Electronic Supplementary Material (ESI) for RSC Advances.

Cationic Palladium(II)-Catalyzed Synthesis of Substituted Pyridines from *α,β*-Unsaturated Oxime Ethers

Supporting Information

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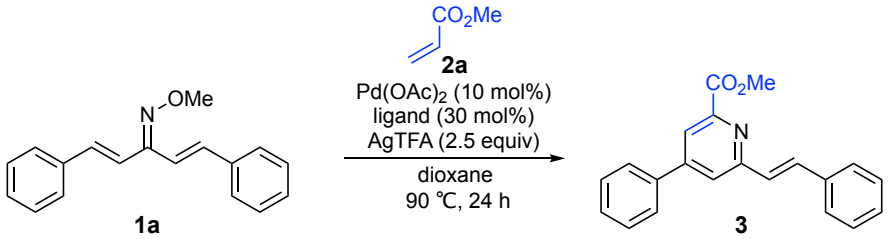
General methods

^{1}H and ^{13}C NMR spectra were recorded with BRUKER AV300M spectrometer at room temperature, with tetramethylsilane (δ = 0) as an internal standard ($CDCl_3$ solution). Chemical shifts were expressed in ppm, and coupling constants (*J*) in Hz. Infrared (IR) spectra were recorded with a Shimadzu IRSpirit. Mass spectra were recorded on JEOL JMS-700 and JMS-T100LP spectrometers. Melting points were determined by using a Yanaco melting point apparatus MP-S3. Merck silica gel 60 F254 and Wako NH_2 silica gel 60 F254 were used for thin layer chromatography (TLC). Merck silica gel 60 (1.09385) and Kanto Chemical silica gel 60 (spherical) NH_2 were used for column chromatography, and the all pyridine products were purified by flash column chromatography on NH_2 silica gel as previously reported.[1] All computations were carried out with the Gaussian 09 series of programs.[2] All compounds were calculated with ωB97X-D/6-311+G(d,p), and an ultrafine grid was used for geometry optimization.

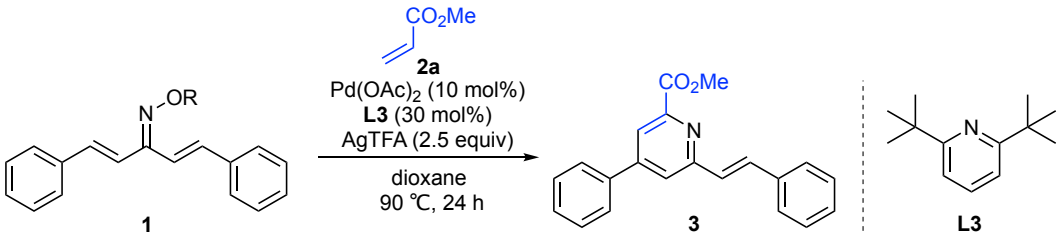
Pyridine ligand optimization



General procedure for pyridine ligand optimization using *α,β*-unsaturated oxime ether 1a[1]

To a solution of *α,β*-unsaturated oxime **1a** (0.2 mmol, 1.0 eq.), methyl acrylate (**2a**, 0.6 mmol, 3.0 eq.), AgTFA (0.5 mmol, 2.5 eq.), and ligand (0.06 mmol, 30 mol%) in dioxane (2.0 mL) was added $Pd(OAc)_2$ (0.02 mmol, 10 mol%). The reaction mixture was stirred at 90 °C (silicone oil bath) for 24 h, then diluted with AcOEt and filtered through a Celite® pad (rinsed with AcOEt). The filtrate was concentrated in *vacuo*, and the crude product was purified by flash column chromatography on NH_2 silica gel (hexane : AcOEt = 3 : 1) to afford the desired pyridine **3** as a white solid.

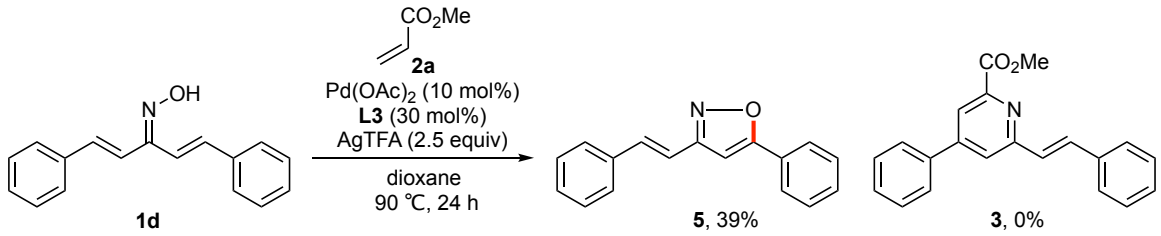
Oxime ether optimization



General procedure for oxime ether optimization[1]

To a solution of α,β-unsaturated oxime **1** (0.2 mmol, 1.0 eq.), methyl acrylate (**2a**, 0.6 mmol, 3.0 eq.), AgTFA (0.5 mmol, 2.5 eq.), and **L3** (0.06 mmol, 30 mol%) in dioxane (2.0 mL) was added $Pd(OAc)_2$ (0.02 mmol, 10 mol%). The reaction mixture was stirred at 90 °C (silicone oil bath) for 24 h, then diluted with AcOEt and filtered through a Celite® pad (rinsed with AcOEt). The filtrate was concentrated in *vacuo*, and the crude product was purified by flash column chromatography on NH_2 silica gel (hexane : AcOEt = 3 : 1) to afford the desired pyridine **3**.

Reaction with oxime 1d

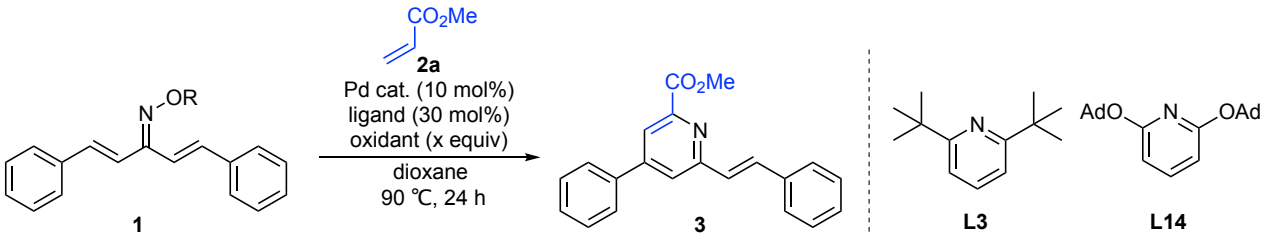


To a solution of α,β-unsaturated oxime **1d** (50 mg, 0.2 mmol, 1.0 eq.), methyl acrylate (**2a**, 0.6 mmol, 3.0 eq.), AgTFA (0.5 mmol, 2.5 eq.), and **L3** (0.06 mmol, 30 mol%) in dioxane (2.0 mL) was added $Pd(OAc)_2$ (0.02 mmol, 10 mol%). The reaction mixture was stirred at 90 °C (silicone oil bath) for 24 h, then diluted with AcOEt and filtered through a Celite® pad (rinsed with AcOEt). The filtrate was concentrated in *vacuo*, and the crude product was purified by flash column chromatography on NH_2 silica gel (hexane : AcOEt = 3 : 1) to afford isoxazole **5**[3] (19.8 mg, 39% yield) as a white solid. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.83 (dd, 2H, J = 10.4, 2.4 Hz), 7.16–7.57 (m, 10H), 6.77 (s, 1H). Spectra data of obtained product was in good agreement with previously reported literature.[3b]

Reaction optimization

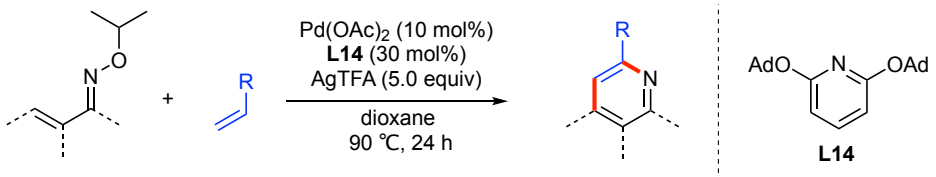
To a solution of α,β-unsaturated oxime **1** (0.2 mmol, 1.0 eq.), methyl acrylate (**2a**, 0.6 mmol, 3.0 eq.), oxidant (x equiv), and ligand (0.06 mmol, 30 mol%) in dioxane (2.0 mL) was added Pd cat. (0.02 mmol, 10 mol%). The reaction mixture was stirred at 90 °C (silicone oil bath) for 24 h, then diluted with AcOEt and filtered through a Celite® pad (rinsed with AcOEt). The filtrate was concentrated in *vacuo*, and the crude product was purified by flash column chromatography on NH_2 silica gel (hexane : AcOEt = 3 : 1) to afford the desired pyridine **3**.

Table S1. Reaction optimization.



entry	OR	Pd cat.	ligand	oxidant	x equiv.	yield
1	OMe	$Pd(OAc)_2$	**L3**	AgTFA	2.5	47%
2	OMe	$Pd(OAc)_2$	**L3**	none	2.5	0%
3	OMe	$PdCl_2$	**L3**	AgTFA	2.5	10%
4	OMe	$Pd(TFA)_2$	**L3**	AgTFA	2.5	53%
5	OMe	$Pd(TFA)_2$	**L3**	AgOAc	2.5	trace
6	O^{i}Pr	$Pd(OAc)_2$	**L3**	AgTFA	2.5	69%
7	O^{i}Pr	$Pd(OAc)_2$	**L14**	AgTFA	2.5	76%
8	O^{i}Pr	$Pd(OAc)_2$	**L14**	AgTFA	4.0	77%
9	O^{i}Pr	$Pd(OAc)_2$	**L14**	AgTFA	5.0	85%

General procedure for substituted pyridine synthesis[1]



All α,β-unsaturated oxime ethers used in this work were *E*-isomer. *E*- and *Z*-isomers were easily separated by flash column chromatography.

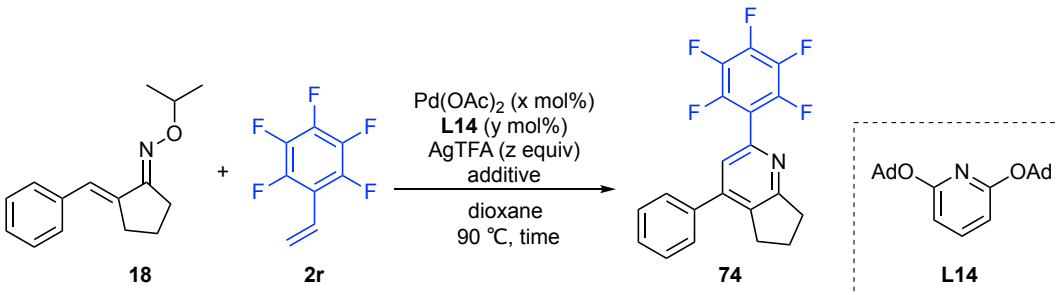
General Procedure A : To a solution of α,β-unsaturated oxime (1.0 eq.), alkene (3.0 eq.), AgTFA (5.0 eq.), and **L14** (30 mol%) in dioxane (2.0 mL) was added $Pd(OAc)_2$ (10 mol%). The reaction mixture was stirred at 90 °C (silicone oil bath) for 24 h, then diluted with AcOEt and filtered through a Celite® pad (rinsed with AcOEt). The filtrate was concentrated in *vacuo*, and the crude product was purified by flash column chromatography on NH_2 silica gel.

General Procedure B : To a solution of α,β-unsaturated oxime (1.0 eq.), alkene (1.5 eq.), AgTFA (5.0 eq.), and **L14** (30 mol%) in dioxane (2.0 mL) was added $Pd(OAc)_2$ (10 mol%). The reaction mixture was stirred at 90 °C (silicone oil bath) for 24 h, then diluted with AcOEt and filtered through a Celite® pad (rinsed with AcOEt). The filtrate was concentrated in *vacuo*, and the crude product was purified by flash column chromatography on NH_2 silica gel.

Investigation of the amount of catalysts and oxidant

To a solution of α,β-unsaturated oxime **18** (0.2 mmol, 1.0 eq.), pentafluorostyrene (**2r**, 0.6 mmol, 3.0 eq.), AgTFA (z equiv), and **L14** (y mol%) in dioxane (2.0 mL) was added $Pd(OAc)_2$ (x mol%). The reaction mixture was stirred at 90 °C (silicone oil bath), then diluted with AcOEt and filtered through a Celite® pad (rinsed with AcOEt). The filtrate was concentrated in *vacuo*, and the crude product was purified by flash column chromatography on NH_2 silica gel (hexane : AcOEt = 3 : 1) to afford the pyridine **74** as a white solid.

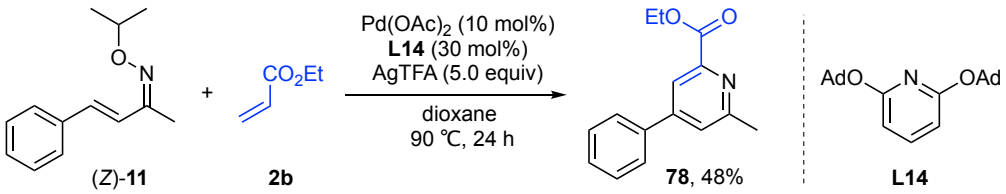
Table S2. Investigation of the amount of catalysts and oxidant.



entry	$Pd(OAc)_2$ (x mol%)	**L14** (y mol%)	AgTFA (z equiv)	time	yield
1	10	30	5.0	24 h	83%
2	1	3	5.0	80 h	77%
3	10	30	1.2	24 h	27%
4	10	30	2.5	24 h	44%
5	10	30	10	24 h	91%

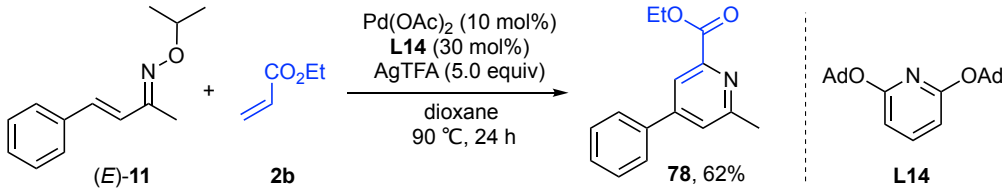
Control experiments with specific substrates and conditions

Pyridine synthesis with *Z*-oxime



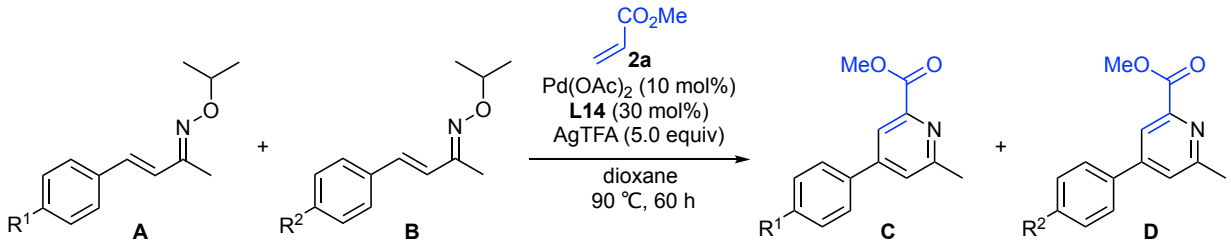
To a solution of (*Z*)-**11** (41 mg, 0.2 mmol, 1.0 eq.), ethyl acrylate (**2b**, 0.6 mmol, 3.0 eq.), AgTFA (1.0 mmol, 5.0 eq.), and **L14** (0.06 mmol, 30 mol%) in dioxane (2.0 mL) was added $Pd(OAc)_2$ (0.02 mmol, 10 mol%). The reaction mixture was stirred at 90 °C (silicone oil bath) for 24 h, then diluted with AcOEt and filtered through a Celite® pad (rinsed with AcOEt). The filtrate was concentrated in *vacuo*, and the crude product was purified by flash column chromatography on NH_2 silica gel (hexane : AcOEt = 3 : 1) to afford the desired pyridine **78** (21 mg, 48% yield) as a pale yellow oil. IR (KBr) 2980, 1716, 1605, 1553, 1379, 1338, 1251, 1145, 1079, 1025, 769, 696, 633 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.18 (d, 1H, J = 1.2 Hz), 7.67 (d, 2H, J = 8.1 Hz), 7.56–7.40 (m, 4H), 4.51 (q, 2H, J = 7.2 Hz), 2.72 (s, 3H), 1.46 (t, 3H, J = 7.2 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 165.5, 159.4, 149.6, 148.4, 137.4, 129.3, 129.1, 127.0, 124.3, 120.5, 61.9, 24.7, 14.3; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{15}H_{15}NO_2$, 241.1103; found, 241.1105.

Pyridine synthesis with *E*-oxime 11



To a solution of (*E*)-**11** (41 mg, 0.2 mmol, 1.0 eq.), ethyl acrylate (**2b**, 0.6 mmol, 3.0 eq.), AgTFA (1.0 mmol, 5.0 eq.), and **L14** (0.06 mmol, 30 mol%) in dioxane (2.0 mL) was added $Pd(OAc)_2$ (0.02 mmol, 10 mol%). The reaction mixture was stirred at 90 °C (silicone oil bath) for 24 h, then diluted with AcOEt and filtered through a Celite® pad (rinsed with AcOEt). The filtrate was concentrated in *vacuo*, and the crude product was purified by flash column chromatography on NH_2 silica gel (hexane : AcOEt = 3 : 1) to afford the pyridine **78** (30 mg, 62% yield) as a pale yellow oil.

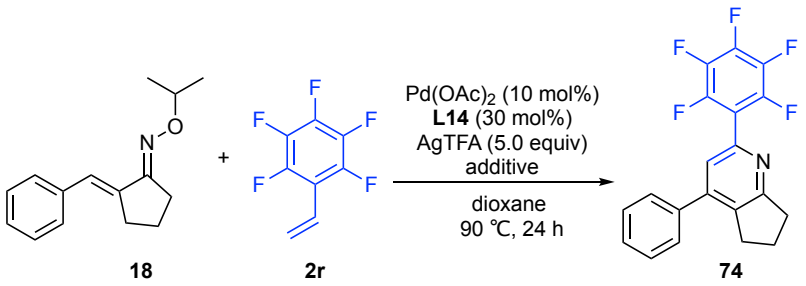
Table S3. Competitive experiments.



entry	Substrates		Product yield		
	R^1 (**A**, **C**)	R^2 (**B**, **D**)	**C**	**D**	**C**/**D**
1	Me	Cl	53%	27%	1.9
2	OMe	Me	52%	29%	1.8
3	Me	H	75%	44%	1.7
4	H	Cl	34%	26%	1.3

To a solution of α,β-unsaturated oxime **A** (0.2 mmol, 1.0 eq.), α,β-unsaturated oxime **B** (0.2 mmol, 1.0 eq.), methyl acrylate (**2a**, 0.6 mmol, 3.0 eq.), AgTFA (1.0 mmol, 5.0 eq.), and **L14** (0.06 mmol, 30 mol%) in dioxane (2.0 mL) was added $Pd(OAc)_2$ (0.02 mmol, 10 mol%). The reaction mixture was stirred at 90 °C (silicone oil bath) for 60 h, then diluted with AcOEt and filtered through a Celite® pad (rinsed with AcOEt). The filtrate was concentrated in *vacuo*, and the crude product was purified by flash column chromatography on NH_2 silica gel (hexane : AcOEt = 2 : 1) to afford the corresponding pyridines **C** and **D** as a mixture. The product yields and the ratio of the pyridine product (**C**/**D**) were determined by ^{1}H NMR analysis of the isolated products.

Table S4. Control experiments.

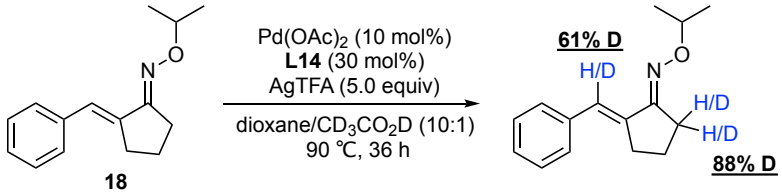


entry	additive	yield (%)
1	none	83
2	MeOH (1.0 equiv)	54
3	^{i}PrOH (1.0 equiv)	66

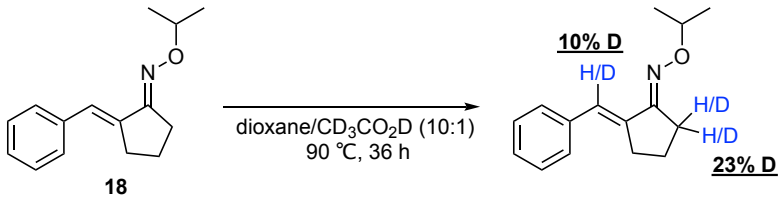
To a solution of α,β-unsaturated oxime **18** (0.2 mmol, 1.0 eq.), pentafluorostyrene (**2r**, 0.6 mmol, 3.0 eq.), AgTFA (1.0 mmol, 5.0 eq.), **L14** (0.06 mmol, 30 mol%), and additive (0.2 mmol, 1.0 eq.) in

dioxane (2.0 mL) was added $Pd(OAc)_2$ (0.02 mmol, 10 mol%). The reaction mixture was stirred at 90 °C (silicone oil bath) for 24 h, then diluted with AcOEt and filtered through a Celite® pad (rinsed with AcOEt). The filtrate was concentrated in *vacuo*, and the crude product was purified by flash column chromatography on NH_2 silica gel (hexane : AcOEt = 3 : 1) to afford the desired pyridine **74** as a white solid. mp 102–103 °C; IR (KBr) 1522, 1501, 1219, 990, 772 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.60–7.30 (m, 5H), 7.26 (s, 1H), 3.25–3.09 (m, 4H), 2.30–2.15 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 167.4, 146.3 (m), 146.0, 144.7, 143.0 (m), 139.4 (m), 138.0, 136.1 (m), 135.3, 128.7, 128.6, 128.2, 123.0, 115.8 (m), 34.6, 30.8, 23.4; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{20}H_{12}F_5N$, 361.0890; found, 361.0888.

Deuterium labeling experiments

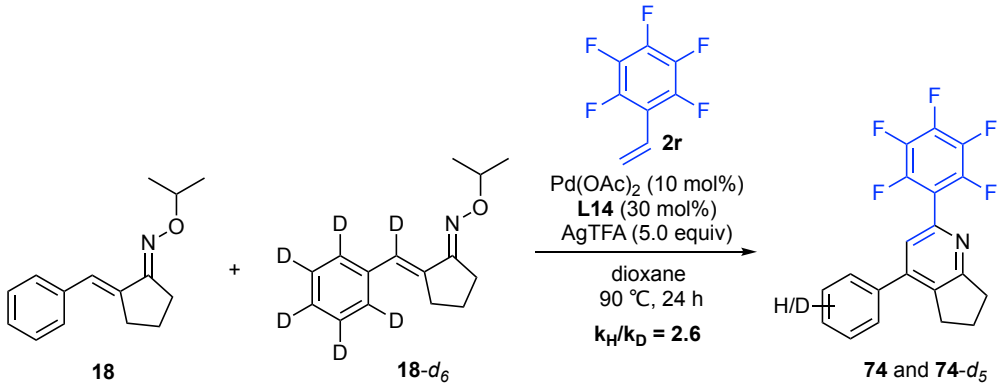


To a solution of α,β-unsaturated oxime **18** (23 mg, 0.1 mmol, 1.0 eq.), AgTFA (0.5 mmol, 5.0 eq.), **L14** (30 mol%), and CD_3CO_2D (0.4 mL, 55 eq.) in dioxane (4.0 mL) was added $Pd(OAc)_2$ (0.01 mmol, 10 mol%). The reaction mixture was stirred at 90 °C (silicone oil bath) for 36 h, then diluted with AcOEt and filtered through a Celite® pad (rinsed with AcOEt). The filtrate was concentrated in *vacuo*, and the crude product was purified by flash column chromatography on NH_2 silica gel (hexane : AcOEt = 10 : 1) to afford the deuterated oxime (16.6 mg) as a pale yellow oil. The deuterium incorporation ratio was determined by ^1H NMR analysis of the isolated product.



To a solution of α,β-unsaturated oxime **18** (23 mg, 0.1 mmol, 1.0 eq.) in dioxane (4.0 mL) was added CD_3CO_2D (0.4 mL, 55 eq.). The reaction mixture was stirred at 90 °C (silicone oil bath) for 36 h, then diluted with AcOEt and filtered through a Celite® pad (rinsed with AcOEt). The filtrate was concentrated in *vacuo*, and the crude product was purified by flash column chromatography on NH_2 silica gel (hexane : AcOEt = 10 : 1) to afford the deuterated oxime (10.0 mg) as a pale yellow oil. The deuterium incorporation ratio was determined by ^1H NMR analysis of the isolated product.

Kinetic isotope effect experiment

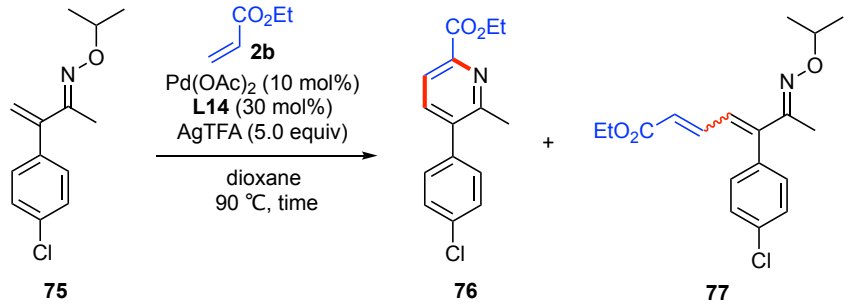


To a solution of α,β-unsaturated oxime **18** (46 mg, 0.2 mmol, 1.0 eq.), **18**-d_6 (47 mg, 0.2 mmol, 1.0 eq.), pentafluorostyrene (**2r**, 0.6 mmol, 3.0 eq.), AgTFA (1.0 mmol, 5.0 eq.), and **L14** (0.06 mmol, 30 mol%) in dioxane (3.0 mL) was added $Pd(OAc)_2$ (0.02 mmol, 10 mol%). The reaction mixture was stirred at 90 °C (silicone oil bath) for 24 h, then diluted with AcOEt and filtered through a Celite® pad (rinsed with AcOEt). The filtrate was concentrated in *vacuo*, and the crude product was purified by flash column chromatography on NH_2 silica gel (hexane : AcOEt = 5 : 1). The obtained product mixture was analyzed by ^{1}H NMR analysis. The conversion of **74**, X_{74}, was determined by integration of the aromatic signals of **74**, which appeared as a multiplet (7.60–7.30 ppm). The total conversion, X_{total}, was determined by integration of the methylene signals of **74** and **74**-d_5, which appeared as multiplet at the same chemical shift (3.25–3.09 ppm for both **74** and **74**-d_5). Conversion of **74**-d_5, $X_{74\text{-}d5}$, could then be determined from the following formula:

$X_{74\text{-}d5} = X_{total} - X_{74}$

$k_H/k_D = X_{74} / X_{74\text{-}d5} = 2.6/1$ (the experiment was repeated two times)

Table S5. Mechanistic studies on pyridine ring formation.[1]

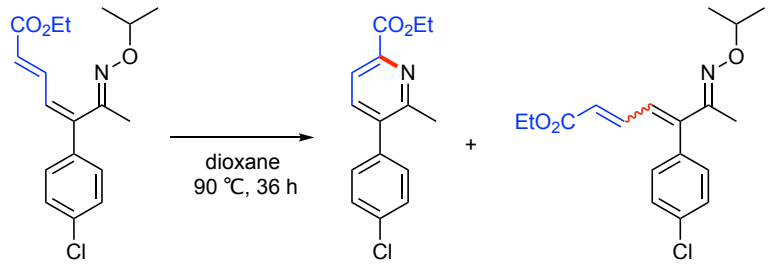


entry	time	**76**	**77**
1	4 h	0%	36% (*E*/*Z* = 1.3/1)
2	36 h	28%	11% (*E*-isomer only)

Procedure for entry 1: To a solution of α,β-unsaturated oxime **75** (60 mg, 0.25 mmol, 1.0 eq.), ethyl acrylate (**2b**, 0.75 mmol, 3.0 eq.), AgTFA (1.25 mmol, 5.0 eq.), and **L14** (0.075 mmol, 30 mol%) in dioxane (3.0 mL) was added $Pd(OAc)_2$ (0.025 mmol, 10 mol%). The reaction mixture was stirred at 90 °C (silicone oil bath) for 4 h, then diluted with AcOEt and filtered through a Celite® pad (rinsed with AcOEt). The filtrate was concentrated in *vacuo*, and the crude product was purified by flash column chromatography on NH_2 silica gel (hexane : AcOEt = 10 : 1) to afford azatriene **77** (pale yellow oil, 30 mg, 36% yield) as a mixture of *E*/*Z* isomers (*E* : *Z* = 1.3 : 1).

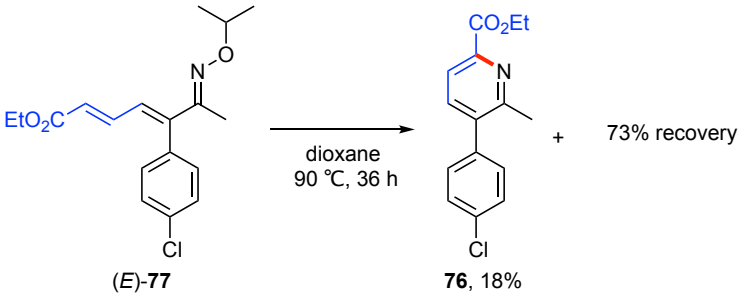
Procedure for entry 2: To a solution of α,β-unsaturated oxime **75** (95 mg, 0.4 mmol, 1.0 eq.), ethyl acrylate (**2b**, 1.2 mmol, 3.0 eq.), AgTFA (2.0 mmol, 5.0 eq.), and **L14** (0.12 mmol, 30 mol%) in dioxane (4.0 mL) was added $Pd(OAc)_2$ (0.04 mmol, 10 mol%). The reaction mixture was stirred at 90 °C (silicone oil bath) for 36 h, then diluted with AcOEt and filtered through a Celite® pad (rinsed with AcOEt). The filtrate was concentrated in *vacuo*, and the crude product was purified by flash column chromatography on NH_2 silica gel (hexane : AcOEt = 3 : 1) to afford **76** (colorless oil, 31 mg, 28% yield) and *E*-**77** (pale yellow oil, 15 mg, 11% yield).

Pyridine ring formation from 1-azatriene[1]



(*Z*)-**77** **76**, 84% **77**, 10% (*E*/*Z* = 3/1)

Z-isomer of **77** (15 mg, 0.045 mmol) was dissolved in dioxane (2 mL) and stirred at 90 °C for 36 h. The reaction mixture was cooled to room temperature and concentrated in *vacuo*. The resulting residue was purified by preparative TLC (silica gel, hexane : AcOEt = 4 :1) to afford **76** (colorless oil, 10.4 mg, 84% yield) and **77** (pale yellow oil, 1.5 mg, 10% yield) as a mixture of *E*/*Z* isomers (*E* : *Z* = 3 : 1).

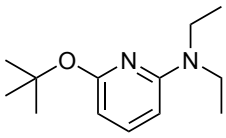


(*E*)-**77** **76**, 18%

E-isomer of **77** (10 mg, 0.03 mmol) was dissolved in dioxane (1 mL) and stirred at 90 °C for 36 h. The reaction mixture was cooled to room temperature and concentrated in *vacuo*. The resulting residue was purified by preparative TLC (silica gel, hexane : AcOEt = 4 :1) to afford **76** (colorless oil, 1.5 mg, 18% yield) and (*E*)-**77** (7.3 mg, 73% recovery).

Preparation of ligands

Ligands **L1**, **L2**, **L3**, **L4**, **L5**, **L9**, **L12**, and **L13** were purchased from commercially sources and used without further purification. **L6**, **L7**, **L10**, **L11**, and **L14** were prepared as previously reported.[1] **L8** was synthesized according to the following procedures.



L8

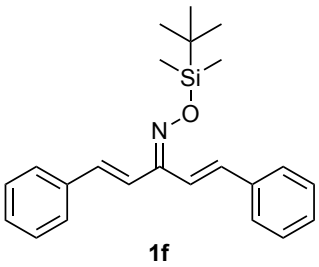
6-(*tert*-butoxy)-*N*,*N*-diethylpyridin-2-amine (**L8**): To a solution of 2-(*tert*-butoxy)-6-chloropyridine (100 mg, 0.54 mmol, 1.0 eq.), diethylamine (0.11 mL, 1.1 mmol, 2.0 eq.), RuPhos (25 mg, 0.054 mmol, 10 mol%), and Cs_2CO_3 (528 mg, 1.6 mmol, 3.0 eq.) in toluene (3.0 mL) and ^{t}BuOH (0.3 mL) was added $Pd(OAc)_2$ (12 mg, 0.054 mmol, 10 mol%). The reaction mixture was stirred at 100 °C (silicone oil bath) for 21 h, then diluted with AcOEt and filtered through a Celite® pad (rinsed with AcOEt). The filtrate was concentrated in *vacuo*, and the crude product was purified by flash column chromatography on silica gel (hexane : AcOEt = 20 : 1) to afford the title compound (95 mg, 80% yield) as a colorless oil. IR (KBr) 2974, 2929, 1589, 1573, 1490, 1434, 1397, 1360, 1297, 1247, 1179, 1156, 1078, 1046, 898, 775, 722 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.28 (dd, 1H, J = 8.1, 7.8 Hz), 5.95 (d, 1H, J = 8.1 Hz), 5.87 (d, 1H, J = 7.8 Hz), 3.46 (q, 4H, J = 6.9 Hz), 1.57 (s, 9H), 1.16 (t, 6H, J = 6.9 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 163.0, 156.2, 139.3, 98.5, 96.3, 78.0, 42.4, 29.0, 13.1; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{13}H_{22}N_2O$, 222.1732; found, 222.1731.

Preparation of substrates

All alkenes used in this work were purchased from commercially sources and used without further purification.

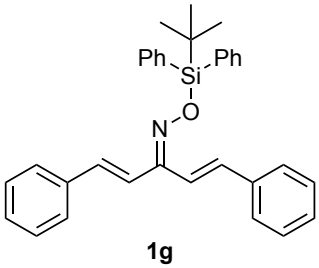
α,β-Unsaturated oximes except for **1f**, **1g**, **1h**, **1i**, **1j**, **1k**, **1l**, **1m**, **1n**, and **1o** were prepared as previously reported.[1]

α,β-Unsaturated oximes **1f**, **1g**, **1h**, **1i**, **1j**, **1k**, **1l**, **1m**, **1n**, and **1o** were synthesized according to the following procedures.



1f

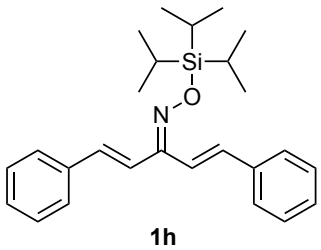
(1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one *O*-(*tert*-butyldimethylsilyl) oxime (**1f**): To a solution of (1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one oxime (200 mg, 0.80 mmol, 1.0 eq.) in CH_2Cl_2 (3 mL) were added *tert*-butyldimethylchlorosilane (133 mg, 0.88 mmol, 1.1 eq.), DMAP (10 mg, 0.08 mmol, 0.1 eq.) and imidazole (109 mg, 1.60 mmol, 2.0 eq.). The reaction mixture was stirred at room temperature for 1.5 h, then quenched with saturated NH_4Cl aq. The aqueous layer was extracted with $CHCl_3$ and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in *vacuo*. The crude product was purified by flash column chromatography on silica gel (hexane : AcOEt = 20 : 1) to afford the title compound (233 mg, 80% yield) as a colorless oil. IR (KBr) 2928, 2856, 1448, 1251, 967, 835, 752, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.57–7.45 (m, 4H), 7.41–7.25 (m, 7H), 7.14 (d, 1H, J = 16.8 Hz), 7.09 (d, 1H, J = 16.8 Hz), 6.93 (d, 1H, J = 16.2 Hz), 1.00 (s, 9H), 0.26 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 158.3, 136.7, 136.60, 136.56, 134.5, 128.82, 128.77, 128.6, 128.3, 127.2, 127.0, 122.8, 117.7, 26.2, 18.2, –5.13; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{30}NOSi$, 364.2097; found, 364.2092.



1g

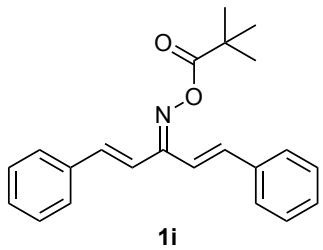
(1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one *O*-(*tert*-butyldimethylsilyl) oxime (**1g**): To a solution of (1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one oxime (100 mg, 0.40 mmol, 1.0 eq.) in THF (2 mL) were added NaH (63% dispersion in mineral oil, 24 mg, 0.60 mmol, 1.5 eq.) and *tert*-butyldiphenylchlorosilane (220 mg, 0.80 mmol, 2.0 eq.). The reaction mixture was stirred at room temperature overnight, then quenched with water. The aqueous layer was extracted with AcOEt and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in *vacuo*. The crude product was purified by flash column chromatography on silica gel (hexane : AcOEt = 10 : 1) to afford the title compound (201 mg, quant.) as a colorless oil. IR (KBr) 3071, 2931, 2857, 1471, 1428, 1262, 1113, 969, 832,

754, 695, 610, 560, 505 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.80–7.75 (m, 4H), 7.65–7.56 (m, 3H), 7.50–7.22 (m, 14H), 7.18 (d, 1H, *J* = 16.8 Hz), 7.10 (d, 1H, *J* = 16.8 Hz), 6.92 (d, 1H, *J* = 16.2 Hz), 1.16 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 159.0, 137.1, 136.6, 136.5, 135.5, 135.1, 133.6, 129.6, 129.0, 128.9, 128.7, 128.4, 127.6, 127.3, 127.0, 122.7, 117.6, 27.2, 19.5; HRMS (ESI-TOF) *m*/*z*: $[M+Na]^+$ Calcd for $C_{33}H_{33}NNaOSi$, 510.2229; found, 510.2216.



1h

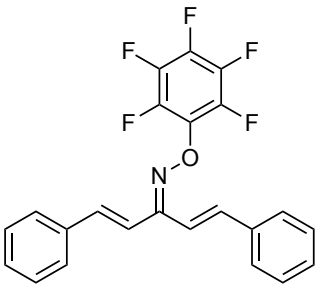
(1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one *O*-triisopropylsilyl oxime (**1h**): To a solution of (1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one oxime (200 mg, 0.80 mmol, 1.0 eq.) in CH_2Cl_2 (3 mL) were added triisopropylsilyl chloride (170 mg, 0.88 mmol, 1.1 eq.), DMAP (10 mg, 0.08 mmol, 0.1 eq.) and imidazole (109 mg, 1.60 mmol, 2.0 eq.). The reaction mixture was stirred at room temperature for 1.5 h, then quenched with saturated NH_4Cl aq. The aqueous layer was extracted with $CHCl_3$ and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in *vacuo*. The crude product was purified by flash column chromatography on silica gel (hexane : AcOEt = 20 : 1) to afford the title compound (241 mg, 74% yield) as a pale yellow oil. IR (KBr) 3026, 2943, 2865, 1635, 1493, 1462, 1448, 1345, 1260, 1200, 967, 882, 826, 754, 690, 460 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.60–7.49 (m, 4H), 7.45–7.28 (m, 7H), 7.13 (d, 1H, *J* = 16.2 Hz), 7.10 (d, 1H, *J* = 16.8 Hz), 6.93 (d, 1H, *J* = 16.2 Hz), 1.40–1.20 (m, 3H), 1.13 (d, 18H, *J* = 6.9 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 157.9, 136.8, 136.7, 136.2, 134.1, 128.8, 128.7, 128.2, 127.2, 126.9, 123.0, 117.7, 18.0, 11.9; HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ Calcd for $C_{26}H_{36}NOSi$, 406.2566; found, 406.2560.



1i

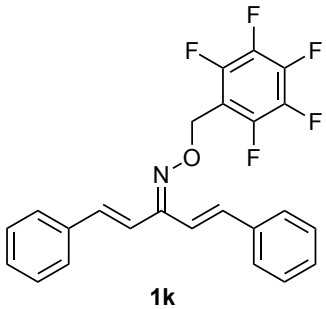
(1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one *O*-pivaloyl oxime (**1i**): To a solution of (1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one oxime (300 mg, 1.20 mmol, 1.0 eq.) in THF (6 mL) were added NaH (63% dispersion in mineral oil, 96 mg, 2.40 mmol, 2.0 eq.) and pivaloyl chloride (0.22 mL, 1.80 mmol, 1.5 eq.). The reaction mixture was stirred at room temperature for 30 min, then quenched with 1M NaOH aq. The aqueous layer was extracted with AcOEt and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in *vacuo*. The crude product was purified by flash column chromatography on silica gel (hexane : AcOEt = 4 : 1) to afford the title compound (388 mg, 96% yield) as a pale yellow solid. mp 105–106 °C; IR (KBr) 2973, 1754, 1636, 1577, 1478, 1448, 1343, 1273, 1202, 1105, 1026, 970, 923, 878, 755, 693 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.55–7.51 (m, 4H), 7.45–7.29 (m, 7H), 7.23 (d, 1H, *J* = 16.5

Hz), 7.19 (d, 1H, J = 16.5 Hz), 7.03 (d, 1H, J = 16.2 Hz), 1.34 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 174.9, 161.1, 139.8, 138.9, 135.8, 135.4, 129.7, 129.2, 129.0, 128.8, 127.4, 127.3, 120.9, 116.8, 38.9, 27.3; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{22}H_{23}NO_2$, 333.1729; found, 333.1716.



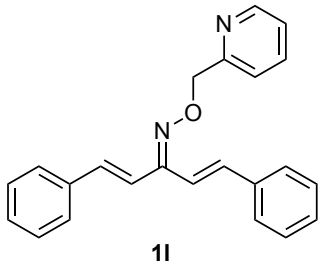
1j

(1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one *O*-pentafluorophenyl oxime (**1j**): To a solution of (1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one oxime (100 mg, 0.40 mmol, 1.0 eq.) in DMF (3 mL) were added NaH (63% dispersion in mineral oil, 32 mg, 0.60 mmol, 1.5 eq.) and hexafluorobenzene (0.1 mL, 0.80 mmol, 2.0 eq.). The reaction mixture was stirred at room temperature for 1 h, then quenched with water. The aqueous layer was extracted with AcOEt and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in *vacuo*. The crude product was purified by flash column chromatography on silica gel (hexane : AcOEt = 10 : 1) to afford the title compound (133 mg, 80% yield) as a pale yellow solid. mp 103–104 °C; IR (KBr) 3027, 1634, 1577, 1515, 1465, 1448, 1344, 1201, 996, 969, 874, 854, 755, 691, 521 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.65–7.30 (m, 11H), 7.23 (d, 1H, J = 15.9 Hz), 7.19 (d, 1H, J = 16.8 Hz), 6.86 (d, 1H, J = 15.9 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 159.4, 140.0, 138.1, 135.8, 135.5, 129.8, 129.2, 128.9, 128.8, 127.7, 127.3, 119.6, 116.1; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{23}H_{14}F_5NO$, 415.0996; found, 415.0987.



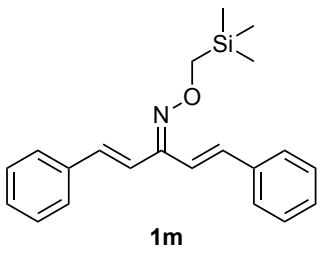
1k

(1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one *O*-(pentafluorophenyl)metyl oxime (**1k**): To a solution of *O*-(pentafluorobenzyl)hydroxylamine hydrochloride (57 mg, 0.23 mmol, 1.1 eq.) and pyridine (42 mg, 0.53 mmol, 2.5 eq.) in MeOH (2 mL) was added *trans*,*trans*-dibenzalacetone (50 mg, 0.21 mmol, 1.0 eq.). The reaction mixture was stirred at room temperature overnight, then quenched with saturated NH_4Cl aq. The aqueous layer was extracted with AcOEt and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in *vacuo* to afford the title compound (89 mg, 99% yield) as a white solid. mp 122–123 °C; IR (KBr) 1655, 1521, 1506, 1448, 1305, 1127, 1025, 962, 941, 755, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.53–7.46 (m, 4H), 7.44–7.30 (m, 6H), 7.19 (d, 1H, J = 16.8 Hz), 7.12 (d, 1H, J = 16.2 Hz), 7.04 (d, 1H, J = 16.8 Hz), 6.83 (d, 1H, J = 16.2 Hz), 5.30 (s, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 155.2, 147.6 (m), 144.1 (m), 139.0 (m), 137.7, 136.3, 136.0, 135.5, 129.0, 128.8 (several signals overlapped.), 127.2, 127.0 (several signals overlapped.), 121.8, 117.0, 111.0 (m), 63.0; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{24}H_{16}F_5NO$, 429.1152; found, 429.1151.



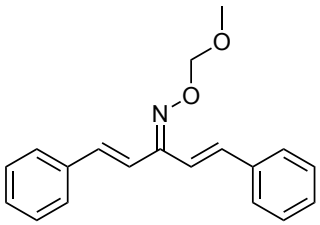
1l

(1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one *O*-(pyridin-2-yl)methyl oxime (**1l**): To a solution of (1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one oxime (300 mg, 1.20 mmol, 1.0 eq.) in DMF (6 mL) were added NaH (63% dispersion in mineral oil, 120 mg, 3.0 mmol, 2.5 eq.) and 2-(bromomethyl)pyridine hydrobromide (364 mg, 1.4 mmol, 1.2 eq.). The reaction mixture was stirred at room temperature for 2.5 h, then quenched with water. The aqueous layer was extracted with AcOEt and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in *vacuo*. The crude product was purified by flash column chromatography on silica gel (hexane : AcOEt = 3 : 1) to afford the title compound (329 mg, 80% yield) as a pale yellow solid. mp 56–57 °C; IR (KBr) 3024, 1590, 1493, 1435, 1356, 1098, 1059, 969, 899, 754, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.60 (dd, 1H, *J* = 3.9, 1.8 Hz), 7.70 (ddd, 1H, *J* = 7.8, 7.8, 1.8 Hz), 7.57–7.26 (m, 12H), 7.23–7.18 (m, 1H), 7.13 (d, 1H, *J* = 16.2 Hz), 7.11 (d, 1H, *J* = 16.5 Hz), 6.89 (d, 1H, *J* = 16.2 Hz), 5.40 (s, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 158.3, 155.0, 149.2, 137.4, 136.6, 136.4, 136.2, 135.2, 129.0, 128.8, 128.7, 128.5, 127.3, 127.0, 122.4, 122.2, 121.7, 117.4, 77.0; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{23}H_{20}N_2O$, 340.1576; found, 340.1581.



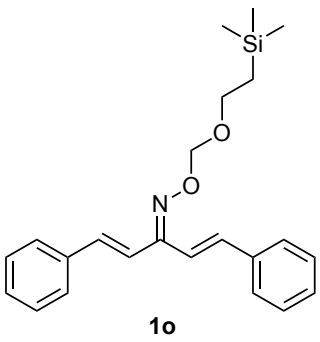
1m

(1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one *O*-(trimethylsilyl)methyl oxime (**1m**): To a solution of (1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one oxime (150 mg, 0.60 mmol, 1.0 eq.) in THF (3 mL) were added NaH (63% dispersion in mineral oil, 36 mg, 0.90 mmol, 1.5 eq.) and chloromethyl trimethylsilane (0.17 mL, 1.20 mmol, 2.0 eq.). The reaction mixture was stirred at 70 °C (silicone oil bath) for 21 h, then quenched with water. The aqueous layer was extracted with AcOEt and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in *vacuo*. The crude product was purified by flash column chromatography on silica gel (hexane : AcOEt = 10 : 1) to afford the title compound (183 mg, 92% yield) as a pale yellow oil. IR (KBr) 2955, 1633, 1494, 1448, 1248, 1027, 968, 854, 754, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.55–7.45 (m, 4H), 7.39–7.22 (m, 7H), 7.12 (d, 1H, *J* = 16.2 Hz), 7.09 (d, 1H, *J* = 16.8 Hz), 6.87 (d, 1H, *J* = 16.2 Hz), 4.02 (s, 2H), 0.15 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 153.6, 136.8, 136.7, 136.5, 134.3, 128.83, 128.78, 128.7, 128.3, 127.1, 126.9, 122.7, 117.4, 69.1, –2.68; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{21}H_{25}NOSi$, 335.1705; found, 335.1703.



1n

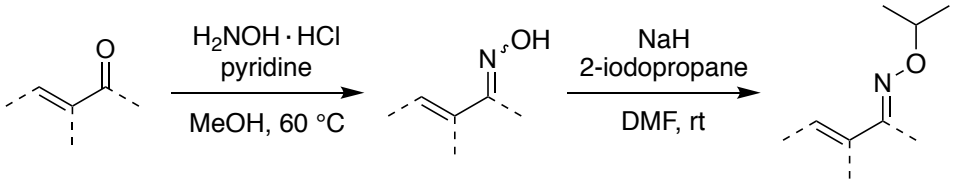
(1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one *O*-methoxymethyl oxime (**1n**): To a solution of (1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one oxime (200 mg, 0.80 mmol, 1.0 eq.) in DMF (3 mL) were added NaH (63% dispersion in mineral oil, 38 mg, 0.96 mmol, 1.2 eq.) and chloromethyl methyl ether (0.12 mL, 1.60 mmol, 2.0 eq.). The reaction mixture was stirred at room temperature for 1 h, then quenched with water. The aqueous layer was extracted with AcOEt and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in *vacuo*. The crude product was purified by flash column chromatography on silica gel (hexane : AcOEt = 5 : 1) to afford the title compound (162 mg, 69% yield) as a colorless oil. IR (KBr) 2933, 1634, 1576, 1494, 1448, 1392, 1345, 1209, 1154, 1086, 997, 970, 924, 896, 855, 755, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.60–7.49 (m, 4H), 7.40–7.29 (m, 7H), 7.17 (d, 1H, *J* = 16.2 Hz), 7.08 (d, 1H, *J* = 16.8 Hz), 6.92 (d, 1H, *J* = 16.2 Hz), 5.24 (s, 2H), 3.50 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 155.7, 137.6, 136.4, 136.1, 135.6, 129.1, 128.8, 128.7, 128.5, 127.3, 127.0, 122.2, 117.4, 98.8, 56.4; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{19}H_{19}NO_2$, 293.1416; found, 293.1415.



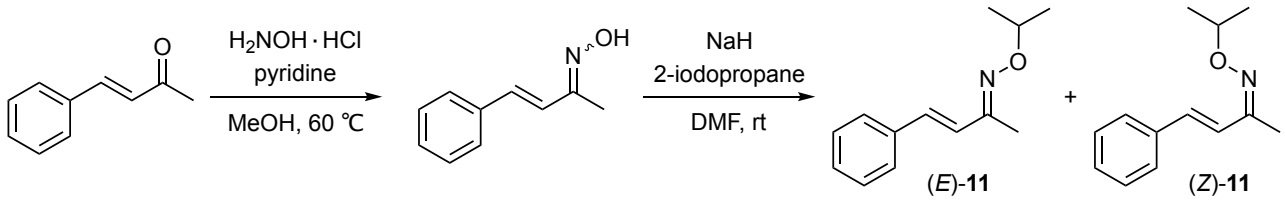
1o

(1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one *O*-((2-(trimethylsilyl)ethoxy)methyl) oxime (**1o**): To a solution of (1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one oxime (200 mg, 0.80 mmol, 1.0 eq.) in DMF (4 mL) were added NaH (63% dispersion in mineral oil, 48 mg, 1.20 mmol, 1.5 eq.) and 2-(chloromethoxy)ethyltrimethylsilane (267 mg, 1.6 mmol, 2.0 eq.). The reaction mixture was stirred at room temperature for 1 h, then quenched with water. The aqueous layer was extracted with AcOEt and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in *vacuo*. The crude product was purified by flash column chromatography on silica gel (hexane : AcOEt = 20 : 1) to afford the title compound (260 mg, 85% yield) as a colorless oil. IR (KBr) 2952, 1448, 1248, 1104, 995, 857, 835, 754, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.55–7.45 (m, 4H), 7.39–7.24 (m, 7H), 7.14 (d, 1H, *J* = 16.2 Hz), 7.05 (d, 1H, *J* = 16.8 Hz), 6.90 (d, 1H, *J* = 16.2 Hz), 5.27 (s, 2H), 3.79–3.73 (m, 2H), 1.02–0.95 (m, 2H), 0.00 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 155.3, 137.3, 136.4, 136.1, 135.4, 129.2, 128.9, 128.7, 128.5, 127.8, 127.5, 122.2, 117.5, 97.3, 66.4, 18.0, –1.44; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{23}H_{29}NO_2Si$, 379.1968; found, 379.1964.

General procedure for the synthesis of *O*-isopropyl *α,β*-unsaturated oxime ethers[1]



To a solution of *α,β*-unsaturated ketone (1.0 eq.) in MeOH (0.5 M) were added hydroxylamine hydrochloride (1.5 eq.) and pyridine (2.0 eq.). The reaction mixture was stirred at 60 °C (silicone oil bath) for 1 h, then quenched with saturated NH_4Cl. The aqueous layer was extracted with AcOEt and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in *vacuo*. The resulting residue was dissolved in DMF (0.3 M) and cooled to 0 °C. After the addition of NaH (63% dispersion in mineral oil, 2.0 eq.) and 2-iodopropane (1.3 eq.) at 0 °C, the reaction mixture was stirred at room temperature for 30 min, then quenched with water. The aqueous layer was extracted with AcOEt and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in *vacuo*. The crude product was purified by flash column chromatography on silica gel to afford the desired *O*-isopropyl *α,β*-unsaturated oxime ethers. *E*- and *Z*-isomers were easily separated by flash column chromatography and the configuration of oximes were determined by ^1H NMR analysis.

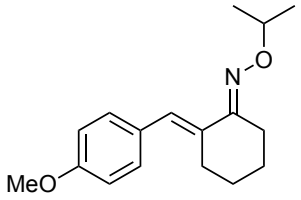


(2*Z*,3*E*)-4-phenylbut-3-en-2-one *O*-isopropyl oxime (*Z*-**11**): Following the general procedure for unsymmetrical *α,β*-unsaturated oxime ether synthesis with (*E*)-4-phenylbut-3-en-2-one (1.0 g, 6.84 mmol), purification by flash column chromatography on silica gel (hexane : CH_2Cl_2 = 3 : 1) afforded (*E*)-**11**[1] (colorless oil, 622 mg, 45% yield) and a small amount of (*Z*)-**11** (colorless oil, 200 mg, 14% yield). The configuration of oximes were determined by ^1H NMR analysis (The vinylene peak of *Z*-oxime was observed at a lower magnetic field than that of *E*-oxime.).

(*E*)-**11**: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.50–7.44 (m, 2H), 7.37–7.25 (m, 3H), 6.90–6.75 (m, 2H), 4.39 (m, 1H), 2.07 (s, 3H), 1.29 (d, 6H, *J* = 6.3 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 154.9, 136.7, 132.2, 128.7, 128.1, 126.7, 126.6, 75.7, 21.8, 10.3.

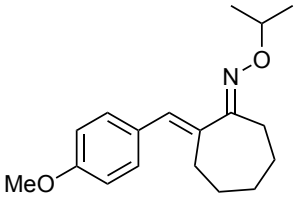
(*Z*)-**11**: IR (KBr) 2973, 2900, 1577, 1493, 1465, 1379, 1368, 1341, 1325, 1301, 1147, 1119, 991, 982, 956, 912, 874, 753, 694, 626, 616, 589, 516 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.54–7.50 (m, 2H), 7.50 (d, 1H, *J* = 16.8 Hz), 7.40–7.30 (m, 3H), 6.89 (d, 1H, *J* = 16.8 Hz), 4.37 (m, 1H), 2.11 (s, 3H), 1.28 (d, 6H, *J* = 6.3 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 151.6, 136.5, 135.5, 128.8, 128.7, 127.4,

117.9, 75.3, 21.7, 17.0; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{13}H_{17}NO$, 203.1310; found, 203.1307.



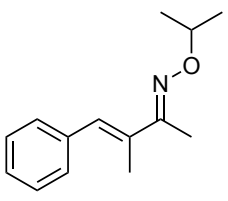
36

(*E*)-2-((*E*)-4-methoxybenzylidene)cyclohexan-1-one *O*-isopropyl oxime (**36**): Following the general procedure for the synthesis of *O*-isopropyl *α*,*β*-unsaturated oxime ethers with (*E*)-2-((*E*)-4-methoxybenzylidene)cyclohexan-1-one oxime (1.10 g, 5.09 mmol), purification by flash column chromatography on silica gel (hexane : AcOEt = 10 : 1) afforded the title compound (white solid, 1.13 g, 81% yield). mp 76–77 °C; IR (KBr) 2971, 2933, 2835, 1605, 1509, 1463, 1367, 1301, 1250, 1177, 1146, 1122, 1035, 969, 889, 835, 749, 531 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.26 (d, 2H, *J* = 8.4 Hz), 6.88 (s, 1H), 6.86 (d, 2H, *J* = 8.4 Hz), 4.45–4.35 (m, 1H), 3.81 (s, 3H), 2.70–2.60 (m, 2H), 2.59–2.56 (m, 2H), 1.70–1.58 (m, 4H), 1.29 (d, 6H, *J* = 6.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 159.0, 158.5, 133.5, 131.1, 129.8, 126.6, 113.4, 75.1, 55.2, 29.0, 25.8, 24.9, 23.3, 21.9; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{17}H_{23}NO_2$, 273.1729; found, 273.1728.



37

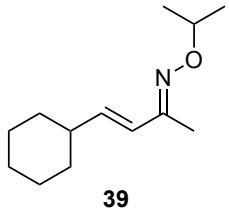
(1*E*)-2-(4-methoxybenzylidene)cycloheptan-1-one *O*-isopropyl oxime (**37**): Following the general procedure for the synthesis of *O*-isopropyl *α*,*β*-unsaturated oxime ethers with (*E*)-2-((*E*)-4-methoxybenzylidene)cycloheptan-1-one oxime (1.31 g, 5.69 mmol), purification by flash column chromatography on silica gel (hexane : AcOEt = 30 : 1) afforded the title compound (colorless oil, 916 mg, 56% yield). IR (KBr) 2971, 2928, 2854, 1606, 1573, 1509, 1455, 1368, 1301, 1251, 1176, 1150, 1123, 1035, 969, 888, 828, 750, 532 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.30 (d, 2H, *J* = 8.4 Hz), 6.87 (d, 2H, *J* = 8.4 Hz), 6.67 (s, 1H), 4.45–4.38 (m, 1H), 3.81 (s, 3H), 2.64–2.56 (m, 4H), 1.70–1.65 (m, 6H), 1.27 (d, 6H, *J* = 6.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 163.9, 158.4, 138.0, 130.4, 129.9, 127.3, 113.5, 74.9, 55.2, 30.5, 30.0, 28.1, 27.7, 24.9, 21.9; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{18}H_{25}NO_2$, 287.1885; found, 287.1886.



38

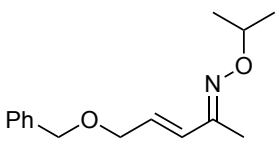
(2*E*,3*E*)-3-methyl-4-phenylbut-3-en-2-one *O*-isopropyl oxime (**38**): Following the general procedure for the synthesis of *O*-isopropyl *α*,*β*-unsaturated oxime ethers with (2*E*,3*E*)-3-methyl-4-phenylbut-3-en-2-one oxime (200 mg, 1.25 mmol), purification by flash column chromatography on silica gel (hexane : AcOEt = 30 : 1) afforded the title compound (colorless oil, 230 mg, 85% yield). IR (KBr) 2973, 1440, 1370, 1324, 1276, 1150, 1124, 1019, 975, 915, 857, 742, 698, 579, 506 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.40–7.24 (m, 5H), 6.83 (s, 1H), 4.44–4.35 (m, 1H), 2.10 (s, 3H), 2.09 (s, 3H), 1.28 (d, 6H, *J* = 6.3 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 155.9, 137.6, 135.6, 129.6, 129.3,

128.1, 126.8, 75.4, 21.7, 14.2, 10.9; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{14}H_{19}NO$, 217.1467; found, 217.1468.



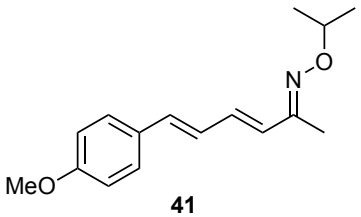
39

(2*E*,3*E*)-4-cyclohexylbut-3-en-2-one *O*-isopropyl oxime (**39**): Following the general procedure for the synthesis of *O*-isopropyl *α*,*β*-unsaturated oxime ethers with (2*E*,3*E*)-4-cyclohexylbut-3-en-2-one oxime (500 mg, 3.28 mmol), purification by flash column chromatography on silica gel (hexane : CH_2Cl_2 = 4 : 1) afforded the title compound (colorless oil, 326 mg, 48% yield). IR (KBr) 2973, 2925, 2852, 1448, 1369, 1323, 1150, 1123, 965, 750, 581 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.10 (dd, 1H, *J* = 16.2, 1.8 Hz), 5.95 (dd, 1H, *J* = 16.2, 6.6 Hz), 4.36–4.27 (m, 1H), 2.15–2.00 (m, 1H), 1.92 (s, 3H), 1.80–1.60 (m, 5H), 1.40–1.10 (m, 5H), 1.24 (d, 6H, *J* = 6.3 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 155.0, 140.8, 125.5, 75.2, 40.9, 32.6, 26.1, 25.9, 21.7, 10.2; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{13}H_{23}NO$, 209.1780; found, 209.1779.



40

(2*E*,3*E*)-5-(benzyloxy)pent-3-en-2-one *O*-isopropyl oxime (**40**): Following the general procedure for the synthesis of *O*-isopropyl *α*,*β*-unsaturated oxime ethers with (2*E*,3*E*)-5-(benzyloxy)pent-3-en-2-one oxime (1.05 g, 5.52 mmol), purification by flash column chromatography on silica gel (hexane : AcOEt = 30 : 1) afforded the title compound (pale yellow oil, 461 mg, 34% yield). IR (KBr) 2974, 1455, 1369, 1274, 1120, 970, 749, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.40–7.28 (m, 5H), 6.37 (dd, 1H, *J* = 16.2, 1.5 Hz), 6.09 (td, 1H, *J* = 16.2, 6.0 Hz), 4.53 (s, 3H), 4.36–4.30 (m, 1H), 4.14 (dd, 1H, *J* = 6.0, 1.5 Hz), 1.95 (s, 3H), 1.25 (d, 6H, *J* = 6.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 154.0, 138.1, 130.4, 130.0, 128.4, 127.7, 127.6, 75.5, 72.3, 70.3, 21.7, 10.2; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{15}H_{21}NO_2$, 247.1572; found, 247.1577.

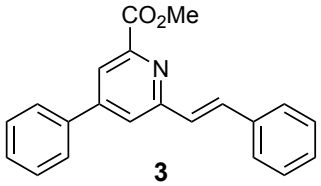


41

(2*E*,3*E*,5*E*)-6-(4-methoxyphenyl)hexa-3,5-dien-2-one *O*-isopropyl oxime (**41**): Following the general procedure for the synthesis of *O*-isopropyl *α*,*β*-unsaturated oxime ethers with (2*E*,3*E*,5*E*)-6-(4-methoxyphenyl)hexa-3,5-dien-2-one oxime (1.08 g, 5.33 mmol), purification by flash column chromatography on silica gel (hexane : AcOEt = 10 : 1) afforded the title compound (pale yellow solid, 605 mg, 44% yield). mp 85–86 °C; IR (KBr) 2968, 2927, 1599, 1511, 1457, 1367, 1257, 1151, 1120, 1027, 990, 971, 840, 818, 806, 749, 539, 516 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.36 (d, 2H, *J* = 8.7 Hz), 6.86 (d, 2H, *J* = 8.7 Hz), 6.80–6.58 (m, 3H), 6.36 (d, 1H, *J* = 15.6 Hz), 4.39–4.30 (m, 1H), 3.81 (s, 3H), 2.00 (s, 3H), 1.27 (d, 6H, *J* = 6.3 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 159.5, 155.0, 133.8, 133.0, 129.8, 129.3, 127.8, 126.7,

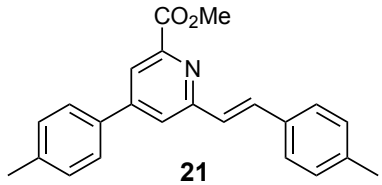
114.1, 75.6, 55.3, 21.7, 10.3; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{16}H_{21}NO_2$, 259.1572; found, 259.1575.

Pd-catalyzed substituted pyridine synthesis[1]



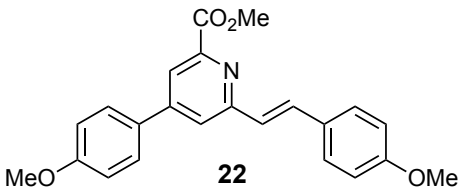
3

methyl (*E*)-4-phenyl-6-styrylpicolinate (**3**): Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **1b** (50 mg, 0.17 mmol) and methyl acrylate (**2a**), purification by flash column chromatography (hexane : AcOEt = 5 : 1) afforded the title compound (white solid, 46 mg, 85% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.23 (d, 1H, *J* = 1.5 Hz), 7.85 (d, 1H, *J* = 1.5 Hz), 7.76–7.69 (m, 2H), 7.67–7.58 (m, 3H), 7.57–7.45 (m, 3H), 7.44–7.28 (m, 4H), 4.06 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 166.0, 156.8, 150.1, 148.4, 137.4, 136.3, 134.3, 129.5, 129.2, 128.8, 128.6, 127.6, 127.3, 127.1, 122.1, 121.5, 53.0; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{21}H_{17}NO_2$, 315.1259; found, 315.1247.



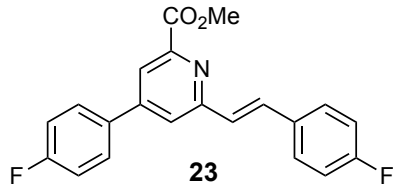
21

methyl (*E*)-6-(4-methylstyryl)-4-(*p*-tolyl)picolinate (**21**): Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **6** (64 mg, 0.20 mmol) and methyl acrylate (**2a**), purification by flash column chromatography (hexane : AcOEt = 4 : 1) afforded the title compound (white solid, 63 mg, 91% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.20 (d, 1H, *J* = 1.8 Hz), 7.82 (d, 1H, *J* = 1.8 Hz), 7.70–7.61 (m, 3H), 7.52 (d, 2H, *J* = 8.1 Hz), 7.35–7.27 (m, 3H), 7.20 (d, 2H, *J* = 7.8 Hz), 4.05 (s, 3H), 2.43 (s, 3H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 166.1, 156.9, 149.9, 148.4, 139.7, 138.7, 134.5, 134.1, 133.6, 129.9, 129.5, 127.2, 126.9, 126.8, 121.7, 121.1, 53.0, 21.3, 21.2; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{23}H_{21}NO_2$, 343.1572; found, 343.1559.



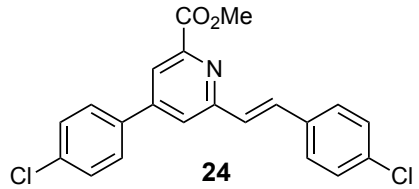
22

methyl (*E*)-4-(4-methoxyphenyl)-6-(4-methoxystyryl)picolinate (**22**): Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **7** (70 mg, 0.20 mmol) and methyl acrylate (**2a**), purification by flash column chromatography (hexane : AcOEt = 3 : 1) afforded the title compound (pale yellow solid, 64 mg, 85% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.17 (d, 1H, *J* = 1.8 Hz), 7.77 (d, 1H, *J* = 1.8 Hz), 7.69 (d, 2H, *J* = 8.7 Hz), 7.63 (d, 1H, *J* = 16.5 Hz), 7.56 (d, 2H, *J* = 8.7 Hz), 7.21 (d, 1H, *J* = 16.5 Hz), 7.04 (d, 2H, *J* = 8.7 Hz), 6.93 (d, 2H, *J* = 8.7 Hz), 4.05 (s, 3H), 3.88 (s, 3H), 3.84 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 166.2, 160.8, 160.1, 157.1, 149.4, 148.3, 133.7, 129.7, 129.1, 128.6, 128.3, 125.6, 121.2, 120.6, 114.6, 114.2, 55.4, 55.3, 53.0; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{23}H_{21}NO_4$, 375.1471; found, 375.1467.



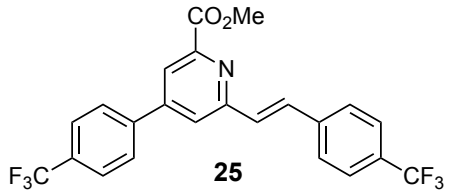
23

methyl (*E*)-4-(4-fluorophenyl)-6-(4-fluorostyryl)picolinate (**23**): Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **8** (65 mg, 0.20 mmol) and methyl acrylate (**2a**), purification by flash column chromatography (hexane : AcOEt = 3 : 1) afforded the title compound (pale yellow oil, 45 mg, 65% yield). H NMR ($CDCl_3$, 300 MHz) δ 8.18 (d, 1H, *J* = 1.5 Hz), 7.77 (d, 1H, *J* = 1.5 Hz), 7.74–7.63 (m, 3H), 7.61–7.55 (m, 2H), 7.28–7.18 (m, 3H), 7.13–7.05 (m, 2H), 4.06 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 165.9, 165.4, 164.6, 162.0, 161.3, 156.7, 149.1, 148.6, 133.5, 133.3, 132.5, 132.4, 129.0, 128.9, 128.8, 127.2, 122.0, 121.3, 116.5, 116.2, 116.0, 115.7, 53.1; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{21}H_{15}F_2NO_2$, 351.1071; found, 351.1058.



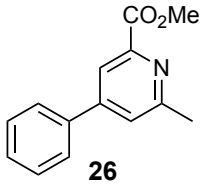
24

methyl (*E*)-4-(4-chlorophenyl)-6-(4-chlorostyryl)picolinate (**24**): Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **9** (43 mg, 0.12 mmol) and methyl acrylate (**2a**), purification by flash column chromatography (hexane : AcOEt = 3 : 1) afforded the title compound (pale yellow solid, 33 mg, 70% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.19 (d, 1H, *J* = 1.5 Hz), 7.77 (d, 1H, *J* = 1.5 Hz), 7.71–7.63 (m, 3H), 7.57–7.48 (m, 4H), 7.36 (d, 2H, *J* = 8.4 Hz), 7.30 (d, 1H, *J* = 16.2 Hz), 4.06 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 165.8, 156.6, 149.0, 148.7, 135.9, 135.8, 134.7, 134.5, 133.2, 129.5, 129.0, 128.4, 128.3, 127.9, 122.1, 121.3, 53.1; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{21}H_{15}Cl_2NO_2$, 383.0480; found, 383.0487.



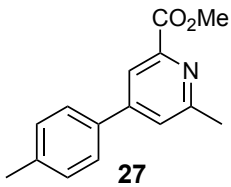
25

methyl (*E*)-4-(4-(trifluoromethyl)phenyl)-6-(4-(trifluoromethyl)styryl)picolinate (**25**): Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **10** (43 mg, 0.10 mmol) and methyl acrylate (**2a**), purification by flash column chromatography (hexane : AcOEt = 3 : 1) afforded the title compound (pale yellow solid, 30 mg, 66% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.26 (d, 1H, J = 1.8 Hz), 7.85–7.63 (m, 10H), 7.42 (d, 1H, J = 16.2 Hz), 4.08 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 165.6, 156.3, 148.9, 140.8, 139.6, 133.2, 131.8, 131.4, 130.6, 130.2, 129.5, 127.6, 127.4, 126.3, 126.2, 125.8, 122.8, 122.0, 53.2; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{23}H_{15}F_6NO_2$, 451.1007; found, 451.1020.



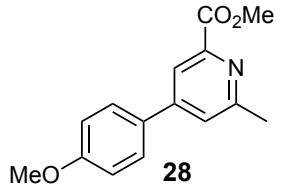
26

methyl 6-methyl-4-phenylpicolinate (**26**): Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **11** (41 mg, 0.20 mmol) and methyl acrylate (**2a**), purification by flash column chromatography (hexane : AcOEt = 3 : 1) afforded the title compound (pale yellow oil, 31 mg, 68% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.21 (d, 1H, J = 1.2 Hz), 7.68 (dd, 2H, J = 9.0, 1.5 Hz), 7.58–7.40 (m, 4H), 4.03 (s, 3H), 2.73 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 166.1, 159.5, 149.7, 148.0, 137.3, 129.4, 129.1, 127.0, 124.5, 120.6, 53.0, 24.7; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{14}H_{13}NO_2$, 227.0946; found, 227.0951.



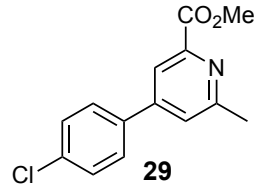
27

methyl 6-methyl-4-(*p*-tolyl)picolinate (**27**): Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **12** (43 mg, 0.20 mmol) and methyl acrylate (**2a**), purification by flash column chromatography (hexane : AcOEt = 3 : 1) afforded the title compound (pale yellow solid, 39 mg, 80% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.20 (d, 1H, J = 1.8 Hz), 7.59 (d, 2H, J = 8.1 Hz), 7.55 (d, 1H, J = 1.8 Hz), 7.30 (d, 2H, J = 8.1 Hz), 4.03 (s, 3H), 2.71 (s, 3H), 2.42 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 166.1, 159.4, 149.6, 148.0, 139.6, 134.4, 129.9, 126.8, 124.2, 120.4, 52.9, 24.7, 21.2; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{15}H_{15}NO_2$, 241.1103; found, 241.1096.



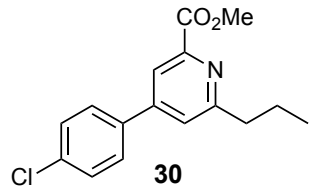
28

methyl 4-(4-methoxyphenyl)-6-methylpicolinate (**28**): Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **13** (41 mg, 0.20 mmol) and methyl acrylate (**2a**), purification by flash column chromatography (hexane : AcOEt = 2 : 1) afforded the title compound (pale yellow solid, 39 mg, 75% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.17 (d, 1H, J = 1.2 Hz), 7.64 (d, 2H, J = 8.7 Hz), 7.52 (d, 1H, J = 1.2 Hz), 7.02 (d, 2H, J = 8.7 Hz), 4.03 (s, 3H), 3.87 (s, 3H), 2.70 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 166.2, 160.7, 159.3, 149.1, 147.9, 129.5, 128.2, 123.7, 120.0, 114.5, 55.3, 52.9, 24.7; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{15}H_{15}NO_3$, 257.1052; found, 257.1057.



29

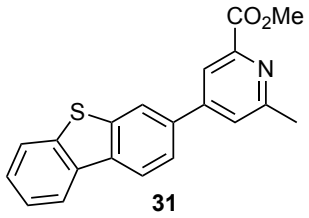
methyl 4-(4-chlorophenyl)-6-methylpicolinate (**29**): Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **14** (48 mg, 0.20 mmol) and methyl acrylate (**2a**), purification by flash column chromatography (hexane : AcOEt = 1 : 1) afforded the title compound (white solid, 34 mg, 64% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.17 (d, 1H, J = 1.2 Hz), 7.62 (d, 2H, J = 8.7 Hz), 7.53 (d, 1H, J = 1.2 Hz), 7.48 (d, 2H, J = 8.7 Hz), 4.03 (s, 3H), 2.73 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 165.9, 159.7, 148.5, 148.2, 135.8, 135.7, 129.4, 128.3, 124.2, 120.4, 53.0, 24.7; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{14}H_{12}ClNO_2$, 261.0557, 263.0527; found, 261.0562, 263.0522.



30

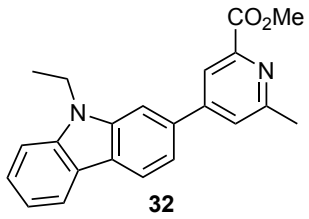
methyl 4-(4-chlorophenyl)-6-propylpicolinate (**30**): Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **15** (53 mg, 0.20 mmol) and methyl acrylate (**2a**), purification by flash column chromatography (hexane : AcOEt = 10 : 1) afforded the title compound (white solid, 37 mg, 64% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.17 (d, 1H, J = 1.2 Hz), 7.62 (d, 2H, J = 8.7 Hz), 7.51 (d, 1H, J = 1.2 Hz), 7.48 (d, 2H, J = 8.7 Hz), 4.03 (s, 3H), 2.94 (t, 2H, J = 8.1 Hz), 1.87–1.78 (m, 2H), 1.02 (t, 3H, J = 7.5 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 166.1, 163.7, 148.4, 148.3,

136.0, 135.7, 129.4, 128.3, 123.5, 120.6, 53.0, 40.5, 23.4, 13.9; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{16}H_{16}ClNO_2$, 289.0870; found, 289.0871.



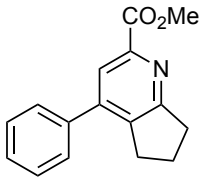
31

methyl 4-(dibenzo[*b*,*d*]thiophen-3-yl)-6-methylpicolinate (**31**): Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **16** (62 mg, 0.20 mmol) and methyl acrylate (**2a**), purification by flash column chromatography (hexane : AcOEt = 2 : 1) afforded the title compound (pale yellow solid, 32 mg, 48% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.42 (d, 1H, *J* = 1.5 Hz), 8.32 (d, 1H, *J* = 1.5 Hz), 8.29–8.22 (m, 1H), 7.96 (d, 1H, *J* = 8.4 Hz), 7.92–7.85 (m, 1H), 7.75 (dd, 1H, *J* = 8.4, 1.8 Hz), 7.67 (d, 1H, *J* = 1.8 Hz), 7.55–7.47 (m, 2H), 4.06 (s, 3H), 2.77 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 166.1, 159.6, 149.7, 148.1, 140.7, 139.9, 136.3, 135.1, 133.8, 127.3, 125.4, 124.7, 124.6, 123.5, 123.0, 121.7, 120.7, 120.0, 53.0, 24.8; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{20}H_{15}NO_2S$, 333.0823; found, 333.0824.



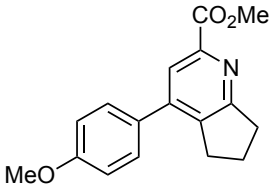
32

methyl 4-(9-ethyl-9*H*-carbazol-2-yl)-6-methylpicolinate (**32**): Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **17** (64 mg, 0.20 mmol) and methyl acrylate (**2a**), purification by flash column chromatography (hexane : AcOEt = 3 : 1) afforded the title compound (yellow oil, 38 mg, 55% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.44 (d, 1H, *J* = 1.5 Hz), 8.35 (d, 1H, *J* = 1.5 Hz), 8.18 (d, 1H, *J* = 7.8 Hz), 7.81 (dd, 1H, *J* = 8.7, 1.8 Hz), 7.70 (d, 1H, *J* = 1.5 Hz), 7.56–7.43 (m, 3H), 7.29 (td, 1H, *J* = 8.7, 1.5 Hz), 4.41 (q, 2H, *J* = 7.2 Hz), 4.06 (s, 3H), 2.75 (s, 3H), 1.47 (t, 3H, *J* = 7.2 Hz).^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 166.4, 159.3, 150.6, 147.9, 140.6, 140.5, 127.9, 126.3, 124.7, 124.3, 123.7, 122.9, 120.6, 119.5, 119.2, 109.0, 108.8, 53.0, 37.8, 24.8, 13.8; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{22}H_{20}N_2O_2$, 344.1525; found, 344.1520.



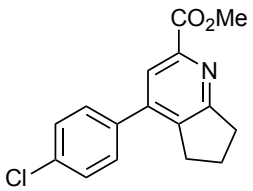
33

methyl 4-phenyl-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine-2-carboxylate (**33**): Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **18** (46 mg, 0.20 mmol) and methyl acrylate (**2a**), purification by flash column chromatography (hexane : AcOEt = 1 : 1) afforded the title compound (white solid, 42 mg, 83% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.03 (s, 1H), 7.60–7.40 (m, 5H), 4.02 (s, 3H), 3.12 (t, 2H, J = 7.5 Hz), 3.10 (t, 2H, J = 7.5 Hz), 2.16 (tt, 2H, J = 7.5, 7.5 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 167.4, 166.3, 146.6, 145.9, 139.0, 137.8, 128.7, 128.2, 123.0, 52.8, 34.6, 31.1, 23.6; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{16}H_{15}NO_2$, 253.1103; found, 253.1104.



34

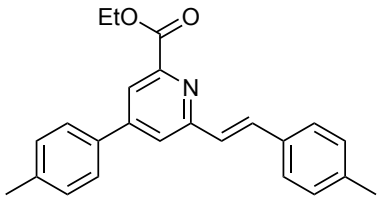
methyl 4-(4-methoxyphenyl)-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine-2-carboxylate (**34**): Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **19** (52 mg, 0.20 mmol) and methyl acrylate (**2a**), purification by flash column chromatography (hexane : AcOEt = 1 : 1) afforded the title compound (white solid, 40 mg, 70% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.01 (s, 1H), 7.48 (d, 2H, J = 9.0 Hz), 7.01 (d, 2H, J = 9.0 Hz), 4.01 (s, 3H), 3.87 (s, 3H), 3.17 (t, 2H, J = 7.5 Hz), 3.10 (t, 2H, J = 7.5 Hz), 2.15 (tt, 2H, J = 7.5, 7.5 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 167.3, 166.4, 160.0, 146.5, 145.5, 138.5, 130.0, 129.5, 122.7, 114.1, 55.3, 52.8, 34.6, 31.3, 23.6; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{17}H_{17}NO_3$, 283.1208; found, 283.1210.



35

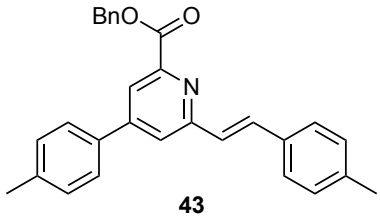
methyl 4-(4-chlorophenyl)-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine-2-carboxylate (**35**): Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **20** (53 mg, 0.20 mmol) and methyl acrylate (**2a**), purification by flash column chromatography (hexane : AcOEt = 5 : 1) afforded

the title compound (white solid, 53 mg, 91% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.99 (s, 1H), 7.50–7.40 (m, 4H), 4.02 (s, 3H), 3.18 (t, 2H, J = 7.8 Hz), 3.07 (t, 2H, J = 7.5 Hz), 2.17 (tt, 2H, J = 7.8, 7.5 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 167.5, 166.1, 146.7, 144.7, 138.8, 136.1, 134.9, 129.5, 129.0, 122.6, 52.8, 34.5, 31.0, 23.5; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{16}H_{14}ClNO_2$, 287.0713, 289.0684; found, 287.0721, 289.0690.



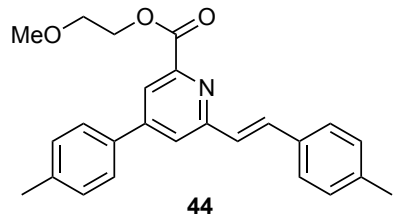
42

ethyl (*E*)-6-(4-methylstyryl)-4-(*p*-tolyl)picolinate (**42**): Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **6** (32 mg, 0.10 mmol) and ethyl acrylate (**2b**), purification by flash column chromatography (hexane : AcOEt = 5 : 1) afforded the title compound (pale yellow oil, 31 mg, 86% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.18 (d, 1H, J = 1.5 Hz), 7.81 (d, 1H, J = 1.5 Hz), 7.67 (d, 1H, J = 15.6 Hz), 7.63 (d, 2H, J = 7.8 Hz), 7.52 (d, 2H, J = 8.1 Hz), 7.35–7.27 (m, 3H), 7.20 (d, 2H, J = 8.1 Hz), 4.52 (q, 2H, J = 7.2 Hz), 2.44 (s, 3H), 2.38 (s, 3H), 1.48 (t, 3H, J = 7.2 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 165.6, 156.9, 149.8, 148.7, 139.6, 138.7, 134.6, 134.1, 129.9, 129.8, 129.5, 127.2, 127.1, 126.9, 121.6, 121.0, 62.0, 21.32, 21.27, 14.4; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{24}H_{23}NO_2$, 356.1729; found, 356.1718.



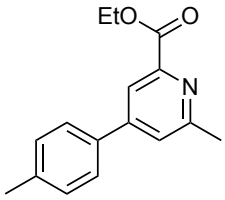
43

benzyl (*E*)-6-(4-methylstyryl)-4-(*p*-tolyl)picolinate (**43**): Following the general procedure B for pyridine synthesis with α,β-unsaturated oxime **6** (32 mg, 0.10 mmol) and benzyl acrylate (**2c**), purification by flash column chromatography (hexane : AcOEt = 5 : 1) afforded the title compound (pale yellow solid, 33 mg, 79% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.16 (d, 1H, J = 1.5 Hz), 7.79 (d, 1H, J = 1.5 Hz), 7.68 (d, 1H, J = 16.2 Hz), 7.61 (d, 2H, J = 8.1 Hz), 7.55–7.47 (m, 4H), 7.45–7.26 (m, 6H), 7.20 (d, 2H, J = 7.8 Hz), 5.50 (s, 2H), 2.43 (s, 3H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 165.4, 157.0, 149.9, 148.5, 139.6, 138.7, 135.8, 134.6, 134.2, 133.6, 129.9, 129.5, 128.6, 128.4, 128.3, 127.2, 126.9, 126.8, 121.8, 121.2, 67.4, 21.3, 21.2; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{29}H_{25}NO_2$, 419.1885; found, 419.1872.



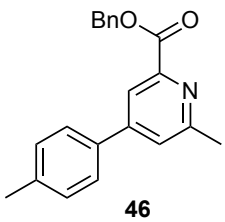
44

2-methoxyethyl (*E*)-6-(4-methylstyryl)-4-(*p*-tolyl)picolinate (**44**): Following the general procedure B for pyridine synthesis with α,β-unsaturated oxime **6** (32 mg, 0.10 mmol) and 2-methoxyethyl acrylate (**2d**), purification by flash column chromatography (hexane : AcOEt = 4 : 1) afforded the title compound (pale yellow solid, 36 mg, 93% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.11 (d, 1H, J = 1.5 Hz), 7.72 (d, 1H, J = 1.5 Hz), 7.61 (d, 1H, J = 16.2 Hz), 7.55 (d, 2H, J = 8.1 Hz), 7.44 (d, 2H, J = 8.1 Hz), 7.26–7.21 (m, 3H), 7.13 (d, 2H, J = 8.1 Hz), 4.54 (t, 2H, J = 4.8 Hz), 3.74 (t, 2H, J = 4.8 Hz), 3.39 (s, 3H), 2.36 (s, 3H), 2.31 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 165.5, 157.0, 149.9, 148.3, 139.6, 138.7, 134.6, 134.1, 133.6, 129.9, 129.5, 127.2, 126.9, 126.8, 121.8, 121.2, 70.4, 64.7, 59.1, 21.3, 21.2; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{25}H_{25}NO_3$, 387.1834; found, 387.1826.



45

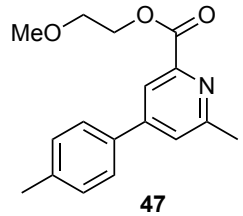
ethyl 6-methyl-4-(*p*-tolyl)picolinate (**45**): Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **12** (43 mg, 0.20 mmol) and ethyl acrylate (**2b**), purification by flash column chromatography (hexane : AcOEt = 5 : 1) afforded the title compound (white solid, 40 mg, 80% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.17 (d, 1H, J = 1.5 Hz), 7.58 (d, 2H, J = 8.1 Hz), 7.53 (d, 1H, J = 1.5 Hz), 7.30 (d, 2H, J = 8.1 Hz), 4.51 (q, 2H, J = 7.2 Hz), 2.71 (s, 3H), 2.42 (s, 3H), 1.45 (t, 3H, J = 7.2 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 165.6, 159.4, 149.5, 148.3, 139.5, 134.5, 129.8, 126.8, 124.0, 120.3, 61.9, 24.7, 21.2, 14.3; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{16}H_{17}NO_2$, 255.1259; found, 255.1268.



46

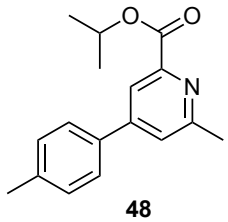
benzyl 6-methyl-4-(*p*-tolyl)picolinate (**46**): Following the general procedure B for pyridine synthesis with α,β-unsaturated oxime **12** (43 mg, 0.20 mmol) and benzyl acrylate (**2c**), purification by flash column chromatography (hexane : AcOEt = 5 : 1) afforded the title compound (white solid, 43 mg, 70% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.15 (d, 1H, J = 1.2 Hz), 7.58–7.48 (m, 5H), 7.40–7.26

(m, 5H), 5.48 (s, 2H), 2.71 (s, 3H), 2.41 (s, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz) δ 165.4, 159.5, 149.6, 148.1, 139.6, 135.9, 134.5, 129.9, 128.5, 128.3, 126.9, 124.2, 120.5, 67.4, 24.7, 21.2; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{21}H_{19}NO_2$, 317.1416; found, 317.1420.



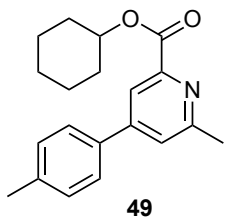
47

2-methoxyethyl 6-methyl-4-(*p*-tolyl)picolinate (**47**): Following the general procedure B for pyridine synthesis with α,β-unsaturated oxime **12** (43 mg, 0.20 mmol) and 2-methoxyethyl acrylate (**2d**), purification by flash column chromatography (hexane : AcOEt = 3 : 1) afforded the title compound (colorless oil, 38 mg, 66% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.09 (d, 1H, *J* = 1.5 Hz), 7.50 (d, 2H, *J* = 8.1 Hz), 7.45 (d, 1H, *J* = 1.5 Hz), 7.22 (d, 2H, *J* = 8.1 Hz), 4.51 (t, 2H, *J* = 4.8 Hz), 3.71 (t, 2H, *J* = 4.8 Hz), 3.36 (s, 3H), 2.63 (s, 3H), 2.34 (s, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz) δ 165.5, 159.5, 149.6, 147.9, 139.5, 134.5, 129.8, 126.9, 124.3, 124.1, 120.5, 120.4, 70.3, 64.5, 59.0, 58.9, 24.7, 21.2; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{17}H_{19}NO_3$, 285.1365; found, 285.1368.



48

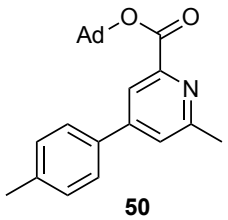
isopropyl 6-methyl-4-(*p*-tolyl)picolinate (**48**): Following the general procedure B for pyridine synthesis with α,β-unsaturated oxime **12** (43 mg, 0.20 mmol) and isopropyl acrylate (**2e**), purification by flash column chromatography (hexane : AcOEt = 3 : 1) afforded the title compound (white solid, 51 mg, 95% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.11 (d, 1H, *J* = 1.5 Hz), 7.57 (d, 2H, *J* = 7.8 Hz), 7.51 (d, 1H, *J* = 1.5 Hz), 7.30 (d, 2H, *J* = 7.8 Hz), 5.40–5.30 (m, 1H), 2.71 (s, 3H), 2.42 (s, 3H), 1.43 (d, 6H, *J* = 6.3 Hz). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz) δ 165.0, 159.4, 149.5, 148.6, 139.4, 134.6, 129.8, 126.9, 123.9, 120.1, 69.4, 24.7, 21.8, 21.2; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{17}H_{19}NO_2$, 269.1416; found, 269.1418.



49

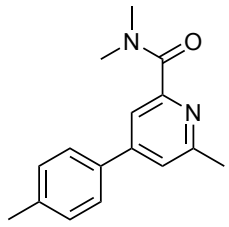
cyclohexyl 6-methyl-4-(*p*-tolyl)picolinate (**49**): Following the general procedure B for pyridine synthesis with α,β-unsaturated oxime **12** (43 mg, 0.20 mmol) and cyclohexyl acrylate (**2f**),

purification by flash column chromatography (hexane : AcOEt = 4 : 1) afforded the title compound (colorless oil, 59 mg, 94% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.10 (d, 1H, *J* = 1.5 Hz), 7.57 (d, 2H, *J* = 8.1 Hz), 7.50 (d, 1H, *J* = 1.5 Hz), 7.30 (d, 2H, *J* = 8.1 Hz), 5.14–5.05 (m, 1H), 2.71 (s, 3H), 2.42 (s, 3H), 2.15–2.00 (m, 2H), 1.90–1.75 (m, 2H), 1.70–1.20 (m, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 164.8, 159.4, 149.4, 148.7, 139.4, 134.7, 129.8, 126.8, 123.9, 120.1, 74.2, 31.6, 25.4, 24.7, 23.9, 21.2; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{20}H_{23}NO_2$, 309.1729; found, 309.1732.



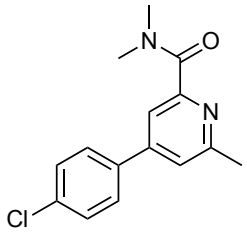
50

(3*s*,5*s*,7*s*)-adamantan-1-yl 6-methyl-4-(*p*-tolyl)picolinate (**50**): Following the general procedure B for pyridine synthesis with α,β-unsaturated oxime **12** (43 mg, 0.20 mmol) and adamantan-1-yl acrylate (**2g**), purification by flash column chromatography (hexane : AcOEt = 4 : 1) afforded the title compound (colorless oil, 60 mg, 83% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.04 (d, 1H, *J* = 1.5 Hz), 7.55 (d, 2H, *J* = 7.8 Hz), 7.48 (d, 1H, *J* = 1.5 Hz), 7.29 (d, 2H, *J* = 7.8 Hz), 2.69 (s, 3H), 2.42 (s, 3H), 2.35–2.30 (m, 6H), 2.25–2.20 (m, 3H), 1.80–1.60 (m, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 164.0, 159.3, 149.5, 149.4, 139.3, 134.8, 129.8, 126.9, 123.6, 119.9, 82.1, 41.2, 36.2, 30.9, 24.7, 21.2; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{24}H_{27}NO_2$, 361.2042; found, 361.2037.



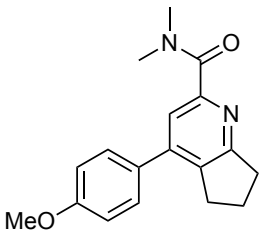
52

N,*N*,6-trimethyl-4-(*p*-tolyl)picolinamide (**52**): Following the general procedure B for pyridine synthesis with α,β-unsaturated oxime **12** (43 mg, 0.20 mmol) and *N*,*N*-dimethylacrylamide (**2i**), purification by flash column chromatography (AcOEt only) afforded the title compound (colorless oil, 22 mg, 43% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.60 (d, 1H, *J* = 1.5 Hz), 7.55 (d, 2H, *J* = 8.1 Hz), 7.39 (d, 1H, *J* = 1.5 Hz), 7.28 (d, 2H, *J* = 8.1 Hz), 3.15 (s, 3H), 3.08 (s, 3H), 2.63 (s, 3H), 2.41 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 169.5, 157.9, 154.5, 149.6, 139.4, 134.8, 129.8, 126.8, 121.4, 118.0, 39.0, 35.6, 24.5, 21.2; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{16}H_{18}N_2O$, 254.1419; found, 254.1418.



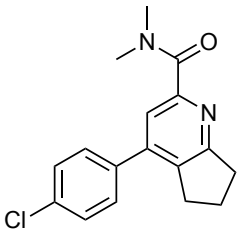
53

4-(4-chlorophenyl)-*N*,*N*,6-trimethylpicolinamide (**53**): Following the general procedure B for pyridine synthesis with α,β-unsaturated oxime **14** (24 mg, 0.10 mmol) and *N*,*N*-dimethylacrylamide (**2i**), purification by flash column chromatography (AcOEt only) afforded the title compound (colorless oil, 17 mg, 62% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.58 (d, 2H, *J* = 8.7 Hz), 7.57 (d, 1H, *J* = 1.2 Hz), 7.46 (d, 2H, *J* = 8.7 Hz), 7.37 (d, 1H, *J* = 1.2 Hz), 3.15 (s, 3H), 3.10 (s, 3H), 2.64 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 169.2, 158.1, 154.7, 148.5, 136.3, 135.5, 129.3, 128.3, 121.4, 118.2, 39.0, 35.7, 24.5; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{15}H_{15}ClN_2O$, 274.0873; found, 274.0869.



54

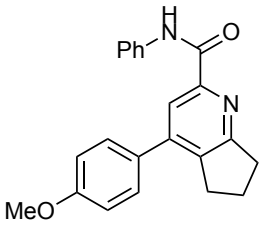
4-(4-methoxyphenyl)-*N*,*N*-dimethyl-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine-2-carboxamide (**54**): Following the general procedure B for pyridine synthesis with α,β-unsaturated oxime **19** (26 mg, 0.10 mmol) and *N*,*N*-dimethylacrylamide (**2i**), purification by flash column chromatography (AcOEt only) afforded the title compound (colorless oil, 26 mg, 88% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.46 (d, 2H, *J* = 8.7 Hz), 7.41 (s, 1H), 6.99 (d, 2H, *J* = 8.7 Hz), 3.86 (s, 3H), 3.14 (s, 3H), 3.11 (s, 3H), 3.10–3.05 (m, 4H), 2.20–2.10 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 169.7, 165.4, 159.9, 152.9, 145.7, 135.1, 130.4, 129.4, 120.0, 114.1, 55.3, 39.1, 35.6, 34.4, 31.1, 23.5; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{18}H_{20}N_2O_2$, 296.1525; found, 296.1523.



55

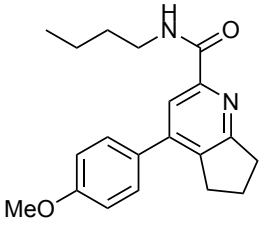
4-(4-chlorophenyl)-*N*,*N*-dimethyl-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine-2-carboxamide (**55**): Following the general procedure B for pyridine synthesis with α,β-unsaturated oxime **20** (26 mg,

0.10 mmol) and *N*,*N*-dimethylacrylamide (**2i**), purification by flash column chromatography (hexane : AcOEt = 2 : 1) afforded the title compound (colorless oil, 28 mg, 94% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.44 (s, 4H), 7.41 (s, 1H), 3.14 (s, 3H), 3.11 (s, 3H), 3.11–3.00 (m, 4H), 2.19–2.13 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 169.4, 165.7, 153.1, 144.9, 136.5, 135.4, 134.7, 129.4, 128.9, 120.2, 39.1, 35.7, 34.4, 30.8, 23.4; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{17}H_{17}ClN_2O$, 300.1029, 302.1000; found, 300.1017, 302.0986.



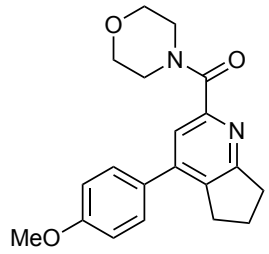
56

4-(4-methoxyphenyl)-*N*-phenyl-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine-2-carboxamide (**56**): Following the general procedure B for pyridine synthesis with α,β-unsaturated oxime **19** (26 mg, 0.10 mmol) and *N*-phenyl acrylamide (**2j**), purification by flash column chromatography (hexane : AcOEt = 5 : 1) afforded the title compound (white solid, 20 mg, 58% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.15 (s, 1H), 7.81 (d, 2H, *J* = 8.4 Hz), 7.51 (d, 2H, *J* = 9.0 Hz), 7.39 (dd, 2H, *J* = 9.0, 7.5 Hz), 7.14 (t, 1H, *J* = 7.5 Hz), 7.01 (d, 2H, *J* = 9.0 Hz), 3.87 (s, 3H), 3.15–3.09 (m, 4H), 2.25–2.15 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 165.5, 162.7, 160.0, 148.5, 146.1, 138.0, 137.8, 130.3, 129.6, 129.0, 124.0, 119.7, 119.6, 114.1, 55.4, 34.2, 31.3, 23.7; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{22}H_{20}N_2O_2$, 344.1525; found, 344.1513.



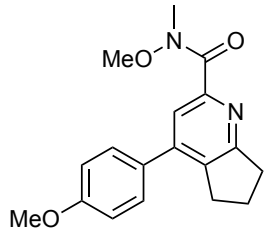
57

N-butyl-4-(4-methoxyphenyl)-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine-2-carboxamide (**57**): Following the general procedure B for pyridine synthesis with α,β-unsaturated oxime **19** (26 mg, 0.10 mmol) and *N*-butyl acrylamide (**2k**), purification by flash column chromatography (hexane : AcOEt = 3 : 1) afforded the title compound (colorless oil, 27 mg, 84% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.15–8.05 (br, 1H), 8.05 (s, 1H), 7.49 (d, 2H, *J* = 9.0 Hz), 6.99 (d, 2H, *J* = 9.0 Hz), 3.87 (s, 3H), 3.48 (q, 2H, *J* = 7.2 Hz), 3.11–3.02 (m, 4H), 2.18–2.10 (m, 2H), 1.70–1.64 (m, 2H), 1.50–1.40 (m, 2H), 0.97 (t, 3H, *J* = 7.2 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 165.4, 164.9, 159.9, 148.8, 145.7, 137.1, 130.4, 129.6, 119.3, 114.0, 55.3, 39.1, 34.2, 31.8, 31.2, 23.7, 20.2, 13.8; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{20}H_{24}N_2O_2$, 324.1838; found, 324.1835.



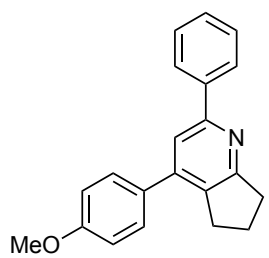
58

(4-(4-methoxyphenyl)-6,7-dihydro-5*H*-cyclopenta[*b*]pyridin-2-yl)(morpholino)methanone (**58**): Following the general procedure B for pyridine synthesis with α,β-unsaturated oxime **19** (26 mg, 0.10 mmol) and 4-acryloylmorpholine (**2l**), purification by flash column chromatography (AcOEt only) afforded the title compound (colorless oil, 30 mg, 90% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.46 (d, 2H, J = 8.7 Hz), 7.45 (s, 1H), 6.99 (d, 2H, J = 8.7 Hz), 3.86 (s, 3H), 3.85–3.75 (m, 4H), 3.75–3.60 (m, 4H), 3.15–3.04 (m, 4H), 2.20–2.09 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 168.2, 165.6, 159.9, 152.0, 145.8, 135.5, 130.2, 129.4, 120.6, 114.1, 67.0, 66.8, 55.3, 47.9, 42.7, 34.5, 31.1, 23.5; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{20}H_{22}N_2O_3$, 338.1630; found, 338.1636.



59

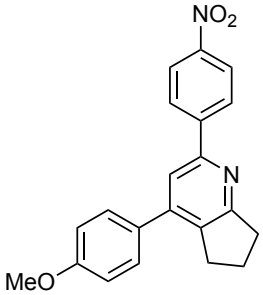
N-methoxy-4-(4-methoxyphenyl)-*N*-methyl-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine-2-carboxamide (**59**): Following the general procedure B for pyridine synthesis with α,β-unsaturated oxime **19** (26 mg, 0.10 mmol) and *N*-methoxy-*N*-methyl acrylamide (**2m**), purification by flash column chromatography (hexane : AcOEt = 3 : 1) afforded the title compound (white solid, 15 mg, 48% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.47 (s, 1H), 7.46 (d, 2H, J = 9.0 Hz), 6.99 (d, 2H, J = 9.0 Hz), 3.86 (s, 3H), 3.79 (s, 3H), 3.42 (s, 3H), 3.13–3.04 (m, 4H), 2.20–2.10 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 165.7, 159.9, 151.4, 145.4, 135.9, 130.4, 129.5, 120.2, 114.1, 61.4, 55.3, 34.4, 31.1, 23.5; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{18}H_{20}N_2NaO_3$, 335.1372; found, 335.1370.



60

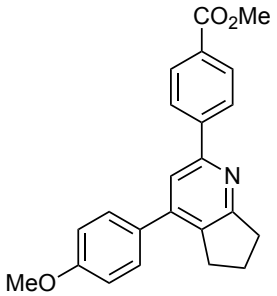
4-(4-methoxyphenyl)-2-phenyl-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine (**60**): Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **19** (26 mg, 0.10 mmol) and styrene

(**2n**), purification by flash column chromatography (hexane : AcOEt = 10 : 1) afforded the title compound (white solid, 10 mg, 33% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.97 (d, 2H, J = 8.7 Hz), 7.53–7.40 (m, 6H), 7.02 (d, 2H, J = 8.7 Hz), 3.88 (s, 3H), 3.15 (t, 2H, J = 7.8 Hz), 3.07 (t, 2H, J = 7.2 Hz), 2.20–2.13 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 166.6, 159.7, 156.4, 145.5, 140.0, 132.9, 131.3, 129.4, 128.6, 128.4, 127.0, 117.9, 114.1, 55.4, 34.8, 30.8, 23.6; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{21}H_{19}NO$, 301.1467; found, 301.1469.



61

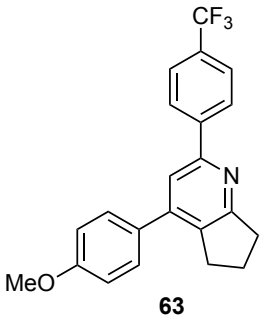
4-(4-methoxyphenyl)-2-(4-nitrophenyl)-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine (**61**): Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **19** (26 mg, 0.10 mmol) and 4-nitrostyrene (**2o**), purification by flash column chromatography (hexane : AcOEt = 4 : 1) afforded the title compound (pale yellow solid, 16 mg, 46% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.30 (d, 2H, J = 9.0 Hz), 8.18 (d, 2H, J = 9.0 Hz), 7.58 (s, 1H), 7.49 (d, 2H, J = 9.0 Hz), 7.03 (d, 2H, J = 9.0 Hz), 3.89 (s, 3H), 3.16 (t, 2H, J = 7.8 Hz), 3.10 (t, 2H, J = 7.8 Hz), 2.25–2.10 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 167.3, 159.9, 153.6, 147.8, 146.1, 145.8, 134.6, 130.7, 129.4, 127.6, 123.9, 118.6, 114.2, 55.4, 34.7, 30.9, 23.5; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{21}H_{18}N_2O_3$, 346.1317; found, 346.1307.



62

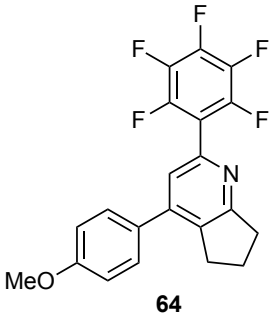
methyl 4-(4-(4-methoxyphenyl)-6,7-dihydro-5*H*-cyclopenta[*b*]pyridin-2-yl)benzoate (**62**): Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **19** (26 mg, 0.10 mmol) and methyl 4-vinylbenzoate (**2p**), purification by flash column chromatography (hexane : AcOEt = 3 : 1) afforded the title compound (white solid, 20 mg, 56% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.13 (d, 2H, J = 8.7 Hz), 8.07 (d, 2H, J = 8.7 Hz), 7.56 (s, 1H), 7.49 (d, 2H, J = 9.0 Hz), 7.02 (d, 2H, J = 9.0 Hz), 3.94 (s, 3H), 3.88 (s, 3H), 3.16 (t, 2H, J = 7.5 Hz), 3.08 (t, 2H, J = 7.5 Hz), 2.20–2.13 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 167.0, 166.9, 159.8, 155.1, 145.6, 144.3, 133.8,

131.1, 130.0, 129.8, 129.4, 126.8, 118.3, 114.1, 55.4, 52.1, 34.7, 30.9, 23.6; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{23}H_{21}NO_3$, 359.1521; found, 359.1522.



63

4-(4-methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine (**63**): Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **19** (26 mg, 0.10 mmol) and 4-trifluoromethylstyrene (**2q**), purification by flash column chromatography (hexane : AcOEt = 4 : 1) afforded the title compound (white solid, 33 mg, 89% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.11 (d, 2H, *J* = 8.1 Hz), 7.71 (d, 2H, *J* = 8.1 Hz), 7.53 (s, 1H), 7.49 (d, 2H, *J* = 8.7 Hz), 7.02 (d, 2H, *J* = 8.7 Hz), 3.88 (s, 3H), 3.16 (t, 2H, *J* = 7.5 Hz), 3.09 (t, 2H, *J* = 7.5 Hz), 2.20–2.13 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 167.0, 159.9, 154.7, 142.6 (q, *J* = 173 Hz), 133.9, 131.0, 129.4, 127.2, 125.6, 125.5, 118.2, 114.1, 55.4, 34.7, 30.9, 23.6; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{22}H_{18}F_3NO$, 369.1340; found, 369.1346.

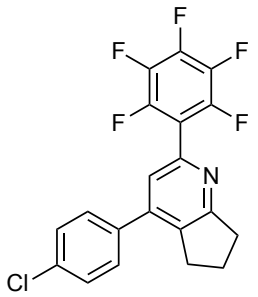


64

4-(4-methoxyphenyl)-2-(perfluorophenyl)-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine (**64**): Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **19** (26 mg, 0.10 mmol) and pentafluorostyrene (**2r**), purification by flash column chromatography (hexane : AcOEt = 10 : 1) afforded the title compound (pale yellow solid, 36 mg, 91% yield).

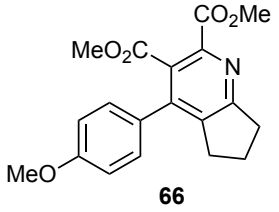
1.0 mmol scale synthesis: Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **19** (259 mg, 1.0 mmol) and pentafluorostyrene (**2r**), purification by flash column chromatography (hexane : AcOEt = 10 : 1) afforded the title compound (pale yellow solid, 290 mg, 74% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.46 (d, 2H, *J* = 8.7 Hz), 7.25 (s, 1H), 7.01 (d, 2H, *J* = 8.1 Hz), 3.87 (s, 3H), 3.20–3.09 (m, 4H), 2.21–2.15 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 167.3, 160.0, 146.3 (m), 145.6, 144.6, 142.9 (m), 139.3 (m), 136.1 (m), 134.9, 130.2, 129.5, 122.7, 115.9

(m), 114.2, 55.4, 34.6, 31.0, 23.4; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{21}H_{14}F_5NO$, 391.0996; found, 391.1001.



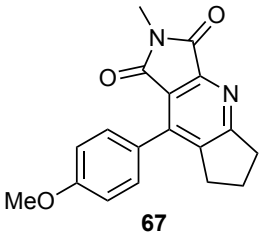
65

4-(4-chlorophenyl)-2-(perfluorophenyl)-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine (**65**): Following the general procedure A for pyridine synthesis with α,β-unsaturated oxime **20** (26 mg, 0.10 mmol) and pentafluorostyrene (**2r**), purification by flash column chromatography (hexane : AcOEt = 4 : 1) afforded the title compound (pale yellow solid, 37 mg, 93% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.60–7.40 (m, 4H), 7.23 (s, 1H), 3.17 (t, 2H, J = 7.5 Hz), 3.09 (t, 2H, J = 7.5 Hz), 2.25–2.15 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 167.6, 146.2 (m), 144.8, 143.0 (m), 139.2 (m), 136.4, 136.1 (m), 135.2, 134.9, 129.5, 129.0, 122.7, 115.6 (m), 34.6, 30.8, 23.3; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{20}H_{11}ClF_5N$, 395.0500; found, 395.0503.



66

dimethyl 4-(4-methoxyphenyl)-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine-2,3-dicarboxylate (**66**): Following the general procedure B for pyridine synthesis with α,β-unsaturated oxime **19** (26 mg, 0.10 mmol) and dimethyl maleate (**2s**), purification by flash column chromatography (hexane : AcOEt = 1 : 1) afforded the title compound (colorless oil, 12 mg, 36% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.22 (d, 2H, J = 9.0 Hz), 6.95 (d, 2H, J = 9.0 Hz), 3.99 (s, 3H), 3.85 (s, 3H), 3.68 (s, 3H), 3.18 (t, 2H, J = 7.2 Hz), 2.86 (t, 2H, J = 7.5 Hz), 2.20–2.10 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 168.3, 166.9, 165.6, 159.8, 144.5, 143.5, 140.1, 130.0, 129.5, 127.7, 113.9, 55.3, 53.2, 52.5, 34.7, 30.6, 23.0; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{19}H_{19}NO_5$, 341.1263; found, 341.1267.

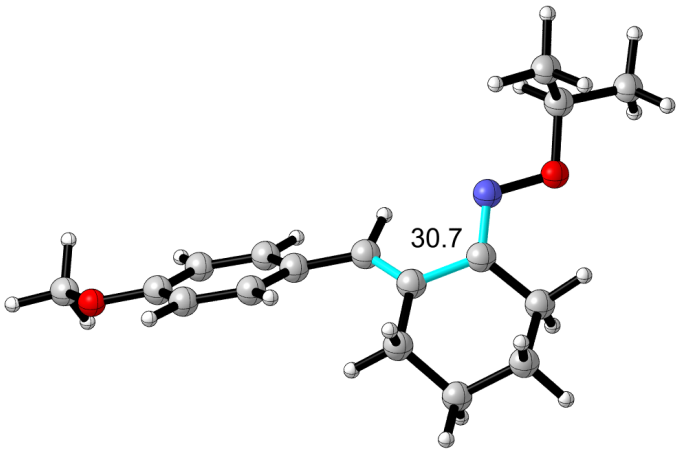


67

8-(4-methoxyphenyl)-2-methyl-6,7-dihydrocyclopenta[*b*]pyrrolo[3,4-*e*]pyridine-1,3(2*H*,5*H*)-dione (**67**): Following the general procedure B for pyridine synthesis with α,β-unsaturated oxime **19** (52 mg, 0.20 mmol) and *N*-methylmaleimide (**2t**), purification by flash column chromatography (hexane : AcOEt = 2 : 1) afforded the title compound (white solid, 32 mg, 52% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.40 (d, 2H, J = 9.0 Hz), 7.20 (d, 2H, J = 9.0 Hz), 3.89 (s, 3H), 3.23 (t, 2H, J = 7.8 Hz), 3.17 (s, 3H), 2.99 (t, 2H, J = 7.5 Hz), 2.22–2.16 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 172.8, 166.8, 160.5, 151.8, 143.8, 141.1, 130.7, 124.7, 121.7, 113.6, 55.3, 34.8, 30.7, 23.8, 23.4; HRMS (EI-quadrupole) *m/z*: $[M]^+$ Calcd for $C_{18}H_{16}N_2O_3$, 308.1161; found, 308.1169.

ωB97X-D/6-311+G(d,p) Calculated cartesian coordinates

6-membered α,β-unsaturated oxime **36**



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C	-5.5571246	-2.2886869	-0.6480961
H	-5.4010911	-2.2410819	-1.7292994
H	-5.9554733	-3.2762538	-0.3964858
H	-6.3056246	-1.5377674	-0.3747898
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H	-3.4540875	-1.8396837	2.0958579
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C	-0.5797720	0.8678899	-0.0107465
C	-2.9241148	1.7612737	-0.6716958
C	-0.1773584	2.2697199	0.4099645
C	-2.5006173	3.1224356	-0.1008374
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H	-3.9594358	1.5262409	-0.4176857
C	-1.0025319	3.3599836	-0.2946245
H	0.8863489	2.4255132	0.2134671
H	-0.3152784	2.3835162	1.4967019

H	-3.0867055	3.9163782	-0.5776835
H	-2.7375356	3.1591209	0.9712329
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C	1.7445609	-0.1959332	-0.0640935
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C	2.4451153	0.4911981	0.9510959
C	3.8861417	-1.1381313	-0.7980756
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H	4.4246856	-1.7826670	-1.4825526
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H	7.7270839	-1.1469469	-0.1017890
H	6.4173190	-2.3280038	-0.3675615
H	6.6223518	-0.9509514	-1.4883176

7-membered α,β-unsaturated oxime **37**

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H	3.7566614	-2.1134710	1.6643107
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H	6.0115116	-1.2808950	1.0081680
H	6.0074457	-3.0565900	1.0483444
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H	2.3537214	-3.3302356	0.0048682
H	3.7513325	-3.4857539	-1.0819891
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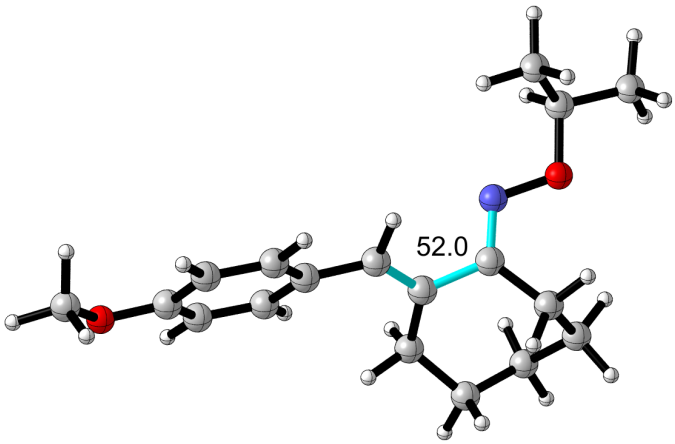

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C	3.4194942	2.3722285	-0.5994091
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H	3.4241954	0.5528500	-1.7803426
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H	0.1426440	2.1369396	1.4888021
H	-0.8865052	2.3755640	0.0909209
C	2.5300527	3.1575088	0.3840731
H	3.7863246	3.0435486	-1.3858378
H	4.3011878	1.9935539	-0.0721461
H	0.9980273	3.4400095	-1.1419141
H	0.6377471	4.2024372	0.3883442
H	2.9645109	4.1531119	0.5318977
H	2.5540478	2.6706605	1.3678997
C	-0.4730123	-0.2512767	-0.2425450
H	-0.0969833	-1.2022522	-0.6139276
C	-1.9297208	-0.2221892	-0.0509590
C	-2.7210646	-1.0753915	-0.8396694
C	-2.6027705	0.5674031	0.9061158
C	-4.1091542	-1.1224243	-0.7268334
H	-2.2340114	-1.7159440	-1.5704086
C	-3.9837165	0.5275605	1.0368468
H	-2.0370512	1.1956461	1.5832518
C	-4.7514980	-0.3096350	0.2152677
H	-4.6729485	-1.7914775	-1.3659418
H	-4.4937886	1.1303356	1.7811329
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H	-6.6904188	-2.1688128	-0.2244587
H	-7.9488732	-0.9167552	-0.0526824
H	-6.8335291	-0.8698565	-1.4437008

Crystallographic description of 2-benzylidenecyclopentenone oxime ether (18)

CCDC-2166741 for 2-benzylidenecyclopentenone oxime ether (**18**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

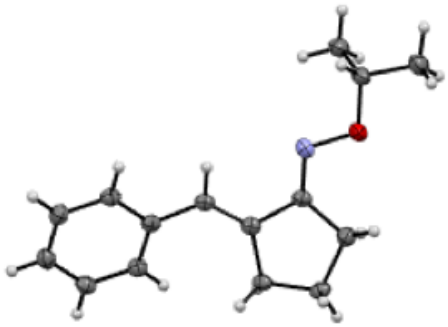
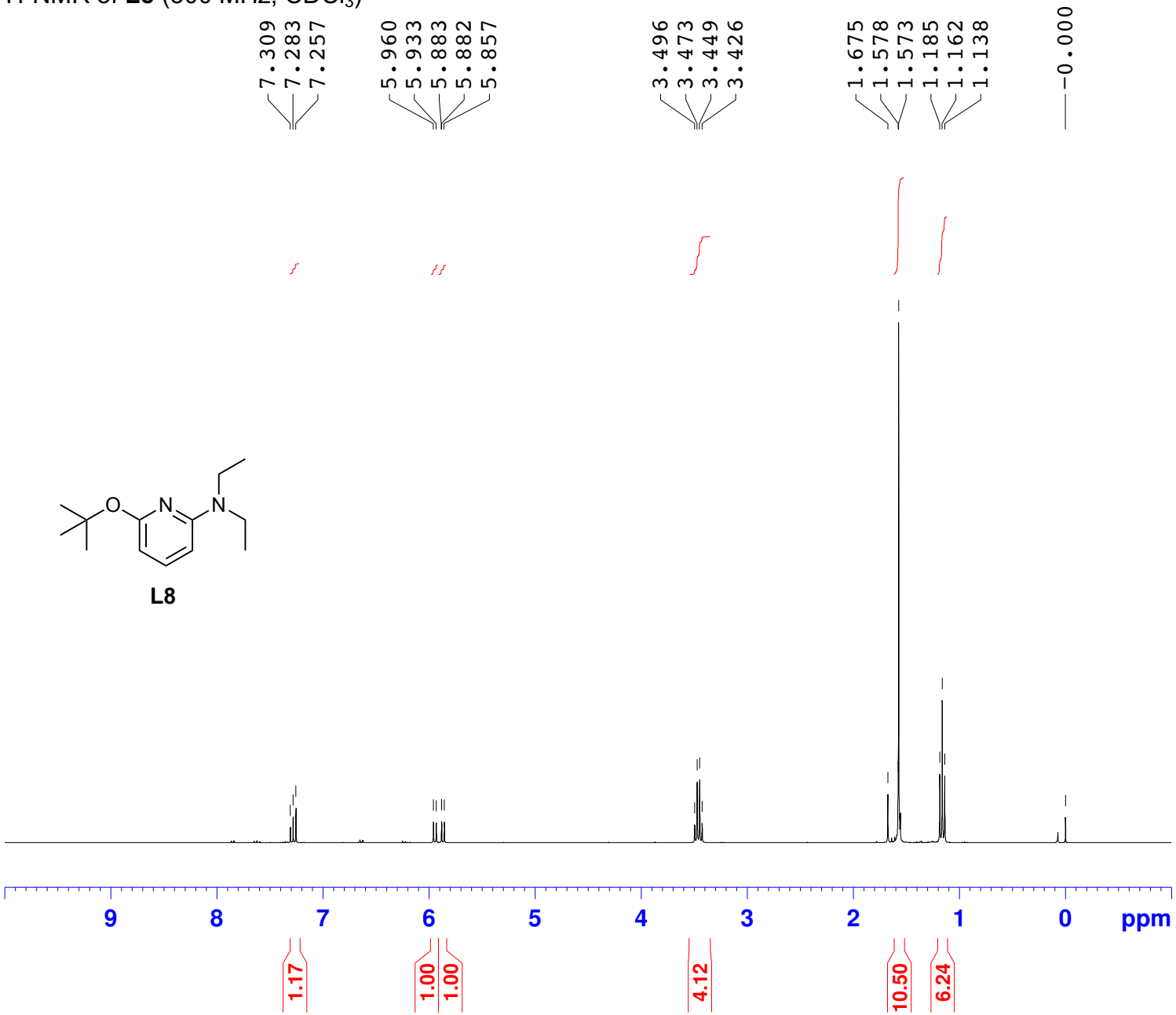


Figure S1. ORTEP view of oxime **18**.

References

1) T. Yamada, Y. Hashimoto, K. Tanaka. III, N. Morita, O. Tamura, *Org. Lett*. **2021**, *23*, 1659–1663.
2) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian 09 Revision D.01; Gaussian, Inc.; Wallingford CT, **2013**.
3) a) J. M. Neely, T. Rovis, *J. Am. Chem. Soc*. **2013**, *135*, 66–69. b) S. Tang, J. He, Y. Sun, L. He, X. She. *Org. Lett*. **2009**, *11*, 3982–3985.

^{1}H-NMR of **L8** (300 MHz, $CDCl_3$)



L8

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AQ              5.2953086 sec
RG                  50.8
DW                80.800 usec
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TE                294.5 K
D1           1.00000000 sec
TD0                    1

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NUC1                   1H
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PLW1          6.19999981 W

F2 - Processing parameters
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SF           300.1300074 MHz
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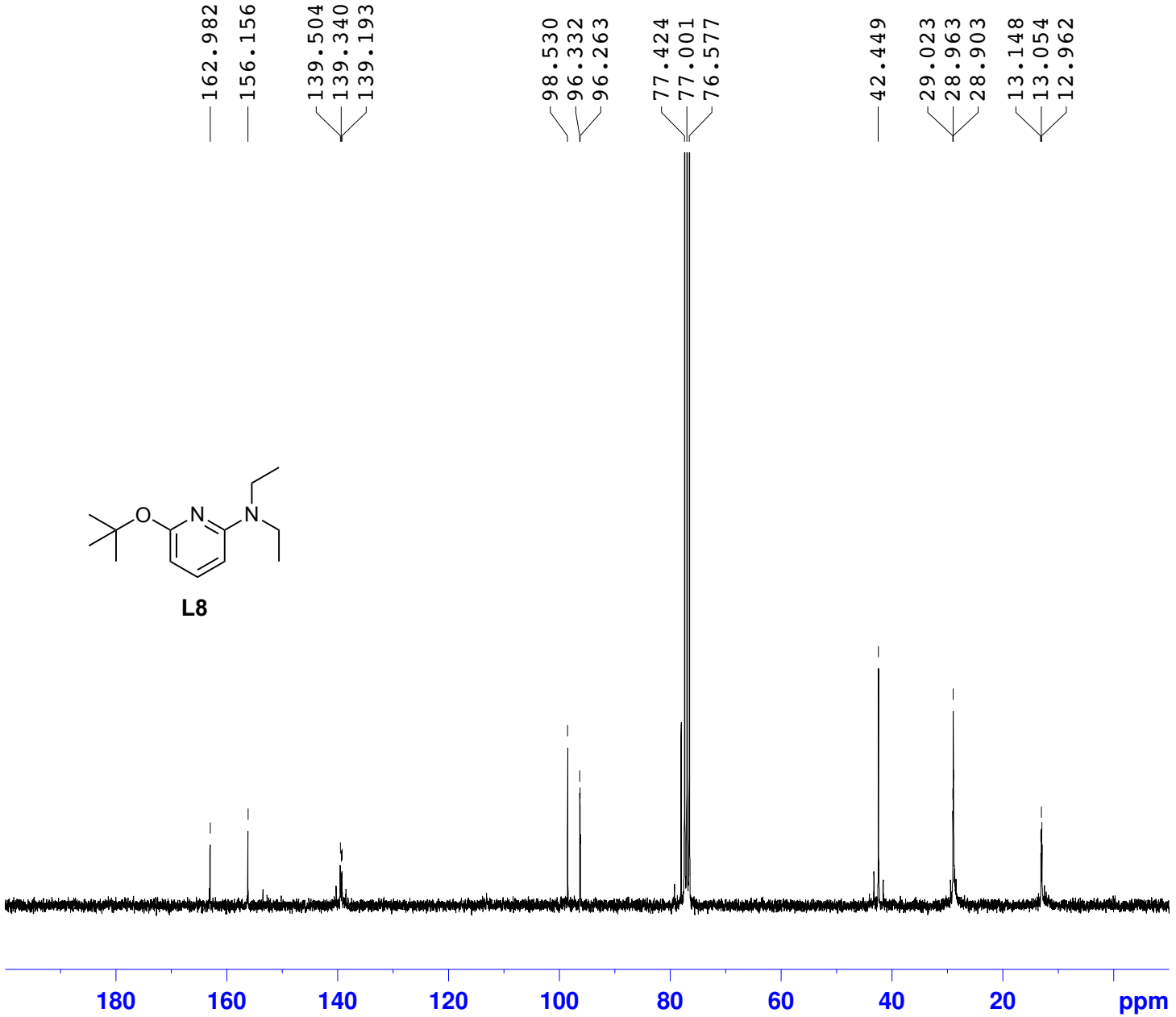
^{13}C-NMR of **L8** (75 MHz, $CDCl_3$)

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AQ            1.8175317 sec
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DW               27.733 usec
DE                6.50 usec
TE               295.6 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

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NUC1                13C
P1                10.00 usec
PLW1        34.50000000 W

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CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         6.19999981 W
PLW12        0.21797000 W
PLW13        0.13950001 W

F2 - Processing parameters
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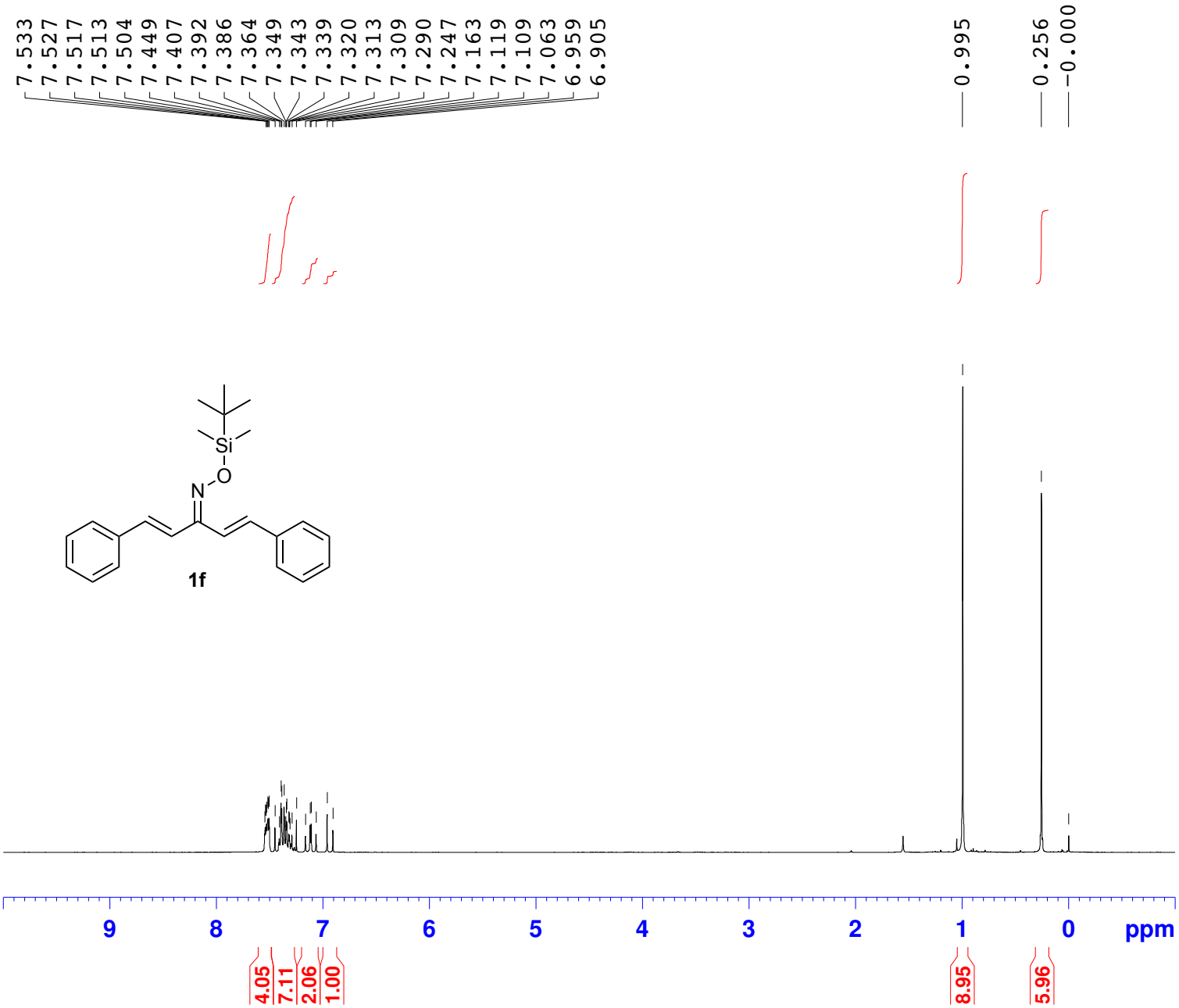
^{1}H-NMR of **1f** (300 MHz, $CDCl_3$)

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DS                     2
SWH             6188.119 Hz
FIDRES          0.094423 Hz
AQ              5.2953086 sec
RG                  40.3
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TE                294.4 K
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F2 - Processing parameters
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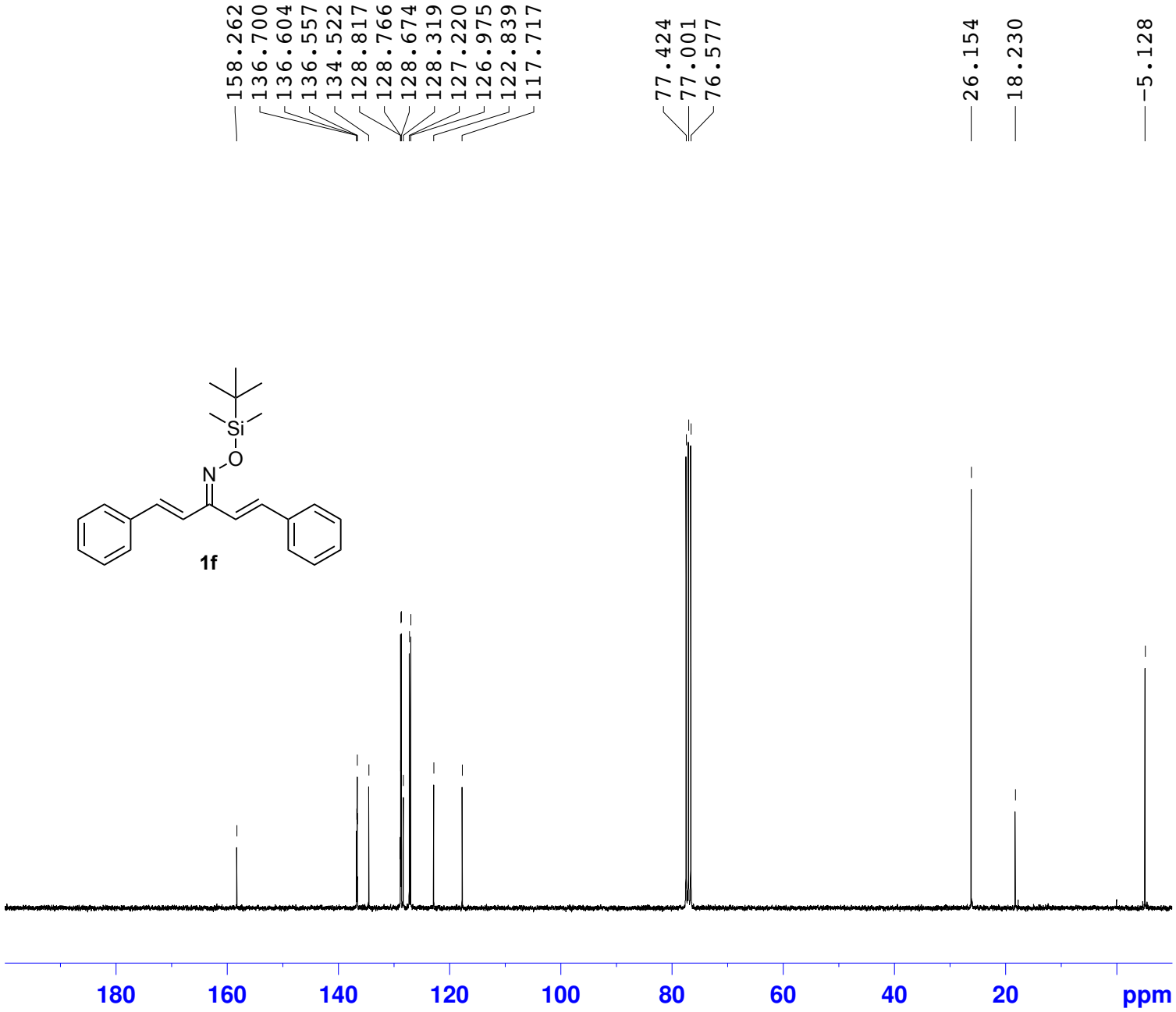
^{13}C-NMR of **1f** (75 MHz, $CDCl_3$)

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FIDRES          0.275098 Hz
AQ             1.8175317 sec
RG                  2050
DW                27.733 usec
DE                  6.50 usec
TE                 295.9 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

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PLW12          0.21797000 W
PLW13          0.13950001 W

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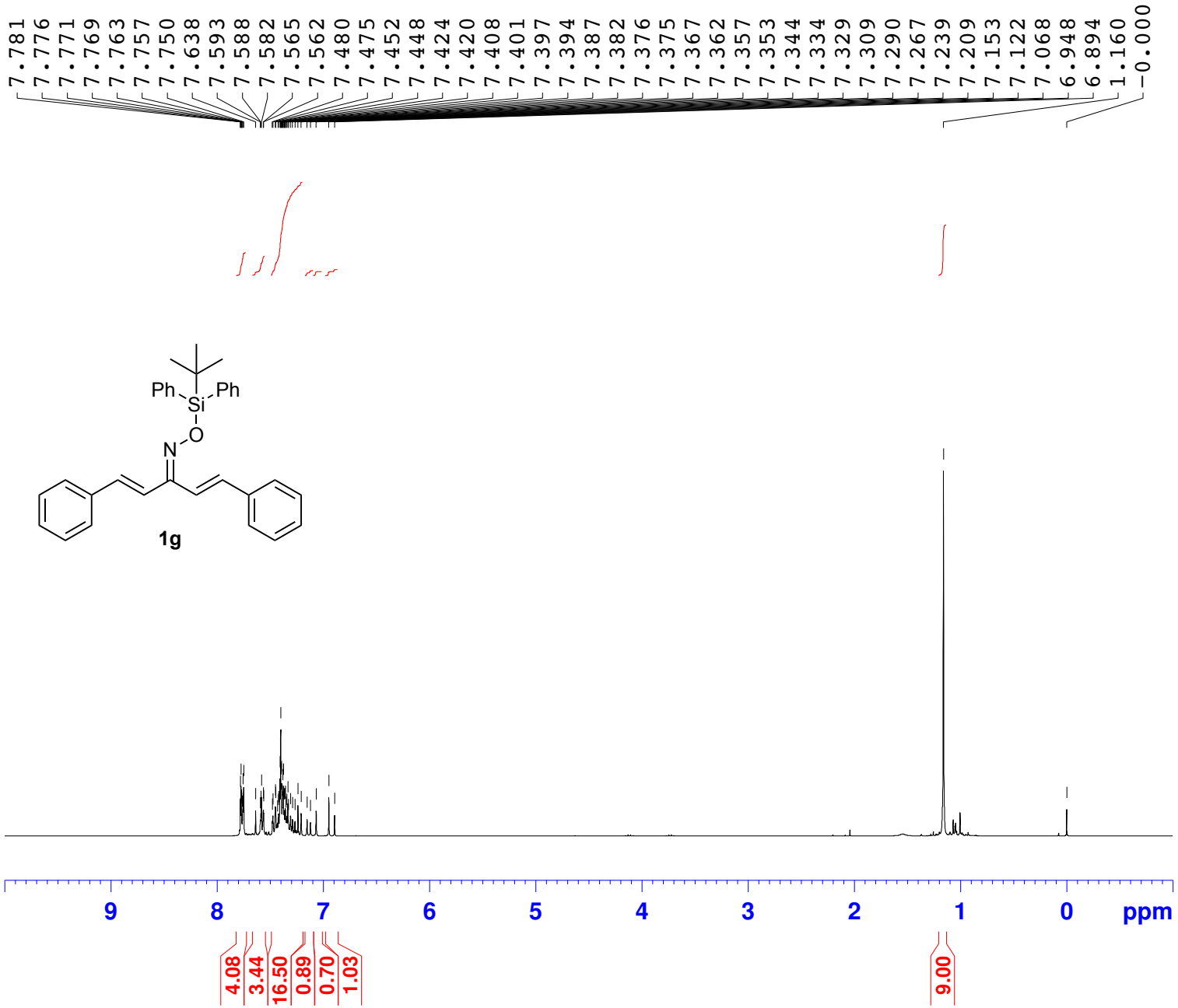
^{1}H-NMR of **1g** (300 MHz, $CDCl_3$)

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SOLVENT            CDCl3
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DS                     2
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FIDRES          0.094423 Hz
AQ             5.2953086 sec
RG                  45.2
DW                80.800 usec
DE                 6.50 usec
TE                294.4 K
D1           1.00000000 sec
TD0                    1

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F2 - Processing parameters
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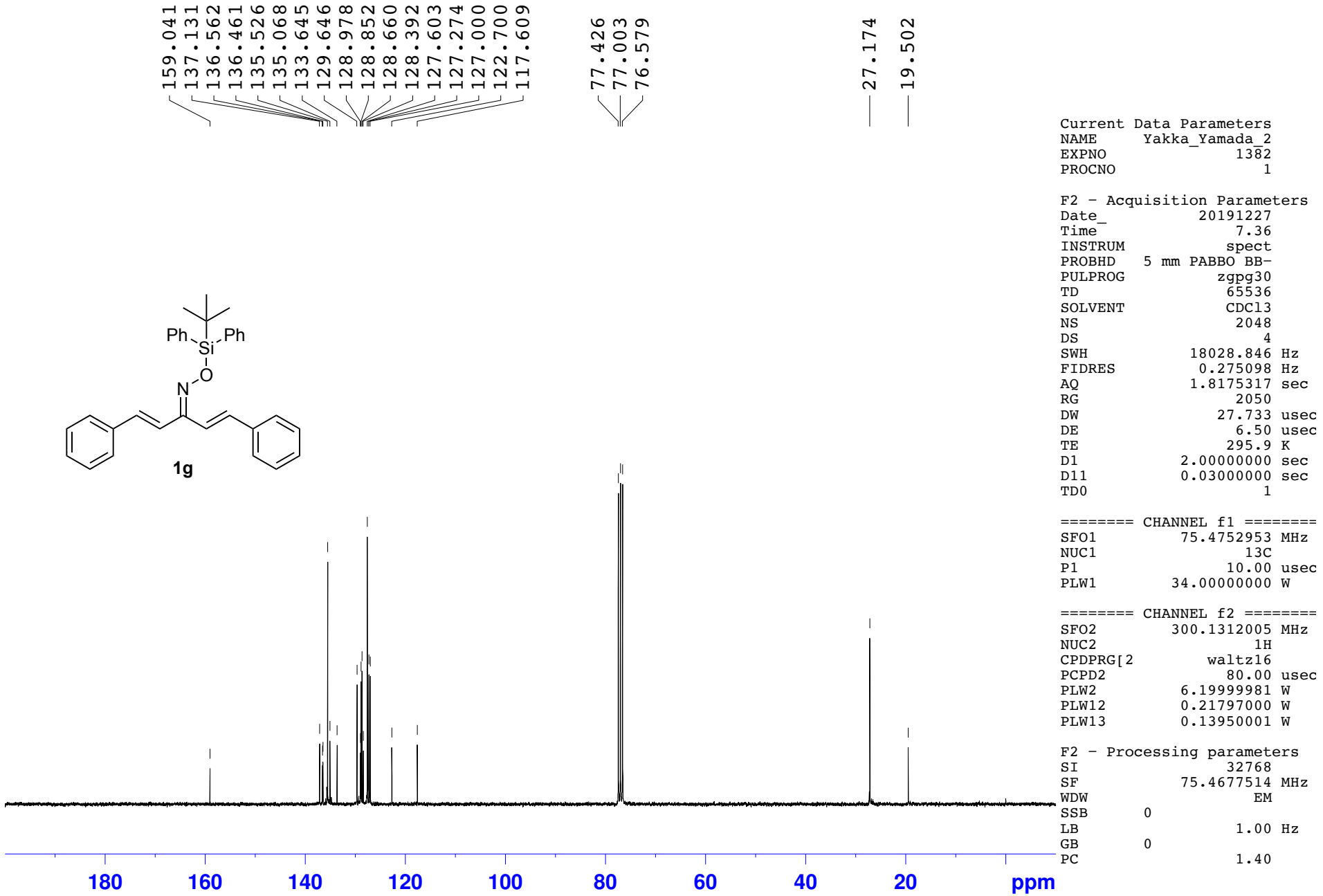
^{13}C-NMR of **1g** (75 MHz, $CDCl_3$)

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RG                 2050
DW               27.733 usec
DE                6.50 usec
TE               295.9 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

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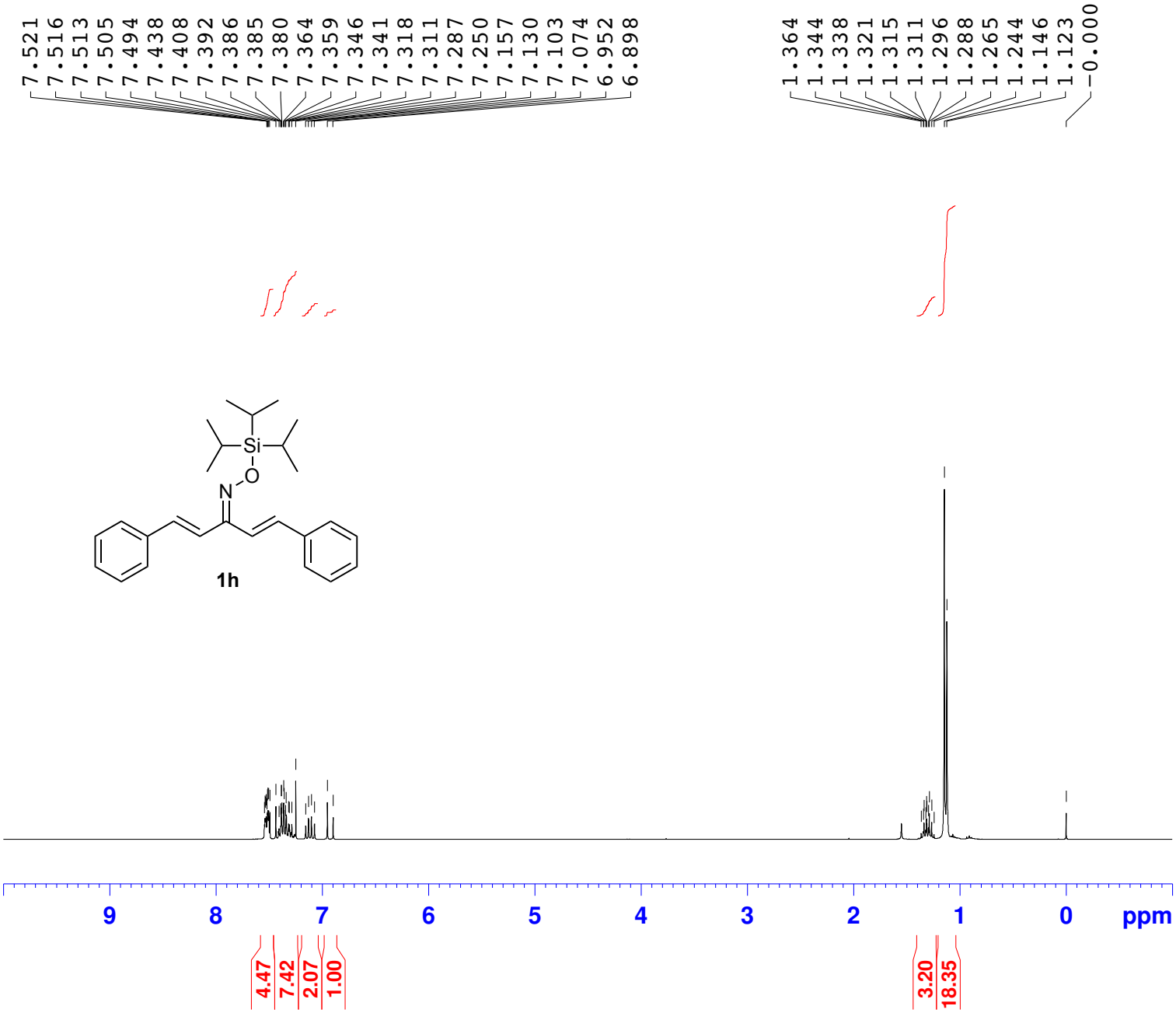
```

^{1}H-NMR of **1h** (300 MHz, $CDCl_3$)



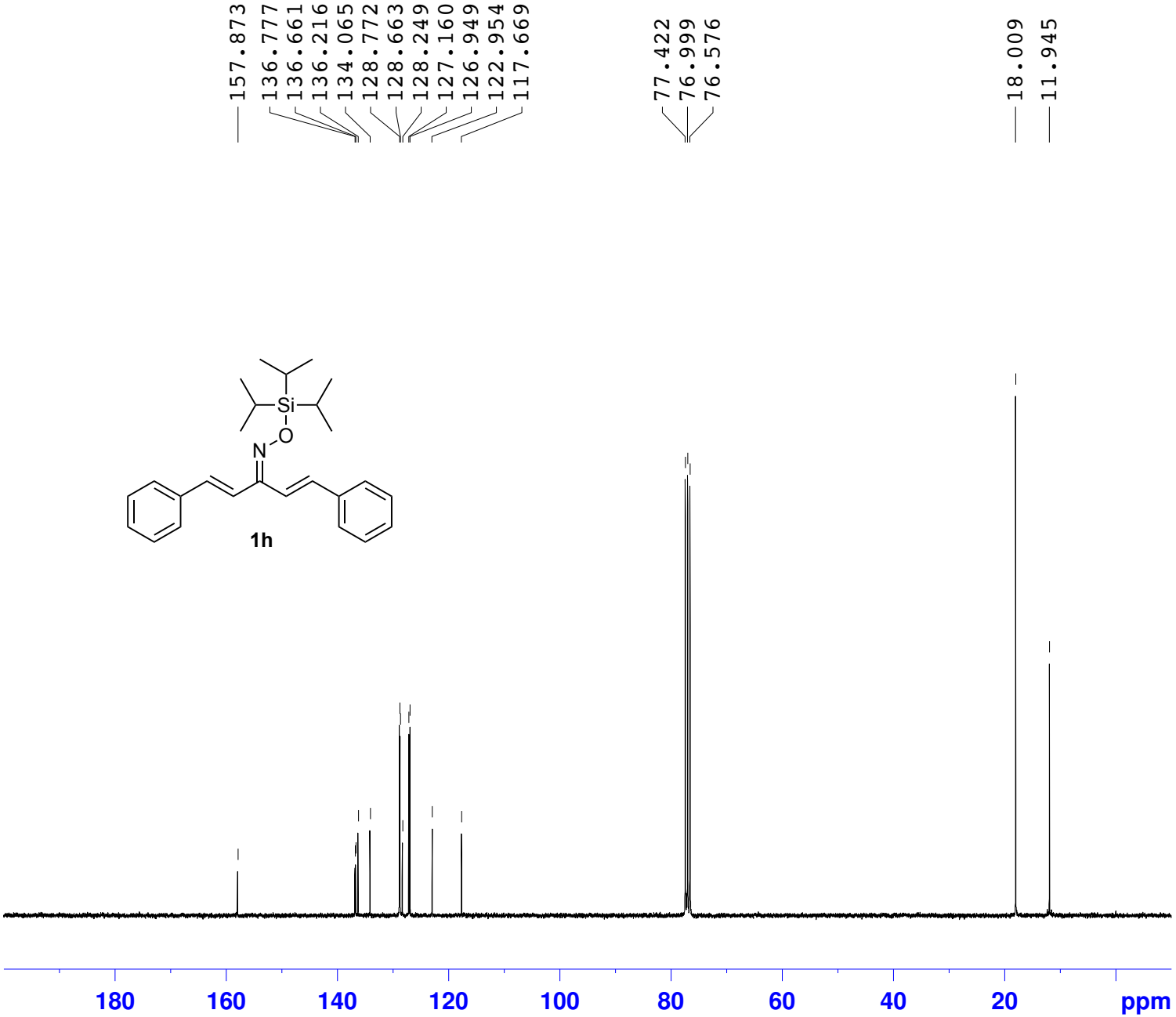

```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               1390
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191226
Time              20.24
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6188.119 Hz
FIDRES        0.094423 Hz
AQ            5.2953086 sec
RG                 45.2
DW                80.800 usec
DE                 6.50 usec
TE                294.4 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        300.1318534 MHz
NUC1                  1H
P1                15.00 usec
PLW1         6.19999981 W

F2 - Processing parameters
SI                32768
SF          300.1300097 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

^{13}C-NMR of **1h** (75 MHz, $CDCl_3$)




```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               1392
PROCNO                 1

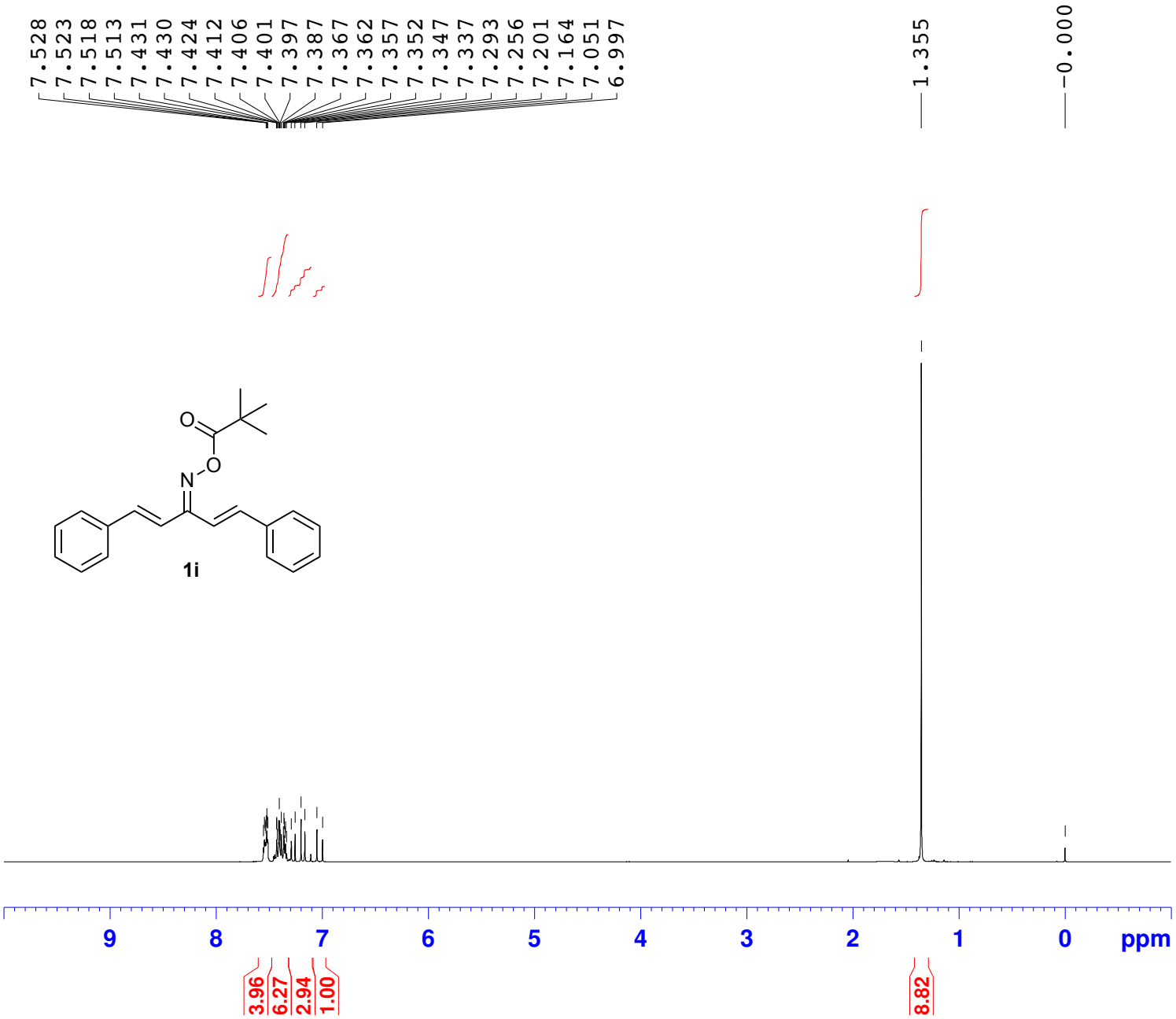
F2 - Acquisition Parameters
Date_           20191228
Time                1.54
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 2048
DS                    4
SWH           18028.846 Hz
FIDRES         0.275098 Hz
AQ            1.8175317 sec
RG                 2050
DW               27.733 usec
DE                6.50 usec
TE                296.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         75.4752953 MHz
NUC1                13C
P1                10.00 usec
PLW1        34.00000000 W

======== CHANNEL f2 ========
SFO2        300.1312005 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2             80.00 usec
PLW2          6.19999981 W
PLW12         0.21797000 W
PLW13         0.13950001 W

F2 - Processing parameters
SI                 32768
SF            75.4677508 MHz
WDW                   EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

^{1}H-NMR of **1i** (300 MHz, $CDCl_3$)



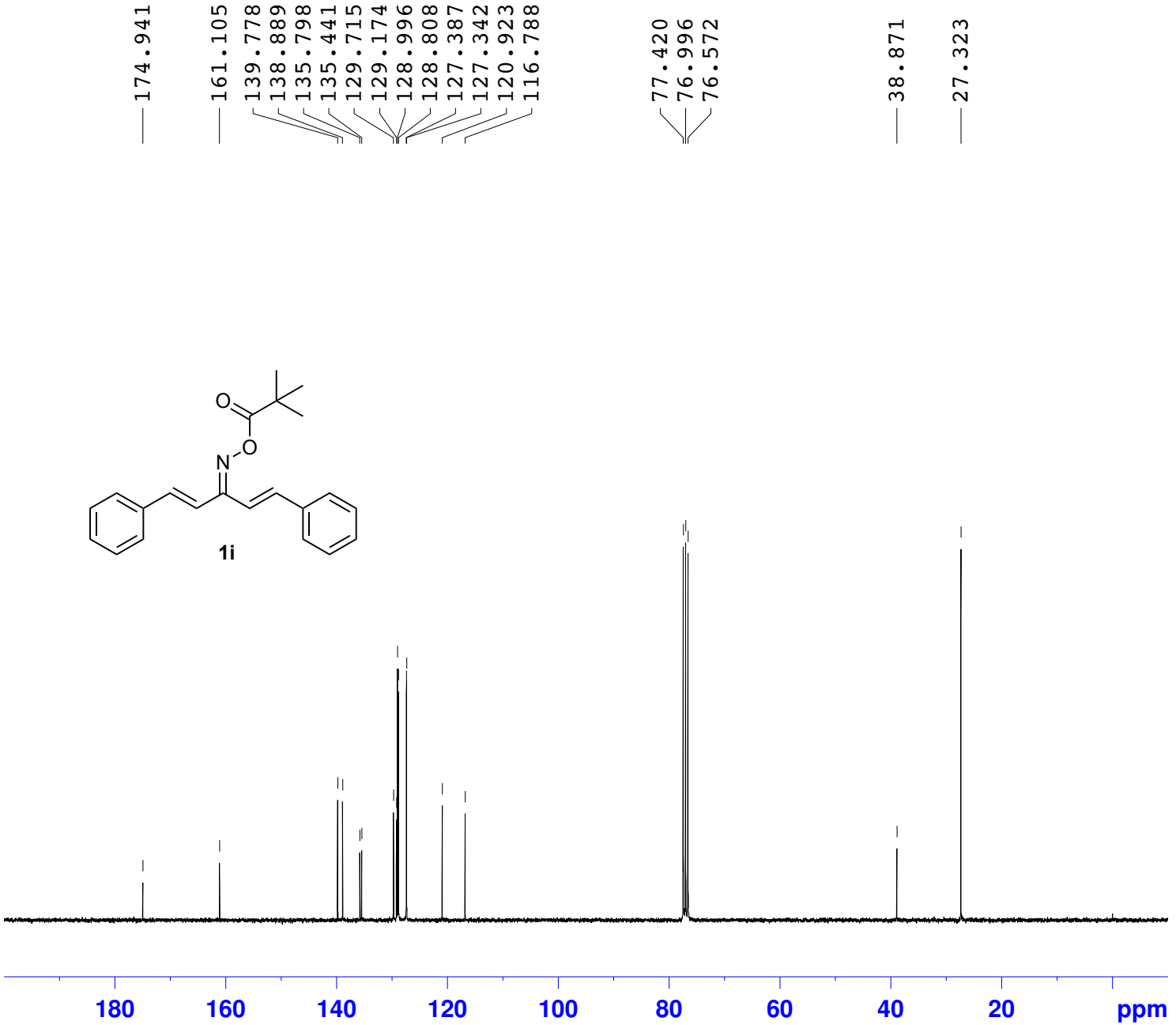

```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               1350
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191226
Time               19.54
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6188.119 Hz
FIDRES          0.094423 Hz
AQ             5.2953086 sec
RG                  45.2
DW                80.800 usec
DE                 6.50 usec
TE                294.4 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         300.1318534 MHz
NUC1                1H
P1                15.00 usec
PLW1          6.19999981 W

F2 - Processing parameters
SI                 32768
SF           300.1300078 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

^{13}C-NMR of **1i** (75 MHz, $CDCl_3$)




```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               1352
PROCNO                 1

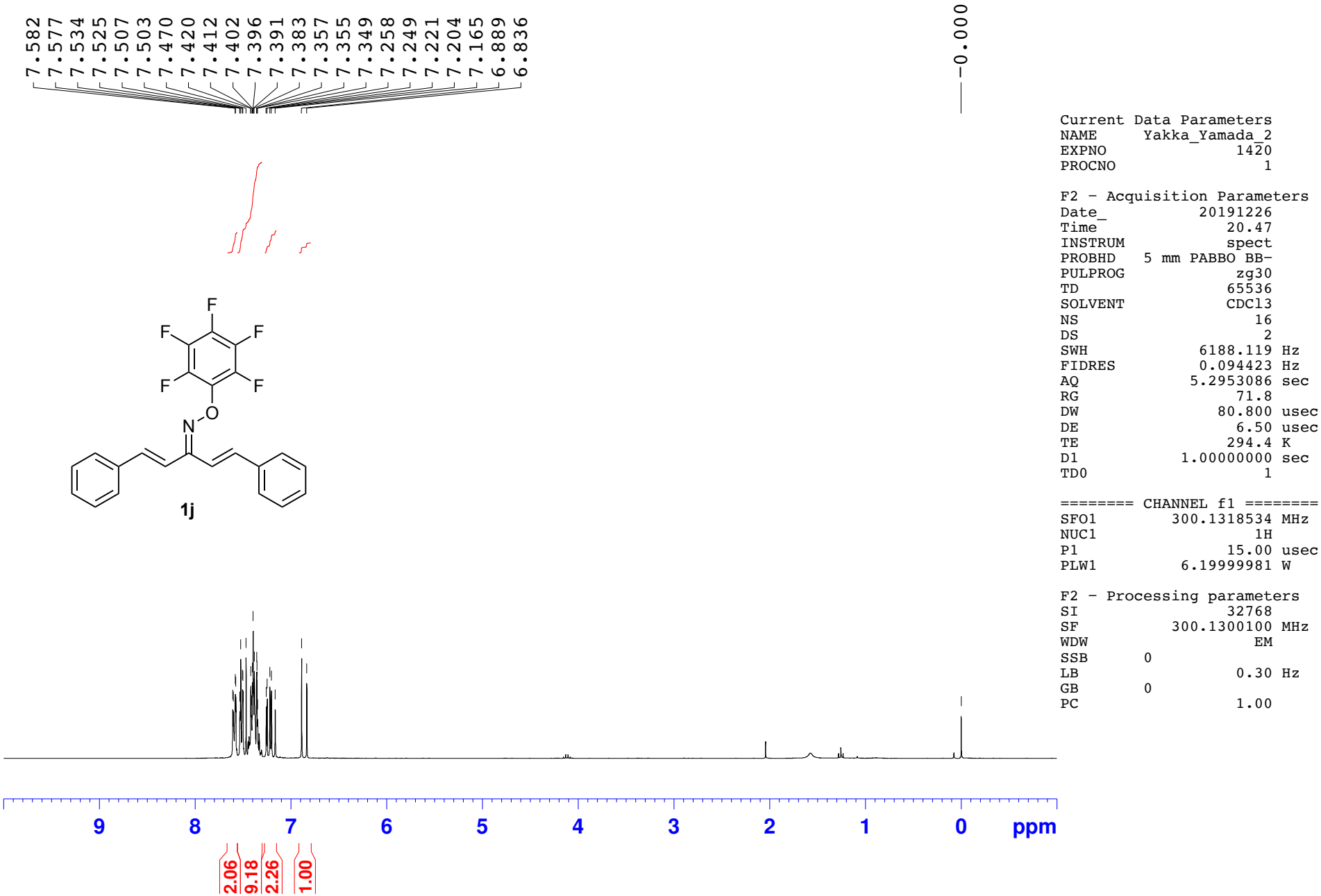
F2 - Acquisition Parameters
Date_           20191227
Time                2.11
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 2048
DS                    4
SWH           18028.846 Hz
FIDRES         0.275098 Hz
AQ            1.8175317 sec
RG                 2050
DW               27.733 usec
DE                6.50 usec
TE               296.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         75.4752953 MHz
NUC1                13C
P1                10.00 usec
PLW1        34.00000000 W

======== CHANNEL f2 ========
SFO2        300.1312005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2          6.19999981 W
PLW12         0.21797000 W
PLW13         0.13950001 W

F2 - Processing parameters
SI                 32768
SF           75.4677526 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

^{1}H-NMR of **1j** (300 MHz, $CDCl_3$)



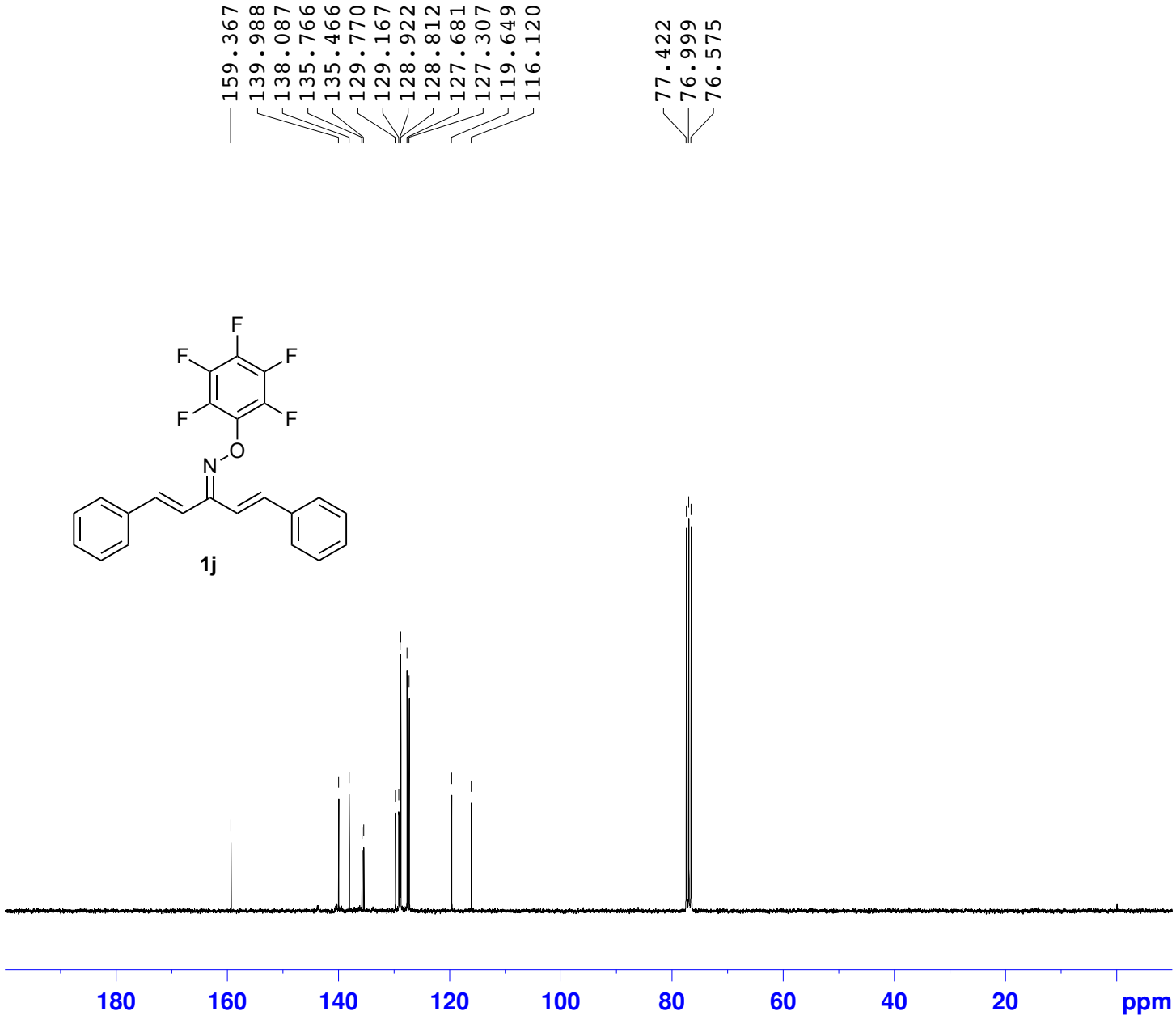

```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               1420
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191226
Time              20.47
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6188.119 Hz
FIDRES        0.094423 Hz
AQ            5.2953086 sec
RG                 71.8
DW               80.800 usec
DE                6.50 usec
TE                294.4 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        300.1318534 MHz
NUC1                   1H
P1                15.00 usec
PLW1         6.19999981 W

F2 - Processing parameters
SI                 32768
SF          300.1300100 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

^{13}C-NMR of **1j** (75 MHz, $CDCl_3$)




```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               1422
PROCNO                 1

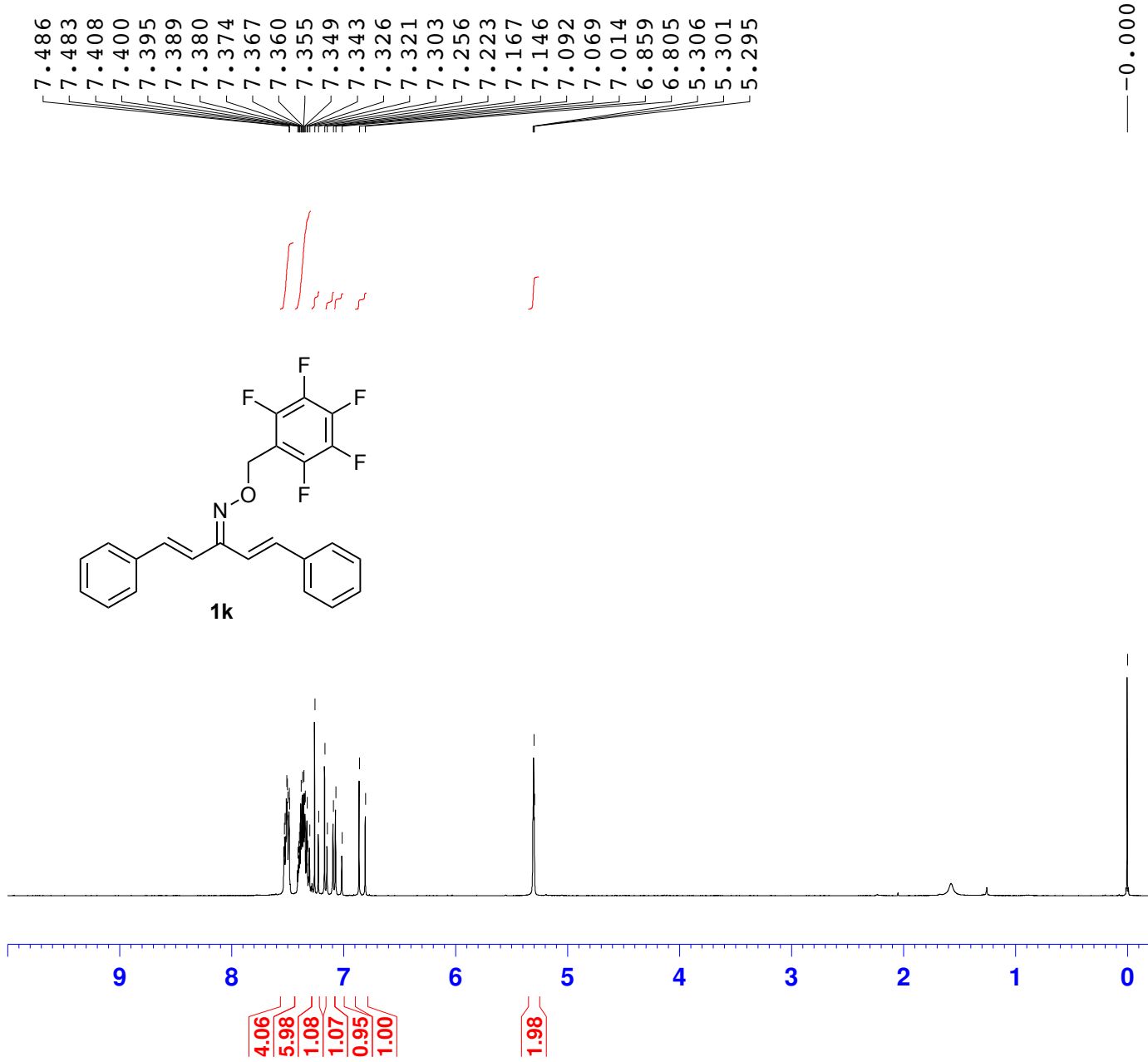
F2 - Acquisition Parameters
Date_           20191228
Time               6.45
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 2048
DS                    4
SWH           18028.846 Hz
FIDRES         0.275098 Hz
AQ            1.8175317 sec
RG                 2050
DW               27.733 usec
DE                6.50 usec
TE                295.9 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         75.4752953 MHz
NUC1                13C
P1                10.00 usec
PLW1        34.00000000 W

======== CHANNEL f2 ========
SFO2        300.1312005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2          6.19999981 W
PLW12         0.21797000 W
PLW13         0.13950001 W

F2 - Processing parameters
SI                 32768
SF            75.4677510 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

^{1}H-NMR of **1k** (300 MHz, $CDCl_3$)



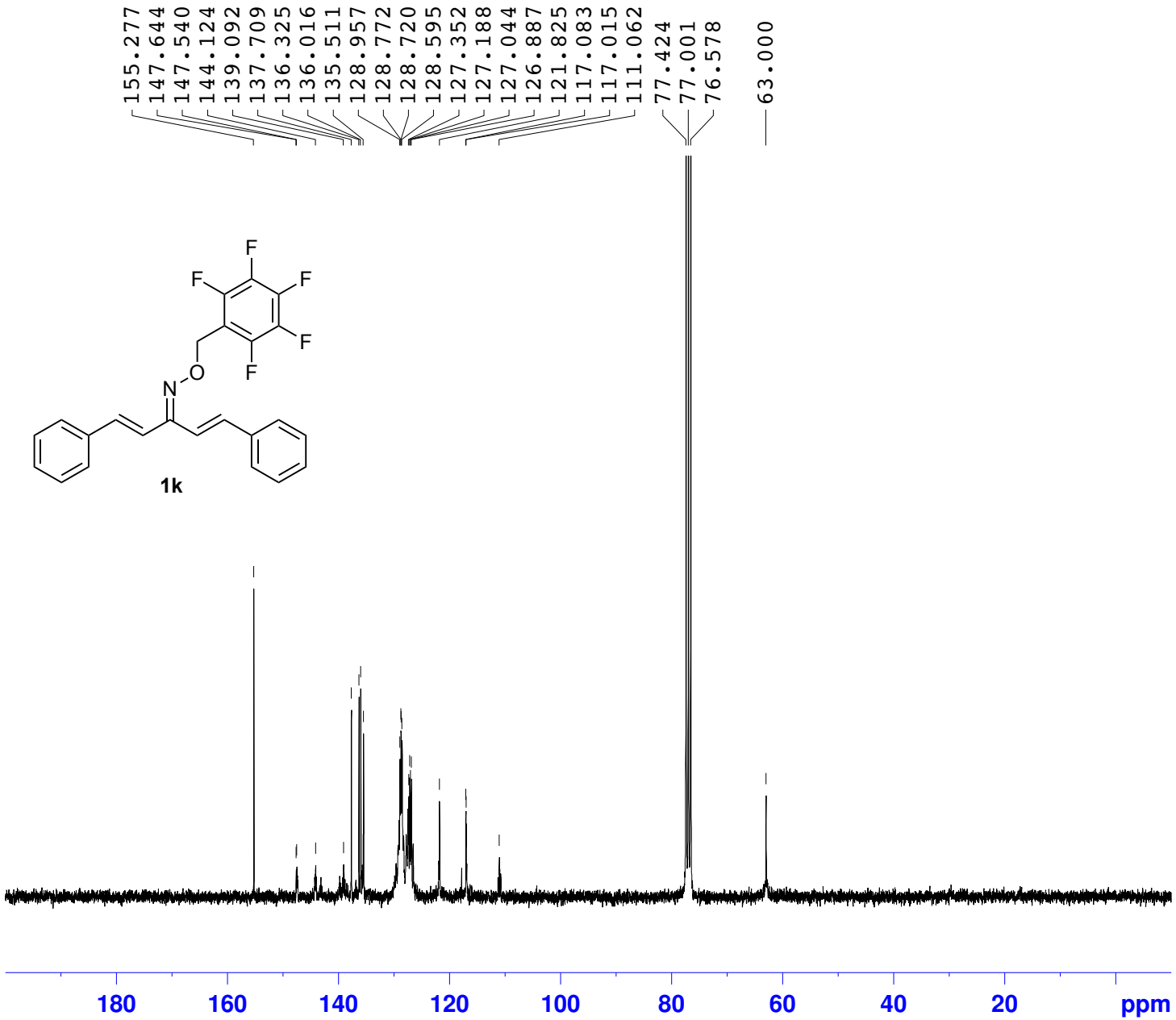

```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               4420
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210313
Time               12.01
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6188.119 Hz
FIDRES          0.094423 Hz
AQ              5.2953086 sec
RG                   101
DW                80.800 usec
DE                 6.50 usec
TE                294.6 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        300.1318534 MHz
NUC1                   1H
P1                 15.00 usec
PLW1          6.19999981 W

F2 - Processing parameters
SI                 32768
SF          300.1300075 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

^{13}C-NMR of **1k** (75 MHz, $CDCl_3$)




```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               4481
PROCNO                 1

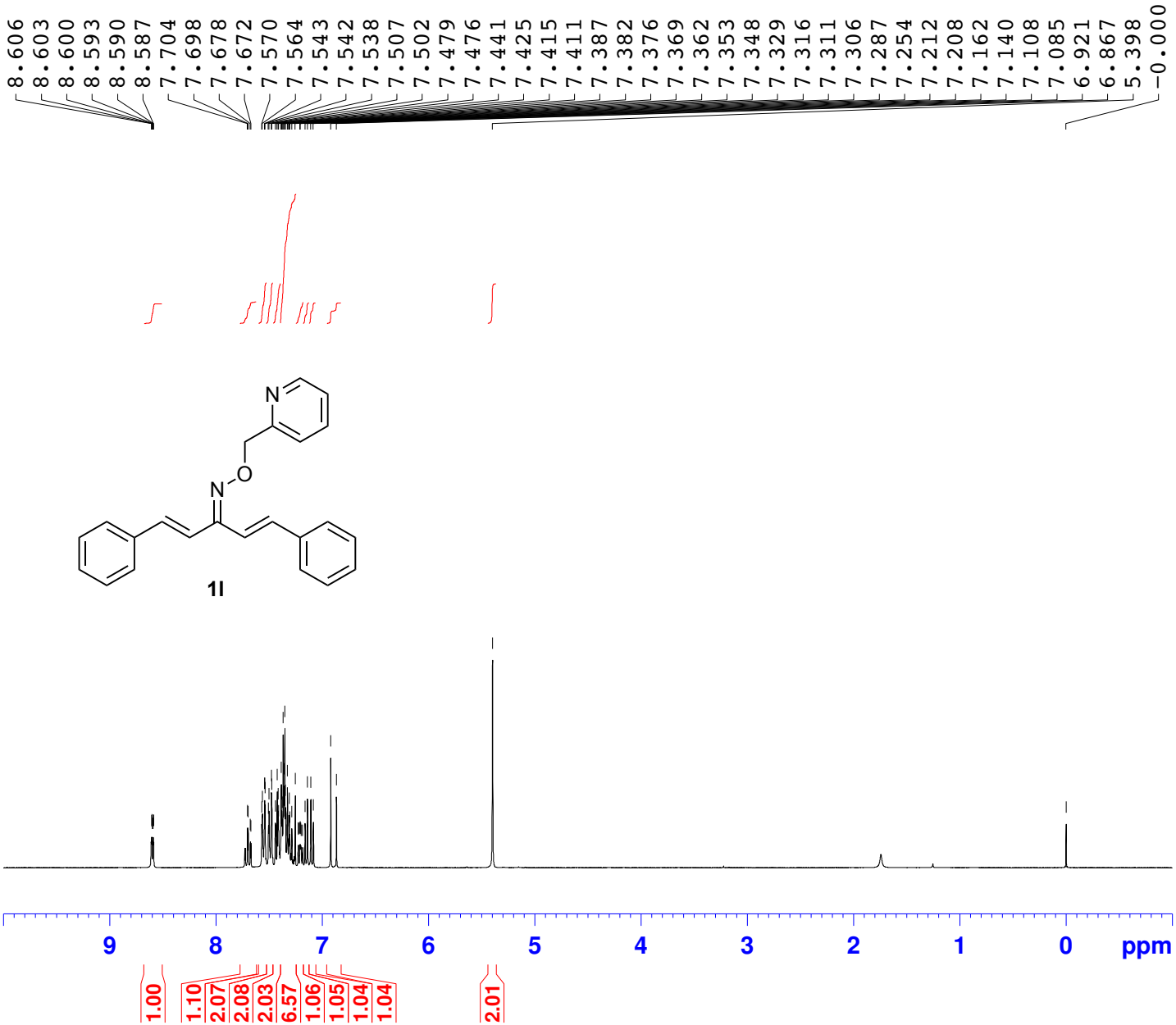
F2 - Acquisition Parameters
Date_           20210320
Time                5.48
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 8000
DS                    4
SWH           18028.846 Hz
FIDRES         0.275098 Hz
AQ             1.8175317 sec
RG                 2050
DW                27.733 usec
DE                 6.50 usec
TE                295.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         75.4752953 MHz
NUC1                13C
P1                 10.00 usec
PLW1         34.50000000 W

======== CHANNEL f2 ========
SFO2        300.1312005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2          6.19999981 W
PLW12         0.21797000 W
PLW13         0.13950001 W

F2 - Processing parameters
SI                 32768
SF            75.4677509 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

^{1}H-NMR of **1l** (300 MHz, $CDCl_3$)



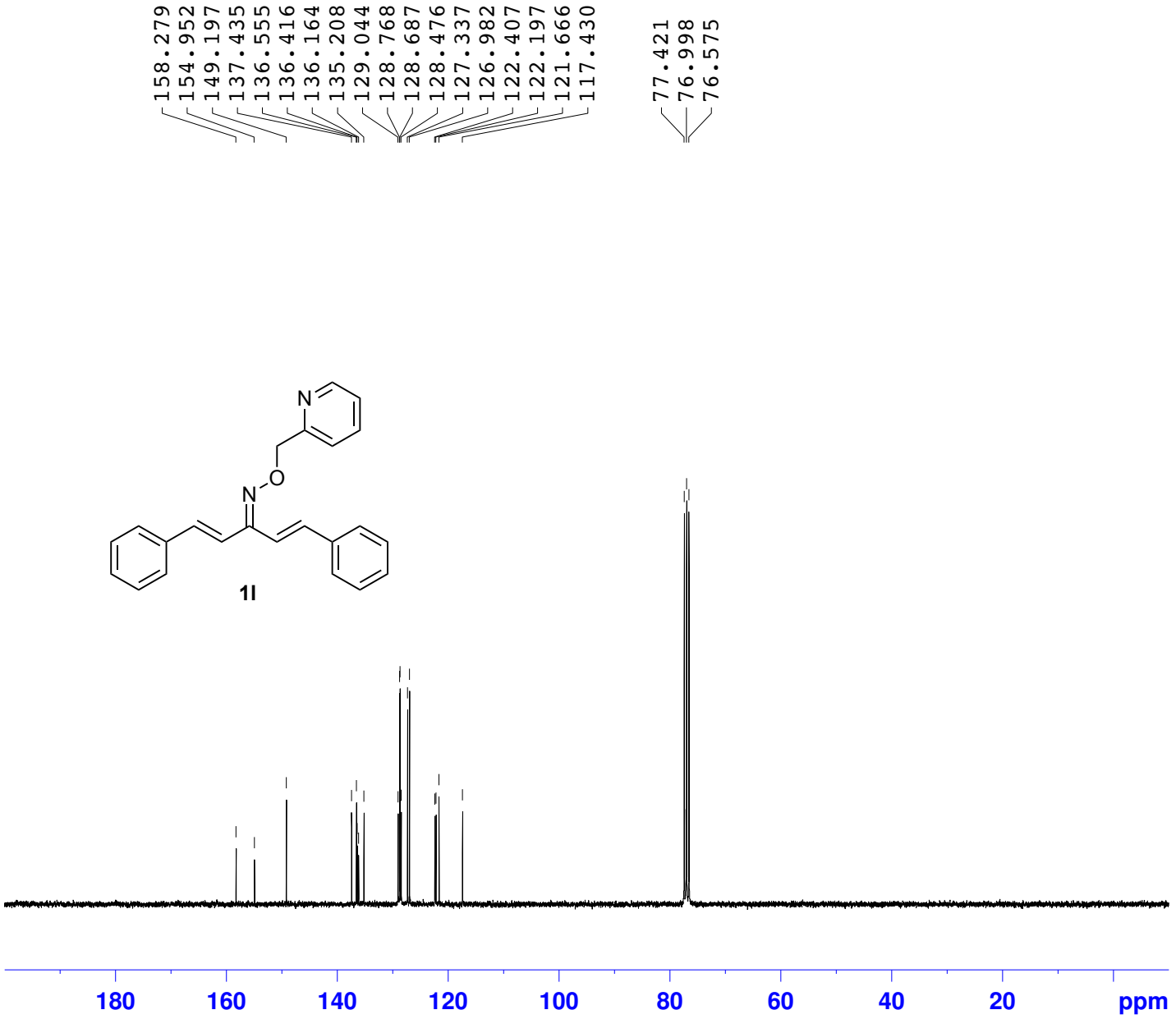

```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               1440
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191227
Time               9.09
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6188.119 Hz
FIDRES        0.094423 Hz
AQ            5.2953086 sec
RG                   57
DW               80.800 usec
DE                6.50 usec
TE                294.4 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        300.1318534 MHz
NUC1                1H
P1                15.00 usec
PLW1         6.19999981 W

F2 - Processing parameters
SI                32768
SF          300.1300085 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

^{13}C-NMR of **1l** (75 MHz, $CDCl_3$)




```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               1444
PROCNO                 1

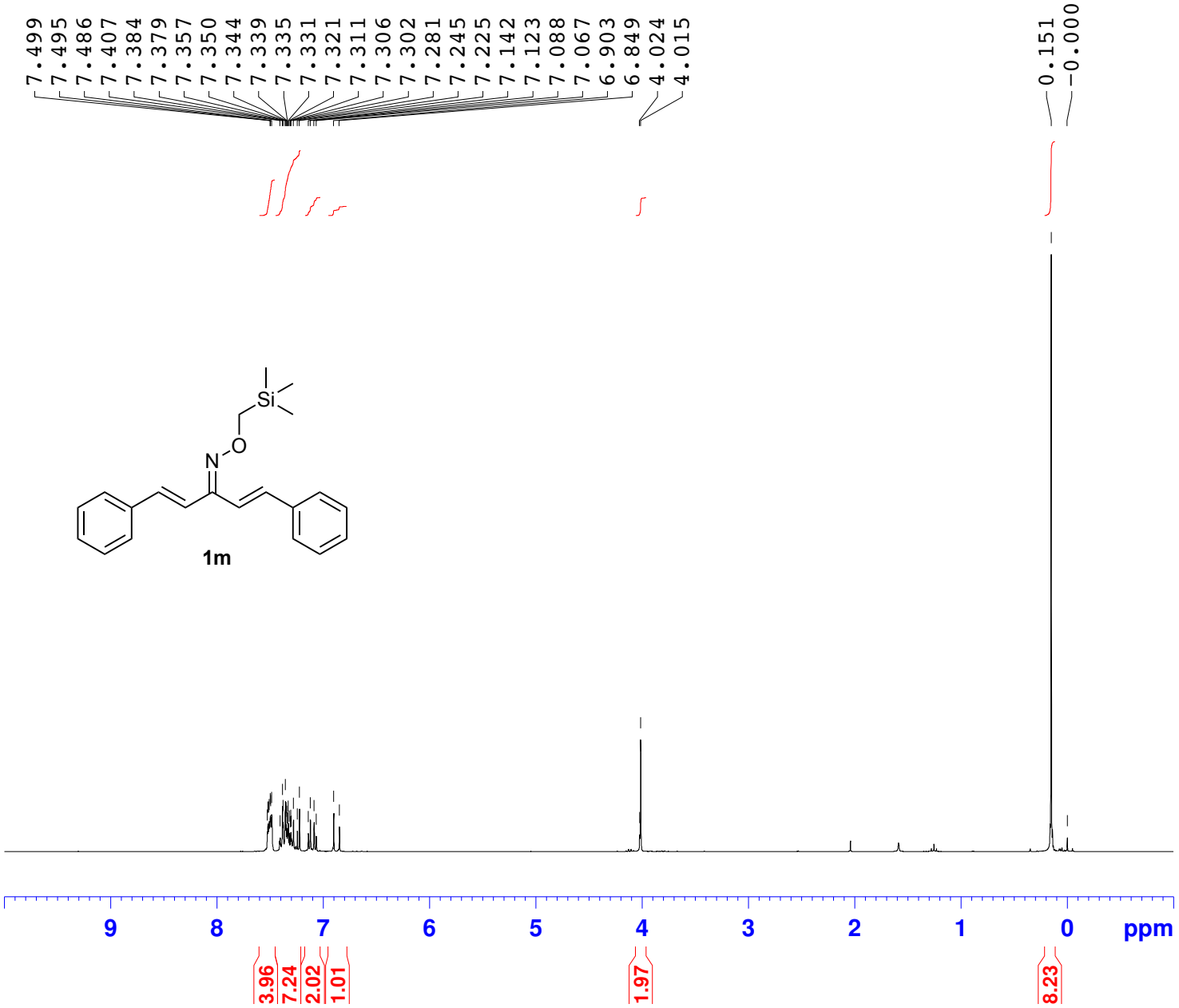
F2 - Acquisition Parameters
Date_           20191228
Time              14.54
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           18028.846 Hz
FIDRES         0.275098 Hz
AQ            1.8175317 sec
RG                 2050
DW               27.733 usec
DE                6.50 usec
TE                295.9 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         75.4752953 MHz
NUC1               13C
P1                10.00 usec
PLW1        34.00000000 W

======== CHANNEL f2 ========
SFO2        300.1312005 MHz
NUC2               1H
CPDPRG[2        waltz16
PCPD2             80.00 usec
PLW2         6.19999981 W
PLW12        0.21797000 W
PLW13        0.13950001 W

F2 - Processing parameters
SI                32768
SF           75.4677521 MHz
WDW                 EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

^{1}H-NMR of **1m** (300 MHz, $CDCl_3$)



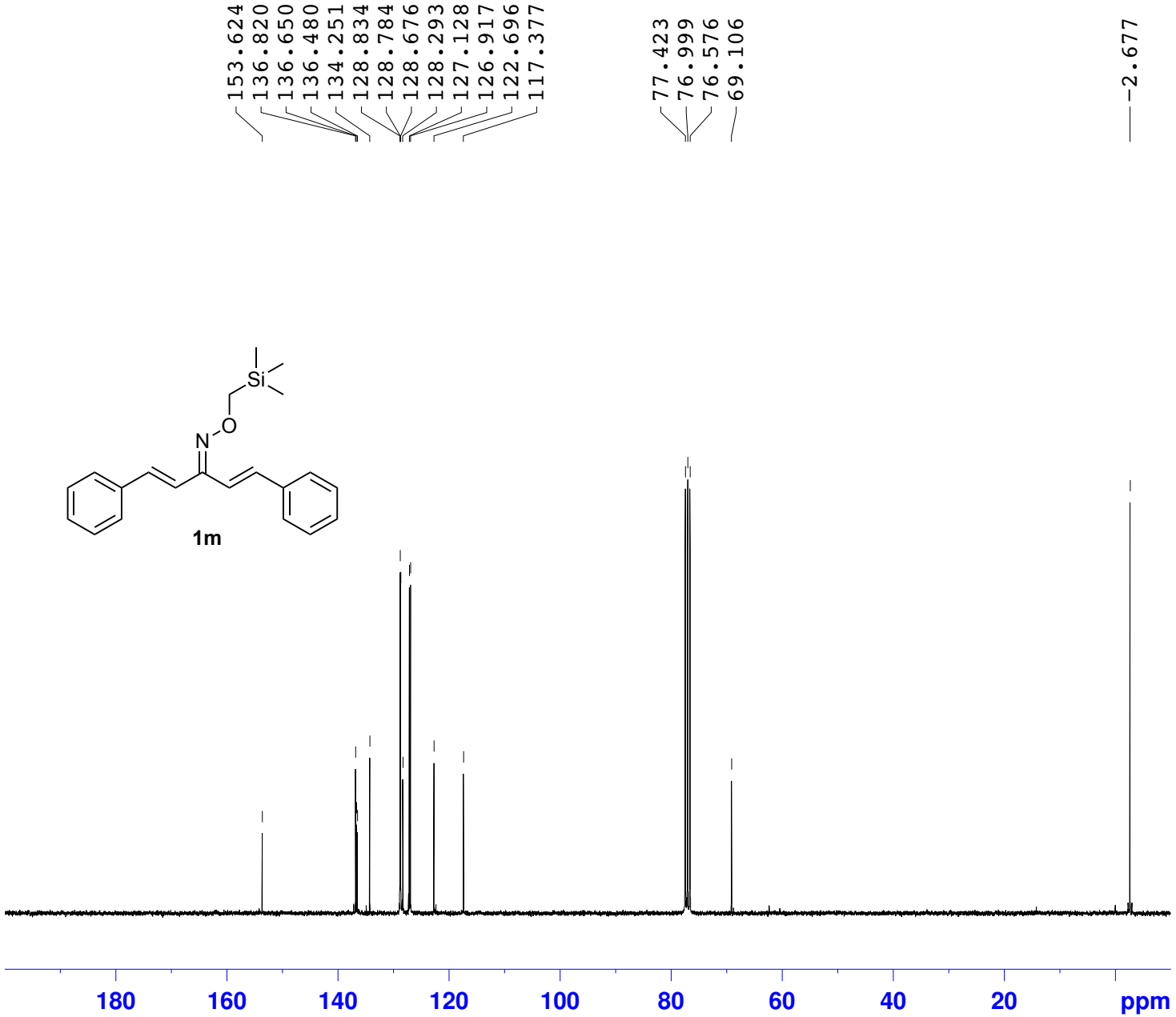

```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               1340
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191226
Time               19.46
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6188.119 Hz
FIDRES          0.094423 Hz
AQ              5.2953086 sec
RG                    36
DW                80.800 usec
DE                 6.50 usec
TE                294.4 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         300.1318534 MHz
NUC1                   1H
P1                 15.00 usec
PLW1          6.19999981 W

F2 - Processing parameters
SI                 32768
SF           300.1300113 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

^{13}C-NMR of **1m** (75 MHz, $CDCl_3$)




```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               1342
PROCNO                 1

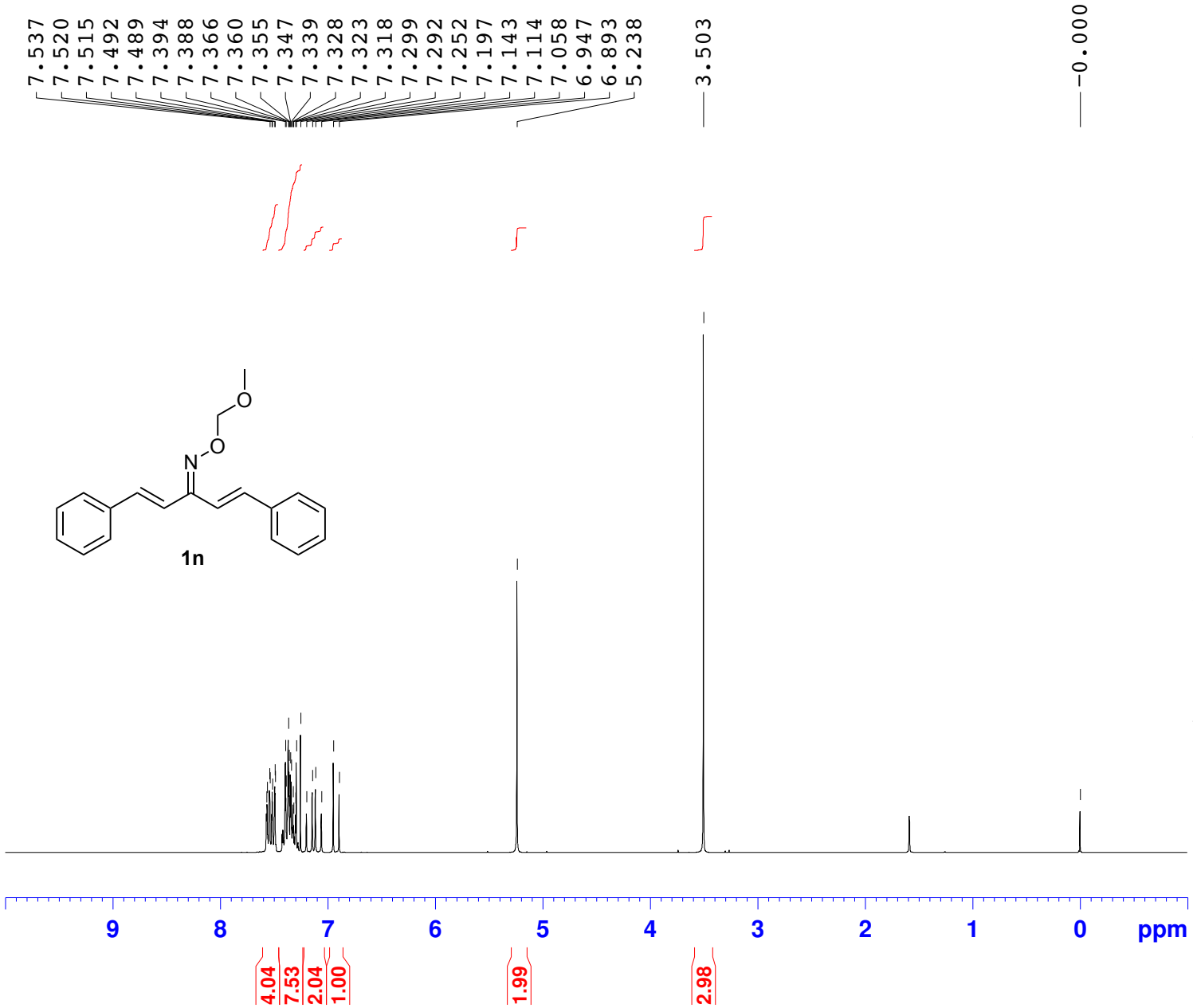
F2 - Acquisition Parameters
Date_           20191226
Time               23.29
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 2048
DS                    4
SWH           18028.846 Hz
FIDRES         0.275098 Hz
AQ            1.8175317 sec
RG                 2050
DW               27.733 usec
DE                6.50 usec
TE                295.9 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         75.4752953 MHz
NUC1                13C
P1                10.00 usec
PLW1        34.00000000 W

======== CHANNEL f2 ========
SFO2        300.1312005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2          6.19999981 W
PLW12         0.21797000 W
PLW13         0.13950001 W

F2 - Processing parameters
SI                 32768
SF           75.4677520 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

^{1}H-NMR of **1n** (300 MHz, $CDCl_3$)



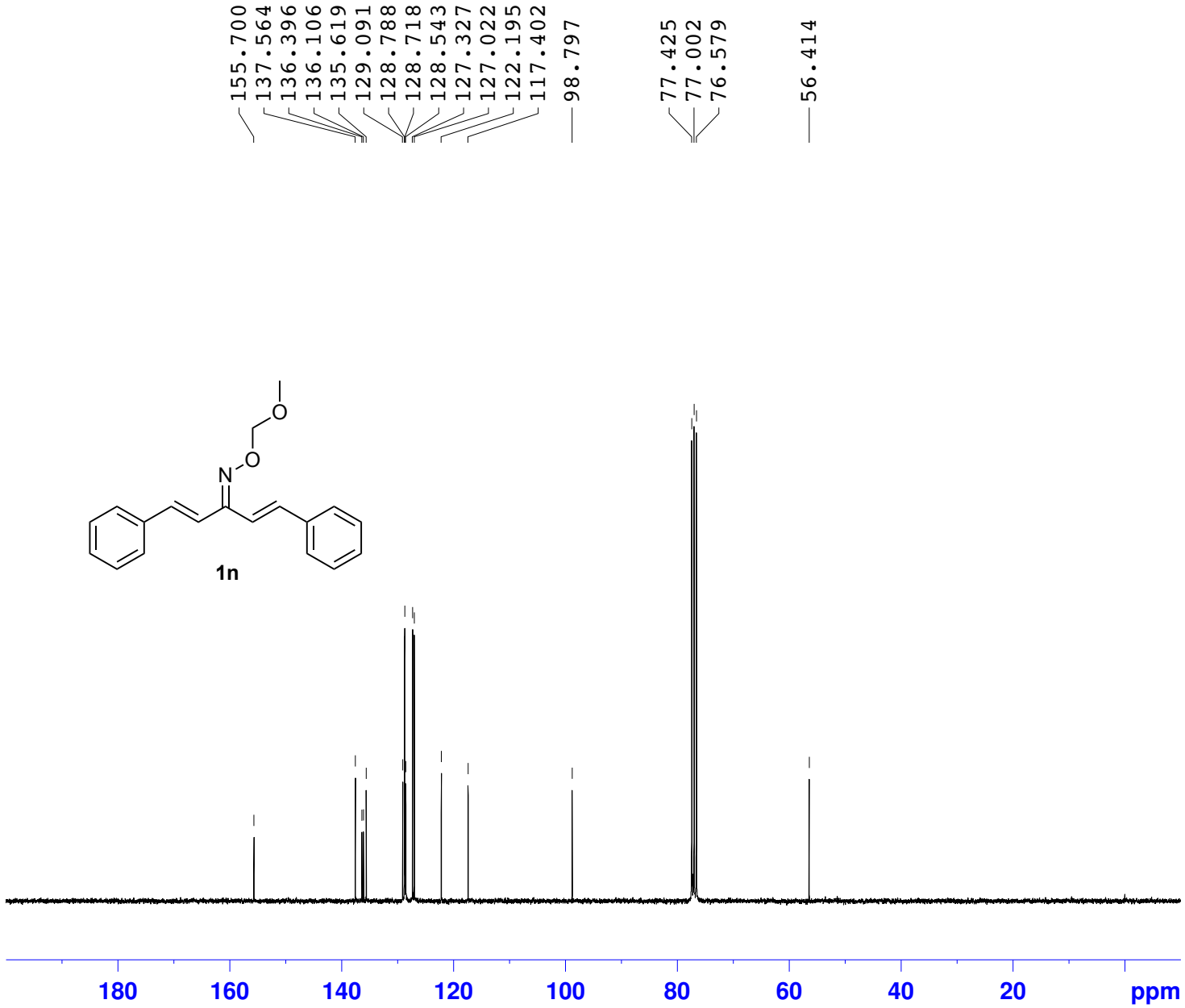

```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               1360
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191226
Time              20.01
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6188.119 Hz
FIDRES         0.094423 Hz
AQ             5.2953086 sec
RG                   57
DW                80.800 usec
DE                 6.50 usec
TE                294.4 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        300.1318534 MHz
NUC1                1H
P1                15.00 usec
PLW1          6.19999981 W

F2 - Processing parameters
SI                32768
SF          300.1300091 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

^{13}C-NMR of **1n** (75 MHz, $CDCl_3$)




```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               1362
PROCNO                 1

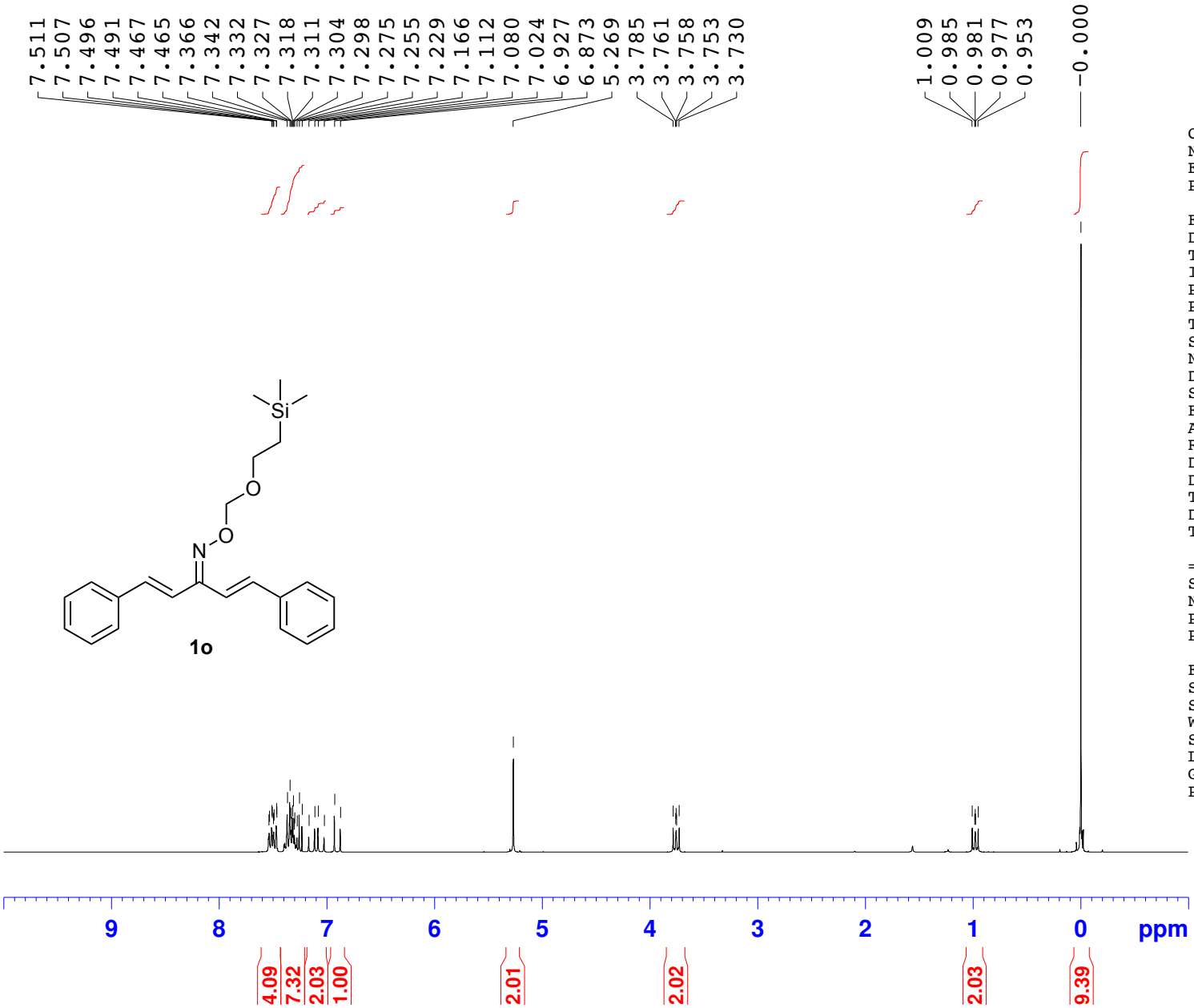
F2 - Acquisition Parameters
Date_           20191227
Time               4.54
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                2048
DS                   4
SWH          18028.846 Hz
FIDRES        0.275098 Hz
AQ            1.8175317 sec
RG                2050
DW              27.733 usec
DE               6.50 usec
TE              295.9 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1         75.4752953 MHz
NUC1                13C
P1                10.00 usec
PLW1        34.00000000 W

======== CHANNEL f2 ========
SFO2        300.1312005 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2             80.00 usec
PLW2         6.19999981 W
PLW12        0.21797000 W
PLW13        0.13950001 W

F2 - Processing parameters
SI                32768
SF           75.4677514 MHz
WDW                  EM
SSB      0
LB                1.00 Hz
GB       0
PC                1.40
```

^{1}H-NMR of **1o** (300 MHz, $CDCl_3$)



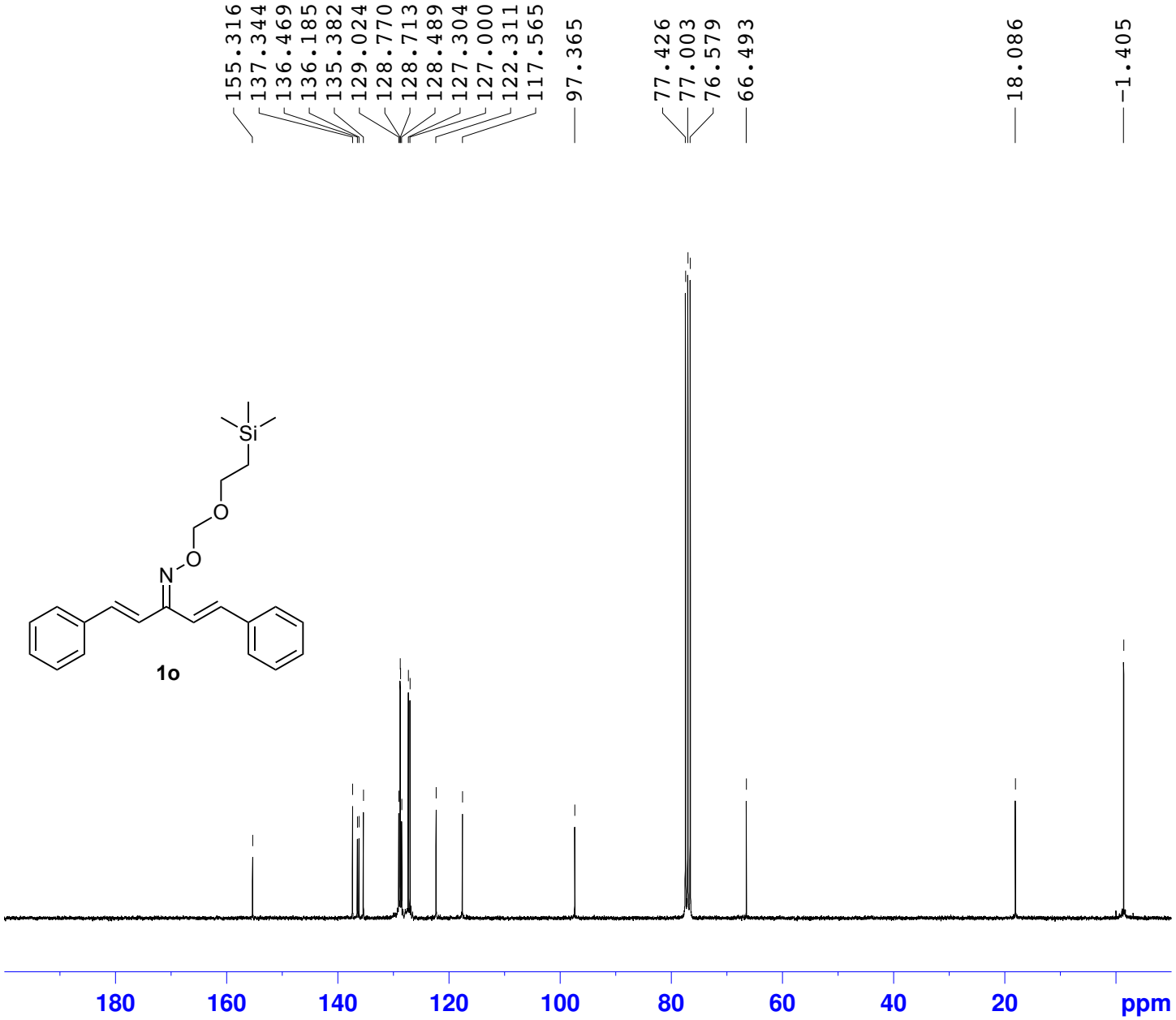

```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               6730
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220312
Time              17.24
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6188.119 Hz
FIDRES        0.094423 Hz
AQ            5.2953086 sec
RG                 45.2
DW               80.800 usec
DE                6.50 usec
TE                294.7 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        300.1318534 MHz
NUC1                1H
P1                15.00 usec
PLW1         8.00000000 W

F2 - Processing parameters
SI                32768
SF          300.1300150 MHz
WDW                 EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

^{13}C-NMR of **1o** (75 MHz, $CDCl_3$)




```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO                6732
PROCNO                  1

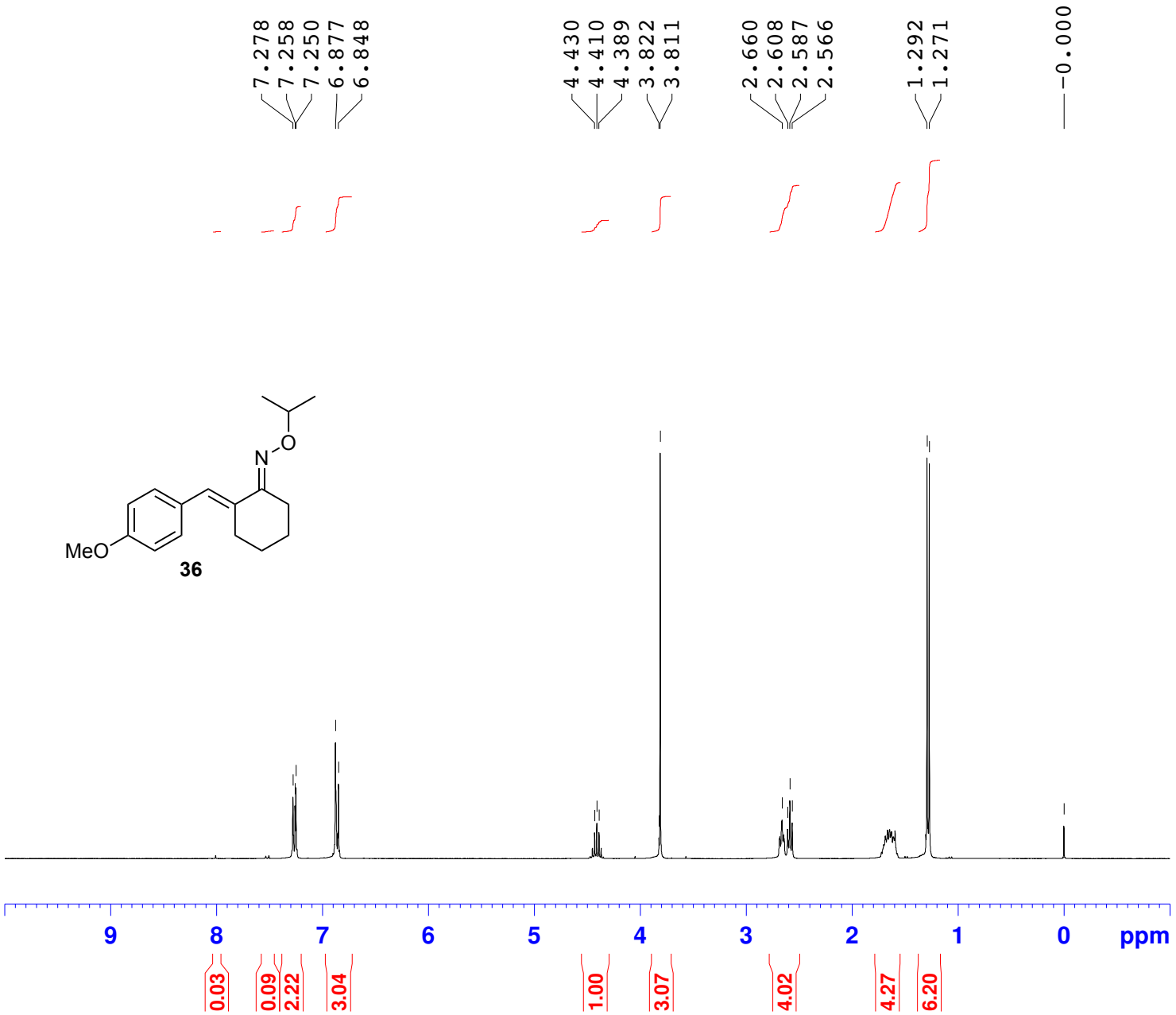
F2 - Acquisition Parameters
Date_            20220313
Time                17.15
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  8000
DS                     4
SWH            18028.846 Hz
FIDRES          0.275098 Hz
AQ              1.8175317 sec
RG                  2050
DW                27.733 usec
DE                 6.50 usec
TE                295.6 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          75.4752953 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         34.50000000 W

======== CHANNEL f2 ========
SFO2         300.1312005 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2          8.00000000 W
PLW12         0.28125000 W
PLW13         0.18000001 W

F2 - Processing parameters
SI                 32768
SF            75.4677509 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

^{1}H-NMR of **36** (300 MHz, $CDCl_3$)



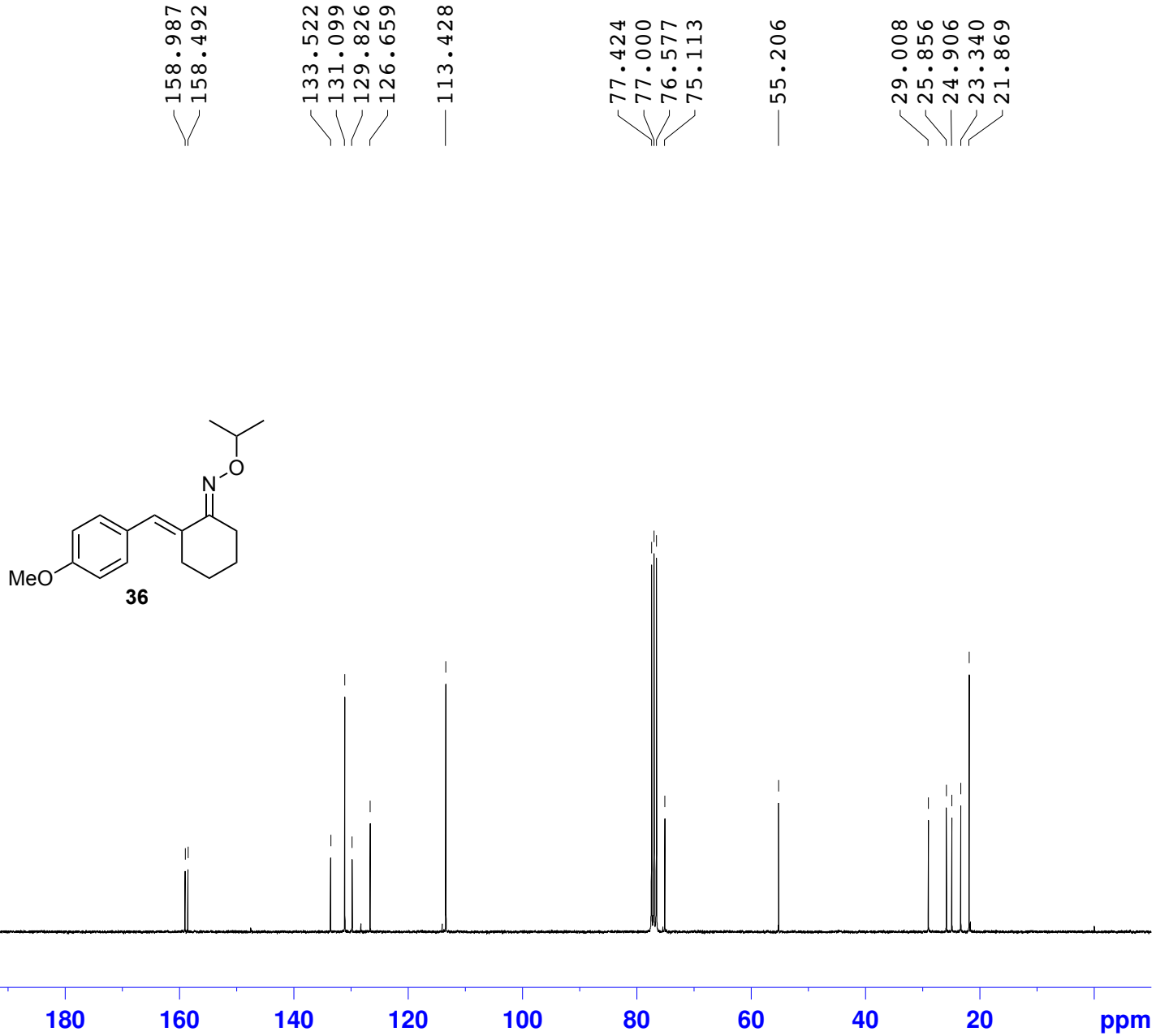

```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               6660
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220305
Time               20.42
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6188.119 Hz
FIDRES          0.094423 Hz
AQ              5.2953086 sec
RG                  45.2
DW                 80.800 usec
DE                  6.50 usec
TE                 294.6 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         300.1318534 MHz
NUC1                1H
P1                 15.00 usec
PLW1          8.00000000 W

F2 - Processing parameters
SI                 32768
SF           300.1300066 MHz
WDW                  EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

^{13}C-NMR of **36** (75 MHz, $CDCl_3$)




```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               6671
PROCNO                 1

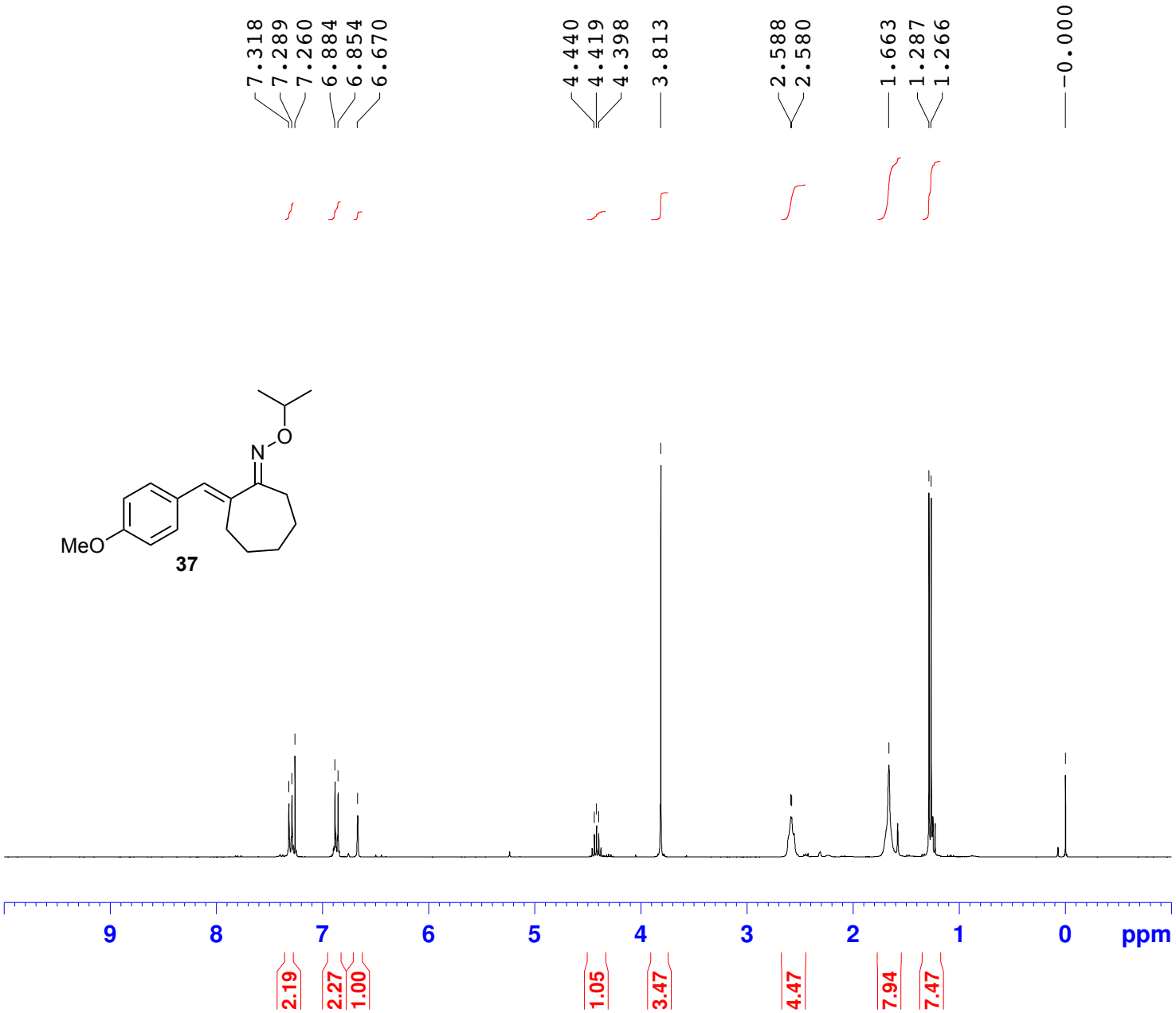
F2 - Acquisition Parameters
Date_           20220306
Time                3.31
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 6000
DS                    4
SWH           18028.846 Hz
FIDRES         0.275098 Hz
AQ            1.8175317 sec
RG                 2050
DW               27.733 usec
DE                6.50 usec
TE                296.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         75.4752953 MHz
NUC1                13C
P1                10.00 usec
PLW1        34.50000000 W

======== CHANNEL f2 ========
SFO2        300.1312005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         8.00000000 W
PLW12        0.28125000 W
PLW13        0.18000001 W

F2 - Processing parameters
SI                 32768
SF           75.4677505 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

^{1}H-NMR of **37** (300 MHz, $CDCl_3$)



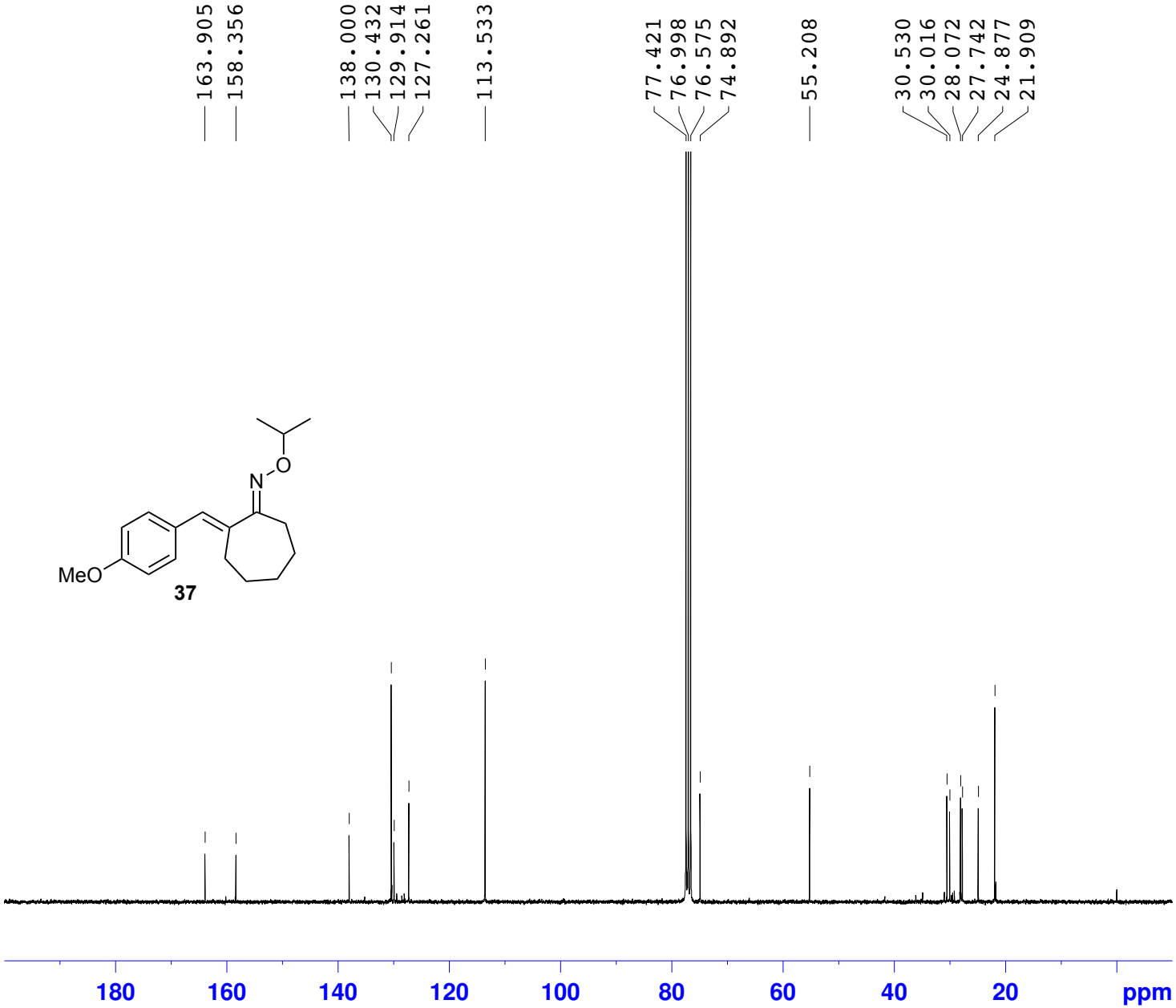

```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               6720
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220312
Time               16.47
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6188.119 Hz
FIDRES         0.094423 Hz
AQ             5.2953086 sec
RG                 80.6
DW               80.800 usec
DE                6.50 usec
TE                294.7 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         300.1318534 MHz
NUC1                1H
P1                15.00 usec
PLW1          8.00000000 W

F2 - Processing parameters
SI                 32768
SF           300.1300058 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

^{13}C-NMR of **37** (75 MHz, $CDCl_3$)




```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               6722
PROCNO                 1

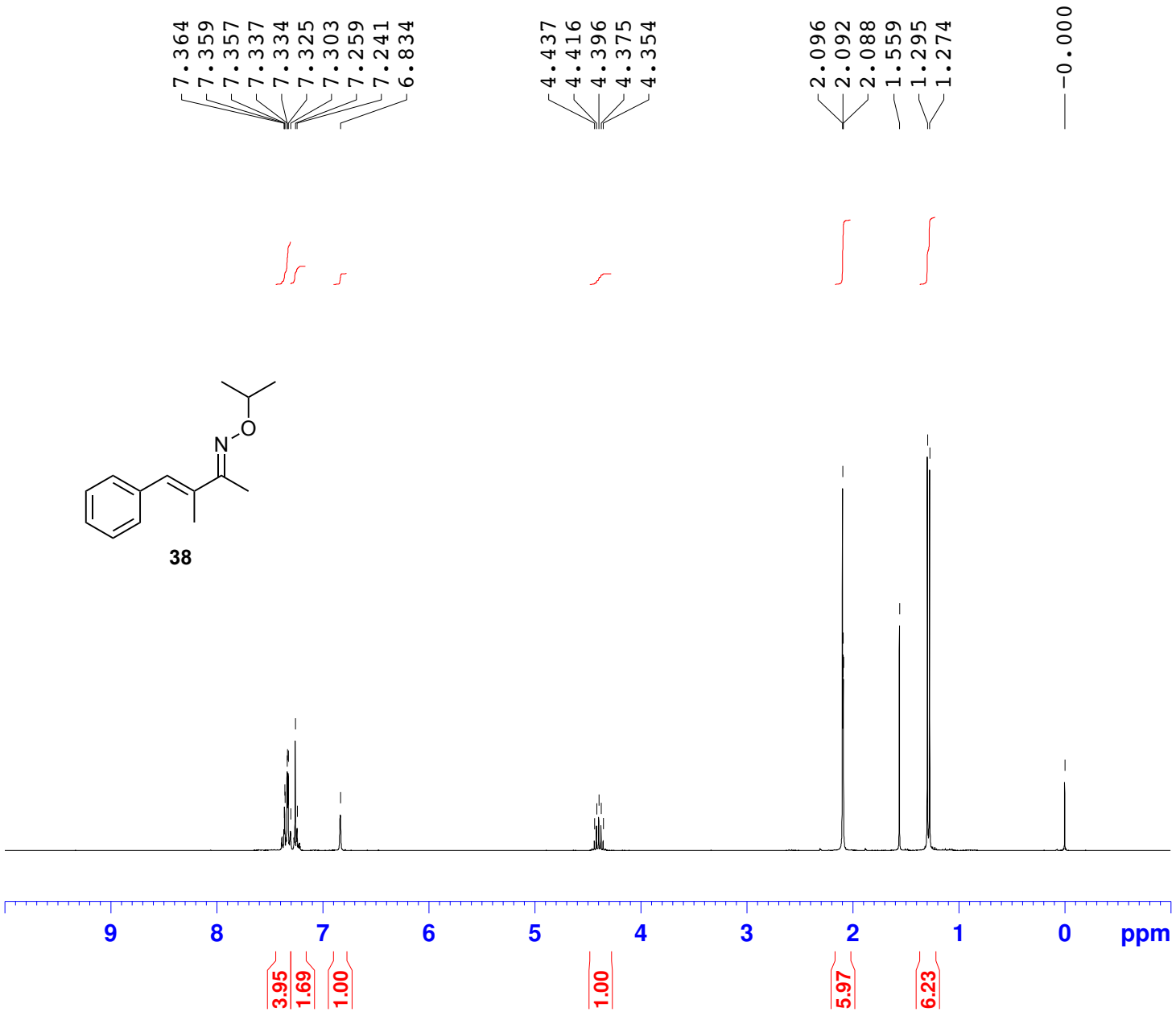
F2 - Acquisition Parameters
Date_           20220313
Time               7.53
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS               10000
DS                   4
SWH          18028.846 Hz
FIDRES        0.275098 Hz
AQ           1.8175317 sec
RG                2050
DW              27.733 usec
DE               6.50 usec
TE               296.5 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1         75.4752953 MHz
NUC1                13C
P1                10.00 usec
PLW1        34.50000000 W

======== CHANNEL f2 ========
SFO2        300.1312005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         8.00000000 W
PLW12        0.28125000 W
PLW13        0.18000001 W

F2 - Processing parameters
SI                 32768
SF           75.4677498 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

^{1}H-NMR of **38** (300 MHz, $CDCl_3$)



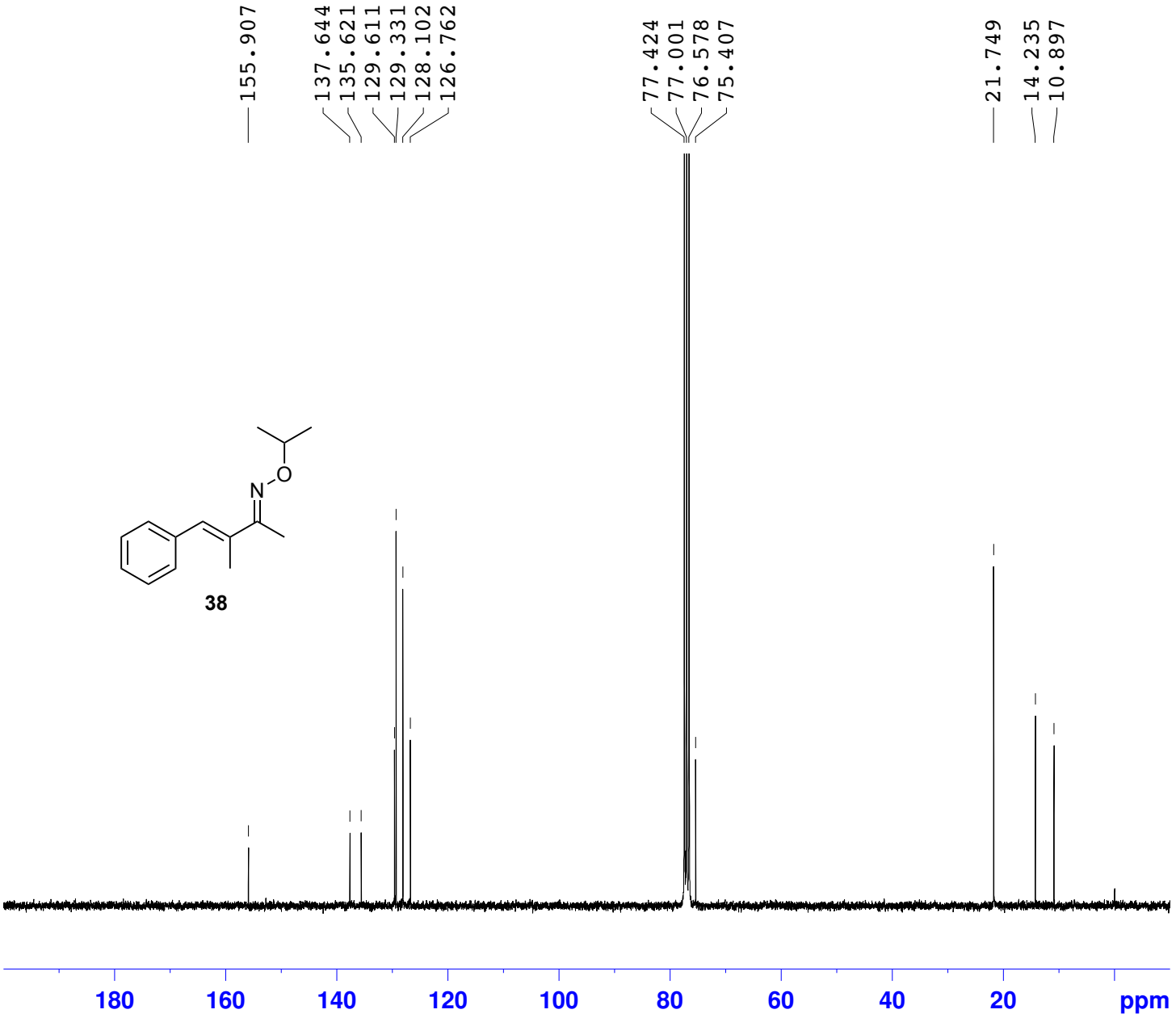

```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               1830
PROCNO                 1

F2 - Acquisition Parameters
Date_          20200314
Time              18.33
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6188.119 Hz
FIDRES         0.094423 Hz
AQ             5.2953086 sec
RG                  114
DW                80.800 usec
DE                 6.50 usec
TE                294.5 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        300.1318534 MHz
NUC1                1H
P1                15.00 usec
PLW1          6.19999981 W

F2 - Processing parameters
SI                32768
SF          300.1300070 MHz
WDW                EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

^{13}C-NMR of **38** (75 MHz, $CDCl_3$)




```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               1831
PROCNO                 1

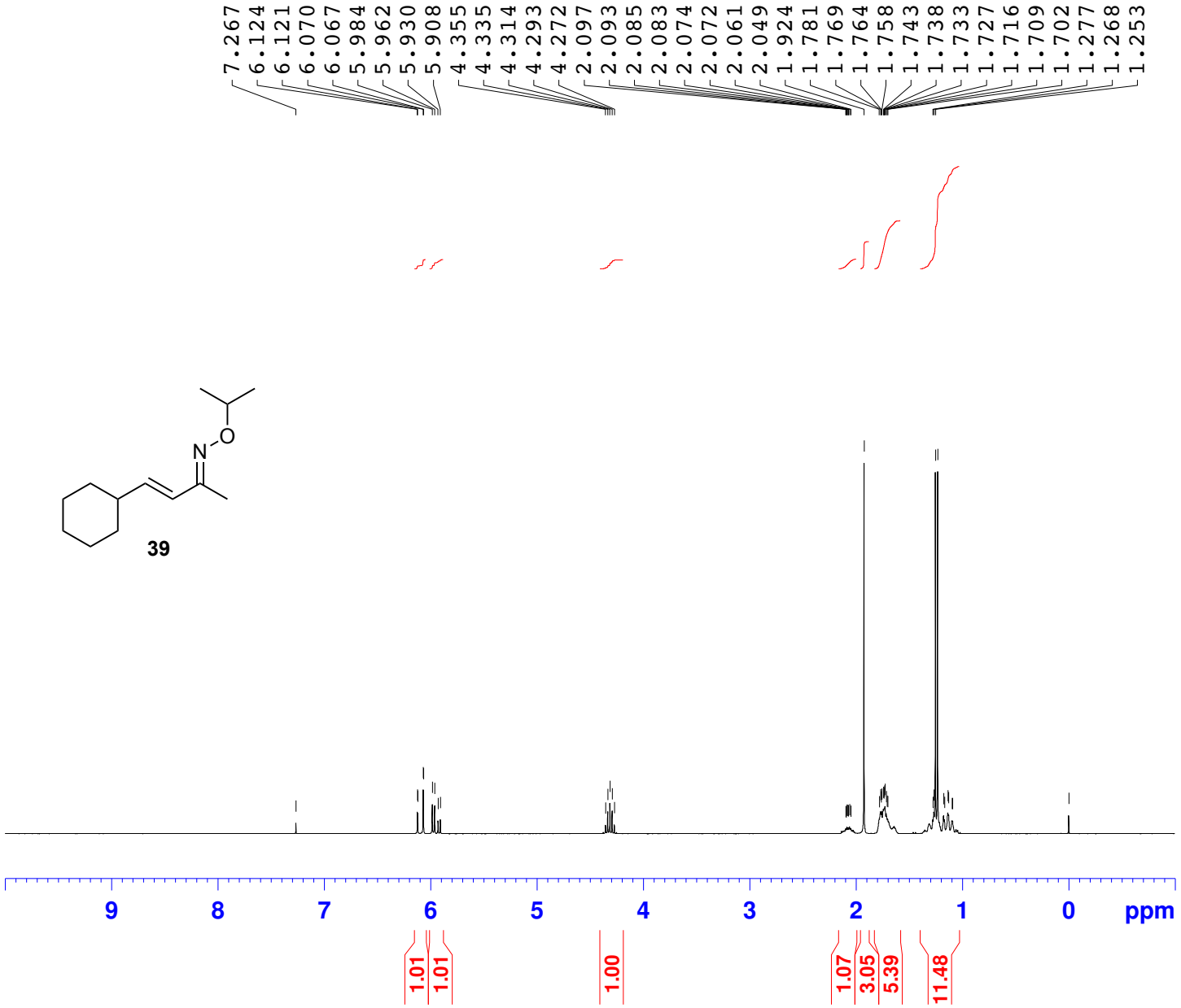
F2 - Acquisition Parameters
Date_           20200315
Time                5.56
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 8192
DS                    4
SWH           18028.846 Hz
FIDRES         0.275098 Hz
AQ            1.8175317 sec
RG                 2050
DW               27.733 usec
DE                6.50 usec
TE               296.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         75.4752953 MHz
NUC1                13C
P1                10.00 usec
PLW1        34.20000076 W

======== CHANNEL f2 ========
SFO2        300.1312005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         6.19999981 W
PLW12        0.17000000 W
PLW13        0.13950001 W

F2 - Processing parameters
SI                 32768
SF           75.4677498 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

^{1}H-NMR of **39** (300 MHz, $CDCl_3$)



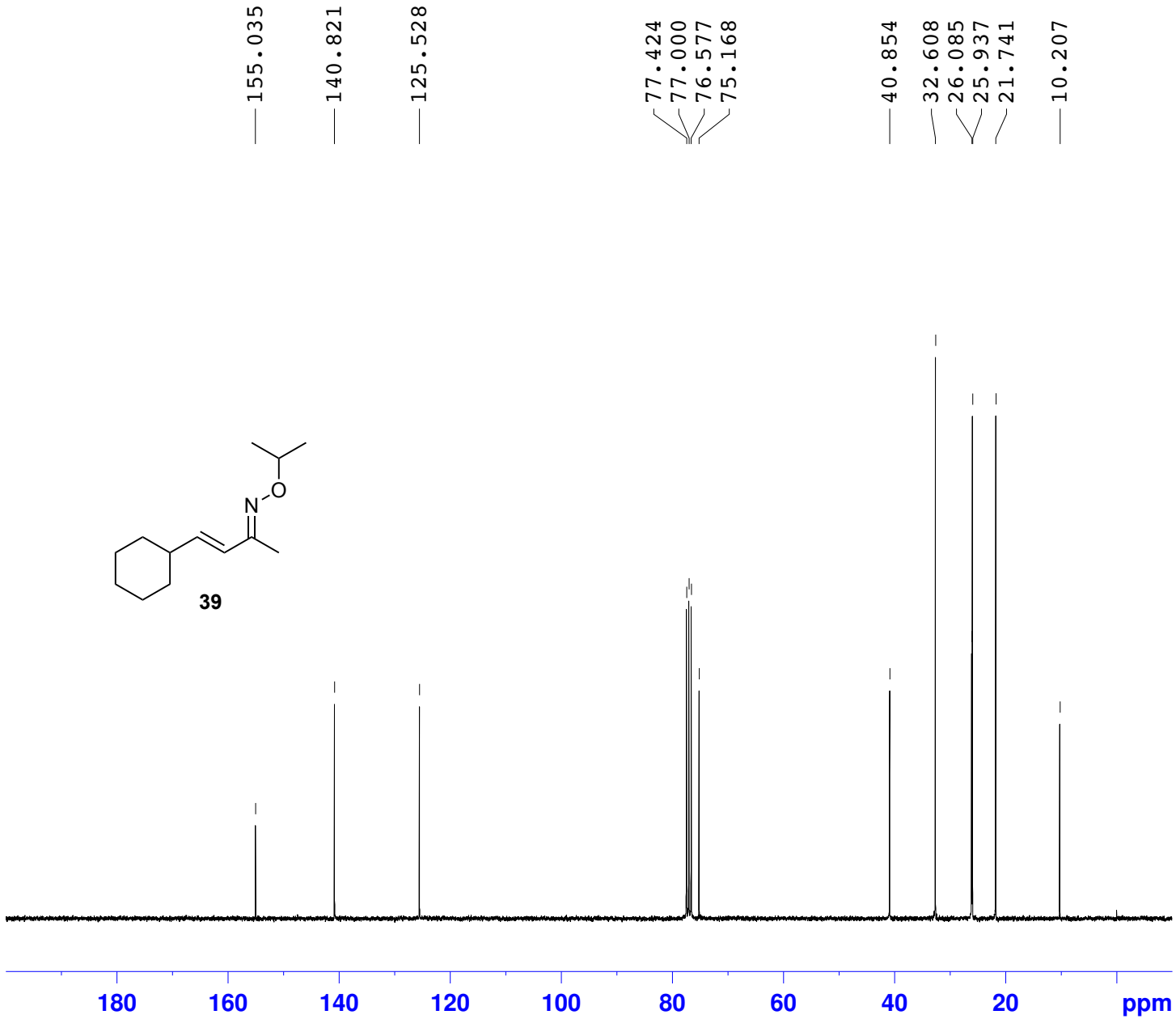

```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               2120
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200625
Time                7.43
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6188.119 Hz
FIDRES          0.094423 Hz
AQ             5.2953086 sec
RG                  20.2
DW                80.800 usec
DE                 6.50 usec
TE                294.8 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         300.1318534 MHz
NUC1                   1H
P1                 15.00 usec
PLW1          6.19999981 W

F2 - Processing parameters
SI                 32768
SF           300.1300042 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

^{13}C-NMR of **39** (75 MHz, $CDCl_3$)




```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               2122
PROCNO                 1

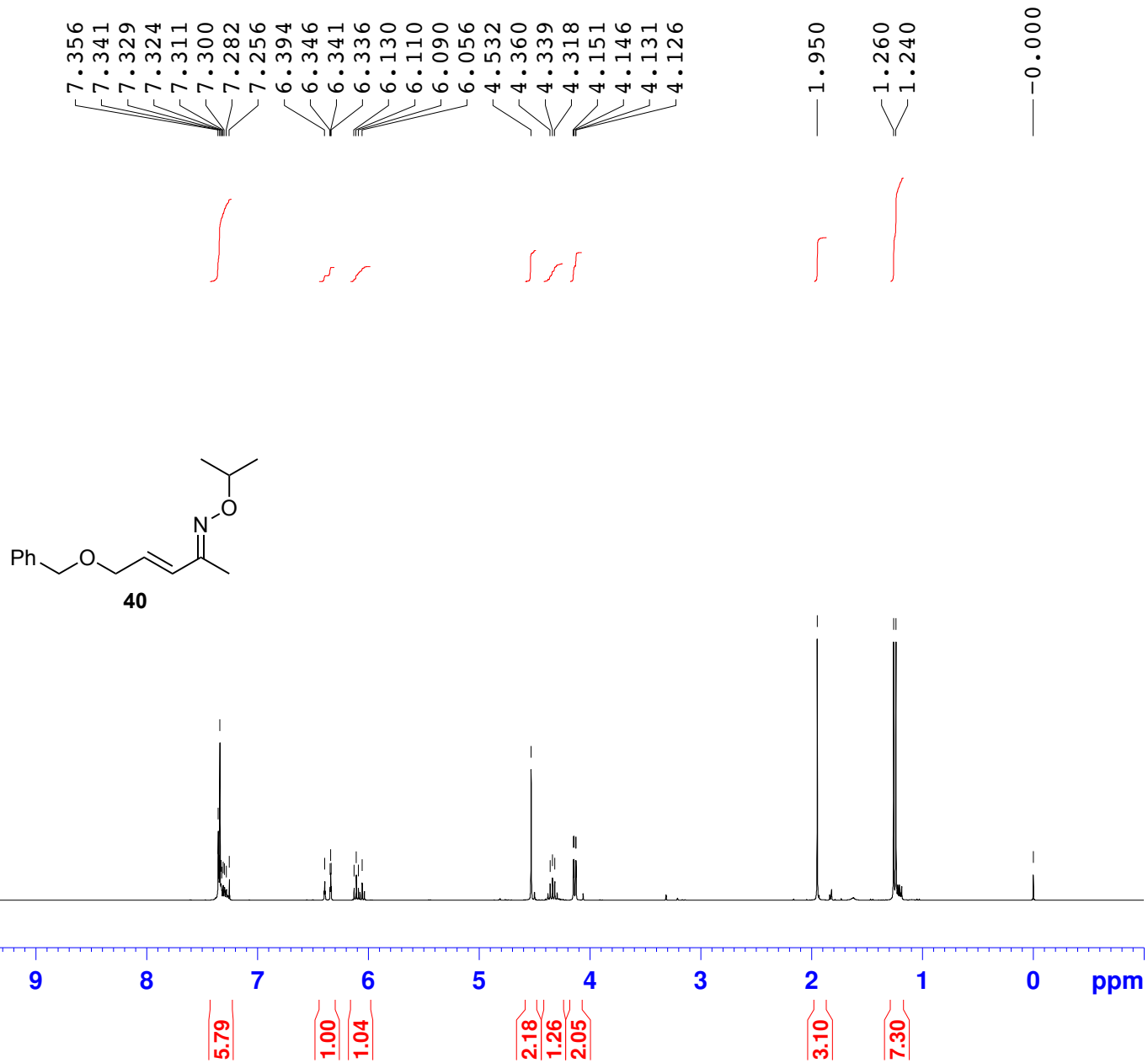
F2 - Acquisition Parameters
Date_           20200625
Time                9.01
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           18028.846 Hz
FIDRES         0.275098 Hz
AQ            1.8175317 sec
RG                 2050
DW               27.733 usec
DE                6.50 usec
TE                296.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         75.4752953 MHz
NUC1                13C
P1                10.00 usec
PLW1        34.20000076 W

======== CHANNEL f2 ========
SFO2        300.1312005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         6.19999981 W
PLW12        0.17000000 W
PLW13        0.13950001 W

F2 - Processing parameters
SI                 32768
SF           75.4677503 MHz
WDW                  EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

^{1}H-NMR of **40** (300 MHz, $CDCl_3$)



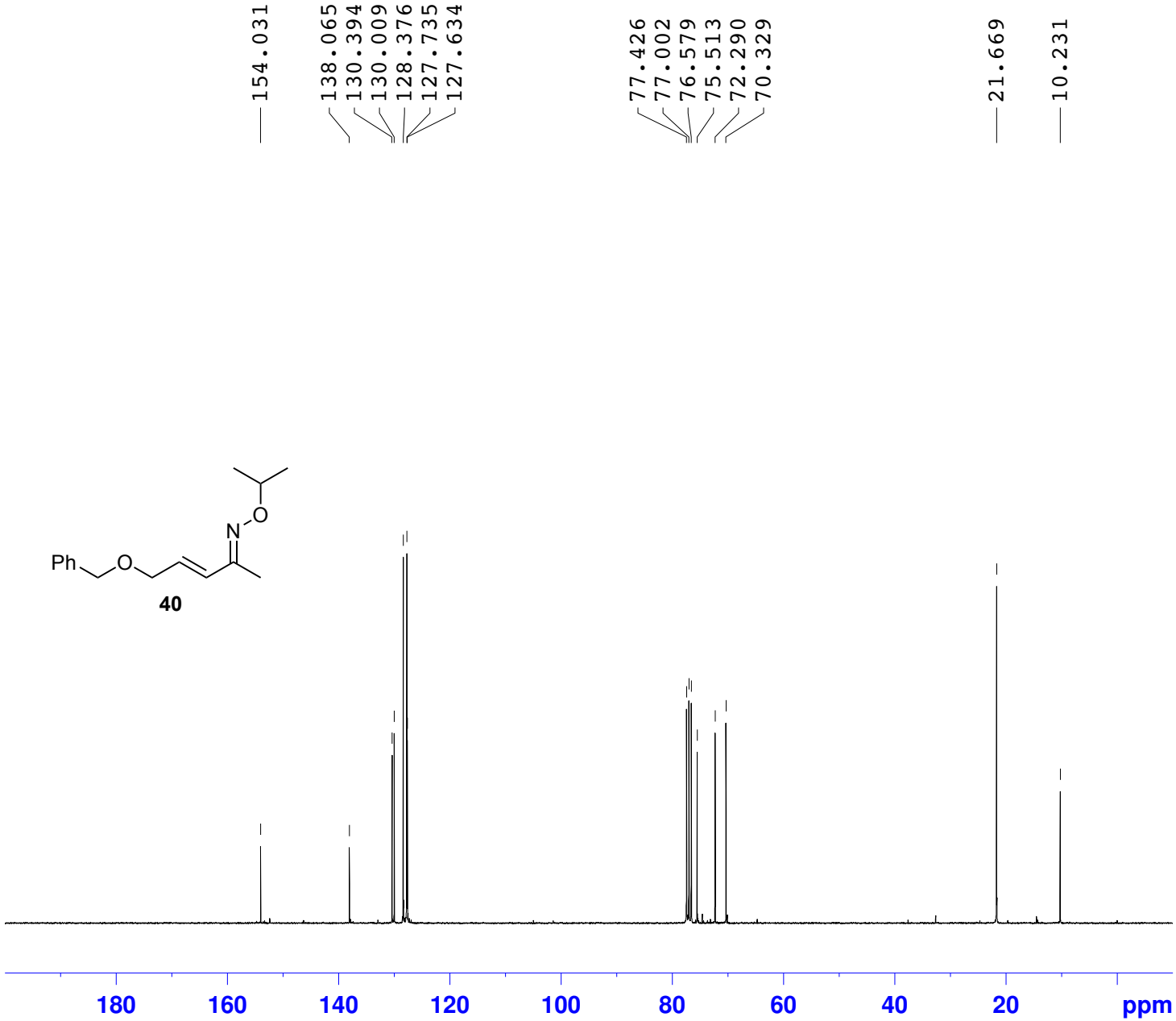

```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               4470
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210313
Time               17.58
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6188.119 Hz
FIDRES          0.094423 Hz
AQ              5.2953086 sec
RG                  45.2
DW                 80.800 usec
DE                  6.50 usec
TE                 294.6 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         300.1318534 MHz
NUC1                   1H
P1                  15.00 usec
PLW1          6.19999981 W

F2 - Processing parameters
SI                 32768
SF           300.1300078 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

^{13}C-NMR of **40** (75 MHz, $CDCl_3$)




```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               4501
PROCNO                 1

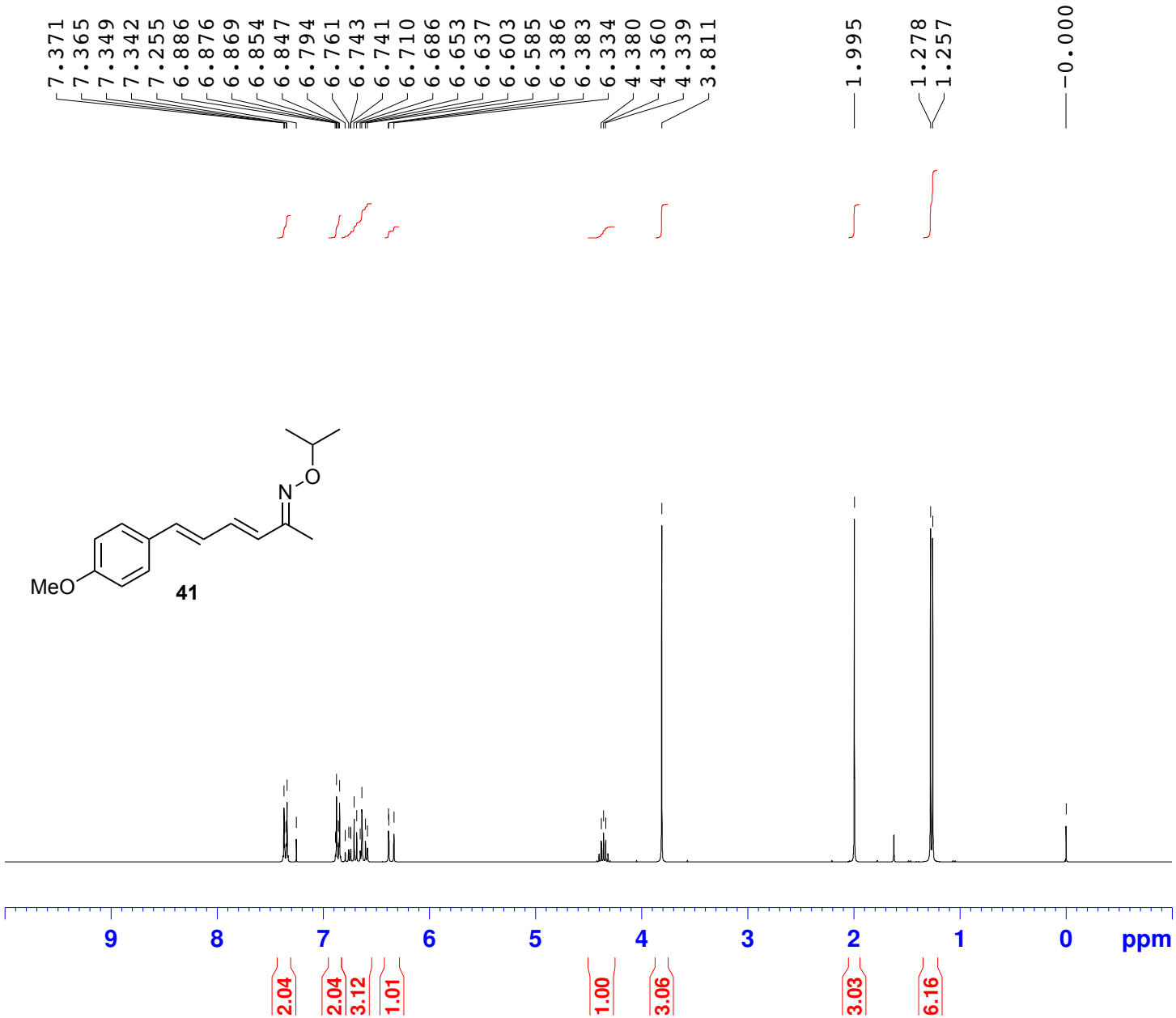
F2 - Acquisition Parameters
Date_           20210321
Time               14.42
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 8000
DS                    4
SWH           18028.846 Hz
FIDRES         0.275098 Hz
AQ             1.8175317 sec
RG                 2050
DW                27.733 usec
DE                 6.50 usec
TE                296.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          75.4752953 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         34.50000000 W

======== CHANNEL f2 ========
SFO2         300.1312005 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2          6.19999981 W
PLW12         0.21797000 W
PLW13         0.13950001 W

F2 - Processing parameters
SI                 32768
SF            75.4677525 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

^{1}H-NMR of **41** (300 MHz, $CDCl_3$)



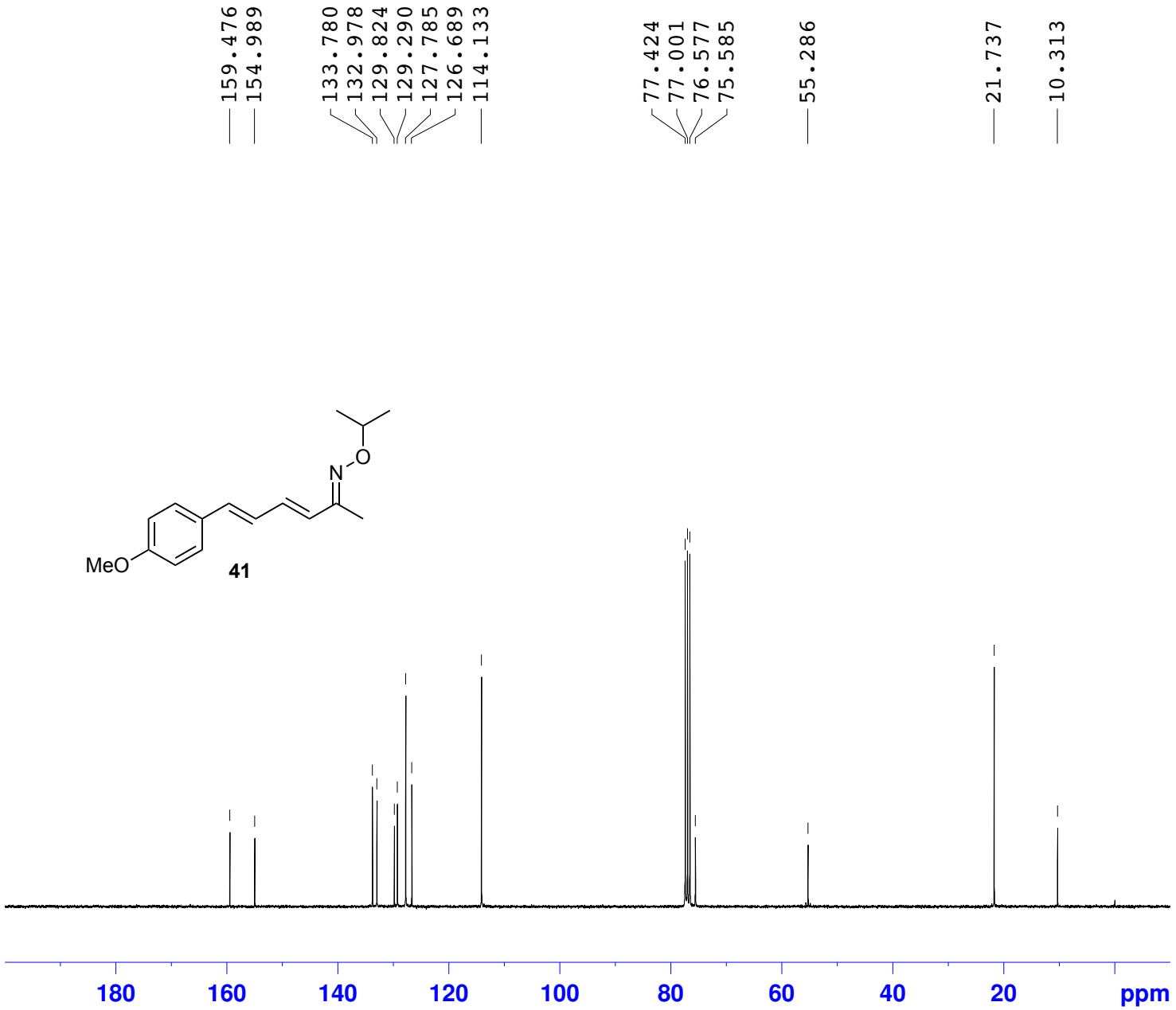

```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               3140
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200817
Time                8.32
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6188.119 Hz
FIDRES          0.094423 Hz
AQ              5.2953086 sec
RG                  45.2
DW                80.800 usec
DE                 6.50 usec
TE                295.6 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         300.1318534 MHz
NUC1                   1H
P1                 15.00 usec
PLW1          6.19999981 W

F2 - Processing parameters
SI                 32768
SF            300.1300068 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

^{13}C-NMR of **41** (75 MHz, $CDCl_3$)




```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               3142
PROCNO                 1

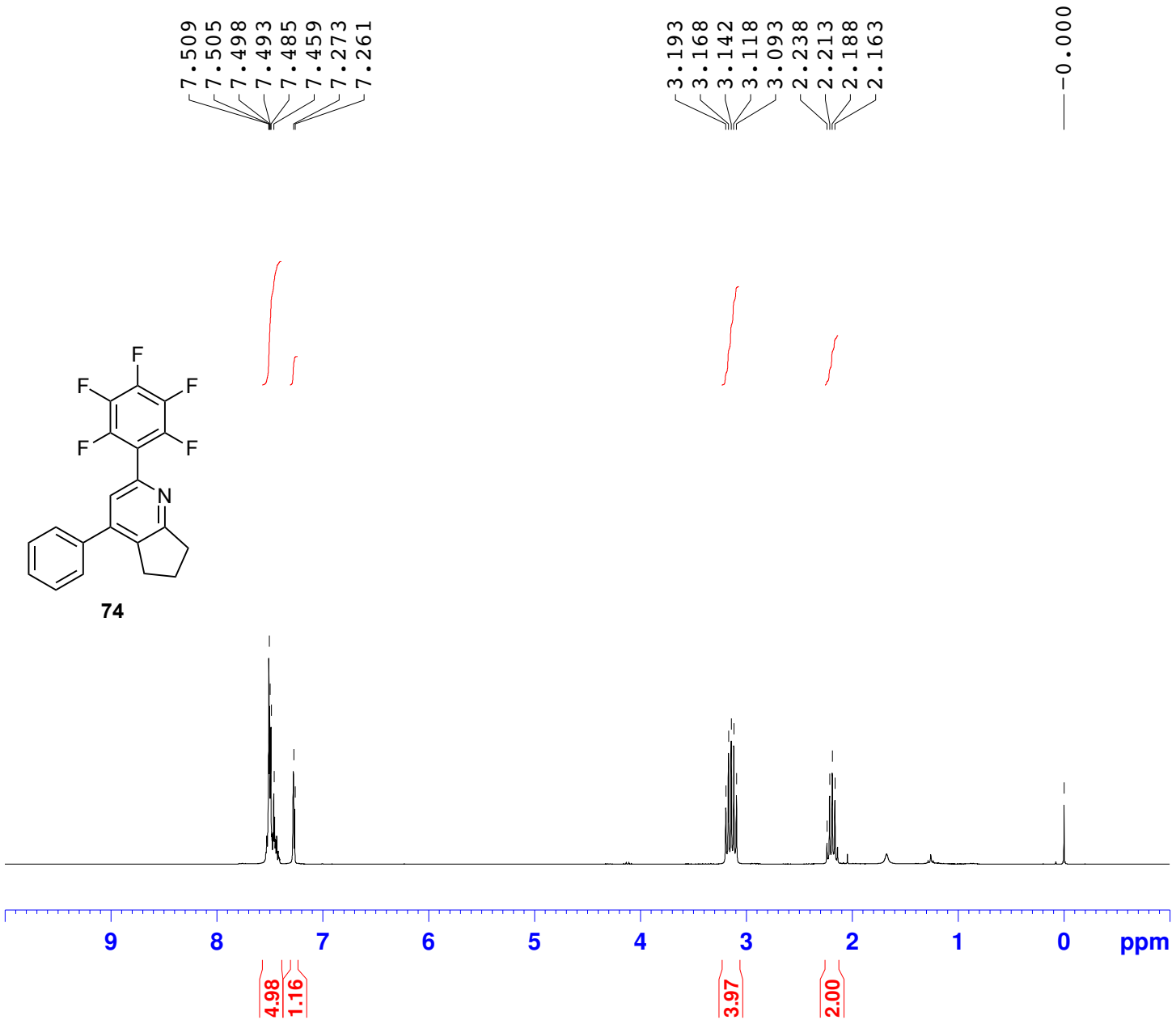
F2 - Acquisition Parameters
Date_           20200817
Time               8.30
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 4096
DS                    4
SWH           18028.846 Hz
FIDRES         0.275098 Hz
AQ            1.8175317 sec
RG                 2050
DW               27.733 usec
DE                6.50 usec
TE                296.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         75.4752953 MHz
NUC1                13C
P1                10.00 usec
PLW1        34.20000076 W

======== CHANNEL f2 ========
SFO2        300.1312005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         6.19999981 W
PLW12        0.17000000 W
PLW13        0.13950001 W

F2 - Processing parameters
SI                 32768
SF           75.4677510 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

^{1}H-NMR of **74** (300 MHz, $CDCl_3$)



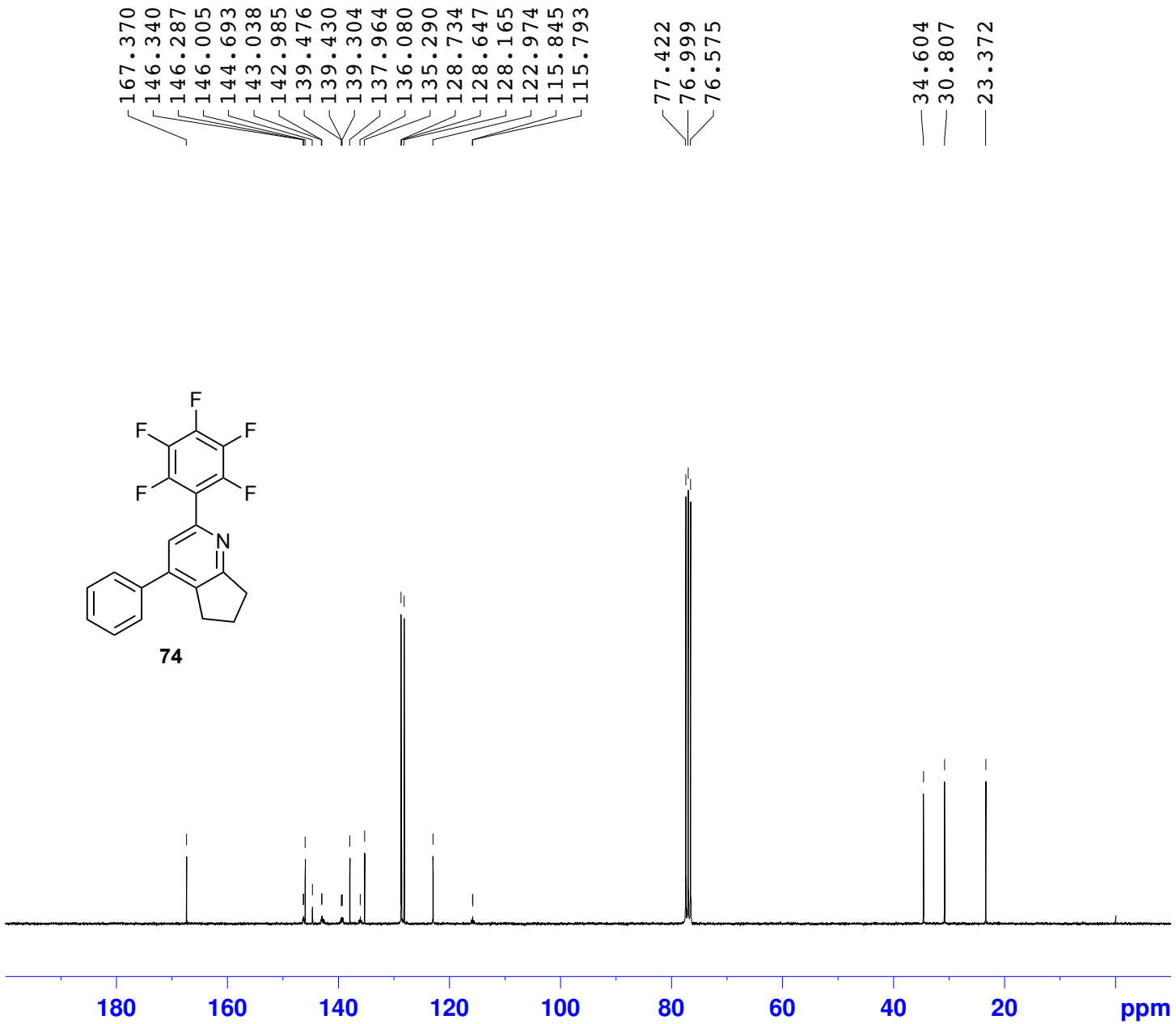

```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               4690
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210605
Time               18.52
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6188.119 Hz
FIDRES          0.094423 Hz
AQ              5.2953086 sec
RG                  80.6
DW                80.800 usec
DE                 6.50 usec
TE                294.8 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         300.1318534 MHz
NUC1                   1H
P1                 15.00 usec
PLW1          6.19999981 W

F2 - Processing parameters
SI                 32768
SF           300.1300055 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

^{13}C-NMR of **74** (75 MHz, $CDCl_3$)




```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               4692
PROCNO                 1

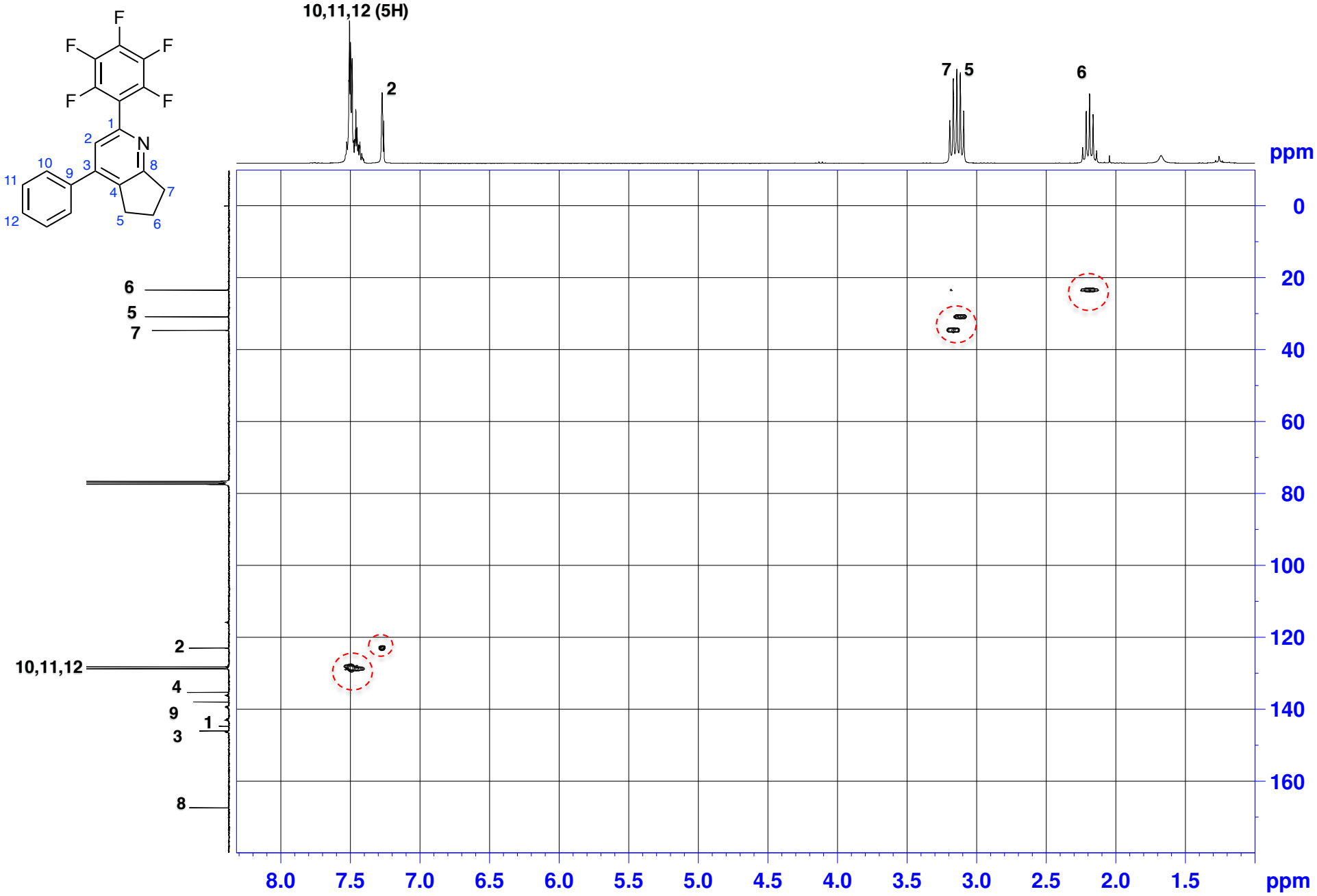
F2 - Acquisition Parameters
Date_           20210606
Time                5.57
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                 8192
DS                    4
SWH           18028.846 Hz
FIDRES         0.275098 Hz
AQ            1.8175317 sec
RG                 2050
DW               27.733 usec
DE                6.50 usec
TE               296.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         75.4752953 MHz
NUC1                13C
P1                10.00 usec
PLW1        34.50000000 W

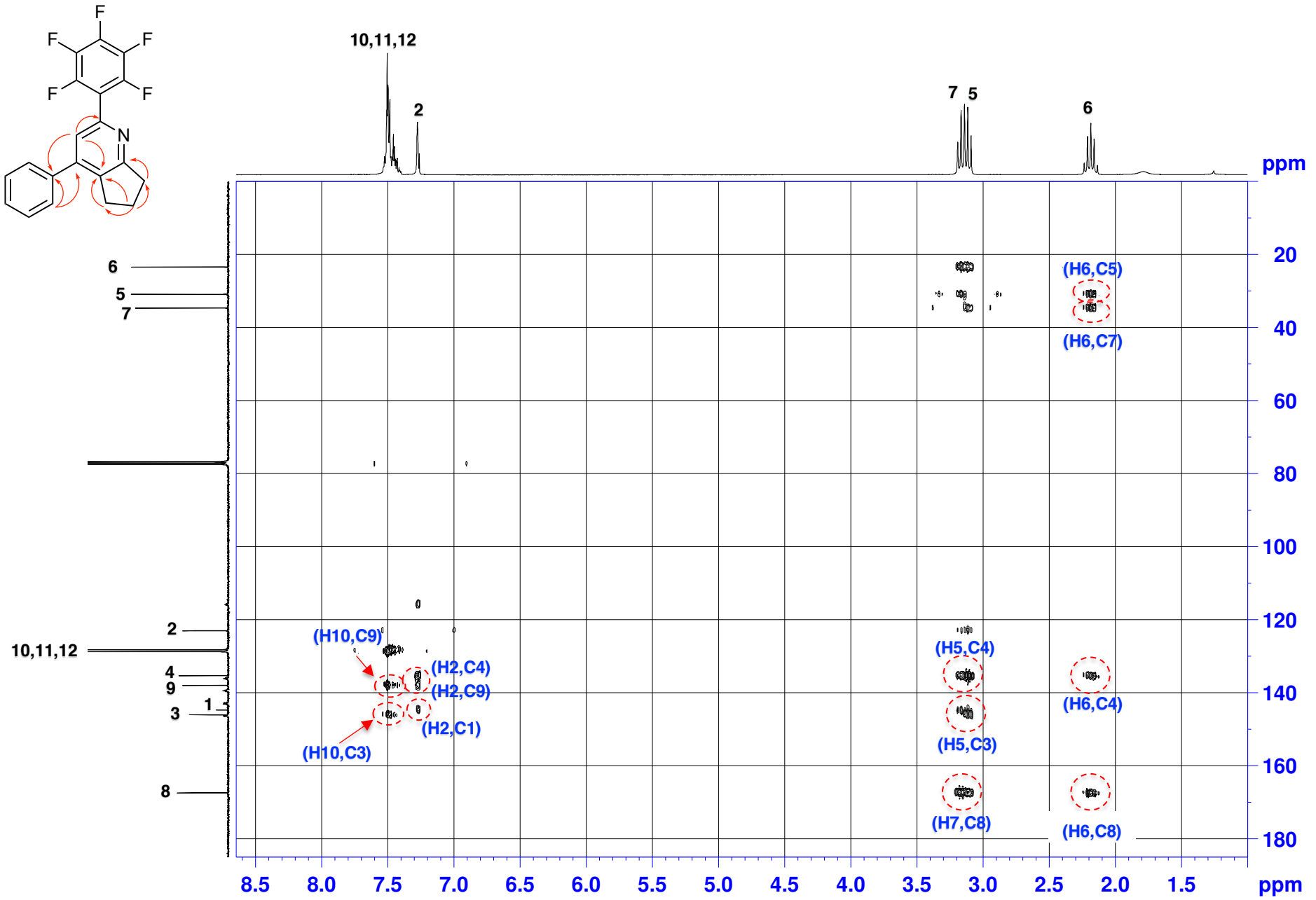
======== CHANNEL f2 ========
SFO2        300.1312005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         6.19999981 W
PLW12        0.21797000 W
PLW13        0.13950001 W

F2 - Processing parameters
SI                32768
SF           75.4677503 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

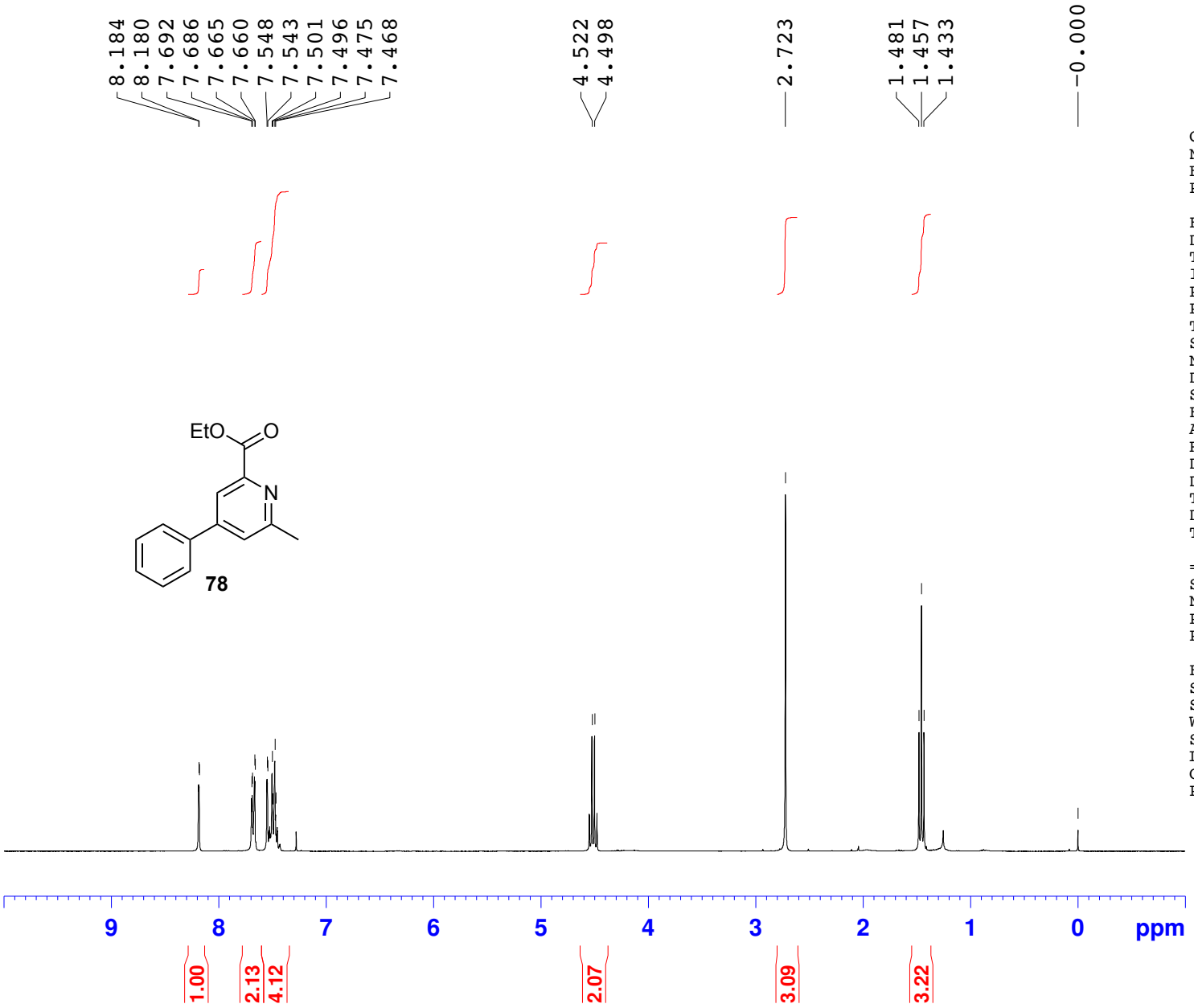
HSQC spectrum of **74**



HMBC spectrum of **74**



^{1}H-NMR of **78** ($CDCl_3$)



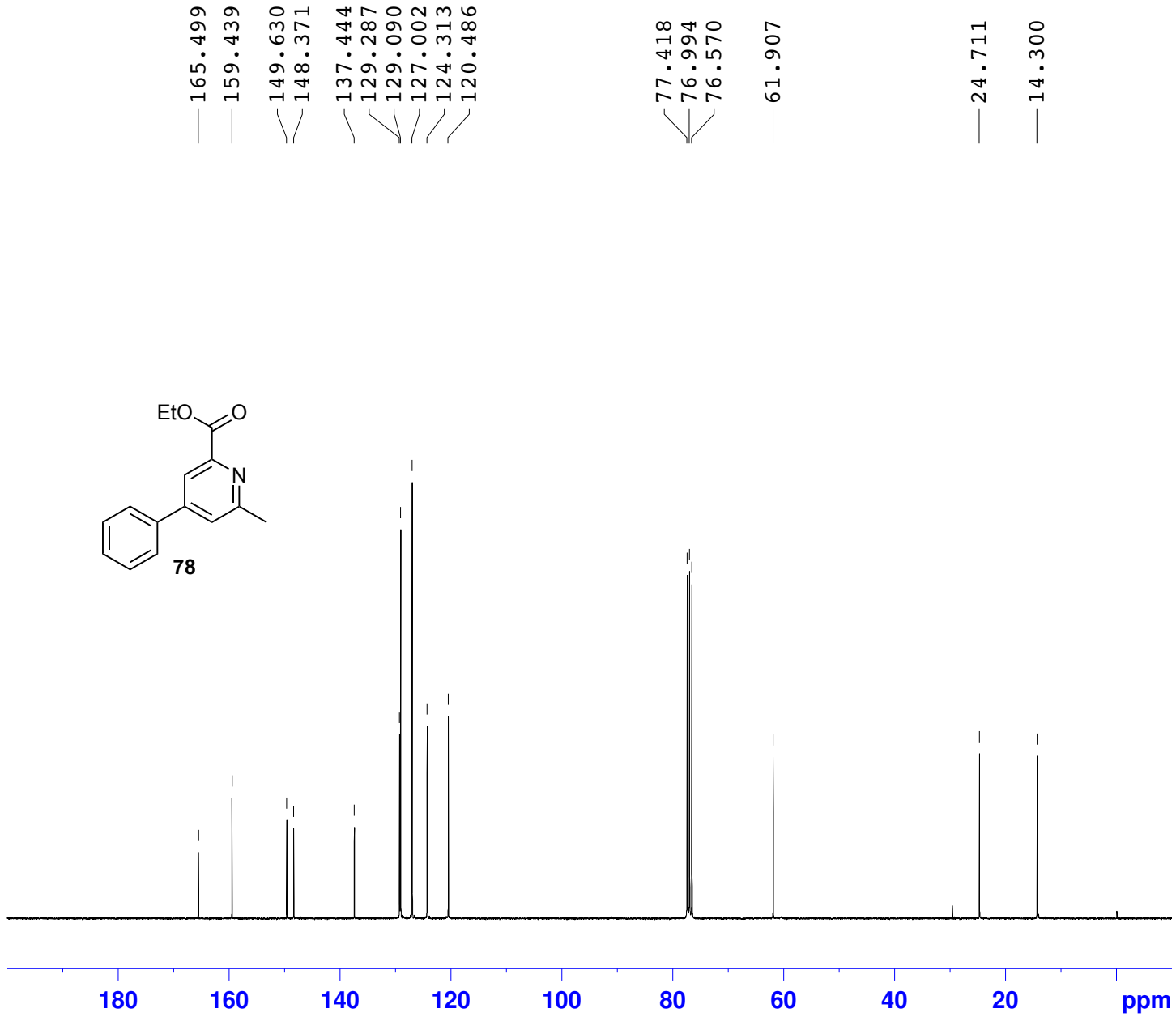

```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               6400
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220129
Time               20.23
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           6188.119 Hz
FIDRES        0.094423 Hz
AQ            5.2953086 sec
RG                    36
DW               80.800 usec
DE                6.50 usec
TE                294.5 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        300.1318534 MHz
NUC1                   1H
P1                15.00 usec
PLW1         8.00000000 W

F2 - Processing parameters
SI                 32768
SF          300.1300012 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

^{13}C-NMR of **78** (75 MHz, $CDCl_3$)




```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               6402
PROCNO                 1

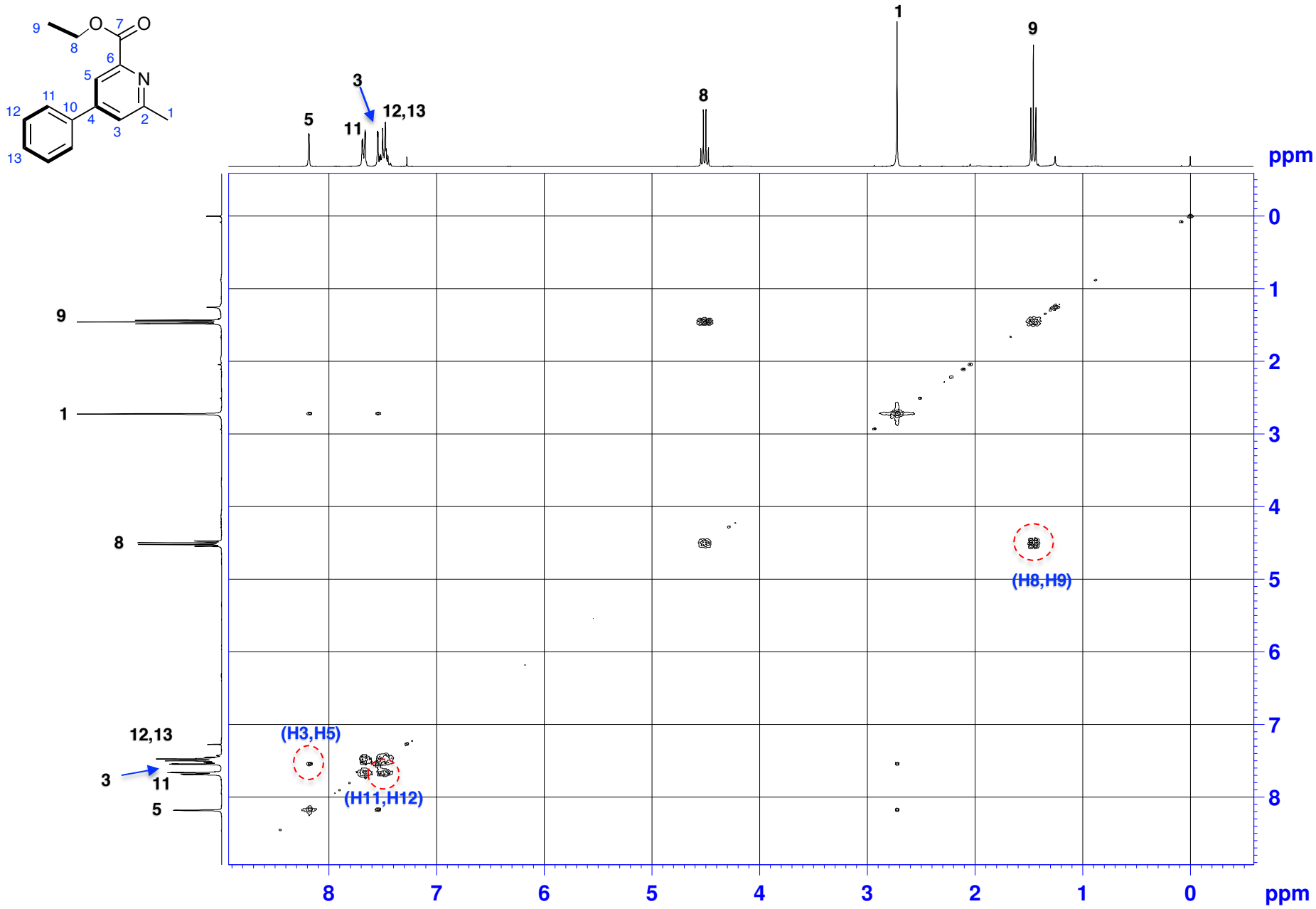
F2 - Acquisition Parameters
Date_           20220130
Time              23.42
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                 8000
DS                    4
SWH           18028.846 Hz
FIDRES         0.275098 Hz
AQ            1.8175317 sec
RG                 2050
DW               27.733 usec
DE                6.50 usec
TE               296.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         75.4752953 MHz
NUC1                13C
P1                10.00 usec
PLW1        34.50000000 W

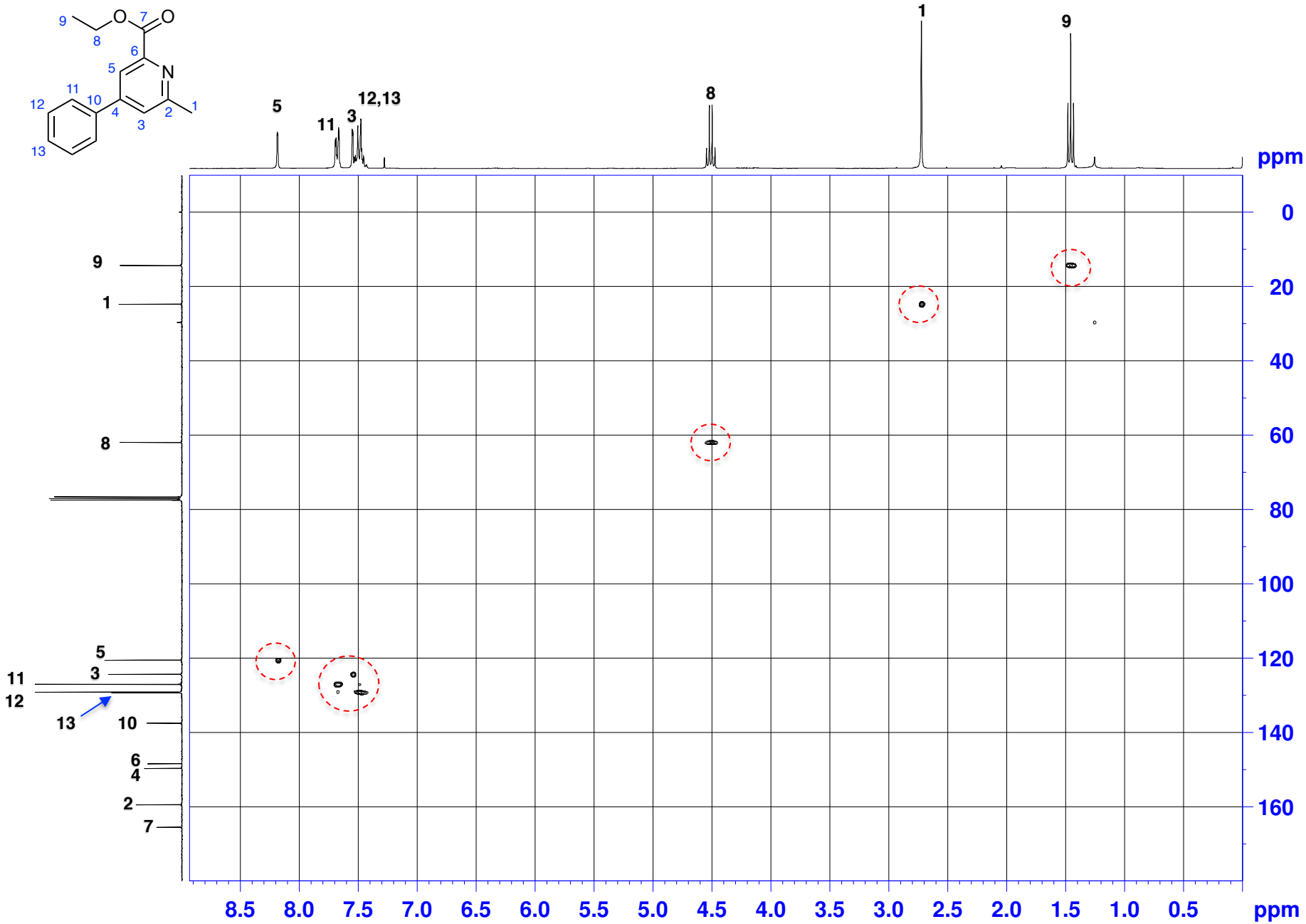
======== CHANNEL f2 ========
SFO2        300.1312005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         8.00000000 W
PLW12        0.28125000 W
PLW13        0.18000001 W

F2 - Processing parameters
SI                 32768
SF            75.4677539 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

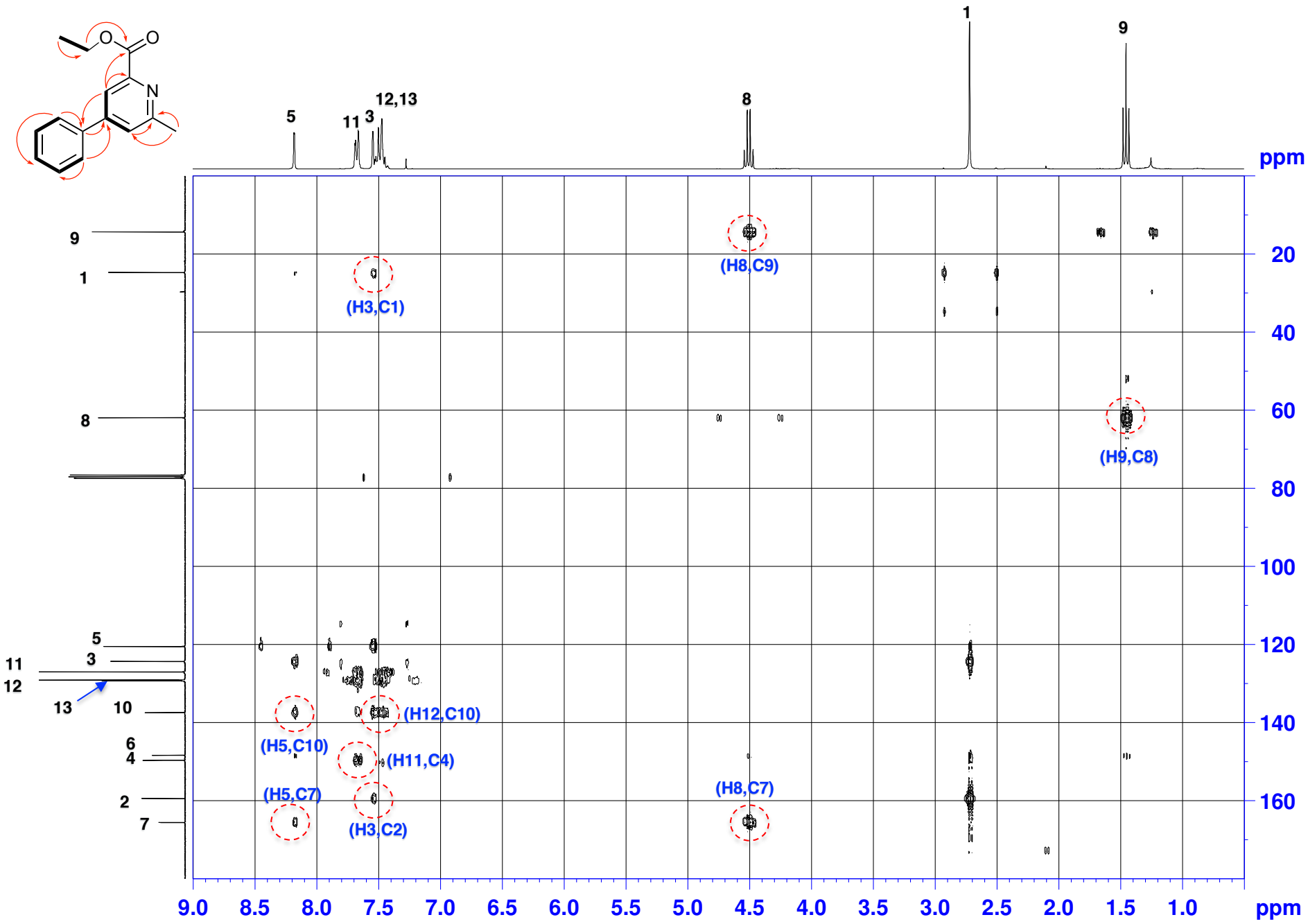
^{1}H-^{1}H COSY spectrum of **78**



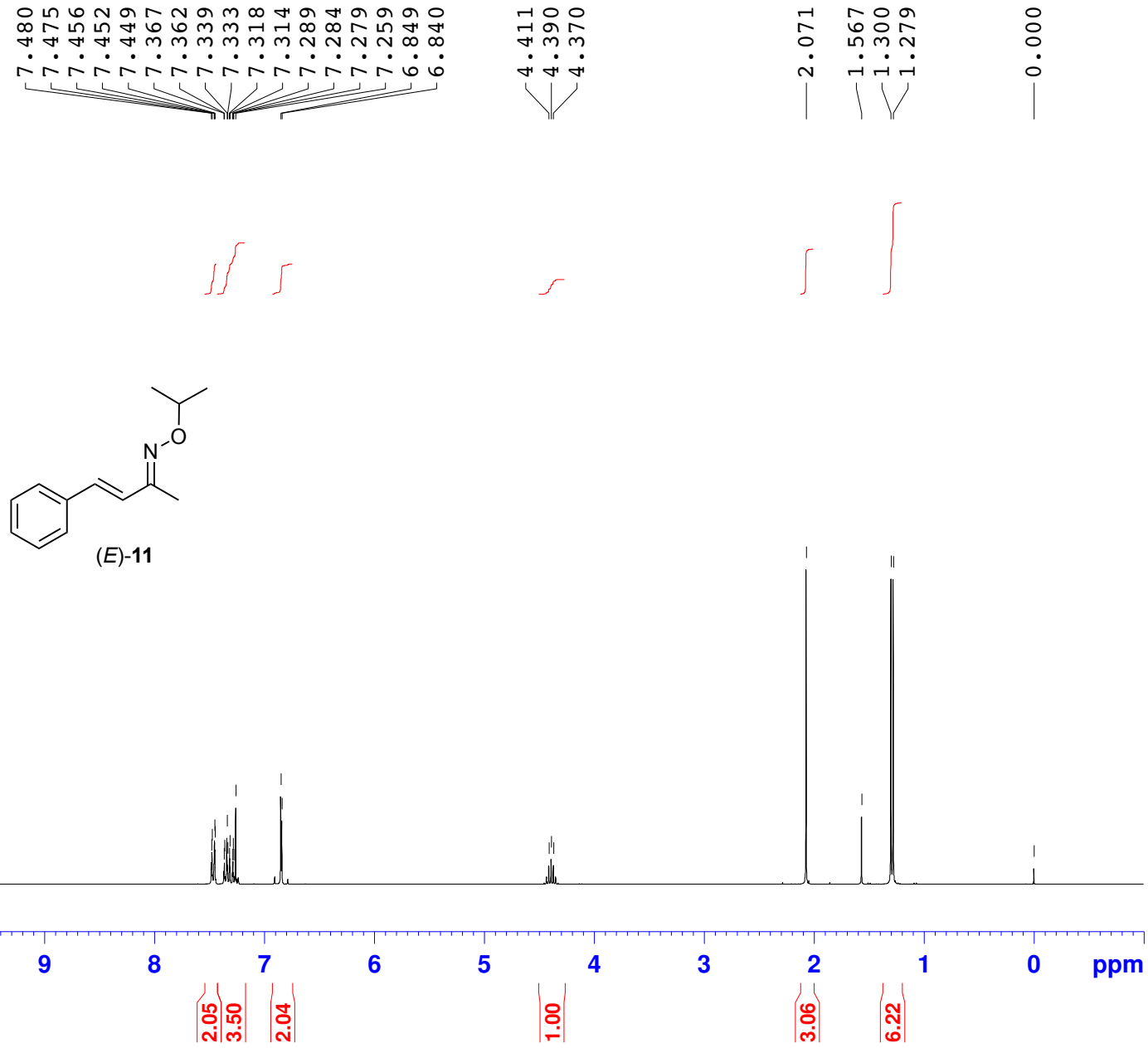
HSQC spectrum of **78**



HMBC spectrum of **78**



^{1}H-NMR of (*E*)-**11** (300 MHz, $CDCl_3$)



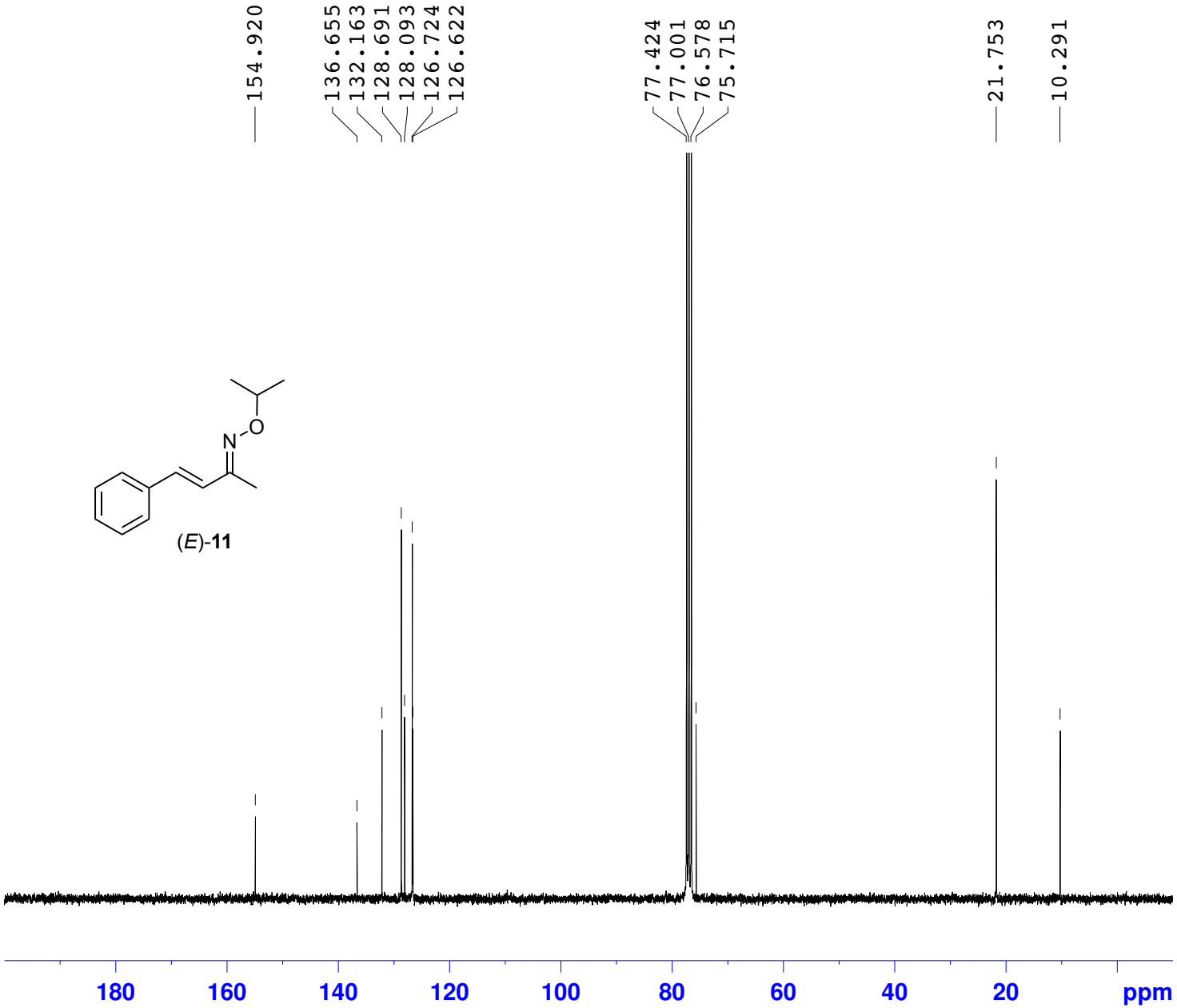

```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               1850
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200324
Time               22.09
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6188.119 Hz
FIDRES          0.094423 Hz
AQ             5.2953086 sec
RG                   101
DW                80.800 usec
DE                 6.50 usec
TE                294.8 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        300.1318534 MHz
NUC1                   1H
P1                 15.00 usec
PLW1          6.19999981 W

F2 - Processing parameters
SI                 32768
SF          300.1300062 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

^{13}C-NMR of (*E*)-**11** (75 MHz, $CDCl_3$)




```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               1871
PROCNO                 1

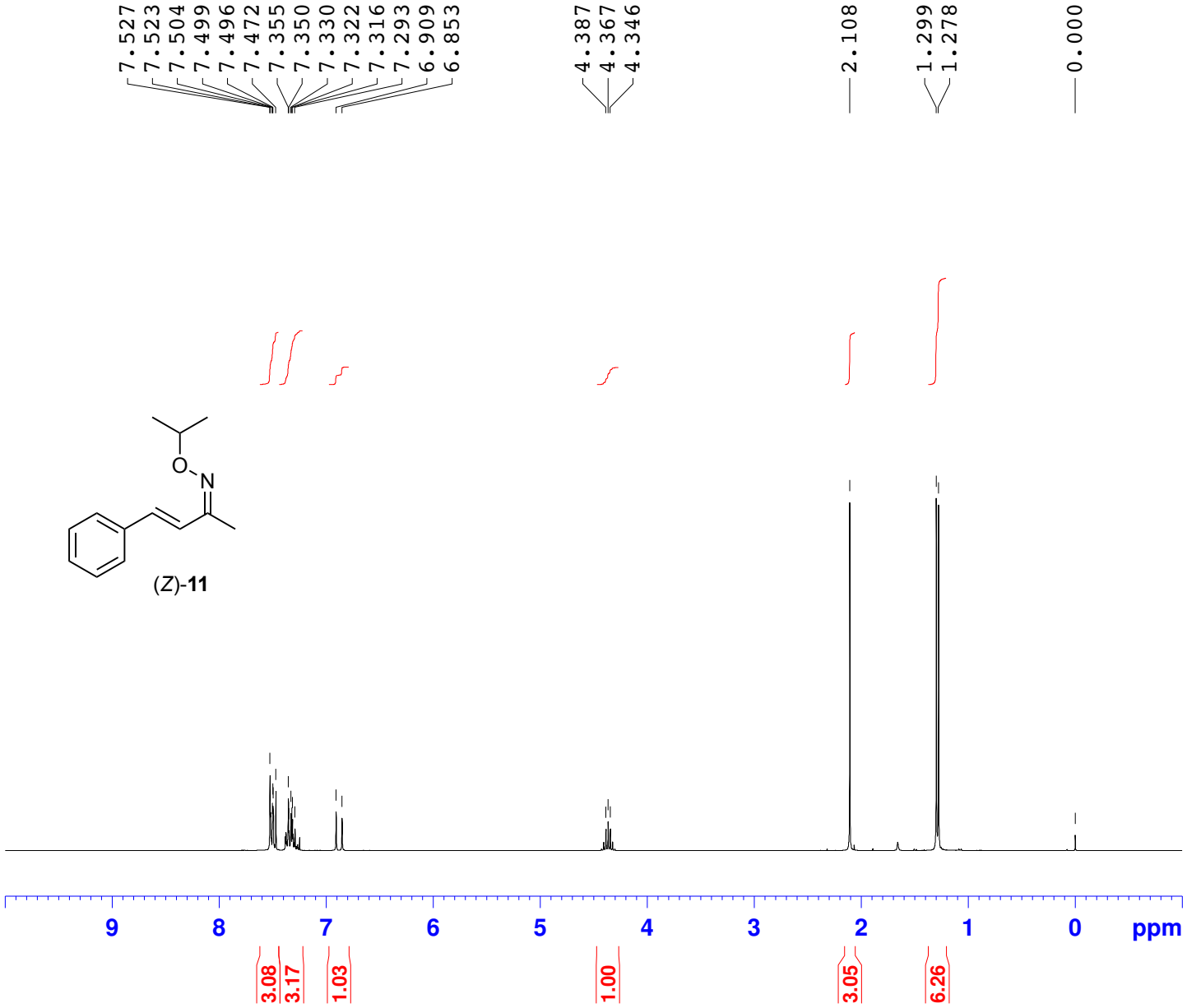
F2 - Acquisition Parameters
Date_           20200325
Time               7.36
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 4096
DS                    4
SWH           18028.846 Hz
FIDRES         0.275098 Hz
AQ            1.8175317 sec
RG                 2050
DW               27.733 usec
DE                6.50 usec
TE                296.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         75.4752953 MHz
NUC1                13C
P1                10.00 usec
PLW1        34.20000076 W

======== CHANNEL f2 ========
SFO2        300.1312005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2          6.19999981 W
PLW12         0.17000000 W
PLW13         0.13950001 W

F2 - Processing parameters
SI                 32768
SF            75.4677498 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

^{1}H-NMR of (*Z*)-**11** (300 MHz, $CDCl_3$)



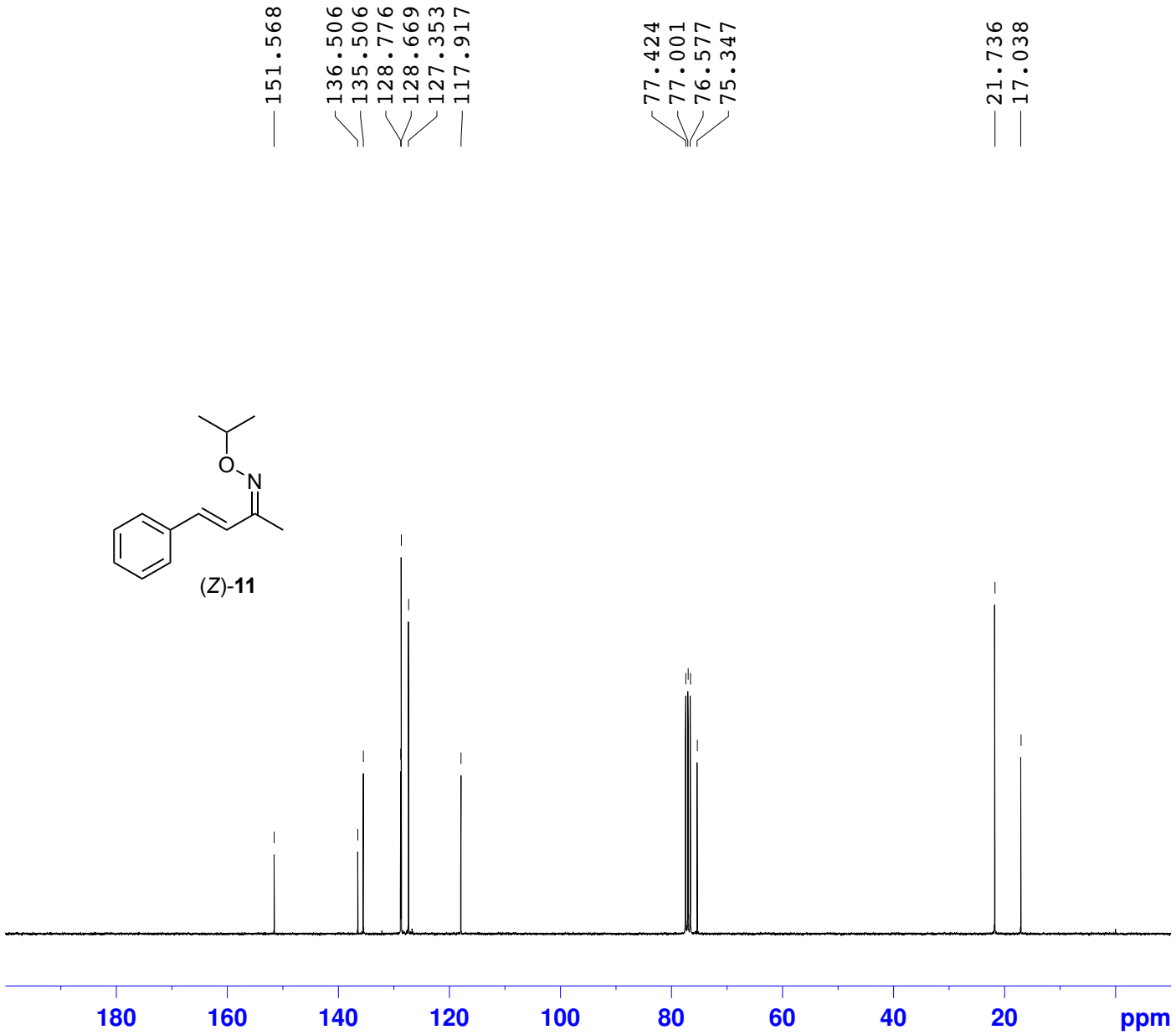

```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               7660
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220709
Time               13.43
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6188.119 Hz
FIDRES          0.094423 Hz
AQ             5.2953086 sec
RG                  20.2
DW                80.800 use
DE                 6.50 use
TE                295.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         300.1318534 MHz
NUC1                   1H
P1                 15.00 use
PLW1          8.00000000 W

F2 - Processing parameters
SI                 32768
SF           300.1300091 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

^{13}C-NMR of (*Z*)-**11** (75 MHz, $CDCl_3$)




```
Current Data Parameters
NAME      Yakka_Yamada_2
EXPNO               7664
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220710
Time               11.39
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 3000
DS                    4
SWH           18028.846 Hz
FIDRES         0.275098 Hz
AQ            1.8175317 sec
RG                 2050
DW               27.733 usec
DE                6.50 usec
TE                296.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         75.4752953 MHz
NUC1                13C
P1                10.00 usec
PLW1        34.50000000 W

======== CHANNEL f2 ========
SFO2        300.1312005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         8.00000000 W
PLW12        0.28125000 W
PLW13        0.18000001 W

F2 - Processing parameters
SI                 32768
SF           75.4677513 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```