Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

for

Chromium-catalyzed olefination of arylaldehydes with haloforms assisted by 2,3,5,6-tetramethyl-*N*,*N*'-bis(trimethylsilyl)-1,4-dihydropyrazine

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1. General Information for Experimental Details

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under argon using standard Schlenk technique or an argon-filled glovebox. THF was dried and deoxygenated by using Grubbs column (Glass Counter Solvent Dispending System, Nikko Hansen & Co., Ltd.). $TiCl_3(thf)_3$, VCl_3, $CrCl_3(thf)_3$ (anhydrous, powder, 97% purity purchased from Sigma-Aldrich), $CrCl_3$ (anhydrous, powder, 99.99% trace metals basis), $CrCl_2$ (anhydrous, powder, 95% purchased from Sigma-Aldrich or anhydrous, powder, 99.99% trace metals basis purchased from Sigma-Aldrich), $Cr(acac)_3$ (anhydrous, powder, 97% purity purchased from Sigma-Aldrich), $MoCl_3(thf)_3$, WCl_4, $NiCl_2$, $CoCl_2$, Mn powder, Zn powder, $MnCl_2$, $ZnCl_2$, and supporting ligands used in Tables 1 and S2 were purchased and used as received. All carbonyl compounds **2a**-**aw** and halomethanes were purchased and, if necessary, purified by distillation over CaH_2. *N*,*N'*-Bis(trimethylsilyl)dihydropyrazine derivatives (**1a**-**1c**) and *N*,*N'*-bis(trimethylsilyl)-4,4'-bipyridinylidene (**1d**) were prepared according to the literature procedure.[1] ^1H and $^{13}C\{^1H\}$ NMR chemical shifts were reported in ppm and referenced to a residual proton signal of $CDCl_3$ (^1H: δ = 7.26), tetramethylsilane (^1H: δ = 0.00), or $CDCl_3$ itself ($^{13}C\{^1H\}$: δ = 77.16 ppm for $CDCl_3$). $^{19}F\{^1H\}$ NMR chemical shifts were reported in ppm relative to the external reference α,α,α-trifluorotoluene at δ –63.9. All melting points were recorded on a BUCHI Melting Point M-565. High resolution mass spectra were recorded on a JEOL JMS-700. Flash column chromatography was performed by using silica gel 60 (0.040–0.0663 nm, 230–400 mesh ASTM). GC-MS analysis were performed with Shimadzu GCMS-QP505A spectrometer with Shimadzu GC-17A GC equipped with J&W Scientific DB-1 column.

2. General Procedure for Chromium-catalyzed Olefination of Arylaldehydes with $CHBr_3$ Assisted by 2,3,5,6-Tetramethyl-*N*,*N*'-bis(trimethylsilyl)-1,4-dihydropyrazine (1a)

For screening reaction conditions (Table 1, except for entry 1)

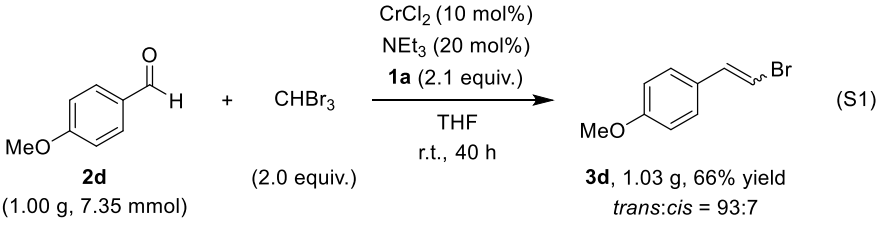
In a glovebox, $CrCl_2$ (0.010 mmol) and ligand (0.010 or 0.020 mmol) were mixed in THF (2.0 mL), and the resulting mixture was stirred for 10 min. Reductant (0.21 or 0.60 mmol), 2-naphthylaldehyde (**2a**, 0.10 mmol), and bromoform (0.20 mmol) were added to the reaction mixture at 30 °C. After 17 h, the reaction mixture was quenched by adding 1 M HCl aq. (2 mL), followed by the addition of 1,3,5-trimethoxybenzene as an internal standard. Organic compounds were extracted with Et_2O (2-3 mL), and then the solvent was removed under reduced pressure. Product yields and ratios of *trans*/*cis* isomers for crude products were determined by their ^{1}H NMR measurements.

For screening reaction conditions (Table 1, entry 1) and scope of arylaldehydes (Tables 2 and 3)

In a glovebox, $CrCl_2$ (0.040 mmol) and NEt_3 (0.080 mmol) were mixed in THF (8.0 mL), and the resulting mixture was stirred for 10 min. 2,3,5,6-Tetramethyl-*N*,*N*'-bis(trimethylsilyl)-1,4-dihydropyrazine (**1a**, 0.84 mmol), arylaldehyde **2** (0.40 mmol), and bromoform (0.80 mmol) were added to the reaction mixture at 30 °C. After 17 h, the reaction mixture was quenched by adding 1 M HCl aq. (8 mL). The aqueous phase was extracted with EtOAc (5 mL x 3). The combined organic extracts were dried over Na_2SO_4, filtered, and the solvent was evaporated. The residue was purified by silica gel chromatography to give olefinated products **3**. Ratios of *trans*/*cis* isomers were determined by their ^{1}H NMR measurements.

Gram-scale synthesis (eq. S1)

In a glovebox, $CrCl_2$ (90.3 mg, 0.735 mmol) and NEt_3 (0.204 mL, 1.47 mmol) were mixed in THF (150 mL), and the resulting mixture was stirred for 10 min. 2,3,5,6-Tetramethyl-*N*,*N'*-bis(trimethylsilyl)-1,4-dihydropyrazine (**1a**, 4.36 g, 15.4 mmol), *p*-methoxybenzaldehyde (**2d**, 1.00g, 7.35 mmol), and bromoform (1.29 mL, 14.7 mmol) were added to the reaction mixture at room temperature. After 40 h, the reaction mixture was quenched by adding 1 M HCl aq. (20 mL) and water (100 mL). The aqueous phase was extracted with EtOAc (80 mL x 3). The combined organic extracts were dried over Na_2SO_4, filtered, and the solvent was evaporated. The residue was purified by silica gel chromatography to give olefinated products **3d** (1.03 g, 66% yield). Ratios of *trans*/*cis* isomers were determined by their ^{1}H NMR measurements.



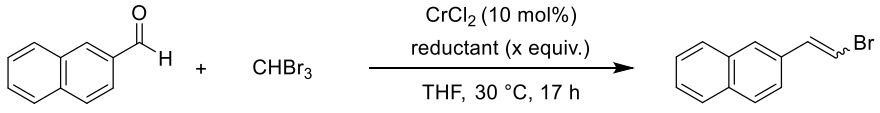
2d (1.00 g, 7.35 mmol)

3d, 1.03 g, 66% yield
trans:*cis* = 93:7

(S1)

3. Optimization for Chromium-catalyzed Olefination of 2-Naphthylaldehyde (2a) with $CHBr_3$

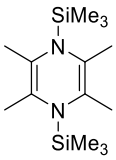
Table S1. Screening of Reductants



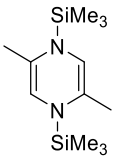
2a (2.0 equiv.) **3a**

entry	reductant (x equiv.)	yield of **3a**[a]	*trans*:*cis*[a]
1	**1a** (2.1)	55%	95:5
2	**1b** (2.1)	n.d.	N/A
3	**1c** (2.1)	n.d.	N/A
4	**1d** (2.1)	n.d.	N/A
5	Zn/TMSBr (6.0)	trace	N/A
6	Mn/TMSBr (6.0)	21%	86:14
7	Mg	n.d.	N/A

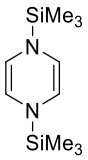
[a] Determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. n.d. = not detected.



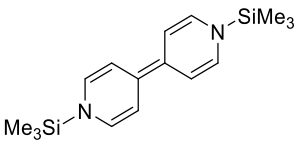
1a



1b

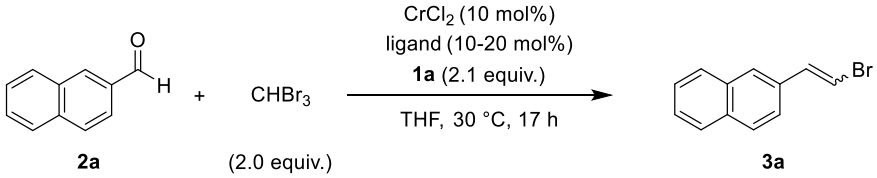


1c



1d

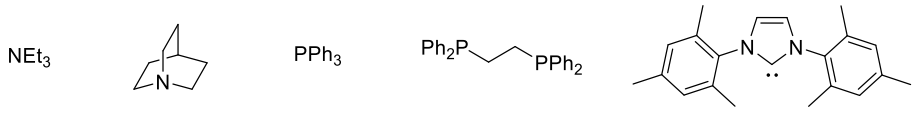
Table S2. Screening of Ligands



2a **3a**

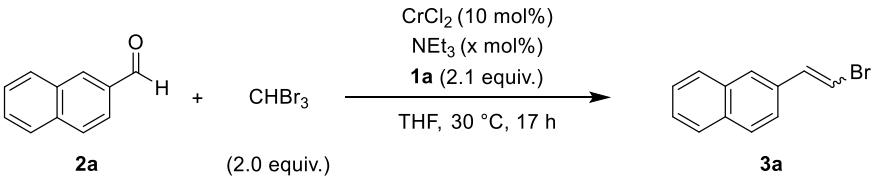
entry	ligand (x mol%)	yield of **3a**[a]	*trans*:*cis*[a]
1	**L1** (20)	74%	93:7
2	**L2** (20)	41%	95:5
3	**L3** (20)	44%	93:7
4	**L4** (10)	41%	90:10
5	**L5** (20)	41%	93:7

[a] Determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.



L1 **L2** **L3** **L4** **L5**

Table S3. Effects for the Amounts of Triethylamine

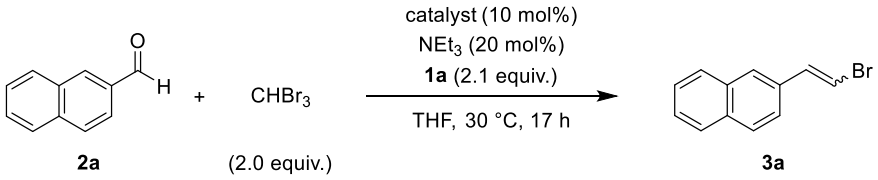


2a **3a**

entry	NEt_3 (x mol%)	yield of **3a**[a]	*trans*:*cis*[a]
1	10	58%	93:7
2	20	74%	93:7
3	30	65%	92:8
4	40	55%	93:7

[a] Determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

Table S4. Screening of Transition Metal Catalysts



2a **3a**

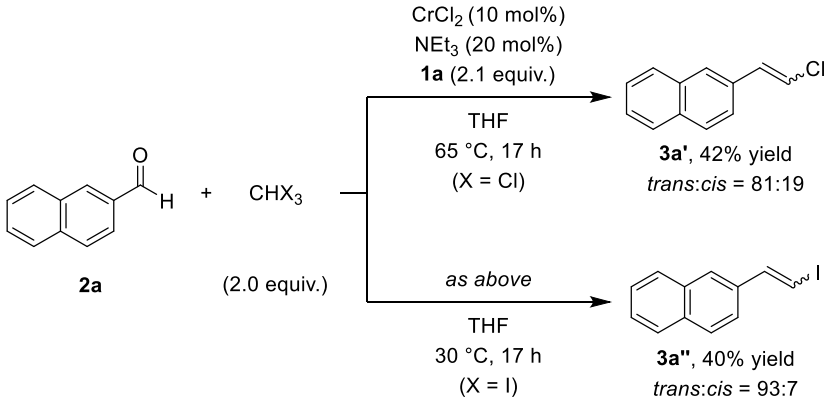
entry	catalyst	yield of **3a**[a]	*trans*:*cis*[a]
1	$TiCl_3(thf)_3$	n.d.	N/A
2	VCl_3	n.d.	N/A
3[b]	$CrCl_2$	74%	93:7
4[c]	$CrCl_2$	70%	91:9
5	$CrCl_3$	62%	92:8
6	$CrCl_3(thf)_3$	68%	91:9
7	$Cr(acac)_3$	n.d.	N/A
8	$MoCl_3(thf)_3$	n.d.	N/A
9	WCl_4	n.d.	N/A
10	$CoCl_2$	n.d.	N/A
11	$NiCl_2$	n.d.	N/A

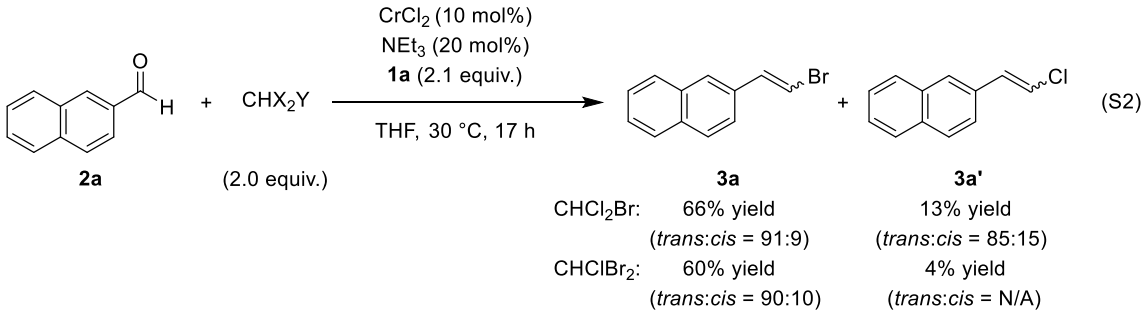
[a] Determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. n.d. = not detected. [b] $CrCl_2$ (anhydrous, powder, 95%) was purchased from Sigma-Aldrich and used as the catalyst. [c] $CrCl_2$ (anhydrous, powder, 99.99% trace metals basis) was purchased from Sigma-Aldrich and used as the catalyst.

3. Scope and Limitations of Carbonyl Compounds and Halomethanes

Chromium-catalyzed olefination with trihalomethanes (Scheme S1 and eq. S2)

Scheme 1 Scope of Haloforms in Cr-catalyzed Olefination with **1a**



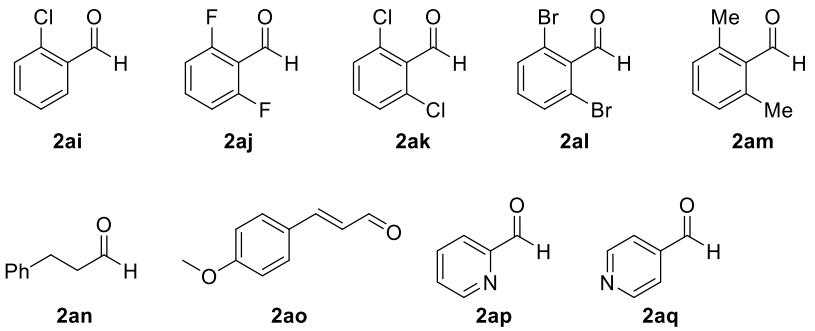


(S2)

Limitations of aldehydes and halomethanes

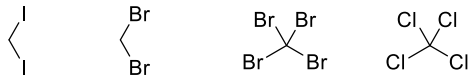
No olefination reaction or quite low yields of corresponding haloalkenes were observed when the following substrates were used for chromium-catalyzed olefination under the optimized reaction conditions.

For aldehydes



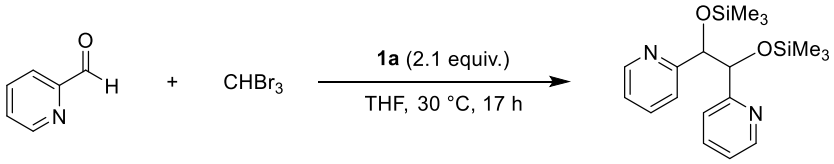
2ai **2aj** **2ak** **2al** **2am** **2an** **2ao** **2ap** **2aq**

For halomethanes



Pinacol coupling reaction of 2-formylpyridine by **1a**

Pinacol coupling reaction of 2-formylpyridine (**2ap**) proceeded quantitatively to afford the corresponding trimethylsilyl-protected pinacol **4ap** in the absence of $CrCl_2$ and NEt_3 (eq. S3). In this reaction, chromium catalyst was not necessary for the reaction progress.

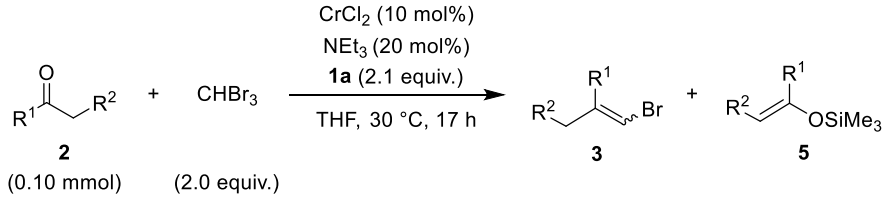


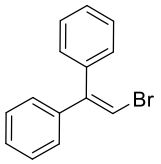
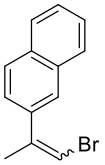
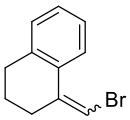
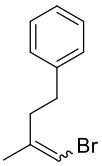
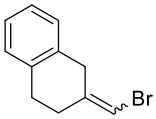
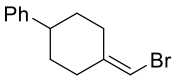
2ap (0.10 mmol) (2.0 equiv.) **4ap**, quant. dl:meso-mixture (S3)

Scope and limitations of ketones

We next investigated the substrate scope of ketones with bromoform, and the results were summarized in Table S5. No olefination product was obtained for diaryl ketone **2ar**, aryl alkyl ketones **2as** and **2at**, and dialkyl ketone **2au**. In the case of cyclic dialkyl ketones **2av** and **2aw**, the corresponding silyl enol ethers **5av** and **5aw** were obtained as major products. When 4-phenylcyclohexanone (**2aw**) was used, the corresponding bromoalkene **3aw** was obtained in 23% NMR yield.

Table S5. Scope and Limitations of Ketones

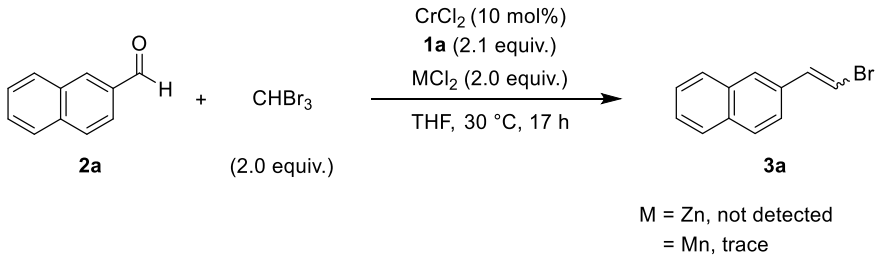


 **3ar**, not detected	 **3as,** not detected	 **3at**, not detected
 **3au**, not detected	 **3av**[a], not detected	 **3aw**[b], 23% yield

^{1}H NMR yields. [a] **5av** in 45% yield. [b] **5aw** in 29% yield.

5. Control Experiments

Scheme S2. Effects of Additional Metal Salts



Olefination of **2x** under reaction conditions reported by Takai *et al.* (eq. S4)[2]

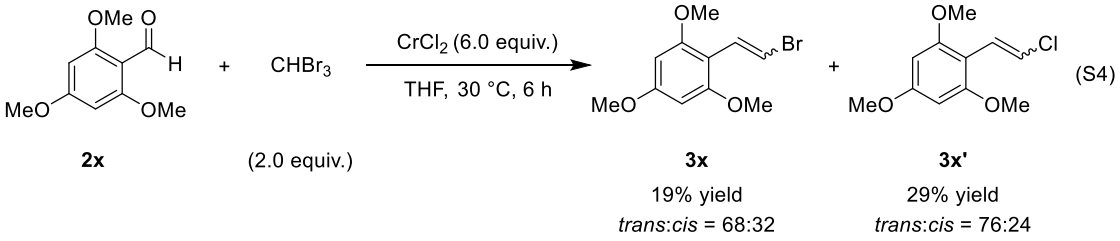
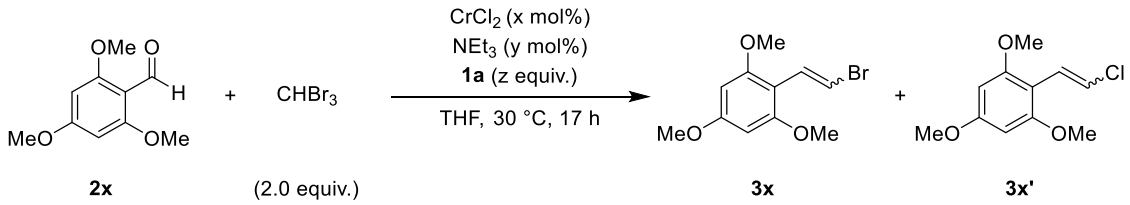


Table S6. Effects of Catalyst Loadings on the Reactivity and *trans*/*cis* Selectivity

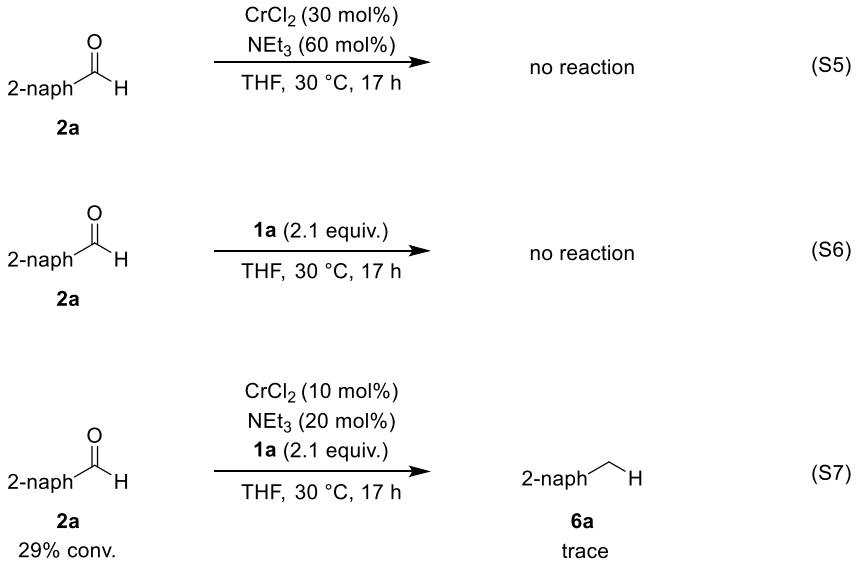


entry	$CrCl_2$ (x mol%)	NEt_3 (y mol%)	**1a** (z equiv.)	yield of **3x**[a]	*trans*:*cis* in **3x**[a]	yield of **3x'**[a]
1	10	20	2.1	78%	18:82	trace
2	20	40	2.1	69%	20:80	2%
3	50	100	1.9	51%	27:73	6%
4	100	200	1.7	33%	39:61	11%

[a]Determined by ^1H NMR analysis using triphenylmethane as an internal standard.

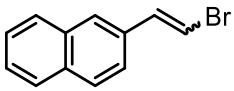
Blank experiments

Following reactions were conducted to evaluate the reactivity of each components in this Cr-catalyzed olefination reaction. Deoxygenative reduction of aldehyde **2a** to **6a** was observed under the optimized reaction conditions in the absence of $CHBr_3$, whereas the substrate **2a** was not consumed without **1a** or $CrCl_2$ (eqs. S5-7). When $MnCl_2$ or $ZnCl_2$ were used with **1a** under the reaction conditions instead of $CrCl_2$, we found over 90% conversion of **2a**, in which reduction and deoxygenation of the carbonyl moiety were observed to afford complicated mixture including **6a** and trimethylsilyl 2-naphthylmethyl ether in the GC-MS analysis.



6. Characterization of Olefinated Products, Trimethylsilyl-protected Pinacol, and Silyl Enol Ethers

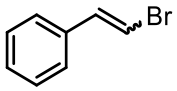
2-(2-Bromovinyl)naphthalene (**3a**)



Isolated as white solid (65.2 mg, 70% yield, *trans*:*cis* = 93:7).

^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3a**: δ 7.81−7.77 (m, 3H), 7.68 (s, 1H), 7.48−7.46 (m, 3H), 7.26 (d, *J* = 14.0 Hz, 1H), 6.89 (d, *J* = 14.0 Hz, 1H) ppm. For *cis*-**3a** (well-resolved signals): δ 8.15 (s, 1H), 6.51 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3a**: δ 137.5, 133.6, 133.5, 133.3, 128.7, 128.2, 127.9, 126.8, 126.5, 126.4, 123.1, 107.0 ppm. Both spectral data are superimposed to the literature values for *trans*-**3a** and *cis*-**3a**.[3,4]

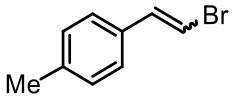
(2-Bromovinyl)benzene (**3b**)



Isolated as colorless oil (50.9 mg, 70% yield, *trans*:*cis* = 93:7).

^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3b**: δ 7.35−7.28 (m, 5H), 7.11 (d, *J* = 14.0 Hz, 1H), 6.76 (d, *J* = 14.0 Hz, 1H) ppm. For *cis*-**3b** (well-resolved signals): δ 7.69−7.67 (m, 2H), 7.40−7.35 (m, 2H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.43 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3b**: δ 137.4, 136.1, 128.9, 128.4, 126.3, 106.7 ppm. Both spectral data are superimposed to the literature values for *trans*-**3b** and *cis*-**3b**.[5]

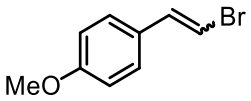
1-(2-Bromovinyl)-4-methylbenzene (3c)



Isolated as colorless oil (53.6 mg, 68% yield, *trans*:*cis* = 93:7).

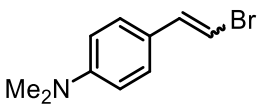
^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3c**: δ 7.19 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 13.9 Hz, 1H), 6.71 (d, *J* = 13.9 Hz, 1H), 2.33 (s, 3H) ppm. For *cis*-**3c** (well-resolved signals): δ 7.59 (d, *J* = 8.2 Hz, 2H), 6.38 (d, *J* = 8.1 Hz, 1H), 2.36 (s, 3H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3c**: δ 138.4, 137.2, 133.4, 129.6, 126.2, 105.5, 21.4 ppm. Both spectral data are superimposed to the literature values for *trans*-**3c** and *cis*-**3c**.[6]

1-(2-Bromovinyl)-4-methoxybenzene (**3d**)



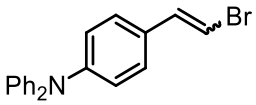
Isolated as colorless oil (64.7 mg, 76% yield, *trans*:*cis* = 92:8). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3d**: δ 7.22 (d, *J* = 8.7 Hz, 2H), 7.03 (d, *J* = 13.9 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.60 (d, *J* = 13.9 Hz, 1H), 3.80 (s, 3H) ppm. For *cis*-**3d**: δ 7.67 (d, *J* = 8.7 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 1H), 6.30 (d, *J* = 8.1 Hz, 2H), 3.82 (s, 3H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3d**: δ 159.8, 136.7, 128.9, 127.5, 114.3, 104.1, 55.4 ppm. Both spectral data are superimposed to the literature values for *trans*-**3d** and *cis*-**3d**.[6]

4-(2-Bromovinyl)-*N*,*N*-dimethylaniline (3e)



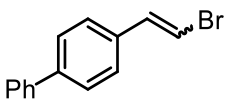
Isolated as white solid (42.9 mg, 47% yield, *trans*:*cis* = 95:5). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3e**: δ 7.18 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 13.9 Hz, 1H), 6.65 (d, *J* = 8.8 Hz, 2H), 6.51 (d, *J* = 13.9 Hz, 1H), 2.96 (s, 6H) ppm. For *cis*-**3e**: δ 7.66 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 8.9 Hz, 2H), 6.17 (d, *J* = 8.0 Hz, 1H), 2.99 (s, 6H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3e**: δ 150.6, 137.1, 127.3, 124.5, 112.4, 101.7, 40.5 ppm. Both spectral data are superimposed to the literature values for *trans*-**3e** and *cis*-**3e**.[7,8]

4-(2-Bromovinyl)-*N*,*N*-diphenylaniline (3f)



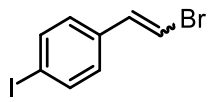
Isolated as white solid (91.7 mg, 66% yield, *trans*:*cis* = 93:7). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3f**: δ 7.26−7.22 (overlapped with signals for *cis*-**3f**, 4H), 7.14 (d, *J* = 8.6 Hz, 2H), 7.07 (dd, *J* = 8.5, 1.0 Hz, 4H), 7.04−6.97 (m, 5H), 6.61 (d, *J* = 13.9 Hz, 1H) ppm. For *cis*-**3f** (well-resolved signals): δ 7.60 (d, *J* = 8.7 Hz, 2H), 6.28 (d, *J* = 8.1 Hz, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3f**: δ 148.1, 147.5, 136.7, 130.0, 129.5, 127.1, 124.8, 123.4, 123.3, 104.6 ppm. HRMS (FAB): *m/z* calcd. For $[C_{20}H_{16}{}^{79}BrN]^+$ 349.0466: found 349.0472. mp: 127−135 °C.

4-(2-Bromovinyl)-1,1'-biphenyl (**3g**)



Isolated as white solid (65.3 mg, 63% yield, *trans*:*cis* = 92:8). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3g**: δ 7.60−7.56 (m, 4H), 7.46−7.36 (m, 5H), 7.15 (d, *J* = 14.0 Hz, 1H), 6.82 (d, *J* = 14.0 Hz, 1H) ppm. For *cis*-**3g** (well-resolved signals): δ 7.79 (d, *J* = 8.3 Hz, 2H), 6.46 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3g**: δ 141.2, 140.6, 136.9, 135.1, 129.0, 127.7, 127.6, 127.1, 126.7, 106.7 ppm. Both spectral data are superimposed to the literature values for *trans*-**3g** and *cis*-**3g**.[5]

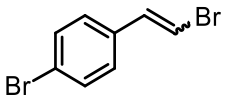
1-(2-Bromovinyl)-4-iodobenzene (3h)



Isolated as white solid (86.5 mg, 70% yield, *trans*:*cis* = 92:8).

^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3h**: δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.04−7.01 (m, 3H), 6.79 (d, *J* = 14.1 Hz, 1H) ppm. For *cis*-**3h** (well-resolved signals): δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 6.47 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3h**: δ 138.1, 136.3, 135.5, 127.9, 107.6, 93.9 ppm. Both spectral data are superimposed to the literature values for *trans*-**3h** and *cis*-**3h**.[5]

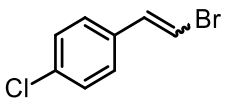
1-Bromo-4-(2-bromovinyl)benzene (**3i**)



Isolated as white solid (55.5 mg, 53% yield, *trans*:*cis* = 93:7).

^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3i**: δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 14.0 Hz, 1H), 6.78 (d, *J* = 14.0 Hz, 1H) ppm. For *cis*-**3i** (well-resolved signals): δ 7.55 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 6.47 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3i**: δ 136.2, 135.0, 132.1, 127.7, 122.4, 107.5 ppm. Both spectral data are superimposed to the literature values for *trans*-**3i** and *cis*-**3i**.[5]

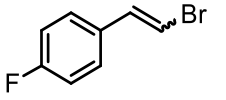
1-(2-Bromovinyl)-4-chlorobenzene (**3j**)



Isolated as colorless oil (38.0 mg, 44% yield, *trans*:*cis* = 93:7).

^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3j**: δ 7.29 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 14.0 Hz, 1H), 6.75 (d, *J* = 14.0 Hz, 1H) ppm. For *cis*-**3j** (well-resolved signals): δ 7.61 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 6.45 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3j**: δ 136.1, 134.6, 134.2, 129.2, 127.4, 107.3 ppm. Both spectral data are superimposed to the literature values for *trans*-**3j** and *cis*-**3j**.[5]

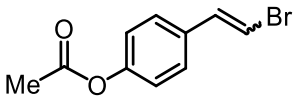
1-(2-Bromovinyl)-4-fluorobenzene (**3k**)



Isolated as colorless oil (22.9 mg, 28% yield, *trans*:*cis* = 94:6).

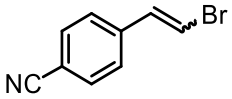
^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3k**: δ 7.28−7.25 (m, 2H), 7.08−6.99 (m, 3H), 6.69 (d, *J* = 14.0 Hz, 1H) ppm. For *cis*-**3k** (well-resolved signals): δ 7.69−7.65 (m, 2H), 6.41 (d, *J* = 8.1 Hz, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3k**: δ 162.8 (d, $J_{C\text{-}F}$ = 246.5 Hz), 136.2, 132.3 (d, $J_{C\text{-}F}$ = 3.6 Hz), 127.9 (d, $J_{C\text{-}F}$ = 8.0 Hz), 116.0 (d, $J_{C\text{-}F}$ = 21.9 Hz), 106.3 (d, $J_{C\text{-}F}$ = 2.2 Hz) ppm. ^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz, 303 K) for *trans*-**3k**: δ -113.00−-113.01 (m) ppm. Both spectral data are superimposed to the literature values for *trans*-**3k** and *cis*-**3k**.[4,9]

4-(2-Bromovinyl)phenyl acetate (**3l**)



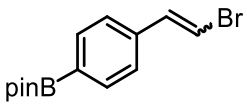
Isolated as white solid (67.4 mg, 70% yield, *trans*:*cis* = 93:7). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3l**: δ 7.32 (d, *J* = 8.6 Hz, 2H), 7.13−7.07 (m, 3H), 6.75 (d, *J* = 14.0 Hz, 1H), 2.32 (s, 3H) ppm. For *cis*-**3l** (well-resolved signals): δ 7.73 (d, *J* = 8.6 Hz, 2H), 6.46 (d, *J* = 8.2 Hz, 1H), 2.33 (s, 3H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3l**: δ 169.4, 150.7, 136.3, 133.8, 127.2, 122.1, 106.8, 21.2 ppm. Both spectral data are superimposed to the literature values for *trans*-**3l** and *cis*-**3l**.[5]

4-(2-Bromovinyl)benzonitrile (**3m**)



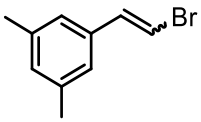
Isolated as white solid (37.0 mg, 45% yield, *trans*:*cis* = 89:11). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3m**: δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 14.1 Hz, 1H), 6.96 (d, *J* = 14.1 Hz, 1H) ppm. For *cis*-**3m** (well-resolved signals): δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 6.63 (d, *J* = 8.3 Hz, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3m**: δ 140.2, 135.8, 132.8, 126.7, 118.7, 111.8, 111.0 ppm. Both spectral data are superimposed to the literature values for *trans*-**3m** and *cis*-**3m**.[5]

2-(4-(2-Bromovinyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3n**)



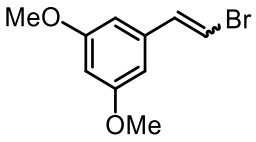
Isolated as white solid (80.5 mg, 65% yield, *trans*:*cis* = 91:9). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3n**: δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 14.0 Hz, 1H), 6.84 (d, *J* = 14.0 Hz, 1H), 1.34 (s, 12H) ppm. For *cis*-**3n** (well-resolved signals): δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 6.47 (d, *J* = 8.0 Hz, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3n**: δ 138.6, 137.4, 135.4, 125.5, 107.8, 84.0, 25.0 ppm. One carbon signal next to the boron atom was not clearly observed. Spectral data are superimposed to the literature values for *trans*-**3n**.[7]

2-(2-Bromovinyl)-1,3-dimethylbenzene (**3o**)



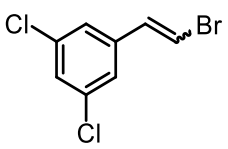
Isolated as colorless oil (59.1 mg, 70% yield, *trans*:*cis* = 94:6). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3o**: δ 7.03 (d, *J* = 14.0 Hz, 1H), 6.92 (s, 1H), 6.90 (s, 2H), 6.72 (d, *J* = 14.0 Hz, 1H), 2.30 (s, 6H) ppm. For *cis*-**3o** (well-resolved signals): δ 7.29 (s, 2H), 6.37 (d, *J* = 8.0 Hz, 1H), 2.33 (s, 6H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3o**: δ 138.4, 137.5, 136.0, 130.1, 124.1, 106.2, 21.3 ppm. Spectral data are superimposed to the literature values for *trans*-**3o**.[10]

2-(2-Bromovinyl)-1,3-dimethoxybenzene (**3p**)



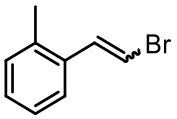
Isolated as colorless oil (73.9 mg, 76% yield, *trans*:*cis* = 93:7). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3p**: δ 7.03 (d, *J* = 13.9 Hz, 1H), 6.75 (d, *J* = 13.9 Hz, 1H), 6.44 (d, *J* = 2.3 Hz, 2H), 6.40 (t, *J* = 2.3 Hz, 1H), 3.79 (s, 6H) ppm. For *cis*-**3p** (well-resolved signals): δ 6.85 (d, *J* = 2.3 Hz, 2H), 3.80 (s, 6H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3p**: δ 161.1, 137.9, 137.3, 107.3, 104.4, 100.6, 55.5 ppm. Spectral data are superimposed to the literature values for *trans*-**3p**.[11]

2-(2-Bromovinyl)-1,3-dichlorobenzene (**3q**)



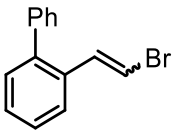
Isolated as colorless oil (40.2 mg, 40% yield, *trans*:*cis* = 88:12). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3q**: δ 7.28 (t, *J* = 1.8 Hz, 1H), 7.17 (d, *J* = 1.8 Hz, 2H), 6.99 (d, *J* = 14.0 Hz, 1H), 6.85 (d, *J* = 14.0 Hz, 1H) ppm. For *cis*-**3q** (well-resolved signals): δ 7.55 (d, *J* = 1.7 Hz, 2H), 7.32 (t, *J* = 1.7 Hz, 1H), 6.56 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3q**: δ 138.8, 135.6, 134.9, 128.2, 124.6, 109.9 ppm. Both spectral data are superimposed to the literature values for *trans*-**3q** and *cis*-**3q**.[12]

1-(2-Bromovinyl)-2-methylbenzene (**3r**)



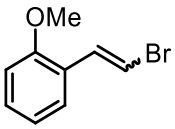
Isolated as colorless oil (32.0 mg, 41% yield, *trans*:*cis* = 78:22). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3r**: δ 7.32−7.29 (m, 2H), 7.22−7.13 (overlapped with signals for *cis*-**3r**, 3H), 6.63 (d, *J* = 13.9 Hz, 1H), 2.33 (s, 3H) ppm. For *cis*-**3r** (well-resolved signals): δ 7.56−7.54 (m, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 2.27 (s, 3H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3r**: δ 135.7, 135.3$_3$, 135.2$_9$, 130.6, 128.4, 126.4, 126.0, 107.4, 19.9 ppm. Both spectral data are superimposed to the literature values for *trans*-**3r** and *cis*-**3r**.[8,13]

1-(2-Bromovinyl)-2-phenylbenzene (**3s**)



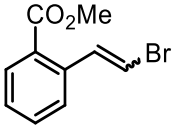
Isolated as colorless oil (63.9 mg, 62% yield, *trans*:*cis* = 73:27). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3s**: δ 7.49−7.30 (overlapped with signals for *cis*-**3s**, 9H), 7.07 (d, *J* = 13.9 Hz, 1H), 6.68 (d, *J* = 13.9 Hz, 1H) ppm. For *cis*-**3s** (well-resolved signals): δ 7.88−7.86 (m, 1H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.41 (d, *J* = 7.9 Hz, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3s**: δ 140.7, 140.5, 136.5, 134.2, 130.5, 129.8, 128.4$_1$, 128.4$_0$, 127.8, 127.5, 126.3, 107.1 ppm. HRMS (EI): *m/z* calcd. for $[C_{14}H_{11}{}^{79}Br]^+$ 258.0044: found 258.0054.

1-(2-Bromovinyl)-2-methoxybenzene (**3t**)



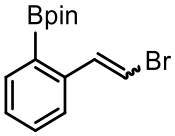
Isolated as colorless oil (62.2 mg, 73% yield, *trans*:*cis* = 71:29). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3t**: δ 7.30 (d, *J* = 13.9 Hz, 1H), 7.27−7.23 (m, 2H), 6.92−6.86 (m, 3H), 3.85 (s, 3H) ppm. For *cis*-**3t**: δ 7.88 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.33−7.25 (m, 2H), 7.00−6.96 (m, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 1H), 3.83 (s, 3H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3t**: δ 156.8, 133.2, 129.4, 128.1, 125.0, 120.9, 111.2, 108.0, 55.6 ppm. For *cis*-**3t**: δ 157.1, 129.7, 129.6, 128.1, 124.0, 120.2, 110.7, 107.2, 55.7 ppm. Both spectral data are superimposed to the literature values for *trans*-**3t** and *cis*-**3t**.[10,14]

Methyl-2-(2-bromovinyl)benzoate (**3u**)



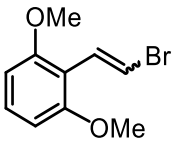
Isolated as colorless oil (51.5 mg, 53% yield, *trans*:*cis* = 64:36). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3u**: δ 7.94−7.91 (m, 2H), 7.56−7.34 (overlapped with signals for *cis*-**3u**, 3H), 6.66 (d, *J* = 13.9 Hz, 1H), 3.91 (s, 3H) ppm. For *cis*-**3u** (well-resolved signals): δ 8.00 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.66−7.62 (m, 2H), 6.51 (d, *J* = 7.9 Hz, 1H), 3.88 (s, 3H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3u**: δ 167.4, 136.5, 132.5, 130.9, 130.7, 128.1, 127.6, 108.5, 52.3 ppm. One carbon signal was not observed due to the overlapping. For *cis*-**3u**: δ 167.2, 137.7, 136.8, 133.4, 132.0, 128.9, 128.1, 107.9, 52.2 ppm. One carbon signal was not observed due to the overlapping. HRMS (CI): *m/z* calcd. for $[C_{10}H_{10}{}^{79}BrO_2]^+$ ($[M+H]^+$) 240.9864: found 240.9862.

2-(2-(2-Bromovinyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3v**)



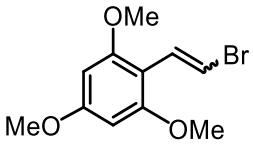
Isolated as colorless oil (74.2 mg, 60% yield, *trans*:*cis* = 74:26). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3v**: δ 7.94 (d, *J* = 13.9 Hz, 1H), 7.80 (d, *J* = 7.3 Hz, 1H), 7.48−7.37 (overlapped with signals for *cis*-**3v**, 2H), 7.33−7.26 (overlapped with signals for *cis*-**3v**, 1H), 6.68 (d, *J* = 13.9 Hz, 1H), 1.37 (s, 12H) ppm. For *cis*-**3v** (well-resolved signals): δ 7.88−7.85 (m, 2H), 7.70 (d, *J* = 8.0 Hz, 1H), 6.44 (d, *J* = 8.0 Hz, 1H), 1.34 (s, 12H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3v**: δ 142.0, 138.3, 136.3, 131.3, 127.4, 125.1, 107.1, 84.1, 25.0 ppm. One carbon signal next to the boron atom was not clearly observed. HRMS (EI): *m/z* calcd. for $[C_{14}H_{18}{}^{11}B^{79}BrO_2]^+$ 308.0583: found 308.0583.

2-(2-Bromovinyl)-1,3-dimethoxybenzene (**3w**)



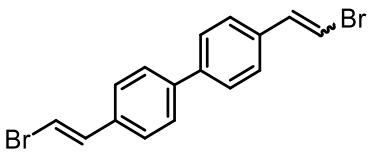
Isolated as colorless oil (73.4 mg, 76% yield, *trans*:*cis* = 24:76). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3w** (well-resolved signals): δ 7.48 (d, *J* = 13.8 Hz, 1H), 7.18 (t, *J* = 8.3 Hz, 1H), 6.54 (d, *J* = 8.3 Hz, 2H), 3.84 (s, 6H) ppm. For *cis*-**3w**: δ 7.29−7.25 (overlapped with signals for *cis*-**3w**, 1H), 6.99 (d, *J* = 7.7 Hz, 1H), 6.62−6.53 (m, 3H), 3.83 (s, 6H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *cis*-**3w**: δ 157.6, 129.6, 127.0, 111.6, 104.$_0$, 103.9, 55.9 ppm. HRMS (EI): *m/z* calcd. for $[C_{10}H_{11}{}^{79}BrO_2]^+$ 241.9942: found 241.9937.

2-(2-Bromovinyl)-1,3,5-trimethoxybenzene (**3x**)



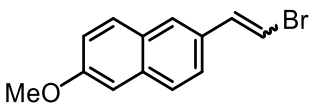
Isolated as colorless oil (85.3 mg, 78% yield, *trans*:*cis* = 18:82). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3x** (well-resolved signals): δ 7.39 (d, *J* = 13.8 Hz, 1H), 7.08 (d, *J* = 13.8 Hz, 1H), 6.11 (s, 2H) ppm. For *cis*-**3x**: δ 6.93 (d, *J* = 7.5 Hz, 1H), 6.54 (d, *J* = 7.5 Hz, 1H), 6.15 (s, 2H), 3.83 (overlapped with signals for *cis*-**3x**, 3H), 3.82 (s, 6 H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *cis*-**3x**: δ 161.6, 158.4, 126.8, 111.0, 90.7$_8$, 90.7$_5$, 55.8, 55.5 ppm. HRMS (EI): *m/z* calcd. For $[C_{11}H_{13}{}^{79}BrO_3]^+$ 272.0048: found 272.0048.

4,4'-Bis(2-bromoethenyl)biphenyl (**3y**)



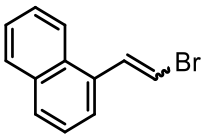
Isolated as white solid (69.0 mg, 47% yield, *trans*/*trans*:*trans*/*cis* = 73:27). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*/*trans*-**3y**: δ 7.55 (d, *J* = 8.4 Hz, 4H), 7.36 (d, *J* = 8.4 Hz, 4H), 7.13 (d, *J* = 14.0 Hz, 2H), 6.82 (d, *J* = 14.0 Hz, 2H) ppm. For *trans*/*cis*-**3y** (well-resolved signals): δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.61−7.57 (m, 4H), 6.46 (d, *J* = 8.1 Hz, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*/*trans*-**3y**: δ 140.3, 136.8, 135.3, 127.4, 126.8, 106.9 ppm. Spectral data are superimposed to the literature values for *trans*/*trans*-**3y**.[15]

2-(2-Bromovinyl)-6-methoxynaphthalene (**3z**)



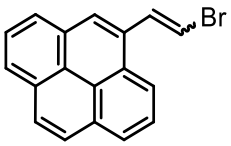
Isolated as white solid (74.7 mg, 71% yield, *trans*:*cis* = 92:8). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3z**: δ 7.70 (t, *J* = 9.6 Hz, 2H), 7.62 (s, 1H), 7.43 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.22 (d, *J* = 14.0 Hz, 1H), 7.16−7.10 (m, 2H), 6.83 (d, *J* = 14.0 Hz, 1H), 3.92 (s, 3H) ppm. For *cis*-**3z** (well-resolved signals): δ 8.10 (s, 1H), 6.45 (d, *J* = 8.0 Hz, 1H), 3.93 (s, 3H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3z**: δ 158.2, 137.4, 134.5, 131.4, 129.7, 129.0, 127.5, 126.2, 123.6, 119.4, 106.1, 105.8, 55.5 ppm. HRMS (EI): *m/z* calcd. For $[C_{13}H_{11}{}^{79}BrO]^+$ 261.9993: found 261.9990. mp: 100−108 °C.

1-(2-Bromovinyl)naphthalene (**3aa**)



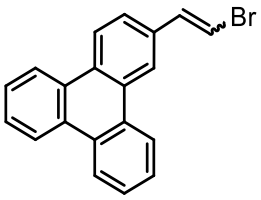
Isolated as colorless oil (56.9 mg, 61% yield, *trans*:*cis* = 87:13). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3aa**: δ 8.05 (d, *J* = 8.0 Hz, 1H), 7.87−7.82 (m, 3H), 7.57−7.42 (m, 4H), 6.78 (d, *J* = 13.8 Hz, 1H) ppm. For *cis*-**3aa** (well-resolved signals): δ 7.71 (d, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3aa**: δ 135.2, 133.8, 133.7, 130.8, 128.9, 128.7, 126.6, 126.3, 125.7, 124.4, 123.9, 108.6 ppm. Both spectral data are superimposed to the literature values for *trans*-**3aa** and *cis*-**3aa**.[5]

1-(2-Bromovinyl)pyrene (**3ab**)



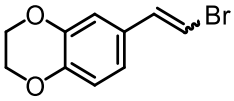
Isolated as yellow solid (49.1 mg, 40% yield, *trans*:*cis* = 93:7). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3ab**: δ 8.30 (d, *J* = 9.3 Hz, 1H), 8.20 (d, *J* = 7.6 Hz, 2H), 8.15 (s, 1H), 8.13−8.00 (m, 6H), 6.96 (d, *J* = 13.7 Hz, 1H) ppm. For *cis*-**3ab** (well-resolved signals): δ 6.87 (d, *J* = 7.9 Hz, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3ab**: δ 135.2, 131.6, 131.5, 131.0, 130.5, 128.2, 128.0, 127.9, 127.5, 126.3, 125.7, 125.5, 125.2, 124.9, 124.1, 123.0, 108.9 ppm. One carbon signal was not observed due to the overlapping. HRMS (EI): *m/z* calcd. For $[C_{18}H_{11}{}^{79}Br]^+$ 306.0044: found 306.0041. mp: 110−120 °C.

2-(2-Bromovinyl)triphenylene (**3ac**)



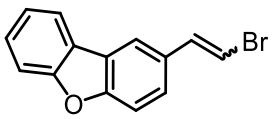
Isolated as white solid (50.0 mg, 38% yield, *trans*:*cis* = 90:10). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3ac**: δ 8.64−8.54 (overlapped with signals for *cis*-**3ac**, 5H), 8.46 (s, 1H), 7.66−7.65 (overlapped with signals for *cis*-**3ac**, 4H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.34 (d, *J* = 14.0 Hz, 1H), 6.97 (d, *J* = 14.0 Hz, 1H) ppm. For *cis*-**3ac** (well-resolved signals): δ 9.03 (s, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3ac**: δ 137.4, 134.7, 130.2, 130.1, 130.0, 129.8, 129.5_6, 129.5_3, 127.7, 127.6_1, 127.5_8, 127.5, 127.4, 124.4, 124.0, 123.5_1, 123.4_9, 123.3, 121.7, 107.2 ppm. HRMS (EI): *m/z* calcd. For $[C_{20}H_{13}{}^{79}Br]^+$ 332.0201: found 332.0200. mp: 144−155 °C.

6-(2-Bromovinyl)-2,3-dihydrobenzo[*b*][1,4]dioxine (**3ad**)



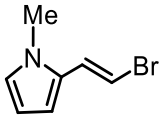
Isolated as colorless oil (60.1 mg, 69% yield, *trans*:*cis* = 93:7). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3ad**: δ 6.97 (d, *J* = 13.9 Hz, 1H), 6.82−6.76 (m, 3H), 6.59 (d, *J* = 13.9 Hz, 1H), 4.25 (s, 4H) ppm. For *cis*-**3ad**: δ 7.34 (d, *J* = 2.0 Hz, 1H), 7.16 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.31 (d, *J* = 8.1 Hz, 1H), 4.27 (s, 4H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3ad**: δ 144.0, 143.8, 136.6, 129.9, 119.8, 117.7, 114.9, 104.8, 64.6, 64.5 ppm. Spectral data are superimposed to the literature values for *trans*-**3ad**.[16]

2-(2-Bromovinyl)dibenzo[b,d]furan (**3ae**)



Isolated as white solid (78.2 mg, 72% yield, *trans*:*cis* = 91:9). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3ae**: δ 7.93 (dd, *J* = 7.5, 0.5 Hz, 1H), 7.85 (d, *J* = 1.8 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.51−7.45 (m, 2H), 7.41−7.34 (m, 2H), 7.25 (d, *J* = 13.9 Hz, 1H), 6.80 (d, *J* = 13.9 Hz, 1H) ppm. For *cis*-**3ae** (well-resolved signals): δ 8.33 (d, *J* = 1.9 Hz, 1H), 7.98−7.96 (m, 1H), 7.75 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.47 (d, *J* = 8.1 Hz, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3ae**: δ 156.8, 156.2, 137.2, 131.2, 127.7, 125.5, 124.9, 124.0, 123.1, 120.9, 118.4, 112.1, 112.0, 105.6 ppm. HRMS (EI): *m/z* calcd. For $[C_{14}H_9{}^{79}BrO]^+$ 271.9837: found 271.9833. mp: 87−92 °C.

***trans*-2-(2-Bromovinyl)-1-methyl-1*H*-pyrrole** (**3af**)

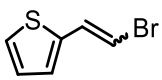


38% NMR yield, *trans*:*cis* = >99:1. (Yield was determined by ^{1}H NMR yield using 1,3,5-trimethoxybenzene as an internal standard.)

^{1}H NMR ($CDCl_3$, 400 MHz, 303 K): δ 6.97 (d, *J* = 13.7 Hz, 1H), 6.61 (s, 1H), 6.48 (d, *J* = 13.7 Hz, 1H), 6.29 (d, *J* = 13.8 Hz, 1H), 6.10−6.08 (m, 1H), 3.61 (s, 3H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K): δ 129.9, 126.4, 123.9, 108.3, 107.6, 103.2, 34.3 ppm.

3af was decomposed upon complete evaporation of the solvent, and the characterization was conducted by the ^{1}H and ^{13}C NMR measurements with contamination of hexane and CH_2Cl_2.

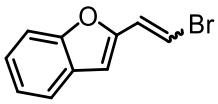
2-(2-Bromovinyl)thiophene (**3ag**)



Isolated as colorless oil (37.8 mg, 50% yield, *trans*:*cis* = 91:9).

^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3ag**: δ 7.20−7.16 (m, 2H), 6.98−6.95 (m, 2H), 6.62 (d, *J* = 13.9 Hz, 1H) ppm. For *cis*-**3ag**: δ 7.37 (d, *J* = 5.2 Hz, 1H), 7.31−7.30 (m, 2H), 7.05 (dd, *J* = 5.2, 3.8 Hz, 1H), 6.31 (d, *J* = 8.0 Hz, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3ag**: δ 140.1, 130.4, 127.6, 126.2, 125.2, 105.3 ppm. Both spectral data are superimposed to the literature values for *trans*-**3ag** and *cis*-**3ag**.[7,17]

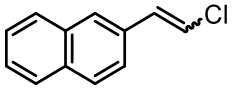
2-(2-Bromovinyl)benzofuran (**3ah**)



Isolated as colorless oil (31.2 mg, 35% yield, *trans*:*cis* = 79:21).

^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3ah**: δ 7.53 (d, *J* = 7.7 Hz, 1H), 7.43 (dd, *J* = 8.2, 0.6 Hz, 1H), 7.32−7.28 (m, 1H), 7.26−7.19 (m, 1H), 7.05 (d, *J* = 13.8 Hz, 1H), 7.01 (d, *J* = 13.8 Hz, 1H), 6.60 (s, 1H) ppm. For *cis*-**3ah** (well-resolved signals): δ 7.61 (d, *J* = 7.5 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3ah**: δ 155.0, 152.8, 128.5, 125.8, 125.3, 123.3, 121.4, 111.2, 109.0, 105.4 ppm. HRMS could not be measured due to the rapid decomposition.

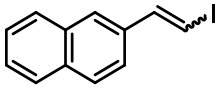
2-(2-Chlorovinyl)naphthalene (**3a'**)



Isolated as white solid (31.7 mg, 42% yield, *trans*:*cis* = 81:19).

^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3a'**: δ 7.86−7.78 (overlapped with signals of *cis*-**3a'**, 3H), 7.68 (s, 1H), 7.50−7.45 (overlapped with signals of *cis*-**3a'**, 3H), 6.99 (d, *J* = 13.7 Hz, 1H), 6.77 (overlapped with signals of *cis*-**3a'**, 1H) ppm. For *cis*-**3a'** (well-resolved signals): δ 8.14 (s, 1H), 6.35 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3a'**: δ 133.6$_4$, 133.5$_7$, 133.3, 132.5, 128.7, 128.2, 127.9, 126.7, 126.4, 126.3, 123.2, 119.2 ppm. Both spectral data are superimposed to the literature values for *trans*-**3a'** and *cis*-**3a'**.[18,19]

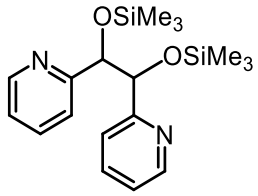
2-(2-Iodovinyl)naphthalene (**3a''**)



Isolated as white solid (45.1 mg, 40% yield, *trans*:*cis* = 93:7). ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) for *trans*-**3a''**: δ 7.86−7.78 (m, 3H), 7.68 (s, 1H), 7.59 (d, *J* = 14.9 Hz, 1H), 7.49−7.46 (m, 3H), 6.97 (d, *J* = 14.9 Hz, 1H) ppm. For *cis*-**3a''** (well-resolved signals): δ 8.11 (s, 1H), 6.66 (d, *J* = 8.6 Hz, 1H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 303 K) for *trans*-**3a''**: δ 145.2, 135.3, 133.5, 133.3, 128.6, 128.3, 127.9, 126.7, 126.6, 126.4, 122.9, 77.0 ppm. Both spectral data are superimposed to the literature values for *trans*-**3a''** and *cis*-**3a''**.[20,21]

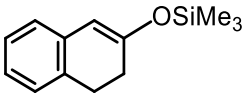
Formation of the corresponding trimethylsilyl-protected pinacol, silyl enol ethers, and bromoalkene were confirmed by comparing with the reported literatures. The underlined signals were used for determining the yield in the ^{1}H NMR spectra with respect to the internal standard.

2,2'-(1,2-Bis-trimethylsilanyloxy-ethane-1,2-diyl)-bis-pyridine (dl:meso-mixture) (**4ap**)



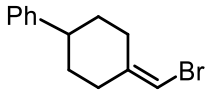
The reaction mixture was quenched by adding $NaHCO_3$ aq. (2.0 mL). Quant. (Yield was determined by ^{1}H NMR yield using 1,3,5-trimethoxybenzene as an internal standard.) ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K, well-resolved signals): δ 8.51−8.49 (m, 2H for both diastereomers), [7.67−7.53 (m) and 7.36 (d, *J* = 7.8 Hz), 4H for both diastereomers], 7.13−7.10 (m, 2H for both diastereomers), [5.21 (s) and 4.97 (s), 2H for both diastereomers], [-0.19 (s) and -0.27 (s) 18H, for both diastereomers]. This data was superimposed to the literature values for **4ap**.[22]

(3,4-Dihydro-naphtalen-1-yloxy)-trimethyl-silane (**5av**)



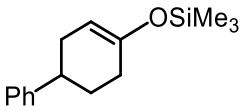
45% NMR yield. (Yield was determined by ^{1}H NMR yield using 1,3,5-trimethoxybenzene as an internal standard.) ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K, well-resolved signals): δ 5.70 (s, 1H), 2.90 (t, *J* = 8.3 Hz, 2H), 2.36 (t, *J* = 8.3 Hz, 2H), 0.28 (s, 9H). This data was superimposed to the literature values for **5av**.[23]

1-(Bromomethylidene)-4-phenylcyclohexane (**3aw**)



23% NMR yield. (Yield was determined by ^{1}H NMR yield using 1,3,5-trimethoxybenzene as an internal standard.) ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K, well-resolved signal): δ 5.93 (s, 1H). This data was superimposed to the literature values for **3aw**.[8]

4-Phenyl-1-trimethylsilyloxy-1-cyclohexene (**5aw**)



29% NMR yield. (Yield was determined by ^{1}H NMR yield using 1,3,5-trimethoxybenzene as an internal standard.) ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K, well-resolved signals): δ 4.95−4.94 (m, 1H), 0.21 (s, 9H). This data was superimposed to the literature values for **5aw**.[24]

7. References

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8. NMR Spectra

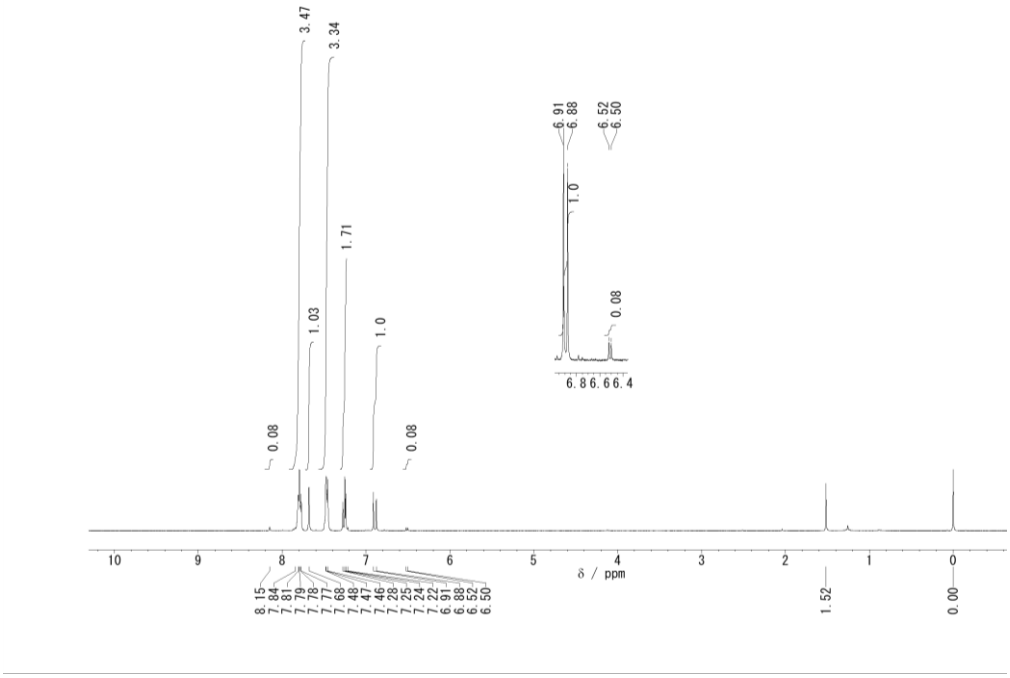

Figure S1. ^{1}H NMR spectrum of **3a** (*trans*/*cis* mixture) in $CDCl_3$.

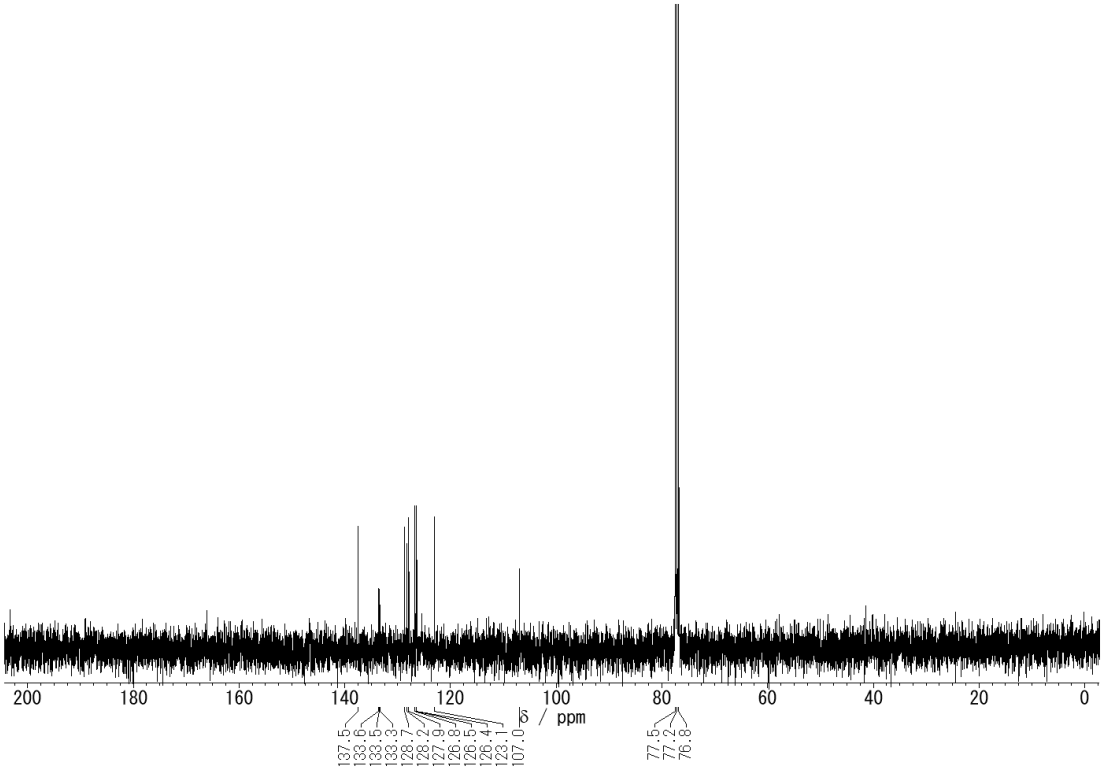

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **3a** (*trans*/*cis* mixture) in $CDCl_3$.

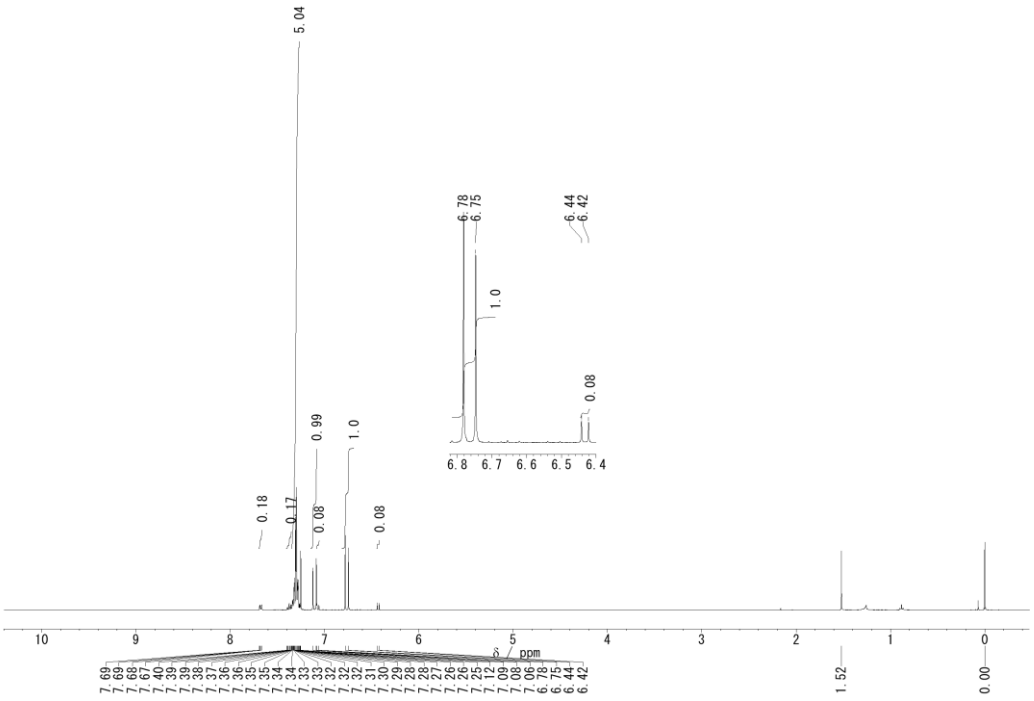

Figure S3. ^{1}H NMR spectrum of **3b** (*trans*/*cis* mixture) in $CDCl_3$.

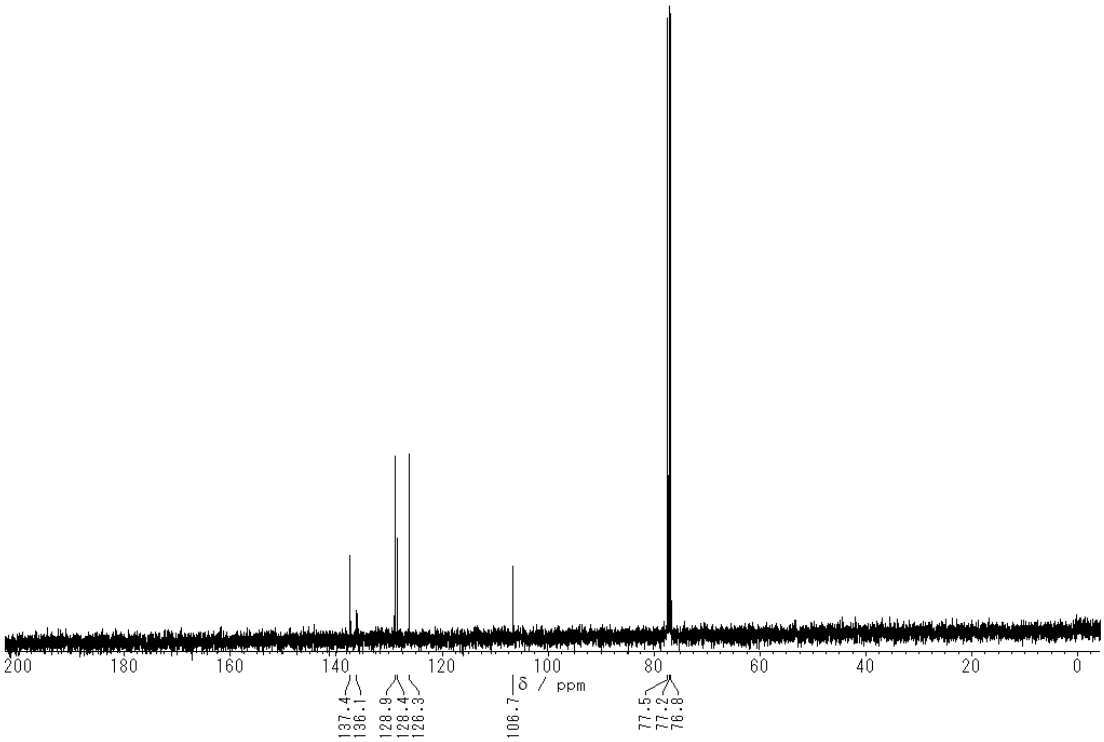

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of **3b** (*trans*/*cis* mixture) in $CDCl_3$.

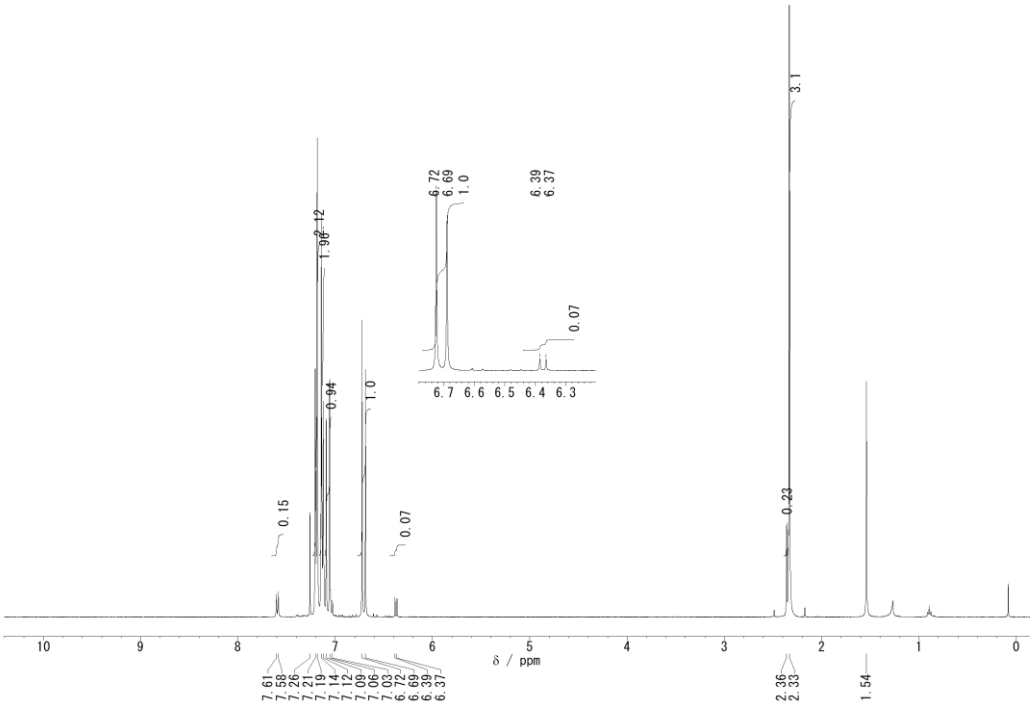

Figure S5. ^{1}H NMR spectrum of **3c** (*trans*/*cis* mixture) in $CDCl_3$.

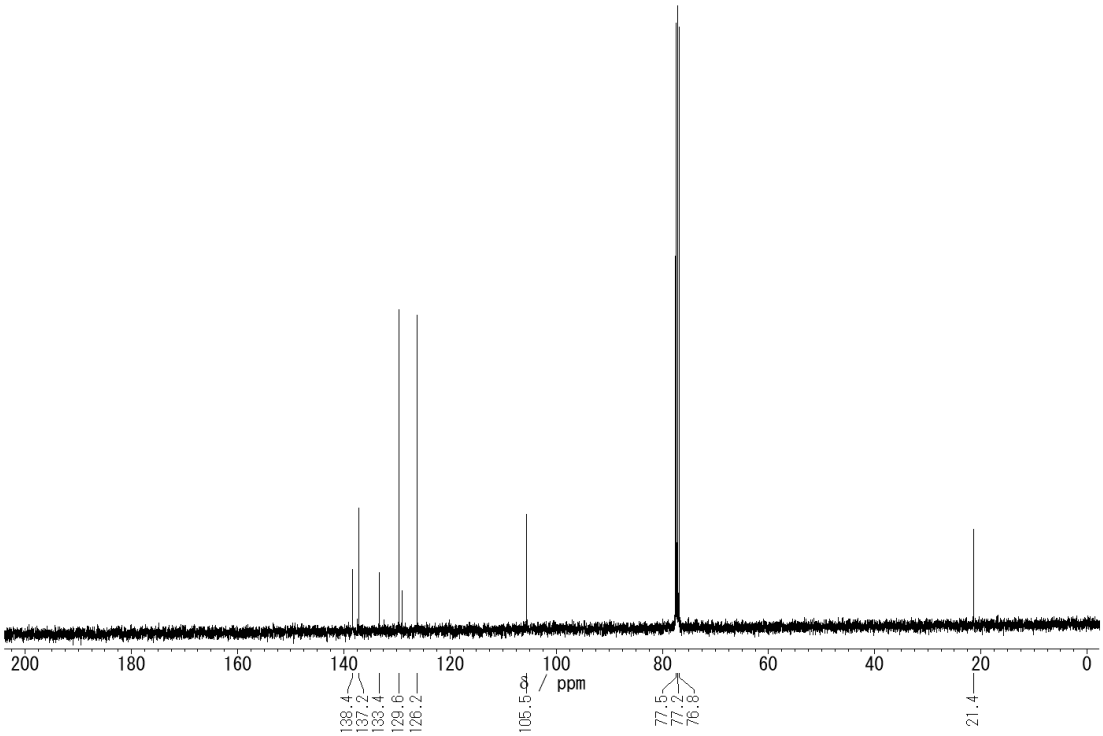

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **3c** (*trans*/*cis* mixture) in $CDCl_3$.

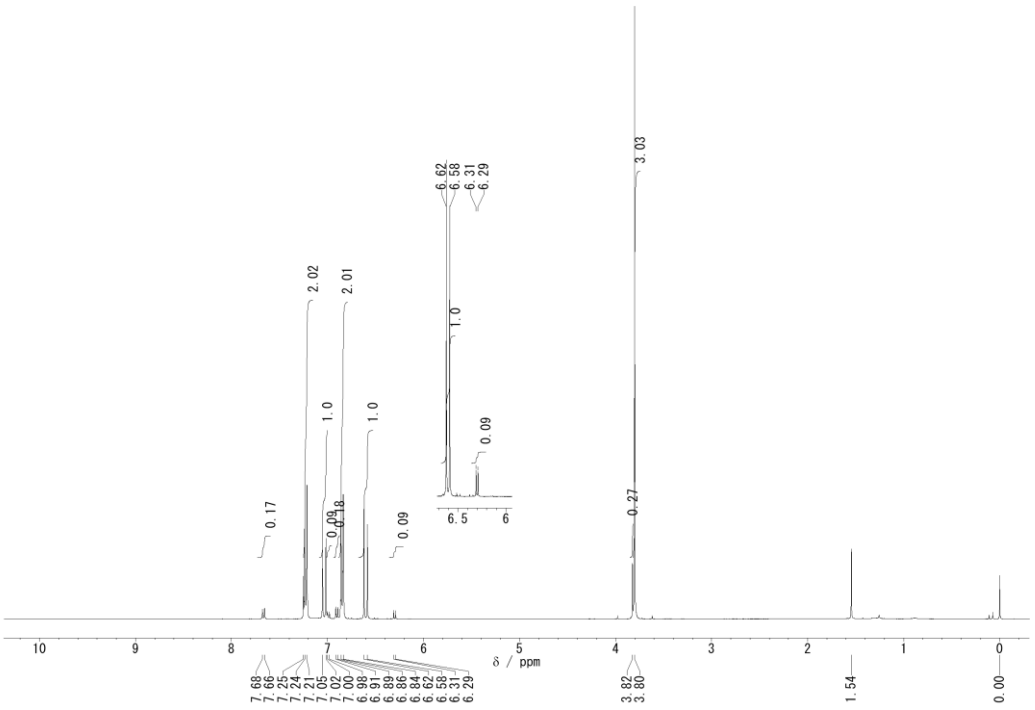

Figure S7. ^{1}H NMR spectrum of **3d** (*trans*/*cis* mixture) in $CDCl_3$.

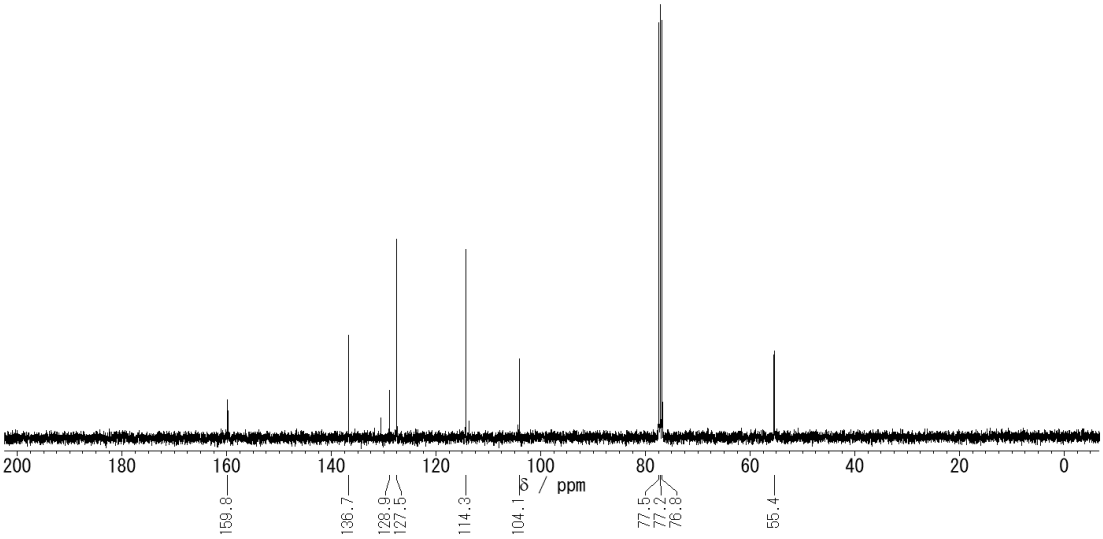

Figure S8. ^{13}C{^{1}H} NMR spectrum of **3d** (*trans*/*cis* mixture) in $CDCl_3$.

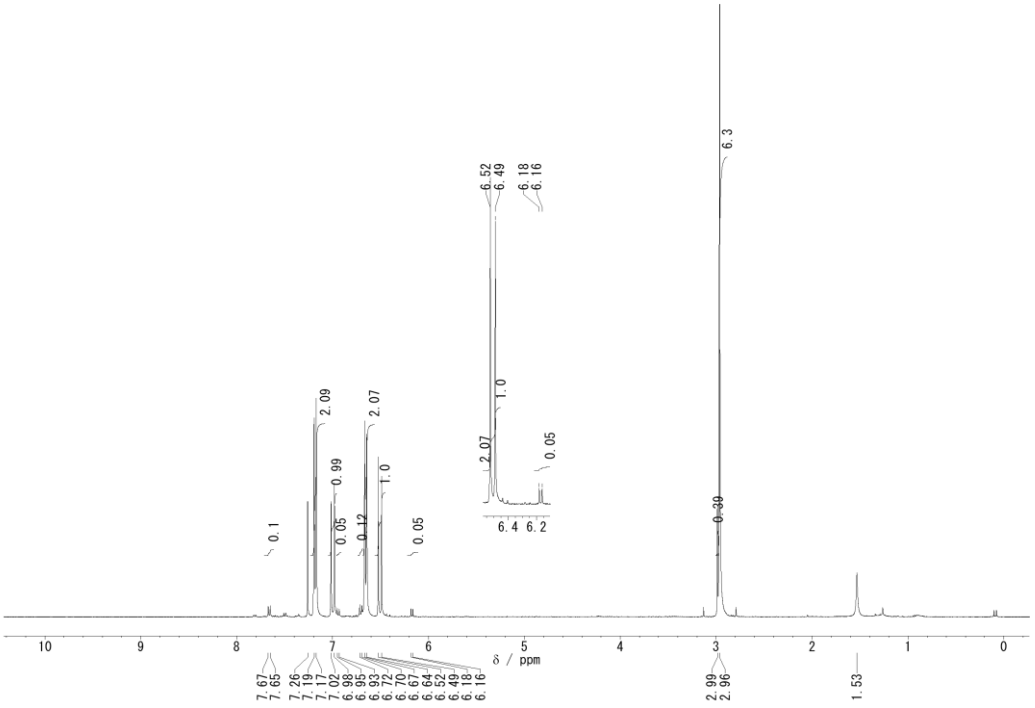

Figure S9. ^{1}H NMR spectrum of **3e** (*trans*/*cis* mixture) in $CDCl_3$.

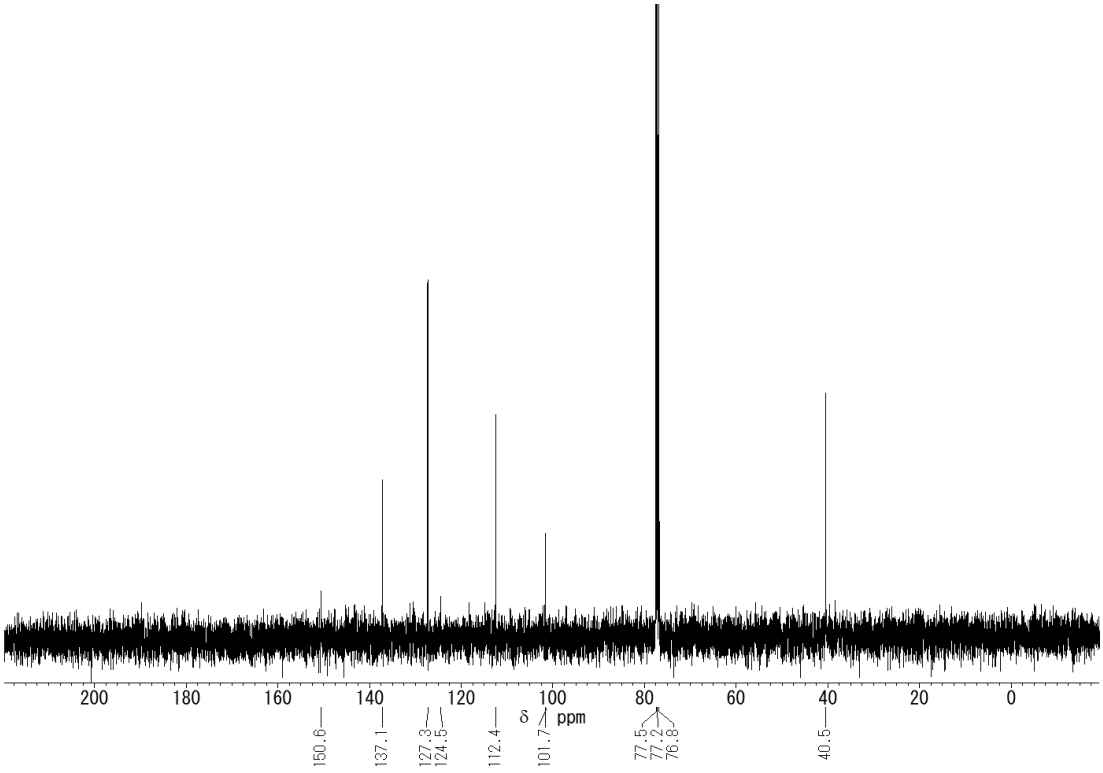

Figure S10. ^{13}C{^{1}H} NMR spectrum of **3e** (*trans*/*cis* mixture) in $CDCl_3$.

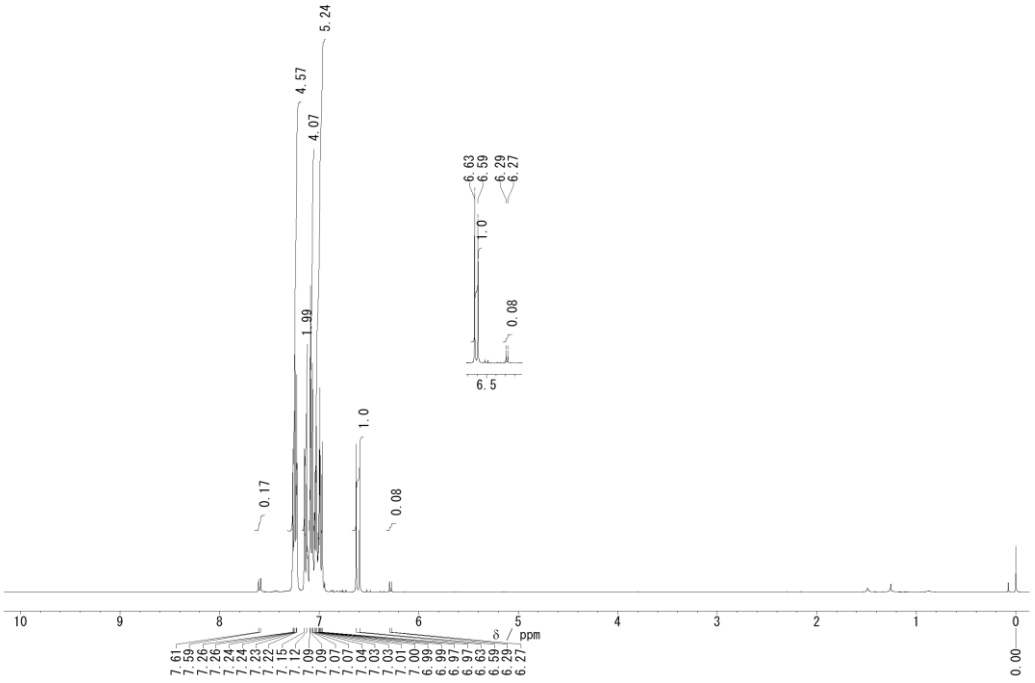

Figure S11. ^{1}H NMR spectrum of **3f** (*trans*/*cis* mixture) in $CDCl_3$.

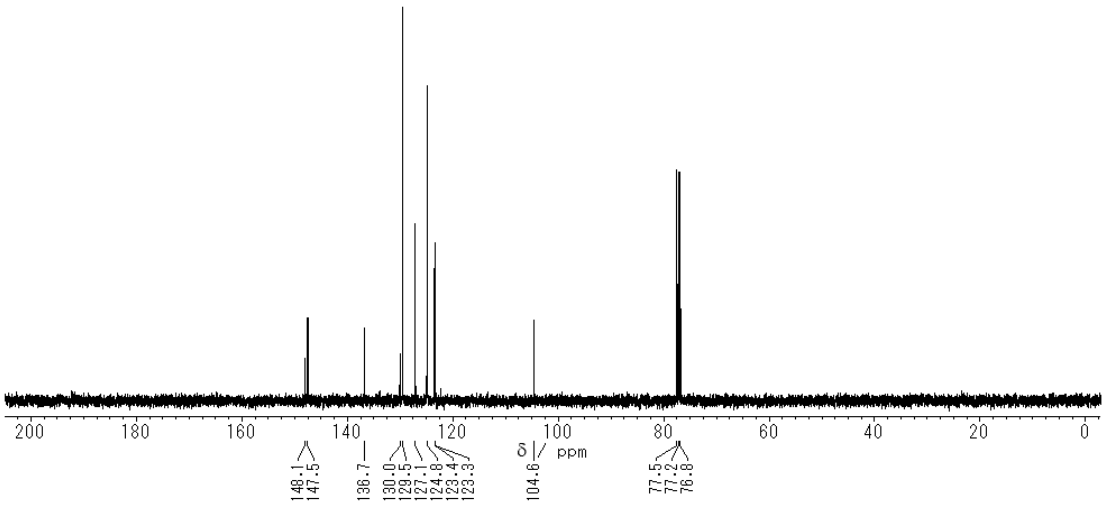

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **3f** (*trans*/*cis* mixture) in $CDCl_3$.

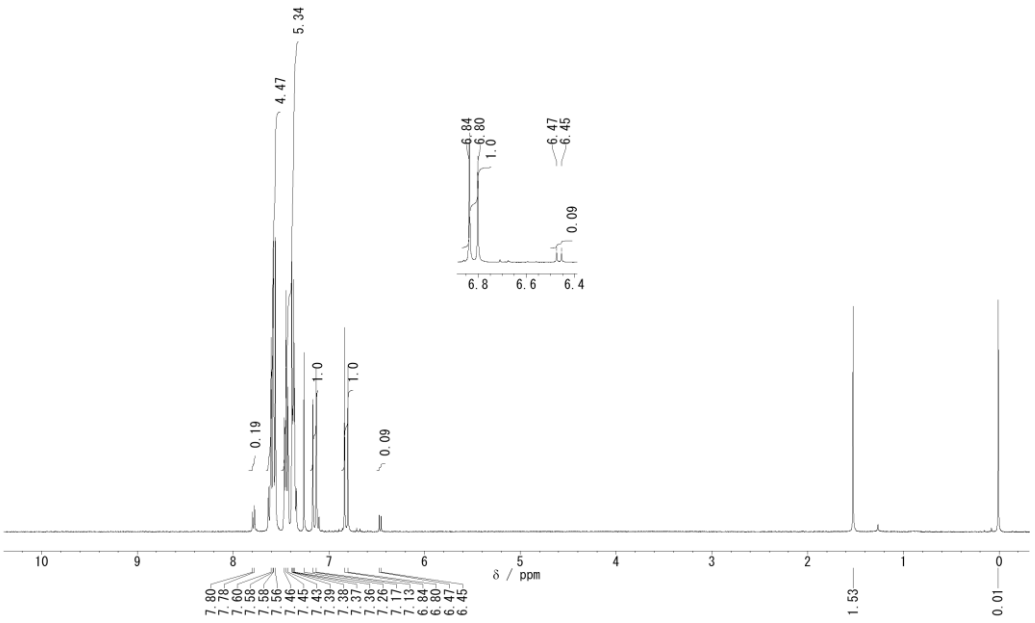

Figure S13. ^{1}H NMR spectrum of **3g** (*trans*/*cis* mixture) in $CDCl_3$.

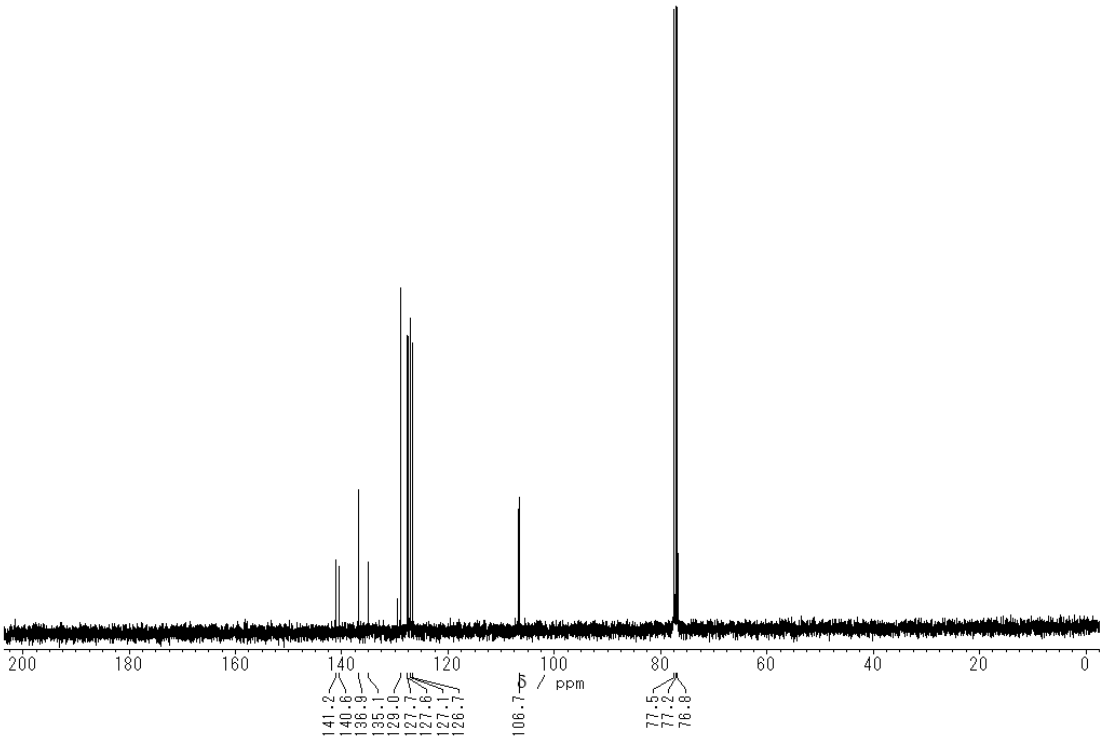

Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **3g** (*trans*/*cis* mixture) in $CDCl_3$.

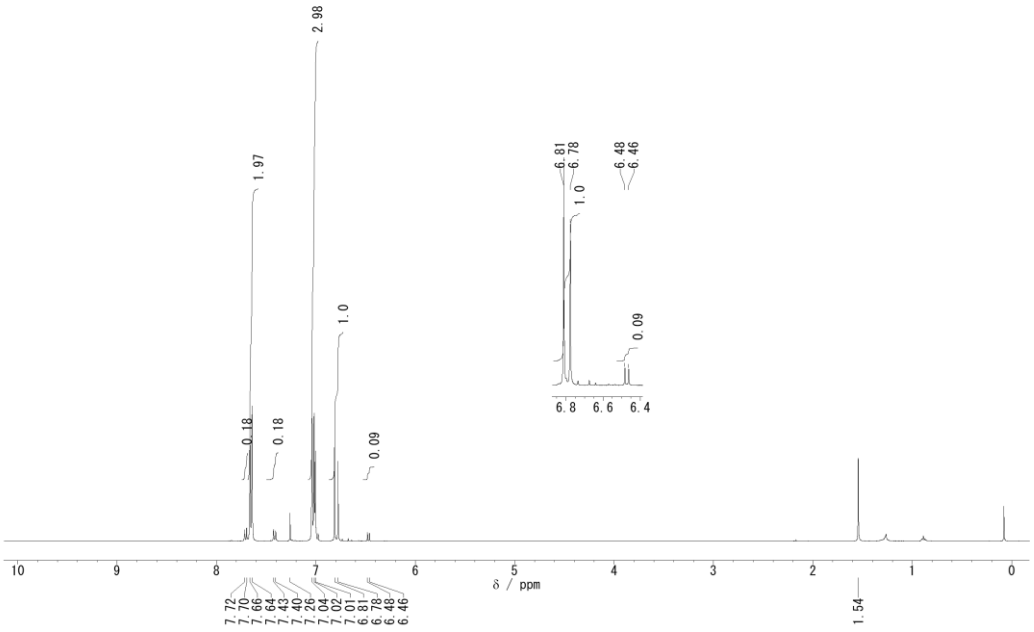

Figure S15. ^{1}H NMR spectrum of **3h** (*trans*/*cis* mixture) in $CDCl_3$.

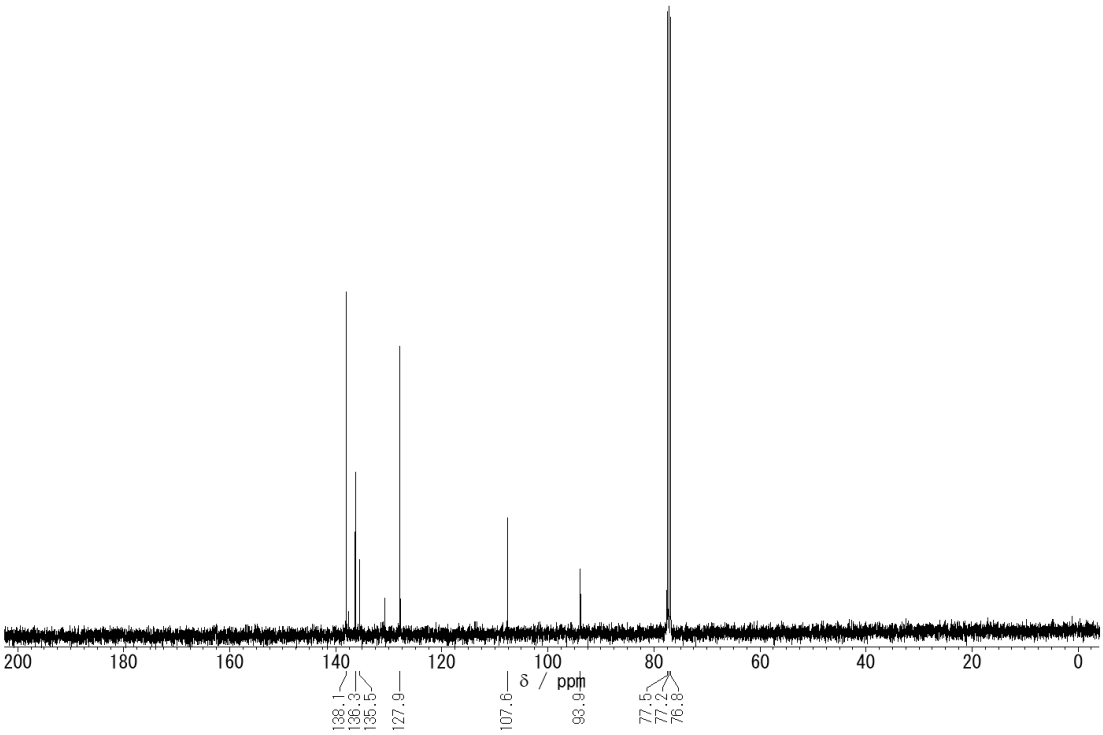

Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of **3h** (*trans*/*cis* mixture) in $CDCl_3$.

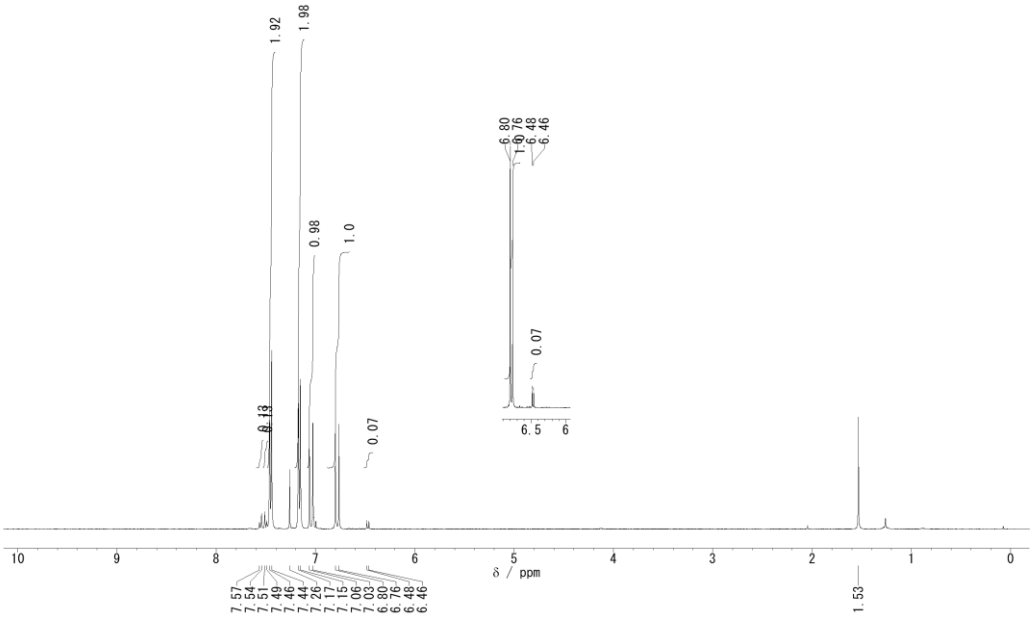

Figure S17. ^{1}H NMR spectrum of **3i** (*trans*/*cis* mixture) in $CDCl_3$.

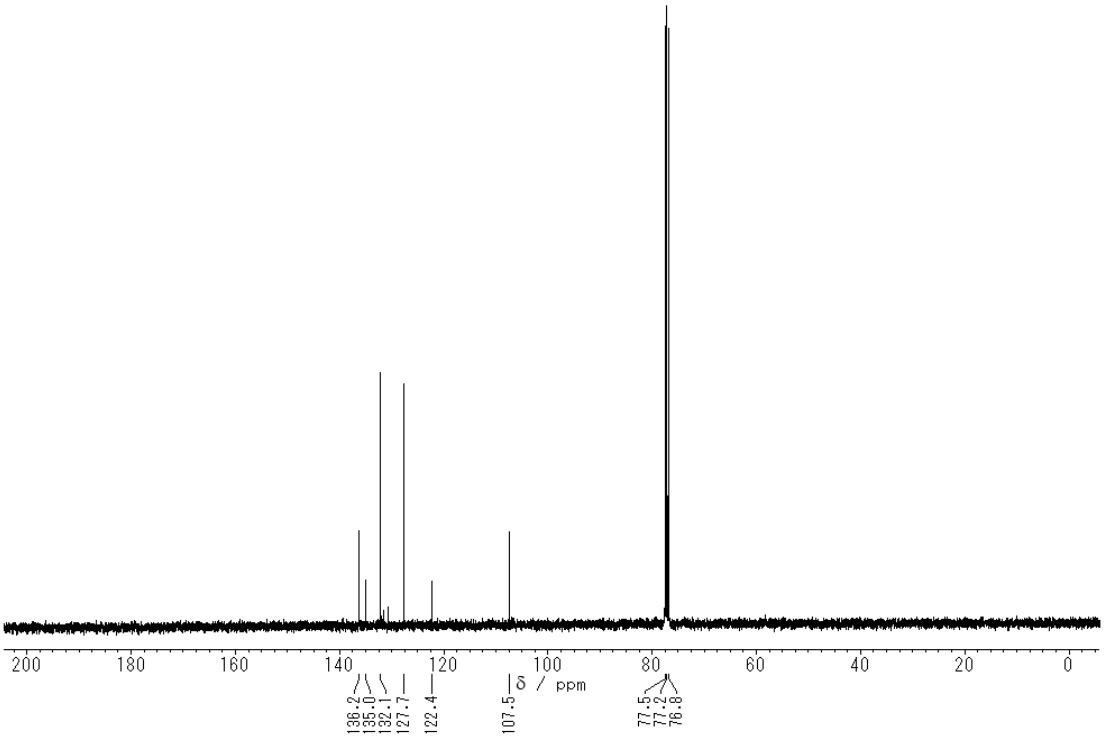

Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of **3i** (*trans*/*cis* mixture) in $CDCl_3$.

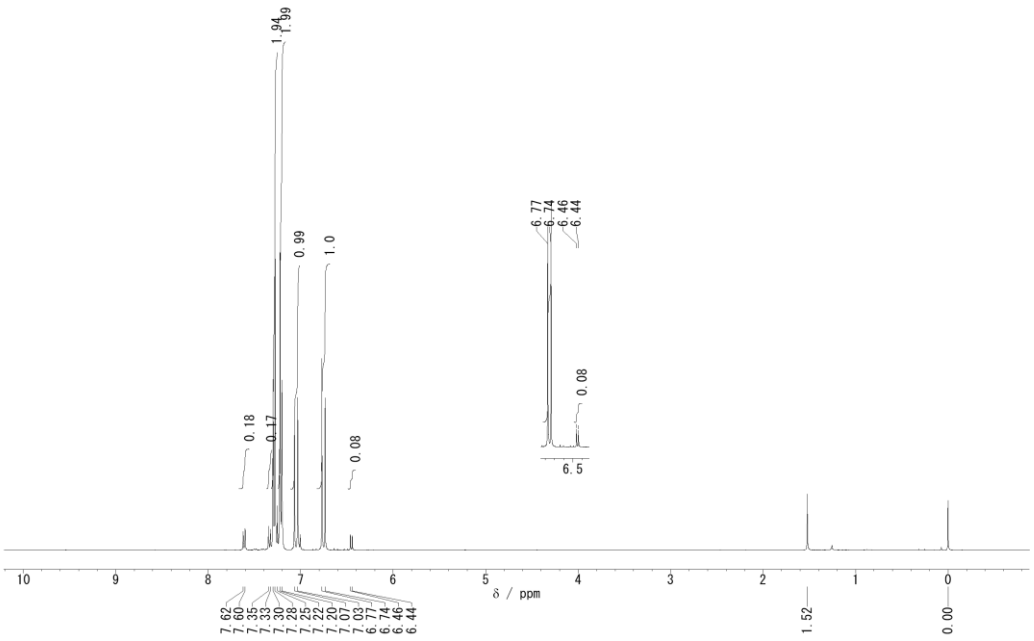

Figure S19. ^{1}H NMR spectrum of **3j** (*trans*/*cis* mixture) in $CDCl_3$.

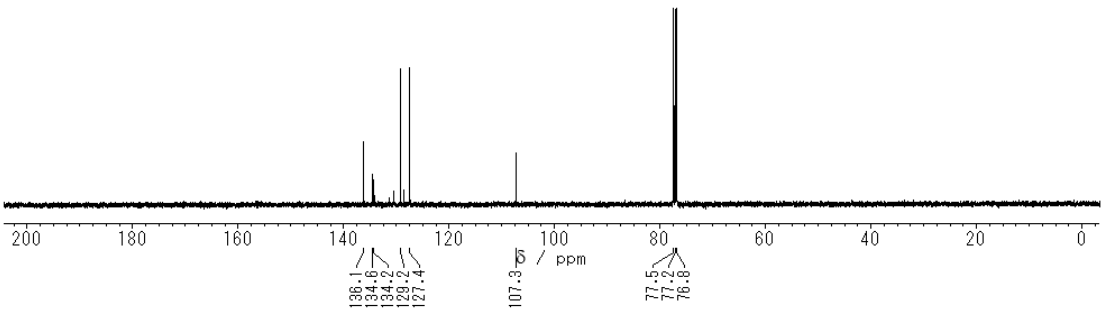

Figure S20. ^{13}C{^{1}H} NMR spectrum of **3j** (*trans*/*cis* mixture) in $CDCl_3$.

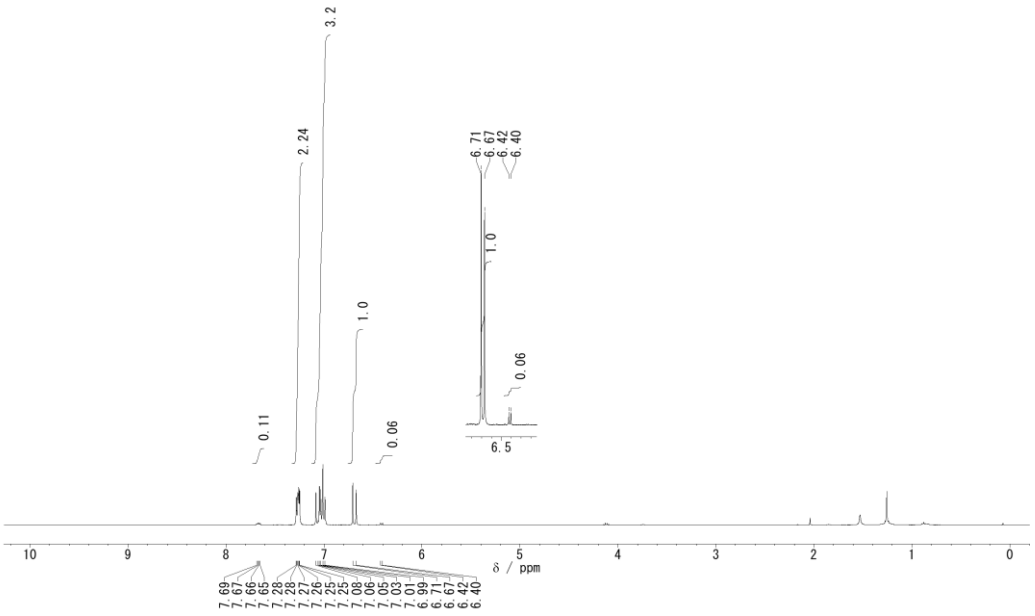

Figure S21. ^{1}H NMR spectrum of **3k** (*trans*/*cis* mixture) in $CDCl_3$.

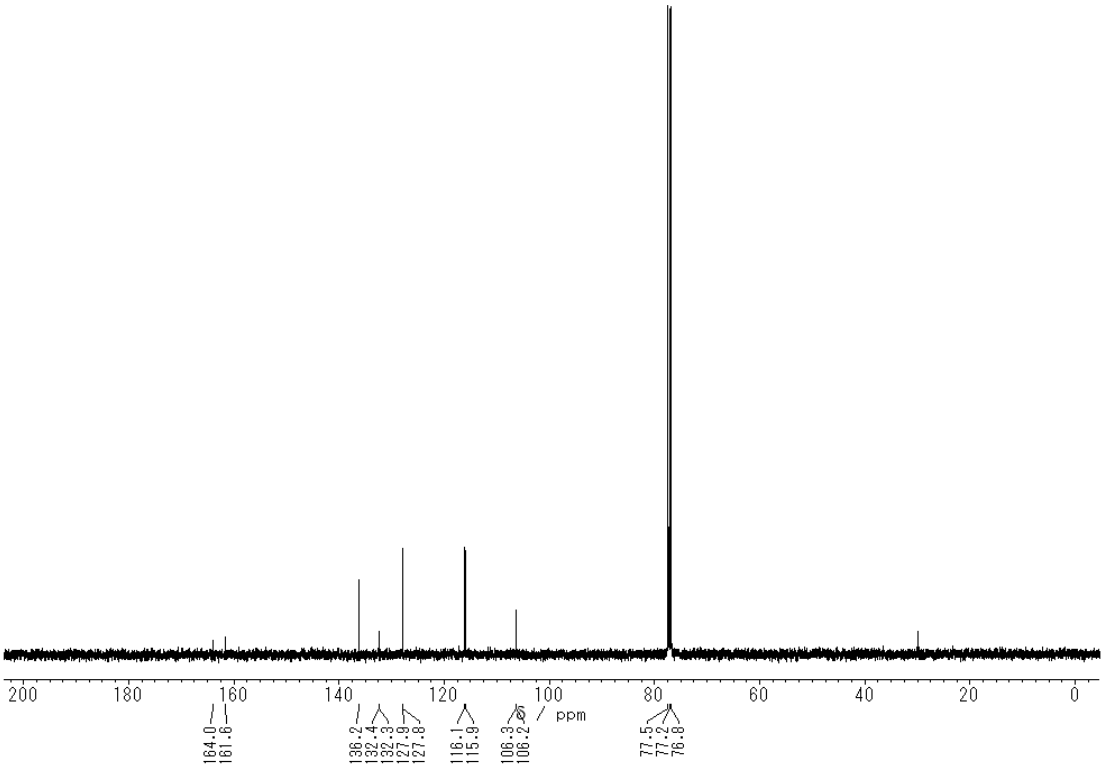

Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of **3k** (*trans*/*cis* mixture) in $CDCl_3$.

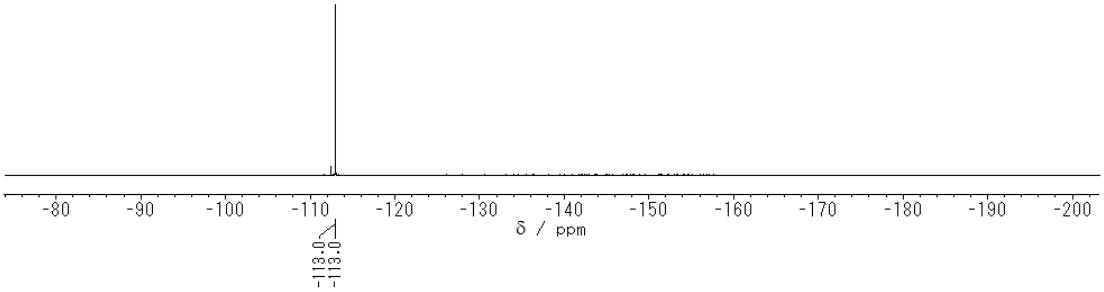

Figure S23. $^{19}F\{^{1}H\}$ NMR spectrum of **3k** (*trans*/*cis* mixture) in $CDCl_3$.

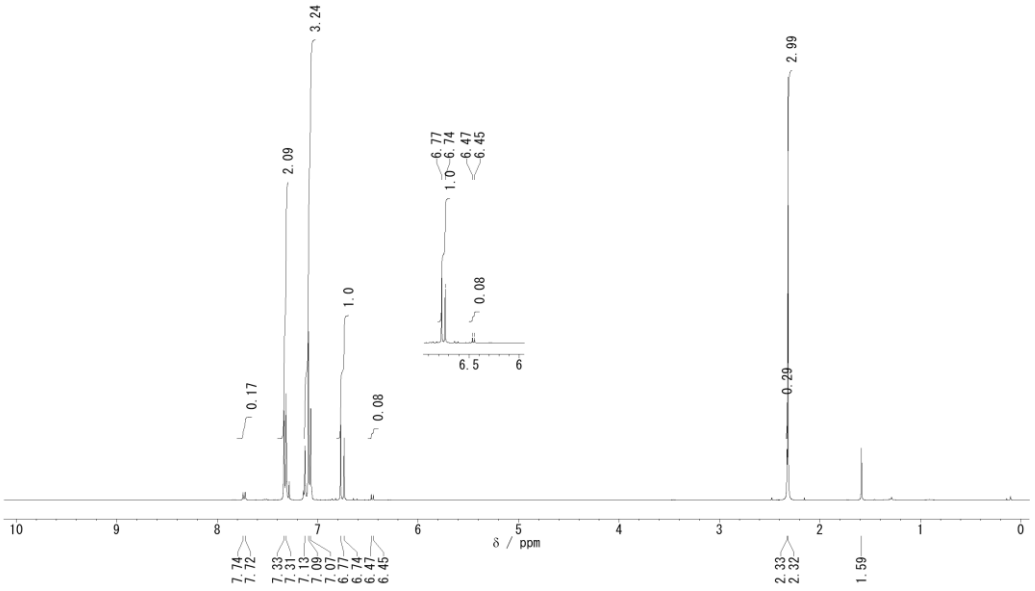

Figure S24. ^{1}H NMR spectrum of **3l** (*trans*/*cis* mixture) in $CDCl_3$.

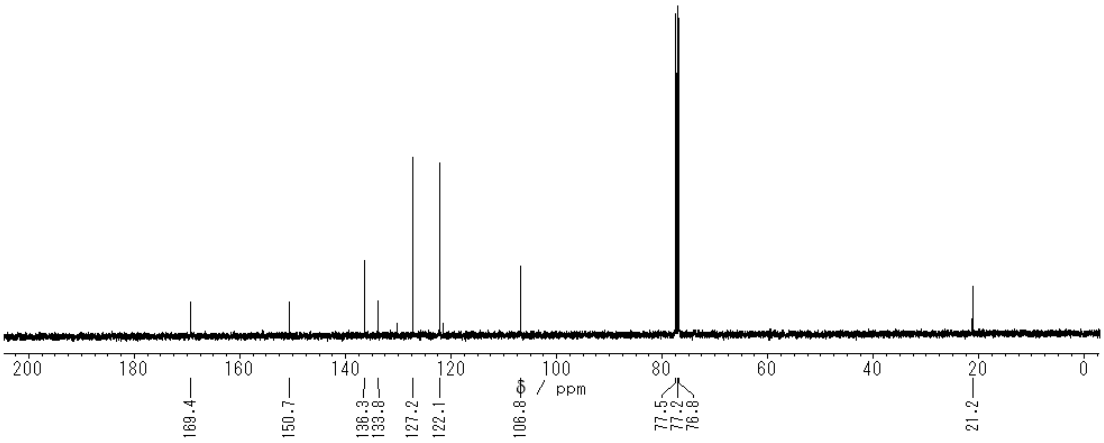

Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of **3l** (*trans*/*cis* mixture) in $CDCl_3$.

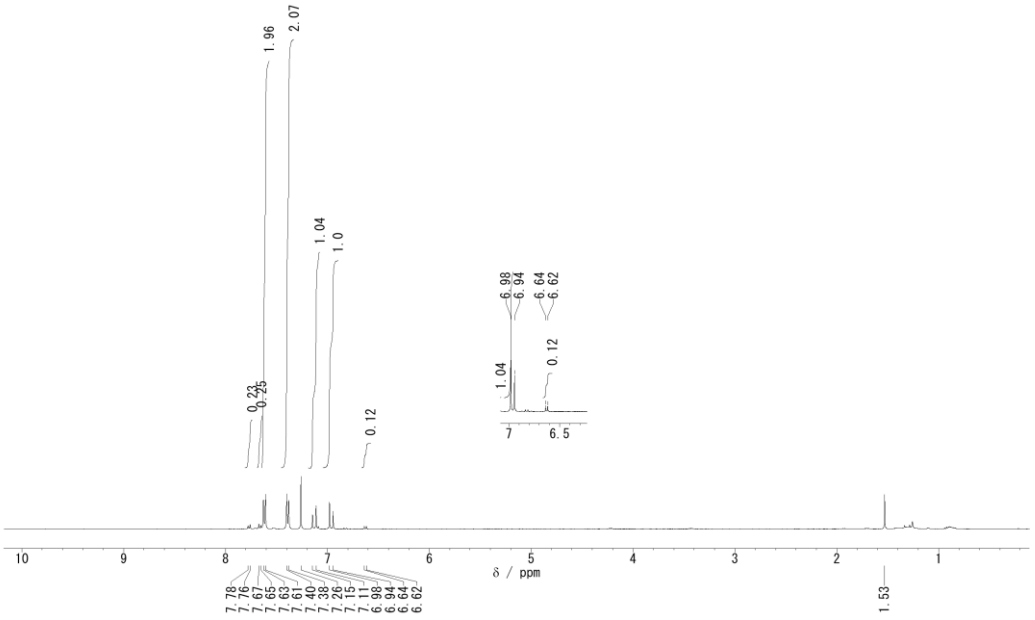

Figure S26. ^{1}H NMR spectrum of **3m** (*trans*/*cis* mixture) in $CDCl_3$.

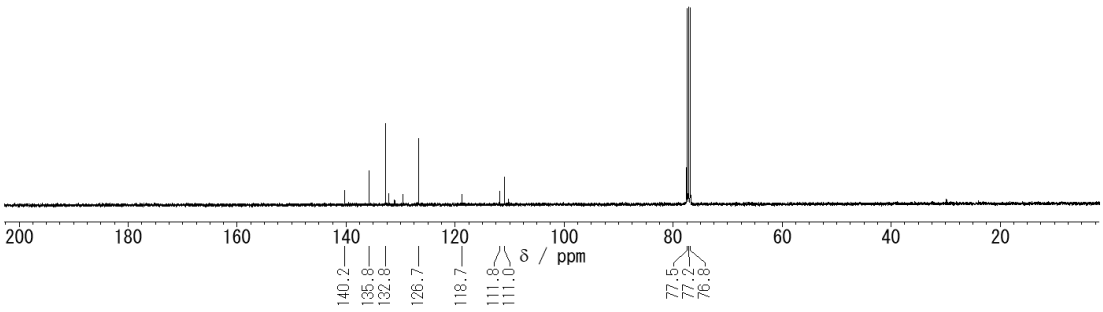

Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of **3m** (*trans*/*cis* mixture) in $CDCl_3$.

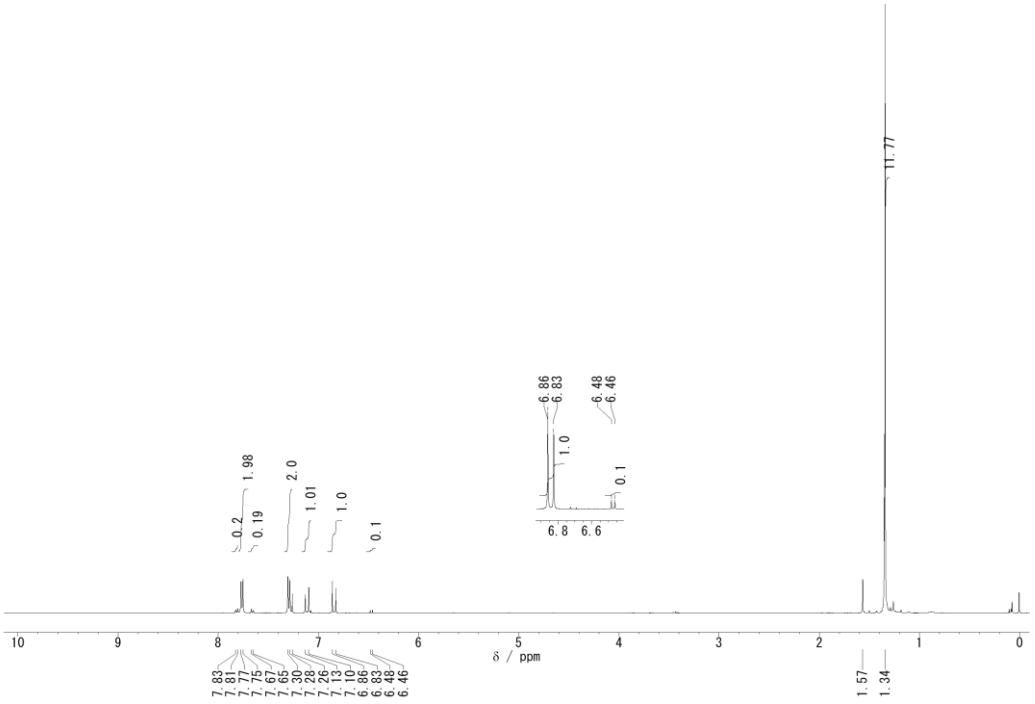

Figure S28. ^{1}H NMR spectrum of **3n** (*trans*/*cis* mixture) in $CDCl_3$.

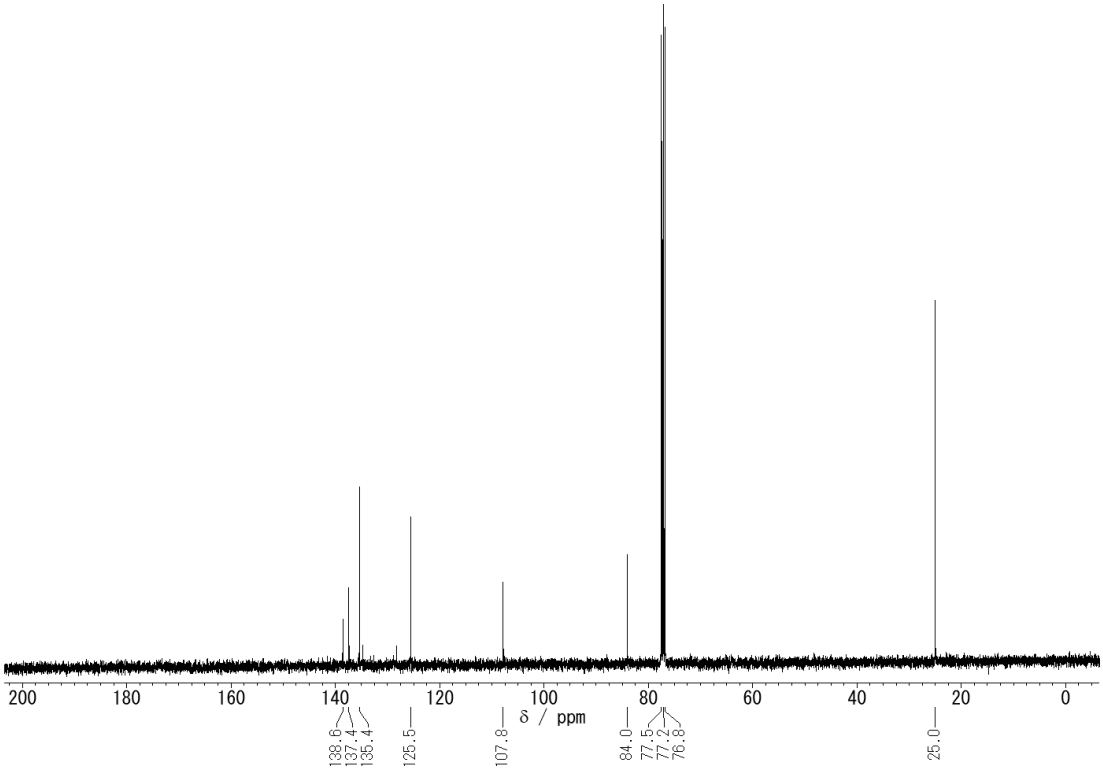

Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of **3n** (*trans*/*cis* mixture) in $CDCl_3$.

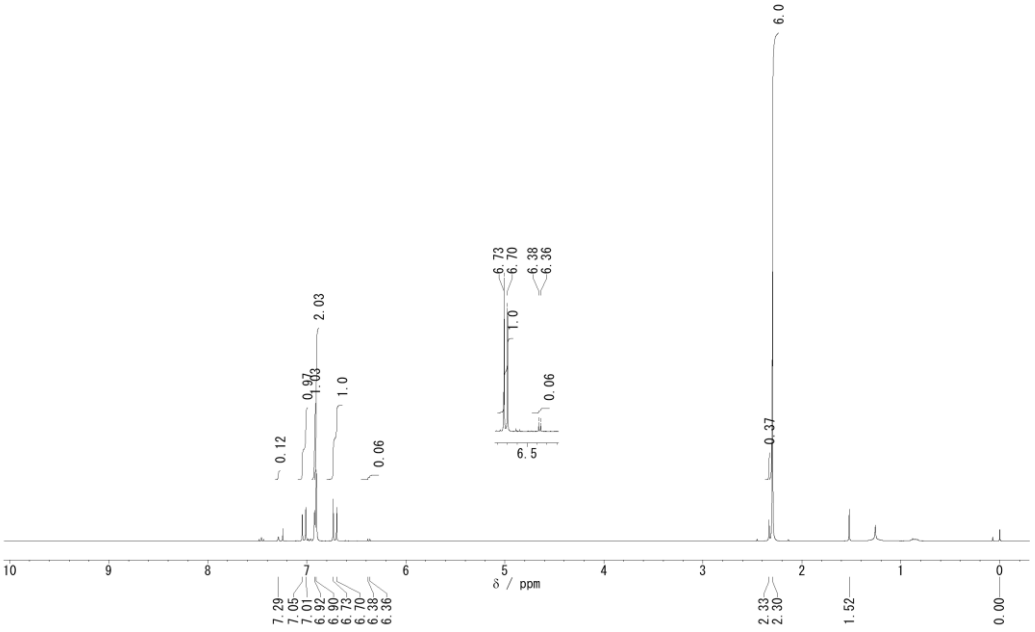

Figure S30. ^{1}H NMR spectrum of **3o** (*trans*/*cis* mixture) in $CDCl_3$.

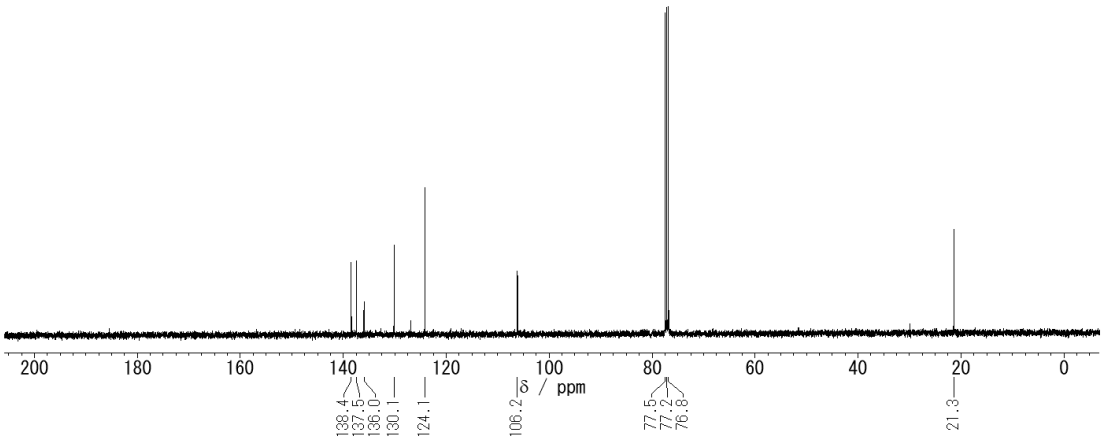

Figure S31. ^{13}C{^{1}H} NMR spectrum of **3o** (*trans*/*cis* mixture) in $CDCl_3$.

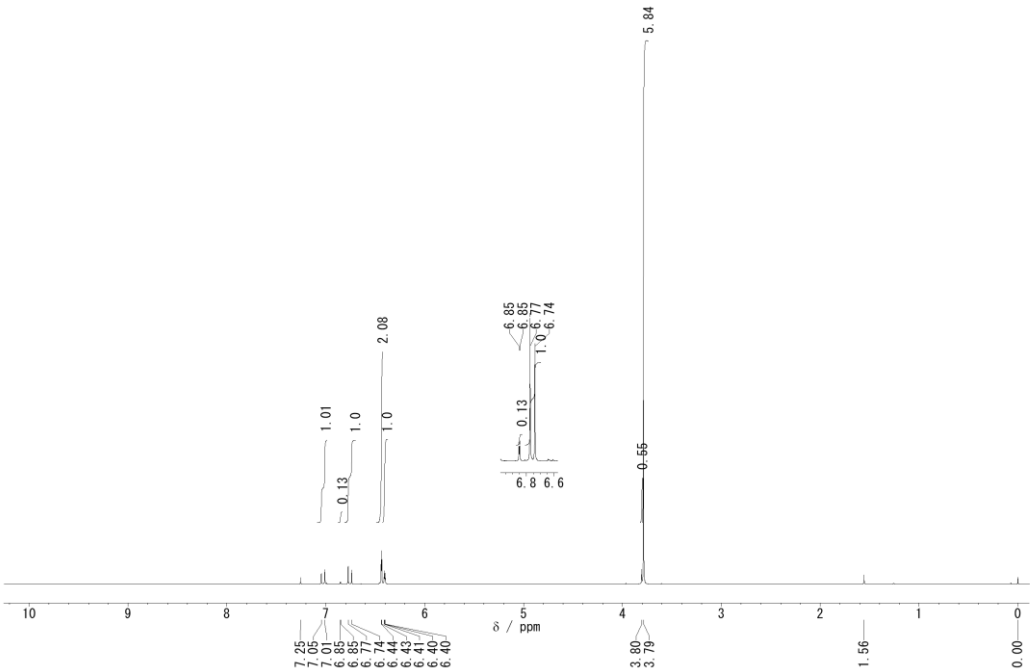

Figure S32. ^{1}H NMR spectrum of **3p** (*trans*/*cis* mixture) in $CDCl_3$.

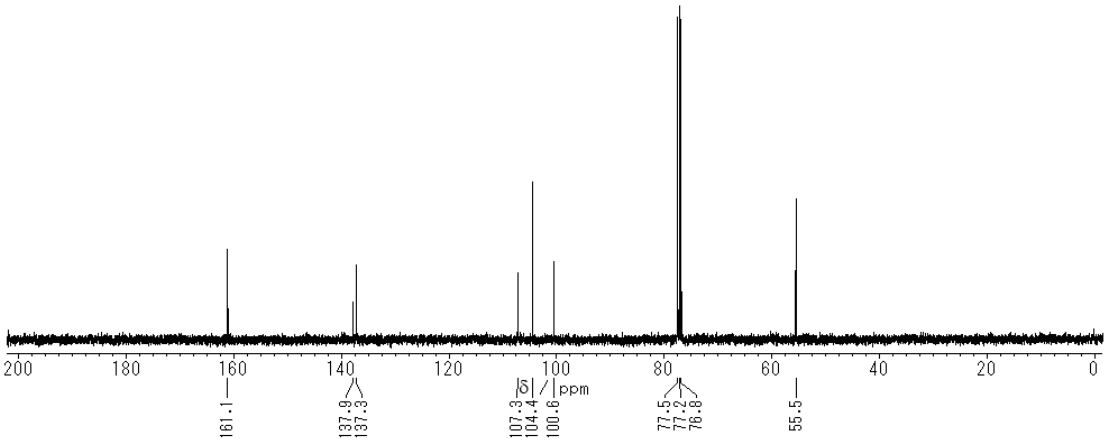

Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum of **3p** (*trans*/*cis* mixture) in $CDCl_3$.

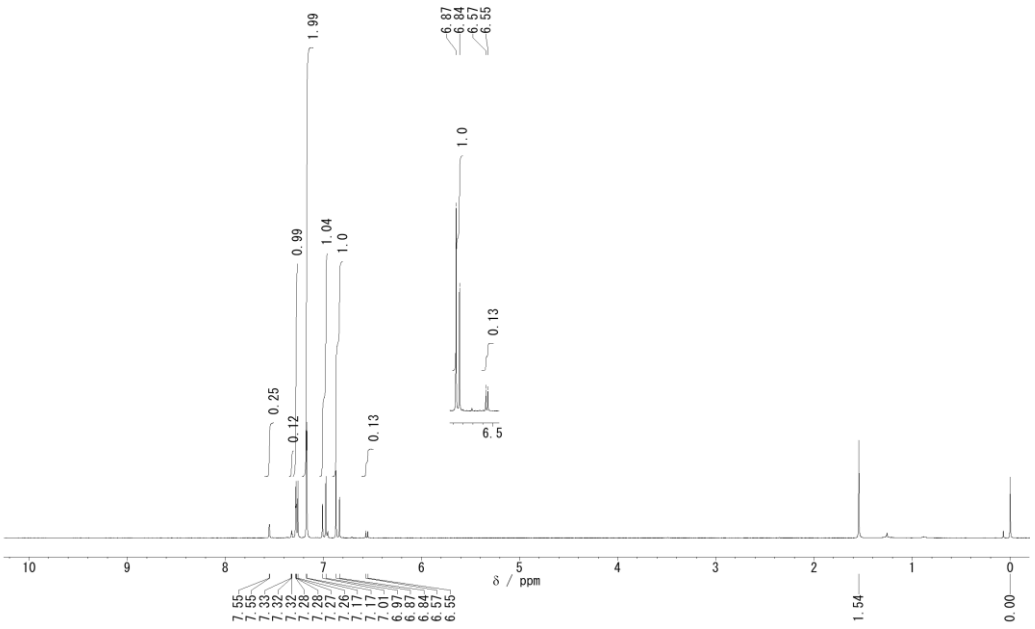

Figure S34. ^{1}H NMR spectrum of **3q** (*trans*/*cis* mixture) in $CDCl_3$.

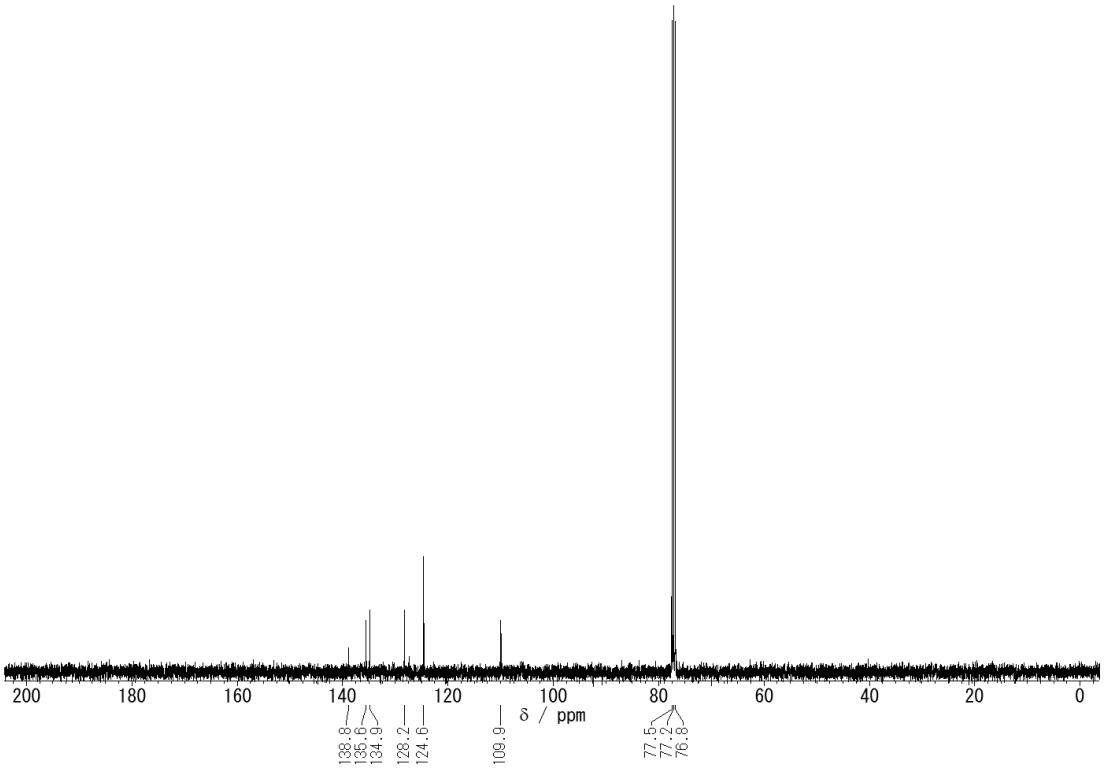

Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of **3q** (*trans*/*cis* mixture) in $CDCl_3$.

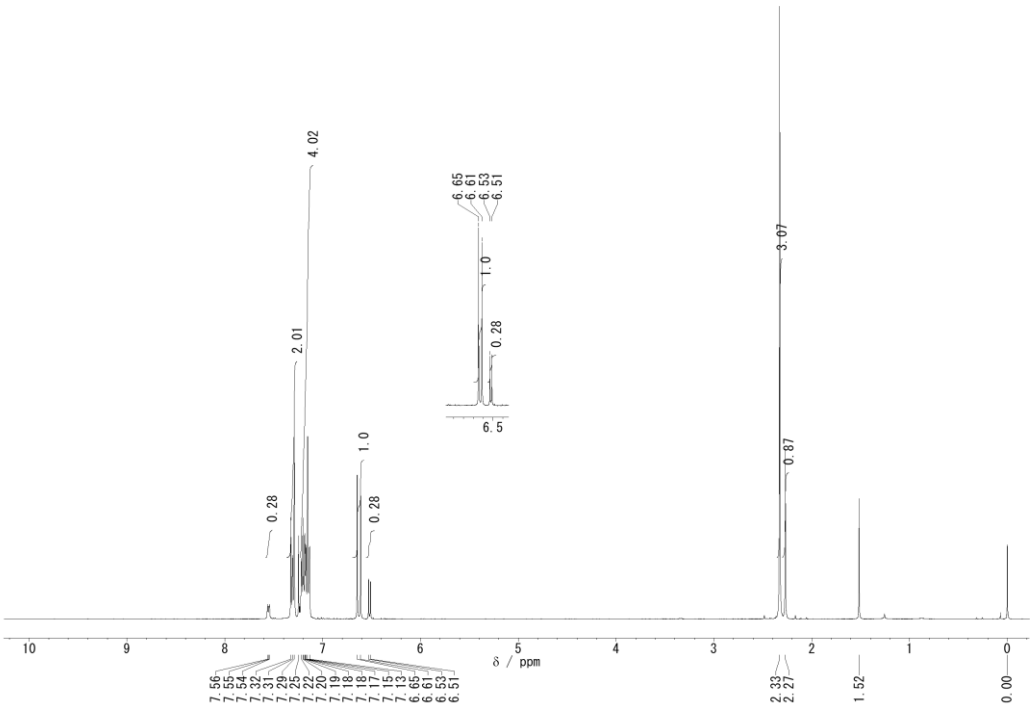

Figure S36. ^{1}H NMR spectrum of **3r** (*trans*/*cis* mixture) in $CDCl_3$.

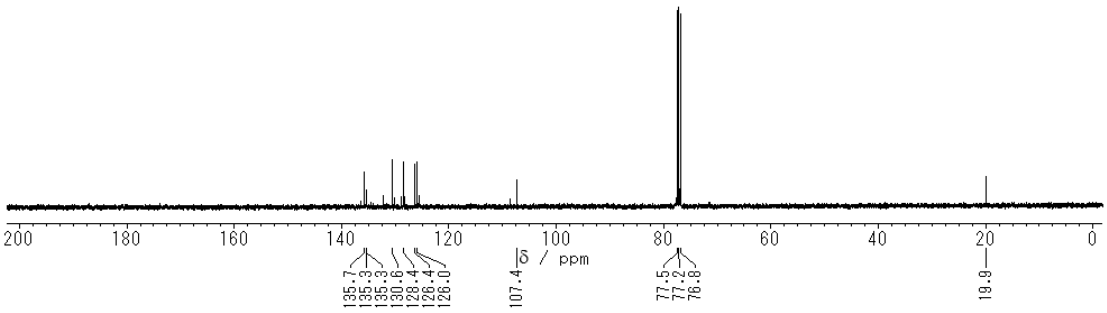

Figure S37. ^{13}C{^{1}H} NMR spectrum of **3r** (*trans*/*cis* mixture) in $CDCl_3$.

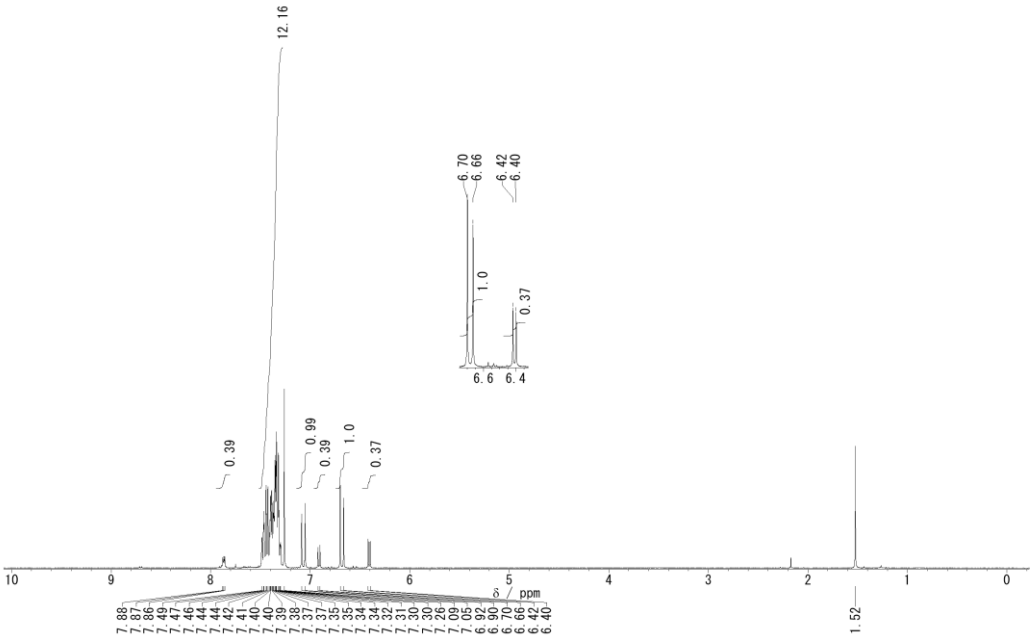

Figure S38. ^{1}H NMR spectrum of **3s** (*trans*/*cis* mixture) in $CDCl_3$.

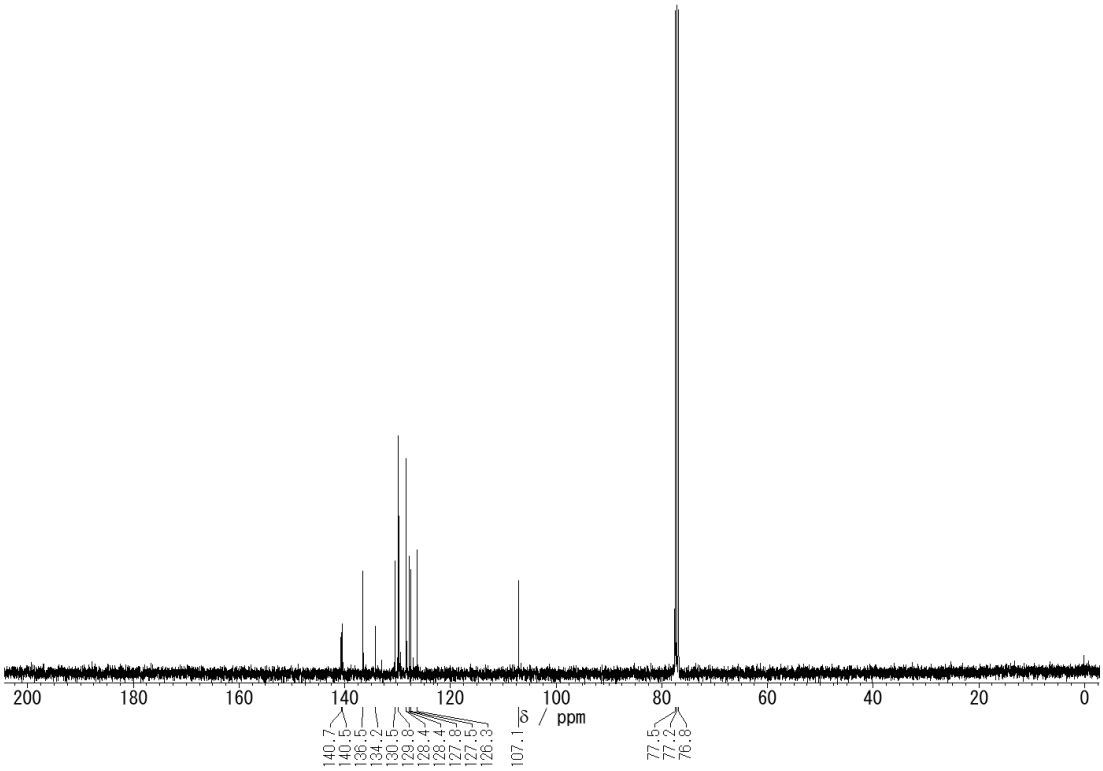

Figure S39. $^{13}C\{^{1}H\}$ NMR spectrum of **3s** (*trans*/*cis* mixture) in $CDCl_3$.

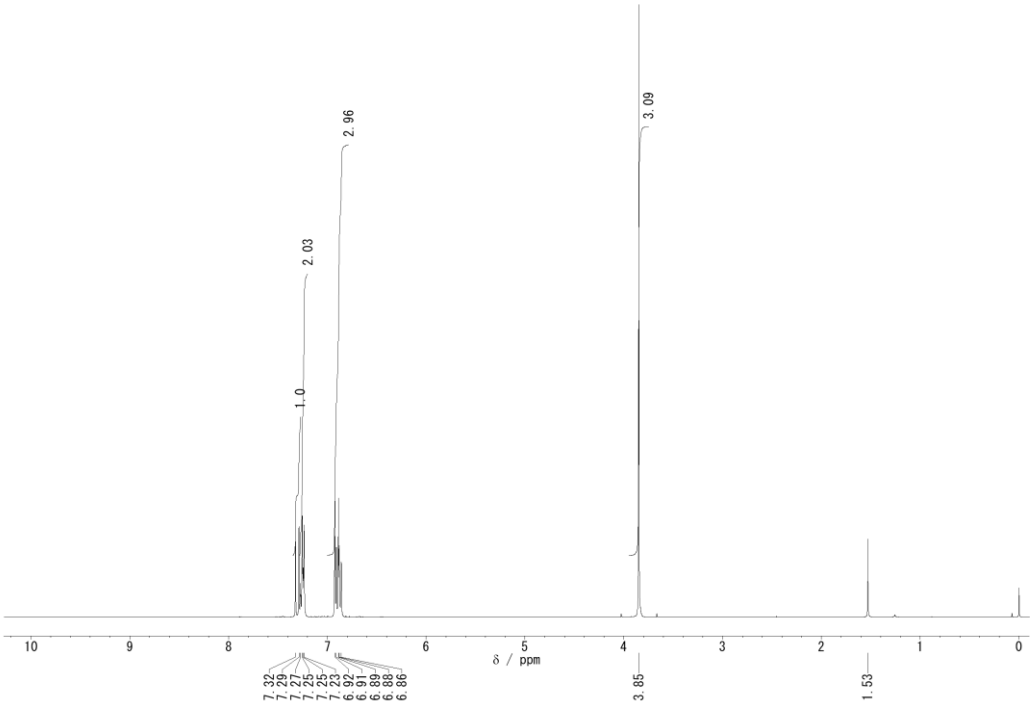

Figure S40. ^{1}H NMR spectrum of *trans*-**3t** in $CDCl_3$.

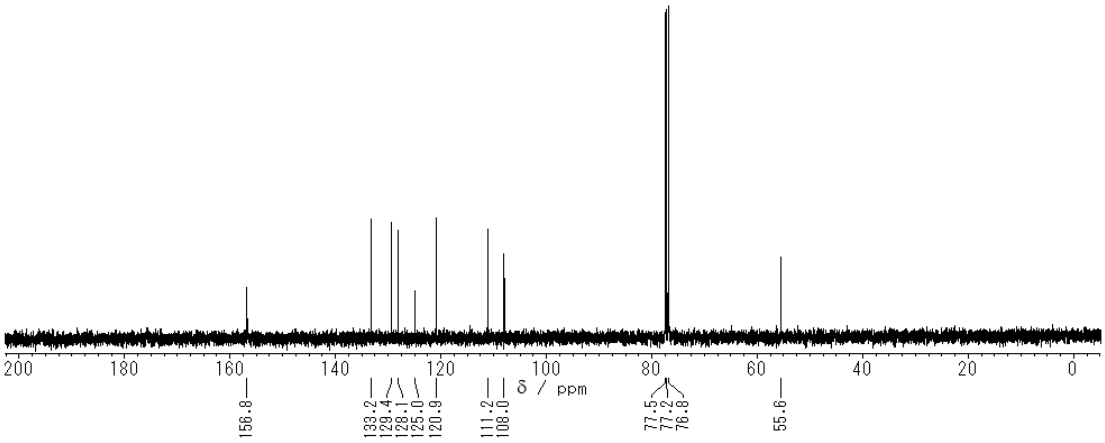

Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum of *trans*-**3t** in $CDCl_3$.

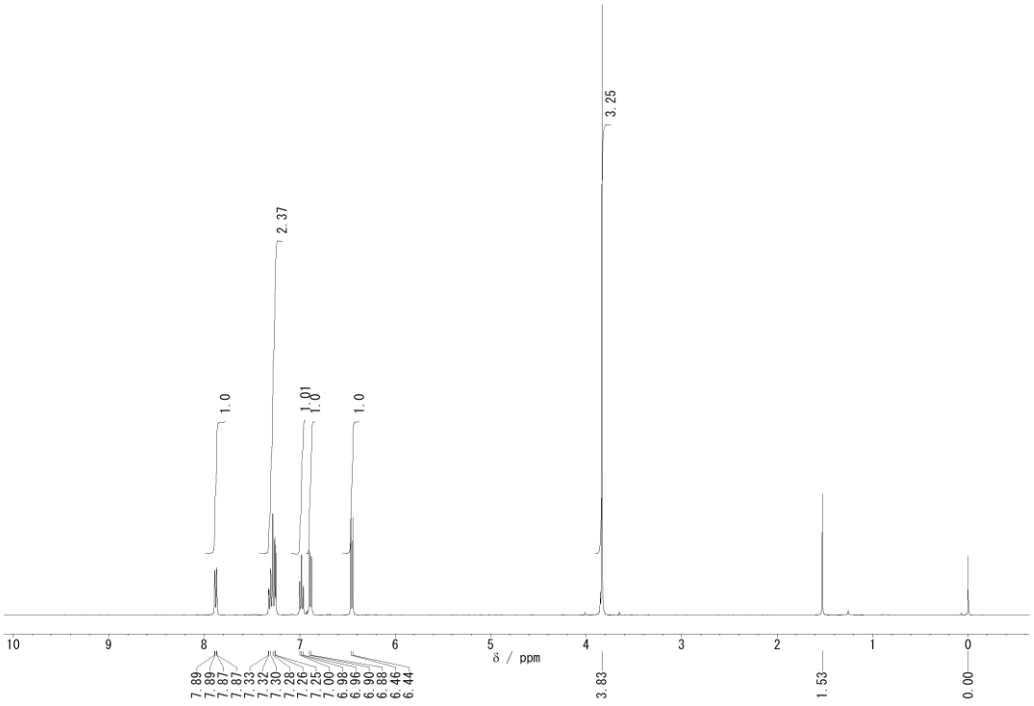

Figure S42. ^{1}H NMR spectrum of *cis*-**3t** in $CDCl_3$.

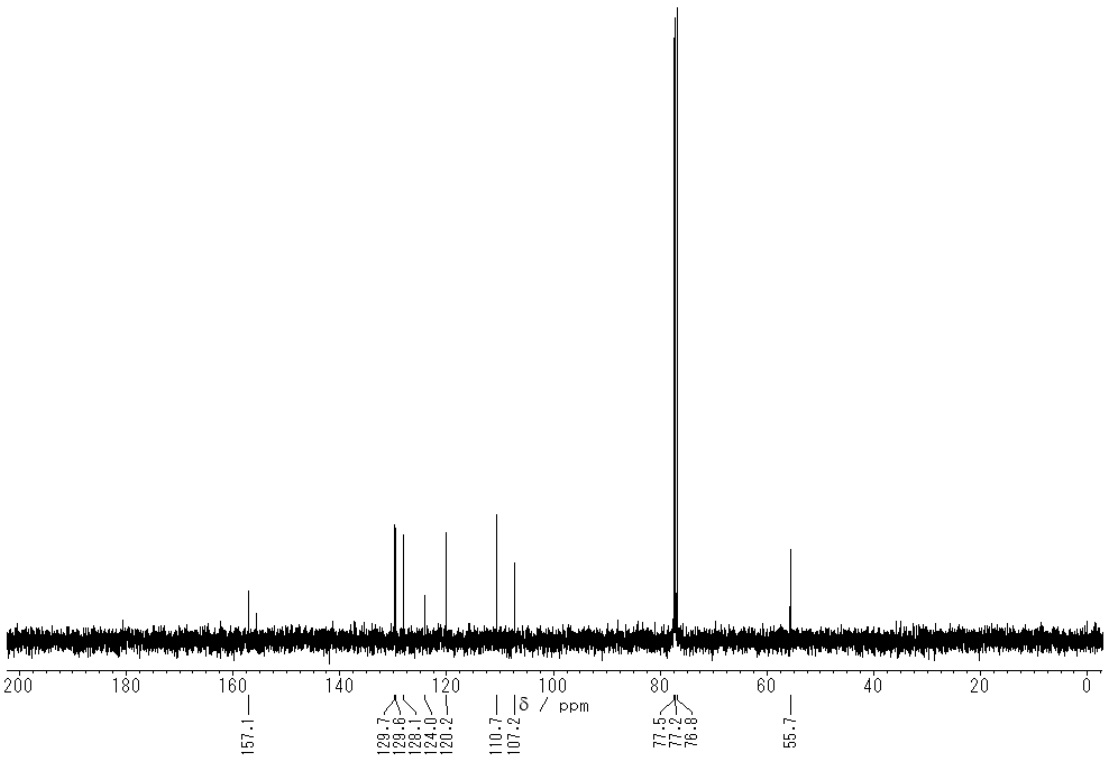

Figure S43. ^{13}C{^{1}H} NMR spectrum of *cis*-**3t** in $CDCl_3$.

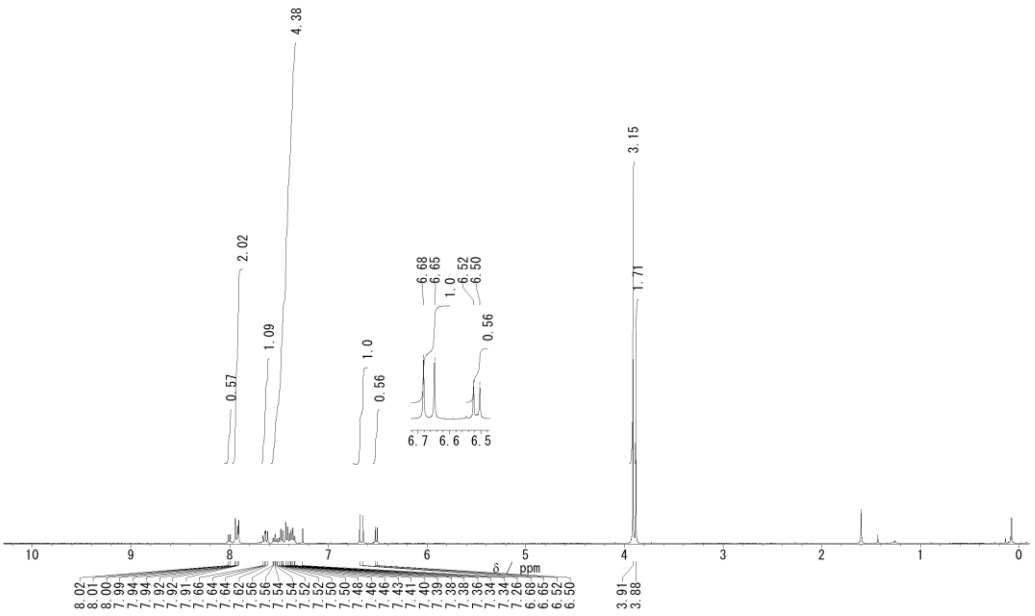

Figure S44. ^{1}H NMR spectrum of **3u** (*trans*/*cis* mixture) in $CDCl_3$.

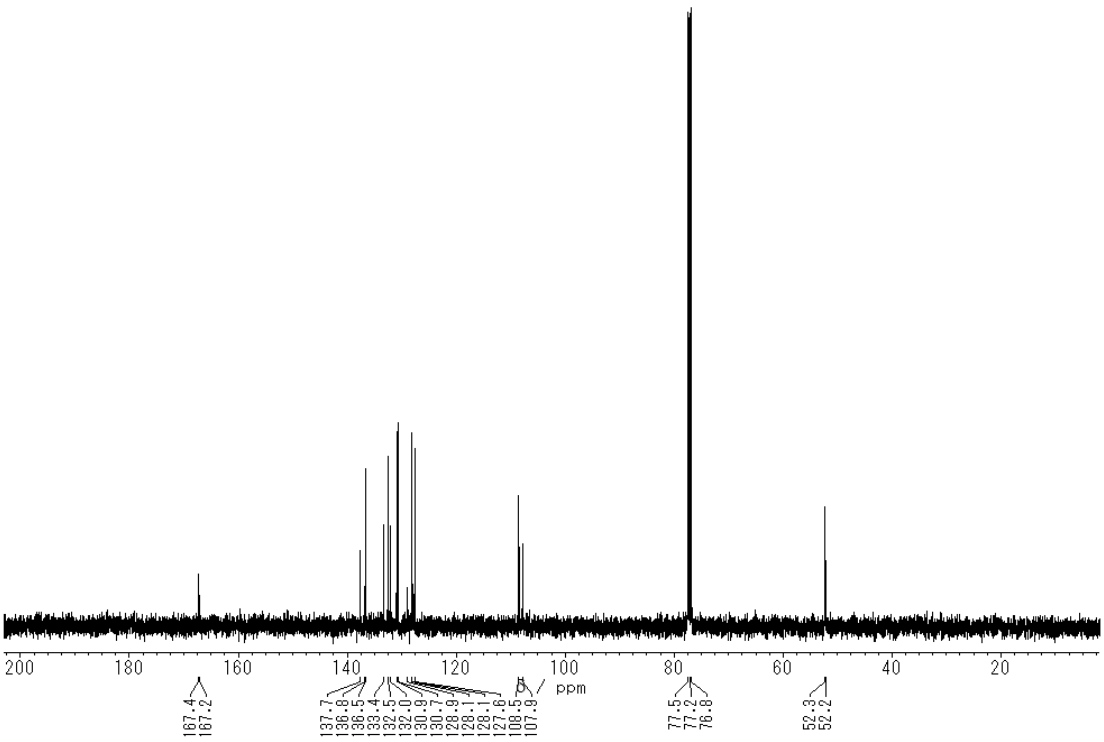

Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum of **3u** (*trans*/*cis* mixture) in $CDCl_3$.

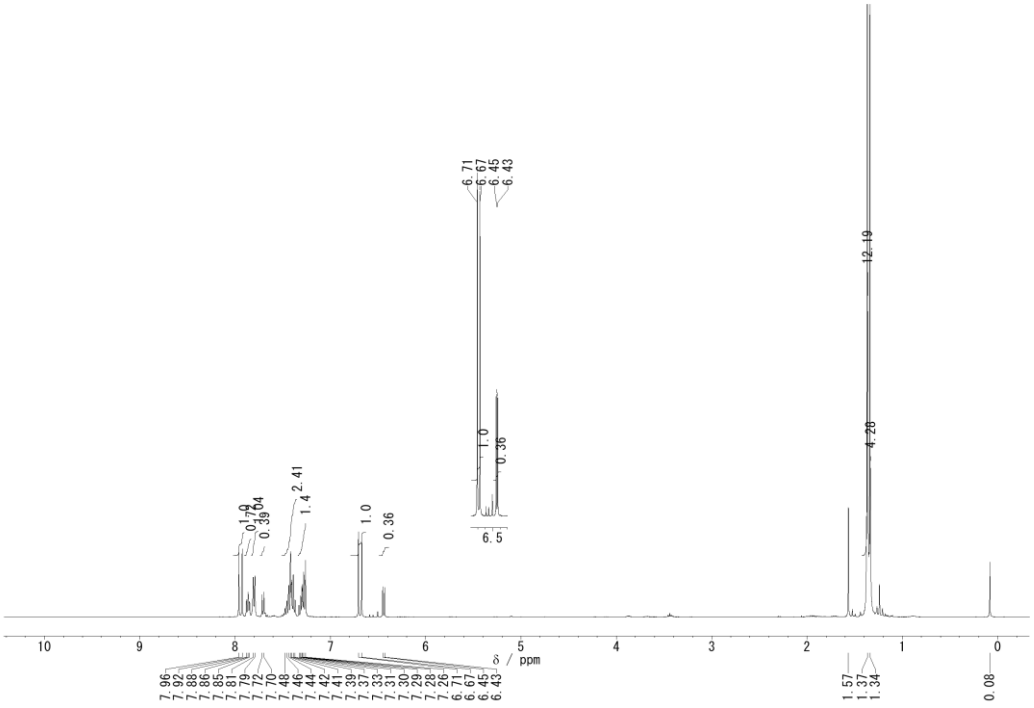

Figure S46. ^{1}H NMR spectrum of **3v** (*trans*/*cis* mixture) in $CDCl_3$.

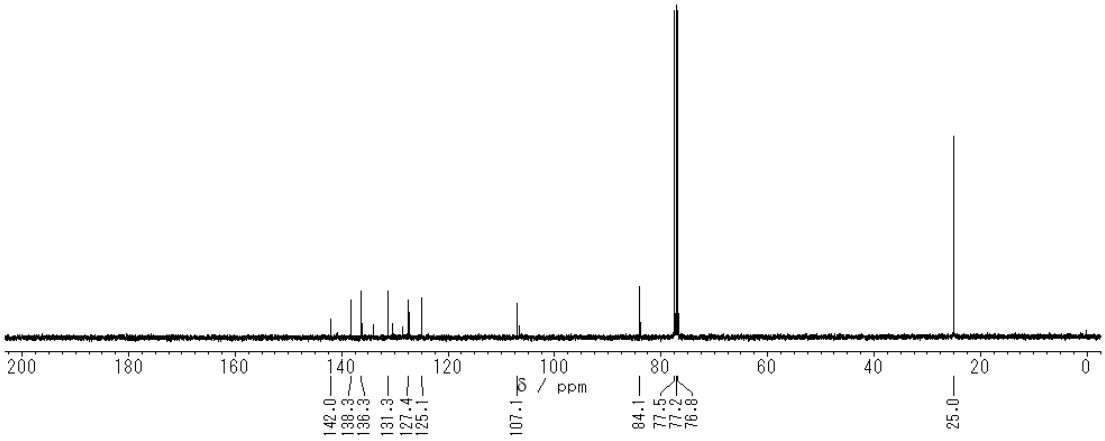

Figure S47. $^{13}C\{^{1}H\}$ NMR spectrum of **3v** (*trans*/*cis* mixture) in $CDCl_3$.

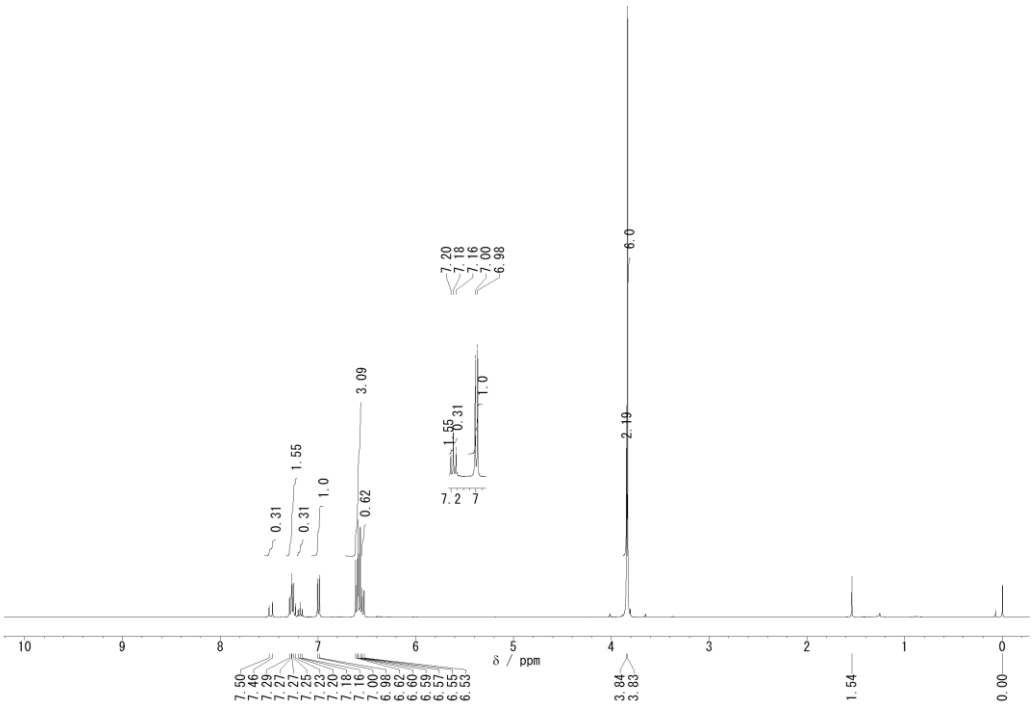

Figure S48. ^{1}H NMR spectrum of **3w** (*trans*/*cis* mixture) in $CDCl_3$.

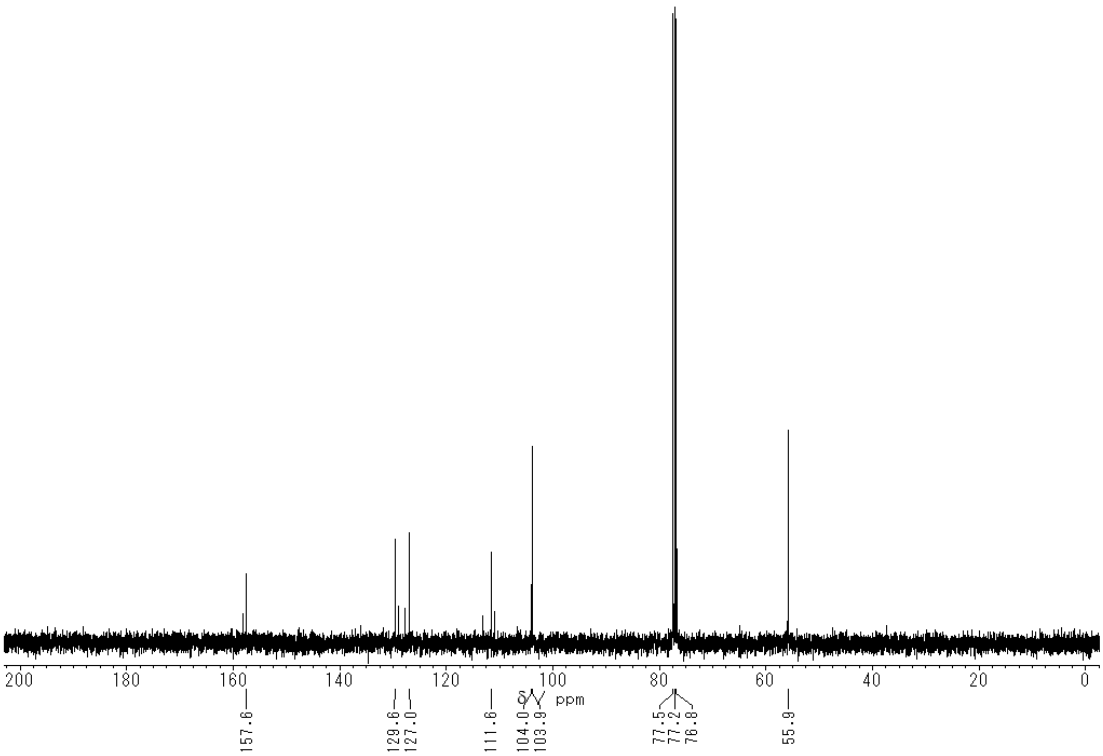

Figure S49. $^{13}C\{^{1}H\}$ NMR spectrum of **3w** (*trans*/*cis* mixture) in $CDCl_3$.

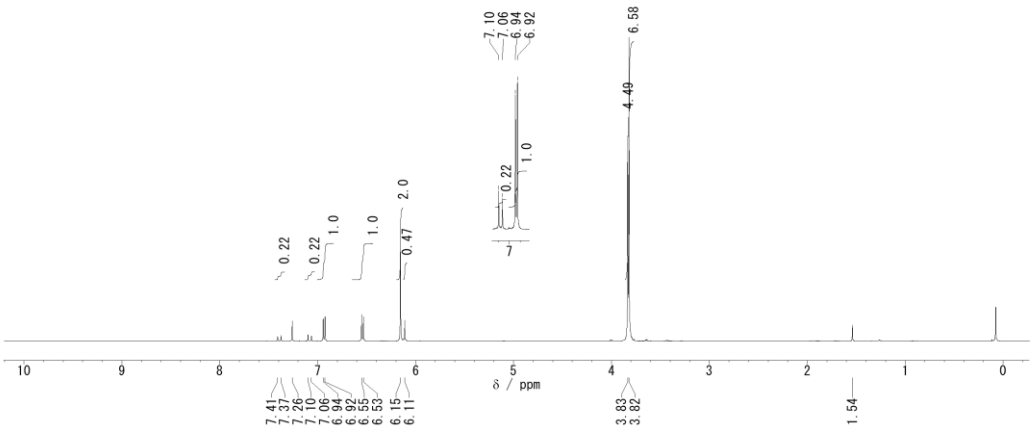

Figure S50. ^{1}H NMR spectrum of **3x** (*trans*/*cis* mixture) in $CDCl_3$.

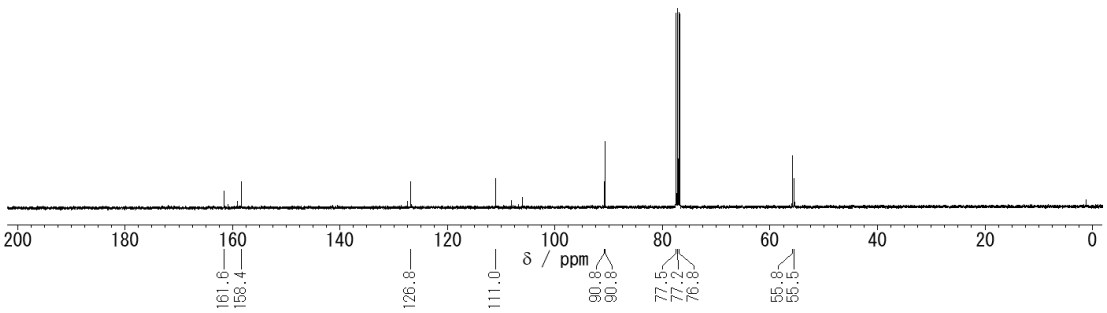

Figure S51. $^{13}C\{^{1}H\}$ NMR spectrum of **3x** (*trans*/*cis* mixture) in $CDCl_3$.

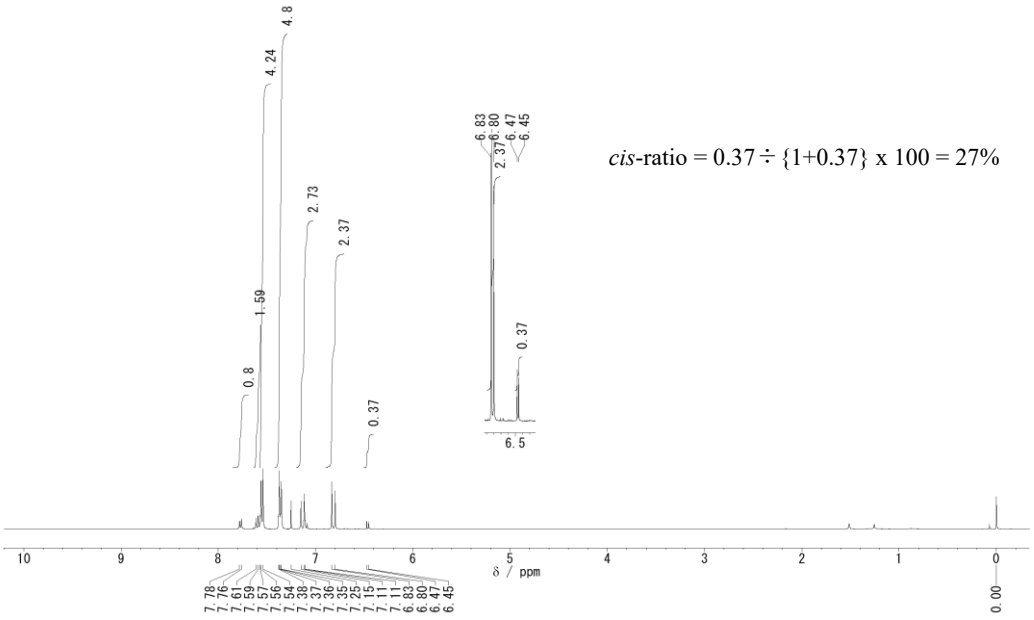

Figure S52. ^{1}H NMR spectrum of **3y** (*trans*/*trans* and *trans*/*cis* mixture) in $CDCl_3$.

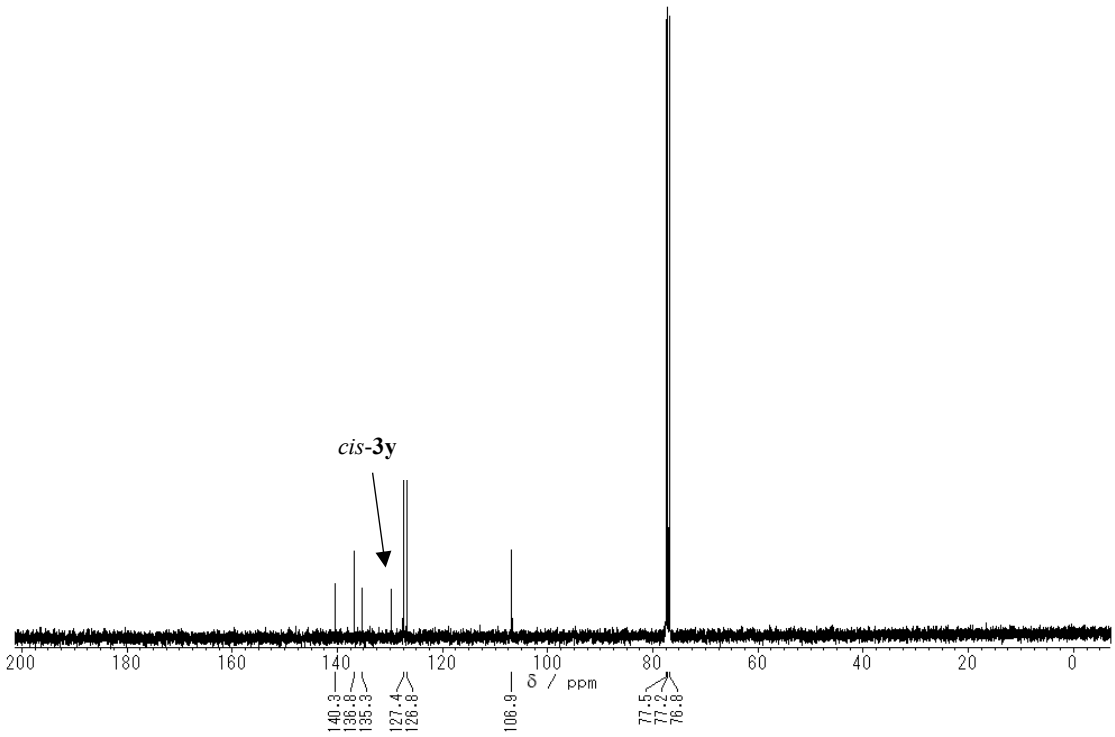

Figure S53. $^{13}C\{^{1}H\}$ NMR spectrum of **3y** (*trans*/*trans* and *trans*/*cis* mixture) in $CDCl_3$.

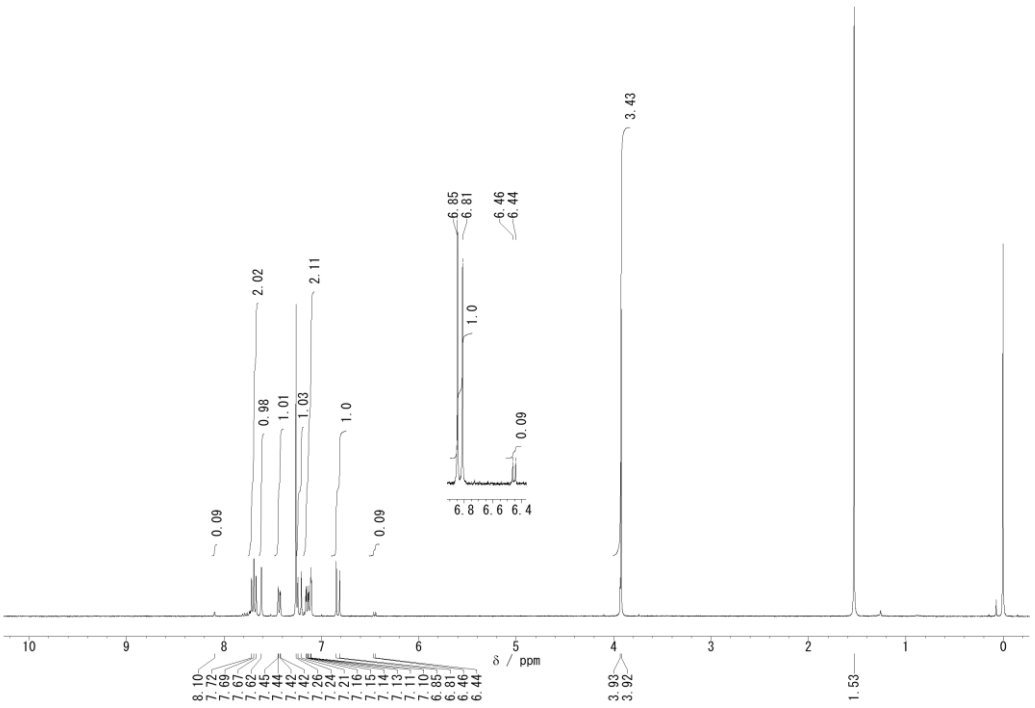

Figure S54. ^{1}H NMR spectrum of **3z** (*trans*/*cis* mixture) in $CDCl_3$.

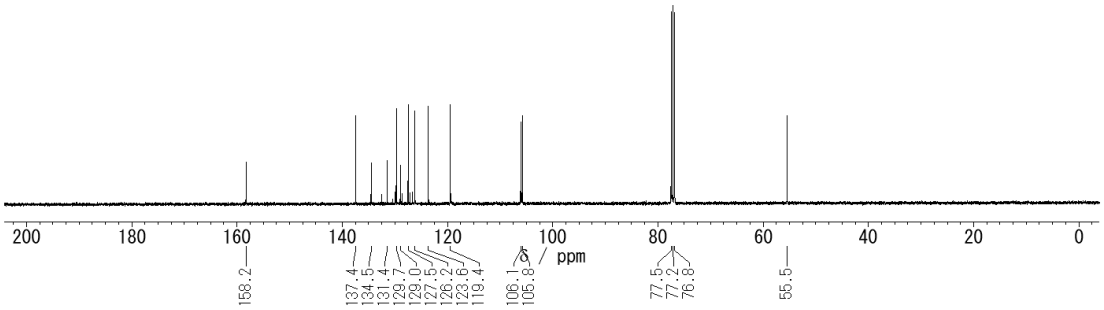

Figure S55. $^{13}C\{^{1}H\}$ NMR spectrum of **3z** (*trans*/*cis* mixture) in $CDCl_3$.

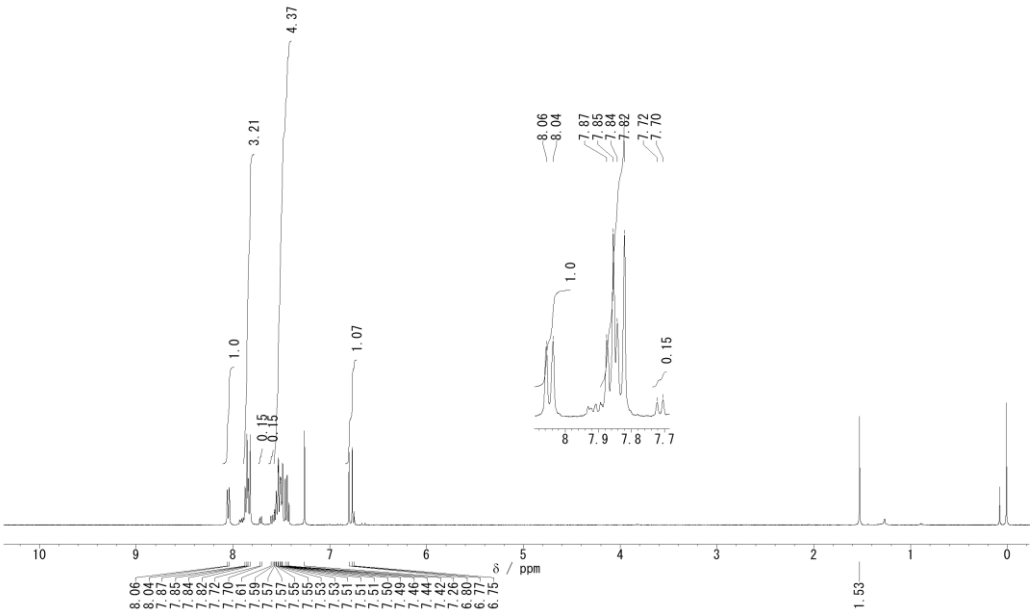

Figure S56. ^{1}H NMR spectrum of **3aa** (*trans*/*cis* mixture) in $CDCl_3$

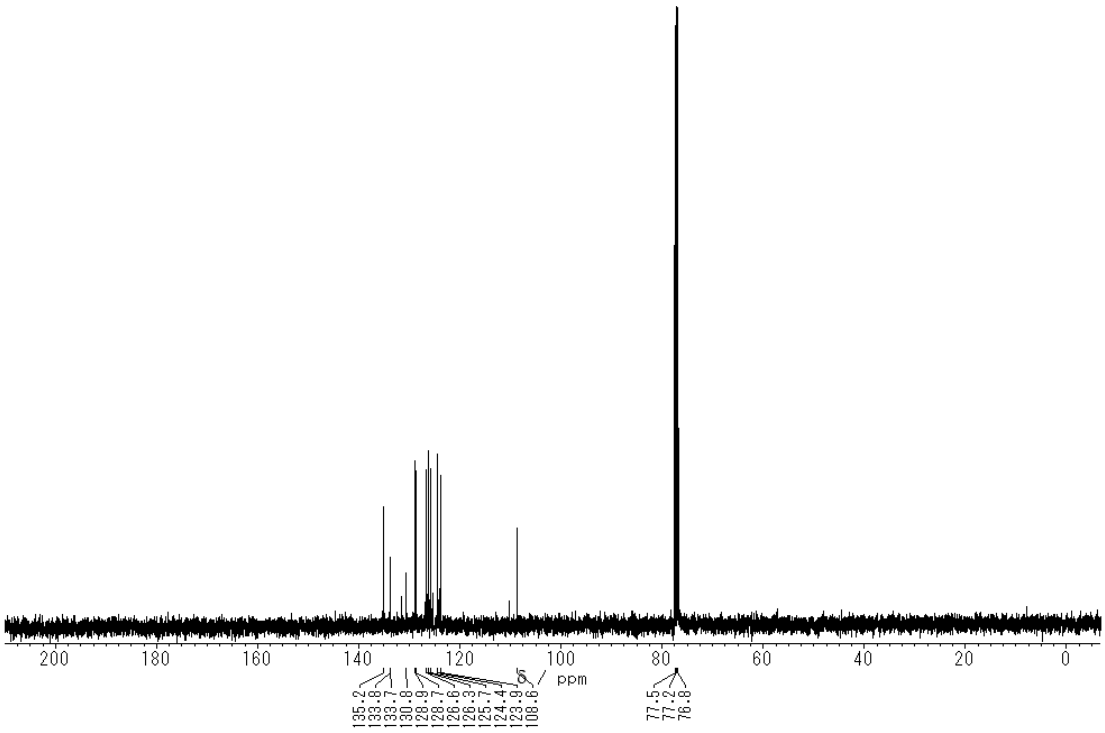

Figure S57. $^{13}C\{^{1}H\}$ NMR spectrum of **3aa** (*trans*/*cis* mixture) in $CDCl_3$.

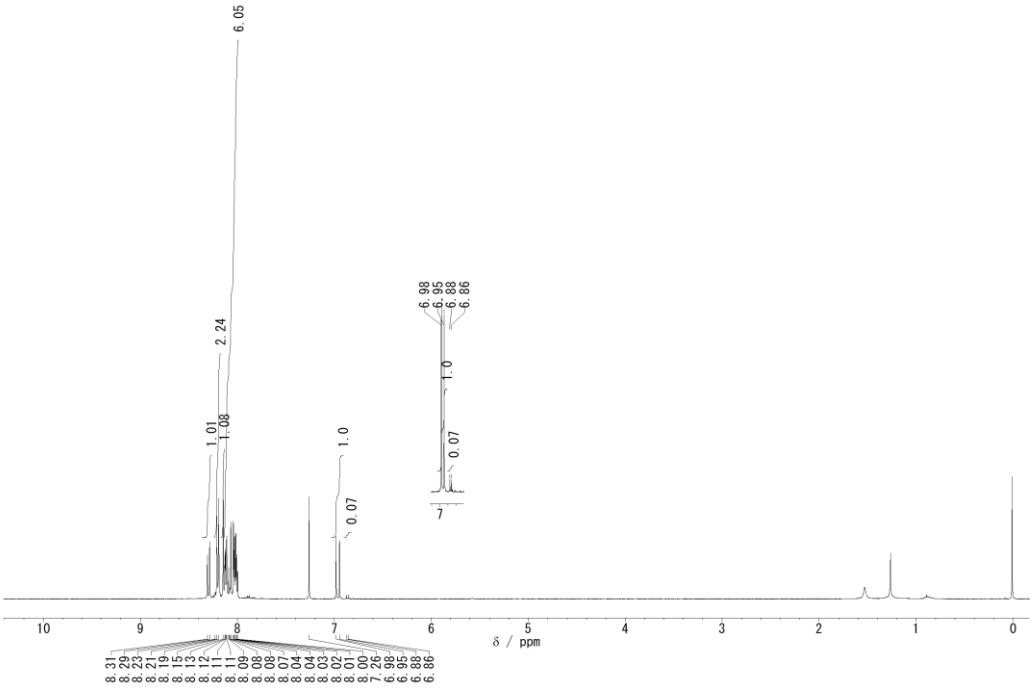

Figure S58. ^{1}H NMR spectrum of **3ab** (*trans*/*cis* mixture) in $CDCl_3$.

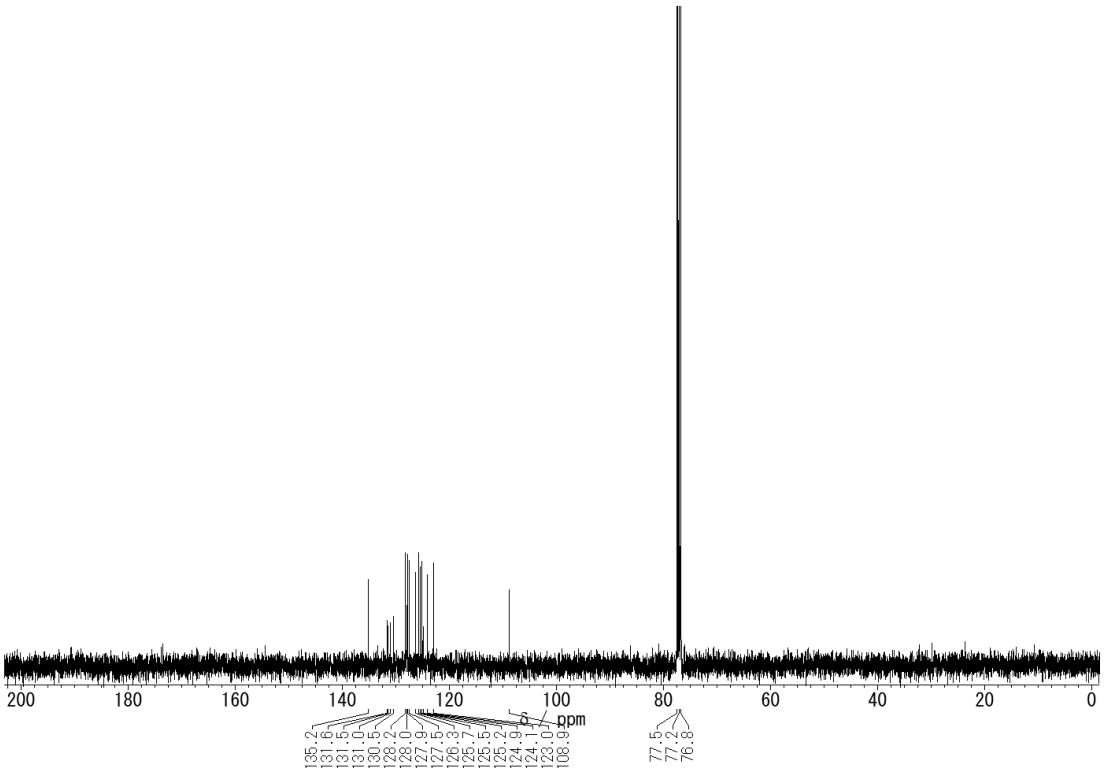

Figure S59. $^{13}C\{^{1}H\}$ NMR spectrum of **3ab** (*trans*/*cis* mixture) in $CDCl_3$.

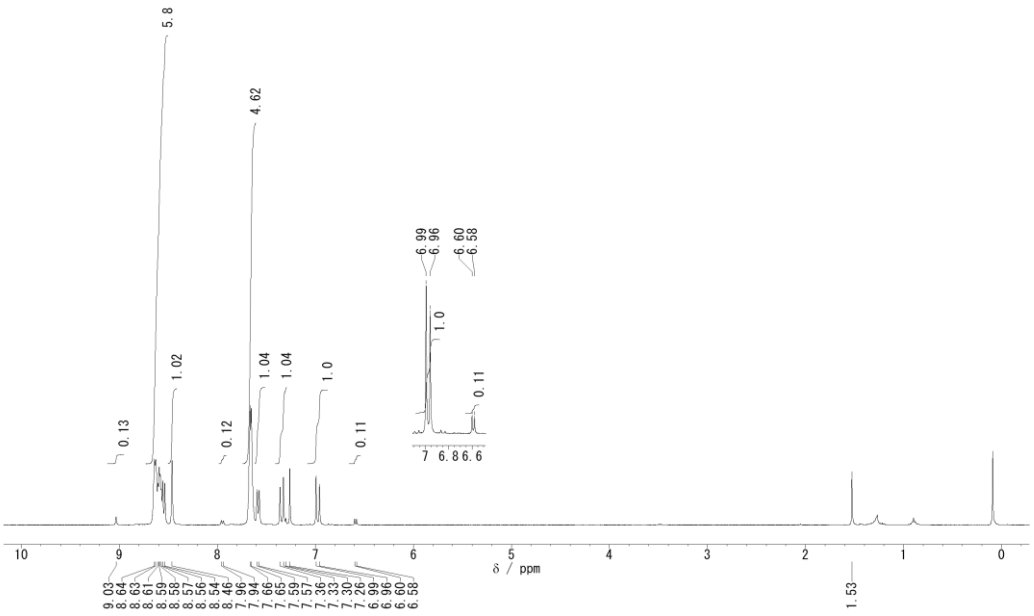

Figure S60. ^{1}H NMR spectrum of **3ac** (*trans*/*cis* mixture) in $CDCl_3$.

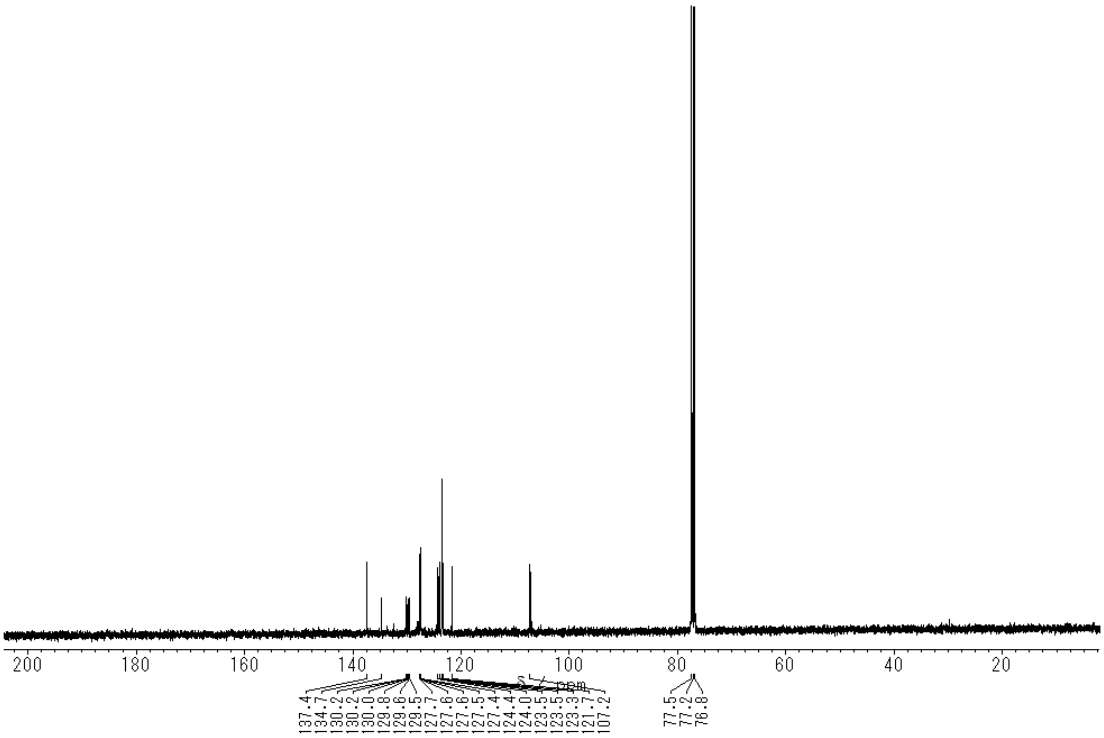

Figure S61. $^{13}C\{^{1}H\}$ NMR spectrum of **3ac** (*trans*/*cis* mixture) in $CDCl_3$.

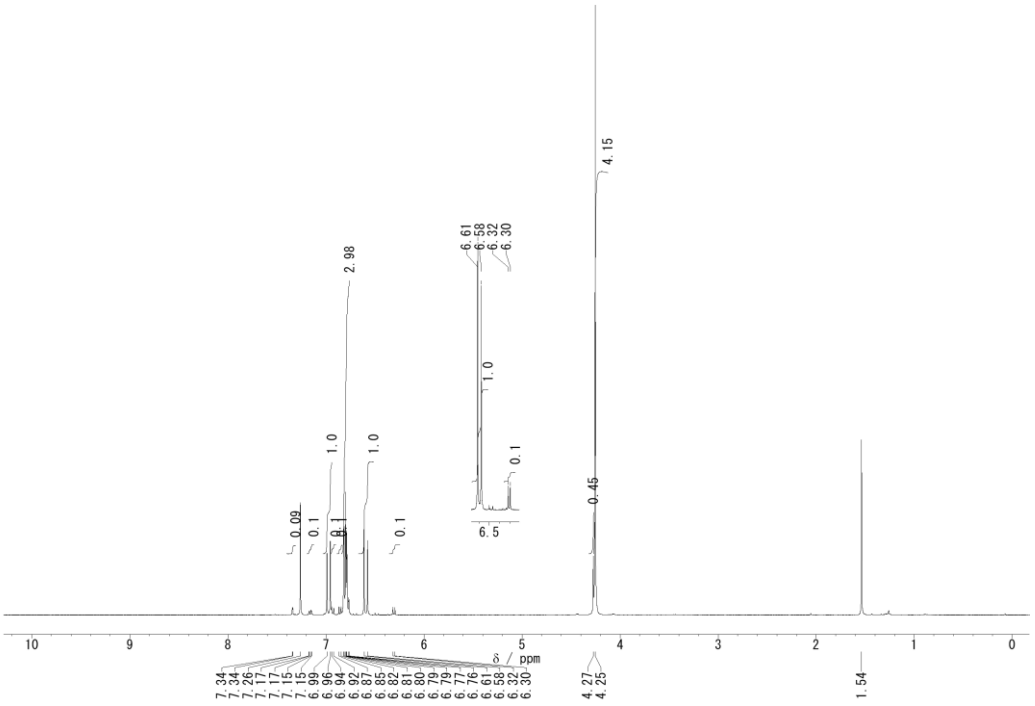

Figure S62. ^{1}H NMR spectrum of **3ad** (*trans*/*cis* mixture) in $CDCl_3$.

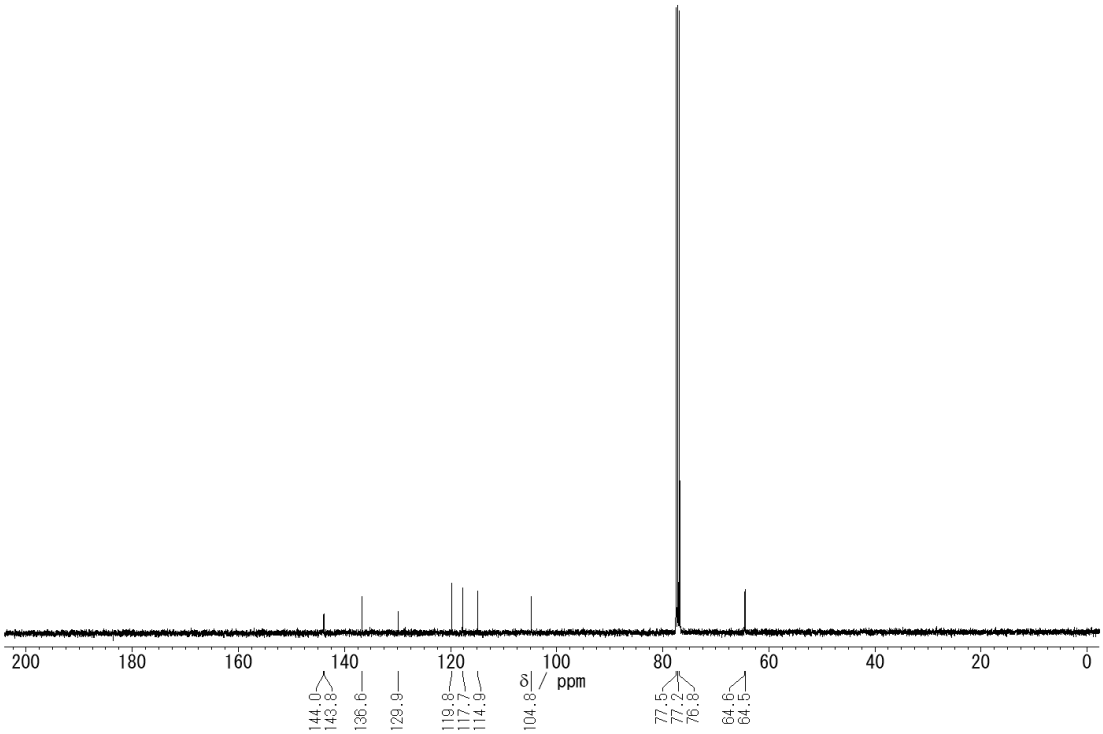

Figure S63. $^{13}C\{^{1}H\}$ NMR spectrum of **3ad** (*trans*/*cis* mixture) in $CDCl_3$.

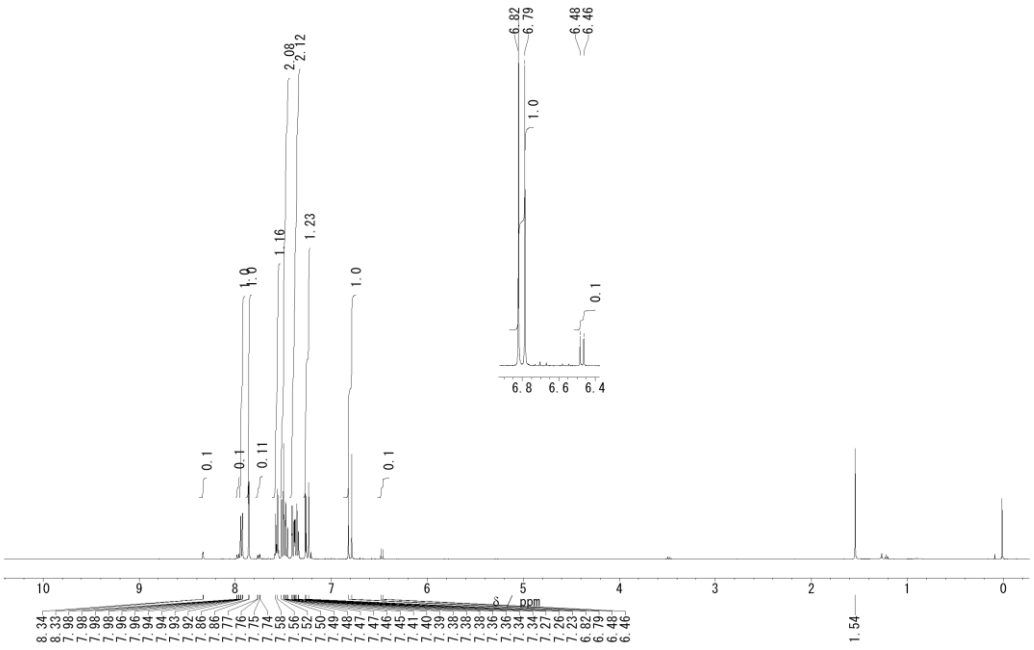

Figure S64. ^{1}H NMR spectrum of **3ae** (*trans*/*cis* mixture) in $CDCl_3$.

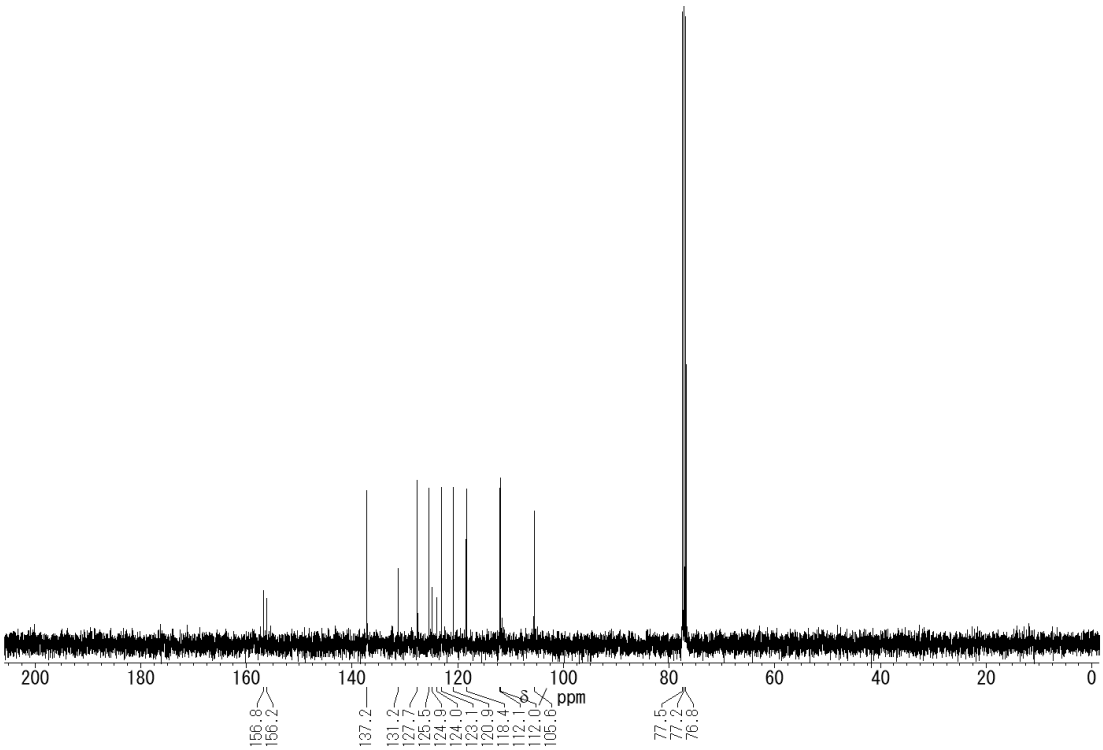

Figure S65. $^{13}C\{^{1}H\}$ NMR spectrum of **3ae** (*trans*/*cis* mixture) in $CDCl_3$.

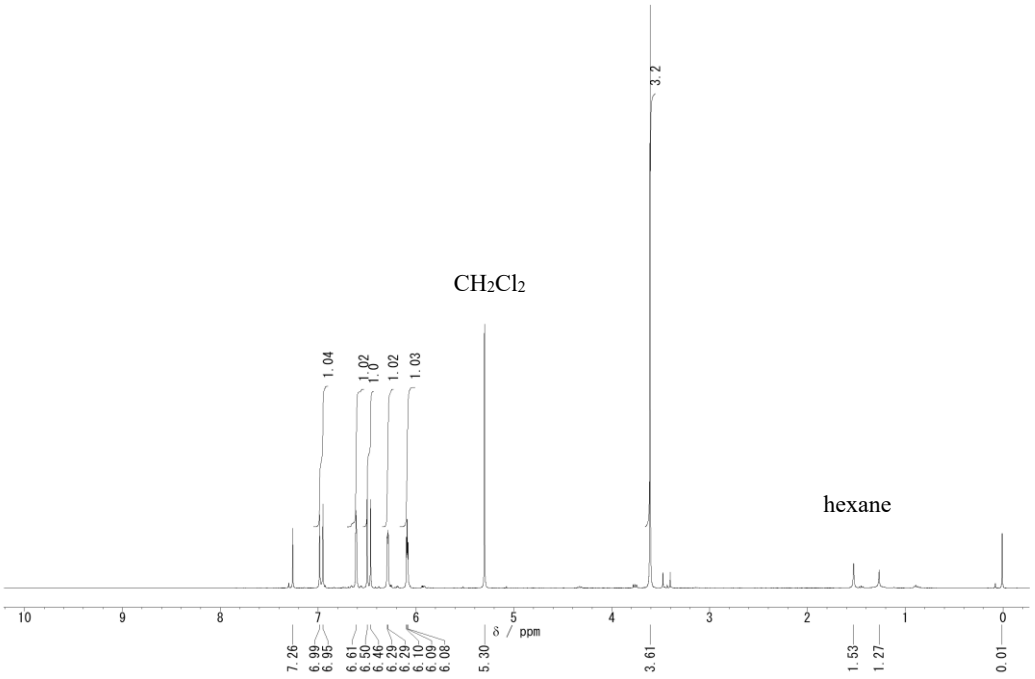

Figure S66. ^{1}H NMR spectrum of **3af** in $CDCl_3$.

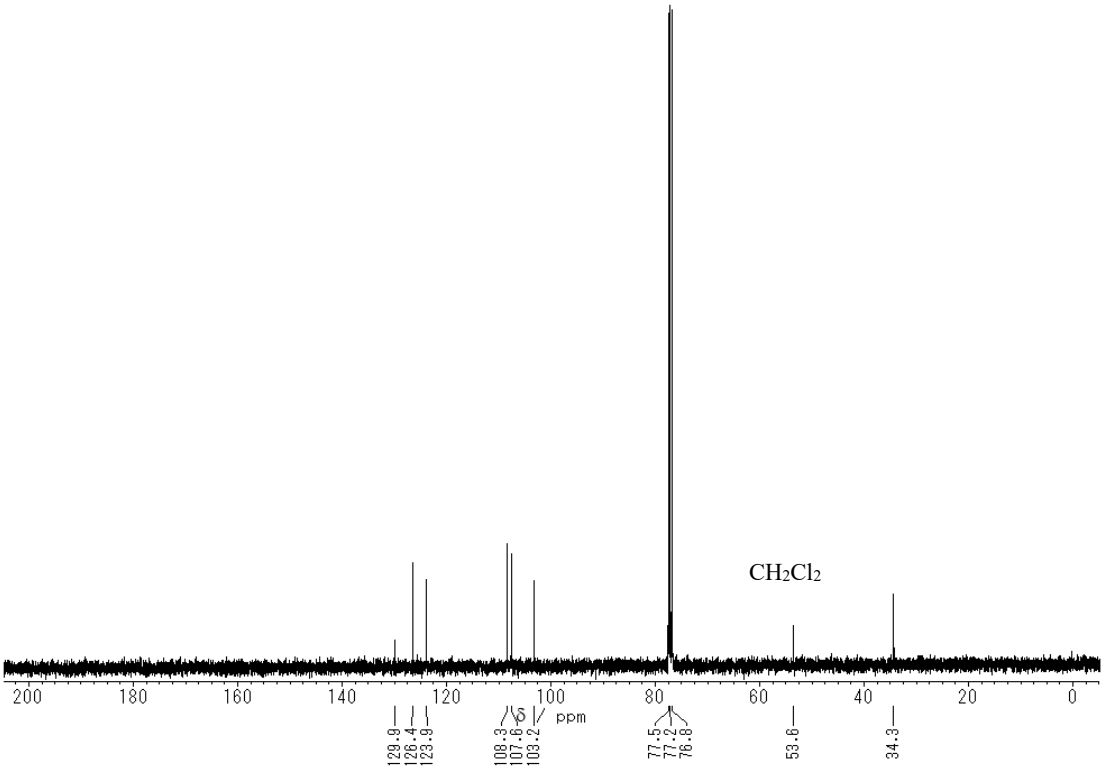

Figure S67. ^{13}C{^{1}H} NMR spectrum of **3af** in $CDCl_3$.

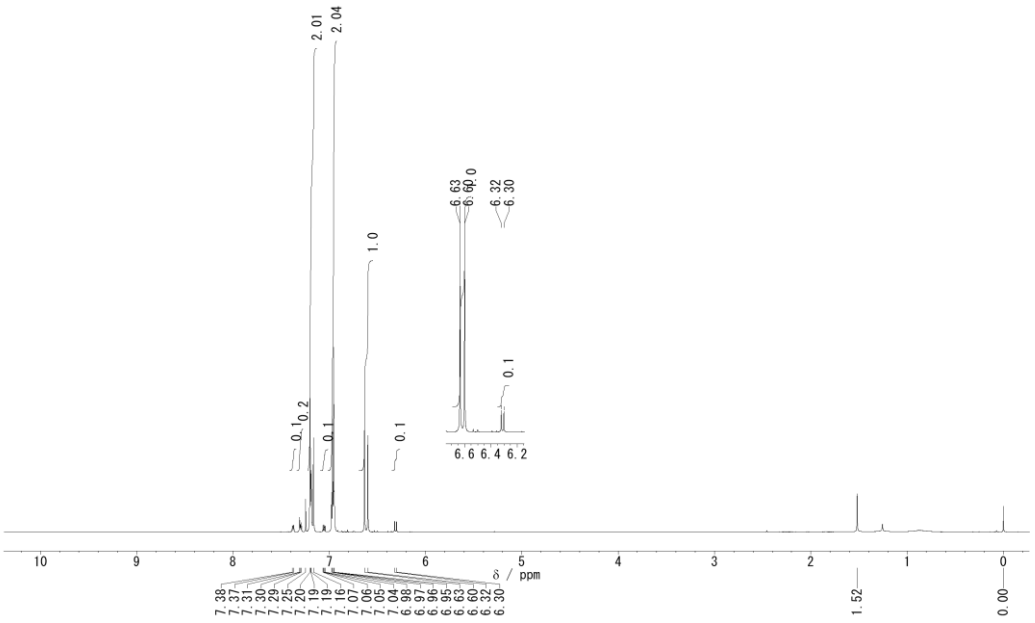

Figure S68. ^{1}H NMR spectrum of **3ag** (*trans*/*cis* mixture) in $CDCl_3$.

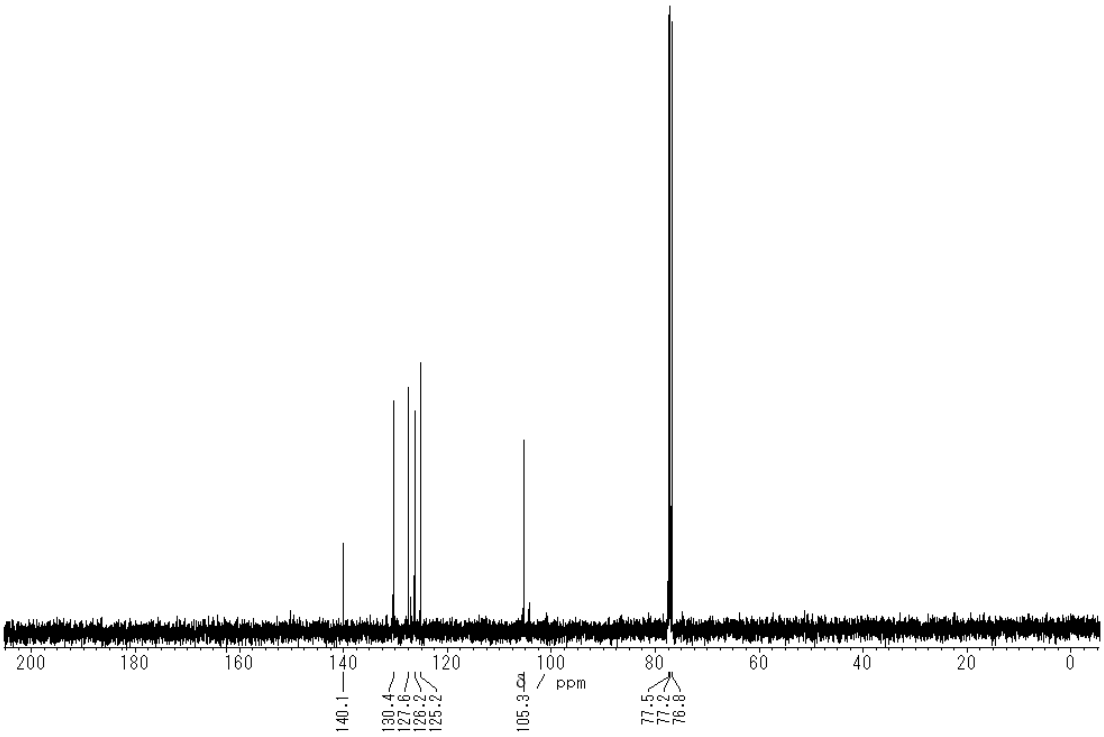

Figure S69. $^{13}C\{^{1}H\}$ NMR spectrum of **3ag** (*trans*/*cis* mixture) in $CDCl_3$.

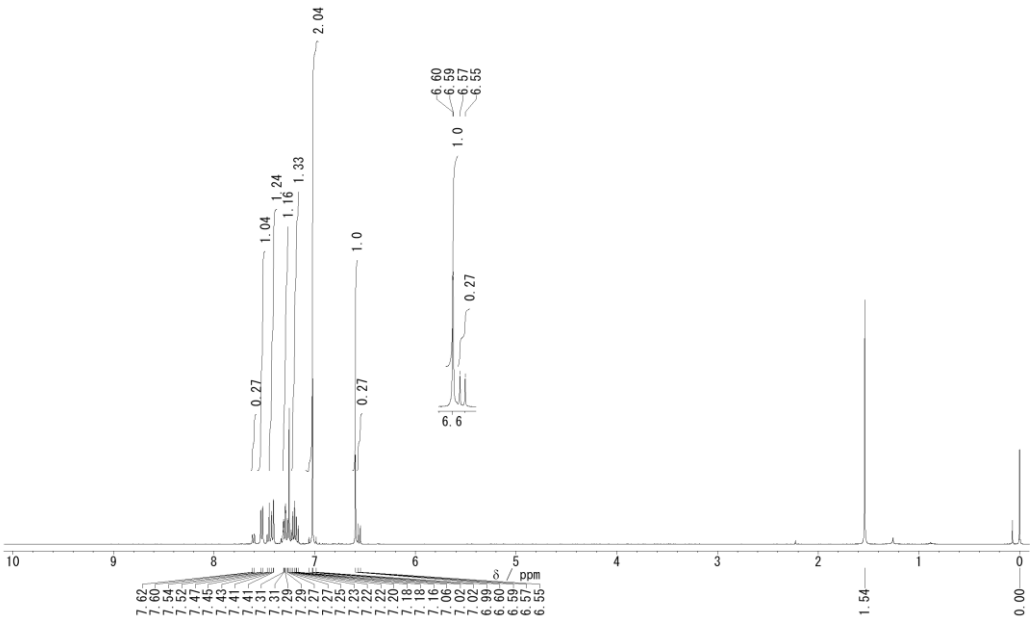

Figure S70. ^{1}H NMR spectrum of **3ah** (*trans*/*cis* mixture) in $CDCl_3$.

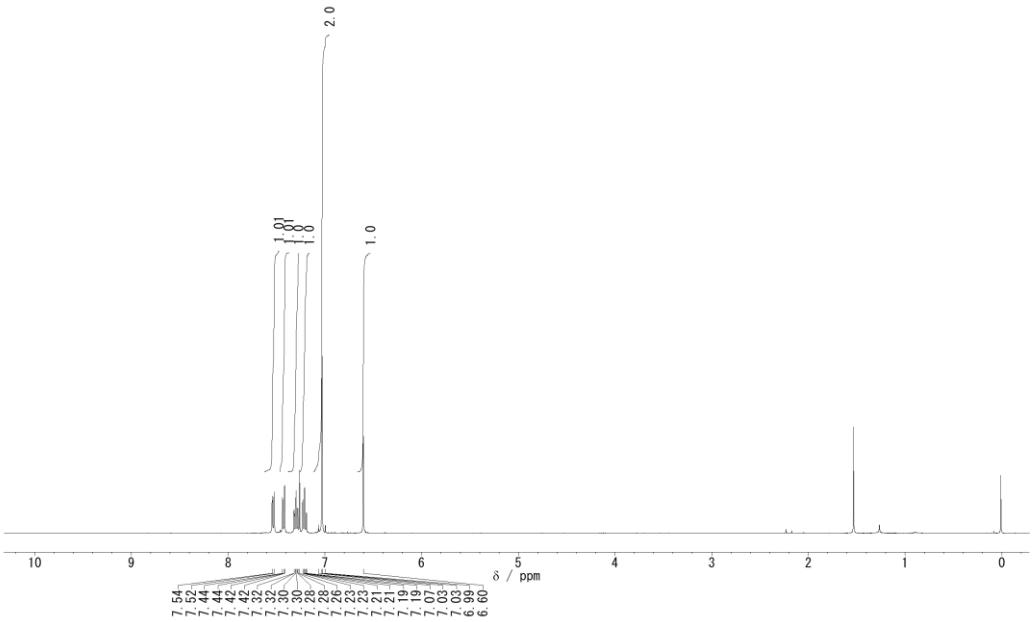

Figure S71. ^{1}H NMR spectrum of *trans*-**3ah** in $CDCl_3$.

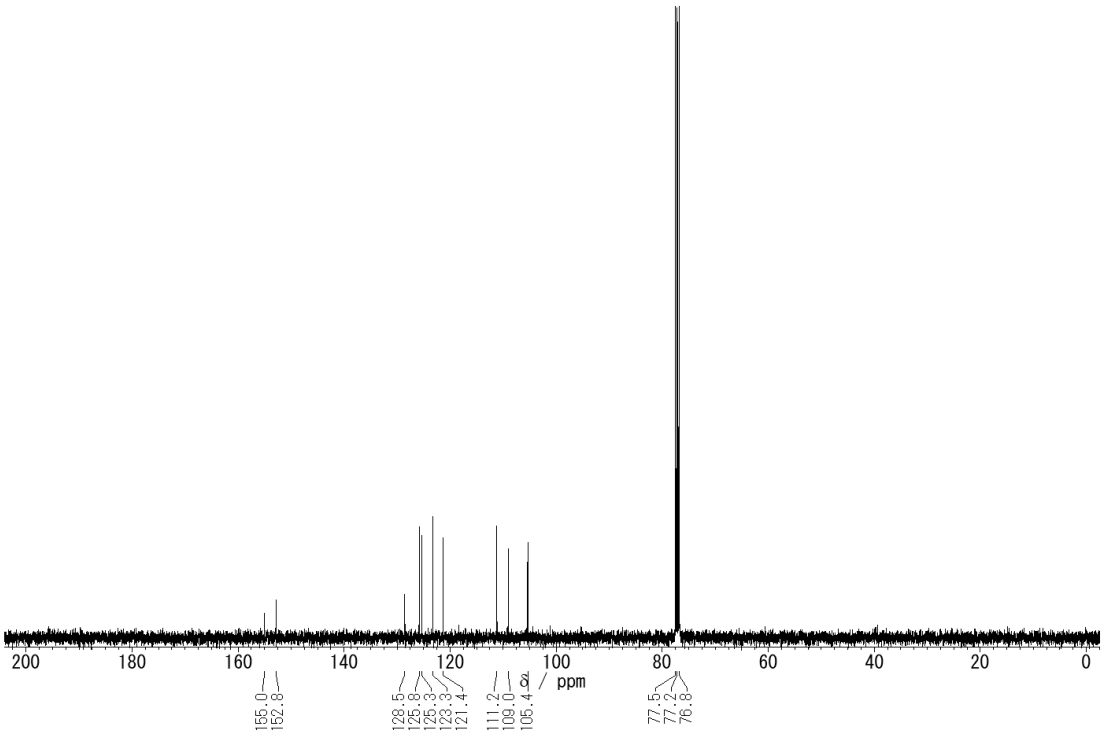

Figure S72. $^{13}C\{^{1}H\}$ NMR spectrum of *trans*-**3ah** in $CDCl_3$.

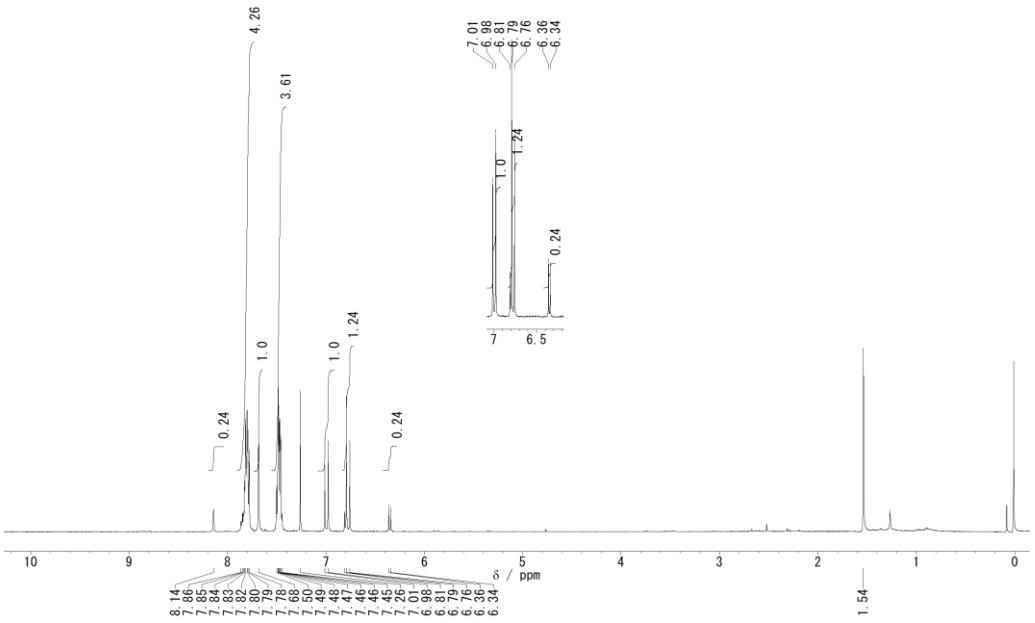

Figure S73. ^{1}H NMR spectrum of **3a'** (*trans*/*cis* mixture) in $CDCl_3$.

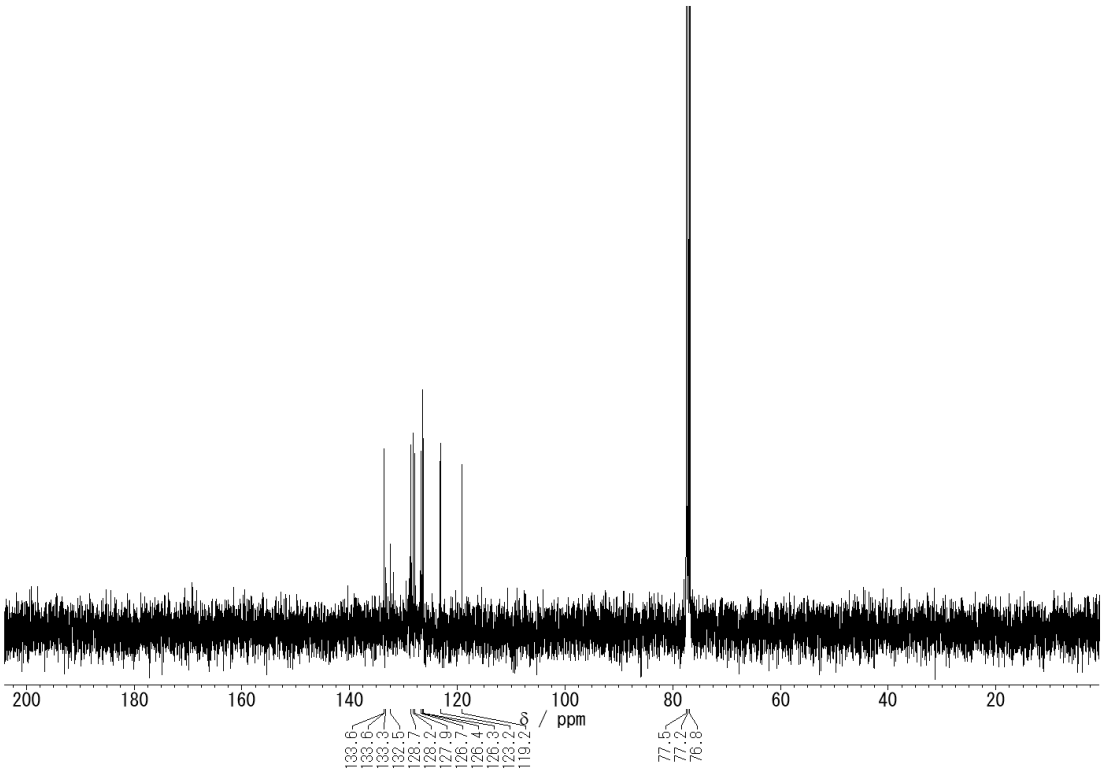

Figure S74. $^{13}C\{^{1}H\}$ NMR spectrum of **3a'** (*trans*/*cis* mixture) in $CDCl_3$.

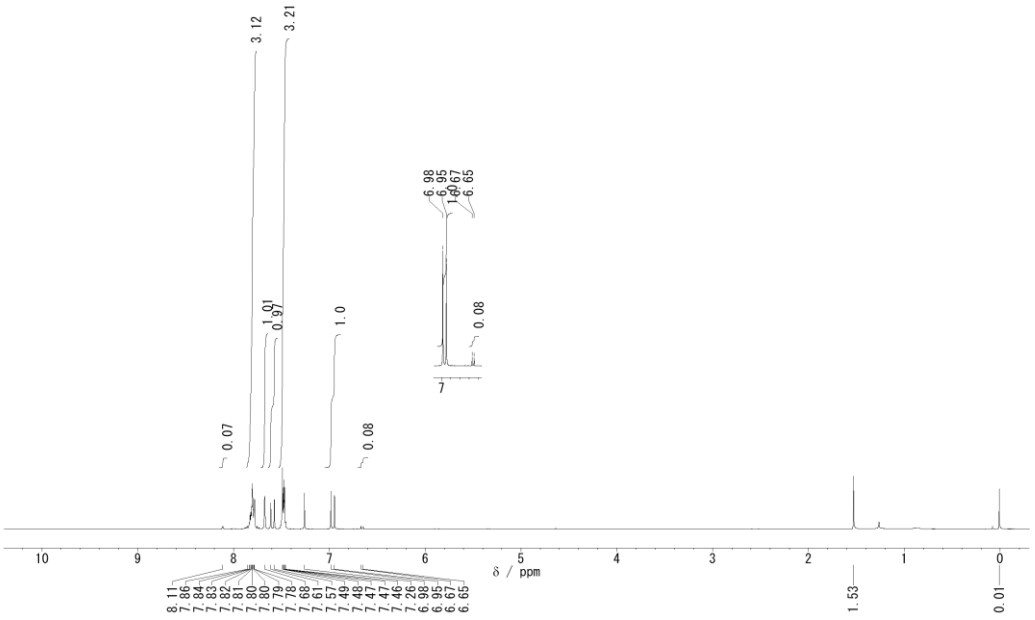

Figure S75. ^{1}H NMR spectrum of **3a''** (*trans*/*cis* mixture) in $CDCl_3$.

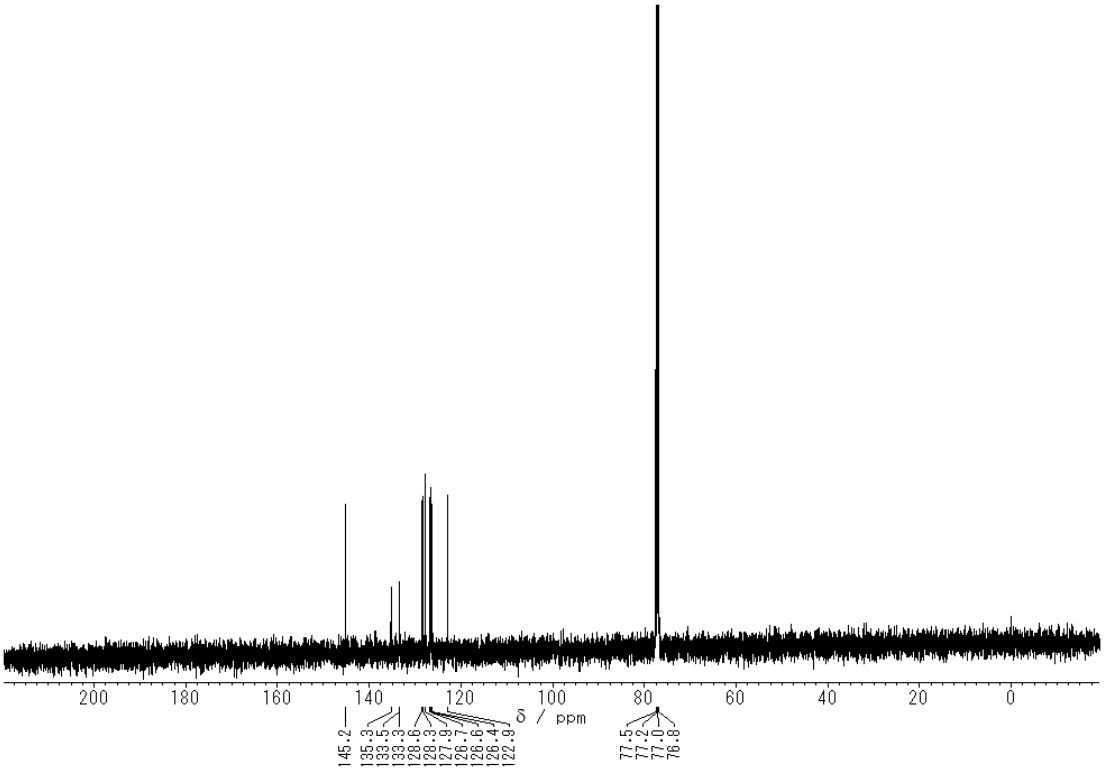

Figure S76. $^{13}C\{^{1}H\}$ NMR spectrum of **3a''** (*trans*/*cis* mixture) in $CDCl_3$.

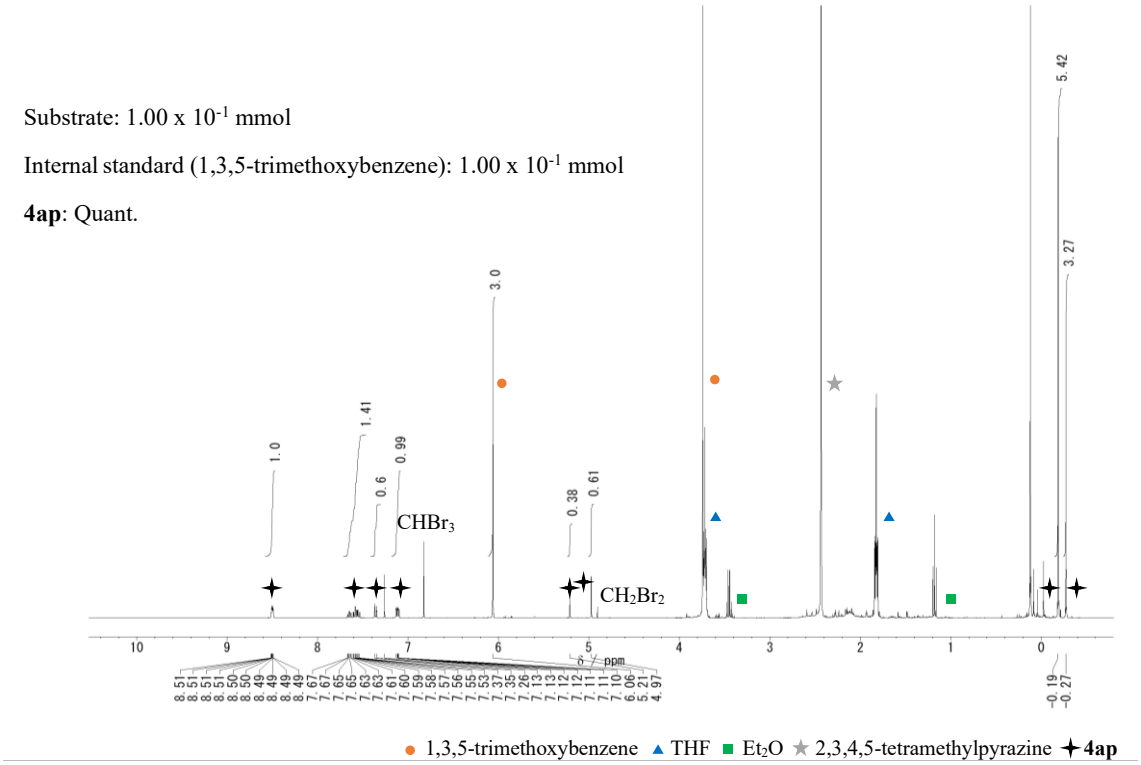

Figure S77. ^{1}H NMR spectrum of the reaction mixture for olefination of **2ap** without $CrCl_2$/ NEt_3.

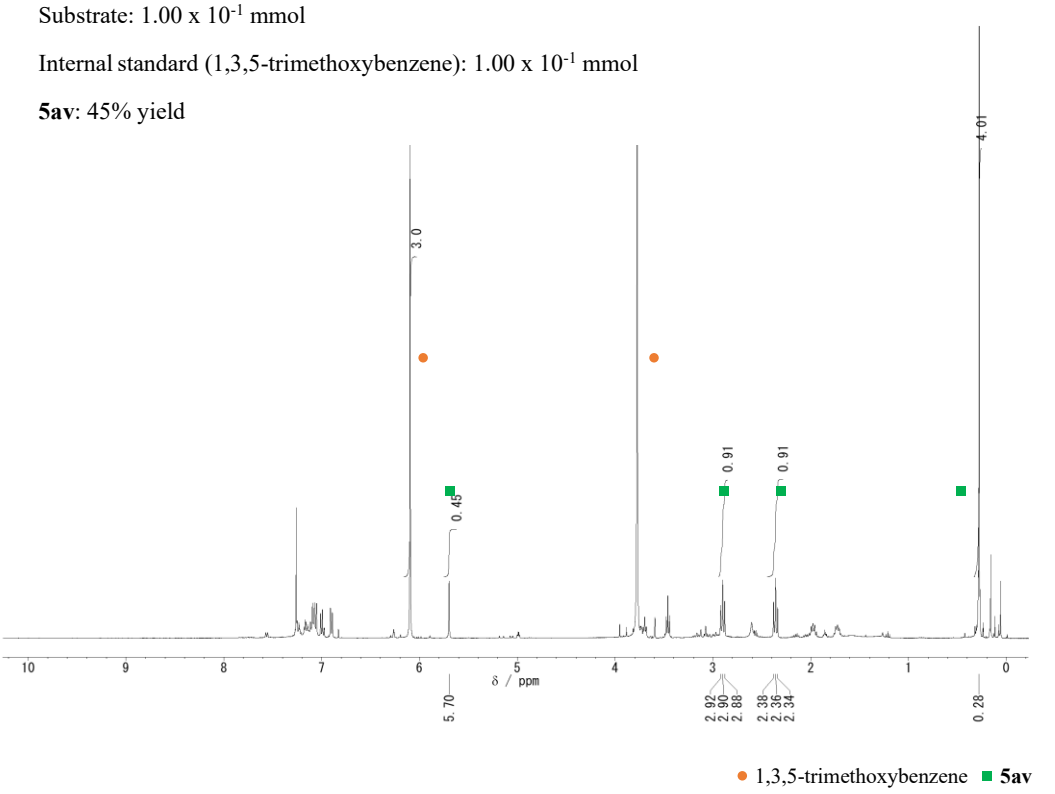

Figure S78. ^{1}H NMR spectrum of the reaction mixture for olefination of **2av**.

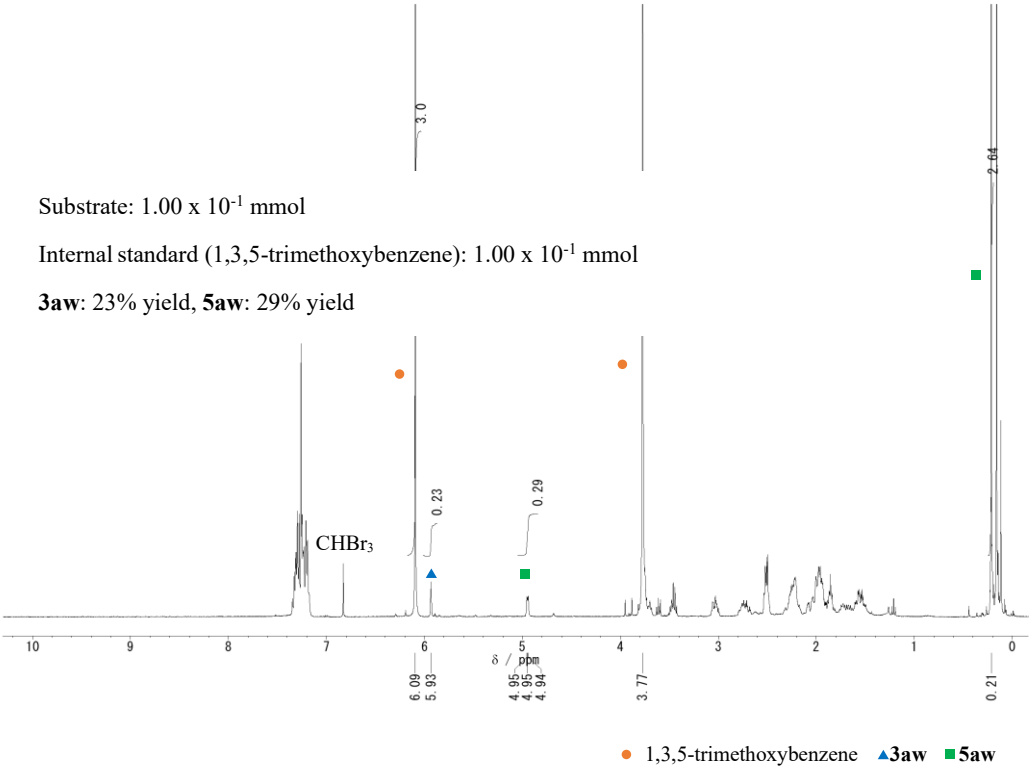

Figure S79. ^{1}H NMR spectrum of the reaction mixture for olefination of **2aw**.