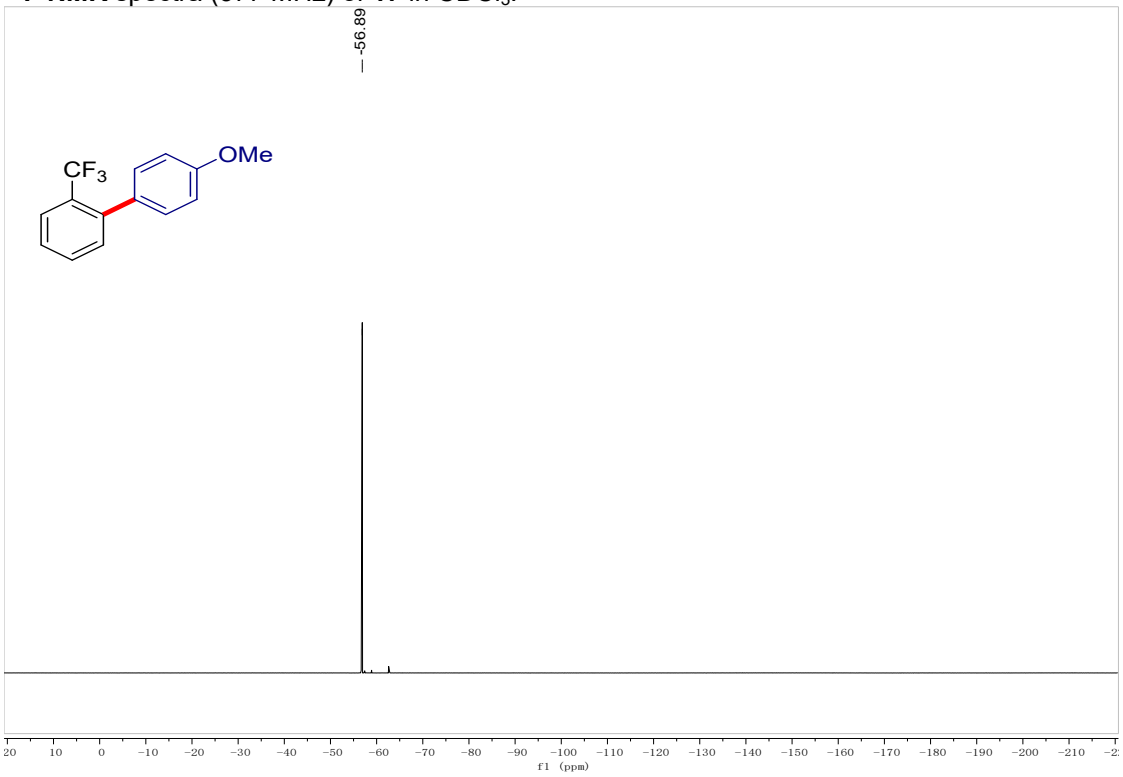
^{1}H NMR spectra (400 MHz) of **17** in $CDCl_3$.



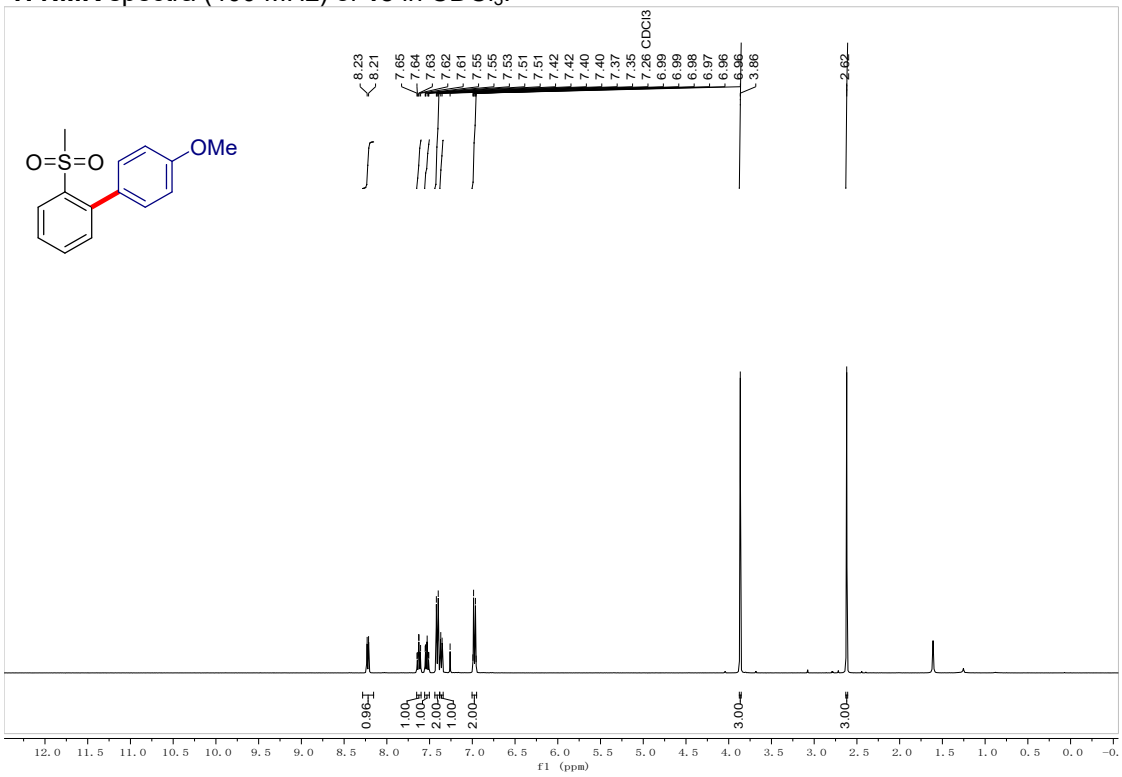
^{13}C NMR spectra (101 MHz) of **17** in $CDCl_3$.



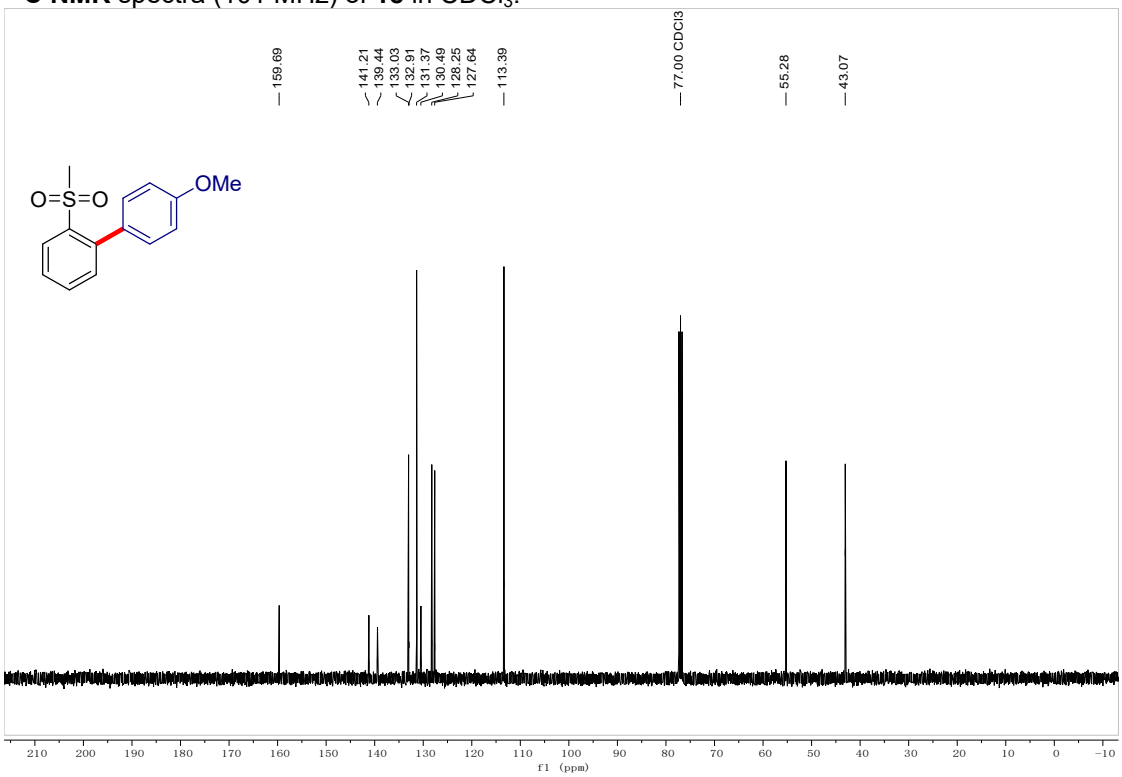
^{19}F NMR spectra (377 MHz) of **17** in $CDCl_3$.



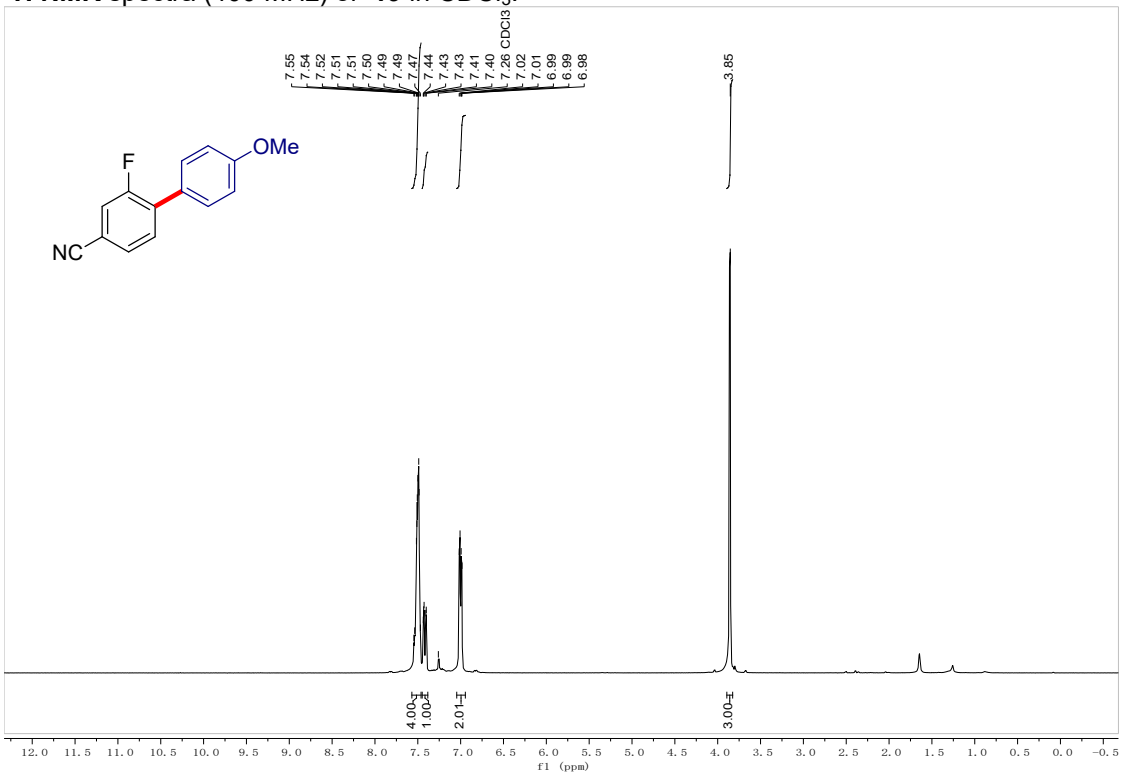
^{1}H NMR spectra (400 MHz) of **18** in $CDCl_3$.



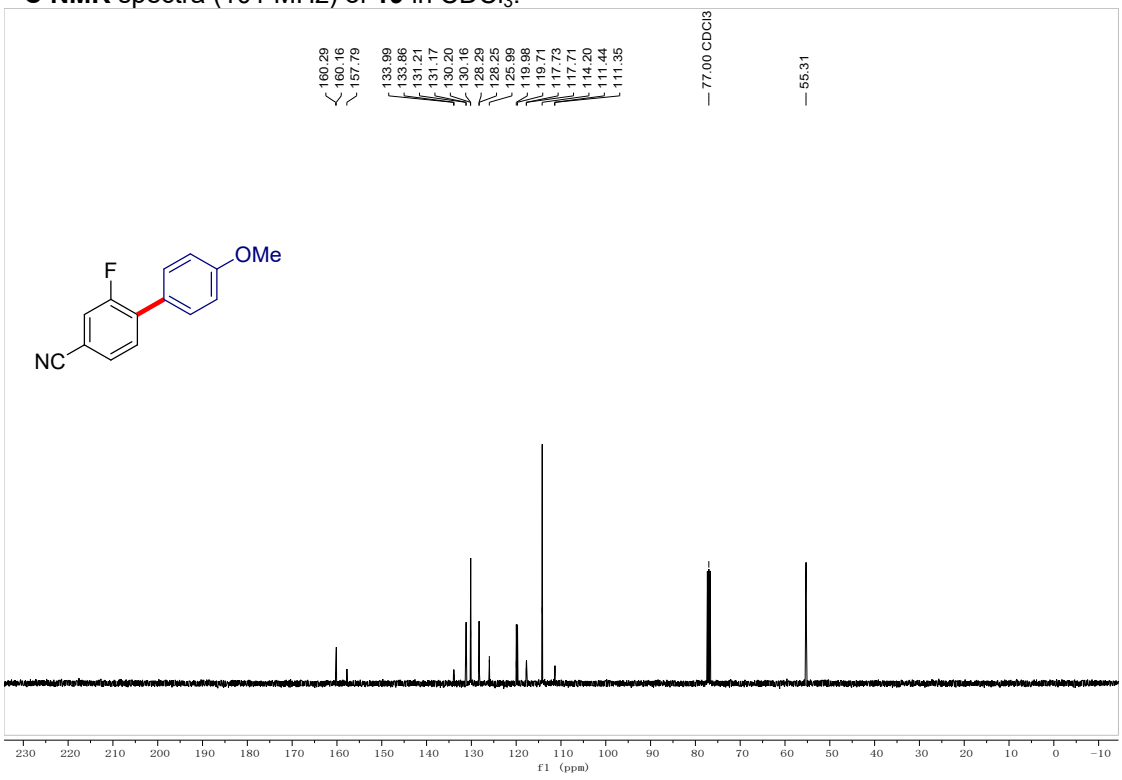
^{13}C NMR spectra (101 MHz) of **18** in $CDCl_3$.



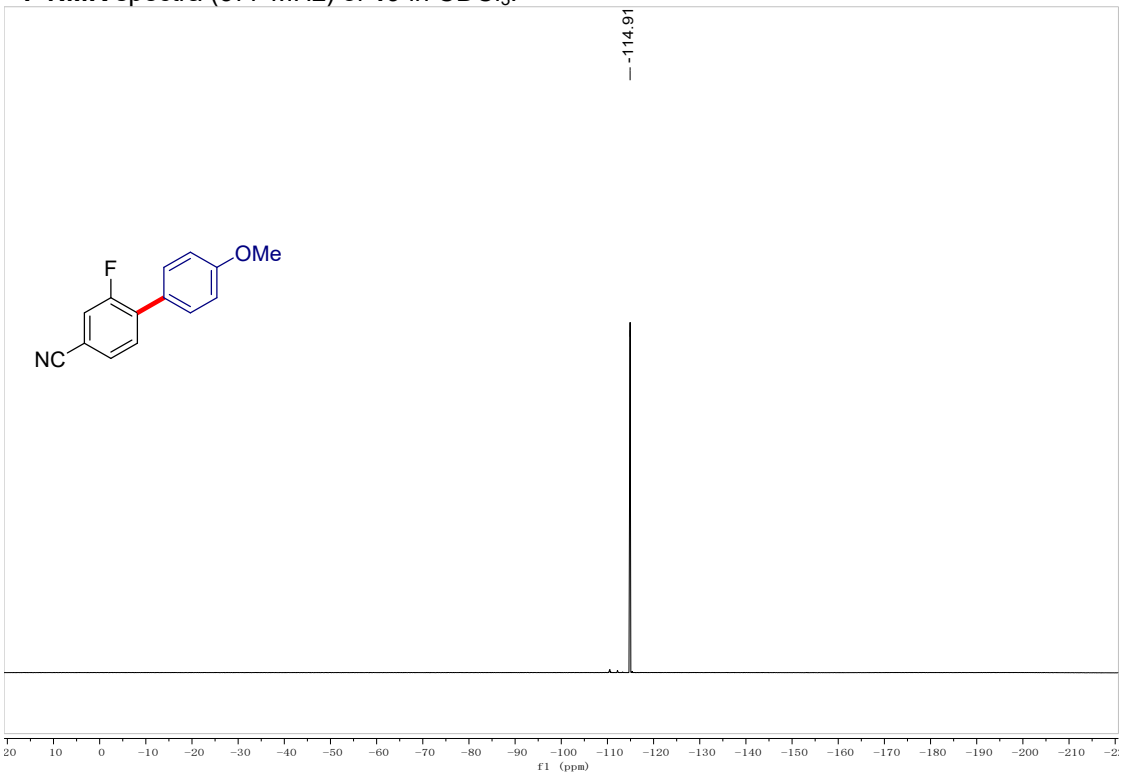
^{1}H NMR spectra (400 MHz) of **19** in $CDCl_3$.



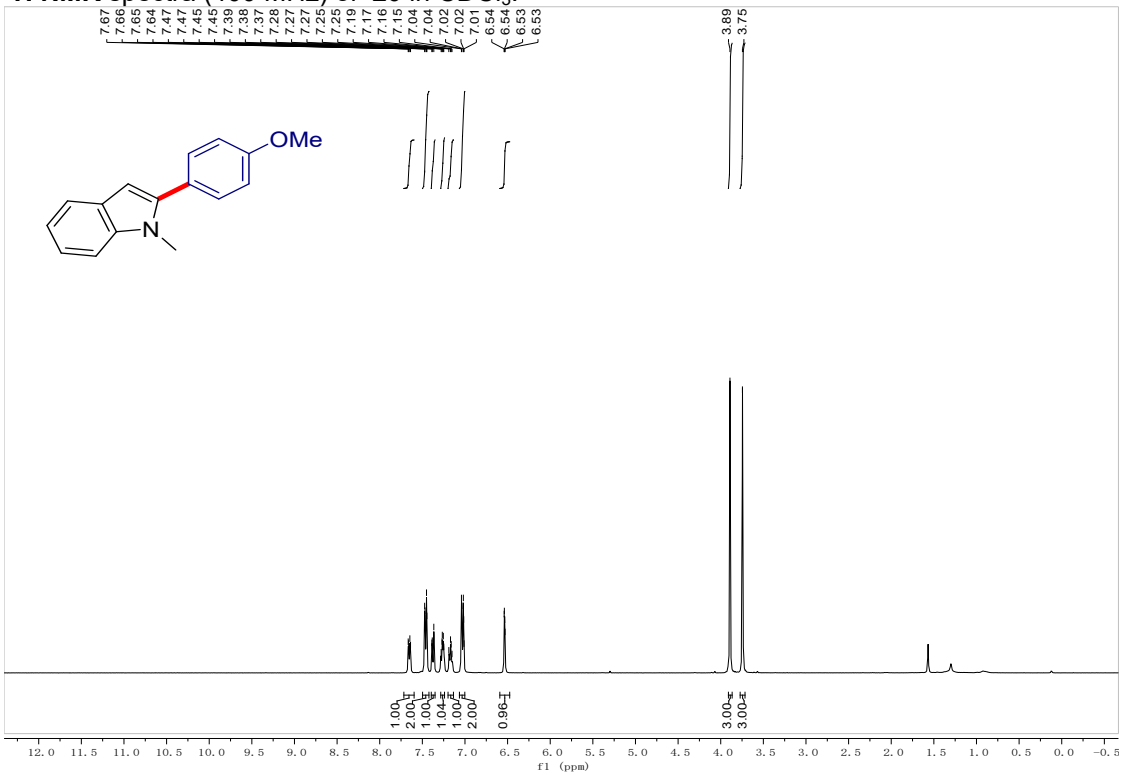
^{13}C NMR spectra (101 MHz) of **19** in $CDCl_3$.



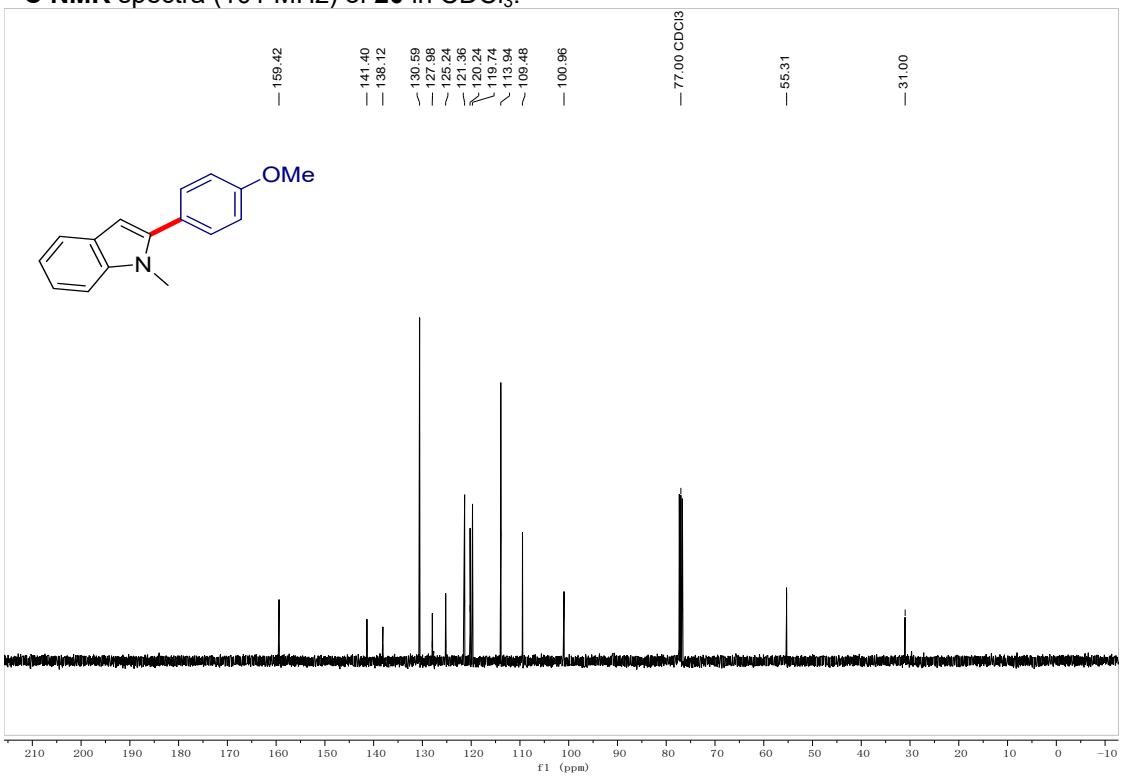
^{19}F NMR spectra (377 MHz) of **19** in $CDCl_3$.



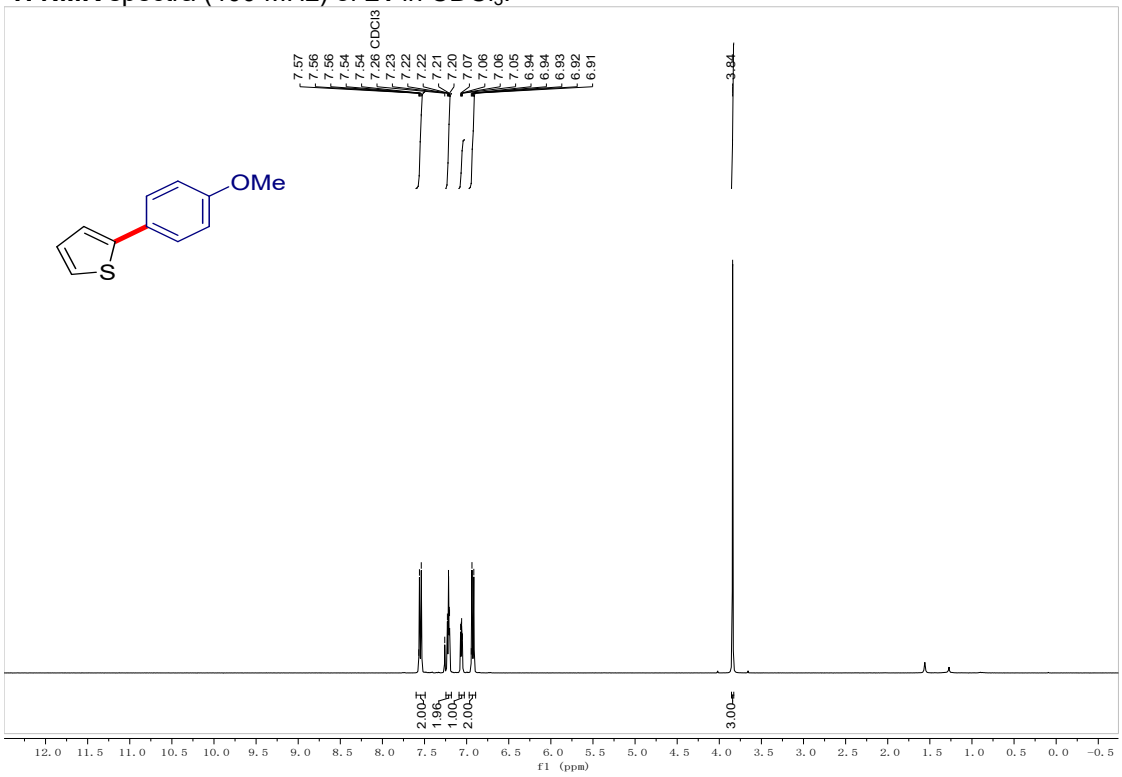
^{1}H NMR spectra (400 MHz) of **20** in $CDCl_3$.



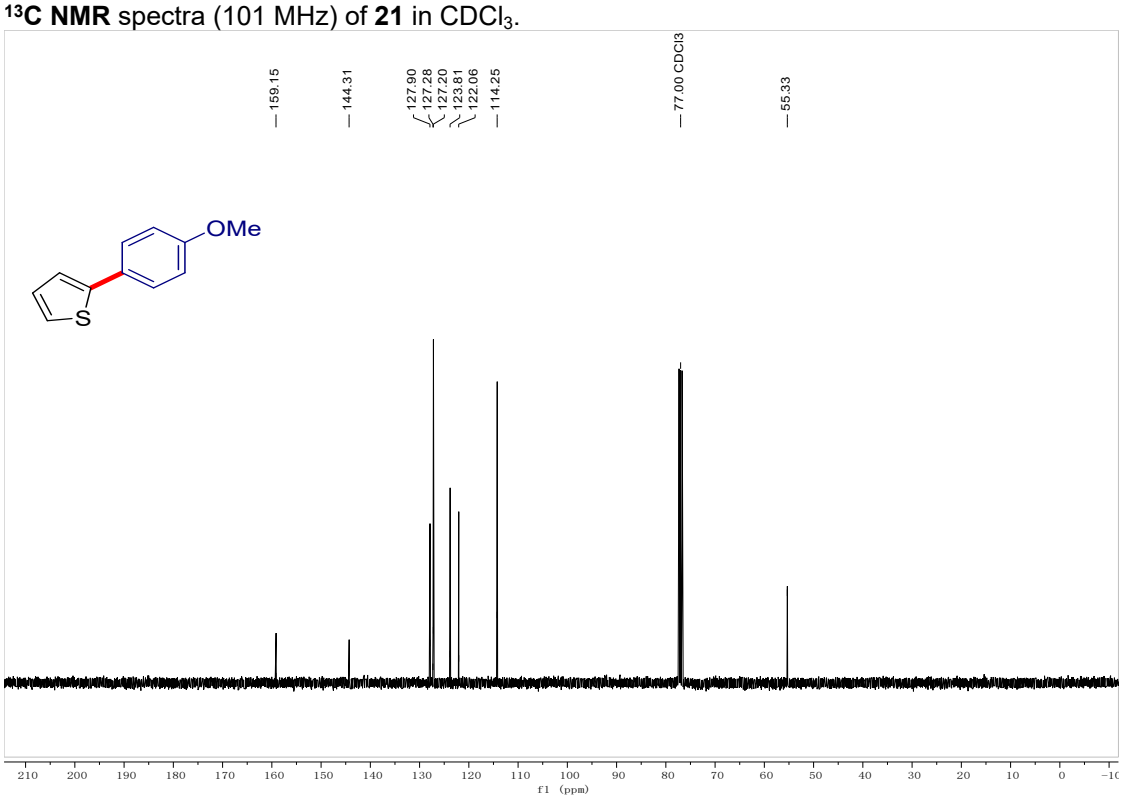
^{13}C NMR spectra (101 MHz) of **20** in $CDCl_3$.



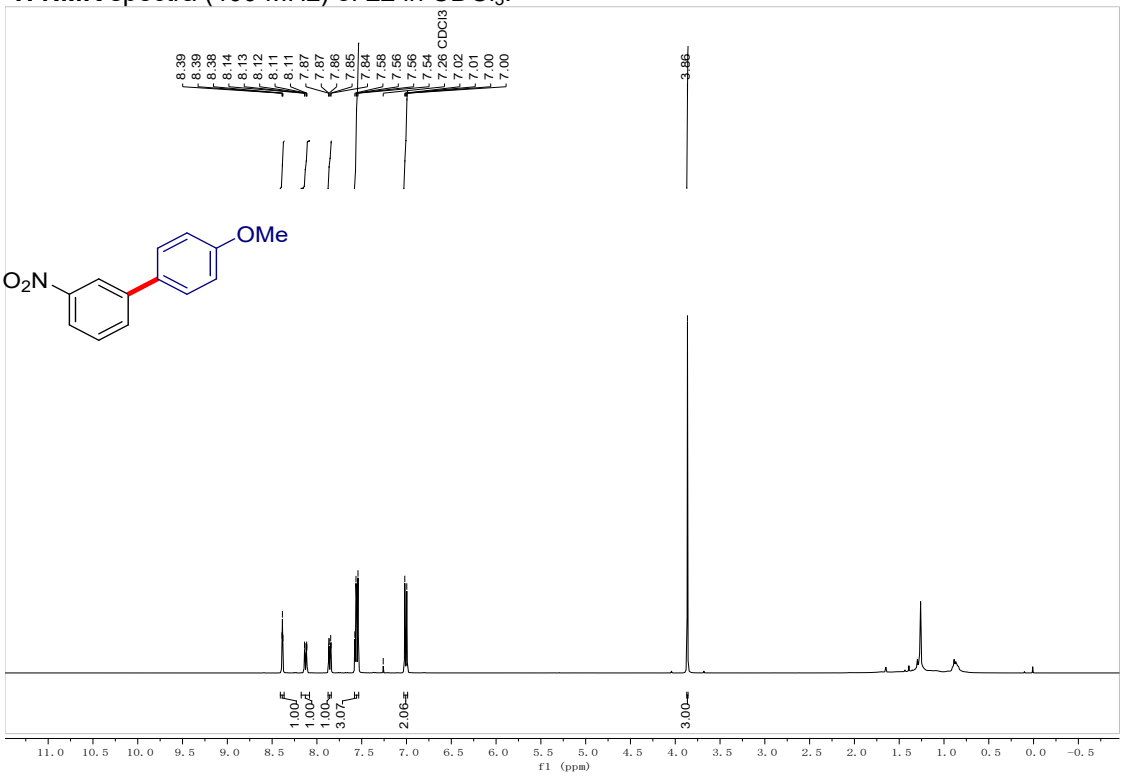
^{1}H NMR spectra (400 MHz) of **21** in $CDCl_3$.



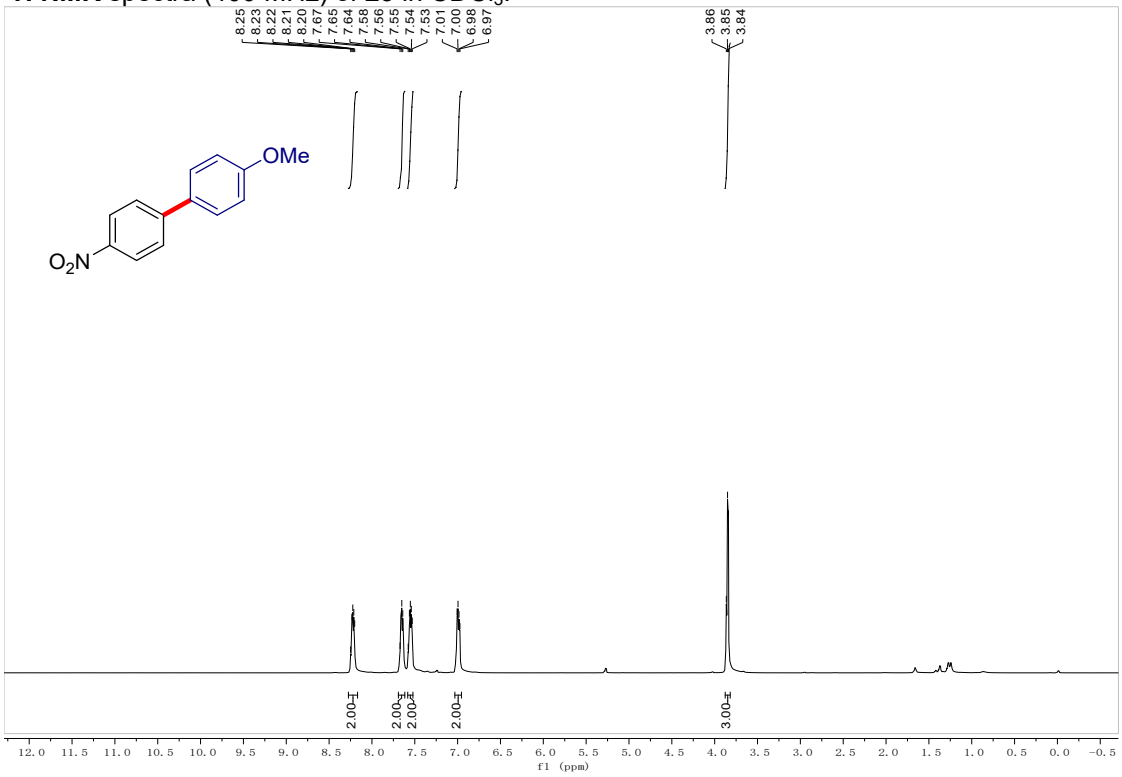
^{13}C NMR spectra (101 MHz) of **21** in $CDCl_3$.



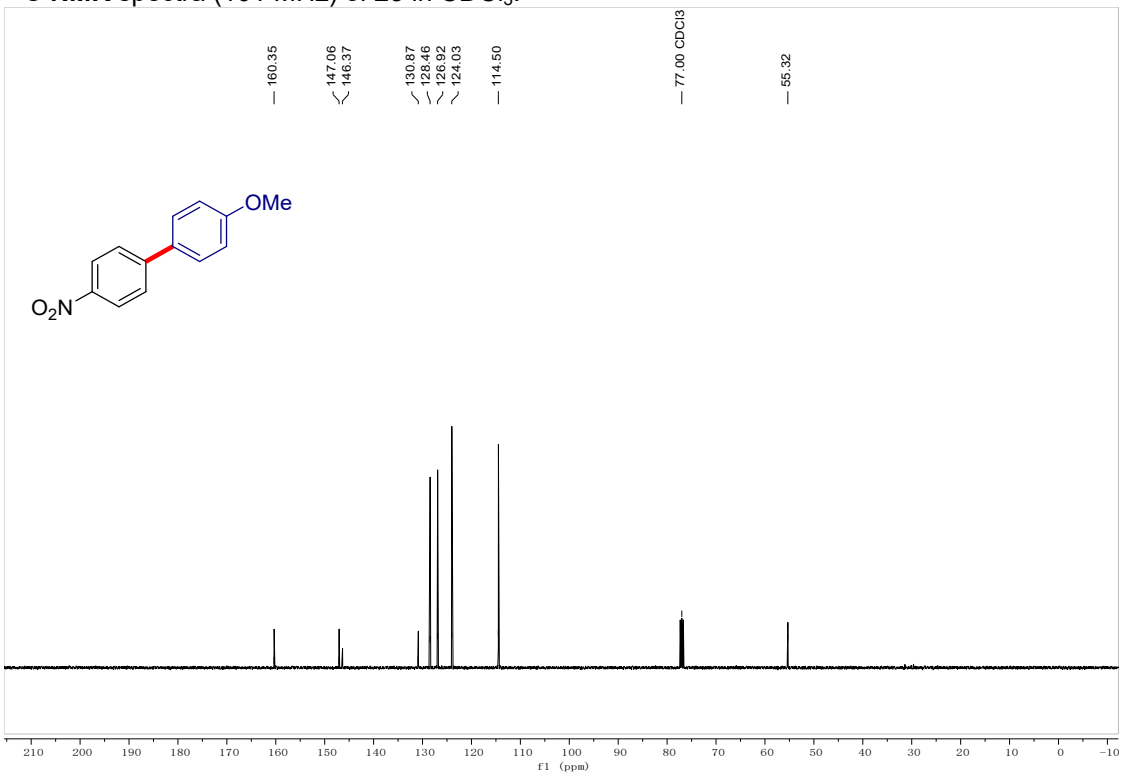
^{1}H NMR spectra (400 MHz) of **22** in $CDCl_3$.



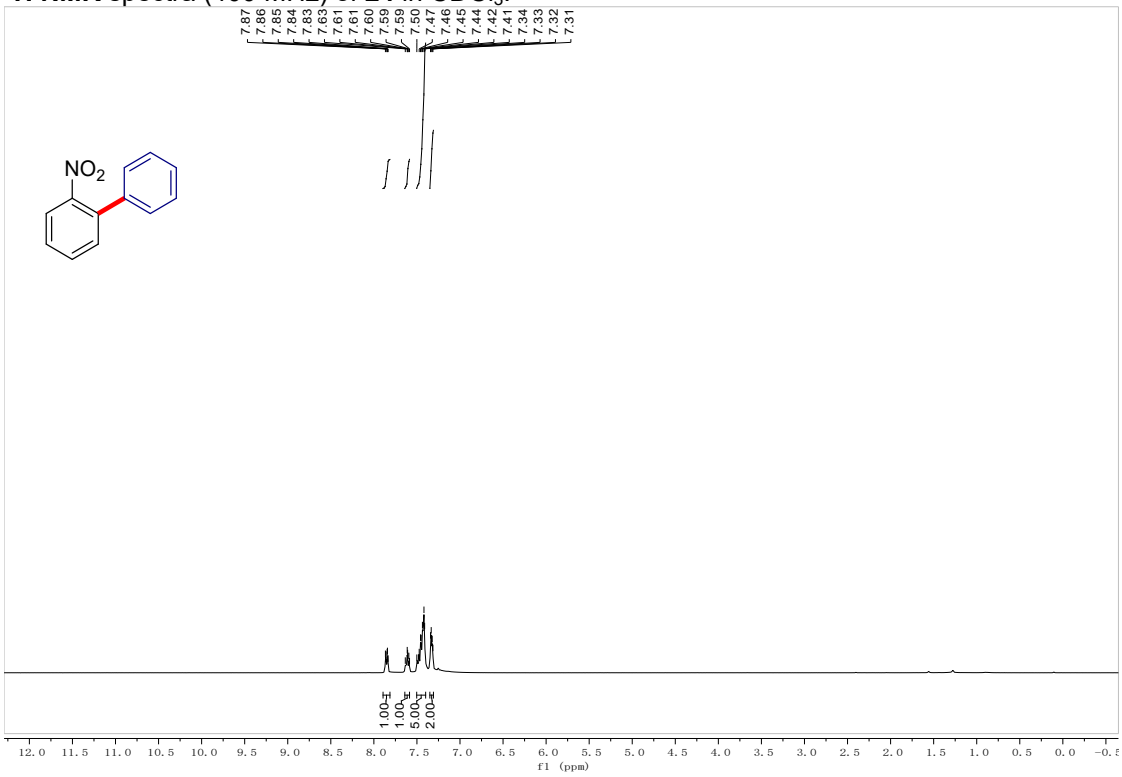
^{1}H NMR spectra (400 MHz) of **23** in $CDCl_3$.



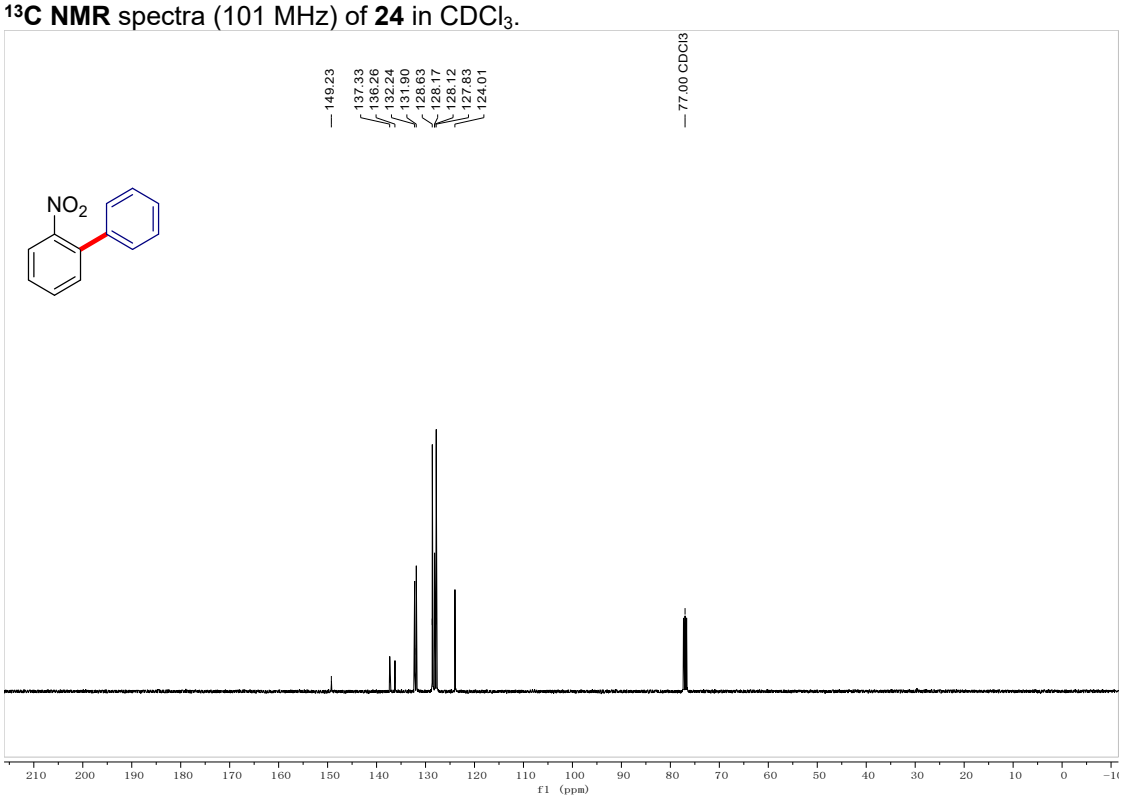
^{13}C NMR spectra (101 MHz) of **23** in $CDCl_3$.



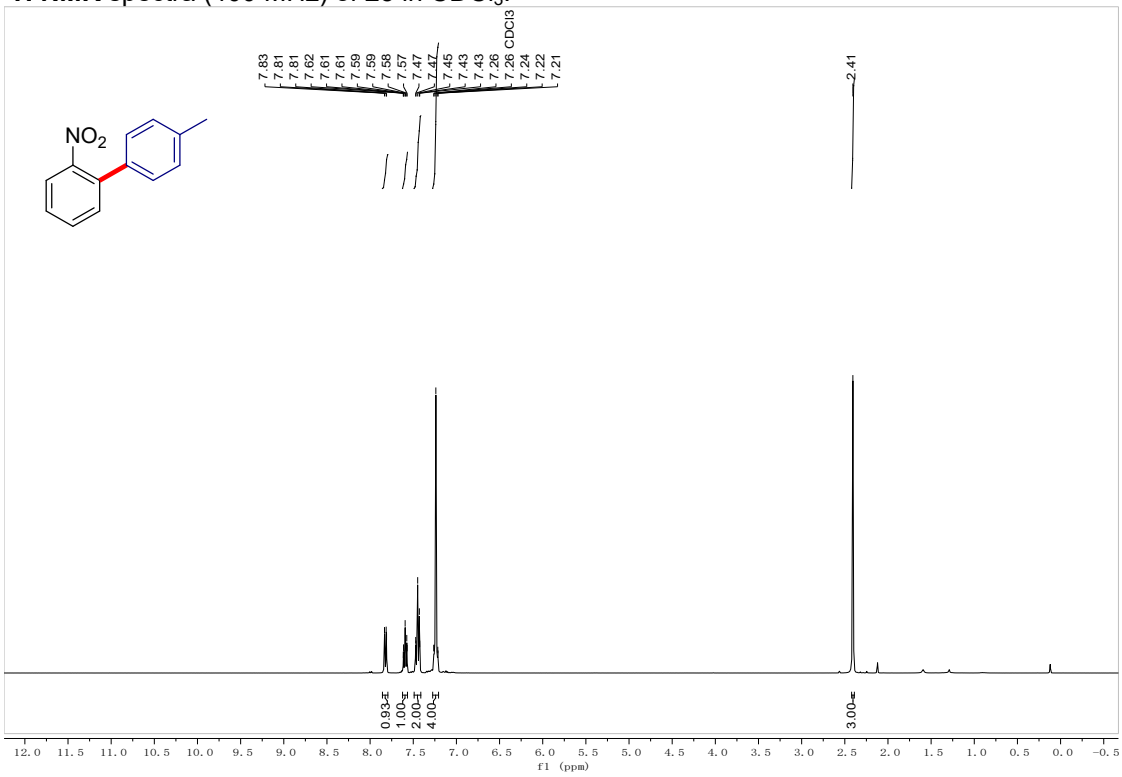
^{1}H NMR spectra (400 MHz) of **24** in $CDCl_3$.



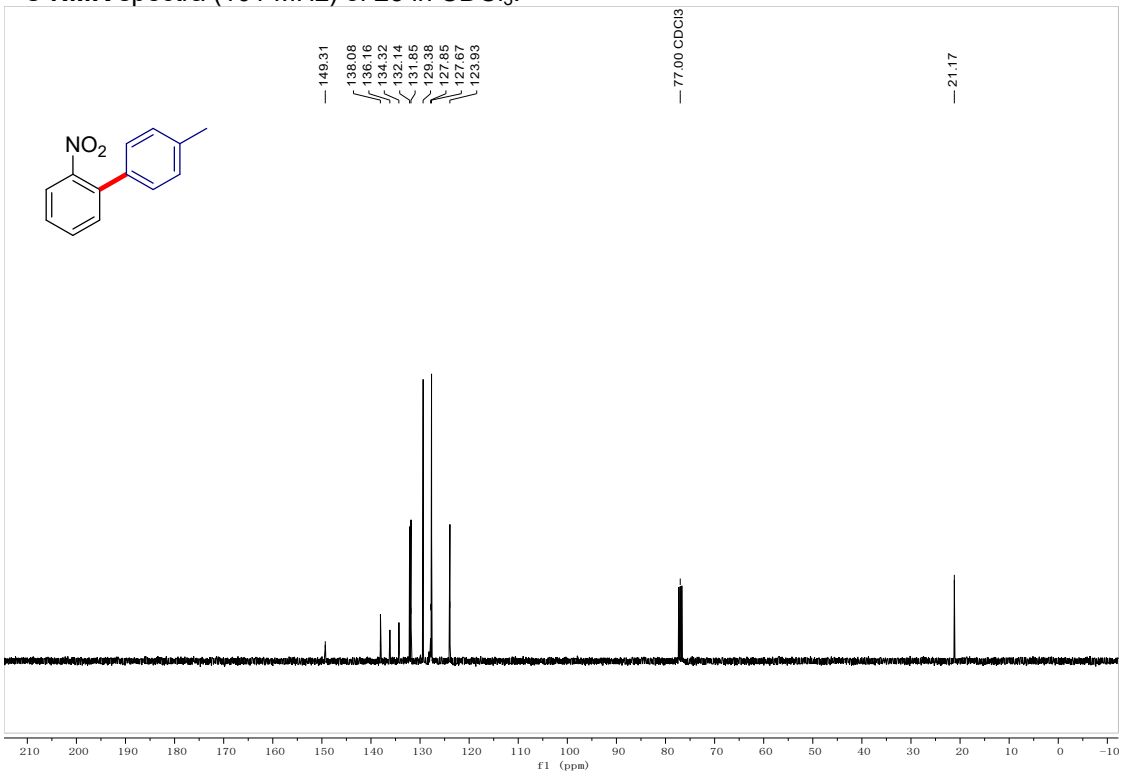
^{13}C NMR spectra (101 MHz) of **24** in $CDCl_3$.



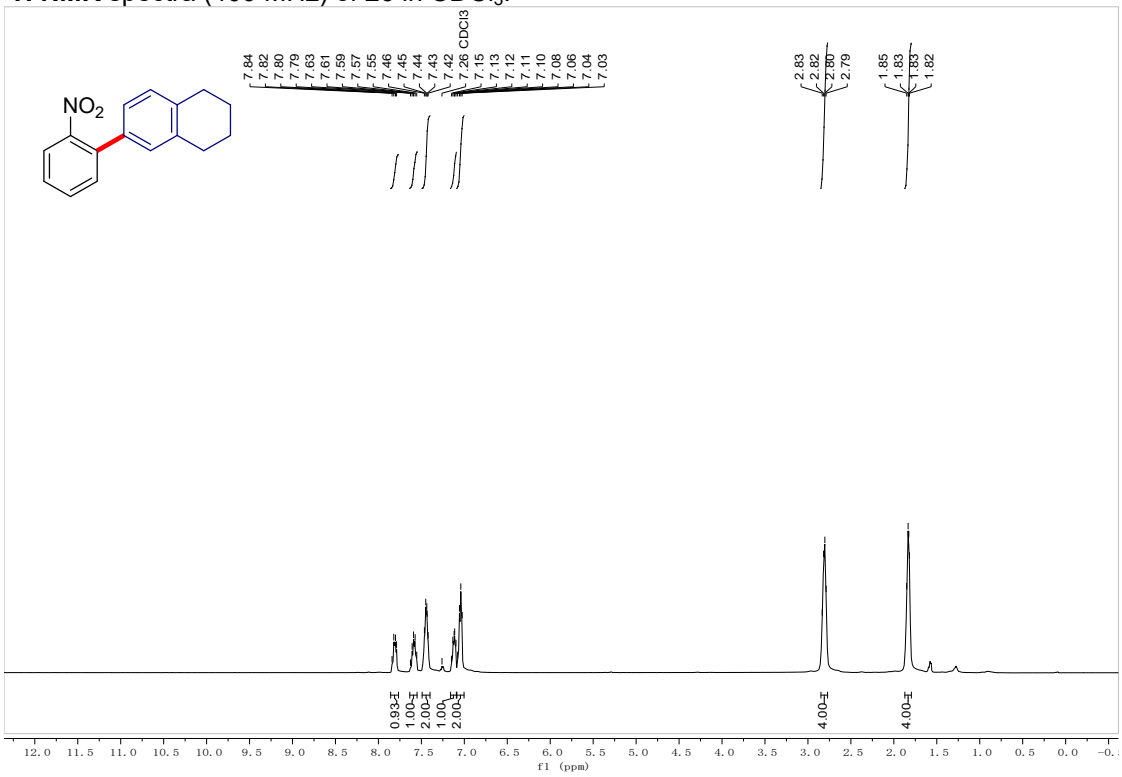
^{1}H NMR spectra (400 MHz) of **25** in $CDCl_3$.



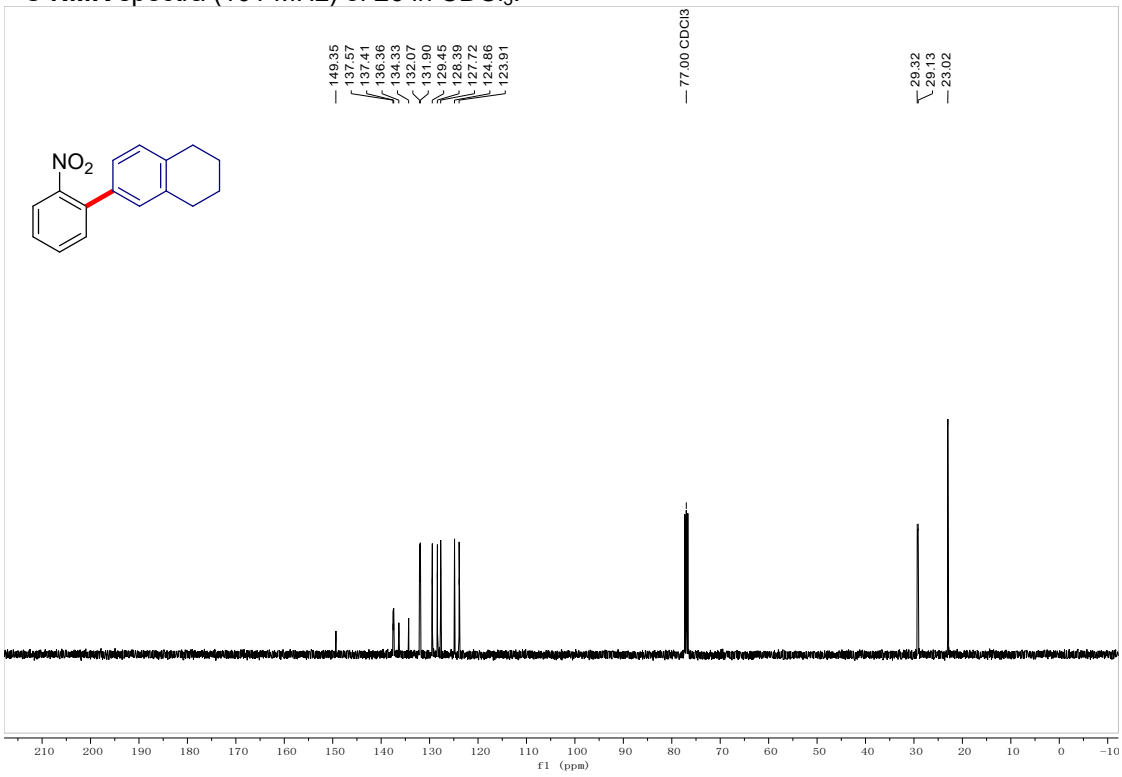
^{13}C NMR spectra (101 MHz) of **25** in $CDCl_3$.



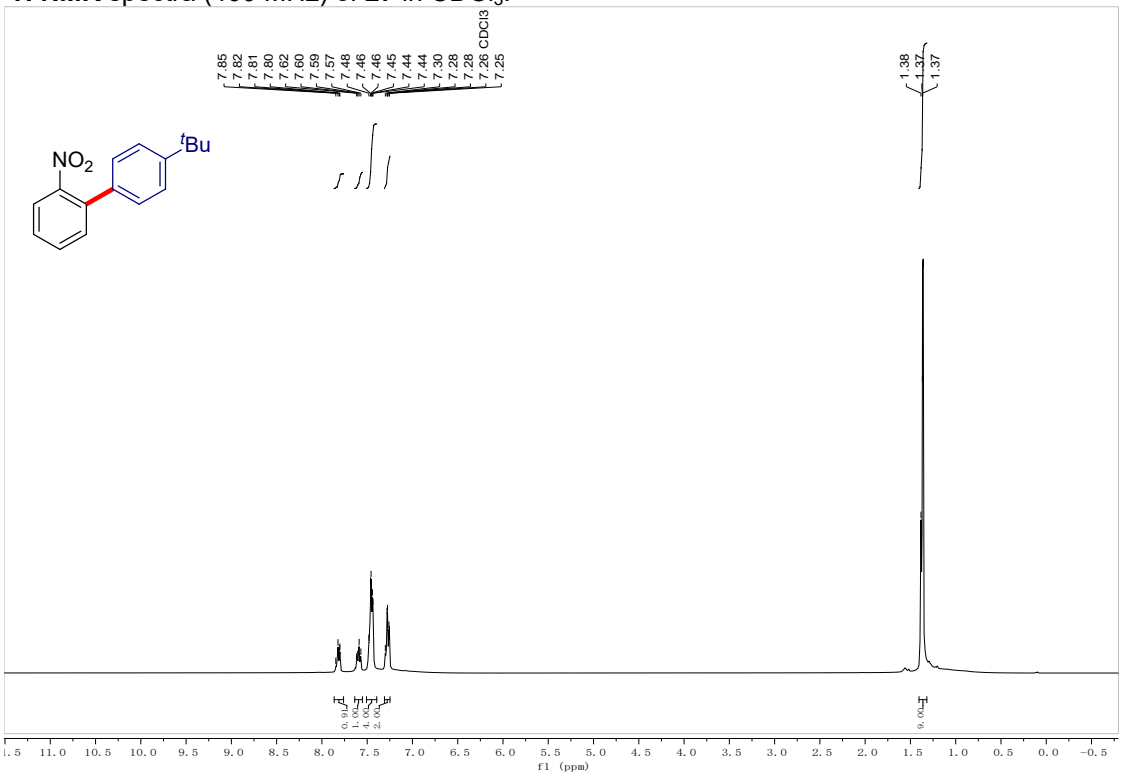
^{1}H NMR spectra (400 MHz) of **26** in $CDCl_3$.



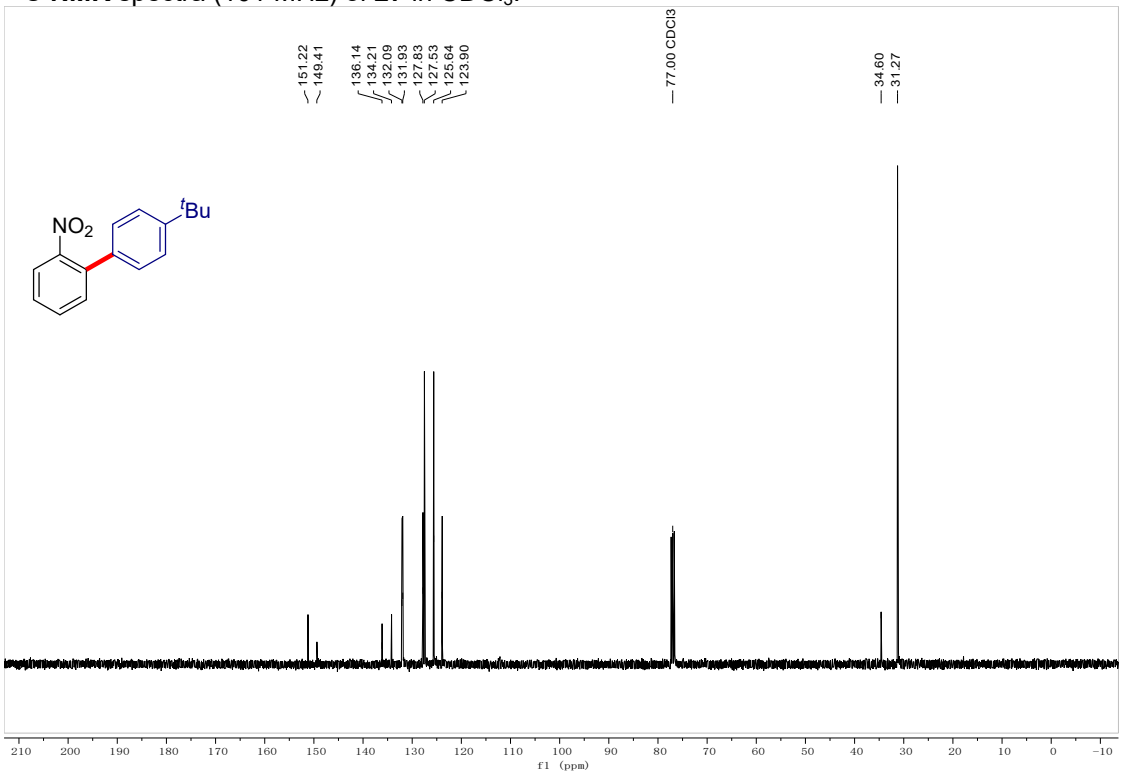
^{13}C NMR spectra (101 MHz) of **26** in $CDCl_3$.



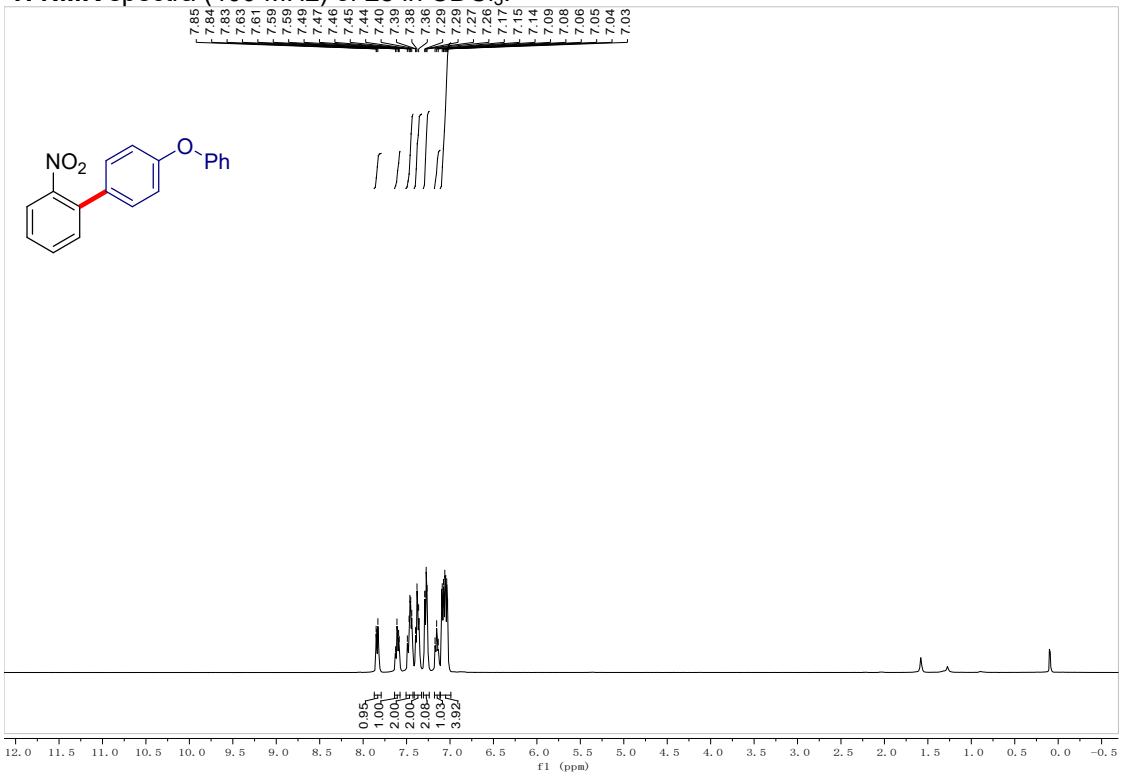
^{1}H NMR spectra (400 MHz) of **27** in $CDCl_3$.



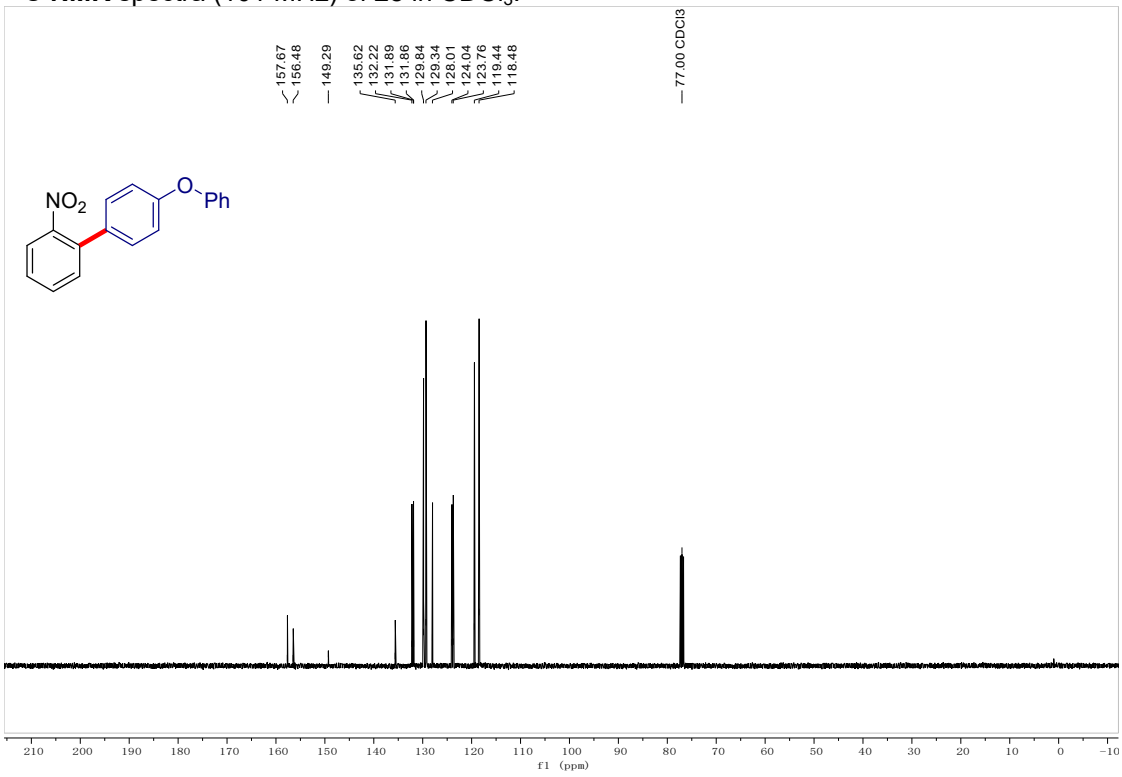
^{13}C NMR spectra (101 MHz) of **27** in $CDCl_3$.



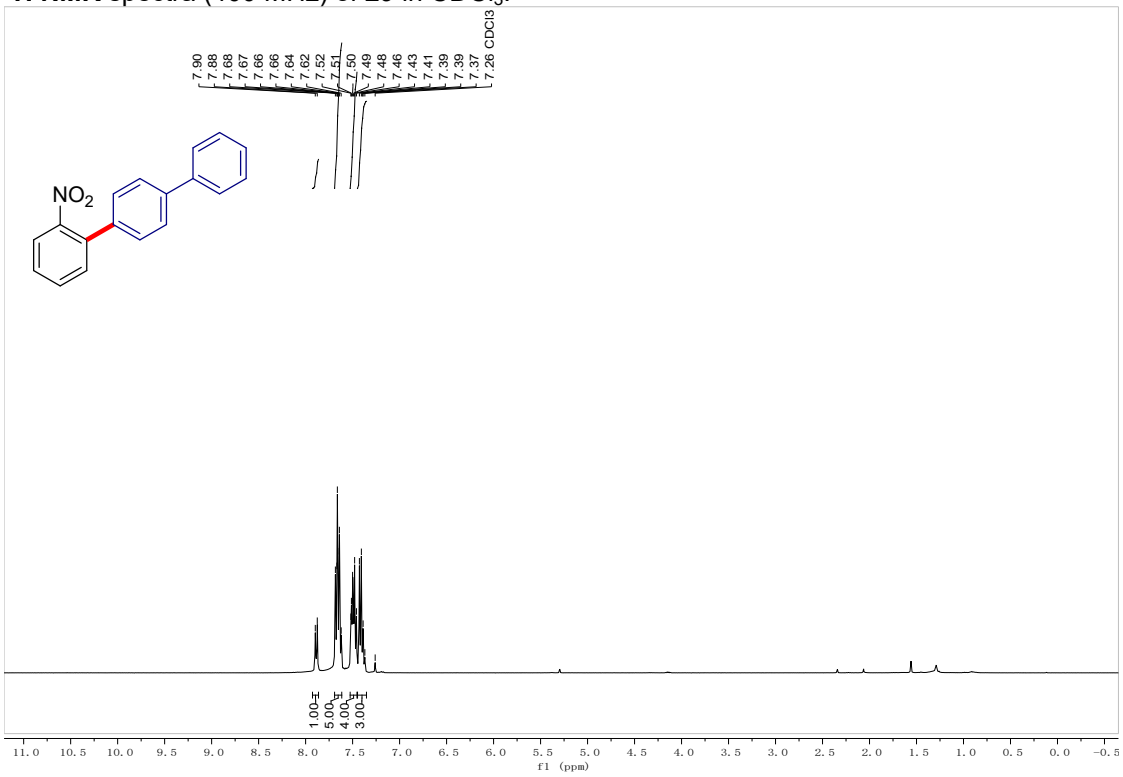
^{1}H NMR spectra (400 MHz) of **28** in $CDCl_3$.



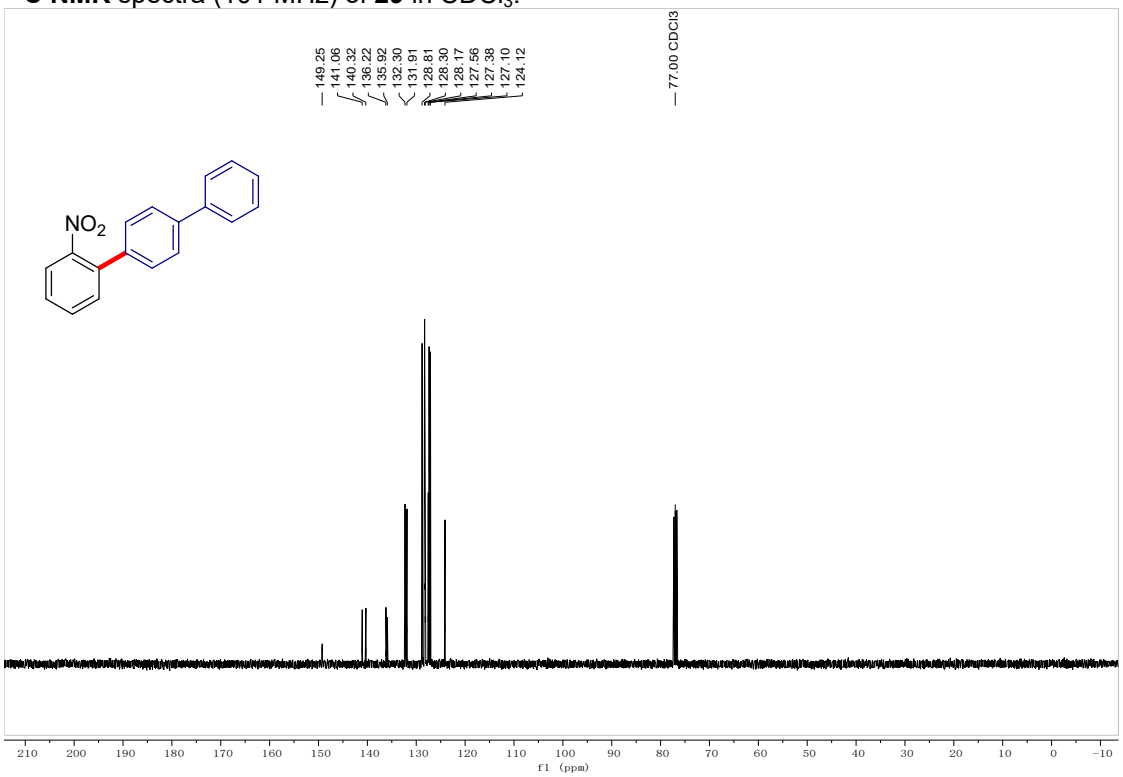
^{13}C NMR spectra (101 MHz) of **28** in $CDCl_3$.



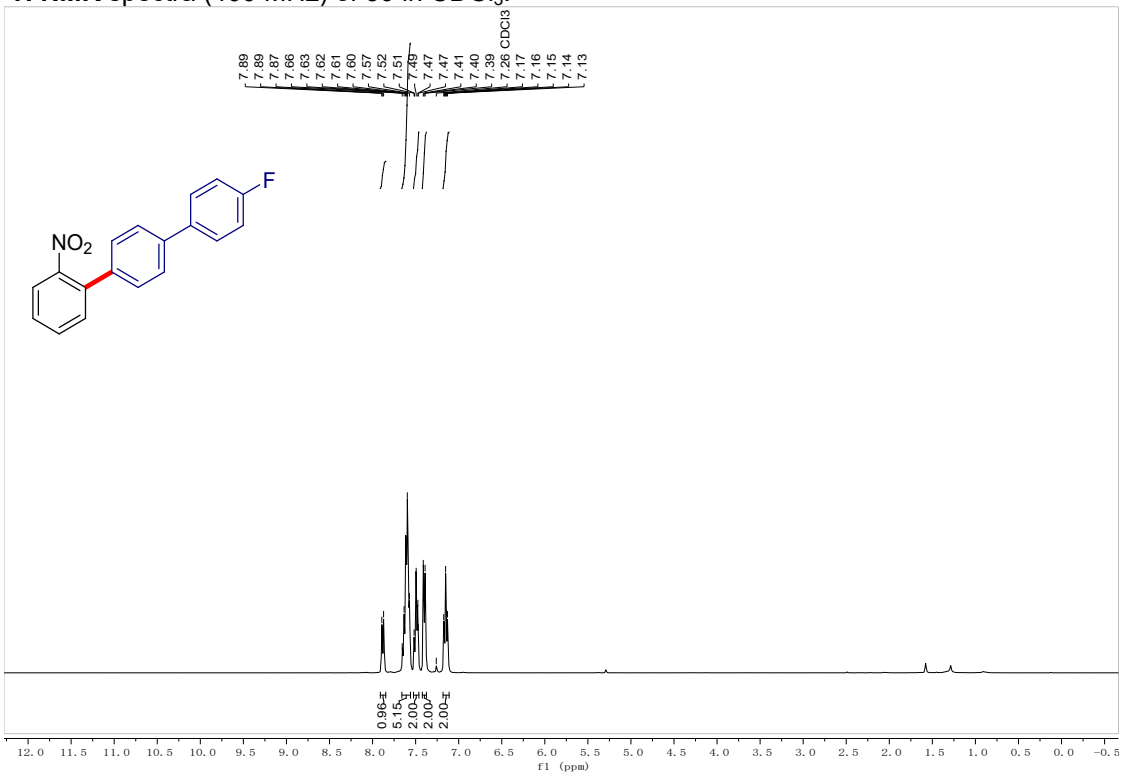
^{1}H NMR spectra (400 MHz) of **29** in $CDCl_3$.



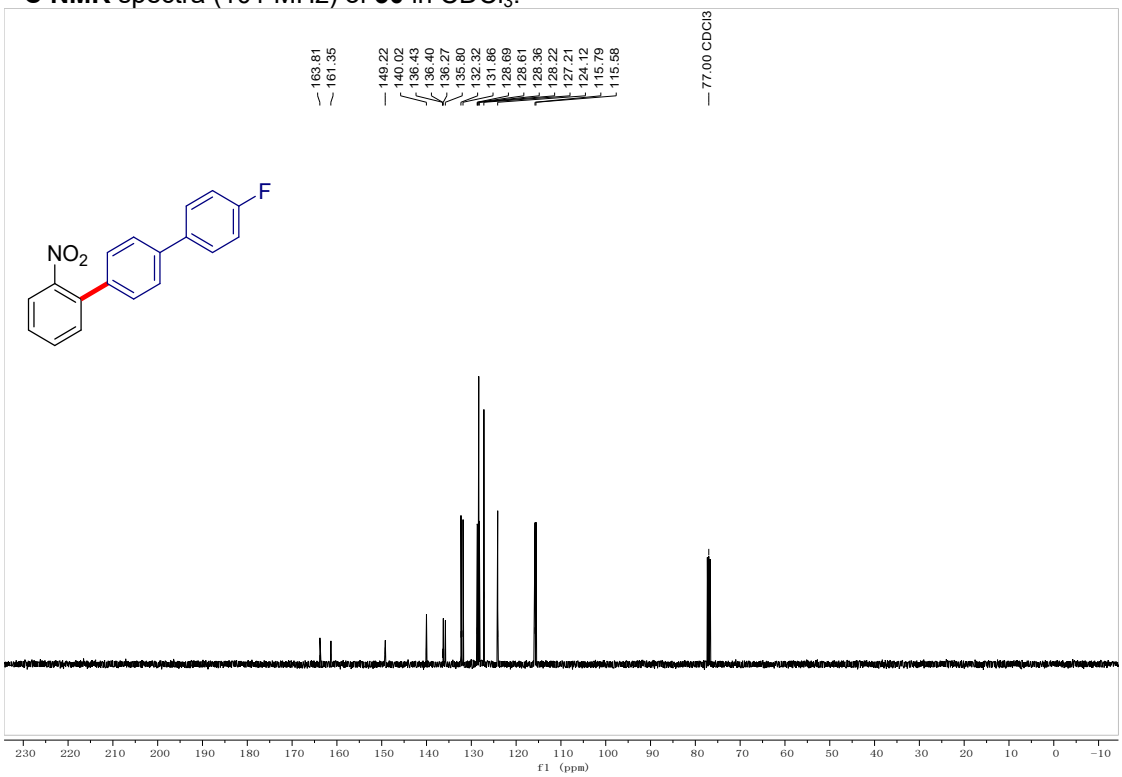
^{13}C NMR spectra (101 MHz) of **29** in $CDCl_3$.



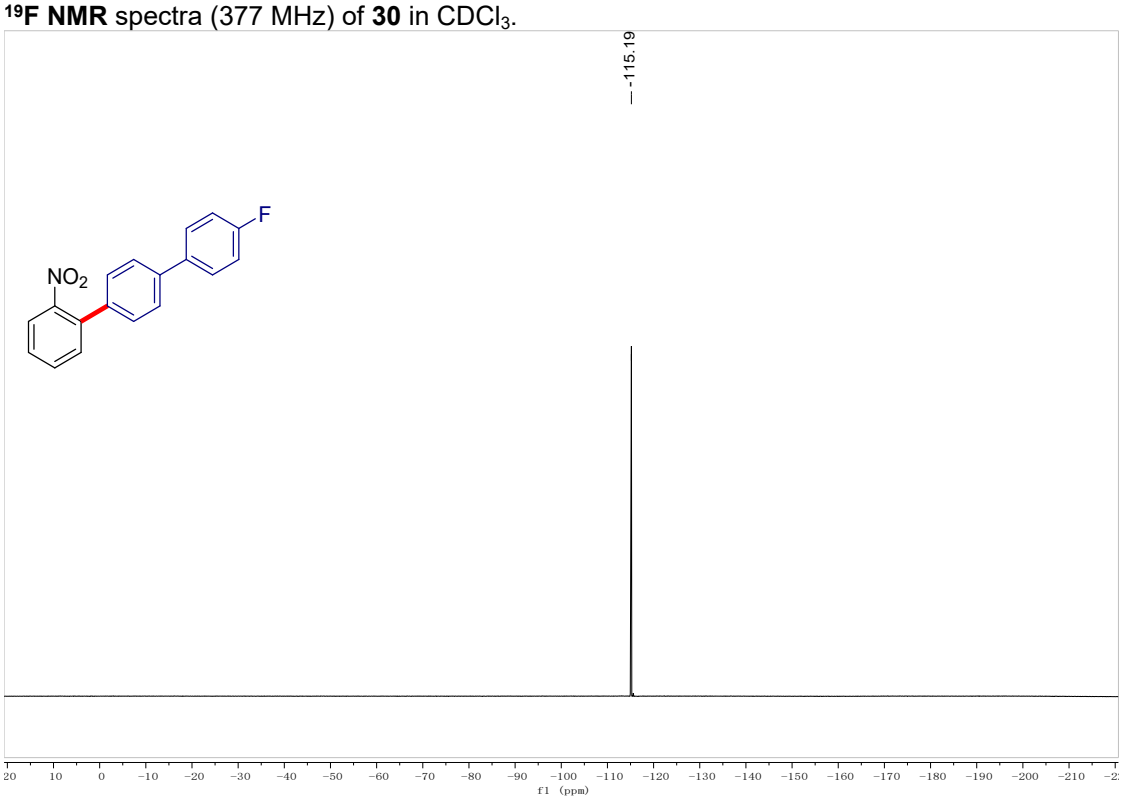
^{1}H NMR spectra (400 MHz) of **30** in $CDCl_3$.



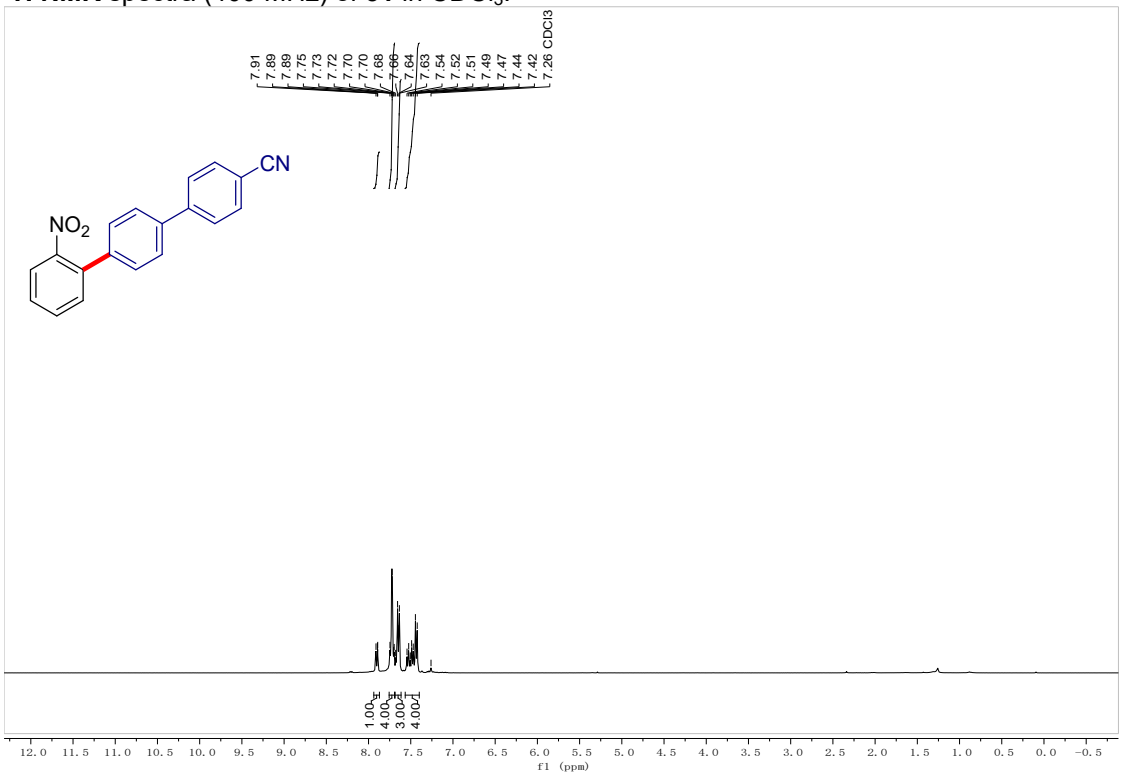
^{13}C NMR spectra (101 MHz) of **30** in $CDCl_3$.



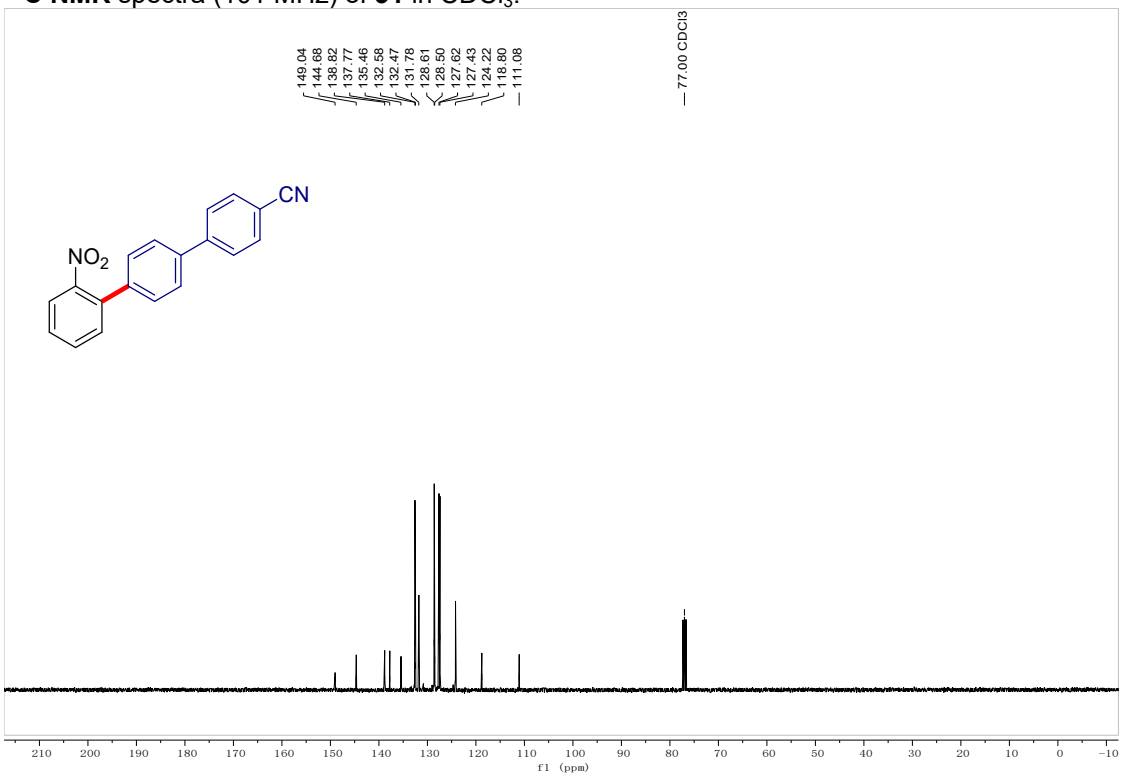
^{19}F NMR spectra (377 MHz) of **30** in $CDCl_3$.



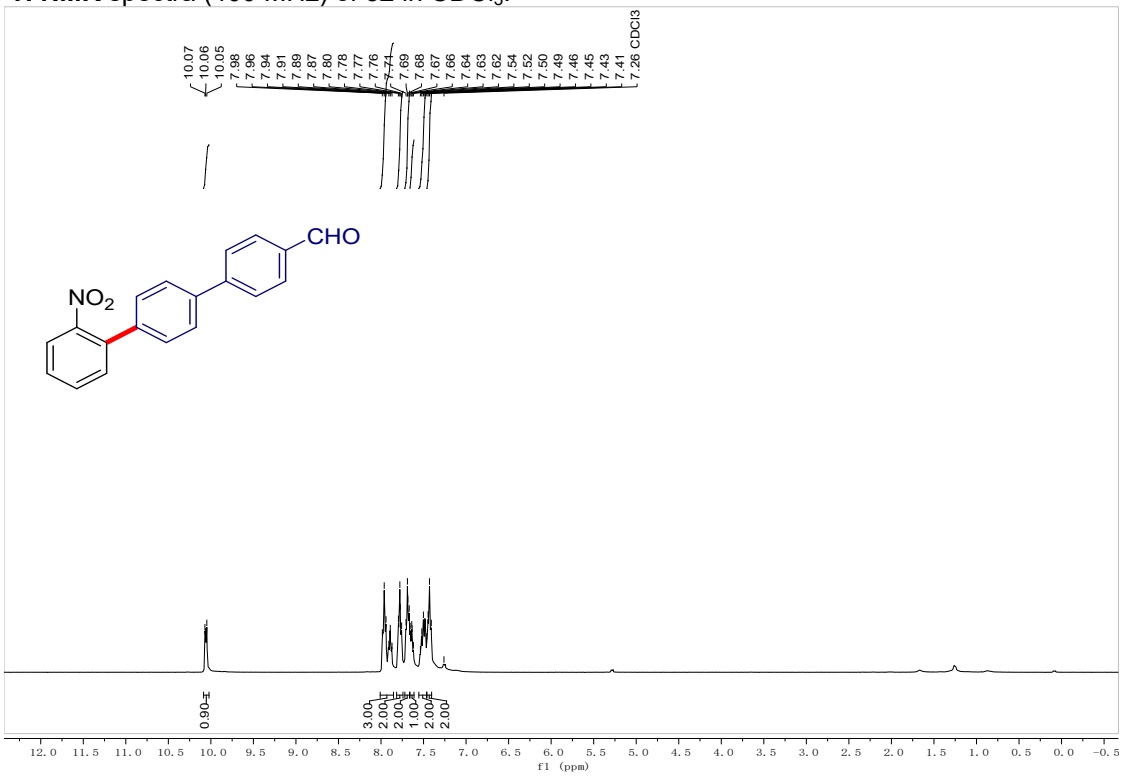
^{1}H NMR spectra (400 MHz) of **31** in $CDCl_3$.



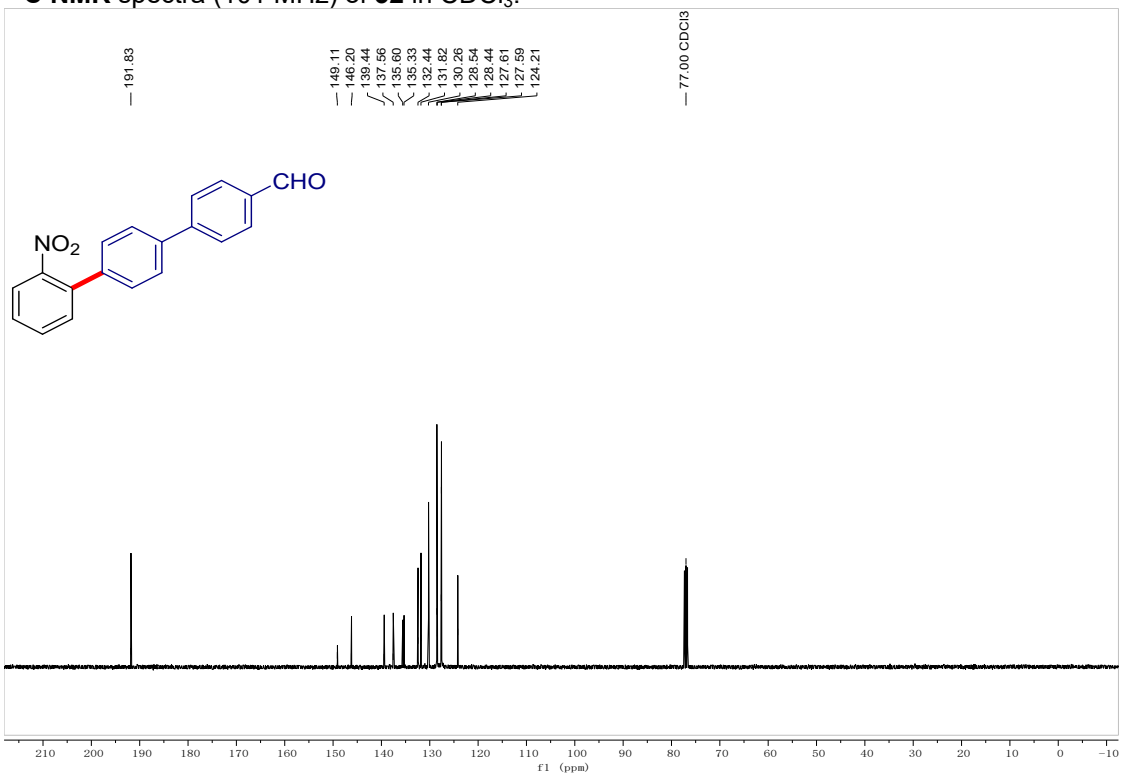
^{13}C NMR spectra (101 MHz) of **31** in $CDCl_3$.



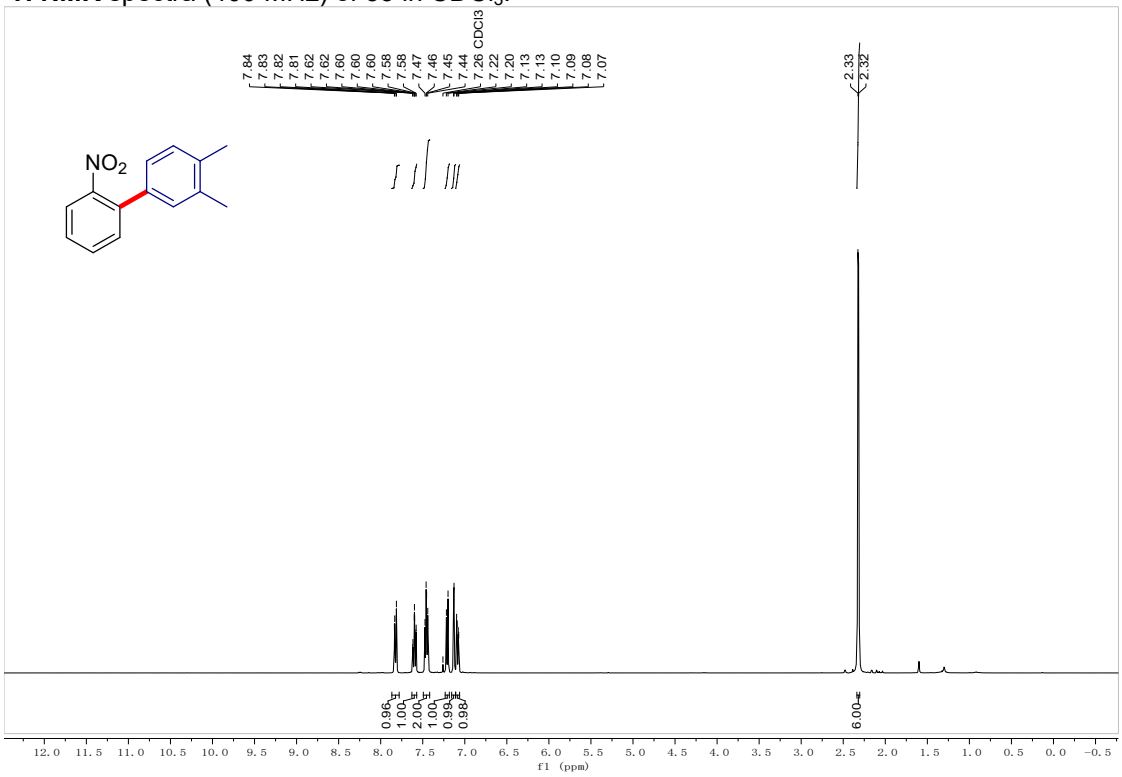
^{1}H NMR spectra (400 MHz) of **32** in $CDCl_3$.



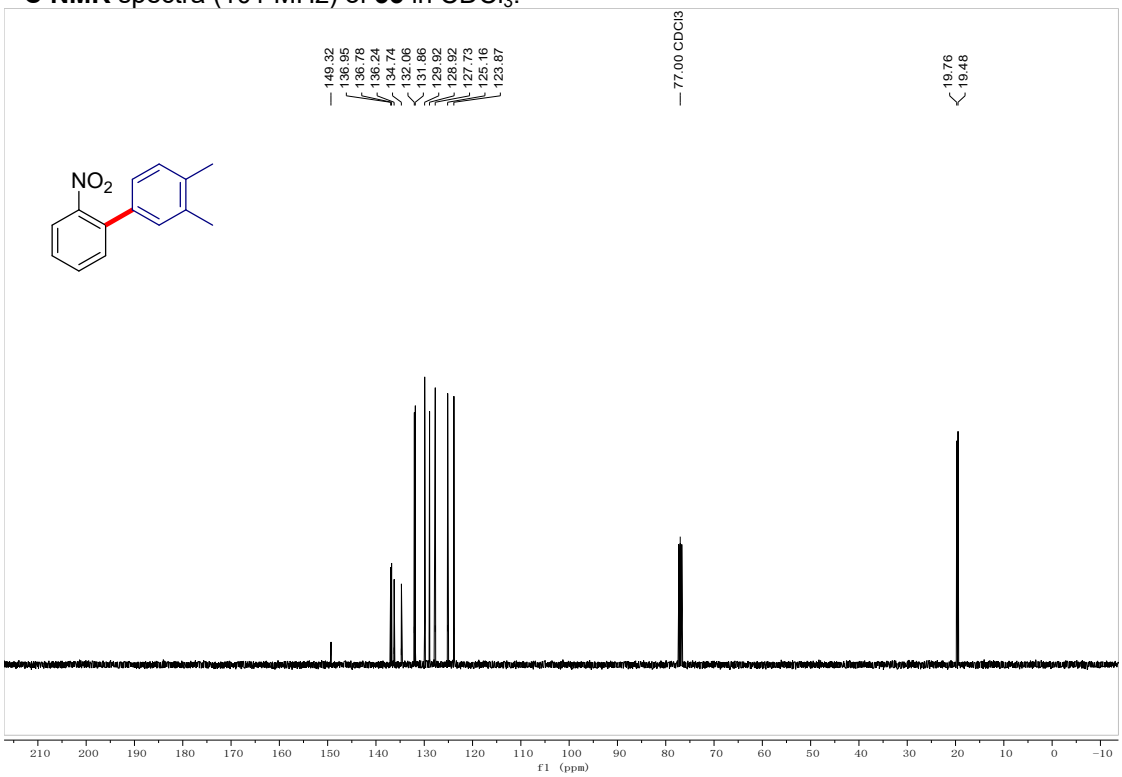
^{13}C NMR spectra (101 MHz) of **32** in $CDCl_3$.



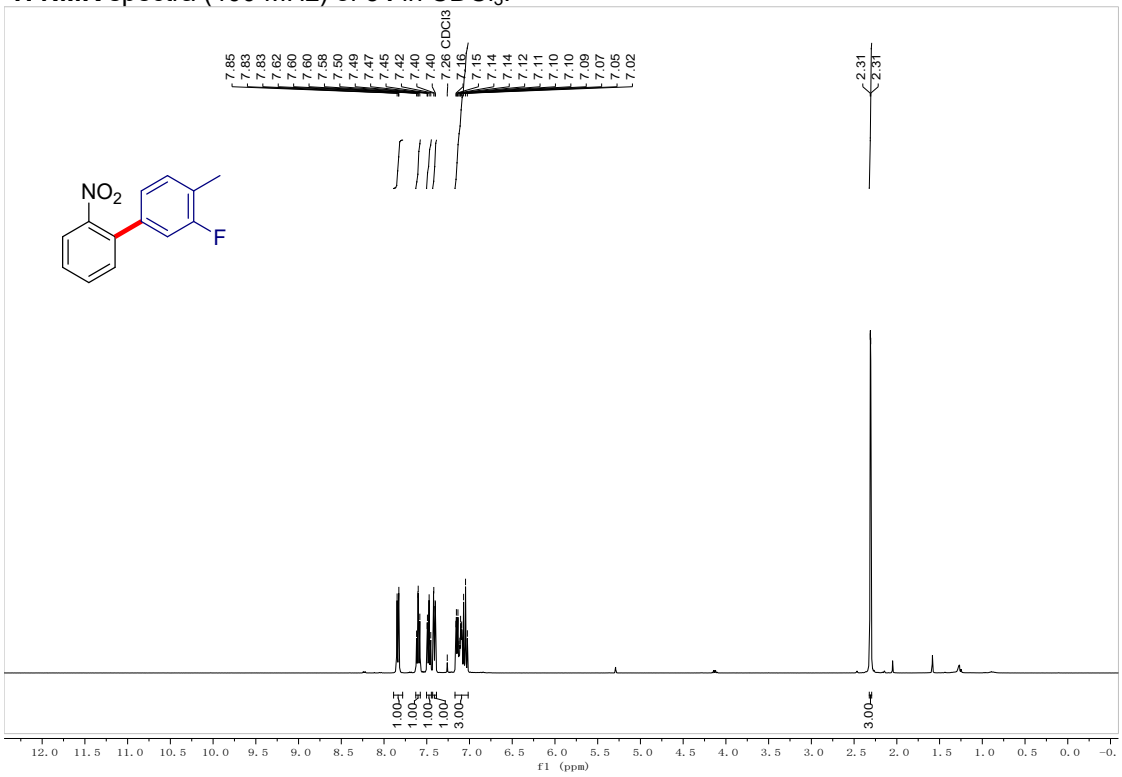
^{1}H NMR spectra (400 MHz) of **33** in $CDCl_3$.



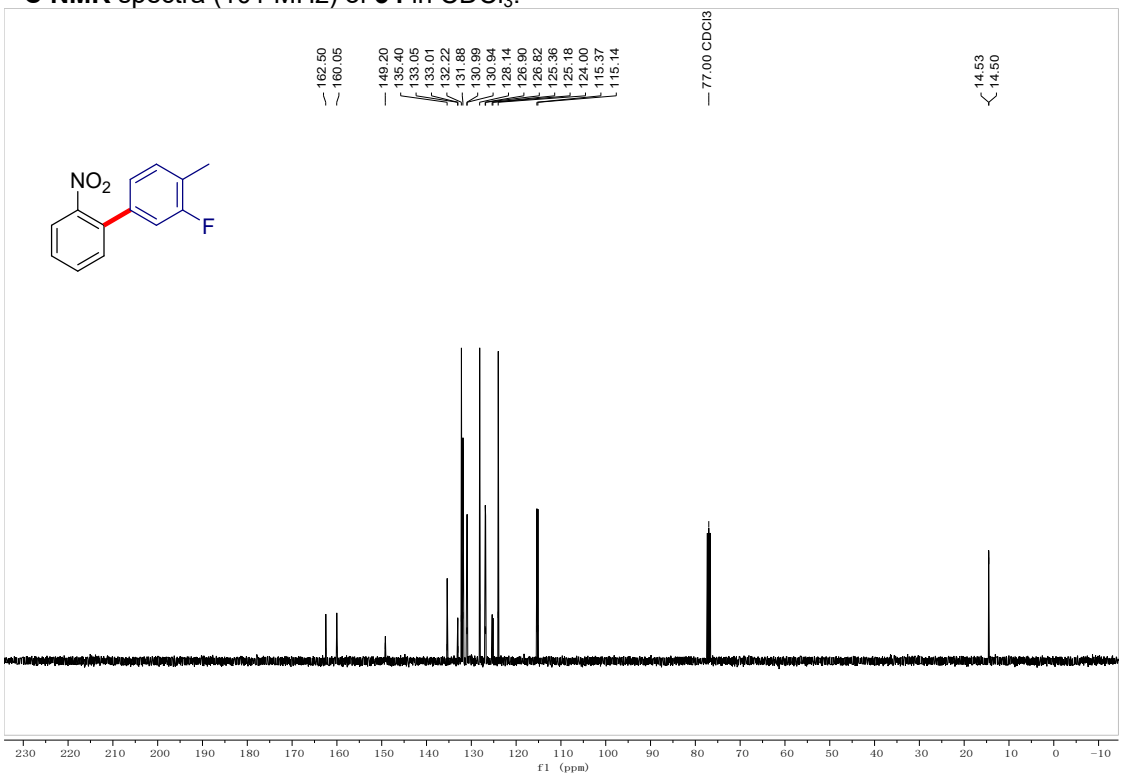
^{13}C NMR spectra (101 MHz) of **33** in $CDCl_3$.



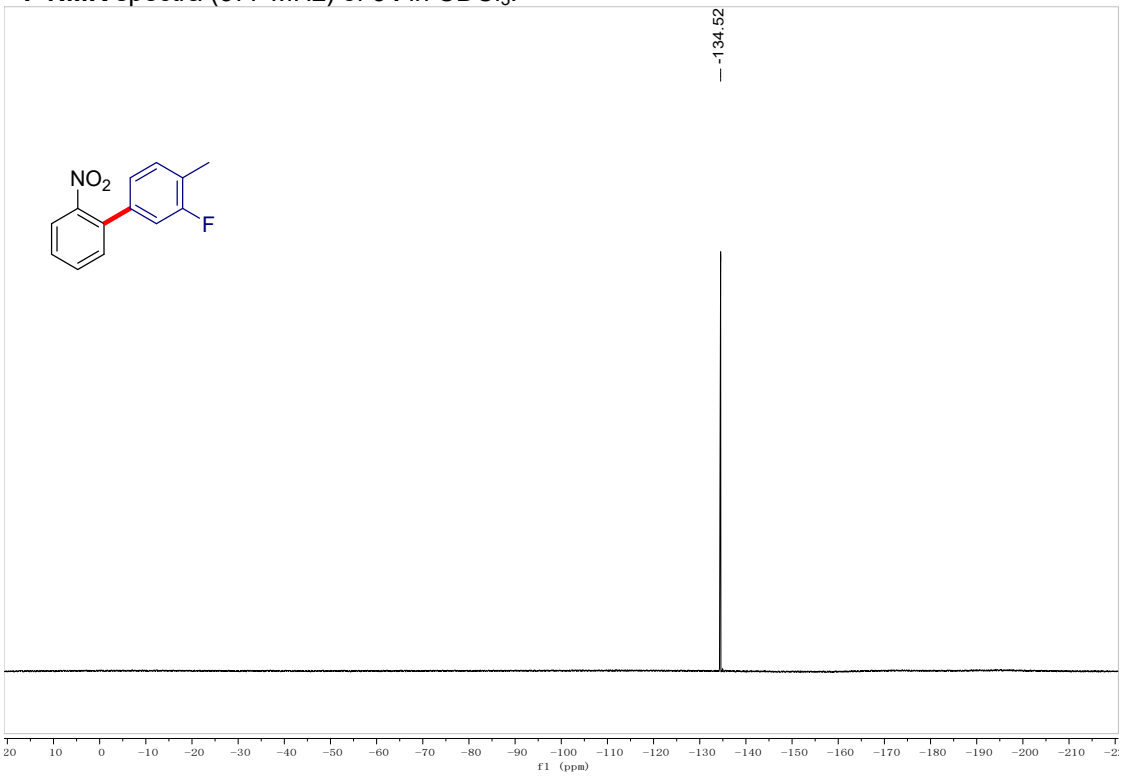
^{1}H NMR spectra (400 MHz) of **34** in $CDCl_3$.



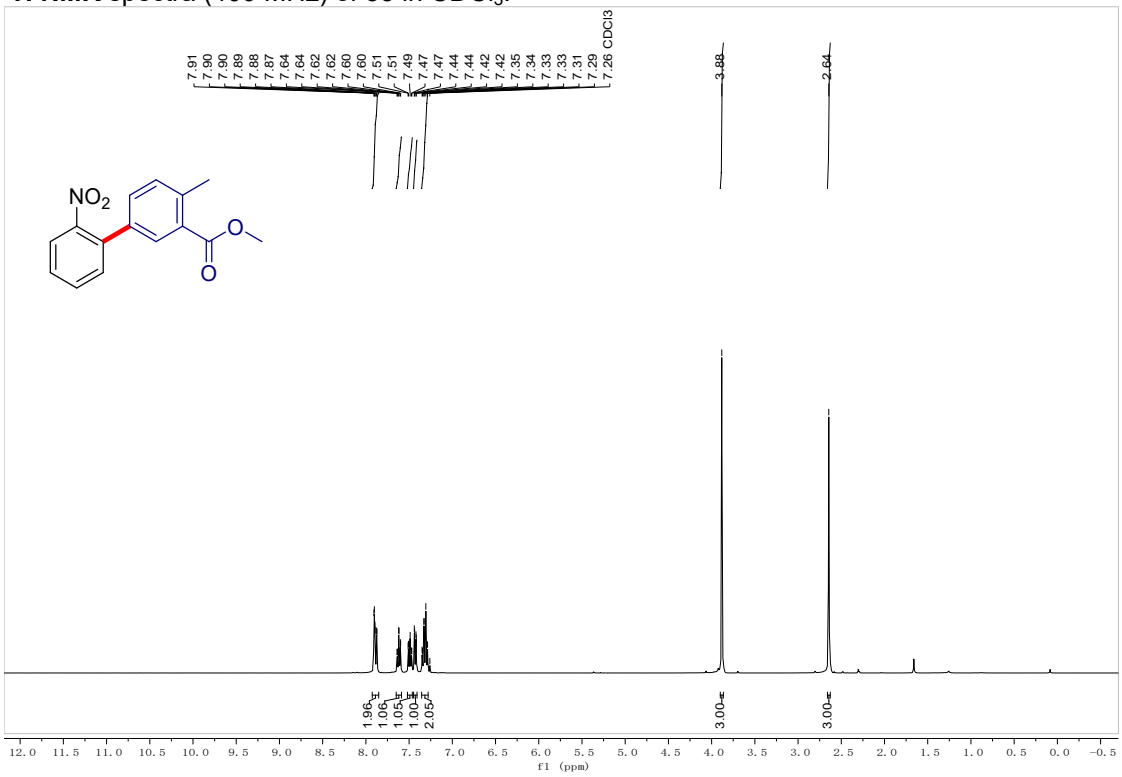
^{13}C NMR spectra (101 MHz) of **34** in $CDCl_3$.



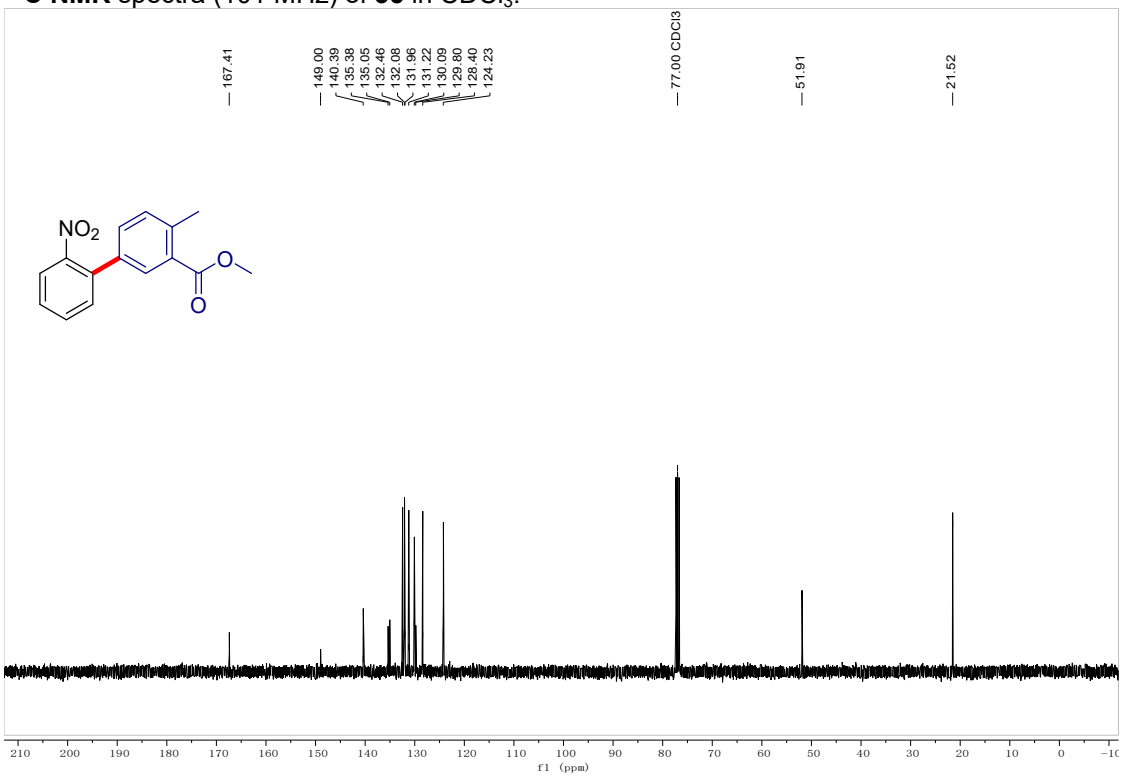
^{19}F NMR spectra (377 MHz) of **34** in $CDCl_3$.



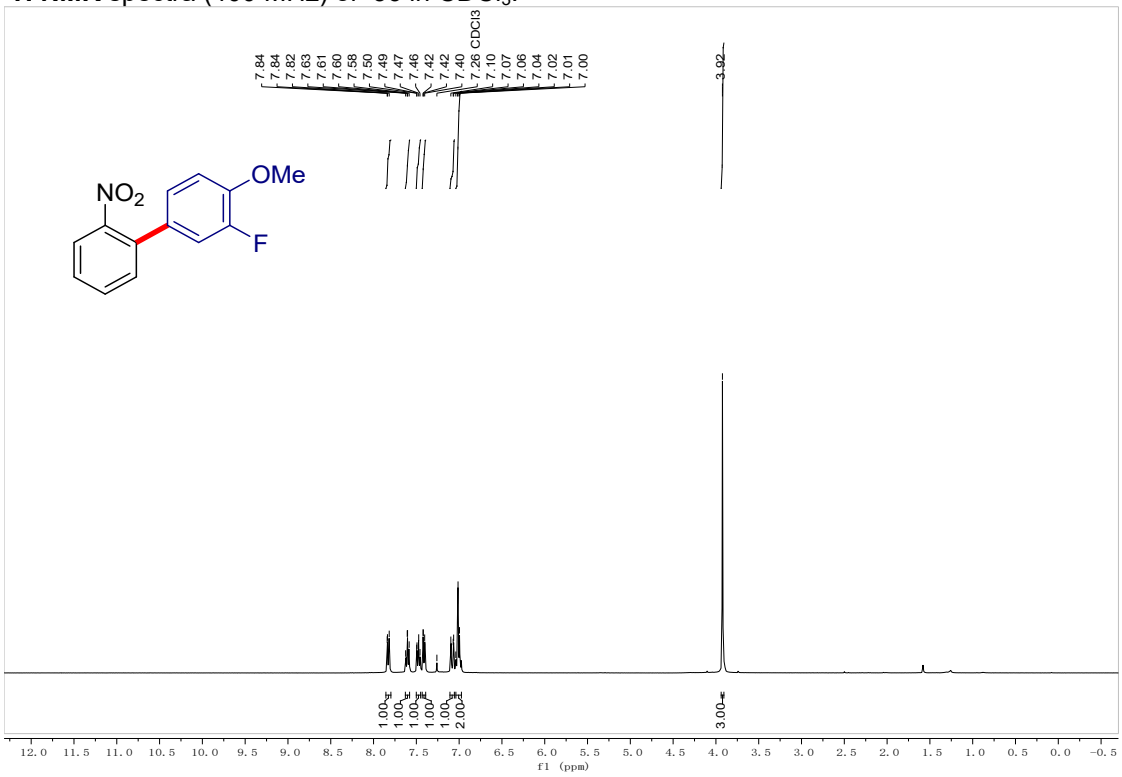
^{1}H NMR spectra (400 MHz) of **35** in $CDCl_3$.



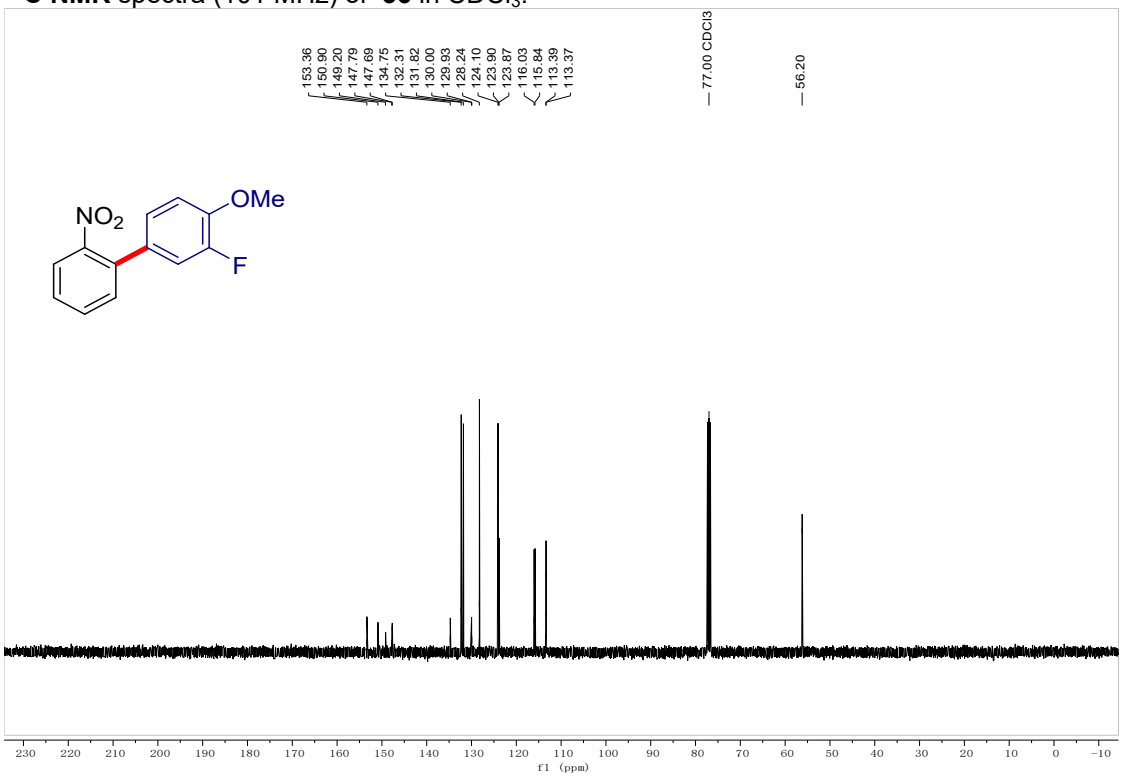
^{13}C NMR spectra (101 MHz) of **35** in $CDCl_3$.



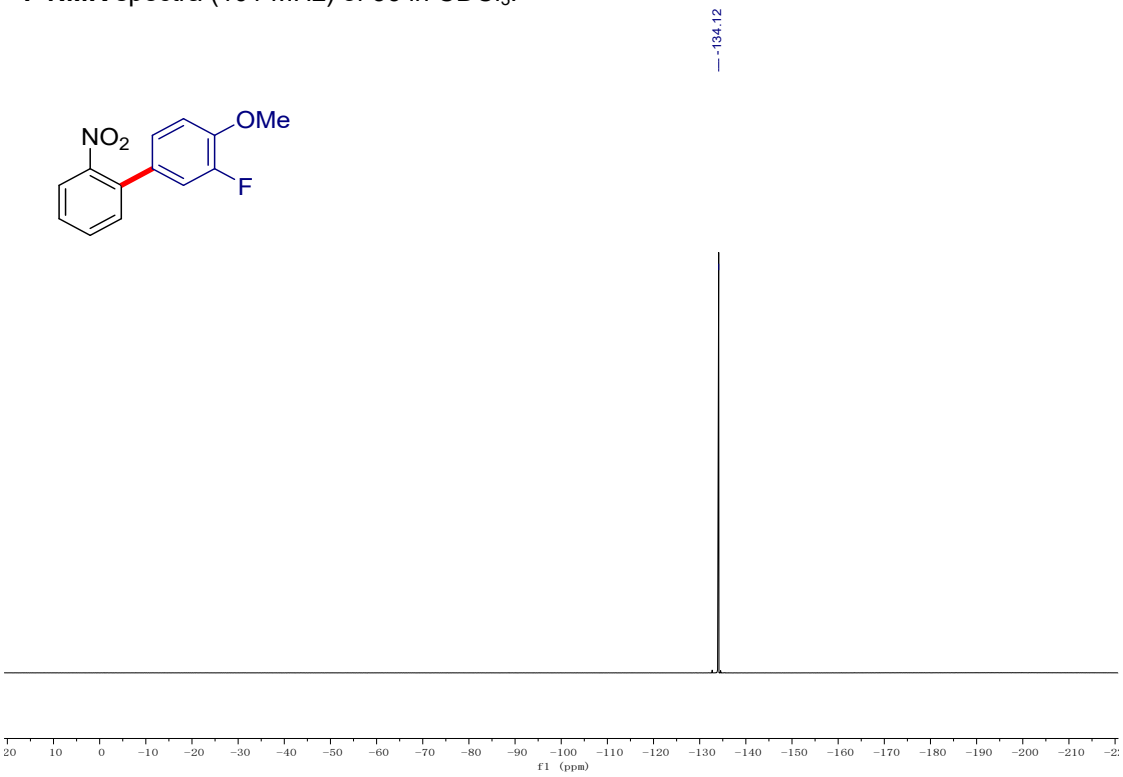
^{1}H NMR spectra (400 MHz) of **36** in $CDCl_3$.



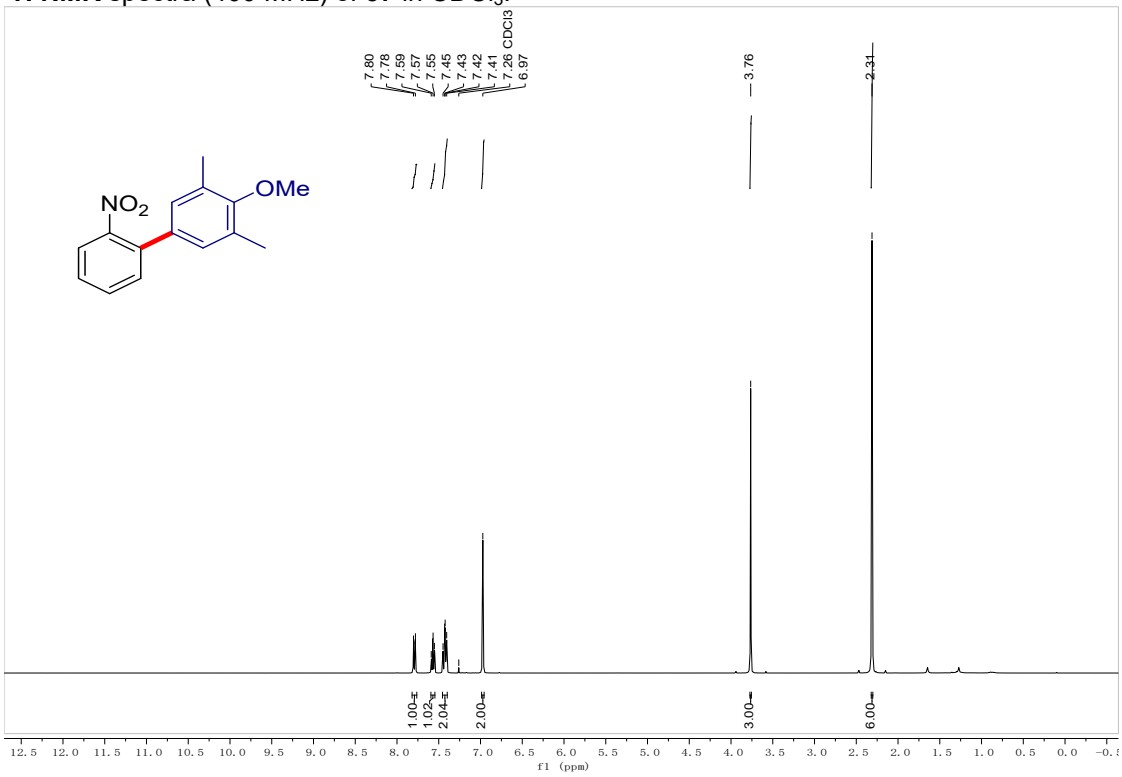
^{13}C NMR spectra (101 MHz) of **36** in $CDCl_3$.



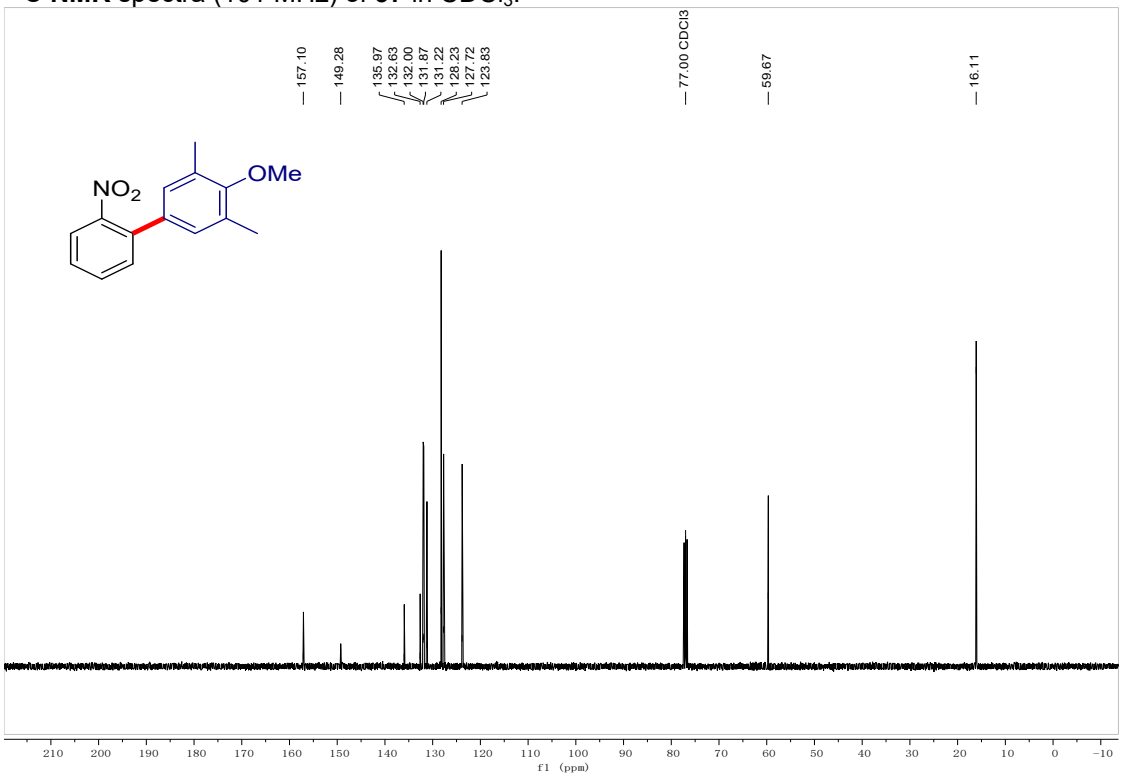
^{19}F NMR spectra (101 MHz) of **36** in $CDCl_3$.



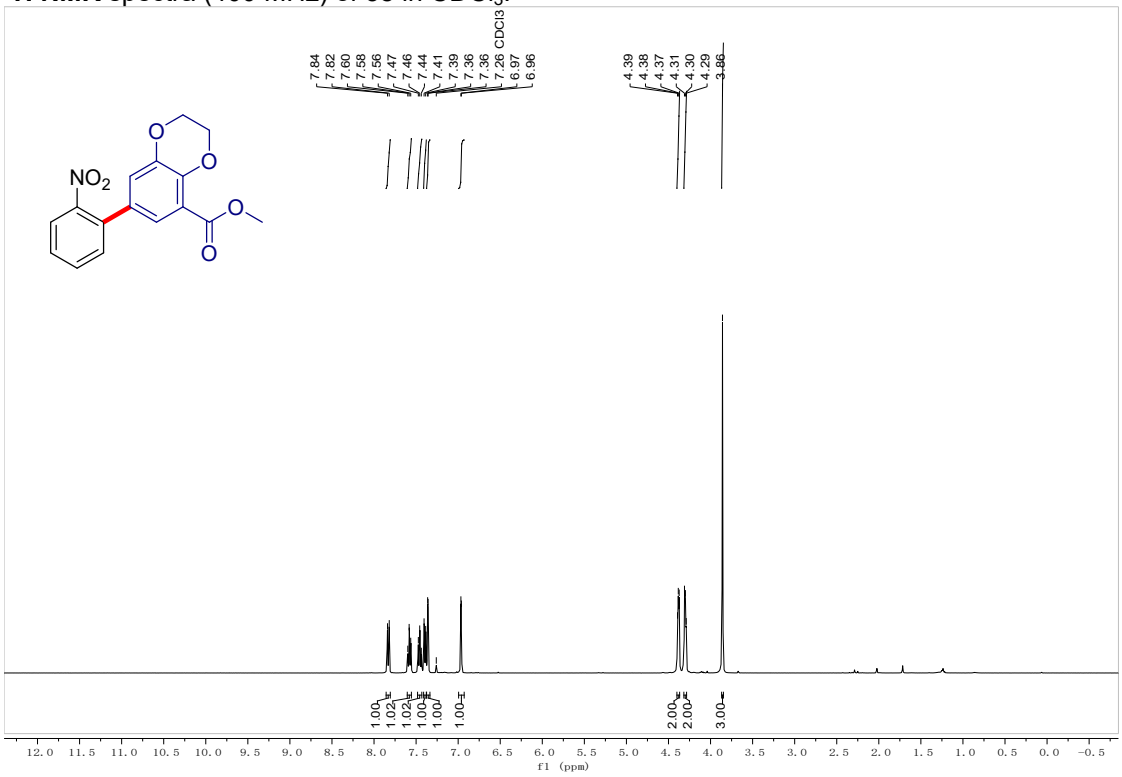
^{1}H NMR spectra (400 MHz) of **37** in $CDCl_3$.



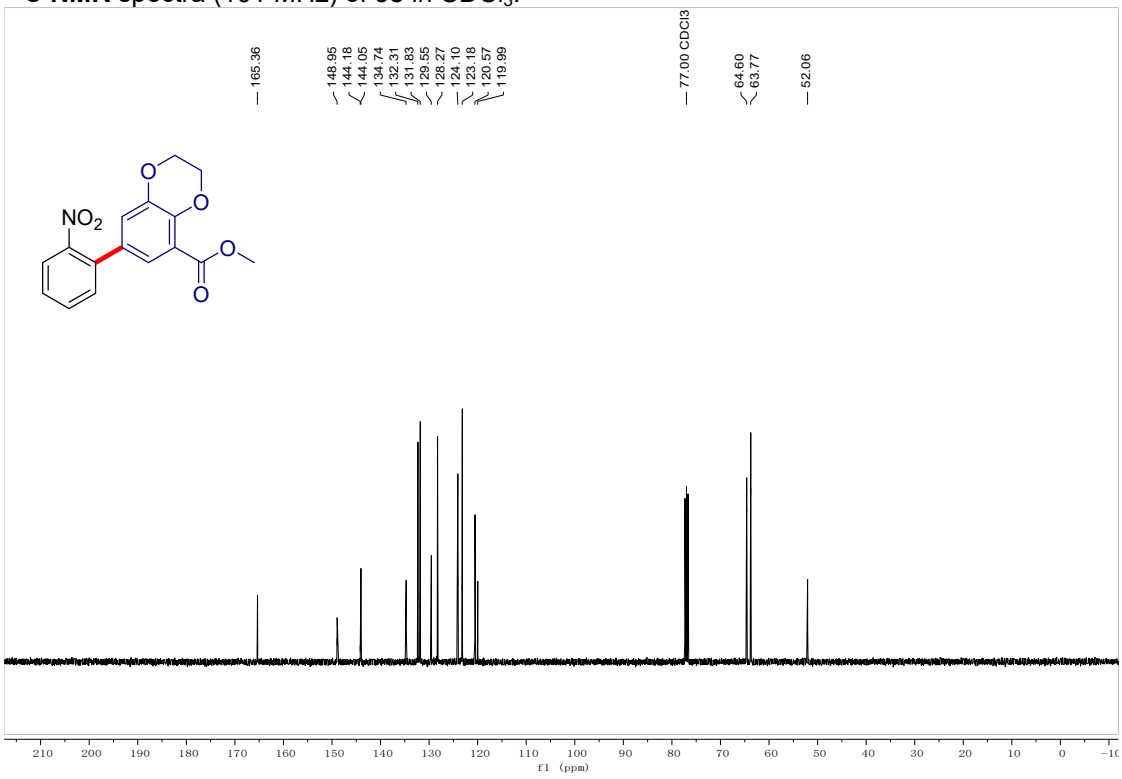
^{13}C NMR spectra (101 MHz) of **37** in $CDCl_3$.



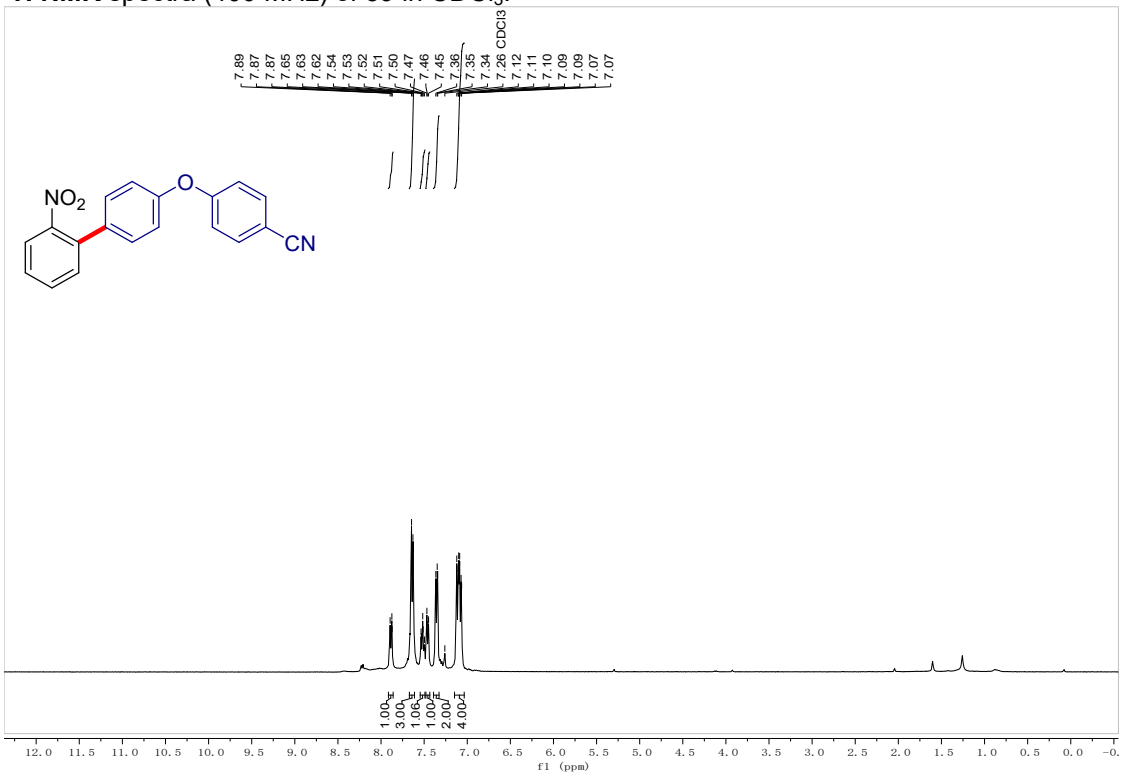
^{1}H NMR spectra (400 MHz) of **38** in $CDCl_3$.



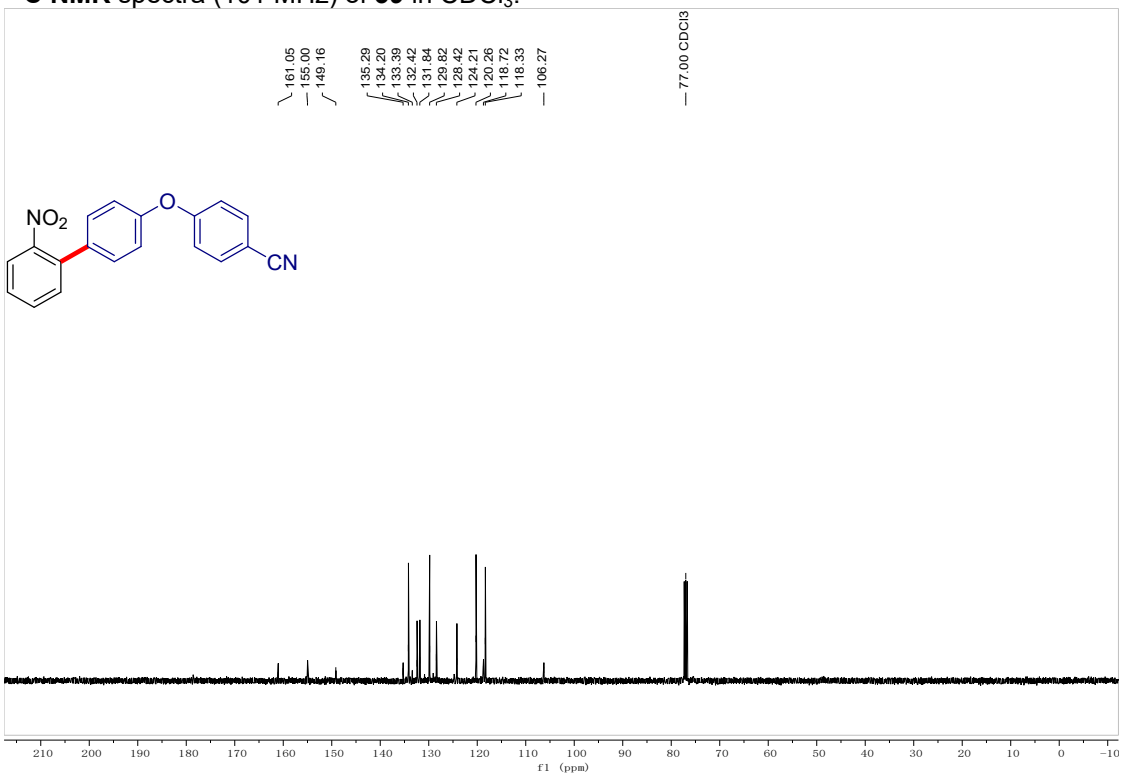
^{13}C NMR spectra (101 MHz) of **38** in $CDCl_3$.



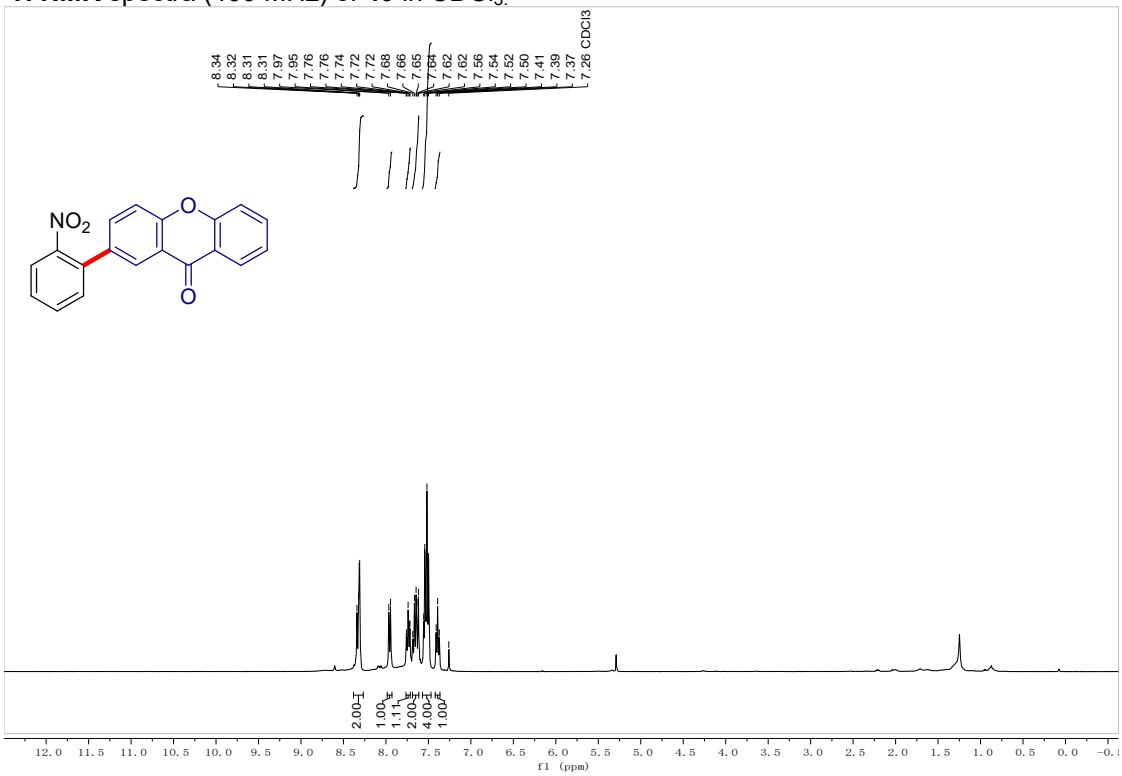
^{1}H NMR spectra (400 MHz) of **39** in $CDCl_3$.



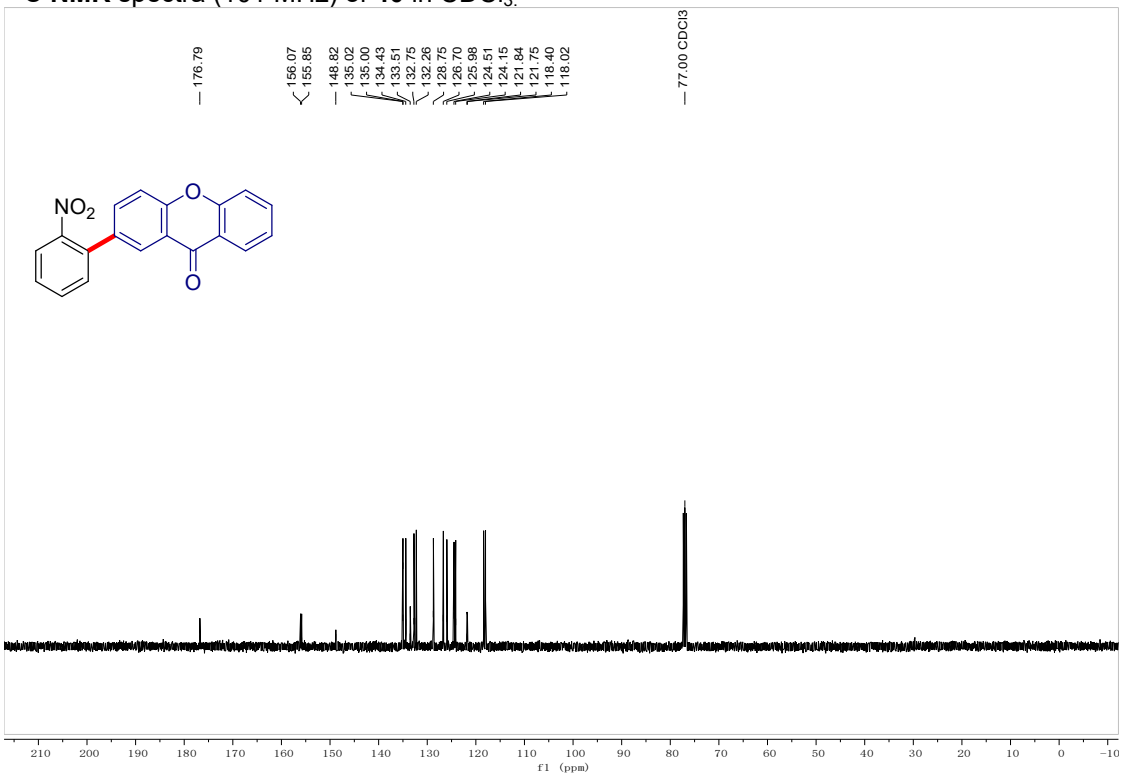
^{13}C NMR spectra (101 MHz) of **39** in $CDCl_3$.



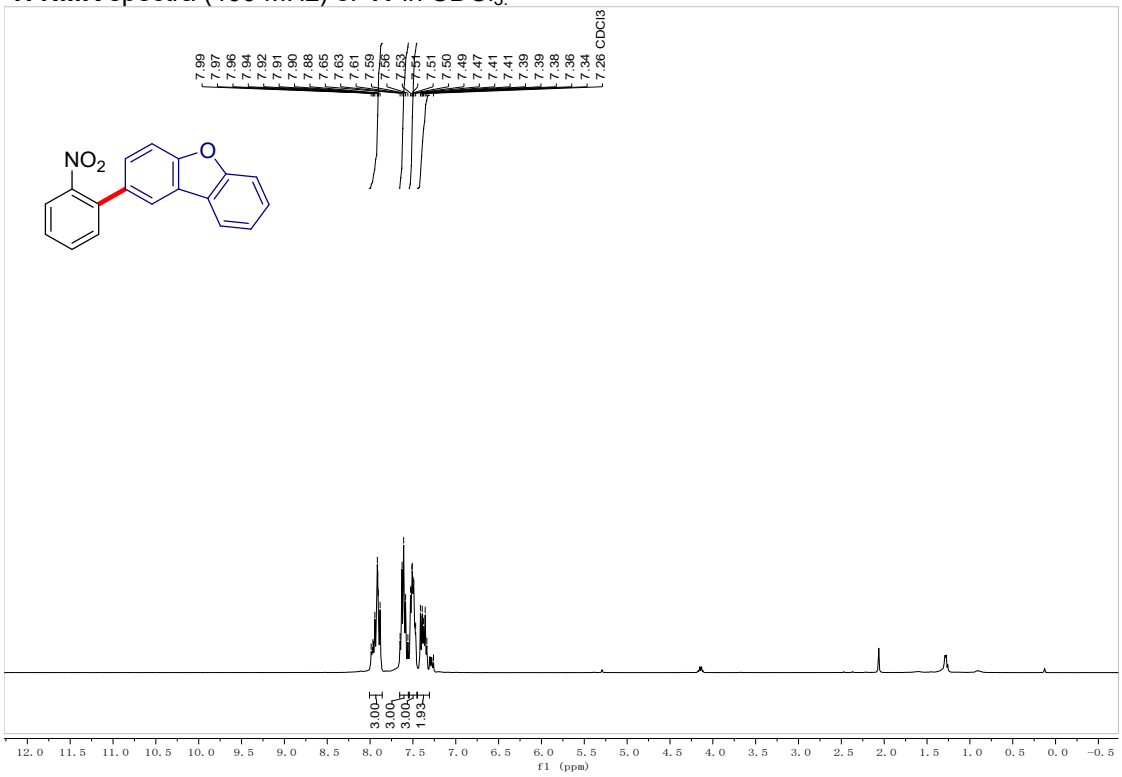
^{1}H NMR spectra (400 MHz) of **40** in $CDCl_3$.



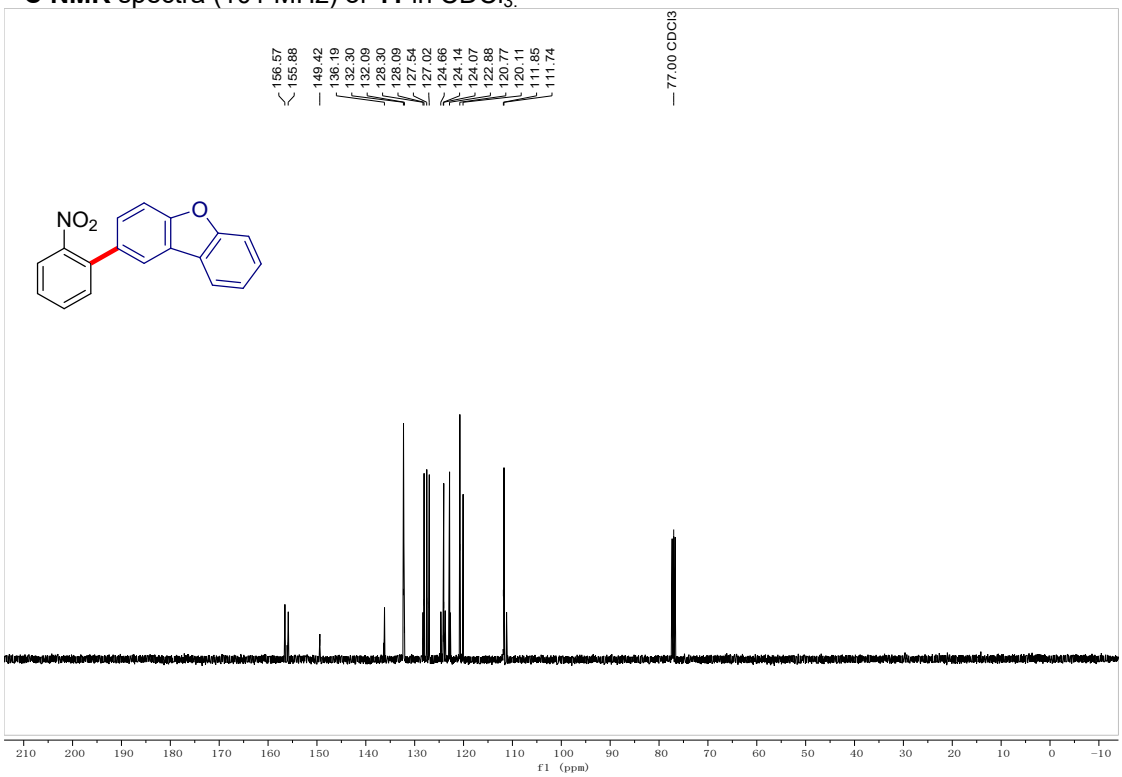
^{13}C NMR spectra (101 MHz) of **40** in $CDCl_3$.



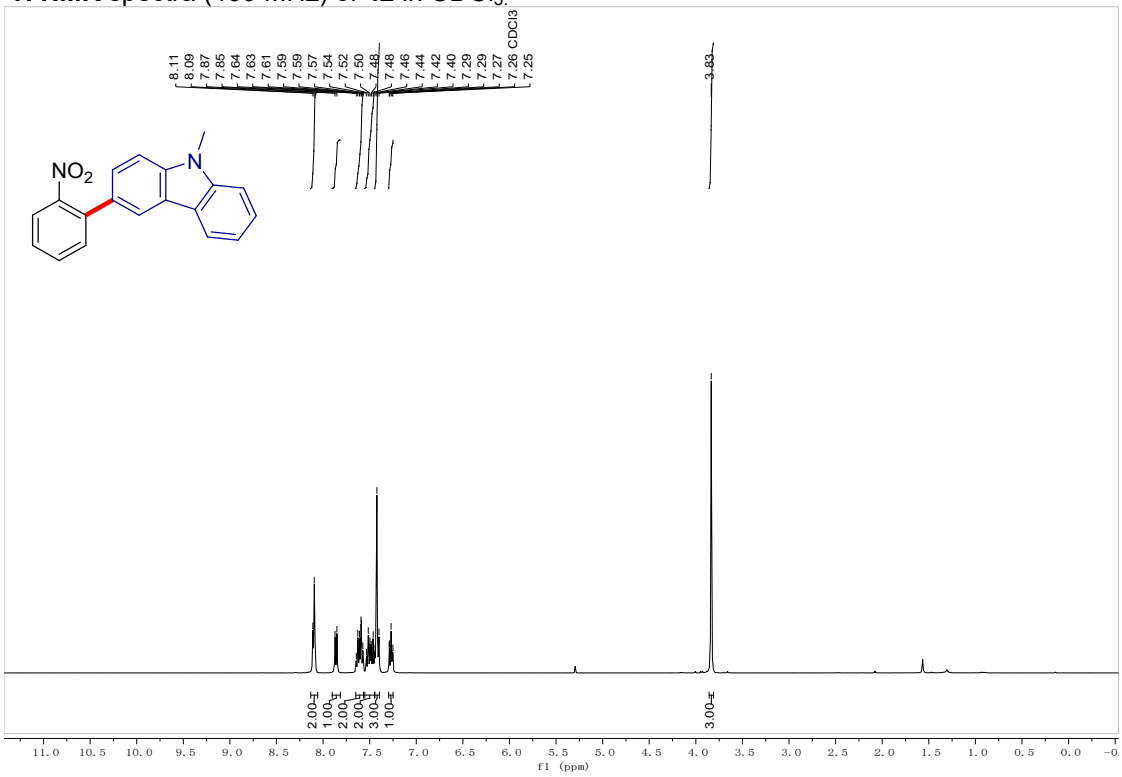
^{1}H NMR spectra (400 MHz) of **41** in $CDCl_3$.



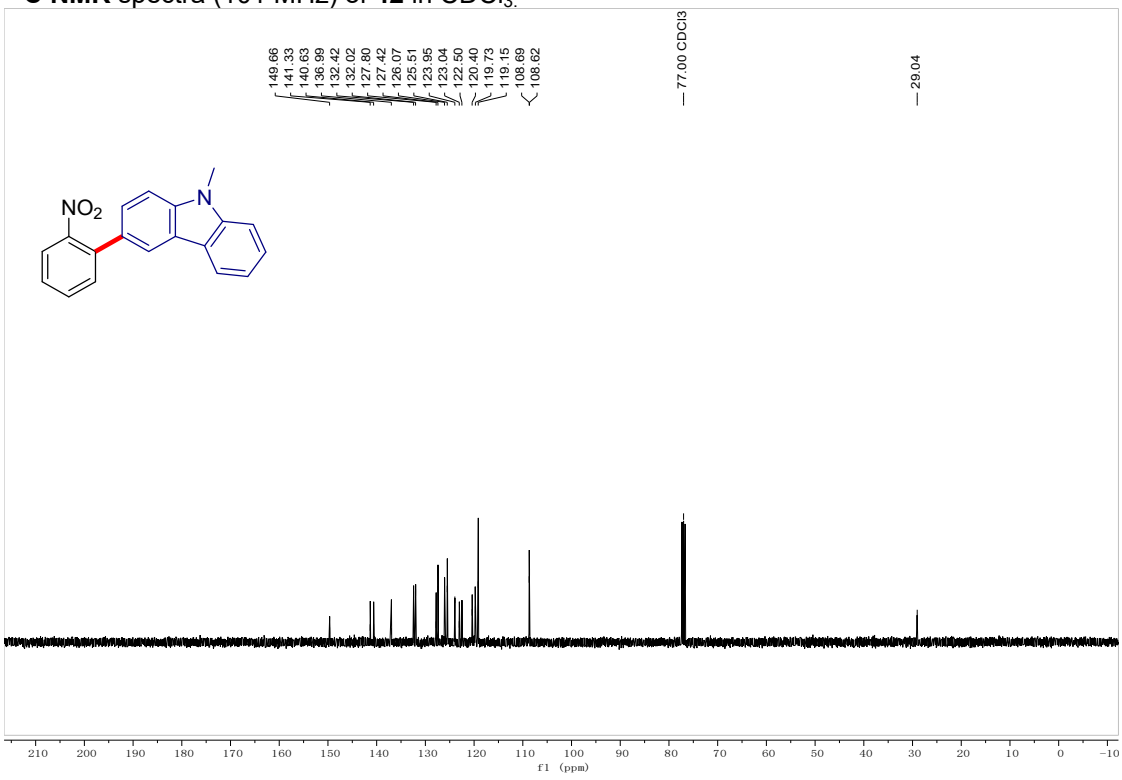
^{13}C NMR spectra (101 MHz) of **41** in $CDCl_3$.



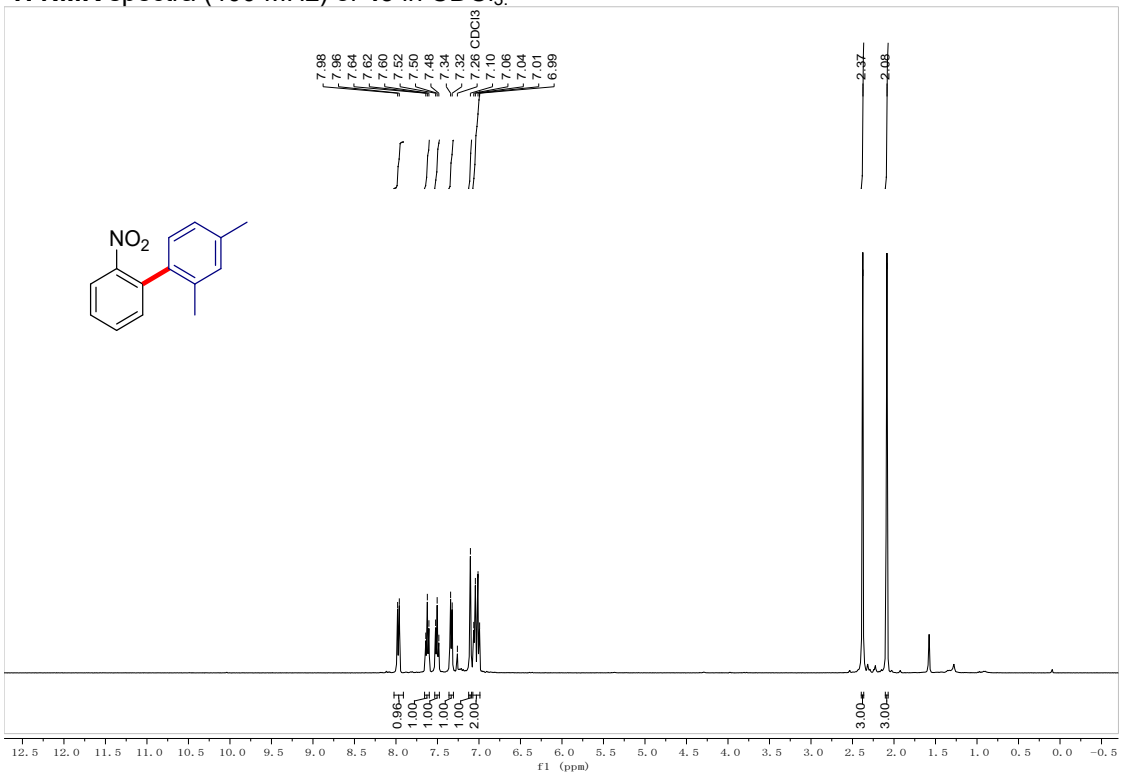
^{1}H NMR spectra (400 MHz) of **42** in $CDCl_3$.



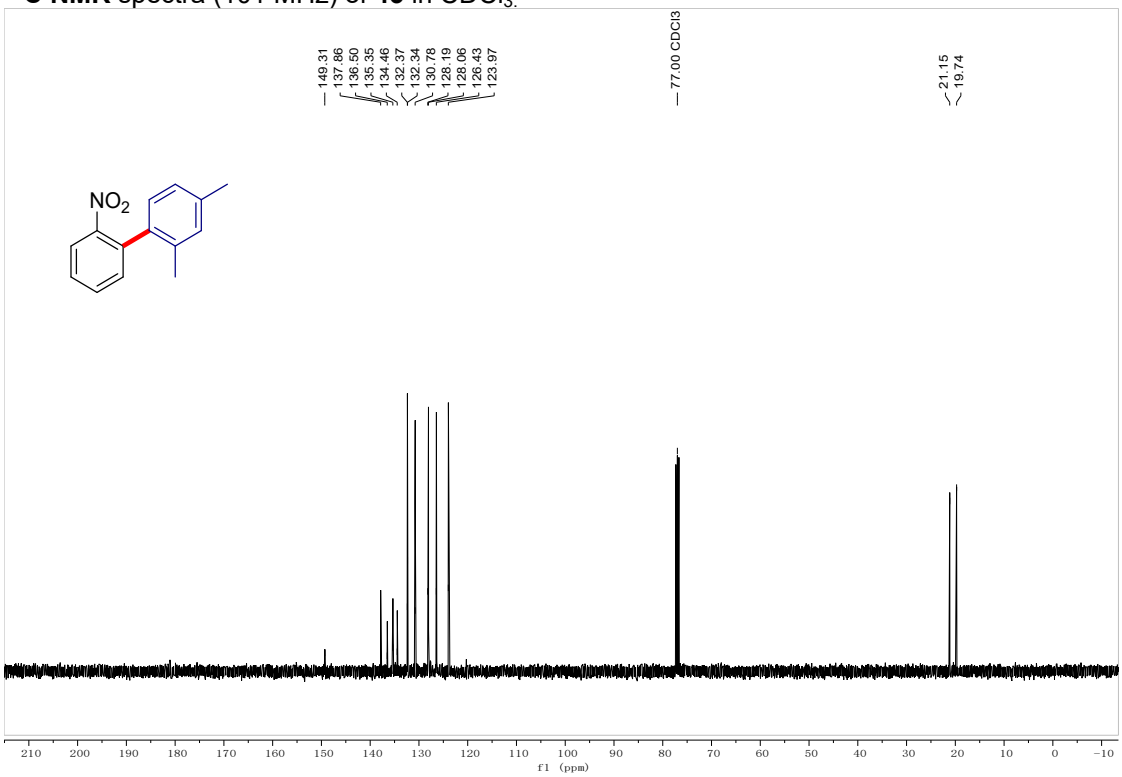
^{13}C NMR spectra (101 MHz) of **42** in $CDCl_3$.



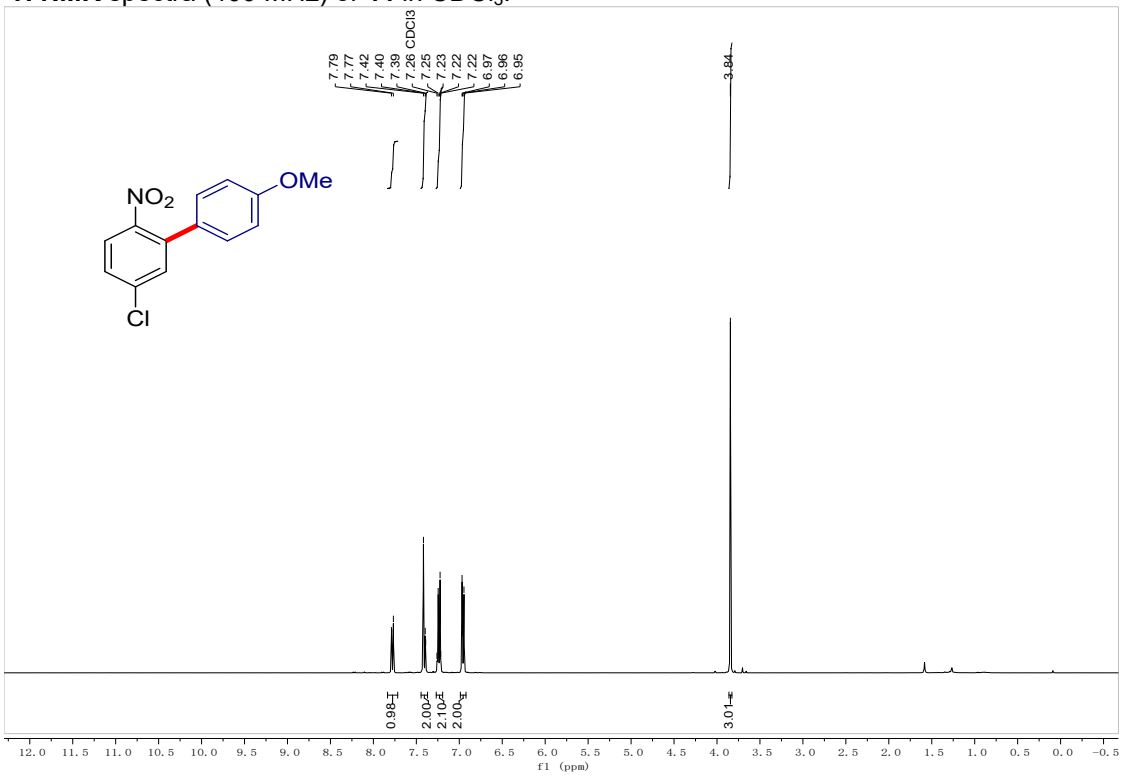
^{1}H NMR spectra (400 MHz) of **43** in $CDCl_3$.



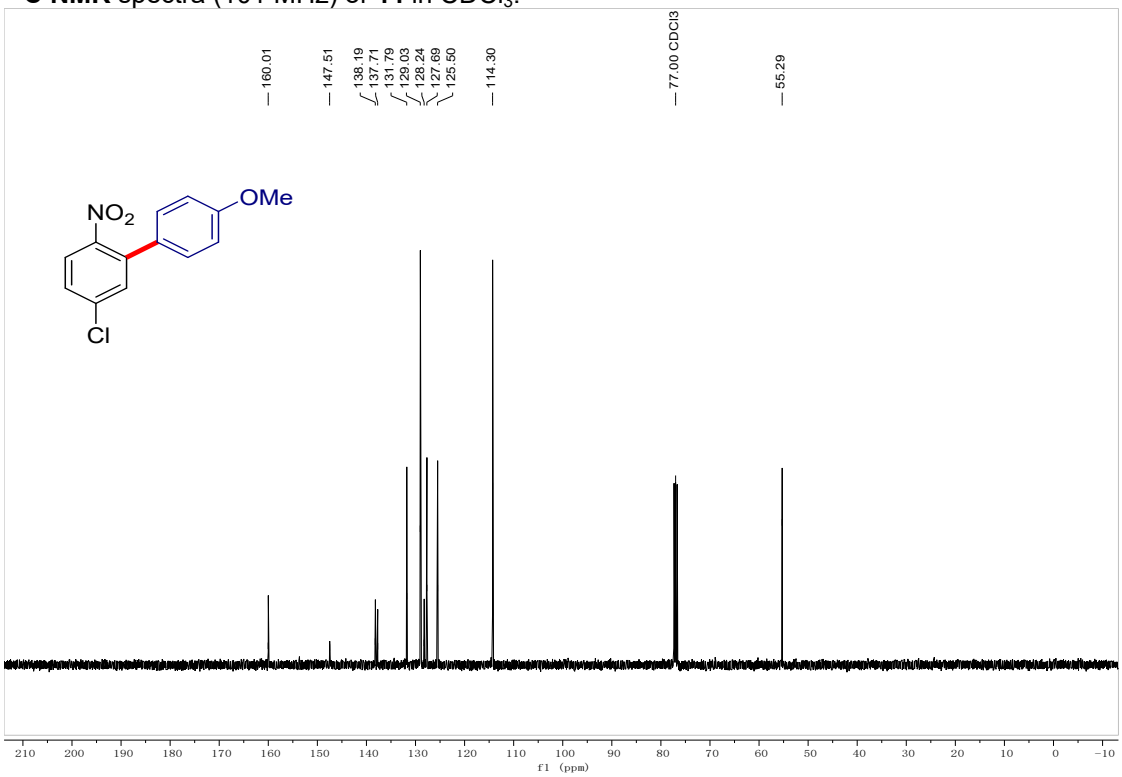
^{13}C NMR spectra (101 MHz) of **43** in $CDCl_3$.



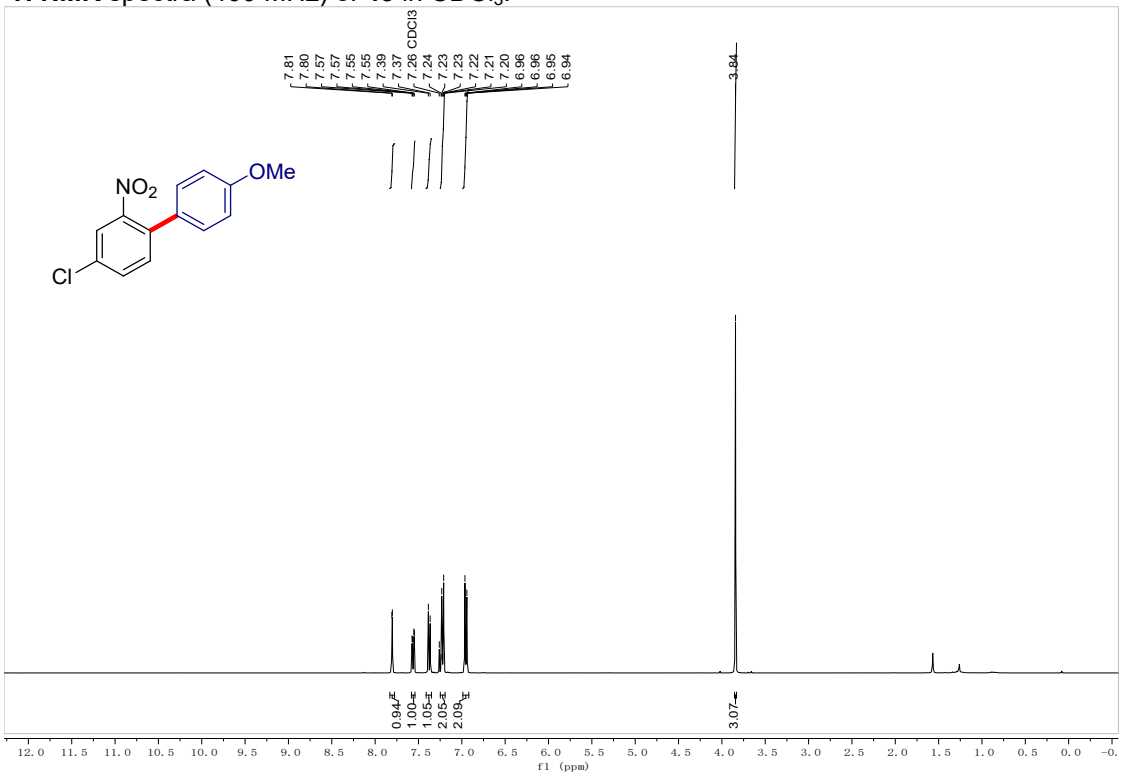
^{1}H NMR spectra (400 MHz) of **44** in $CDCl_3$.



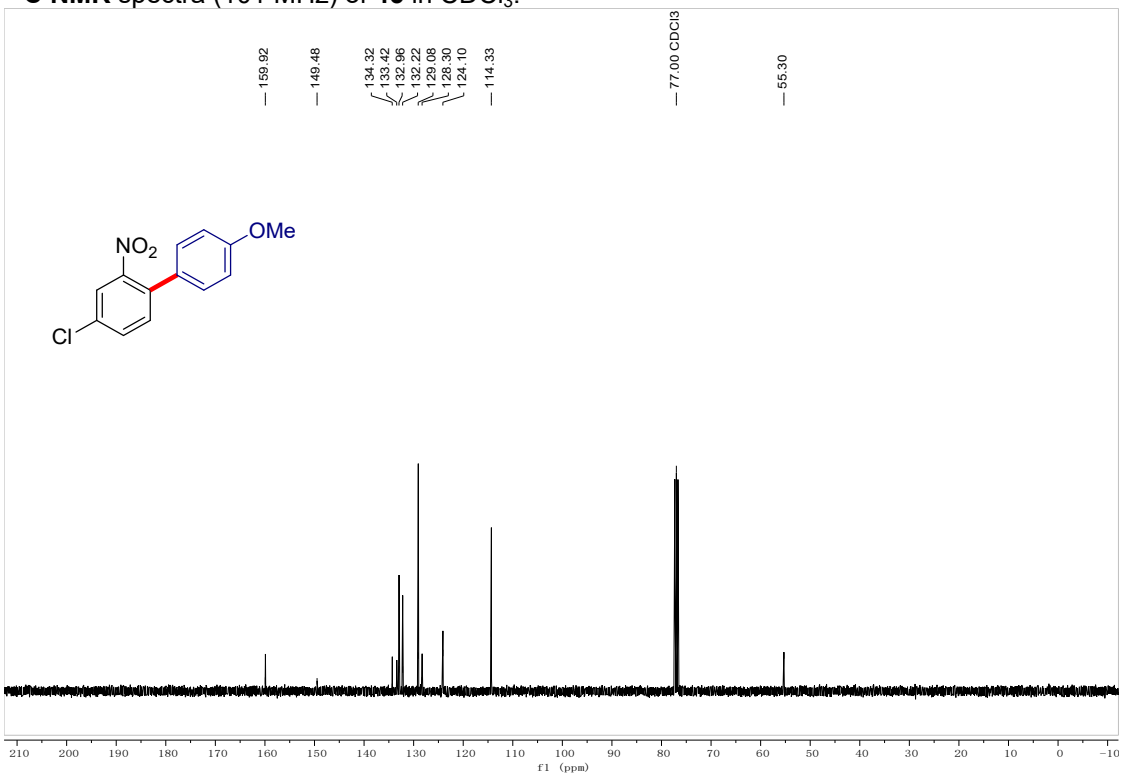
^{13}C NMR spectra (101 MHz) of **44** in $CDCl_3$.



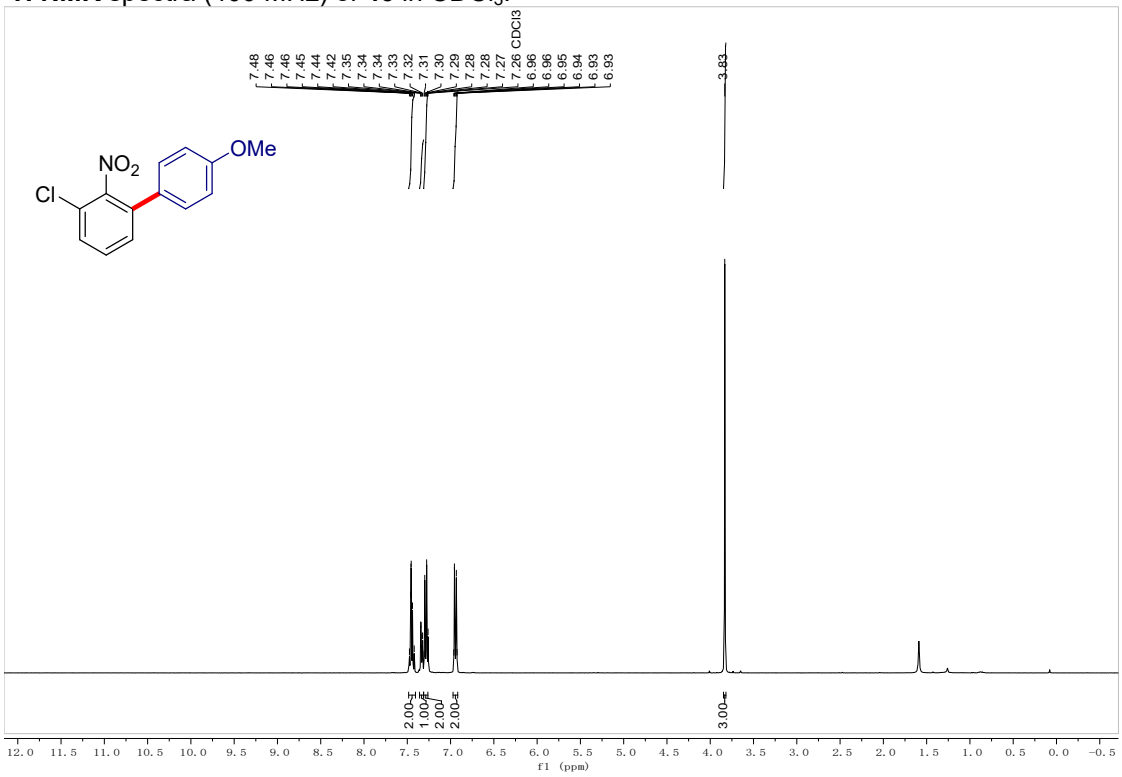
^{1}H NMR spectra (400 MHz) of **45** in $CDCl_3$.



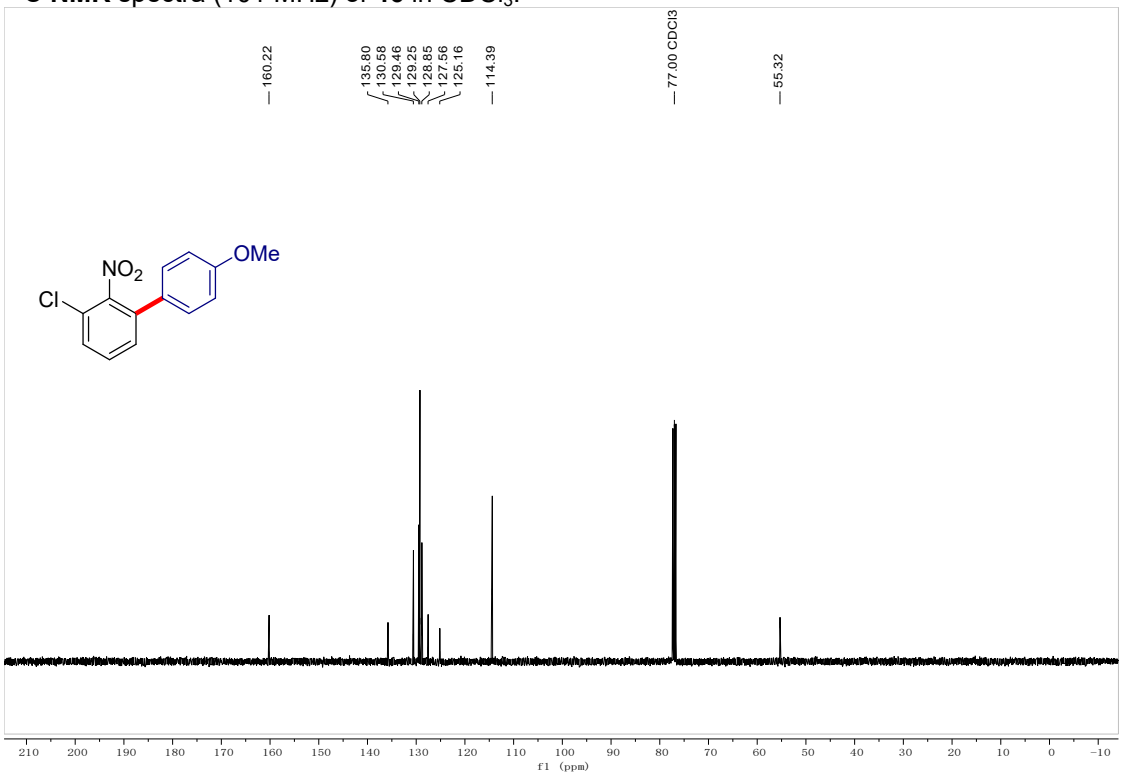
^{13}C NMR spectra (101 MHz) of **45** in $CDCl_3$.



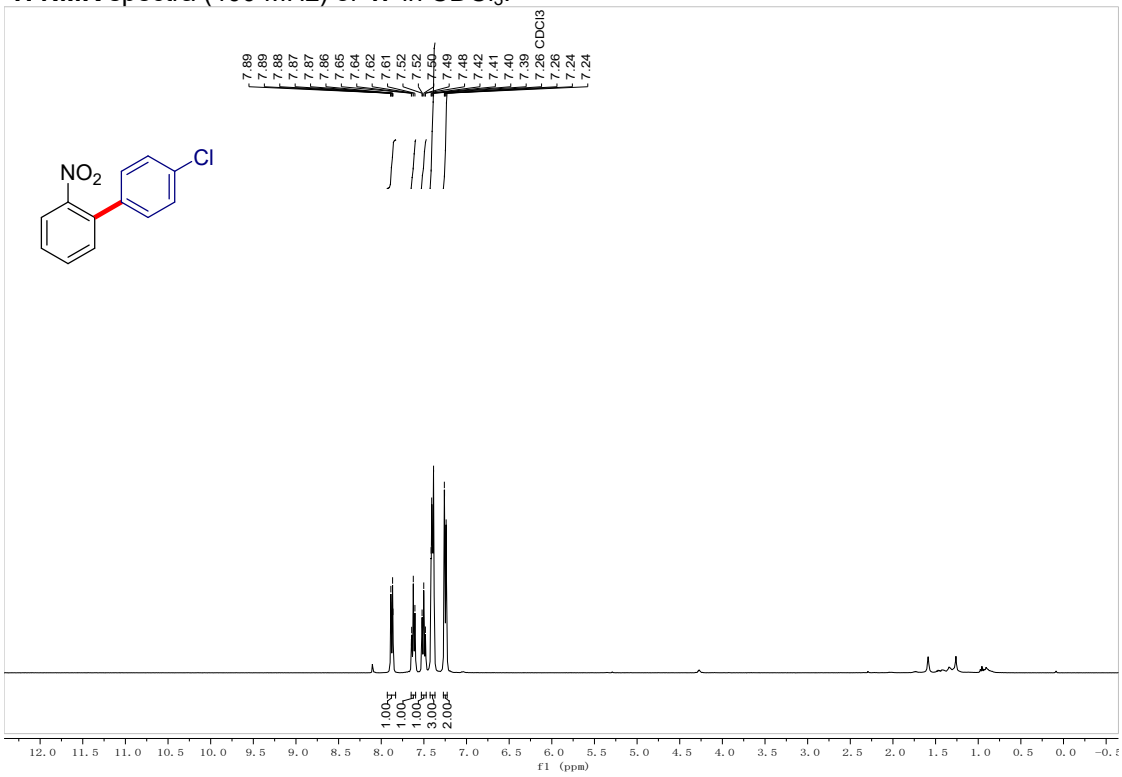
^{1}H NMR spectra (400 MHz) of **46** in $CDCl_3$.



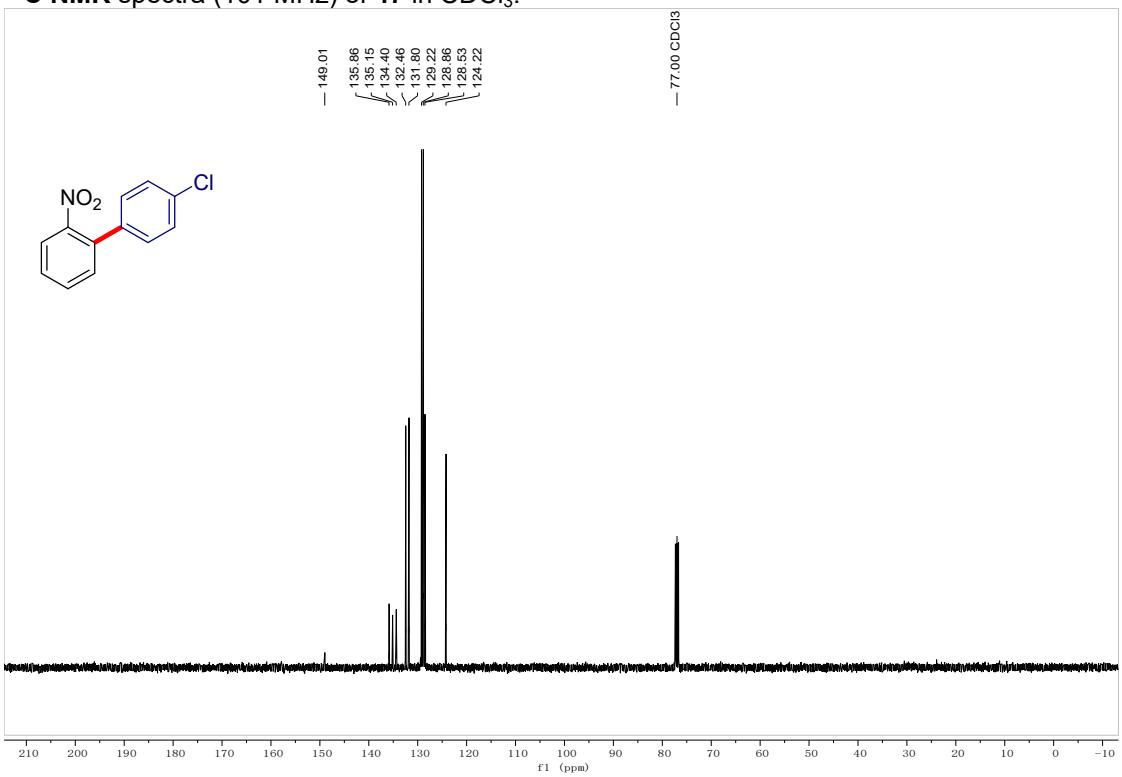
^{13}C NMR spectra (101 MHz) of **46** in $CDCl_3$.



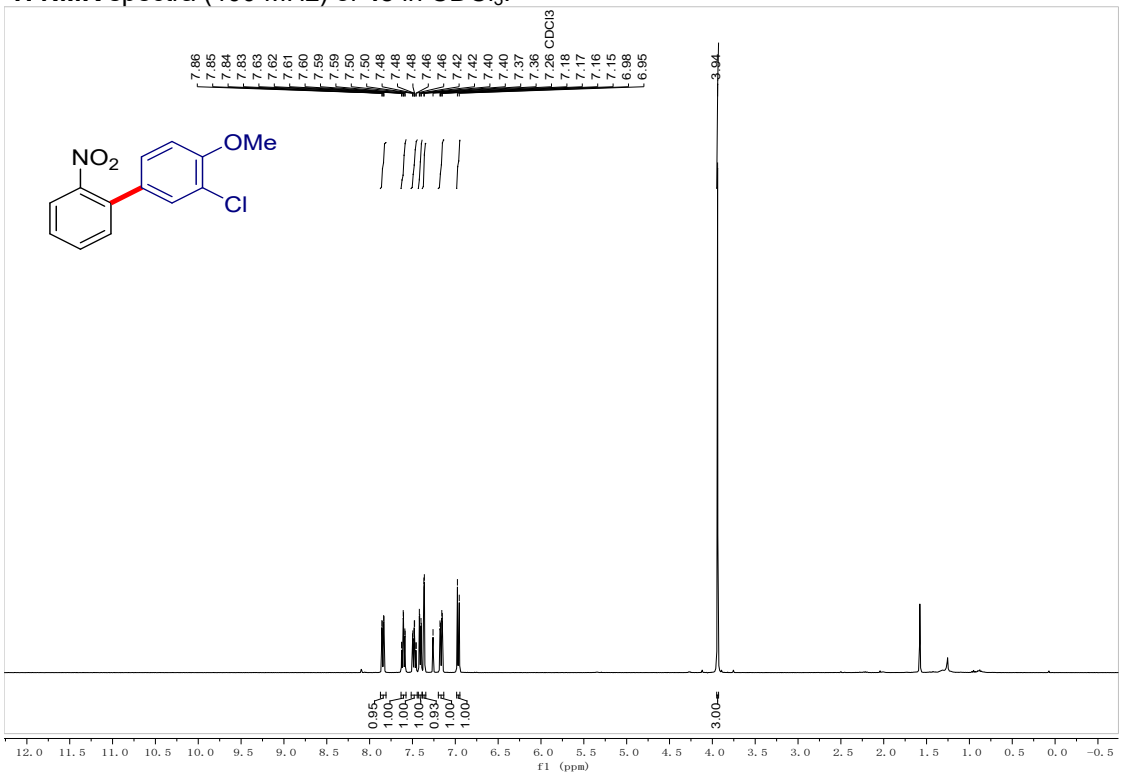
^{1}H NMR spectra (400 MHz) of **47** in $CDCl_3$.



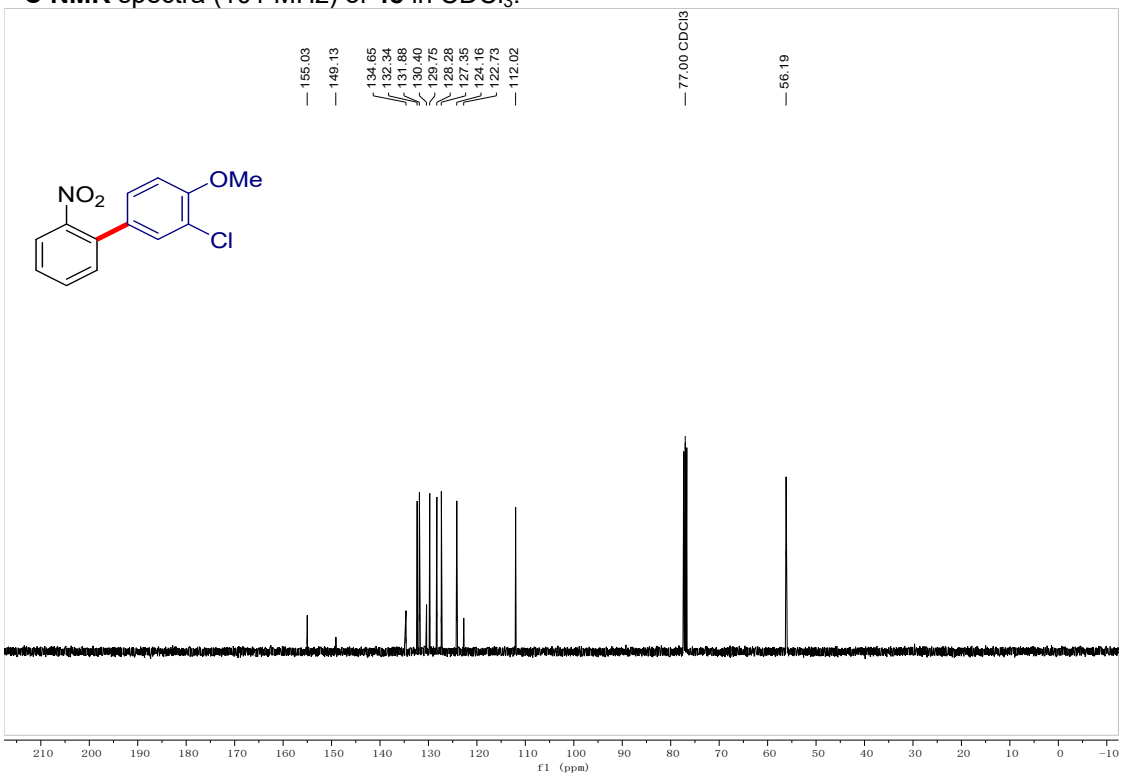
^{13}C NMR spectra (101 MHz) of **47** in $CDCl_3$.



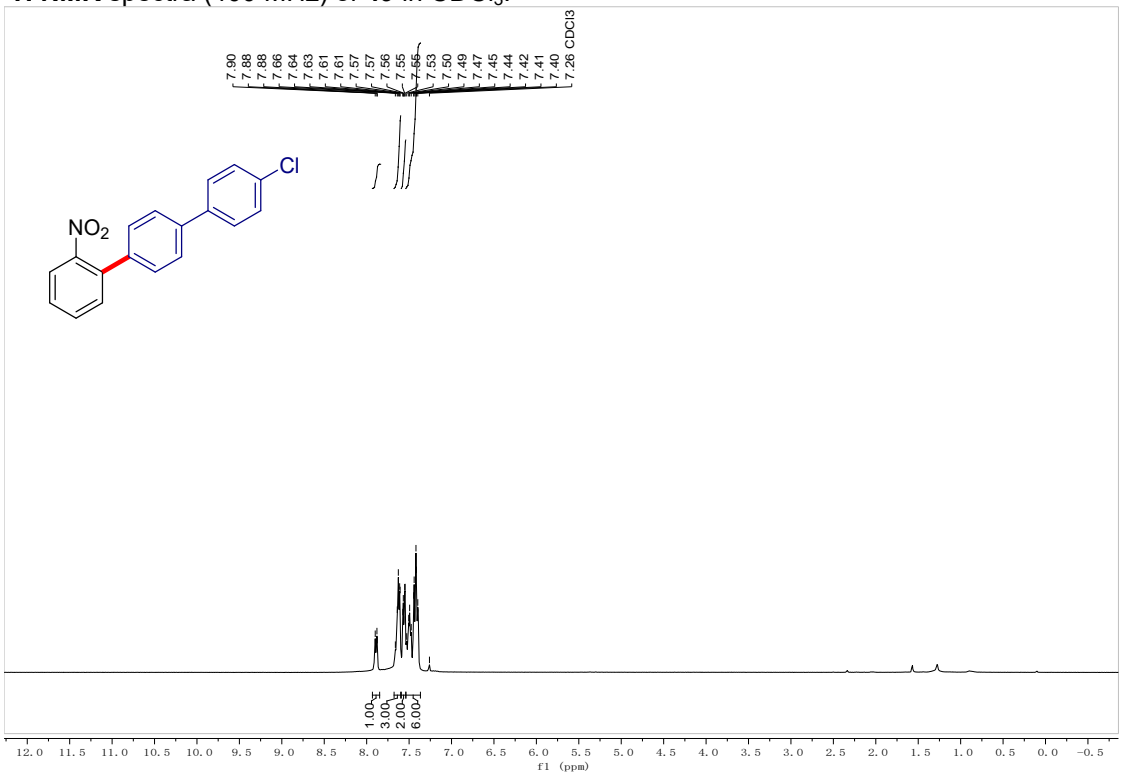
^{1}H NMR spectra (400 MHz) of **48** in $CDCl_3$.



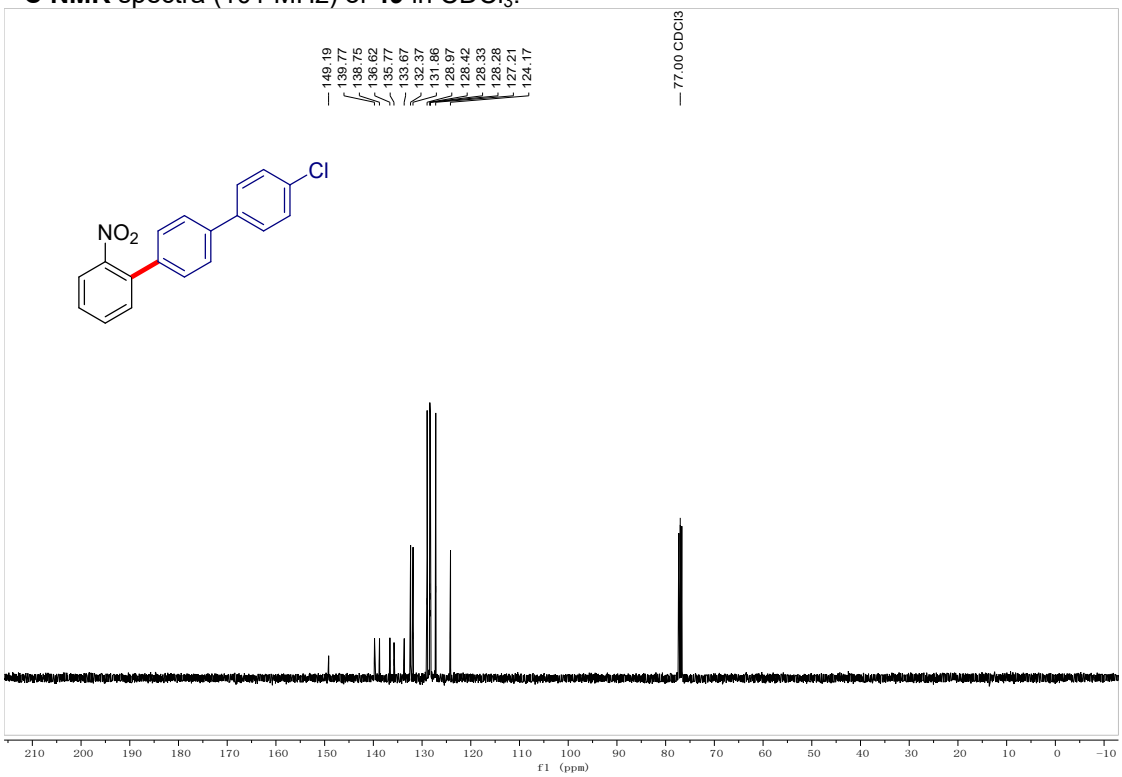
^{13}C NMR spectra (101 MHz) of **48** in $CDCl_3$.



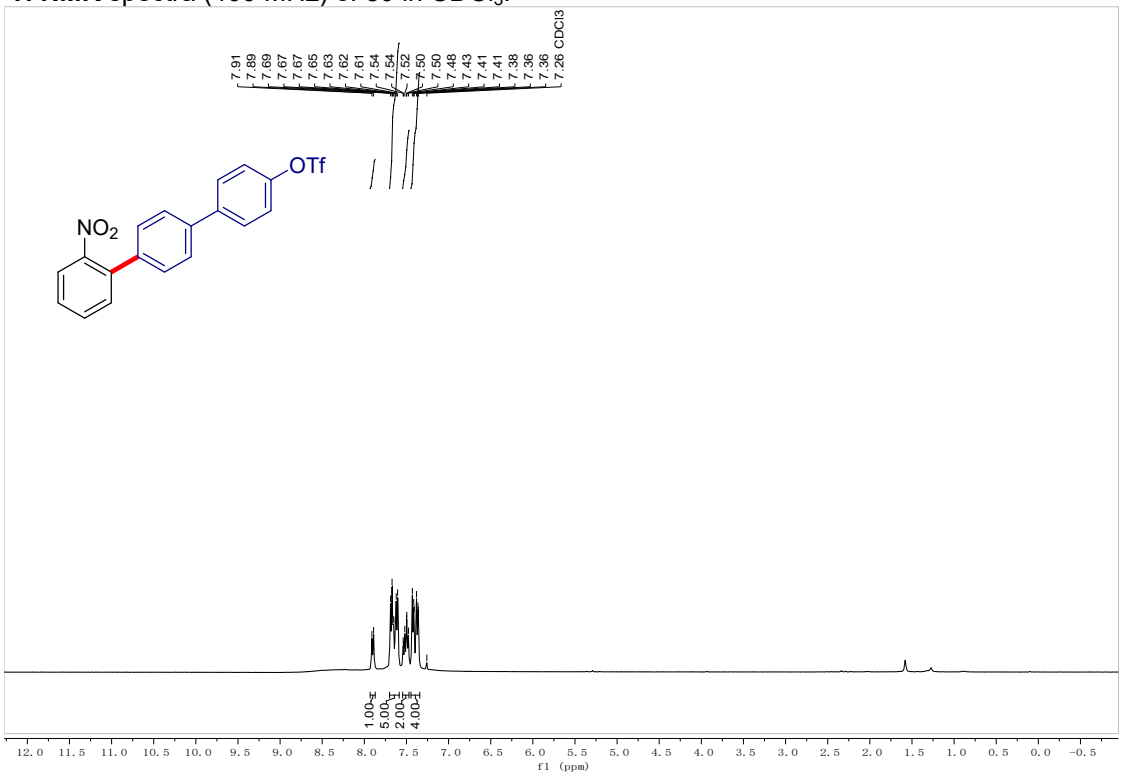
^{1}H NMR spectra (400 MHz) of **49** in $CDCl_3$.



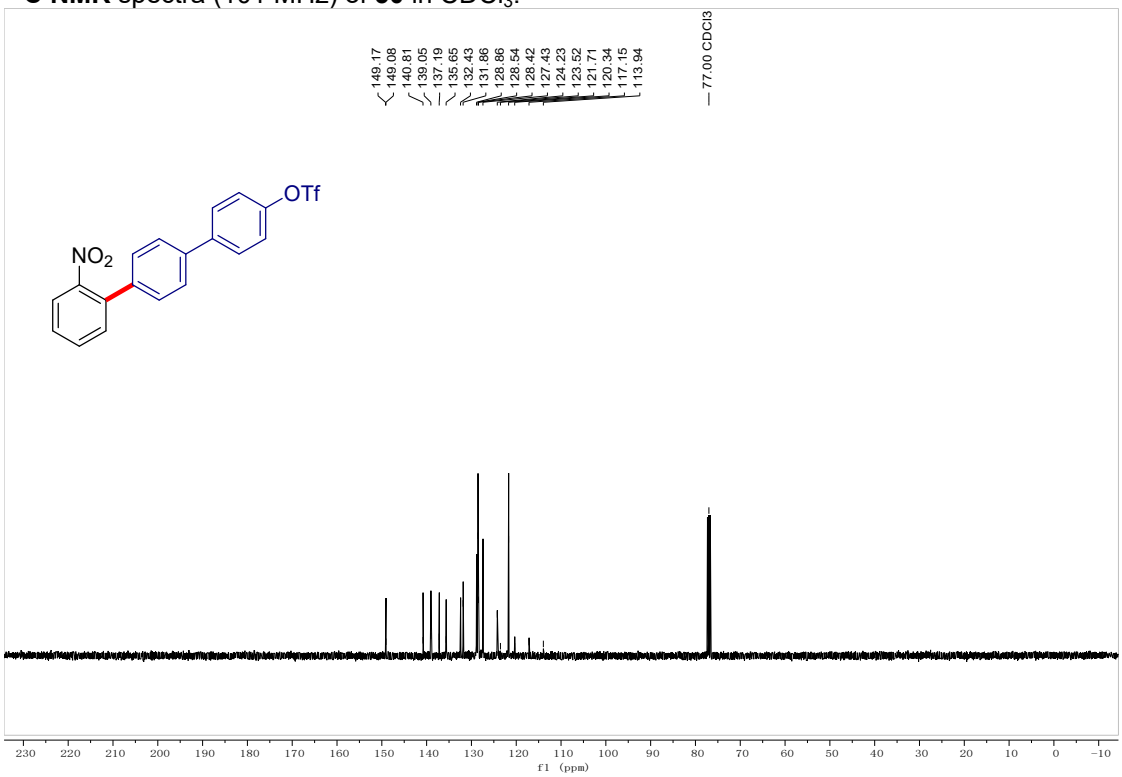
^{13}C NMR spectra (101 MHz) of **49** in $CDCl_3$.



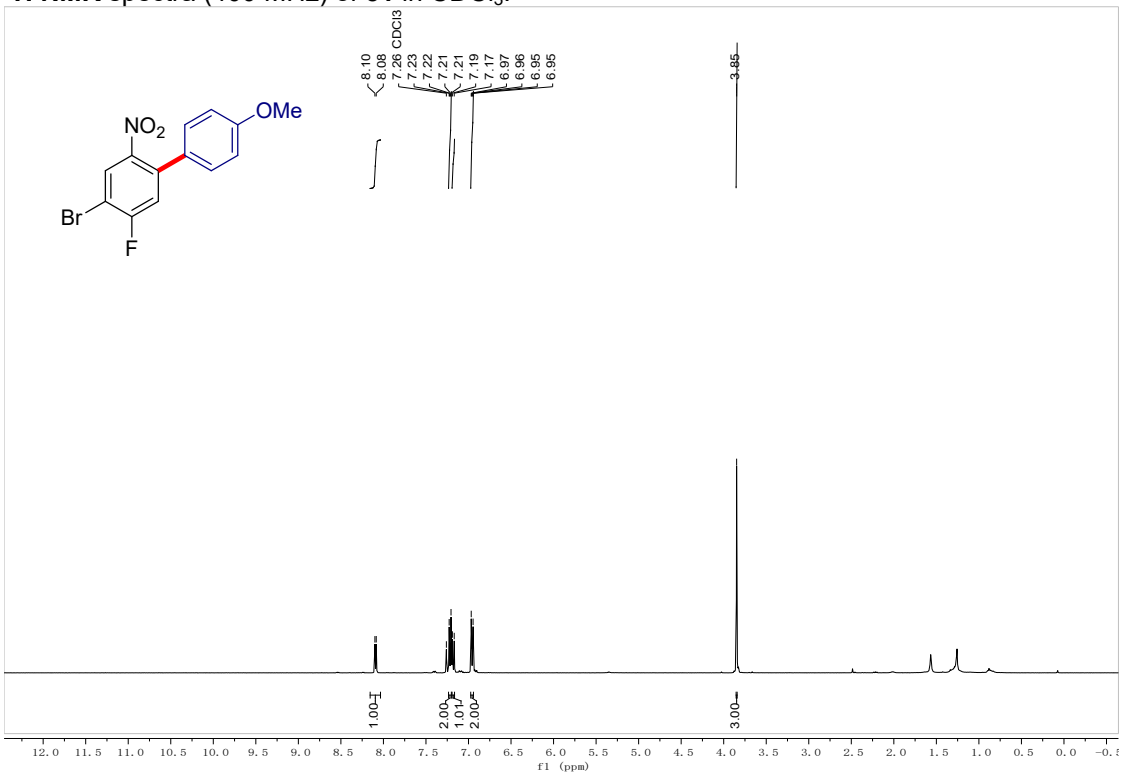
^{1}H NMR spectra (400 MHz) of **50** in $CDCl_3$.



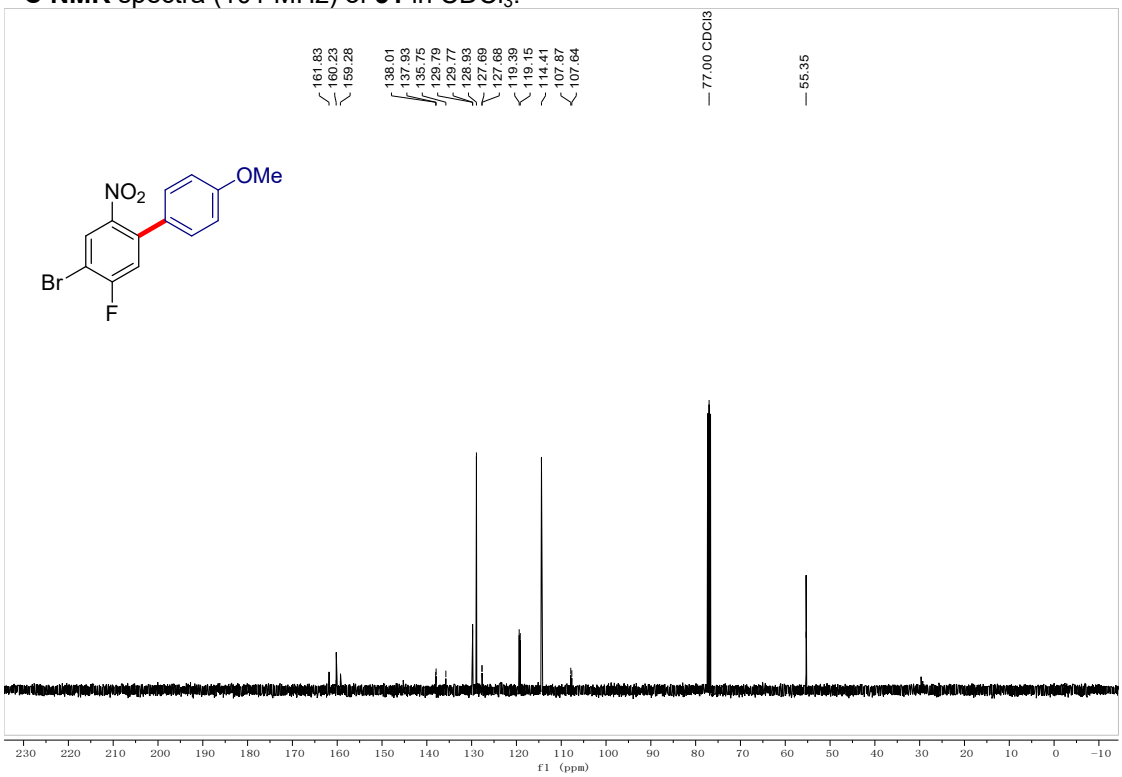
^{13}C NMR spectra (101 MHz) of **50** in $CDCl_3$.



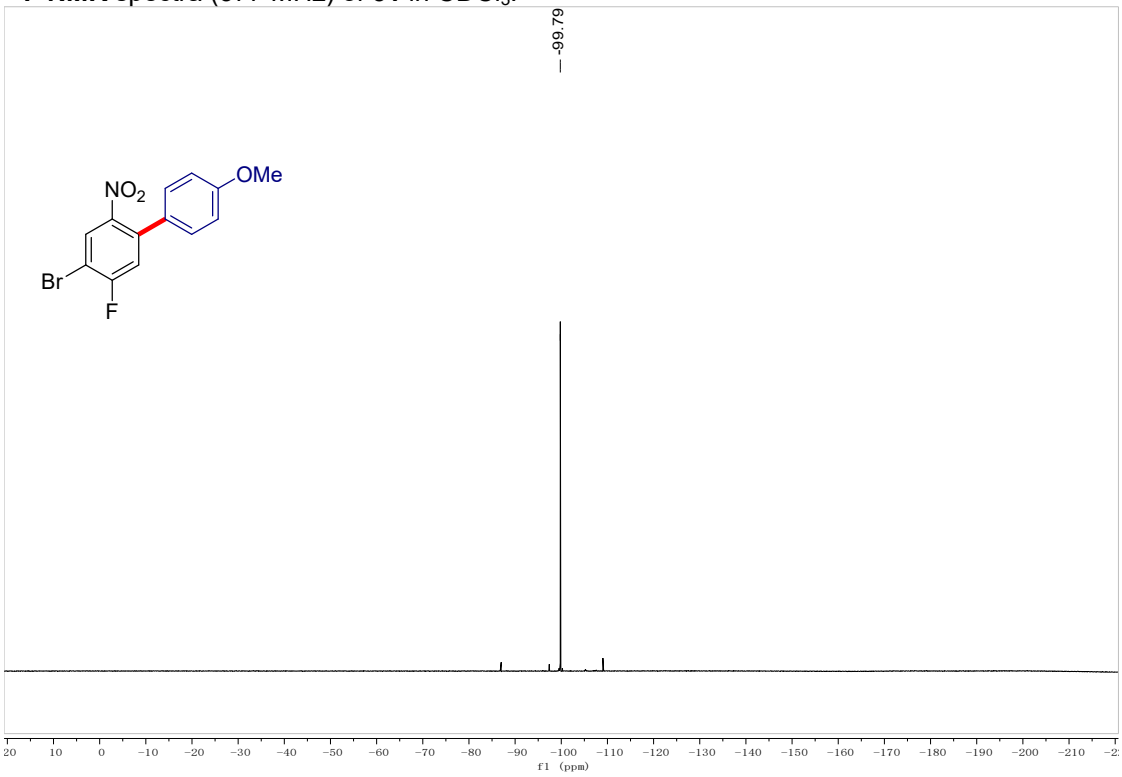
^{1}H NMR spectra (400 MHz) of **51** in $CDCl_3$.



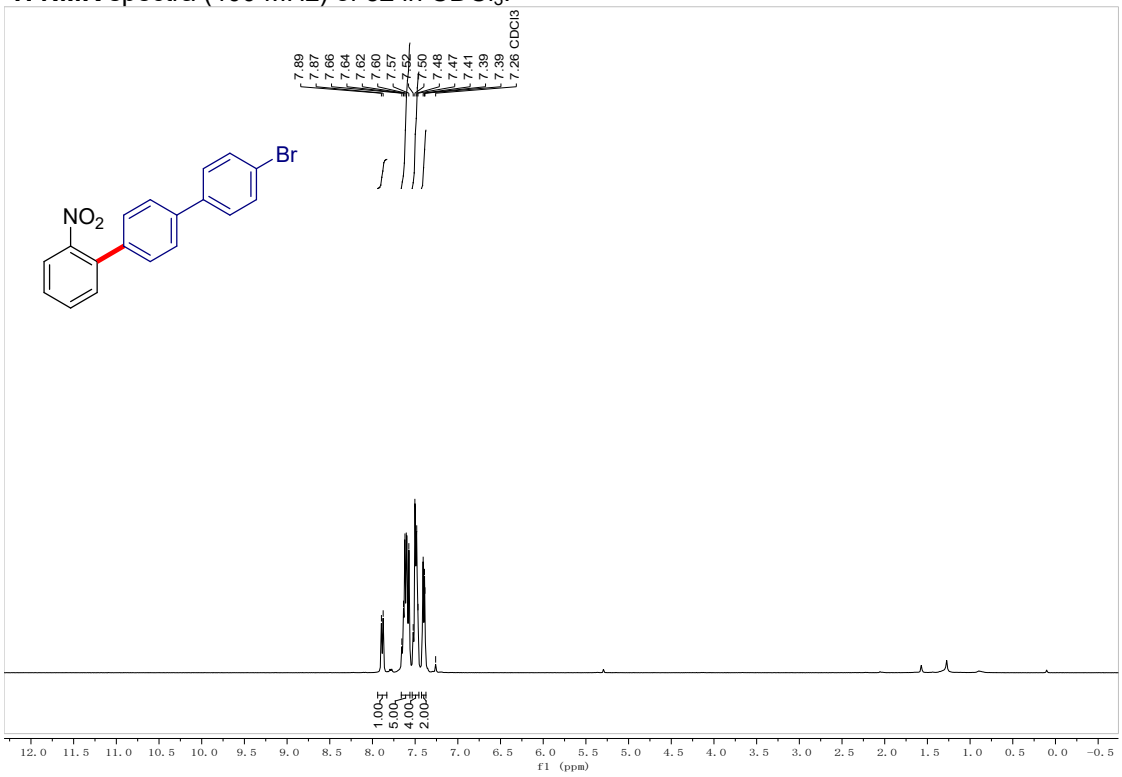
^{13}C NMR spectra (101 MHz) of **51** in $CDCl_3$.



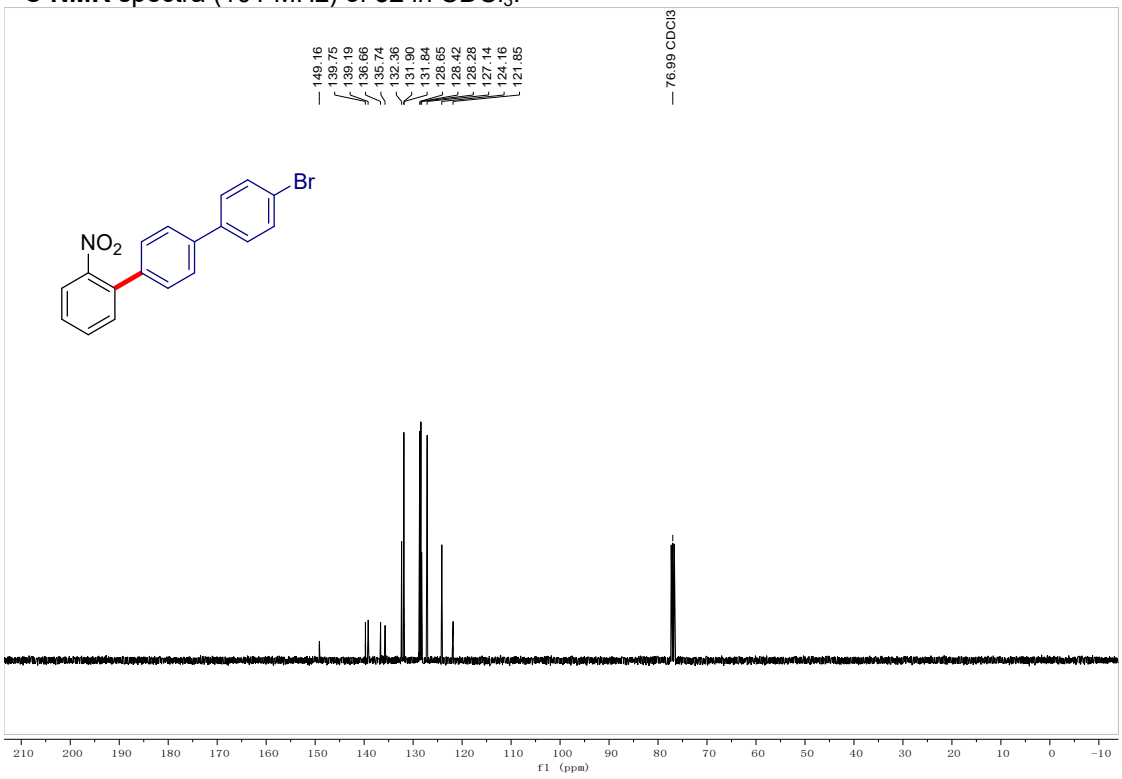
^{19}F NMR spectra (377 MHz) of **51** in $CDCl_3$.



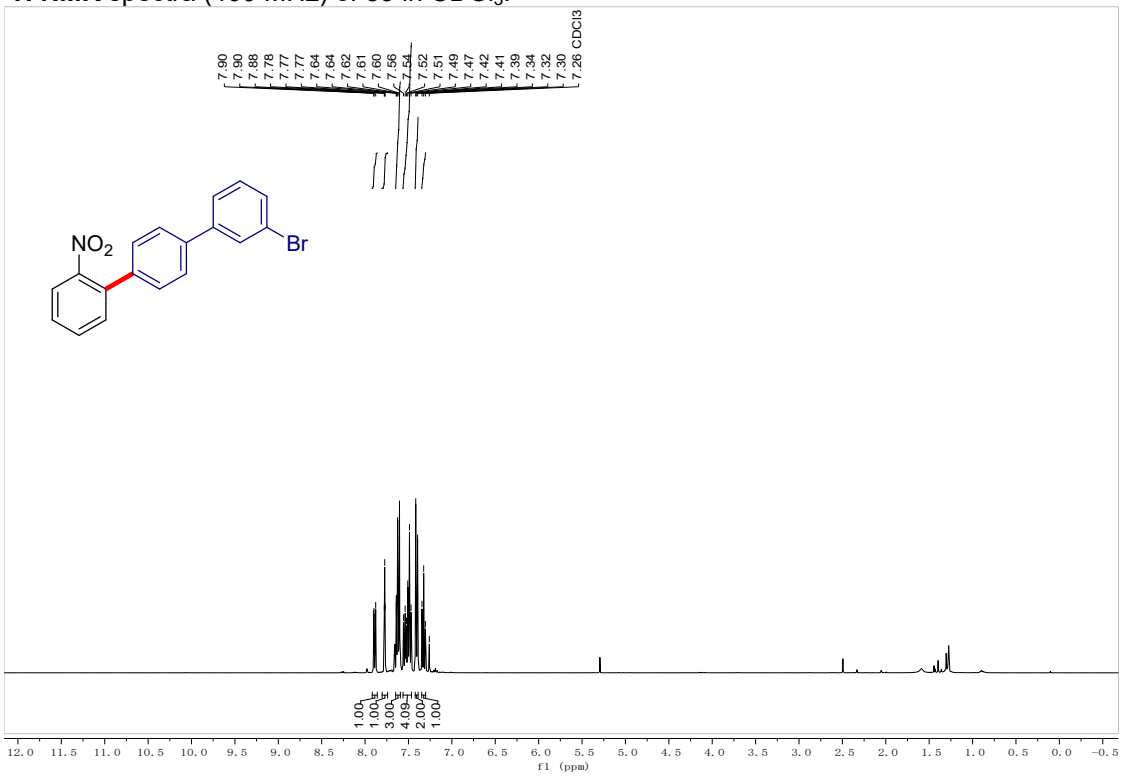
^{1}H NMR spectra (400 MHz) of **52** in $CDCl_3$.



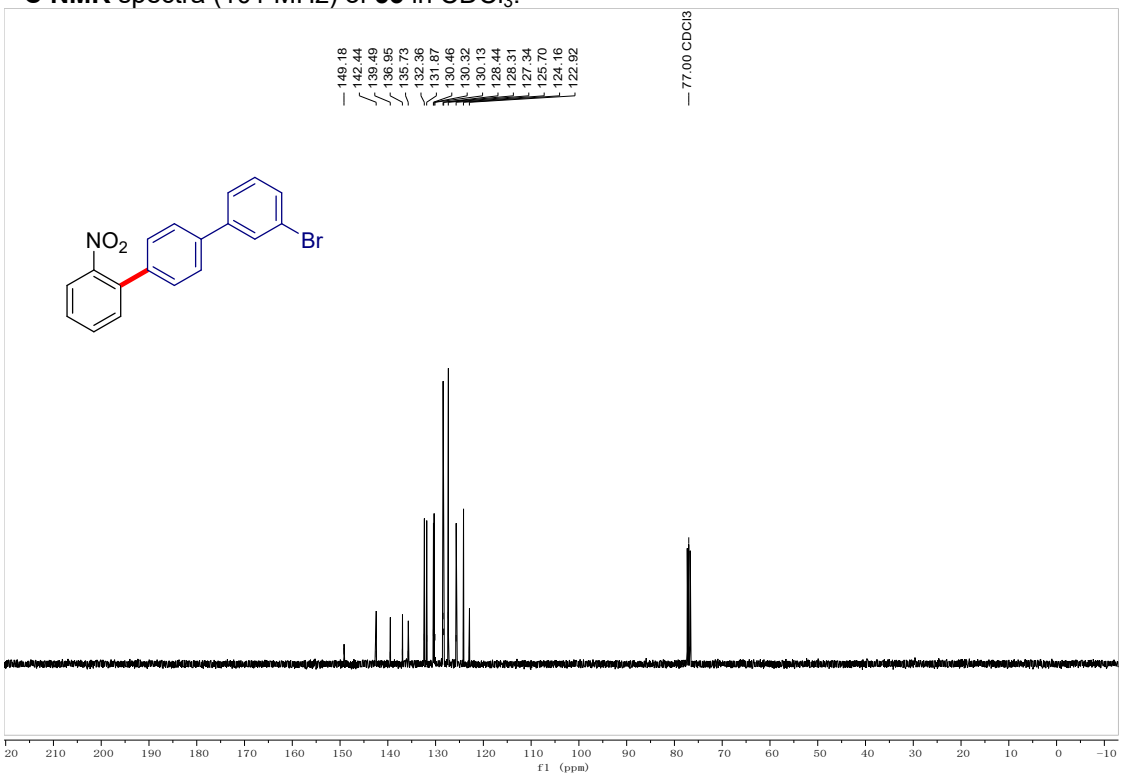
^{13}C NMR spectra (101 MHz) of **52** in $CDCl_3$.



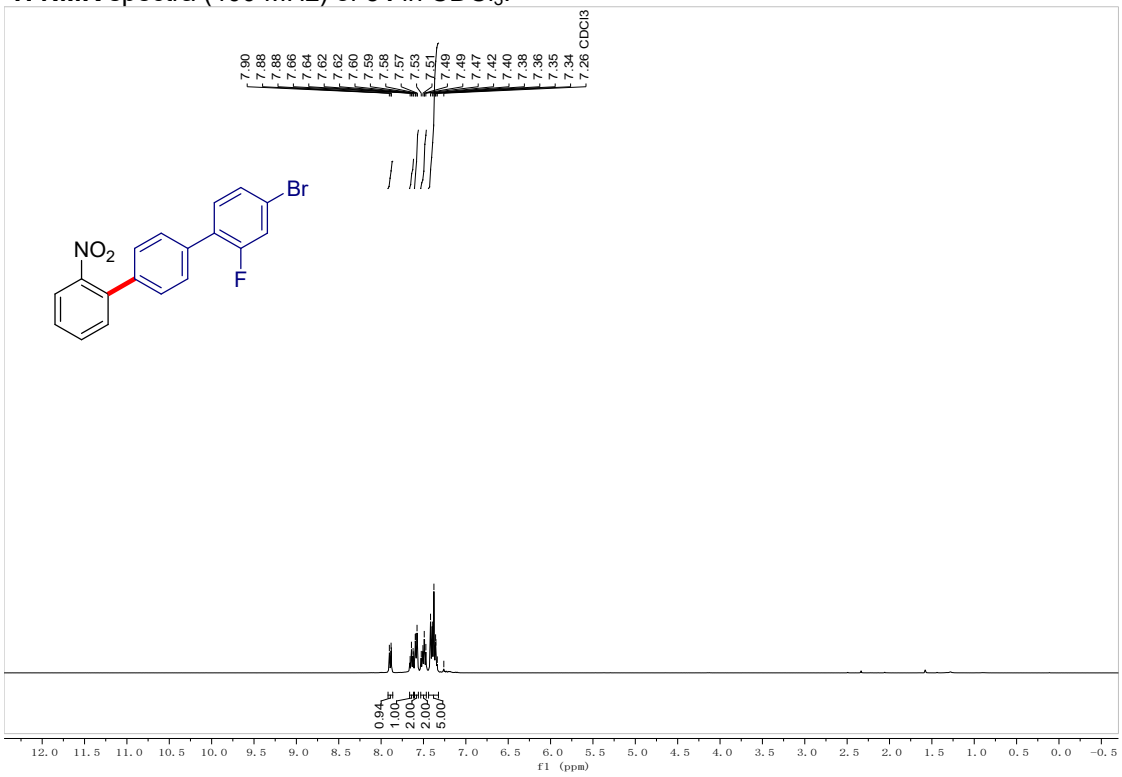
^{1}H NMR spectra (400 MHz) of **53** in $CDCl_3$.



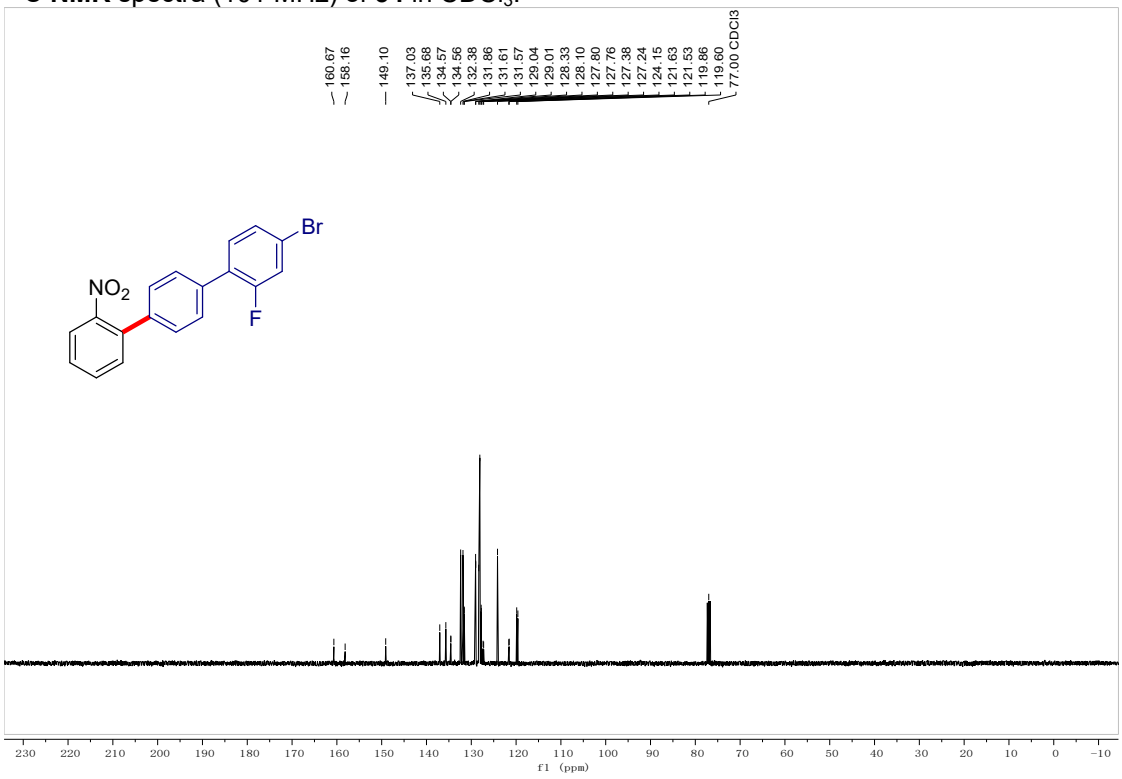
^{13}C NMR spectra (101 MHz) of **53** in $CDCl_3$.



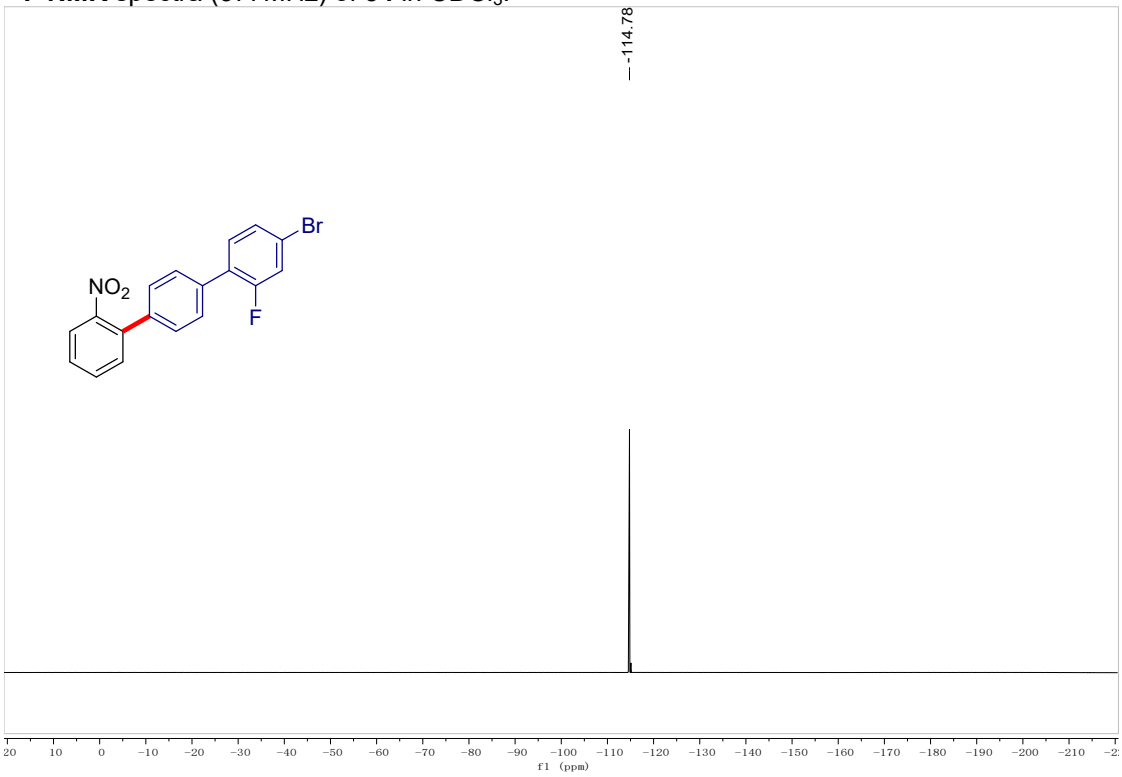
^{1}H NMR spectra (400 MHz) of **54** in $CDCl_3$.



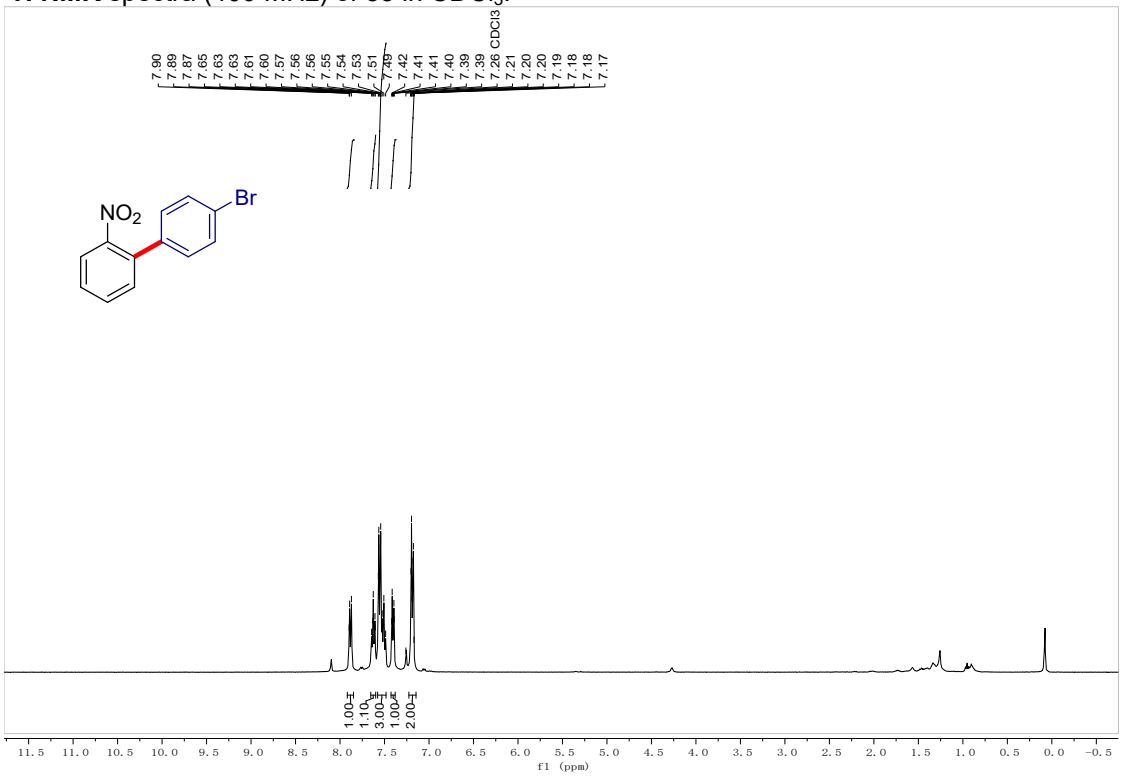
^{13}C NMR spectra (101 MHz) of **54** in $CDCl_3$.



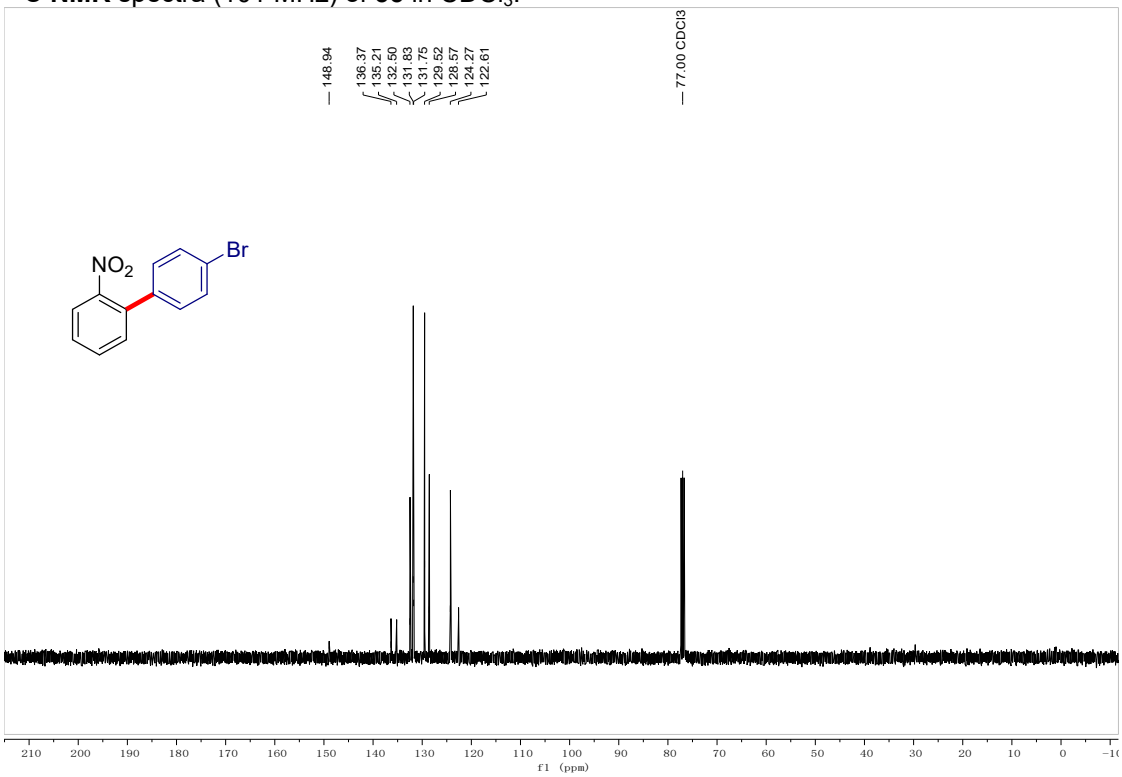
^{19}F NMR spectra (377MHz) of **54** in $CDCl_3$.



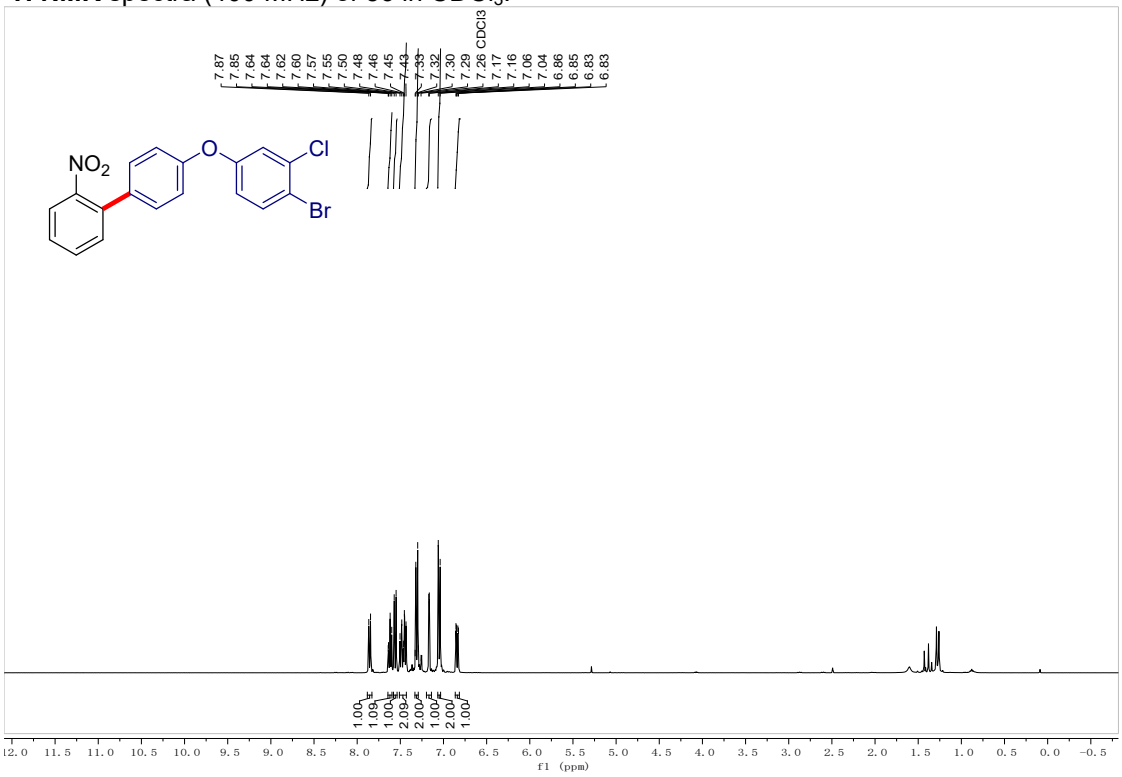
^{1}H NMR spectra (400 MHz) of **55** in $CDCl_3$.



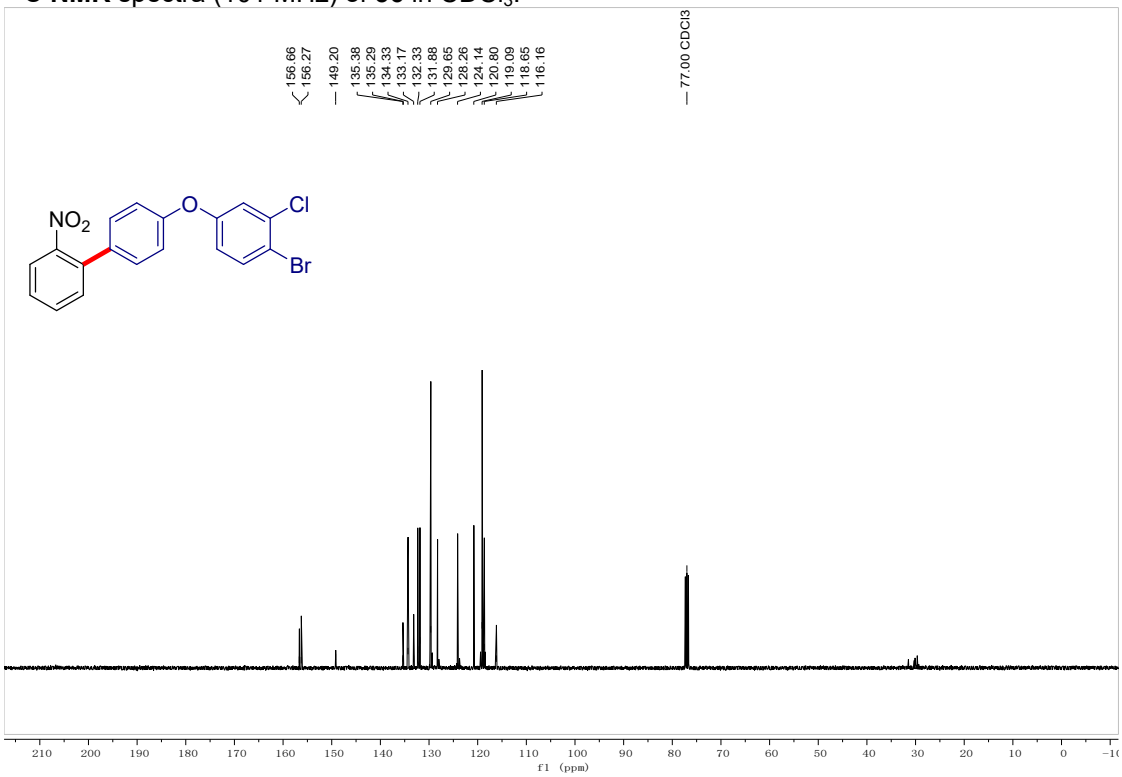
^{13}C NMR spectra (101 MHz) of **55** in $CDCl_3$.



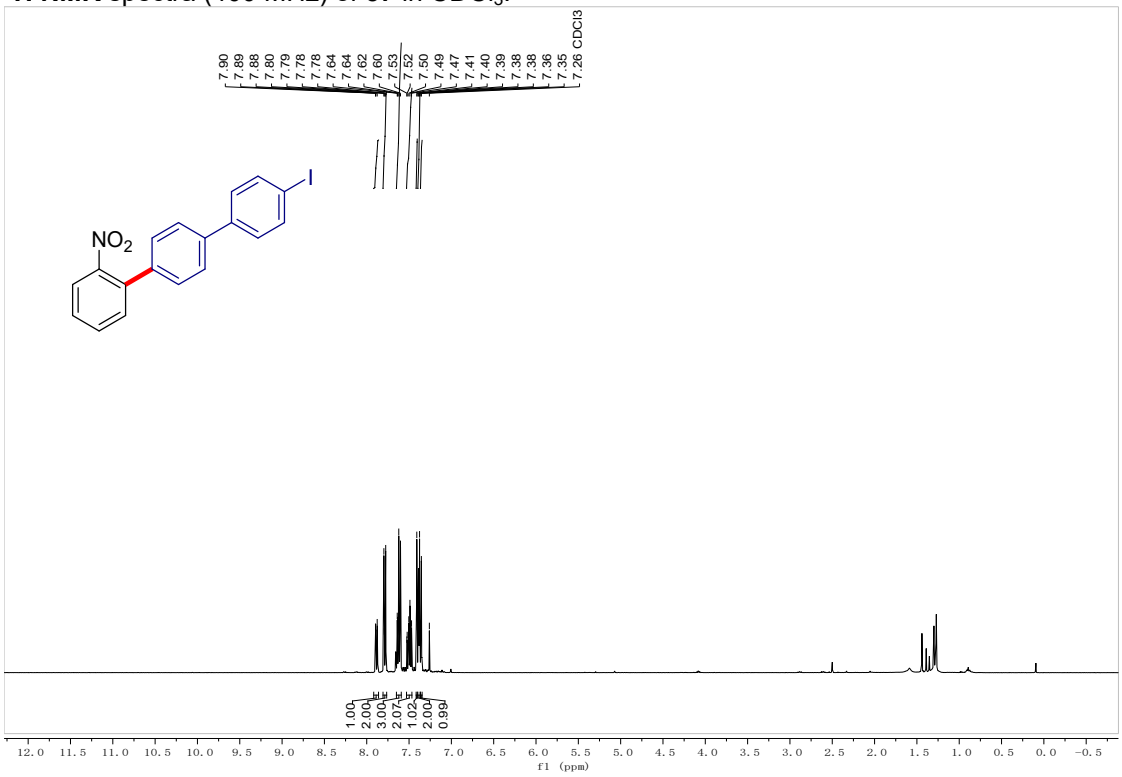
^{1}H NMR spectra (400 MHz) of **56** in $CDCl_3$.



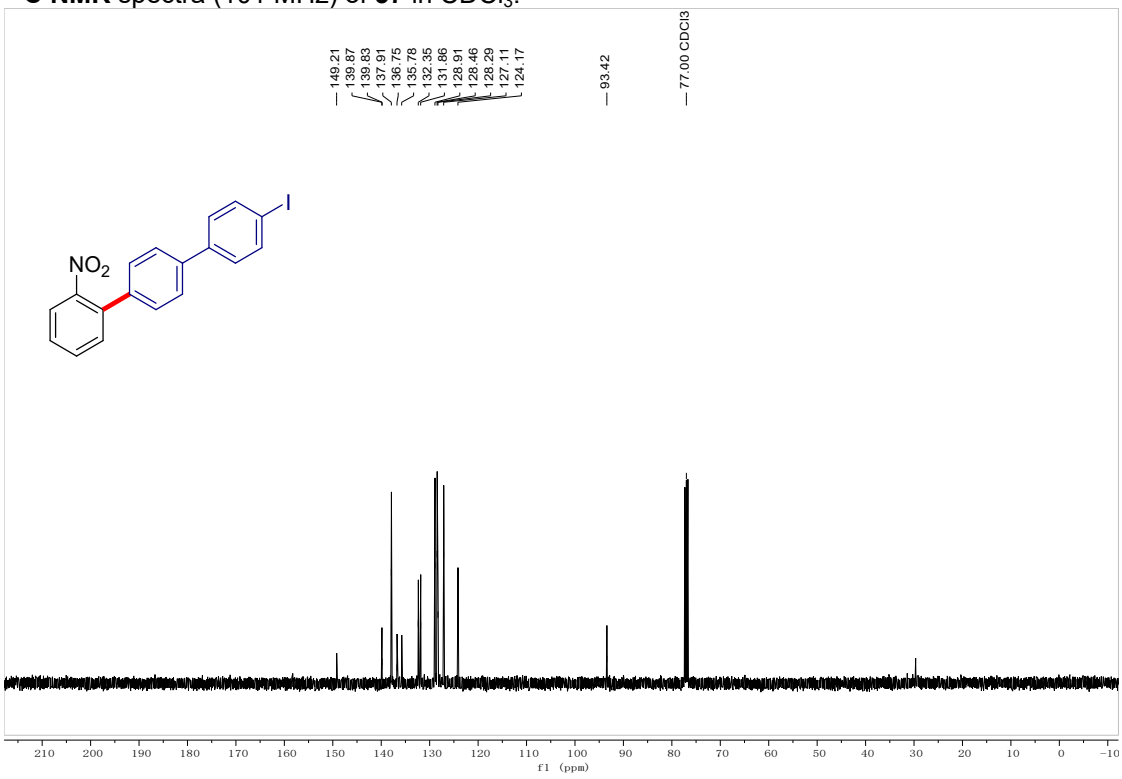
^{13}C NMR spectra (101 MHz) of **56** in $CDCl_3$.



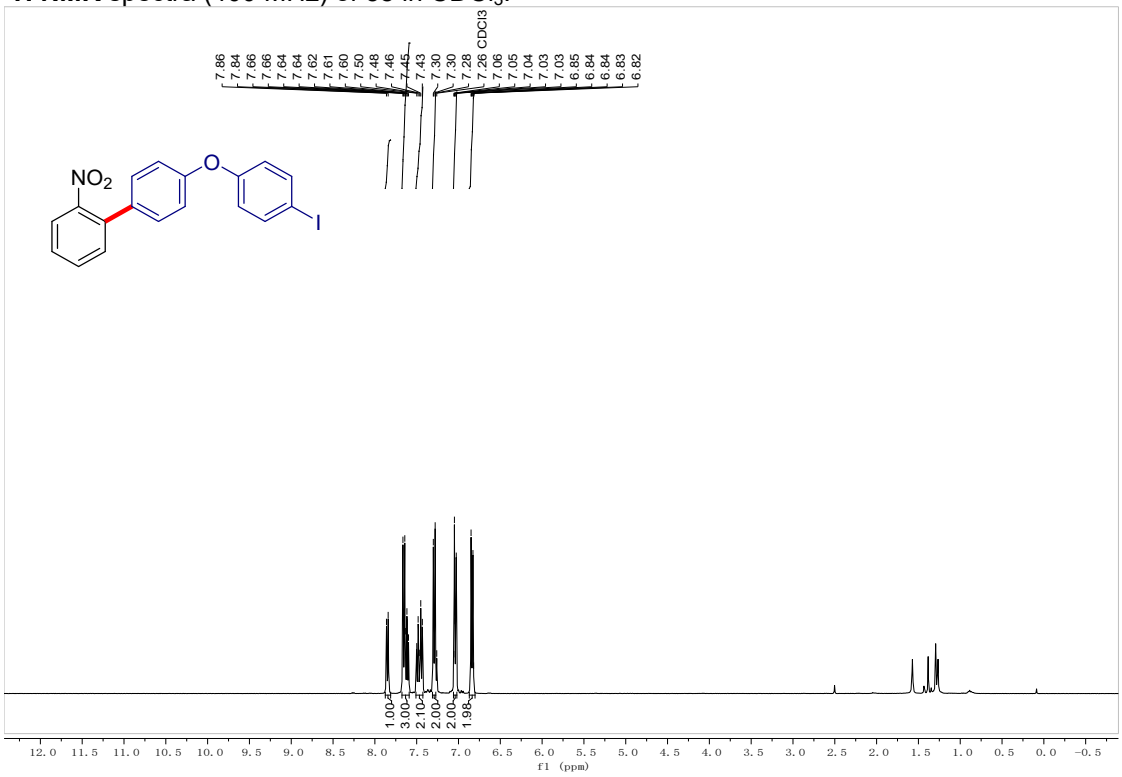
^{1}H NMR spectra (400 MHz) of **57** in $CDCl_3$.



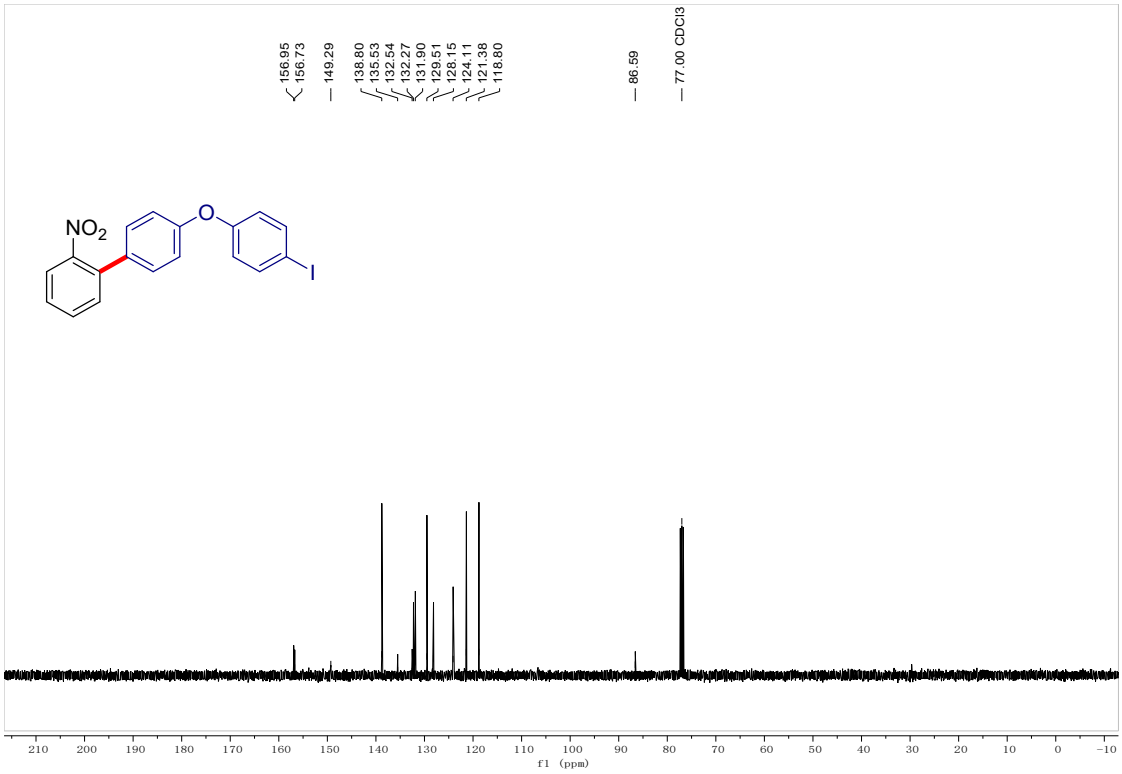
^{13}C NMR spectra (101 MHz) of **57** in $CDCl_3$.



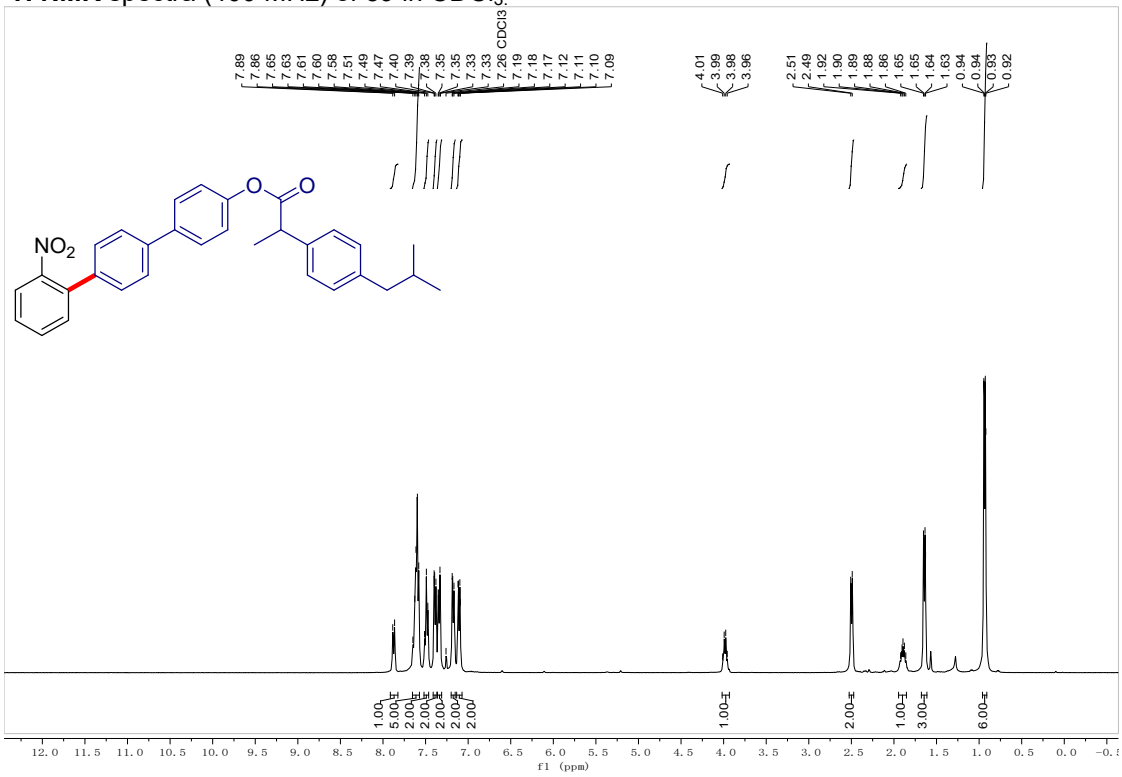
^{1}H NMR spectra (400 MHz) of **58** in $CDCl_3$.



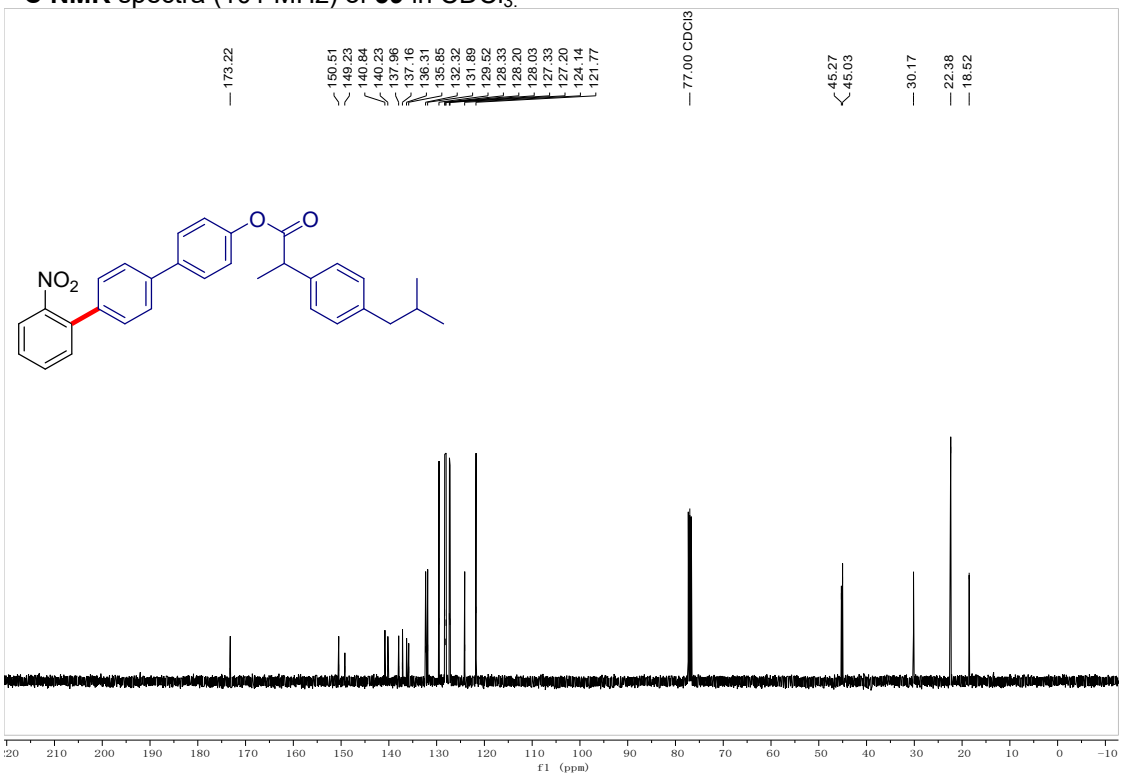
^{13}C NMR spectra (101 MHz) of **58** in $CDCl_3$.



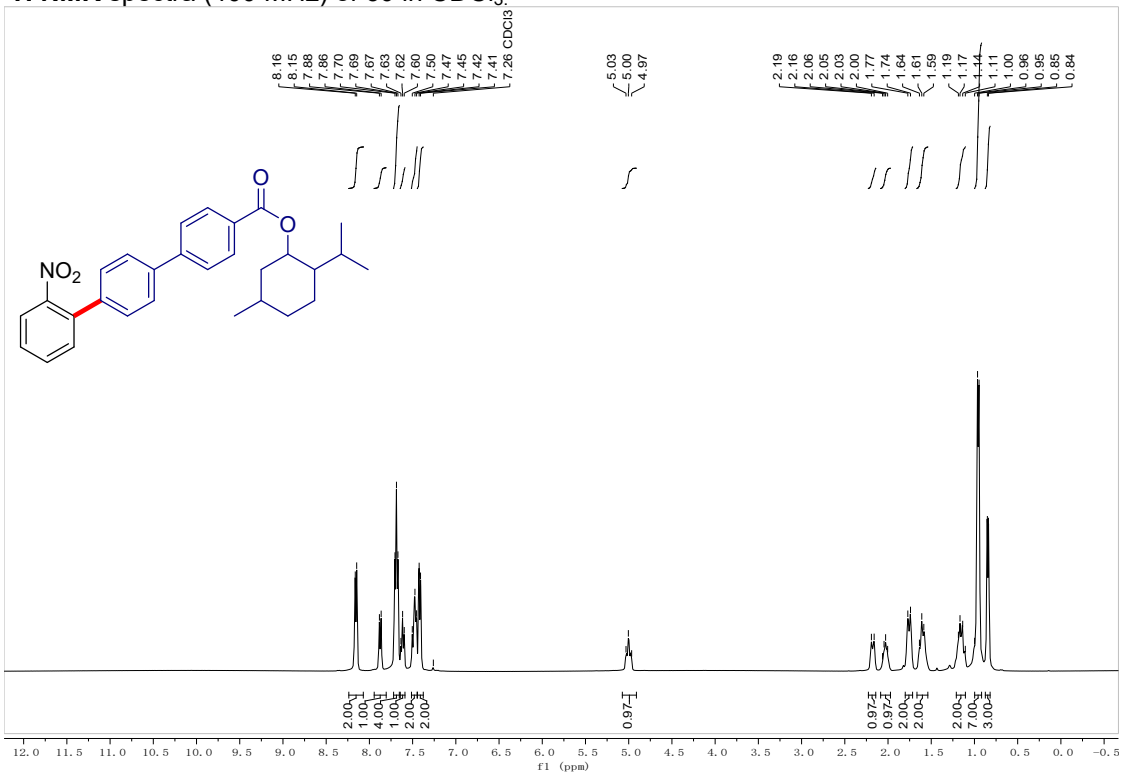
^{1}H NMR spectra (400 MHz) of **59** in $CDCl_3$.



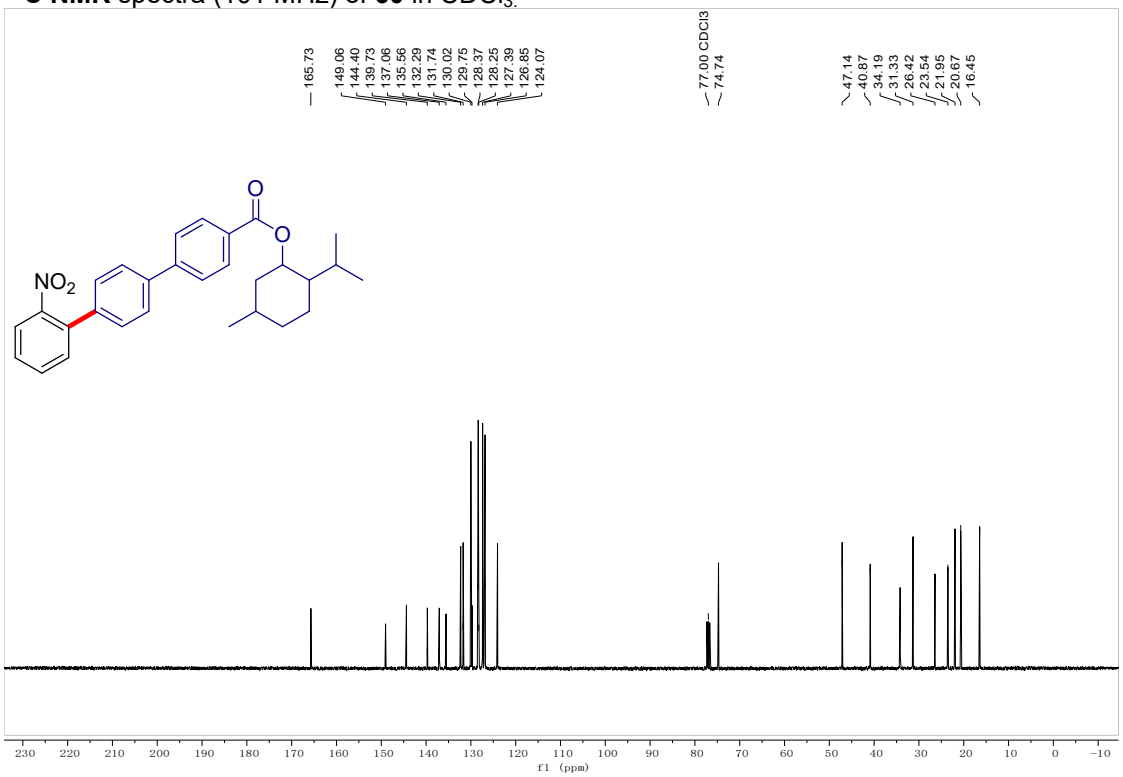
^{13}C NMR spectra (101 MHz) of **59** in $CDCl_3$.



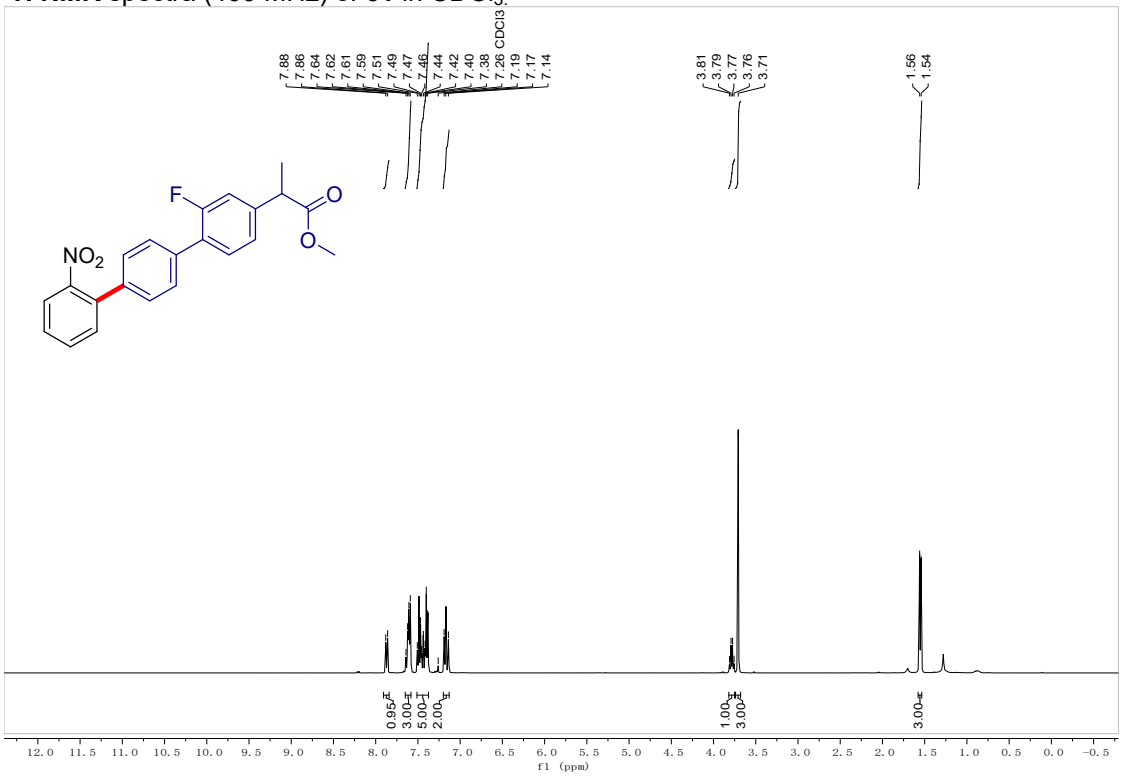
^{1}H NMR spectra (400 MHz) of **60** in $CDCl_3$.



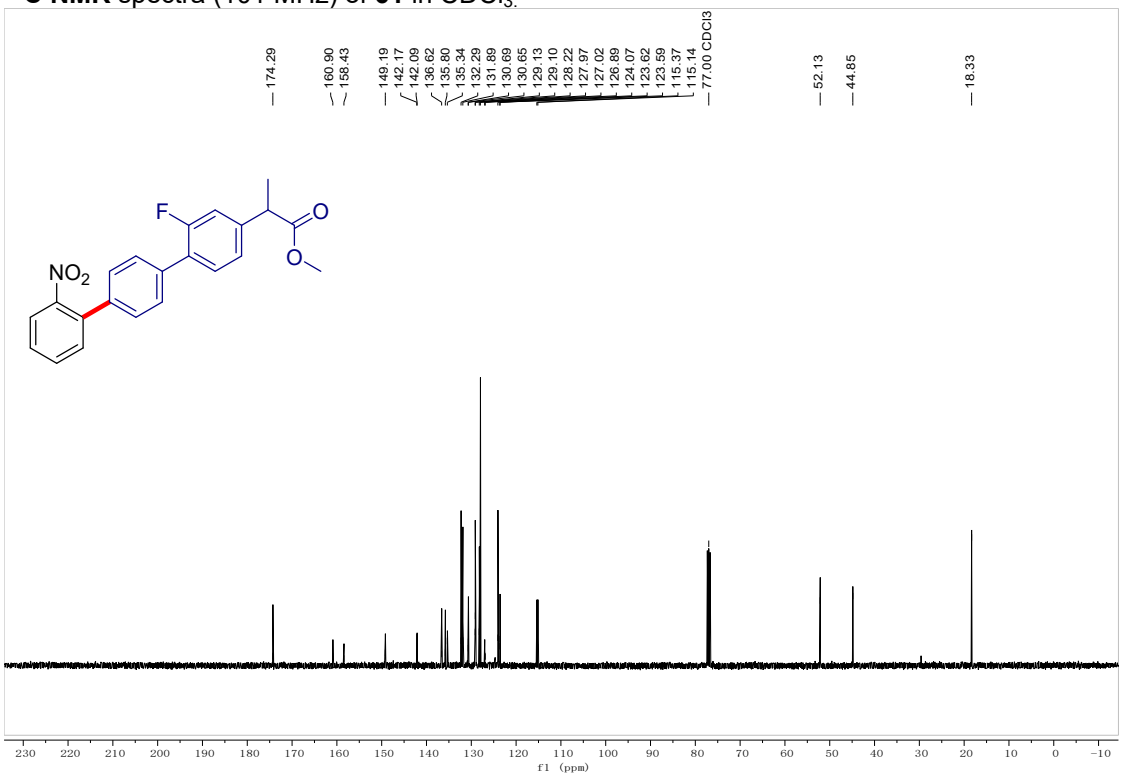
^{13}C NMR spectra (101 MHz) of **60** in $CDCl_3$.



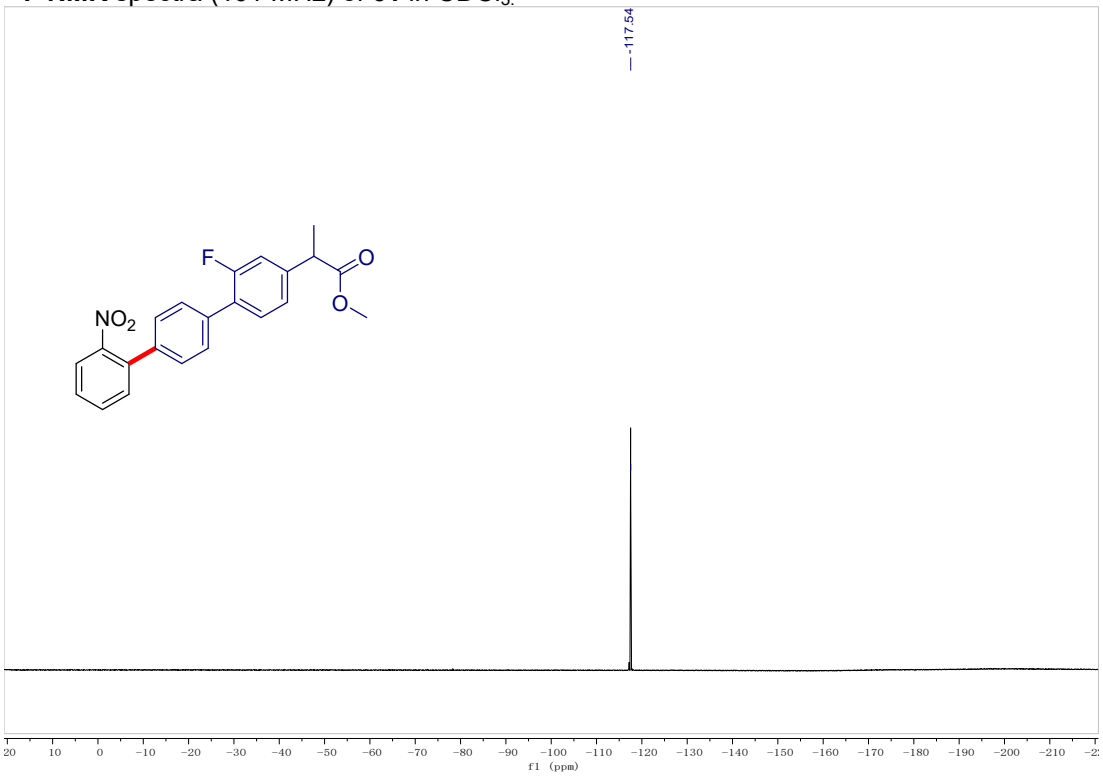
^{1}H NMR spectra (400 MHz) of **61** in $CDCl_3$.



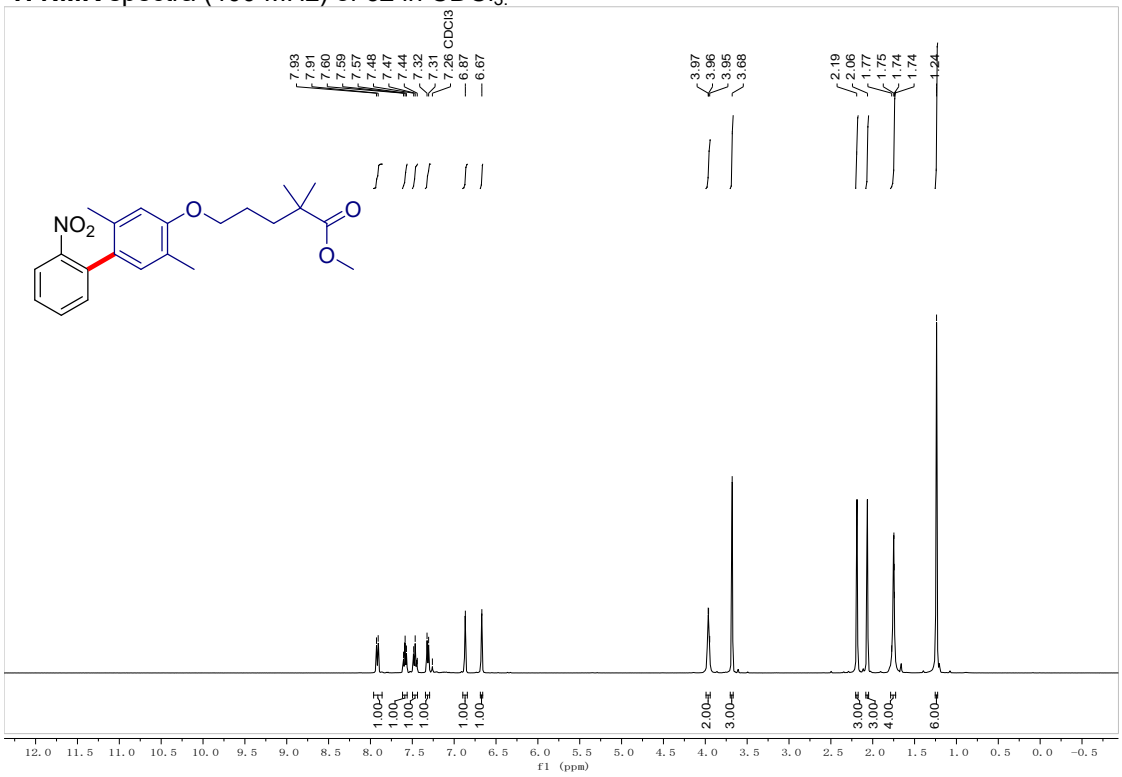
^{13}C NMR spectra (101 MHz) of **61** in $CDCl_3$.



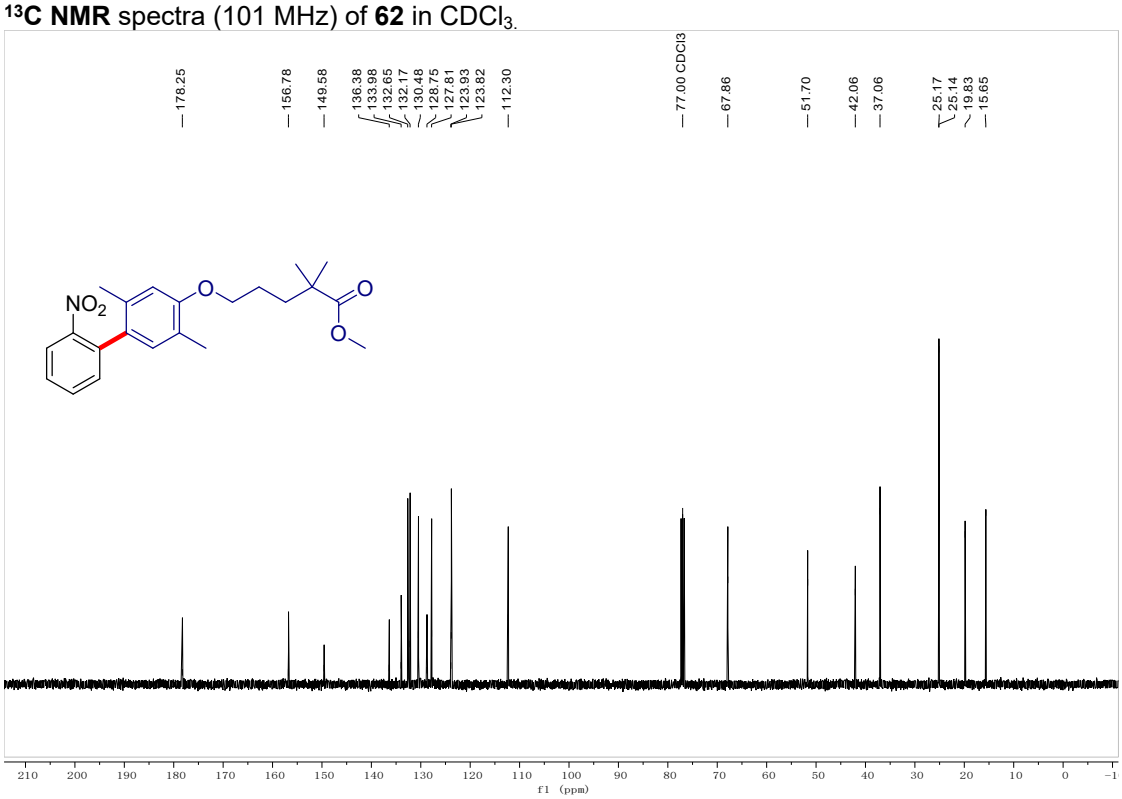
^{19}F NMR spectra (101 MHz) of **61** in $CDCl_3$.



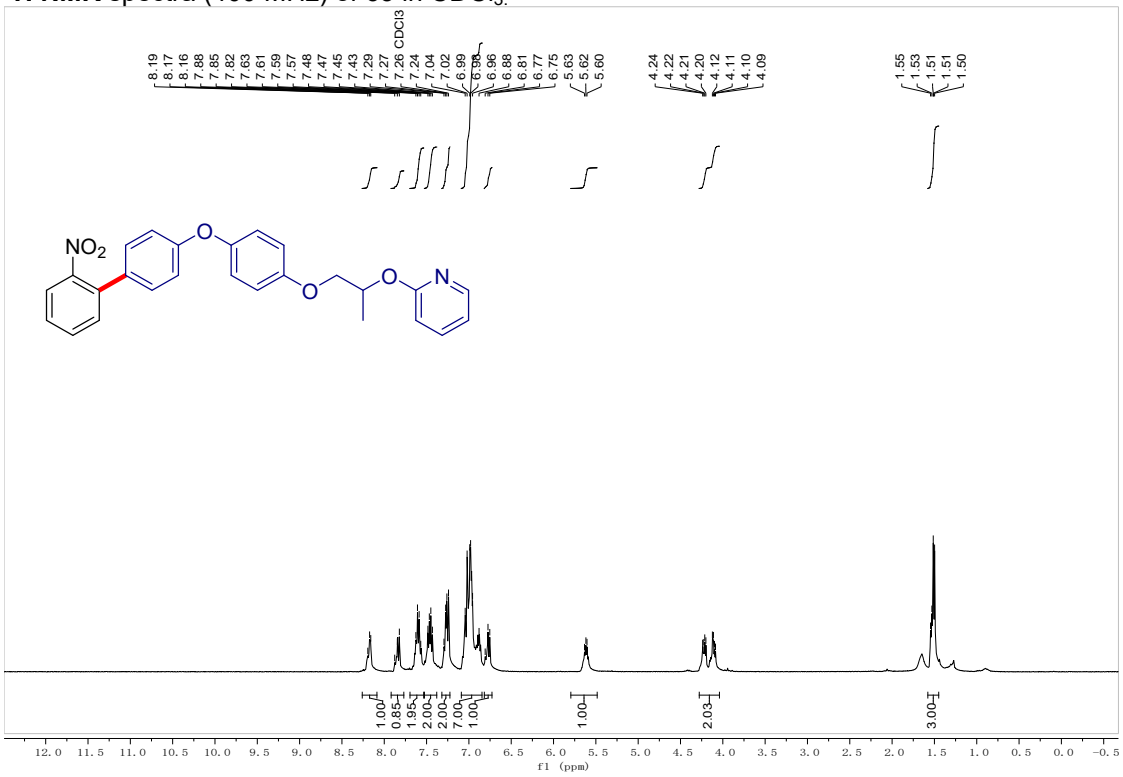
^{1}H NMR spectra (400 MHz) of **62** in $CDCl_3$.



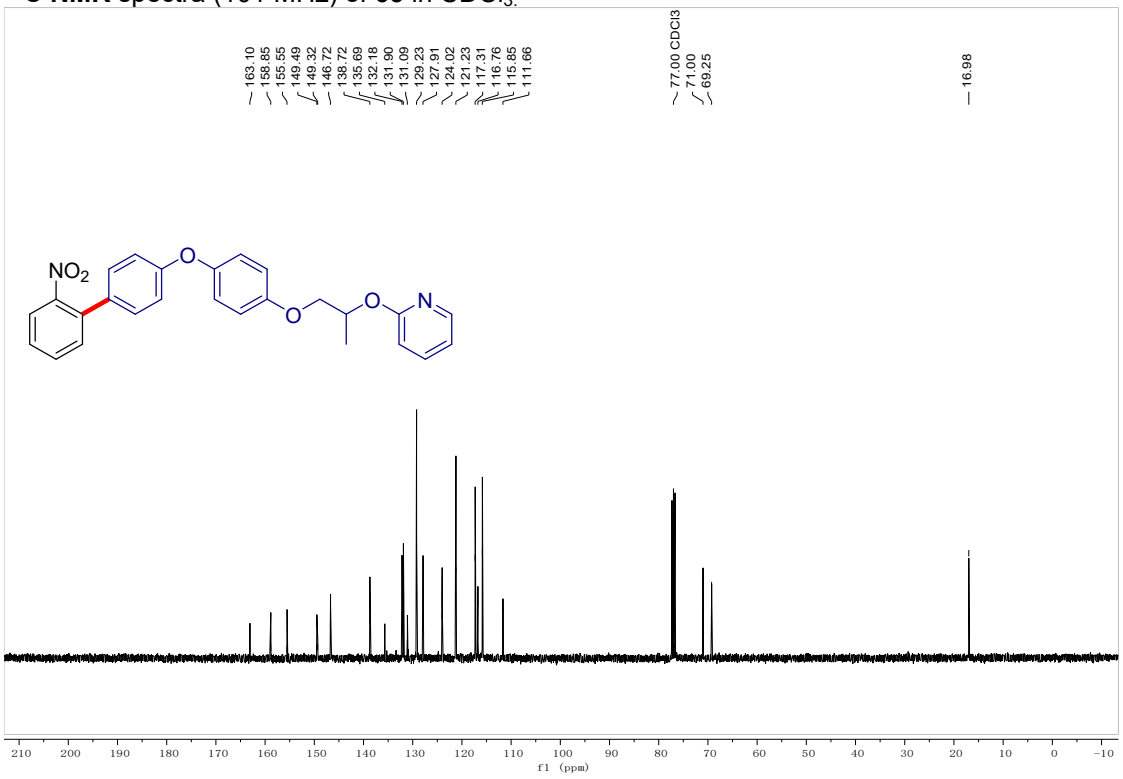
^{13}C NMR spectra (101 MHz) of **62** in $CDCl_3$.



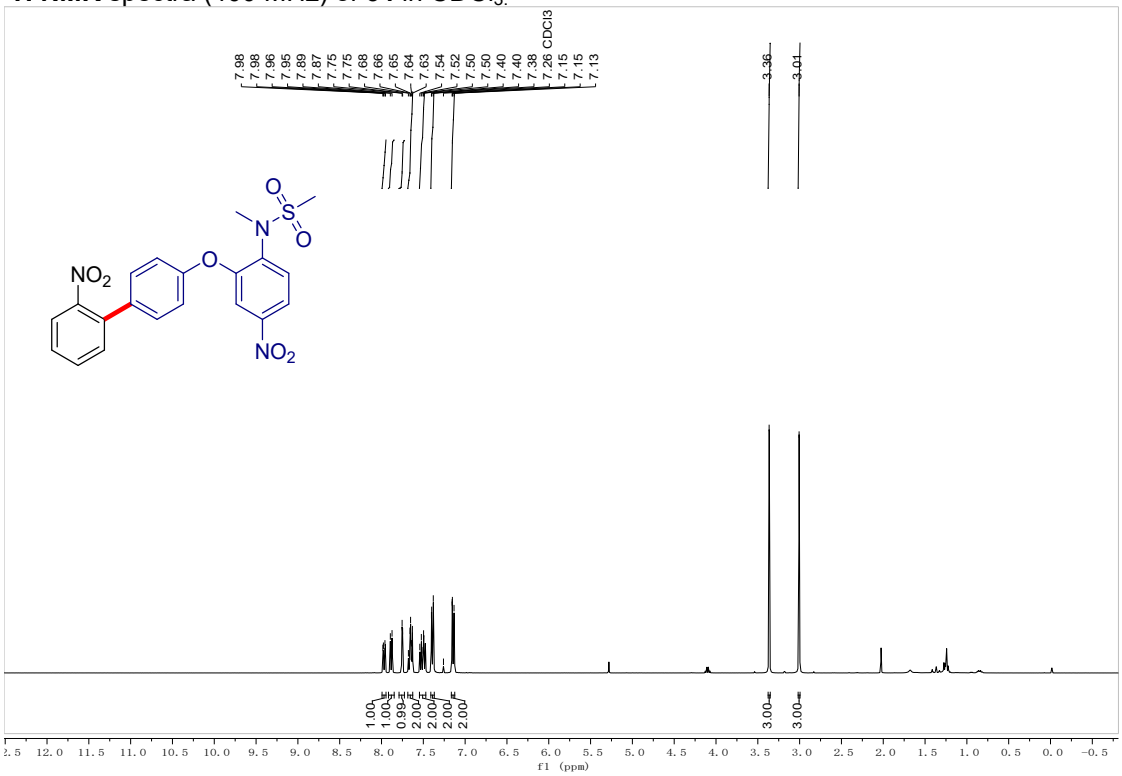
^{1}H NMR spectra (400 MHz) of **63** in $CDCl_3$.



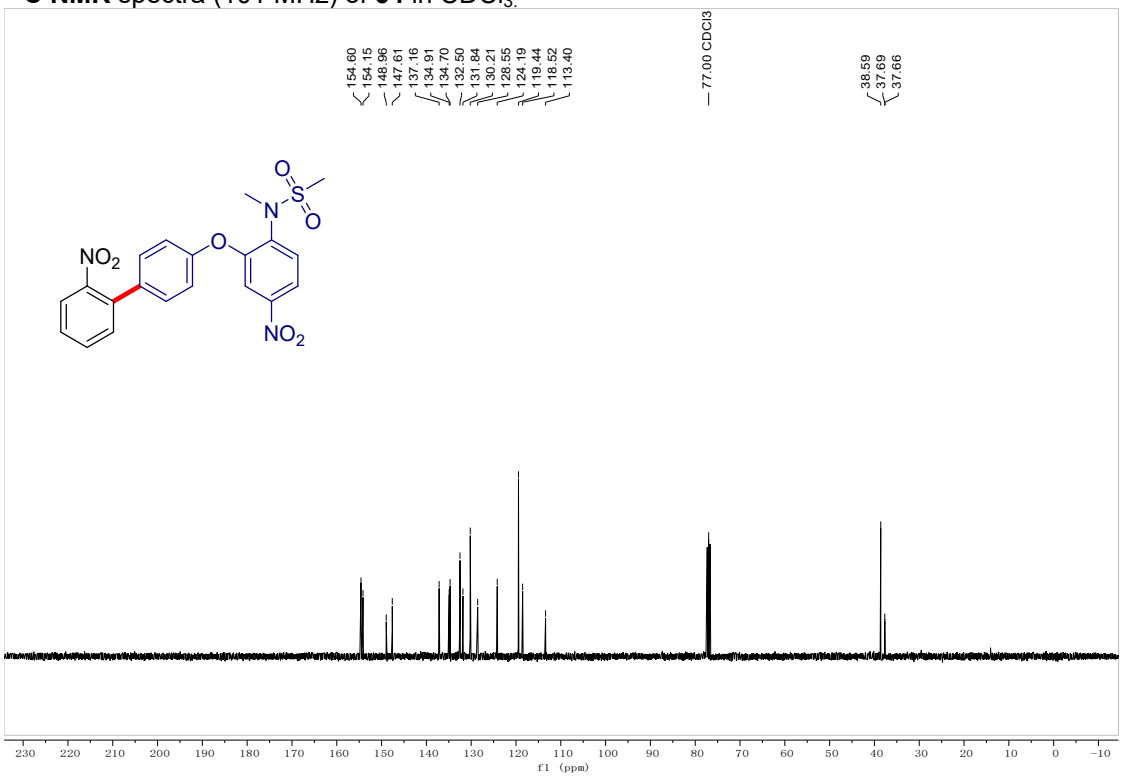
^{13}C NMR spectra (101 MHz) of **63** in $CDCl_3$.



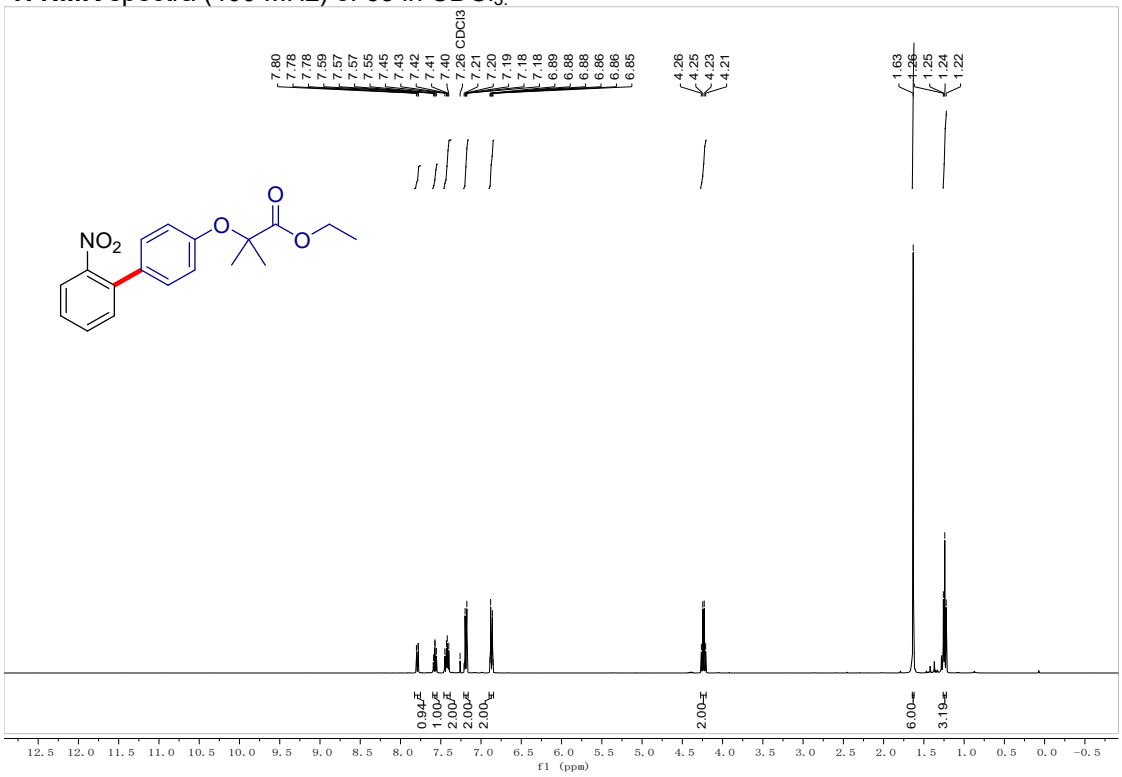
^{1}H NMR spectra (400 MHz) of **64** in $CDCl_3$.



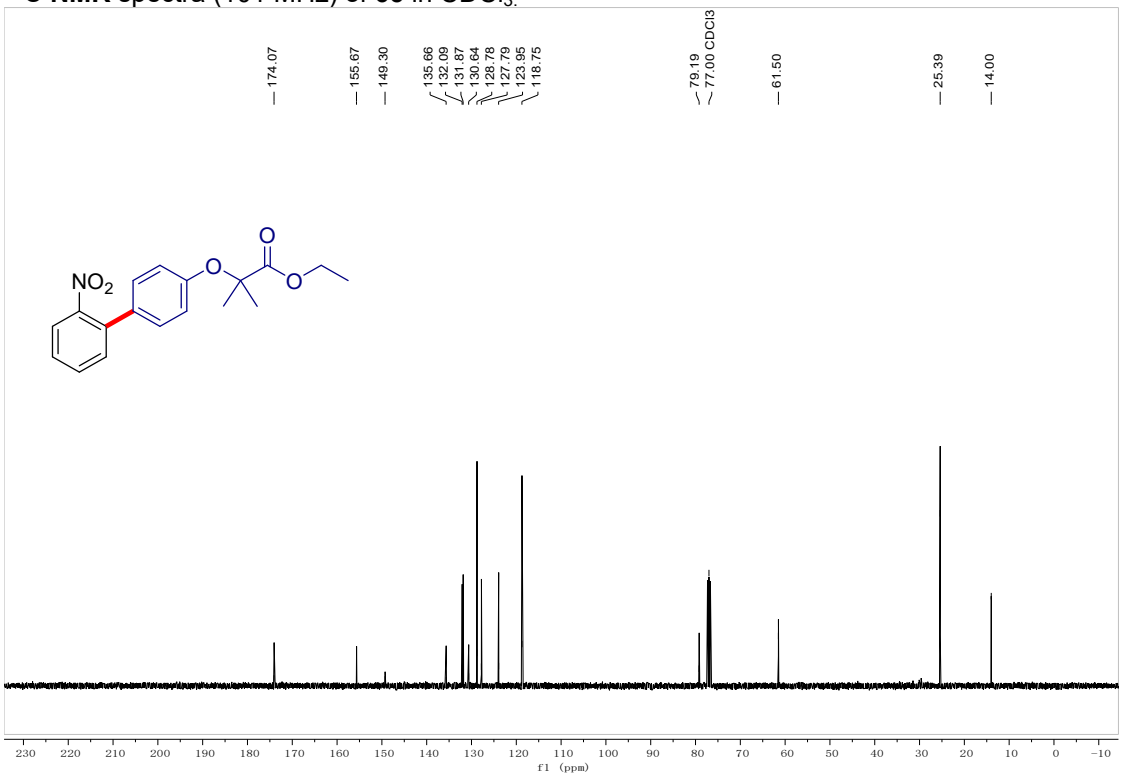
^{13}C NMR spectra (101 MHz) of **64** in $CDCl_3$.



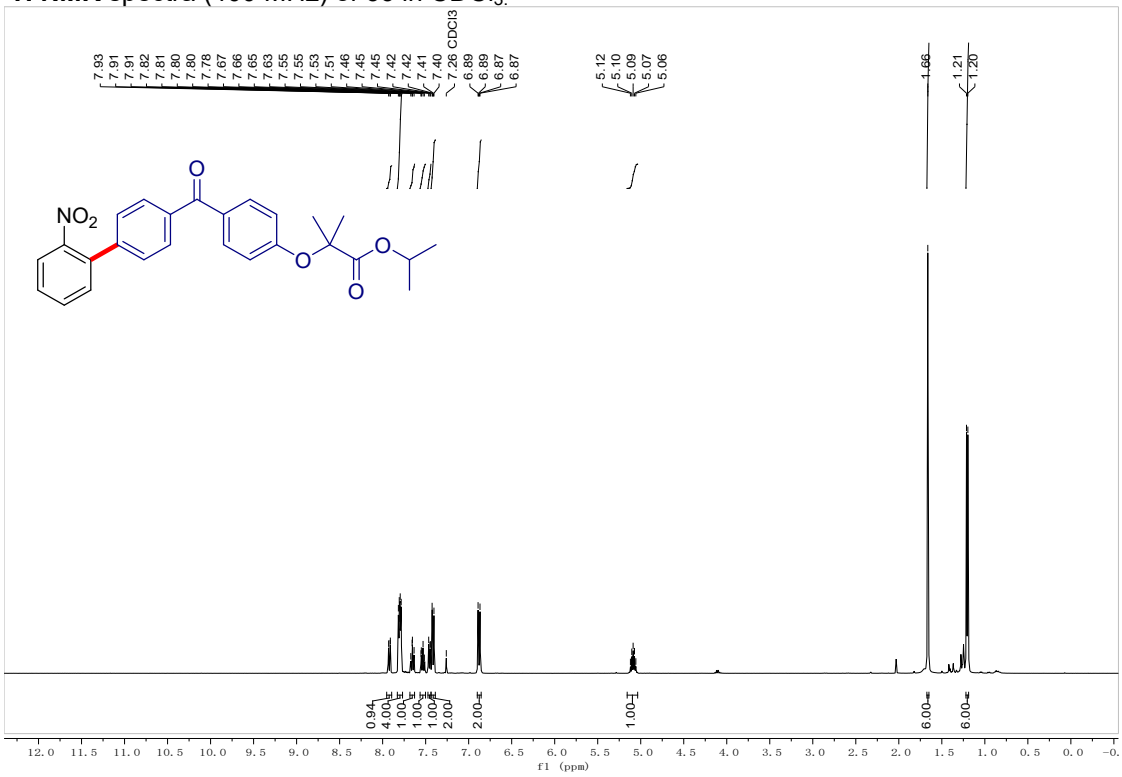
^{1}H NMR spectra (400 MHz) of **65** in $CDCl_3$.



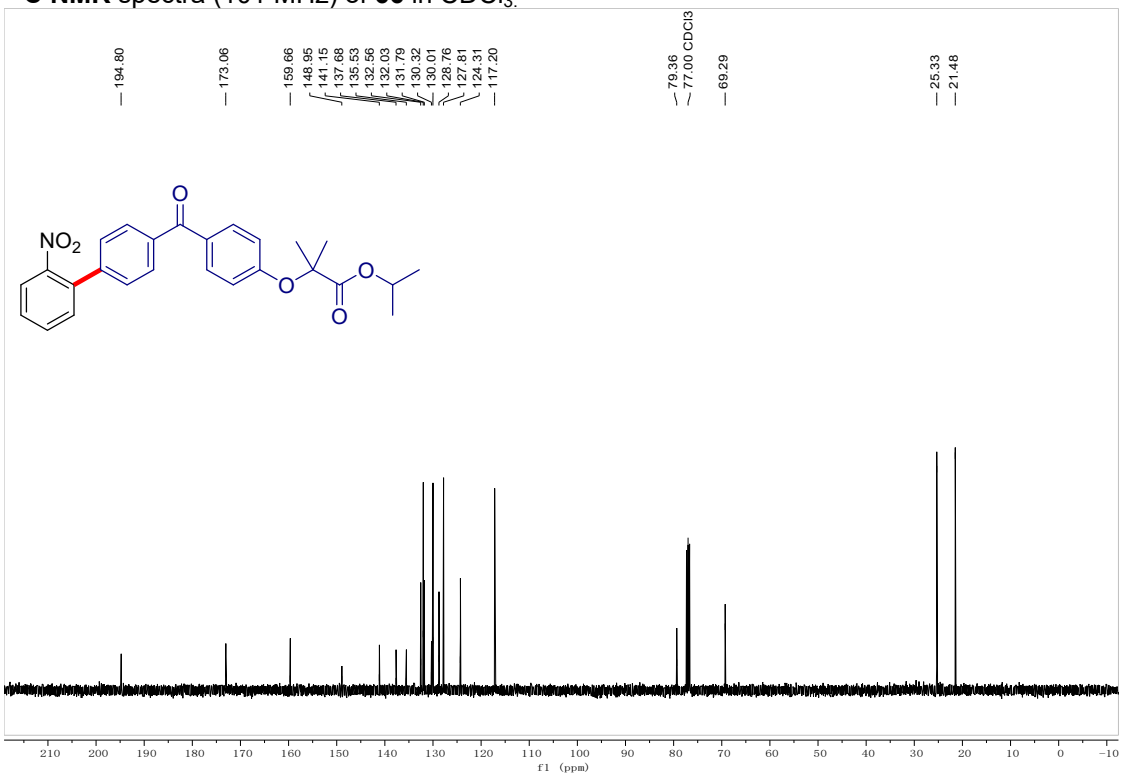
^{13}C NMR spectra (101 MHz) of **65** in $CDCl_3$.



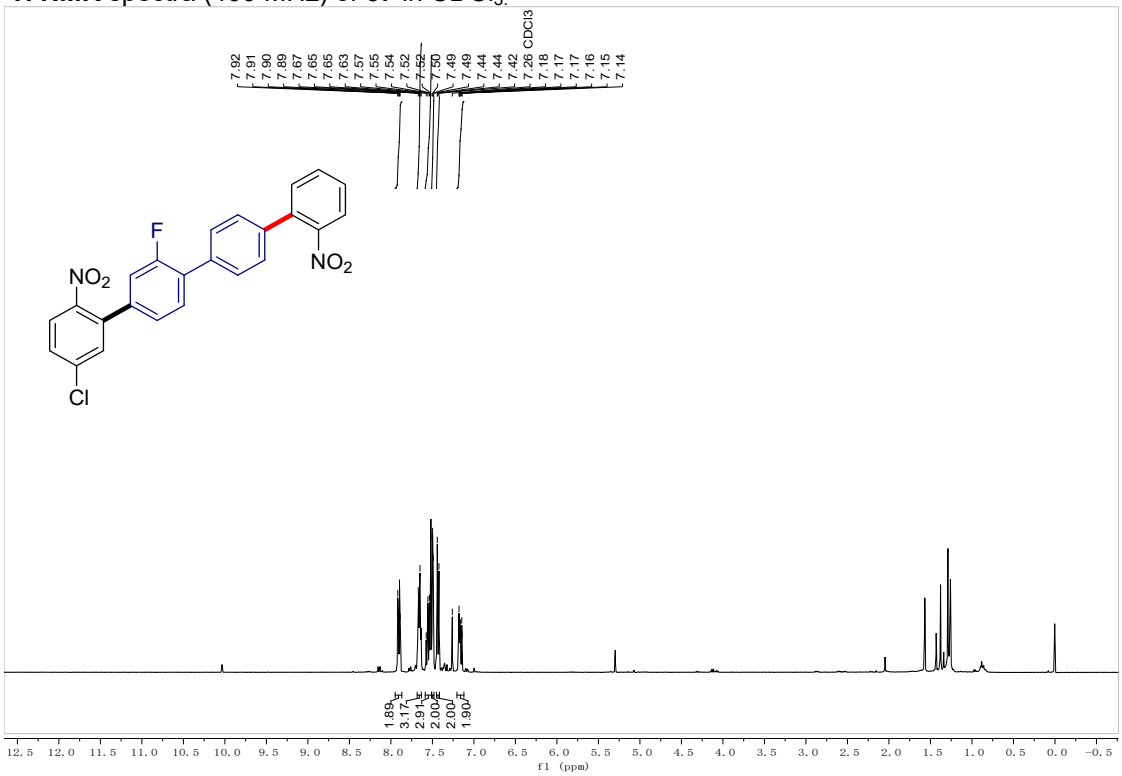
^{1}H NMR spectra (400 MHz) of **66** in $CDCl_3$.



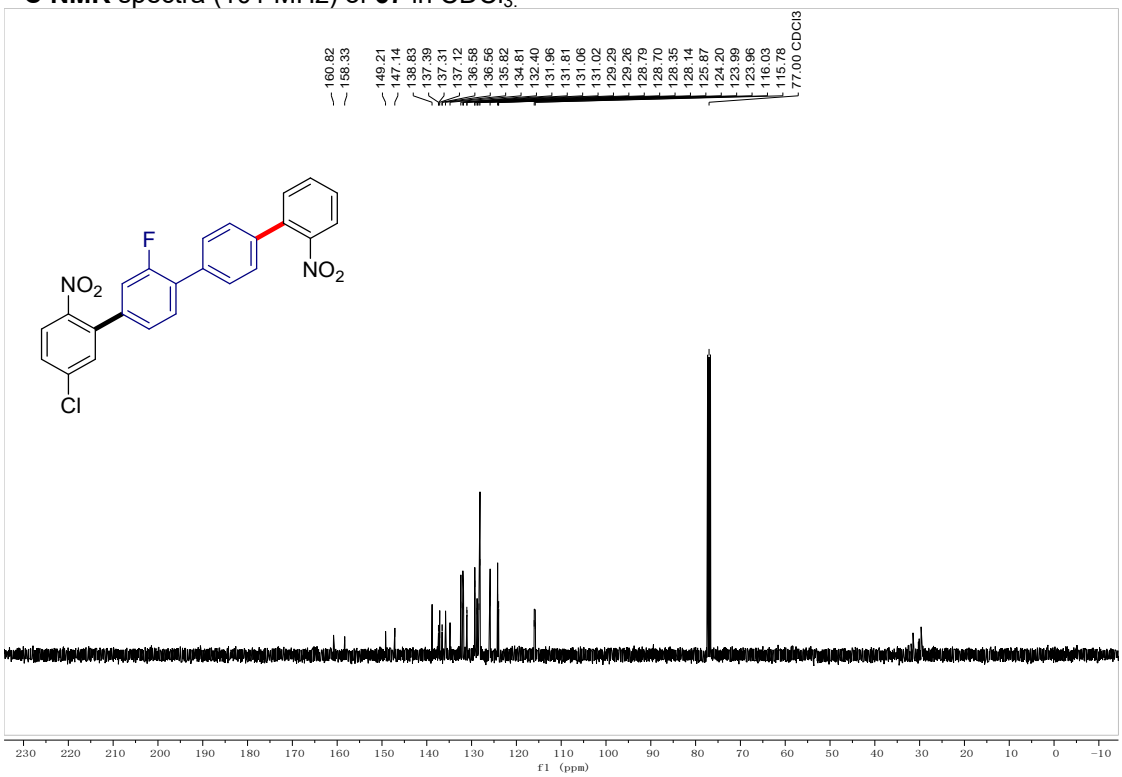
^{13}C NMR spectra (101 MHz) of **66** in $CDCl_3$.



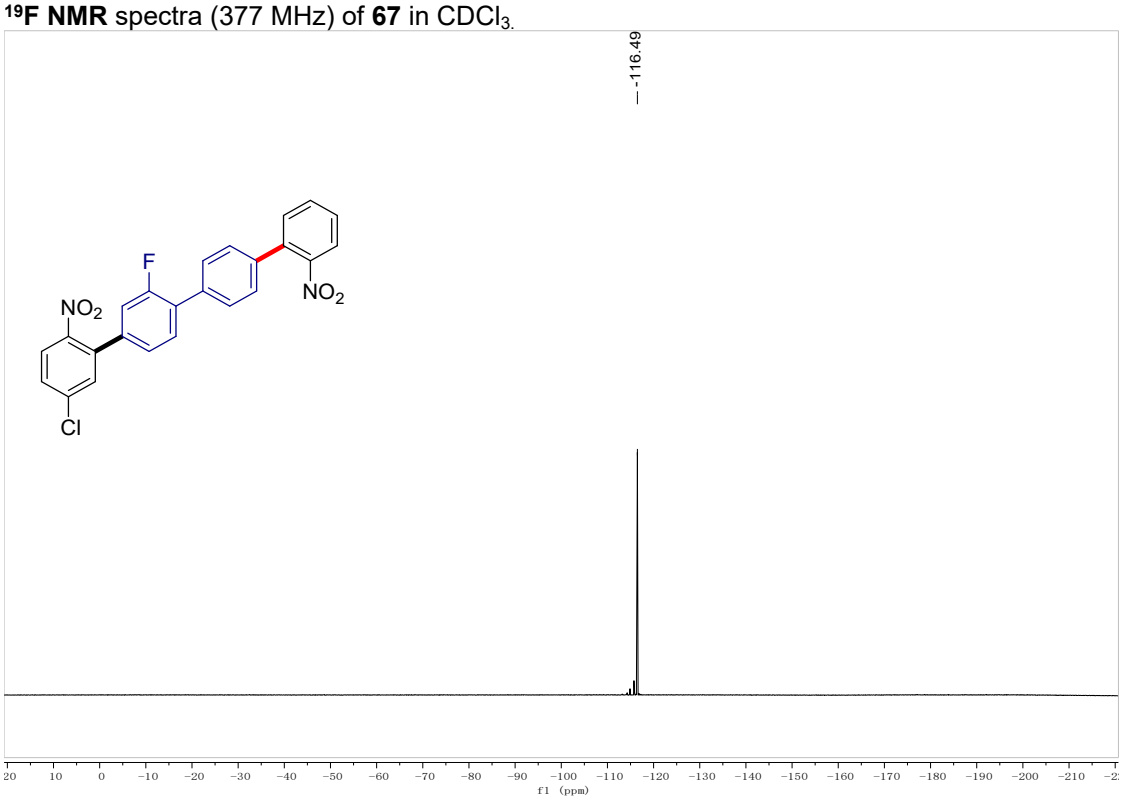
^{1}H NMR spectra (400 MHz) of **67** in $CDCl_3$.



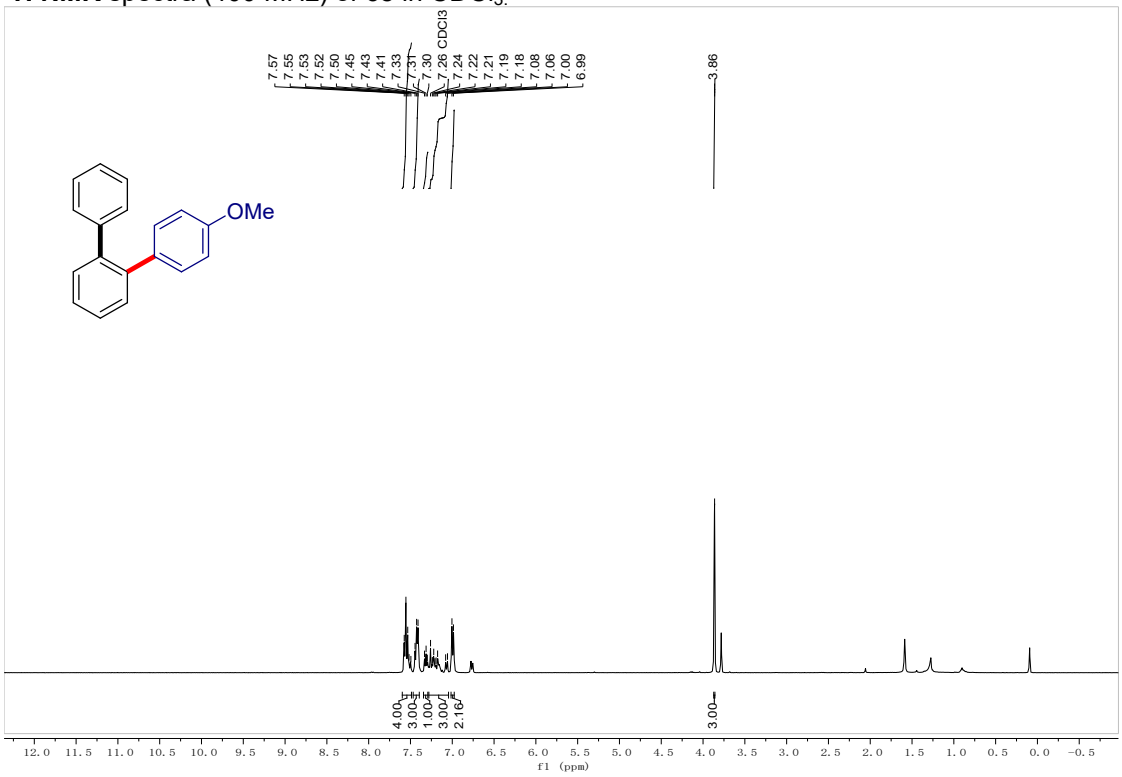
^{13}C NMR spectra (101 MHz) of **67** in $CDCl_3$.



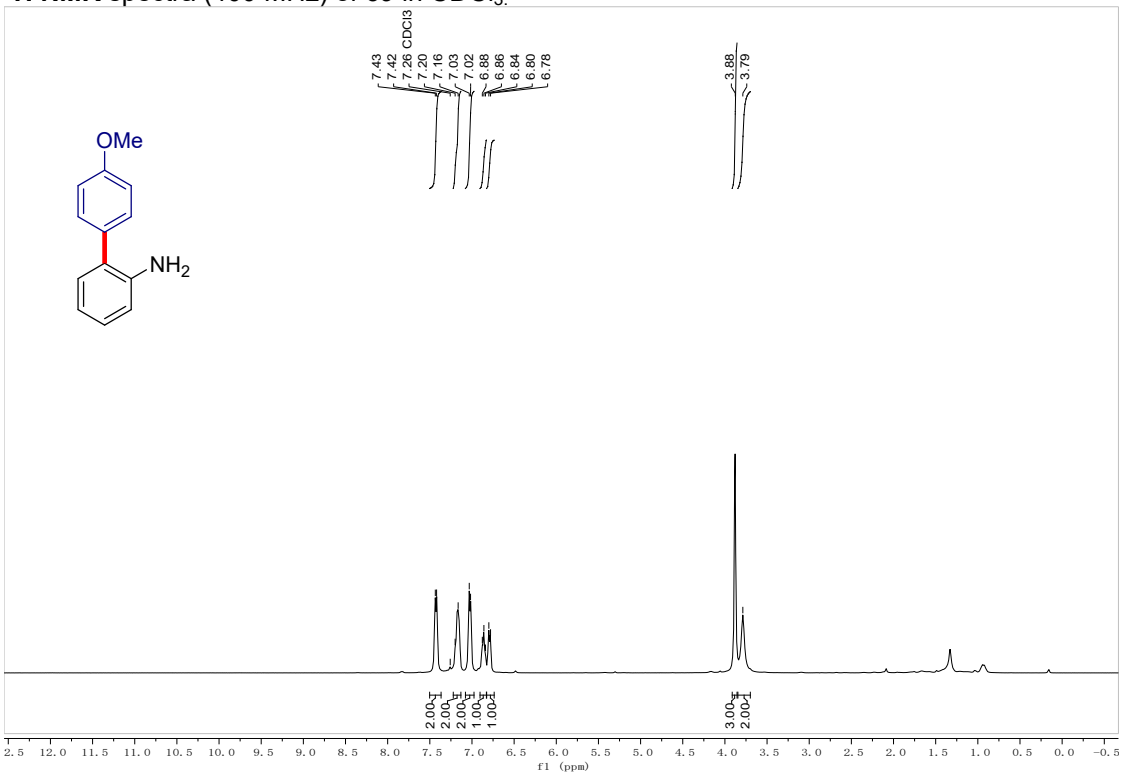
^{19}F NMR spectra (377 MHz) of **67** in $CDCl_3$.



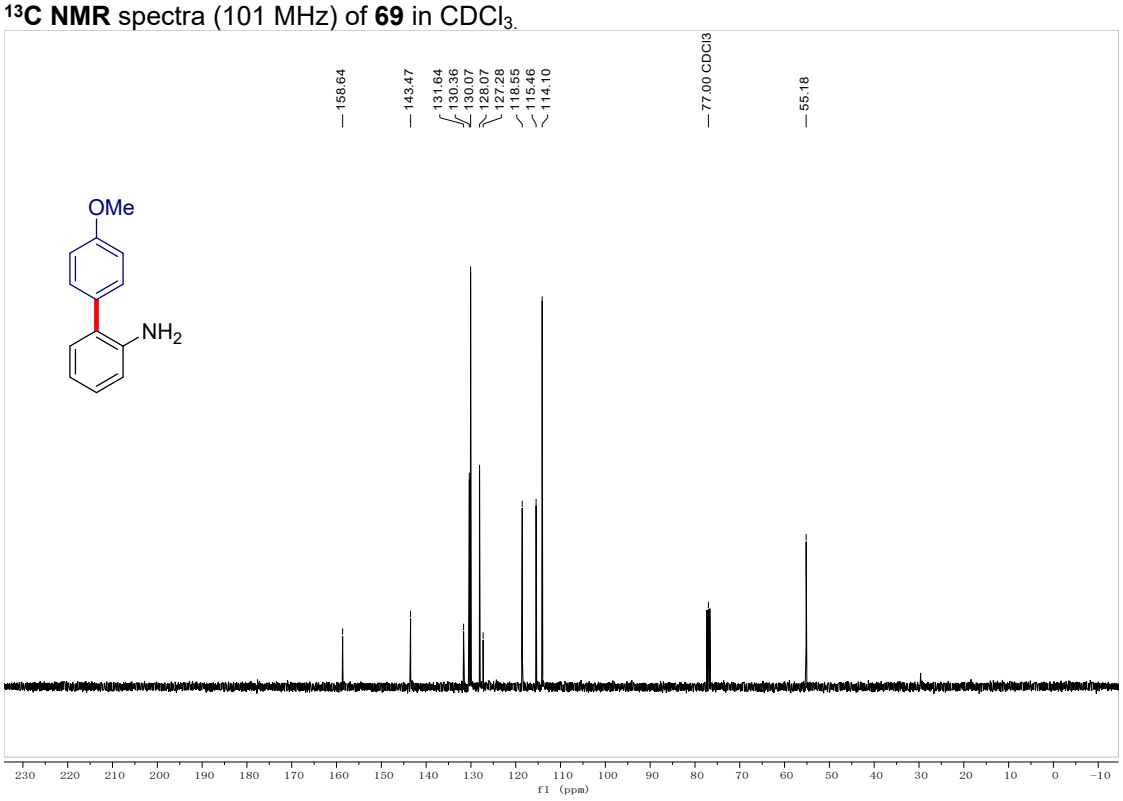
^{1}H NMR spectra (400 MHz) of **68** in $CDCl_3$.



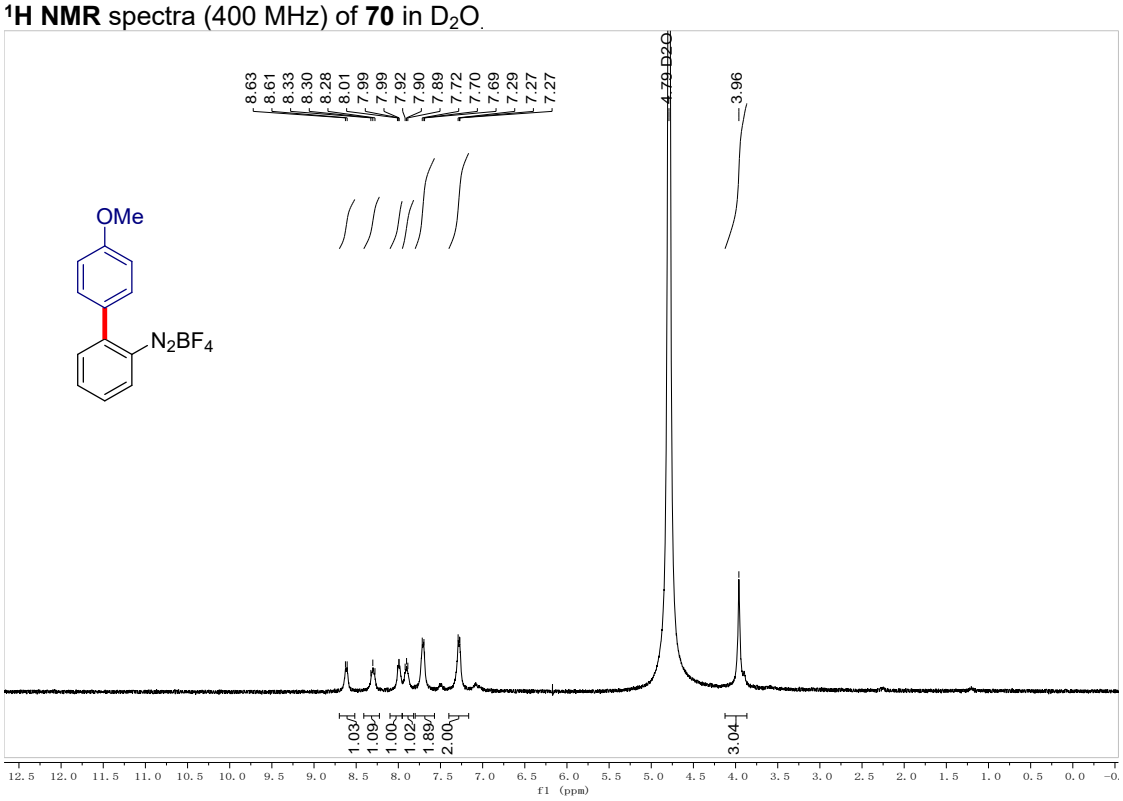
^{1}H NMR spectra (400 MHz) of **69** in $CDCl_3$.



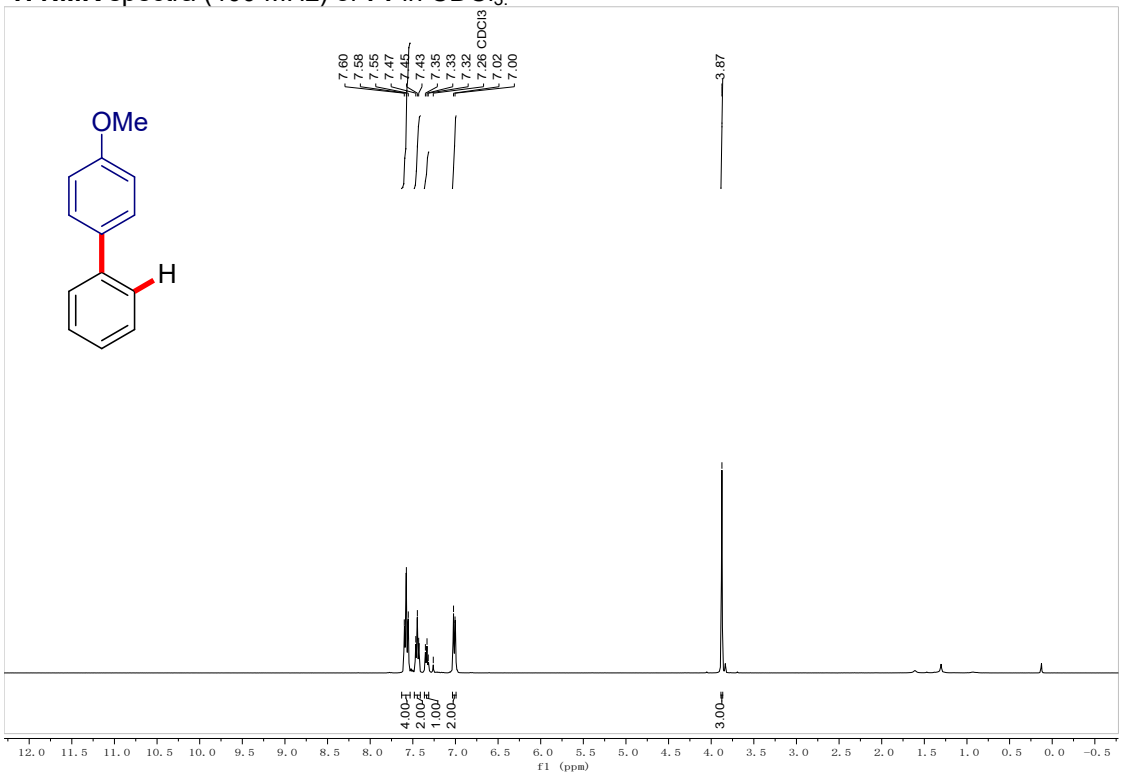
^{13}C NMR spectra (101 MHz) of **69** in $CDCl_3$.



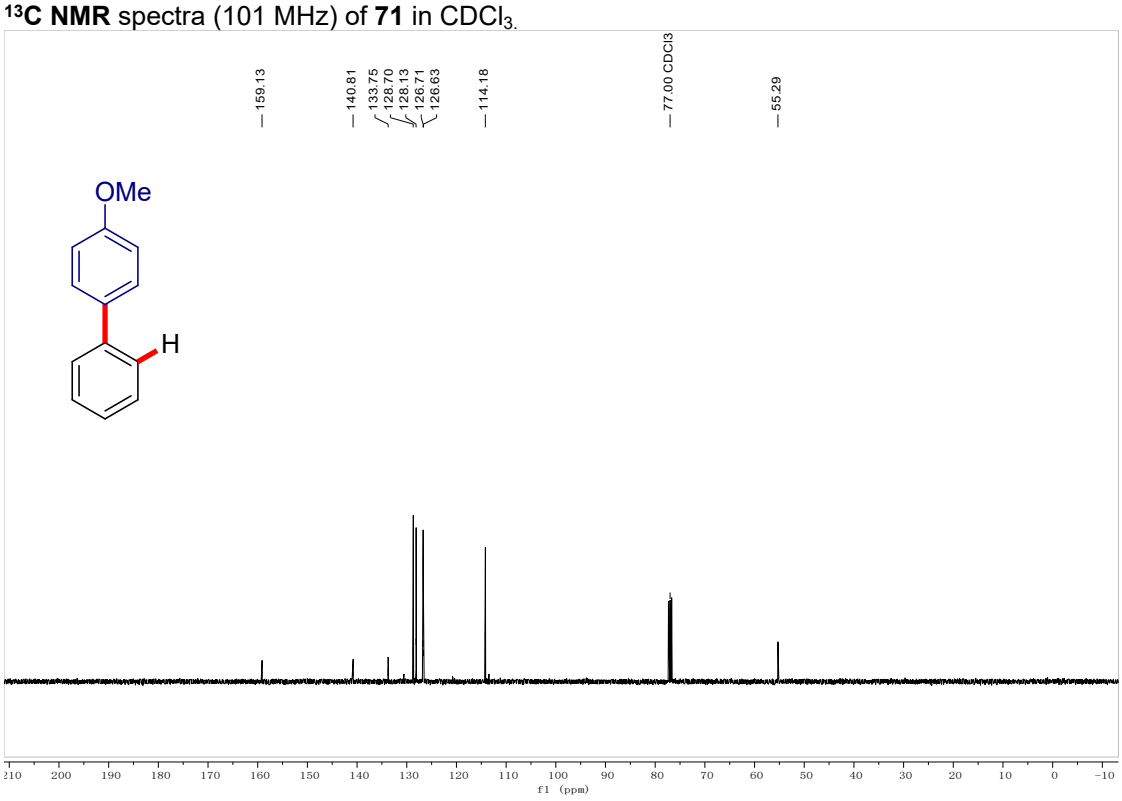
^{1}H NMR spectra (400 MHz) of **70** in D_2O.



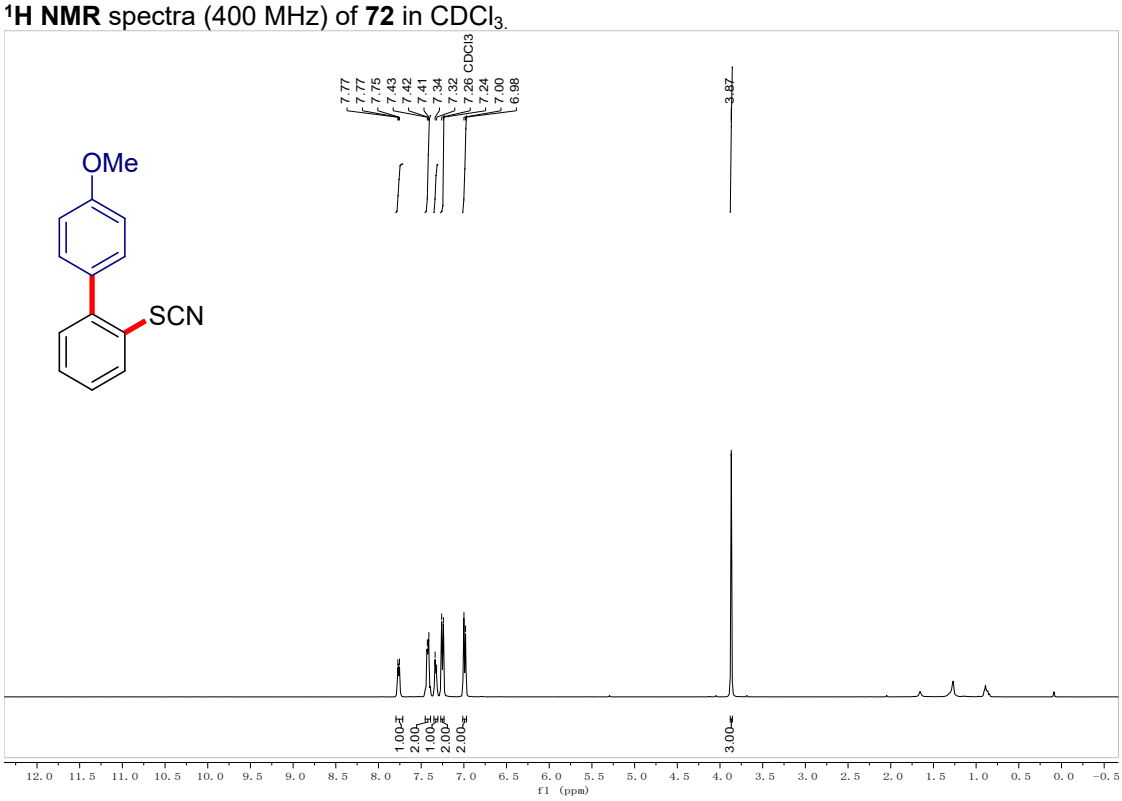
^{1}H NMR spectra (400 MHz) of **71** in $CDCl_3$.



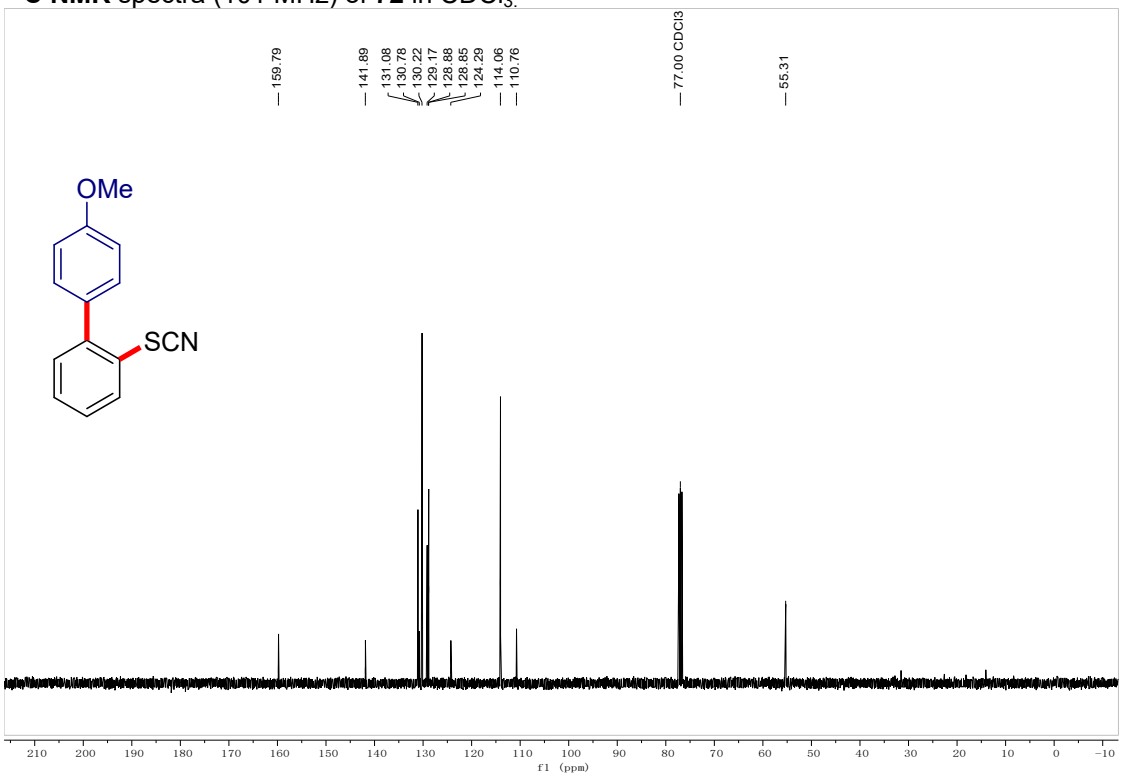
^{13}C NMR spectra (101 MHz) of **71** in $CDCl_3$.



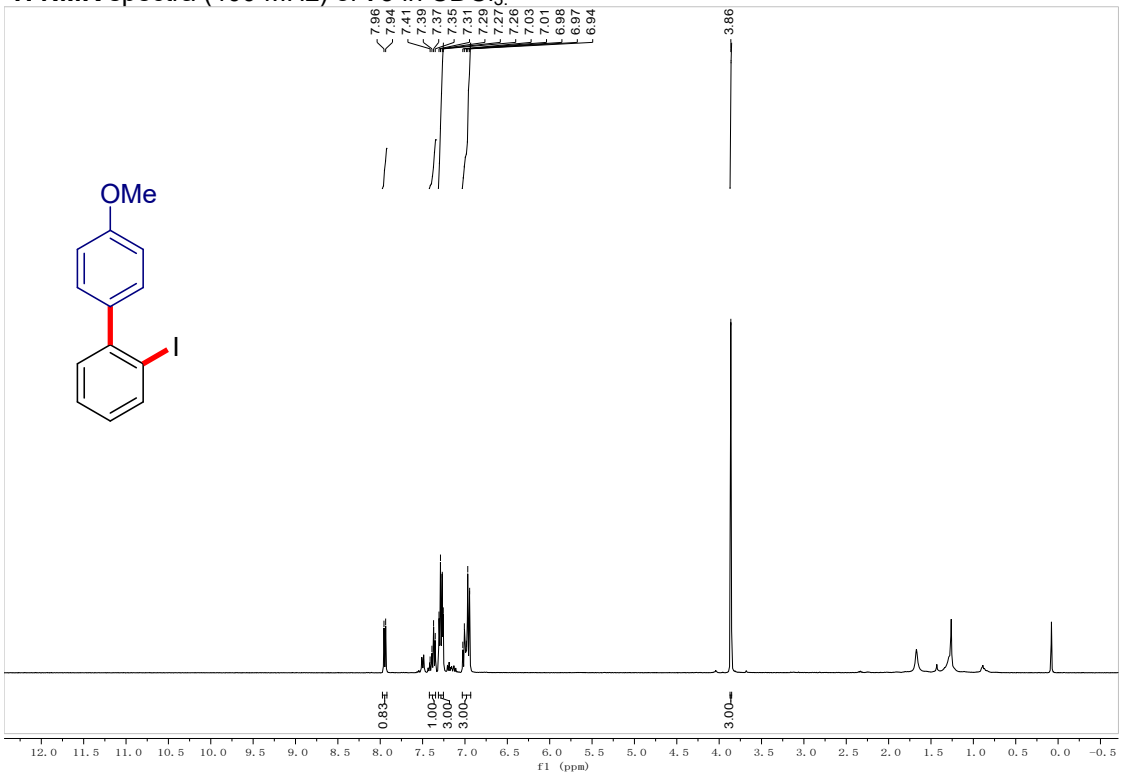
^{1}H NMR spectra (400 MHz) of **72** in $CDCl_3$.



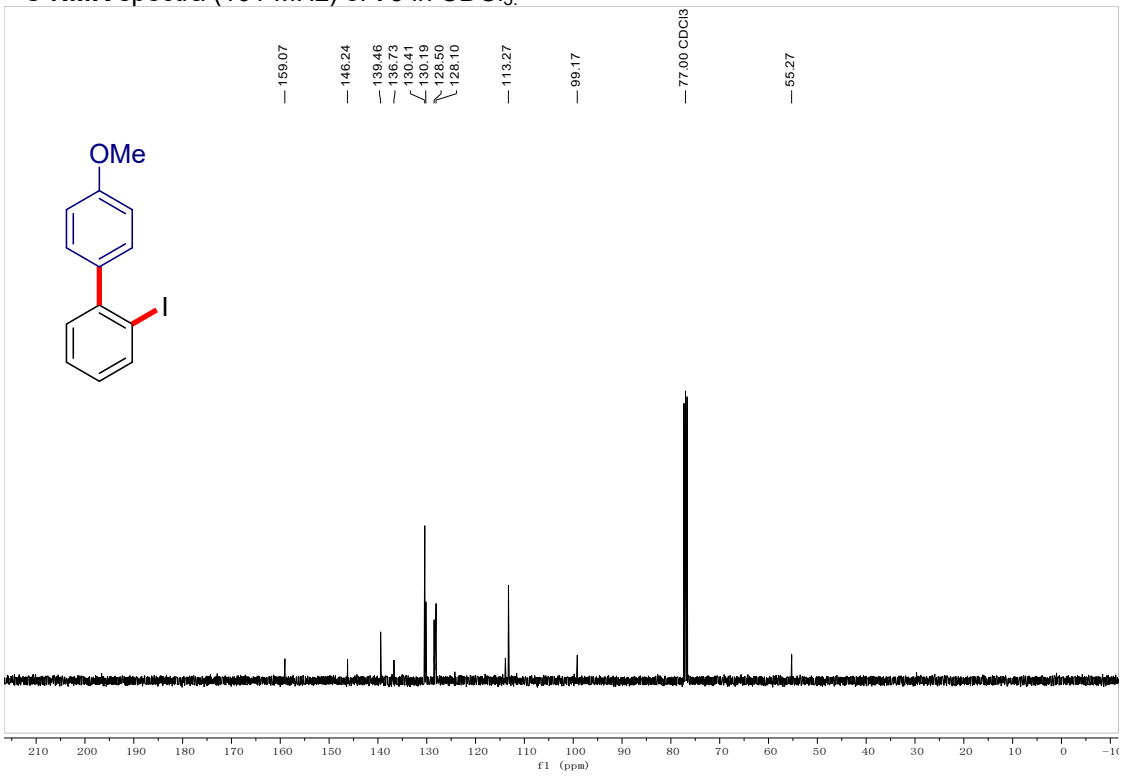
^{13}C NMR spectra (101 MHz) of **72** in $CDCl_3$.



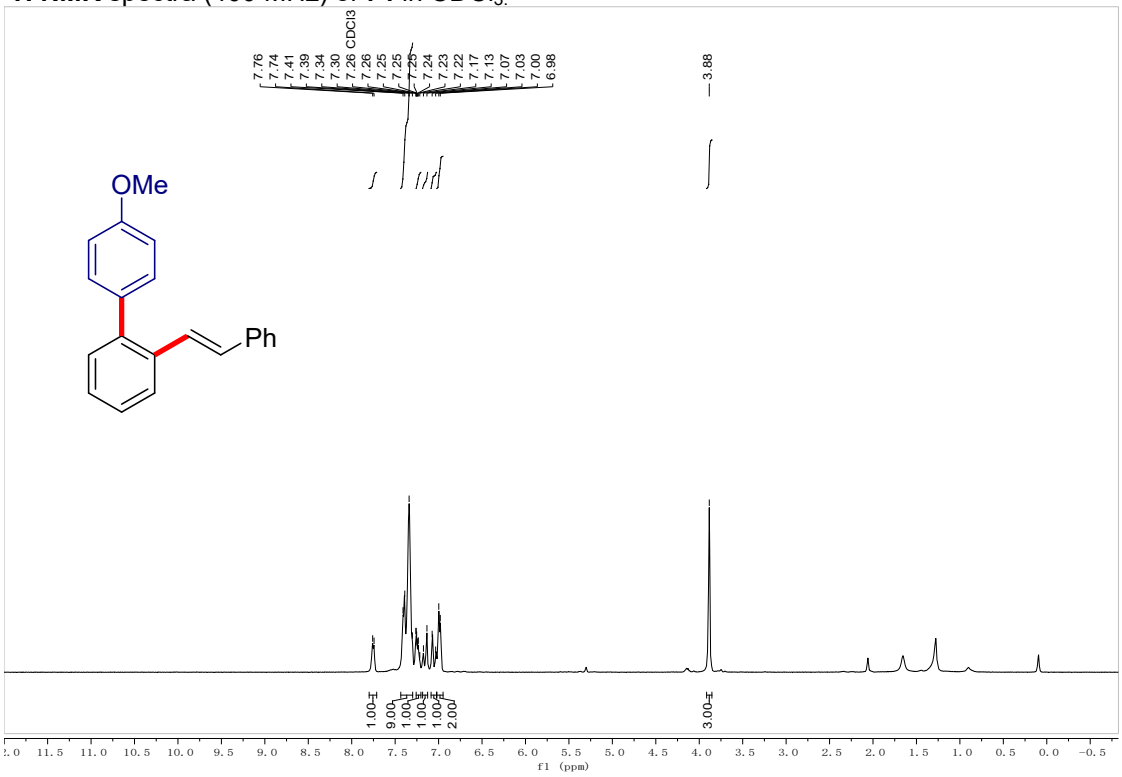
^{1}H NMR spectra (400 MHz) of **73** in $CDCl_3$.



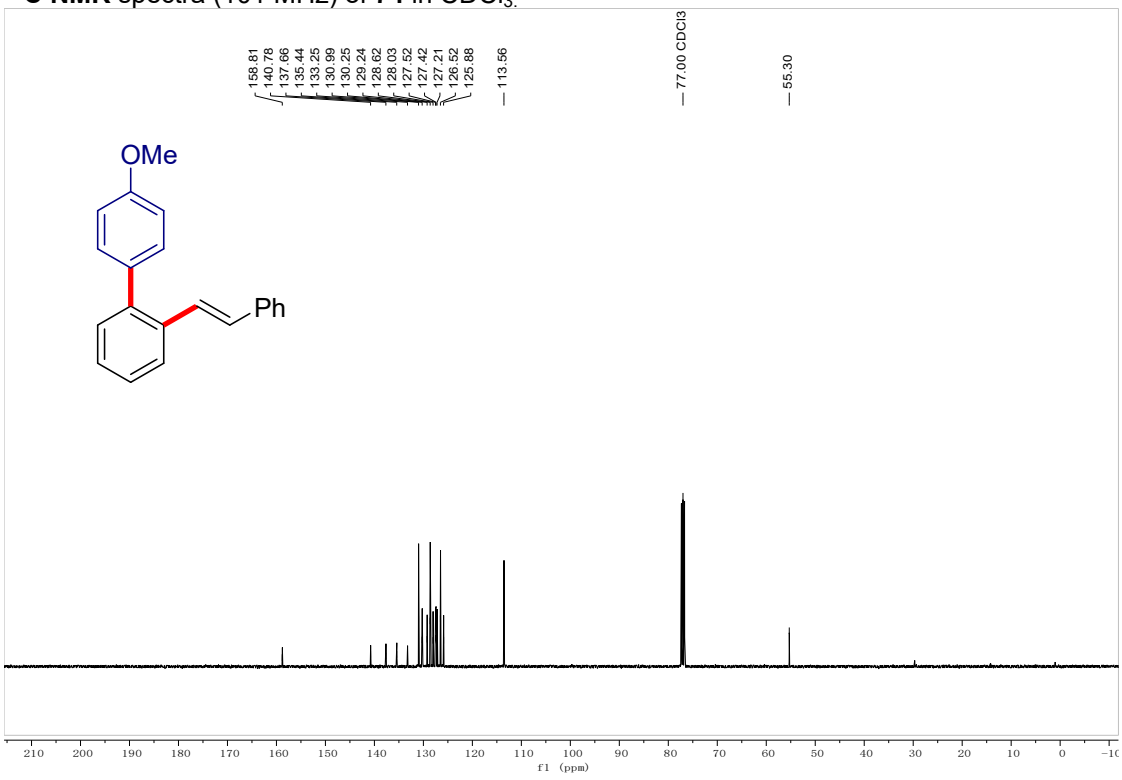
^{13}C NMR spectra (101 MHz) of **73** in $CDCl_3$.



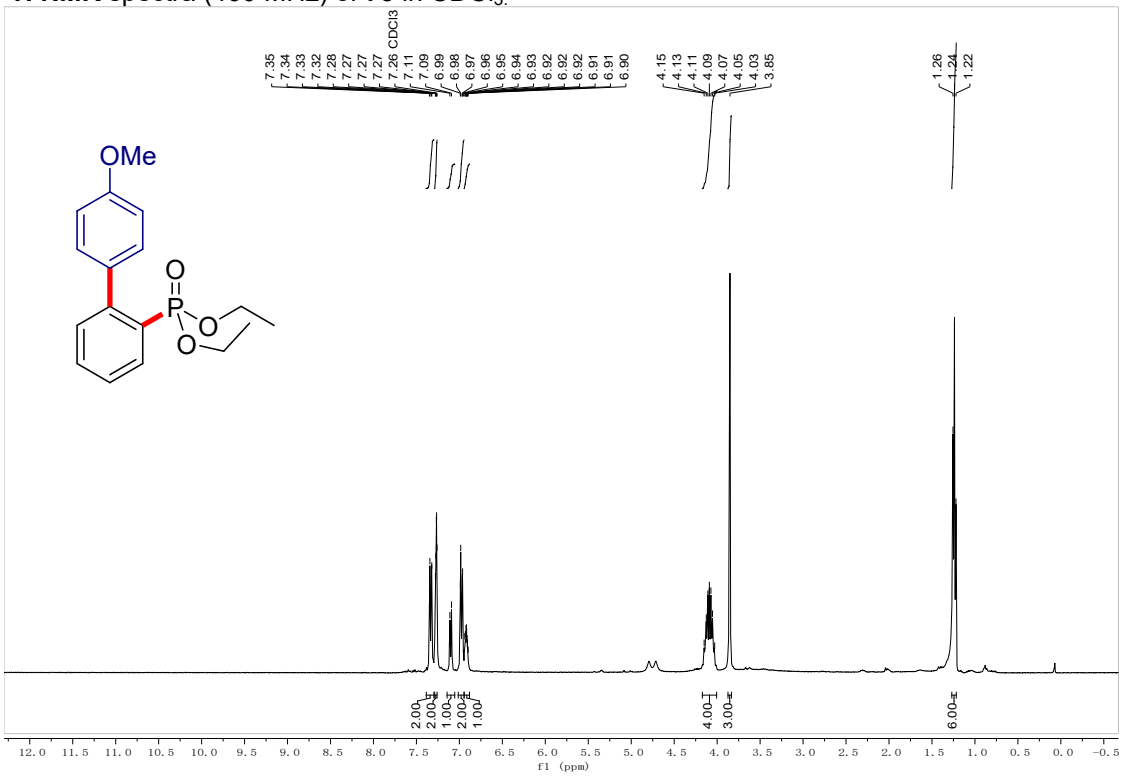
^{1}H NMR spectra (400 MHz) of **74** in $CDCl_3$.



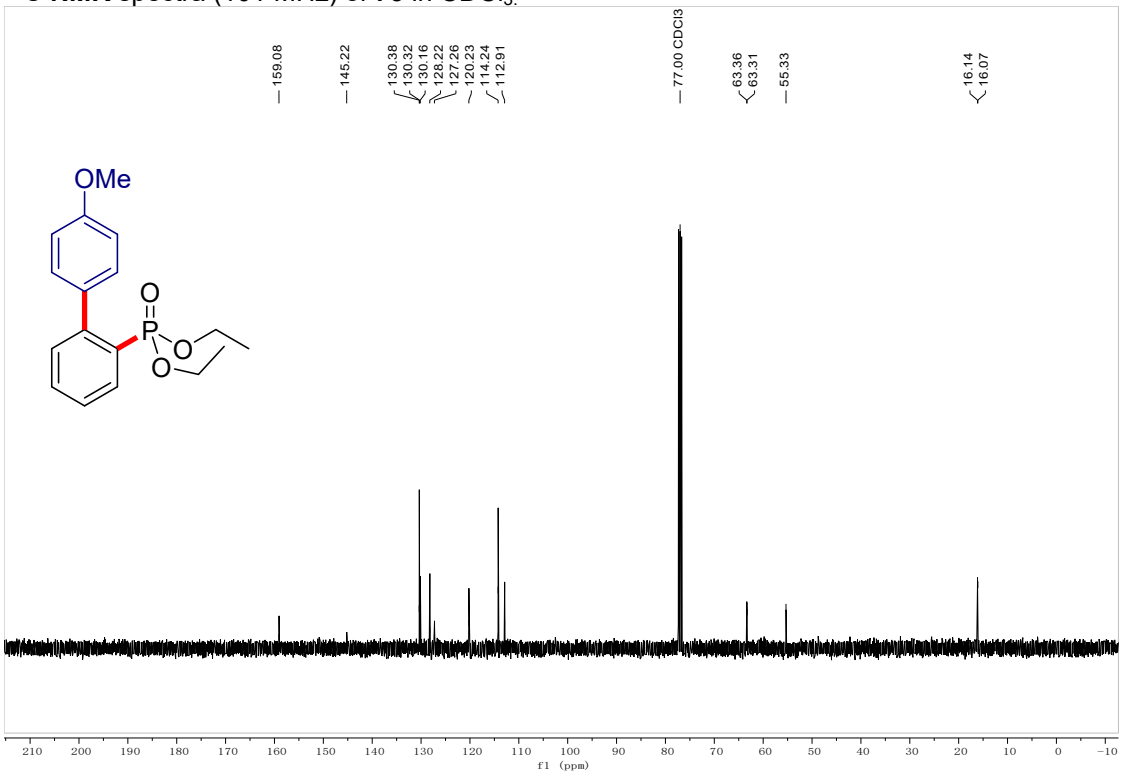
^{13}C NMR spectra (101 MHz) of **74** in $CDCl_3$.



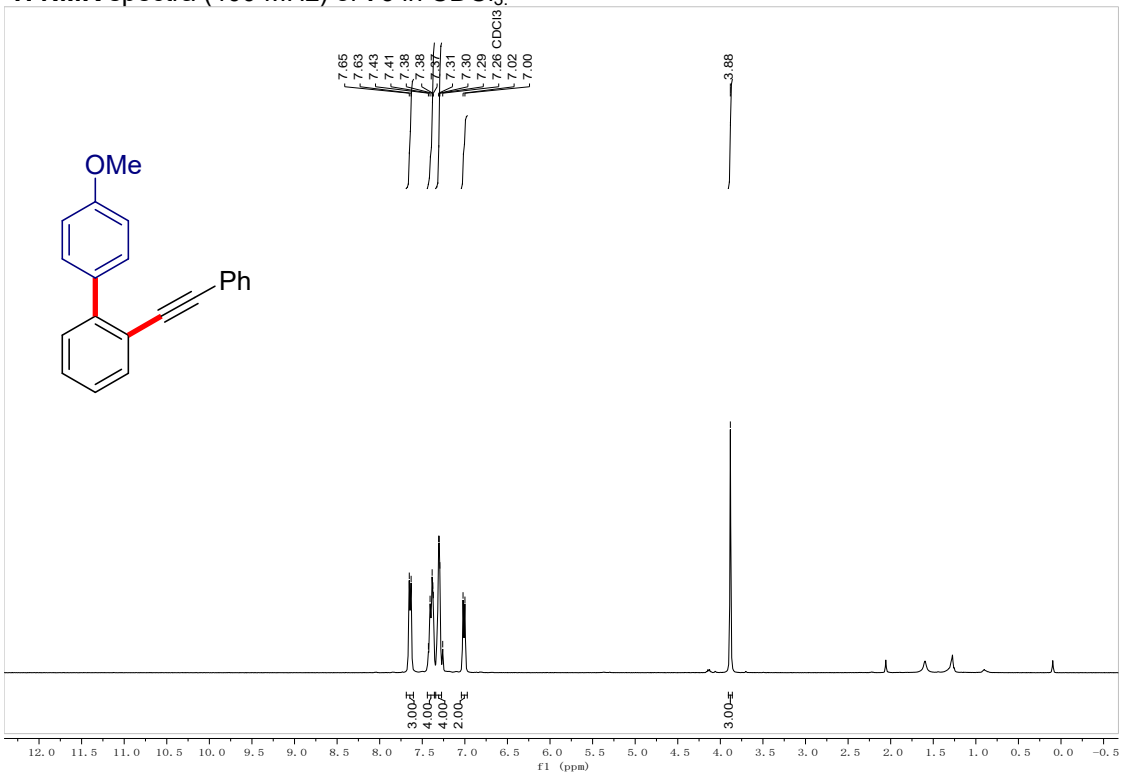
^{1}H NMR spectra (400 MHz) of **75** in $CDCl_3$.



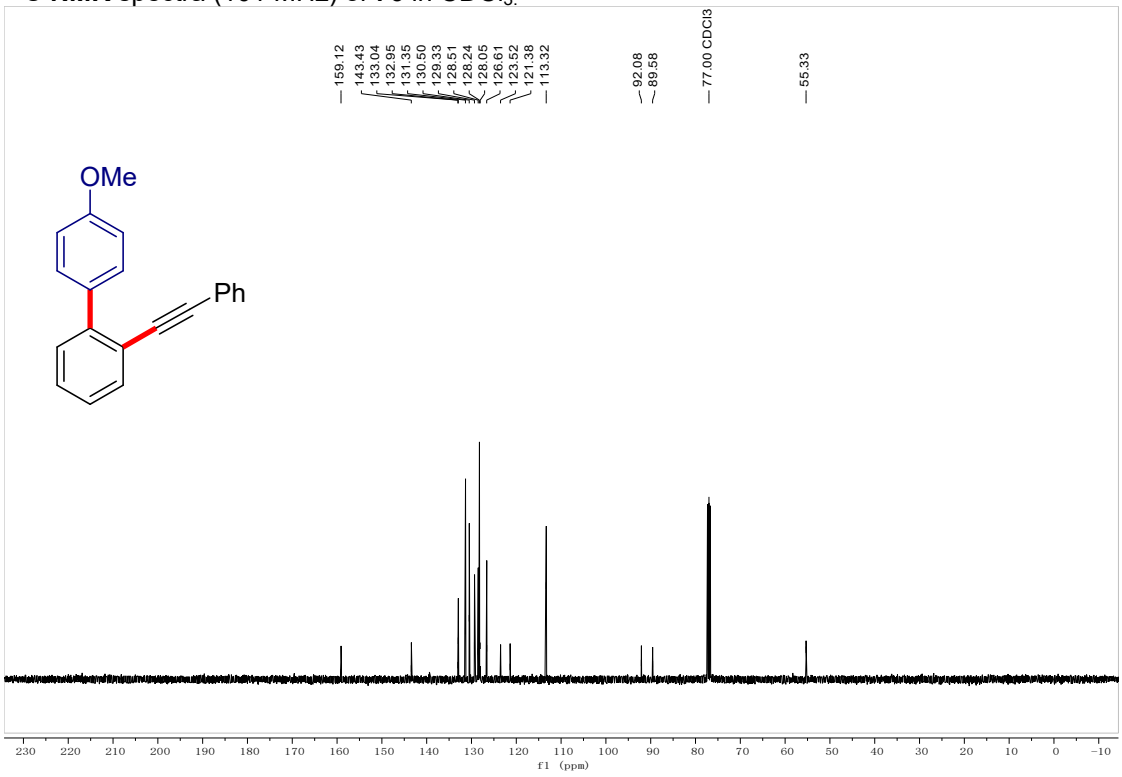
^{13}C NMR spectra (101 MHz) of **75** in $CDCl_3$.



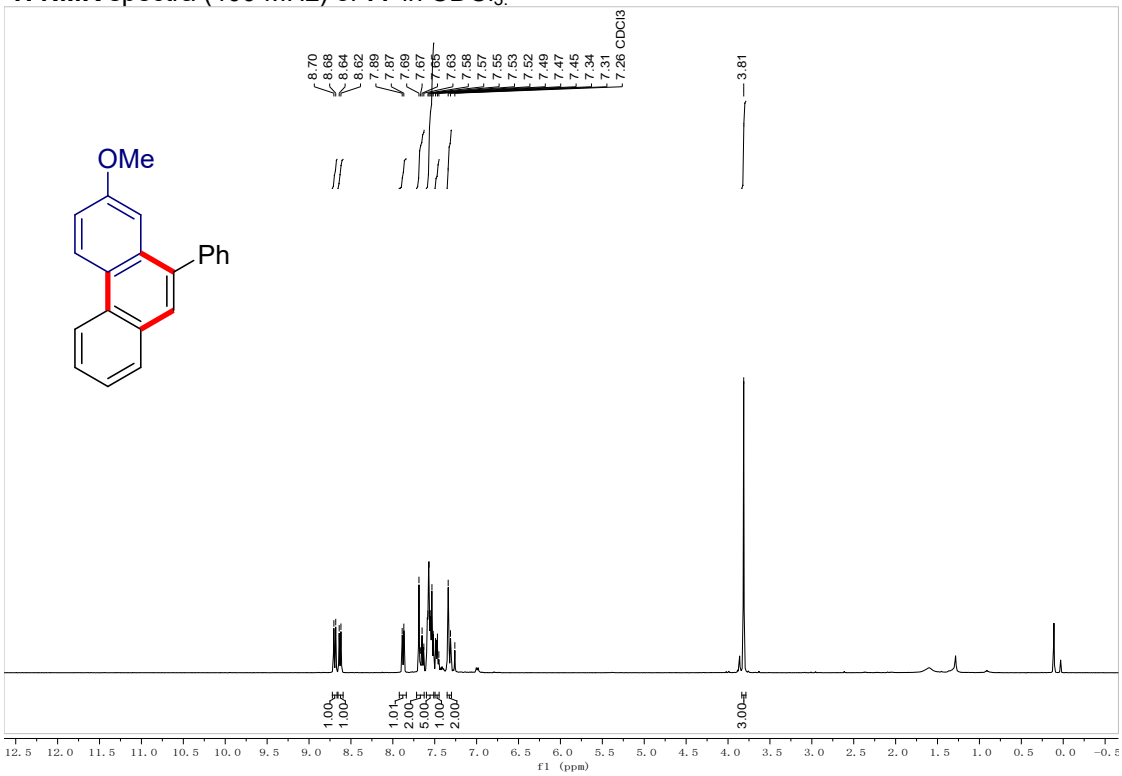
^{1}H NMR spectra (400 MHz) of **76** in $CDCl_3$.



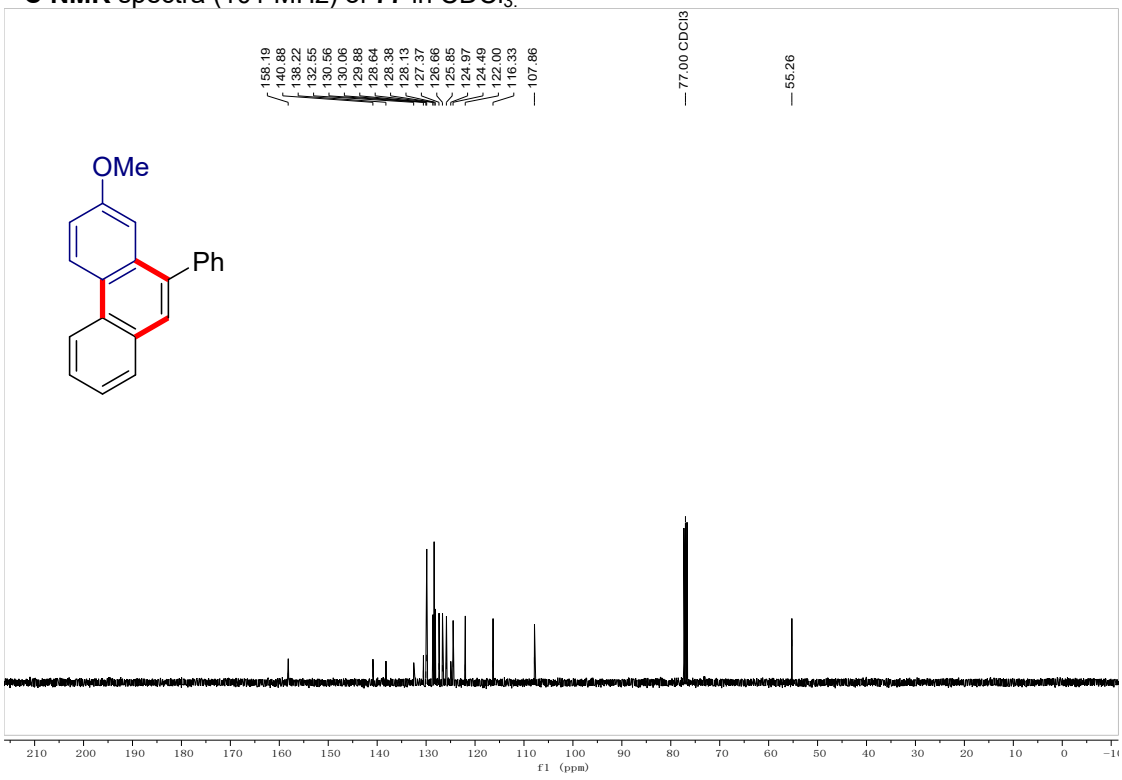
^{13}C NMR spectra (101 MHz) of **76** in $CDCl_3$.



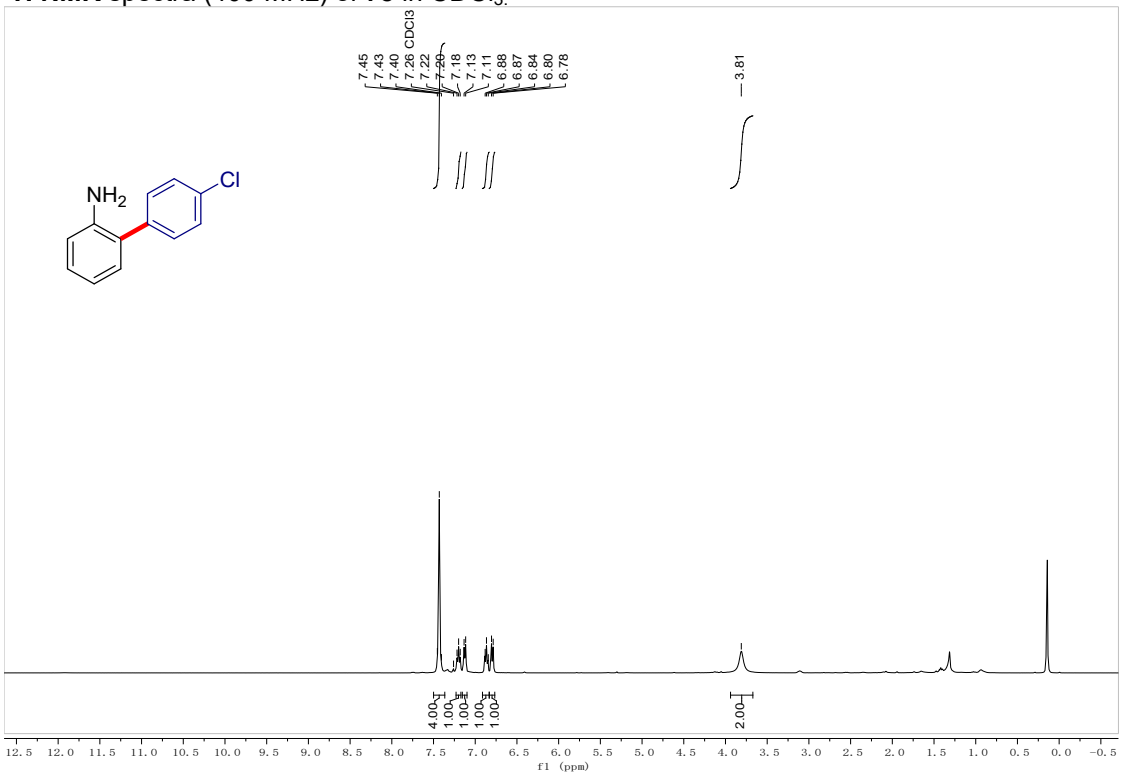
^{1}H NMR spectra (400 MHz) of **77** in $CDCl_3$.



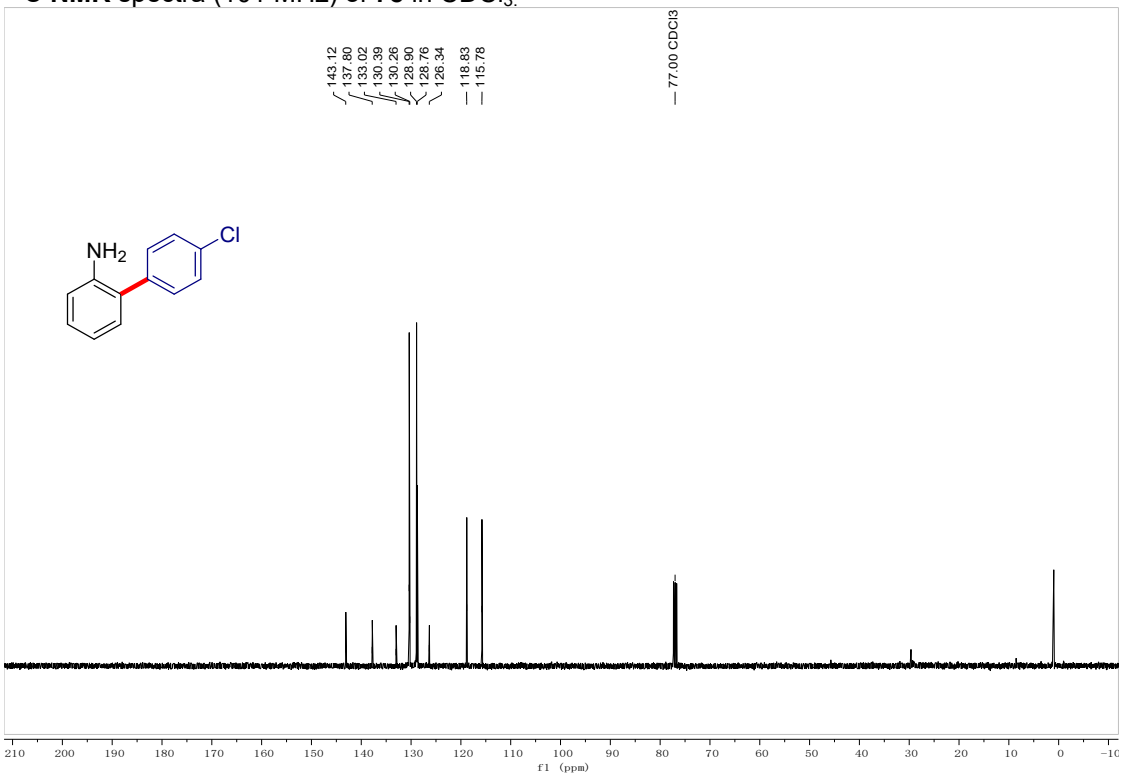
^{13}C NMR spectra (101 MHz) of **77** in $CDCl_3$.



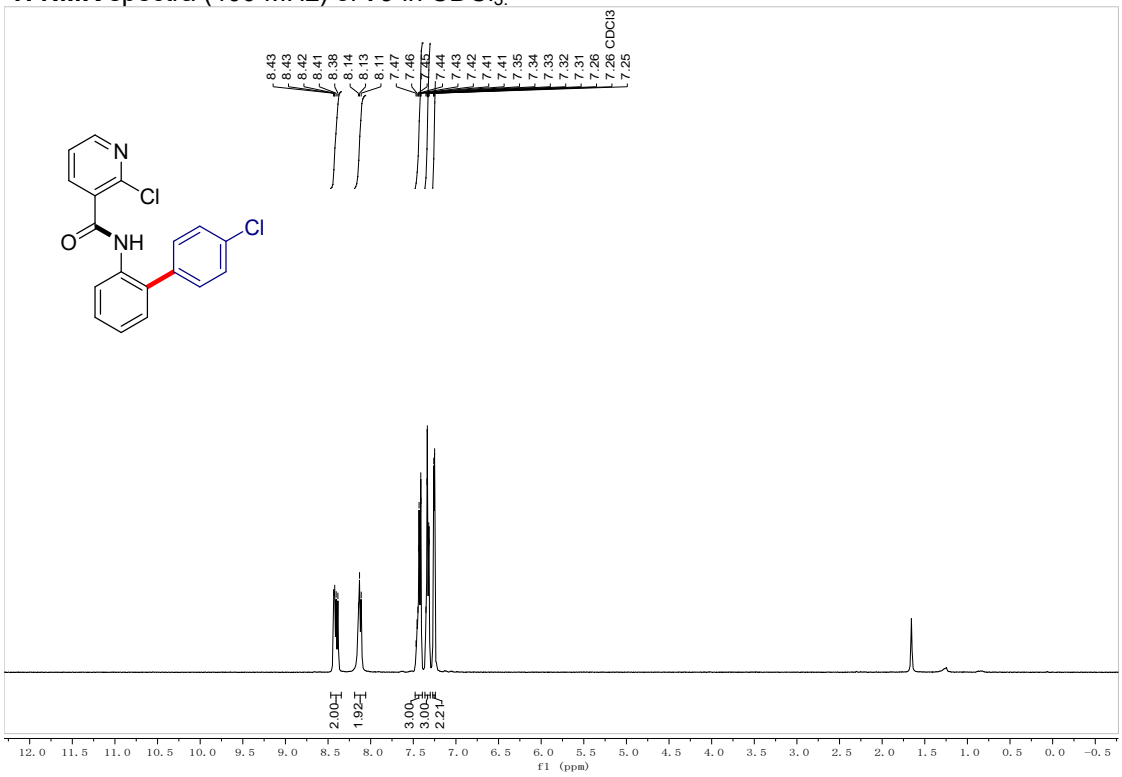
^{1}H NMR spectra (400 MHz) of **78** in $CDCl_3$.



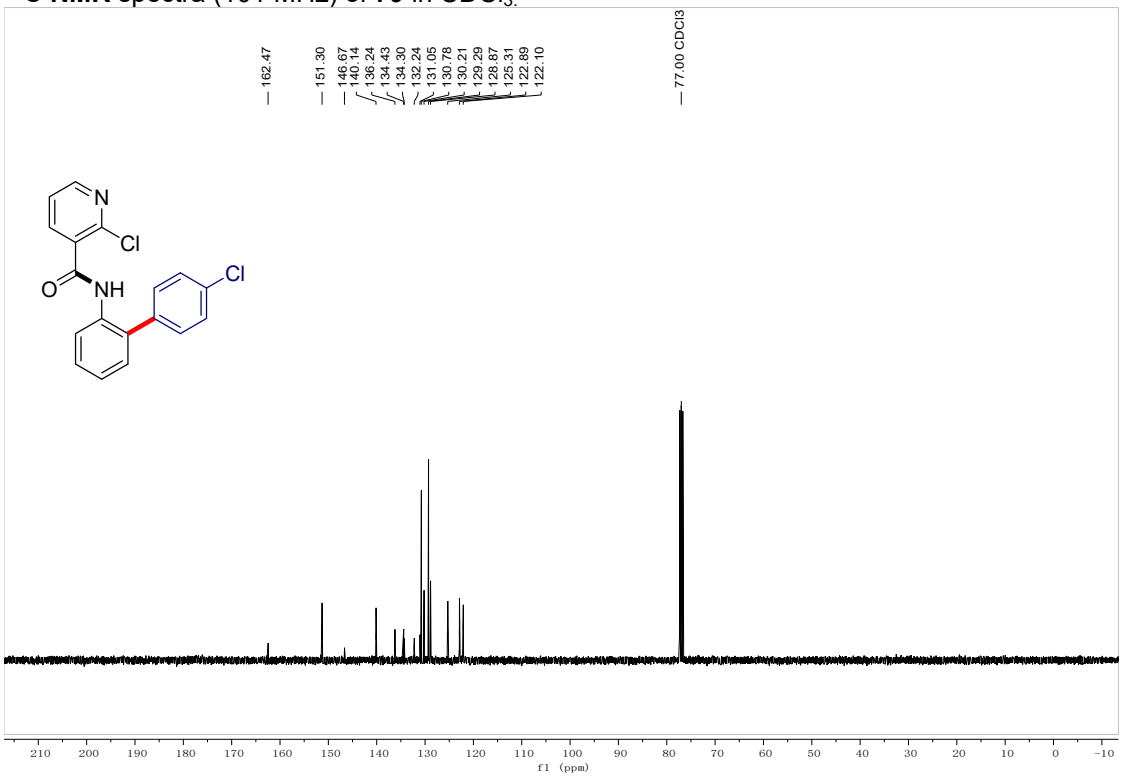
^{13}C NMR spectra (101 MHz) of **78** in $CDCl_3$.



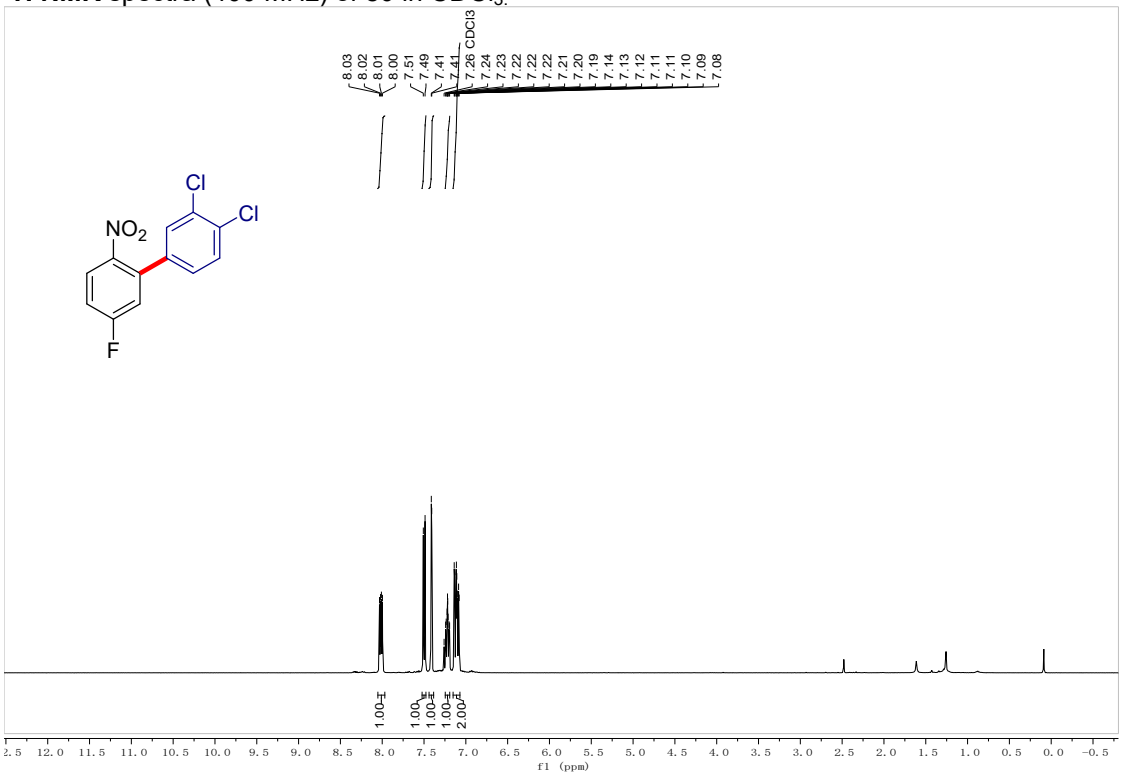
^{1}H NMR spectra (400 MHz) of **79** in $CDCl_3$.



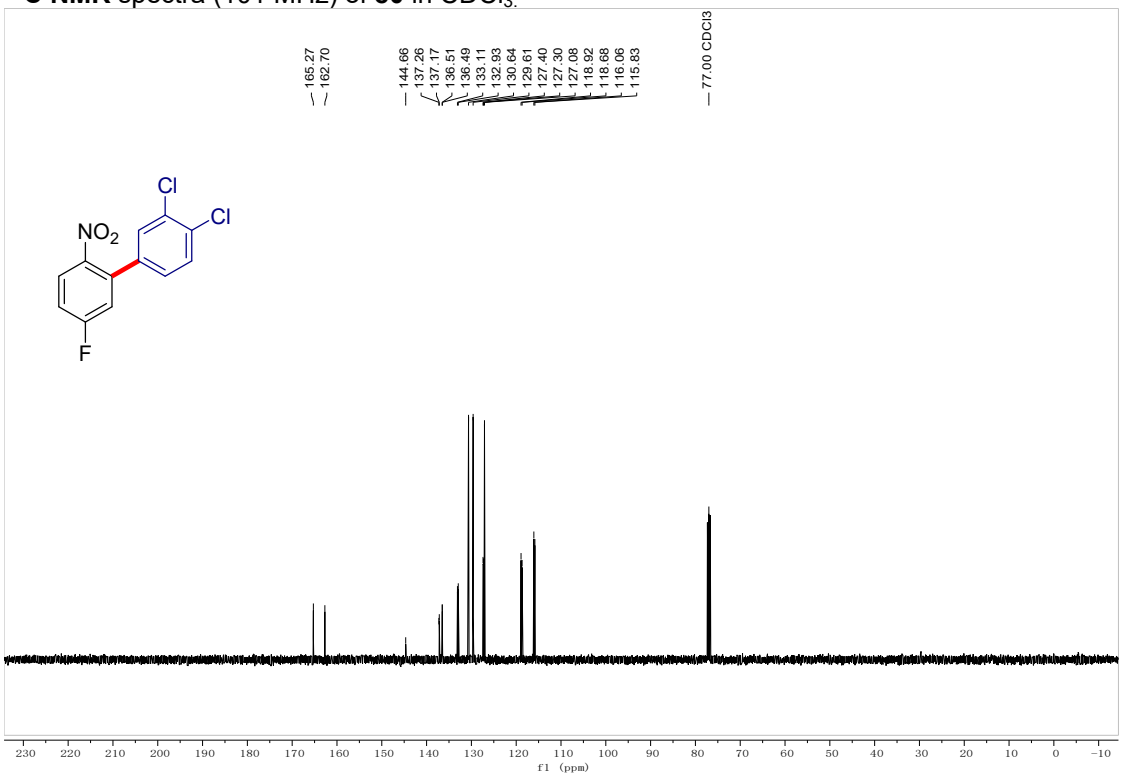
^{13}C NMR spectra (101 MHz) of **79** in $CDCl_3$.



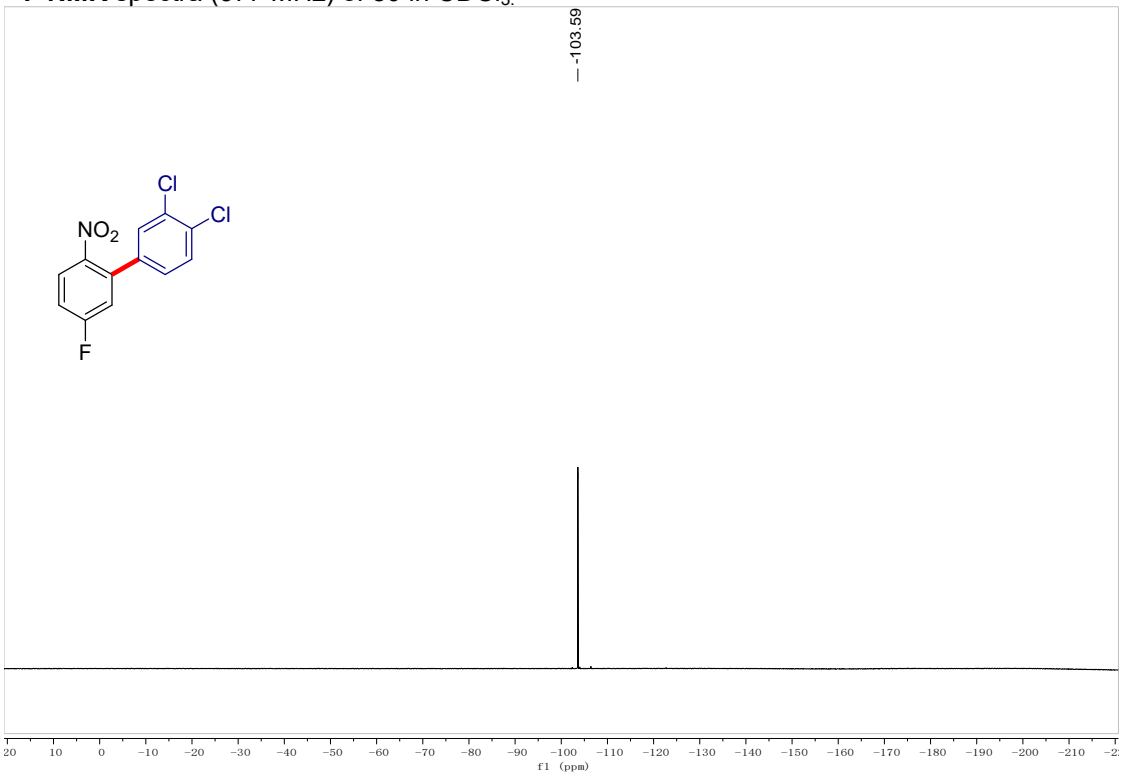
^{1}H NMR spectra (400 MHz) of **80** in $CDCl_3$.



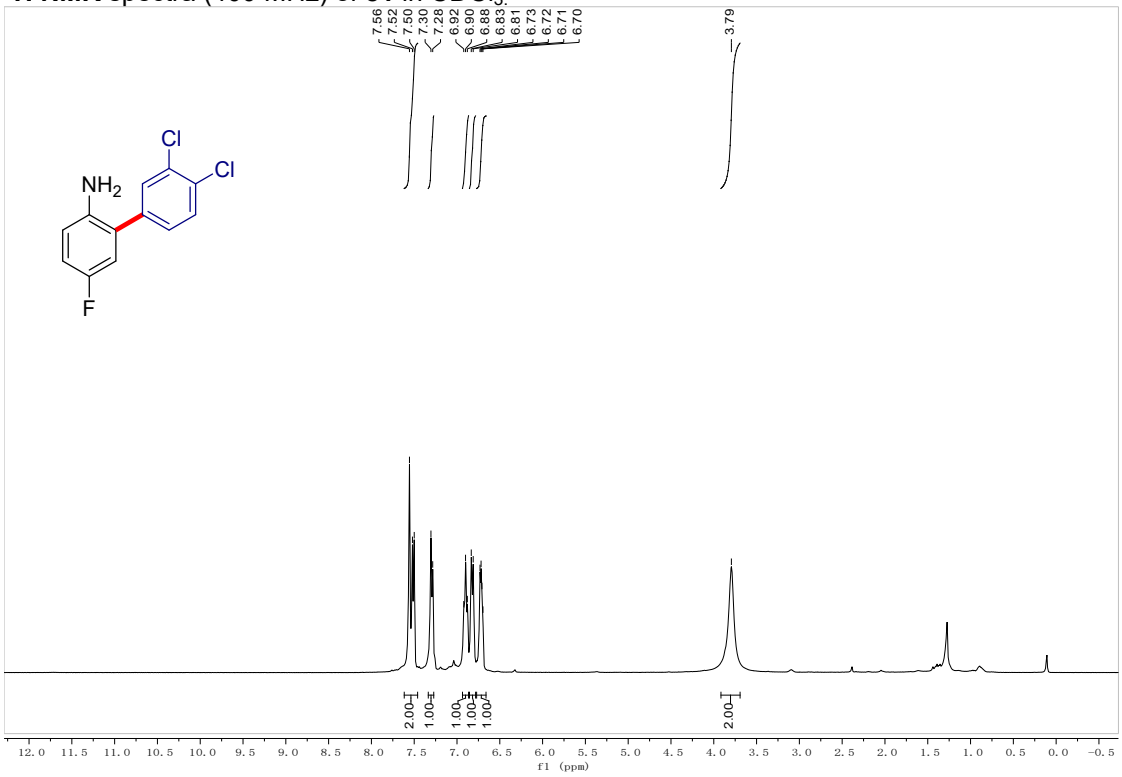
^{13}C NMR spectra (101 MHz) of **80** in $CDCl_3$.



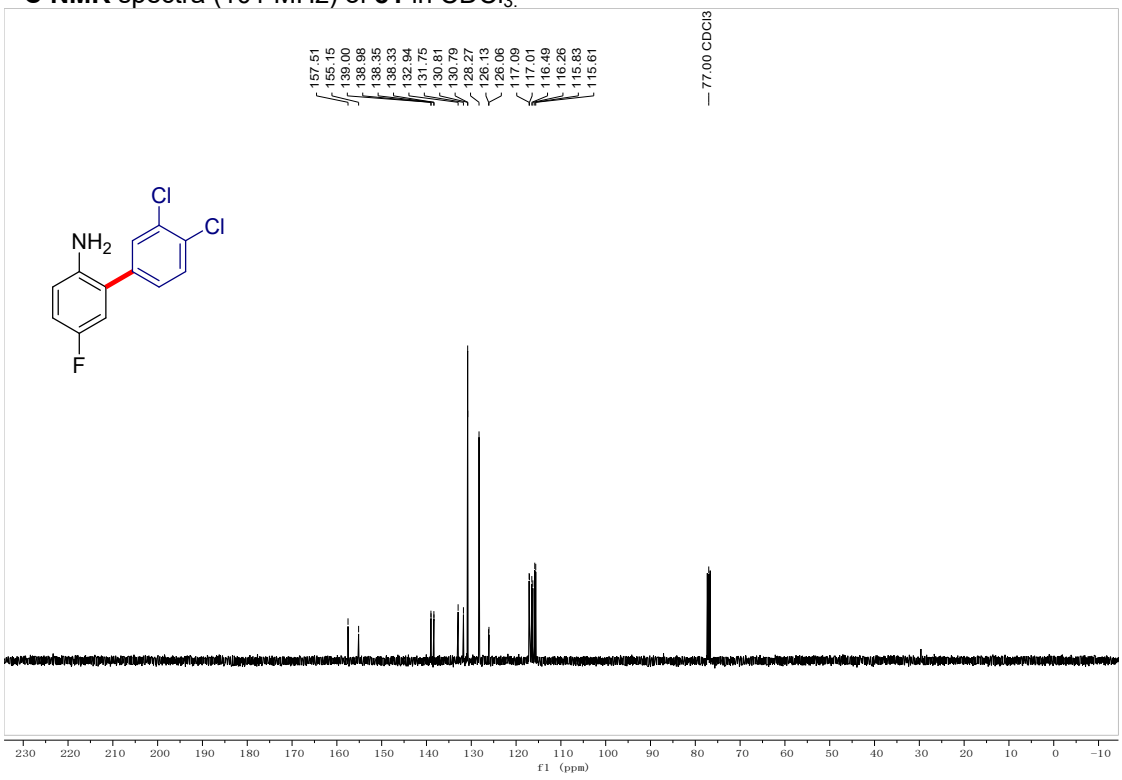
^{19}F NMR spectra (377 MHz) of **80** in $CDCl_3$.



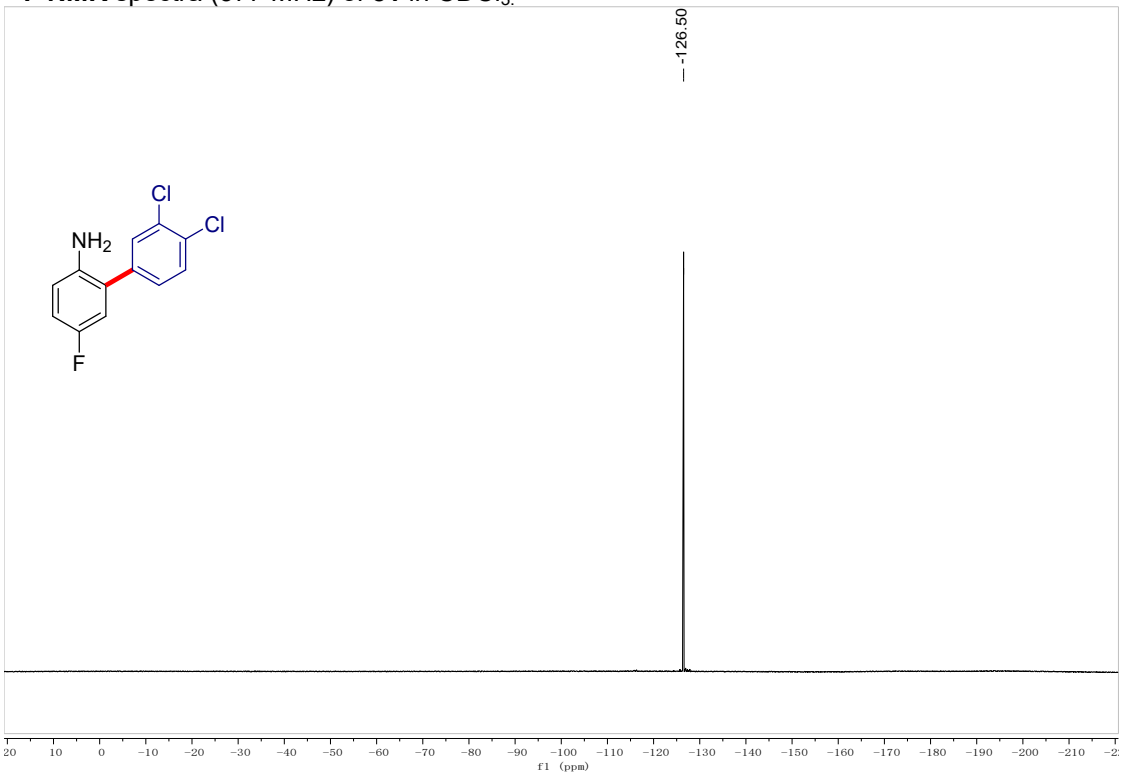
^{1}H NMR spectra (400 MHz) of **81** in $CDCl_3$.



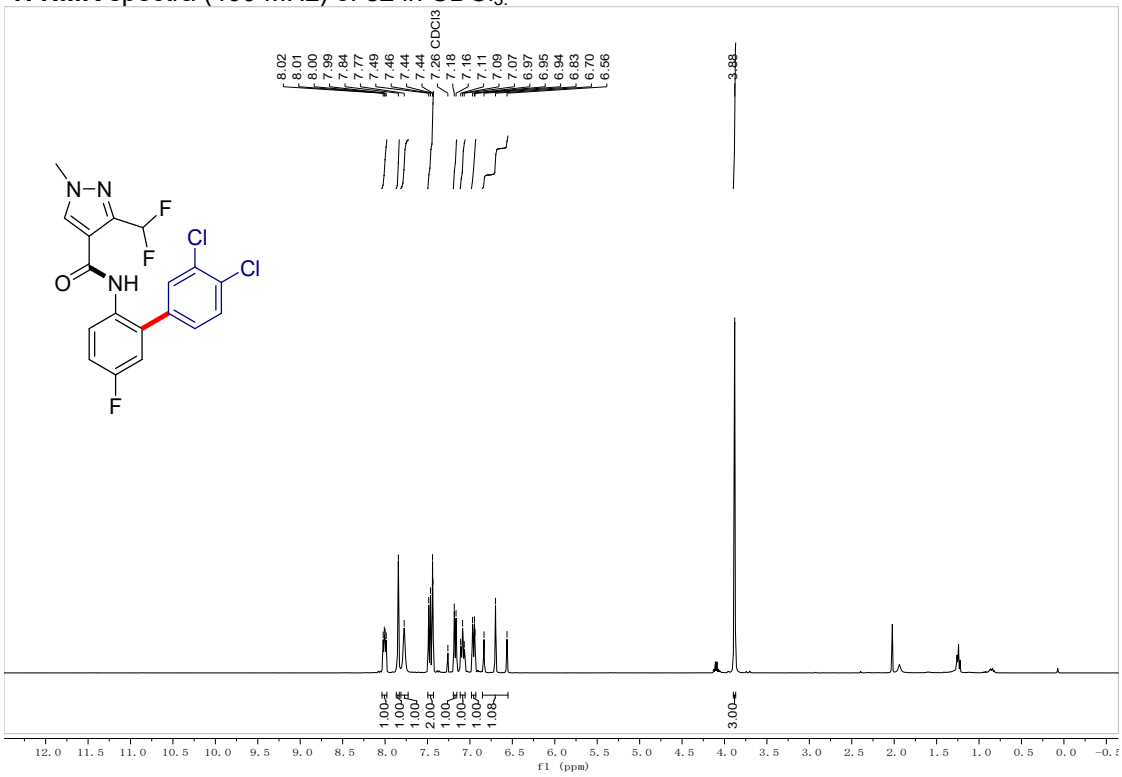
^{13}C NMR spectra (101 MHz) of **81** in $CDCl_3$.



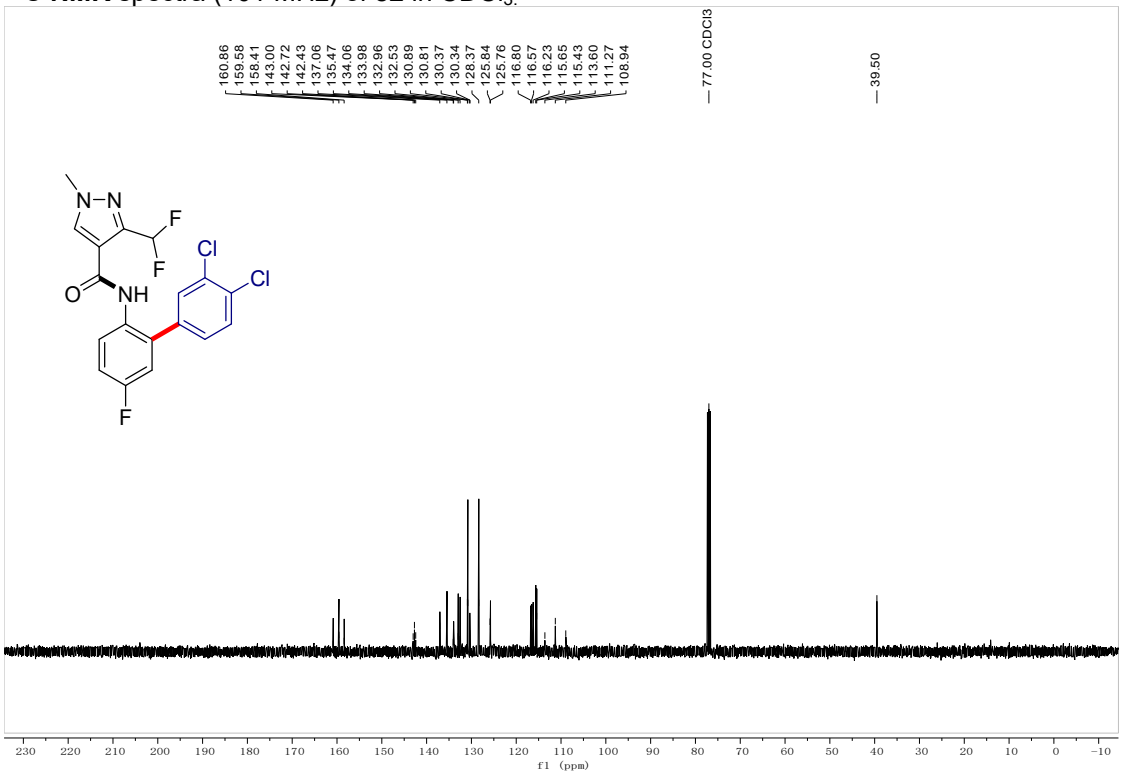
^{19}F NMR spectra (377 MHz) of **81** in $CDCl_3$.



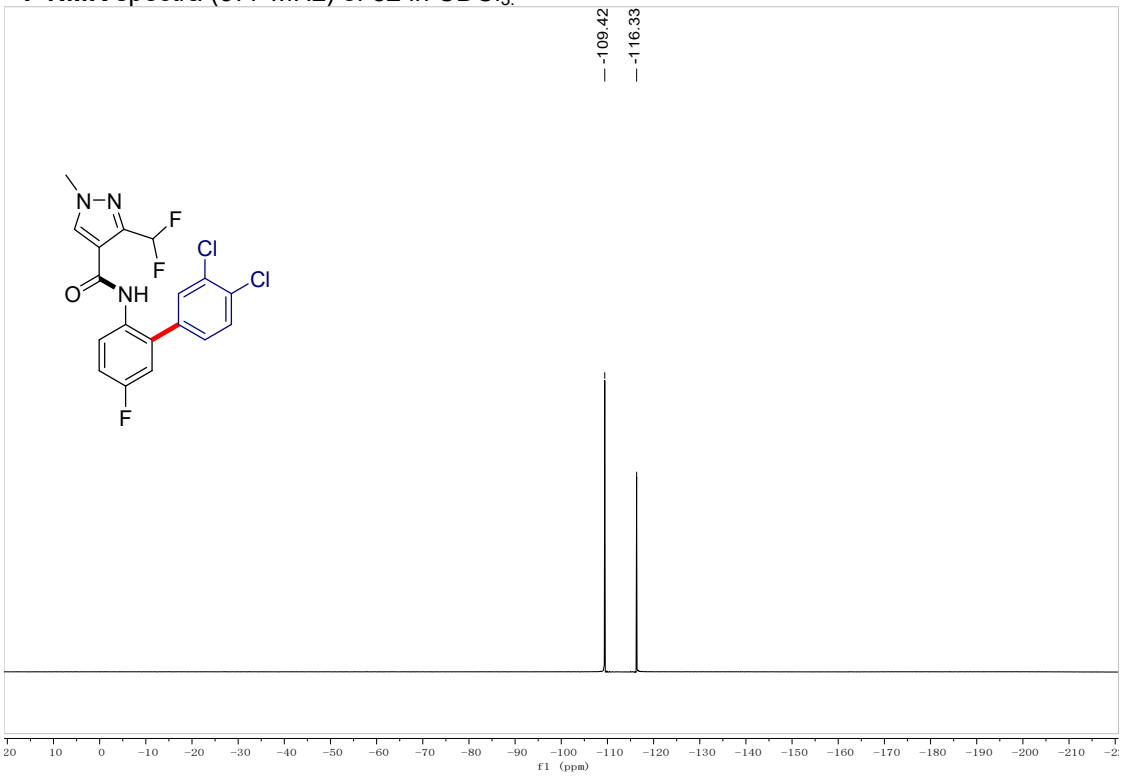
^{1}H NMR spectra (400 MHz) of **82** in $CDCl_3$.



^{13}C NMR spectra (101 MHz) of **82** in $CDCl_3$.



^{19}F NMR spectra (377 MHz) of **82** in $CDCl_3$.



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