Supporting Information

For the article entitled

Chelation-Assisted α and β C−H Functionalization of Aryl Alkenes with Alkynes and Alkenes

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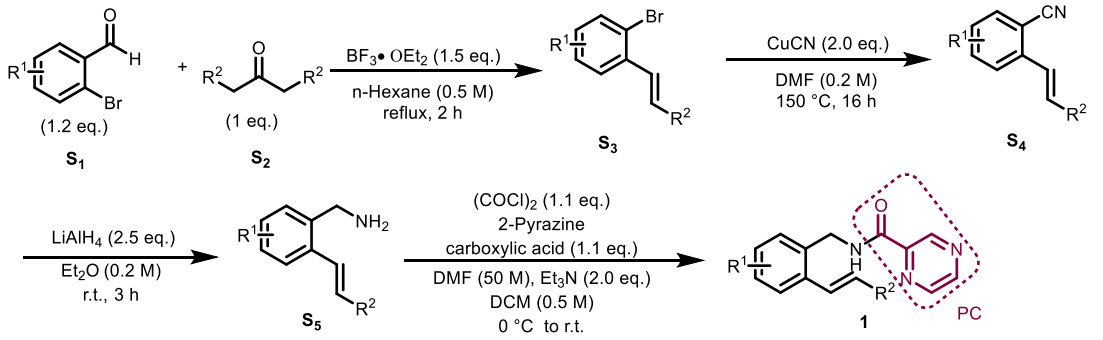
1. General Methods

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate. Flash column chromatography was performed using Merck aluminium oxide 90 active neutral with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on Bruker AMX 400 spectrophotometer ($CDCl_3$ as solvent), and Bruker AMX 500 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 7.26, singlet). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartets), dd (doublets of doublet) or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.0, triplet). Mass spectrometry was performed by Waters Q-Tof Premier Micromass instrument, using Electro Spray Ionization (ESI) mode. IR spectra were recorded as thin films on KBr plates on a Bio-Rad FTS 165 FTIR spectrometer and are reported in frequency of absorption (cm^{-1}). $Pd(OAc)_2$ were purchased from TCI or Energy Chemical and used directly. Other reagents, unless otherwise noted below, are commercially available from TCI, Energy Chemical or Alfa Aesar (China) Chemical Co. Ltd. and used without further purification.

2. General Procedure for Substrate Synthesis

The benzyl amides are prepared according to previous methods and the synthetic route is shown as following. The data of benzyl amides is also consistent with the previous data.

2.1 General Procedure A for *trans*-Styrenes



General Procedure for Tandem Aldol-Grob Reaction[1]: An oven-dried Schlenk flask was charged with 2-bromobenzaldehyde (**S_1**, 1.2 equiv), 5-nonanone (**S_2**, 1.0 equiv) and dry *n*-hexane (0.2 M). A solution of boron trifluoride diethyl etherate (BF_3• OEt_2) (1.5 equiv) was added to the Schlenk flask, and the mixture was heated to reflux with stirring for 2 hours. The reaction was cooling down to room temperature and quenched with water. The aqueous layer was extracted three times with diethyl ether. The combined organic phase was dried over anhydrous Na_2SO_4. The organic phase was filtrated and concentrated in vacuo, and the crude product was purified by silica gel chromatography and eluted by hexane to obtain compound (**S_3**) as a colorless liquid.

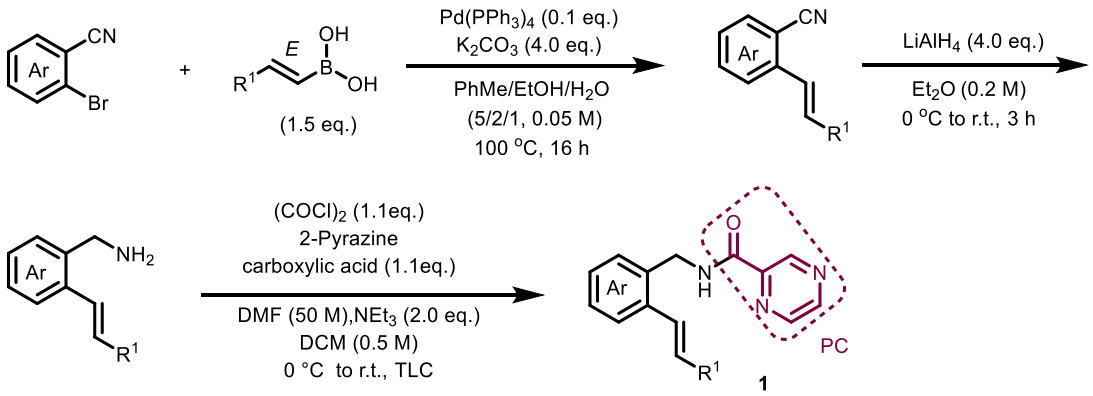
General Procedure for Cyanation Reaction[2]: To a mixture of CuCN (2.0 equiv) in DMF (0.2 M) was added 1-bromo-2-(pent-1-yn-1-yl) benzene **(**S_3, 1.0 equiv**)** at room temperature. The reaction was heated to 150 °C with stirring for 16 h until the substrate was completely consumed. After that, the reaction was cooled down to room temperature and the mixture was diluted with H_2O and extracted with EtOAc. The organic layer was combined and dried over anhydrous Na_2SO_4. The organic phase was filtrated and concentrated in vacuo, and the resulting residue was purified by silica gel column chromatography (PE / EA) to give compound **S4**.

General Procedure for Benzonitrile Reduction[3]: A solution of substituted benzonitrile **(**S_4**)** in Et_2O (0.2 M) was added $LiAlH_4$ (4.0 equiv, 1.0 M in THF) over 30 min at 0°C and stirred at room temperature for 2 h. Then, 2 N NaOH was added slowly until a clear solution was obtained. The Et_2O layer was separated and the aqueous phase was extracted with Et_2O. The organic layers were combined and dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the resulting amine **(**S_5**)** was obtained and used in the next step without further purification.

General Procedure for Amide Preparation[4]: A 50 mL round-bottomed flask

immersed in a 0°C bath (ice and water) was charged with 2-pyrazinecarboxylic acid (1.0 equiv) and CH_2Cl_2 (0.5 M). To the stirred suspension was added oxalyl chloride (1.1 equiv, 2.0 M in methylene chloride) dropwise over a 15 minute period followed by the addition of DMF (50 M, catalytic amount) in one portion, producing a rust-red color and the evolution of a gas. The mixture was kept in the cooling bath for 1 h and then allowed to warm to room temperature. After gas evolution ceased, the mixture was again cooled to 0°C and NEt_3 (2.0 equiv) was added dropwise over a 15 minute period followed by the addition of benzylamine (1.1 equiv) over a 15 minute period. The brown mixture was left in the cooling bath for 30 minutes and then allowed to warm to room temperature. Stirring was continued at room temperature for 8 h. After the reaction was finished, the solvent was removed under vacuo to give the crude product as a brown solid that was extracted with CH_2Cl_2. The organic phases were combined and dried over anhydrous Na_2SO_4. The organic phase was filtrated and concentrated in vacuo, the resulting residue was purified by silica gel column chromatography (PE/EA = 8/1) to obtain the corresponding *trans*-styrenes **1**.

2.2 General Procedure B for *trans*-Styrenes



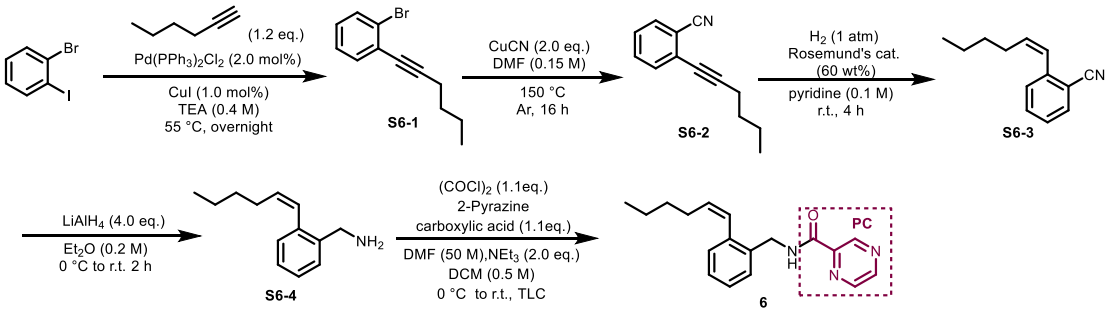
General Procedure for synthesis (*E*)-alkenyl boronic acid[5]: To a solution of terminal alkyl alkyne (1.0 equiv) in DCM (1 M) was added $HBBr_2Me_2S$ (1.0 equiv, 1 M in DCM) at 0°C. After addition, the mixture was warm to room temperature and stirred for 4 h. The resulting solution was then dropwise added to an ice-cooled mixture of Et_2O/H_2O (0.5 M, *v: v* =2/1) and continued stirring for 15 min. The aqueous layer was extracted with Et_2O. The organic phase was combined and dried over anhydrous Na_2SO_4. After filtration and concentration in vacuo to afford (*E*)-alkenyl boronic acid which could be used directly.

Suzuki Reaction[5]: A solution of (*E*)-pent-1-en-1-yl boronic acid (1.5 equiv), $Pd(PPh_3)_4$ (0.1 equiv), K_2CO_3 (4.0 equiv), K_3PO_4 (3.0 equiv), and ortho-bromoarene (1.0 equiv) in toluene/EtOH/H_2O (100 mL, *v :v :v* = 5/2/1, 0.05 M) was heated to 100°C with stirring for 16 h in a sealed tube under an argon atmosphere. Then the reaction was cooled to room temperature and diluted with H_2O followed by extraction with EtOAc. The organic phase was combined and dried over anhydrous Na_2SO_4. After filtration and

concentration in vacuo, the crude product was purified by silica gel chromatography (SiO_2, PE/EA) to afford the corresponding product.

Benzonitrile Reduction and Amide Preparation was performed following **the general procedure A** to obtain *trans*-styrenes **1**.

2.3 Procedure C for Synthesis of *cis*-Styrenes



Alkynylation Reaction[7]: A solution of $Pd(PPh_3)_2Cl_2$ (1.0 mol%), CuI (1.0 mol%), 1-bromo-2-iodobenzene (1.0 equiv) and 1-pentyne (1.2 equiv) in NEt_3 (0.4 M) was heated to 55°C with stirring for overnight. Then, the reaction was cooled to room temperature and diluted with H_2O, and extracted with EtOAc. The organic phase was combined and dried over anhydrous Na_2SO_4. After filtration and concentration in vacuo, the crude product was purified by silica gel chromatography (SiO_2, PE / EA) to obtain the corresponding product (**S6-1)**.

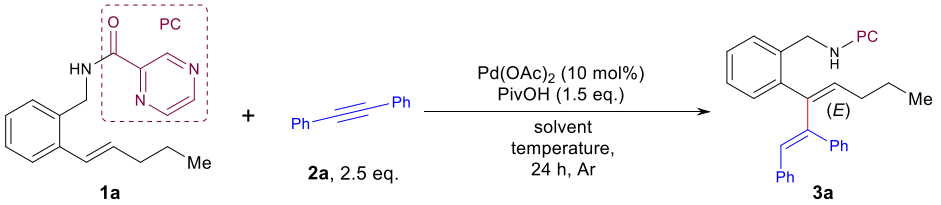
Cyanation Reaction was performed following **the general procedure A** to obtain the corresponding product (**S6-2)**

Hydrogenation Reaction: Following the previously reported procedure with a slight modification, a two-necked flask was changed with Rosenmund's catalyst (60 wt%, 5% Pd on $BaSO_4$), alkyne (**S6-2)** (1.0 equiv) and pyridine (0.1 M). The reaction bottle was vacuumed three times and then backfilled with H_2 three times. And then, the solution was allowed to stir at room temperature for 4 h until the reaction was completed (monitored by TLC). The reaction solution was diluted with ethyl acetate and washed with HCl (2 N), water and brine. The organic phase was then dried over anhydrous Na_2SO_4. After filtration and concentration in vacuo, the crude product was purified by silica gel chromatography (SiO_2, PE/EA) to obtain olefin (**S6-3)**.

Benzonitrile Reduction and Amide Preparation was performed following **the general procedure A** to obtain *cis*-styrenes **6**.

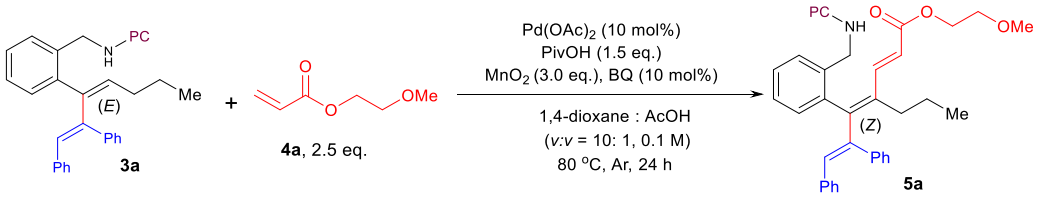
3. General Procedure for Alkenyl C-H Alkenylation

3.1 Condition optimization



Entry [a]	Temperature (℃)	Solvent	Yield (%[b], *E/Z*[c])
1	40	EtOH	NR
2	70	EtOH	58% (86:14)
3	100	EtOH	96% (81:19)
4	100	MeOH	93% (65:34)
5	100	MeCN	90% (68:32)
6	100	DMSO	96% (42:58)
7	100	DMF	91% (74:26)
8	100	1,4-dioxane	97% (89:11)
9	80	1,4-dioxane	81% (96:4)
10	90	1,4-dioxane	87% (96:4)

[a] Conditions: **1a** (0.1 mmol), **2a** (0.25 mmol, 2.5 equiv.), $Pd(OAc)_2$ (10 mol%), PivOH (1.5 equiv.) in a solvent (0.15 M), 24 h under Ar; [b] Isolated yields; [c] *E/Z* ratios of the isomer given in parentheses were determined by ^1H NMR analysis.

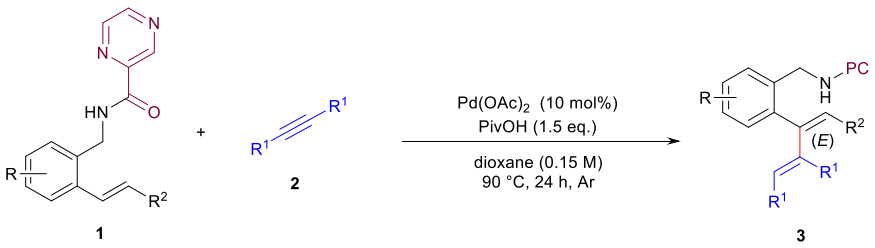


Entry[a]	Solvent	Additive/Catalyst	Yield (%, *E/Z*) [b,c]
1	dioxane/AcOH=10:1	PivOH	61% (>99:1)
2	DMF	PivOH	trace
3	DMSO	PivOH	trace
4	dioxane	PivOH	65% (87:13)
5	MeCN	PivOH	34% (63:37)
6	Toluene	PivOH	77% (82:18)
7	DME	PivOH	52% (>99:1)
8	EtOH	PivOH	32% (>99:1)
9	EtOH	15mol% [Pd]	41% (>99:1)
10[d]	dioxane /AcOH=10:1	PivOH	51% (>99:1)
11[e]	dioxane /AcOH=10:1	PivOH	43% (>99:1)
12[f]	dioxane /AcOH=10:1	PivOH	27% (>99:1)

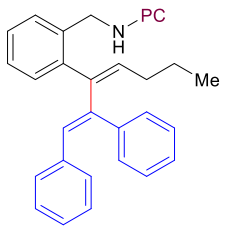
13	dioxane /AcOH=12:1	PivOH	53% (98:2)
14	dioxane /AcOH=8:1	PivOH	44% (>99:1)
15	dioxane /AcOH=1:1	PivOH	35% (>99:1)
16	EtOH/AcOH=10:1	PivOH	Trace
17	dioxane /AcOH=10:1	15mol% [Pd]	48% (>99:1)
18	dioxane /AcOH=10:1	PivOH	55% (>99:1)
19	dioxane /AcOH=10:1	PivOH (2.5 eq)	50% (>99:1)
20	dioxane /AcOH=10:1	PivOH (1.0 eq)	Trace

[a] Conditions: **3a** (0.1 mmol), **4a** (0.25 mmol, 2.5 eq.), $Pd(OAc)_2$ (10 mol%), PivOH, MnO_2 (3.0 equiv.) and BQ (10 mol%) in solvent (0.1 M) heat and stir for 24 h under Ar; [b] Isolated yields; [c] *E/Z* ratios of the isomer given in parentheses were determined by ^{1}H NMR analysis; [d] 90 °C; [e]100 °C; [f] 110 °C.

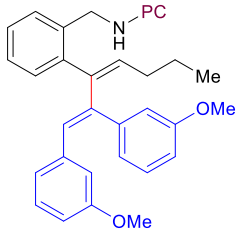
3.2 General Procedure 1 for Cross-Coupling-1 between *trans*-Styrenes and Alkynes



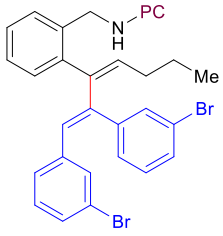
A screw-cap vial was charged with $Pd(OAc)_2$ (10 mol%, 0.015 mmol), *trans*-styrenes **1** (1.0 equiv, 0.15 mmol), alkyne **2** (2.5 equiv, 0.38 mmol) and 1,4-dioxane (1.0 mL). Then, pivalic acid (1.5 equiv, 0.23 mmol) were added into the solution. The vial was sealed under argon atmosphere and heated to 90°C with stirring for 24 h. After cooling down, the mixture was concentrated and directly applied to a flash column chromatography (PE/EA mixtures) for separation to obtain the corresponding product **3**.



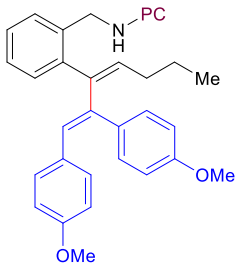
***N*-(2-((1*E*,3*E*)-1,2-Diphenylhepta-1,3-dien-3-yl) benzyl) pyrazine-2-carboxamide (3a)** Following the **General Procedure 1**, **3a** was obtained as a yellow oil (60.0 mg, 87% yield, *E/Z*=96:4). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.42 (d, *J* = 1.5 Hz, 1H), 8.68 (d, *J* = 2.5 Hz, 1H), 8.32 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.93 (s, 1H), 7.31-7.28 (m, 1H), 7.18-7.12 (m, 6H), 7.08 (dd, *J* = 5.6, 2.5 Hz, 5H), 7.00-6.94 (m, 2H), 6.65 (s, 1H), 5.66 (t, *J* = 7.4 Hz, 1H), 4.73 (d, *J* = 5.8 Hz, 2H), 2.33 (q, *J* = 7.4 Hz, 2H), 1.55-1.46 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.58, 147.08, 144.55, 144.36, 142.44, 142.41, 142.25, 140.83, 139.16, 136.65, 135.33, 135.04, 130.99, 130.89, 129.48, 129.21, 129.09, 128.40, 127.89, 127.43, 127.32, 127.20, 126.88, 41.48, 31.66, 23.35, 14.08. **HRMS (ESI)** *m/z* calculated for $C_{31}H_{29}N_3ONa$ $[M+Na]^+$: 482.2203, found: 482.2207.



***N*-(2-((1*E*,3*E*)-1,2-bis(3-methoxyphenyl) hepta-1,3-dien-3-yl) benzyl) pyrazine-2-carboxamide (3b)** Following the **General Procedure 1**, **3b** was obtained as a yellow oil (36.6 mg, 47% yield, *E/Z*= 90:10). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.42 (d, *J* = 1.6 Hz, 1H), 8.69 (d, *J* = 2.5 Hz, 1H), 8.38 – 8.32 (m, 1H), 7.92 (t, *J* = 5.9 Hz, 1H), 7.32 (dd, *J* = 5.2, 2.6 Hz, 1H), 7.22 – 7.16 (m, 3H), 7.11 (t, *J* = 7.9 Hz, 1H), 7.03 (t, *J* = 7.9 Hz, 1H), 6.73 – 6.68 (m, 2H), 6.68 – 6.60 (m, 4H), 6.53 (s, 1H), 5.67 (t, *J* = 7.4 Hz, 1H), 4.73 (d, *J* = 5.8 Hz, 2H), 3.61 (s, 3H), 3.52 (s, 3H), 2.36 (q, *J* = 7.3 Hz, 2H), 1.52 (h, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.53, 158.55, 157.95, 146.06, 143.48, 143.33, 141.33, 141.22, 141.14, 139.79, 139.56, 136.81, 134.37, 133.96, 129.85, 129.82, 128.41, 128.09, 127.81, 126.42, 126.29, 121.30, 120.59, 113.36, 112.74, 112.53, 112.11, 54.06, 53.80, 40.42, 30.59, 22.30, 13.03. **HRMS (ESI)** *m/z* calculated for $C_{33}H_{33}N_3O_3Na$ $[M+Na]^+$: 542.2414, found: 542.2409.

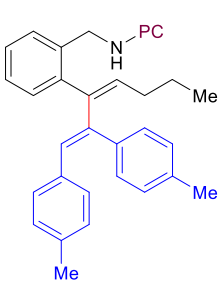


***N*-(2-((1*E*,3*E*)-1,2-bis (3-bromophenyl) hepta-1,3-dien-3-yl) benzyl) pyrazine-2-carboxamide (3c)** Following the **General Procedure 1**, **3c** was obtained as a yellow oil (42.3 mg, 46% yield, *E/Z*=93:7). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.43 (d, *J* = 1.5 Hz, 1H), 8.70 (d, *J* = 2.4 Hz, 1H), 8.37 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.91 (s, 1H), 7.34-7.27 (m, 2H), 7.25-7.21 (m, 2H), 7.21-7.16 (m, 2H), 7.11 (dd, *J* = 8.8, 1.8 Hz, 2H), 7.04 (t, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.7 Hz, 1H), 6.93 (t, *J* = 7.9 Hz, 1H), 6.84 (s, 1H), 6.59 (s, 1H), 5.72 (t, *J* = 7.4 Hz, 1H), 4.72 (d, *J* = 5.7 Hz, 2H), 2.28 (q, *J* = 7.4 Hz, 2H), 1.54-1.45 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.56, 147.22, 144.41, 144.37, 142.45, 141.69, 141.43, 140.73, 140.67, 138.23, 136.18, 135.21, 132.42, 132.04, 130.95, 130.61, 130.28, 130.08, 130.05, 129.44, 129.38, 127.93, 127.84, 127.76, 127.60, 122.45, 122.06, 41.56, 31.69, 23.25, 14.05. **HRMS (ESI)** *m/z* calculated for $C_{31}H_{27}Br_2N_3ONa$ $[M+Na]^+$: 638.0413, found: 638.0417.

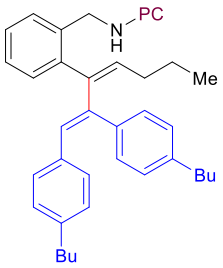


***N*-(2-((1*E*,3*E*)-1,2-Bis(4-methoxyphenyl) hepta-1,3-dien-3-yl) benzyl) pyrazine-2-carboxamide (3d)** Following the **General Procedure 1**, **3d** was obtained as a yellow oil (40.1 mg, 51% yield, *E/Z*=76:24). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.44-9.39 (m, 1H), 8.68 (d, *J* = 2.4 Hz, 1H), 8.34 (dd, *J* = 2.3, 1.5 Hz, 1H), 7.90 (s, 1H), 7.16 (t, *J* = 3.4 Hz, 3H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 6.63 (d, *J* = 8.8 Hz, 2H), 6.55 (s, 1H), 6.54-6.47 (m, 1H), 5.62 (t, *J* = 7.3 Hz, 1H), 4.73 (d, *J* = 5.8 Hz, 2H), 3.72 (d, *J* = 2.7 Hz, 6H), 2.33 (q, *J* = 7.3 Hz, 2H), 1.55-1.45 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, CDCl3) δ 162.55, 158.56, 158.39, 147.06, 144.56, 144.37, 142.83, 142.41, 142.27, 138.47, 135.30, 134.59, 131.55, 131.15, 130.83, 130.66, 130.40, 130.08, 129.50, 129.11, 127.29, 113.85, 113.35, 77.31, 77.06, 76.81, 55.17,

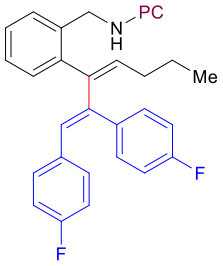
55.05, 41.46, 31.63, 23.39, 14.08. **HRMS (ESI)** *m/z* calculated for $C_{33}H_{33}N_3O_3Na$ $[M+Na]^+$: 542.2414, found: 542.2419.



***N*-(2-((1*E*,3*E*)-1,2-Di-p-tolylhepta-1,3-dien-3-yl) benzyl) pyrazine-2-carboxamide (3e)** Following the **General Procedure 1**, **3e** was obtained as a yellow oil (60.7 mg, 83% yield, *E/Z*= 94:6). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.42 (d, *J* = 1.5 Hz, 1H), 8.67 (d, *J* = 2.5 Hz, 1H), 8.33 (t, *J* = 1.9 Hz, 1H), 7.91 (s, 1H), 7.31-7.26 (m, 1H), 7.15 (q, *J* = 4.7, 4.2 Hz, 3H), 6.96 (s, 4H), 6.89 (s, 4H), 6.59 (s, 1H), 5.62 (d, *J* = 7.4 Hz, 1H), 4.72 (d, *J* = 5.8 Hz, 2H), 2.33 (q, *J* = 7.3 Hz, 2H), 2.24 (s, 3H), 2.24 (s, 3H), 1.54 – 1.45 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.57, 147.04, 144.60, 144.42, 142.74, 142.45, 142.38, 139.90, 136.68, 136.59, 136.21, 135.35, 134.75, 133.95, 130.83, 130.60, 129.36, 129.11, 129.06, 128.61, 127.30, 127.25, 41.45, 31.65, 23.38, 21.27, 21.15, 14.08. **HRMS (ESI)** *m/z* calculated for $C_{33}H_{33}N_3ONa$ $[M+Na]^+$: 510.2516, found: 510.2525.

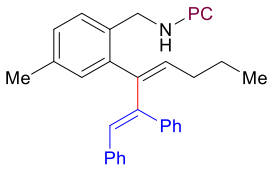


***N*-(2-((1*E*,3*E*)-1,2-bis (4-butylphenyl) hepta-1,3-dien-3-yl) benzyl) pyrazine-2-carboxamide (3f)** Following the **General Procedure 1**, **3f** was obtained as a yellow liquid (40.3 mg, 47% yield, *E/Z*= 95:5). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.43-9.40 (m, 1H), 8.66 (d, *J* = 2.4 Hz, 1H), 8.30 (dd, *J* = 2.4, 1.5 Hz, 1H), 7.96 (s, 1H), 7.32-7.26 (m, 1H), 7.18-7.13 (m, 3H), 6.98 (s, 4H), 6.88 (s, 4H), 6.56 (s, 1H), 5.62 (t, *J* = 7.4 Hz, 1H), 4.72 (d, *J* = 5.9 Hz, 2H), 2.51 (dt, *J* = 13.7, 7.7 Hz, 4H), 2.29 (q, *J* = 7.4 Hz, 2H), 1.58-1.45 (m, 6H), 1.37 -1.22 (m, 4H), 0.95-0.87 (m, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$)δ 162.56, 147.02, 144.59, 144.41, 142.74, 142.60, 142.35, 141.72, 141.64, 140.07, 136.57, 135.37, 134.66, 134.15, 130.90, 130.70, 129.36, 129.01, 128.43, 127.90, 127.27, 127.23, 41.50, 35.32, 35.30, 33.48, 33.36, 31.63, 23.36, 22.36, 22.23, 14.07, 13.98, 13.95. **HRMS (ESI)** *m/z* calculated for $C_{39}H_{45}N_3ONa$ $[M+Na]^+$: 594.3455, found: 594.3464.

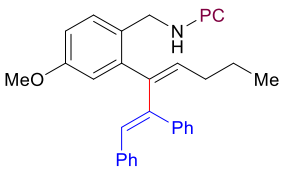


***N*-(2-((1*E*,3*E*)-1,2-bis (4-fluorophenyl) hepta-1,3-dien-3-yl) benzyl) pyrazine-2-carboxamide (3g)** Following the **General Procedure 1**, **3g** was obtained as a yellow liquid (49.5 mg, 67% yield, *E/Z*= 94:6). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.43 (s, 1H), 8.71 (d, *J* = 2.3 Hz, 1H), 8.38 (dd, *J* = 2.4, 1.5 Hz, 1H), 7.82 (s, 1H), 7.30 (dd, *J* = 5.6, 3.3 Hz, 1H), 7.20-7.12 (m, 3H), 7.02 (dd, *J* = 8.6, 5.5 Hz, 2H), 6.94 (dd, *J* = 8.6, 5.6 Hz, 2H), 6.86 (t, *J* = 8.7 Hz, 2H), 6.79 (t, *J* = 8.7 Hz, 2H), 6.62 (s, 1H), 5.67 (t, *J* = 7.4 Hz, 1H), 4.71 (d, *J* = 5.7 Hz, 2H), 2.33 (q, *J* = 7.3 Hz, 2H), 1.55 – 1.46 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.54, 161.95 (d, J_{CF} = 246.9 Hz), 161.64 (d, J_{CF} = 247.6 Hz), 147.20, 144.43, 144.39, 142.44, 141.97 (d, J_{CF} = 19.3 Hz), 139.45 (d, J_{CF} = 1.4 Hz), 135.26, 135.23, 134.80 (d, J_{CF} = 3.4 Hz), 132.50 (d, J_{CF} = 3.4 Hz), 131.05, 130.99, 130.90,

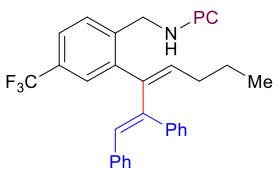
130.83, 130.75, 130.08, 129.17, 127.49 (d, J_{CF} = 20.6 Hz), 115.59 (d, J_{CF} = 21.3 Hz), 114.95 (d, J_{CF} = 21.4 Hz), 41.35, 31.66, 23.33, 14.07. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -114.22, -114.31. **HRMS (ESI)** *m/z* calculated for $C_{31}H_{27}F_2N_3ONa$ $[M+Na]^+$: 518.2014, found: 518.2020.



***N*-(2-((1*E*,3*E*)-1,2-diphenyl hepta-1,3-dien-3-yl)-4-methyl benzyl) pyrazine-2-carboxamide (3i)** Following the **General Procedure 1**, **3i** was obtained as a yellow solid (87.1mg, 77% yield, *E/Z*=95:5, m.p. = 102.6-103.7 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.41 (d, *J* = 1.5 Hz, 1H), 8.65 (d, *J* = 2.4 Hz, 1H), 8.30 (s, 1H), 7.88 (s, 1H), 7.17 (dd, *J* = 14.0, 7.7 Hz, 4H), 7.10-7.04 (m, 5H), 7.00-6.94 (m, 4H), 6.63 (s, 1H), 5.64 (t, *J* = 7.4 Hz, 1H), 4.68 (d, *J* = 5.7 Hz, 2H), 2.30 (q, *J* = 7.4 Hz, 2H), 2.25 (s, 3H), 1.54 – 1.43 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.52, 147.04, 144.60, 144.34, 142.47, 142.40, 142.21, 140.96, 139.27, 136.95, 136.73, 134.88, 132.38, 131.43, 130.98, 129.48, 129.24, 129.19, 128.40, 128.18, 127.89, 127.19, 126.85, 41.27, 31.68, 23.36, 21.06, 14.10. **HRMS (ESI)** *m/z* calculated for $C_{32}H_{31}N_3ONa$ $[M+Na]^+$: 496.2359, found: 496.2362.

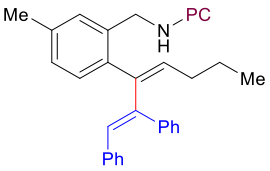


***N*-(2-((1*E*, 3*E*)-1,2-diphenyl hepta-1,3-dien-3-yl)-4-methoxy benzyl) pyrazine-2-carboxamide (3j)** Following the **General Procedure 1**, **3j** was obtained as a light yellow oil (55.9 mg, 76% yield, *E/Z*=99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.41 (d, *J* = 1.5 Hz, 1H), 8.66 (d, *J* = 2.5 Hz, 1H), 8.30 (t, *J* = 2.0 Hz, 1H), 7.87 (s, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.16 (q, *J* = 6.1 Hz, 3H), 7.11-7.05 (m, 5H), 6.96 (dd, *J* = 6.4, 2.9 Hz, 2H), 6.73-6.66 (m, 2H), 6.64 (s, 1H), 5.67 (t, *J* = 7.4 Hz, 1H), 4.66 (d, *J* = 5.7 Hz, 2H), 3.70 (s, 3H), 2.32 (q, *J* = 7.4 Hz, 2H), 1.54-1.45 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.46, 158.55, 147.02, 144.60, 144.32, 143.67, 142.39, 142.35, 140.68, 139.14, 136.63, 134.95, 130.99, 130.60, 129.48, 129.24, 128.42, 127.87, 127.65, 127.22, 126.88, 116.34, 112.74, 55.23, 41.03, 31.63, 23.33, 14.07. **HRMS (ESI)** *m/z* calculated for $C_{32}H_{31}N_3O_2Na$ $[M+Na]^+$: 521.2308, found: 521.2316.

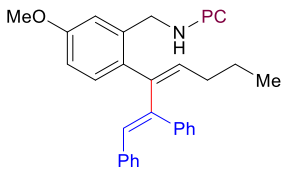


***N*-(2-((1*E*, 3*E*)-1,2-diphenyl hepta-1,3-dien-3-yl)-4-(trifluoromethyl) benzyl)-1-methylphosphanamine (3k)** Following the **General Procedure 1**, **3k** was obtained as a light yellow oil (66.5 mg, 84% yield, *E/Z*=95:5). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.70 (s, 1H), 8.35 (s, 1H), 7.97 (s, 1H), 7.39 (dd, *J* = 19.2, 7.2 Hz, 3H), 7.17 (d, *J* = 6.2 Hz, 3H), 7.13 – 7.08 (m, 3H), 7.06 (dd, *J* = 7.3, 2.1 Hz, 2H), 7.03 – 6.98 (m, 2H), 6.69 (s, 1H), 5.70 (t, *J* = 7.4 Hz, 1H), 4.77 (d, *J* = 6.1 Hz, 2H), 2.38 (q, *J* = 7.4 Hz, 2H), 1.59 – 1.49 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.82, 147.32, 144.43, 144.26, 142.71, 142.44, 141.40, 140.12, 139.52, 138.73, 136.32, 136.03, 131.47, 129.53, 129.19,

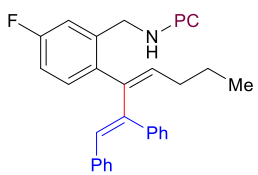
129.11, 128.58, 127.99, 127.55 (q, J_{CF} = 3.6 Hz), 127.47, 127.16, 124.09 (q, J_{CF} = 3.6 Hz), 123.97 (d, J_{CF} = 272.3 Hz), 40.93, 31.69, 23.29, 14.10. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.56. **HRMS (ESI)** *m/z* calculated for $C_{32}H_{28}F_3N_3ONa$ $[M+Na]^+$: 550.2077, found: 550.2078.



***N*-(2-((1*E*, 3*E*)-1,2-Diphenyl hepta-1,3-dien-3-yl)-5-methyl benzyl) pyrazine-2-carboxamide (3l)** Following the **General Procedure 1**, **3l** was obtained as a light yellow oil (66.2 mg, 93% yield, *E/Z*=90:10). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.42 (d, *J* = 1.5 Hz, 1H), 8.67 (d, *J* = 2.5 Hz, 1H), 8.32 (dd, *J* = 2.4, 1.5 Hz, 1H), 7.91 (s, 1H), 7.15 (q, *J* = 5.5 Hz, 3H), 7.11-7.03 (m, 7H), 6.99-6.93 (m, 3H), 6.64 (s, 1H), 5.64 (t, *J* = 7.4 Hz, 1H), 4.69 (d, *J* = 5.8 Hz, 2H), 2.32 (q, *J* = 7.3 Hz, 2H), 2.25 (s, 3H), 1.53-1.45 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.52, 147.06, 144.60, 144.39, 142.38, 142.36, 141.01, 139.39, 139.22, 137.08, 136.73, 135.08, 134.92, 130.82, 130.79, 129.88, 129.48, 129.24, 128.37, 128.12, 127.87, 127.15, 126.82, 41.48, 31.68, 23.37, 21.06, 14.08. **HRMS (ESI)** *m/z* calculated for $C_{32}H_{31}N_3ONa$ $[M+Na]^+$: 496.2359, found: 496.2354.

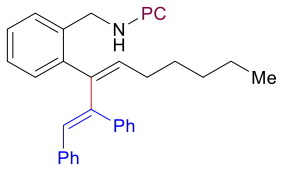


***N*-(2-((1*E*,3*E*)-1,2-Diphenylhepta-1,3-dien-3-yl)-5-methoxy benzyl) pyrazine-2-carboxamide (3m)** Following the **General Procedure 1**, **3m** was obtained as a yellow oil (89.2 mg, 74% yield, *E/Z*=93:7). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.41 (d, *J* = 1.4 Hz, 1H), 8.66 (d, *J* = 2.4 Hz, 1H), 8.32 (dd, *J* = 2.3, 1.5 Hz, 1H), 7.94 (s, 1H), 7.20-7.11 (m, 3H), 7.10-7.04 (m, 6H), 6.98 (dd, *J* = 6.8, 2.8 Hz, 2H), 6.83 (d, *J* = 2.7 Hz, 1H), 6.69 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.65 (s, 1H), 5.63 (d, *J* = 7.4 Hz, 1H), 4.70 (d, *J* = 5.8 Hz, 2H), 3.71 (s, 3H), 2.34 (q, *J* = 7.3 Hz, 2H), 1.55 – 1.45 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.62, 158.68, 147.11, 144.53, 144.35, 142.44, 142.11, 141.10, 139.26, 136.73, 136.67, 134.92, 134.64, 131.99, 130.72, 129.47, 129.21, 128.40, 127.90, 127.16, 126.84, 114.21, 112.79, 55.20, 41.60, 31.73, 23.41, 14.11. **HRMS (ESI)** *m/z* calculated for $C_{32}H_{31}N_3O_2Na$ $[M+Na]^+$: 512.2308, found: 512.2302.

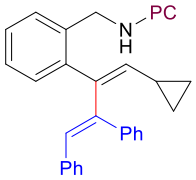


***N*-(2-((1*E*, 3*E*)-1,2-Diphenylhepta-1,3-dien-3-yl)-5-fluorobenzyl) pyrazine-2-carboxamide (3n)** Following the **General Procedure 1**, **3n** was obtained as a yellow oil (78.6 mg, 69% yield, *E/Z*=97:3). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.42 (d, *J* = 1.5 Hz, 1H), 8.69 (d, *J* = 2.5 Hz, 1H), 8.36 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.97 (s, 1H), 7.20-7.14 (m, 3H), 7.12-7.05 (m, 6H), 6.99 (dt, *J* = 6.1, 2.4 Hz, 3H), 6.82 (td, *J* = 8.4, 2.7 Hz, 1H), 6.66 (s, 1H), 5.65 (t, *J* = 7.4 Hz, 1H), 4.71 (d, *J* = 6.0 Hz, 2H), 2.37 (q, *J* = 7.3 Hz, 2H), 1.58 – 1.47 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.78, 161.80 (d, J_{CF} = 244.5 Hz), 147.27, 144.43, 144.34, 142.45, 141.61, 140.65, 139.03, 137.88 (d, J_{CF} = 3.2 Hz), 137.78 (d, J_{CF} = 7.1 Hz),

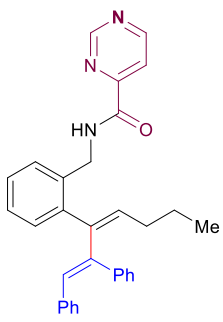
136.51, 135.39, 132.40 (d, J_{CF} = 7.9 Hz), 131.02, 129.48, 129.14, 128.49, 127.95, 127.31, 127.01, 115.25 (d, J_{CF} = 21.8 Hz), 114.09 (d, J_{CF} = 20.9 Hz), 41.09, 31.69, 23.35, 14.10. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -114.86. **HRMS (ESI)** *m/z* calculated for $C_{31}H_{28}FN_3ONa$ $[M+Na]^+$: 500.2109, found: 500.2110.



***N*-(2-((1*E*,3*E*)-1,2-Diphenylnona-1,3-dien-3-yl) benzyl) pyrazine-2-carboxamide (3o)** Following the **General Procedure 1**, **3o** was obtained as a light yellow oil (59.7 mg, 82% yield, *E/Z*=93:7). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.42 (d, *J* = 1.5 Hz, 1H), 8.68 (d, *J* = 2.5 Hz, 1H), 8.33 (t, *J* = 2.0 Hz, 1H), 7.92 (s, 1H), 7.31-7.28 (m, 1H), 7.19-7.13 (m, 6H), 7.11-7.05 (m, 5H), 6.99-6.93 (m, 2H), 6.64 (s, 1H), 5.66 (t, *J* = 7.4 Hz, 1H), 4.72 (d, *J* = 5.8 Hz, 2H), 2.33 (q, *J* = 7.4 Hz, 2H), 1.51 – 1.41 (m, 2H), 1.35-1.27 (m, 4H), 0.87 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 147.08, 144.54, 144.40, 142.36, 142.29, 142.18, 140.86, 139.17, 136.67, 135.35, 135.28, 130.98, 130.88, 129.46, 129.22, 129.12, 128.38, 127.87, 127.40, 127.31, 127.18, 126.84, 41.48, 31.67, 29.84, 29.59, 22.53, 14.03. **HRMS (ESI)** *m/z* calculated for $C_{33}H_{33}N_3ONa$ $[M+Na]^+$: 510.2516, found: 510.2509.



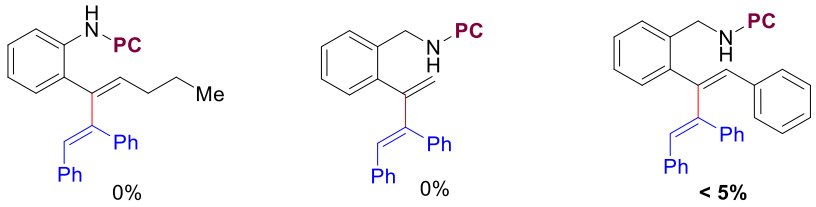
N-(2-((1E,3E)-1-cyclopropyl-3,4-diphenylbuta-1,3-dien-2-l) benzyl) pyrazine-2-carboxamide (3p). Following the general procedure 1, **3p** was obtainedas a yellow liquid (21.8 mg, 32% yield, , *E/Z* = 99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.42 (d, *J* = 1.5 Hz, 1H), 8.68 (d, *J* = 2.4 Hz, 1H), 8.32 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.99 – 7.93 (m, 1H), 7.29 (ddd, *J* = 5.4, 3.4, 2.1 Hz, 1H), 7.17 (ddt, *J* = 9.3, 5.6, 2.9 Hz, 9H), 7.08 – 7.05 (m, 3H), 6.97 (dd, *J* = 6.8, 3.0 Hz, 2H), 6.76 (s, 1H), 5.00 (d, *J* = 10.1 Hz, 1H), 1.73 (dddd, *J* = 12.8, 9.7, 8.1, 4.7 Hz, 1H), 0.77 – 0.69 (m, 2H), 0.49 – 0.41 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.56 , 147.10 , 144.54 , 144.41 , 142.36 , 142.33 , 141.23 , 140.35 , 139.62 , 139.33 , 136.86 , 135.46 , 131.29 , 130.97 , 129.48 , 129.45 , 129.14 , 128.40 , 127.86 , 127.39 , 127.38 , 127.21 , 126.77 , 41.52 , 12.13 , 8.13 . **HRMS (ESI)** for $C_{31}H_{27}N_3O$ $[M+Na]^+$: 480.2046, found: 480.2048. **FTIR** (KBr, cm^{-1}) 3433.64, 2962.62, 2828.04, 2715.89, 1611.21, 1358.88, 1064.49, 767.29



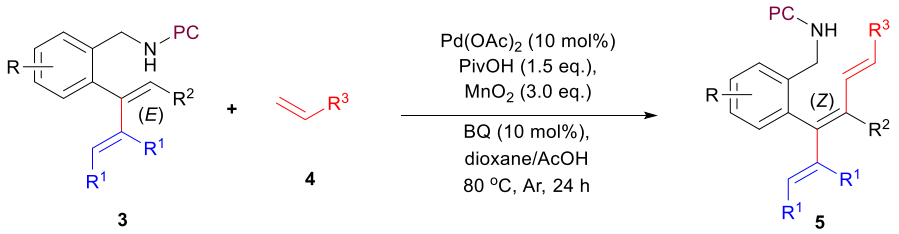
***N*-(2-((1*E*, 3*E*)-1,2-Diphenyl hepta-1,3-dien-3-yl) benzyl) pyrimidine-4-carboxamide** Following the **General Procedure 1**, This compound was obtained as a light yellow oil (61.1 mg, 89% yield, *E/Z*=91:9). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.05 (d, *J* = 1.4 Hz, 1H), 8.94 (d, *J* = 5.0 Hz, 1H), 8.13 (dd, *J* = 5.0, 1.5 Hz, 2H), 7.31-7.25 (m, 1H), 7.19-7.12 (m, 6H), 7.11-7.04 (m, 5H), 7.01-6.95 (m, 2H), 6.65 (s, 1H), 5.67 (t, *J* = 7.4 Hz, 1H), 4.72 (d, *J* = 5.8 Hz, 2H), 2.34 (q, *J* = 7.3 Hz, 2H), 1.55-1.46 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.20, 159.10, 157.59, 156.31, 142.44, 142.25, 140.79, 139.12, 136.63, 135.12, 135.07, 130.99, 130.92, 129.48, 129.19, 129.07, 128.41,

127.90, 127.44, 127.38, 127.23, 126.93, 118.54, 41.62, 31.67, 23.35, 14.08. **HRMS (ESI)** *m/z* calculated for $C_{31}H_{29}N_3ONa$ $[M+Na]^+$: 482.2203, found: 482.2201.

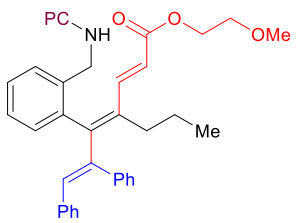
Unsuccessful substrates:



3.3 General Procedure 2 for Cross-Coupling-2 between Dienes and Alkenes

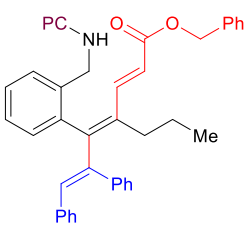


A screw-cap vial was charged with $Pd(OAc)_2$ (10 mol%, 0.015 mmol), MnO_2 (3.0 equiv, 0.45 mmol), BQ (10 mol%, 0.015 mmol), amide **3** (1.0 equiv, 0.15 mmol), olefin **2** (2.5 equiv, 0.38 mmol) and 1,4-dioxane/AcOH (0.1 M, 10: 1). Then, pivalic acid (1.5 equiv, 0.23 mmol) were added into the solution in sequence. The vial was sealed under argon atmosphere and heated to 80 °C with stirring for 24 h. After cooling down, the mixture was concentrated and directly applied to a flash column chromatography (PE/EA mixtures) for separation to obtain the corresponding product **5**.

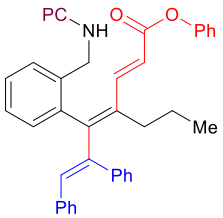


2-Methoxyethyl (2*E*, 4*Z*, 6*E*)-6,7-diphenyl-4-propyl-5-(2-((pyrazine-2-carboxamido) methyl) phenyl) hepta-2,4,6-trienoate (5a) Following the **General Procedure 2**, **5a** was obtained as a yellow oil (53.8 mg, 61% yield, *Z*/*E* > 99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.38 (d, *J* = 1.5 Hz, 1H), 8.67 (d, *J* = 2.4 Hz, 1H), 8.34 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.69 (s, 1H), 7.33 (d, *J* = 7.3 Hz, 1H), 7.25-7.19 (m, 1H), 7.19-7.14 (m, 4H), 7.10 (dd, *J* = 8.7, 7.0 Hz, 4H), 6.99 – 6.91 (m, 5H), 6.78 (s, 1H), 6.03 (d, *J* = 15.9 Hz, 1H), 4.57 (dd, *J* = 14.6, 6.4 Hz, 1H), 4.33 (dd, *J* = 14.6, 5.3 Hz, 1H), 4.19-4.12 (m, 2H), 3.53 (dd, *J* = 5.6, 4.0 Hz, 2H), 3.31 (s, 3H), 2.73-2.65 (m, 2H), 1.67-1.57 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.91, 162.57, 149.66, 147.06, 144.43, 144.33, 144.25, 142.35, 141.97, 138.57, 138.40, 136.78, 136.11, 136.02, 131.15, 130.70, 129.53, 129.25, 129.08, 128.57, 128.34, 128.00, 127.51, 127.41, 127.33, 118.96, 70.41, 63.55, 59.06, 41.01, 32.06, 23.61, 14.81. **HRMS (ESI)** *m/z* calculated for $C_{37}H_{37}N_3O_4Na$ $[M+Na]^+$:

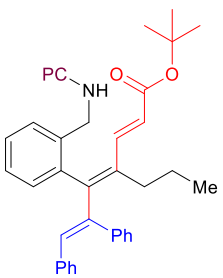
610.2676, found: 610.2672.



Benzyl (2*E*, 4*Z*, 6*E*)-6,7-diphenyl-4-propyl-5-(2-((pyrazine-2-carboxamido) methyl) phenyl) hepta-2,4,6-trienoate (5b) Following the **General Procedure 2**, **5b** was obtained as a yellow oil (45.7 mg, 49% yield, *Z/E* =95:5). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.34 (s, 1H), 8.60 (s, 1H), 8.22 (s, 1H), 7.70 (s, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 3H), 7.25 (d, *J* = 4.4 Hz, 1H), 7.21-7.13 (m, 7H), 7.12-7.06 (m, 3H), 6.96 (dd, *J* = 7.6, 4.8 Hz, 5H), 6.79 (s, 1H), 6.00 (d, *J* = 15.9 Hz, 1H), 5.04 (s, 2H), 4.56 (dd, *J* = 14.5, 6.3 Hz, 1H), 4.35 (dd, *J* = 14.5, 5.5 Hz, 1H), 2.70 (t, *J* = 8.2 Hz, 2H), 1.67-1.53 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.66, 162.52, 149.82, 146.99, 144.39, 144.27, 142.30, 141.92, 138.57, 138.52, 136.77, 136.15, 136.02, 135.99, 131.26, 130.68, 129.54, 129.40, 129.10, 128.59, 128.49, 128.36, 128.05, 128.01, 127.78, 127.53, 127.48, 127.35, 118.94, 65.91, 41.04, 31.99, 23.59, 14.80. **HRMS (ESI)** *m/z* calculated for $C_{41}H_{37}N_3O_3Na$ $[M+Na]^+$: 642.2727, found: 642.2724.

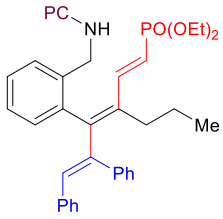


Phenyl (2*E*,4*Z*,6*E*)-6,7-diphenyl-4-propyl-5-(2-((pyrazine-2-carboxamido) methyl) phenyl) hepta-2,4,6-trienoate (5c) Following the **General Procedure 2**, **5c** was obtained as a green oil (45.4 mg, 50% yield, *Z/E* =96:4). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.39 (s, 1H), 8.63 (d, *J* = 2.0 Hz, 1H), 8.25 (s, 1H), 7.73 (s, 1H), 7.36-7.30 (m, 3H), 7.29 (d, *J* = 12.1 Hz, 1H), 7.23-7.14 (m, 6H), 7.12-7.07 (m, 3H), 7.04-6.94 (m, 7H), 6.82 (s, 1H), 6.15 (d, *J* = 15.9 Hz, 1H), 4.58 (dd, *J* = 14.6, 6.3 Hz, 1H), 4.37 (dd, *J* = 14.6, 5.4 Hz, 1H), 2.76 (t, *J* = 8.2 Hz, 2H), 1.77-1.58 (m, 2H), 1.01 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.31, 162.60, 150.75, 150.56, 147.09, 145.65, 144.38, 144.31, 142.40, 141.96, 138.52, 138.33, 136.74, 136.11, 135.98, 131.38, 130.62, 129.57, 129.29, 129.25, 129.11, 128.63, 128.53, 128.05, 127.60, 127.50, 127.43, 125.58, 121.44, 118.44, 41.03, 32.10, 23.63, 14.86. **HRMS (ESI)** *m/z* calculated for $C_{40}H_{35}N_3O_3Na$ $[M+Na]^+$: 628.2571, found: 628.2575.

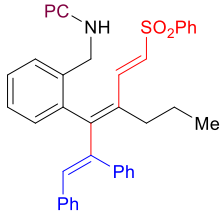


Tert-butyl (2*E*, 4*Z*, 6*E*)-6,7-diphenyl-4-propyl-5-(2-((pyrazine-2-carboxamido) methyl) phenyl) hepta-2,4,6-trienoate (5d) Following the **General Procedure 2**, **5d** was obtained as a yellow oil (55.1 mg, 63% yield, *Z/E* =98:2). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.39 (s, 1H), 8.67 (d, *J* = 2.3 Hz, 1H), 8.34 (s, 1H), 7.69 (s, 1H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.21 (t, *J* = 7.0 Hz, 1H), 7.18-7.12 (m, 4H), 7.08 (dt, *J* = 6.2, 3.0 Hz, 3H), 7.01-6.93 (m, 6H), 6.78 (s, 1H), 5.89 (d, *J* = 15.9 Hz, 1H), 4.59 (dd, *J* = 14.6, 6.4 Hz, 1H), 4.34 (dd, *J* = 14.6, 5.3 Hz, 1H), 2.77-2.63 (m, 2H), 1.68-1.58 (m, 2H), 1.36 (s, 9H), 0.98 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.33, 162.59, 148.75, 147.03, 144.48, 144.34, 142.71, 142.36,

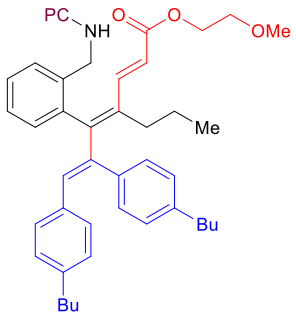
142.08, 138.67, 138.53, 136.81, 136.12, 136.07, 130.97, 130.69, 129.51, 129.12, 129.10, 128.53, 128.24, 127.98, 127.47, 127.36, 127.26, 121.29, 80.11, 41.00, 32.03, 28.07, 23.67, 14.84. **HRMS (ESI)** *m/z* calculated for $C_{38}H_{39}N_3O_3Na$ $[M+Na]^+$: 608.2884, found: 608.2891.



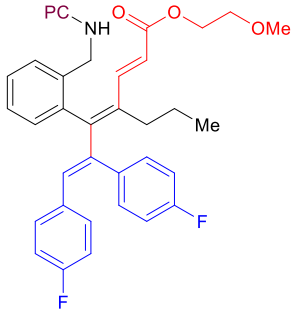
Diethyl ((1*E*,3*Z*,5*E*)-5,6-diphenyl-3-propyl-4-(2-((pyrazine-2-carboxamido) methyl) phenyl) hexa-1,3,5-trien-1-yl) phosphonate (5e) Following the **General Procedure 2**, **5e** was obtained as a yellow oil (43.1 mg, 46% yield, *Z/E* >99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.39 (s, 1H), 8.68 (d, *J* = 2.3 Hz, 1H), 8.45-8.32 (m, 1H), 7.71 (t, *J* = 4.9 Hz, 1H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.22-7.15 (m, 4H), 7.14-7.06 (m, 4H), 7.00 -6.88 (m, 5H), 6.82-6.72 (m, 2H), 5.84 (dd, *J* = 19.2, 17.6 Hz, 1H), 4.66 (dd, *J* = 14.7, 6.6 Hz, 1H), 4.34 (dd, *J* = 14.7, 5.1 Hz, 1H), 4.01-3.88 (m, 4H), 2.79-2.64 (m, 2H), 1.67-1.57 (m, 2H), 1.17 (q, *J* = 7.2 Hz, 6H), 0.97 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.66, 148.45, 147.12, 146.35 (d, J_{CP} = 6.7 Hz), 144.37, 144.28, 142.46, 141.82 (d, J_{CP} = 2.2 Hz), 138.55, 138.25, 137.18, 137.00, 136.00 (d, J_{CP} = 2.1 Hz), 131.00 (d, J_{CP} = 5.7 Hz), 129.52, 129.07, 129.00, 128.55, 128.28, 127.99, 127.52, 127.37, 127.32, 116.31, 114.79, 61.80 (dd, J_{CP} = 8.3, 5.8 Hz), 40.96, 31.72, 23.53, 16.23 (d, J_{CP} = 6.6 Hz), 14.81. **^{31}P NMR** (202 MHz, $CDCl_3$) δ 19.44. **HRMS (ESI)** *m/z* calculated for $C_{37}H_{40}N_3O_4PNa$ $[M+Na]^+$: 644.2649, found: 644.2651.



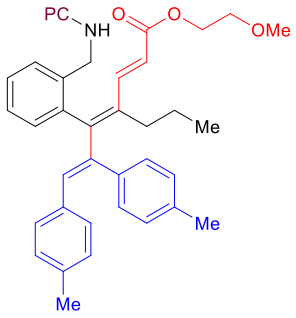
N-(2-((1*E*, 3*Z*)-1,2-diphenyl-4-((*E*)-2-(phenyl sulfonyl) vinyl) hepta-1,3-dien-3-yl)benzyl)pyrazine-2-carboxamide (5f) Following the **General Procedure 2**, **5f** was obtained as a yellow solid (49.7 mg, 53% yield, *Z/E* =97:3, m.p. = 132.2 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.39 (s, 1H), 8.69 (d, *J* = 2.1 Hz, 1H), 8.40 (s, 1H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.72 (s, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.2 Hz, 1H), 7.18-7.13 (m, 4H), 7.12-7.05 (m, 3H), 6.99-6.90 (m, 5H), 6.88 (d, *J* = 7.5 Hz, 1H), 6.78 (s, 1H), 6.41 (d, *J* = 15.4 Hz, 1H), 4.62 (dd, *J* = 14.6, 6.6 Hz, 1H), 4.28 (dd, *J* = 14.6, 5.0 Hz, 1H), 2.69-2.52 (m, 2H), 1.58-1.47 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.66, 151.58, 147.23, 144.28, 144.25, 142.59, 141.63, 141.29, 140.60, 138.28, 137.79, 135.83, 135.76, 135.11, 133.25, 131.78, 130.93, 129.57, 129.26, 129.04, 128.74, 128.73, 128.63, 128.04, 127.65, 127.56, 127.53, 127.52, 41.01, 32.26, 23.25, 14.71. **HRMS (ESI)** *m/z* calculated for $C_{39}H_{35}N_3O_3SNa$ $[M+Na]^+$: 648.2291, found: 648.2296.



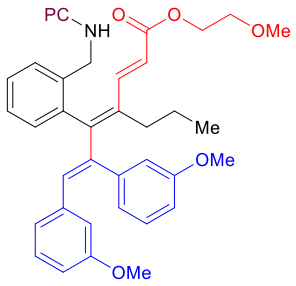
2-Methoxy ethyl (2*E*, 4*Z*, 6*E*)-6,7-bis (4-butylphenyl)-4-propyl-5-(2-((pyrazine-2-carboxamido) methyl) phenyl) hepta-2,4,6-trienoate (5g) Following the **General Procedure 2**, **5g** was obtained as a yellow oil (66.5 mg, 63% yield, *Z/E* >99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.38 (s, 1H), 8.68-8.64 (m, 1H), 8.31 (s, 1H), 7.74 (s, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 15.9 Hz, 1H), 6.99 (d, *J* = 7.9 Hz, 2H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.91-6.83 (m, 6H), 6.70 (s, 1H), 6.01 (d, *J* = 15.9 Hz, 1H), 4.55 (dd, *J* = 14.6, 6.4 Hz, 1H), 4.34 (dd, *J* = 14.6, 5.4 Hz, 1H), 4.20-4.11 (m, 2H), 3.57-3.49 (m, 2H), 3.30 (s, 3H), 2.71-2.64 (m, 2H), 2.55-2.47 (m, 4H), 1.66-1.48 (m, 6H), 1.38-1.21 (m, 4H), 0.95 (t, *J* = 7.3 Hz, 3H), 0.92-0.86 (m, 6H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.95, 162.55, 150.19, 146.98, 144.51, 144.36, 142.34, 142.21, 142.08, 141.18, 138.76, 136.48, 136.09, 135.97, 133.53, 131.09, 130.73, 129.45, 129.17, 128.90, 128.59, 128.20, 128.01, 127.32, 118.60, 70.41, 63.52, 59.05, 41.07, 35.30, 33.41, 33.32, 31.98, 23.51, 22.34, 22.18, 14.79, 13.95, 13.93. **HRMS (ESI)** *m/z* calculated for $C_{45}H_{53}N_3O_4Na$ $[M+Na]^+$: 722.3928, found: 722.3927.



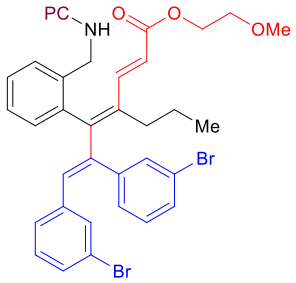
2-Methoxyethyl (2*E*,4*Z*,6*E*)-6,7-bis (4-fluorophenyl)-4-propyl-5-(2-((pyrazine-2-carboxamido) methyl) phenyl) hepta-2,4,6-trienoate (5h) Following the **General Procedure 2**, **5h** was obtained as a yellow oil (53.4 mg, 57% yield, *Z/E* >99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.38 (s, 1H), 8.69 (d, *J* = 2.3 Hz, 1H), 8.38 (s, 1H), 7.59 (t, *J* = 5.2 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 7.1 Hz, 1H), 7.08 (d, *J* = 15.9 Hz, 1H), 6.98-6.93 (m, 3H), 6.92-6.85 (m, 4H), 6.84-6.77 (m, 3H), 6.03 (d, *J* = 15.9 Hz, 1H), 4.61 (dd, *J* = 14.5, 6.7 Hz, 1H), 4.29 (dd, *J* = 14.6, 5.1 Hz, 1H), 4.18 (dd, *J* = 5.7, 3.5 Hz, 2H), 3.55 (dd, *J* = 5.7, 3.6 Hz, 2H), 3.33 (s, 3H), 2.68 (t, *J* = 8.3 Hz, 2H), 1.71-1.53 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.82, 162.53, 162.12 (d, J_{CF} = 247.6 Hz), 161.89 (d, J_{CF} = 248.4 Hz), 148.98, 147.17, 144.31, 144.28, 143.91, 142.43, 140.54 (d, J_{CF} = 1.53 Hz), 138.06, 136.97, 136.08, 134.27 (d, J_{CF} = 3.5 Hz), 131.90 (d, J_{CF} = 3.3 Hz), 131.12 (d, J_{CF} = 8.0 Hz), 130.79 (d, J_{CF} = 7.9 Hz), 130.57, 130.29, 129.33, 128.49, 127.54, 119.30, 115.82 (d, J_{CF} = 21.4 Hz), 115.11 (d, J_{CF} = 21.4 Hz), 70.40, 63.56, 59.04, 40.87, 32.09, 23.66, 14.80. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -113.47, -113.50. **HRMS (ESI)** *m/z* calculated for $C_{37}H_{35}F_2N_3O_4Na$ $[M+Na]^+$: 646.2488, found: 646.2493.



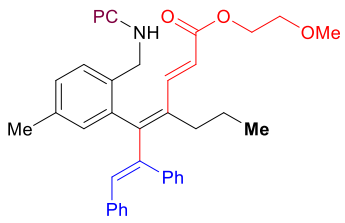
2-Methoxyethyl (2*E*,4*Z*,6*E*)-4-propyl-5-(2-((pyrazine-2-carboamido) methyl) phenyl)-6,7-di-p-tolylhepta-2,4,6-trienoate (5i) Following the **General Procedure 2**, **5i** was obtained as a yellow oil (41.6 mg, 45% yield, *Z/E* =95:5). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.38 (s, 1H), 8.67 (d, *J* = 2.2 Hz, 1H), 8.34 (s, 1H), 7.66 (t, *J* = 5.1 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 15.9 Hz, 1H), 6.98 (d, *J* = 7.7 Hz, 3H), 6.89 (q, *J* = 8.2 Hz, 4H), 6.82 (d, *J* = 7.8 Hz, 2H), 6.71 (s, 1H), 6.02 (d, *J* = 15.9 Hz, 1H), 4.56 (dd, *J* = 14.6, 6.5 Hz, 1H), 4.31 (dd, *J* = 14.6, 5.3 Hz, 1H), 4.19-4.13 (m, 2H), 3.56-3.50 (m, 2H), 3.31 (s, 3H), 2.72-2.65 (m, 2H), 2.25 (s, 3H), 2.24 (s, 3H), 1.68-1.54 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.95, 162.57, 150.08, 147.00, 144.49, 144.39, 142.36, 141.12, 138.58, 137.16, 137.07, 136.53, 136.15, 135.62, 133.31, 130.79, 130.60, 129.43, 129.27, 129.17, 128.92, 128.72, 128.23, 127.35, 118.72, 70.42, 63.53, 59.06, 40.97, 32.05, 23.60, 21.27, 21.16, 14.81. **HRMS (ESI)** *m/z* calculated for $C_{39}H_{41}N_3O_4Na$ $[M+Na]^+$: 638.2989, found: 638.2987.



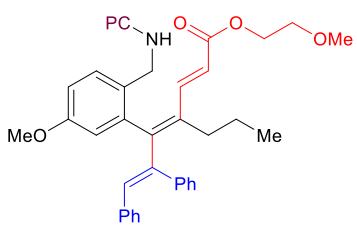
2-Methoxyethyl (2*E*,4*Z*,6*E*)-6,7-bis(3-methoxy phenyl)-4-propyl-5-(2-((pyrazine-2-carboxamido) methyl) phenyl) hepta-2,4,6-trienoate (5j) Following the **General Procedure 2**, **5j** was obtained as a yellow oil (66.1 mg, 68% yield, *Z/E* >99:1). **^{1}H NMR** (500 MHz, $CDCl_3$)δ 9.38 (s, 1H), 8.68 (s, 1H), 8.36 (s, 1H), 7.70 (s, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.15-7.09 (m, 2H), 7.05 (t, *J* = 7.9 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.78-6.65 (m, 4H), 6.60 (d, *J* = 7.4 Hz, 1H), 6.52 (s, 1H), 6.46 (s, 1H), 6.05 (d, *J* = 15.9 Hz, 1H), 4.57 (dd, *J* = 14.5, 6.4 Hz, 1H), 4.34 (dd, *J* = 14.5, 5.2 Hz, 1H), 4.20-4.14 (m, 2H), 3.58 (s, 3H), 3.56-3.53 (m, 2H), 3.51 (s, 3H), 3.33 (s, 3H), 2.77-2.69 (m, 2H), 1.70-1.60 (m, 2H), 1.00 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.86, 162.55, 159.65, 159.04, 149.42, 147.05, 144.42, 144.30, 144.19, 142.33, 141.90, 139.95, 138.34, 137.21, 136.73, 136.23, 131.00, 130.67, 129.63, 129.29, 128.98, 128.38, 127.45, 122.49, 121.40, 119.03, 114.24, 114.04, 113.72, 113.49, 70.39, 63.55, 59.05, 55.10, 54.81, 40.99, 32.03, 23.64, 14.80. **HRMS (ESI)** *m/z* calculated for $C_{39}H_{41}N_3O_6Na$ $[M+Na]^+$: 670.2888, found: 670.2885.



2-Methoxyethyl (2*E*,4*Z*,6*E*)-6,7-bis(3-bromophenyl)-4-propyl-5-(2-((pyrazine-2-carboxamido) methyl) phenyl) hepta-2,4,6-trienoate (5k) Following the **General Procedure 2**, **5k** was obtained as a yellow oil (47.4 mg, 43% yield, *Z/E* =95:5). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.39 (d, *J* = 1.1 Hz, 1H), 8.69 (d, *J* = 2.4 Hz, 1H), 8.41-8.33 (m, 1H), 7.73 (s, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 8.8 Hz, 1H), 7.28 -7.23 (m, 2H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.14-7.11 (m, 2H), 7.10-7.03 (m, 2H), 6.95 (t, *J* = 7.9 Hz, 1H), 6.92-6.83 (m, 3H), 6.76 (s, 1H), 6.04 (d, *J* = 15.9 Hz, 1H), 4.60 (dd, *J* = 14.5, 6.4 Hz, 1H), 4.38 (dd, *J* = 14.5, 5.1 Hz, 1H), 4.18 (dd, *J* = 5.3, 3.9 Hz, 2H), 3.60-3.48 (m, 2H), 3.33 (s, 3H), 2.64 (dd, *J* = 10.8, 7.3 Hz, 2H), 1.72-1.52 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.76, 162.52, 148.15, 147.19, 144.34, 144.27, 143.74, 142.41, 141.77, 140.14, 137.90, 137.77, 137.63, 135.91, 132.47, 131.87, 130.95, 130.90, 130.53, 130.52, 130.18, 129.60, 129.54, 128.66, 127.88, 127.83, 127.71, 122.57, 122.17, 119.61, 70.39, 63.59, 59.05, 41.18, 32.11, 23.63, 14.78. **HRMS (ESI)** *m/z* calculated for $C_{37}H_{35}Br_2N_3O_4Na$ $[M+Na]^+$: 766.0887, found: 766.0888.

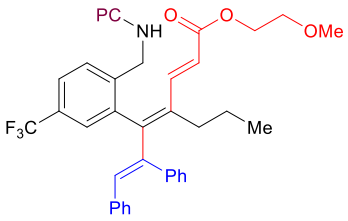


2-Methoxyethyl (2*E*,4*Z*,6*E*)-5-(5-methyl-2-((pyrazine-2-carboxamido) methyl) phenyl)-6,7-diphenyl-4-propylhepta-2,4,6-trienoate (5l) Following the **General Procedure 2**, **5l** was obtained as a yellow oil (49.1 mg, 54% yield, *Z/E* >99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.37 (s, 1H), 8.66 (d, *J* = 2.3 Hz, 1H), 8.41-8.26 (m, 1H), 7.60 (s, 1H), 7.23-7.15 (m, 4H), 7.14-7.06 (m, 4H), 7.03 (d, *J* = 7.7 Hz, 1H), 6.99-6.92 (m, 4H), 6.79 (s, 1H), 6.75 (s, 1H), 6.02 (d, *J* = 15.9 Hz, 1H), 4.47 (dd, *J* = 14.5, 6.4 Hz, 1H), 4.24 (dd, *J* = 14.5, 5.3 Hz, 1H), 4.19-4.12 (m, 2H), 3.57-3.50 (m, 2H), 3.31 (s, 3H), 2.68 (p, *J* = 7.5 Hz, 2H), 2.22 (s, 3H), 1.68-1.52 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.94, 162.49, 149.83, 147.01, 144.50, 144.41, 144.32, 142.33, 142.14, 138.65, 138.27, 137.04, 136.54, 136.10, 133.22, 131.02, 130.89, 129.51, 129.19, 129.16, 129.08, 128.54, 128.00, 127.48, 127.29, 118.79, 70.42, 63.54, 59.05, 40.70, 32.06, 23.56, 21.00, 14.81. **HRMS (ESI)** *m/z* calculated for $C_{38}H_{39}N_3O_4Na$ $[M+Na]^+$: 624.2833, found: 624.2833.

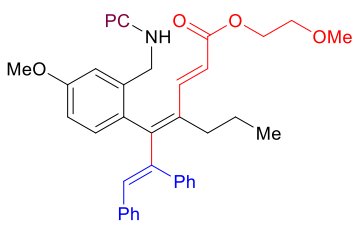


2-Methoxyethyl (2*E*, 4*Z*, 6*E*)-5-(5-methoxy-2-((pyrazine-2-carboxamido) methyl) phenyl)-6,7-diphenyl-4-propylhepta-2,4,6-trienoate (5m) Following the **General Procedure 2**, **5m** was obtained as a brown oil (58.4 mg, 63% yield, *Z/E* = 98:2). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.37 (s, 1H), 8.66 (s, 1H), 8.32 (s, 1H), 7.63 (d, *J* = 5.1 Hz, 1H), 7.25 (s, 1H), 7.21-7.16 (m, 3H), 7.15-7.04 (m, 4H), 6.99-6.94 (m, 4H), 6.80-6.73 (m, 2H), 6.43 (d, *J* = 2.6 Hz, 1H), 6.02 (d, *J* = 15.9

Hz, 1H), 4.50 (dd, *J* = 14.5, 6.4 Hz, 1H), 4.27 (dd, *J* = 14.5, 5.2 Hz, 1H), 4.17 (dd, *J* = 5.7, 3.2 Hz, 2H), 3.64 (s, 3H), 3.54 (dd, *J* = 5.3, 3.5 Hz, 2H), 3.32 (s, 3H), 2.76-2.62 (m, 2H), 1.69-1.55 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.87, 162.45, 158.51, 149.43, 147.00, 144.49, 144.30, 144.22, 142.32, 141.83, 139.72, 138.59, 136.64, 136.01, 131.03, 130.72, 129.52, 129.13, 128.58, 128.36, 127.98, 127.53, 127.32, 119.02, 115.61, 114.13, 70.41, 63.55, 59.05, 55.21, 40.51, 32.02, 23.62. **HRMS (ESI)** *m/z* calculated for $C_{38}H_{39}N_3O_5Na$ $[M+Na]^+$: 640.2782, found: 640.2788.

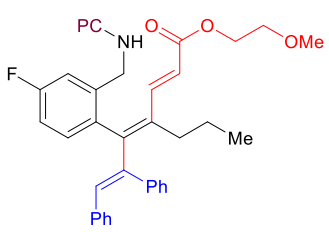


2-Methoxyethyl (2E, 4Z, 6E)-6,7-diphenyl-5-(2-(((phosphaneyl methyl) amino) methyl)-5-(trifluoromethyl) phenyl)-4-propyl hepta-2,4,6-trienoate (5n) Following the **General Procedure 2**, **5n** was obtained as a brown oil (62.4 mg, 63% yield, *Z/E* > 99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.38 (s, 1H), 8.70 (d, *J* = 2.2 Hz, 1H), 8.37 (s, 1H), 7.73 (s, 1H), 7.48 (s, 2H), 7.22 – 7.18 (m, 4H), 7.15 – 7.09 (m, 3H), 7.05 – 6.97 (m, 3H), 6.92 (dd, *J* = 6.5, 2.9 Hz, 2H), 6.84 (s, 1H), 6.09 (d, *J* = 15.9 Hz, 1H), 4.64 – 4.56 (m, 1H), 4.35 (dd, *J* = 14.9, 5.5 Hz, 1H), 4.24 – 4.11 (m, 2H), 3.53 (t, *J* = 4.6 Hz, 2H), 3.31 (s, 3H), 2.83 – 2.71 (m, 2H), 1.74 – 1.61 (m, 2H), 1.00 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.60, 161.76, 146.71, 146.26, 143.35, 143.12, 142.23, 141.37, 140.30, 139.32, 137.99, 137.15, 136.46, 134.66, 130.50, 128.55 (d, J_{CF} = 32.6 Hz), 128.55, 128.50, 127.95, 127.74, 127.07, 126.76, 126.59, 126.19 (q, J_{CF} = 3.7 Hz), 123.94 (d, J_{CF} = 3.6 Hz), 122.70 (d, J_{CF} = 272.4 Hz), 119.01, 69.32, 62.61, 57.96, 39.41, 31.03, 22.66, 13.78. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.65. **HRMS (ESI)** *m/z* calculated for $C_{38}H_{36}F_3N_3O_4Na$ $[M+Na]^+$: 678.2550, found: 678.2551.

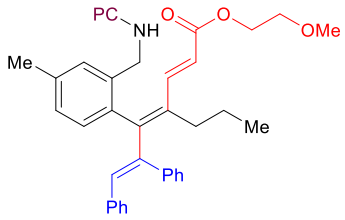


2-Methoxyethyl (2*E*, 4*Z*, 6*E*)-5-(4-methoxy-2-((pyrazine-2-carboxamido) methyl) phenyl)-6,7-diphenyl-4-propylhepta-2,4,6-trienoate (5o) Following the **General Procedure 2**, **5o** was obtained as a yellow oil (44.8 mg, 48% yield, *Z/E* =93:7). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.37 (s, 1H), 8.69-8.66 (m, 1H), 8.38-8.34 (m, 1H), 7.68 (s, 1H), 7.20-7.13 (m, 4H), 7.12-7.06 (m, 3H), 6.99-6.93 (m, 4H), 6.89 (d, *J* = 8.5 Hz, 1H), 6.86 (d, *J* = 2.6 Hz, 1H), 6.75 (s, 1H), 6.70 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.03 (d, *J* = 15.9 Hz, 1H), 4.52 (dd, *J* = 14.6, 6.5 Hz, 1H), 4.28 (dd, *J* = 14.6, 5.4 Hz, 1H), 4.18 (dd, *J* = 5.9, 3.4 Hz, 2H), 3.74 (s, 3H), 3.55 (dd, *J* = 5.9, 4.0 Hz, 2H), 3.33 (s, 3H), 2.73-2.65 (m, 2H), 1.68-1.53 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.03, 162.57, 159.34, 149.62, 147.06, 144.46, 144.42, 144.33, 142.34, 142.30, 138.71, 137.64, 137.03, 136.10, 131.91, 130.83, 130.57, 129.50, 129.06, 128.56, 127.99, 127.45, 127.27, 118.73, 114.26, 113.17, 70.45, 63.53, 59.04, 55.18, 41.12, 32.21, 23.60, 14.81. **HRMS (ESI)** *m/z* calculated for

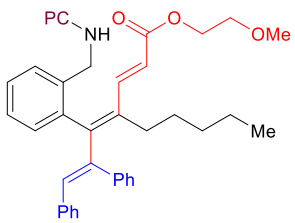
$C_{38}H_{39}N_3O_5Na$ [M+Na]$^+$: 640.2782, found: 640.2782.



2-Methoxyethyl (2*E*, 4*Z*, 6*E*)-5-(4-fluoro-2-((pyrazine-2-carboxamido) methyl) phenyl)-6,7-diphenyl-4-propylhepta-2,4,6-trienoate (5p) Following the **General Procedure 2**, **5p** was obtained as a yellow oil (52.2 mg, 57% yield, *Z*/*E* =98:2). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.38 (d, *J* = 1.2 Hz, 1H), 8.70 (d, *J* = 2.4 Hz, 1H), 8.37 (dd, *J* = 2.3, 1.5 Hz, 1H), 7.72 (t, *J* = 5.8 Hz, 1H), 7.22-7.16 (m, 3H), 7.14-7.03 (m, 5H), 7.01-6.97 (m, 2H), 6.96-6.92 (m, 3H), 6.88-6.82 (m, 1H), 6.79 (s, 1H), 6.06 (d, *J* = 15.9 Hz, 1H), 4.53 (dd, *J* = 14.8, 6.6 Hz, 1H), 4.30 (dd, *J* = 14.8, 5.6 Hz, 1H), 4.23-4.14 (m, 2H), 3.58-3.51 (m, 2H), 3.33 (s, 3H), 2.72 (t, *J* = 8.2 Hz, 2H), 1.69-1.57 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.85, 162.73, 162.29 (d, J_{CF} = 247.9 Hz), 148.52, 147.22, 144.37, 144.24, 143.85, 142.40, 141.81, 138.73 (d, J_{CF} = 7.2 Hz), 138.46, 137.31, 135.87, 134.09 (d, J_{CF} = 3.3 Hz), 132.33 (d, J_{CF} = 8.1 Hz), 131.18, 129.53, 129.02, 128.68, 128.06, 127.64, 127.46, 119.37, 115.68 (d, J_{CF} = 21.8 Hz), 114.54 (d, J_{CF} = 21.2 Hz), 70.41, 63.58, 59.02, 40.68, 32.11, 23.65, 14.80. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -113.18. **HRMS (ESI)** *m/z* calculated for $C_{37}H_{36}FN_3O_4Na$ [M+Na]$^+$: 628.2582, found: 628.2578.

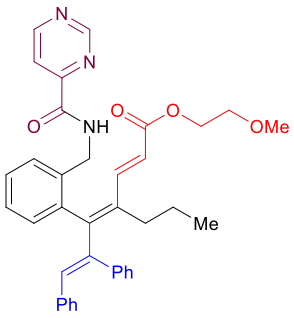


2-Methoxyethyl (2*E*, 4*Z*, 6*E*)-5-(4-methyl-2-((pyrazine-2-carboxamido) methyl) phenyl)-6,7-diphenyl-4-propylhepta-2,4,6-trienoate (5q) Following the **General Procedure 2**, **5q** was obtained as a yellow oil (47.0 mg, 52% yield, *Z*/*E* >99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.38 (s, 1H), 8.73-8.61 (m, 1H), 8.34 (s, 1H), 7.67 (s, 1H), 7.19-7.05 (m, 8H), 7.00-6.90 (m, 5H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.75 (s, 1H), 6.02 (d, *J* = 15.9 Hz, 1H), 4.52 (dd, *J* = 14.4, 6.4 Hz, 1H), 4.29 (dd, *J* = 14.5, 5.2 Hz, 1H), 4.21-4.12 (m, 2H), 3.60-3.50 (m, 2H), 3.32 (s, 3H), 2.74-2.63 (m, 2H), 2.27 (s, 3H), 1.67-1.53 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.01, 162.52, 149.86, 147.03, 144.49, 144.47, 144.35, 142.32, 142.19, 138.64, 138.08, 136.82, 136.12, 135.86, 135.43, 130.96, 130.58, 129.96, 129.51, 129.11, 128.54, 128.29, 127.97, 127.46, 127.25, 118.70, 70.44, 63.55, 59.04, 40.99, 32.13, 23.58, 21.16, 14.80. **HRMS (ESI)** *m/z* calculated for $C_{38}H_{39}N_3O_4Na$ [M+Na]$^+$: 624.2833, found: 624.2830.



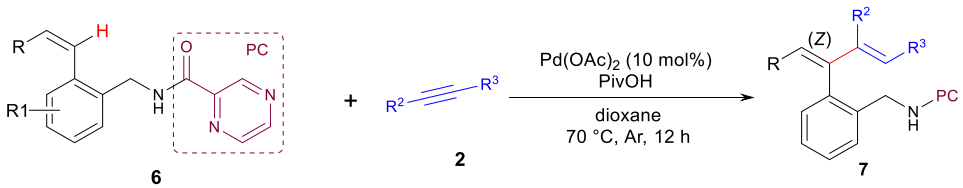
2-Methoxyethyl (2*E*,4*Z*)-4-((*E*)-2,3-diphenyl-1-(2-((pyrazine-2-carboxamido) methyl) phenyl) allylidene) non-2-enoate (5r) Following the **General Procedure 2**, **5r** was obtained as a yellow oil (59.1 mg, 64% yield, *Z*/*E* > 99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.38 (s, 1H), 8.67 (d, *J* = 2.2 Hz, 1H), 8.34 (s, 1H), 7.70 (t, *J* = 5.0 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.19-7.14 (m, 4H), 7.13-7.06 (m, 4H), 7.00-6.92 (m,

5H), 6.79 (s, 1H), 6.02 (d, *J* = 15.9 Hz, 1H), 4.58 (dd, *J* = 14.6, 6.4 Hz, 1H), 4.34 (dd, *J* = 14.6, 5.3 Hz, 1H), 4.21-4.13 (m, 2H), 3.55-3.49 (m, 2H), 3.31 (s, 3H), 2.75-2.67 (m, 2H), 1.64-1.51 (m, 2H), 1.31 (q, *J* = 13.2, 12.7 Hz, 4H), 0.86 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.92, 162.56, 149.55, 147.06, 144.43, 144.34, 144.28, 142.33, 141.93, 138.60, 138.43, 136.89, 136.12, 136.02, 131.19, 130.74, 129.52, 129.28, 129.09, 128.56, 128.32, 127.99, 127.51, 127.41, 127.31, 118.92, 70.41, 63.56, 59.06, 41.05, 32.51, 30.02, 29.97, 22.45, 14.05. **HRMS (ESI)** *m/z* calculated for $C_{39}H_{41}N_3O_4Na$ $[M+Na]^+$: 638.2989, found: 638.2987.

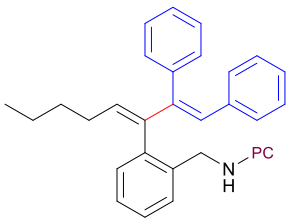


2-Methoxyethyl (2*E*,4*Z*,6*E*)-6,7-diphenyl-4-propyl-5-(2-((pyrimidine-4-carboxamido) methyl) phenyl) hepta-2,4,6-trienoate Following the **General Procedure 2**, This compound was obtained as a yellow oil (44.2 mg, 50% yield *Z/E* =93:7). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.04 (d, *J* = 1.1 Hz, 1H), 8.93 (d, *J* = 5.0 Hz, 1H), 8.09 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.87 (s, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.25-7.20 (m, 1H), 7.19-7.13 (m, 4H), 7.09 (dt, *J* = 7.3, 4.3 Hz, 4H), 7.00-6.92 (m, 5H), 6.78 (s, 1H), 6.04 (d, *J* = 15.9 Hz, 1H), 4.58 (dd, *J* = 14.6, 6.6 Hz, 1H), 4.30 (dd, *J* = 14.6, 5.2 Hz, 1H), 4.20-4.14 (m, 2H), 3.54 (t, *J* = 4.5 Hz, 2H), 3.32 (s, 3H), 2.75-2.67 (m, 2H), 1.69-1.56 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.90, 162.20, 159.03, 157.54, 156.17, 149.58, 144.19, 142.00, 138.54, 138.39, 136.82, 136.01, 135.90, 131.12, 130.71, 129.53, 129.20, 129.07, 128.58, 128.38, 128.01, 127.56, 127.49, 127.37, 119.02, 118.50, 70.43, 63.53, 59.05, 41.12, 32.09, 23.62, 14.81. **HRMS (ESI)** *m/z* calculated for $C_{37}H_{37}N_3O_4Na$ $[M+Na]^+$: 610.2676, found: 610.2675.

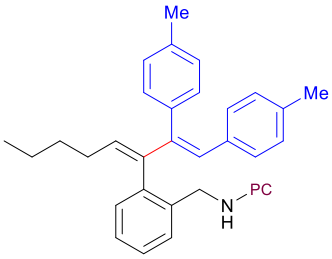
3.4 General Procedure 3 for α-C-H Functionalization of *cis*-Styrenes



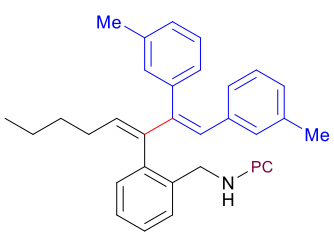
An oven-dried vial was charged with $Pd(OAc)_2$ (2.3 mg, 10 mol%), PivOH (19.5 mg, 1.5 equiv.) and dioxane (0.67 mL). Then, alkyne **2** (0.25 mmol, 2.5 equiv.) and *cis*-styrene **6** (0.1 mmol, 1.0 equiv.) were added into the solution in sequence. The vial was sealed under argon and heated to 70 ℃ with stirring for 12 hours. After cooling down, the mixture was concentrated and directly applied to a flash column chromatography for separation (PE/EA mixtures) to obtain the corresponding product **7**.



***N*-(2-((1*E*, 3*Z*)-1,2-diphenylocta-1,3-dien-3-yl) benzyl) pyrazine-2-carboxamide (7a).** Following **the General Procedure 3**, **7a** was obtained as a yellow liquid (80%, 37 mg, *Z*/*E* = 92:8). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.37 (d, 1H), 8.54 (d, *J* = 2.5 Hz, 1H), 8.09 (s, 1H), 7.95 (d, *J* = 1.9 Hz, 1H), 7.55 (dd, *J* = 7.1, 1.9 Hz, 1H), 7.46 – 7.33 (m, 5H), 7.32 – 7.22 (m, 3H), 6.95 (ddd, *J* = 14.1, 7.7, 5.9 Hz, 3H), 6.66 – 6.53 (m, 2H), 5.97 (s, 1H), 5.50 (t, *J* = 7.5 Hz, 1H), 4.76 (dd, *J* = 14.3, 6.7 Hz, 1H), 4.61 (dd, *J* = 14.3, 5.1 Hz, 1H), 1.85 – 1.75 (m, 2H), 1.24 – 1.18 (m, 2H), 1.17 – 1.10 (m, 2H), 0.76 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.51, 146.93, 144.32, 144.31, 144.17, 142.86, 142.24, 139.48, 139.16, 136.99, 135.86, 135.65, 130.88, 129.98, 129.69, 129.63, 129.37, 128.84, 128.10, 127.91, 127.60, 127.28, 126.33, 41.72, 31.47, 29.87, 22.37, 13.89. **HRMS (ESI)** *m/z* calculated for $C_{32}H_{31}N_3ONa$ $[M+Na]^+$: 496.2359, found: 496.2352. **FTIR** (KBr, cm^{-1}) 3447.66, 2958.68, 2830.84, 2715.89, 1597.20, 1364.49, 1070.09, 781.30.

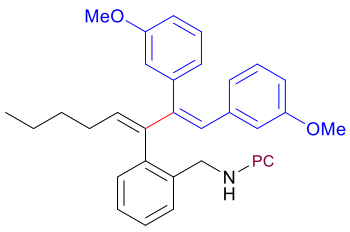


***N*-(2-((1*E*,3*Z*)-1,2-di-p-tolylocta-1,3-dien-3-yl) benzyl) pyrazine-2-carboxamide (7b).** Following **the General Procedure 3**, **7b** was obtained as a yellow liquid (68%, 34 mg, *Z*/*E* = 94:6). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.35 (d, *J* = 1.5 Hz, 1H), 8.54 (d, *J* = 2.4 Hz, 1H), 8.06 (s, 1H), 7.97 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.53 (dd, *J* = 7.3, 1.7 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.23 – 7.17 (m, 3H), 7.16 – 7.10 (m, 2H), 6.75 (d, *J* = 8.0 Hz, 2H), 6.48 (d, *J* = 8.2 Hz, 2H), 5.90 (s, 1H), 5.47 (t, *J* = 7.5 Hz, 1H), 4.73 (dd, *J* = 14.3, 6.6 Hz, 1H), 4.58 (dd, *J* = 14.3, 5.1 Hz, 1H), 2.41 (s, 3H), 2.18 (s, 3H), 1.83 – 1.71 (m, 2H), 1.22 – 1.16 (m, 2H), 1.15 – 1.10 (m, 1H), 0.74 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.53, 146.84, 144.37, 144.17, 143.42, 143.05, 142.24, 139.40, 136.74, 136.53, 136.00, 135.84, 134.96, 134.29, 130.88, 129.82, 129.56, 129.54, 129.29, 128.33, 128.02, 127.78, 41.73, 31.53, 29.85, 22.39, 21.38, 21.03, 13.90. **HRMS (ESI)** *m/z* calculated for $C_{34}H_{35}N_3ONa$ $[M+Na]^+$: 524.2672, found: 524.2678. **FTIR** (KBr, cm^{-1}) 3447.79, 2962.75, 2836.58, 2713.22, 1608.56, 1361.83, 1073.05, 775.85.

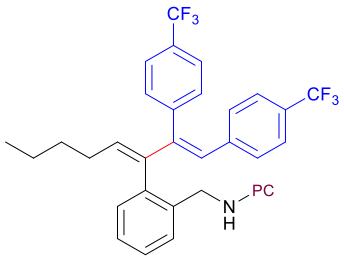


***N*-(2-((1*E*, 3*Z*)-1,2-di-m-tolylocta-1,3-dien-3-yl) benzyl) pyrazine-2-carboxamide (7c).** Following **the General Procedure 3**, **7c** was obtained as a yellow liquid (70%, 35 mg, *Z*/*E* = 97:3). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.36 (d, *J* = 1.5 Hz, 1H), 8.53 (d, *J* = 2.5 Hz, 1H), 8.09 (s, 1H), 7.98 – 7.88 (m, 1H), 7.54 (dd, *J* = 7.0, 2.0 Hz, 1H), 7.39 (td, *J* = 6.5, 1.8 Hz, 2H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.22 (dd, *J* = 6.8, 2.1 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 8.5 Hz, 2H), 6.84 – 6.75 (m, 2H), 6.43 – 6.28 (m, 2H), 5.89

(s, 1H), 5.50 (t, *J* = 7.5 Hz, 1H), 4.74 (dd, *J* = 14.3, 6.7 Hz, 1H), 4.58 (dd, *J* = 14.3, 5.1 Hz, 1H), 2.35 (s, 3H), 2.03 (s, 3H), 1.84 – 1.72 (m, 2H), 1.22 – 1.18 (m, 2H), 1.17 – 1.09 (m, 2H), 0.75 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.56, 146.87, 144.37, 144.21, 144.16, 142.94, 142.22, 139.50, 139.27, 138.32, 136.93, 136.90, 135.87, 135.42, 130.88, 130.51, 130.46, 129.63, 129.59, 128.66, 128.06, 127.90, 127.83, 127.46, 127.06, 126.98, 126.21, 41.79, 31.50, 29.87, 22.39, 21.48, 21.19, 13.90. **HRMS (ESI)**: *m/z* calculated for $C_{34}H_{35}N_3ONa$ $[M+Na]^+$: 524.2672, found: 524.2673. **FTIR** (KBr, cm^{-1}): 3439.38, 2957.14, 2839.39, 2712.22, 1597.34, 1364.63, 1073.05, 781.46.

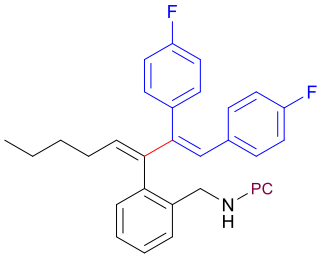


***N*-(2-((1*E*, 3*Z*)-1,2-bis (3-methoxyphenyl) octa-1,3-dien-3-yl) benzyl) pyrazine-2-carboxamide (7d).** Following **the General Procedure 3**, **7d** was obtained as a yellow liquid (60%, 32 mg, *Z/E* = 96:4). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.35 (d, *J* = 1.5 Hz, 1H), 8.54 (d, *J* = 2.4 Hz, 1H), 8.04 (s, 1H), 8.00 – 7.97 (m, 1H), 7.54 (dd, *J* = 7.1, 2.0 Hz, 1H), 7.40 (td, *J* = 6.5, 1.7 Hz, 2H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.23 (dd, *J* = 6.7, 2.2 Hz, 1H), 6.94 – 6.83 (m, 4H), 6.56 – 6.51 (m, 1H), 6.26 (d, *J* = 7.6 Hz, 1H), 6.11 (t, *J* = 2.1 Hz, 1H), 5.90 (s, 1H), 5.53 (t, *J* = 7.5 Hz, 1H), 4.72 (dd, *J* = 14.3, 6.5 Hz, 1H), 4.59 (dd, *J* = 14.3, 5.2 Hz, 1H), 3.78 (s, 3H), 3.38 (s, 3H), 1.87 – 1.72 (m, 2H), 1.24 – 1.17 (m, 2H), 1.16 – 1.09 (m, 2H), 0.75 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.49, 160.15, 158.74, 146.94, 144.28, 144.19, 144.12, 142.57, 142.27, 140.99, 139.10, 138.16, 135.82, 135.81, 130.89, 129.92, 129.70, 129.33, 128.49, 128.15, 127.92, 122.59, 122.43, 115.25, 113.44, 113.10, 113.06, 55.32, 54.69, 41.78, 31.45, 29.87, 22.39, 13.88. **HRMS (ESI)** *m/z* calculated for $C_{34}H_{36}N_3O_3$ $[M+H]^+$: 534.2751, found: 534.2753. **FTIR** (KBr, cm^{-1}) 3442.06, 2954.21, 2828.04, 2718.69, 1591.59, 1364.49, 1070.09, 775.70.

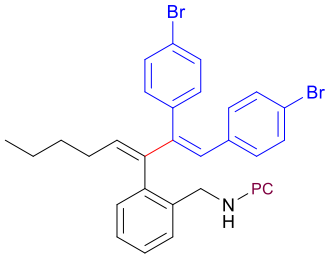


***N*-(2-((1*E*, 3*Z*)-1,2-bis(4-(trifluoromethyl) phenyl) octa-1,3-dien-3-yl) benzyl) pyrazine-2-carboxamide (7e).** Following **the General Procedure 3**, **7e** was obtained as a yellow liquid (65%, 40 mg, *Z/E* = 98:2). **^{1}H NMR** (500 MHz, $CDCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.36 (s, 1H), 8.57 (s, 1H), 8.03 (s, 1H), 7.94 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.56 (dd, *J* = 6.8, 2.2 Hz, 1H), 7.47 – 7.38 (m, 4H), 7.26 – 7.22 (m, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.61 (d, *J* = 8.2 Hz, 2H), 6.01 (s, 1H), 5.46 (t, *J* = 7.5 Hz, 1H), 4.74 – 4.60 (m, 2H), 1.88 – 1.73 (m, 2H), 1.24 – 1.16 (m, 2H), 1.17 – 1.09 (m, 2H), 0.75 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.41, 147.16, 144.99, 144.32, 144.10, 142.80, 142.14 (d, J_{CF} = 5.3 Hz), 139.98, 138.30, 137.52, 135.76, 130.84, 130.47, 130.08, 129.82, 129.71, 129.56, 129.25, 128.72, 128.34 (d, J_{CF} = 6.2 Hz), 128.12, 125.94 (q, J_{CF} = 3.5 Hz), 124.60 (q, J_{CF} = 3.8 Hz), 124.10 (d, J_{CF} = 272.4 Hz), 123.94 (d, J_{CF} = 271.9 Hz), 41.61, 31.30, 29.99, 22.39,

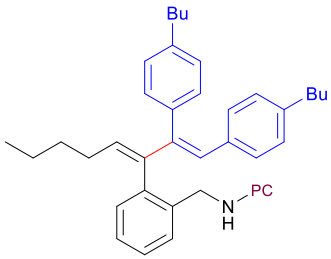
13.82. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.42, -62.67. **HRMS (ESI)** *m/z* calculated for $C_{34}H_{30}F_6N_3O$ $[M+H]^+$: 610.2288, found: 610.2287. **FTIR** (KBr, cm^{-1}) 3456.07, 2962.62, 2830.84, 2715.89, 1600.00, 1358.88, 1070.09, 775.70.



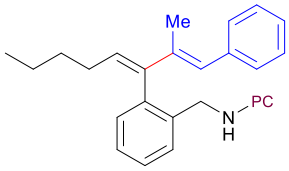
***N*-(2-((1*E*,3*Z*)-1,2-bis (4-fluorophenyl) octa-1,3-dien-3-yl) benzyl) pyrazine-2-carboxamide (7f).** Following **the General Procedure 3**, **7f** was obtained as a yellow liquid (55%, 28 mg, *Z/E* = 91:9). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.36 (d, 1H), 8.59 (d, *J* = 2.5 Hz, 1H), 8.06 (t, *J* = 1.9 Hz, 1H), 7.99 (s, 1H), 7.53 (dd, *J* = 6.5, 2.2 Hz, 1H), 7.46 – 7.37 (m, 2H), 7.24 – 7.20 (m, 3H), 7.11 (t, *J* = 8.7 Hz, 2H), 6.66 – 6.60 (m, 2H), 6.58 – 6.49 (m, 2H), 5.92 (s, 1H), 5.46 (t, *J* = 7.5 Hz, 1H), 4.74 – 4.51 (m, 2H), 1.84 – 1.73 (m, 2H), 1.24 – 1.16 (m, 2H), 1.16 – 1.09 (m, 2H), 0.75 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.45, 162.16 (d, J_{CF} = 246.6 Hz), 161.20 (d, J_{CF} = 247.5 Hz), 147.06, 144.29, 144.25, 142.95 (d, J_{CF} = 1.9 Hz), 142.67, 142.18, 138.90, 135.75, 135.64, 134.95 (d, J_{CF} = 3.4 Hz), 132.94 (d, J_{CF} = 3.4 Hz), 131.70 (d, J_{CF} = 7.8 Hz), 130.84, 130.81, 130.78, 129.57, 128.77, 128.10 (d, J_{CF} = 20.7 Hz), 116.02 (d, J_{CF} = 21.2 Hz), 114.60 (d, J_{CF} = 21.3 Hz), 41.65, 31.45, 29.83, 22.36, 13.86. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -114.56, -114.98. **HRMS (ESI)** *m/z* calculated for $C_{32}H_{30}N_3OF_2$ $[M+H]^+$: 510.2351, found: 510.2358. **FTIR** (KBr, cm^{-1}) 3442.06, 2962.62, 2833.64, 2718.69, 1602.80, 1361.68, 1227.10, 1064.49, 778.50..



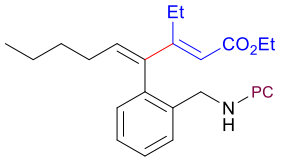
***N*-(2-((1*E*, 3*Z*)-1,2-bis (4-bromophenyl) octa-1,3-dien-3-yl) benzyl) pyrazine-2-carboxamide (7g).** Following **the General Procedure 3**, **7g** was obtained as a white solid (73%, 46 mg, *Z/E* = 98:2). **^{1}H NMR** (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.35 (d, *J* = 1.5 Hz, 1H), 8.60 (d, *J* = 2.4 Hz, 1H), 8.05 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.95 (s, 1H), 7.54 (dd, *J* = 8.9, 3.0 Hz, 3H), 7.44 – 7.38 (m, 2H), 7.22 – 7.18 (m, 1H), 7.13 (d, *J* = 8.3 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.42 (d, *J* = 8.6 Hz, 2H), 5.88 (s, 1H), 5.47 (t, *J* = 7.5 Hz, 1H), 4.69 – 4.57 (m, 2H), 1.84 – 1.71 (m, 2H), 1.23 – 1.16 (m, 2H), 1.15 – 1.09 (m, 2H), 0.75 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125MHz, $CDCl_3$) δ 162.43, 147.09, 144.28, 144.16, 143.72, 142.36, 142.19, 138.65, 137.96, 136.40, 135.73, 135.57, 132.21, 131.77, 130.84, 130.82, 130.73, 129.66, 128.70, 128.25, 128.12, 121.63, 120.42, 41.64, 31.38, 29.91, 22.38, 13.87. **HRMS (ESI)** *m/z* calculated for $C_{32}H_{29}N_3OBr_2Na$ $[M+Na]^+$: 652.0570, found: 652.0574. **FTIR** (KBr, cm^{-1}) 3456.07, 2954.21, 2830.84, 2718.69, 1608.41, 1364.49, 1072.90, 775.70.



***N*-(2-((1*E*,3*Z*)-1,2-bis (4-butylphenyl) octa-1,3-dien-3-yl)benzyl) pyrazine-2-carboxamide (7h).** Following **the General Procedure 3**, **7h** was obtained as a yellow liquid (69%, 41 mg, *Z/E* > 99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.35 (d, *J* = 1.5 Hz, 1H), 8.51 (d, *J* = 2.5 Hz, 1H), 8.09 (s, 1H), 7.91 (dd, *J* = 2.4, 1.5 Hz, 1H), 7.53 (dd, *J* = 6.9, 2.0 Hz, 1H), 7.45 – 7.32 (m, 2H), 7.21 (d, *J* = 8.3 Hz, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 8.1 Hz, 2H), 6.46 (d, *J* = 8.2 Hz, 2H), 5.89 (s, 1H), 5.48 (t, *J* = 7.6 Hz, 1H), 4.74 (dd, *J* = 14.2, 6.8 Hz, 1H), 4.56 (dd, *J* = 14.3, 5.0 Hz, 1H), 2.68 (t, *J* = 7.7 Hz, 2H), 2.43 (t, *J* = 7.7 Hz, 2H), 1.85 – 1.73 (m, 2H), 1.71 – 1.62 (m, 2H), 1.53 – 1.44 (m, 2H), 1.43 – 1.35 (m, 2H), 1.32 – 1.26 (m, 2H), 1.23 – 1.17 (m, 2H), 1.16 – 1.09 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H), 0.74 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (125MHz, $CDCl_3$) δ 162.51, 146.80, 144.36, 144.15, 143.50, 143.05, 142.22, 141.79, 141.09, 139.41, 136.81, 135.85, 134.98, 134.50, 130.87, 129.72, 129.61, 129.58, 129.32, 128.92, 128.02, 127.77, 127.66, 41.74, 35.45, 35.18, 33.56, 33.47, 31.53, 29.84, 29.71, 22.38, 22.31, 14.04, 13.92, 13.89. **HRMS (ESI)** *m/z* calculated for $C_{40}H_{47}N_3ONa$ $[M+Na]^+$: 608.3611, found: 608.3613. **FTIR** (KBr, cm^{-1}) 3467.29, 2962.62, 2830.84, 2718.69, 1602.80, 1361.68, 1070.09, 781.31.

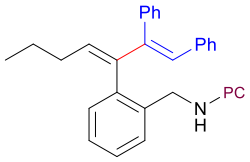


***N*-(2-((1*E*,3*Z*)-2-methyl-1-phenylocta-1,3-dien-3-yl) benzyl) pyrazine-2-carboxamide (7i).** Following **the General Procedure 3**, **7i** was obtained as a yellow liquid (44%, 18 mg, *Z/E* > 99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.29 (s, 1H), 8.53 (d, *J* = 2.5 Hz, 1H), 8.06 (d, *J* = 1.9 Hz, 1H), 7.87 (s, 1H), 7.44 – 7.38 (m, 1H), 7.29 – 7.23 (m, 2H), 7.15 (t, *J* = 7.5 Hz, 2H), 7.10 – 6.99 (m, 4H), 5.98 (t, *J* = 7.3 Hz, 1H), 5.89 (s, 1H), 4.53 (dd, *J* = 14.4, 6.5 Hz, 1H), 4.38 (dd, *J* = 14.4, 5.3 Hz, 1H), 2.06 (s, 3H), 1.87 – 1.70 (m, 2H), 1.32 – 1.23 (m, 2H), 1.18 – 1.11 (m, 2H), 0.74 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.48, 146.95, 144.45, 144.24, 142.30, 142.25, 139.51, 138.24, 138.22, 135.78, 130.87, 130.76, 129.72, 129.32, 127.82, 127.80, 127.65, 126.21, 41.62, 31.80, 29.76, 22.42, 15.33, 13.95. **HRMS (ESI)** *m/z* calculated for $C_{27}H_{29}N_3ONa$ $[M+Na]^+$: 434.2203, found: 434.2203. **FTIR** (KBr, cm^{-1}) 3436.58, 2954.34, 2828.17, 2718.83, 1594.54, 1359.03, 1073.05, 770.25.

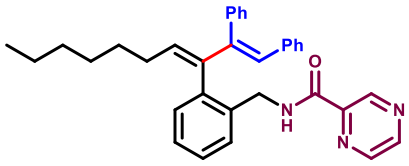


Ethyl (2*E*, 4*Z*)-3-ethyl-4-(2-((pyrazine-2-carboxamido) methyl) phenyl) nona-2,4-dienoate (7j). Following **the General Procedure 3**, **7j** was obtained as a yellow liquid (26%, 11 mg, *Z/E* > 99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.39 (d, 1H), 8.72 (d, *J* = 2.4 Hz, 1H), 8.44 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.90 (s, 1H), 7.49 – 7.46 (m, 1H), 7.36 – 7.32 (m, 2H), 7.05 – 7.00 (m, 1H), 6.37 (t, *J* = 7.4 Hz, 1H), 5.20 (s, 1H), 4.53 (dd, *J* = 14.7, 6.5 Hz, 1H), 4.39 (dd, *J* = 14.7, 5.5 Hz, 1H), 4.10 – 3.97 (m, 2H), 3.07 – 2.98 (m, 1H), 2.96 – 2.81 (m, 1H), 1.99 – 1.76 (m, 2H), 1.28 – 1.22 (m, 4H),

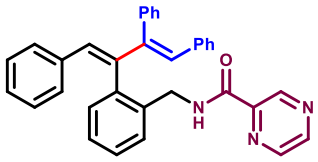
1.21 – 1.14 (m, 6H), 0.81 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.71, 162.53, 160.66, 147.16, 144.43, 142.39, 139.61, 137.99, 136.73, 135.66, 130.55, 129.22, 128.04, 117.48, 59.62, 41.34, 31.33, 30.09, 22.41, 21.34, 14.44, 14.24, 13.88. **HRMS (ESI)** *m/z* calculated for $C_{25}H_{31}N_3O_3Na$ $[M+Na]^+$: 444.2258, found: 444.2256. **FTIR** (KBr, cm^{-1}) 3453.27, 2954.21, 2830.84, 2718.69, 1608,41, 1367.29, 1067.29, 778.50.



***N*-(2-((1*E*, 3*Z*)-1,2-diphenylhepta-1,3-dien-3-yl) benzyl) pyrazine-2-carboxamide (7k).** Following **the General Procedure 3**, **7k** was obtained as a yellow liquid (87%, 40 mg, *Z/E* > 99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.36 (d, *J* = 1.3 Hz, 1H), 8.53 (d, *J* = 2.4 Hz, 1H), 8.08 (s, 1H), 7.95 (dd, *J* = 2.4, 1.5 Hz, 1H), 7.54 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.43 – 7.35 (m, 5H), 7.29 – 7.21 (m, 3H), 6.99 – 6.90 (m, 3H), 6.60 – 6.53 (m, 2H), 5.96 (s, 1H), 5.49 (t, *J* = 7.5 Hz, 1H), 4.75 (dd, *J* = 14.3, 6.7 Hz, 1H), 4.60 (dd, *J* = 14.3, 5.1 Hz, 1H), 1.84 – 1.70 (m, 2H), 1.25 – 1.20 (m, 2H), 0.74 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.53, 146.94, 144.30, 144.18, 143.05, 142.24, 139.49, 139.17, 136.99, 135.86, 135.47, 130.90, 129.99, 129.72, 129.61, 129.38, 128.84, 128.10, 127.91, 127.61, 127.29, 126.35, 41.72, 32.10 , 22.48, 13.85. **HRMS (ESI)** *m/z* calculated for $C_{31}H_{29}N_3ONa$ $[M+Na]^+$: 482.2203, found: 482.2204.

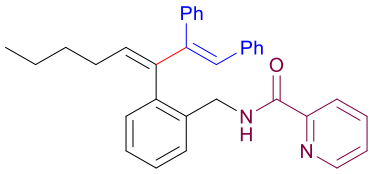


N-(2-((1*E*, 3*Z*)-1,2-diphenyl deca-1,3-dien-3-yl) benzyl) pyrazine-2-carboxamide (7l). Following the general experiment procedure, **7l** was obtained as a yellow liquid (78%, 39 mg, *Z/E* > 99:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.36 (d, *J* = 1.5 Hz, 1H), 8.53 (d, *J* = 2.4 Hz, 1H), 8.08 (s, 1H), 7.94 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.54 (dd, *J* = 7.0, 1.9 Hz, 1H), 7.43 – 7.34 (m, 5H), 7.28 – 7.19 (m, 3H), 6.98 – 6.88 (m, 3H), 6.65 – 6.37 (m, 2H), 5.96 (s, 1H), 5.49 (t, *J* = 7.5 Hz, 1H), 4.74 (dd, *J* = 14.3, 6.6 Hz, 1H), 4.59 (dd, *J* = 14.3, 5.1 Hz, 1H), 1.84 – 1.67 (m, 2H), 1.22 – 1.15 (m, 4H), 1.13 – 1.06 (m, 4H), 0.81 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.52 , 146.94 , 144.32 , 144.18 , 142.84 , 142.23 , 139.49 , 139.17 , 137.00 , 135.87 , 135.72 , 130.88 , 129.99 , 129.69 , 129.64 , 129.37 , 128.84 , 128.10 , 127.91 , 127.61 , 127.28 , 126.34 , 41.73 , 31.52 , 30.13 , 29.20 , 28.93 , 22.48 , 14.02. **HR-MS (ESI)**: m/z calculated for $C_{34}H_{35}N_3ONa$: $[M+Na]^+$: 524.2672, found: 524.2676.

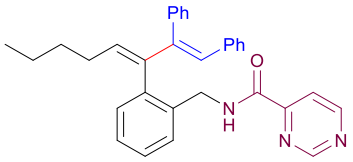


N-(2-((1*Z*, 3*E*)-1,3,4-triphenyl buta-1,3-dien-2-yl) benzyl) pyrazine-2-carboxamide (7m). Following the general experiment procedure, **7m** was obtained as a colorless liquid (41%, 20 mg, *Z/E* > 99:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.28 (d, *J* = 1.5 Hz, 1H), 8.50 (d, *J* = 2.4 Hz,

1H), 7.92 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.91 (s, 1H), 7.61 – 7.56 (m, 1H), 7.48 – 7.44 (m, 4H), 7.43 – 7.40 (m, 1H), 7.39 – 7.32 (m, 3H), 7.04 – 6.92 (m, 6H), 6.68 – 6.57 (m, 4H), 6.37 (s, 1H), 6.17 (s, 1H), 4.64 – 4.53 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.50 , 146.77 , 145.06 , 144.25 , 144.08 , 142.96 , 142.14 , 139.23 , 139.12 , 136.81 , 136.57 , 135.80 , 132.73 , 131.66 , 131.07 , 130.54 , 130.18 , 129.53 , 129.20 , 129.07 , 128.83 , 128.51 , 128.09 , 127.72 , 127.58 , 127.14 , 126.74 , 41.83. **HR-MS (ESI)**: m/z calculated for $C_{34}H_{27}N_3O$: $[M+H]^+$: 494.2227, found: 494.2222.



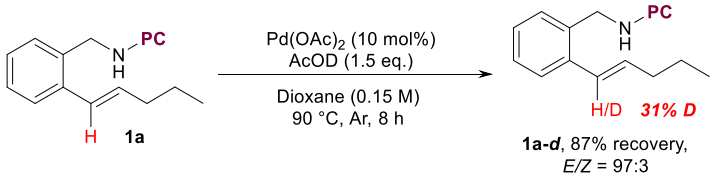
***N*-(2-((1*E*,3*Z*)-1,2-diphenylocta-1,3-dien-3-yl) benzyl) picolinamide (7n).** Following **the General Procedure 3**, **7n** was obtained as a yellow liquid (89%, 42 mg, *Z/E* > 99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 8.13 (d, *J* = 4.6 Hz, 1H), 7.76 (td, *J* = 7.7, 1.8 Hz, 1H), 7.55 (dd, *J* = 7.0, 2.1 Hz, 1H), 7.43 – 7.32 (m, 5H), 7.29 – 7.24 (m, 3H), 7.23 – 7.21 (m, 1H), 6.98 – 6.89 (m, 3H), 6.65 – 6.54 (m, 2H), 5.99 (s, 1H), 5.48 (t, *J* = 7.5 Hz, 1H), 4.75 (dd, *J* = 14.5, 6.7 Hz, 1H), 4.60 (dd, *J* = 14.5, 5.3 Hz, 1H), 1.92 – 1.70 (m, 2H), 1.24 – 1.16 (m, 2H), 1.16 – 1.07 (m, 2H), 0.74 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.01, 149.78, 147.88, 144.18, 142.93, 139.61, 139.01, 137.14, 137.10, 136.39, 135.50, 130.74, 130.14, 129.64, 129.44, 129.29, 128.74, 127.79, 127.56, 127.16, 126.23, 125.91, 122.08, 41.53, 31.51, 29.88, 22.39, 13.90. **HRMS (ESI)** *m/z* calculated for $C_{33}H_{32}N_2OK$ $[M+K]^+$: 511.2146, found: 511.2147. **FTIR** (KBr, cm^{-1}) 3836.45, 2965.42, 2833.64, 2718.69, 1591.59, 1361.68, 1072.90, 775.70.



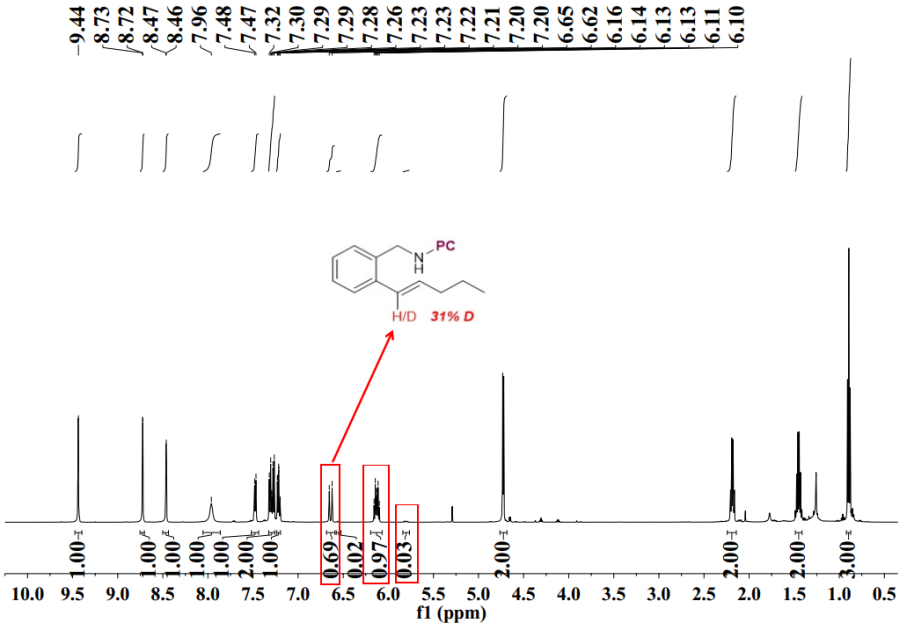
***N*-(2-((1*E*,3*Z*)-1,2-diphenylocta-1,3-dien-3-yl) benzyl) pyrimidine-4-carboxamide (7o).** Following **the General Procedure 3**, **7o** was obtained as a yellow liquid (52%, 25 mg, *Z/E* > 99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.78 (d, *J* = 5.1 Hz, 1H), 8.62 (s, 1H), 8.19 (s, 1H), 7.98 (d, *J* = 4.9 Hz, 1H), 7.45 (d, *J* = 7.0 Hz, 1H), 7.38 – 7.28 (m, 5H), 7.18 (q, *J* = 7.9, 5.9 Hz, 4H), 6.88 (dd, *J* = 12.4, 7.1 Hz, 3H), 6.51 (d, *J* = 7.5 Hz, 1H), 5.89 (s, 1H), 5.41 (t, *J* = 7.5 Hz, 1H), 4.66 (dd, *J* = 14.5, 6.6 Hz, 1H), 4.52 (dd, *J* = 14.4, 5.2 Hz, 1H), 1.88 – 1.52 (m, 2H), 1.19 – 1.10 (m, 2H), 1.09 – 1.02 (m, 2H), 0.67 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.16, 158.94, 157.50, 156.08, 144.22, 142.84, 139.47, 139.18, 136.93, 135.63, 130.90, 130.00, 129.74, 129.56, 129.38, 128.83, 128.16, 127.93, 127.63, 127.29, 126.48, 118.35, 41.82, 31.48, 29.87, 22.38, 13.88. **HRMS (ESI)** *m/z* calculated for $C_{32}H_{31}N_3ONa$ $[M+Na]^+$: 496.2359, found: 496.2360. **FTIR** (KBr, cm^{-1}) 3461.68, 2962.62, 2830.84, 2721.50, 1600.00, 1367.29, 1064.49, 772.90.

4. Pd-Catalyzed H/D Exchange

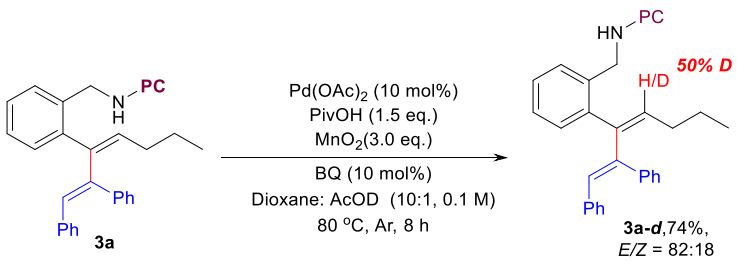
4.1 Pd-Catalyzed H/D Exchange in Cross-Coupling-1



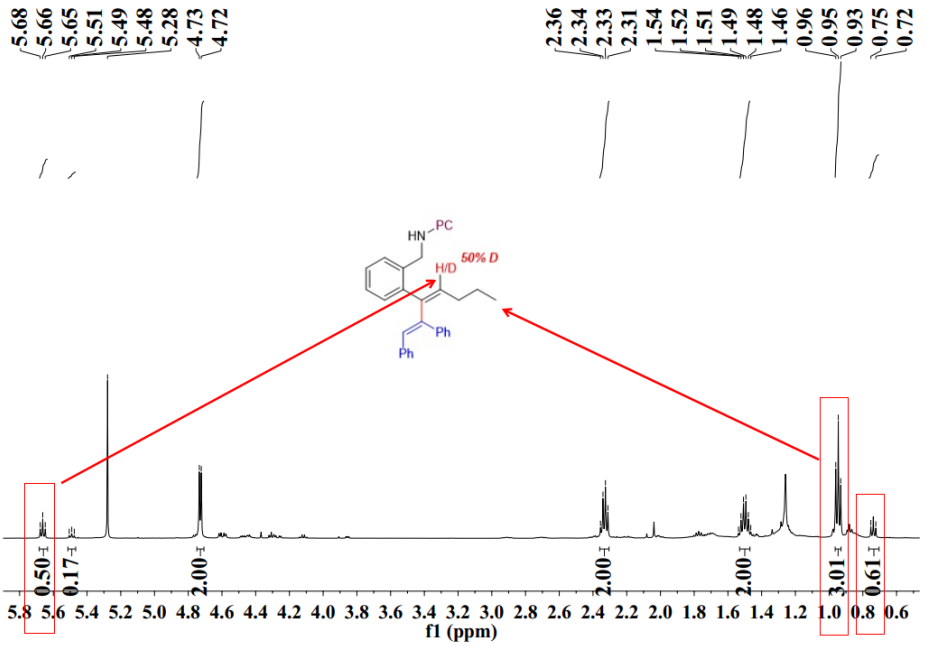
A screw-cap vial was charged with $Pd(OAc)_2$ (10 mol%, 0.015 mmol), amide **1a** (1.0 equiv, 0.15 mmol) and 1,4-dioxane (1.0 mL). Then, AcOD (1.5 equiv, 0.23 mmol) were added into the solution in sequence. The vial was sealed under argon atmosphere and heated to 90 °C with stirring for 8 h. After cooling down, the mixture was directly applied to a flash column chromatography (PE/EA mixtures) for separation to obtain **1a** and **1a-*d***. Deuterium incorporation and isomeric ratio were determined by ^{1}H NMR analysis.



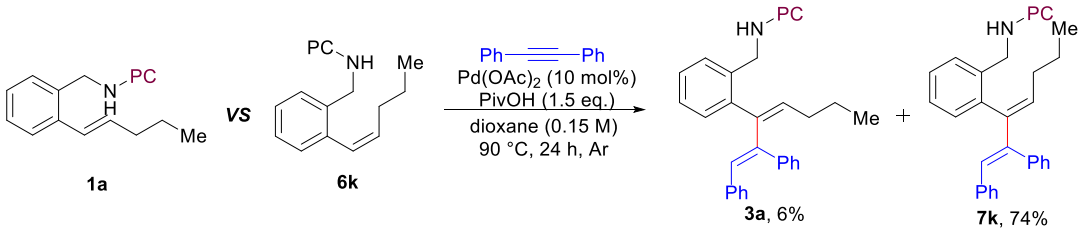
4.2 Pd-Catalyzed H/D Exchange in Cross-Coupling-2



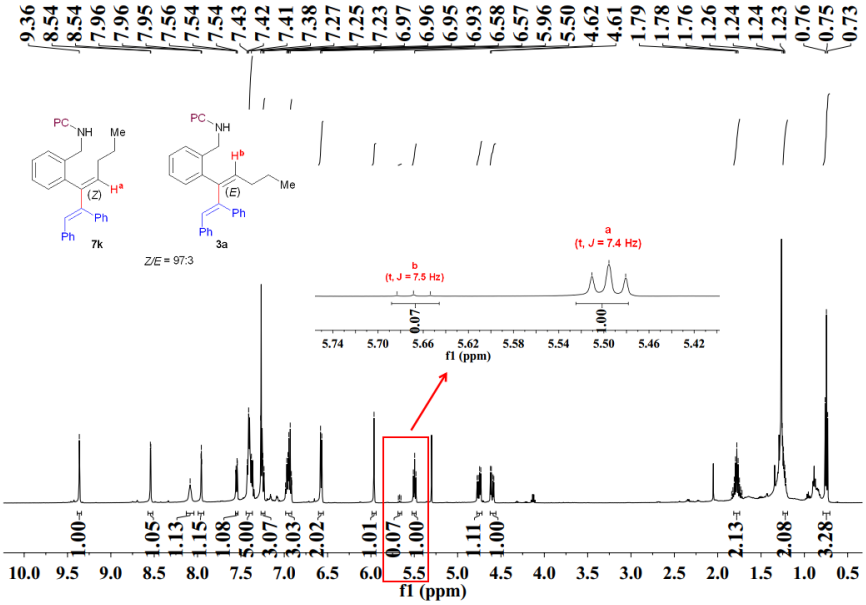
A screw-cap vial was charged with $Pd(OAc)_2$ (10 mol%, 0.015 mmol), MnO_2 (3.0 equiv, 0.45 mmol), BQ (10 mol%, 0.015 mmol), amide **3a** (1.0 equiv, 0.15 mmol) and dioxane/AcOD (*v*: *v* = 10: 1, 0.1 M,). Then, pivalic acid (1.5 equiv, 0.23 mmol) was added into the solution. The vial was sealed under argon atmosphere and heated to 80°C with stirring for 8 h. After cooling down, the mixture was directly applied to a flash column chromatography (PE/EA mixtures) for separation to obtain a mixture of **3a** and **3a-*d***. Deuterium incorporation and isomeric ratio were determined by ^{1}H NMR analysis.

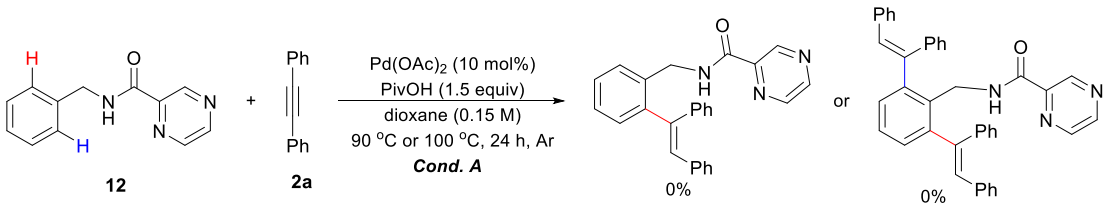


5. Competition Experiment for *trans*- and *cis*-Styrenes



A screw-cap vial was charged with $Pd(OAc)_2$ (10 mol%, 0.015 mmol), alkyne **2** (1.0equiv, 0.1 mmol), amide **1a** (1.0 equiv, 0.1 mmol) and **6k** (1.0 equiv, 0.1 mmol) and 1,4-dioxane (0.7 mL). Then, PivOH (1.5 equiv, 0.15 mmol) were added into the solution in sequence. The vial was sealed under argon atmosphere and heated to 70 °C with stirring for 12 h. After cooling down, the mixture was directly applied to a flash column chromatography (PE/EA mixtures) for separation to obtain a mixture of **3a** and **7k** (36.7 mg, 80%). The yields of **3a** or **7k** were determined by ^{1}H NMR analysis.

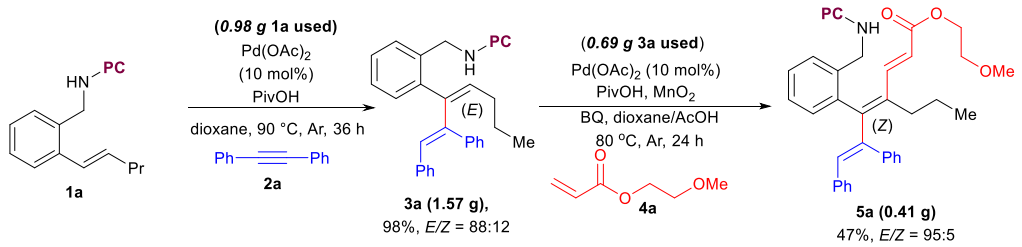




A screw-cap vial was charged with $Pd(OAc)_2$ (10 mol%, 0.015 mmol), alkyne **2** (1.0equiv, 0.1 mmol) and benzyl amide **12** (1.0 equiv, 0.1 mmol) in 1,4-dioxane (0.7 mL). Then, PivOH (1.5 equiv, 0.15 mmol) were added into the solution in sequence. The vial was sealed under argon atmosphere and heated to 90 °C or 100 °C with stirring for 24 h. No reaction occurred and the amide **12** was totally recovered.

6. Synthetic Applications

6.1 Scaled-up preparation

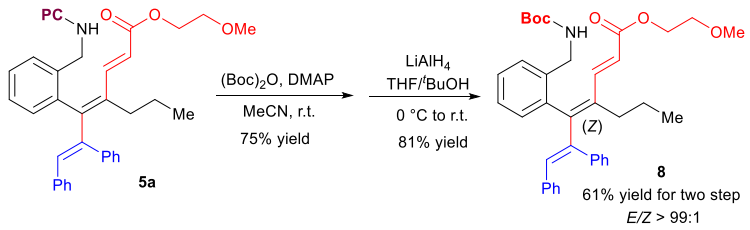


A screw-cap vial was charged with $Pd(OAc)_2$ (10 mol%, 0.35 mmol, 78.6 mg), amide **1a** (1.0 equiv, 3.5 mmol, 0.98 g), diarylacetylene **2a** (2.5 equiv, 8.75 mmol, 1.56 g) and 1,4-dioxane (0.15 M, 40 mL). Then, pivalic acid (1.5 equiv, 5.25 mmol, 0.54 g) were added into the solution in sequence. The vial was sealed under argon atmosphere and heated to 90 °C with stirring for 36 h. After cooling down, the mixture was directly applied to a flash column chromatography (PE/EA mixtures) for separation to obtain

the corresponding product **3a** (1.57 g, 3.4 mmol, 98%, *E/Z* = 88: 12).

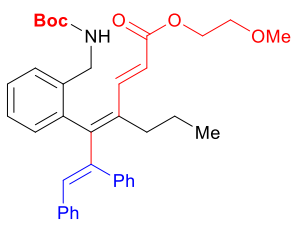
A screw-cap vial was charged with $Pd(OAc)_2$ (10 mol%, 0.15 mmol, 33.7 mg), MnO_2 (3.0 equiv, 4.5 mmol, 0.37 g), BQ (10 mol%, 0.15 mmol, 16.2 mg), amide **3a** (1.0 equiv, 1.5 mmol, 0.69 g), olefin **4a** (2.5 equiv, 3.8 mmol, 0.49 g) and 1,4-dioxane/ AcOH (*v*: *v* = 10: 1, 15 mL, 0.1 M). Then, pivalic acid (1.5 equiv, 2.3 mmol, 0.23 g) were added into the solution in sequence. The vial was sealed under Ar atmosphere and heated to 80 °C with stirring for 24 h. After cooling down, the mixture was directly applied to a flash column chromatography (PE/EA mixtures) for separation to obtain the corresponding product **5a** (0.41 g, 0.7 mmol, 47%, *E/Z* = 95: 5).

6.2 DG Removal



DG remove experiment according to previous literature[11]: Boc-anhydride (436.5 mg, 1.5 mmol, 10 equiv) was added to a solution of **5a** (117.5 mg, 0.2 mmol, 1.0 equiv) and DMAP (57.7 mg，0.3 mmol，2.0 equiv) in MeCN (1.0 mL,0.2 M) and the reaction mixture was stirred overnight. The reaction mixture was quenched with NH_4Cl (10 Ml, sat. aq) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were dried Na_2SO_4, concentrated under reduced pressure and purified by column chromatography (SiO_2, PE / EA=40:1 to 20: 1) to give N-Boc-amide (103.18 mg, 75% yield, *E/Z* > 99: 1).

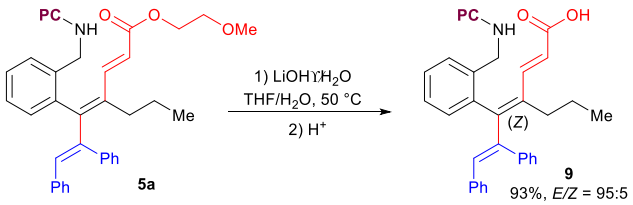
Then to a solution of *N*-Boc-amide in THF/^{t}BuOH (1: 1, 0.02 M) was added $LiAlH_4$ (2.0 equiv, 2.5 M in THF) dropwisely over 30 min at 0°C and stirred at room temperature for 2 h, and 2 N NaOH was added slowly at 0°C until a clear solution was obtained. The organic layer was separated and the aqueous phase was extracted with Et_2O (20 mL × 3). Combined the organic layers and dried over Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with PE/EA and the resulting amine **11** was obtained as a light yellow oil (71.0 mg, 81% yield, 61% yield for two steps, *E/Z* > 99:1).



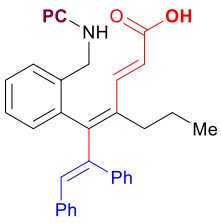
2-Methoxyethyl (2*E*,4*Z*,6*E*)-5-(2-(((tert-butoxycarbonyl) amino) methyl) phenyl)-6,7-diphenyl-4-propylhepta-2,4,6-trienoate (8) According to previous literature reports, **8** was obtained as a light yellow oil (71.0 mg, 61% yield, *Z/E* > 99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.6 Hz, 1H), 7.23-

7.14 (m, 5H), 7.13-7.10 (m, 3H), 7.08 (d, *J* = 16.2 Hz, 1H), 7.03-6.96 (m, 3H), 6.93-6.88 (m, 2H), 6.73 (s, 1H), 6.04 (d, *J* = 15.9 Hz, 1H), 4.31 (s, 1H), 4.25-4.17 (m, 2H), 4.12 (dd, *J* = 14.4, 6.1 Hz, 1H), 3.92 (dd, *J* = 14.4, 5.0 Hz, 1H), 3.55 (t, *J* = 4.7 Hz, 2H), 3.32 (s, 3H), 2.75-2.63 (m, 2H), 1.70-1.55 (m, 2H), 1.42 (s, 9H), 0.97 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.04, 155.78, 149.48, 144.40, 142.15, 138.65, 137.94, 137.27, 136.19, 136.14, 130.91, 130.06, 129.46, 129.11, 128.90, 128.55, 128.19, 128.05, 127.50, 127.29, 127.01, 118.68, 79.06, 70.44, 63.49, 59.00, 41.85, 32.03, 28.43, 23.57, 14.80. **HRMS (ESI)** *m/z* calculated for $C_{37}H_{43}NO_4$ Na $[M+Na]^+$: 604.3033, found: 604.3033.

6.3 Ester Hydrolysis

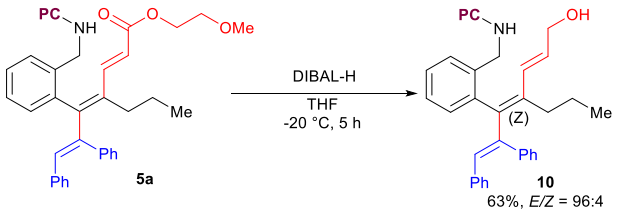


A solution of **5a** (58.8 mg, 0.1 mmol, 1.0 equiv) in THF/H_2O (0.1 M, 1.0 mL, *v/v* = 1: 1) was treated with LiOH·H_2O (0.42 g, 1.0 mmol, 10.0 equiv). The reaction heated to 50 °C and stirred overnight. Solvent was removed in vacuo, followed by the addition of HCl (1 N) to PH < 7. The organic layer was separated and the aqueous phase was extracted with EA. The organic layers were combined and dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with PE/EA (1: 4) to obtained **9** as a light yellow solid (49.4 mg, 93 % yield, *E/Z* = 95:5).

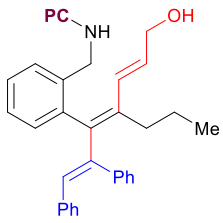


(2*E*, 4*Z*, 6*E*)-6,7-Diphenyl-4-propyl-5-(2-((pyrazine-2-carboxamido) methyl) phenyl) hepta-2,4,6-trienoic acid (9) According to the above method, **7** was obtained as a light yellow solid (49.4 mg, 93 % yield, *Z/E* = 95:5). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.36 (s, 1H), 8.62 (d, *J* = 2.3 Hz, 1H), 8.30 (s, 1H), 7.74 (t, *J* = 5.7 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.25-7.20 (m, 1H), 7.20-7.05 (m, 8H), 7.01-6.90 (m, 5H), 6.79 (s, 1H), 5.93 (d, *J* = 15.9 Hz, 1H), 4.52 (dd, *J* = 14.5, 6.2 Hz, 1H), 4.33 (dd, *J* = 14.5, 5.5 Hz, 1H), 2.72 (t, *J* = 8.2 Hz, 2H), 1.70-1.53 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.95, 162.61, 150.51, 147.01, 145.79, 144.40, 144.20, 142.45, 141.94, 138.47, 138.29, 136.60, 136.10, 135.96, 131.29, 130.56, 129.55, 129.42, 129.07, 128.61, 128.51, 128.04, 127.58, 127.51, 127.41, 118.64, 41.01, 32.06, 23.57, 14.80. **HRMS (ESI)** *m/z* calculated for $C_{34}H_{31}N_3O_3Na$ $[M+Na]^+$: 552.2258, found: 552.2259.

6.4 Ester Reduction

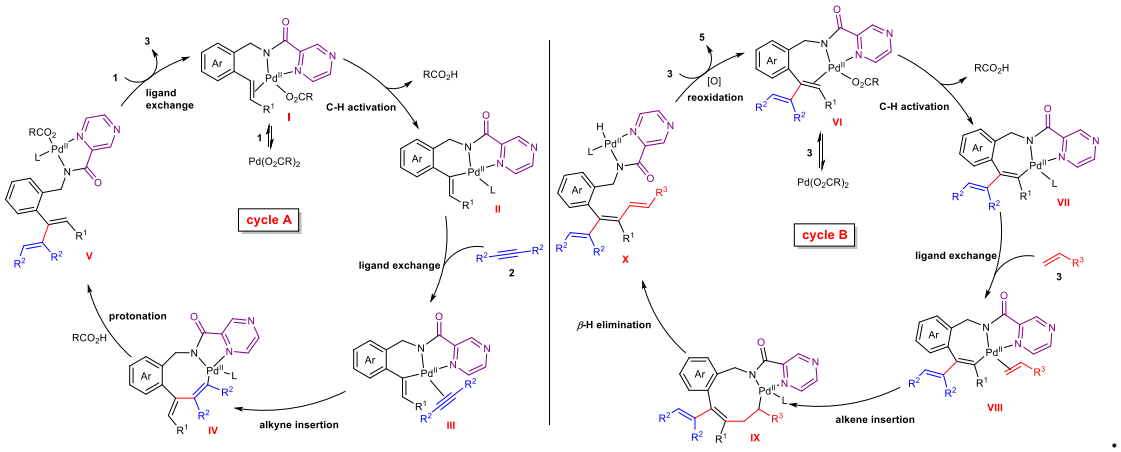


A solution of **5a** (58.8 mg, 0.1 mmol, 1.0 equiv) in THF (0.1 M, 1.0 mL) was cooled down to -20 °C and treated with DIBAL-H (5.0 equiv, 1.5 mol/L in THF). The reaction was stirred for 5 h under -20 °C until the materials are completely consumed. The organic phase was quenched with 1 N hydrochloric acid at -20 ℃, and then diluted with water and ethyl acetate. The aqueous phase was extracted with EA. The organic phase was combined and dried over anhydrous Na_2SO_4. The EA was removed under reduced pressure. The resulting mixture was purified by silica gel column chromatography (PE: EA = 1: 2). Allyl alcohol **10** was obtained as a colorless oil (32.5 mg, 63% yield, *E/Z* = 95:5)



***N*-(2-((1*E*, 3*Z*, 5*E*)-7-Hydroxy-1,2-diphenyl-4-propylhepta-1,3,5-trien-3-yl) benzyl) pyrazine-2-carboxamide (10)** According to the above method, **10** was obtained as a colorless oil (32.5 mg, 63% yield, *Z/E* = 95:5). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.42 – 9.36 (m, 1H), 8.72 (d, *J* = 2.3 Hz, 1H), 8.46 – 8.40 (m, 1H), 7.81 (s, 1H), 7.24 – 7.20 (m, 1H), 7.19 – 7.14 (m, 5H), 7.12 – 7.06 (m, 4H), 6.97 (dd, *J* = 6.7, 2.9 Hz, 2H), 6.93 (dd, *J* = 6.5, 3.0 Hz, 2H), 6.74 (s, 1H), 6.04 (d, *J* = 5.4 Hz, 2H), 4.64 (dd, *J* = 15.2, 6.9 Hz, 1H), 4.16 – 4.03 (m, 3H), 2.81 – 2.67 (m, 2H), 1 1.76 – 1.58 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.78, 147.33, 144.63, 144.34, 142.81, 142.36, 141.70, 139.28, 138.84, 136.77, 136.53, 136.36, 130.83, 130.28, 130.08, 129.81, 129.35, 129.01, 128.41, 127.97, 127.69, 127.44, 127.23, 127.15, 126.95, 63.66, 40.87, 32.38, 23.84, 14.91. **HRMS (ESI)** *m/z* calculated for $C_{34}H_{33}N_3O_2Na$ $[M+Na]^+$: 538.2465, found: 538.2464

6.5 Proposed Mechanism



Plausible catalytic cycles are shown in Scheme 4. In α C−H functionalization of E-aryl alkenes, N,N-bidentate chelation assisted insertion of Pd(II) into the α C−H bond of E-styrene 1 results in six-membered exo-palladacycle species II. Then II coordinates with alkyne 2 and undergoes 1,2-migratory insertion, followed by protonation to generate the hydro-alkenylation product 3 (Scheme 4, cycle A). Functional-group-directed insertion of Pd(II) into the β C–H bond of diene 3 results in seven-membered endo-palladacycle species VII. Then VII coordinates with alkene 4 and undergoes 1,2-migratory insertion, followed by β-hydride elimination to generate triene product 5. Pd(0) is then re-oxidized by MnO2 and re-enters the next catalytic cycle (cycle B).

6.6 Photophysical Properties

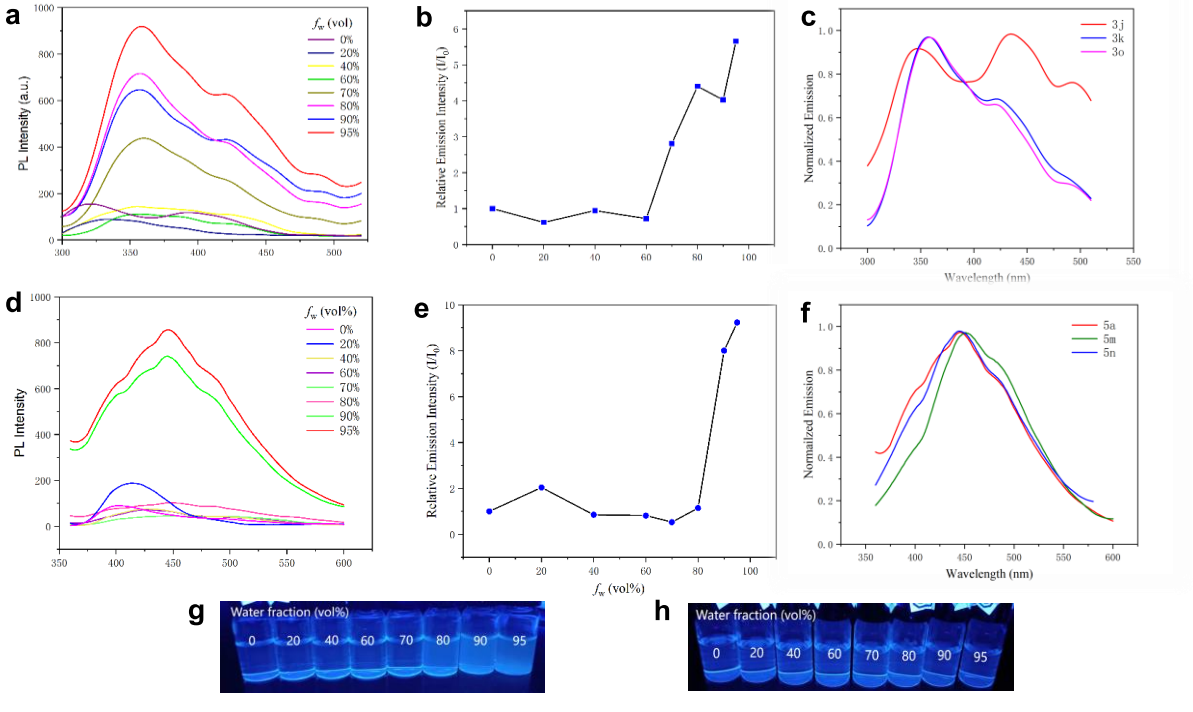


Figure S1. Photophysical Property Test. (a) Emission spectra of **3o** obtained at different water fractions of the 1,4-dixoane/ H_2O mixtures. (b) Relative emission intensity of compound **3o** in 1,4-dioxane/H_2O mixture with increasing water fractions (fw) to 95% (c =150 μM, λ_{ex} = 269 nm, λ_{em} = 365 nm). (c) Normalized fluorescence emission spectra in 1,4-dixoane/water mixtures (c =150 μM, 95% water) of dienes **3**. (d) Emission spectra of **5a** obtained at different water fractions of the 1,4-dixoane/H_2O mixtures. (e) Relative emission intensity of **5a** in 1,4-dioxane/H_2O mixture with increasing water fractions (fw) to 95% (c =150 μM, λ_{ex} = 320 nm, λ_{em} = 445 nm). (f) Normalized fluorescence emission spectra in 1,4-dixoane/H_2O mixtures (c =150 μ M, 95% water) of trienes **5**. (g) **3o** (c = 150 μM) in 1,4- dioxane/water mixtures with different volume fractions of H_2O. (h) **5a** (c = 150 μM) in 1,4- dioxane/H_2O mixtures with different volume fractions of H_2O.

With the library of these tetrasubstituted dienes **3** and trienes **5** in hand, we then examined their photophysical properties. Although compound **3o** and **5a** showed almost no fluorescence in 1,4-dixoane, the emission intensity increased gradually with the increasing of water fraction. Notably, the emission intensity of **3o** and **5a** increased significantly when water fraction exceeded 95% due to the restriction of intra-molecular rotation (Fig. 1a, b, d, e). Polyenes bearing electro-withdrawing and electro-donating groups were measured by fluorescence emission spectra, and the emission maxima of all the AIE-gens altered from 356 to 436 nm and 447 to 451 nm (Fig. 1f). The results showed that the substituents on alkyne **2** and functionality on benzyl amides **1** were vital for the AIE-activity of the polyene products. In this regard, these dienes exhibited potential applications in OLEDs and living animal imaging by structural derivations.

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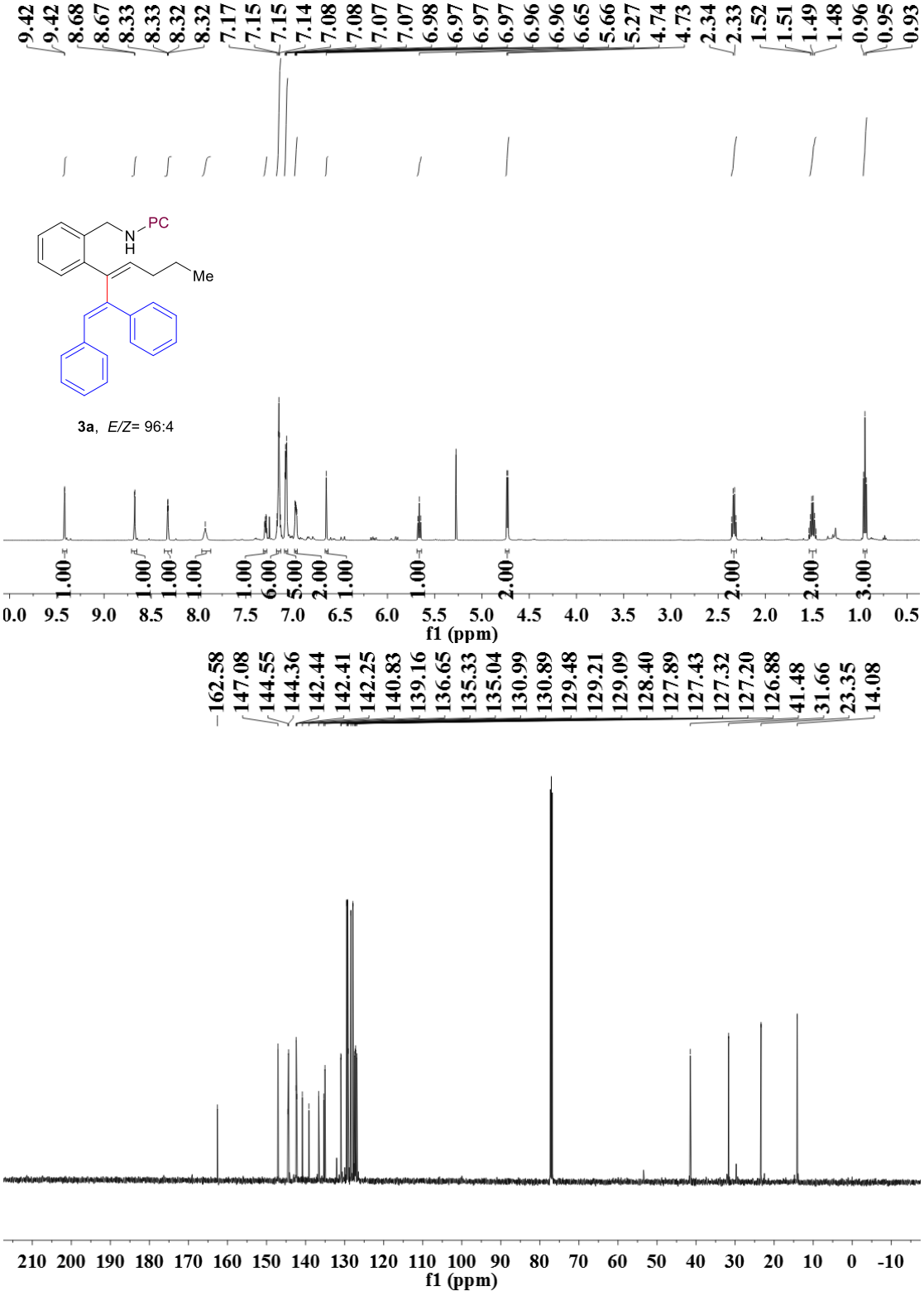
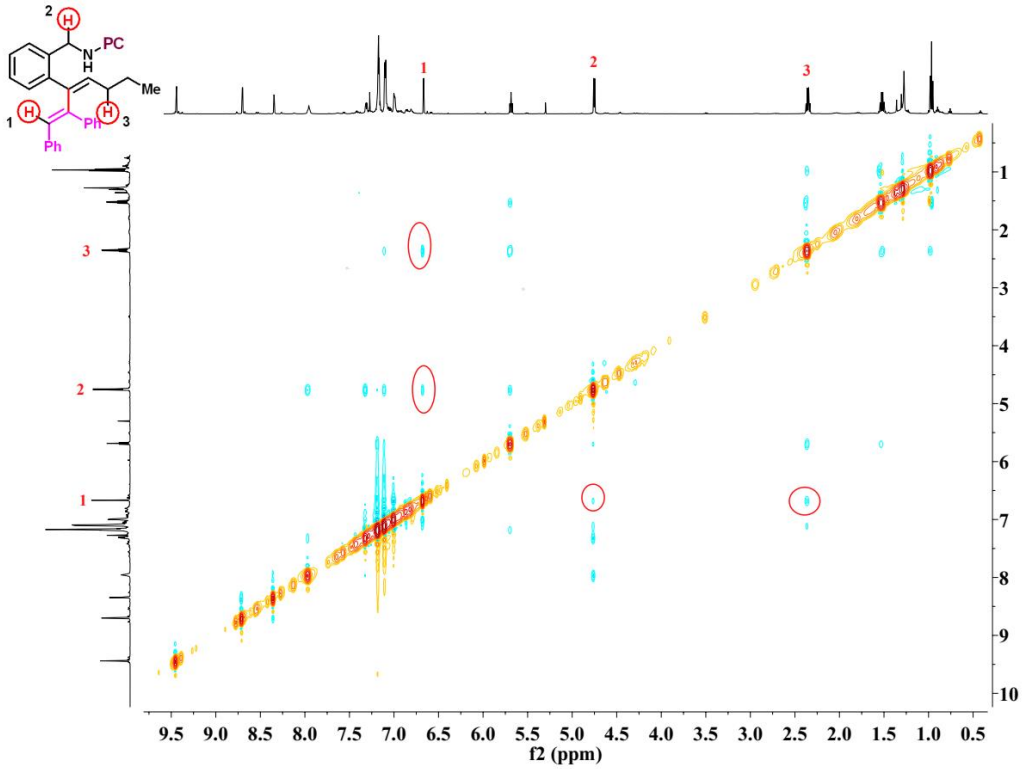
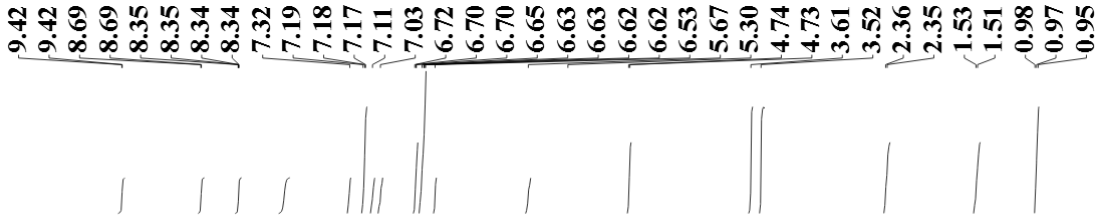
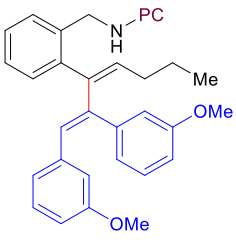
8. NMR Spectra

8.1 NMR Spectra of the Products 3

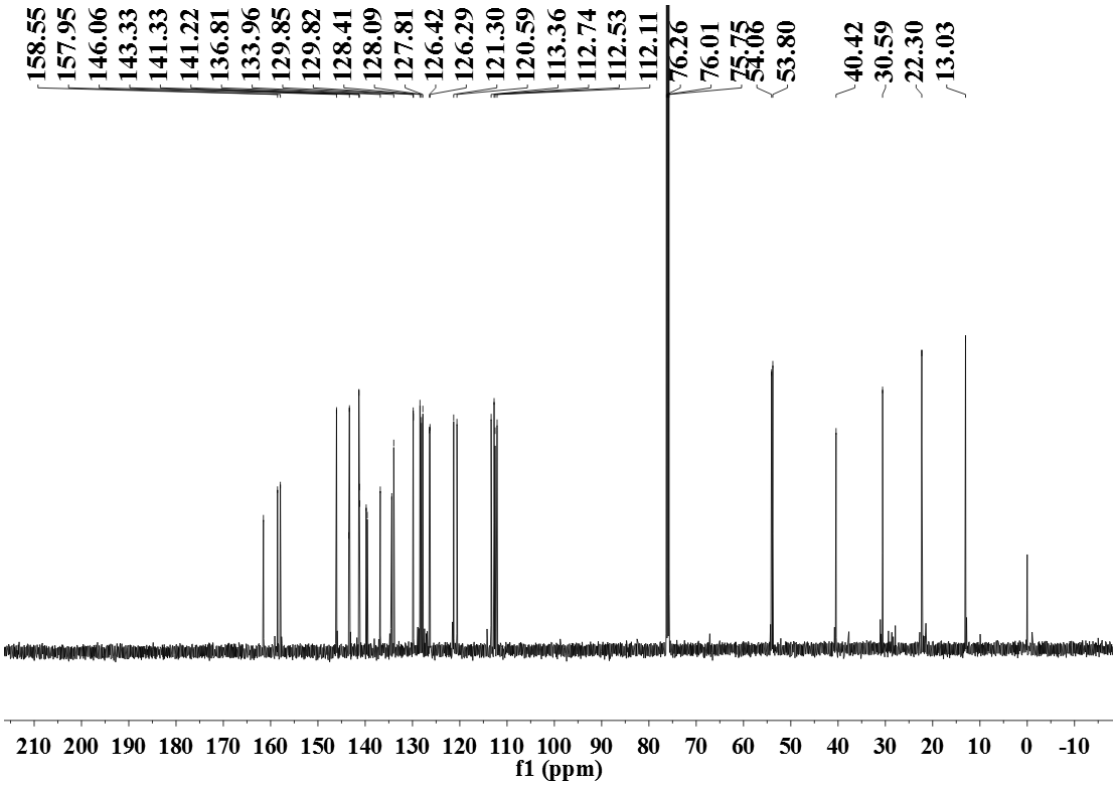








3b, *E*/*Z*= 90:10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127.81
126.42
126.29
121.30
120.59
113.36
112.74
112.53
112.11
76.26
76.01
75.75
54.06
53.80
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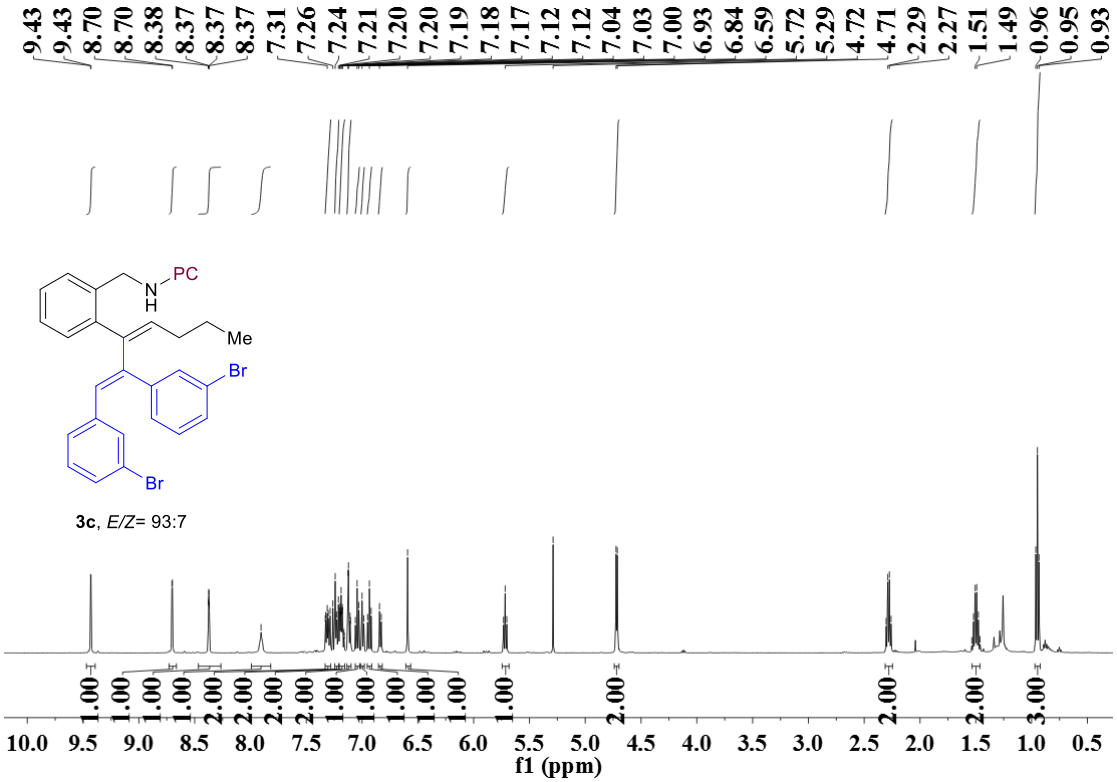
30.59
22.30
13.03
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.20
7.19
7.18
7.17
7.12
7.12
7.04
7.03
7.00
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6.84
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5.29
4.72
4.71
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Br
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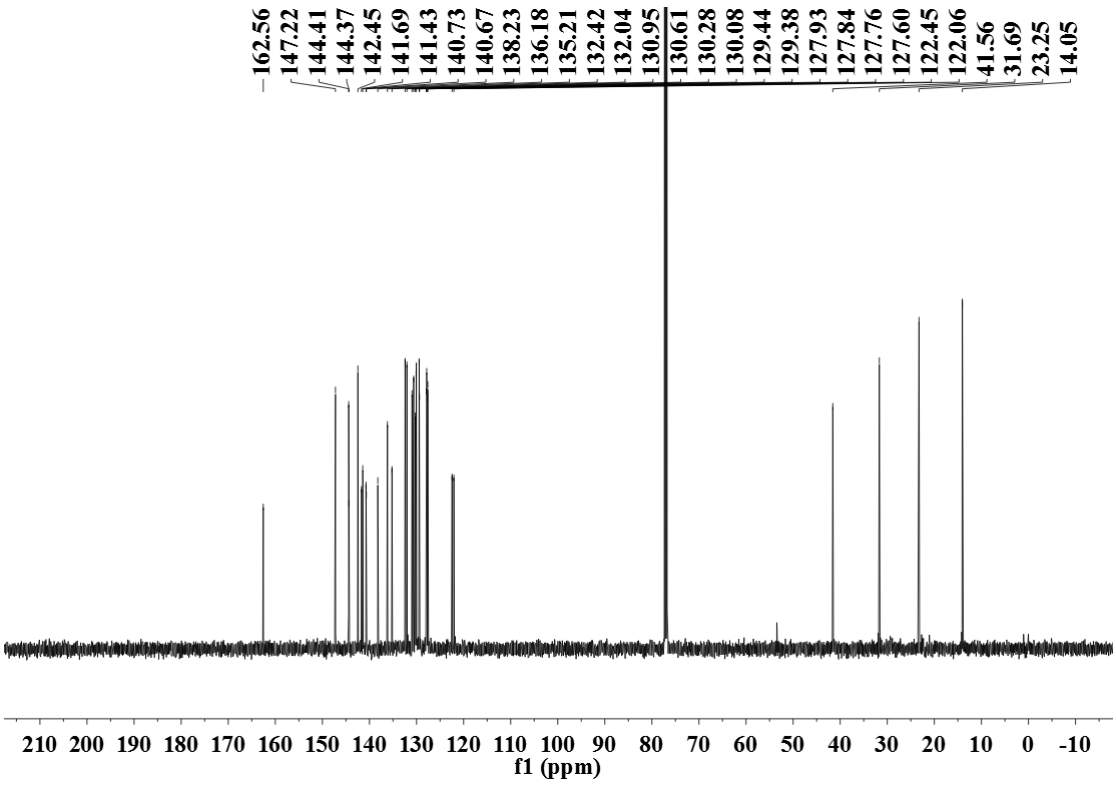
3c, *E*/*Z*= 93:7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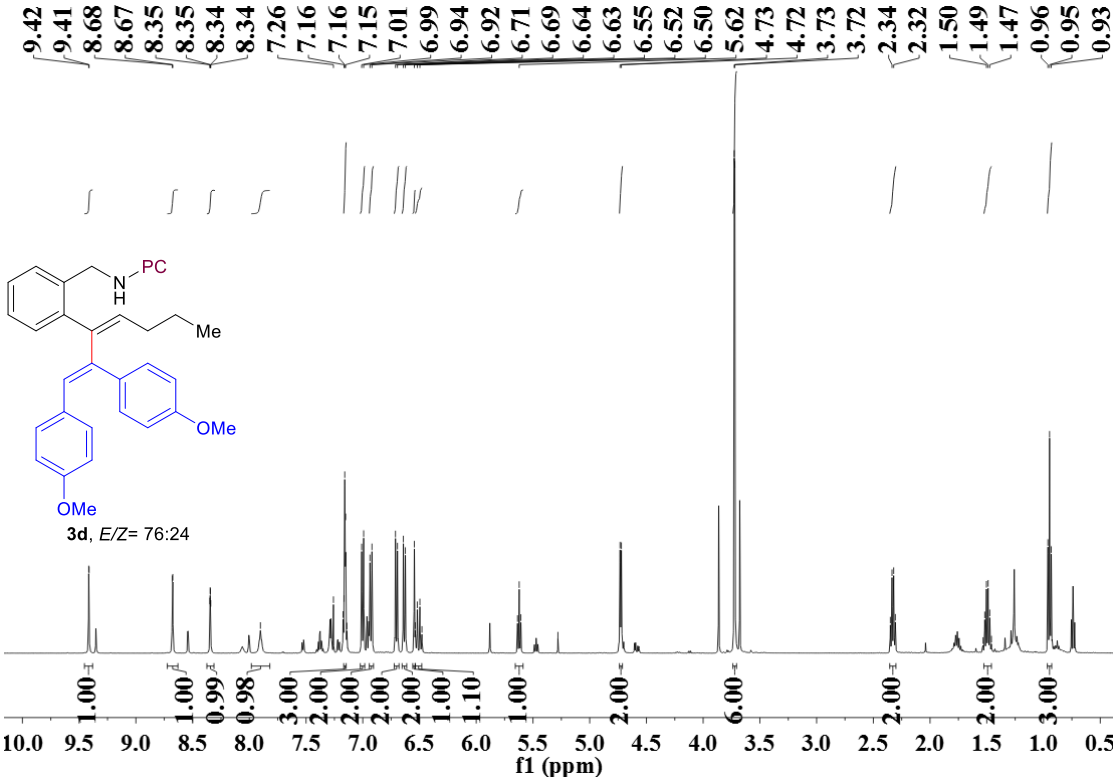
f1 (ppm)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6.50
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OMe
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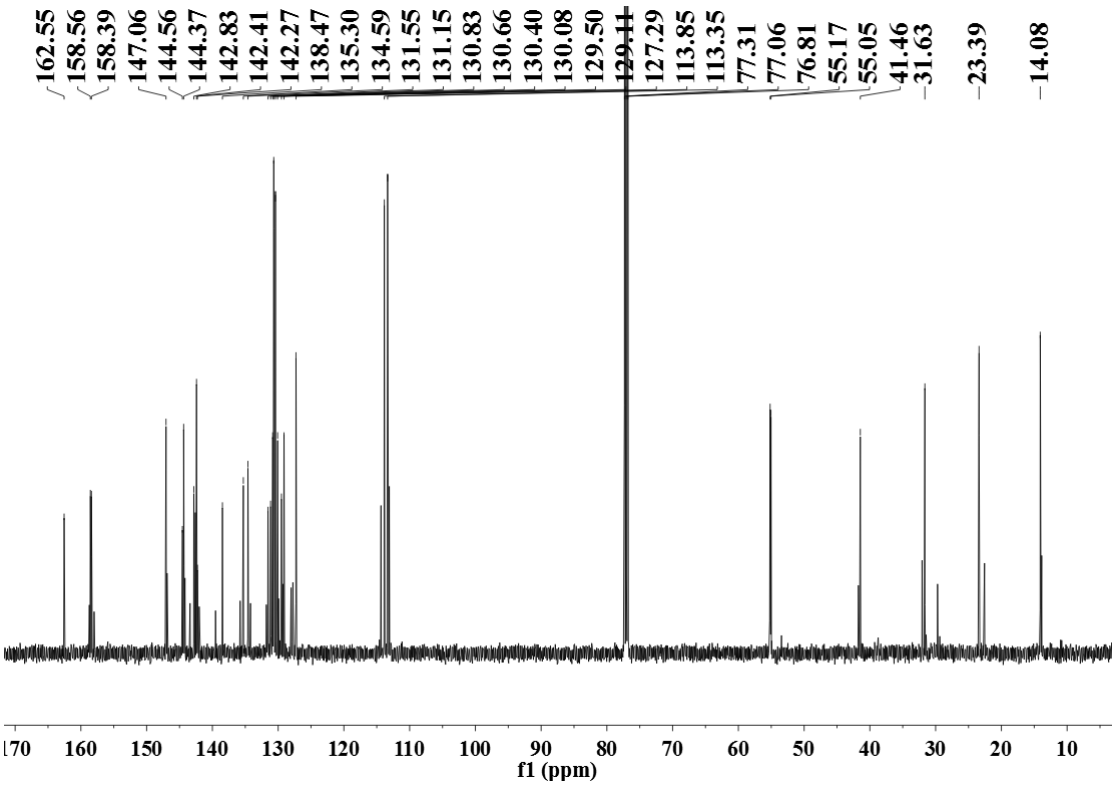
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23.39
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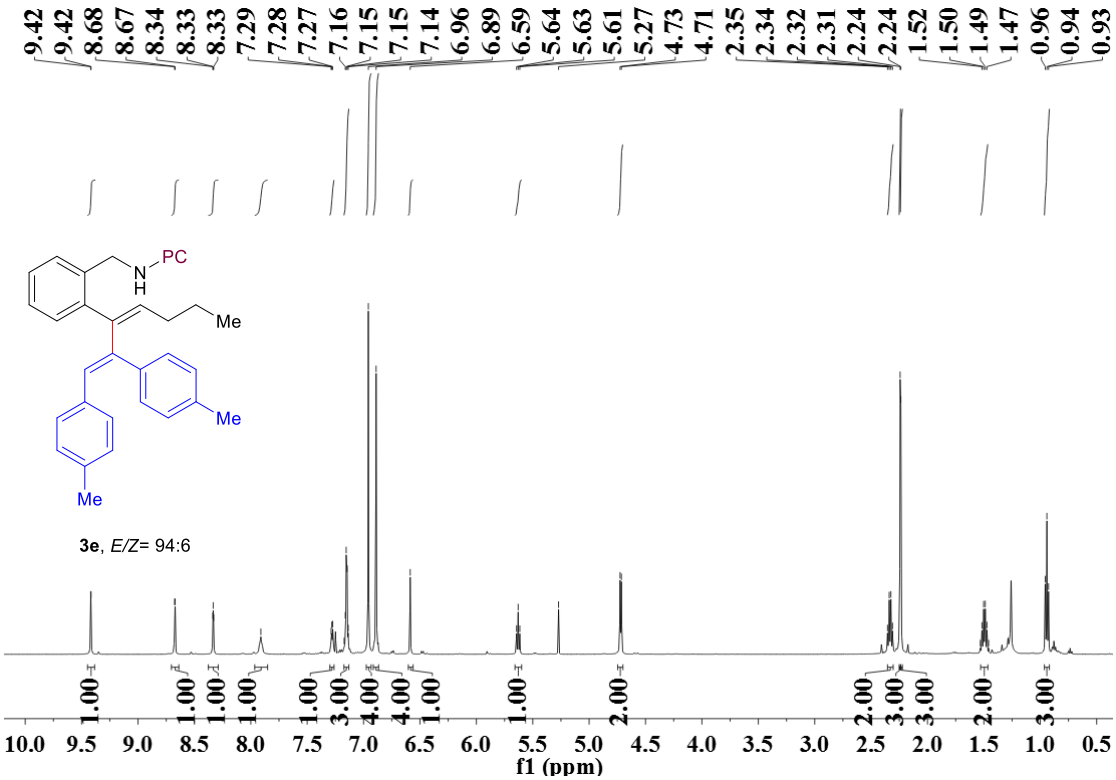
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Me
Me
3e, E/Z= 94:6
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1.00
1.00
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1.00
3.00
4.00
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3.00
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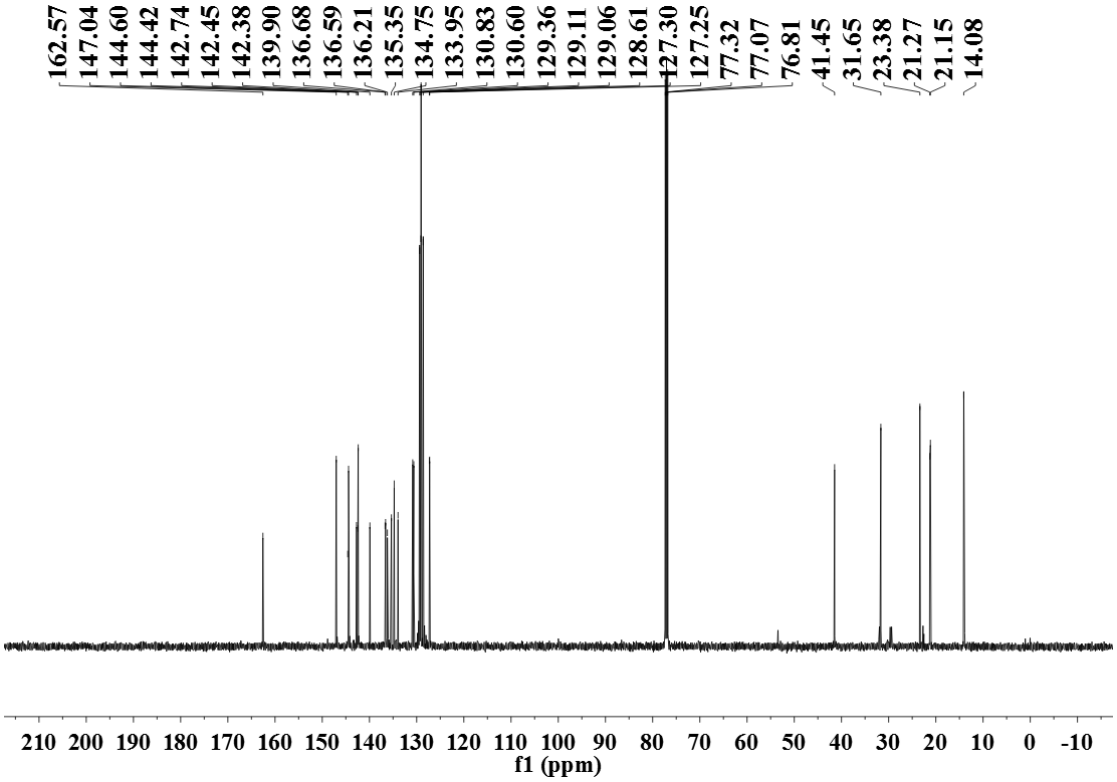
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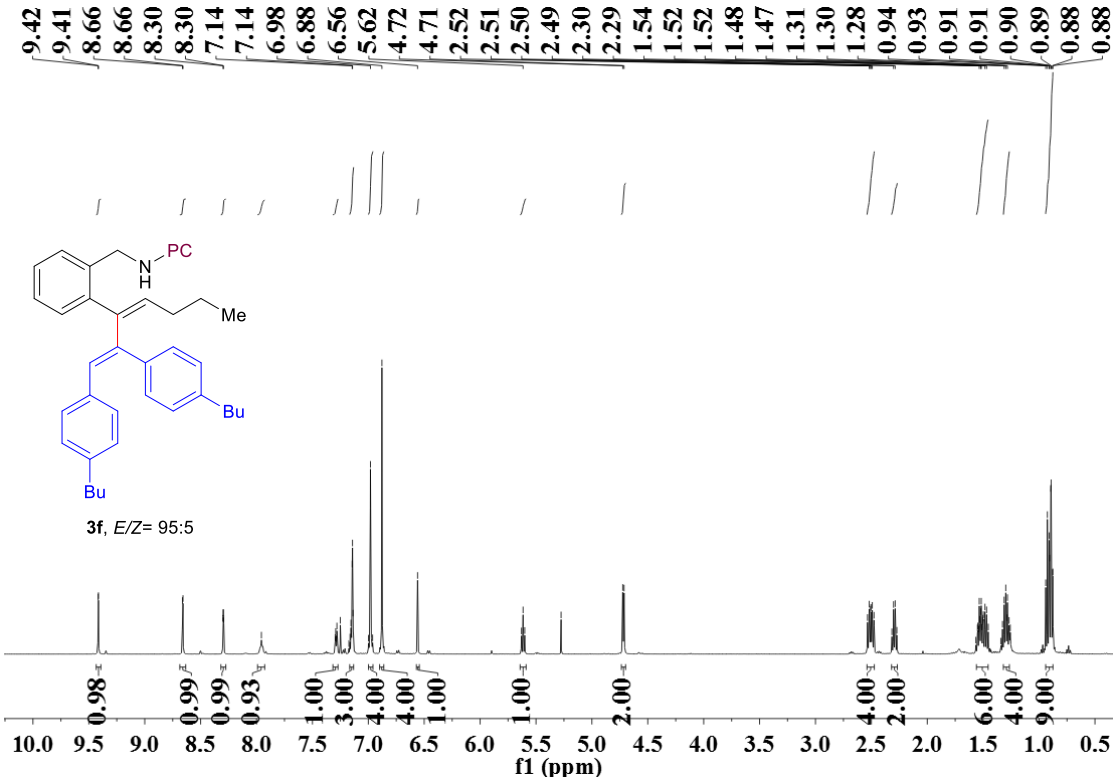
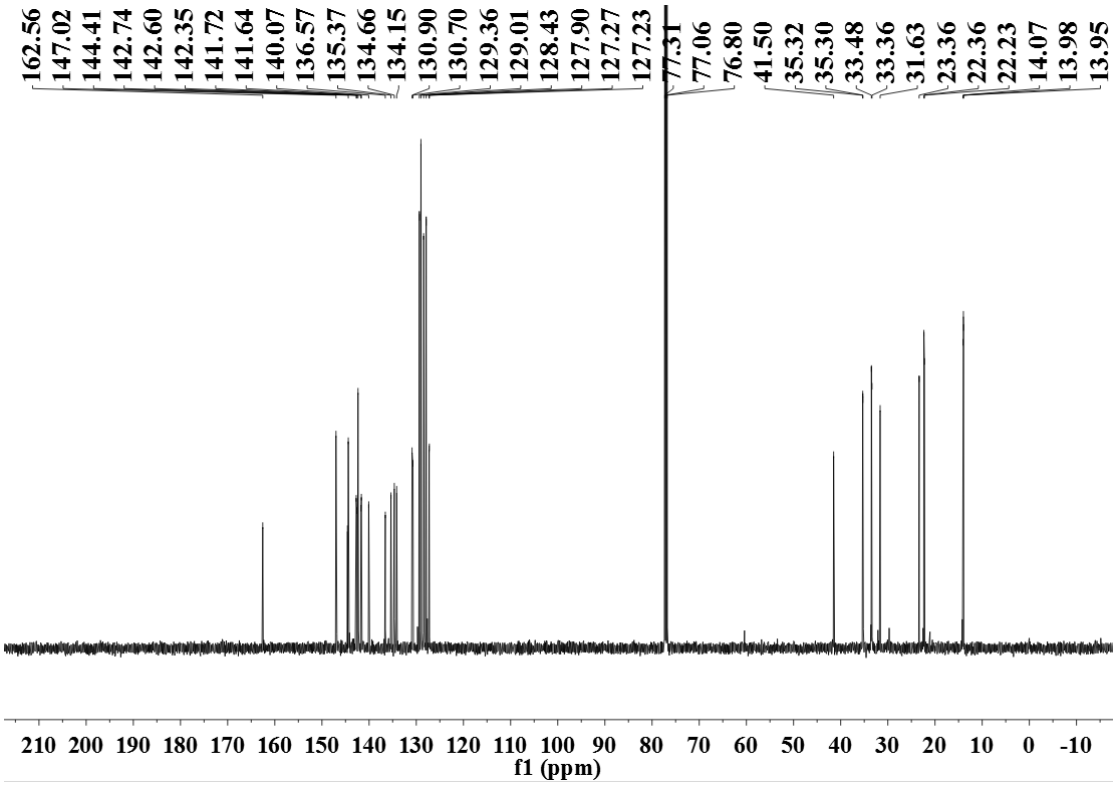
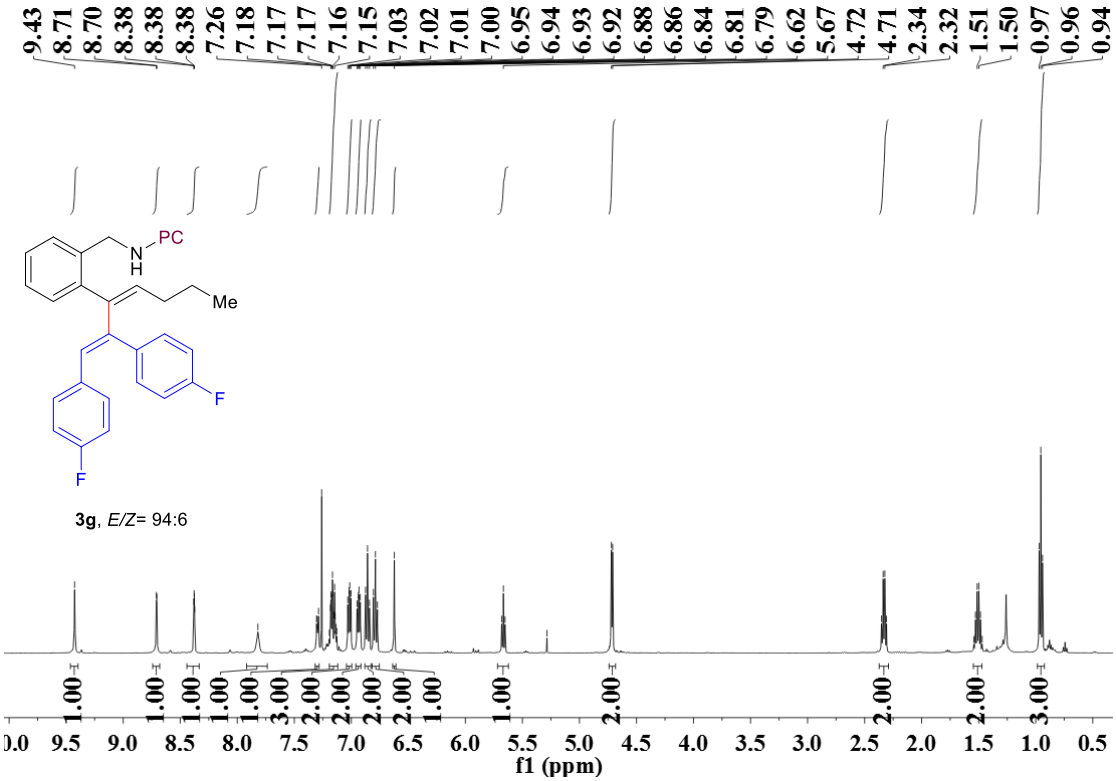
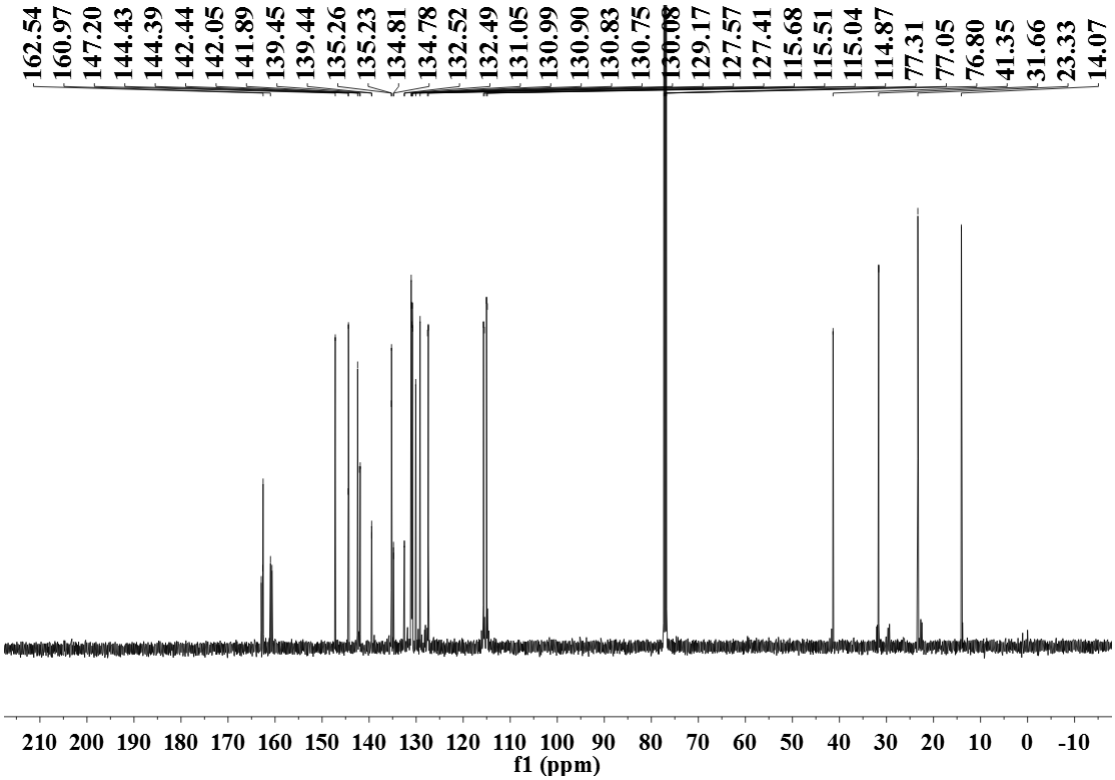
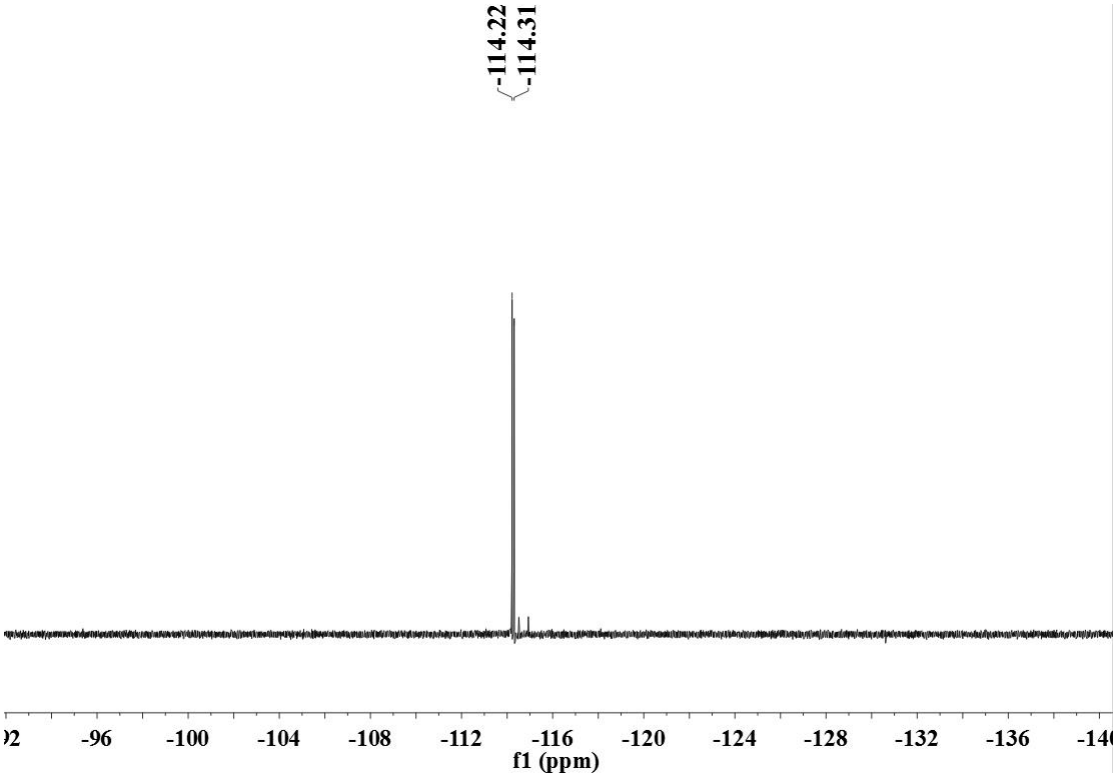
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

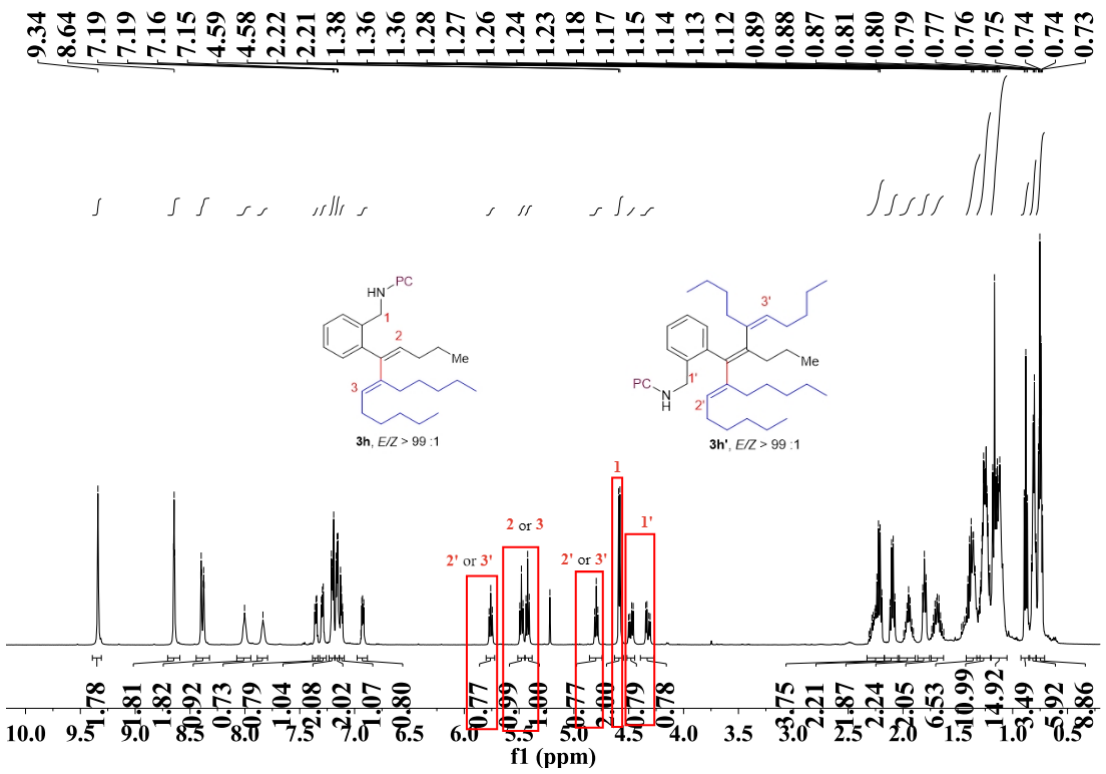

9.42
9.41
8.66
8.66
8.30
8.30
7.14
7.14
6.98
6.88
6.56
5.62
4.72
4.71
2.52
2.51
2.50
2.49
2.30
2.29
1.54
1.52
1.52
1.48
1.47
1.31
1.30
1.28
0.94
0.93
0.91
0.91
0.90
0.89
0.88
0.88
PC
N
H
Me
Bu
Bu
3f, E/Z= 95:5
0.98
0.99
0.99
0.93
1.00
3.00
4.00
4.00
1.00
1.00
2.00
4.00
2.00
6.00
4.00
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

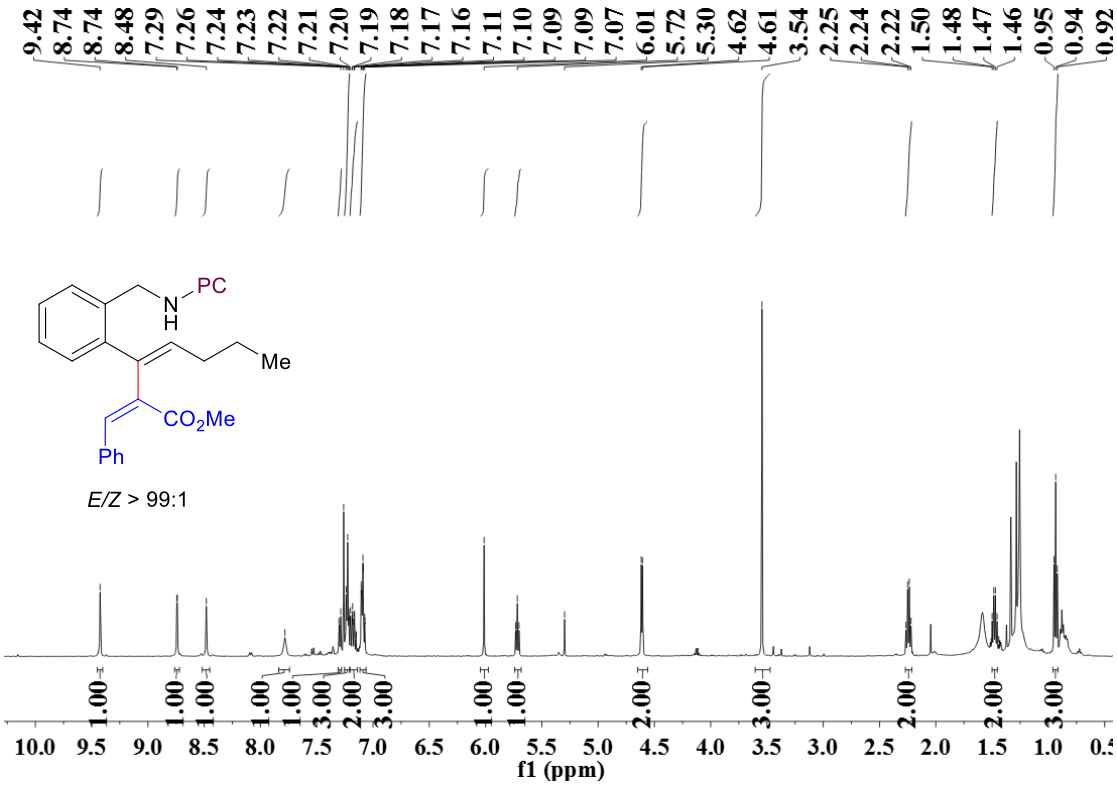

162.56
147.02
144.41
142.74
142.60
142.35
141.72
141.64
140.07
136.57
135.37
134.66
134.15
130.90
130.70
129.36
129.01
128.43
127.90
127.27
127.23
77.31
77.06
76.80
41.50
35.32
35.30
33.48
33.36
31.63
23.36
22.36
22.23
14.07
13.98
13.95
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

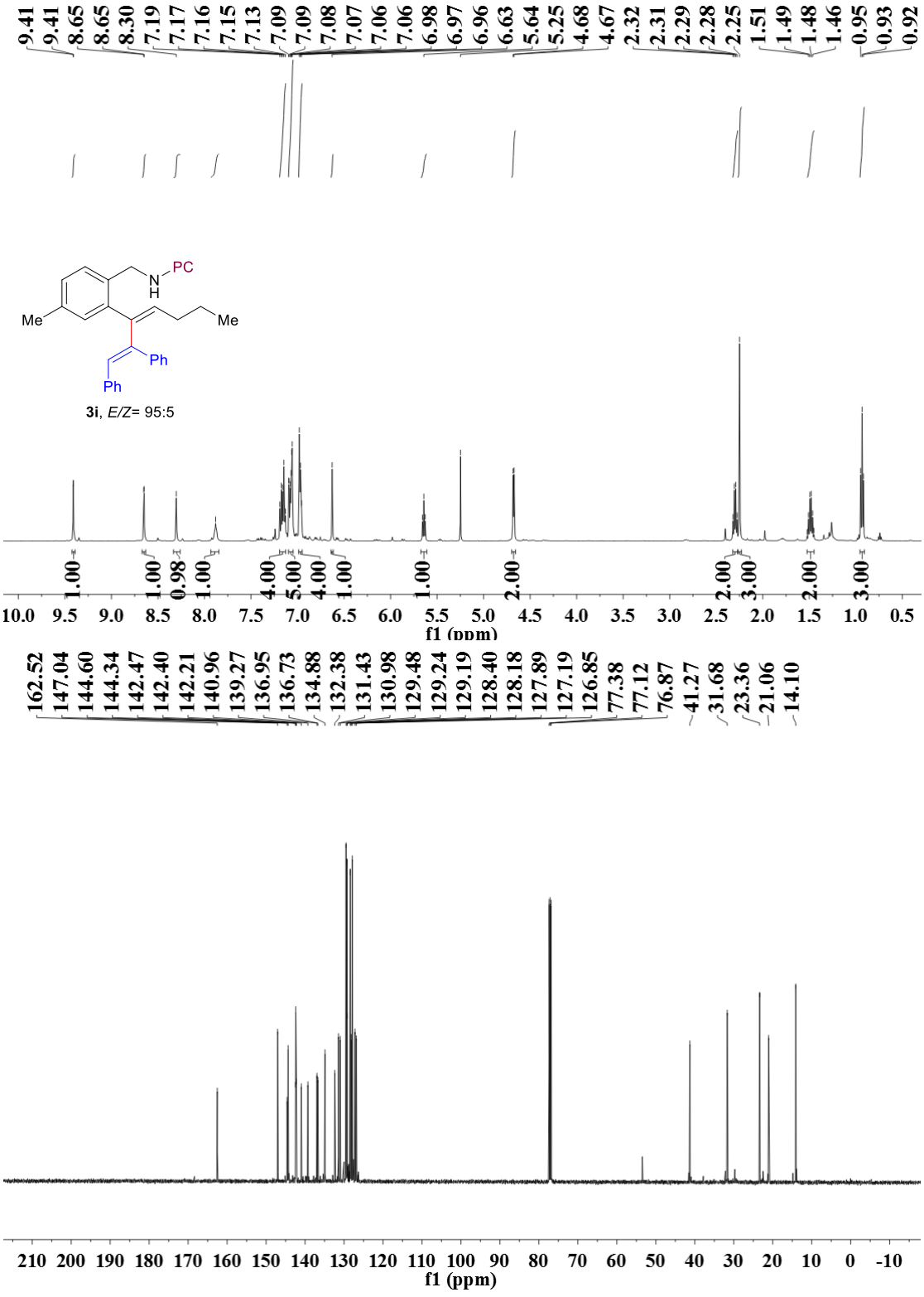

9.43
8.71
8.70
8.38
8.38
8.38
7.26
7.18
7.17
7.17
7.16
7.15
7.03
7.02
7.01
7.00
6.95
6.94
6.93
6.92
6.88
6.86
6.84
6.81
6.79
6.62
5.67
4.72
4.71
2.34
2.32
1.51
1.50
0.97
0.96
0.94
PC
N
H
Me
F
F
3g, E/Z= 94:6
1.00
1.00
1.00
1.00
1.00
3.00
2.00
2.00
2.00
2.00
1.00
1.00
2.00
2.00
2.00
3.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

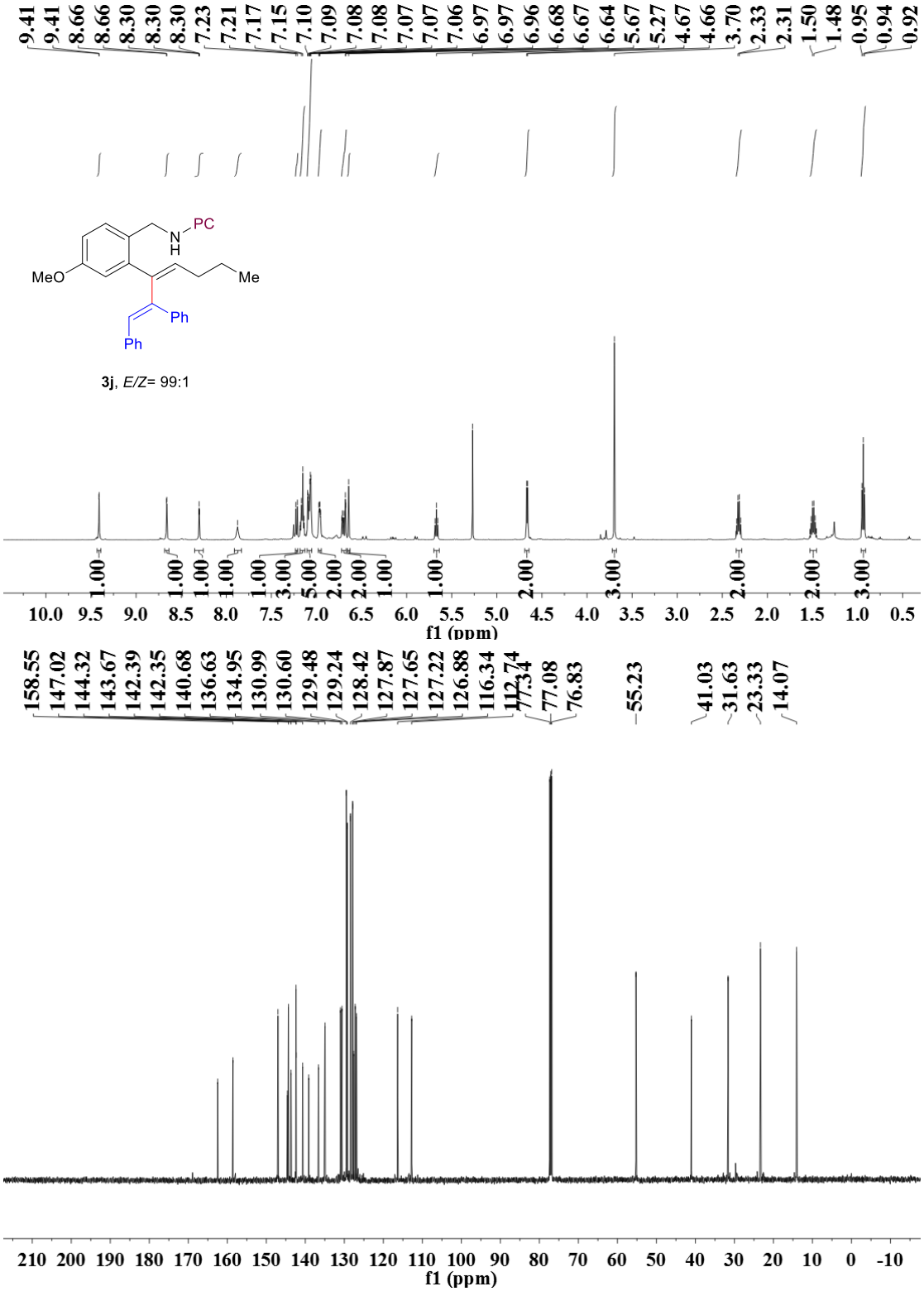

162.54
160.97
147.20
144.43
144.39
142.44
142.05
141.89
139.45
139.44
135.26
135.23
134.81
134.78
132.52
132.49
131.05
130.99
130.90
130.83
130.75
130.08
129.17
127.57
127.41
115.68
115.51
115.04
114.87
77.31
77.05
76.80
41.35
31.66
23.33
14.07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

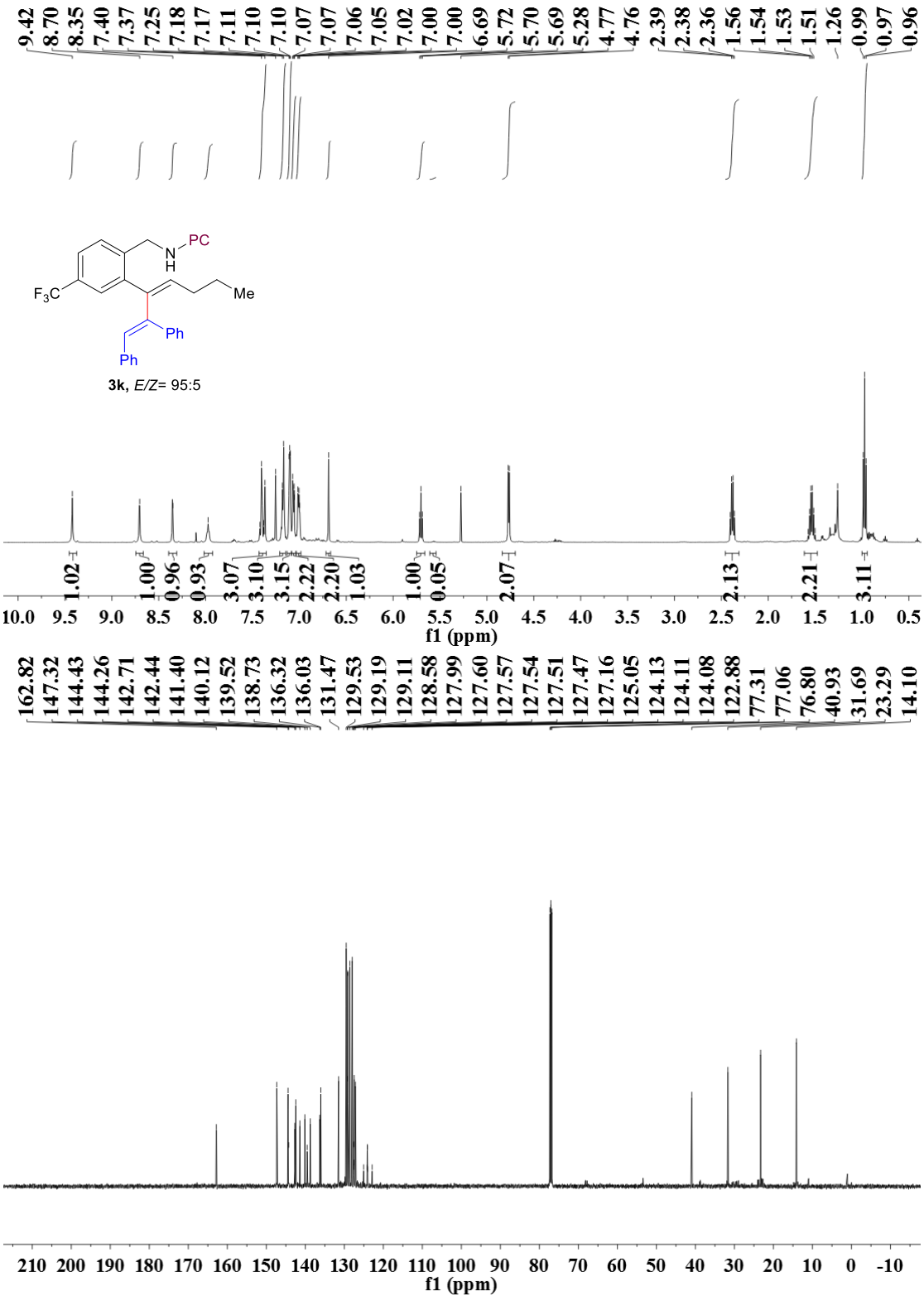

-114.22
-114.31
-96 -100 -104 -108 -112 -116 -120 -124 -128 -132 -136
f1 (ppm)

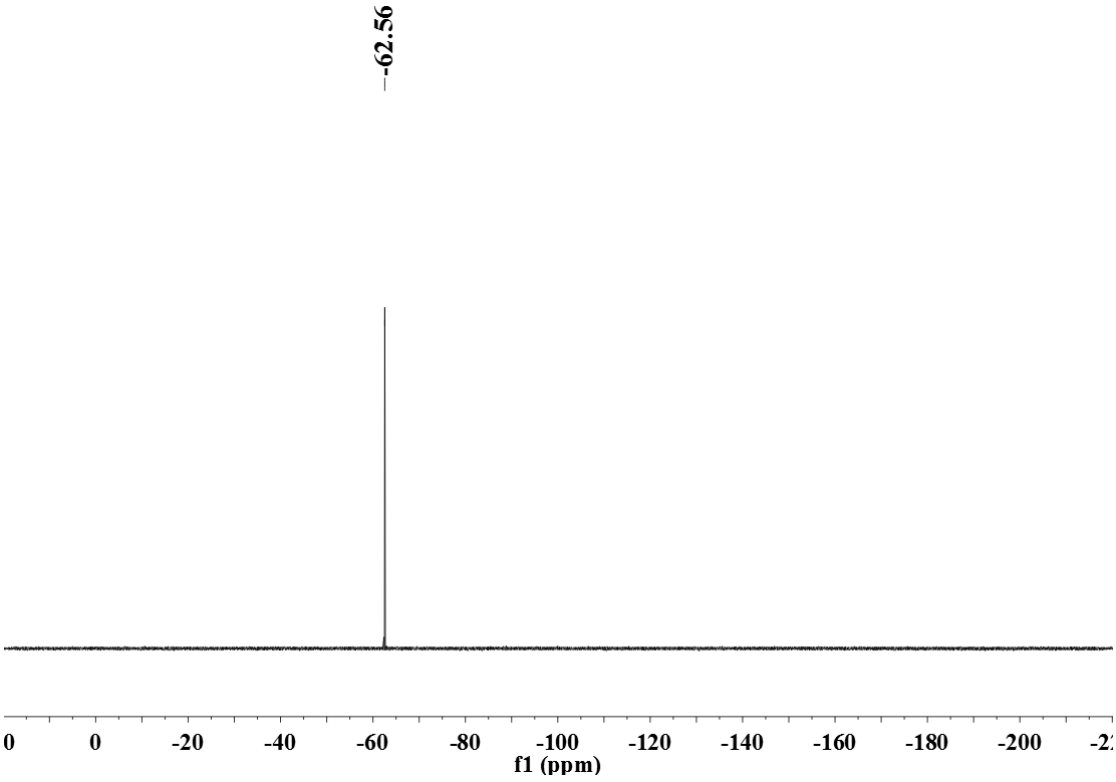

HN
PC
1
2
3
Me
3h, E/Z > 99 :1
PC
N
H
1'
2'
3'
Me
3h', E/Z > 99 :1
2' or 3'
2 or 3
2' or 3'
1
1'
f1 (ppm)

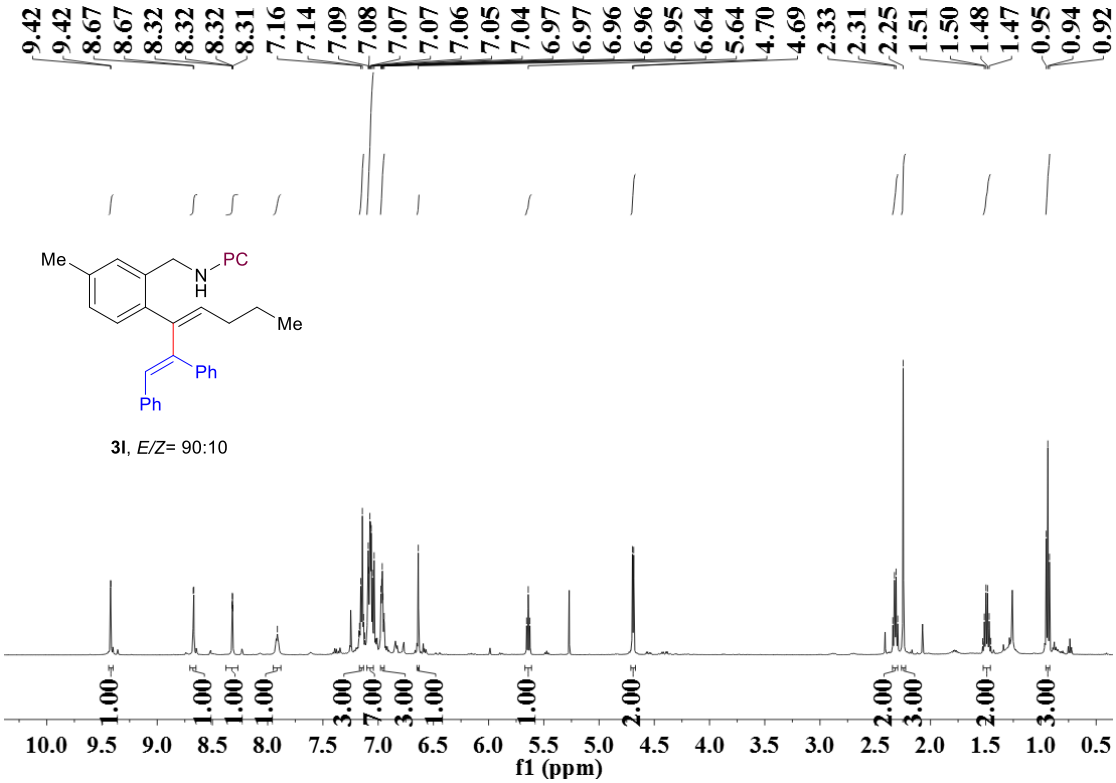

N
H
PC
Me
CO2Me
Ph
E/Z > 99:1
f1 (ppm)


9.41 9.41 8.65 8.65 8.30 7.19 7.17 7.16 7.15 7.13 7.09 7.09 7.08 7.07 7.06 7.06 6.98 6.97 6.96 6.63 5.64 5.25 4.68 4.67 2.32 2.31 2.29 2.28 2.25 1.51 1.49 1.48 1.46 0.95 0.93 0.92
PC
N
H
Me
Me
Ph
Ph
3i, E/Z= 95:5
1.00 1.00 0.98 1.00 4.00 5.00 4.00 1.00 1.00 2.00 2.00 3.00 2.00 3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
162.52 147.04 144.60 144.34 142.47 142.40 142.21 140.96 139.27 136.95 136.73 134.88 132.38 131.43 130.98 129.48 129.24 129.19 128.40 128.18 127.89 127.19 126.85 77.38 77.12 76.87 41.27 31.68 23.36 21.06 14.10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

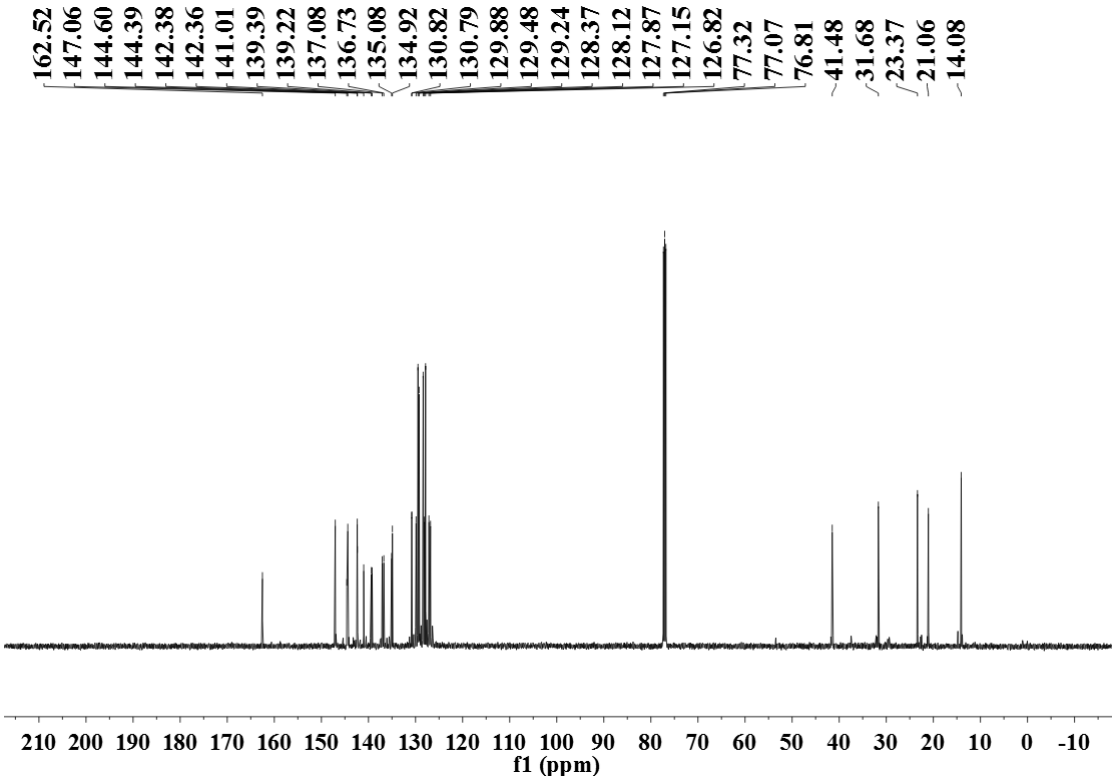

9.41 9.41 8.66 8.66 8.30 8.30 8.30 7.23 7.21 7.17 7.15 7.10 7.09 7.08 7.08 7.07 7.07 7.06 6.97 6.97 6.96 6.68 6.67 6.64 5.67 5.27 4.67 4.66 3.70 2.33 2.31 1.50 1.48 0.95 0.94 0.92
PC
N
H
MeO
Me
Ph
Ph
3j, E/Z= 99:1
1.00 1.00 1.00 1.00 3.00 5.00 2.00 2.00 1.00 1.00 2.00 3.00 2.00 2.00 3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
158.55 147.02 144.32 143.67 142.39 142.35 140.68 136.63 134.95 130.99 130.60 129.48 129.24 128.42 127.87 127.65 127.22 126.88 116.34 112.74 77.34 77.08 76.83 55.23 41.03 31.63 23.33 14.07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

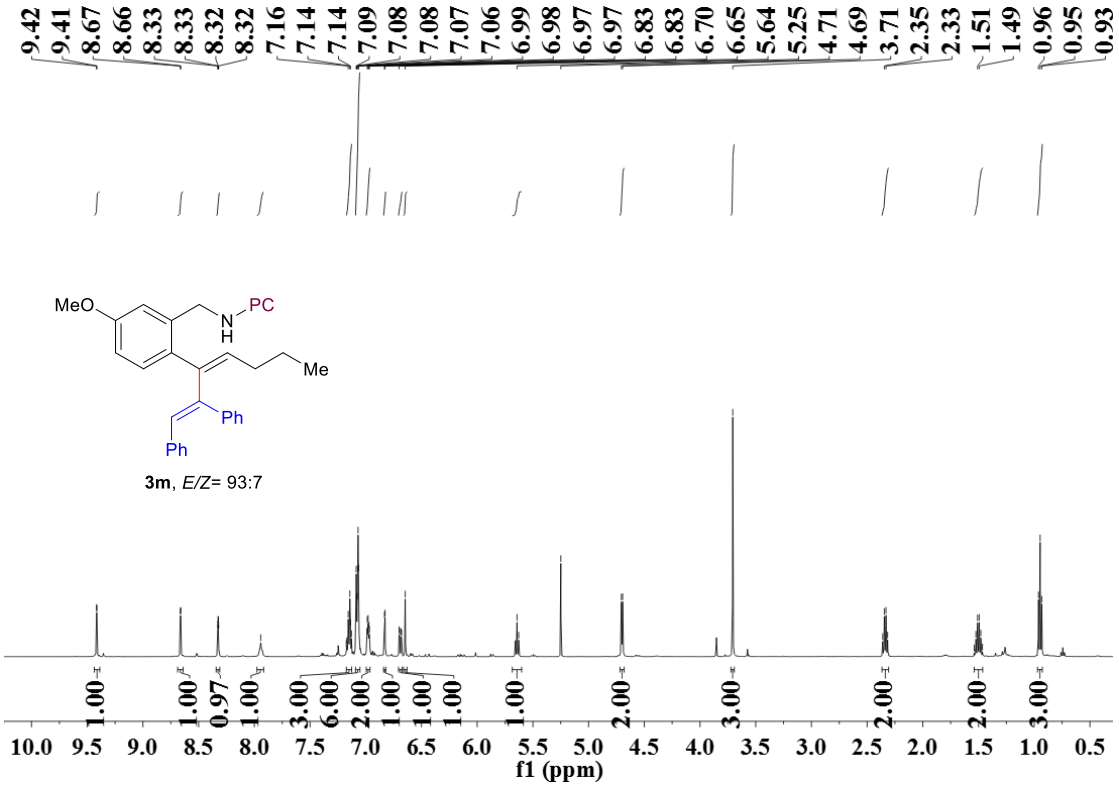

9.42 8.70 8.35 7.40 7.37 7.25 7.18 7.17 7.11 7.10 7.10 7.07 7.07 7.06 7.05 7.02 7.00 7.00 6.69 5.72 5.70 5.69 5.28 4.77 4.76 2.39 2.38 2.36 1.56 1.54 1.53 1.51 1.26 0.99 0.97 0.96
PC
N
H
F3C
Me
Ph
Ph
3k, E/Z= 95:5
1.02 1.00 0.96 0.93 3.07 3.10 3.15 2.22 2.20 1.03 1.00 0.05 2.07 2.13 2.21 3.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
162.82 147.32 144.43 144.26 142.71 142.44 141.40 140.12 139.52 138.73 136.32 136.03 131.47 129.53 129.19 129.11 128.58 127.99 127.60 127.57 127.54 127.51 127.47 127.16 125.05 124.13 124.11 124.08 122.88 77.31 77.06 76.80 40.93 31.69 23.29 14.10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-62.56
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

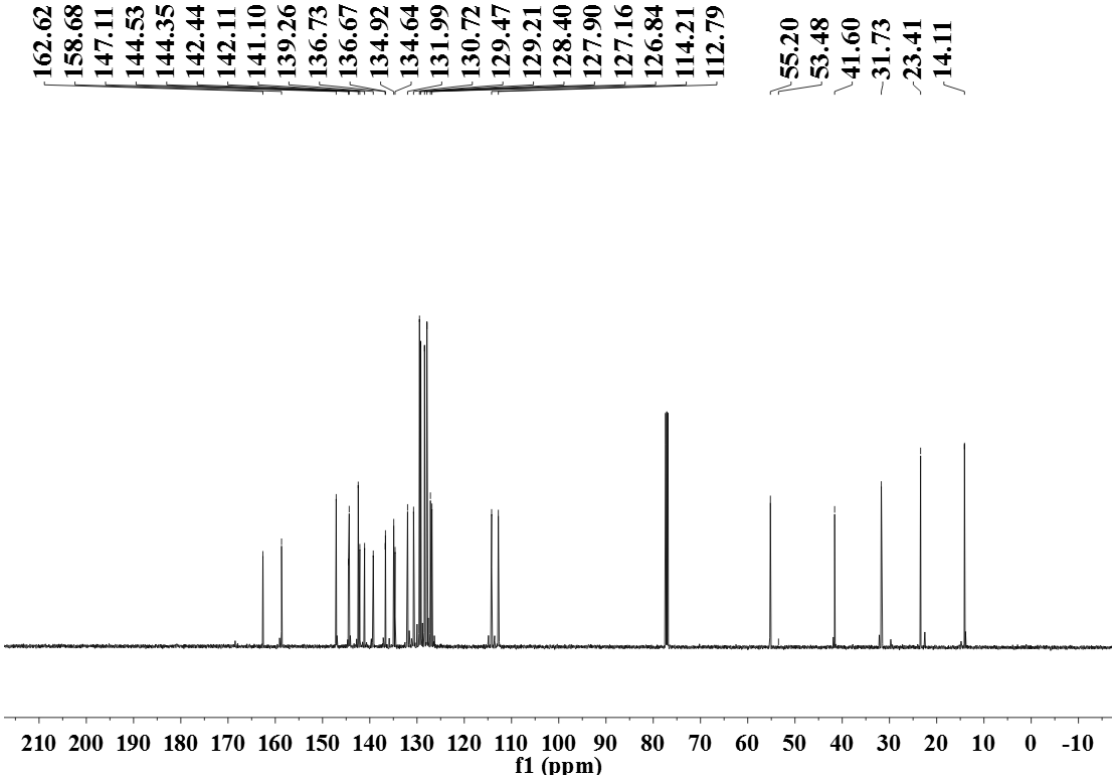

9.42
9.42
8.67
8.67
8.32
8.32
8.32
8.31
7.16
7.14
7.09
7.08
7.07
7.07
7.06
7.05
7.04
6.97
6.97
6.96
6.96
6.95
6.64
5.64
4.70
4.69
2.33
2.31
2.25
1.51
1.50
1.48
1.47
0.95
0.94
0.92
Me
N
H
PC
Me
Ph
Ph
1.00
1.00
1.00
1.00
3.00
7.00
3.00
1.00
1.00
2.00
2.00
3.00
2.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

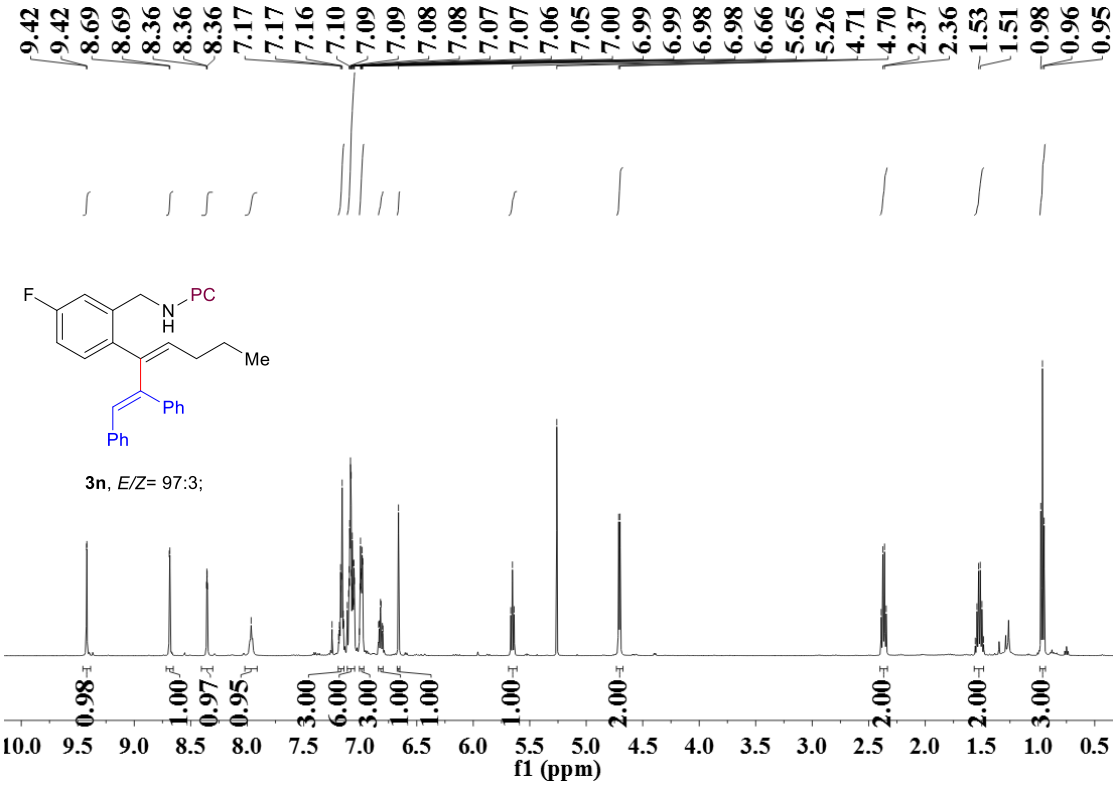
3l, *E*/*Z*= 90:10

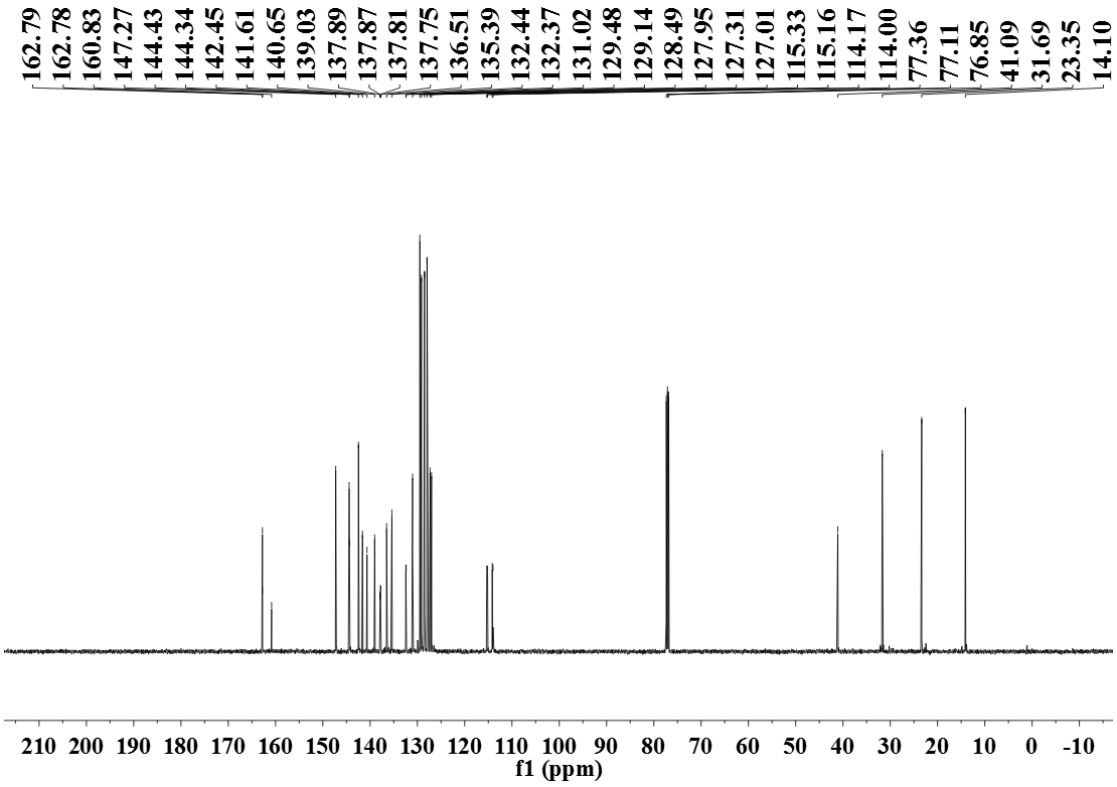

162.52
147.06
144.60
144.39
142.38
142.36
141.01
139.39
139.22
137.08
136.73
135.08
134.92
130.82
130.79
129.88
129.48
129.24
128.37
128.12
127.87
127.15
126.82
77.32
77.07
76.81
41.48
31.68
23.37
21.06
14.08
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

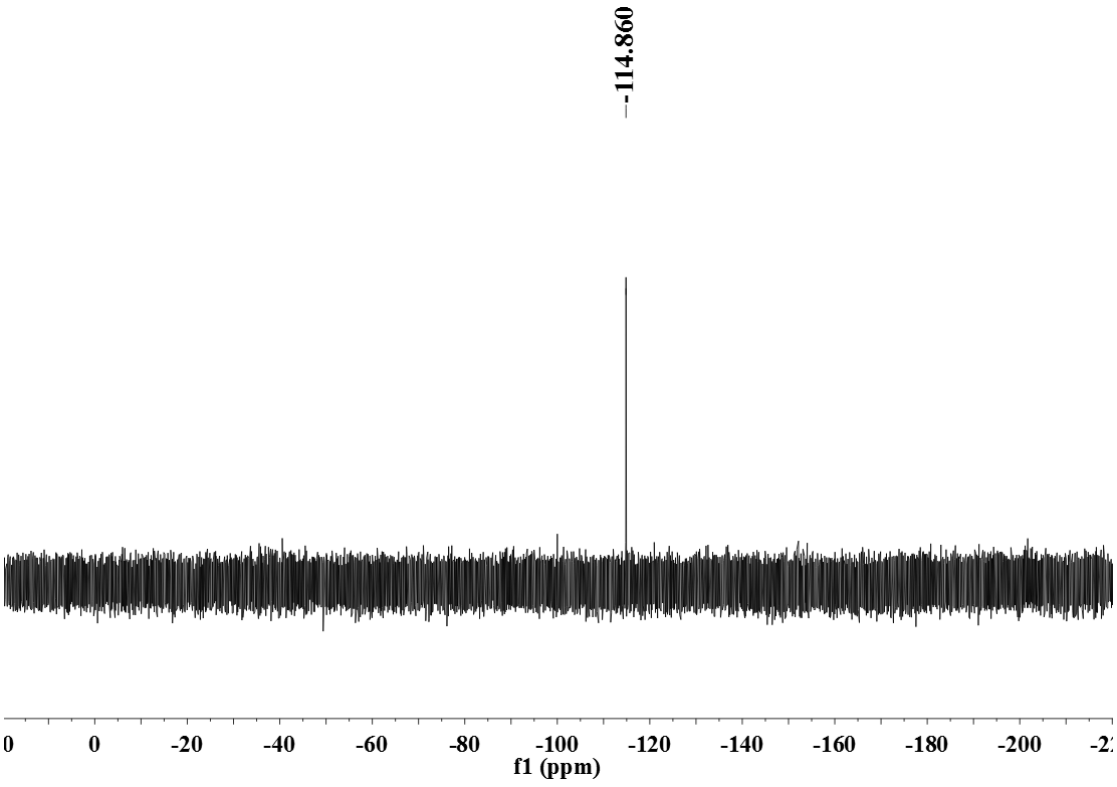

9.42
9.41
8.67
8.66
8.33
8.33
8.32
8.32
7.16
7.14
7.14
7.09
7.08
7.08
7.07
7.06
6.99
6.98
6.97
6.97
6.83
6.83
6.70
6.65
5.64
5.25
4.71
4.69
3.71
2.35
2.33
1.51
1.49
0.96
0.95
0.93
MeO
N
H
PC
Me
Ph
Ph
1.00
1.00
0.97
1.00
3.00
6.00
2.00
1.00
1.00
1.00
1.00
2.00
3.00
2.00
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

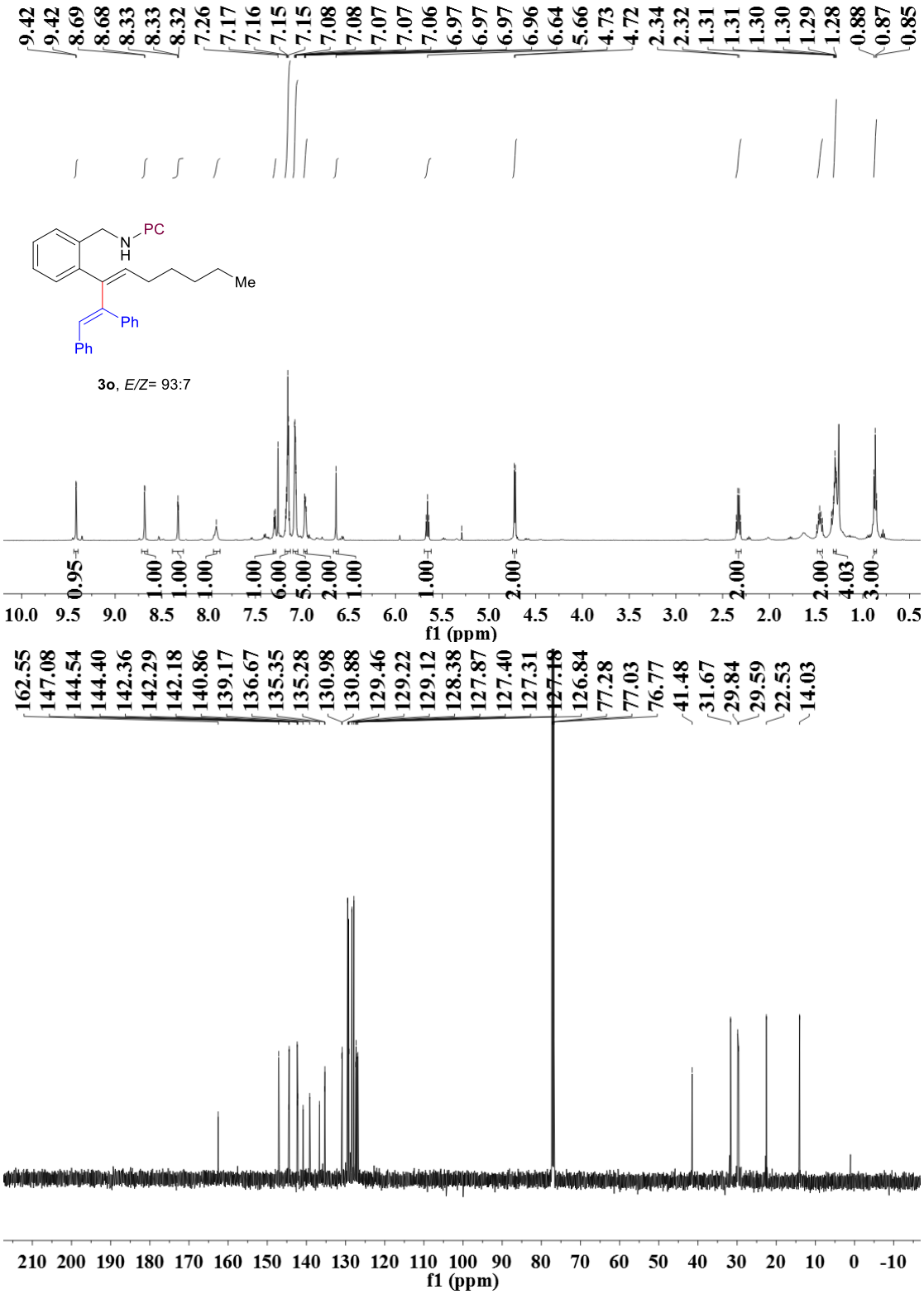
3m, *E*/*Z*= 93:7

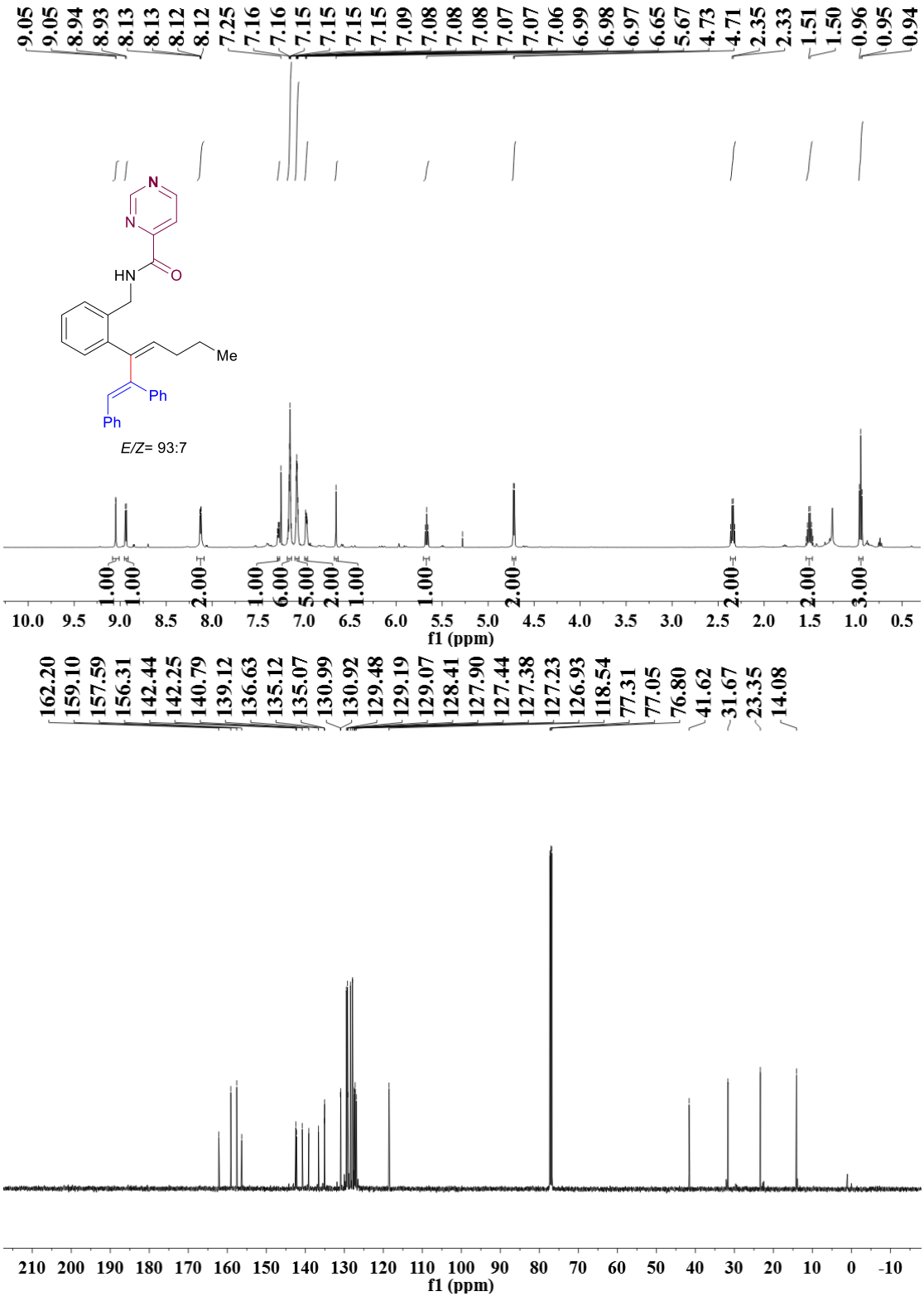

162.62
158.68
147.11
144.53
144.35
142.44
142.11
141.10
139.26
136.73
136.67
134.92
134.64
131.99
130.72
129.47
129.21
128.40
127.90
127.16
126.84
114.21
112.79
55.20
53.48
41.60
31.73
23.41
14.11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

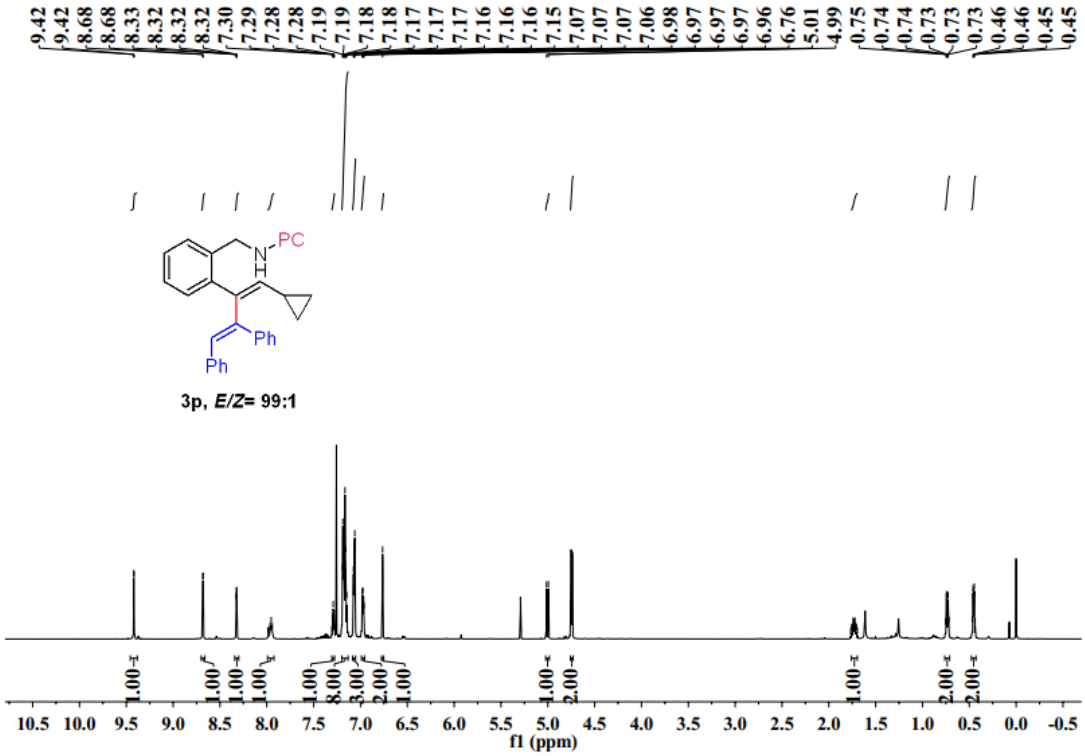

9.42
9.42
8.69
8.69
8.36
8.36
8.36
7.17
7.17
7.16
7.10
7.09
7.09
7.08
7.08
7.07
7.07
7.06
7.05
7.00
6.99
6.99
6.98
6.98
6.66
5.65
5.26
4.71
4.70
2.37
2.36
1.53
1.51
0.98
0.96
0.95
F
N
H
PC
Me
Ph
Ph
3n, E/Z= 97:3;
0.98
1.00
0.97
0.95
3.00
6.00
3.00
1.00
1.00
1.00
2.00
2.00
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

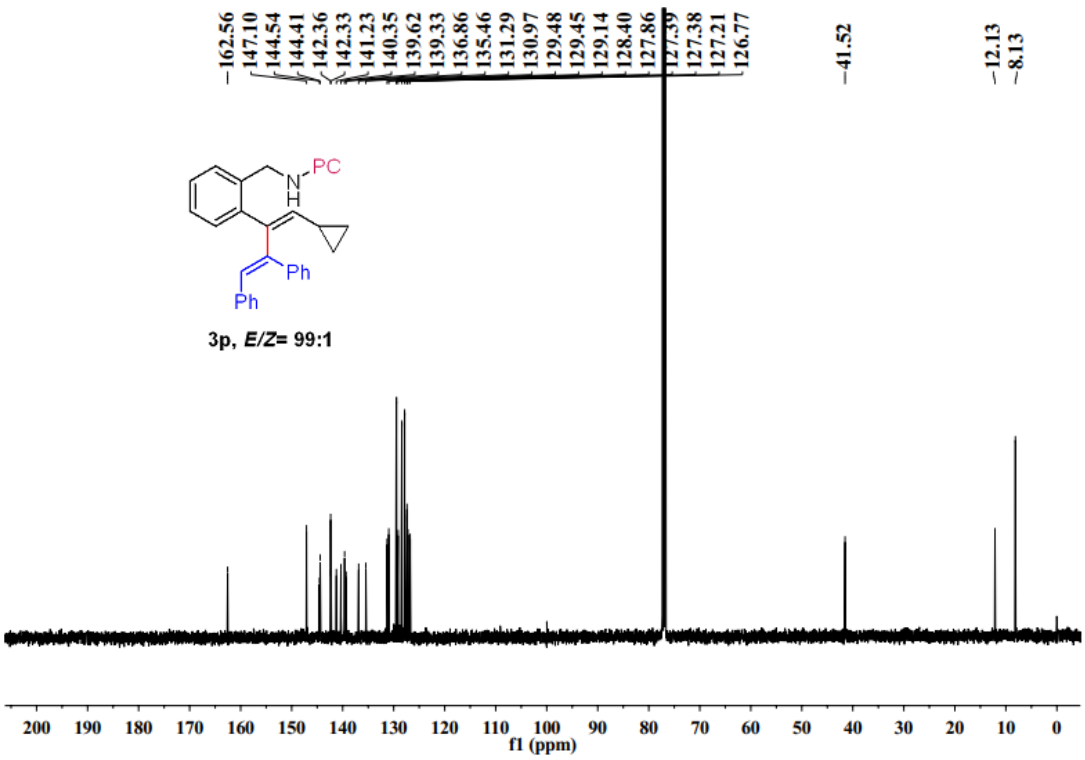

162.79
162.78
160.83
147.27
144.43
144.34
142.45
141.61
140.65
139.03
137.89
137.87
137.81
137.75
136.51
135.39
132.44
132.37
131.02
129.48
129.14
128.49
127.95
127.31
127.01
115.33
115.16
114.17
114.00
77.36
77.11
76.85
41.09
31.69
23.35
14.10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-114.860
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

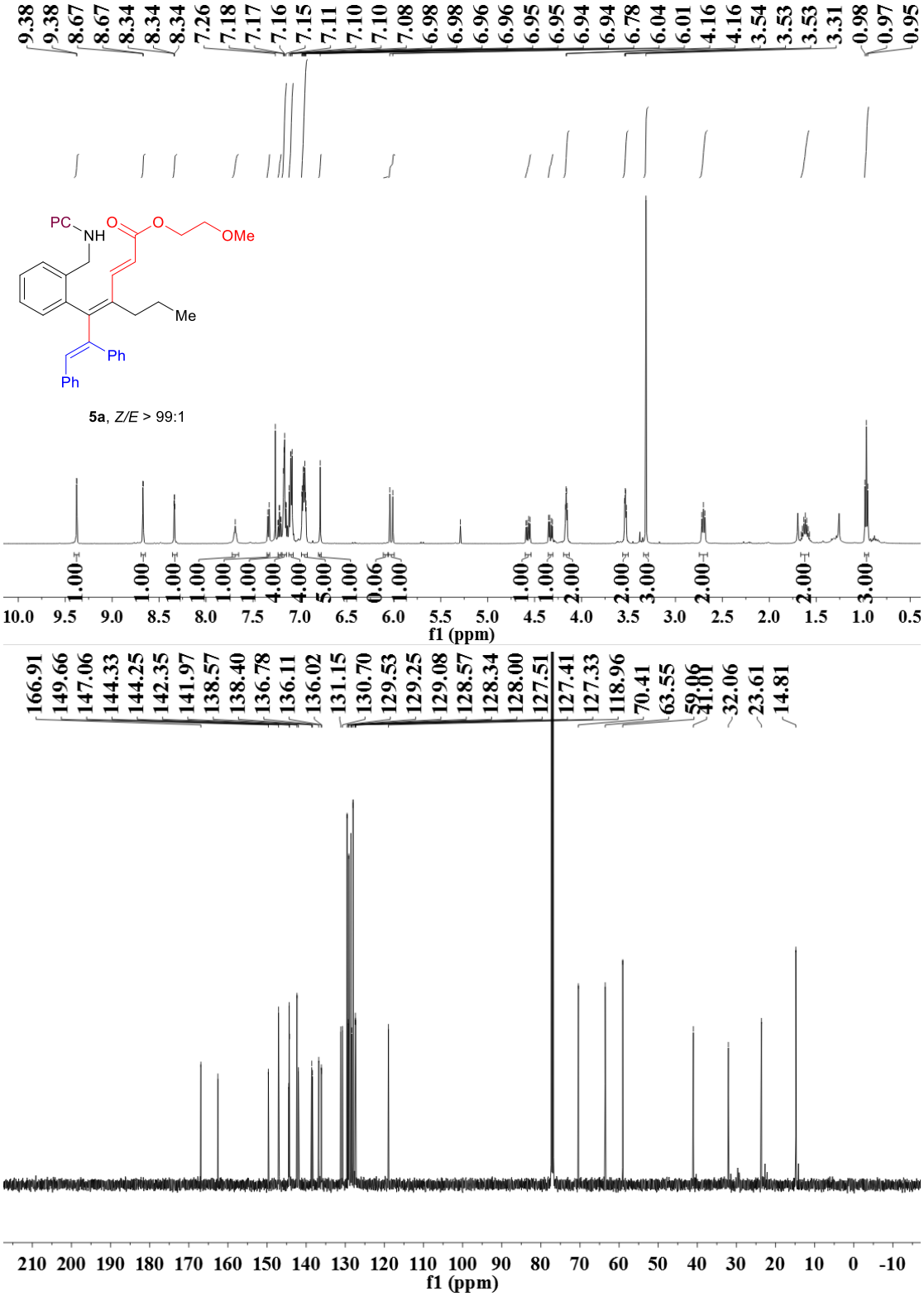

9.42 9.42 8.69 8.68 8.33 8.33 8.32 7.26 7.17 7.16 7.15 7.15 7.08 7.08 7.07 7.07 7.06 6.97 6.97 6.97 6.96 6.64 5.66 4.73 4.72 2.34 2.32 1.31 1.31 1.30 1.30 1.29 1.28 0.88 0.87 0.85
PC
N
H
Me
Ph
Ph
3o, E/Z= 93:7
0.95 1.00 1.00 1.00 1.00 6.00 5.00 2.00 1.00 1.00 2.00 2.00 2.00 4.03 3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
162.55 147.08 144.54 144.40 142.36 142.29 142.18 140.86 139.17 136.67 135.35 135.28 130.98 130.88 129.46 129.22 129.12 128.38 127.87 127.40 127.31 127.18 126.84 77.28 77.03 76.77 41.48 31.67 29.84 29.59 22.53 14.03
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

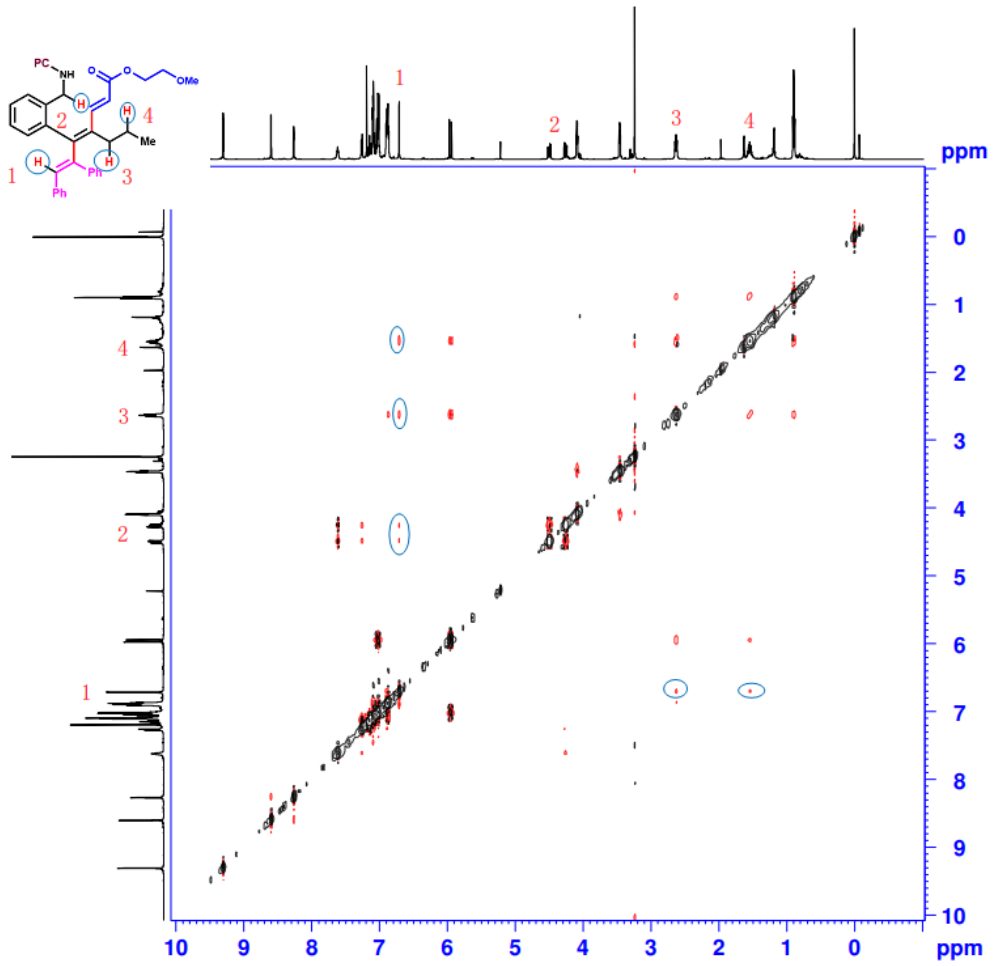

9.05 9.05 8.94 8.93 8.13 8.13 8.12 8.12 7.25 7.16 7.16 7.15 7.15 7.15 7.15 7.09 7.08 7.08 7.08 7.07 7.07 7.06 6.99 6.98 6.97 6.65 5.67 4.73 4.71 2.35 2.33 1.51 1.50 0.96 0.95 0.94
N
N
HN
O
Me
Ph
Ph
E/Z= 93:7
1.00 1.00 2.00 1.00 6.00 5.00 2.00 1.00 1.00 2.00 2.00 2.00 3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
162.20 159.10 157.59 156.31 142.44 142.25 140.79 139.12 136.63 135.12 135.07 130.99 130.92 129.48 129.19 129.07 128.41 127.90 127.44 127.38 127.23 126.93 118.54 77.31 77.05 76.80 41.62 31.67 23.35 14.08
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

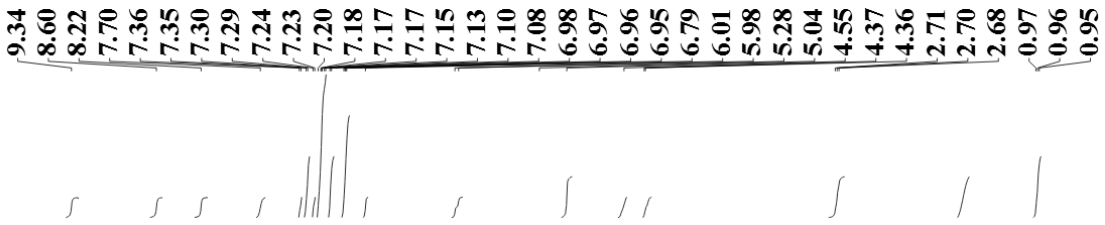

9.42 9.42 8.68 8.68 8.33 8.32 8.32 8.32 7.30 7.29 7.28 7.28 7.19 7.19 7.18 7.18 7.17 7.17 7.17 7.16 7.16 7.16 7.15 7.07 7.07 7.07 7.06 6.98 6.97 6.97 6.97 6.96 6.76 5.01 4.99 0.75 0.74 0.74 0.73 0.73 0.73 0.46 0.46 0.45 0.45
PC
N
H
Ph
Ph
3p, E/Z= 99:1
1.00 1.00 1.00 1.00 1.00 8.00 3.00 2.00 1.00 1.00 2.00 1.00 2.00 2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

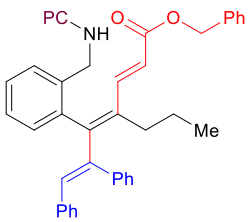

162.56 147.10 144.54 144.41 142.36 142.33 141.23 140.35 139.62 139.33 136.86 135.46 131.29 130.97 129.48 129.45 129.14 128.40 127.86 127.39 127.38 127.21 126.77 41.52 12.13 8.13
PC
N
H
Ph
Ph
3p, E/Z= 99:1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

8.2 NMR Spectra of the Products 5

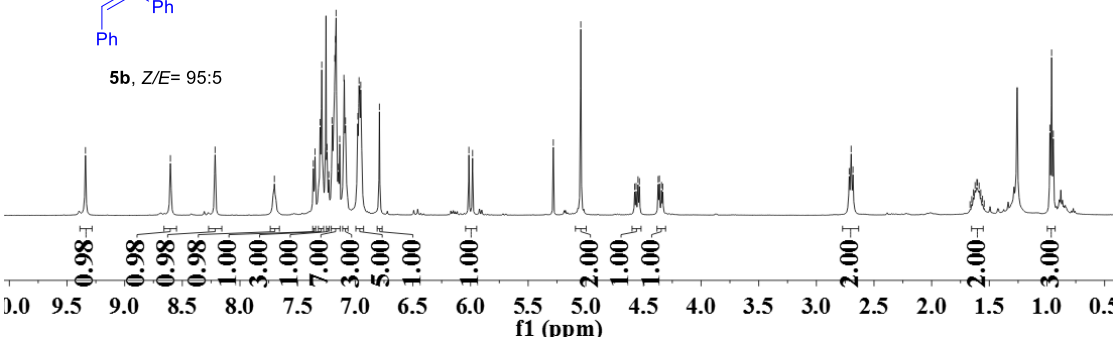


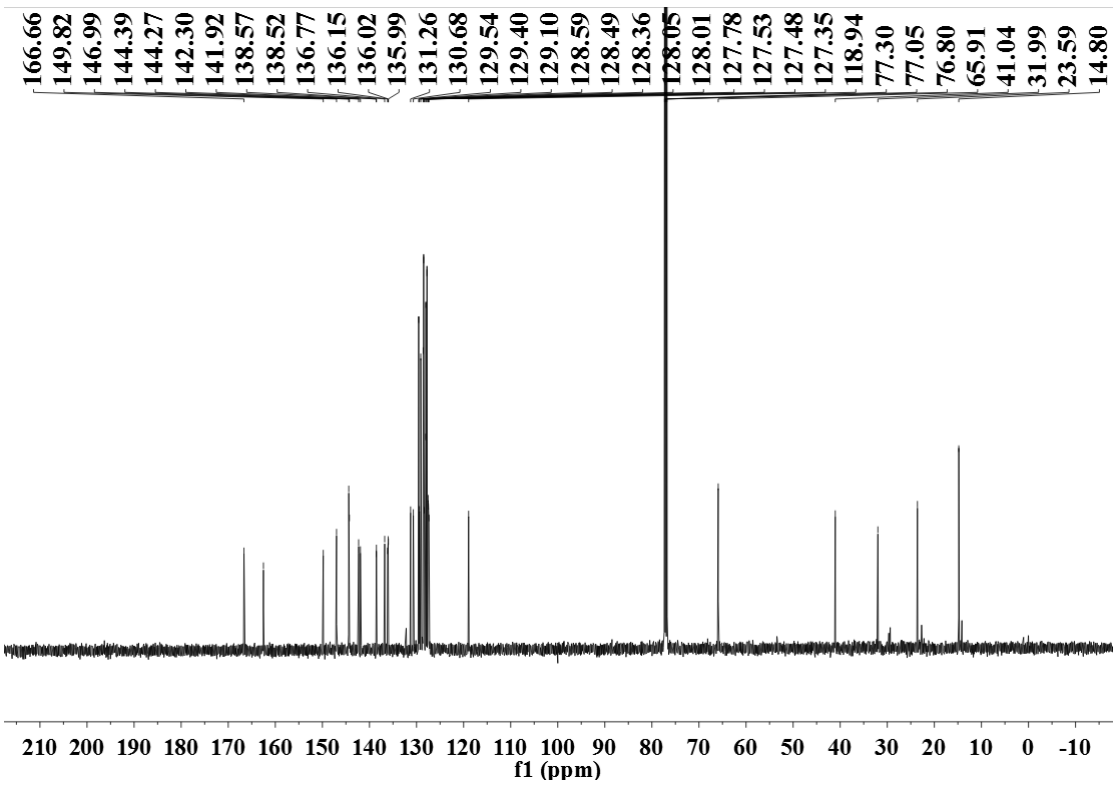

PC
NH
OMe
Ph
Me
ppm

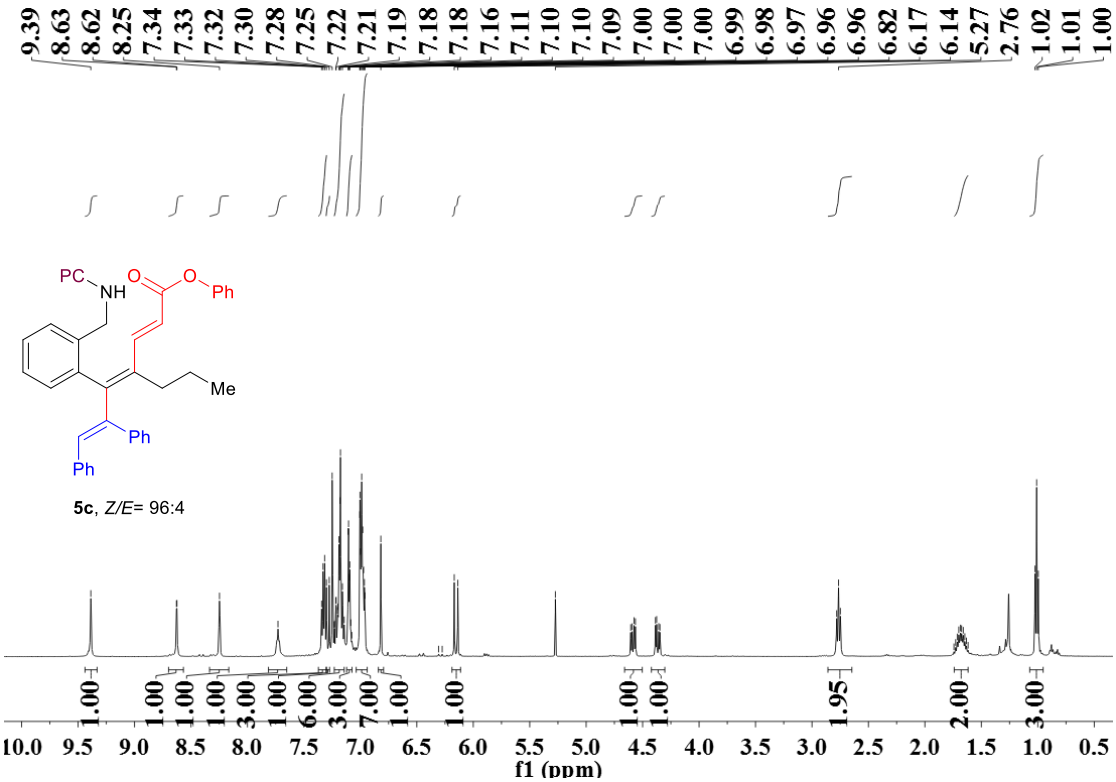

9.34
8.60
8.22
7.70
7.36
7.35
7.30
7.29
7.24
7.23
7.20
7.18
7.17
7.17
7.15
7.13
7.10
7.08
6.98
6.97
6.96
6.95
6.79
6.01
5.98
5.28
5.04
4.55
4.37
4.36
2.71
2.70
2.68
0.97
0.96
0.95

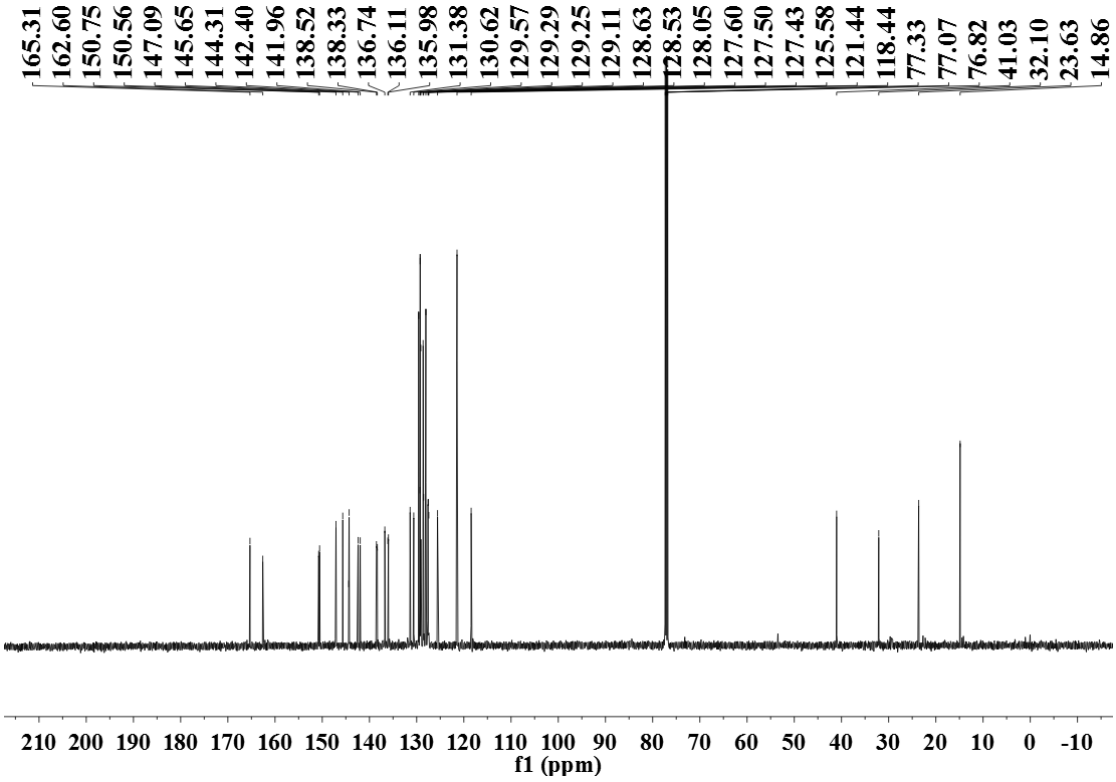

PC
NH
O
O
Ph
Me
Ph
Ph

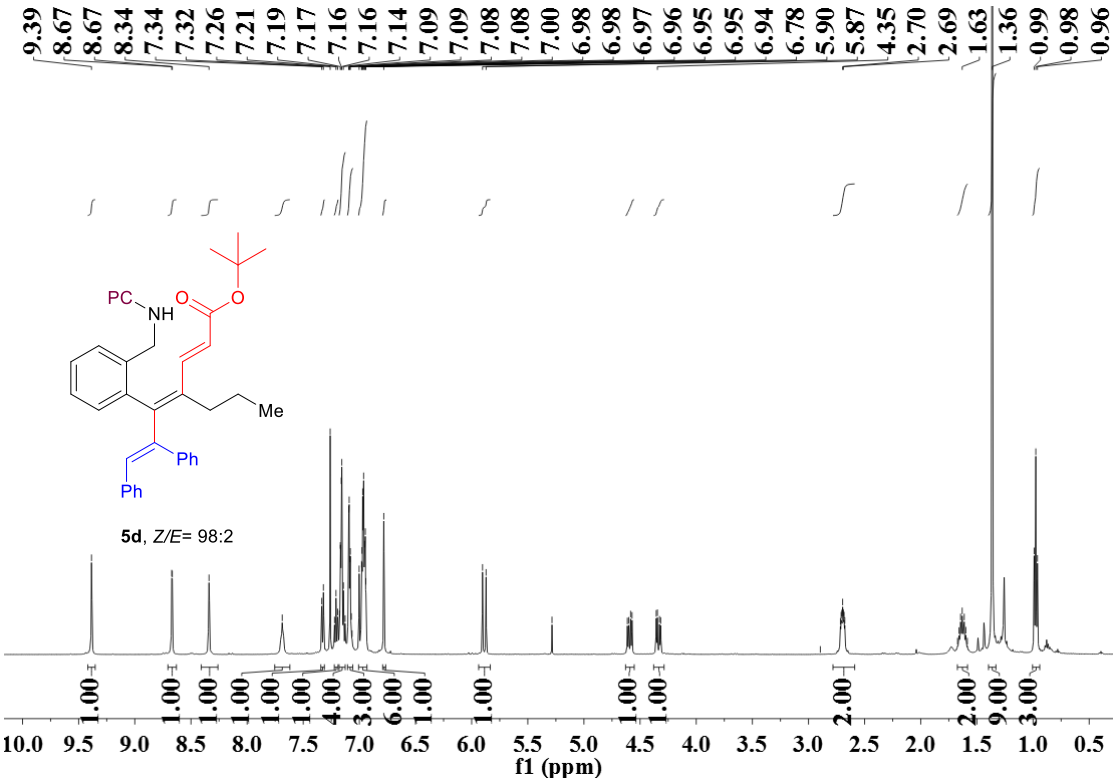
5b, *Z*/*E*= 95:5

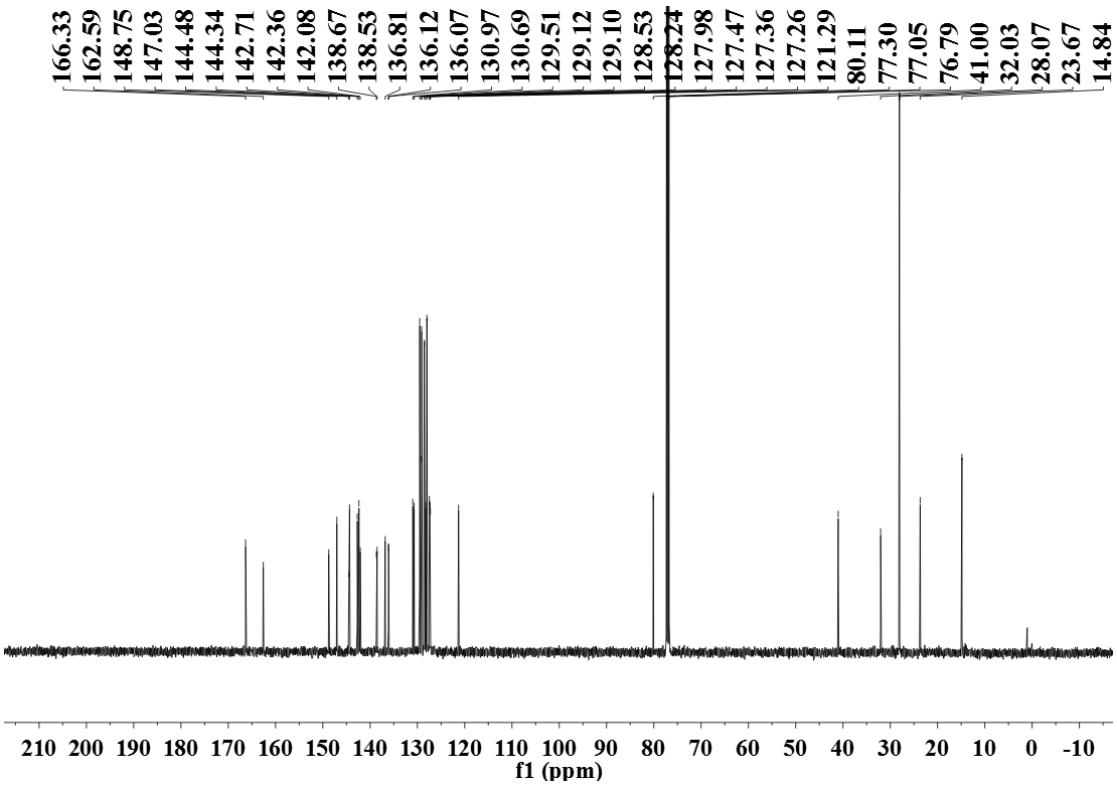

0.98
0.98
0.98
0.98
1.00
3.00
1.00
7.00
3.00
5.00
1.00
1.00
2.00
1.00
1.00
2.00
2.00
3.00
f1 (ppm)

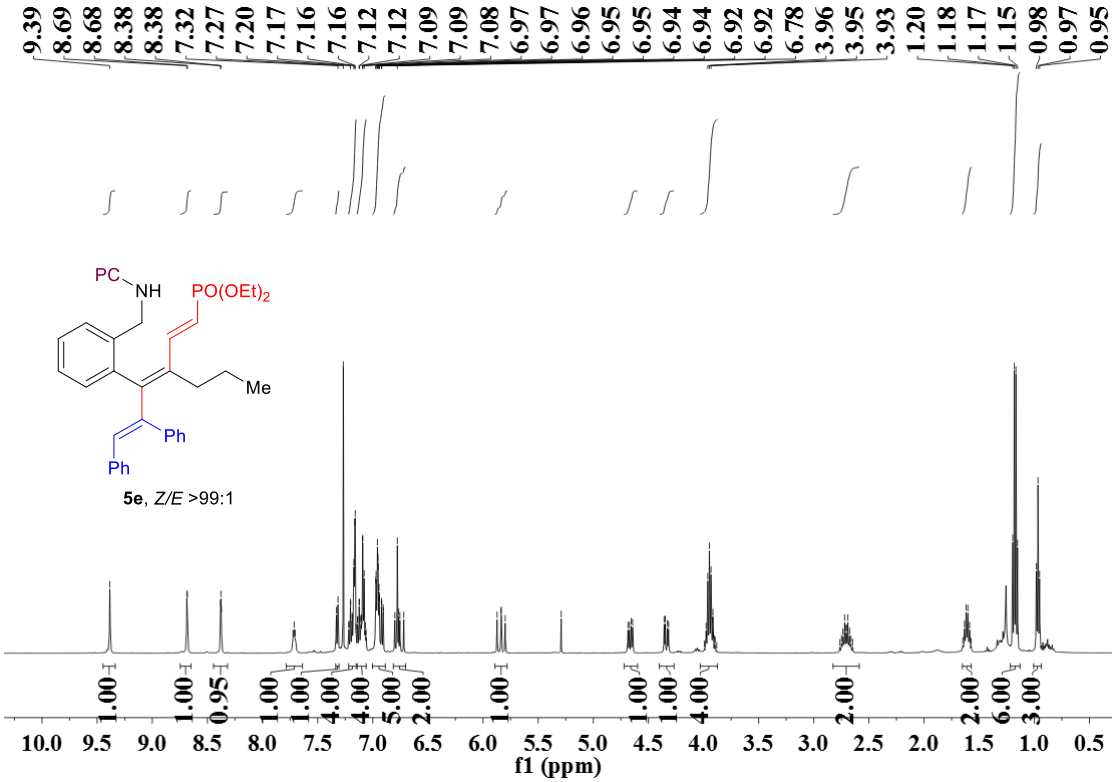

166.66
149.82
146.99
144.39
144.27
142.30
141.92
138.57
138.52
136.77
136.15
136.02
135.99
131.26
130.68
129.54
129.40
129.10
128.59
128.49
128.36
128.05
128.01
127.78
127.53
127.48
127.35
118.94
77.30
77.05
76.80
65.91
41.04
31.99
23.59
14.80
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


9.39
8.63
8.62
8.25
7.34
7.33
7.32
7.30
7.28
7.25
7.22
7.21
7.19
7.18
7.18
7.16
7.11
7.10
7.10
7.09
7.00
7.00
7.00
6.99
6.98
6.97
6.96
6.96
6.82
6.17
6.14
5.27
2.76
1.02
1.01
1.00
PC
NH
O
O
Ph
Me
Ph
Ph
5c, Z/E= 96:4
1.00
1.00
1.00
1.00
3.00
1.00
6.00
3.00
7.00
1.00
1.00
1.00
1.00
1.95
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

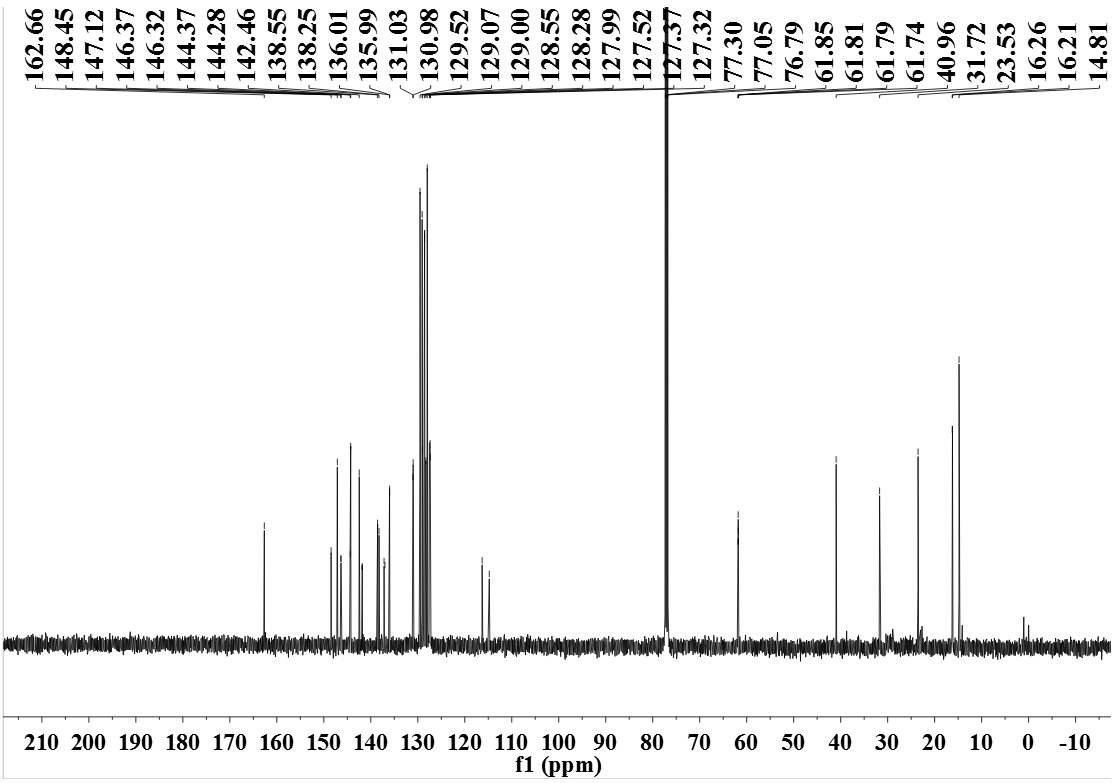

165.31
162.60
150.75
150.56
147.09
145.65
144.31
142.40
141.96
138.52
138.33
136.74
136.11
135.98
131.38
130.62
129.57
129.29
129.25
129.11
128.63
128.53
128.05
127.60
127.50
127.43
125.58
121.44
118.44
77.33
77.07
76.82
41.03
32.10
23.63
14.86
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

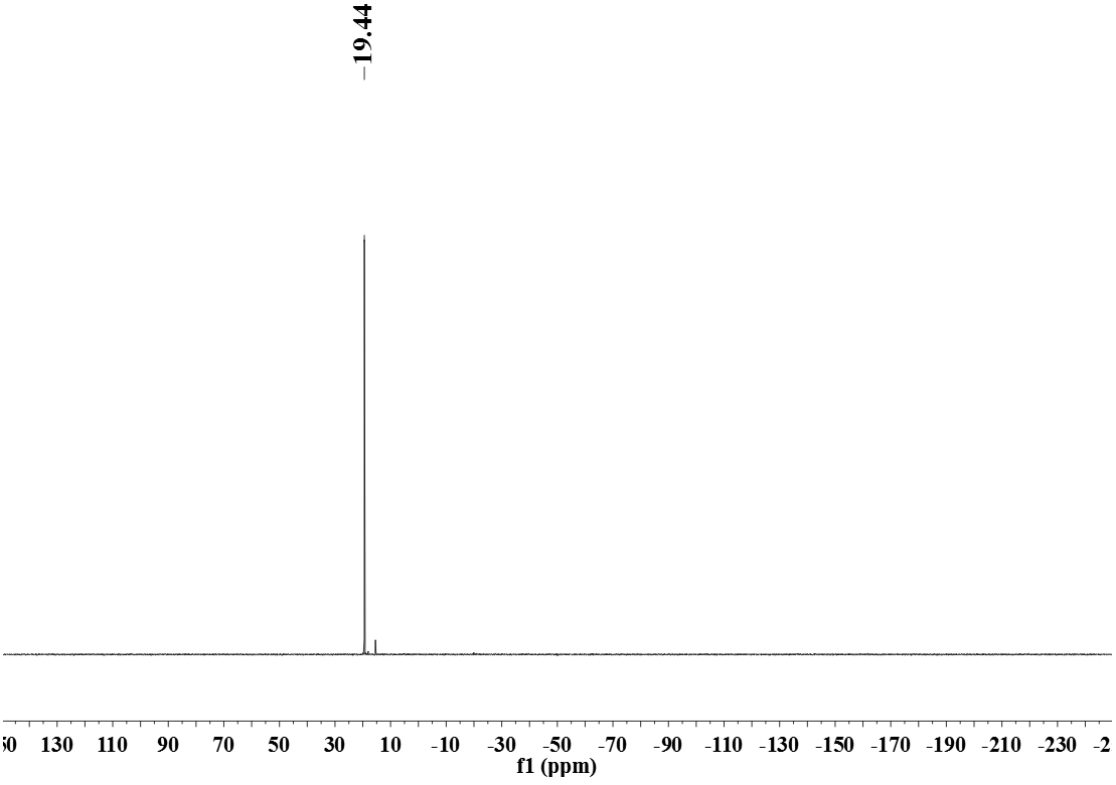

9.39
8.67
8.67
8.34
7.34
7.32
7.26
7.21
7.19
7.17
7.16
7.16
7.14
7.09
7.09
7.08
7.08
7.00
6.98
6.98
6.97
6.96
6.95
6.95
6.94
6.78
5.90
5.87
4.35
2.70
2.69
1.63
1.36
0.99
0.98
0.96
PC
NH
O
O
Me
Ph
Ph
5d, Z/E= 98:2
1.00
1.00
1.00
1.00
1.00
1.00
4.00
3.00
6.00
1.00
1.00
1.00
1.00
2.00
2.00
9.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

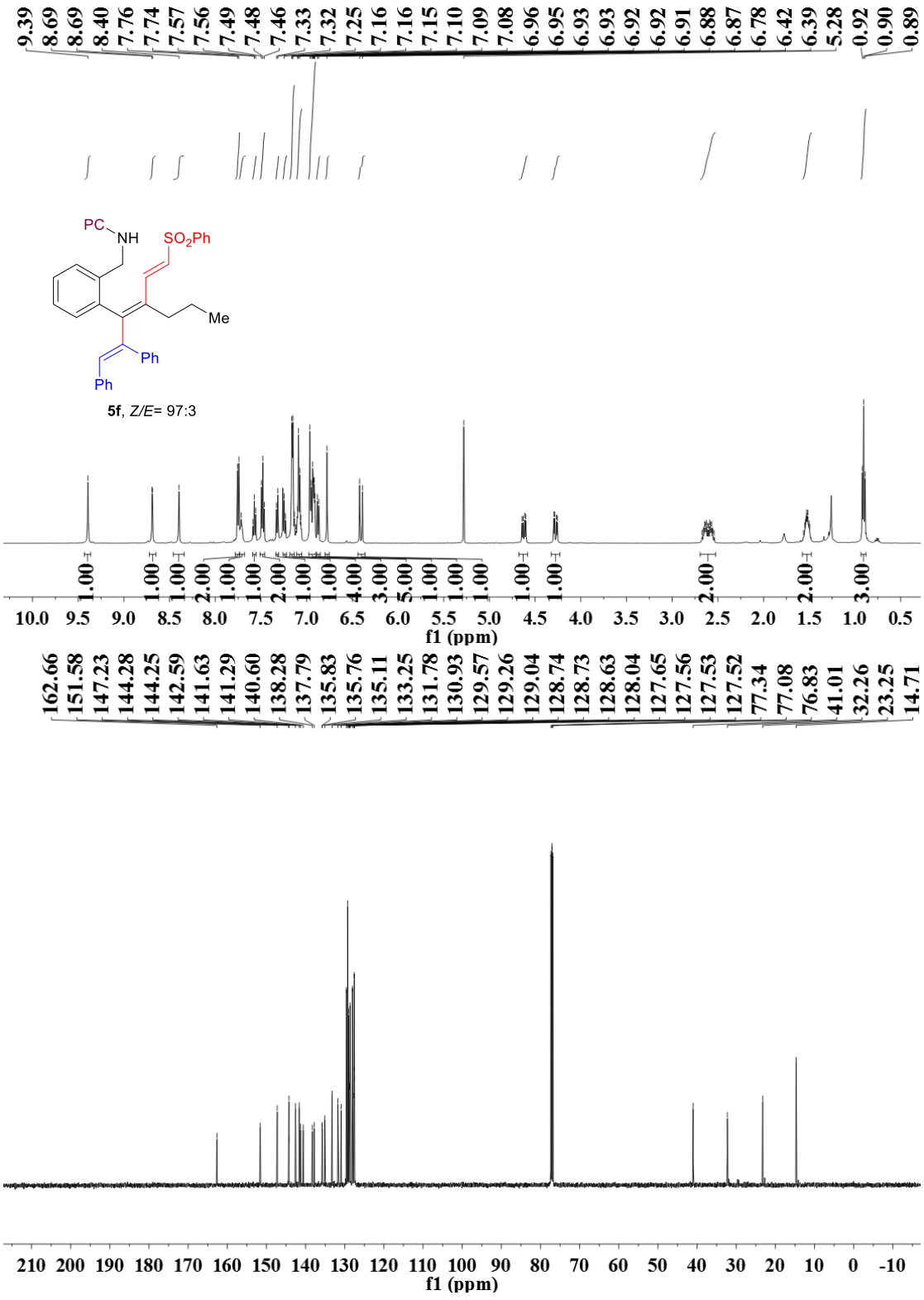

166.33
162.59
148.75
147.03
144.48
144.34
142.71
142.36
142.08
138.67
138.53
136.81
136.12
136.07
130.97
130.69
129.51
129.12
129.10
128.53
128.24
127.98
127.47
127.36
127.26
121.29
80.11
77.30
77.05
76.79
41.00
32.03
28.07
23.67
14.84
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

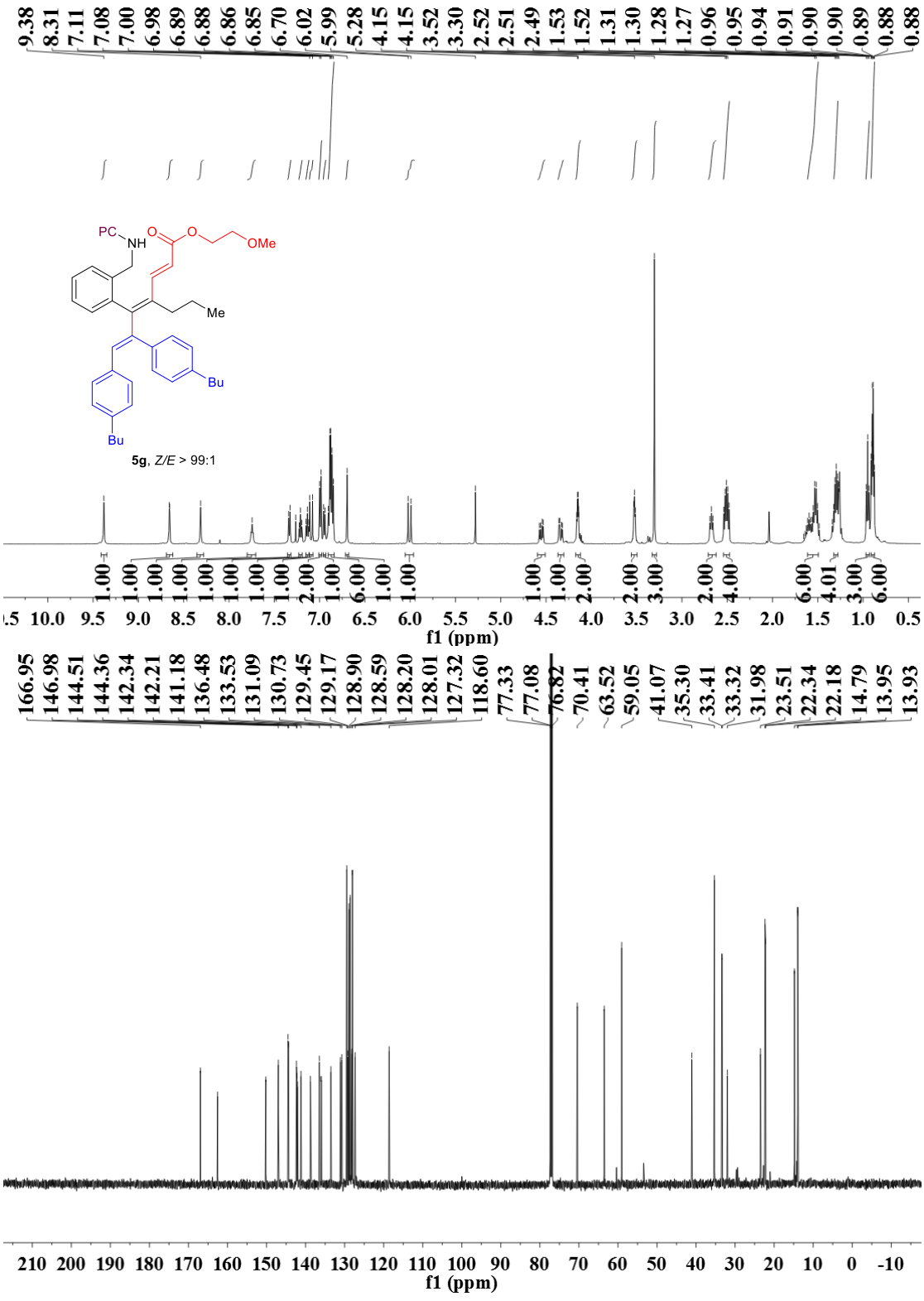

9.39
8.69
8.68
8.38
8.38
7.32
7.27
7.20
7.17
7.16
7.16
7.12
7.12
7.09
7.09
7.08
6.97
6.97
6.96
6.95
6.95
6.94
6.94
6.92
6.92
6.78
3.96
3.95
3.93
1.20
1.18
1.17
1.15
0.98
0.97
0.95
PC
NH
PO(OEt)2
Me
Ph
Ph
1.00
1.00
0.95
1.00
1.00
4.00
4.00
5.00
2.00
1.00
1.00
1.00
4.00
2.00
2.00
6.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

5e, *Z*/*E* >99:1

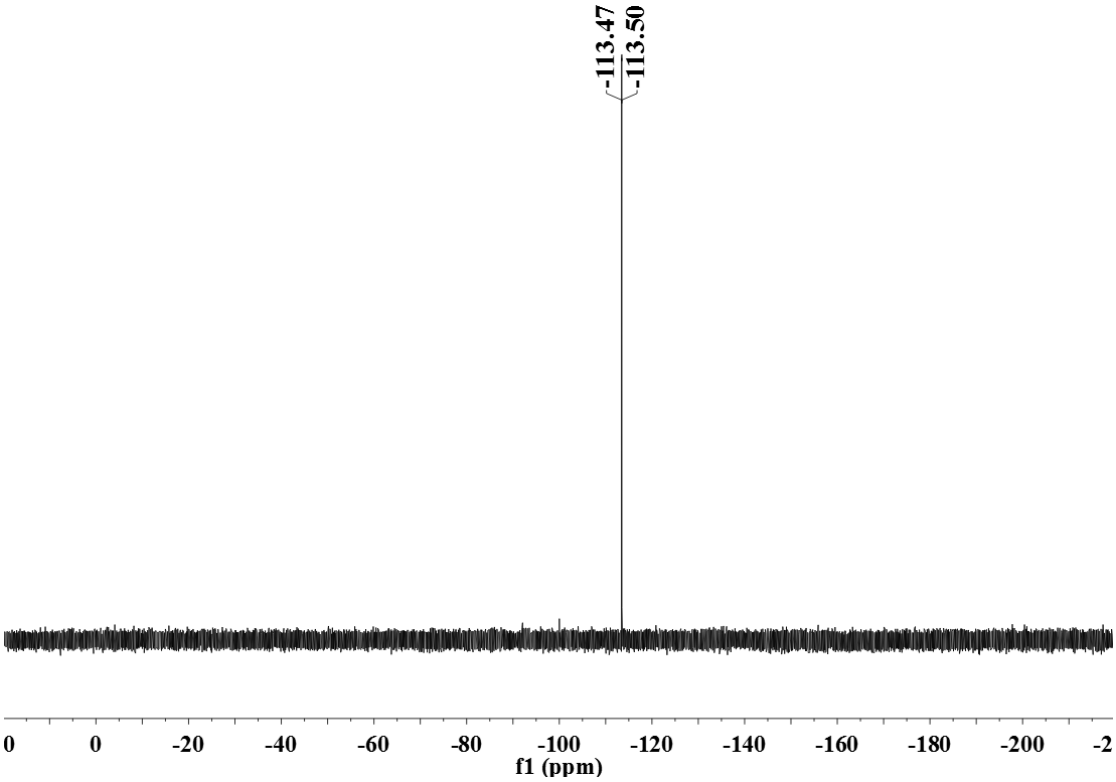

162.66
148.45
147.12
146.37
146.32
144.37
144.28
142.46
138.55
138.25
136.01
135.99
131.03
130.98
129.52
129.07
129.00
128.55
128.28
127.99
127.52
127.37
127.32
77.30
77.05
76.79
61.85
61.81
61.79
61.74
40.96
31.72
23.53
16.26
16.21
14.81
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

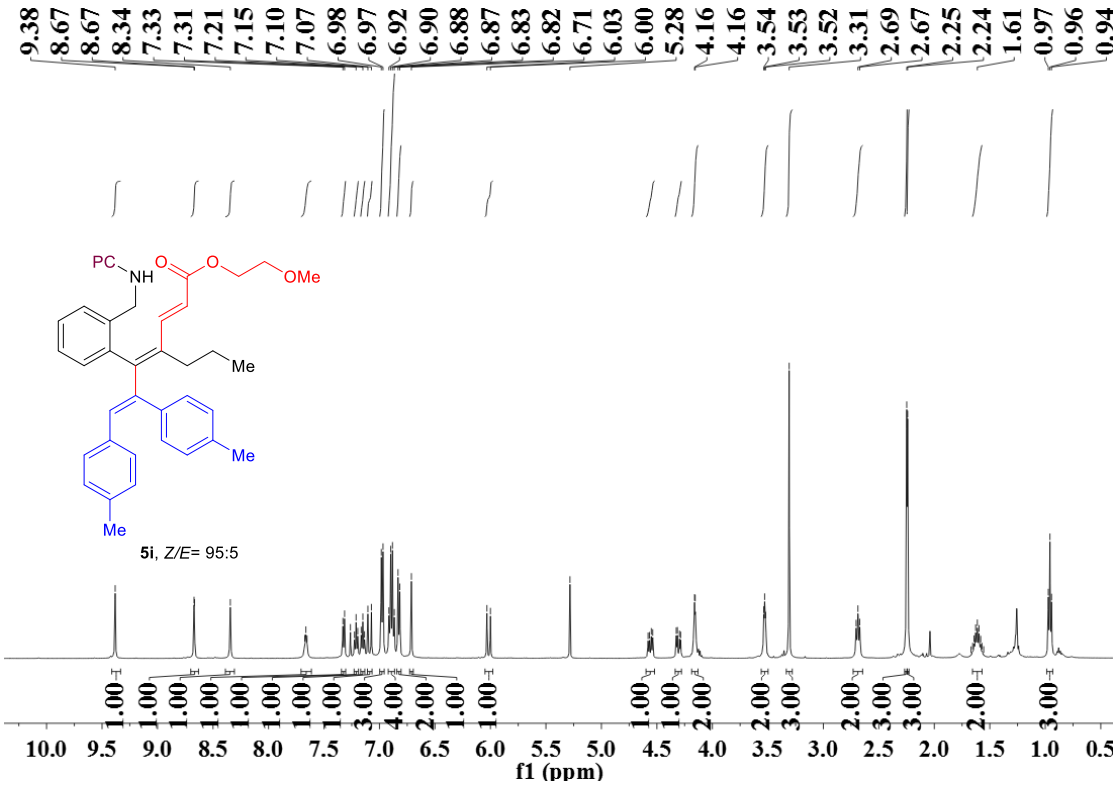

19.44
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -2
f1 (ppm)

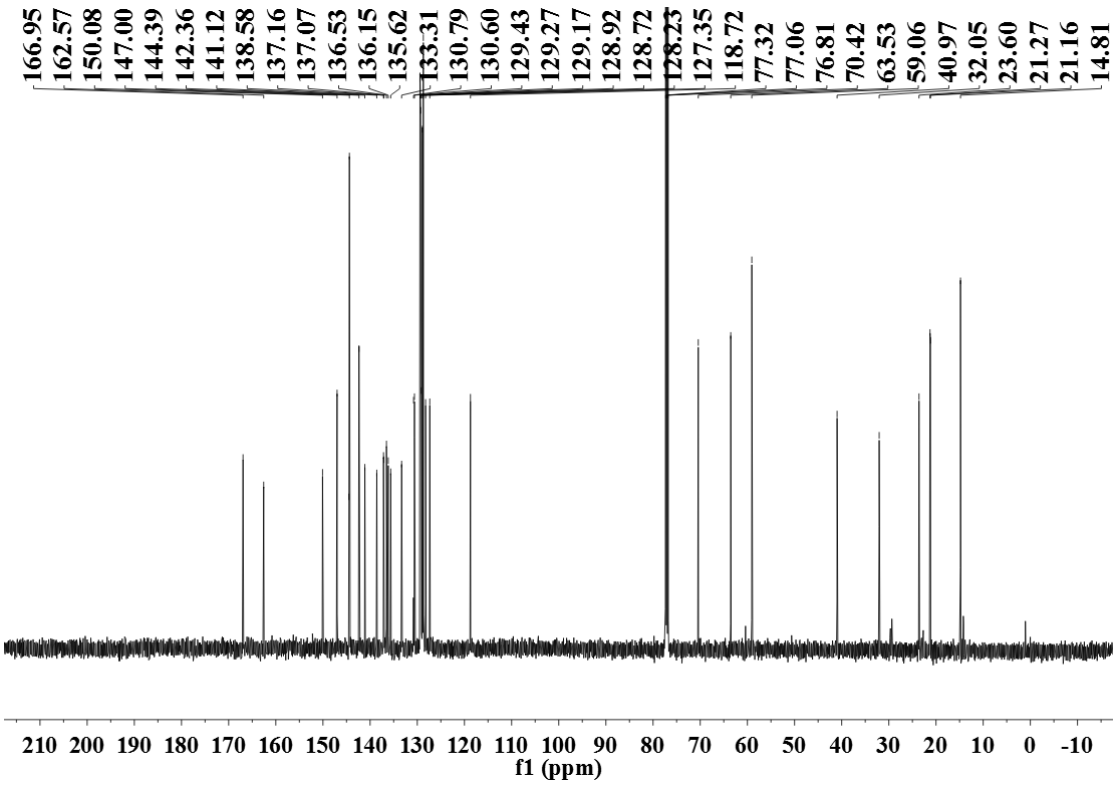

9.39 8.69 8.69 8.40 7.76 7.74 7.57 7.56 7.49 7.48 7.46 7.33 7.32 7.25 7.16 7.16 7.15 7.10 7.09 7.08 6.96 6.95 6.93 6.93 6.92 6.92 6.91 6.88 6.87 6.78 6.42 6.39 5.28 0.92 0.90 0.89
PC
NH
SO2Ph
Me
Ph
Ph
5f, Z/E= 97:3
1.00 1.00 1.00 2.00 1.00 1.00 2.00 1.00 1.00 4.00 3.00 5.00 1.00 1.00 1.00 1.00 1.00 2.00 2.00 3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
162.66 151.58 147.23 144.28 144.25 142.59 141.63 141.29 140.60 138.28 137.79 135.83 135.76 135.11 133.25 131.78 130.93 129.57 129.26 129.04 128.74 128.73 128.63 128.04 127.65 127.56 127.53 127.52 77.34 77.08 76.83 41.01 32.26 23.25 14.71
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

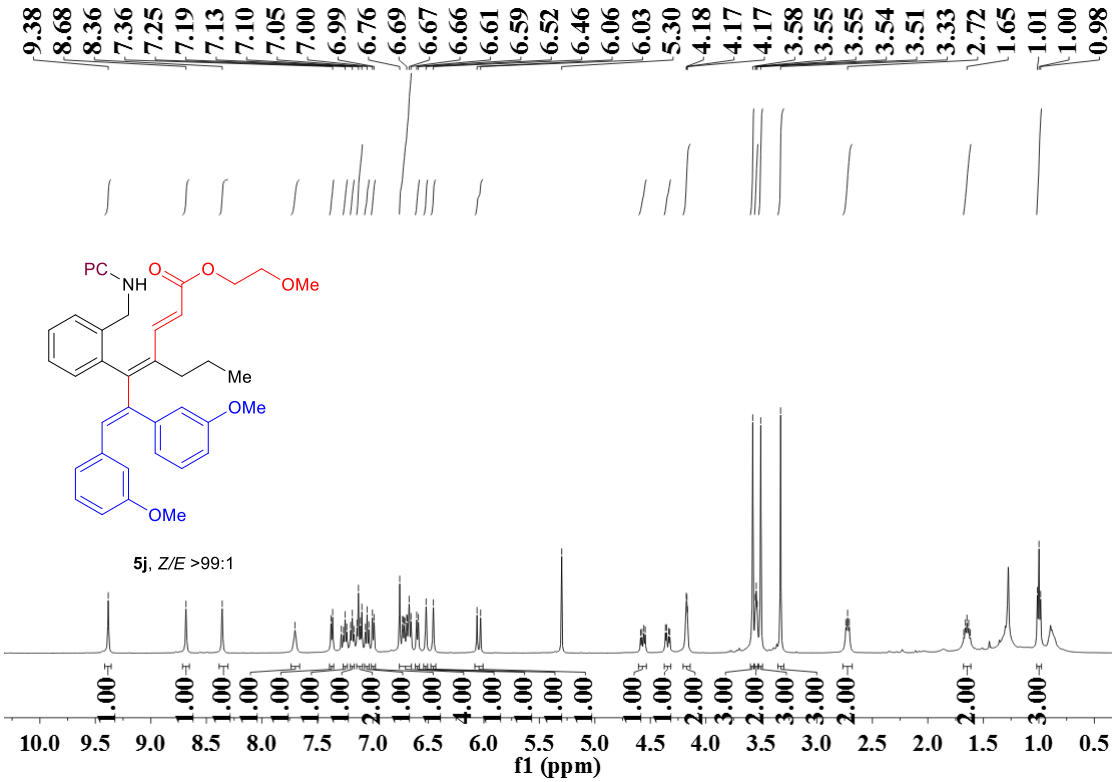

9.38 8.31 7.11 7.08 7.00 6.98 6.89 6.88 6.86 6.85 6.70 6.02 5.99 5.28 4.15 4.15 3.52 3.30 2.52 2.51 2.49 1.53 1.52 1.31 1.30 1.28 1.27 0.96 0.95 0.94 0.91 0.90 0.90 0.89 0.88 0.88
PC
NH
O
O
OMe
Me
Bu
Bu
5g, Z/E > 99:1
1.00 1.00 1.00 1.00 1.00 1.00 1.00 2.00 1.00 6.00 1.00 1.00 1.00 1.00 2.00 2.00 3.00 2.00 4.00 6.00 4.01 3.00 6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
166.95 146.98 144.51 144.36 142.34 142.21 141.18 136.48 133.53 131.09 130.73 129.45 129.17 128.90 128.59 128.20 128.01 127.32 118.60 77.33 77.08 76.82 70.41 63.52 59.05 41.07 35.30 33.41 33.32 31.98 23.51 22.34 22.18 14.79 13.95 13.93
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

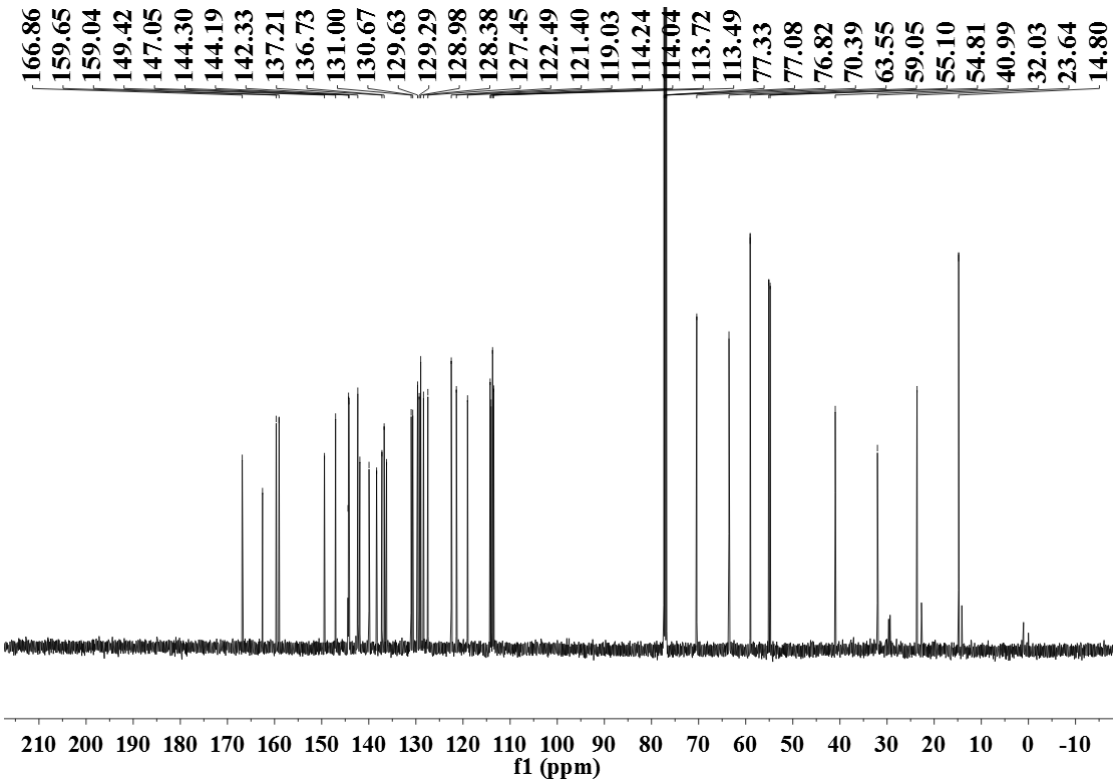

9.38 8.70 8.69 8.38 7.34 7.33 7.23 7.17 7.09 7.06 6.96 6.94 6.93 6.89 6.89 6.88 6.87 6.82 6.81 6.78 6.04 6.01 5.29 4.19 4.18 4.18 4.17 3.56 3.55 3.54 3.54 3.33 2.68 0.99 0.97 0.96
PC
NH
O
O
OMe
Me
F
F
5h, Z/E > 99:1
1.01 1.00 1.00 1.00 1.00 1.00 1.00 1.00 3.00 4.00 3.00 1.00 1.00 1.00 2.00 2.00 3.00 2.00 2.00 3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
166.82 162.53 148.98 147.17 144.31 144.28 143.91 142.43 140.54 138.06 136.97 136.08 131.15 131.09 130.82 130.76 130.57 130.29 129.33 128.49 127.54 119.30 115.90 115.73 115.20 115.03 77.31 77.06 76.80 70.40 63.56 59.04 40.87 32.09 23.66 14.80
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

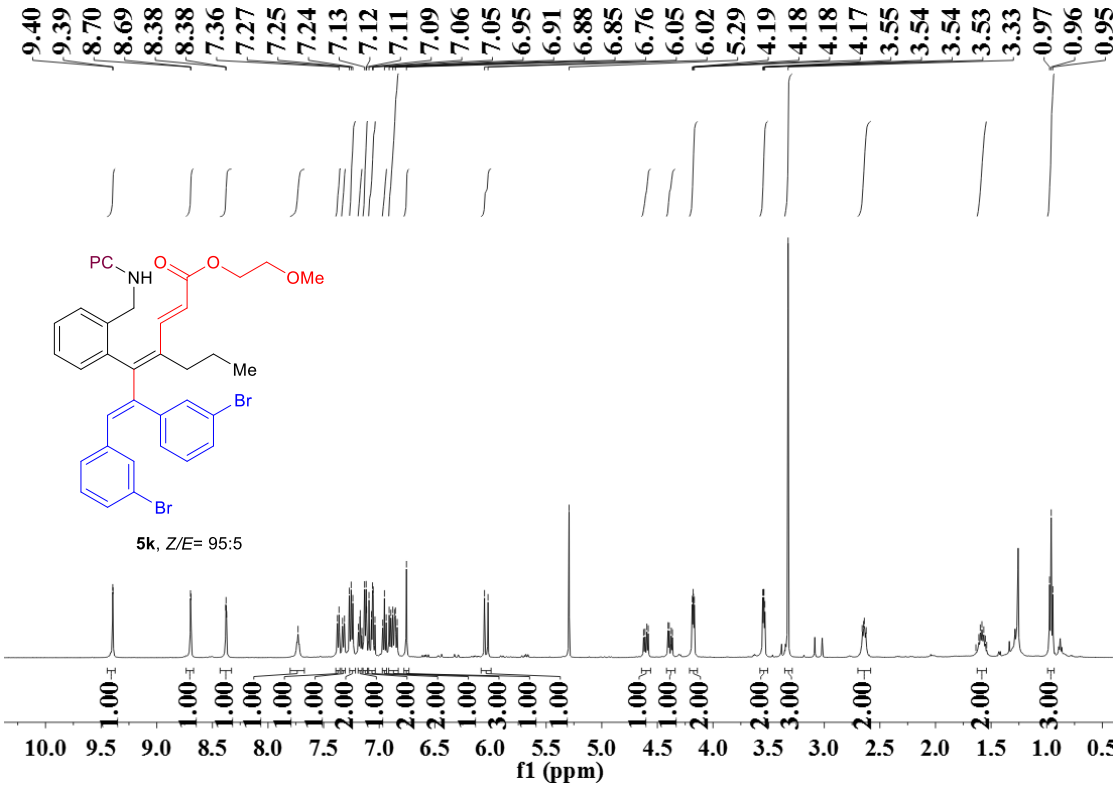

-113.47
-113.50
0
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-2
f1 (ppm)

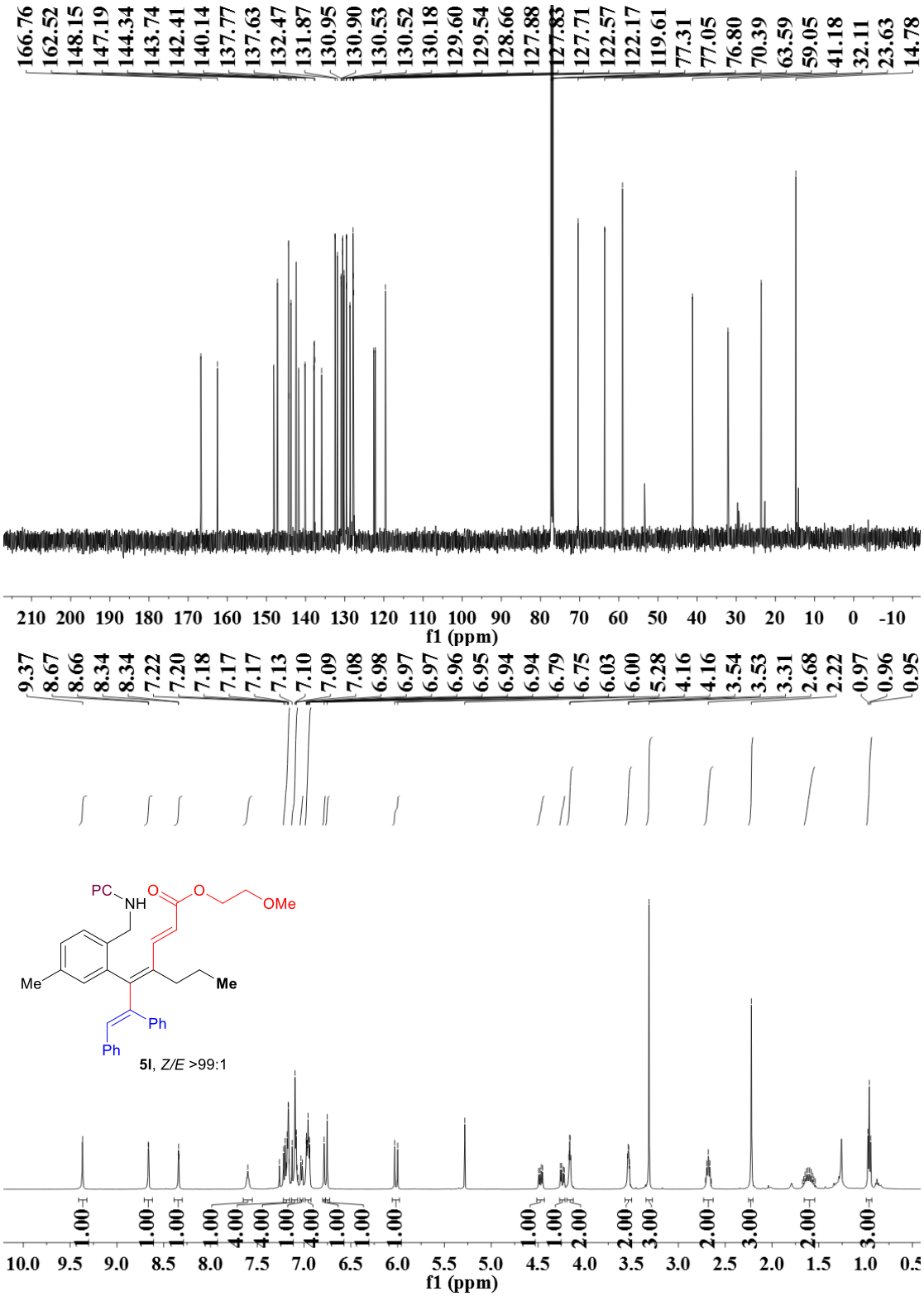

9.38
8.67
8.67
8.34
7.33
7.31
7.21
7.15
7.10
7.07
6.98
6.97
6.92
6.90
6.88
6.87
6.83
6.82
6.71
6.03
6.00
5.28
4.16
4.16
3.54
3.53
3.52
3.31
2.69
2.67
2.25
2.24
1.61
0.97
0.96
0.94
PC
NH
O
O
OMe
Me
Me
Me
5i, Z/E= 95:5
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
4.00
2.00
1.00
1.00
1.00
1.00
2.00
2.00
3.00
2.00
3.00
3.00
2.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

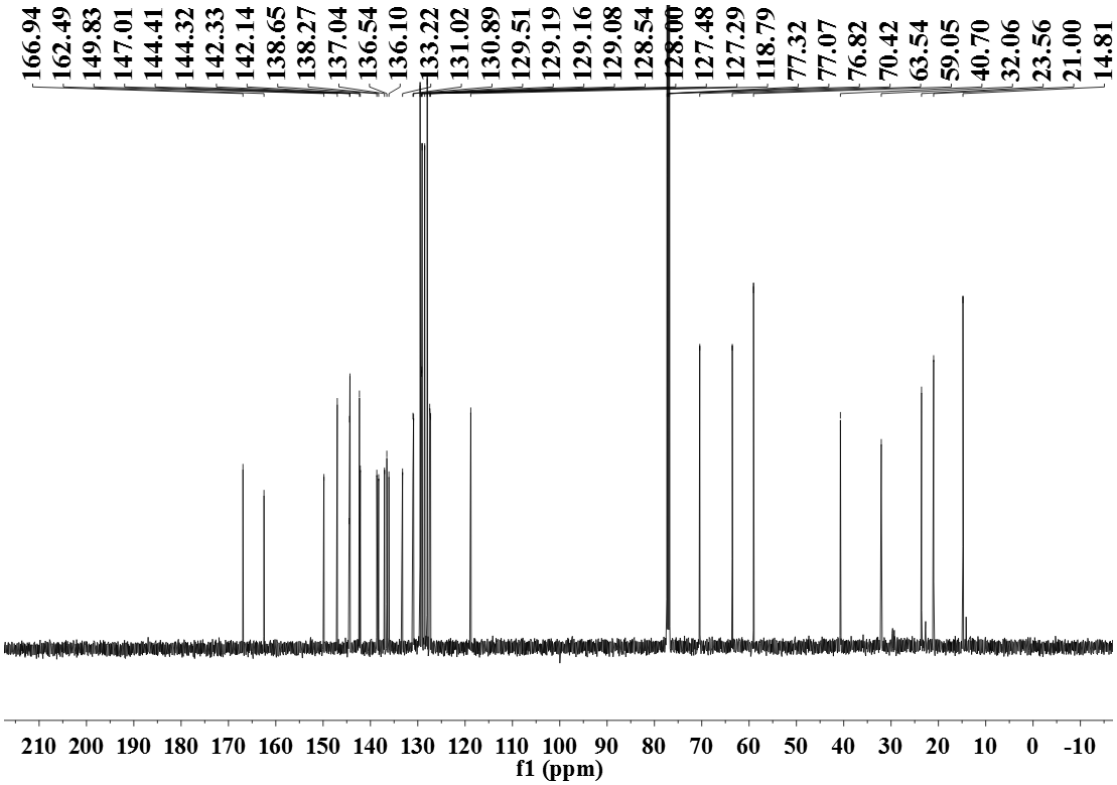

166.95
162.57
150.08
147.00
144.39
142.36
141.12
138.58
137.16
137.07
136.53
136.15
135.62
133.31
130.79
130.60
129.43
129.27
129.17
128.92
128.72
128.23
127.35
118.72
77.32
77.06
76.81
70.42
63.53
59.06
40.97
32.05
23.60
21.27
21.16
14.81
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

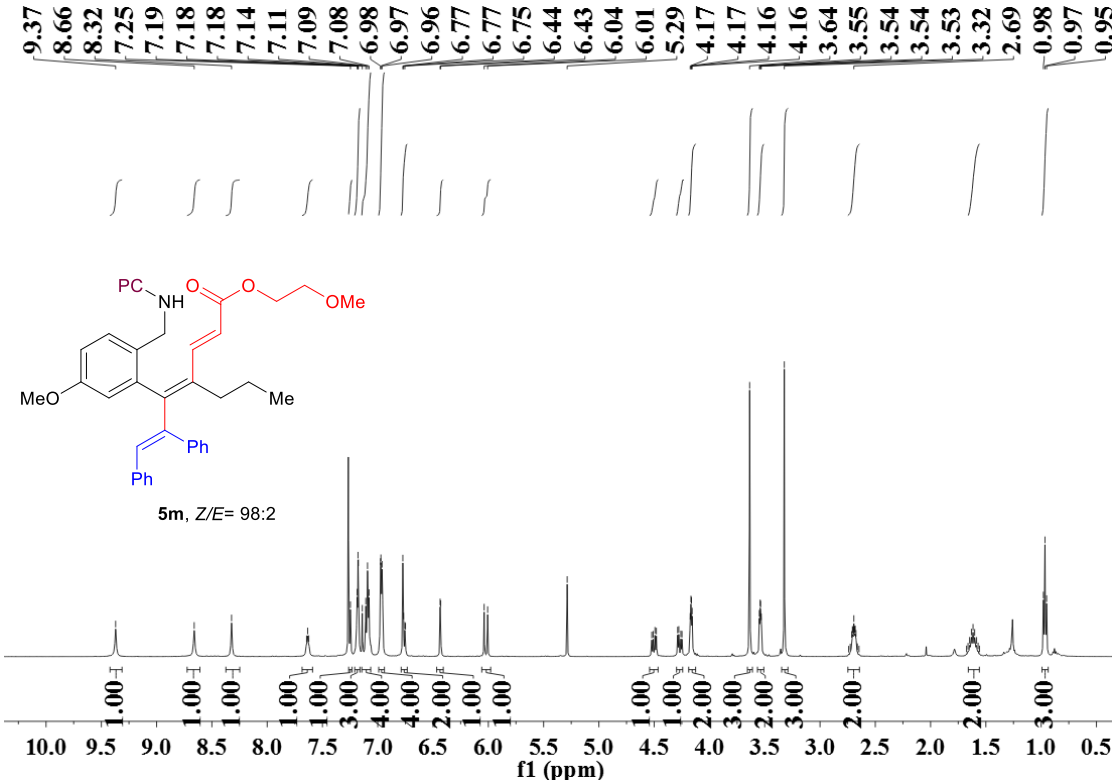

9.38
8.68
8.36
7.36
7.25
7.19
7.13
7.10
7.05
7.00
6.99
6.76
6.69
6.67
6.66
6.61
6.59
6.52
6.46
6.06
6.03
5.30
4.18
4.17
4.17
3.58
3.55
3.55
3.54
3.51
3.33
2.72
1.65
1.01
1.00
0.98
PC
NH
O
O
OMe
Me
OMe
OMe
5j, Z/E >99:1
1.00
1.00
1.00
1.00
1.00
1.00
1.00
2.00
1.00
1.00
4.00
1.00
1.00
1.00
1.00
1.00
1.00
2.00
3.00
2.00
3.00
3.00
2.00
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


166.86
159.65
159.04
149.42
147.05
144.30
144.19
142.33
137.21
136.73
131.00
130.67
129.63
129.29
128.98
128.38
127.45
122.49
121.40
119.03
114.24
114.04
113.72
113.49
77.33
77.08
76.82
70.39
63.55
59.05
55.10
54.81
40.99
32.03
23.64
14.80
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

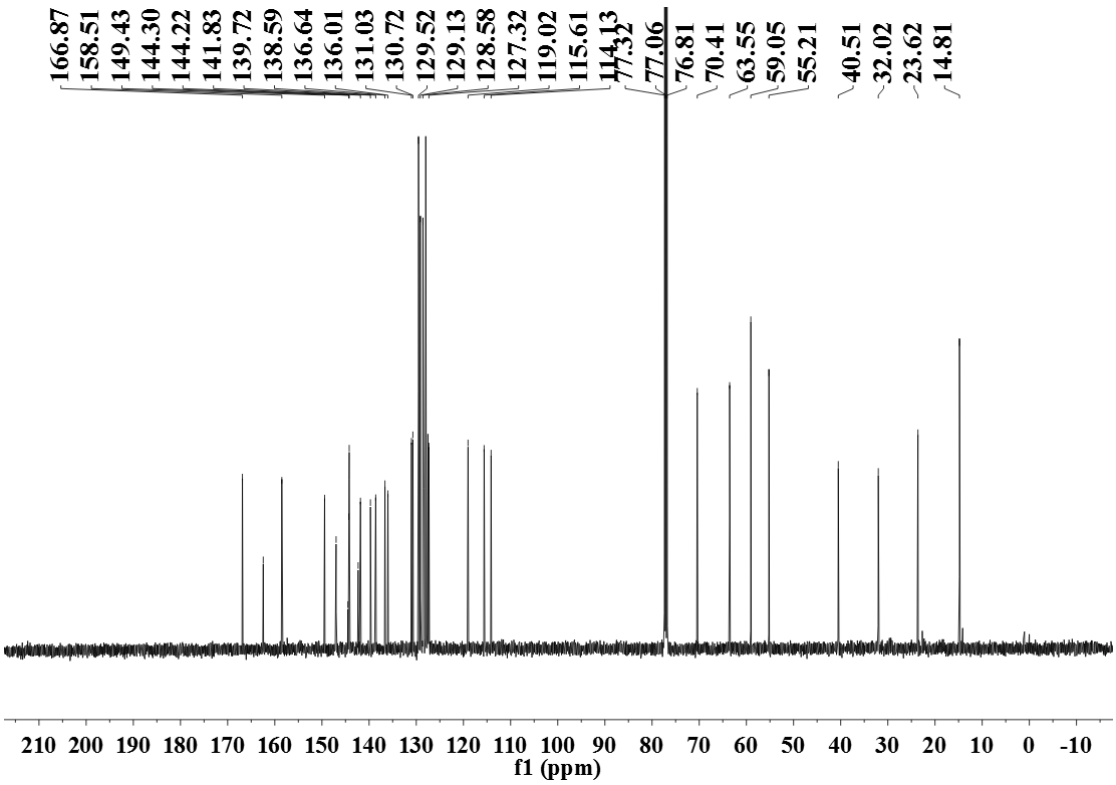

9.40
9.39
8.70
8.69
8.38
8.38
7.36
7.27
7.25
7.24
7.13
7.12
7.11
7.09
7.06
7.05
6.95
6.91
6.88
6.85
6.76
6.05
6.02
5.29
4.19
4.18
4.18
4.17
3.55
3.54
3.54
3.53
3.33
0.97
0.96
0.95
PC
NH
O
O
OMe
Me
Br
Br
5k, Z/E= 95:5
1.00
1.00
1.00
1.00
1.00
1.00
2.00
1.00
2.00
2.00
1.00
3.00
1.00
1.00
1.00
1.00
2.00
2.00
3.00
2.00
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

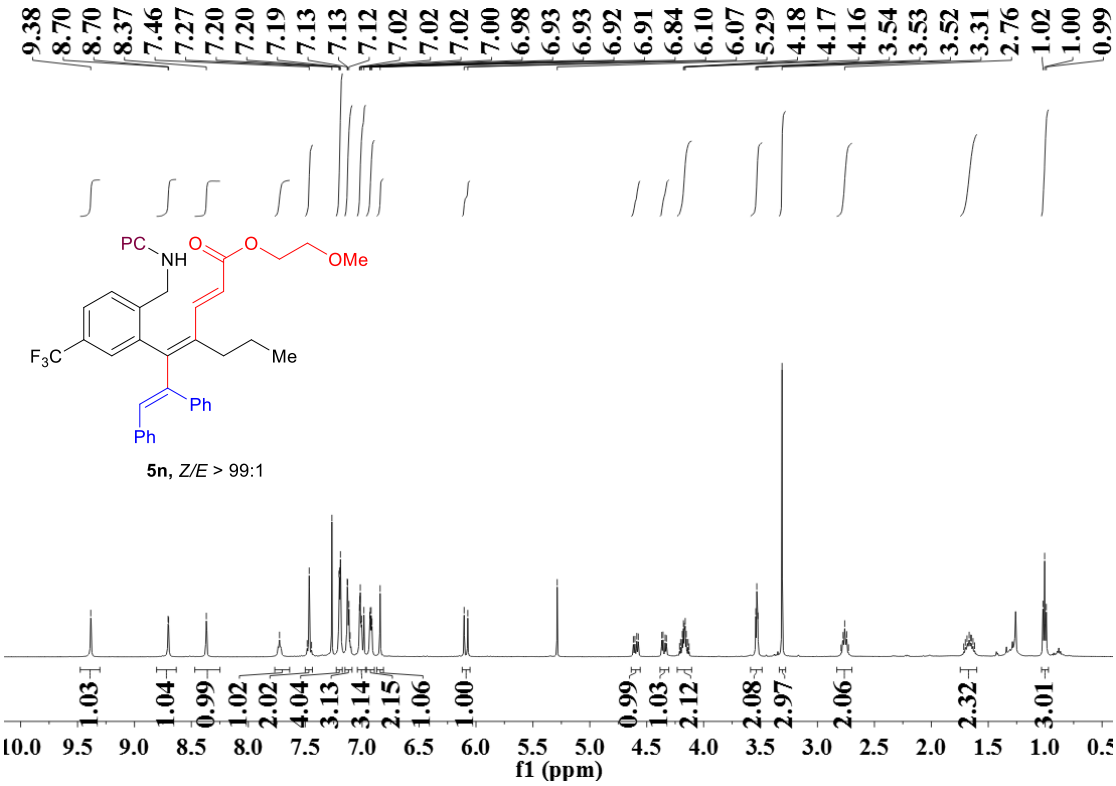

166.76
162.52
148.15
147.19
144.34
143.74
142.41
140.14
137.77
137.63
132.47
131.87
130.95
130.90
130.53
130.52
130.18
129.60
129.54
128.66
127.88
127.83
127.71
122.57
122.17
119.61
77.31
77.05
76.80
70.39
63.59
59.05
41.18
32.11
23.63
14.78
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
9.37
8.67
8.66
8.34
8.34
7.22
7.20
7.18
7.17
7.17
7.13
7.10
7.09
7.08
6.98
6.97
6.97
6.96
6.95
6.94
6.94
6.79
6.75
6.03
6.00
5.28
4.16
4.16
3.54
3.53
3.31
2.68
2.22
0.97
0.96
0.95
PC
NH
O
O
OMe
Me
Me
Ph
Ph
5l, Z/E >99:1
1.00
1.00
1.00
1.00
4.00
4.00
1.00
4.00
1.00
1.00
1.00
1.00
1.00
2.00
2.00
3.00
2.00
3.00
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


166.94
162.49
149.83
147.01
144.41
144.32
142.33
142.14
138.65
138.27
137.04
136.54
136.10
133.22
131.02
130.89
129.51
129.19
129.16
129.08
128.54
128.00
127.48
127.29
118.79
77.32
77.07
76.82
70.42
63.54
59.05
40.70
32.06
23.56
21.00
14.81
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

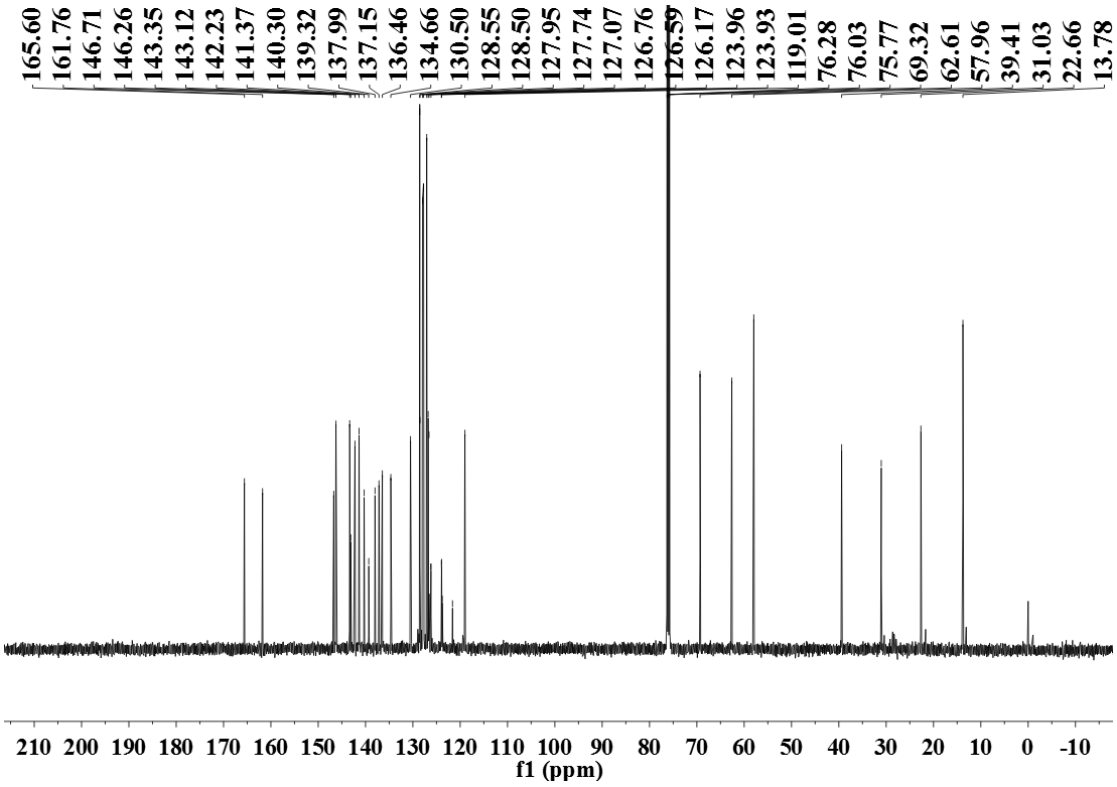

9.37
8.66
8.32
7.25
7.19
7.18
7.18
7.14
7.11
7.09
7.08
6.98
6.97
6.96
6.77
6.77
6.75
6.44
6.43
6.04
6.01
5.29
4.17
4.17
4.16
4.16
3.64
3.55
3.54
3.54
3.53
3.32
2.69
0.98
0.97
0.95
PC
NH
O
O
OMe
MeO
Me
Ph
Ph
1.00
1.00
1.00
1.00
1.00
3.00
4.00
4.00
2.00
1.00
1.00
1.00
1.00
2.00
3.00
2.00
3.00
2.00
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

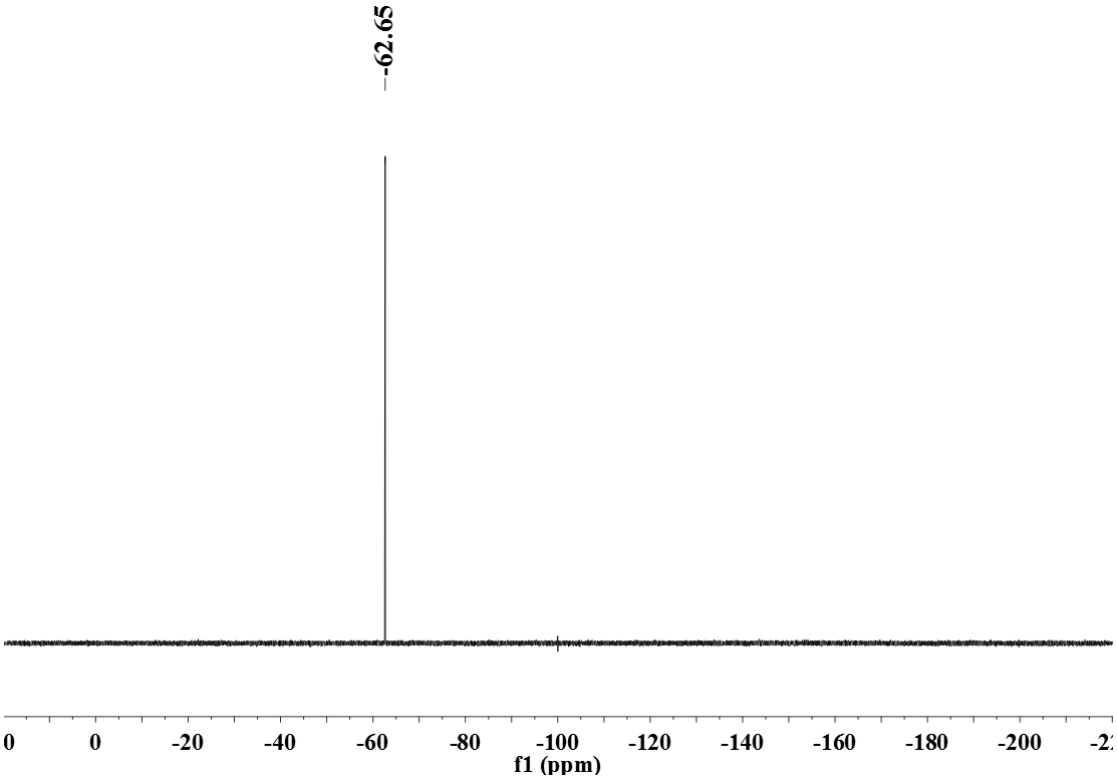
5m, *Z*/*E*= 98:2

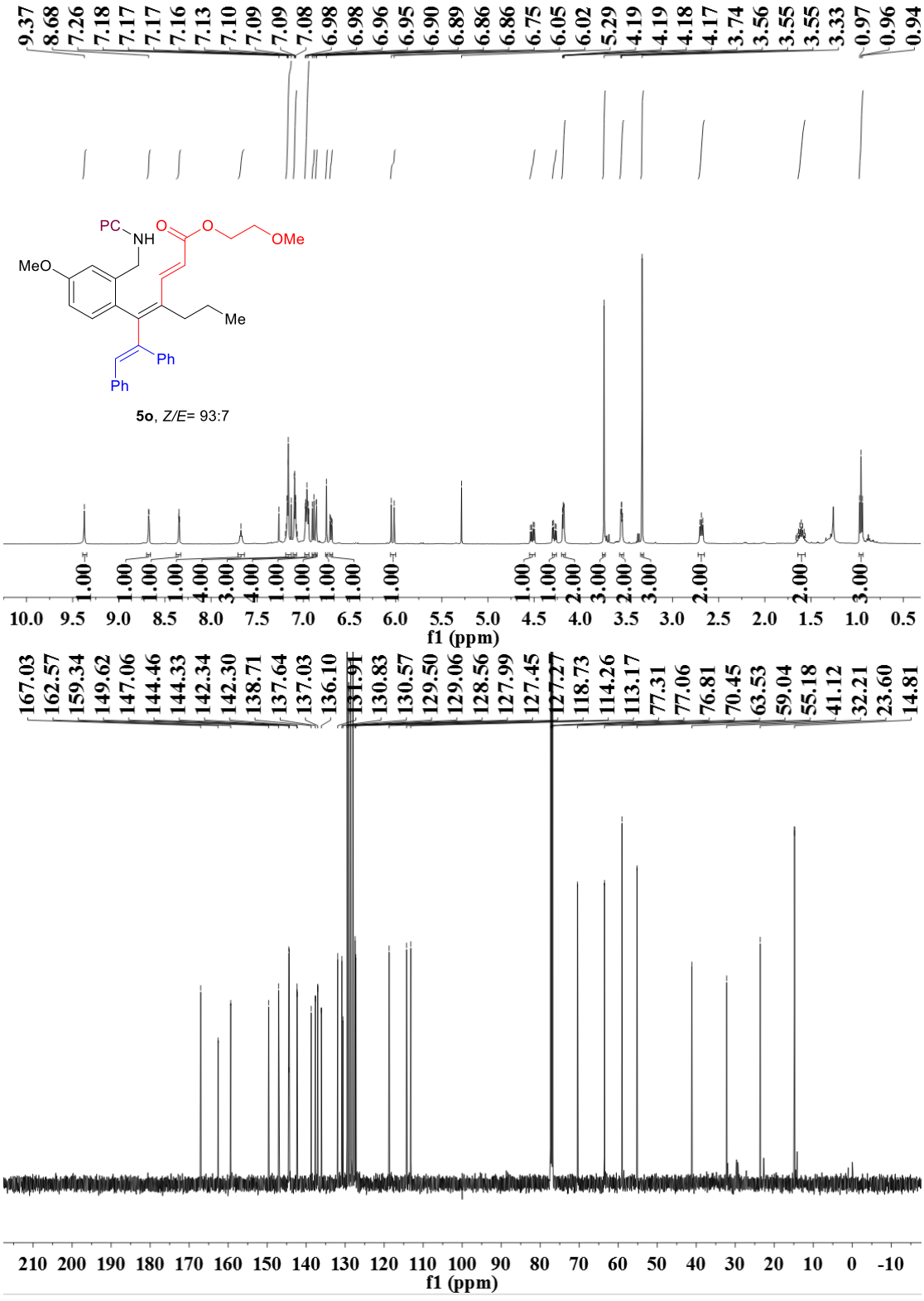

166.87
158.51
149.43
144.30
144.22
141.83
139.72
138.59
136.64
136.01
131.03
130.72
129.52
129.13
128.58
127.32
119.02
115.61
114.13
77.32
77.06
76.81
70.41
63.55
59.05
55.21
40.51
32.02
23.62
14.81
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


9.38
8.70
8.70
8.37
7.46
7.27
7.20
7.20
7.19
7.13
7.13
7.12
7.02
7.02
7.02
7.00
6.98
6.93
6.93
6.92
6.91
6.84
6.10
6.07
5.29
4.18
4.17
4.16
3.54
3.53
3.52
3.31
2.76
1.02
1.00
0.99
PC
NH
O
O
OMe
F3C
Me
Ph
Ph
1.03
1.04
0.99
1.02
2.02
4.04
3.13
3.14
2.15
1.06
1.00
0.99
1.03
2.12
2.08
2.97
2.06
2.32
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

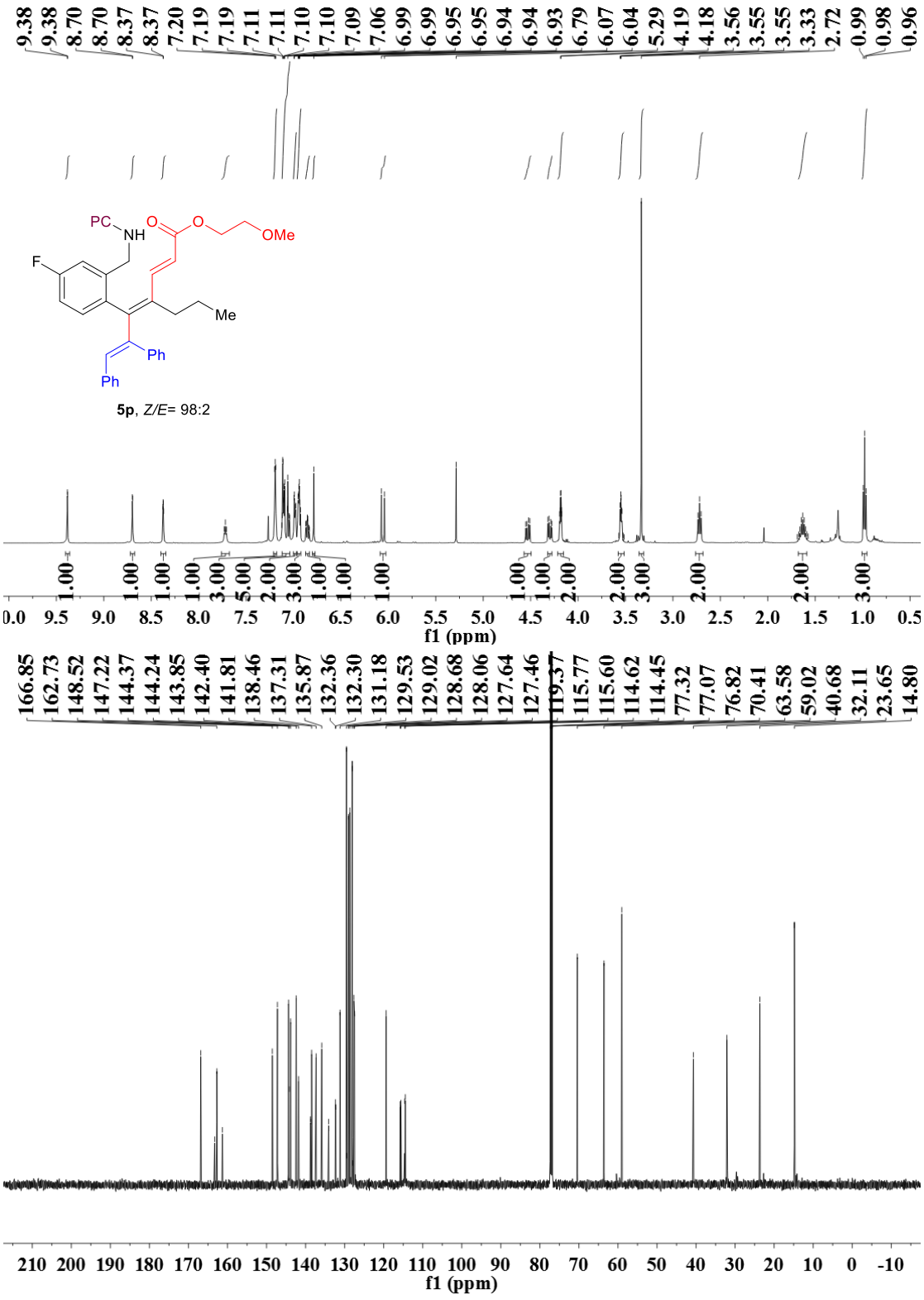
5n, *Z*/*E* > 99:1


165.60
161.76
146.71
146.26
143.35
143.12
142.23
141.37
140.30
139.32
137.99
137.15
136.46
134.66
130.50
128.55
128.50
127.95
127.74
127.07
126.76
126.59
126.17
123.96
123.93
119.01
76.28
76.03
75.77
69.32
62.61
57.96
39.41
31.03
22.66
13.78
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

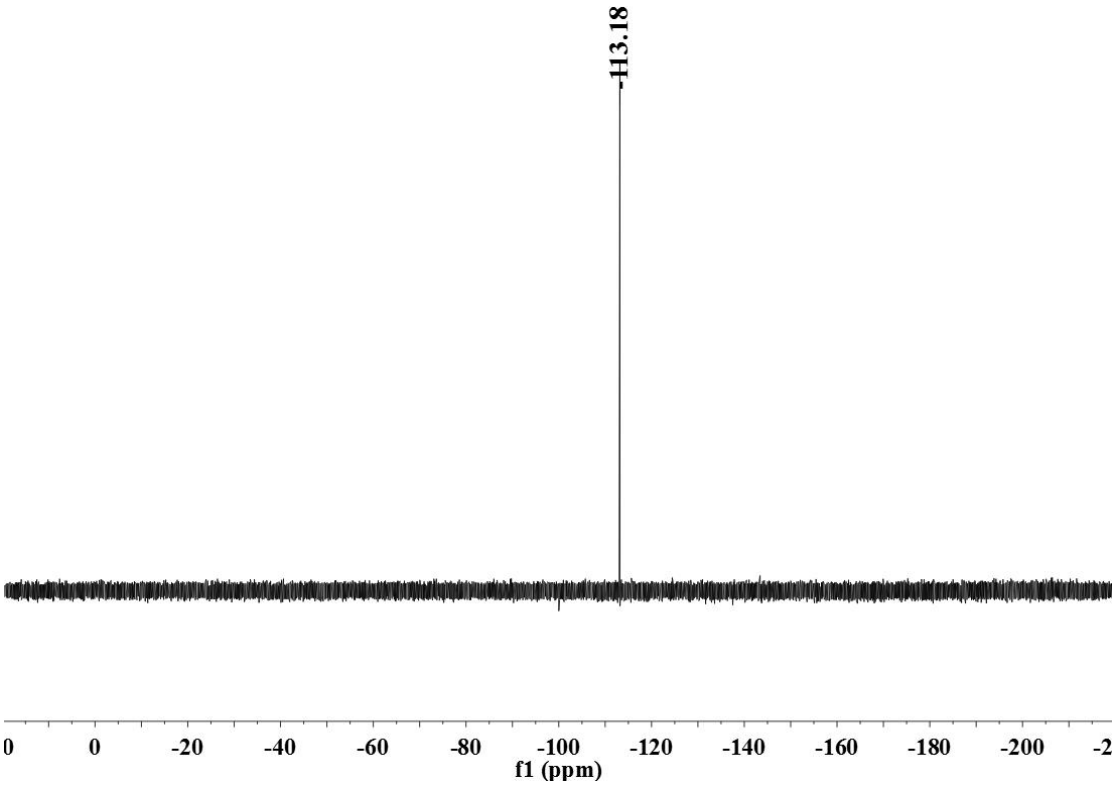

-62.65
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

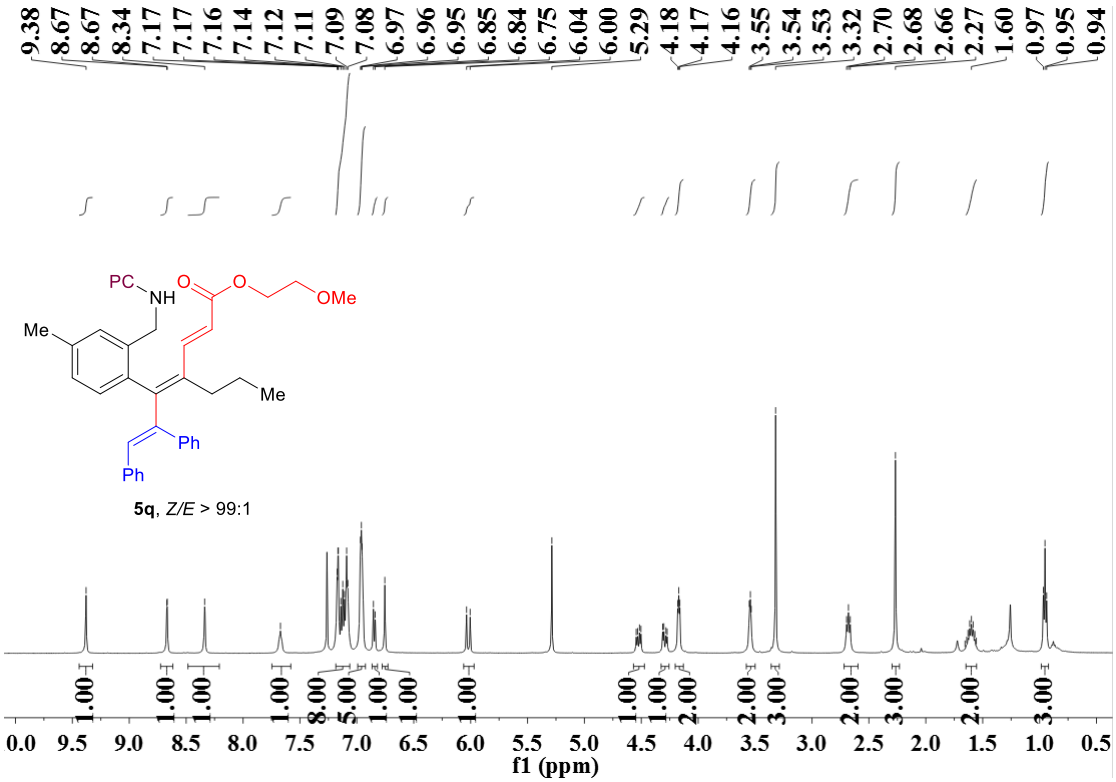

9.37 8.68 7.26 7.18 7.17 7.17 7.16 7.13 7.10 7.09 7.09 7.08 6.98 6.98 6.96 6.95 6.90 6.89 6.86 6.86 6.75 6.05 6.02 5.29 4.19 4.19 4.18 4.17 3.74 3.56 3.55 3.55 3.33 0.97 0.96 0.94
PC
NH
O
O
OMe
MeO
Me
Ph
Ph
1.00 1.00 1.00 1.00 4.00 3.00 4.00 1.00 1.00 1.00 1.00 1.00 1.00 2.00 3.00 2.00 3.00 2.00 2.00 3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
167.03 162.57 159.34 149.62 147.06 144.46 144.33 142.34 142.30 138.71 137.64 137.03 136.10 131.91 130.83 130.57 129.50 129.06 128.56 127.99 127.45 127.27 118.73 114.26 113.17 77.31 77.06 76.81 70.45 63.53 59.04 55.18 41.12 32.21 23.60 14.81
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

5o, *Z*/*E*= 93:7

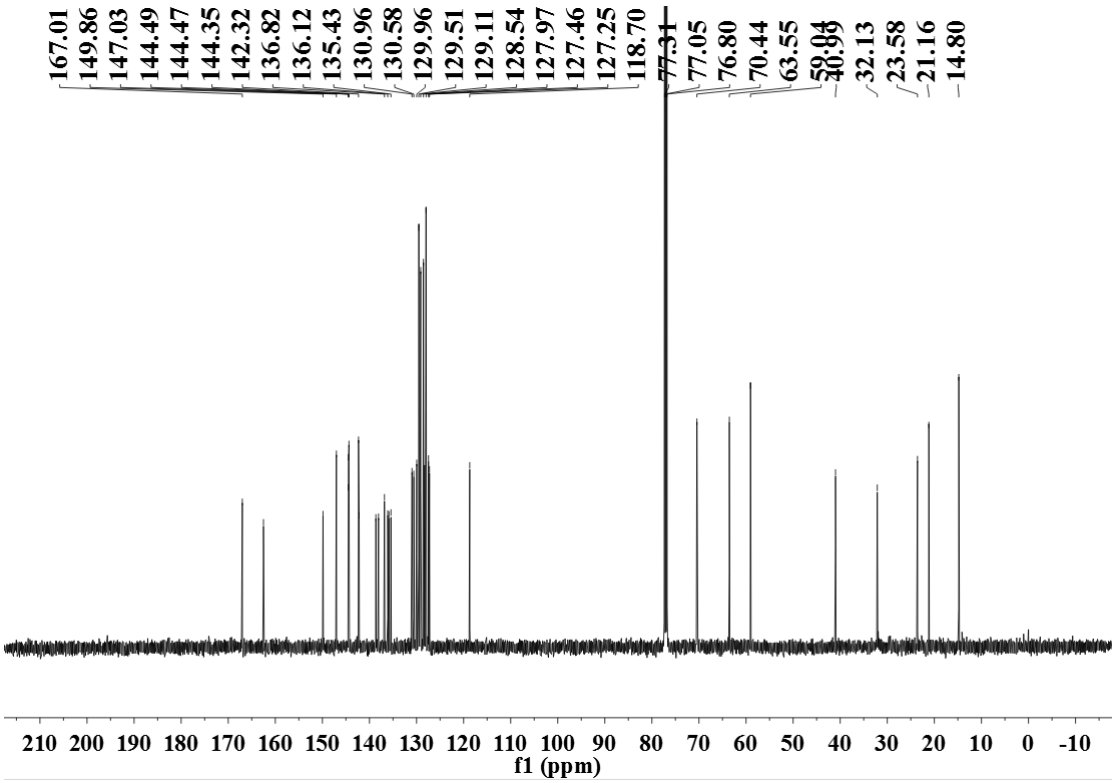

9.38 9.38 8.70 8.70 8.37 8.37 7.20 7.19 7.19 7.11 7.11 7.10 7.10 7.09 7.06 6.99 6.99 6.95 6.95 6.94 6.94 6.93 6.79 6.07 6.04 5.29 4.19 4.18 3.56 3.55 3.55 3.33 2.72 0.99 0.98 0.96
PC
NH
O
O
OMe
F
Me
Ph
Ph
1.00 1.00 1.00 1.00 3.00 5.00 2.00 3.00 1.00 1.00 1.00 1.00 1.00 2.00 2.00 3.00 2.00 2.00 3.00
f1 (ppm)
166.85 162.73 148.52 147.22 144.37 144.24 143.85 142.40 141.81 138.46 137.31 135.87 132.36 132.30 131.18 129.53 129.02 128.68 128.06 127.64 127.46 119.37 115.77 115.60 114.62 114.45 77.32 77.07 76.82 70.41 63.58 59.02 40.68 32.11 23.65 14.80
f1 (ppm)

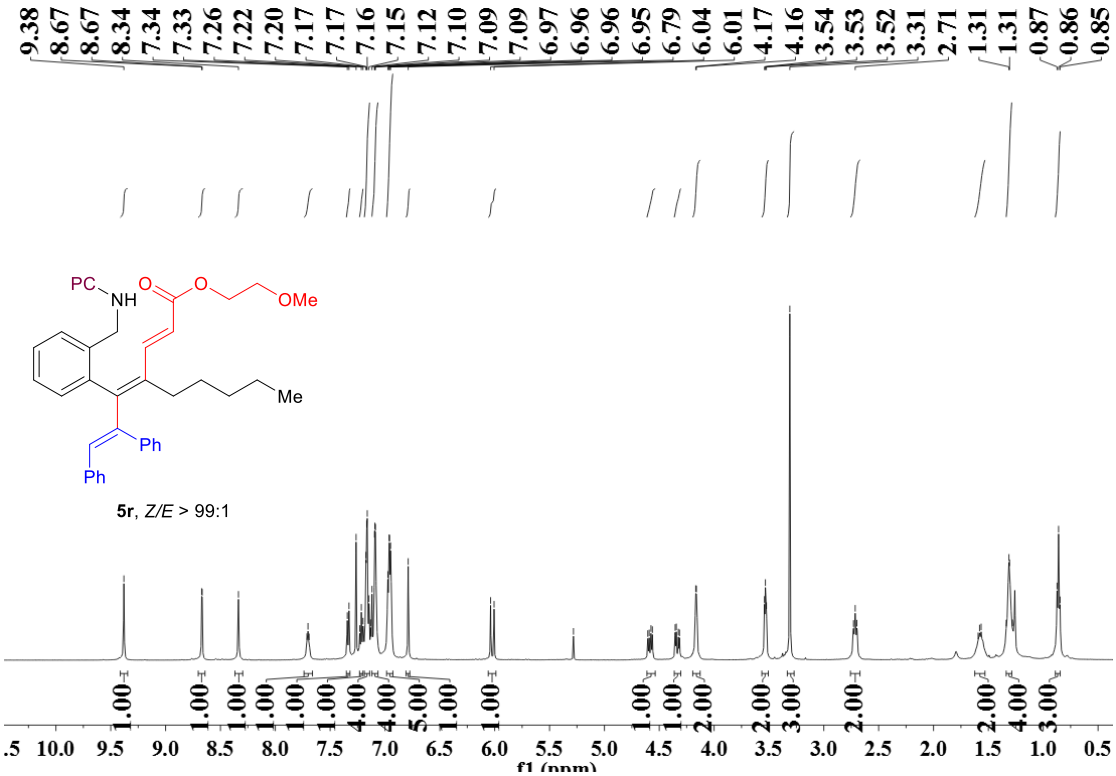
5p, *Z*/*E*= 98:2

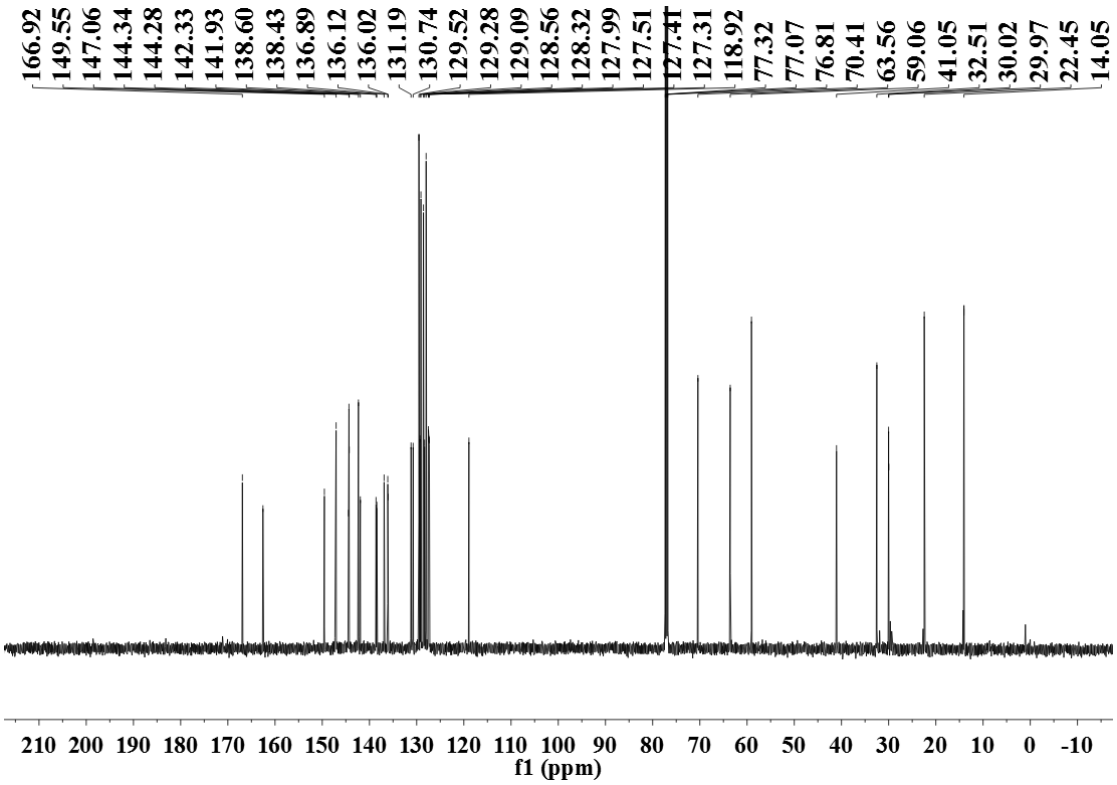

-113.18
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)

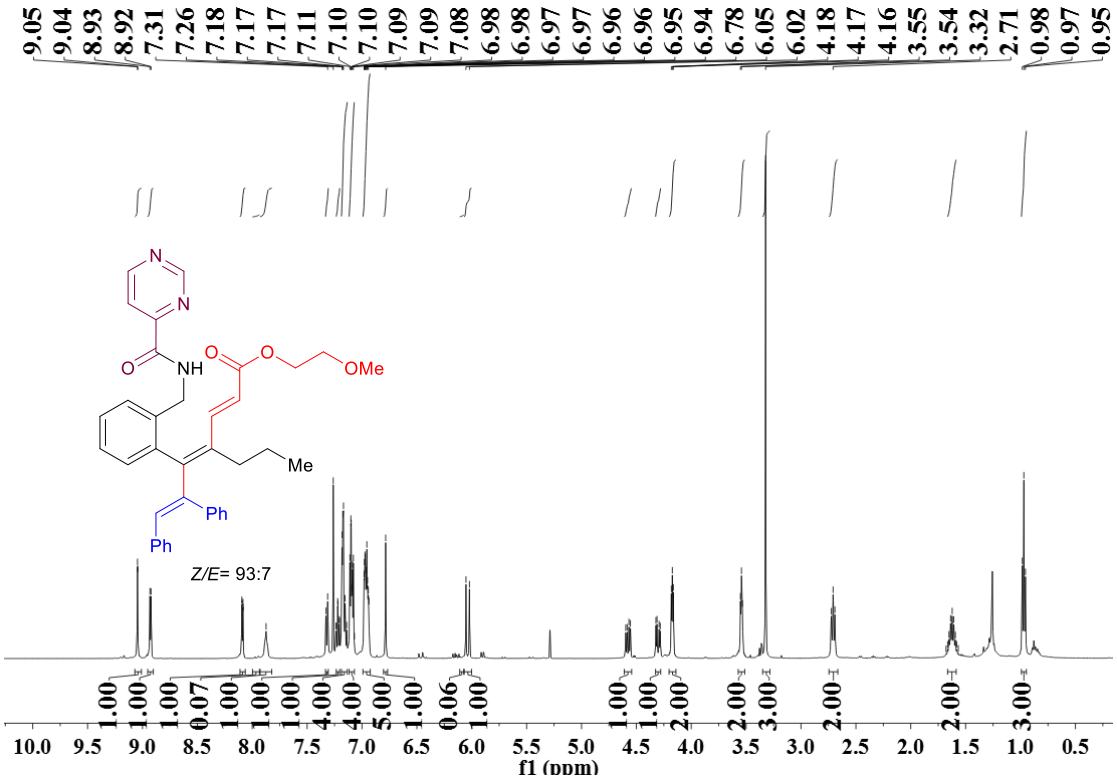

9.38 8.67 8.67 8.34 7.17 7.17 7.16 7.14 7.12 7.11 7.09 7.08 6.97 6.96 6.95 6.85 6.84 6.75 6.04 6.00 5.29 4.18 4.17 4.16 3.55 3.54 3.53 3.32 2.70 2.68 2.66 2.27 1.60 0.97 0.95 0.94
PC
NH
O
O
OMe
Me
Me
Ph
Ph
1.00 1.00 1.00 1.00 8.00 5.00 1.00 1.00 1.00 1.00 1.00 2.00 2.00 3.00 2.00 3.00 2.00 3.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

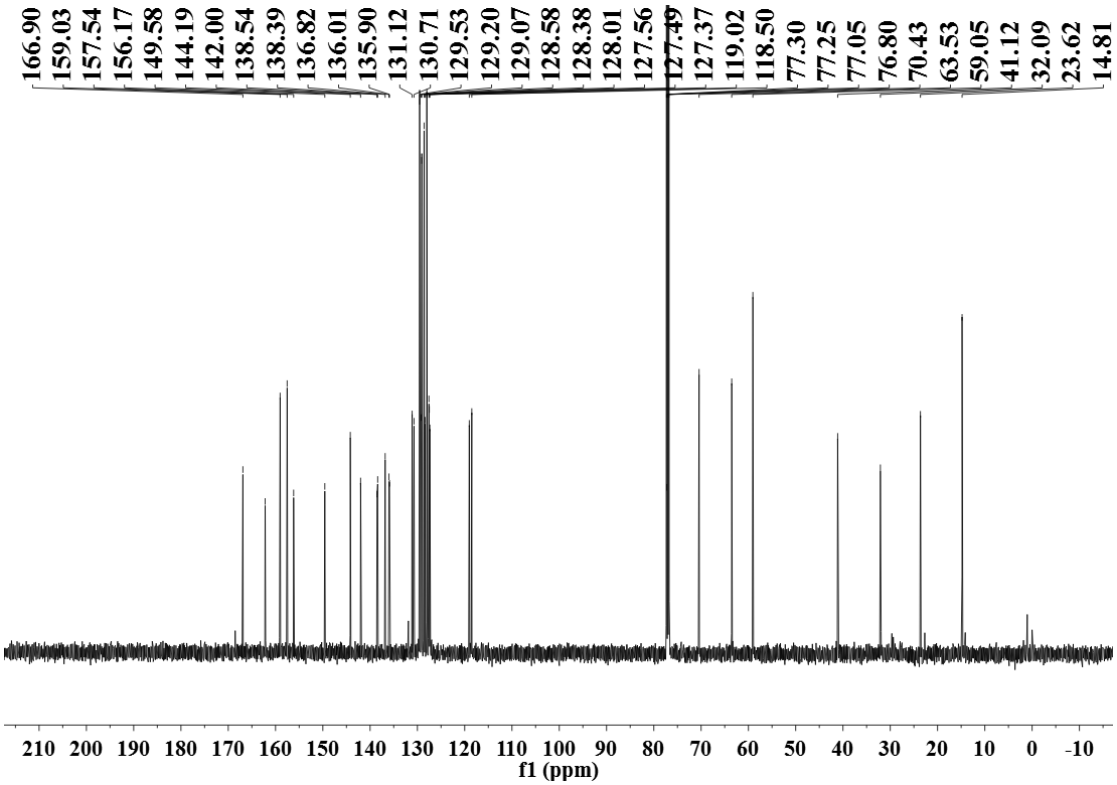
5q, *Z*/*E* > 99:1


167.01
149.86
147.03
144.49
144.47
144.35
142.32
136.82
136.12
135.43
130.96
130.58
129.96
129.51
129.11
128.54
127.97
127.46
127.25
118.70
77.31
77.05
76.80
70.44
63.55
59.04
40.99
32.13
23.58
21.16
14.80
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

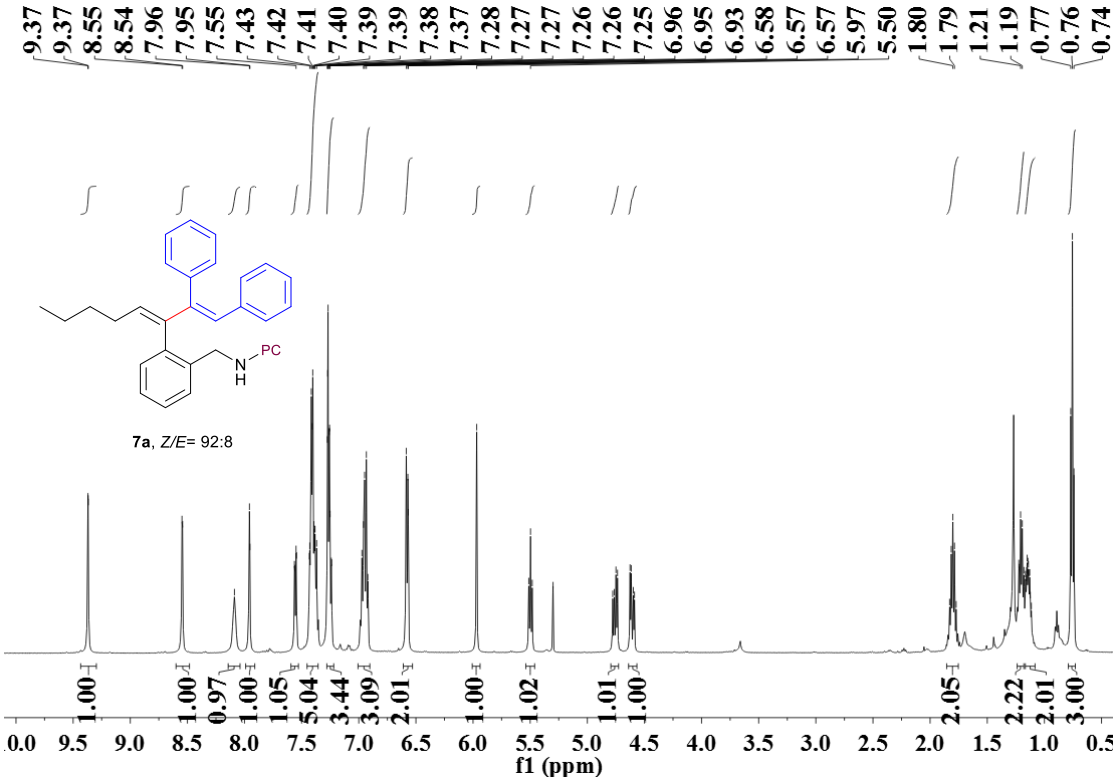

9.38
8.67
8.67
8.34
7.34
7.33
7.26
7.22
7.20
7.17
7.17
7.16
7.15
7.12
7.10
7.09
7.09
6.97
6.96
6.96
6.95
6.79
6.04
6.01
4.17
4.16
3.54
3.53
3.52
3.31
2.71
1.31
1.31
0.87
0.86
0.85
PC
NH
O
O
OMe
Me
Ph
Ph
5r, Z/E > 99:1
1.00
1.00
1.00
1.00
1.00
4.00
4.00
5.00
1.00
1.00
1.00
1.00
2.00
2.00
3.00
2.00
2.00
4.00
3.00
.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

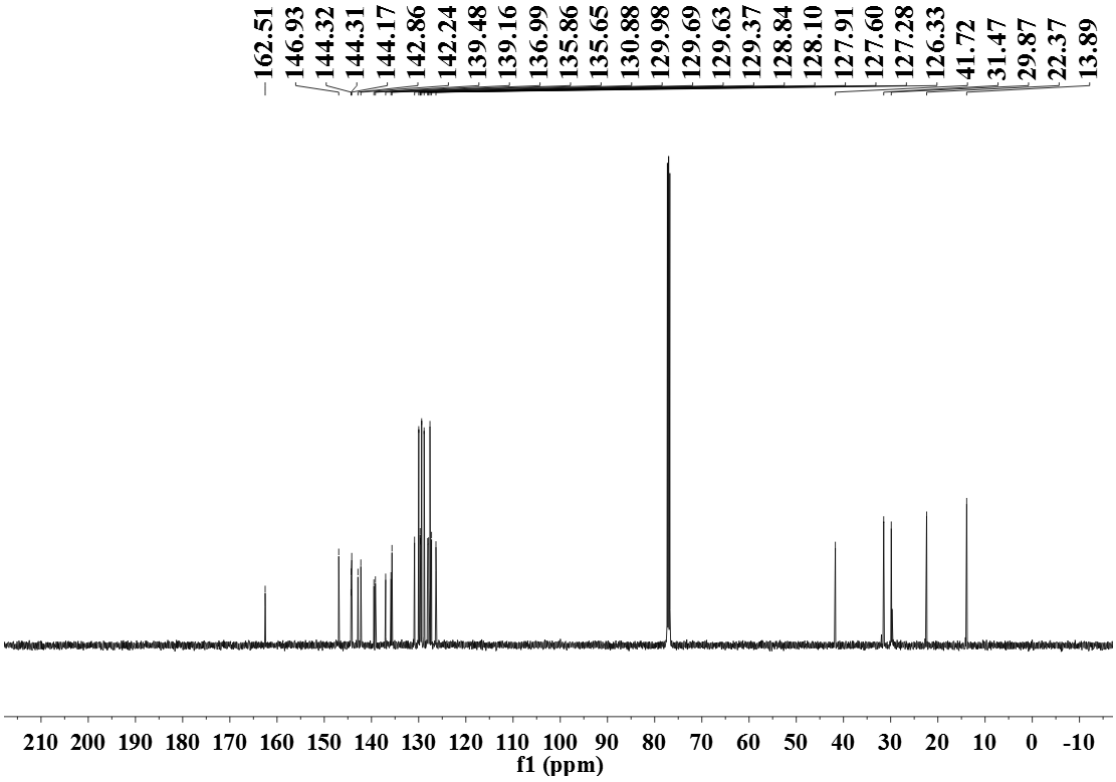

166.92
149.55
147.06
144.34
144.28
142.33
141.93
138.60
138.43
136.89
136.12
136.02
131.19
130.74
129.52
129.28
129.09
128.56
128.32
127.99
127.51
127.41
127.31
118.92
77.32
77.07
76.81
70.41
63.56
59.06
41.05
32.51
30.02
29.97
22.45
14.05
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

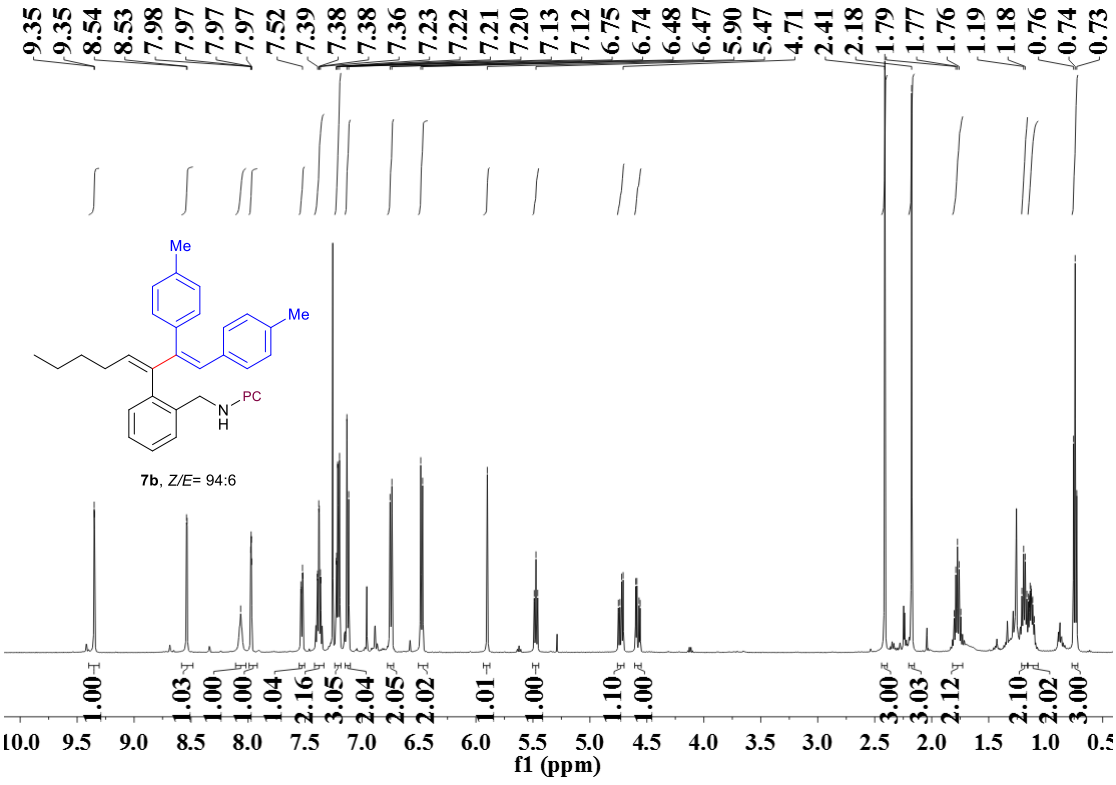

9.05
9.04
8.93
8.92
7.31
7.26
7.18
7.17
7.17
7.11
7.10
7.10
7.09
7.09
7.08
6.98
6.98
6.97
6.97
6.96
6.96
6.95
6.94
6.78
6.05
6.02
4.18
4.17
4.16
3.55
3.54
3.32
2.71
0.98
0.97
0.95
N
N
O
NH
O
O
OMe
Me
Ph
Ph
Z/E= 93:7
1.00
1.00
1.00
0.07
1.00
1.00
1.00
4.00
4.00
5.00
1.00
0.06
1.00
1.00
1.00
2.00
2.00
3.00
2.00
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

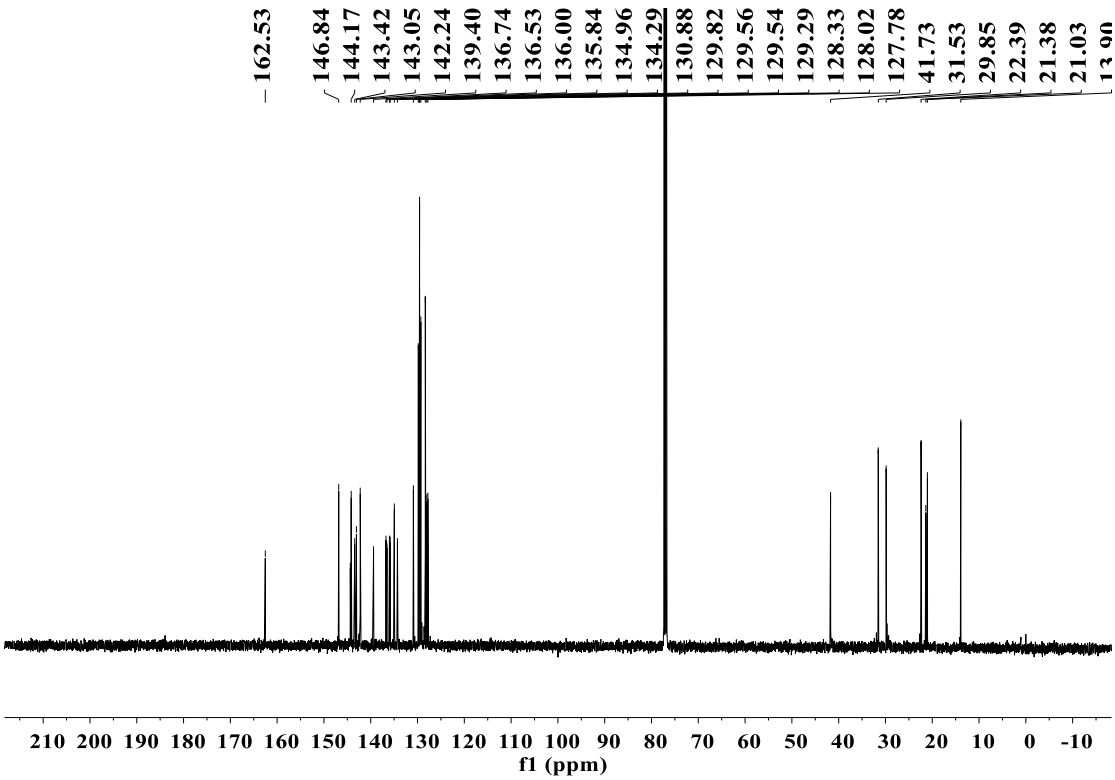


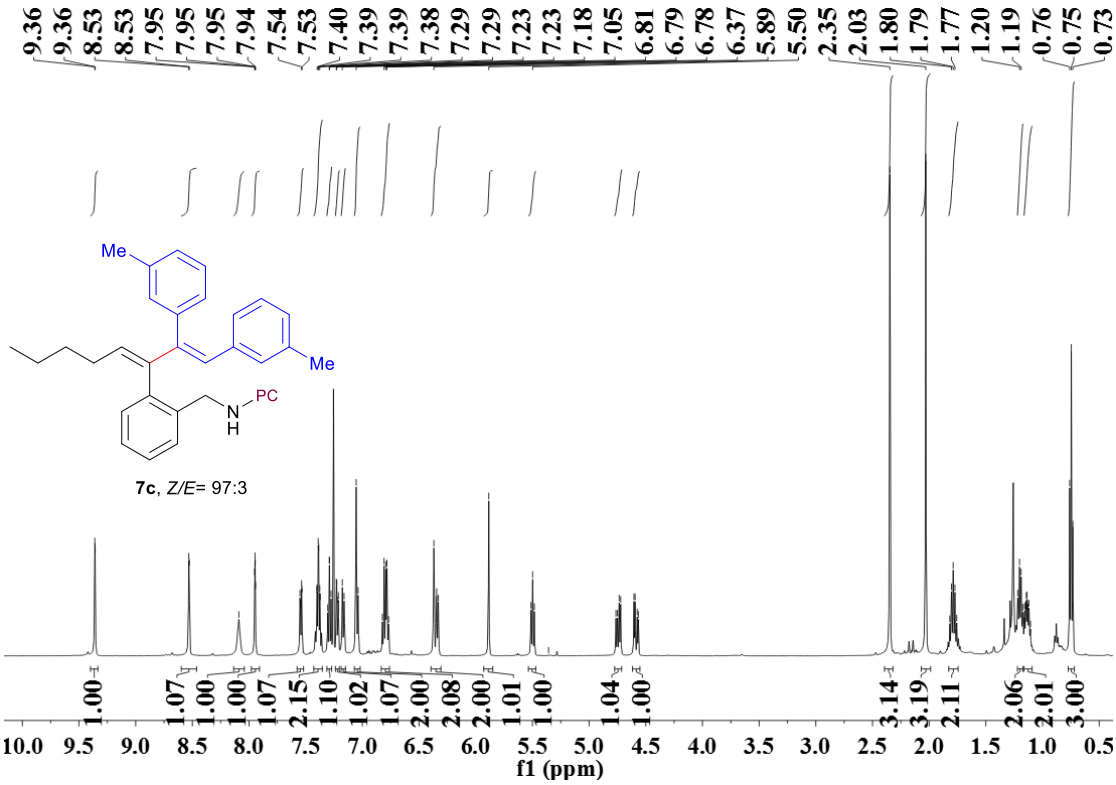
8.3 NMR Spectra of the Products 7

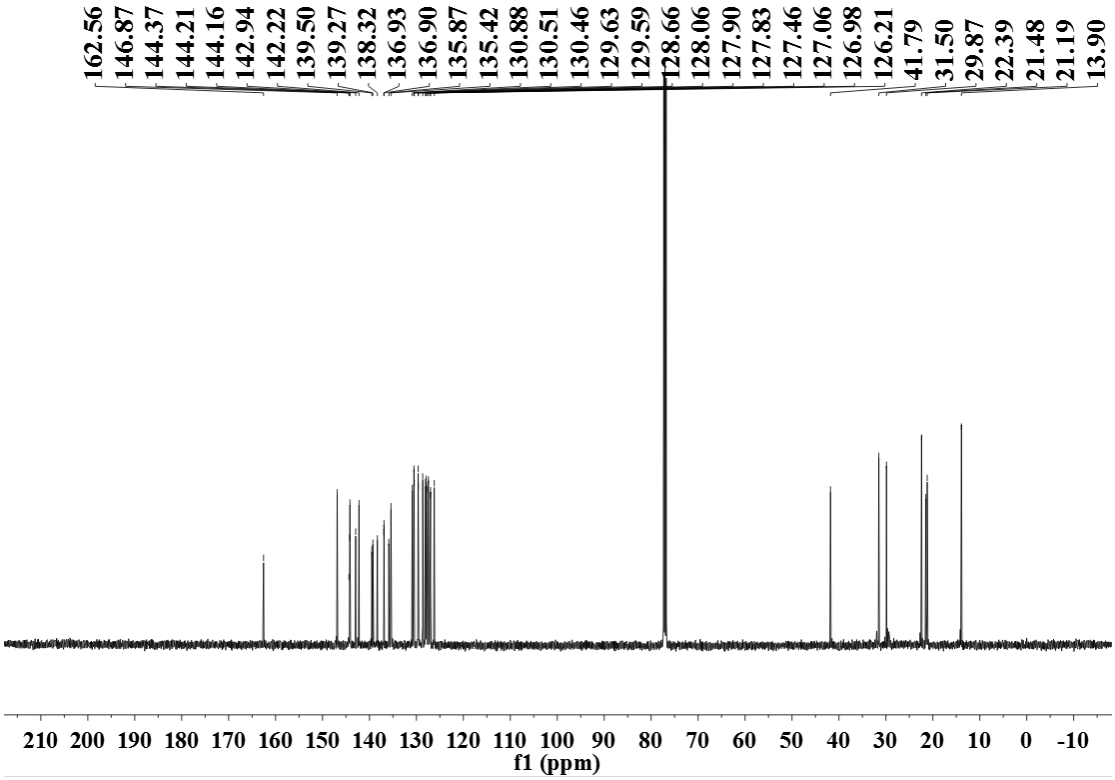


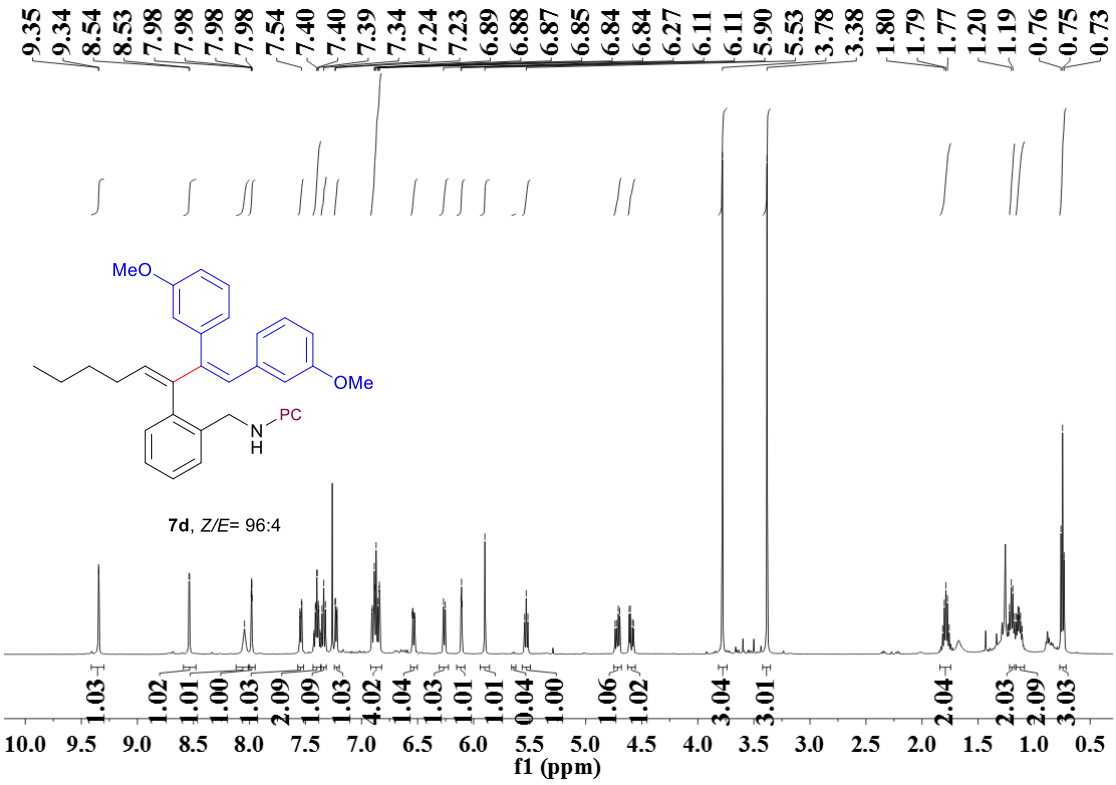

162.51
146.93
144.32
144.31
144.17
142.86
142.24
139.48
139.16
136.99
135.86
135.65
130.88
129.98
129.69
129.63
129.37
128.84
128.10
127.91
127.60
127.28
126.33
41.72
31.47
29.87
22.37
13.89
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

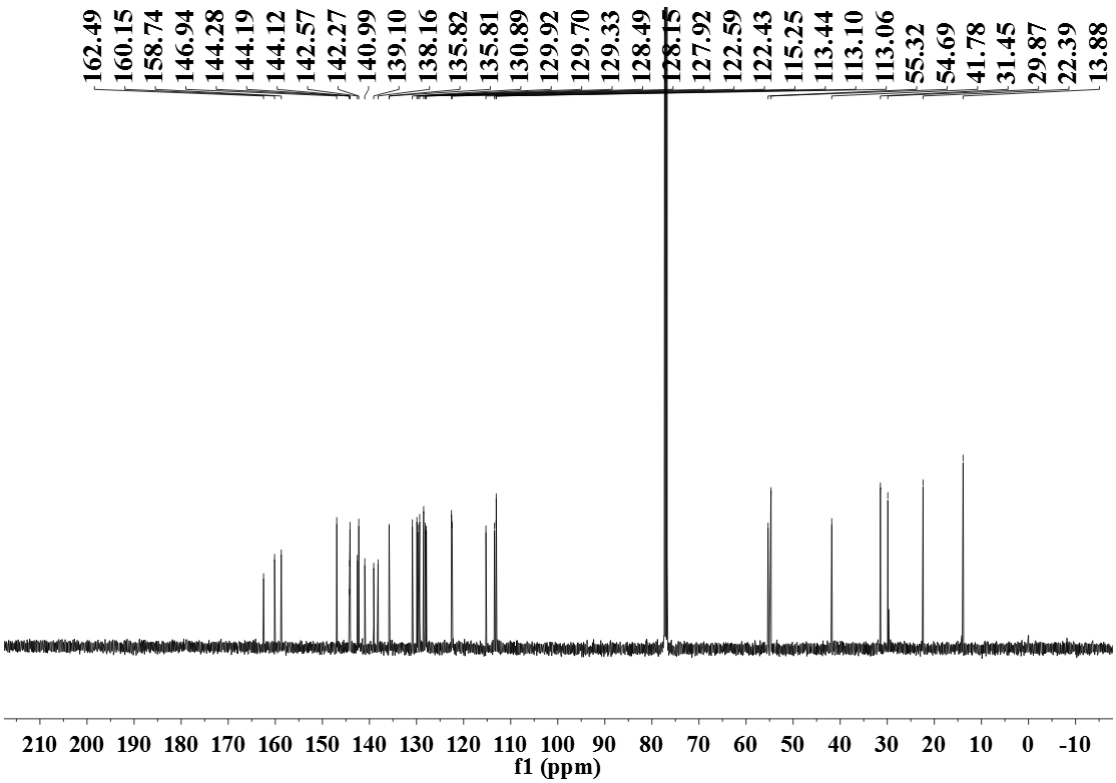

9.35
9.35
8.54
8.53
7.98
7.97
7.97
7.97
7.52
7.39
7.38
7.38
7.36
7.23
7.22
7.21
7.20
7.13
7.12
6.75
6.74
6.48
6.47
5.90
5.47
4.71
2.41
2.18
1.79
1.77
1.76
1.19
1.18
0.76
0.74
0.73
Me
Me
N
H
PC
7b, Z/E= 94:6
1.00
1.03
1.00
1.00
1.04
2.16
3.05
2.04
2.05
2.02
1.01
1.00
1.10
1.00
3.00
3.03
2.12
2.10
2.02
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

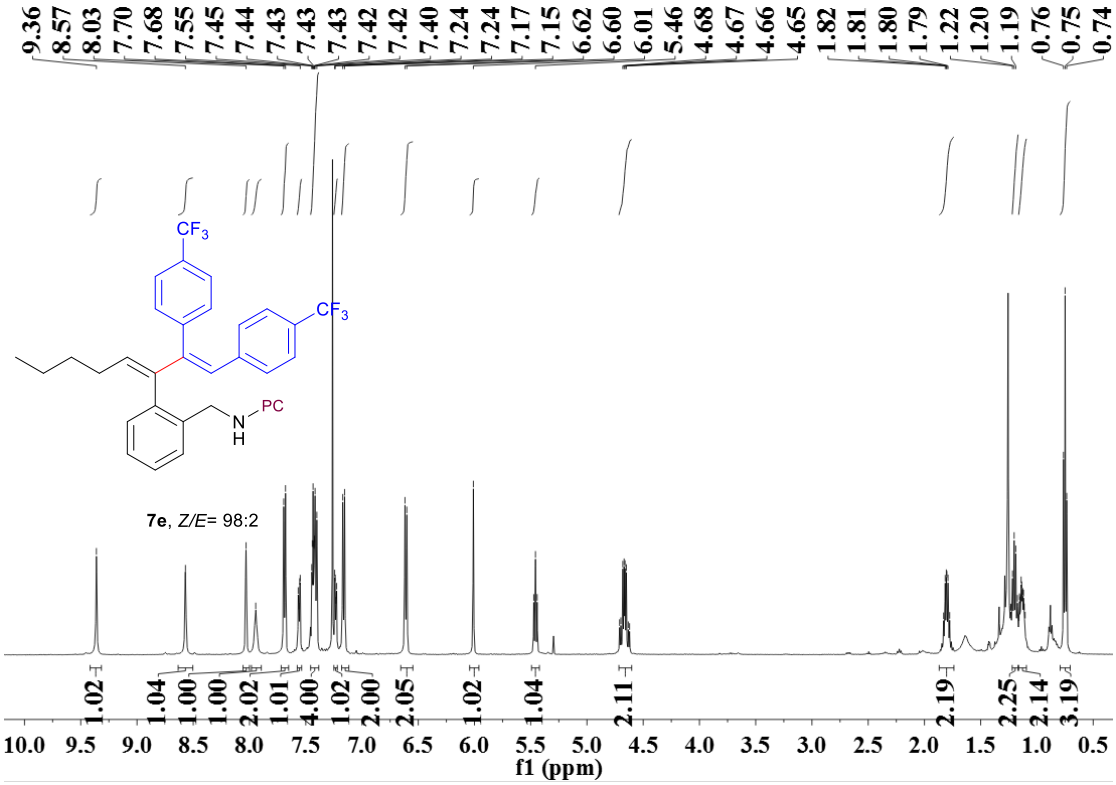

162.53
146.84
144.17
143.42
143.05
142.24
139.40
136.74
136.53
136.00
135.84
134.96
134.29
130.88
129.82
129.56
129.54
129.29
128.33
128.02
127.78
41.73
31.53
29.85
22.39
21.38
21.03
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

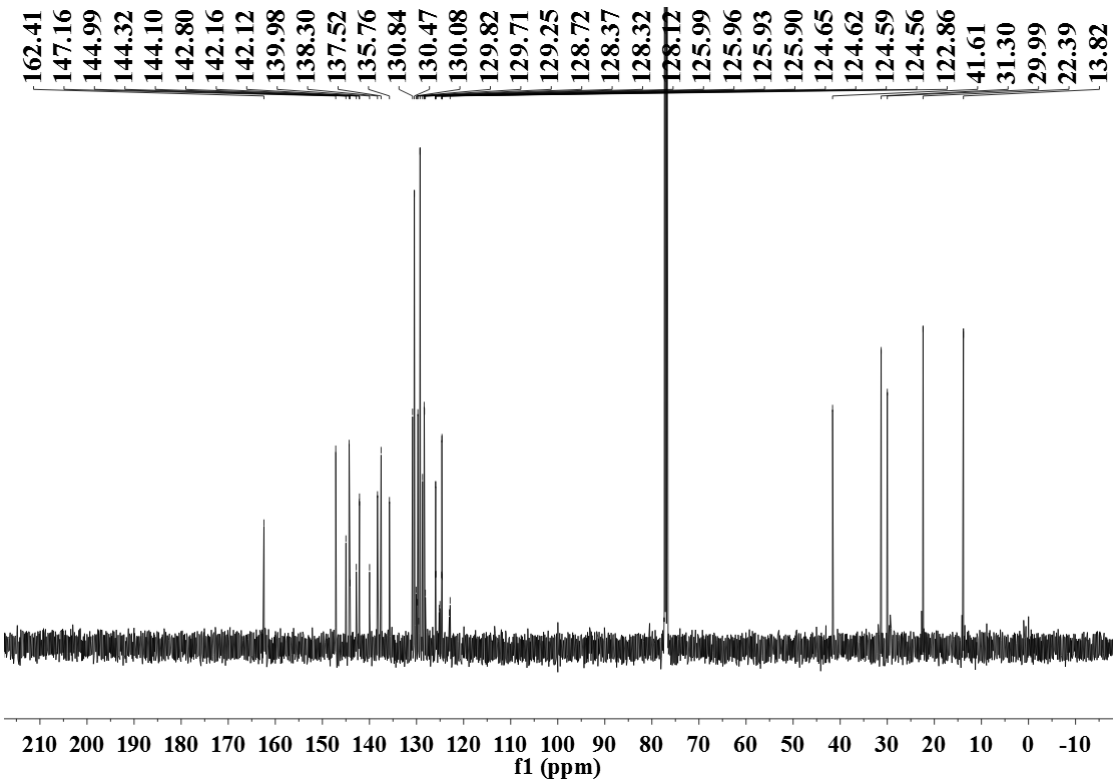

9.36
9.36
8.53
8.53
7.95
7.95
7.95
7.94
7.54
7.53
7.40
7.39
7.39
7.38
7.29
7.29
7.23
7.23
7.18
7.05
6.81
6.79
6.78
6.37
5.89
5.50
2.35
2.03
1.80
1.79
1.77
1.20
1.19
0.76
0.75
0.73
Me
Me
N
H
PC
7c, Z/E= 97:3
1.00
1.07
1.00
1.00
1.07
2.15
1.10
1.02
1.07
2.00
2.08
2.00
1.01
1.00
1.04
1.00
3.14
3.19
2.11
2.06
2.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

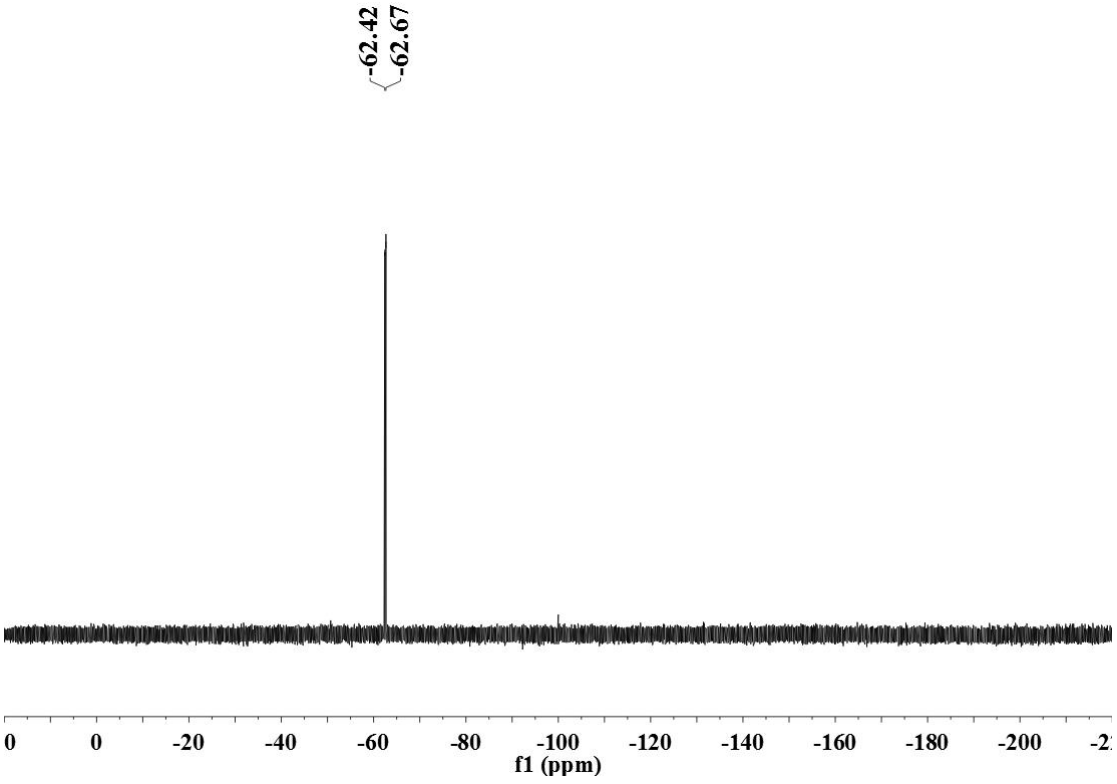

162.56
146.87
144.37
144.21
144.16
142.94
142.22
139.50
139.27
138.32
136.93
136.90
135.87
135.42
130.88
130.51
130.46
129.63
129.59
128.66
128.06
127.90
127.83
127.46
127.06
126.98
126.21
41.79
31.50
29.87
22.39
21.48
21.19
13.90
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

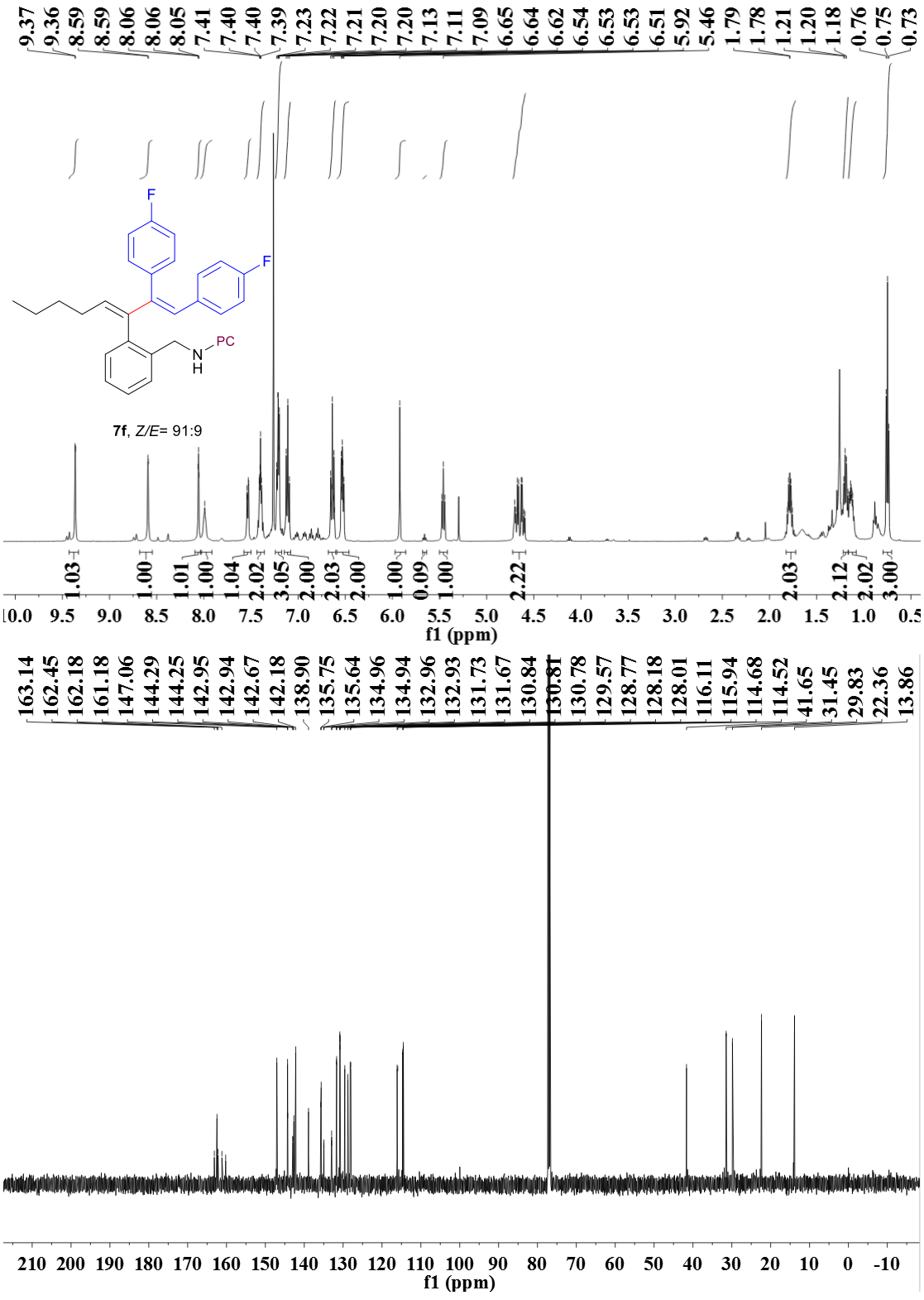

9.35
9.34
8.54
8.53
7.98
7.98
7.98
7.98
7.54
7.40
7.40
7.39
7.34
7.24
7.23
6.89
6.88
6.87
6.85
6.84
6.84
6.27
6.11
6.11
5.90
5.53
3.78
3.38
1.80
1.79
1.77
1.20
1.19
0.76
0.75
0.73
MeO
OMe
PC
N
H
7d, Z/E= 96:4
1.03
1.02
1.01
1.00
1.03
2.09
1.09
1.03
4.02
1.04
1.03
1.01
1.01
0.04
1.00
1.06
1.02
3.04
3.01
2.04
2.03
2.09
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

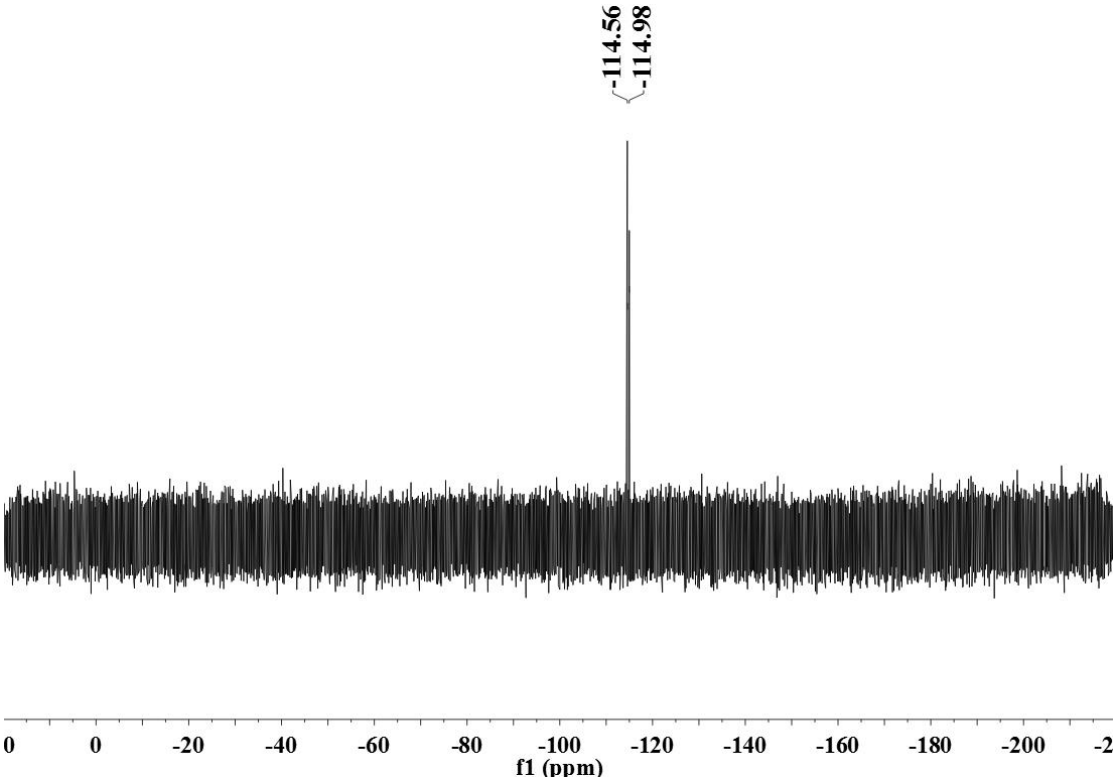

162.49
160.15
158.74
146.94
144.28
144.19
144.12
142.57
142.27
140.99
139.10
138.16
135.82
135.81
130.89
129.92
129.70
129.33
128.49
128.15
127.92
122.59
122.43
115.25
113.44
113.10
113.06
55.32
54.69
41.78
31.45
29.87
22.39
13.88
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

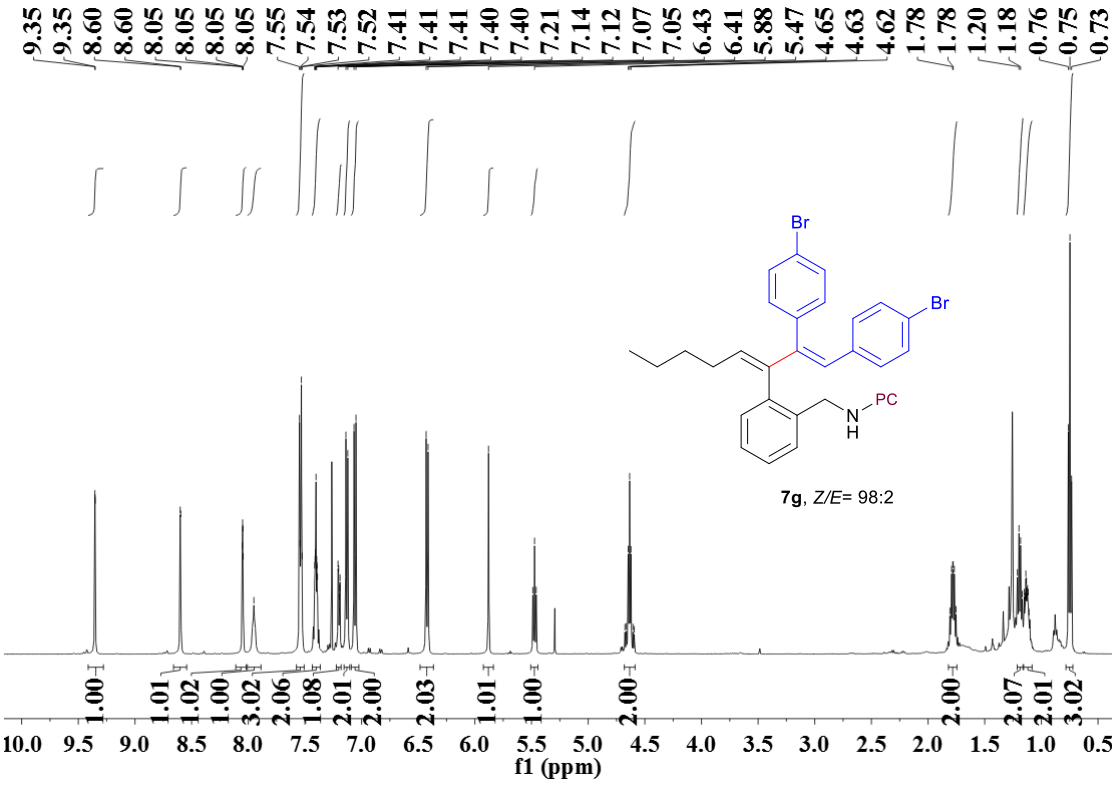

9.36
8.57
8.03
7.70
7.68
7.55
7.45
7.44
7.43
7.43
7.43
7.42
7.42
7.40
7.24
7.24
7.17
7.15
6.62
6.60
6.01
5.46
4.68
4.67
4.66
4.65
1.82
1.81
1.80
1.79
1.22
1.20
1.19
0.76
0.75
0.74
CF3
CF3
PC
N
H
7e, Z/E= 98:2
1.02
1.04
1.00
1.00
2.02
1.01
4.00
1.02
2.00
2.05
1.02
1.04
2.11
2.19
2.25
2.14
3.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


162.41
147.16
144.99
144.32
144.10
142.80
142.16
142.12
139.98
138.30
137.52
135.76
130.84
130.47
130.08
129.82
129.71
129.25
128.72
128.37
128.32
128.12
125.99
125.96
125.93
125.90
124.65
124.62
124.59
124.56
122.86
41.61
31.30
29.99
22.39
13.82
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

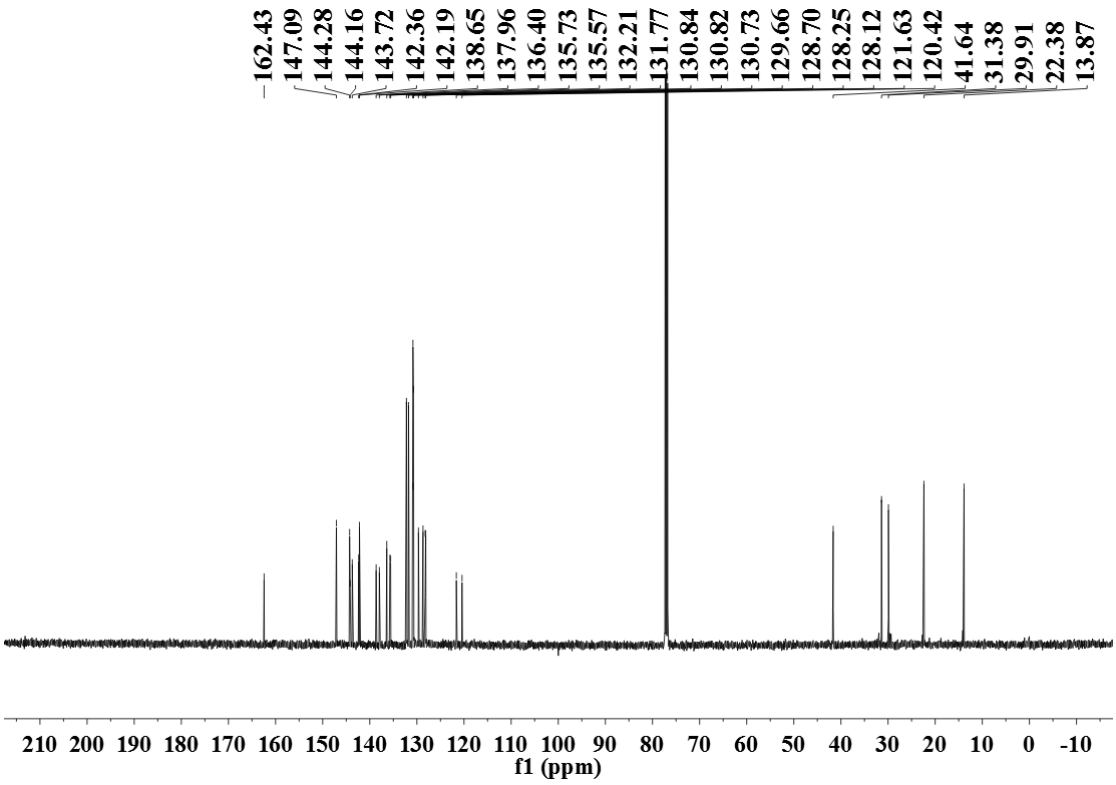

-62.42
-62.67
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

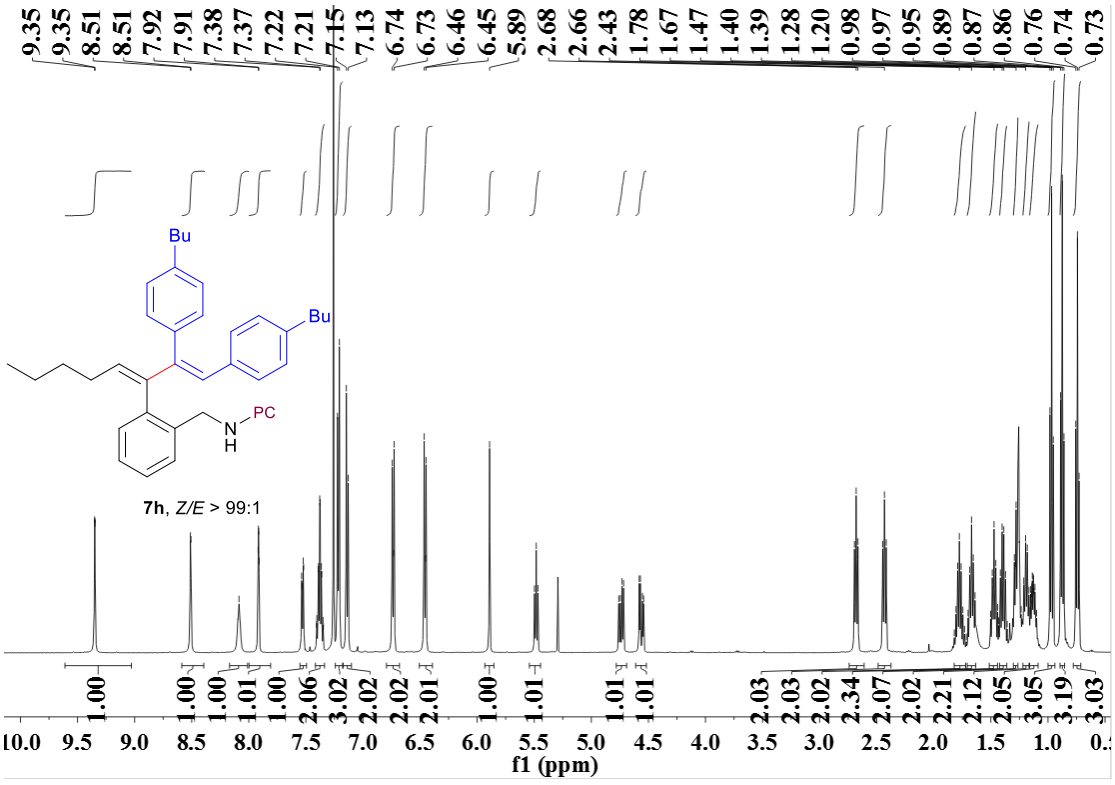

9.37 9.36 8.59 8.59 8.06 8.06 8.05 7.41 7.40 7.40 7.39 7.23 7.22 7.21 7.20 7.20 7.13 7.11 7.09 6.65 6.64 6.62 6.54 6.53 6.53 6.51 5.92 5.46 1.79 1.78 1.21 1.20 1.18 0.76 0.75 0.73
F
F
PC
N
H
7f, Z/E= 91:9
1.03 1.00 1.01 1.00 1.04 2.02 3.05 2.00 2.03 2.00 1.00 0.09 1.00 2.22 2.03 2.12 2.02 3.00
f1 (ppm)
163.14 162.45 162.18 161.18 147.06 144.29 144.25 142.95 142.94 142.67 142.18 138.90 135.75 135.64 134.96 134.94 132.96 132.93 131.73 131.67 130.84 130.81 130.78 129.57 128.77 128.18 128.01 116.11 115.94 114.68 114.52 41.65 31.45 29.83 22.36 13.86
f1 (ppm)

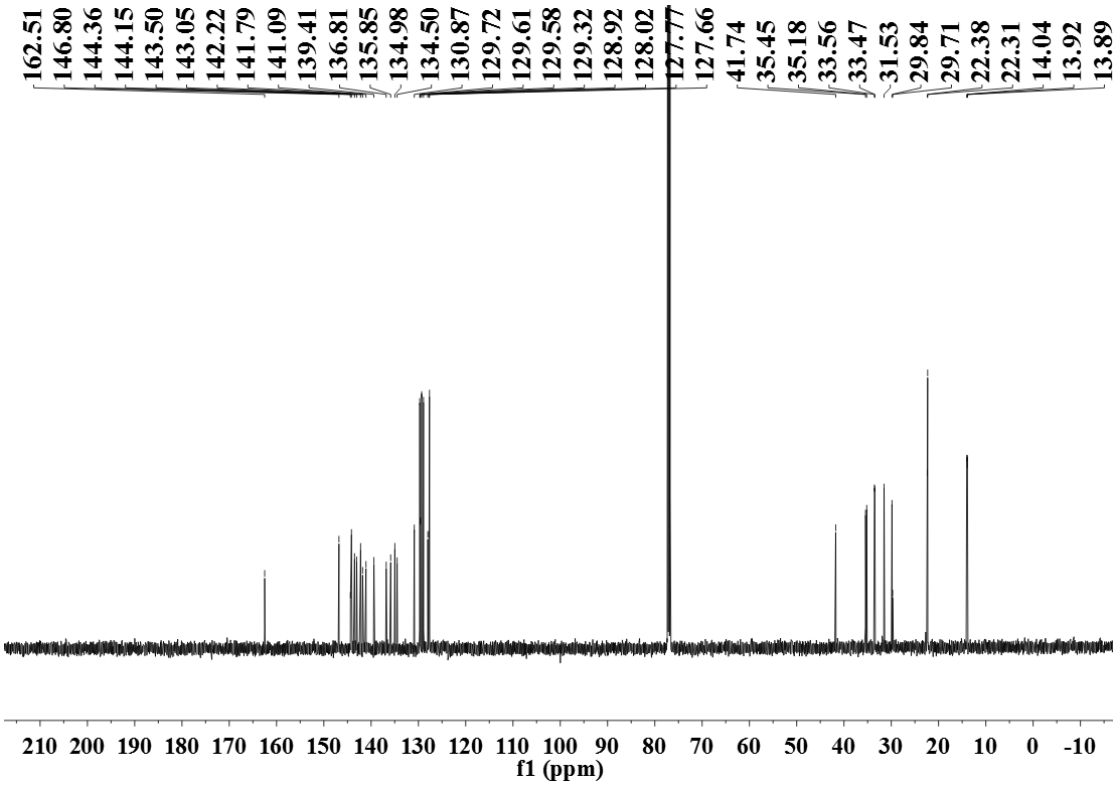

-114.56
-114.98
0
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-2
f1 (ppm)

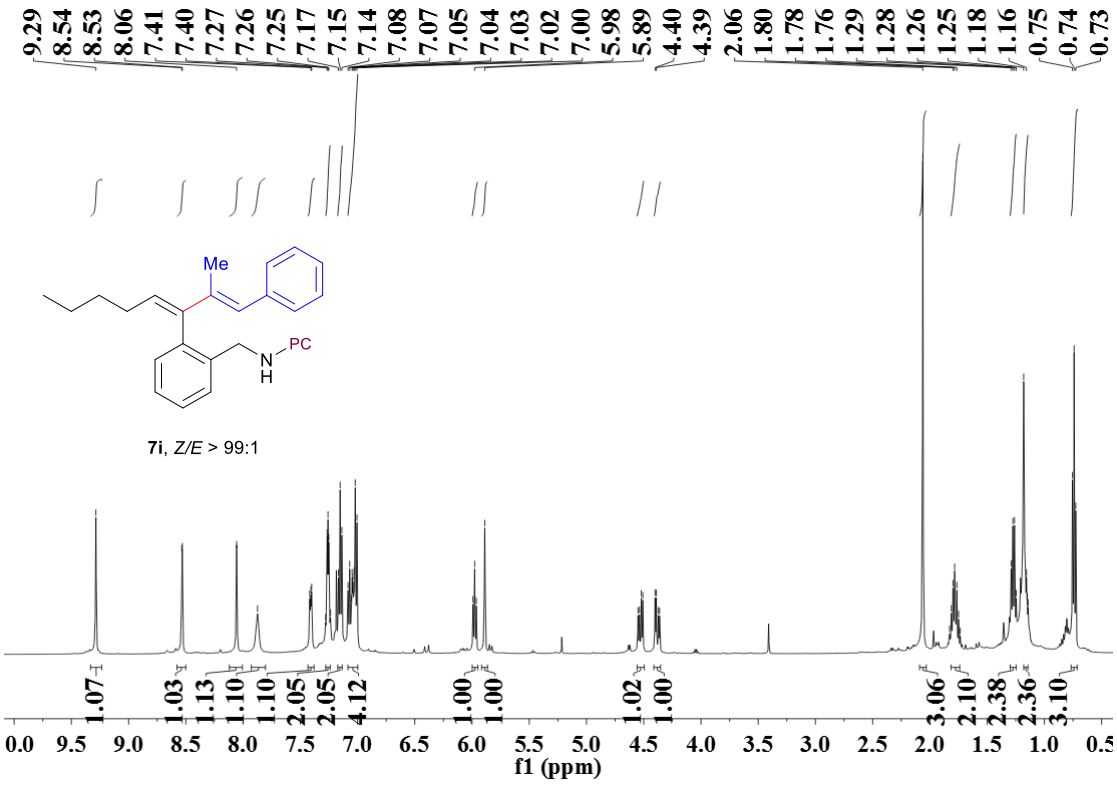

9.35
9.35
8.60
8.60
8.05
8.05
8.05
8.05
7.55
7.54
7.53
7.52
7.41
7.41
7.41
7.40
7.40
7.21
7.14
7.12
7.07
7.05
6.43
6.41
5.88
5.47
4.65
4.63
4.62
1.78
1.78
1.20
1.18
0.76
0.75
0.73
Br
Br
N
H
PC
1.00
1.01
1.02
1.00
3.02
2.06
1.08
2.01
2.00
2.03
1.01
1.00
2.00
2.00
2.07
2.01
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

7g, *Z*/*E*= 98:2

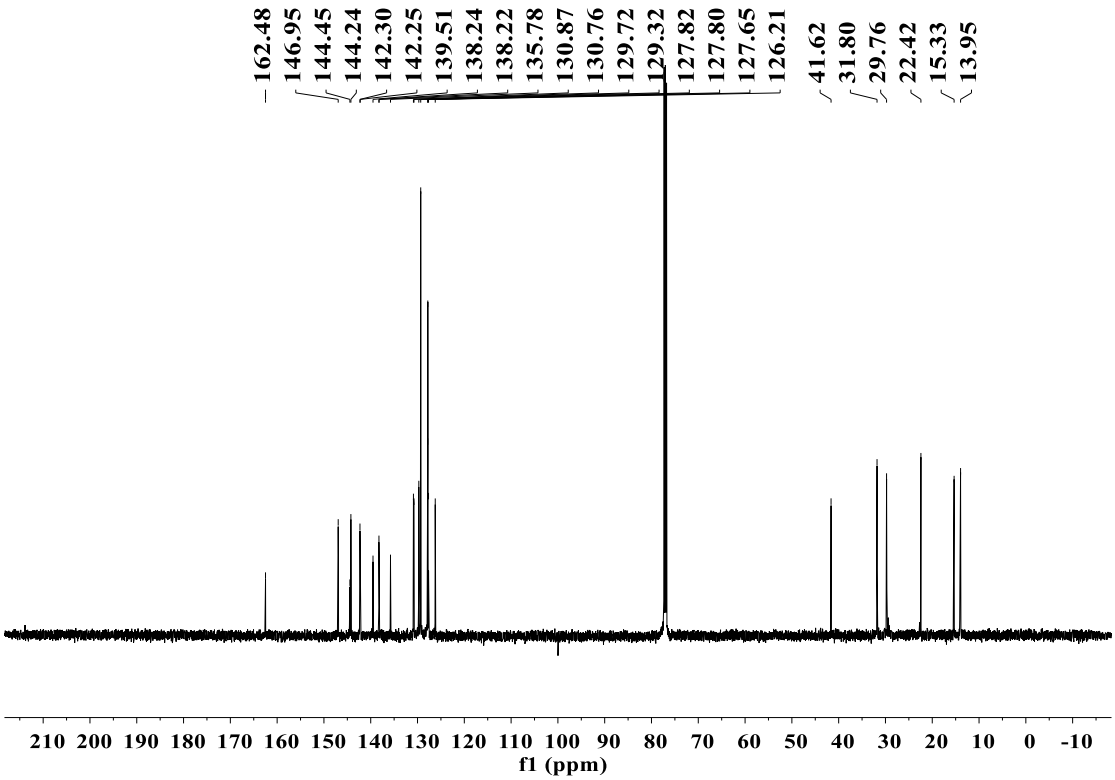

162.43
147.09
144.28
144.16
143.72
142.36
142.19
138.65
137.96
136.40
135.73
135.57
132.21
131.77
130.84
130.82
130.73
129.66
128.70
128.25
128.12
121.63
120.42
41.64
31.38
29.91
22.38
13.87
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

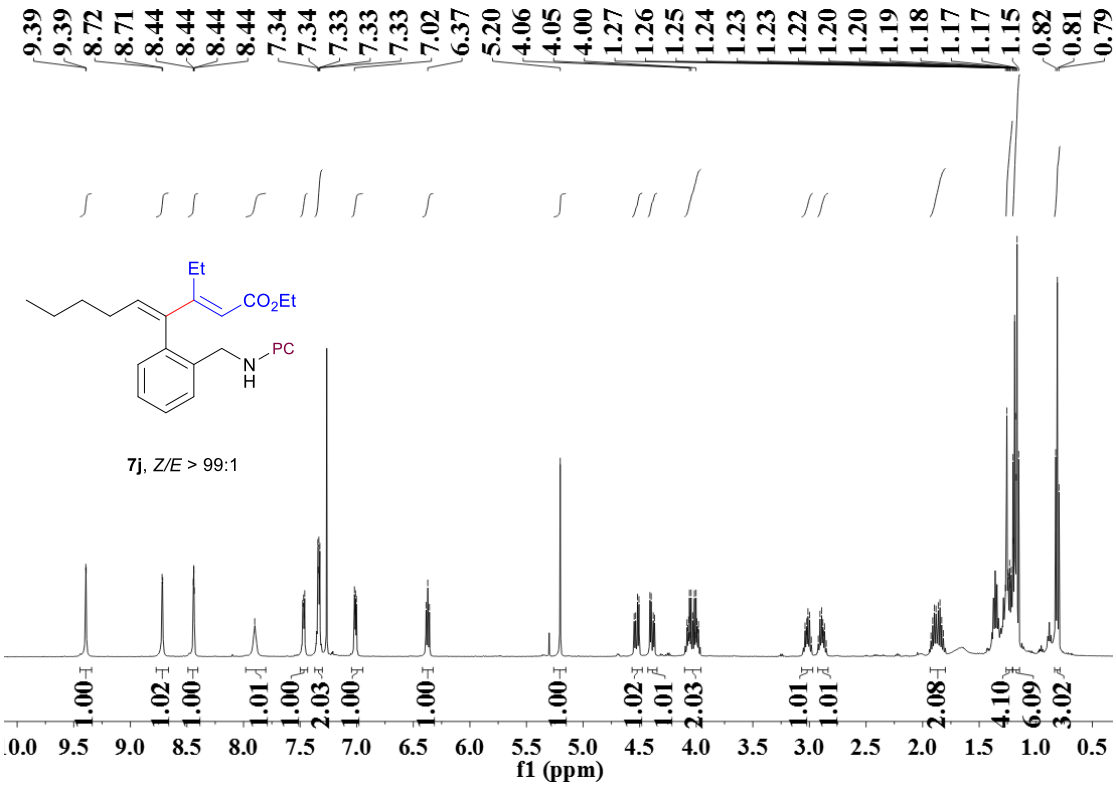

9.35
9.35
8.51
8.51
7.92
7.91
7.38
7.37
7.22
7.21
7.15
7.13
6.74
6.73
6.46
6.45
5.89
2.68
2.66
2.43
1.78
1.67
1.47
1.40
1.39
1.28
1.20
0.98
0.97
0.95
0.89
0.87
0.86
0.76
0.74
0.73
Bu
Bu
N
H
PC
7h, Z/E > 99:1
1.00
1.00
1.00
1.01
1.00
2.06
3.02
2.02
2.02
2.01
1.00
1.01
1.01
1.01
2.03
2.03
2.02
2.34
2.07
2.02
2.21
2.12
2.05
3.05
3.19
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

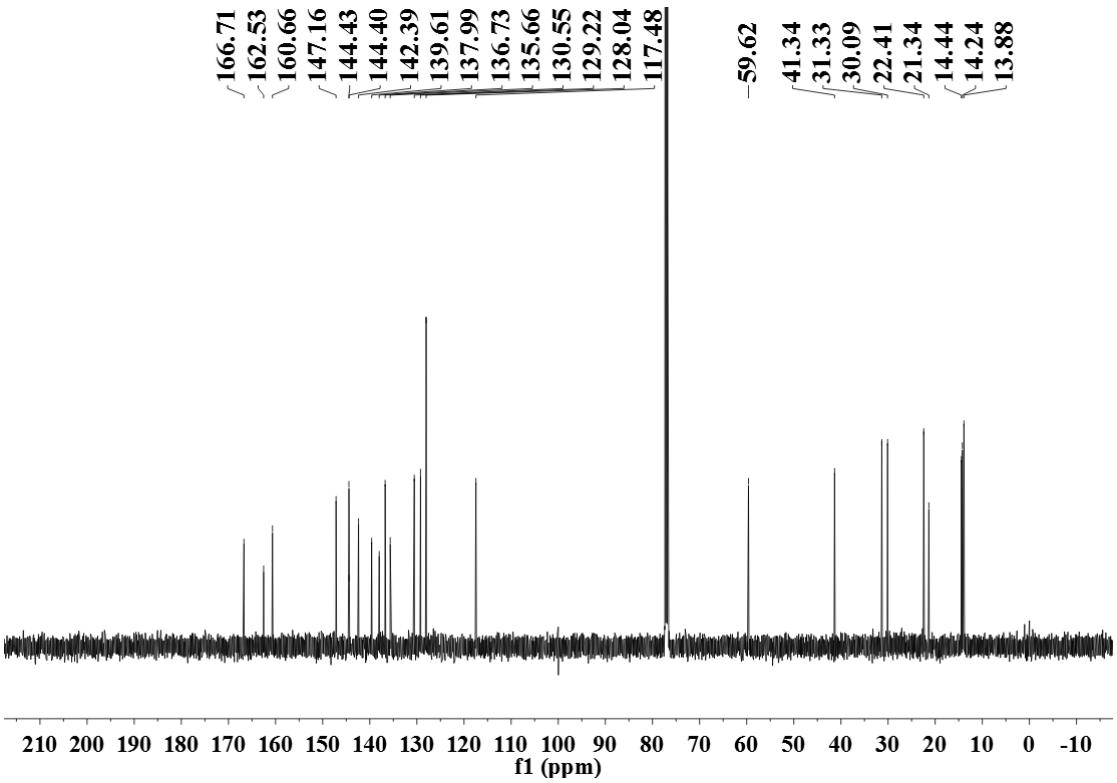

162.51
146.80
144.36
144.15
143.50
143.05
142.22
141.79
141.09
139.41
136.81
135.85
134.98
134.50
130.87
129.72
129.61
129.58
129.32
128.92
128.02
127.77
127.66
41.74
35.45
35.18
33.56
33.47
31.53
29.84
29.71
22.38
22.31
14.04
13.92
13.89
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

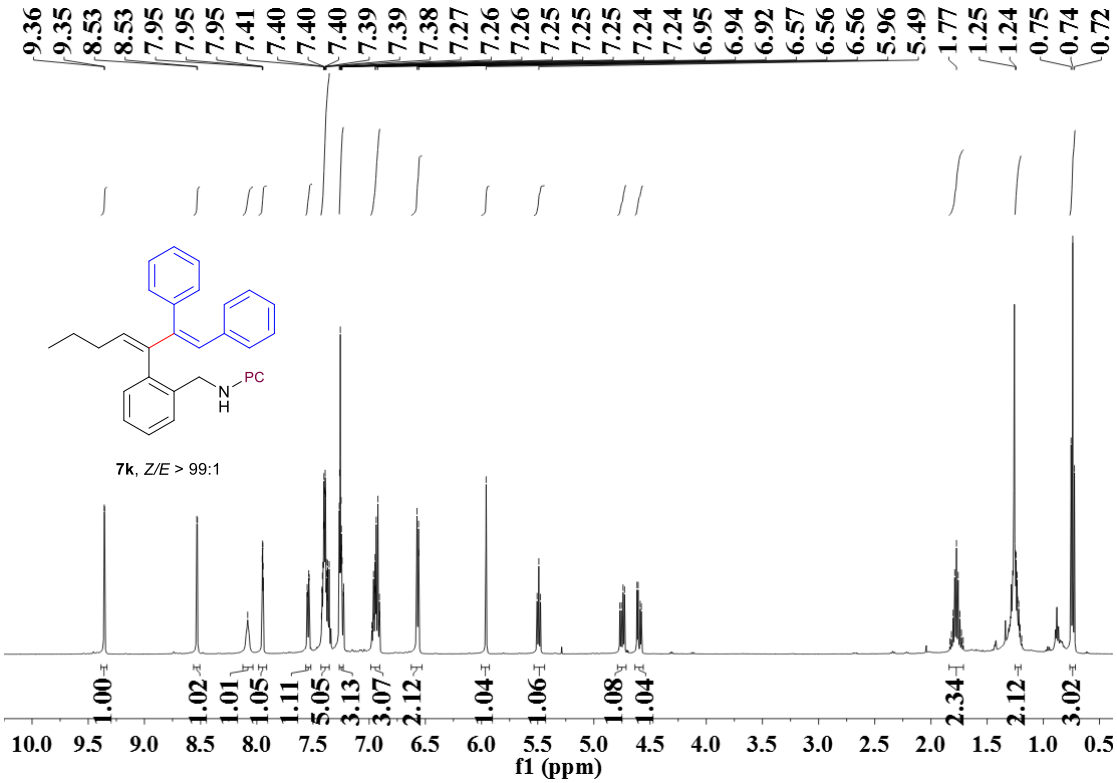

9.29
8.54
8.53
8.06
7.41
7.40
7.27
7.26
7.25
7.17
7.15
7.14
7.08
7.07
7.05
7.04
7.03
7.02
7.00
5.98
5.89
4.40
4.39
2.06
1.80
1.78
1.76
1.29
1.28
1.26
1.25
1.18
1.16
0.75
0.74
0.73
Me
PC
N
H
1.07
1.03
1.13
1.10
1.10
2.05
2.05
4.12
1.00
1.00
1.02
1.00
3.06
2.10
2.38
2.36
3.10
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

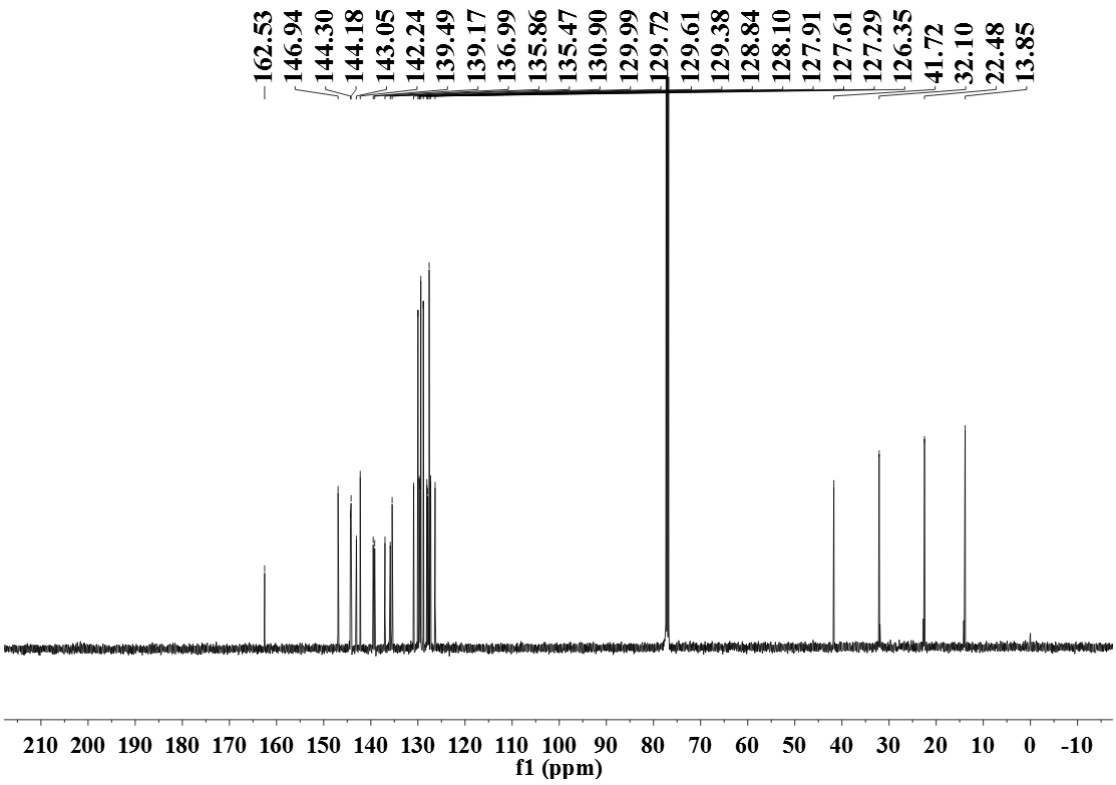
7i, *Z*/*E* > 99:1

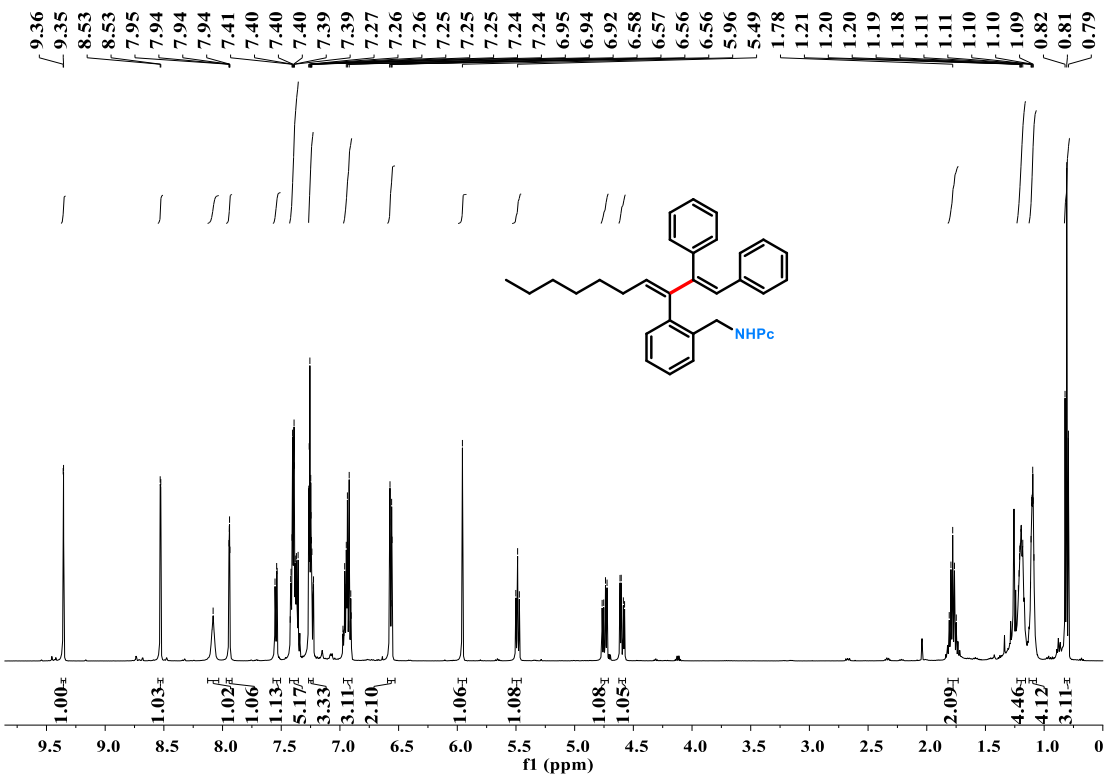

162.48
146.95
144.45
144.24
142.30
142.25
139.51
138.24
138.22
135.78
130.87
130.76
129.72
129.32
127.82
127.80
127.65
126.21
41.62
31.80
29.76
22.42
15.33
13.95
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

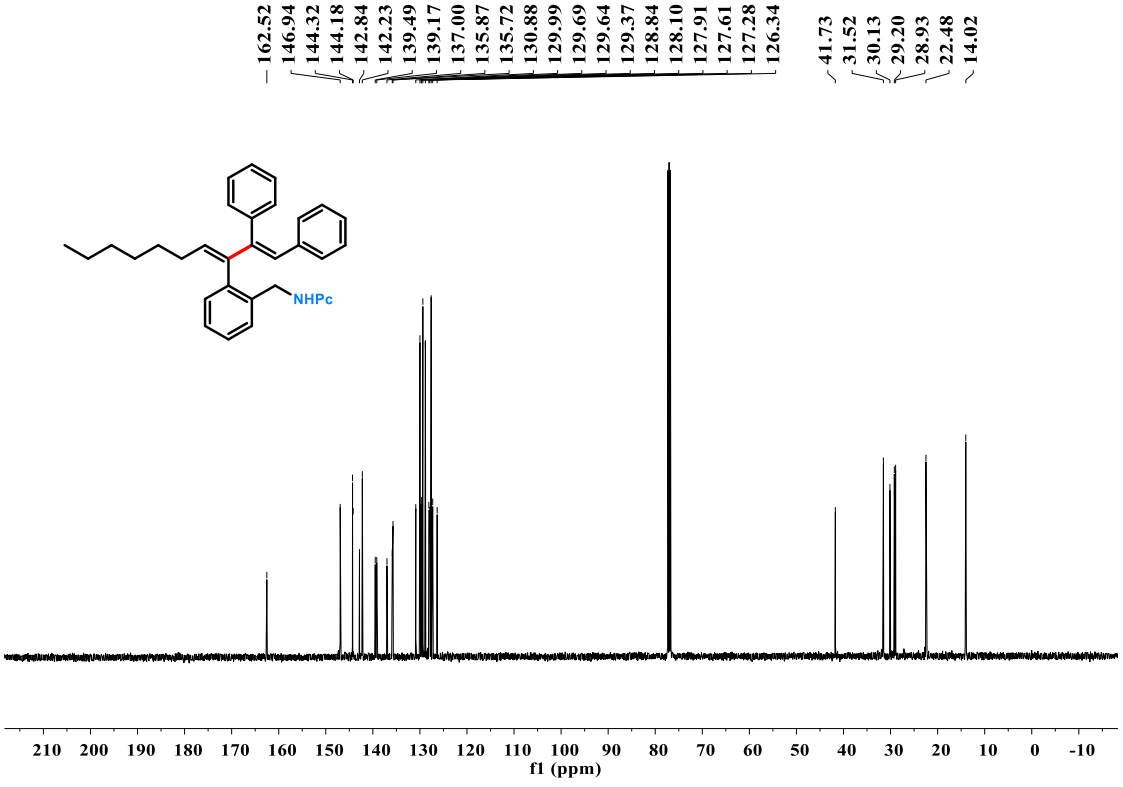

9.39
9.39
8.72
8.71
8.44
8.44
8.44
8.44
7.34
7.34
7.33
7.33
7.33
7.02
6.37
5.20
4.06
4.05
4.00
1.27
1.26
1.25
1.24
1.23
1.23
1.22
1.20
1.20
1.19
1.18
1.17
1.17
1.15
0.82
0.81
0.79
Et
CO2Et
PC
N
H
7j, Z/E > 99:1
1.00
1.02
1.00
1.01
1.00
2.03
1.00
1.00
1.00
1.02
1.01
2.03
1.01
1.01
2.08
4.10
6.09
3.02
.0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

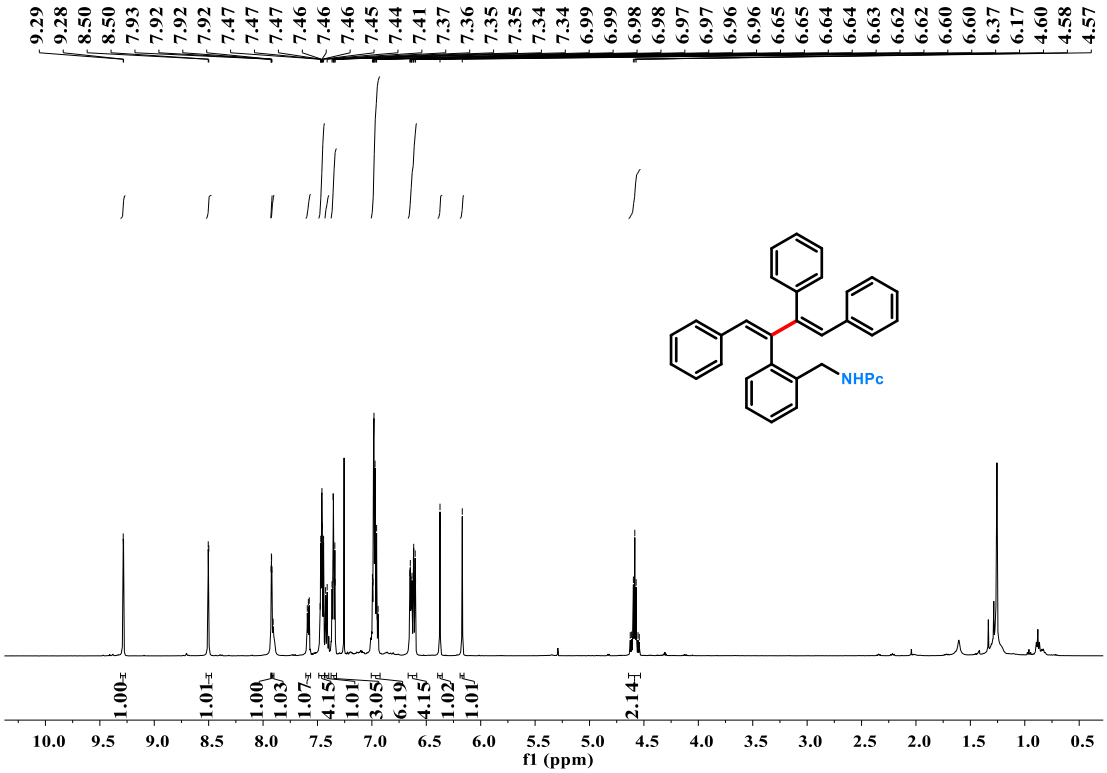

166.71
162.53
160.66
147.16
144.43
144.40
142.39
139.61
137.99
136.73
135.66
130.55
129.22
128.04
117.48
59.62
41.34
31.33
30.09
22.41
21.34
14.44
14.24
13.88
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

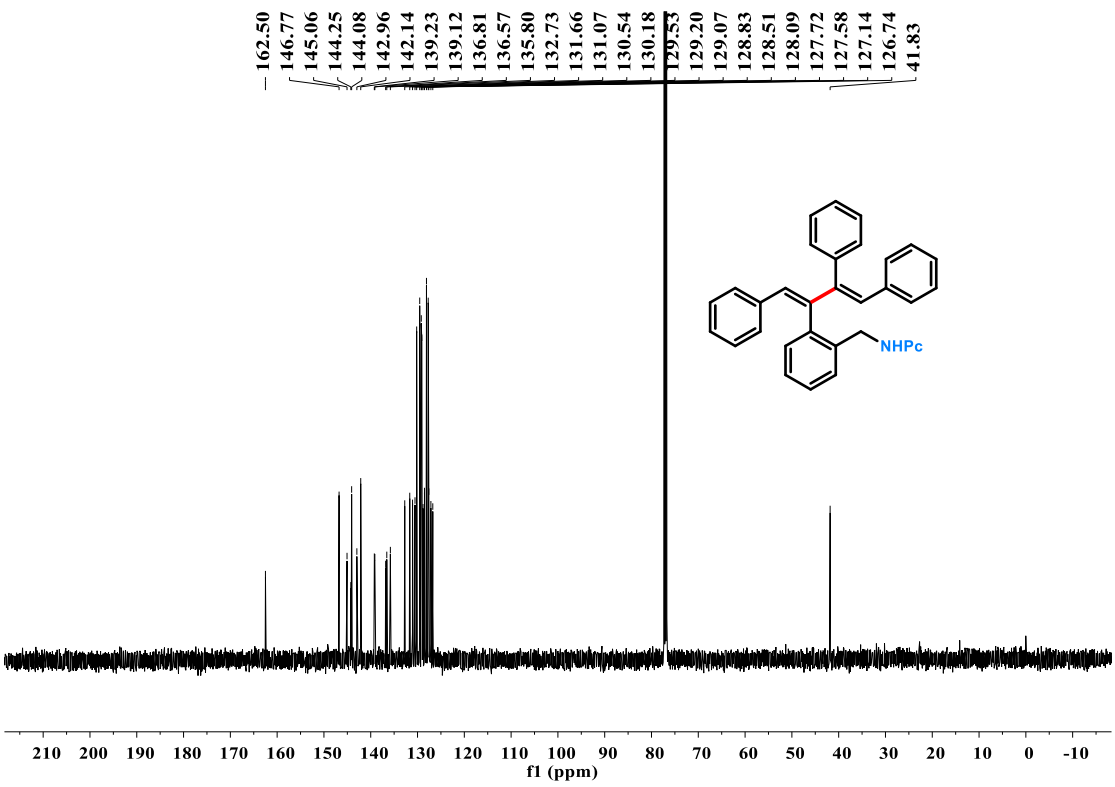

9.36
9.35
8.53
8.53
7.95
7.95
7.95
7.41
7.40
7.40
7.40
7.39
7.39
7.38
7.27
7.26
7.26
7.25
7.25
7.25
7.24
7.24
6.95
6.94
6.92
6.57
6.56
6.56
5.96
5.49
1.77
1.25
1.24
0.75
0.74
0.72
PC
N
H
7k, Z/E > 99:1
1.00
1.02
1.01
1.05
1.11
5.05
3.13
3.07
2.12
1.04
1.06
1.08
1.04
2.34
2.12
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

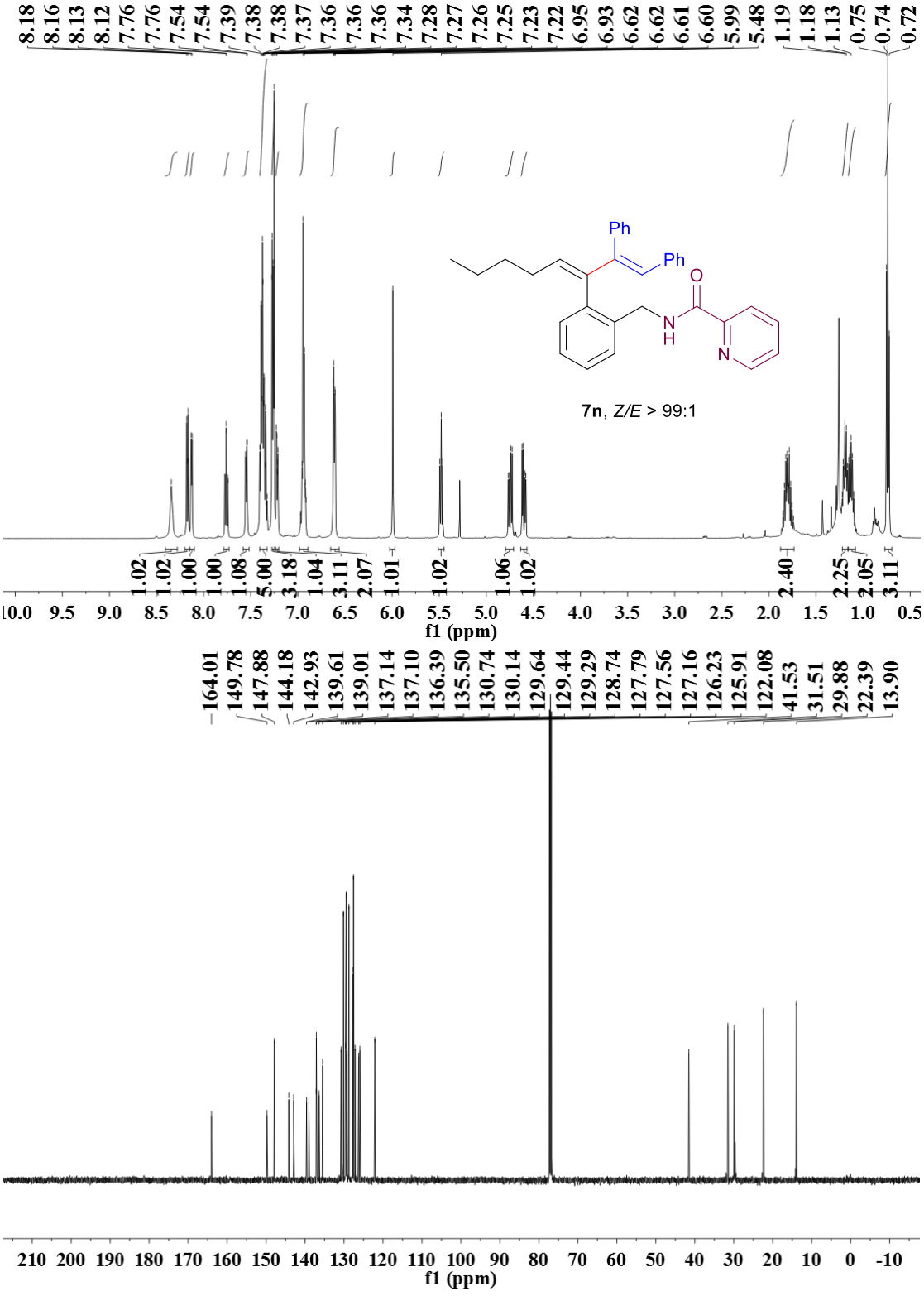

162.53
146.94
144.30
144.18
143.05
142.24
139.49
139.17
136.99
135.86
135.47
130.90
129.99
129.72
129.61
129.38
128.84
128.10
127.91
127.61
127.29
126.35
41.72
32.10
22.48
13.85
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

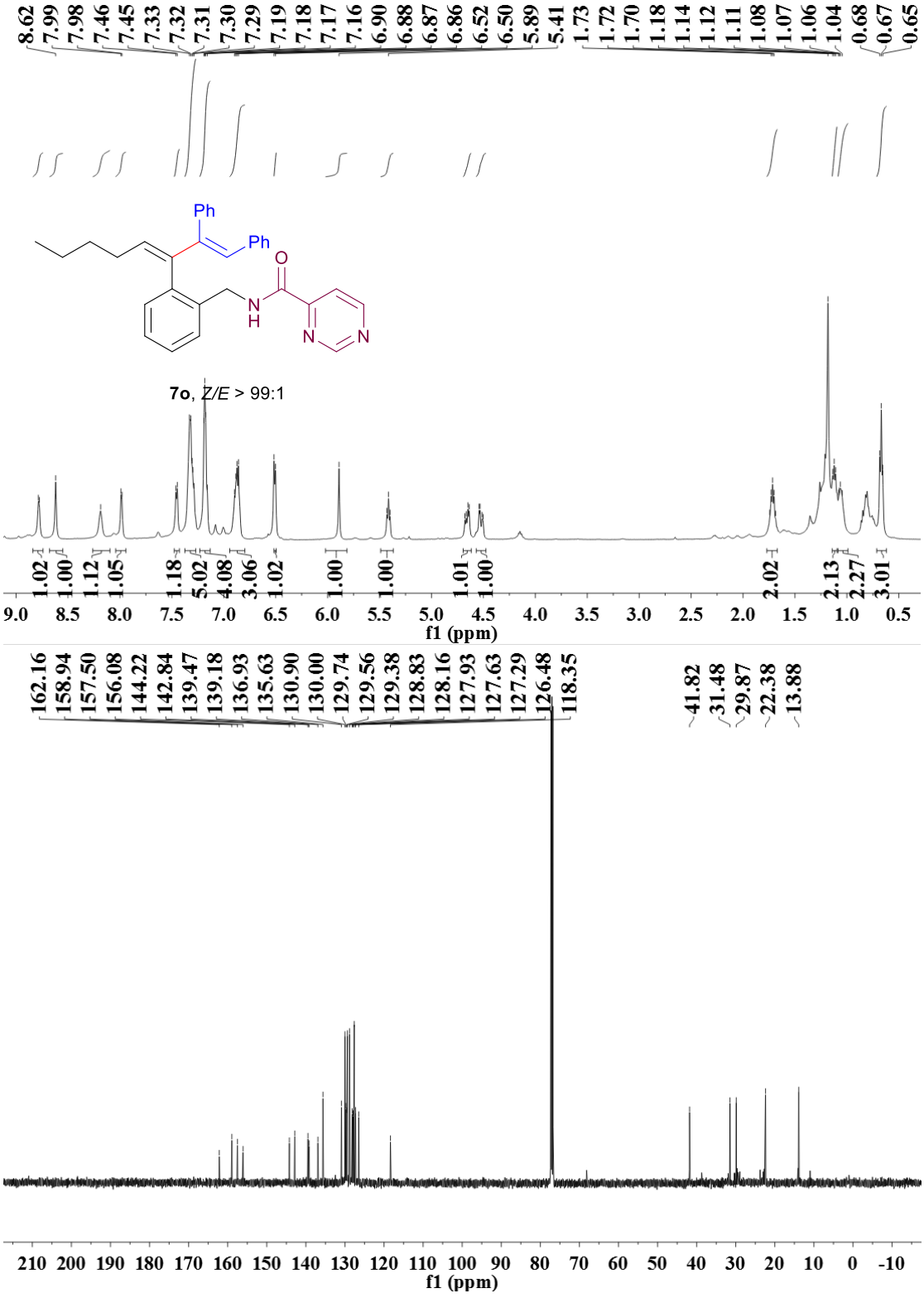

9.36 9.35 8.53 8.53 7.95 7.94 7.94 7.94 7.41 7.40 7.40 7.40 7.39 7.39 7.27 7.26 7.26 7.25 7.25 7.24 7.24 6.95 6.94 6.92 6.58 6.57 6.56 6.56 5.96 5.49 1.78 1.21 1.20 1.20 1.19 1.18 1.11 1.11 1.10 1.10 1.09 0.82 0.81 0.79
NHPc
1.00 1.03 1.02 1.06 1.13 5.17 3.33 3.11 2.10 1.06 1.08 1.08 1.05 2.09 4.46 4.12 3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0
f1 (ppm)


162.52 146.94 144.32 144.18 142.84 142.23 139.49 139.17 137.00 135.87 135.72 130.88 129.99 129.69 129.64 129.37 128.84 128.10 127.91 127.61 127.28 126.34
41.73 31.52 30.13 29.20 28.93 22.48 14.02
NHPc
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

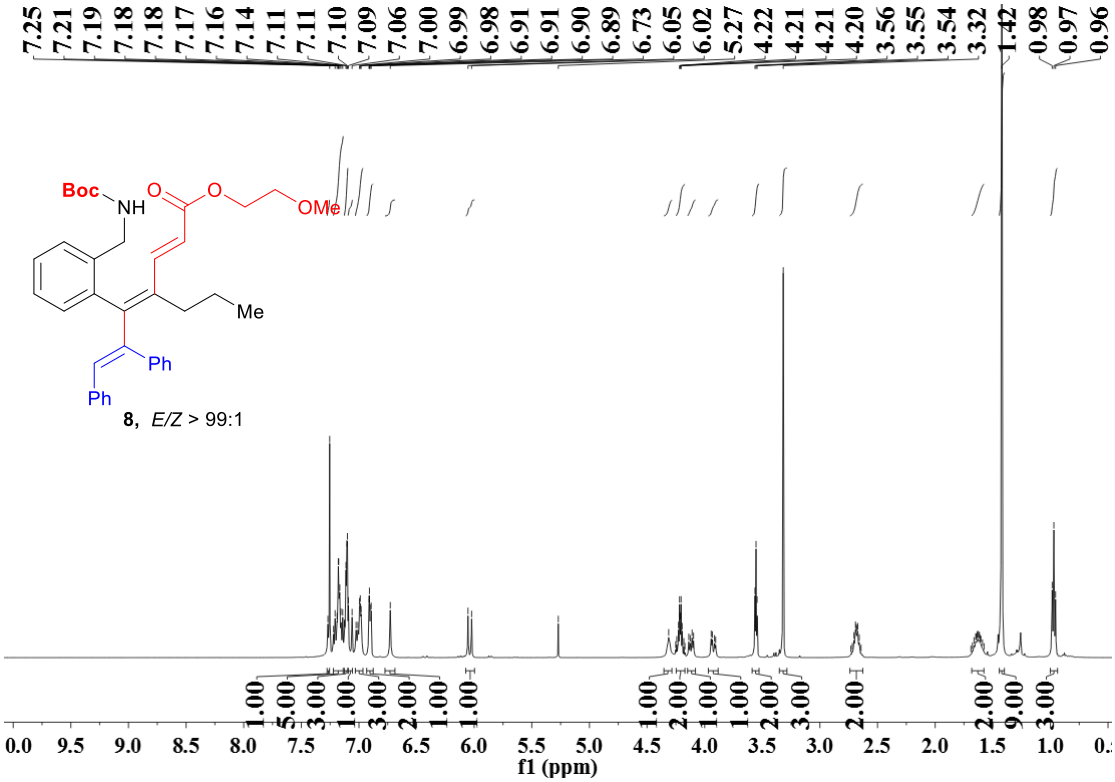

9.29 9.28 8.50 8.50 7.93 7.92 7.92 7.92 7.47 7.47 7.47 7.46 7.46 7.46 7.45 7.44 7.41 7.37 7.36 7.35 7.35 7.34 7.34 6.99 6.99 6.98 6.98 6.97 6.97 6.96 6.96 6.65 6.65 6.64 6.64 6.63 6.62 6.62 6.60 6.60 6.37 6.17 4.60 4.58 4.57
NHPc
1.00 1.01 1.00 1.03 1.07 4.15 1.01 3.05 6.19 4.15 1.02 1.01 2.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

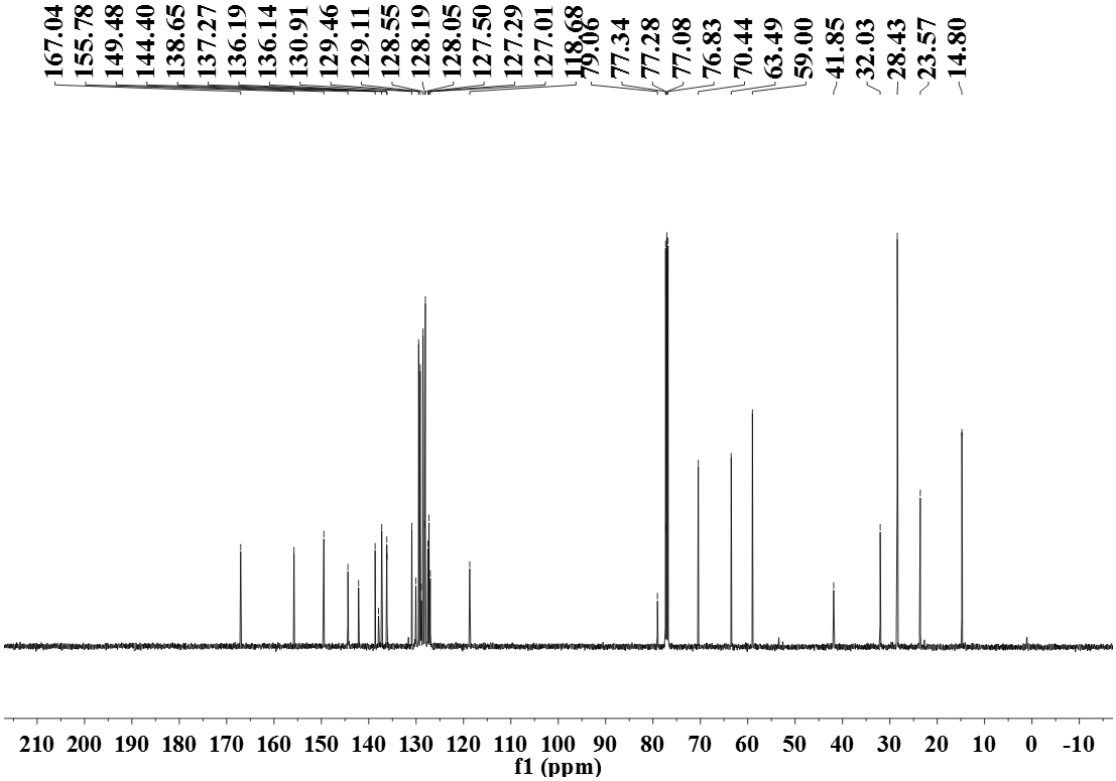

162.50 146.77 145.06 144.25 144.08 142.96 142.14 139.23 139.12 136.81 136.57 135.80 132.73 131.66 131.07 130.54 130.18 129.53 129.20 129.07 128.83 128.51 128.09 127.72 127.58 127.14 126.74 41.83
NHPc
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.18 8.16 8.13 8.12 7.76 7.76 7.54 7.54 7.39 7.38 7.38 7.37 7.36 7.36 7.36 7.34 7.28 7.27 7.26 7.25 7.23 7.22 6.95 6.93 6.62 6.62 6.61 6.60 5.99 5.48 1.19 1.18 1.13 0.75 0.74 0.72
Ph
Ph
O
N
H
N
7n, Z/E > 99:1
1.02 1.02 1.00 1.00 1.08 5.00 3.18 1.04 3.11 2.07 1.01 1.02 1.06 1.02 2.40 2.25 2.05 3.11
f1 (ppm)
164.01 149.78 147.88 144.18 142.93 139.61 139.01 137.14 137.10 136.39 135.50 130.74 130.14 129.64 129.44 129.29 128.74 127.79 127.56 127.16 126.23 125.91 122.08 41.53 31.51 29.88 22.39 13.90
f1 (ppm)

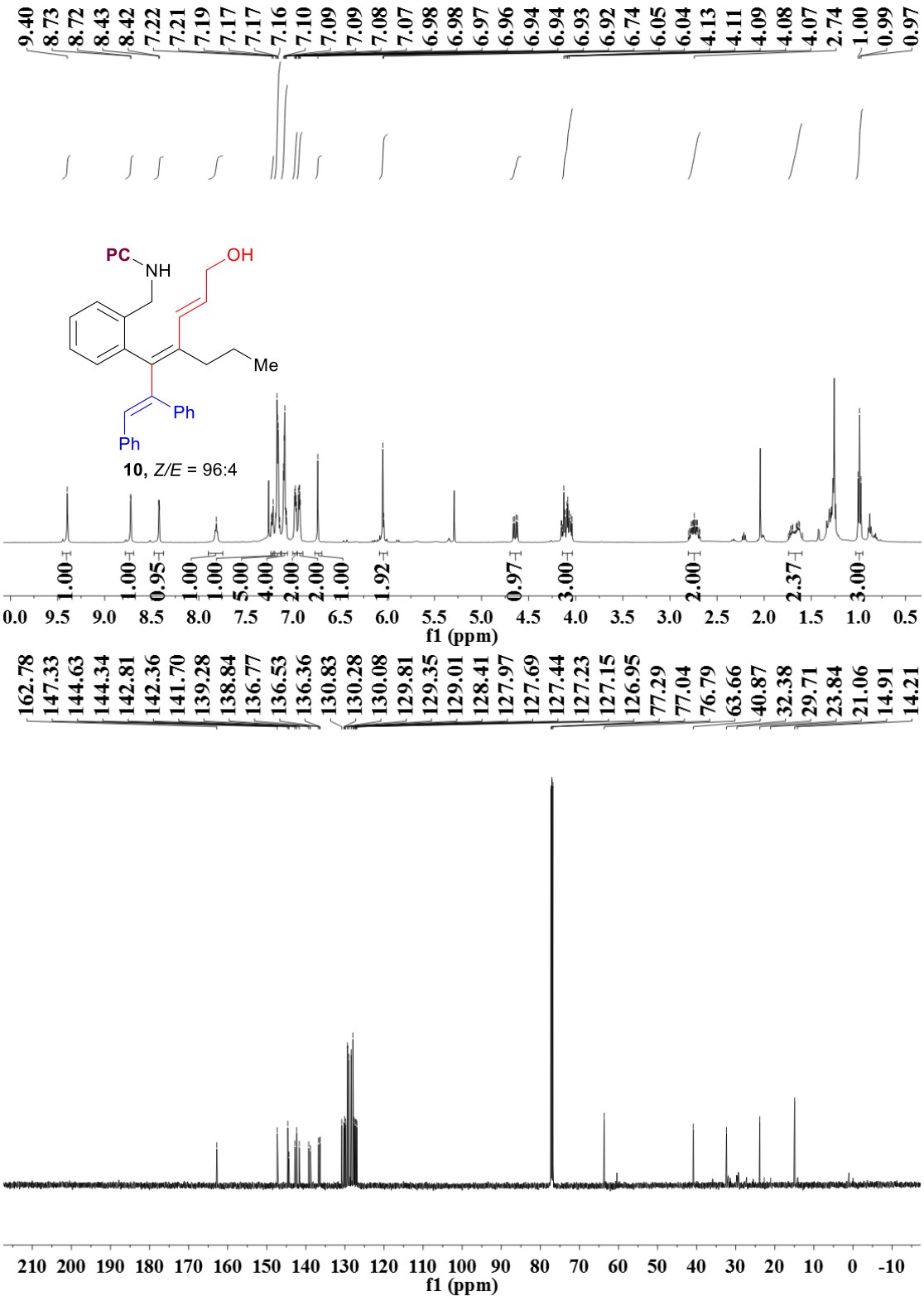

8.62 7.99 7.98 7.46 7.45 7.33 7.32 7.31 7.30 7.29 7.19 7.18 7.17 7.16 6.90 6.88 6.87 6.86 6.52 6.50 5.89 5.41 1.73 1.72 1.70 1.18 1.14 1.12 1.11 1.08 1.07 1.06 1.04 0.68 0.67 0.65
Ph
Ph
O
N
H
N
N
7o, Z/E > 99:1
1.02 1.00 1.12 1.05 1.18 5.02 4.08 3.06 1.02 1.00 1.00 1.01 1.00 2.02 2.13 2.27 3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
162.16 158.94 157.50 156.08 144.22 142.84 139.47 139.18 136.93 135.63 130.90 130.00 129.74 129.56 129.38 128.83 128.16 127.93 127.63 127.29 126.48 118.35
41.82 31.48 29.87 22.38 13.88
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

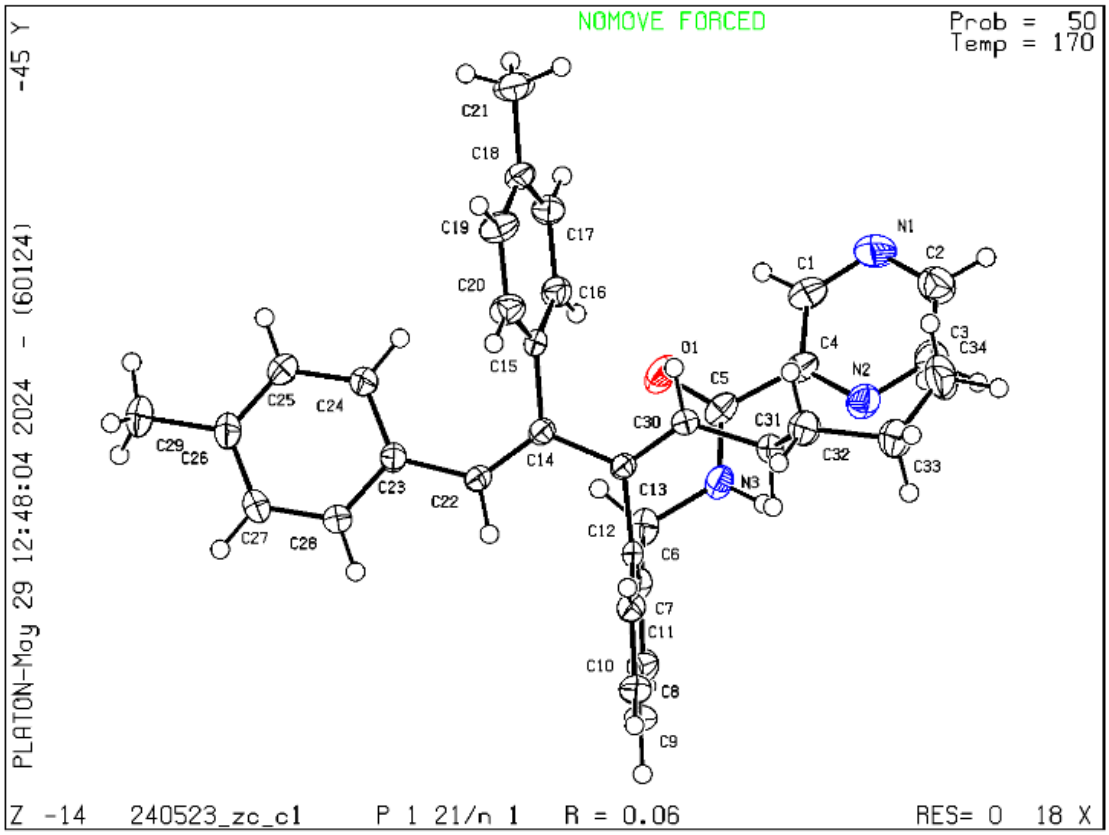
8.4 NMR Spectra of Synthetic Applications






PC
NH
O
OH
Me
Ph
Ph
9, Z/E = 95:5
f1 (ppm)
f1 (ppm)


9.40 8.73 8.72 8.43 8.42 7.22 7.21 7.19 7.17 7.17 7.16 7.10 7.09 7.09 7.08 7.07 6.98 6.98 6.97 6.96 6.94 6.94 6.93 6.92 6.74 6.05 6.04 4.13 4.11 4.09 4.08 4.07 2.74 1.00 0.99 0.97
PC
NH
OH
Me
Ph
Ph
10, Z/E = 96:4
1.00 1.00 0.95 1.00 1.00 5.00 4.00 2.00 2.00 1.00 1.92 0.97 3.00 2.00 2.37 3.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
162.78 147.33 144.63 144.34 142.81 142.36 141.70 139.28 138.84 136.77 136.53 136.36 130.83 130.28 130.08 129.81 129.35 129.01 128.41 127.97 127.69 127.44 127.23 127.15 126.95 77.29 77.04 76.79 63.66 40.87 32.38 29.71 23.84 21.06 14.91 14.21
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



240523_ZC_C1

Table 1 Crystal data and structure refinement for 240523_ZC_C1.

Identification code	240523_ZC_C1
Empirical formula	$C_{34}H_{35}N_3O$
Formula weight	501.65
Temperature/K	170.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	15.9469(6)
b/Å	10.8747(4)
c/Å	16.2725(6)
α/°	90
β/°	96.083(2)
γ/°	90
Volume/Å^3	2806.05(18)
Z	4
ρ_{calc}g/cm^3	1.187
μ/mm^{-1}	0.354
F(000)	1072.0
Crystal size/mm^3	0.09 × 0.07 × 0.03
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	6.42 to 121.408
Index ranges	-20 ⩽ h ⩽ 20, -11 ⩽ k ⩽ 14, -21 ⩽ l ⩽ 21
Reflections collected	42541

Independent reflections	6394 [R_{int} = 0.0640, R_{sigma} = 0.0530]
Data/restraints/parameters	6394/0/346
Goodness-of-fit on F^2	1.149
Final R indexes [I>=2σ (I)]	R_1 = 0.0596, wR_2 = 0.1530
Final R indexes [all data]	R_1 = 0.0744, wR_2 = 0.1601
Largest diff. peak/hole / e $Å^{-3}$	0.27/-0.27

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for 240523_ZC_C1. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	6372.5(8)	6005.8(11)	6141.5(8)	42.0(3)
N1	8404.5(11)	6215.0(14)	7926.3(11)	46.5(4)
C1	7775.9(12)	6114.4(16)	7319.3(12)	40.9(4)
N2	7473.9(9)	4046.5(13)	7639.1(9)	35.4(3)
C2	8563.6(12)	5212.6(18)	8382.2(12)	42.1(4)
N3	6178.0(8)	3973.3(12)	6370.5(8)	28.7(3)
C3	8114.8(11)	4133.9(18)	8236.1(12)	41.4(4)
C4	7303.9(10)	5052.4(14)	7182.9(10)	30.0(4)
C5	6574.9(10)	5042.4(14)	6512.5(11)	30.3(4)
C6	5455.9(10)	3880.6(16)	5737.2(10)	31.4(4)
C7	4830.4(9)	2919.7(14)	5934.4(9)	26.2(3)
C8	4733.7(11)	1840.5(16)	5469.3(11)	36.7(4)
C9	4167.3(12)	939.8(16)	5650.9(12)	40.9(5)
C10	3687.6(11)	1100.6(15)	6296.4(12)	36.8(4)
C11	3765.6(10)	2178.4(14)	6757.1(10)	28.2(3)
C12	4325.2(9)	3098.9(13)	6576.7(9)	21.7(3)
C13	4350.2(8)	4276.7(13)	7058.8(9)	21.0(3)
C14	3858.4(9)	5330.8(13)	6678.2(9)	21.7(3)
C15	3963.9(9)	6532.5(13)	7125.6(9)	22.3(3)
C16	4660.6(9)	7278.8(14)	7056.8(10)	27.6(3)
C17	4734.2(10)	8401.5(15)	7463.9(10)	31.1(4)
C18	4130.4(11)	8808.5(14)	7952.3(10)	29.8(4)
C19	3436.2(11)	8062.2(15)	8017.3(11)	35.4(4)
C20	3360.3(10)	6933.4(15)	7613.7(11)	31.8(4)
C21	4229.8(13)	10011.6(16)	8414.7(12)	42.4(5)
C22	3334.7(9)	5192.0(13)	5979.8(9)	23.3(3)
C23	2796.5(9)	6095.2(13)	5497.1(9)	23.6(3)
C24	2877.6(11)	7375.6(15)	5548.2(11)	34.2(4)
C25	2351.1(12)	8138.1(15)	5041.7(11)	39.0(4)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 240523_ZC_C1. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C26	1723.8(10)	7671.2(16)	4471.9(10)	32.0(4)
C27	1641.6(10)	6404.0(15)	4417.1(10)	31.5(4)
C28	2171.6(9)	5635.4(14)	4911.2(10)	28.2(3)
C29	1153.3(12)	8514.7(18)	3927.9(12)	45.7(5)
C30	4780.6(9)	4359.0(13)	7810.2(9)	24.0(3)
C31	5318.2(10)	3389.9(14)	8253.5(9)	26.8(3)
C32	5095.1(11)	3147.2(16)	9128.0(10)	34.9(4)
C33	5751.5(13)	2368.8(17)	9647.0(12)	45.2(5)
C34	6579.0(14)	3032(2)	9878.8(14)	57.0(6)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for 240523_ZC_C1. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	45.8(7)	25.8(6)	54.1(8)	10.0(5)	2.9(6)	6.4(5)
N1	51.4(10)	32.0(8)	54.7(10)	-3.5(7)	-0.9(8)	-10.6(7)
C1	49.6(11)	23.2(8)	49.4(11)	1.2(7)	2.7(9)	-2.1(7)
N2	30.6(7)	27.8(7)	47.4(9)	6.0(6)	1.5(6)	-2.8(6)
C2	38.4(10)	43.1(11)	43.9(11)	-1.3(8)	0.2(8)	-5.5(8)
N3	25.3(6)	24.8(7)	35.8(7)	6.1(5)	2.4(5)	2.7(5)
C3	36.0(9)	37.7(10)	49.1(11)	10.0(8)	-1.7(8)	-4.3(8)
C4	30.8(8)	22.4(8)	38.2(9)	-0.5(6)	10.3(7)	2.3(6)
C5	30.5(8)	23.9(8)	37.9(9)	2.3(7)	9.8(7)	6.0(6)
C6	29.7(8)	36.0(9)	28.6(8)	5.4(7)	3.6(6)	5.6(7)
C7	25.5(7)	25.6(8)	26.0(8)	0.7(6)	-4.7(6)	7.5(6)
C8	40.0(9)	37.0(10)	31.9(9)	-8.4(7)	-2.2(7)	13.2(8)
C9	47.4(10)	25.3(8)	45.9(11)	-13.5(7)	-13.8(8)	6.1(8)
C10	35.0(9)	22.6(8)	49.8(11)	-2.5(7)	-9.7(8)	-2.9(7)
C11	26.9(8)	22.1(8)	34.2(9)	1.1(6)	-3.3(6)	0.5(6)
C12	19.8(7)	18.3(7)	25.2(7)	-0.5(5)	-6.8(5)	3.9(5)
C13	19.0(7)	16.9(7)	26.9(7)	0.2(5)	0.8(5)	0.5(5)
C14	19.9(7)	18.2(7)	26.7(7)	0.7(6)	1.7(5)	0.5(5)
C15	23.1(7)	18.0(7)	24.5(7)	1.7(6)	-3.8(6)	3.3(6)
C16	24.1(7)	26.2(8)	32.4(8)	-0.1(6)	2.7(6)	0.8(6)
C17	29.7(8)	23.5(8)	39.3(9)	0.9(7)	-0.4(7)	-6.1(6)
C18	40.4(9)	18.8(7)	28.8(8)	0.2(6)	-3.0(7)	2.6(6)
C19	39.6(9)	28.3(9)	40.3(10)	-5.4(7)	13.4(7)	3.0(7)
C20	28.0(8)	26.0(8)	42.3(10)	-2.7(7)	7.5(7)	-2.7(6)
C21	62.7(12)	23.8(9)	39.9(10)	-5.8(7)	1.7(9)	-1.0(8)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 240523_ZC_C1. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C22	23.0(7)	16.8(7)	29.5(8)	-0.1(6)	-0.5(6)	0.8(5)
C23	21.8(7)	23.7(7)	24.7(8)	1.9(6)	-0.1(6)	1.9(6)
C24	36.8(9)	22.3(8)	39.8(10)	1.3(7)	-13.4(7)	-0.5(7)
C25	45.9(10)	21.6(8)	46.1(10)	3.1(7)	-11.4(8)	2.8(7)
C26	30.0(8)	34.7(9)	30.1(9)	5.7(7)	-2.9(7)	6.5(7)
C27	28.3(8)	33.9(9)	30.0(8)	0.7(7)	-7.6(6)	1.0(7)
C28	29.1(8)	22.8(7)	31.2(8)	-0.7(6)	-3.2(6)	-0.1(6)
C29	48.8(11)	39.0(10)	45.3(11)	10.3(8)	-13.8(9)	10.9(9)
C30	24.8(7)	19.2(7)	27.2(8)	-2.1(6)	-1.4(6)	0.8(6)
C31	29.1(8)	22.9(7)	26.8(8)	0.1(6)	-4.9(6)	2.7(6)
C32	40.8(9)	31.1(9)	31.7(9)	5.5(7)	-0.8(7)	0.3(7)
C33	60.0(12)	35.0(10)	37.0(10)	11.4(8)	-11.9(9)	0.7(9)
C34	61.5(13)	53.4(13)	49.5(12)	14.3(10)	-24.5(10)	-2.1(10)

Table 4 Bond Lengths for 240523_ZC_C1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C5	1.2349(19)	C14	C22	1.346(2)
N1	C1	1.335(2)	C15	C16	1.390(2)
N1	C2	1.328(2)	C15	C20	1.382(2)
C1	C4	1.384(2)	C16	C17	1.388(2)
N2	C3	1.337(2)	C17	C18	1.385(2)
N2	C4	1.334(2)	C18	C19	1.386(2)
C2	C3	1.382(3)	C18	C21	1.509(2)
N3	C5	1.332(2)	C19	C20	1.391(2)
N3	C6	1.465(2)	C22	C23	1.475(2)
C4	C5	1.508(2)	C23	C24	1.400(2)
C6	C7	1.503(2)	C23	C28	1.397(2)
C7	C8	1.396(2)	C24	C25	1.387(2)
C7	C12	1.399(2)	C25	C26	1.386(2)
C8	C9	1.385(3)	C26	C27	1.386(2)
C9	C10	1.375(3)	C26	C29	1.511(2)
C10	C11	1.390(2)	C27	C28	1.384(2)
C11	C12	1.393(2)	C30	C31	1.495(2)
C12	C13	1.5003(19)	C31	C32	1.526(2)
C13	C14	1.4865(19)	C32	C33	1.529(2)
C13	C30	1.340(2)	C33	C34	1.516(3)
C14	C15	1.497(2)			

Table 5 Bond Angles for 240523_ZC_C1.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	N1	C1	115.47(16)	C22	C14	C13	121.21(13)
N1	C1	C4	122.70(17)	C22	C14	C15	122.44(13)
C4	N2	C3	116.17(15)	C16	C15	C14	121.34(13)
N1	C2	C3	122.42(17)	C20	C15	C14	120.39(13)
C5	N3	C6	120.37(13)	C20	C15	C16	118.26(14)
N2	C3	C2	121.84(17)	C17	C16	C15	120.20(15)
C1	C4	C5	119.13(15)	C18	C17	C16	121.75(15)
N2	C4	C1	121.35(16)	C17	C18	C19	117.80(14)
N2	C4	C5	119.51(14)	C17	C18	C21	121.37(15)
O1	C5	N3	124.11(16)	C19	C18	C21	120.81(16)
O1	C5	C4	119.29(15)	C18	C19	C20	120.73(15)
N3	C5	C4	116.59(14)	C15	C20	C19	121.24(15)
N3	C6	C7	112.81(13)	C14	C22	C23	130.48(14)
C8	C7	C6	120.43(15)	C24	C23	C22	125.86(13)
C8	C7	C12	118.87(15)	C28	C23	C22	117.25(13)
C12	C7	C6	120.69(14)	C28	C23	C24	116.83(13)
C9	C8	C7	121.05(17)	C25	C24	C23	120.85(15)
C10	C9	C8	120.09(15)	C26	C25	C24	121.79(15)
C9	C10	C11	119.62(16)	C25	C26	C27	117.62(14)
C10	C11	C12	121.01(16)	C25	C26	C29	121.11(16)
C7	C12	C13	121.60(13)	C27	C26	C29	121.27(15)
C11	C12	C7	119.32(14)	C28	C27	C26	121.02(15)
C11	C12	C13	119.04(14)	C27	C28	C23	121.87(15)
C14	C13	C12	117.18(12)	C13	C30	C31	127.24(13)
C30	C13	C12	121.11(12)	C30	C31	C32	113.17(13)
C30	C13	C14	121.68(13)	C31	C32	C33	113.40(15)
C13	C14	C15	116.33(12)	C34	C33	C32	113.65(15)

Table 6 Torsion Angles for 240523_ZC_C1.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	C1	C4	N2	-2.4(3)	C13	C14	C15	C16	79.63(18)
N1	C1	C4	C5	176.67(16)	C13	C14	C15	C20	-101.06(16)
N1	C2	C3	N2	-2.0(3)	C13	C14	C22	C23	-179.58(14)
C1	N1	C2	C3	0.5(3)	C13	C30	C31	C32	-128.31(17)
C1	C4	C5	O1	-5.5(2)	C14	C13	C30	C31	-178.07(14)
C1	C4	C5	N3	175.60(15)	C14	C15	C16	C17	178.59(14)
N2	C4	C5	O1	173.56(15)	C14	C15	C20	C19	-

Table 6 Torsion Angles for 240523_ZC_C1.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
									178.31(15)
N2	C4	C5	N3	-5.3(2)	C14	C22	C23	C24	17.7(3)
C2	N1	C1	C4	1.7(3)	C14	C22	C23	C28	-165.11(16)
N3	C6	C7	C8	-110.33(16)	C15	C14	C22	C23	2.0(2)
N3	C6	C7	C12	70.77(18)	C15	C16	C17	C18	0.6(2)
C3	N2	C4	C1	0.8(2)	C16	C15	C20	C19	1.0(2)
C3	N2	C4	C5	-178.25(15)	C16	C17	C18	C19	-0.8(2)
C4	N2	C3	C2	1.3(3)	C16	C17	C18	C21	177.99(15)
C5	N3	C6	C7	-149.87(15)	C17	C18	C19	C20	1.0(3)
C6	N3	C5	O1	0.5(2)	C18	C19	C20	C15	-1.2(3)
C6	N3	C5	C4	179.27(13)	C20	C15	C16	C17	-0.7(2)
C6	C7	C8	C9	179.16(15)	C21	C18	C19	C20	-177.73(16)
C6	C7	C12	C11	-178.48(13)	C22	C14	C15	C16	-101.88(17)
C6	C7	C12	C13	3.6(2)	C22	C14	C15	C20	77.4(2)
C7	C8	C9	C10	0.1(3)	C22	C23	C24	C25	177.78(16)
C7	C12	C13	C14	80.65(17)	C22	C23	C28	C27	-178.99(15)
C7	C12	C13	C30	-101.10(17)	C23	C24	C25	C26	0.4(3)
C8	C7	C12	C11	2.6(2)	C24	C23	C28	C27	-1.6(2)
C8	C7	C12	C13	-175.33(13)	C24	C25	C26	C27	-0.6(3)
C8	C9	C10	C11	0.9(2)	C24	C25	C26	C29	179.71(18)
C9	C10	C11	C12	-0.2(2)	C25	C26	C27	C28	-0.4(3)
C10	C11	C12	C7	-1.6(2)	C26	C27	C28	C23	1.5(3)
C10	C11	C12	C13	176.41(13)	C28	C23	C24	C25	0.6(3)
C11	C12	C13	C14	-97.29(16)	C29	C26	C27	C28	179.33(17)
C11	C12	C13	C30	80.96(18)	C30	C13	C14	C15	8.0(2)
C12	C7	C8	C9	-1.9(2)	C30	C13	C14	C22	-170.50(14)
C12	C13	C14	C15	-173.75(12)	C30	C31	C32	C33	-167.74(14)
C12	C13	C14	C22	7.7(2)	C31	C32	C33	C34	69.6(2)
C12	C13	C30	C31	3.8(2)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 240523_ZC_C1.

Atom	*x*	*y*	*z*	U(eq)
H1	7647.59	6800.04	6966.51	49
H2	9002.21	5238.03	8825.04	50
H3	6350.5	3319.04	6658.73	34
H3A	8265.91	3434.6	8569.25	50
H6A	5662.25	3680.7	5200.21	38
H6B	5168.89	4688.06	5680.23	38
H8	5061.51	1721.9	5021.18	44
H9	4110.37	210.07	5328.84	49
H10	3304.96	478.49	6426.89	44
H11	3432.17	2289.06	7201.86	34
H16	5087.67	7019.68	6730.13	33
H17	5211.67	8904.08	7405.84	37
H19	3007.42	8324.22	8340.91	42
H20	2884.6	6428.88	7674.91	38
H21A	4463.57	9856.25	8986.69	64
H21B	3678.17	10410.14	8410.75	64
H21C	4612.1	10549.73	8146.86	64
H22	3307.05	4380.52	5762.42	28
H24	3298.5	7726.92	5934.66	41
H25	2422.47	9003.67	5086.56	47
H27	1214.91	6057.77	4034.6	38
H28	2108.64	4770.53	4850.07	34
H29A	1160.55	8273.28	3348.44	69
H29B	1352.61	9364.07	4001.46	69
H29C	576.66	8454.03	4080.81	69
H30	4739.42	5117.68	8092.54	29
H31A	5916.37	3645.46	8281.37	32
H31B	5256.07	2615.8	7932.61	32
H32A	4543.53	2722.13	9094.99	42
H32B	5034.62	3944.39	9409.49	42
H33A	5515.96	2111.54	10159.12	54
H33B	5862.45	1615.98	9333.95	54
H34A	6816.94	3291.91	9375.55	85
H34B	6974.88	2476.59	10196.07	85
H34C	6480.28	3755.1	10214.51	85

Experimental

Single crystals of $C_{34}H_{35}N_3O$ **[240523_ZC_C1]** were **[]**. A suitable crystal was selected and **[]** on a diffractometer. The crystal was kept at 170.00 K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [240523_ZC_C1]

Crystal Data for $C_{34}H_{35}N_3O$ (M =501.65 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 15.9469(6) Å, b = 10.8747(4) Å, c = 16.2725(6) Å, β = 96.083(2)°, V = 2806.05(18) Å^3, Z = 4, T = 170.00 K, μ(GaKα) = 0.354 mm^{-1}, *Dcalc* = 1.187 g/cm^3, 42541 reflections measured (6.42° ≤ 2Θ ≤ 121.408°), 6394 unique (R_{int} = 0.0640, R_{sigma} = 0.0530) which were used in all calculations. The final R_1 was 0.0596 (I > 2σ(I)) and wR_2 was 0.1601 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.
Details:

```
   1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups, All N(H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Secondary CH2 refined with riding coordinates:
 C6(H6A,H6B), C31(H31A,H31B), C32(H32A,H32B), C33(H33A,H33B)
2.b Aromatic/amide H refined with riding coordinates:
 C1(H1), C2(H2), N3(H3), C3(H3A), C8(H8), C9(H9), C10(H10), C11(H11),
C16(H16),
  C17(H17), C19(H19), C20(H20), C22(H22), C24(H24), C25(H25), C27(H27),
 C28(H28), C30(H30)
2.c Idealised Me refined as rotating group:
 C21(H21A,H21B,H21C), C29(H29A,H29B,H29C), C34(H34A,H34B,H34C)
```

This report has been created with Olex2, compiled on 2022.04.07 svn.rca3783a0 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.