Supporting Information

Palladium-catalyzed formal arylacylation of allenes employing acid chlorides and arylboronic acids

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1. Instrument

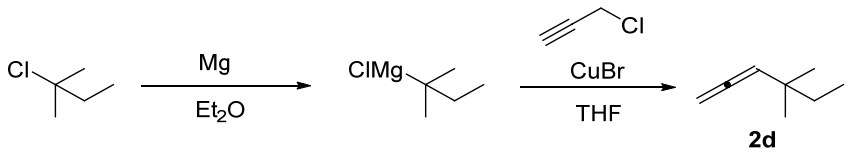
All manipulations were performed under an atmosphere of argon, using standard Schlenk-type glasswares on a dual-manifold Schlenk line. All solvents were dried and purified by usual procedures.[1] ^{1}H and $^{13}C\{^{1}H\}$ NMR were measured with a JEOL ECX-400 spectrometer. The ^{1}H NMR chemical shifts are reported relative to tetramethylsilane (TMS, 0.00 ppm) or residual protiated solvent (7.26 ppm) in $CDCl_3$. The ^{13}C NMR chemical shifts are reported relative to $CDCl_3$ (77.0 ppm). EI-MS were recorded on a Shimadzu GCMS-QP2010. IR spectra were obtained on Shimazu IRTracer-100 FT-IR Spectrometer equipped with Shimazu MIRacle A (Ge) Single Reflecion HATR. APCI-HRMS were obtained with Thermo Scientific Exactive. Elemental analysis was carried out at Center for Organic Elemental Microanalysis, Graduate School of Pharmaceutical Science, Kyoto University. Melting points were measured on a Yanako MP-J3 apparatus. Medium pressure liquid chromatography (MPLC) was performed on Biotage Isorera One with a silica gel column (Biotage SNAP Ultra 25 g, HP-Sphere 25μm). Preparative recycling GPC was performed with SHIMADZU LC-20AP System equipped with Shodex K-4002.5L column, a SHIMADZU SPD-20A, and SHIMADZU RID-10A using $CHCl_3$ as the eluent at a flow rate of 14 mL min^{-1}. GC analysis was carried out using Shimadzu GC-17A with a capillary column (CBP-5, 0.25 mm i.d. × 25 μm).

2. Preparation of Substrate

Unless otherwise noted, commercially available chemicals were used as received. Anhydrous toluene was purchased from Kanto Chemical and further purified by passage through activated alumina under positive argon pressure as described by Grubbs et al.[2]

$Pd_2(dba)_3 \cdot CHCl_3$ was synthesized according to a literature.[3] CuCl was purified according to a literature.[1] Acid chlorides **1a**–**j** were used after distillation under vacuum. Boronic acids **3a**–**i** were used after recrystallization from water. Allenes **2a**–**e**,[4] **2f** and **2g**[5] were synthesized according to literatures.

Preparation of **2d**



2d

Mg turnings (8.76 g, 360 mmol) were activated by evacuation and heating with stirring in a flask equipped with a reflux condenser and a dropping funnel. The flask was backfilled with argon and Et_2O (15 mL) was added. Then, *t*-amyl chloride (37.2 mL, 300 mmol) was transferred to the dropping funnel. After, a small portion of *t*-amyl chloride was added to the reaction flask (ca. 1 mL), the remaining *t*-amyl chloride was diluted with Et_2O (45 mL) in the dropping funnel. The solution was slowly added to the flask in 2 h. Then, the reaction mixture was stirred under reflux for 1 h. The mixture was filtered with a Celite pad to afford Grignard-reagent solution. Next, a mixture of propargyl chloride (12.6 mL, 175 mmol) and CuBr (1.0 g, 7.0 mmol) in THF (120 mL) was cooled to –40 °C. Then, the Grignard-reagent solution was added dropwise in 1 h and stirred at –40 °C for 30 min. The resulting mixture was slowly warmed up to room temperature and stirred overnight at room temperature. The reaction mixture was poured

into NH_4Cl aq. The product was extracted with Et_2O, dried over $MgSO_4$, and evaporated in vacuo. After distillation (200 tor, 30–40 ºC), **2d** was obtained in 34 % yield (6.61 g, 60 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.02 (t, J = 6.6 Hz, 1H), 4.70 (d, J = 6.8 Hz, 2H), 1.34 (q, J = 7.6 Hz, 2H), 0.99 (s, 6H), 0.84 (t, J = 7.5 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 206.70, 100.34, 76.02, 35.63, 34.32, 27.31, 8.98. **IR (ATR)**: 839.0, 869.9, 1014.6, 1057.0, 1095.6, 1261.5, 1462.0, 1955.8, 2964.6 cm^{-1}. **HRMS (APCI)**: Calcd. for C_8H_{15} ($[M+H]^+$), 111.1168. Found, 111.1173.

3. Experimental Procedure

3.1. Typical procedure in Table 1 (Entry 1)

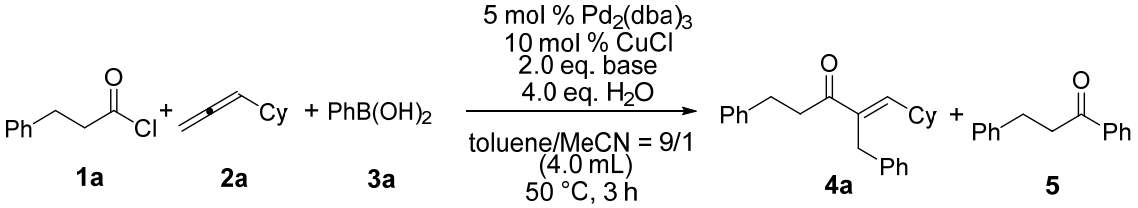
To a 10-mL Schlenk flask with a reflux condenser was added $K_3PO_4 \cdot H_2O$ (92 mg, 0.40 mmol), and the whole system was dried under evacuation and heating with stirring. The flask was backfilled with argon and $Pd_2(dba_3) \cdot CHCl_3$ (10.3 mg, 0.010 mmol, 5.0 mol %), CuCl (0.020 mmol, 10 mol %) and phenylboronic acid (**3a**, 36.6 mg, 0.30 mmol) were charged. The flask was evacuated and backfilled with argon three times. Then, toluene (3.6 mL) and MeCN (0.4 mL) were added to the flask. To the mixture, H_2O (14 μL, 0.80 mmol), cyclohexylallene (**2a**, 30 μL, 0.20 mmol) and 3-phenylpropionyl chloride (**1a**, 60 μL, 0.40 mmol) were added in this order, and the mixture was stirred at 50 °C for 3 h. After cooling to room temperature, the reaction mixture was analyzed by GC using tetradecane (50 μL) as an internal standard.

Regarding the isolation of (*E*)-**4a**, the reaction mixture was filtrated through a pad of silica gel and all volatiles were removed in vacuo. (*E*)-**4a** was obtained by MPLC (Hexane/EtOAc = 98/2) in 80% yield. The stereochemistry of the product (*E*)-**4a** was determined by 2D NMR measurements (See pages S41).

3.2. Effect of base and additives

To a 10-mL Schlenk flask with a reflux condenser was added a base (0.40 mmol), and the whole system was dried under evacuation and heating with stirring. The flask was backfilled with argon, then $Pd_2(dba_3) \cdot CHCl_3$ (10.3 mg, 0.010 mmol, 5.0 mol %), an additive (0.020 mmol, 10 mol %) and phenylboronic acid (**3a**, 36.6 mg, 0.30 mmol) were charged. The flask was evacuated and backfilled with argon three times. Then, toluene (3.6 mL) and MeCN (0.4 mL) were added to the flask. To the mixture, H_2O (14 μL, 0.80 mmol), cyclohexylallene (**2a**, 30 μL, 0.20 mmol) and 3-phenylpropionyl chloride (**1a**, 60 μL, 0.40 mmol) were added in this order, and the mixture was stirred at 50 °C for 3 h. After cooling to room temperature, the reaction mixture was analyzed by GC using tetradecane (50 μL) as an internal standard.

Table S1. Effect of bases[a]

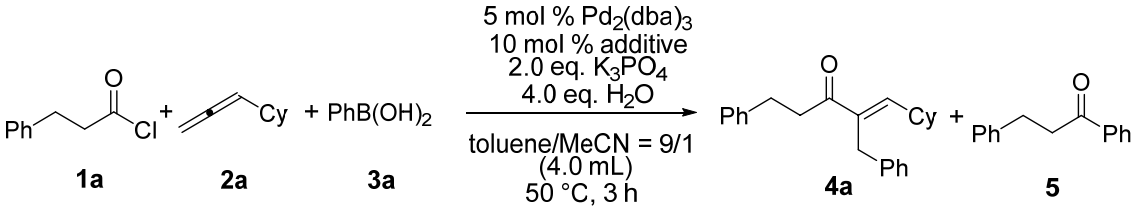


1a **2a** **3a** **4a** **5**

		4a		
Entry	Base	Total Yield of **4a** (%)[b]	(*E*)-**4a**/Other Isomer[c]	**5** (mmol)
1	K_3PO_4	86 (80)[d]	96/4	0.034
2	Na_3PO_4	53	97/3	0.030
3	K_2CO_3	32	96/4	0.019
4	Cs_2CO_3	67	97/3	0.020
5	Na_2CO_3	47	97/3	0.018
6	KOAc	13	-	0.004
7	KF	35	97/3	0.015
8	KOH	42	96/4	0.016
9	KO*t*Bu	40	96/4	0.020

[a] Reaction conditions: 3-phenypropionyl chloride (**1a**, 0.40 mmol), cyclohexylallene (**2a**, 0.20 mmol), phenylboronic acid (**3a**, 0.30 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (0.010 mmol, 5.0 mol %), CuCl (0.020 mmol, 10 mol %), base (0.40 mmol), H_2O (0.80 mmol) in toluene/MeCN = 9/1 (4.0 mL), at 50 ºC, for 3 h. [b] Yield by the GC internal standard method. [c] Determined by GC. [d] Isolated yield of (*E*)-**4a**.

Table S2. Effect of additives[a]



1a **2a** **3a** **4a** **5**

		4a		
Entry	Additive	Total Yield of **4a** (%)[b]	(*E*)-**4a**/Other Isomer[c]	**5** (mmol)
1	None	31	96/4	0.014
2	CuCl	86 (80)[d]	96/4	0.034
3	CuBr	61	97/3	0.024
4	CuI	73	94/6	0.023
5	CuOAc	52	96/4	0.025
6	$CuCl_2$	79	96/4	0.043
7	$CuBr_2$	78	96/4	0.042
8	$CuOAc_2$	79	96/4	0.024

[a] Reaction conditions: 3-phenypropionyl chloride (**1a**, 0.40 mmol), cyclohexylallene (**2a**, 0.20 mmol), phenylboronic acid (**3a**, 0.30 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (0.010 mmol, 5.0 mol %), additive (0.020 mmol, 10 mol %), K_3PO_4 (0.40 mmol), H_2O (0.80 mmol) in toluene/MeCN = 9/1 (4.0 mL), at 50 ºC, for 3 h. [b] Yield by the GC internal standard method. [c] Determined by GC. [d] Isolated yield of (*E*)-**4a**.

3.3. General procedure in Table 2

To a 10-mL Schlenk flask with a reflux condenser was added $K_3PO_4 \cdot H_2O$ (92 mg, 0.40 mmol), and the whole system was dried under evacuation and heating with stirring. The flask was backfilled with argon, then $Pd_2dba_3 \cdot CHCl_3$ (10.3 mg, 0.010 mmol, 5.0 mol %), CuCl (2.0 mg, 0.020 mmol, 10 mol %) and phenylboronic acid (**3a**, 36.6 mg, 0.30 mmol) were charged. The flask was evacuated and backfilled with argon three times. Then, toluene (3.6 mL) and MeCN (0.4 mL) were added to the flask. To the mixture, H_2O, cyclohexylallene (**2a**, 30 μL, 0.20 mmol) and acid chloride (0.40 mmol) were added in this order, and the mixture was stirred at 50 °C for 3 h. After cooling to room temperature, all volatiles were removed in vacuo. The product was isolated by MPLC or preparative recycling GPC. The stereochemistry of the product **4b**–**j** was determined by 2D NMR measurements. As typical examples, NOESY spectra of **4g** and **4h** was shown in Section 5 (See pages S41 and S42).

3.4. General procedure in Table 3

To a 10-mL Schlenk flask with a reflux condenser was added $K_3PO_4 \cdot H_2O$ (92 mg, 0.40 mmol), and the whole system was dried under evacuation and heating with stirring. The flask was backfilled with argon, then

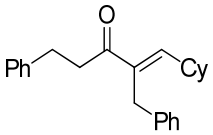
$Pd_2dba_3 \cdot CHCl_3$ (10.3 mg, 0.010 mmol, 5.0 mol %), CuCl (2.0 mg, 0.020 mmol, 10 mol %) and phenylboronic acid (**3a**, 36.6 mg, 0.30 mmol) were charged. The flask was evacuated and backfilled with argon three times. Then, toluene (3.6 mL) and MeCN (0.4 mL) were added to the flask. To the mixture, H_2O, allene (0.20 mmol) and 3-phenylpropionyl chloride (**1a**, 60 μL, 0.40 mmol) were added in this order, and the mixture was stirred at 50 °C for 3 h. After cooling to room temperature, all volatiles were removed in vacuo. The product was isolated by MPLC or preparative recycling GPC. The stereochemistry of the product **4k–p** was determined by 2D NMR measurements. As a typical example, a NOESY spectrum of **4n** was shown in Section 5 (See page S42).

3.5. General procedure in Table 4

To a 10-mL Schlenk flask with a reflux condenser was added $K_3PO_4 \cdot H_2O$ (92 mg, 0.40 mmol), and the whole system was dried under evacuation and heating with stirring. The flask was backfilled with argon, then $Pd_2dba_3 \cdot CHCl_3$ (10.3 mg, 0.010 mmol, 5.0 mol %), CuCl (2.0 mg, 0.020 mmol, 10 mol %) and boronic acid (0.30 mmol) were charged. The flask was evacuated and backfilled with argon three times. Then, toluene (3.6 mL) and MeCN (0.4 mL) were added to the flask. To the mixture, H_2O, cyclohexylallene (**2a**, 30 μL, 0.20 mmol) and 3-phenylpropionyl chloride (**1a**, 60 μL, 0.40 mmol) were added in this order, and the mixture was stirred at 50 °C for 3 h. After cooling to room temperature, all volatiles were removed in vacuo. The product was isolated by MPLC or preparative recycling GPC. The stereochemistry of the product **4q–x** was determined by 2D NMR measurements. As a typical example, a NOESY spectrum of **4x** was shown in Section 5 (See page S43).

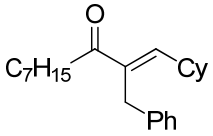
4. Characterization of the Compounds.

(*E*)-2-benzyl-1-cyclohexyl-5-phenylpent-1-en-3-one (**4a**)



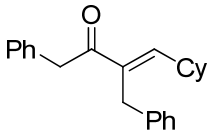
Isolated by MPLC (hexane/EtOAc = 98/2). Colorless oil. 53.3 mg, 80% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.28-7.10 (m, 10H), 6.52 (d, J = 9.5 Hz, 1H), 3.69 (s, 2H), 2.98-2.93 (m, 2H), 2.90-2.85 (m, 2H), 2.48 (tdt, J = 10.9, 10.0, 3.6 Hz, 1H), 1.76-1.55 (m, 5H), 1.33-1.06 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 200.66, 148.93, 141.53, 140.23, 138.13, 128.41, 128.38, 128.29, 128.17, 125.96, 125.77, 39.37, 38.35, 32.03, 31.41, 30.63, 25.74, 25.41. **IR (ATR)**: 902.7, 974.1, 1030.0, 1074.4, 1126.4, 1178.5, 1450.5, 1494.8, 1602.9, 1633.7, 1668.4, 2850.8, 2926.0, 3026.3 cm^{-1}. **HRMS (APCI)**: Calcd. for $C_{24}H_{29}O$ ([M+H]$^+$), 333.2213. Found, 333.2200.

(*E*)-2-benzyl-1-cyclohexyldec-1-en-3-one (**4b**)



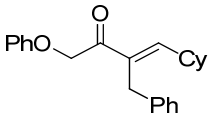
Isolated by MPLC (hexane/EtOAc = 98/2). Colorless oil. 52.2 mg, 80% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.25-7.20 (m, 2H), 7.15-7.11 (m, 3H), 6.53 (d, J = 9.5 Hz, 1H), 3.68 (s, 2H), 2.61 (t, J = 7.5 Hz, 2H), 2.49 (tdt, J = 10.9, 10.0, 3.6 Hz, 1H), 1.77-1.51 (m, 7H), 1.33-1.12 (m, 13H), 0.86 (t, J = 6.8 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 202.12, 148.34, 140.36, 138.24, 128.23, 128.16, 125.70, 38.31, 37.50, 32.10, 31.66, 31.41, 29.22, 29.07, 25.77, 25.44, 24.88, 22.56, 14.04. **IR (ATR)**: 734.9, 900.8, 972.1, 1030.0, 1074.4, 1132.2, 1450.5, 1494.8, 1668.4, 2852.7, 2926.0 cm^{-1}. **Anal**. Calcd. for $C_{23}H_{34}O$: C, 84.60; H,10.50. Found: C, 84.64; H, 10.64. **EIMS**: *m/z* 327 (26%, [M+1]$^+$), 326 (100, [M]$^+$), 243 (76), 227 (82), 117 (74), 91 (96).

(*E*)-3-benzyl-4-cyclohexyl-1-phenylbut-3-en-2-one (**4c**)



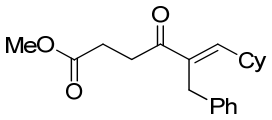
Isolated by MPLC (hexane/EtOAc = 98/2). Pale yellow oil. 51.2 mg, 80% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.28-7.03 (m, 10H), 6.66 (d, J = 10.0 Hz, 1H), 3.95 (s, 2H), 3.67 (s, 2H), 2.48 (tdt, J = 10.9, 10.0, 3.6 Hz, 1H), 1.76-1.56 (m, 5H), 1.32-1.09 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 199.19, 150.01, 139.96, 137.65, 135.32, 129.25, 128.40, 128.21, 128.14, 126.50, 125.72, 44.64, 38.37, 31.96, 31.47, 25.72, 25.33. **IR (ATR)**: 746.5, 974.1, 1030.0, 1074.4, 1122.6, 1450.5, 1494.8, 1602.9, 1664.6, 2850.8, 2926.0 cm^{-1}. **HRMS (APCI)**: Calcd. for $C_{23}H_{27}O$ ([M+H]$^+$), 319.2056. Found, 319.2053.

(*E*)-3-benzyl-4-cyclohexyl-1-phenoxybut-3-en-2-one (**4d**)



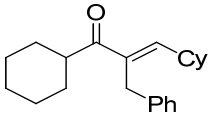
Isolated by preparative recycling GPC. Pale yellow oil. 56.0 mg, 84% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.24-7.18 (m, 4H), 7.17-7.09 (m, 3H), 6.93 (tt, J = 7.5, 1.1 Hz, 1H), 6.80-6.75 (m, 2H), 6.63 (d, J = 10.0 Hz, 1H), 4.92 (s, 2H), 3.71 (s, 2H), 2.53 (tdt, J = 10.9, 10.4, 3.6 Hz, 1H), 1.77-1.60 (m, 5H), 1.33-1.12 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 196.08, 157.93, 149.85, 139.60, 136.32, 129.43, 128.38, 128.24, 125.96, 121.32, 114.68, 70.27, 38.33, 31.93, 31.45, 25.70, 25.36. **IR (ATR)**: 752.2, 785.0, 1030.0, 1130.3, 1174.7, 1230.6, 1450.5, 1494.8, 1599.0, 1631.8, 1687.7, 2850.8, 2926.0 cm^{-1}. **Anal**. Calcd. for $C_{23}H_{26}O_2$: C, 82.60; H,7.84. Found: C, 82.86; H, 7.99. **EIMS**: *m/z* 334 (9%, $[M]^+$), 227 (100), 117 (50), 91 (59).

methyl (*E*)-5-benzyl-6-cyclohexyl-4-oxohex-5-enoate (**4e**)



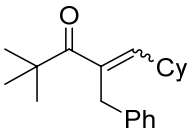
Isolated by MPLC (hexane/EtOAc = 95/5). Colorless oil. 43.5 mg, 69% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.25-7.20 (m, 2H), 7.16-7.11 (m, 3H), 6.62 (d, J = 10.0 Hz, 1H), 3.69 (s, 2H), 3.65 (s, 3H), 3.00 (t, J = 6.8 Hz, 2H), 2.58 (t, J = 6.8 Hz, 2H), 2.50 (tdt, J = 10.9, 10.4, 3.6 Hz, 1H), 1.79-1.57 (m, 5H), 1.34-1.11 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 199.21, 173.51, 149.16, 140.09, 137.75, 128.25, 128.04, 125.74, 51.62, 38.32, 32.30, 31.98, 31.37, 28.18, 25.70, 25.37. **IR (ATR)**: 842.9, 902.7, 1030.0, 1076.3, 1126.4, 1166.9, 1215.2, 1361.7, 1437.0, 1450.5, 1494.8, 1670.4, 1737.9, 2850.8, 2926.0 cm^{-1}. **HRMS (APCI)**: Calcd. for $C_{20}H_{27}O_3$ ($[M+H]^+$), 315.1955. Found, 315.1951.

(*E*)-2-benzyl-1,3-dicyclohexylprop-2-en-1-one (**4f**)



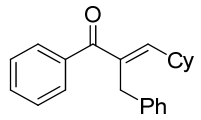
Isolated by MPLC (hexane/EtOAc = 98/2). Colorless oil. 37.5 mg, 60% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.25-7.20 (m, 2H), 7.14-7.10 (m, 3H), 6.49 (d, J = 10.0 Hz, 1H), 3.68 (s, 2H), 2.98 (tt, J = 11.1, 3.2 Hz, 1H), 2.50 (tdt, J = 10.9, 10.0, 3.9 Hz, 1H), 1.77-1.60 (m, 10H), 1.37-1.12 (m, 10H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 205.39, 147.57, 140.43, 137.22, 128.20, 128.14, 125.65, 44.38, 38.34, 32.13, 31.52, 29.71, 25.89, 25.83, 25.78, 25.47. **IR (ATR)**: 734.9, 821.7, 906.5, 1030.0, 1074.4, 1118.7, 1141.9, 1255.7, 1311.6, 1450.5, 1494.8, 1664.6, 2852.7, 2926.0 cm^{-1}. **Anal**. Calcd. for $C_{22}H_{30}O$: C, 85.11; H,9.74. Found: C, 84.91; H, 9.70. **EIMS**: *m/z* 310 (52%, $[M]^+$), 227 (100), 117 (42), 91 (40).

(*E*)-2-benzyl-1-cyclohexyl-4,4-dimethylpent-1-en-3-one (**4g**)



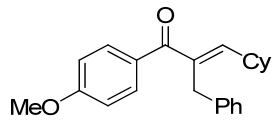
Isolated by preparative recycling GPC as mixture of inseparable isomers (*E*/*Z* = 89/11). Colorless oil. 32.4 mg, 57% yield. **^{1}H NMR (400 MHz, CDCl$_3$)** δ: 7.30-7.12 (m , 5H), 6.09 (d, *J* = 9.5 Hz, 1H), 3.66 (s, 2H), 2.46 (tdt, *J* = 10.9, 9.5, 3.4 Hz, 1H), 1.79-1.59 (m, 5H), 1.36-1.07 (m, 5H), 1.11 (s, 9H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ: 210.51, 142.27, 139.82, 136.86, 128.49, 128.25, 125.87, 43.79, 37.80, 33.92, 32.47, 28.55, 25.84, 25.53. **IR (ATR)**: 742.6, 902.7, 966.3, 1030.0, 1074.4, 1114.9, 1365.6, 1394.5, 1450.5, 1477.5, 1494.8, 1672.3, 2850.8, 2926.0 cm^{-1}. **Anal**. Calcd. for $C_{20}H_{28}O$: C, 84.45; H,9.92. Found: C, 84.33; H, 9.96. **HRMS (APCI)**: Calcd. for $C_{20}H_{29}O$ ([M+H]$^+$), 285.2213. Found, 285.2211.

(*E*)-2-benzyl-3-cyclohexyl-1-phenylprop-2-en-1-one (**4h**)



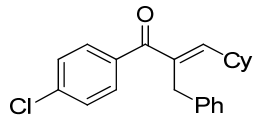
Isolated by MPLC (hexane/EtOAc = 98/2). Pale yellow oil. 44.3 mg, 73% yield. **^{1}H NMR (400 MHz, CDCl$_3$)** δ: 7.63-7.59 (m, 2H), 7.49-7.45 (m, 1H), 7.40-7.35 (m, 2H), 7.27-7.22 (m, 4H), 7.18-7.12 (m, 1H), 6.16 (d, *J* = 10.0 Hz, 1H), 3.87 (s, 2H), 2.59 (tdt, *J* = 10.9, 10.4, 3.6 Hz, 1H), 1.76-1.61 (m, 5H), 1.36-1.04 (m, 5H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ: 198.51, 151.67, 139.98, 138.71, 137.53, 131.50, 129.44, 128.37, 128.33, 127.99, 125.89, 38.44, 32.48, 32.05, 25.71, 25.40. **IR (ATR)**: 711.7, 785.0, 960.6, 1028.1, 1070.5, 1176.6, 1226.7, 1276.9, 1315.5, 1446.6, 1494.8, 1597.1, 1649.1, 2850.8, 2924.1 cm^{-1}. **Anal**. Calcd. for $C_{22}H_{24}O$: C, 86.80; H,7.95. Found: C, 86.95; H, 8.19. **EIMS**: *m/z* 305 (23%, [M+1]$^+$), 304 (100, [M]$^+$), 221 (55), 105 (81), 91 (43), 77 (42).

(*E*)-2-benzyl-3-cyclohexyl-1-(4-methoxyphenyl)prop-2-en-1-one (**4i**)



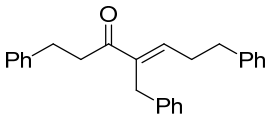
Isolated by MPLC (hexane/EtOAc = 98/2). Pale yellow oil. 44.1 mg, 66% yield. **^{1}H NMR (400 MHz, CDCl$_3$)** δ: 7.66 (dt, *J* = 9.4, 2.5 Hz, 2H), 7.25-7.21 (m, 4H), 7.17-7.11 (m, 1H), 6.88 (dt, *J* = 9.4, 2.4 Hz, 2H), 6.08 (d, *J* = 10.0 Hz, 1H), 3.86 (s, 2H), 3.83 (s, 3H), 2.58 (tdt, *J* = 10.9, 10.4, 3.5 Hz, 1H), 1.75-1.64 (m, 5H), 1.36-1.08 (m, 5H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ: 197.41, 162.59, 149.48, 140.04, 137.41, 131.86, 131.10, 128.38, 125.87, 113.29, 55.37, 38.29, 32.93, 32.22, 25.77, 25.48. (One aromatic carbon peak was overlapped.) **IR (ATR)**: 761.9, 842.9, 1030.0, 1168.9, 1228.7, 1253.7, 1448.5, 1508.3, 1599.0, 1641.4, 2924.1 cm^{-1}. **HRMS (APCI)**: Calcd. for $C_{23}H_{27}O_2$ ([M+H]$^+$), 335.2006. Found, 335.1998.

(*E*)-2-benzyl-1-(4-chlorophenyl)-3-cyclohexylprop-2-en-1-one (**4j**)



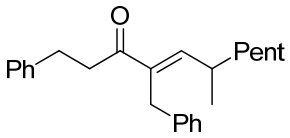
Isolated by MPLC (hexane/EtOAc = 98/2). White solid. 49.1 mg, 72% yield. **M.p.** 80-81 ºC **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.55 (dt, J = 8.8, 2.3 Hz, 2H), 7.36 (dt, J = 8.9, 2.0 Hz, 2H), 7.27-7.20 (m, 4H), 7.17-7.12 (m, 1H), 6.12 (d, J = 9.5 Hz, 1H), 3.85 (s, 2H), 2.59 (tdt, J = 11.3, 10.0, 3.9 Hz, 1H), 1.76-1.62 (m, 5H), 1.36-1.05 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 197.25, 151.60, 139.76, 137.85, 137.47, 136.97, 130.82, 128.43, 128.32, 128.29, 125.99, 38.43, 32.53, 32.06, 25.69, 25.37. **IR (ATR)**: 740.7, 754.2, 825.5, 947.1, 1014.6, 1226.7, 1275.0, 1302.0, 1446.6, 1494.8, 1589.3, 1645.3, 2846.9, 2924.1 cm^{-1}.**Anal**. Calcd. for $C_{22}H_{23}OCl$: C, 77.98; H, 6.84. Found: C, 77.76; H, 6.97. **EIMS**: *m/z* 340 (34%, $[M+2]^+$), 339 (26, $[M+1]^+$), 338 (100, $[M]^+$), 255 (48), 139 (79), 111 (39), 91 (62).

(*E*)-4-benzyl-1,7-diphenylhept-4-en-3-one (**4k**)



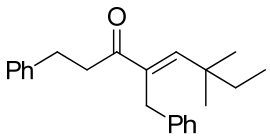
Isolated by MPLC (hexane/EtOAc = 98/2). Pale yellow oil. 42.5 mg, 60% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.29-7.11 (m, 13H), 7.07-7.04 (m, 2H), 6.75 (t, J = 7.2 Hz, 1H), 3.64 (s, 2H), 2.96-2.91 (m, 2H), 2.89-2.85 (m, 2H), 2.71 (t, J = 7.7 Hz, 2H), 2.64-2.58 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 200.17, 142.83, 141.36, 140.76, 140.72, 139.75, 128.50, 128.40, 128.34, 128.32, 128.29, 128.21, 126.23, 125.97, 125.83, 39.27, 34.74, 31.24, 31.10, 30.65. **IR (ATR)**: 939.3, 1030.0, 1452.4, 1494.8, 1602.9, 1678.1, 2927.9, 3026.3 cm^{-1}. **HRMS (APCI)**: Calcd. for $C_{26}H_{27}O$ ($[M+H]^+$), 355.2056. Found, 355.2046.

(*E*)-4-benzyl-6-methyl-1-phenylundec-4-en-3-one (**4l**)



Isolated by MPLC (hexane/EtOAc = 98/2). Colorless oil. 55.0 mg,79% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.29-7.09 (m, 10H), 6.47 (d, J = 10.4 Hz, 1H), 3.68 (s, 2H), 3.00-2.95 (m, 2H), 2.92-2.86 (m, 2H), 2.68-2.57 (m, 1H), 1.37-1.14 (m, 8H), 0.96 (d, J = 6.8 Hz, 3H), 0.85 (t, J = 6.8 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 200.59, 150.05, 141.49, 140.21, 138.67, 128.41, 128.37, 128.25, 128.20, 125.97, 125.74, 39.38, 36.82, 33.78, 31.85, 31.39, 30.70, 27.09, 22.51, 20.02, 13.99. **IR (ATR)**: 734.9, 1030.0, 1076.3, 1124.5, 1452.4, 1494.8, 1602.9, 1668.4, 2926.0, 2956.9 cm^{-1}. **Anal**. Calcd. for $C_{25}H_{32}O$: C, 86.15; H,9.25. Found: C, 86.08; H, 9.44. **EIMS**: *m/z* 348 (11%, $[M]^+$), 250 (20), 149 (100), 105 (18), 91 (55).

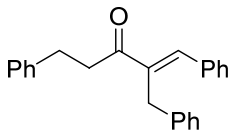
(*E*)-4-benzyl-6,6-dimethyl-1-phenyloct-4-en-3-one (**4m**)



Isolated by MPLC (hexane/EtOAc = 98/2). Colorless oil. 57.6 mg, 90% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.27-7.11 (m, 8H), 7.07 (d, J = 7.2 Hz, 2H), 6.67 (s, 1H), 3.86 (s, 2H), 2.97-2.93 (m, 2H), 2.88-2.83 (m, 2H), 1.47 (q, J = 7.4 Hz, 2H), 1.13 (s, 6H), 0.84 (t, J = 7.5 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 201.72, 151.76, 141.47, 139.97,

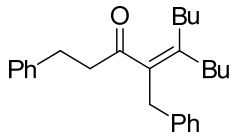
139.00, 128.38, 128.35, 128.23, 127.89, 125.94, 125.65, 39.82, 37.13, 36.61, 31.62, 30.72, 27.66, 9.22. **IR (ATR)**: 729.1, 748.4, 987.6, 1030.0, 1076.3, 1155.4, 1452.4, 1494.8, 1602.9, 1672.3, 2962.7 cm^{-1}. **Anal**. Calcd. for $C_{23}H_{28}O$: C, 86.20; H,8.81. Found: C, 86.41; H, 8.69. **EIMS**: *m/z* 320 (10, $[M]^+$), 250 (23), 249 (100), 105 (31), 91 (81).

(*E*)-2-benzyl-1,5-diphenylpent-1-en-3-one (**4n**)



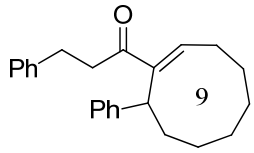
Isolated by MPLC (hexane/EtOAc = 98/2). Pale yellow oil. 25.1 mg, 38% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.71 (s, 1H), 7.35-7.23 (m, 9H), 7.22-7.16 (m, 4H), 7.12 (d, *J* = 7.2 Hz, 2H), 3.95 (s, 2H), 3.12 (t, *J* = 7.5 Hz, 2H), 2.96 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 200.82, 141.35, 140.35, 139.48, 139.42, 135.30, 129.18, 128.87, 128.59, 128.54, 128.46, 128.41, 127.93, 126.03, 39.82, 32.35, 30.54. (One aromatic carbon peak was overlapped.) **IR (ATR)**: 750.3, 993.3, 1030.0, 1076.3, 1159.2, 1211.3, 1452.4, 1494.8, 1602.9, 1668.4, 3026.3 cm^{-1}. **Anal**. Calcd. for $C_{24}H_{22}O$: C, 88.31; H,6.79. Found: C, 88.45; H, 6.96. **EIMS**: *m/z* 327 (21%, $[M+1]^+$), 326 (81, $[M]^+$), 235 (41), 221 (50), 115 (71), 91 (100).

4-benzyl-5-butyl-1-phenylnon-4-en-3-one (**4o**)



Isolated by MPLC (hexane/EtOAc = 97/3). Colorless oil.58.8 mg, 81% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.28-7.11 (m, 8H), 7.05-7.02 (m, 2H), 3.63 (s, 2H), 2.75-2.66 (m, 2H), 2.63-2.57 (m, 2H), 2.15-2.06 (m, 4H), 1.46-1.23 (m, 8H), 0.89 (t, *J* = 7.2 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 207.33, 145.24, 141.28, 139.02, 135.23, 128.51, 128.30, 126.21, 125.84, 44.70, 35.06, 33.35, 31.87, 31.31, 30.60, 29.78, 23.01, 22.97, 13.95, 13.93. (2 aromatic carbon peaks were overlapped.) **IR (ATR)**: 1030.0, 1074.4, 1138.0, 1454.3, 1494.8, 1602.9, 1687.7, 2929.9, 2956.9 cm^{-1}. **HRMS (APCI)**: Calcd. for $C_{26}H_{35}O$ ($[M+H]^+$), 363.2682. Found, 363.2674.

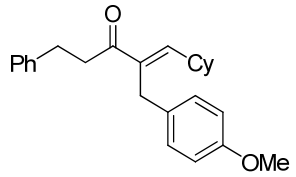
3-phenyl-1-[(*E*)-9-phenylcyclonon-1-en-1-yl]propan-1-one (**4p**)



Isolated by MPLC (hexane/EtOAc = 98/2). Colorless oil. 60.4 mg, 91% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.27-7.20 (m, 6H), 7.17-7.08 (m, 4H), 6.84 (dd, *J* = 10.0, 8.2 Hz, 1H), 4.33 (dd, *J* = 12.2, 5.0 Hz, 1H), 2.98-2.78 (m, 4H), 2.71-2.62 (m, 1H), 2.47-2.33 (m, 2H), 1.98-1.90 (m, 1H), 1.75-1.42 (m, 8H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 200.94, 144.24, 144.05, 143.32, 141.46, 128.33, 128.26, 128.09, 127.28, 125.87, 125.62, 42.11, 40.13, 31.46, 30.62, 28.45, 27.23, 26.42, 26.38, 25.82. **IR (ATR)**: 750.3, 1138.0, 1452.4, 1494.8, 1600.9, 1668.4, 2924.1, 3026.3 cm^{-1}. **Anal**.

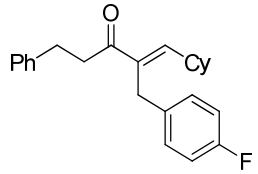
Calcd. for $C_{24}H_{28}O$: C, 86.70; H,8.49. Found: C, 86.73; H, 8.71. **EIMS**: *m/z* 332 (24%, $[M]^+$), 228 (27), 227 (88), 105 (56), 91 (100).

(*E*)-1-cyclohexyl-2-[(4-methoxyphenyl)methyl]-5-phenylpent-1-en-3-one (**4q**)



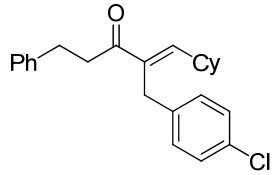
Isolated by MPLC (hexane/EtOAc = 97/3). Colorless oil. 59.1 mg, 82% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.28-7.23 (m, 2H), 7.20-7.13 (m, 3H), 7.04 (dt, *J* = 8.6, 2.5 Hz, 2H), 6.78 (dt, *J* = 9.4, 2.5 Hz, 2H), 6.49 (d, *J* = 9.5 Hz, 1H), 3.76 (s, 3H), 3.62 (s, 2H), 2.97-2.92 (m, 2H), 2.90-2.85 (m, 2H), 2.49 (tdt, *J* = 10.9, 10.0, 3.6 Hz, 1H), 1.76-1.57 (m, 5H), 1.33-1.06 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 200.77, 157.69, 148.55, 141.54, 138.47, 132.26, 129.11, 128.39, 128.37, 125.95, 113.71, 55.19, 39.40, 38.30, 32.08, 30.63, 30.54, 25.75, 25.43. **IR (ATR)**: 750.3, 817.8, 1035.8, 1126.4, 1176.6, 1246.0, 1300.0, 1448.5, 1510.3, 1610.6, 1668.4, 2850.8, 2926.0 cm^{-1}. **Anal**. Calcd. for $C_{25}H_{30}O_2$: C, 82.83; H,8.34. Found: C, 82.73; H, 8.43. **EIMS**: *m/z* 362 (47%, $[M]^+$), 279 (87), 257 (32), 163 (32), 121 (100), 108 (35), 91 (54).

(*E*)-1-cyclohexyl-2-[(4-fluorophenyl)methyl]-5-phenylpent-1-en-3-one (**4r**)



Isolated by MPLC (hexane/EtOAc = 97/3). Colorless oil. 60.7 mg, 87% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.26 (t, *J* = 7.2 Hz, 2H), 7.20-7.14 (m, 3H), 7.07 (dd, *J* = 8.8, 5.7 Hz, 2H), 6.90 (tt, *J* = 8.8, 2.3 Hz, 2H), 6.51 (d, *J* = 10.0 Hz, 1H), 3.64 (s, 2H), 2.98-2.94 (m, 2H), 2.91-2.86 (m, 2H), 2.45 (tdt, *J* = 10.9, 10.4, 3.6 Hz, 1H), 1.76-1.54 (m, 5H), 1.32-1.06 (m, 5H). **^{13}C NMR (100MHz, $CDCl_3$)** δ: 200.60, 161.14 (d, *J* = 244.1 Hz), 149.05, 141.41, 138.14, 135.88 (d, *J* = 3.8 Hz), 129.51 (d, *J* = 7.6 Hz), 128.40, 128.35, 125.97, 114.97 (d, *J* = 21.0 Hz), 39.22, 38.39, 31.99, 30.61, 30.58, 25.68, 25.37. **IR (ATR)**: 750.3, 821.7, 902.7, 1016.5, 1093.6, 1126.4, 1157.3, 1220.9, 1448.5, 1506.4, 1602.9, 1668.4, 2850.8, 2926.0 cm^{-1}. **HRMS (APCI)**: Calcd. for $C_{24}H_{28}FO$ ($[M+H]^+$), 351.2119. Found, 351.2106.

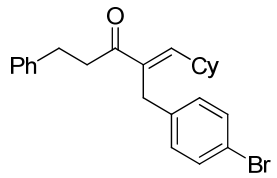
(*E*)-2-[(4-chlorophenyl)methyl]-1-cyclohexyl-5-phenylpent-1-en-3-one (**4s**)



Isolated by MPLC (hexane/EtOAc = 98/2). Colorless oil. 66.0 mg, 90% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.29-7.22 (m, 2H), 7.22-7.13 (m, 5H), 7.04 (dt, *J* = 8.8, 2.3 Hz, 2H), 6.52 (d, *J* = 10.0 Hz, 1H), 3.63 (s, 2H), 2.99-2.93 (m, 2H), 2.91-2.86 (m, 2H), 2.44 (tdt, *J* = 10.9, 10.0, 4.1 Hz, 1H), 1.77-1.54 (m, 5H), 1.33-1.06 (m, 5H). **^{13}C NMR (100**

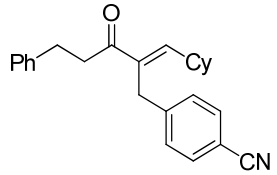
MHz, $CDCl_3$) δ: 200.55, 149.28, 141.39, 138.76, 137.87, 131.48, 129.52, 128.42, 128.37, 126.01, 39.21, 38.44, 32.01, 30.79, 30.63, 25.69, 25.38. (One aromatic carbon peak was overlapped.) **IR (ATR)**: 750.3, 902.7, 1014.6, 1091.7, 1126.4, 1178.5, 1448.5, 1491.0, 1668.4, 2850.8, 2926.0 cm^{-1}. **Anal**. Calcd. for $C_{24}H_{27}OCl$: C, 78.56; H,7.42. Found: C, 78.48; H, 7.49. **EIMS**: *m/z* 366 (11%, $[M]^+$), 285 (33), 284 (21), 283 (100), 125 (30), 91 (41).

(*E*)-2-[(4-bromophenyl)methyl]-1-cyclohexyl-5-phenylpent-1-en-3-one (**4t**)



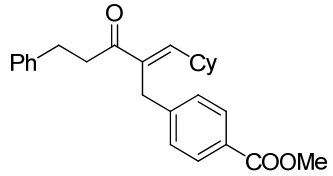
Isolated by preparative recycling GPC. Colorless oil. 69.3 mg, 84% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.33 (dt, *J* = 9.1, 2.2 Hz, 2H), 7.28-7.24 (m, 2H), 7.20-7.14 (m, 3H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.52 (d, *J* = 10.0 Hz, 1H), 3.61 (s, 2H), 2.98-2.94 (m, 2H), 2.90-2.86 (m, 2H), 2.43 (tdt, *J* = 10.9, 10.0, 3.6 Hz, 1H), 1.76-1.54 (m, 5H), 1.32-1.06 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 200.49, 149.30, 141.35, 139.27, 137.76, 131.28, 129.92, 128.40, 128.35, 125.99, 119.52, 39.18, 38.42, 31.98, 30.83, 30.60, 25.66, 25.35. **IR (ATR)**: 750.3, 794.7, 902.7, 1010.7, 1072.4, 1126.4, 1178.5, 1406.1, 1448.5, 1487.1, 1666.5, 2850.8, 2926.0 cm^{-1}. **HRMS (APCI)**: Calcd. for $C_{24}H_{28}BrO$ ($[M+H]^+$), 411.1318. Found, 411.1305.

4-[(*E*)-2-(cyclohexylmethylidene)-3-oxo-5-phenylpentyl]benzonitrile (**4u**)



Isolated by preparative recycling GPC. Pale yellow oil. 52.0 mg, 73% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.51 (d, *J* = 8.2 Hz, 2H), 7.27-7.25 (m, 2H), 7.20-7.14 (m, 5H), 6.58 (d, *J* = 10.0 Hz, 1H), 3.71 (s, 2H), 3.01-2.96 (m, 2H), 2.91-2.88 (m, 2H), 2.40 (tdt, *J* = 10.9, 10.3, 3.4 Hz, 1H), 1.77-1.53 (m, 5H), 1.31-1.08 (m, 5H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ: 200.30, 150.08, 146.07, 141.17, 137.07, 132.07, 128.90, 128.40, 128.33, 126.04, 119.03, 109.59, 38.96, 38.57, 31.90, 31.62, 30.56, 25.57, 25.28. **IR (ATR)**: 750.3, 819.8, 1126.4, 1176.6, 1448.5, 1496.8, 1606.7, 1666.5, 2225.9, 2850.8, 2926.0 cm^{-1}. **HRMS (APCI)**: Calcd. for $C_{25}H_{28}NO$ ($[M+H]^+$), 358.2165. Found, 358.2159.

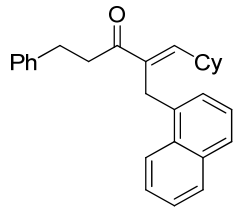
methyl 4-[(*E*)-2-(cyclohexylmethylidene)-3-oxo-5-phenylpentyl]benzoate (**4v**)



Isolated by MPLC (hexane/EtOAc = 95/5). Pale yellow oil. 61.9 mg, 79% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.91 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.28-7.24 (m, 2H), 7.20-7.15 (m, 5H), 6.55 (d, *J* = 10.0 Hz, 1H), 3.88 (s, 3H), 3.72 (s, 2H), 2.99-2.97 (m, 2H), 2.91-2.87 (m, 2H), 2.43 (tdt, *J* = 10.9, 10.0, 3.9 Hz, 1H), 1.74-1.54 (m, 5H), 1.30-1.06 (m,

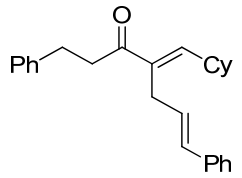
5H). **^{13}C NMR (100 MHz, $CDCl_3$)** *δ*: 200.42, 167.04, 149.62, 145.90, 141.33, 137.53, 129.62, 128.40, 128.34, 128.13, 127.73, 125.99, 51.90, 39.14, 38.49, 31.91, 31.46, 30.62, 25.64, 25.32. **IR (ATR)**: 752.2, 902.7, 1020.3, 1107.1, 1178.5, 1278.8, 1435.0, 1496.8, 1608.6, 1668.4, 1720.5, 2850.8, 2926.0 cm^{-1}. **HRMS (APCI)**: Calcd. for $C_{26}H_{31}O_3$ ($[M+H]^+$), 391.2268. Found, 391.2254.

(*E*)-1-cyclohexyl-2-(naphthalen-1-ylmethyl)-5-phenylpent-1-en-3-one (**4w**)



Isolated by preparative recycling GPC. Pale yellow oil. 68.1 mg, 89% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** *δ*: 8.13 (d, *J* = 8.6 Hz, 1H), 7.86-7.83 (m, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.56-7.46 (m, 2H), 7.32-7.24 (m, 3H), 7.22-7.15 (m, 3H), 6.98 (dd, *J* = 7.2, 0.9 Hz, 1H), 6.71 (d, *J* = 10.0 Hz, 1H), 4.13 (s, 2H), 3.07-3.02 (m, 2H), 2.94-2.89 (m, 2H), 2.36-2.26 (m, 1H), 1.68-1.54 (m, 5H), 1.26-1.07 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** *δ*: 200.70, 150.07, 141.53, 137.19, 135.56, 133.73, 132.03, 128.69, 128.45, 126.61, 126.01, 125.84, 125.51, 125.44, 123.95, 123.50, 39.41, 38.22, 32.00, 30.72, 28.05, 25.71, 25.28. (One aromatic carbon peak was overlapped.) **IR (ATR)**: 750.3, 771.5, 790.8, 902.7, 1076.3, 1126.4, 1398.4, 1448.5, 1494.8, 1668.4, 2850.8, 2924.1 cm^{-1}. **HRMS (APCI)**: Calcd. for $C_{28}H_{31}O$ ($[M+H]^+$), 383.2369. Found, 383.2361.

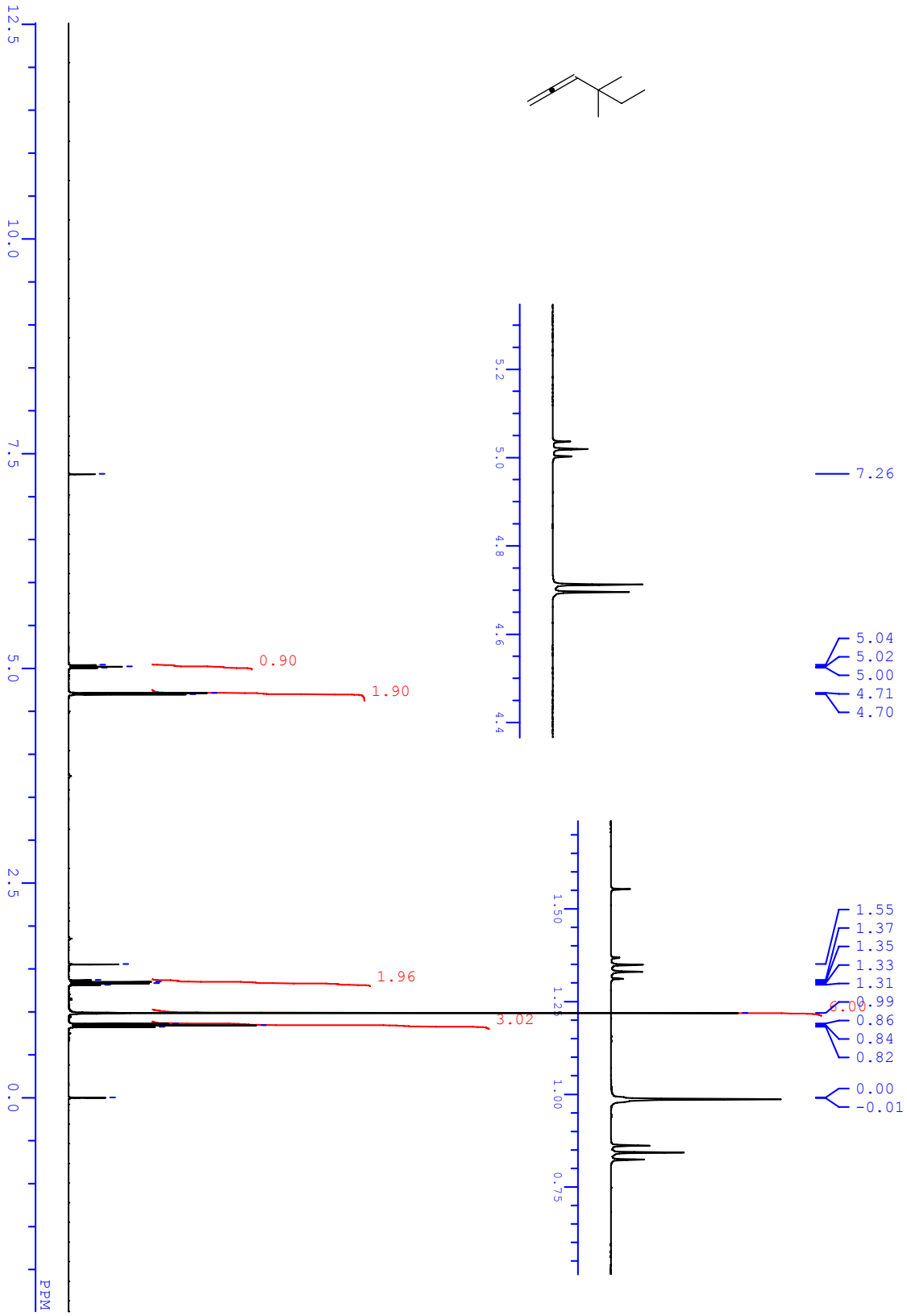
(4*E*,6*E*)-4-(cyclohexylmethylidene)-1,7-diphenylhept-6-en-3-one (**4x**)



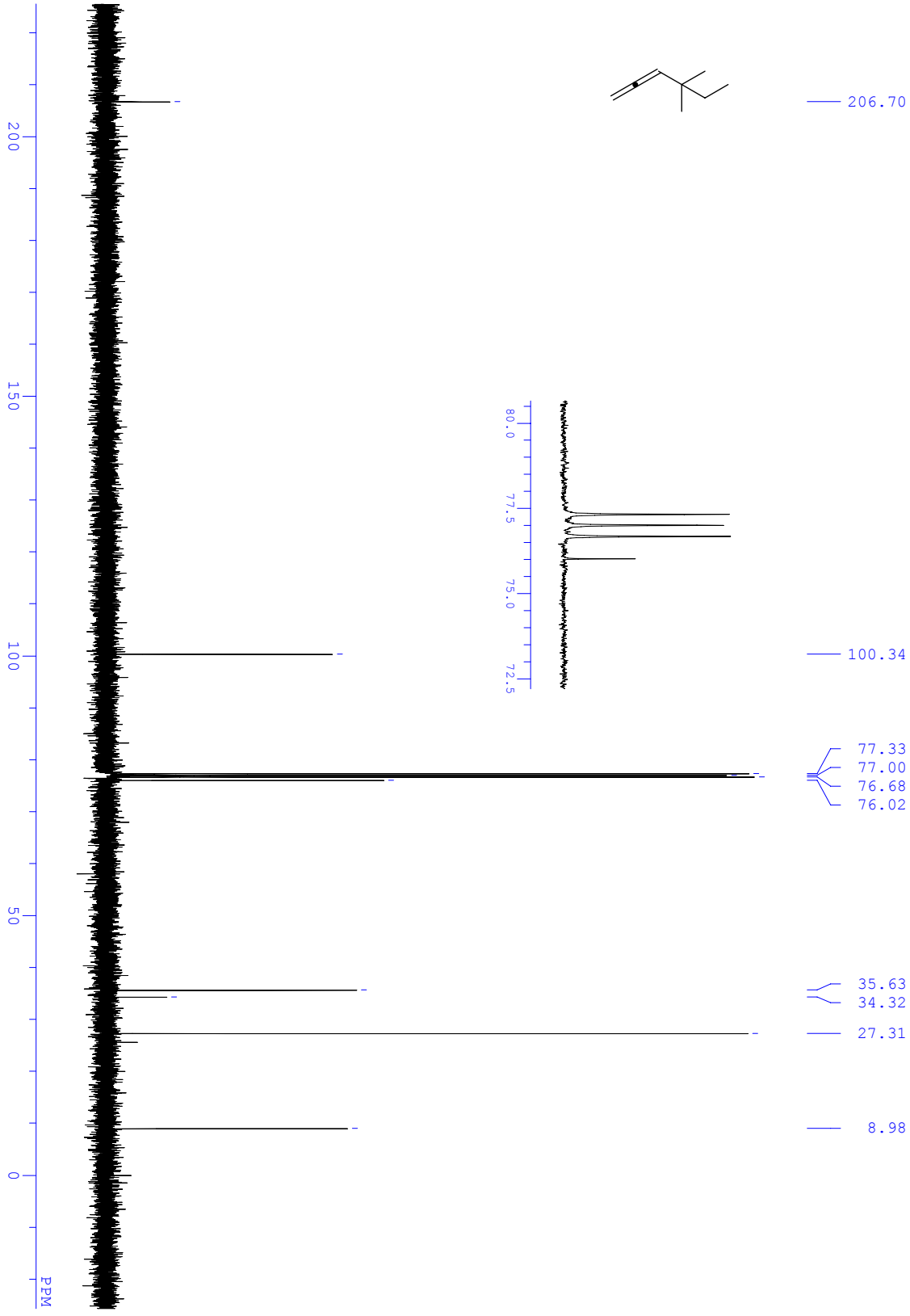
Isolated by MPLC (hexane/EtOAc = 98/2). Colorless oil. 44.2 mg, 62% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** *δ*: 7.31-7.24 (m, 6H), 7.21-7.15 (m, 4H), 6.48 (d, *J* = 10.0 Hz, 1H), 6.34 (d, *J* = 15.9 Hz, 1H), 6.14 (dt, *J* = 15.9, 6.3 Hz, 1H), 3.22 (dd, *J* = 6.6, 1.1 Hz, 2H), 3.01-2.97 (m, 2H), 2.95-2.90 (m, 2H), 2.45 (tdt, *J* = 10.8, 10.0, 3.6 Hz, 1H), 1.77-1.63 (m, 5H), 1.36-1.07 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** *δ*: 200.41, 148.98, 141.53, 137.58, 137.15, 130.18, 128.42, 128.40, 128.30, 126.90, 125.98, 39.21, 38.15, 32.14, 30.73, 29.20, 25.75, 25.44. (2 aromatic carbon peaks were overlapped.) **IR (ATR)**: 900.8, 964.4, 1030.0, 1074.4, 1126.4, 1178.5, 1448.5, 1494.8, 1668.4, 2850.8, 2924.1, 3026.3 cm^{-1}. **Anal**. Calcd. for $C_{26}H_{30}O$: C, 87.10; H,8.43. Found: C, 86.79; H, 8.48. **EIMS**: *m/z* 359 (18%, $[M+1]^+$), 358 (46, $[M]^+$), 275 (81), 207 (27), 105 (64), 91(100).

5. NMR Charts

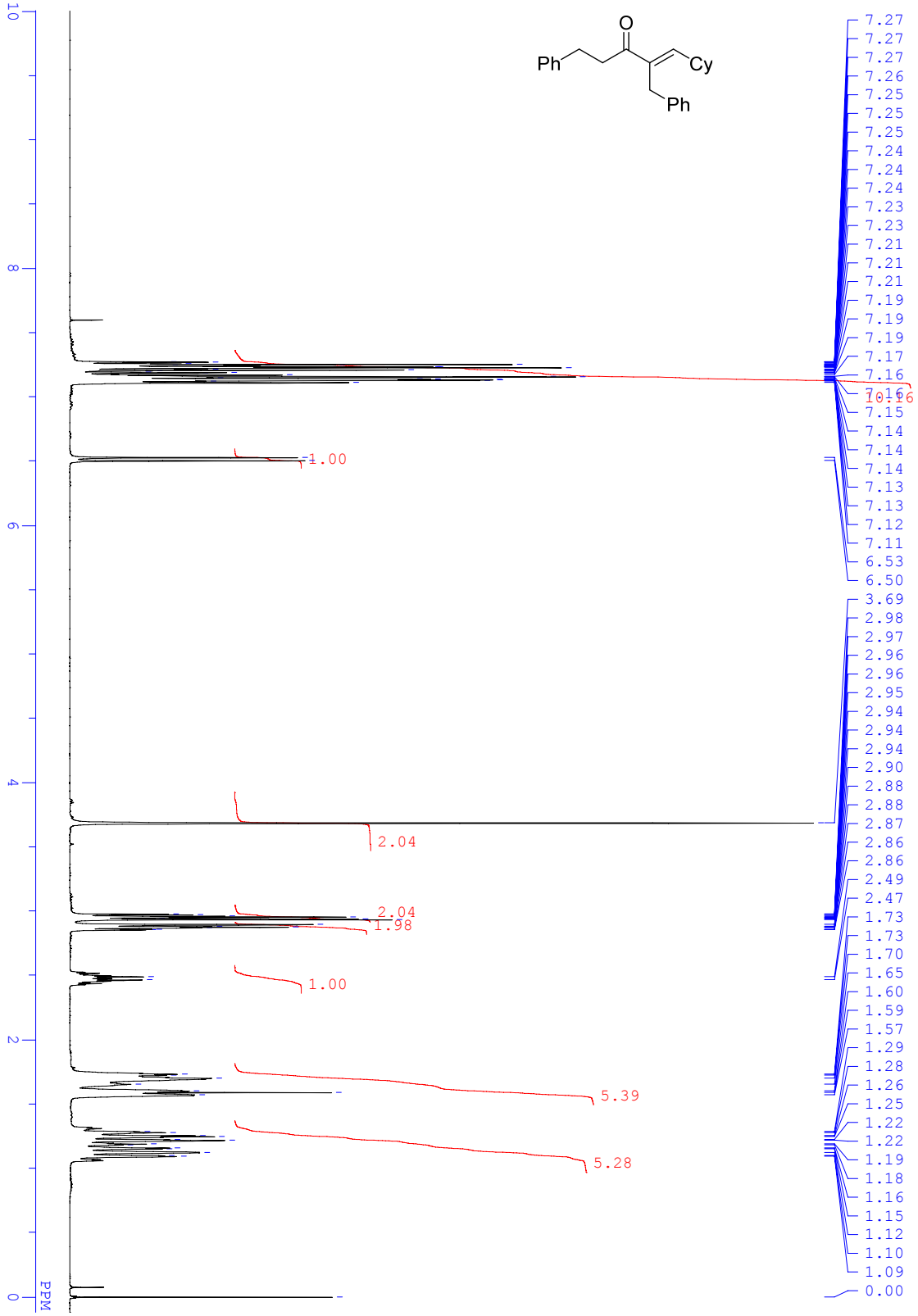
^{1}H NMR spectrum of **2d**



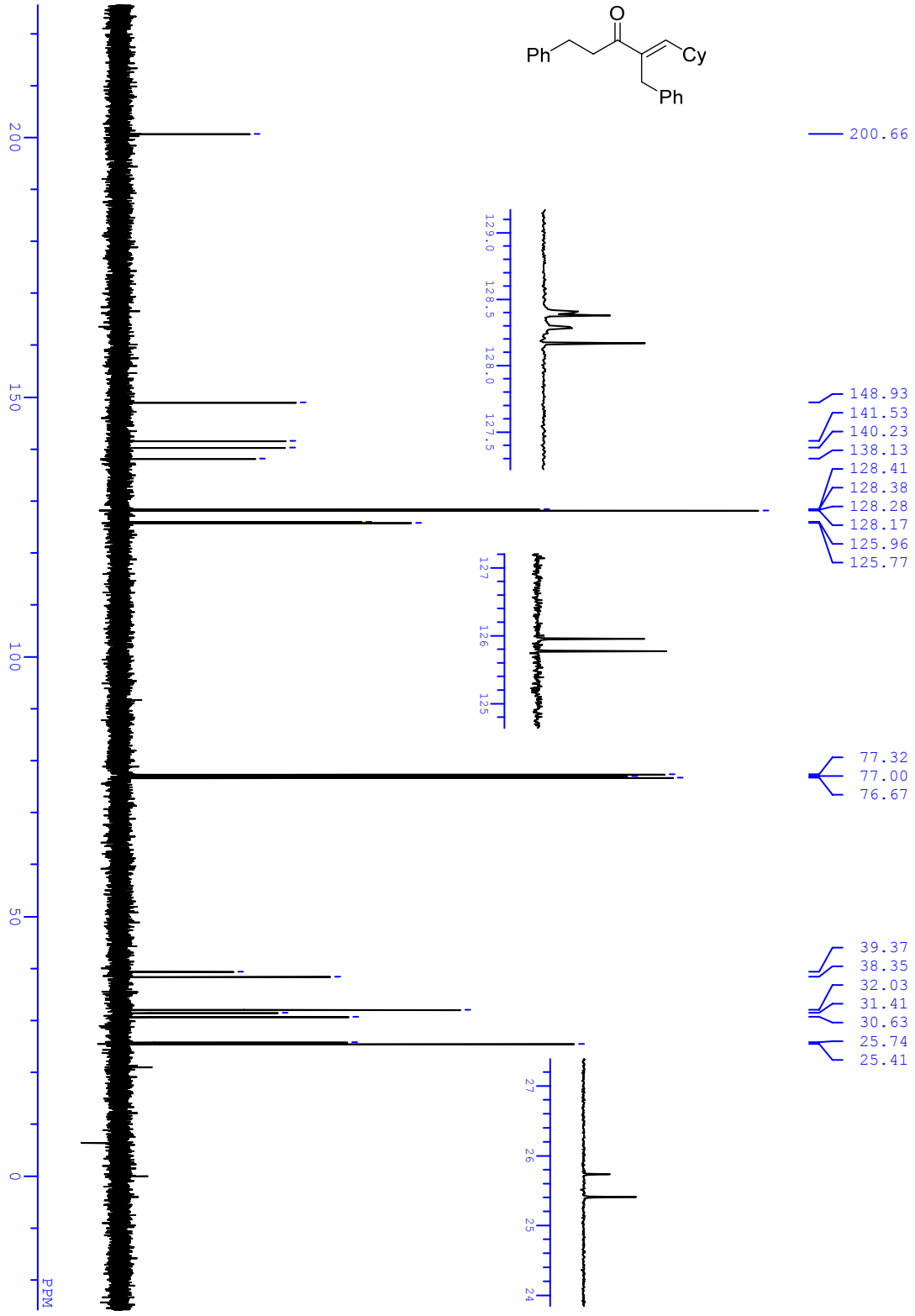
^{13}C {^{1}H} NMR spectrum of **2d**



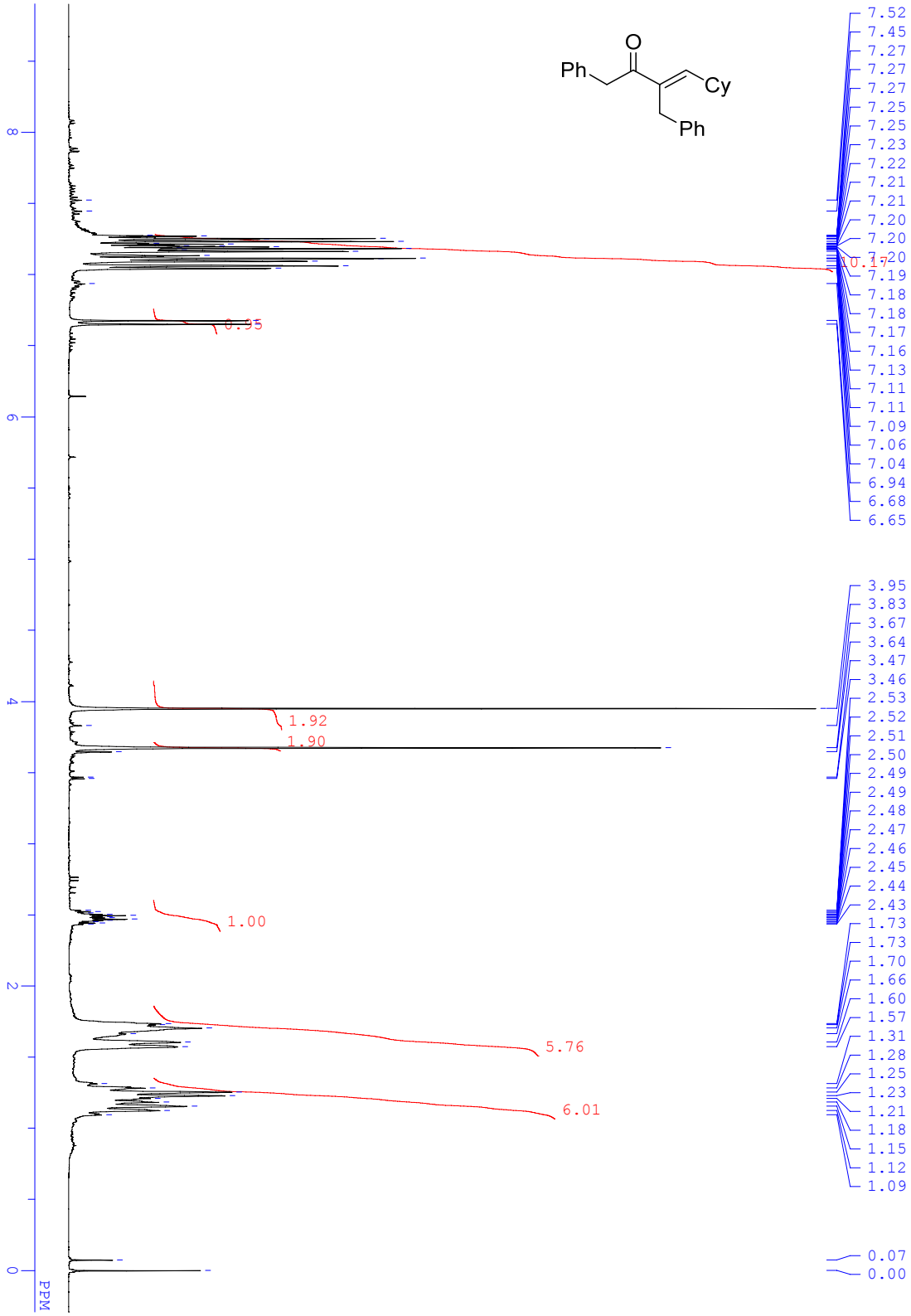
^{1}H NMR spectrum of **4a**



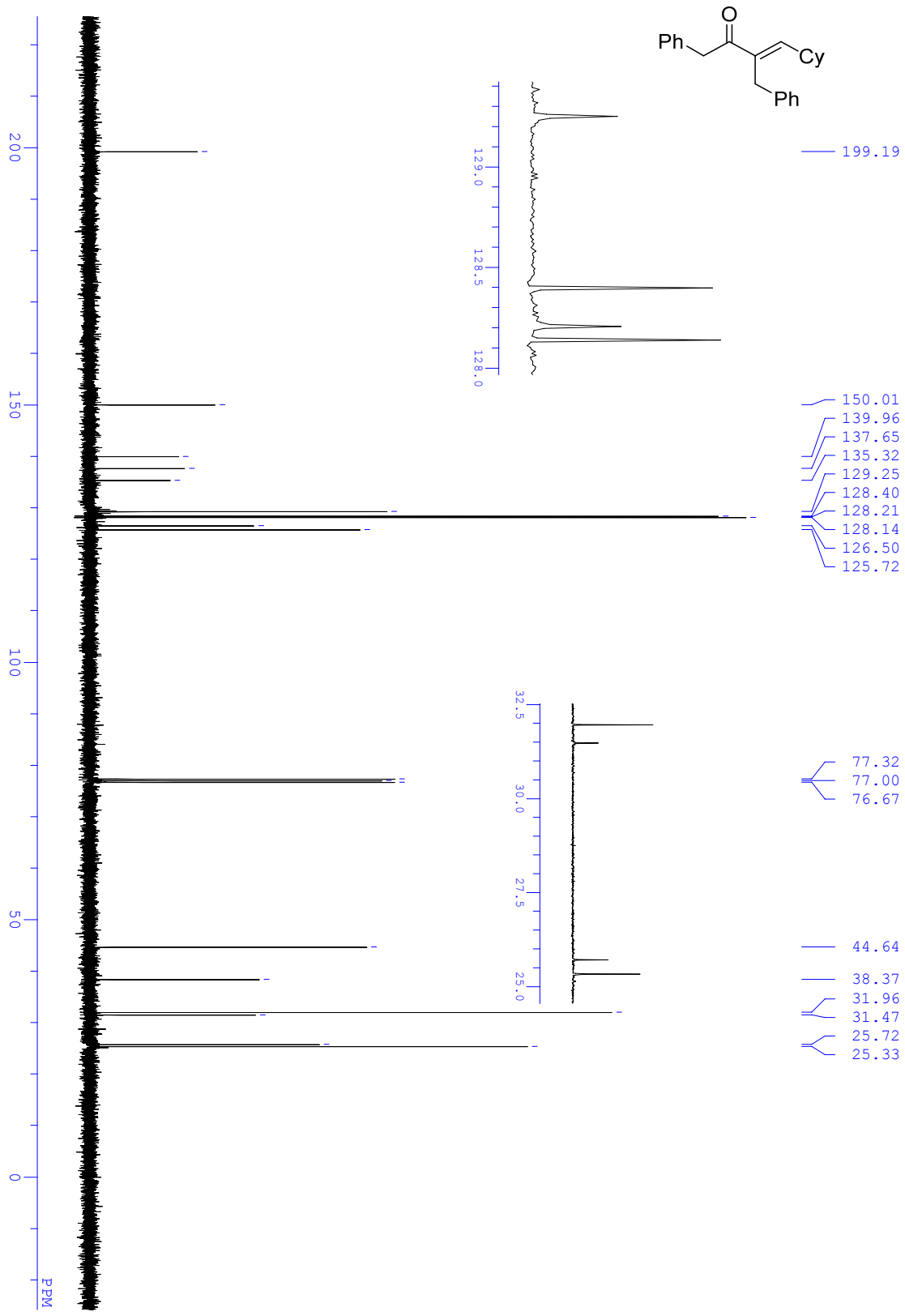
^{13}C {^{1}H} NMR spectrum of **4a**



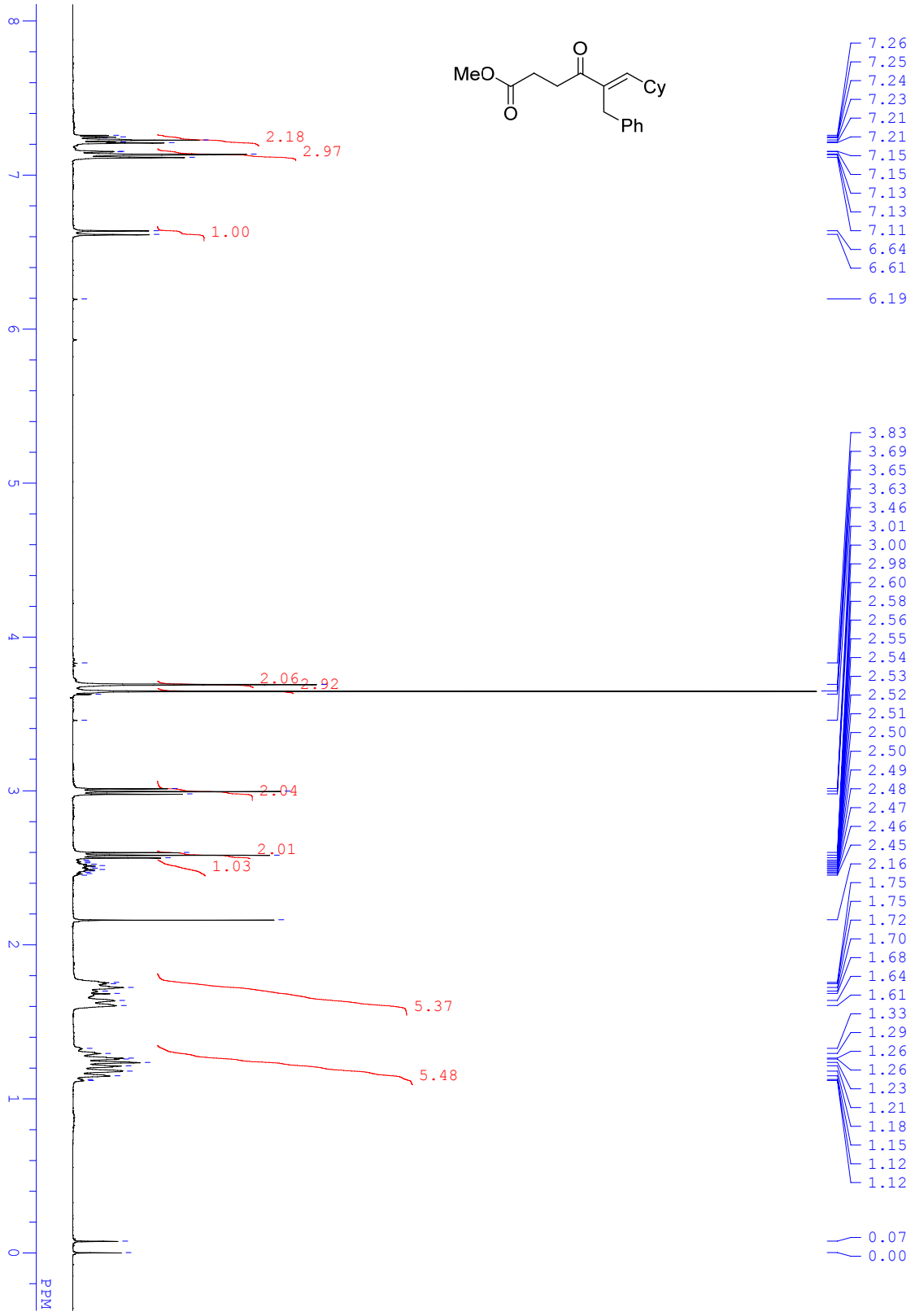
^{1}H NMR spectrum of **4c**



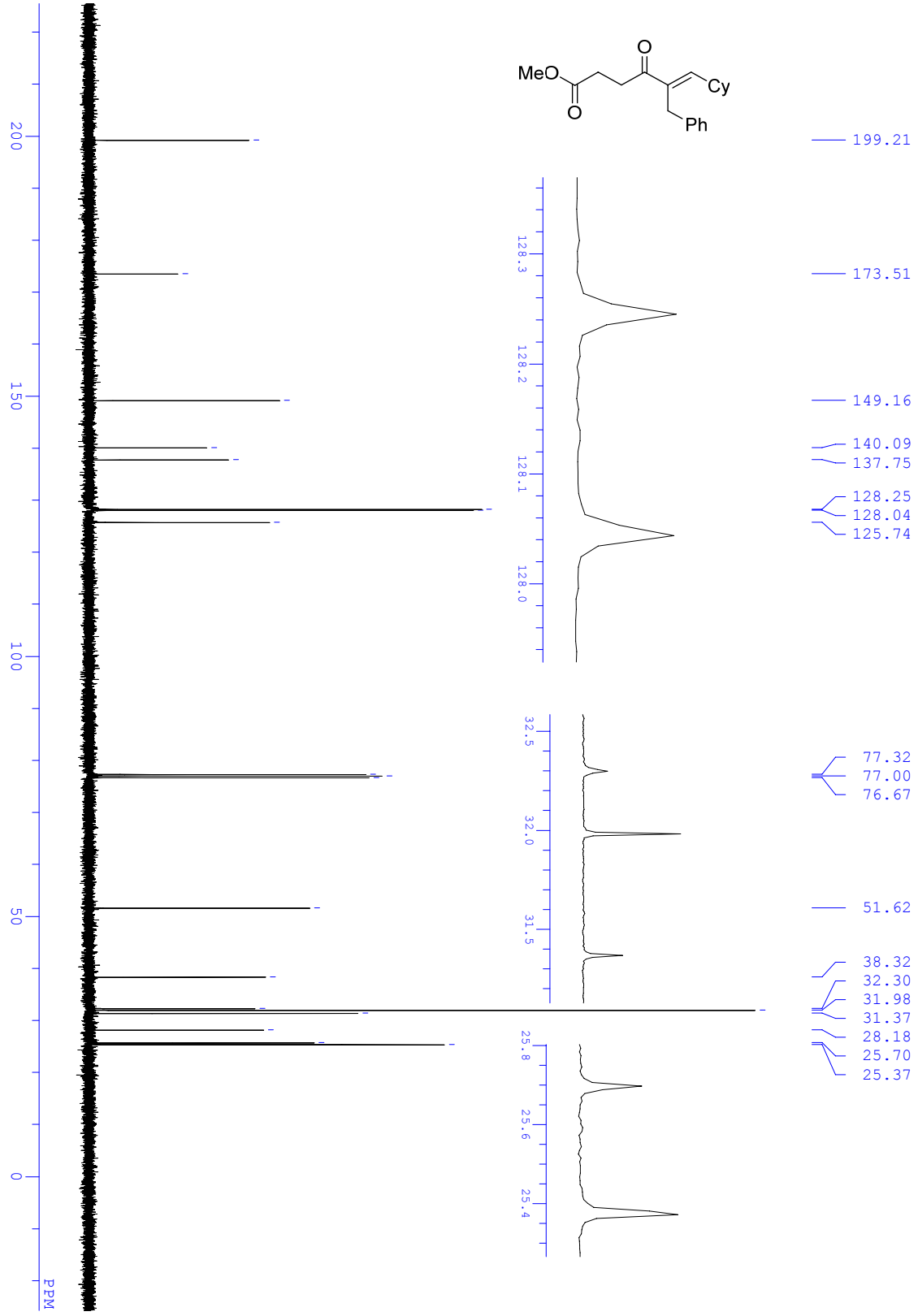
^{13}C {^{1}H} NMR spectrum of **4c**



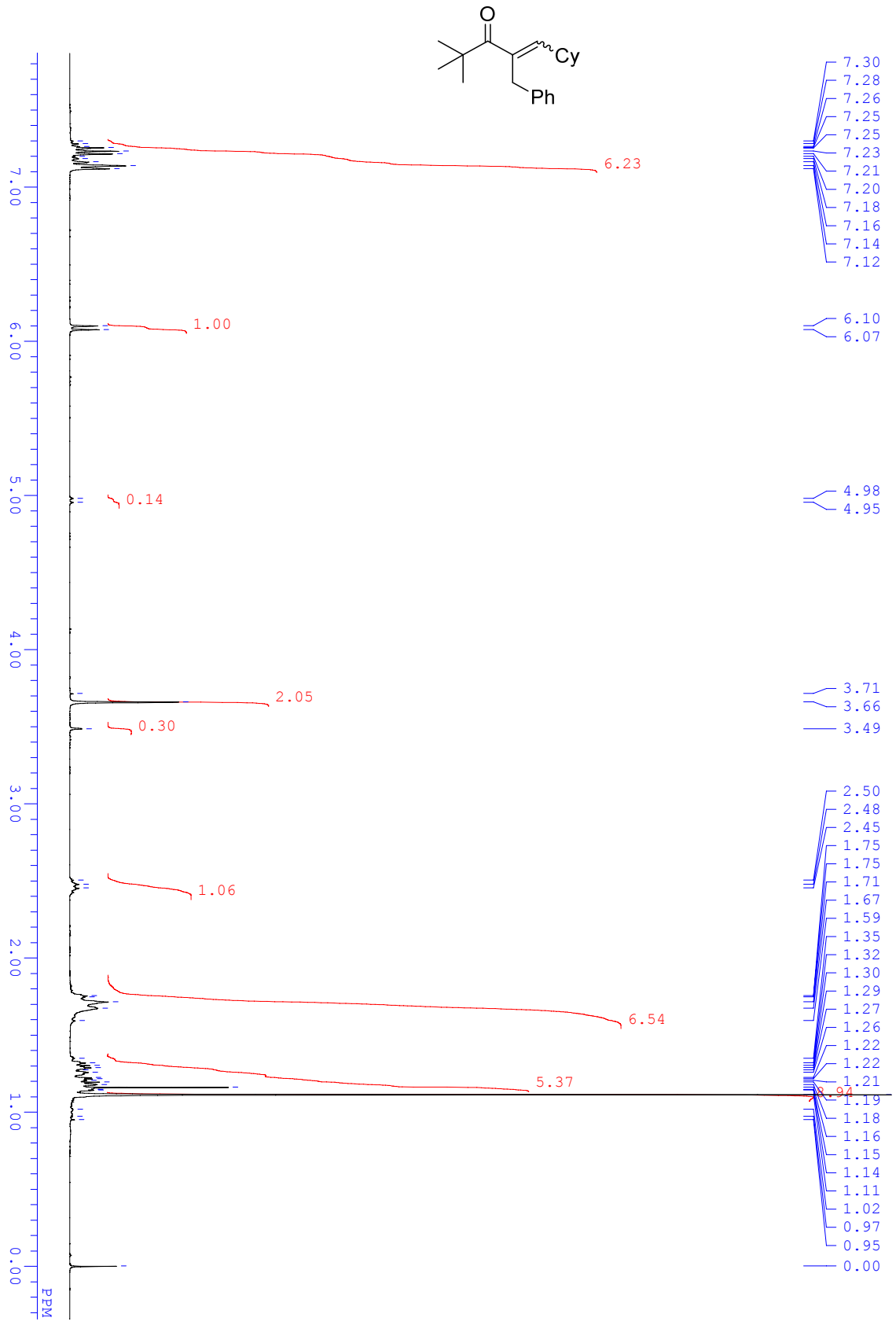
^{1}H NMR spectrum of **4e**



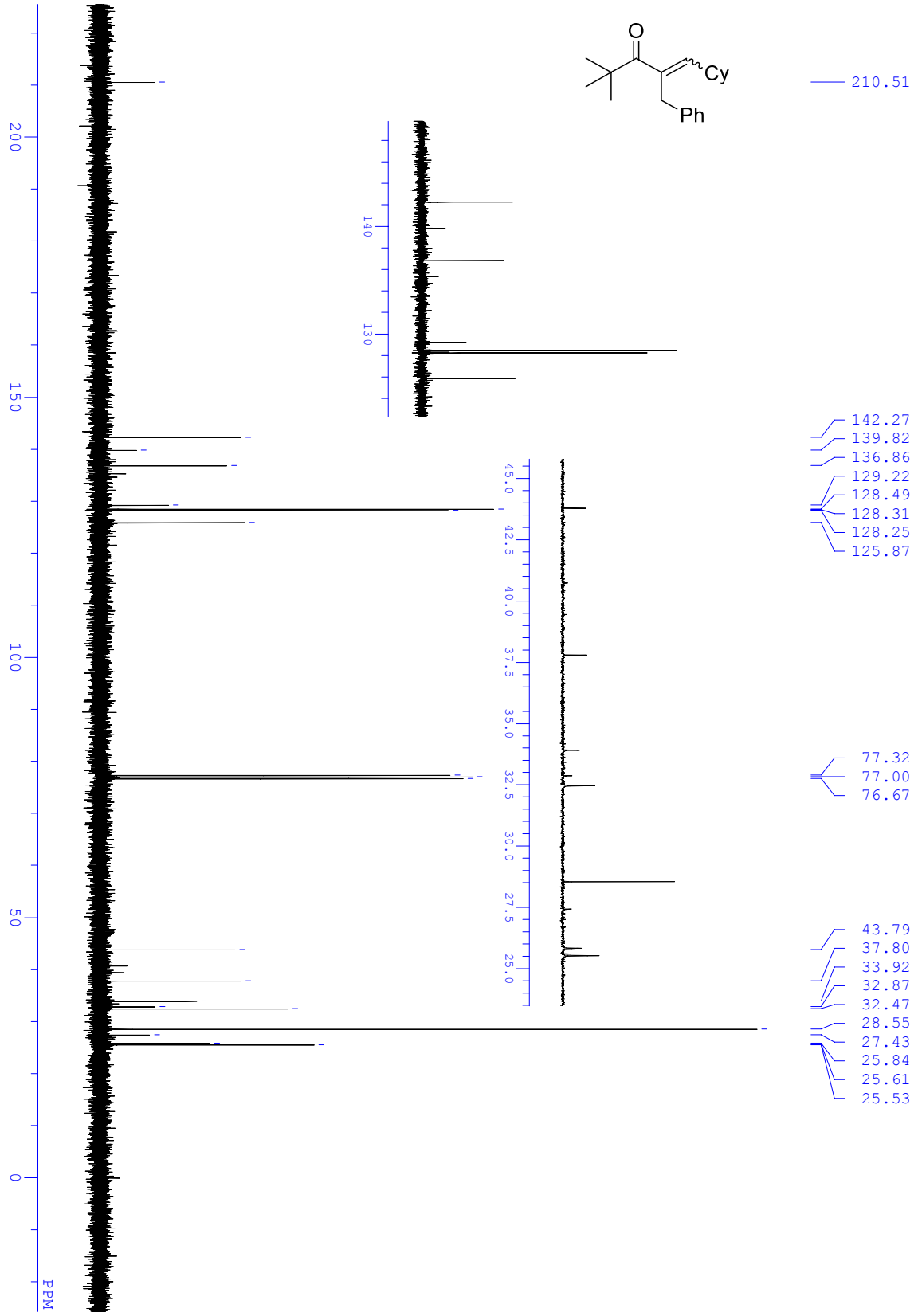
^{13}C {^{1}H} NMR spectrum of **4e**



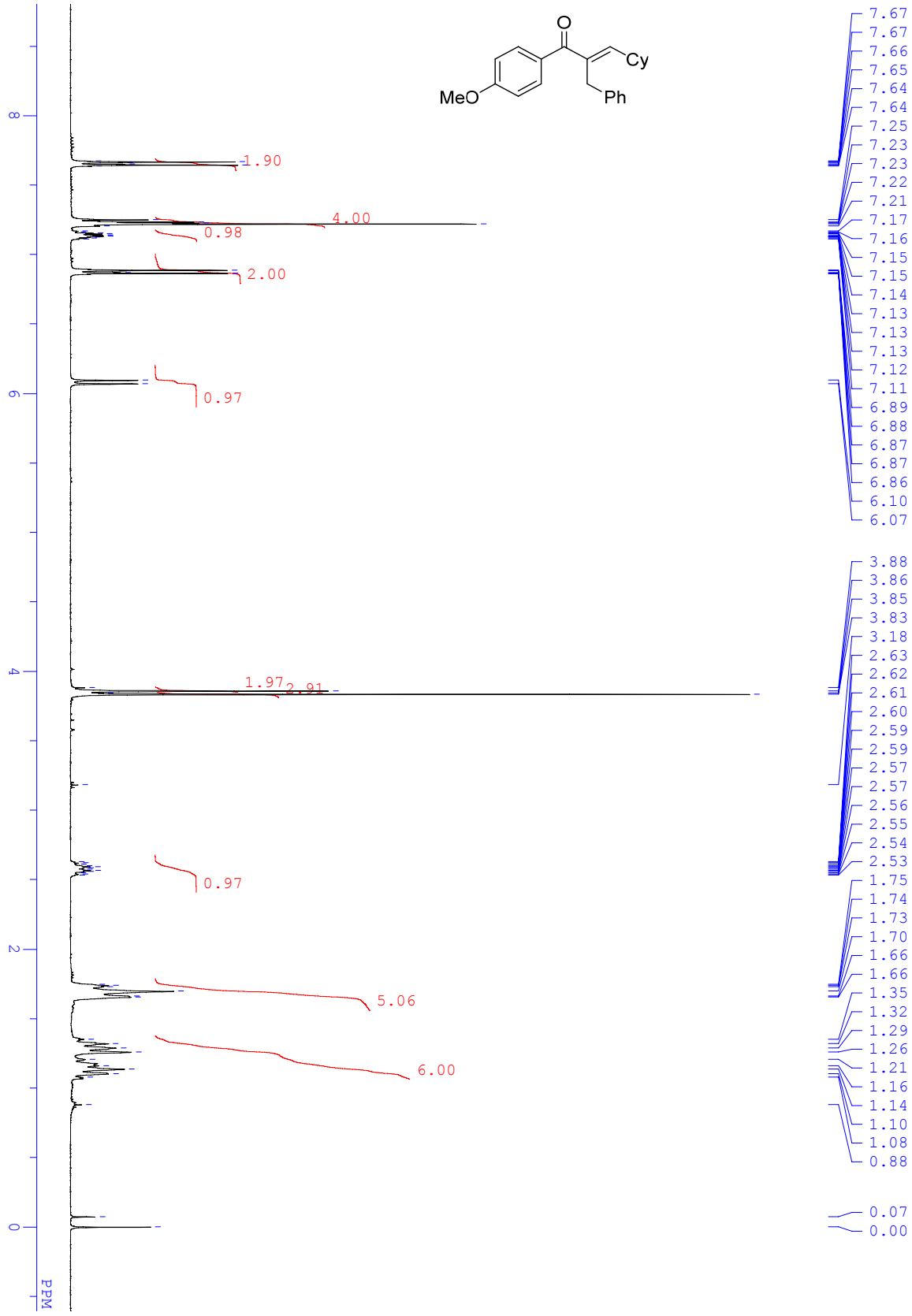
^{1}H NMR spectrum of **4g**



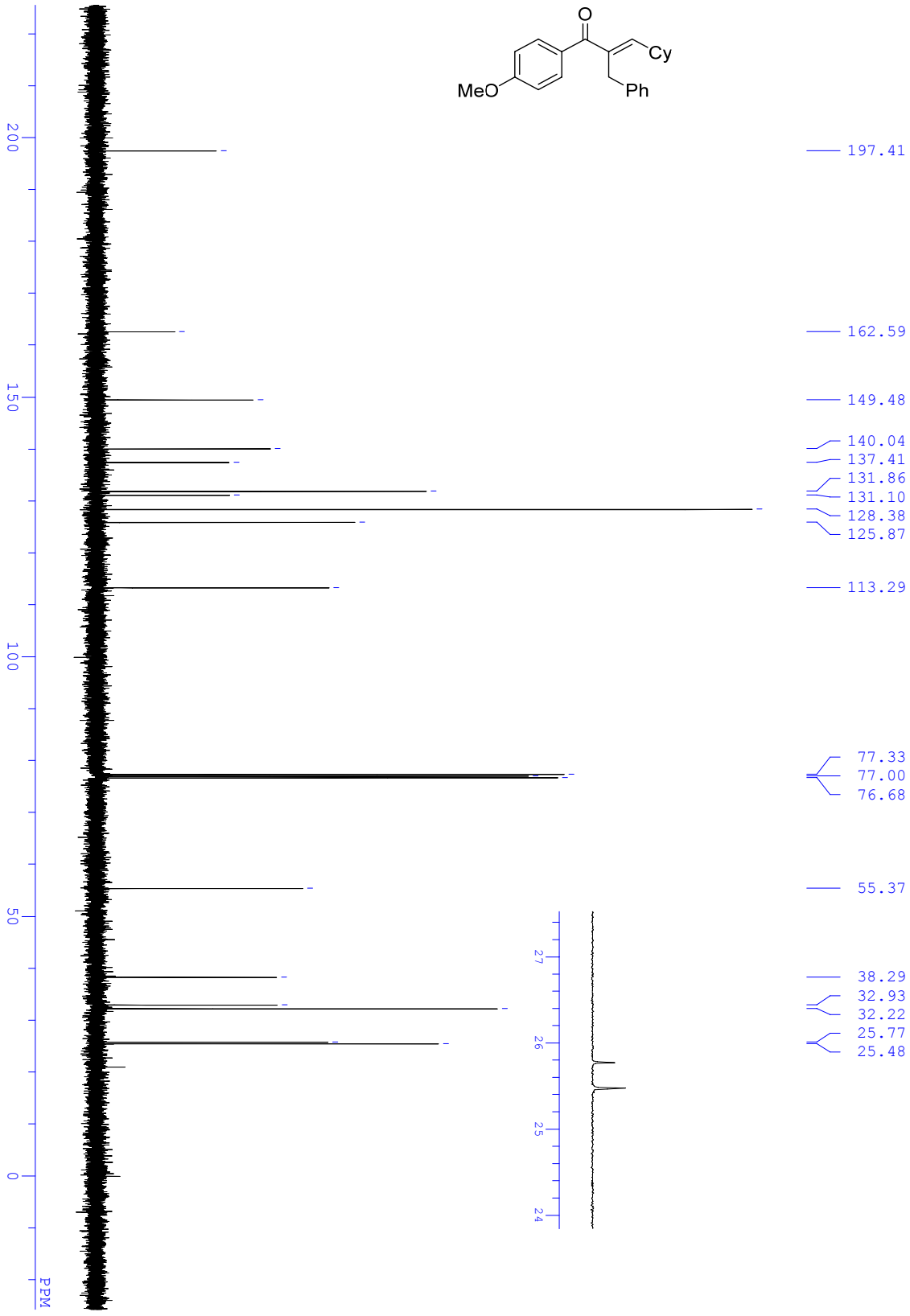
^{13}C {^{1}H} NMR spectrum of **4g**



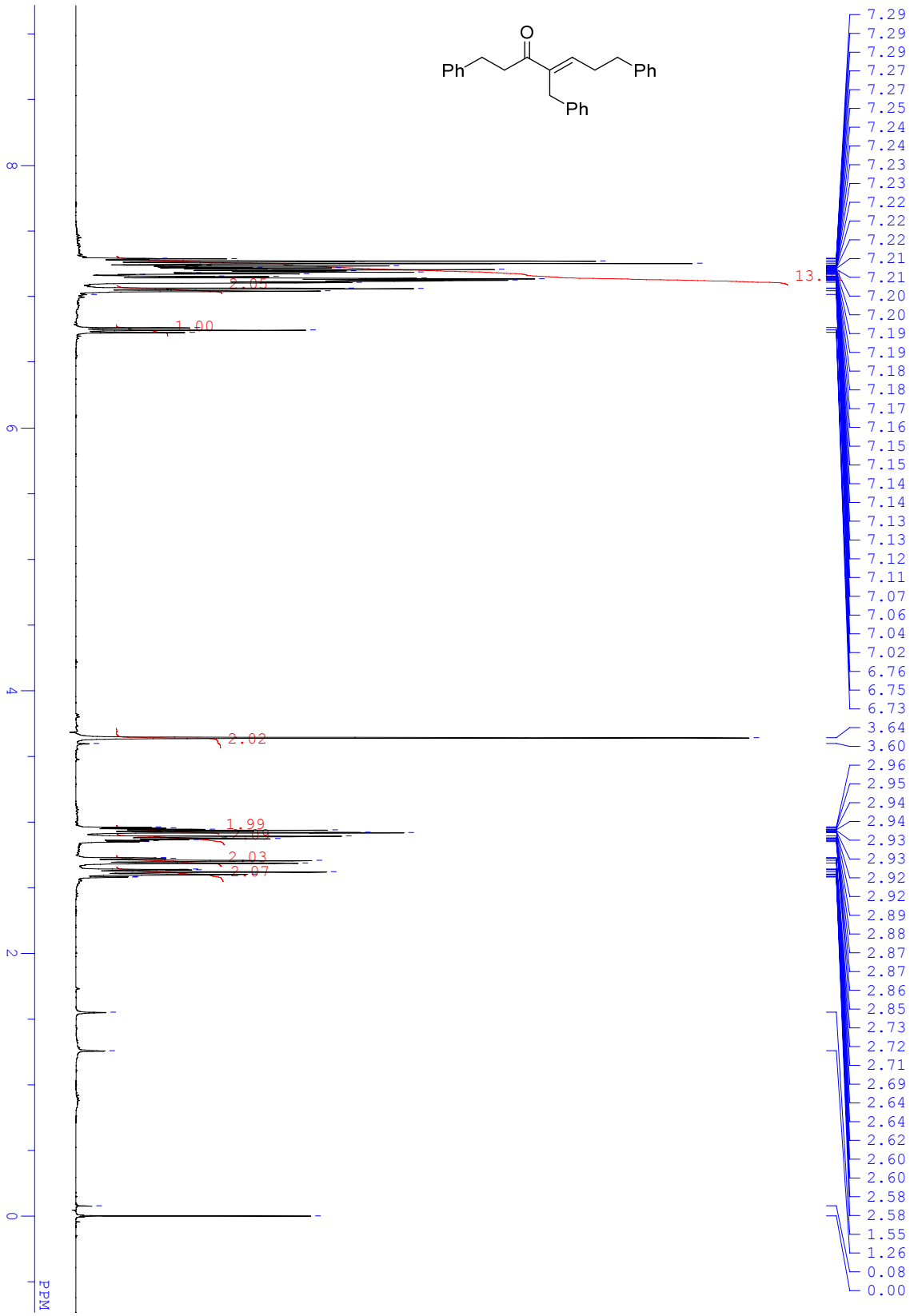
^{1}H NMR spectrum of **4i**



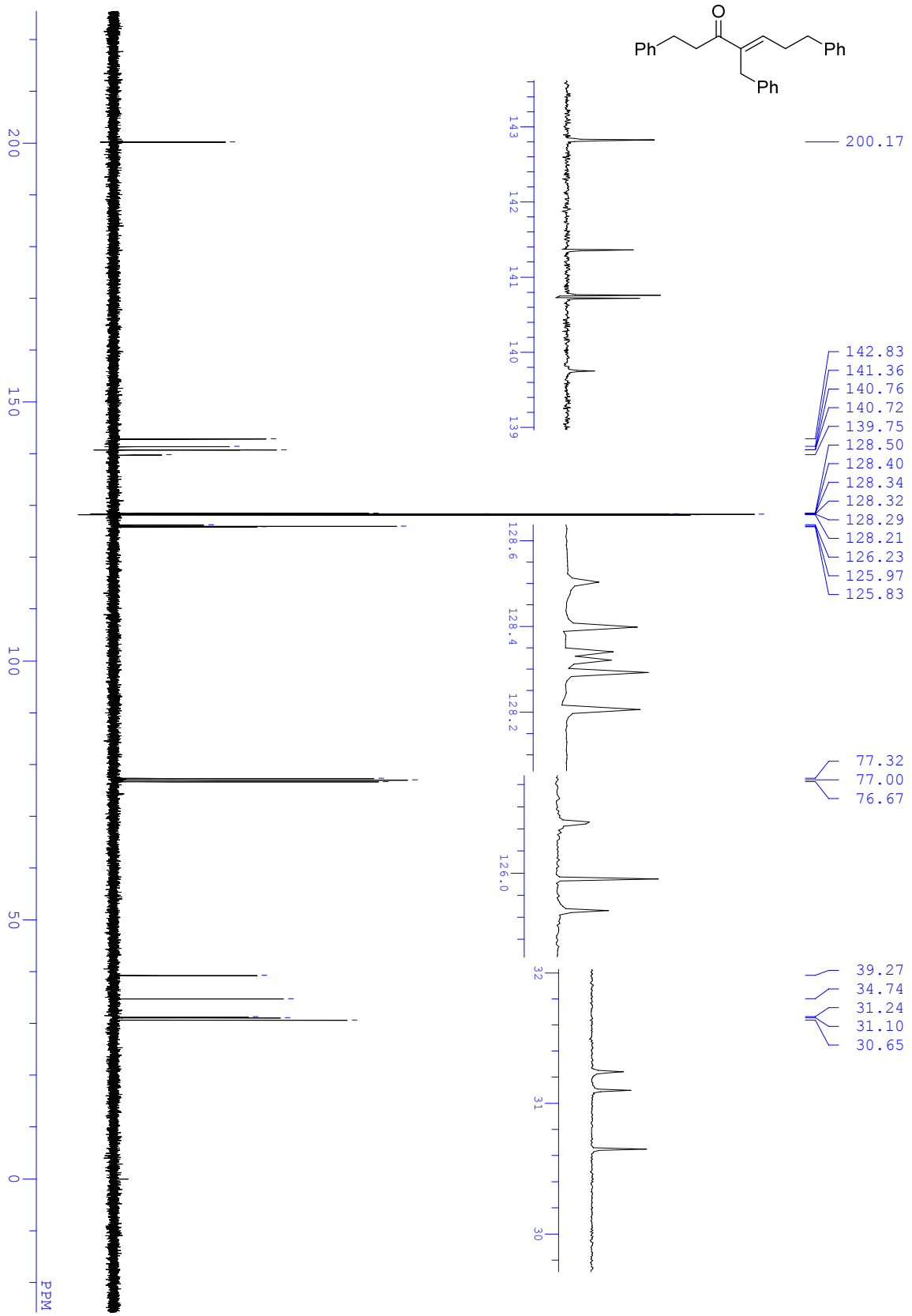
^{13}C {^{1}H} NMR spectrum of **4i**



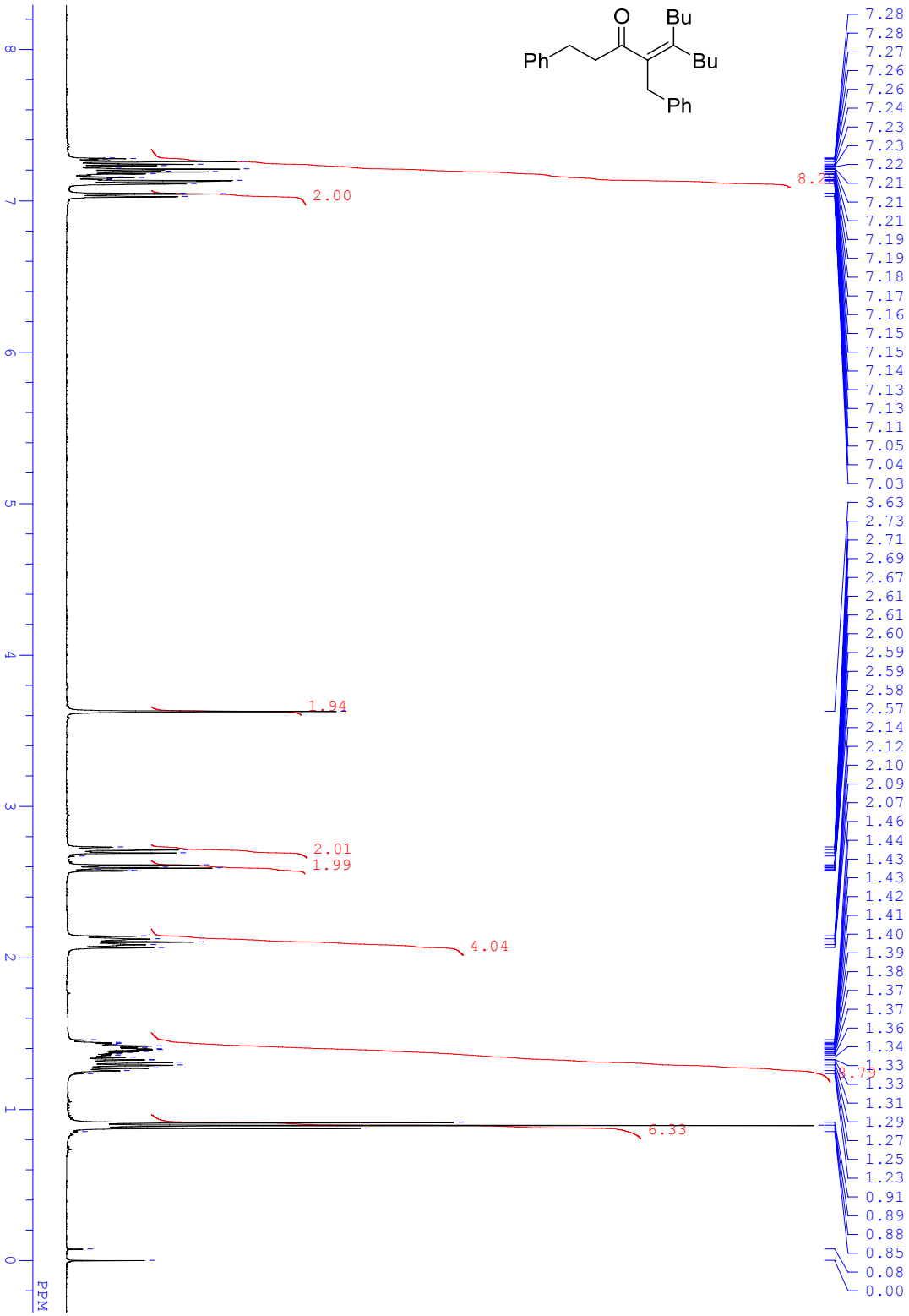
^{1}H NMR spectrum of **4k**



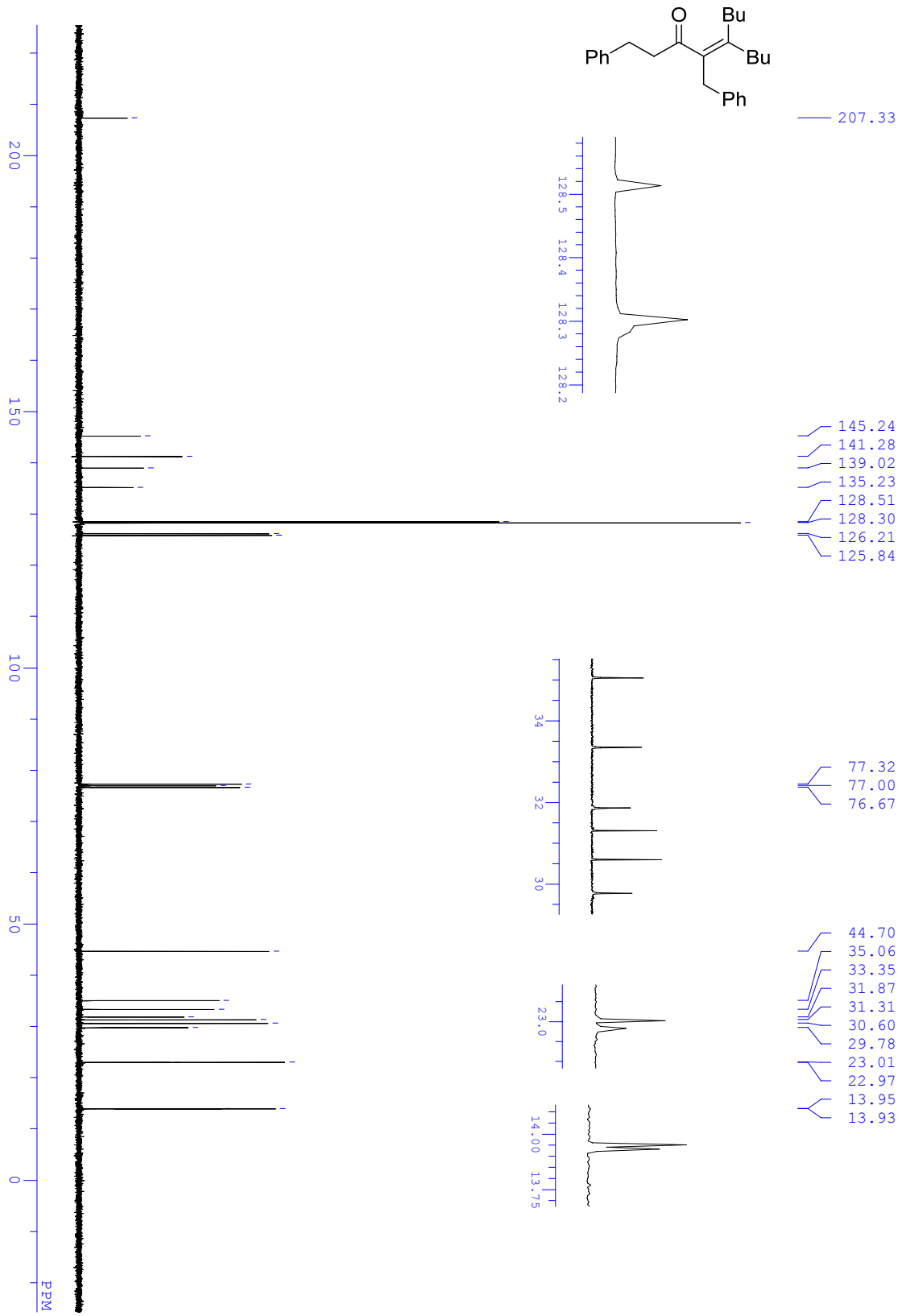
^{13}C {^{1}H} NMR spectrum of **4k**



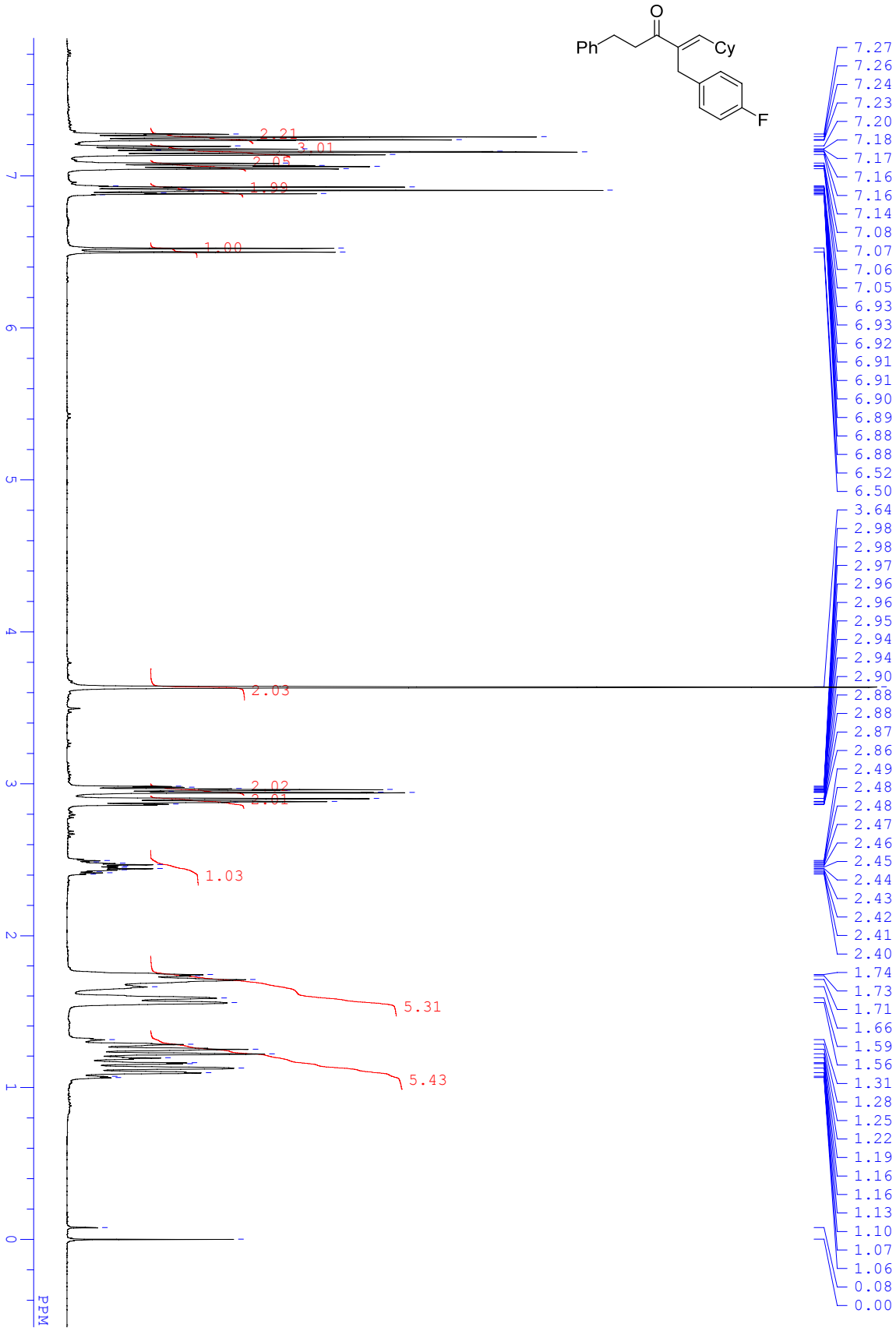
^{1}H NMR spectrum of **4o**



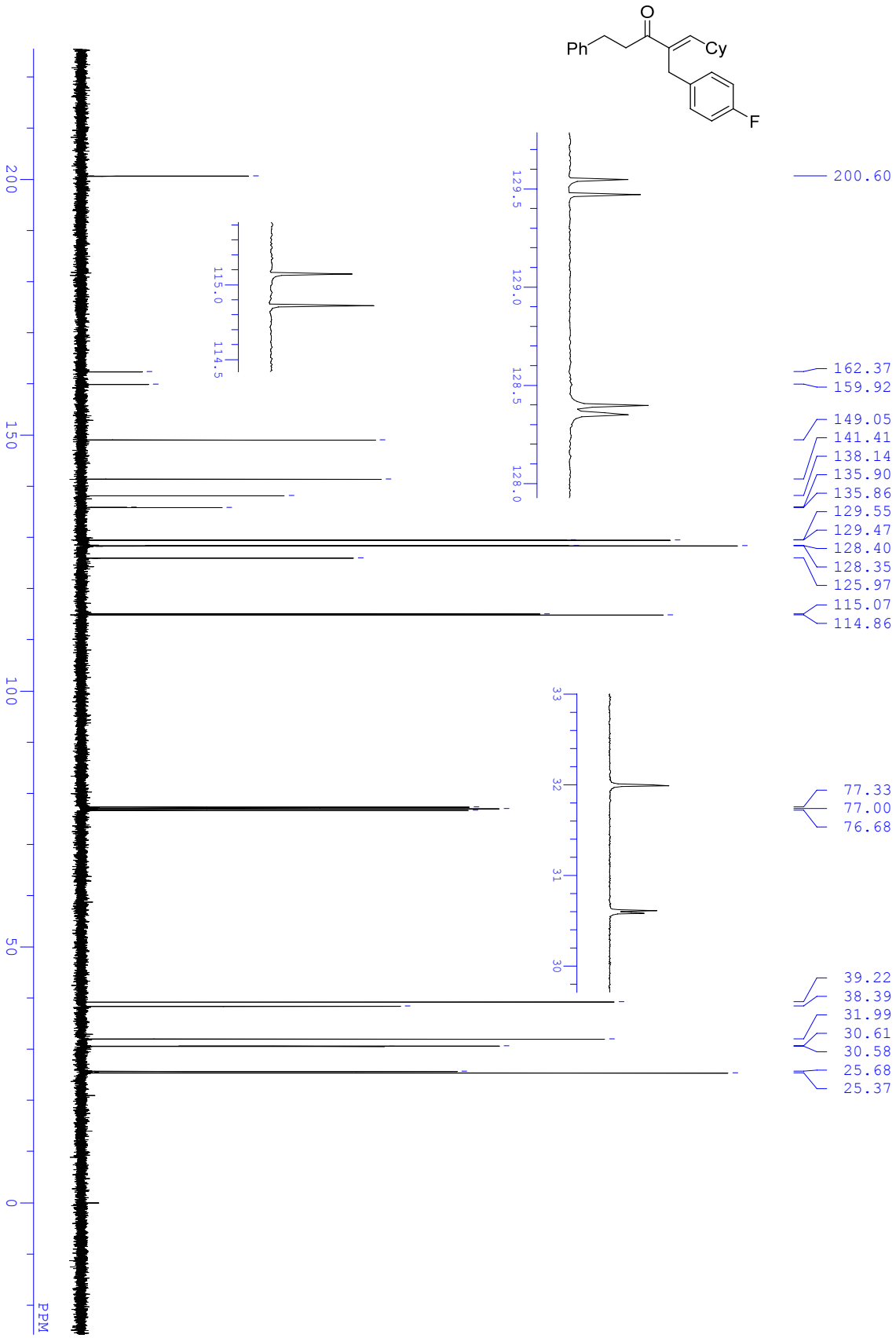
^{13}C {^{1}H} NMR spectrum of **4o**



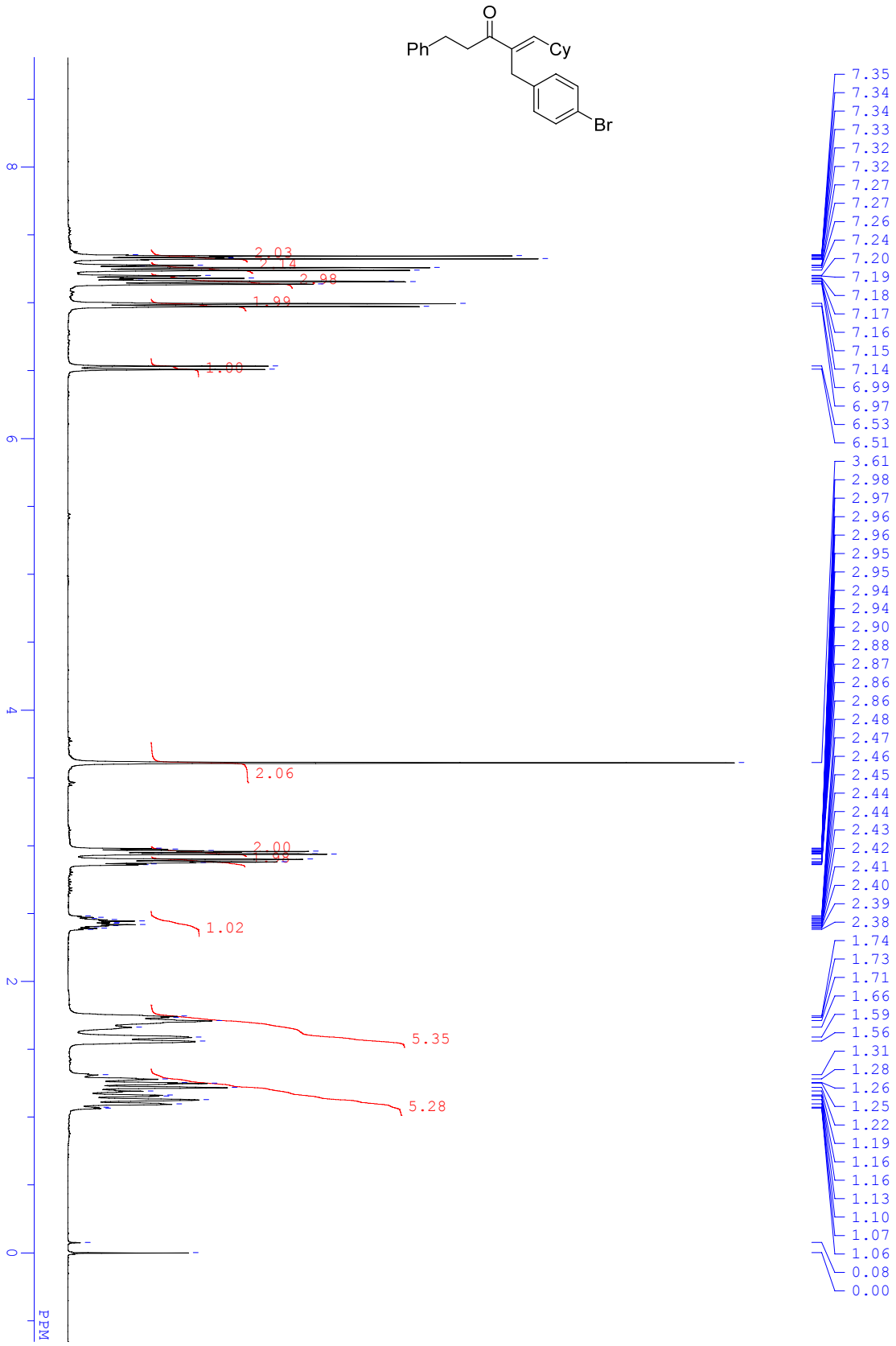
^{1}H NMR spectrum of **4r**



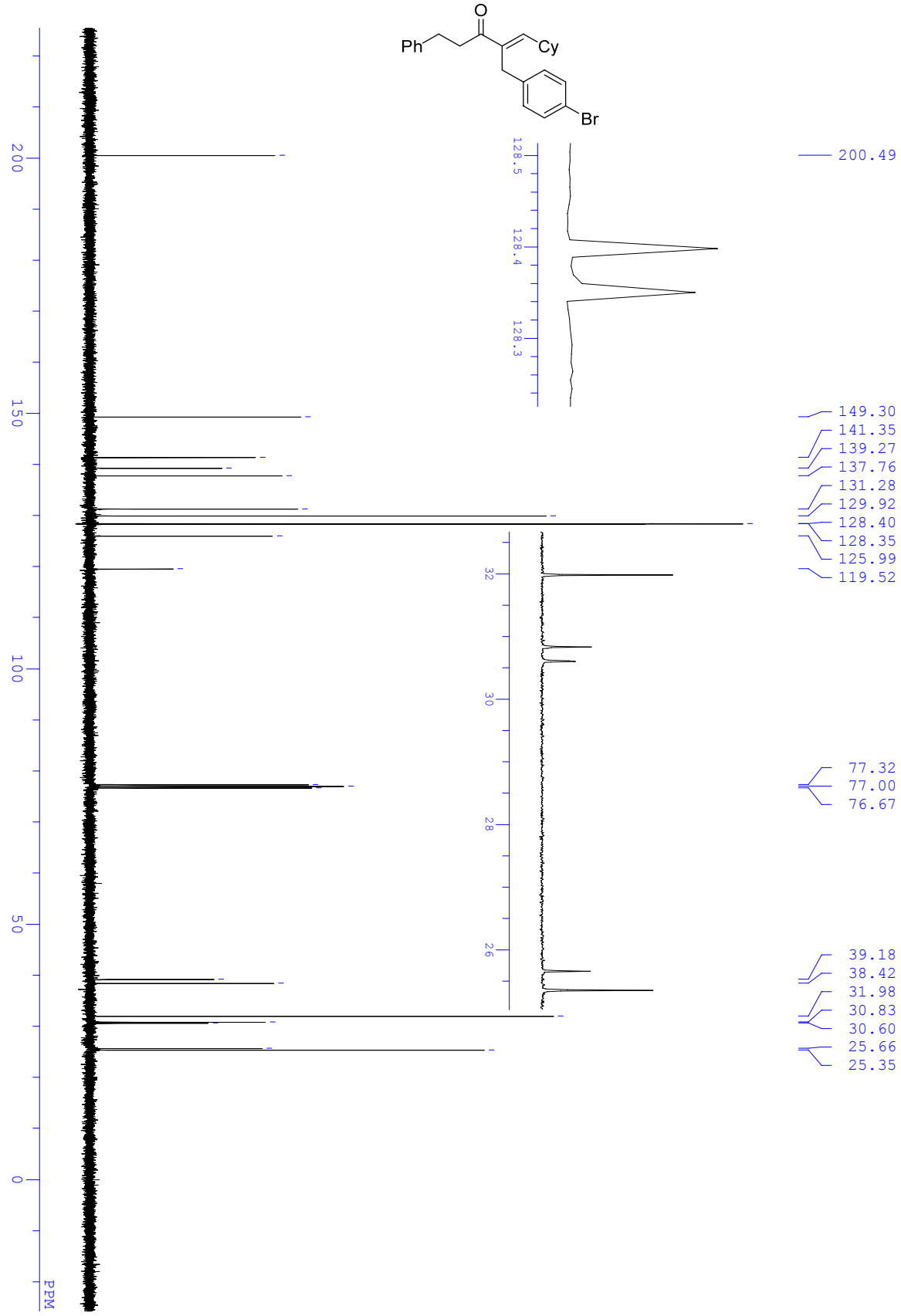
^{13}C {^{1}H} NMR spectrum of **4r**



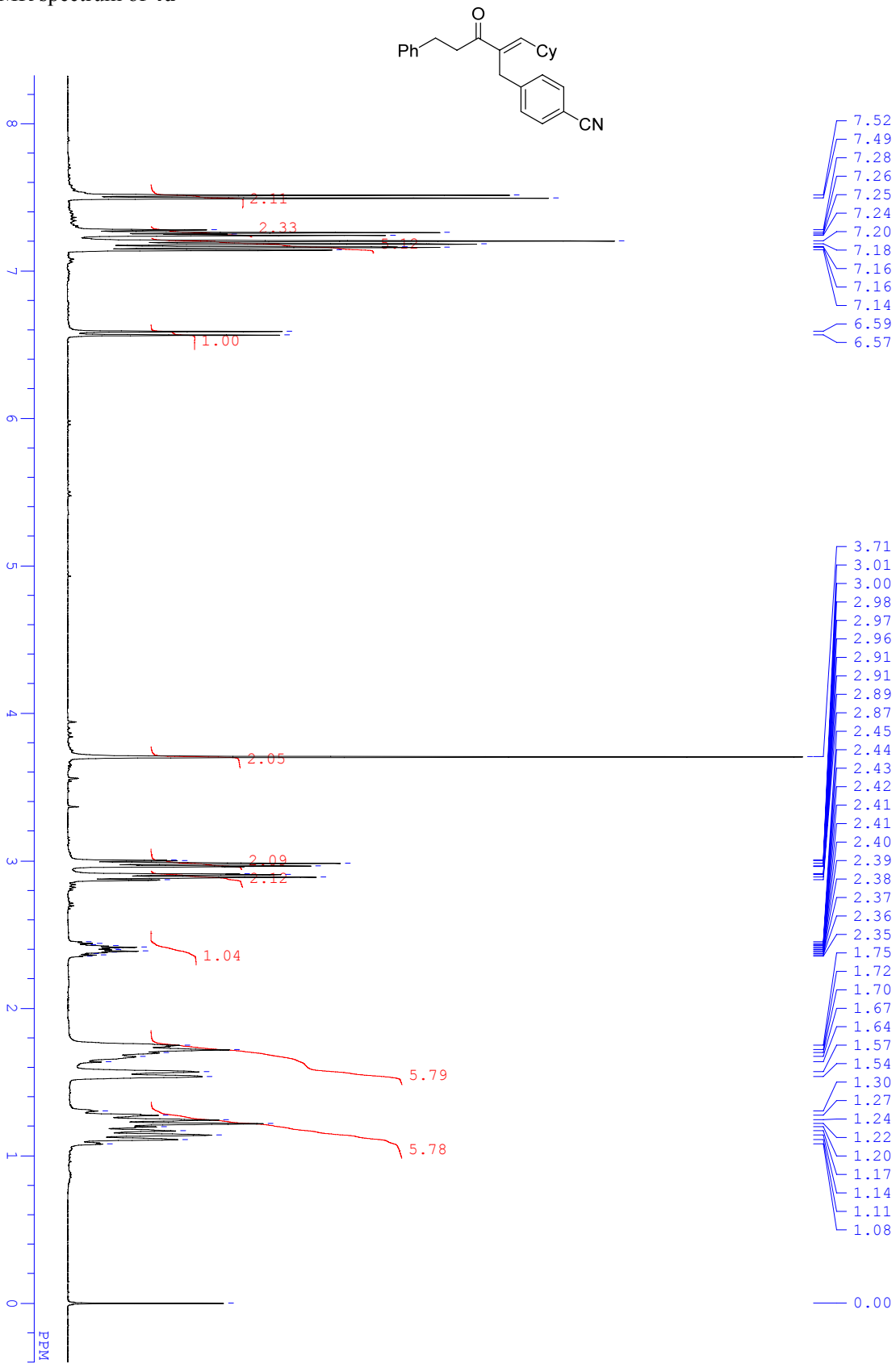
^{1}H NMR spectrum of **4t**



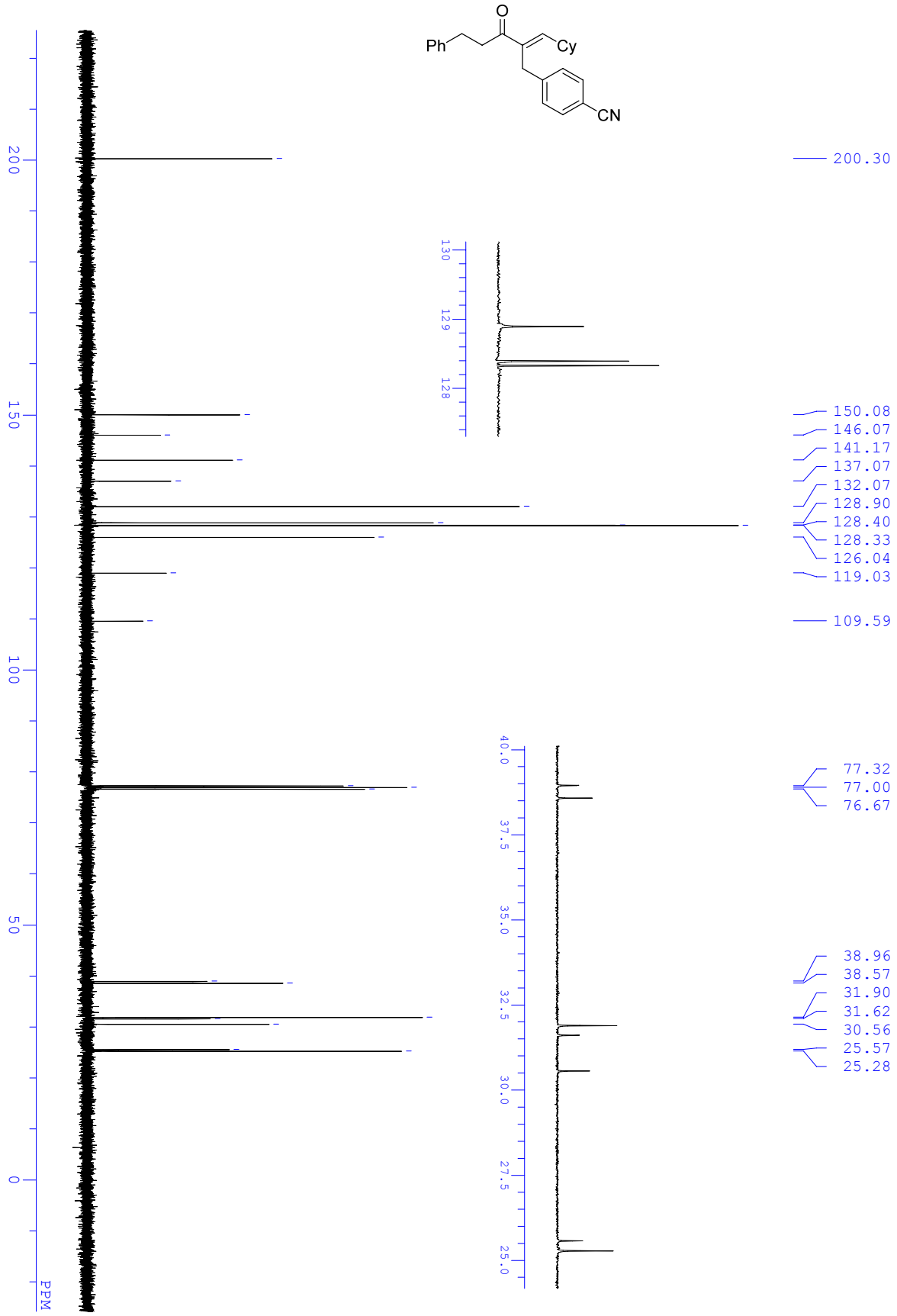
^{13}C {^{1}H} NMR spectrum of **4t**



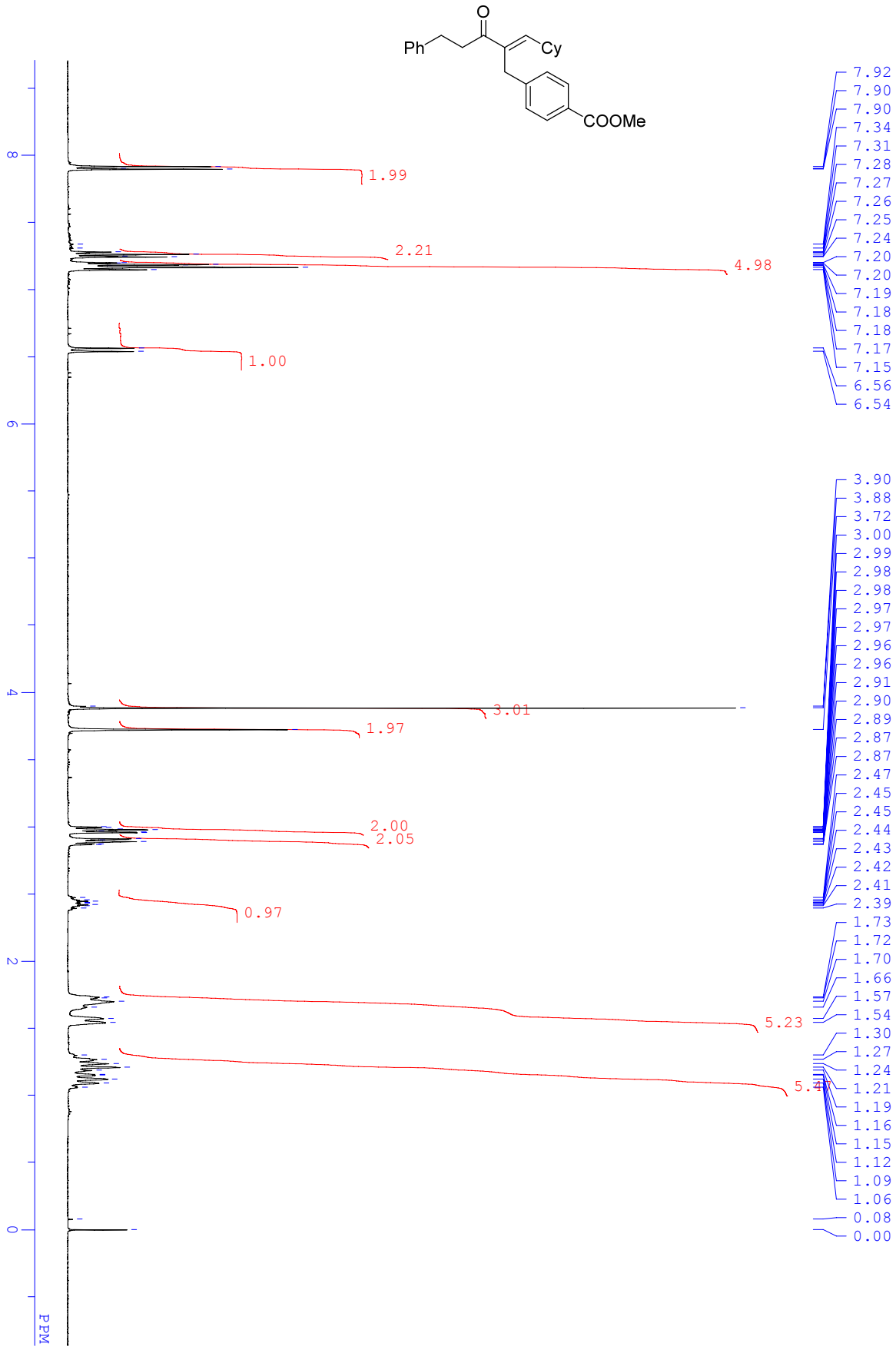
^{1}H NMR spectrum of **4u**



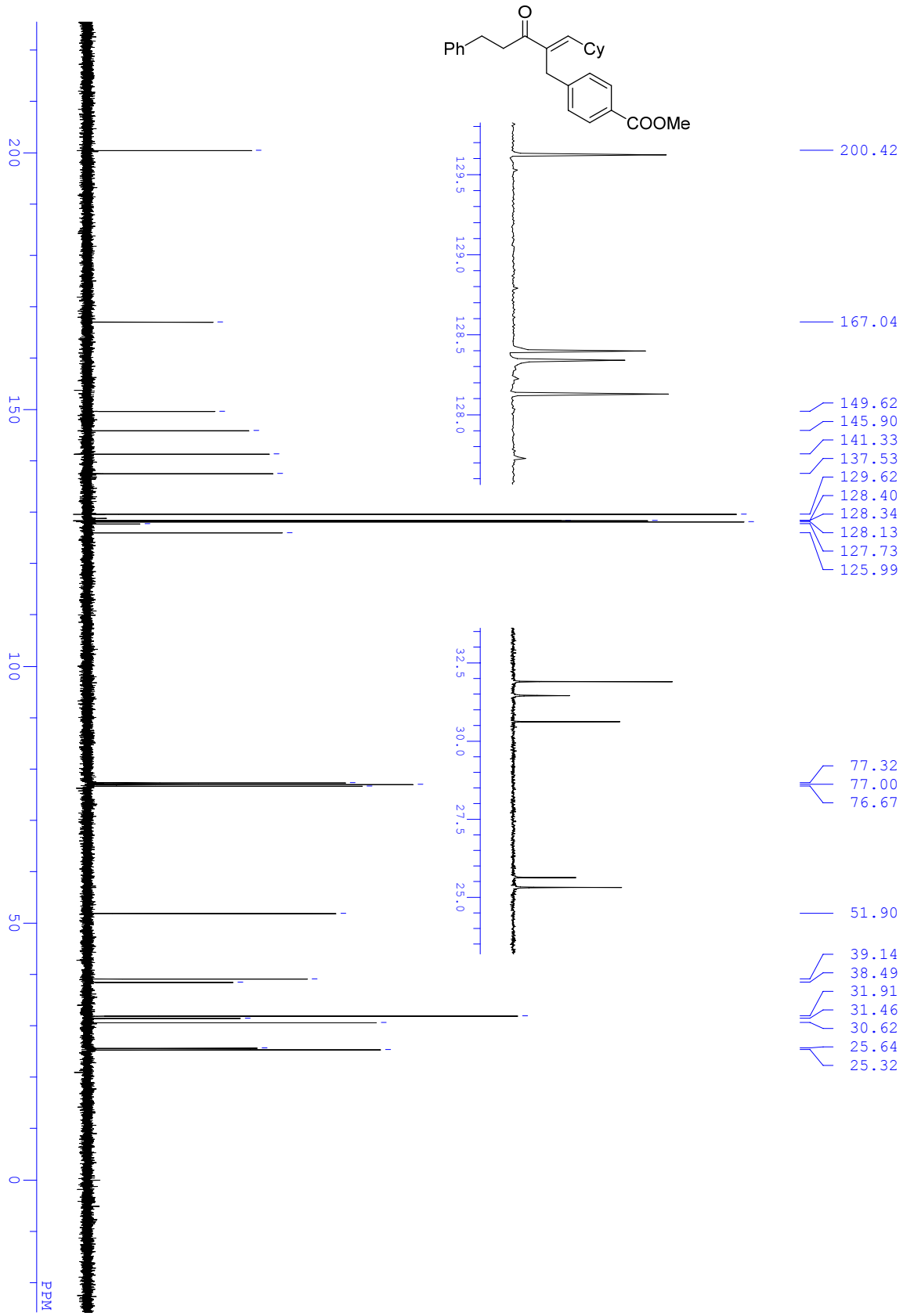
^{13}C {^{1}H} NMR spectrum of **4u**



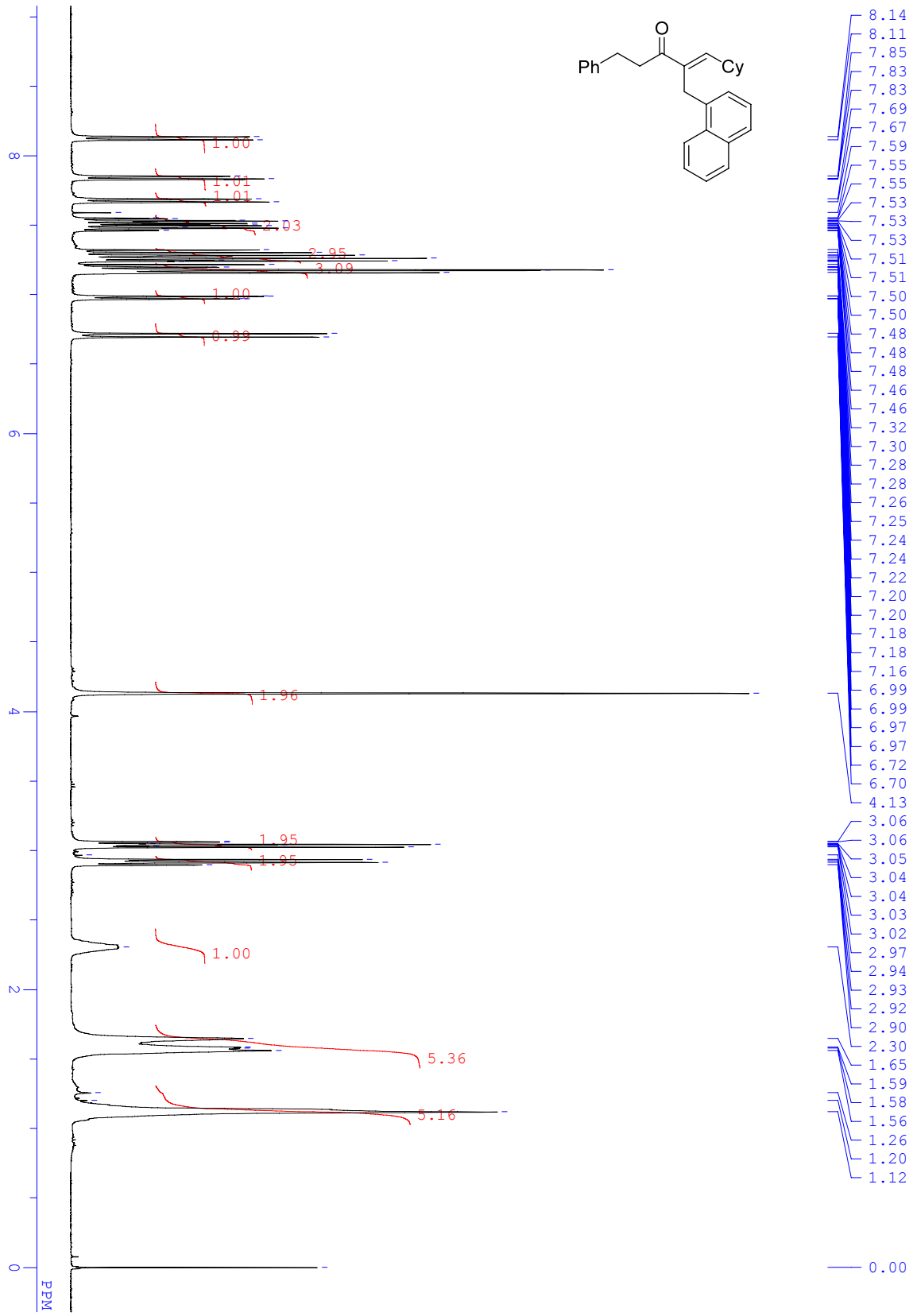
^{1}H NMR spectrum of **4v**



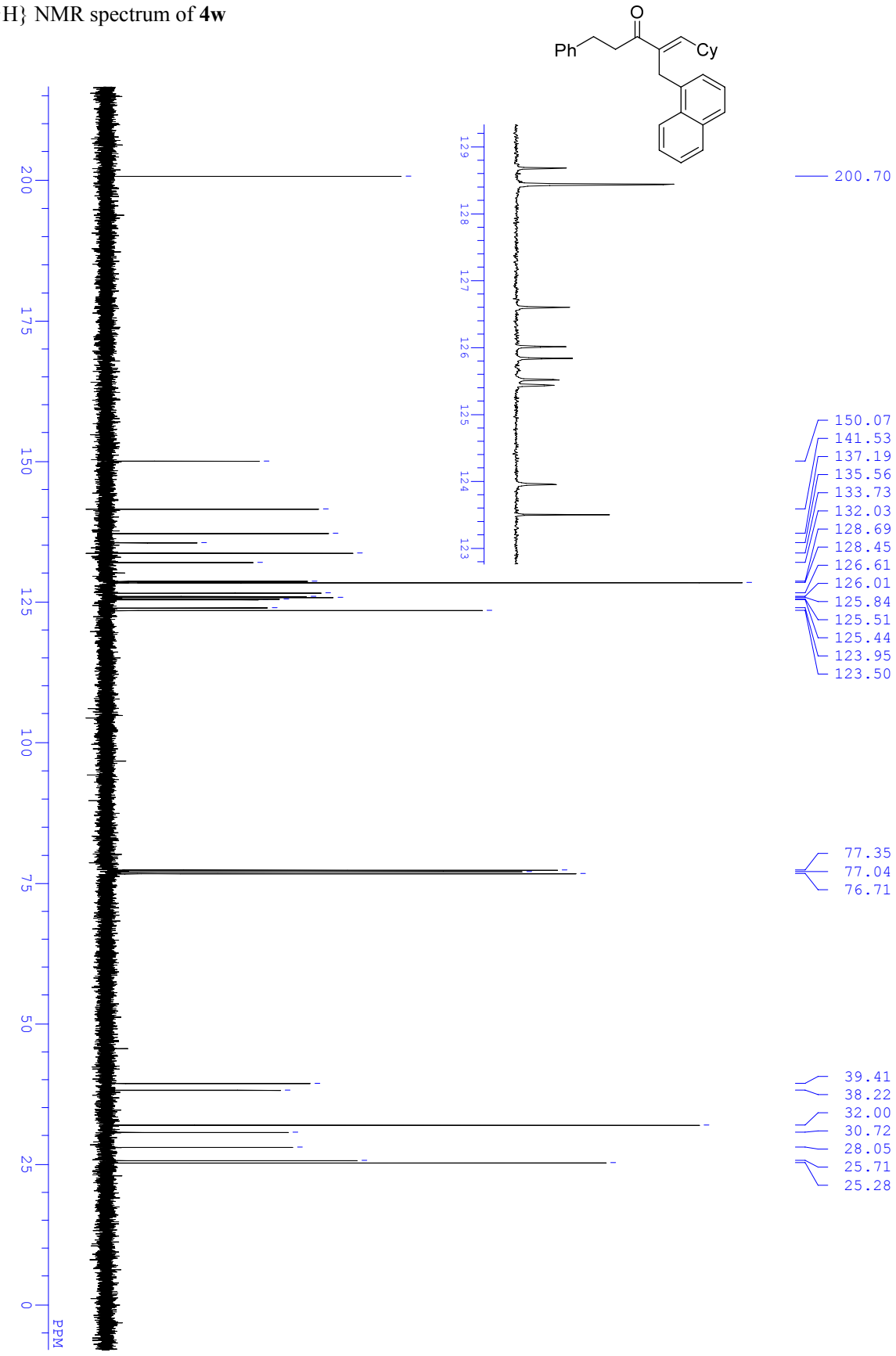
^{13}C {^{1}H} NMR spectrum of **4v**



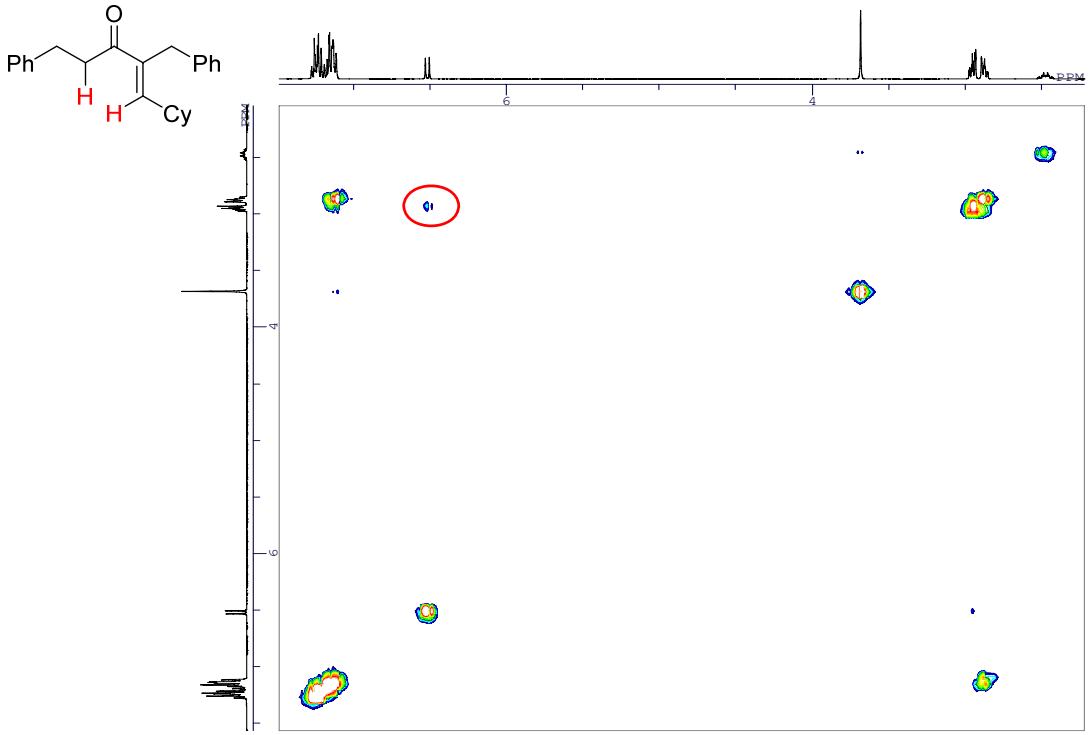
^{1}H NMR spectrum of **4w**



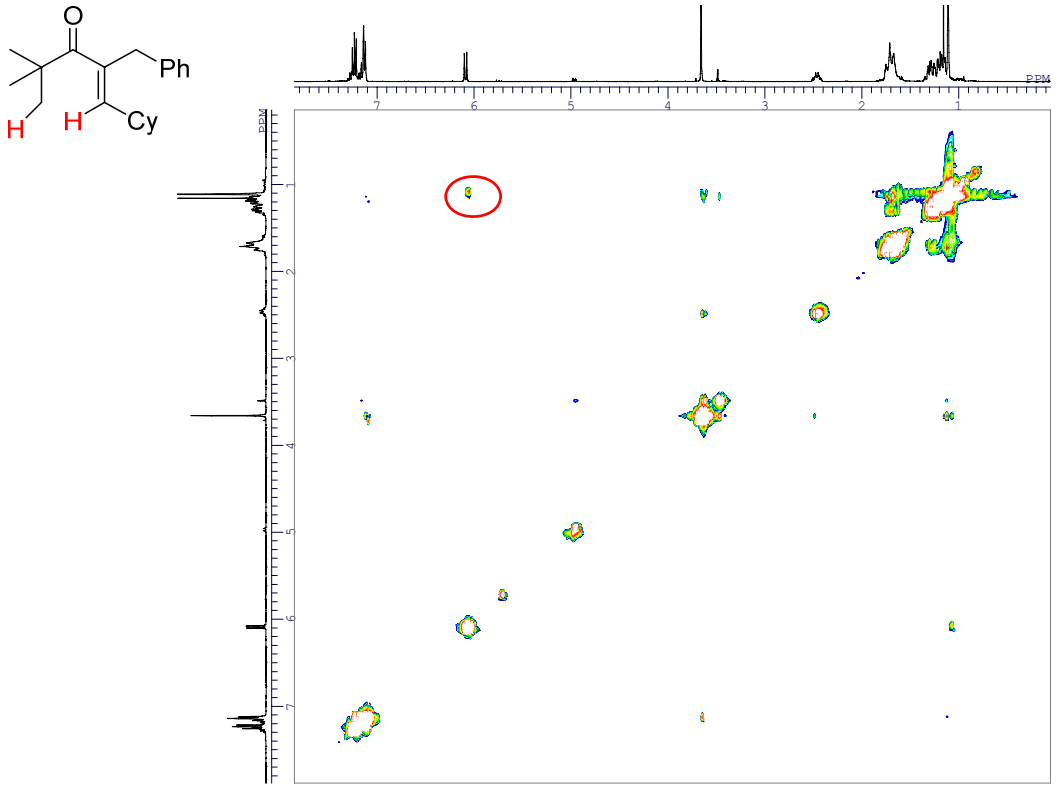
^{13}C {^{1}H} NMR spectrum of **4w**



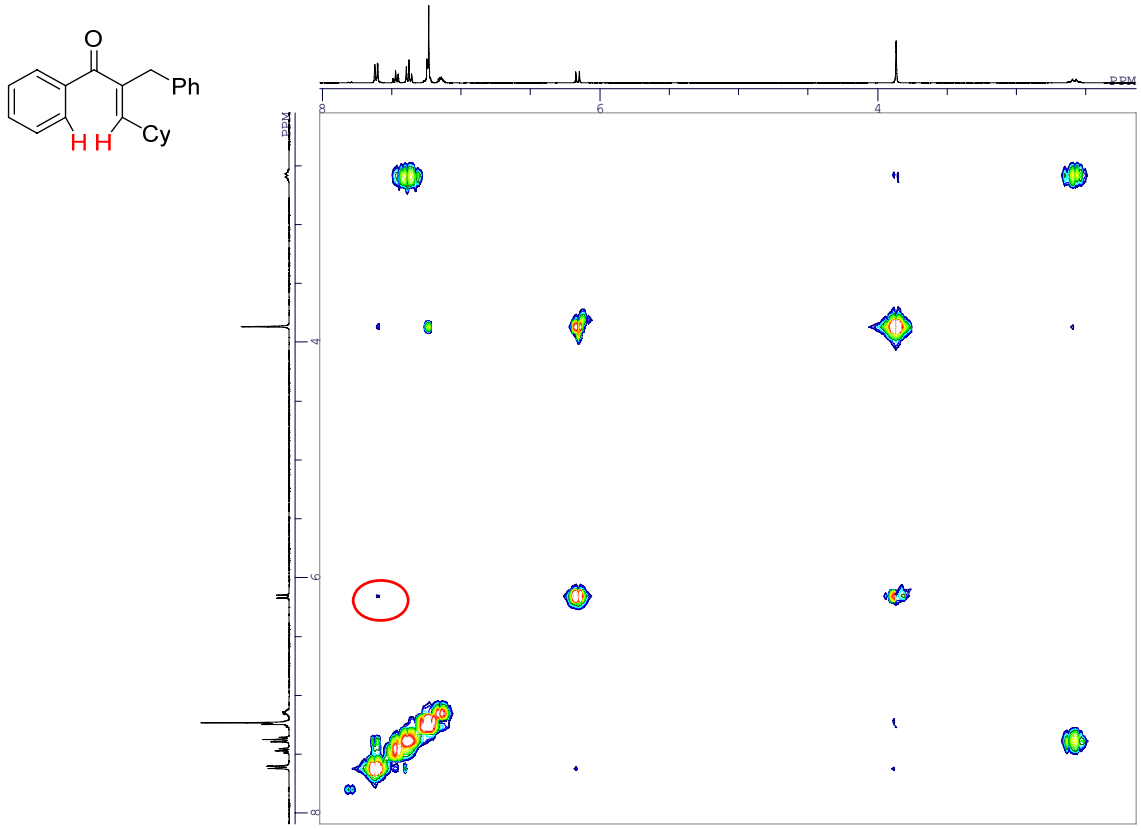
noesy spectrum of **4a**



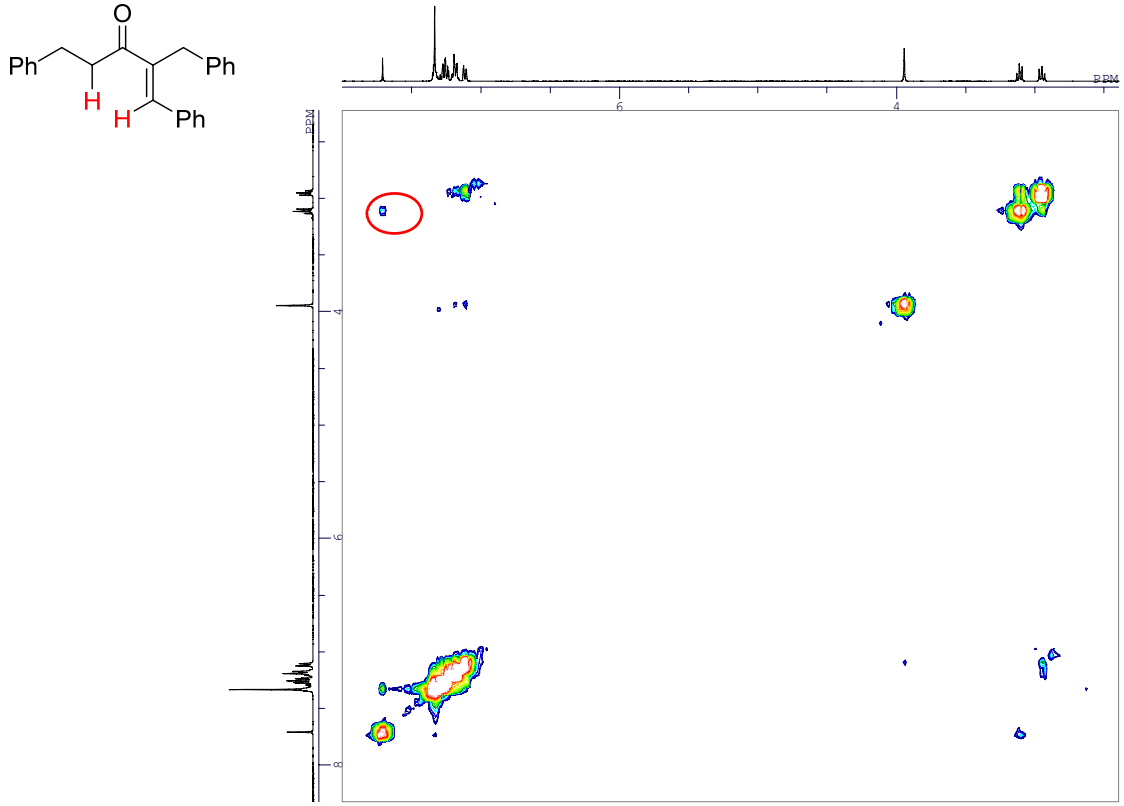
noesy spectrum of **4g**



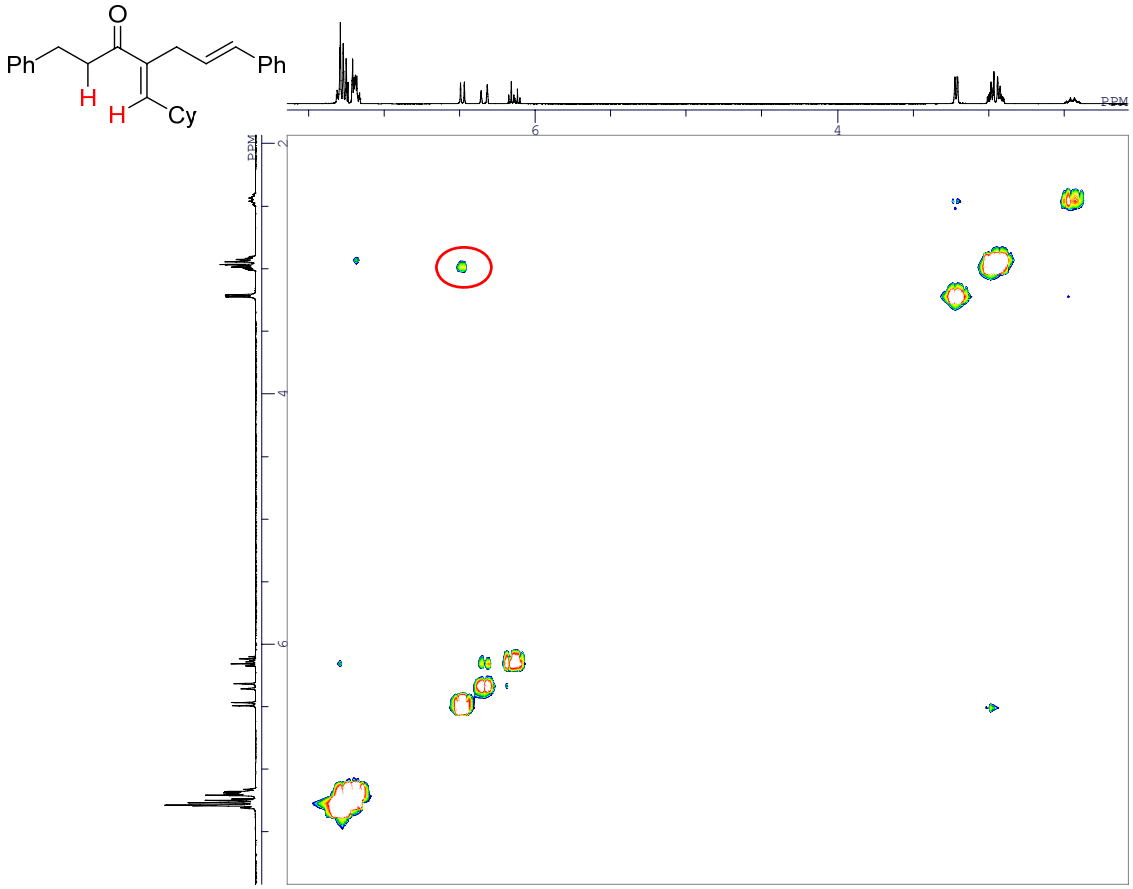
noesy spectrum of **4h**



noesy spectrum of **4n**



noesy spectrum of **4x**



6. Reference

(1) W. L. F. Armargo and C. L. L. Chai, *Purification of Laboratory Chemicals*, *5th Ed*.; Burrerworth-Heinemann: Oxford. U. K., **2003**.

(2) A. B. Pangbon, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics,* 1996, **15**, 1518-1520.

(3) T. Ukai, H. Kawazura and Y. Ishii, *J. Organomet. Chem.,* 1974, **65**, 253.

(4) K. Semba, M. Shinomiya, T. Fujihara, J. Terao and Y. Tsuji, *Chem. Eur. J.,* 2013, **19**, 7125-7132.

(5) T. Kippo, T. Fukuyama and I. Ryu, *Org. Lett*., 2011, **13**, 3864-3867.