Supporting Information

Pd-Catalyzed Relay Heck Arylation of Alkenyl Alcohols with Arylsulfonium Salts

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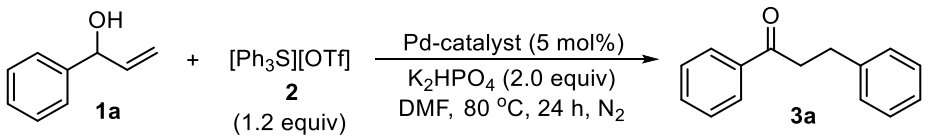
1. General information

All reactions were carried out under a nitrogen atmosphere. Unless otherwise specified, NMR spectra were recorded in $CDCl_3$ or acetone-d_6 on a 500 MHz (for ^1H), 471 MHz (for ^{19}F), 202 MHz (for ^{31}P), and 126 MHz (for ^{13}C) spectrometer. All chemical shifts were reported in ppm relative to TMS (0 ppm for ^1H NMR) or $PhCF_3$ (-63.5 ppm for ^{19}F NMR) or 85% H_3PO_4 (0 ppm for ^{31}P NMR) as an internal or external standard. The HPLC experiments were conducted on a Wufeng LC-100 II instrument (column: Shodex, C18, 5 μm, 4.6 × 250 mm), and the yields of products were determined by using the corresponding pure compounds as external standards. The coupling constants were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet, dd = doublet of doublets, td = triplet of doublets, dm = doublet of multiplets, and tm = triplet of multiplets. Melting points of solid products were measured and uncorrected. MS experiments were performed on a TOF-Q ESI instrument. Dibenzo[*b*,*d*]thiophene 5-oxide (DBTO),[1] thianthrene 5-oxide (TTO),[2] phenoxathiine 10-oxide,[3] 10-methyl-10*H*-phenothiazine 5-oxide,[4] and tetraphenylphosphonium triflate[5] were prepared according to the literature. Solvents were dried before use according to the literature. Other reagents in the reactions were all purchased from the commercial sources and used without further purification. Reactions that require heating employed oil bath as the heat source.

2. Screening of the optimal reaction conditions for the relay Heck arylation of alkenyl alcohols (1) with triphenylsulfonium triflate (2).

Table S1. The relay Heck reactions of **1a** with **2** in the presence of different Pd-catalysts.[a]

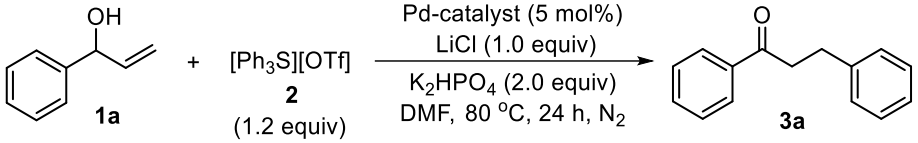


Entry	Pd-catalyst	Yield (**3a**, %)
1	$Pd[P(t\text{-}Bu)_3]_2$	19
2	$Pd(OAc)_2$	5
3	$Pd(dba)_2$	9

4	$Pd(PPh_3)_4$	4
5	$Pd(MeCN)_2Cl_2$	55
6	$Pd(PPh_3)_2Cl_2$	62
7	$PdCl_2$	58

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.24 mmol), K_2HPO_4 (0.4 mmol), Pd-catalyst (0.01 mmol), DMF (2 mL), 80 °C, N_2, and 24 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 9.0 min, λ_{max} = 242 nm, water / methanol = 20 / 80 (v / v)).

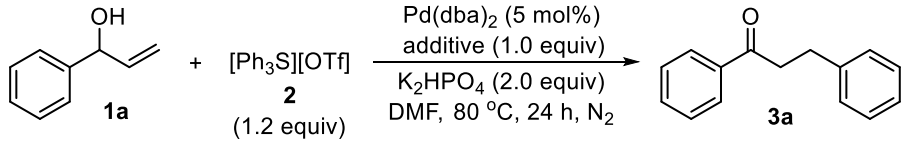
Table S2. The relay Heck reactions of **1a** with **2** and LiCl in the presence of different Pd-catalysts.[a]



Entry	Pd-catalyst	Yield (**3a**, %)
1	$Pd[P(t\text{-}Bu)_3]_2$	24
2	$Pd(OAc)_2$	86
3	$Pd(dba)_2$	90
4	$Pd(PPh_3)_4$	46
5	$Pd(MeCN)_2Cl_2$	90
6	$Pd(PPh_3)_2Cl_2$	68
7	$PdCl_2$	89

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.24 mmol), LiCl (0.2 mmol), K_2HPO_4 (0.4 mmol), Pd-catalyst (0.01 mmol), DMF (2 mL), 80 °C, N_2, and 24 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 9.0 min, λ_{max} = 242 nm, water / methanol = 20 / 80 (v / v)).

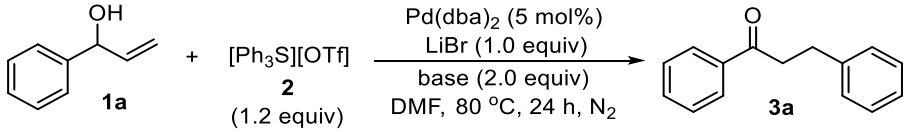
Table S3. The relay Heck reactions of **1a** with **2** and $Pd(dba)_2$ in the presence of different additives.[a]



Entry	Additive	Yield (**3a**, %)
1	LiCl	90
2	LiF	18
3	LiBr	94
4	LiI	83
5	NaBr	75
6	KF	30
7	KBr	73
8	none	9

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.24 mmol), additive (0.2 mmol), K_2HPO_4 (0.4 mmol), $Pd(dba)_2$ (0.01 mmol), DMF (2 mL), 80 °C, N_2, and 24 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 9.0 min, λ_{max} = 242 nm, water / methanol = 20 / 80 (v / v)).

Table S4. The relay Heck reactions of **1a** with **2**, LiBr, and $Pd(dba)_2$ in the presence of different bases.[a]

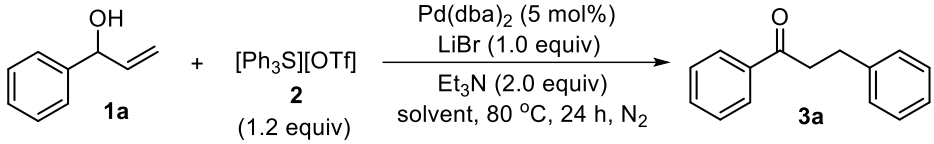


Entry	Base	Yield (**3a**, %)
1	K_2HPO_4	94
2	KH_2PO_4	14
3	K_3PO_4	66
4	KOAc	68
5	Na_2CO_3	89
6	K_2CO_3	94
7	$NaHCO_3$	91
8	DBU	21
9	Et_3N	98
10	CsF	97
11	none	5

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.24 mmol), LiBr (0.2 mmol), base (0.4

mmol), $Pd(dba)_2$ (0.01 mmol), DMF (2 mL), 80 °C, N_2, and 24 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 9.0 min, λ_{max} = 242 nm, water / methanol = 20 / 80 (v / v)).

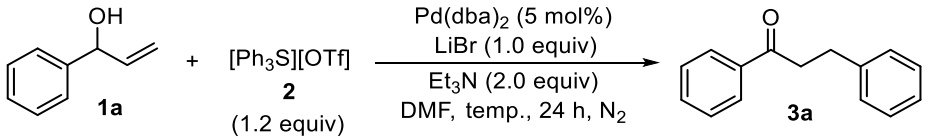
Table S5. The relay Heck reactions of **1a** with **2** in different solvents.[a]



Entry	Solvent	Yield (**3a**, %)
1	DMF	98
2	DMAc	79
3	1,4-dioxane	80
4	DCE	51
5	toluene	72
6	THF	77
7	MeCN	94
8	DMSO	73

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.24 mmol), LiBr (0.2 mmol), Et_3N (0.4 mmol), $Pd(dba)_2$ (0.01 mmol), solvent (2 mL), 80 °C, N_2, and 24 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 9.0 min, λ_{max} = 242 nm, water / methanol = 20 / 80 (v / v)).

Table S6. The relay Heck reactions of **1a** with **2** at different temperatures.[a]

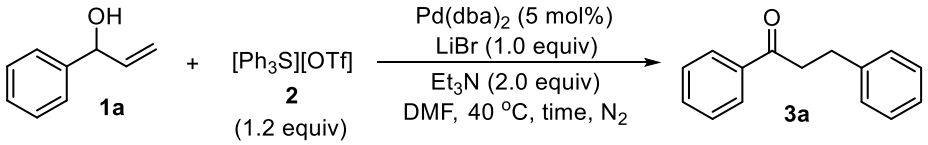


Entry	Temperature (°C)	Yield (**3a**, %)
1	25	94
2	40	97
3	60	96
4	80	98

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.24 mmol), LiBr (0.2 mmol), Et_3N (0.4

mmol), $Pd(dba)_2$ (0.01 mmol), DMF (2 mL), 25-80 °C, N_2, and 24 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 9.0 min, λ_{max} = 242 nm, water / methanol = 20 / 80 (v / v)).

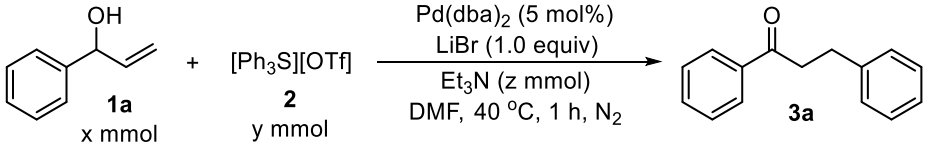
Table S7. The relay Heck reactions of **1a** with **2** in different times.[a]



Entry	Time (h)	Yield (**3a**, %)
1	0.5	51
2	1	95
3	3	97
4	6	98
5	9	97
6	12	98
7	24	97

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.24 mmol), LiBr (0.2 mmol), Et_3N (0.4 mmol), $Pd(dba)_2$ (0.01 mmol), DMF (2 mL), 40 °C, N_2, and 0.5-24 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 9.0 min, λ_{max} = 242 nm, water / methanol = 20 / 80 (v / v)).

Table S8. The relay Heck reactions of **1a** with **2** using different reactant ratios.[a]

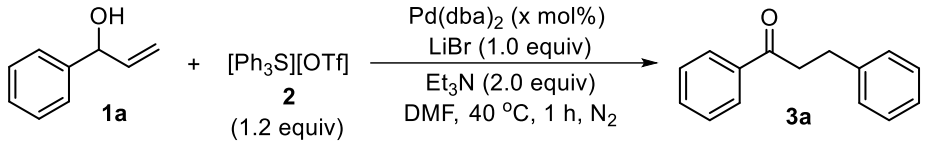


Entry	x : y : z	Yield (**3a**, %)
1	1:1.2:2	95
2	1:1.2:1.5	89
3	1:1.2:1.2	85
4	1:1:1	78

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.2 or 0.24 mmol), LiBr (0.2 mmol), Et_3N

(0.2, 0.24, 0.3 or 0.4 mmol), $Pd(dba)_2$ (0.01 mmol), DMF (2 mL), 40 °C, N_2, and 1 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 9.0 min, λ_{max} = 242 nm, water / methanol = 20 / 80 (v / v)).

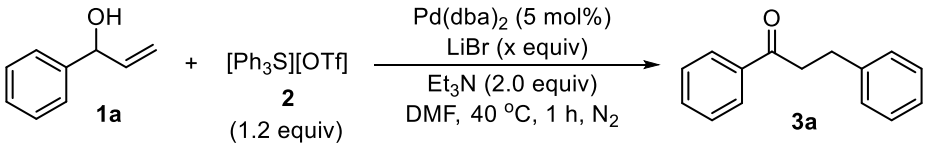
Table S9. The relay Heck reactions of **1a** with **2** using different dosages of catalyst.[a]



Entry	x	Yield (**3a**, %)
1	2.5	70, 90 [b]
2	5	95

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.24 mmol), LiBr (0.2 mmol), Et_3N (0.4 mmol), $Pd(dba)_2$ (0.005 or 0.01 mmol), DMF (2 mL), 40 °C, N_2, and 1 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 9.0 min, λ_{max} = 242 nm, water / methanol = 20 / 80 (v / v)). [b] The reaction was run at 80 °C.

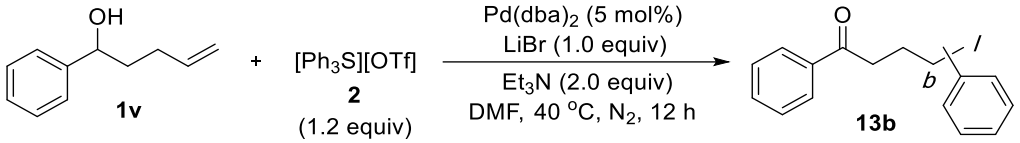
Table S10. The relay Heck reactions of **1a** with **2** using different amounts of LiBr.[a]



Entry	x	Yield (**3a**, %)
1	0.2	81
2	0.5	84
3	1	95

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.24 mmol), LiBr (x mmol), Et_3N (0.4 mmol), $Pd(dba)_2$ (0.01 mmol), DMF (2 mL), 40 °C, N_2, and 1 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 9.0 min, λ_{max} = 242 nm, water / methanol = 20 / 80 (v / v)).

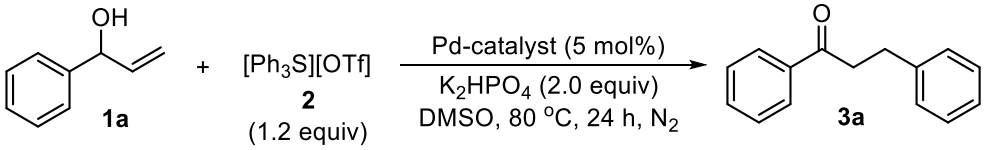
Table S11. The relay Heck reactions of 1-phenylpent-4-en-1-ol (**1v**) with **2** under different conditions.



Entry	Variation from the standard conditions	Yield (**13b**, %)
1	none	47
2	$Pd(OAc)_2$ instead of $Pd(dba)_2$	45
3	$NaHCO_3$ instead of Et_3N	76
4	LiCl instead of LiBr	65

[a] Reaction conditions: **1v** (0.2 mmol), **2** (0.24 mmol), LiBr (0.2 mmol), Et_3N (0.4 mmol), $Pd(dba)_2$ (0.01 mmol), DMF (2 mL), 40 °C, N_2, and 12 h. Isolated yields.

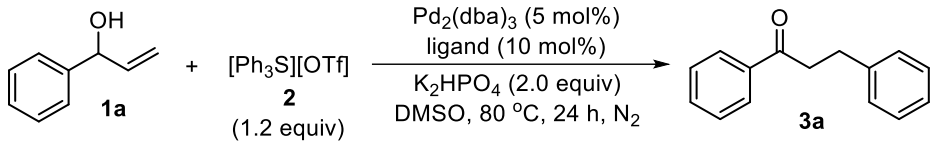
Table S12. The relay Heck reactions of **1a** with **2** in DMSO in the presence of different Pd-catalysts.[a]



Entry	Pd-catalyst	Yield (**3a**, %)
1	$Pd(dba)_2$	60
2	$Pd_2(dba)_3$	64
3	$Pd(PPh_3)_2Cl_2$	64
4	$Pd(PPh_3)_4$	58
5	$Pd[(P(t\text{-}Bu)_3)_2]$	33
6	$Pd(OAc)_2$	35

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.24 mmol), K_2HPO_4 (0.4 mmol), $Pd(dba)_2$ (0.01 mmol), DMSO (2 mL), 80 °C, N_2, and 24 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 9.0 min, λ_{max} = 242 nm, water / methanol = 20 / 80 (v / v)).

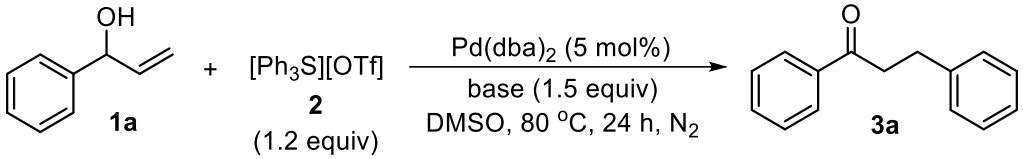
Table S13. The effects of ligand on the $Pd_2(dba)_3$-catalyzed relay Heck reaction of **1a** with **2** in DMSO.[a]



Entry	Ligand	Yield (**3a**, %)
1	PPh_3	63
2	X-Phos	69
3	Xantphos	64
4	dppe	13
5	bpy	52
6	dtbpy	62
7	S-Phos	67

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.24 mmol), K_2HPO_4 (0.4 mmol), $Pd_2(dba)_3$ (0.01 mmol), ligand (0.02 mmol), DMSO (2 mL), 80 °C, N_2, and 24 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 9.0 min, λ_{max} = 242 nm, water / methanol = 20 / 80 (v / v)).

Table S14. The relay Heck reactions of **1a** with **2** in DMSO in the presence of different bases.[a]

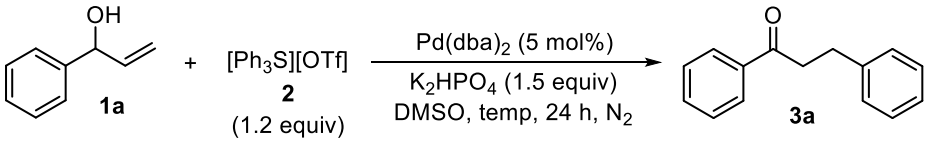


Entry	Base	Yield (**3a**, %)
1	NaOH	1
2	K_2HPO_4	72
3	CsOH	3
4	Na_2CO_3	44
5	Cs_2CO_3	3
6	K_3PO_4	trace
7	NaH	trace
8	KH_2PO_4	14

9	K_2CO_3	31
10	DBU	49
11	Et_3N	39
12	CsF	31
13	LiOH	7
14	$NaHCO_3$	56
15	$(CH_3)_3COK$	trace
16	none	trace

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.24 mmol), base (0.3 mmol), $Pd(dba)_2$ (0.01 mmol), DMSO (2 mL), 80 °C, N_2, and 24 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 9.0 min, λ_{max} = 242 nm, water / methanol = 20 / 80 (v / v)).

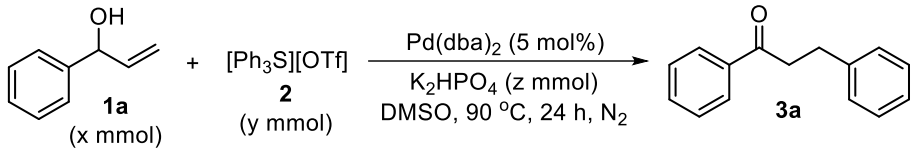
Table S15. The relay Heck reactions of **1a** with **2** in DMSO at different temperatures.[a]



Entry	Temperature (°C)	yield (**3a**, %)
1	25	2
2	40	2
3	60	25
4	80	72
5	90	77
6	100	77

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.24 mmol), K_2HPO_4 (0.3 mmol), $Pd(dba)_2$ (0.01 mmol), DMSO (2 mL), 25-100 °C, N_2, and 24 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 9.0 min, λ_{max} = 242 nm, water / methanol = 20 / 80 (v / v)).

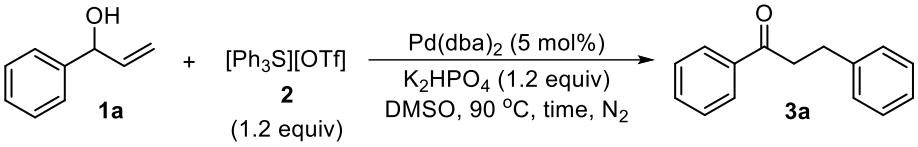
Table S16. The relay Heck reactions of **1a** with **2** in DMSO using different reactant ratios.[a]



Entry	x : y : z	Yield (**3a**, %)
1	1 : 2 : 2	75
2	1 : 1.5 : 2	75
3	1 : 1.2 : 2	74
4	1 : 1.2 : 1.5	72
5	1 : 1.5 : 1.5	78
6	1 : 1.2 : 1.2	77
7	1 : 1.2 : 1	73
8	1 : 1 : 1	63

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.2, 0.24, 0.3, or 0.4 mmol), K_2HPO_4 (0.2, 0.24, 0.3, or 0.4 mmol), $Pd(dba)_2$ (0.01 mmol), DMSO (2 mL), 90 °C, N_2, and 24 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 9.0 min, λ_{max} = 242 nm, water / methanol = 20 / 80 (v / v)).

Table S17. The relay Heck reactions of **1a** with **2** in DMSO in different times.[a]

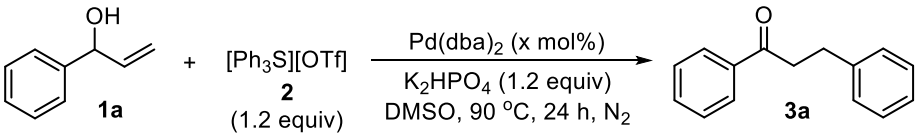


Entry	time (h)	Yield (**3a**, %)
1	12	72
2	24	77
3	36	75

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.24 mmol), K_2HPO_4 (0.24 mmol), $Pd(dba)_2$ (0.01 mmol), DMSO (2 mL), 90 °C, N_2, and 12-36 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 9.0 min, λ_{max} = 242 nm, water / methanol = 20 / 80 (v / v)).

Table S18. The relay Heck reactions of **1a** with **2** in DMSO using different dosages of

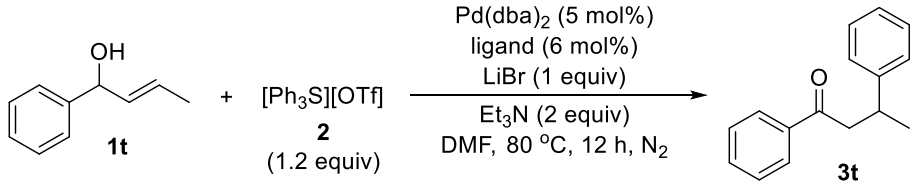
catalyst.[a]



Entry	x	Yield (**3a**, %)
1	2.5	79 (75[b])
2	5	77
3	7.5	73
4	10	70

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.24 mmol), K_2HPO_4 (0.24 mmol), $Pd(dba)_2$ (0.005-0.02 mmol), DMSO (2 mL), 90 °C, N_2, and 24 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 9.0 min, λ_{max} = 242 nm, water / methanol = 20 / 80 (v / v)). [b] Isolated yield.

Table S19. The Pd-catalyzed relay Heck reactions of **1t** with **2** in DMF using extra ligands.[a]



Entry	Ligand	Yield (**3t**, %)	ee value (%)
1	**L1**	0	0
2	**L2**	0	0
3	**L3**	54	5
4	**L4**	trace	-[b]
5	**L5**	29	15
6	**L6**	18	16
7	**L7**	35	11
8 [c]	none	68	0

[a] Reaction conditions: **1t** (0.1 mmol), **2** (0.12 mmol), LiBr (0.1 mmol), Et_3N (0.2 mmol), $Pd(dba)_2$ (0.005 mmol), ligand (0.006 mmol), DMF (1 mL), 80 °C for 12 hours. The yields and ee of **3t** were determined by chiral HPLC using racemic **3t** as an external standard (t_R = 11.7 min and 13.2 min, λ = 254 nm, *n*-hexane / isopropanol

= 90 / 10 (v / v)). [b] Not determined. [c] The reaction was run for 5 h. Isolated yield.

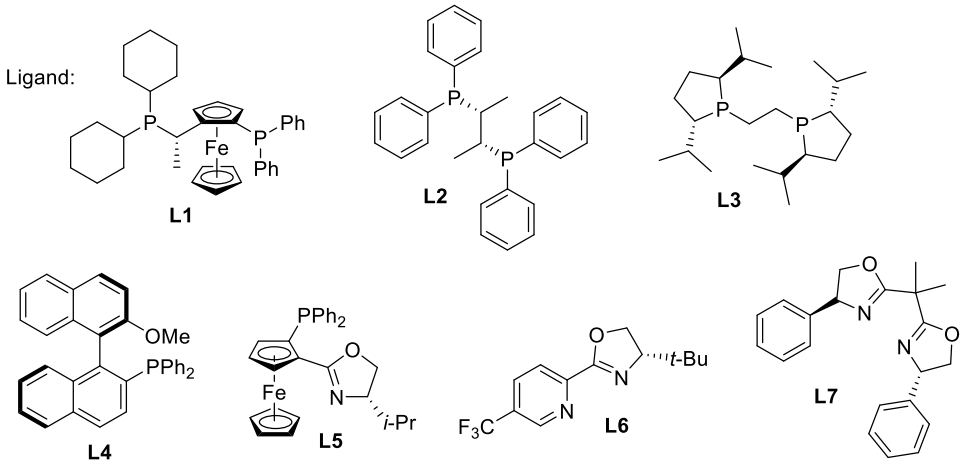
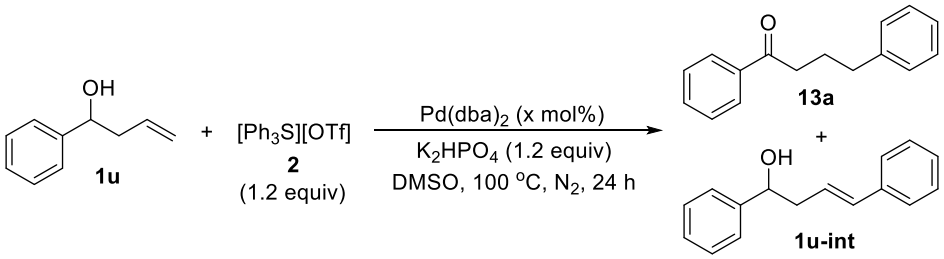


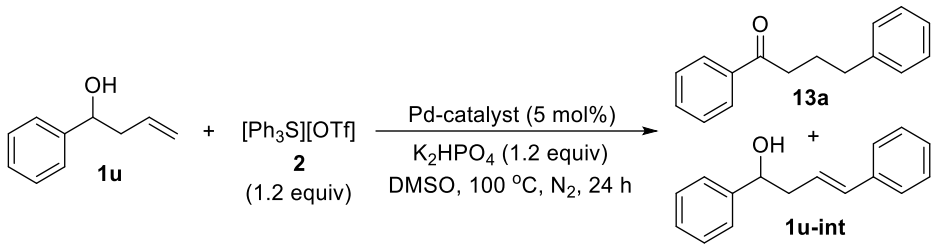
Table S20. The relay Heck reactions of **1u** with **2** in DMSO under the above optimal conditions.[a]



Entry	x	Yield (**13a**, %)	Yield (**1u-int**, %)
1	5	11	75
2	10	12	77
3	15	12	74
4	20	13	77

[a] Reaction conditions: **1u** (0.1 mmol), **2** (0.12 mmol), K_2HPO_4 (0.12 mmol), $Pd(dba)_2$ (0.005-0.02 mmol), DMSO (1 mL), 100 °C, N_2, and 24 h. The yields of **13a** and **1u-int** were determined by HPLC using pure **13a** (t_R = 11.2 min, λ_{max} = 241 nm, water / methanol = 20 / 80 (v / v) and **1u-int** (t_R = 7.8 min, λ = 241 nm, water / methanol = 20 / 80 (v / v) as external standards, respectively.

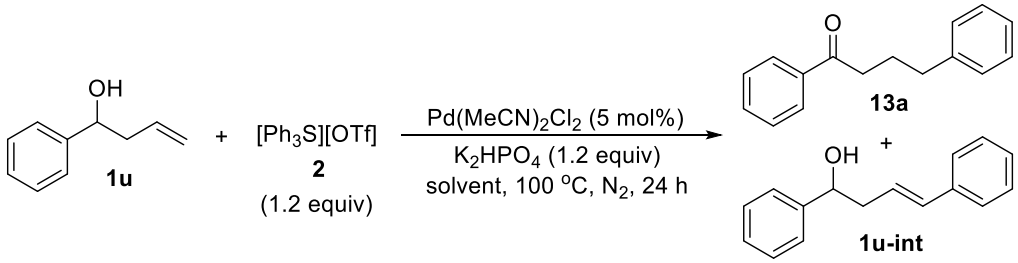
Table S21. The relay Heck reactions of **1u** with **2** in DMSO in the presence of different Pd-catalysts.[a]



Entry	Pd-catalyst	Yield (**13a,** %)	Yield (**1u-int**, %)
1	$Pd(dba)_2$	11	75
2	$Pd(PPh_3)_2Cl_2$	10	83
3	$Pd(dppf)_2Cl_2$	12	73
4	$Pd(TFA)_2$	trace	38
5	$Pd(MeCN)Cl_2$	23	56

[a] Reaction conditions: **1u** (0.1 mmol), **2** (0.12 mmol), K_2HPO_4 (0.12 mmol), Pd-catalyst (0.005 mmol), DMSO (1 mL), 100 °C, N_2, and 24 h. The yields of **13a** and **1u-int** were determined by HPLC using pure **13a** (t_R = 11.2 min, λ_{max} = 241 nm, water / methanol = 20 / 80 (v / v) and **1u-int** (t_R = 7.8 min, λ = 241 nm, water / methanol = 20 / 80 (v / v) as external standards, respectively.

Table S22. The relay Heck reactions of **1u** with **2** and $Pd(MeCN)_2Cl_2$ without using additives in different solvents.[a]

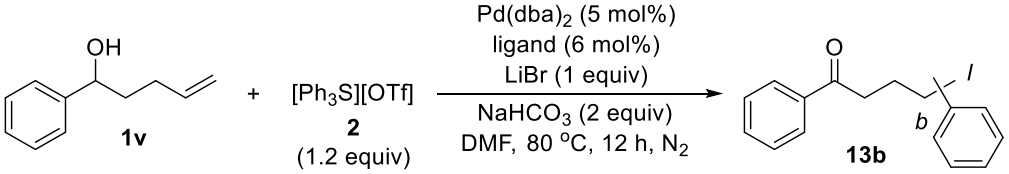


Entry	Solvent	Yield (**13a**, %)	Yield (**1u-int**, %)
1	DMF	38	31
2	DMAc	28	34
3	DMSO	23	56
4	DG	8	18
5	MeCN	trace	3
6	DCE	trace	5

7	DME	7	35
8	toluene	4	23
9	TFA	trace	trace
10	1,4-dioxane	7	16
11	DMC	trace	14
12	EA	6	32
13	*n*-octane	trace	trace
14	mesitylene	5	10

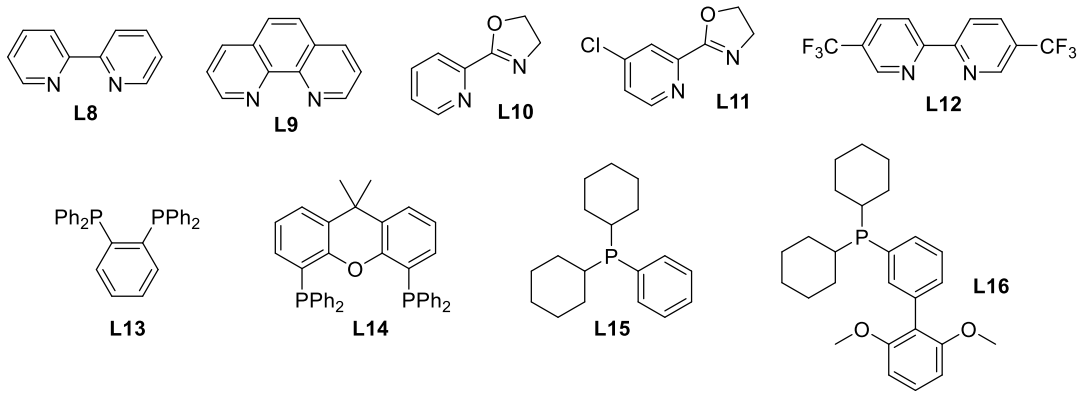
[a] Reaction conditions: **1u** (0.1 mmol), **2** (0.12 mmol), K_2HPO_4 (0.12 mmol), $Pd(MeCN)_2Cl_2$ (0.005 mmol), solvent (1 mL), 100 °C, N_2, and 24 h. The yields of **13a** and **1u-int** were determined by HPLC using pure **13a** (t_R = 11.2 min, λ_{max} = 241 nm, water / methanol = 20 / 80 (v / v) and **1u-int** (t_R = 7.8 min, λ = 241 nm, water / methanol = 20 / 80 (v / v) as external standards, respectively.

Table S23. The relay Heck reactions of **1v** with **2** in the presence of $Pd(dba)_2$ using extra ligands.[a]



Entry	Ligand	Yield (**13b**, %)	*l*/*b*
1	**L8**	30	2.6/1
2	**L9**	0	0
3	**L10**	51	4.1/1
4	**L11**	75	4.3/1
5	**L12**	63	4.6/1
6	**L13**	0	0
7	**L14**	0	0
8	**L15**	trace	-[b]
9	**L16**	79	3.8/1
10	none	76	4.9/1

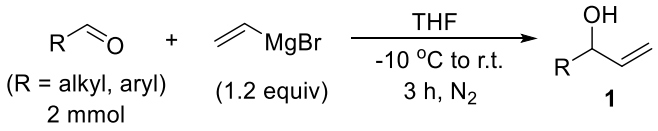
[a] Reaction conditions: **1v** (0.1 mmol), **2** (0.12 mmol), LiBr (0.1 mmol), $NaHCO_3$ (0.2 mmol), $Pd(dba)_2$ (0.005 mmol), ligand (0.006 mmol), DMF (1 mL), 80 °C, N_2, and 12 h. Isolated yields. The *l*/*b* ratios were determined by ^1H NMR. [b] Not determined.



3. The relay Heck reactions of diverse allylic alcohols (1) with triphenylsulfonium triflate (2).

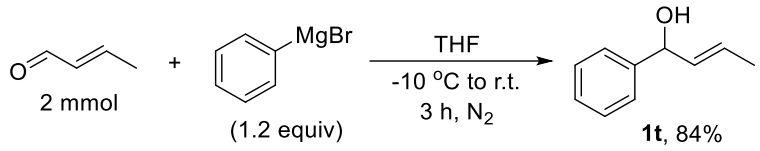
3.1. General procedure for the synthesis of allylic alcohols (1) from aldehydes.[6]

Procedure A:[6a] Under a nitrogen atmosphere, a sealed tube was charged with aldehyde (2 mmol) and THF (1 mL) with stirring and cooled to -10 ^{o}C. Vinyl magnesium bromide (2.4 mmol, 1.0 M in THF) was slowly added. The mixture was then warmed to room temperature, reacted for 3 h, quenched by a saturated aqueous ammonium chloride solution (20 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with water, dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluents to give the desired product (**1**).



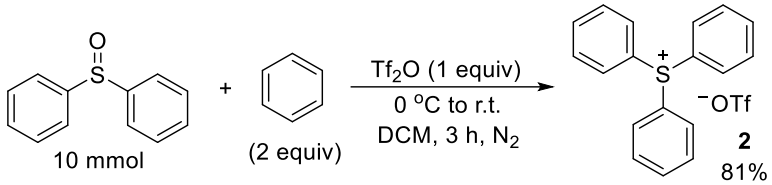
Procedure B:[6b] Under a nitrogen atmosphere, a sealed tube was charged with crotonaldehyde (140 mg, 2 mmol) and THF (1 mL) with stirring and cooled to -10 ^{o}C. Phenyl magnesium bromide (2.4 mmol, 1.0 M in THF) was slowly added. The mixture was then warmed to room temperature, reacted for 3 h, quenched by a saturated aqueous ammonium chloride solution (20 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with water, dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (10/1, v/v) as eluents to give the desired product (**1t**)

as a colorless oil (249 mg, 84%).



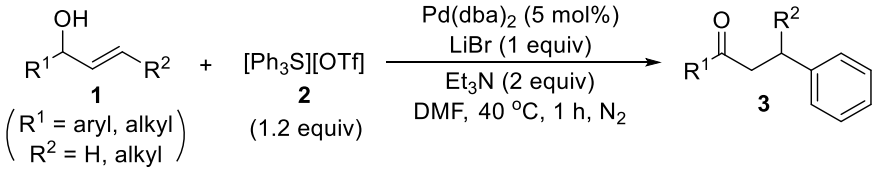
3.2. Procedure for the synthesis of triphenylsulfonium triflate (2).[7]

To a stirred mixture of diphenyl sulfoxide (2.02 g, 10 mmol) and benzene (1.56 g, 20 mmol) in CH_2Cl_2 (20 mL) was slowly added trifluoromethanesulfonic anhydride (2.82 g, 10 mmol) at 0 °C. The mixture was reacted at room temperature for 3 h, poured into water (20 mL), and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were concentrated to dryness under reduced pressure. The residue was crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford triphenylsulfonium triflate (**2**) as a white solid (3.34 g, 81%).

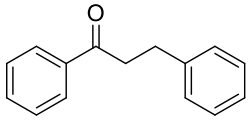


3.3. General procedure for the relay Heck arylation of diverse allylic alcohols (1) with triphenylsulfonium triflate (2).

In a nitrogen-filled glovebox, a sealed tube was charge with **1** (0.2 mmol), triphenylsulfonium triflate (**2**, 99.0 mg, 0.24 mmol), LiBr (17.4 mg, 0.2 mmol), $Pd(dba)_2$ (5.8 or 11.6 mg, 0.01 or 0.02 mmol), Et_3N (40.5 mg, 0.4 mmol), and DMF (2 mL) with vigorous stirring. The mixture was reacted at 40, 50 or 80 °C for 1, 3 or 5 hours, cooled to room temperature, diluted with water (30 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether (PE) and ethyl acetate (EA) as eluents to give the desired product (**3**).

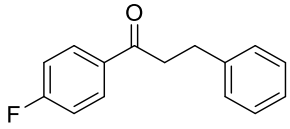


3-Phenylpropiophenone (**3a**)[8]



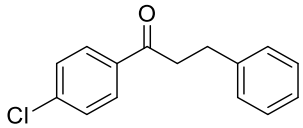
White solid (40.1 mg, 95%, eluents: PE/EA = 80/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.28 (d, *J* = 7.3 Hz, 2H), 7.23 (t, *J* = 7.1 Hz, 1H), 3.32 (t, *J* = 7.6 Hz, 2H), 3.09 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 141.3, 136.9, 133.1, 128.6, 128.6, 128.5, 128.1, 126.2, 40.5, 30.2.

1-(4-Fluorophenyl)-3-phenylpropan-1-one (**3b**)[8]



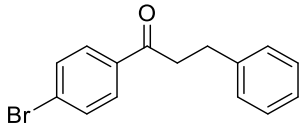
Yellow solid (33.4 mg, 73%, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.8 Hz, 5.4 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.25 (d, *J* = 7.1 Hz, 2H), 7.21 (tm, *J* = 7.2 Hz, 1H), 7.12 (t, *J* = 8.6 Hz, 2H), 3.28 (t, *J* = 7.7 Hz, 2H), 3.07 (t, *J* = 7.7 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -105.3 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.6, 165.7 (d, *J* = 255.3 Hz), 141.2, 133.3 (d, *J* = 2.9 Hz), 130.7 (d, *J* = 9.3 Hz), 128.6, 128.4, 126.2, 115.7 (d, *J* = 21.8 Hz), 40.4, 30.1.

1-(4-Chlorophenyl)-3-phenylpropan-1-one (**3c**)[8]



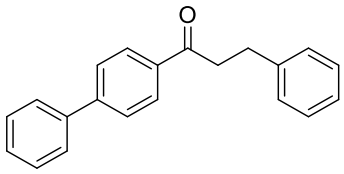
White solid (38.1 mg, 78%, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 3.27 (t, *J* = 7.6 Hz, 2H), 3.06 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.0, 141.1, 139.5, 135.2, 129.5, 128.9, 128.6, 128.4, 126.2, 40.4, 30.1.

1-(4-Bromophenyl)-3-phenylpropan-1-one (**3d**)[8]



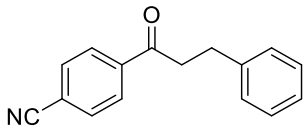
White solid (47.8 mg, 83%, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 7.1 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 3.27 (t, *J* = 7.6 Hz, 2H), 3.06 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.2, 141.1, 135.6, 131.9, 129.6, 128.6, 128.4, 128.2, 126.3, 40.4, 30.1.

1-([1,1'-Biphenyl]-4-yl)-3-phenylpropan-1-one (**3e**)[9]



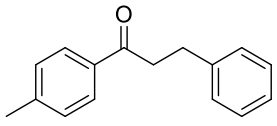
White solid (45.9 mg, 80%, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.28 (d, *J* = 7.0 Hz, 2H), 7.22 (t, *J* = 7.1 Hz, 1H), 3.34 (t, *J* = 7.6 Hz, 2H), 3.11 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.9, 145.8, 141.3, 139.9, 135.6, 129.0, 128.7, 128.6, 128.5, 128.3, 127.3, 127.3, 126.2, 40.5, 30.2.

4-(3-Phenylpropanoyl)benzonitrile (**3f**)[10]



Yellow solid (38.2 mg, 81%, eluents: PE/EA = 10/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 6.9 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 3.31 (t, *J* = 7.6 Hz, 2H), 3.08 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.8, 140.7, 139.8, 132.5, 128.6, 128.5, 128.4, 126.4, 117.9, 116.4, 40.8, 29.9.

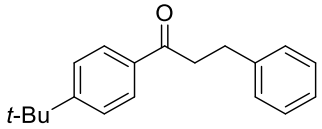
3-Phenyl-1-(*p*-tolyl)propan-1-one (**3g**)[8]



White solid (40.6 mg, 91%, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.26-7.22 (m, 4H), 7.2 (t, *J* = 7.2 Hz, 1H), 3.27 (t, *J* = 7.8 Hz, 2H), 3.06 (t, *J* = 7.8 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (126

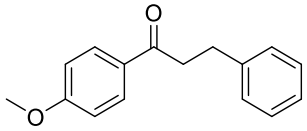
MHz, $CDCl_3$) δ 198.9, 143.8, 141.4, 134.4, 129.3, 128.5, 128.4, 128.2, 126.1, 40.4, 30.3, 21.6.

1-(4-(*tert*-Butyl)phenyl)-3-phenylpropan-1-one (**3h**)[9]



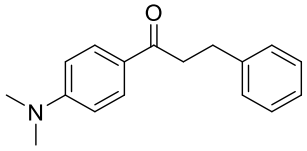
Light yellow oil (41.5 mg, 78%, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 6.8 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 3.32 (t, *J* = 7.6 Hz, 2H), 3.10 (t, *J* = 7.7 Hz, 2H), 1.38 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.9, 156.8, 141.5, 134.4, 128.5, 128.4, 128.1, 126.1, 125.6, 40.4, 35.1, 31.1, 30.2.

1-(4-Methoxyphenyl)-3-phenylpropiophenone (**3i**)[8]



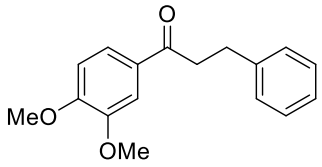
White solid (46.5 mg, 97%, eluents: PE/EA = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.0 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.26 (d, *J* = 6.8 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H), 3.25 (t, *J* = 7.5 Hz, 2H), 3.06 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.9, 163.5, 141.5, 130.3, 130.0, 128.5, 128.5, 126.1, 113.8, 55.5, 40.1, 30.4.

1-(4-(Dimethylamino)phenyl)-3-phenylpropan-1-one (**3j**)[11]



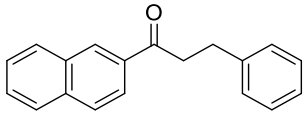
Light yellow solid (32.2 mg, 64%, eluents: PE/EA = 10/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 9.1 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 2H), 7.26 (d, *J* = 6.7 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 8.9 Hz, 2H), 3.21 (t, *J* = 7.7 Hz, 2H), 3.07-3.04 (m, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.4, 153.4, 141.9, 130.3, 128.5, 128.5, 126.0, 124.9, 110.7, 40.0, 39.8, 30.7.

1-(3,4-Dimethoxyphenyl)-3-phenylpropan-1-one (**3k**)[9]



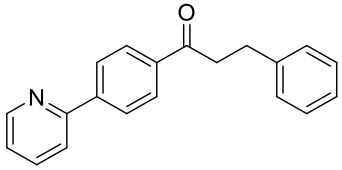
White solid (31.7 mg, 59%, eluents: PE/EA = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.25 (d, *J* = 6.8 Hz, 2H), 7.20 (t, *J* = 7.1 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.26 (t, *J* = 7.7 Hz, 2H), 3.06 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.9, 153.3, 149.1, 141.5, 130.2, 128.5, 128.5, 126.1, 122.7, 110.2, 110.0, 56.1, 56.0, 40.0, 30.5.

1-(Naphthalen-2-yl)-3-phenylpropan-1-one (**3l**)[8]



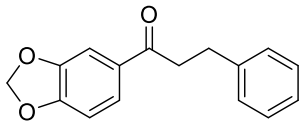
White solid (45.3 mg, 87%, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.05 (dd, *J* = 8.6 Hz, 1.8 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.89 (t, *J* = 8.6 Hz, 2H), 7.60 (tm, *J* = 7.5 Hz, 1H), 7.55 (tm, *J* = 7.5 Hz, 1H), 7.35-7.30 (m, 4H), 7.24 (m, 1H), 3.45 (t, *J* = 7.7 Hz, 2H), 3.15 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 141.4, 135.6, 134.2, 132.6, 129.7, 129.6, 128.6, 128.5, 128.5, 128.5, 127.8, 126.8, 126.2, 123.9, 40.6, 30.3.

3-Phenyl-1-(4-(pyridin-2-yl)phenyl)propan-1-one (**3m**)



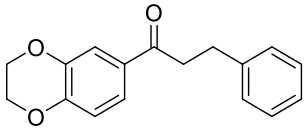
White solid (40.3 mg, 70%, eluents: PE/EA = 5/1). M.p.: 94-96 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (d, *J* = 4.8 Hz, 1H), 8.10-8.05 (m, 4H), 7.78 (m, 2H), 7.33-7.26 (m, 5H), 7.21 (t, *J* = 7.1 Hz, 1H), 3.35 (t, *J* = 7.7 Hz, 2H), 3.10 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.9, 156.1, 149.9, 143.6, 141.3, 136.9, 136.9, 128.6, 128.5, 127.1, 126.2, 122.9, 121.0, 40.6, 30.2. IR (KBr): 3061, 3025, 2914, 2861, 1673, 1605, 1584, 1462, 1443, 1405, 1291, 1276, 1258, 1210, 1152, 1093, 1027, 1006, 980, 831, 769, 753, 738, 701 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{20}H_{18}NO]^{+}$ ($[M + H]^{+}$): 288.1383; found: 288.1389.

1-(Benzo[*d*][1,3]dioxol-5-yl)-3-phenylpropan-1-one (**3n**)[12]



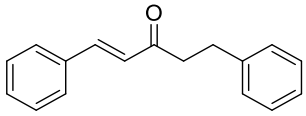
Light yellow solid (40.0 mg, 79%, eluents: PE/EA = 10/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.1 Hz, 1.7 Hz, 1H), 7.44 (d, *J* = 1.7 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.25 (d, *J* = 7.1 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.03 (s, 2H), 3.22 (t, *J* = 7.7 Hz, 2H), 3.05 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.3, 151.7, 148.2, 141.4, 131.8, 128.5, 128.4, 126.1, 124.3, 107.9, 107.9, 101.8, 40.2, 30.4.

1-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)-3-phenylpropan-1-one (**3o**)[13]



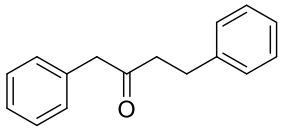
White solid (35.7 mg, 67%, eluents: PE/EA = 10/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55-7.50 (m, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.27 (d, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.1 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 4.34-4.27 (m, 4H), 3.24 (t, *J* = 7.7 Hz, 2H), 3.07 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.7, 148.0, 143.4, 141.4, 130.8, 128.5, 128.4, 126.1, 122.2, 117.6, 117.2, 64.7, 64.1, 40.1, 30.3.

(*E*)-1,5-diphenylpent-1-en-3-one (**3p**)[14]



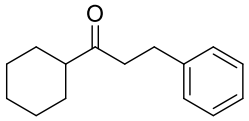
Yellow solid (37.0 mg, 78%, eluents: PE/EA = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.56 (m, 3H), 7.43 (m, 3H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.29 (d, *J* = 7.3 Hz, 2H), 7.25 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 16.3 Hz, 1H), 3.05 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.3, 142.7, 141.3, 134.5, 130.5, 129.0, 128.6, 128.4, 128.3, 126.2, 126.2, 42.5, 30.2.

1,4-Diphenylbutan-2-one (**3q**)[15]



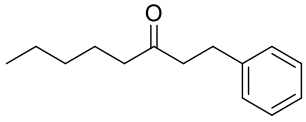
Light yellow solid (28.7 mg, 64%, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.3 Hz, 2H), 7.30-7.27 (m, 3H), 7.23-7.19 (m, 3H), 7.16 (d, *J* = 7.5 Hz, 2H), 3.70 (s, 2H), 2.90 (t, *J* = 7.5 Hz, 2H), 2.80 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.5, 140.9, 134.1, 129.4, 128.8, 128.5, 128.3, 127.1, 126.1, 50.4, 43.5, 29.8.

1-Cyclohexyl-3-phenylpropan-1-one (**3r**)[11]



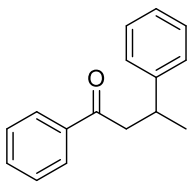
Colorless oil (30.2 mg, 70%, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.5 Hz, 2H), 7.11-7.09 (m, 3H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.67 (t, *J* = 7.5 Hz, 2H), 2.23 (m, 1H), 1.74-1.67 (m, 4H), 1.58 (m, 1H), 1.29-1.08 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 213.2, 141.4, 128.5, 128.3, 126.0, 51.0, 42.3, 29.8, 28.4, 25.9, 25.7.

1-Phenyloctan-3-one (**3s**)[10]



Colorless oil (28.6 mg, 71%, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.6 Hz, 2H), 7.23-7.20 (m, 3H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.40 (t, *J* = 7.5 Hz, 2H), 1.59 (m, 2H), 1.35-1.25 (m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.4, 141.2, 128.5, 128.3, 126.1, 44.3, 43.1, 31.4, 29.8, 23.5, 22.5, 13.9.

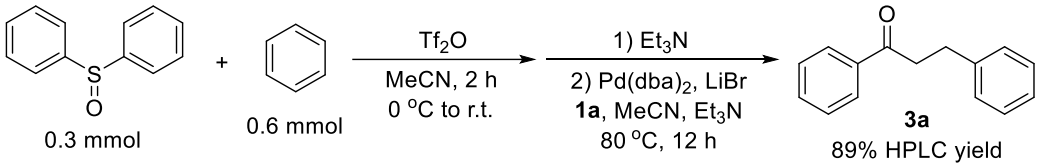
1,3-Diphenylbutan-1-one (**3t**)[11]



White solid (30.4 mg, 68%, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ

7.93 (d, *J* = 8.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.32-7.27 (m, 4H), 7.20 (tm, *J* = 6.9 Hz, 1H), 3.51 (m, 1H), 3.31 (dd, *J* = 16.4 Hz, 5.9 Hz, 1H), 3.19 (dd, *J* = 16.5 Hz, 8.3 Hz, 1H), 1.35 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.1, 146.6, 137.2, 133.0, 128.6, 128.6, 128.1, 126.9, 126.3, 47.1, 35.6, 21.9.

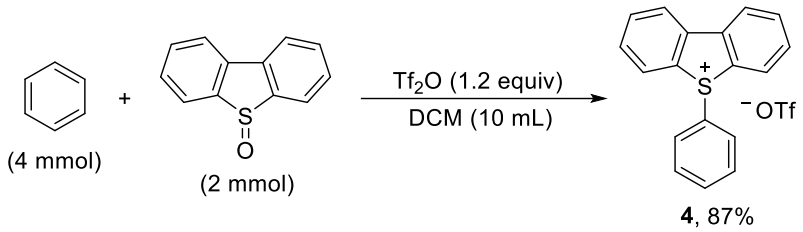
An example of two-step reaction in one-pot fashion from arene.



Procedure: Under a N_2 atmosphere, trifluoromethanesulfonic anhydride (60 μL, 0.36 mmol) was added slowly to a mixture of diphenyl sulfoxide (60.7 mg, 0.3 mmol) and benzene (46.9 mg, 0.6 mmol) in MeCN (1 mL) at 0 °C with stirring. The mixture was reacted at room temperature for 2 h. Then, Et_3N (60.7 mg, 0.6 mmol) was added to neutralize the reaction mixture. After 2 h, **1a** (26.8 mg, 0.2 mmol), $Pd(dba)_2$ (5.8 mg, 5 mol%), LiBr (17.4 mg, 1 equiv), Et_3N (20.2 mg, 0.2 mmol), and MeCN (1 mL) were added. The resulting mixture was heated at 80 °C under N_2 for 12 h. The yield was determined by HPLC using pure **3a** as an external standard (t_R = 9.0 min, λ_{max} = 242 nm, water / methanol = 20 / 80 (v / v)).

4. The relay Heck reactions of 1-phenylprop-2-en-1-ol (1a) with different arylsulfonium salts.

4.1 Procedure for the synthesis of 5-phenyl-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (4)[16]

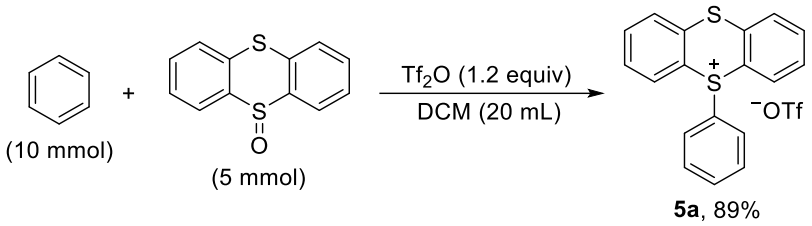


Under a N_2 atmosphere, Tf_2O (0.4 mL, 2.4 mmol) was added to a mixture of benzene (0.312 g, 4 mmol), dibenzo[*b,d*]thiophene 5-oxide (401 mg, 2 mmol), and DCM (10 mL) at -40 °C. The mixture was reacted at room temperature for 3 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to

dryness under reduced pressure. The residue was crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford 5-phenyl-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**4**) as a white solid (714 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.8 Hz, 2H), 8.11 (d, *J* = 8.1 Hz, 2H), 7.84 (t, *J* = 7.7 Hz, 2H), 7.65-7.58 (m, 5H), 7.50 (t, *J* = 7.8 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.0, 135.0, 134.6, 131.8, 131.7, 131.6, 130.6, 128.6, 126.5, 124.3, 120.9 (q, *J* = 321.0 Hz).

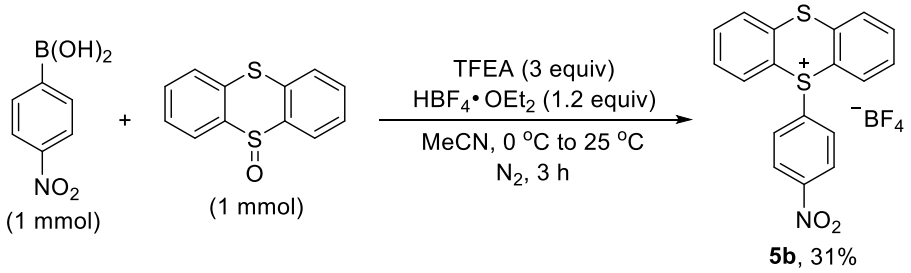
4.2 Procedures for the synthesis of arylthianthrenium salts (5).

5-Phenyl-5*H*-thianthren-5-ium trifluoromethanesulfonate (**5a**)[16]



Under a N_2 atmosphere, Tf_2O (1.0 mL, 6 mmol) was added to a mixture of benzene (0.781 g, 10 mmol), thianthrene 5-oxide (1.16 g, 5 mmol), and DCM (20 mL) at -40 ^{o}C. The mixture was reacted at room temperature for 3 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford 5-phenyl-5*H*-thianthren-5-ium trifluoromethanesulfonate (**5a**) as a white solid (1.96 g, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (d, *J* = 7.8 Hz, 2H), 7.85-7.80 (m, 4H), 7.76 (tm, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.7, 135.6, 135.0, 133.0, 130.7, 130.3, 130.3, 128.0, 124.1, 120.1 (q, *J* = 320.3 Hz), 118.8.

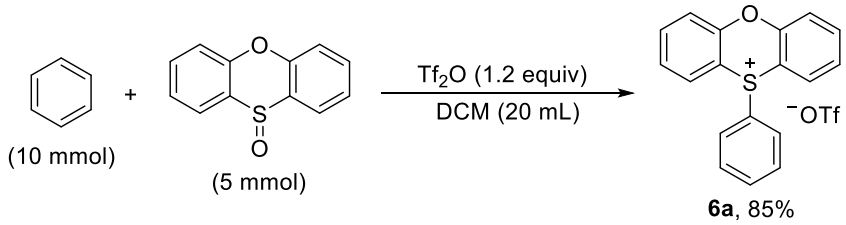
5-(4-Nitrophenyl)-5*H*-thianthren-5-ium tetrafluoroborate (**5b**)[17]



Under a N_2 atmosphere, a flask was charged with thianthrene 5-oxide (232 mg, 1 mmol), 4-nitrophenylboronic acid (167 mg, 1 mmol), and dry MeCN (5 mL) with stirring. After cooling to 0 °C, trifluoroacetic anhydride (0.42 mL, 0.64 g, 3.0 mmol) was added, followed by addition of HBF_4•OEt_2 (174 μL, 1.20 mmol). The deep purple mixture was kept at 0 °C for 1 h and warmed to 25 °C over a period of 1 h. After another 1 h, the reaction mixture was concentrated to dryness under reduced pressure. The residue was diluted with DCM (10 mL) and washed with a saturated aqueous $NaHCO_3$ solution (10 mL). The aqueous layer was extracted with DCM (2 ×10 mL). The DCM solutions were collected, washed with aqueous $NaBF_4$ solutions (2 × 10 mL, 5 % w/w), dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel (eluents: DCM/MeCN = 3/1 (v/v)) and then crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford 5-(4-nitrophenyl)-5H-thianthren-5-ium tetrafluoroborate (**5b**) as a white solid (132 mg, 31%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (m, 2H), 8.22 (d, *J* = 9.1 Hz, 2H), 7.87-7.83 (m, 6H), 7.35 (d, *J* = 9.1 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -149.9 (brs), -149.9 (brs). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.1, 136.8, 136.3, 135.4, 131.2, 130.7, 130.5, 129.4, 125.1, 118.4.

4.3 Procedures for the synthesis of arylphenoxathiinium salt (6).

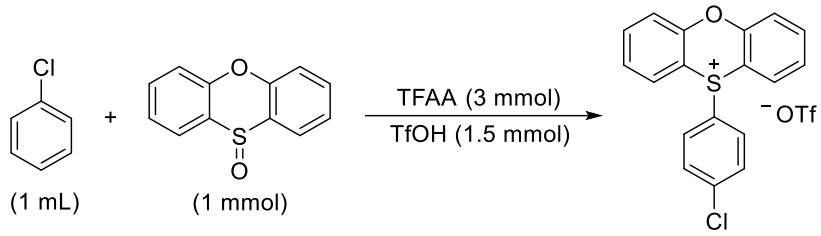
10-Phenyl-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6a**)[16]



Under a N_2 atmosphere, Tf_2O (1.0 mL, 6 mmol) was added to a mixture of benzene (0.781 g, 10 mmol), phenoxathiine 10-oxide (1.08 g, 5 mmol), and DCM (20 mL) at -40 ^{o}C. The mixture was reacted at room temperature for 3 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford 10-phenyl-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6a**) as a white solid (1.82 g, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.0 Hz, 2H), 7.83 (t, *J* = 7.9 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H),

7.61 (d, *J* = 8.4 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.54-7.47 (m, 4H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.7, 136.9, 134.5, 132.0, 131.6, 131.3, 129.0, 127.6, 120.9 (q, *J* = 321.0 Hz), 120.4, 105.7.

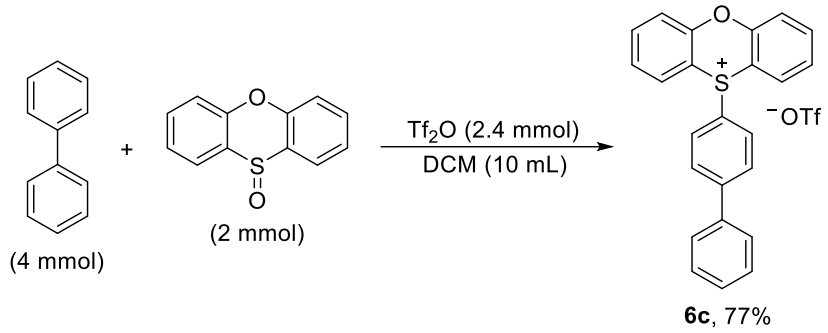
10-(4-Chlorophenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6b**)



6b, 55%

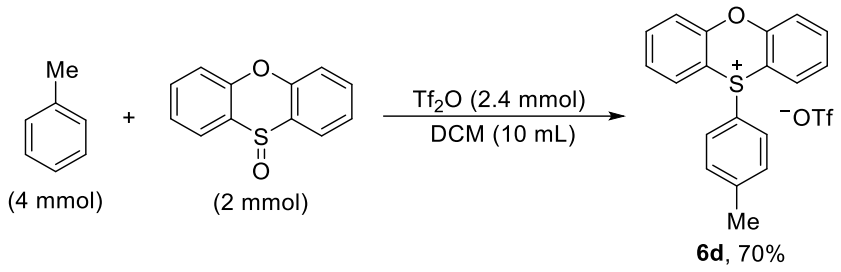
Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.42 mL, 3 mmol) and trifluoromethanesulfonic acid (TfOH, 0.13 mL, 1.5 mmol) were successively added to a mixture of chlorobenzene (1 mL) and phenoxathiine 10-oxide (216 mg, 1 mmol) at room temperature. The mixture was reacted at room temperature for 12 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were washed with aqueous NaOTf solutions (2 × 20 mL, 5% (w/w)), dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel (eluents: DCM/MeCN = 3/1 (v/v)) and then crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford 10-(4-chlorophenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6b**) as a gray solid (253 mg, 55%). M.p.: 137-139 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.8 Hz, 2H), 7.83 (t, *J* = 7.8 Hz, 2H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.2 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.7, 141.5, 136.9, 132.4, 131.8, 130.5, 129.6, 127.8, 120.8 (q, *J* = 320.5 Hz), 120.3, 105.8. IR (KBr): 3082, 3059, 1590, 1582, 1479, 1461, 1442, 1276, 1257, 1223, 1159, 1151, 1093, 1062, 1026, 1005, 882, 831, 770, 636 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{18}H_{12}ClOS]^+$ ($[M]^+$): 313.0262, found: 313.0270.

10-([1,1'-Biphenyl]-4-yl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6c**)



Under a N_2 atmosphere, Tf_2O (0.4 mL, 2.4 mmol) was added to a mixture of 1,1'-biphenyl (616 mg, 4 mmol), phenoxathiine 10-oxide (432 mg, 2 mmol), and DCM (10 mL) at -40 °C. The mixture was reacted at room temperature for 3 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel (eluents: DCM/MeCN = 3/1 (v/v)) and then crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford 10-([1,1'-biphenyl]-4-yl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6c**) as a white solid (777 mg, 77%). M.p.: 168-169 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.9 Hz, 2H), 7.84-7.81 (m, 4H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.43-7.39 (m, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.7, 147.6, 138.0, 136.7, 132.2, 130.0, 129.7, 129.4, 129.2, 129.2, 127.6, 127.3, 120.9 (q, *J* = 319.8 Hz), 120.3, 106.1. IR (KBr): 3070, 3026, 1595, 1586, 1468, 1439, 1272, 1256, 1224, 1182, 1151, 1061, 1028, 1003, 889, 850, 771, 758, 704, 640 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{24}H_{17}OS]^+$ ($[M]^+$): 353.0995; found: 353.0996.

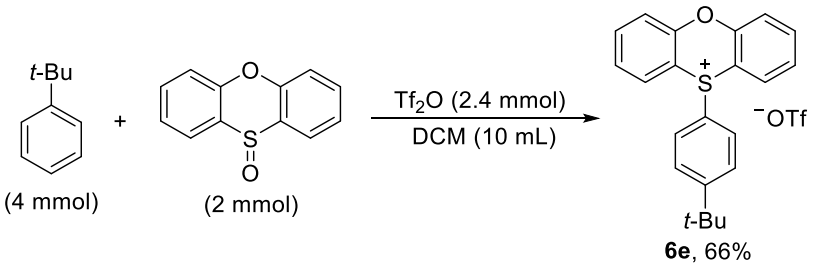
10-(*p*-Tolyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6d**)[3]



Under a N_2 atmosphere, Tf_2O (0.4 mL, 2.4 mmol) was added to a mixture of toluene (368 mg, 4 mmol), phenoxathiine 10-oxide (432 mg, 2 mmol), and DCM (10 mL) at -40 °C. The mixture was reacted at room temperature for 3 h, neutralized by a saturated

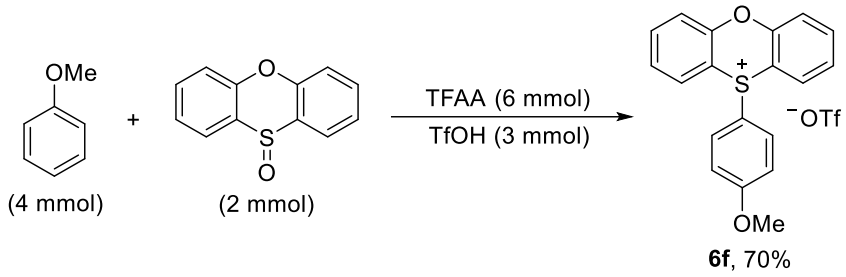
aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel (eluents: DCM/MeCN = 3/1 (v/v)) and then crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford 10-(*p*-tolyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6d**) as a white solid (618 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 8.0 Hz, 1.5 Hz, 2H), 7.80 (tm, *J* = 7.9 Hz, 2H), 7.61-7.58 (m, 4H), 7.47 (tm, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 2.31 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.3 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.6, 146.1, 136.6, 132.2, 132.1, 129.2, 127.9, 127.6, 120.9 (q, *J* = 321.4 Hz), 120.2, 106.2, 21.6.

10-(4-(*Tert*-butyl)phenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6e**)[18]



Under a N_2 atmosphere, Tf_2O (0.4 mL, 2.4 mmol) was added to a mixture of *tert*-butylbenzene (536 mg, 4 mmol), phenoxathiine 10-oxide (432 mg, 2 mmol), and DCM (10 mL) at -40 °C. The mixture was reacted at room temperature for 3 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel (eluents: DCM/MeCN = 3/1 (v/v)) and then crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford 10-(4-(*tert*-butyl)phenyl)-10H-phenoxathiin-10-ium trifluoromethanesulfonate (**6e**) as a white solid (639 mg, 66%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 8.1 Hz, 1.5 Hz, 2H), 7.81 (tm, *J* = 7.9 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.61 (dd, *J* = 8.4 Hz, 1.1 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.48 (tm, *J* = 7.8 Hz, 2H), 1.21 (s, 9H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.0 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 151.7, 136.6, 132.1, 129.1, 128.8, 127.8, 127.6, 121.0 (q, *J* = 320.1 Hz), 120.3, 106.3, 35.4, 30.8.

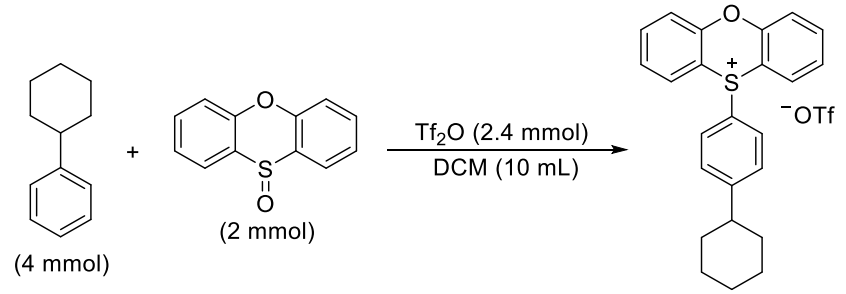
10-(4-Methoxyphenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6f**)



6f, 70%

Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.84 mL, 6 mmol) and trifluoromethanesulfonic acid (TfOH, 0.26 mL, 3 mmol) were successively added to a mixture of anisole (432 mg, 4 mmol) and phenoxathiine 10-oxide (432 mg, 2 mmol) in MeCN (4 mL) at -40 °C. The mixture was reacted at room temperature for 5 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were washed with aqueous NaOTf solutions (2 × 20 mL, 5% (w/w)), dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel (eluents: DCM/MeCN = 3/1 (v/v)) and then crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford 10-(4-methoxyphenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6f**) as a white solid (638 mg, 70%). M.p.: 132-134 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 2H), 7.79 (t, *J* = 7.9 Hz, 2H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 151.4, 136.5, 131.9, 131.4, 127.5, 120.9 (q, *J* = 320.6 Hz), 120.9, 120.3, 117.1, 106.7, 56.1. IR (KBr): 3093, 3026, 2990, 2946, 1589, 1575, 1499, 1471, 1439, 1317, 1273, 1258, 1222, 1183, 1155, 1070, 1030, 1020, 889, 838, 779, 758, 636 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{19}H_{15}O_2S]^+$ ($[M]^+$): 308.0821; found: 308.0826.

10-(4-Cyclohexylphenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6g**)

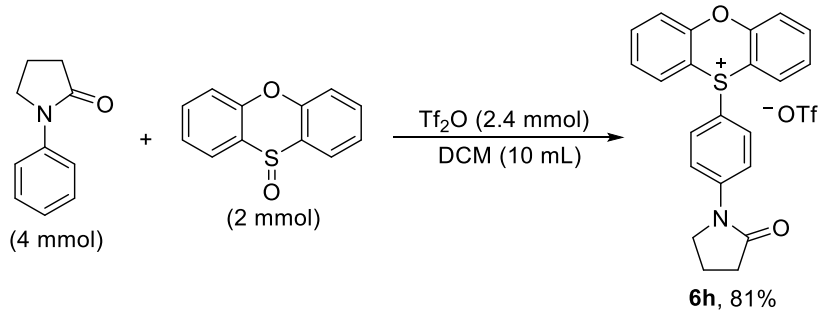


6g, 77%

Under a N_2 atmosphere, Tf_2O (0.4 mL, 2.4 mmol) was added to a mixture of

cyclohexylbenzene (641 mg, 4 mmol), phenoxathiine 10-oxide (432 mg, 2 mmol), and DCM (10 mL) at -40 °C. The mixture was reacted at room temperature for 3 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel (eluents: DCM/MeCN = 3/1 (v/v)) and then crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford 10-(4-cyclohexylphenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6g**) as a white solid (784 mg, 77%). M.p.: 75-76 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.7 Hz, 2H), 7.80 (t, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 2.48 (m, 1H), 1.80-1.70 (m, 5H), 1.35-1.24 (m, 5H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 151.6, 136.7, 131.9, 130.2, 129.3, 127.9, 127.5, 120.9 (q, *J* = 320.6 Hz), 120.4, 106.1, 44.5, 33.8, 26.4, 25.7. IR (KBr): 3089, 3067, 3026, 2924, 2852, 1592, 1583, 1466, 1440, 1272, 1259, 1224, 1150, 1066, 1029, 887, 771, 637 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{24}H_{23}OS]^+$ ($[M]^+$): 359.1464; found: 359.1473.

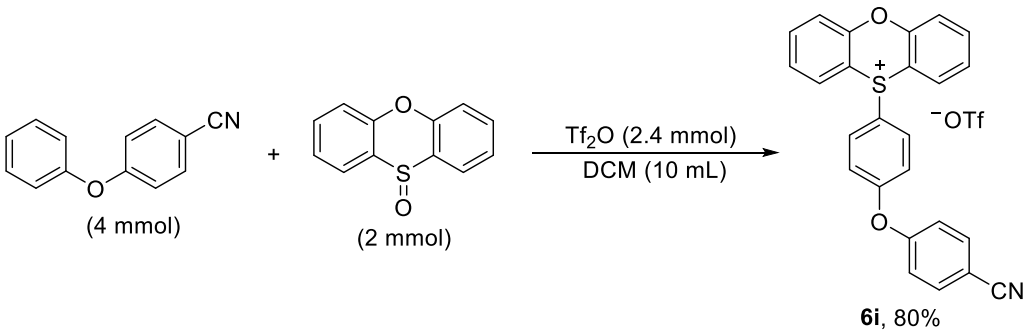
10-(4-(2-Oxopyrrolidin-1-yl)phenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6h**)



Under a N_2 atmosphere, Tf_2O (0.4 mL, 2.4 mmol) was added to a mixture of 1-phenylpyrrolidin-2-one (644 mg, 4 mmol), phenoxathiine 10-oxide (432 mg, 2 mmol), and DCM (10 mL) at -40 °C. The mixture was reacted at room temperature for 3 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel (eluents: DCM/MeCN = 3/1 (v/v)) and then crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford 10-(4-(2-

oxopyrrolidin-1-yl)phenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6h**) as a white solid (825 mg, 81%). M.p.: 138-140 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.9 Hz, 2H), 7.81-7.76 (m, 4H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 3.82 (t, *J* = 7.1 Hz, 2H), 2.58 (t, *J* = 8.0 Hz, 2H), 2.15 (m, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.2, 151.5, 144.9, 136.5, 132.0, 130.5, 127.6, 124.3, 121.3, 120.9 (q, *J* = 320.3 Hz), 120.2, 106.3, 48.3, 32.7, 17.7. IR (KBr): 3100, 3069, 3027, 2956, 2895, 1701, 1585, 1496, 1486, 1469, 1438, 1421, 1388, 1329, 1309, 1272, 1262, 1225, 1150, 1030, 889, 839, 765, 636 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{22}H_{18}NO_2S]^+$ ($[M]^+$): 360.1053; found: 360.1058.

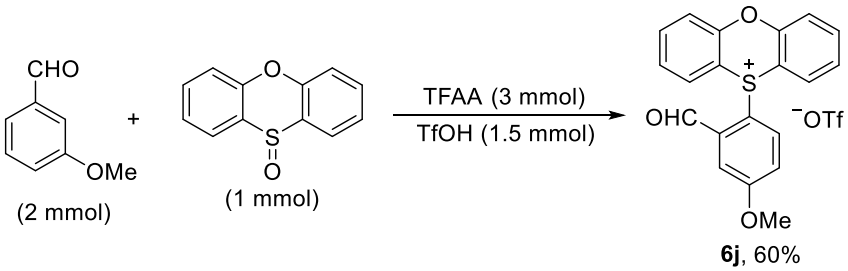
10-(4-(4-Cyanophenoxy)phenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6i**)



Under a N_2 atmosphere, Tf_2O (0.4 mL, 2.4 mmol) was added to a mixture of 4-phenoxybenzonitrile (780 mg, 4 mmol), phenoxathiine 10-oxide (432 mg, 2 mmol), and DCM (10 mL) at -40 °C. The mixture was reacted at room temperature for 3 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel (eluents: DCM/MeCN = 3/1 (v/v)) and then crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford 10-(4-(4-cyanophenoxy)phenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6i**) as a white solid (870 mg, 80%). M.p.: 190-192 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.9 Hz, 2H), 7.83 (t, *J* = 7.6 Hz, 2H), 7.79 (d, *J* = 8.9 Hz, 2H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.0, 158.3, 151.6, 136.8, 134.6, 132.1, 132.0, 127.7, 125.3,

121.1, 120.9 (q, *J* = 320.7 Hz), 120.4, 120.4, 118.1, 108.7, 106.0. IR (KBr): 3097, 3064, 3025, 2226, 1579, 1501, 1486, 1470, 1438, 1276, 1261, 1228, 1156, 1031, 888, 876, 836, 763, 637 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{25}H_{16}NO_2S]^+$ ($[M]^+$): 394.0896; found: 396.0905.

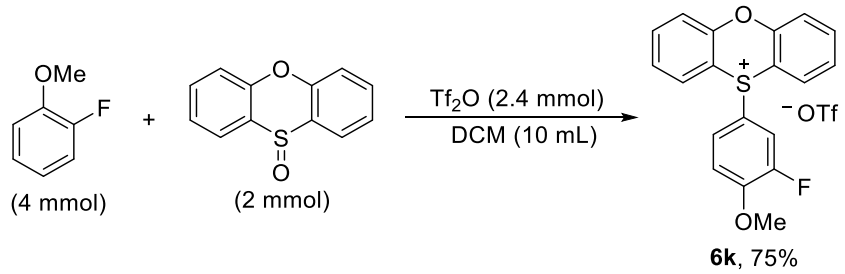
10-(2-Formyl-4-methoxyphenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6j**)



6j, 60%

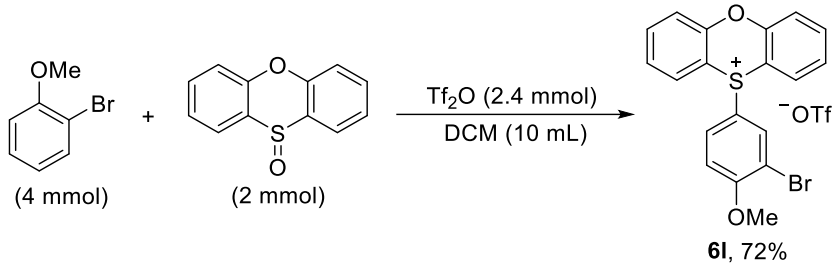
Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.42 mL, 3 mmol) and trifluoromethanesulfonic acid (TfOH, 0.13 mL, 1.5 mmol) were successively added to a mixture of 3-methoxybenzaldehyde (272 mg, 2 mmol) and phenoxathiine 10-oxide (216 mg, 1 mmol) in MeCN (2 mL) at -40 °C. The mixture was reacted at room temperature for 12 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were washed with aqueous NaOTf solutions (2 × 20 mL, 5% (w/w)), dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel (eluents: DCM/MeCN = 3/1 (v/v)) and then crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford 10-(2-formyl-4-methoxyphenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6j**) as a white solid (292 mg, 60%). M.p.: 157-159 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.16 (s, 1H), 8.29 (d, *J* = 8.0 Hz, 2H), 7.83 (t, *J* = 7.6 Hz, 2H), 7.71 (d, *J* = 2.3 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.16 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 6.99 (d, *J* = 9.0 Hz, 1H), 3.89 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.2 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.1, 164.4, 153.3, 136.8, 136.8, 132.0, 127.5, 122.5, 121.2, 120.8 (q, *J* = 320.6 Hz), 120.5, 117.7, 106.6, 56.8. IR (KBr): 3082, 3026, 2946, 2891, 1694, 1591, 1479, 1462, 1440, 1324, 1271, 1263, 1252, 1224, 1149, 1032, 882, 784, 765, 637 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{20}H_{15}O_3S]^+$ ($[M]^+$): 335.0736; found: 335.0742.

10-(3-Fluoro-4-methoxyphenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6k**)



Under a N_2 atmosphere, Tf_2O (0.4 mL, 2.4 mmol) was added to a mixture of 1-fluoro-2-methoxybenzene (504 mg, 4 mmol), phenoxathiine 10-oxide (432 mg, 2 mmol), and DCM (10 mL) at -40 ^oC. The mixture was reacted at room temperature for 12 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel (eluents: DCM/MeCN = 3/1 (v/v)) and then crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford 10-(3-fluoro-4-methoxyphenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6k**) as a white solid (712 mg, 75%). M.p.: 128-130 ^oC. ^1H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 8.7 Hz, 1H), 7.82 (t, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.25 (m, 1H), 7.15 (t, *J* = 8.4 Hz, 1H), 3.88 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.1 (s, 3F), -126.4 (t, *J* = 9.8 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.6 (d, *J* = 10.2 Hz), 152.9 (d, *J* = 257.9 Hz), 151.4, 136.8, 131.9, 128.5 (d, *J* = 3.6 Hz), 127.7, 121.0 (d, *J* = 6.2 Hz), 120.9 (q, *J* = 319.7 Hz), 120.5, 116.2 (d, *J* = 21.9 Hz), 115.2 (d, *J* = 2.0 Hz), 106.1, 56.8 (d, *J* = 1.2 Hz). IR (KBr): 3070, 3029, 3014, 2974, 2939, 2847, 1598, 1585, 1510, 1469, 1439, 1325, 1278, 1222, 1165, 1149, 1071, 1032, 1016, 888, 861, 762, 636 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{19}H_{14}FO_2S]^+$ ($[M]^+$): 326.0727; found: 326.0737.

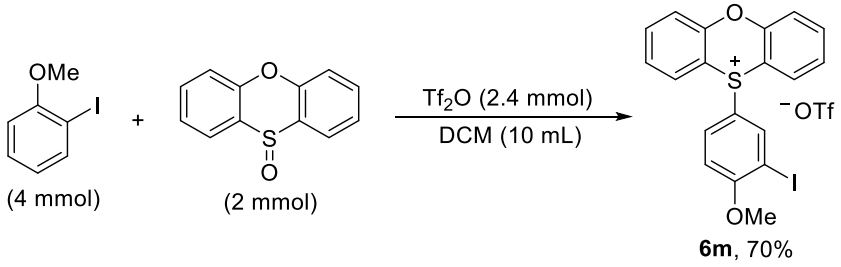
10-(3-Bromo-4-methoxyphenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6l**)



6l, 72%

Under a N_2 atmosphere, Tf_2O (0.4 mL, 2.4 mmol) was added to a mixture of 1-bromo-2-methoxybenzene (748 mg, 4 mmol), phenoxathiine 10-oxide (432 mg, 2 mmol), and DCM (10 mL) at -40 °C. The mixture was reacted at room temperature for 12 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel (eluents: DCM/MeCN = 3/1 (v/v)) and then crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford 10-(3-bromo-4-methoxyphenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6l**) as a white solid (770 mg, 72%). M.p.: 112-114 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.8 Hz, 2H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.82 (t, *J* = 7.6 Hz, 2H), 7.64-7.61 (m, 3H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 9.0 Hz, 1H), 3.89 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.1, 151.4, 136.8, 133.1, 132.0, 131.8, 127.7, 122.1, 120.9 (q, *J* = 321.1 Hz), 120.5, 114.8, 113.9, 106.1, 57.1. IR (KBr): 3092, 3024, 2942, 2847, 1583, 1574, 1484, 1470, 1439, 1329, 1292, 1282, 1277, 1228, 1159, 1049, 1026, 887, 822, 783, 772, 635 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{19}H_{14}BrO_2S]^+$ ($[M]^+$): 384.9892; found: 384.9899.

10-(3-Iodo-4-methoxyphenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6m**)

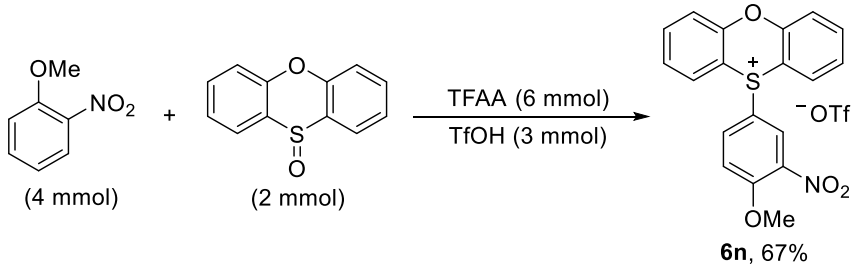


6m, 70%

Under a N_2 atmosphere, Tf_2O (0.4 mL, 2.4 mmol) was added to a mixture of 1-iodo-2-methoxybenzene (936 mg, 4 mmol), phenoxathiine 10-oxide (432 mg, 2 mmol), and DCM (10 mL) at -40 °C. The mixture was reacted at room temperature for 12 h,

neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel (eluents: DCM/MeCN = 3/1 (v/v)) and then crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford 10-(3-iodo-4-methoxyphenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6m**) as a white solid (815 mg, 70%). M.p.: 112-114 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.0 Hz, 2H), 8.03 (d, *J* = 8.7 Hz, 1H), 7.83-7.80 (m, 3H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 1H), 3.88 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2, 151.4, 139.1, 136.8, 132.8, 131.8, 127.7, 122.5, 120.9 (q, *J* = 320.4 Hz), 120.5, 112.7, 106.1, 88.6, 57.3. IR (KBr): 3064, 3025, 2977, 2946, 1584, 1473, 1437, 1276, 1261, 1222, 1163, 1029, 1011, 888, 819, 766, 637 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{19}H_{14}IO_2S]^+$ ($[M]^+$): 432.9754; found: 432.9761.

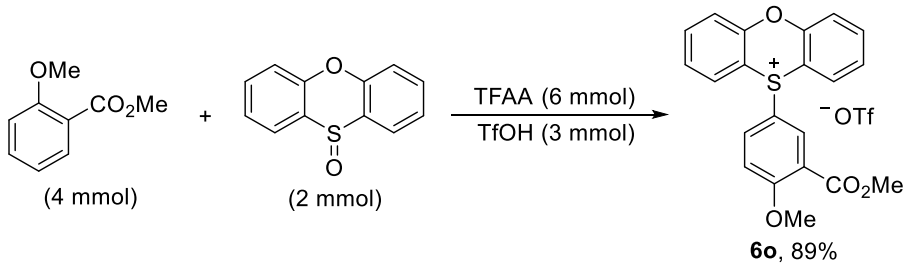
10-(4-Methoxy-3-nitrophenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6n**)



Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.84 mL, 6 mmol) and trifluoromethanesulfonic acid (TfOH, 0.26 mL, 3 mmol) were successively added to a mixture of 1-methoxy-2-nitrobenzene (612 mg, 4 mmol) and phenoxathiine 10-oxide (432 mg, 2 mmol) in MeCN (4 mL) at -40 °C. The mixture was reacted at room temperature for 12 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were washed with aqueous NaOTf solutions (2 × 20 mL, 5% (w/w)), dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel (eluents: DCM/MeCN = 3/1 (v/v)) and then crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford 10-(4-methoxy-3-nitrophenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate

(**6n**) as a white solid (672 mg, 67%). M.p.: 186-188 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 2H), 8.17 (dd, *J* = 9.2 Hz, 2.0 Hz, 1H), 8.11 (d, *J* = 2.4 Hz, 1H), 7.85 (t, *J* = 7.8 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 9.2 Hz, 1H), 3.98 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.2 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.3, 151.6, 140.1, 137.2, 135.9, 131.9, 127.9, 126.8, 121.8, 120.8 (q, *J* = 321.6 Hz), 120.7, 117.4, 105.3, 57.7. IR (KBr): 3064, 3024, 2952, 2852, 1604, 1572, 1531, 1470, 1438, 1354, 1274, 1260, 1226, 1162, 1030, 1005, 887, 809, 778, 750, 637 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{19}H_{14}NO_4S]^+$ ($[M]^+$): 353.0672; found: 353.0679.

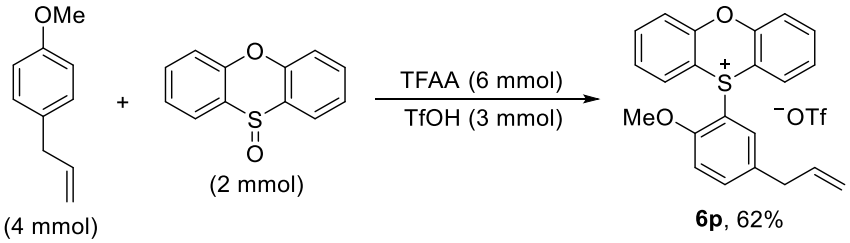
10-(4-Methoxy-3-(methoxycarbonyl)phenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6o**)



Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.84 mL, 6 mmol) and trifluoromethanesulfonic acid (TfOH, 0.26 mL, 3 mmol) were successively added to a mixture of methyl 2-methoxybenzoate (664 mg, 4 mmol) and phenoxathiine 10-oxide (432 mg, 2 mmol) in MeCN (4 mL) at -40 °C. The mixture was reacted at room temperature for 12 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were washed with aqueous NaOTf solutions (2 × 20 mL, 5% (w/w)), dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel (eluents: DCM/MeCN = 3/1 (v/v)) and then crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford 10-(4-methoxy-3-(methoxycarbonyl)phenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6o**) as a white solid (916 mg, 89%). M.p.: 111-113 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18-8.15 (m, 3H), 7.94 (d, *J* = 2.7 Hz, 1H), 7.81 (tm, *J* = 7.9 Hz, 2H), 7.61 (dd, *J* = 8.4 Hz, 1.0 Hz, 2H), 7.50 (tm, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 9.2 Hz, 1H), 3.90 (s, 3H), 3.84 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.2 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2, 163.5, 151.5, 136.7, 135.7, 132.7, 131.9, 127.7,

123.2, 121.2, 120.9 (q, *J* = 321.0 Hz), 120.4, 115.2, 106.1, 56.9, 52.8. IR (KBr): 3085, 3060, 3022, 2998, 2949, 1708, 1595, 1491, 1466, 1438, 1410, 1323, 1303, 1278, 1263, 1225, 1162, 1147, 1105, 1029, 1005, 886, 815, 776, 762, 638 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{21}H_{17}O_4S]^+$ ($[M]^+$): 366.0876; found: 366.0885.

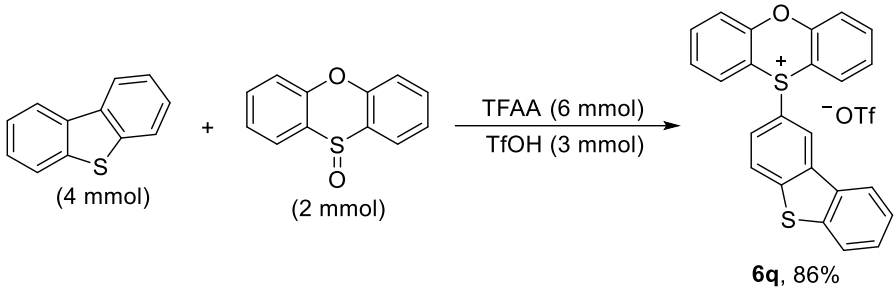
10-(5-Allyl-2-methoxyphenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6p**)



Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.84 mL, 6 mmol) and trifluoromethanesulfonic acid (TfOH, 0.26 mL, 3 mmol) were successively added to a mixture of 1-allyl-4-methoxybenzene (592 mg, 4 mmol) and phenoxathiine 10-oxide (432 mg, 2 mmol) in MeCN (4 mL) at -40 °C. The mixture was reacted at room temperature for 12 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were washed with aqueous NaOTf solutions (2 × 20 mL, 5% (w/w)), dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel (eluents: DCM/MeCN = 3/1 (v/v)) and then crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford 10-(5-allyl-2-methoxyphenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6p**) as a white solid (616 mg, 62%). M.p.: 144-146 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.9 Hz, 2H), 7.79 (t, *J* = 7.9 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.09 (s, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 5.77 (m, 1H), 5.04 (d, *J* = 9.9 Hz, 1H), 4.98 (d, *J* = 17.2 Hz, 1H), 3.89 (s, 3H), 3.27 (d, *J* = 6.6 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.6, 152.6, 137.4, 136.5, 135.6, 135.1, 132.0, 129.9, 127.1, 120.9 (q, *J* = 320.7 Hz), 119.7, 117.3, 116.2, 113.7, 103.6, 56.9, 38.6. IR (KBr): 3079, 3023, 2935, 2827, 1638, 1594, 1571, 1500, 1469, 1437, 1271, 1261, 1166, 1029, 1009, 889, 783, 757, 637 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{22}H_{19}O_2S]^+$ ($[M]^+$): 347.1100; found: 347.1108.

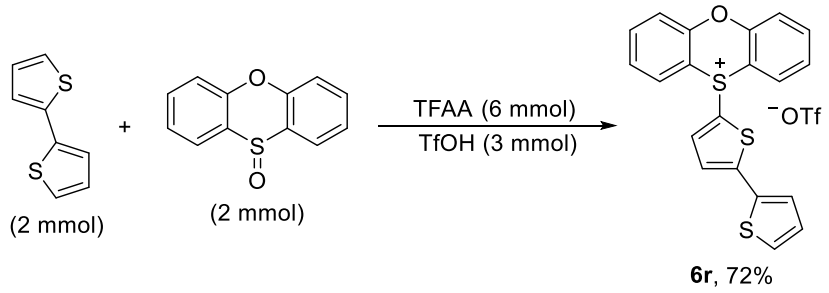
10-(Dibenzo[*b*,*d*]thiophen-2-yl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate

(**6q**)



Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.84 mL, 6 mmol) and trifluoromethanesulfonic acid (TfOH, 0.26 mL, 3 mmol) were successively added to a mixture of dibenzo[*b*,*d*]thiophene (737 mg, 4 mmol) and phenoxathiine 10-oxide (432 mg, 2 mmol) in MeCN (4 mL) at -40 °C. The mixture was reacted at room temperature for 5 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were washed with aqueous NaOTf solutions (2 × 20 mL, 5% (w/w)), dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel (eluents: DCM/MeCN = 3/1 (v/v)) and then crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford 10-(dibenzo[*b*,*d*]thiophen-2-yl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6q**) as a light yellow solid (915 mg, 86%, with impurity). This impure product was used for the relay Heck reaction without further purification.

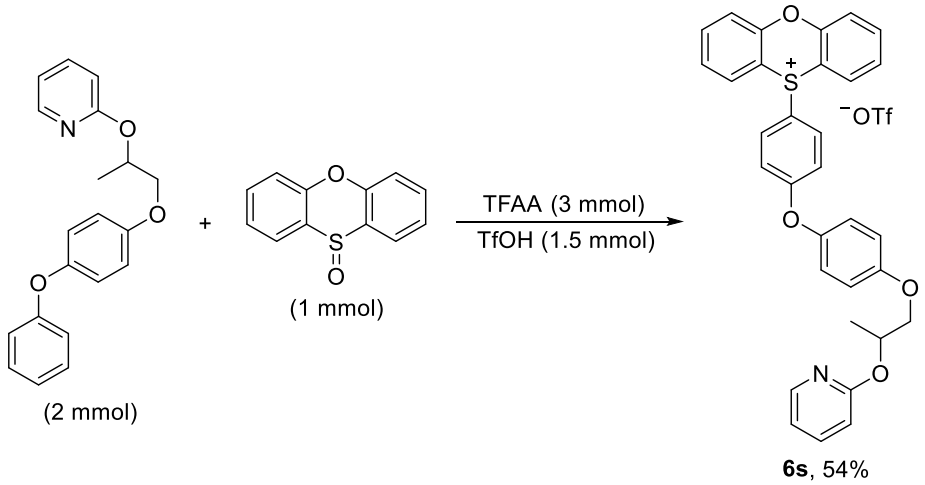
10-([2,2'-Bithiophen]-5-yl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6r**)



Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.84 mL, 6 mmol) and trifluoromethanesulfonic acid (TfOH, 0.26 mL, 3 mmol) were successively added to a mixture of 2,2'-bithiophene (332 mg, 2 mmol) and phenoxathiine 10-oxide (432 mg, 2 mmol) in MeCN (4 mL) at -78 °C. The mixture was reacted at room temperature for 12 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were washed with aqueous NaOTf

solutions (2 × 20 mL, 5% (w/w)), dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel (eluents: DCM/MeCN = 3/1 (v/v)) and then crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford 10-([2,2'-bithiophen]-5-yl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6r**) as a light yellow solid (742 mg, 72%). M.p.: 80-82 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 4.2 Hz, 1H), 8.23 (dd, *J* = 8.0 Hz, 1.2 Hz, 2H), 7.82 (t, *J* = 7.9 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 5.0 Hz, 1H), 7.16 (d, *J* = 3.1 Hz, 1H), 7.08 (d, *J* = 4.1 Hz, 1H), 6.98 (t, *J* = 4.3 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.4, 150.8, 141.3, 136.7, 133.9, 131.7, 128.5, 128.4, 127.5, 127.1, 124.9, 124.3, 120.9 (q, *J* = 321.0 Hz), 120.4, 108.2. IR (KBr): 3089, 3023, 1581, 1544, 1464, 1429, 1271, 1260, 1225, 1158, 1029, 1001, 885, 843, 779, 766, 709, 637 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{20}H_{13}OS_3]^+$ ($[M]^+$): 365.0123; found: 365.0130.

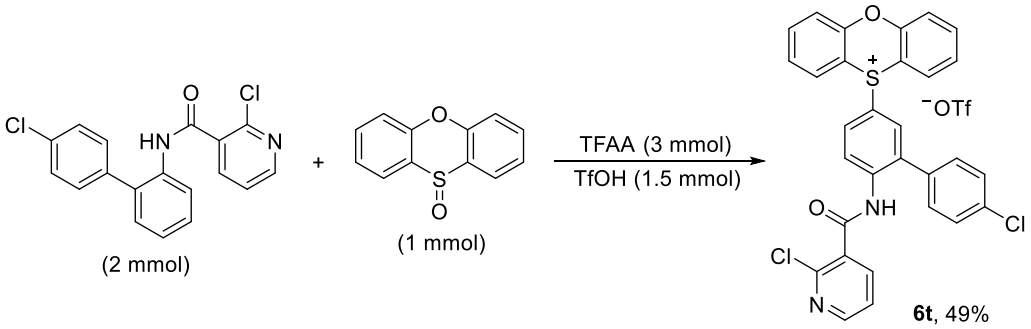
10-(4-(4-((1-(Pyridin-2-yloxy)propan-2-yl)oxy)phenoxy)phenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6s**)



Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.42 mL, 3 mmol) and trifluoromethanesulfonic acid (TfOH, 0.13 mL, 1.5 mmol) were successively added to a mixture of 2-((1-(4-phenoxyphenoxy)propan-2-yl)oxy)pyridine (642 mg, 2 mmol) and phenoxathiine 10-oxide (216 mg, 1 mmol) in MeCN (4 mL) at -40 °C. The mixture was reacted at room temperature for 12 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were washed with aqueous NaOTf solutions (2 × 20 mL, 5% (w/w)), dried over

anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel (eluents: DCM/MeCN = 3/1 (v/v)) and then crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford 10-(4-(4-((1-(pyridin-2-yloxy)propan-2-yl)oxy)phenoxy)phenyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6s**) as a white solid (362 mg, 54%). M.p.: 59-61 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.1 Hz, 1.4 Hz, 2H), 8.14 (d, *J* = 3.7 Hz, 1H), 7.78 (tm, *J* = 7.9 Hz, 2H), 7.72 (d, *J* = 9.1 Hz, 2H), 7.60-7.56 (m, 3H), 7.50 (tm, *J* = 7.7 Hz, 2H), 6.97-6.92 (m, 4H), 6.89-6.86 (m, 3H), 6.74 (d, *J* = 8.4 Hz, 1H), 5.56 (m, 1H), 4.18 (dd, *J* = 10.0 Hz, 5.2 Hz, 1H), 4.06 (dd, *J* = 10.0 Hz, 4.8 Hz, 1H), 1.47 (d, *J* = 6.4 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.2 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2, 163.1, 156.7, 151.5, 147.3, 146.7, 138.9, 136.4, 132.1, 131.9, 127.6, 122.4, 121.8, 120.9 (q, *J* = 320.0 Hz), 120.1, 119.0, 116.9, 116.3, 111.7, 106.8, 71.1, 69.2, 17.0. IR (KBr): 3090, 3065, 3024, 2980, 2934, 2875, 1595, 1584, 1573, 1504, 1487, 1469, 1433, 1273, 1233, 1194, 1155, 1066, 1029, 954, 885, 832, 762, 637 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{32}H_{26}NO_4S]^+$ ($[M]^+$): 520.1577; found: 520.1583.

10-(4'-Chloro-6-(2-chlorobenzamido)-[1,1'-biphenyl]-3-yl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6t**)[18]

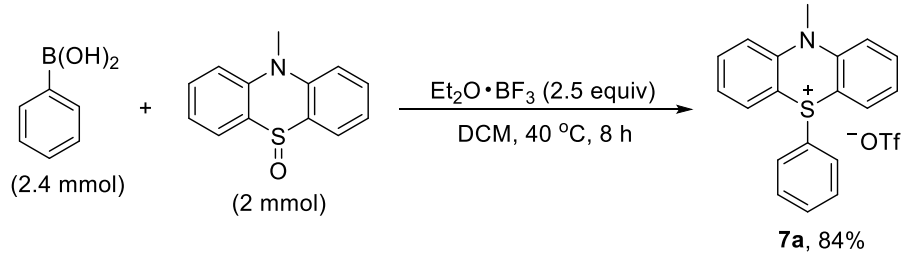


Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.42 mL, 3 mmol) and trifluoromethanesulfonic acid (TfOH, 0.13 mL, 1.5 mmol) were successively added to a mixture of 2-chloro-*N*-(4'-chloro-[1,1'-biphenyl]-2-yl)benzamide (684 mg, 2 mmol) and phenoxathiine 10-oxide (216 mg, 1 mmol) in MeCN (4 mL) at -40 °C. The mixture was reacted at room temperature for 12 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were washed with aqueous NaOTf solutions (2 × 20 mL, 5% (w/w)), dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The crude

product was purified by column chromatography on silica gel (eluents: DCM/MeCN = 3/1 (v/v)) and then crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford 10-(4'-chloro-6-(2-chlorobenzamido)-[1,1'-biphenyl]-3-yl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (**6t**) as a white solid (338 mg, 49%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (d, *J* = 9.1 Hz, 1H), 8.59 (s, 1H), 8.42 (dd, *J* = 4.8 Hz, 1.9 Hz, 1H), 8.26 (dd, *J* = 8.0 Hz, 1.5 Hz, 2H), 8.06 (dd, *J* = 7.8 Hz, 1.9 Hz, 1H), 7.86 (d, *J* = 2.5 Hz, 1H), 7.82 (tm, *J* = 7.9 Hz, 2H), 7.60 (dd, *J* = 8.4 Hz, 0.9 Hz, 2H), 7.55-7.51 (m, 3H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.34-7.32 (m, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.2 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.9, 151.9, 151.7, 146.5, 140.4, 140.3, 136.7, 136.0, 134.4, 133.1, 132.3, 131.6, 130.7, 130.0, 130.0, 129.2, 127.7, 125.9, 124.0, 123.1, 120.8 (q, *J* = 320.6 Hz), 120.3, 106.2.

4.4 Procedures for the synthesis of arylphenothiazinium salts (7)

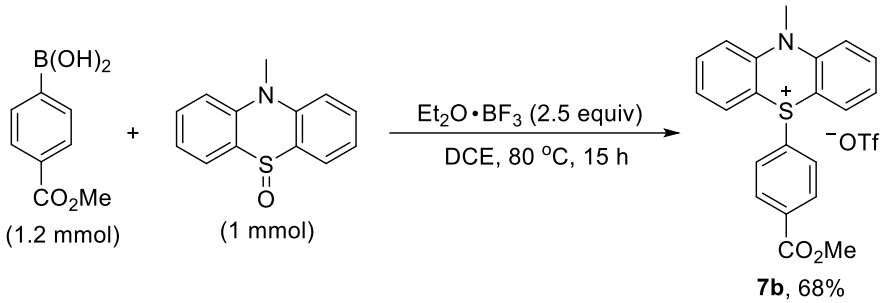
10-Methyl-5-phenyl-5,10-dihydrophenothiazin-5-ium trifluoromethanesulfonate (**7a**)[19]



Under a N_2 atmosphere, a flask was charged with $Et_2O{\bullet}BF_3$ (0.68 mL, 5.0 mmol), 10-methyl-10*H*-phenothiazine 5-oxide (458 mg, 2 mmol), phenylboronic acid (293 mg, 2.4 mmol), and DCM (10 mL) with stirring. The mixture was reacted at 40 °C for 8 h, quenched by moisture, concentrated under reduced pressure, and diluted with DCM (20 mL). 2-(Bis(2-hydroxyethyl)amino)-2-(hydroxymethyl)propane-1,3-diol (Bis-Tris, 4.2 g, 20 mmol) and a saturated aqueous NaOTf solution (20 mL) were added to the DCM solution. After shaking for at least 5 min, the aqueous layer was extracted with DCM (3 × 15 mL). The organic layers were collected, dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The residue was crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford 10-methyl-5-phenyl-5,10-dihydrophenothiazin-5-ium trifluoromethanesulfonate (**7a**) as a white solid (738 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 8.0 Hz, 1.4 Hz, 2H), 7.82 (tm, *J* = 7.8 Hz, 2H), 7.51-7.48 (m, 3H), 7.46-7.41 (m, 4H), 7.23 (d, *J* = 8.1 Hz, 2H), 3.67 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.1 (s, 3F). ^{13}C NMR (126 MHz,

CD_3CN) δ 143.3, 135.9, 133.1, 132.1, 130.9, 129.5, 127.0, 124.4, 121.3 (q, *J* = 321.5 Hz), 117.9, 104.9, 35.7.

5-(4-(Methoxycarbonyl)phenyl)-10-methyl-5,10-dihydrophenothiazin-5-ium trifluoromethanesulfonate (**7b**)

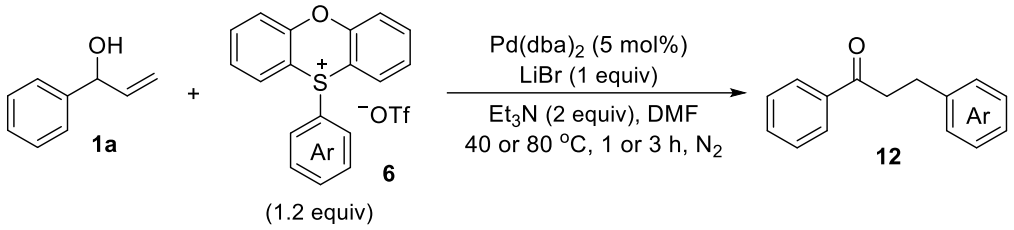


Under a N_2 atmosphere, a flask was charged with 10-methyl-10*H*-phenothiazine 5-oxide (230 mg, 1 mmol), (4-(methoxycarbonyl)phenyl)boronic acid (216 mg, 1.2 mmol), $Et_2O•BF_3$ (0.34 mL, 2.5 mmol), and DCE (15 mL) with stirring. The mixture was reacted at 80 °C for 15 h, quenched by moisture, concentrated under reduced pressure, and diluted with DCM (10 mL). Bis-Tris (2.1 g, 10 mmol) and a saturated aqueous NaOTf solution (20 mL) were added to the DCM solution. After shaking for at least 5 min, the aqueous layer was extracted with DCM (3 × 15 mL). The organic layers were collected, dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The residue was crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to give 5-(4-(methoxycarbonyl)phenyl)-10-methyl-5,10-dihydrophenothiazin-5-ium trifluoromethanesulfonate (**7b**) as a gray solid (338.3 mg, 68%). M.p.: 131-133 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 7.9 Hz, 1.3 Hz, 2H), 8.01 (d, *J* = 8.7 Hz, 2H), 7.85 (tm, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H), 3.64 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.9, 143.2, 136.4, 134.2, 133.6, 132.7, 131.5, 127.1, 125.0, 120.9 (q, *J* = 320.6 Hz), 117.5, 104.6, 52.8, 36.0. IR (KBr): 3066, 3027, 2962, 2840, 1732, 1581, 1464, 1398, 1354, 1267, 1192, 1163, 1136, 1111, 1057, 1030, 1010, 959, 878, 766, 756, 637 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{21}H_{18}NO_2S]^+$ ($[M]^+$): 348.1053; found: 348.1062.

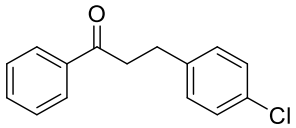
4.5. General procedure for the relay Heck arylation of 1-phenylprop-2-en-1-ol (1a) with different arylsulfonium salts (4-7).

In a nitrogen-filled glovebox, a sealed tube was charge with **1a** (26.8 mg, 0.2 mmol),

arylsulfonium salt (**4**, **5a**, **6** or **7a**, 0.24 mmol), LiBr (17.4 mg, 0.2 mmol), $Pd(dba)_2$ (5.8 mg, 0.01 mmol), Et_3N (40.5 mg, 0.4 mmol), and DMF (2 mL) with stirring. The mixture was reacted at 40 or 80 °C for 1 or 3 hours, cooled to room temperature, diluted with water (30 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether (PE) and ethyl acetate (EA) as eluents to give the desired product (**12**).

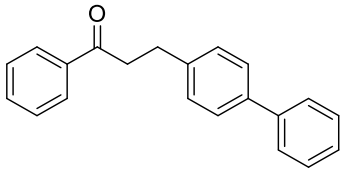


3-(4-Chlorophenyl)-1-phenylpropan-1-one (**12a**)[8]



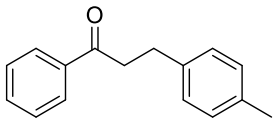
White solid (35.4 mg, 72%, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 6.9 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 3.31 (t, *J* = 7.5 Hz, 2H), 3.07 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.9, 139.8, 136.8, 133.2, 131.9, 129.8, 128.7, 128.6, 128.0, 40.2, 29.4.

3-([1,1'-Biphenyl]-4-yl)-1-phenylpropan-1-one (**12b**)[20]



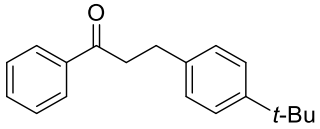
White solid (50.2 mg, 88%, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.4 Hz, 2H), 7.59 (d, *J* = 7.4 Hz, 2H), 7.57 (t, 7.4 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.35-7.33 (m, 3H), 3.36 (t, *J* = 7.5 Hz, 2H), 3.13 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 141.0, 140.3, 139.2, 136.9, 133.1, 128.9, 128.8, 128.7, 128.1, 127.3, 127.1, 127.0, 40.4, 29.8.

1-Phenyl-3-(*p*-tolyl)propan-1-one (**12c**)[8]



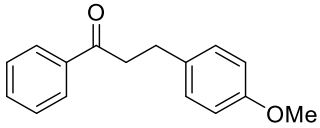
White solid (37.6 mg, 84%, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.16 (d, 7.9 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 3.29 (t, *J* = 7.6 Hz, 2H), 3.04 (t, *J* = 7.7 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.3, 137.2, 135.9, 134.6, 132.0, 128.2, 127.6, 127.3, 127.0, 39.6, 28.7, 20.0.

3-(4-(*Tert*-butyl)phenyl)-1-phenylpropan-1-one (**12d**)[11]



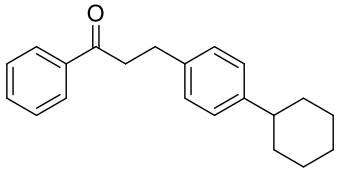
Light yellow solid (50.4 mg, 95%, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 3.32 (t, *J* = 7.7 Hz, 2H), 3.07 (t, *J* = 7.7 Hz, 2H), 1.34 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.4, 149.0, 138.2, 136.9, 133.0, 128.6, 128.1, 128.1, 125.4, 40.5, 34.4, 31.4, 29.6.

3-(4-Methoxyphenyl)-1-phenylpropan-1-one (**12e**)[8]



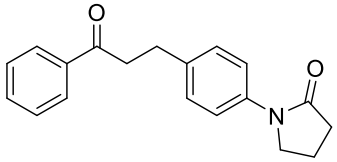
Colorless oil (43.1 mg, 90%, eluents: PE/EA = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 3.79 (s, 3H), 3.27 (t, *J* = 7.5 Hz, 2H), 3.02 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.4, 158.0, 136.9, 133.3, 133.0, 129.4, 128.6, 128.1, 114.0, 55.3, 40.7, 29.3.

3-(4-Cyclohexylphenyl)-1-phenylpropan-1-one (**12f**)



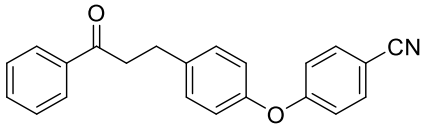
White solid (43.8 mg, 75%, eluents: PE/EA = 40/1). M.p.: 67-69 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 3.30 (t, *J* = 7.6 Hz, 2H), 3.04 (t, *J* = 7.6 Hz, 2H), 2.48 (m, 1H), 1.86 (m, 4H), 1.75 (m, 1H), 1.41 (m, 4H), 1.27 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.4, 146.0, 138.6, 136.9, 133.0, 128.6, 128.3, 128.1, 127.0, 44.2, 40.6, 34.6, 29.8, 27.0, 26.2. IR (KBr): 3083, 3050, 3024, 2920, 2848, 1683, 1596, 1515, 1447, 1435, 1403, 1359, 1239, 1176, 1000, 972, 927, 819, 762, 734, 688 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{21}H_{24}NaO]^+$ ($[M + Na]^+$): 315.1719; found: 315.1729.

1-(4-(3-Oxo-3-phenylpropyl)phenyl)pyrrolidin-2-one (**12g**)



Yellow solid (44.4 mg, 76%, eluents: PE/EA = 5/1). M.p.: 94-95 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 3.86 (t, *J* = 6.9 Hz, 2H), 3.30 (t, *J* = 7.5 Hz, 2H), 3.07 (t, *J* = 7.6 Hz, 2H), 2.62 (t, *J* = 8.0 Hz, 2H), 2.17 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 174.1, 137.6, 137.6, 136.9, 133.1, 128.8, 128.6, 128.0, 120.3, 48.9, 40.4, 32.7, 29.5, 18.1. IR (KBr): 3062, 2930, 2891, 1694, 1679, 1597, 1579, 1514, 1488, 1447, 1396, 1365, 1331, 1225, 1205, 1182, 973, 817, 745, 691 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{19}H_{19}NNaO_2]^+$ ($[M + Na]^+$): 316.1308; found: 316.1314.

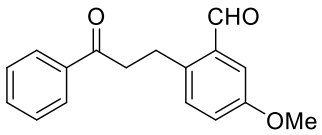
4-(4-(3-Oxo-3-phenylpropyl)phenoxy)benzonitrile (**12h**)



White solid (54.8 mg, 84%, eluents: PE/EA = 5/1). M.p.: 64-66 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.4 Hz, 2H), 7.58-7.55 (m, 3H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.6 Hz, 2H), 3.33 (t, *J* = 7.5 Hz, 2H), 3.10 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.0, 161.9, 153.0, 138.3, 136.8, 134.1, 133.2, 130.2, 128.7, 128.1, 120.6, 118.9, 117.7, 105.6,

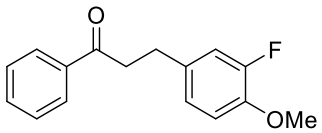
40.2, 29.4. IR (KBr): 3067, 2926, 2224, 1682, 1595, 1494, 1447, 1292, 1246, 1200, 1165, 875, 840, 746, 696 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{22}H_{17}NNaO_2]^+$ ([M + Na]$^+$): 350.1151; found: 350.1152.

5-Methoxy-2-(3-oxo-3-phenylpropyl)benzaldehyde (**12i**)



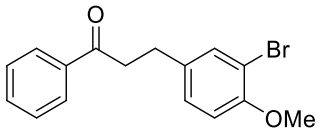
Light yellow oil (36.4 mg, 68%, eluents: PE/EA = 5/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.95 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 2.2 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.07 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 3.85 (s, 3H), 3.40 (t, *J* = 7.3 Hz, 2H), 3.29 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.0, 192.2, 158.5, 136.8, 136.1, 134.6, 133.1, 132.7, 128.6, 128.1, 120.6, 116.2, 55.5, 40.6, 26.3. IR (KBr): 3062, 3003, 2934, 2837, 1685, 1608, 1579, 1499, 1449, 1403, 1326, 1286, 1259, 1206, 1164, 1036, 975, 826, 744, 691 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{17}H_{16}NaO_3]^+$ ([M + Na]$^+$): 291.0992; found: 291.0999.

3-(3-Fluoro-4-methoxyphenyl)-1-phenylpropan-1-one (**12j**)



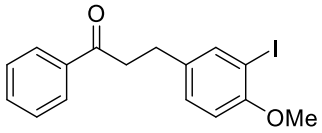
Light yellow solid (44.5 mg, 86%, eluents: PE/EA = 20/1). M.p.: 87-89 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 6.98 (dd, *J* = 12.3 Hz, 2.0 Hz, 1H), 6.95 (d, *J* = 8.7 Hz, 1H), 6.88 (t, *J* = 8.5 Hz, 1H), 3.86 (s, 3H), 3.26 (t, *J* = 7.5 Hz, 2H), 3.00 (t, *J* = 7.5 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -135.3 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.0, 152.3 (d, *J* = 245.3 Hz), 145.9 (d, *J* = 10.7 Hz), 136.8, 134.4 (d, *J* = 6.1 Hz), 133.1, 128.6, 128.0, 124.0 (d, *J* = 3.6 Hz), 116.2 (d, *J* = 18.1 Hz), 113.6 (d, *J* = 2.1 Hz), 56.4, 40.2, 29.1. IR (KBr): 3094, 3063, 2999, 2927, 2842, 1678, 1623, 1596, 1522, 1448, 1364, 1293, 1274, 1226, 1123, 1030, 1024, 978, 876, 811, 761, 745, 691, 639 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{16}H_{16}FO_2]^+$ ([M + H]$^+$): 259.1129; found: 259.1136.

3-(3-Bromo-4-methoxyphenyl)-1-phenylpropan-1-one (**12k**)[21]



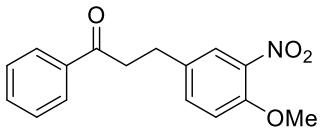
Light yellow solid (54.0 mg, 85%, eluents: PE/EA = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.43 (s, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 3.86 (s, 3H), 3.26 (t, *J* = 7.5 Hz, 2H), 2.99 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.9, 154.3, 136.8, 135.0, 133.2, 133.2, 128.7, 128.5, 128.0, 112.1, 111.6, 56.3, 40.3, 28.8.

3-(3-Iodo-4-methoxyphenyl)-1-phenylpropan-1-one (**12l**)



Light yellow solid (59.4 mg, 81%, eluents: PE/EA = 20/1). M.p.: 67-69 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* =7.5 Hz, 2H), 7.67 (d, *J* = 1.9 Hz, 1H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.19 (dd, *J* = 8.3 Hz, 2.0 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 3.85 (s, 3H), 3.26 (t, *J* = 7.5 Hz, 2H), 2.98 (t, *J* = 7.5 Hz, H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.0, 156.6, 139.3, 136.8, 135.6, 133.1, 129.6, 128.7, 128.0, 111.0, 86.0, 56.4, 40.4, 28.7. IR (KBr): 3057, 3036, 2999, 2931, 2853, 2837, 1679, 1595, 1579, 1493, 1461, 1447, 1360, 1281, 1251, 1207, 1180, 1155, 1047, 1016, 976, 826, 745, 690 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{16}H_{15}INaO_2]^+$ ([M + Na]$^+$): 389.0009; found: 389.0018.

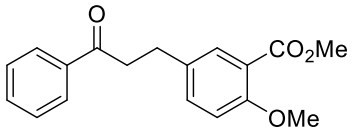
3-(4-Methoxy-3-nitrophenyl)-1-phenylpropan-1-one (**12m**)



Light yellow solid (54.6 mg, 96%, eluents: PE/EA = 5/1). M.p.: 104-106 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.4 Hz, 2H), 7.74 (s, 1H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.47-7.44 (m, 3H), 7.01 (d, *J* = 8.7 Hz, 1H), 3.93 (s, 3H), 3.31 (t, *J* = 7.3 Hz, 2H), 3.07 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.5, 151.4, 139.5, 136.6, 134.5, 133.7, 133.3, 128.7, 128.0, 125.4, 113.7, 56.6, 39.8, 28.6. IR (KBr): 3125, 3064, 3007, 2941, 2849, 1679, 1622, 1571, 1528, 1469, 1449, 1352, 1316, 1279, 1260, 1207, 1183, 1161, 1089, 1003, 976, 937, 825, 765, 742, 688 cm^{-1}. HRMS-ESI (m/z)

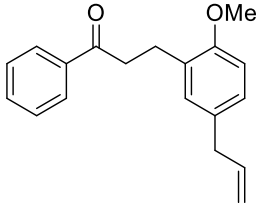
calcd. for $[C_{16}H_{16}NO_4]^+$ ([M + H]$^+$): 286.1074; found: 286.1070.

Methyl 2-methoxy-5-(3-oxo-3-phenylpropyl)benzoate (**12n**)



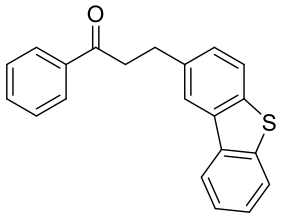
White solid (52.9 mg, 89%, eluents: PE/EA = 5/1). M.p.: 72-74 ^oC. ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.5 Hz, 2H), 7.68 (d, *J* = 2.3 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.36 (dd, *J* = 8.6 Hz, 2.3 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.28 (t, *J* = 7.4 Hz, 2H), 3.03 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.0, 166.8, 157.6, 136.9, 133.6, 133.1, 133.0, 131.4, 128.6, 128.0, 120.0, 112.4, 56.2, 52.0, 40.3, 29.0. IR (KBr): 3037, 3006, 2983, 2947, 2928, 2841, 1720, 1681, 1643, 1585, 1502, 1464, 1447, 1436, 1362, 1303, 1257, 1203, 1183, 1085, 1021, 974, 835, 788, 747, 690 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{18}H_{18}NaO_4]^+$ ([M + Na]$^+$): 321.1097; found: 321.1102.

3-(5-Allyl-2-methoxyphenyl)-1-phenylpropan-1-one (**12o**)



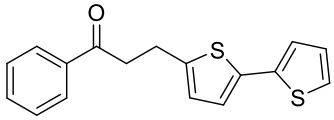
Light yellow oil (30.1 mg, 54%, eluents: PE/EA = 20/1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.02-7.00 (m, 2H), 6.79 (d, *J* = 9.0 Hz, 1H), 5.98-5.90 (m, 1H), 5.08-5.03 (m, 2H), 3.81 (s, 3H), 3.31 (d, *J* = 6.8 Hz, 2H), 3.25 (t, *J* = 7.8 Hz, 2H), 3.02 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.0, 156.0, 137.9, 137.0, 132.9, 132.0, 130.5, 129.5, 128.5, 128.1, 127.3, 115.4, 110.3, 55.4, 39.4, 39.1, 25.9. IR (KBr): 3063, 3002, 2928, 2853, 1686, 1598, 1502, 1465, 1449, 1283, 1251, 1205, 1181, 1123, 1033, 914, 812, 742, 691 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{19}H_{21}O_2]^+$ ([M + H]$^+$): 281.1536; found: 281.1533.

3-(Dibenzo[*b*,*d*]thiophen-2-yl)-1-phenylpropan-1-one (**12p**)



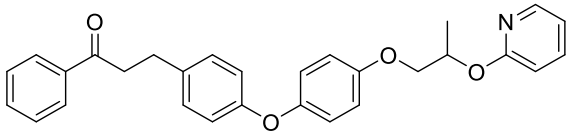
Light yellow oil (48.8 mg, 77%, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (m, 1H), 8.04 (s, 1H), 7.98 (d, *J* = 7.9 Hz, 2H), 7.84 (m, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.48-7.43 (m, 4H), 7.37 (dd, *J* = 8.1 Hz, 1.2 Hz, 1H), 3.41 (t, *J* = 7.6 Hz, 2H), 3.26 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 139.9, 137.7, 137.3, 136.9, 135.9, 135.4, 133.1, 128.7, 128.1, 127.5, 126.7, 124.3, 122.9, 122.8, 121.6, 121.3, 40.9, 30.2. IR (KBr): 3051, 2921, 2852, 1682, 1594, 1468, 1446, 1430, 1358, 1288, 1229, 1207, 1158, 1077, 1025, 975, 764, 745, 733, 691 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{21}H_{17}OS]^+$ ($[M + H]^+$): 317.0995; found: 317.0999.

3-([2,2'-Bithiophen]-5-yl)-1-phenylpropan-1-one (**12q**)



Yellow solid (47.2 mg, 79%, eluents: PE/EA = 40/1). M.p.: 65-66 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 5.0 Hz, 1H), 7.10 (d, *J* = 3.1 Hz, 1H), 7.00-6.98 (m, 2H), 6.77 (d, *J* = 2.6 Hz, 1H), 3.38 (t, *J* = 7.2 Hz, 2H), 3.27 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.4, 143.3, 137.7, 136.7, 135.5, 133.2, 128.7, 128.1, 127.7, 125.5, 124.0, 123.5, 123.3, 40.3, 24.4. IR (KBr): 3064, 2929, 2878, 1676, 1596, 1579, 1448, 1428, 1376, 1322, 1304, 1277, 1207, 977, 839, 803, 781, 774, 741, 670 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{17}H_{14}NaOS_2]^+$ ($[M + Na]^+$): 321.0378; found: 321.0389.

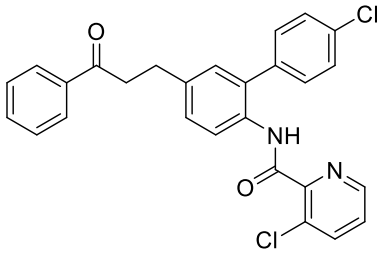
1-Phenyl-3-(4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)phenyl)propan-1-one (**12r**)



Colorless oil (75.1 mg, 83%, eluents: PE/EA = 5/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 4.9 Hz, 1.8 Hz, 1H), 7.96 (dm, *J* = 7.9 Hz, 2H), 7.58-7.54 (m, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.95-6.90 (m, 4H), 6.88 (dm, *J* = 8.5 Hz,

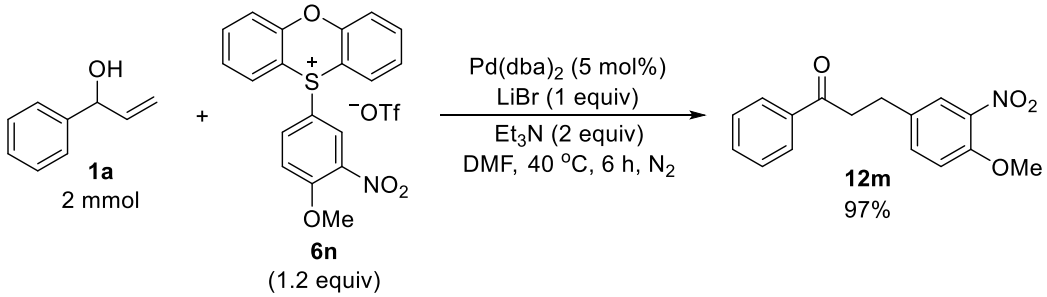
2H), 6.85 (m, 1H), 6.74 (d, *J* = 8.3 Hz, 1H), 5.58 (m, 1H), 4.19 (dd, *J* = 9.9 Hz, 5.3 Hz, 1H), 4.07 (dd, *J* = 9.9 Hz, 4.9 Hz, 1H), 3.29 (t, *J* = 7.6 Hz, 2H), 3.04 (t, *J* = 7.6 Hz, 2H), 1.48 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.3, 163.2, 156.8, 155.1, 150.7, 146.8, 138.7, 137.0, 135.4, 133.1, 129.6, 128.6, 128.1, 120.5, 117.9, 116.8, 115.8, 111.7, 71.2, 69.3, 40.6, 29.4, 17.0. IR (KBr): 3057, 2979, 2931, 1686, 1596, 1570, 1499, 1471, 1432, 1287, 1224, 1079, 1046, 956, 875, 827, 780, 741, 690 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{29}H_{28}NO_4]^+$ ($[M + H]^+$): 454.2013; found: 454.2018.

2-Chloro-*N*-(4'-chloro-5-(3-oxo-3-phenylpropyl)-[1,1'-biphenyl]-2-yl)benzamide (**12s**)



White solid (81.7 mg, 86%, eluents: PE/EA = 2/1). M.p.: 198-200 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 4.6 Hz, 1.6 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 8.13 (s, 1H), 8.07 (dd, *J* = 7.6 Hz, 1.4 Hz, 1H), 7.94 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.34-7.30 (m, 4H), 7.16 (d, *J* = 1.6 Hz, 1H), 3.32 (t, *J* = 7.6 Hz, 2H), 3.09 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.0, 162.7, 151.2, 146.8, 139.9, 138.7, 136.8, 136.4, 134.3, 133.2, 132.9, 132.4, 131.2, 130.8, 130.3, 129.2, 128.8, 128.7, 128.1, 122.9, 122.8, 40.2, 29.5. IR (KBr): 3335, 3054, 2924, 2897, 1671, 1580, 1516, 1481, 1450, 1399, 1303, 1287, 1206, 1130, 1086, 1067, 977, 851, 826, 746, 689 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{27}H_{20}Cl_2N_2NaO_2]^+$ ($[M + Na]^+$): 497.0794; found: 497.0804.

An example for the scale-up synthesis of the product

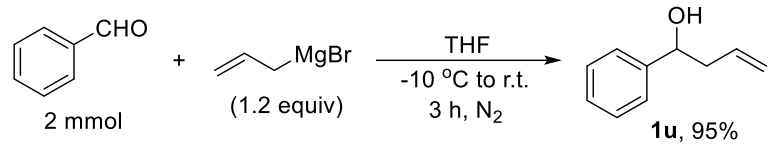


In a nitrogen-filled glovebox, a flask was charge with **1a** (268 mg, 2 mmol), **6n** (1.2 g,

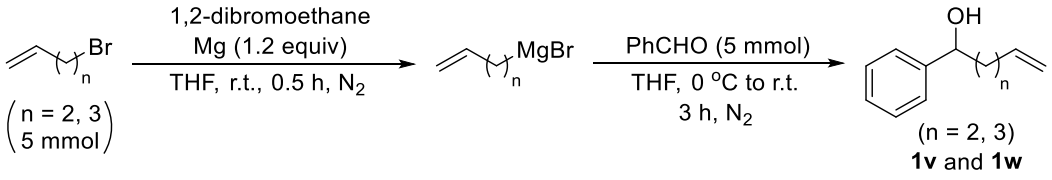
2.4 mmol), LiBr (174 mg, 2 mmol), $Pd(dba)_2$ (58 mg, 0.1 mmol), Et_3N (405 mg, 4 mmol), and DMF (20 mL) with stirring. The mixture was reacted at 40 °C for 6 hours, cooled to room temperature, diluted with water (80 mL), and extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (5/1, v/v) as eluents to give the desired product **12m** (556 mg, 97%).

5. The relay Heck reactions of non-allylic alcohols with diverse arylsulfonium salts.

5.1. Procedures for the synthesis of non-allylic alcohols.

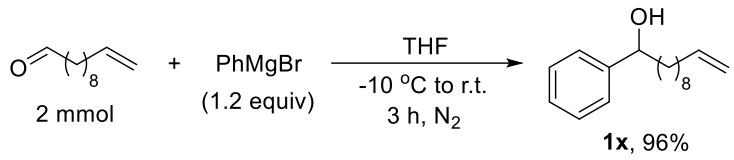


Procedure A:[22] Under a nitrogen atmosphere, a sealed tube was charged with benzaldehyde (212 mg, 2 mmol) and THF (1 mL) with stirring and cooled to -10 °C. Allylmagnesium bromide (2.4 mL, 1.0 M in THF, 2.4 mmol) was slowly added. The mixture was then warmed to room temperature, reacted for 3 h, quenched by a saturated aqueous ammonium chloride solution (20 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with water, dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (10/1, v/v) as eluents to give the desired product (**1u**).

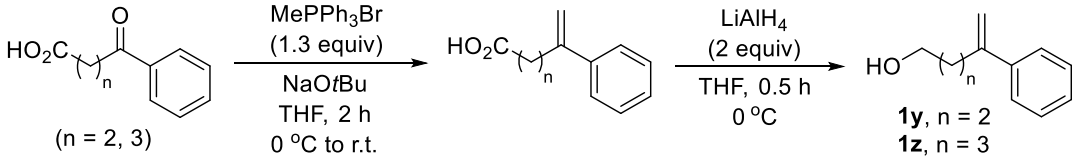


Procedure B:[23] Under a nitrogen atmosphere, alkenyl bromide (5 mmol) was slowly added to a mixture of magnesium turning (146 mg, 6 mmol) and 1,2-dibromoethane (about 50 μL) in THF (15 mL) with vigorous stirring. The mixture was reacted at room temperature for 0.5 h. Then, benzaldehyde (530 mg, 5 mmol) was slowly added to the mixture with a syringe at 0 °C. The resulting mixture was returned to room

temperature, reacted for another 3 h, quenched by a saturated aqueous ammonium chloride solution (50 mL), and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with water, dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (10/1, v/v) as eluents to give the desired product (**1v** or **1w**).



Procedure C:[24] Under a nitrogen atmosphere, a sealed tube was charged with undec-10-enal (336 mg, 2 mmol) and THF (1 mL) with stirring and cooled to -10 °C. Phenylmagnesium bromide (2.4 mL, 1.0 M in THF, 2.4 mmol) was slowly added. The mixture was warmed to room temperature, reacted for 3 h, quenched by a saturated aqueous ammonium chloride solution (20 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with water, dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (10/1, v/v) as eluents to give the desired product (**1x**).



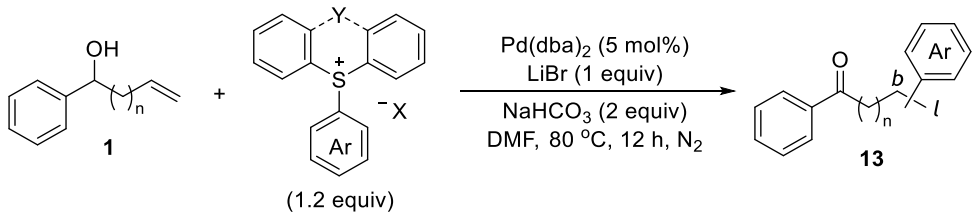
Procedure D:[25] To a suspension of methyltriphenylphosphonium bromide (1.4 g, 3.9 mmol) in THF (5 mL) was added sodium *tert*-butoxide (0.75 g, 7.8 mmol) at 0 °C. The mixture was reacted at 0 °C for 30 min, and then 3-benzoylpropionic acid or 4-benzoylpropionic acid (3 mmol) was added. The reaction mixture was warmed to room temperature, reacted for another 2 h, and concentrated to dryness under reduced pressure. The residue was dissolved in a mixture of DCM (20 mL) and 10% aqueous NaOH solution (20 mL). The aqueous layer was washed with DCM (the resulting DCM solution was discarded), acidified by 10% aqueous HCl solution until pH = 2, and extracted with DCM (2 × 20 mL). The DCM extracts were collected, washed with brine (20 mL), dried over anhydrous Na_2SO_4, and concentrated to dryness under

reduced pressure to give the crude product for next step without further purification.

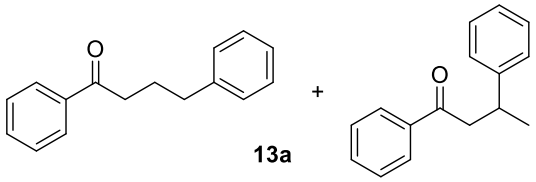
To a solution of $LiAlH_4$ (0.24 g, 6 mmol) in THF (5 mL) was slowly added a solution of the above crude product in THF (5 mL) at 0 °C. The mixture was reacted at 0 °C for 0.5 h, slowly quenched by H_2O (1.5 mL) and 10% aqueous NaOH solution (0.5 mL), poured onto a pad of celite, and washed with ethyl acetate (50 mL). The ethyl acetate solution was collected, washed with brine, dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluents to give the desired product (**1y** or **1z**).

5.2. General procedure for the relay Heck arylation of non-allylic alcohols (1) with diverse arylsulfonium salts (2, 5-7).

In a nitrogen-filled glovebox, a sealed tube was charge with non-allylic alcohol (**1**, 0.2 mmol), arylsulfonium salt (**2**, **5b**, **6** or **7b**, 0.24 mmol), LiBr (17.4 mg, 0.2 mmol), $NaHCO_3$ (33.6 mg, 0.4 mmol), $Pd(dba)_2$ (5.8 mg, 0.01 mmol), and DMF (2 mL) with stirring. The mixture was reacted at 40 or 80 °C for 12, 24 or 48 hours, diluted with water (30 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether (PE) and ethyl acetate (EA) as eluents to give the desired product (**13**).



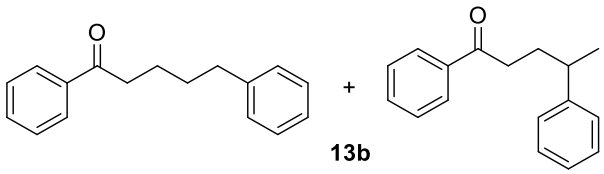
A mixture of 1,4-diphenylbutan-1-one and 1,3-diphenylbutan-1-one (**13a**)[26]



Colorless oil (37.6 mg, 84%, *l*/*b* = 24/1, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.24-7.18 (m, 3H), 3.51 (m, 0.04H), 3.30 (dd, *J* = 16.5 Hz,

5.9 Hz, 0.04H), 3.19 (dd, *J* = 16.5 Hz, 8.2 Hz, 0.04H), 2.98 (t, *J* = 7.3 Hz, 1.93H), 2.73 (t, *J* = 7.5 Hz, 1.93H), 2.10 (m, 1.93H), 1.35 (d, *J* = 4.8 Hz, 0.12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.1, 141.7, 137.1, 132.9, 128.6, 128.5, 128.4, 128.1, 126.0, 37.7, 35.3, 25.8.

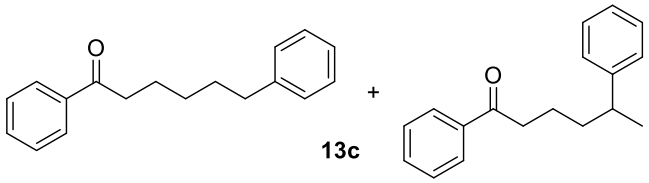
A mixture of 1,5-diphenylpentan-1-one and 1,4-diphenylpentan-1-one (**13b**)[27]



13b

Colorless oil (36.3 mg, 76%, *l*/*b* = 4.9/1, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.8 Hz, 1.66H), 7.86 (d, *J* = 7.8 Hz, 0.34H), 7.56 (t, *J* = 7.4 Hz, 0.83H), 7.53 (t, *J* = 7.4 Hz, 0.17H), 7.46 (t, *J* = 7.8 Hz, 1.65H), 7.42 (t, *J* = 7.8 Hz, 0.36H), 7.32 (t, *J* = 7.7 Hz, 0.34H), 7.29 (t, *J* = 7.7 Hz, 1.66H), 7.24-7.17 (m, 3H), 3.00 (t, *J* = 7.1 Hz, 1.66H), 2.91-2.76 (m, 0.51H), 2.69 (t, *J* = 7.5 Hz, 1.66H), 2.14-1.96 (m, 0.34H), 1.82 (m, 1.66H), 1.74 (m, 1.66H) 1.33 (d, *J* = 6.9 Hz, 0.51H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.4, 200.3, 146.6, 142.3, 137.1, 137.0, 132.9, 132.9, 128.6, 128.5, 128.5, 128.4, 128.3, 128.1, 128.0 127.1, 126.2, 125.8, 39.6, 38.4, 36.7, 35.8, 32.5, 31.1, 24.0, 22.6.

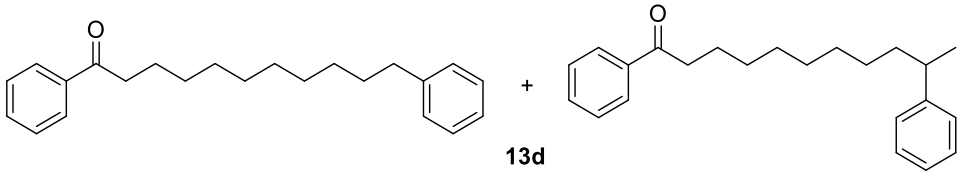
A mixture of 1,6-diphenylhexan-1-one and 1,5-diphenylhexan-1-one (**13c**)[28]



13c

Colorless oil (37.2 mg, 74%, *l*/*b* = 4.9/1, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.9 Hz, 1.66H), 7.92 (d, *J* = 7.9 Hz, 0.34H), 7.58-7.53 (m, 1H), 7.49-7.42 (m, 2H), 7.32-7.27 (m, 2H), 7.23-7.17 (m, 3H), 2.97 (t, *J* = 7.4 Hz, 1.66H), 2.93 (m, 0.34H), 2.76 (m, 0.17H), 2.65 (t, *J* = 7.7 Hz, 1.66H), 1.79 (m, 1.67H), 1.73-1.67 (m, 2.33H), 1.45 (m, 1.66H), 1.28 (d, *J* = 6.9 Hz, 0.51H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.5, 200.3, 147.3, 142.6, 137.1, 137.0, 132.9, 132.9, 128.6, 128.6, 128.4, 128.4, 128.3, 128.1, 128.0, 127.0, 126.0, 125.7, 39.9, 38.6, 38.5, 37.9, 35.8, 31.3, 29.0, 24.2, 22.6, 22.4.

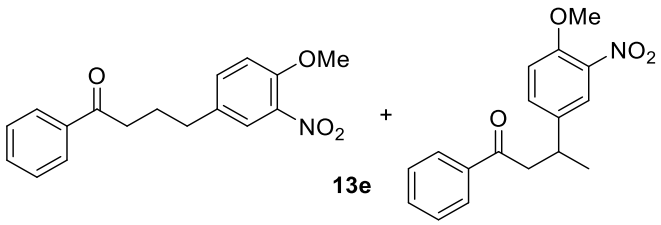
A mixture of 1,11-diphenylundecan-1-one and 1,10-diphenylundecan-1-one (**13d**)[29]



13d

Colorless oil (34.2 mg, 53%, *l*/*b* = 4.6/1, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, acetone-D_6) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.25-7.19 (m, 3H), 3.03-2.98 (m, 2H), 2.68 (m, 0.18H), 2.60 (t, *J* = 7.8 Hz, 1.65H), 1.73-1.66 (m, 2H), 1.64-1.57 (m, 2H), 1.42-1.25 (m, 11.64H), 1.21 (d, *J* = 6.9 Hz, 0.55H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.6, 148.0, 143.0, 137.2, 132.9, 128.6, 128.4, 128.3, 128.2, 128.1, 127.0, 125.8, 125.6, 40.0, 38.7, 38.5, 36.0, 31.5, 29.7, 29.6, 29.5, 29.5, 29.5, 29.4, 29.4, 29.4, 27.7, 24.4, 24.4, 22.4.

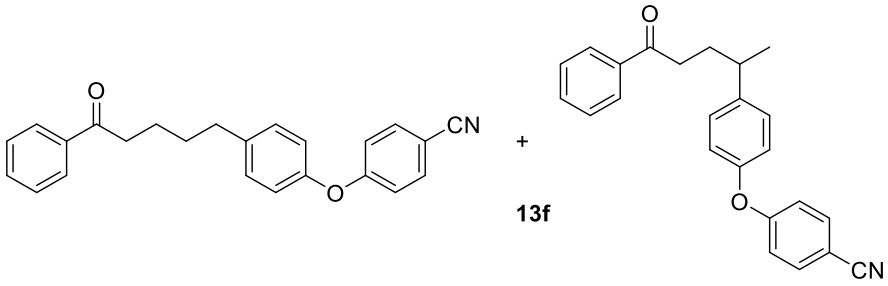
A mixture of 4-(4-methoxy-3-nitrophenyl)-1-phenylbutan-1-one and 3-(4-methoxy-3-nitrophenyl)-1-phenylbutan-1-one (**13e**)



13e

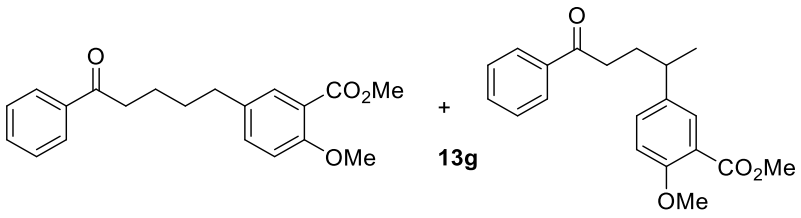
Light yellow oil (44.2 mg, 74%, *l*/*b* = 5.7/1, eluents: PE/EA = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93-7.90 (m, 2H), 7.76 (d, *J* = 2.2 Hz, 0.15H), 7.69 (d, *J* = 2.2 Hz, 0.85H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.47-7.43 (m, 2H), 7.39 (dd, *J* = 8.6 Hz, 2.2 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 1H), 3.93 (s, 2.55H), 3.92 (s, 0.45H), 3.54 (m, 0.15H), 3.30-3.18 (m, 0.30H), 2.99 (t, *J* = 7.1 Hz, 1.71H), 2.71 (t, *J* = 7.6 Hz, 1.71H), 2.07 (m, 1.70H), 1.34 (d, *J* = 7.0 Hz, 0.45H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.6, 198.3, 151.5, 151.3, 139.5, 139.0, 136.9, 136.9, 134.2, 134.2, 133.2, 133.2, 133.1, 128.7, 128.6, 128.0, 128.0, 125.3, 123.7, 113.7, 56.6, 56.6, 46.7, 37.4, 34.4, 33.8, 29.7, 25.4. IR (KBr): 3058, 3017, 2937, 2867, 2840, 1681, 1622, 1573, 1529, 1449, 1349, 1279, 1261, 1184, 1159, 1088, 1014, 820, 758, 733, 689 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{17}H_{18}NO_4]^+$ ($[M + H]^+$): 300.1230; found: 300.1232.

A mixture of 4-(4-(5-oxo-5-phenylpentyl)phenoxy)benzonitrile and 4-(4-(5-oxo-5-phenylpentan-2-yl)phenoxy)benzonitrile (**13f**)



Colorless oil (48.3 mg, 68%, *l*/*b* = 3.8/1, eluents: PE/EA = 10/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.7 Hz, 1.58H), 7.87 (d, *J* = 7.7 Hz, 0.42H), 7.58-7.53 (m, 3H), 7.47-7.42 (m, 2H), 7.25-7.21 (m, 2H), 7.00-6.96 (m, 4H), 3.01 (t, *J* = 7.1 Hz, 1.58H), 2.91-2.82 (m, 0.63H), 2.69 (t, *J* = 7.4 Hz, 1.58H), 2.10-2.00 (m, 0.42H), 1.81 (m, 1.58H), 1.74 (m, 1.58H), 1.33 (d, *J* = 6.8 Hz, 0.63H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.2, 200.1, 162.0, 161.9, 153.0, 152.7, 143.7, 139.3, 137.0, 137.0, 134.1, 134.1, 133.0, 130.1, 128.7, 128.6, 128.6, 128.0, 128.0, 120.5, 120.4, 118.9, 118.9, 117.8, 117.7, 105.7, 105.6, 38.9, 38.3, 36.6, 35.2, 32.6, 31.1, 23.9, 22.5. IR (KBr): 3061, 2932, 2860, 2226, 1684, 1597, 1498, 1448, 1286, 1248, 1201, 1168, 1106, 1016, 874, 837, 751, 691 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{24}H_{22}NO_2]^+$ ($[M + H]^+$): 356.1645; found: 356.1657.

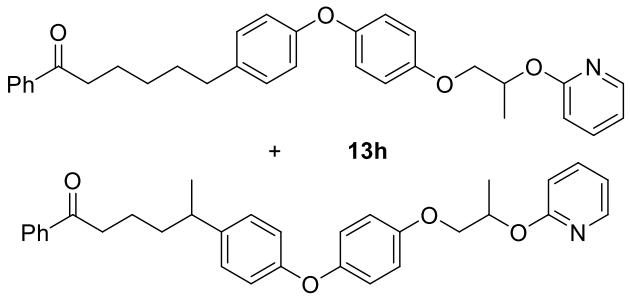
A mixture of methyl 2-methoxy-5-(5-oxo-5-phenylpentyl)benzoate and methyl 2-methoxy-5-(5-oxo-5-phenylpentan-2-yl)benzoate (**13g**)



Colorless oil (41.2 mg, 63%, *l*/*b* = 2.6/1, eluents: PE/EA = 10/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.7 Hz, 1.45H), 7.85 (d, *J* = 7.7 Hz, 0.55H), 7.62 (m, 1H), 7.57-7.51 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 1.45H), 7.42 (t, *J* = 7.6 Hz, 0.55H), 7.29 (m, 1H), 6.93-6.88 (m, 1H), 3.88 (m, 6H), 2.99 (t, *J* = 7.1 Hz, 1.45H), 2.85-2.77 (m, 0.83H), 2.63 (t, *J* = 7.5 Hz, 1.45H), 2.09-2.03 (m, 0.28H), 2.00-1.93 (m, 0.28H), 1.78 (m, 1.45H), 1.69 (m, 1.45H), 1.29 (d, *J* = 7.0 Hz, 0.83H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.2, 200.2, 166.9, 157.6, 157.4, 138.3, 137.0, 137.0, 134.0, 133.4, 132.9, 132.9, 132.0, 131.4, 130.1, 128.6, 128.5, 128.0, 128.0, 120.0, 119.8, 112.4, 112.2, 56.2, 56.1, 52.0, 52.0, 38.6, 38.3, 36.6, 34.6, 32.5, 31.1, 23.9, 22.6. IR (KBr): 3059, 3002, 2947, 2857, 1729, 1684, 1613, 1597, 1581, 1501, 1449, 1436, 1304, 1258, 1201, 1083, 1025,

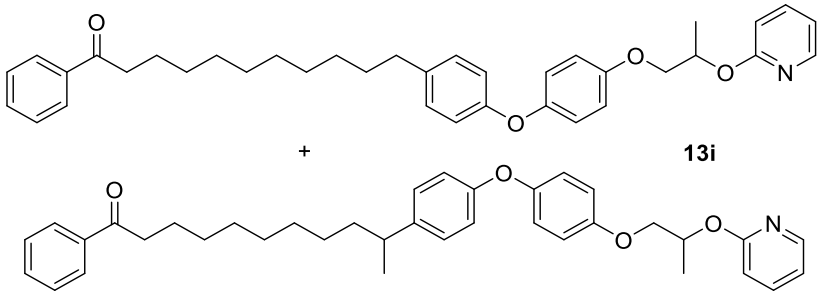
974, 820, 788, 751, 692 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{20}H_{22}NaO_4]^+$ ($[M + Na]^+$): 349.1410; found: 349.1411.

A mixture of 1-phenyl-6-(4-(4-((1-(pyridin-2-yloxy)propan-2-yl)oxy)phenoxy)phenyl) hexan-1-one and 1-phenyl-5-(4-(4-((1-(pyridin-2-yloxy)propan-2-yl)oxy)phenoxy)phenyl)hexan-1-one (**13h**)



Colorless oil (60.6 mg, 61%, *l*/*b* = 3.4/1, eluents: PE/EA = 5/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 5.0 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 1.55H), 7.91 (d, *J* = 7.6 Hz, 0.45H), 7.58-7.53 (m, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.12-7.08 (m, 2H), 6.95-6.90 (m, 4H), 6.87-6.84 (m, 3H), 6.74 (d, *J* = 8.3 Hz, 1H), 5.58 (m, 1H), 4.18 (dd, *J* = 9.9 Hz, 5.3 Hz, 1H), 4.07 (dd, *J* = 9.9 Hz, 4.9 Hz, 1H), 2.96 (t, *J* = 7.4 Hz, 1.55H), 2.92 (m, 0.45H), 2.71 (m, 0.22H), 2.59 (t, *J* = 7.7 Hz, 1.55H), 1.78 (m, 1.55H), 1.69-1.63 (m, 2.45H), 1.48 (d, *J* = 6.5 Hz, 3H), 1.43 (m, 1.55H), 1.27 (d, *J* = 7.1 Hz, 0.67H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.4, 200.3, 163.2, 156.5, 156.4, 155.1, 155.0, 150.8, 150.7, 146.8, 141.4, 138.7, 137.1, 137.1, 136.8, 132.9, 129.4, 128.6, 128.6, 128.1, 128.0, 128.0, 120.5, 120.4, 117.7, 117.7, 116.8, 115.8, 111.7, 71.2, 69.3, 60.4, 39.2, 38.6, 38.5, 38.1, 35.0, 31.4, 29.0, 24.2, 22.5, 22.5, 21.0, 17.0, 14.2. IR (KBr): 3057, 2932, 2857, 1688, 1596, 1570, 1499, 1471, 1432, 1308, 1287, 1223, 1143, 1080, 1045, 958, 874, 831, 780, 691 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{32}H_{34}NO_4]^+$ ($[M + H]^+$): 496.2482; found: 496.2488.

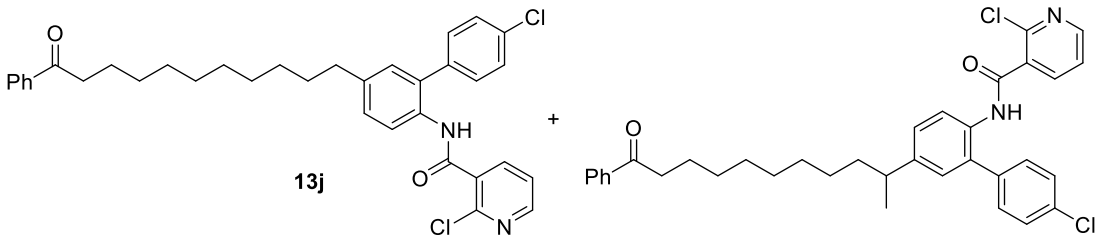
A mixture of 1-phenyl-11-(4-(4-((1-(pyridin-2-yloxy)propan-2-yl)oxy)phenoxy)phenyl)undecan-1-one and 1-phenyl-10-(4-(4-((1-(pyridin-2-yloxy)propan-2-yl)oxy)phenoxy)phenyl)undecan-1-one (**13i**)



13i

Colorless oil (59.9 mg, 53%, *l*/*b* = 3.5/1, eluents: PE/EA = 5/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 4.9 Hz, 1H), 7.96 (d, *J* = 7.5 Hz, 2H), 7.58-7.53 (m, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.96-6.89 (m, 4H), 6.87-6.84 (m, 3H), 6.74 (d, *J* = 8.3 Hz, 1H), 5.58 (m, 1H), 4.18 (dd, *J* = 9.9 Hz, 5.4 Hz, 1H), 4.07 (dd, *J* = 9.9 Hz, 4.8 Hz, 1H), 2.97-2.93 (m, 2H), 2.64 (m, 0.22H), 2.56 (t, *J* = 7.8 Hz, 1.56H), 1.77-1.69 (m, 2.22H), 1.59 (m, 1.78H), 1.48 (d, *J* = 6.4 Hz, 3H), 1.38-1.25 (m, 11.56H), 1.21 (d, *J* = 7.0 Hz, 0.66H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.6, 163.2, 156.3, 156.2, 155.0, 155.0, 150.9, 150.8, 146.8, 142.2, 138.7, 137.2, 137.2, 132.8, 129.4, 129.0, 128.6, 128.4, 128.1, 128.0, 127.5, 125.9, 120.5, 120.4, 117.7, 117.6, 116.8, 115.8, 111.7, 74.7, 71.2, 69.3, 39.2, 39.1, 38.6, 38.6, 35.2, 33.8, 31.6, 29.7, 29.5, 29.5, 29.4, 29.4, 29.4, 29.3, 27.7, 25.8, 24.4, 24.4, 22.4, 17.0. IR (KBr): 3052, 2917, 2848, 1681, 1596, 1570, 1501, 1471, 1431, 1375, 1308, 1286, 1272, 1222, 1143, 1077, 1050, 960, 831, 779, 746, 690 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{37}H_{44}NO_4]^+$ ([M + H]$^+$): 566.3265; found: 566.3264.

A mixture of 2-chloro-*N*-(4'-chloro-5-(11-oxo-11-phenylundecyl)-[1,1'-biphenyl]-2-yl)nicotinamide and 2-chloro-*N*-(4'-chloro-5-(11-oxo-11-phenylundecan-2-yl)-[1,1'-biphenyl]-2-yl)nicotinamide (**13j**)

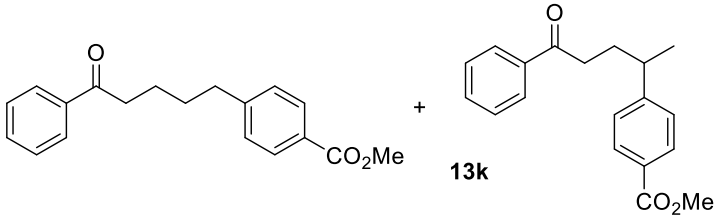


13j

Colorless oil (66.9 mg, 57%, *l*/*b* = 4.6/1, eluents: PE/EA = 2/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, *J* = 4.8 Hz, 1H), 8.24-8.20 (m, 1H), 8.12 (s, 1H), 8.07 (d, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.40 (dm, *J* = 8.1 Hz, 2H), 7.35-7.30 (m, 3H), 7.25 (m, 1H), 7.08 (m, 1H), 2.96-2.92 (m, 2H), 2.70 (m, 0.18H), 2.63 (t, *J* = 7.7 Hz, 1.64H), 1.74-1.68 (m, 2.18H), 1.66-1.60 (m,

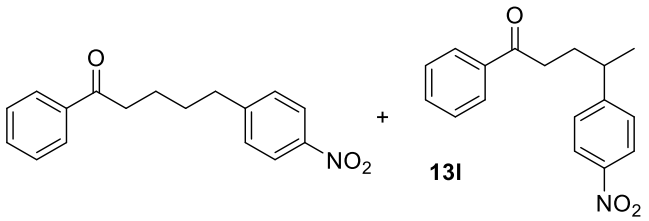
1.82H), 1.38-1.24 (m, 12.18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.6, 162.6, 151.3, 151.2, 146.8, 145.5, 140.4, 139.9, 137.1, 136.8, 136.7, 134.2, 132.9, 132.6, 132.6, 131.9, 131.8, 131.3, 130.8, 130.8, 130.3, 130.2, 129.3, 129.2, 128.9, 128.8, 128.6, 128.1, 127.3, 122.9, 122.6, 39.5, 38.6, 38.3, 35.4, 31.4, 29.6, 29.5, 29.5, 29.5, 29.4, 29.3, 29.3, 27.7, 24.4, 22.3. IR (KBr): 3266, 3057, 2926, 2854, 1682, 1581, 1520, 1484, 1448, 1399, 1310, 1223, 1150, 1089, 1066, 1014, 899, 835, 755, 691 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{35}H_{36}Cl_2N_2NaO_2]^+$ ([M + Na]$^+$): 609.2046; found: 609.2048.

A mixture of methyl 4-(5-oxo-5-phenylpentyl)benzoate and methyl 4-(5-oxo-5-phenylpentan-2-yl)benzoate (**13k**)[30]



Yellow oil (16.5 mg, 56%, *l*/*b* = 9/1, eluents: PE/EA = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95-7.93 (m, 3.80H), 7.88-7.85 (m, 0.20H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 2H), 3.90 (m, 3H), 2.99 (t, *J* = 7.0 Hz, 1.80H), 2.90-2.81 (m, 0.30H), 2.72 (t, *J* = 7.5 Hz, 1.80H), 2.12-2.08 (m, 0.10H), 2.03-2.00 (m, 0.10H), 1.83-1.71 (m, 3.60H), 1.32 (d, *J* = 7.0 Hz, 0.30H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.1, 167.2, 147.8, 137.0, 133.0, 129.7, 128.6, 128.5, 128.0, 127.8, 52.0, 38.3, 35.9, 30.7, 23.9.

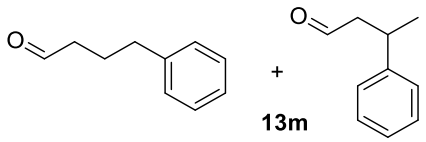
A mixture of 5-(4-Nitrophenyl)-1-phenylpentan-1-one and 4-(4-nitrophenyl)-1-phenylpentan-1-one (**13l**)[31]



Yellow solid (11.9 mg, 42%, *l*/*b* = 13/1, eluents: PE/EA = 10/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17-8.13 (m, 2H), 7.94 (d, *J* = 7.7 Hz, 1.86H), 7.86 (d, *J* = 7.7 Hz, 0.14H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.48-7.43 (m, 2H), 7.38-7.33 (m, 2H), 3.01 (t, *J* = 6.8 Hz, 1.86H), 2.90-2.82 (m, 0.21H), 2.78 (t, *J* = 7.4 Hz, 1.86H), 2.15-2.02 (m, 0.14H), 1.84-

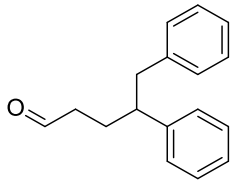
1.72 (m, 3.72H), 1.34 (d, *J* = 7.2 Hz, 0.21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.8, 150.1, 146.4, 137.0, 133.0, 129.1, 128.6, 128.3, 128.0, 127.9, 124.4, 123.9, 123.6, 38.1, 35.7, 30.5, 23.7.

A mixture of 4-phenylbutanal and 3-phenylbutanal (**13m**)[32]



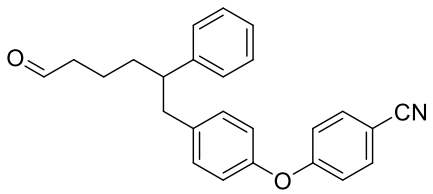
Colorless oil (17.8 mg, 60%, *l*/*b* = 7.3/1, eluents: PE/EA = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.76 (s, 0.88H), 9.71 (s, 0.12H), 7.33-7.28 (m, 2H), 7.23-7.17 (m, 3H), 3.36 (m, 0.12H), 2.76 (dd, *J* = 16.6 Hz, 6.8 Hz, 0.12H), 2.69-2.65 (m, 1.88H), 2.45 (t, *J* = 7.3 Hz, 1.76H), 1.97 (m, 1.76H), 1.32 (d, *J* = 6.9 Hz, 0.36H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.3, 201.8, 145.5, 141.2, 128.7, 128.5, 126.8, 126.6, 126.1, 51.8, 43.1, 35.0, 34.3, 23.7, 22.2.

4,5-Diphenylpentanal (**13n**)[33]



Colorless oil (25.8 mg, 54%, eluents: PE/EA = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.23-7.18 (m, 3H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 7.5 Hz, 2H), 7.05 (d, *J* = 7.4 Hz, 2H), 2.96-2.89 (m, 2H), 2.86-2.80 (m, 1H), 2.25 (t, *J* = 7.5 Hz, 2H), 2.09-2.02 (m, 1H), 1.93-1.85 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.2, 143.7, 140.1, 129.1, 128.5, 128.2, 127.7, 126.6, 126.0, 47.3, 43.8, 42.1, 27.7.

4-(4-(6-Oxo-2-phenylhexyl)phenoxy)benzonitrile (**13o**)

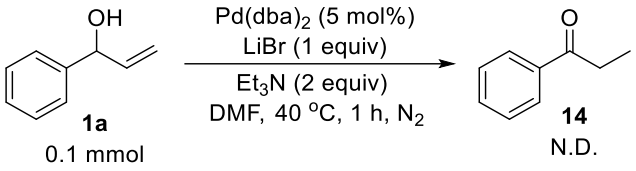


Colorless oil (36.2 mg, 49%, eluents: PE/EA = 5/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.69 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H),

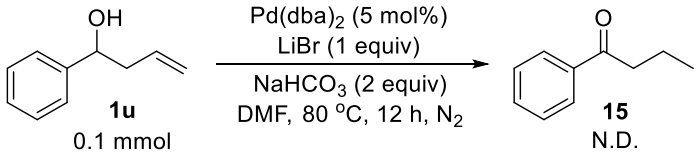
7.11 (d, *J* = 7.7 Hz, 2H), 7.04 (d, *J* = 8.1 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.1 Hz, 2H), 2.98-2.88 (m, 2H), 2.87-2.80 (m, 1H), 2.38 (m, 2H), 1.73 (m, 2H), 1.53 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.3, 161.9, 152.8, 144.0, 137.5, 134.1, 130.8, 128.4, 127.7, 126.4, 120.1, 118.9, 117.7, 105.6, 48.1, 43.8, 43.1, 35.0, 20.2. IR (KBr): 3060, 3029, 2926, 2844, 2226, 1707, 1597, 1498, 1452, 1413, 1248, 1201, 1168, 1016, 874, 836, 758, 701 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{25}H_{24}NO_2]^+$ ([M + H]$^+$): 370.1802; found: 370.1802.

6. Control experiments for mechanistic insights.

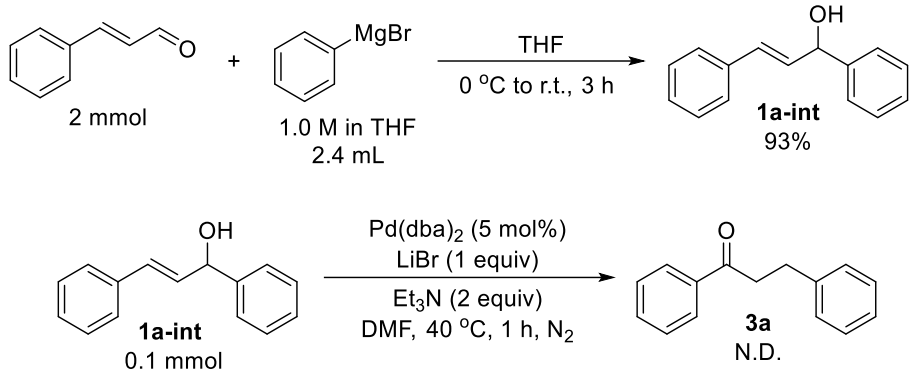
6.1 Reactions of alkenyl alcohols without using arylsulfonium salt under the standard conditions.



In a nitrogen-filled glovebox, a sealed tube was charged with **1a** (13.4 mg, 0.1 mmol), Et_3N (20 mg, 0.2 mmol), LiBr (8.7 mg, 0.1 mmol), $Pd(dba)_2$ (2.9 mg, 0.005 mmol), and DMF (1 mL) with stirring. The mixture was reacted at 40 °C for 1 h, and no desired isomerization product (**14**) was formed.

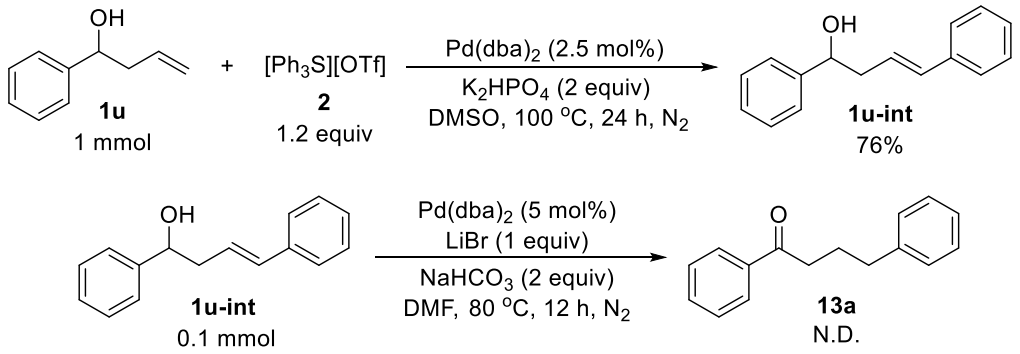


In a nitrogen-filled glovebox, a sealed tube was charged with **1u** (14.8 mg, 0.1 mmol), $NaHCO_3$ (16.8 mg, 0.2 mmol), LiBr (8.7 mg, 0.1 mmol), $Pd(dba)_2$ (2.9 mg, 0.005 mmol), and DMF (1 mL) with stirring. The mixture was reacted at 80 °C for 12 h, and no desired isomerization product (**15**) was formed.



Under a nitrogen atmosphere, a sealed tube was charged with cinnamaldehyde (264 mg, 2 mmol) and THF with stirring and cooled to 0 °C. Phenylmagnesium bromide (2.4 mL, 1.0 M in THF, 2.4 mmol) was slowly added. The mixture was reacted at room temperature for 3 h, quenched by a saturated aqueous ammonium chloride solution (20 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with water, dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (10/1, v/v) as eluents to give the desired product (**1a-int**). (*E*)-1,3-diphenylprop-2-en-1-ol (**1a-int**):[34] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.4 Hz, 2H), 7.41-7.37 (m, 4H), 7.38-7.31 (m, 3H), 7.26 (t, *J* = 6.9 Hz, 1H), 6.71 (d, *J* = 15.9 Hz, 1H), 6.41 (dd, *J* = 15.9 Hz, 6.5 Hz, 1H), 5.40 (d, *J* = 6.4 Hz, 1H), 2.15 (brs, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.8, 136.6, 131.6, 130.6, 128.6, 128.6, 127.8, 127.8, 126.6, 126.4, 75.1.

In a nitrogen-filled glovebox, a sealed tube was charged with **1a-int** (21.0 mg, 0.1 mmol), Et_3N (20 mg, 0.2 mmol), LiBr (8.7 mg, 0.1 mmol), $Pd(dba)_2$ (2.9 mg, 0.005 mmol), and DMF (1 mL) with stirring. The mixture was reacted at 40 °C for 1 h, and no desired isomerization product (**3a**) was formed.



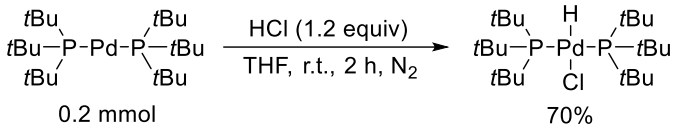
In a nitrogen-filled glovebox, a flask was charge with **1u** (148 mg, 1 mmol), **2** (494.9

mg, 1.2 mmol), K_2HPO_4 (348.4 mg, 2 mmol), $Pd(dba)_2$ (14.2 mg, 0.025 mmol), and DMF (5 mL) with stirring. The mixture was reacted at 100 °C for 24 h, cooled to room temperature, diluted with water (50 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (10/1, v/v) as eluents to give the desired product (**1u-int**). (*E*)-1,4-diphenylbut-3-en-1-ol (**1u-int**):[35] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.34 (m, 6H), 7.32-7.29 (m, 3H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.52 (d, *J* = 15.9 Hz, 1H), 6.21 (dt, *J* = 15.9 Hz, 7.4 Hz, 1H), 4.82 (t, *J* = 6.4 Hz, 1H), 2.68 (m, 2H), 2.05 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.9, 137.2, 133.5, 128.5, 128.5, 127.6, 127.3, 126.2, 125.9, 125.8, 73.8, 43.1.

In a nitrogen-filled glovebox, a sealed tube was charged with **1u-int** (22.4 mg, 0.1 mmol), $NaHCO_3$ (16.8 mg, 0.2 mmol), LiBr (8.7 mg, 0.1 mmol), $Pd(dba)_2$ (2.9 mg, 0.005 mmol), and DMF (1 mL) with stirring. The mixture was reacted at 80 °C for 12 h, and no desired isomerization product (**13a**) was formed.

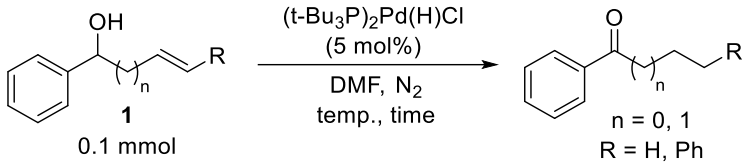
6.2 Isomerization of alkenyl alcohols in the presence of Pd-H complexes without using arylsulfonium salt.

Synthesis of (*t*-Bu$_3$P)$_2$Pd(H)Cl.[36]



In a nitrogen-filled glovebox, a sealed tube was charged with Pd[P(*t*-Bu)$_3$]$_2$ (102.2 mg, 0.2 mmol) and THF (2 mL) with stirring. A solution of anhydrous HCl in 1,4-dioxane (60 μL, 4.0 mol/L, 0.24 mmol) was slowly added via a micro-syringe outside of the glovebox. The mixture was reacted at 25 °C for 2 h, and the volatiles were removed inside of the glovebox under reduced pressure. The residue was washed with hexane (2 × 1 mL) and dried overnight under vacuum to afford (*t*-Bu$_3$P)$_2$Pd(H)Cl as a gray solid (76.6 mg, 70% yield). ^{1}H NMR (500 MHz, acetone-d_6) δ 1.58 (m, 54H), -16.58 (t, *J* = 6.5 Hz, 1H). ^{31}P NMR (202 MHz, acetone-d_6) δ 82.5 (m).

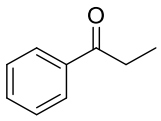
Table S24. Isomerization of allylic alcohols in the presence of (*t*-Bu$_3$P)$_2$Pd(H)Cl.



Procedure: In a nitrogen-filled glovebox, a sealed tube was charged with **1** (0.1 mmol), (*t*-$Bu_3P)_2Pd(H)Cl$ (2.7 mg, 0.005 mmol), and DMF (1 mL) with stirring. The mixture was reacted at 20-120 °C for 12-36 hours, cooled to room temperature, diluted with water (30 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (40/1, v/v) as eluents to give the product.

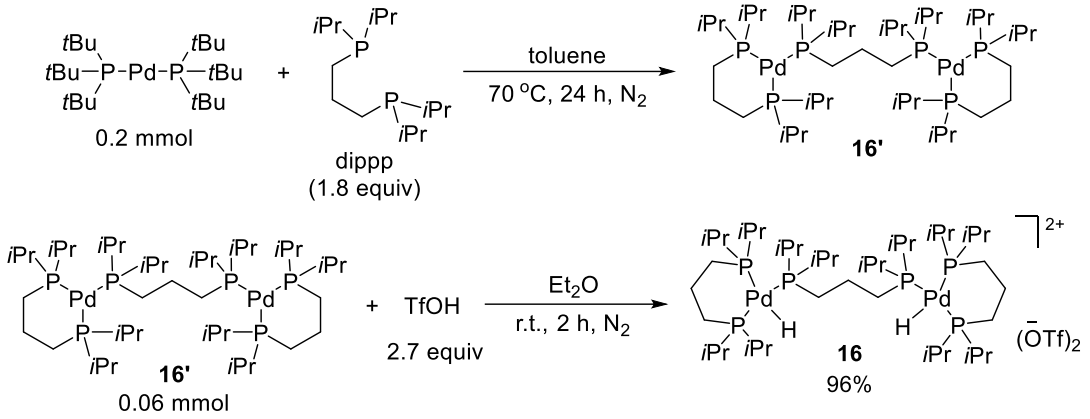
Entry	Allyl alcohol	Temp. (°C)	Time (h)	Isolated yield (%)
1	**1a**	20	12	**14**, 14%
2	**1a**	80	12	**14**, 89%
3	**1a-int**	80	12	**3a**, 0%
4	**1a-int**	120	36	**3a**, 0%
5	**1u**	80	24	**15**, trace
6	**1u-int**	80	24	**13a**, 0%

Propiophenone (**14**)[37]



Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 3.01 (q, *J* = 7.3 Hz, 2H), 1.23 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.8, 137.0, 132.9, 128.6, 128.0, 31.8, 8.3.

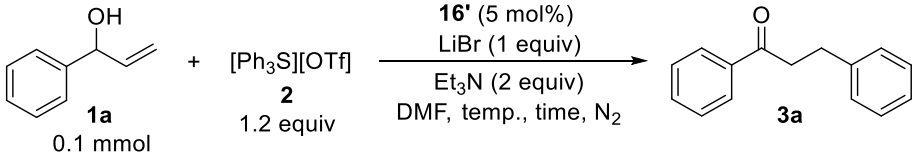
Synthesis of Pd-H complex 16.[38]



In a nitrogen-filled glovebox, a sealed tube was charged with Pd[P(*t*-Bu)$_3$]$_2$ (102.2 mg, 0.2 mmol), toluene (0.5 mL), and dippp (99.5 mg, 0.36 mmol) with vigorous stirring. The mixture was reacted at 70 °C for 24 h and cooled to room temperature. Yellow precipitates were formed by addition of dry acetonitrile (2 mL) to the reaction mixture, which were collected and washed with acetonitrile (2 × 2.0 mL) to afford the desired product **16'** as a yellow solid (90.7 mg, 87%).

In a nitrogen-filled glovebox, a sealed tube was charged with **16'** (62.5 mg, 0.06 mmol) and Et$_2$O (1 mL) with stirring. TfOH (24.4 mg, 0.16 mmol) was added to the solution via a micro-syringe at room temperature outside of the glovebox. The reaction mixture immediately turned colorless and formed a thick oily residue. The volatiles were removed under reduced pressure inside of the glovebox. The resulting solid was washed with Et$_2$O (2 × 1 mL) and dried overnight under vacuum to afford **16** (77.3 mg, 96% yield) as a gray solid. ^{1}H NMR (500 MHz, acetone-d$_6$) δ 2.52-1.93 (m, 30H), 1.58-1.16 (m, 72H), -6.78 (dd, *J* = 16.0 Hz, 5.6 Hz), -7.13 (dd, *J* = 17.0 Hz, 6.0 Hz). ^{31}P NMR (202 MHz, acetone-d$_6$) δ 44.2 (d, *J* = 311.0 Hz), 37.1 (d, *J* = 309.2 Hz), 15.5 (d, *J* = 168.3 Hz).

Table S25. The relay Heck reaction of 1a with 2 in the presence of 16'.

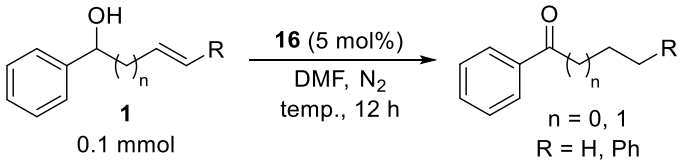


Procedure: In a nitrogen-filled glovebox, a sealed tube was charged with **1a** (13.4 mg, 0.1 mmol), **2** (49.5 mg, 0.12 mmol), Et$_3$N (20 mg, 0.2 mmol), LiBr (8.7 mg, 0.1 mmol), **16'** (5.2 mg, 0.005 mmol), and DMF (1 mL) with stirring. The mixture was reacted at 40 or 100 °C for 1 or 12 hours. The yields of product were determined by

HPLC using **3a** as an external standard (t_R = 9.0 min, λ_{max} = 242 nm, water / methanol = 20 / 80 (v / v)).

Entry	Temp. (°C)	Time (h)	Yield (**3a**, %)
1	40	1	trace
2	40	12	trace
3	100	12	57

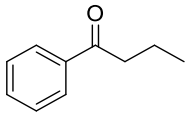
Table S26. Isomerization of alkenyl alcohols in the presence of 16.



Procedure: In a nitrogen-filled glovebox, a sealed tube was charged with **1** (0.1 mmol), **16** (6.7 mg, 0.005 mmol), and DMF (1 mL) with stirring. The mixture was reacted at 40 or 80 °C for 12 h, cooled to room temperature, diluted with water (30 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (40/1, v/v) as eluents to give the desired product.

Entry	Allyl alcohol	Temp. (°C)	Isolated yield (%)
1	**1a**	40	**14**, 61
2	**1a-int**	40	**3a**, 28
3	**1u**	80	**15**, 54
4	**1u-int**	80	**13a**, 78

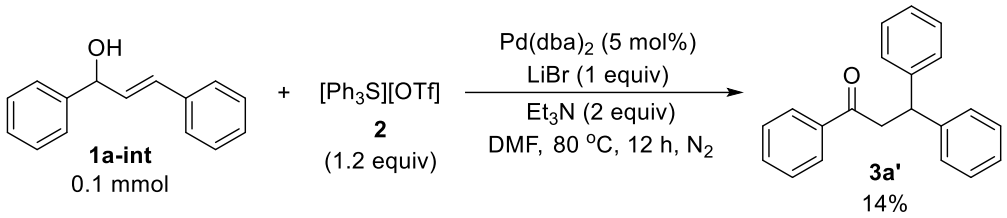
1-Phenylbutan-1-one (**15**)[39]



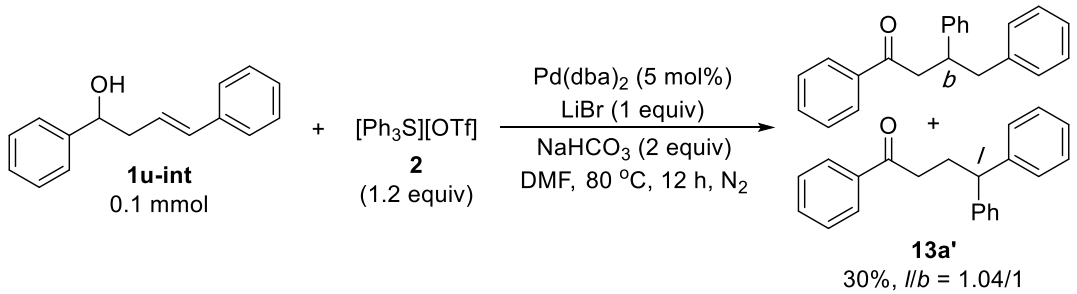
Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 2.95 (t, *J* = 7.3 Hz, 2H), 1.78 (m, 2H), 1.01 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.4, 137.2, 132.8, 128.5, 128.0, 40.5,

17.8, 13.9.

6.3 Treatment of 1a-int and 1u-int with 2 under the standard relay Heck reaction conditions.



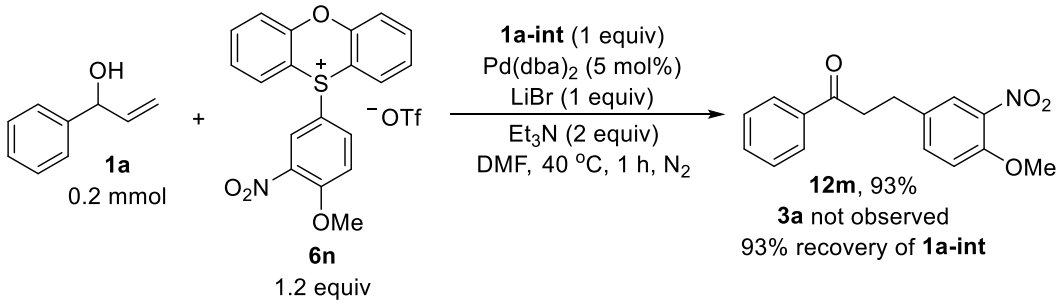
In a nitrogen-filled glovebox, a sealed tube was charged with **1a-int** (21.0 mg, 0.1 mmol), **2** (49.5 mg, 0.12 mmol), Et_3N (20 mg, 0.2 mmol), LiBr (8.7 mg, 0.1 mmol), $Pd(dba)_2$ (2.9 mg, 0.005 mmol), and DMF (1 mL) with stirring. The mixture was reacted at 80 °C for 12 hours, diluted with water (30 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (40/1, v/v) as eluents to give the product **3a'** as a colorless oil (3.9 mg, 14%). 1,3,3-Triphenylpropan-1-one (**3a'**):[40] ^1H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.27-7.26 (m, 8H), 7.18-7.15 (m, 2H), 4.83 (t, *J* = 7.3 Hz, 1H), 3.74 (d, *J* = 7.3 Hz, 2H).



In a nitrogen-filled glovebox, a sealed tube was charged with **1u-int** (22.4 mg, 0.1 mmol), **2** (49.5 mg, 0.12 mmol), $NaHCO_3$ (16.8 mg, 0.2 mmol), LiBr (8.7 mg, 0.1 mmol), $Pd(dba)_2$ (2.9 mg, 0.005 mmol), and DMF (1 mL) with stirring. The mixture was reacted at 80 °C for 12 hours, diluted with water (30 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether and

ethyl acetate (40/1, v/v) as eluents to give the product **13a'** with regioisomers (9.0 mg, 30%, *l*/*b* = 1.04/1).[41] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86-7.83 (m, 2H), 7.54-7.51 (m, 1H), 7.43-7.39 (m, 2H), 7.31-7.28 (m, 4.08H), 7.24-7.14 (m, 4.94H), 7.07 (d, *J* = 7.3 Hz, 0.98H), 4.02 (t, *J* = 7.9 Hz, 0.51H), 3.67 (m, 0.49H), 3.36 (dd, *J* = 16.7 Hz, 7.3 Hz, 0.49H), 3.28 (dd, *J* = 16.8 Hz, 6.6 Hz, 0.49H), 3.01 (dd, *J* = 13.5 Hz, 7.1 Hz, 0.49H), 2.98-2.92 (m, 1.51H), 2.51 (m, 1.02H).

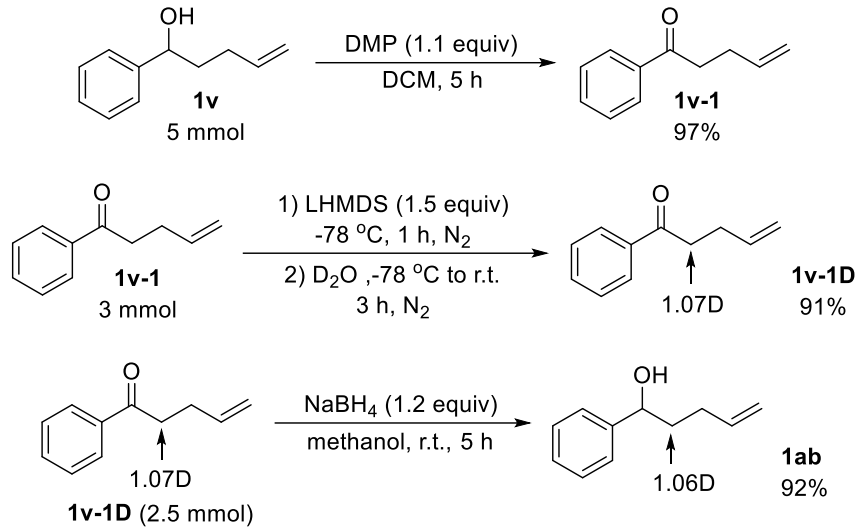
6.4 The Pd-catalyzed relay Heck reaction of 1a with 6n in the presence of 1a-int



Procedure: In a nitrogen-filled glovebox, a sealed tube was charged with **1a** (26.8 mg, 0.2 mmol), **6n** (120.3 mg, 0.24 mmol), **1a-int** (42.0 mg, 0.2 mmol), Et_3N (20 mg, 0.2 mmol), LiBr (17.4 mg, 0.2 mmol), $Pd(dba)_2$ (5.8 mg, 0.01 mmol), and DMF (2 mL) with stirring. The mixture was reacted at 40 °C for 1 h, diluted with water (30 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (10/1 to 5/1, v/v) as eluents to give product **12m** (53.0 mg, 93%) with recovery of **1a-int** (39.1 mg, 93%). The product **3a** was not generated in the reaction.

6.5 The relay Heck arylation of deuterated non-allylic alcohol under the standard conditions.

Synthesis of deuterated non-allylic alcohol (1ab).[27]



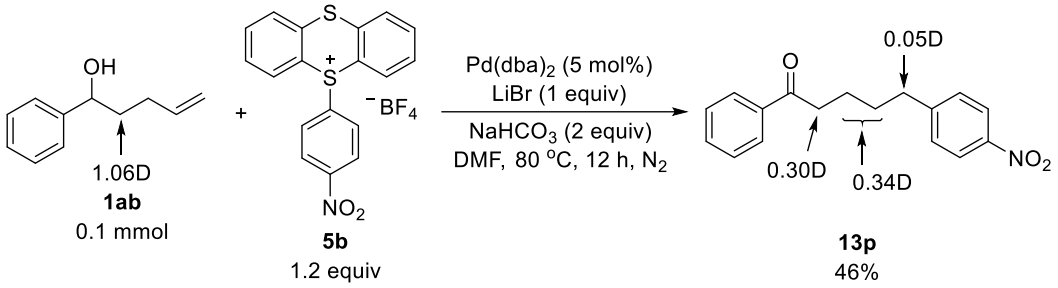
To a solution of **1v** (811 mg, 5 mmol) in DCM (15 mL) was added Dess-Martin periodinane (2.3 g, 5.5 mmol). The mixture was reacted at room temperature for 5 h and concentrated to dryness with silica gel under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (40/1, v/v) as eluents to give product **1v-1** (777 mg, 97%) as a light yellow liquid.

Under a nitrogen atmosphere, LHMDS (4.5 mL, 1.0 M in THF, 4.5 mmol) was added to a solution of **1v-1** (481 mg, 3 mmol) in anhydrous THF (15 mL) at -78 °C with stirring. The mixture was kept at -78 °C for 1 h, followed by addition of deuterium oxide (D_2O, 1.6 mL, 90 mmol), and then warmed to room temperature over 3 h. Water (20 mL) and ethyl acetate (20 mL) was added to the reaction mixture. The aqueous layer was extracted with ethyl acetate (3 × 20 mL). All ethyl acetate solutions were collected, washed with brine, dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure, affording product **1v-1D** as a colorless oil (440 mg, 91%). 1-Phenylpent-4-en-1-one-2-*d* (**1v-1D**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 5.95-5.86 (m, 1H), 5.09 (dm, *J* = 17.0 Hz, 1H), 5.02 (dm, *J* = 10.2 Hz, 1H), 3.10-3.03 (m, 0.93H), 2.50 (t, *J* = 7.0 Hz, 2H).

To a solution of **1v-1D** (403 mg, 2.5 mmol) in methanol (10 mL) was added $NaBH_4$ (113.5 mg, 3 mmol). The mixture was reacted at room temperature for 5 h and concentrated to dryness with silica gel under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (10/1, v/v) as eluents to give product **1ab** (375 mg, 93%) as a colorless oil. 1-Phenylpent-4-en-2-*d*-1-ol (**1ab**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-

7.33 (m, 4H), 7.29 (m, 1H), 5.89-5.81 (m, 1H), 5.05 (dm, *J* = 17.1 Hz, 1H), 4.99 (dm, *J* = 10.1 Hz, 1H), 4.70 (d, *J* = 6.3 Hz, 1H), 2.20-2.09 (m, 2H), 1.90 (s, 1H), 1.90-1.76 (m, 0.94H).

Procedure for the relay Heck arylation of deuterated non-allylic alcohol (1ab)



In a nitrogen-filled glovebox, a sealed tube was charged with **1ab** (16.3 mg, 0.1 mmol), **5b** (51.0 mg, 0.12 mmol), $NaHCO_3$ (16.8 mg, 0.2 mmol), LiBr (8.7 mg, 0.1 mmol), $Pd(dba)_2$ (2.9 mg, 0.005 mmol), and DMF (2 mL) with stirring. The mixture was reacted at 80 °C for 12 h, cooled to room temperature, diluted with water (30 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (10/1, v/v) as eluents to give product **13p** (13.1 mg, 46%) as a light yellow liquid. Deuterated 5-(4-nitrophenyl)-1-phenylpentan-1-one (**13p**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.6 Hz, 2H), 7.94 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 3.02-2.97 (m, 1.70H), 2.78 (t, *J* = 7.4 Hz, 1.95H), 1.83-1.72 (m, 3.66H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.8, 150.1, 146.4, 136.9, 133.1, 129.2, 128.6, 128.0, 123.7, 38.1, 38.1, 35.8, 35.8, 30.5, 30.4, 23.7, 23.7.

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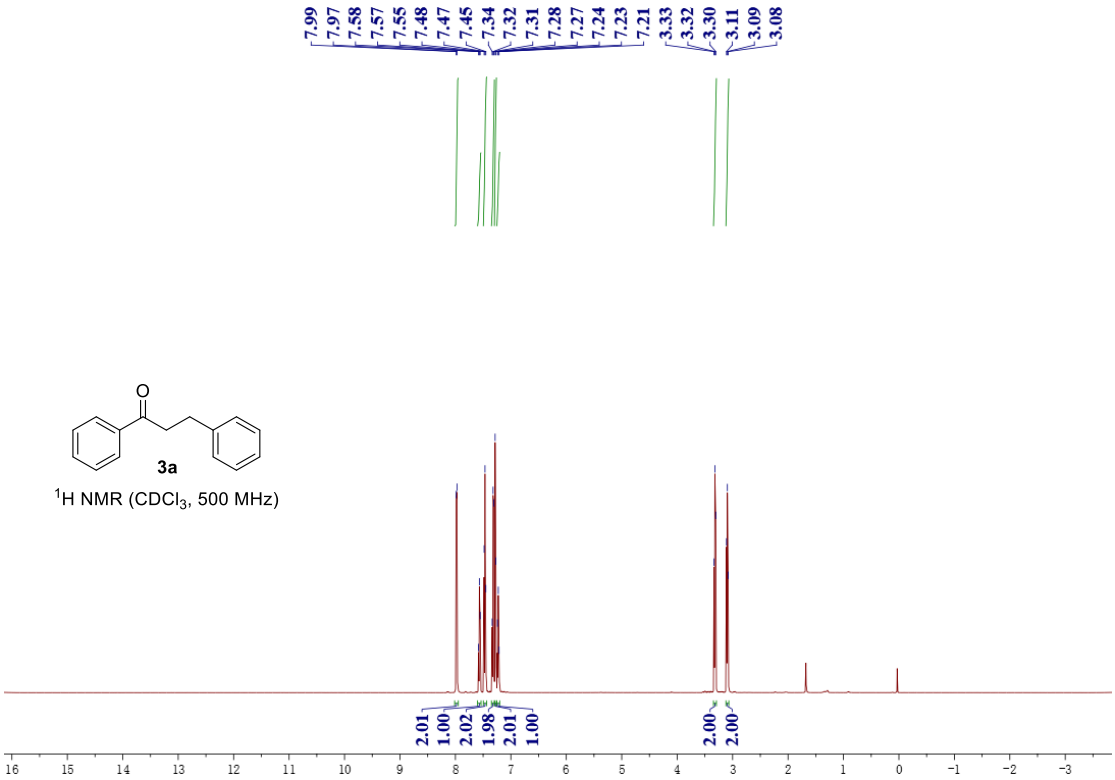
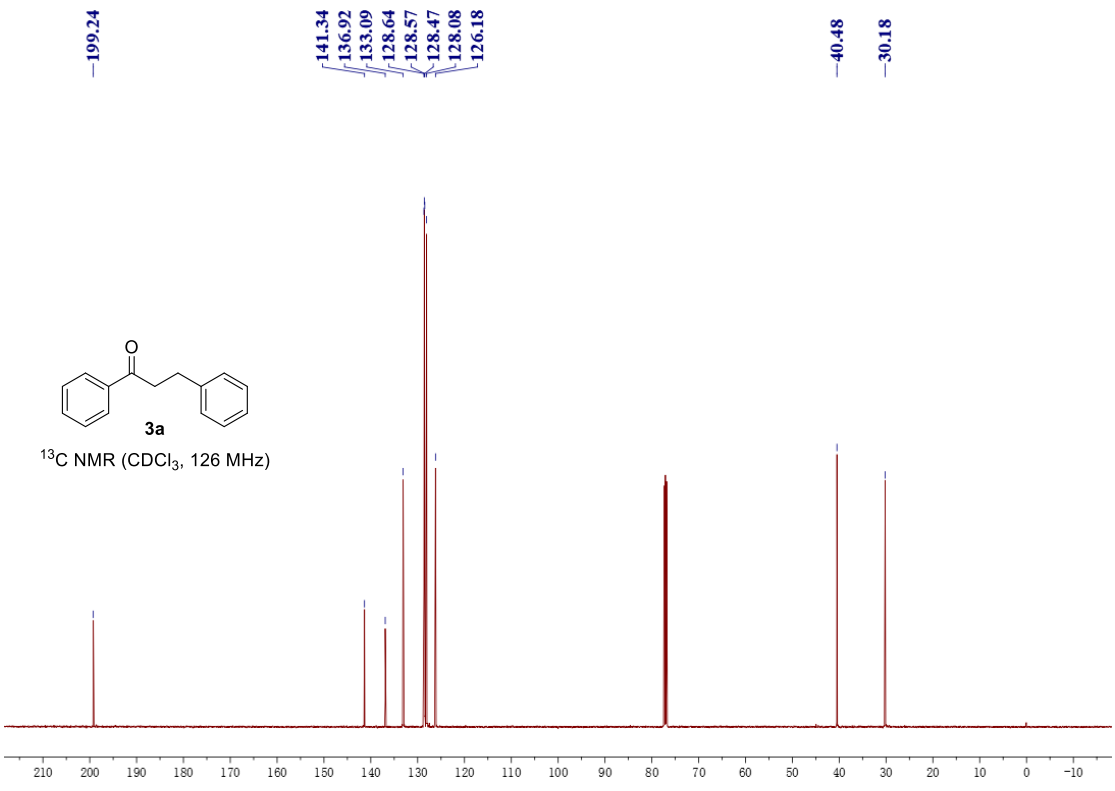
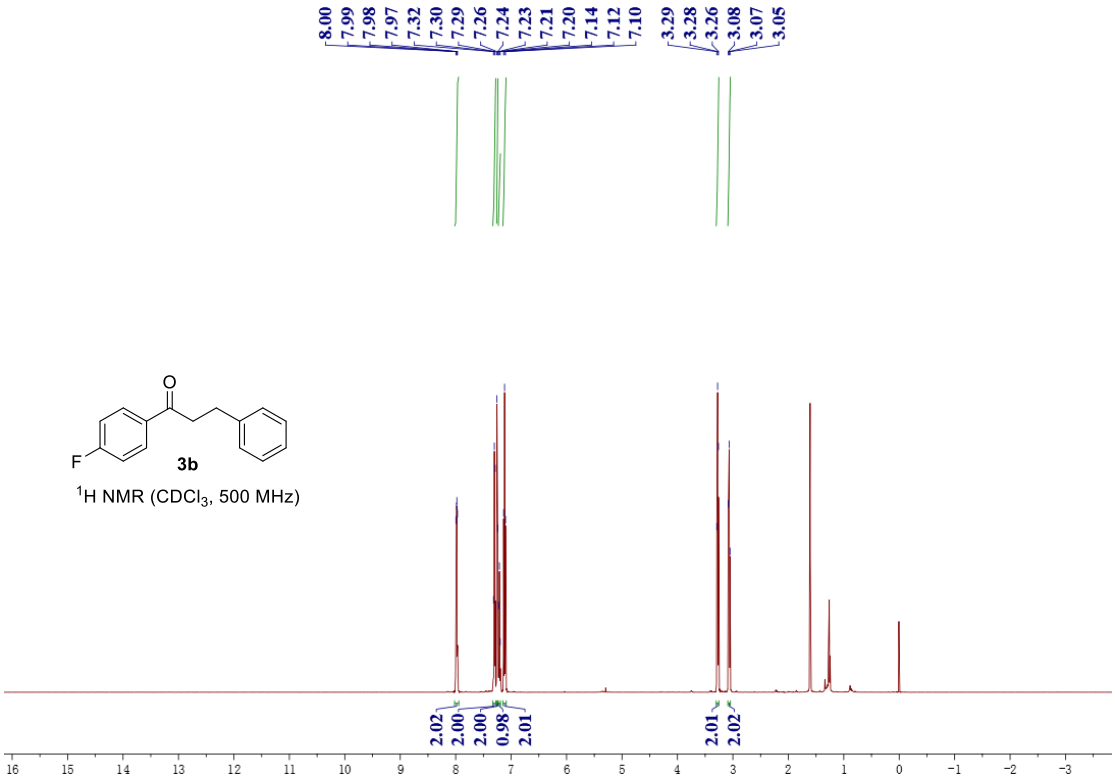
7. NMR spectra of the products



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7.30
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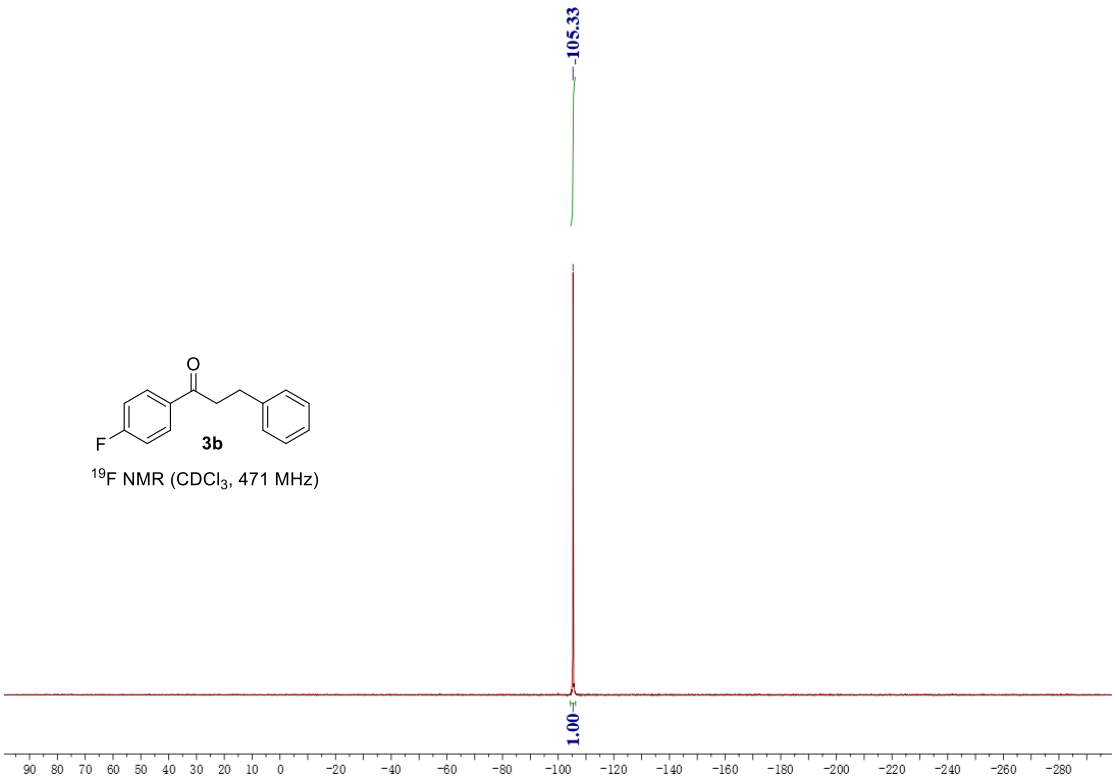
7.26
7.24
7.23
7.21
7.20
7.14
7.12
7.10
3.29
3.28
3.26
3.08
3.07
3.05
O
F
3b
1H NMR (CDCl3, 500 MHz)
2.02
2.00
2.00
0.98
2.01
2.01
2.02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O
F
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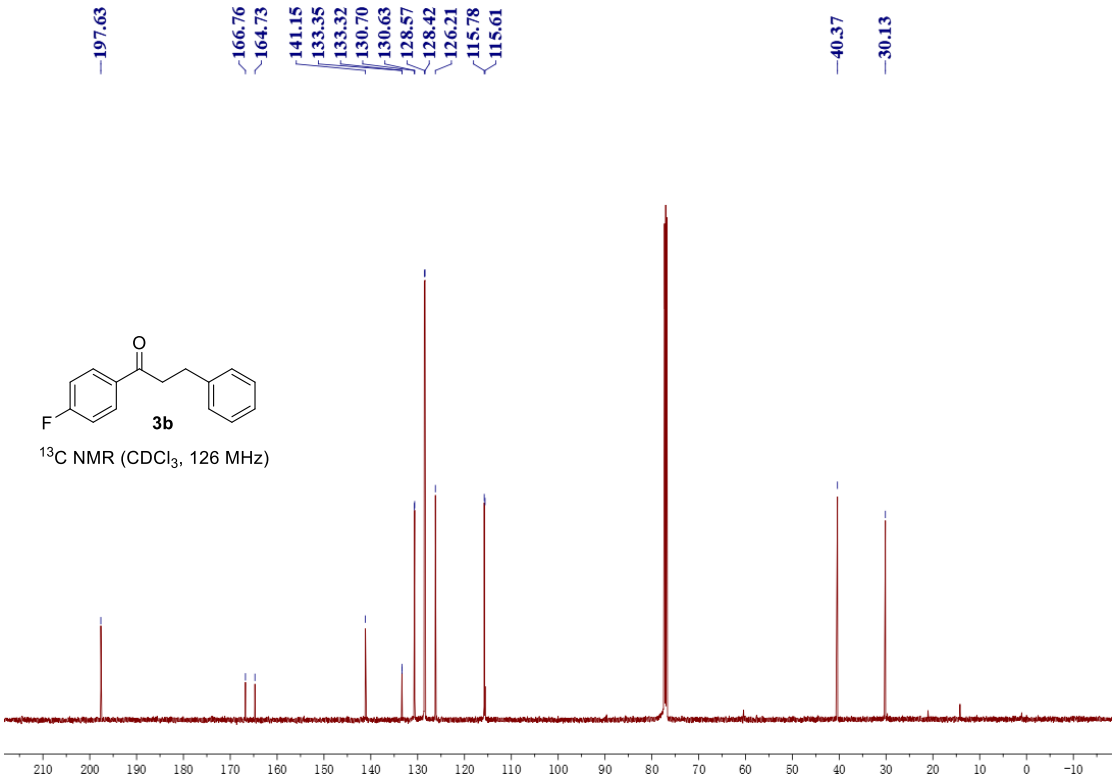
19F NMR (CDCl3, 471 MHz)
1.00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133.32
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130.63
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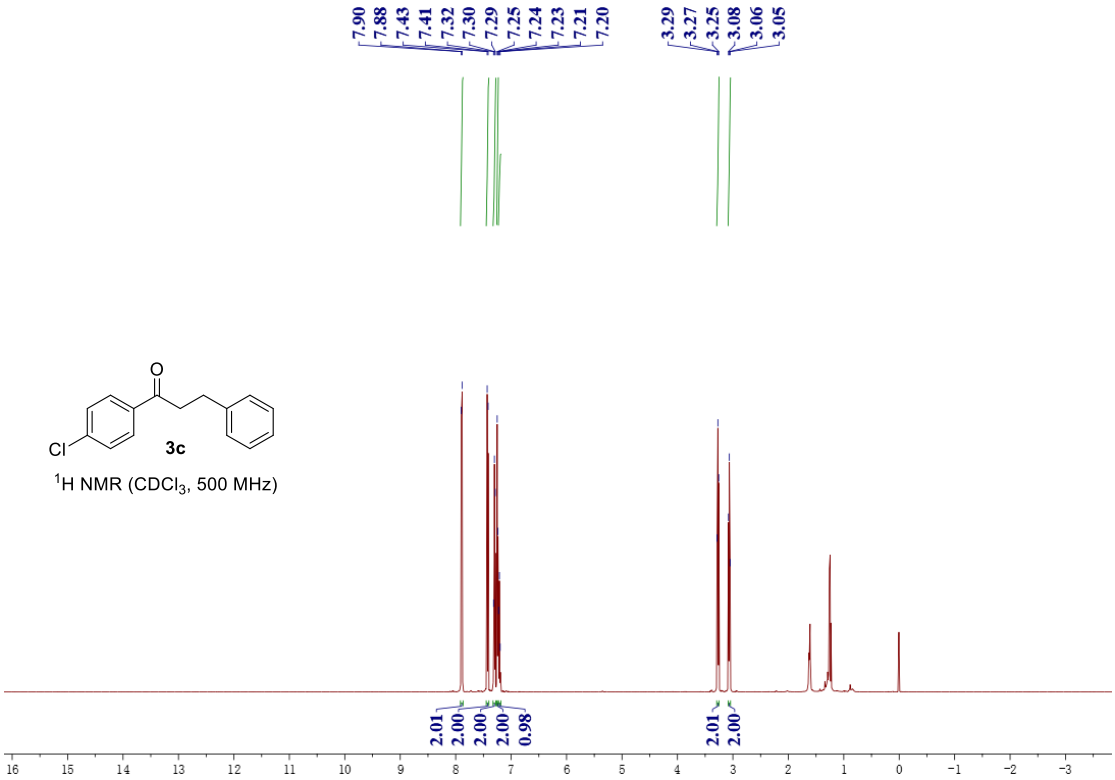
128.42
126.21
115.78
115.61
40.37
30.13
O
F
3b
13C NMR (CDCl3, 126 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10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7.30
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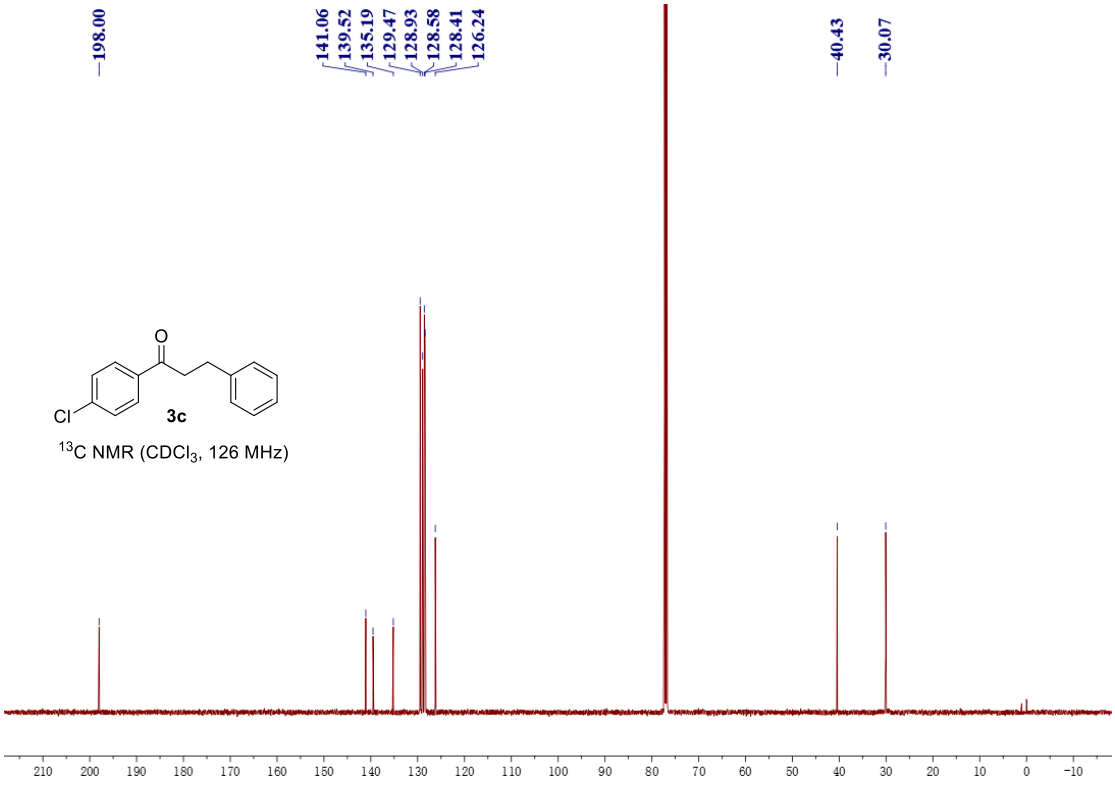
7.25
7.24
7.23
7.21
7.20
3.29
3.27
3.25
3.08
3.06
3.05
O
Cl
3c
1H NMR (CDCl3, 500 MHz)
2.01
2.00
2.00
2.00
0.98
2.01
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3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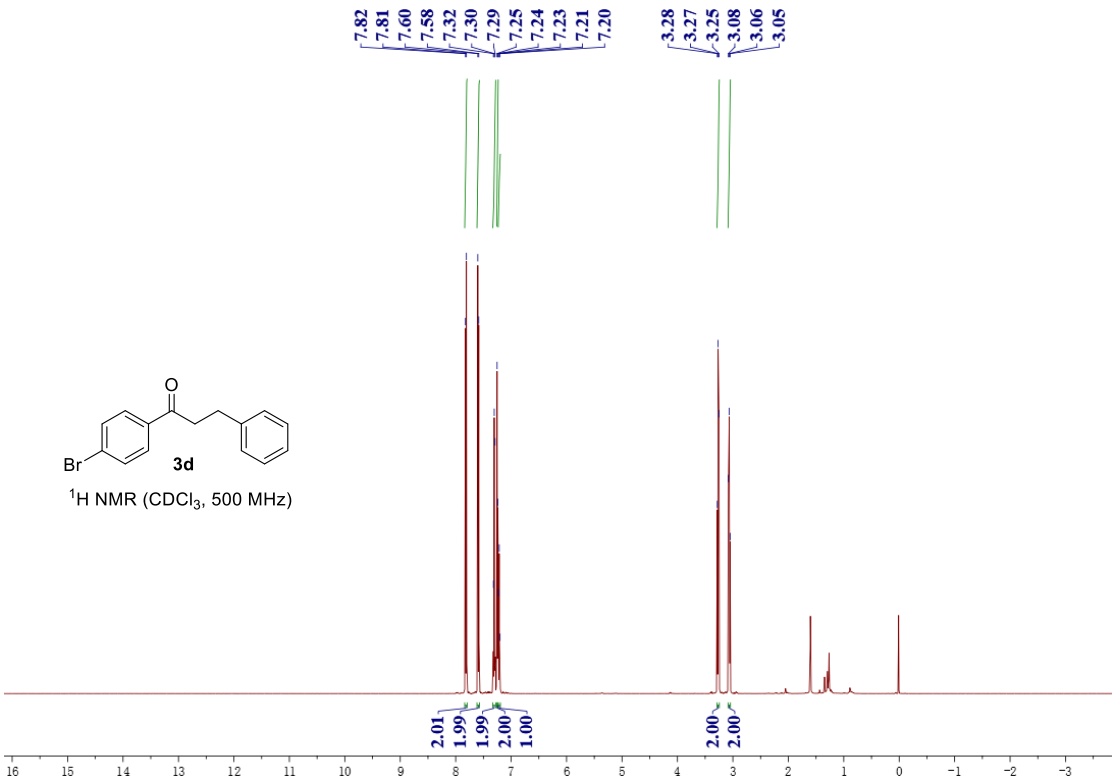
O
Cl
3c
13C NMR (CDCl3, 126 MHz)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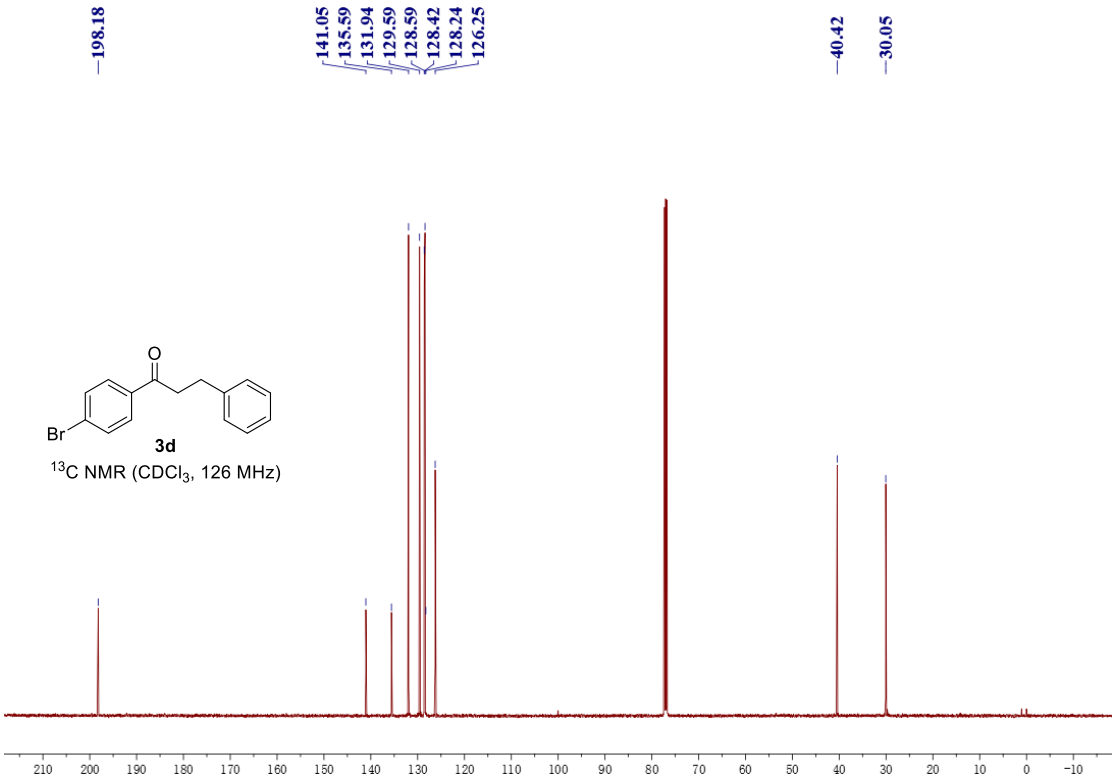
7.21
7.20
3.28
3.27
3.25
3.08
3.06
3.05
2.01
1.99
1.99
2.00
1.00
2.00
2.00
O
Br
3d
1H NMR (CDCl3, 500 MHz)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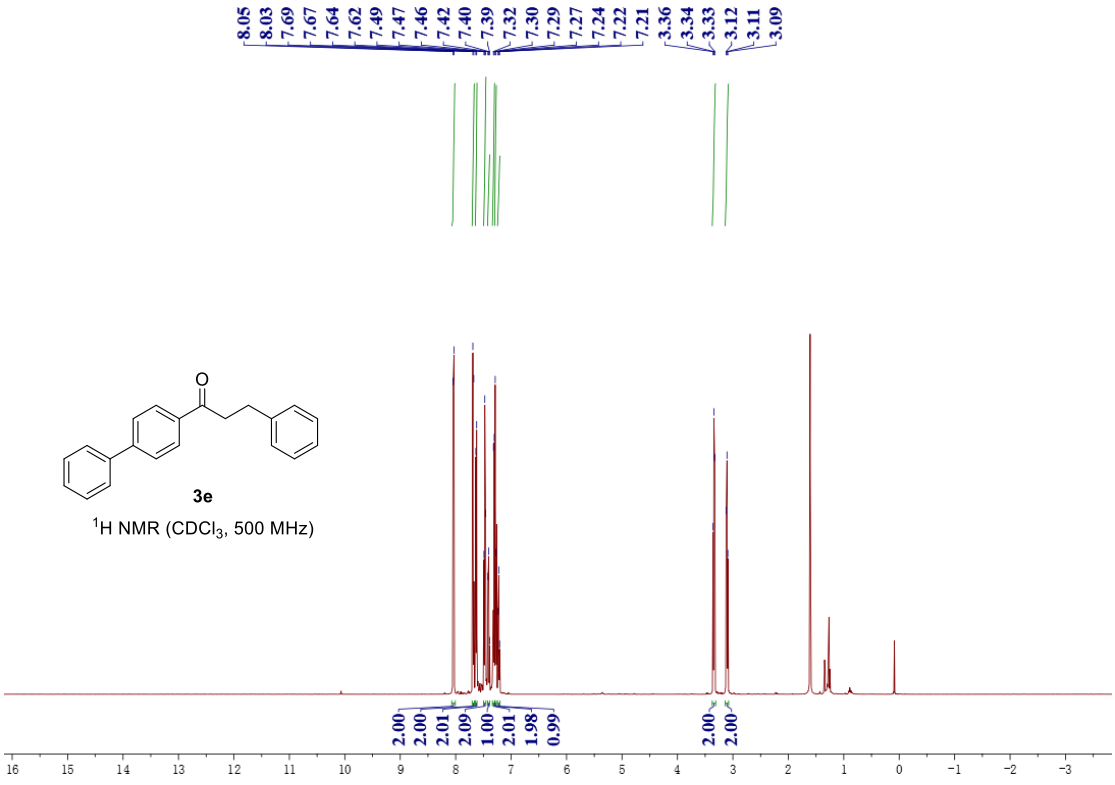
O
Br
3d
13C NMR (CDCl3, 126 MHz)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7.47
7.46
7.42
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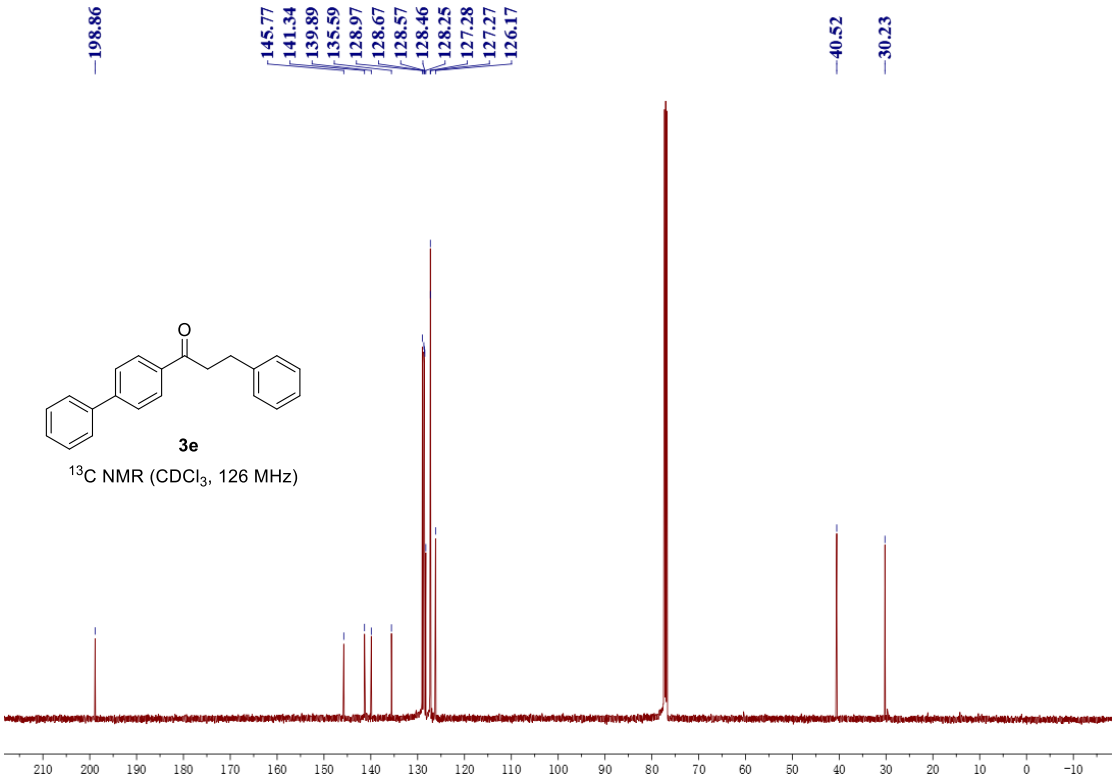
7.39
7.32
7.30
7.29
7.27
7.24
7.22
7.21
3.36
3.34
3.33
3.12
3.11
3.09
O
3e
1H NMR (CDCl3, 500 MHz)
2.00
2.00
2.01
2.09
1.00
2.01
1.98
0.99
2.00
2.00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127.28
127.27
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O
3e
13C NMR (CDCl3, 126 MHz)
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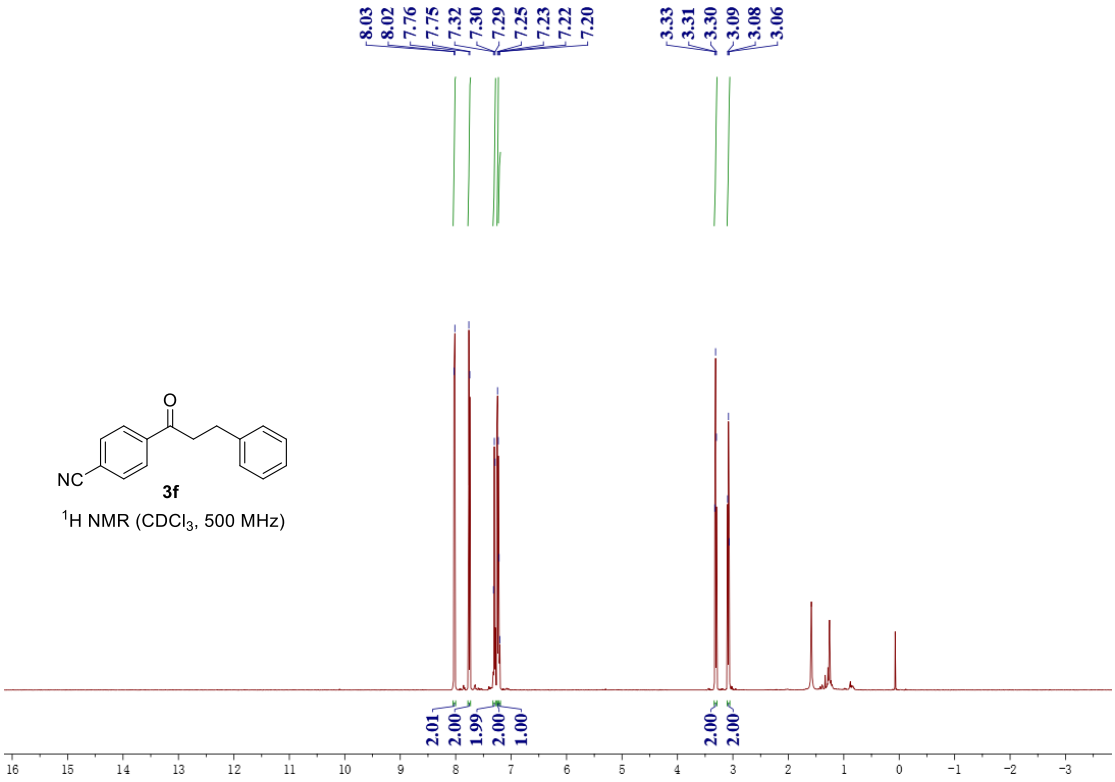
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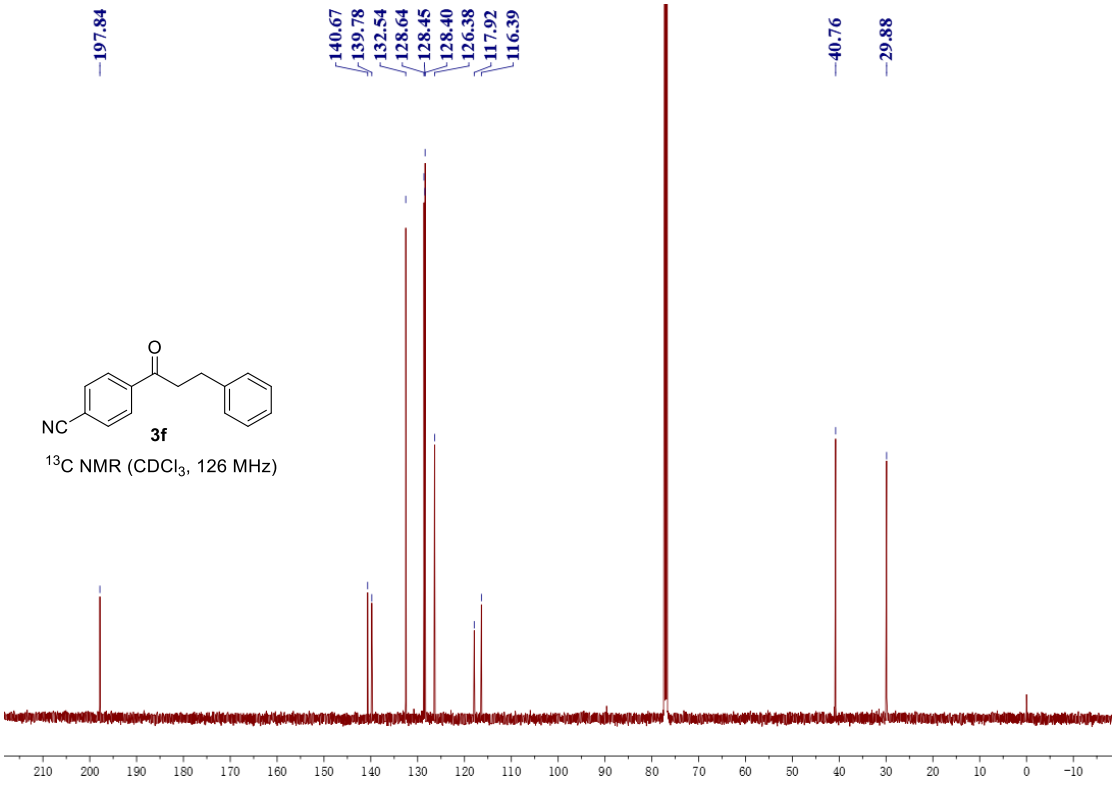
7.22
7.20
3.33
3.31
3.30
3.09
3.08
3.06
O
NC
3f
1H NMR (CDCl3, 500 MHz)
2.01
2.00
1.99
2.00
1.00
2.00
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3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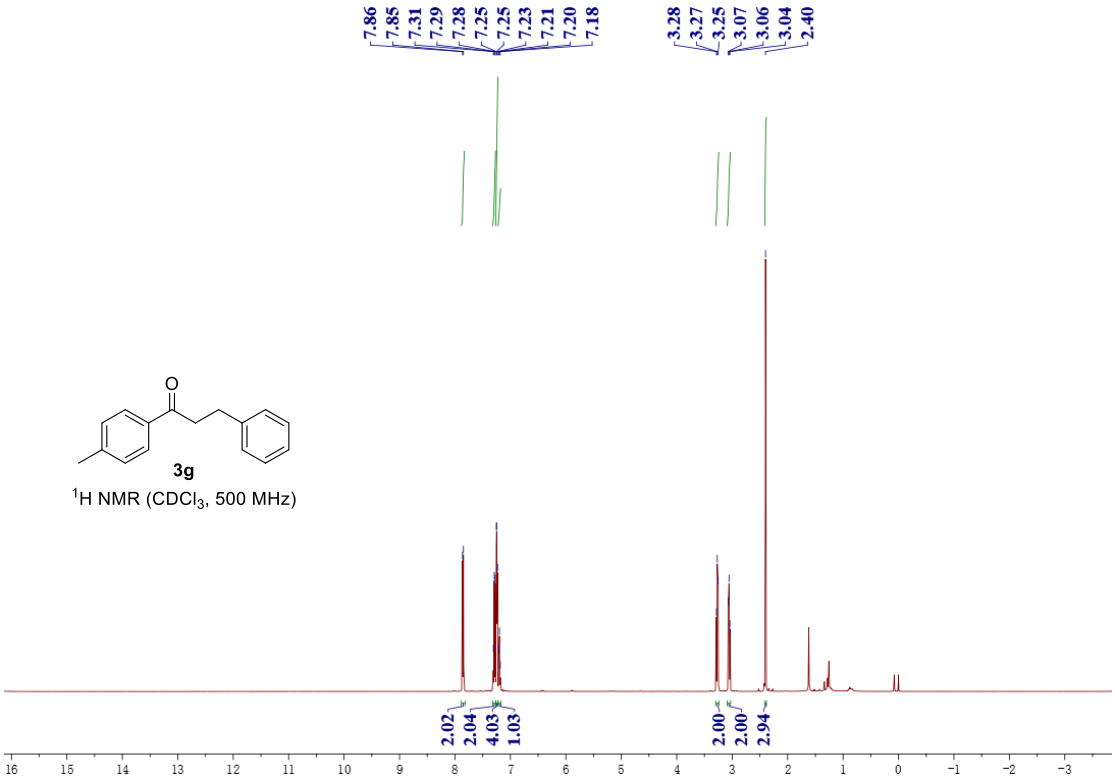
O
NC
3f
^{13}C NMR ($CDCl_3$, 126 MHz)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7.23
7.21
7.20
7.18
3.28
3.27
3.25
3.07
3.06
3.04
2.40
O
3g
^{1}H NMR ($CDCl_3$, 500 MHz)
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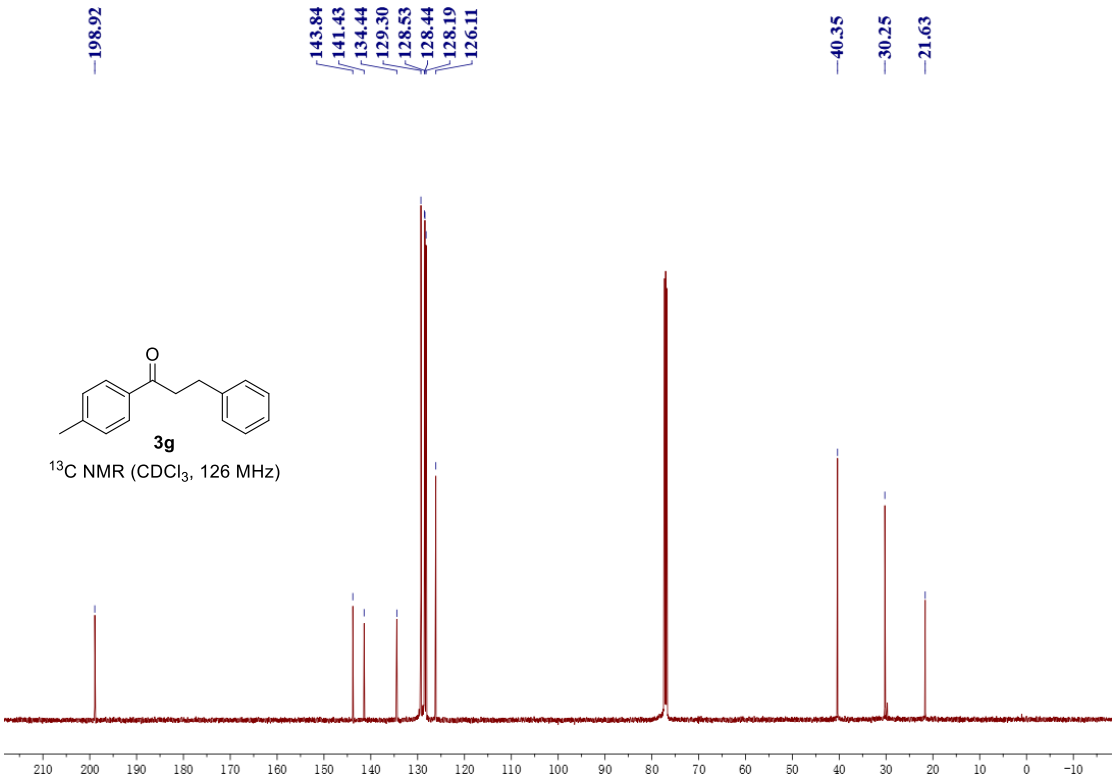
2.04
4.03
1.03
2.00
2.00
2.94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21.63
O
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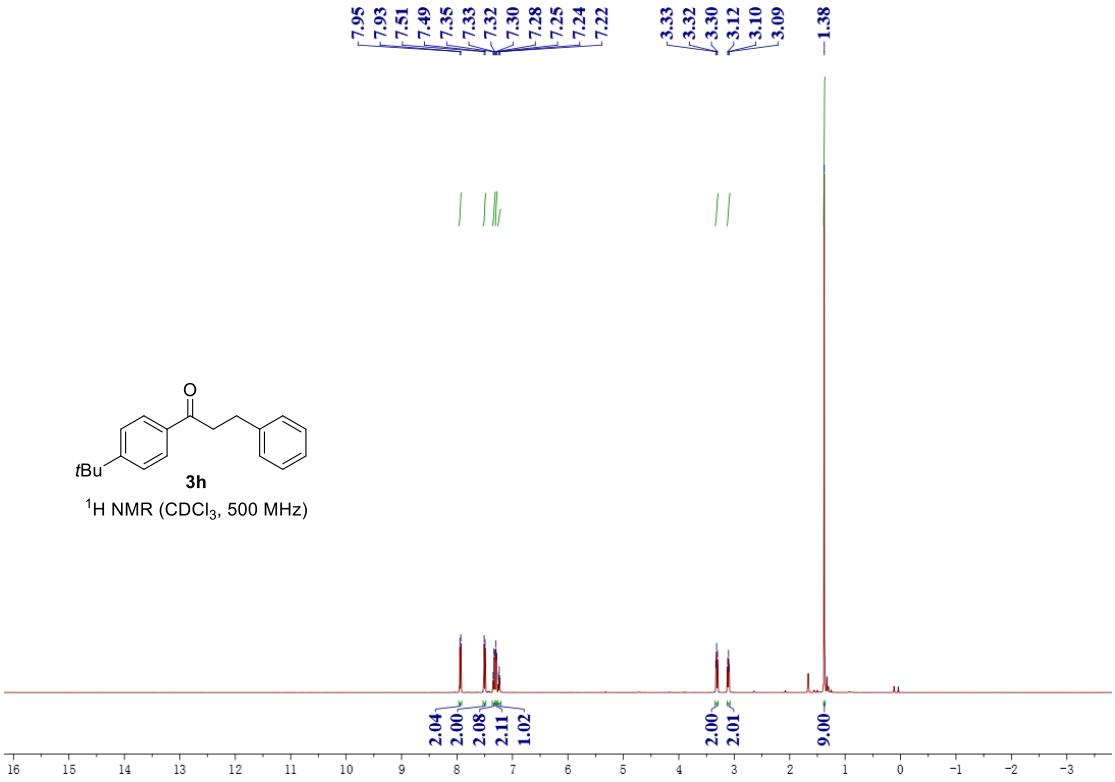
13C NMR (CDCl3, 126 MHz)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3.33
3.32
3.30
3.12
3.10
3.09
1.38
O
tBu
3h
1H NMR (CDCl3, 500 MHz)
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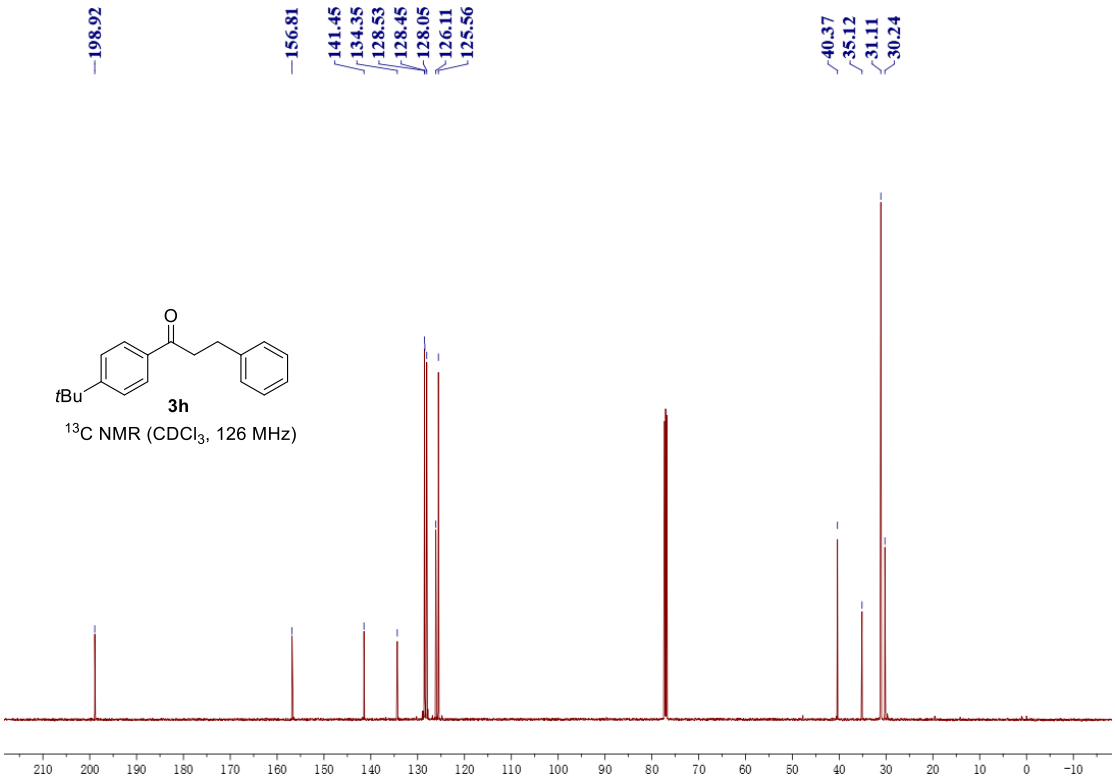
2.00
2.08
2.11
1.02
2.00
2.01
9.00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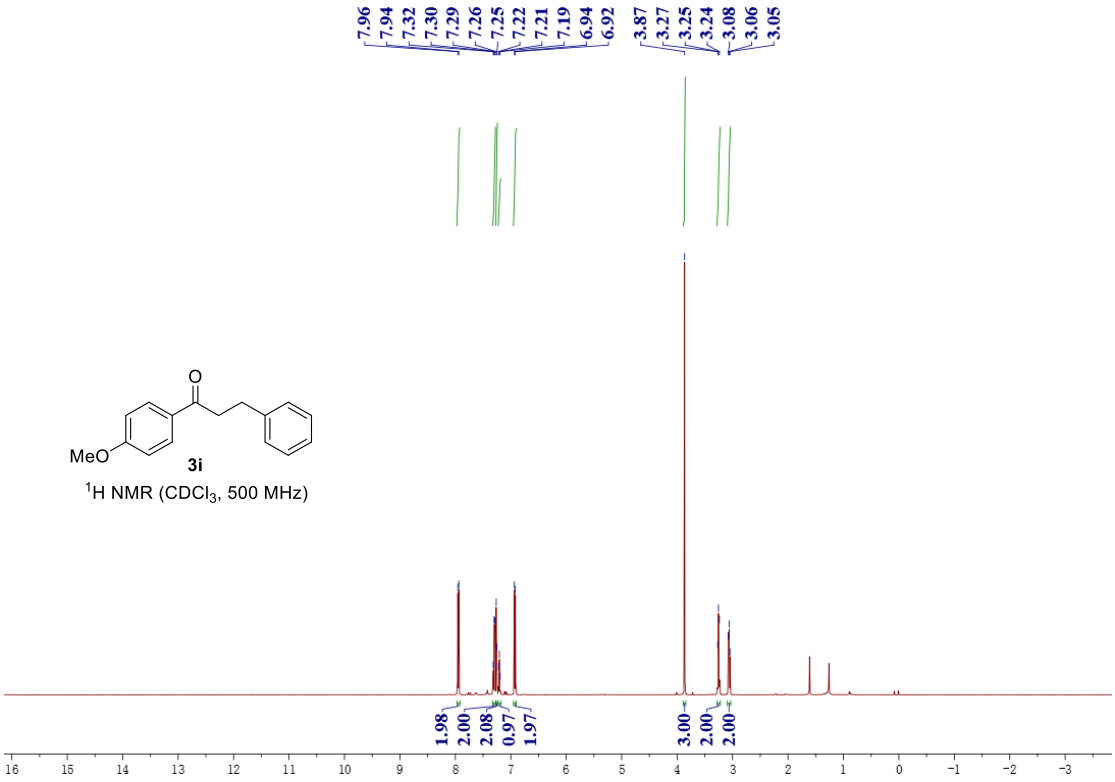
O
tBu
3h
13C NMR (CDCl3, 126 MHz)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3.27
3.25
3.24
3.08
3.06
3.05
O
MeO
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0.97
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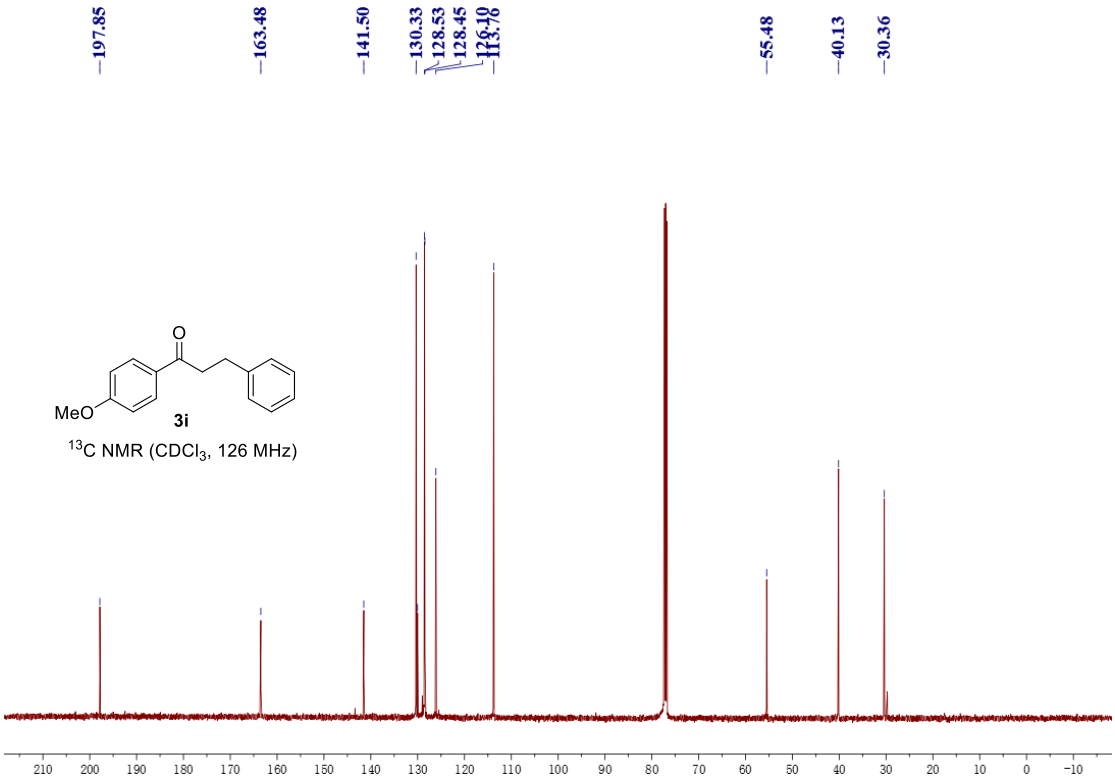
2.00
2.00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O
MeO
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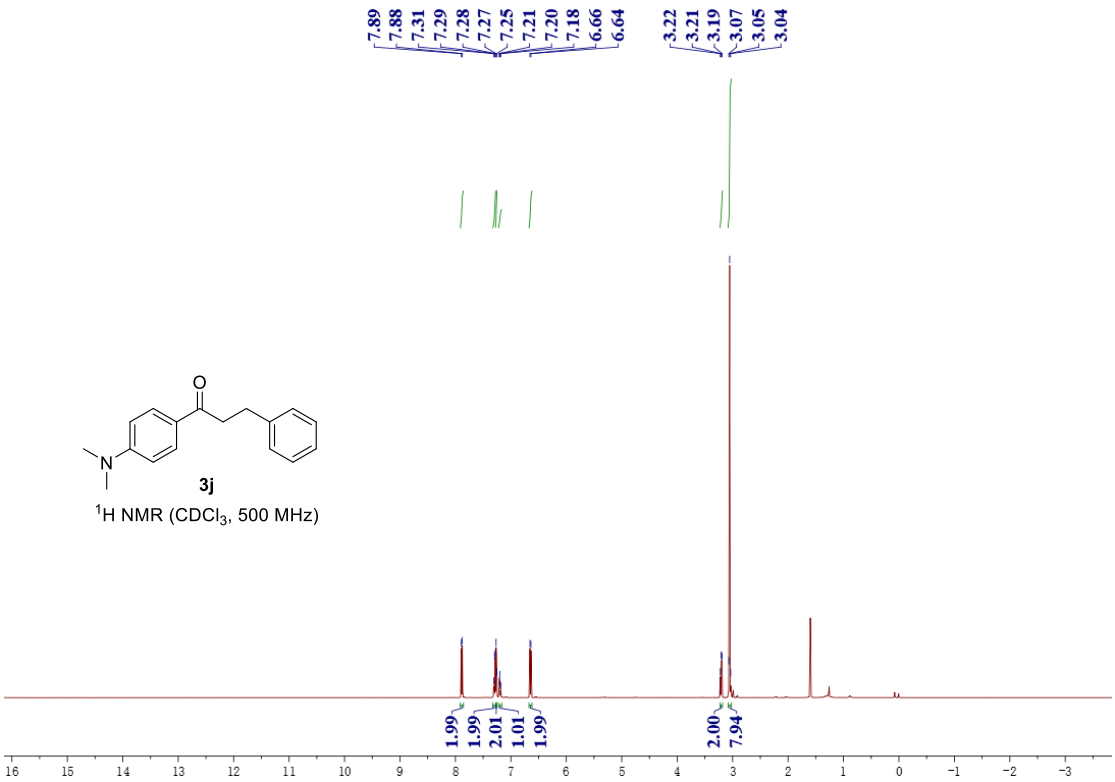
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7.18
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6.64
3.22
3.21
3.19
3.07
3.05
3.04
O
N
3j
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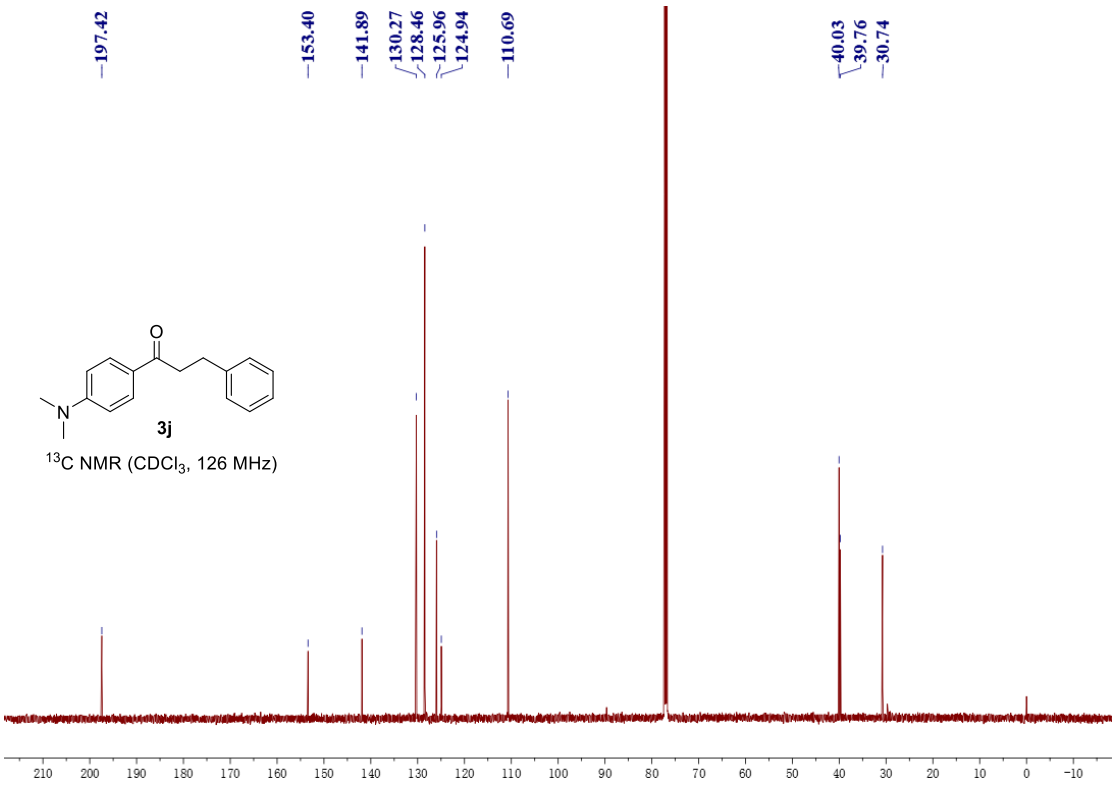
1.99
2.01
1.01
1.99
2.00
7.94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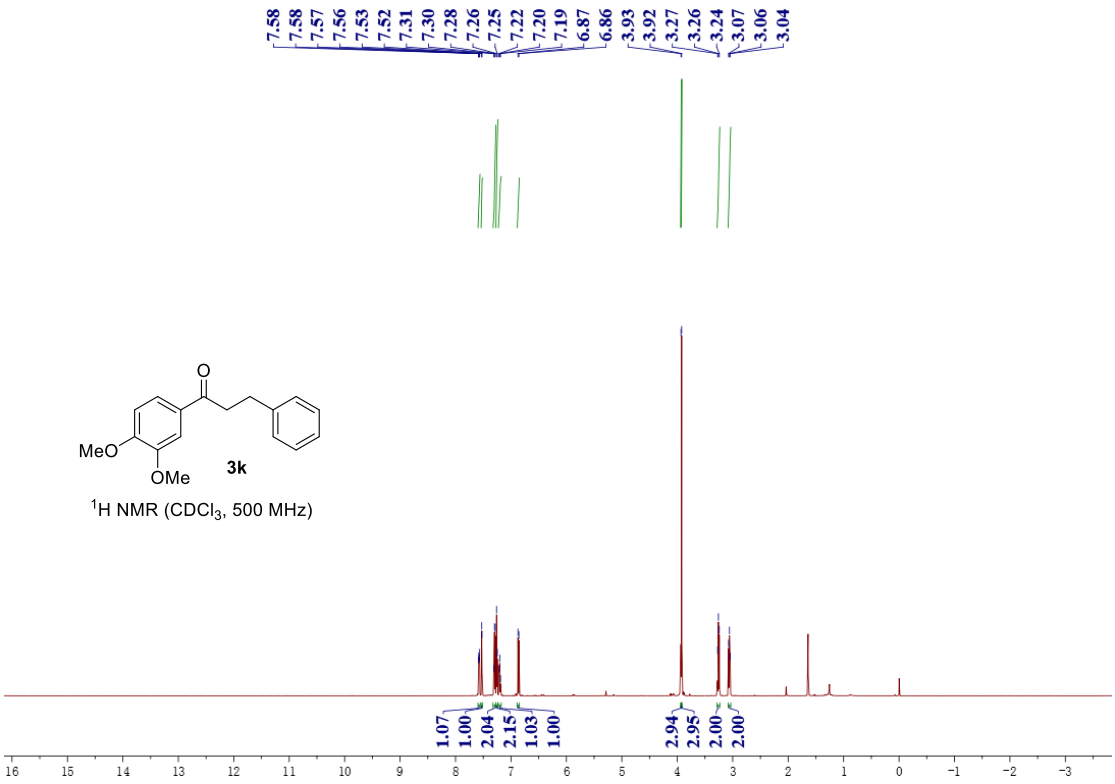
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6.87
6.86
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3.92
3.27
3.26
3.24
3.07
3.06
3.04
O
MeO
OMe
3k
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1.00
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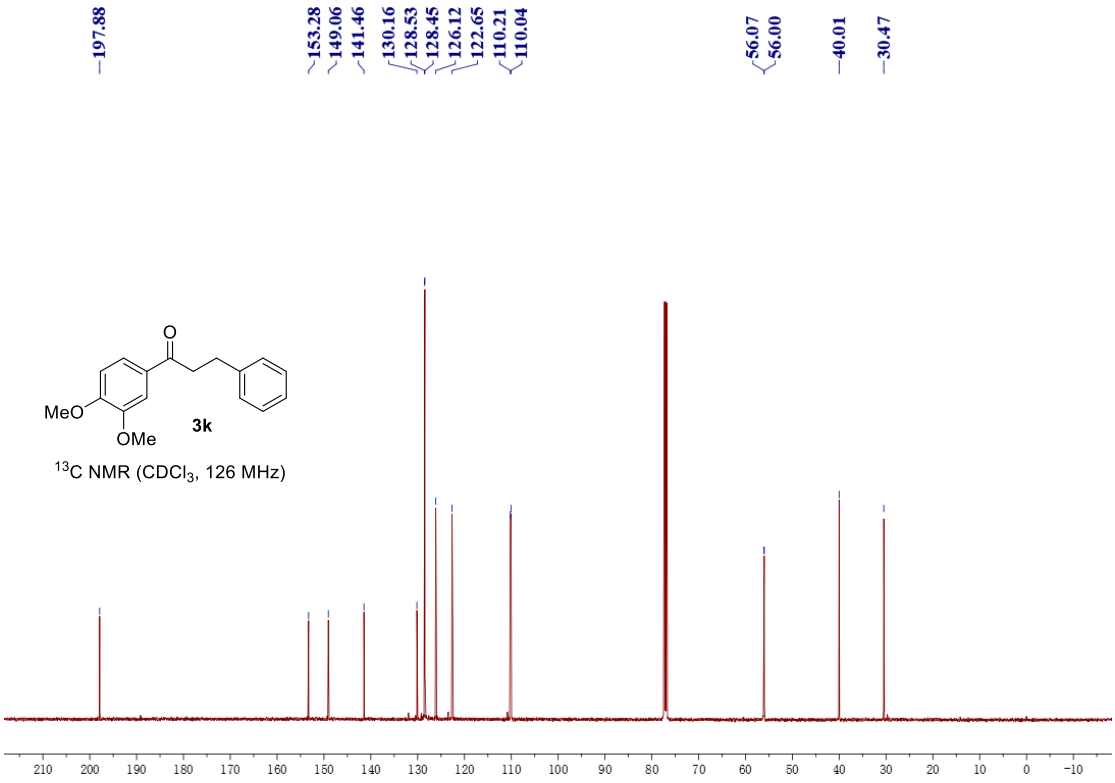
2.00
2.00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MeO
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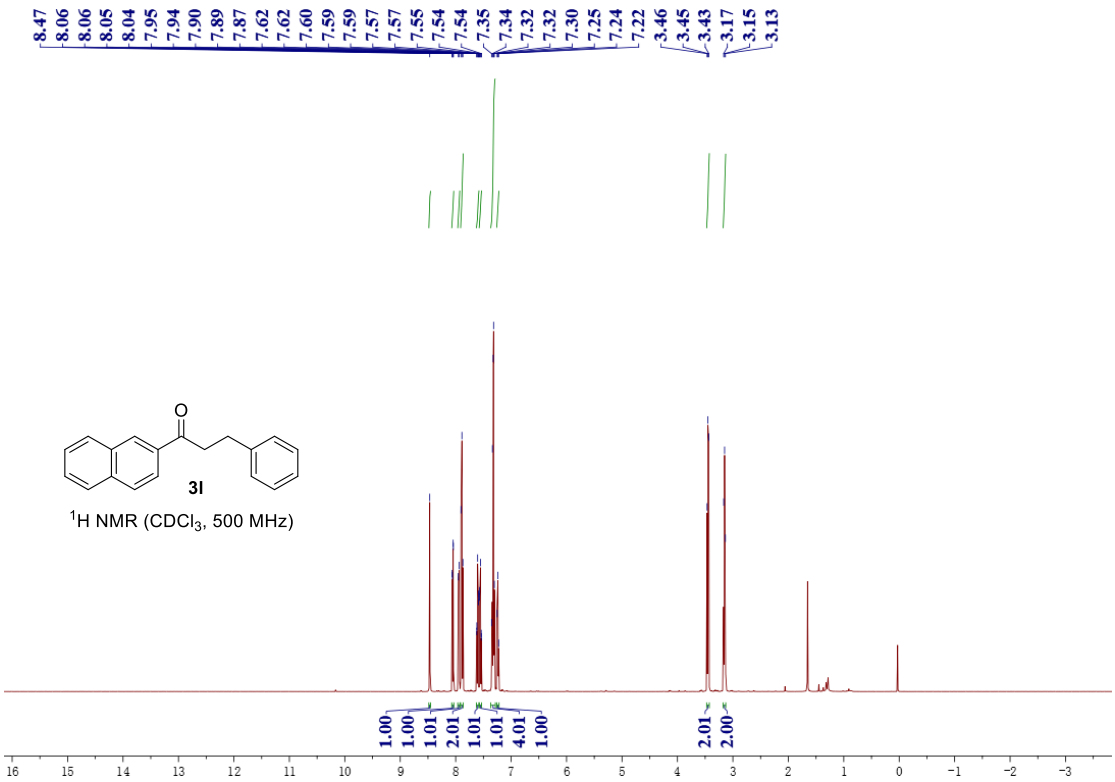
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7.57
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7.32
7.32
7.30
7.25
7.24
7.22
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3.45
3.43
3.17
3.15
3.13
3l
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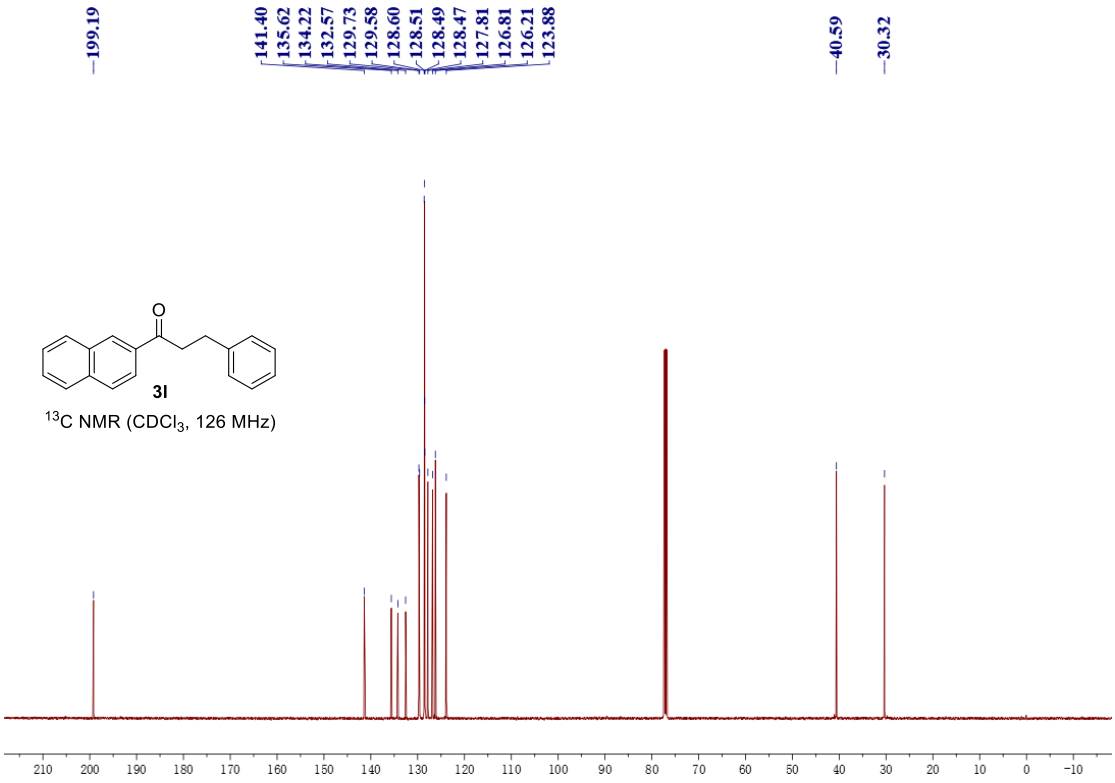
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30.32
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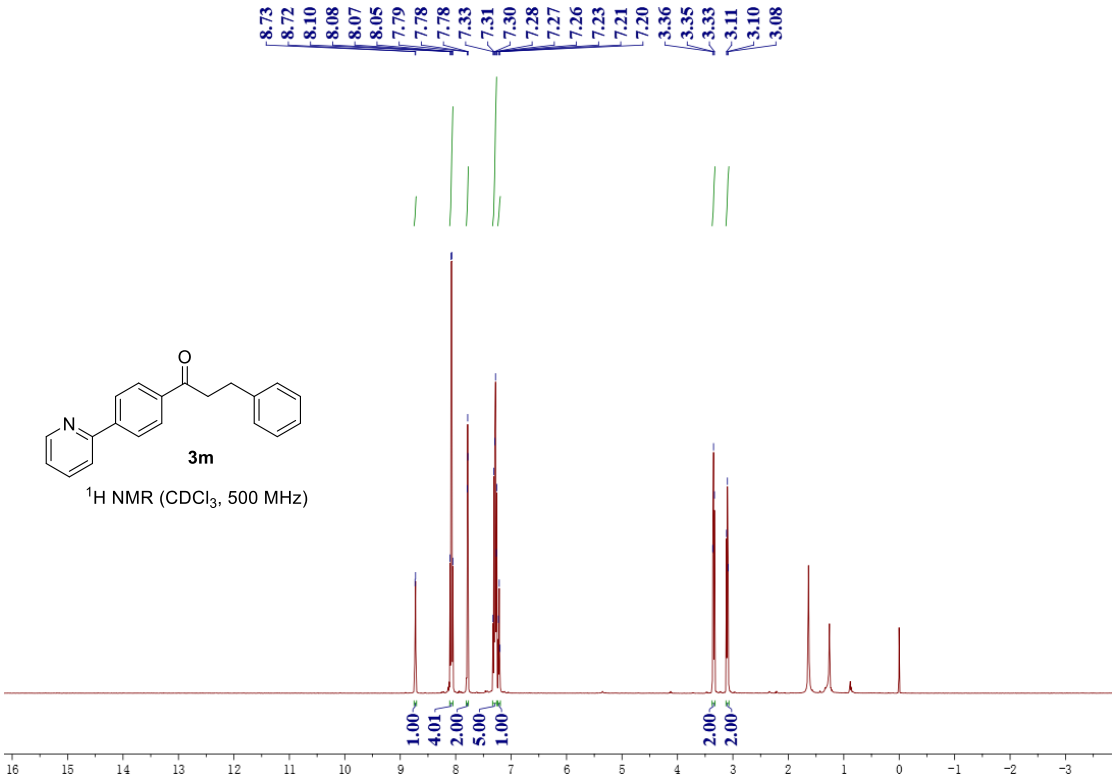
3l
13C NMR (CDCl3, 126 MHz)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7.27
7.26
7.23
7.21
7.20
3.36
3.35
3.33
3.11
3.10
3.08
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N
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1H NMR (CDCl3, 500 MHz)
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2.00
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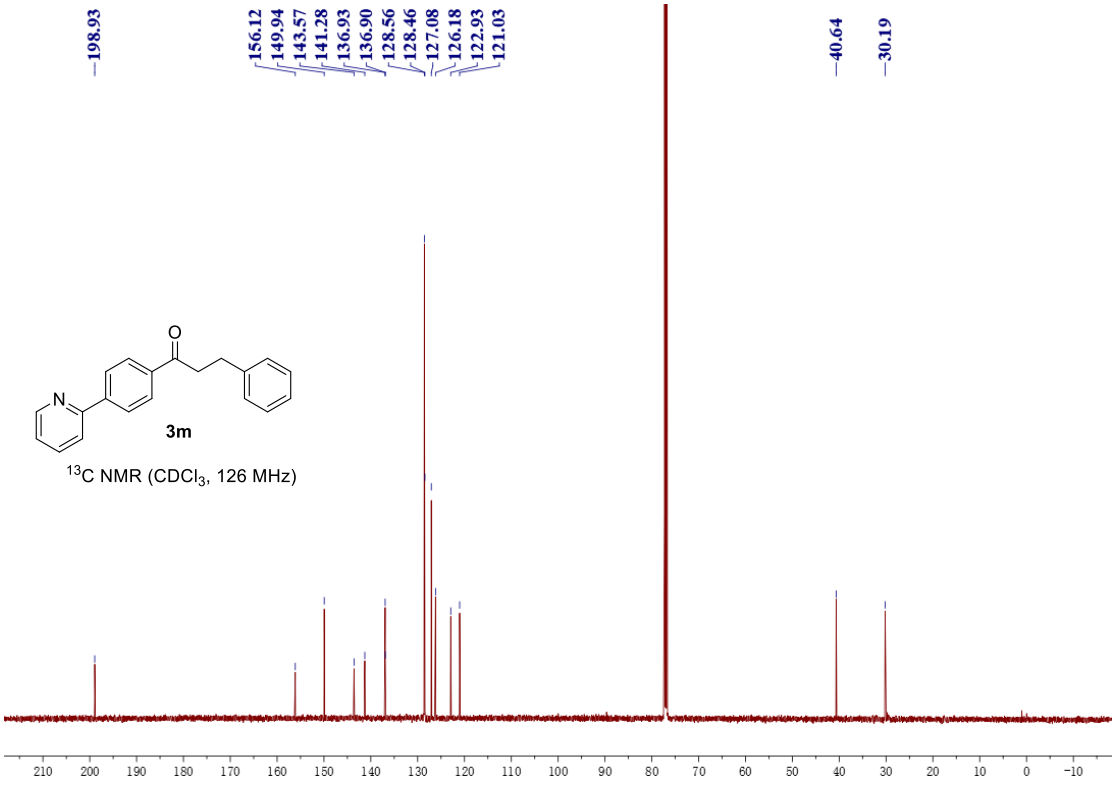
2.00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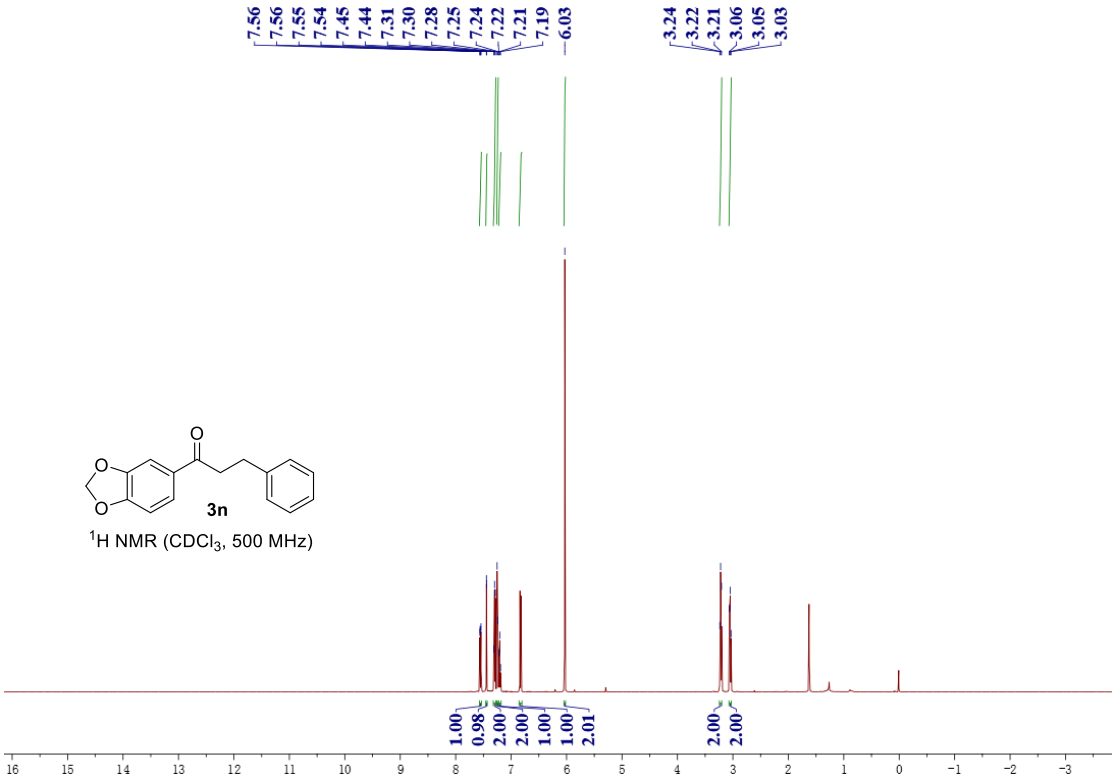
121.03
40.64
30.19
O
N
3m
13C NMR (CDCl3, 126 MHz)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7.21
7.19
6.03
3.24
3.22
3.21
3.06
3.05
3.03
O
O
O
3n
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1.00
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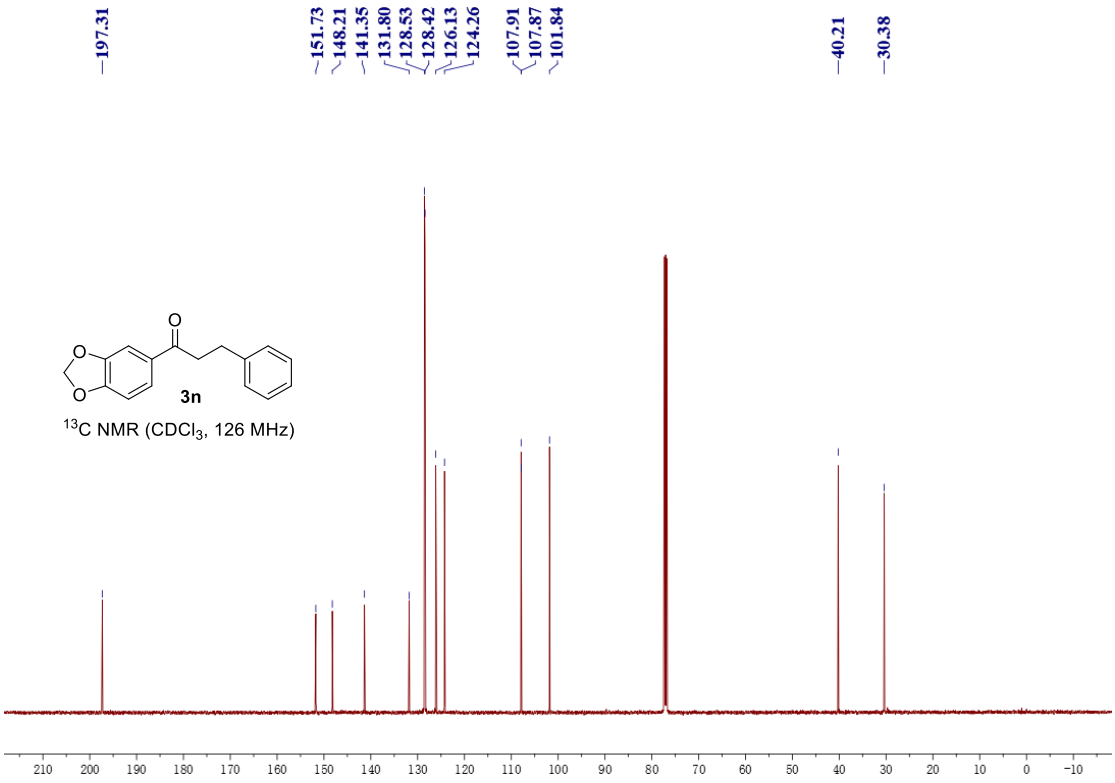
2.00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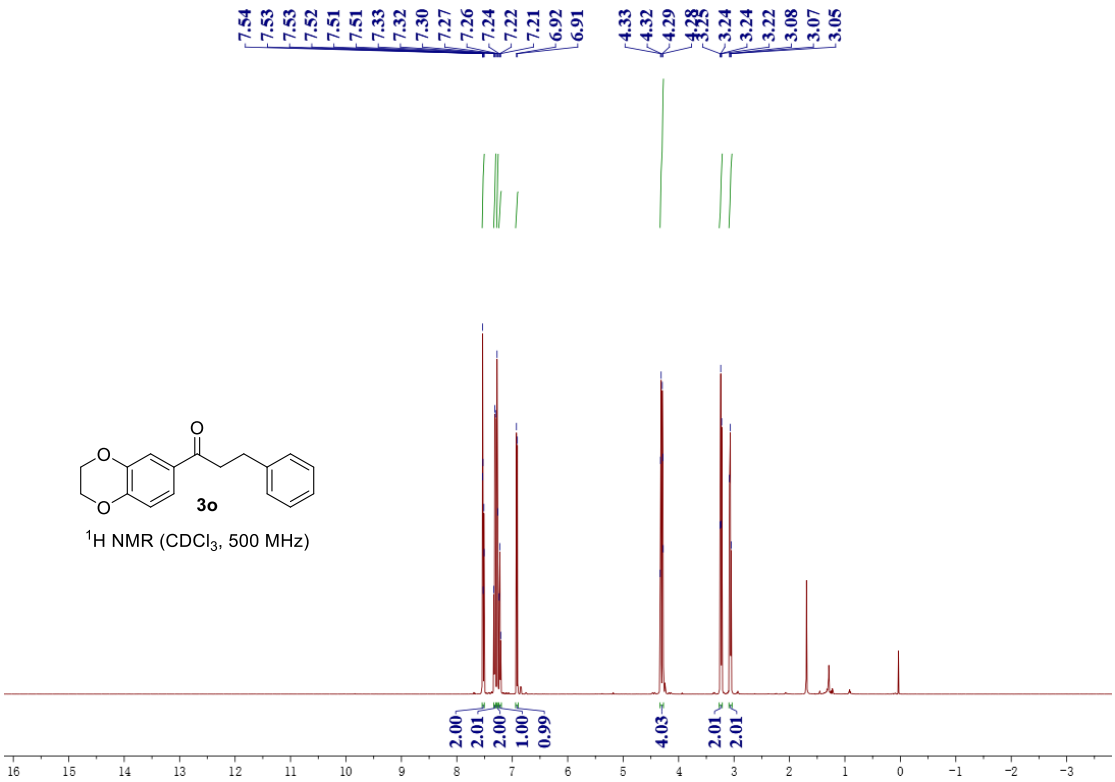
128.42
126.13
124.26
107.91
107.87
101.84
40.21
30.38
3n
13C NMR (CDCl3, 126 MHz)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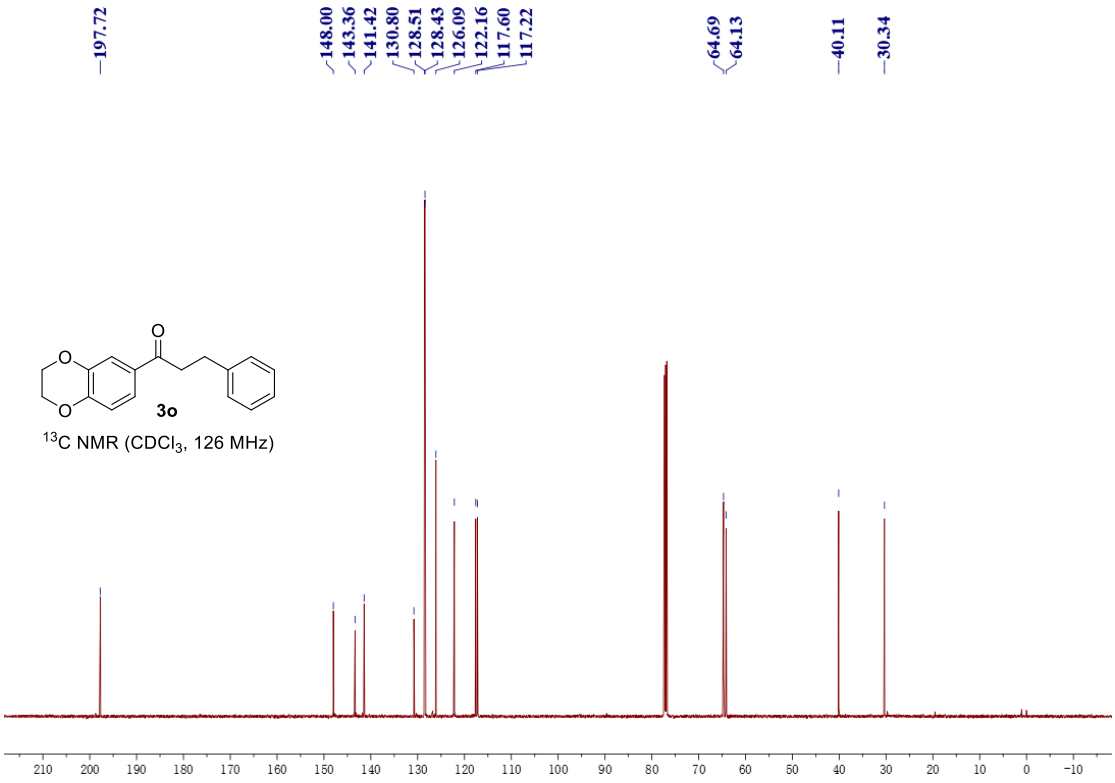
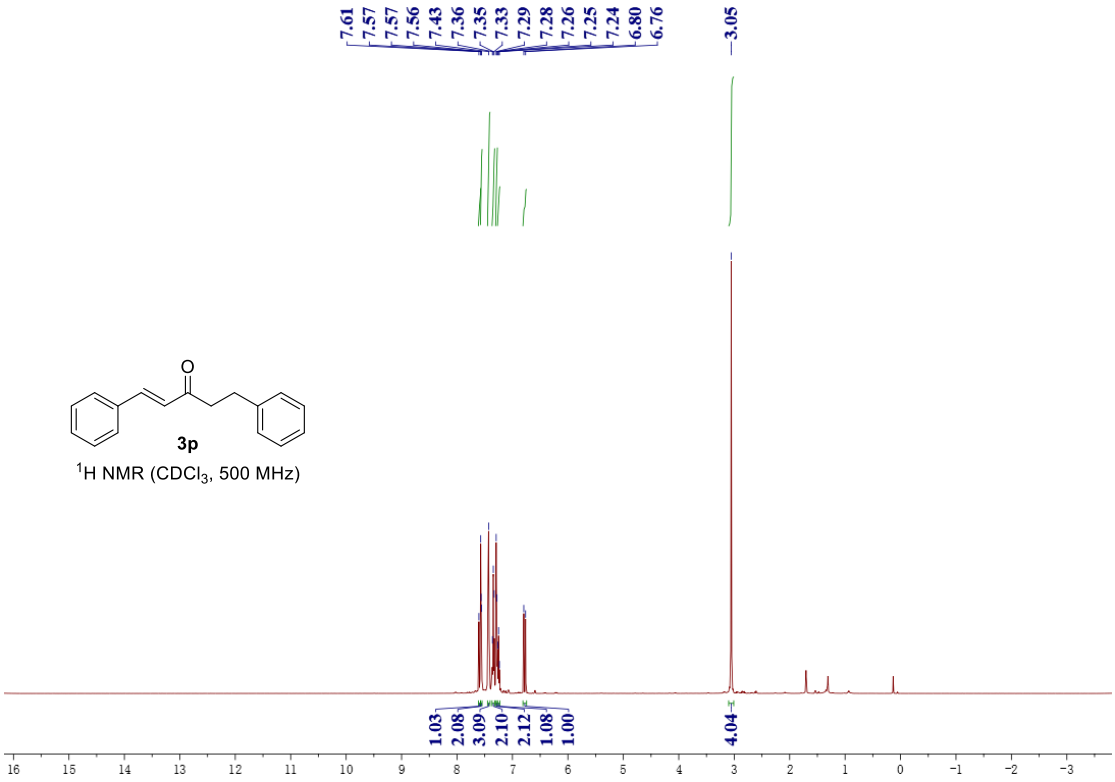
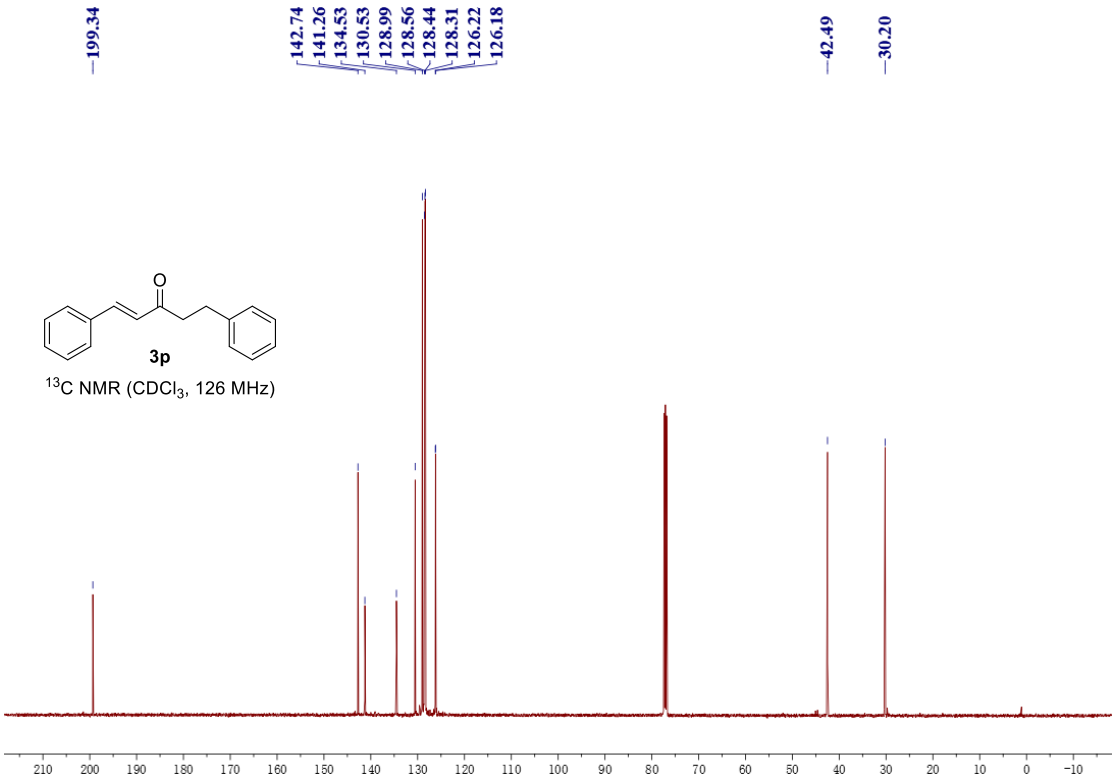
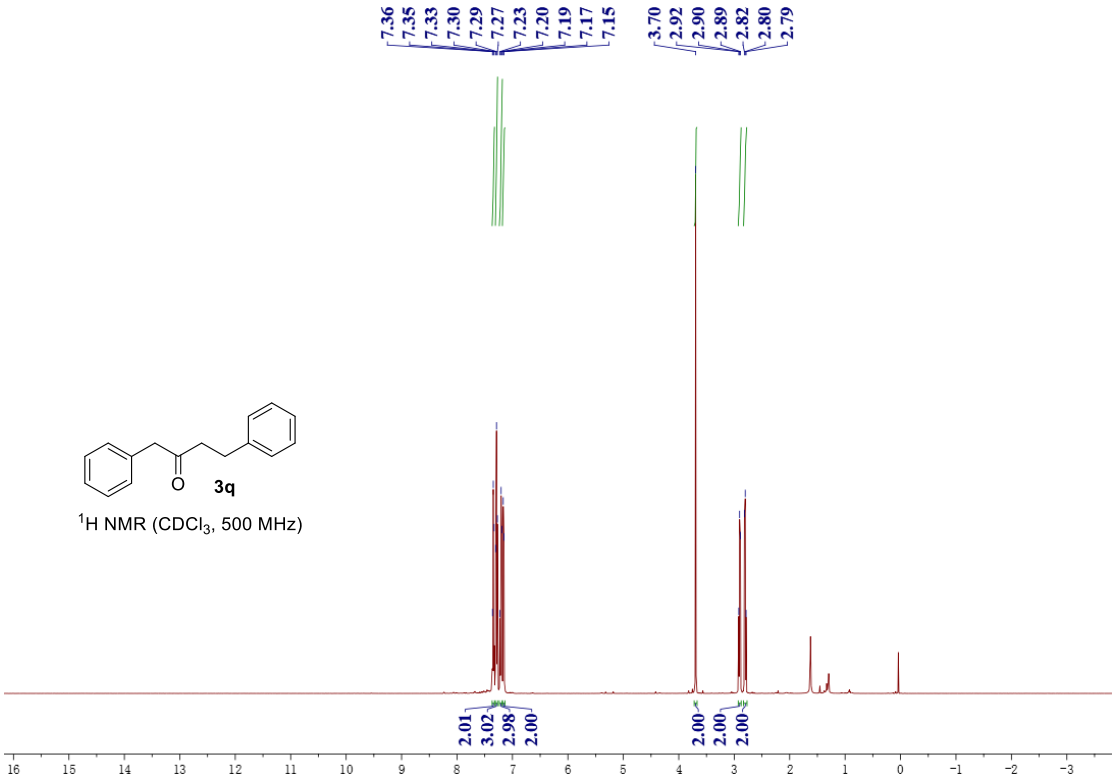
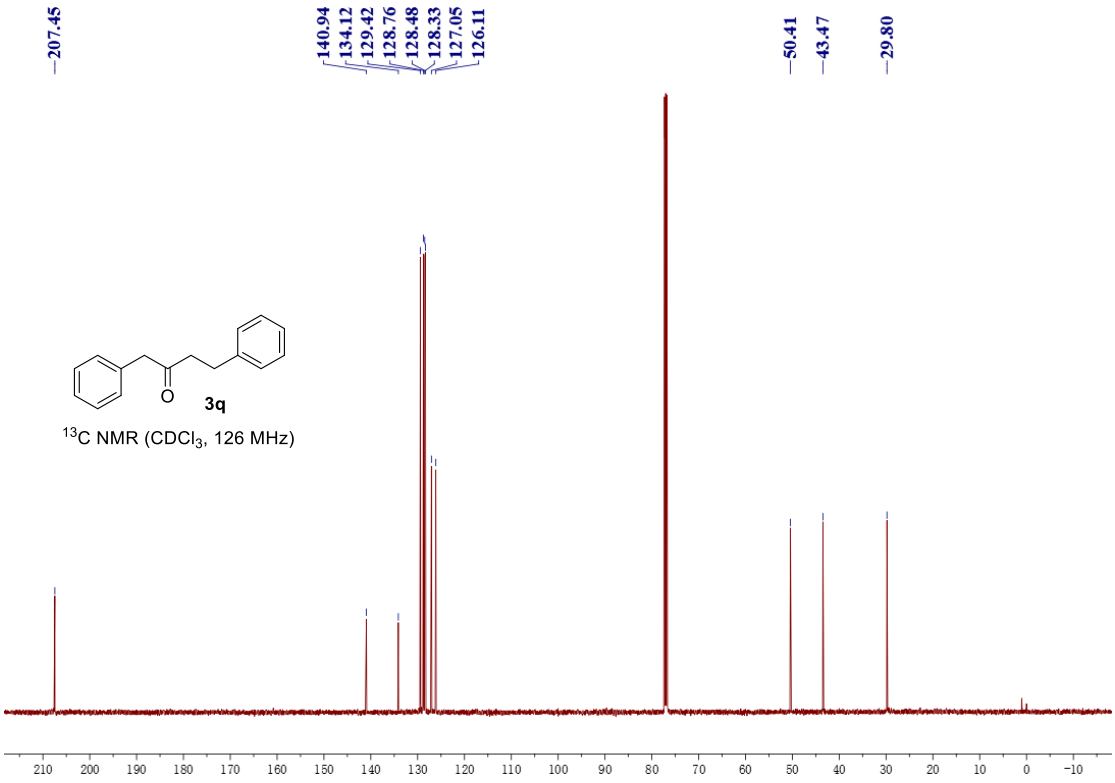
7.53
7.53
7.52
7.51
7.51
7.33
7.32
7.30
7.27
7.26
7.24
7.22
7.21
6.92
6.91
4.33
4.32
4.29
3.25
3.24
3.24
3.22
3.08
3.07
3.05
3o
1H NMR (CDCl3, 500 MHz)
2.00
2.01
2.00
1.00
0.99
4.03
2.01
2.01

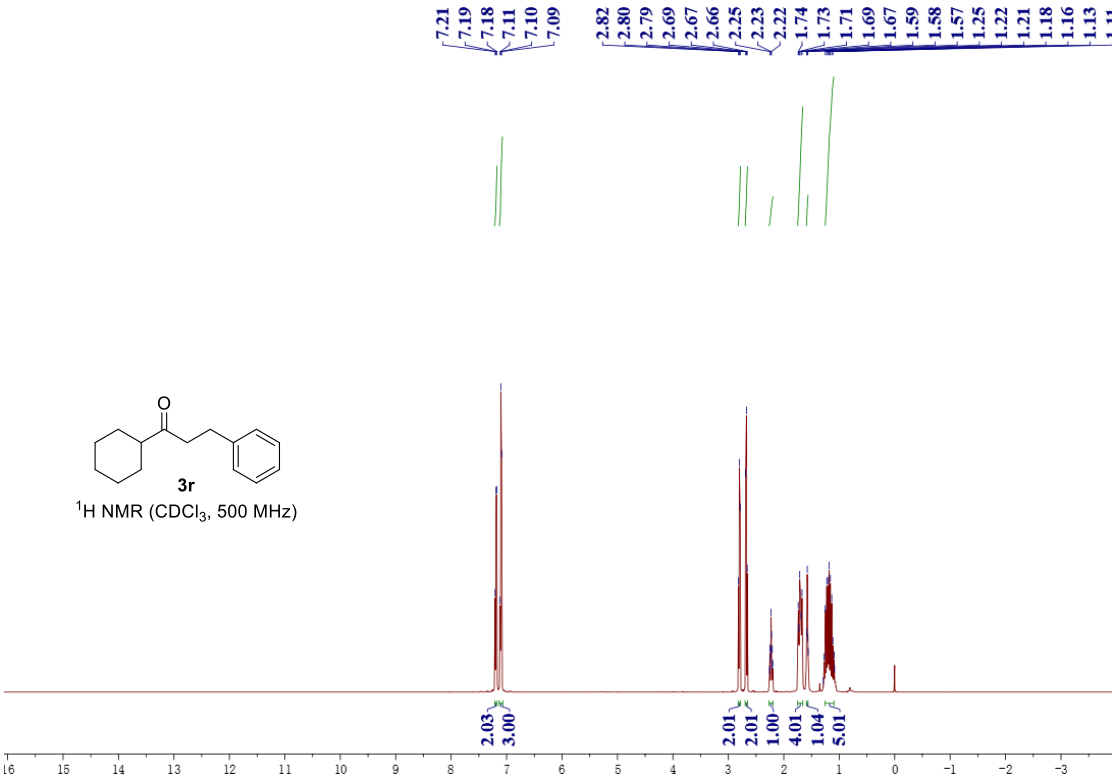

197.72
148.00
143.36
141.42
130.80
128.51
128.43
126.09
122.16
117.60
117.22
64.69
64.13
40.11
30.34
O
O
O
3o
13C NMR (CDCl3, 126 MHz)

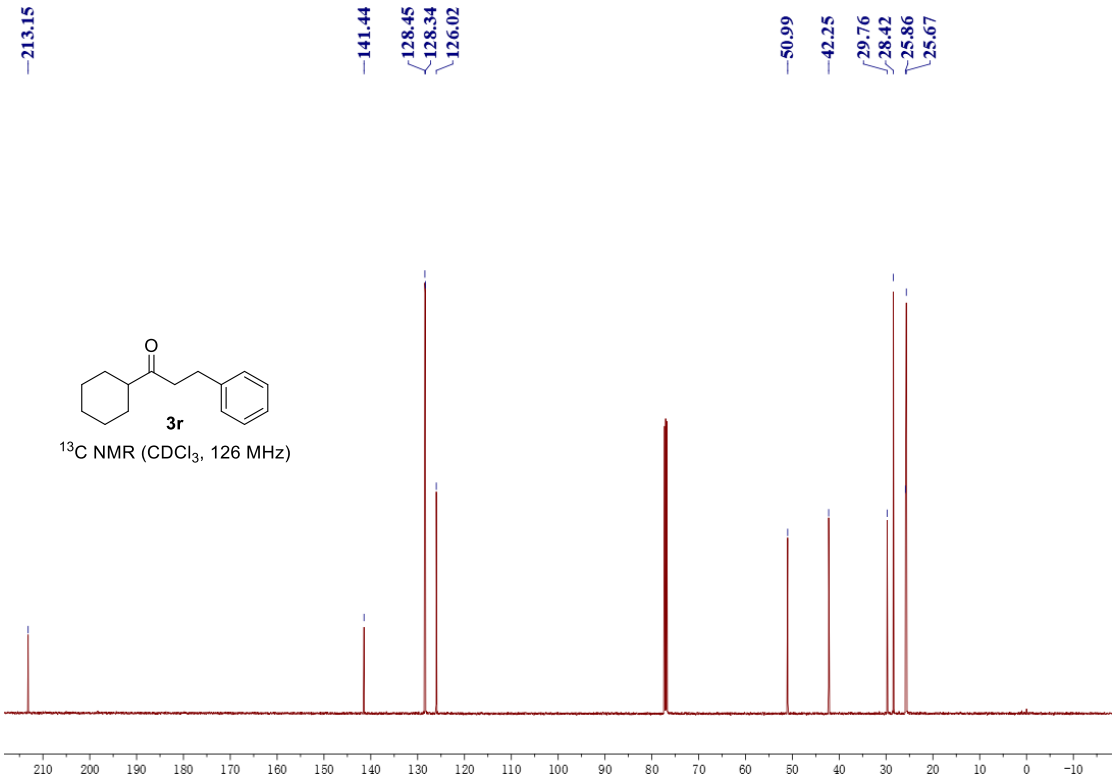

7.61
7.57
7.57
7.56
7.43
7.36
7.35
7.33
7.29
7.28
7.26
7.25
7.24
6.80
6.76
3.05
O
3p
1H NMR (CDCl3, 500 MHz)
1.03
2.08
3.09
2.10
2.12
1.08
1.00
4.04

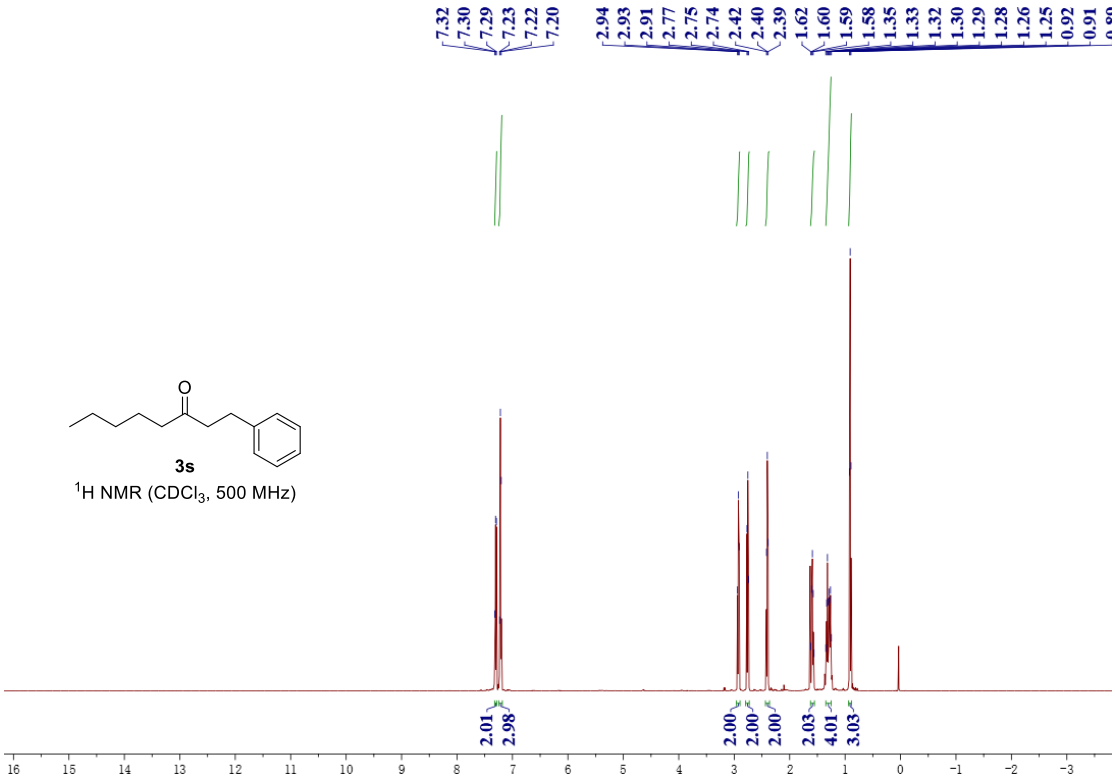

199.34
142.74
141.26
134.53
130.53
128.99
128.56
128.44
128.31
126.22
126.18
42.49
30.20
O
3p
13C NMR (CDCl3, 126 MHz)

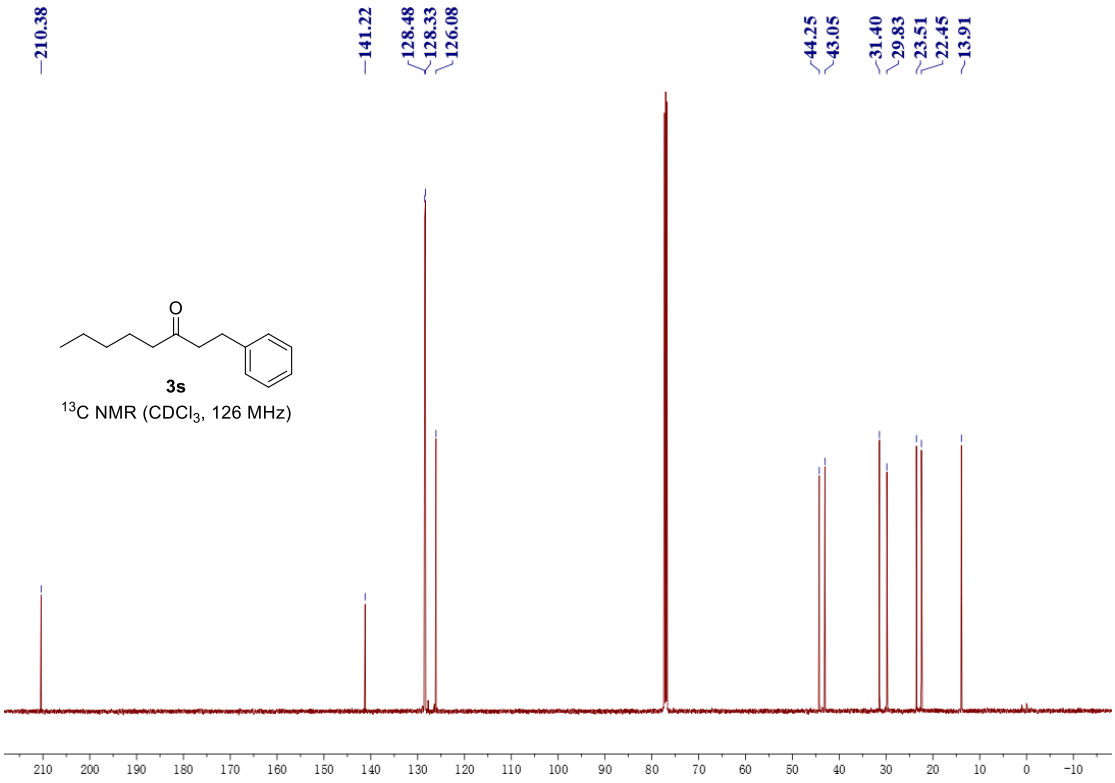

7.36
7.35
7.33
7.30
7.29
7.27
7.23
7.20
7.19
7.17
7.15
3.70
2.92
2.90
2.89
2.82
2.80
2.79
O
3q
1H NMR (CDCl3, 500 MHz)
2.01
3.02
2.98
2.00
2.00
2.00
2.00

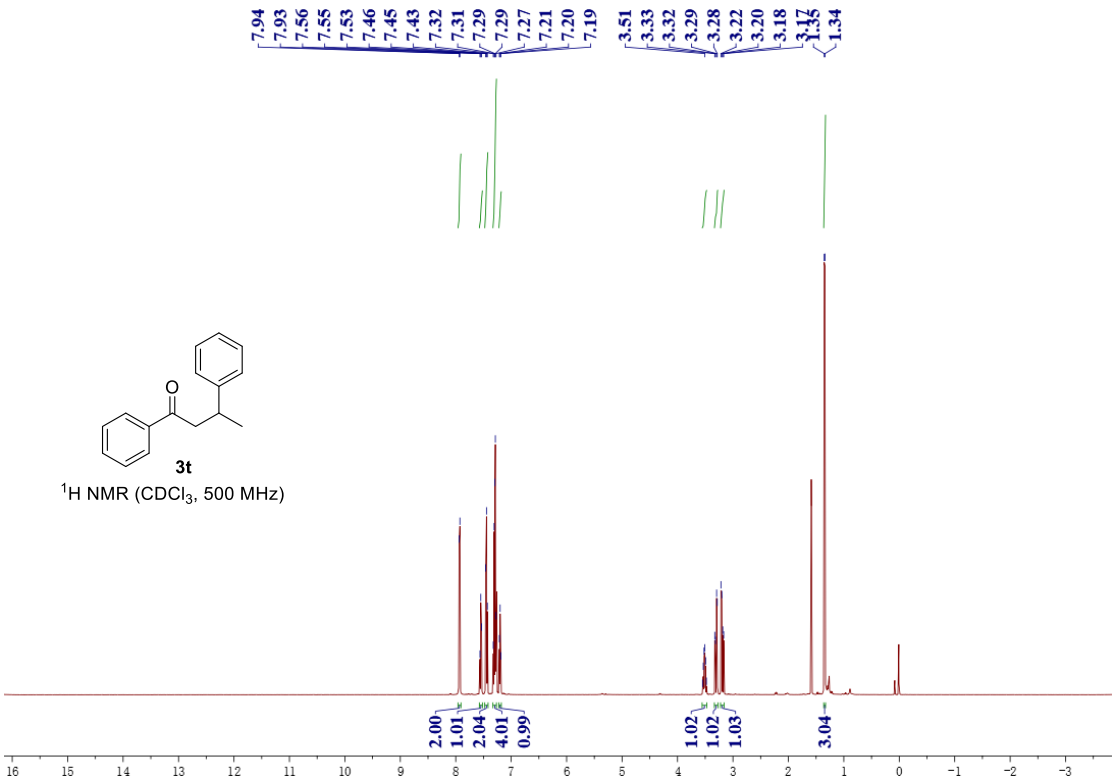

207.45
140.94
134.12
129.42
128.76
128.48
128.33
127.05
126.11
50.41
43.47
29.80
O
3q
13C NMR (CDCl3, 126 MHz)

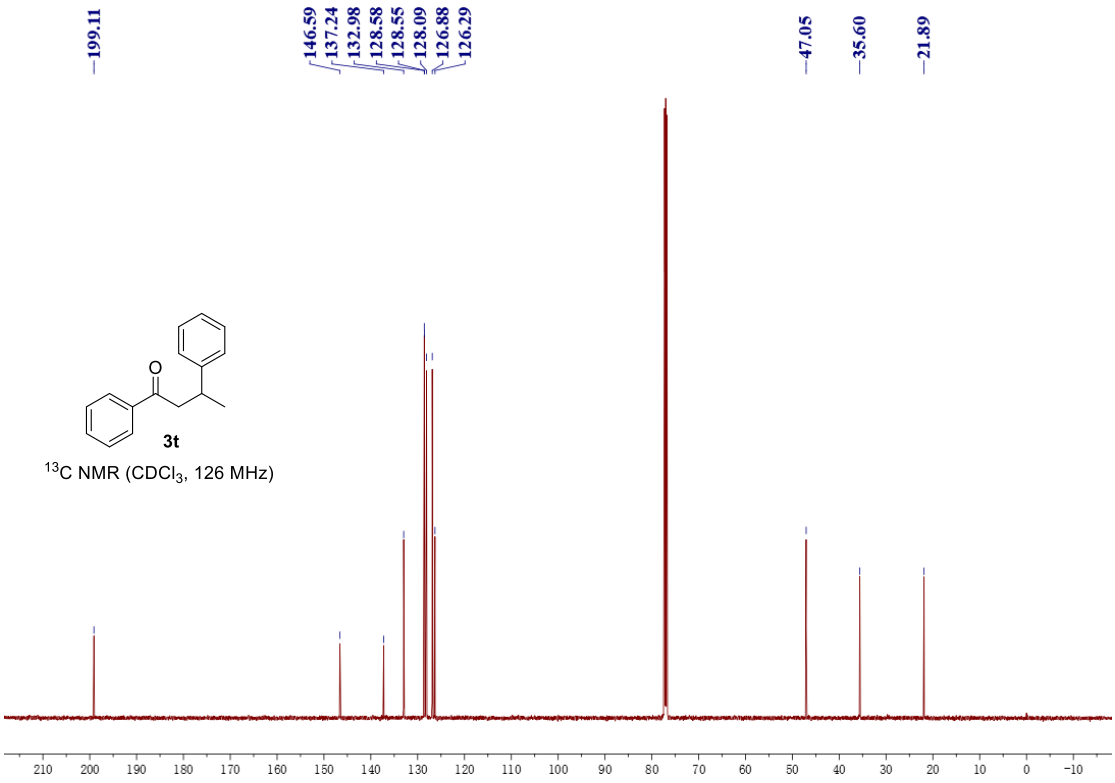

7.21
7.19
7.18
7.11
7.10
7.09
2.82
2.80
2.79
2.69
2.67
2.66
2.25
2.23
2.22
1.74
1.73
1.71
1.69
1.67
1.59
1.58
1.57
1.25
1.22
1.21
1.18
1.16
1.13
O
3r
1H NMR (CDCl3, 500 MHz)
2.03
3.00
2.01
2.01
1.00
4.01
1.04
5.01

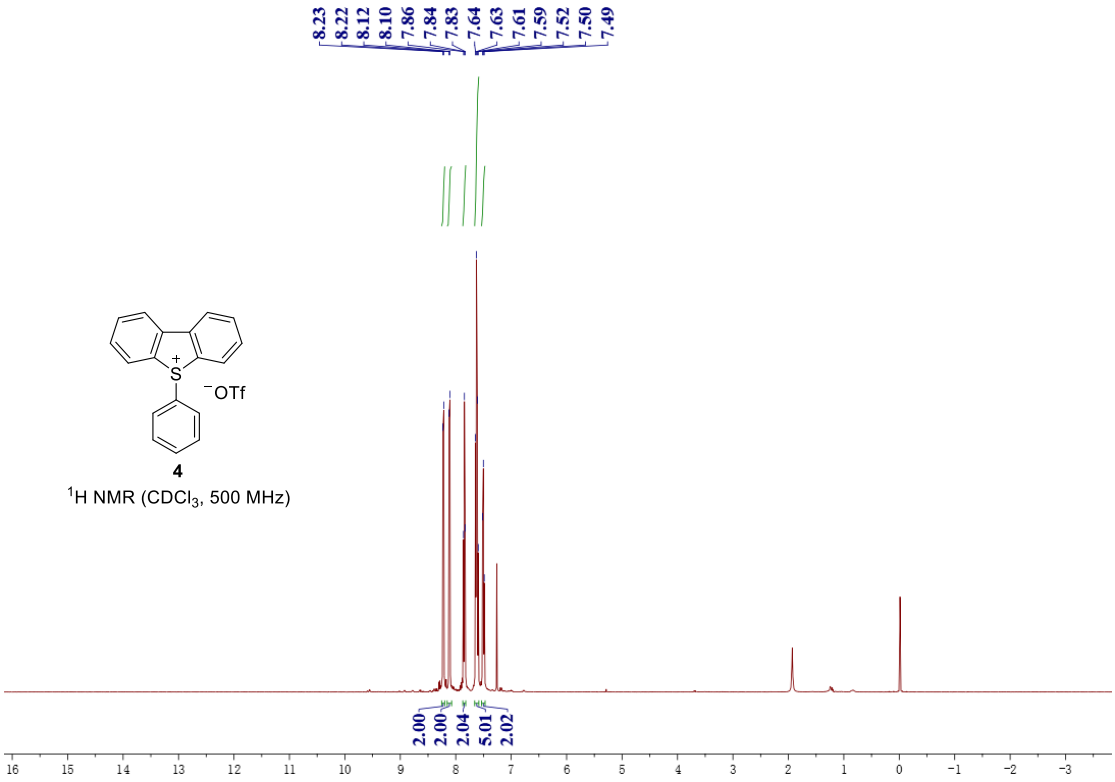

213.15
141.44
128.45
128.34
126.02
50.99
42.25
29.76
28.42
25.86
25.67
O
3r
13C NMR (CDCl3, 126 MHz)

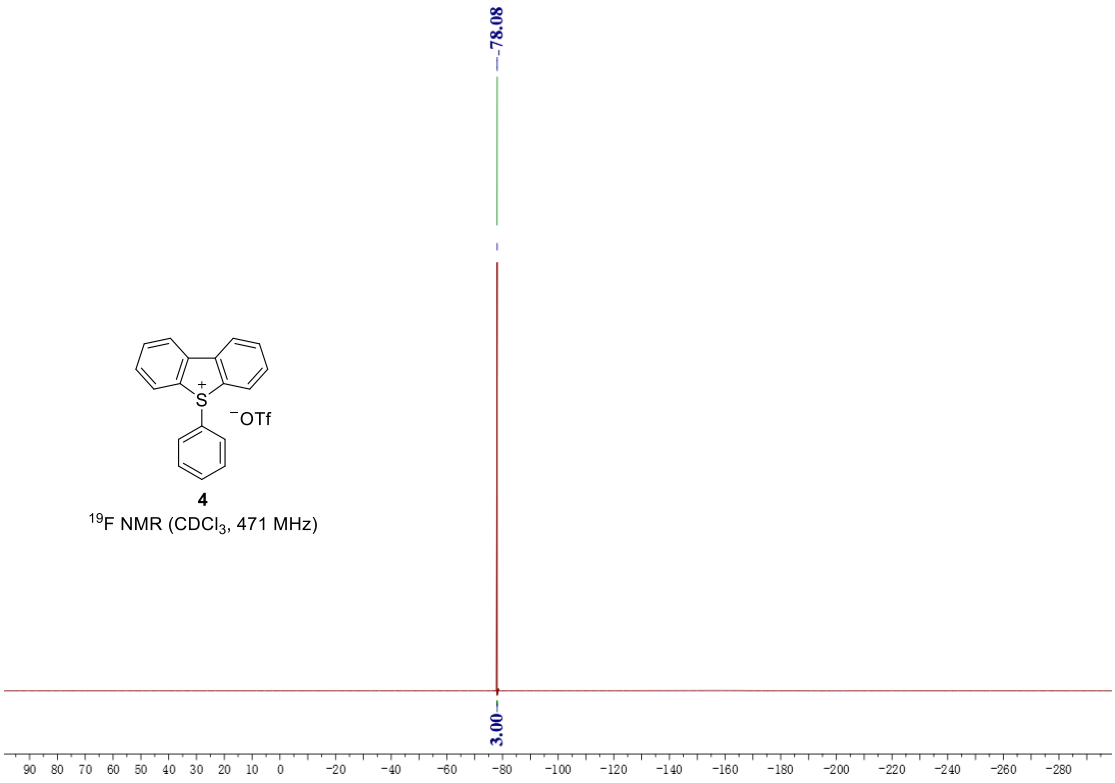

7.32
7.30
7.29
7.23
7.22
7.20
2.94
2.93
2.91
2.77
2.75
2.74
2.42
2.40
2.39
1.62
1.60
1.59
1.58
1.35
1.33
1.32
1.30
1.29
1.28
1.26
1.25
0.92
0.91
O
3s
1H NMR (CDCl3, 500 MHz)
2.01
2.98
2.00
2.00
2.00
2.03
4.01
3.03


210.38
141.22
128.48
128.33
126.08
44.25
43.05
31.40
29.83
23.51
22.45
13.91
O
3s
13C NMR (CDCl3, 126 MHz)


7.94
7.93
7.56
7.55
7.53
7.46
7.45
7.43
7.32
7.31
7.29
7.29
7.27
7.21
7.20
7.19
3.51
3.33
3.32
3.29
3.28
3.22
3.20
3.18
3.17
1.35
1.34
O
3t
1H NMR (CDCl3, 500 MHz)
2.00
1.01
2.04
4.01
0.99
1.02
1.02
1.03
3.04

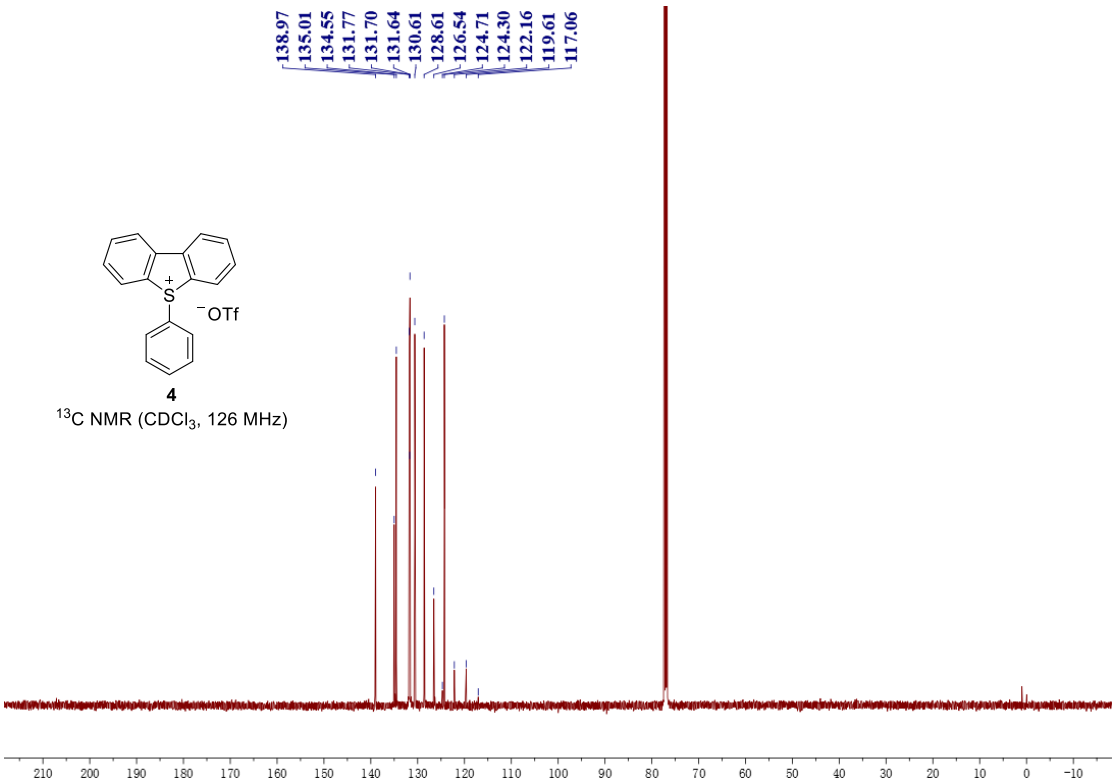

199.11
146.59
137.24
132.98
128.58
128.55
128.09
126.88
126.29
47.05
35.60
21.89
O
3t
13C NMR (CDCl3, 126 MHz)


8.23
8.22
8.12
8.10
7.86
7.84
7.83
7.64
7.63
7.61
7.59
7.52
7.50
7.49
S
OTf
4
1H NMR (CDCl3, 500 MHz)
2.00
2.00
2.04
5.01
2.02



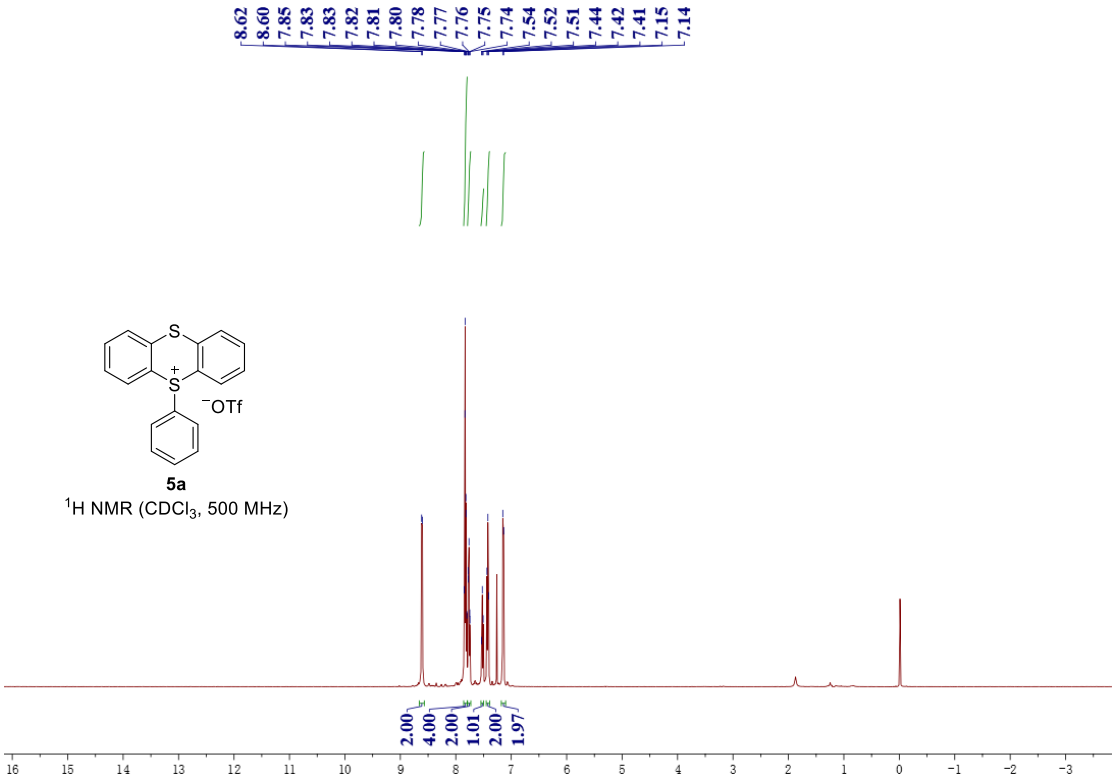
4

^{19}F NMR ($CDCl_3$, 471 MHz)



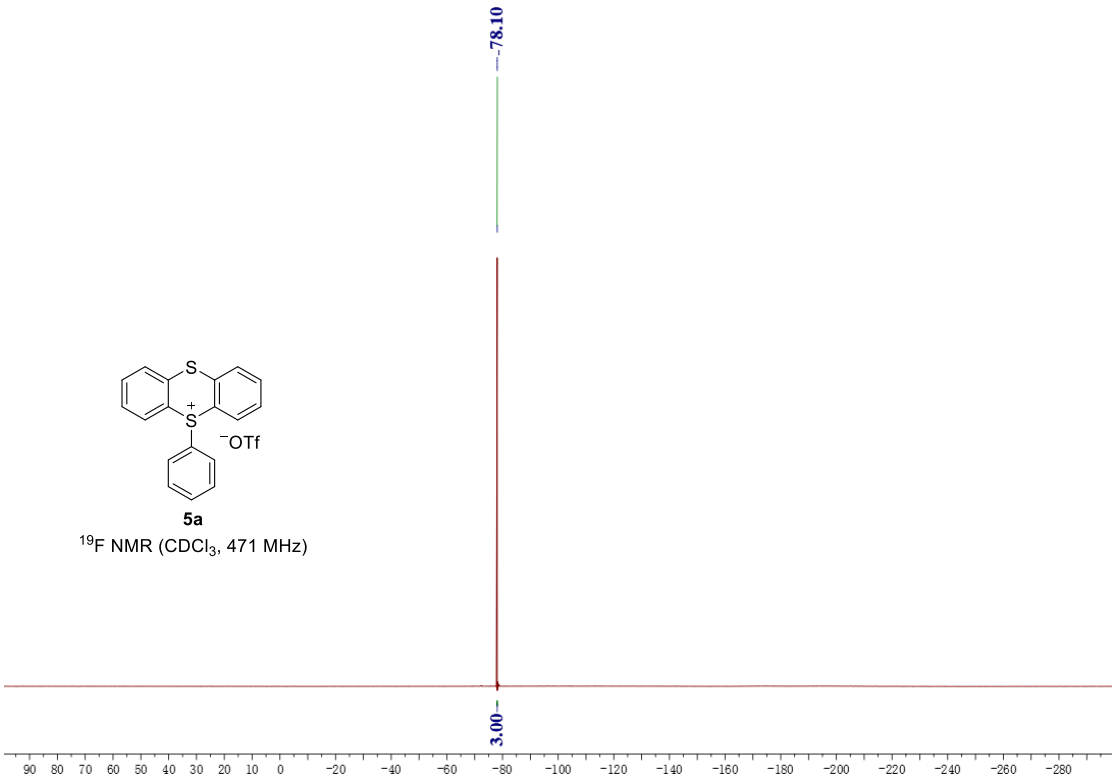
4

^{13}C NMR ($CDCl_3$, 126 MHz)



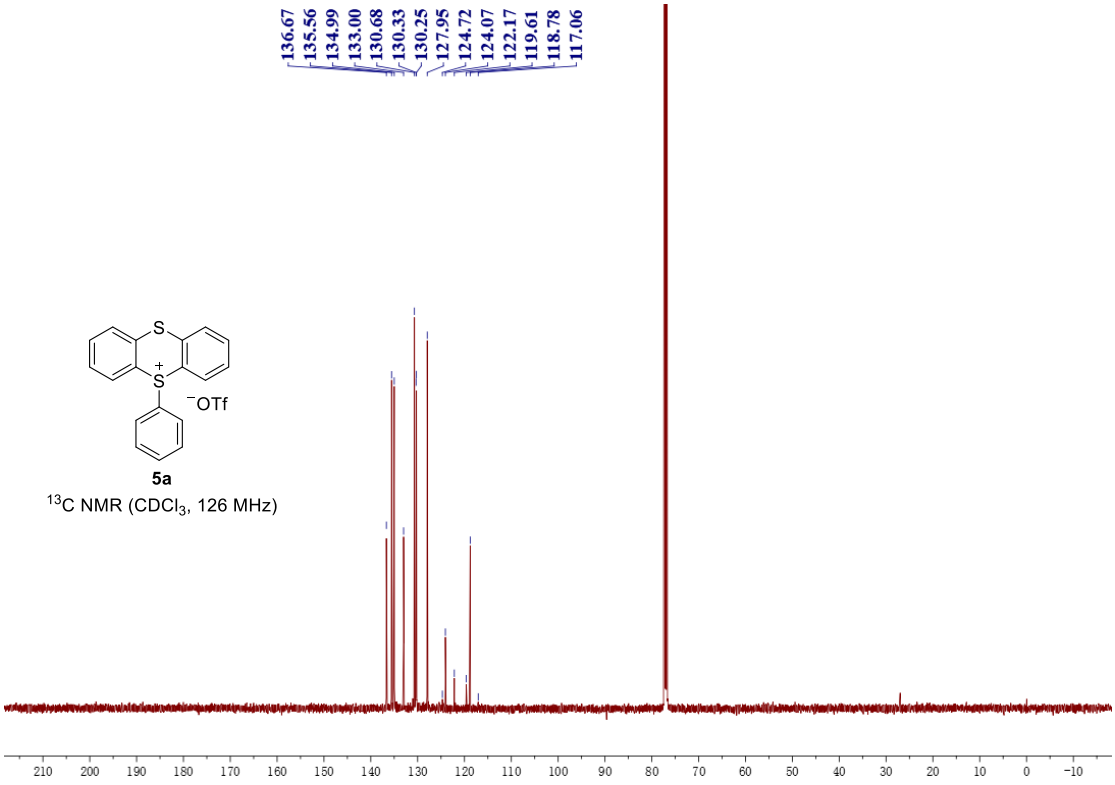
5a

^{1}H NMR ($CDCl_3$, 500 MHz)



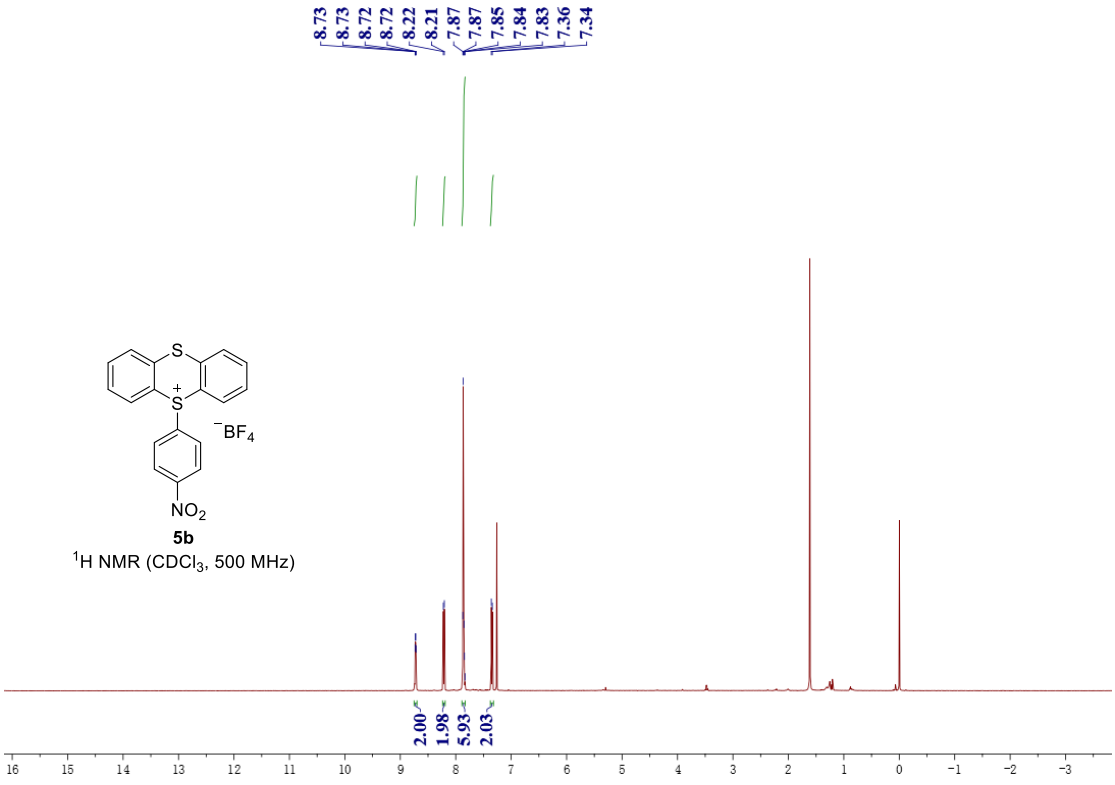
5a

^{19}F NMR ($CDCl_3$, 471 MHz)



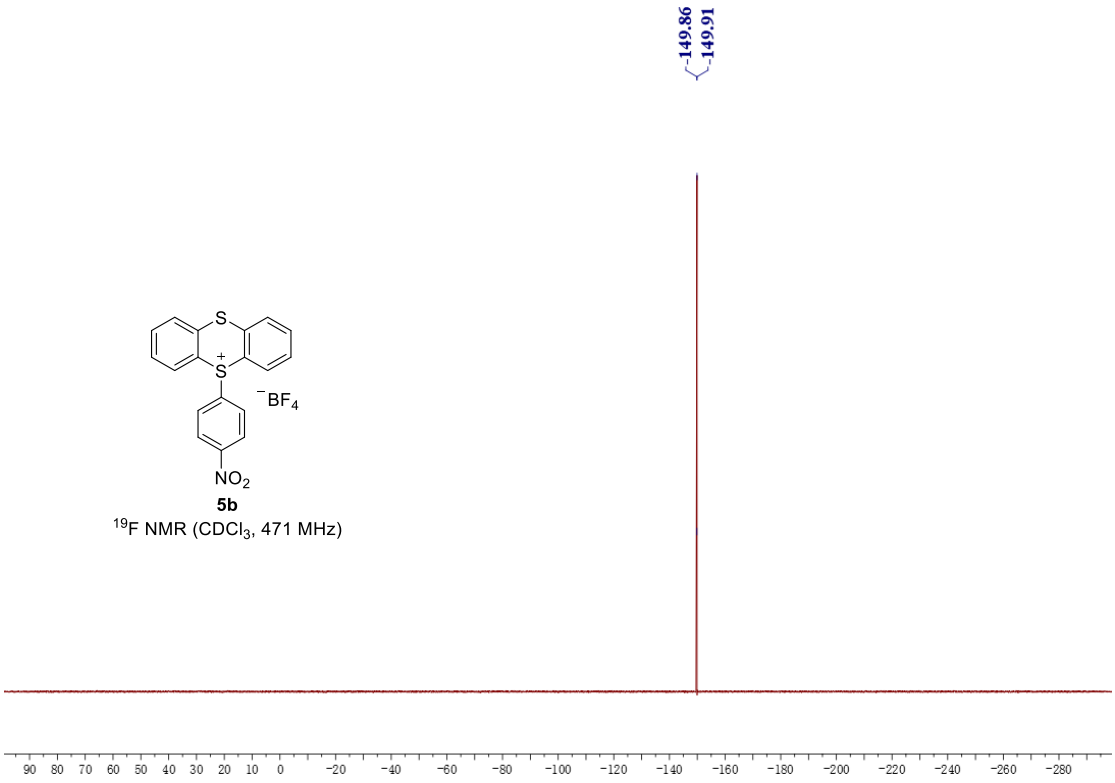
5a

^{13}C NMR ($CDCl_3$, 126 MHz)



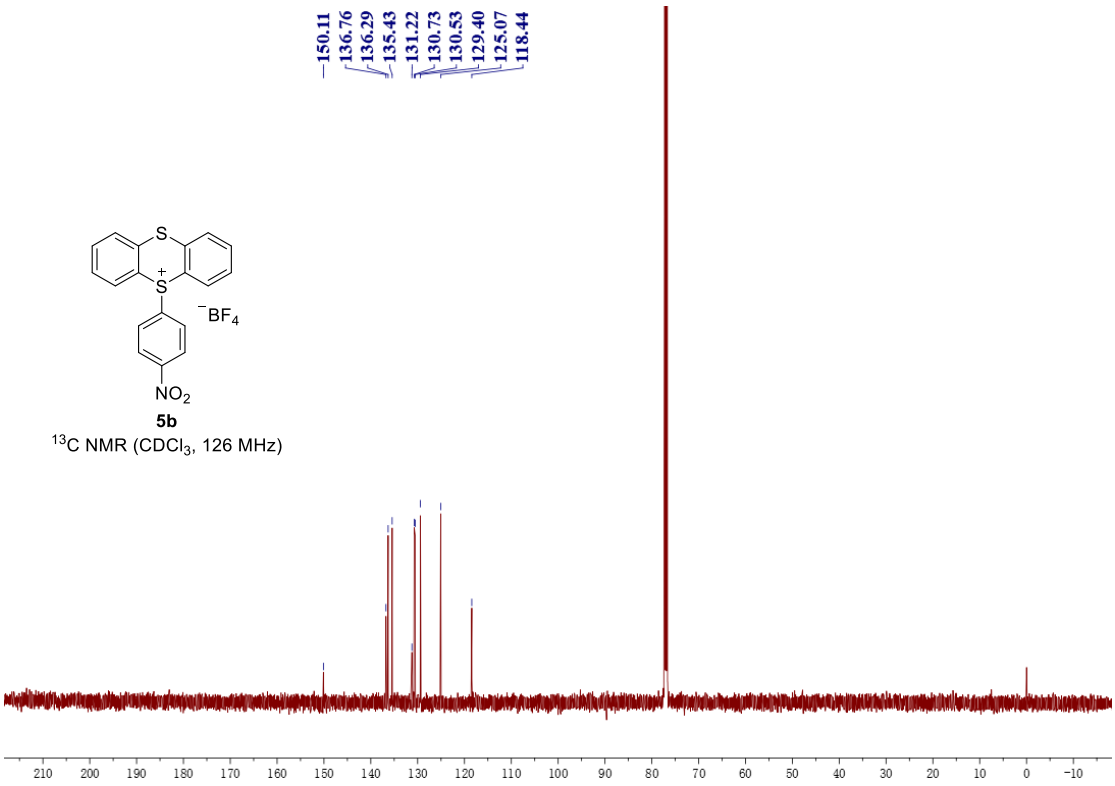
5b

^{1}H NMR ($CDCl_3$, 500 MHz)



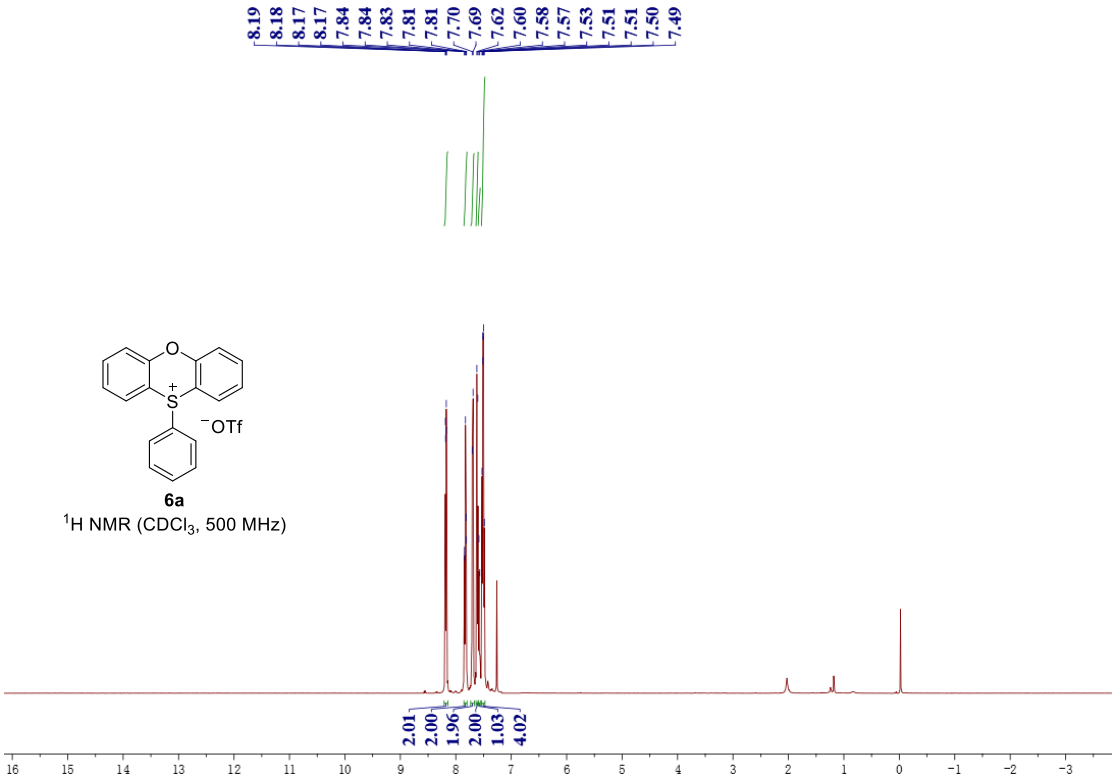
5b

^{19}F NMR ($CDCl_3$, 471 MHz)



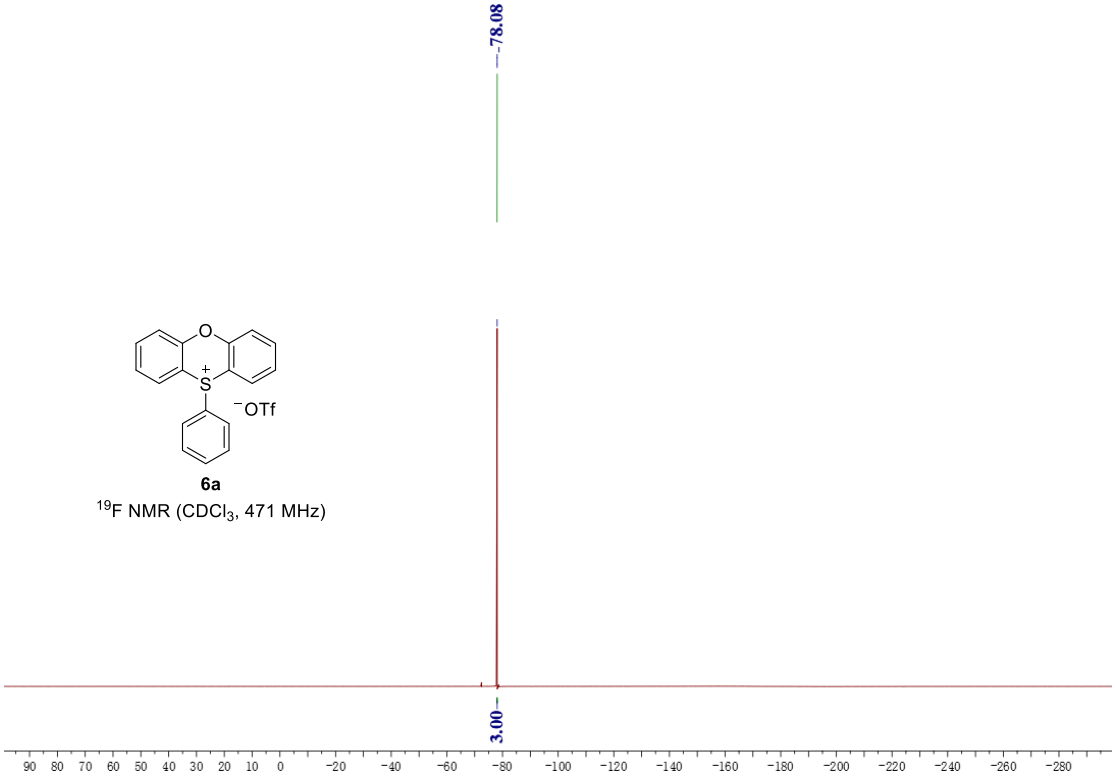
5b

^{13}C NMR ($CDCl_3$, 126 MHz)



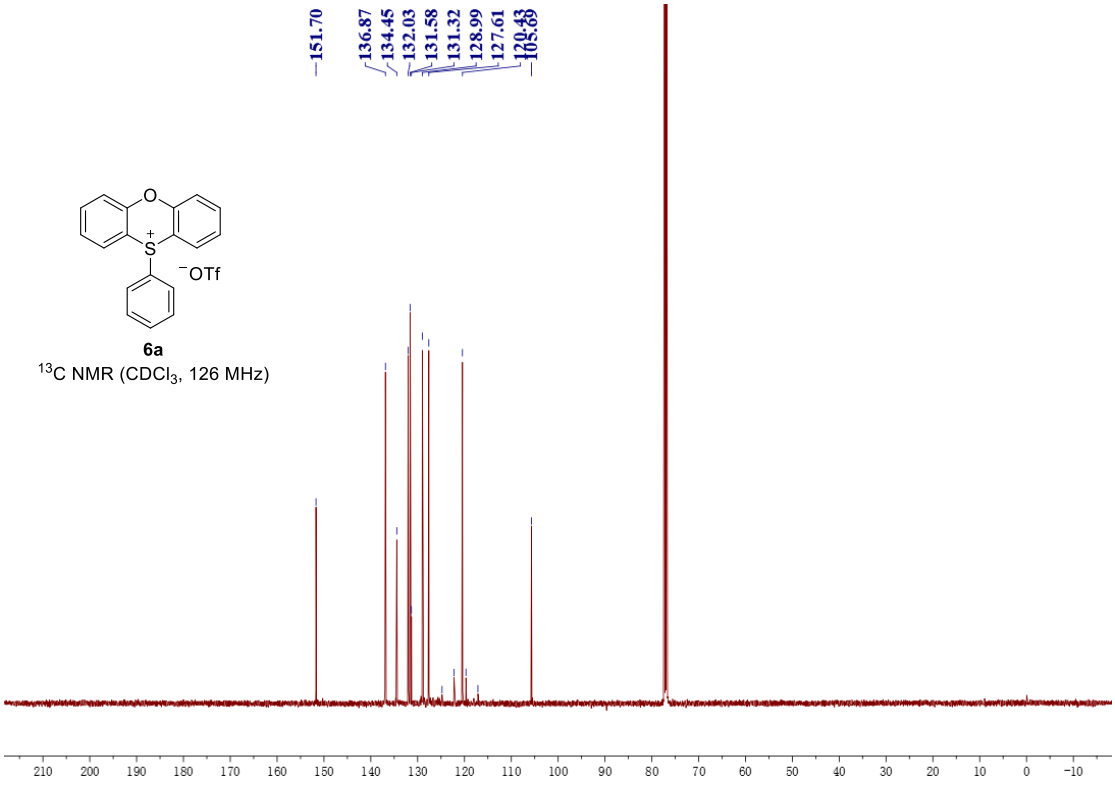
6a

^{1}H NMR ($CDCl_3$, 500 MHz)



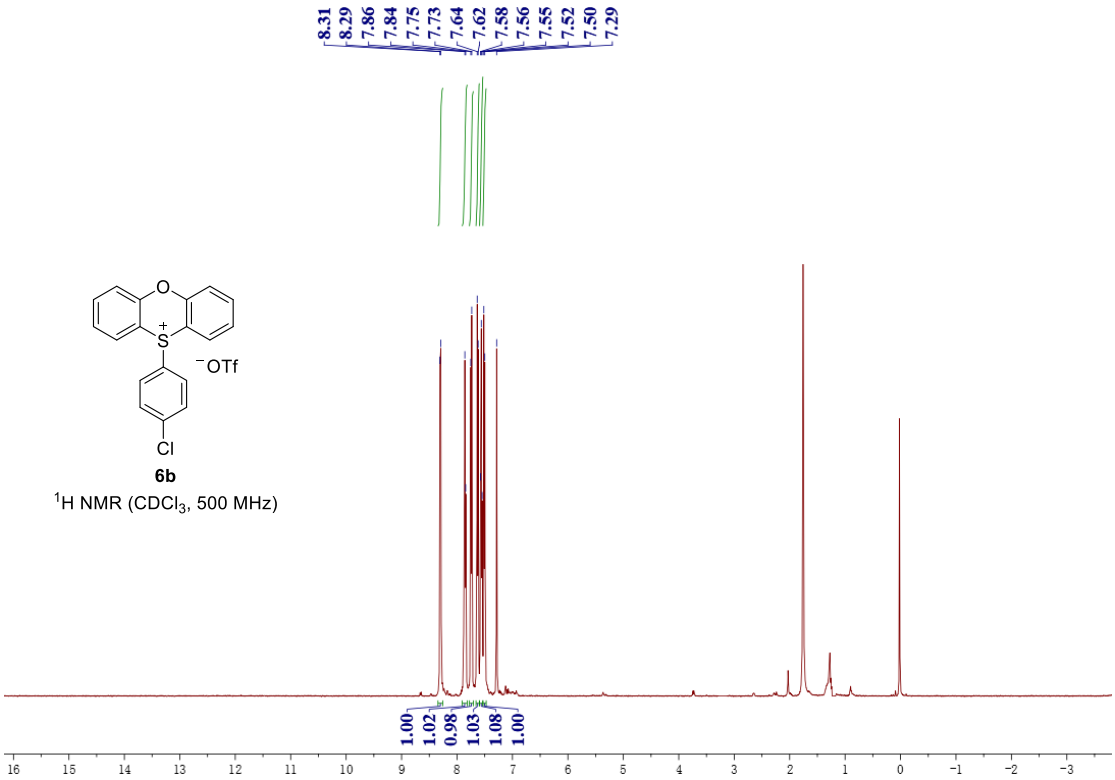
6a

^{19}F NMR ($CDCl_3$, 471 MHz)



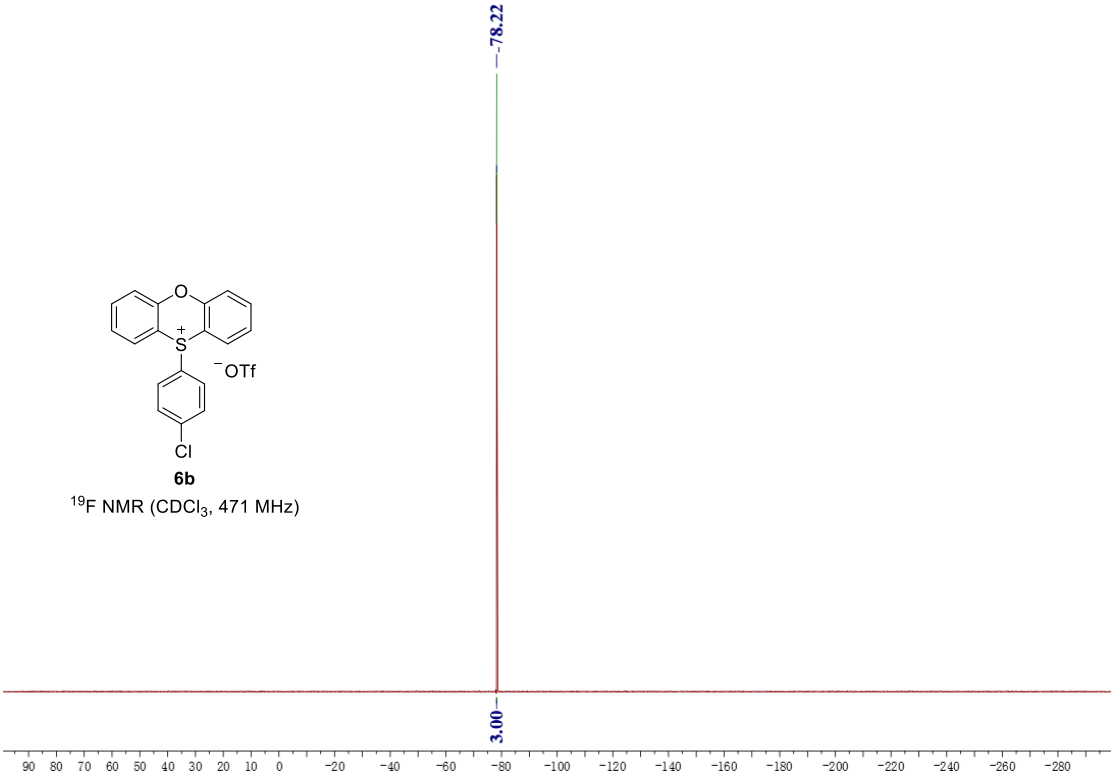
6a

^{13}C NMR ($CDCl_3$, 126 MHz)



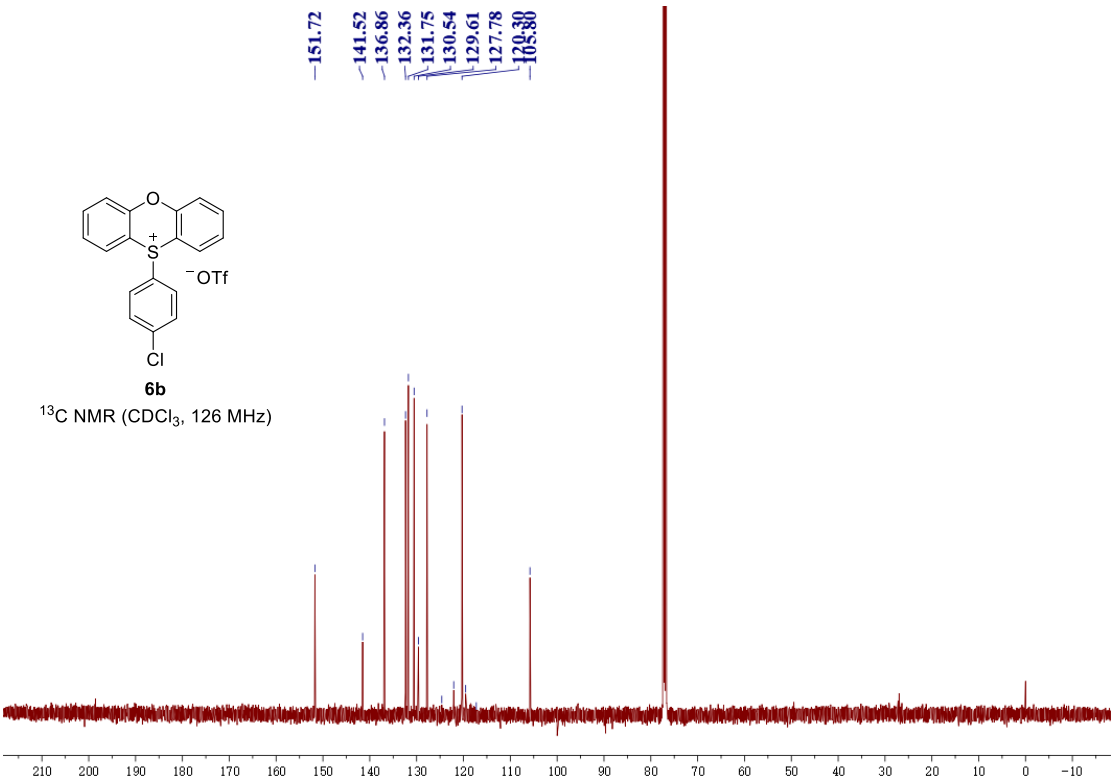
6b

^{1}H NMR ($CDCl_3$, 500 MHz)



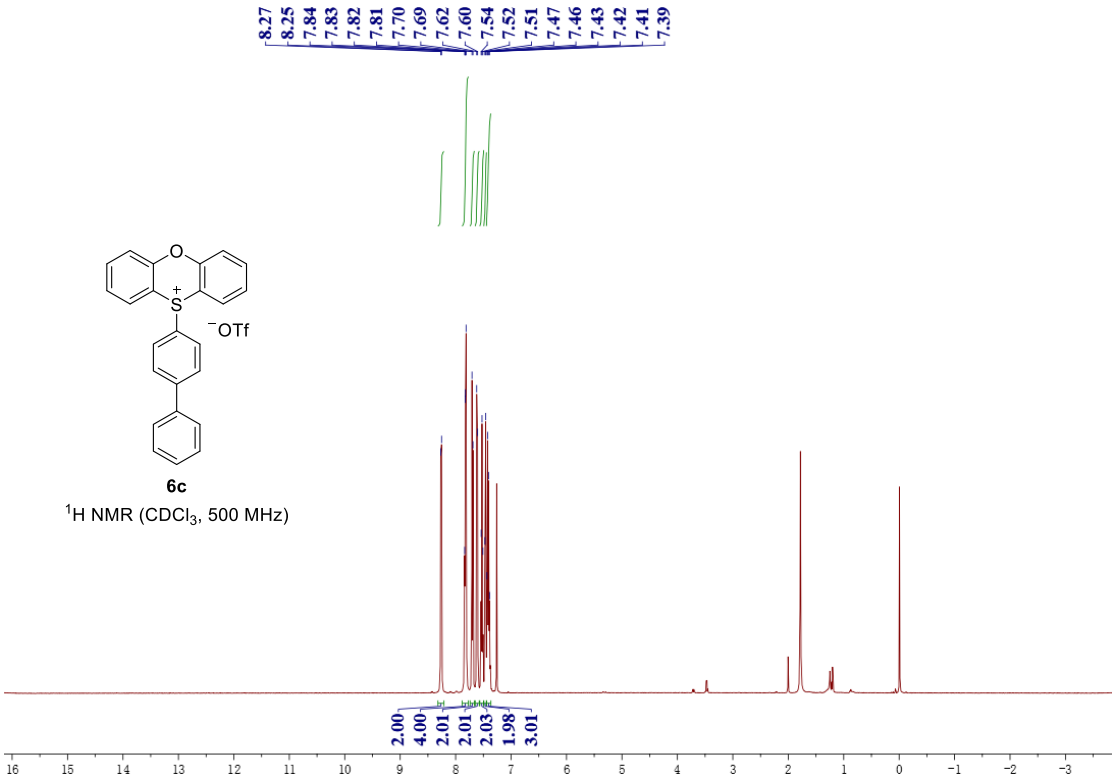
6b

^{19}F NMR ($CDCl_3$, 471 MHz)



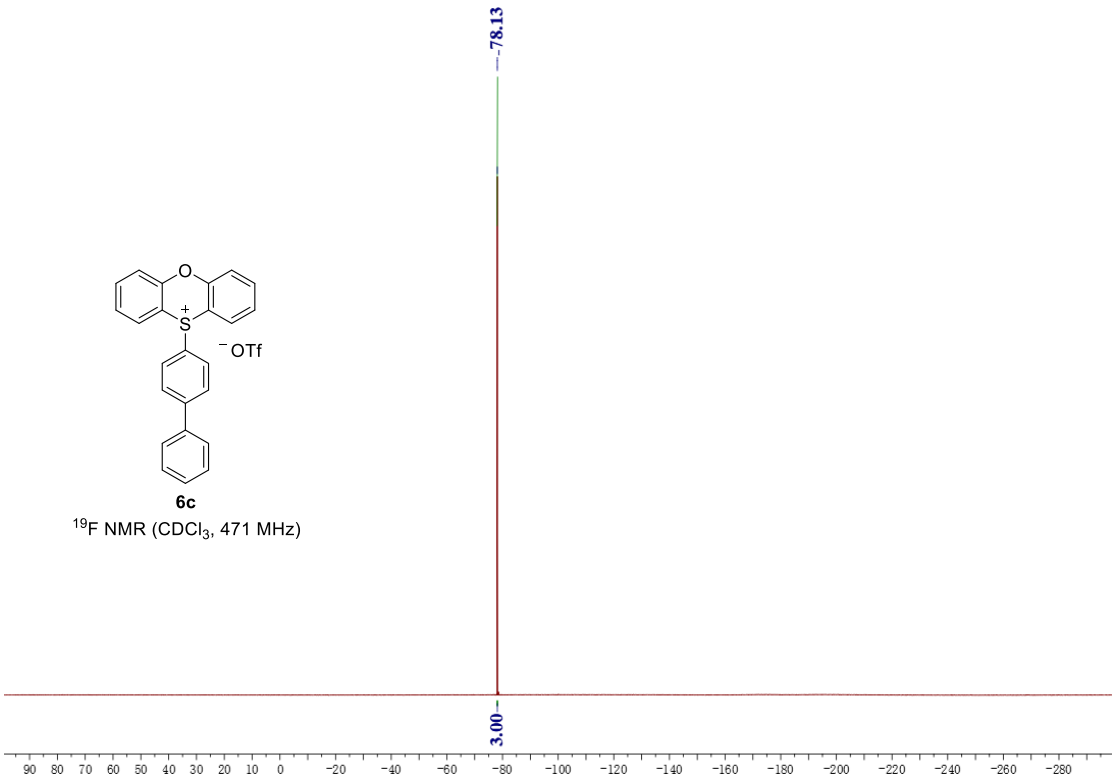
6b

^{13}C NMR ($CDCl_3$, 126 MHz)



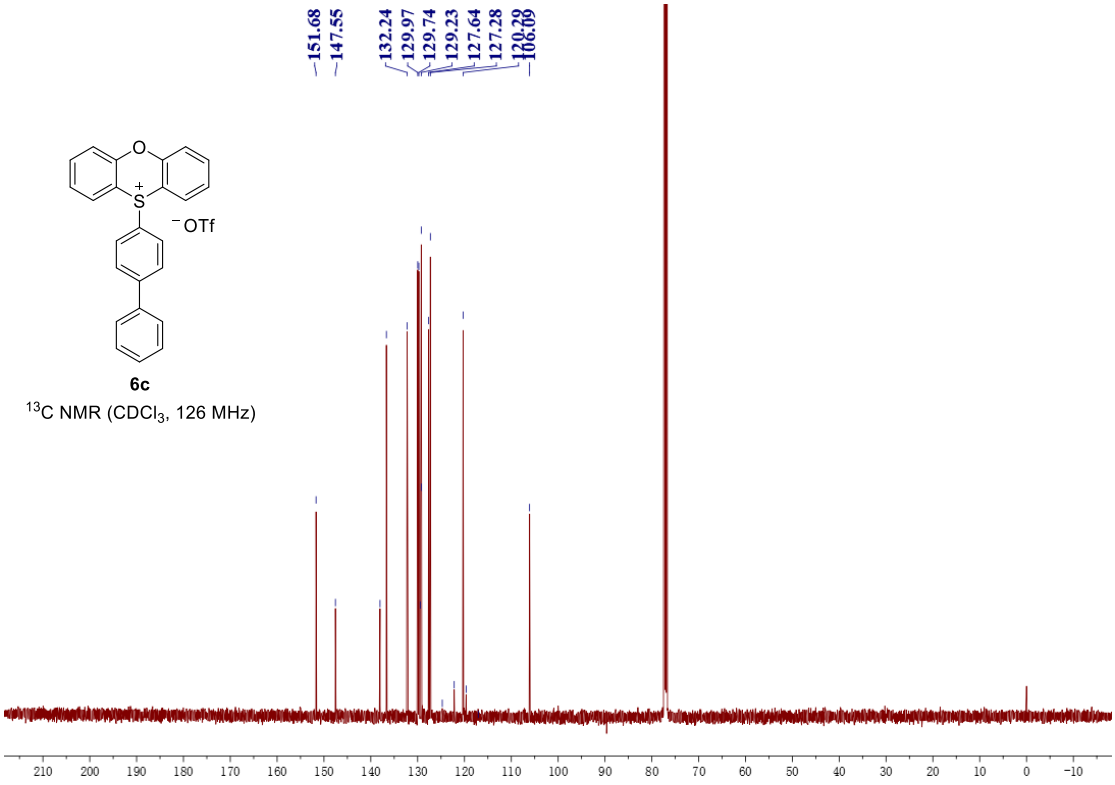
6c

^{1}H NMR ($CDCl_3$, 500 MHz)



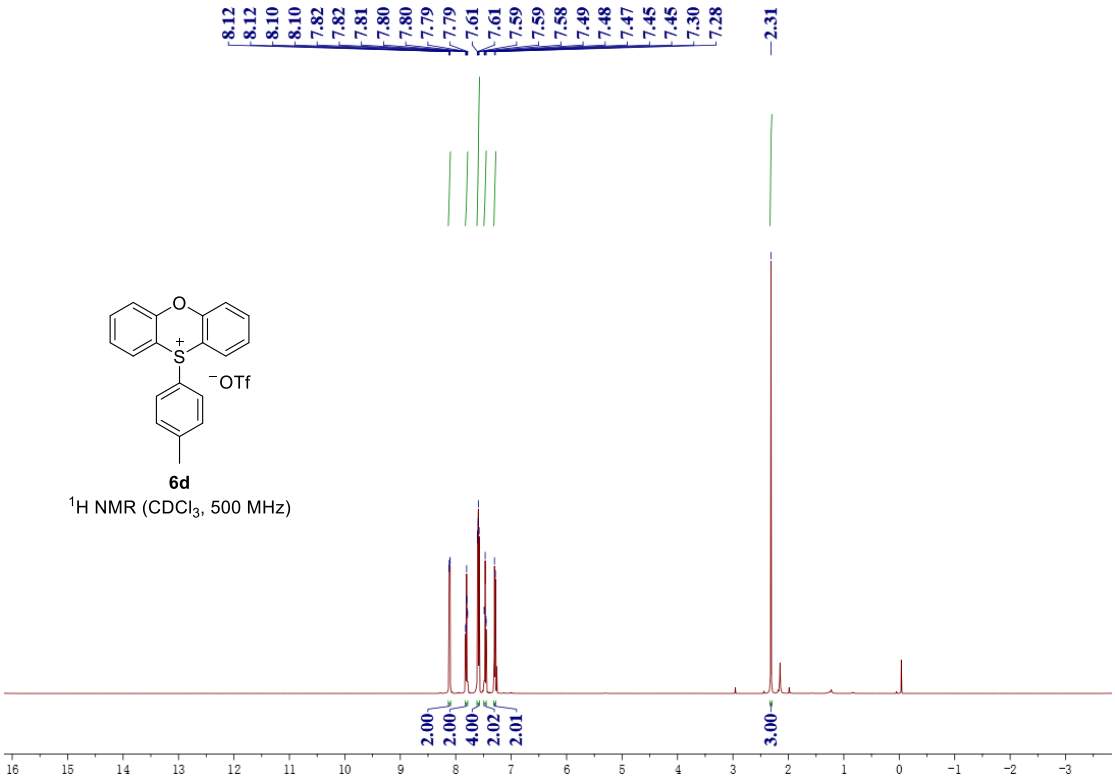
6c

^{19}F NMR ($CDCl_3$, 471 MHz)



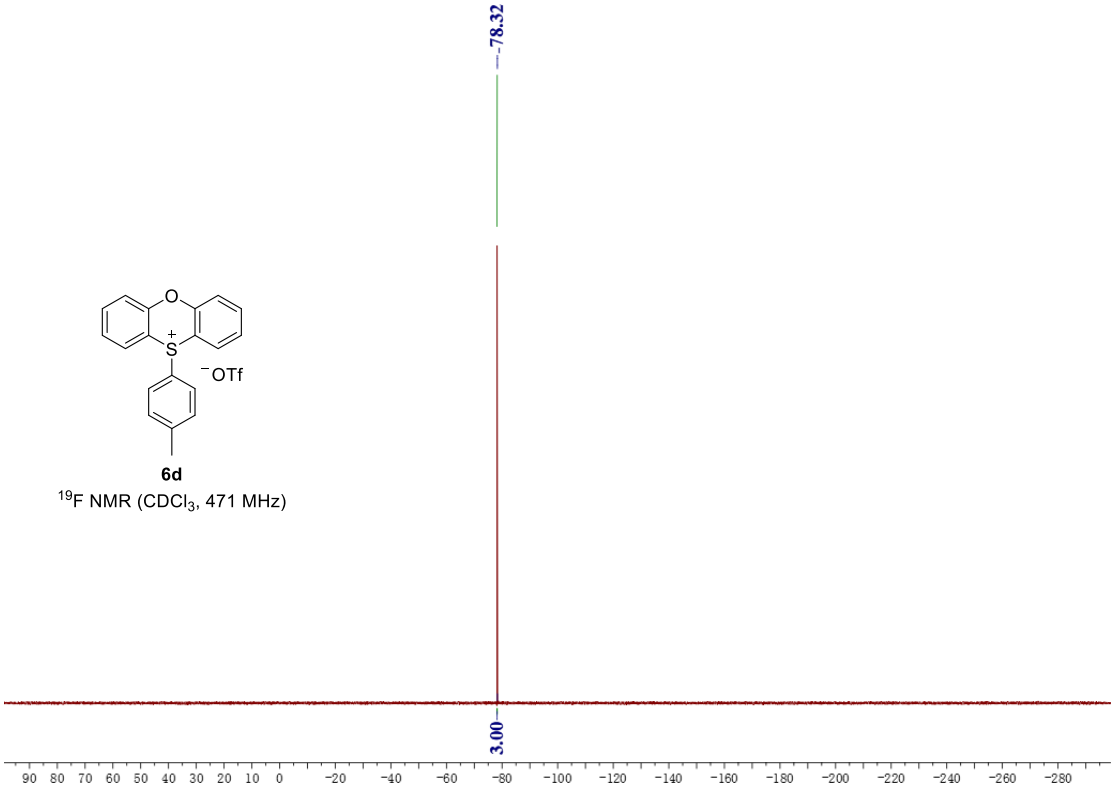
6c

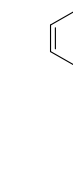
^{13}C NMR ($CDCl_3$, 126 MHz)



6d

^{1}H NMR ($CDCl_3$, 500 MHz)



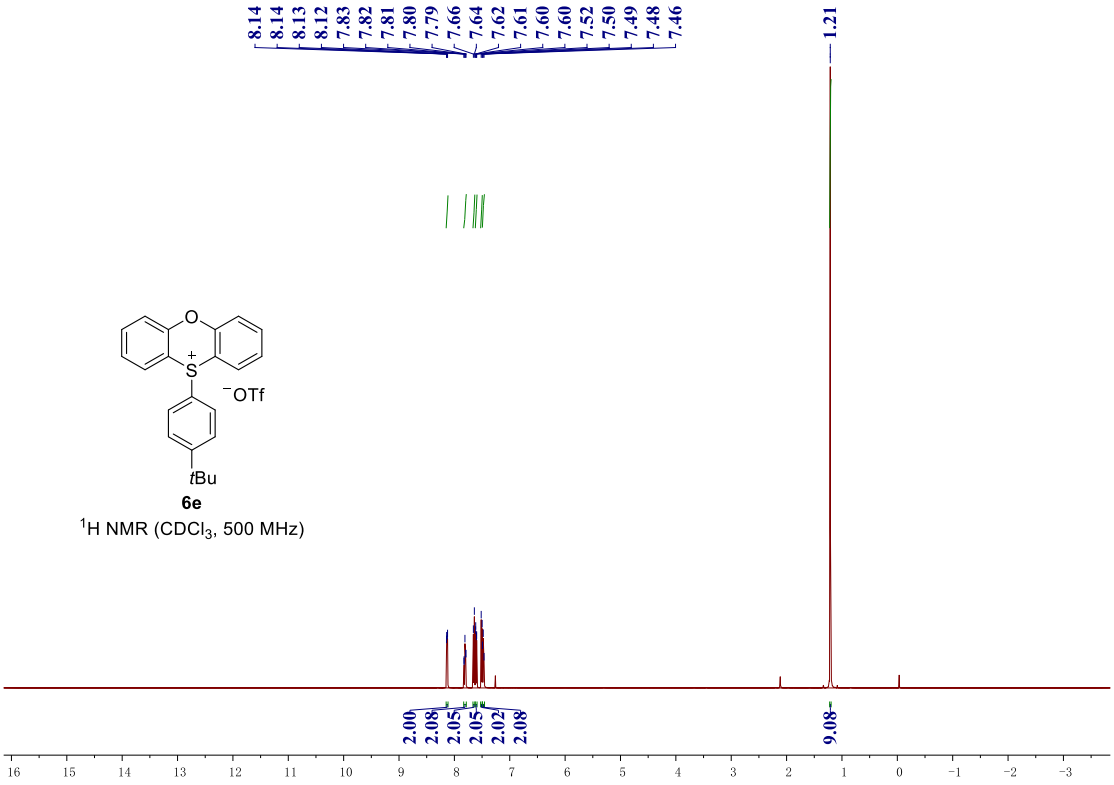


6d

^{19}F NMR ($CDCl_3$, 471 MHz)

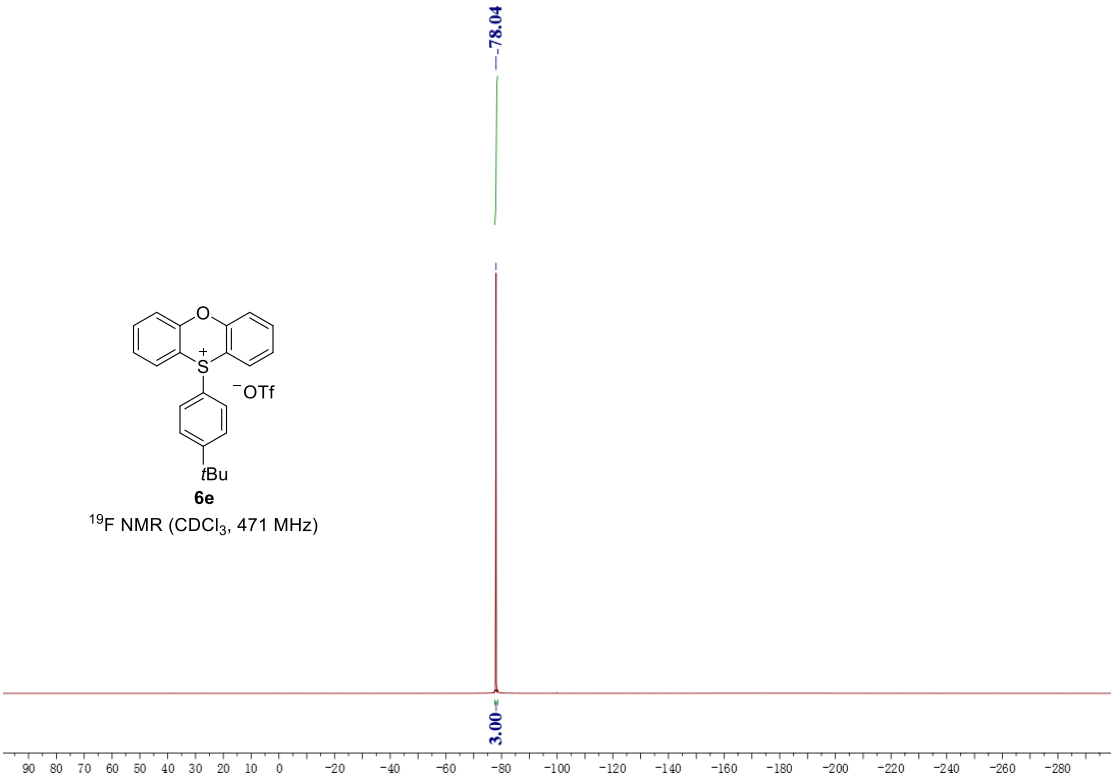
6d

^{13}C NMR ($CDCl_3$, 126 MHz)



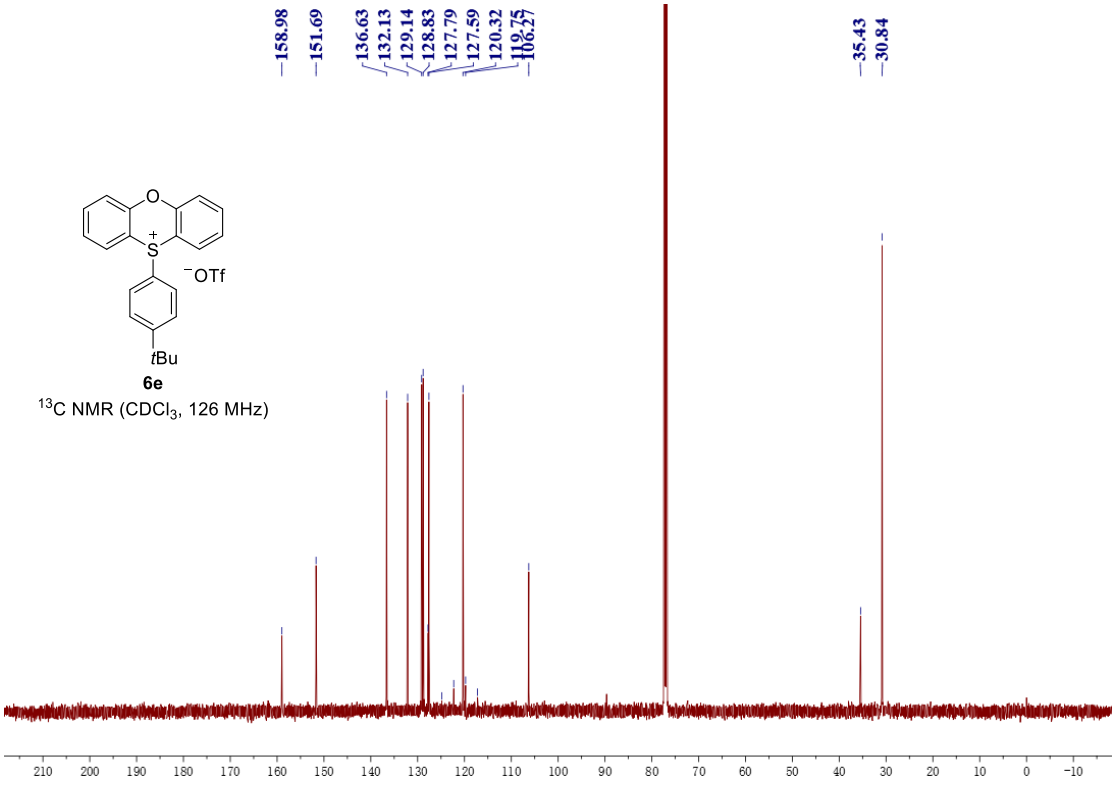
6e

^{1}H NMR ($CDCl_3$, 500 MHz)



6e

^{19}F NMR ($CDCl_3$, 471 MHz)


158.98
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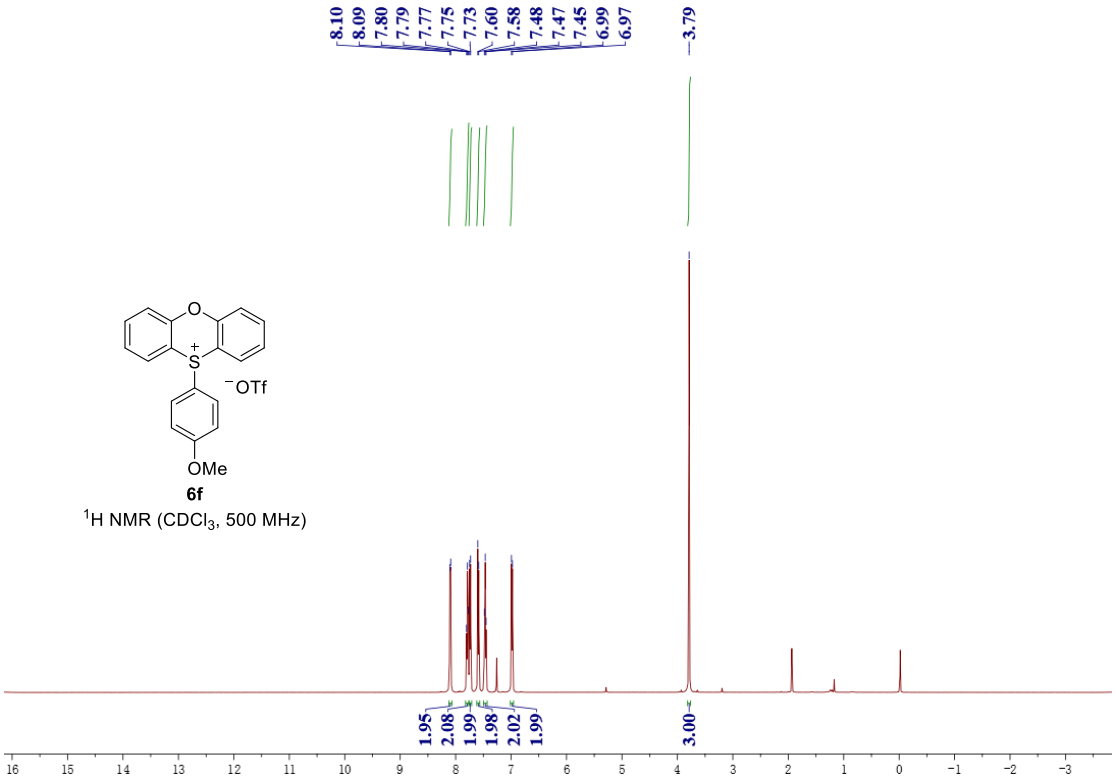
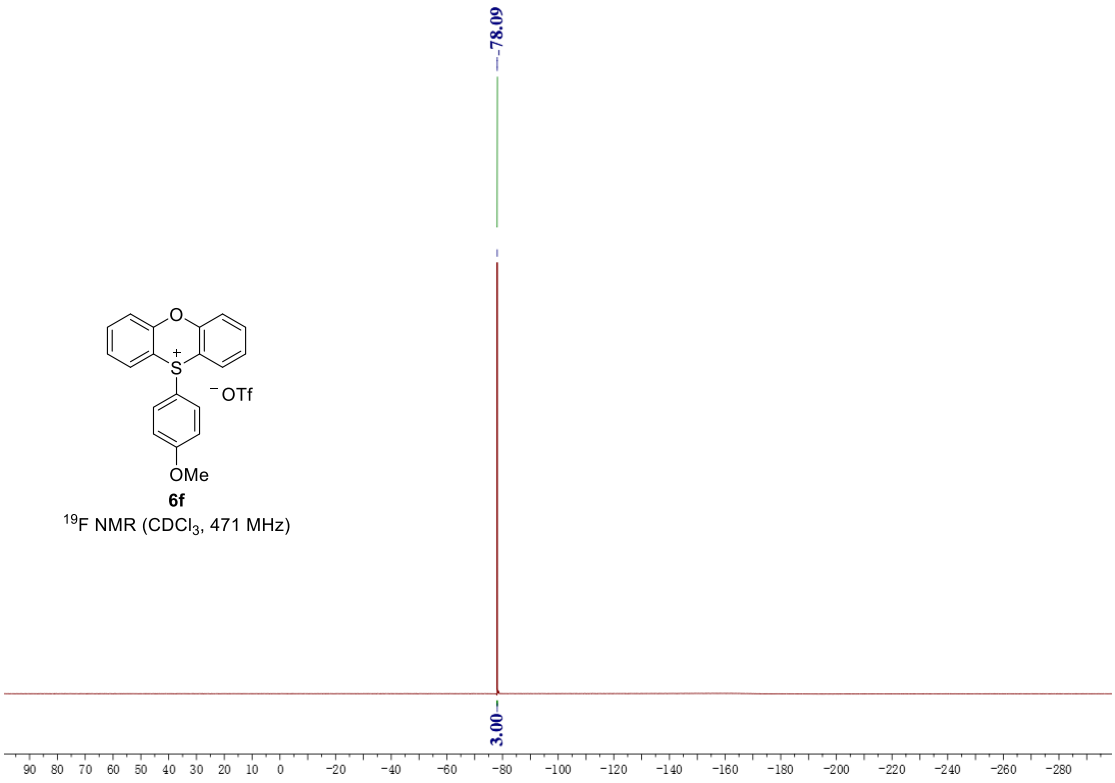
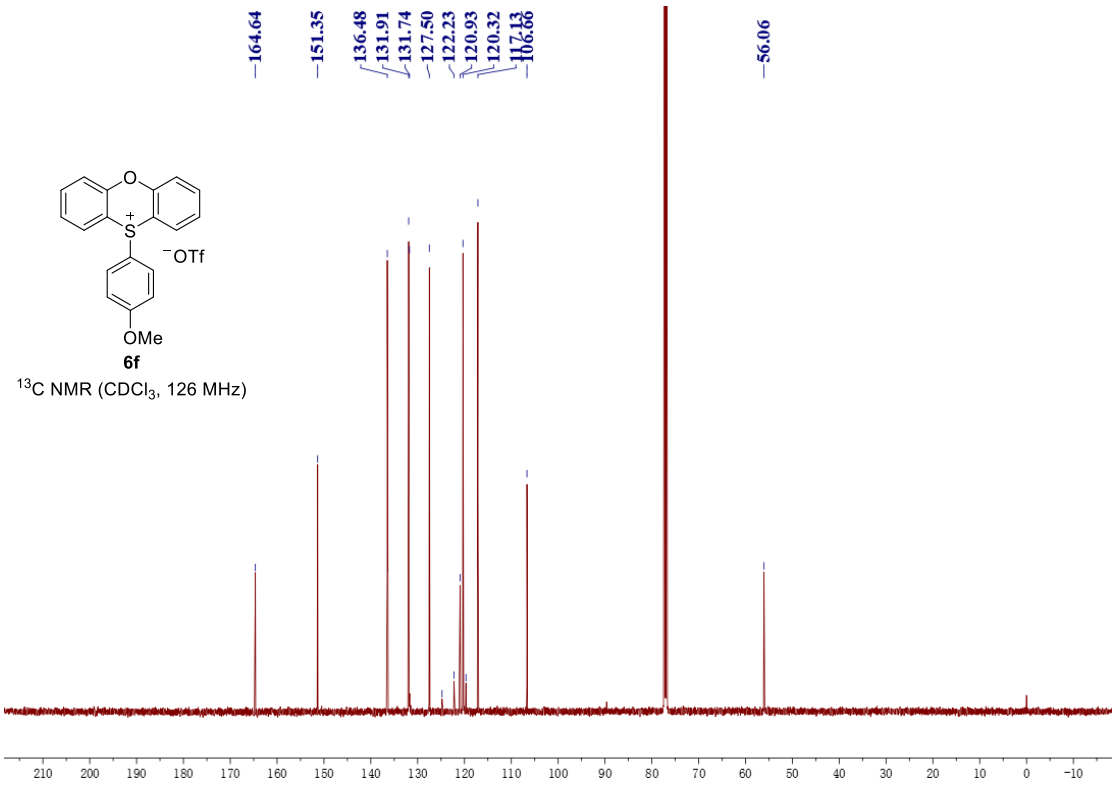
132.13
129.14
128.83
127.79
127.59
120.32
119.75
106.27
35.43
30.84
O
S
+
−OTf
tBu
6e
13C NMR (CDCl3, 126 MHz)


8.10
8.09
7.80
7.79
7.77
7.75
7.73
7.60
7.58
7.48
7.47
7.45
6.99
6.97
3.79
O
S
+
−OTf
OMe
6f
1H NMR (CDCl3, 500 MHz)
1.95
2.08
1.99
1.98
2.02
1.99
3.00



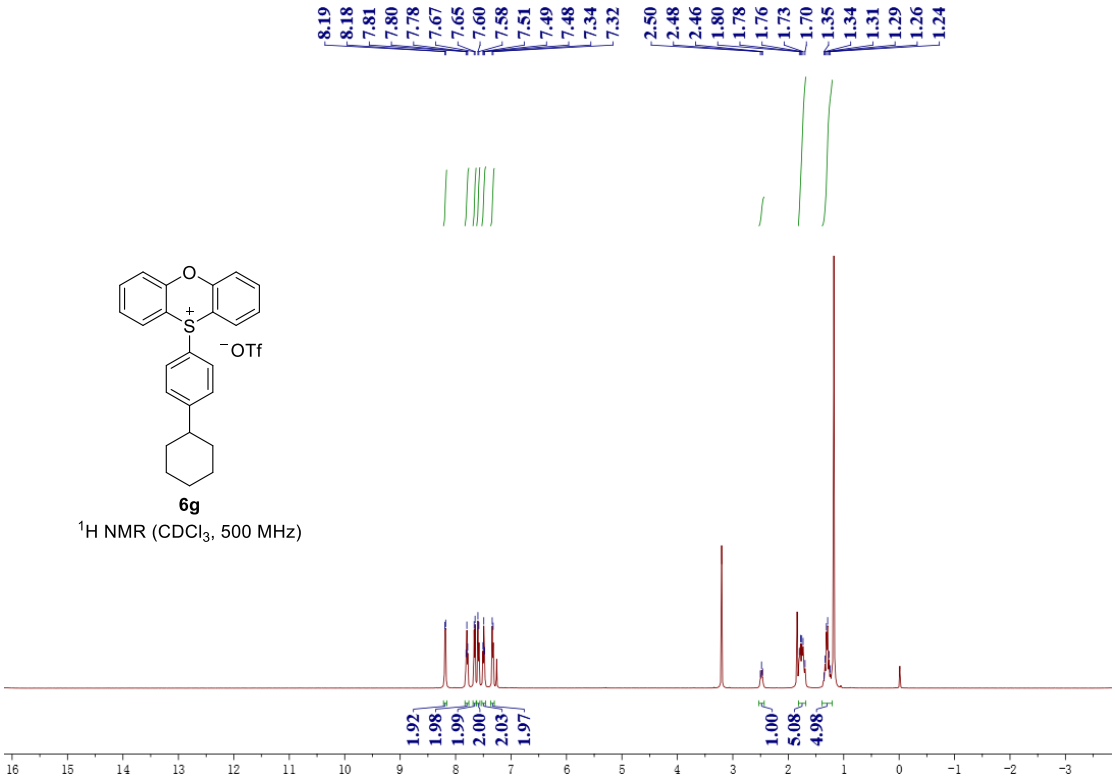
6f

^{19}F NMR ($CDCl_3$, 471 MHz)



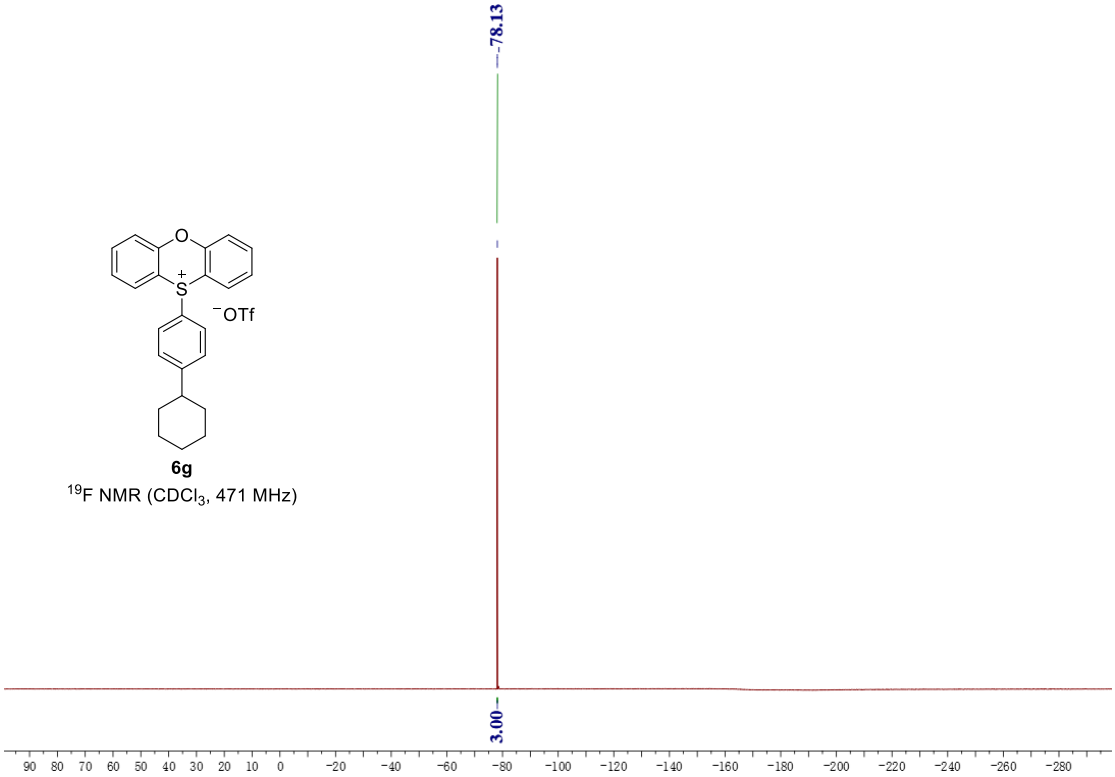
6f

^{13}C NMR ($CDCl_3$, 126 MHz)



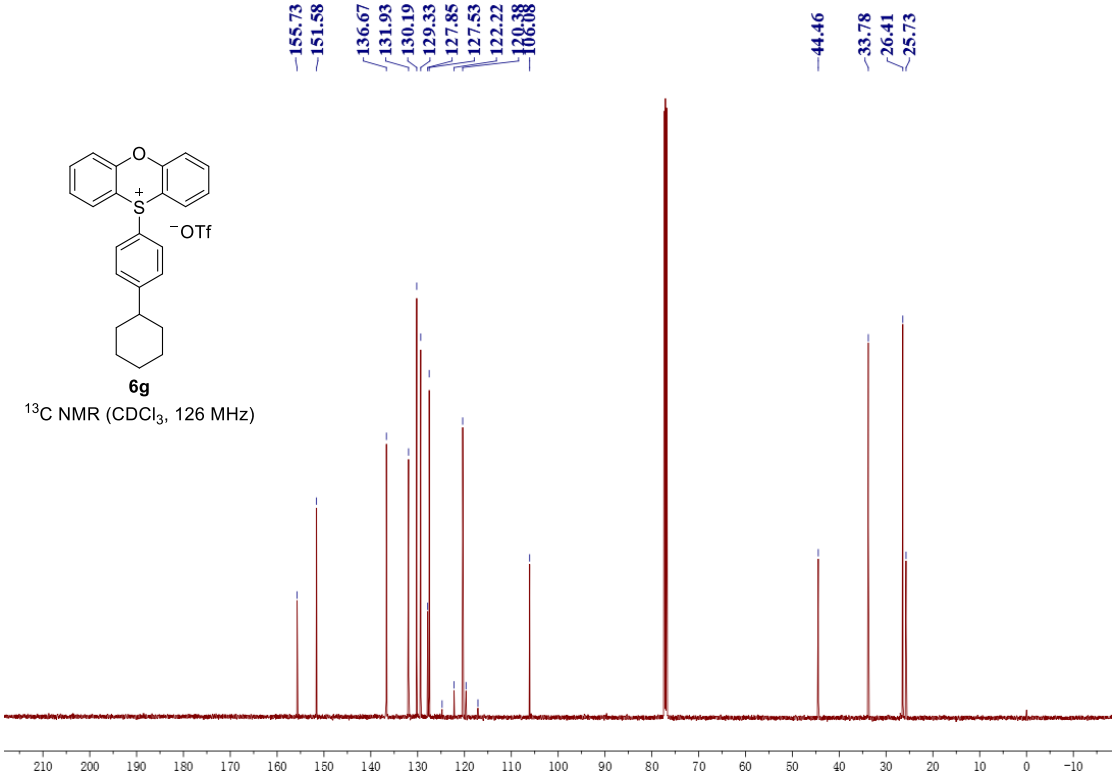
6g

^{1}H NMR ($CDCl_3$, 500 MHz)



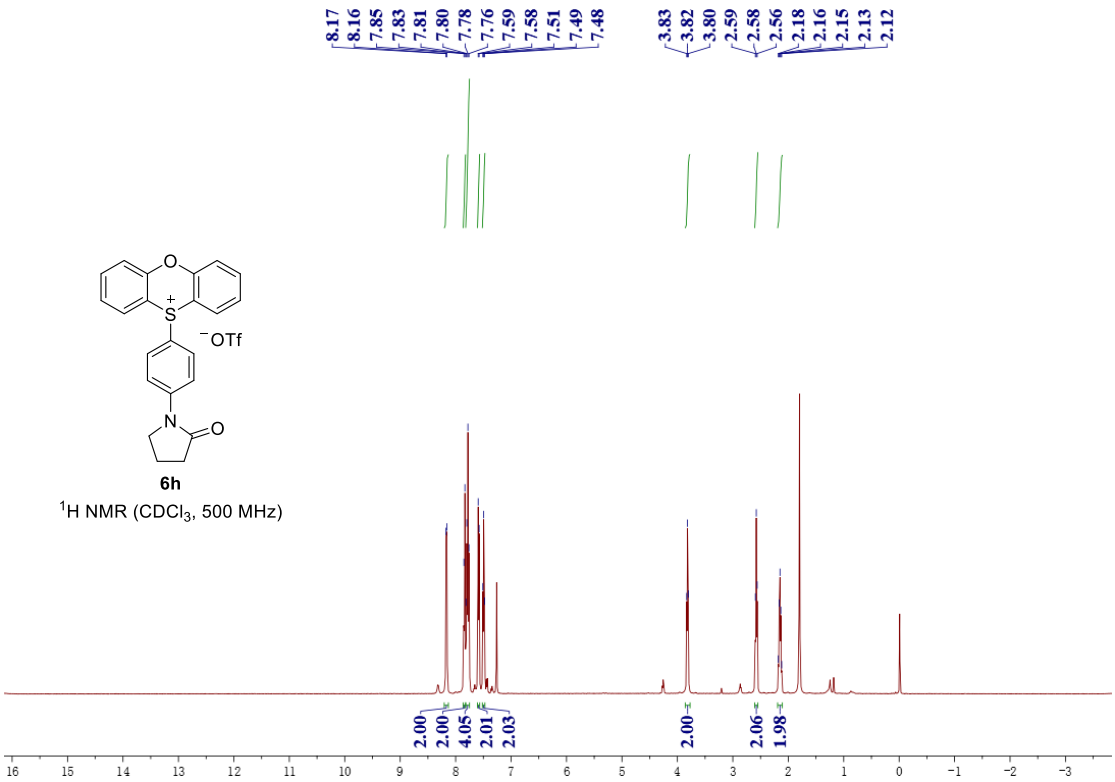
6g

^{19}F NMR ($CDCl_3$, 471 MHz)



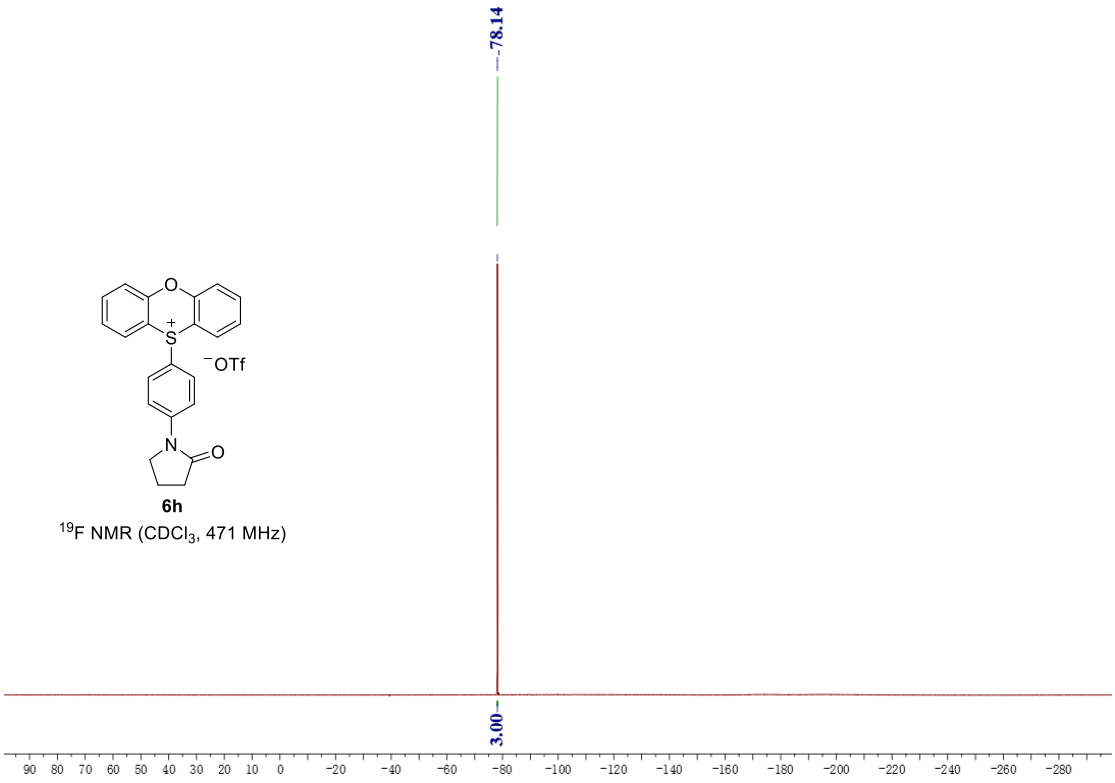
6g

^{13}C NMR ($CDCl_3$, 126 MHz)



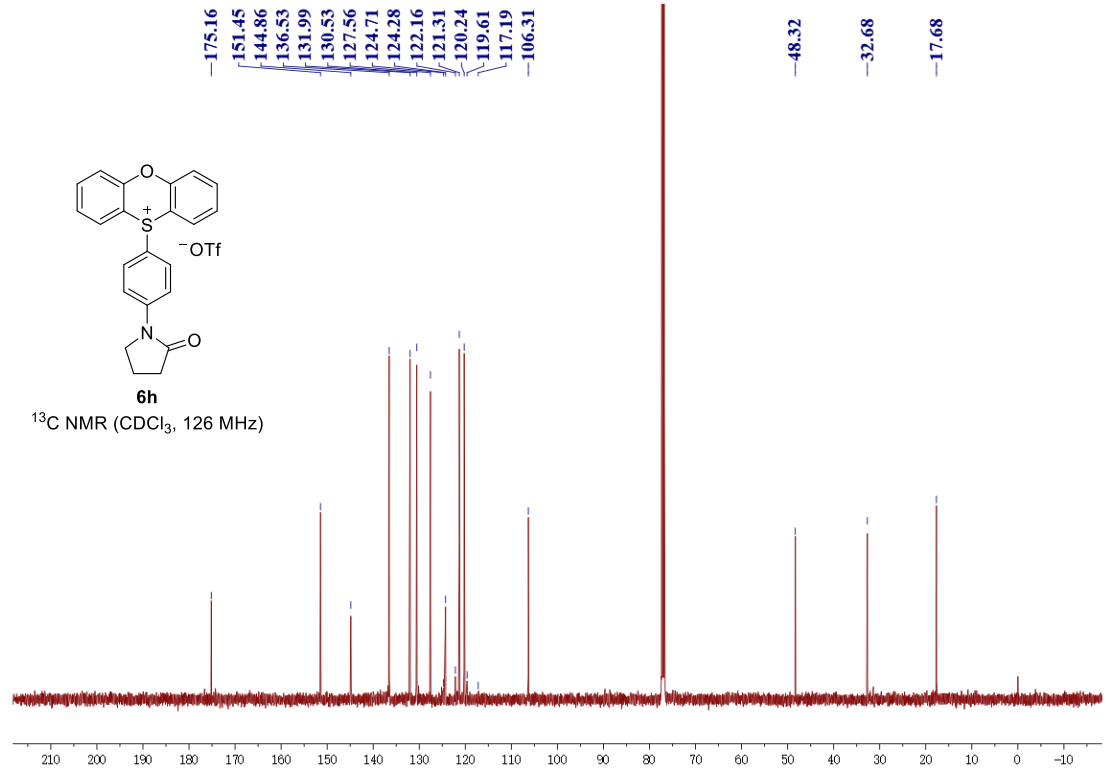
6h

^{1}H NMR ($CDCl_3$, 500 MHz)



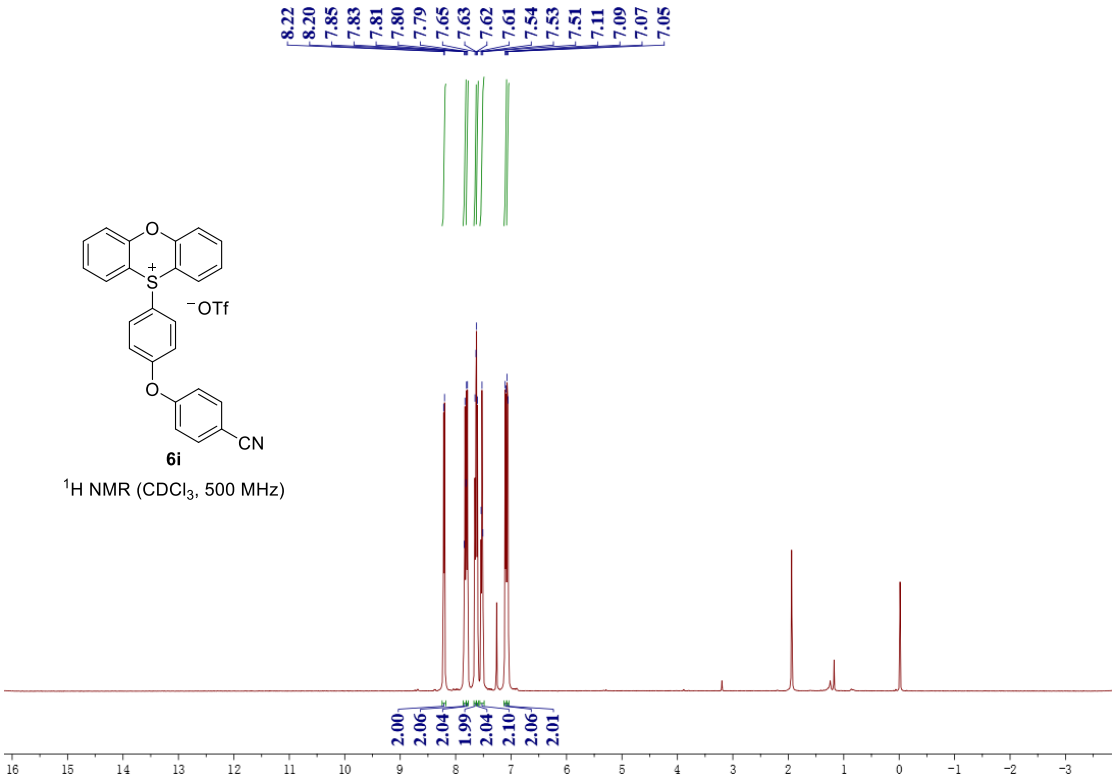
6h

^{19}F NMR ($CDCl_3$, 471 MHz)



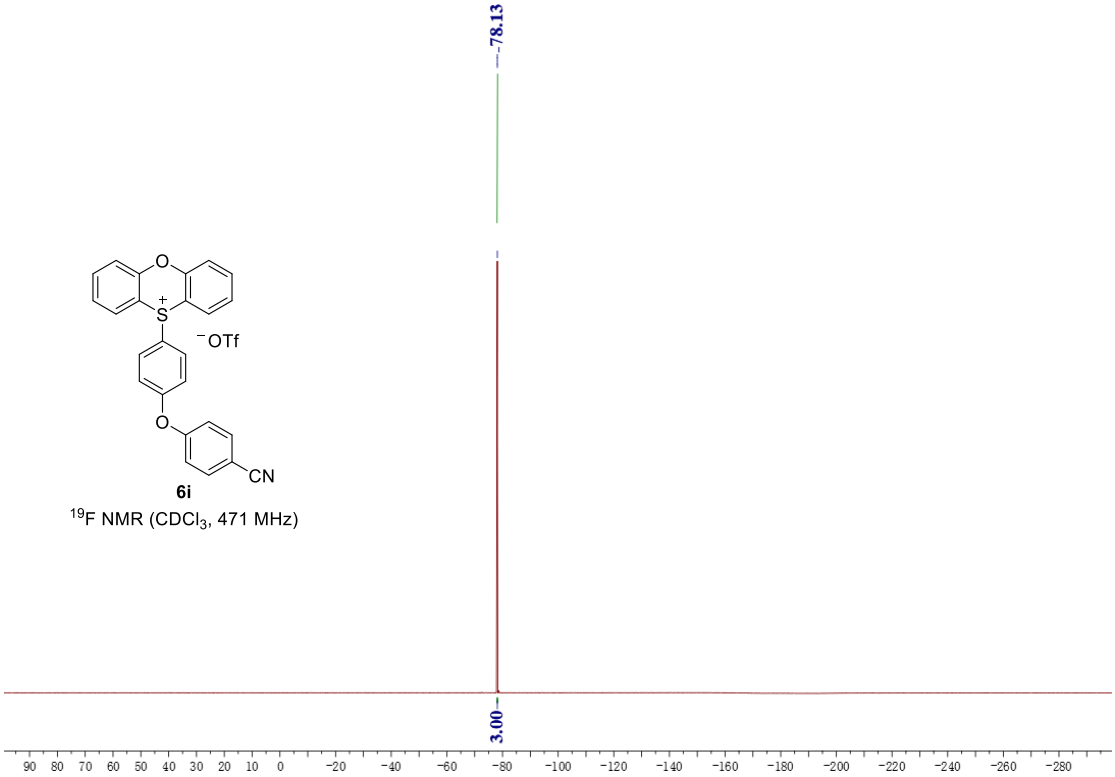
6h

^{13}C NMR ($CDCl_3$, 126 MHz)



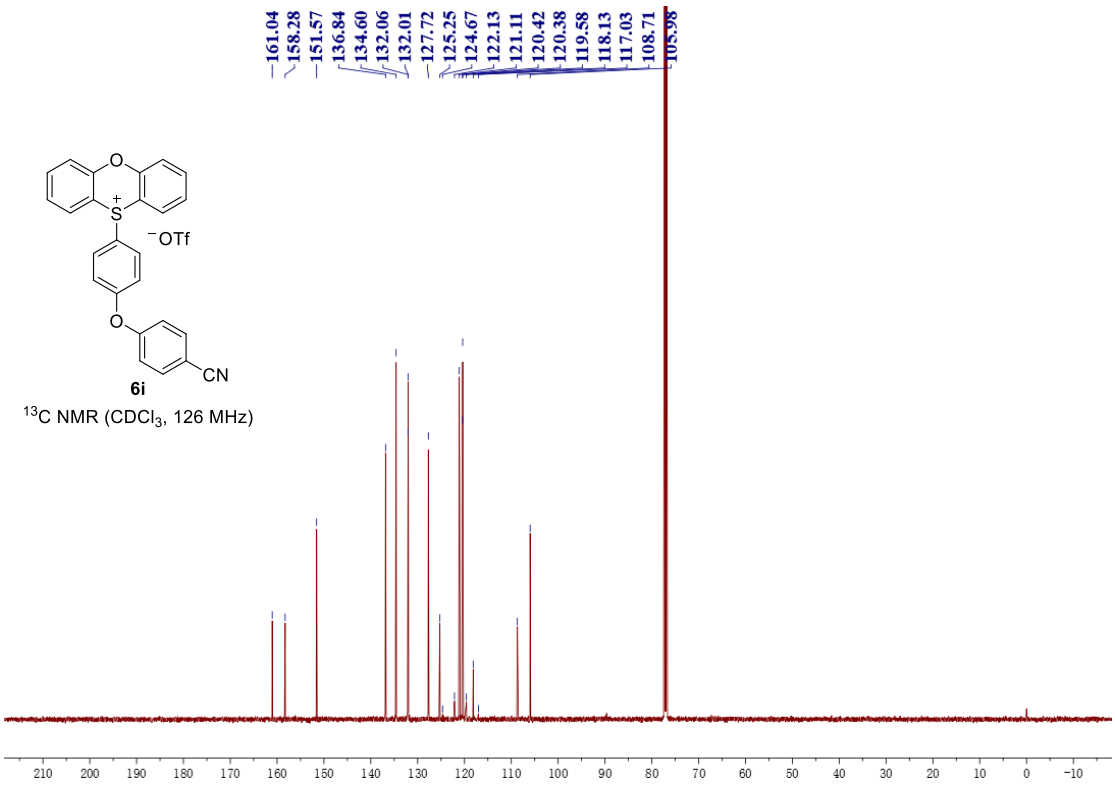
6i

^{1}H NMR ($CDCl_3$, 500 MHz)



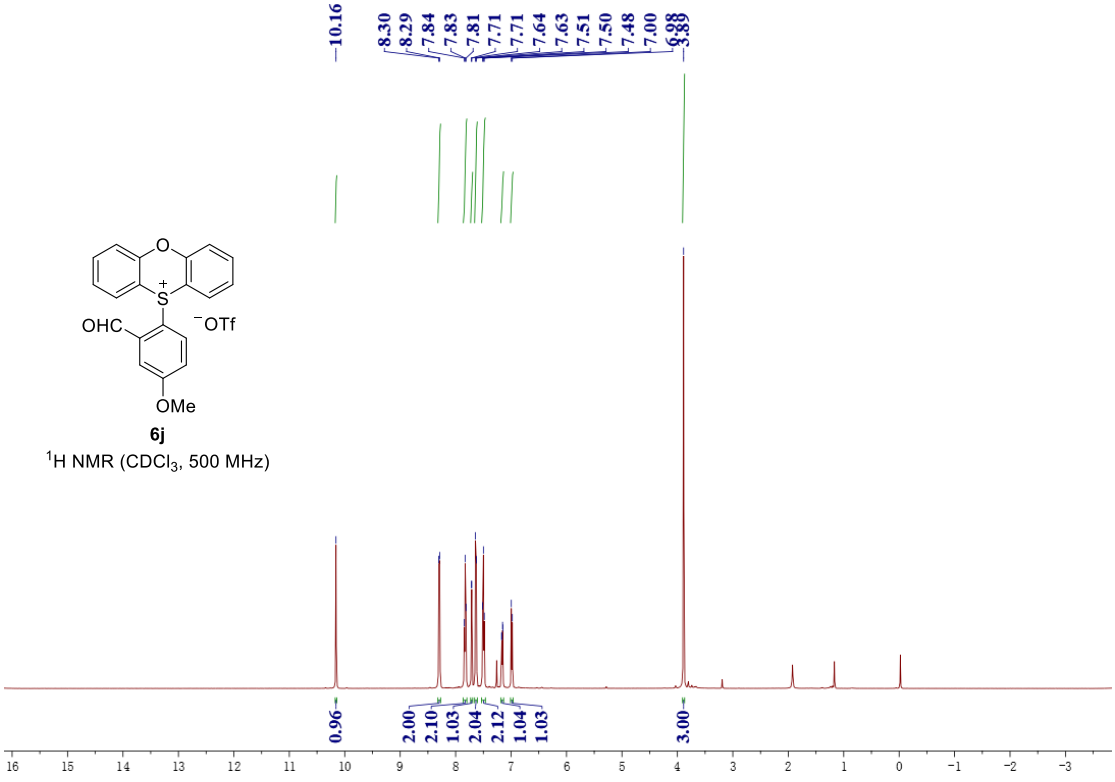
6i

^{19}F NMR ($CDCl_3$, 471 MHz)



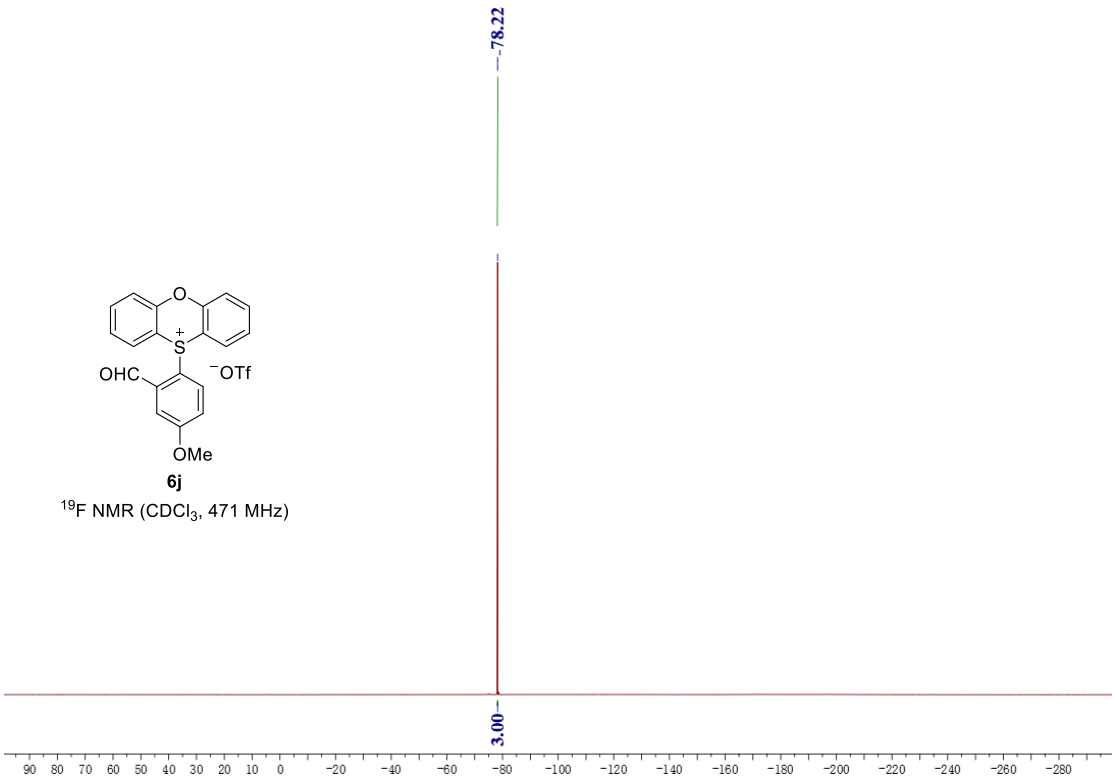
6i

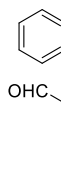
^{13}C NMR ($CDCl_3$, 126 MHz)



6j

^{1}H NMR ($CDCl_3$, 500 MHz)



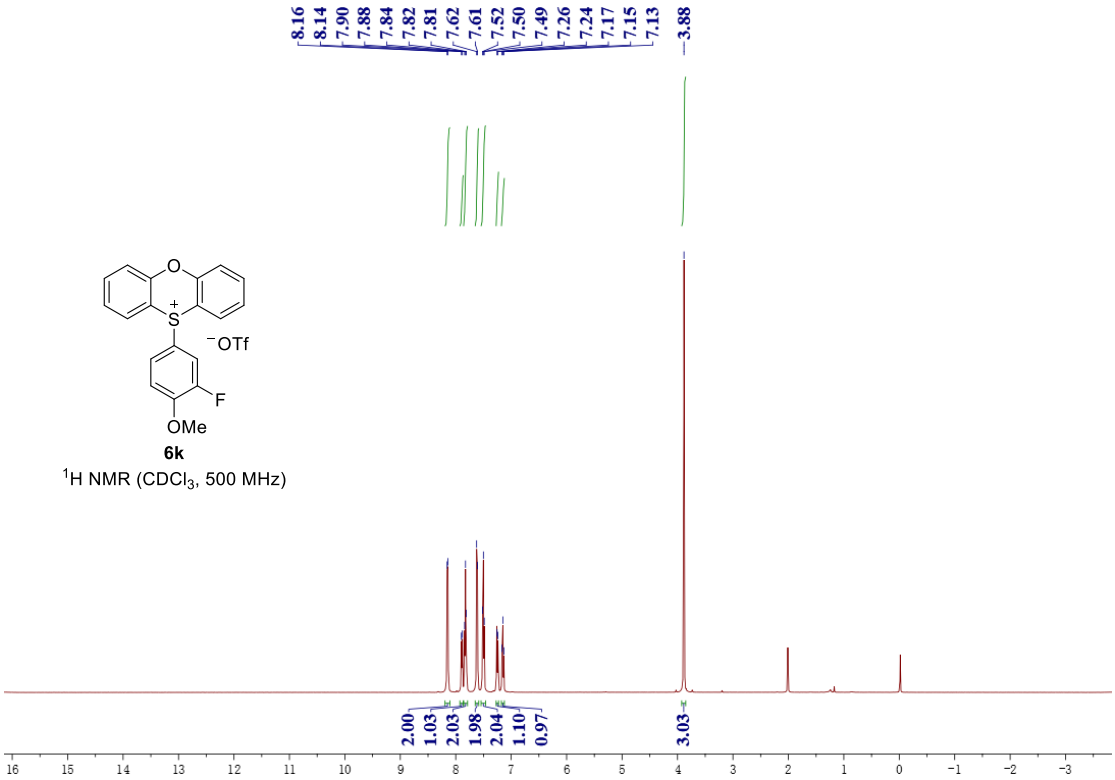


6j

^{19}F NMR ($CDCl_3$, 471 MHz)

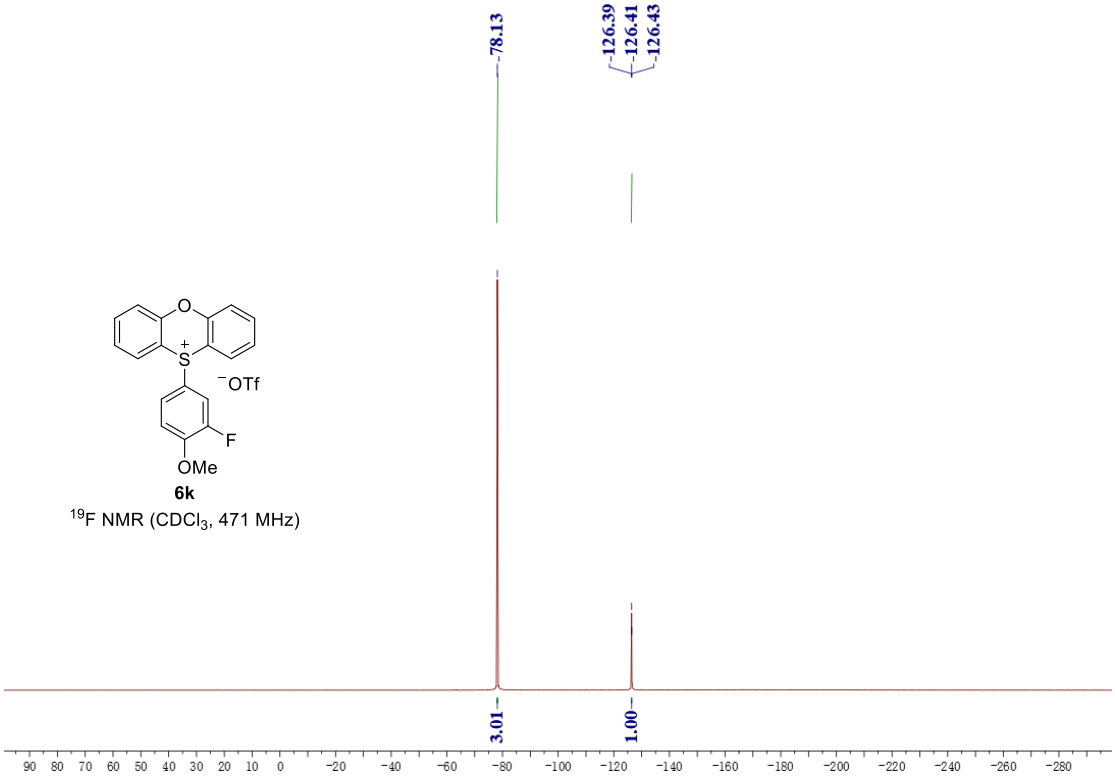
6j

^{13}C NMR ($CDCl_3$, 126 MHz)



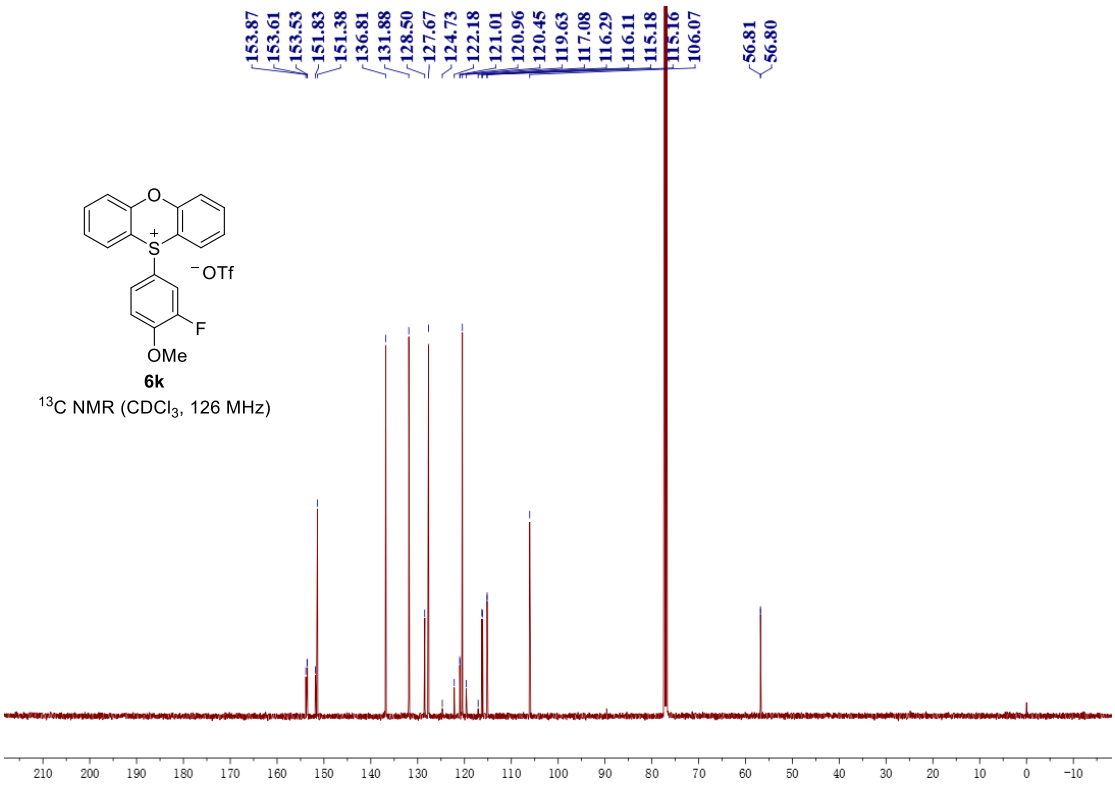
6k

^{1}H NMR ($CDCl_3$, 500 MHz)



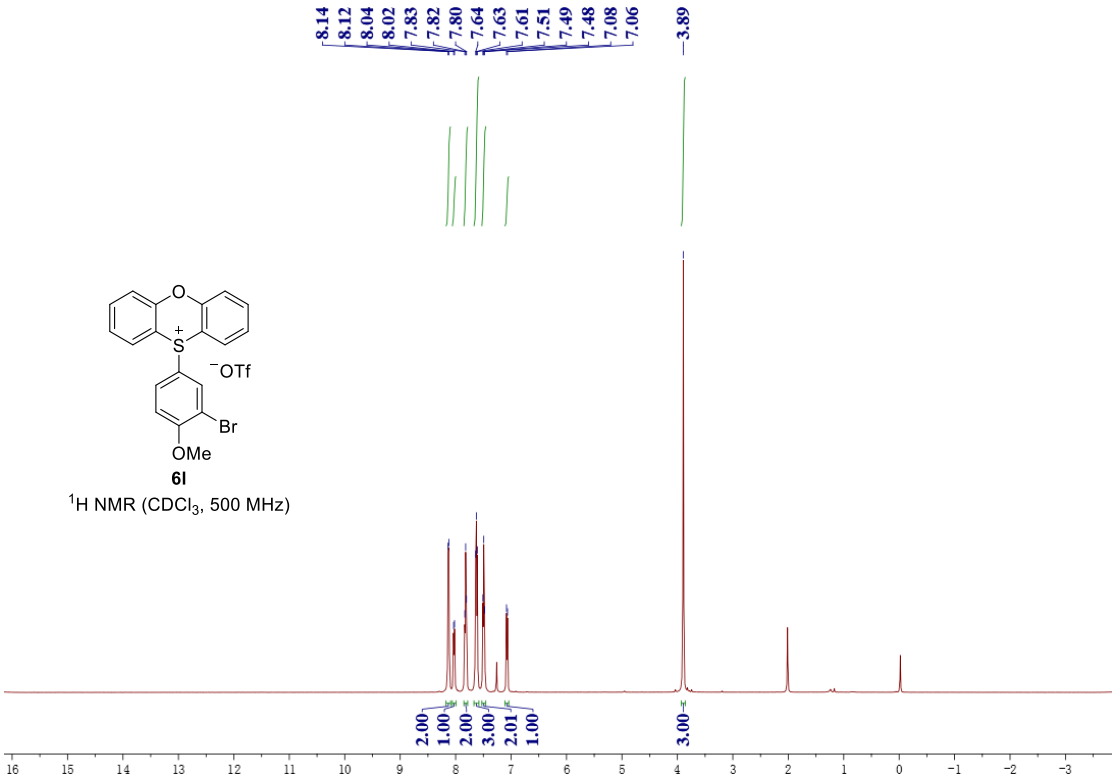
6k

^{19}F NMR ($CDCl_3$, 471 MHz)



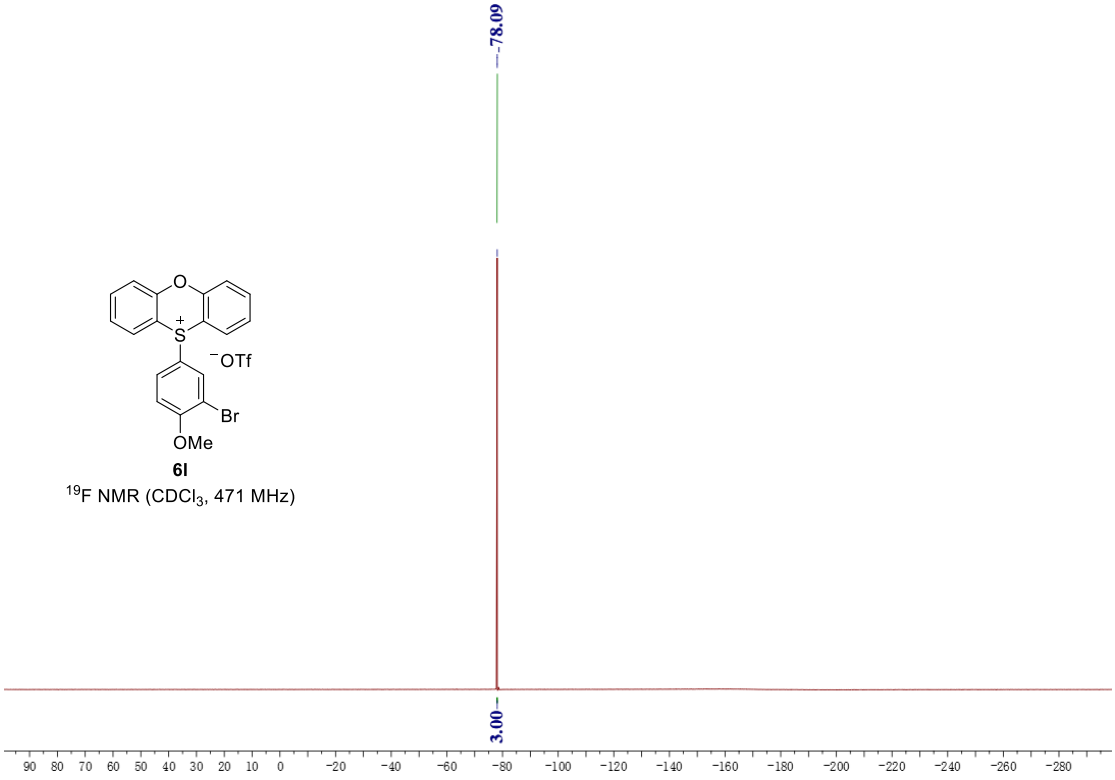
6k

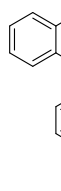
^{13}C NMR ($CDCl_3$, 126 MHz)



6l

^{1}H NMR ($CDCl_3$, 500 MHz)



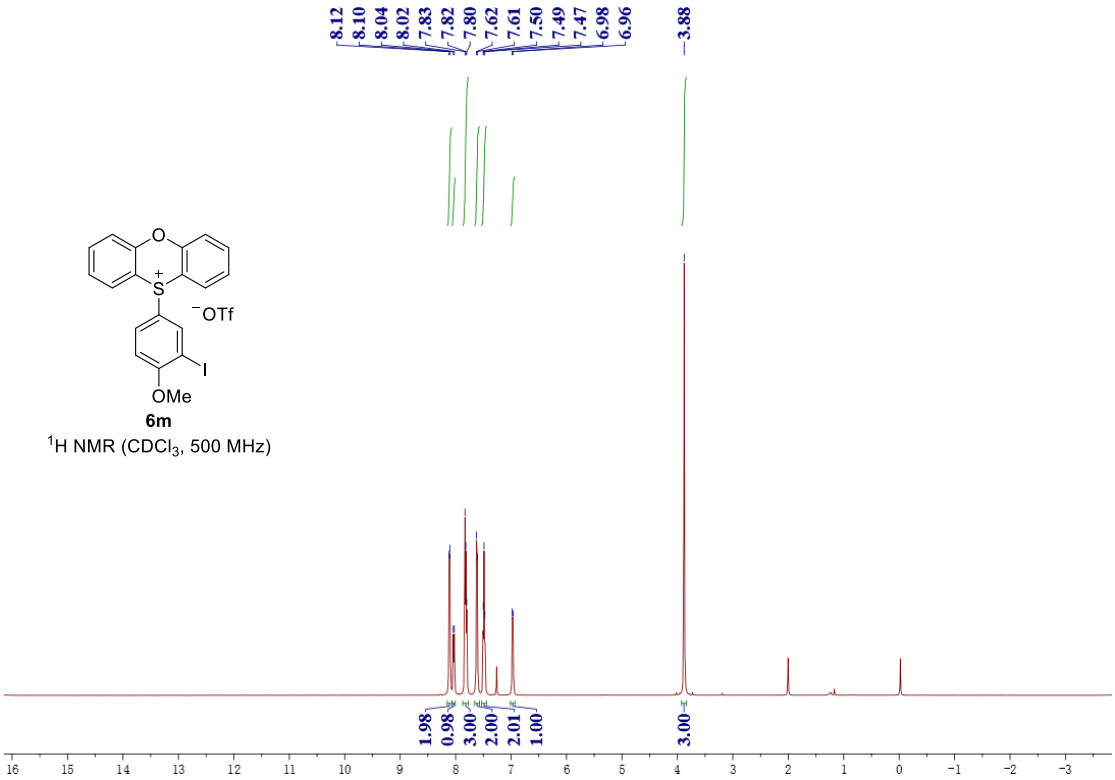


6l

^{19}F NMR ($CDCl_3$, 471 MHz)

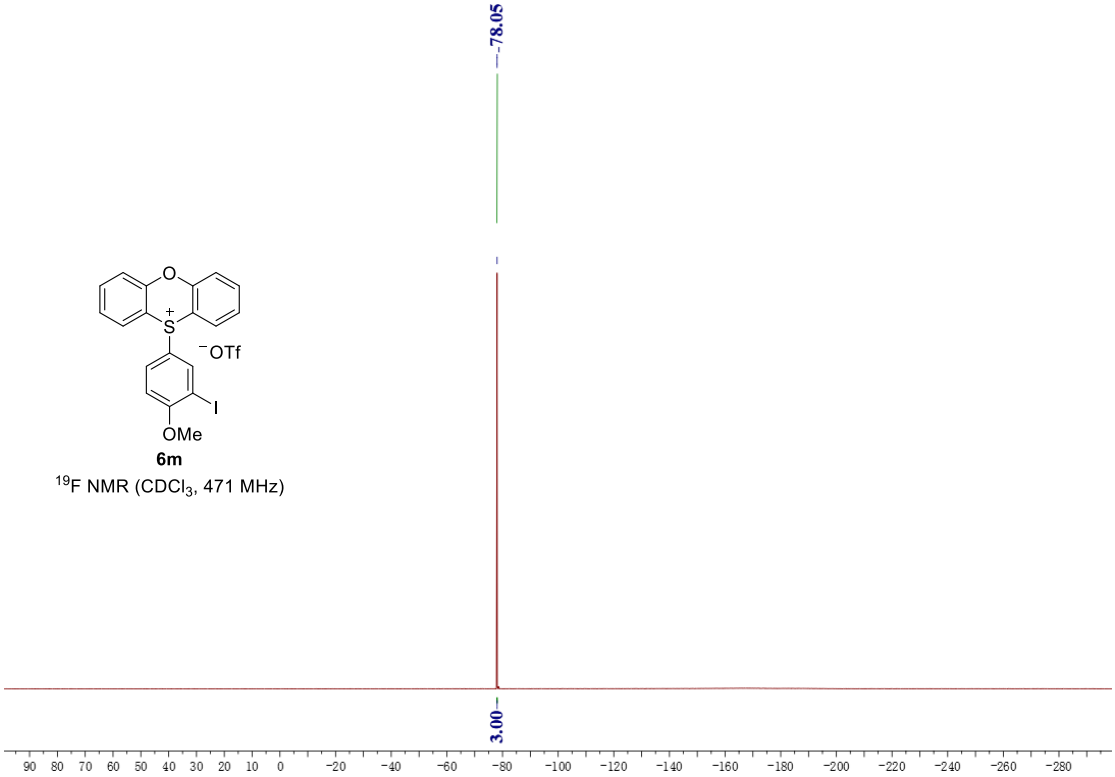
6l

^{13}C NMR ($CDCl_3$, 126 MHz)



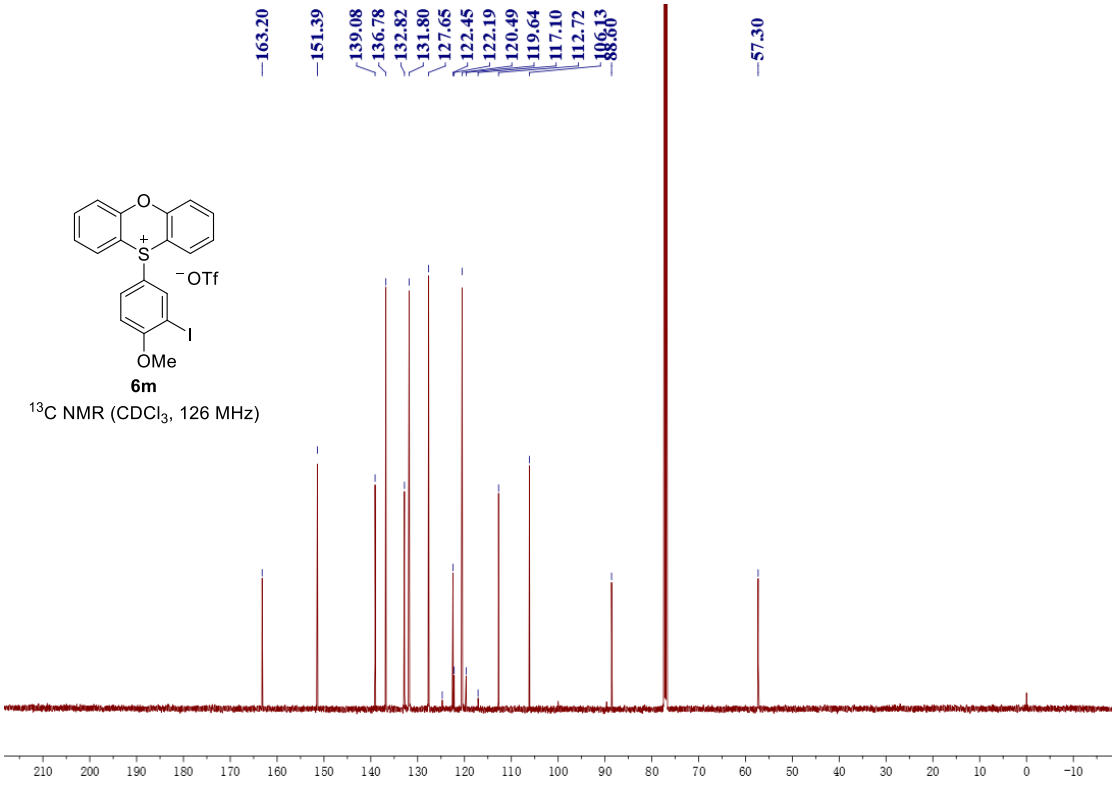
6m

^{1}H NMR ($CDCl_3$, 500 MHz)



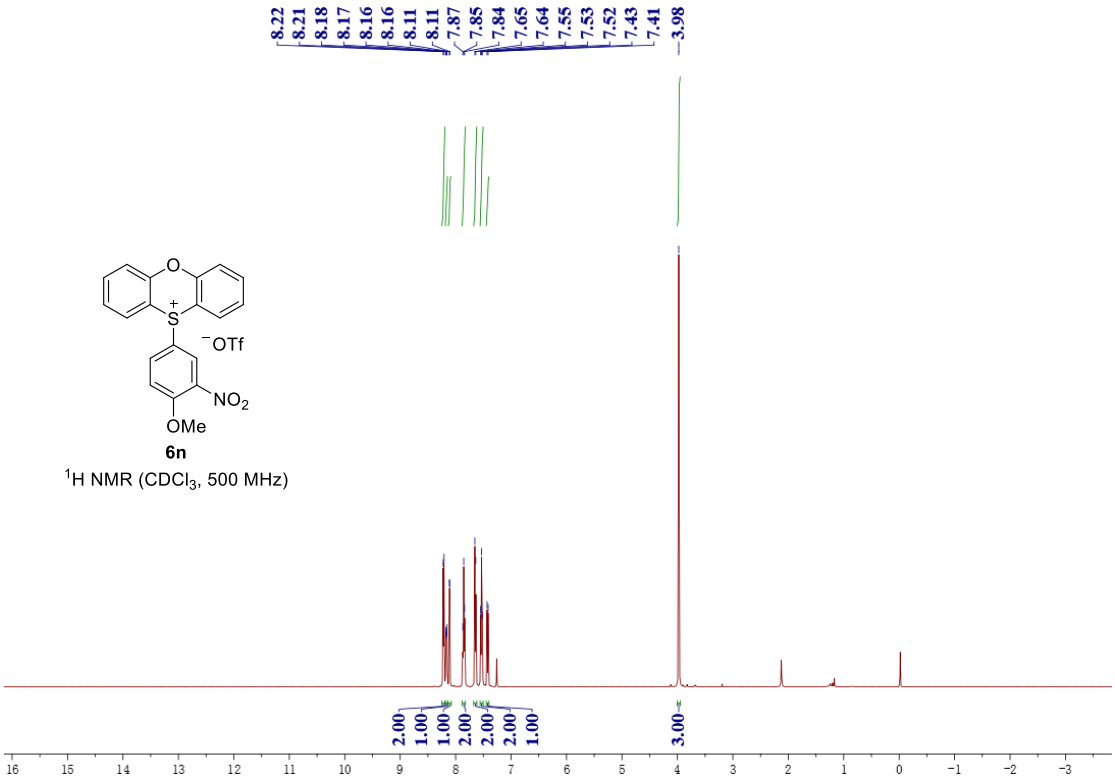
6m

^{19}F NMR ($CDCl_3$, 471 MHz)



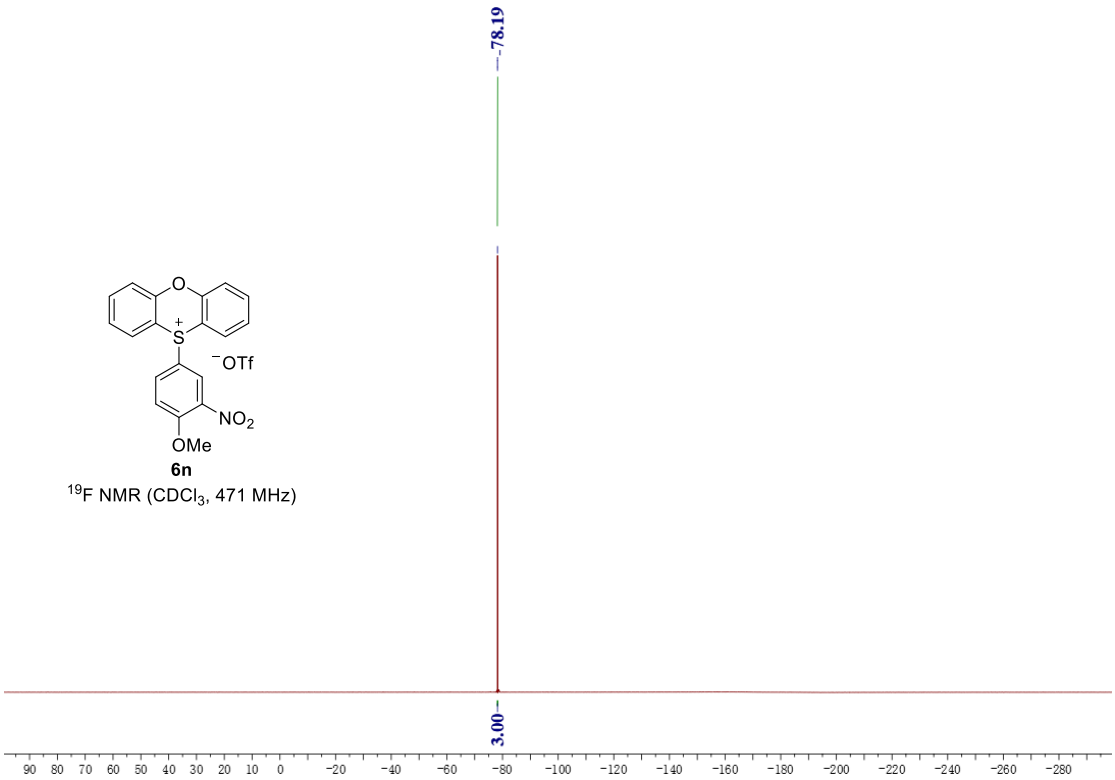
6m

^{13}C NMR ($CDCl_3$, 126 MHz)



6n

^{1}H NMR ($CDCl_3$, 500 MHz)

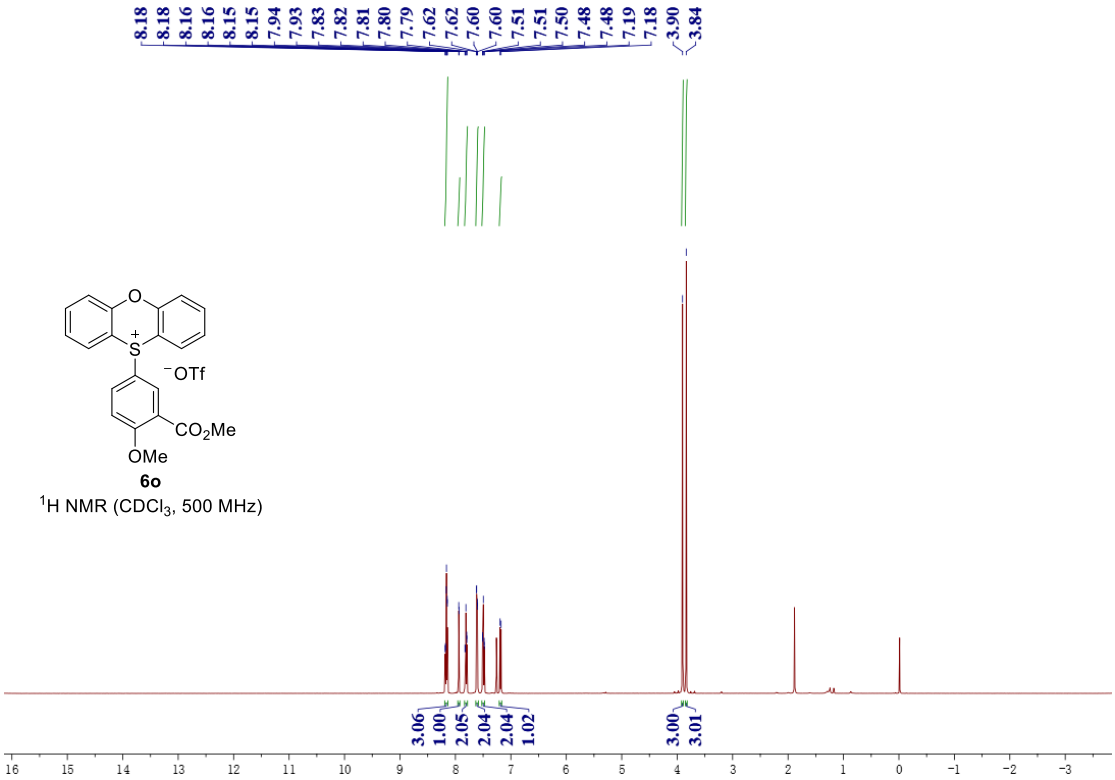


6n

^{19}F NMR ($CDCl_3$, 471 MHz)

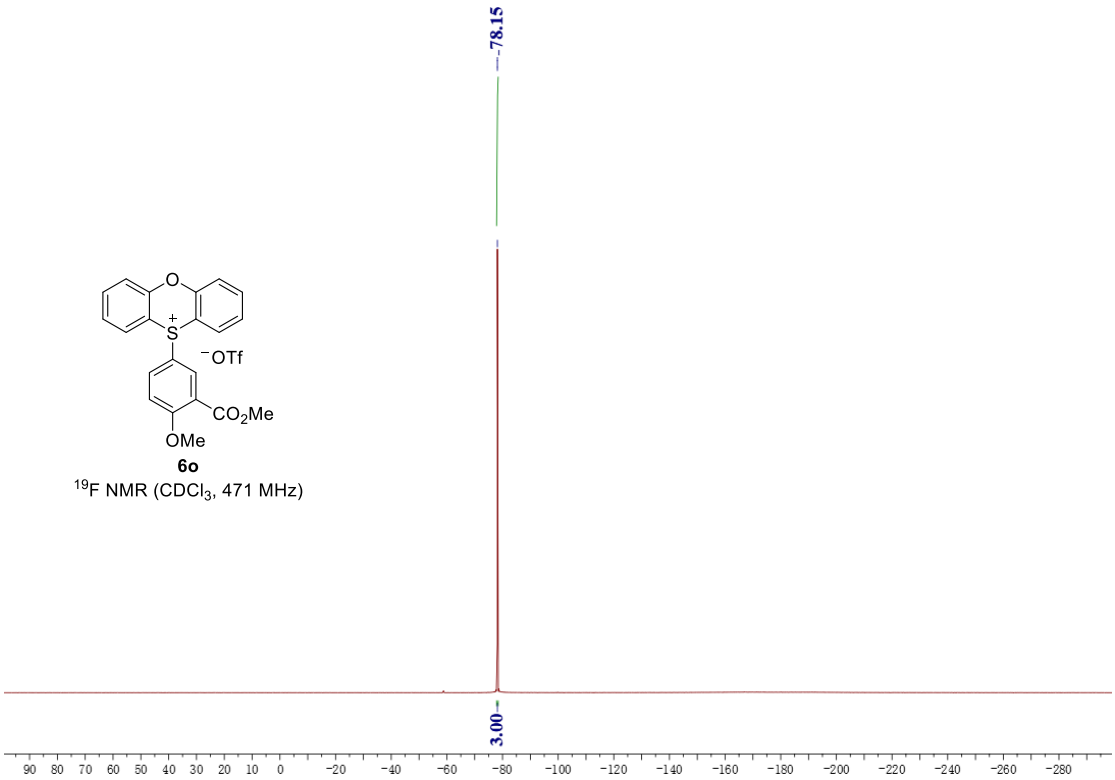
6n

^{13}C NMR ($CDCl_3$, 126 MHz)



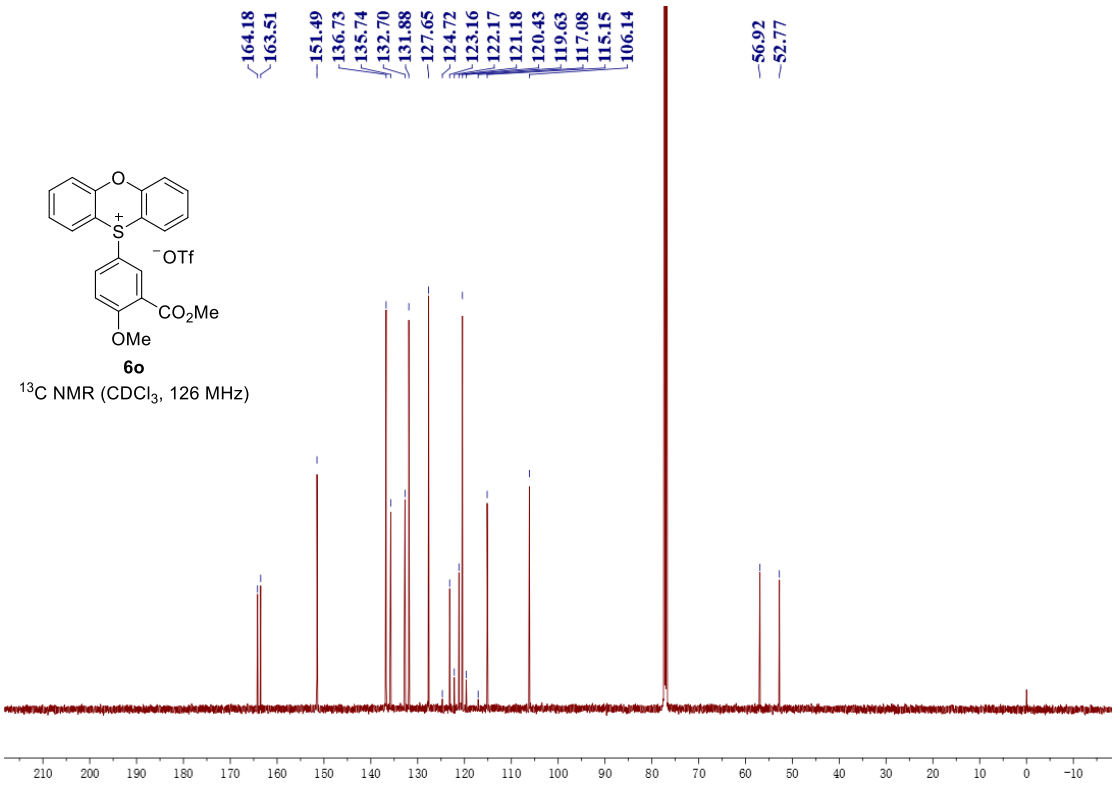
6o

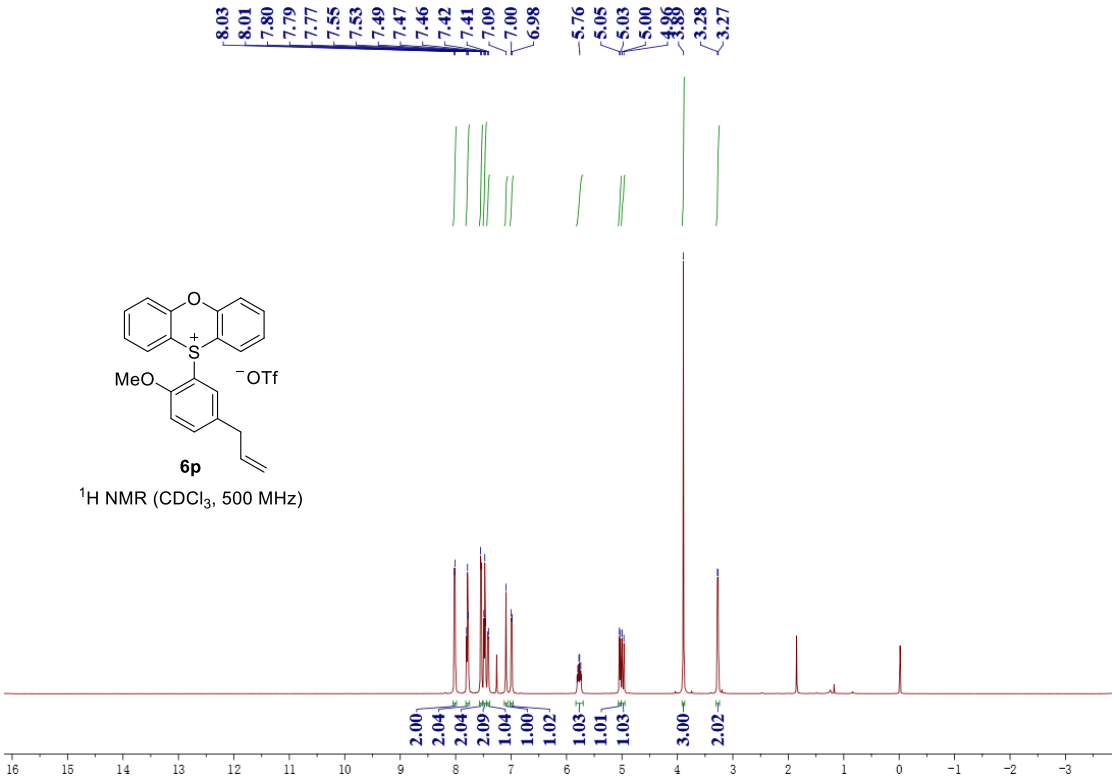
^{1}H NMR ($CDCl_3$, 500 MHz)

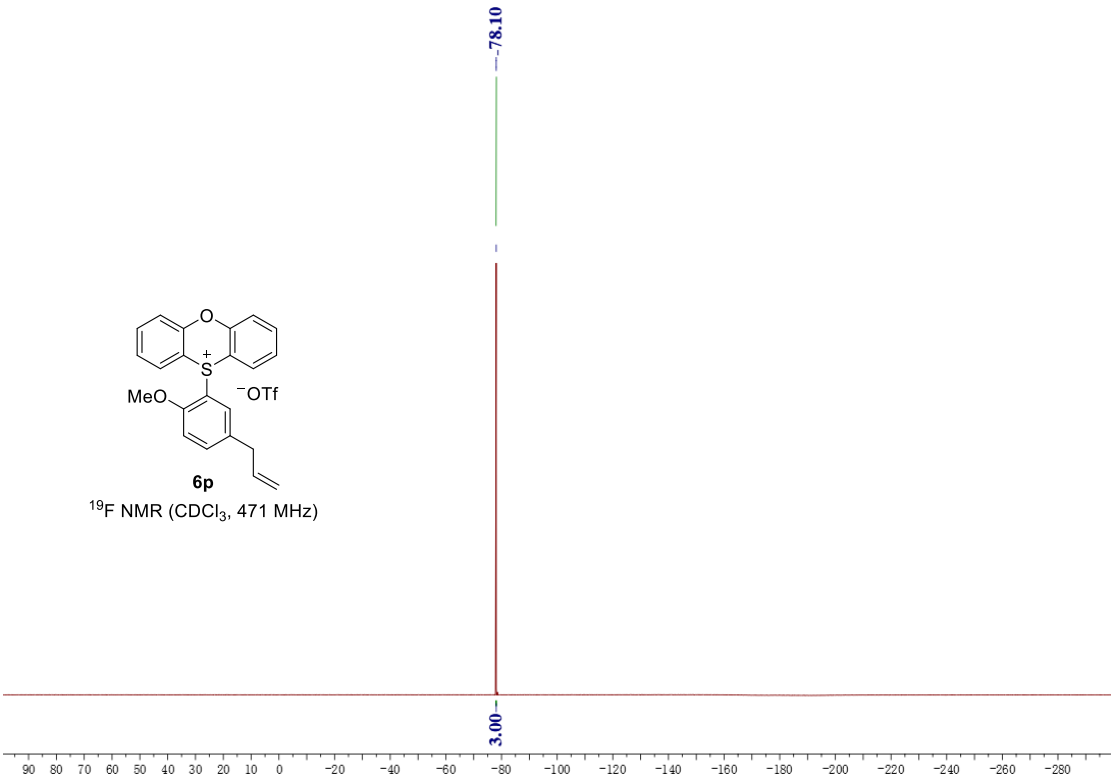


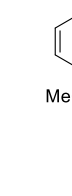
6o

^{19}F NMR ($CDCl_3$, 471 MHz)


164.18
163.51
151.49
136.73
135.74
132.70
131.88
127.65
124.72
123.16
122.17
121.18
120.43
119.63
117.08
115.15
106.14
56.92
52.77
O
S
+
⁻OTf
CO2Me
OMe
6o
13C NMR (CDCl3, 126 MHz)


8.03
8.01
7.80
7.79
7.77
7.55
7.53
7.49
7.47
7.46
7.42
7.41
7.09
7.00
6.98
5.76
5.05
5.03
5.00
4.96
3.89
3.28
3.27
O
S
+
MeO
⁻OTf
6p
1H NMR (CDCl3, 500 MHz)
2.00
2.04
2.04
2.09
1.04
1.00
1.02
1.03
1.01
1.03
3.00
2.02



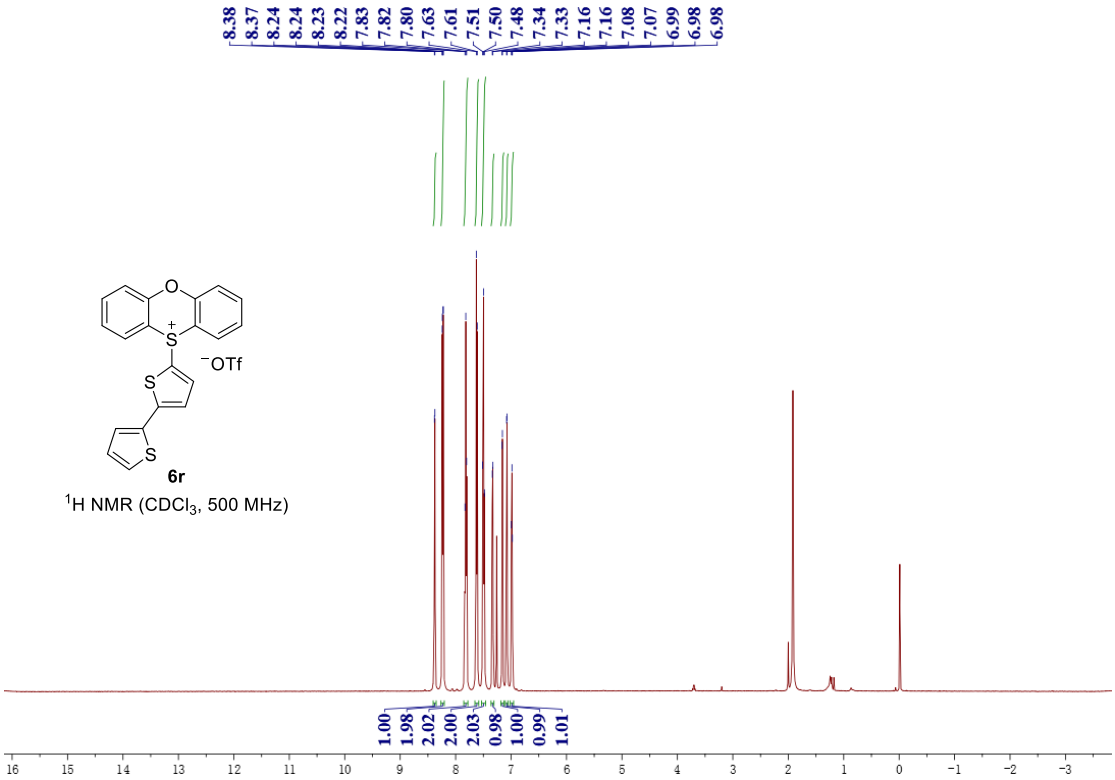


6p

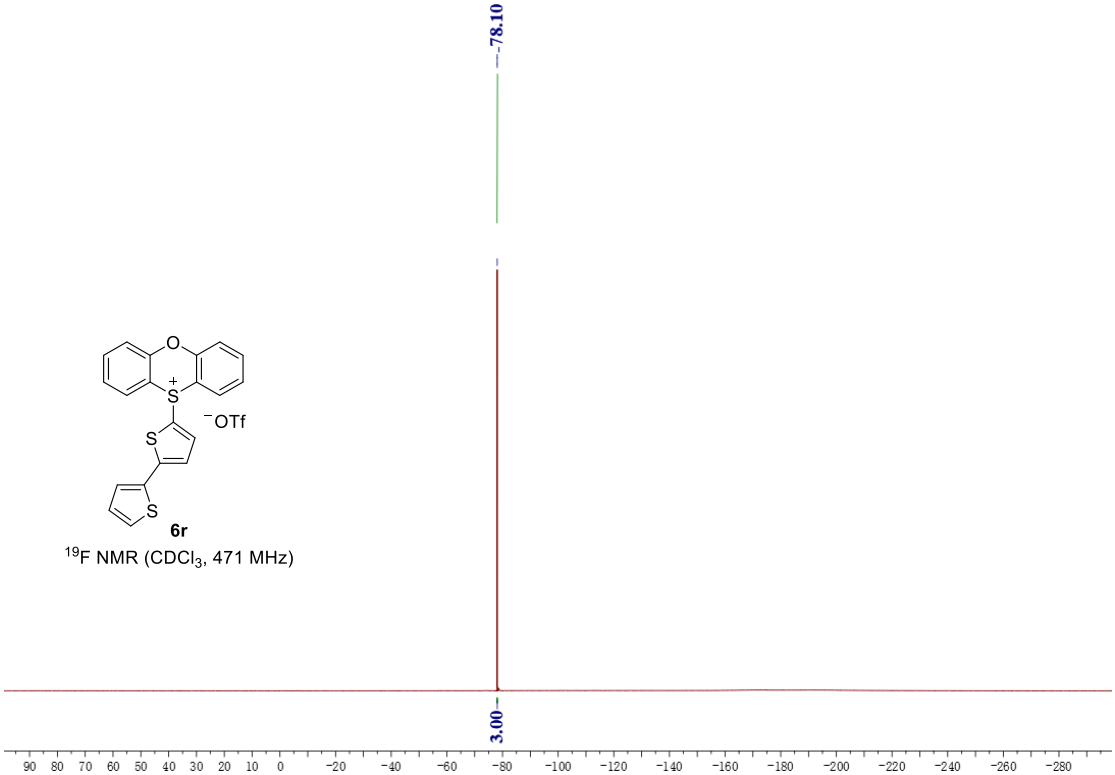
^{19}F NMR ($CDCl_3$, 471 MHz)

6p

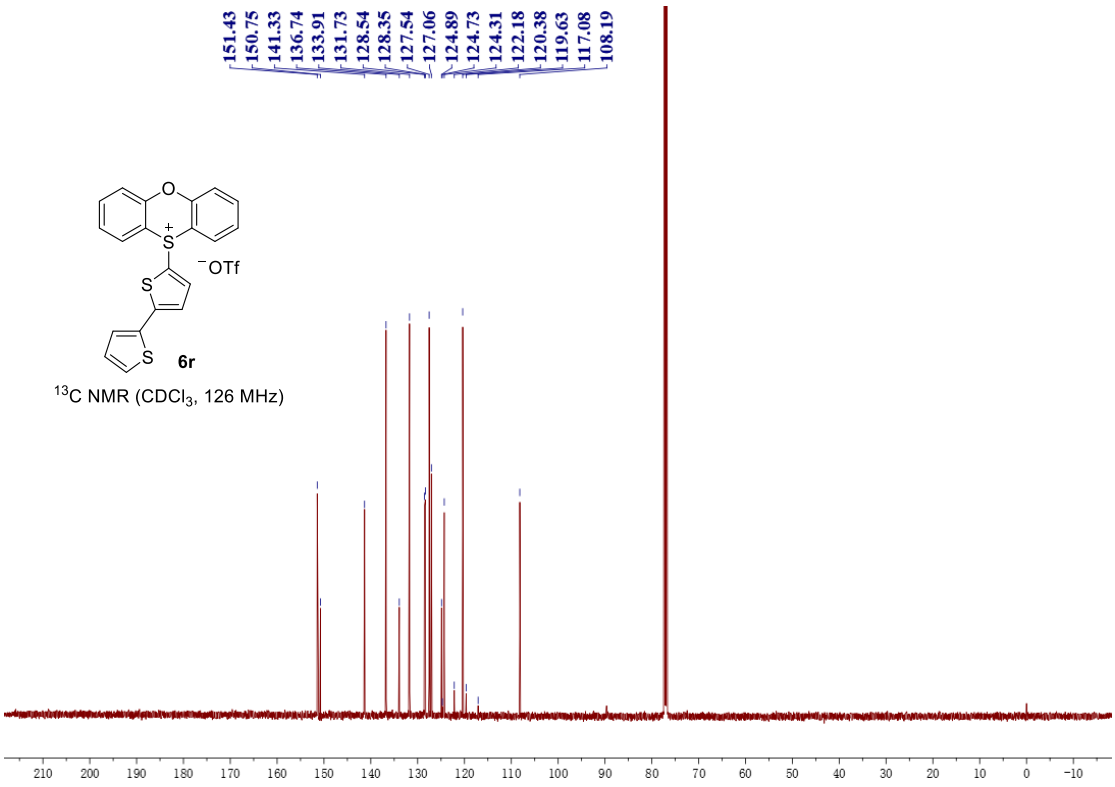
^{13}C NMR ($CDCl_3$, 126 MHz)

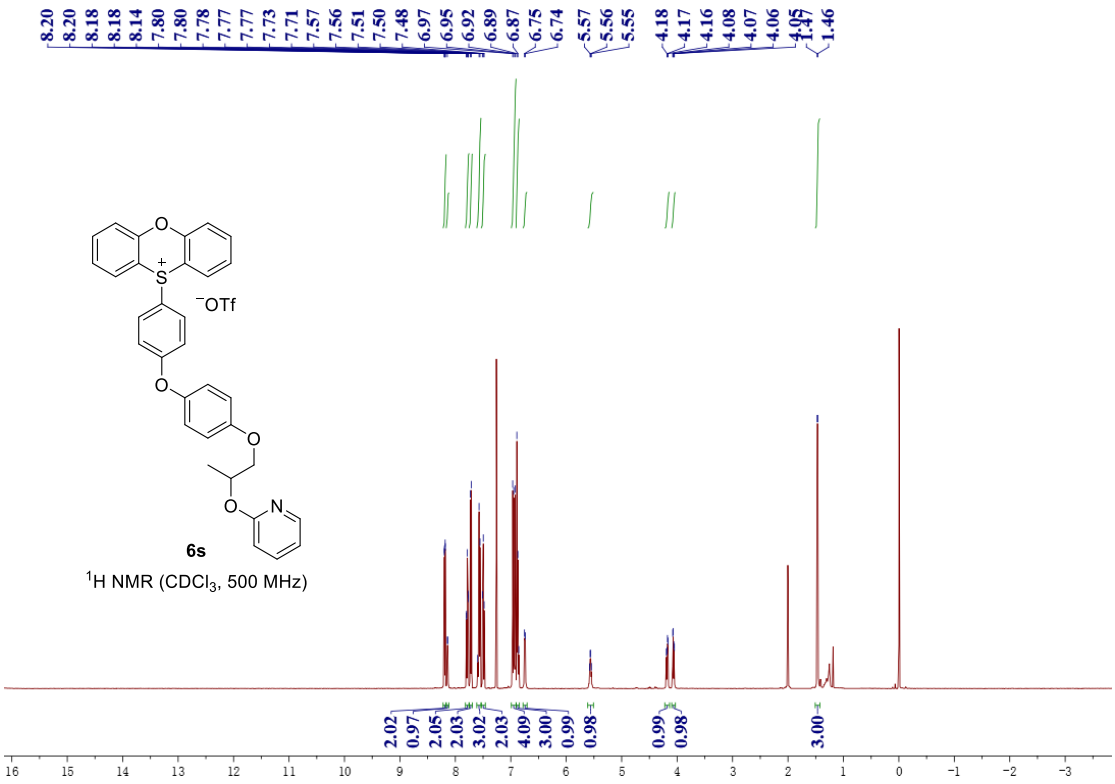


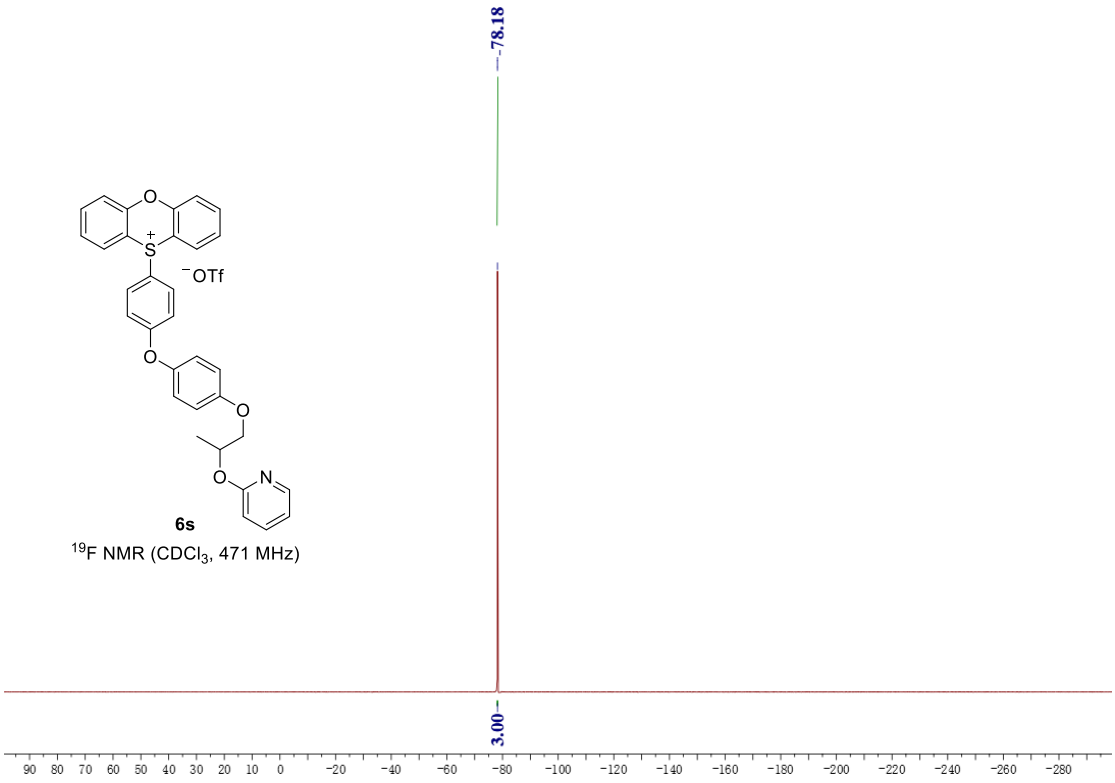
^{1}H NMR ($CDCl_3$, 500 MHz)



^{19}F NMR ($CDCl_3$, 471 MHz)

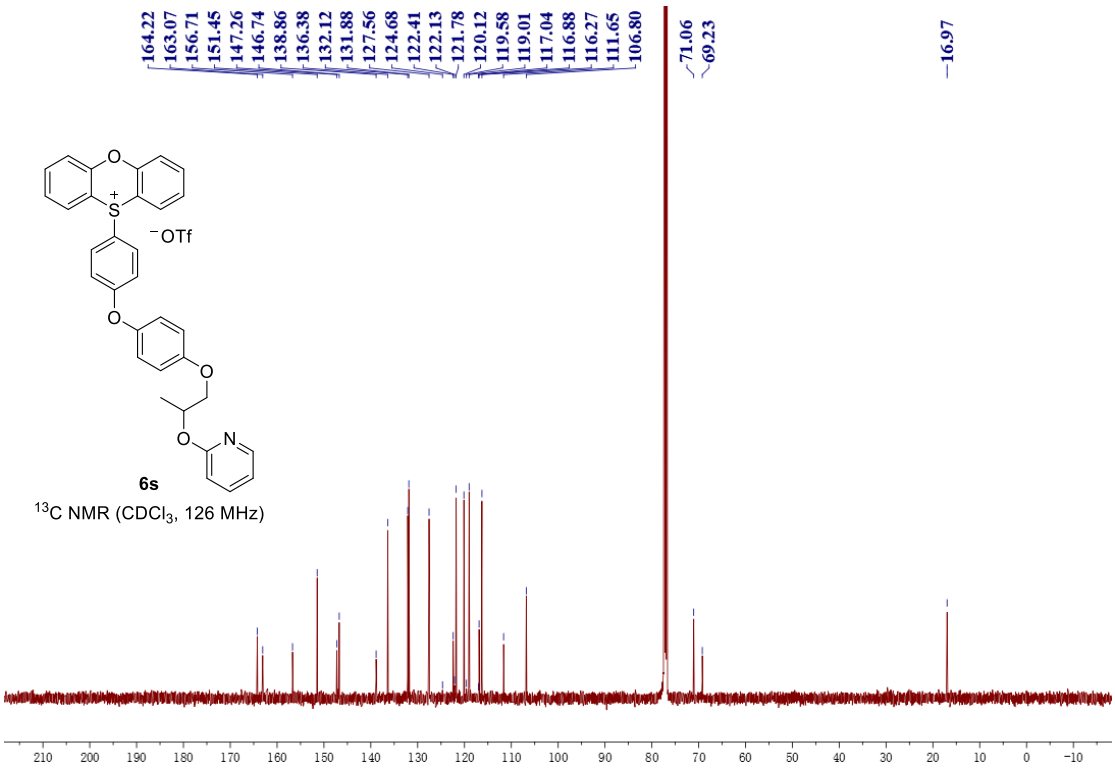

151.43
150.75
141.33
136.74
133.91
131.73
128.54
128.35
127.54
127.06
124.89
124.73
124.31
122.18
120.38
119.63
117.08
108.19
O
S
+
−OTf
S
S
6r
13C NMR (CDCl3, 126 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10


8.20
8.20
8.18
8.18
8.14
7.80
7.80
7.78
7.77
7.77
7.73
7.71
7.57
7.56
7.51
7.50
7.48
6.97
6.95
6.92
6.89
6.87
6.75
6.74
5.57
5.56
5.55
4.18
4.17
4.16
4.08
4.07
4.06
4.05
1.47
1.46
O
S
+
−OTf
O
O
O
O
N
6s
1H NMR (CDCl3, 500 MHz)
2.02
0.97
2.05
2.03
3.02
2.03
4.09
3.00
0.99
0.98
0.99
0.98
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3



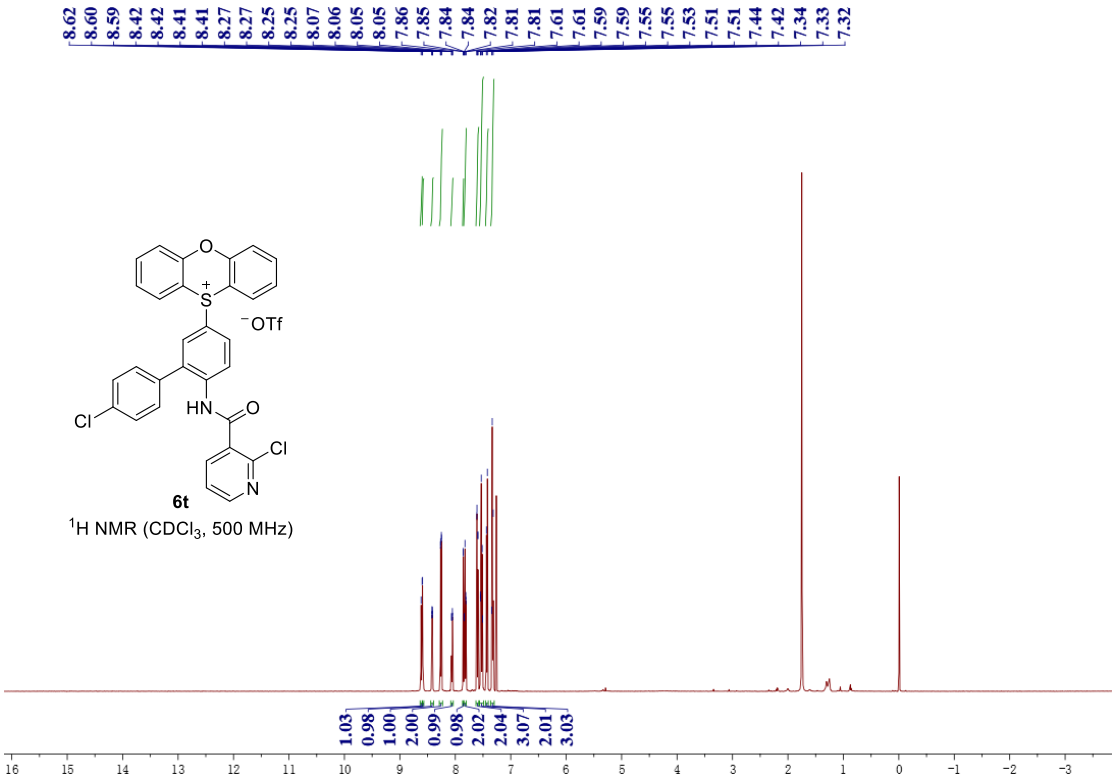
6s

^{19}F NMR ($CDCl_3$, 471 MHz)



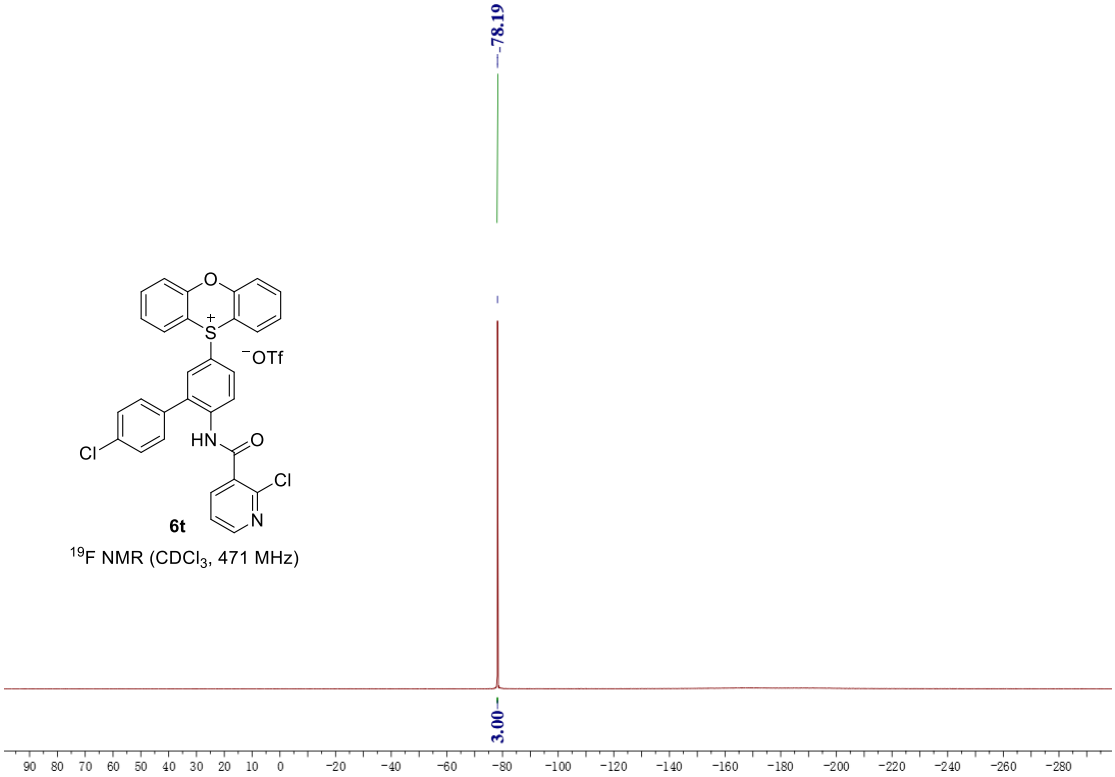
6s

^{13}C NMR ($CDCl_3$, 126 MHz)



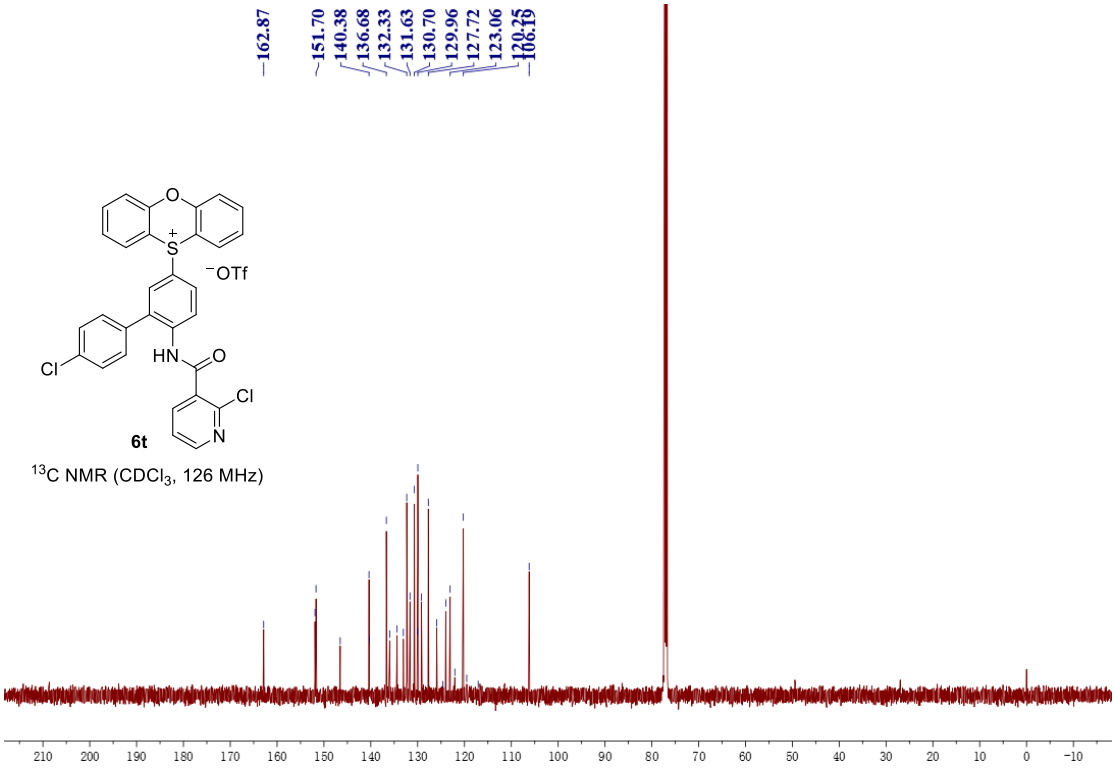
6t

^{1}H NMR ($CDCl_3$, 500 MHz)



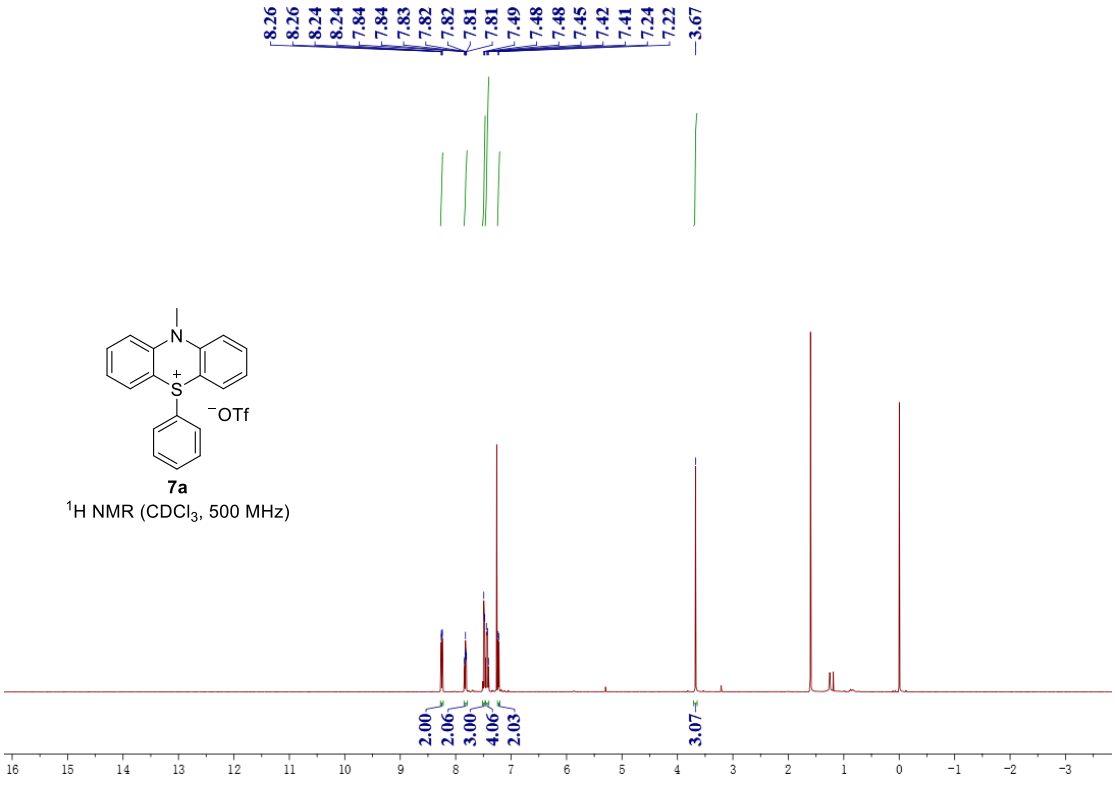
6t

^{19}F NMR ($CDCl_3$, 471 MHz)



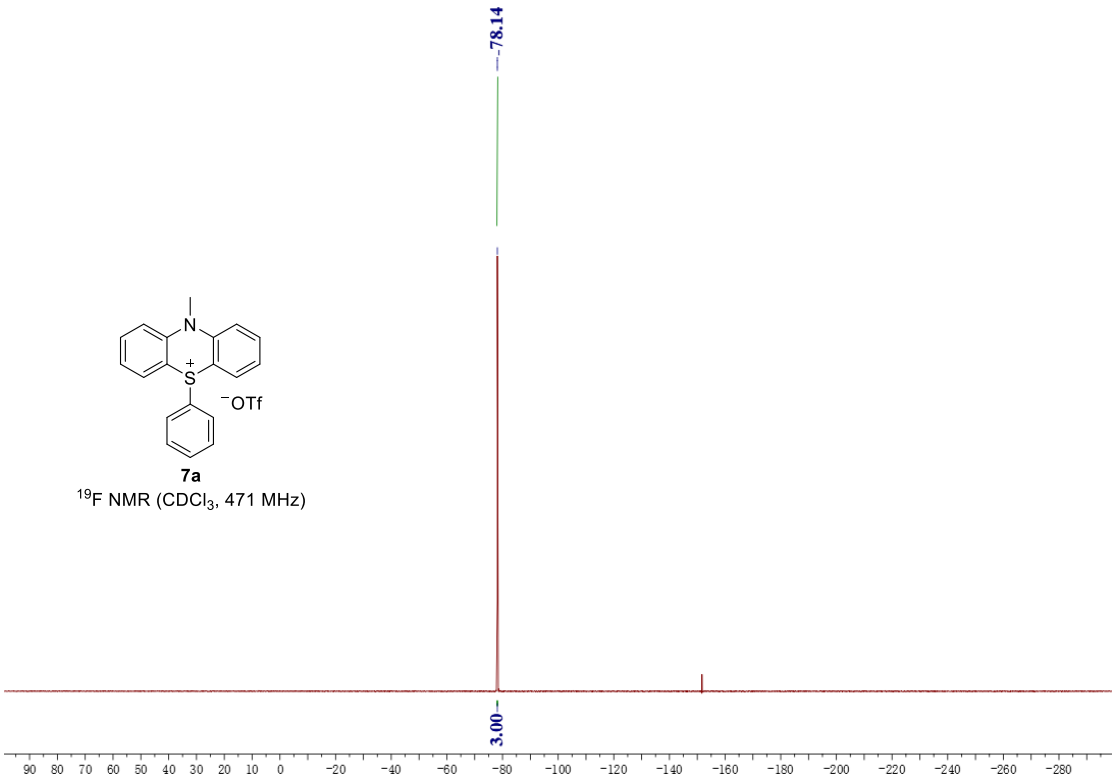
6t

^{13}C NMR ($CDCl_3$, 126 MHz)



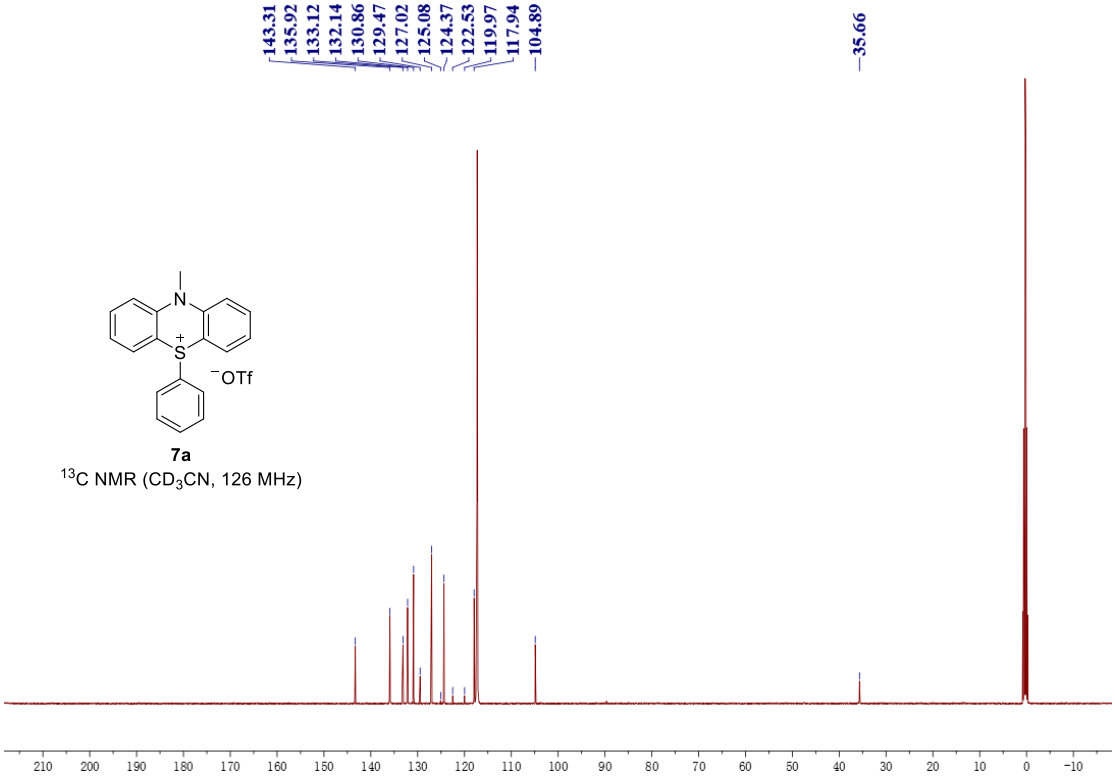
7a

^{1}H NMR ($CDCl_3$, 500 MHz)



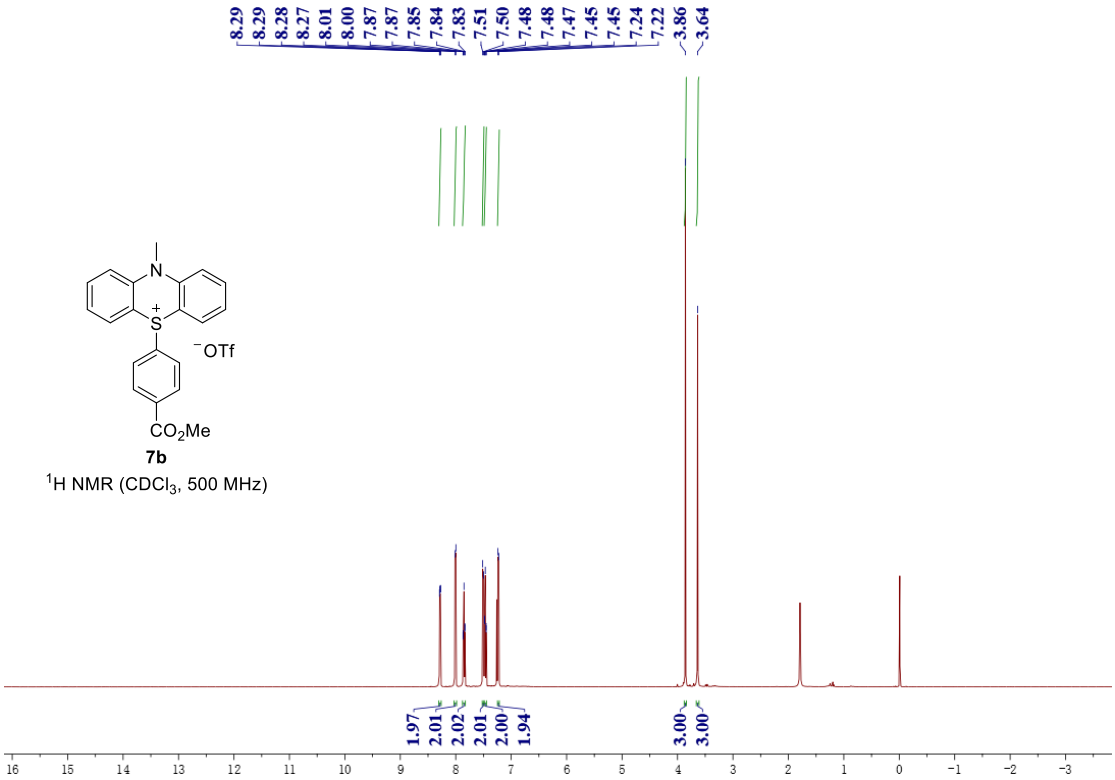
7a

^{19}F NMR ($CDCl_3$, 471 MHz)



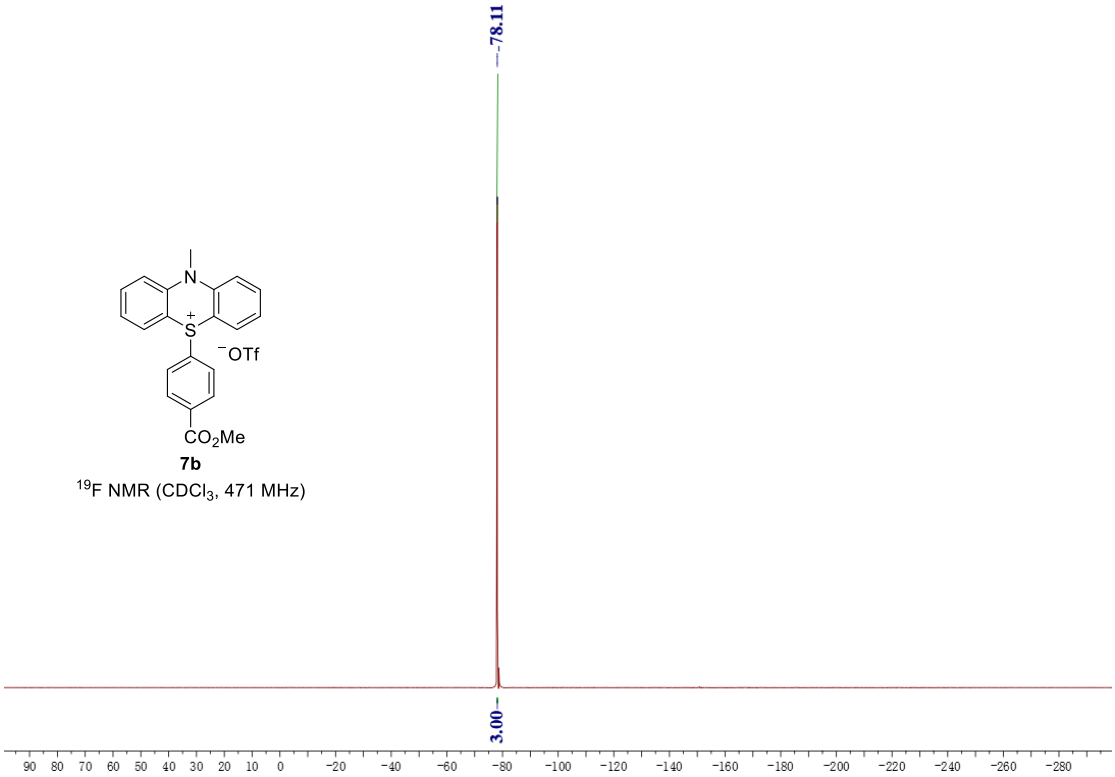
7a

^{13}C NMR (CD_3CN, 126 MHz)



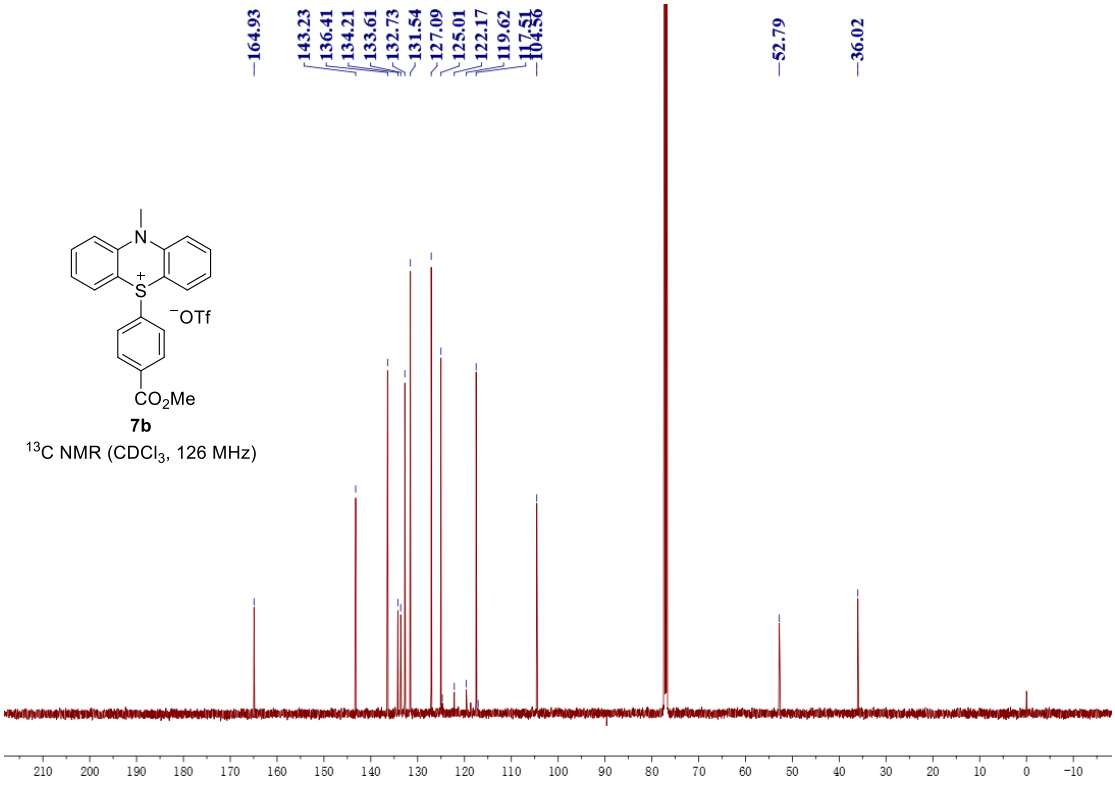
7b

^{1}H NMR ($CDCl_3$, 500 MHz)



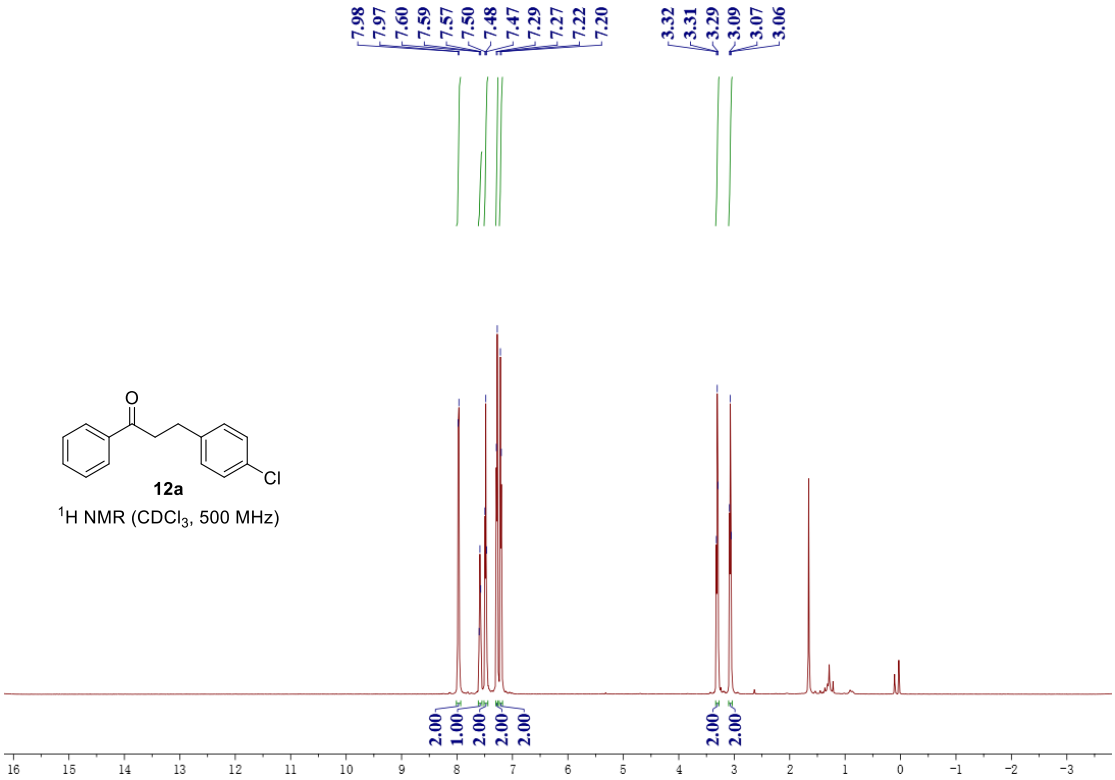
7b

^{19}F NMR ($CDCl_3$, 471 MHz)



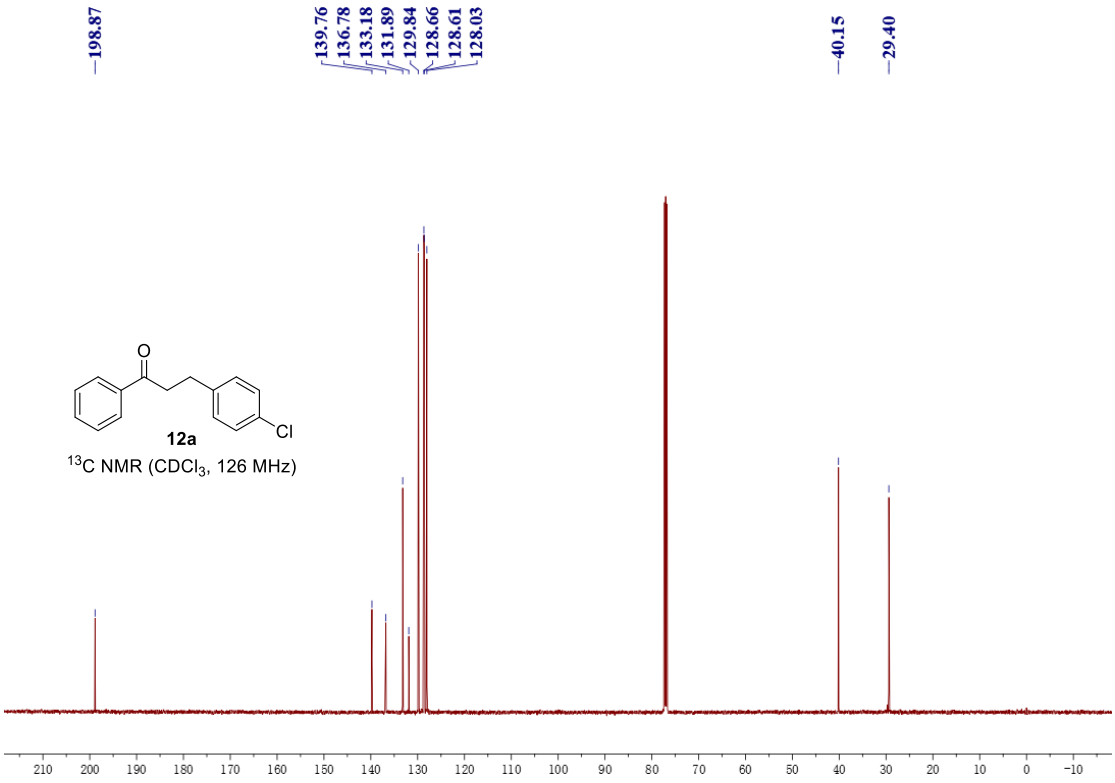
7b

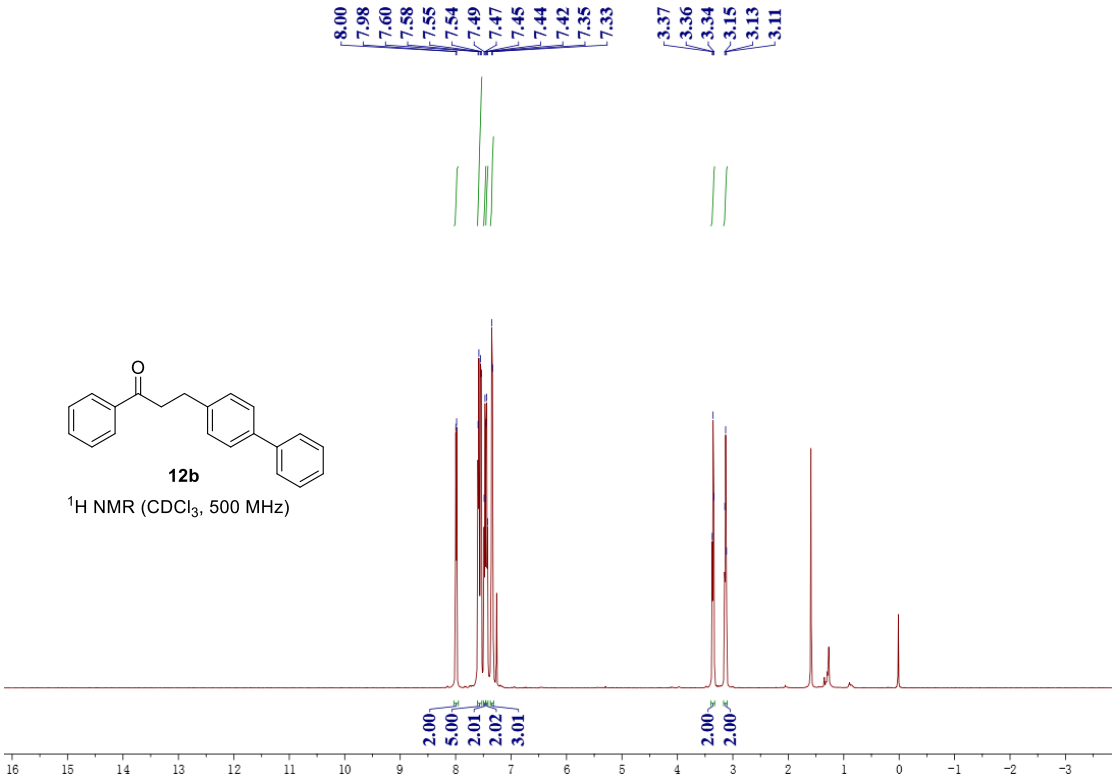
^{13}C NMR ($CDCl_3$, 126 MHz)

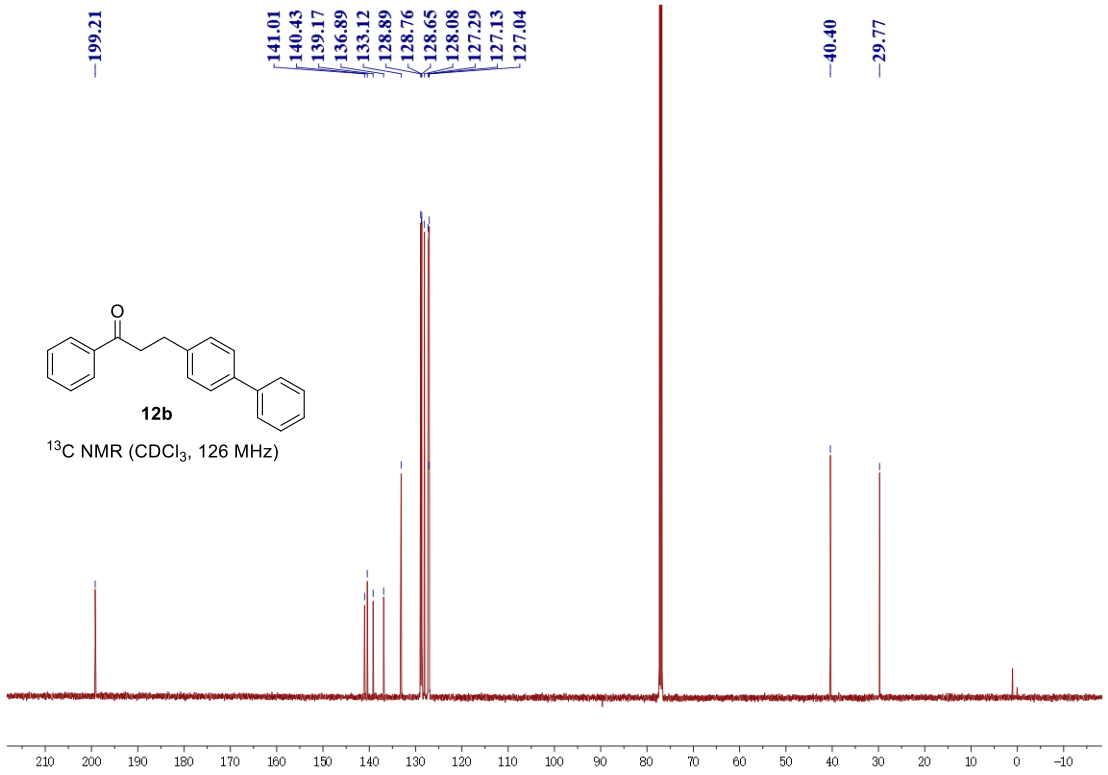


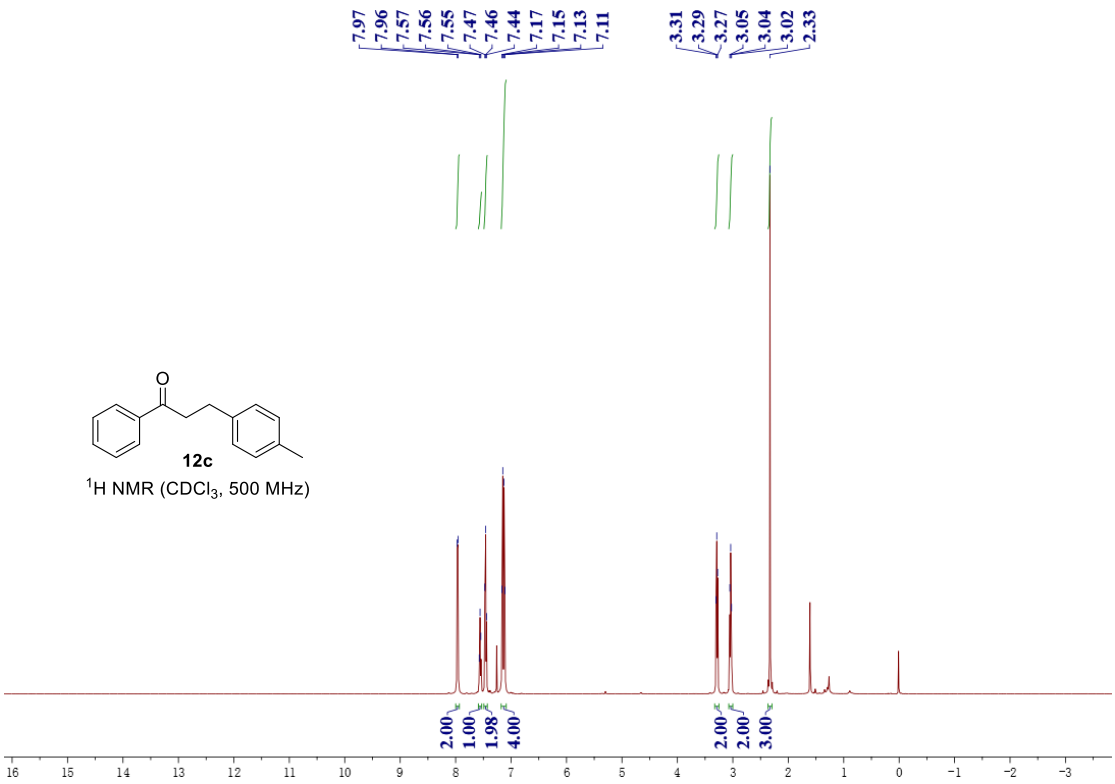
12a

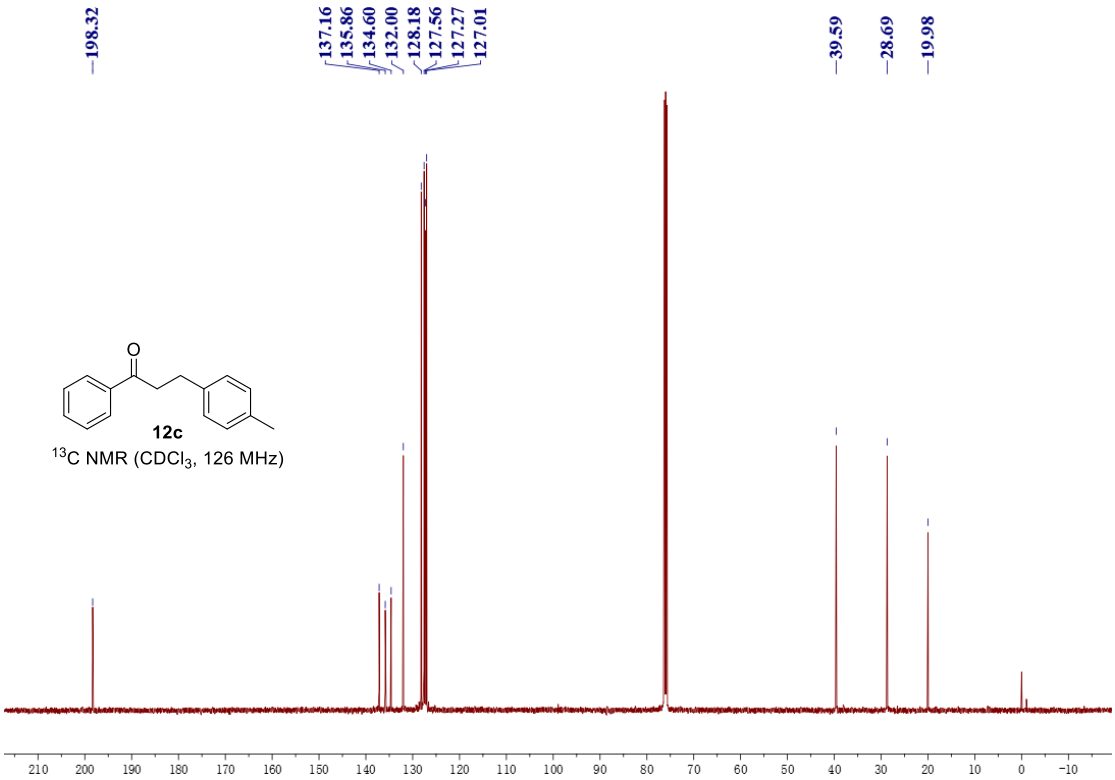
^{1}H NMR ($CDCl_3$, 500 MHz)

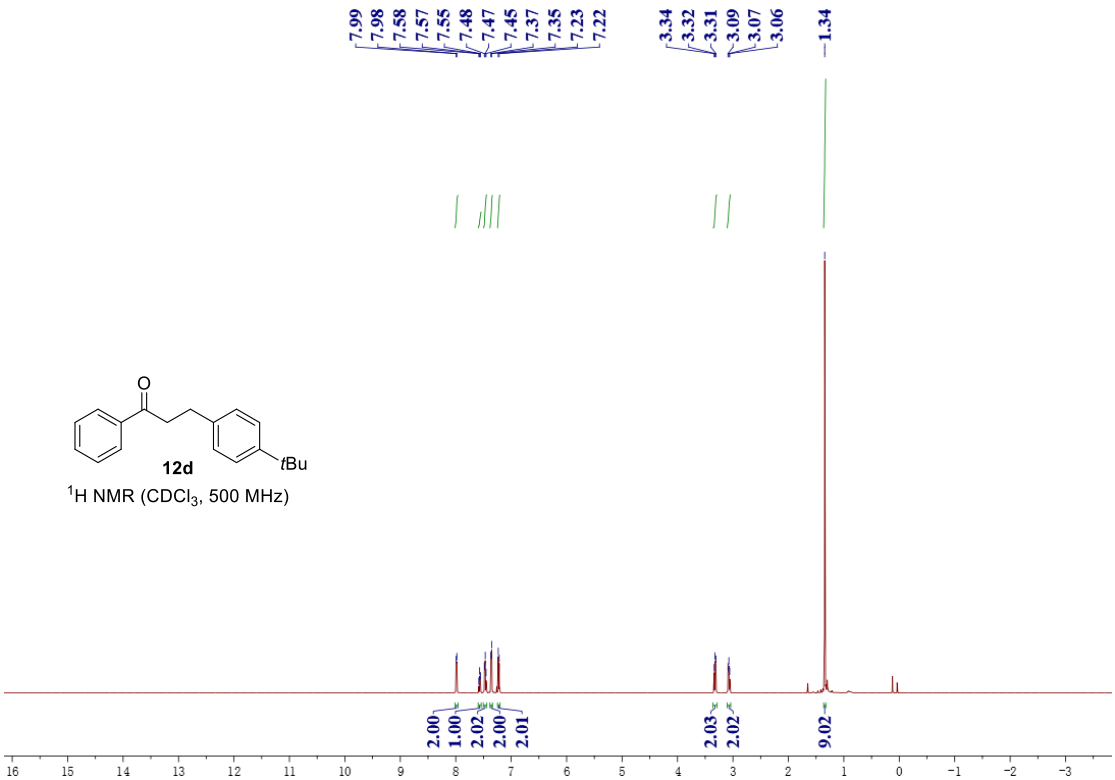

198.87
139.76
136.78
133.18
131.89
129.84
128.66
128.61
128.03
40.15
29.40
O
Cl
12a
13C NMR (CDCl3, 126 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

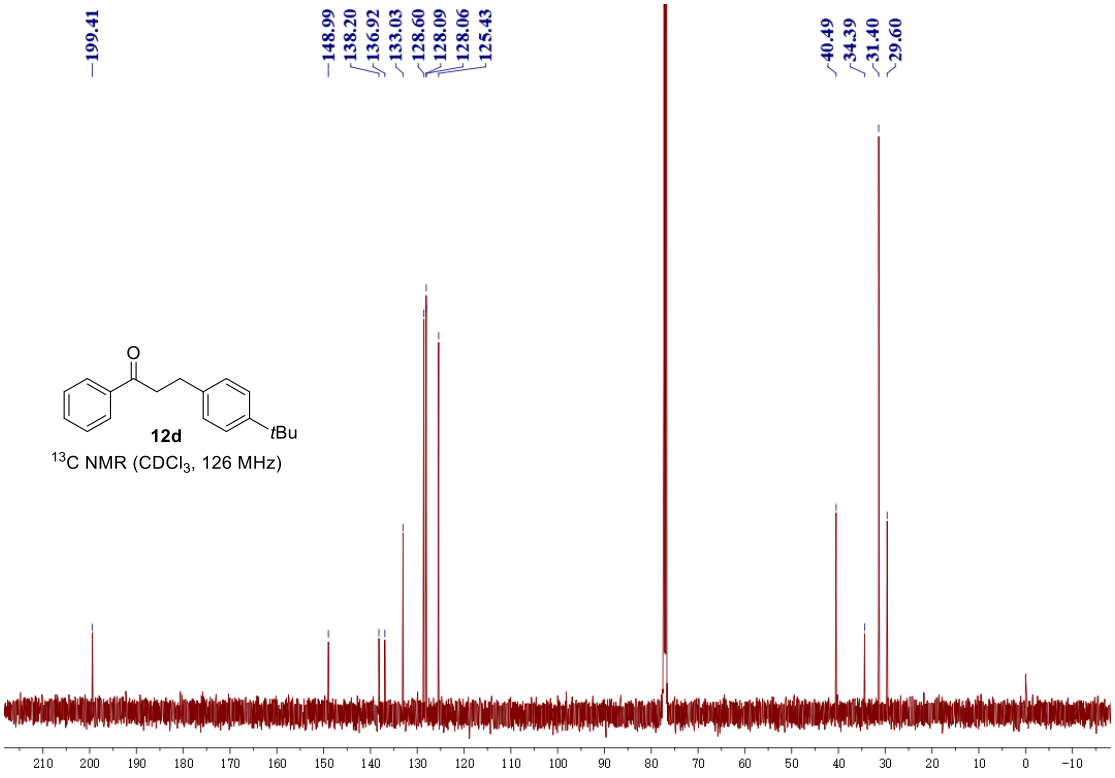

8.00
7.98
7.60
7.58
7.55
7.54
7.49
7.47
7.45
7.44
7.42
7.35
7.33
3.37
3.36
3.34
3.15
3.13
3.11
O
12b
1H NMR (CDCl3, 500 MHz)
2.00
5.00
2.01
2.02
3.01
2.00
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3


199.21
141.01
140.43
139.17
136.89
133.12
128.89
128.76
128.65
128.08
127.29
127.13
127.04
40.40
29.77
O
12b
13C NMR (CDCl3, 126 MHz)


7.97
7.96
7.57
7.56
7.55
7.47
7.46
7.44
7.17
7.15
7.13
7.11
3.31
3.29
3.27
3.05
3.04
3.02
2.33
O
12c
1H NMR (CDCl3, 500 MHz)
2.00
1.00
1.98
4.00
2.00
2.00
3.00


198.32
137.16
135.86
134.60
132.00
128.18
127.56
127.27
127.01
39.59
28.69
19.98
O
12c
13C NMR (CDCl3, 126 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10


7.99
7.98
7.58
7.57
7.55
7.48
7.47
7.45
7.37
7.35
7.23
7.22
3.34
3.32
3.31
3.09
3.07
3.06
1.34
O
12d
tBu
1H NMR (CDCl3, 500 MHz)
2.00
1.00
2.02
2.00
2.01
2.03
2.02
9.02
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3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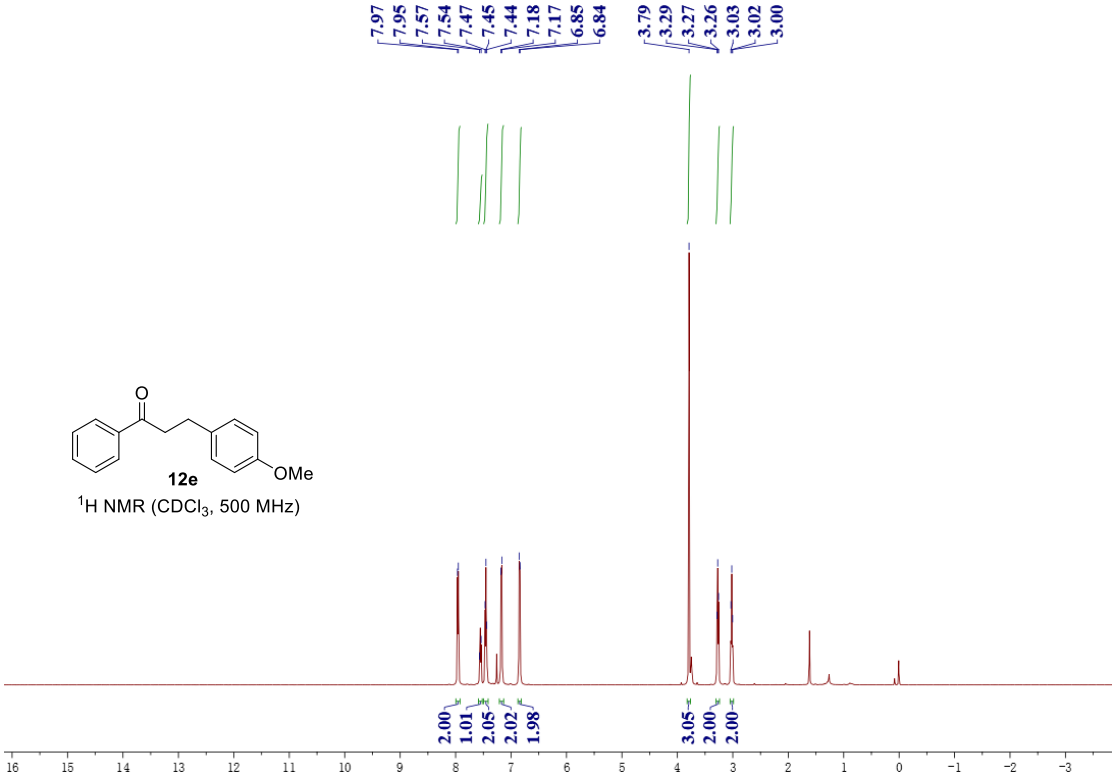
148.99
138.20
136.92
133.03
128.60
128.09
128.06
125.43
40.49
34.39
31.40
29.60
O
tBu
12d
13C NMR (CDCl3, 126 MHz)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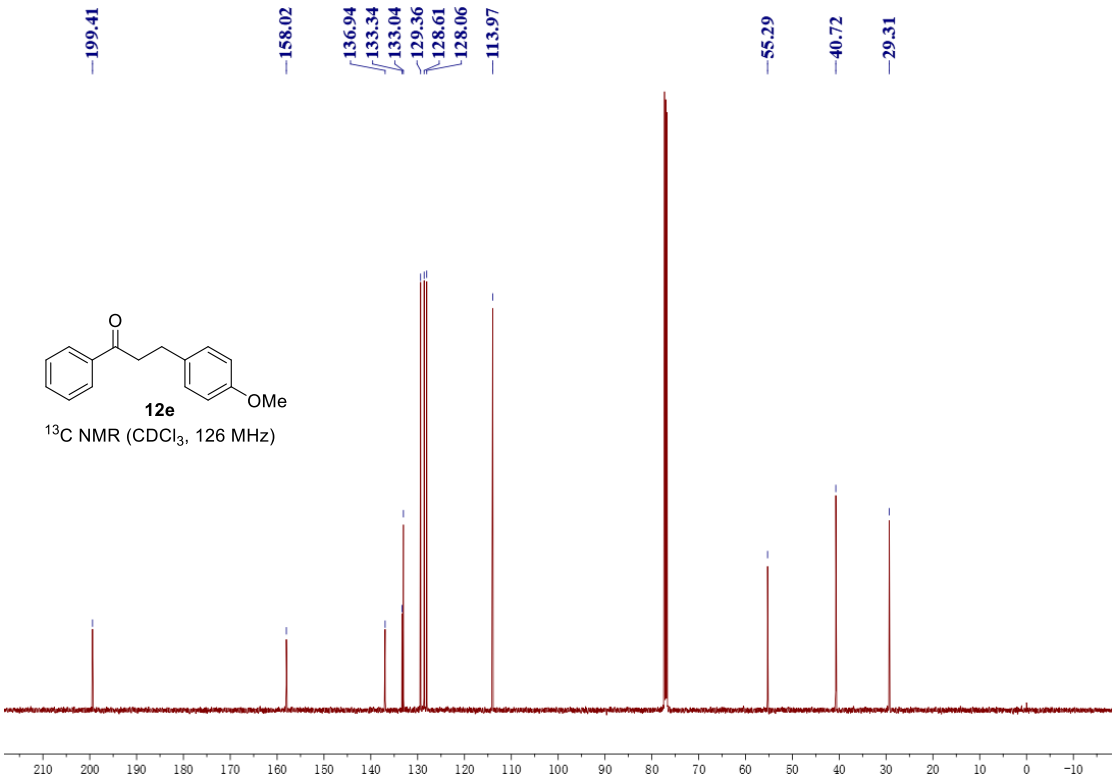
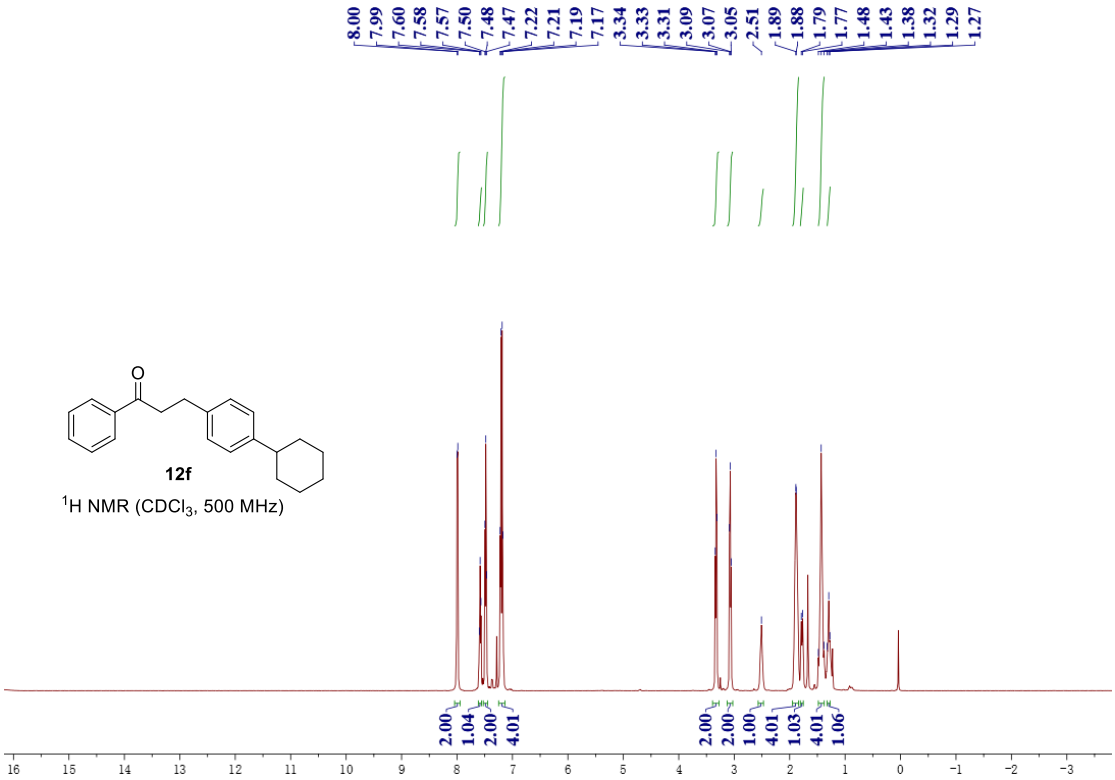
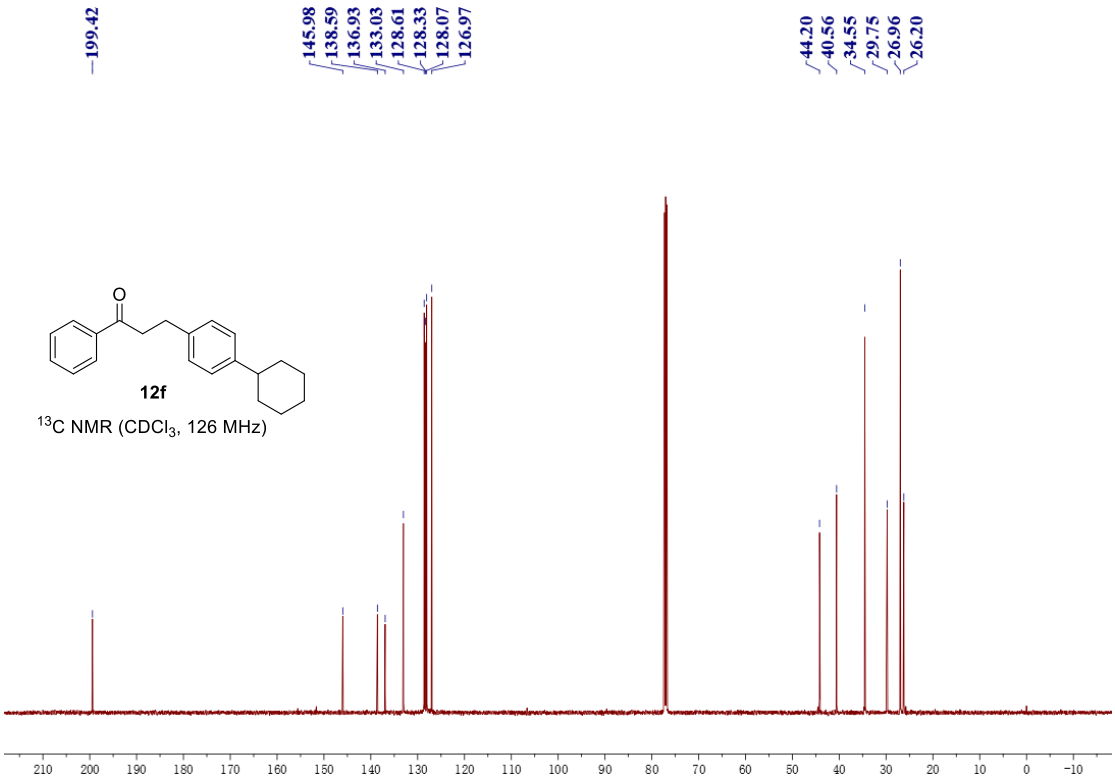
7.95
7.57
7.54
7.47
7.45
7.44
7.18
7.17
6.85
6.84
3.79
3.29
3.27
3.26
3.03
3.02
3.00
O
OMe
12e
1H NMR (CDCl3, 500 MHz)
2.00
1.01
2.05
2.02
1.98
3.05
2.00
2.00


199.41
158.02
136.94
133.34
133.04
129.36
128.61
128.06
113.97
55.29
40.72
29.31
O
OMe
12e
13C NMR (CDCl3, 126 MHz)


8.00
7.99
7.60
7.58
7.57
7.50
7.48
7.47
7.22
7.21
7.19
7.17
3.34
3.33
3.31
3.09
3.07
3.05
2.51
1.89
1.88
1.79
1.77
1.48
1.43
1.38
1.32
1.29
1.27
O
12f
1H NMR (CDCl3, 500 MHz)
2.00
1.04
2.00
4.01
2.00
2.00
1.00
4.01
1.03
4.01
1.06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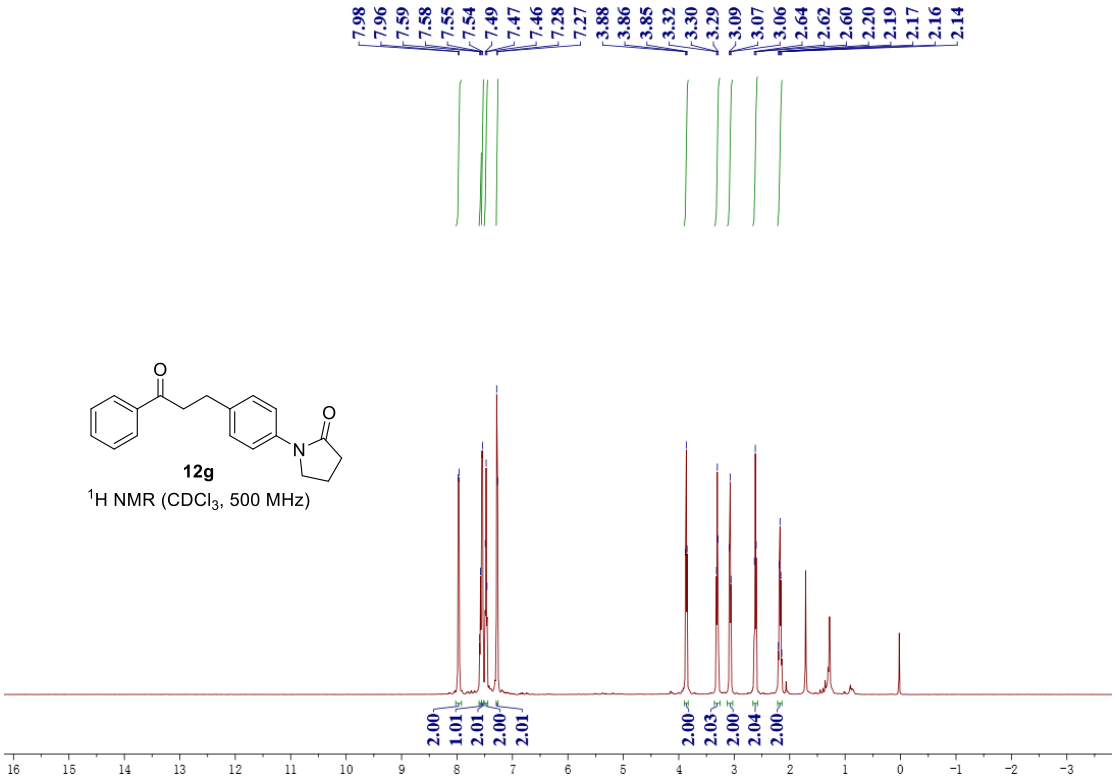
145.98
138.59
136.93
133.03
128.61
128.33
128.07
126.97
44.20
40.56
34.55
29.75
26.96
26.20
O
12f
13C NMR (CDCl3, 126 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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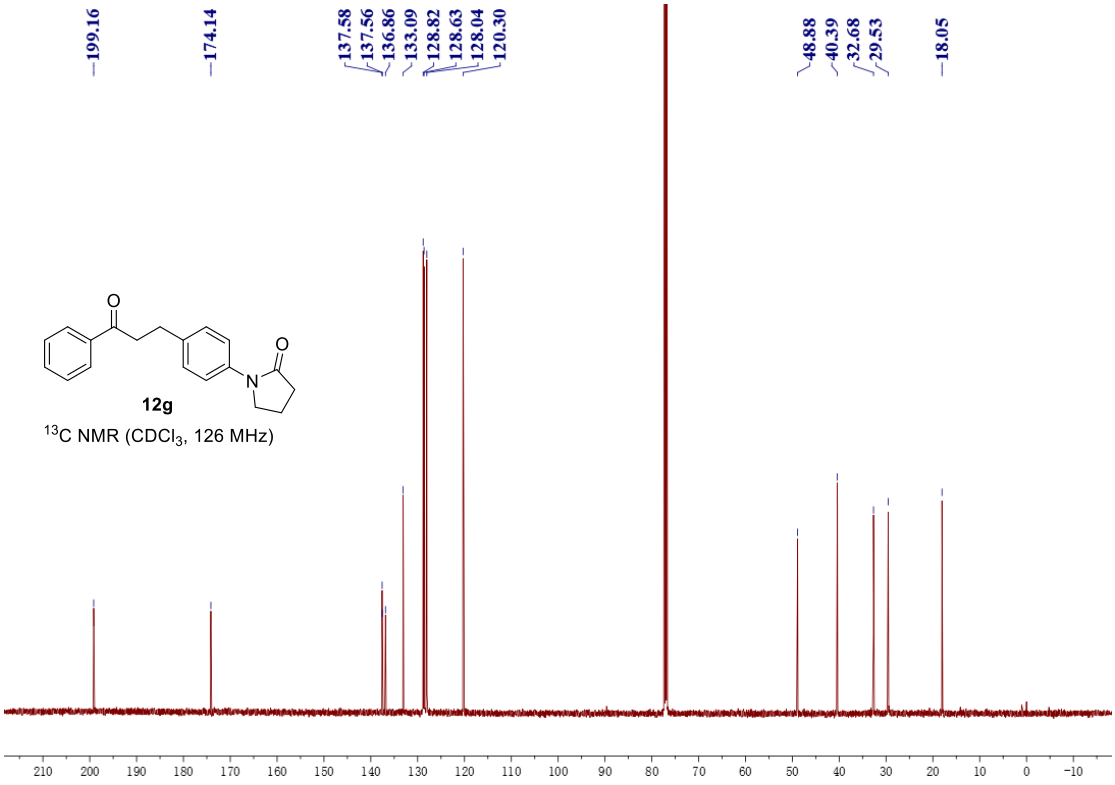
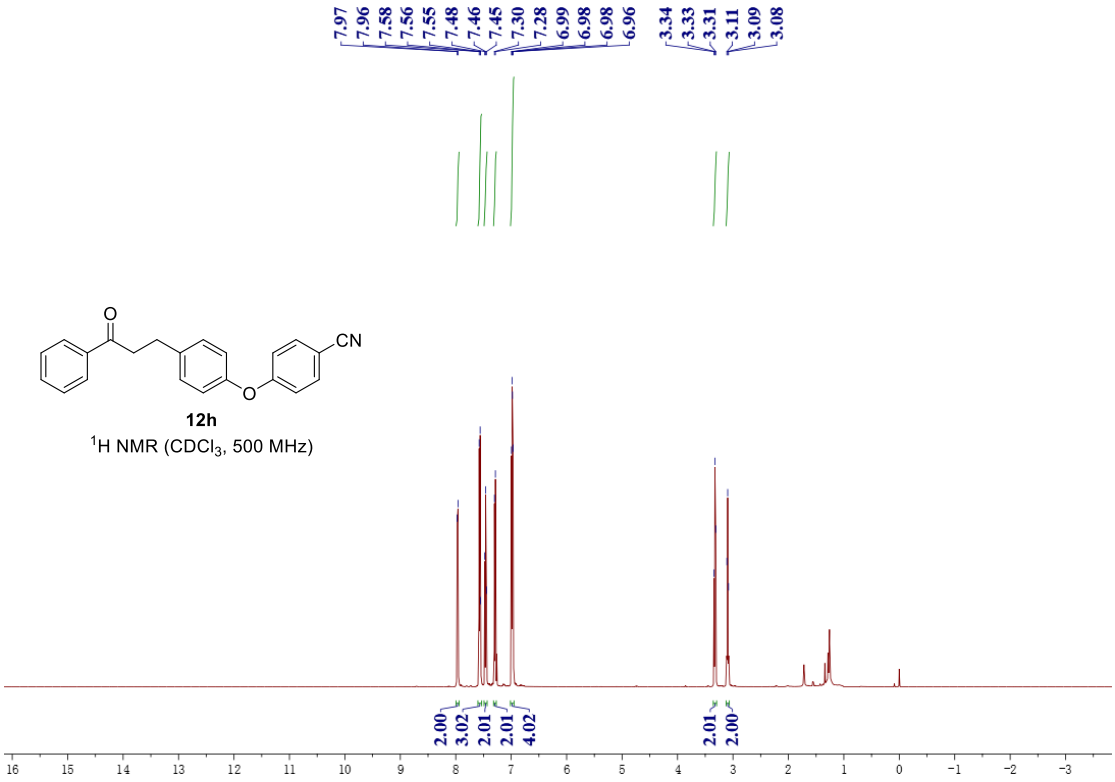
7.96
7.59
7.58
7.55
7.54
7.49
7.47
7.46
7.28
7.27
3.88
3.86
3.85
3.32
3.30
3.29
3.09
3.07
3.06
2.64
2.62
2.60
2.20
2.19
2.17
2.16
2.14
O
N
O
12g
1H NMR (CDCl3, 500 MHz)
2.00
1.01
2.01
2.00
2.01
2.00
2.03
2.00
2.04
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3


199.16
174.14
137.58
137.56
136.86
133.09
128.82
128.63
128.04
120.30
48.88
40.39
32.68
29.53
18.05
O
O
N
12g
13C NMR (CDCl3, 126 MHz)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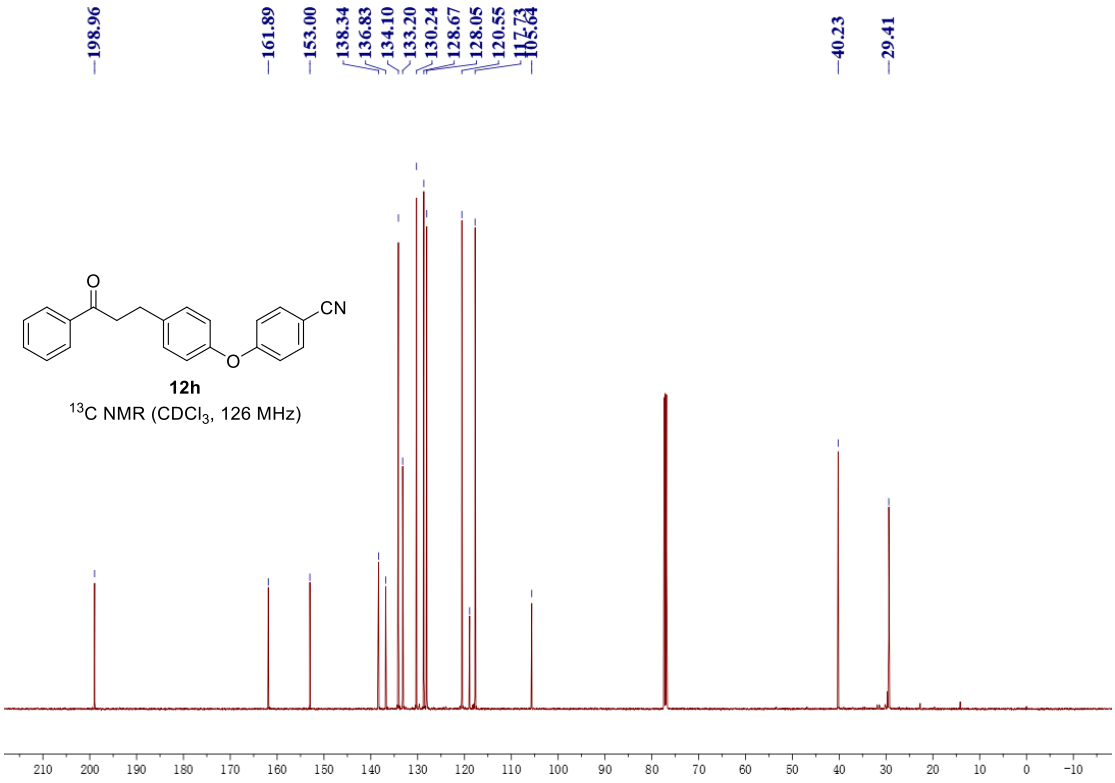
7.96
7.58
7.56
7.55
7.48
7.46
7.45
7.30
7.28
6.99
6.98
6.98
6.96
3.34
3.33
3.31
3.11
3.09
3.08
O
O
CN
12h
1H NMR (CDCl3, 500 MHz)
2.00
3.02
2.01
2.01
4.02
2.01
2.00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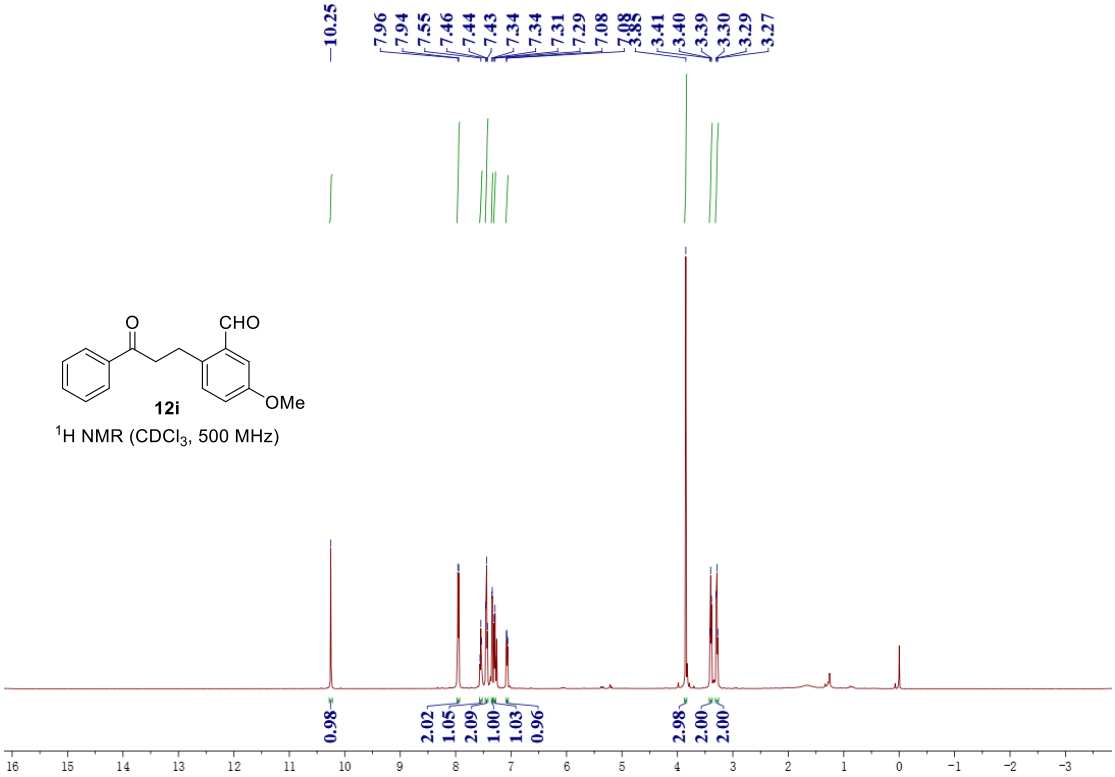
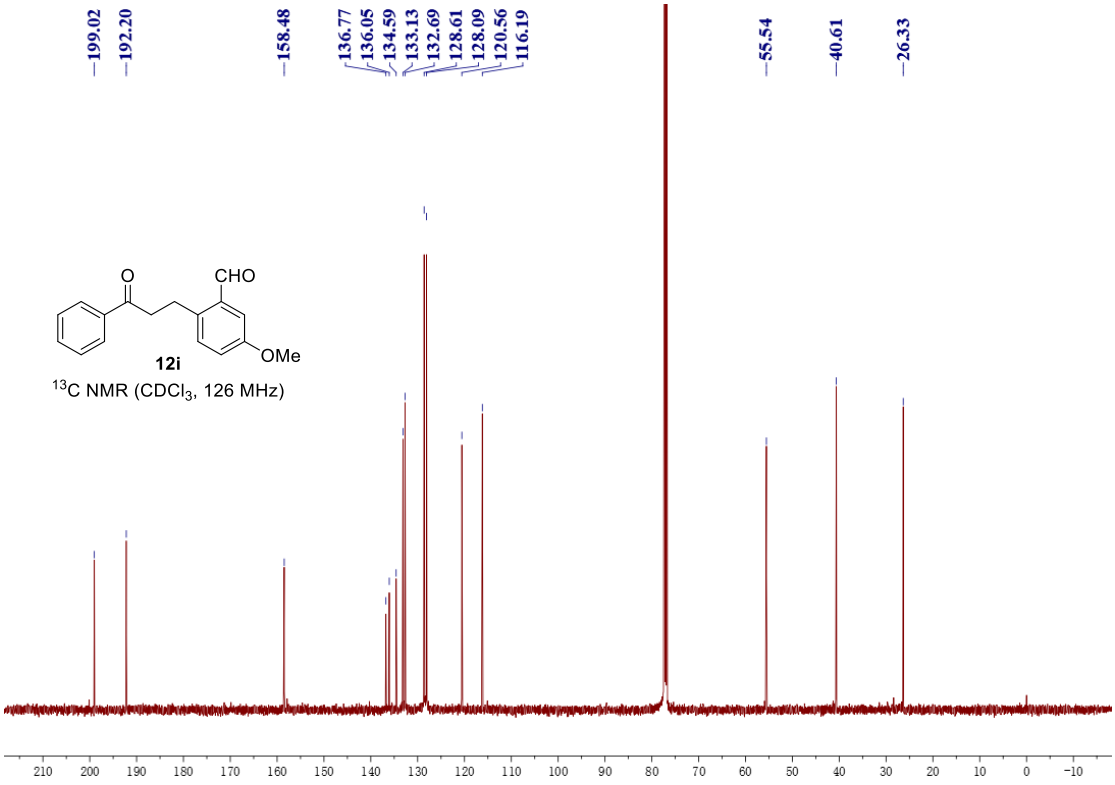
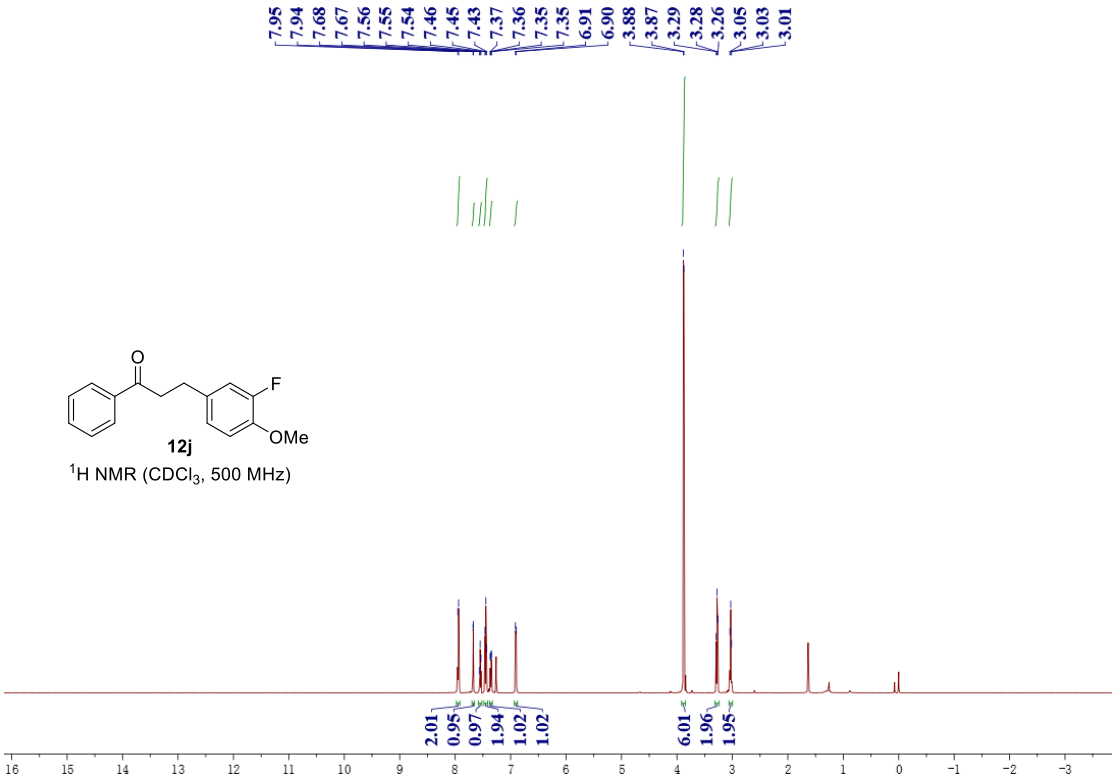
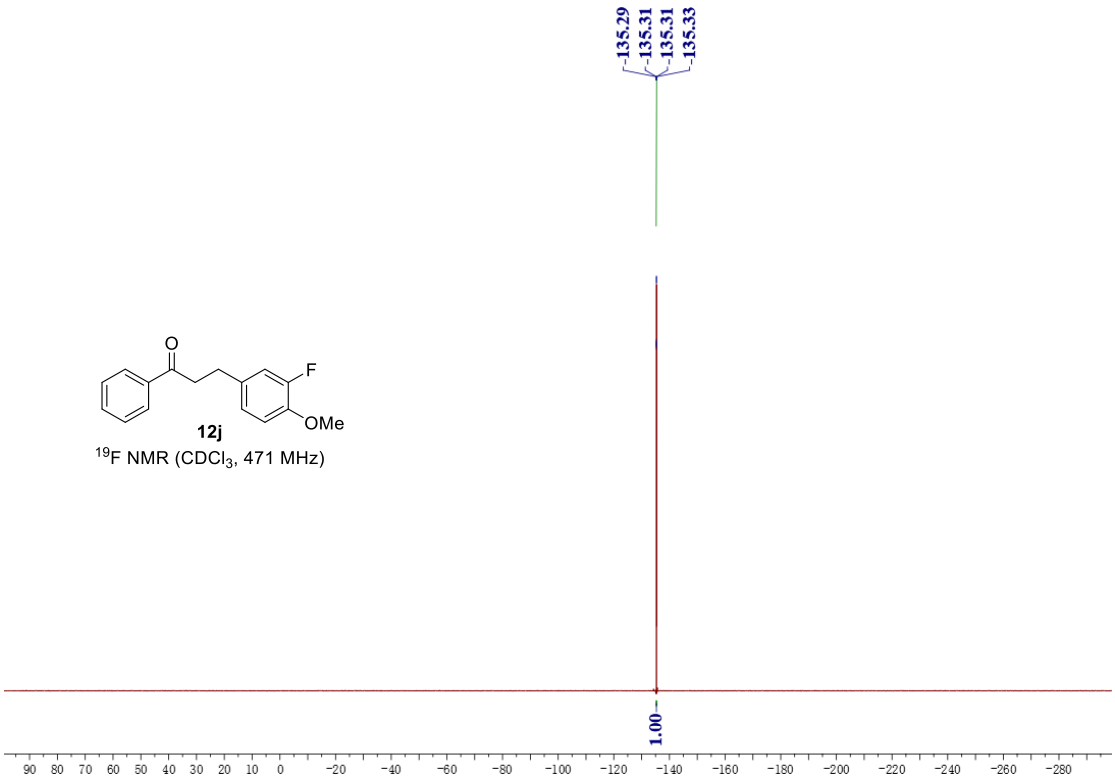
161.89
153.00
138.34
136.83
134.10
133.20
130.24
128.67
128.05
120.55
117.73
116.84
40.23
29.41
O
CN
O
12h
13C NMR (CDCl3, 126 MHz)

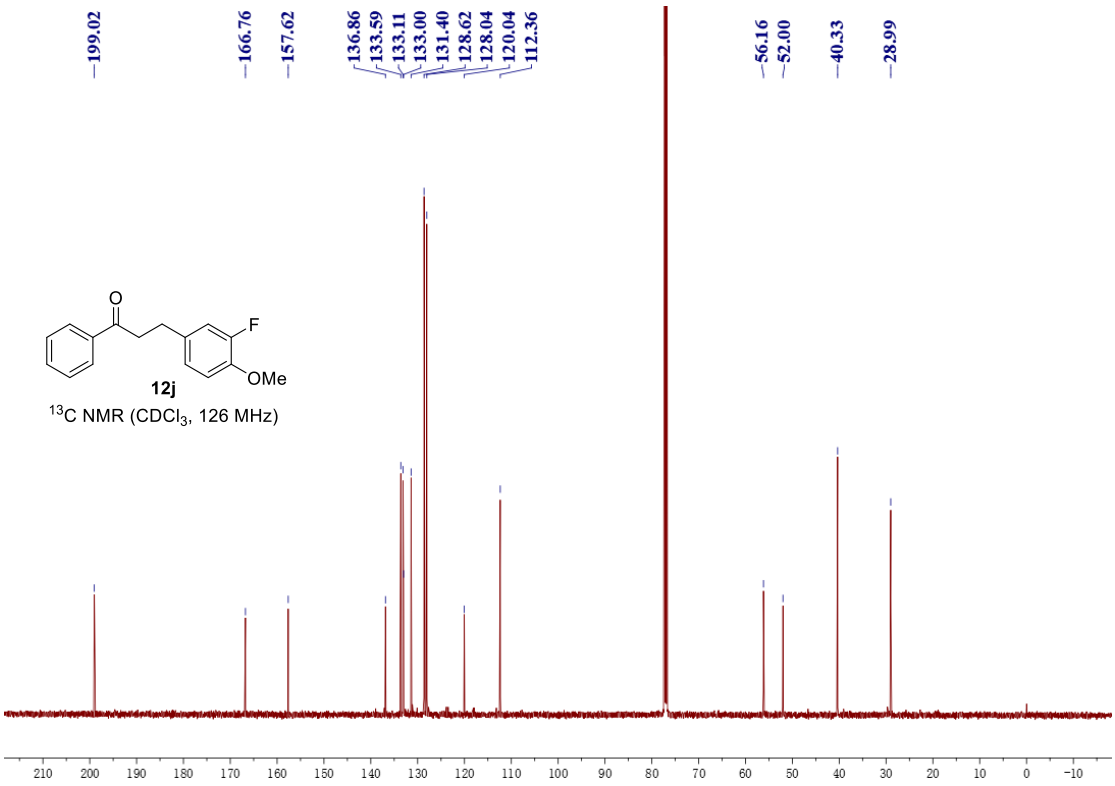

10.25
7.96
7.94
7.55
7.46
7.44
7.43
7.34
7.34
7.31
7.29
7.08
3.41
3.40
3.39
3.30
3.29
3.27
O
CHO
OMe
12i
1H NMR (CDCl3, 500 MHz)
0.98
2.02
1.05
2.09
1.00
1.03
0.96
2.98
2.00
2.00


199.02
192.20
158.48
136.77
136.05
134.59
133.13
132.69
128.61
128.09
120.56
116.19
55.54
40.61
26.33
O
CHO
OMe
12i
13C NMR (CDCl3, 126 MHz)

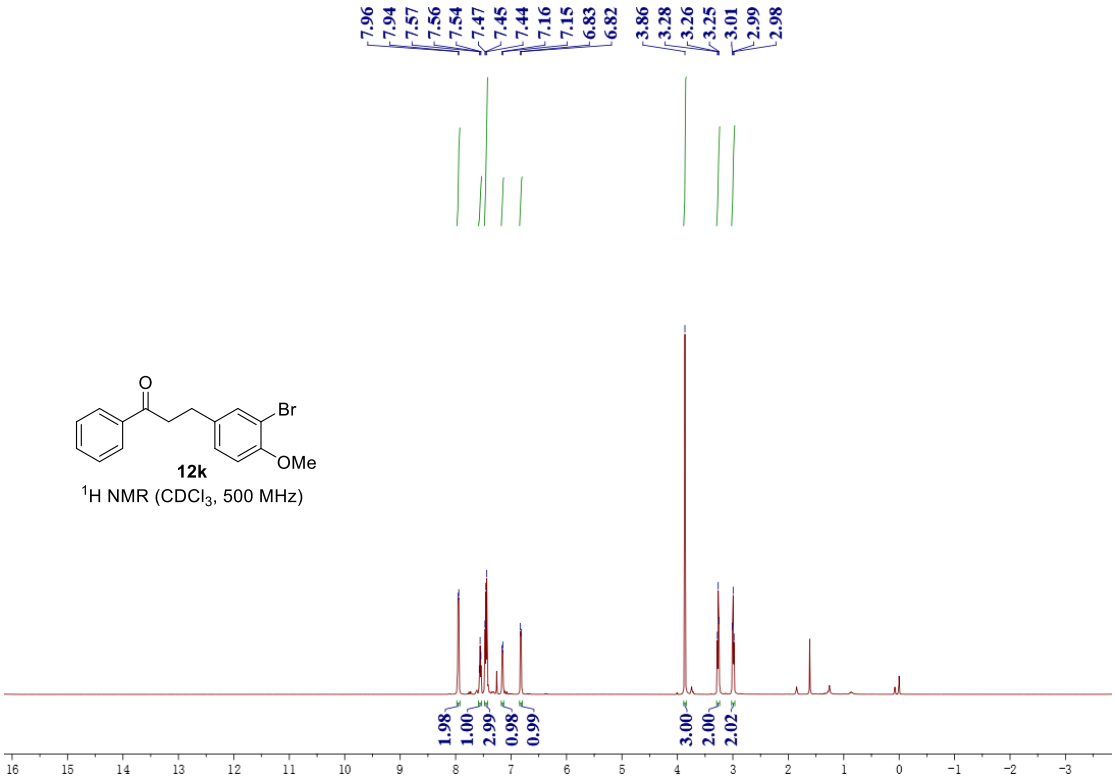

7.95
7.94
7.68
7.67
7.56
7.55
7.54
7.46
7.45
7.43
7.37
7.36
7.35
7.35
6.91
6.90
3.88
3.87
3.29
3.28
3.26
3.05
3.03
3.01
O
F
OMe
12j
1H NMR (CDCl3, 500 MHz)
2.01
0.95
0.97
1.94
1.02
1.02
6.01
1.96
1.95

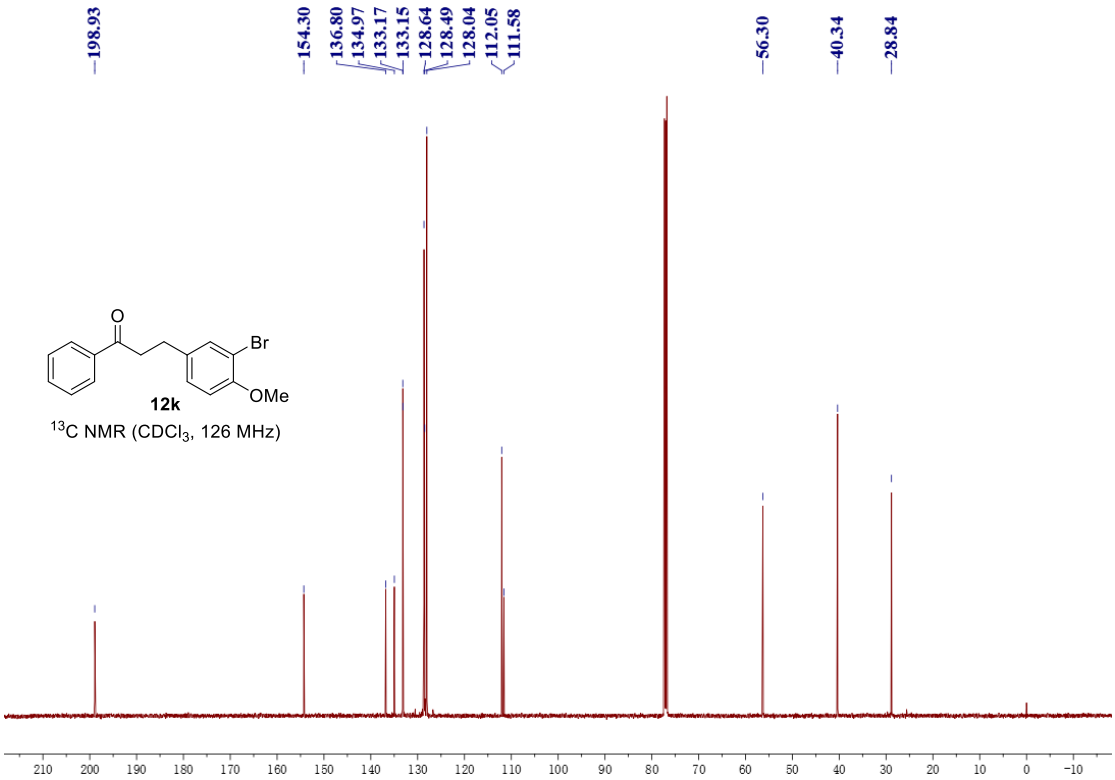


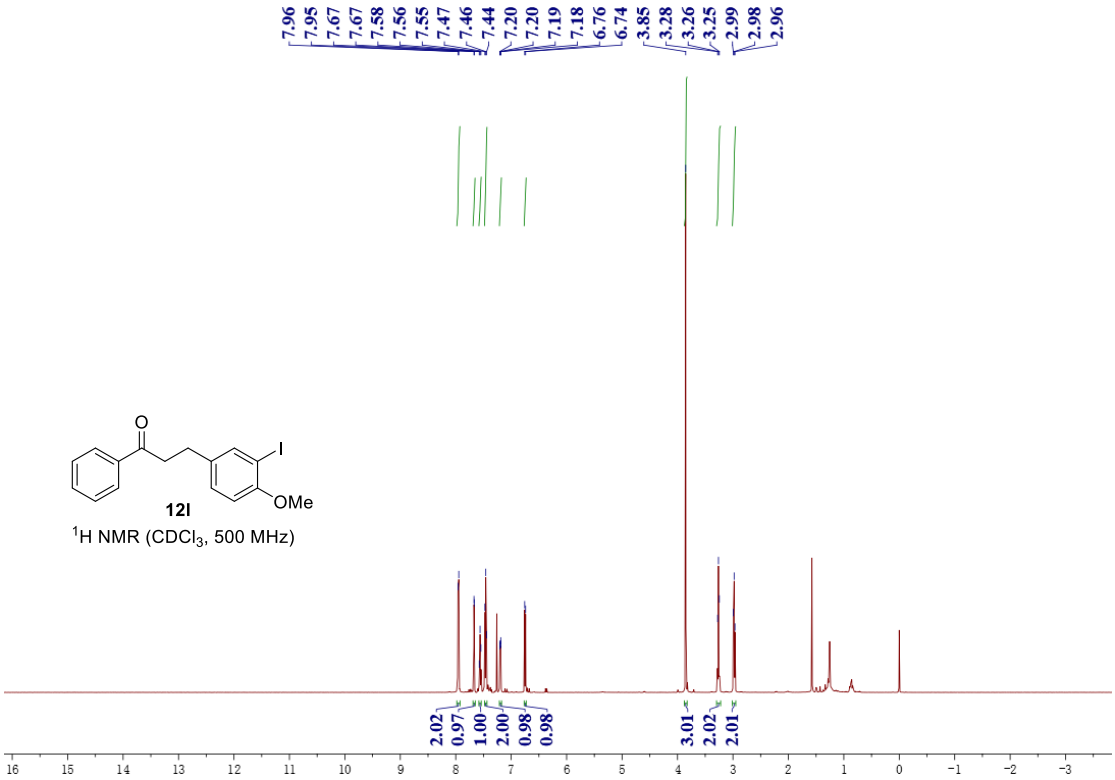
^{19}F NMR ($CDCl_3$, 471 MHz)

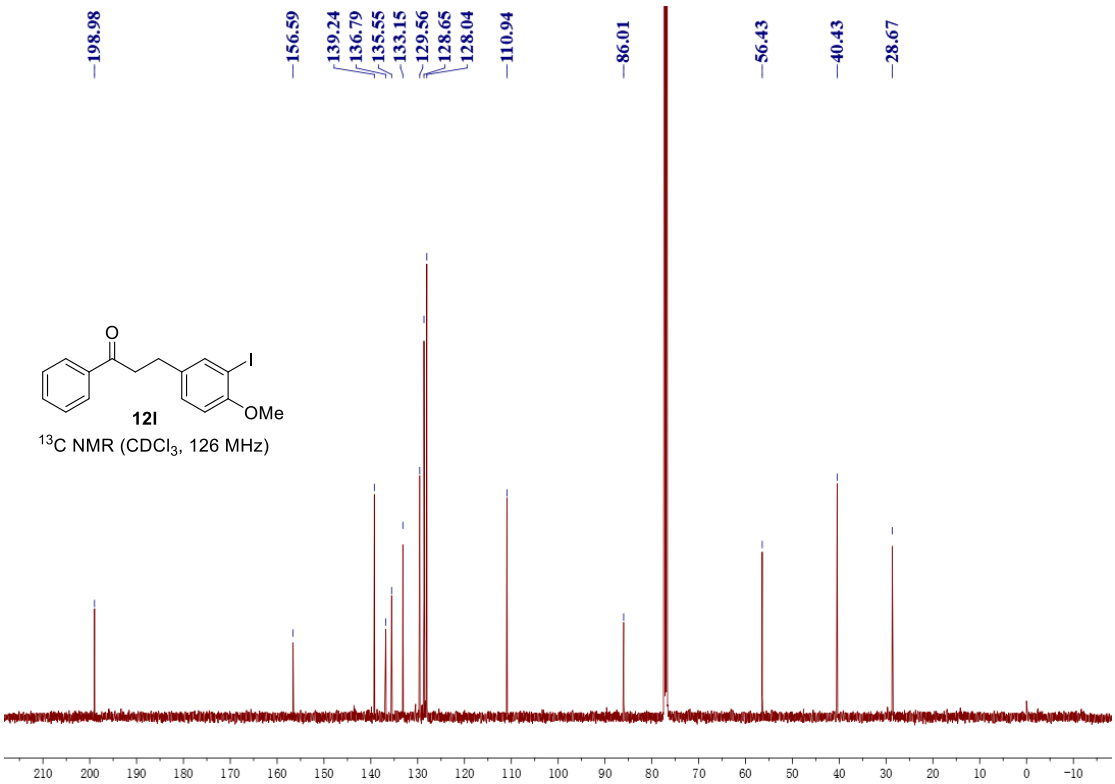


^{13}C NMR ($CDCl_3$, 126 MHz)


7.96
7.94
7.57
7.56
7.54
7.47
7.45
7.44
7.16
7.15
6.83
6.82
3.86
3.28
3.26
3.25
3.01
2.99
2.98
O
Br
OMe
12k
1H NMR (CDCl3, 500 MHz)
1.98
1.00
2.99
0.98
0.99
3.00
2.00
2.02


198.93
154.30
136.80
134.97
133.17
133.15
128.64
128.49
128.04
112.05
111.58
56.30
40.34
28.84
O
Br
OMe
12k
13C NMR (CDCl3, 126 MHz)


7.96
7.95
7.67
7.67
7.58
7.56
7.55
7.47
7.46
7.44
7.20
7.20
7.19
7.18
6.76
6.74
3.85
3.28
3.26
3.25
2.99
2.98
2.96
O
I
OMe
12l
1H NMR (CDCl3, 500 MHz)
2.02
0.97
1.00
2.00
0.98
0.98
3.01
2.02
2.01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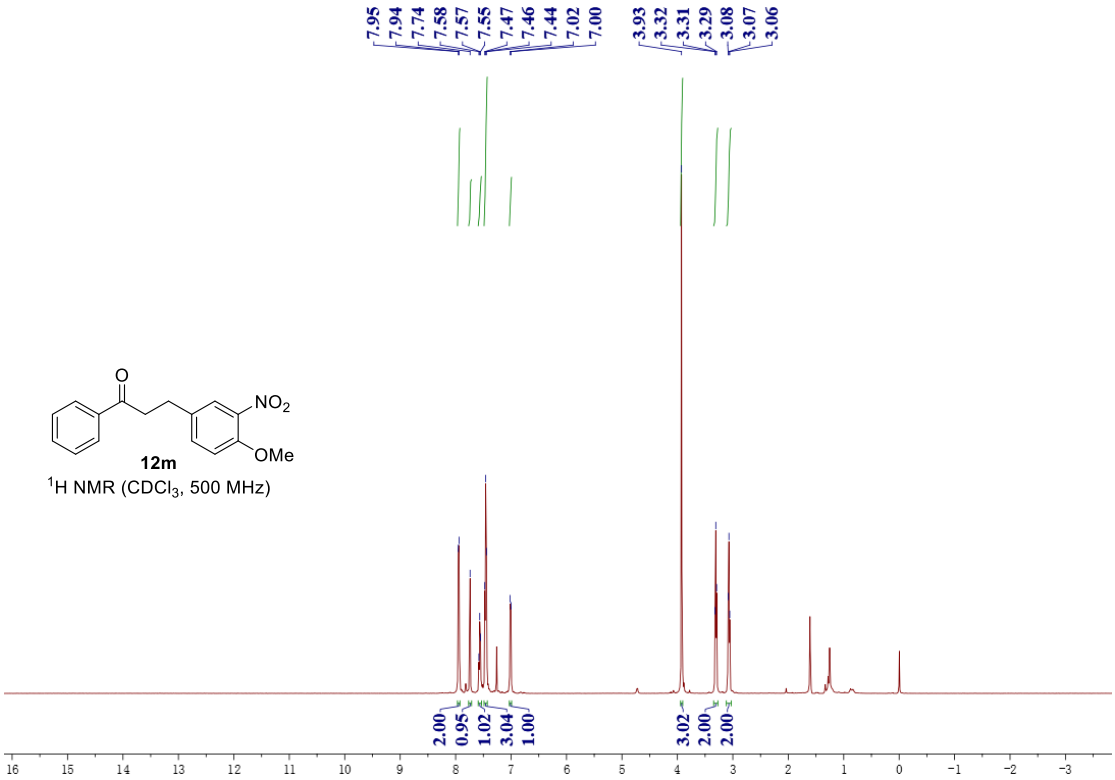
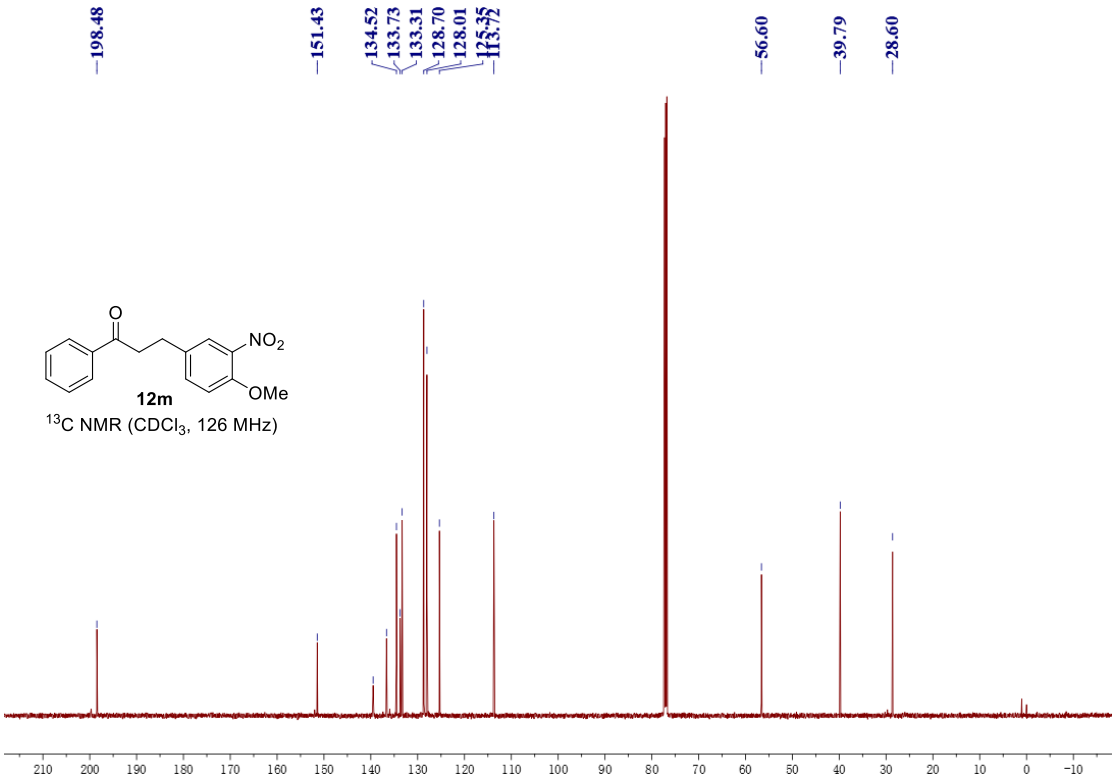
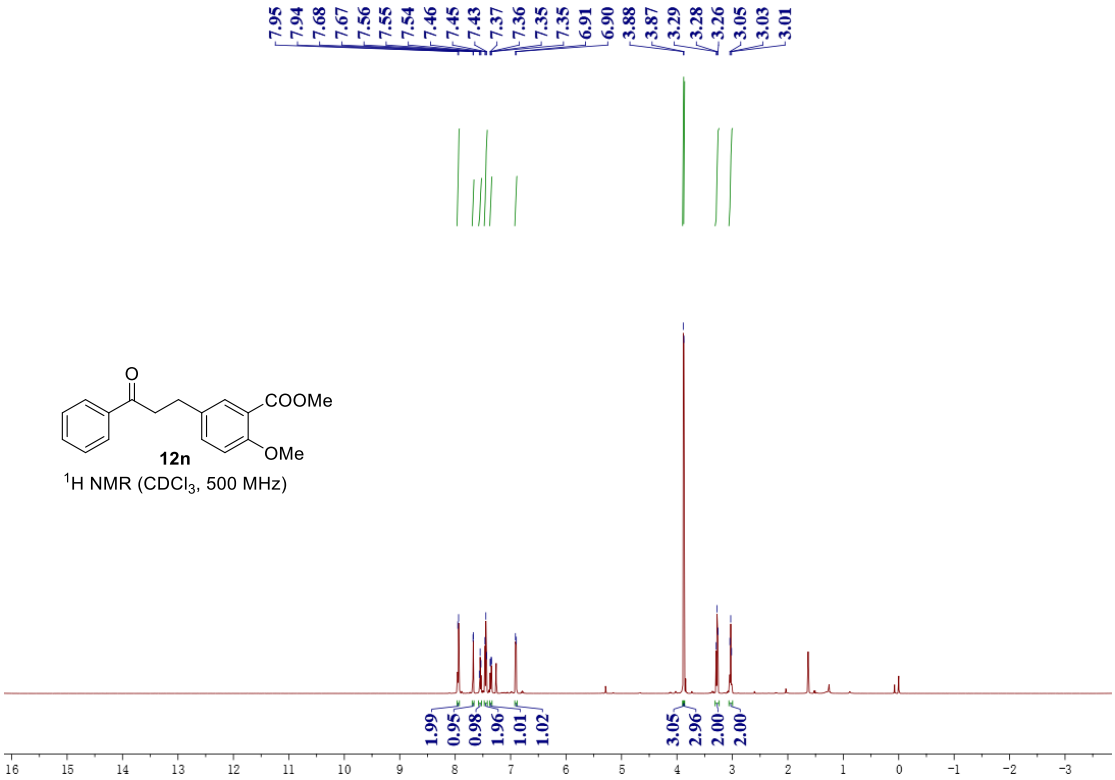
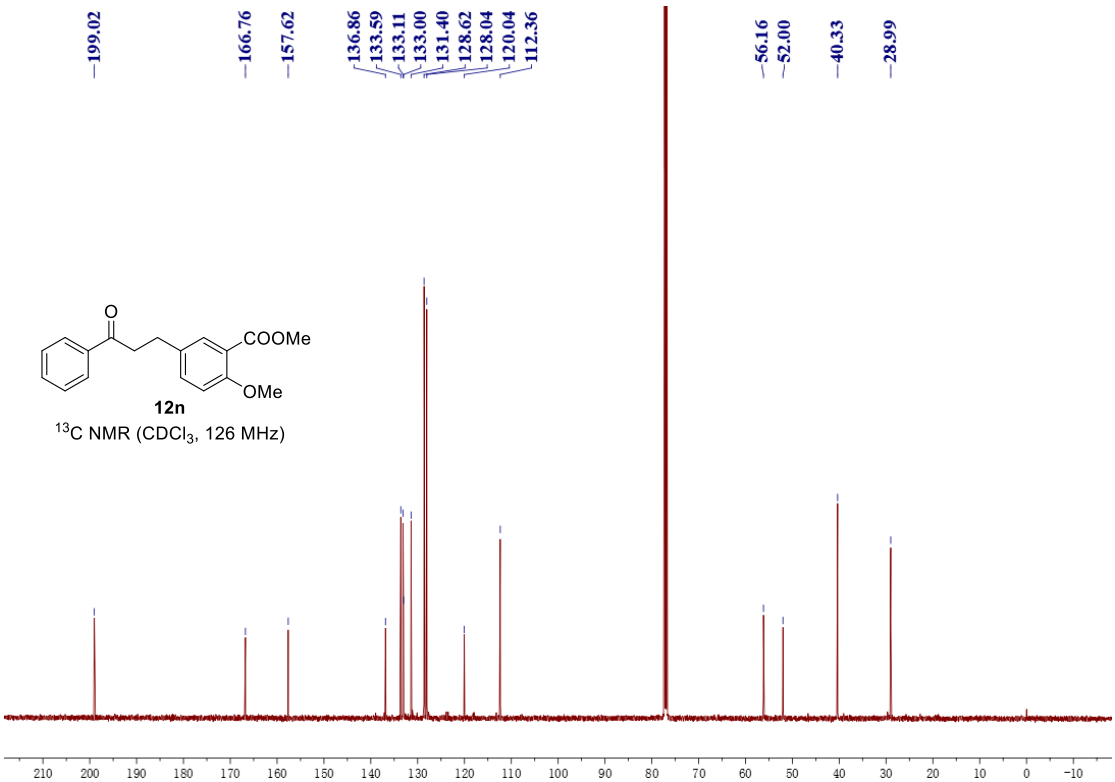
156.59
139.24
136.79
135.55
133.15
129.56
128.65
128.04
110.94
86.01
56.43
40.43
28.67
O
I
OMe
12l
13C NMR (CDCl3, 126 MHz)


7.95
7.94
7.74
7.58
7.57
7.55
7.47
7.46
7.44
7.02
7.00
3.93
3.32
3.31
3.29
3.08
3.07
3.06
O
NO2
OMe
12m
1H NMR (CDCl3, 500 MHz)
2.00
0.95
1.02
3.04
1.00
3.02
2.00
2.00


198.48
151.43
134.52
133.73
133.31
128.70
128.01
56.60
39.79
28.60
O
NO2
OMe
12m
13C NMR (CDCl3, 126 MHz)


7.95
7.94
7.68
7.67
7.56
7.55
7.54
7.46
7.45
7.43
7.37
7.36
7.35
7.35
6.91
6.90
3.88
3.87
3.29
3.28
3.26
3.05
3.03
3.01
O
COOMe
OMe
12n
1H NMR (CDCl3, 500 MHz)
1.99
0.95
0.98
1.96
1.01
1.02
3.05
2.96
2.00
2.00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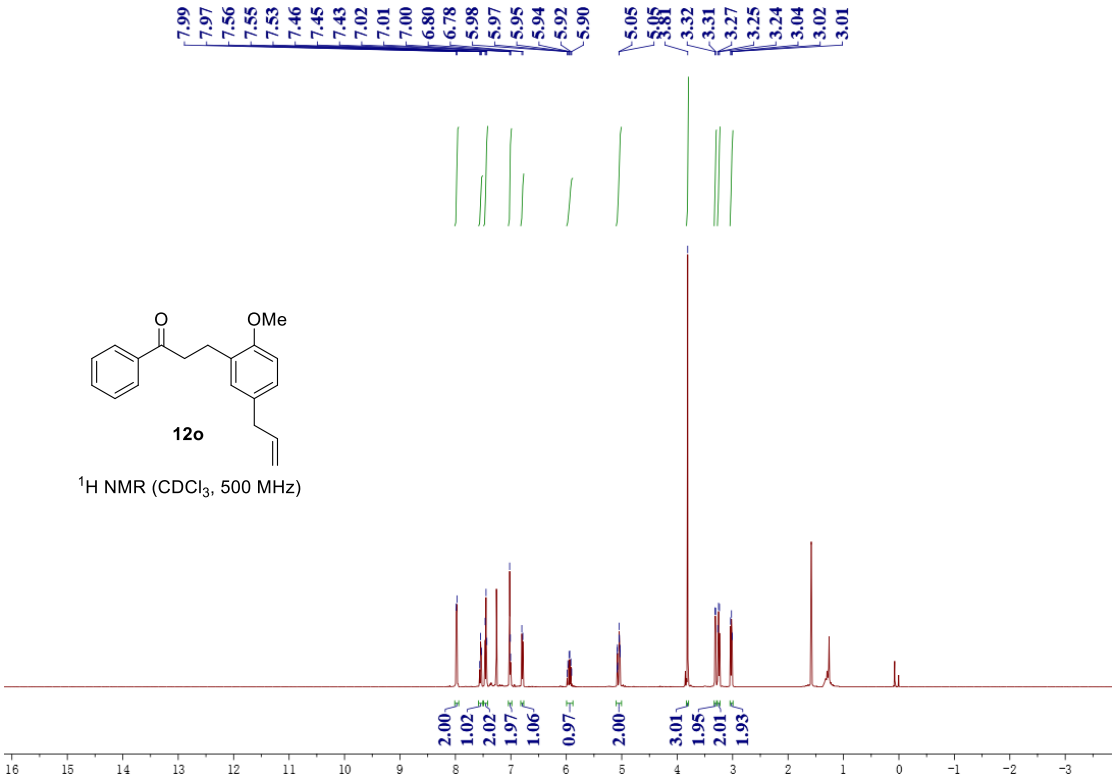
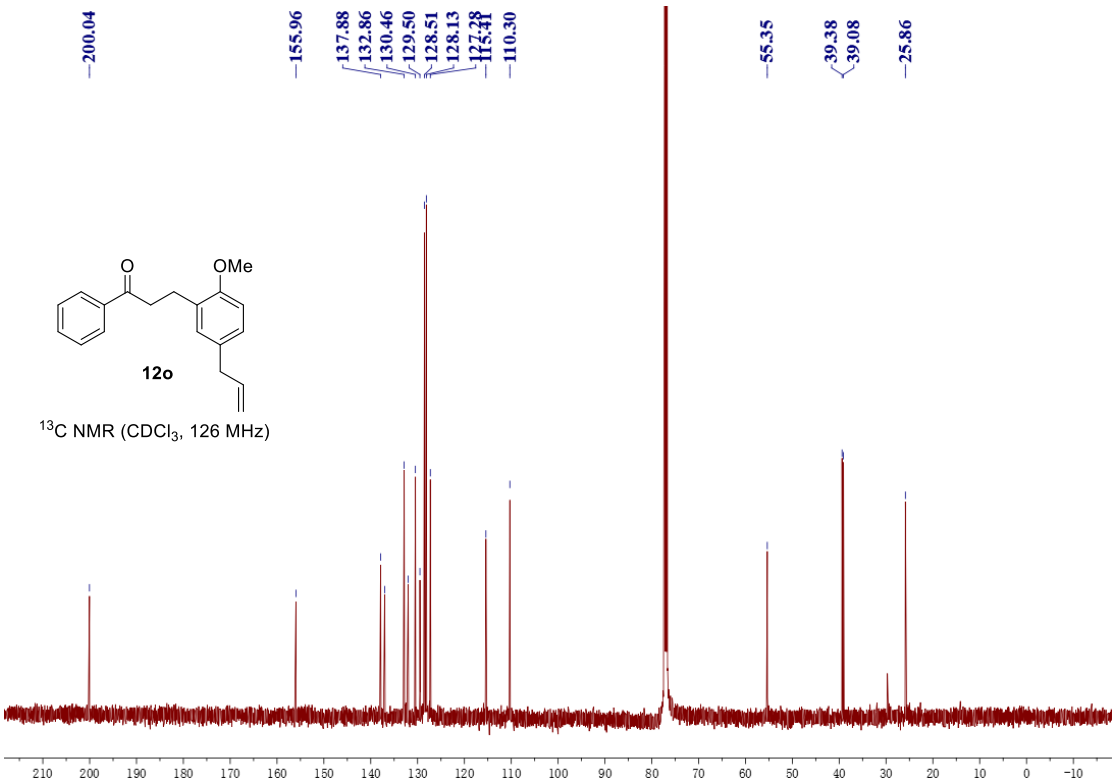
133.59
133.11
133.00
131.40
128.62
128.04
120.04
112.36
56.16
52.00
40.33
28.99
O
COOMe
OMe
12n
13C NMR (CDCl3, 126 MHz)


7.99
7.97
7.56
7.55
7.53
7.46
7.45
7.43
7.02
7.01
7.00
6.80
6.78
5.98
5.97
5.95
5.94
5.92
5.90
5.05
3.81
3.32
3.31
3.27
3.25
3.24
3.04
3.02
3.01
O
OMe
12o
1H NMR (CDCl3, 500 MHz)
2.00
1.02
2.02
1.97
1.06
0.97
2.00
3.01
1.95
2.01
1.93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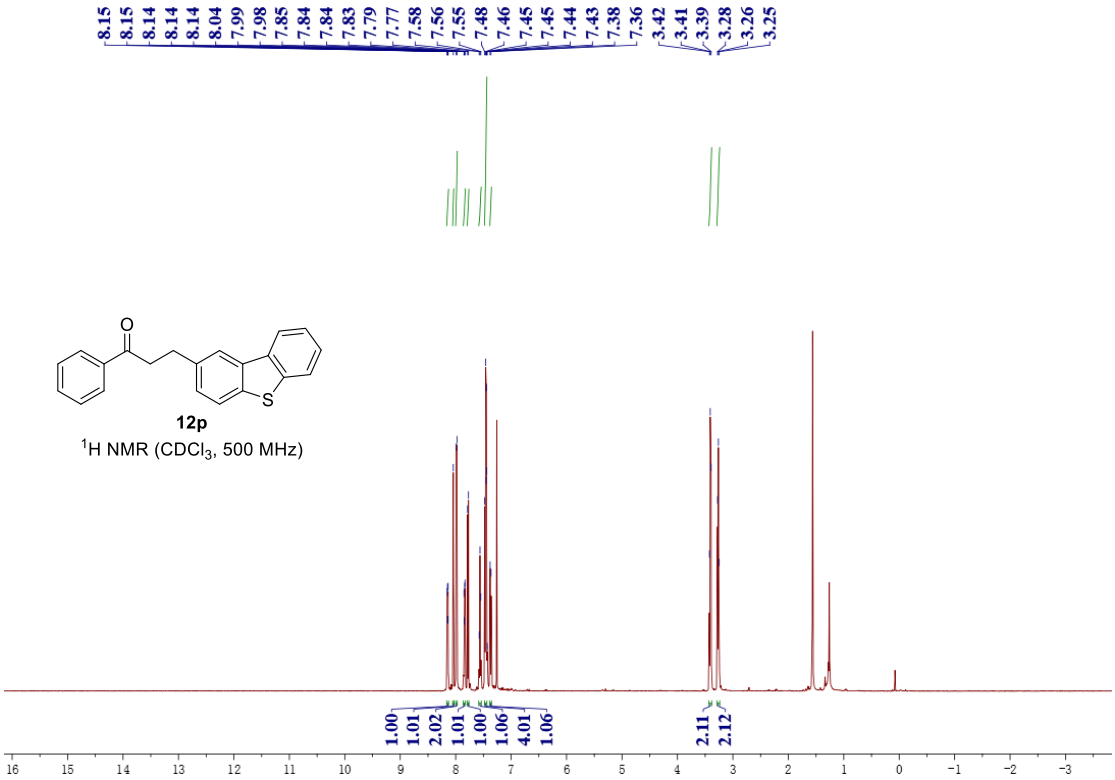
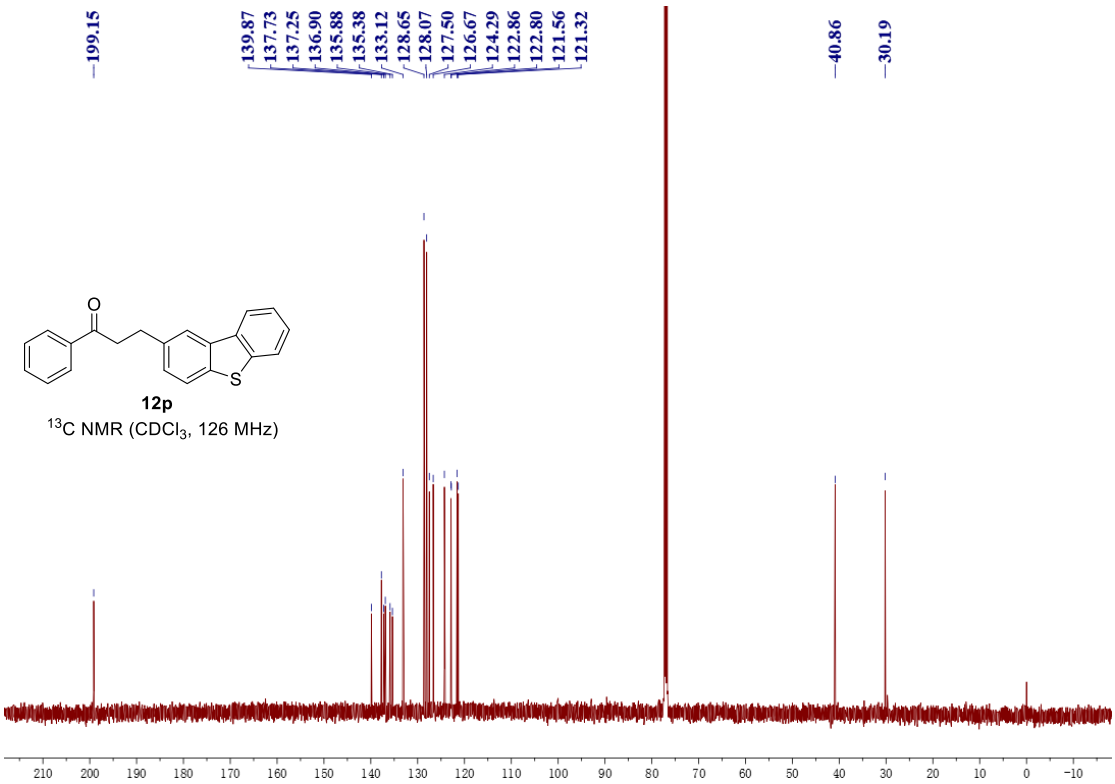
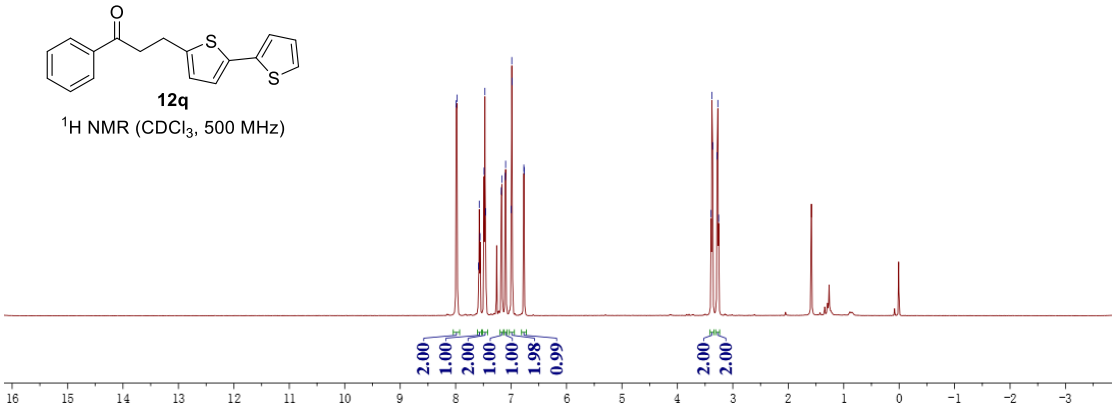
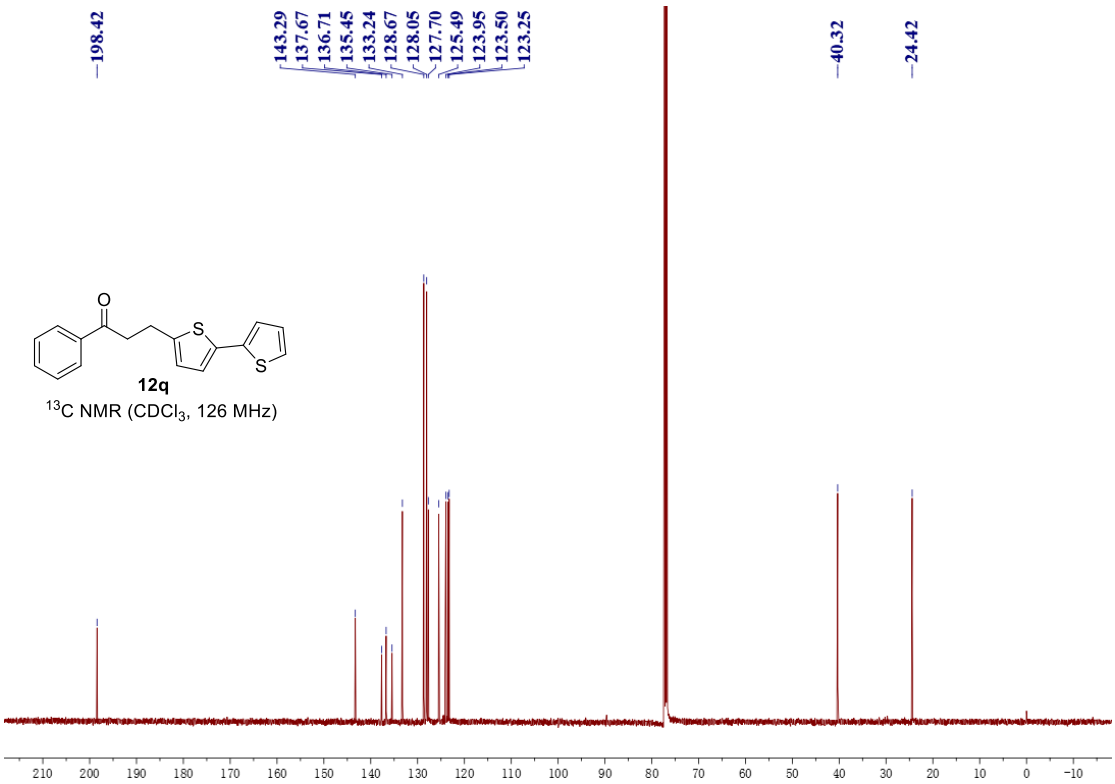
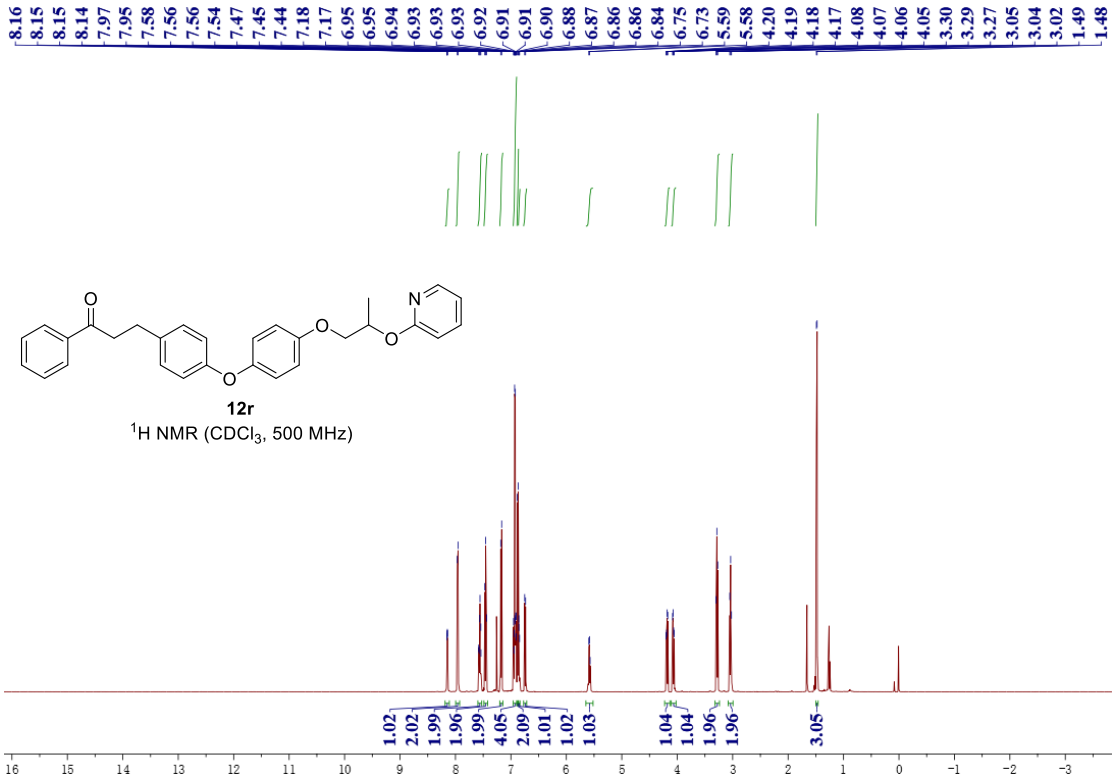
132.86
130.46
129.50
128.51
128.13
127.28
115.41
110.30
55.35
39.38
39.08
25.86
O
OMe
12o
13C NMR (CDCl3, 126 MHz)


8.15
8.15
8.14
8.14
8.14
8.04
7.99
7.98
7.85
7.84
7.84
7.83
7.79
7.77
7.58
7.56
7.55
7.48
7.46
7.45
7.45
7.44
7.43
7.38
7.36
3.42
3.41
3.39
3.28
3.26
3.25
O
S
12p
1H NMR (CDCl3, 500 MHz)
1.00
1.01
2.02
1.01
1.00
1.06
4.01
1.06
2.11
2.12


199.15
139.87
137.73
137.25
136.90
135.88
135.38
133.12
128.65
128.07
127.50
126.67
124.29
122.86
122.80
121.56
121.32
40.86
30.19
O
S
12p
13C NMR (CDCl3, 126 MHz)


12q
1H NMR (CDCl3, 500 MHz)


12q
13C NMR (CDCl3, 126 MHz)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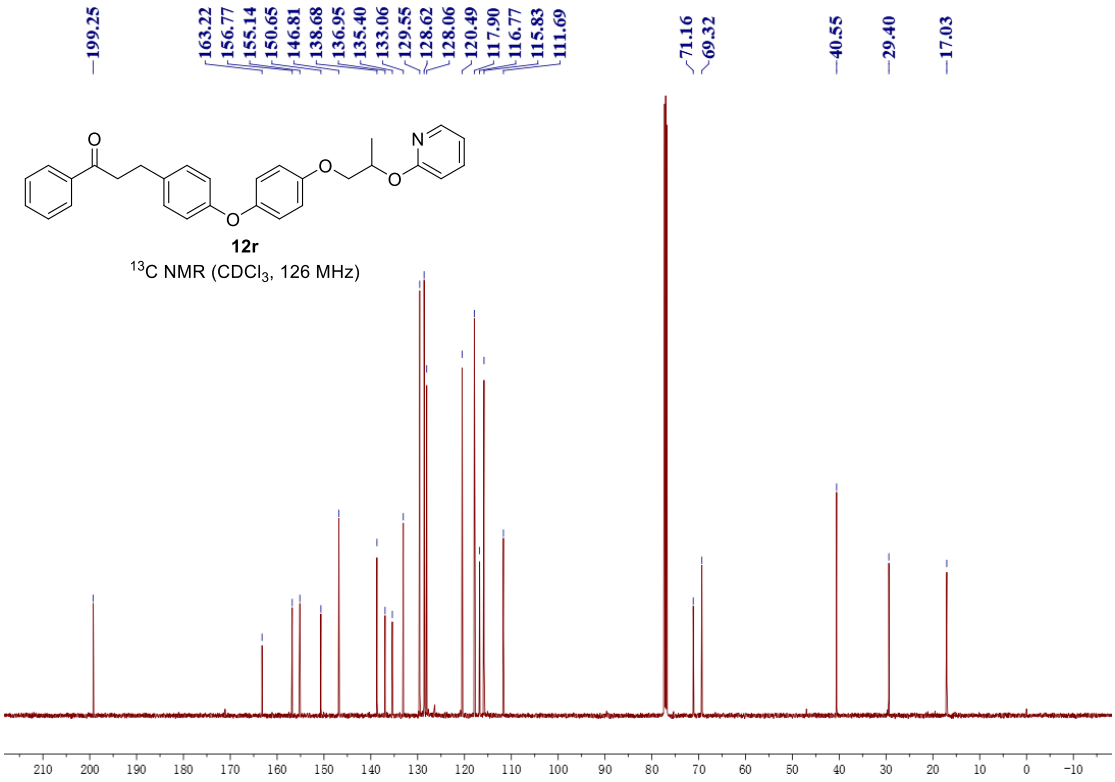
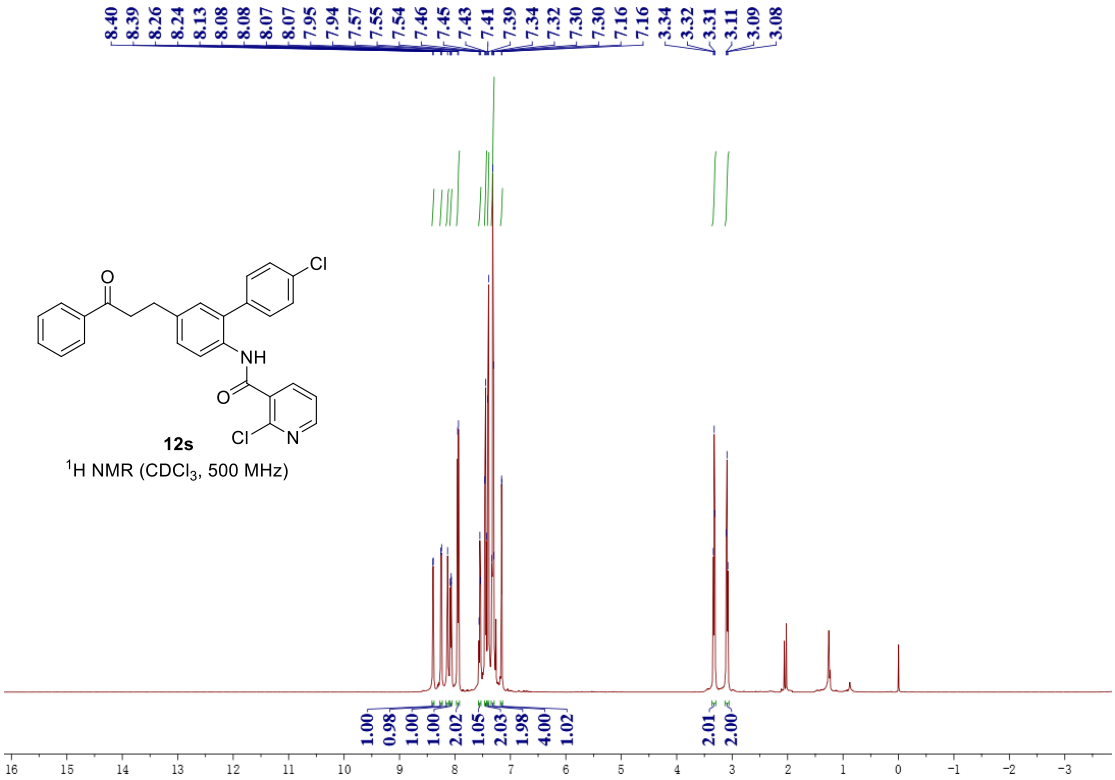
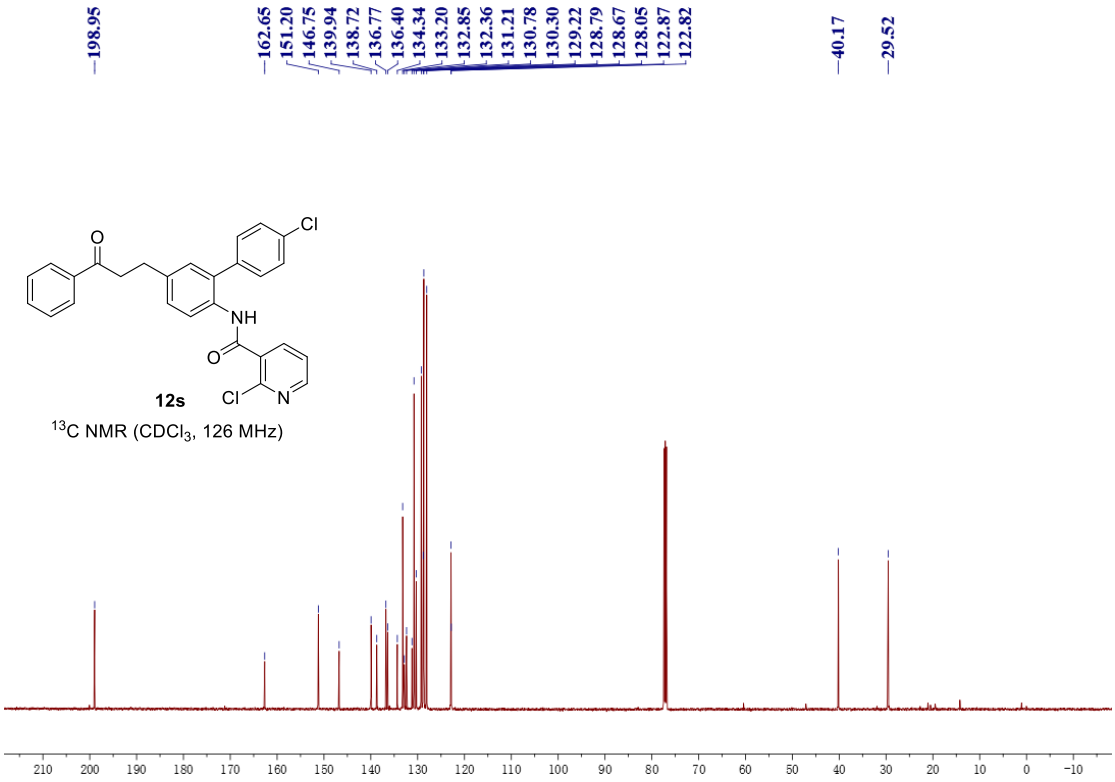
O
N
O
O
O
12r
1H NMR (CDCl3, 500 MHz)
1.02 2.02 1.99 1.96 1.99 4.05 2.09 1.01 1.02 1.03 1.04 1.04 1.96 1.96 3.05
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3


199.25
163.22 156.77 155.14 150.65 146.81 138.68 136.95 135.40 133.06 129.55 128.62 128.06 120.49 117.90 116.77 115.83 111.69
71.16 69.32
40.55
29.40
17.03
O
N
O
O
O
12r
13C NMR (CDCl3, 126 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10



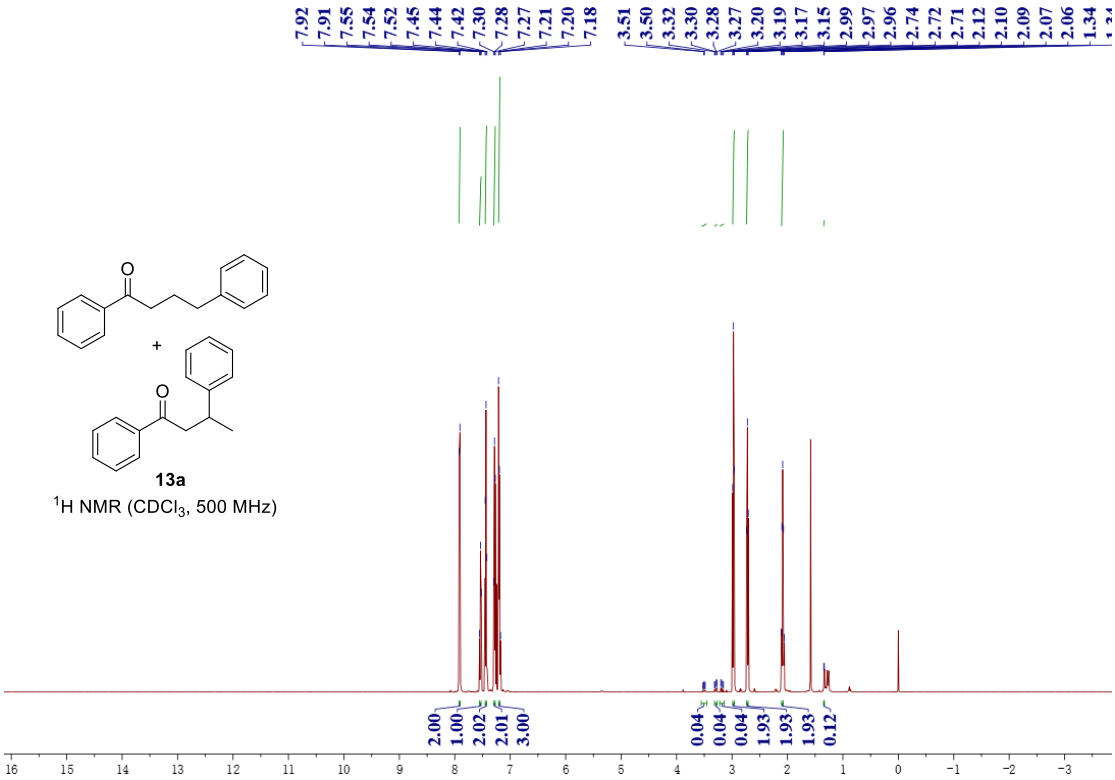
12s

^{1}H NMR ($CDCl_3$, 500 MHz)



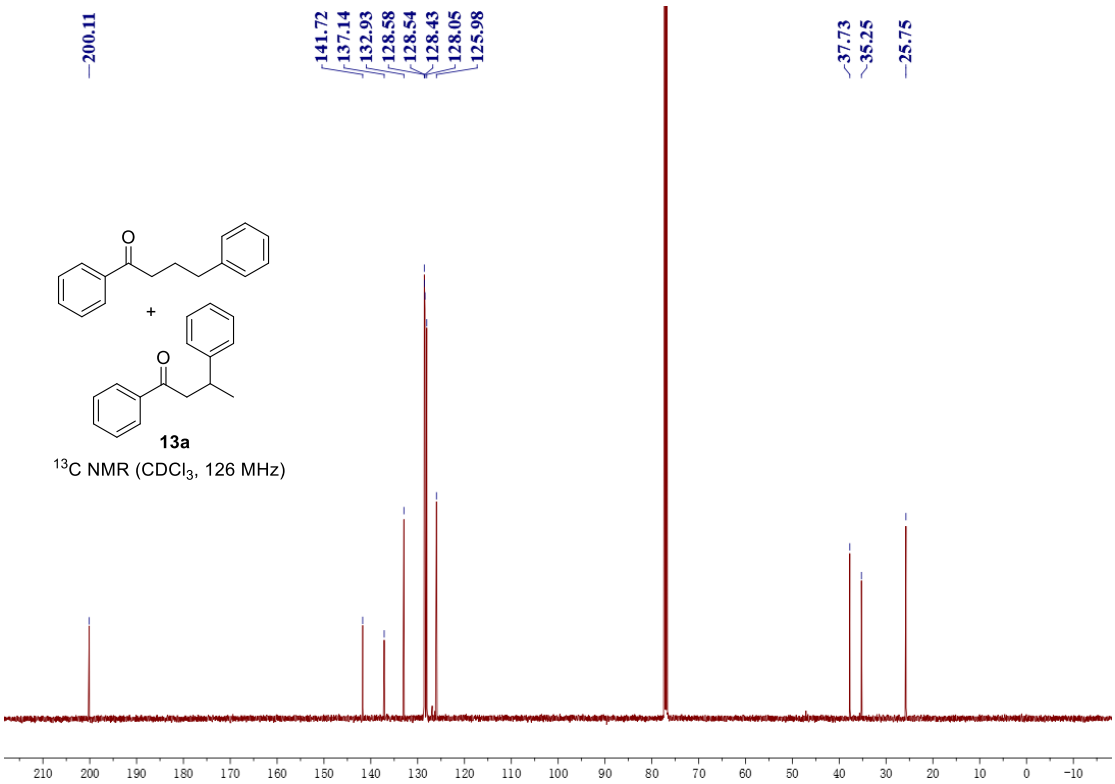
12s

^{13}C NMR ($CDCl_3$, 126 MHz)



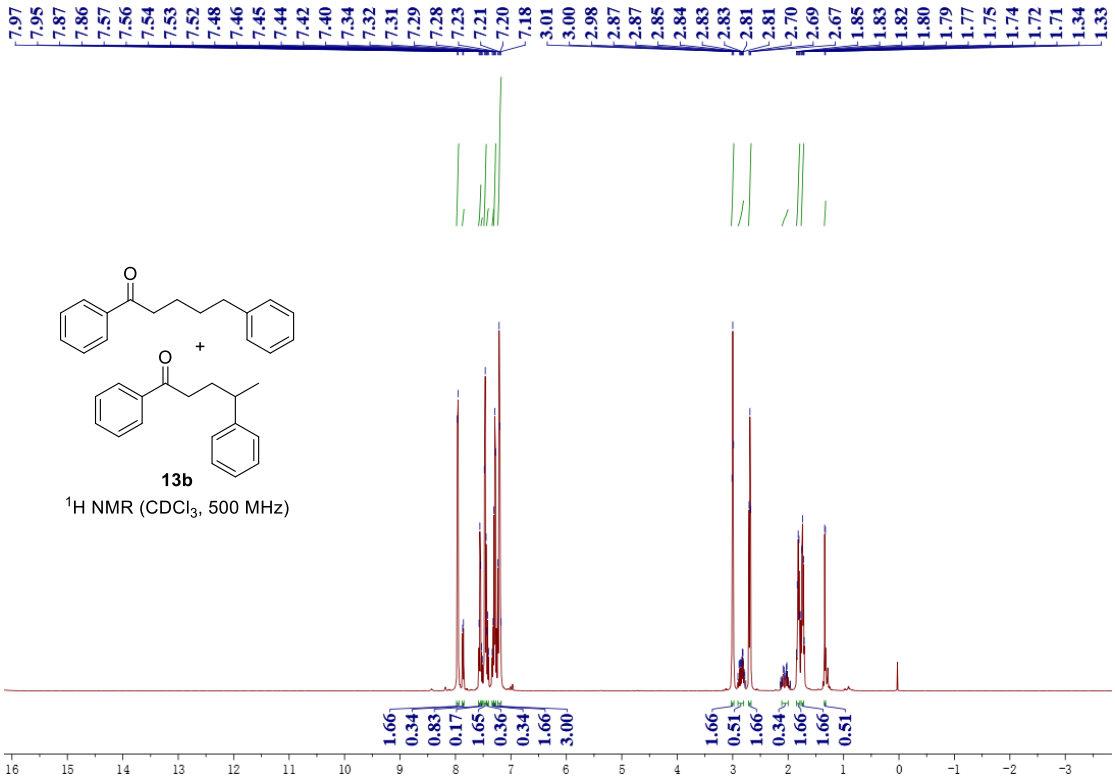
13a

^{1}H NMR ($CDCl_3$, 500 MHz)



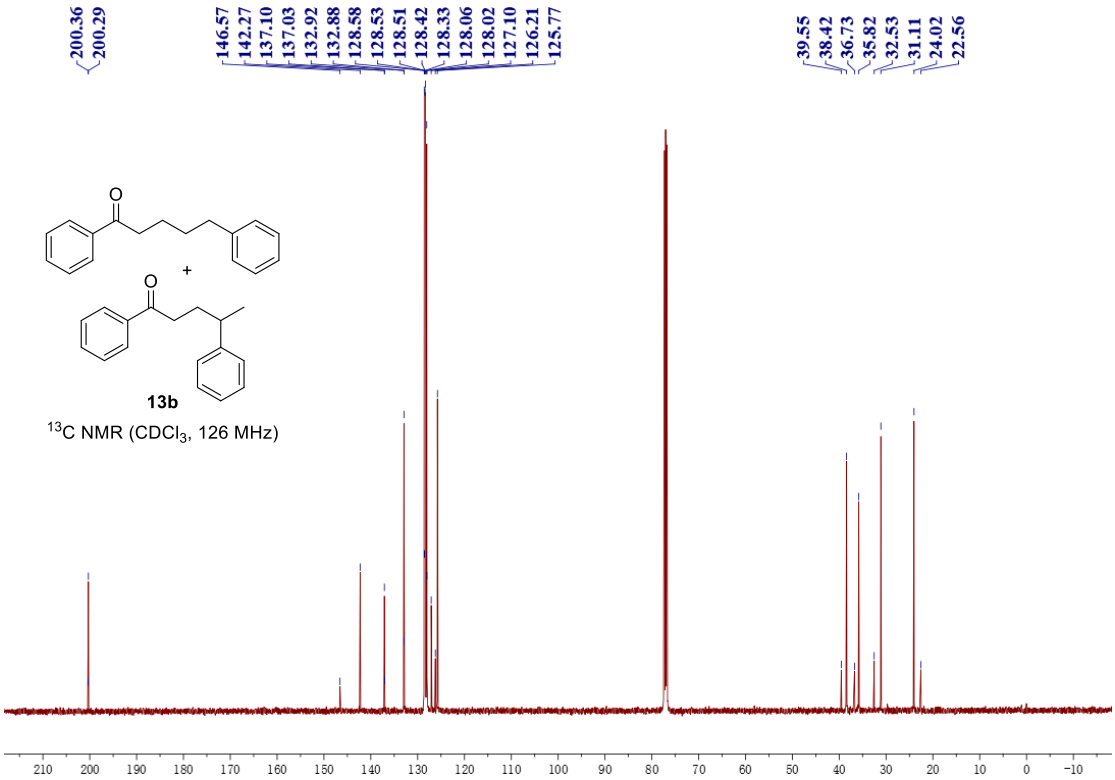
13a

^{13}C NMR ($CDCl_3$, 126 MHz)



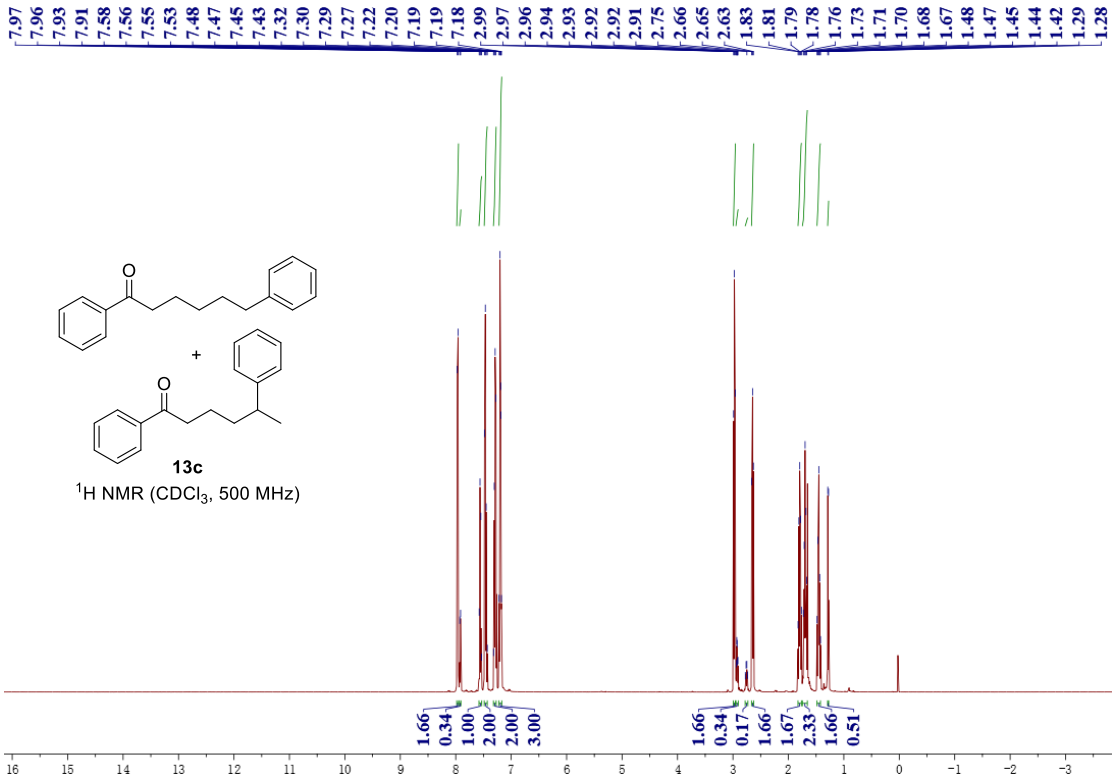
13b

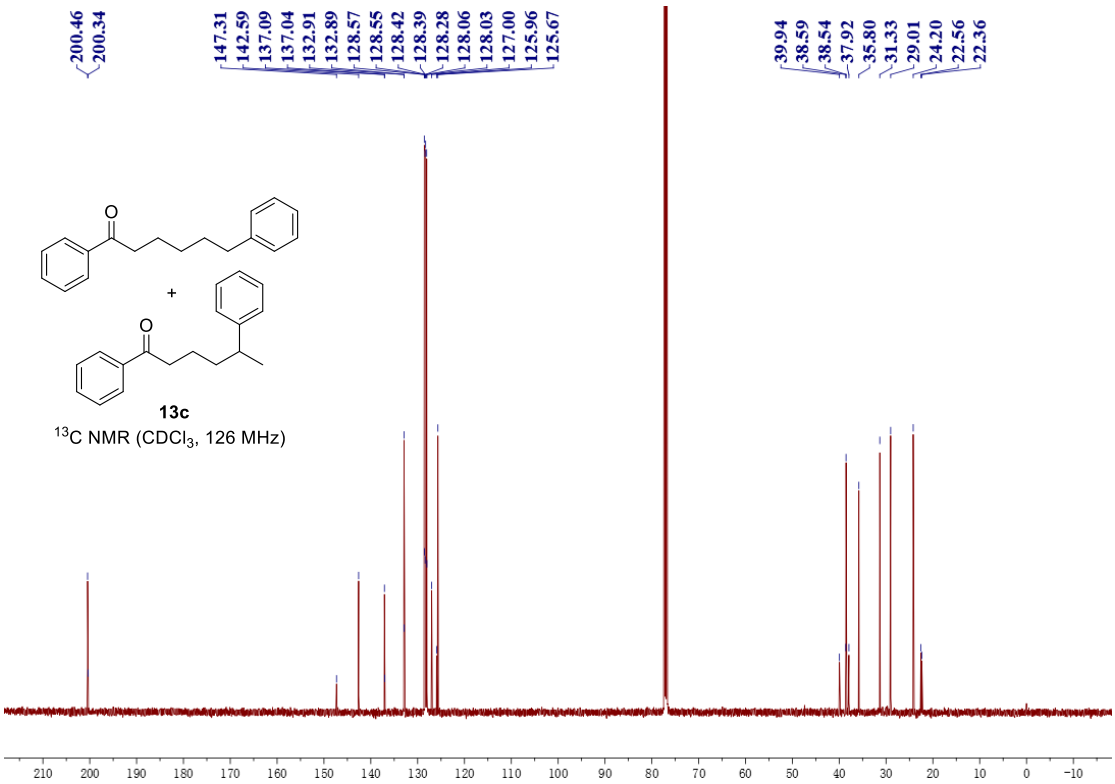
^{1}H NMR ($CDCl_3$, 500 MHz)

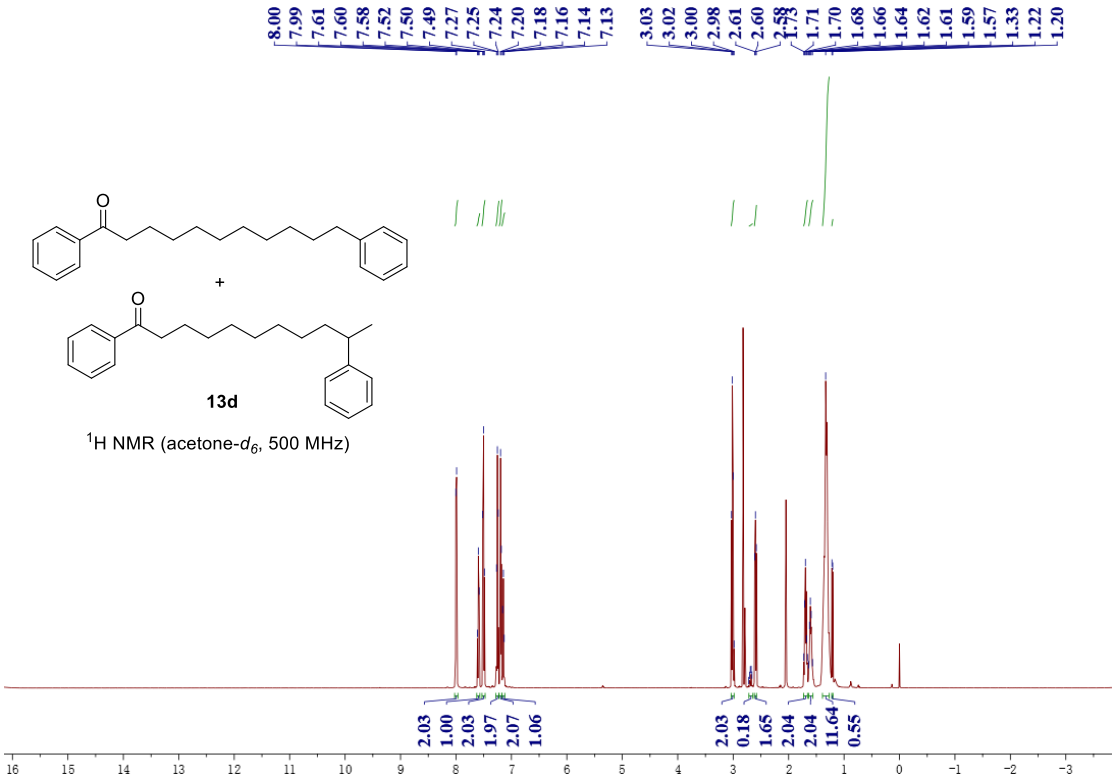


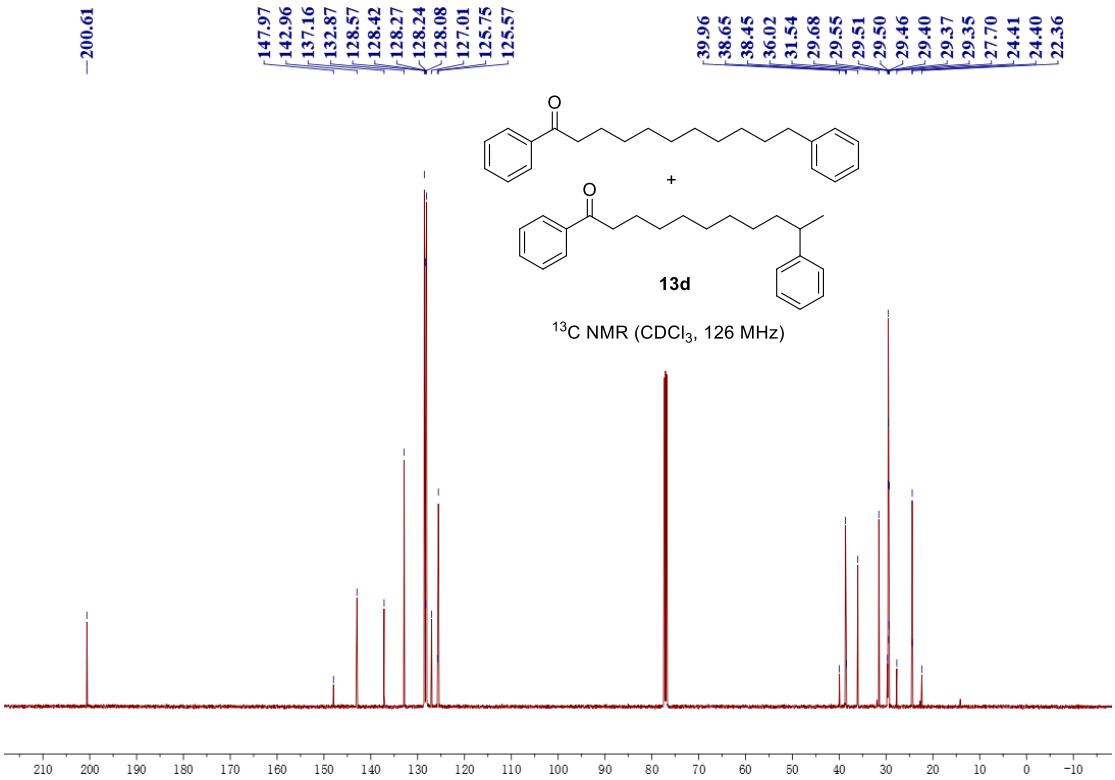
13b

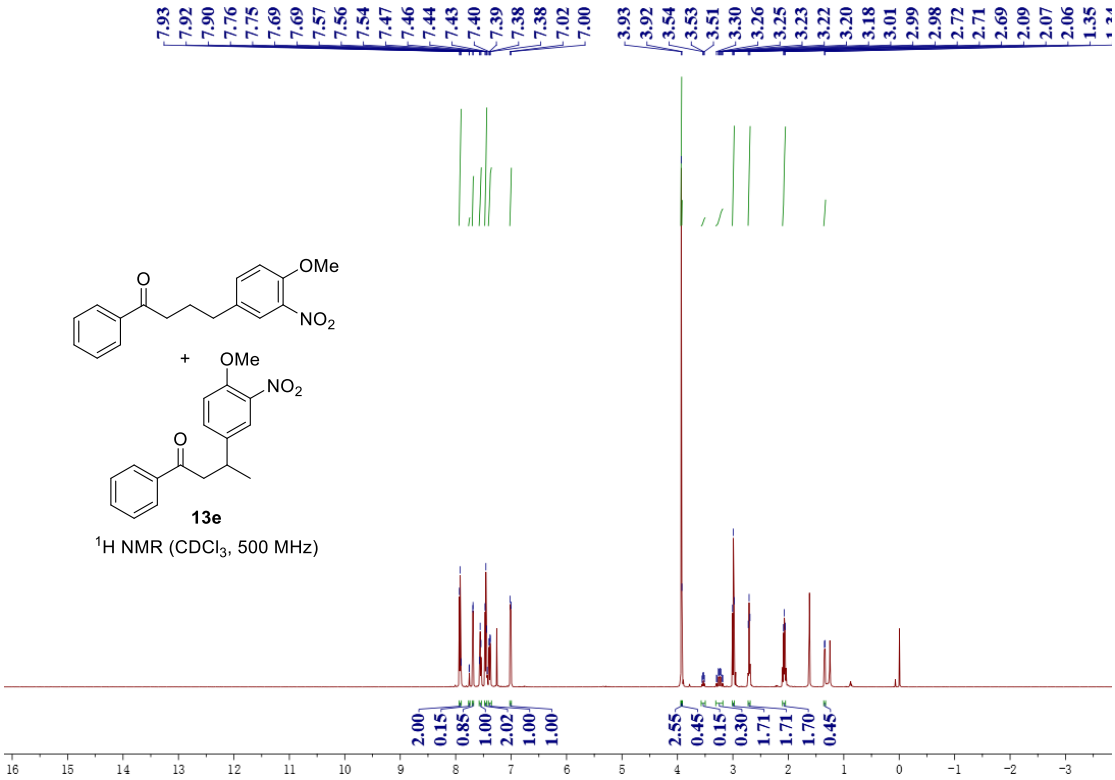
^{13}C NMR ($CDCl_3$, 126 MHz)

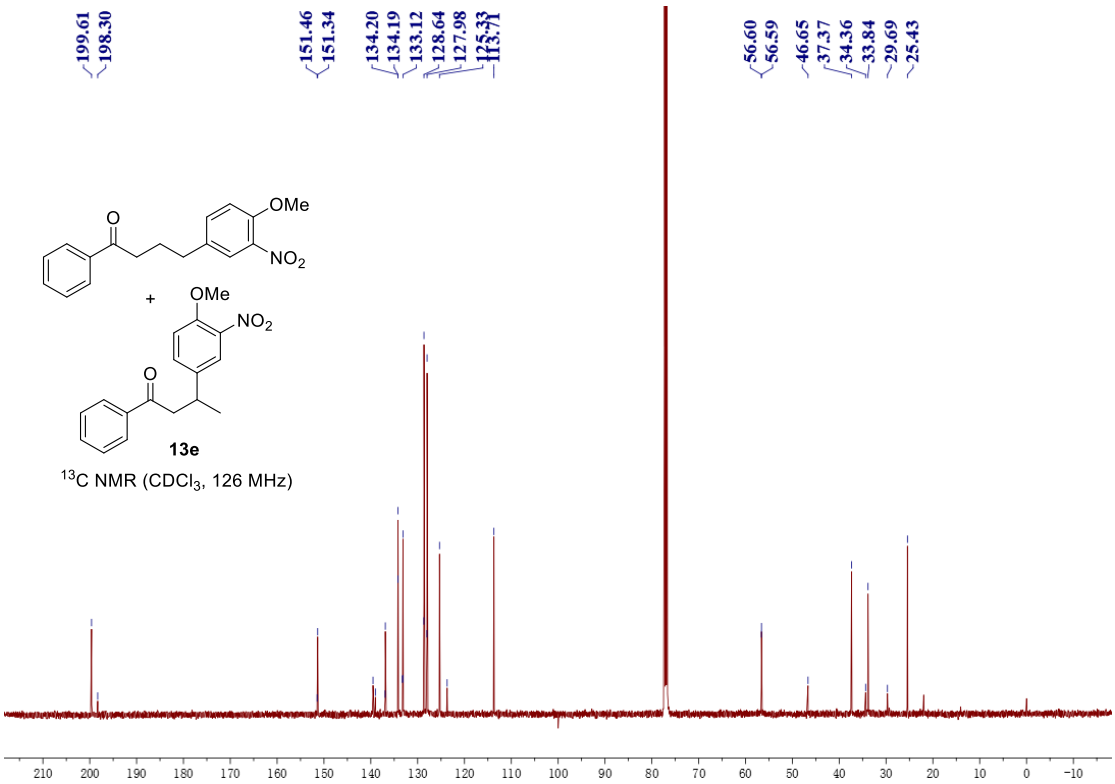

7.97
7.96
7.93
7.91
7.58
7.56
7.55
7.53
7.48
7.47
7.45
7.43
7.32
7.30
7.29
7.27
7.22
7.20
7.19
7.19
7.18
2.99
2.97
2.96
2.94
2.93
2.92
2.92
2.91
2.75
2.66
2.65
2.63
1.83
1.81
1.79
1.78
1.76
1.73
1.71
1.70
1.68
1.67
1.48
1.47
1.45
1.44
1.42
1.29
1.28
O
+
O
13c
1H NMR (CDCl3, 500 MHz)
1.66
0.34
1.00
2.00
2.00
3.00
1.66
0.34
0.17
1.66
1.67
2.33
1.66
0.51
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3

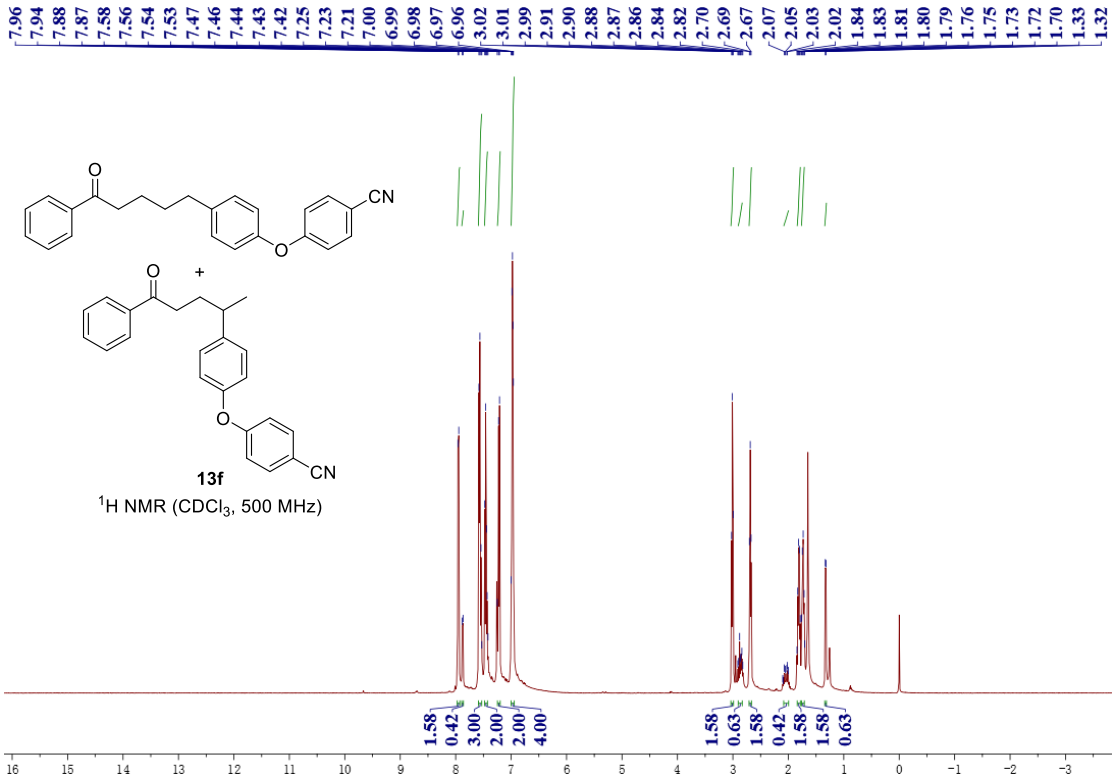

200.46
200.34
147.31
142.59
137.09
137.04
132.91
132.89
128.57
128.55
128.42
128.39
128.28
128.06
128.03
127.00
125.96
125.67
39.94
38.59
38.54
37.92
35.80
31.33
29.01
24.20
22.56
22.36
O
+
O
13c
13C NMR (CDCl3, 126 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

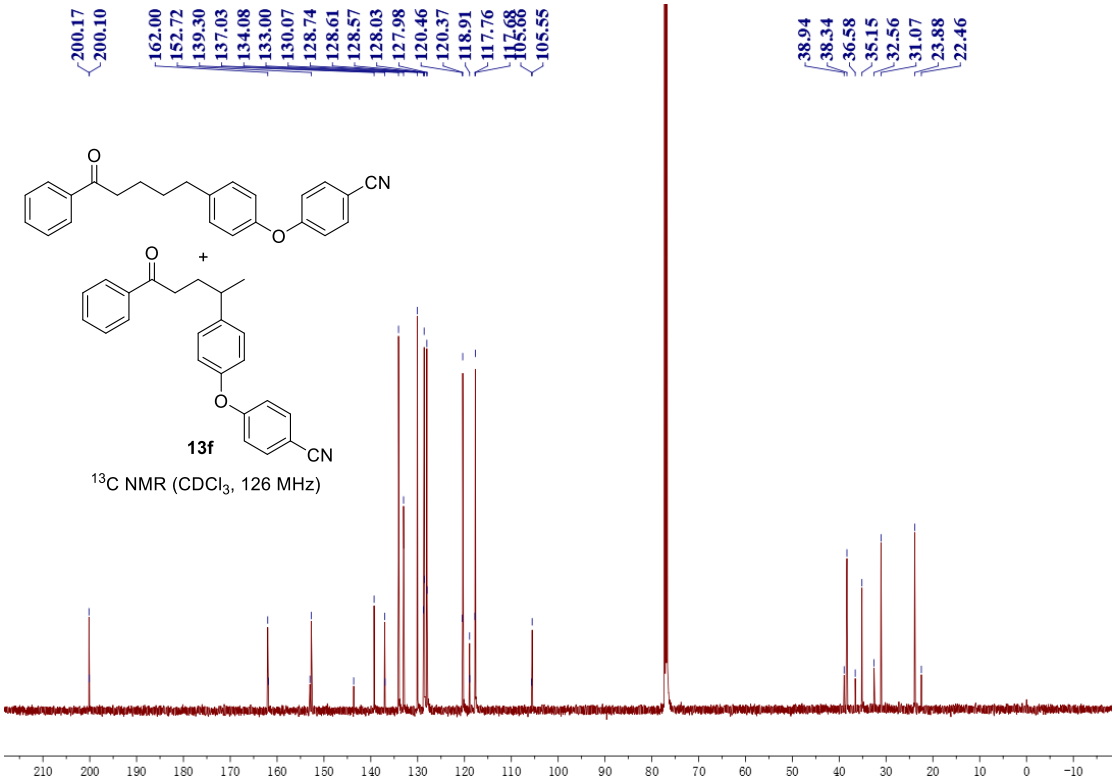

8.00
7.99
7.61
7.60
7.58
7.52
7.50
7.49
7.27
7.25
7.24
7.20
7.18
7.16
7.14
7.13
3.03
3.02
3.00
2.98
2.61
2.60
2.58
1.73
1.71
1.70
1.68
1.66
1.64
1.62
1.61
1.59
1.57
1.33
1.22
1.20
O
+
O
13d
1H NMR (acetone-d6, 500 MHz)
2.03
1.00
2.03
1.97
2.07
1.06
2.03
0.18
1.65
2.04
2.04
11.64
0.55
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3

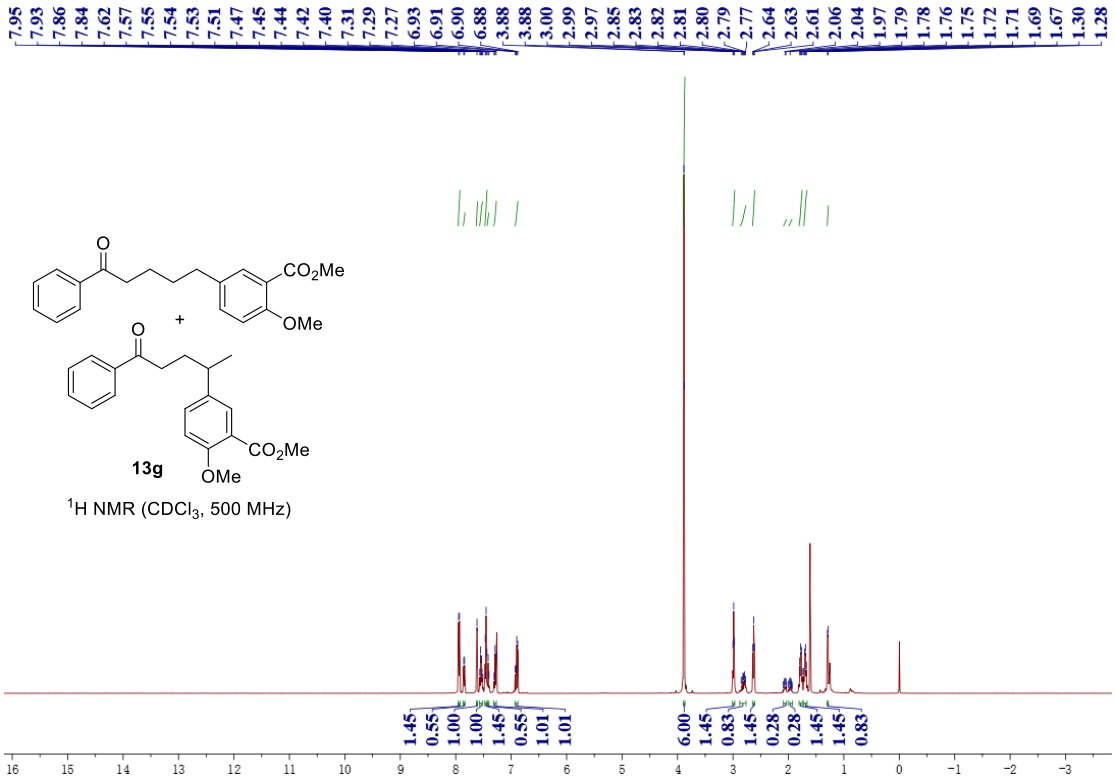

200.61
147.97
142.96
137.16
132.87
128.57
128.42
128.27
128.24
128.08
127.01
125.75
125.57
39.96
38.65
38.45
36.02
31.54
29.68
29.55
29.51
29.50
29.46
29.40
29.37
29.35
27.70
24.41
24.40
22.36
O
+
O
13d
13C NMR (CDCl3, 126 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

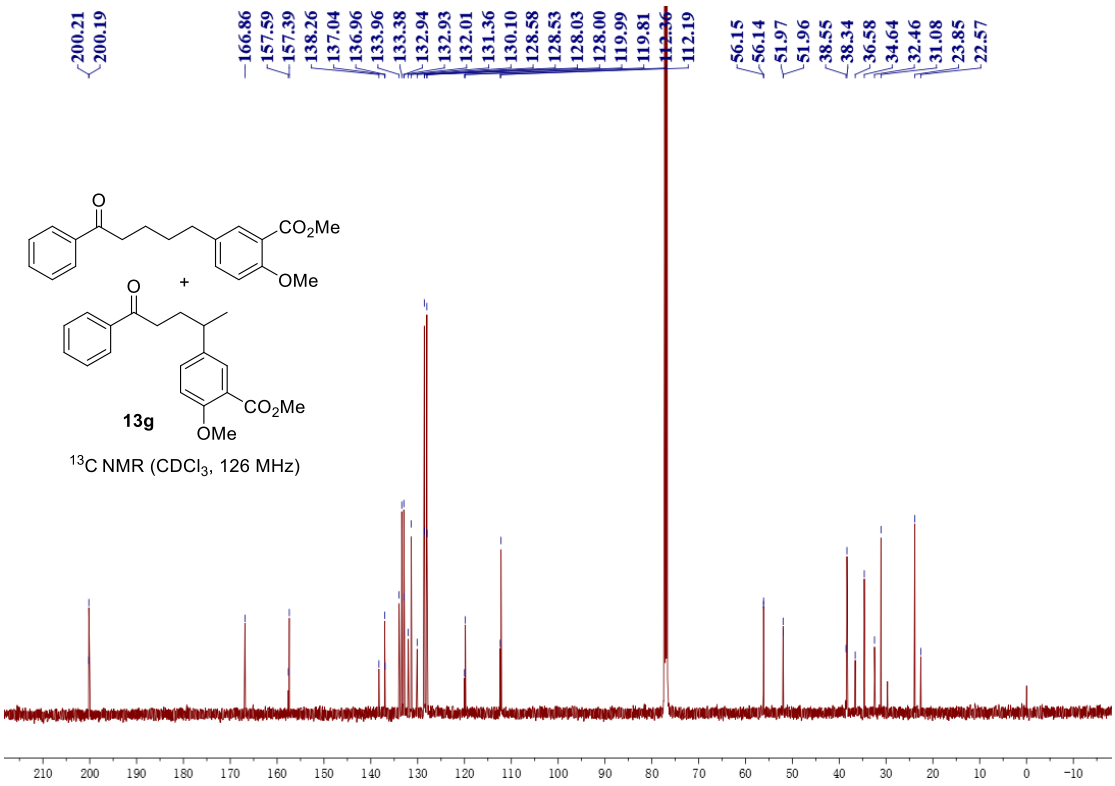

7.93
7.92
7.90
7.76
7.75
7.69
7.69
7.57
7.56
7.54
7.47
7.46
7.44
7.43
7.40
7.39
7.38
7.38
7.02
7.00
3.93
3.92
3.54
3.53
3.51
3.30
3.26
3.25
3.23
3.22
3.20
3.18
3.01
2.99
2.98
2.72
2.71
2.69
2.09
2.07
2.06
1.35
OMe
NO2
+
OMe
NO2
O
13e
1H NMR (CDCl3, 500 MHz)
2.00
0.15
0.85
1.00
2.02
1.00
1.00
2.55
0.45
0.15
0.30
1.71
1.71
1.70
0.45

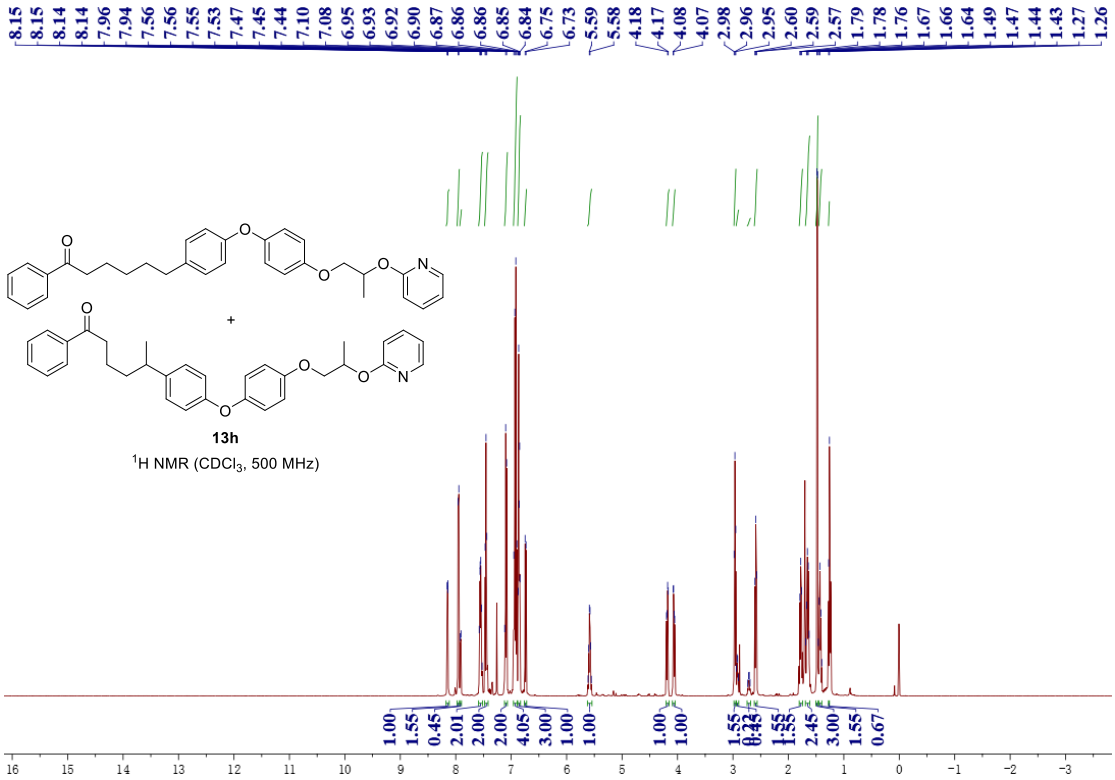

199.61
198.30
151.46
151.34
134.20
134.19
133.12
128.64
127.98
56.60
56.59
46.65
37.37
34.36
33.84
29.69
25.43
OMe
NO2
+
OMe
NO2
O
13e
13C NMR (CDCl3, 126 MHz)

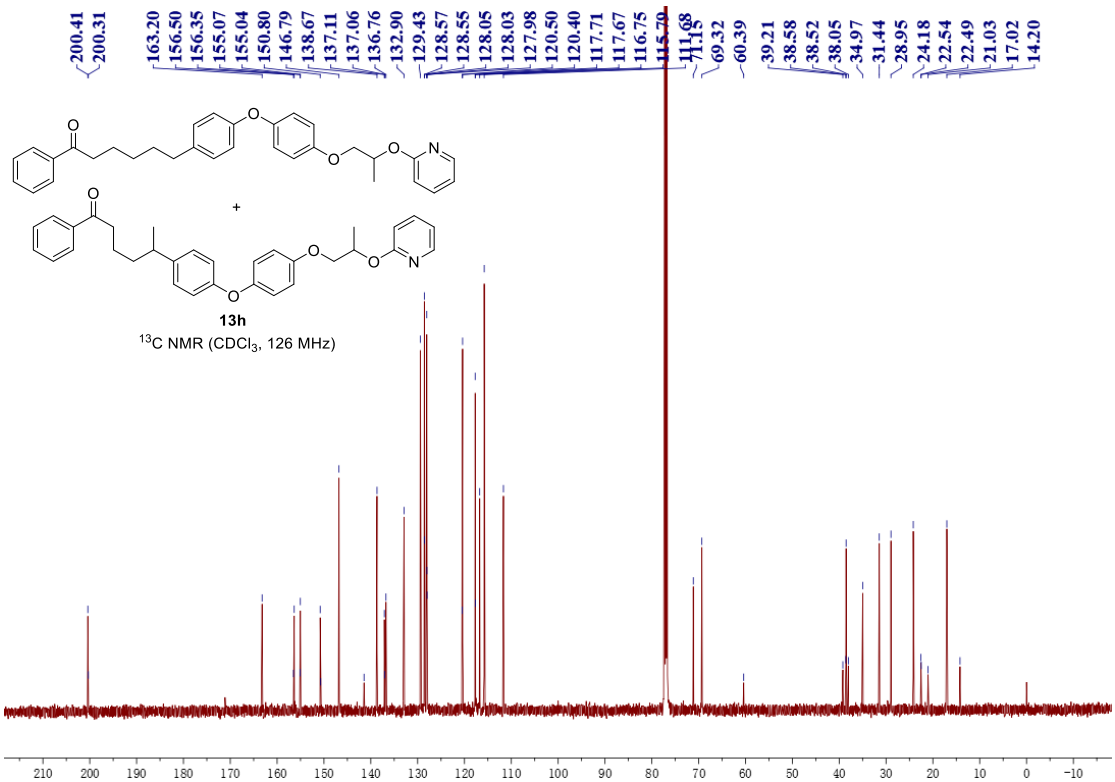

7.96 7.94 7.88 7.87 7.58 7.56 7.54 7.53 7.47 7.46 7.44 7.43 7.42 7.25 7.23 7.21 7.00 6.99 6.98 6.97 6.96 3.02 3.01 2.99 2.91 2.90 2.88 2.87 2.86 2.84 2.82 2.70 2.69 2.67 2.07 2.05 2.03 2.02 1.84 1.83 1.81 1.80 1.79 1.76 1.75 1.73 1.72 1.70 1.33 1.32
O
CN
O
+
O
O
CN
13f
1H NMR (CDCl3, 500 MHz)
1.58 0.42 3.00 2.00 2.00 4.00 1.58 0.63 1.58 0.42 1.58 1.58 0.63
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3

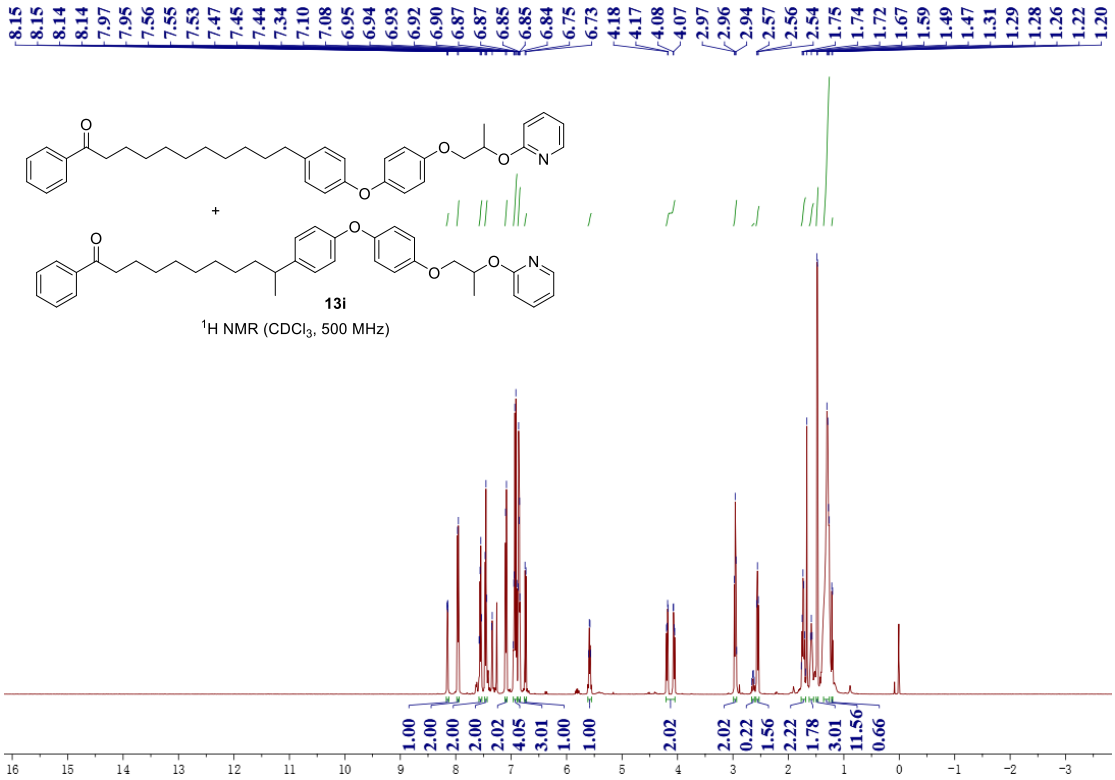

200.17 200.10 162.00 152.72 139.30 137.03 134.08 133.00 130.07 128.74 128.61 128.57 128.03 127.98 120.46 120.37 118.91 117.76 117.68 105.86 105.55 38.94 38.34 36.58 35.15 32.56 31.07 23.88 22.46
O
CN
O
+
O
O
CN
13f
13C NMR (CDCl3, 126 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

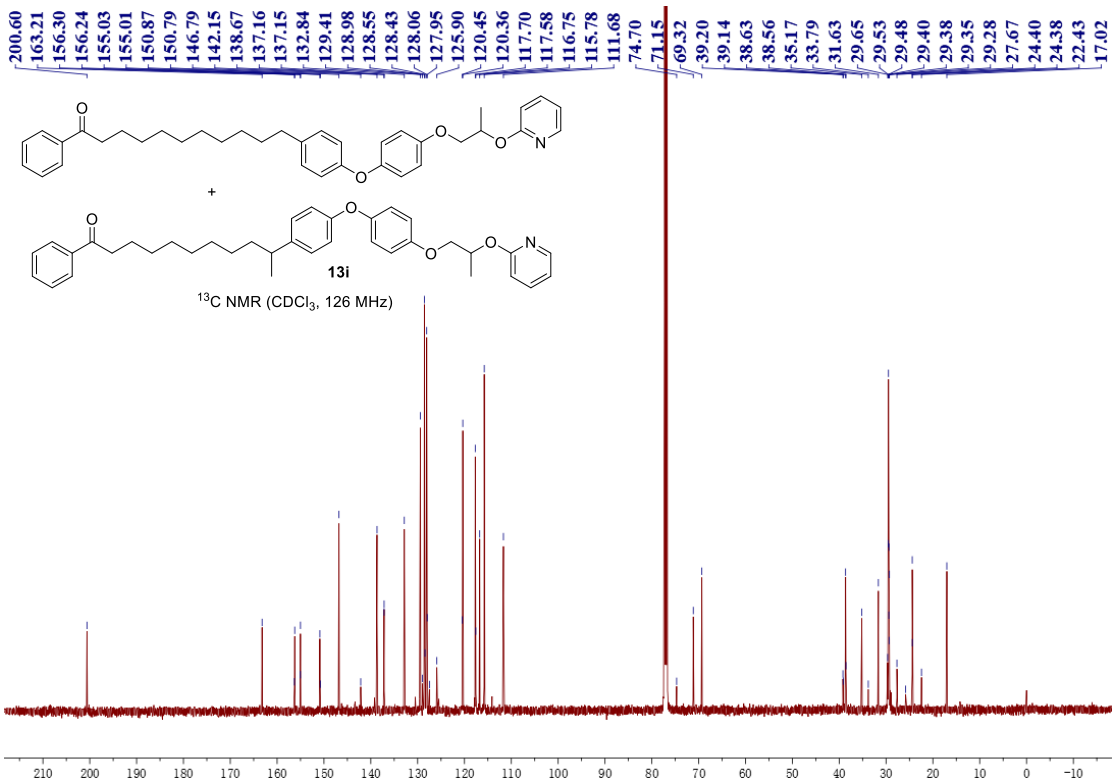

7.95 7.93 7.86 7.84 7.62 7.57 7.55 7.54 7.53 7.51 7.47 7.45 7.44 7.42 7.40 7.31 7.29 7.27 6.93 6.91 6.90 6.88 3.88 3.88 3.00 2.99 2.97 2.85 2.83 2.82 2.81 2.80 2.79 2.77 2.64 2.63 2.61 2.06 2.04 1.97 1.79 1.78 1.76 1.75 1.72 1.71 1.69 1.67 1.30 1.28
CO2Me
OMe
CO2Me
OMe
13g
1H NMR (CDCl3, 500 MHz)
1.45 0.55 1.00 1.00 1.45 0.55 1.01 1.01 6.00 1.45 0.83 1.45 0.28 0.28 1.45 1.45 0.83
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3

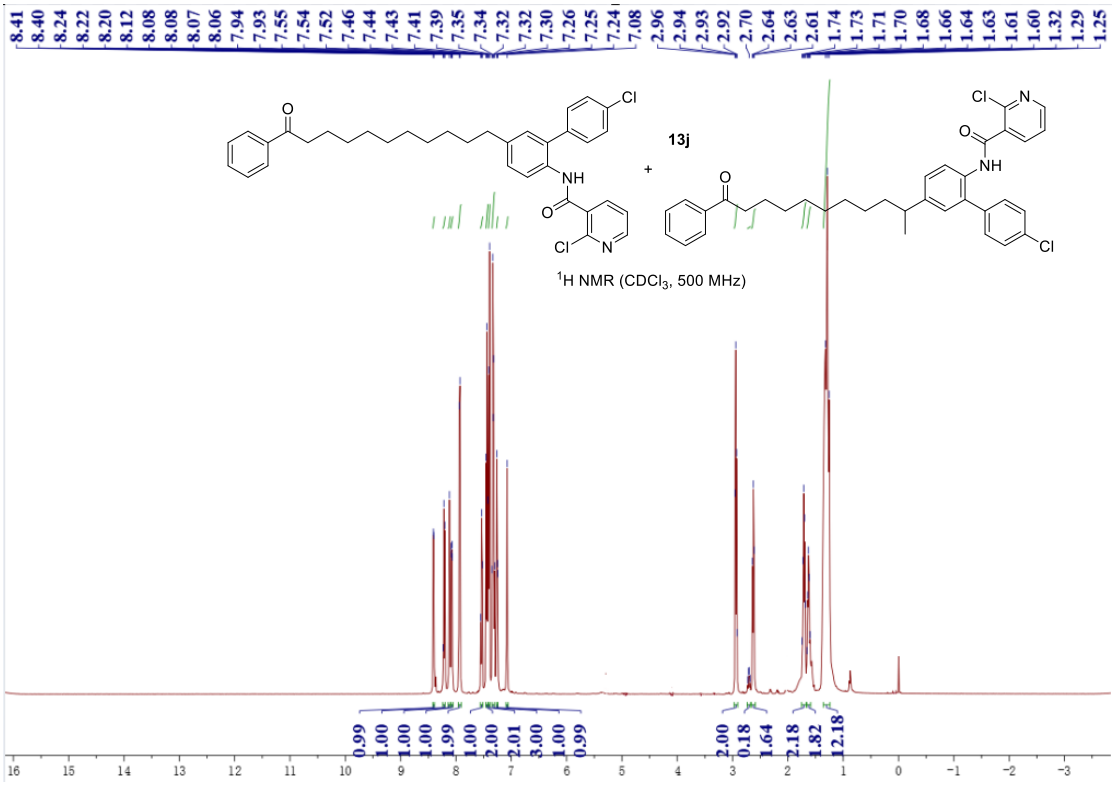

200.21 200.19 166.86 157.59 157.39 138.26 137.04 136.96 133.96 133.38 132.94 132.93 132.01 131.36 130.10 128.58 128.53 128.03 128.00 119.99 119.81 112.36 112.19 56.15 56.14 51.97 51.96 38.55 38.34 36.58 34.64 32.46 31.08 23.85 22.57
CO2Me
OMe
CO2Me
OMe
13g
13C NMR (CDCl3, 126 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

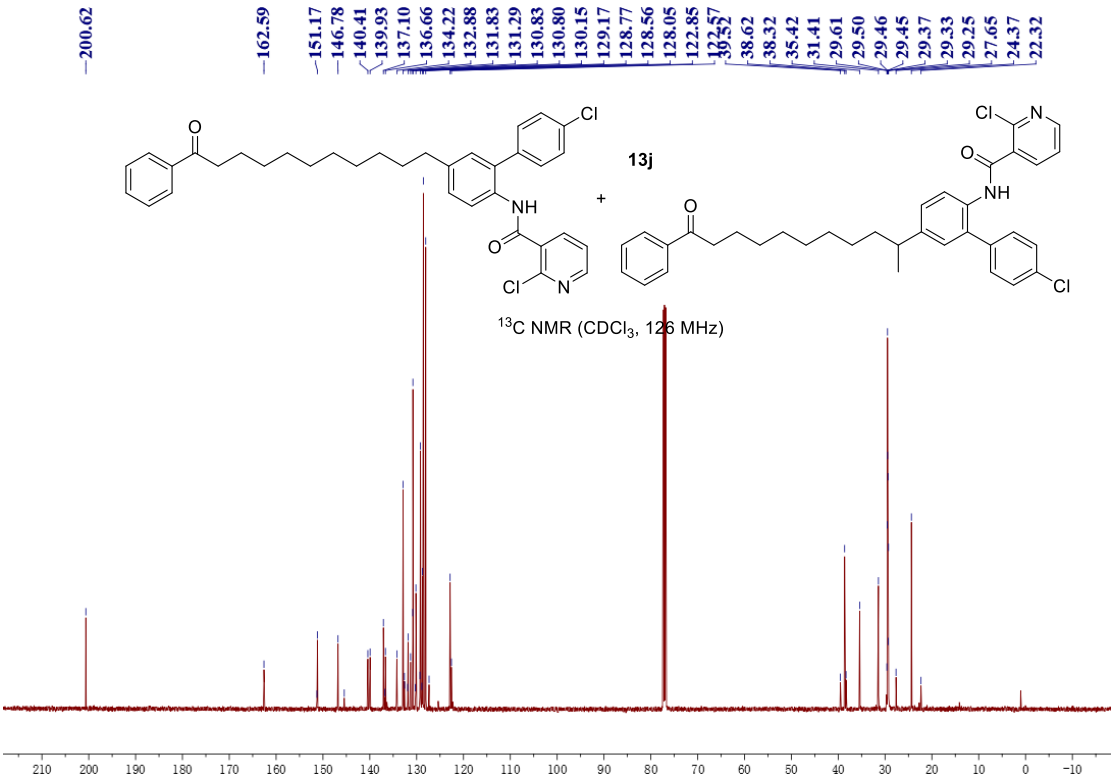

13h
^{1}H NMR ($CDCl_3$, 500 MHz)

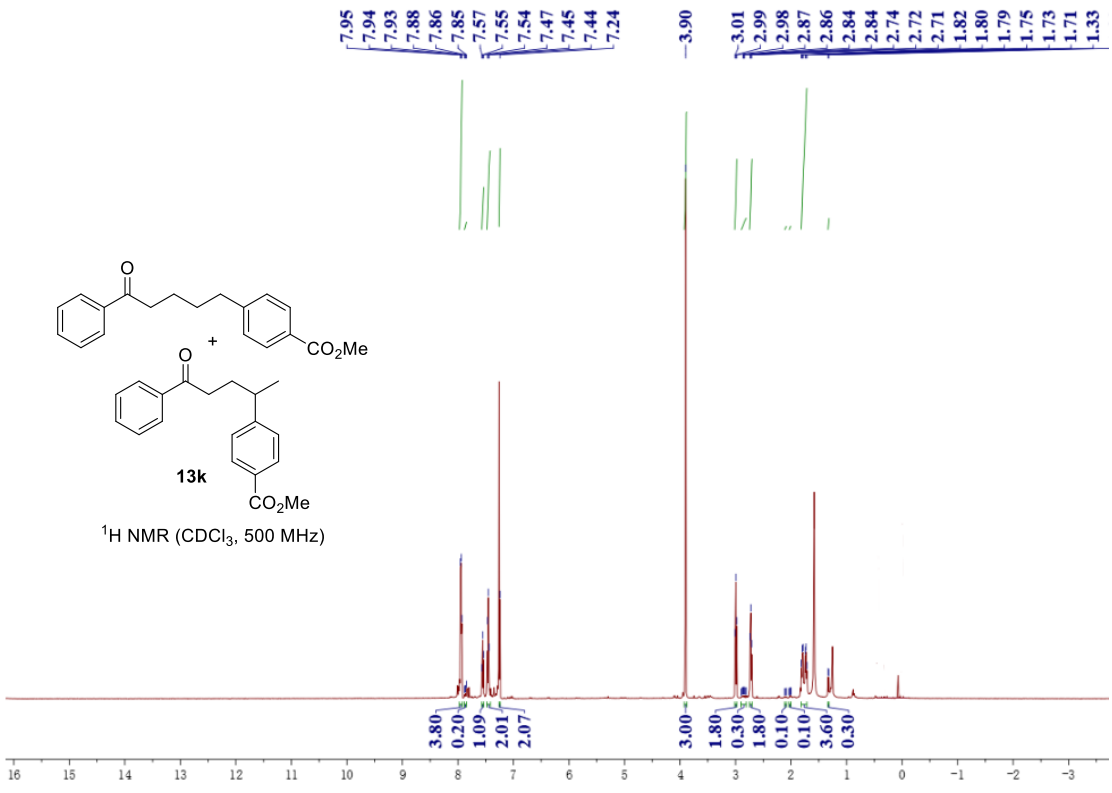

13h
^{13}C NMR ($CDCl_3$, 126 MHz)


13i
^{1}H NMR ($CDCl_3$, 500 MHz)

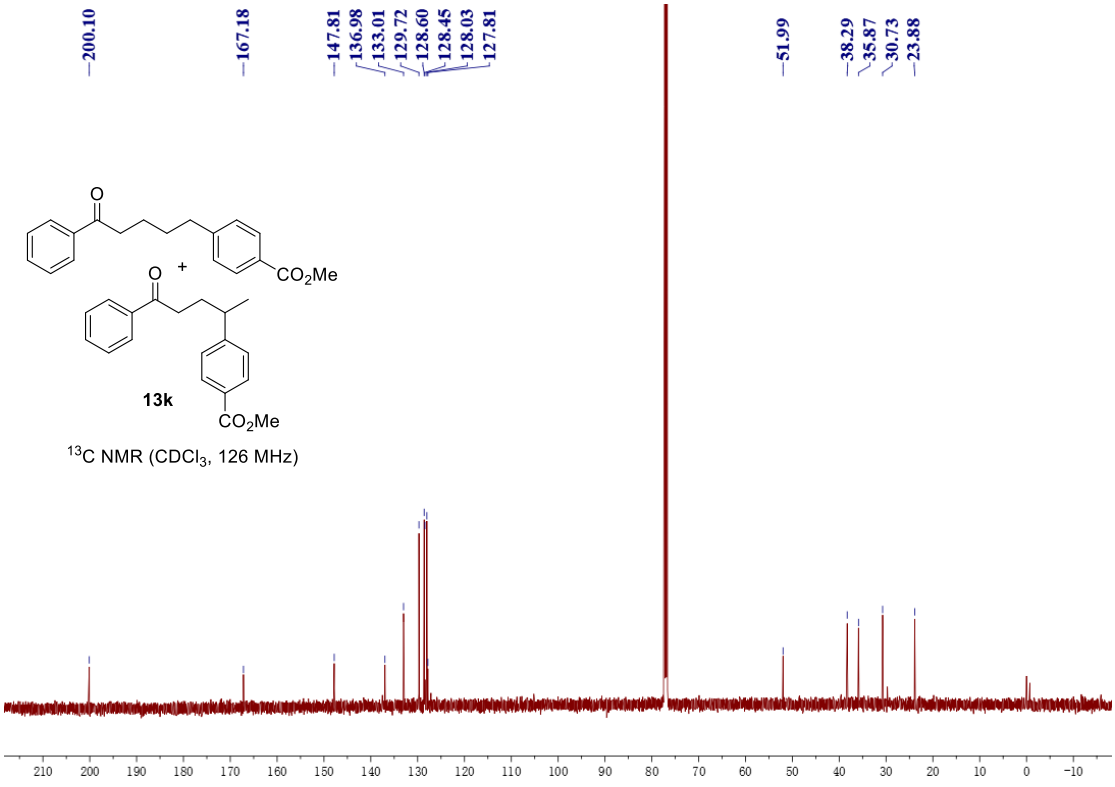

13i
^{13}C NMR ($CDCl_3$, 126 MHz)


13j
^{1}H NMR ($CDCl_3$, 500 MHz)

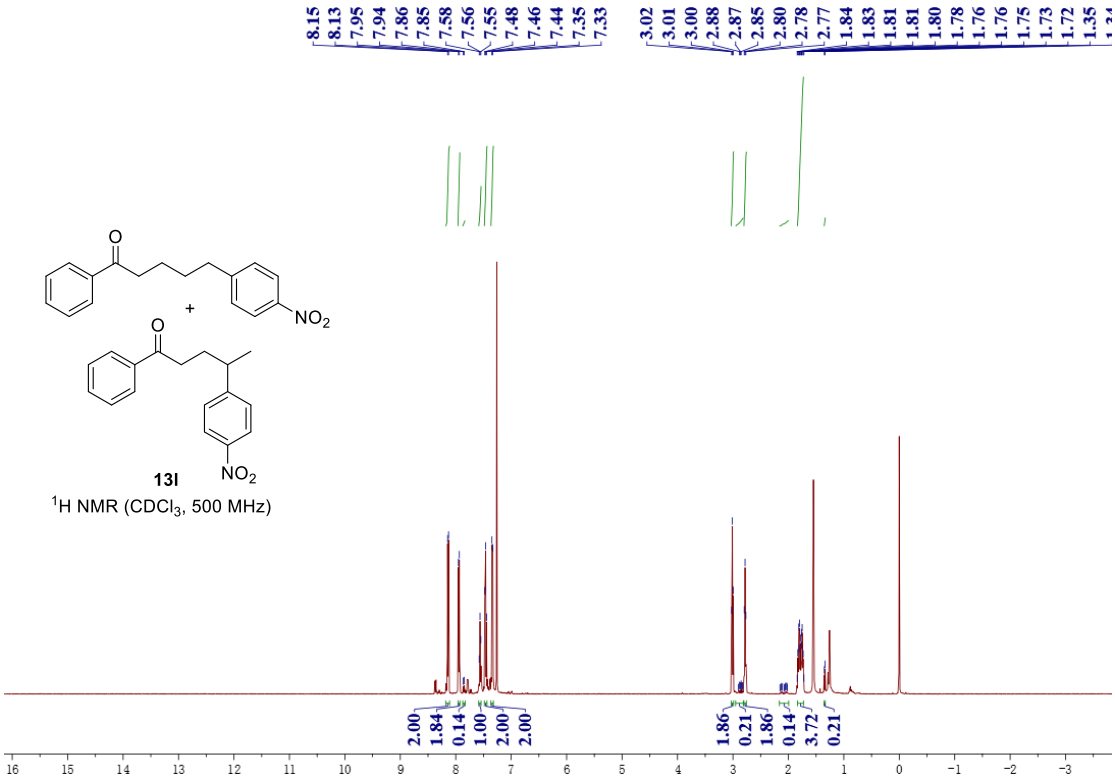

13j
^{13}C NMR ($CDCl_3$, 126 MHz)



^{1}H NMR ($CDCl_3$, 500 MHz)

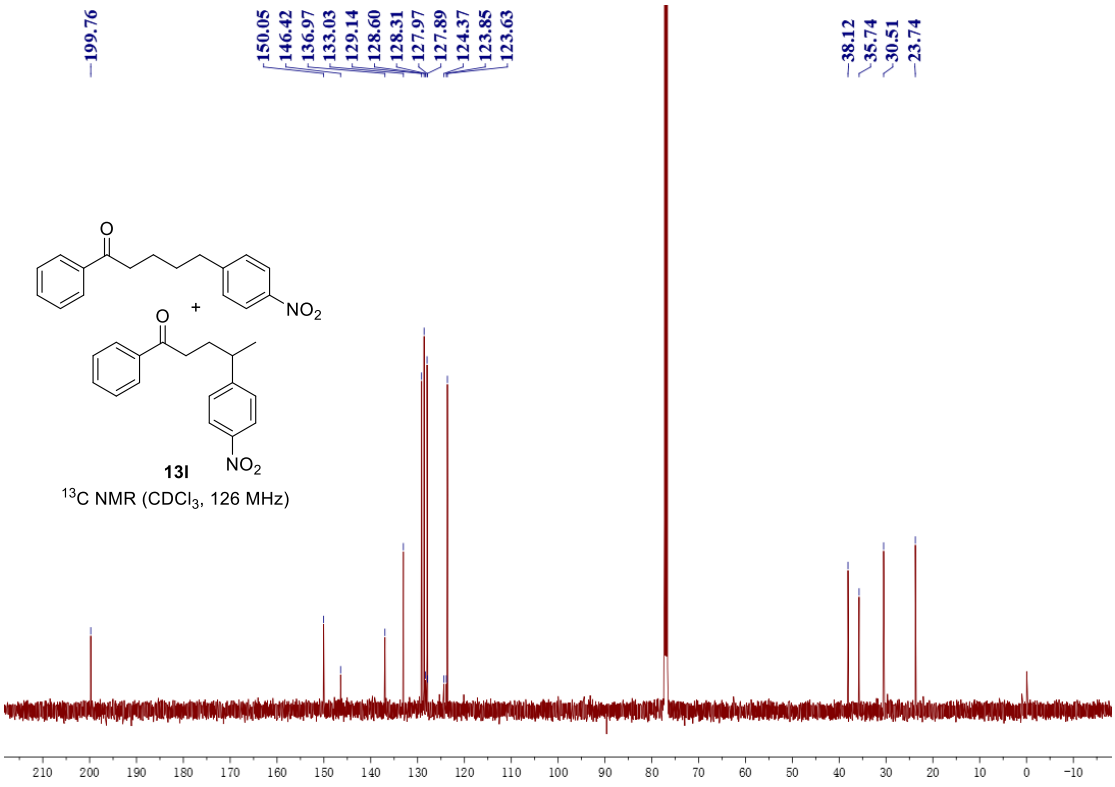


^{13}C NMR ($CDCl_3$, 126 MHz)



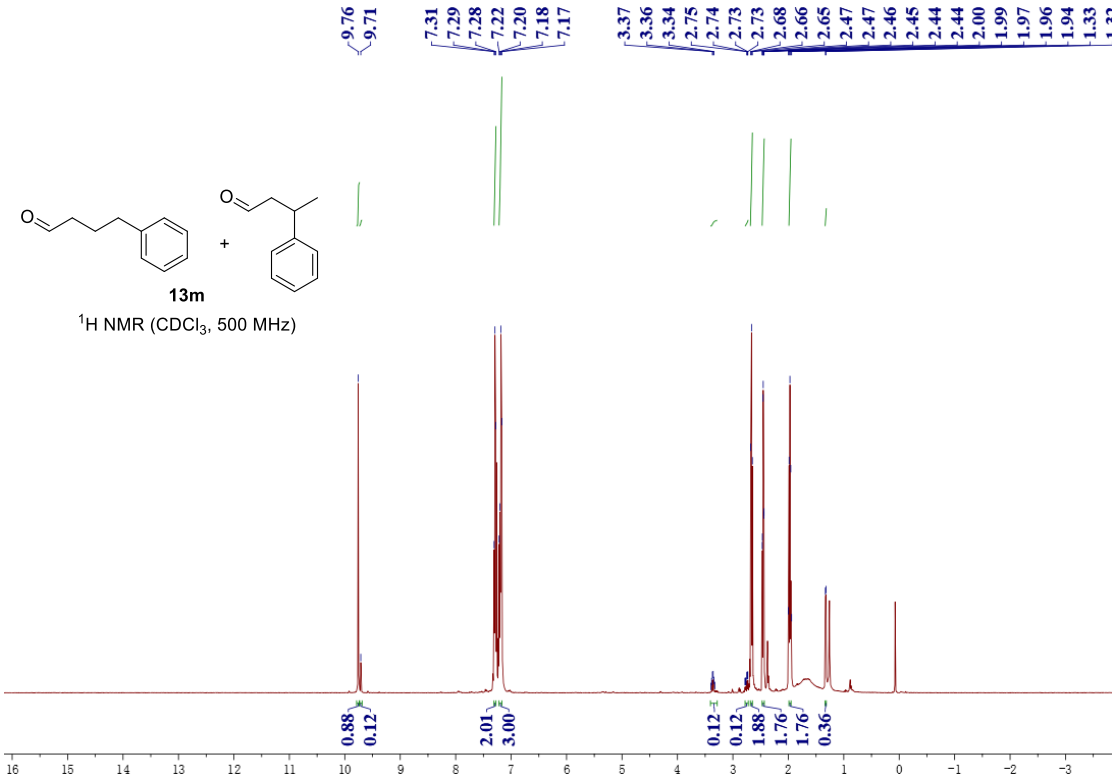
13l

^{1}H NMR ($CDCl_3$, 500 MHz)



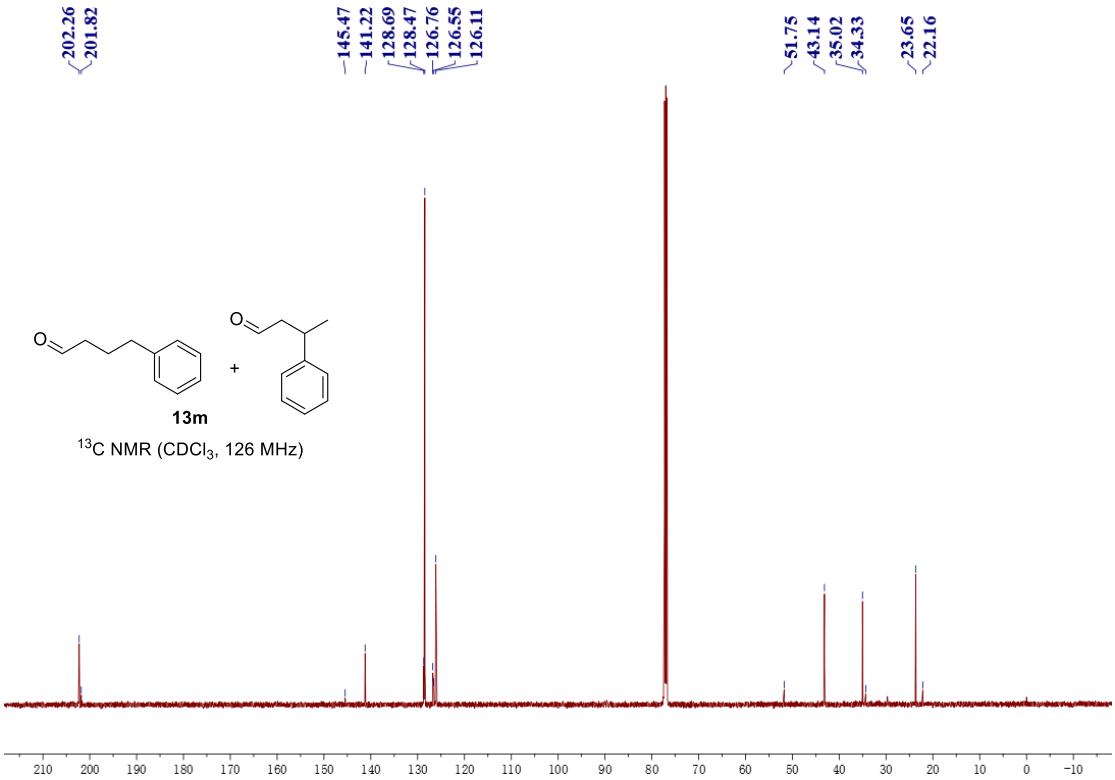
13l

^{13}C NMR ($CDCl_3$, 126 MHz)



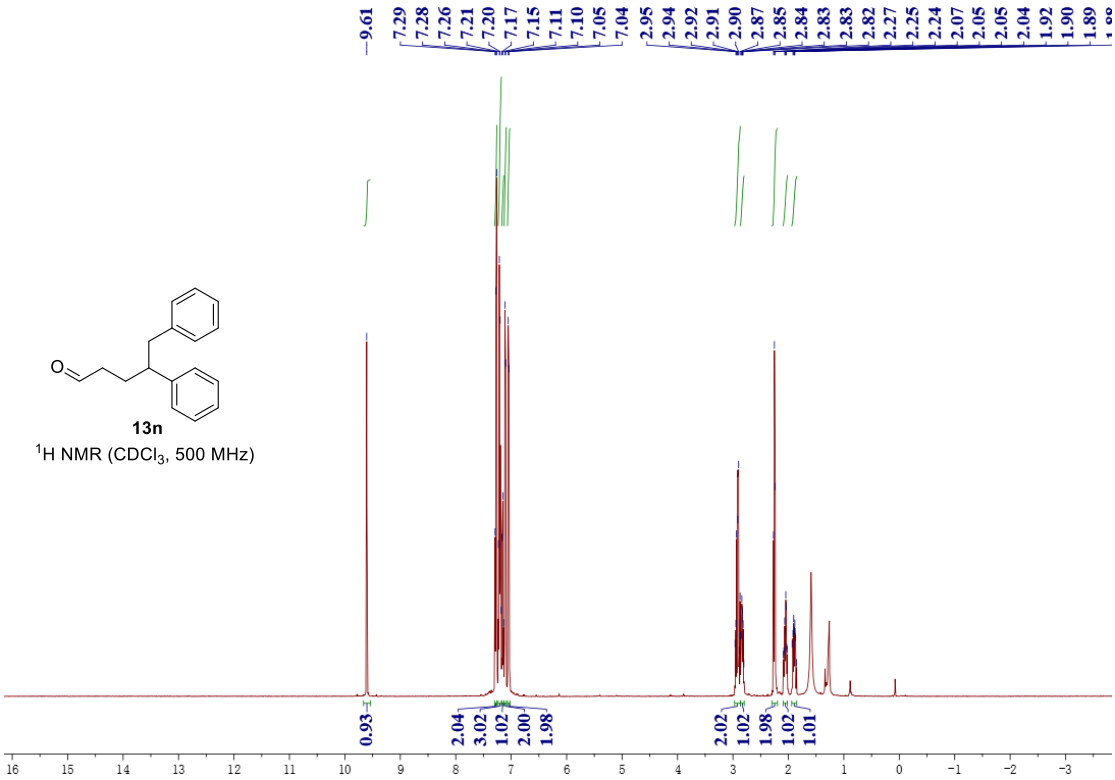
13m

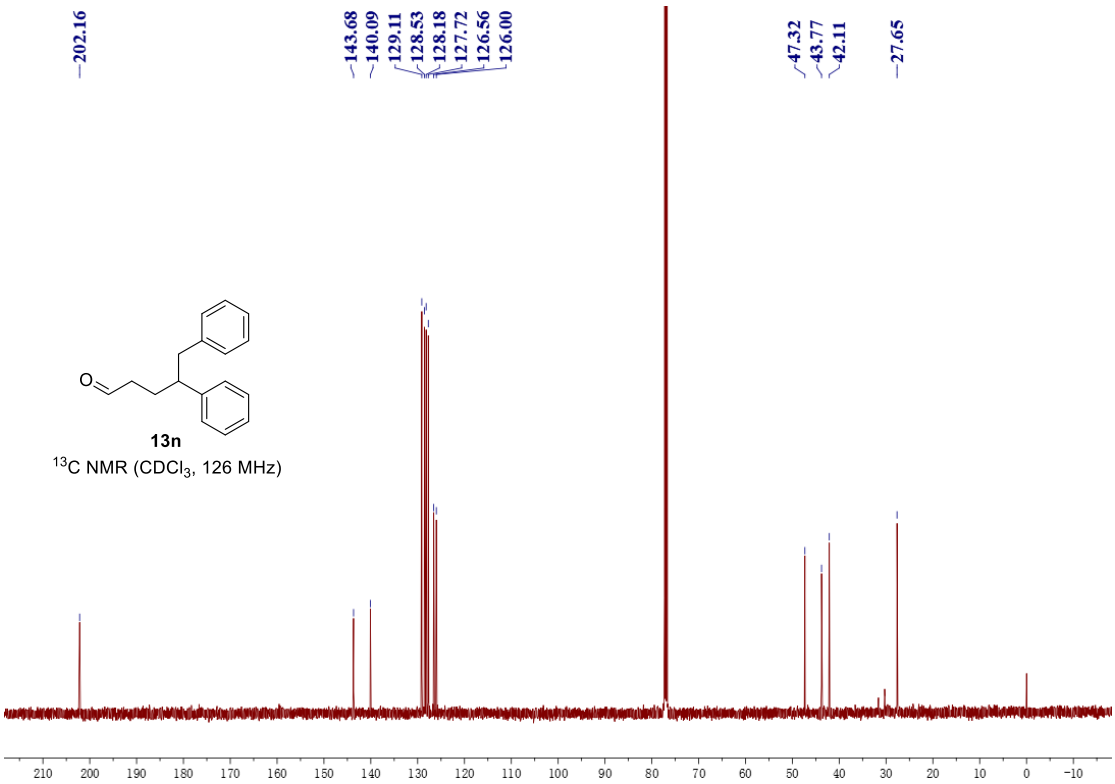
^{1}H NMR ($CDCl_3$, 500 MHz)

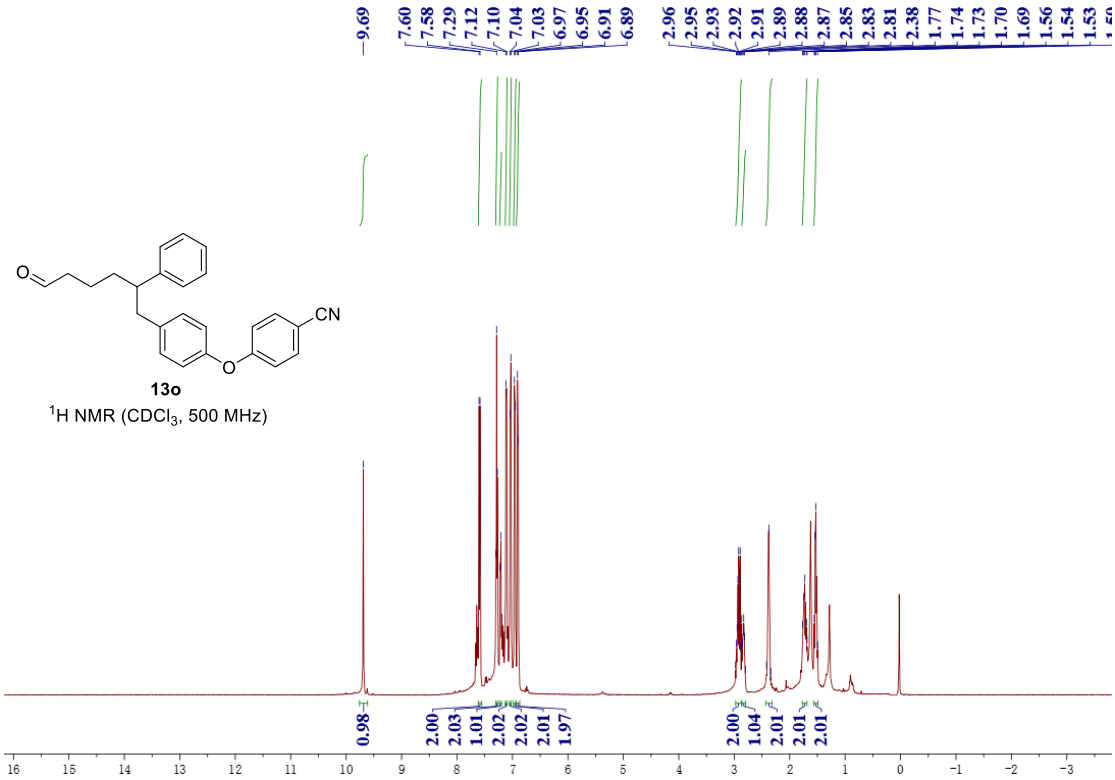


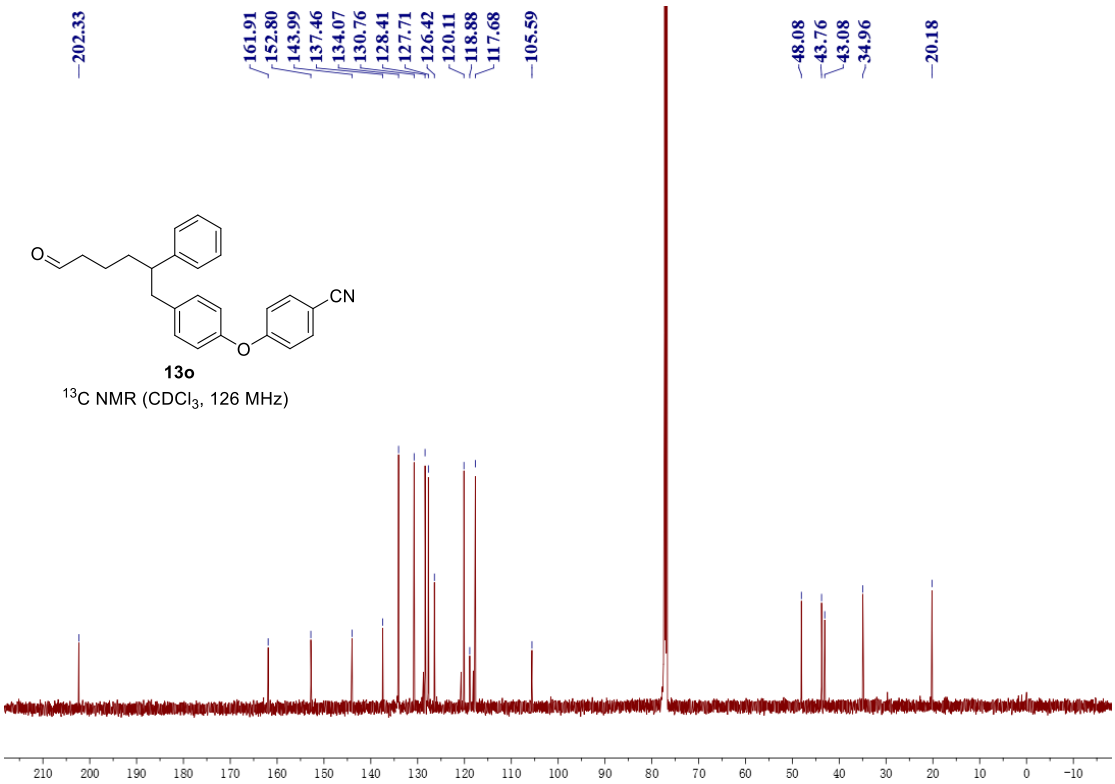
13m

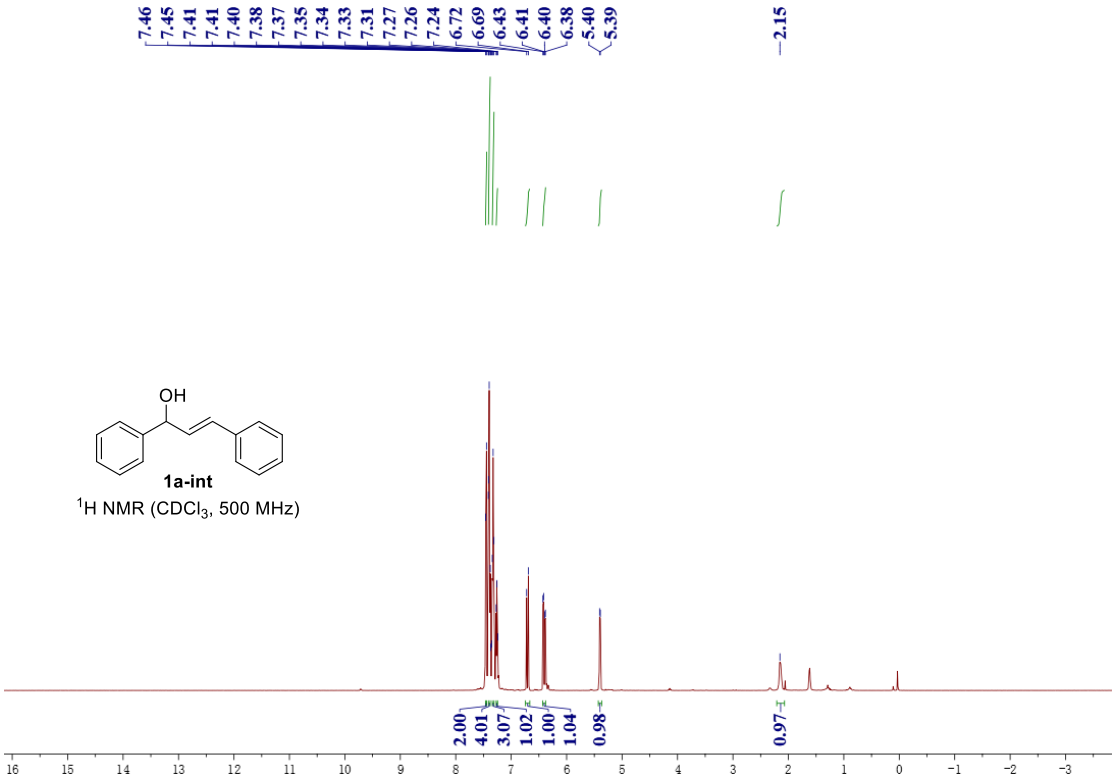
^{13}C NMR ($CDCl_3$, 126 MHz)

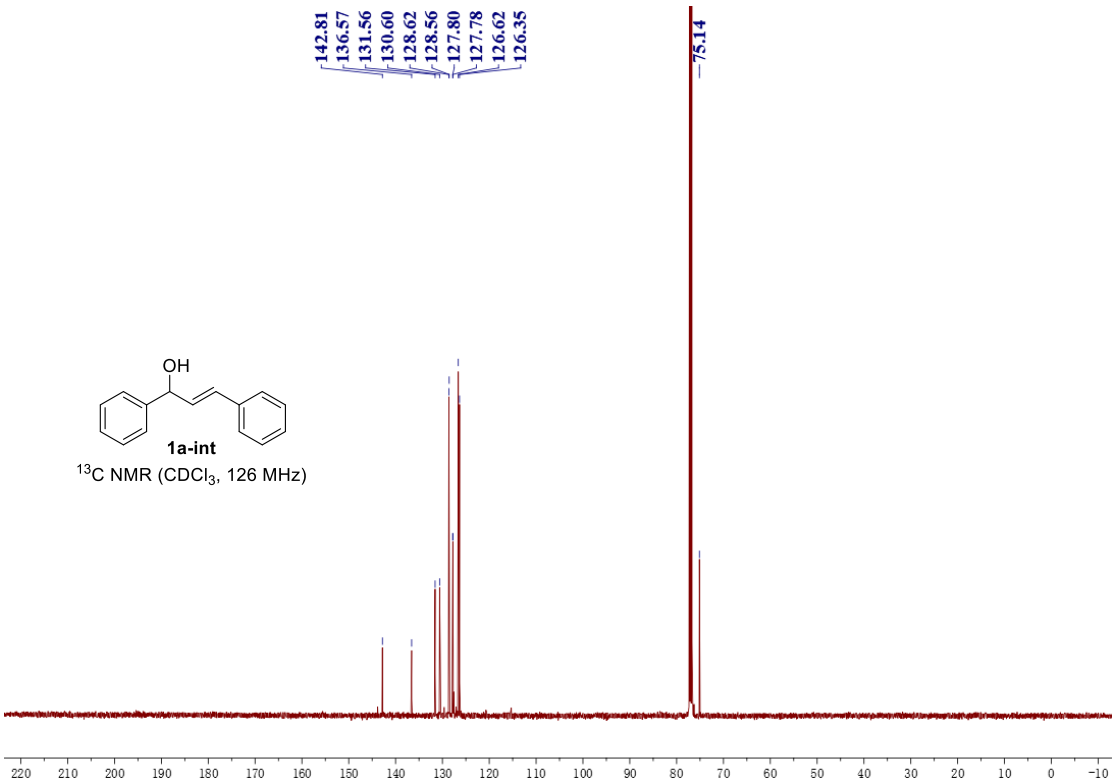

9.61
7.29
7.28
7.26
7.21
7.20
7.17
7.15
7.11
7.10
7.05
7.04
2.95
2.94
2.92
2.91
2.90
2.87
2.85
2.84
2.83
2.83
2.82
2.27
2.25
2.24
2.07
2.05
2.05
2.04
1.92
1.90
1.89
0.93
2.04
3.02
1.02
2.00
1.98
2.02
1.02
1.98
1.02
1.01
O
13n
1H NMR (CDCl3, 500 MHz)

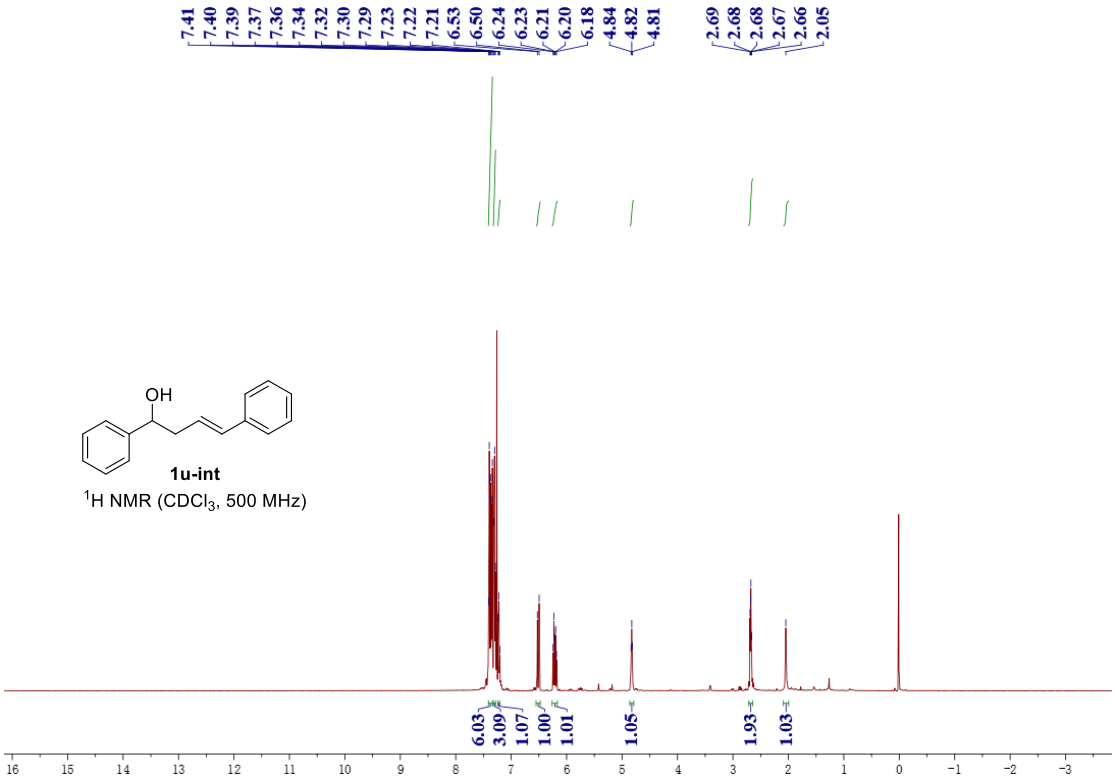

202.16
143.68
140.09
129.11
128.53
128.18
127.72
126.56
126.00
47.32
43.77
42.11
27.65
O
13n
13C NMR (CDCl3, 126 MHz)

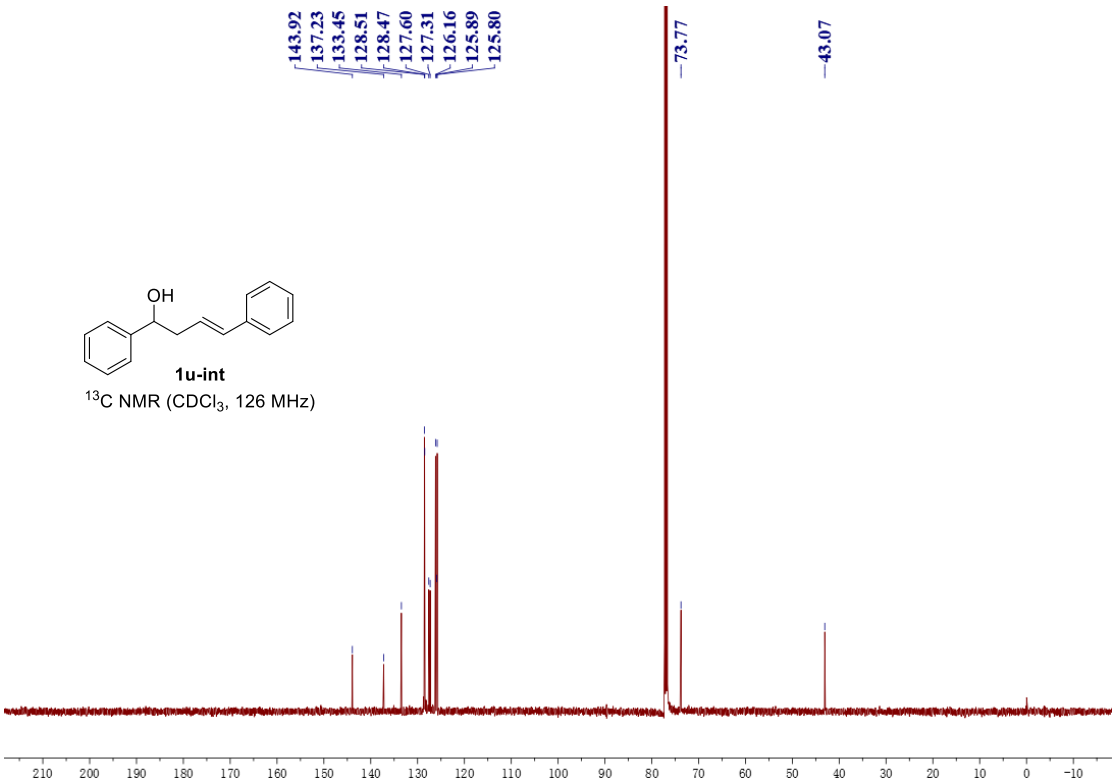

9.69
7.60
7.58
7.29
7.12
7.10
7.04
7.03
6.97
6.95
6.91
6.89
2.96
2.95
2.93
2.92
2.91
2.89
2.88
2.87
2.85
2.83
2.81
2.38
1.77
1.74
1.73
1.70
1.69
1.56
1.54
1.53
O
CN
O
13o
1H NMR (CDCl3, 500 MHz)
0.98
2.00
2.03
1.01
2.02
2.02
2.01
1.97
2.00
1.04
2.01
2.01
2.01

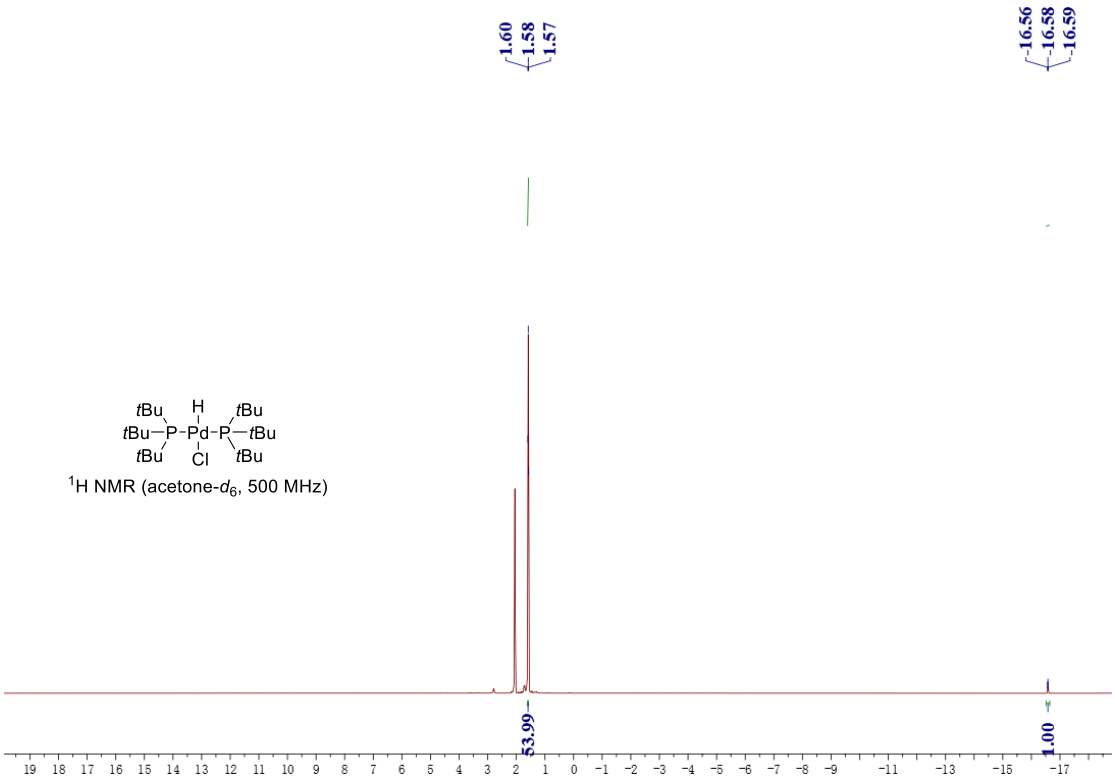

202.33
161.91
152.80
143.99
137.46
134.07
130.76
128.41
127.71
126.42
120.11
118.88
117.68
105.59
48.08
43.76
43.08
34.96
20.18
O
CN
O
13o
13C NMR (CDCl3, 126 MHz)


7.46
7.45
7.41
7.41
7.40
7.38
7.37
7.35
7.34
7.33
7.31
7.27
7.26
7.24
6.72
6.69
6.43
6.41
6.40
6.38
5.40
5.39
2.15
OH
1a-int
1H NMR (CDCl3, 500 MHz)
2.00
4.01
3.07
1.02
1.00
1.04
0.98
0.97

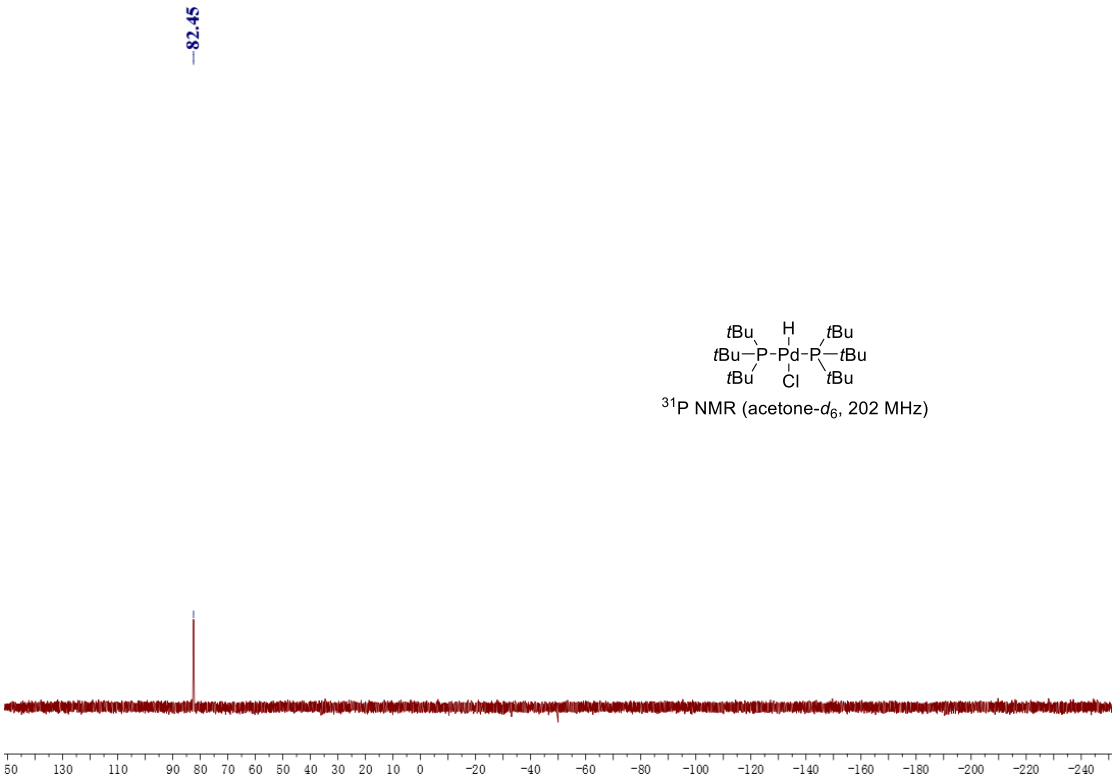

142.81
136.57
131.56
130.60
128.62
128.56
127.80
127.78
126.62
126.35
75.14
OH
1a-int
13C NMR (CDCl3, 126 MHz)


7.41
7.40
7.39
7.37
7.36
7.34
7.32
7.30
7.29
7.23
7.22
7.21
6.53
6.50
6.24
6.23
6.21
6.20
6.18
4.84
4.82
4.81
2.69
2.68
2.68
2.67
2.66
2.05
OH
1u-int
1H NMR (CDCl3, 500 MHz)
6.03
3.09
1.07
1.00
1.01
1.05
1.93
1.03

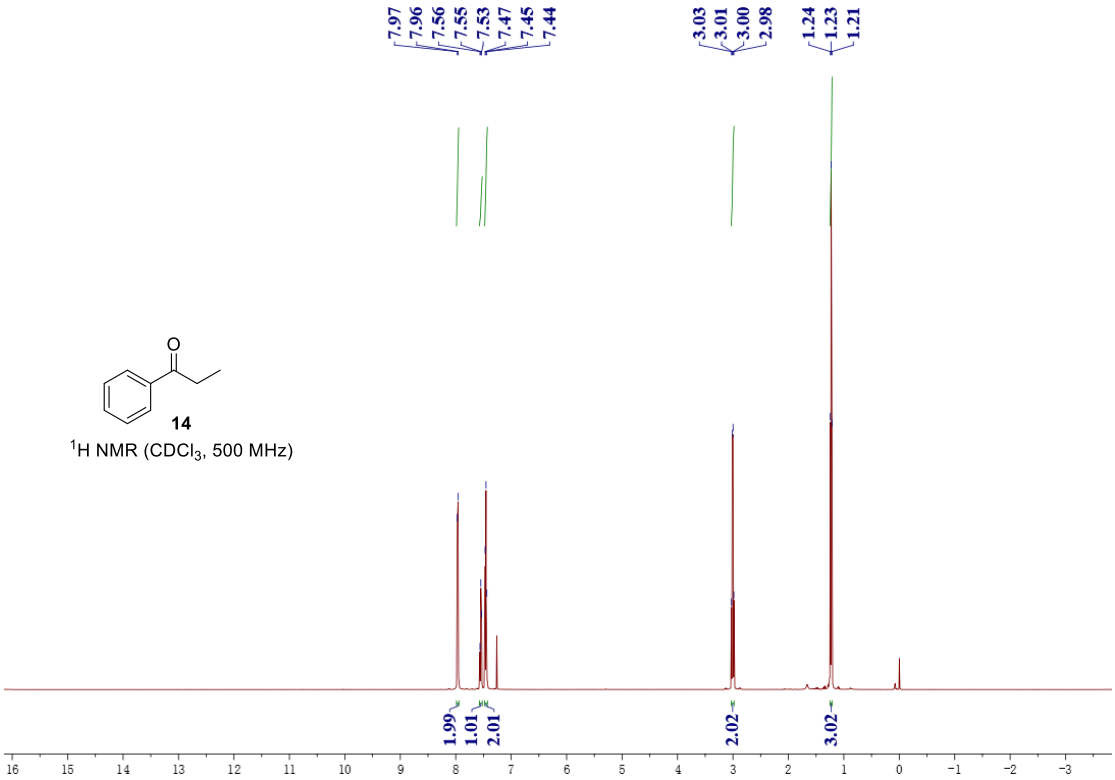

143.92
137.23
133.45
128.51
128.47
127.60
127.31
126.16
125.89
125.80
73.77
43.07
OH
1u-int
13C NMR (CDCl3, 126 MHz)

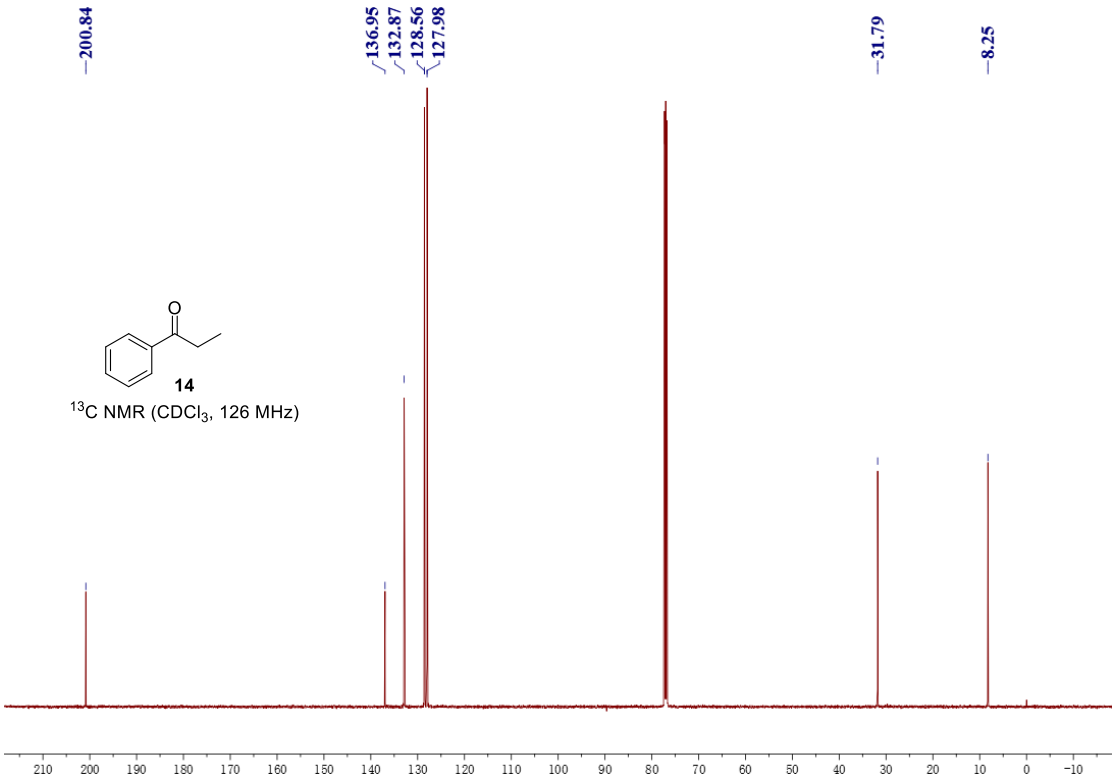


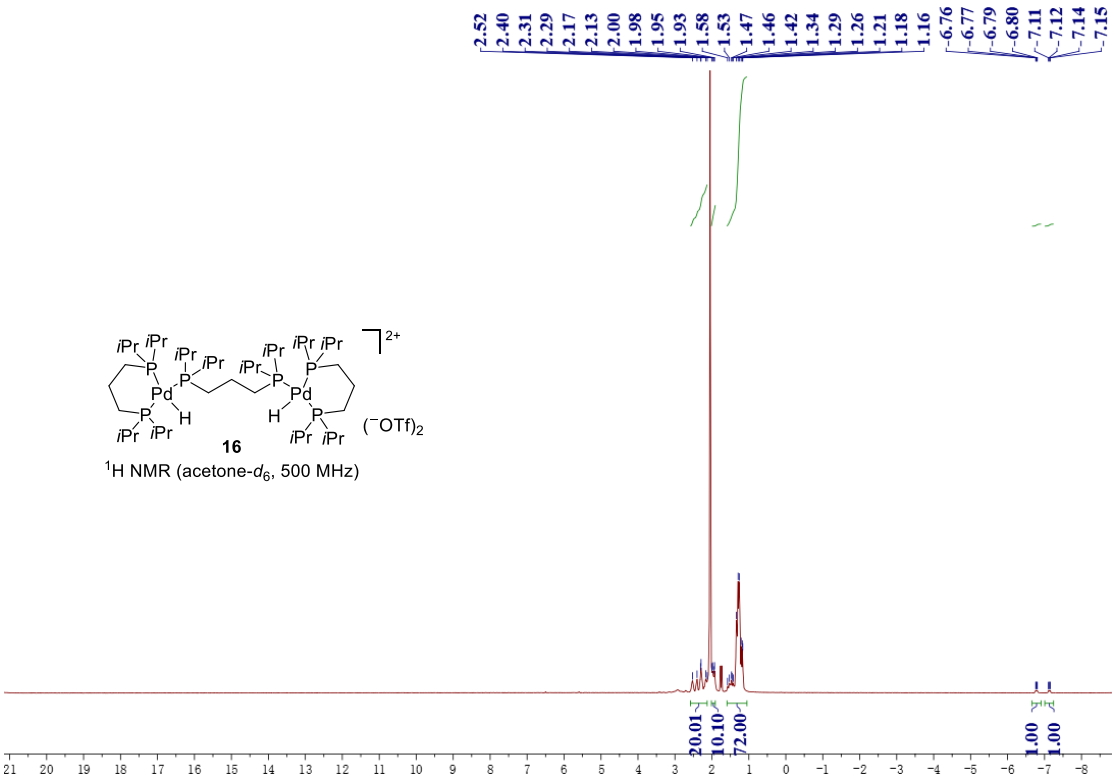
^{1}H NMR (acetone-d_6, 500 MHz)



^{31}P NMR (acetone-d_6, 202 MHz)

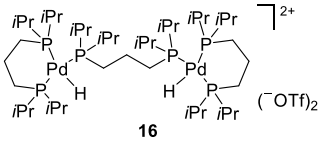

7.97
7.96
7.56
7.55
7.53
7.47
7.45
7.44
3.03
3.01
3.00
2.98
1.24
1.23
1.21
O
14
1H NMR (CDCl3, 500 MHz)
1.99
1.01
2.01
2.02
3.02
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3


200.84
136.95
132.87
128.56
127.98
31.79
8.25
O
14
13C NMR (CDCl3, 126 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10



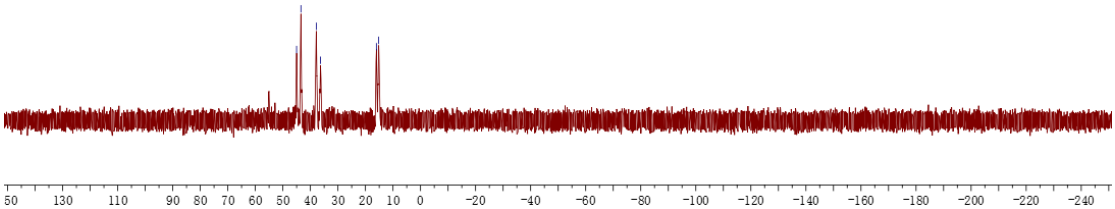
16

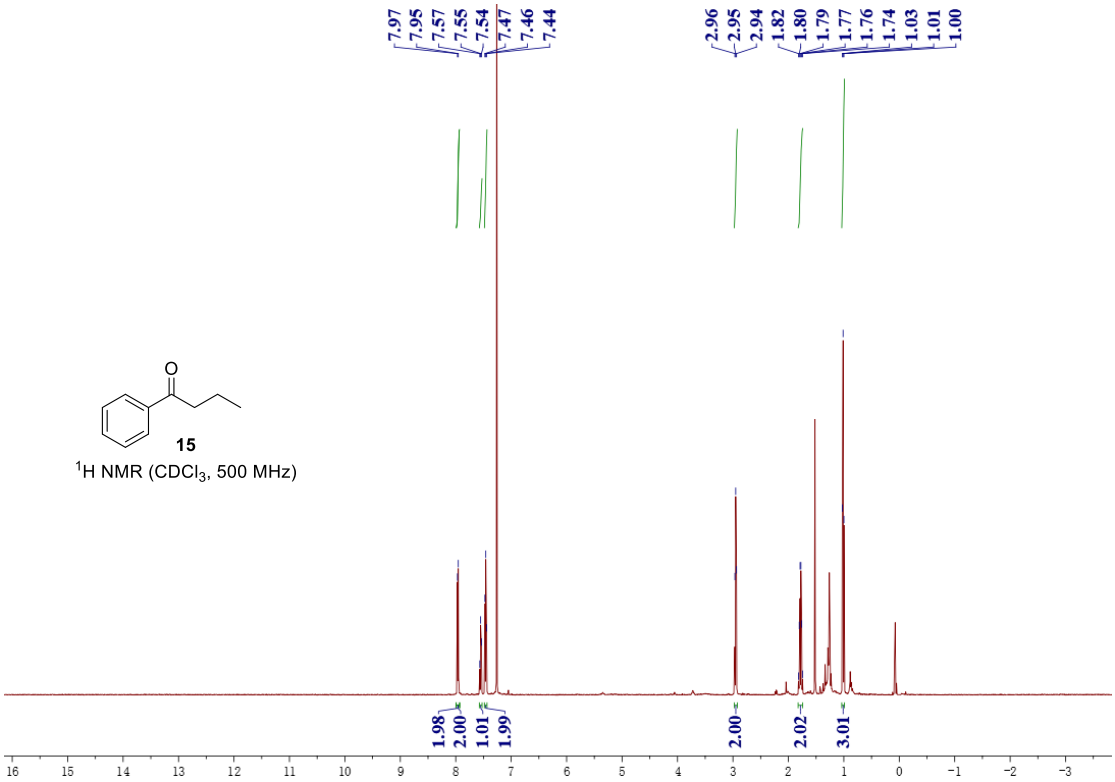
^{1}H NMR (acetone-d_6, 500 MHz)

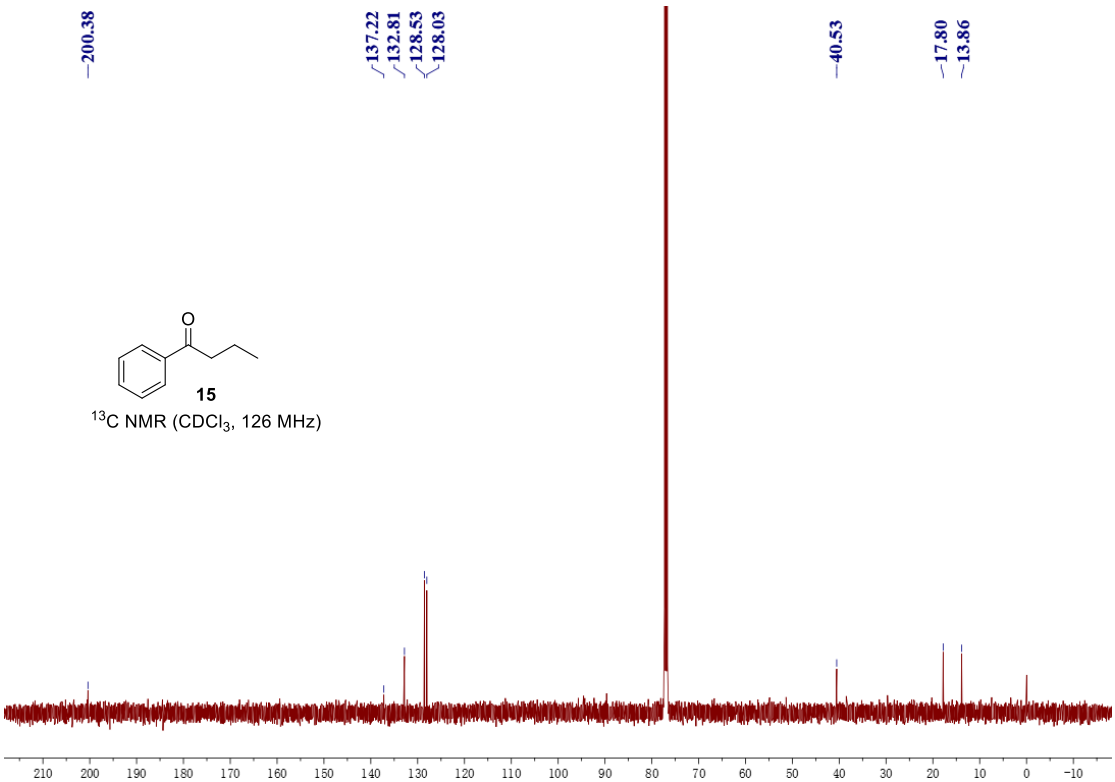


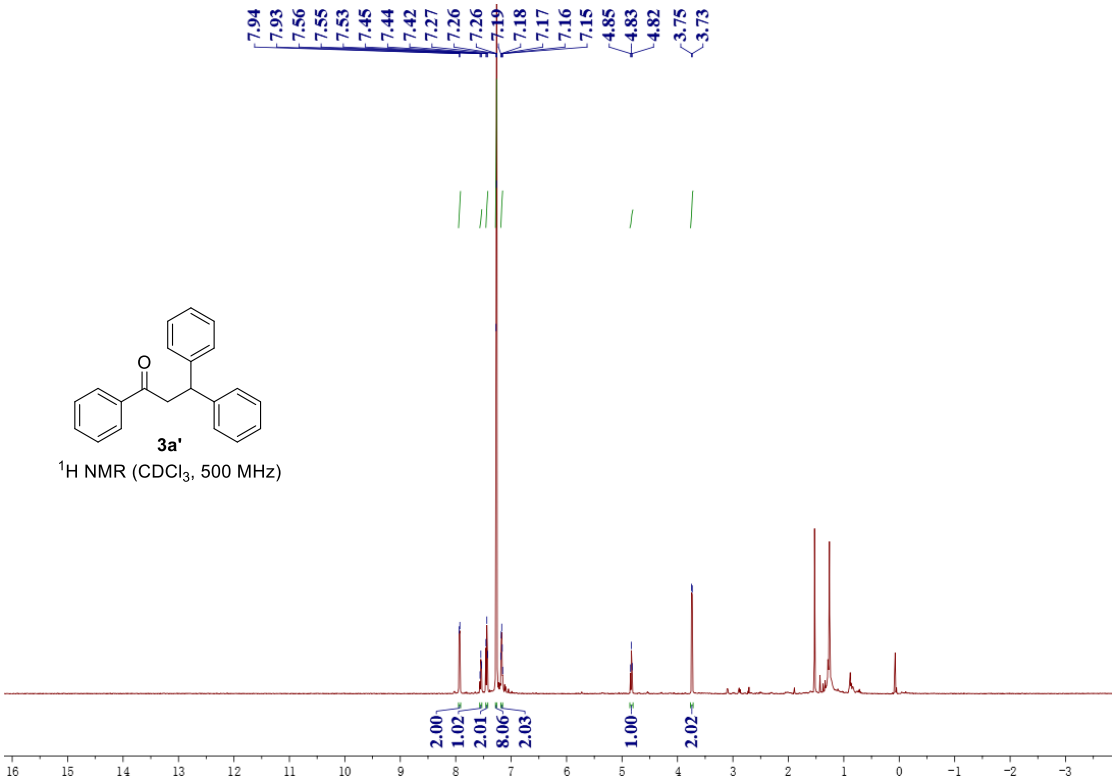
16

^{31}P NMR (acetone-d_6, 202 MHz)



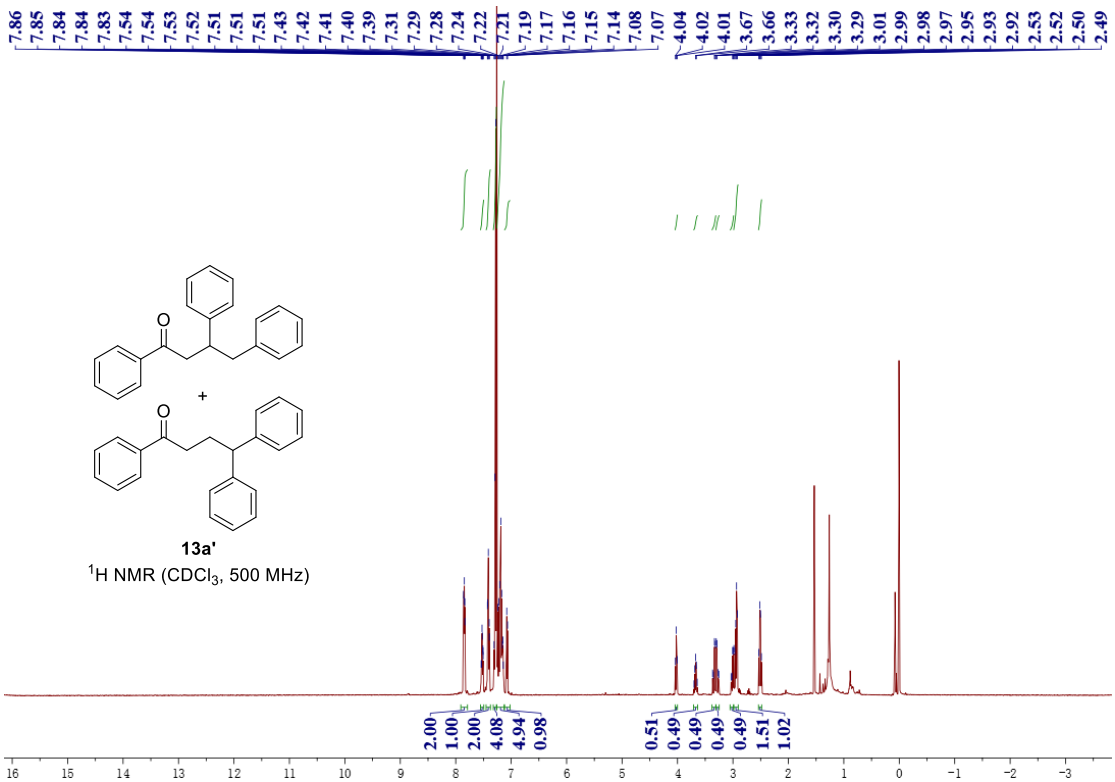

7.97
7.95
7.57
7.55
7.54
7.47
7.46
7.44
2.96
2.95
2.94
1.82
1.80
1.79
1.77
1.76
1.74
1.03
1.01
1.00
O
15
1H NMR (CDCl3, 500 MHz)
1.98
2.00
1.01
1.99
2.00
2.02
3.01


200.38
137.22
132.81
128.53
128.03
40.53
17.80
13.86
O
15
13C NMR (CDCl3, 126 MHz)



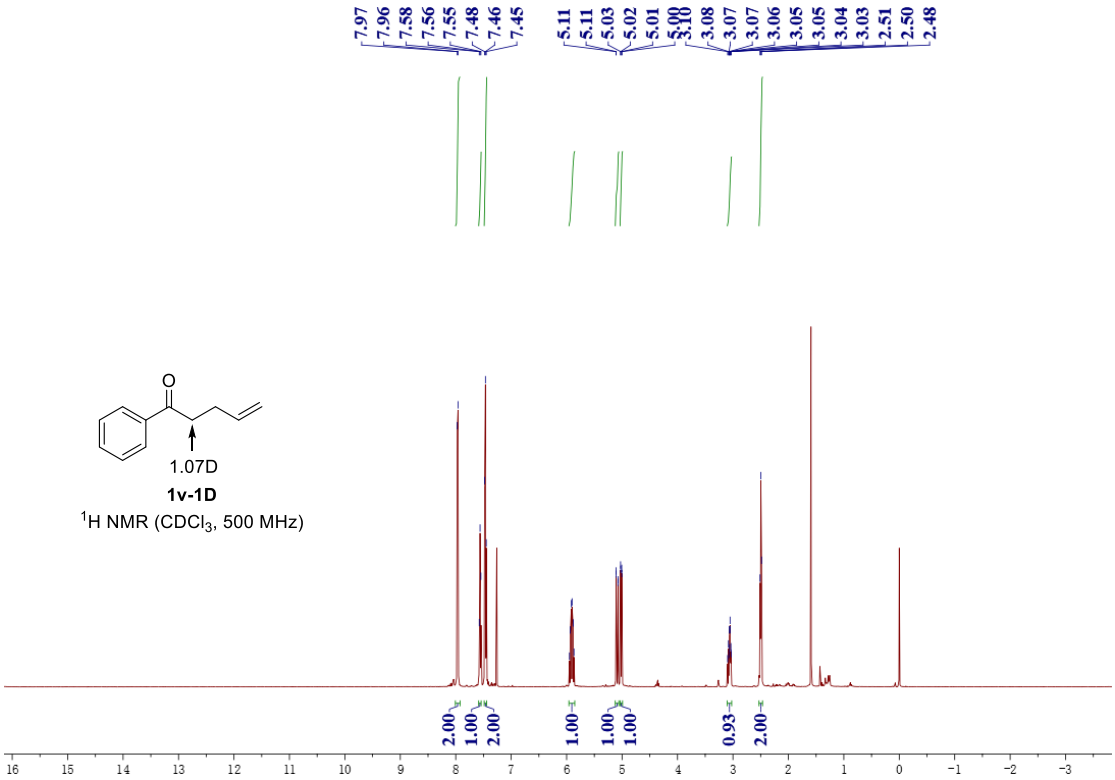
3a'

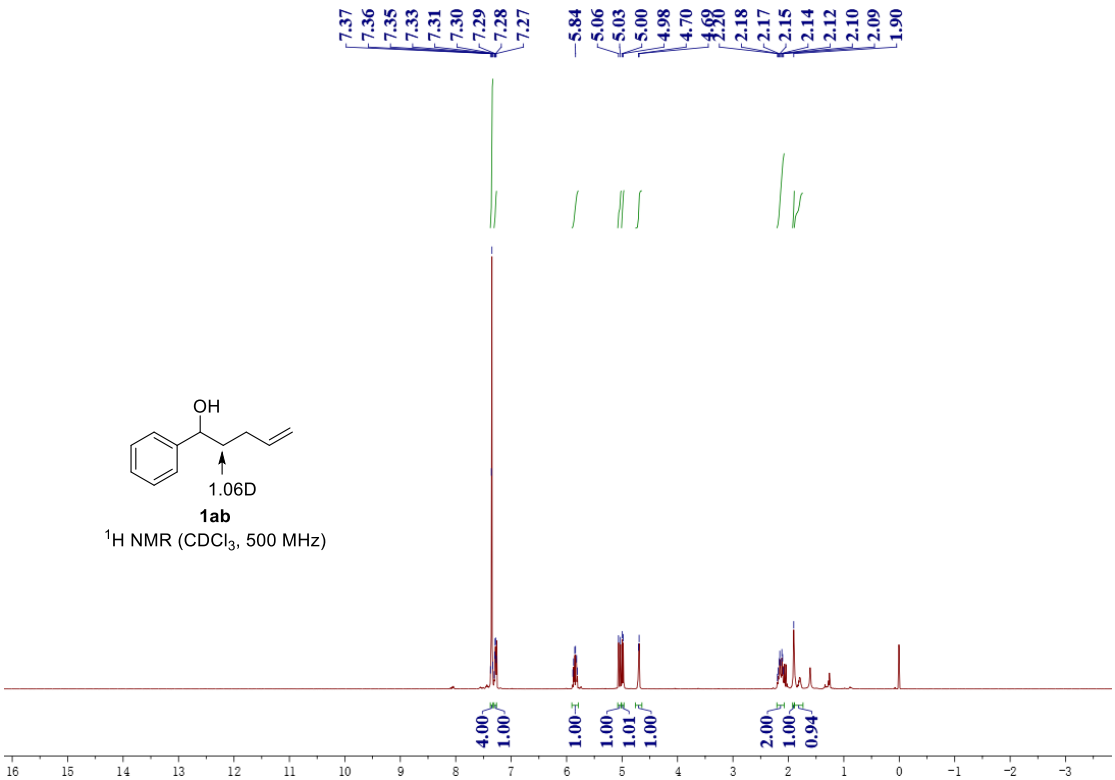
^{1}H NMR ($CDCl_3$, 500 MHz)

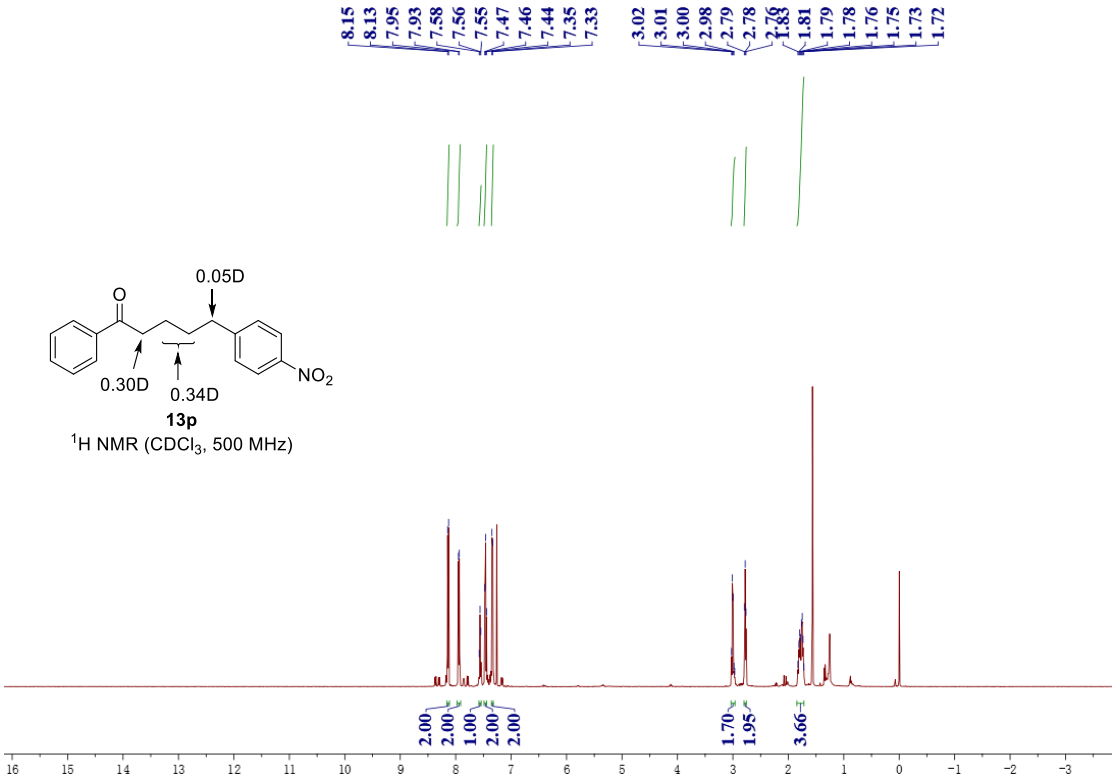


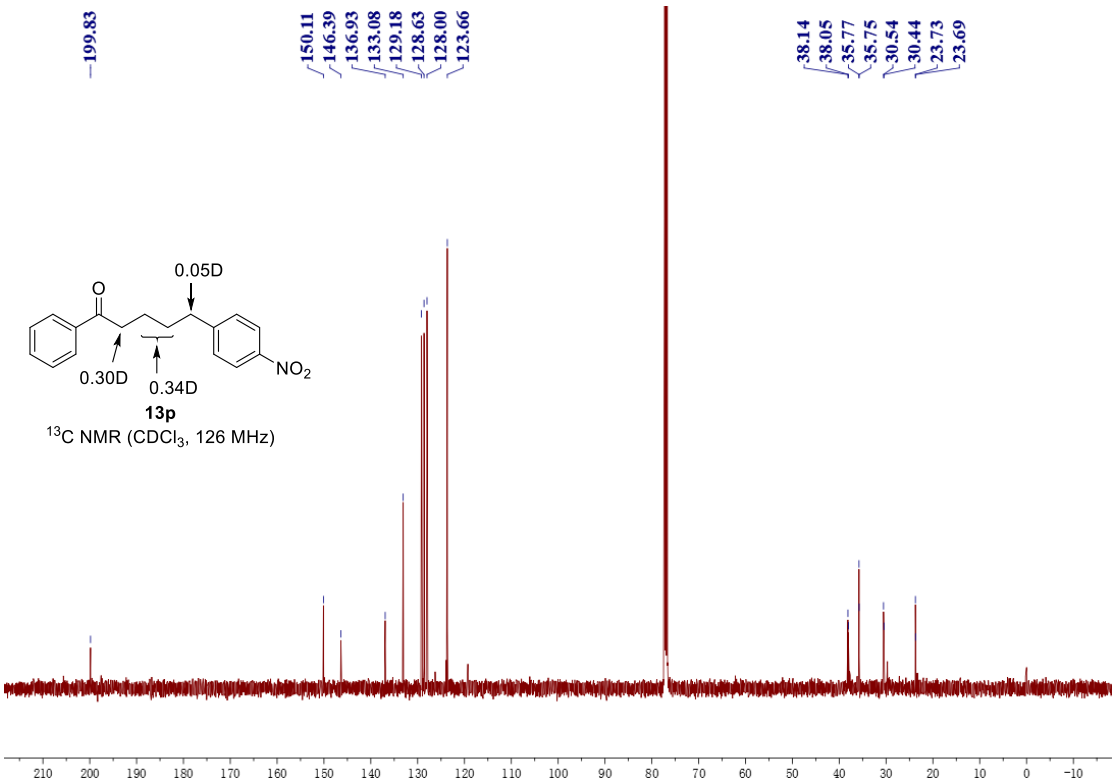
13a'

^{1}H NMR ($CDCl_3$, 500 MHz)


7.97
7.96
7.58
7.56
7.55
7.48
7.46
7.45
5.11
5.11
5.03
5.02
5.01
3.10
3.08
3.07
3.07
3.06
3.05
3.05
3.04
3.03
2.51
2.50
2.48
O
1.07D
1v-1D
1H NMR (CDCl3, 500 MHz)
2.00
1.00
2.00
1.00
1.00
1.00
0.93
2.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3


7.37
7.36
7.35
7.33
7.31
7.30
7.29
7.28
7.27
5.84
5.06
5.03
5.00
4.98
4.70
2.18
2.17
2.15
2.14
2.12
2.10
2.09
1.90
OH
1.06D
1ab
1H NMR (CDCl3, 500 MHz)
4.00
1.00
1.00
1.00
1.01
1.00
2.00
1.00
0.94
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3


8.15
8.13
7.95
7.93
7.58
7.56
7.55
7.47
7.46
7.44
7.35
7.33
3.02
3.01
3.00
2.98
2.79
2.78
1.83
1.81
1.79
1.78
1.76
1.75
1.73
1.72
0.05D
O
0.30D
0.34D
NO2
13p
1H NMR (CDCl3, 500 MHz)
2.00
2.00
1.00
2.00
2.00
1.70
1.95
3.66


199.83
150.11
146.39
136.93
133.08
129.18
128.63
128.00
123.66
38.14
38.05
35.77
35.75
30.54
30.44
23.73
23.69
0.05D
O
0.30D
0.34D
NO2
13p
13C NMR (CDCl3, 126 MHz)