Supporting information for…

Reductive Ni-Catalysis for Stereoselective Carboarylation of Terminal Aryl Alkynes

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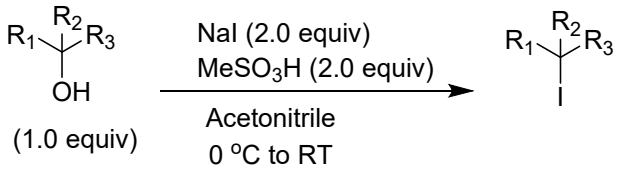
I. General Information

All reagents were purchased from standard suppliers (Sigma-Aldrich, Alfa Aesar, or TCI) and were used without further purification. Few starting materials were prepared and the methods for preparation and characterization data have been provided below. Unless otherwise stated, all the solid chemicals were weighed out on the benchtop outside the glovebox and the difunctionalization reactions were performed using Schlenk techniques under N_2 atmosphere. Liquid chemicals were added to the screw-top Schlenk tube via microsyringe. Reactions were monitored by thin-layer chromatography (TLC) using Merck silica gel 60F254 glass plate with 0.25 mm thickness. The glass plates were visualized by an ultra-violet lamp (254 nm). Flash column chromatography was performed using Merck silica gel 60 (mesh 230−400). ^{1}H, broadband proton-decoupled ^{13}C NMR spectra were recorded on a Bruker Avance III HD 400 MHz instrument. The chemical shift values (δ) are reported in parts per million (ppm) with respect to residual solvent signals. Data are given as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br s = broad singlet, m = multiplet), coupling constant (*J*, Hz), and integration. High-resolution mass spectrometry (HRMS) data

were measured on a Thermo Scientific Q Exactive Plus Hybrid Quadrupole-Orbitrap mass spectrometer. Melting points of the compounds were measured by using a digital melting point apparatus (KRUSS, Germany). Fourier transform infrared spectroscopy (FTIR) spectra in attenuated total reflectance (ATR) mode were recorded on a Shimadzu IRTracer-100 and reported in wave number (cm^{-1}).

Preparation of tertiary alkyl iodides:

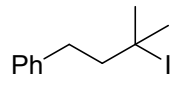
2-Iodo-2-methyl-propane (*tert*-butyl iodide) was purchased from Sigma-Aldrich and stored properly to avoid decomposition. Use of non-decomposed colourless *tert*-butyl iodide was essential to conduct the reactions. Following mentioned two tertiary alkyl iodides were prepared from corresponding tertiary alkyl alcohol by following literature report.[1]



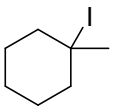
The corresponding tertiary alcohol (1.0 equiv.) and sodium iodide (2.0 equiv.) were dissolved in acetonitrile and cooled to 0 ºC. Methanesulfonic acid (2 equiv.) was added dropwise to the reaction mixture, which was then warmed to room temperature and stirred for an additional 30 minutes. Minimizing light exposure, the mixture was then concentrated on a rotary evaporator, re-dissolved in diethyl ether and washed with aqueous saturated $NaHCO_3$ solution followed by a wash with saturated $Na_2S_2O_3$. The organic layer was dried over $MgSO_4$ and concentrated. Purification by silica gel column chromatography was carried out rapidly (prolonged residence on the stationary phase resulted in H-I elimination) using *n*-hexane as eluent. The compounds were stored in a freezer by wrapping the vial with aluminium foil. Yields of *tert*-alkyl iodides were not optimized.

2-Iodo-2-methylbutane (SM-1)[2]: The title compound was synthesized from the corresponding alcohol 2-methylbutan-2-ol. Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.91 (s, 6H), 1.64 (q, J = 8 Hz, 2H), 1.06 (t, J = 8 Hz, 3H).). The spectral data was in accordance with the literature.

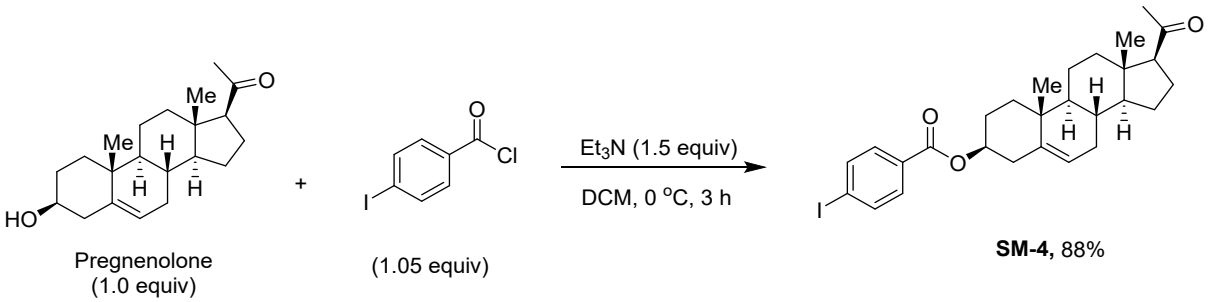
(3-Iodo-3-methylbutyl)benzene (SM-2)[3]: The title compound was synthesized from the corresponding alcohol 2-methyl-4-phenylbutan-2-ol. Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, J = 8 Hz, 2H), 7.24-7.21 (m, 3H), 2.86 (t, J = 8 Hz, 2H), 2.01 (s, 6H), 1.92 (t, J = 8 Hz, 2H). The spectral data was in accordance with the literature.



1-Iodo-1-methylcyclohexane (SM-3)[1]: The title compound was synthesized from the corresponding alcohol 1-methylcyclohexan-1-ol. Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.17-2.12 (m, 2H), 2.10 (s, 3H), 1.68-1.65 (m, 5H), 1.27-1.20 (m, 1H), 1.04-0.97 (m, 2H). The spectral data was in accordance with the literature.

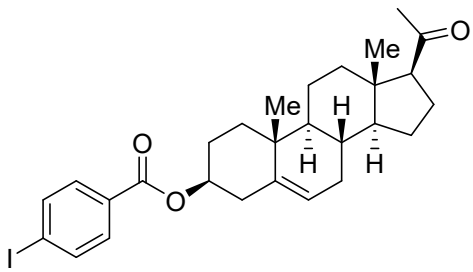


Preparation of steroid derived aryl iodide substrate(SM-4):



To a stirred solution of Pregnenolone (300 mg, 0.94 mmol) in DCM taken in a 100 mL round bottom flask, triethylamine (198 µL, 1.41 mmol) was added and the flask was cooled at 0 °C. Subsequently 4-iodobenzoyl chloride (265 mg, 0.99 mmol) was introduced and the resulting solution was stirred untill the alcohol was fully consumed. Then, saturated aqueous solution of ammonium chloride was added to quench the reaction. The resulting solution was extracted with DCM three times. The organic layer was separated and passed through anhydrous sodium sulphate, followed by evaporation of solvent under reduced pressure in rotary evaporator. The residue was separated by column chromatography using hexane and ethyl acetate as eluent to get the product **SM-4** as white solid (454 mg, 0.831 mmol).

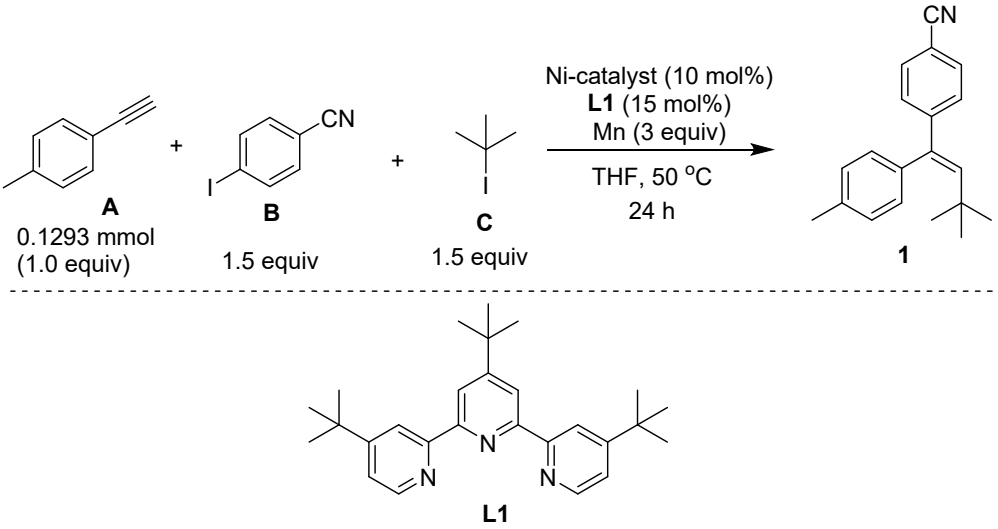
(3S,8S,9S,10R,13S,14S,17S)-17-Acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-iodobenzoate (SM-4): White solid (454 mg, 88%); mp 206-208 °C;



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8 Hz, 2H), 7.74 (d, *J* = 8 Hz, 2H), 5.42 (d, *J* = 4 Hz, 1H), 4.89-4.81 (m, 1H), 2.55 (t, *J* = 8 Hz, 1H), 2.46 (d, *J* = 8 Hz, 2H), 2.13 (s, 3H), 2.08-1.90 (m, 4H), 1.72-1.61 (m, 5H), 1.54-1.47 (m, 4H), 1.26-1.18 (m, 3H), 1.07 (s, 3H), .064 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 209.7, 165.6, 137.8, 131.2, 100.6, 74.9, 63.8, 56.9, 50.0, 44.1, 38.9, 38.2, 37.1, 36.8, 32.0, 31.9, 31.7, 27.9, 24.6, 22.9, 21.2, 19.5, 13.4; IR (ATR) $\tilde{\nu}$: 2940, 1710, 1584, 1392, 1355, 1272, 1116, 1007, 758 cm^{-1}; HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{28}H_{36}IO_3$, 547.1703; found, 547.1705.

II. Screening of reaction parameters for alkylarylation

Table S1. Catalyst screening

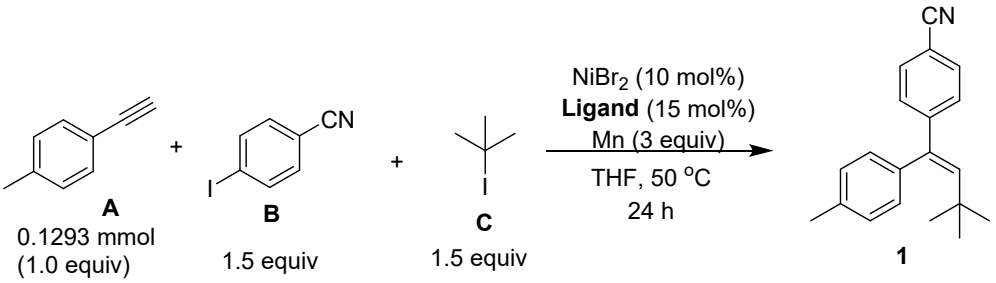


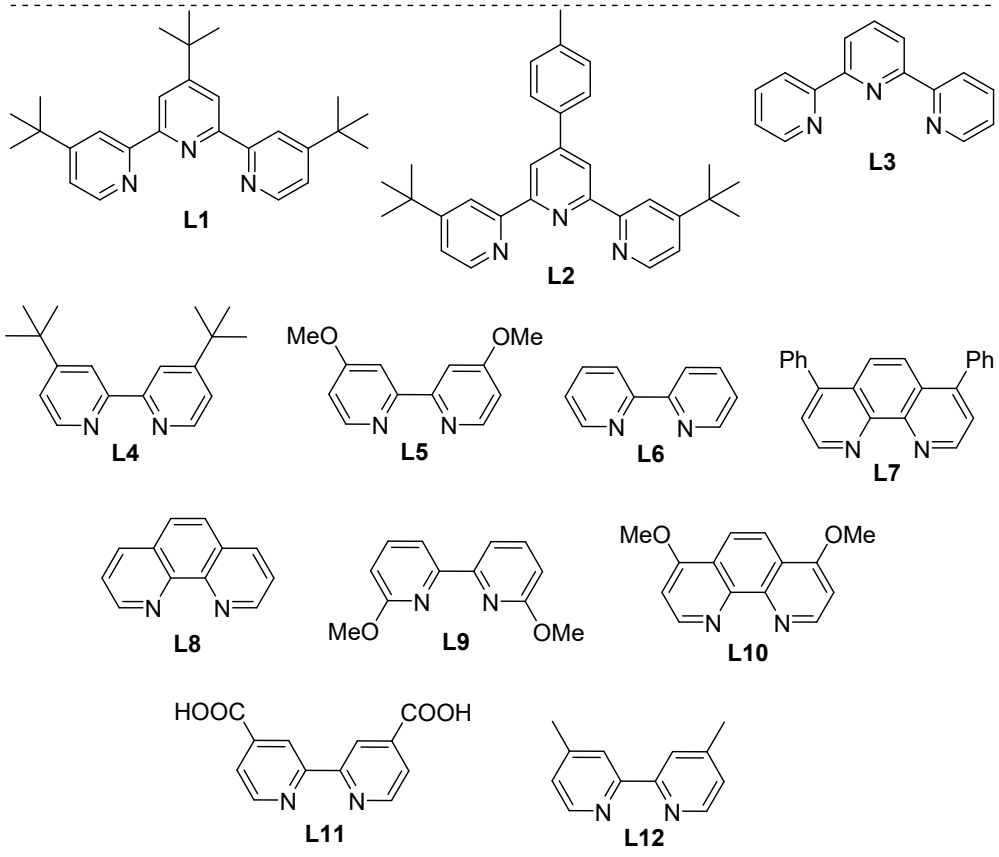
Entry	Catalyst	Yield (%)
1	$NiCl_2$	82
2	**$NiBr_2$**	**87**
3	$NiBr_2$.dme	83
4	NiI_2	79
5	$NiCl_2.6H_2O$	76
6	$NiCl_2(PPh_3)_2$	25
7	$Ni(OAc)_2.4H_2O$	72
8	$NiCl_2(dppp)_2$	56
9	$Ni(acac)_2$	9

10	$NiCl_2(Py)_4$	42
11	$NiBr_2.3H_2O$	<5
12	$Ni(NO_3)_2.6H_2O$	0
13	$NiClCp(PPh_3)$	23

Reaction condition: 0.129 mmol **A**, 0.193 mmol **B** (1.5 equiv), 0.193 mmol **C** (1.5 equiv). Yields are after column chromatographic purification of **1**. N_2 condition.

Table S2. Ligand screening



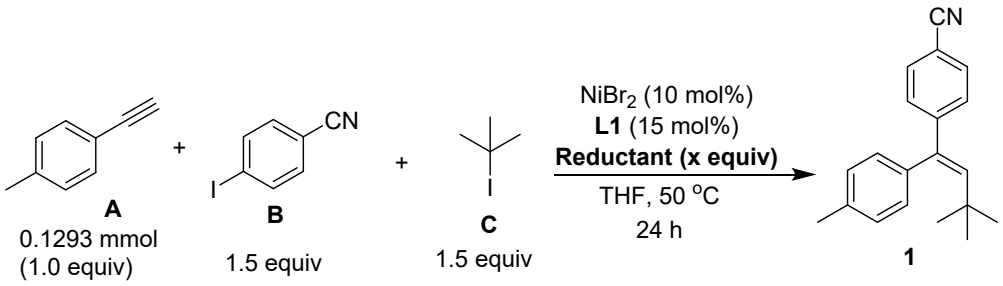


Entry	Ligand	Yield (%)
1	**L1**	**87**
2	**L2**	69
3	**L3**	<5
4	**L4**	75
5	**L5**	28
6	**L6**	<5
7	**L7**	10
8	**L8**	20
9	Xantphos	0
10	1,3-Bis(diphenylphosphino)propane (dppp)	0
11	**L9**	0

12	**L10**	<5
12	**L11**	<5
13	**L12**	12
14	1,1'-Bis(diphenylphosphino)ferrocene	0

Reaction condition: 0.129 mmol **A**, 0.193 mmol **B** (1.5 equiv), 0.193 mmol **C** (1.5 equiv). Yields are after column chromatographic purification of **1**. N_2 condition.

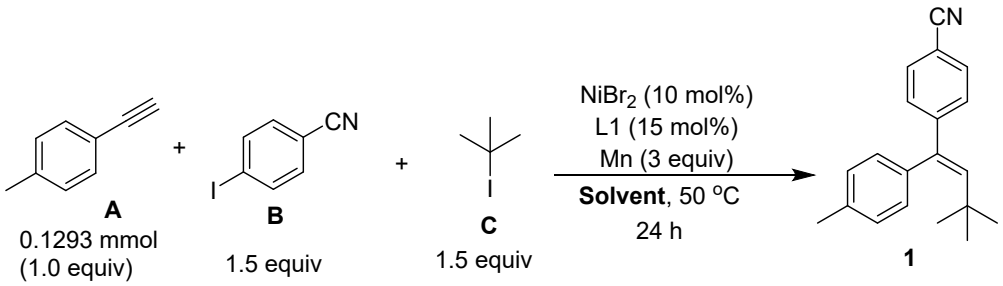
Table S3. Reducing agent screening



Entry	Reductant (equivalent)	Yield (%)
1	**Mn (3)**	**87**
2	Zn (3)	38
3	TDAE (3)	<5
4	Mn (2)	70
5	Mn (1)	47
6	Mn (3) at room temperature	0
7	TDAE (3) at room temperature	0

Reaction condition: 0.129 mmol **A**, 0.193 mmol **B** (1.5 equiv), 0.193 mmol **C** (1.5 equiv). Yields are after column chromatographic purification of **1**. N_2 condition. TDAE = Tetrakis(dimethylamino)ethylene

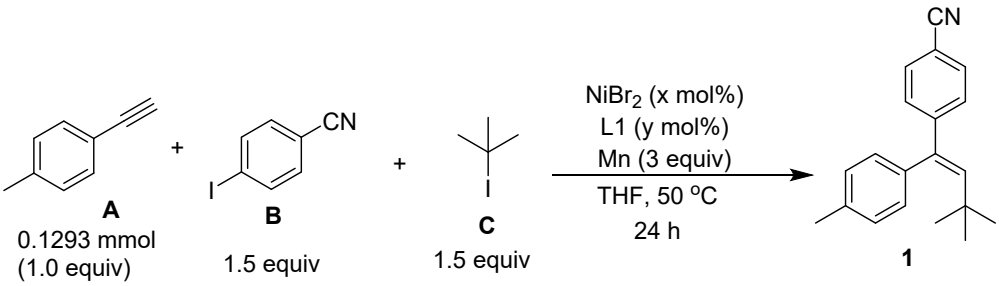
Table S4. Solvent screening



Entry	Solvent	Yield (%)
1	**Tetrahydrofuran**	**87**
2	1,2-Dimethoxyethane	63
3	1,2-Dichlorobenzene	0
4	Toluene	0
5	N,N-Dimethylacetamide	0
6	Acetonitrile	<5
7	N,N-Dimethylformamide	0
8	Ethylacetate	10
9	2,2,2-Trifluoroethanol	0
10	Methanol	<5
11	Benzene	0
12	Chloroform	0
13	1,4-Dioxane	0
14	Non anhydrous THF	0

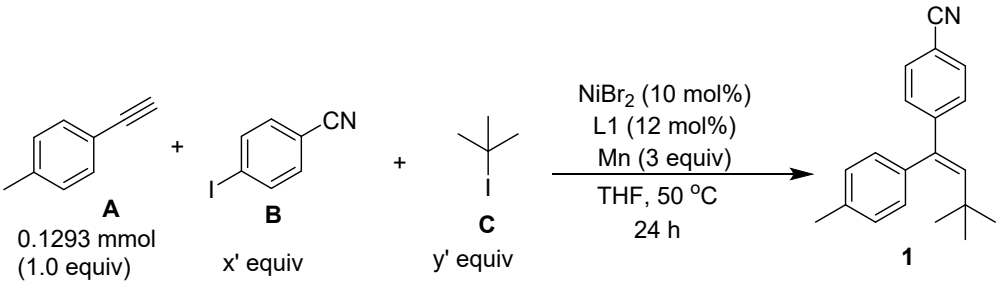
Reaction condition: 0.129 mmol **A**, 0.193 mmol **B** (1.5 equiv), 0.193 mmol **C** (1.5 equiv). Yields are after column chromatographic purification of **1**.

Table S5. Catalyst to ligand ratio optimization



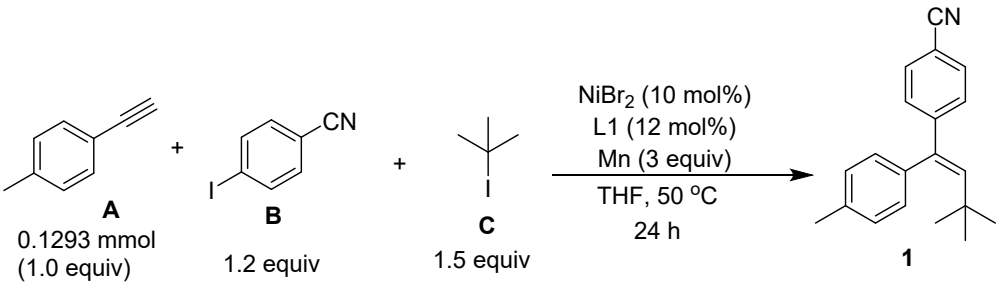
Entry	x / y (mol%)	Yield (%)
1	10 / 15	87
2	10 / 10	83
3	5 / 10	80
4	5 / 5	72
5	2.5 / 5	67
6	2.5 / 2.5	61
7	**10 / 12**	**87**

Table S6. Substrate ratio optimization



Entry	x' / y' (equiv)	Yield (%)
1	1.5 / 1.5	87
2	1.5 / 1.0	76
3	1.0 / 1.5	85
4	1.2 / 1.2	71
5	**1.2 / 1.5**	**87**

Table S7. Other variation



Entry	Variation form standard condition	Yield (%)
1	**No variation**	**87**
2	No catalyst	0
3	No ligand	0
4	No Mn	0
5	Reaction at 25 °C	0
6	Reaction at 45 °C	85

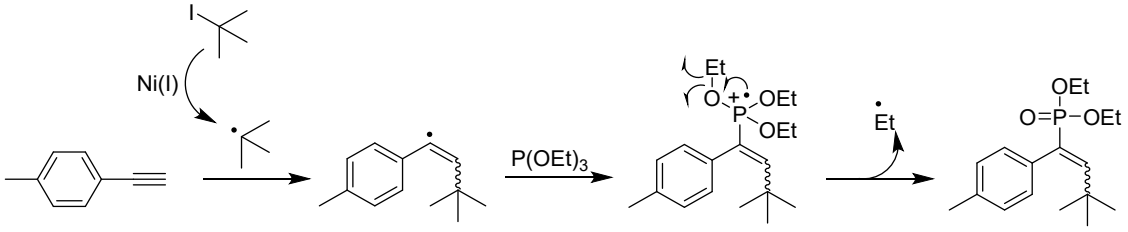
NOTES:

The stereochemistry of the synthesized products were assigned by comparing 1H-NMR of vinylic proton of compounds with previously reported similar compounds (made through redox-neutral Ni-catalysis).[4]

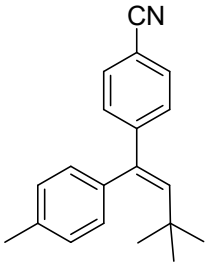
Representative Procedure for the Synthesis of (*E*)-4-(3,3-Dimethyl-1-(*p*-tolyl)but-1-en-1-yl)benzonitrile (1): An oven dried Schlenk tube was charged with 4-iodobenzonitrile (68.7 mg, 0.3 mmol, 1.2 equiv), $NiBr_2$ (5.4 mg, 0.025 mmol, 10 mol%), ligand **L1** (12 mg, 0.03 mmol, 12 mol%), Mn (41 mg, 0.75 mmol, 3 equiv) powder. The reaction vessel was evacuated and back filled with nitrogen three times. 2.5 mL of dry THF was added to the tube under positive flow of N_2 and followed by addition of 4-ethynyl toluene (31.6 µL, 0.25 mmol, 1.0 equiv) and 2-iodo-2-methylpropane (45 µL, 0.375 mmol, 1.5 equiv). The Schenk tube was immediately transferred to a preheated oil bath at 50 °C and allowed to stir for additional 24 h. The reaction was monitored by TLC by checking the consumption of alkyene. Once the alkyne was completely consumed, the reaction mixture were transferred into a round bottom flask and the solvent was evaporated under reduced pressure. The residue was dissolved in minimum amount of dichloromethane and loaded in column for chromatographic purification. The

product was isolated as white solid (60 mg, 0.218 mmol, 87% yield) by using 1% diethyl ether in hexane as eluent.

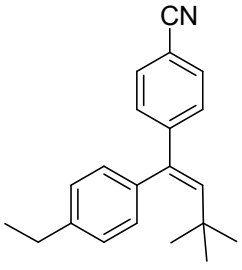
Mechanism of formation of vinyl radical trapped phosphite (45 & 46)[5]:



III. Spectral data:

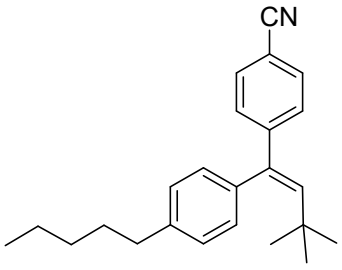


(*E*)-4-(3,3-Dimethyl-1-(*p*-tolyl)but-1-en-1-yl)benzonitrile (1): White solid (60 mg, 87%); mp 53−54 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8 Hz, 2H), 7.26 (d, *J* = 8 Hz, 2H), 7.17 (d, *J* = 8 Hz, 2H), 7.03 (d, *J* = 8 Hz, 2H), 6.16 (s, 1H), 2.39 (s, 3H), 0.97 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.8, 143.3, 138.1, 137.1, 136.4, 131.9, 130.2, 128.9, 127.5, 119.3, 109.9, 34.4, 31.2, 21.4; IR (ATR) $\tilde{\nu}$: 2953, 2922, 2863, 2225, 1600, 1460, 1247, 1021, 835 cm^{-1}; HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{20}H_{22}N$, 276.1747; found, 276.1743.

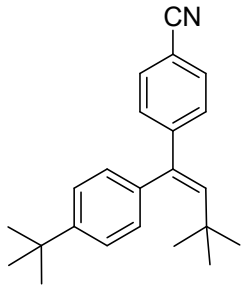


(*E*)-4-(1-(4-Ethylphenyl)-3,3-dimethylbut-1-en-1-yl)benzonitrile (2): White solid (53 mg, 73%); mp 75−76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8 Hz, 2H), 7.26 (d, *J* = 8 Hz, 2H), 7.18 (d, *J* = 8 Hz, 2H), 7.05 (d, *J* = 8 Hz, 2H), 6.16 (s, 1H), 2.69 (q, *J* = 8 Hz, 2H), 1.27 (t, *J* = 8 Hz, 3H), 0.97 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.9, 143.5, 143.3, 138.1, 136.56, 131.9, 130.2, 127.6, 127.5, 119.3, 109.9, 34.4, 31.2, 28.7, 15.6; IR (ATR) $\tilde{\nu}$: 2958, 2924, 2855, 2225, 1600, 1461, 1247, 1113, 832 cm^{-1}; HRMS (ESI^+): m/z $[M + Na]^+$ calcd for $C_{21}H_{23}NNa$, 312.1723; found, 312.1722.

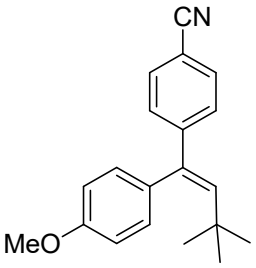
(*E*)-4-(1-(4-Butylphenyl)-3,3-dimethylbut-1-en-1-yl)benzonitrile (3): Colourless liquid (62 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8 Hz, 2H), 7.27 (d, *J* = 8 Hz, 2H), 7.17 (d, *J* = 8 Hz, 2H), 7.05 (d, *J* = 8 Hz, 2H), 6.17 (s, 1H), 2.65 (t, *J* = 8 Hz, 2H), 1.68-1.60 (m, 2H), 1.43-1.34 (m, 2H), 0.97 (s, 9H), 0.96 (t, *J* = 8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.8, 143.2, 142.1, 138.1, 136.5, 131.9, 130.2, 128.2, 127.5, 119.3, 109.9, 35.5, 34.4, 33.7, 31.2, 22.5, 14.1; IR (ATR) $\tilde{\nu}$: 2958, 2927, 2859, 2226, 1600, 1498, 1364, 1261, 835 cm^{-1}; HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{23}H_{28}N$, 318.2216; found, 318.2211.



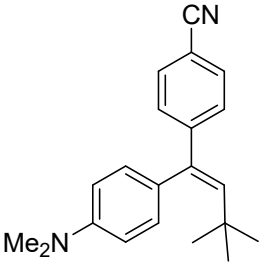
(*E*)-4-(3,3-Dimethyl-1-(4-pentylphenyl)but-1-en-1-yl)benzonitrile (4): Colourless liquid (71 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8 Hz, 2H), 7.27 (d, *J* = 8 Hz, 2H), 7.17 (d, *J* = 8 Hz, 2H), 7.05 (d, *J* = 8 Hz, 2H), 6.17 (s, 1H), 2.64 (t, *J* = 8 Hz, 2H), 1.66 (pent, *J* = 8 Hz, 2H), 1.39-1.34 (m, 4H), 0.97 (s, 9H), 0.91 (t, *J* = 8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.8, 143.2, 142.2, 138.1, 136.5, 131.9, 130.1, 128.2, 127.5, 119.3, 109.9, 35.8, 34.4, 31.6, 31.2, 29.8, 22.6, 14.2; IR (ATR) $\tilde{\nu}$: 2955, 2925, 2855, 2225, 1600, 1461, 1409, 1247, 1114, 833 cm^{-1}; HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{24}H_{29}NNa$, 354.2192; found, 354.2192.



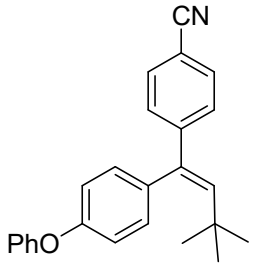
(*E*)-4-(1-(4-(*tert*-butyl)phenyl)-3,3-dimethylbut-1-en-1-yl)benzonitrile (5): Colourless liquid (72 mg, 91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8 Hz, 2H), 7.36 (d, *J* = 8 Hz, 2H), 7.27 (d, *J* = 8 Hz, 2H), 7.06 (d, *J* = 8 Hz, 2H), 6.17 (s, 1H), 1.35 (s, 9H), 0.96 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.4, 148.8, 143.3, 138.1, 136.2, 131.9, 129.9, 127.5, 125.0, 119.3, 109.9, 34.7, 34.4, 31.5, 31.2; IR (ATR) $\tilde{\nu}$: 2958, 2927, 2862, 2224, 1610, 1467, 1244, 1031, 835 cm^{-1}; HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{23}H_{28}N$, 318.2216; found, 318.2214.



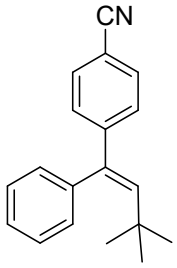
(*Z*)-4-(1-(4-Methoxyphenyl)-3,3-dimethylbut-1-en-1-yl)benzonitrile (6): White solid (56 mg, 77%); mp 79−80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8 Hz, 2H), 7.26 (d, *J* = 8 Hz, 2H), 7.05 (d, *J* = 8 Hz, 2H), 6.90 (d, *J* = 8 Hz, 2H), 6.17 (s, 1H), 3.84(s, 3H), 0.97 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.0, 149.0, 143.5, 137.7, 131.9, 131.6, 131.4, 127.5, 119.3, 113.6, 109.9, 55.3, 34.4, 31.2; IR (ATR) $\tilde{\nu}$: 2955, 2927, 2863, 2225, 1604, 1508, 1461, 1285, 1241, 1173, 1032, 830 cm^{-1}; HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{20}H_{22}NO$, 292.1696; found, 292.1691.



(*Z*)-4-(1-(4-(Dimethylamino)phenyl)-3,3-dimethylbut-1-en-1-yl)benzonitrile (7): White solid (30 mg, 40%); mp 137−139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8 Hz, 2H), 7.28 (d, *J* = 8 Hz, 2H), 6.98 (d, *J* = 8 Hz, 2H), 6.71 (d, *J* = 8 Hz, 2H), 6.13 (s, 1H), 2.99 (s, 6H), 0.99 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.6, 143.2, 138.3, 131.9, 131.1, 127.6, 119.4, 112.3, 112.2, 112.0, 109.7, 40.8, 34.4, 31.3; IR (ATR) $\tilde{\nu}$: 2953, 2922, 2853, 2224, 1607, 1519, 1351, 1196, 835 cm^{-1}; HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{21}H_{25}N_2$, 305.2012; found, 305.2012.

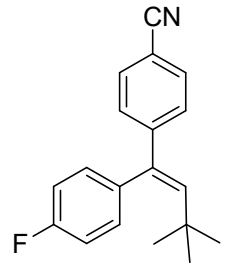


(*Z*)-4-(3,3-Dimethyl-1-(4-phenoxyphenyl)but-1-en-1-yl)benzonitrile (8): Colourless liquid (58 mg, 66%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = Hz, 2H), 7.37 (t, *J* = 8 Hz, 2H), 7.28 (t, *J* = 8 Hz, 2H), 7.15-7.10 (m, 3H), 7.06 (d, *J* = 8 Hz, 2 H), 7.01 (d, *J* = Hz, 2H), 6.19 (s, 1H), 1.0 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.9, 156.8, 148.6, 143.7, 137.4, 134.1, 131.9, 131.7, 129.9, 127.5, 123.6, 119.2, 119.2, 118.4, 110.1, 34.5, 31.2; IR (ATR) $\tilde{\nu}$: 2954, 2923, 2858, 2225, 1609, 1462, 1241, 1016, 837 cm^{-1}; HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{25}H_{24}NO$, 354.1852; found, 354.1849.

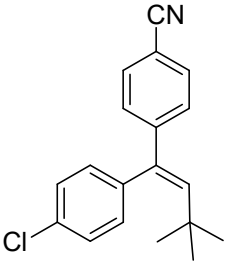


(*E*)-4-(3,3-Dimethyl-1-phenylbut-1-en-1-yl)benzonitrile (9): White solid (64 mg, 98%); mp 93−94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8 Hz, 2H), 7.34 (t, *J* = 4 Hz, 3H), 7.25 (d, *J* = 4 Hz, 2H), 7.14 (d, *J* = 8 Hz, 2H), 6.17 (s, 1H), 0.95 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.6, 143.3, 139.4,

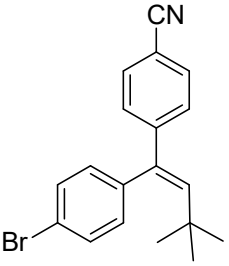
138.0, 131.9, 130.34, 128.2, 127.45, 127.4, 119.3, 110.0, 34.4, 31.2; IR (ATR) $\tilde{\nu}$: 2958, 2923, 2854, 2222, 1603, 1358, 1180, 1070, 836 cm^{-1}; HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{19}H_{20}N$, 262.1590; found, 262.1590.



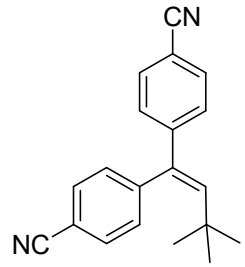
(*Z*)-4-(1-(4-Fluorophenyl)-3,3-dimethylbut-1-en-1-yl)benzonitrile (10): White solid (62 mg, 89%); mp 101−102 °C; ^{19}F NMR (377 MHz, $CDCl_3$) δ -114.67 − -114.74 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8 Hz, 2H), 7.24 (d, *J* = 8 Hz, 2H), 7.14-7.04 (m, 4H), 6.20 (s, 1H), 0.97 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.3 (d, *J* = 246 Hz), 148.3, 143.9, 136.9, 135.3 (d, *J* = 4 Hz) 132.0, 131.9 (d, *J* = 8 Hz), 127.4, 119.2, 115.3 (d, *J* = 22 Hz), 110.2, 34.5, 31.2; IR (ATR) $\tilde{\nu}$: 2958, 2926, 2862, 2227, 1601, 1503, 1220, 1089, 833 cm^{-1}; HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{19}H_{19}FN$, 280.1496; found, 280.1494.



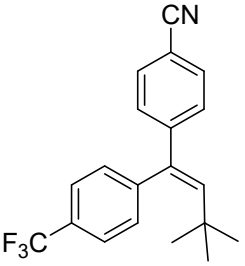
(*Z*)-4-(1-(4-Chlorophenyl)-3,3-dimethylbut-1-en-1-yl)benzonitrile (11): White solid (52 mg, 71%); mp 81−83 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8 Hz, 2H), 7.35 (d, *J* = 8 Hz, 2H), 7.23 (d, *J* = 8 Hz, 2H), 7.10 (d, *J* = 8 Hz, 2H), 6.20 (s, 1H), 0.97 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.1, 144.0, 137.9, 136.8, 133.6, 132.1, 131.7, 128.5, 127.5, 119.1, 110.3, 34.5, 31.2; IR (ATR) $\tilde{\nu}$: 2956, 2923, 2854, 2226, 1602, 1487, 1361, 1092, 1016, 828 cm^{-1}; HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{19}H_{19}ClN$, 296.1201; found, 296.1200.



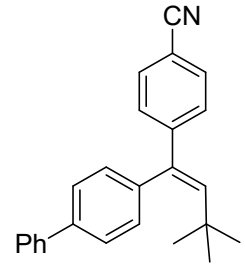
(*Z*)-4-(1-(4-Bromophenyl)-3,3-dimethylbut-1-en-1-yl)benzonitrile (12): White solid (43 mg, 51%); mp 39−40 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 4 Hz, 2H), 7.50 (d, *J* = 4 Hz, 2H), 7.23 (d, *J* = 8 Hz, 2H), 7.04 (d, *J* = 8 Hz, 2H), 6.20 (s, 1H), 0.97 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.9, 143.9, 138.4, 137.4, 136.8, 132.1, 131.5, 127.5, 121.7, 119.1, 110.3, 34.5, 31.2; IR (ATR) $\tilde{\nu}$: 2953, 2921, 2852, 2226, 1602, 1461, 1247, 1071, 1012, 835 cm^{-1}; HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{19}H_{19}BrN$, 340.0695; found, 340.0694.



4,4'-(3,3-Dimethylbut-1-ene-1,1-diyl)dibenzonitrile (13): White solid (31 mg, 44%); mp 88−89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8 Hz, 2H), 7.53 (d, *J* = 8 Hz, 2H), 7.30 (d, *J* = 8 Hz, 2H), 7.19 (d, *J* = 8 Hz, 2H), 6.23 (s, 1H), 0.97 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.2, 144.8, 144.5, 136.3, 132.2, 132.1, 131.2, 127.5, 118.9, 118.7, 111.7, 110.7, 34.6, 31.2; IR (ATR) $\tilde{\nu}$: 2958, 2924, 2854, 2227, 1599, 1503, 1410, 1362, 836 cm^{-1}; HRMS (ESI^{+}): m/z [M + H]$^{+}$ calcd for $C_{20}H_{19}N_2$, 287.1542; found, 287.1543.

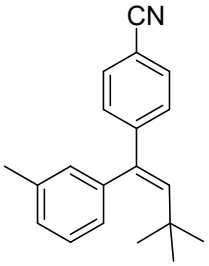


(*Z*)-4-(3,3-Dimethyl-1-(4-(trifluoromethyl)phenyl)but-1-en-1-yl)benzonitrile (14): White solid (64 mg, 78%); mp 99−100 °C; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.48 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8 Hz, 2H), 7.52 (d, *J* = 8 Hz, 2H), 7.30 (d, *J* = 8 Hz, 2H), 7.22 (d, *J* = 8 Hz, 2H), 6.24 (s, 1H), 0.97 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.6, 144.2, 143.4, 136.7, 132.1, 130.8, 130.1, 129.7, 127.5, 125.2 (q, *J* = 4 Hz), 119.1, 110.5, 34.5, 31.2; IR (ATR) $\tilde{\nu}$: 2960, 2927, 2864, 2227, 1599, 1405, 1323, 1170, 1065, 837 cm^{-1}; HRMS (ESI^{+}): m/z [M + H]$^{+}$ calcd for $C_{20}H_{19}F_3N$, 330.1464; found, 330.1462.



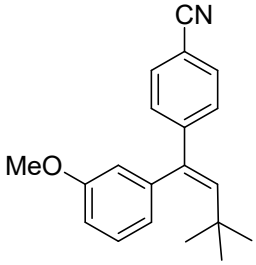
(*E*)-4-(1-([1,1'-Biphenyl]-4-yl)-3,3-dimethylbut-1-en-1-yl)benzonitrile (15): White solid (55 mg, 65%); mp 106−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8 Hz, 2H), 7.61 (d, *J* = 8 Hz, 2H), 7.52 (d, *J* = 8 Hz, 2H), 7.46 (t, *J* = 8 Hz, 2H), 7.36 (t, *J* = 8 Hz, 1H), 7.31 (d, *J* = 8 Hz, 2H), 7.23 (d, *J* = 8 Hz, 2H), 6.21 (s, 1H), 1.01 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.6, 143.6, 140.6, 140.2, 138.5, 137.7, 132.0, 131.2, 130.8, 128.9, 127.6, 127.1, 126.8, 119.3, 110.1, 34.5, 31.3; IR (ATR) $\tilde{\nu}$: 2956, 2925, 2862, 2225, 1599, 1409, 1350, 833 cm^{-1}; HRMS (ESI^{+}): m/z [M + H]$^{+}$ calcd for $C_{25}H_{24}N$, 338.1903; found, 338.1903.

(*Z*)-4-(3,3-Dimethyl-1-(*m*-tolyl)but-1-en-1-yl)benzonitrile (16):



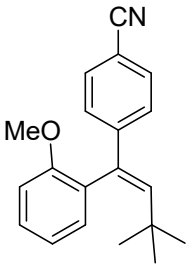
Colourless liquid (47 mg, 68%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8 Hz, 2H), 7.28 (d, *J* = 8 Hz, 2H), 7.24 (s, 1H), 7.15 (d, *J* = 8 Hz, 1H), 6.97 (d, *J* = 8 HZ, 2H), 6.17 (s, 1H), 2.37 (s, 3H), 0.99 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.7, 143.1, 139.3, 138.2, 137.8, 131.9, 130.9, 128.1, 128.0, 127.5, 127.5, 119.3, 109.9, 34.4, 31.2, 21.6; IR (ATR) $\tilde{\nu}$: 2957, 2925, 2863, 2225, 1599, 1462, 1360, 1248, 834 cm^{-1}; HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{20}H_{22}N$, 276.1746; found, 276.1747.

(*Z*)-4-(1-(3-Methoxyphenyl)-3,3-dimethylbut-1-en-1-yl)benzonitrile (17):



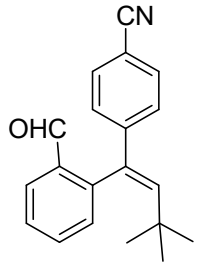
Colourless liquid (55 mg, 76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8 Hz, 2H), 7.30-7.27 (m, 3H), 6.88 (dd, *J* = 4 Hz, 1H), 6.76 (d, *J* = 8 Hz, 1H), 6.70 (s, 1H), 6.17 (s, 1H), 3.80 (s, 3H), 0.99 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.4, 148.3, 143.1, 140.7, 137.8, 131.9, 129.2, 127.4, 122.9, 119.2, 116.1, 112.7, 110.0, 55.3, 34.4, 31.1; IR (ATR) $\tilde{\nu}$: 2956, 2927, 2854, 2225, 1595, 1483, 1284, 1228, 1046, 834 cm^{-1}; HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{20}H_{21}NONa$, 314.1515; found, 314.1515.

(*Z*)-4-(1-(2-Methoxyphenyl)-3,3-dimethylbut-1-en-1-yl)benzonitrile (18):



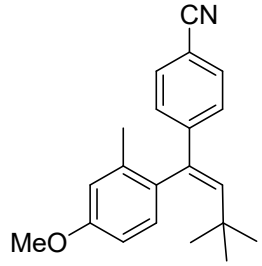
White solid (61 mg, 84%); mp 46−47 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8 Hz, 2H), 7.34 (t, *J* = 8 Hz, 1H), 7.28 (d, *J* = 8 Hz, 2H), 7.09 (dd, *J* = 4 Hz, 1H), 6.96 (t, *J* = 4 Hz, 1H), 6.91 (d, *J* = 8 Hz, 1H), 6.21 (s, 1H), 0.95 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.2, 148.2, 143.7, 134.3, 131.9, 131.9, 129.3, 128.3, 127.0, 120.3, 119.5, 110.9, 109.8, 55.4, 34.3, 30.5; IR (ATR) $\tilde{\nu}$: 2955, 2922, 2853, 2223, 1601, 1490, 1242, 1109, 1027, 837 cm^{-1}; HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{20}H_{22}NO$, 292.1696; found, 292.1695.

(*Z*)-4-(1-(2-Formylphenyl)-3,3-dimethylbut-1-en-1-yl)benzonitrile (19):

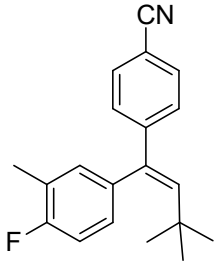


Colourless liquid (35 mg, 49%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.73 (d, *J* = 8 Hz, 1H), 7.39 (t, *J* = 8 Hz, 1H), 7.29-7.26 (m, 3H), 7.05 (d, *J* = 8 Hz, 1H), 6.99 (d, *J* = 8 Hz, 2H), 6.16 (s, 1H), 0.67 (s, 9H); ^{13}C{^{1}H} NMR

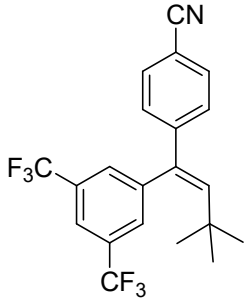
(100 MHz, $CDCl_3$) δ 191.8, 147.3, 145.2, 142.3, 134.4, 133.9, 133.5, 132.3, 132.1, 128.7, 128.5, 127.1, 118.9, 110.7, 34.7, 30.8; IR (ATR) $\tilde{\nu}$: 2956, 2922, 2853, 2226, 1694, 1594, 1463, 1362, 1197, 837 cm^{-1}; HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{20}H_{20}NO$, 290.1539; found, 290.1539.



(*Z*)-4-(1-(4-Methoxy-2-methylphenyl)-3,3-dimethylbut-1-en-1-yl)benzonitrile (20): Colourless liquid (55 mg, 72%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8 Hz, 2H), 7.26 (d, *J* = 8 Hz, 2H), 7.05 (d, *J* = 8 Hz, 1H), 6.78-6.74 (m, 2H), 6.22 (s, 1H), 3.82 (s, 3H), 1.99 (s, 3H), 0.95 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.3, 148.0, 143.4, 137.9, 136.6, 132.1, 131.9, 130.8, 127.0, 119.3, 115.7, 110.6, 109.9, 55.2, 34.5, 30.6, 20.3; IR (ATR) $\tilde{\nu}$: 2956, 2925, 2861, 2225, 1603, 1500, 1292, 1242, 1048, 837 cm^{-1}; HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{21}H_{24}NO$, 306.1852; found, 306.1851.

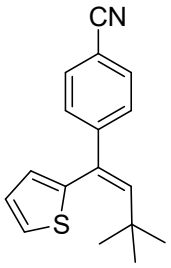


(*Z*)-4-(1-(4-Fluoro-3-methylphenyl)-3,3-dimethylbut-1-en-1-yl)benzonitrile (21): White solid (55 mg, 75%); mp 88−89 °C; ^{19}F NMR (377 MHz, $CDCl_3$) δ -119.21 − -119.27 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8 Hz, 2H), 7.25 (d, *J* = 8 Hz, 2H), 7.02-6.92 (m, 3H), 6.16 (s, 1H), 2.28 (s, 3H), 0.97 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.8 (d, *J* = 276 Hz), 148.5, 143.6, 137.2, 135.0 (d, *J* = 4 Hz), 133.2 (d, *J* = 5 Hz), 132.0, 129.3 (d, *J* = 8 Hz), 127.4, 124.8 (d, *J* = 17 Hz), 119.2, 114.8 (d, *J* = 22 Hz), 110.1, 34.4, 31.2, 14.8, 14.7 cm^{-1}; IR (ATR) $\tilde{\nu}$: 2960, 2927, 2865, 2227, 1601, 1454, 1237, 1029, 829 cm^{-1}; HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{20}H_{21}FN$, 294.1653; found, 294.1652.

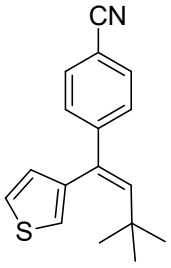


(*Z*)-4-(1-(3,5-Bis(trifluoromethyl)phenyl)-3,3-dimethylbut-1-en-1-yl)benzonitrile (22): White solid (58 mg, 59%); mp 97−98 °C; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.88 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.64 (s, 2H), 7.57 (d, *J* = 12 Hz, 2H), 7.20 (d, *J* = 8 Hz, 2H), 6.30 (s, 1H), 0.96 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.7, 145.7, 141.7, 135.1, 131.8 (q, *J* = 36 Hz), 130.5, 127.5, 124.6, 121.9, 121.7 (q, *J* = 4 Hz), 118.8, 111.1, 34.6, 31.2; IR (ATR) $\tilde{\nu}$: 2963, 2929, 2864, 2228,

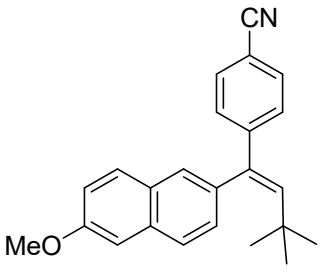
1504, 1345, 1276, 1130, 827 cm^{-1}; HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{21}H_{18}F_6N$, 398.1338; found, 398.1338.



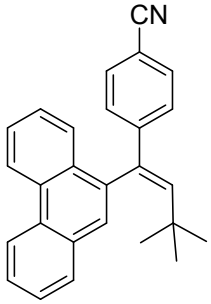
(*Z*)-4-(3,3-Dimethyl-1-(thiophen-2-yl)but-1-en-1-yl)benzonitrile (23): White solid (42 mg, 63%); mp 87−88 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8 Hz, 2H), 7.37 (dd, *J* = 4 Hz, 1H), 7.32 (d, *J* = 8 Hz, 2H), 7.05 (dd, *J* = 4 Hz, 1H), 6.91 (dd, *J* = 4 Hz, 1H), 6.29 (s, 1H), 1.06 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.3, 147.5, 139.6, 132.1, 130.8, 128.8, 127.3, 126.8, 126.4, 119.2, 110.4, 34.7, 30.8; IR (ATR) $\tilde{\nu}$: 2958, 2924, 2866, 2225, 1602, 1502, 1461, 1354, 1247, 1034, 836 cm^{-1}; HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{17}H_{18}NS$, 268.1154; found, 268.1155.



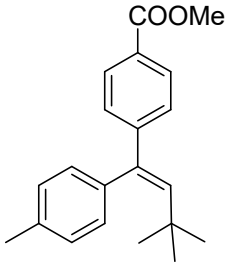
(*Z*)-4-(3,3-Dimethyl-1-(thiophen-3-yl)but-1-en-1-yl)benzonitrile (24): Yellow solid (64 mg, 96%); mp 72−74 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8 Hz, 2H), 7.34 (dd, *J* = 4 Hz, 1H), 7.27 (d, *J* = 8 Hz, 2H), 7.08 (dd, *J* = 4 Hz, 1H), 6.86 (d, *J* = 8 Hz, 1H), 6.23 (s, 1H), 1.00 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.1, 144.9, 138.9, 133.1, 132.0, 129.8, 127.2, 125.5, 124.2, 119.3, 110.2, 34.3, 30.9; IR (ATR) $\tilde{\nu}$: 2954, 2922, 2853, 2220, 1500, 1418, 1189, 1077, 853 cm^{-1}; HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{17}H_{18}NS$, 268.1154; found, 268.1154.



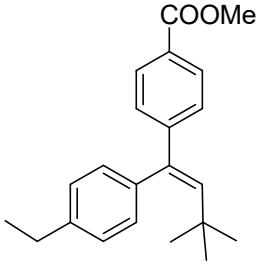
(*Z*)-4-(1-(6-Methoxynaphthalen-2-yl)-3,3-dimethylbut-1-en-1-yl)benzonitrile (25): White solid (68 mg, 80%); mp 152−153 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 4 Hz, 2H), 7.57 (s, 1H), 7.49 (d, *J* = 8 Hz, 2H), 7.29 (d, *J* = 8 Hz, 2H), 7.21 (dd, *J* = 4 Hz, 2H), 7.17 (s, 2H), 6.26 (s, 1H), 3.94 (s, 3H), 0.98 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.1, 148.7, 143.7, 138.1, 134.6, 133.8, 131.9, 129.6, 129.1, 129.0, 128.6, 127.6, 126.7, 119.3, 119.3, 110.1, 105.8, 55.5, 34.5, 31.3; IR (ATR) $\tilde{\nu}$: 2954, 2930, 2862, 2223, 1630, 1597, 1484, 1268, 1211, 1032, 836 cm^{-1}; HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{24}H_{23}NO$, 342.1852; found, 342.1850.



(*Z*)-4-(3,3-Dimethyl-1-(phenanthren-9-yl)but-1-en-1-yl)benzonitrile (26): White solid (30 mg, 33%); mp 148−149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8 Hz, 2H), 7.90 (d, *J* = 8 Hz, 1H), 7.76 (d, *J* = 8 Hz, 1H), 7.68-7.61 (m, 4H), 7.51-7.46 (m, 3H), 7.40 (d, *J* = 12 Hz, 2H), 6.53 (s, 1H), 0.95 (s 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.8, 145.2, 135.8, 135.2, 132.2, 131.6, 131.3, 130.6, 130.4, 129.0, 128.8, 127.2, 127.1, 127.1, 127.0, 126.9, 126.8, 123.1, 122.8, 119.2, 110.3, 34.8, 30.7; IR (ATR) $\tilde{\nu}$: 2955, 2923, 2854, 2225, 1601, 1423, 1262, 835 cm^{-1}; HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{27}H_{24}N$, 362.1903; found, 362.1902.

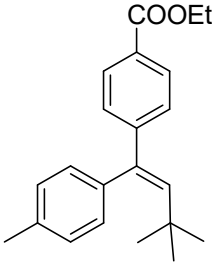


(*E*)-Methyl 4-(3,3-dimethyl-1-(*p*-tolyl)but-1-en-1-yl)benzoate (27): White solid (75.4 mg, 98%); mp 50−52 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 12 Hz, 2H), 7.23 (d, *J* = 8 Hz, 2H), 7.16 (d, *J* = 8 Hz, 2H), 7.05 (d, *J* = 8 Hz, 2H), 6.16 (s, 1H), 3.88 (s, 3H), 2.38 (s, 3H), 0.97 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.2, 148.9, 142.3, 138.6, 137.1, 136.8, 130.3, 129.4, 128.7, 128.1, 126.9, 52.1, 34.3, 31.3, 21.4; IR (ATR) $\tilde{\nu}$: 2951, 2922, 2853, 1723, 1604, 1276, 1104, 852 cm^{-1}; HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{21}H_{24}O_2Na$, 331.1669; found, 331.1649.



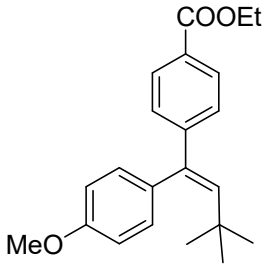
(*E*)-Methyl 4-(1-(4-ethylphenyl)-3,3-dimethylbut-1-en-1-yl)benzoate (28): Colourless semi-solid (66 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89(d, *J* = 8 Hz, 2H), 7.25 (d, *J* = 8 Hz, 2H), 7.18 (d, *J* = 8 Hz, 2H), 7.08 (d, *J* = 8 Hz, 2H), 6.18 (s, 1H), 3.88 (s, 3H), 2.69 (q, *J* = 8 Hz, 2H), 1.28 (t, *J* = 8 Hz, 3H), 0.98 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.2, 148.9, 143.1, 142.2, 138.7, 137.2, 130.3, 129.4, 128.1, 127.5, 126.9, 52.1, 34.3, 31.3, 28.7, 15.6; IR (ATR) $\tilde{\nu}$: 2957, 2928, 2865, 1721, 1604, 1434, 1275, 1182, 1103, 1017, 852 cm^{-1}; HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{22}H_{27}O_2$, 323.2006; found, 323.2005.

(*E*)-Ethyl 4-(3,3-dimethyl-1-(*p*-tolyl)but-1-en-1-yl)benzoate (29): Colourless semi-solid (44 mg, 55%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8 Hz, 2H), 7.24 (d, *J* = 8 Hz, 2H), 7.16 (d, *J* = 8 Hz, 2H), 7.06 (d, *J* = 8 Hz, 2H), 6.17 (s, 1H), 4.35 (q, *J* = 8 Hz, 2H), 2.39 (s, 3H), 1.37 (t, *J* = 8 Hz, 3H), 0.98 (s, 9H);

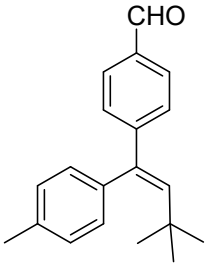


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.7, 148.8, 142.1, 138.6, 137.1, 136.7, 130.3, 129.4, 128.7, 128.5, 126.8, 60.9, 34.3, 31.3, 21.4, 14.5; IR (ATR) $\tilde{\nu}$: 2955, 2925, 2864, 1715, 1603, 1364, 1271, 1101, 1020, 852 cm^{-1}; HRMS (ESI^+): m/z $[M + Na]^+$ calcd for $C_{22}H_{26}O_2Na$, 345.1825; found, 345.1825.

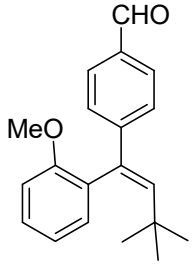
(*Z*)-Ethyl 4-(1-(4-methoxyphenyl)-3,3-dimethylbut-1-en-1-yl)benzoate (30): White solid



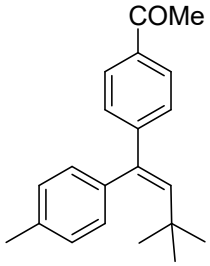
(49 mg, 58%); mp 63−64 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8 Hz, 2H), 7.23 (d, *J* = 8 Hz, 2H), 7.07 (d, *J* = 8 Hz, 2H), 6.89 (d, *J* = 8 Hz, 2H), 6.16 (s, 1H), 4.35 (q, *J* = 8 Hz, 2H), 3.84 (s, 3H), 1.37 (t, *J* = 8 Hz, 3H), 0.98 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.7, 158.8, 149.0, 142.4, 138.3, 132.3, 131.4, 129.4, 128.5, 126.8, 113.4, 60.9, 55.3, 34.3, 31.3, 14.5; IR (ATR) $\tilde{\nu}$: 2956, 2927, 2866, 1715, 1606, 1511, 1275, 1244, 1104, 1034 cm^{-1}; HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{22}H_{27}O_3$, 339.1955; found, 339.1954.



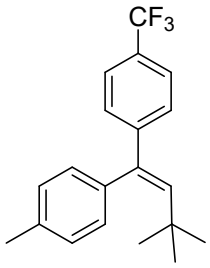
(*E*)-4-(3,3-Dimethyl-1-(*p*-tolyl)but-1-en-1-yl)benzaldehyde (31): White solid (41 mg, 59%); mp 104−105 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.73 (d, *J* = 8 Hz, 2H), 7.33 (d, *J* = 8 Hz, 2H), 7.17 (d, *J* = 8 Hz, 2H), 7.06 (d, *J* = 8 Hz, 2H), 6.21 (s, 1H), 2.39 (s, 3H), 0.98 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 192.1, 150.5, 143.2, 138.6, 136.9, 136.8, 134.7, 130.3, 129.7, 128.8, 127.5, 34.4, 31.3, 21.4; IR (ATR) $\tilde{\nu}$: 2955, 2924, 2862, 1698, 1597, 1511, 1360, 1213, 1170, 827 cm^{-1}; HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{20}H_{23}O$, 279.1743; found, 279.1744.



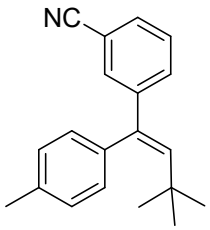
(*Z*)-4-(1-(2-Methoxyphenyl)-3,3-dimethylbut-1-en-1-yl)benzaldehyde (32): White solid (39 mg, 53%); mp 63−64 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.73 (d, *J* = 12 Hz, 2H), 7.37-7.32 (m, 3H), 7.11 (d, *J* = 8 Hz, 1H), 6.97 (t, *J* = 8 Hz, 1H), 6.92 (d, *J* = 8 Hz, 1H), 6.27 (s, 1H), 3.72 (s, 3H), 0.96 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 192.1, 157.3, 149.9, 143.6, 134.7, 134.7, 131.9, 129.7, 129.1, 128.7, 127.0, 120.3, 110.9, 55.4, 34.4, 30.6; IR (ATR) $\tilde{\nu}$: 2954, 2927, 2863, 1697, 1599, 1489, 1242, 1026, 827 cm^{-1}; HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{20}H_{23}O_2$, 295.1693; found, 295.1692.



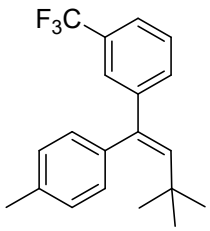
(*E*)-1-(4-(3,3-Dimethyl-1-(*p*-tolyl)but-1-en-1-yl)phenyl)ethanone (33): White solid (42 mg, 58%); mp 84−85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8 Hz, 2H), 7.26 (d, *J* = 8 Hz, 2H), 7.16 (d, *J* = 8 Hz, 2H), 7.05 (d, *J* = 8 Hz, 2H), 6.18 (s, 1H), 2.55 (s, 3H), 2.39 (s, 3H), 0.98 (s, 9H): ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.9, 149.1, 142.5, 138.5, 137.0, 136.8, 135.2, 130.3, 128.8, 128.3, 127.1, 34.3, 31.3, 26.7, 21.4; IR (ATR) $\tilde{\nu}$: 2954, 2923, 2857, 1681, 1598, 1357, 1266, 821 cm^{-1}; HRMS (ESI^{+}): m/z [M + H]$^{+}$ calcd for $C_{21}H_{25}O$, 293.1900; found, 293.1897.



(*E*)-1-(3,3-Dimethyl-1-(4-(trifluoromethyl)phenyl)but-1-en-1-yl)-4-methylbenzene (34): Colourless semi-solid (42 mg, 53%); ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.36 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8 Hz, 2H), 7.28 (d, *J* = 8 Hz, 2H), 7.16 (d, *J* = 8 Hz, 2H), 7.06 (d, *J* = 8 Hz, 2H), 6.13 (s, 1H), 2.39 (s, 3H), 0.98 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.9, 142.2, 138.3, 137.0, 136.9, 130.2, 128.8, 127.2, 125.8, 125.0 (q, *J* = 4 Hz) 123.1, 34.3, 31.3, 21.4; IR (ATR) $\tilde{\nu}$: 2953, 2922, 2865, 1615, 1462, 1323, 1164, 1125, 1058, 838 cm^{-1}; HRMS (ESI^{+}): m/z [M + H]$^{+}$ calcd for $C_{20}H_{22}F_3$, 319.1668; found, 319.1666.



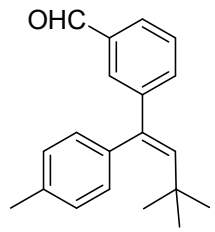
(*E*)-3-(3,3-Dimethyl-1-(*p*-tolyl)but-1-en-1-yl)benzonitrile (35): White solid (56 mg, 82%); mp 56−57 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.41 (m, 3H), 7.31 (t, *J* = 8 Hz, 1H), 7.17 (d, *J* = 8 Hz, 2H), 7.03 (d, *J* = 8 Hz, 2H), 6.09 (s, 1H), 2.39 (s, 3H), 0.97 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.6, 142.3, 137.5, 137.1, 136.4, 131.2, 130.7, 130.2, 130.0, 128.9, 128.8, 119.3, 112.2, 34.3, 31.3, 21.4; IR (ATR) $\tilde{\nu}$: 2955, 2923, 2854, 2229, 1597, 1462, 1360, 1255, 831 cm^{-1}; HRMS (ESI^{+}): m/z [M + H]$^{+}$ calcd for $C_{20}H_{22}N$, 276.1747; found, 276.1741.



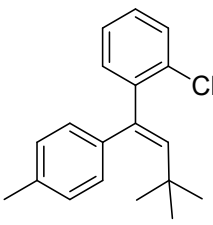
(*E*)-1-(3,3-Dimethyl-1-(*p*-tolyl)but-1-en-1-yl)-3-(trifluoromethyl)benzene (36): Colourless liquid (39 mg, 49%); ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.50 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H),

7.43-7.41 (m, 1H), 7.32-7.30 (m, 2H), 7.17 (d, J = 8 Hz, 2H), 7.07 (d, J = 8 Hz, 2H), 6.10 (s, 1H), 2.39 (s, 3H), 0.99 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.3, 141.8, 138.3, 136.9, 136.8, 130.5, 130.2, 128.8, 128.5, 125.7, 123.4 (q, J = 4 Hz), 123.2 (q, J = 4 Hz), 123.0, 34.2, 31.3, 21.4; IR (ATR) $\tilde{\nu}$: 2956, 2925, 2858, 1511, 1474, 1327, 1164, 1124, 1074 cm^{-1}; HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{20}H_{22}F_3$, 319.1668; found, 319.1666.

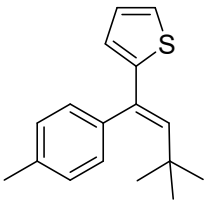
(*E*)-3-(3,3-Dimethyl-1-(*p*-tolyl)but-1-en-1-yl)benzaldehyde (37): Colorless semi-solid (39 mg, 56%); ^1H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.74-7.68 (m, 2H), 7.43-7.35 (m, 2H), 7.17 (d, J = 8 Hz, 2H), 7.07 (d, J = 8 Hz, 2H), 6.14 (s, 1H), 2.39 (s, 3H), 0.99 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 192.7, 145.5, 141.7, 138.2, 137.0, 136.8, 136.4, 133.1, 130.2, 128.8, 128.7, 128.1, 127.8, 34.2, 31.4, 21.4; IR (ATR) $\tilde{\nu}$: 2953, 2922, 2853, 1703, 1577, 1461, 1363, 1199, 793 cm^{-1}; HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{20}H_{23}O$, 279.1743; found, 279.1742.



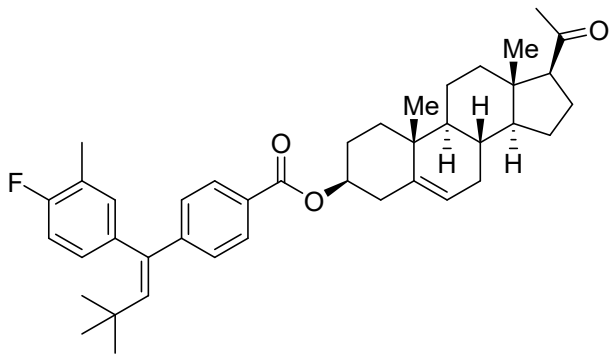
(*E*)-2-(3,3-Dimethyl-1-(*p*-tolyl)but-1-en-1-yl)benzonitrile (38): Colourless semi-solid (38.5 mg, 56%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8 Hz, 1H), 7.38 (t, J = 8 Hz, 1H), 7.27-7.23 (m, 1H), 7.17-7.12 (m, 5H), 5.98 (s, 1H), 2.35 (s, 3H), 1.04 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 149.1, 145.7, 137.1, 136.2, 133.5, 132.1, 129.9, 129.9, 128.7, 126.8, 119.1, 111.4, 31.0, 29.8, 21.4; IR (ATR) $\tilde{\nu}$: 2953, 2921, 2852, 2223, 1595, 1510, 1460, 1376, 1109, 822 cm^{-1}; HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{20}H_{22}N$, 276.1747; found, 276.1742.



(*E*)-2-(3,3-Dimethyl-1-(*p*-tolyl)but-1-en-1-yl)thiophene (39): Colourless liquid (19 mg, 30%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.18-7.12 (m 4H), 7.08 (d, J = 8 Hz, 1H), 6.83 (dd, J = 4 Hz, 1H), 6.43 (d, J = 4 Hz, 1H), 6.19 (s, 1H), 2.39 (s, 3H), 0.95 (s, 9 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 149.6, 138.4, 136.9, 136.8, 133.6, 130.1, 128.6, 127.2, 124.6, 123.5, 34.1, 31.4, 21.4; IR (ATR) $\tilde{\nu}$: 2955, 2923, 2856, 1728, 1509, 1461, 1360, 1272, 1217, 822, 691 cm^{-1}; HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{17}H_{21}S$, 257.1358; found, 257.1359.

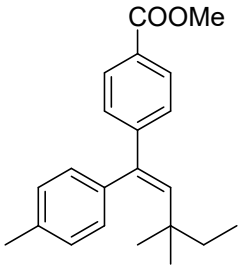


(3S,8S,9S,10R,13S,14S,17S)-17-Acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-((Z)-1-(4-fluoro-3-methylphenyl)-3,3-dimethylbut-1-en-1-yl)benzoate (40): White solid



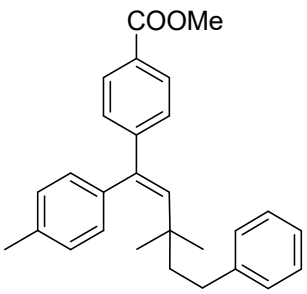
(98 mg, 64%); mp 163–164 °C; ^{19}F NMR (377 MHz, $CDCl_3$) δ -119.83−-119.89 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8 Hz, 2H), 7.20 (d, *J* = 8 Hz, 2H), 6.98-6.95 (m, 3H), 6.15 (s, 1H), 5.40 (d, *J* = 4 Hz, 1H), 4.87-4.79 (m, 1H), 2.54 (t, *J* = 8 Hz, 1H), 2.48-2.43 (m, 2H), 2.27 (s, 3H), 2.13 (s, 3H), 2.07-1.99 (m, 4H), 1.69-1.63 (m, 6H), 1.52-1.46 (m, 3H), 1.25-1.18 (m, 4H), 1.06 (s, 3H), 0.97 (s, 9H), 0.64 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 209.7, 166.0, 160.7 (d, *J* = 243 Hz), 148.5, 142.5, 139.4, 137.8, 135.7 (d, *J* = 6 Hz), 130.3 (d, *J* = 5 Hz), 129.7, 129.5, 129.3 (d, *J* = 8 Hz), 128.9, 126.8, 122.5, 114.5 (d, *J* = 22 Hz), 74.4, 63.8, 57.0, 50.0, 44.1, 38.9, 38.3, 37.2, 36.8, 34.3, 31.9 (d, *J* = 4 Hz), 31.7, 31.3, 28.0, 24.6, 22.9, 21.2, 19.5, 14.7, 14.6, 13.4; IR (ATR) $\tilde{\nu}$: 2945, 2902, 1704, 1603, 1498, 1464, 1356, 1271, 1114, 1015, cm^{-1}; HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{41}H_{52}FO_3$, 611.3895; found, 611.3897.

Methyl (*E*)-4-(3,3-dimethyl-1-(*p*-tolyl)pent-1-en-1-yl)benzoate (41): Colourless liquid (62



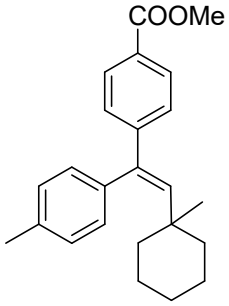
mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8 Hz, 2H), 7.27 (d, *J* = 8 Hz, 2H), 7.17 (d, *J* = 8 Hz, 2H), 7.08 (d, *J* = 8 Hz, 2H), 6.10 (s, 1H), 3.90 (s, 3H), 2.40 (s, 3H), 1.38 (q, *J* = 8 Hz, 2H), 0.91 (s, 6H), 0.90 (t, *J* = 8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.1, 149.1, 141.3, 139.4, 137.1, 136.7, 130.2, 129.4, 128.7, 128.1, 126.8, 52.1, 37.6, 37.3, 28.5, 21.4, 9.5; IR (ATR) $\tilde{\nu}$: 2957, 2922, 2854, 1721, 1604, 1511, 1434, 1273, 1182, 1103, 1017 cm^{-1}; HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{22}H_{27}O_2$, 323.2006; found, 323.2002.

(*E*)-Methyl 4-(3,3-dimethyl-5-phenyl-1-(*p*-tolyl)pent-1-en-1-yl)benzoate (42): Colorless



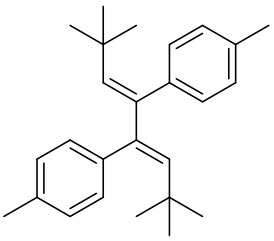
semi-solid (38 mg, 38%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 12 Hz, 2H), 7.29-7.23 (m, 4H), 7.19-7.13 (m, 5H), 7.09 (d, *J* = 8

Hz, 2H), 6. 14 (s, 1H), 3.89 (s, 3H), 2.63 (t, J = 8 Hz, 2H), 2.39 (s, 3H), 1.65 (t, J = 8 Hz, 2H), 0.98 (s, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 167.2, 149.0, 143.1, 140.8, 139.7, 137.0, 136.9, 130.2, 129.5, 128.8, 128.5, 128.4, 128.3, 126.9, 125.7, 52.1, 46.9, 37.6, 29.8, 29.1, 21.4; IR (ATR) $\tilde{\nu}$: 2959, 2920, 2851, 1725, 1604, 1455, 1275, 1182, 1105, 1018 cm^{-1}; HRMS (ESI^+): m/z $[M + Na]^+$ calcd for $C_{28}H_{30}NO_2Na$, 421.2138; found, 421.2135.



(*E*)-Methyl 4-(2-(1-methylcyclohexyl)-1-(*p*-tolyl)vinyl)benzoate (43): White solid (64 mg, 74%); mp 102−103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8 Hz, 2H), 7.24 (d, J = 8 Hz, 2H), 7.15 (d, J = 8 Hz, 2H), 7.06 (d, J = 8 Hz, 2H), 6.10 (s, 1H), 3.88 (s, 3H), 2.38 (s, 3H), 1.48-1.38 (m, 6H), 1.24-1.20 (m, 2H), 1.11-1.04 (m, 2H), 1.00 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl^3$) δ 167.2, 149.3, 141.4, 139.9, 137.3, 136.8, 129.9, 129.4, 128.8, 128.1, 126.9, 52.1, 39.5, 37.5, 26.2, 23.1, 21.4; IR (ATR) $\tilde{\nu}$: 2961, 2921, 2850, 1720, 1603, 1434, 1273, 1180, 1103, 773 cm^{-1}; HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{24}H_{29}O_2$, 349.2162; found, 349.2160.

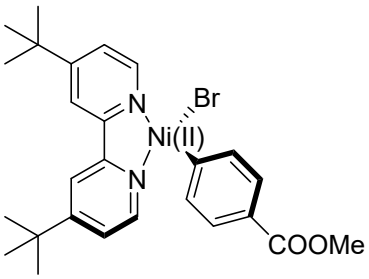
4,4'-((3*E*,5*E*)-2,2,7,7-Tetramethylocta-3,5-diene-4,5-diyl)bis(methylbenzene) (44): White solid (33 mg, 76%) (Reaction done with 0.25 mmol, yield calculated with respect to 0.125 mmol as homocoupling happened); mp 162−164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, J = 8 Hz, 2H), 6.97 (d, J = 8 Hz, 2H), 5.10 (s, 1H), 2.36 (s, 3H), 0.71 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 143.6, 141.0, 137.7, 135.7, 130.6, 128.0, 33.5, 31.4, 21.4; IR (ATR) $\tilde{\nu}$: 2959, 2920, 2853, 1509, 1458, 1357, 1258, 1199, 1108 cm^{-1}; HRMS (ESI^+): m/z $[M + Na]^+$ calcd for $C_{26}H_{35}$, 347.2733; found, 347.2731.



Diethyl (*E*)-(3,3-dimethyl-1-(*p*-tolyl)but-1-en-1-yl)phosphonate (45): Colorless liquid (50 mg, 65%); Stereochemistry was defined by ^{1}H-^{1}H NOESY spectra and also by comparing with the chemical shift and coupling constant of *β*-olefinic H in the ^{1}H NMR spectroscopy of structurally similar compound[6]; ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.83 (dt); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, J = 12 Hz, 2H), 7.03 (d, J = 8 Hz, 2H), 6.79 (d, J = 28 Hz, 1H), 4.0 (pent, J = 8 Hz, 4 H), 2.34 (s,

3H), 1.24 (t, J = 8 Hz, 6H), 0.92 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 156.8 (d, $J_{C,P}$ = 9 Hz), 137.0 (d, $J_{C,P}$ = 2 Hz), 132.5 (d, $J_{C,P}$ = 8 Hz), 129.9 (d, $J_{C,P}$ = 5 Hz), 129.3 (d, $J_{C,P}$ = 175 Hz), 128.5 (d, $J_{C,P}$ = 2 Hz), 62.0 (d, $J_{C,P}$ = 6 Hz), 35.6 (d, $J_{C,P}$ = 29 Hz), 30.6 (d, $J_{C,P}$ = 2 Hz), 21.3, 16.4 (d, $J_{C,P}$ = 7 Hz); IR (ATR) $\tilde{\nu}$: 2959, 2928, 2858, 1475, 1241, 1054, 1022, 963 cm^{-1}; HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{17}H_{28}O_3P$, 311.1771; found, 311.1772.

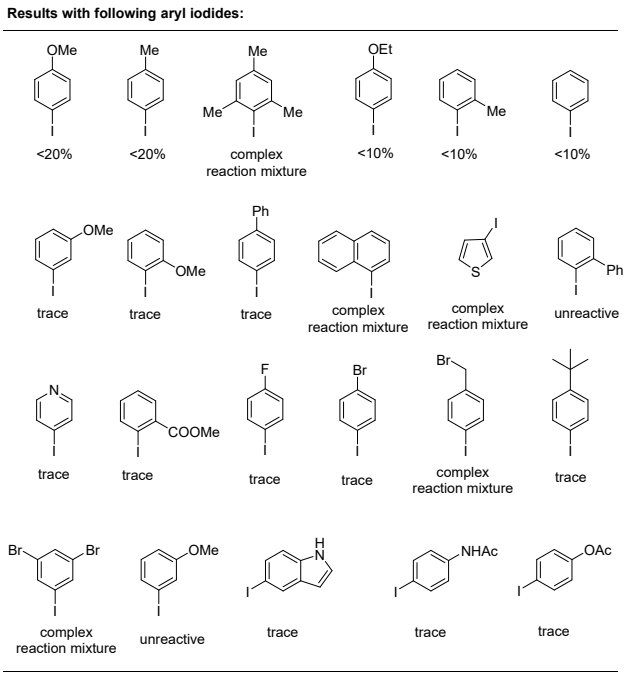
Diethyl (*Z*)-(3,3-dimethyl-1-(*p*-tolyl)but-1-en-1-yl)phosphonate (46): Colorless liquid (3 mg, 4%); Stereochemistry was defined by ^1H-^1H NOESY spectra. ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.71 (dt); ^1H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, J = 8 Hz, 2H), 7.09 (d, J = 8 Hz, 2H), 6.37 (d, J = 52 Hz, 1H), 4.04-3.92 (m, 4H), 2.33 (s, 3H), 1.34 (s, 9H), 1.19 (t, J = 8 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.0 (d, $J_{C,P}$ = 12 Hz), 139.7 (d, $J_{C,P}$ = 12 Hz), 136.7 (d, $J_{C,P}$ = 2 Hz), 130.8, 129.0 (d, $J_{C,P}$ = 5 Hz), 128.7 (d, $J_{C,P}$ = 4 Hz), 128.6 (d, $J_{C,P}$ = 1 Hz), 61.7 (d, $J_{C,P}$ = 7 Hz), 34.6 (d, $J_{C,P}$ = 6 Hz), 30.6 (d, $J_{C,P}$ = 1 Hz), 21.2, 16.3 (d, $J_{C,P}$ = 7 Hz); HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{17}H_{28}O_3P$, 311.1771; found, 311.1769.

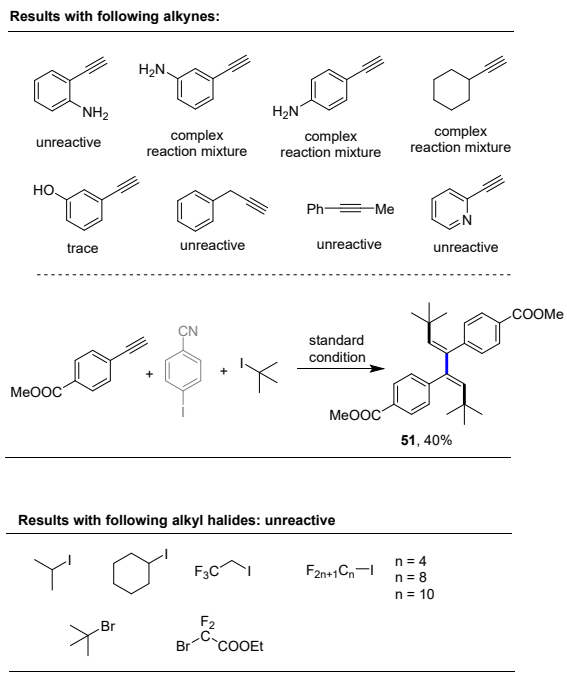


Ni(II) Complex-I (47)[7]: Brown solid (quantitative yield); ^1H NMR (400 MHz, CD_2Cl_2) δ 9.21 (s, 1H), 7.85 (d, J = 8 Hz, 2H), 7.72 (brs, 2H), 7.54 (m, 3H), 7.08 (m, 3H), 3.83 (s, 3H), 1.36 (m, 18H). Data matched with literature report.

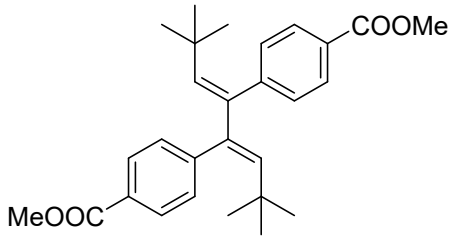
Additional results for arylalkylation of alkynes:

- Internal alkynes and aliphatic alkynes remained unreactive under the reaction protocol.
- Electron donating group substituted aryl iodides were not so favourable in the reductive coupling reaction as it mostly led to very trace amount of the desired products formation.
- Attempt to use secondary or primary alkyl iodides or fluoroalkyl iodides were found to be unsuccessful for the dicarbofunctionalization method.
- The nonproductivity of aliphatic alkynes could be realized by the lack of pi-conjugation stabilizing effect of vinyl radical relative to aromatic alkynes.[8]





Dimethyl 4,4'-((3*E*,5*E*)-2,2,7,7-tetramethylocta-3,5-diene-4,5-diyl)dibenzoate (51): White solid (22 mg, 40%) (Reaction done with 0.25 mmol, yield calculated with respect to 0.125 mmol as homocoupling happened); mp 216−217 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8 Hz, 2H), 7.18 (d, J = 8 Hz, 2H), 5.09 (s, 1H), 3.93 (s, 3H), 0.70 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.3, 145.8, 142.1, 142.0, 130.8, 128.9, 128.6, 52.2, 33.7, 31.3; IR (ATR) $\tilde{\nu}$: 2960, 2924, 2856, 1726, 1273, 1113, 716 cm^{-1}; HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{28}H_{35}O_4$, 435.2530; found, 435.2531.



IV. Reference:

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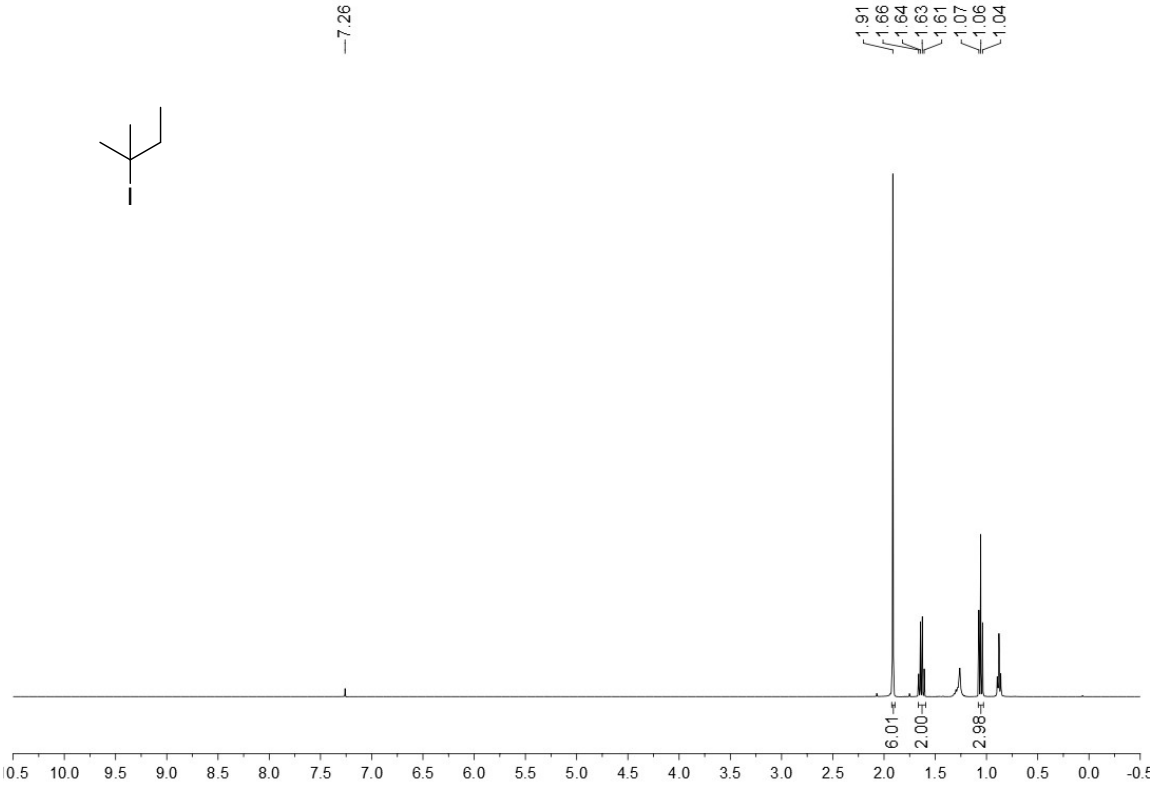
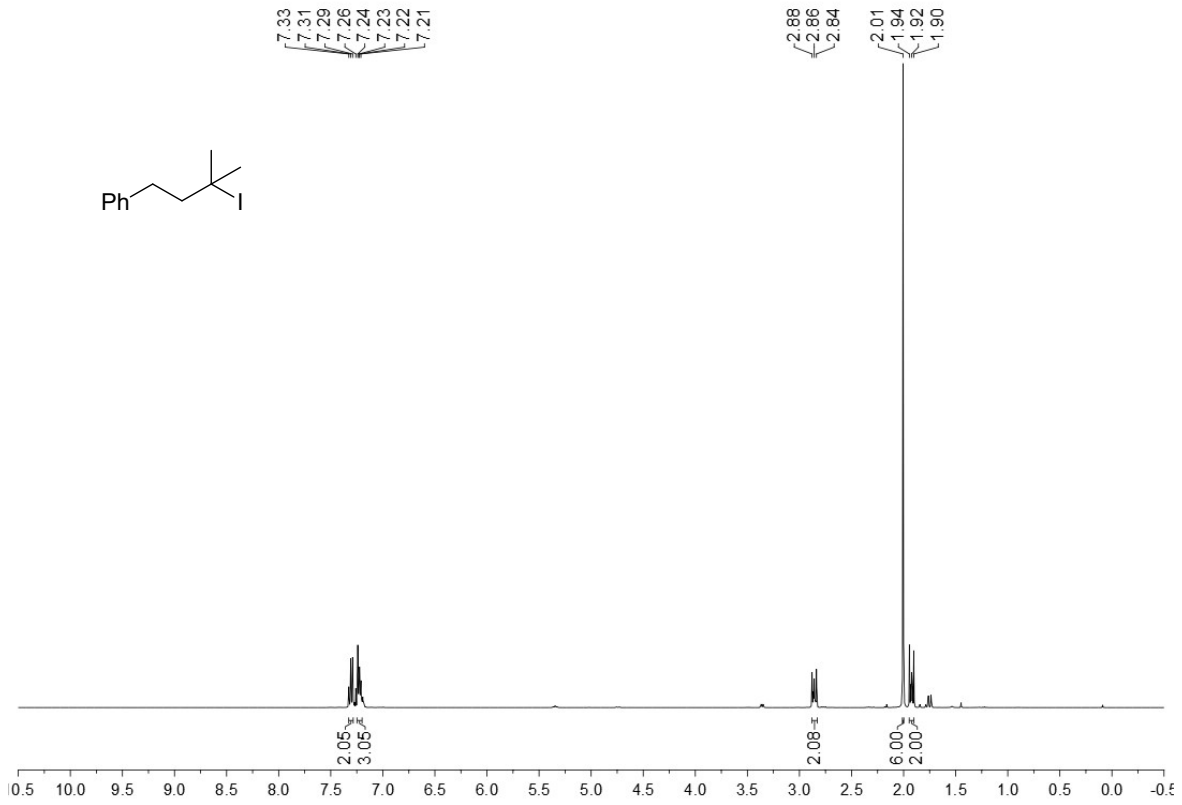
7. L. Guo, F. Song, S. Zhu, H. Li and L. Chu, *Nat. Commun.*, 2018, **9**, 4543.

8. C. Galli, A. Guarnieri, H. Koch, P. Mencarelli and Z. Rappoport, *J. Org. Chem.*, 1997, **62**, 4072.

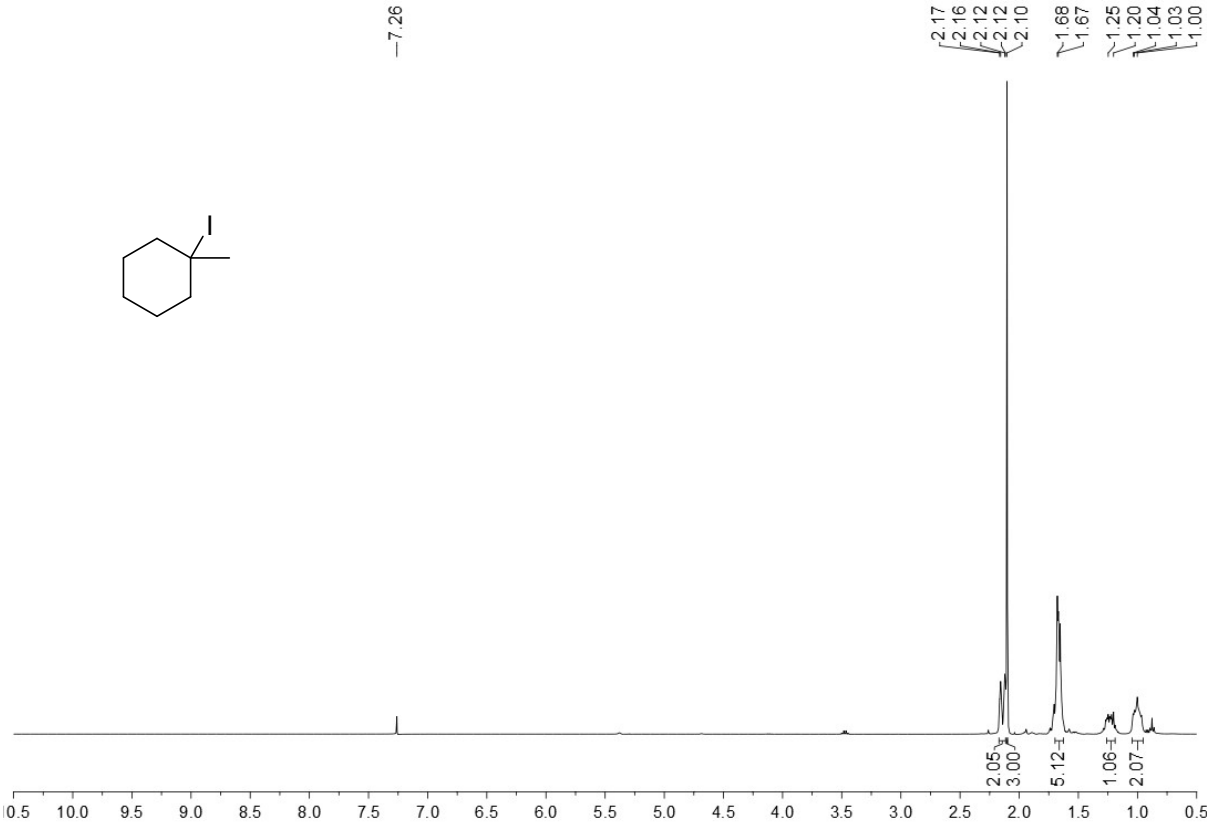
V. NMR spectra



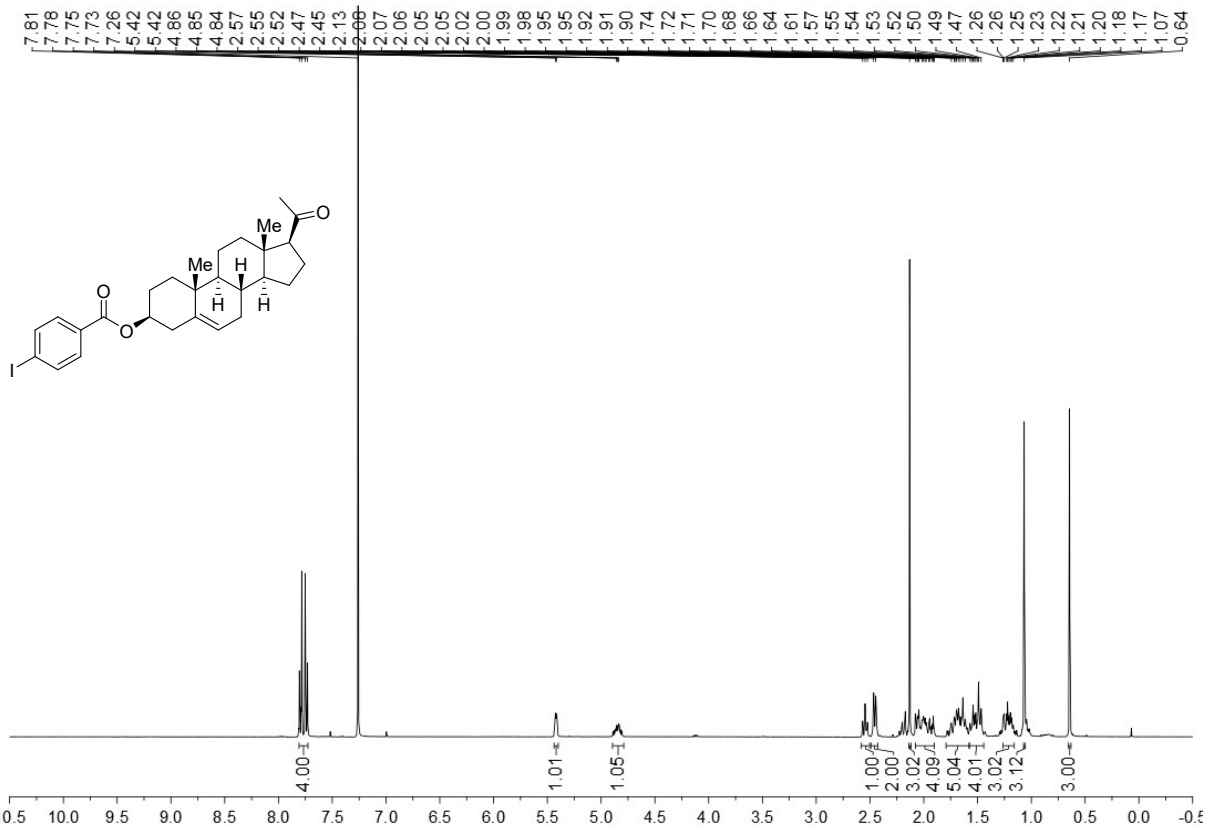
^{1}H NMR (400 MHz, $CDCl_3$) of **SM-1**.



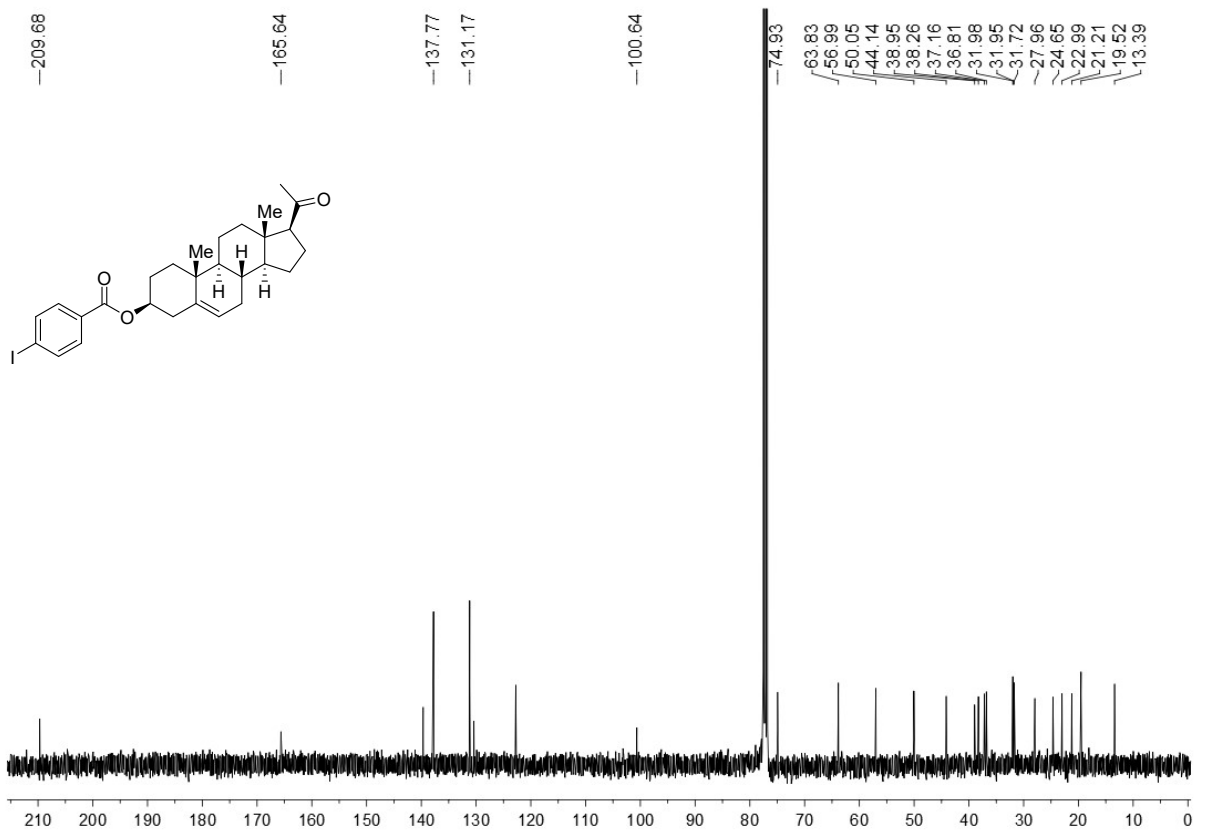
^{1}H NMR (400 MHz, $CDCl_3$) of **SM-2**.



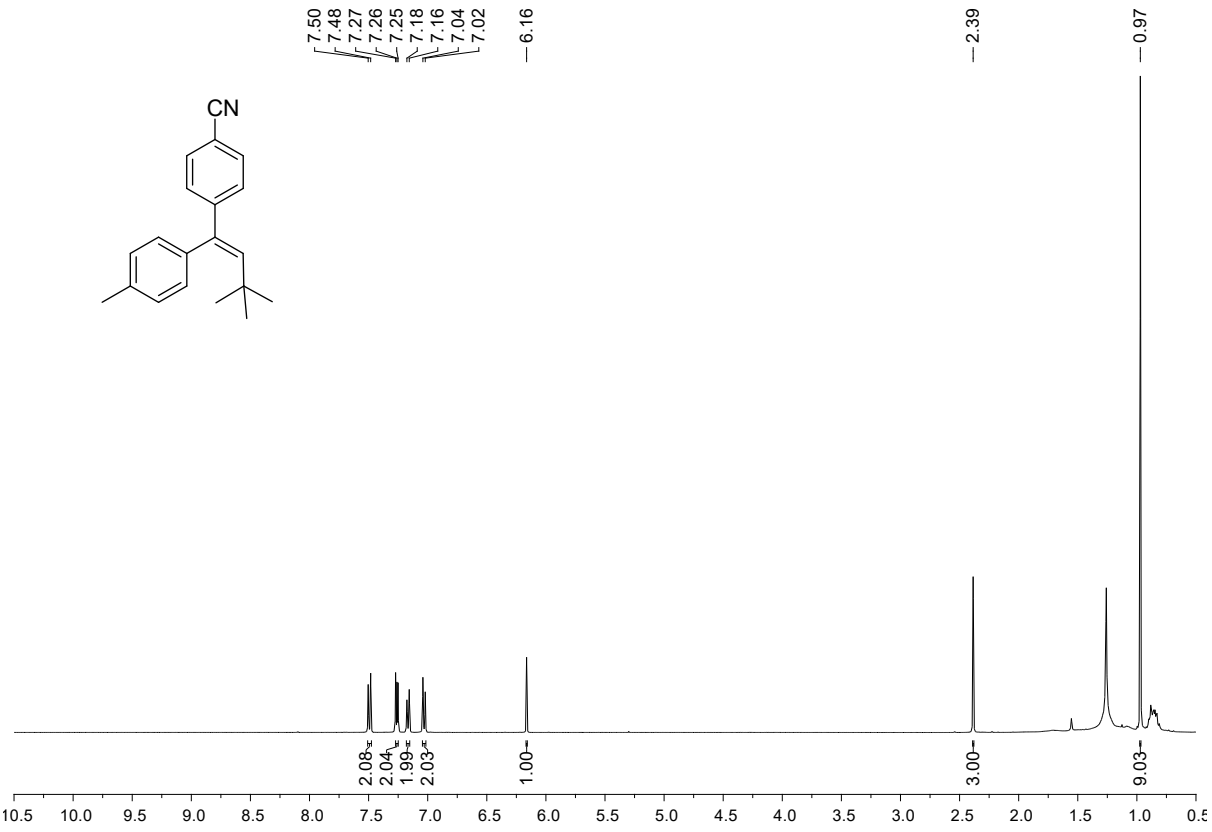
^{1}H NMR (400 MHz, $CDCl_3$) of **SM-3**.



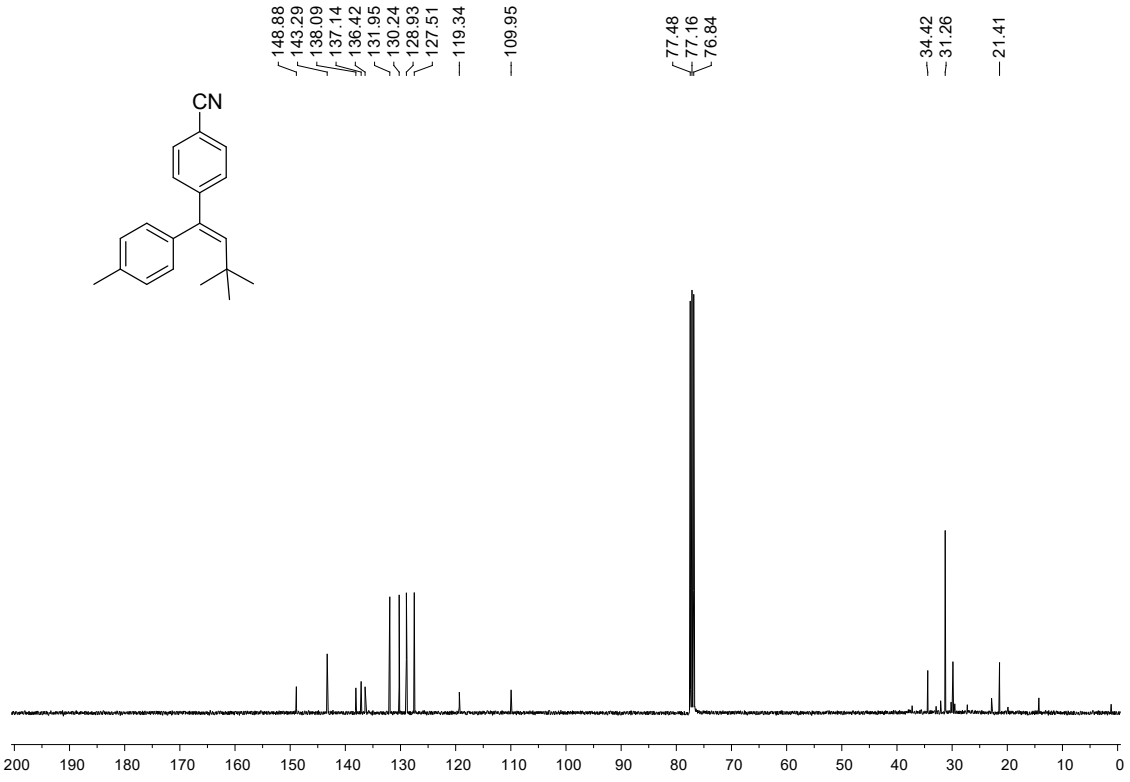
^{1}H NMR (400 MHz, $CDCl_3$) of **SM-4**.



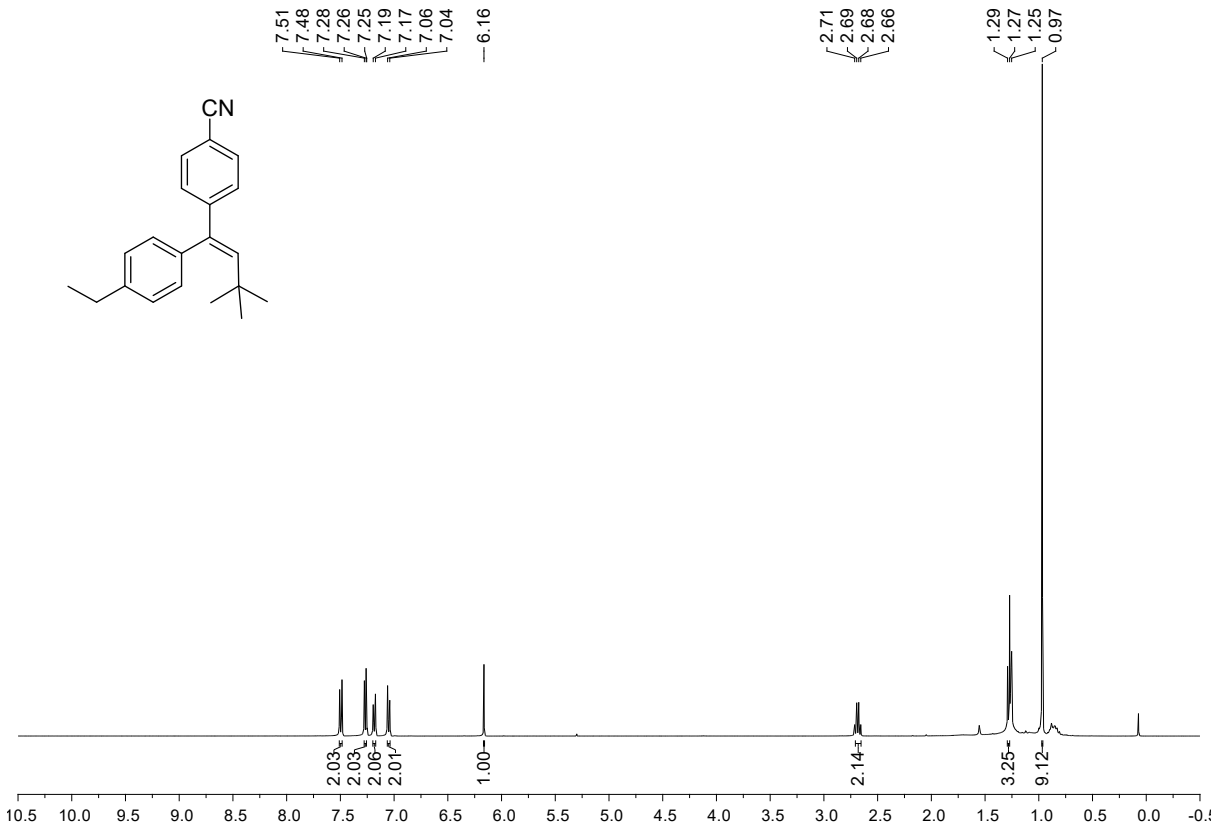
^{13}C NMR (100 MHz, $CDCl_3$) of **SM-4**.



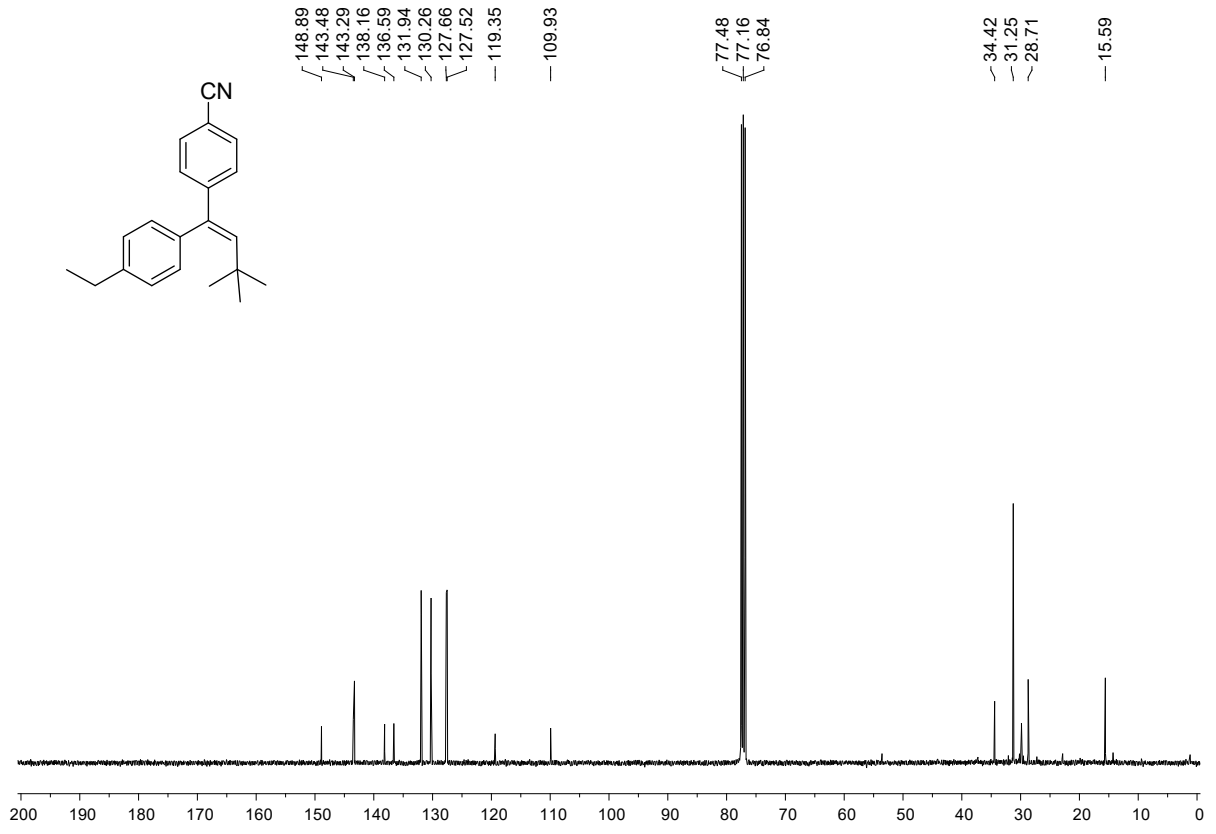
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **1**.



^{13}C NMR (100 MHz, $CDCl_3$) of the compound **1**.

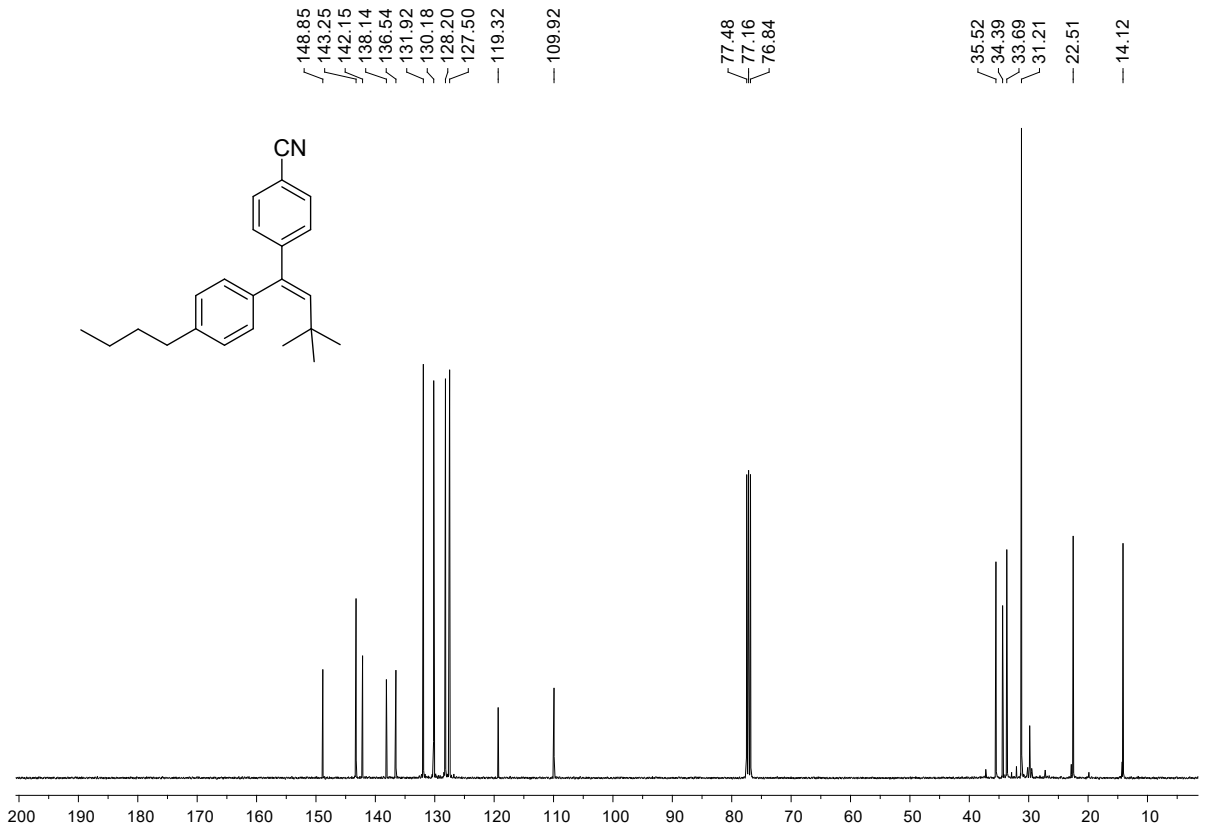


^{1}H NMR (400 MHz, $CDCl_3$) of the compound **2**.



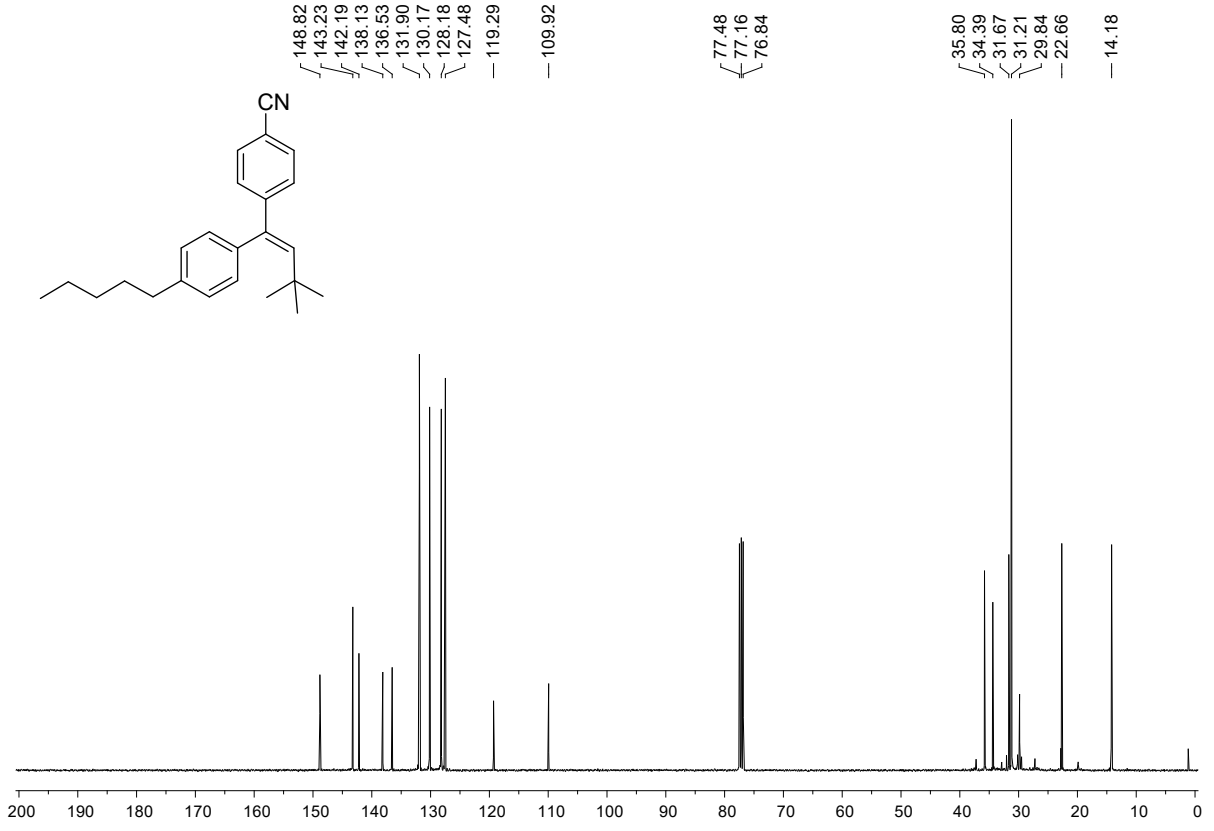
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **2**.

^{1}H NMR (400 MHz, $CDCl_3$) of the compound **3**.

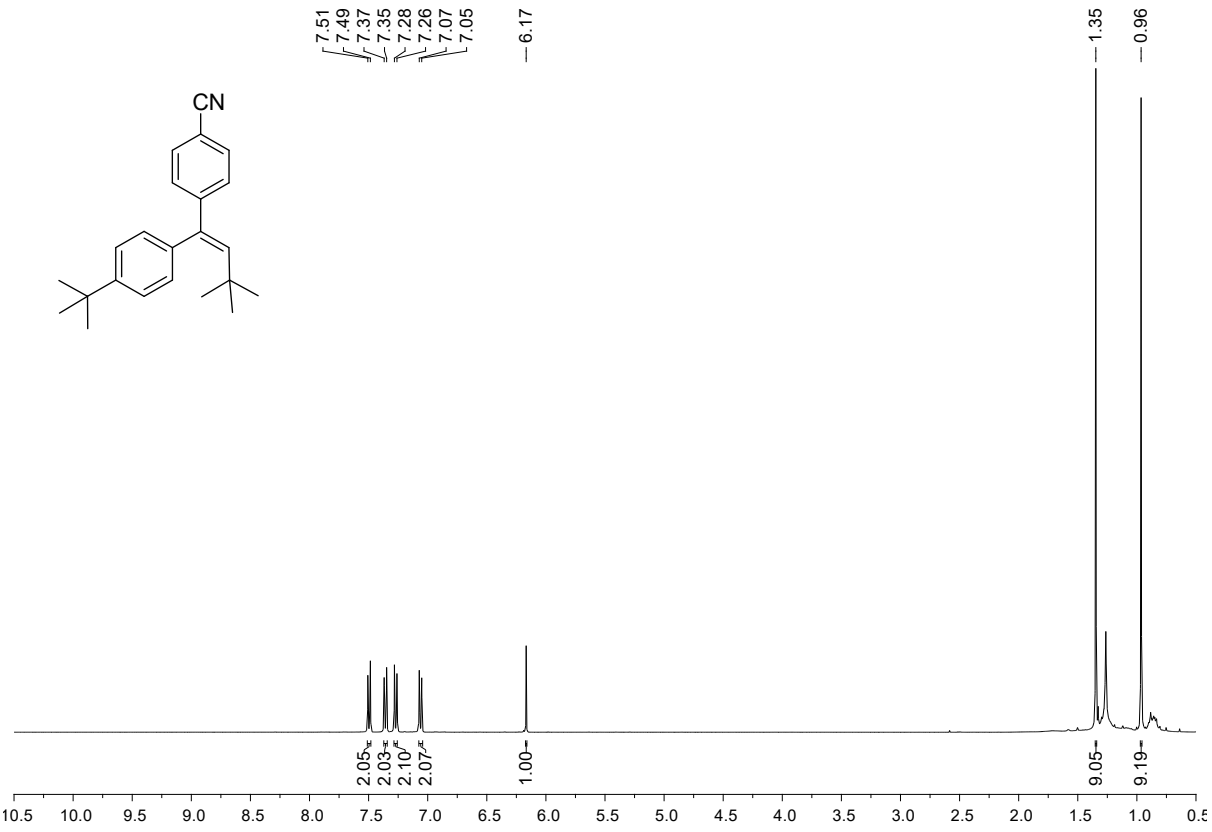


^{13}C NMR (100 MHz, $CDCl_3$) of the compound **3**.

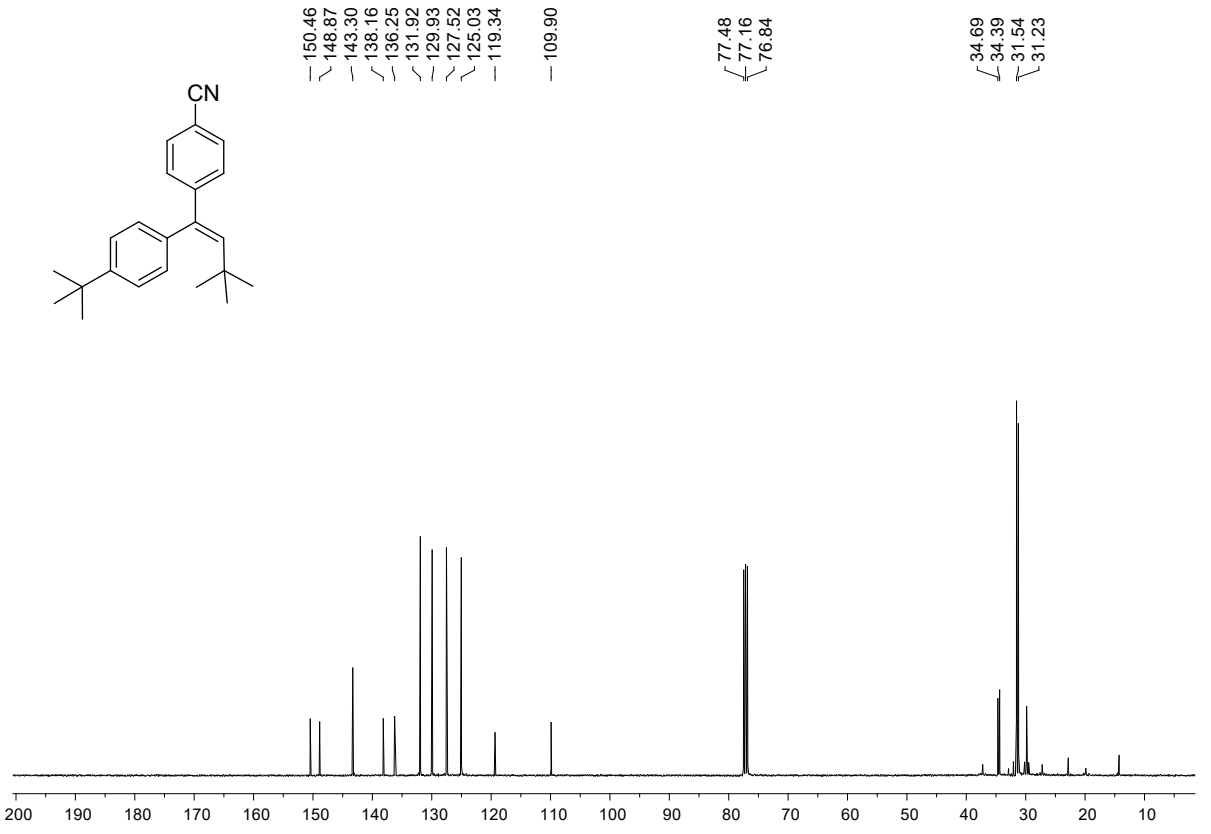
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **4**.



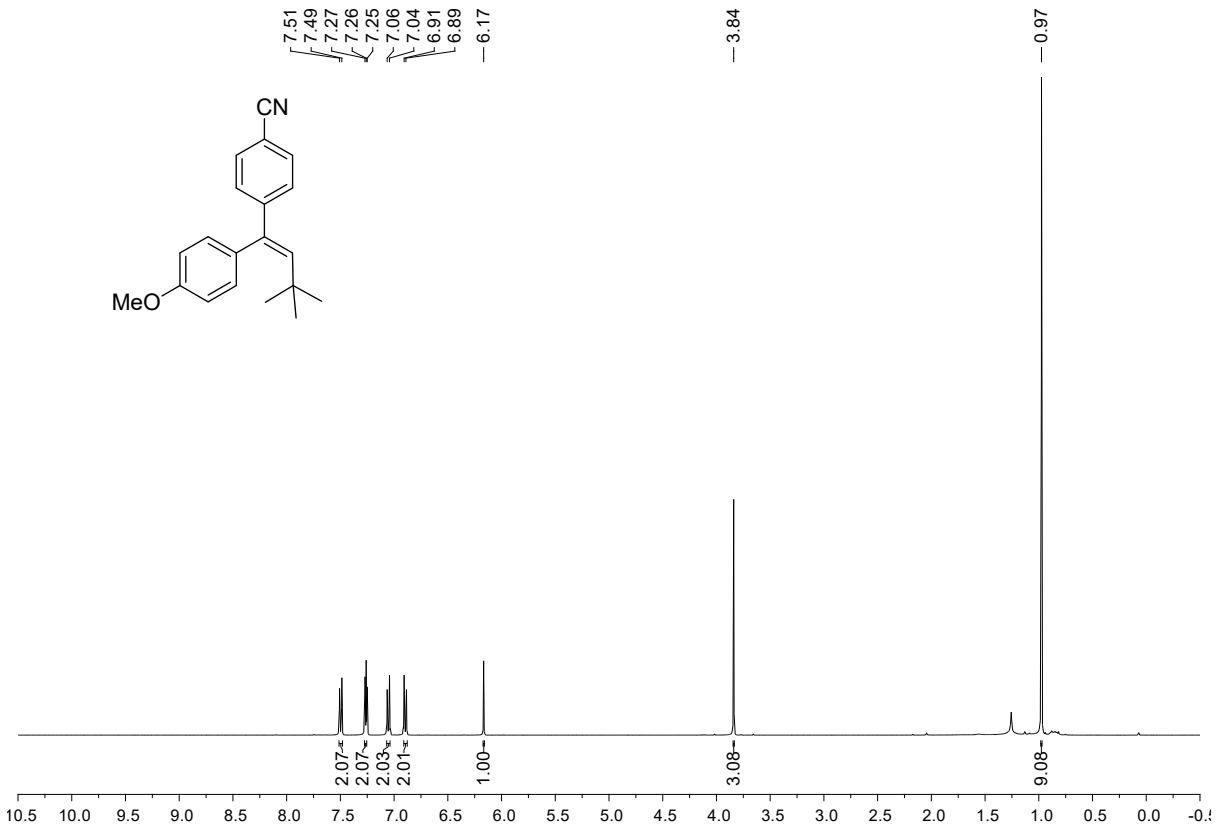
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **4**.



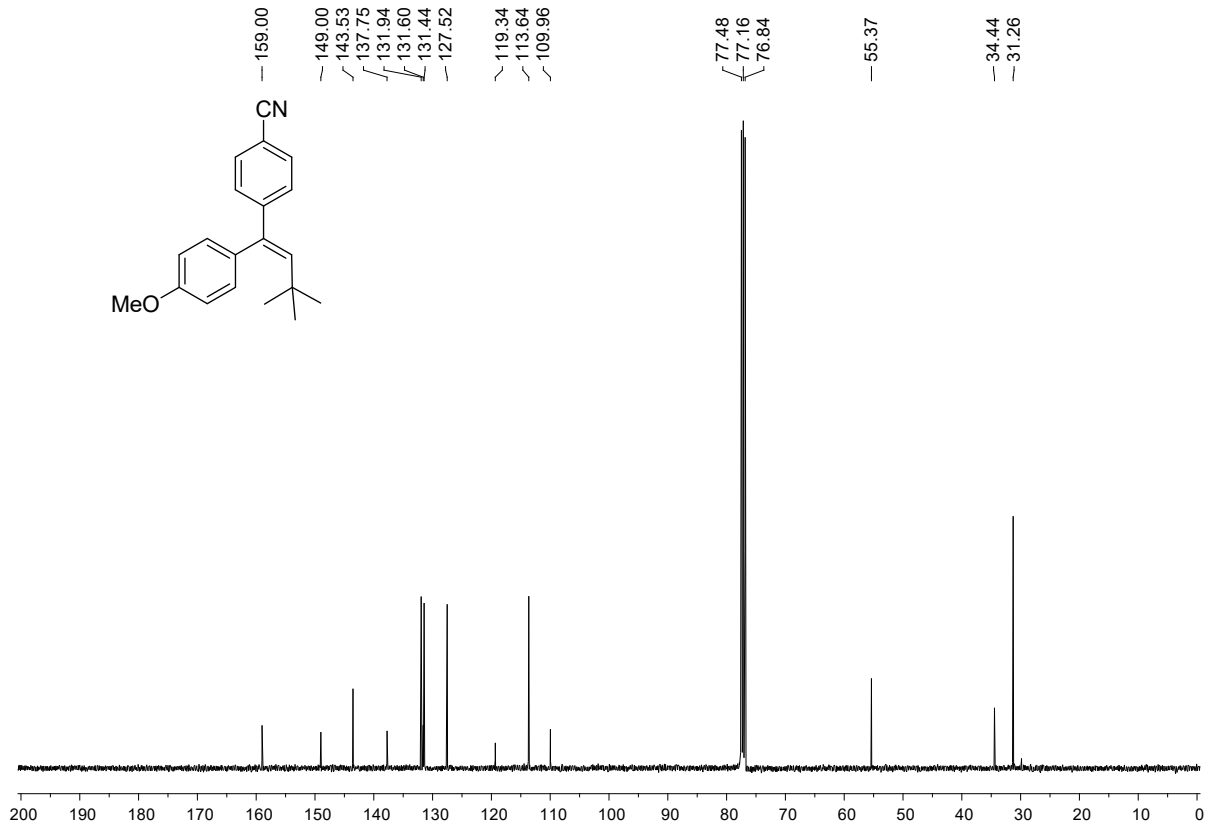
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **5**.



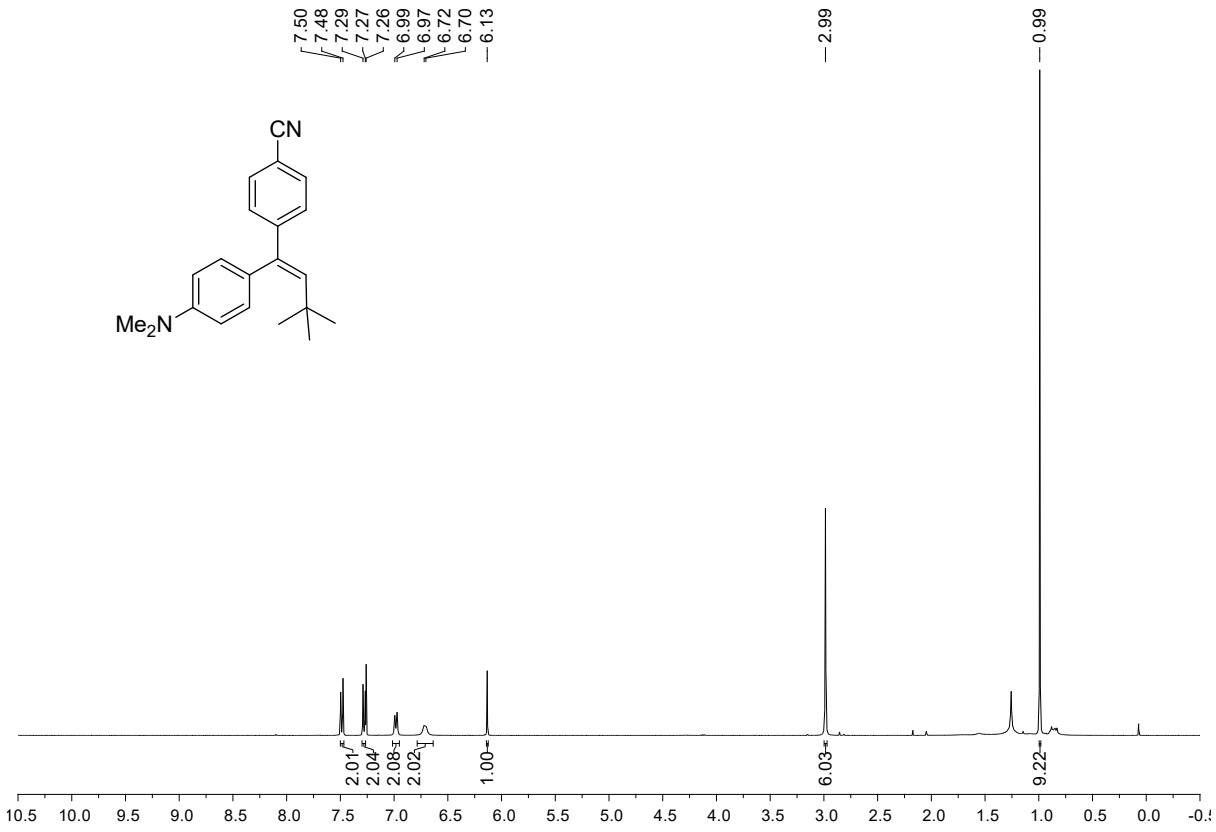
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **5**.



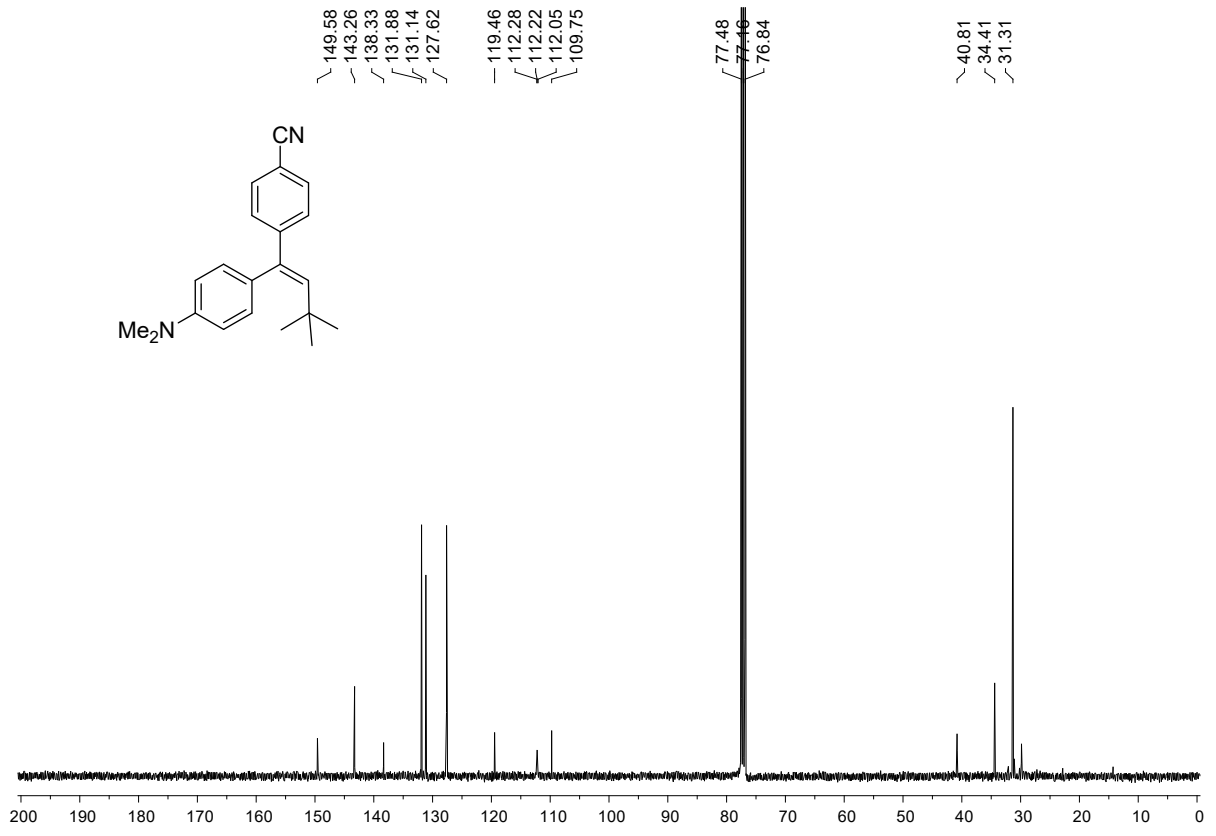
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **6**.



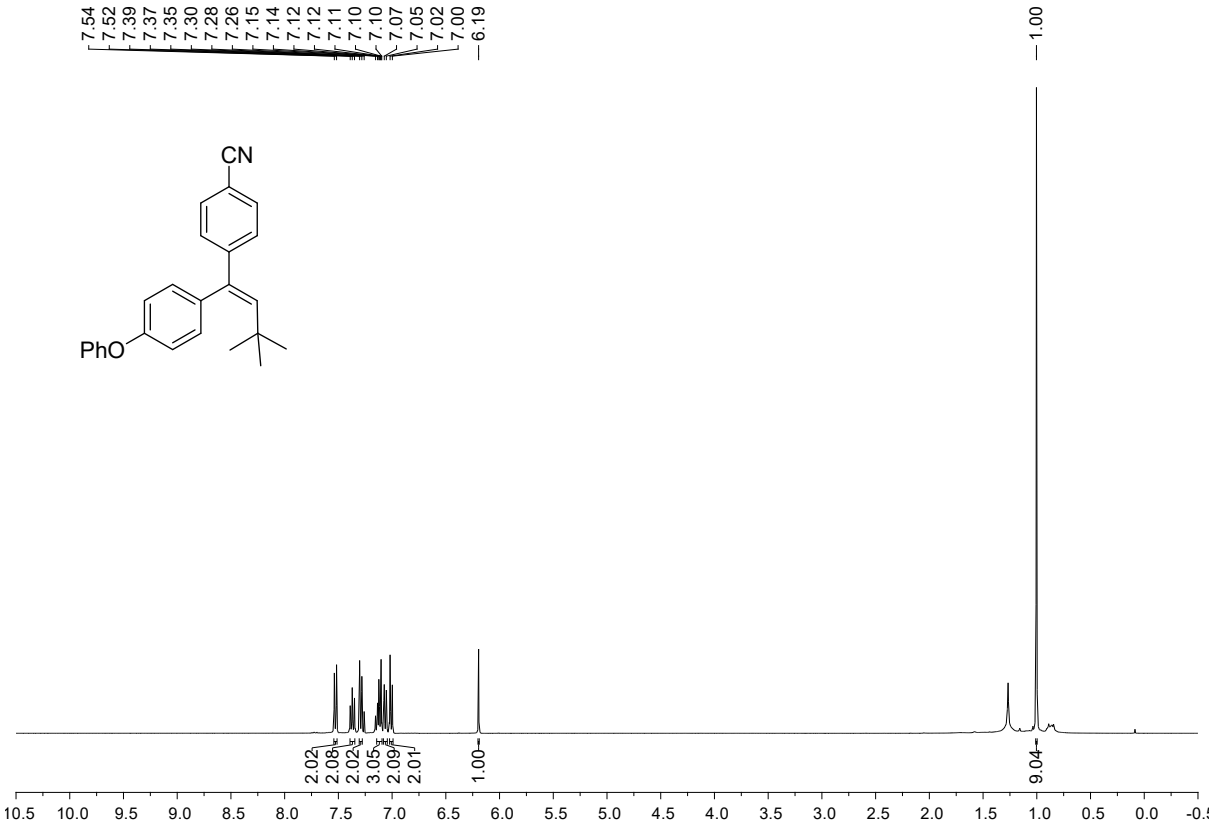
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **6**.



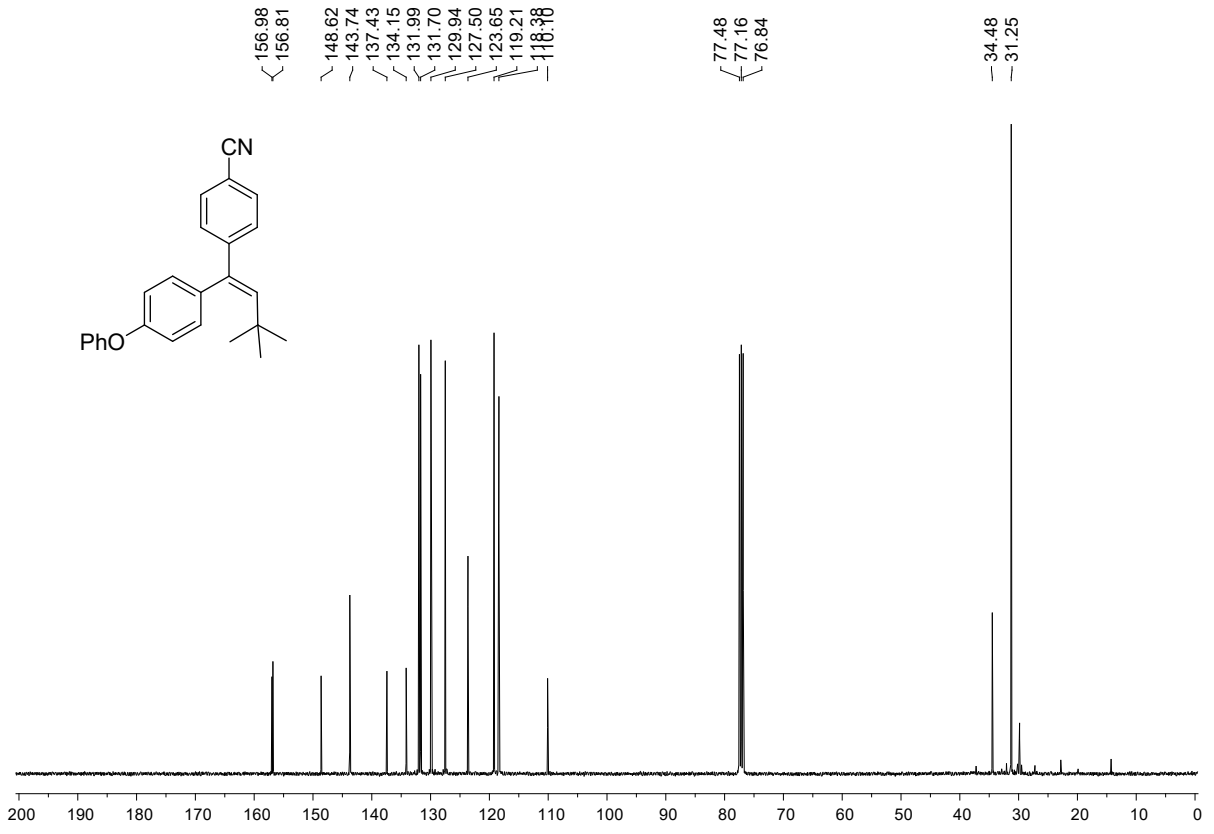
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **7**.



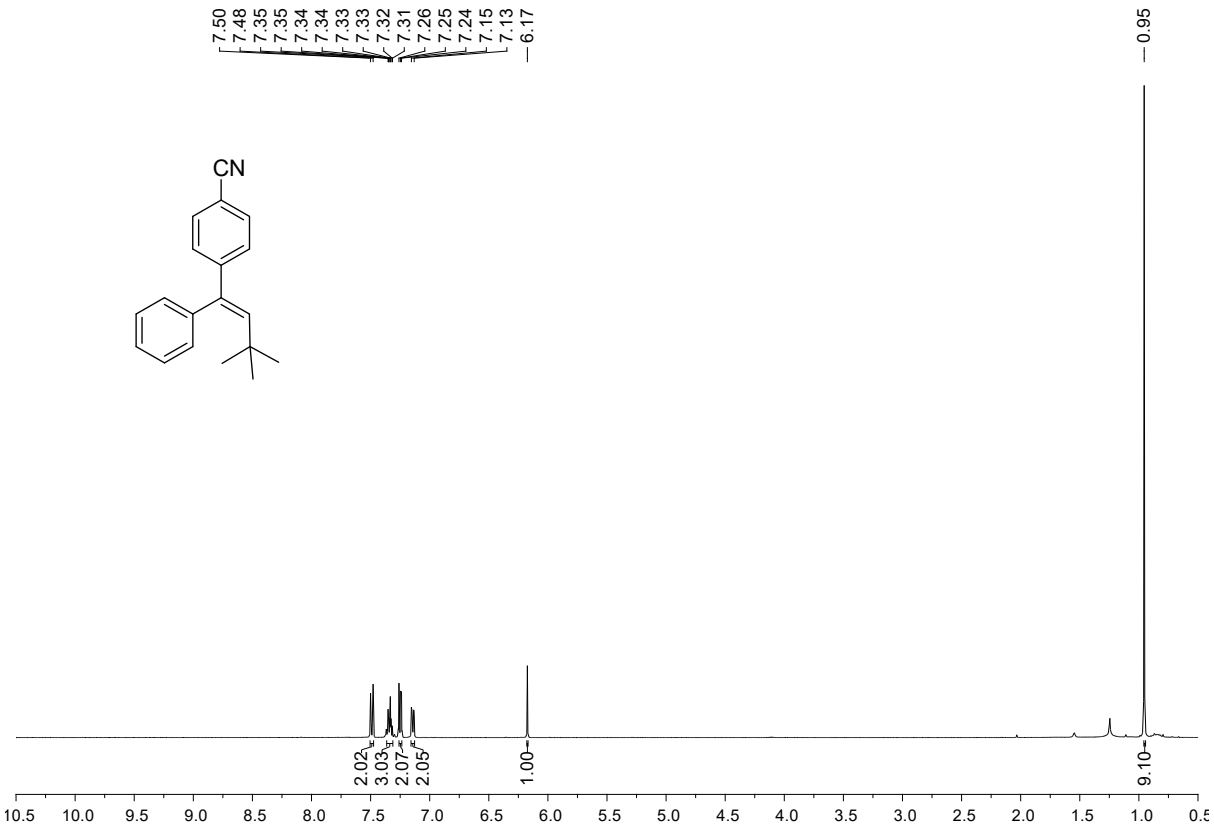
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **7**.



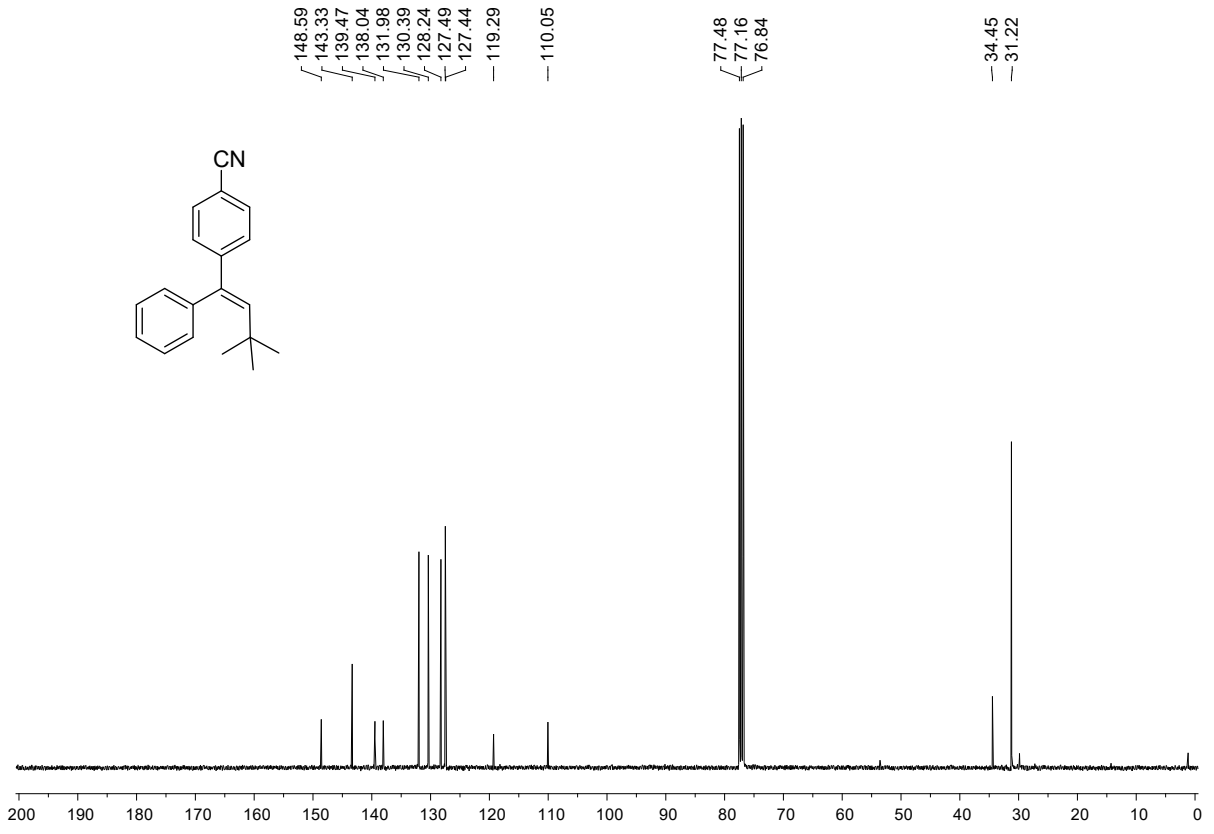
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **8**.



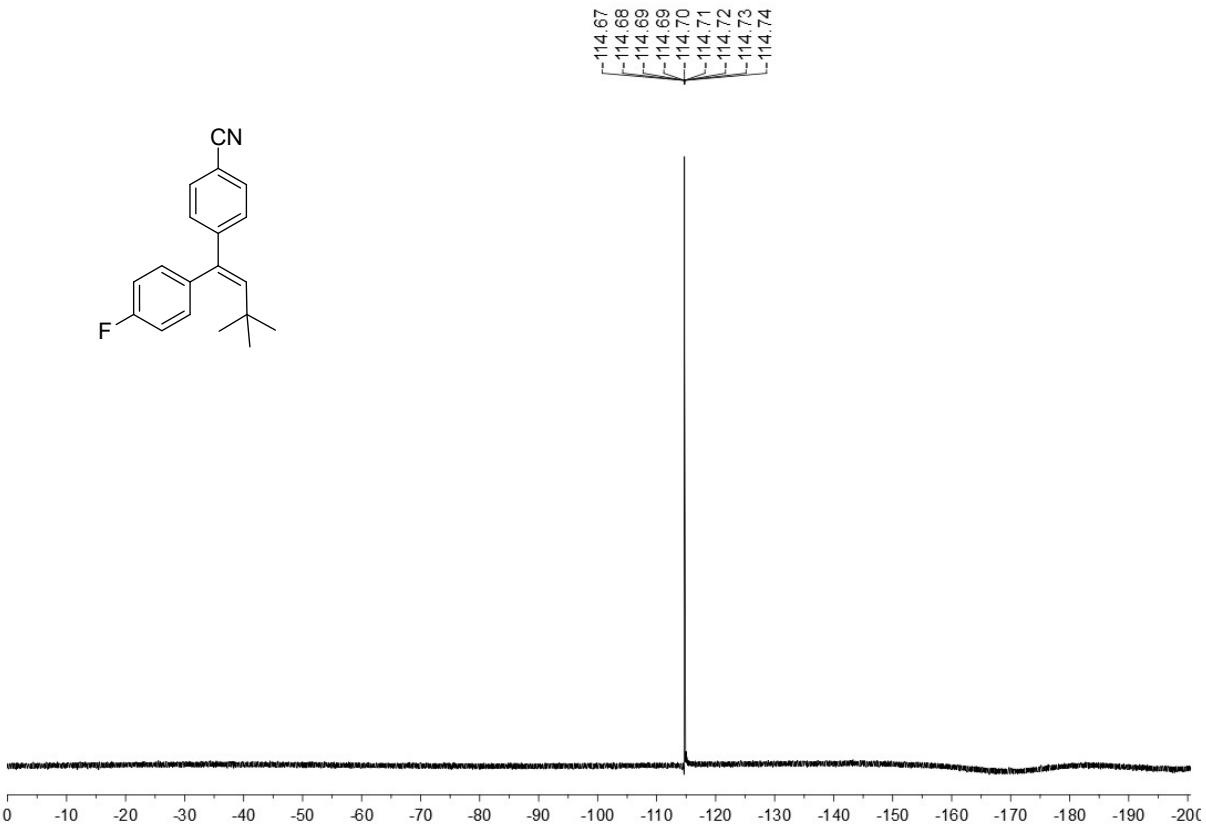
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **8**.



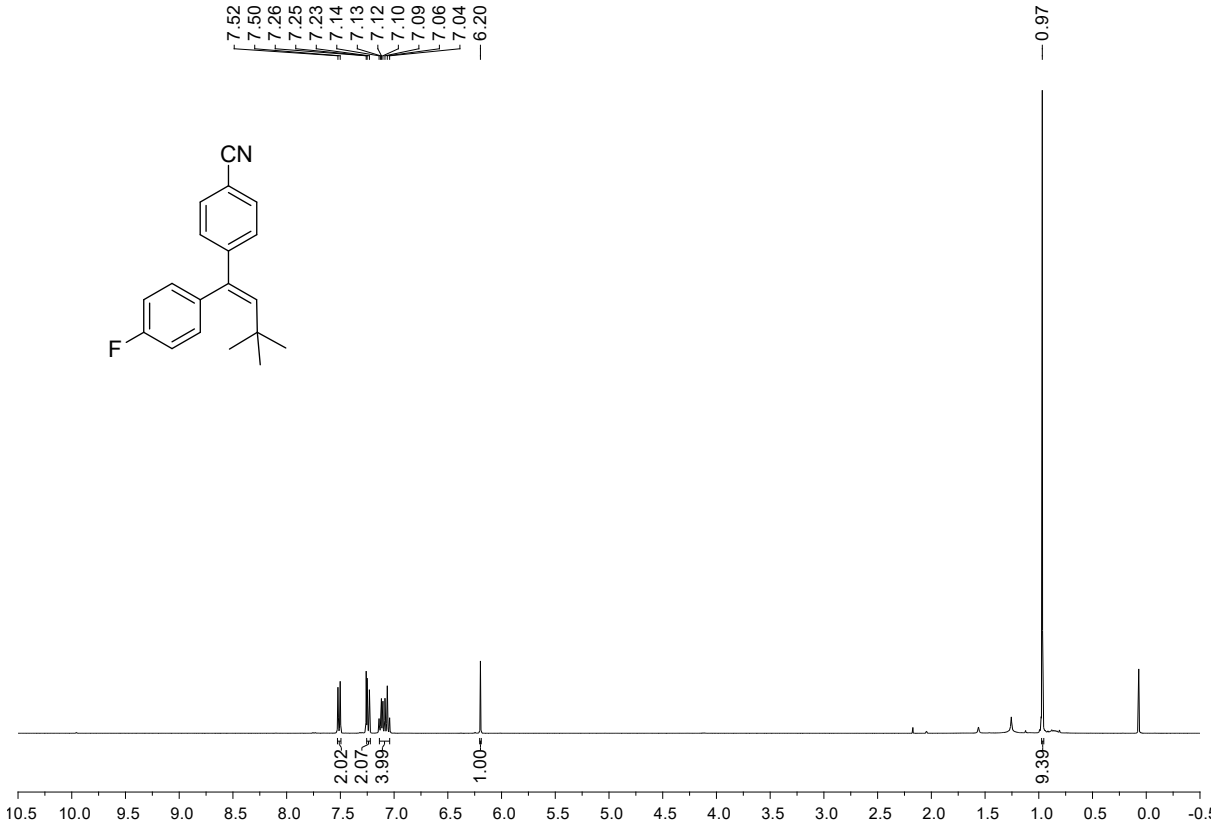
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **9**.



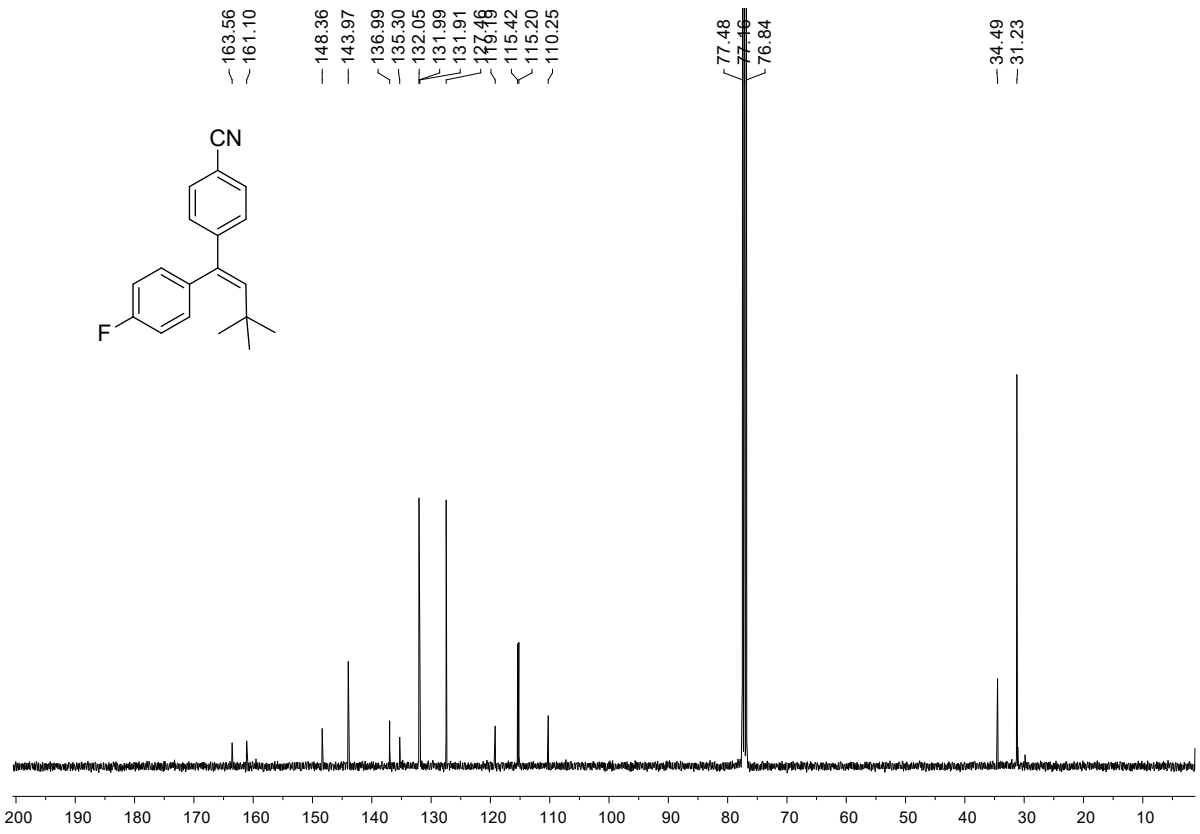
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **9**.



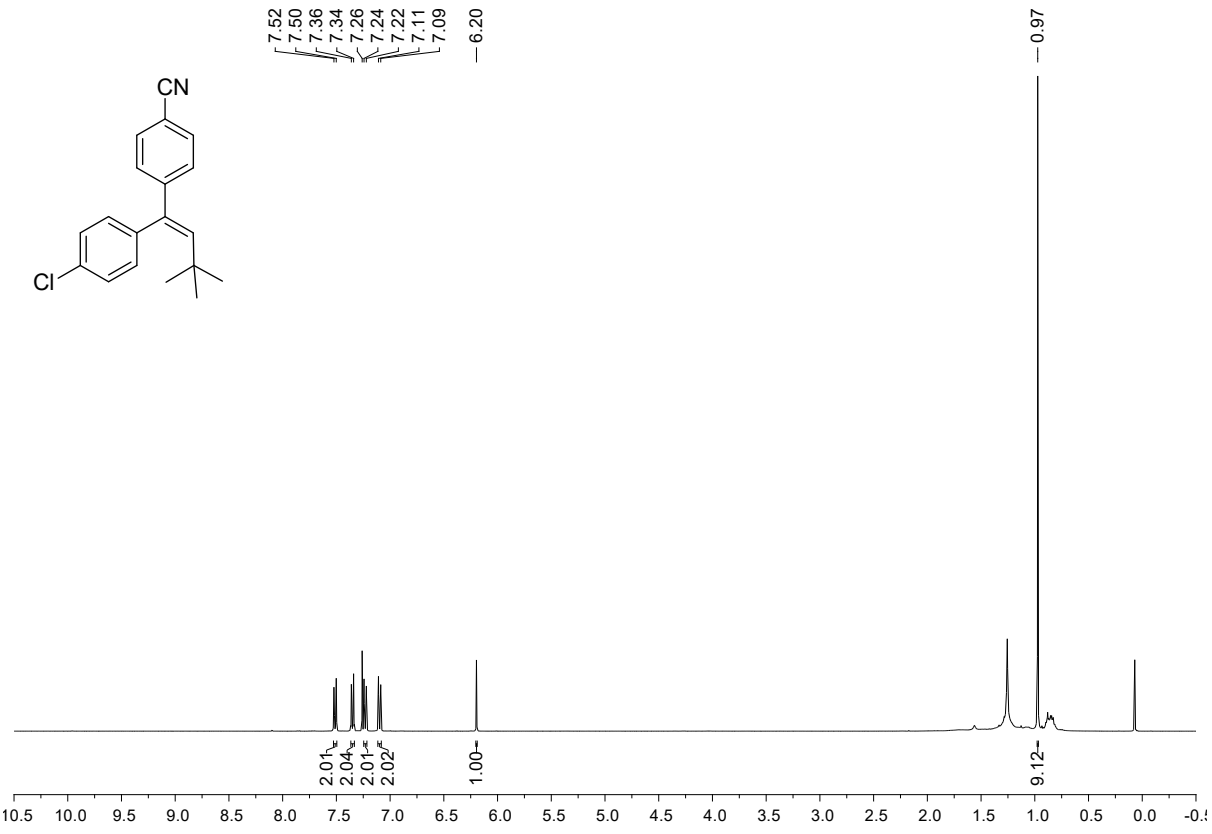
^{19}F NMR (377 MHz, $CDCl_3$) of the compound **10**.



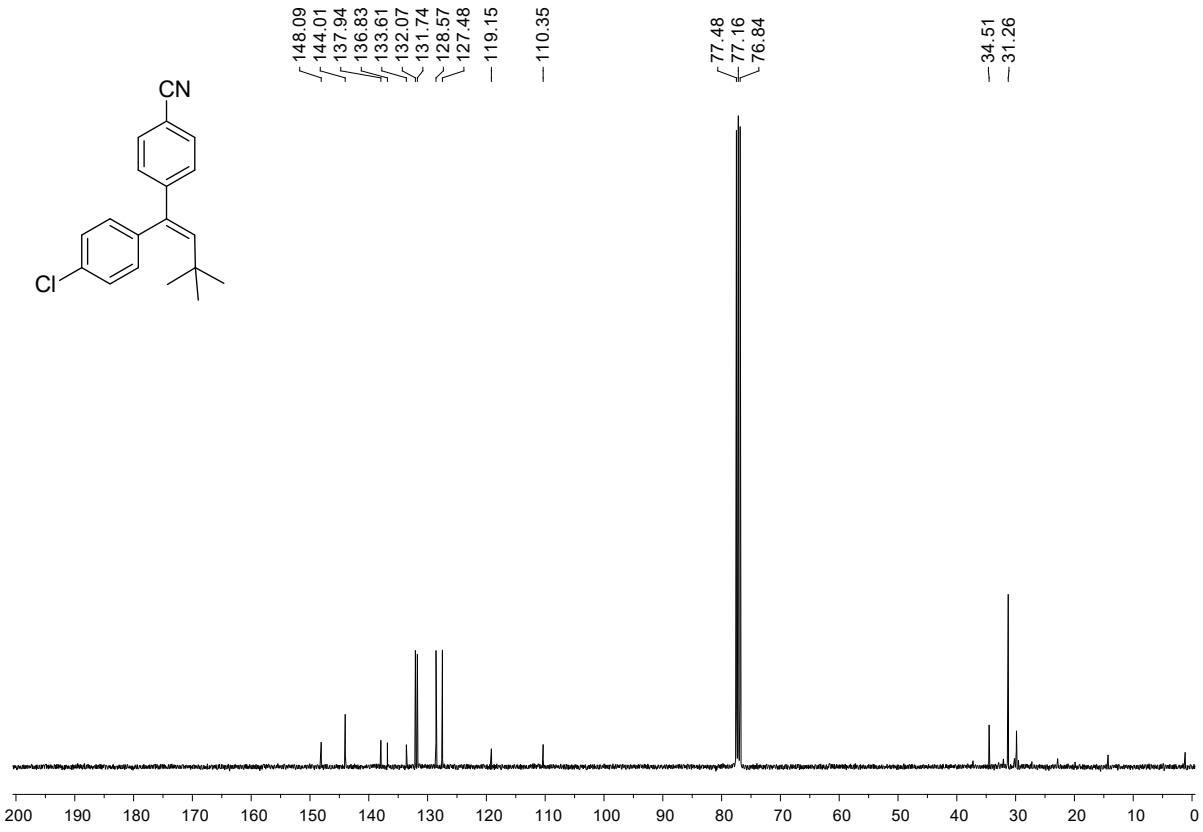
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **10**.



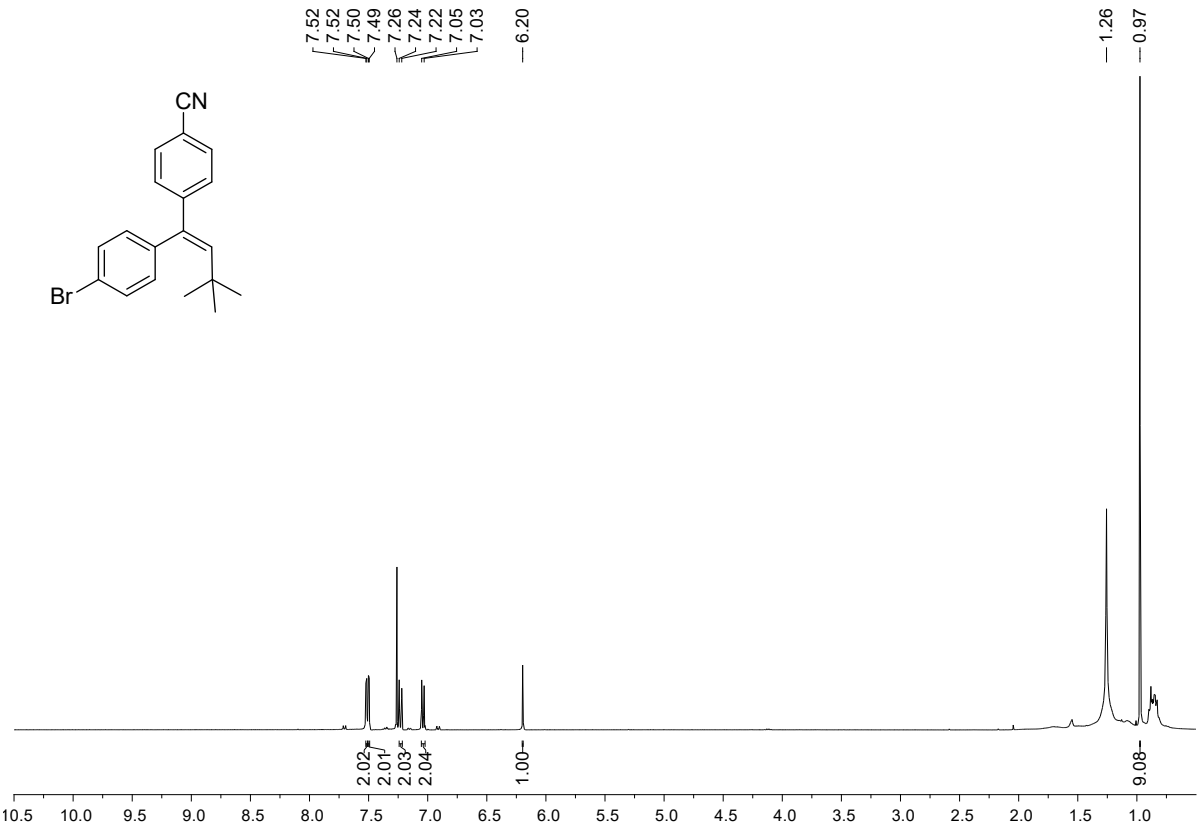
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **10**.



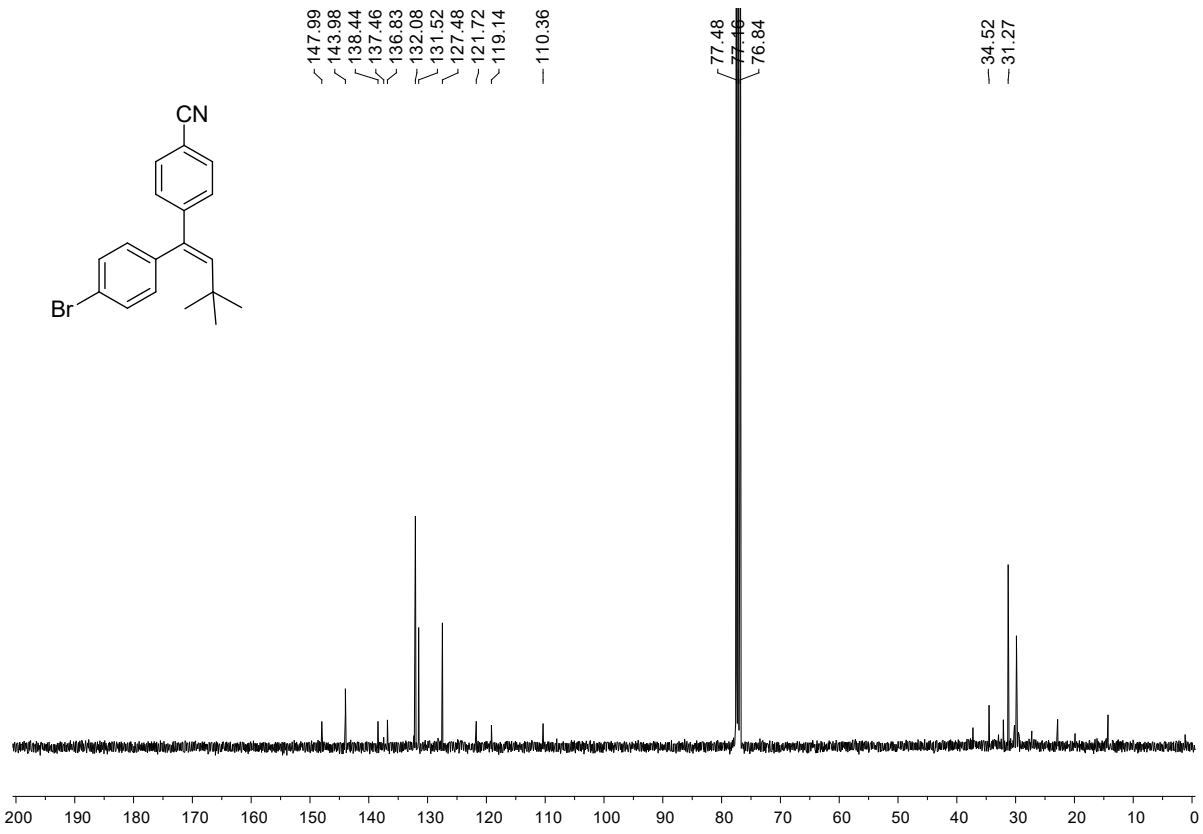
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **11**.



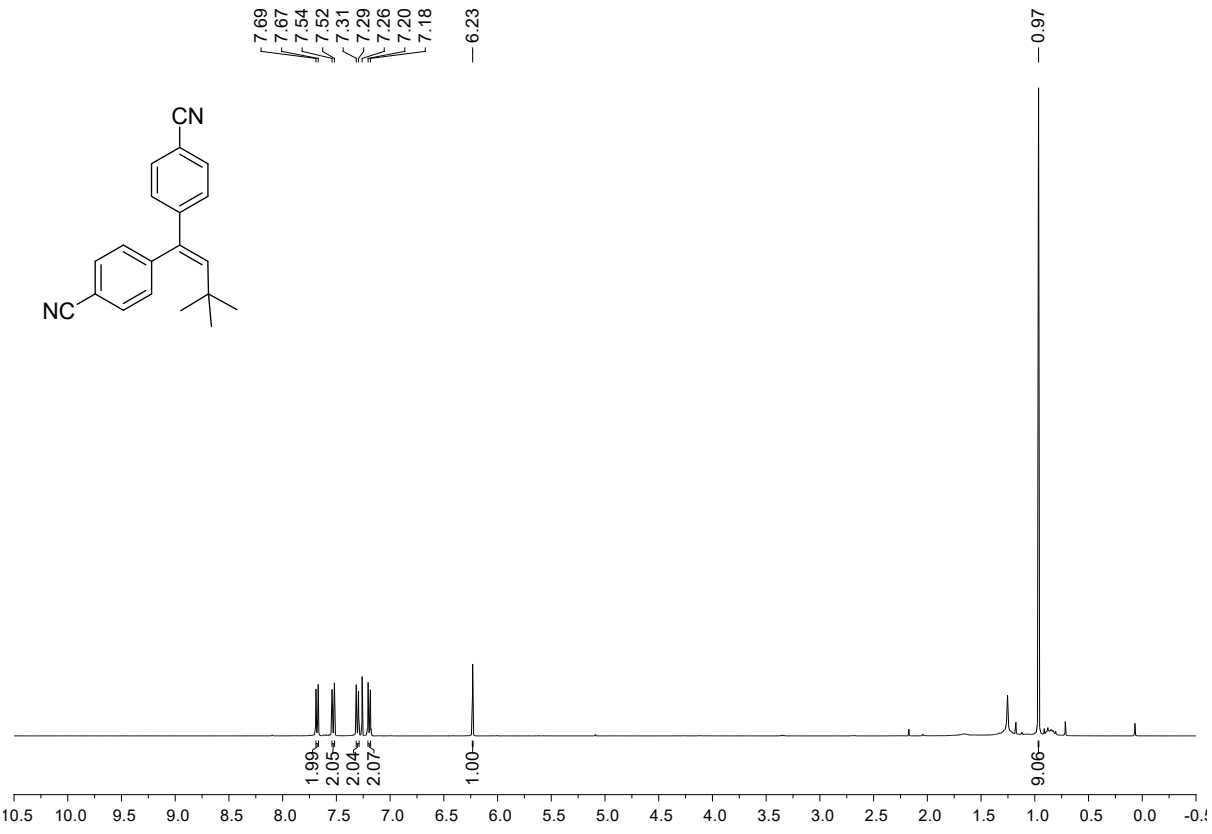
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **11**.



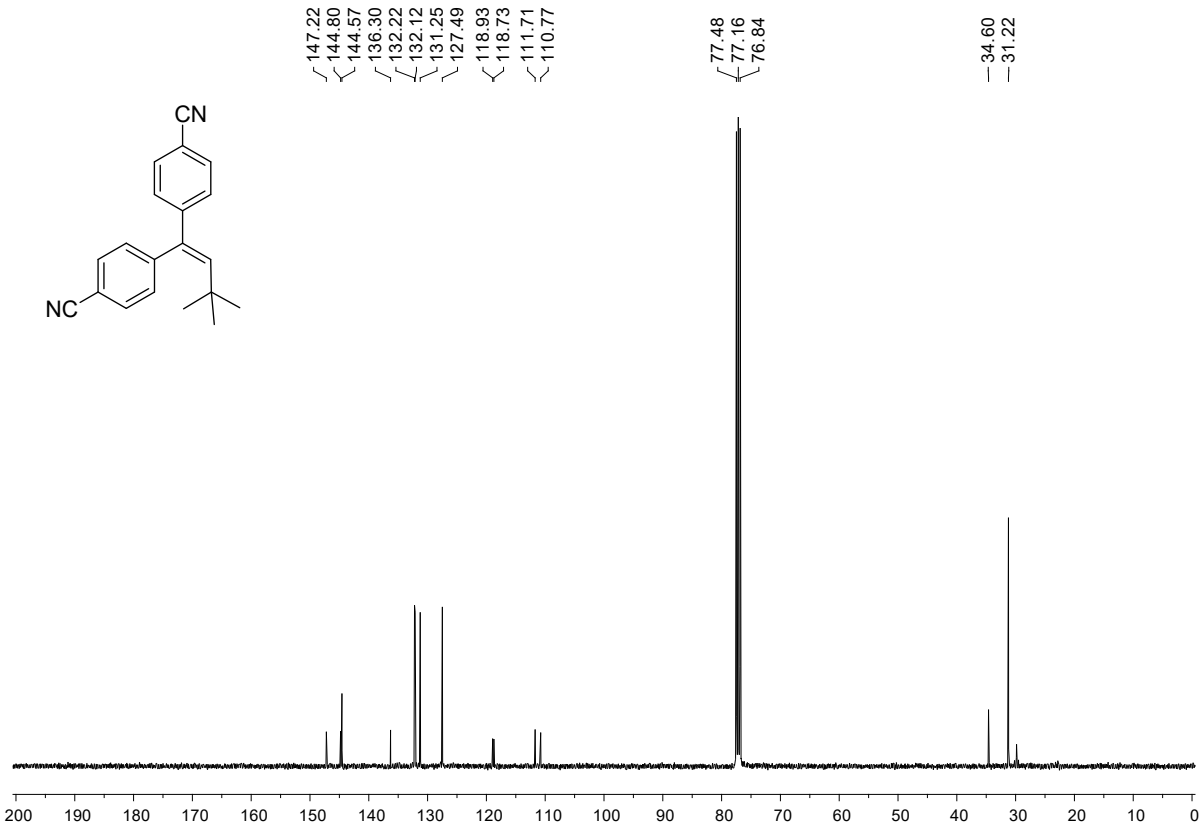
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **12**.



^{13}C NMR (100 MHz, $CDCl_3$) of the compound **12**.

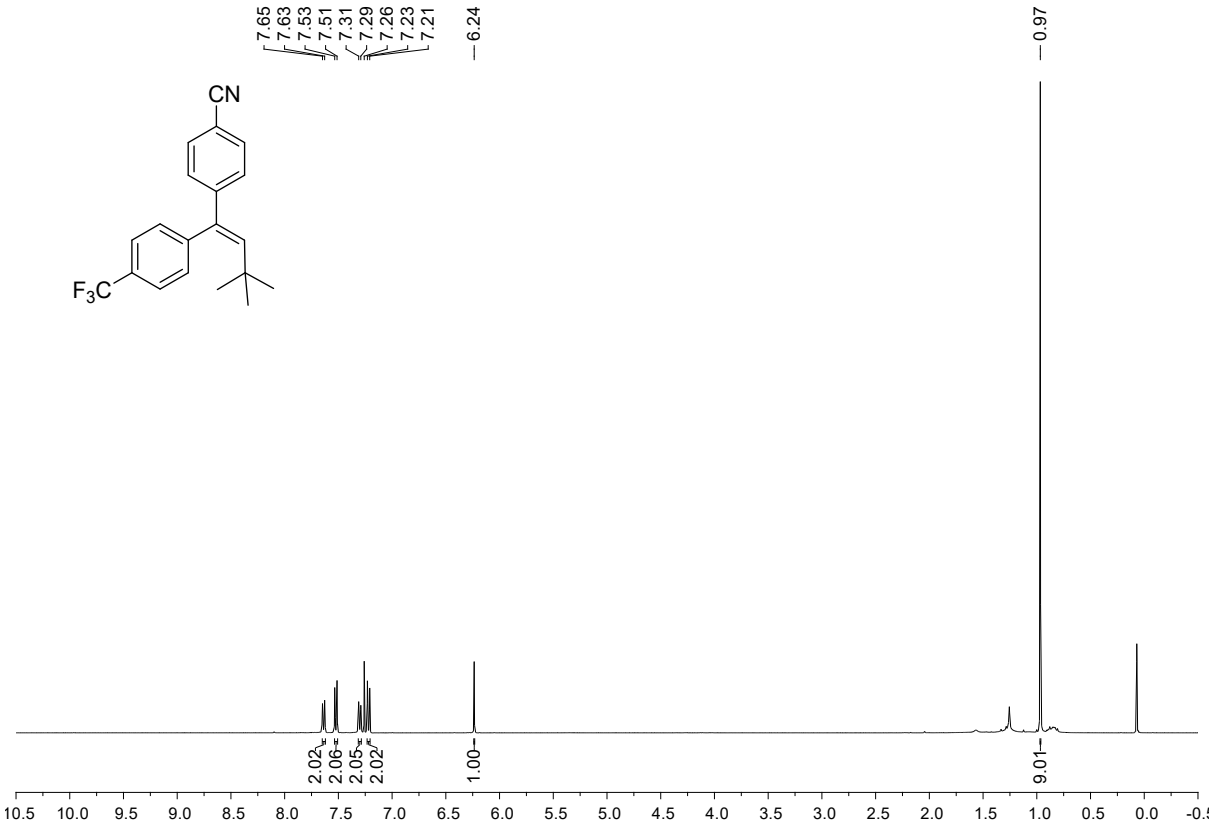


^{1}H NMR (400 MHz, $CDCl_3$) of the compound **13**.

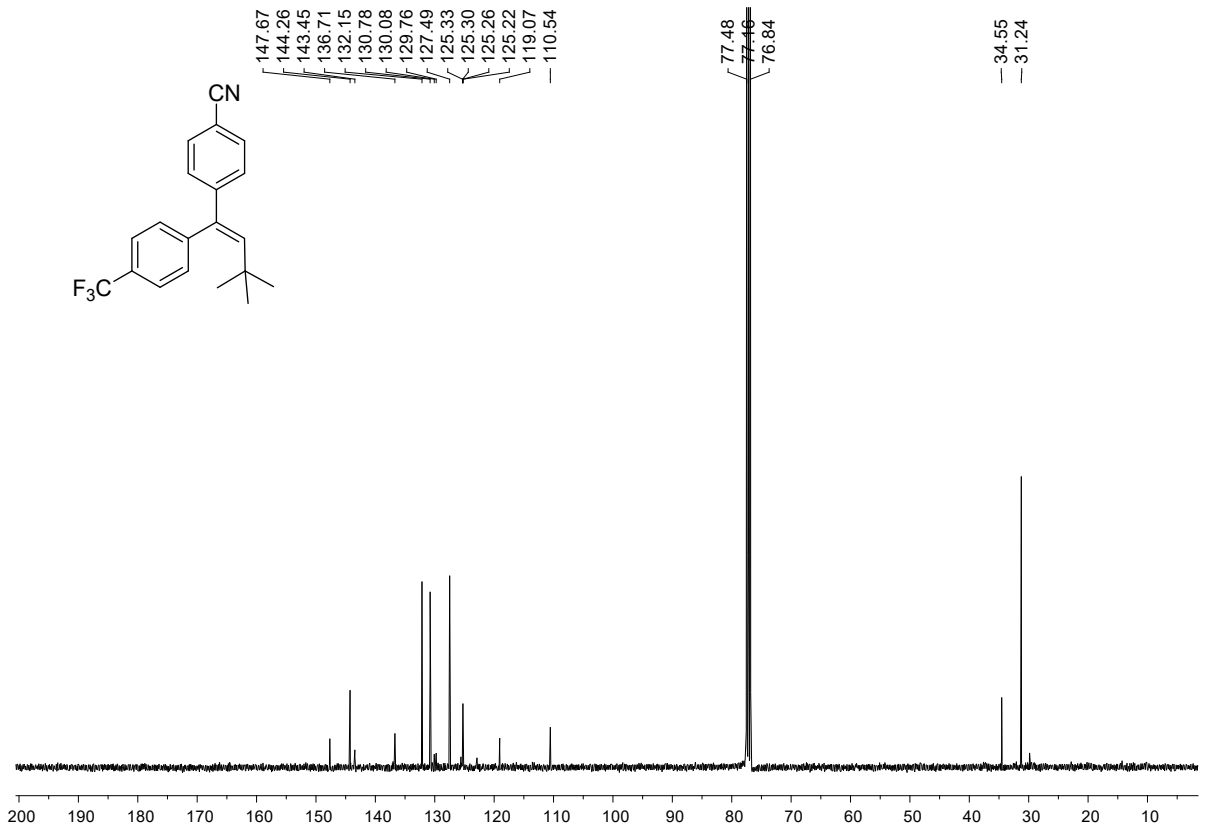


^{13}C NMR (100 MHz, $CDCl_3$) of the compound **13**.

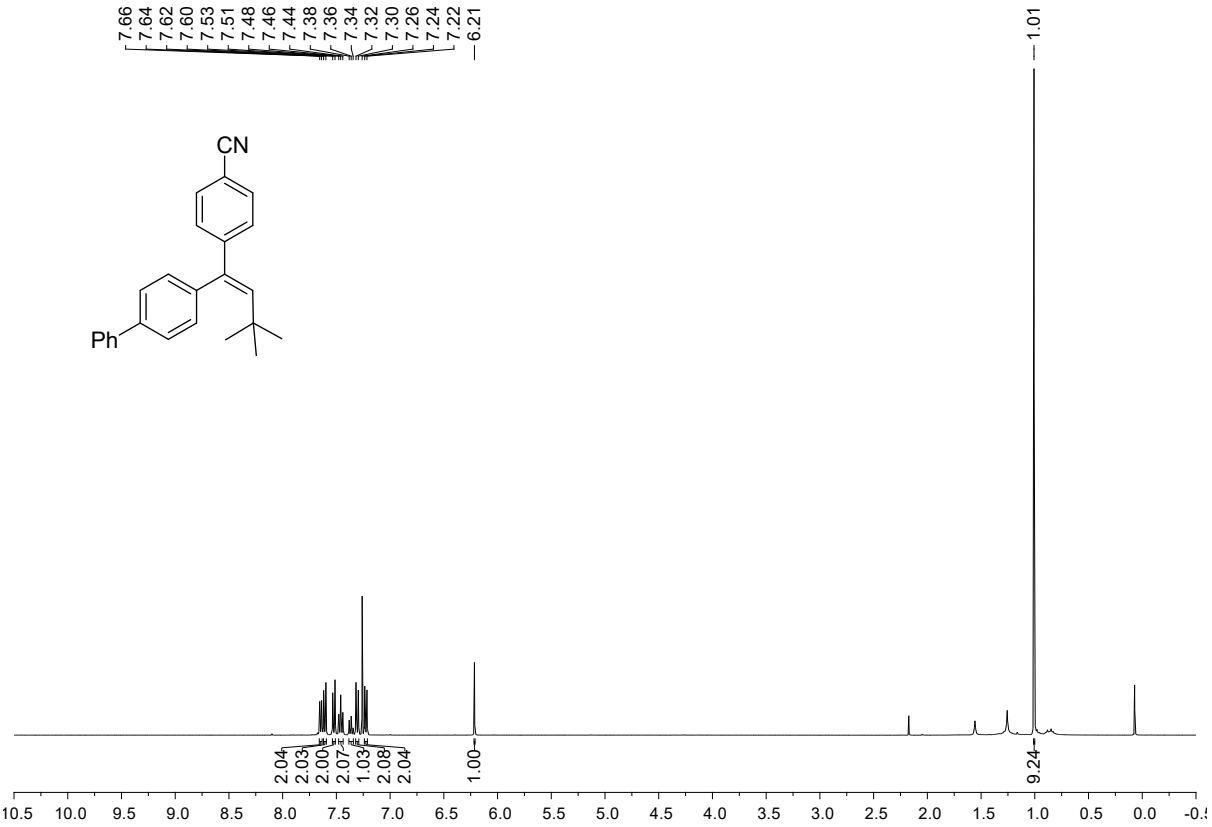
^{19}F NMR (377 MHz, $CDCl_3$) of the compound **14**.



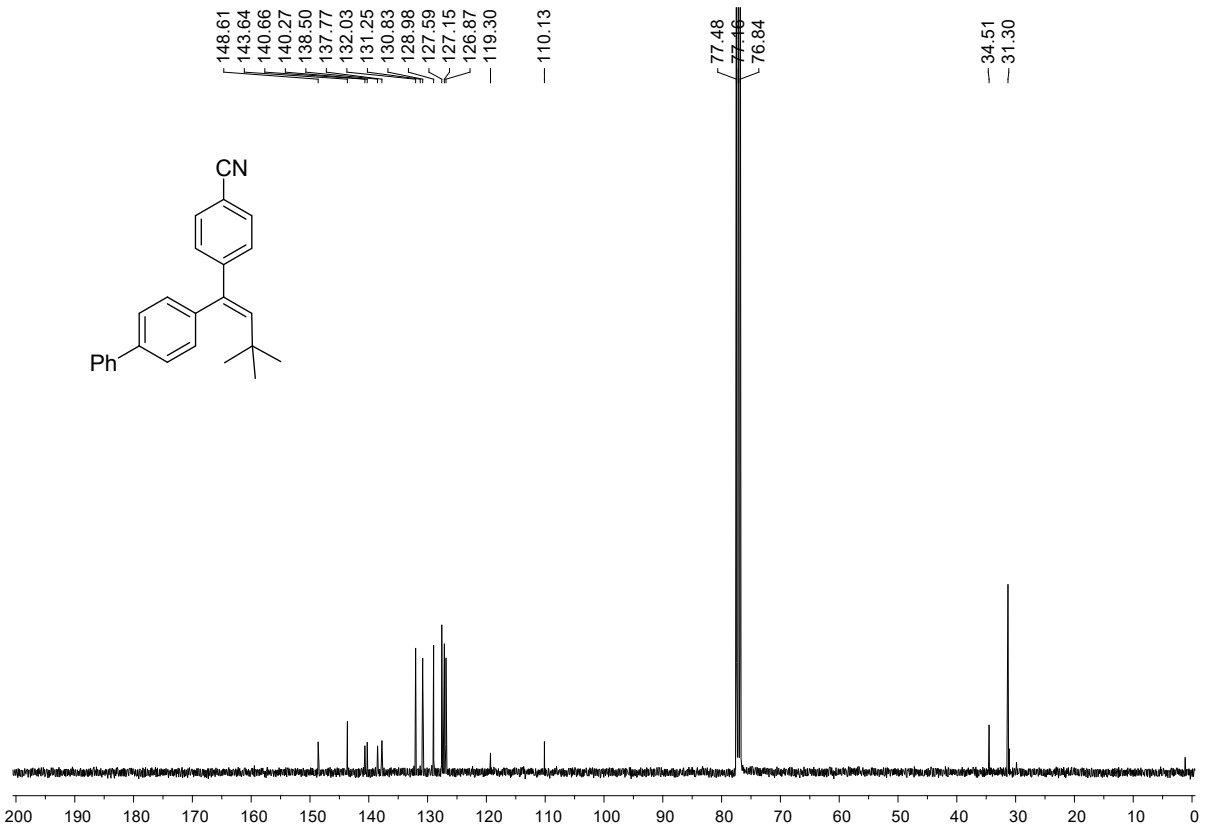
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **14**.



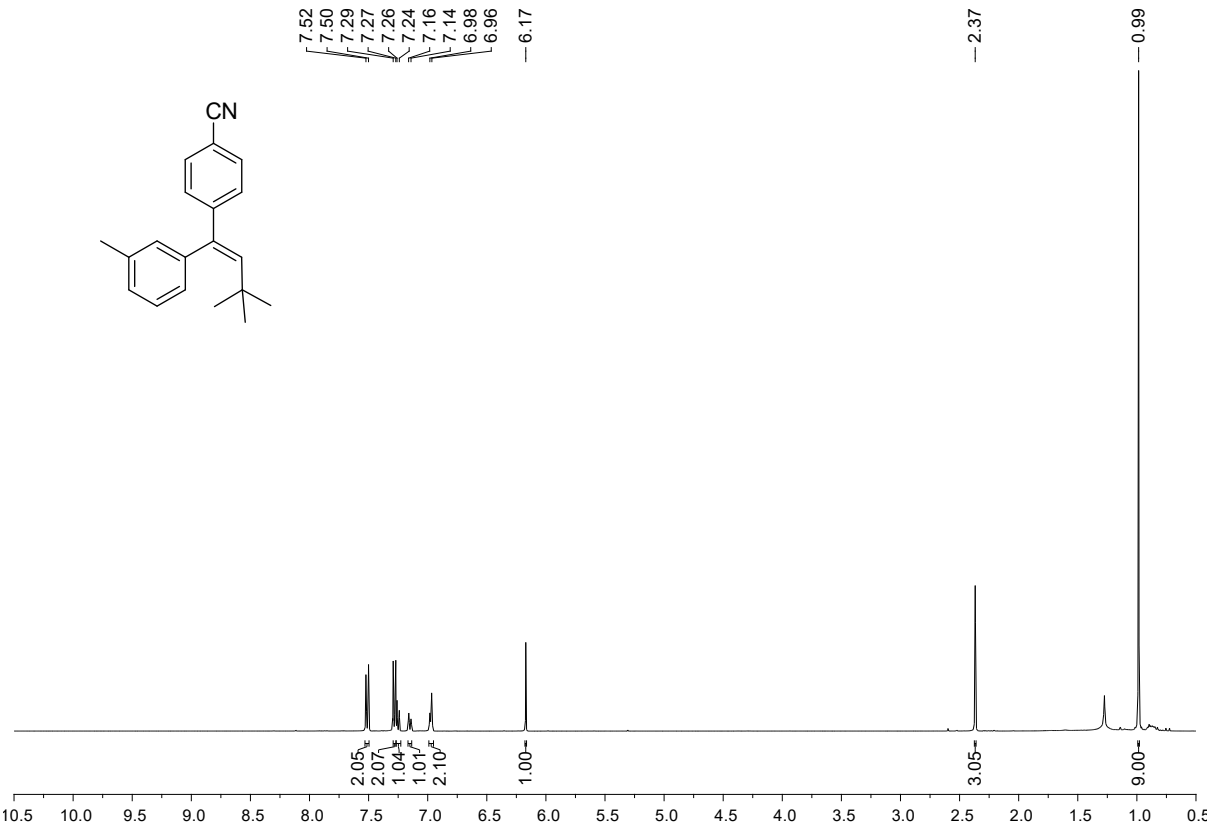
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **14**.



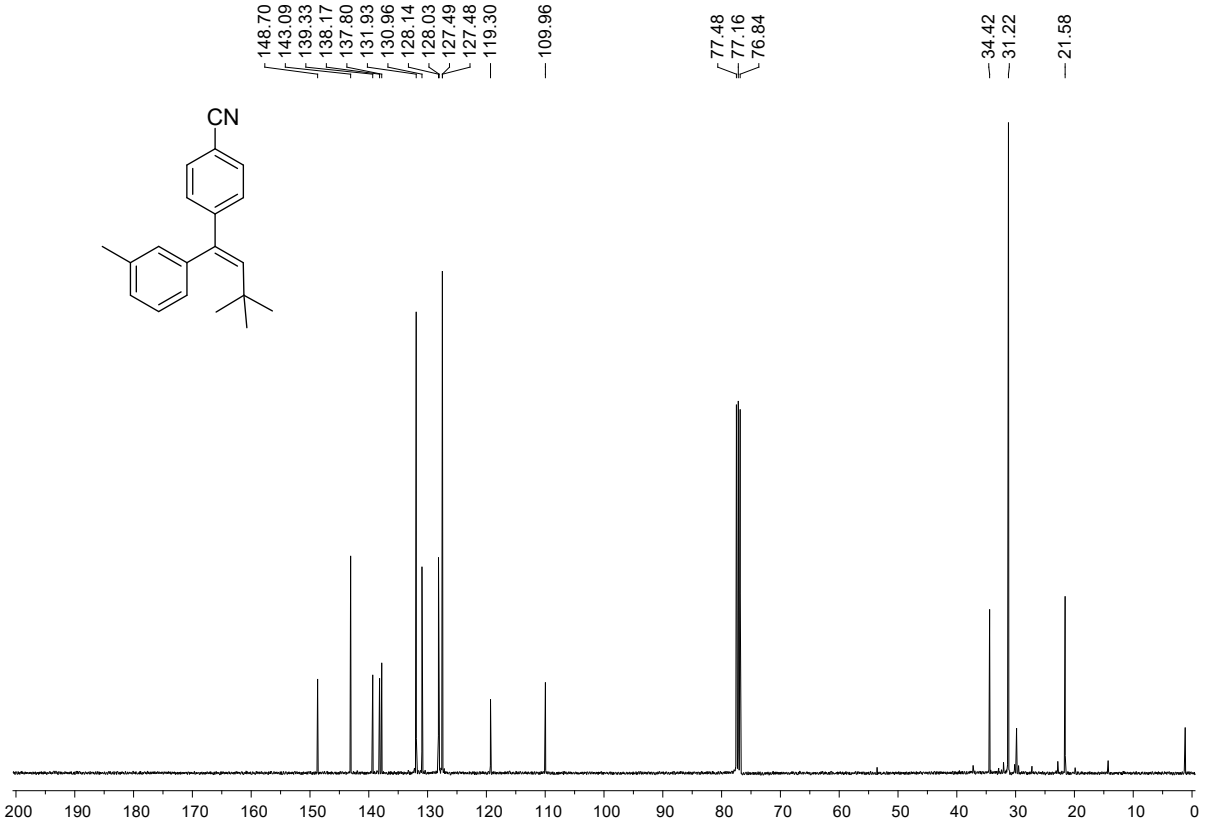
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **15**.



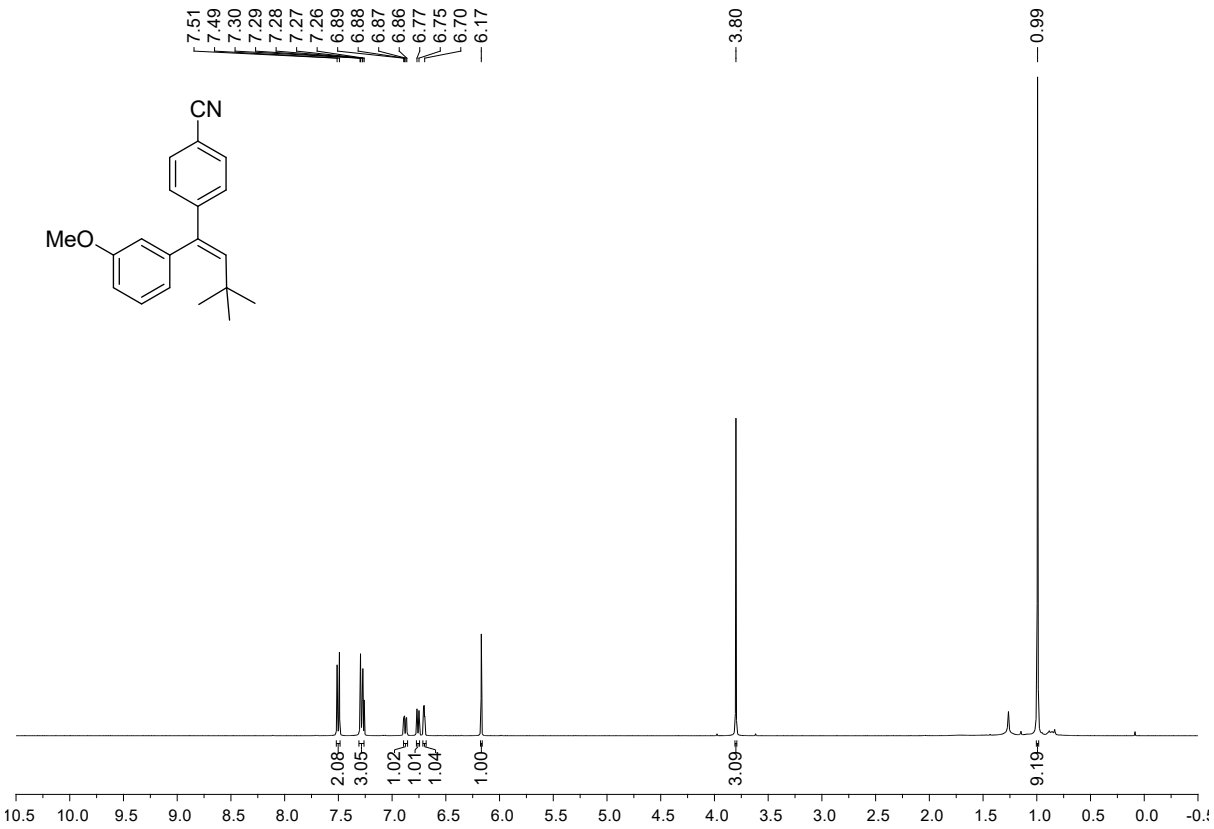
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **15**.



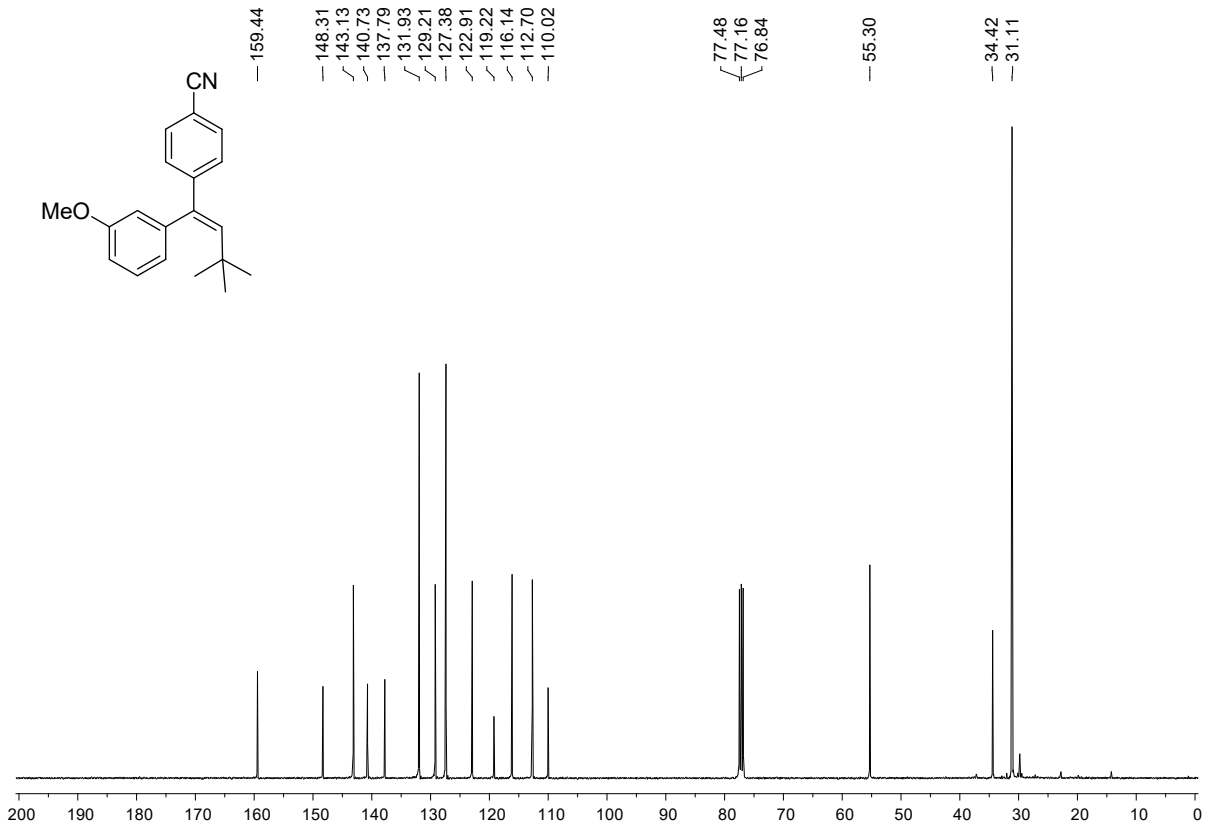
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **16**.



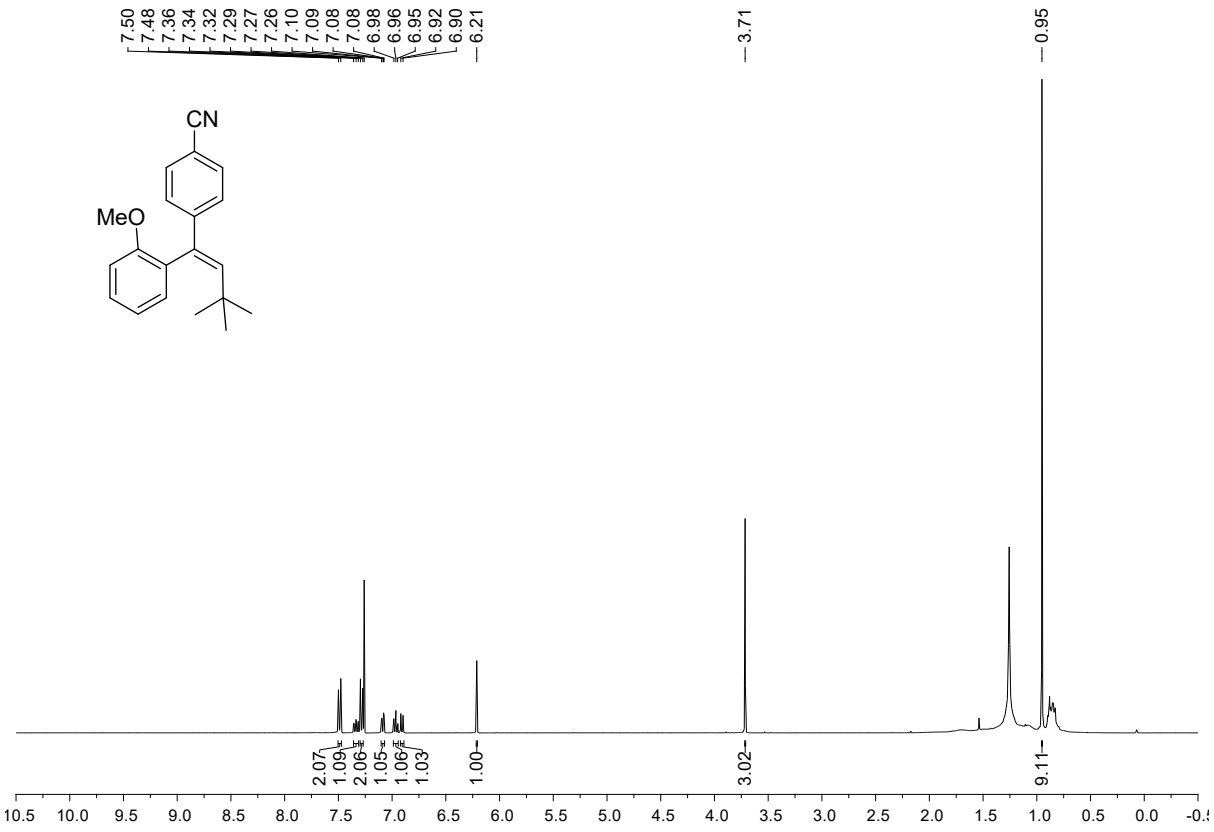
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **16**.



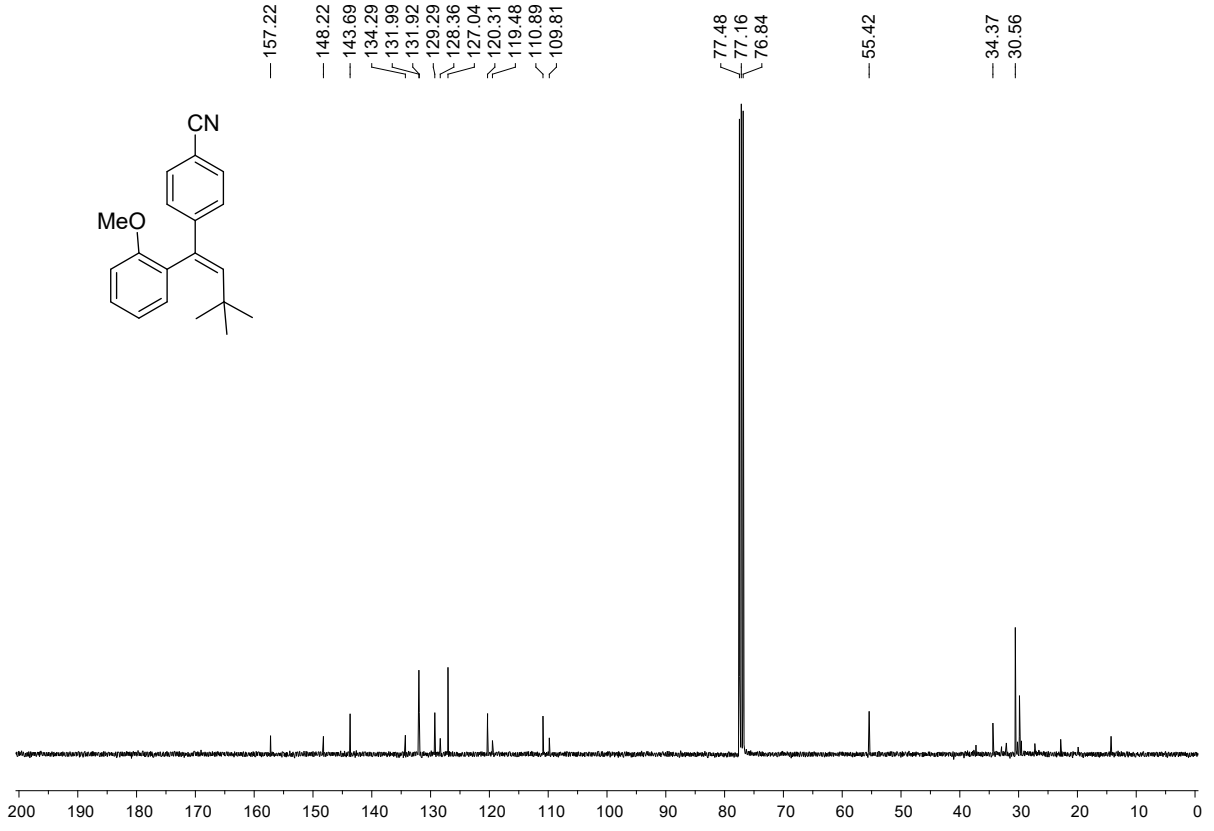
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **17**.



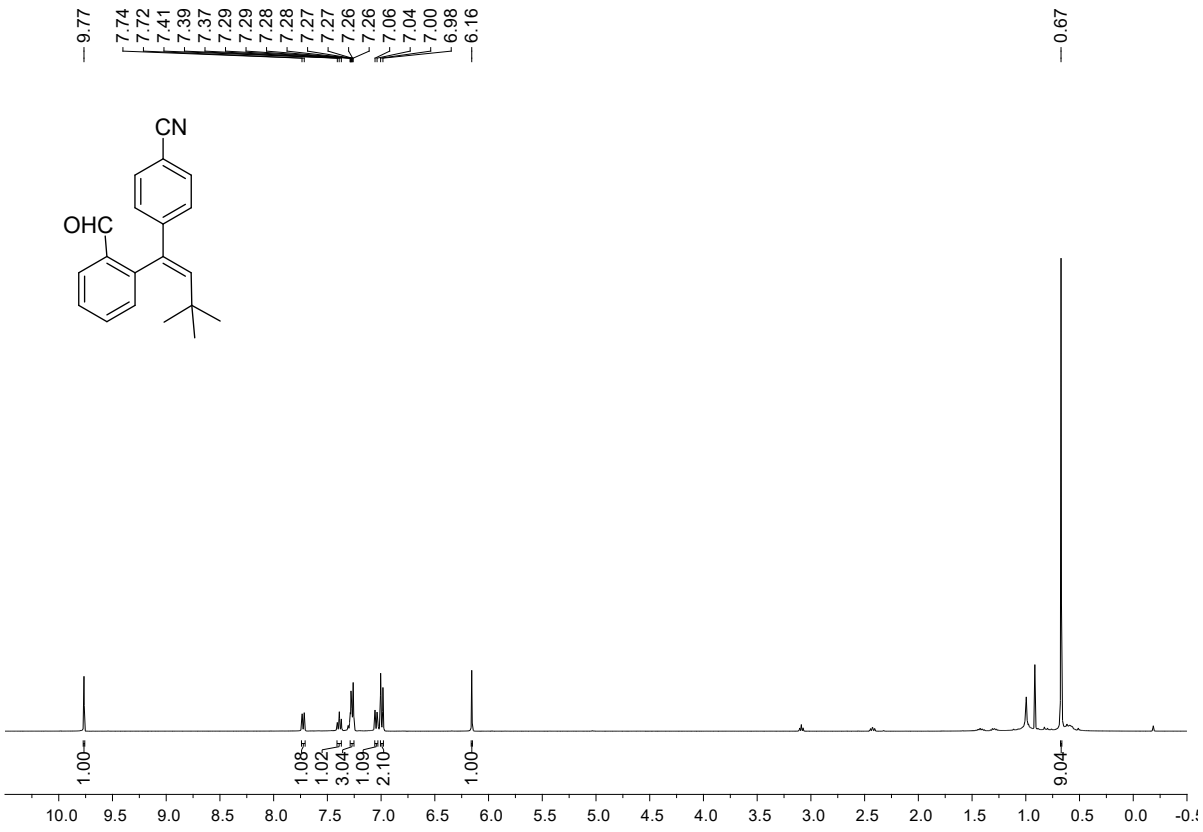
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **17**.



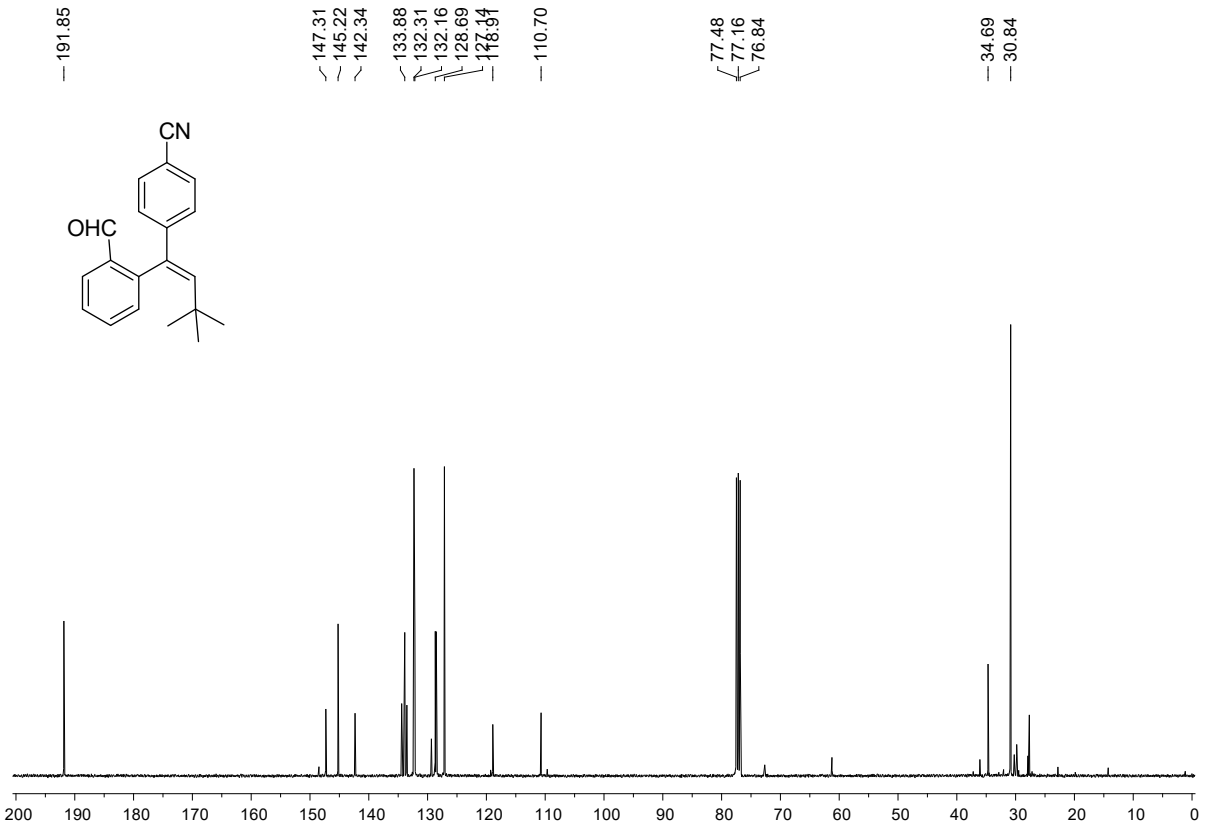
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **18**.



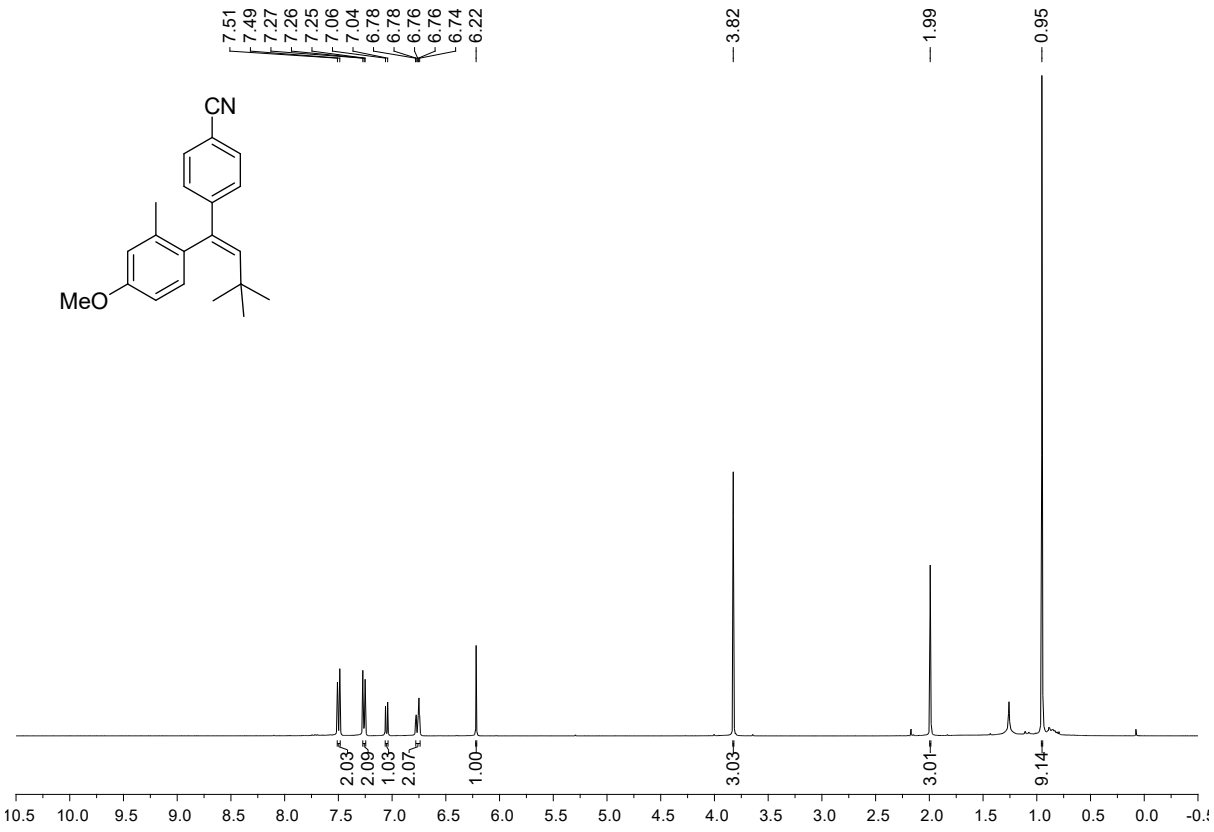
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **18**.



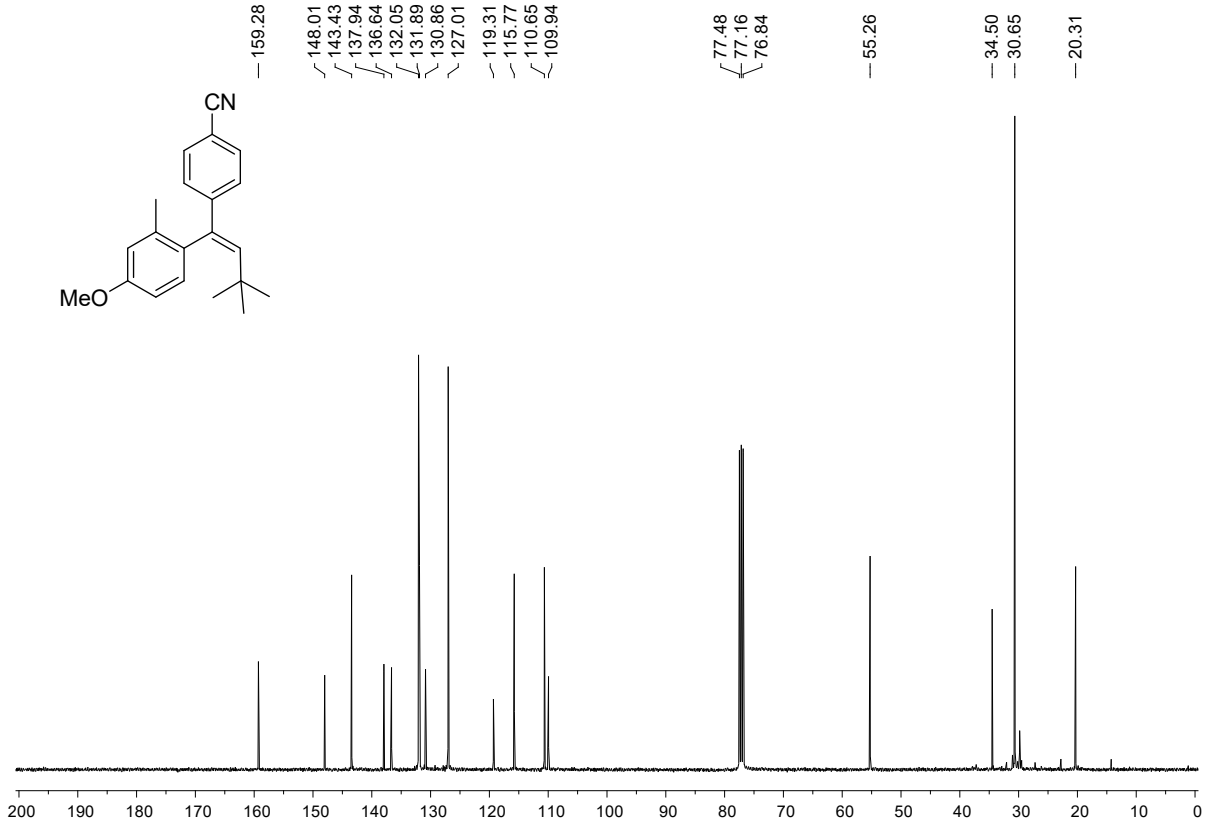
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **19**.



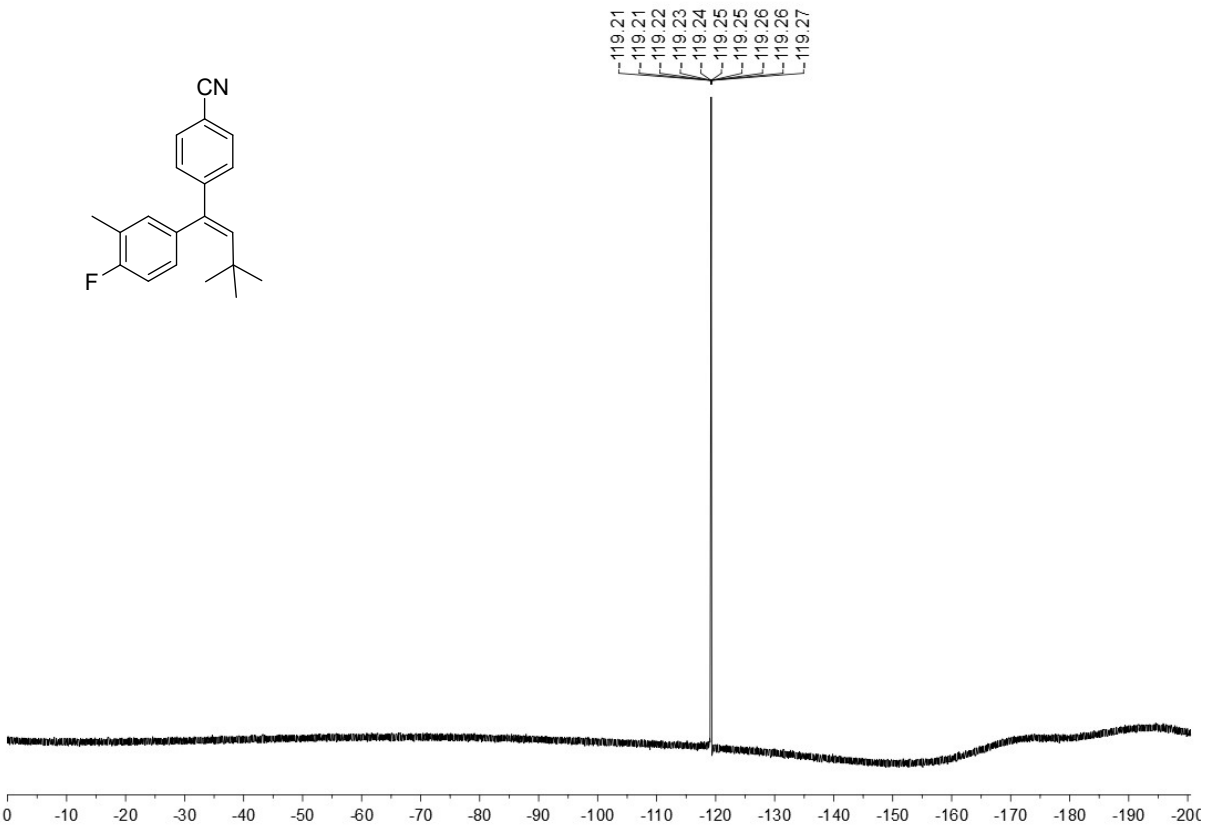
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **19**.



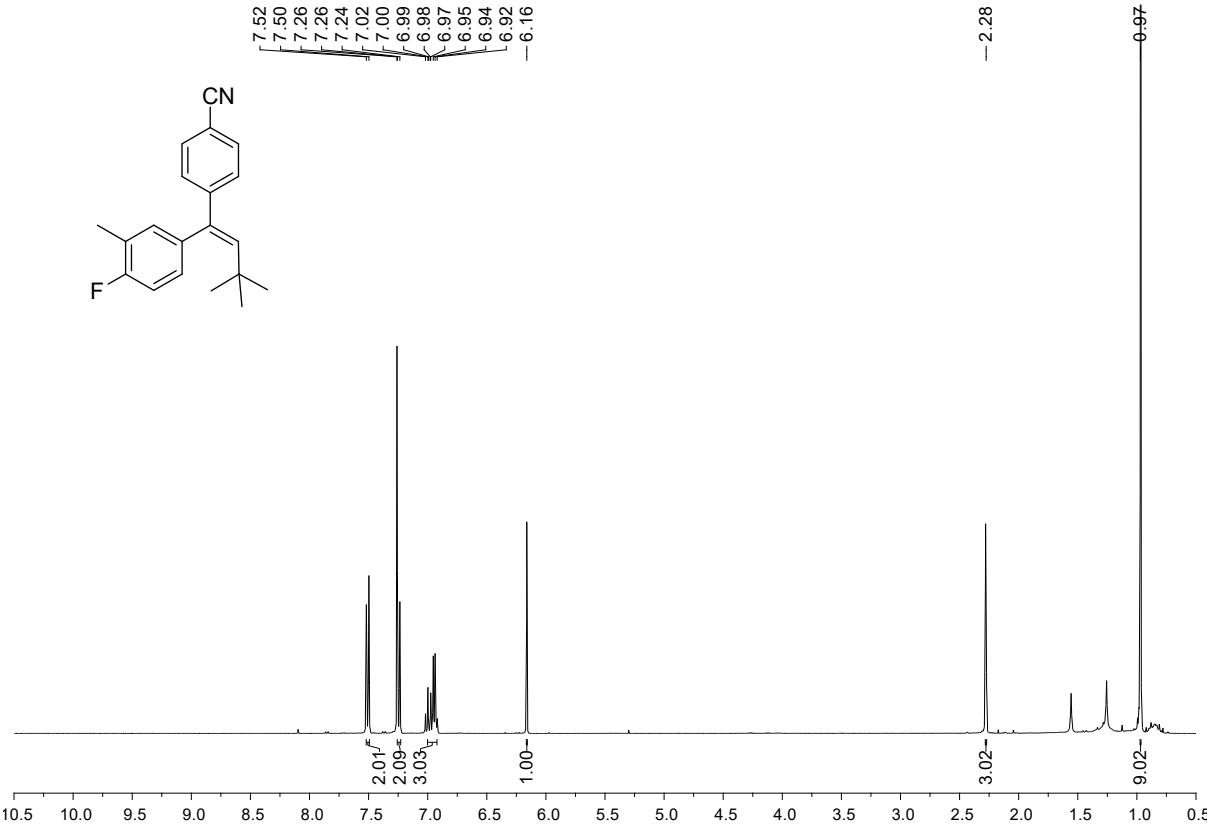
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **20**.



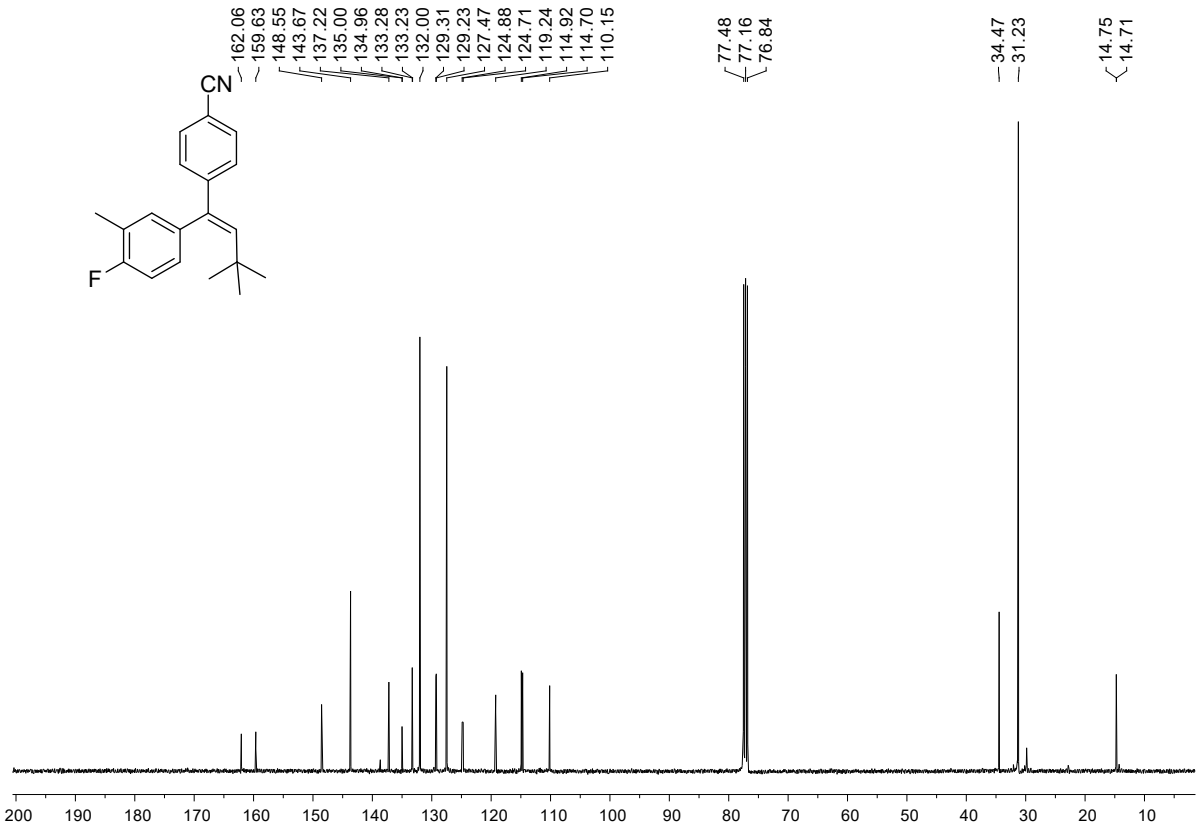
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **20**.



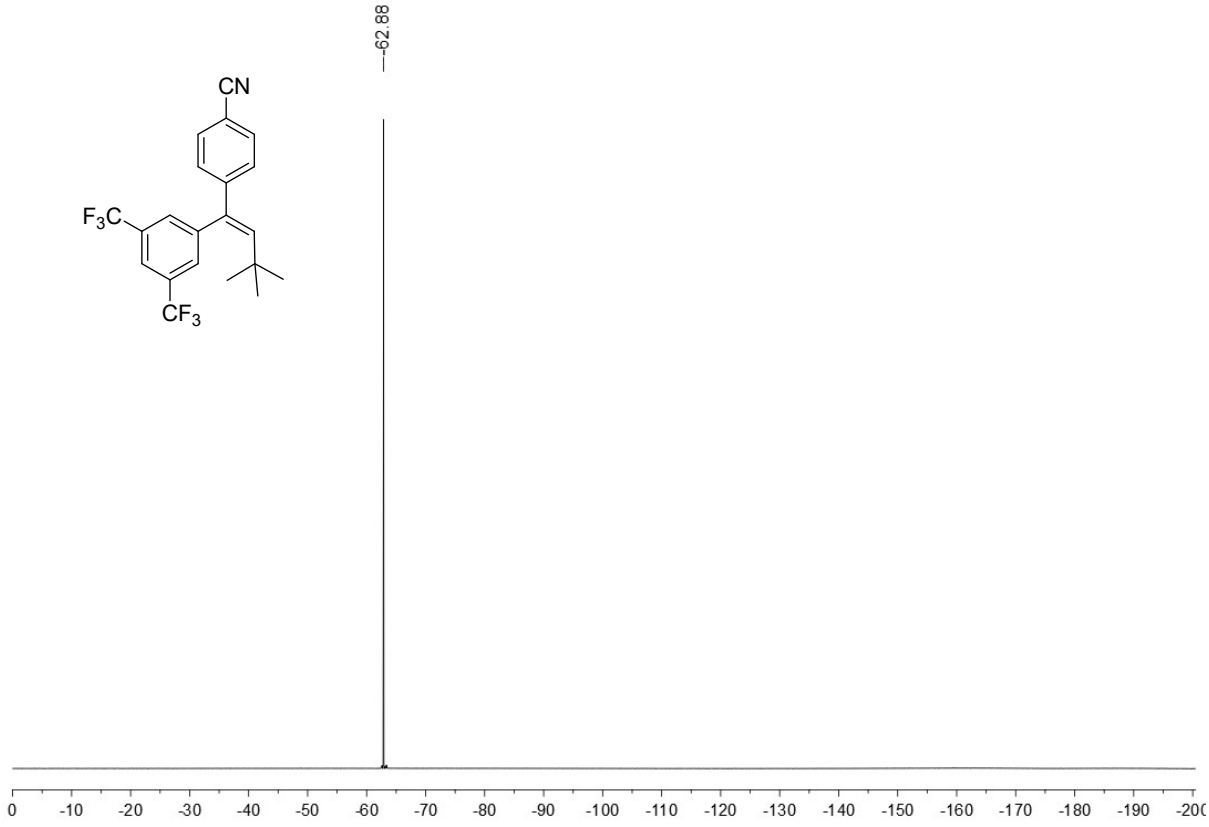
^{19}F NMR (377 MHz, $CDCl_3$) of the compound **21**.



^{1}H NMR (400 MHz, $CDCl_3$) of the compound **21**.

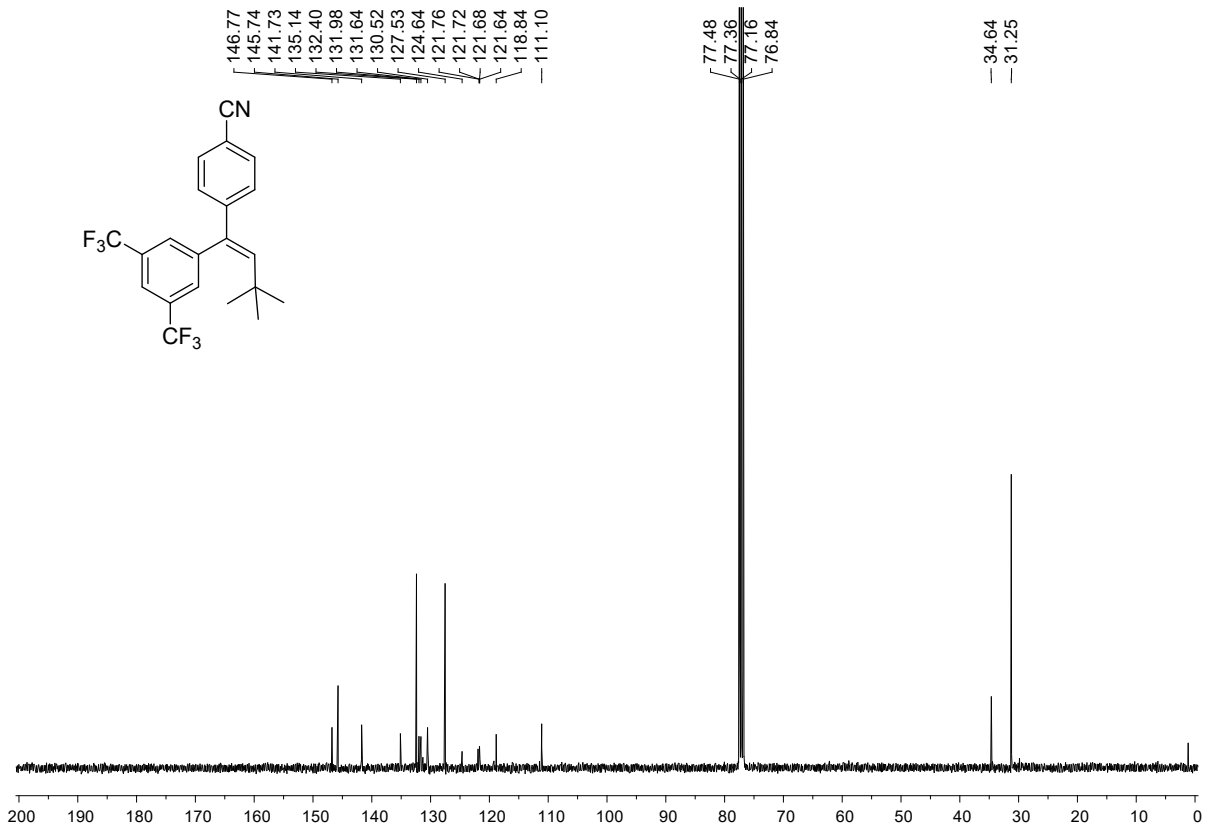


^{13}C NMR (100 MHz, $CDCl_3$) of the compound **21**.

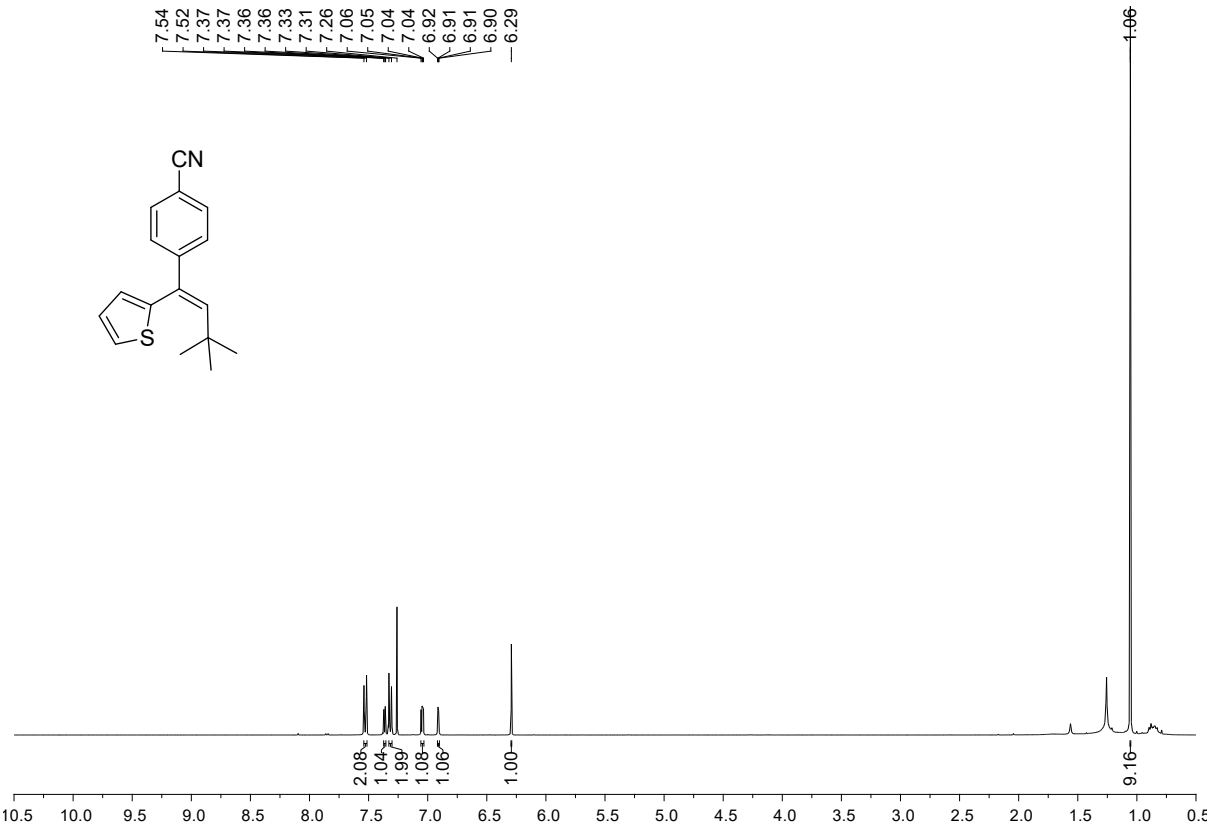


^{19}F NMR (377 MHz, $CDCl_3$) of the compound **22**.

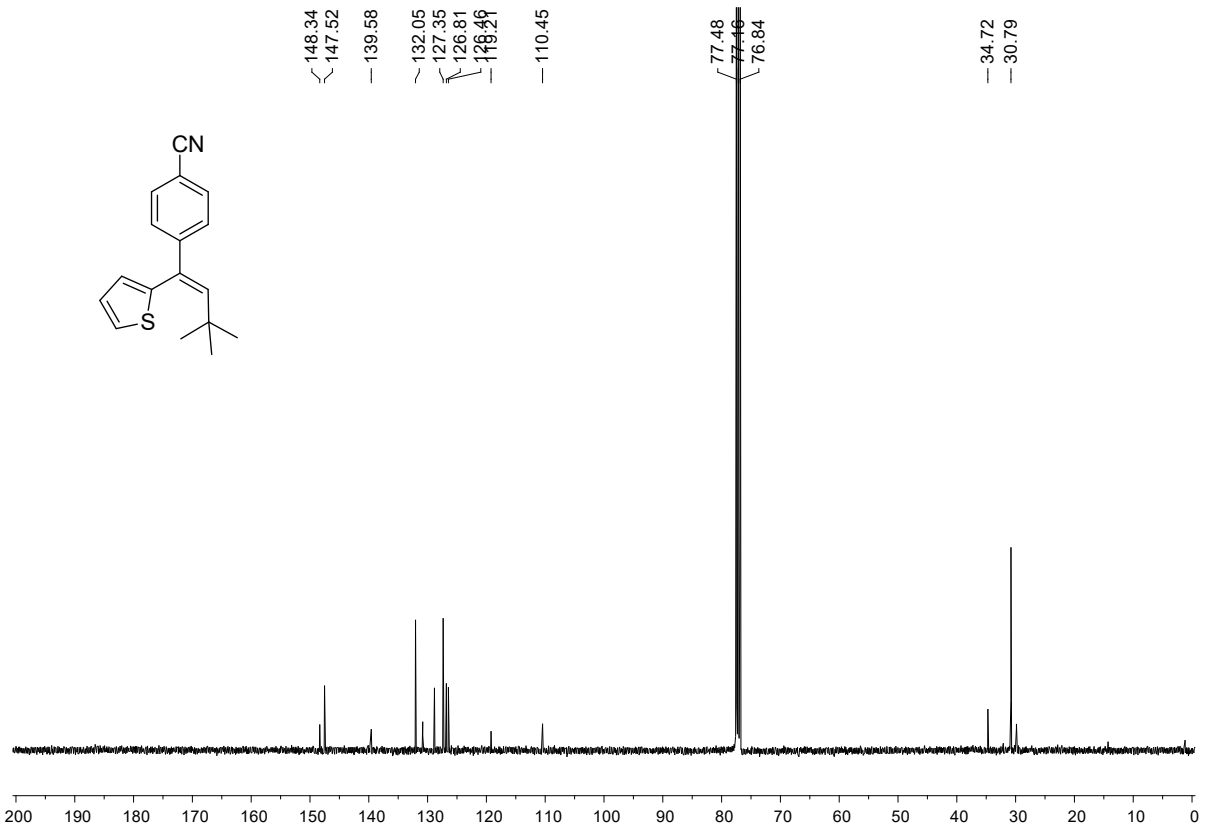
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **22**.



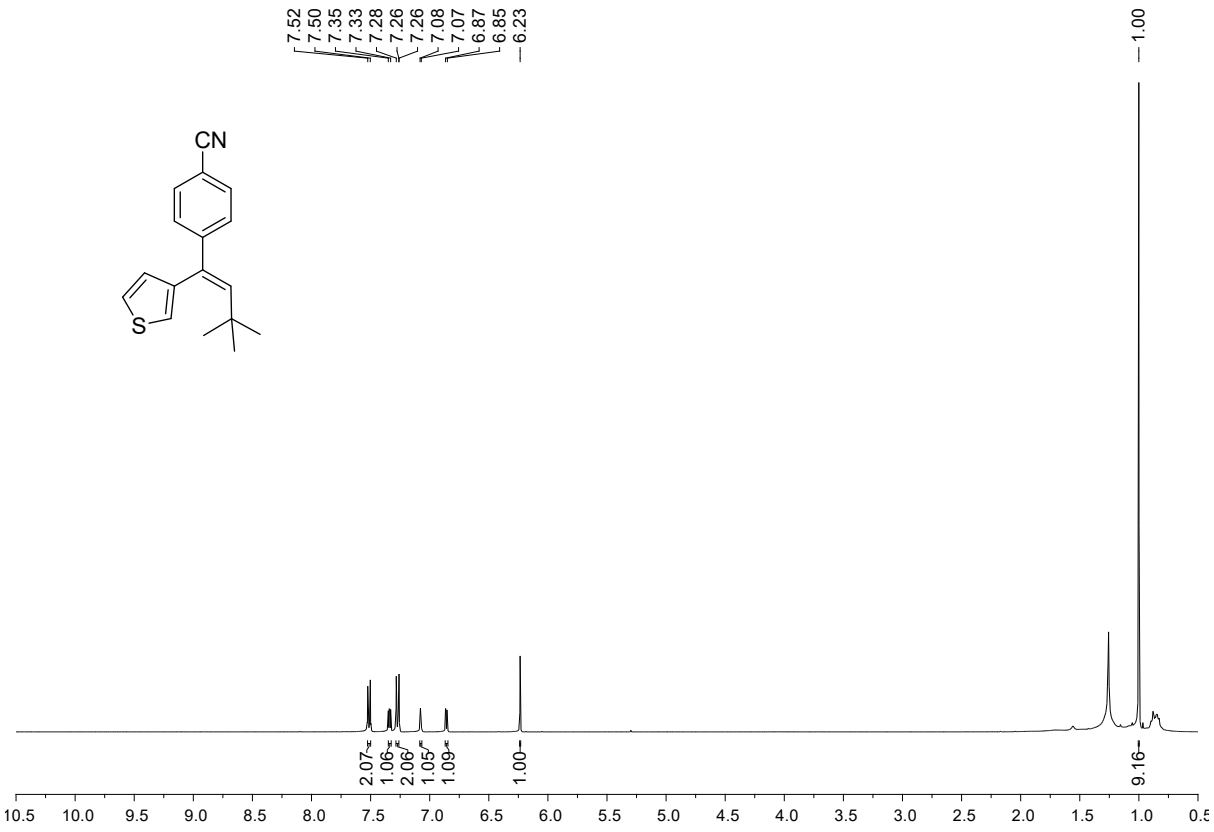
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **22**.



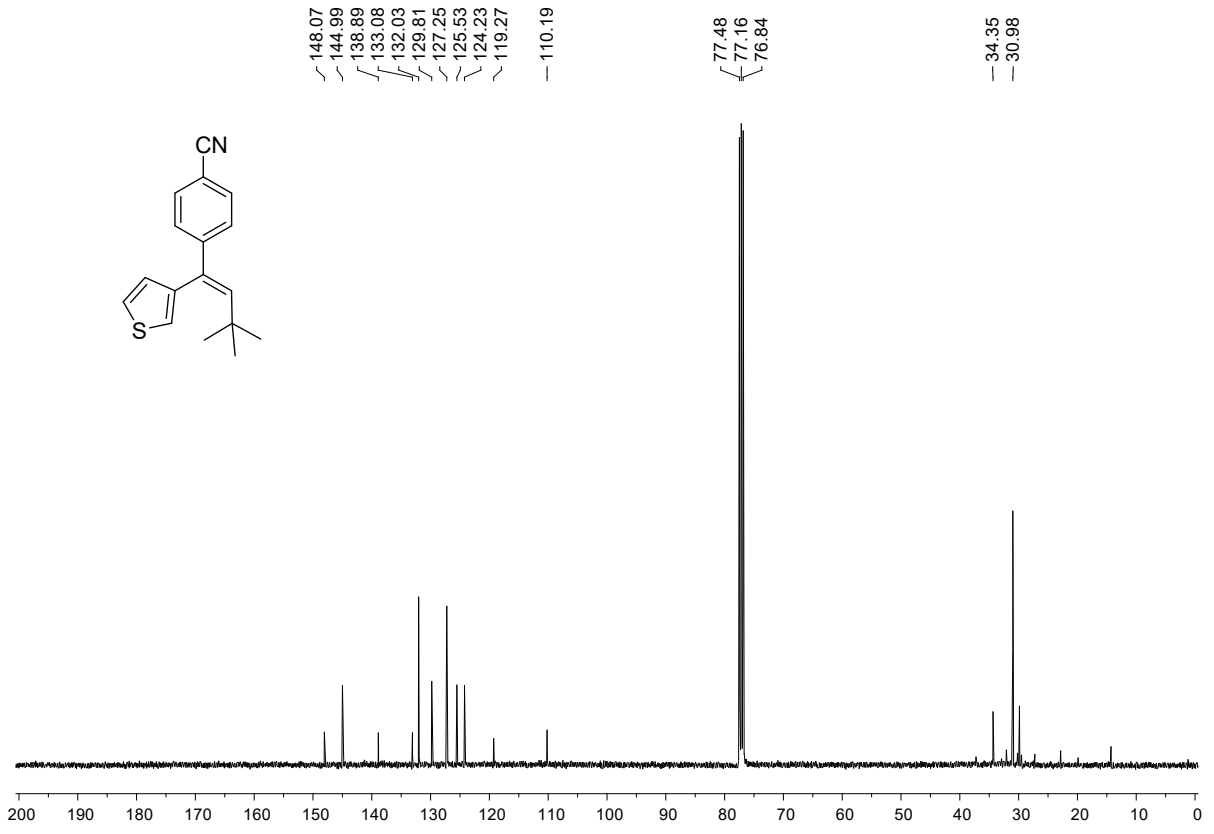
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **23**.



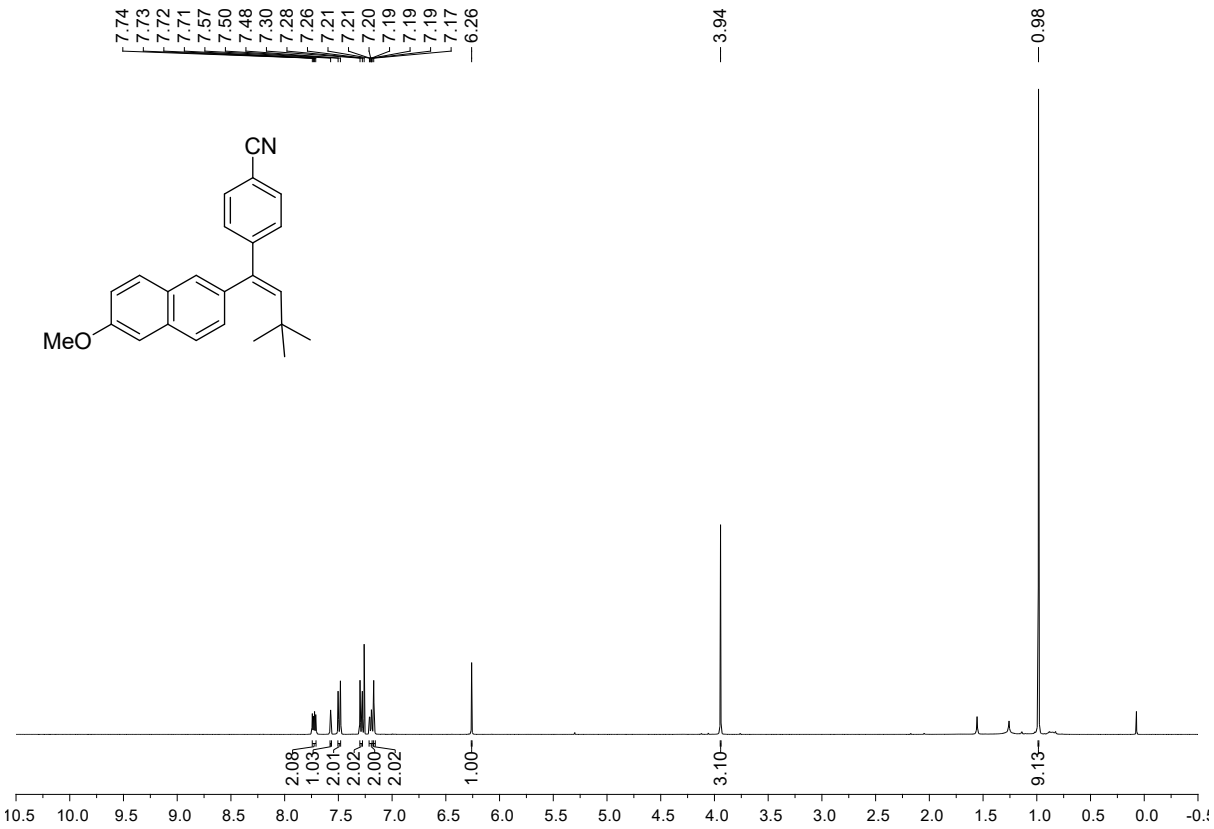
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **23**.



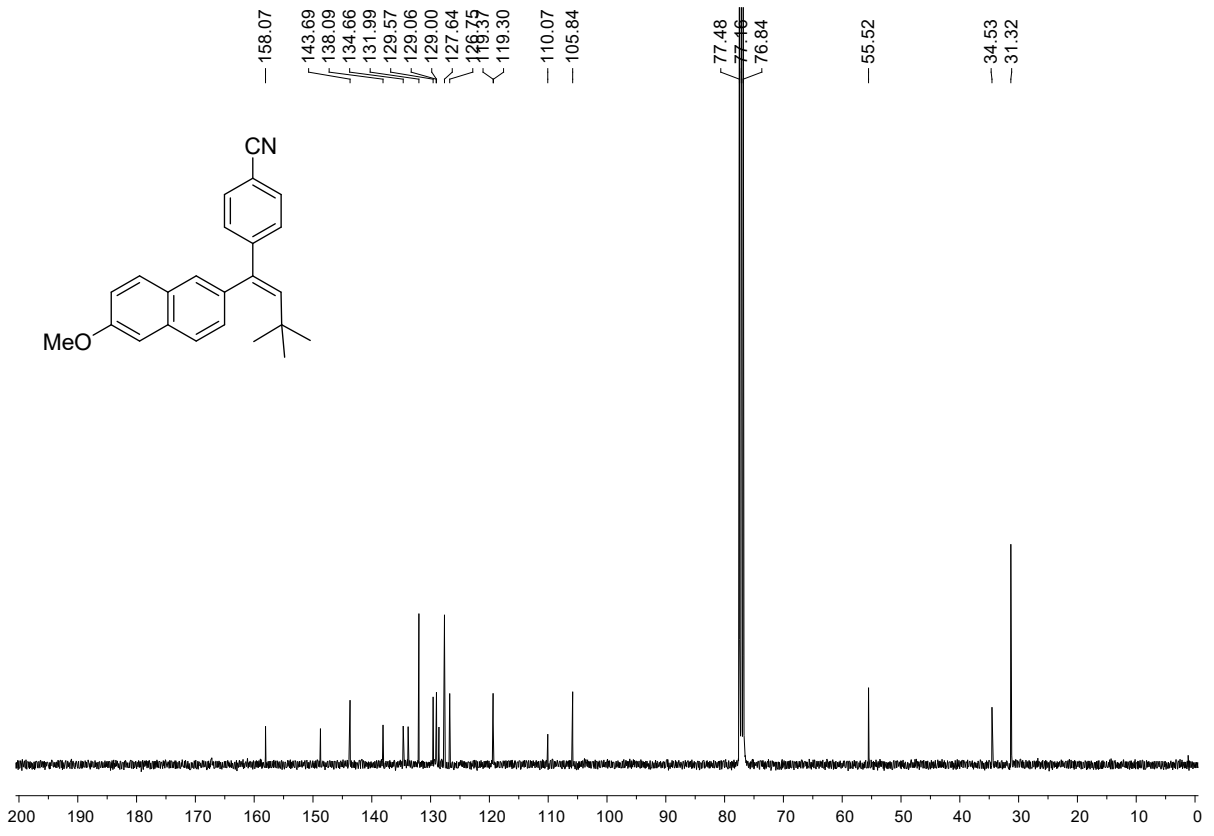
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **24**.



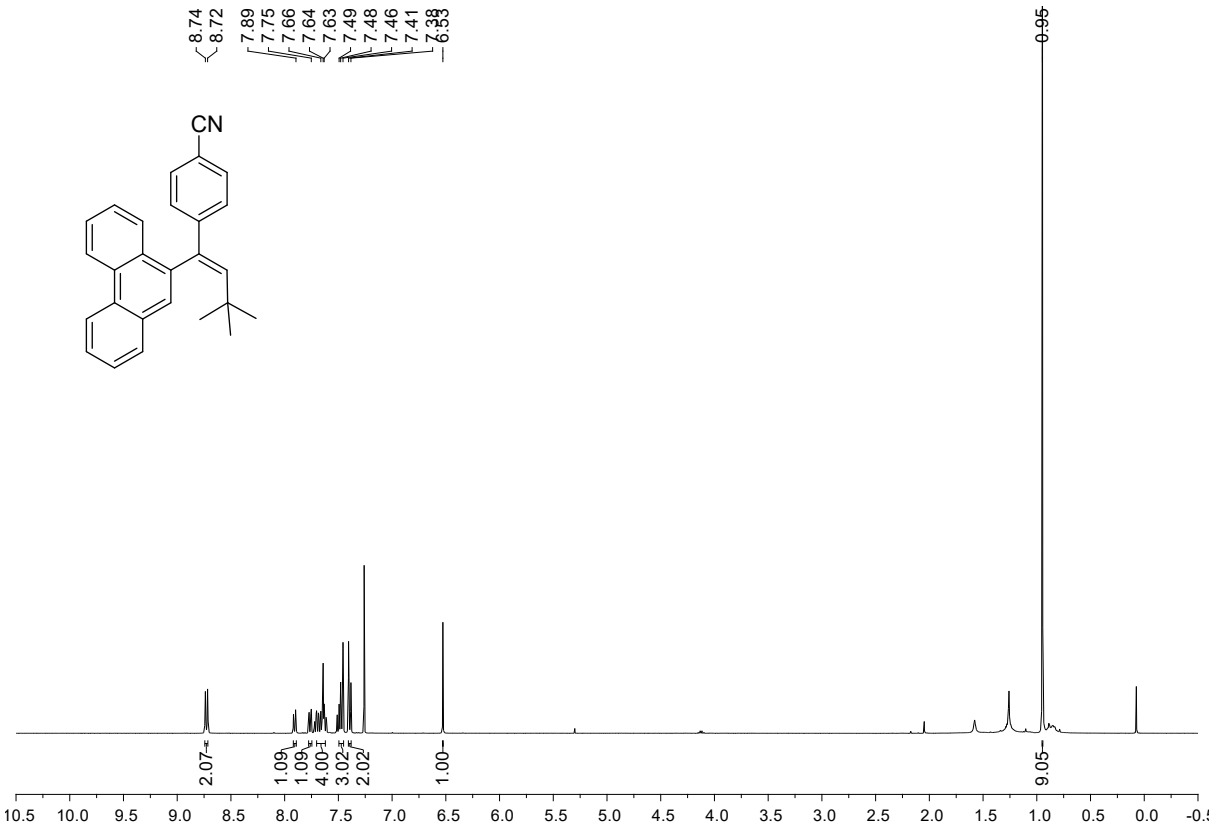
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **24**.



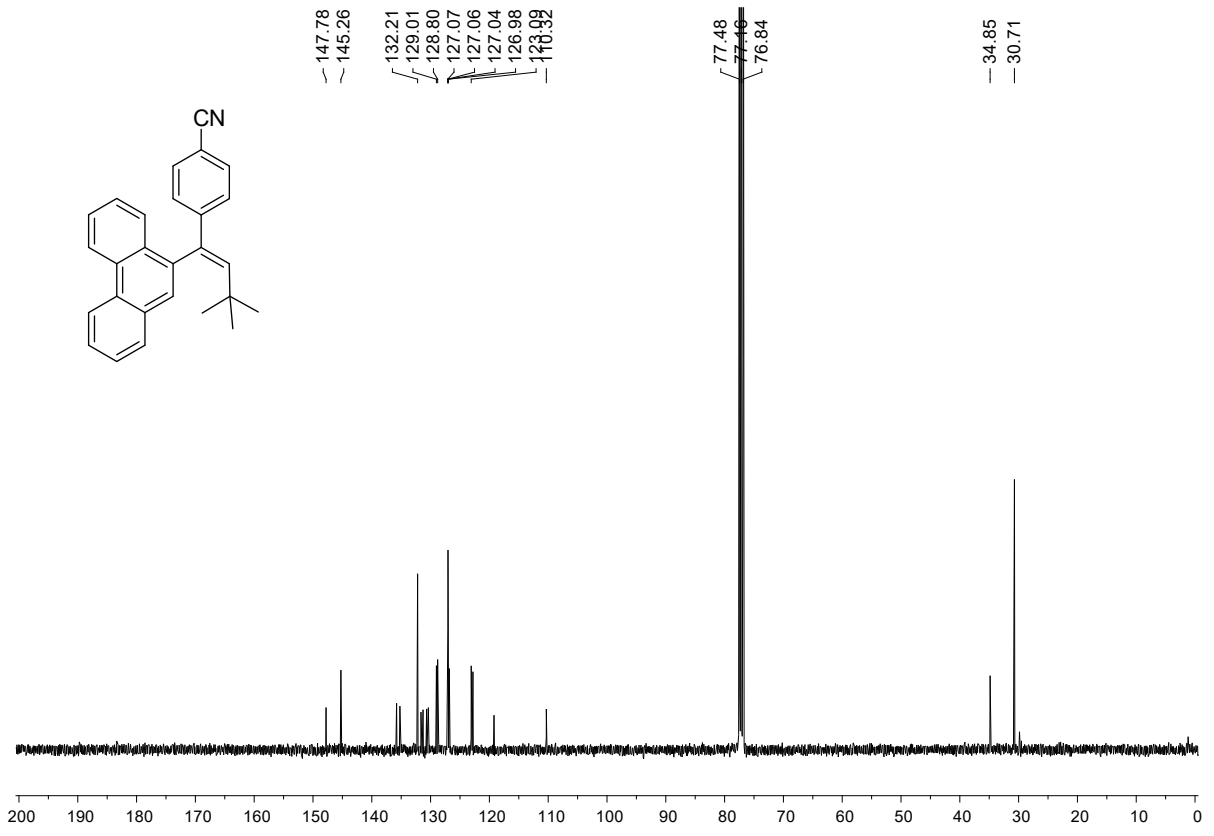
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **25**.



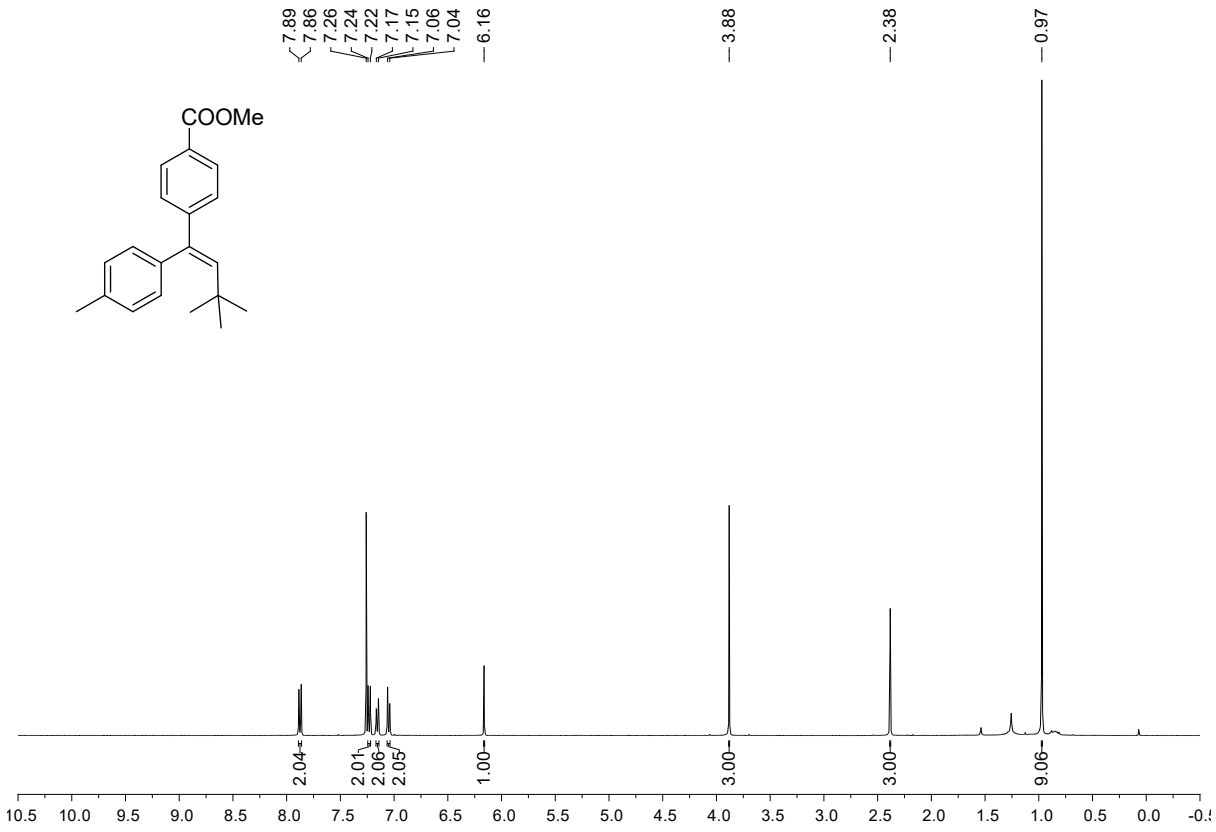
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **25**.



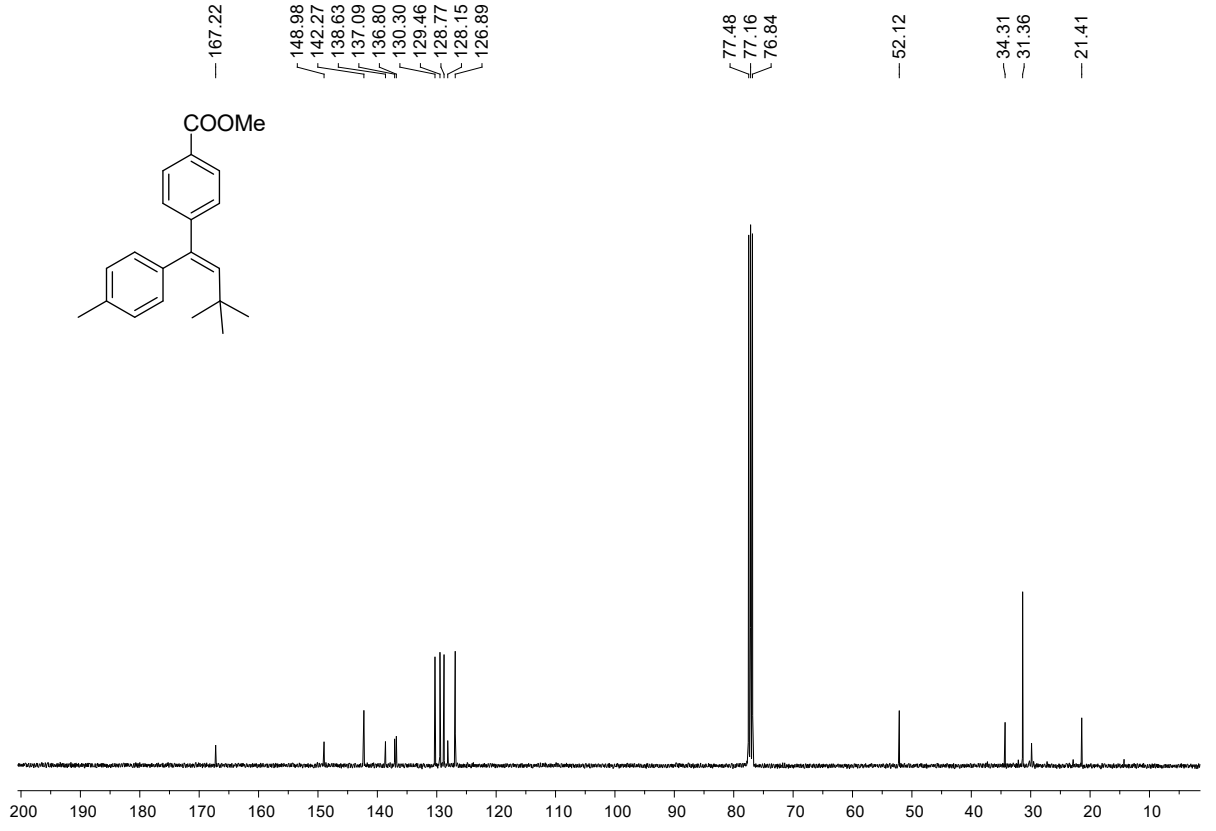
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **26**.



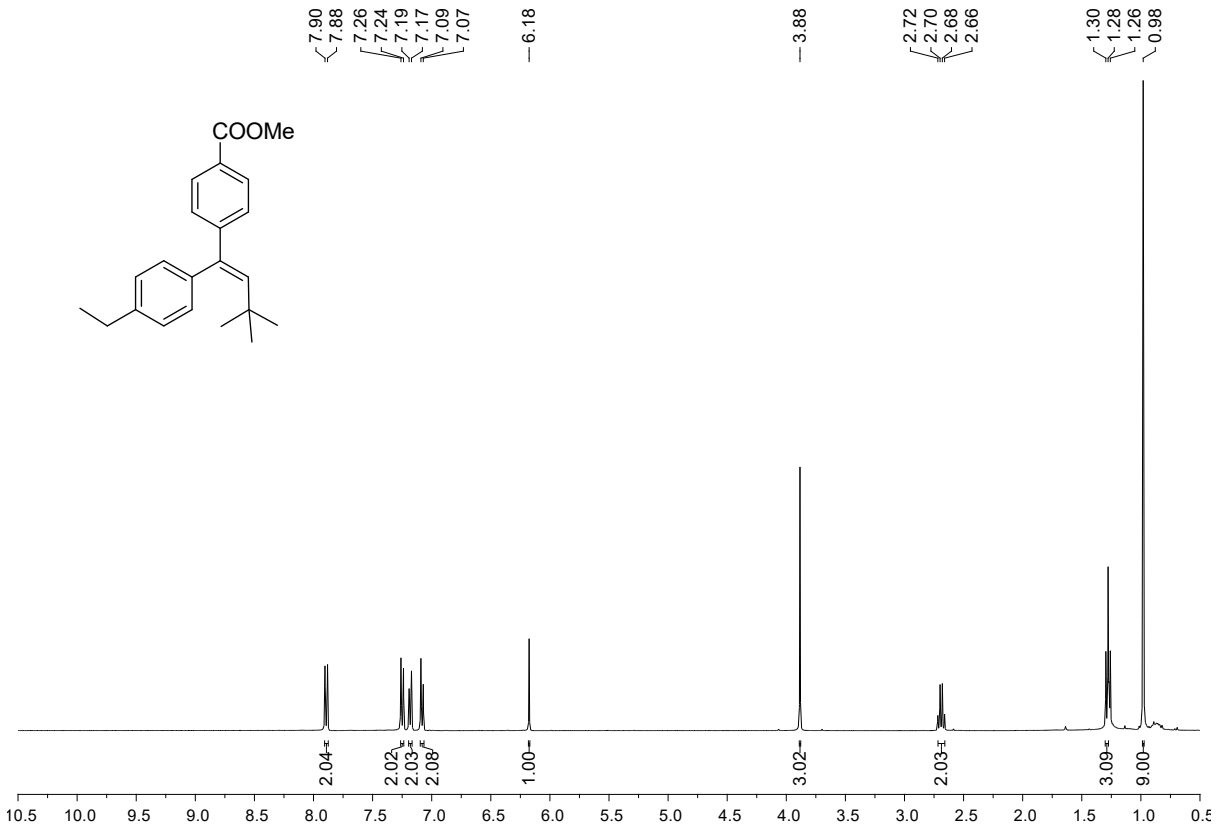
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **26**.



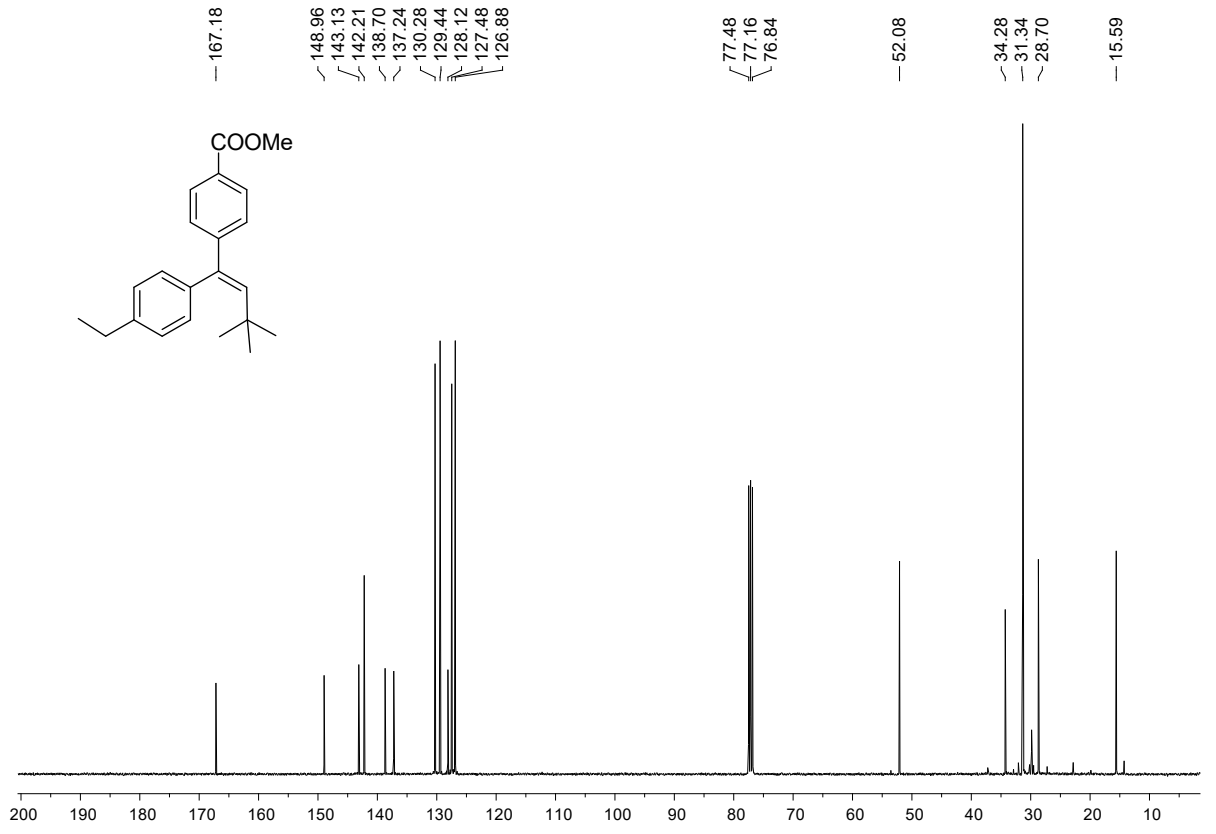
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **27**.



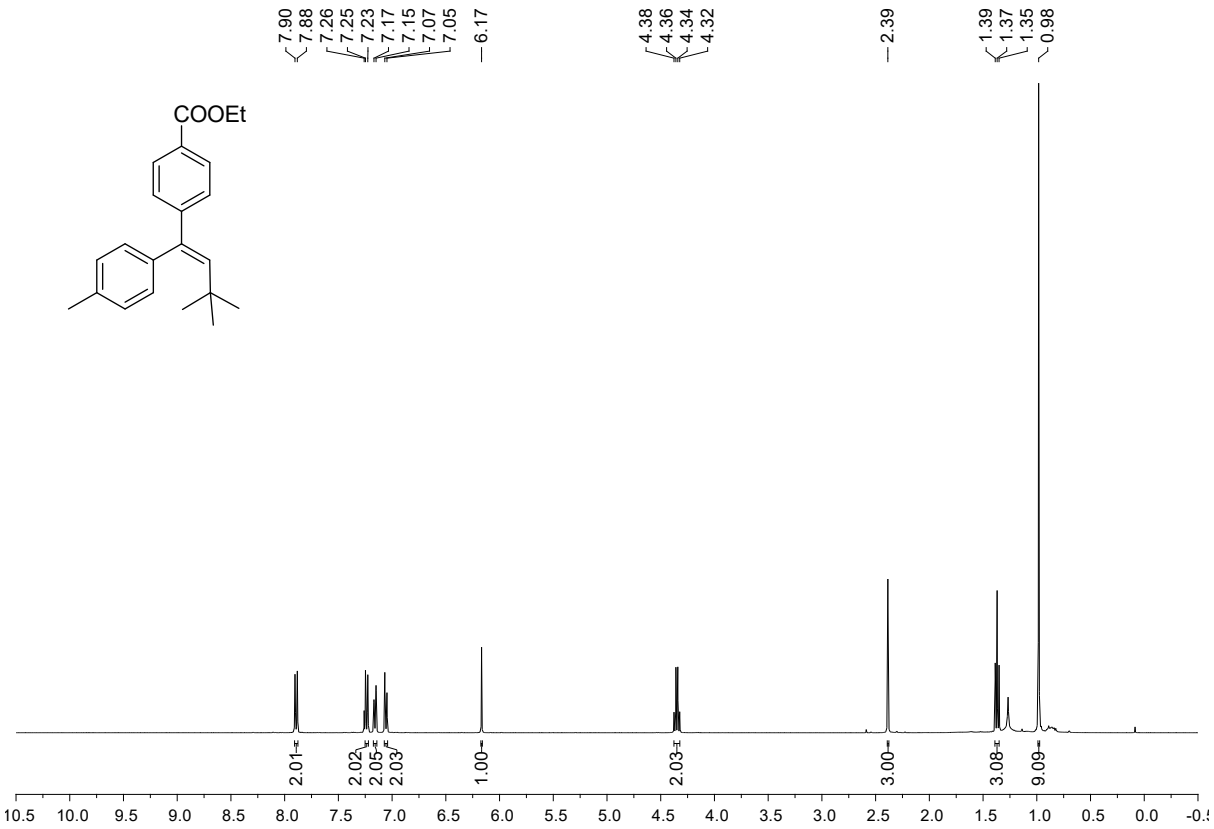
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **27**.



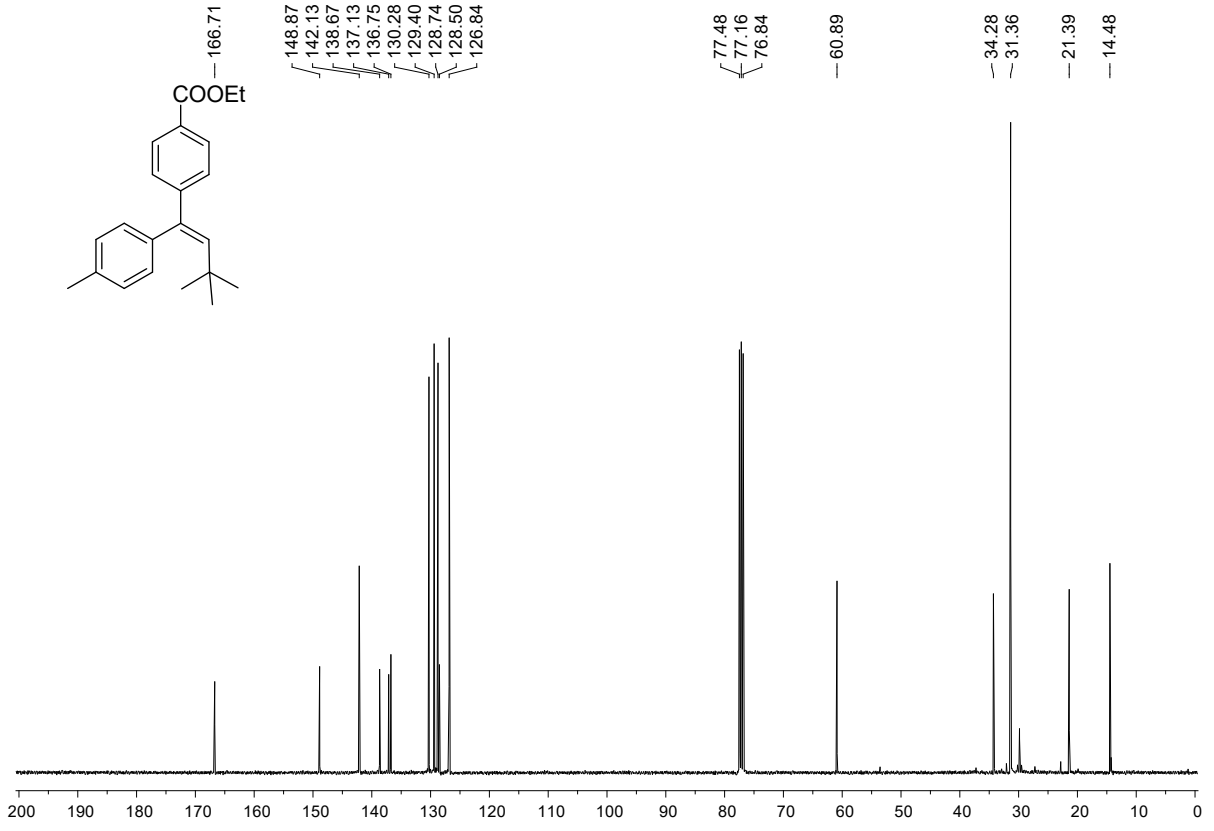
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **28**.



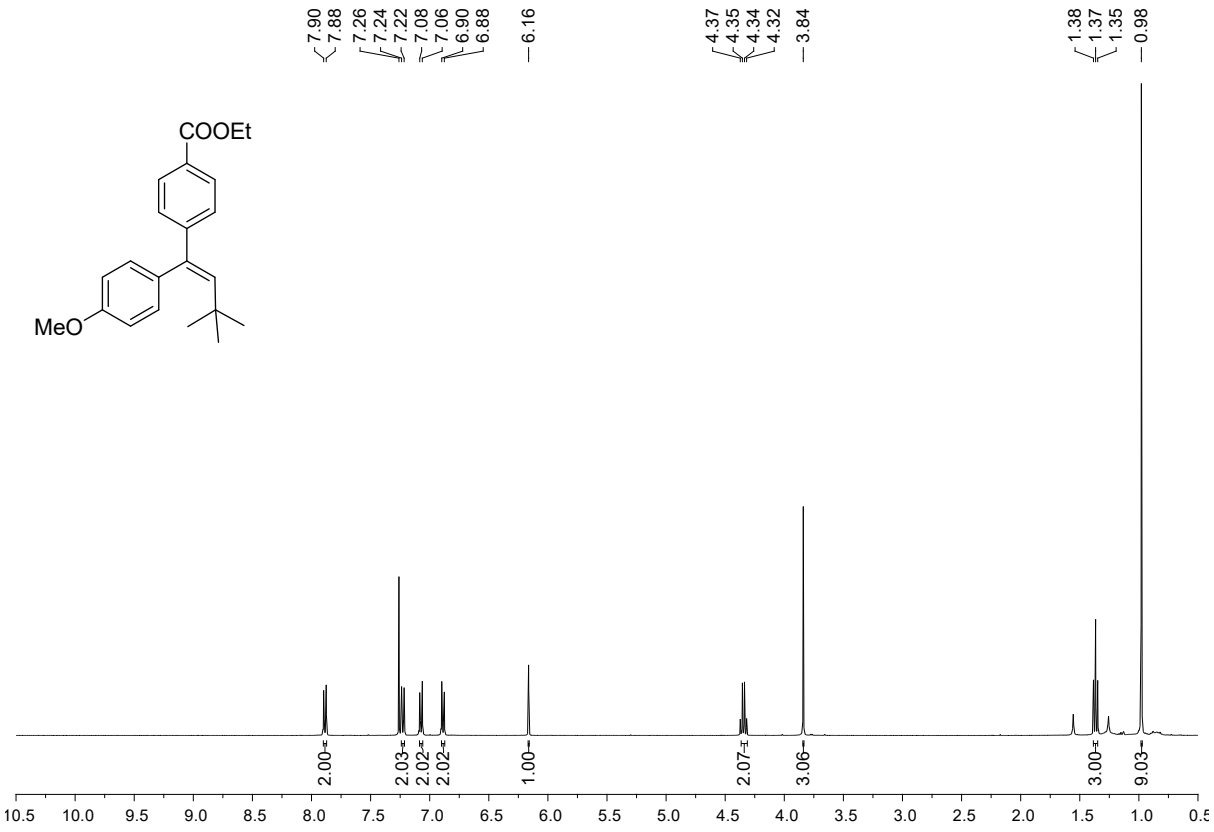
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **28**.



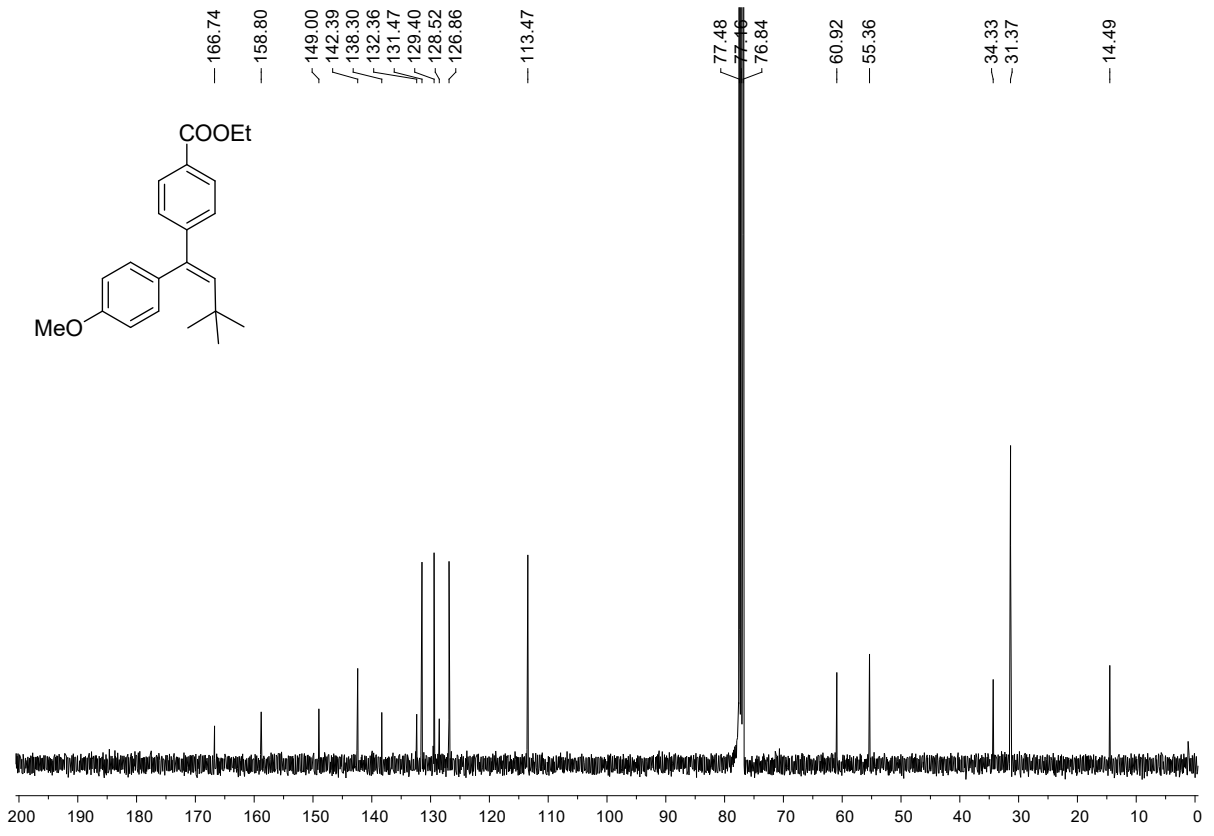
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **29**.



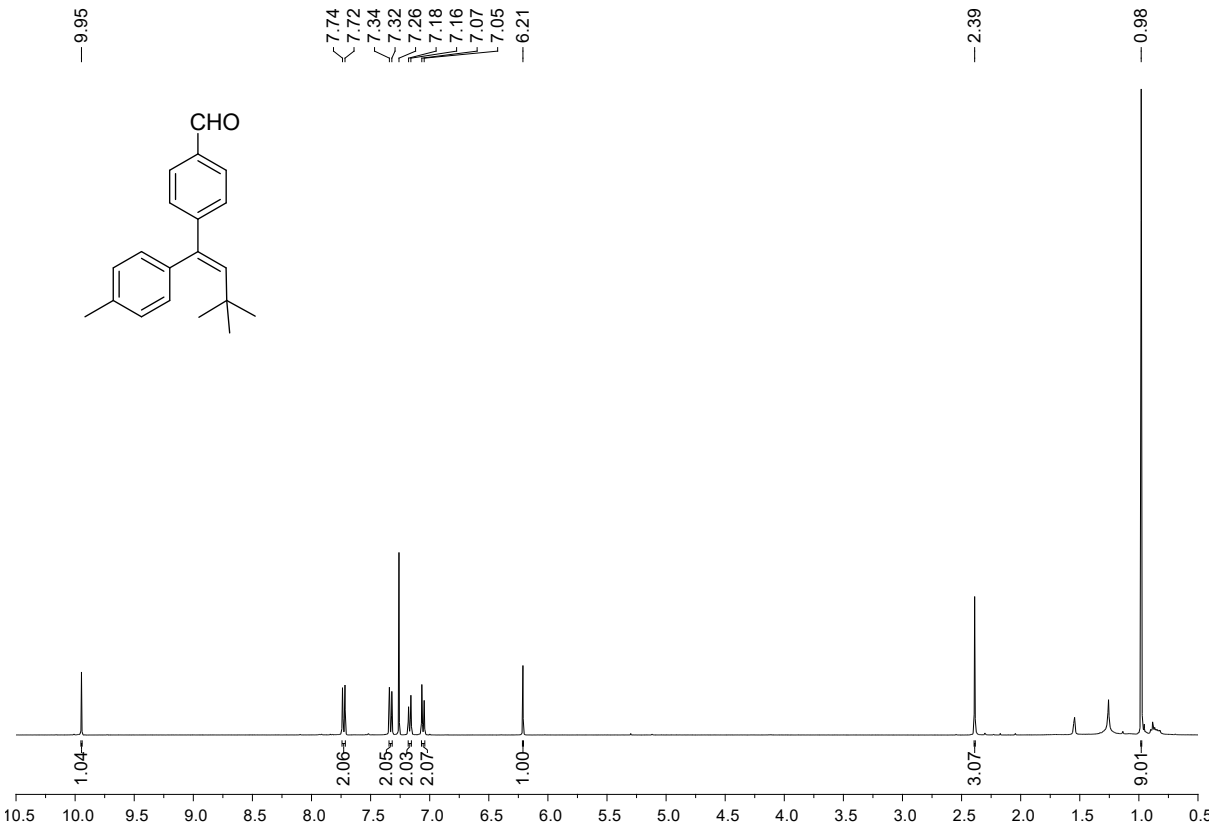
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **29**.



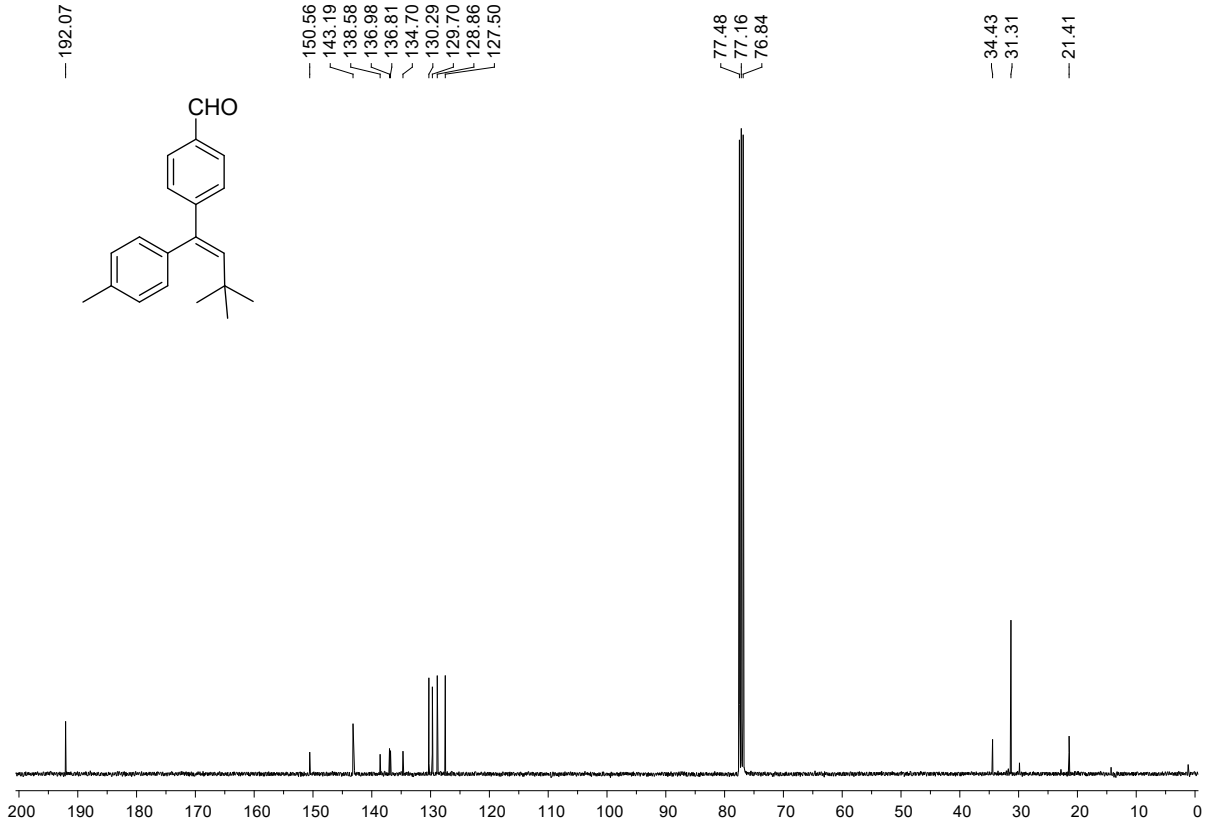
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **30.**



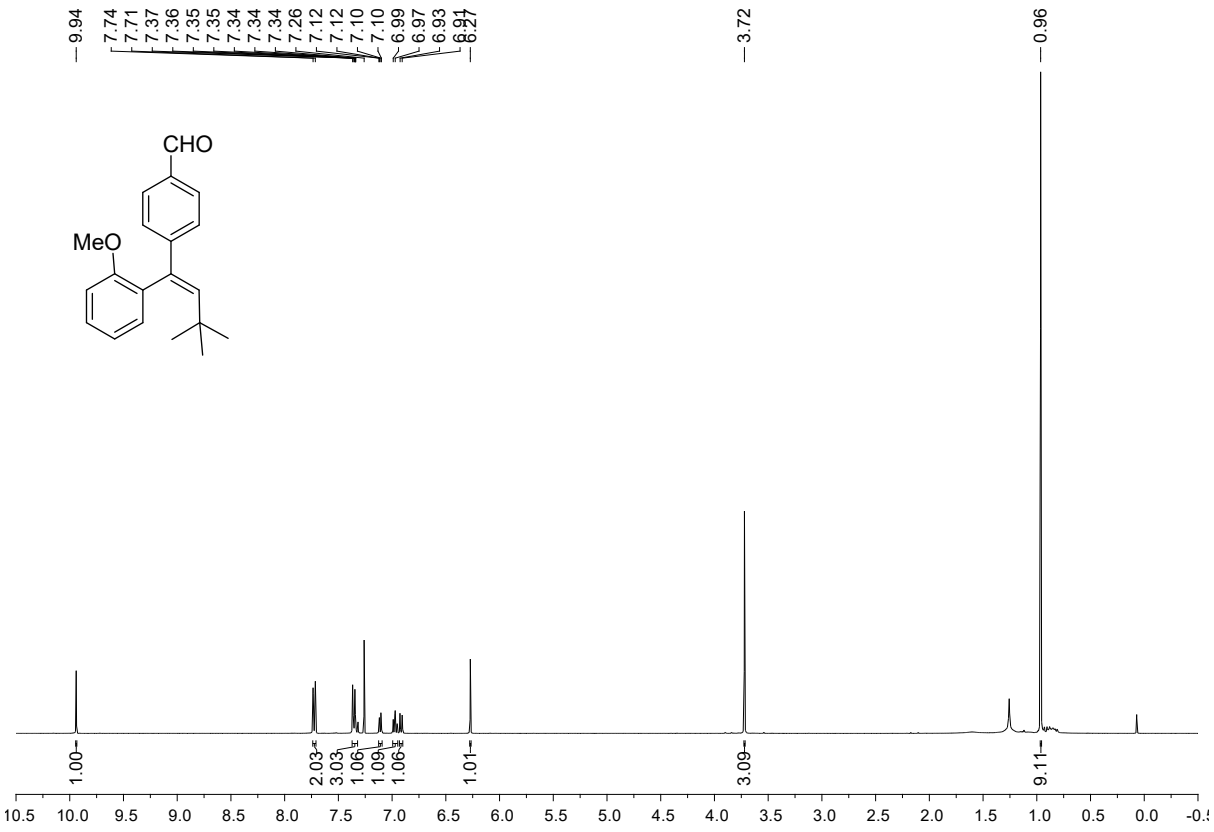
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **30**.



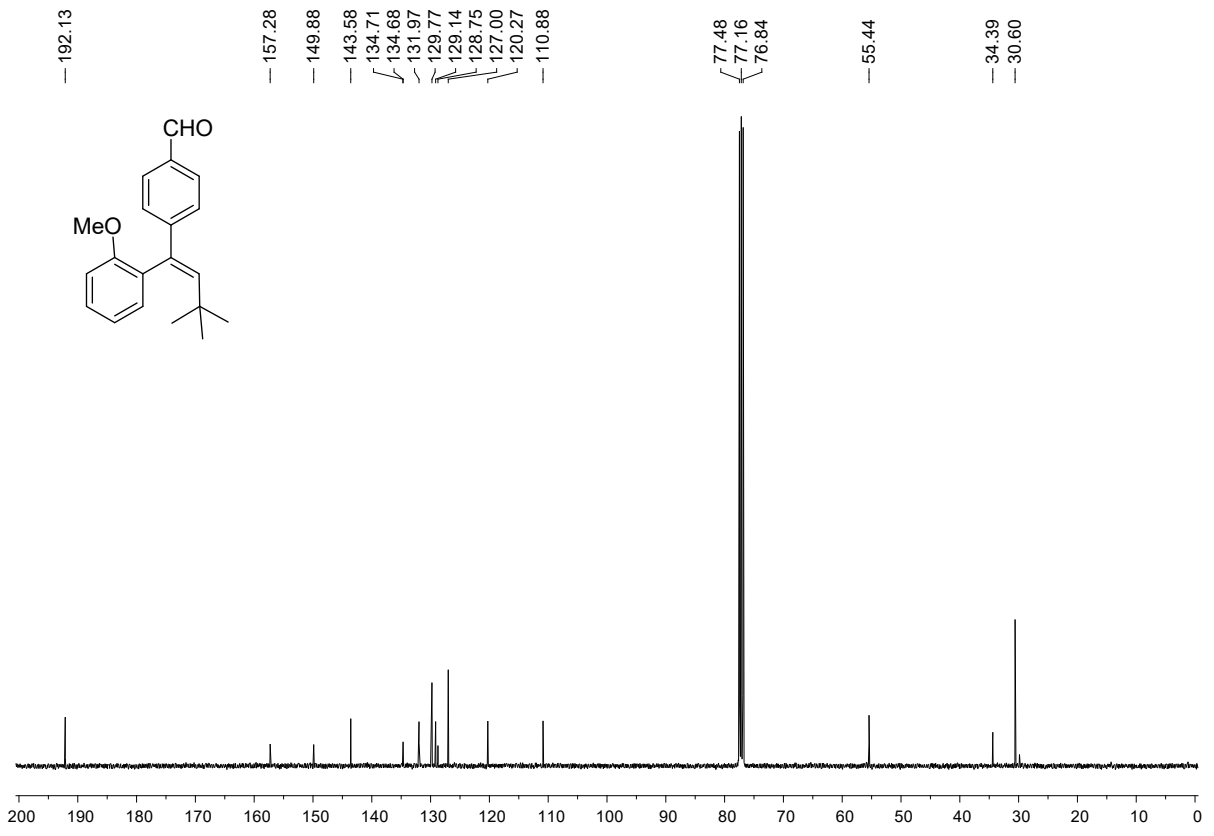
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **31.**



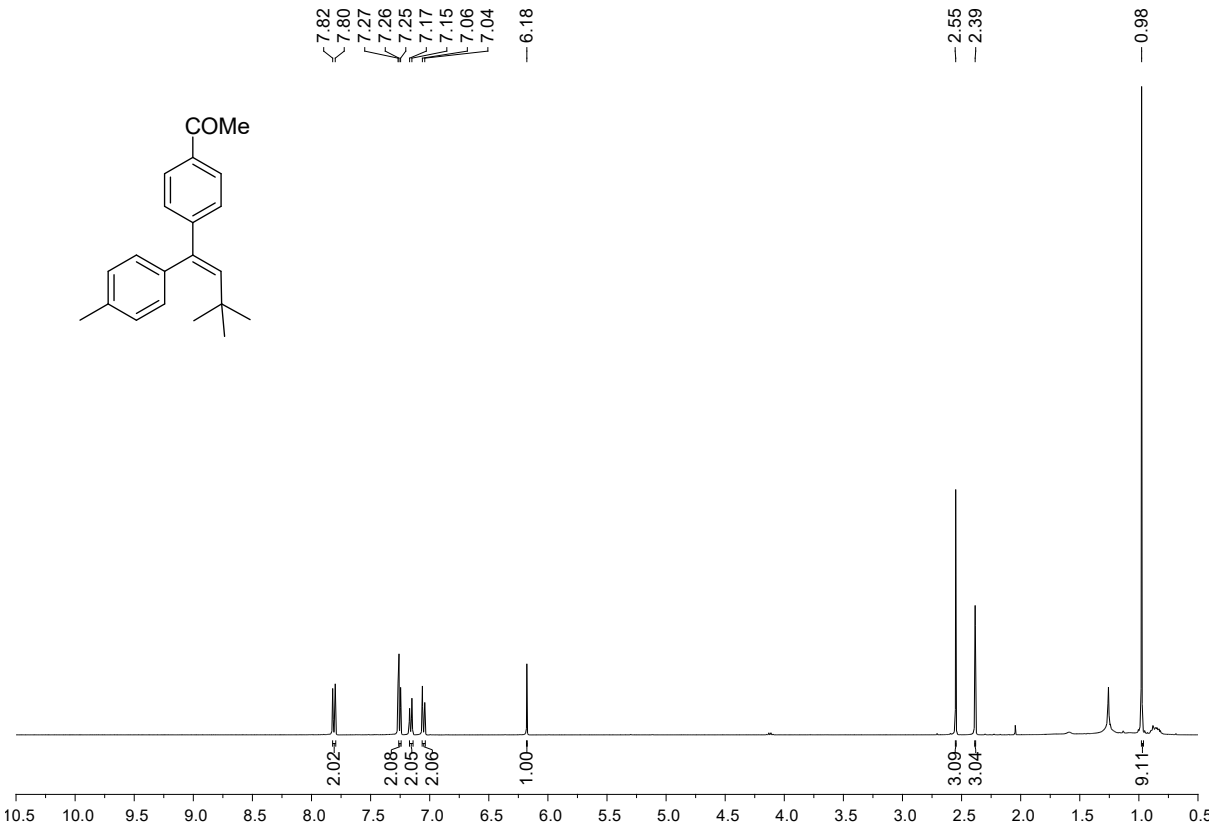
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **31**.



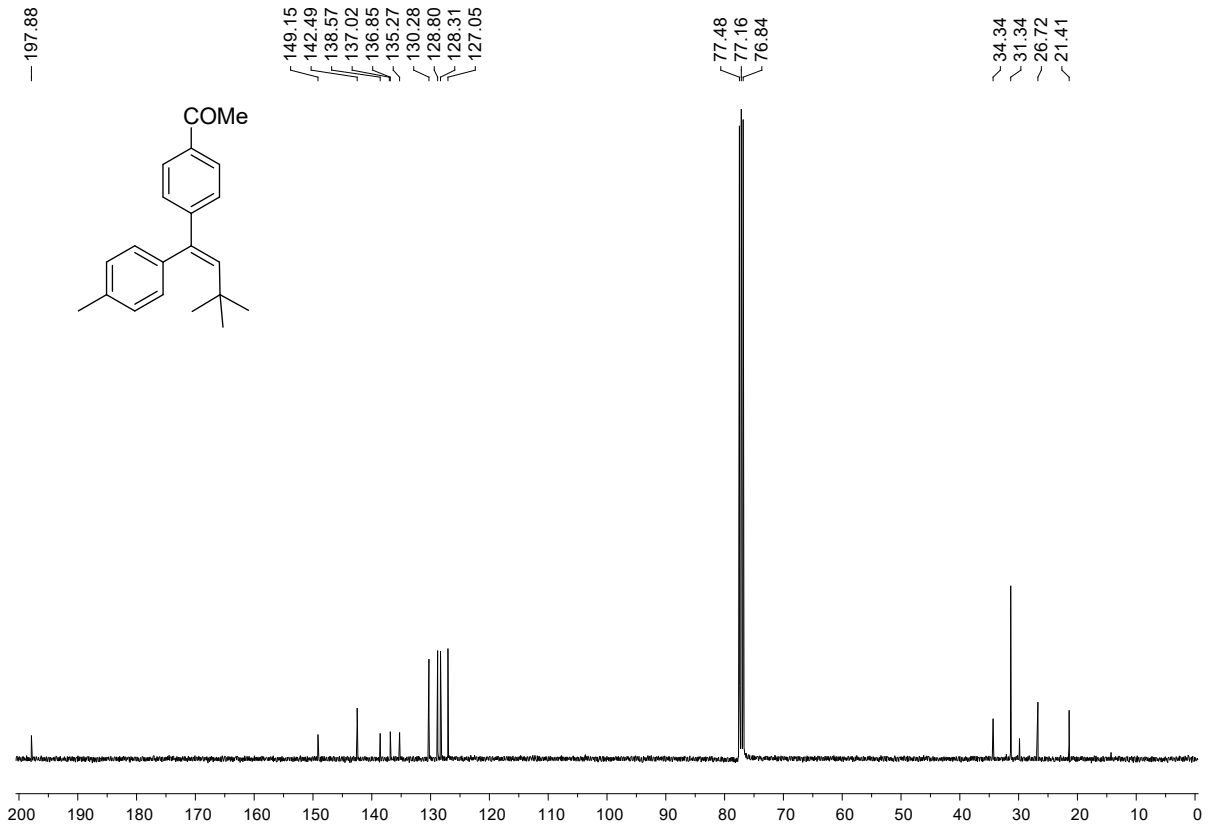
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **32.**



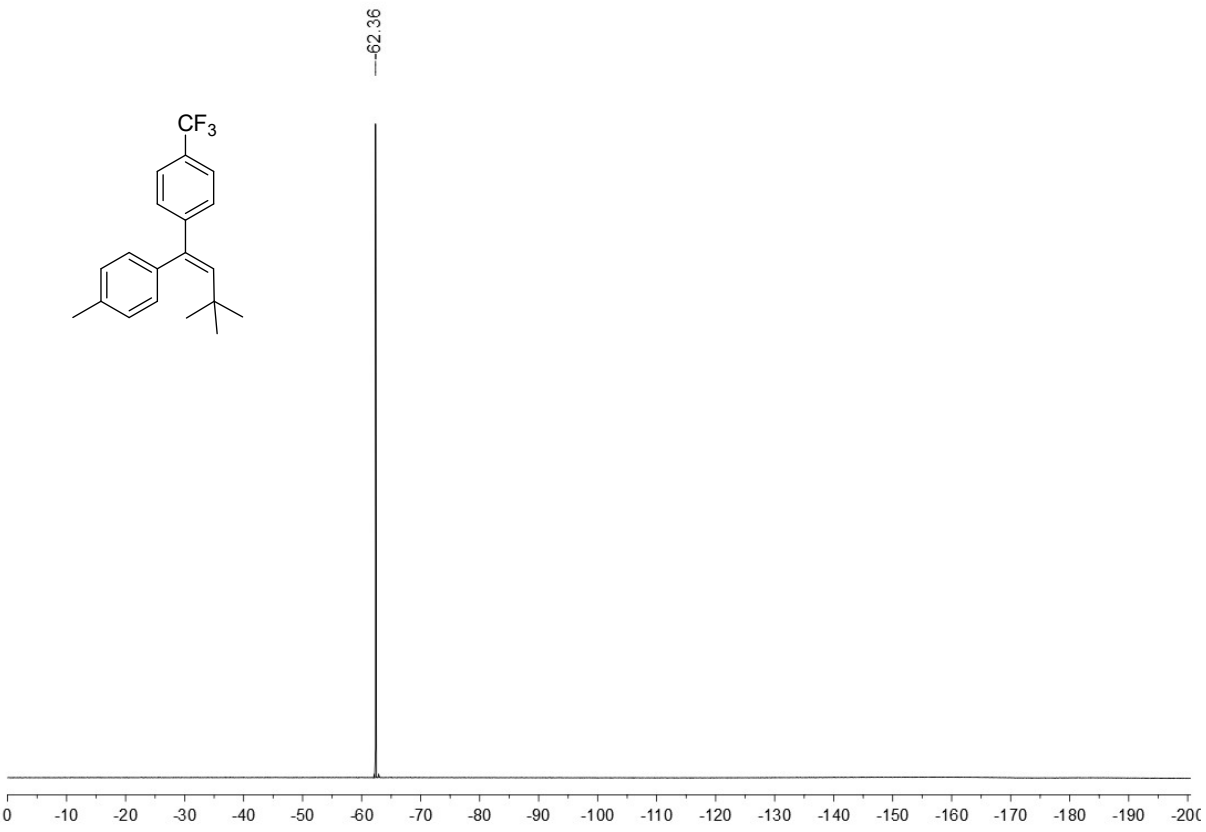
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **32**.



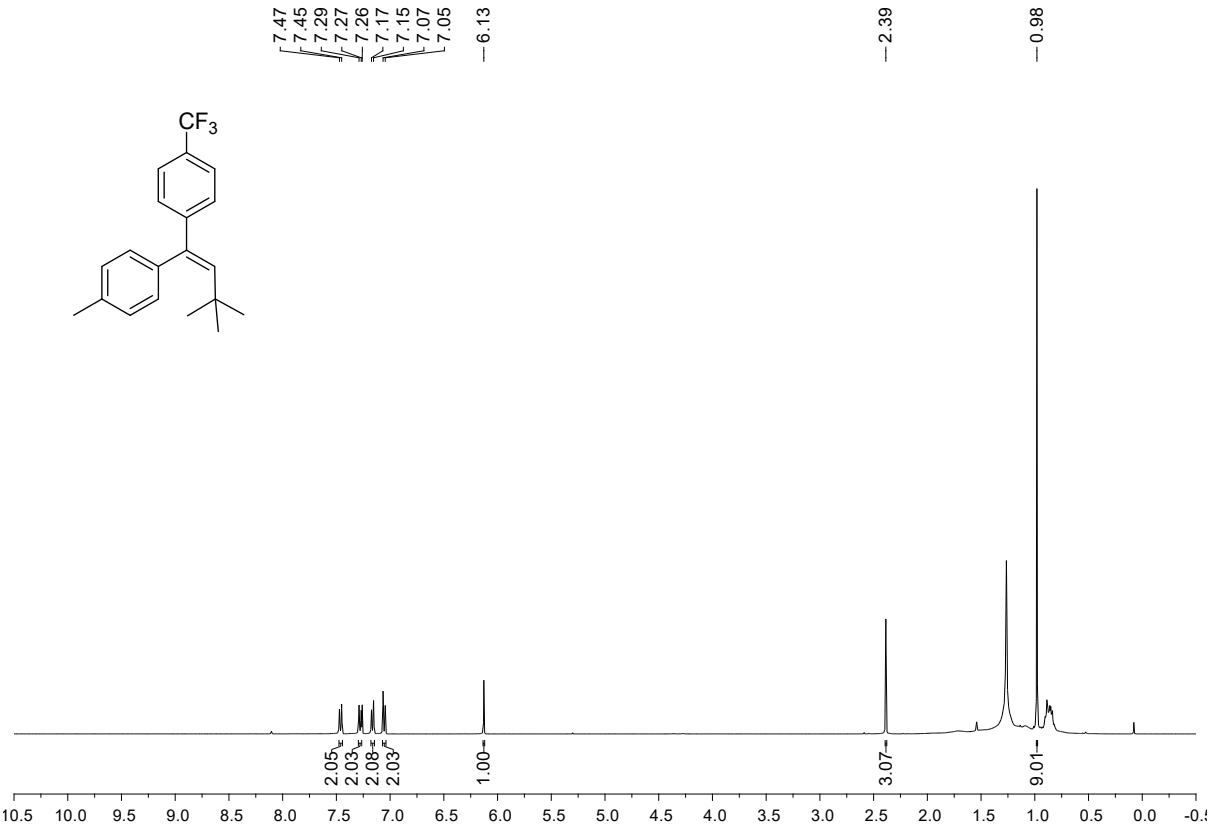
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **33.**



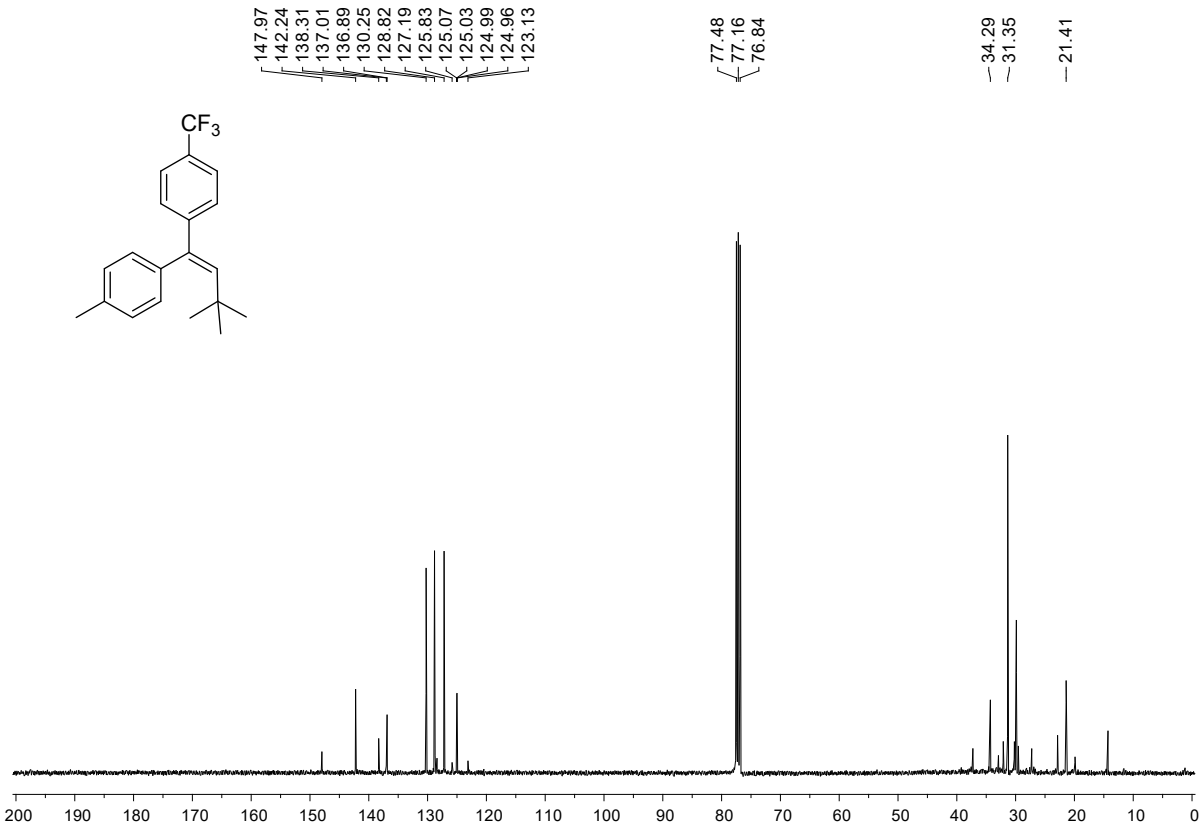
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **33**.



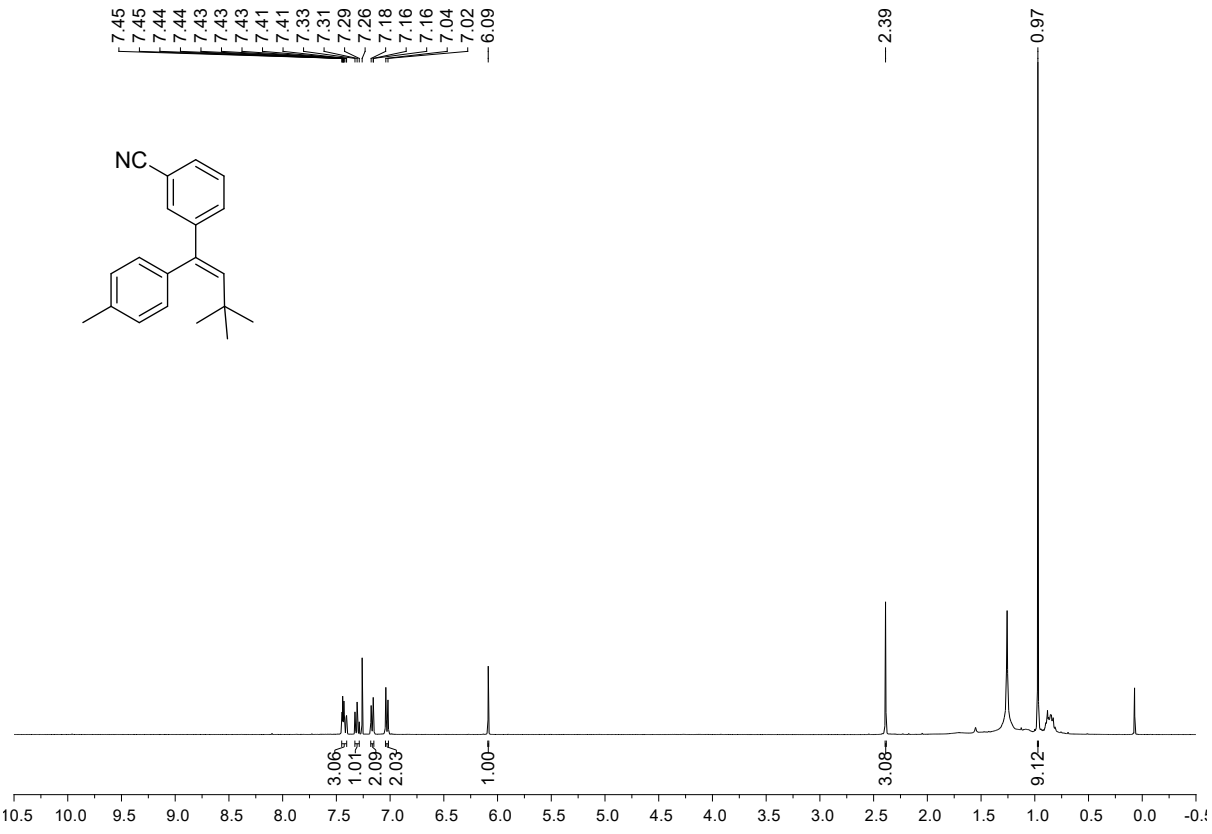
^{19}F NMR (377 MHz, $CDCl_3$) of the compound **34.**



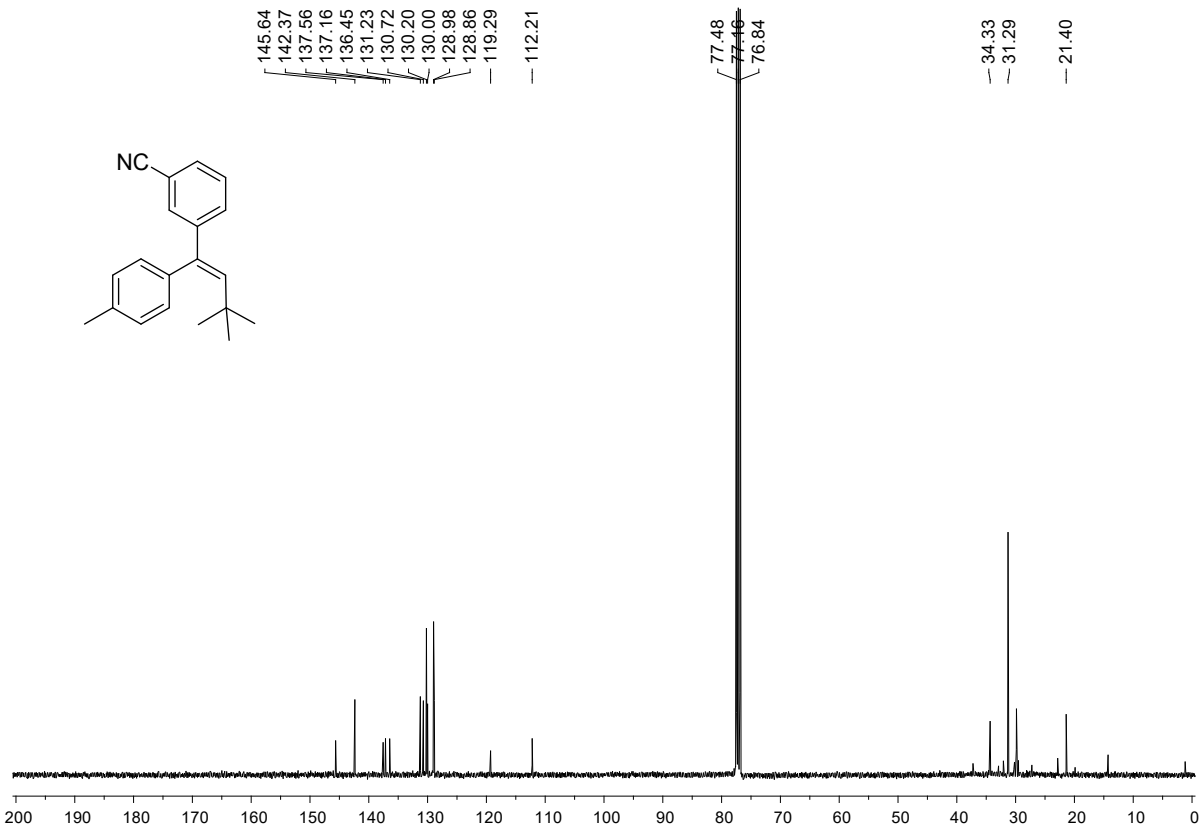
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **34.**



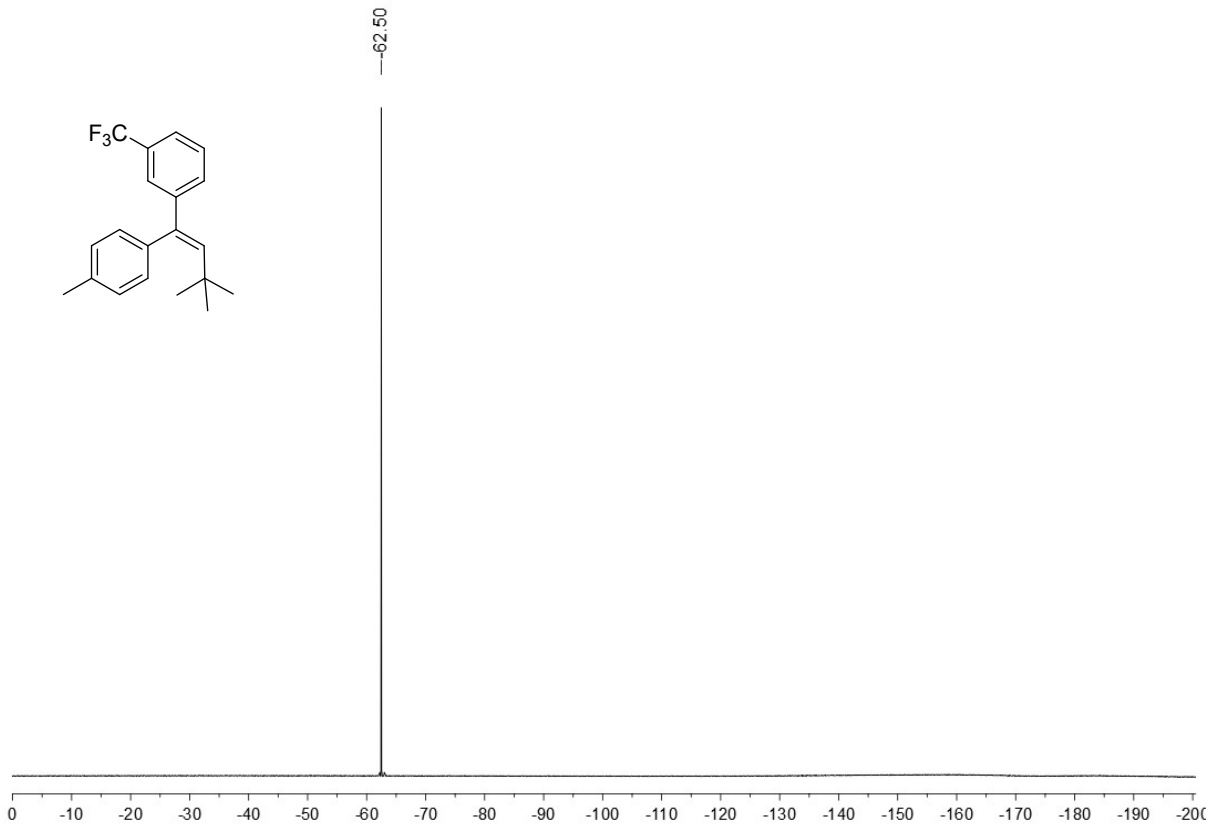
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **34**.



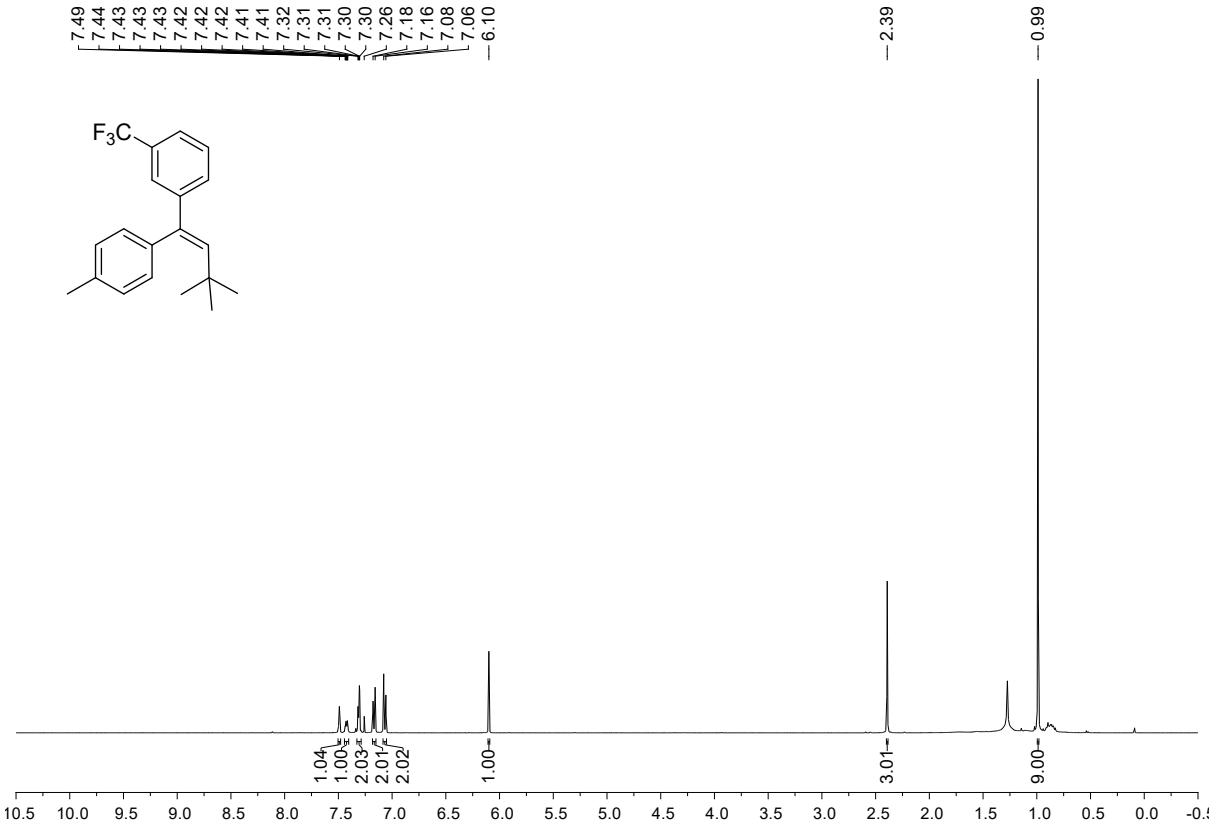
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **35.**



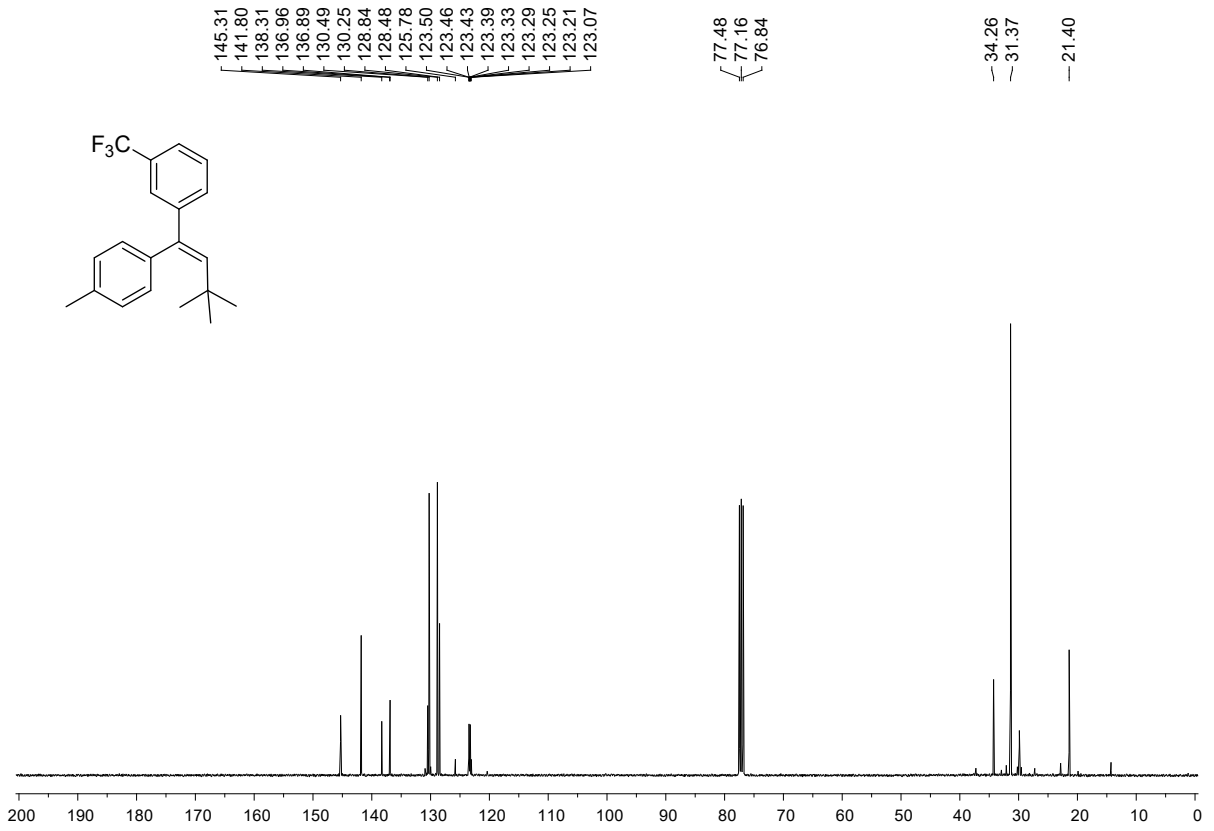
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **35**.



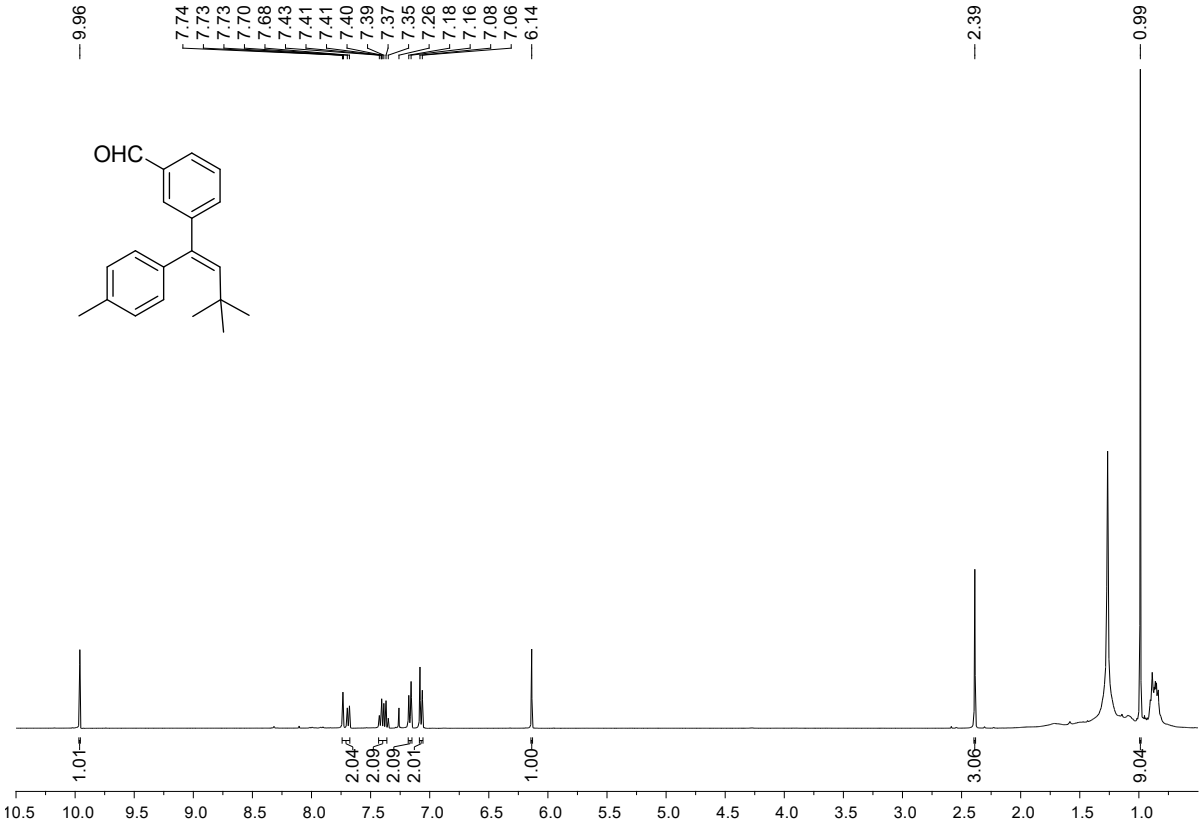
^{19}F NMR (37 MHz, $CDCl_3$) of the compound **36.**



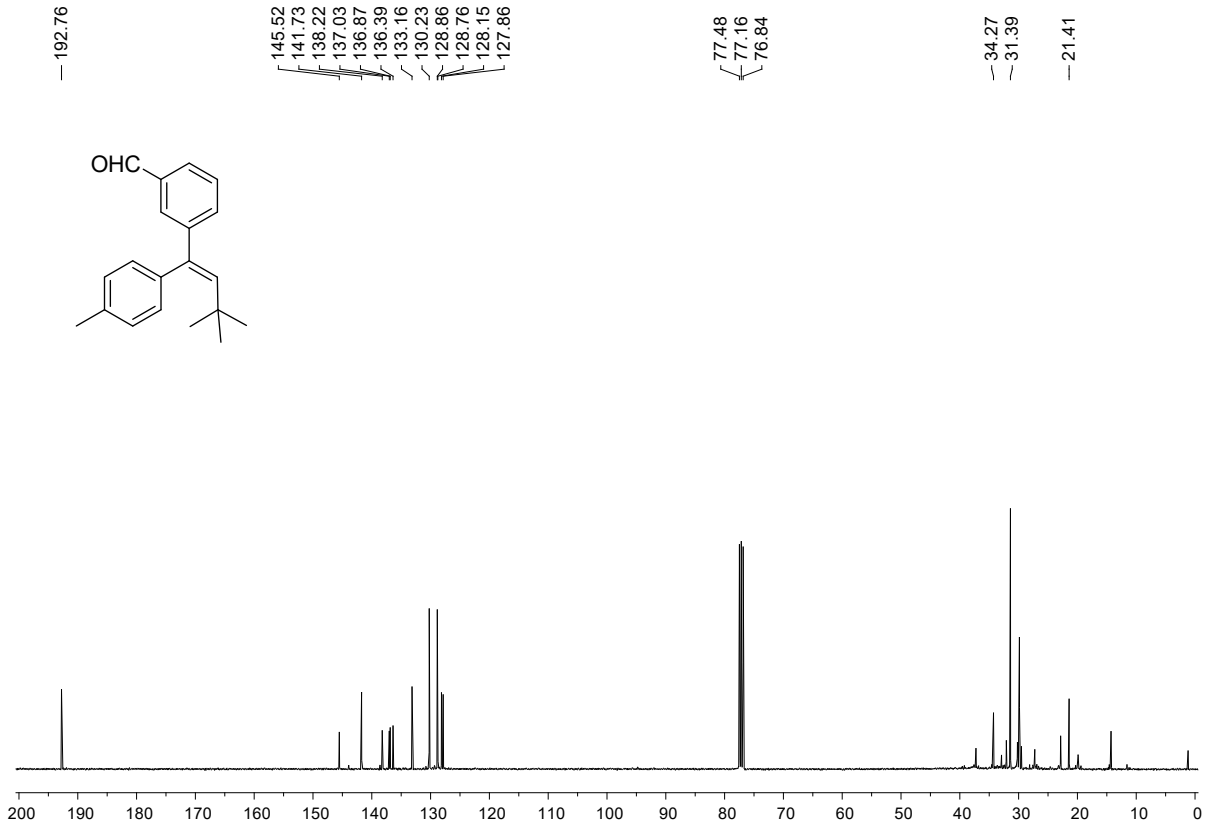
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **36.**



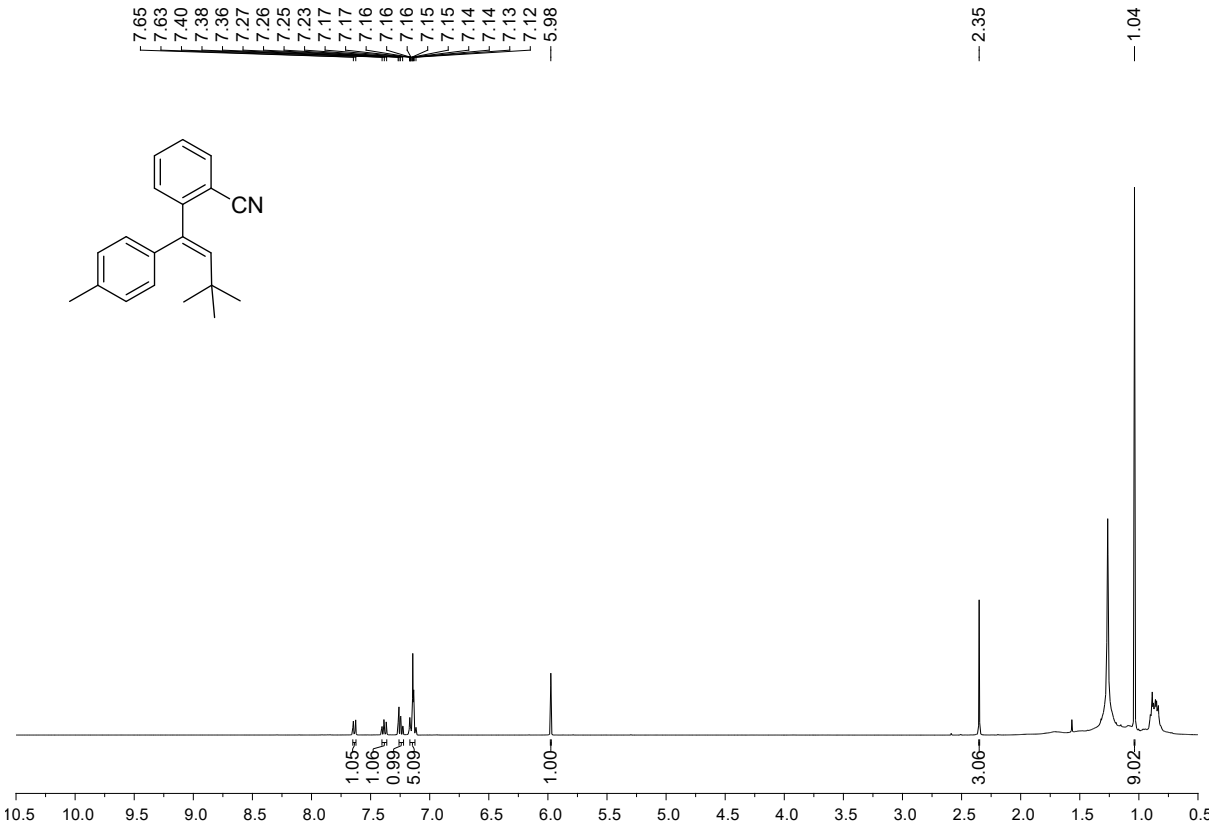
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **36**.



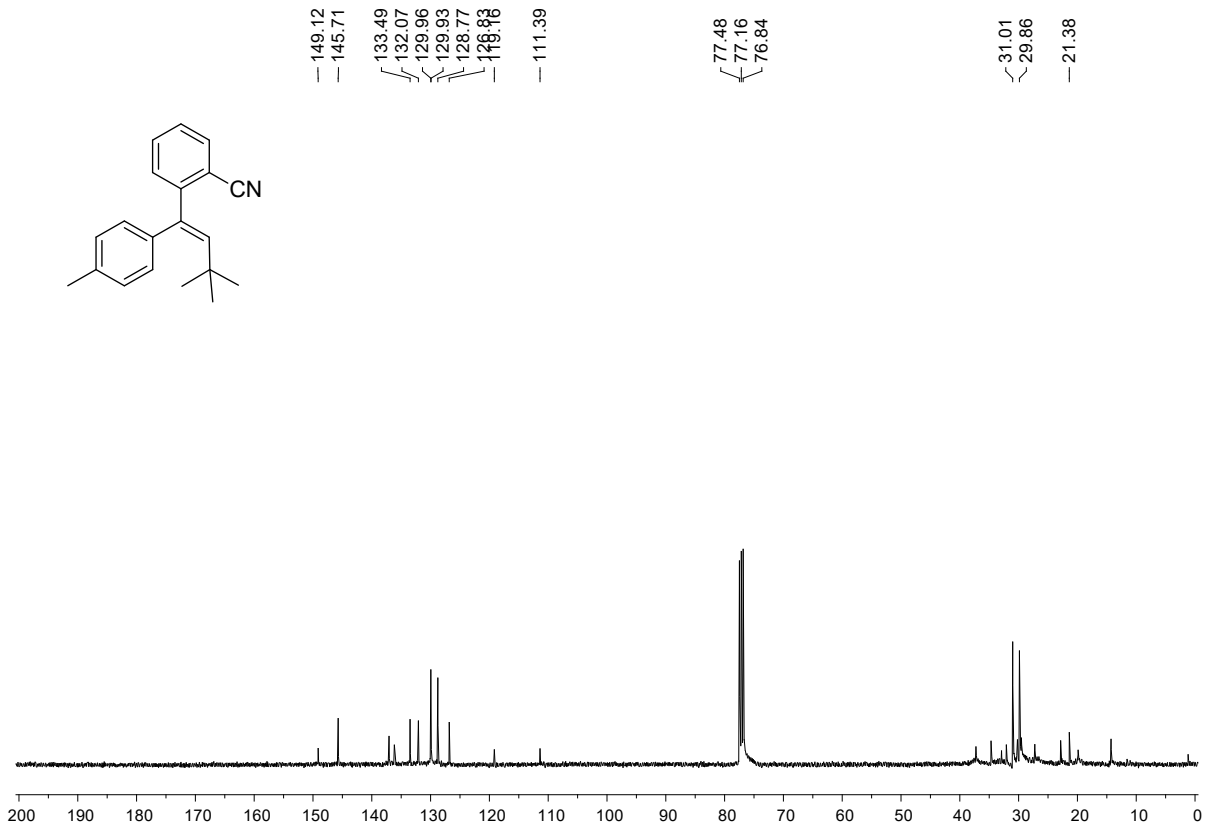
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **37.**



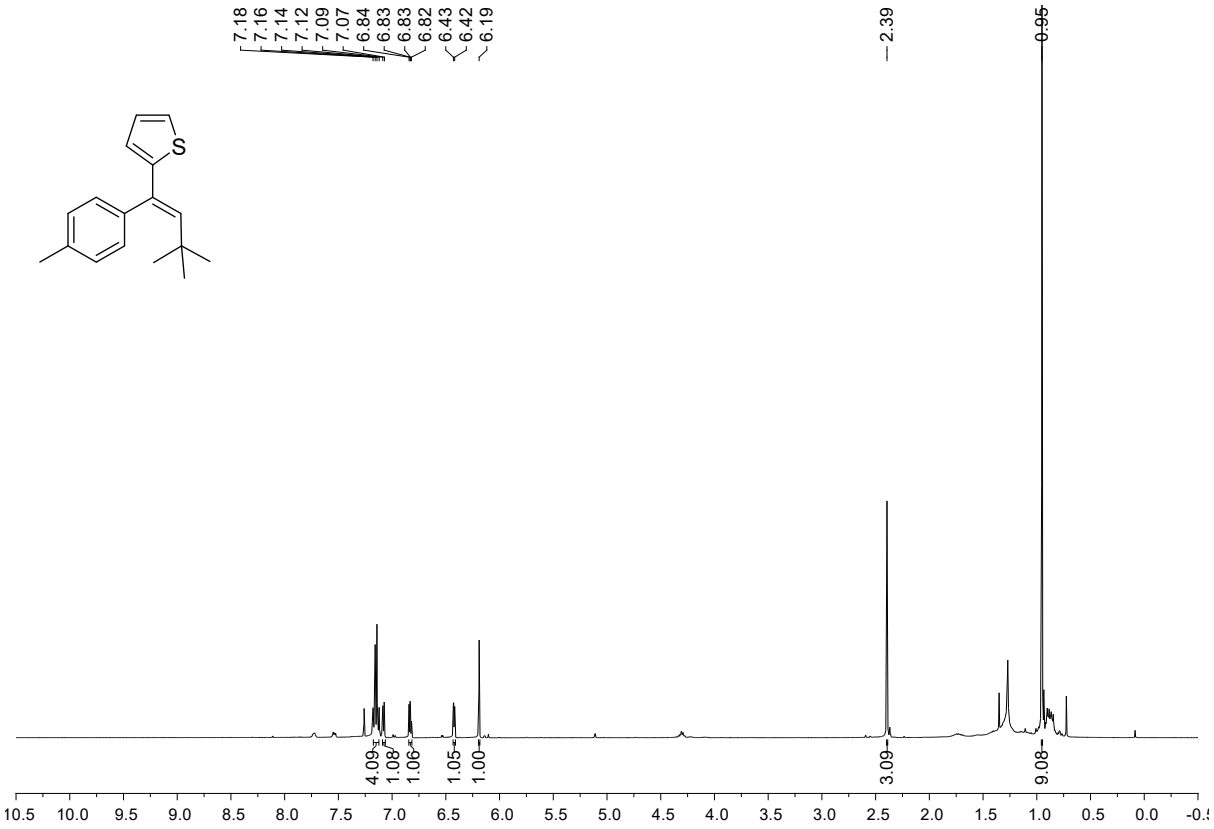
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **37**.



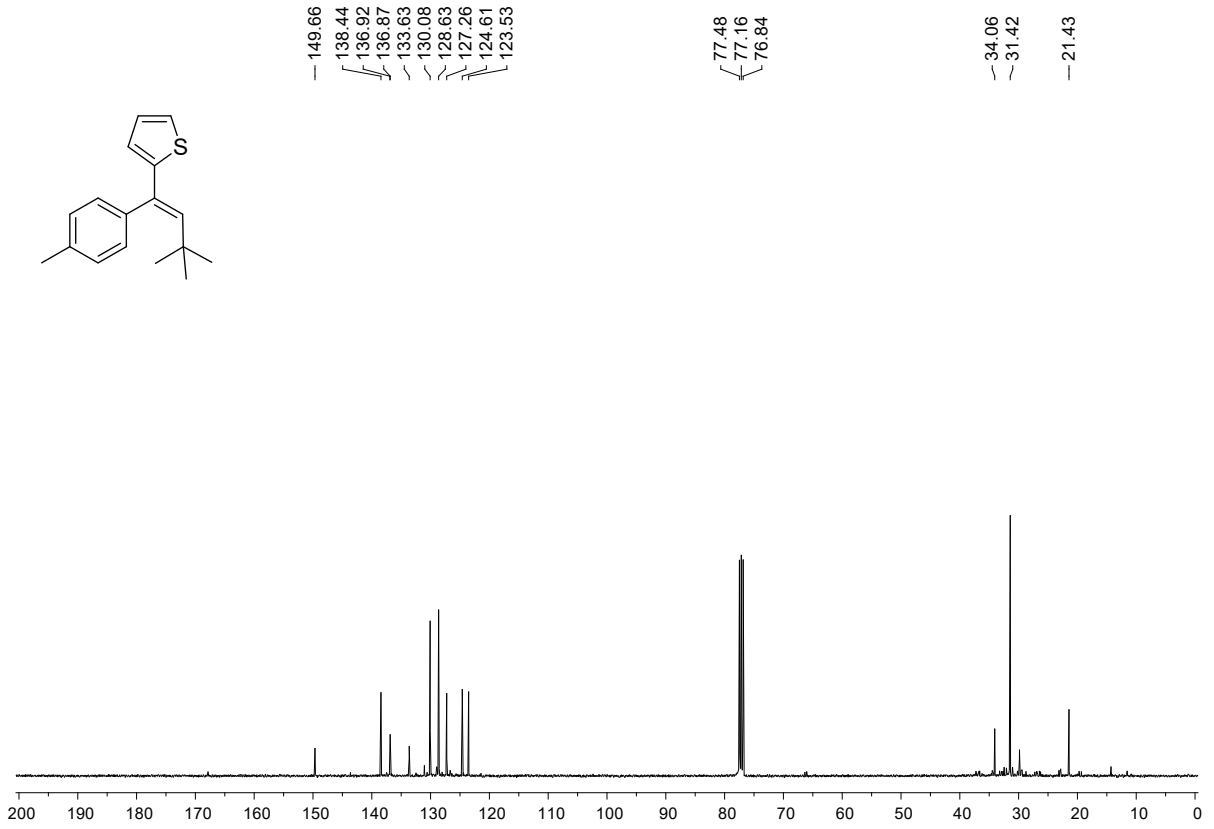
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **38.**



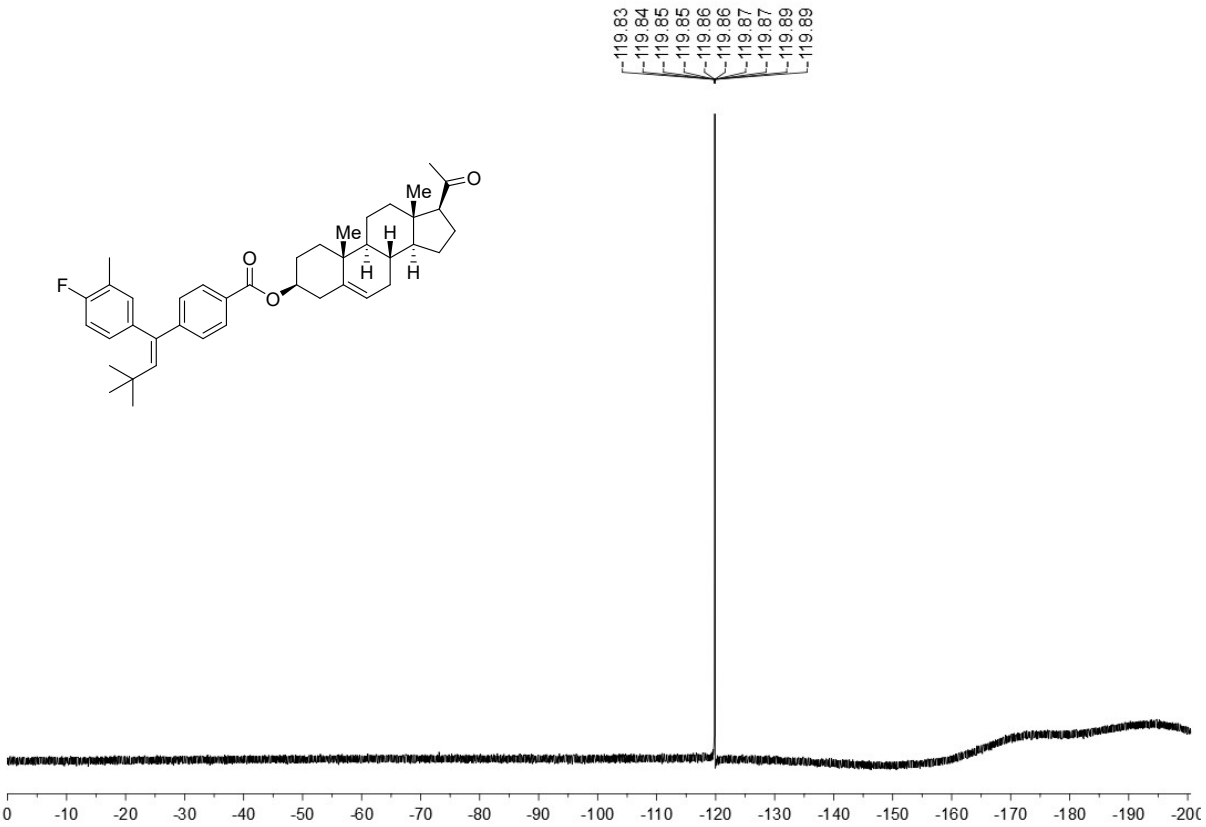
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **38**.



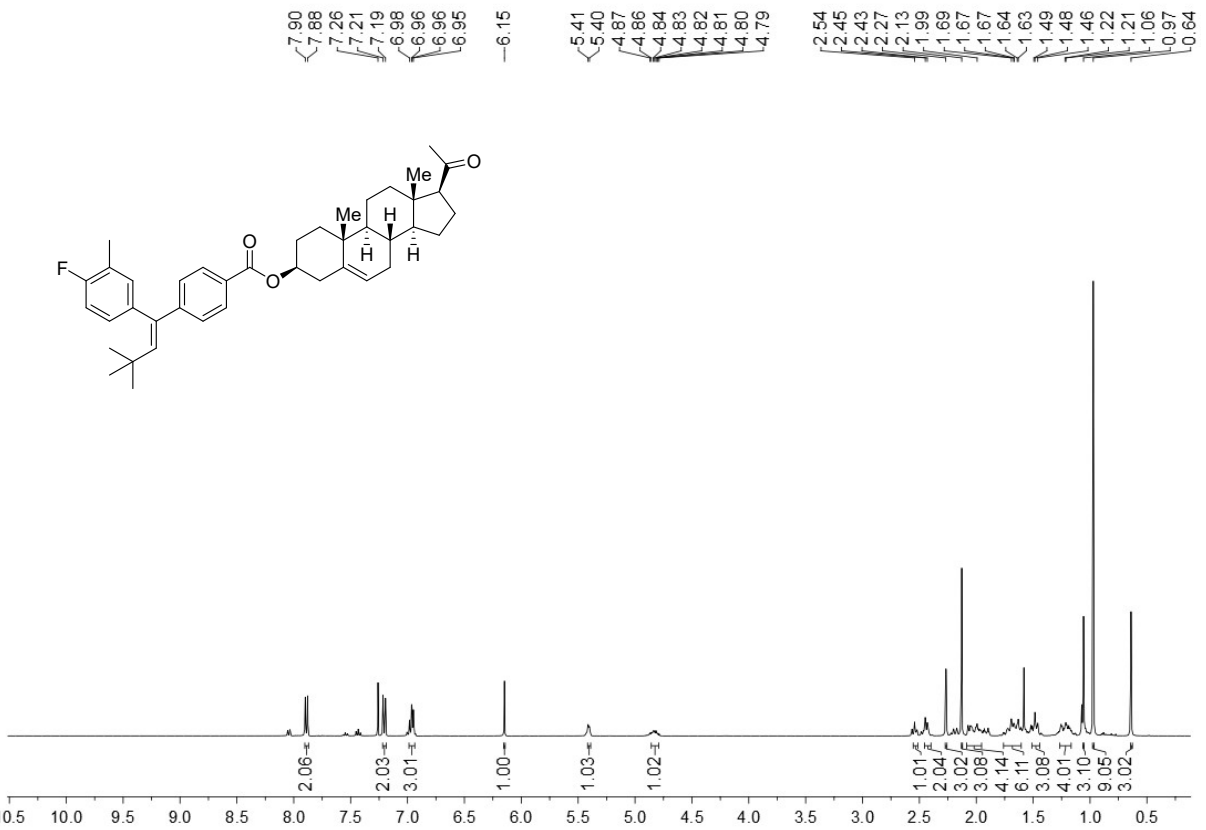
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **39.**



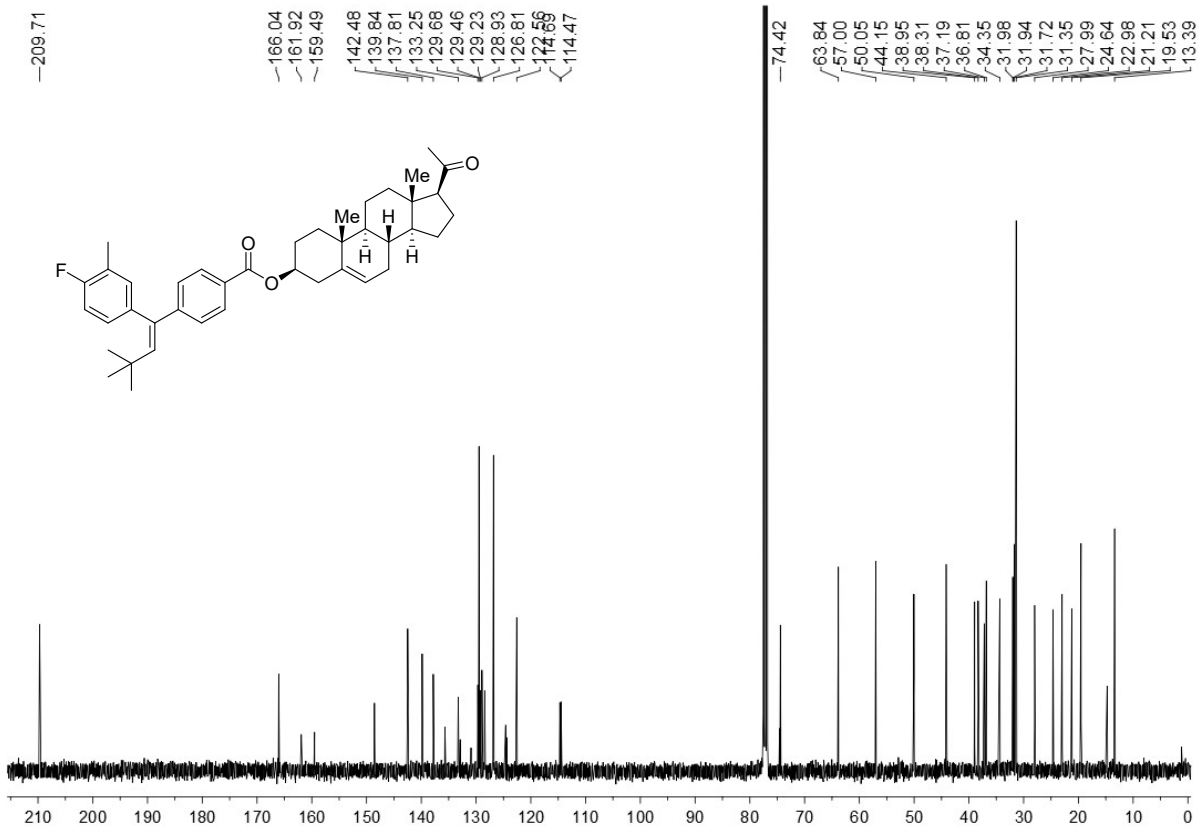
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **39**.



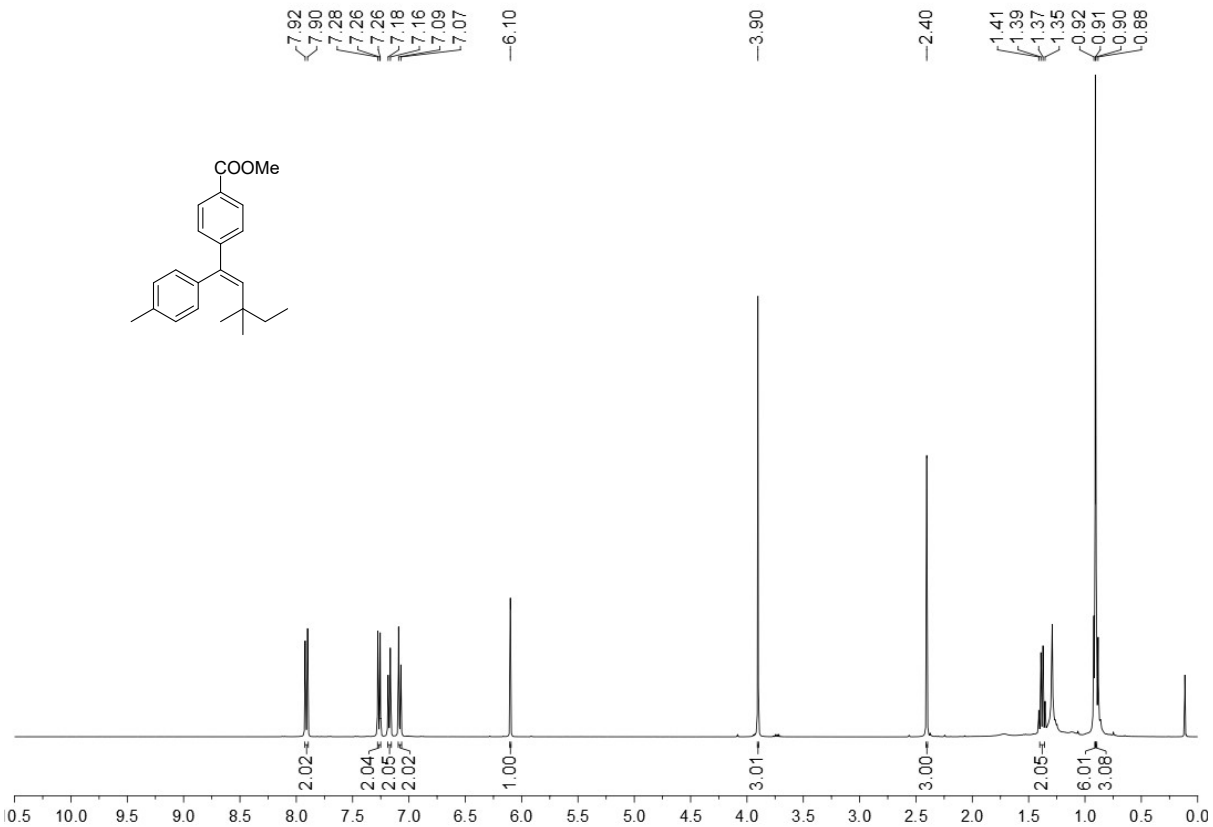
^{19}F NMR (377 MHz, $CDCl_3$) of the compound **40.**



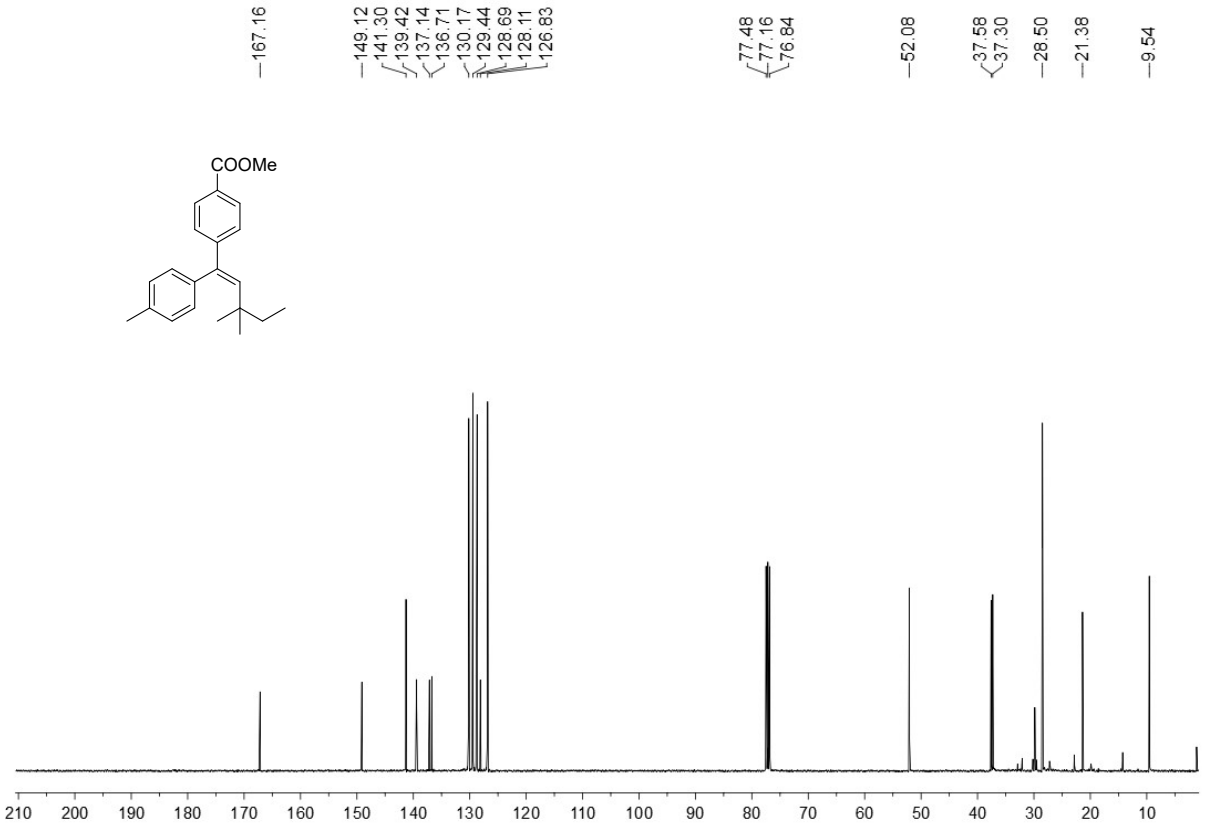
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **40.**



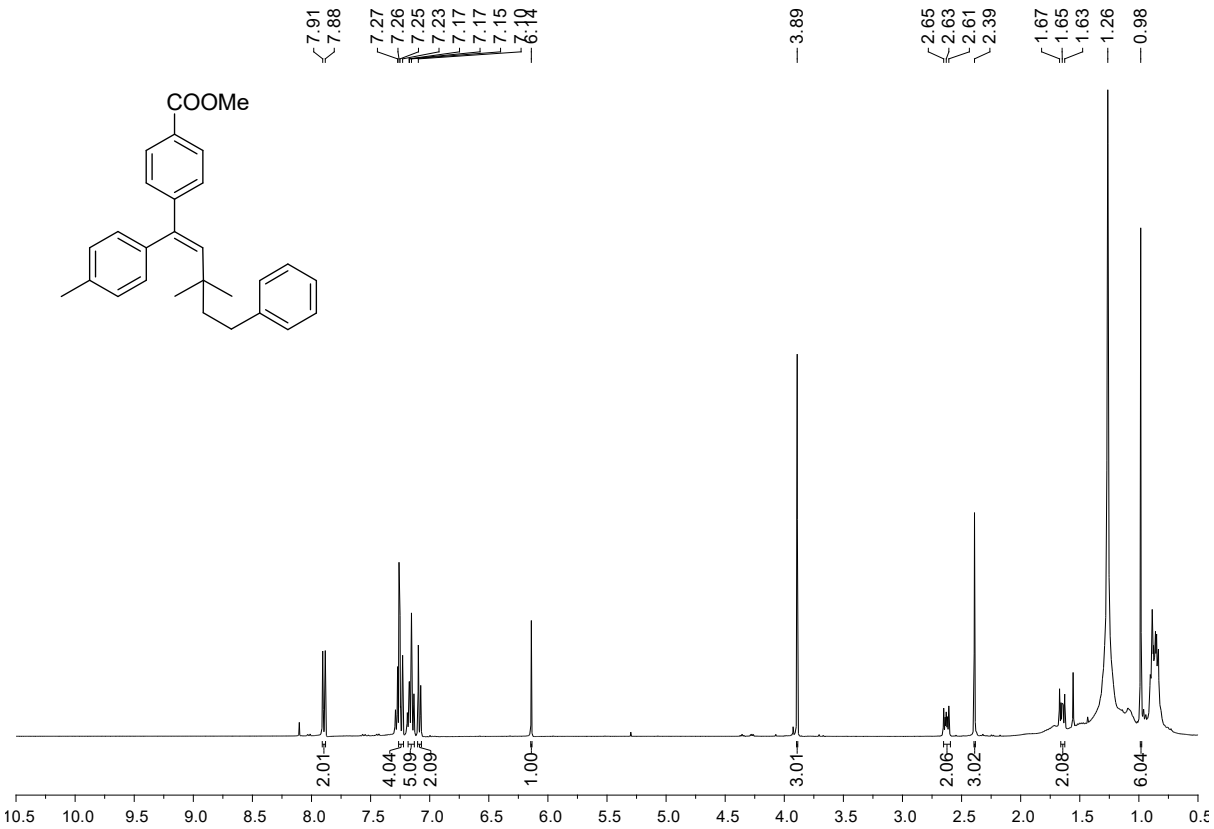
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **40.**



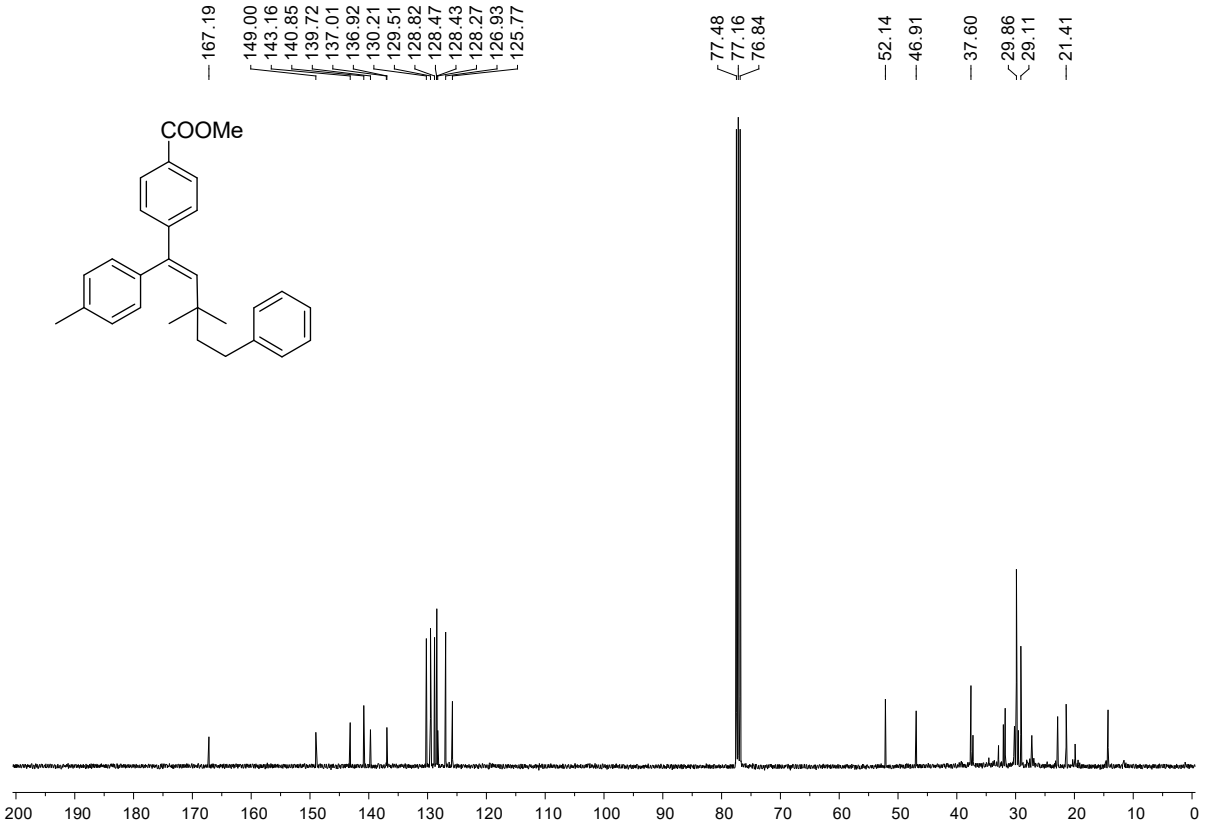
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **41.**



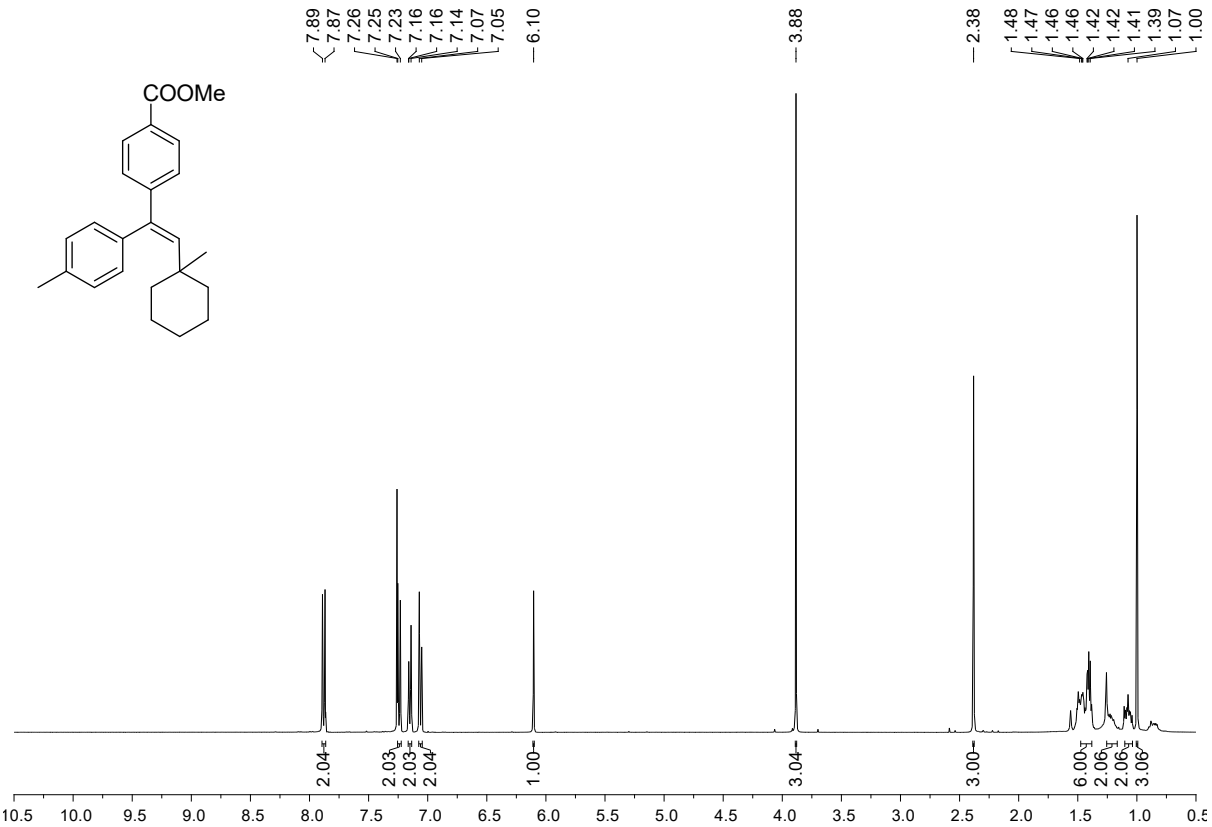
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **41.**



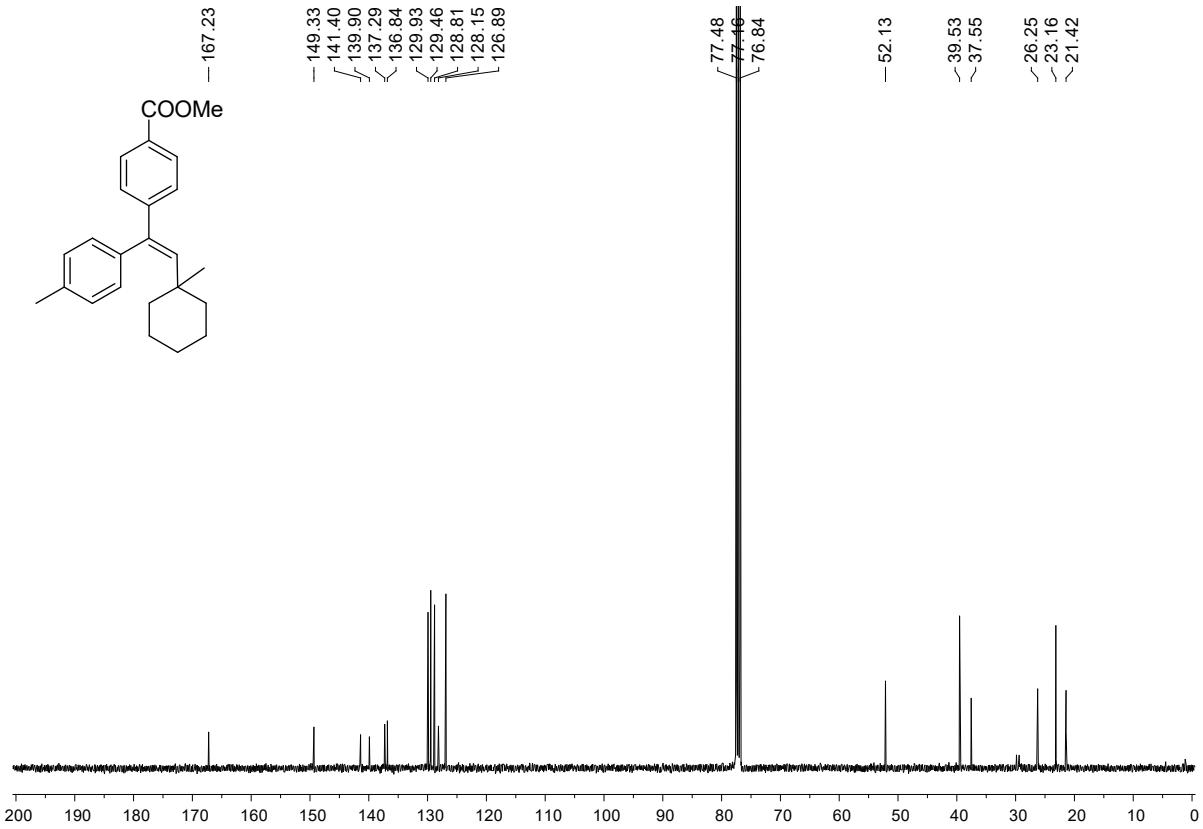
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **42.**



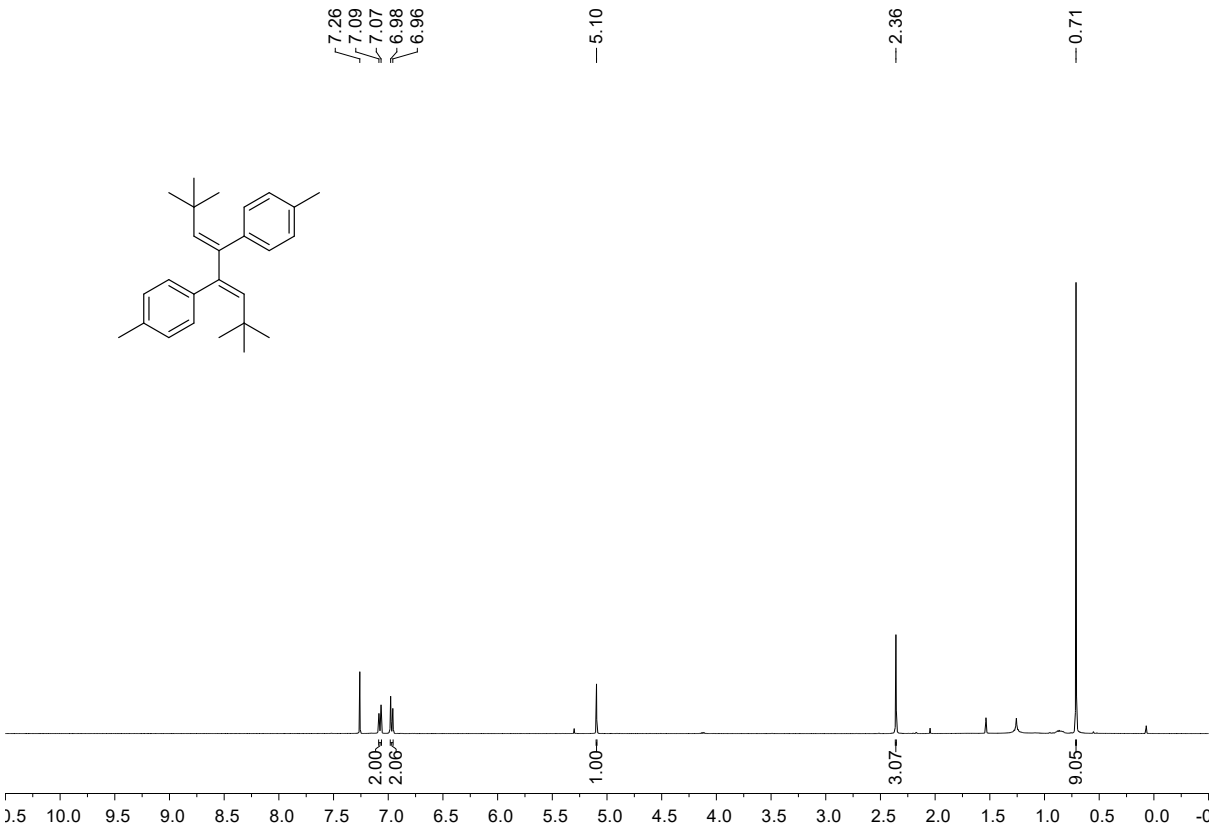
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **42**.



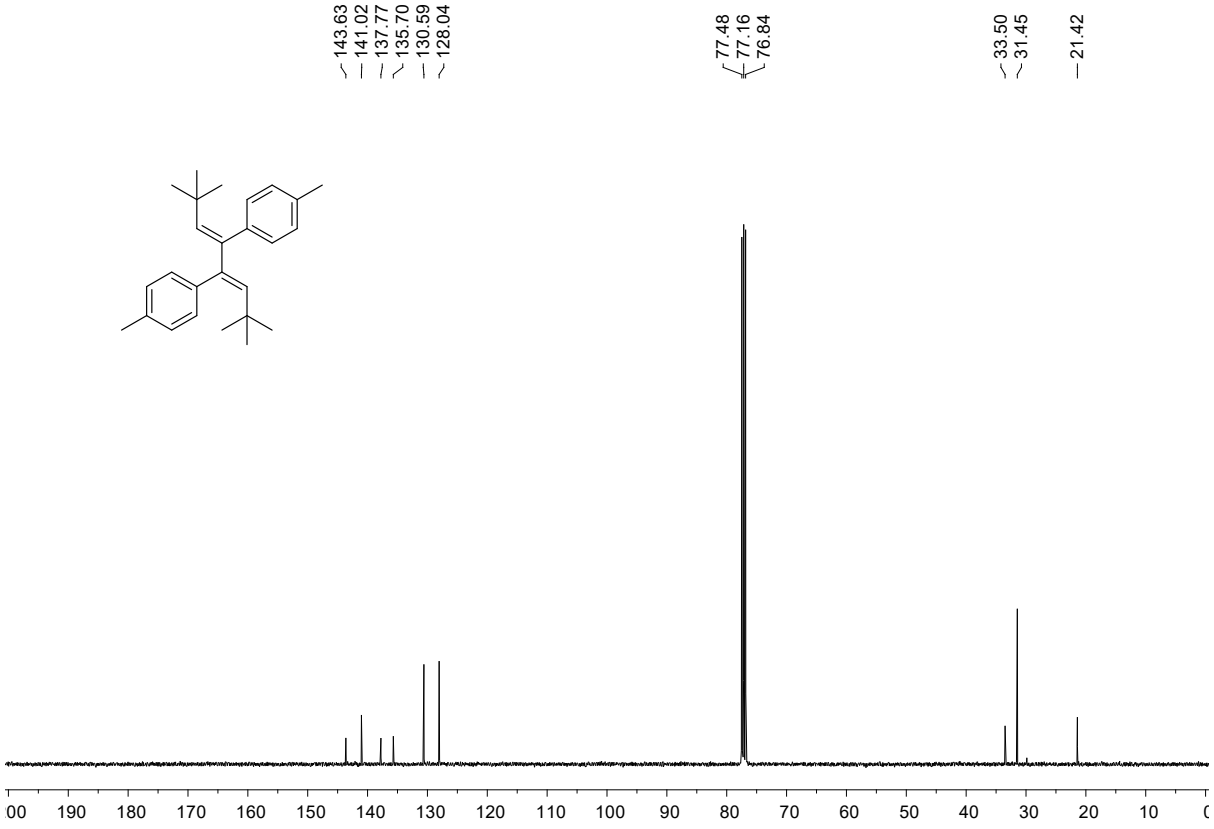
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **43.**



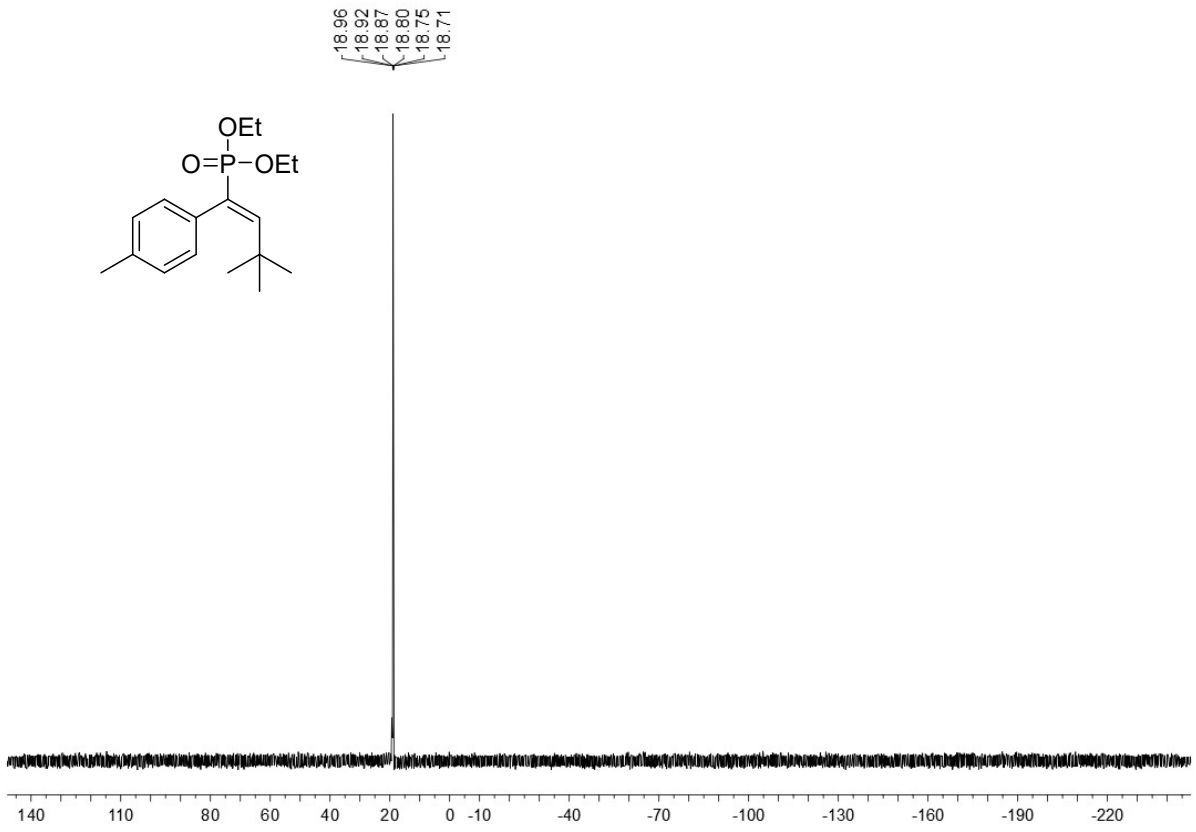
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **43**.



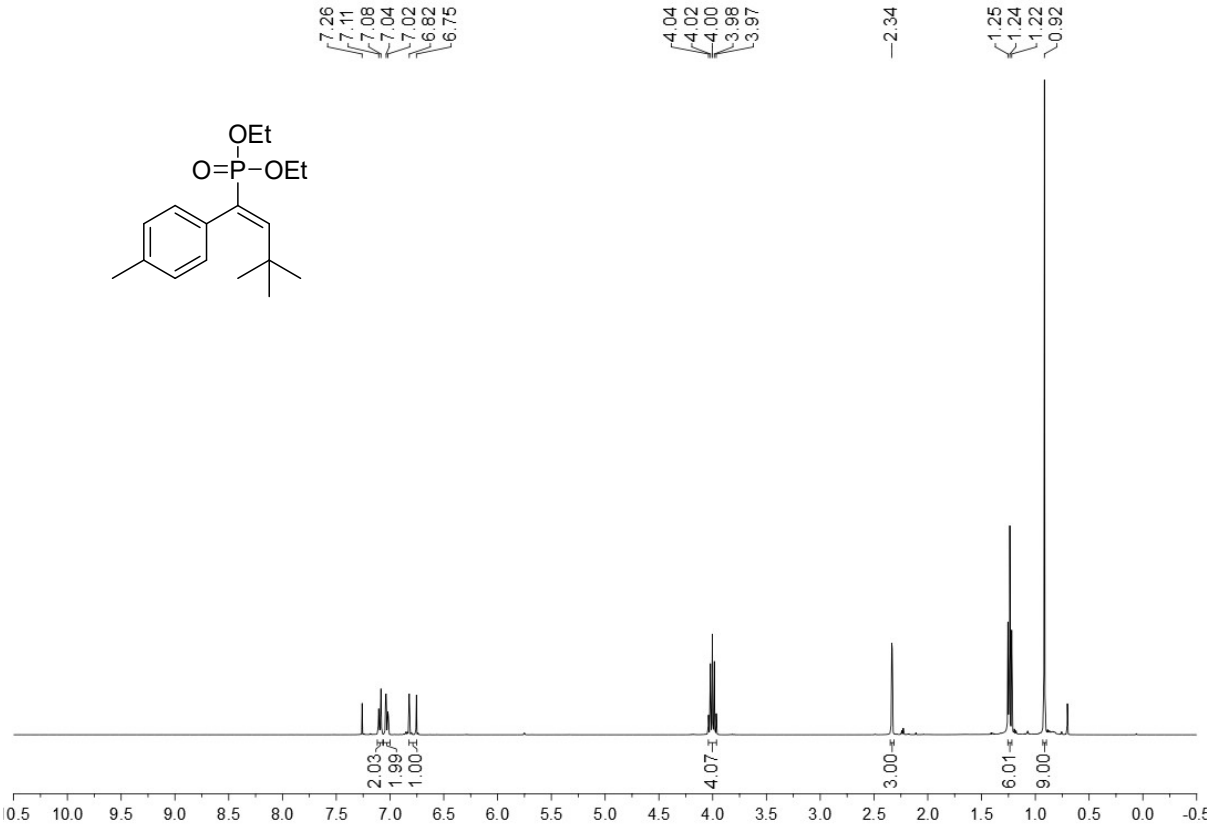
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **44.**



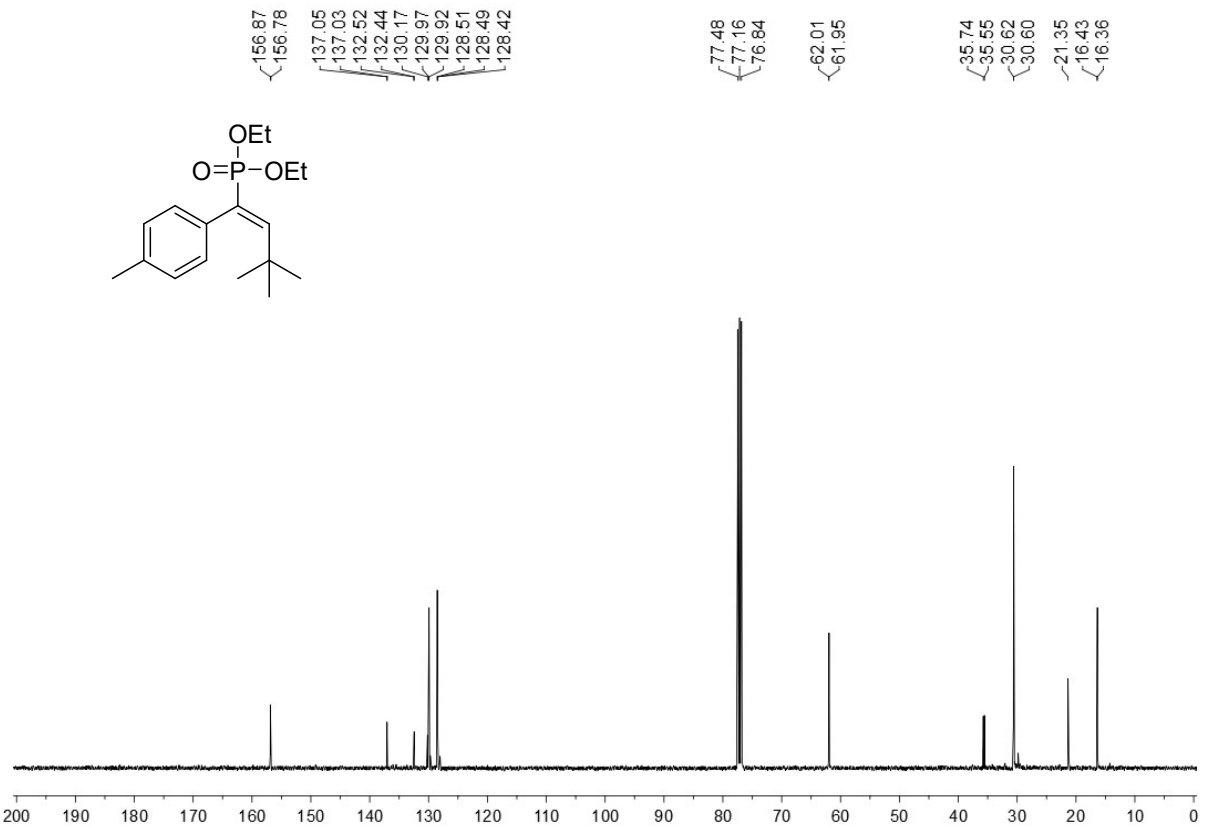
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **44.**



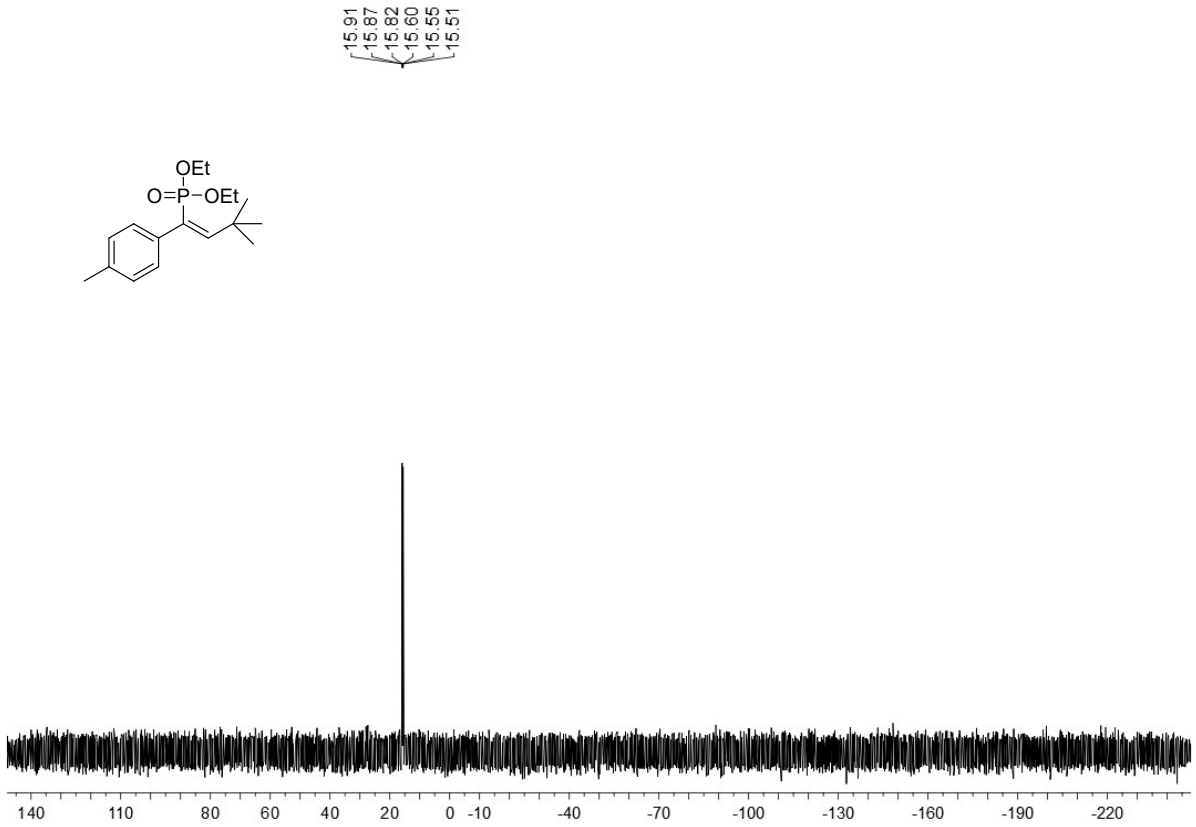
^{31}P NMR (162 MHz, $CDCl_3$) of the compound **45.**



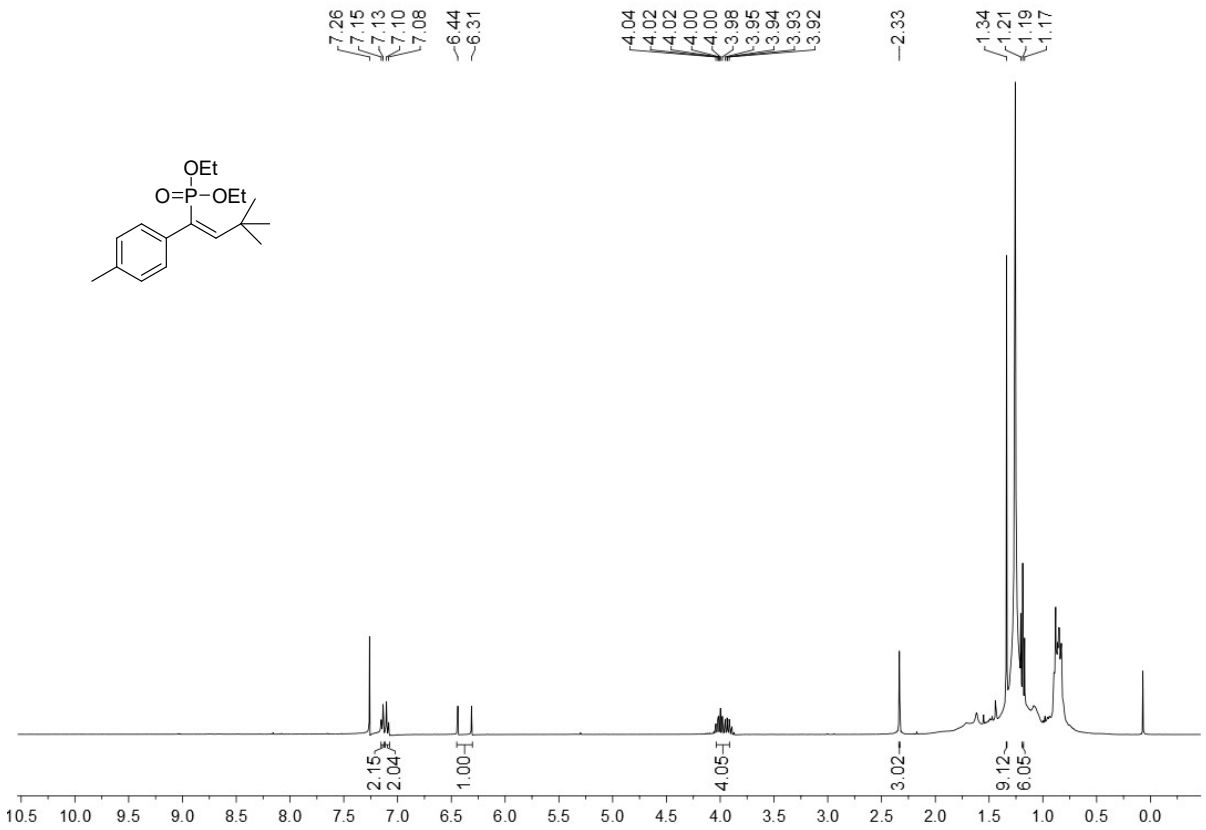
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **45.**



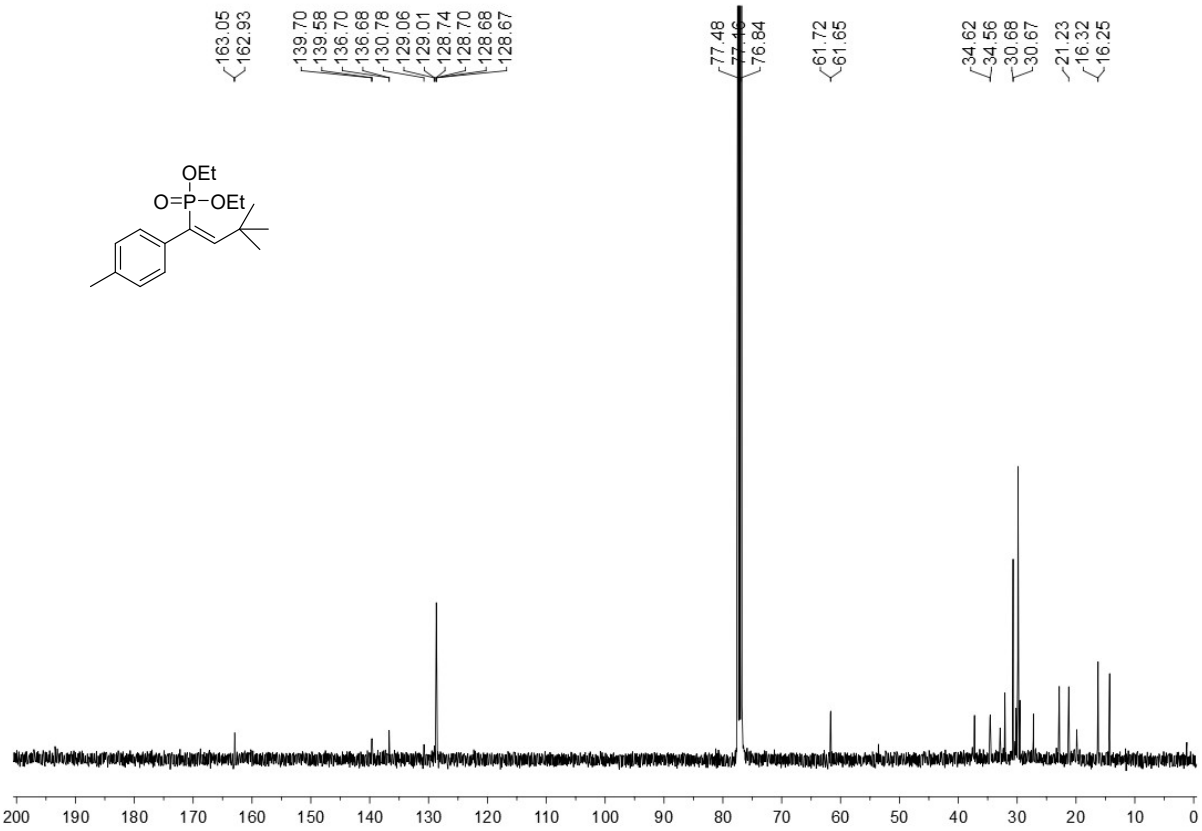
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **45.**



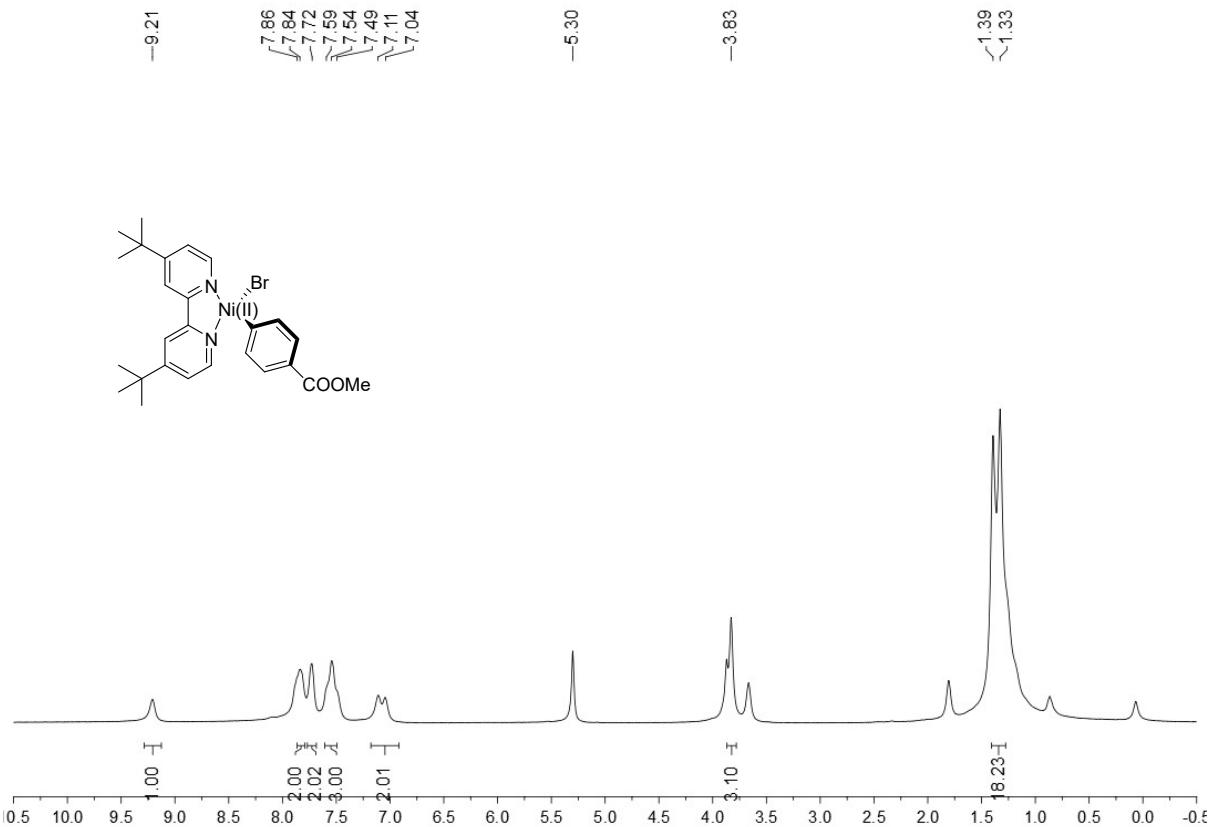
^{31}P NMR (162 MHz, $CDCl_3$) of the compound **46**.



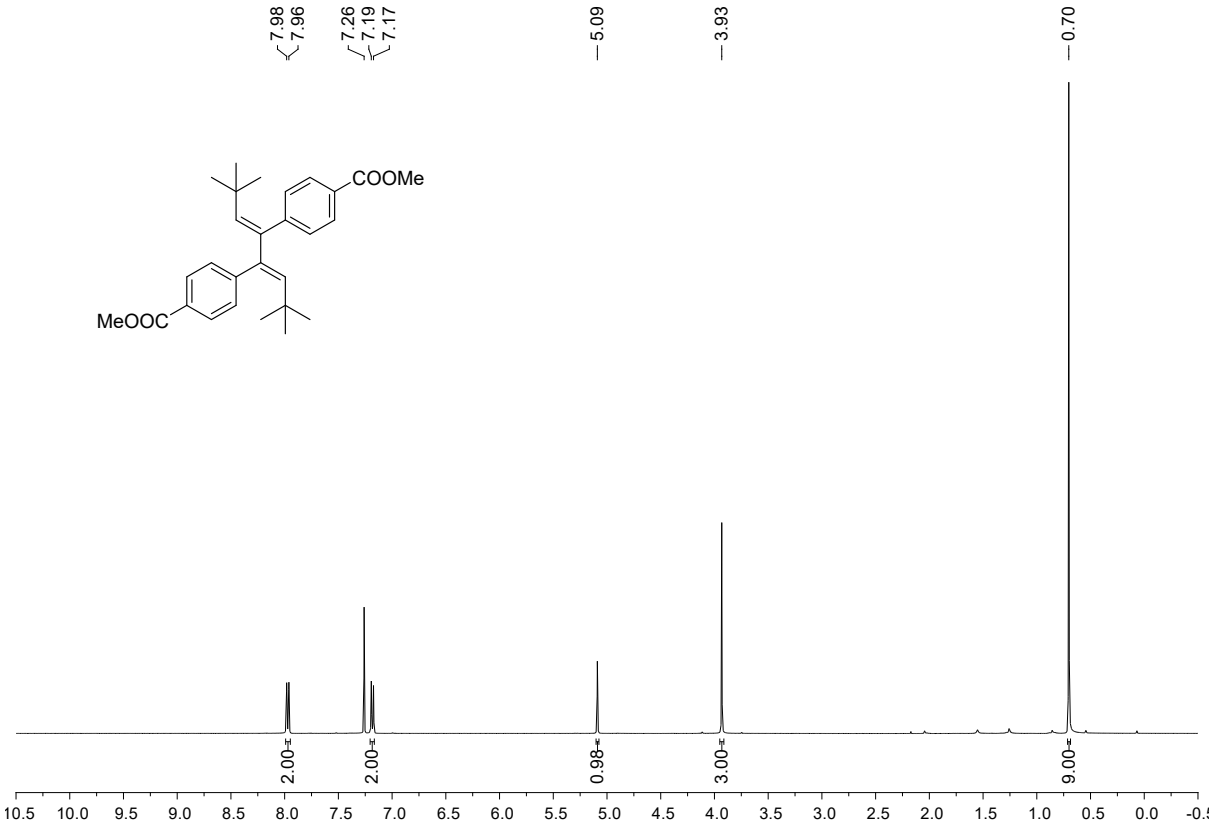
^{1}H NMR (400 MHz, $CDCl_3$) of the compound **46**.



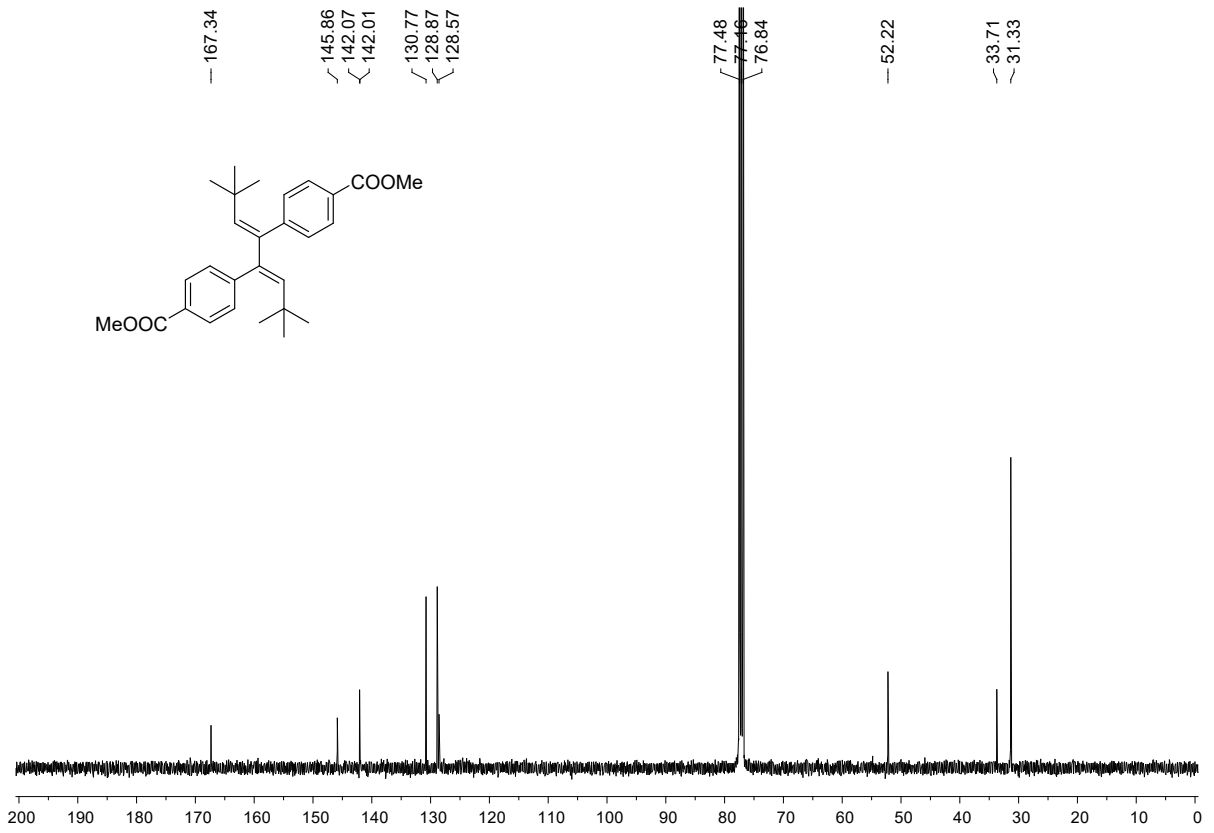
^{13}C NMR (100 MHz, $CDCl_3$) of the compound **46**.



^{1}H NMR (400 MHz, CD_2Cl_2) of the compound **47.**

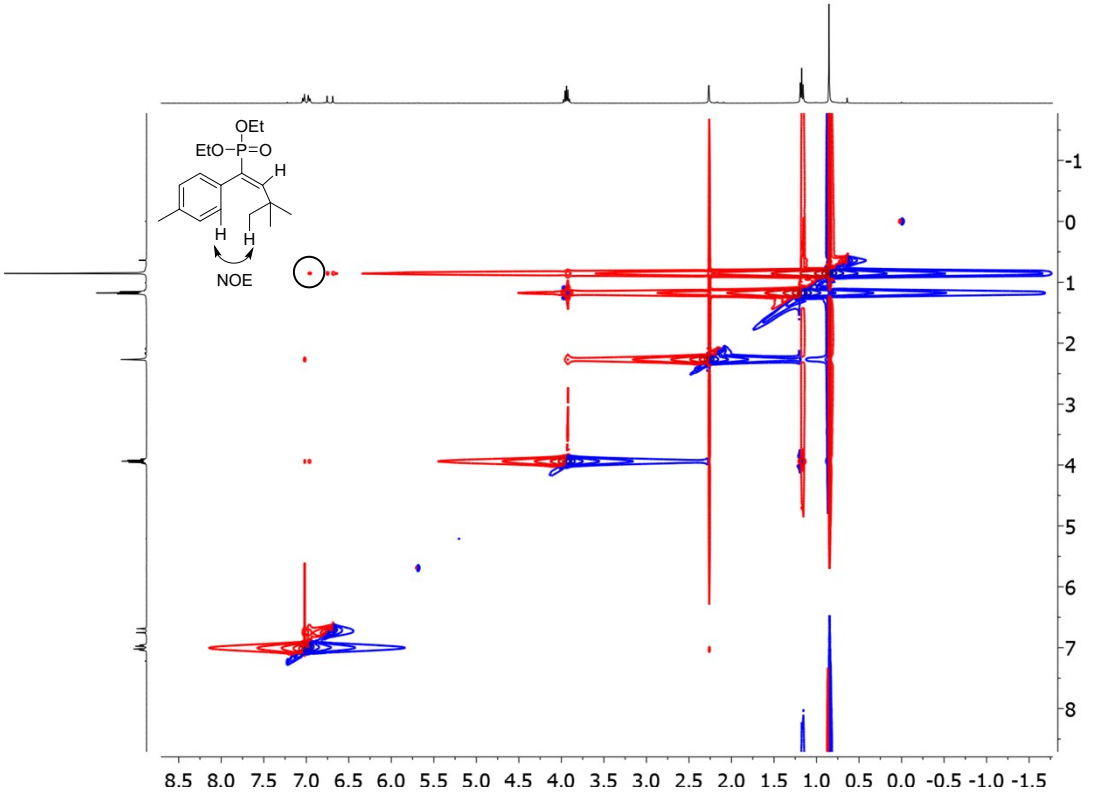


^{1}H NMR (400 MHz, $CDCl_3$) of the compound **51.**

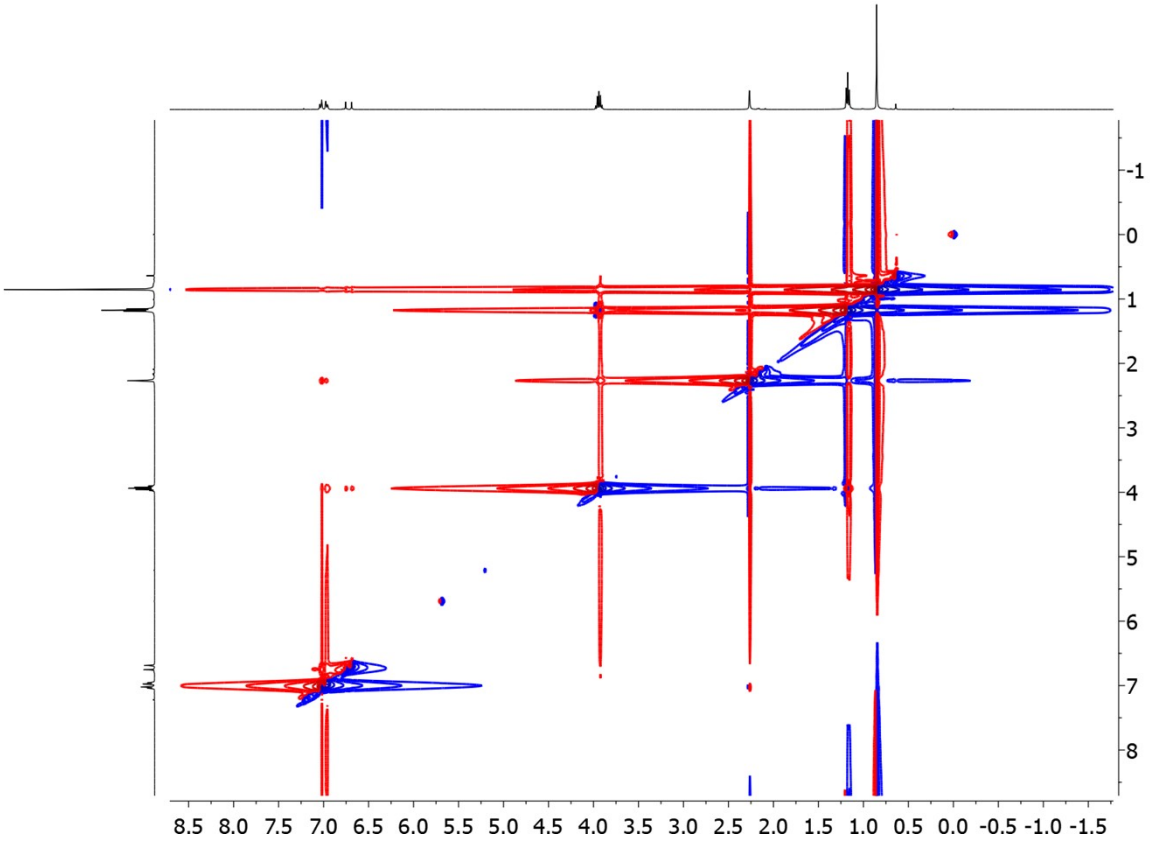


^{13}C NMR (100 MHz, $CDCl_3$) of the compound **51**.

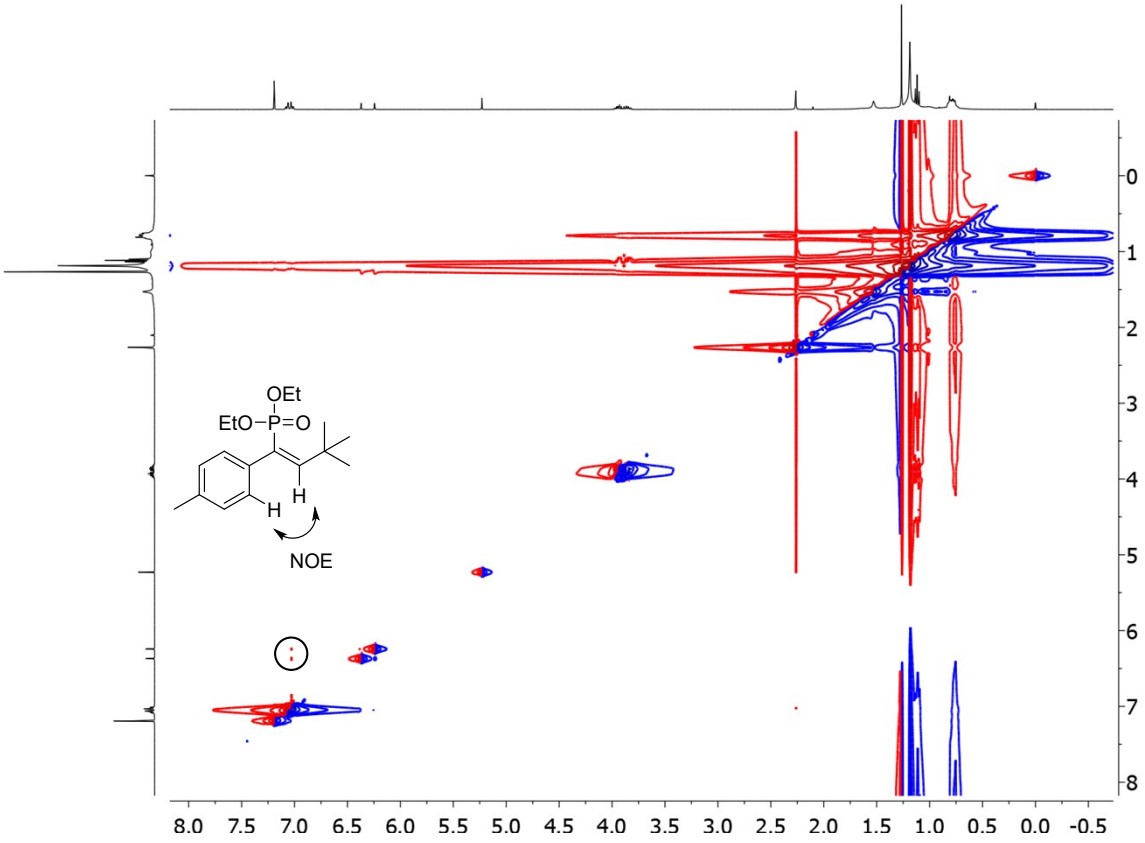
IX. ^{1}H-^{1}H NOESY of some selected compounds



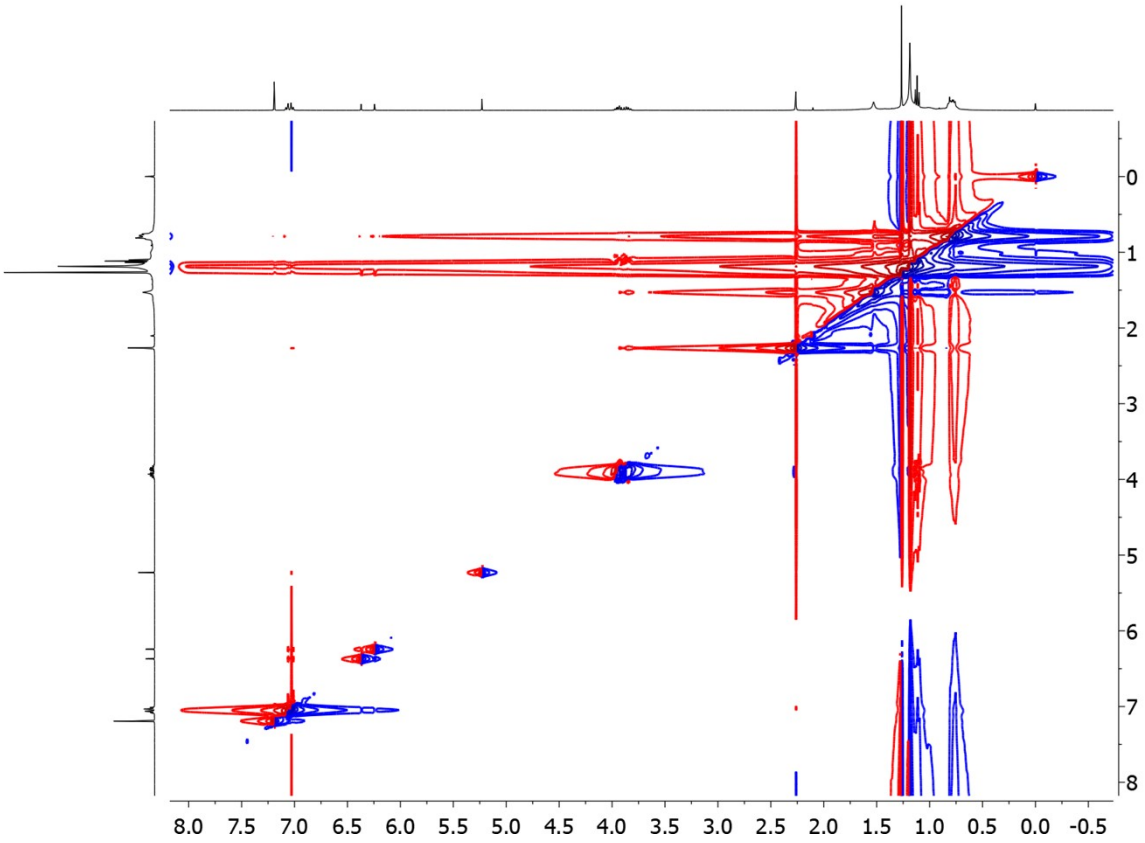
^{1}H-^{1}H NOESY of the compound **45.**



Zoomed ^{1}H-^{1}H NOESY spectrum of the compound **45**.



^{1}H-^{1}H NOESY of the compound **46**.



Zoomed ^{1}H-^{1}H NOESY spectrum of the compound **46**.