Supplementary Information (SI) for Catalysis Science & Technology.

Supporting Information

Platinum-Group-Metal-on-Carbon Catalyzed Dehydration of Tertiary Alcohols and its Application to the One-Pot Synthesis of Aromatics

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1. General information.

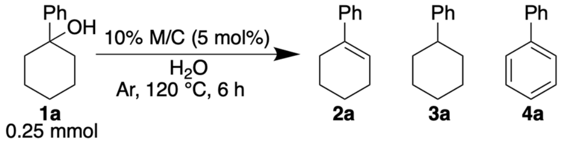
Unless otherwise noted, all substrates and solvents were purchased from commercial sources and were used without further purification. Flash column chromatography was performed with 40-50 mm Silica Gel 60 N (Kanto Chemical Co., Inc.) or Silica Gel 30 µm 60 Å (YAMAZEN CORPORATION). Melting points were measured on Yanaco MP-S3 and were uncorrected. IR spectra were recorded on SHIMADZU IRAffinity-1S as a thin film on NaCl. ^{1}H, ^{13}C NMR spectra were recorded on a JEOL AL-300 (^{1}H: 300 MHz, ^{2}H: 46 MHz), a JEOL JMN-ECS-400 (^{1}H: 400 MHz, ^{13}C: 100 MHz), a BRUKER 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz), a JEOL JMN-ECA-500 or JMN-ECZ-500 (^{1}H: 500 MHz, ^{13}C: 125 MHz), with chemical shifts reported in d (ppm) relative to the residual solvent signal for ^{1}H ($CDCl_3$: d = 7.26 ppm) or internal standard for ^{1}H (TMS in $CDCl_3$: 0.00 ppm) and relative to the deuterated solvent signal for ^{13}C ($CDCl_3$: 77.0 ppm) and relative to the deuterated solvent signal for ^{2}H ($CDCl_3$: 7.26 ppm). High resolution mass spectra were measured on JEOL JMS-S3000 (MALDI).

2. Optimization of dehydration

Experimental procedure for Table S1:

To a mixture of **1a** (44 mg, 0.25 mmol) and H_2O (1 mL) were added 10% M/C (0.0125 mmol) under argon. The reaction mixture was refluxed at 120 °C. After stirring for 6 h, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove M/C. The filtrate was extracted with EtOAc (10 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The yield was calculated by ^{1}H NMR analysis of a crude mixture using 1,1,2,2-tetrachloroethane (26.5 µL, 0.25 mmol) as an internal standard.

Table S1 The catalyst efficiencies towards the dehydration of 1-phenyl-1-cyclohexanol (**1a**) as a *tert*-alcohol

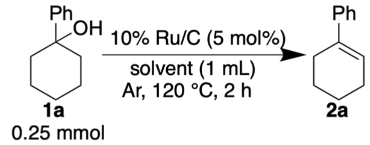


entry	M/C	yield (%)			
		1a	**2a**	**3a**	**4a**
1	Pd/C	trace	trace	53	36
2	Ru/C	65	20	0	trace
3	Rh/C	86	13	0	trace
4	Ir/C	quant	0	0	0
5	Pt/C	trace	0	45	38
6	Au/C	quant	0	0	0
7	Ag/C	quant	0	0	0
8	Cu/C	quant	0	0	0

Experimental procedure for Table S2:

To a solution of **1a** (44 mg, 0.25 mmol) in solvent (1 mL) was added 10% Ru/C (0.0125 mmol) under argon. The reaction mixture was refluxed or heated at 120 °C. After stirring for 2 h, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove 10% Ru/C. The filtrate was concentrated in vacuo. The yield was calculated by ^{1}H NMR analysis of a crude mixture using 1,1,2,2-tetrachloroethane (26.5 µL, 0.25 mmol) as an internal standard.

Table S2 The solvent effect

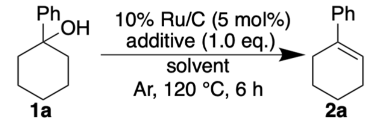


entry	solvent	yield (%)	
		1a	**2a**
1	H_2O	65	20
2	toluene	0	99
3	*n*-heptane	0	99
4	cyclohexane	0	99
5	*n*-decane	0	99
6	EtOH	99	0
7	*t*-BuOH	99	0
8	DMSO	99	0
9	THF	99	0
10	1,1,2,2-TCE	trace	95

Experimental procedure for Table S3:

To a solution of **1a** (44 mg, 0.25 mmol) and additive (1.0 equiv., 0.25 mmol) in toluene or H_2O (1 mL) was added 10% Ru/C (0.0125 mmol) under argon. The reaction mixture was refluxed or heated at 120 °C. After stirring for 6 h, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove 10% Ru/C. The filtrate was concentrated in vacuo. The yield was calculated by ^{1}H NMR analysis of a crude mixture using 1,1,2,2-tetrachloroethane (26.5 μL, 0.25 mmol) as an internal standard.

Table S3 The Ruthenium catalyst efficiencies towards the dehydration of 1-phenyl-1-cyclohexanol (**1a**) as a *tert*-alcohol



1a
0.25 mmol

2a

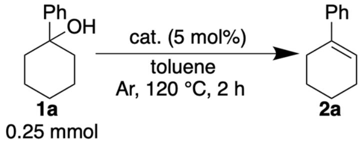
entry	solvent	additive	yield (%)	
			1a	**2a**
1	H_2O	—	65	20
2	toluene	—	0	99
3	H_2O	K_2CO_3	quant.	0
4	toluene	K_2CO_3	0	99
5	toluene	NEt_3	quant.	0

The base, such as NEt_3, sometimes works as catalyst poison for Ru/C, Pt/C, and so on. Therefore, the reactivity dramatically decreased in the reaction with base.

Experimental procedure for Table S4:

To a solution of **1a** (44 mg, 0.25 mmol) in toluene (1 mL) was added catalyst (0.0125 mmol) under argon. The reaction mixture was refluxed or heated at 120 °C. After stirring for 2 h, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove catalyst. The filtrate was concentrated in vacuo. The yield was calculated by ^{1}H NMR analysis of a crude mixture using 1,1,2,2-tetrachloroethane (26.5 μL, 0.25 mmol) as an internal standard.

Table S4 The Ruthenium catalyst efficiencies towards the dehydration of 1-phenyl-1-cyclohexanol (**1a**) as a *tert*-alcohol



entry	catalyst	yield (%)	
		1a	**2a**
1	10% Ru/C (N. E. Chemcat)	0	99
2	4.3% Ru/C (Aldrich)	0	95
3	5% Ru/C with water	91	9
4	washed 10% Ru/C (N. E. Chemcat)	0	98
5	C[a]	37	63
6	washed C[a]	98	trace
7	$RuCl_3$	68	32
8	RuO_2	99	0
9[b]	RuO_2	99	0

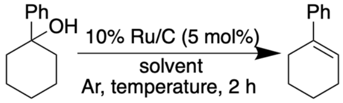
[a]Actvated carbon [b]crushed with ball mill

entry 4: Commercially available activated carbon is known to sometimes include some metals (magnesium ion, calcium ion, etc.) and acid, which facilitated the present reaction. So, we investigated the present reaction using washed Ru/C and activated carbon (See, Fig. 2A, entries 8 and 9). These results clearly indicated the importance of Ru species.

Experimental procedure for Table S5:

To a solution of **1a** (44 mg, 0.25 mmol) in toluene or *n*-heptane (1 mL) was added 10% Ru/C (0.0125 mmol) under argon. The reaction mixture was refluxed or heated at each temperature. After stirring for 2 h, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove 10% Ru/C. The filtrate was concentrated in vacuo. The yield was calculated by ^{1}H NMR analysis of a crude mixture using 1,1,2,2-tetrachloroethane (26.5 µL, 0.25 mmol) as an internal standard.

Table S5 The temperature effects



1a
0.25 mmol

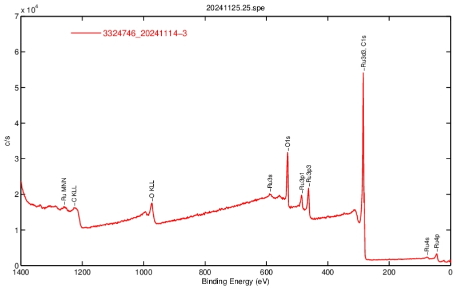
2a

entry	solvent	temperature (°C)	yield (%)	
			1a	**2a**
1	toluene	120	0	99
2		100	47	53
3	*n*-heptane	120	0	99
4		100	0	99
5		80	62	38

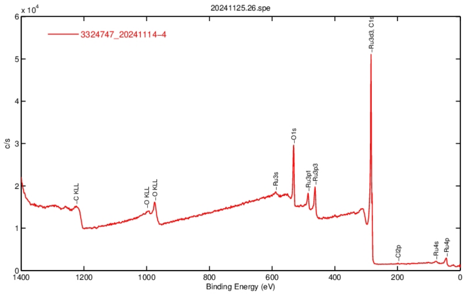
3. Analyses of fresh catalyst and used catalyst.

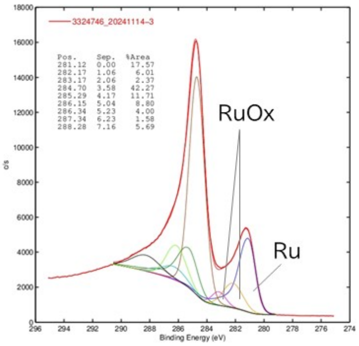
3-1. Ru/C

XPS before reaction

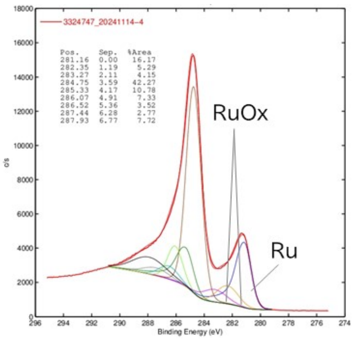


XPS after reaction



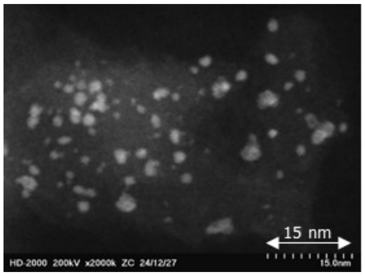


Ru : RuO_x = 68 : 32 (%)



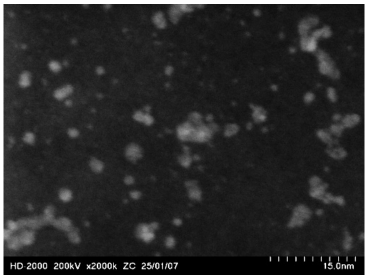
Ru : RuO_x = 63 : 37 (%)

STEM before reaction



particle size; ave. 1.6 nm

STEM after reaction



particle size; ave. 1.8 nm

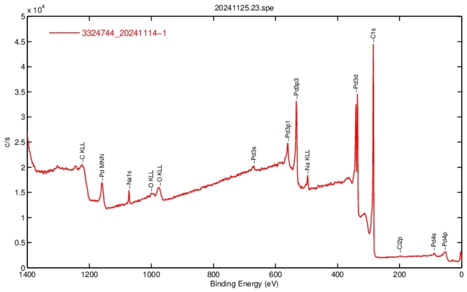
leaching test

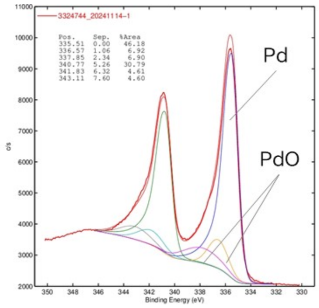
A mixture of a 1-phenylcyclohexan-1-ol (0.25 mmol, 44 mg) and 10% Ru/C (12.6 mg, 0.0125 mol% of the substrate) in toluene (1.0 mL) in a test tube was stirred under ordinary (balloon) Argon pressure at 120 °C for 3 h. The reaction mixture was filtrated through a membrane filter (Millipore Corporation, Billerica, MA, USA; Omnipore, 0.20 um). The filtrate was dilluted with toluene to 10 mL of the total volume, and the ruthenium leaching

(<10 ppm: below the detection limit) in the filtrate was observed by SHIMADZU ICPS-8100.

3-2. Pd/C

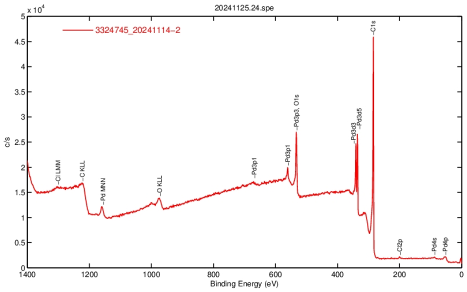
XPS before reaction

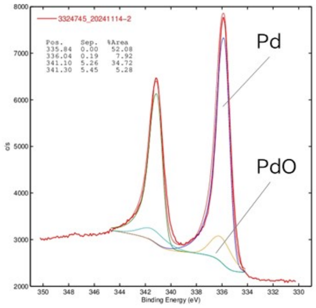




Pd : PdO_x = 77 : 23 (%)

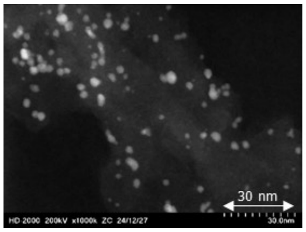
XPS after reaction





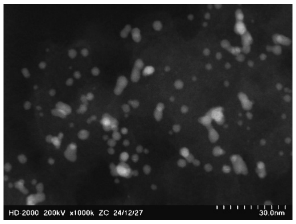
Pd : PdO_x = 87 : 13 (%)

STEM before reaction



particle size; ave. 2.3 nm

STEM after reaction



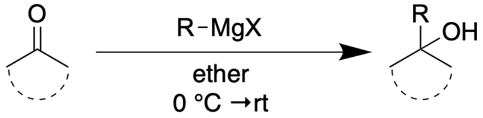
particle size; ave. 2.8 nm

leaching test

A mixture of a 1-phenylcyclohexan-1-ol (0.25 mmol, 44 mg), 10% Pd/C (13.3 mg, 0.0125 mol% of the substrate), (*E*)-pent-3-en-2-one (10 mmol, 245 μL) in H_2O (1.0 mL) in a test tube was stirred under ordinary (balloon) Argon pressure at 120 °C for 24 h. The reaction mixture was filtrated through a membrane filter (Millipore Corporation, Billerica, MA, USA; Omnipore, 0.20 um). The filtrate was dilluted with H_2O to 10 mL of the total volume, and the palladium leaching (<1 ppm: below the detection limit) in the filtrate was observed by SHIMADZU ICPS-8100.

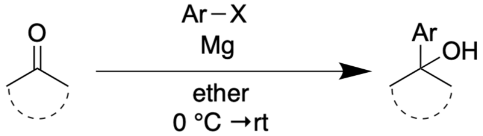
4. Preparation of substrates

General Procedure A: Grignard Reaction



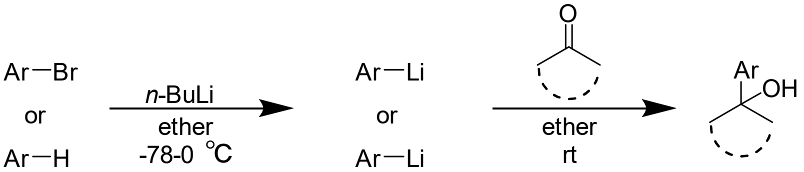
To a solution of ketone in anhydrous ethers was slowly added RMgX at 0 °C under argon atmosphere. Then the reaction mixture was warmed up to room temperature and stirred until the ketone was completely consumed (monitored by TLC). The reaction was quenched by slow addition of saturated NH_4Cl aq. The aqueous layer was extracted with EtOAc three times. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to provide the corresponding product.

General Procedure B: Grignard Reaction



To a solution of Mg in anhydrous ethers was added ArX and 0.25 mL of 1,2-dibromoethane at 0 °C under argon atmosphere. Then the reaction mixture was slowly added ketone in anhydrous ethers and warmed up to room temperature and stirred until the ketone was completely consumed (monitored by TLC). The reaction was quenched by slow addition of saturated NH_4Cl aq. The aqueous layer was extracted with EtOAc three times. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to provide the corresponding product.

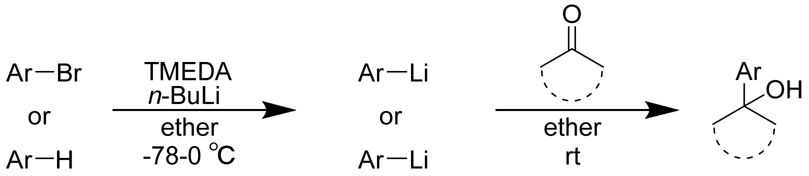
General Procedure C: Lithiation Reaction



A two-neck round-bottom flask equipped with a stir bar under Ar atmosphere was added n-butyllithium (2.66-2.69 M solution in hexane, 1.0 equiv) slowly to a solution of aryl bromide (1.0 equiv.) or aryl compounds (1.0 equiv) in THF (0.2 M) at -78 °C. The reaction mixture was stirred for 1–2 h at -78 ℃ - 0 ℃ and then the corresponding ketone (1.0 equiv.) was added dropwise.

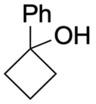
The mixture was allowed to warm up to room temperature and stirred for overnight. After completion, the reaction mixture was quenched by slow addition of saturated NH_4Cl aq. The aqueous layer was extracted with EtOAc three times. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to provide the corresponding product.

General Procedure D: Lithiation Reaction



A two-neck round-bottom flask equipped with a stir bar under Ar atmosphere was added *n*-butyllithium (2.66-2.69 M solution in hexane, 1.0 equiv) slowly to a solution of TMEDA (1.0 equiv.) in THF (0.5 M) at -78 °C. After that, aryl compounds (1.0 equiv) was added to the reaction mixture and the reaction mixture was stirred for 1 h at -78 ℃ and then the corresponding ketone (0.2 equiv.) was added dropwise. The mixture was stirred for 1 h at -78 ℃. After completion, the reaction mixture was quenched by slow addition of saturated NH_4Cl aq. The aqueous layer was extracted with EtOAc three times. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to provide the corresponding product.

1-phenylcyclobutan-1-ol (1b)



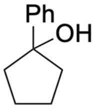
1b

The compound was prepared from cyclobutanone (1.0 equiv., 5.0 mmol) and PhMgBr (1.5 equiv., 7.5 mmol) following the general procedure A. Purification by column chromatography (silica gel, 10 : 1 = hexane : EtOAc) afforded 765 mg (99%) of the title compound **1b**.

Colorless solid; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.52–7.50 (m, 2H), 7.40–7.37 (m, 2H), 7.31–7.27 (m, 1H), 2.60–2.55 (m, 2H), 2.41–2.35 (m, 2H), 2.06–1.99 (m, 2H), 1.72–1.67 (m, 1H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [1].

1-phenylcyclopentan-1-ol (1c)



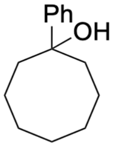
1c

The compound was prepared from cyclopentanone (1.0 equiv., 5.0 mmol) and PhMgBr (1.5 equiv., 7.5 mmol) following the general procedure A. Purification by column chromatography (silica gel, 12 : 1 = hexane : EtOAc) afforded 648 mg (80%) of the title compound **1c**.

Colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.50–7.48 (m, 2H), 7.36–7.32 (m, 2H), 7.26–7.23 (m, 1H), 2.04–1.97 (m, 6H), 1.86–1.83 (m, 2H), 1.54 (s, 1H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [2].

1-phenylcyclooctan-1-ol (1d)



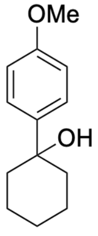
1d

The compound was prepared from cyclooctanone (1.0 equiv., 5.0mmol) and PhMgBr (1.5 equiv., 7.5 mmol) following the general procedure A. Purification by column chromatography (silica gel, 10 : 1 = hexane : EtOAc) afforded 489.4 mg (48%) of the title compound **1d**.

Colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.58–7.47 (m, 2H), 7.41–7.31 (m, 2H), 7.29–7.20 (m, 1H), 2.14–1.91 (m, 4H), 1.83–1.65 (m, 5H), 1.62–1.47 (m, 6H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [2].

1-(4-methoxyphenyl) cyclohexan-1-ol (1e)



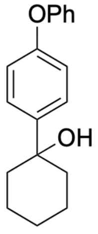
1e

The compound was prepared from cyclohexanone (1.0 equiv., 10 mmol), Mg (1.2 equiv., 12 mmol) and 1-bromo-4-methoxybenzene (1.0 equiv., 10 mmol) following the general procedure B. Purification by column chromatography (silica gel, 40 : 1 = toluene : acetone) afforded 580 mg (28%) of the title compound **1e**.

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45–7.42 (m, 2H), 6.90–6.87 (m, 2H), 3.81 (s, 3H), 1.86–1.70 (m, 7H), 1.65–1.60 (m, 2H), 1.52 (s, 1H), 1.33–1.24 (m, 1H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [2].

1-(4-phenoxyphenyl)cyclohexan-1-ol (1f)



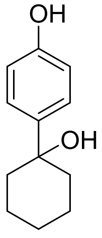
1f

The compound was prepared from cyclohexanone (1.0 equiv., 5.0 mmol), 2.66% *n*-BuLi *n*-hexane solution (1.3 equiv., 6.5 mmol) and 1-bromo-4-phenoxybenzene (1.3 equiv., 6.5 mmol) following the general procedure C. Purification by column chromatography (silica gel, 10 : 1 = hexane : EtOAc) afforded 512 mg (30%) of the title compound **1f**.

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48–7.45 (m, 2H), 7.35–7.31 (m, 2H), 7.12–7.08 (m, 1H), 7.03–6.96 (m, 4H), 1.87–1.71 (m, 7H), 1.66–1.59 (m, 3H), 1.33–1.26 (m, 1H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [3].

1-(4-Hydroxyphenyl)cyclohexan-1-ol (1g)



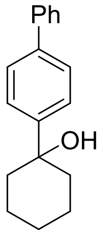
1g

The compound was prepared from cyclohexanone (1.0 equiv., 3.0 mmol), 2.66% *n*-BuLi *n*-hexane solution (4.5 equiv., 13.5 mmol) and 4-bromophenol (1.5 equiv., 4.5 mmol) following the general procedure C. Purification by column chromatography (silica gel) afforded 247 mg (43%) of the title compound **1g**.

White solid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.14 (s, 1H), 7.26–7.23 (m, 2H), 6.68–6.65 (m, 2H), 4.46 (s, 1H), 1.71–1.55 (m, 7H), 1.46–1.43 (m, 2H), 1.25–1.16 (m, 1H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [4].

1-([1,1'-biphenyl]-4-yl)cyclohexan-1-ol (1h)



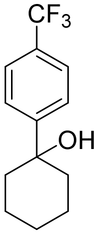
1h

The compound was prepared from cyclohexanone (1.0 equiv., 5.0 mmol), 2.66% *n*-BuLi *n*-hexane solution (1.3 equiv., 6.5 mmol) and 4-bromo-1,1'-biphenyl (1.3 equiv., 6.5 mmol) following the general procedure C. Purification by column chromatography (silica gel, 10 : 1 = hexane : EtOAc) afforded 223 mg (14%) of the title compound **1h**.

White solid; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.62–7.59 (m, 6H), 7.45–7.42 (m, 2H), 7.36–7.32 (m, 1H), 1.92–1.74 (m, 7H), 1.69–1.65 (m, 2H), 1.61 (s, 1H), 1.36–1.26 (m, 1H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [3].

1-(4-(trifluoromethyl)phenyl)cyclohexan-1-ol (1i)



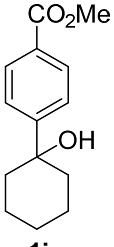
1i

The compound was prepared from cyclohexanone (1.0 equiv., 10 mmol), 2.69% *n*-BuLi *n*-hexane solution (1.2 equiv., 12 mmol) and 1-bromo-4-(trifluoromethyl)benzene (1.1 equiv., 11 mmol) following the general procedure C. Purification by column chromatography (silica gel, 30 : 1 = toluene : EtOAc) afforded 2.17 mg (89%) of the title compound **1i**.

Colorless solid; ^{1}H NMR (500 MHz, CDCl$_3$); δ 7.61 (m, 4H), 1.86–1.65 (m, 10H), 1.57 (s, 1H), 1.35–1.27 (m, 1H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [5].

1-(4-Methoxycarbonylphenyl) cyclohexanol (1j)



1j

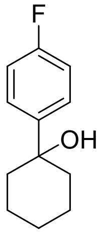
A solution of *i*-PrMgCl (0.79 equiv., 15.8 mmol) was added dropwise to the solution of methyl 4-iodobenzoate (0.75 equiv., 15 mmol) in THF (40 mL) at −20 °C. After being stirred for 1.5 h, cyclohexanone (1.0 equiv., 20 mmol) was added dropwise to the reaction mixture. Then, after being stirred at room temperature for 1 h, the reaction mixture was quenched with sat. NH$_4$Cl aq. at 0 °C. The resulting mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. Purification by column chromatography (silica gel, 10 : 1 = hexane : EtOAc) afforded 1.99 g (85%) of the title compound **1j.**

White solid; m.p. 76–77 °C; IR (ATR) cm^{-1}: 3482, 2934, 2858, 1723, 1706, 1609, 1436, 1283, 1190, 1113, 1106, 1014; ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.00 (dt, *J* = 8.7, 2.0 Hz, 2H), 7.58 (dt, *J* = 8.7, 2.0 Hz, 2H), 3.91 (s, 3H), 1.86–1.71 (m, 8H), 1.67–1.63 (m, 2H), 1.34–1.27 (m, 1H)

^{13}C NMR (125 MHz, CDCl$_3$) δ: 167.0, 154.6, 129.5, 128.4, 124.6, 73.3, 52.0, 38.6, 25.3, 21.9.

HRMS (EI+): calcd. for $C_{14}H_{18}O_3^+$ $(M)^+$ 234.1256, found 234.1252

1-(4-fluorophenyl) cyclohexan-1-ol (1k)

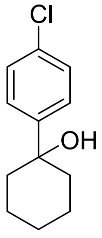

1k

The compound was prepared from cyclohexanone (1.0 equiv., 20 mmol), Mg (1.2 equiv., 24 mmol) and 1-bromo-4-fluorobenzene (1.0 equiv., 20 mmol) following the general procedure B. Purification by column chromatography (silica gel, 20 : 1 = hexane : acetone) afforded 1.90 g (49%) of the title compound **1k**.

White solid; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.47 (m, 2H), 7.01 (m, 2H), 1.84–1.70 (m, 7H), 1.64 (dt, J = 12.4, 3.6 Hz, 2H), 1.59 (d, J = 1.7 Hz, 1H), 1.33–1.25 (m, 1H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [2].

1-(4-chlorophenyl) cyclohexan-1-ol (1l)

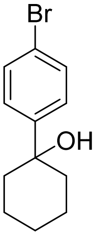

1l

The compound was prepared from cyclohexanone (1.0 equiv., 10 mmol), Mg (8.0 equiv., 80 mmol) and 1-chloro-4-iodobenzene (4.0 equiv., 40 mmol) following the general procedure B. Purification by column chromatography (silica gel, 20 : 1 = hexane : acetone) afforded 1.90 g (49%) of the title compound **1l**.

White solid; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.47–7.43 (m, 2H), 7.32–7.29 (m, 2H), 1.83–1.69 (m, 7H), 1.67–1.62 (m, 2H), 1.58 (s, 1H), 1.32–1.24 (m, 1H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [2].

1-(4-Bromophenyl)cyclohexanol (1m)



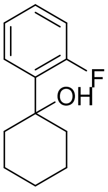
1m

The compound was prepared from cyclohexanone (1.0 equiv., 14 mmol), 2.69% *n*-BuLi *n*-hexane solution (1.0 equiv., 14 mmol) and dibromobenzene (0.91 equiv., 12.7 mmol) following the general procedure C. Purification by column chromatography (silica gel, 75 : 1 = toluene : EtOAc) afforded 2.69 g (83%) of the title compound **1m**.

Colorless solid; ^{1}H NMR (500 MHz, CDCl$_3$); δ 7.46 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 1.82–1.61 (m, 10H), 1.32–1.24 (m, 1H).

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [2].

1-(2-fluorophenyl)cyclohexan-1-ol (1n)



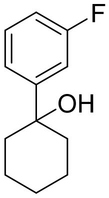
1n

The compound was prepared from cyclohexanone (1.0 equiv., 11 mmol), 2.69% *n*-BuLi *n*-hexane solution (0.93 equiv., 10.2 mmol) and 1-bromo-2-fluorobenzene (0.91 equiv., 10 mmol) following the general procedure C. Purification by column chromatography (silica gel, 40 : 1 = toluene : acetone) afforded 1.82 mg (85%) of the title compound **1n**.

Colorless solid; ^{1}H NMR (500 MHz, CDCl$_3$); δ 7.55 (td, *J* = 8.1, 1.7 Hz, 1H), 7.25–7.21 (m, 1H), 7.13 (td, *J* = 7.5, 1.3 Hz, 1H), 7.05–7.00 (m, 1H), 2.08–2.02 (m, 2H), 1.98 (d, *J* = 4.0 Hz, 1H), 1.82–1.72 (m, 5H), 1.66–1.62 (m, 2H), 1.37–1.28 (m, 1H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [2].

1-(3-fluorophenyl) cyclohexan-1-ol (1o)



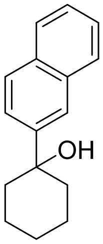
1o

The compound was prepared from cyclohexanone (1.0 equiv., 10 mmol), Mg (1.2 equiv., 12 mmol) and 1-bromo-3-fluorobenzene (1.0 equiv., 10 mmol) following the general procedure B. Purification by column chromatography (silica gel, 30 : 1 = toluene : acetone) afforded 1.24 g (64%) of the title compound **1o**.

White solid; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.34–7.21 (m, 3H), 6.96–6.90 (m, 1H), 1.87–1.62 (m, 10H), 1.37–1.25 (m, 1H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [2].

1-(naphthalen-2-yl) cyclohexan-1-ol (1p)



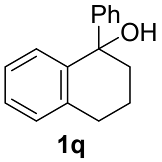
1p

The compound was prepared from cyclohexanone (1.0 equiv., 10 mmol), Mg (1.2 equiv., 12 mmol) and 2-bromonaphthalene (1.0 equiv., 10 mmol) following the general procedure B. Purification by column chromatography (silica gel, 20 : 1 = hexane : acetone) afforded 1.37 g (60%) of the title compound **1p**.

White solid; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.96 (d, J = 1.7 Hz, 1H), 7.86–7.81 (m, 3H), 7.64 (dd, J = 8.6, 1.7 Hz, 1H), 7.50–7.42 (m, 2H), 2.05–1.66 (m, 10H), 1.42–1.28 (m, 1H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [3].

1-phenyl-1,2,3,4-tetrahydronaphthalen-1-ol (1q)



1q

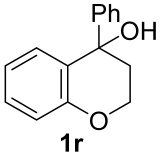
The compound was prepared from 3,4-dihydronaphthalen-1(2*H*)-one (1.0 equiv., 10 mmol) and

PhMgBr (2.5 equiv., 25 mmol) following the general procedure A. Purification by column chromatography (silica gel, 40 : 1 = toluene : acetone) afforded 1.39 g (62%) of the title compound **1q**.

Colorless oil; ^{1}HNMR (500 MHz, $CDCl_3$): δ 7.35–7.29 (m, 4H), 7.26–7.19 (m, 2H), 7.17 (d, *J* = 7.0 Hz, 1H), 7.14–7.11 (m, 1H), 7.04 (d, *J* = 7.7 Hz, 1H), 2.94–2.89 (m, 2H), 2.18–2.09 (m, 3H), 2.05–1.96 (m, 1H), 1.83–1.76 (m, 1H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [6].

4-phenylchroman-4-ol (1r)



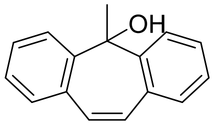
1r

The compound was prepared from chroman-4-one (1.0 equiv., 5.0 mmol) and PhMgBr (1.5 equiv., 7.5 mmol) following the general procedure A. Purification by column chromatography (silica gel, 10 : 1 = hexane : EtOAc) afforded 181 mg (20%) of the title compound **1r**.

White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41–7.38 (m, 2H), 7.35–7.32 (m, 2H), 7.29–7.26 (m, 1H), 7.23–7.20 (m, 1H), 6.96–6.90 (m, 2H), 6.86–6.83 (m, 1H), 4.40 (m, 1H), 4.24 (m, 1H), 2.38–2.32 (m, 1H), 2.27 (m, 1H), 2.20 (m, 1H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [7].

5-methyl-5*H*-dibenzo[*a*,*d*][7]annulen-5-ol (1s)



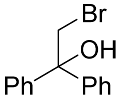
1s

The compound was prepared from 5*H*-dibenzo[*a*,*d*][7]annulen-5-one (1.0 equiv., 5.0 mmol) and MeMgBr (1.5 equiv., 7.5 mmol) following the general procedure A. Purification by column chromatography (silica gel, 10 : 1 = hexane : EtOAc) afforded 401 mg (36%) of the title compound **1s**.

White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (s, 2H), 7.41–7.28 (m, 8H), 2.26 (br, 1H), 1.59 (br, 3H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [10].

2-bromo-1,1-diphenylethan-1-ol (1u)



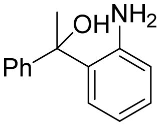
1u

Compound **2t** (1.0 equiv., 1.5 mmol) and NBS (1.09, 1.64 mmol) were stirred in acetone-H_2O (1.36 mL; 5:1) at room temperature (25 °C) for 2 hours. After completion of reaction (TLC), acetone was removed in vacuo and residue 10 was dissolved in ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The crude was purified by column chromatography (silica gel, 20 : 1 = hexane : EtOAc) afforded 205 mg (49%) of the title compound **1u**.

White solid ; ^1H NMR (500 MHz, $CDCl_3$): δ 7.46–7.44 (m, 4H), 7.36–7.33 (m, 4H), 7.29 (d, *J* = 7.4 Hz, 2H), 4.13 (s, 2H), 3.09 (s, 1H)

Spectroscopic data of ^1H NMR was identical to those reported in reference [8].

1-(2-aminophenyl)-1-phenylethan-1-ol (1v)



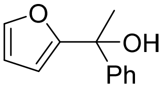
1v

The compound was prepared from (2-aminophenyl)(phenyl)methanone (1.0 equiv., 5.0 mmol) and MeMgBr (1.6 equiv., 8.0 mmol) following the general procedure A. Purification by column chromatography (silica gel, 10 : 1 = hexane : EtOAc) afforded 496 mg (47%) of the title compound **1v**.

Yellow solid; ^1H NMR (500 MHz, $CDCl_3$): δ 7.43–7.39 (m, 3H), 7.32–7.29 (m, 2H), 7.25–7.22 (m, 1H), 7.15 (td, *J* = 7.6, 1.4 Hz, 1H), 6.88 (td, *J* = 7.5, 1.3 Hz, 1H), 6.65 (dd, *J* = 7.8, 1.2 Hz, 1H), 3.93 (s, 1H), 3.66 (s, 2H), 1.88 (s, 3H)

Spectroscopic data of ^1H NMR was identical to those reported in reference [9].

1-(furan-2-yl)-1-phenylethan-1-ol (1x)



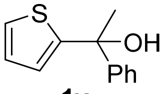
1x

The compound was prepared from 1-(furan-2-yl)ethan-1-one (1.0 equiv., 5.0 mmol) and PhMgBr (1.5 equiv., 7.5 mmol) following the general procedure A. Purification by column chromatography (silica gel, 10 : 1 = hexane : EtOAc) afforded 794 mg (90%) of the title compound **1x**.

Colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.42–7.31 (m, 5H), 7.30–7.25 (m, 1H), 6.34 (q, *J* = 1.6 Hz, 1H), 6.25 (dd, *J* = 3.3, 0.9 Hz, 1H), 2.49 (s, 1H), 1.88 (s, 3H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [11].

1-phenyl-1-(thiophen-2-yl) ethan-1-ol (1y)



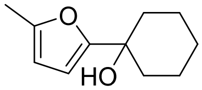
1y

The compound was prepared from 1-(thiophen-2-yl)ethan-1-one (1.0 equiv., 5.0 mmol) and PhMgBr (1.5 equiv., 7.5 mmol) following the general procedure A. Purification by column chromatography (silica gel, 10 : 1 = hexane : EtOAc) afforded 873 mg (85%) of the title compound **1y**.

Colorless solid; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.51–7.49 (m, 2H), 7.36–7.33 (m, 2H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.24 (dd, *J* = 5.0, 1.3 Hz, 1H), 6.93 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.90 (dd, *J* = 3.6, 1.3 Hz, 1H), 2.39 (s, 1H), 2.02 (s, 3H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [12].

1-(5-methylfuran-2-yl)cyclohexan-1-ol (1z)



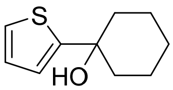
1z

The compound was prepared from cyclohexanone (0.2 equiv., 1.0 mmol), 2.69% *n*-BuLi *n*-hexane solution (1.0 equiv., 5.0 mmol) and 2-methylfuran (1.0 equiv., 5.0 mmol) following the general procedure D. Purification by column chromatography (silica gel, 10 : 1 = hexane : EtOAc) afforded 86.7 mg (48%) of the title compound **1z**.

Colorless solid; ^{1}HNMR (500 MHz, CDCl$_3$): δ 6.08 (d, *J* = 3.2 Hz, 1H), 5.89–5.88 (m, 1H), 2.28 (d, *J* = 0.9 Hz, 3H), 1.98–1.93 (m, 2H), 1.85–1.81 (m, 2H), 1.75–1.68 (m, 3H), 1.53–1.46 (m, 3H), 1.40–1.36 (m, 1H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [13].

1-(thiophen-2-yl)cyclohexan-1-ol (1aa)



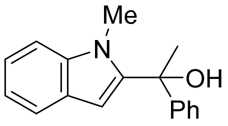
1aa

The compound was prepared from cyclohexanone (1.0 equiv., 11 mmol), 2.69% *n*-BuLi *n*-hexane solution (0.93 equiv., 10.2 mmol) and 2-bromothiophene (0.91 equiv., 10 mmol) following the general procedure C. Purification by column chromatography (silica gel, 40 : 1 = toluene : acetone) afforded 1.23 g (61%) of the title compound **1aa**.

White solid; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.21–7.20 (m, 1H), 6.99 (t, *J* = 1.7 Hz, 1H), 6.96 (dd, *J* = 4.9, 3.7 Hz, 1H), 1.98–1.89 (m, 4H), 1.83 (d, *J* = 1.7 Hz, 1H), 1.78–1.70 (m, 2H), 1.68–1.58 (m, 3H), 1.37–1.30 (m, 1H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [14].

1-(1-methyl-1*H*-indol-2-yl)-1-phenylethan-1-ol (1ab)



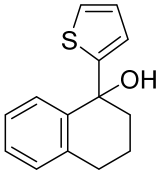
1ab

The compound was prepared from acetophenone (1.0 equiv., 10 mmol) and 1-methyl-1*H*-indole (1.0 equiv., 10 mmol) following the general procedure C. Purification by column chromatography (silica gel, 10 : 1 = hexane : EtOAc) afforded 955 mg (38%) of the title compound **1ab**.

Yellow solid; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.65 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.36–7.28 (m, 4H), 7.26–7.20 (m, 3H), 7.14–7.11 (m, 1H), 6.70 (d, *J* = 0.6 Hz, 1H), 3.40 (s, 3H), 2.19 (s, 1H), 2.02 (s, 3H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [15].

1-(thiophen-2-yl)-1,2,3,4-tetrahydronaphthalen-1-ol (1ac)



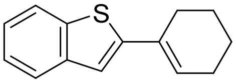
1ac

The compound was prepared from 3,4-dihydronaphthalen-1(2*H*)-one (1.0 equiv., 10 mmol) and thiophen (1.0 equiv., 10 mmol) following the general procedure C. Purification by column chromatography (silica gel, 10 : 1 = hexane : EtOAc) afforded 1.08 g (47%) of the title compound **1ac**.

White solid; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.39 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.25–7.21 (m, 2H), 7.20–7.13 (m, 2H), 6.90 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.63 (dd, *J* = 3.6, 1.3 Hz, 1H), 2.93–2.81 (m, 2H), 2.44 (s, 1H), 2.32–2.22 (m, 2H), 2.03–1.95 (m, 1H), 1.84–1.76 (m, 1H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [16].

1-(benzo[*b*]thiophen-2-yl)cyclohexan-1-ol (1ad)



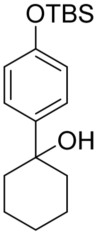
1ad

The compound was prepared from cyclohexanone (1.0 equiv., 10 mmol) and benzothiophen (1.0 equiv., 10 mmol) following the general procedure C. Purification by column chromatography (silica gel, 10 : 1 = hexane : EtOAc) afforded 1.79 g (77%) of the title compound **1ad**.

Colorless solid; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.81 (d, J = 7.9 Hz, 1H), 7.72–7.70 (m, 1H), 7.34–7.27 (m, 2H), 7.20 (s, 1H), 2.02–1.95 (m, 4H), 1.93 (s, 1H), 1.82–1.61 (m, 5H), 1.40–1.33 (m, 1H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [14].

1-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)cyclohexan-1-ol (1ae)



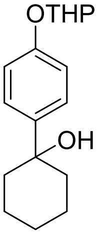
1ae

The compound was prepared from cyclohexanone (1.0 equiv., 2.45 mmol), 2.66% *n*-BuLi *n*-hexane solution (1.43 equiv., 3.5 mmol) and (4-bromophenoxy)(*tert*-butyl)dimethylsilane (1.43 equiv., 3.5 mmol) following the general procedure C. Purification by column chromatography (silica gel, 20 : 1 = hexane : EtOAc) afforded 617 mg (85%) of the title compound **1ae**.

White solid; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.35 (dd, J = 6.6, 2.1 Hz, 2H), 6.81–6.79 (m, 2H), 1.80–1.75 (m, 7H), 1.57–1.67 (2H), 1.51 (s, 1H), 1.17–1.38 (1H), 0.98 (s, 9H), 0.19 (s, 6H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [3].

1-(4-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)cyclohexan-1-ol (1af)



1af

The compound was prepared from cyclohexanone (1.0 equiv., 4.0 mmol), 2.66% *n*-BuLi *n*-hexane solution (1.1 equiv., 4.8 mmol) and 2-(4-bromophenoxy)tetrahydro-2*H*-pyran (1.0 equiv., 4.0 mmol) following the general procedure C. Purification by column chromatography (silica gel, 10 : 1 = hexane : EtOAc) afforded 656 mg (60%) of the title compound **1af**.

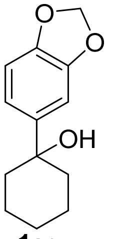
White solid; m.p.75–77 ℃; IR (NaCl) cm^{-1}: 3445, 2934, 2853, 1608, 1582, 1510, 1447, 1355, 1237, 1201, 1179, 1147, 1125, 1109, 1076, 1036, 1022, 969, 921, 906, 871, 849, 828, 756, 645

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.48–7.38 (m, 2H), 7.14–6.95 (m, 2H), 5.53–5.38 (m, 1H), 3.98–3.86 (m, 1H), 3.64–3.58 (m, 1H), 3.49–3.45 (m, 1H), 2.05–1.95 (m, 1H), 1.91–1.56 (m, 13H), 1.53–1.47 (m, 1H), 1.36–1.24 (m, 1H)

^{13}C NMR (125 MHz, CDCl$_3$) δ 155.9, 142.6, 125.8, 116.1, 96.4, 72.9, 62.1, 39.0, 30.5, 25.6, 25.3, 22.4, 18.9

HRMS (ESI+): calcd. for $C_{17}H_{24}NaO_3^+$ (M+Na)$^+$ 299.1618, found 299.1620

1-(benzo[*d*][1,3]dioxol-5-yl)cyclohexan-1-ol (1ag)



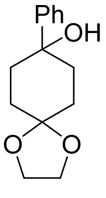
1ag

The compound was prepared from cyclohexanone (1.0 equiv., 3.0 mmol) and 5-bromobenzo[*d*][1,3]dioxole (1.0 equiv., 3.0 mmol) following the general procedure C. Purification by column chromatography (silica gel, 10 : 1 = hexane : EtOAc) afforded 338 mg (51%) of the title compound **1af**.

Colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.03 (d, *J* = 1.9 Hz, 1H), 6.96 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 5.94 (s, 2H), 1.82–1.67 (m, 8H), 1.64–1.59 (m, 2H), 1.58 (s, 1H), 1.31–1.23 (m, 1H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [17].

8-phenyl-1,4-dioxaspiro [4.5]decan-8-ol (1ah)



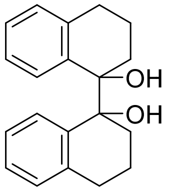
1ah

The compound was prepared from 1,4-dioxaspiro[4.5]decan-8-one (1.0 equiv., 5.0 mmol) and PhMgBr (1.5 equiv., 7.5 mmol) following the general procedure A. Purification by column chromatography (silica gel, 10 : 1 = hexane : EtOAc) afforded 197 mg (16.8%) of the title compound **1ah**.

White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54–7.52 (m, 2H), 7.37–7.34 (m, 2H), 7.27–7.24 (m, 1H), 4.02–3.96 (m, 4H), 2.22–2.08 (m, 4H), 1.82 (dd, *J* = 13.1, 1.5 Hz, 2H), 1.70 (dd, *J* = 12.5, 1.4 Hz, 2H), 1.56 (s, 1H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [18].

3,3',4,4'-tetrahydro-[1,1'-binaphthalene]-1,1'(2*H*,2'*H*)-diol (1ai)



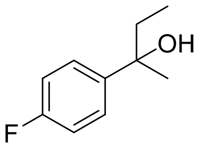
1ai

$TiCl_4$ was added to the mixture of 3,4-dihydronaphthalen-1(2*H*)-one (1.0 equiv., 5.0 mmol) and anhydrous THF (15 mL) at -78 °C. After stirring for 0.5 h at 0 ℃, Zn powder (3.0 equiv., 15.0 mmol) was added to the reaction mixture. After stirring for 20 h of reaction, the reaction mixture was quenched by slow addition of saturated $NaHCO_3$ aq. The aqueous layer was extracted with EtOAc three times. The combined organic layers were washed with brine, dried over anhydrous MgSO4, and concentrated under reduced pressure. The crude product was purified by recrystallization with EtOH and afforded 252 mg (34%) of the title compound **1ai**.

White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.26–7.19 (m, 4H), 7.10 (d, *J* = 7.4 Hz, 2H), 3.16 (d, *J* = 1.0 Hz, 2H), 2.74–2.70 (m, 2H), 2.58–2.52 (m, 2H), 1.70–1.58 (m, 6H), 1.30–1.24 (m, 2H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [55].

2-(4-fluorophenyl)butan-2-ol (1ak)



1ak

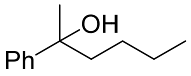
The compound was prepared from 1-(4-fluorophenyl)ethan-1-one (1.0 equiv., 5.0 mmol) and EtMgBr (1.5 equiv., 7.5 mmol) following the general procedure A. Purification by column chromatography (silica gel, 10 : 1 = hexane : EtOAc) afforded 388 mg (46%) of the title compound **1ak**.

Colorless oil; ^{1}HNMR (500 MHz, $CDCl_3$): δ 7.40–7.38 (m, 2H), 7.03–6.99 (m, 2H), 1.86–1.77

(m, 2H), 1.54 (s, 3H), 0.78 (t, J = 7.4 Hz, 3H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [57].

2-phenylhexan-2-ol (1al)



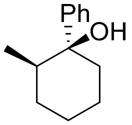
1al

The compound was prepared from 1-phenylpentan-1-one (1.0 equiv., 5.0 mmol) and MeMgBr (1.5 equiv., 7.5 mmol) following the general procedure A. Purification by column chromatography (silica gel, 10 : 1 = hexane : EtOAc) afforded 891 mg (100%) of the title compound **1al**.

Colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.44–7.42 (m, 2H), 7.36–7.32 (m, 2H), 7.26–7.22 (m, 1H), 1.86–1.75 (m, 2H), 1.71 (s, 1H), 1.56 (s, 3H), 1.30–1.19 (m, 3H), 1.14–1.08 (m, 1H), 0.86–0.83 (m, 3H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [11].

(1*S*,2*R*)-2-methyl-1-phenylcyclohexan-1-ol (1am)



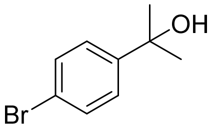
(±)-**1am**

The compound was prepared from 2-methylcyclohexan-1-one (1.0 equiv., 10 mmol), Mg (3.0 equiv., 30 mmol) and bromobenzene (1.4 equiv., 14 mmol) following the general procedure B. Purification by column chromatography (silica gel, 10 : 1 = hexane : EtOAc) afforded 882 mg (46%) of the title compound **1am**.

Colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.46–7.43 (m, 2H), 7.35–7.32 (m, 2H), 7.24–7.20 (m, 1H), 1.97–1.90 (m, 1H), 1.82–1.70 (m, 3H), 1.69–1.59 (m, 4H), 1.52–1.36 (m, 2H), 0.62 (d, J = 6.7 Hz, 3H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [19].

2-(4-bromophenyl) propan-2-ol (1an)



1an

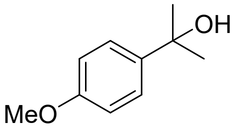
The compound was prepared from 1-(4-bromophenyl)ethan-1-one (1.0 equiv., 5.0 mmol) and

MeMgBr (1.2 equiv., 6.0 mmol) following the general procedure A. Purification by column chromatography (silica gel, 7 : 1 = hexane : EtOAc) afforded 485 mg (45%) of the title compound **1an**.

White solid; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.47–7.44 (m, 2H), 7.38–7.36 (m, 2H), 1.70 (s, 1H), 1.57 (s, 6H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [58].

2-(4-methoxyphenyl) propan-2-ol (1ao)



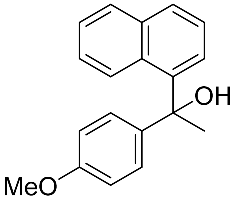
1ao

The compound was prepared from 1-(4-methoxyphenyl)ethan-1-one (1.0 equiv., 6.0 mmol) and MeMgBr (1.2 equiv., 7.2 mmol) following the general procedure A. Purification by column chromatography (silica gel, 4 : 1 = hexane : EtOAc) afforded 405 mg (41%) of the title compound **1ao.**

Colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.43–7.41 (m, 2H), 6.88–6.87 (m, 2H), 3.81 (d, *J* = 1.0 Hz, 3H), 1.70 (d, *J* = 5.4 Hz, 1H), 1.58 (d, *J* = 4.3 Hz, 6H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [58].

1-(4-methoxyphenyl)-1-(naphthalen-1-yl)ethan-1-ol (1ap)



1ap

The compound was prepared from 1-(naphthalen-1-yl)ethan-1-one (1.0 equiv., 5.0 mmol), 2.66% *n*-BuLi *n*-hexane solution (1.23 equiv., 6.15 mmol) and thiophen (1.0 equiv., 5.0 mmol) following the general procedure C. Purification by column chromatography (silica gel, 5 : 1 = hexane : EtOAc) afforded 873 mg (58%) of the title compound **1ap**.

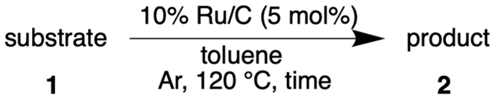
White solid; m.p.73–74 ℃; IR (NaCl) cm^{-1}: 3565, 3472, 3048, 3003, 2974, 2933, 2906, 2835, 1608, 1588, 1582, 1509, 1463, 1456, 1441, 1370, 1346, 1325, 1298, 1247, 1179, 1108, 1094, 1071, 1030, 919, 905, 857, 833, 802, 779, 759, 667; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.89–7.86 (m, 2H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.50 (dd, *J* = 8.2, 7.3 Hz, 1H), 7.37–7.34 (m, 1H), 7.30–7.27 (m, 2H), 7.24–7.21 (m, 1H), 6.81–6.78 (m, 2H), 3.76 (s, 3H), 2.35 (s, 1H), 2.07 (s, 3H); ^{13}C NMR

(125 MHz, $CDCl_3$): δ 158.3, 142.3, 140.7, 134.8, 130.6, 128.9, 128.8, 127.3, 126.5, 125.3, 125.1, 124.7, 123.9, 113.6, 55.2, 32.5

HRMS (ESI+): calcd. for $C_{19}H_{18}NaO_2^+$ (M+Na) $^+$ 301.1199, found 301.1210

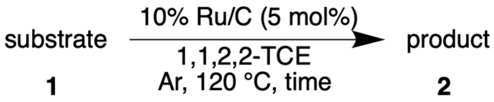
5. General Procedure of dehydration.

Method A



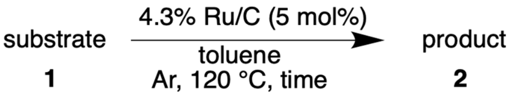
To a solution of **1** (0.25 mmol) in toluene (1 mL) was added 10% Ru/C (0.0125 mmol) under argon. The reaction mixture was refluxed at 120 °C. After stirring, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove Ru/C. The filtrate was concentrated in vacuo. The yield was calculated by the amount of product after purified by column chromatography purification.

Method B



To a solution of **1** (0.25 mmol) in 1,1,2,2-tetrachloroethane (1 mL) was added 10% Ru/C (0.0125 mmol) under argon. The reaction mixture was refluxed at 120 °C. After stirring, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove Ru/C. The filtrate was concentrated in vacuo. The yield was calculated by the amount of product after purified by column chromatography purification.

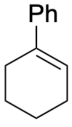
Method C



To a solution of **1** (0.25 mmol) in toluene (1 mL) was added 4.3% Ru/C (0.0125 mmol) under argon. The reaction mixture was refluxed at 120 °C. After stirring, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove Ru/C. The filtrate was concentrated in vacuo. The yield was calculated by the amount of product after purified by column chromatography purification.

6. Spectroscopic data in dehydration.

2,3,4,5-tetrahydro-1,1'-biphenyl (2a)



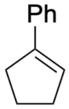
2a

When using **1a** (44 mg, 0.25 mmol) according to Method A, 2,3,4,5-tetrahydro-1,1'-biphenyl (**2a**: 37 mg, 0.2 mmol) was obtained for 2 h in 80% yield. The crude product was purified by column chromatography purification (silica gel, Hexane).

Colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.41–7.38 (m, 2H), 7.33–7.30 (m, 2H), 7.24–7.20 (m, 1H), 6.15–6.13 (m, 1H), 2.45–2.41 (m, 2H), 2.22 (qd, *J* = 6.3, 2.6 Hz, 2H), 1.82–1.77 (m, 2H), 1.70–1.65 (m, 2H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [22].

cyclopent-1-en-1-ylbenzene (2c)



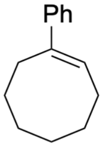
2c

When using **1c** (40.5 mg, 0.25 mmol) according to Method A, cyclopent-1-en-1-ylbenzene (**2c**: 18.9 mg, 0.131 mmol) was obtained for 2 h in 52% yield. The crude product was purified by column chromatography purification (silica gel, Hexane).

Colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.45–7.43 (m, 2H), 7.32–7.29 (m, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.20–6.18 (m, 1H), 2.73–2.69 (m, 2H), 2.55–2.51 (m, 2H), 2.05–1.99 (m, 2H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [23].

(*E*)-1-phenylcyclooct-1-ene (2d)



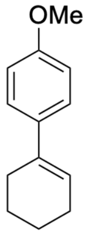
2d

When using **1d** (51.1 mg, 0.25 mmol) according to Method A, (*E*)-1-phenylcyclooct-1-ene (**2d**:37.3 mg, 0.200 mmol) was obtained for 24 h in 80% yield. The crude product was purified by column chromatography purification (silica gel, Hexane).

Colorless oil ; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42–7.37 (m, 2H), 7.34–7.28 (m, 2H), 7.23–7.18 (m, 1H), 6.03–5.98 (m, 1H), 2.67–2.58 (m, 2H), 2.31–2.24 (m, 2H), 1.65–1.64 (m, 2H), 1.59–1.56 (m, 2H), 1.54–1.51 (m, 4H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [23].

4'-methoxy-2,3,4,5-tetrahydro-1,1'-biphenyl (2e)



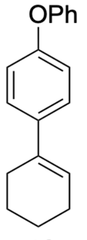
2e

When using **1e** (51.6 mg, 0.25 mmol) according to Method A, 4'-methoxy-2,3,4,5-tetrahydro-1, 1'-biphenyl (**2e**: 46.9 mg, 0.249 mmol) was obtained for 2 h in 99% yield without further column chromatography purification (silica gel, Hexane).

White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (dd, J = 6.7, 2.1 Hz, 2H), 6.85 (dd, J = 6.7, 2.1 Hz, 2H), 6.04–6.02 (m, 1H), 3.80 (s, 3H), 2.38 (qd, J = 4.1, 2.0 Hz, 2H), 2.20–2.17 (m, 2H), 1.78–1.75 (m, 2H), 1.67–1.64 (m, 2H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [22].

4’-phenoxy-2,3,4,5-tetrahydro-1,1’-biphenyl (2f)



2f

When using **1f** (67.1 mg, 0.25 mmol) according to Method A, 4’-phenoxy-2,3,4,5-tetrahydro-1, 1’-biphenyl (**2f**: 62 mg, 0.248 mmol) was obtained for 3 h in 99% yield. The crude product was purified by column chromatography purification (silica gel, Hexane).

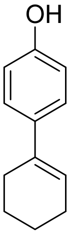
Colorless oil; IR (ATR) cm^{-1}: 3038, 2928, 2857, 2833, 1588, 1505, 1168, 870, 827, 800, 754, 691

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38–7.29 (m, 4H), 7.08 (t, J = 7.4 Hz, 1H), 7.02–6.93 (m, 4H), 6.10–6.07 (m, 1H), 2.42–2.37 (m, 2H), 2.24–2.18 (m, 2H), 1.82–1.74 (m, 2H), 1.70–1.64 (m, 2H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6, 155.9, 138.0, 135.9, 129.8, 126.3, 124.3, 123.1, 118.8, 118.8, 27.6, 26.0, 23.2, 22.3

HRMS (MALDI$^+$): calcd. For $C_{18}H_{18}O^+$ (M^+) 250.1345, found 250.1352

4'-hydroxy-2,3,4,5-tetrahydro-1,1'-biphenyl (2g)



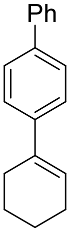
2g

When using **1g** (48.7 mg, 0.253 mmol) according to Method A, 2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-ol (**2g**: 43.8 mg, 0.251 mmol) was obtained for 1 h in 99% yield. The crude product was purified by colum chromatography purification (silica gel, 10 : 1 = hexane : EtOAc).

White solid; ^{1}H NMR (500 MHz, DMSO-d_6): 9.33 (s, 1H), 7.21–7.18 (m, 2H), 6.70–6.67 (m, 2H), 5.98–5.96 (m, 1H)2.30–2.28 (m, 2H), 2.15–2.11 (m, 2H), 1.71–1.66 (m, 2H), 1.59–1.54 (m, 2H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [61].

2,3,4,5-tetrahydro-1,1':4',1''-terphenyl (2h)



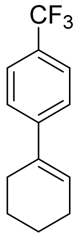
2h

When using **1h** (63.1 mg, 0.25 mmol) according to Method A, 2,3,4,5-tetrahydro-1,1':4',1''-terphenyl (**2h**: 54 mg, 0.23 mmol) was obtained for 1.5 h in 92% yield. The crude product was purified by column chromatography purification (silica gel, Hexane).

White solid; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.61–7.54 (m, 4H), 7.47–7.41 (m, 4H), 7.34–7.31 (m, 1H), 6.20–6.18 (m, 1H), 2.45 (tt, J = 6.2, 2.0 Hz, 2H), 2.25–2.21 (m, 2H), 1.83–1.78 (m, 2H), 1.70–1.66 (m, 2H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [24].

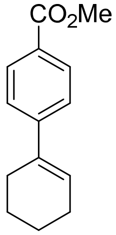
4'-(trifluoromethyl)-2,3,4,5-tetrahydro-1,1'-biphenyl (2i)



2i

When using **1i** (61.1 mg, 0.25 mmol) according to Method A, 4’-(trifluoromethyl)-2,3,4,5-tetrahydro-1,1’-biphenyl (**2i**: 48.9 mg, 0.216 mmol) was obtained for 22 h in 86% yield. The crude product was purified by column chromatography purification (silica gel, 20 : 1 = hexane : EtOAc). Colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 6.22–6.21 (m, 1H), 2.43–2.40 (m, 2H), 2.25–2.23 (m, 2H), 1.83–1.78 (m, 2H), 1.71–1.66 (m, 2H) Spectroscopic data of ^{1}H NMR was identical to those reported in reference [22].

Methyl 2’,3’,4’,5’-tetrahydro-[1,1’-biphenyl]-4-carboxylate (2j)

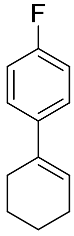


2j

When using **1j** (58.6 mg, 0.25 mmol) according to Method A, methyl 2’,3’,4’,5’-tetrahydro-[1,1’-biphenyl]-4-carboxylate (**2j**: 48.1 mg, 0.222 mmol) was obtained for 24 h in 82% yield. The crude product was purified by column chromatography purification (silica gel, 20 : 1 = hexane : EtOAc). White solid; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.97 (dd, *J* = 8.4, 1.7 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 6.26–6.25 (m, 1H), 3.91 (s, 3H), 2.42 (tt, *J* = 6.1, 2.1 Hz, 2H), 2.24 (qd, *J* = 6.3, 2.5 Hz, 2H), 1.82–1.77 (m, 2H), 1.70–1.65 (m, 2H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [25].

4’-fluoro-2,3,4,5-tetrahydro-1,1’-biphenyl (2k)



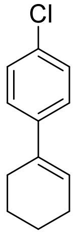
2k

When using **1k** (48.6 mg, 0.25 mmol) according to Method A, 4’-fluoro-2,3,4,5-tetrahydro- 1,1’-biphenyl (**2k**: 39.3 mg, 0.223 mmol) was obtained for 1 h in 89% yield. The crude product was purified by column chromatography purification (silica gel, Hexane).

Colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.33 (ddd, *J* = 12.0, 5.4, 3.2 Hz, 2H), 7.00–6.96 (m, 2H), 6.06–6.04 (m, 1H), 2.39–2.35 (m, 2H), 2.19 (qd, *J* = 6.3, 2.5 Hz, 2H), 1.80–1.75 (m, 2H), 1.68–1.63 (m, 2H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [22].

4’-chloro-2,3,4,5-tetrahydro-1,1’-biphenyl (2l)



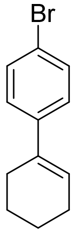
2l

When using **1l** (52.7 mg, 0.25 mmol) according to Method A, 4’-chloro-2,3,4,5-tetrahydro-1,1’-biphenyl (**2l**: 45.4 mg, 0.236 mmol) was obtained for 1.5 h in 94% yield. The crude product was purified by column chromatography purification (silica gel, Hexane).

White solid; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.30–7.28 (m, 2H), 7.25 (td, *J* = 4.4, 2.3 Hz, 2H), 6.11–6.09 (m, 1H), 2.38–2.34 (m, 2H), 2.22–2.17 (m, 2H), 1.80–1.75 (m, 2H), 1.67–1.63 (m, 2H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [23].

4’-bromo-2,3,4,5-tetrahydro-1,1’-biphenyl (2m)



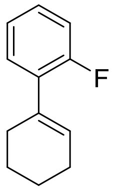
2m

When using **1m** (63.8 mg, 0.25 mmol) according to Method A, 4'-bromo-2,3,4,5-tetrahydro-1,1'-biphenyl (**2m**: 54.9 mg, 0.232 mmol) was obtained for 1 h in 93% yield. The crude product was purified by column chromatography purification (silica gel, Hexane).

White solid; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.42–7.40 (m, 2H), 7.25–7.22 (m, 2H), 6.12–6.10 (m, 1H), 2.38–2.34 (m, 2H), 2.19 (qd, *J* = 6.3, 2.5 Hz, 2H), 1.80–1.75 (m, 2H), 1.68–1.63 (m, 2H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [26].

2'-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (2n)



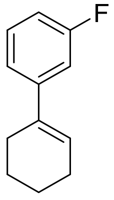
2n

When using **1n** (48.6 mg, 0.25 mmol) according to Method A, 2'-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (**2n**: 37 mg, 0.21 mmol) was obtained for 5 h in 84% yield. The crude product was purified by column chromatography purification (silica gel, Hexane).

Colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.24–7.15 (m, 2H), 7.07 (td, *J* = 7.5, 1.2 Hz, 1H), 7.01 (ddd, *J* = 11.1, 8.1, 1.3 Hz, 1H), 5.93–5.92 (m, 1H), 2.39–2.35 (m, 2H), 2.23–2.18 (m, 2H), 1.79–1.74 (m, 2H), 1.71–1.66 (m, 2H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [25].

3'-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (2o)



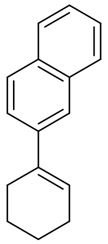
2o

When using **1o** (48.6 mg, 0.25 mmol) according to Method A, 3'-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (**2o**: 38.6 mg, 0.219 mmol) was obtained for 2 h in 88% yield. The crude product was purified by column chromatography purification (silica gel, Hexane).

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28–7.23 (m, 1H), 7.16 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.09–7.06 (m, 1H), 6.92–6.88 (m, 1H), 6.17–6.15 (m, 1H), 2.40–2.37 (m, 2H), 2.24–2.20 (m, 2H), 1.81–1.76 (m, 2H), 1.69–1.64 (m, 2H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [28].

2-(cyclohex-1-en-1-yl) naphthalene (2p)



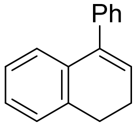
2p

When using **1p** (56.6 mg, 0.25 mmol) according to Method A, 2-(cyclohex-1-en-1-yl) naphthalene (**2p**: 51.6 mg, 0.248 mmol) was obtained for 1.3 h in 99% yield. The crude product was purified by column chromatography purification (silica gel, Hexane).

White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81–7.76 (m, 4H), 7.60 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.46–7.39 (m, 2H), 6.31–6.28 (m, 1H), 2.56–2.52 (m, 2H), 2.29–2.25 (m, 2H), 1.86–1.81 (m, 2H), 1.73–1.68 (m, 2H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [27].

4-phenyl-1,2-dihydronaphthalene (2q)



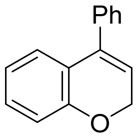
2q

When using **1q** (56.1 mg, 0.25 mmol) according to Method A, 4-phenyl-1,2-dihydronaphthalene (**2q**: 46.2 mg, 0.224 mmol) was obtained for 2 h in 90% yield. The crude product was purified by column chromatography purification (silica gel, Hexane).

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40–7.31 (m, 5H), 7.21–7.20 (m, 1H), 7.16 (td, *J* = 7.3, 1.4 Hz, 1H), 7.11 (td, *J* = 7.5, 1.6 Hz, 1H), 7.00 (dd, *J* = 7.7, 0.9 Hz, 1H), 6.09 (t, *J* = 4.7 Hz, 1H), 2.86 (t, *J* = 7.9 Hz, 2H), 2.43–2.39 (m, 2H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [29].

4-phenyl-2*H*-chromene (2r)



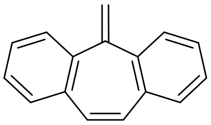
2r

When using **1r** (56.6 mg, 0.25 mmol) according to Method A, 4-phenyl-2*H*-chromene (**2r**: 28.3 mg, 0.136 mmol) was obtained for 2 h in 54% yield. The crude product was purified by column chromatography purification (silica gel, 10 : 1 = hexane : EtOAc).

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42–7.33 (m, 5H), 7.16 (td, *J* = 7.7, 1.5 Hz, 1H), 7.01 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.90 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.85 (td, *J* = 7.5, 1.2 Hz, 1H), 5.80 (t, *J* = 3.9 Hz, 1H), 4.86 (d, *J* = 4.0 Hz, 2H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [30].

5-methylene-5*H*-dibenzo[*a*,*d*][7]annulene (2s)



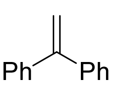
2s

When using **1s** (55.6 mg, 0.25 mmol) according to Method A, 5-methylene-5*H*-dibenzo[*a*,*d*]-[7]annulene (**2s**: 42.7 mg, 0.209 mmol) was obtained for 1.5 h in 84% yield. The crude product was purified by column chromatography purification (silica gel, Hexane).

White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (dd, *J* = 7.5, 1.4 Hz, 2H), 7.37–7.34 (m, 2H), 7.32–7.27 (m, 4H), 6.84 (s, 2H), 5.26 (s, 2H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [34].

Ethene-1,1-diyldibenzene (2t)



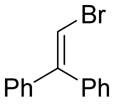
2t

When using 1,1-diphenylethan-1-ol (**1t**) (396.5 mg, 2.0 mmol) according to Method A, ethene-1,1-diyldibenzene (**2t**: 356 mg, 1.98 mmol) was obtained for 1 h in 99% yield without further column chromatography purification.

Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35–7.32 (m, 10H), 5.46 (s, 2H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [31].

(2-bromoethene-1,1-diyl) dibenzene (2u)



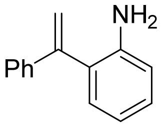
2u

When using **1u** (41.5 mg, 0.15 mmol) according to Method A, (2-bromoethene-1,1-diyl) dibenzene (**2u**: 31.8 mg, 0.123 mmol) was obtained for 24 h in 82% yield. The crude product was purified by column chromatography purification (silica gel, = 10 : 1 hexane : EtOAc).

White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43–7.35 (m, 3H), 7.32–7.28 (m, 5H), 7.23–7.20 (m, 2H), 6.77 (d, *J* = 0.6 Hz, 1H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [32].

2-(1-phenylvinyl) aniline (2v)



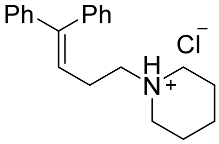
2v

When using **1v** (53.3 mg, 0.25 mmol) according to Method A, 2-(1-phenylvinyl) aniline (**2v**: 39.7 mg, 0.203 mmol) was obtained for 17 h in 81% yield. The crude product was purified by column chromatography purification (silica gel, = 10 : 1 hexane : EtOAc).

Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39–7.36 (m, 2H), 7.34–7.29 (m, 3H), 7.18–7.11 (m, 2H), 6.79 (td, *J* = 7.4, 1.1 Hz, 1H), 6.70 (dd, *J* = 8.0, 1.0 Hz, 1H), 5.80 (d, *J* = 1.4 Hz, 1H), 5.36 (d, *J* = 1.3 Hz, 1H), 3.55 (s, 2H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [33].

1-(4,4-diphenylbut-3-en-1-yl) piperidine Hydrochloride (2w)



2w

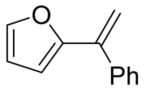
When using diphenidol hydrochloride (**1w**) (86.5 mg, 0.25 mmol) according to Method B, 1-(4,4-diphenylbut-3-en-1-yl) piperidine Hydrochloride (**2w**: 69 mg, 0.21 mmol) was obtained for 42 h in 84% yield. The crude product was purified by washing with EtOAc and filteration.

Yellow Solid; m.p. 172–174 ℃; IR (NaCl) cm^{-1}: 3408, 3053, 3025, 2946, 2860, 2635, 2534, 2378, 1730, 1598, 1495, 1444, 1074, 1031, 963, 951, 763, 702, 633; ^{1}H NMR (500 MHz, $CDCl_3$): δ

12.19 (s, 1H), 7.44–7.39 (m, 2H), 7.38–7.35 (m, 1H), 7.31–7.25 (m, 2H), 7.23–7.20 (m, 2H), 7.17–7.15 (m, 2H), 6.04 (t, *J* = 7.4 Hz, 1H), 3.39 (d, *J* = 11.3 Hz, 2H), 3.00–2.97 (m, 2H), 2.75–2.70 (m, 2H), 2.50 (t, *J* = 10.2 Hz, 2H), 2.27 (m, 2H), 1.88 (d, *J* = 12.9 Hz, 1H), 1.78 (d, *J* = 14.7 Hz, 2H), 1.34 (q, *J* = 12.9 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 129.5, 128.7, 128.4, 127.8, 127.3, 56.6, 53.0, 24.1, 22.6, 22.2

HRMS (MALDI$^+$): calcd. For $C_{21}H_{28}N^+$ (M+H)$^+$ 292.2055, found 292.2059

2-(1-phenylvinyl) furan (2x)



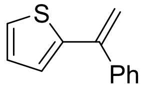
2x

When using **1x** (47.05 mg, 0.25 mmol) according to Method A, 2-(1-phenylvinyl) furan (**2x**: 41.8 mg, 0.245 mmol) was obtained for 1 h in 98% yield without further column chromatography purification (silica gel, Hexane).

Colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.46–7.43 (m, 3H), 7.39–7.35 (m, 3H), 6.39 (q, *J* = 1.7 Hz, 1H), 6.20 (d, *J* = 3.3 Hz, 1H), 5.75 (d, *J* = 1.2 Hz, 1H), 5.23 (d, *J* = 1.2 Hz, 1H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [30].

2-(1-phenylvinyl) thiophene (2y)



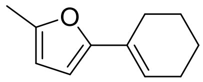
2y

When using **1y** (51.07 mg, 0.25 mmol) according to Method A, 2-(1-phenylvinyl) thiophene (**2y**: 40.3, 0.216 mmol) was obtained for 3 h in 87% yield without further column chromatography purification (silica gel, Hexane).

Colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.45–7.43 (m, 2H), 7.38–7.35 (m, 3H), 7.24 (dd, *J* = 5.1, 0.9 Hz, 1H), 6.99–6.97 (m, 1H), 6.91 (dd, *J* = 3.6, 1.0 Hz, 1H), 5.59 (s, 1H), 5.25 (s, 1H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [30].

2-(cyclohex-1-en-1-yl)-5-methylfuran (2z)

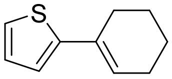


2z

When using **1z** (45.1 mg, 0.25 mmol) according to Method A, 2-(cyclohex-1-en-1-yl)-5-methylfuran (**2z**: 22.6 mg, 0.139 mmol) was obtained for 3 h in 56% yield. The crude product was purified by column chromatography purification (silica gel, Hexane).

Colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.22–6.21 (m, 1H), 6.02 (d, *J* = 3.0 Hz, 1H), 5.93–5.92 (m, 1H), 2.28 (s, 3H), 2.25 (tt, *J* = 6.2, 2.1 Hz, 2H), 2.21–2.17 (m, 2H), 1.74–1.61 (m, 4H)
Spectroscopic data of ^{1}H NMR was identical to those reported in reference [35].

2-(cyclohex-1-en-1-yl) thiophene (2aa)

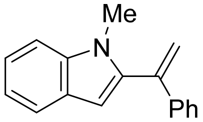


2aa

When using **1aa** (45.6 mg, 0.25 mmol) according to Method A, 2-(cyclohex-1-en-1-yl) thiophene (**2aa**: 37.6 mg, 0.229 mmol) was obtained for 2 h in 92% yield. The crude product was purified by column chromatography purification (silica gel, Hexane).

Colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.08 (dd, *J* = 5.0, 1.0 Hz, 1H), 6.96–6.92 (m, 2H), 6.20–6.18 (m, 1H), 2.43–2.40 (m, 2H), 2.18 (qd, *J* = 6.2, 2.5 Hz, 2H), 1.79–1.62 (m, 4H)
Spectroscopic data of ^{1}H NMR was identical to those reported in reference [14].

1- methyl-2-(1-phenylvinyl)-1*H*-indole (2ab)

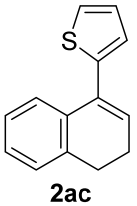


2ab

When using **1ab** (62.8 mg, 0.25 mmol) according to Method A, 1-methyl-2-(1-phenylvinyl)-1*H*-indole (**2ab**: 45.6 mg, 0.195 mmol) was obtained for 1.5 h in 78% yield. The crude product was purified by column chromatography purification (silica gel, 10 : 1 = hexane : EtOAc).

White solid; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.64 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.34–7.28 (m, 6H), 7.25–7.22 (m, 1H), 7.15–7.12 (m, 1H), 6.58 (d, *J* = 0.7 Hz, 1H), 5.81 (d, *J* = 1.6 Hz, 1H), 5.53 (d, *J* = 1.4 Hz, 1H), 3.40 (s, 3H)
Spectroscopic data of ^{1}H NMR was identical to those reported in reference [36].

2-(3,4-dihydronaphthalen-1-yl) thiophene (2ac)



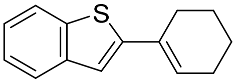
2ac

When using **1ac** (57.6 mg, 0.25 mmol) according to Method C, 2-(3,4-dihydronaphthalen-1-yl) thiophene (**2ac**: 52.8 mg, 0.249 mmol) was obtained for 0.5 h in quant. Yield. The crude product was purified by column chromatography purification (silica gel, Hexane).

Yellow oil ; IR (NaCl) cm^{-1}: 3067, 3025, 2935, 2884, 2829, 1485, 1450, 1434, 1253, 1220, 1100, 1041, 1020, 854, 823, 806, 765, 737, 696; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.36–7.34 (m, 1H), 7.26–7.24 (m, 1H), 7.21–7.16 (m, 3H), 7.06 (q, *J* = 3.6 Hz, 2H), 6.29 (t, *J* = 4.9 Hz, 1H), 2.84–2.81 (m, 2H), 2.41–2.37 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 142.7, 136.8, 134.5, 133.0, 129.3, 127.7, 127.4, 127.1, 126.4, 125.7, 125.3, 124.1, 28.1, 23.5

HRMS (MALDI$^+$): calcd. For $C_{14}H_{12}S^+$ (M)$^+$ 212.0659, found 212.0654

2-(cyclohex-1-en-1-yl) benzo[*b*]thiophene (2ad)



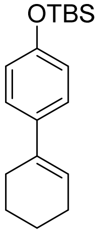
2ad

When using **1ad** (58.1 mg, 0.25 mmol) according to Method C, 2-(cyclohex-1-en-1-yl) benzo-[*b*]thiophene (**2ad**: 49.9 mg, 0.233 mmol) was obtained for 1.5 h in 93% yield. The crude product was purified by column chromatography purification (silica gel, 10 : 1 = hexane : EtOAc).

Colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.74–7.72 (m, 1H), 7.66 (dd, *J* = 7.1, 1.4 Hz, 1H), 7.30–7.23 (m, 2H), 7.11 (s, 1H), 6.31–6.29 (m, 1H), 2.52–2.48 (m, 2H), 2.26–2.23 (m, 2H), 1.83–1.78 (m, 2H), 1.71–1.66 (m, 2H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [14].

***Tert*-butyldimethyl((2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-yl) oxy) silane (2ae)**



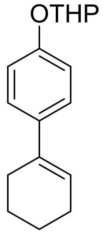
2ae

When using **1ae** (76.6 mg, 0.25 mmol) according to Method A, *tert*-butyldimethyl((2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-yl) oxy) silane (**2ae**: 37 mg, 0.2 mmol) was obtained for 24 h in 94% yield. The crude product was purified by column chromatography purification (silica gel, Hexane).

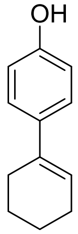
Colorless oil ; IR (NaCl) cm^{-1}: 3035, 2930, 2859, 2835, 1605, 1510, 1472, 1256, 1173, 1006, 916, 838, 826, 805, 780, 706, 668; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.26–7.24 (m, 2H), 6.78–6.76 (m, 2H), 6.04 (d, *J* = 1.0 Hz, 1H), 2.37 (d, *J* = 1.3 Hz, 2H), 2.20–2.18 (m, 2H), 1.79–1.74 (m, 2H), 1.67–1.62 (m, 2H), 0.98 (d, *J* = 1.0 Hz, 9H), 0.19 (d, *J* = 1.0 Hz, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 154.5, 136.0, 135.8, 125.8, 123.2, 119.8, 27.5, 25.9, 25.8, 23.2, 22.3, 18.3, -4.3

HRMS (ESI$^+$): calcd. For $C_{18}H_{29}OSi^+$ (M+H)$^+$ 289.1982, found 289.1969

2-((2’,3’,4’,5’-tetrahydro-[1,1’-biphenyl]-4-yl)oxy)tetrahydro-2*H*-pyran (2af)



2af



2af'

When using **1ae** (69.1 mg, 0.25 mmol) according to Method A, 2-((2’,3’,4’,5’-tetrahydro-[1,1’-biphenyl]-4-yl)oxy)tetrahydro-2*H*-pyran (**2af**:25.3 mg, 0.098 mmol) was obtained for 2 h in 40% yield and 2’,3’,4’,5’-tetrahydro-[1,1’-biphenyl]-4-ol (**2af’**:15.9 mg, 0.091 mmol) was obtained as a byproduct in 37% yield. The crude product was purified by column chromatography purification (silica gel, 10 : 1 = hexane : EtOAc).

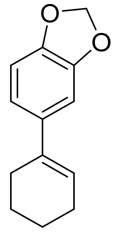
2af; Colorless oil; IR (NaCl) cm^{-1}: 2930, 2874, 2856, 2834, 1606, 1510, 1440, 1357, 1276, 1234, 1202, 1179, 1125, 1110, 1077, 1038, 1020, 967, 921, 823, 800; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32–7.29 (m, 2H), 7.00–6.97 (m, 2H), 6.04–6.02 (m, 1H), 5.41 (t, *J* = 3.3 Hz, 1H), 3.94–3.89 (m, 1H), 3.62–3.58 (m, 1H), 2.39–2.36 (m, 2H), 2.21–2.16 (m, 2H), 2.04–1.97 (m, 1H), 1.90–1.83 (m, 2H), 1.79–1.74 (m, 2H), 1.72–1.58 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 155.9, 136.3, 136.0, 125.9, 123.4, 116.2, 96.5, 62.1, 30.5, 27.5, 25.9, 25.3, 23.2, 22.3, 18.9

HRMS (ESI+): calcd. For C17H23O2^{+} (M+H)$^{+}$ 259.1693, found 259.1690

2af’ (same as **2g**); white solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28–7.26 (m, 2H), 6.79–6.76 (m, 2H), 6.03–6.01 (m, 1H), 4.63 (s, 1H), 2.39–2.35 (m, 2H), 2.21–2.16 (m, 2H), 1.79–1.74 (m, 2H), 1.67–1.62 (m, 2H)

Spectroscopic data of ^{1}H NMR was identical to that reported in the reference [59].

5-(cyclohex-1-en-1-yl)benzo[*d*][1,3]dioxole (2ag)



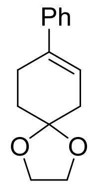
2ag

When using **1ag** (55.1 mg, 0.25 mmol) according to Method A, 5-(cyclohex-1-en-1-yl) benzo[*d*]-[1,3]dioxole (**2ag**: 27.5 mg, 0.136 mmol) was obtained for 2 h in 54% yield. The crude product was purified by column chromatography purification (silica gel, 10: 1 = hexane: EtOAc).

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.89 (d, *J* = 1.9 Hz, 1H), 6.84 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.75 (d, J = 8.2 Hz, 1H), 6.00–5.99 (m, 1H), 5.93 (s, 2H), 2.36–2.33 (m, 2H), 2.19–2.17 (m, 2H), 1.77–1.74 (m, 2H), 1.65–1.63 (m, 2H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [22].

8-phenyl-1,4-dioxaspiro[4.5]dec-7-ene (2ah)



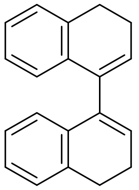
2ah

When using **1ah** (58.6 mg, 0.25 mmol) according to Method A, 8-phenyl-1,4-dioxaspiro-[4.5]dec-7-ene (**2ah**: 44 mg, 0.203 mmol) was obtained for 21.6 h in 81% yield. The crude product was purified by column chromatography purification (silica gel, 10 : 1 = hexane : EtOAc).

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40–7.38 (m, 2H), 7.32–7.29 (m, 2H), 7.24–7.21 (m, 1H), 6.00–5.98 (m, 1H), 4.03 (s, 4H), 2.69–2.65 (m, 2H), 2.47 (t, J = 1.9 Hz, 2H), 1.93 (t, J = 6.5 Hz, 2H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [41].

3,3’,4,4’-tetrahydro-1,1’-binaphthalene (2ai)



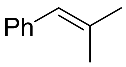
2ai

When using **1ai** (58.9 mg, 0.20 mmol) according to Method A, 8-phenyl-1,4-dioxaspiro- [4.5]dec-7-ene (**2ai**: 27.4 mg, 0.106 mmol) was obtained for 6 h in 53% yield. The crude product was purified by column chromatography purification (silica gel, hexane).

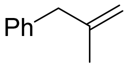
White solid; ^{1}HNMR (500 MHz, $CDCl_3$): δ 7.16 (d, J = 6.9 Hz, 2H), 7.09 (td, J = 7.4, 1.3 Hz, 2H), 7.00 (td, J = 7.5, 1.1 Hz, 2H), 6.91 (d, J = 7.4 Hz, 2H), 6.08 (t, J = 4.5 Hz, 2H), 2.89 (t, J = 7.2 Hz, 4H), 2.40 (td, J = 7.9, 4.6 Hz, 4H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [60].

(2-methylprop-1-en-1-yl)benzene (2ai), (2-methylallyl)benzene (2aj’)



2aj



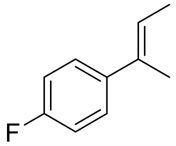
2aj’

When using 2-methyl-1-phenylpropan-2-ol (**1aj**) (37.6 mg, 0.25 mmol) according to Method A, 91% of **2aj** and 9% of **2aj’** was obtained for 24 h and the yield was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. Because products easily vapored, the yields of products were determined by ^{1}H NMR with toluene solvent.

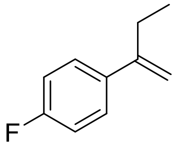
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.43 (**2aj**; s, 1H), 4.97 (**2aj’**; s, 1H), 4.89 (**2aj’**; s, 1H), 3.46 (**2aj’**; s, 2H), 2.05 (**2aj**; s, 3H), 2.00 (**2aj**; s, 3H), 1.83 (**2aj’**; s, 3H)

Spectroscopic data of ^{1}H NMR was identical to those reported in references [37] and [38].

1-(but-2-en-2-yl)-4-fluorobenzene (2ak), 1-(but-1-en-2-yl)-4-fluorobenzene (2ak’)



2ak



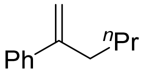
2ak’

When using **1ak** (42.1 mg, 0.25 mmol) according to Method A, 56% of **2ak** and 35% of **2ak’** was obtained for 1 h and the yield was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. Because products easily vapored, the yields of products were determined by ^{1}H NMR with toluene solvent.

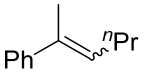
Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$); δ 7.07–6.97 (m, 2H), 5.85–5.78 (**2ak**; m, 1H), 5.24 (**2ak’**; s, 1H), 5.06 (**2ak’**; d, J = 1.4 Hz, 1H), 2.02 (**2ak**; s, 3H), 1.81 (**2ak**; d, J = 6.9 Hz, 3H), 1.11 (**2ak’**; t, J = 7.4 Hz, 3H)

Spectroscopic data of ^{1}H NMR was identical to those reported in references [53] and [54].

Hex-1-en-2-ylbenzene (2ak), hex-2-en-2-ylbenzene (2al’)



2al



2al’

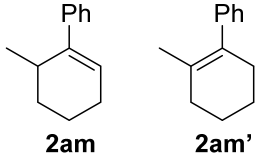
When using **1al** (44.6 mg, 0.25 mmol) according to Method A, 45% of **2al** and 52% of **2al’** was obtained for 4 h and the yield was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43–7.38 (**2al**; m, 2H/**2al’**; m, 2H), 7.35–7.29 (**2al**; m, 2H/**2al’**; m, 2H), 7.24–7.18 (**2al**; m, 1H/ **2al’**; m, 1H), 5.81–5.78 (**2al’;** m, 1H), 5.27 (**2al**; d, J = 1.6 Hz, 1H), 5.06 (**2al**; d, J = 1.4 Hz, 1H), 2.53–2.49 (**2al**; m, 2H), 2.21–2.17 (**2al’**; m, 2H), 2.04 (**2al’**; d, J = 1.1 Hz, 2H), 1.54–1.41 (**2al**; m, 2H), 1.39–1.32 (**2al**; m, 2H), 0.97 (**2al’**; t, J =

7.4 Hz, 2H), 0.90 (**2al**; t, *J* = 7.3 Hz, 3H)

Spectroscopic data of ^{1}H NMR was identical to those reported in references [39] and [40].

2-methyl-2,3,4,5-tetrahydro-1,1'-biphenyl and 6-methyl-2,3,4,5-tetrahydro-1,1'-biphenyl (2am, 2am')



When using **1j** (47.6 mg, 0.25 mmol) according to Method A, 60% of **2am** and 10% of **2am'** was obtained for 24 h and the yield was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. By column chromatography purification (silica gel, hexane) of the crude product, an inseparable mixture (**2am/2am'**: 6/1; 18.1 mg) was obtained in 36% of **2am** and 6% of **2am'**.

Colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.33–7.28 (**2am**; m, 4H/ **2am'**; m, 2H), 7.24–7.18 (**2am**; m, 1H/ **2am'**; m, 2H), 7.15–7.13 (**2am'**; m, 2H), 5.88 (**2am**; td, *J* = 3.9, 1.1 Hz, 1H), 2.85–2.81 (**2am**; m, 1H), 2.24–2.22 (**2am'**; m, 2H), 2.18–2.14 (**2am**; m, 2H), 2.08–2.06 (**2am'**; m, 2H), 1.90–1.85 (**2am**; m, 1H), 1.74–1.66 (**2am**; m, 1H/**2am'**; m, 4H), 1.65–1.56 (**2am**; m, 2H), 1.55 (**2am'**; s, 3H), 0.93 (**2am**; d, *J* = 7.0 Hz, 3H)

Spectroscopic data of ^{1}H NMR was identical to those reported in reference [42], [43].

7. Procedure of Figure 3B

7-1. Procedure of Figure 3B-(i)

To a solution of **5a** (0.25 mmol) in toluene (1 mL) was added 10% Ru/C (0.0125 mmol) under argon. The reaction mixture was refluxed at 120 °C. After stirring for 18 h, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove Ru/C. The filtrate was concentrated in vacuo. Then, 36% of **6a**, 11% of **7a** and 14% of **8a** were obtained. The yield was calculated by the amount of product after purified by column chromatography purification.

7-2. Procedure of Figure 3B-(ii)

To a solution of **9a** (0.25 mmol) in toluene (1 mL) was added 10% Ru/C (0.0125 mmol) under argon. The reaction mixture was refluxed at 120 °C. After stirring for 18 h, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove Ru/C. The filtrate was concentrated in vacuo. Then, olefin was not obtained and 76% of **9a** was recovered. The yield was calculated by the amount of product after purified by column chromatography purification.

7-3. Procedure of Figure 3B-(iii)

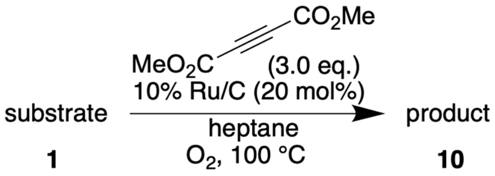
To a solution of **1t** (0.25 mmol) and **5a** (0.25 mmol) in toluene (1 mL) was added 10% Ru/C (0.0125 mmol) under argon. The reaction mixture was refluxed at 120 °C. After stirring for 24 h, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove Ru/C. The filtrate was concentrated in vacuo. Then, 99% of **2t** was obtained from **1t** and 46% of **6a**, 19% of **7a** and 13% of **8a** were obtained from **5a**. The yield was calculated by the amount of product after purified by column chromatography purification.

7-4. Procedure of Figure 3B-(iv)

To a solution of **1t** (0.25 mmol) and **5a** (0.25 mmol) in toluene (1 mL) was added 10% Ru/C (0.025 mmol) under O_2. The reaction mixture was refluxed at 120 °C. After stirring for 48 h, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove Ru/C. The filtrate was concentrated in vacuo. Then, 91% of **2t** was obtained from **1t** and trace **6a** and 86% of **7a** were obtained from **5a**. The yield was calculated by the amount of product after purified by column chromatography purification.

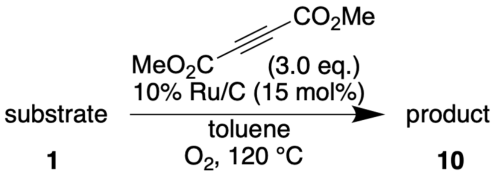
8. Gneral procedure in one-pot synthesis.

Method A



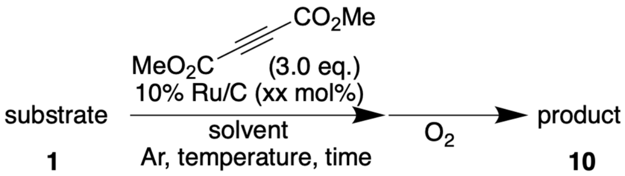
To a solution of **1** (0.25 mmol, 1.0 equiv.) in heptane (1 mL) was added catalyst amount of 10% Ru/C (20 mol%) and Dimethyl acetylene dicarboxylate (0.75 mmol, 3.0 equiv.) under O_2. The reaction mixture was refluxed at 100 ℃. After stirring, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove Ru/C. The filtrate was concentrated in vacuo. The yield was calculated by the amount of product after purified by column chromatography purification.

Method B



To a solution of **1** (0.25 mmol, 1.0 equiv.) in toluene (1 mL) was added catalyst amount of 10% Ru/C (15 mol%) and Dimethyl acetylene dicarboxylate (0.75 mmol, 3.0 equiv.) under O_2. The reaction mixture was refluxed at 120 °C. After stirring, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove Ru/C. The filtrate was concentrated in vacuo. The yield was calculated by the amount of product after purified by column chromatography purification.

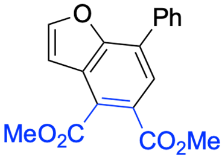
Method C



To a solution of **1** (0.25 mmol, 1.0 equiv.) in xylene (1 mL) was added catalyst amount of 10% Ru/C (xx mol%) and Dimethyl acetylene dicarboxylate (0.75 mmol, 3.0 equiv.) under Ar. The reaction mixture was stirred at 140 °C. After stirring, Replace argon with oxygen and the reaction mixture was stirred at 100 ℃. After that, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove Ru/C. The filtrate was concentrated in vacuo. The yield was calculated by the amount of product after purified by column chromatography purification.

9. Spectroscopic data in one-pot synthesis.

dimethyl 7-phenylbenzofuran-4,5-dicarboxylate (10a)



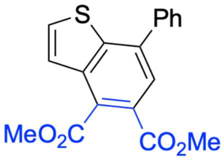
10a

When using **1x** (47.05 mg, 0.25 mmol) according to Method A, 65% of dimethyl 7-phenylbenzofuran-4,5-dicarboxylate (**10a)** was obtained for 48 h and the yield is determined by 1H NMR using 1,1,2,2-tetrachloroethane as an internal standard. By column chromatography purification (silica gel, 4 : 1 = hexane : EtOAc) of the crude product, the pure compound (**10a**: 47.4 mg, 0.15 mmol) was obtained in 61% yield.

Yellow solid; m.p. 69–70 ℃; IR (NaCl) cm^{-1}: 2952, 1723, 1433, 1316, 1269, 1206, 1165, 1127, 1043, 761, 697; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89–7.80 (m, 4H), 7.54–7.51 (m, 2H), 7.47–7.44 (m, 1H), 7.11–7.10 (m, 1H), 4.01 (s, 3H), 3.95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.2, 167.4, 153.4, 147.5, 134.7, 128.9, 128.9, 128.8, 128.1, 127.9, 127.4, 124.8, 124.4, 107.2, 52.8, 52.8

HRMS (MALDI$^+$): calcd. for $C_{18}H_{14}NaO_5^+$ (M+Na)$^+$ 333.0729, found 333.0733

dimethyl 7-phenylbenzo[*b*]thiophene-4,5-dicarboxylate (10b)



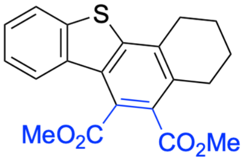
10b

When using **1y** (51.07 mg, 0.25 mmol) according to Method A, 85% of dimethyl 7-phenylbenzo[*b*]thiophenne-4,5-dicarboxylate (**10b)** was obtained for 48 h and the yield is determined by 1H NMR using 1,1,2,2-tetrachloroethane as an internal standard. By column chromatography purification (silica gel, 4 : 1 = hexane : EtOAc) of the crude product, the pure compound (**10b**: 44.7 mg, mmol) was obtained in 55% yield.

Yellow solid; m.p.106–108 ℃; ; IR (NaCl) cm^{-1}: 2950, 1725, 1447, 1362, 1287, 1253, 1196, 1166, 1111, 813, 755, 700; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.73–7.70 (m, 2H), 7.62 (d, *J* = 5.6 Hz, 1H), 7.55–7.51 (m, 3H), 7.49–7.46 (m, 1H), 4.04 (s, 3H), 3.95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.0, 167.1, 143.2, 139.2, 138.4, 137.9, 129.7, 129.1, 128.9, 128.6, 128.3, 126.2, 124.5, 123.5, 53.0, 52.8

HRMS (MALDI$^+$): calcd. for $C_{18}H_{14}NaO_4S^+$ (M+Na)$^+$ 349.0498, found 349.0505

dimethyl 1,2,3,4-tetrahydrobenzo[*b*]naphtho[2,1-*d*]thiophene-5,6-dicarboxylate (10c)



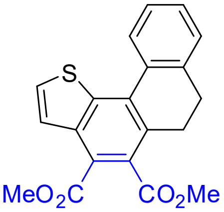
10c

When using **1ad** (58.1 mg, 0.25 mmol) according to Method B, 56% of dimethyl 1,2,3,4-tetrahydrobenzo[*b*]naphtho[2,1-*d*]thiophene-5,6-dicarboxylate (**10c)** was obtained for 24 h and the yield is determined by 1H NMR using 1,1,2,2-tetrachloroethane as an internal standard. By column chromatography purification (silica gel, 4 : 1 = hexane : EtOAc) of the crude product, the pure compound (**10c**: 50.2 mg, 0.14 mmol) was obtained in 56% yield.

White solid; m.p.135–136 ℃; IR (NaCl) cm^{-1}: 2948, 1732, 1563, 1435, 1275, 1245, 1209, 1163, 1125, 1038, 991, 762, 732; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.99–7.97 (m, 1H), 7.87–7.85 (m, 1H), 7.47–7.40 (m, 2H), 4.04 (s, 3H), 3.93 (s, 3H), 2.98–2.93 (m, 4H), 1.99–1.94 (m, 2H), 1.91–1.86 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 169.2, 168.8, 143.2, 139.5, 134.3, 133.7, 133.4, 128.8, 128.6, 127.0, 126.2, 124.9, 123.8, 123.0, 52.9, 52.6, 28.9, 27.7, 22.9, 22.2

HRMS (MALDI$^+$): calcd. for $C_{20}H_{18}NaO_4S^+$ (M+Na)$^+$ 377.0815, found 377.0818

dimethyl 6,7-dihydrophenanthro[4,3-*b*]thiophene-4,5-dicarboxylate (10d)



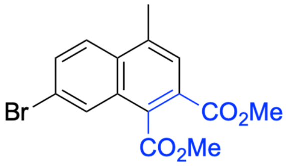
10d

When using **1ac** (57.6 mg, 0.25 mmol) according to Method C, 50% of dimethyl 6,7-dihydrophenanthro[4,3-*b*]thiophene-4,5-dicarboxylate (**10d**) was obtained after purification by silica-gel column chromatography (silica gel, 4 : 1 = hexane : EtOAc).

Yellow solid; m.p.128–129 °C; IR (NaCl) cm^{-1}: 2950, 2916, 2849, 1729, 1545, 1458, 1438, 1355, 1283, 1257, 1200, 1233, 1178, 1125, 910, 773, 749, 668; ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.35 (d, *J* = 7.9 Hz, 1H), 7.99 (dd, *J* = 5.7, 0.3 Hz, 1H), 7.62 (d, *J* = 5.7 Hz, 1H), 7.45–7.41 (m, 1H), 7.38–7.35 (m, 2H), 3.99 (s, 3H), 3.98 (d, 3H), 2.94–2.91 (m, 2H), 2.84–2.82 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 169.9, 167.1, 139.5, 138.6, 138.1, 134.1, 133.2, 132.2, 131.8, 129.0, 128.7, 128.1, 126.9, 126.3, 124.7, 122.6, 52.8, 52.7, 28.7, 26.5

HRMS (MALDI$^+$): calcd. for $C_{20}H_{16}NaO_4S^+$ (M+Na)$^+$ 375.0661, found 375.0658

dimethyl 7-bromo-4-methylnaphthalene-1,2-dicarboxylate (10e)



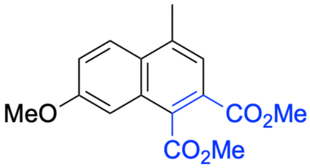
10e

When using **1an** (53.7 mg, 0.25 mmol) according to Method A, 60% of dimethyl 7-bromo-4-methylnaphthalene-1,2-dicarboxylate (**10e)** was obtained for 24 h and the yield is determined by 1H NMR using 1,1,2,2-tetrachloroethane as an internal standard. By column chromatography purification (silica gel, 4 : 1 = hexane : EtOAc) of the crude product, the pure compound (**10e**: 51.7 mg, 0.144 mmol) was obtained in 58% yield.

White solid; m.p.131–132 ℃; IR (NaCl) cm^{-1}: 2951, 1726, 1592, 1573, 1438, 1349, 1330, 1257, 1228, 1161, 1141, 1088, 1042, 1006, 894, 824, 792, 759; ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.04 (d, *J* = 1.7 Hz, 1H), 7.90 (d, *J* = 8.9 Hz, 1H), 7.86 (d, *J* = 0.9 Hz, 1H), 7.71 (dd, *J* = 9.0, 1.9 Hz, 1H), 4.07 (s, 3H), 3.96 (s, 3H), 2.72 (d, *J* = 0.9 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 169.2, 166.3, 136.9, 132.8, 132.2, 131.8, 130.7, 128.9, 126.1, 126.0, 125.8, 122.0, 53.2, 52.9, 19.6

HRMS (ESI$^+$): calcd. for $C_{15}H_{13}BrNaO_4^+$ (M+Na)$^+$ 358.9889, found 358.9888

dimethyl 7-methoxy-4-methylnaphthalene-1,2-dicarboxylate (10f)



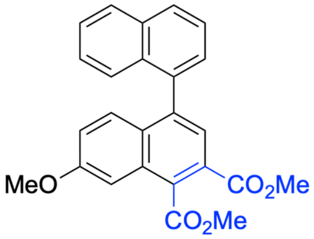
10f

When using **1ao** (41.5 mg, 0.25 mmol) according to Method B, 43% of dimethyl 7-methoxy-4-methylnaphthalene-1,2-dicarboxylate (**10f)** was obtained for 24 h and the yield is determined by 1H NMR using 1,1,2,2-tetrachloroethane as an internal standard. By column chromatography purification (silica gel, 4 : 1 = hexane : EtOAc) of the crude product, the pure compound (**10f**: 23.7mg, 0.082 mmol) was obtained in 33% yield.

White solid; m.p.126–129 ℃; IR (NaCl) cm^{-1}: 2954, 1724, 1623, 1599, 1580, 1516, 1436, 1376, 1347, 1268, 1234,1226, 1194, 1155, 1139, 1039, 1023, 952, 828, 791, 706; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.95 (d, *J* = 9.3 Hz, 1H), 7.71 (d, *J* = 0.6 Hz, 1H), 7.30 (dd, *J* = 9.3, 2.6 Hz, 1H), 7.16 (d, *J* = 2.6 Hz, 1H), 4.05 (s, 3H), 3.95 (s, 3H), 3.92 (s, 3H), 2.70 (d, *J* = 0.7 Hz, 3H); ^{13}CNMR (125 MHz, CDCl$_3$): δ 170.1, 166.8, 158.6, 136.6, 131.6, 131.0, 130.0, 126.0, 125.5, 123.5, 121.1, 104.6, 55.4, 52.9, 52.7, 19.7

HRMS (ESI$^+$): calcd. for $C_{16}H_{16}NaO_5^+$ (M+Na)$^+$ 311.0890, found 311.0887

dimethyl 6-methoxy-[1,1'-binaphthalene]-3,4-dicarboxylate (10g)



10g

When using **1ap** (69.58 mg, 0.25 mmol) according to Method B, 54% of dimethyl 6-methoxy-[1,1'-binaphthalene]-3,4-dicarboxylate (**10g)** was obtained for 24 h and the yield is determined by 1H NMR using 1,1,2,2-tetrachloroethane as an internal standard. By column chromatography purification (silica gel, 4 : 1 = hexane : EtOAc) of the crude product, the pure compound (**10g**: 43.1mg, 0.107 mmol) was obtained in 43% yield.

White solid; m.p.115–116 ℃; IR (NaCl) cm^{-1}: 3008, 2951, 2833, 1729, 1622, 1575, 1511, 1455, 1442, 1435, 1420, 1354, 1261, 1232, 1138, 1028, 904, 832, 804, 781, 756; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 12.2, 8.2 Hz, 2H), 7.91 (s, 1H), 7.59 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.51–7.47 (m, 1H), 7.47–7.45 (m, 1H), 7.34 (d, *J* = 9.3 Hz, 1H), 7.31–7.29 (m, 2H), 7.22 (d, *J* = 2.6 Hz, 1H), 7.07 (dd, *J* = 9.3, 2.6 Hz, 1H), 4.13 (s, 3H), 3.93 (s, 3H), 3.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.0, 166.6, 158.9, 140.5, 137.1, 133.6, 133.0, 132.5, 131.1, 130.4, 128.6, 128.4, 127.8, 126.4, 126.2, 126.1, 125.4, 125.3, 124.8, 121.5, 104.1, 55.5, 53.1, 52.8

HRMS (ESI$^+$): calcd. for $C_{25}H_{20}NaO_5^+$ (M+Na)$^+$ 423.1203, found 423.1195

10. Gneral procedure in aromatization.

General procedure A using H_2 acceptor (10 equiv.) for 24 h

To a mixture of **1** (0.25 mmol) and H_2O (1 mL) were added Pd/C (13.3 mg, 0.0125 mmol) and 3-pentan-2-one (244 µL, 2.5 mmol) as a H_2 acceptor under argon. The reaction mixture was refluxed at 120 °C. After stirring for 24 h, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove Pd/C. The filtrate was extracted with EtOAc (10 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

General procedure B using H_2 acceptor (10 equiv.) for 6 h

To a mixture of **1** (0.25 mmol) and H_2O (1 mL) were added Pd/C (13.3 mg, 0.0125 mmol) and 3-pentan-2-one (244 µL, 2.5 mmol) as a H_2 acceptor under argon. The reaction mixture was refluxed at 120 °C. After stirring for 6 h, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove Pd/C. The filtrate was extracted with EtOAc (10 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

General procedure C using H_2 acceptor (5 equiv.) for 24 h

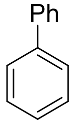
To a mixture of **1** (0.25 mmol) and H_2O (1 mL) were added Pd/C (13.3 mg, 0.0125 mmol) and 3-pentan-2-one (122 µL, 1.25 mmol) as a H_2 acceptor under argon. The reaction mixture was refluxed at 120 °C. After stirring for 24 h, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove Pd/C. The filtrate was extracted with EtOAc (10 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

General procedure D using Pd/C and Ru/C

To a mixture of **1** (0.25 mmol) and H_2O (1 mL) were added Pd/C (13.3 mg, 0.0125 mmol), Ru/C (12.6 mg, 0.0125 mmol) and 3-pentan-2-one (122 µL, 1.25 mmol) as a H_2 acceptor under argon. The reaction mixture was refluxed at 120 °C. After stirring for 24 h, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove Pd/C. The filtrate was extracted with EtOAc (10 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

11. Spectroscopic data in aromatization.

1,1'-biphenyl (3a)



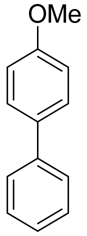
3a

When using **1a** (44.0 mg, 0.25 mmol) according to general procedure A, 91% of 1,1'-biphenyl (**3a)** and 9% of cyclohexylbenzene (**4a**) was obtained and the yield is determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. By column chromatography purification (silica gel, 40 : 1 = hexane : EtOAc) of the crude product, the pure compound (**3a**: 34.0mg, 0.22 mmol) was obtained in 88% yield.

Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61–7.59 (m, 4H), 7.46–7.43 (m, 4H), 7.37–7.33 (m, 2H).

Spectroscopic data of ^{1}H NMR was identical to that reported in the reference [45].

4-methoxy-1,1'-biphenyl (3b)



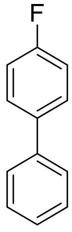
3b

When using **1e** (52.0 mg, 0.25 mmol) according to general procedure B, 77% of 4-methoxy-1,1'-biphenyl (**3b)** and 23% of 1-cyclohexyl-4-methoxybenzene (**4b**) was obtained and the yield is determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. By column chromatography purification (silica gel, hexane) of the crude product, an inseparable mixture (**3b/4b**: 4/1; 40.4mg) was obtained in 70% of **3b** and 17% of **4b**.

The spectroscopic data of **3b**; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57–7.52 (m, 4H), 7.44–7.41 (m, 2H), 7.33–7.29 (m, 1H), 7.00–6.97 (m, 2H), 3.86 (s, 1H).

Spectroscopic data of ^{1}H NMR was identical to that reported in the reference [46].

4-fluoro-1,1'-biphenyl (3c)



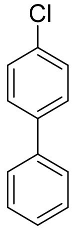
3c

When using **1j** (48.6 mg, 0.25 mmol) according to general procedure C, 99% of 4-fluoro-1,1’-biphenyl (**3a)** and 1% of 1-cyclohexyl-4-fluorobenzene (**4c**) was obtained and the yield is determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. By column chromatography purification (silica gel, 40 : 1 = hexane : EtOAc) of the crude product, the pure compound (**3c**: 33.6mg, 0.20 mmol) was obtained in 78% yield.

Colorless solid; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.58–7.53 (m, 4H), 7.47–7.42 (m, 2H), 7.36–7.33 (m, 1H), 7.15–7.10 (m, 2H).

Spectroscopic data of ^{1}H NMR was identical to that reported in the reference [47].

4-chloro-1,1’-biphenyl (3d)



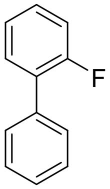
3d

When using **1k** (52.7 mg, 0.25 mmol) according to general procedure C, 73% of 4-chloro-1,1'-biphenyl (**3d)** and 26% of 1,1'-biphenyl (**3a**) was obtained and the yield is determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. By column chromatography purification (silica gel, hexane) of the crude product, an inseparable mixture (**3d/3a**: 4/1; 32.1 mg) was obtained in 56% of **3d** and 14% of **3a**.

The spectroscopic data of **3d**; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.60–7.50 (m, 4H), 7.50–7.35 (m, 5H).

Spectroscopic data of ^{1}H NMR was identical to that reported in the reference [48].

2-fluoro-1,1'-biphenyl (3e)



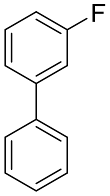
3e

When using **1m** (48.6 mg, 0.25 mmol) according to general procedure D, 87% of 2-fluoro-1,1'-biphenyl (**3e)** and 11% of 1-cyclohexyl-2-fluorobenzene (**4e**) was obtained and the yield is determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. By column chromatography purification (silica gel, 40 : 1 = hexane : EtOAc) of the crude product, the pure compound (**3e**) was obtained in 87% yield.

Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57–7.54 (m, 2H), 7.46–7.43 (m, 3H), 7.39–7.36 (m, 1H), 7.34–7.30 (m, 1H), 7.21 (td, *J* = 7.5, 1.2 Hz, 1H), 7.15 (ddd, *J* = 10.7, 8.2, 1.2 Hz, 1H).

Spectroscopic data of ^{1}H NMR was identical to that reported in the reference [51].

3-fluoro-1,1'-biphenyl (3f)



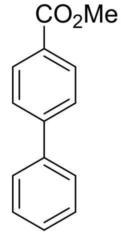
3f

When using **1n** (48.6 mg, 0.25 mmol) according to general procedure D, 58% of 3-fluoro-1,1'-biphenyl (**3f)** and 16% of 1-cyclohexyl-3-fluorobenzene (**4f**) was obtained and the yield is determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. By column chromatography purification (silica gel, 40 : 1 = hexane : EtOAc) of the crude product, the pure compound (**3f**) was obtained in 58% yield.

Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58–7.56 (m, 2H), 7.46–7.43 (m, 2H), 7.42–7.36 (m, 3H), 7.30–7.28 (m, 1H), 7.06–7.02 (m, 1H).

Spectroscopic data of ^{1}H NMR was identical to that reported in the reference [48].

methyl [1,1'-biphenyl]-4-carboxylate (3g)

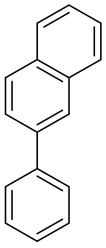


3g

When using **1i** (58.6 mg, 0.25 mmol) according to general procedure D, 45% of methyl [1,1'-biphenyl]-4-carboxylate (**3g)** and 10% of methyl 4-cyclohexylbenzoate (**4g**) was obtained and the yield is determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. By column chromatography purification (silica gel, 40 : 1 = hexane : EtOAc) of the crude product, the pure compound (**3g**) was obtained in 45% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13–8.10 (m, 2H), 7.69–7.62 (m, 4H), 7.50–7.42 (m, 2H), 7.42–7.35 (m, 1H), 3.94 (s, 3H). Spectroscopic data of ^{1}H NMR was identical to that reported in the reference [50].

2-phenylnaphthalene (3h)



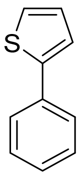
3h

When using **1o** (56.6 mg, 0.25 mmol) according to general procedure A, 69% of 2-phenylnaphthalene (**3h)** and 31% of 2-cyclohexylnaphthalene (**4h**) was obtained and the yield is determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. By column chromatography purification (silica gel, 40 : 1 = hexane : EtOAc) of the crude product, the pure compound (**3h**: 36.8mg, 0.18 mmol) was obtained in 72% yield.

Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 1.2 Hz, 1H), 7.93–7.86 (m, 3H), 7.77–7.72 (m, 3H), 7.53–7.47 (m, 4H), 7.40–7.37 (m, 1H).

Spectroscopic data of ^{1}H NMR was identical to that reported in the reference [48].

2-phenylthiophene (3i)



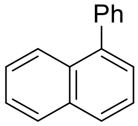
3i

When using **1z** (45.6 mg, 0.25 mmol) according to general procedure A, 50% of 2-phenylthiophene (**3i)** and 41% of 2-cyclohexylthiophene (**4i**) was obtained and the yield is determined by 1H NMR using 1,1,2,2-tetrachloroethane as an internal standard. By column chromatography purification (silica gel, 40 : 1 = hexane : EtOAc) of the crude product, the pure compound (**3i**) was obtained in 46% yield.

Colorless solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63–7.59 (m, 2H), 7.41–7.27 (m, 5H), 7.08 (dd, *J* = 5.2, 3.4 Hz, 1H).

Spectroscopic data of ^{1}H NMR was identical to that reported in the reference [46].

1-phenylnaphthalene (3j)



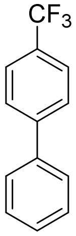
3j

When using **1p** (56.0 mg, 0.25 mmol) according to general procedure B, 91% of 1-phenylnaphthalene (**3j)** and 9% of 1-phenyl-1,2,3,4-tetrahydronaphthalene (**4j**) was obtained and the yield is determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. By column chromatography purification (silica gel, 40 : 1 = hexane : EtOAc) of the crude product, an inseparable mixture (**3j/4j**: 8.4/1; 43.7 mg) was obtained in 76% of **3j** and 9% of **4j**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91–7.90 (m, 2H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.54–7.41 (m, 9H).

Spectroscopic data of ^{1}H NMR was identical to that reported in the reference [52].

4-(trifluoromethyl)-1,1'-biphenyl (3k)



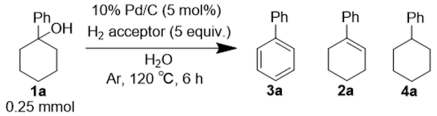
3k

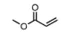
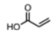
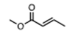
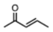
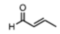
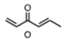
To a mixture of **2i** (40.9 mg, 0.18 mmol) and H_2O (0.72 mL) were added Pd/C (9.6 mg, 0.009 mmol) and 3-pentan-2-one (88 μL, 0.90 mmol) as a H_2 acceptor under argon. The reaction mixture was refluxed at 120 °C. After stirring for 24 h, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove Pd/C. The filtrate was extracted with EtOAc (10 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The yield of **3k** (69%) was calculated based on ^{1}H NMR analysis of a crude mixture using 1,1,2,2-tetrachloroethane (26.5 μL, 0.25 mmol) as an internal standard. After purification by silica-gel column chromatography (silica gel, = 40 : 1 = hexane : EtOAc), **3k** (22.3 mg) was obtained in 56% yield.

Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 4H), 7.61–7.59 (m, 2H), 7.50–7.46 (m, 2H), 7.43–7.39 (m, 1H).

Spectroscopic data of ^{1}H NMR was identical to that reported in the reference [46].

12. Screening of H_2 acceptor in one-pot synthesis of biaryl



entry	H_2 acceptor	yield (%)[c]			
		1a (SM)	**3a**	**2a**	**4a**
1[d]		trace	64	15	trace
2		trace	47	13	trace
3[d]		0	55	19	trace
4		0	63	37	0
5		24	24	50	trace
6		0	**81**	19	0
7		0	40	48	0
8		85	0	0	15
9		0	61	39	0

[a]Reations were conducted on a 0.25 mmol scale and 1 mL of H_2O was used. [b]10 w/w% palladium/carbon catalyst (N.E.ChemCat) was used. [c]Determined by ^1H NMR using 1,1,2,2-tetrachloroethane as an internal standard. [d]Using H_2 acceptor (10 equiv)

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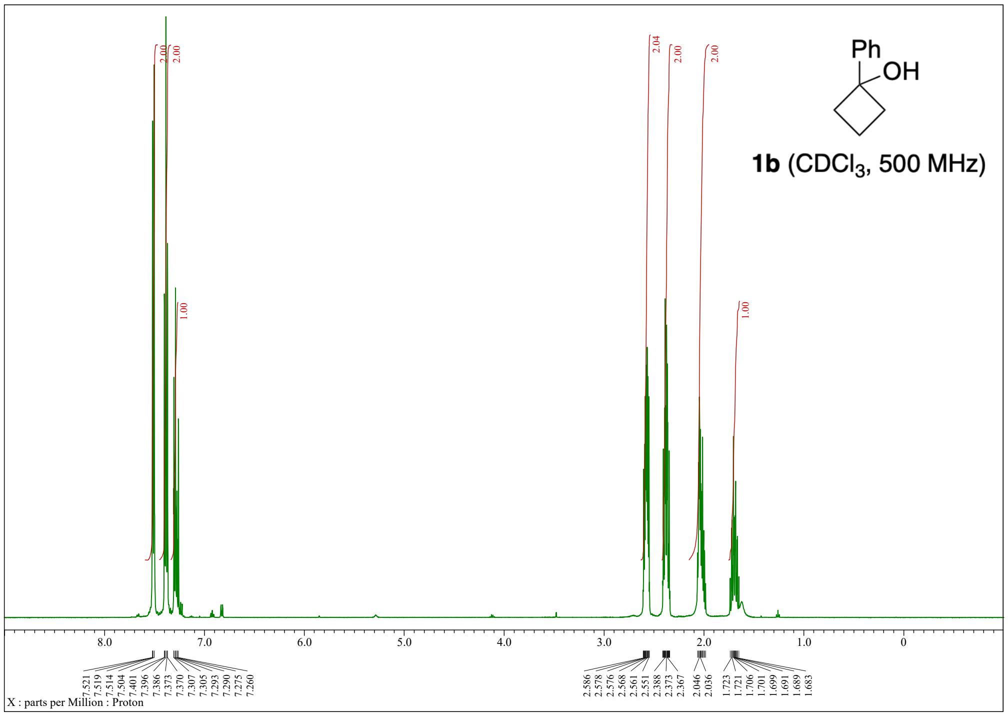
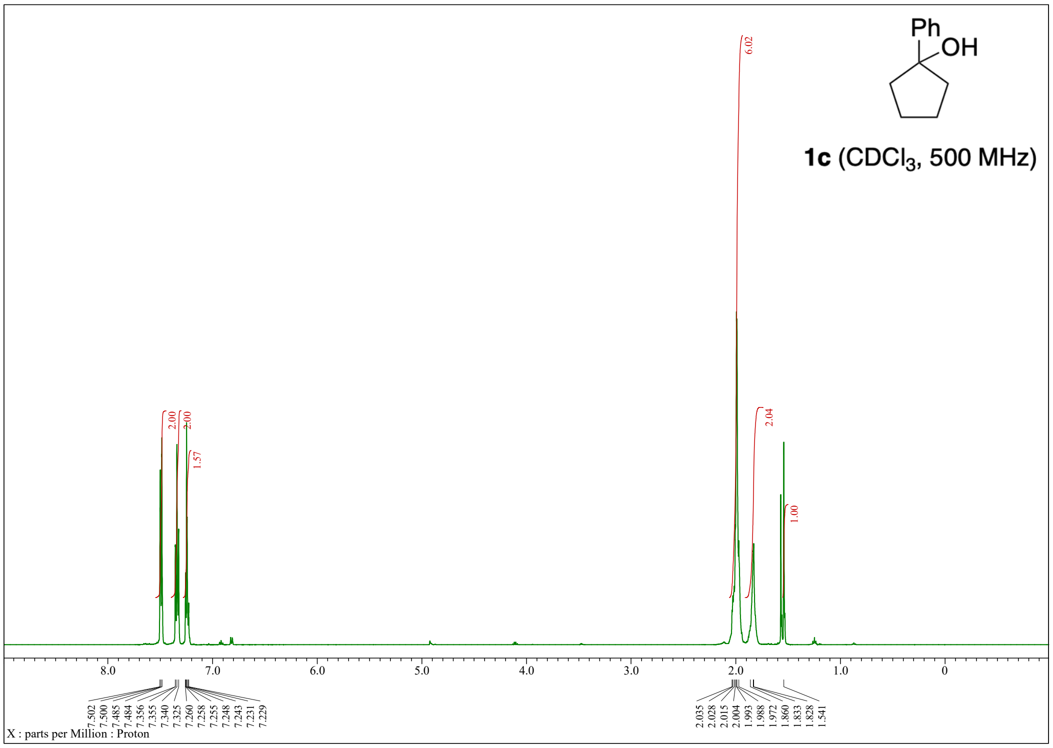
14. ^{1}H NMR spectra of the substrates and products.

^{1}H NMR spectra of 1-phenylcyclobutan-1-ol **(1b)**



^{1}H NMR spectra of 1-phenylcyclopentan-1-ol **(1c)**



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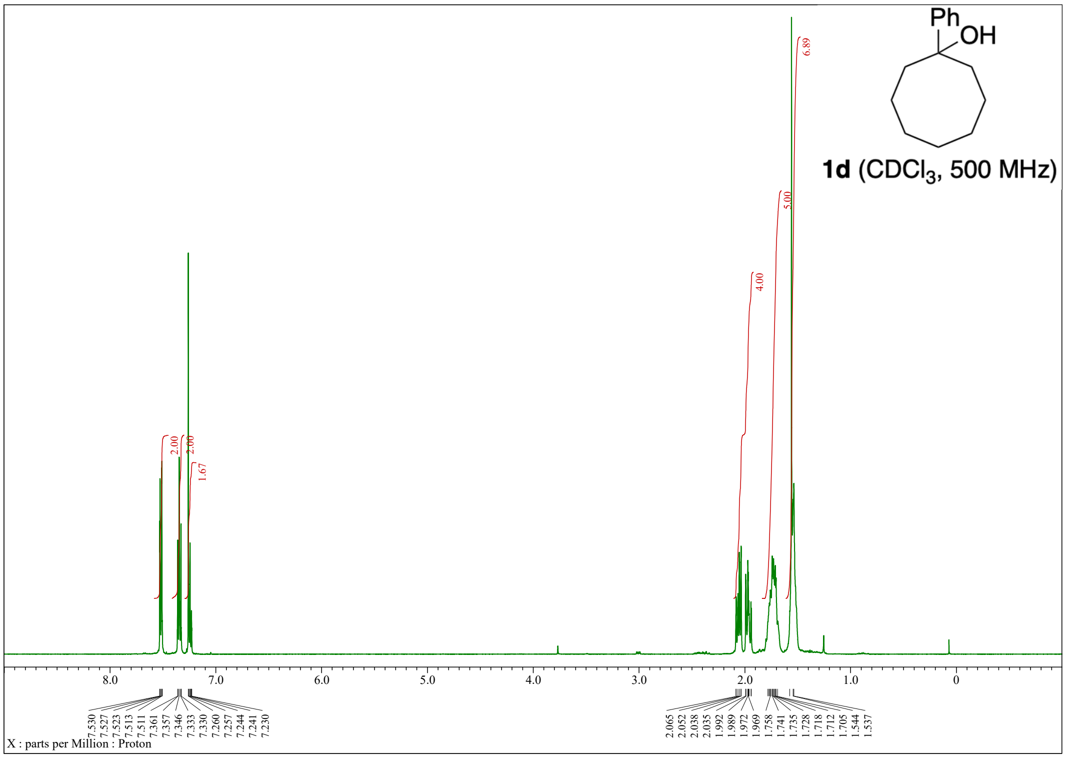
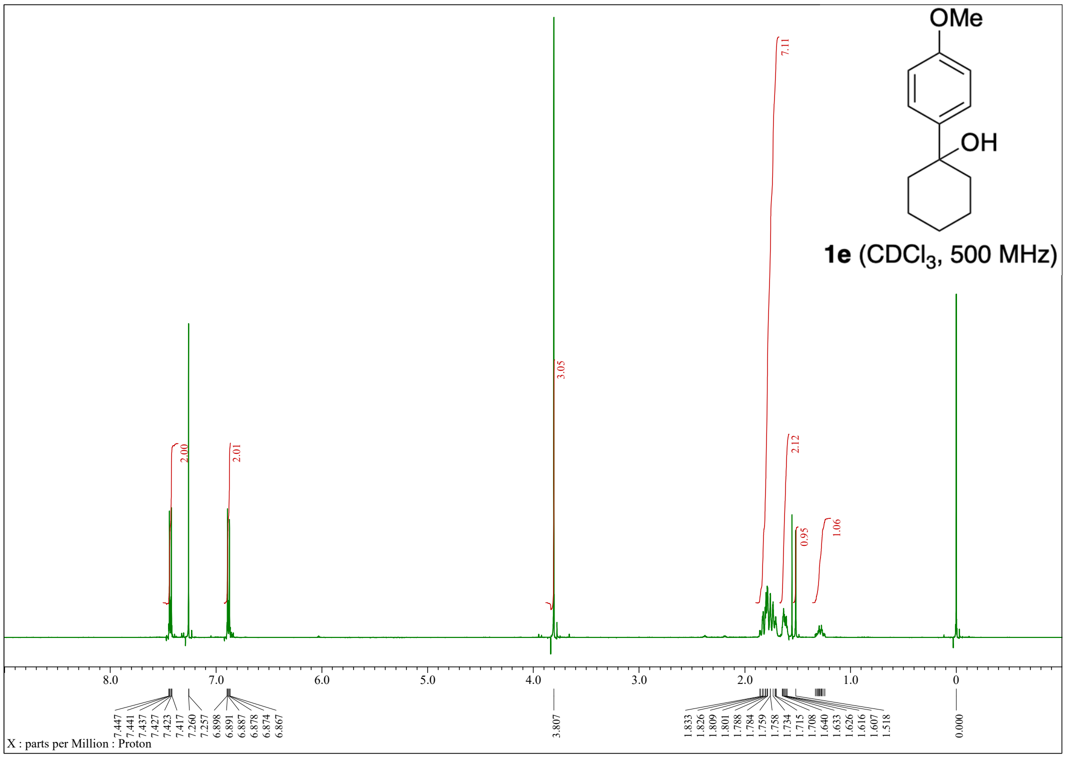
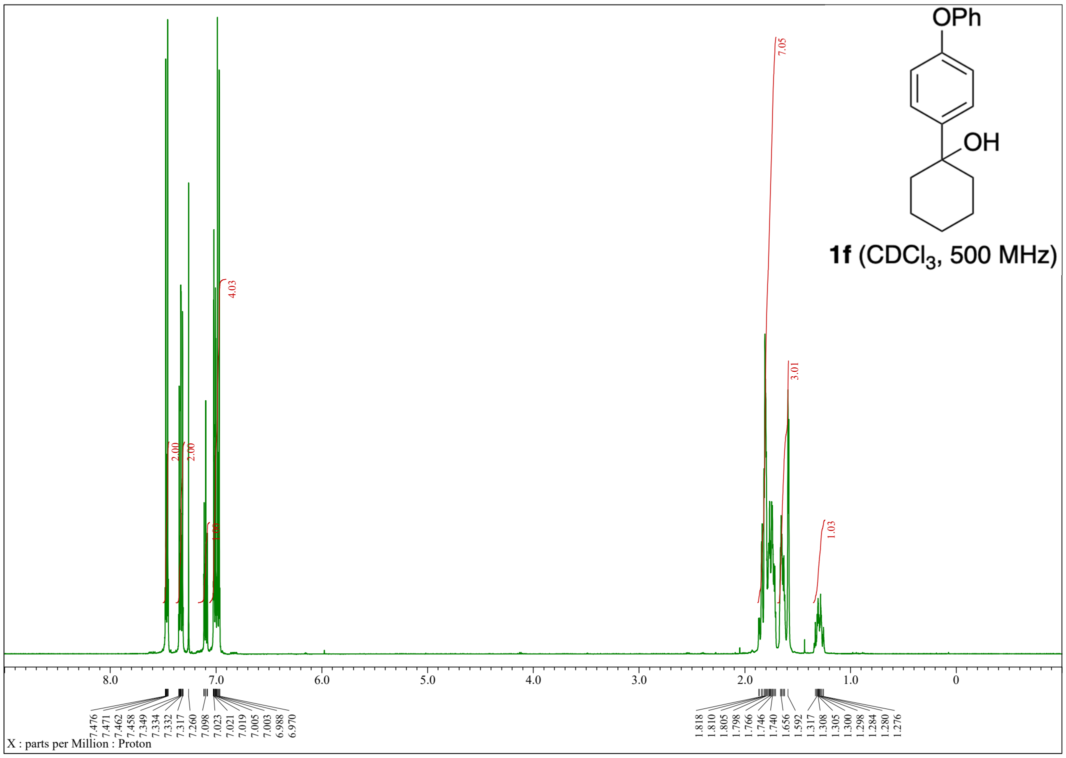


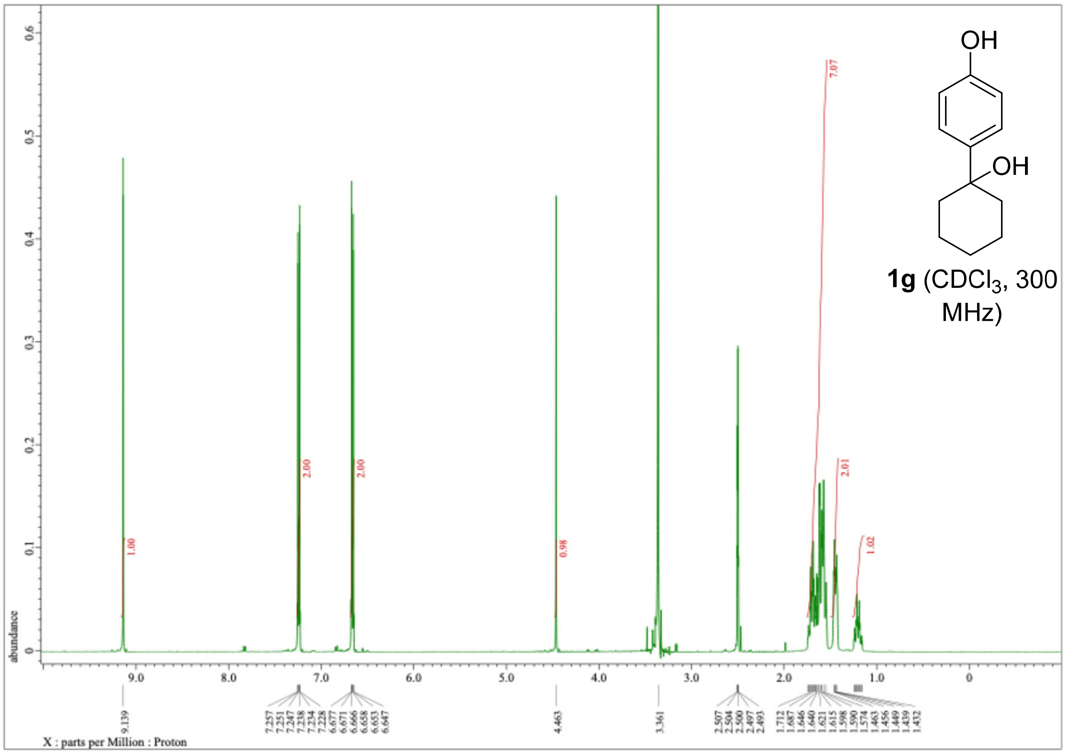
^{1}H NMR spectra of 1-(4-methoxyphenyl)cyclohexan-1-ol **(1e)**



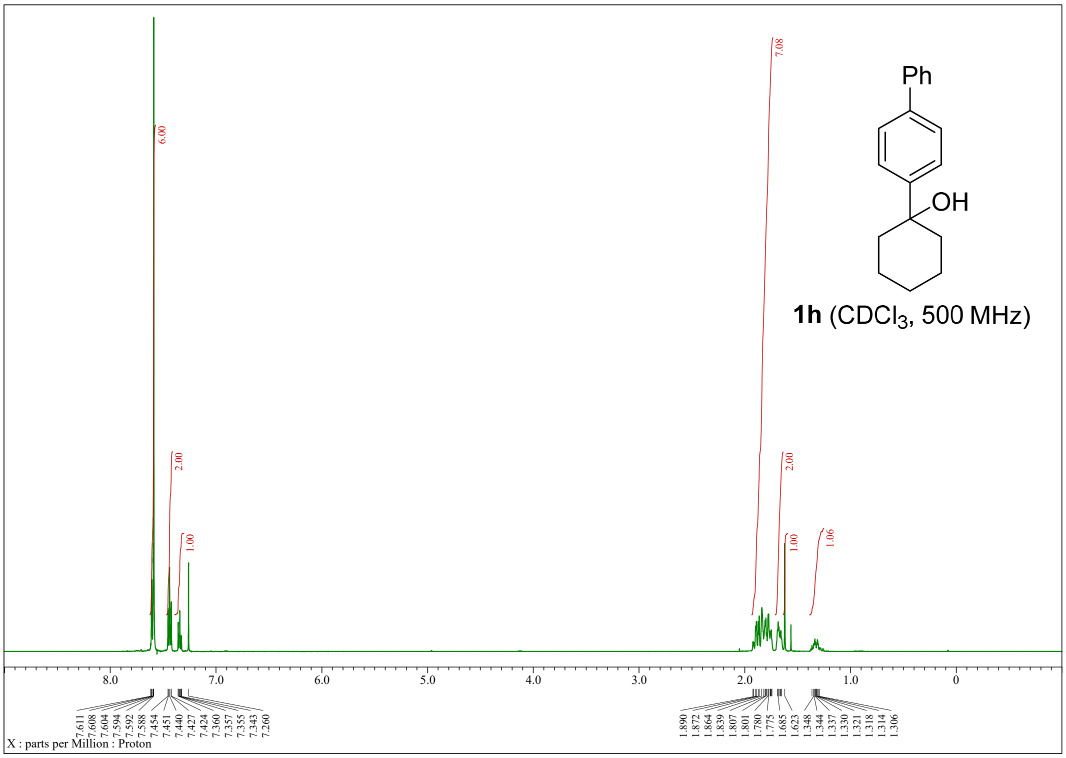
^{1}H NMR spectra of 1-(4-phenoxyphenyl)cyclohexan-1-ol **(1f)**



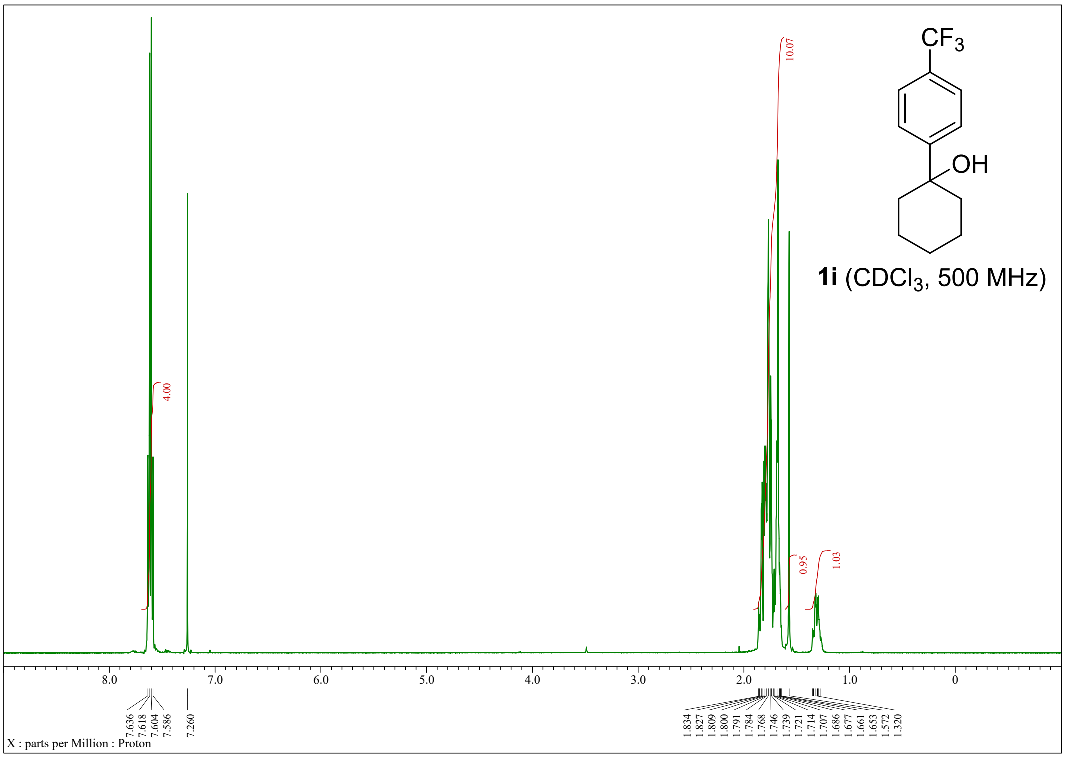
^{1}H NMR spectra of 4-(1-hydroxycyclohexyl)phenol **(1g)**



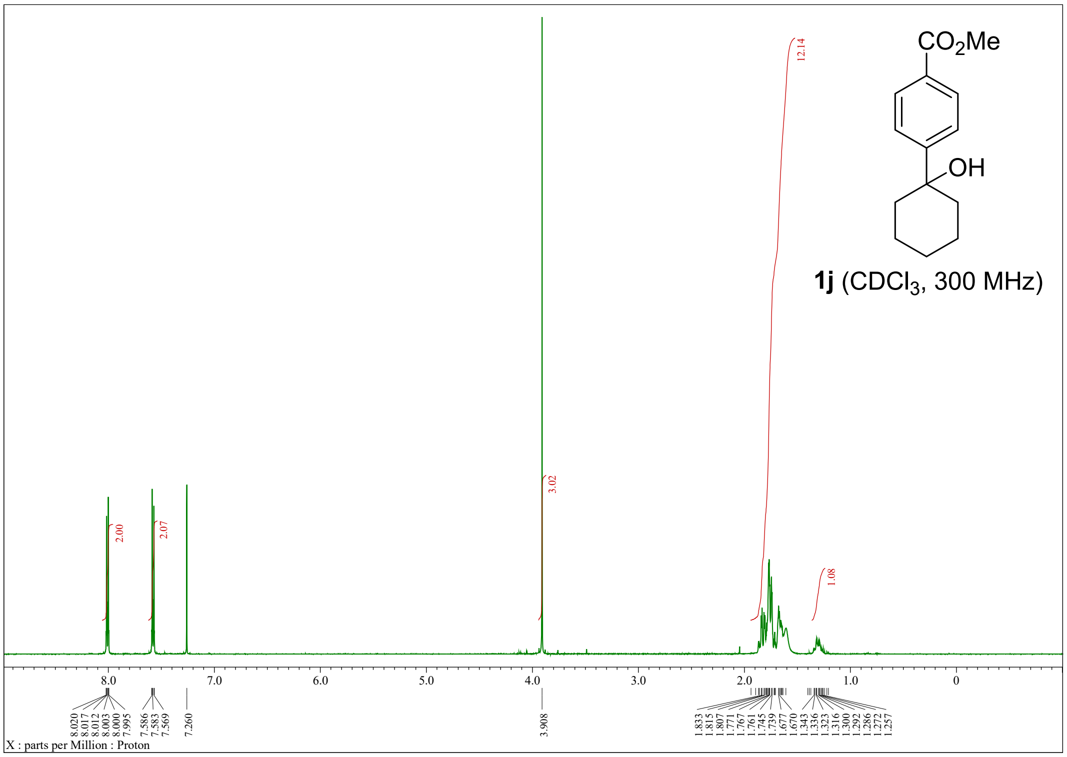
^{1}H NMR spectra of 1-([1,1'-biphenyl]-4-yl)cyclohexan-1-ol **(1h)**



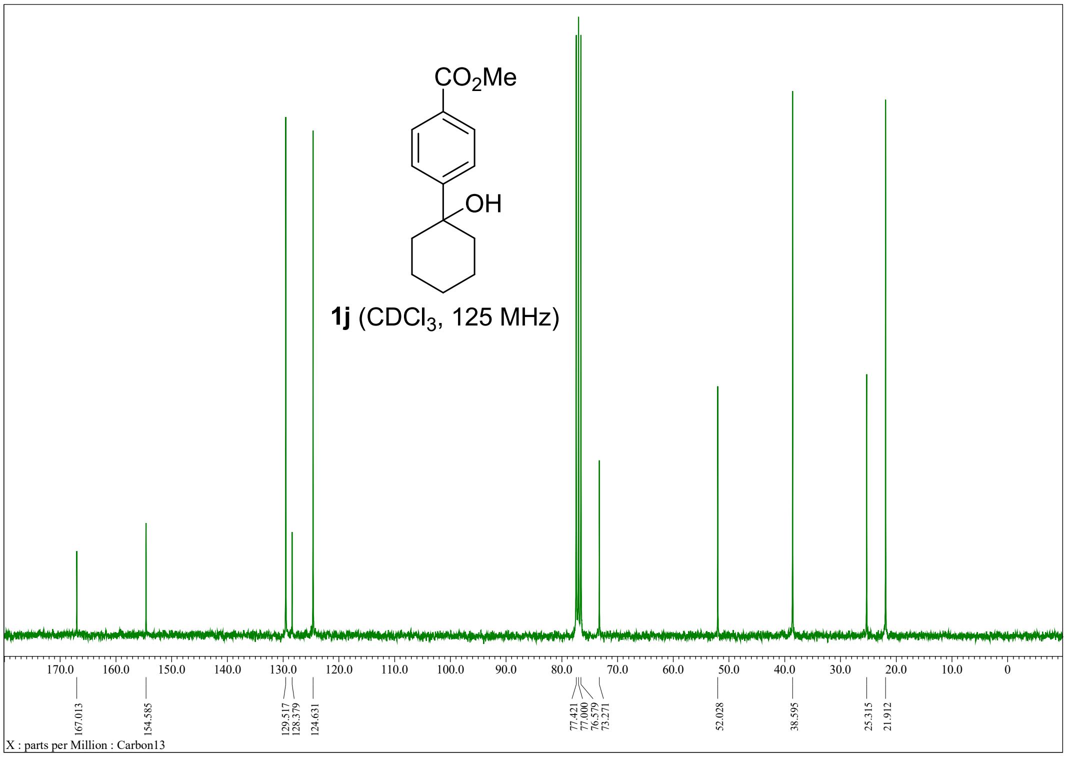
^{1}H NMR spectra of 1-(4-(trifluoromethyl)phenyl)cyclohexan-1-ol **(1i)**



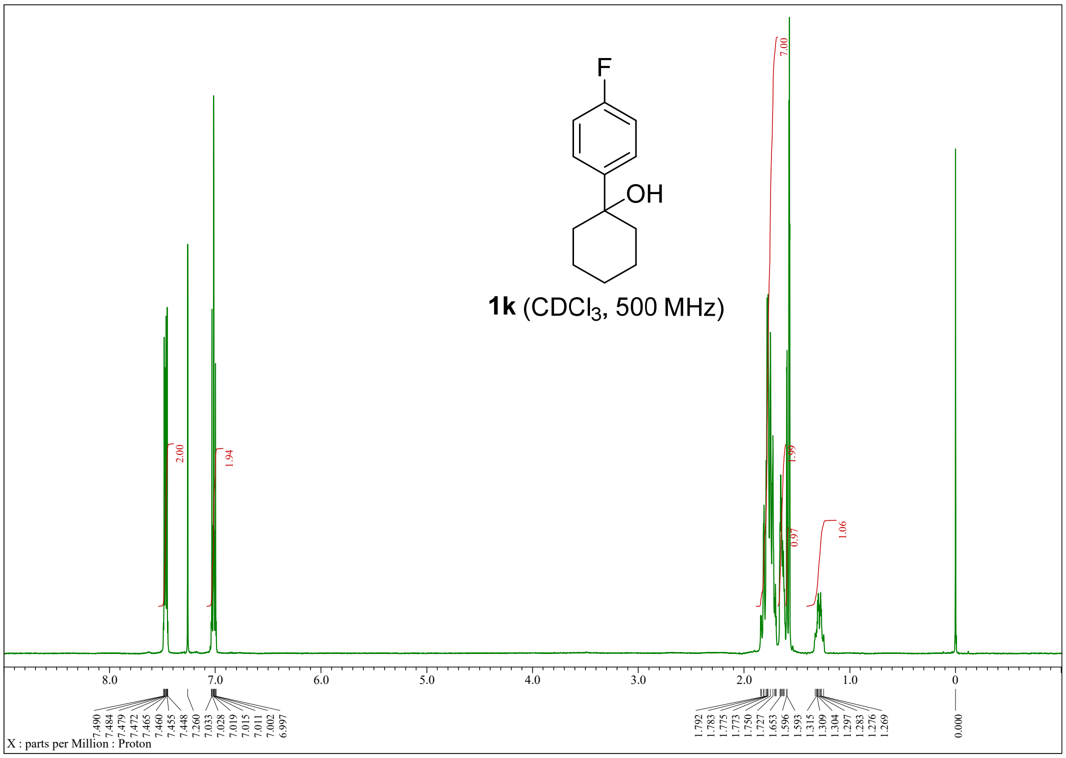
^1H NMR spectra of methyl 4-(1-hydroxycyclohexyl)benzoate (**1j**)



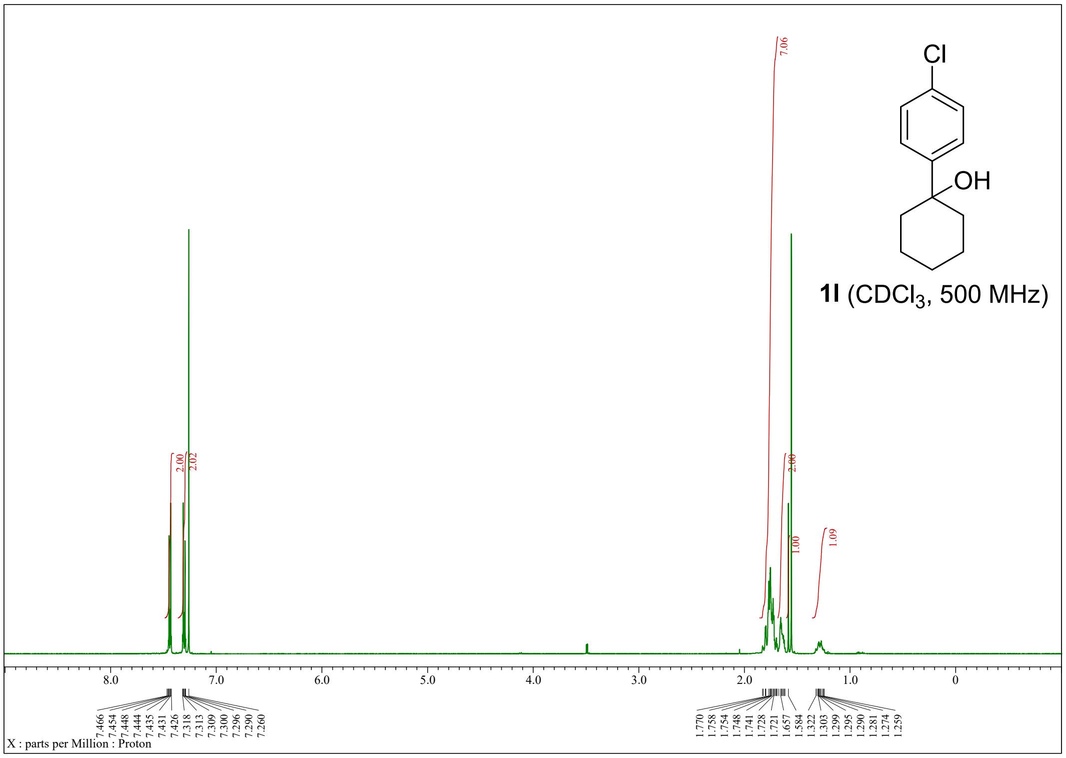
^{13}C NMR spectra of methyl 4-(1-hydroxycyclohexyl)benzoate (**1j**)



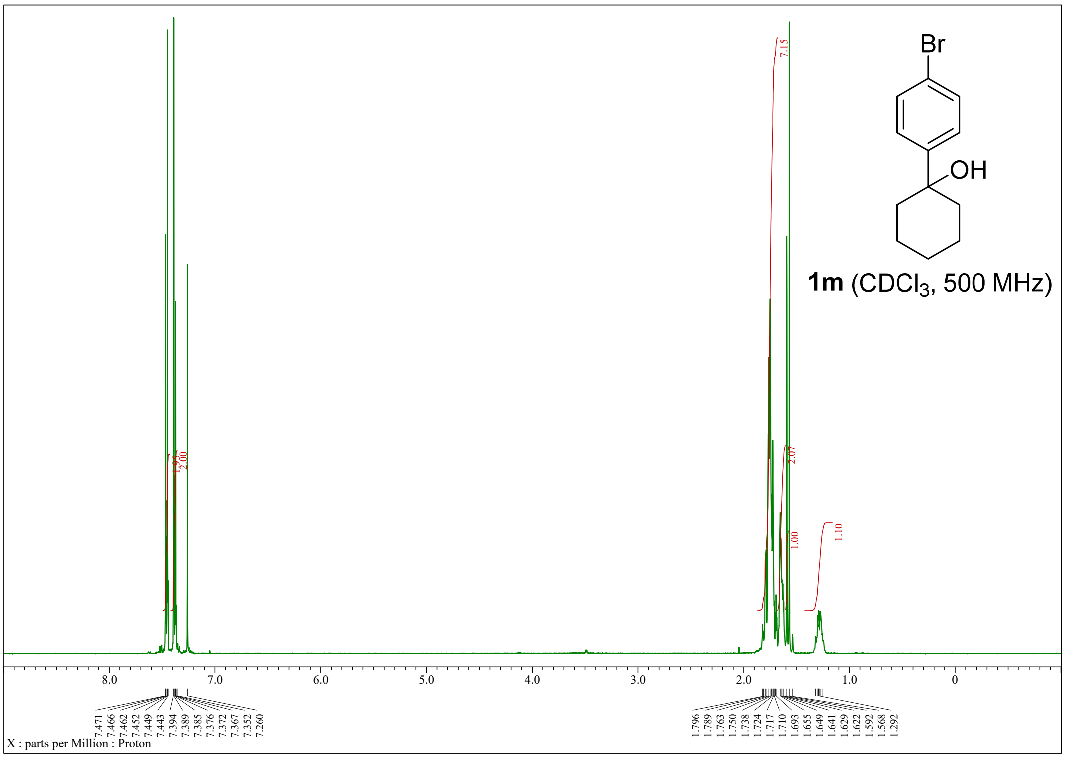
^{1}H NMR spectra of 1-(4-fluorophenyl)cyclohexan-1-ol **(1k)**



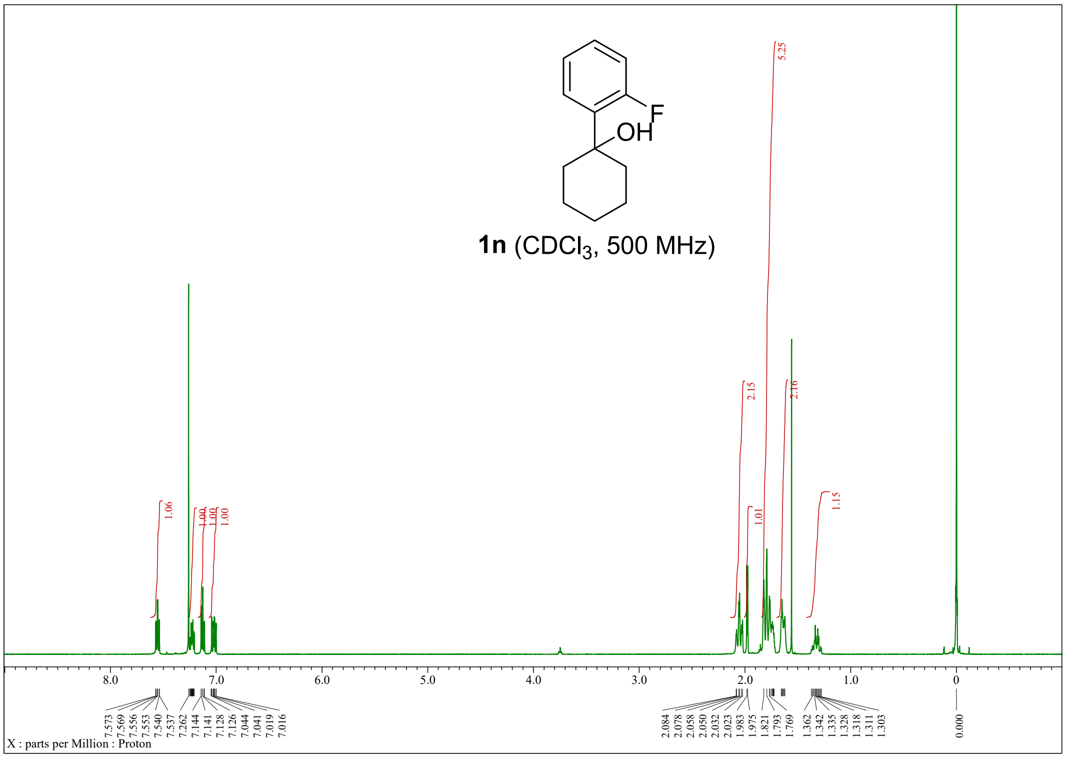
^{1}H NMR spectra of 1-(4-chlorophenyl)cyclohexan-1-ol **(1l)**



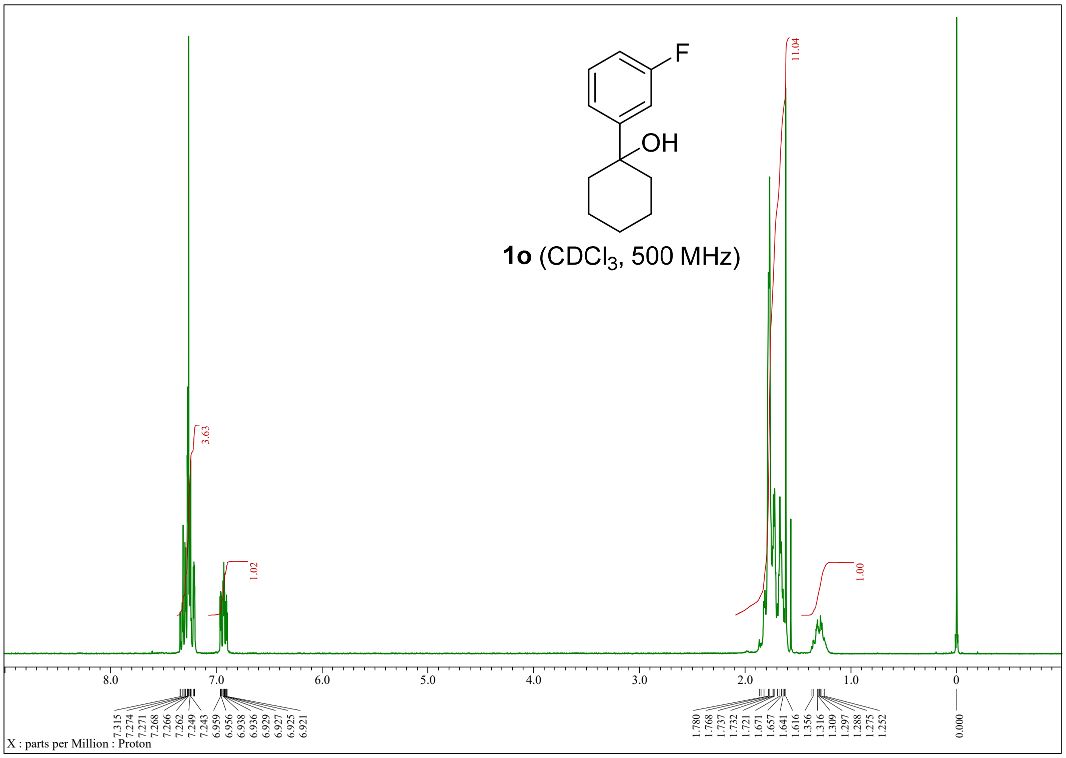
^{1}H NMR spectra of 1-(4-bromophenyl)cyclohexan-1-ol **(1m)**



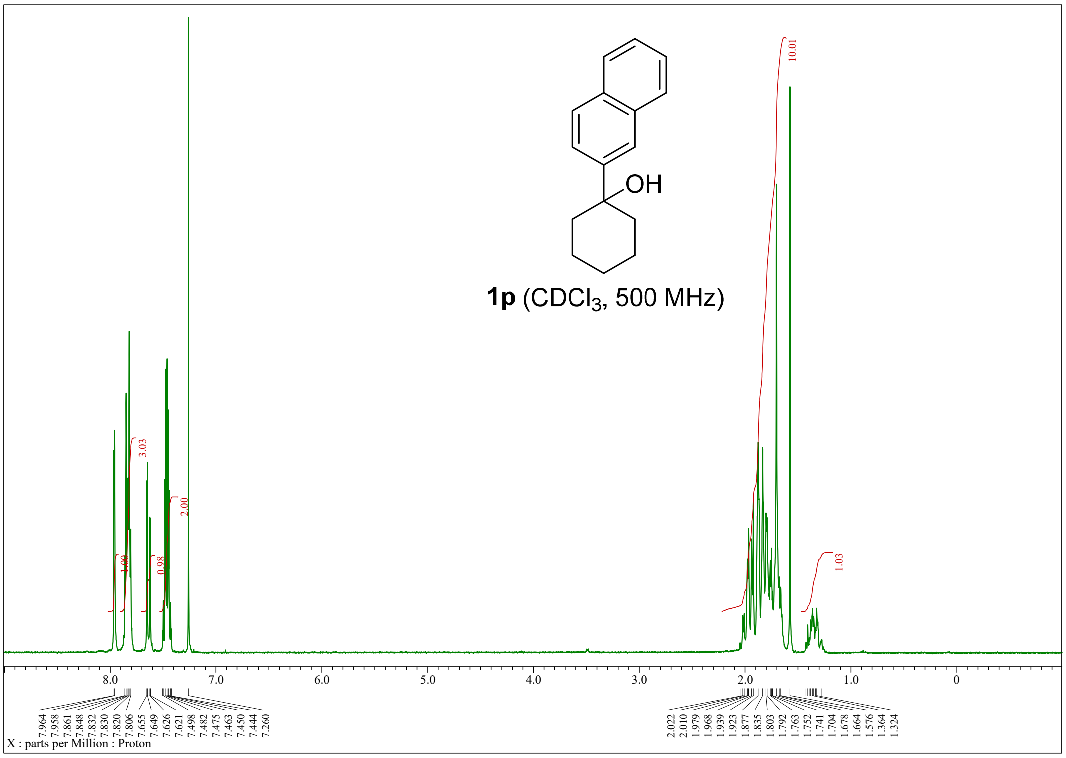
^{1}H NMR spectra of 1-(2-fluorophenyl)cyclohexan-1-ol **(1n)**



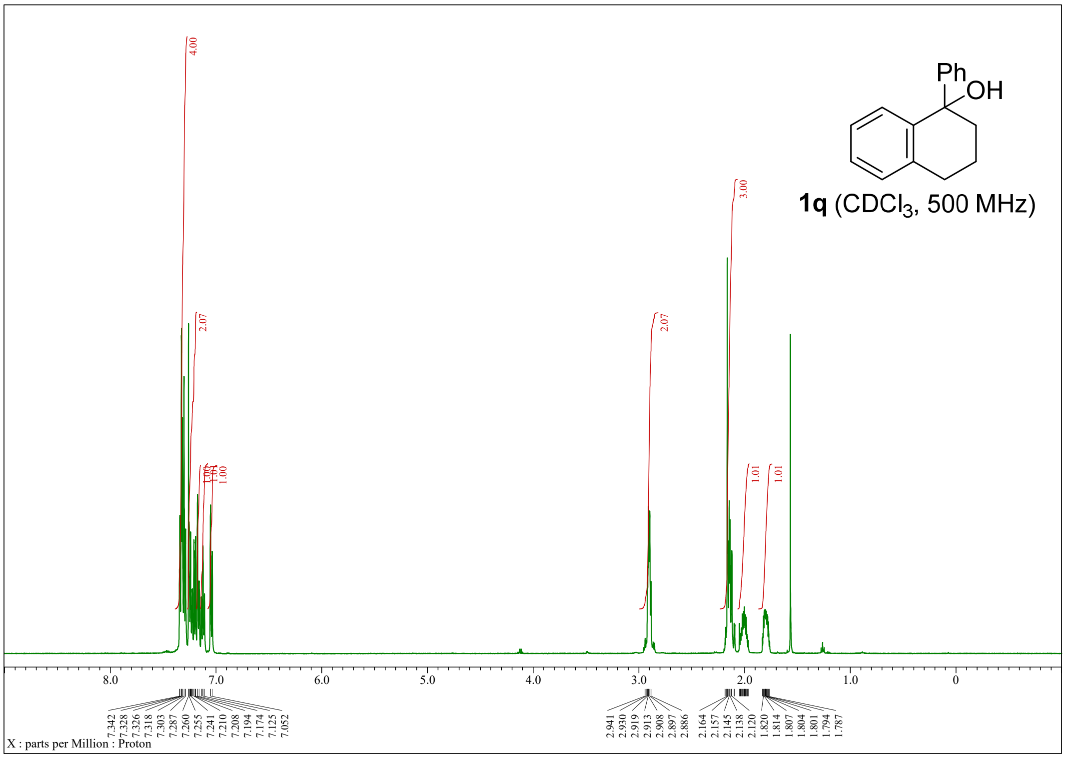
^{1}H NMR spectra of 1-(3-fluorophenyl)cyclohexan-1-ol **(1o)**



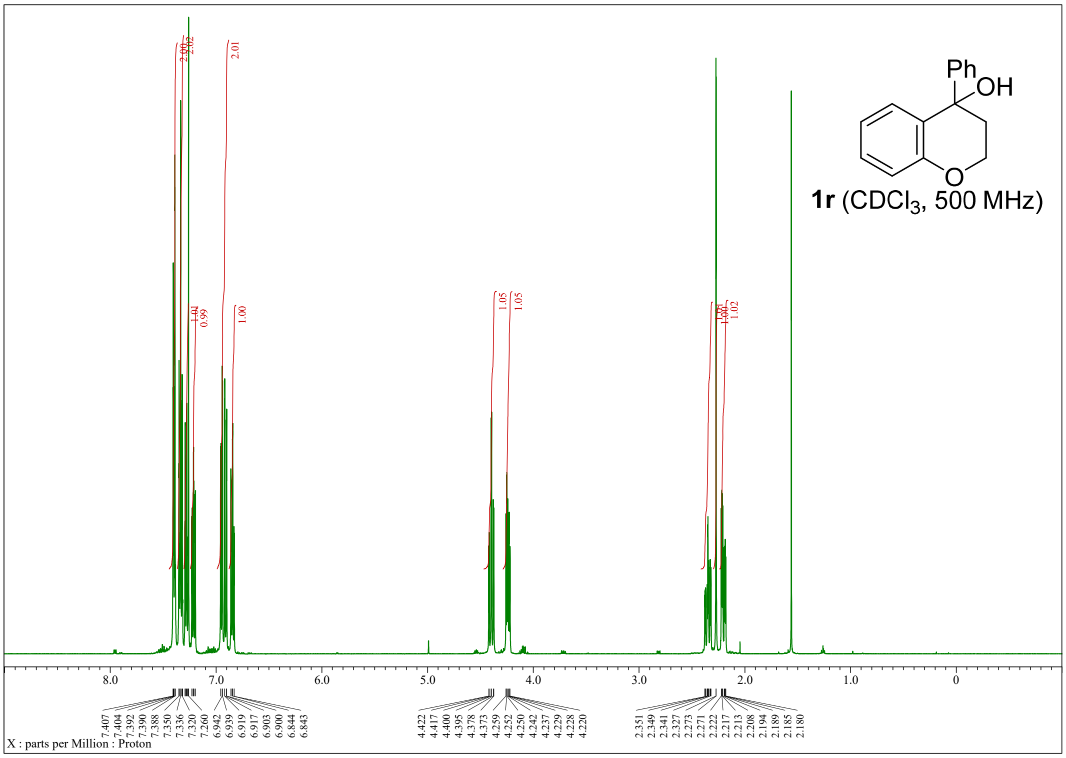
^{1}H NMR spectra of 1-(naphthalen-2-yl)cyclohexan-1-ol **(1p)**



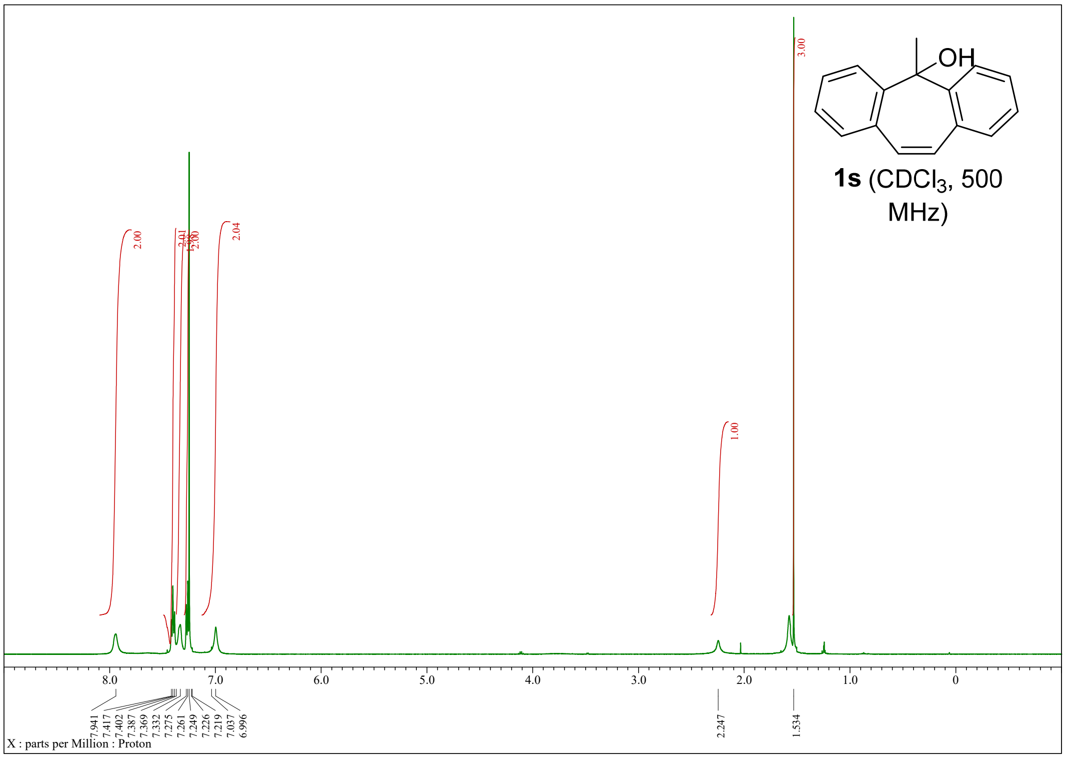
^{1}H NMR spectra of 1-phenyl-1,2,3,4-tetrahydronaphthalen-1-ol **(1q)**



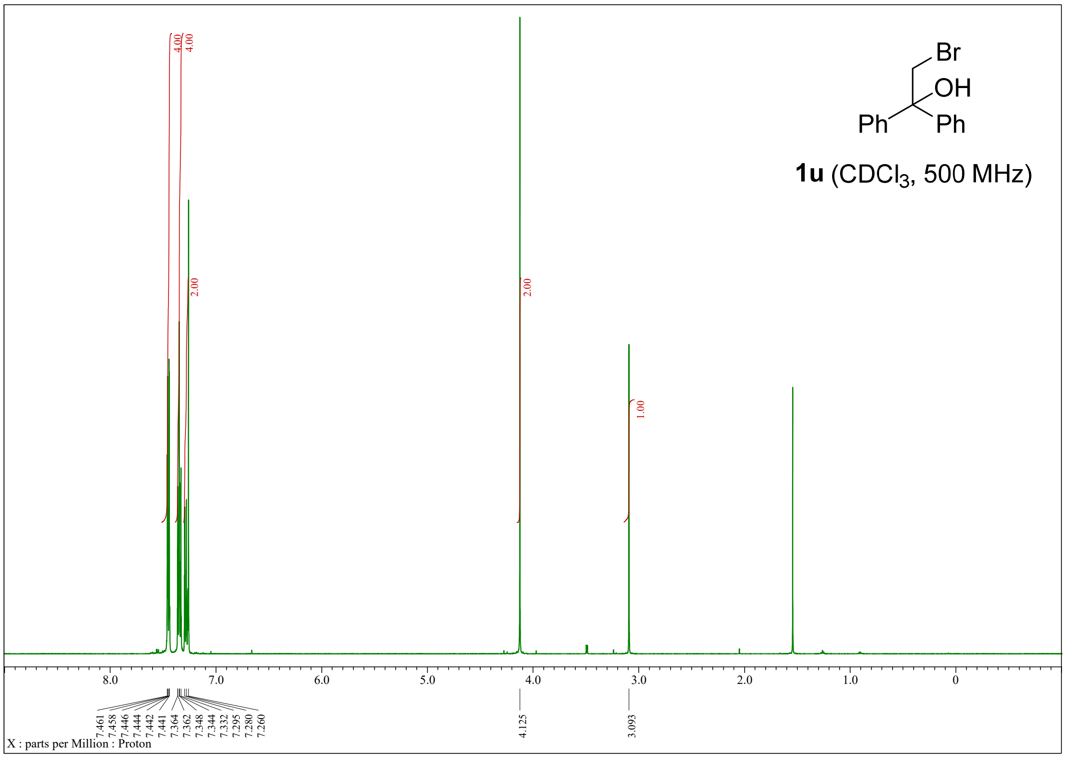
^{1}H NMR spectra of 4-phenylchroman-4-ol **(1r)**



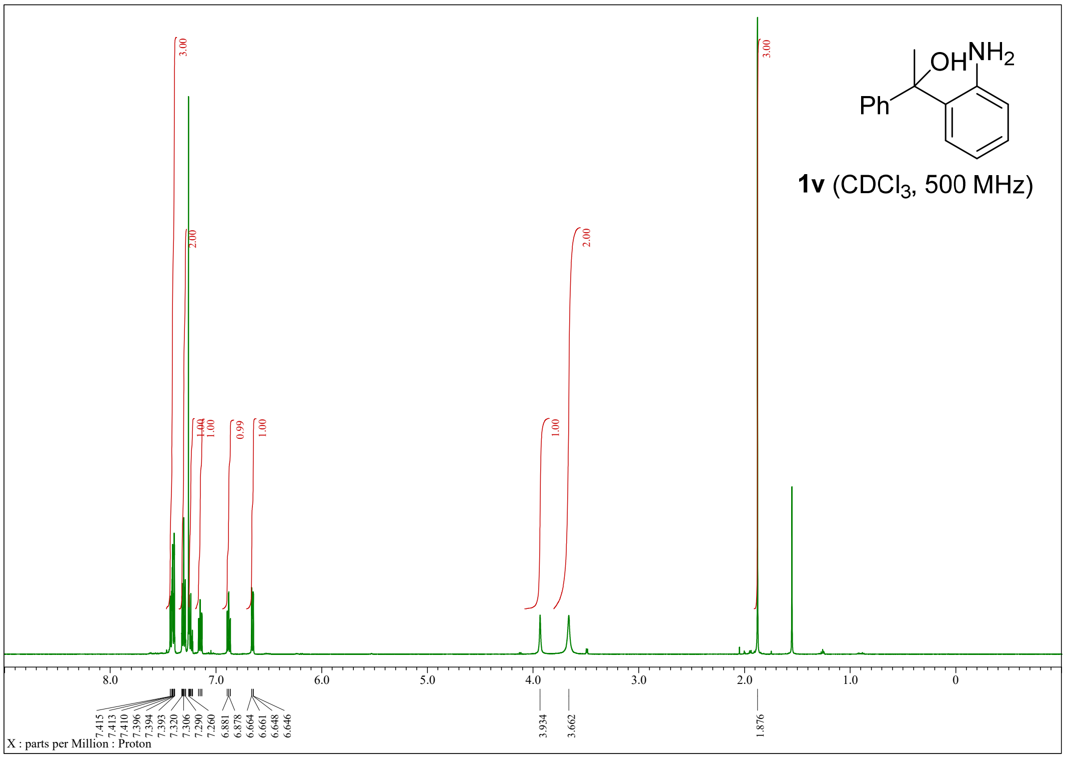
^{1}H NMR spectra of 5-methyl-5*H*-dibenzo[*a*,*d*][7]annulen-5-ol **(1s)**



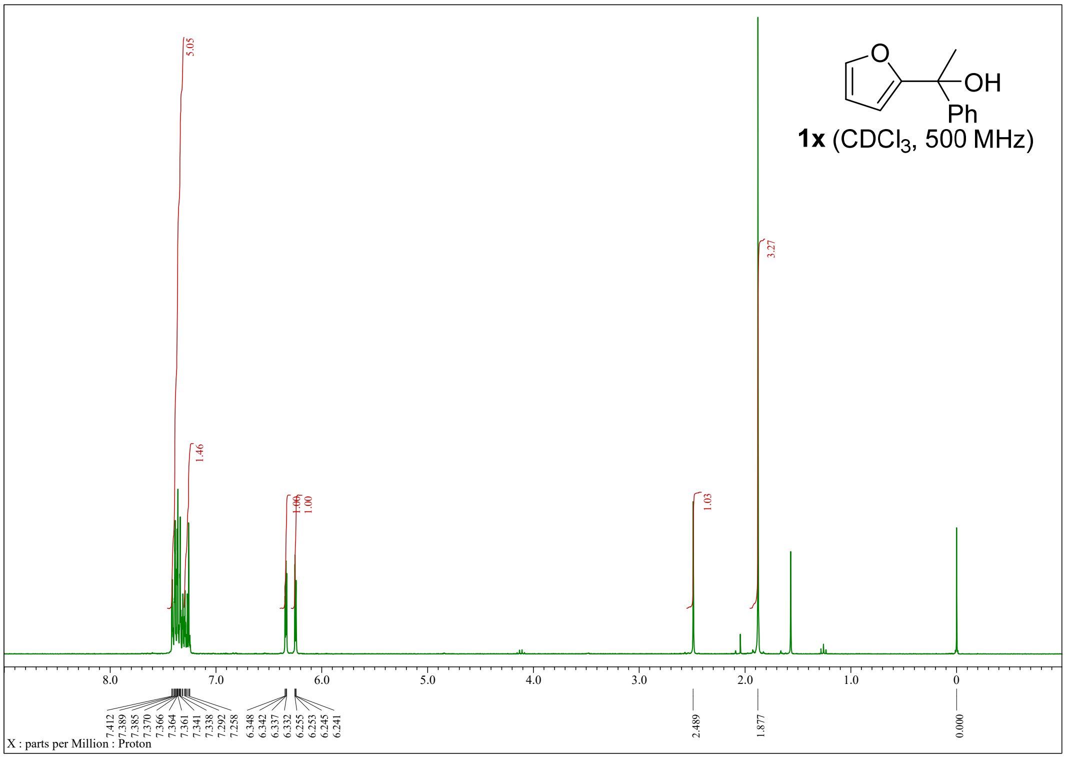
^{1}H NMR spectra of 2-bromo-1,1-diphenylethan-1-ol **(1u)**



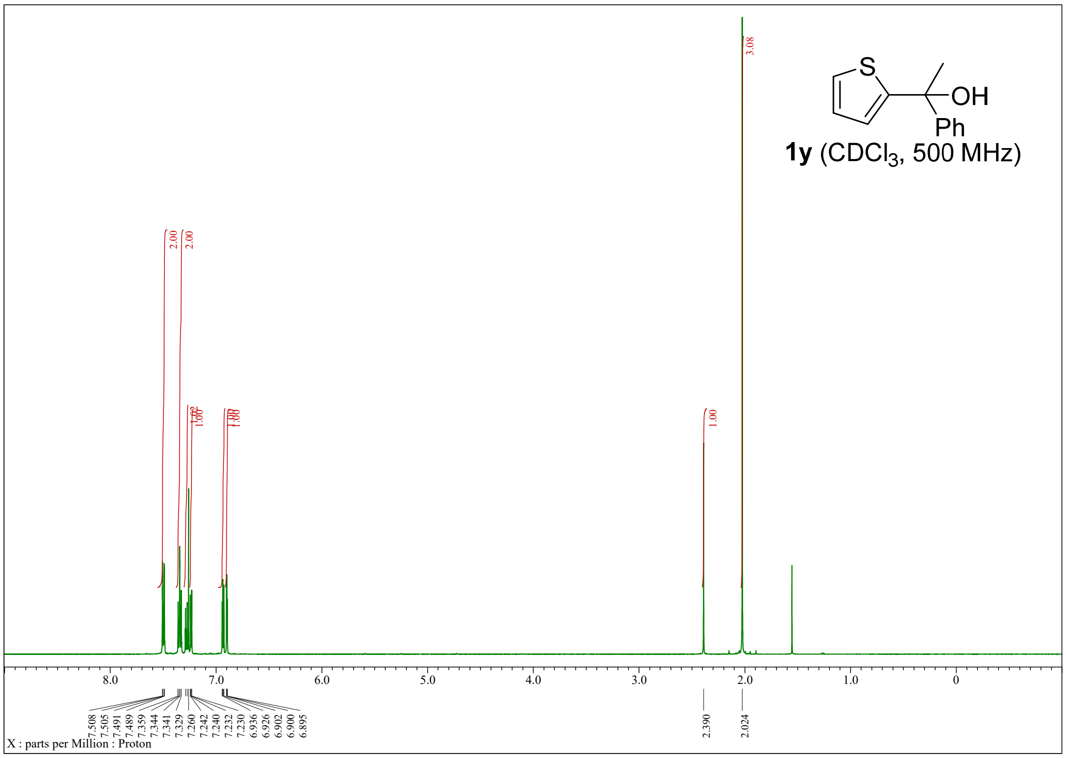
^{1}H NMR spectra of 1-(2-aminophenyl)-1-phenylethan-1-ol **(1v)**



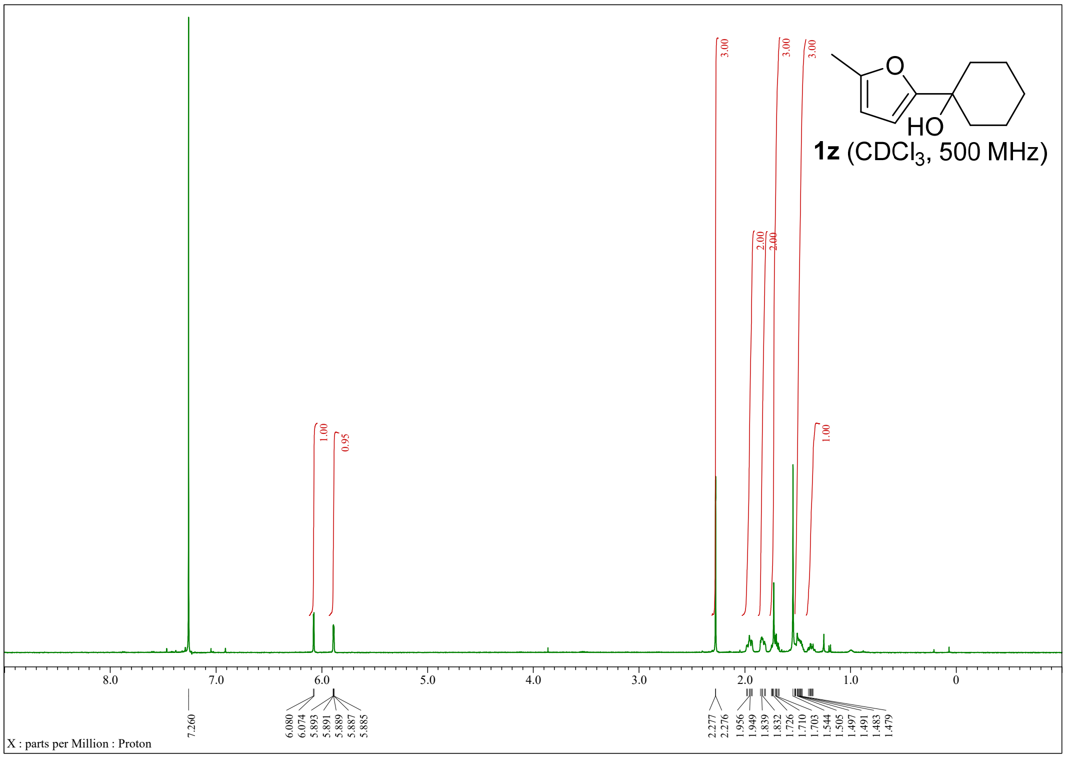
^{1}H NMR spectra of 1-(furan-2-yl)-1-phenylethan-1-ol **(1x)**



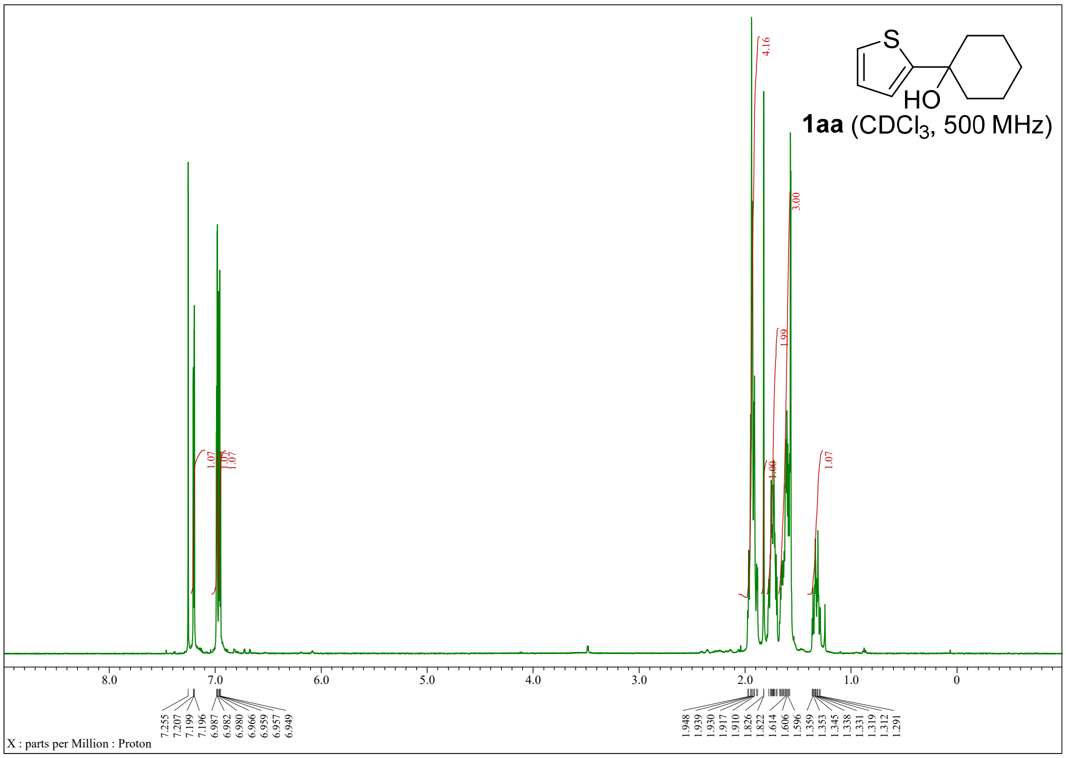
^{1}H NMR spectra of 1-phenyl-1-(thiophen-2-yl)ethan-1-ol **(1y)**



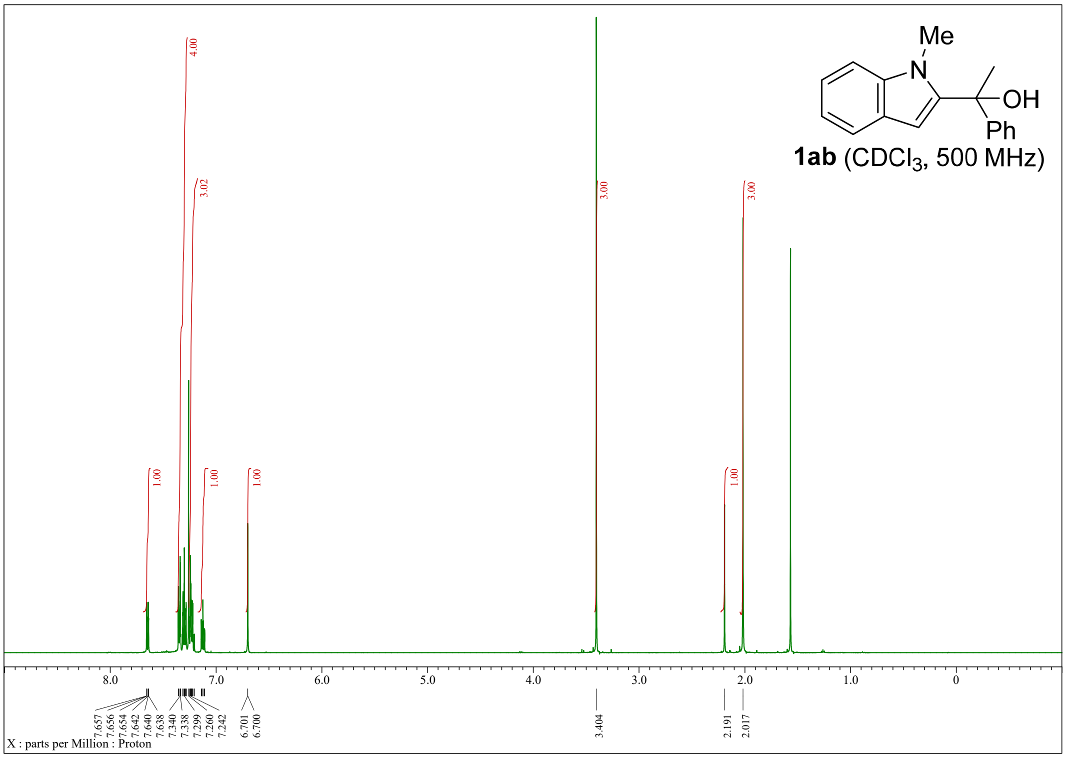
^{1}H NMR spectra of 1-(5-methylfuran-2-yl)cyclohexan-1-ol **(1z)**



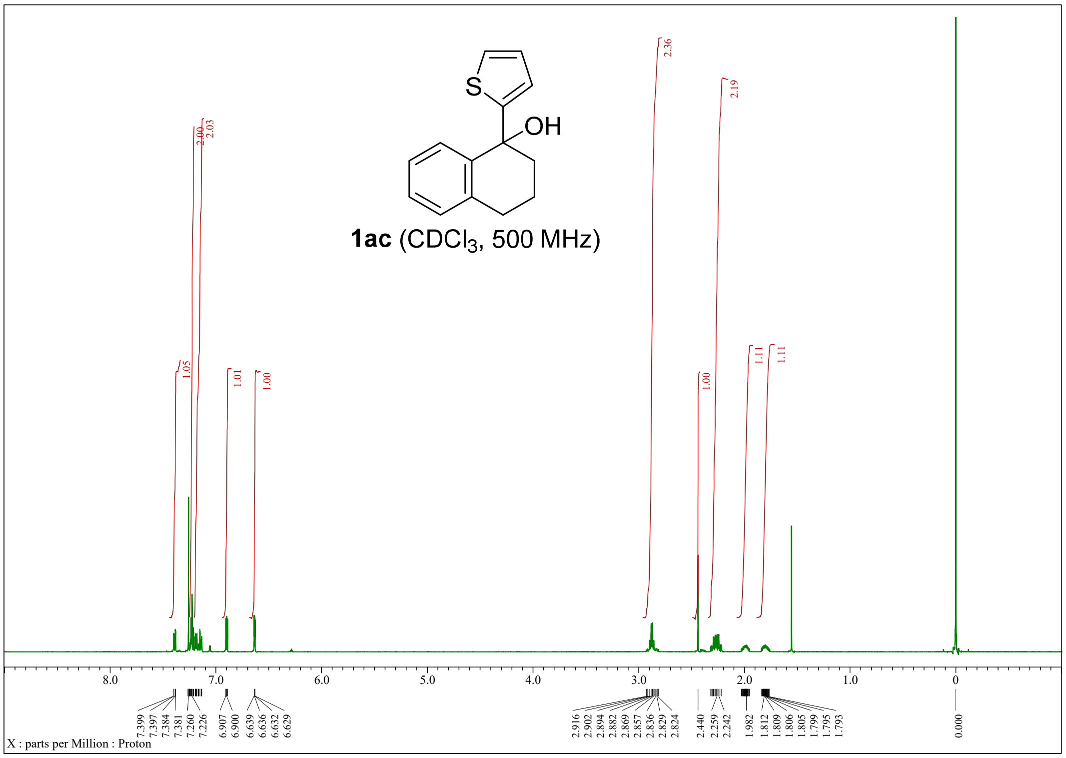
^{1}H NMR spectra of 1-(thiophen-2-yl)cyclohexan-1-ol **(1aa)**



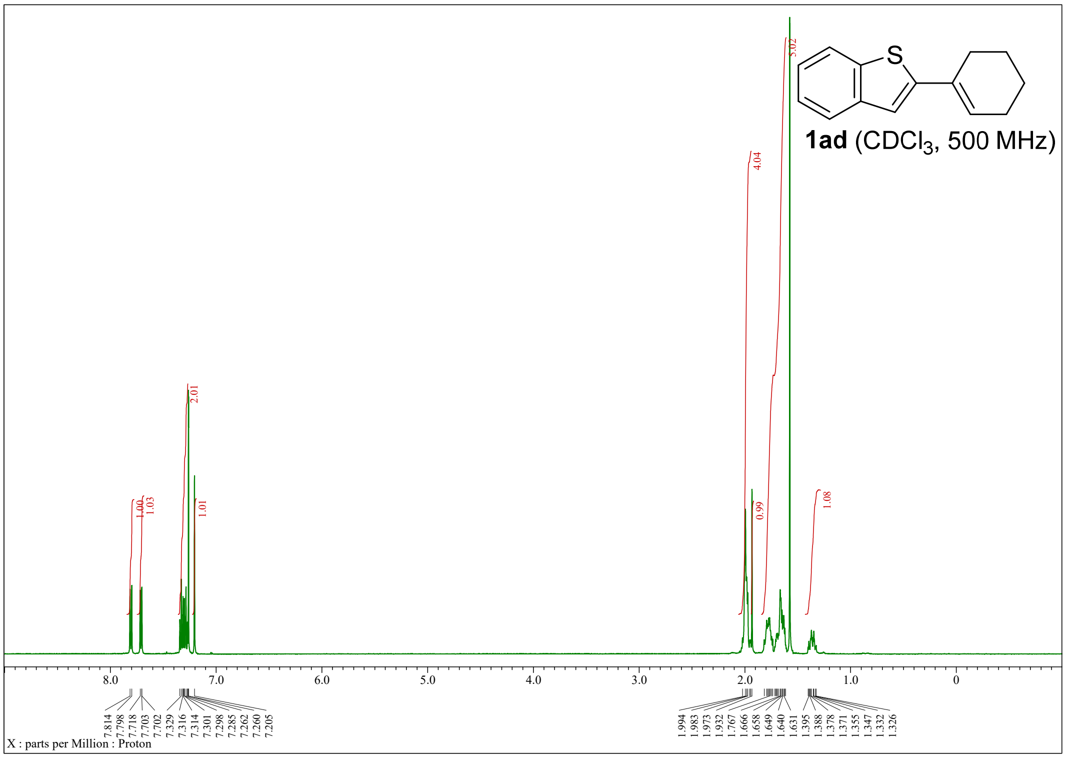
^{1}H NMR spectra of 1-(1-methyl-1*H*-indol-2-yl)-1-phenylethan-1-ol **(1ab)**



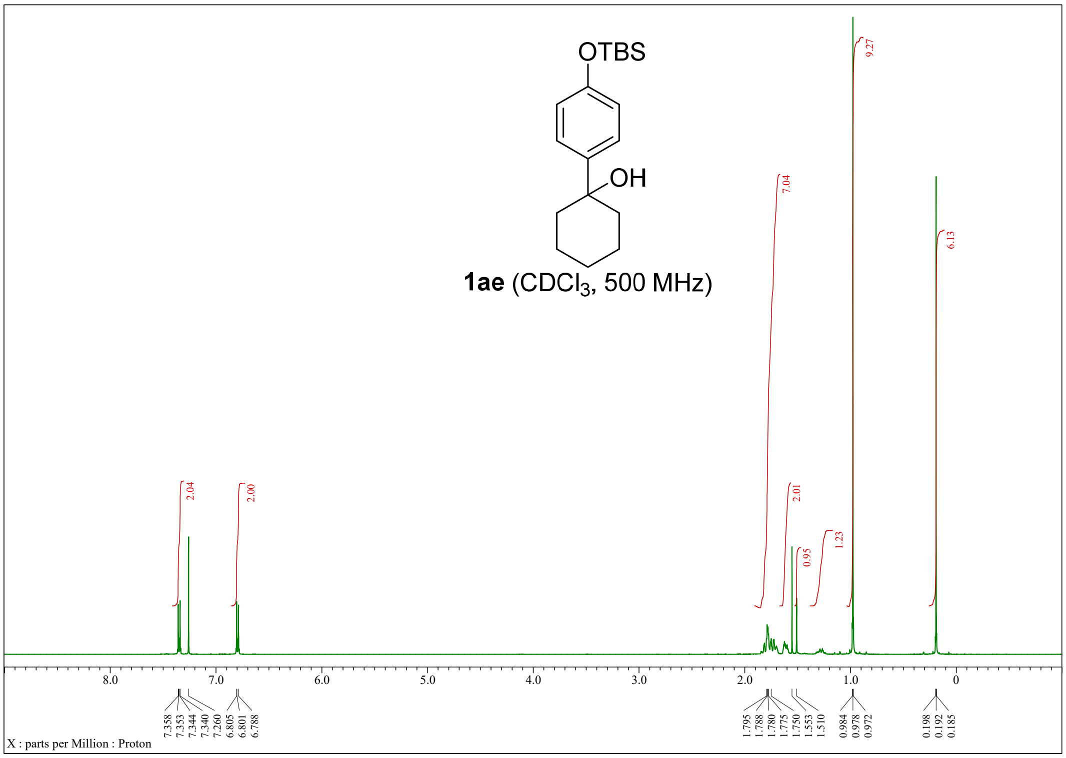
^{1}H NMR spectra of 1-(thiophen-2-yl)-1,2,3,4-tetrahydronaphthalen-1-ol **(1ac)**



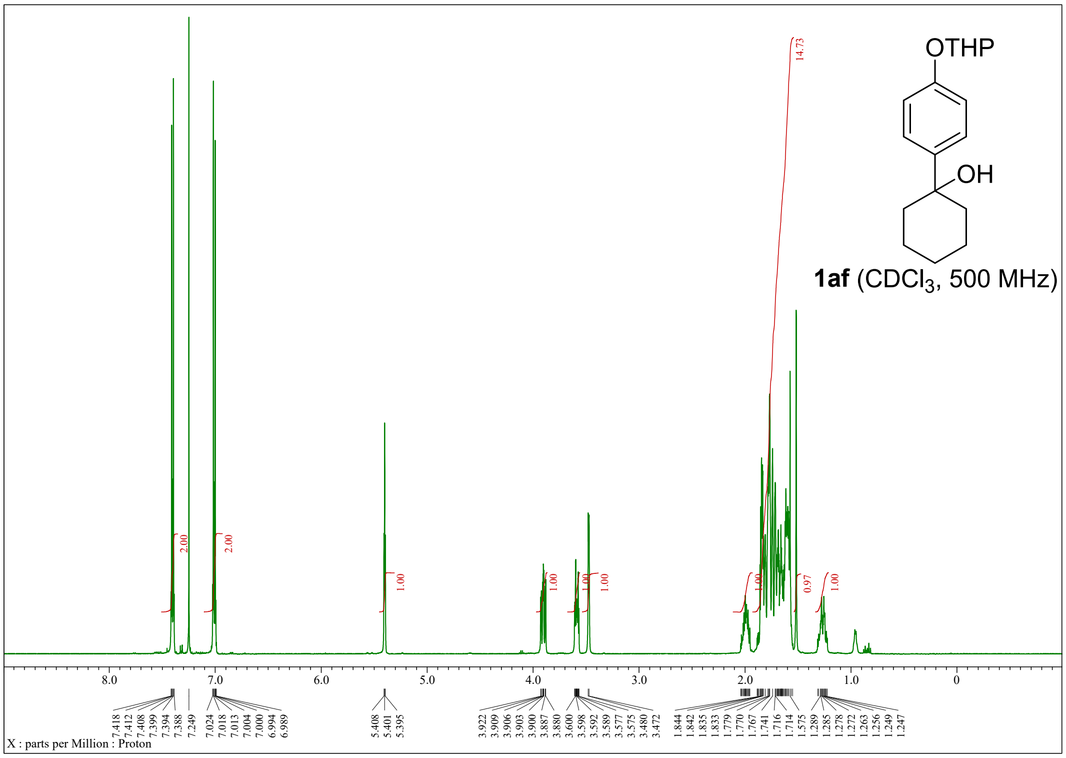
^{1}H NMR spectra of 1-(benzo[*b*]thiophen-2-yl)cyclohexan-1-ol **(1ad)**



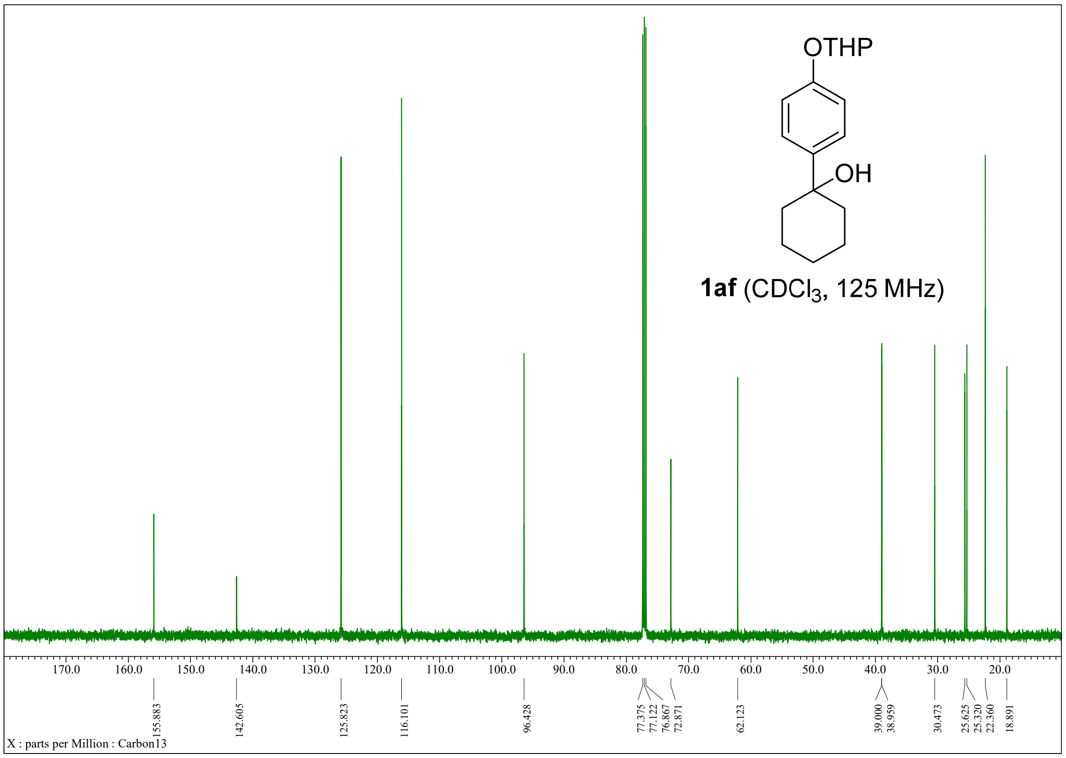
^{1}H NMR spectra of 1-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)cyclohexan-1-ol **(1ae)**



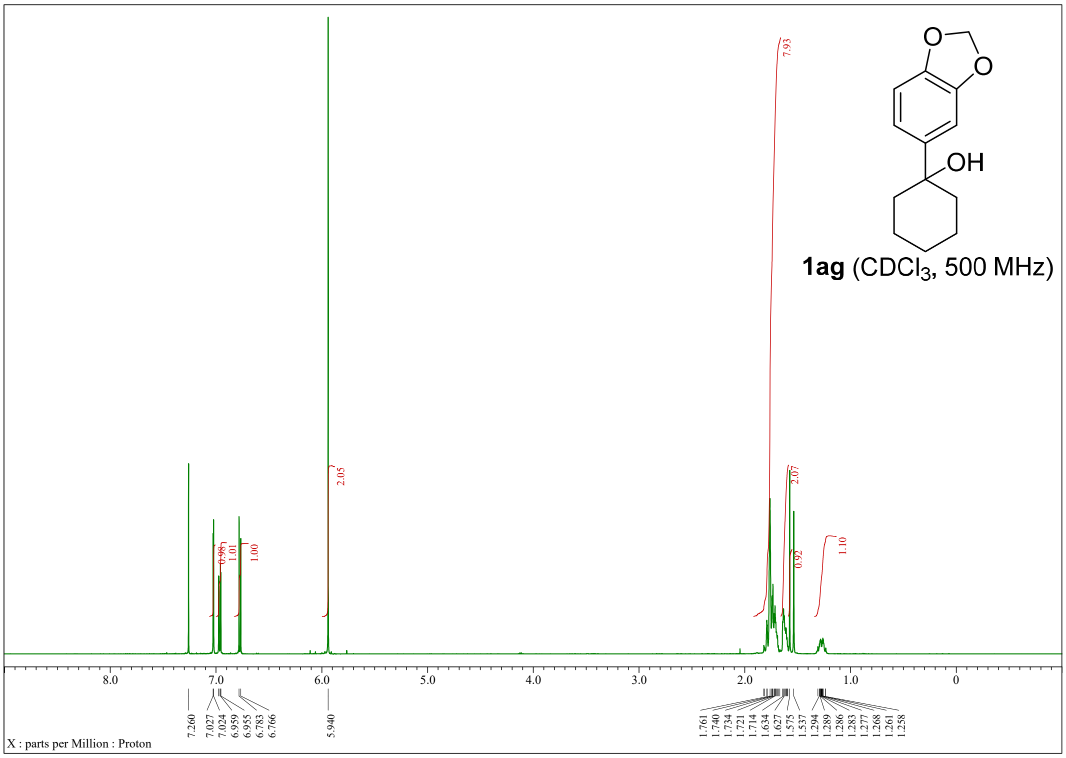
^{1}H NMR spectra of 1-(4-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)cyclohexan-1-ol **(1af)**



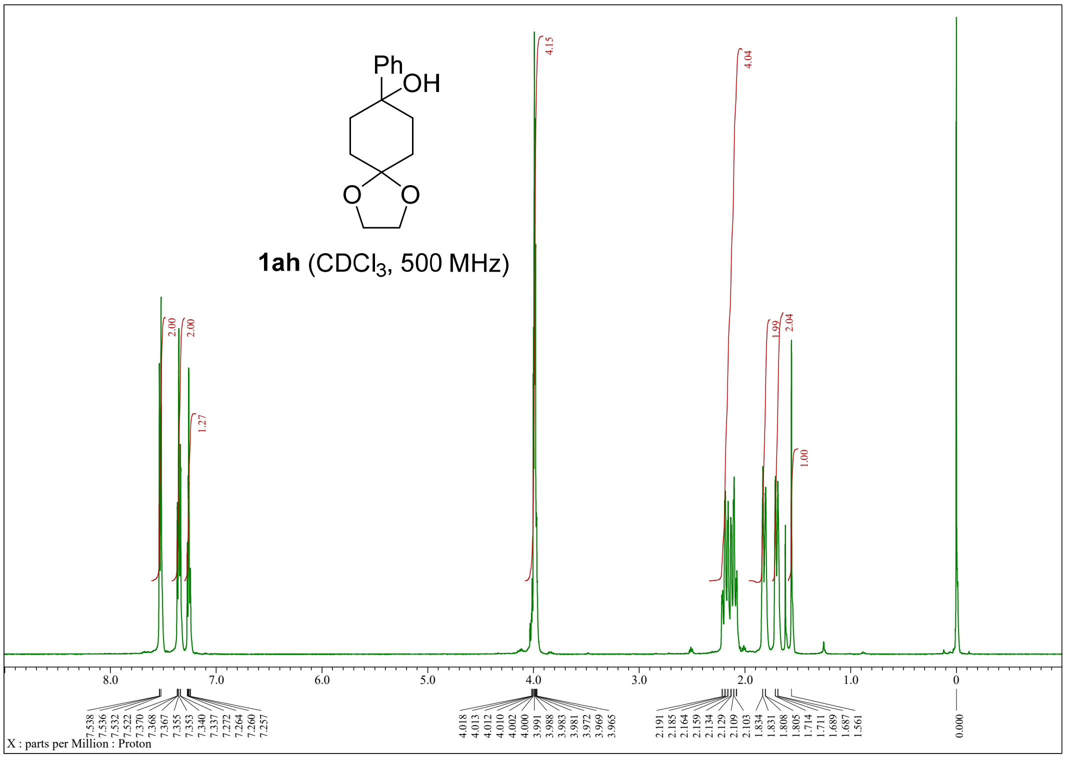
^{13}C NMR spectra of 1-(4-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)cyclohexan-1-ol **(1af)**



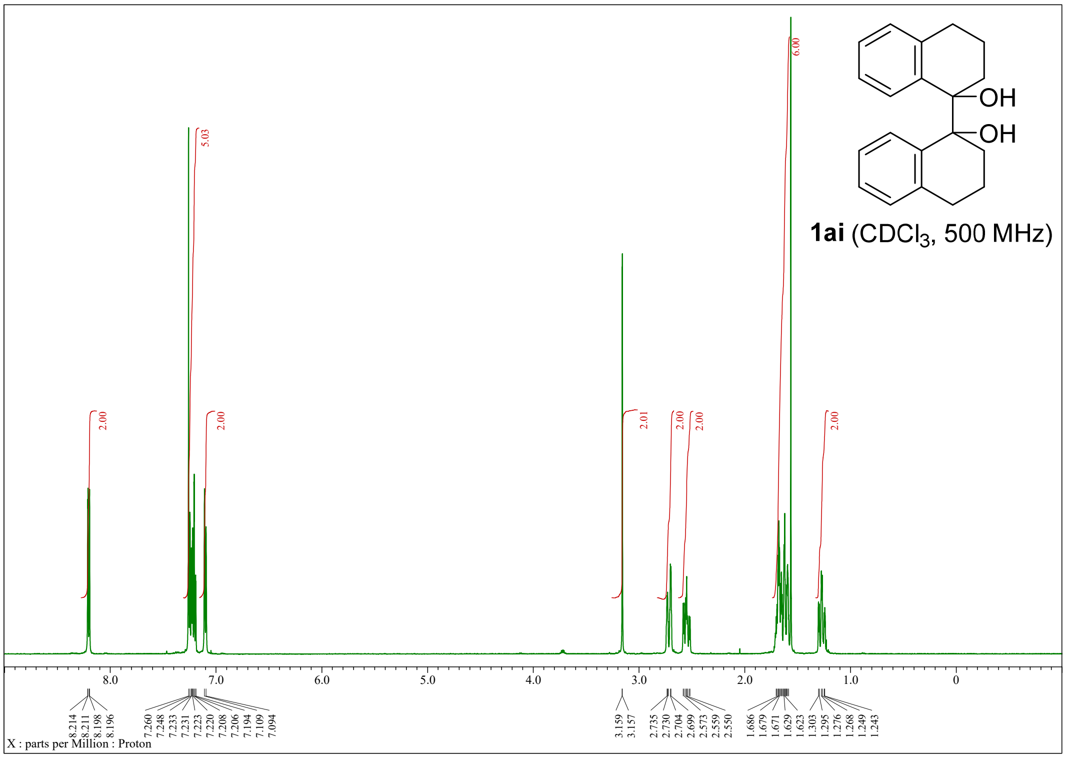
^{1}H NMR spectra of 1-(benzo[*d*][1,3]dioxol-5-yl)cyclohexan-1-ol **(1ag)**



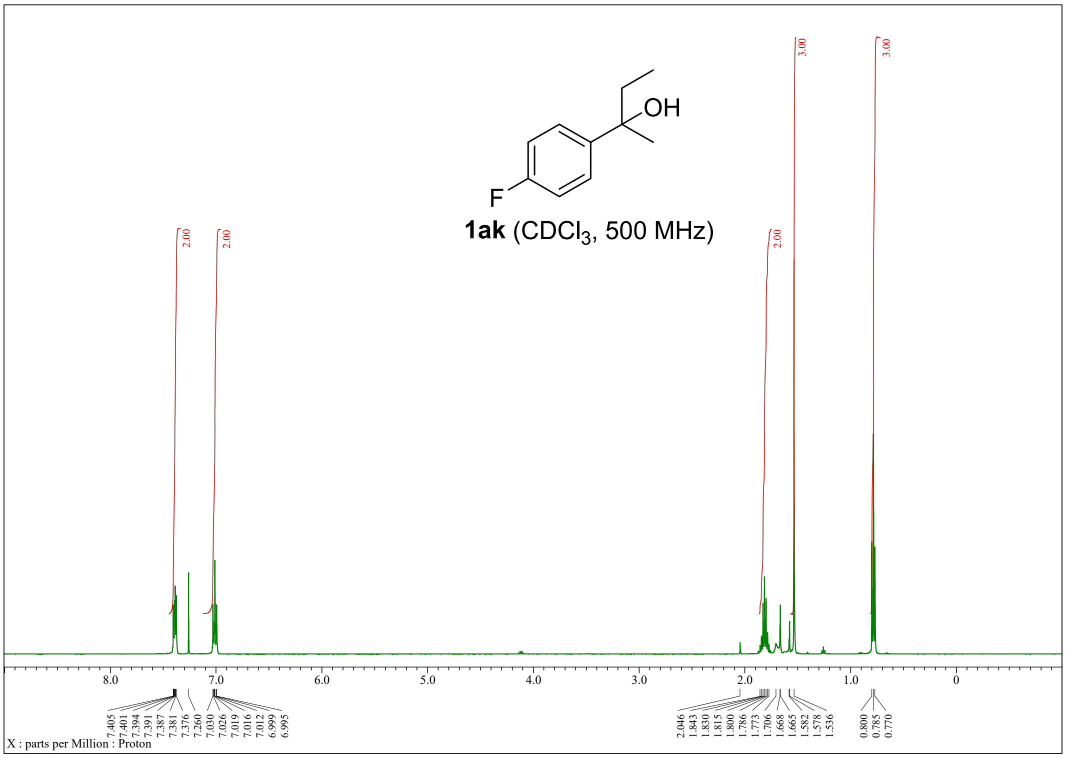
^{1}H NMR spectra of 8-phenyl-1,4-dioxaspiro[4.5]decan-8-ol **(1ah)**



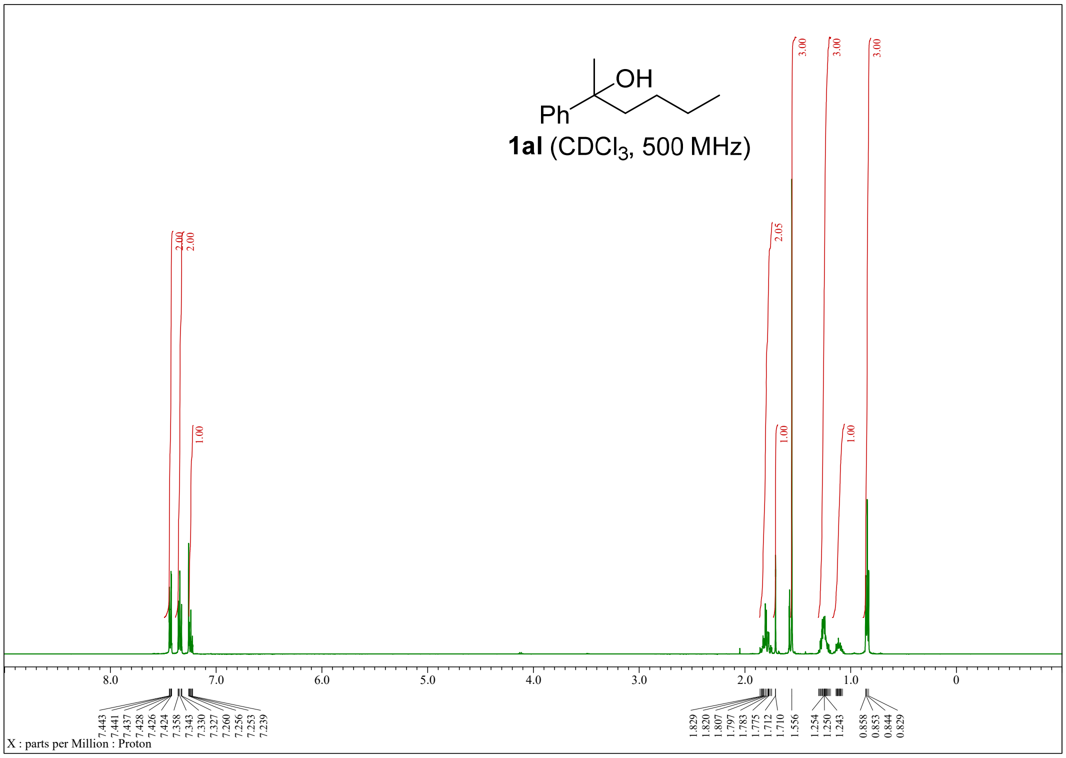
^{1}H NMR spectra of 3,3',4,4'-tetrahydro-[1,1'-binaphthalene]-1,1'(2*H*,2'*H*)-diol **(1ai)**



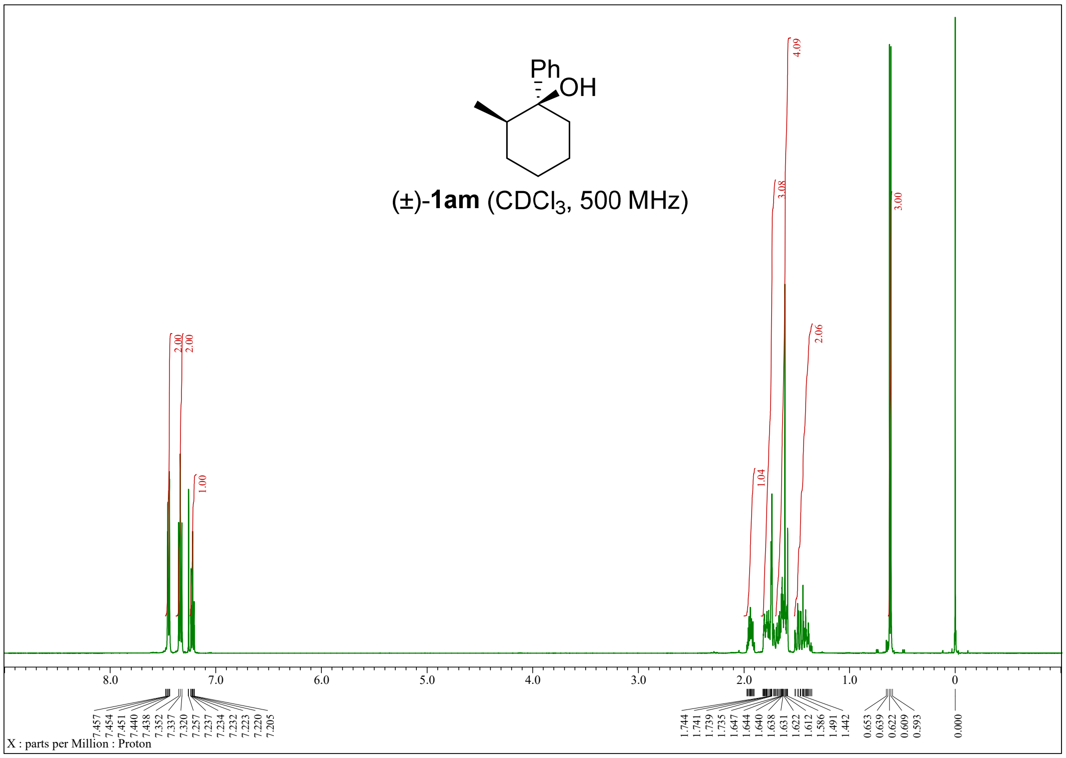
^{1}H NMR spectra of 2-(4-fluorophenyl)butan-2-ol **(1ak)**



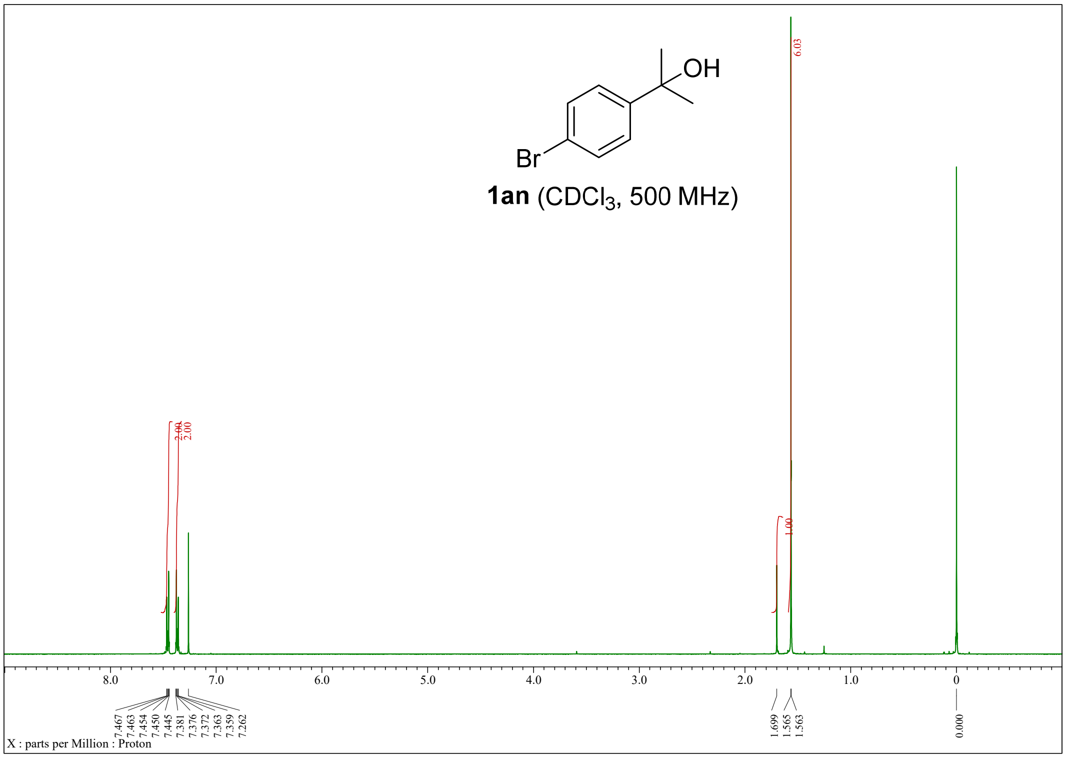
^{1}H NMR spectra of 2-phenylhexan-2-ol **(1al)**



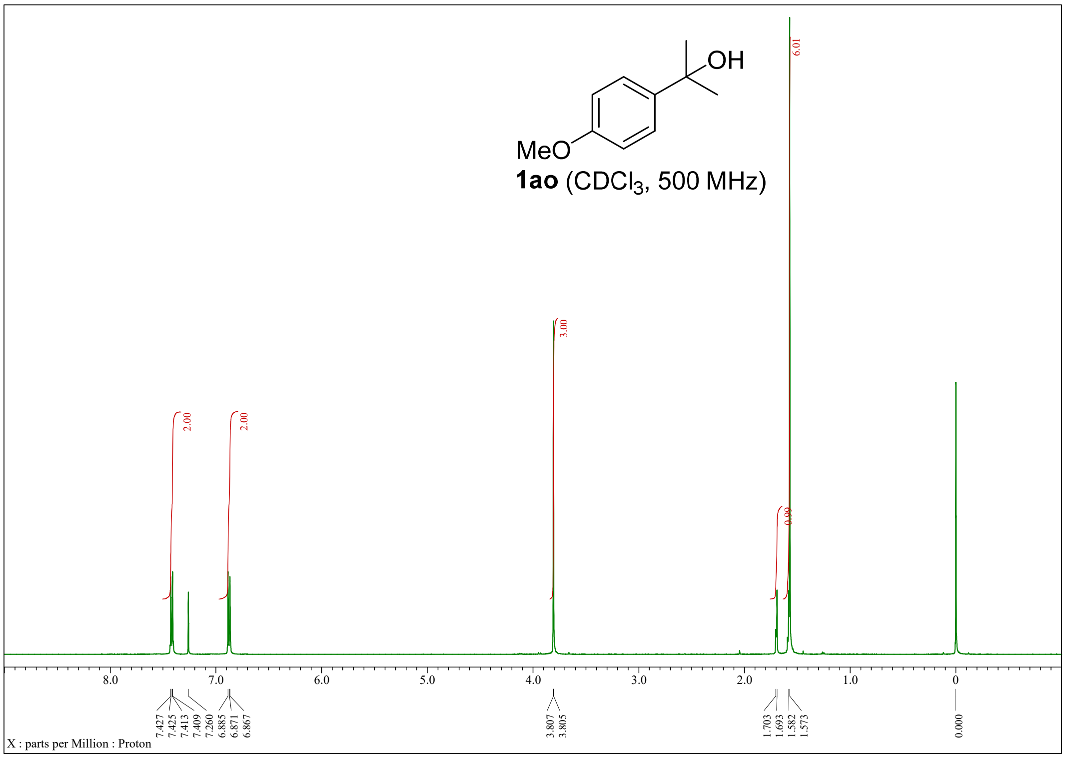
^{1}H NMR spectra of (1R,2S) / (1S,2R)-2-methyl-1-phenylcyclohexan-1-ol **(1am)**



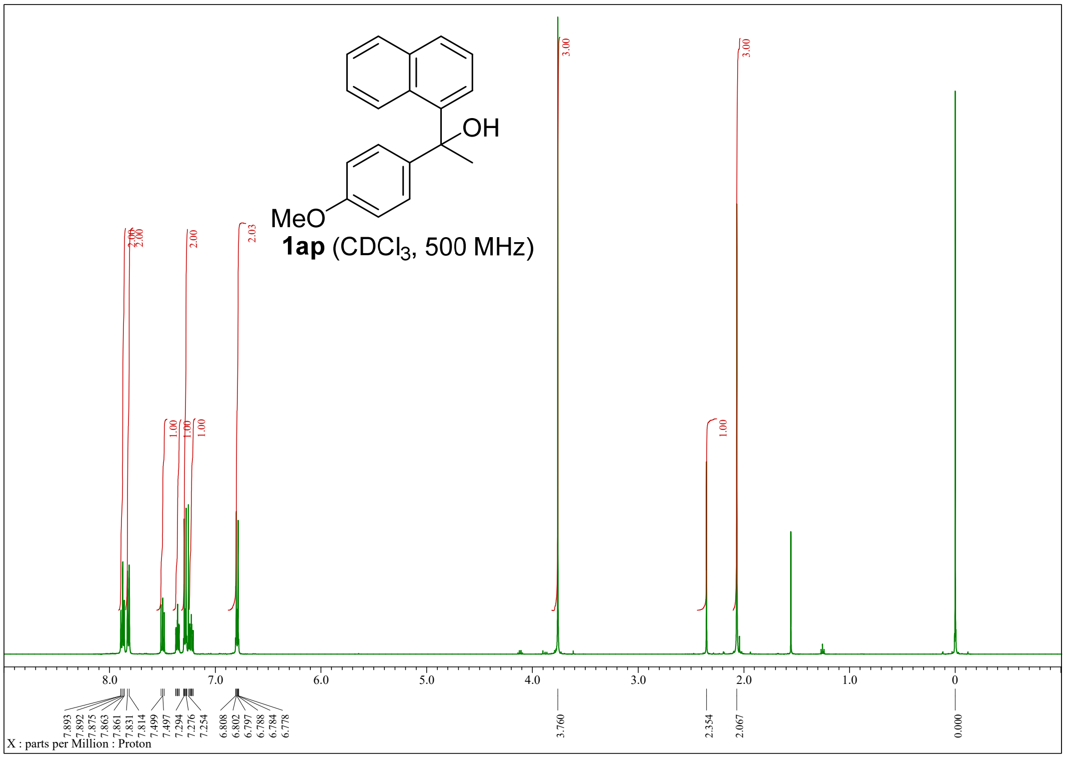
^{1}H NMR spectra of 2-(4-bromophenyl)propan-2-ol (**1an**)



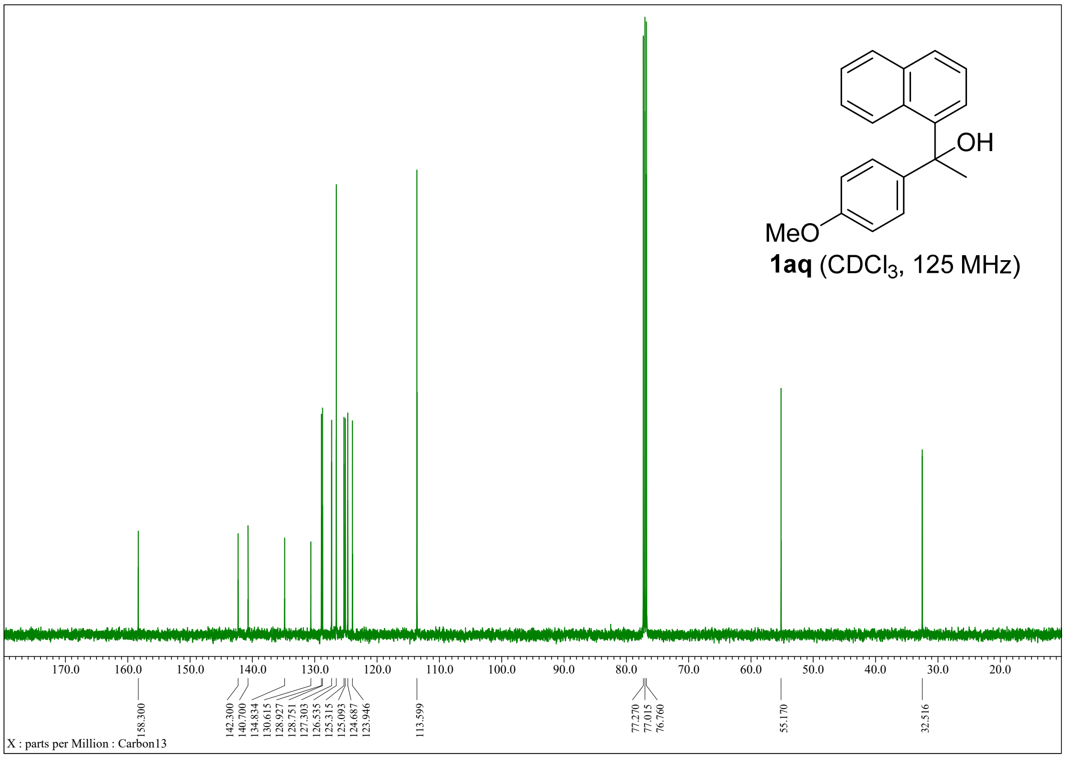
H NMR spectra of 2-(4-methoxyphenyl)propan-2-ol (**1ao**)



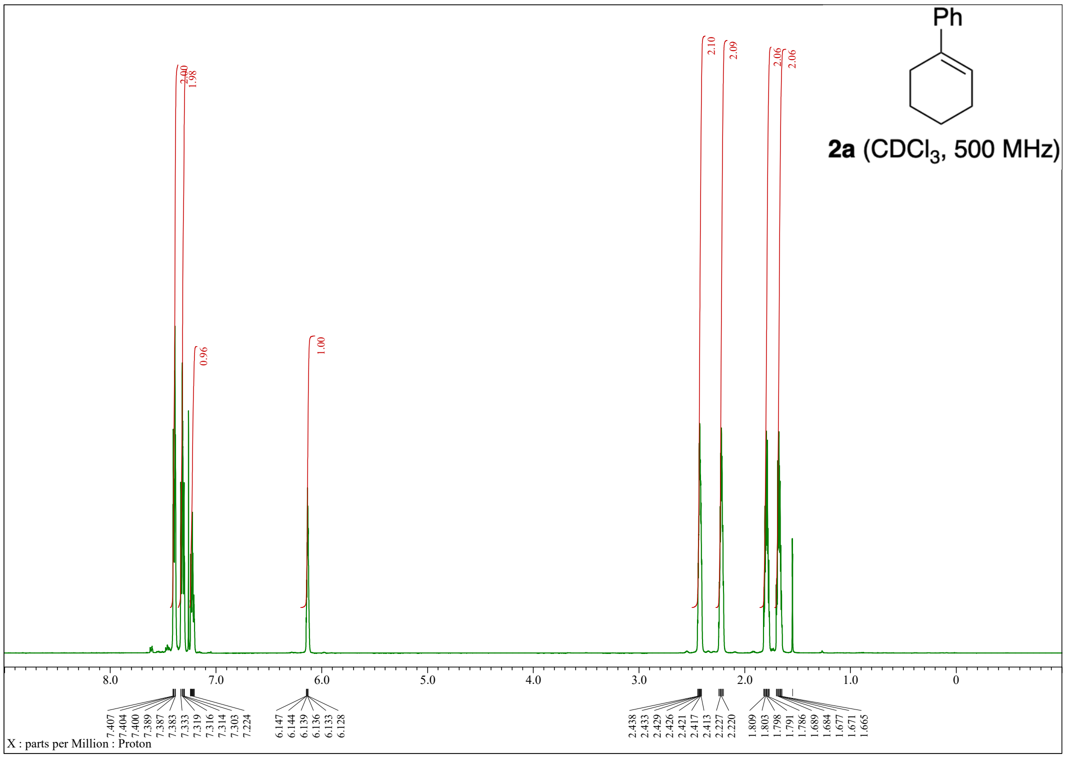
^{1}H NMR spectra of 1-(4-methoxyphenyl)-1-(naphthalen-1-yl)ethan-1-ol (**1ap**)



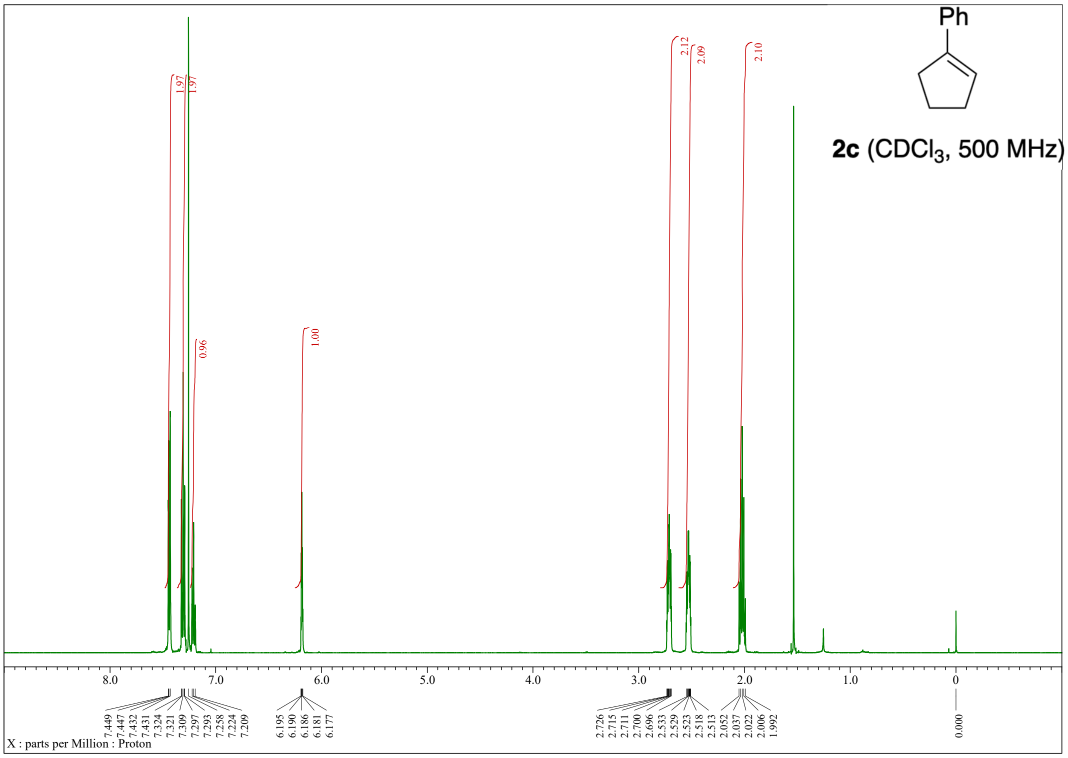
^{13}C NMR spectra of 1-(4-methoxyphenyl)-1-(naphthalen-1-yl)ethan-1-ol (**1aq**)



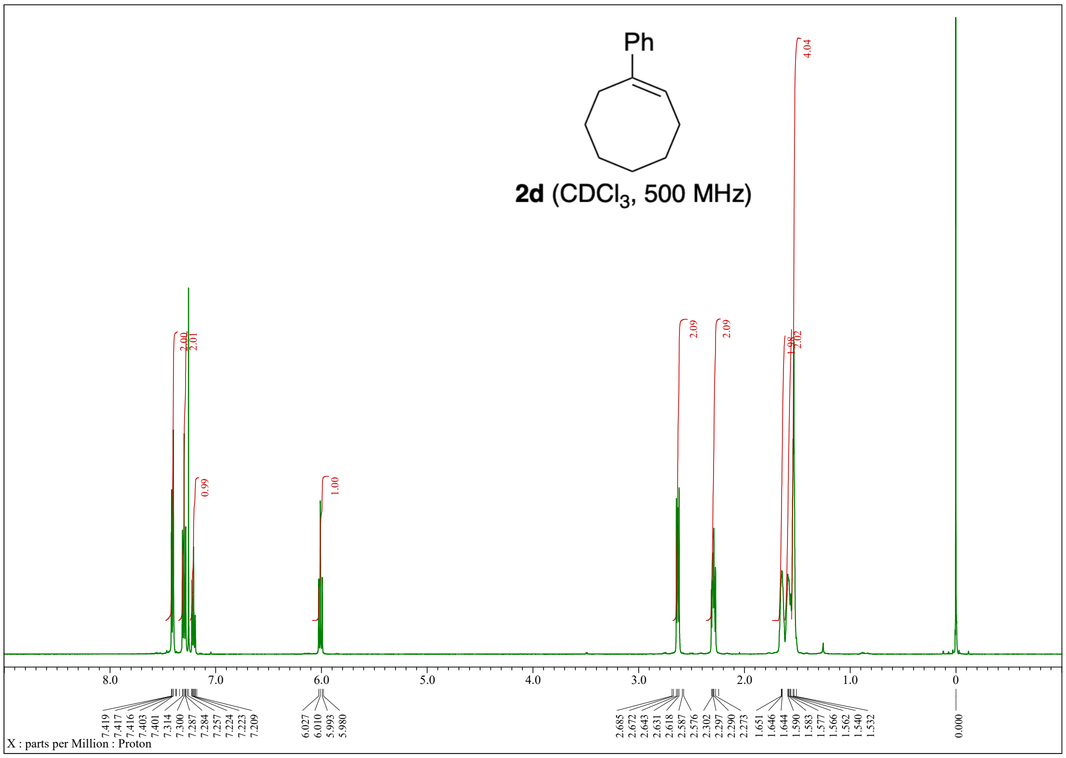
^{1}H NMR spectra of 2,3,4,5-tetrahydro-1,1'-biphenyl **(2a)**



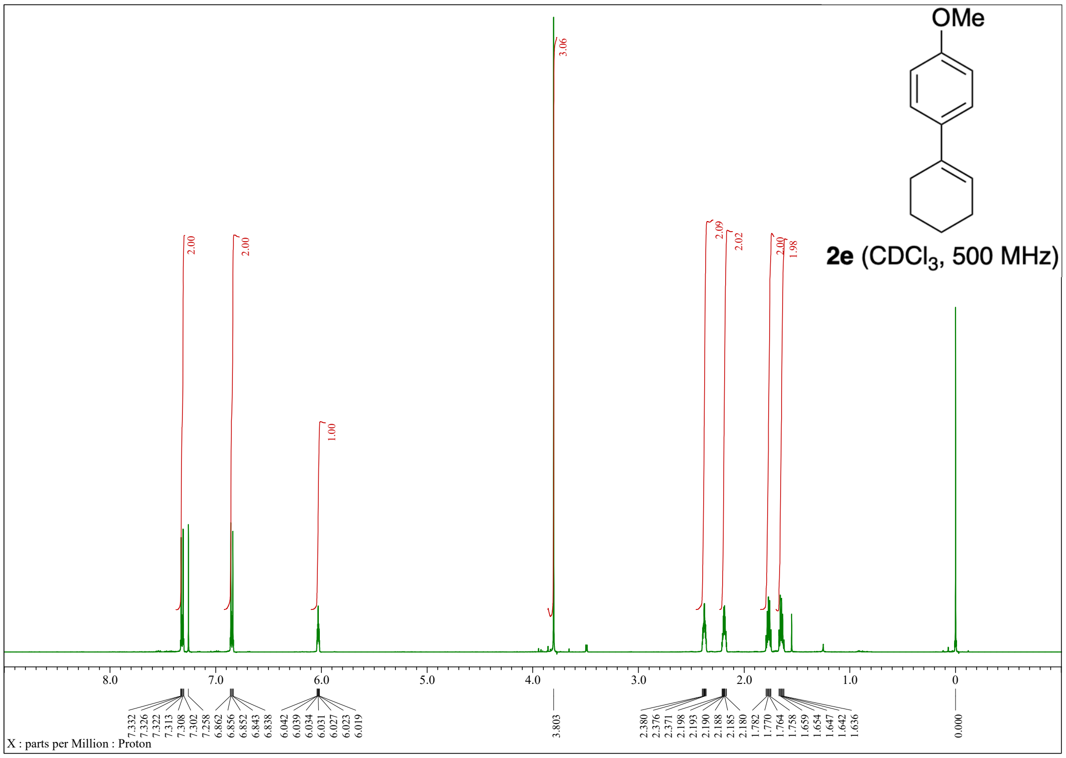
^{1}H NMR spectra of cyclopent-1-en-1-ylbenzene (**2c**).



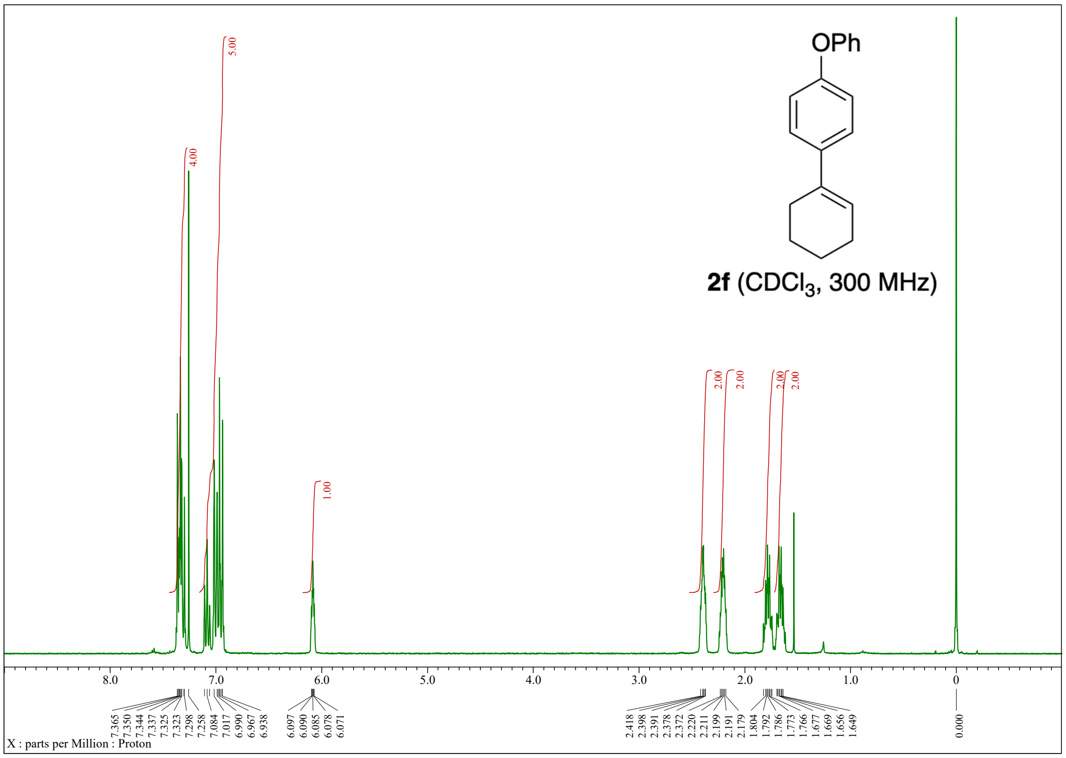
^{1}H NMR spectra of (*E*)-1-phenylcyclooct-1-ene (**2d**).



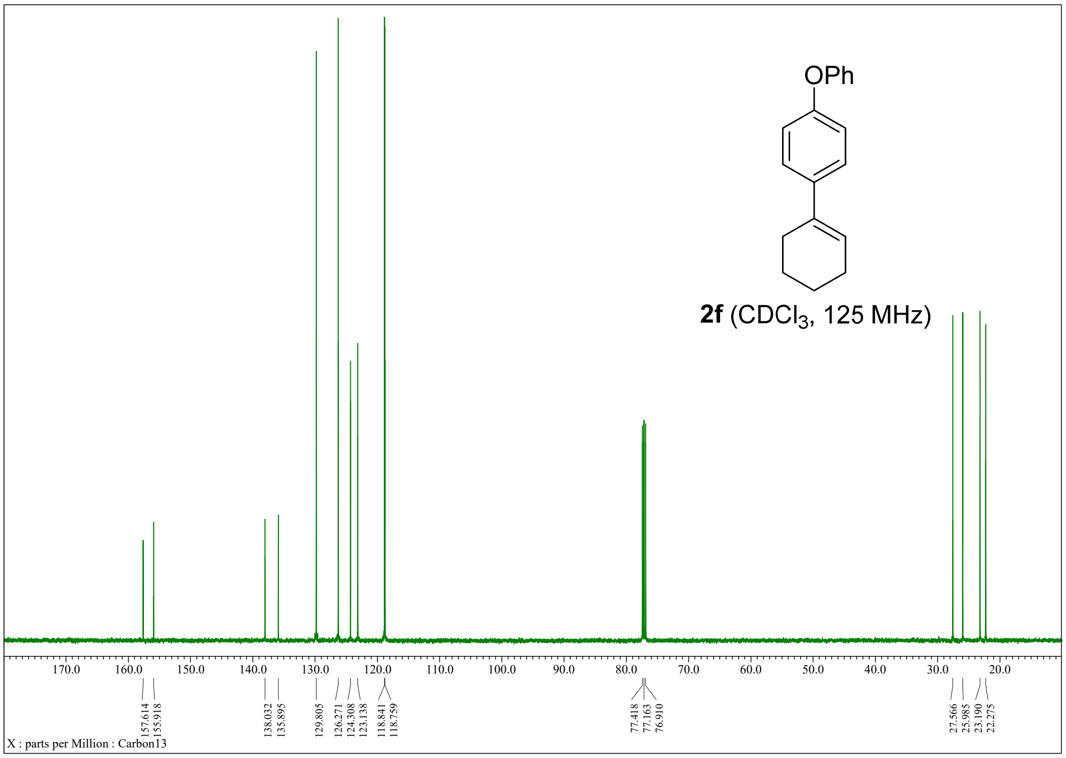
^{1}H NMR spectra of 4'-methoxy-2,3,4,5-tetrahydro-1,1'-biphenyl **(2e).**



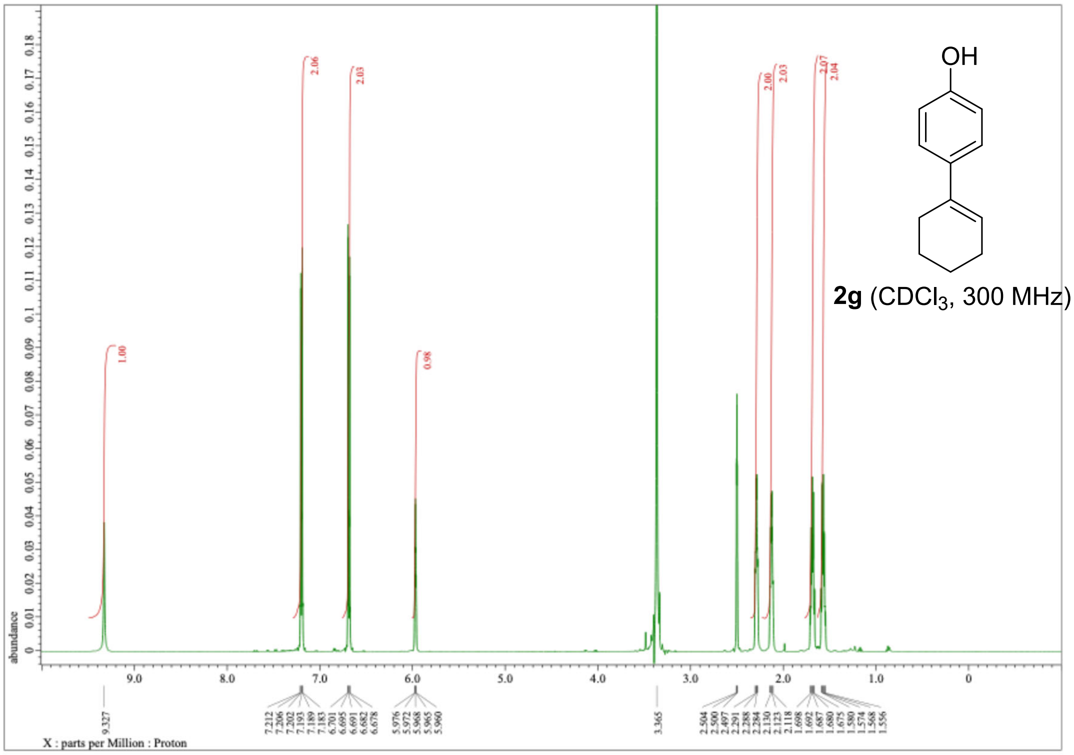
^{1}H NMR spectra of 4'-phenoxy-2,3,4,5-tetrahydro-1,1'-biphenyl **(2f)**



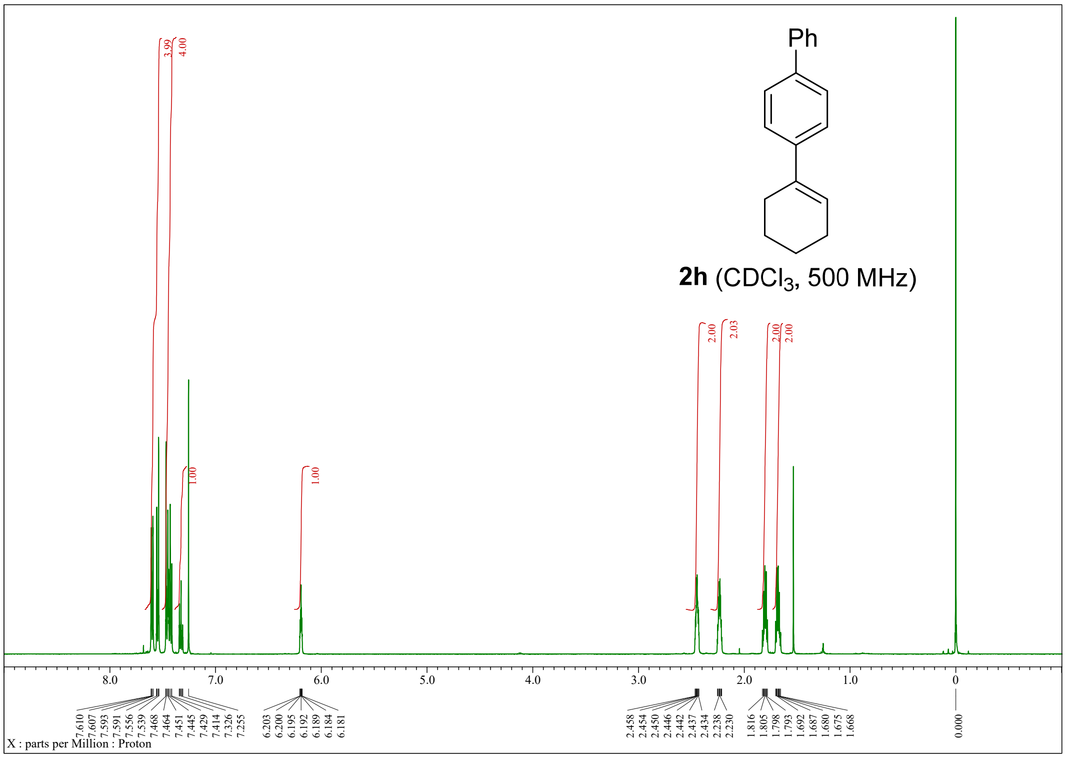
^{13}C NMR spectra of 4'-phenoxy-2,3,4,5-tetrahydro-1,1'-biphenyl **(2f)**



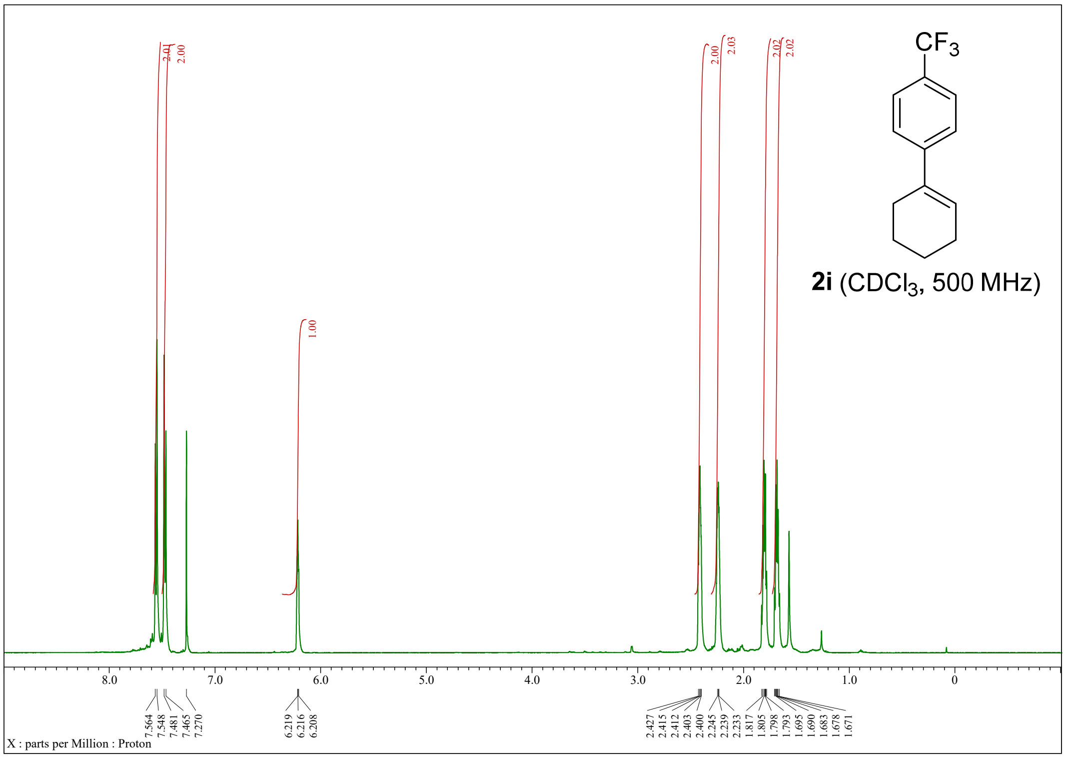
^{1}H NMR spectra of 4-(1-hydroxycyclohexyl)phenol **(2g)**



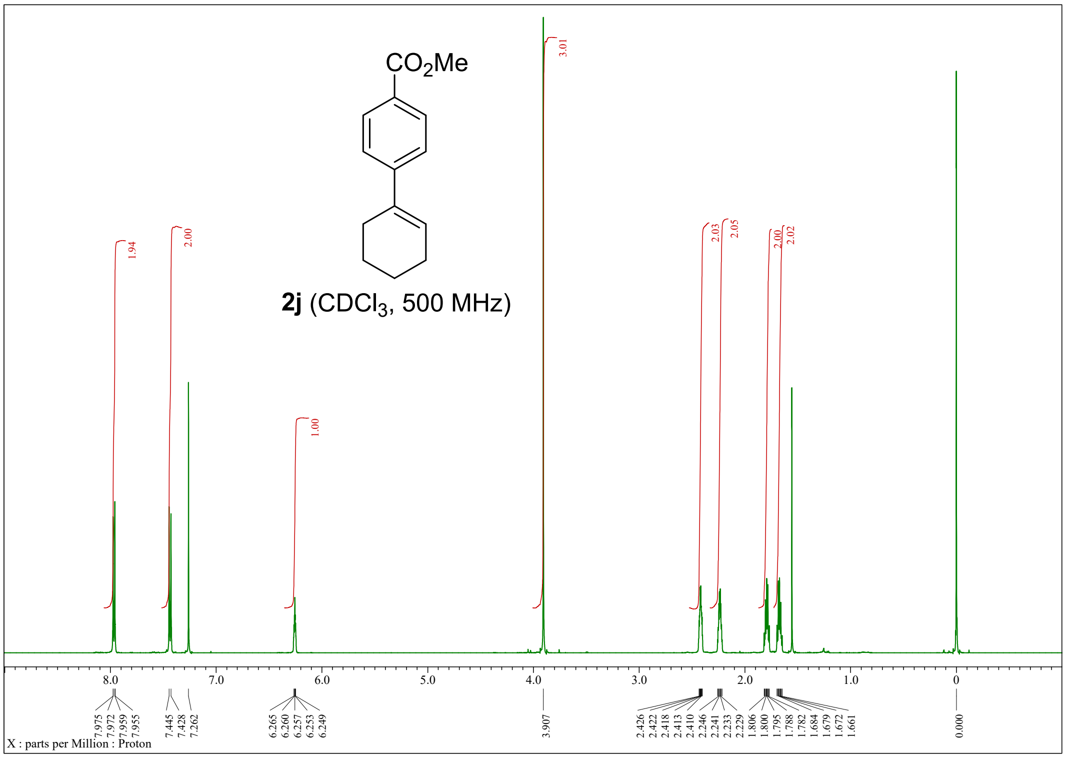
^{1}H NMR spectra of 2,3,4,5-tetrahydro-1,1':4',1''-terphenyl **(2h)**



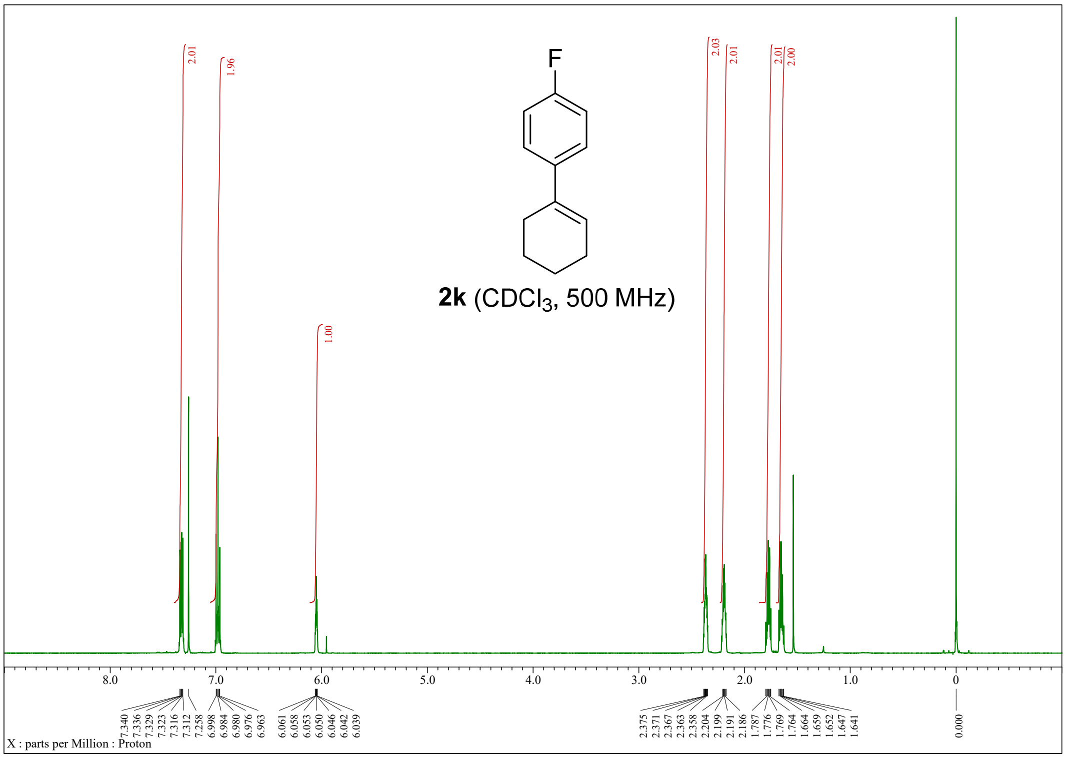
^{1}H NMR spectra of 4'-(trifluoromethyl)-2,3,4,5-tetrahydro-1,1'-biphenyl **(2i)**



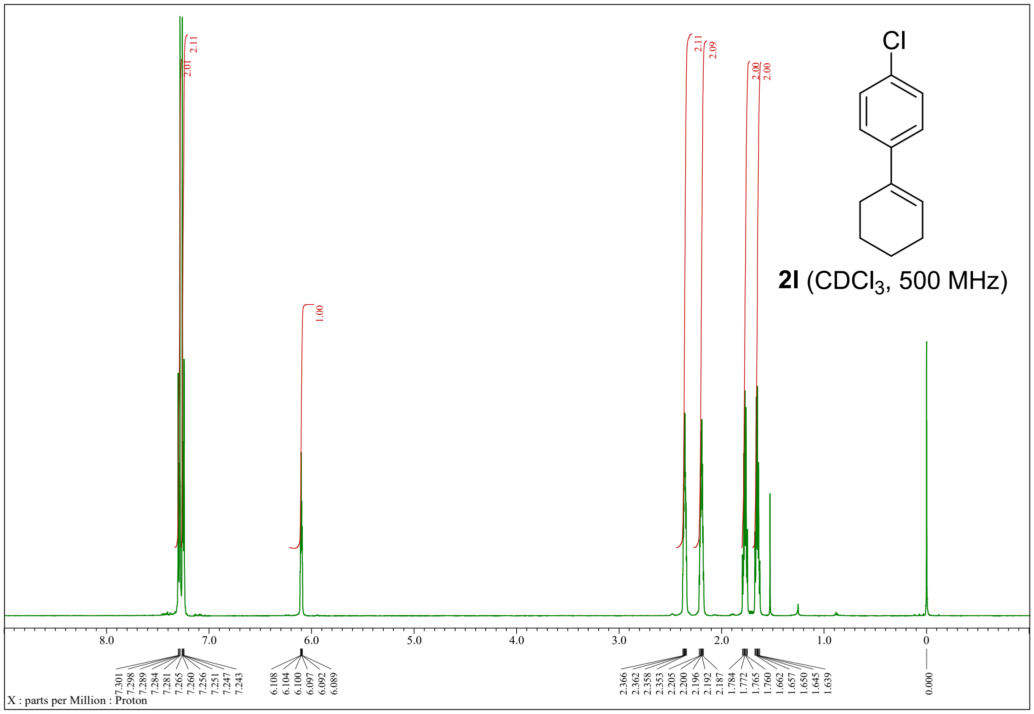
^{1}H NMR spectra of methyl 2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-carboxylate **(2j)**



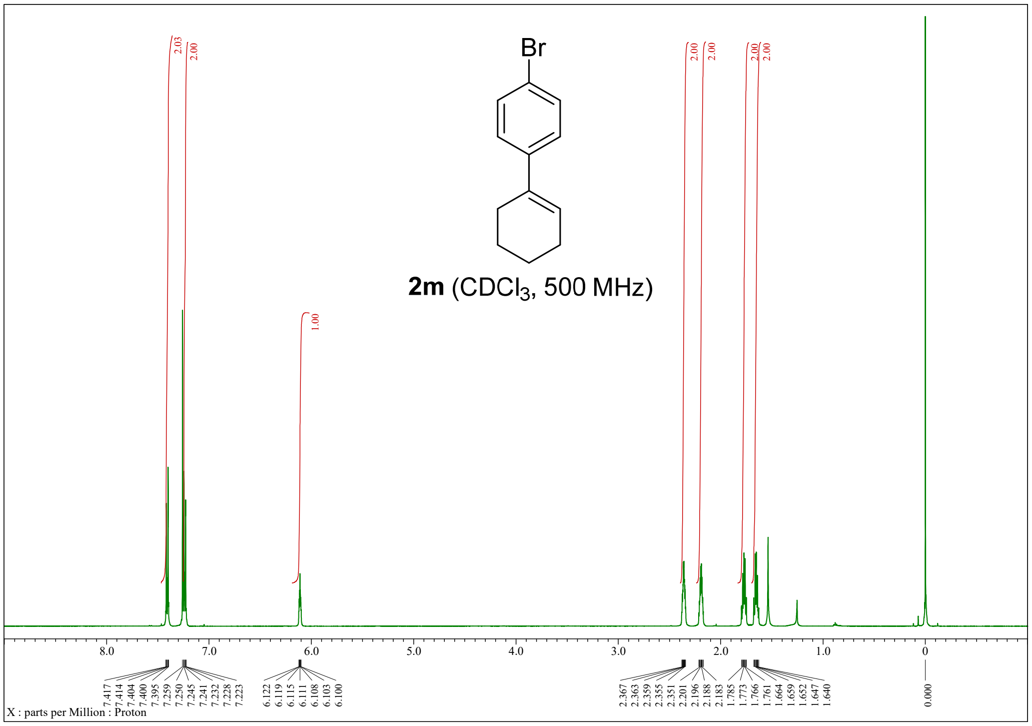
^{1}H NMR spectra of 4'-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl **(2k)**



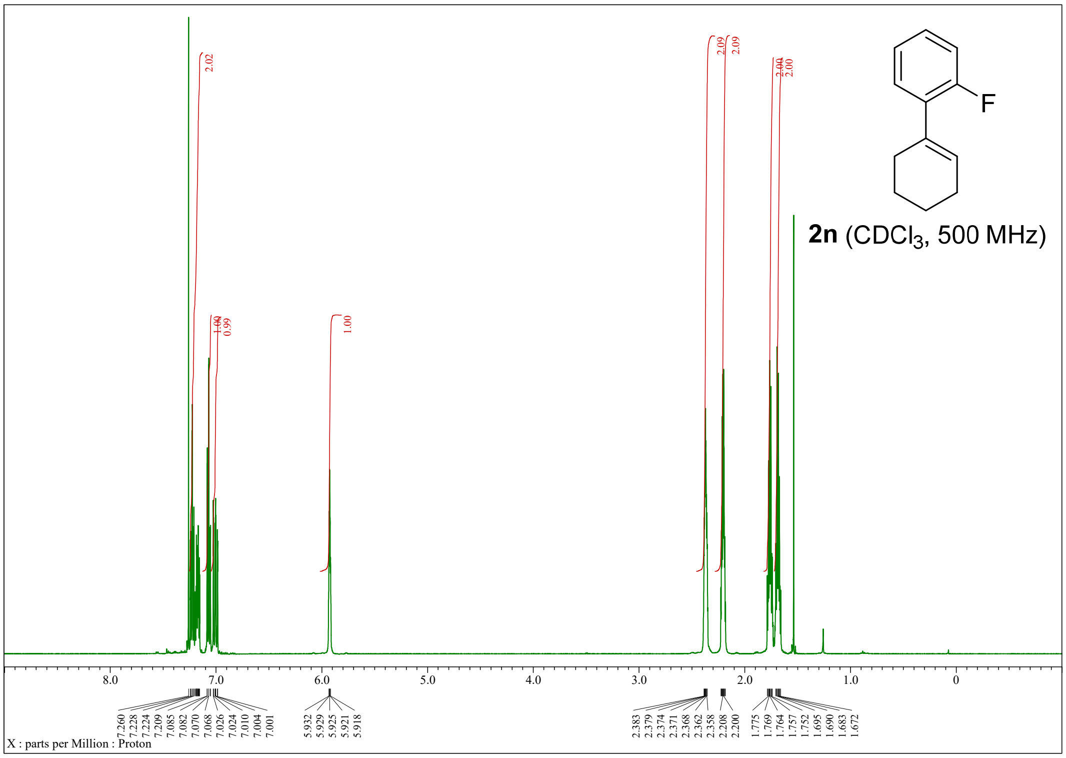
^{1}H NMR spectra of 4'-chloro-2,3,4,5-tetrahydro-1,1'-biphenyl **(2l)**



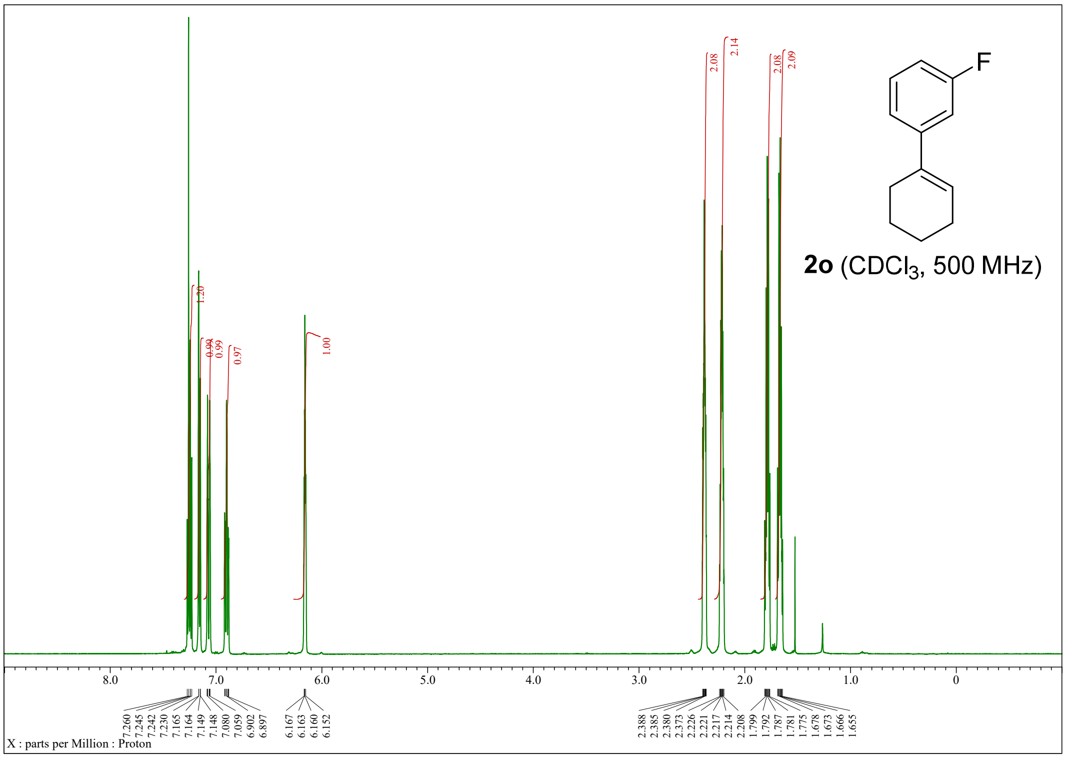
^{1}H NMR spectra of 4'-bromo-2,3,4,5-tetrahydro-1,1'-biphenyl **(2m)**



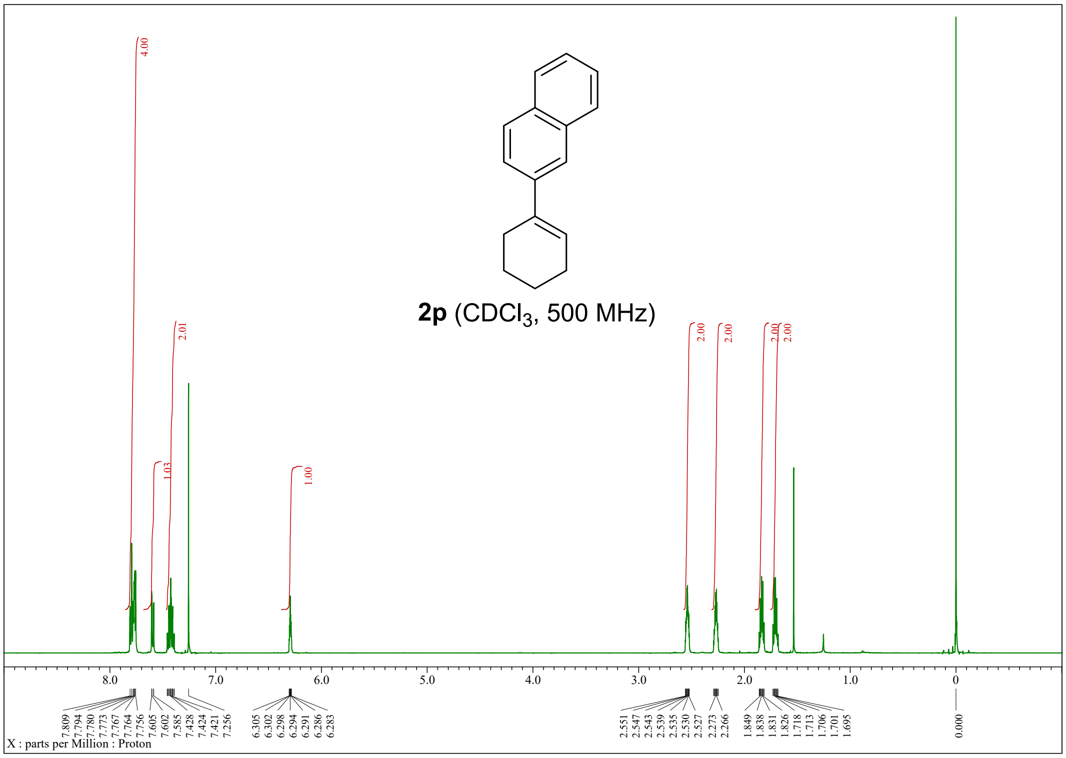
^{1}H NMR spectra of 2'-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl **(2n)**



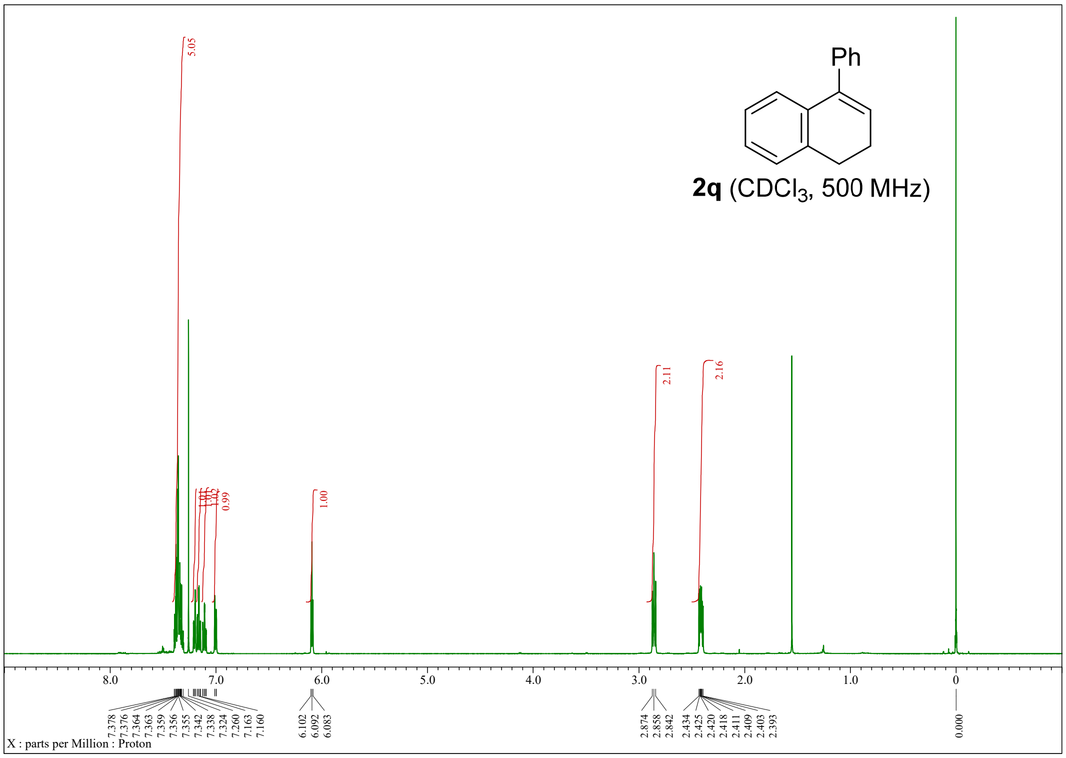
^{1}H NMR spectra of 3'-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl **(2o)**



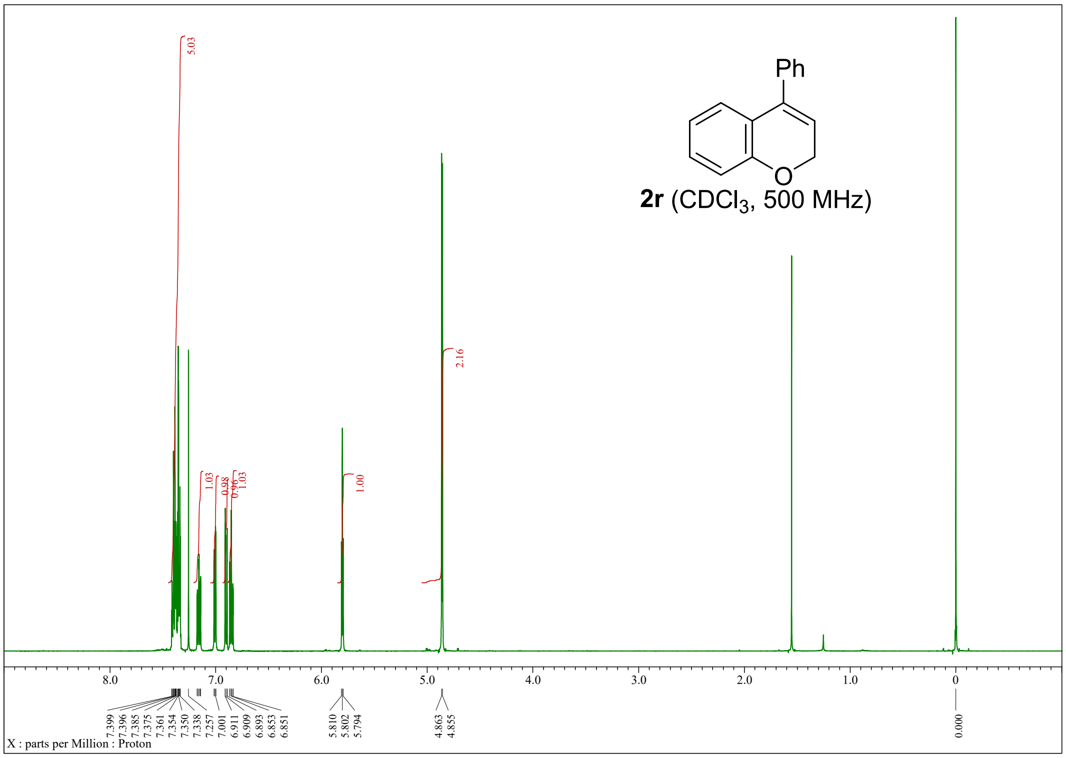
^{1}H NMR spectra of 2-(cyclohex-1-en-1-yl) naphthalene **(2p)**



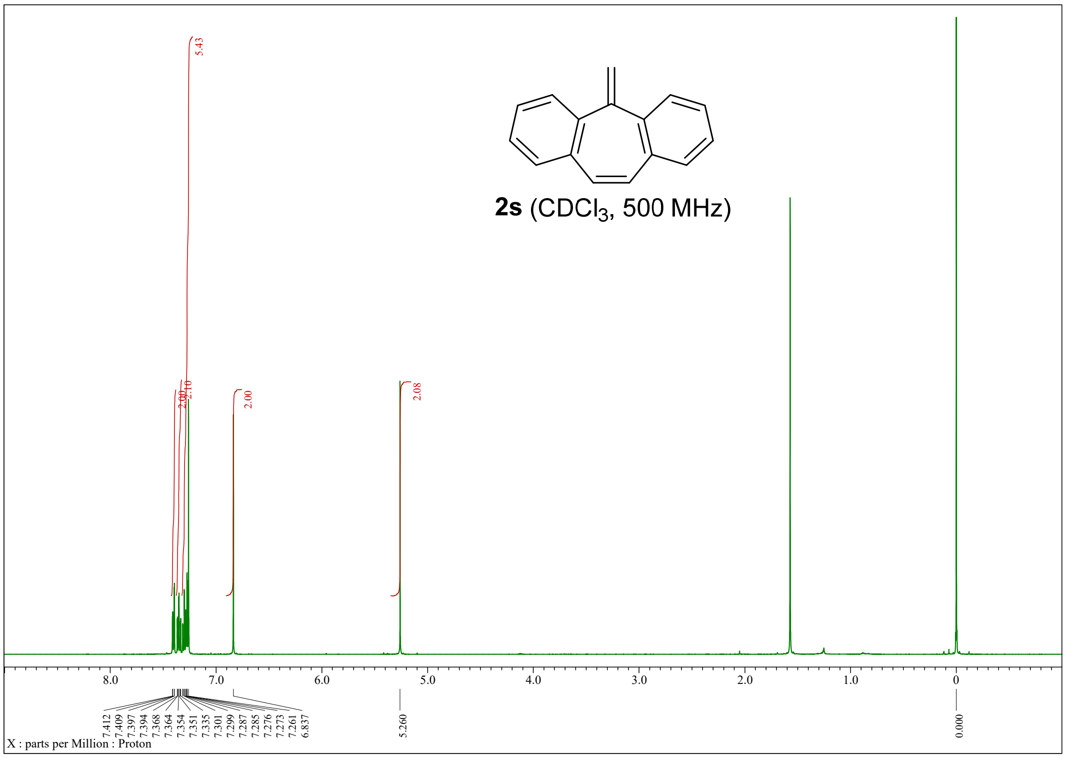
^{1}H NMR spectra of 4-phenyl-1,2-dihydronaphthalene **(2q)**



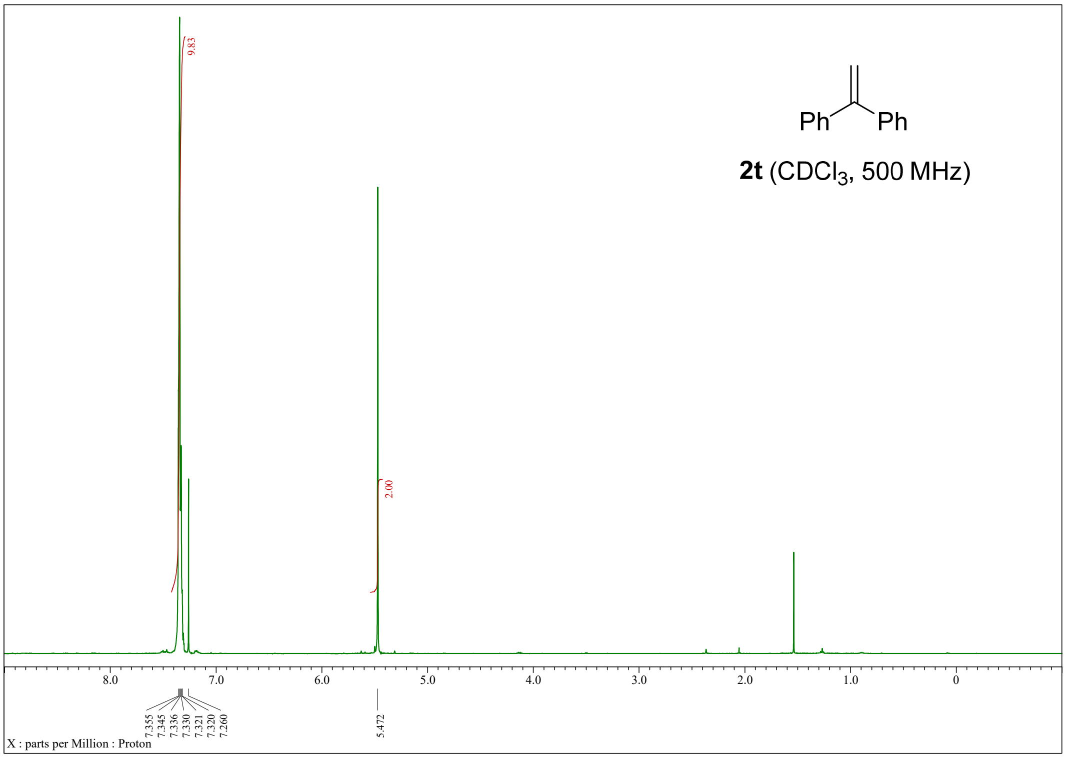
^{1}H NMR spectra of 4-phenyl-2*H*-chromene **(2r)**



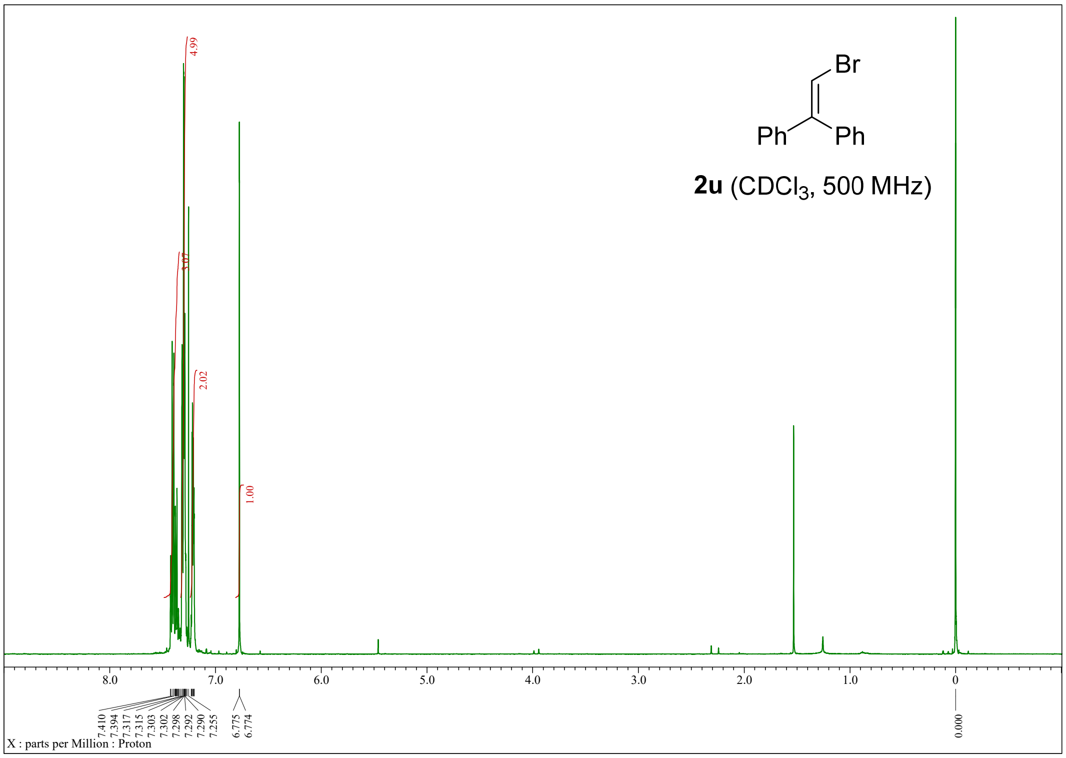
^{1}H NMR spectra of 5-methylene-5*H*-dibenzo[*a*,*d*][7]annulene **(2s)**



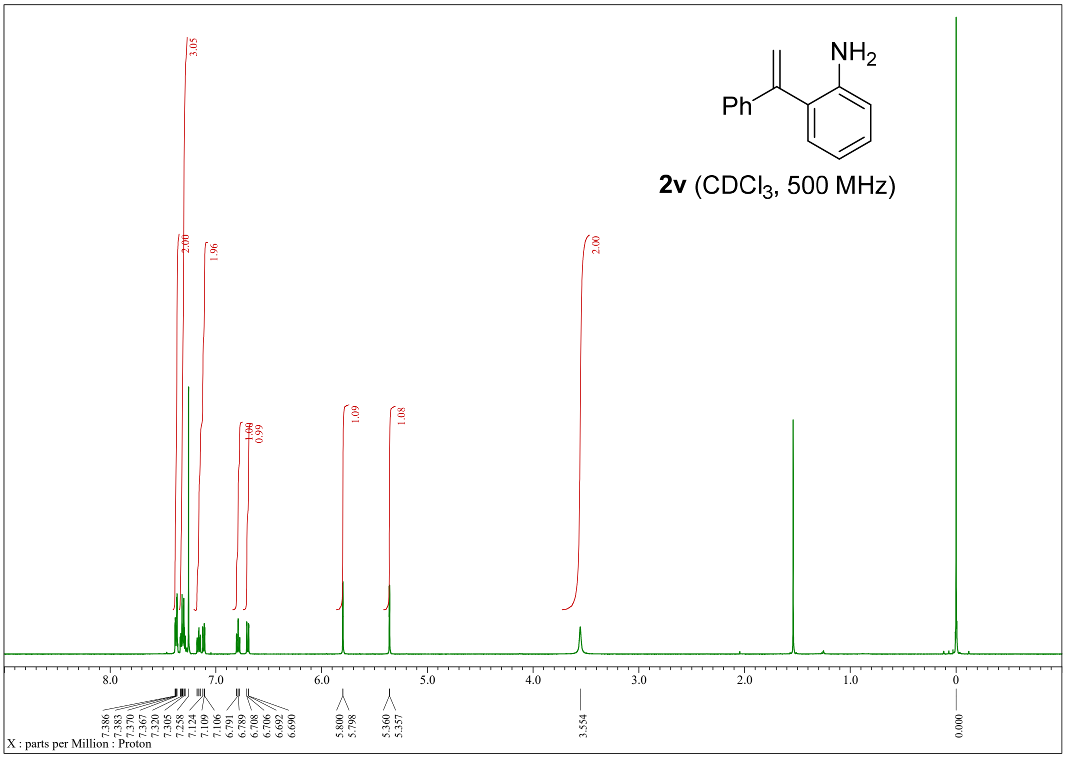
^{1}H NMR spectra of ethene-1,1-diyldibenzene **(2t)**



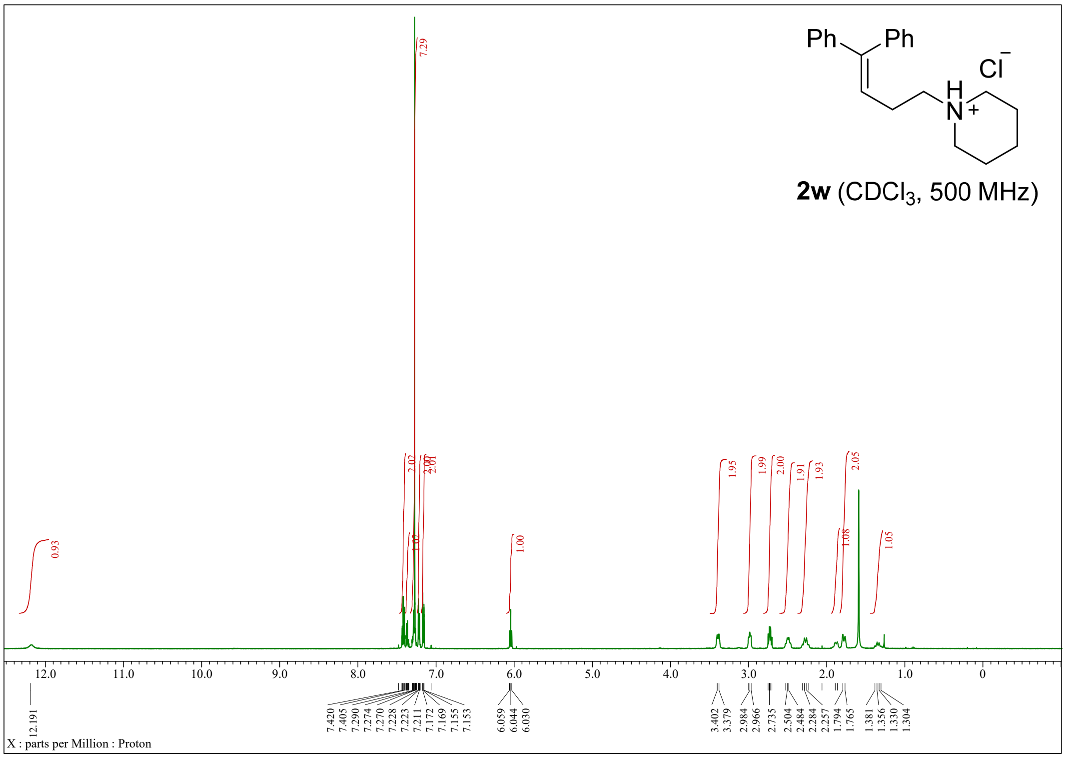
^{1}H NMR spectra of (2-bromoethene-1,1-diyl) dibenzene **(2u)**



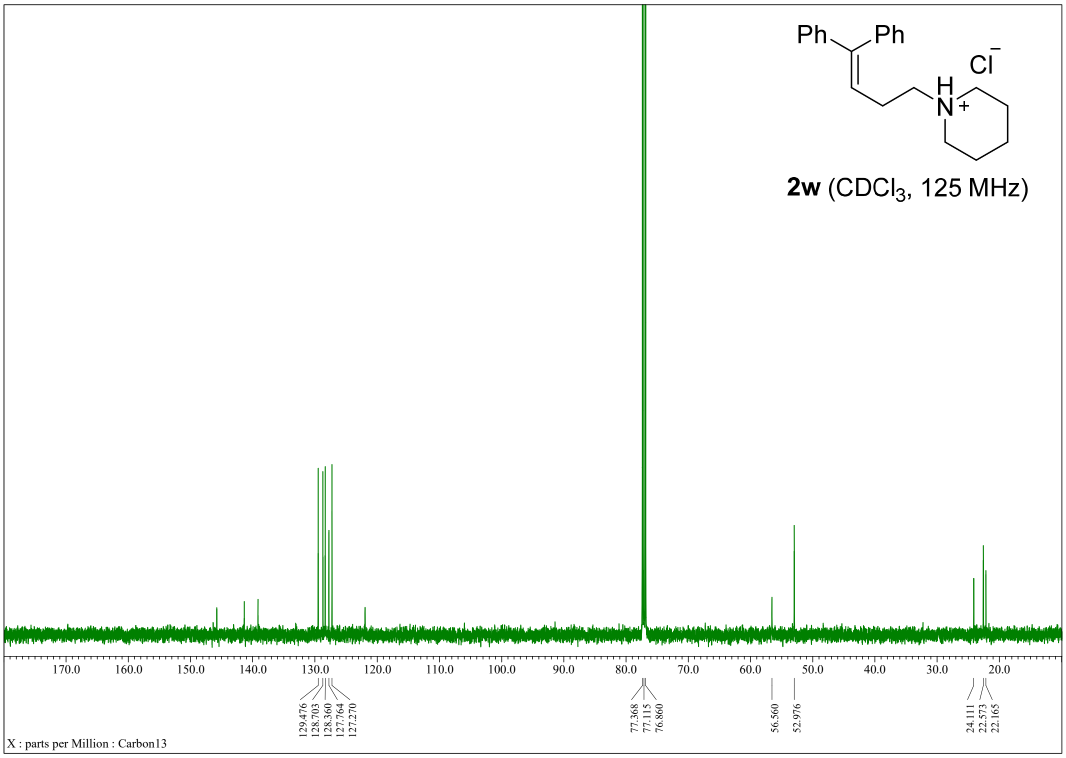
^{1}H NMR spectra of 2-(1-phenylvinyl) aniline **(2v)**



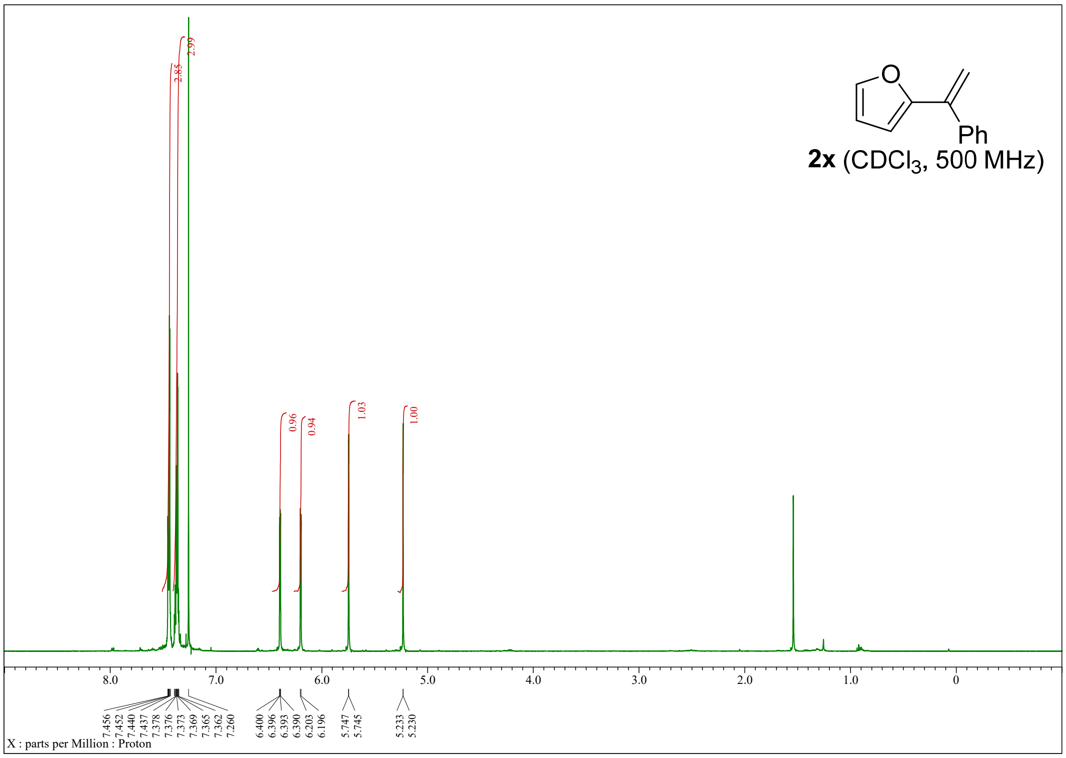
^{1}H NMR spectra of 1-(4,4-diphenylbut-3-en-1-yl)piperidin-1-ium chloride **(2w)**



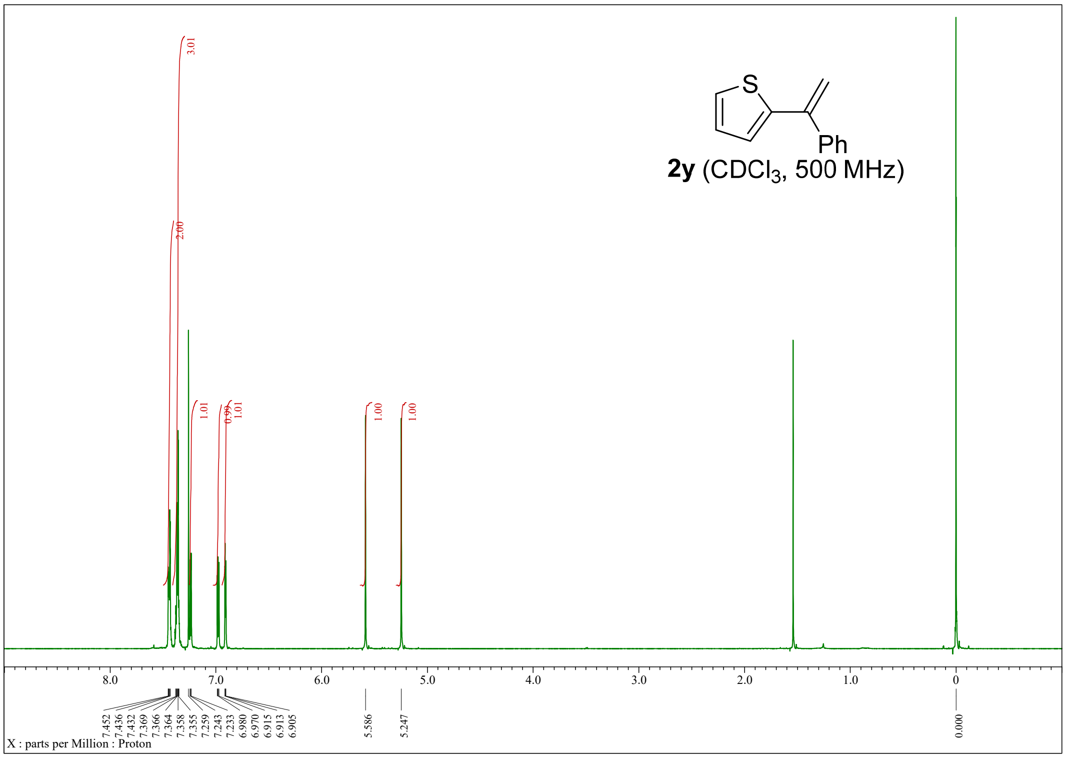
^{13}C NMR spectra of 1-(4,4-diphenylbut-3-en-1-yl)piperidin-1-ium chloride **(2w)**



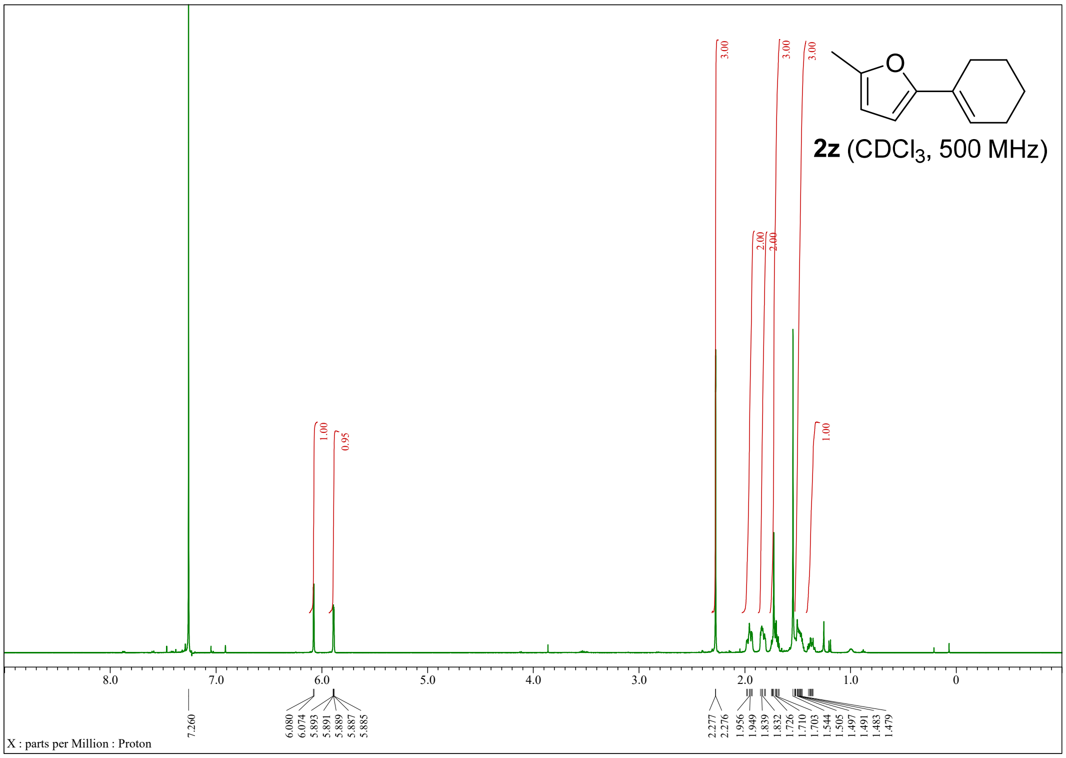
^{1}H NMR spectra of 2-(1-phenylvinyl) furan **(2x)**



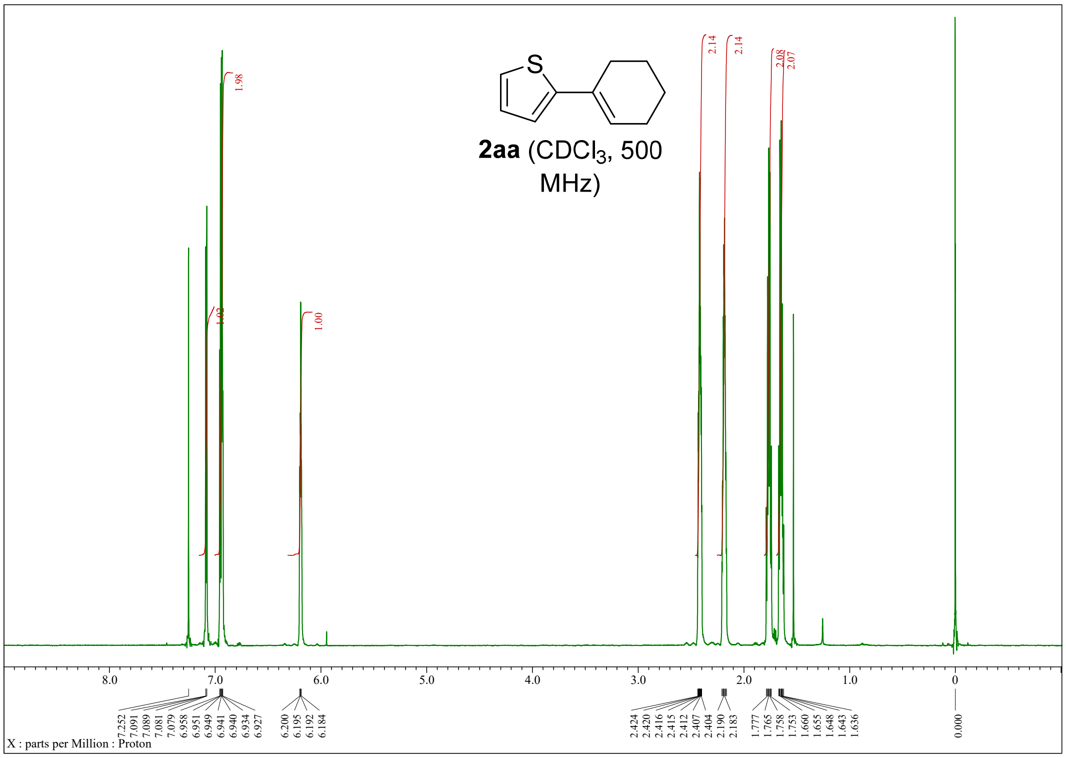
^{1}H NMR spectra of 2-(1-phenylvinyl) thiophene **(2y)**



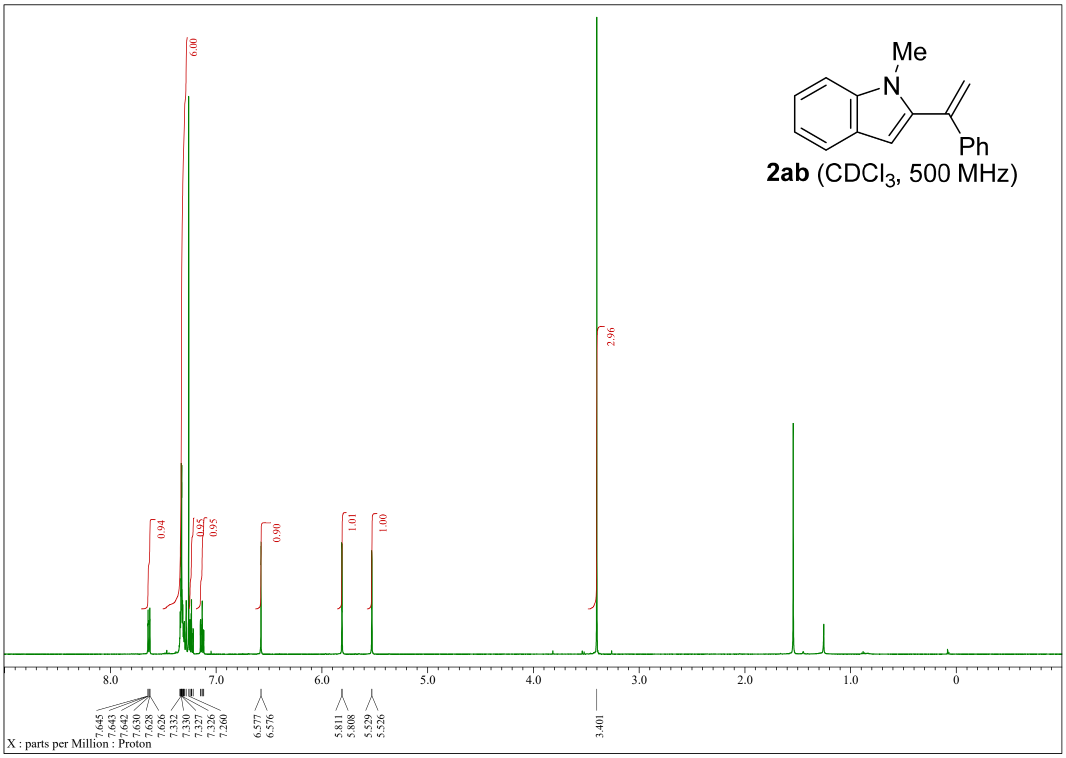
^{1}H NMR spectra of 2-(cyclohex-1-en-1-yl)-5-methylfuran **(2z)**



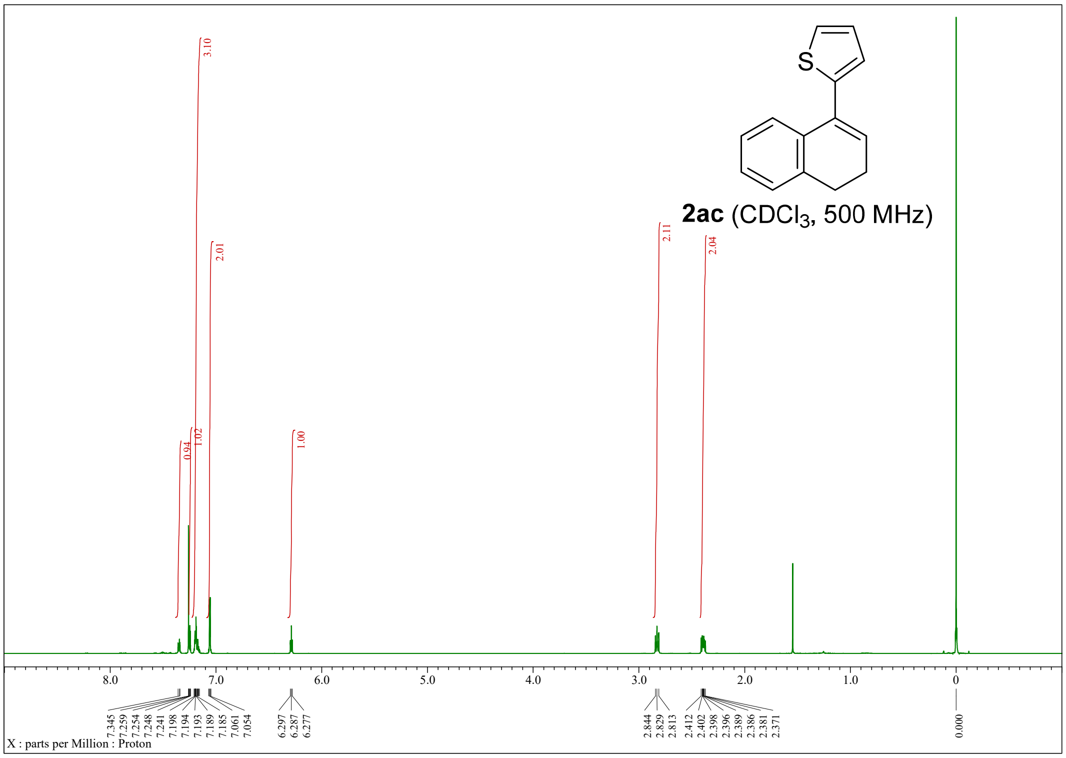
^{1}H NMR spectra of 2-(cyclohex-1-en-1-yl) thiophene **(2aa)**



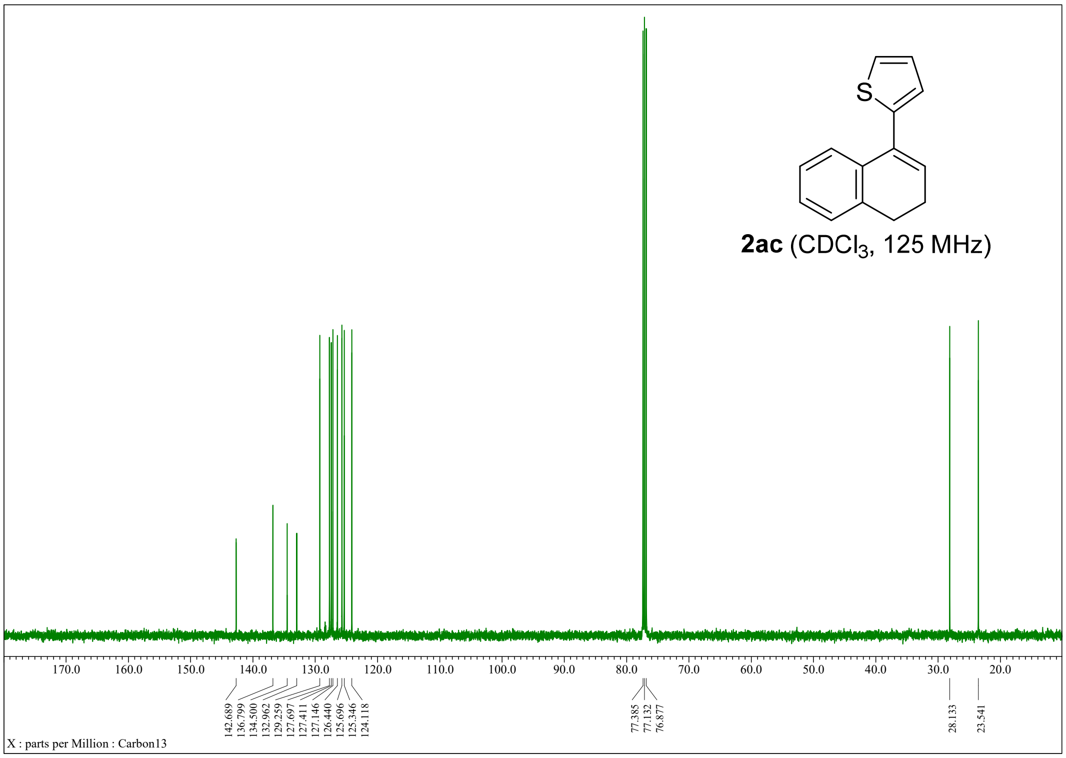
^{1}H NMR spectra of 1-methyl-2-(1-phenylvinyl)-1*H*-indole **(2ab)**



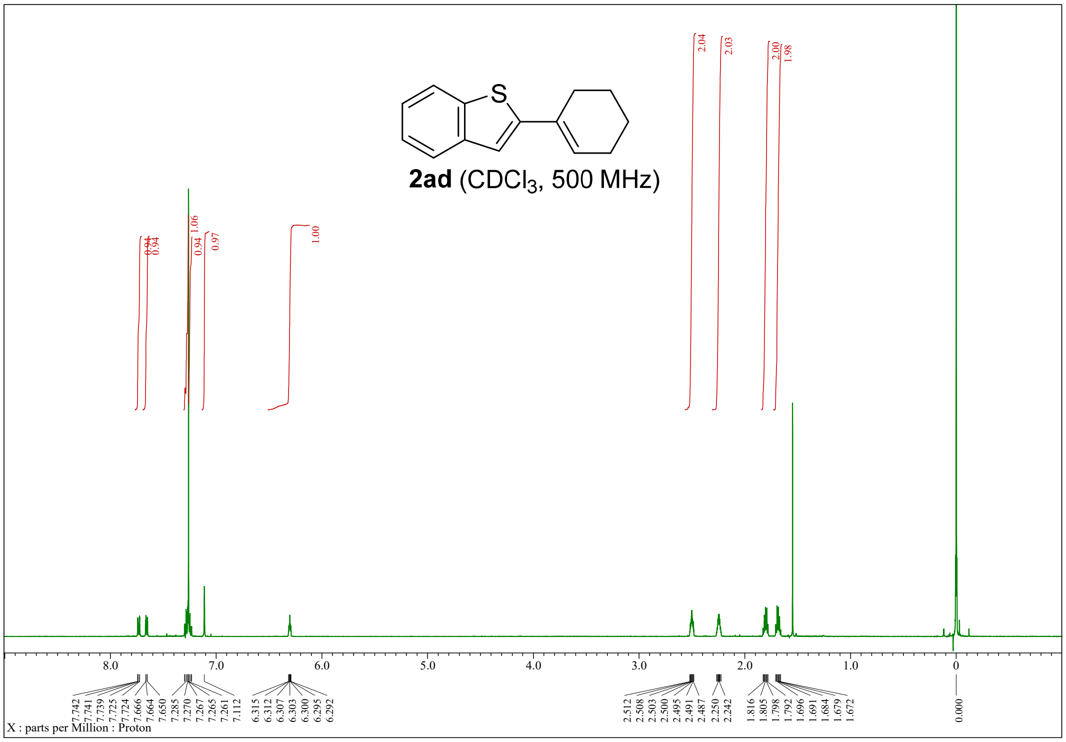
^{1}H NMR spectra of 2-(3,4-dihydronaphthalen-1-yl) thiophene **(2ac)**



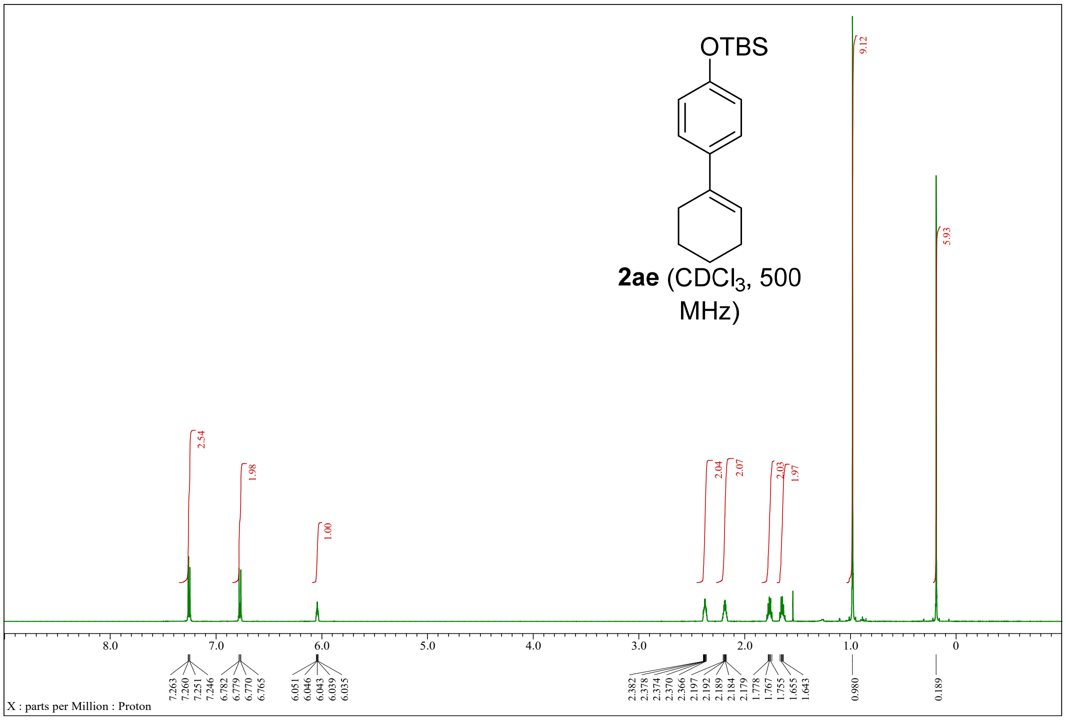
^{13}C NMR spectra of 2-(3,4-dihydronaphthalen-1-yl) thiophene **(2ac)**



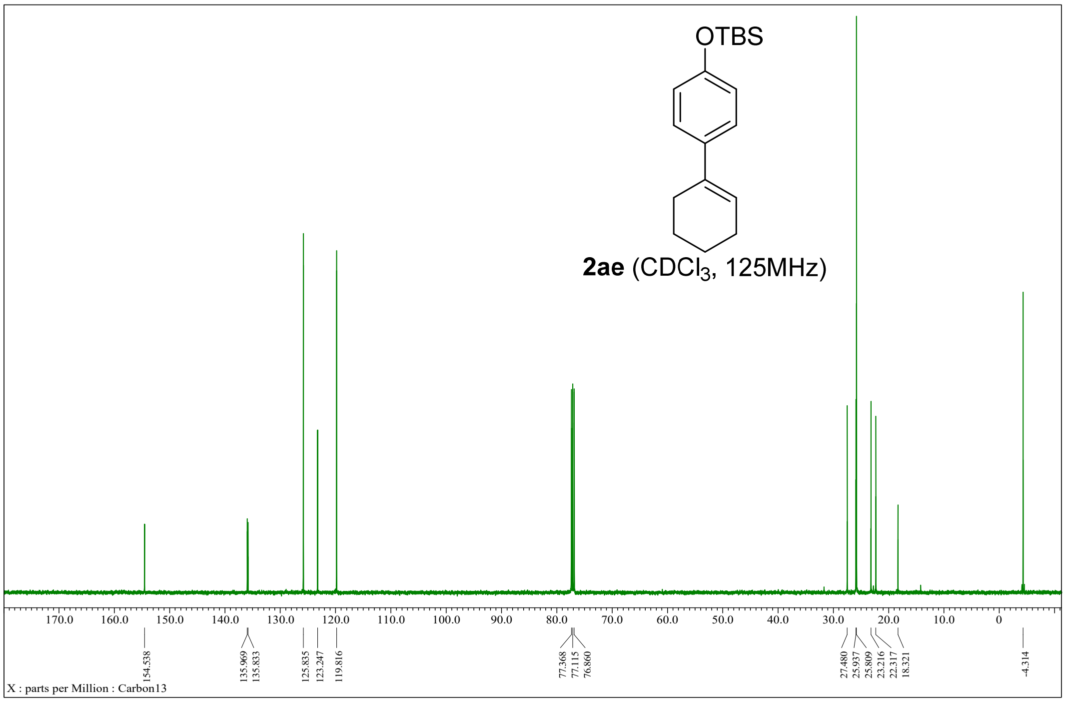
^{1}H NMR spectra of 2-(cyclohex-1-en-1-yl) benzo[*b*]thiophene **(2ad)**



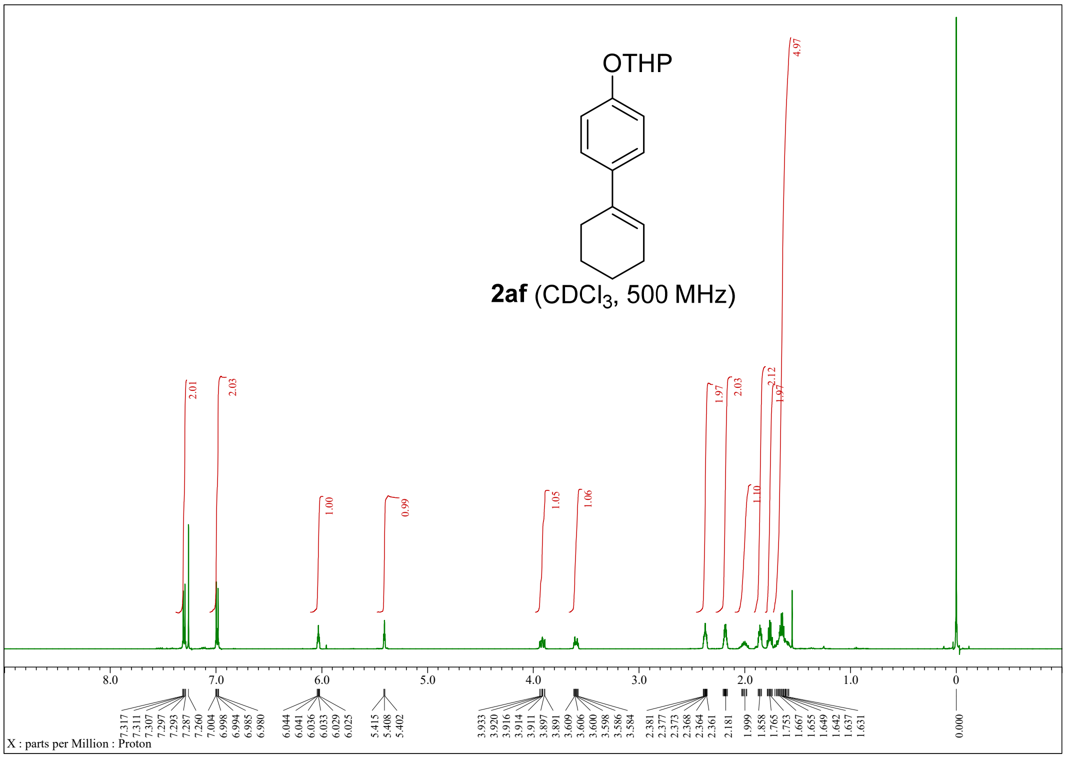
^{1}H NMR spectra of *tert*-butyldimethyl((2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-yl) oxy) silane **(2ae)**



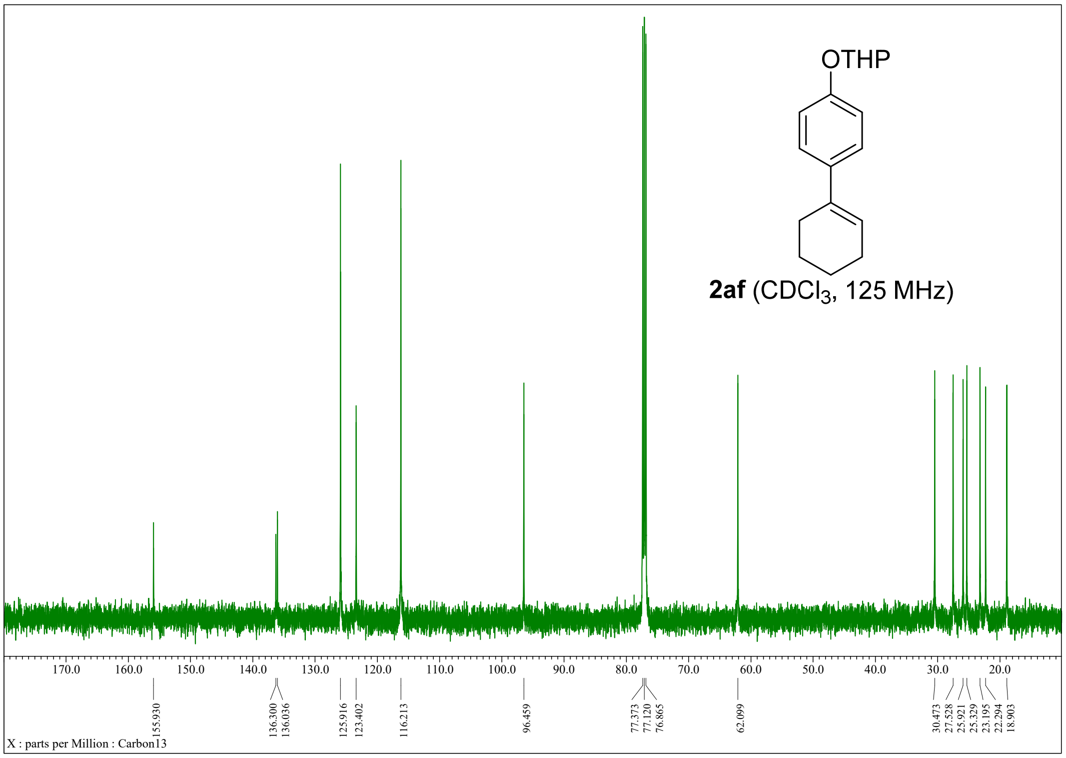
^{13}C NMR spectra of *tert*-butyldimethyl((2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-yl) oxy) silane **(2ae)**



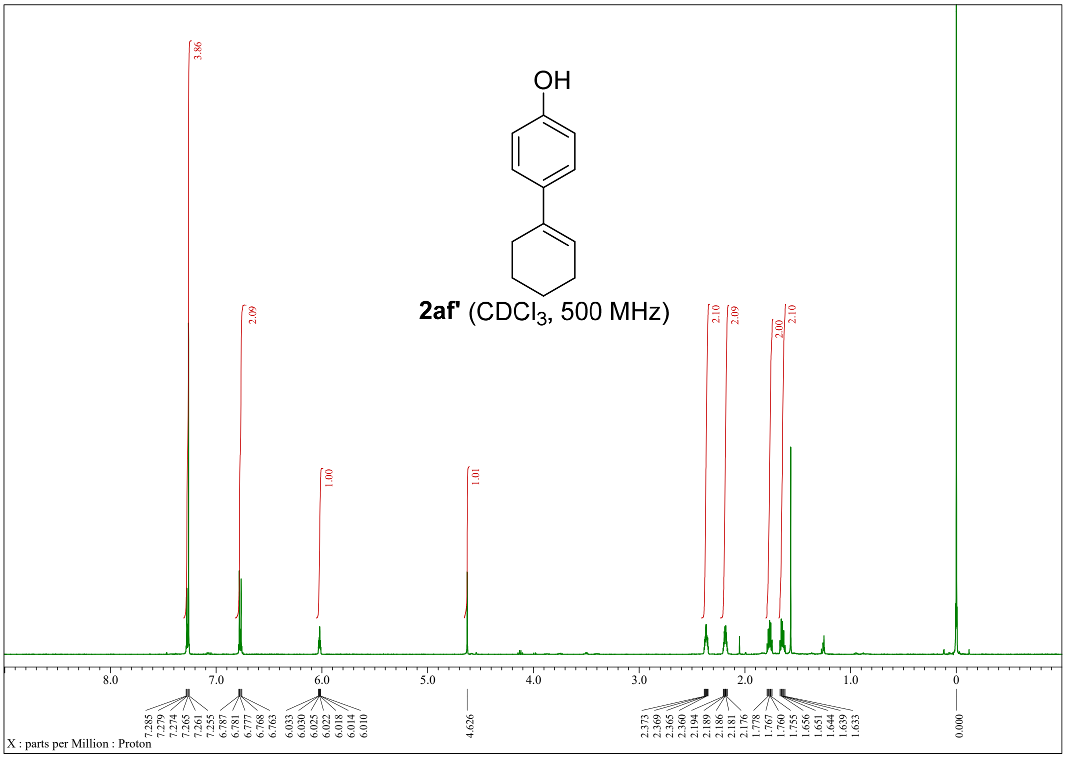
^{1}H NMR spectra of 2-((2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-yl)oxy)tetrahydro-2*H*-pyran **(2af)**



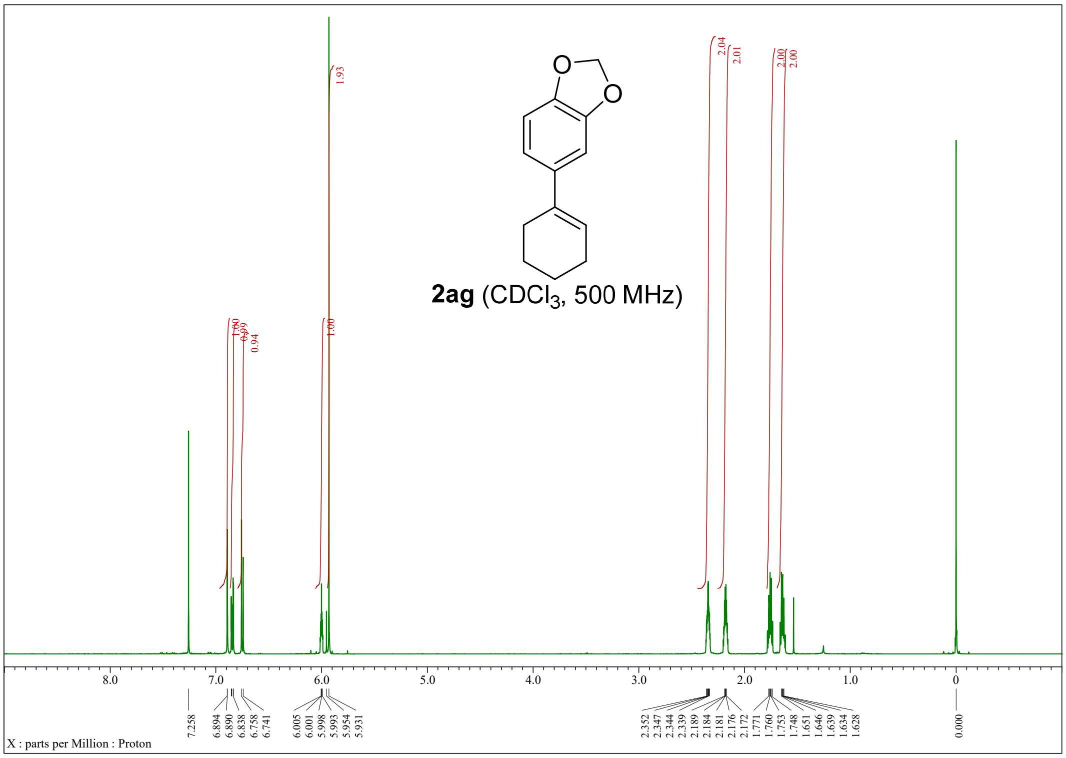
^{13}C NMR spectra of 2-((2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-yl)oxy)tetrahydro-2*H*-pyran **(2af)**



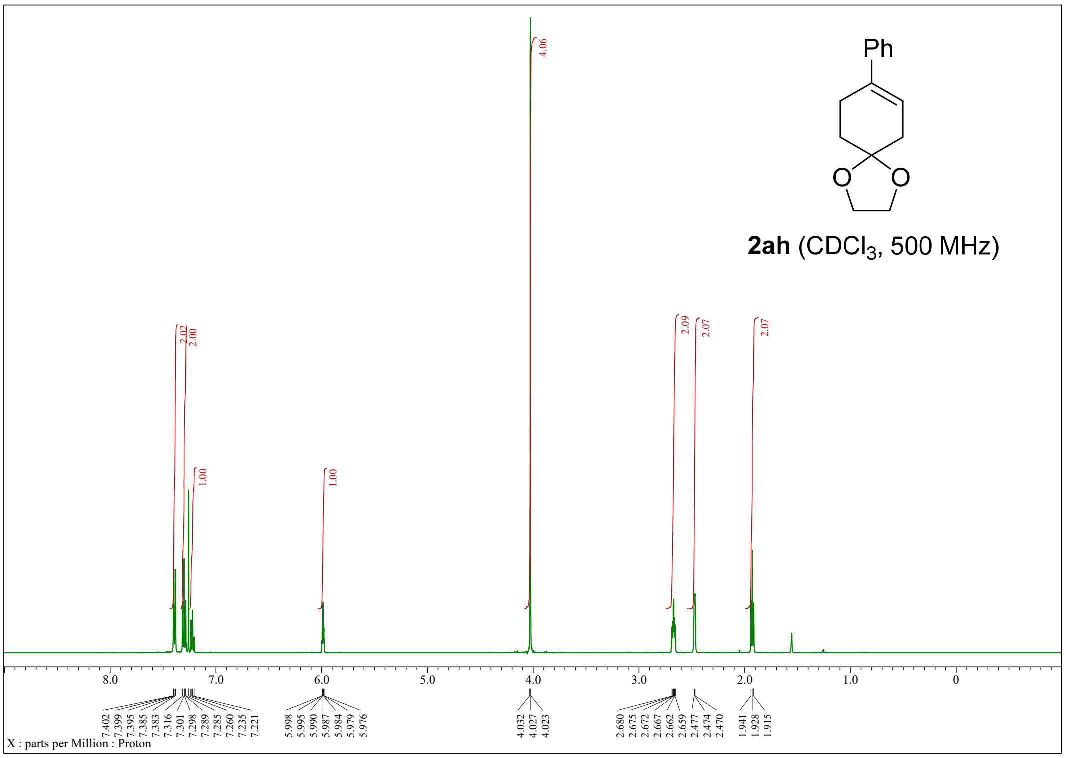
^{1}H NMR spectra of 2’,3’,4’,5’-tetrahydro-[1,1’-biphenyl]-4-ol (**2af’**)



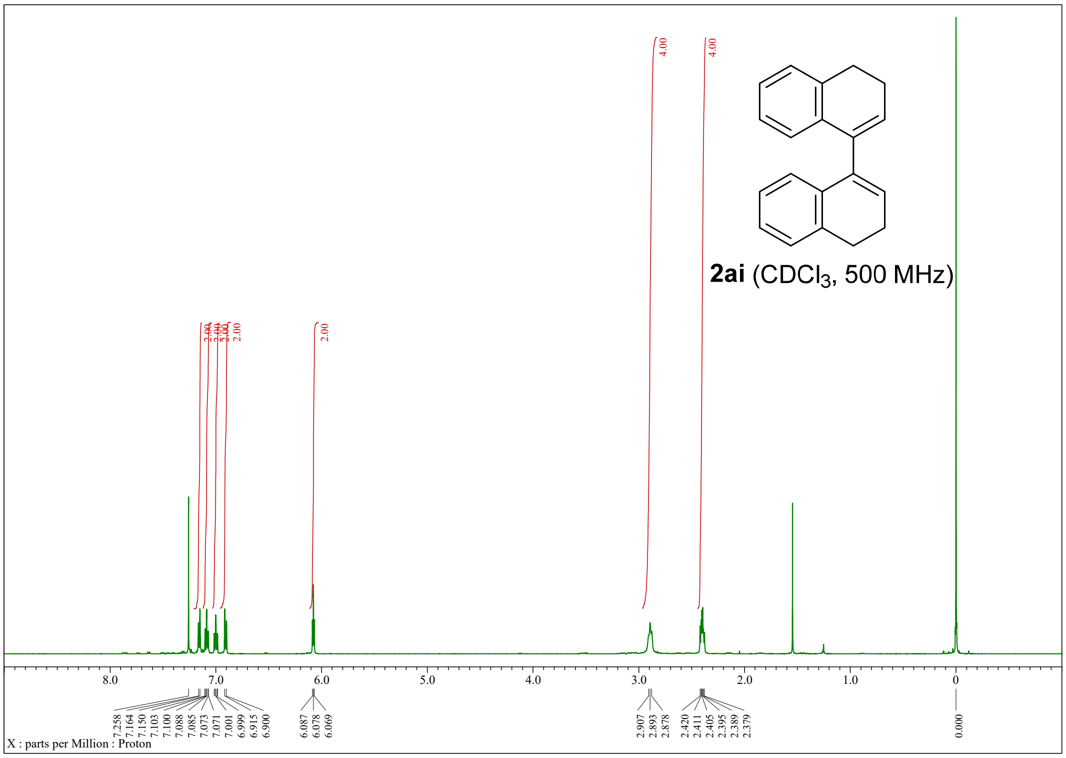
^{1}H NMR spectra of 5-(cyclohex-1-en-1-yl)benzo[*d*][1,3]dioxole **(2ag)**



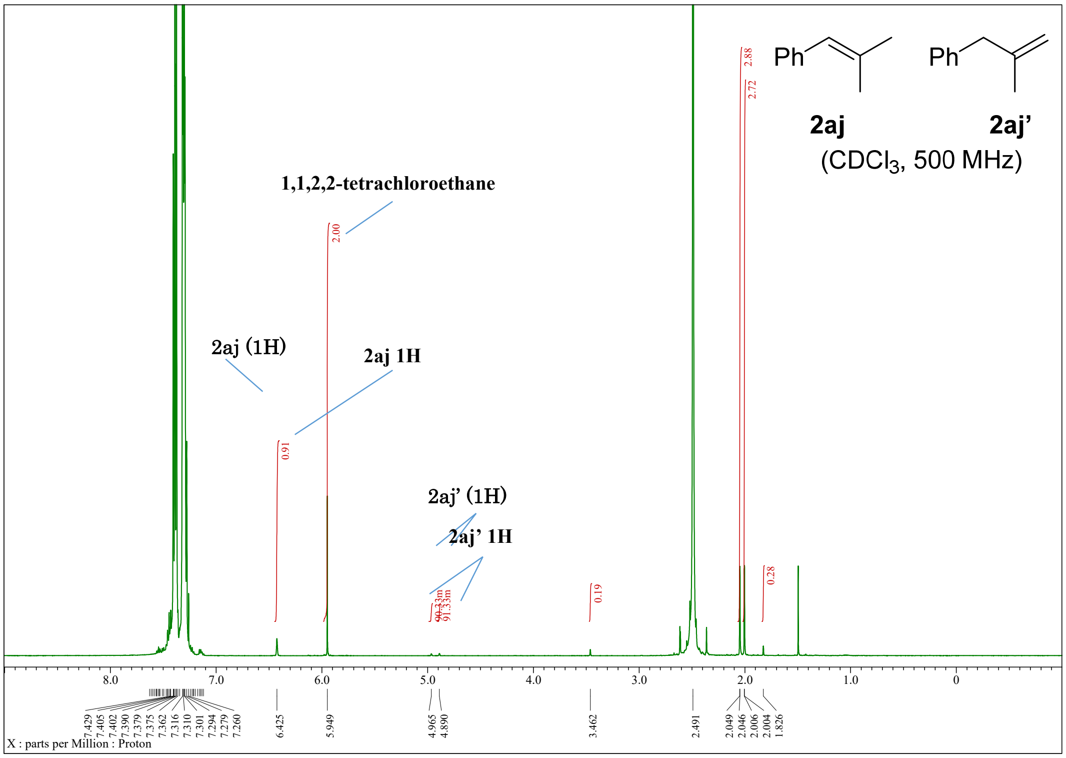
^{1}H NMR spectra of 8-phenyl-1,4-dioxaspiro[4.5]dec-7-ene **(2ah)**



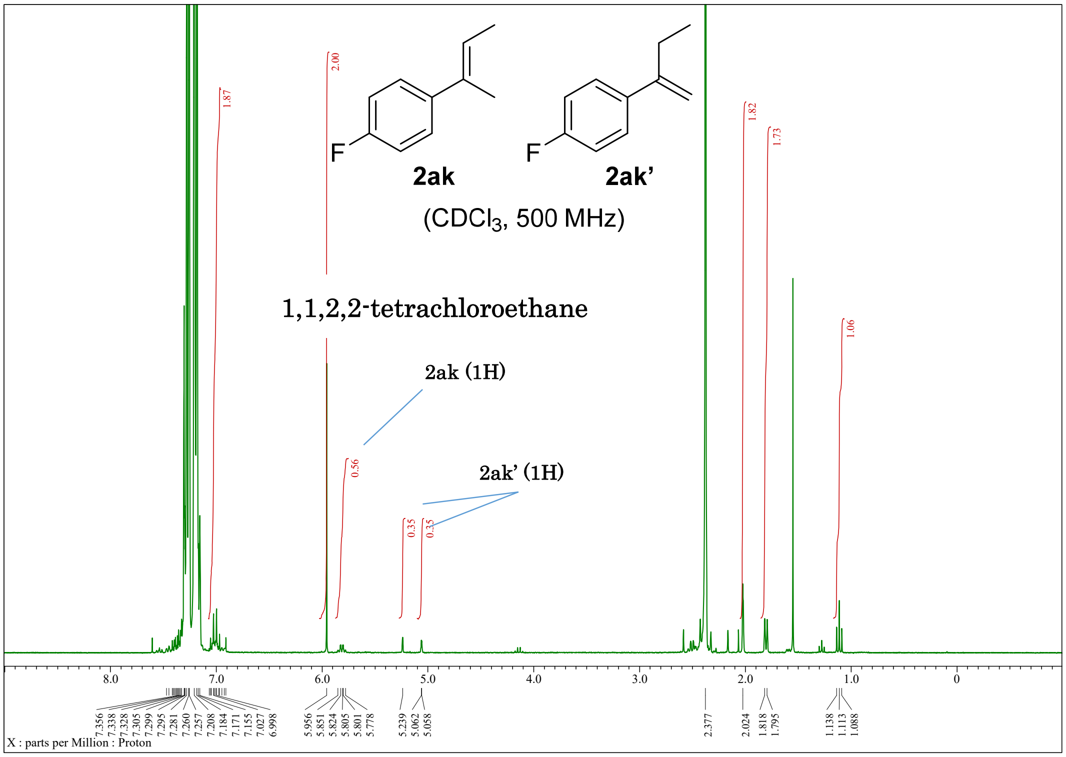
^{1}H NMR spectra of 3,3',4,4'-tetrahydro-1,1'-binaphthalene (**2ai**)



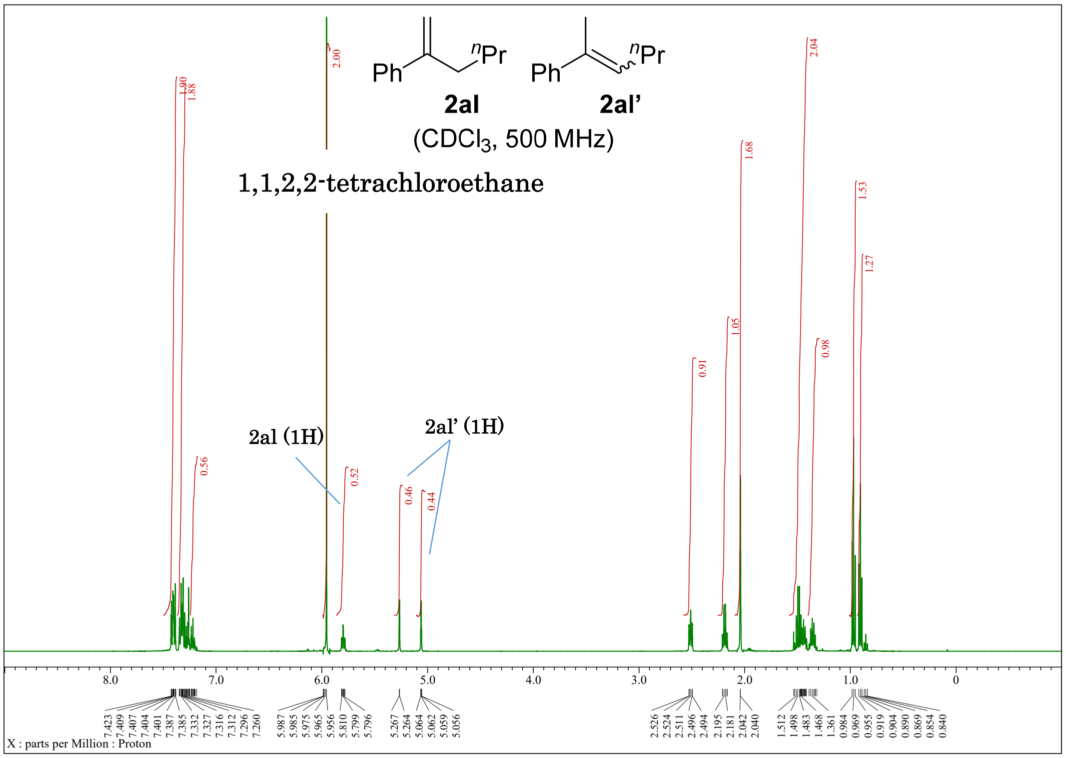
^{1}H NMR spectra of (2-methylprop-1-en-1-yl)benzene **(2aj)**, (2-methylallyl)benzene **(2aj')**



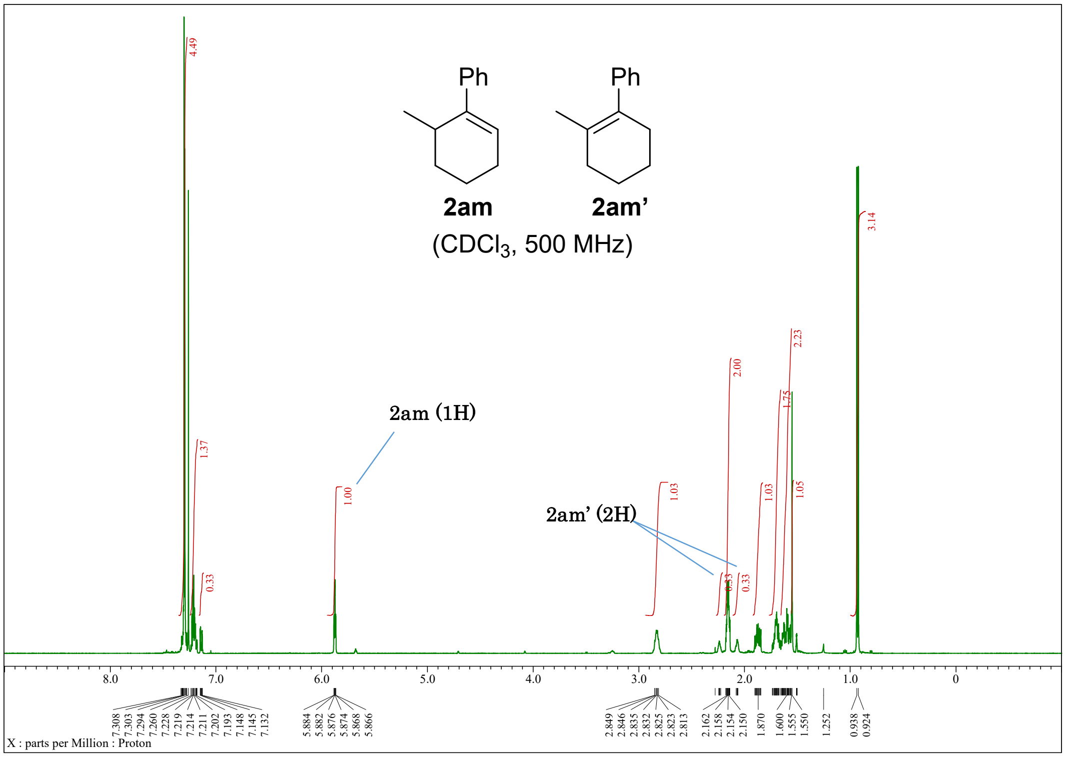
^{1}H NMR spectra of 1-(but-2-en-2-yl)-4-fluorobenzene (**2ak**), 1-(but-1-en-2-yl)-4-fluorobenzene (**2ak’**)



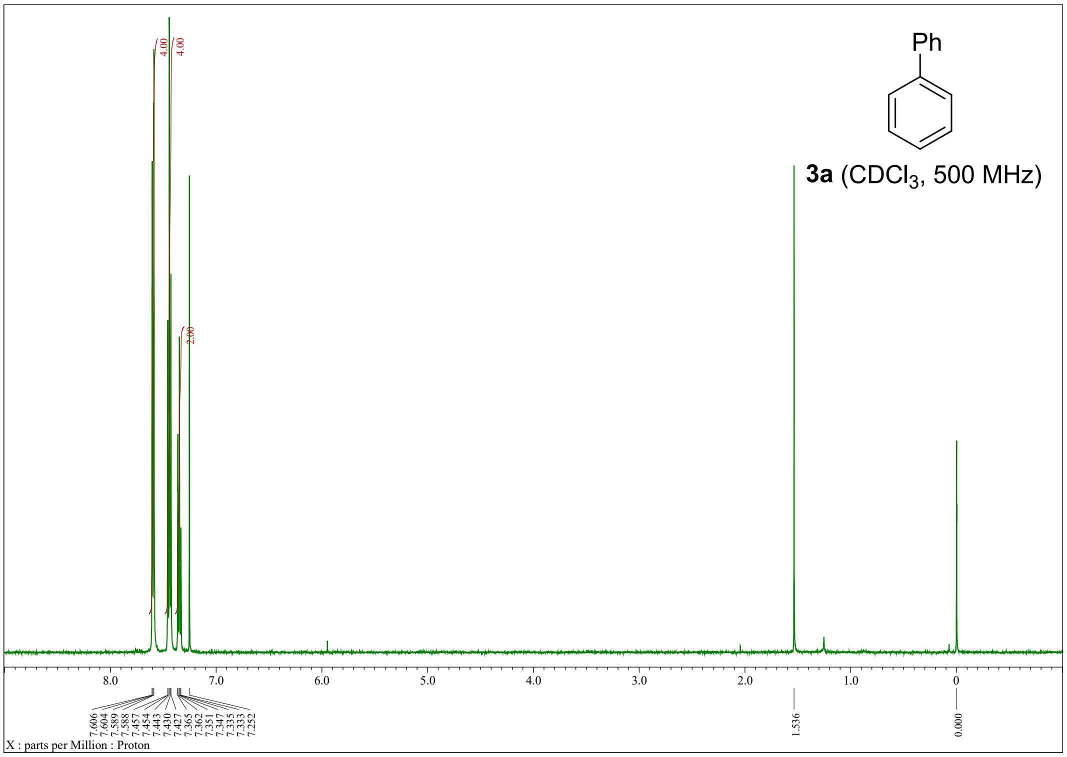
^{1}H NMR spectra of hex-1-en-2-ylbenzene **(2al),** hex-2-en-2-ylbenzene **(2al')**



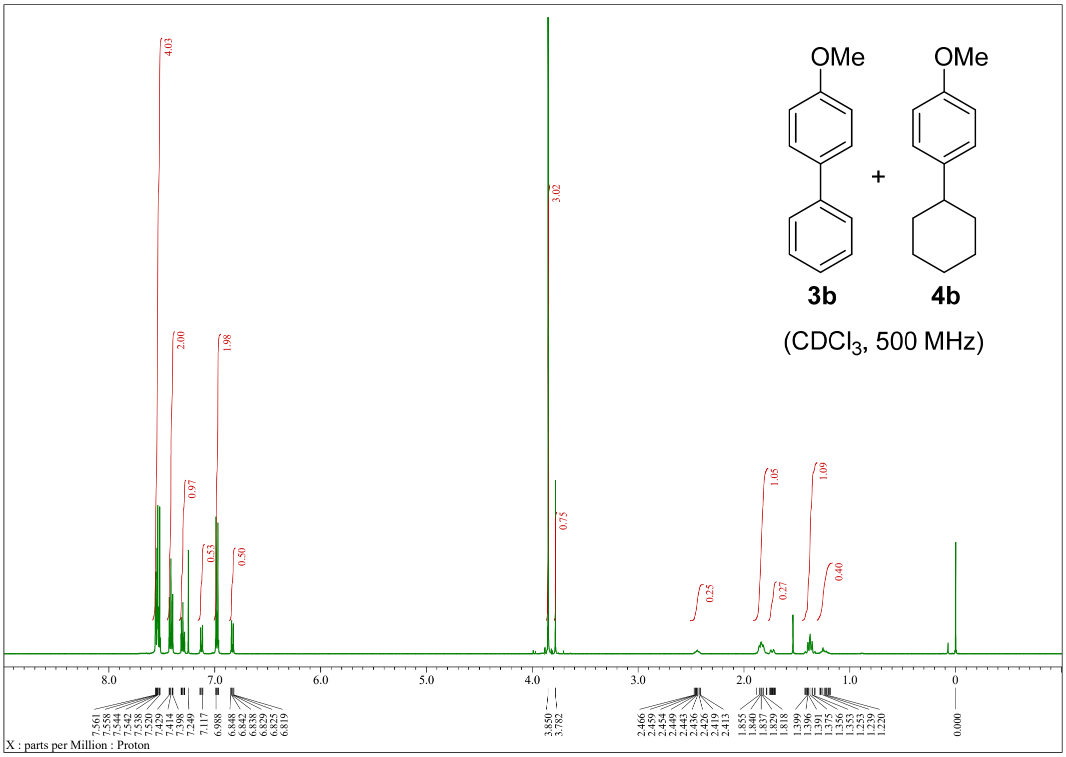
^{1}H NMR spectra of 2-methyl-2,3,4,5-tetrahydro-1,1'-biphenyl **(2am)** and 6-methyl-2,3,4,5-tetrahydro-1,1'-biphenyl **(2am')**



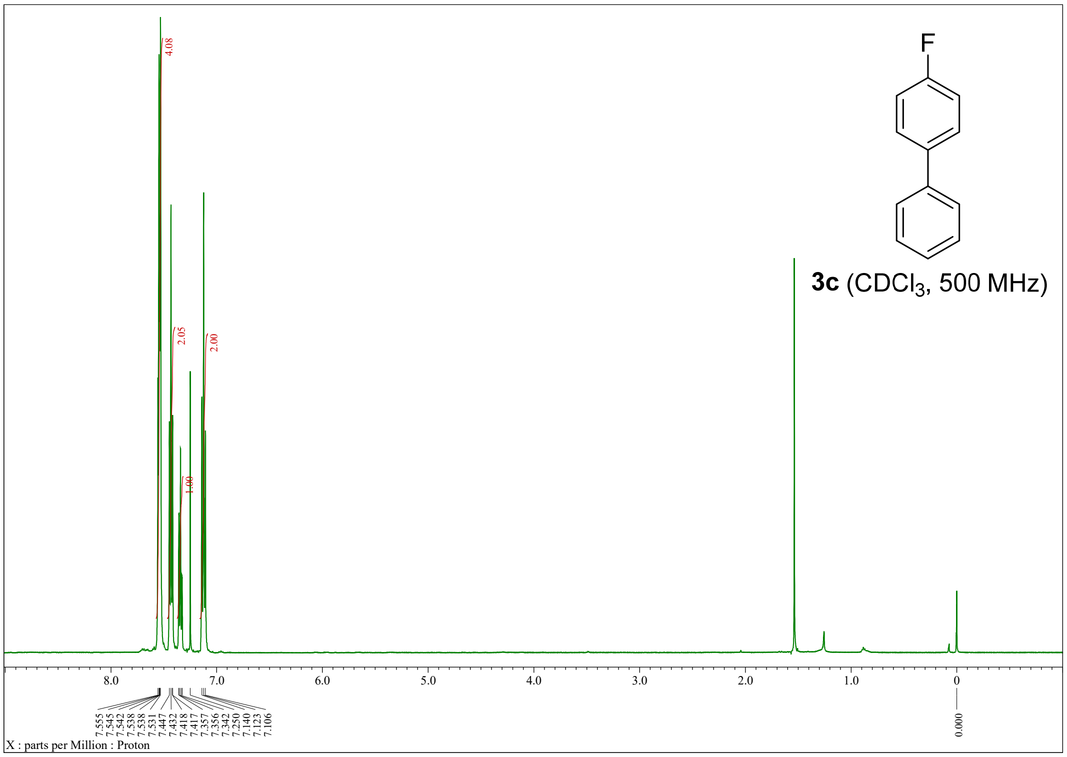
^{1}H NMR spectra of 1,1'-biphenyl **(3a)**



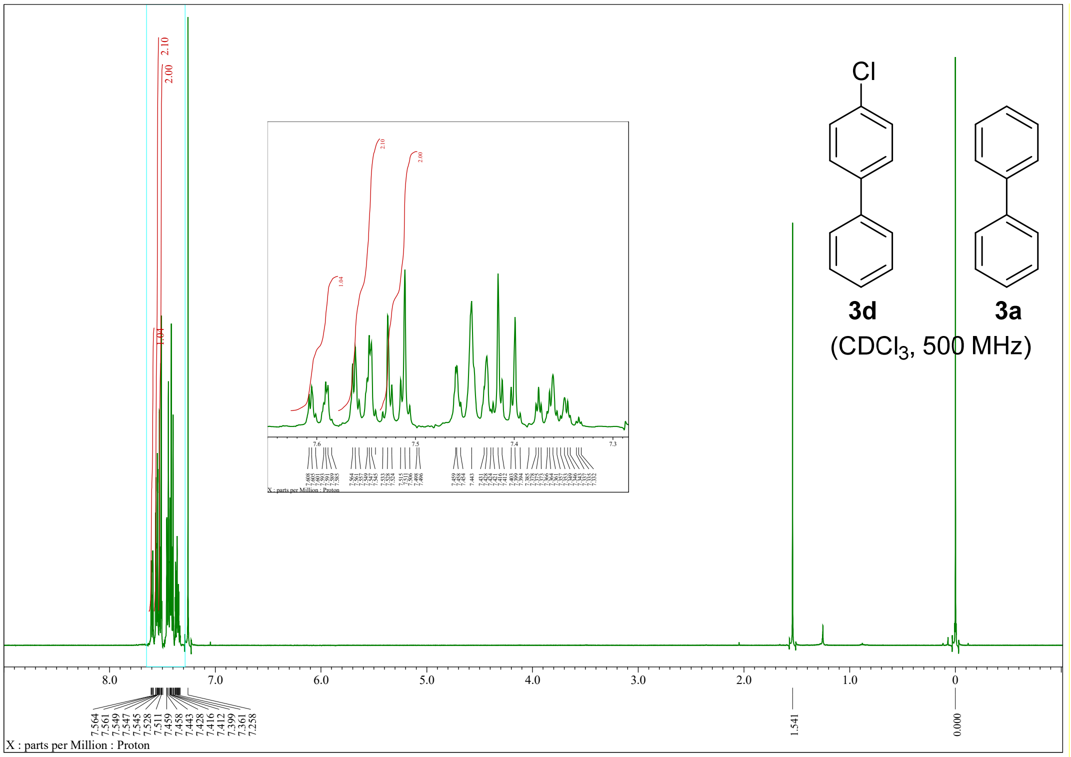
^{1}H NMR spectra of 4-methoxy-1,1'-biphenyl **(3b)** and 1-cyclohexyl-4-methoxybenzene **(4b)**



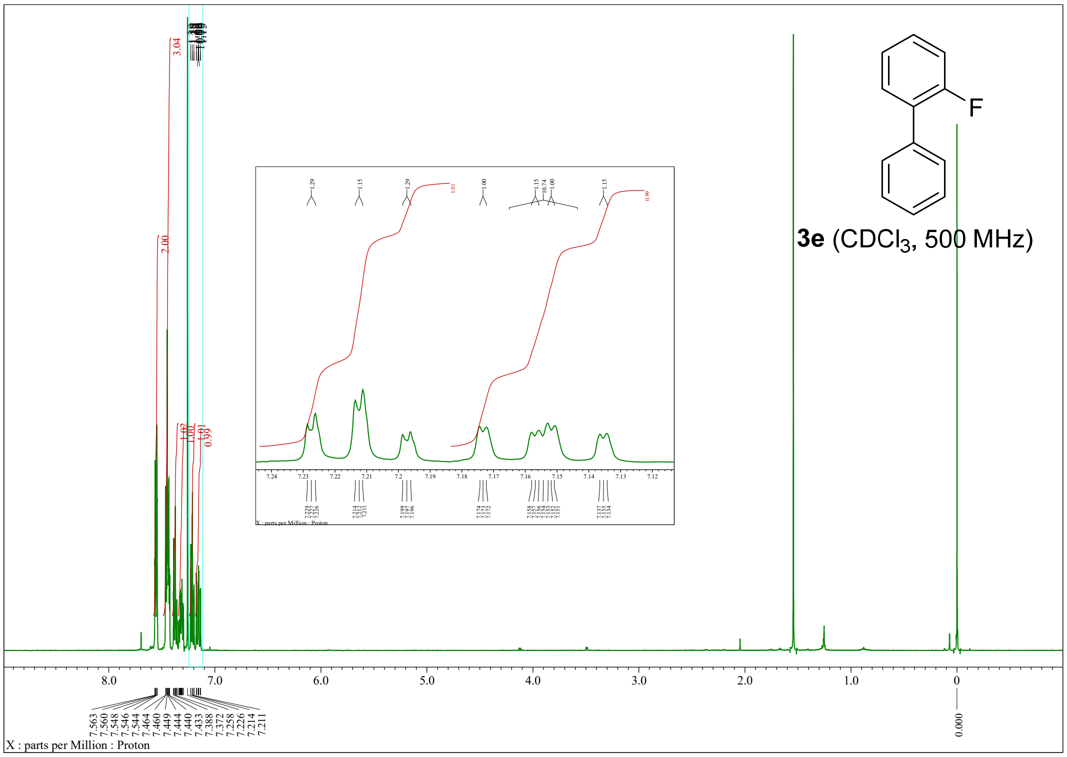
^{1}H NMR spectra of 4-fluoro-1,1'-biphenyl **(3c)**



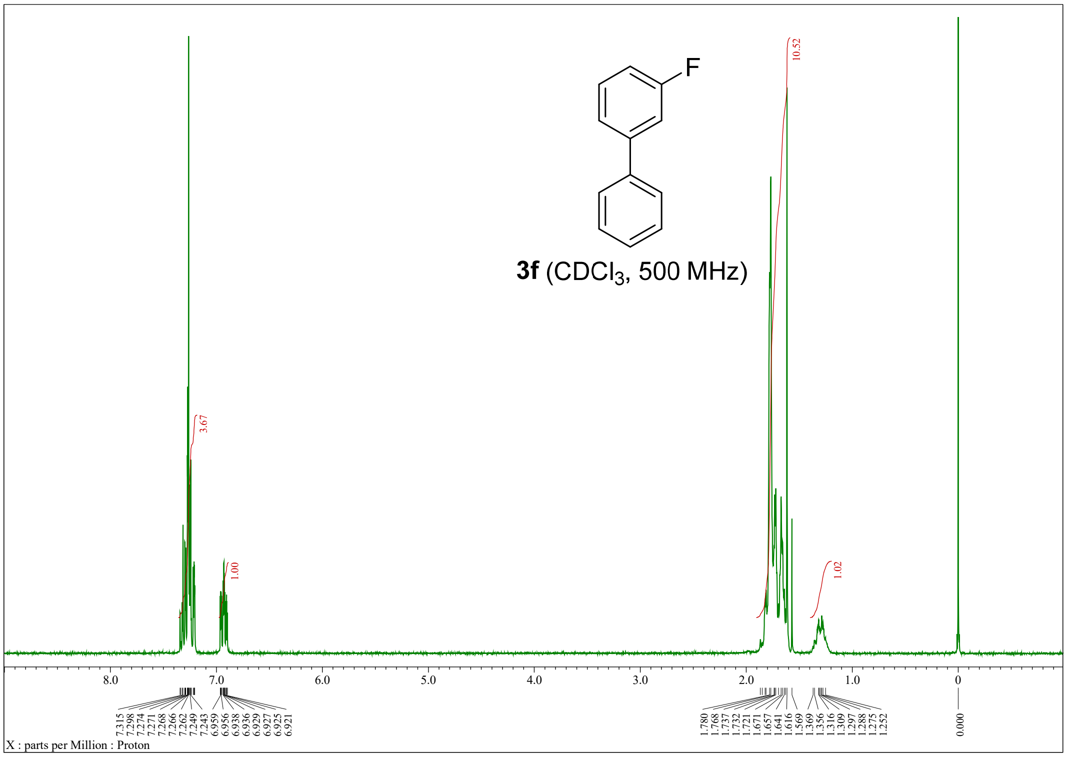
^{1}H NMR spectra of 4-chloro-1,1'-biphenyl **(3d)** and 1,1'-biphenyl **(3a)**



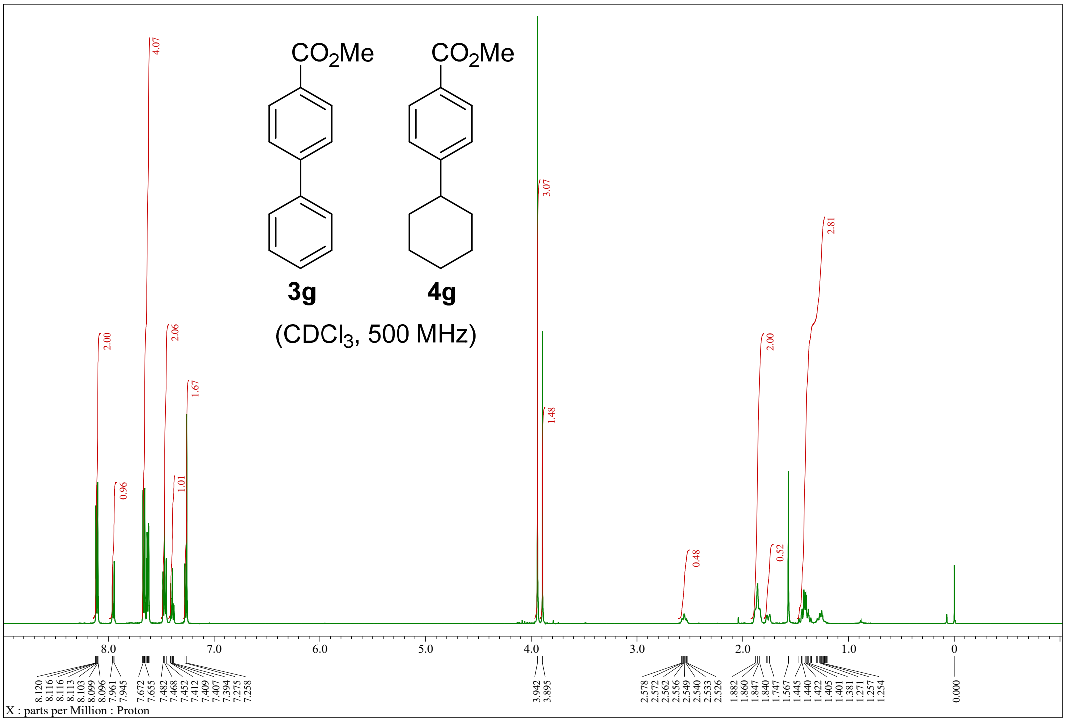
^{1}H NMR spectra of 2-fluoro-1,1'-biphenyl **(3e)**



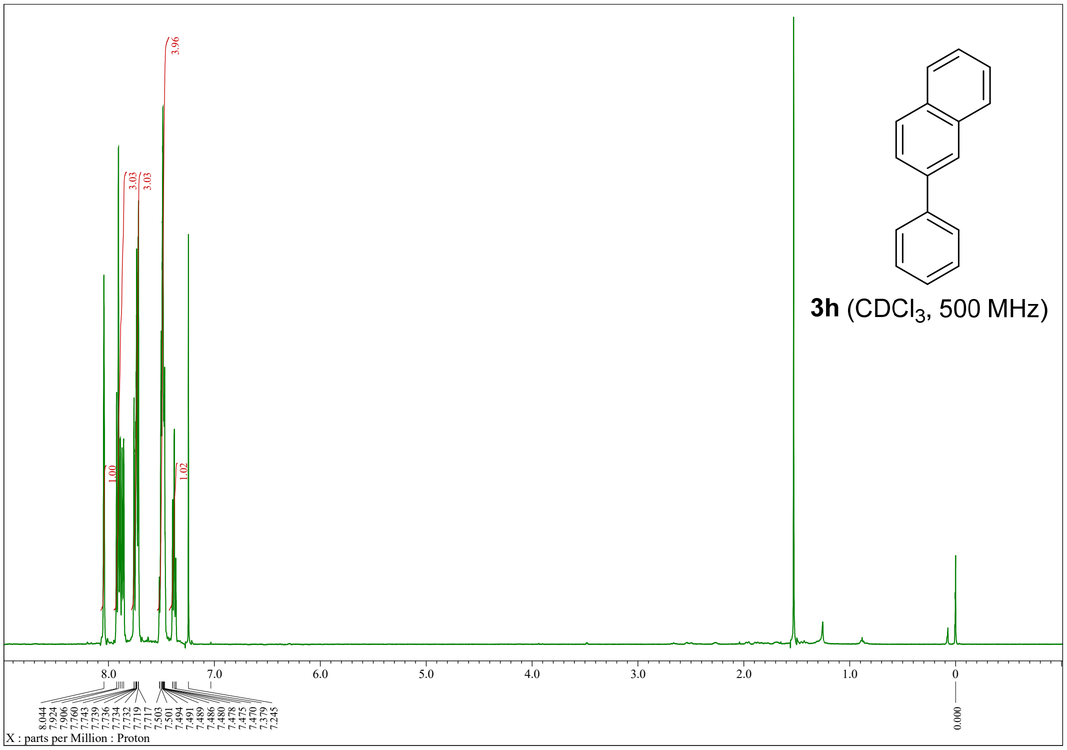
^{1}H NMR spectra of 3-fluoro-1,1'-biphenyl **(3f)**



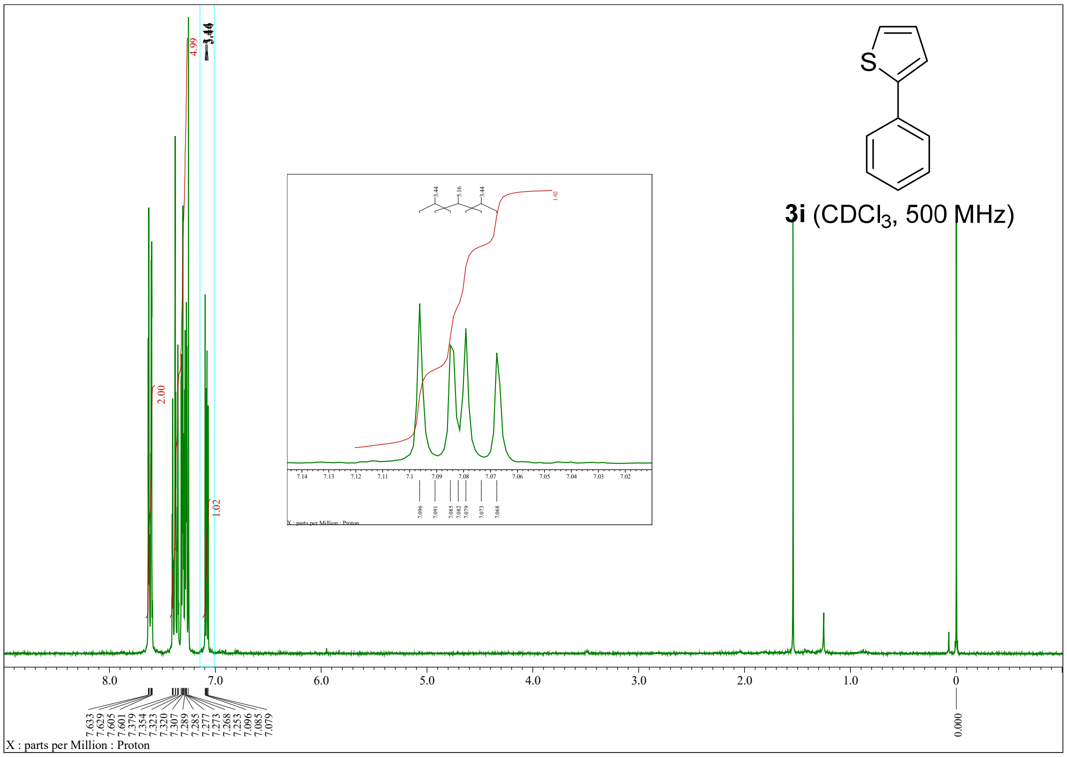
^{1}H NMR spectra of methyl [1,1'-biphenyl]-4-carboxylate **(3g)** and methyl 4-cyclohexylbenzoate **(4g)**



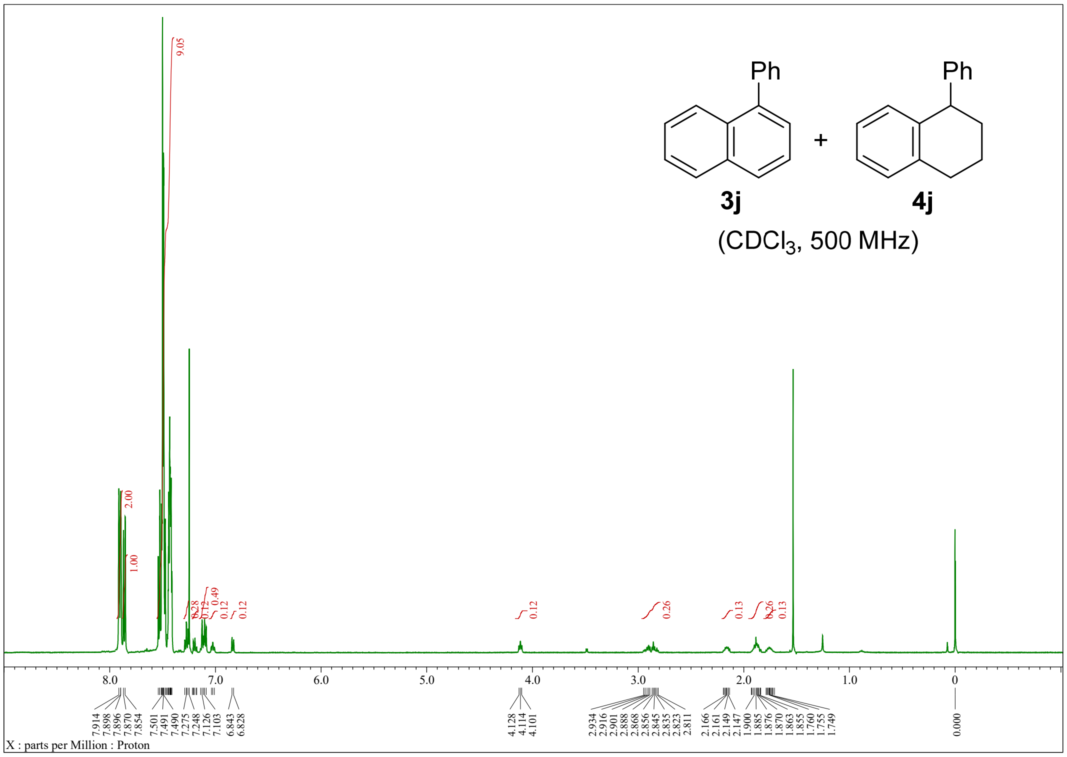
^{1}H NMR spectra of 2-phenylnaphthalene **(3h)**



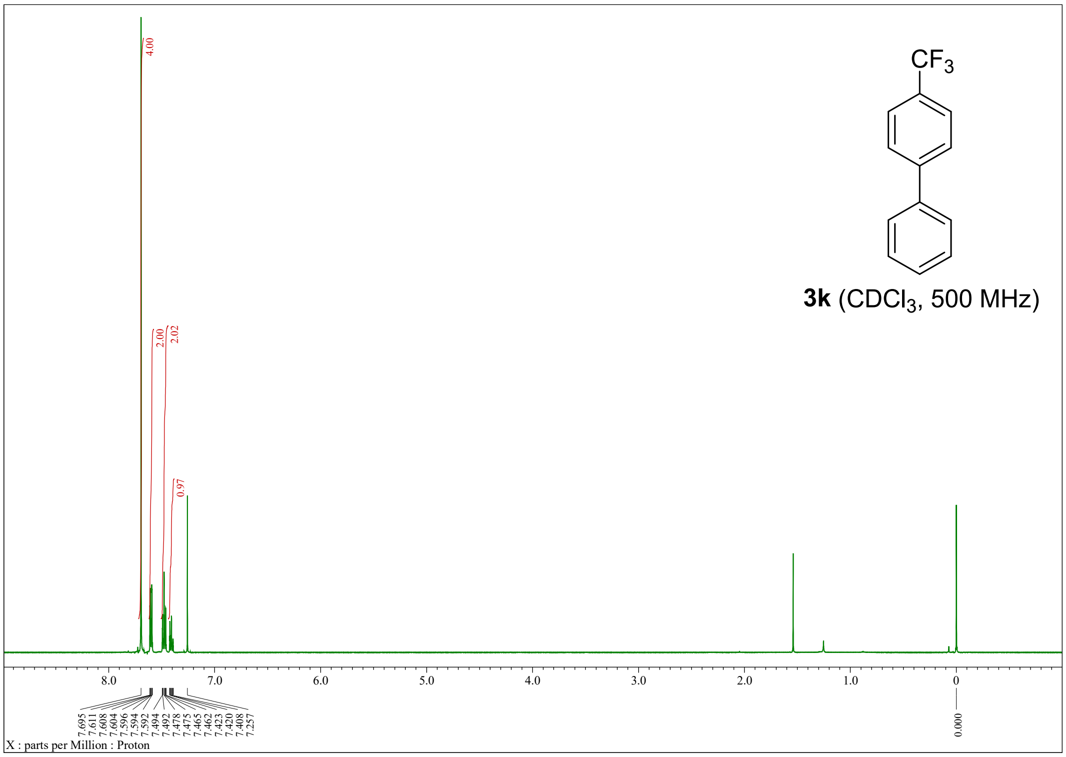
^{1}H NMR spectra of 2-phenylthiophene (**3i**)



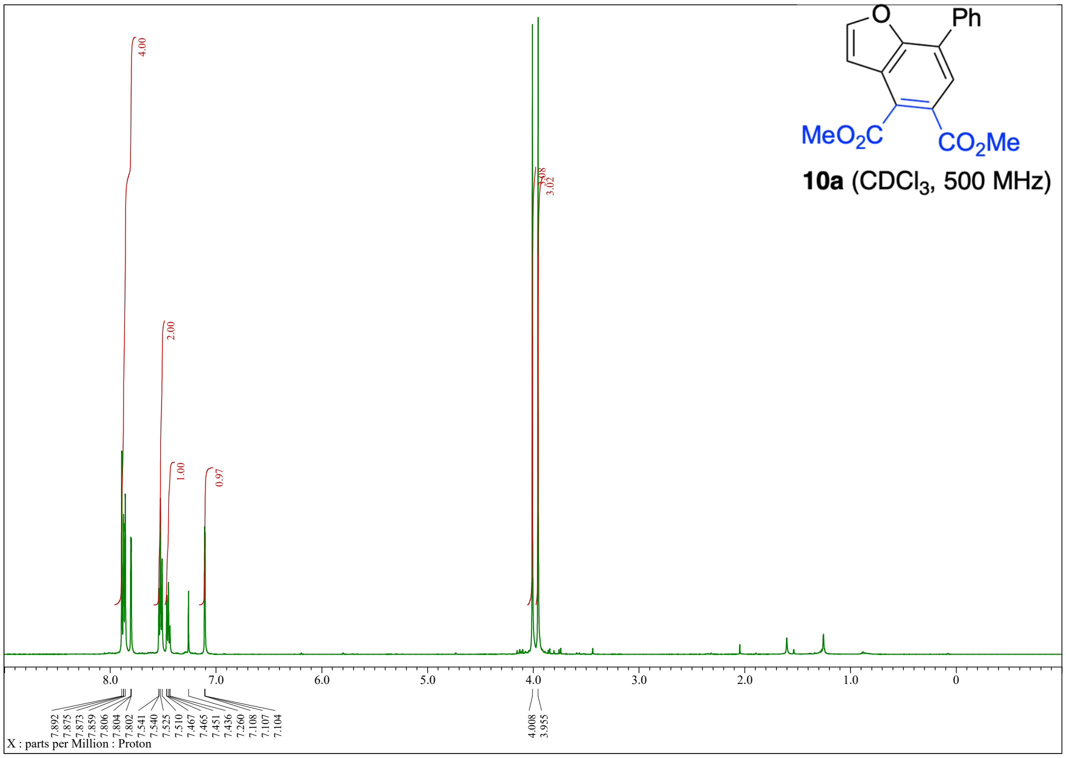
^{1}H NMR spectra of 1-phenylnaphthalene (**3j**) and **4j**



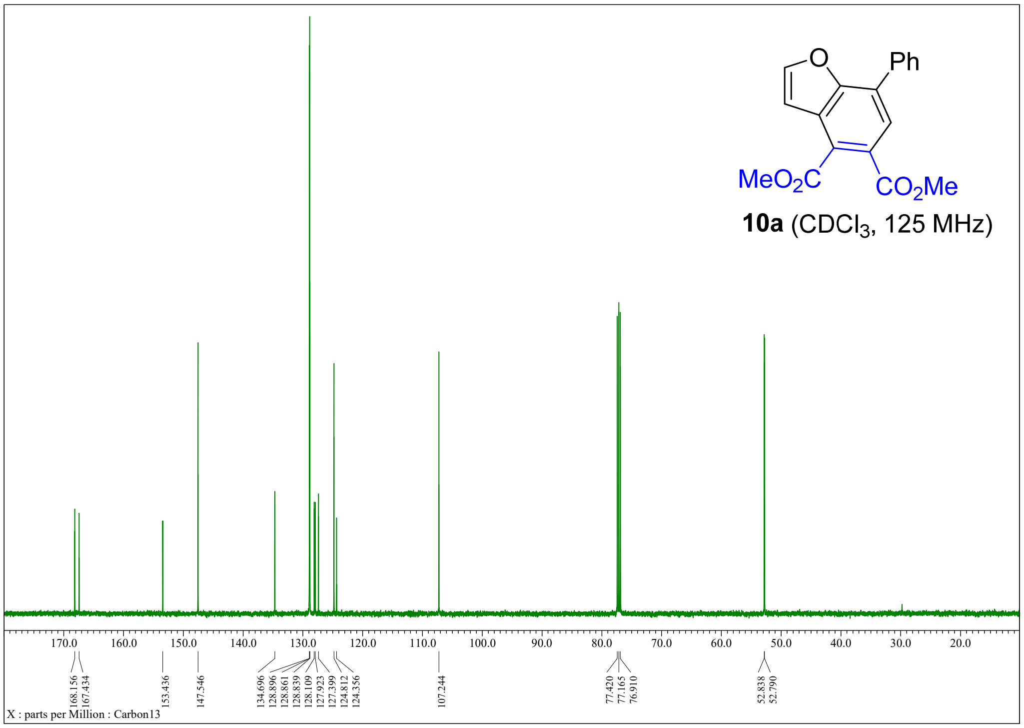
^{1}H NMR spectra of 4-(trifluoromethyl)-1,1'-biphenyl **(3k)**



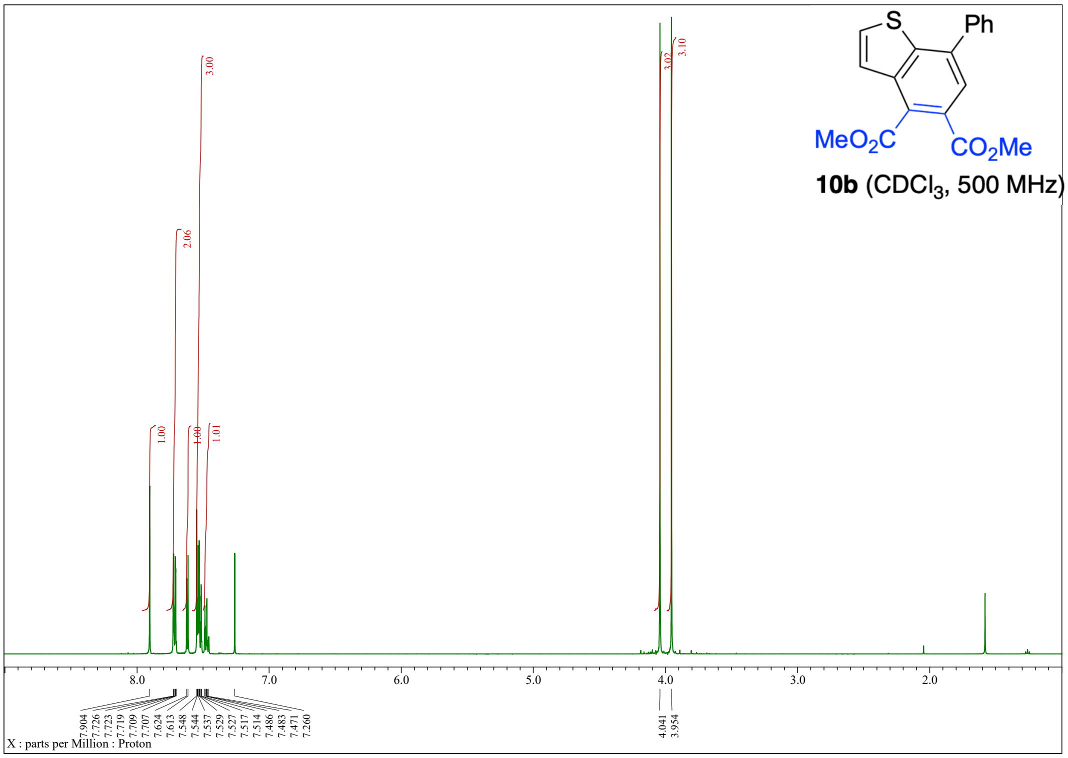
^{1}H NMR of dimethyl 7-phenylbenzofuran-4,5-dicarboxylate **(10a)**



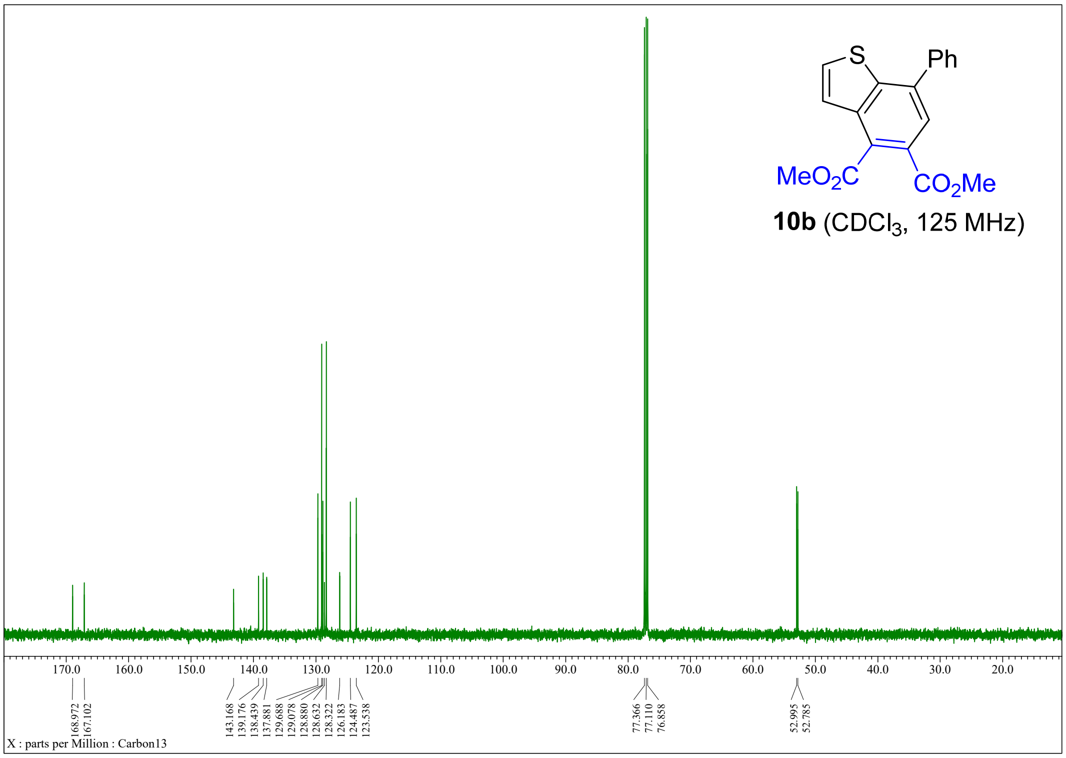
^{13}C NMR of dimethyl 7-phenylbenzofuran-4,5-dicarboxylate **(10a)**



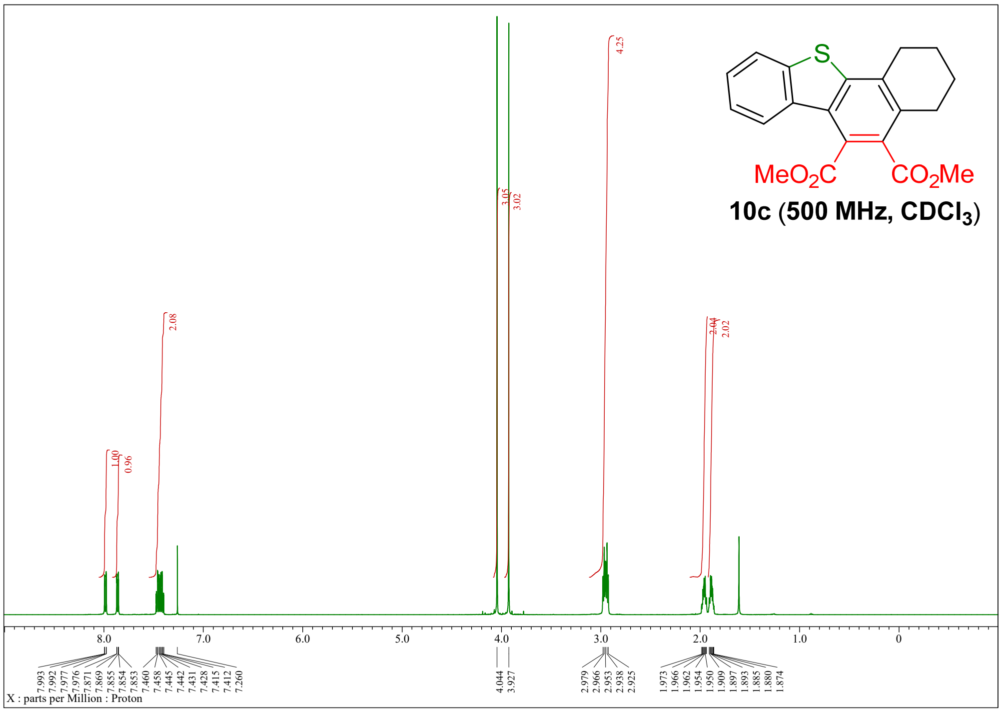
^{1}H NMR spectra of dimethyl 7-phenylbenzo[*b*]thiophene-4,5-dicarboxylate **(3x)**



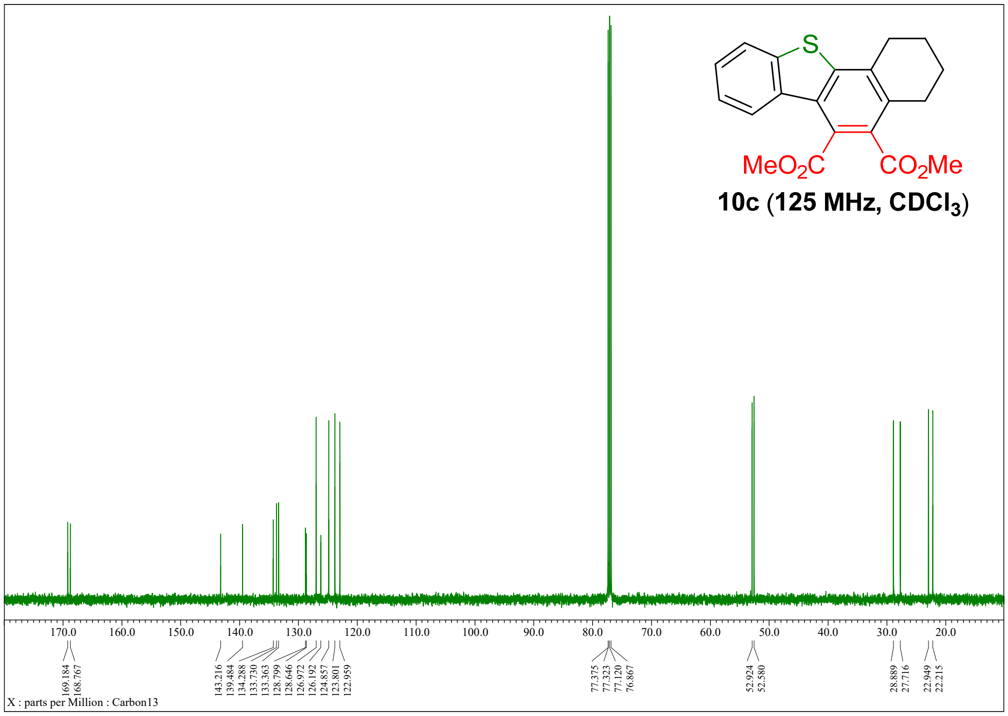
^{13}C NMR spectra of dimethyl 7-phenylbenzo[*b*]thiophene-4,5-dicarboxylate **(10b)**



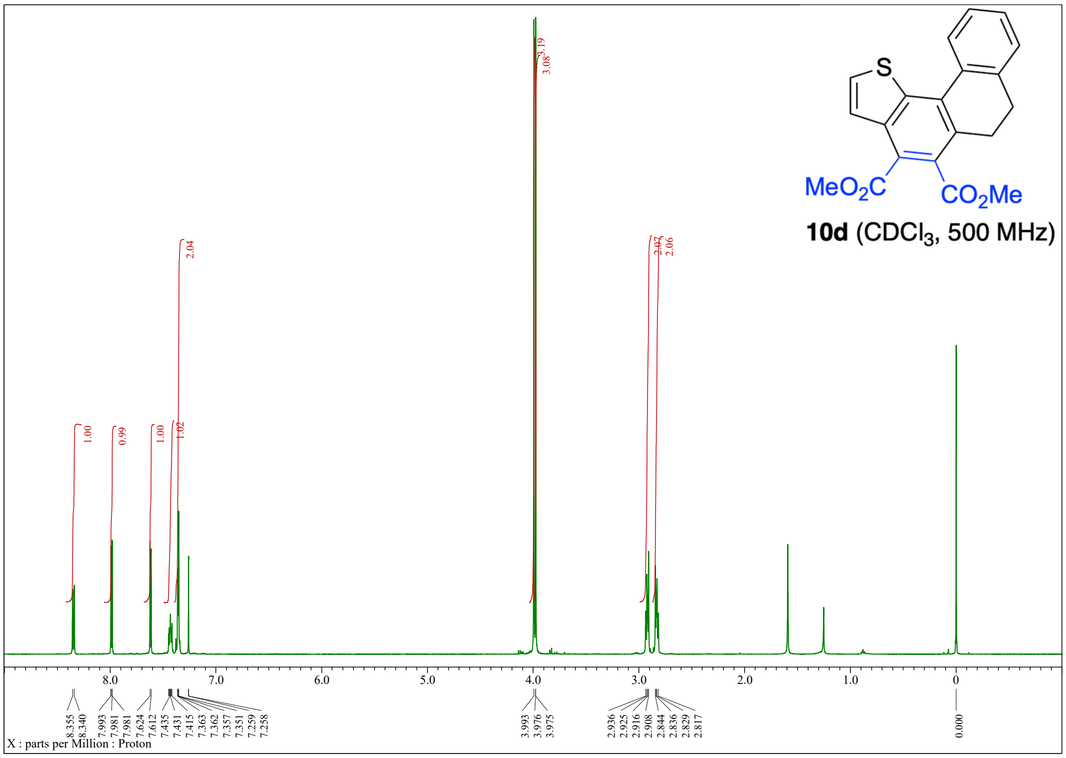
^{1}H NMR spectra of dimethyl 1,2,3,4-tetrahydrobenzo[*b*]naphtho[2,1-*d*]thiophene-5,6-dicarboxylate **(10c)**



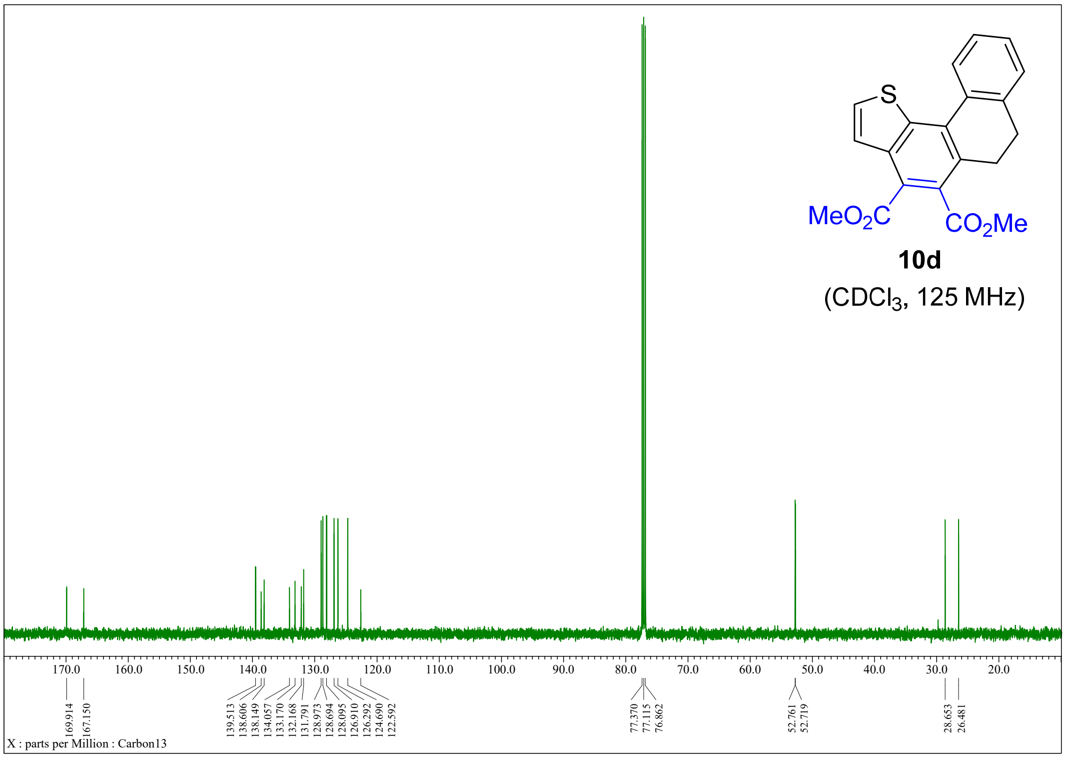
^{13}C NMR spectra of dimethyl 1,2,3,4-tetrahydrobenzo[*b*]naphtho[2,1-*d*]thiophene-5,6-dicarboxylate **(10c)**



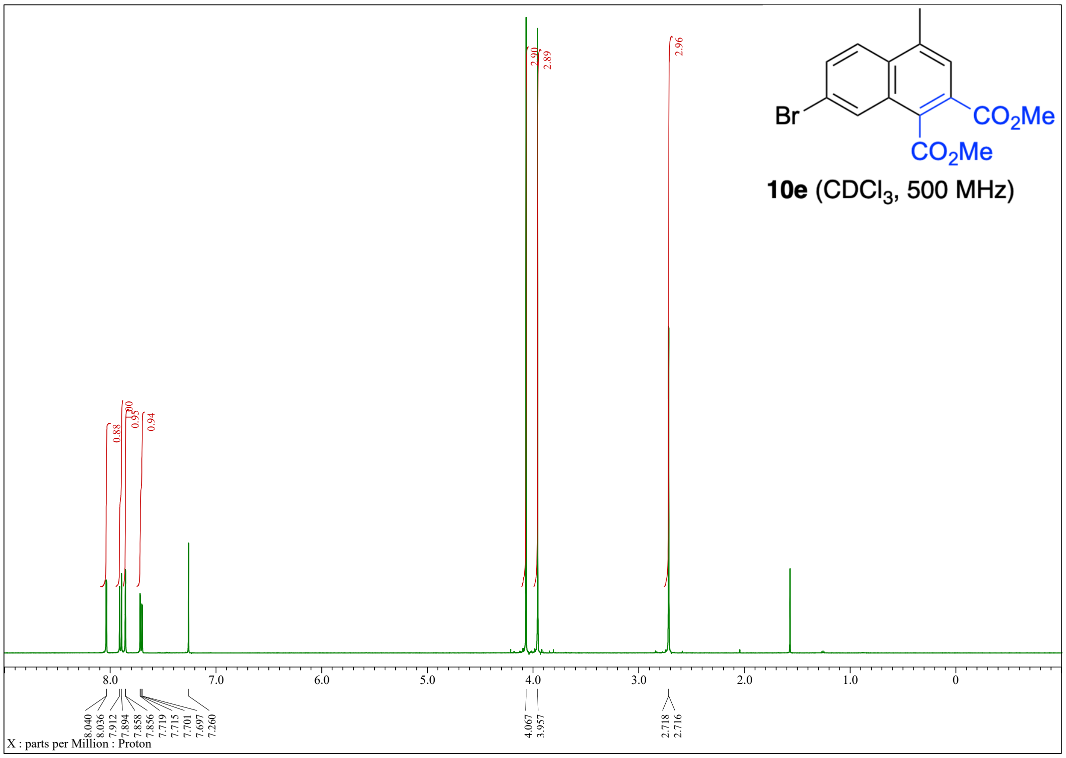
^{1}H NMR spectra of dimethyl 6,7-dihydrophenanthro[4,3-*b*]thiophene-4,5-dicarbox- ylate **(10d)**



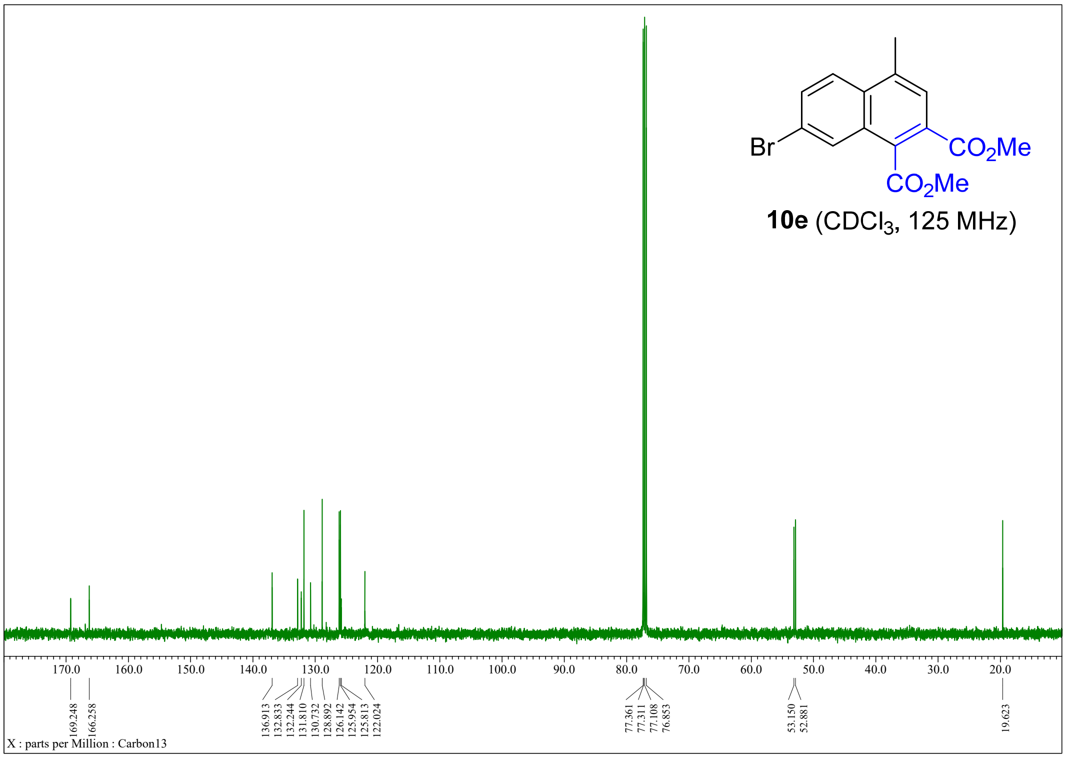
^{13}C NMR spectra of dimethyl 6,7-dihydrophenanthro[4,3-*b*]thiophene-4,5-dicarboxylate **(10d)**



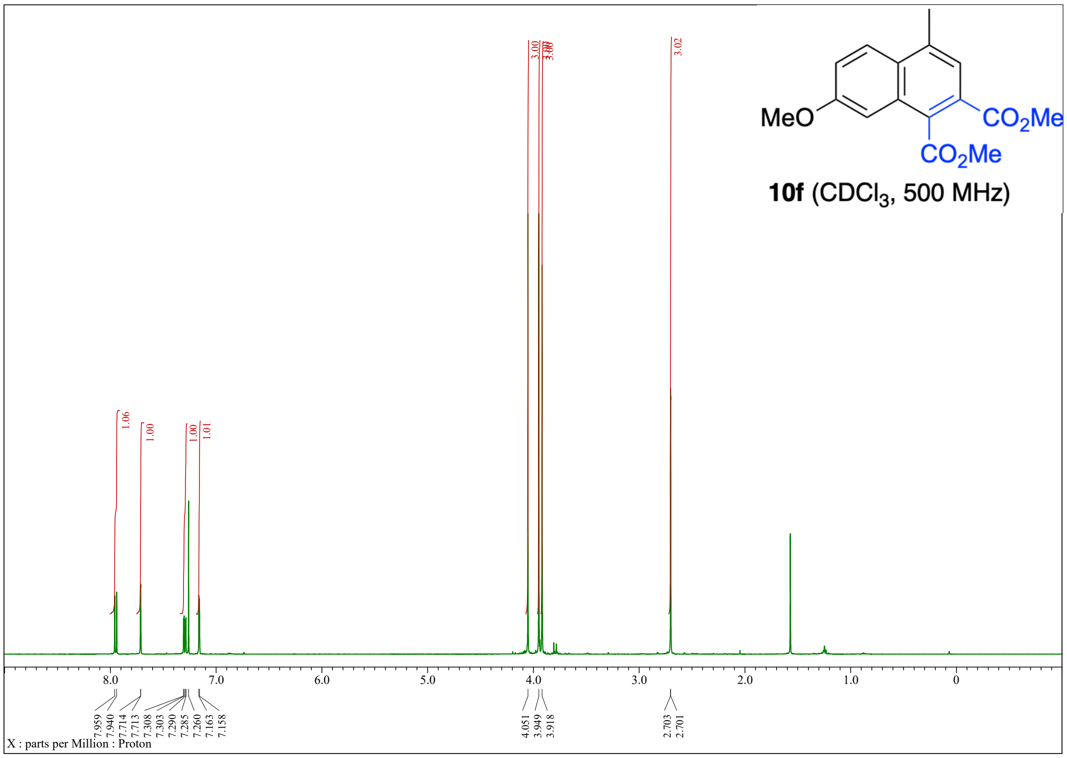
^{1}H NMR spectra of dimethyl 7-bromo-4-methylnaphthalene-1,2-dicarboxylate (**10e**)



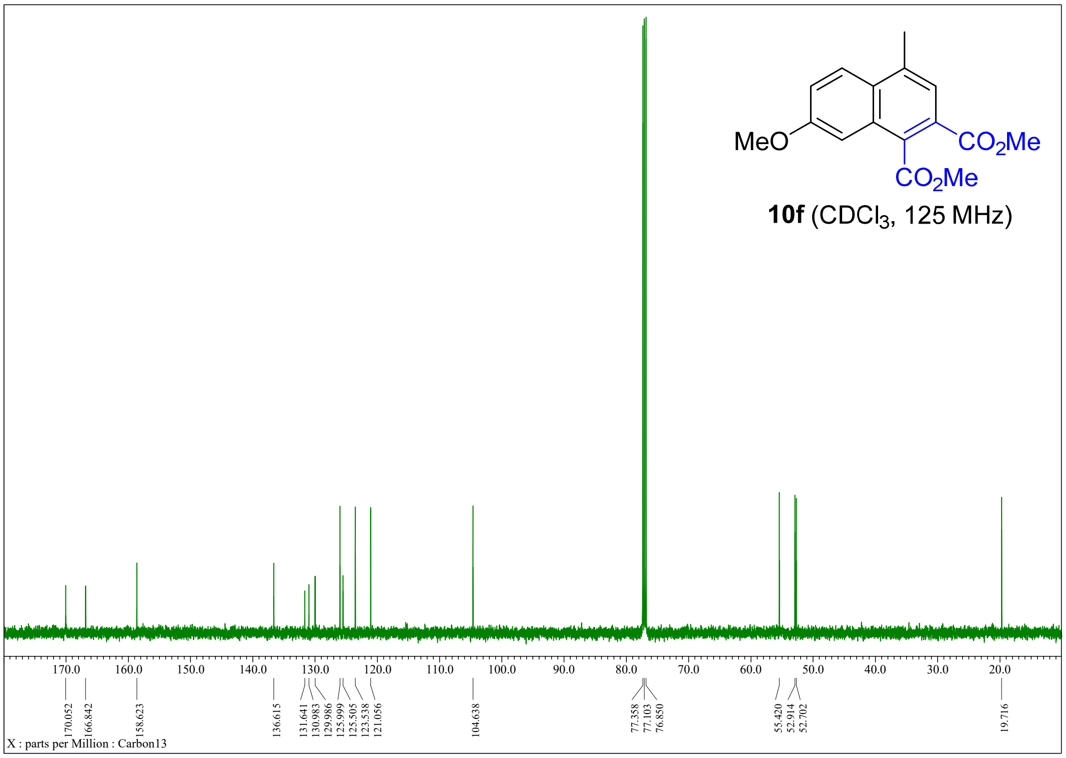
^{13}C NMR spectra of dimethyl 7-bromo-4-methylnaphthalene-1,2-dicarboxylate (**10e**)



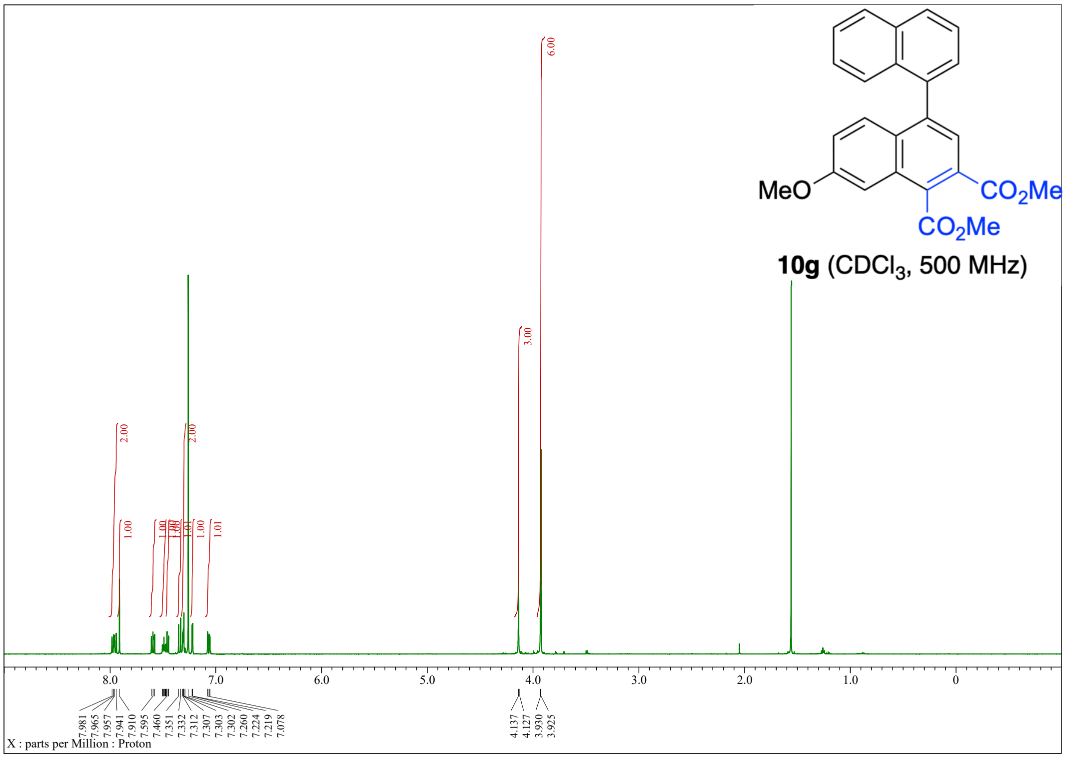
^{1}H NMR spectra of dimethyl 7-methoxy-4-methylnaphthalene-1,2-dicarboxylate (**10f**)



^{13}C NMR spectra of dimethyl 7-methoxy-4-methylnaphthalene-1,2-dicarboxylate (**10f**)



^{1}H NMR spectra of dimethyl 6-methoxy-[1,1'-binaphthalene]-3,4-dicarboxylate (**10g**)



^{13}C NMR spectra of dimethyl 6-methoxy-[1,1'-binaphthalene]-3,4-dicarboxylate (**10g**)