Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry


# Base catalysed synthesis of thiochromans and azo-linked chromenes using allenylphosphonates

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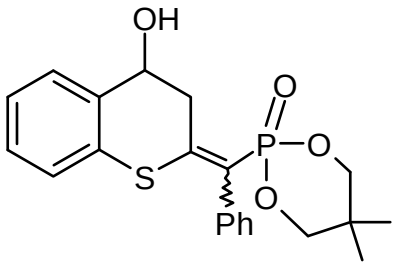
**General experimental details**

Chemicals were purified when required according to standard procedures.[1] All reactions, unless stated otherwise, were performed in a dry nitrogen atmosphere. $^{1}H$, $^{13}C$and $^{31}P$NMR spectra were recorded using a 400 MHz spectrometer in $CDCl_3$ (unless stated otherwise) with shifts referenced to $SiMe_4$ ($\delta = 0$) or 85 % $H_3PO_4$ ($\delta = 0$). Infrared spectra were recorded neat or by using KBr pellets on an FT/IR spectrometer. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected. Microanalyses were performed using a CHNS analyzer. For TLC, glass microslides were coated with silica-gel-$GF_{254}$ (mesh size 75μ) and spots were identified using iodine or UV chamber as appropriate. For column chromatography, silica gel of100-200 mesh size was used. LC-MS and HRMs equipment was used to record mass spectra for isolated compounds where appropriate. LC-MS data were obtained using electrospray ionization (positive mode) on a C-18 column at a flow rate 0.2 mL/ min using MeOH/water (90:10) as eluent.

## Synthesis of thiochromans 8,9 and 11-31

### Compound 8



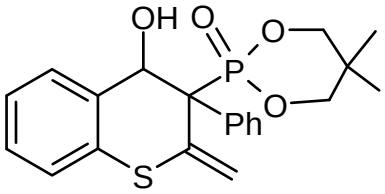

### Compound (*Z*)-8 (isomeric purity ~95%)

White solid, yield 0.09 g (23%). Mp 144-148 $^{o}$C; IR (KBr) $\nu$ 3299, 1557, 1472, 1441, 1236, 1053, 1007 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.15-7.40 (m, 9H), 4.73-4.74 (m, 1H), 3.98-4.07 (m, 2H), 3.51-3.67 (m, 2H), 2.84-2.90 (m, 1H), 2.61-2.67 (m, 1H), 1.02 (s, 3H), 0.62 (s, 3H). The O*H* peak was broad; $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 151.5 (d, *J*(PC) = 8.5 Hz), 136.5 (d, *J*(PC) = 8.8 Hz), 130.7, 130.1, 128.6, 127.8, 127.0, 126.5, 126.0, 122.8 (d, *J*(PC) = 182.7 Hz), 75.7, 67.8, 38.5 (d, *J*(PC) = 14.7 Hz), 32.3 (d, *J*(PC) = 6.2 Hz), 21.7, 21.1; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 9.8; LC/MS *m/z*: 385 $[M-18+H]^+$.

### Compound (*E*)-8

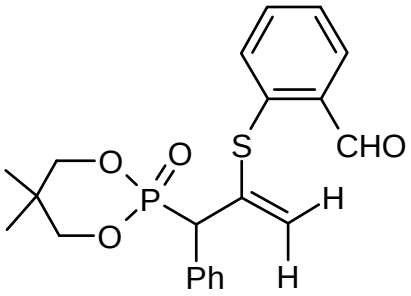
White solid, yield 0.22 g (57%). Mp 244-248 $^{o}$C; IR (KBr) $\nu$ 3302, 1557, 1472, 1235, 1119, 1053, 1007 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.01-7.47 (m, 9H), 4.95-4.96 (m, 1H) 4.01-4.06 (m, 2H), 3.81-3.87 (m, 1H), 3.57-3.63 (m, 2H), 3.47-3.53 (m, 1H), 3.11 (br, 1H), 0.98 (s, 3H), 0.64 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 155.7 (d, *J*(PC) = 21.0 Hz), 136.7, 135.5 (d, *J*(PC) = 8.2 Hz), 130.0 (d, *J*(PC) = 4.5 Hz), 129.7, 128.5, 128.1, 127.8, 126.3, 125.9, 125.6, 120.8 (d, *J*(PC) = 187.1 Hz), 75.7 (d, *J*(PC) = 5.3 Hz), 67.0, 37.4 (d, *J*(PC) = 5.4 Hz), 31.9 (d, *J*(PC) = 6.3 Hz), 21.1, 20.3; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 9.0; LC/MS *m/z*: 402 $[M]^+$; HRMS (ESI) calcd. for $C_{21}H_{23}O_4PSNa$ $[M + Na]^+$ 425.0953, found 425.0953. Anal. Calcd. for $C_{21}H_{23}O_4PS$: C, 62.67; H, 5.76 Found: C, 62.61; H, 5.79. X-ray structure was determined for this sample.

**Compound 9**

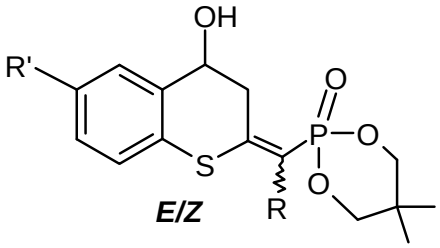



White solid, yield 0.12 g (38%). Mp 236-240 $^{o}$C; IR (KBr) $\nu$ 3221, 1588, 1468, 1238, 1067, 1013, 897 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.13-7.47 (m, 9H), 5.81 (d, 1H, $J$ = 4.0 Hz), 5.68 (d, 1H, $J$ = 4.0 Hz), 5.56 (d, 1H, $J$ = 8.0 Hz), 4.67 (s, 1H), 4.16-4.29 (m, 2H), 3.53-3.91 (dt, 2H), 1.14 (s, 3H), 0.86 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$ + 5% MeOH) $\delta$ (ppm) 139.3, 136.5, 136.4, 134.1, 130.7, 130.5, 127.4, 127.2, 126.2, 125.1, 124.4, 116.4, 77.8 (d, $J$(PC) = 7.7 Hz), 73.3, 59.3 (d, $J$(PC) = 135.6 Hz), 32.4 (d, $J$(PC) = 8.6 Hz), 21.6, 20.6; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 20.3; LC/MS $m/z$: 403 [M+ H]$^{+}$; Anal. Calcd. for $C_{21}H_{23}O_4PS$: C, 62.67; H, 5.76. Found: C, 62.48; H, 5.81. X-ray structure was determined for this sample.

**Compound 10**




White solid, yield 0.05 g (16%). Mp 136-140 $^{o}$C; IR (KBr) $\nu$ 1692, 1584, 1478, 1260, 1057, 1009 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 10.2 (s, 1H), 7.26-7.92 (m, 9H), 6.22 (s, 1H), 5.50 (s, 1H), 4.09-4.18 (m, 2H), 3.97 (d, 1H, $J$(PH) = 24.4 Hz), 3.58-3.69 (m, 2H), 0.97 (s, 3H), 0.66 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 191.4, 139.0, 136.8, 136.1, 134.4, 133.5, 130.0, 129.6, 129.5, 128.7, 128.6, 128.1, 122.2, 75.9, 50.1 (d, $J$(PC) = 133.0 Hz), 32.6 (d, $J$(PC) = 7.0 Hz), 21.5, 21.3; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 17.3; LC/MS $m/z$: 403 [M+ H]$^{+}$.




| | | | |
|---|---|---|---|
| R' = H, R = 4-Me-$C_6H_4$ | (**11**) | R' = Me, R = Ph | (**17**) |
| R' = H, R = 4-MeO-$C_6H_4$ | (**12**, X-ray) | R' = Me, R = 4-Me-C6H4 | (**18**) |
| R' = H, R = 4-Cl-$C_6H_4$ | (**13**) | R' = Me, R = 4-MeO-C6H4 | (**19**) |
| R' = H, R = 4-$NO_2$-$C_6H_4$ | (**14**) | R' = Me, R = 4-Cl-C6H4 | (**20**) |
| R' = H, R = 1-Naphtyl | (**15**) | R' = Me, R = 4-NO2-C6H4 | (**21**) |
| R' = H, R = Me | (**16**, X-ray) | R' = Me, R = 1-Naphthyl | (**22**) |
| | | R' = Me, R = Me | (**23**) |

**Compound (*Z*)-11**

White solid, yield 0.05 g (18%). Mp 186-190 $^{o}$C; IR (KBr) $\nu$ 3391, 1572, 1508, 1472, 1439, 1233 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.15-7.39 (m, 8H), 4.72-4.74 (m, 1H), 3.96-4.06 (m, 2H), 3.52-3.68 (m, 2H), 2.86-2.93 (m, 1H), 2.61-2.66 (m, 1H), 2.37 (s, 3H), 1.04 (s, 3H), 0.68 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 151.3 (d, *J*(PC) = 8.0 Hz), 137.6, 137.0, 133.4 (d, *J*(PC) = 8.0 Hz), 130.6, 130.4, 129.3, 128.4, 126.8, 126.4, 126.0, 122.6 (d, *J*(PC) = 180.0 Hz), 75.9 (d, *J*(PC) = 6.0 Hz), 67.8, 38.6 (d, *J*(PC) = 15.0 Hz), 32.3 (d, *J*(PC) = 7.0 Hz), 21.8, 21.3, 21.0; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 9.7; LC/MS *m/z*: 417 $[M+ H]^+$; Anal. Calcd. for $C_{22}H_{25}O_4PS$: C, 63.45; H, 6.05. Found: C, 63.55; H, 6.10.

**Compound (*E*)-11**

White solid, yield 0.18 g (60%). Mp 252-256 $^{o}$C; IR (KBr) $\nu$ 3312, 1557, 1507, 1470, 1233, 1057, 1009 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.02-7.48 (m, 8H), 4.94-4.96 (m, 1H), 3.98-4.04 (m, 2H), 3.81-3-3.88 (m, 1H), 3.58-3.65 (m, 2H), 3.42-3.47 (m, 1H), 2.40 (s, 3H), 1.01 (s, 3H), 0.68 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 154.5 (d, *J*(PC) = 21.8 Hz), 138.2, 136.3, 133.0 (d, *J*(PC) = 8.1 Hz), 130.6, 130.1 (d, *J*(PC) = 4.5 Hz), 129.4, 128.3, 127.5, 125.9, 122.9 (d, *J*(PC) = 185.6 Hz), 75.7 (d, *J*(PC) = 6.9 Hz), 67.8, 37.5 (d, *J*(PC) = 5.3 Hz), 32.3 (d, *J*(PC) = 6.4 Hz), 21.7, 21.4, 21.0; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) δ 9.2; LC/MS *m/z*: 417 $[M+ H]^+$; Anal. Calcd. for

$C_{22}H_{25}O_4PS$: C, 63.45; H, 6.05. Found: C, 63.51; H, 6.03

**Compound (*Z*)-12**

White solid, yield 0.04 g (13%). Mp 174-176 $^oC$; IR (KBr) $\nu$ 3308, 1696, 1539, 1250, 1055, 1007 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 6.84-7.43 (m, 8H), 4.70-4.72 (m, 1H), 3.88-4.01 (m, 2H), 3.80 (s, 3H), 3.47-3.68 (m, 2H), 2.76-2.79 (m, 1H), 2.67-2.72 (m, 1H), 1.03 (s, 3H), 0.67 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 159.1, 151.7 (d, *J*(PC) = 9.3 Hz), 137.1, 131.6, 130.7, 128.6 (d, *J*(PC) = 8.3 Hz), 128.4, 126.8, 126.4, 126.0, 122.1 (d, *J*(PC) = 181.7 Hz), 114.0, 75.8 (d, *J*(PC) = 5.0 Hz), 67.8, 55.3, 38.7 (d, *J*(PC) = 14.4 Hz), 32.6 (d, *J*(PC) = 6.4 Hz), 21.8, 21.1; $^{31}P$ NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 9.9; LC/MS *m/z*: 432 $[M]^+$; Anal. Calcd. for $C_{22}H_{25}O_5PS$: C, 61.10; H, 5.83. Found: C, 61.22; H, 5.85. X-ray structure was determined for this sample.

**Compound (*E*)-12**

White solid, yield 0.19 g (66%). Mp 212-214 $^oC$; IR (KBr) $\nu$ 3328, 1605, 1562, 1505, 1233, 1057, 1007 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 6.94-7.48 (m, 8H), 4.93-4.95 (m, 1H), 4.00-4.05 (m, 2H), 3.85 (s, 3H), 3.78-3.83 (m, 1H), 3.58-3.64 (m, 2H), 3.45-3.50 (m, 1H), 1.00 (s, 3H), 0.67 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) $159.5_0$, $159.4_8$, 155.3 (d, *J*(PC) = 23.0 Hz), 136.6, 131.6 (d, *J*(PC) = 4.0 Hz), 130.6, 128.2 (d, *J*(PC) = 6.0 Hz), 127.3, 126.0, 125.9, 122.1 (d, *J*(PC) = 187.0 Hz), 114.1, 75.6 (d, *J*(PC) = 5.0 Hz), 67.7, 55.2, 37.5 (d, *J*(PC) = 5.0 Hz), 32.3 (d, *J*(PC) = 6.0 Hz), 21.7, 21.1; $^{31}P$ NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 9.4; LC/MS *m/z*: 432 $[M]^+$; Anal. Calcd. for $C_{22}H_{25}O_5PS$: C, 61.10; H, 5.83. Found: C, 61.25; H, 5.80. X-ray structure was determined for this sample.

**Compound (*Z*)-13**

White solid, yield 0.05 g (18%). Mp 158-162 $^oC$; IR (KBr) $\nu$ 3400, 1701, 1460, 1262, 1092, 1057, 1013 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.19-7.40 (m, 8H), 4.73-4.75 (m, 1H), 4.02-4.12 (m, 2H), 3.53-3.69 (m, 2H), 2.84-2.87 (m, 1H), 2.59-2.63 (m, 1H), 1.00 (s, 3H), 0.69 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 152.7 (d, *J*(PC) =

8.6 Hz), 136.4, 135.0 (d, *J*(PC) = 8.4 Hz), 133.9 (d, *J*(PC) = 2.4 Hz), 131.9, 130.5, 128.8, 128.7, 127.0, 126.5, 126.1, 121.2 (d, *J*(PC) = 183.7 Hz), 75.6 (d, *J*(PC) = 6.3 Hz), 67.7, 38.5 (d, *J*(PC) = 14.5 Hz), 32.3 (d, *J*(PC) = 6.1 Hz) , 21.6, 21.1; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) δ 9.8; LC/MS *m/z*: 419 $[M-18]^+$and 421 $[M-18+2H]^+$; Anal. Calcd. for $C_{21}H_{22}O_4ClPS$: C, 57.73; H, 5.08. Found: C, 57.65; H, 5.12.

**Compound (*E*)-13**

White solid, yield: 0.18 g (62%); Mp 226-230 $^oC$; IR (KBr) $\nu$ 3324, 1555, 1480, 1346, 1236, 1055, 1009 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.03-7.48 (m, 8H), 4.94-4.96 (m, 1H), 4.08-4.13 (m, 2H), 3.86-3.93 (m, 1H), 3.58-3.65 (m, 2H), 3.43-3.48 (m, 1H), 0.96 (s, 3H), 0.69 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 157.3 (d, *J*(PC) = 21.6 Hz), 136.8, 134.4, 134.3 (d, *J*(PC) = 8.0 Hz), 131.8 (d, *J*(PC) = 4.0 Hz), 129.7, 129.0, 128.2, 126.8, 126.3, 125.8, 119.8 (d, *J*(PC) = 191.0 Hz), 75.6 (d, *J*(PC) = 5.9 Hz), $75.5_6$ (d, *J*(PC) = 5.8 Hz), 67.2, 37.6, 32.3 (d, *J*(PC) = 6.1 Hz), 21.4, 21.0; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 9.2; LC/MS *m/z*: 419 $[M-18]^+$and 421 $[M-18+2H]^+$; Anal. Calcd. for $C_{21}H_{22}O_4ClPS$: C, 57.73; H, 5.08 Found: C, 57.85; H, 5.01.

**Compound (*E*)-14**

(The *Z*–isomer was only a minor product and hence not isolated)

White solid, yield 0.18 g (63%). Mp 250-254 $^oC$; IR (KBr) $\nu$3322, 1734, 1653, 1238, 1055 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.03-7.48 (m, 8H), 4.94-4.96 (m, 1H), 4.08-4.13 (m, 2H), 3.87-3.92 (m, 1H), 3.58-3.65 (m, 2H), 3.43-3.47 (m, 1H), 0.96 (s, 3H), 0.69 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 157.3 (d, *J*(PC) = 21.4 Hz), 136.8, 134.4, 134.2 (d, *J*(PC) = 8.1 Hz), 131.8 (d, *J*(PC) = 3.9 Hz), 129.6, 129.0, 128.2, 126.7, 126.3, 125.8, 119.7 (d, *J*(PC) = 190.5 Hz), 75.6 (d, *J*(PC) = 6.0 Hz), 67.2, 37.6 (d, *J*(PC) = 4.6 Hz), 32.3 (d, *J*(PC) = 6.0 Hz), 21.3, 21.0; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 9.2; LC/MS *m/z*: 421 $[M-18+H]^+$; Anal. Calcd. for $C_{21}H_{22}NO_6PS$: C, 56.37; H, 4.96; N, 3.13. Found: C, 56.38; H, 4.85; N, 3.07.

**Compound (*E*/*Z*)-15**

White solid, yield 0.20 g (68%). Mp 206-210 $^oC$; IR (KBr) $\nu$ 3312, 1574, 1447, 1198, 1051, 997 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 6.89-8.07 (m, 11H), 5.02-5.06 (m,

1H), 4.01-4.05 (m, 1H), 3.88-4.00 (m, 2H), 3.54-3.60 (m, 1H), 3.32-3.40 (m, 2H), 0.92 (s, 3H), 0.48 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 136.6, 133.8, 133.5, 131.6, 130.4, 129.0, 128.7, 128.5, 128.3, 128.1, 127.2, 126.8, 126.6, 126.2, 126.0, 125.9, 125.7, 125.5, 125.3, 119.8, 75.6, 67.9, 37.7, 32.3, 21.6, 21.0; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 9.2 and 9.0 (5:2); LC/MS *m/z*: 452 $[M]^+$; Anal. Calcd. for $C_{25}H_{25}O_4PS$: C, 66.36; H, 5.57. Found: C, 66.41; H, 5.52.

**Compound (*E*)-16**

The *Z*–isomer was not observed in the reaction mixture ($^{31}$P NMR).

White solid, yield 0.29 g (86%). Mp 168-172 $^{o}$C; IR (KBr) $\nu$ 3295, 1572, 1472, 1447, 1217, 1196, 1047, 992 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.18-7.47 (m, 4H), 4.86-4.89 (m, 1H), 4.22-4.28 (m, 2H), 3.78-3.89 (m, 2H), 3.64-3.70 (m, 1H), 3.23-3.28 (m, 1H), 2.07-2.10 (dd, $J$ = 13.4 and 1.2 Hz, 3H), 1.15 (s, 3H), 1.04 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 150.5 (d, $J$(PC) = 20.4 Hz), 136.9, 129.8, 128.3, 127.4, $126.1_2$, $126.0_7$, 114.7 (d, $J$(PC) = 185.1 Hz), 75.0 (d, $J$(PC) = 4.8 Hz), 67.7, 37.7 (d, $J$(PC) = 6.1 Hz), 32.5 (d, $J$(PC) = 5.6 Hz), 21.8, 21.6, 16.5 (d, $J$(PC) = 9.2 Hz); $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 14.9; LC/MS *m/z*: 341 $[M+H]^+$. X-ray structure was determined for this sample (see Fig. S1 in Supporting Information).

**Compound (*Z*)-17**

White solid, yield 0.06 g (18%). Mp 182-186 $^{o}$C; IR (KBr) $\nu$ 3376, 1684, 1543, 1474, 1262, 1061 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.06-7.39 (m, 8H), 4.69-4.70 (m, 1H), 3.98-4.06 (m, 2H), 3.50-3.67 (m, 2H), 2.84-2.90 (m, 1H), 2.59-2.64 (m, 1H), 2.32 (s, 3H), 1.01 (s, 3H), 0.64 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 152.0 (d, $J$(PC) = 8.0 Hz), 136.7 (d, $J$(PC) = 8.0 Hz), 136.4, 136.0, 130.7, 129.4, 128.6, 127.8, 127.7, 127.2, 126.5, 122.4 (d, $J$(PC) = 182.0 Hz), 75.8 (d, $J$(PC) = 3.0 Hz), , 75.7 (d, $J$(PC) = 2.0 Hz), 68.0, 38.8 (d, $J$(PC) = 15.0 Hz), 32.3 (d, $J$(PC) = 6.0 Hz), 21.8, $21.0_8$, $21.0_6$; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 9.7; LC/MS *m/z*: 417 $[M+H]^+$; Anal. Calcd. for $C_{22}H_{25}O_4PS$: C, 63.45; H, 6.05. Found: C, 63.56; H, 6.11.

**Compound (*E*)-17**

White solid, yield 0.19 g (61%). Mp 220-224 $^{o}$C; IR (KBr) $\nu$ 3283, 1561, 1472, 1204, 1121, 1049, 1003 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 6.91-7.44 (m, 8H), 4.91-4.93 (m, 1H), 4.01-4.06 (m, 2H), 3.83-3.89 (m, 1H), 3.56-3.63 (m, 2H), 3.43-3.48 (m, 1H), 2.31 (s, 3H), 0.98 (s, 3H), 0.64 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 155.7 (d, $J$(PC) = 22.0 Hz), 136.5, 136.3 (d, $J$(PC) = 7.9 Hz), 135.9, 130.4 (d, $J$(PC) = 4.4 Hz), 129.0, 128.6, 128.2, 127.9 (d, $J$(PC) = 4.7 Hz), 126.9, 125.8, 122.0 (d, $J$(PC) = 177.2 Hz), 75.6 (d, $J$(PC) = 3.9 Hz), 75.5 (d, $J$(PC) = 3.9 Hz), 67.8, 37.6 (d, $J$(PC) = 4.9 Hz), 32.3 (d, $J$(PC) = 6.3 Hz), 21.6, $21.0_3$, $20.9_8$; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 9.2; LC/MS *m/z*: 416 $[M]^+$; Anal. Calcd. for $C_{22}H_{25}O_4PS$: C, 63.45; H, 6.05. Found: C, 63.51; H, 6.01.

**Compound (*Z*)-18 (~95%)**

White solid, yield 0.02 g (7%). Mp 150-154 $^{o}$C; IR (KBr) $\nu$ 3351, 1696, 1605, 1507, 1464, 1262, 1057, 1009 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.06-7.26 (m, 7H), 4.68-4.69 (m, 1H), 3.96-4.05 (m, 2H), 3.52-3.68 (m, 2H), 2.85-2.88 (m, 1H), 2.60-2.64 (m, 1H), 2.37 (s, 3H), 2.32 (s, 3H), 1.04 (s, 3H), 0.68 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 151.4 (d, $J$(PC) = 8.8 Hz), 137.5, 136.4, 135.8, 134.2, 133.5 (d, $J$(PC) = 8.3 Hz), 130.1, 129.2, 127.6, 127.1, 126.3, 122.4 (d, $J$(PC) = 181.1 Hz), 75.7 (d, $J$(PC) = 6.1 Hz), 67.9, 38.6 (d, $J$(PC) = 14.7 Hz), 32.3 (d, $J$(PC) = 6.4 Hz), 21.8, 21.2, 21.0; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 9.8; LC/MS *m/z*: 413 $[M-18+H]^+$.

**Compound *(E)*-18**

White solid, yield 0.21 g (69%). Mp 230-234 $^{o}$C; IR (KBr) $\nu$ 3287, 1564, 1474, 1215, 1196, 1047, 993 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 6.91-7.30 (m, 7H), 4.90-4.91 (m, 1H), 3.97-4.04 (m, 2H), 3.73-3.79 (m, 1H), 3.58-3.64 (m, 2H), 3.45-3.49 (m, 1H), 2.40 (s, 3H), 2.31 (s, 3H), 1.00 (s, 3H), 0.67 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 155.2 (d, $J$(PC) = 21.6), 138.1, 136.5, 135.9, 133.2 (d, $J$(PC) = 8.0 Hz), 130.2 (d, $J$(PC) = 4.3 Hz), 129.5, 129.0, 128.0, 127.0, 125.9, 122.2 (d, $J$(PC) = 186.1 Hz), 75.7 (d, $J$(PC) = 5.7 Hz), 67.8, 37.8 (d, $J$(PC) = 5.2 Hz), 32.4 (d, $J$(PC) = 6.2 Hz), 21.8, 21.5, 21.1; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 9.4; LC/MS *m/z*: 430 $[M]^+$; Anal. Calcd. for $C_{23}H_{27}O_4PS$: C, 64.17; H, 6.32. Found: C, 64.25; H, 6.28.

**Compound (*Z*)-19**

White gummy solid, yield 0.04 g (13%). IR (neat) $\nu$ 3364, 1605, 1543, 1507, 1474, 1250, 1177 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 6.87-7.23 (m, 7H), 4.68-4.69 (m, 1H), 3.93-4.02 (m, 2H), 3.82 (s, 3H), 3.51-3.68 (m, 2H), 2.81-2.87 (m, 1H), 2.63-2.67 (m, 1H), 2.31 (s, 3H), 1.04 (s, 3H), 0.68 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 159.1, 151.8 (d, *J*(PC) = 9.2 Hz), 136.5, 135.9, 132.1 (d, *J*(PC) = 10.0 Hz), 131.8, 131.3, 129.3, 128.7 (d, *J*(PC) = 8.1 Hz), 127.7, 127.2, 126.4, 122.0 (d, *J*(PC) = 181.7 Hz), 114.0, 75.8, 68.0, 55.3, 38.7 (d, *J*(PC) = 14.4 Hz), 32.4 (d, *J*(PC) = 6.2 Hz), 21.8, 21.1; $^{31}P$ NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 10.3; LC/MS *m/z*: 447 $[M+H]^+$; Anal. Calcd. for $C_{23}H_{27}O_5PS$: C, 61.87; H, 6.10. Found: C, 61.75; H, 6.14.

**Compound (*E*)-19**

White solid, yield 0.20 g (65%). Mp 232-236 $^oC$; IR (KBr) $\nu$ 3277, 1605, 1562, 1505, 1246, 1202, 999 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 6.92-7.29 (m, 7H), 4.90-4.91 (m, 1H), 4.00-4.05 (m, 2H), 3.85 (s, 3H), 3.79-4.05 (m, 1H), 3.58-3.64 (m, 2H), 3.42-3.47 (m, 1H), 2.31 (s, 3H), 1.00 (s, 3H), 0.67 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 159.5, 155.7 (d, *J*(PC) = 22.6 Hz), 136.4, 135.9, 131.7 (d, *J*(PC) = 4.4 Hz), 129.1, 128.4 (d, *J*(PC) = 8.3 Hz), 128.1, 127.1, 125.9, 121.9 (d, *J*(PC) = 187.0 Hz), 114.1, 75.6 (d, *J*(PC) = 6.0 Hz), 67.9, 55.3, 37.7 (d, *J*(PC) = 5.1 Hz) , 32.4 (d, *J*(PC) = 6.3 Hz), 21.7, 21.1, 21.0; $^{31}P$ NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 9.4; LC/MS *m/z*: 445 $[M-H]^+$; Anal. Calcd. for $C_{23}H_{27}O_5PS$: C, 61.87; H, 6.10. Found: C, 61.95; H, 6.14.

**Compound (*Z*)-20**

White solid, yield 0.04 g (14%). Mp 168-172 $^oC$; IR (KBr) $\nu$ 3364, 1686, 1545, 1474, 1260, 1055, 1003 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.08-7.40 (m, 7H), 4.70-4.71 (m, 1H), 4.04-4.13 (m, 2H), 3.53-3.69 (m, 2H), 2.83-2.87 (m, 1H), 2.56-2.60 (m, 1H), 2.33 (s, 3H), 1.00 (s, 3H), 0.69 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 153.5 (d, *J*(PC) = 8.7 Hz), 136.6, 136.1, 135.0 (d, *J*(PC) = 8.3 Hz), 133.8, 131.9, 129.3, 128.8, 127.7, 126.7, 126.3, 120.1 (d, *J*(PC) = 183.6 Hz), 75.7 (d, *J*(PC) = 5.8 Hz), 67.6, 38.8 (d, *J*(PC) = 14.3 Hz), 32.4 (d, *J*(PC) = 6.1 Hz), 21.6, 21.1, 20.8; $^{31}P$ NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 10.0; LC/MS *m/z*: 451 $[M]^+$ and 453 $[M+2H]^+$; Anal. Calcd. for $C_{22}H_{24}ClO_4PS$:

C, 58.60; H, 5.36. Found: C, 58.75; H, 5.26.

**Compound (*E*)-20**

White solid, yield 0.20 g (67%). Mp 218-222 $^{o}$C; IR (KBr) $\nu$ 3314, 1576, 1564, 1476, 1208, 1047 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 6.91-7.41 (m, 7H), 4.90-4.92 (m, 1H), 4.07-4.12 (m, 2H), 3.84-3.90 (m, 1H), 3.57-3.65 (m, 2H), 3.41-3.45 (m, 1H), 2.32 (s, 3H), 0.96 (s, 3H), 0.68 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 156.7 (d, *J*(PC) = 21.3 Hz), 136.3, 136.1, 134.7 (d, *J*(PC) = 7.9 Hz), 134.3, 131.9 (d, *J* = 4.0 Hz), 129.1, 129.0, 128.0, 126.6, 125.8, 120.7 (d, *J*(PC) = 189.6 Hz), 75.4 (d, *J*(PC) = 3.8 Hz), 67.7, 37.5 (d, *J*(PC) = 4.8 Hz), 32.3 (d, *J*(PC) = 5.9 Hz), 21.5, 21.2, 21.1; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 9.4; LC/MS *m/z*: 433 $[M-18]^+$and 435 $[M-18+2H]^+$; Anal. Calcd. for $C_{22}H_{24}ClO_4PS$: C, 58.60; H, 5.36. Found: C, 58.56; H, 5.41.

**Compound (*E*)-21**

The *Z*–isomer was only a minor product and hence not isolated.

White solid, yield 0.19 g (64%). Mp 244-248 $^{o}$C; IR (KBr) $\nu$ 3316, 2971, 1576, 1559, 1476, 1208, 1047 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 6.91-7.41 (m, 7H), 4.90-4.92 (m, 1H), 4.07-4.13 (m, 2H), 3.80-3.86 (m, 1H), 3.57-3.65 (m, 2H), 3.45-3.49 (m, 1H), 2.32 (s, 3H), 0.96 (s, 3H), 0.68 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 156.8 (d, *J*(PC) = 21.5 Hz), 136.3 (d, *J*(PC) = 8.4 Hz), 134.7, 134.3, 132.0, 129.2, 129.0, 128.1, 126.6, 125.9, 120.7 (d, *J*(PC) = 189.7 Hz), 75.5, 67.8, 37.6, 32.4 (d, *J*(PC) = 5.8 Hz), 21.6, 21.2, 21.1; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 9.4; LC/MS *m/z*: 462 $[M+H]^+$; Anal. Calcd. for $C_{22}H_{24}NO_6PS$: C, 57.26; H, 5.24; N, 3.04. Found: C, 57.18; H, 5.31; N, 3.13.

**Compound (*E/Z*)-22**

White solid, yield 0.20 g (67%). Mp 208-212 $^{o}$C; IR (KBr) $\nu$ 3297, 1572, 1559, 1476, 1198, 1051, 997 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 6.77-8.07 (m, 10H), 4.98-5.02 (m, 1H), 3.96-4.05 (m, 1H), 3.85-3.93 (m, 2H), 3.54-3.62 (m, 1H), 3.31-3.39 (m, 2H), 2.29 (s, 3H), 0.92 (s, 3H), 0.48 (s, 3H).The other isomer was also present, but no distinct signal except for the one at 0.49 ppm could be observed; $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 156.8, 156.5, 138.6, 136.4, 135.8, 135.6, 133.8, 133.6, 133.5, 131.7,

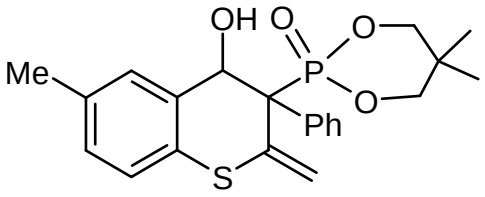
131.6, 131.3, 129.1, 128.9, 128.8, $128.7_4$, $128.6_8$, 128.6, 128.5, 128.4, 128.3, 127.8, 127.4, 126.8, 126.7, 126.6, 126.3, 126.2, 125.9, 125.8, 125.7, 125.5, 125.3, 120.3 (d, *J*(PC) = 188.4 Hz), 75.6 (d, *J*(PC) = 6.0 Hz), 68.0, 53.4, 37.9 (d, *J*(PC) = 4.9 Hz), 37.5 (d, *J*(PC) = 5.7 Hz), 32.3 (d, *J*(PC) = 6.3 Hz), 21.6, $20.9_5$, $20.9_1$; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 9.4 and 9.2 (2:3); LC/MS *m/z*: 467 $[M+H]^+$; Anal. Calcd. for $C_{26}H_{27}O_4PS$: C, 66.94; H, 5.83. Found: C, 66.85; H, 5.87.

**Compound (*E*)-23**

The *Z*–isomer was not observed.

White solid, yield 0.30 g (85%). Mp 204-208 $^oC$; IR (KBr) $\nu$ 3378, 1730, 1698, 1549, 1472, 1262, 1061 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.06-7.29 (m, 3H), 4.82-4.85 (m, 1H), 4.21-4.27 (m, 2H), 3.80-3.88 (m, 2H), 3.77-3.80 (m, 1H), 3.23-3.26 (m, 1H), 2.33 (s, 3H), 2.05-2.09 (dd, *J* = 14.0 and 1.2 Hz, 3H), 1.15 (s, 3H), 1.03 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 151.2 (d, *J*(PC) = 20.4), 136.9, 136.1, 129.0, 128.0, 126.2, 126.0, 114.0 (d, *J*(PC) = 185.4 Hz), 75.1 (d, *J*(PC) = 5.9 Hz), 67.8, 37.9 (d, *J*(PC) = 6.2 Hz), 32.5 (d, *J*(PC) = 5.5 Hz), 21.8, 21.6, 21.1, 16.5 (d, *J*(PC) = 9.3 Hz); $^{31}$P NMR (80 MHz, $CDCl_3$) δ 15.0; LC/MS *m/z*: 354 $[M]^+$; Anal. Calcd. for $C_{17}H_{23}O_4PS$: C, 57.61; H, 6.54. Found: C, 57.68; H, 6.51.

**Compound 24**

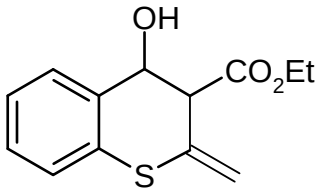



This compound was prepared by a procedure similar to that for **9** by the reaction of allene **1a** with 5-methyl-2-mercapto-benzaldehyde **5** in ethanol using the same molar quantities of the reactants and isolated by column chromatography on silica gel (hexane/ EtOAc; 1:1).

White solid, yield 0.08 g (25%). Mp 202-206 $^oC$; IR (KBr) $\nu$ 3264, 1605, 1480, 1240, 1069, 1005 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 6.97-7.30 (m, 8H), 5.79 (d, 1H, *J* = 5.2 Hz), 5.64 (d, 1H, *J* = 4.0 Hz), 5.51 (d, 1H, *J* = 8.4 Hz), 4.79 (s, 1H), 4.16-4.28 (m,

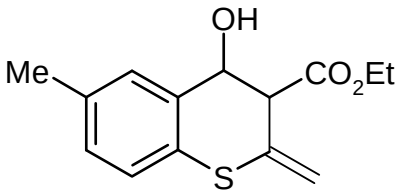
2H), 3.56-3.91 (dt, 2H), 2.26 (s, 3H), 1.15 (s, 3H), 0.85 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 140.7 (d, *J*(PC) = 7.5 Hz), 136.4 (d, *J*(PC) = 12.4 Hz), 136.0, 135.8, 130.4 (d, *J*(PC) = 6.9 Hz), 128.3, 127.5, 127.4, 127.3, 127.2, 125.9, 118.8 (d, *J*(PC) = 7.8 Hz), 77.8 (d, *J*(PC) = 7.7 Hz), 72.8, 60.4 (d, *J*(PC) = 132.8 Hz), 33.0 (d, *J*(PC) = 8.1 Hz), 22.0, 21.5, 21.3; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 20.4; LC/MS *m/z*: 417 $[M+H]^+$; Anal. Calcd. for $C_{22}H_{25}O_4PS$: C, 63.45; H, 6.05. Found: C, 63.34; H, 6.12.

**Compound 25**




The procedure was the same as above using **2** and **4** at room temperature using the same molar quantities. White solid, yield 0.30 g (84%). Mp 54-56 $^{o}$C; IR (KBr) $\nu$ 3457, 1732, 1713, 1589, 1445, 1260 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.13-7.46 (m, 4H), 5.48 (s, 1H), 5.31 (s, 1H), 5.13 (d, *J* ~ 6.2 Hz, 1H), 4.11-4.18 (m, 2H), 3.77 (d, *J* ~ 6.2 Hz, 1H), 1.14 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 169.6, 134.0, 133.7, 131.0, 129.0, 128.7, 125.7, 125.3, 114.3, 69.8, 61.4, 54.5, 14.0; LC/MS *m/z*: 250 $[M]^+$; HRMS (ESI) calcd for $C_{13}H_{14}O_3SNa$ $[M + Na]^+$ 273.0562, found 273.0562. Anal. Calcd. for $C_{13}H_{14}O_3S$: C, 62.38; H, 5.64. Found: C, 62.25; H, 5.68.

**Compound 26**

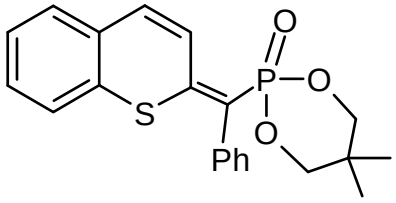



The procedure was the same as above using **2** and **5** at room temperature using the same molar quantities. White solid, yield 0.28 g (85%); Mp 42-46 $^{o}$C; IR (KBr) $\nu$ 3401, 1732,

1605, 1474, 1370, 1331, 1179 $cm^{-1}$; $^{1}H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.00-7.27 (m, 3H), 5.46 (s, 1H), 5.29 (s, 1H), 5.06-5.09 (m, 1H), 4.11-4.16 (m, 2H), 3.74 (d, $J$ = 8.0 Hz, 1H), 2.31 (s, 3H), 1.14 (t, $J$ = 8.0 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 169.7, 135.2, 134.3, 133.6, $129.7_4$, $129.6_7$, 127.4, 125.6, 114.2, 70.0, 61.4, 54.7, 21.0, 14.1; LC/MS *m/z*: 264 $[M]^+$; Anal. Calcd. for $C_{14}H_{16}O_3S$: C, 63.61; H, 6.10. Found: C, 63.75; H, 6.16.

**Synthesis of phosphono-thiochromene 27**

The quantities, procedure and the work up were the same as that for compound [procedure (ii) in the main paper] except that the reaction time was 24 h (instead of 4 h).

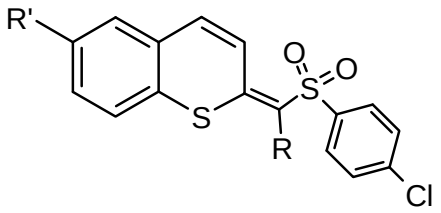



**Compound (*E*)-27 (isomeric purity ~95%)**

White solid, yield 0.22 g (70%). Mp 150-154 $^{o}C$; IR (KBr) $\nu$ 1611, 1514, 1485, 1385, 1260, 1219, 1057 $cm^{-1}$; $^{1}H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 6.85-8.12 (m, 11H), 4.09-4.14 (m, 2H), 3.54-3.61 (m, 2H), 0.92 (s, 3H), 0.60 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 152.1 (d, $J$(PC) = 22.1 Hz), 136.8 (d, $J$(PC) = 6.4 Hz), 133.4, 132.7, 130.4, 129.7, 129.4, 128.7, 128.2, 127.6, 126.1, 124.8, 122.1 (d, $J$(PC) = 6.6 Hz), 113.7 (d, $J$(PC) = 193.5 Hz), 75.2 (d, $J$(PC) = 6.0 Hz), 32.2 (d, $J$(PC) = 5.8 Hz), 21.6, 21.1; $^{31}P$ NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 10.1 (other isomer 12.4 (5%)); LC/MS *m/z*: 385 $[M+H]^+$.

**Synthesis of -thiochromene 28-31**

These compounds were prepared by a procedure similar to that for **8**] procedure (ii)] by the reaction of allenylsulfones **3a-b** with mercapto-benzaldehyde **4-5** in DMSO using the same molar quantities of the reactants and isolated by column chromatography on silica gel (hexane/ EtOAc; 3:2).




R = Ph, R' = H (**28**)
R = Ph, R' = Me (**29**)
R = Me, R' = H (**30**)
R = Me, R' = Me (**31**)

**Compound-28**

Yellow solid, yield 0.24 g (77%); Mp 162-164 $^{o}$C. IR (KBr) $\nu$ 1611, 1514, 1485, 1385, 1260, 1219, 1057 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.34 (d, $J$ = 10.8 Hz, 1H), 7.60-7.62 (m, 2H), 7.39-7.43 (m, 5H), 7.30-7.33 (m, 1H), 7.18-7.20 (m, 2H), 7.01-7.07 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 147.8, 140.3, 139.5, 134.4, 133.8, 133.3, 132.5, 131.6, 130.1, 129.7, 129.6, 129.4, 129.1, 129.0, 128.9, 128.8, 127.2, 126.6, 124.9, 119.1; LC/MS *m/z*: 411, 409 $[M]^+$; Anal. Calcd. for $C_{22}H_{15}ClO_2S_2$: C, 64.30; H, 3.68. Found: C, 64.21; H, 3.72.

**Compound 29**

Yellow solid, yield 0.23 g (72%); Mp 140-142 $^{o}$C. IR (KBr) $\nu$ 1611, 1514, 1485, 1385, 1260, 1219, 1057 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.33 (d, $J$ = 10.4 Hz, 1H), 7.61 (d, $J$ = 8.4 Hz, 2H), 7.38-7.42 (m, 5H), 6.92-7.13 (m, 6H), 2.32 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 148.2, 140.4, 139.4, 136.5, 134.5, 133.9, 132.5, 131.7, 130.5, 130.4, 130.1, 129.7, 129.5, 129.1, 129.0, 128.9, 127.0, 124.7, 123.6, 119.0, 21.0; LC/MS *m/z*: 425, 423 $[M]^+$; HRMS (ESI) calcd for $C_{23}H_{17}ClO_2S_2Na$ $[M + Na]^+$ 447.0256, found 447.0256. Anal. Calcd. for $C_{23}H_{17}ClO_2S_2$: C, 65.01; H, 4.03. Found: C, 64.12; H, 4.11.

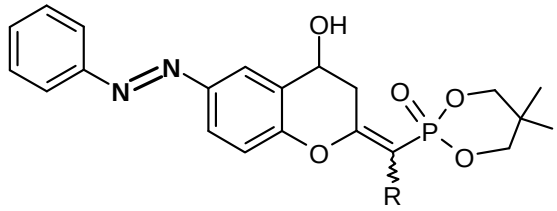
**Compound 30**

Yellow solid, yield 0.19 g (73%); Mp 137-139 $^{o}$C. IR (KBr) $\nu$ 1615, 1520, 1474, 1393, 1308, 1269, 1224, 1142 1084, 804 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.11 (d, $J$ = 10.8 Hz, 1H), 7.81-7.83 (m, 2H), 7.48-7.50 (m, 2H), 7.27-7.32 (m, 4H), 6.88 (d, $J$ = 11.2 Hz, 1H), 2.04 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 144.6, 140.8, 139.4, 132.6, 132.3, 130.2, 129.6, 129.2, 128.1, 127.4, 126.8, 125.1, 119.5, 118.3, 17.1; LC/MS *m/z*: 349, 351 $[M]^+$; Anal. Calcd. for $C_{17}H_{13}ClO_2S_2$: C, 58.53; H, 3.76. Found: C, 58.45; H, 3.81.

**Compound 31**

Yellow solid, yield 0.19 g (70%); Mp 172-174 $^{o}$C. IR (KBr) $\nu$ 1613, 1507, 1476, 1304, 1236, 1134, 1086, 1011, 810 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.09 (d, $J$ = 10.8 Hz, 1H), 7.81-7.83 (m, 2H), 7.47-7.49 (m, 2H), 7.10-7.20 (m, 4H), 6.85 (d, $J$ = 10.8 Hz, 1H), 2.35 (s, 3H), 2.03 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 145.1, 140.9, 139.4, 136.8, 132.4, 130.6, 130.3, 129.5, 129.4, 128.1, 127.3, 124.9, 119.5, 117.7, 21.0, 17.1; LC/MS *m/z*: 363, 365 $[M]^+$; Anal. Calcd. for $C_{18}H_{15}ClO_2S_2$: C, 59.58; H, 4.17. Found: C, 59.45; H, 4.23.

***Azo*-substituted phosphono-chromans 32-33 [procedure (iii) in the main paper]**




R = Ph **32**
R = *p*-Anisyl **33**

**Compound (*E*)-32**

Red solid, yield 0.10 g (27%). Mp 206-208 $^{o}$C; IR (KBr) $\nu$ 3358, 1644, 1609, 1480, 1235, 1059, 1005 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.24-7.95 (m, 13H), 4.88 (m, 1H), 3.69-3.91 (m, 4H), 3.19 (br, 1H), 2.93-2.97 (m, 1H), 2.64-2.67 (m, 1H), 1.20 (s, 3H), 0.79 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm) 159.3, 153.3, 152.1, 147.5, 134.2 (d, $J$(PC) = 6.2 Hz), 131.5, 129.6 (d, $J$(PC) = 4.8 Hz), 129.7, 128.7, 127.8, 127.5, 124.9, 122.6, 122.1, 117.3, 108.3 (d, $J$(PC) = 169.1 Hz), 75.9, 61.9, 33.0 (d, $J$(PC) = 9.6 Hz), 32.2 (d, $J$(PC) = 6.3 Hz), 21.5, 20.2; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 10.4; LC/MS *m/z*: 473 $[M-18+H]^+$; Anal. Calcd. for $C_{27}H_{27}N_2O_5P$: C, 66.12; H, 5.55; N, 5.71. Found: C, 66.35; H, 5.48; N, 5.65.

**Compound (*Z*)-32**

Red solid, yield 0.20 g (53%). Mp 206-208 $^{o}$C; IR (KBr) $\nu$ 3310, 1636, 1607, 1483, 1236, 1165, 1057 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 6.86-8.01 (m, 13H), 5.08 (m, 1H),

3.93-4.10 (m, 2H), 3.56-3.71 (m, 2H), 3.30-3.34 (m, 1H), 3.13-3.14 (m, 1H), 0.99 (s, 3H), 0.64 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm) 160.0 (d, $J$(PC) = 32.2 Hz), 153.3, 152.3, 147.8, 134.0, 131.9, 130.7, 130.0, 128.6, 128.1, 127.8, 124.9, 122.9, 122.3, 117.5, 108.9 (d, $J$(PC) = 188.4 Hz), 75.9 (d, $J$(PC) = 15.4 Hz), 62.0, 33.5, 32.2, 21.5, 20.4; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 14.5; LC/MS *m/z*: 473 $[M-18+H]^+$; Anal. Calcd. for $C_{27}H_{27}N_2O_5P$: C, 66.12; H, 5.55; N, 5.71. Found: C, 66.35; H, 5.46; N, 5.88.

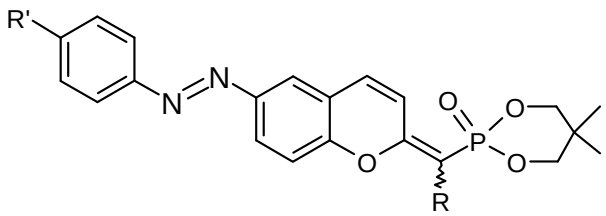
**Compound (*E*)-33**

Red solid, yield 0.10 g (28%). Mp 206-208 $^o$C; IR (KBr) $\nu$ 3368, 1638, 1605, 1510, 1480, 1244, 1061 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 6.90-7.90 (m, 12H), 4.87 (br m, 1H), 3.85-3.90 (m, 2H), 3.82 (s, 3H), 3.70-3.78 (m, 2H), 2.93-2.94 (m, 1H), 2.63-2.67 (m, 1H), 1.20 (s, 3H), 0.77 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm) 159.5, 159.1, 153.6, 152.3, 147.7, 132.1, 131.8, 130.0, 127.7, 126.3 (d, $J$(PC) = 5.8 Hz), 125.2, 122.8, 122.4, 117.5, 114.3, 107.9 (d, $J$(PC) = 169.1 Hz), 76.2, 62.0, 55.6, 33.2, 32.1 (d, $J$(PC) = 5.8 Hz), 21.8, 20.2; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 10.9; LC/MS *m/z*: 503 $[M-18+H]^+$; HRMS (ESI) calcd for $C_{28}H_{29}N_2O_6PNa$ $[M + Na]^+$ 543.1661, found 543.1661. Anal. Calcd. for $C_{28}H_{29}N_2O_6P$: C, 64.61; H, 5.62; N, 5.38. Found: C, 64.48; H, 5.55; N, 5.45.

**Compound (*Z*)-33**

Red solid, yield 0.16 g (46%). Mp 206-208 $^o$C; IR (KBr) $\nu$ 3306, 1636, 1605, 1510, 1481, 1242, 1177, 1059, 1007 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 6.88-8.02 (m, 12H), 5.07 (m, 1H), 3.99-4.09 (m, 2H), 3.85 (s, 3H), 3.67-3.90 (m, 2H), 3.56-3.62 (m, 1H), 3.32-3.36 (m, 1H), 1.00 (s, 3H), 0.68 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm) 159.8 (d, $J$(PC) = 32.7 Hz), 158.7, 153.4, 152.3, 147.7, 131.8, 130.0, 128.2, 125.9, 124.8, 122.8, 122.2, 117.5, 113.9, 108.4 (d, $J$(PC) = 188.1 Hz), 75.9 (d, $J$(PC) = 14.6 Hz), 62.1, 55.5, 33.5, 32.1 (d, $J$(PC) = 5.8 Hz), 21.6, 20.4; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 14.9; LC/MS *m/z*: 503 $[M-18+H]^+$; Anal. Calcd. for $C_{28}H_{29}N_2O_6P$: C, 64.61; H, 5.62; N, 5.38. Found: C, 64.75; H, 5.56; N, 5.45.

**Azo substituted phosphono-chromenes 34-43 [procedure (iii) in the main paper]**




| | | | |
|---|---|---|---|
| R' = H, R = Ph | **34** | R' = NO2, R = Ph | **39** |
| R' = H, R = 4-Me-$C_6H_4$ | **35** | R' = NO2, R = 4-Me-C6H4 | **40** |
| R' = H, R = 4-MeO-$C_6H_4$ | **36** | R' = NO2, R = 4-MeO-C6H4 | **41** |
| R' = H, R = 4-Cl-$C_6H_4$ Ph | **37** | R' = NO2, R = 4-Cl-C6H4 | **42** |
| R' = H, R = Me | **38** | R' = NO2, R = Me | **43** |

**Compound (*E*)-34**

Red solid, yield 0.14 g (40%). Mp 202-206 $^{o}$C; IR (KBr) $\nu$ 1630, 1562, 1470, 1260, 1235, 1055, 1003 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.27-7.89 (m, 13H), 7.05 (d, $J$ = 10.0 Hz, 1H), 6.87 (d, $J$ = 10.0 Hz, 1H), 4.10-4.15 (m, 2H), 3.58-3.64 (m, 2H), 0.94 (s, 3H), 0.65 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 159.0 (d, $J$(PC) = 35.0 Hz), 154.6, 152.5, 148.5, 133.9, 131.1, 130.9 (d, $J$(PC) = 5.0 Hz), 130.1, 129.1, 128.1, 127.3, 125.5, 122.8, 120.9, 120.7, 120.5, 116.5, 102.1 (d, $J$(PC) = 201.0 Hz), 75.2 (d, $J$(PC) = 6.0 Hz), 32.3 (d, $J$(PC) = 6.0 Hz), 21.6, 21.2; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 14.9; LC/MS *m/z*: 473 $[M+H]^+$; HRMS (ESI) calcd for $C_{27}H_{25}N_2O_4P$ $[M + H]^+$ 473.1630, found 473.1630. Anal. Calcd. for $C_{27}H_{25}N_2O_4P$: C, 68.64; H, 5.33; N, 5.93. Found: C, 68.43; H, 5.41; N, 5.85.

**Compound (*Z*)-34**

Red solid, yield 0.13 g (36%). Mp 164-168 $^{o}$C; IR (KBr) $\nu$ 1628, 1574, 1555, 1472, 1433, 1258, 1059, 1009 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.27-7.95 (m, 13H), 6.86 (dd, $J$ = 10.0 and ~2.0 Hz, 1H), 6.37 (d, $J$ = 10.0 Hz, 1H), 3.88-3.95 (m, 2H), 3.72-3.76 (m, 2H), 1.21 (s, 3H), 0.81 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 158.5, 154.7, 152.5, 148.5, 133.9 (d, $J$(PC) = 5.2 Hz), 131.1, 130.5, 129.2, 128.9, 127.8, 126.3, 122.8, 121.0, 120.4, 120.2, 119.3 (d, $J$(PC) = 12.8 Hz), 116.9, 102.2 (d, $J$(PC) = 181.9 Hz), 75.9, 32.4 (d, $J$(PC) = 5.7 Hz), 21.9, 21.1; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 11.7; LC/MS *m/z*: 473 $[M+H]^+$; Anal. Calcd. for $C_{27}H_{25}N_2O_4P$: C, 68.64; H, 5.33; N, 5.93. Found: C,

68.71; H, 5.25; N, 6.07.

**Compound (*E*)-35**

Red solid, yield 0.11 g (32%). Mp 176-178 $^{o}$C; IR (KBr) $\nu$ 1628, 1559, 1468, 1445, 1262, 1235 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.20-7.89 (m, 12H), 7.02 (d, $J$ = 8.0 Hz, 1H), 6.90 (d, $J$ = 8.0 Hz), 4.07-4.12 (m, 2H), 3.59-3.65 (m, 2H), 2.41 (s, 3H), 0.98 (s, 3H), 0.69 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 158.7 (d, $J$(PC) = 34.9 Hz), 154.7, 152.4, 148.5, 136.9, 131.0, 130.7, 130.6 (d, $J$(PC) = 4.7 Hz), 129.9, 129.1, 128.9, 125.5, 122.8, 120.9, 120.7, 120.6, 116.5, 102.1 (d, $J$(PC) = 191.0 Hz), 75.3 (d, $J$(PC) = 5.3 Hz), 32.3 (d, $J$(PC) = 5.7 Hz), 21.7, 21.4, 21.2; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 15.2; LC/MS *m/z*: 487 $[M+H]^+$; Anal. Calcd. for $C_{28}H_{27}N_2O_4P$: C, 69.13; H, 5.59; N, 5.76. Found: C, 69.32; H, 5.51; N, 5.66. X-ray structure was determined for this sample.

**Compound (*Z*)-35**

Red solid, yield 0.14 g (40%). Mp 190-194 $^{o}$C; IR (KBr) $\nu$ 1630, 1615, 1574, 1476, 1435, 1258, 1236 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.20-7.96 (m, 12H), 6.81 (dd, $J$ = 10.0 and ~2.0 Hz, 1H), 6.38 (d, $J$ = 10.0 Hz, 1H), 3.85-3.92 (m, 2H), 3.73-3.77 (m, 2H), 2.38 (s, 3H), 1.21 (s, 3H), 0.81 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 158.0, 154.7, 152.4, 148.4, 137.5, 131.0, 130.7 (d, $J$(PC) = 5.1 Hz), 130.1, 129.5, 129.1, 129.0, 126.1, 122.7, 120.9, 120.4, 119.4 (d, $J$(PC) = 13.1 Hz), 116.7, 102.3 (d, $J$(PC) = 179.6 Hz), 76.0 (d, $J$(PC) = 5.8 Hz), 32.3 (d, $J$(PC) = 5.6 Hz), 21.9, 21.2, 21.0; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 11.9; LC/MS *m/z*: 487 $[M+H]^+$; Anal. Calcd. for $C_{28}H_{27}N_2O_4P$: C, 69.13; H, 5.59; N, 5.76. Found: C, 69.05; H, 5.63; N, 5.82.

**Compound (*E*)-36**

Red solid, yield 0.10 g (30%). Mp 162-166 $^{o}$C; IR (KBr) $\nu$ 1628, 1607, 1561, 1468, 1262, 1231 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 6.94-7.96 (m, 12H), 7.02 (d, $J$ = 8.0 Hz, 1H), 6.90 (d, $J$ = 8.0 Hz, 1H), 4.09-4.14 (m, 2H), 3.87 (s, 3H), 3.59-3.65 (m, 2H), 0.96 (s, 3H), 0.69 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 159.0 (d, $J$(PC) = 36.7 Hz), 154.7, 152.5, 148.5, 132.0 (d, $J$(PC) = 4.7 Hz), 131.1, 129.9, 129.2, 126.0, 125.5, 122.8, 120.9, 120.8, 120.6, 120.1, 116.5, 101.7 (d, $J$(PC) = 200.2 Hz), 75.3 (d, $J$(PC) = 5.7 Hz), 55.3, 32.3 (d, $J$(PC) = 5.7 Hz), 21.7, 21.3; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 15.3;

LC/MS *m/z*: 503 $[M+H]^+$; Anal. Calcd. for $C_{28}H_{27}N_2O_5P$: C, 66.93; H, 5.42; N, 5.57. Found: C, 66.85; H, 5.39; N, 5.62.

**Compound (*Z*)-36**

Red solid, yield 0.15 g (43%). Mp 172-175 $^oC$; IR (KBr) $\nu$ 1630, 1613, 1574, 1435, 1236 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 6.93-7.94 (m, 12H), 6.85 (dd, $J$ = 10.0 and 3.0 Hz, 1H), 6.38 (d, $J$ = 10.0 Hz, 1H), 3.88-3.95 (m, 2H), 3.85 (s, 3H), 3.73-3.77 (m, 2H), 1.21 (s, 3H), 0.82 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 159.1, 158.1, 154.8, 152.5, 148.5, 132.1, 131.1, 130.1, 129.2, 126.2, 125.9, 122.8, 121.0, 120.5, 119.5 (d, $J$(PC) = 12.0 Hz), 116.8, 114.3, 102.0 (d, $J$(PC) = 180.8 Hz), 76.0, 55.3, 32.4, 22.0, 21.1; $^{31}P$ NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 12.0; LC/MS *m/z*: 503 $[M+H]^+$; Anal. Calcd. for $C_{28}H_{27}N_2O_5P$: C, 66.93; H, 5.42; N, 5.57. Found: C, 66.78; H, 5.35; N, 5.66.

**Compound (*E*)-37**

Red solid, yield 0.16 g (37%). Mp 200-202 $^oC$; IR (KBr) $\nu$ 1628, 1578, 1468, 1445, 1262, 1235 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.33-7.90 (m, 12H), 7.07 (d, $J$ = 10.0 Hz, 1H), 6.90 (d, $J$ = 10.0 Hz, 1H), 4.16-4.21 (m, 2H), 3.59-3.66 (m, 2H), 0.93 (s, 3H), 0.70 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 159.6 (d, $J$(PC) = 34.6 Hz), 154.5, 152.5, 148.7, 133.2, 132.6, 132.4 (d, $J$(PC) = 4.6 Hz), 131.2, 130.6, 129.2, 128.4, 125.6, 122.9, 121.1, 120.7, 120.3, 116.5, 100.5 (d, $J$(PC) = 202.9 Hz), 75.1 (d, $J$(PC) = 5.5 Hz), 32.3 (d, $J$(PC) = 5.6 Hz), 21.6, 21.4; $^{31}P$ NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 15.0; LC/MS *m/z*: 507 $[M]^+$ and 509 $[M+2H]^+$; Anal. Calcd. for $C_{27}H_{24}N_2O_4ClP$: C, 63.97; H, 4.77; N, 5.53. Found: C, 63.85; H, 4.71; N, 5.65.

**Compound (*Z*)-37**

Red solid, yield 0.16 g (37%). Mp 188-192 $^oC$; IR (KBr) $\nu$ 1630, 1574, 1480, 1435, 1258, 1236 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.32-7.89 (m, 12H), 6.91 (dd, $J$ = 10.4 and ~2.0 Hz, 1H), 6.34 (d, $J$ = 10.4 Hz, 1H), 3.93-4.00 (m, 2H), 3.72-3.77 (m, 2H), 1.20 (s, 3H), 0.85 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 158.5, 154.6, 152.5, 148.6, 133.8, 132.7, 132.4, 131.2, 131.0, 129.2, 126.4, 122.9, 121.2, 120.3, 118.9 (d, $J$(PC) = 12.6 Hz), 116.9, 101.2 (d, $J$(PC) = 182.0 Hz), 76.0, 32.5, 22.0, 21.2; $^{31}P$ NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 11.4; LC/MS *m/z*: 507 $[M]^+$ and 509 $[M+2H]^+$ ; Anal. Calcd. for

$C_{27}H_{24}N_2O_4ClP$: C, 63.97; H, 4.77; N, 5.53. Found: C, 63.85; H, 4.69; N, 5.61.

**Compound (*E*)-38**

Red solid, yield 0.20 g (50%). Mp 238-242 $^oC$; IR (KBr) $\nu$ 1634, 1609, 1578, 1472, 1433, 1231 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.47-7.91 (m, 8H), 7.19 (d, $J$ = 10.0 Hz, 1H), 6.86 (d, $J$ = 10.0 Hz, 1H), 4.34-4.38 (m, 2H), 3.76-3.83 (m, 2H), 2.02 (d, $J$ = 14.0 Hz, 3H), 1.27 (s, 3H), 0.97 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 159.0 (d, $J$(PC) = 36.1 Hz), 154.9, 152.5, 148.5, 131.0, 129.1, 128.0, 125.4, 122.8, 120.9, 120.7, 116.1, 94.6 (d, $J$(PC) = 202.6 Hz), 74.5 (d, $J$(PC) = 5.3 Hz), 32.5 (d, $J$(PC) = 5.0 Hz), 22.3, 21.5, 12.1 (d, $J$(PC) = 4.0 Hz); $^{31}P$ NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 20.9; LC/MS *m/z*: 411 $[M+H]^+$; Anal. Calcd. for $C_{22}H_{23}N_2O_4P$: C, 64.39; H, 5.65; N, 6.83. Found: C, 64.55; H, 5.58; N, 6.75.

**Compound (*Z*)-38**

Red solid, yield 0.12 g (30%). Mp 196-200 $^oC$; IR (KBr) $\nu$ 1628, 1580, 1472, 1262, 1231 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.18-7.90 (m, 8H), 6.93 (dd, $J$ = 13.2 and ~3.6 Hz, 1H), 6.61 (d, $J$ = 10.0 Hz, 1H), 4.12-4.18 (m, 2H), 3.87-3.92 (m, 2H), 1.94 (d, $J$ = 14.8 Hz, 3H), 1.22 (s, 3H), 1.05 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 156.2, 155.0, 152.5, 148.3, 131.0, 129.8, 129.1, 126.2, 122.8, 121.0, 120.3, 118.0 (d, $J$(PC) = 14.2 Hz), 116.3, 93.0 (d, $J$(PC) = 182.5 Hz), 75.6 (d, $J$(PC) = 5.9 Hz), 32.5 (d, $J$(PC) = 5.6 Hz), 21.9, 21.6, 12.3 (d, $J$(PC) = 6.9 Hz); $^{31}P$ NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 17.0; LC/MS *m/z*: 411 $[M+H]^+$; Anal. Calcd. for $C_{22}H_{23}N_2O_4P$: C, 64.39; H, 5.65; N, 6.83. Found: C, 64.51; H, 5.71; N, 6.75.

**Compound (*E*)-39**

Red solid, yield 0.16 g (40%). Mp 234-236 $^oC$; IR (KBr) $\nu$ 1630, 1559, 1522, 1460, 1339, 1235 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.35-8.37 (m, 12H), 7.04 (d, $J$ = 10.0 Hz, 1H), 6.89 (d, $J$ = 10.0 Hz, 1H), 4.12-4.16 (m, 2H), 3.58-3.64 (m, 2H), 0.94 (s, 3H), 0.64 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 158.9, 158.5, 155.6 (d, $J$(PC) = 5.9 Hz), 148.5 (d, $J$(PC) = 30.8 Hz), 133.8, 130.8 (d, $J$(PC) = 4.6 Hz), 129.7, 128.2, 127.4, 126.2, 124.8, 123.4, 121.6, 121.0, 116.8, 102.9 (d, $J$(PC) = 200.5 Hz), 75.3 (d, $J$(PC) = 5.8 Hz), 32.3 (d, $J$(PC) = 5.8 Hz), 21.6, 21.2; $^{31}P$ NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 14.5;

LC/MS *m/z*: 518 $[M+H]^+$; Anal. Calcd. for $C_{27}H_{24}N_3O_6P$: C, 62.67; H, 4.67; N, 8.12. Found: C, 62.55; H, 4.72; N, 8.28.

**Compound (*Z*)-39**

Red solid, yield 0.16 g (40%). Mp 218-222 °C; IR (KBr) $\nu$ 1612, 1572, 1518, 1343, 1273, 1240 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.27-8.39 (m, 12H), 6.86 (dd, $J$ = 10.4 and ~3.0 Hz, 1H), 6.39 (d, $J$ = 9.6 Hz, 1H), 3.88-3.94 (m, 2H), 3.71-3.75 (m, 2H), 1.20 (s, 3H), 0.80 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 158.0, 155.7 (d, $J$(PC) = 17.4 Hz), 148.5 (d, $J$(PC) = 29.1 Hz), 133.8, 130.9, 130.0, 129.0, 128.0, 126.9, 124.8, 123.8, 123.4, 123.3, 121.8, 120.7, 119.8 (d, $J$(PC) = 13.1 Hz), 117.2, 103.4 (d, $J$(PC) = 180.0 Hz), 76.1, 32.4 (d, $J$(PC) = 5.6 Hz), 22.0, 21.0; $^{31}P$ NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 11.2; LC/MS *m/z*: 518 $[M+H]^+$; Anal. Calcd. for $C_{27}H_{24}N_3O_6P$: C, 62.67; H, 4.67; N, 8.12. Found: C, 62.54; H, 4.58; N, 8.22.

**Compound (*E*)-40**

Red solid, yield 0.18 g (48%). Mp 238-240 °C; IR (KBr) $\nu$ 1630, 1609, 1557, 1520, 1460, 1339, 1262, 1235 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.21-8.36 (m, 11H), 7.01 (d, $J$ = 10.0 Hz, 1H), 6.92 (d, $J$ = 10.0 Hz, 1H), 4.08-4.13 (m, 2H), 3.59-3.65 (m, 2H), 2.41 (s, 3H), 0.97 (s, 3H), 0.69 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 158.6, 158.3, 155.7 (d, $J$(PC) = 11.8 Hz), 148.5 (d, $J$(PC) = 32.0 Hz), 137.1, 130.6, 130.5, 129.4, 128.9, 126.1, 124.8, 123.4, 121.6, 121.1, 116.8, 103.1 (d, $J$(PC) = 198.7 Hz), 75.4 (d, $J$(PC) = 5.8 Hz), 32.3 (d, $J$(PC) = 5.8 Hz), 21.7, 21.4, 21.3; $^{31}P$ NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 14.7; LC/MS *m/z*: 532 $[M+H]^+$; Anal. Calcd. for $C_{28}H_{26}N_3O_6P$: C, 63.27; H, 4.93; N, 7.91. Found: C, 63.12; H, 4.88; N, 7.85.

**Compound (*Z*)-40**

Red solid, yield 0.11 g (28%). Mp 244-246 °C; IR (KBr) $\nu$ 1611, 1559, 1524, 1456, 1435, 1260 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.21-8.40 (m, 11H), 6.83 (dd, $J$ = 13.2 and ~3.2 Hz, 1H), 6.41 (d, $J$ = 9.6 Hz, 1H), 3.87-3.94 (m, 2H), 3.72-3.76 (m, 2H), 2.39 (s, 3H), 1.21 (s, 3H), 0.81 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 157.7, 155.8, 155.6, 148.3 (d, $J$(PC) = 29.0 Hz), 137.7, 130.7 (d, $J$(PC) = 4.0 Hz), 129.7, 129.6, 126.8, 124.8, 123.4, 121.7, 120.7, 119.8 (d, $J$(PC) = 13.0 Hz), 117.1, 103.4 (d, $J$(PC) = 179.0

Hz), 76.1 (d, *J*(PC) = 6.0 Hz), 32.3 (d, *J*(PC) = 6.0 Hz), 22.0, 21.3, 21.0; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 11.5; LC/MS *m/z*: 532 $[M+H]^+$; Anal. Calcd. for $C_{28}H_{26}N_3O_6P$: C, 63.27; H, 4.93; N, 7.91. Found: C, 63.41; H, 4.88; N, 7.81.

**Compound (*E*)-41**

Red solid, yield 0.14 g (38%). Mp 238-242 $^{o}$C; IR (KBr) $\nu$ 1630, 1609, 1553, 1522, 1341, 1227 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 6.91-8.36 (m, 13H), 4.10-4.15 (m, 2H), 3.87 (s, 3H), 3.59-3.65 (m, 2H), 0.96 (s, 3H), 0.69 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 158.9, 158.5, 155.7, 155.6, 148.5 (d, *J*(PC) = 30.9 Hz), 132.0 (d, *J*(PC) = 5.8 Hz), 129.5, 126.2, 125.8, 124.8, 123.4, 121.6, 121.1, 116.8, 113.7, 102.6 (d, *J*(PC) = 199.8 Hz), 75.4 (d, *J*(PC) = 5.8 Hz), 55.3, 32.3 (d, *J*(PC) = 5.9 Hz), 21.7, 21.3; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 14.9; LC/MS *m/z*: 548 $[M+H]^+$; Anal. Calcd. for $C_{28}H_{26}N_3O_7P$: C, 61.43; H, 4.79; N, 7.67. Found: C, 61.32; H, 4.68; N, 7.56.

**Compound (*Z*)-41**

Red solid, yield 0.14 g (38%). Mp 206-208 $^{o}$C; IR (KBr) $\nu$ 1628, 1611, 1578, 1528, 1343, 1238 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 6.93-8.01 (m, 11H), 6.83 (dd, *J* = 13.6 and ~3.6 Hz, 1H), 6.40 (d, *J* = 10.0 Hz, 1H), 3.88-3.95 (m, 2H), 3.85 (s, 3H), 3.71-3.76 (m, 2H), 1.21 (s, 3H), 0.82 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 159.3, 157.9, 155.8, 155.6, 148.5 (d, *J*(PC) = 29.6 Hz), 132.1 (d, *J*(PC) = 4.9 Hz), 129.8, 126.8, 125.7 (d, *J*(PC) = 5.6 Hz), 124.8, 123.4, 121.7, 120.8, 119.9 (d, *J*(PC) = 12.8 Hz), 117.1, 114.4, 102.9 (d, *J*(PC) = 180.4 Hz), 76.0 (d, *J*(PC) = 6.0 Hz), 55.4, 32.4 (d, *J*(PC) = 6.0 Hz), 22.0, 21.1; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 11.6; LC/MS *m/z*: 548 $[M+H]^+$; Anal. Calcd. for $C_{28}H_{26}N_3O_7P$: C, 61.43; H, 4.79; N, 7.67. Found: C, 61.55; H, 4.65; N, 7.58.

**Compound (*E*)-42**

Red solid, yield 0.14 g (39%). Mp. 226-228 $^{o}$C; IR (KBr) $\nu$ 1628, 1611, 1572, 1557, 1524, 1385, 1339, 1238 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.33-8.39 (m, 11H), 7.07 (d, *J* = 10.0 Hz, 1H), 6.92 (d, *J* = 10.0 Hz, 1H), 4.17-4.22 (m, 2H), 3.59-3.66 (m, 2H), 0.92 (s, 3H), 0.69 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 159.4, 159.0, 155.5 (d, *J*(PC) = 7.5 Hz), 148.5 (d, *J*(PC) = 26.7 Hz), 133.3, 132.3 (d, *J*(PC) = 4.7 Hz), 130.1, 128.5, 126.2, 124.8, 123.4, 121.8, 120.9, 120.7, 116.8, 101.4 (d, *J*(PC) = 202.3 Hz), 75.2

(d, *J*(PC) = 5.6 Hz), 32.3 (d, *J*(PC) = 5.5 Hz), 21.5, 21.3; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 14.6; LC/MS *m/z*: 552 $[M]^+$ and 554 $[M+2H]^+$; Anal. Calcd. for $C_{27}H_{23}ClN_3O_6P$: C, 58.76; H, 4.20; N, 7.61. Found: C, 58.62; H, 4.28; N, 7.88.

**Compound (*Z*)-42**

Red solid, yield 0.14 g (39%). Mp. 202-204 $^oC$; IR (KBr) $\nu$ 1626, 1559, 1522, 1458, 1343, 1458, 1244, 1049 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.33-8.38 (m, 11H), 6.90 (dd, *J* = 10.0 and ~2.0 Hz, 1H), 6.37 (d, *J* = 9.6 Hz, 1H), 3.95-4.01 (m, 2H), 3.71-3.76 (m, 2H), 1.19 (s, 3H), 0.85 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 158.2, 155.6 (d, *J*(PC) = 7.4 Hz), 148.5 (d, *J*(PC) = 26.3 Hz), 134.0, 132.4, 132.3, 130.6, 129.2, 126.9, 124.8, 123.5, 121.9, 120.6, 119.4 (d, *J*(PC) = 12.7 Hz), 117.2, 102.1 (d, *J*(PC) = 182.2 Hz), 76.0 (d, *J*(PC) = 6.0 Hz), 32.4 (d, *J*(PC) = 6.0 Hz), 21.9, 21.2; $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 11.0; LC/MS *m/z*: 552 $[M]^+$ and 554 $[M+2H]^+$; Anal. Calcd. for $C_{27}H_{23}ClN_3O_6P$: C, 58.76; H, 4.20; N, 7.61. Found: C, 58.85; H, 4.31; N, 7.55.

**Compound (*E*)-43**

Red solid, yield 0.22 g (49%). Mp. 244-248 $^oC$; IR (KBr) $\nu$ 1632, 1562, 1510, 1339, 1231, 1051 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.81-8.03 (m, 7H), 7.22 (d, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 4.35-4.39 (m, 2H), 3.76-3.83 (m, 2H), 2.03 (d, *J* = 12.0 Hz, 3H), 1.28 (s, 3H), 0.97 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 158.7 (d, *J*(PC) = 36.2 Hz), 155.9 (d, *J*(PC) = 3.1 Hz), 155.6, 148.6, 148.4, 127.5, 126.0, 124.8, 123.3, 121.5, 121.2, 121.1, 116.4, 94.6 (d, *J*(PC) = 202.0 Hz), 74.5 (d, *J*(PC) = 5.4 Hz), 32.5 (d, *J*(PC) = 5.3 Hz), 22.3, 21.5, 12.1 (d, *J*(PC) = 4.3 Hz); $^{31}$P NMR (80 MHz, $CDCl_3$) $\delta$ (ppm) 20.5; LC/MS *m/z*: 456 $[M+H]^+$; Anal. Calcd. for $C_{22}H_{22}N_3O_6P$: C, 58.02; H, 4.87; N, 9.23: Found: C, 58.21; H, 4.78; N, 9.45.

**Compound (*Z*)-43** (~90%; the remaining was the *E*-isomer)

Red solid, yield 0.11 g (25%); Mp. 146-150 $^oC$; IR (KBr) $\nu$ 1638, 1605, 1526, 1462, 1343, 1262, 1053 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) (major) $\delta$ (ppm) 7.21-8.40 (m, 7H), 6.94 (dd, *J* = 10.0 and ~2.0 Hz, 1H), 6.63 (d, *J* = 9.6 Hz, 1H), 4.14-4.20 (m, 2H), 3.87-3.92 (m, 2H), 1.95 (d, *J* = 14.8 Hz, 3H), 1.21 (s, 3H), 1.07 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 155.6 (d, *J*(PC) = 31.1 Hz) 148.7, 148.4, 127.5, 126.0, $124.7_8$, $124.7_7$,

123.4, 121.5, 121.2, 116.4, 92.1, 74.5 (d, *J*(PC) = 5.7 Hz), 32.5 (d, *J*(PC) = 5.0 Hz), 22.3, 21.5, 12.2; The doublet due to P-*C* carbon could not be clearly identified due to low intensity; $^{31}$P NMR $\delta$ (ppm) 16.6; LC/MS *m/z*: 456 $[M+H]^+$; Anal. Calcd. for $C_{22}H_{22}N_3O_6P$: C, 58.02; H, 4.87; N, 9.23: Found: C, 58.12; H, 4.91; N, 9.12.

***Crystal data*:**

(*E*)-**8:** $C_{21}H_{23}O_4PS$, *M* = 402.43, Monoclinic, Space group P2(1)/c, *a* = 10.667(2), *b* = 9.913(2), *c* = 20.138(4) Å, $\beta$ = 111.543(9), *V* = 1980.7(7) Å$^3$, *Z* = 4, $\mu$ = 0.268 mm$^{-1}$, data/restraints/parameters: 3484/ 0/ 246, R indices ($I > 2\sigma(I)$): R1 = 0.0697, *wR*2 (all data) = 0.1355

**9:** $C_{21}H_{23}O_4PS$, *M* = 402.43, Monoclinic, Space group P2(1)/c, *a* = 9.127(2), *b* = 17.133(3), *c* = 12.580(3) Å, $\beta$ = 93.34(2), *V* = 1980.7(7) Å$^3$, *Z* = 4, $\mu$ = 0.270 mm$^{-1}$, data/restraints/parameters: 3436/ 0/ 251, R indices ($I > 2\sigma(I)$): R1 = 0.0415, *wR*2 (all data) = 0.0871

(*E*)-**12:** $C_{22}H_{25}O_5PS$, *M* = 432.35, Monoclinic, Space group P2(1)/c, *a* = 5.952(2), *b* = 9.834(4), *c* = 36.141(14) Å, $\beta$ = 94.321(7), *V* = 2109.4(14) Å$^3$, *Z* = 4, $\mu$ = 0.260 mm$^{-1}$, data/restraints/parameters: 3712/ 0/ 266, R indices ($I > 2\sigma(I)$): R1 = 0.0593, *wR*2 (all data) = 0.1458

(*Z*)-**12:** $C_{22}H_{25}O_5PS$, *M* = 432.46, Monoclinic, Space group P2(1)/c, *a* = 12.3185(7), *b* = 12.0813(7), *c* = 18.8019(8) Å, *β* = 130.587(2), *V* = 2124.98(19) Å$^3$, *Z* = 4, μ = 0.258 mm$^{-1}$, data/restraints/parameters: 3752/ 0/ 265, R indices (*I* > 2σ(*I*)): R1 = 0.0687, *wR*2 (all data) = 0.1544

(*E*)-**16:** $C_{16}H_{21}O_4PS$, *M* = 340.37, Monoclinic, Space group P2(1)/c, *a* = 6.8884(5), *b* = 22.6134(16), *c* = 11.3005(7) Å, *β* = 111.284(3), *V* = 1640.22(19) Å$^3$, *Z* = 4, μ = 0.309 mm$^{-1}$, data/restraints/parameters: 2884/ 0/ 202, R indices (*I* > 2σ(*I*)): R1 = 0.0497, *wR*2 (all data) = 0.1166

**(*E*)-35:** $C_{28}H_{27}N_2O_4P$, *M* = 486.49, Monoclinic, Space group P2(1)/c, *a* = 21.0466(15), *b* = 11.4539(8), *c* = 9.9034(7) Å, *β* = 91.0190(10), *V* = 2387.0(3) Å$^3$, *Z* = 4, μ = 0.154 mm$^{-1}$, data/restraints/parameters: 4198/ 0/ 319, R indices (*I* > 2σ(*I*)): R1 = 0.0474, *wR*2 (all data) = 0.1156

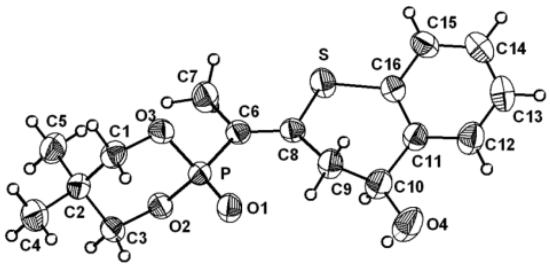



**Figure S1.** An ORTEP diagram of compound (*E*)-**16**. Selected bond lengths [Å] with esd's in parentheses. P-C(6) 1.772(3), C(6)-C(8) 1.346(4), C(8)-C(9) 1.500(3), C(9)-C(10) 1.532(4), S-C(8) 1.765(2), O(4)-C(10) 1.389(3). [Hydrogen bond parameters: O(4)-H(4)**…**O(1) 0.82 1.90 2.699(3) 164.3 °; symmetry code: 1-x, 1-y, 1-z].

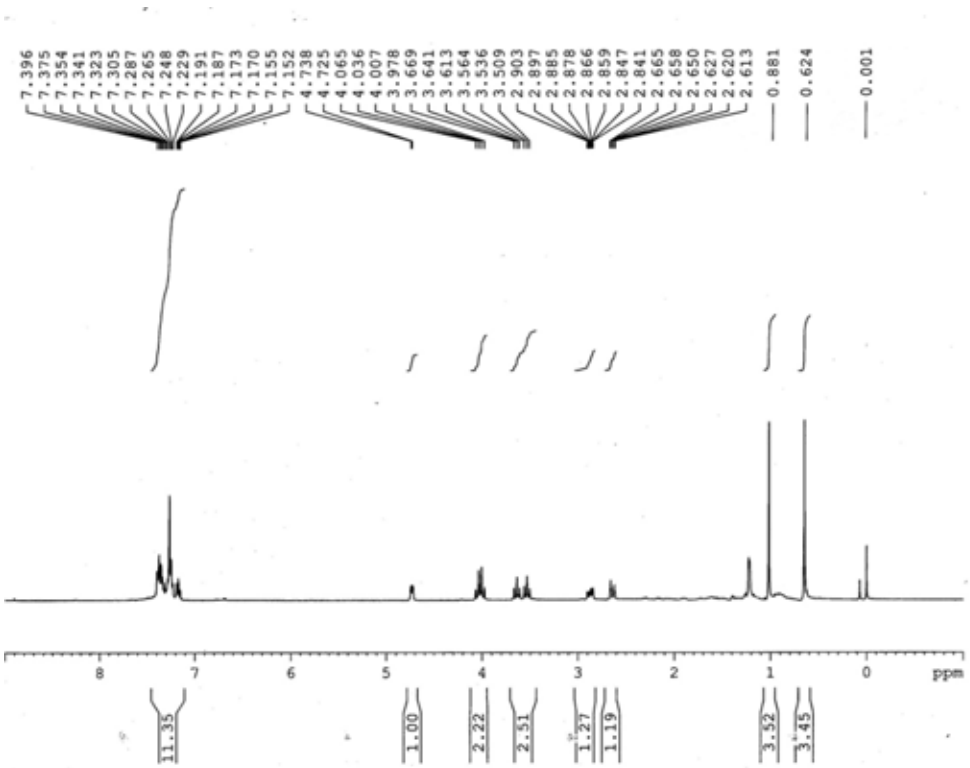



**Figure S2a**. $^{1}$H NMR spectrum of compound (***Z***)-**8**

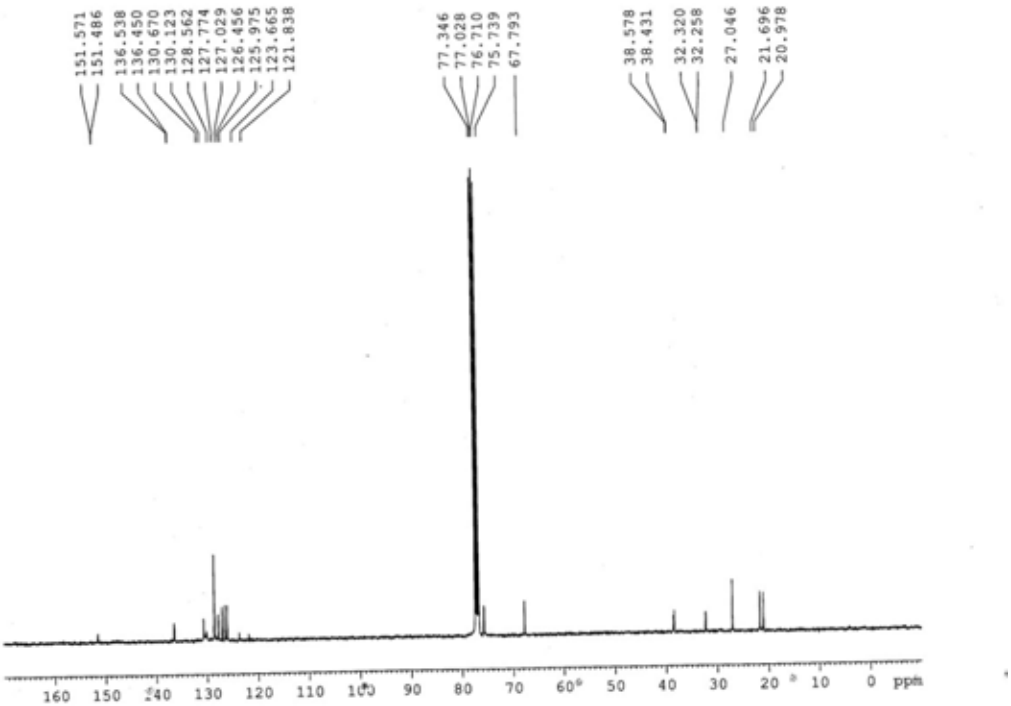



**Figure S2b**. $^{13}$C NMR spectrum of compound (***Z***)-**8**

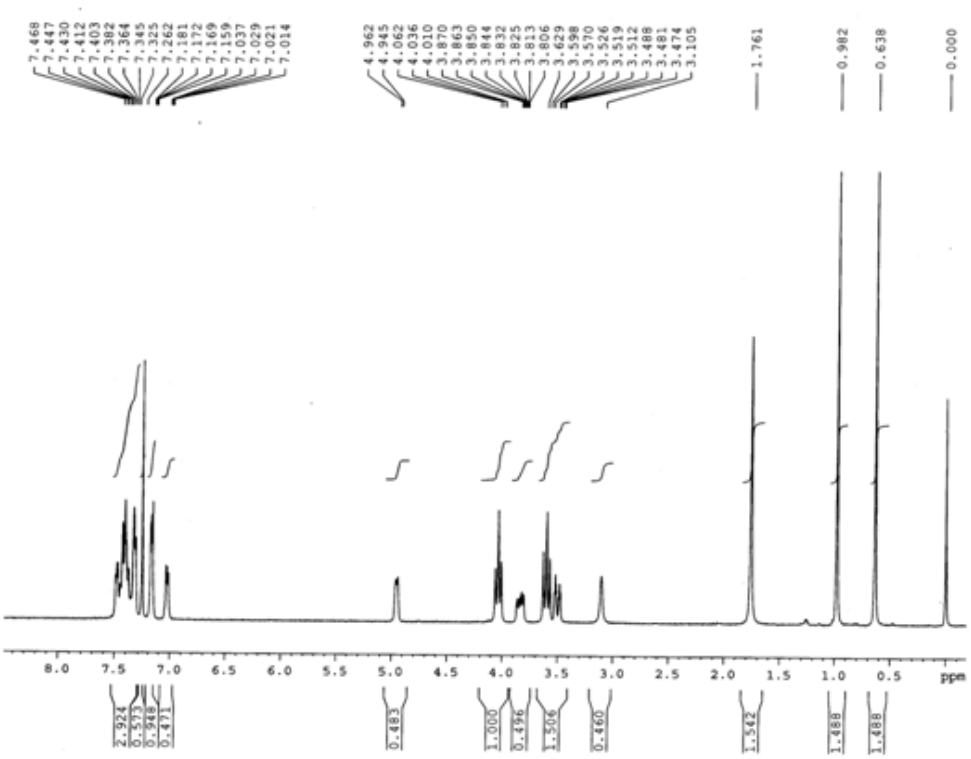



**Figure S3a**. $^{1}$H NMR spectrum of compound (***E***)-**8**

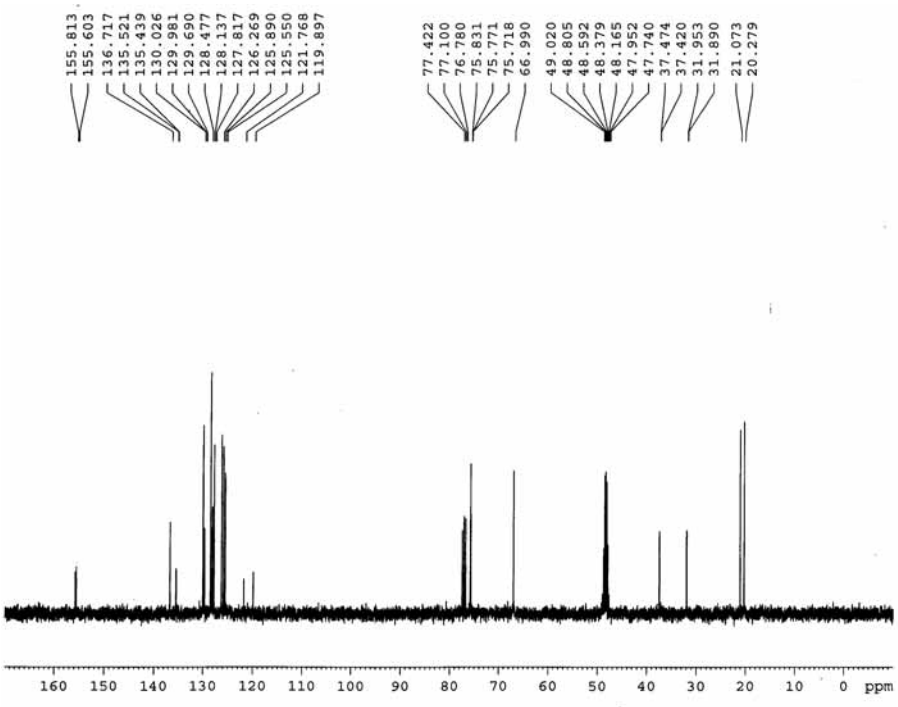



**Figure S3b**. $^{13}$C NMR spectrum of compound (***E***)-**8**

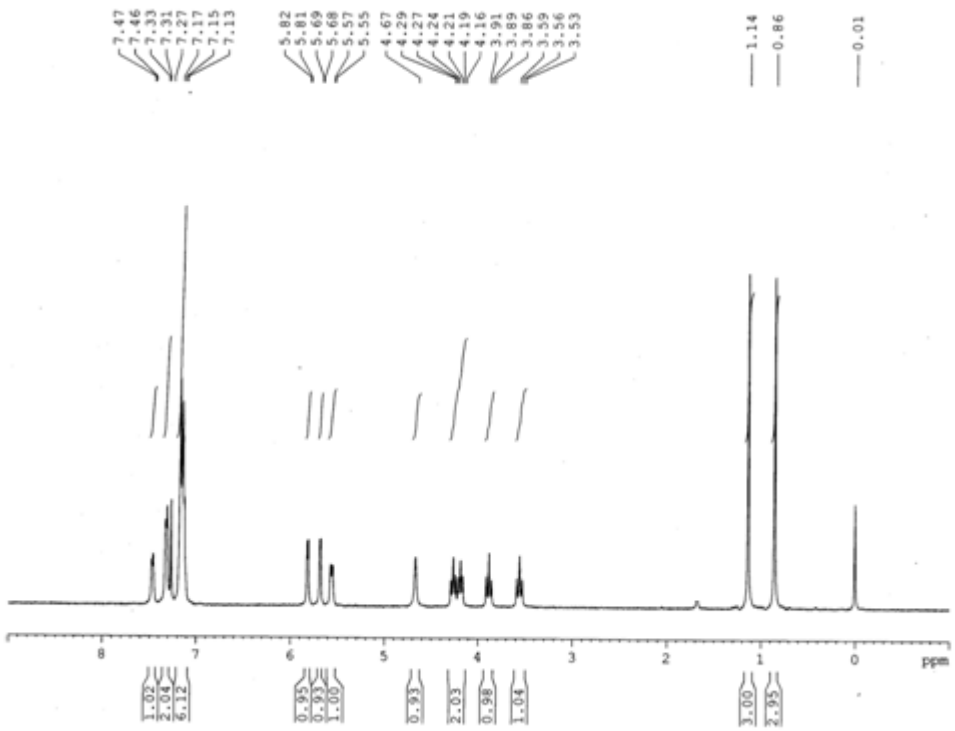



**Figure S4a**. $^{1}$H NMR spectrum of compound **9**

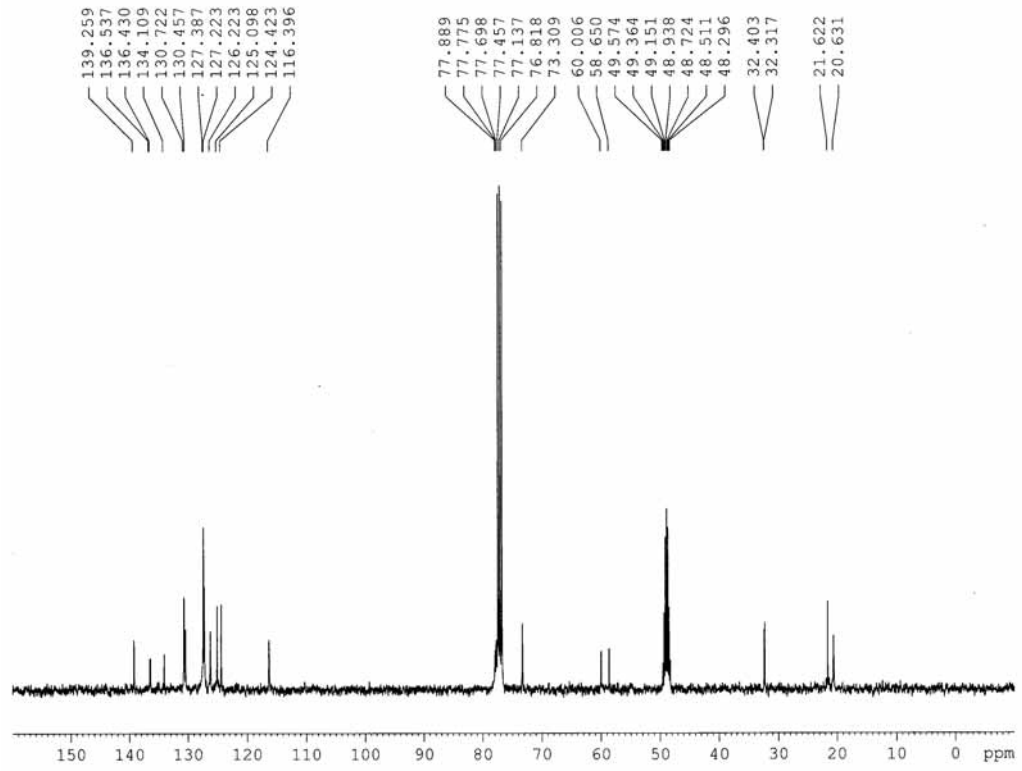



**Figure S4b**. $^{13}$C NMR spectrum of compound **9**

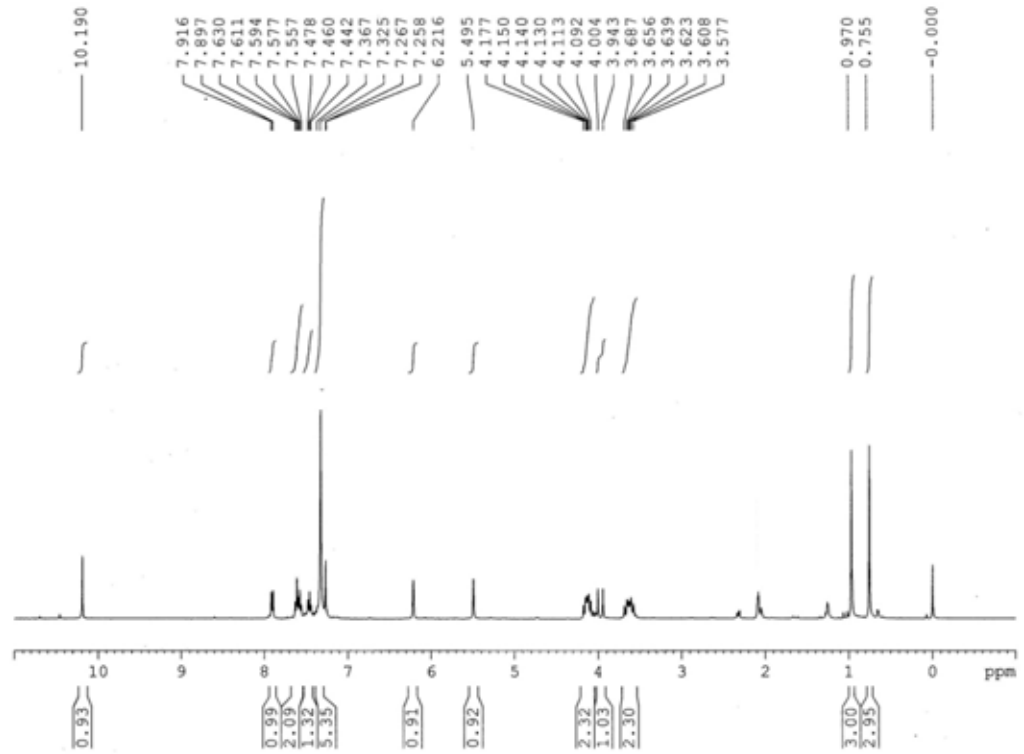



**Figure S5a**. $^{1}$H NMR spectrum of compound **10**

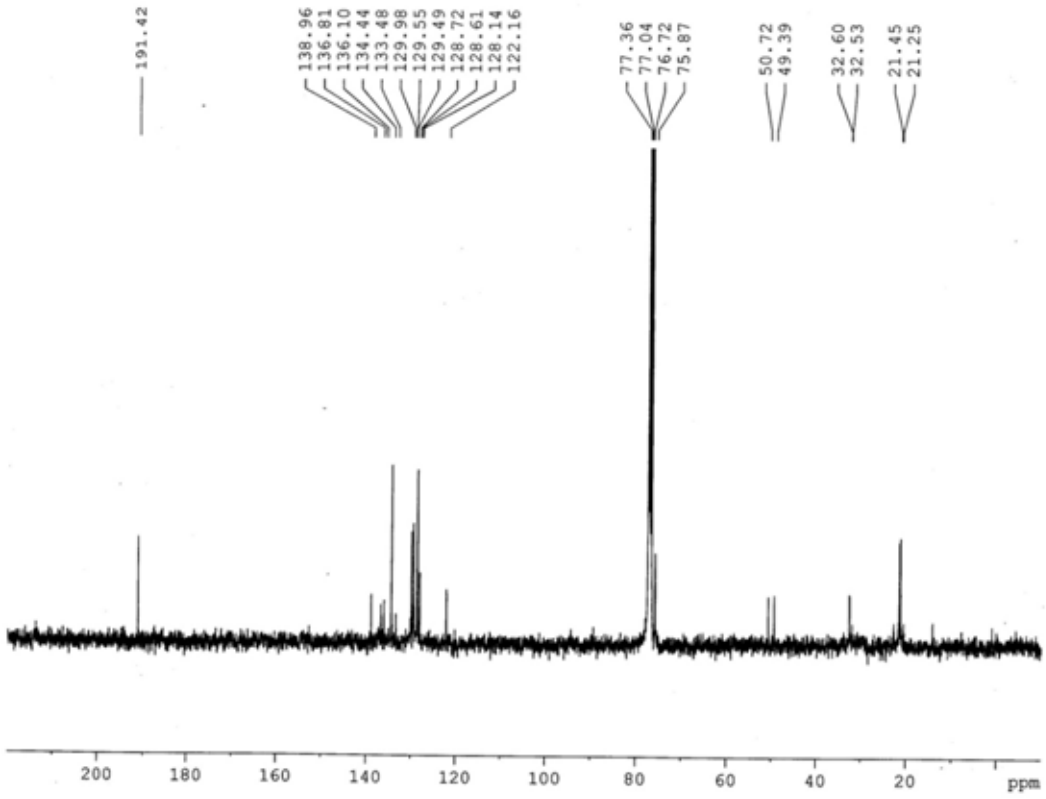



**Figure S5b**. $^{13}$C NMR spectrum of compound **10**

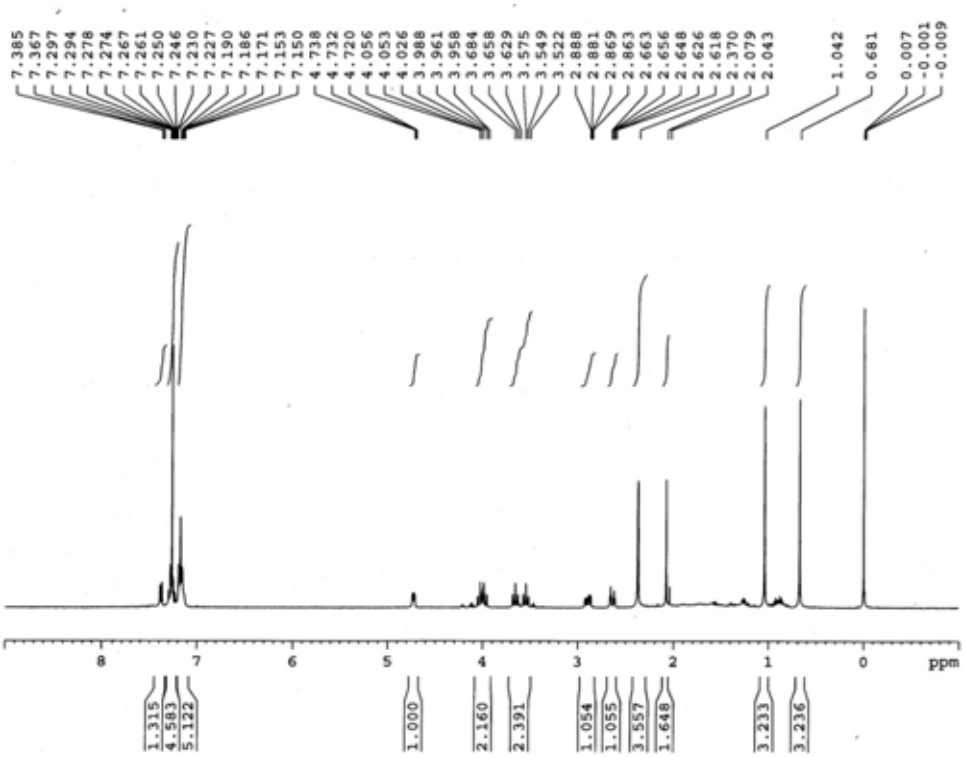



**Figure S6a**. $^{1}$H NMR spectrum of compound **(*Z*)-11**

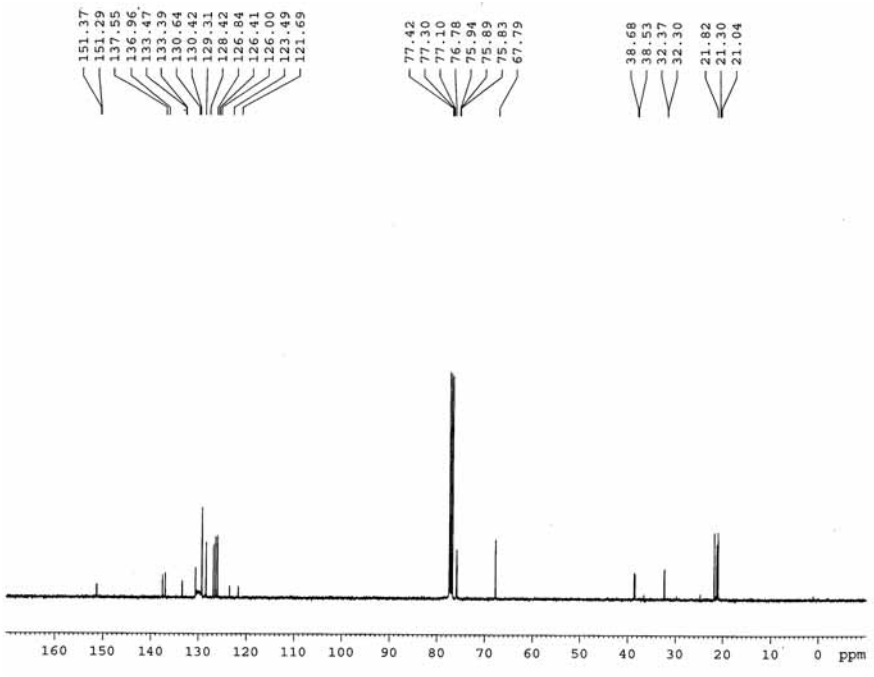



**Figure S6b**. $^{13}$C NMR spectrum of compound **(*Z*)-11**

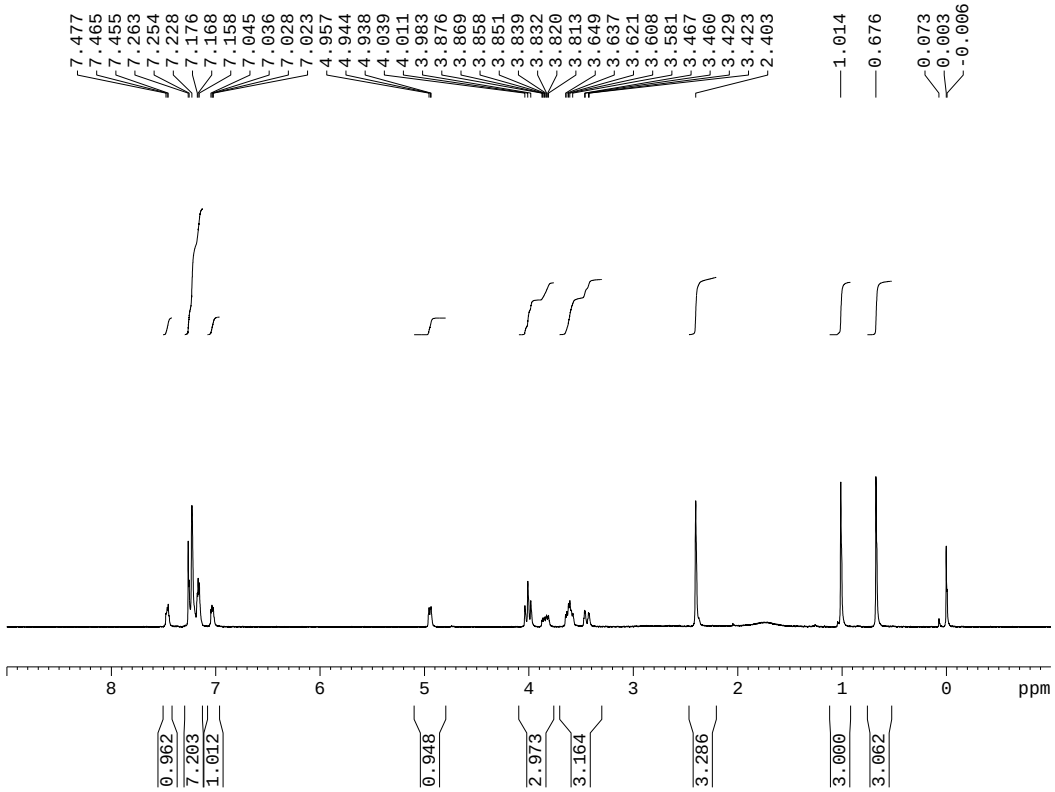



**Figure S7a**. $^{1}$H NMR spectrum of compound **(*E*)-11**

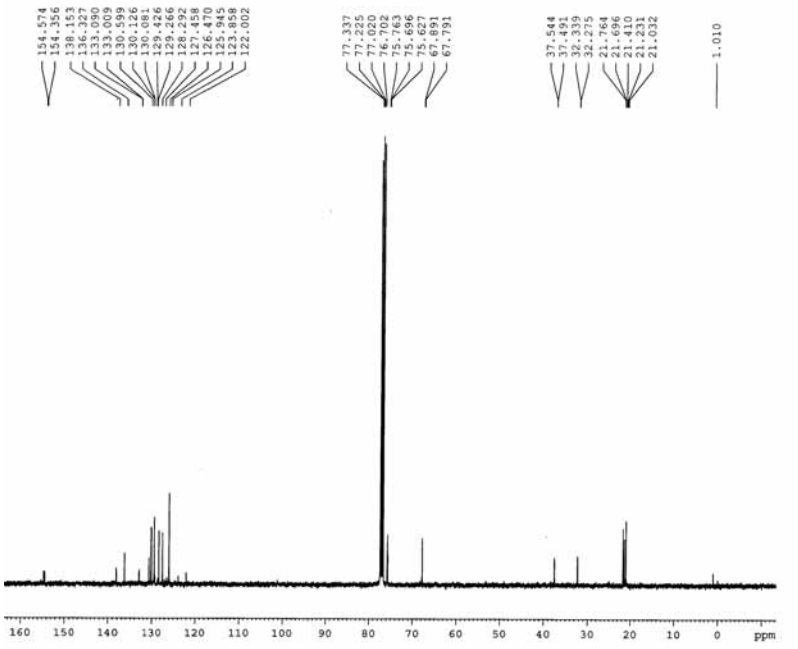



**Figure S7b**. $^{13}$C NMR spectrum of compound **(*E*)-11**

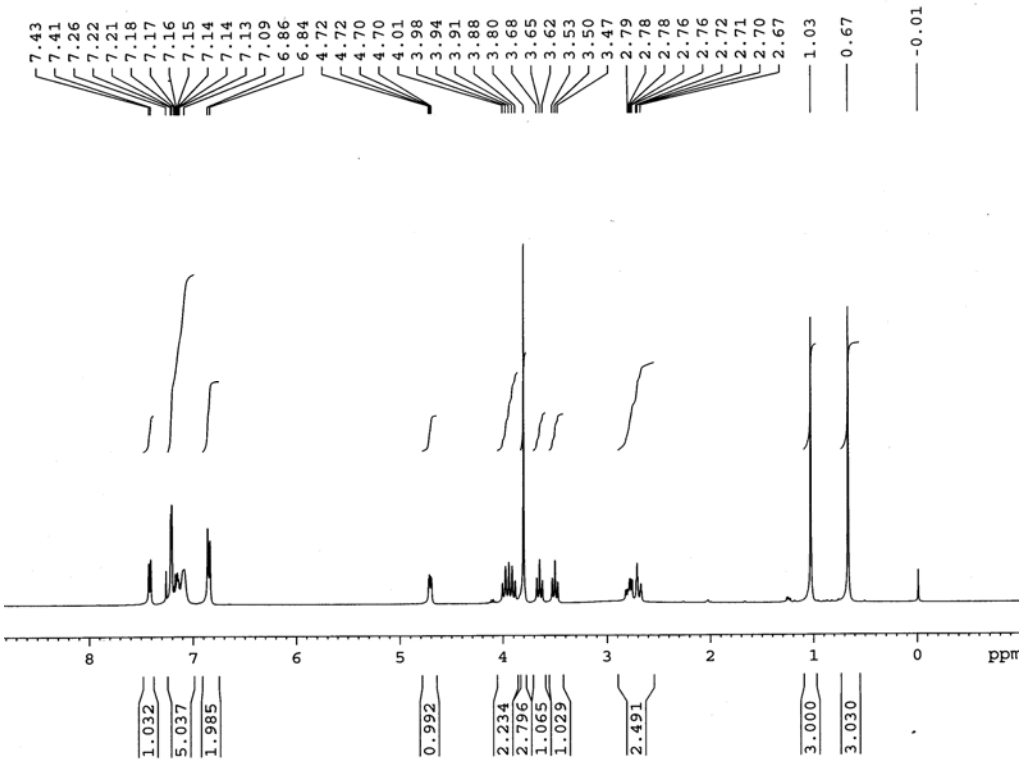



**Figure S8a**. $^{1}$H NMR spectrum of compound **(*Z*)-12**

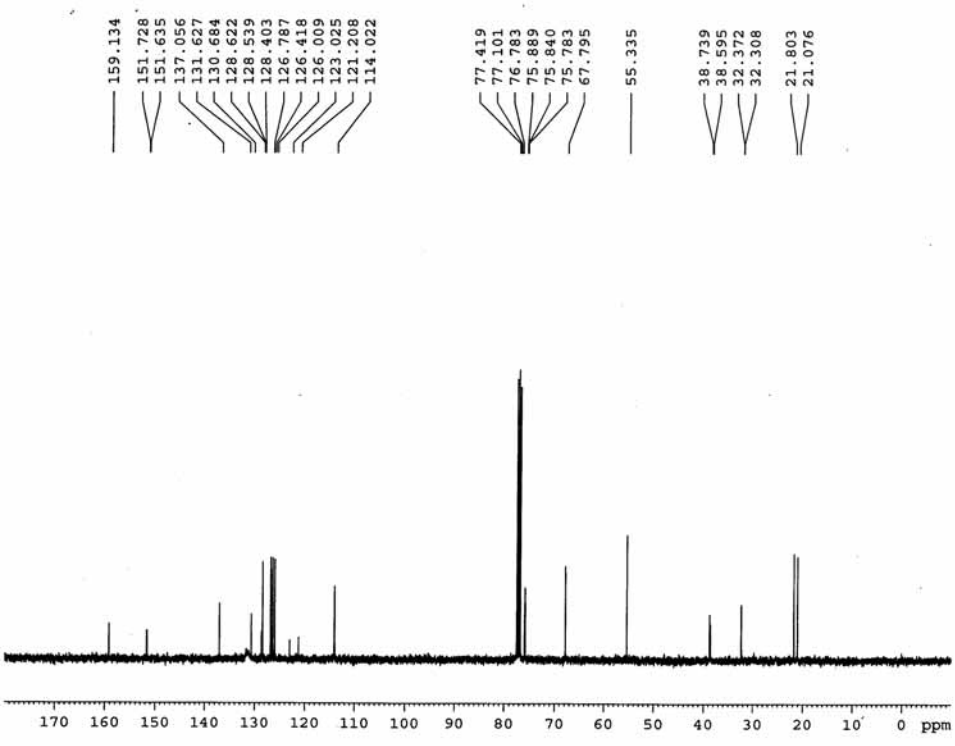



**Figure S8b**. $^{13}$C NMR spectrum of compound **(*Z*)-12**

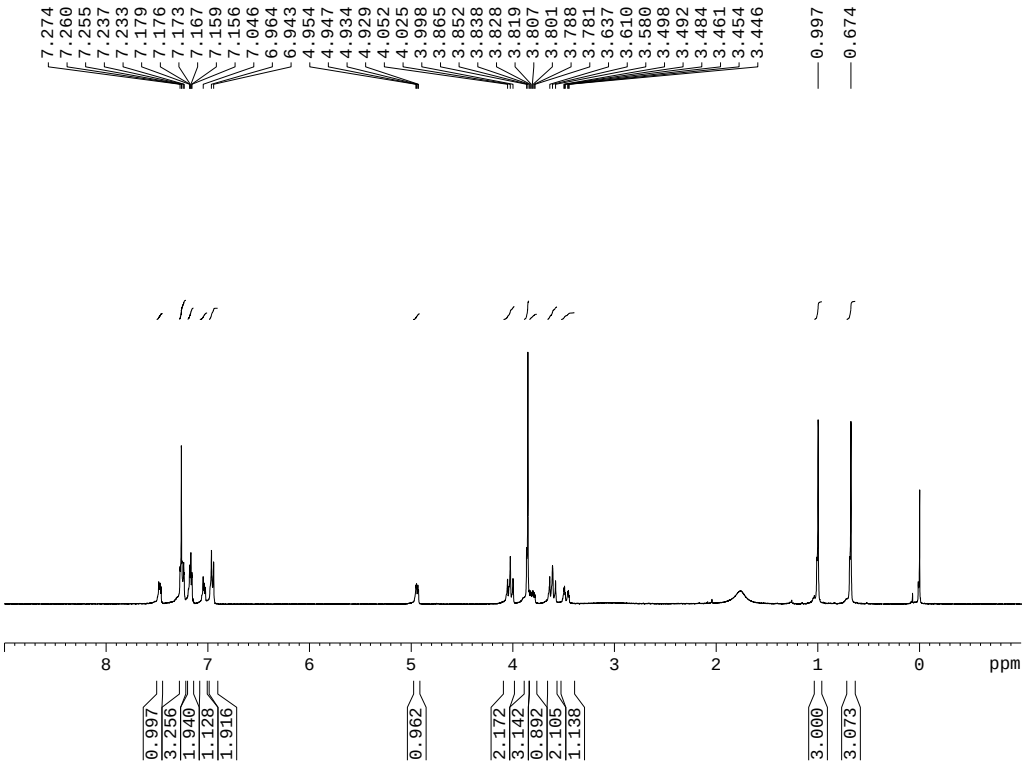



**Figure S9a**. $^{1}$H NMR spectrum of compound **(*E*)-12**

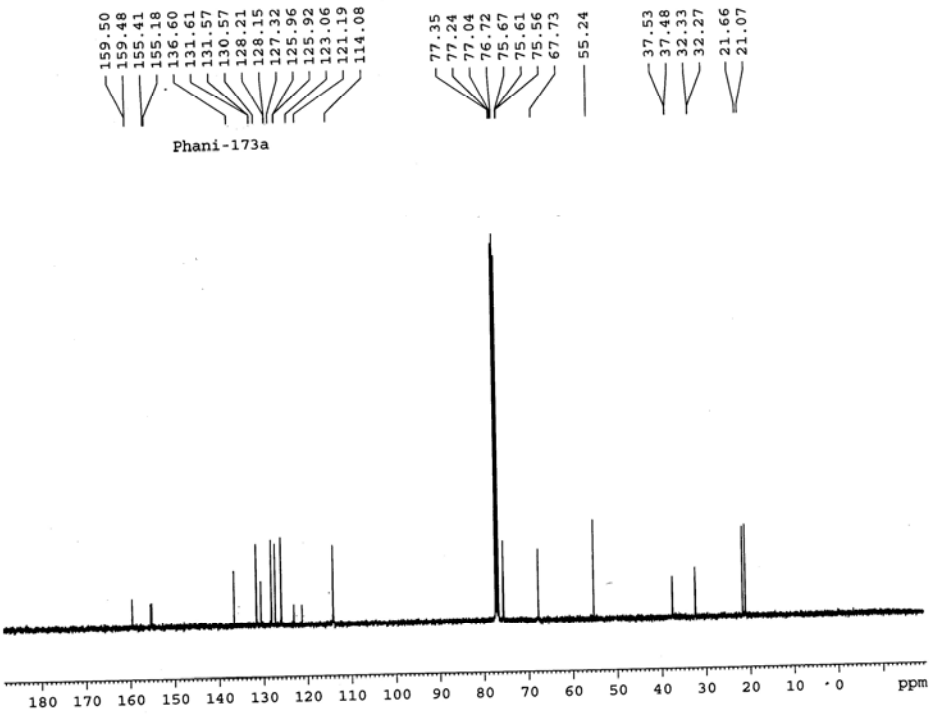



**Figure S9b**. $^{13}$C NMR spectrum of compound **(*E*)-**12

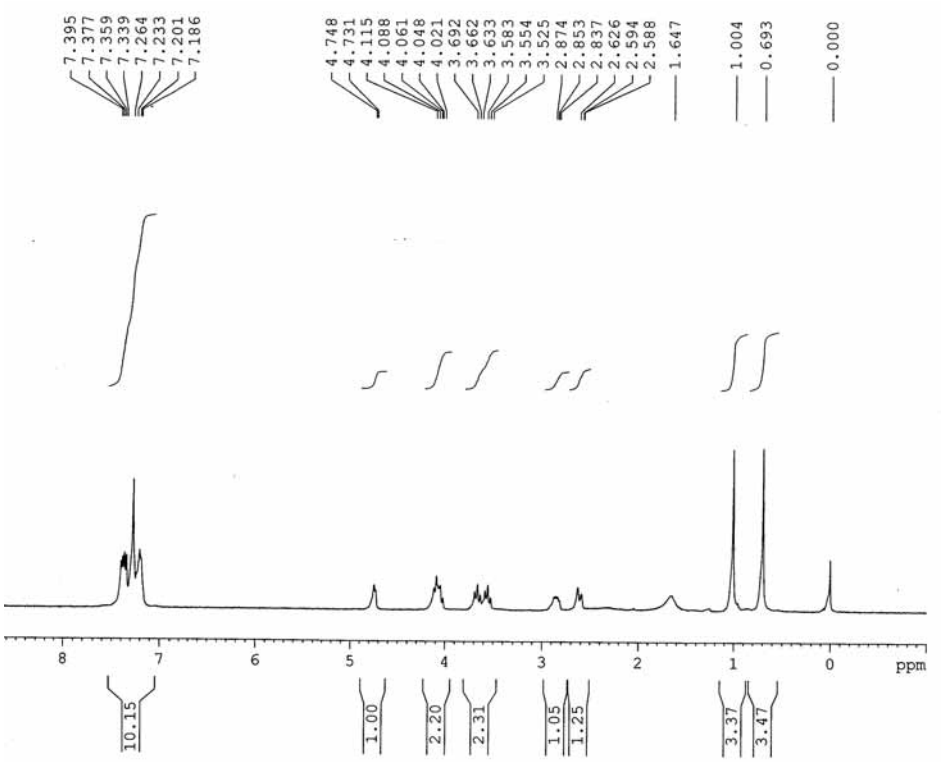



**Figure S10a**. $^{1}$H NMR spectrum of compound **(*Z*)-13**

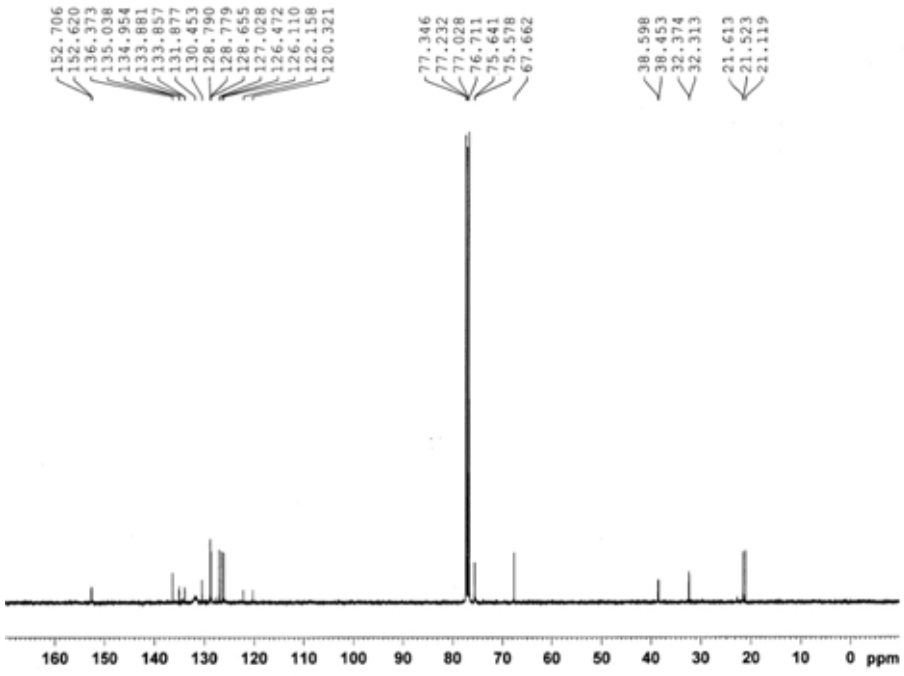



**Figure S10b**. $^{13}$C NMR spectrum of compound **(*Z*)-13**

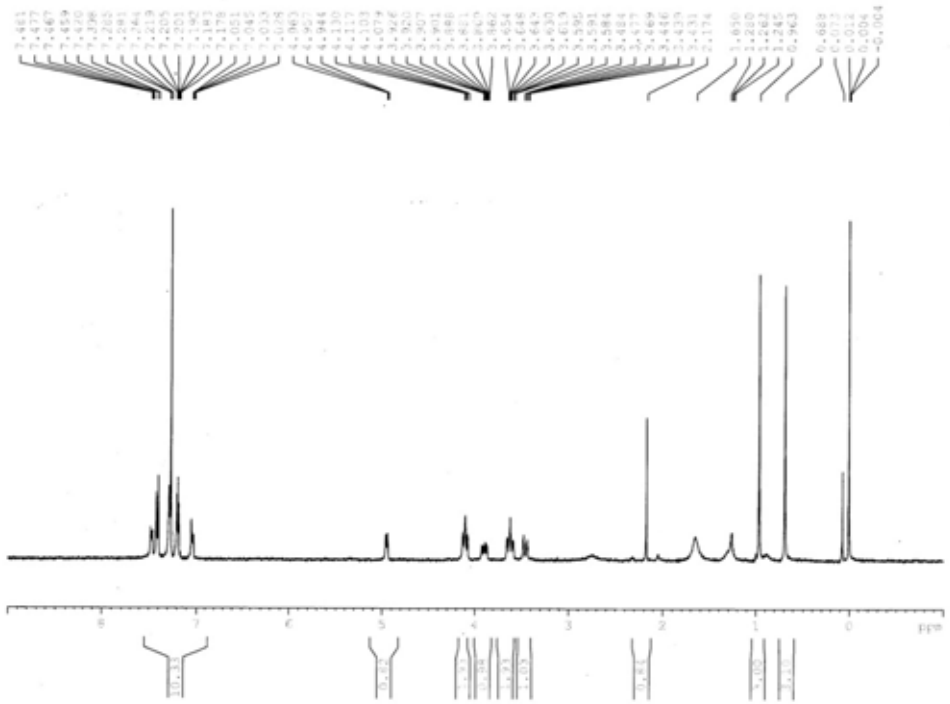


**Figure S11a**. $^{1}$H NMR spectrum of compound **(*E*)-13**

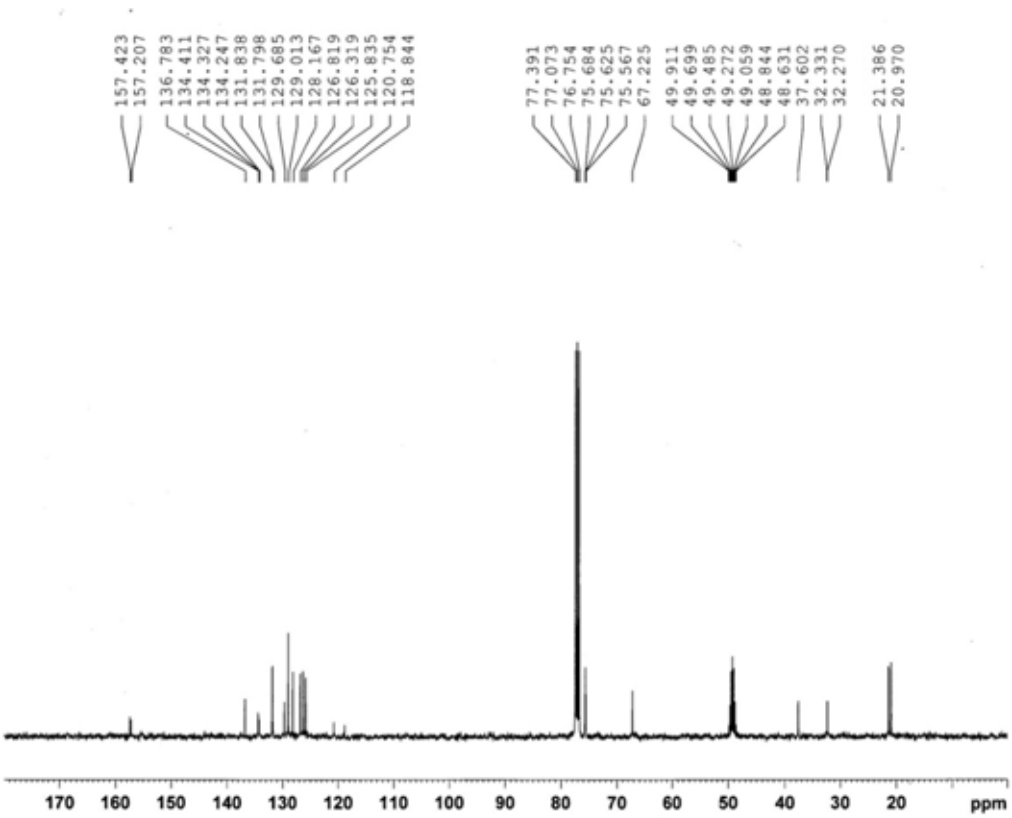



**Figure S11b**. $^{13}$C NMR spectrum of compound **(*E*)-13**

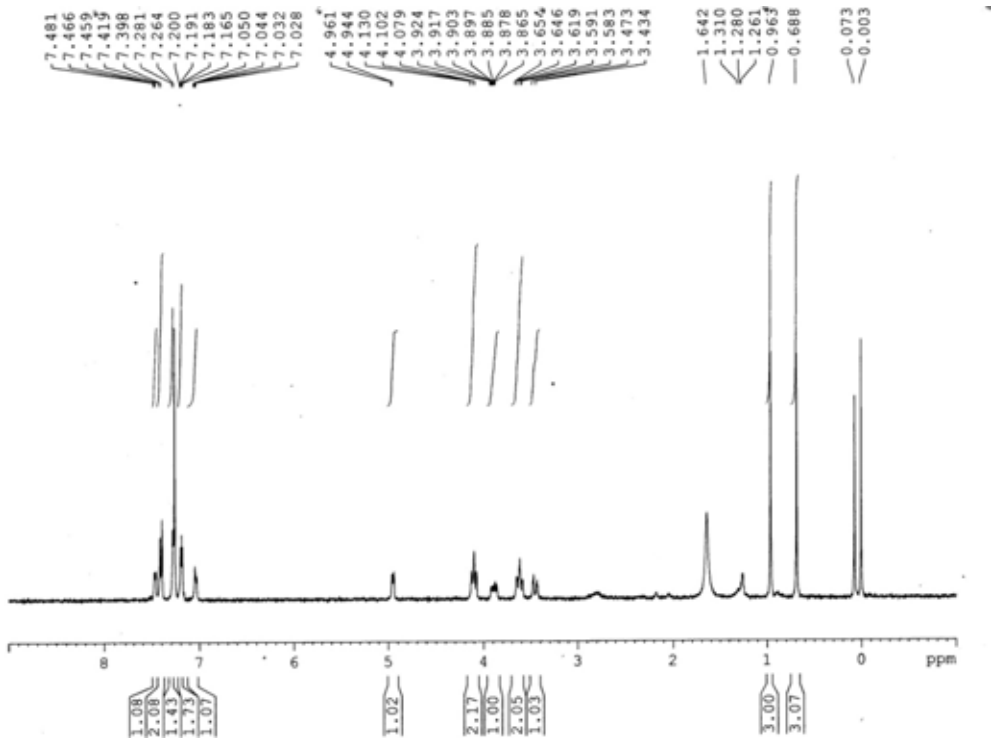



**Figure S12a**. $^{1}$H NMR spectrum of compound **(*E*)-14**

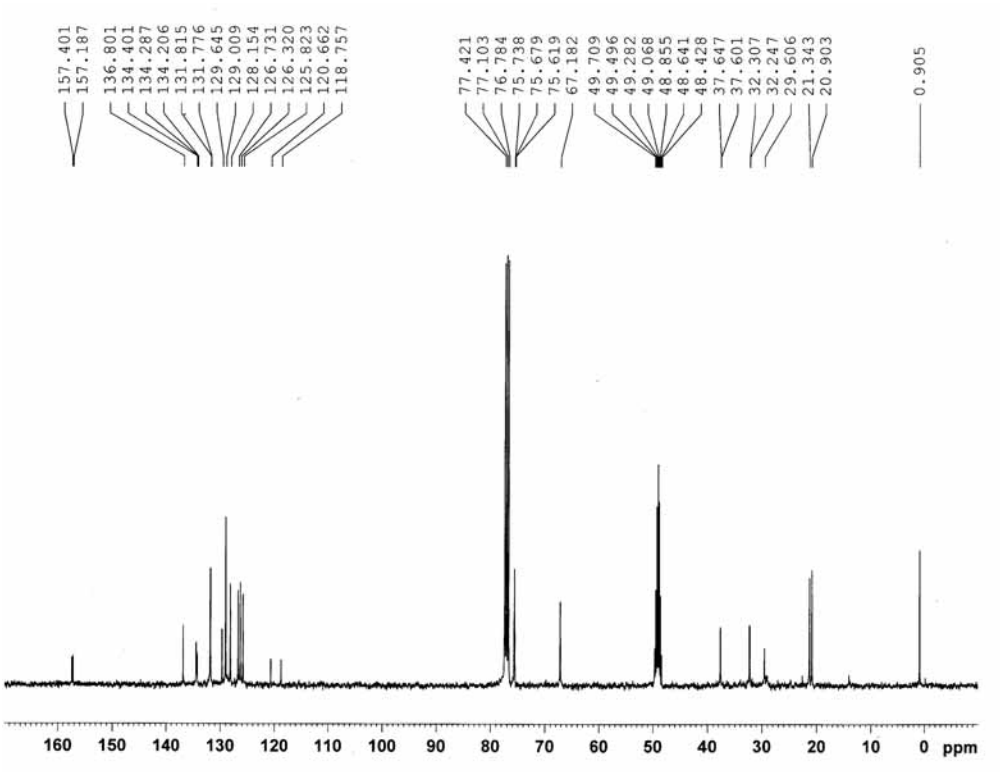



**Figure S12b**. $^{13}$C NMR spectrum of compound **(*E*)-14**

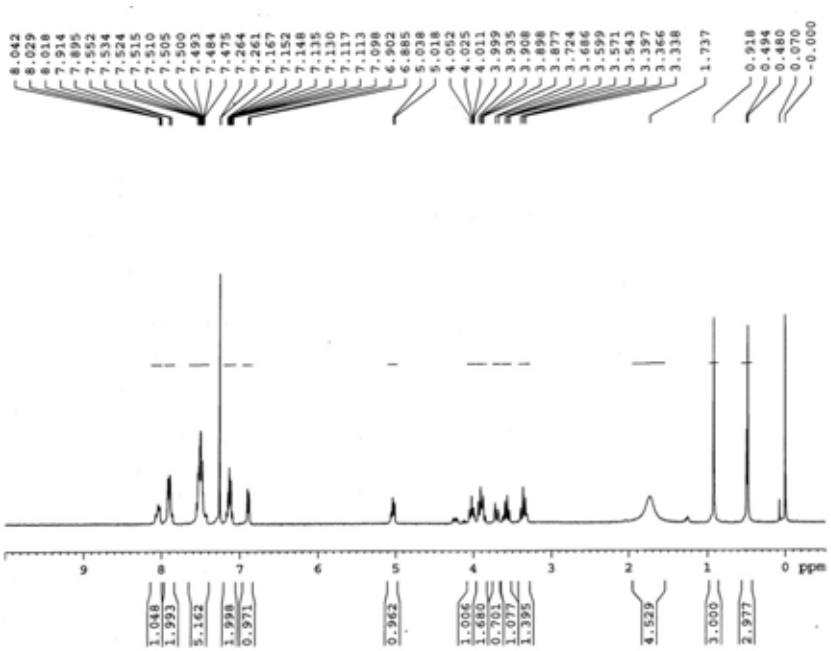



**Figure S13a**. $^{1}$H NMR spectrum of compound **15**

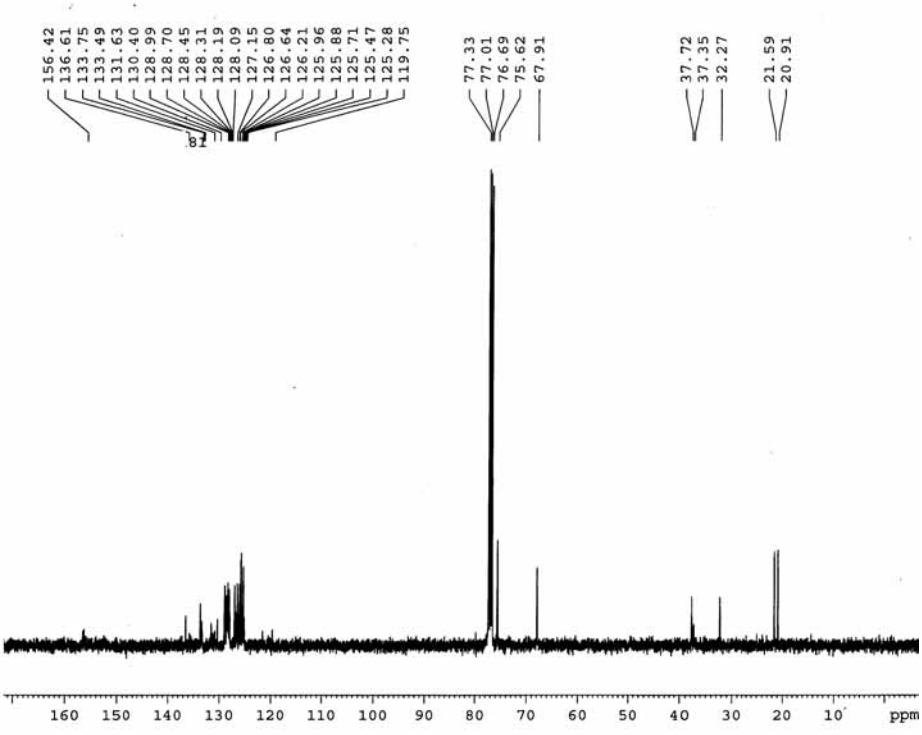



**Figure S13b**. $^{13}$C NMR spectrum of compound **15**

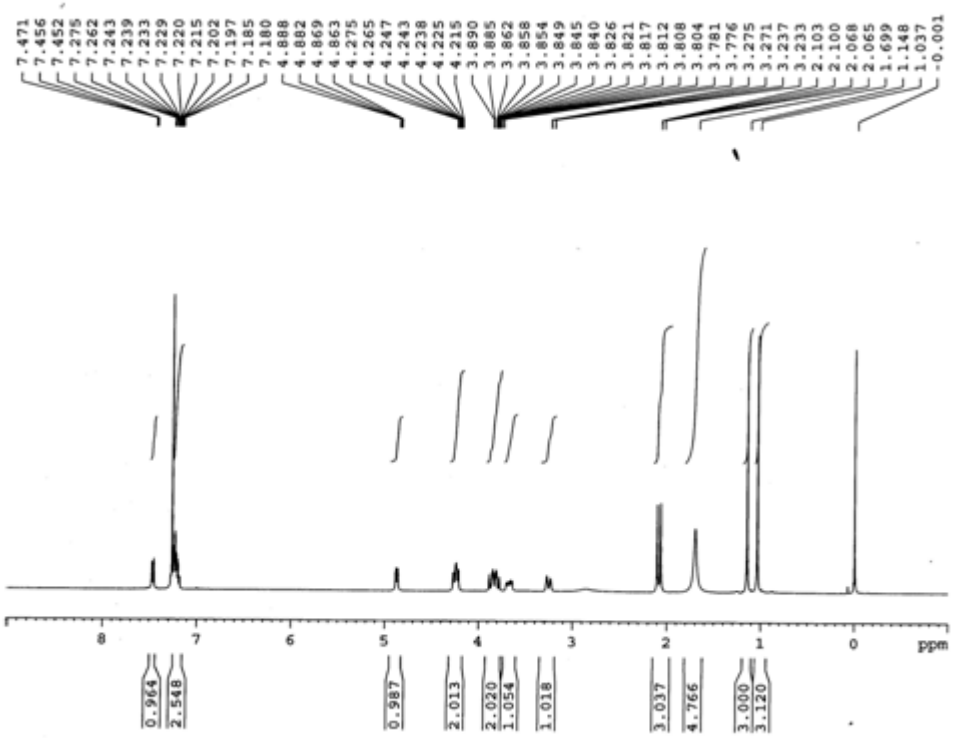



**Figure S14a**. $^{1}$H NMR spectrum of compound **(*E*)-16**

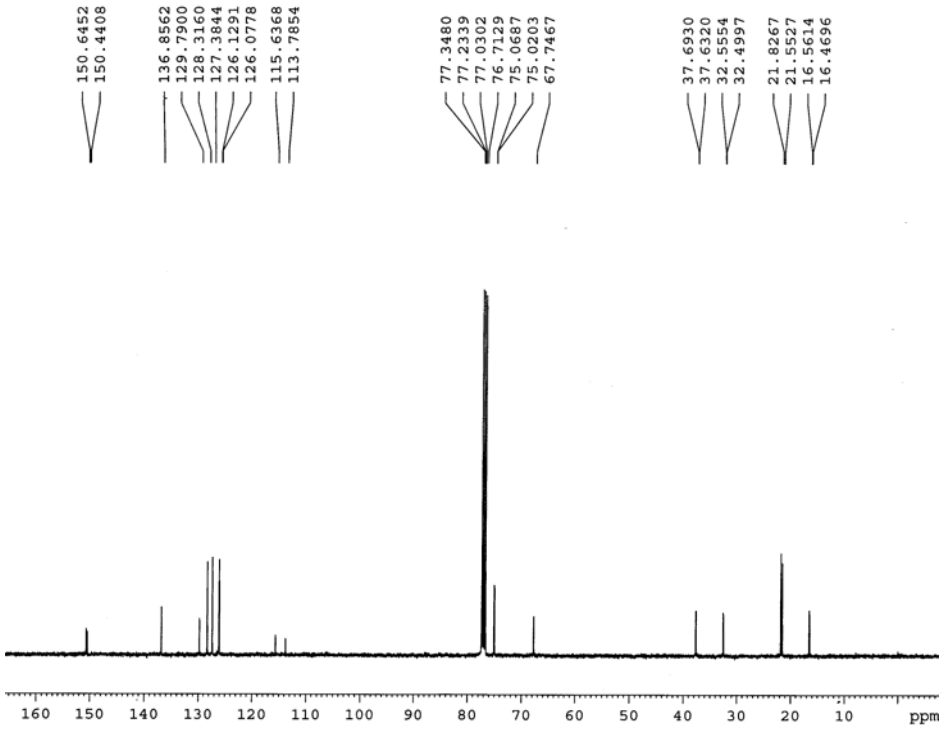



**Figure S14b**. $^{13}$C NMR spectrum of compound **(*E*)-16**

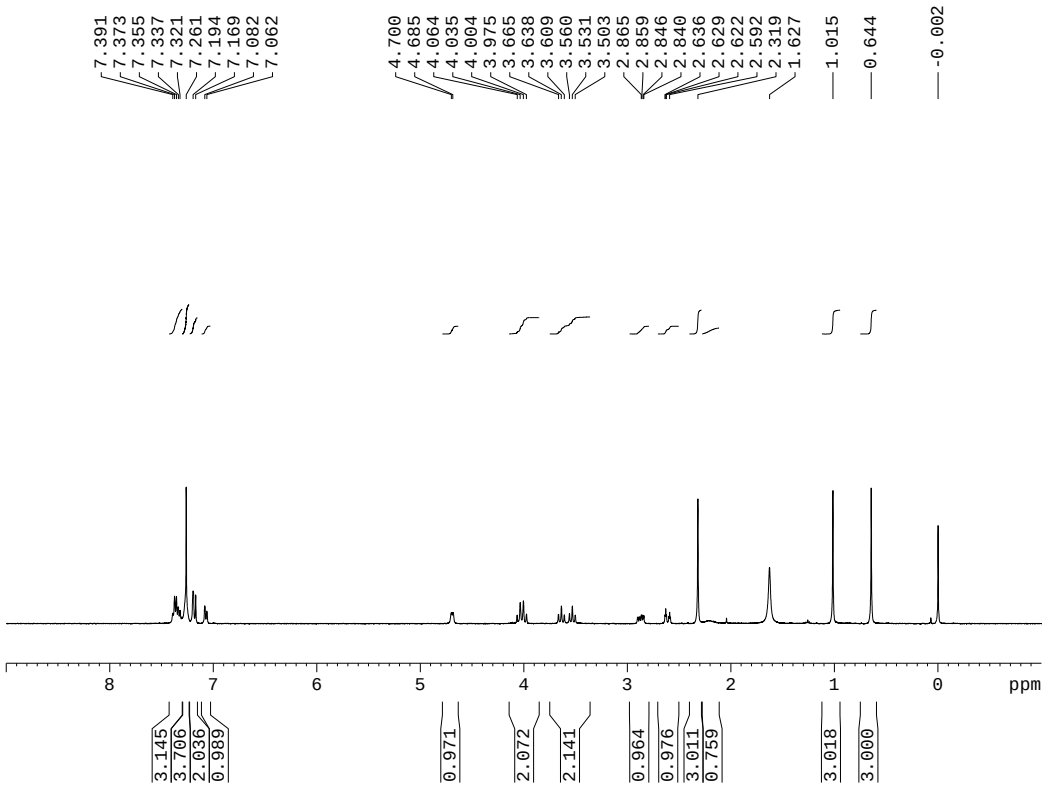



**Figure S15a**. $^{1}$H NMR spectrum of compound **(*Z*)-17**

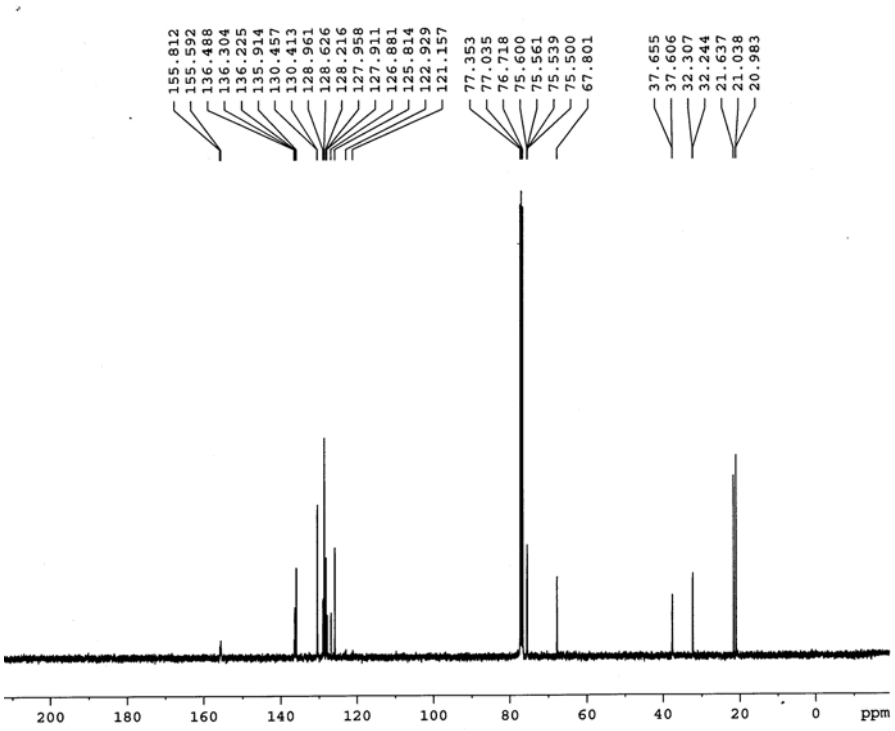



**Figure S15b**. $^{13}$C NMR spectrum of compound **(*Z*)-17**

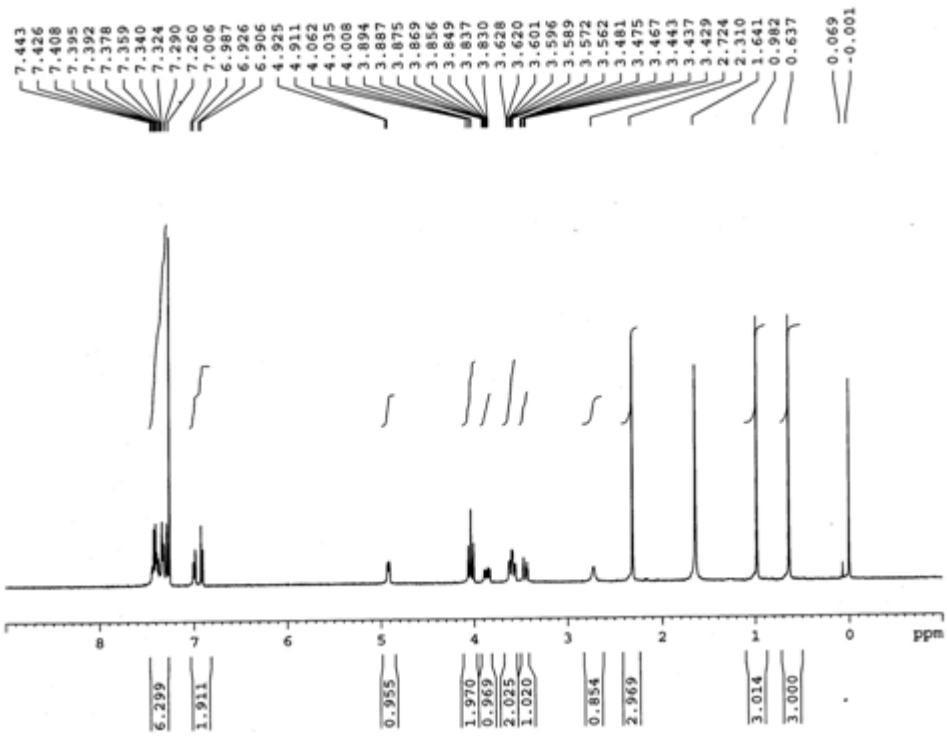



**Figure S16a**. $^{1}$H NMR spectrum of compound **(*E*)-17**

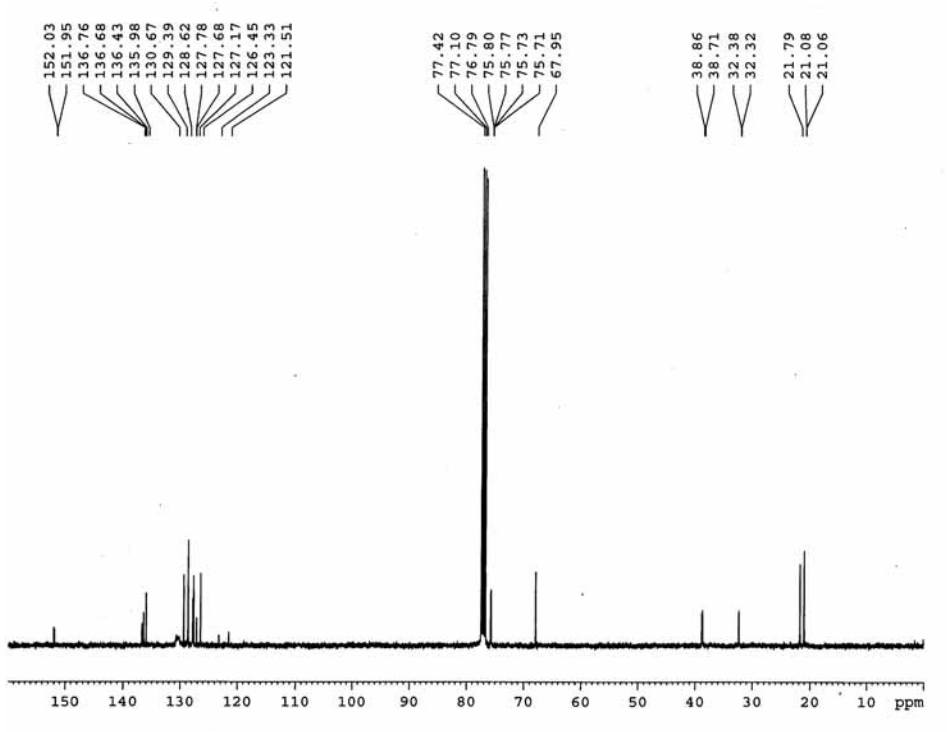



**Figure S16b**. $^{13}$C NMR spectrum of compound **(*E*)-17**

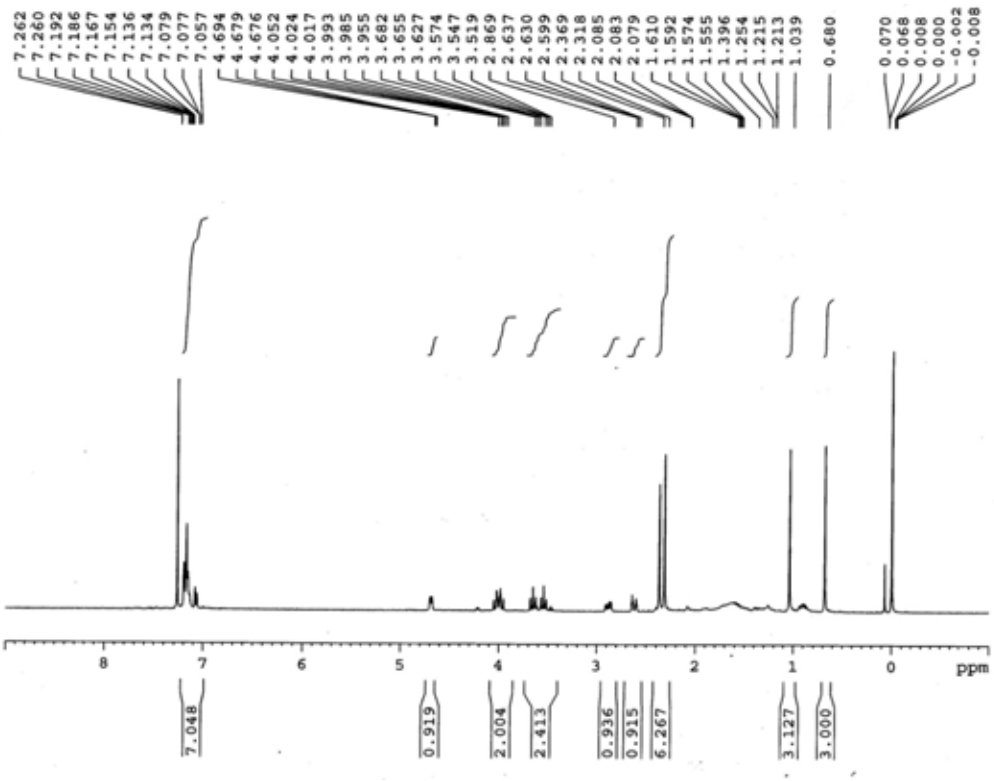



**Figure S17a**. $^{1}$H NMR spectrum of compound **(*Z*)-18**

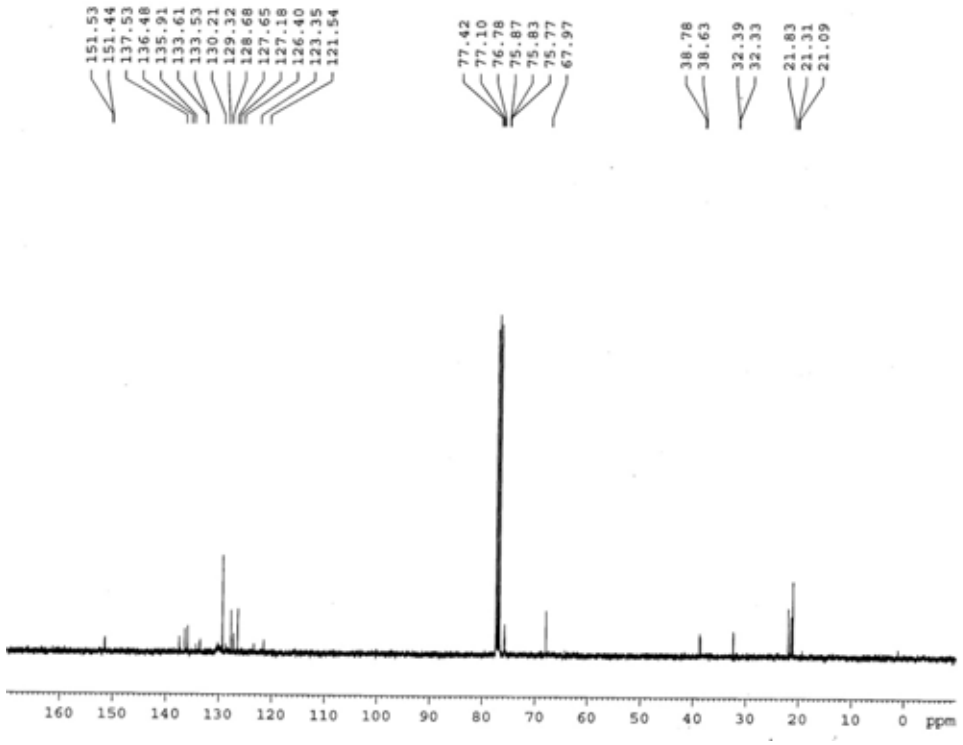



**Figure S17b**. $^{13}$C NMR spectrum of compound **(*Z*)-18**

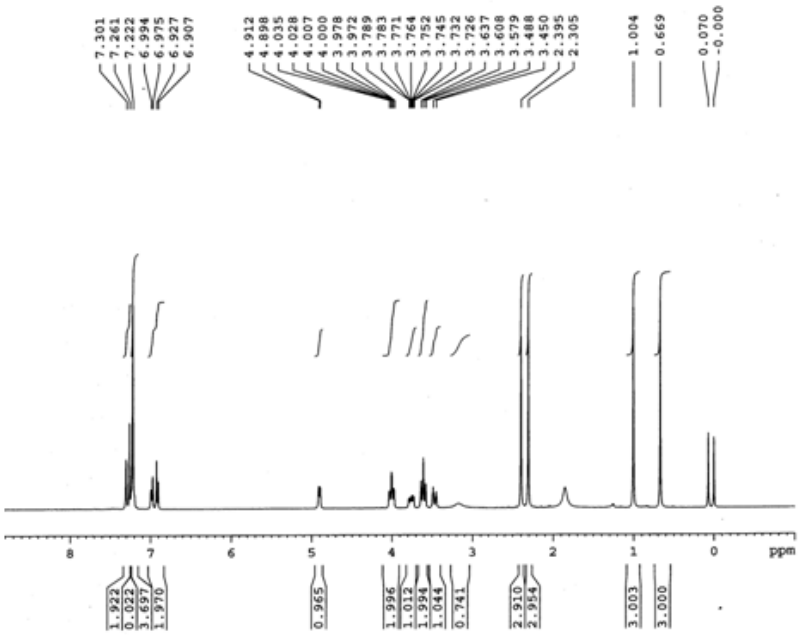



**Figure S18a**. $^{1}$H NMR spectrum of compound **(*E*)-18**

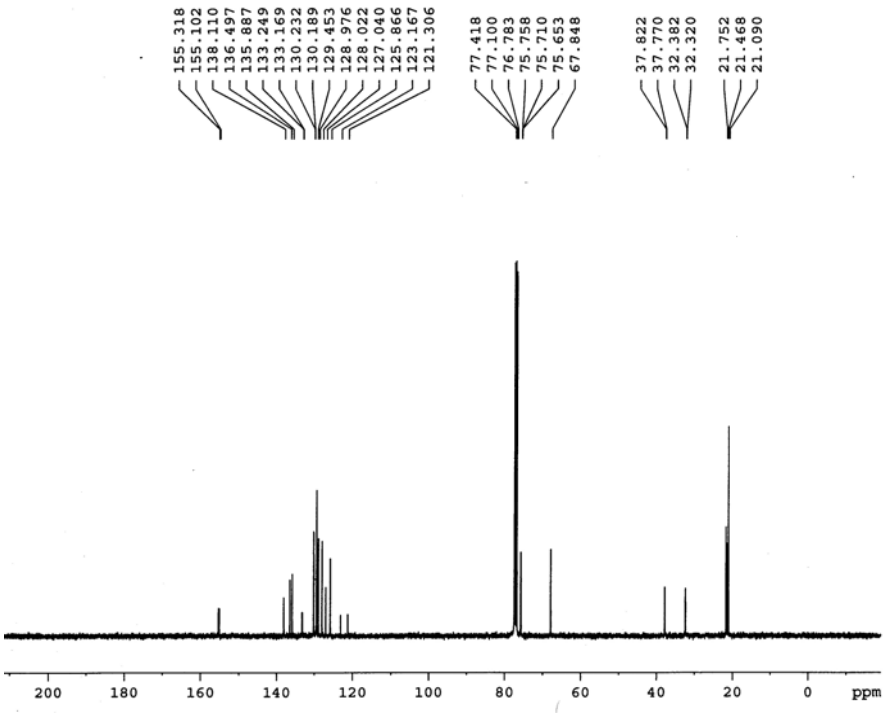



**Figure S18b**. $^{13}$C NMR spectrum of compound **(*E*)-18**

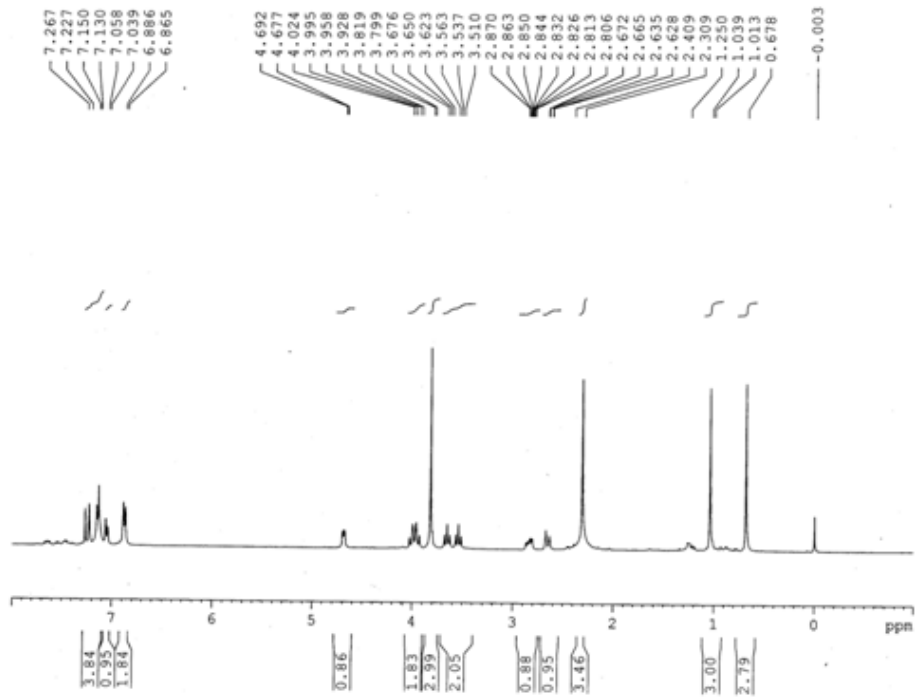



**Figure S19a**. $^{1}$H NMR spectrum of compound **(*Z*)-19**

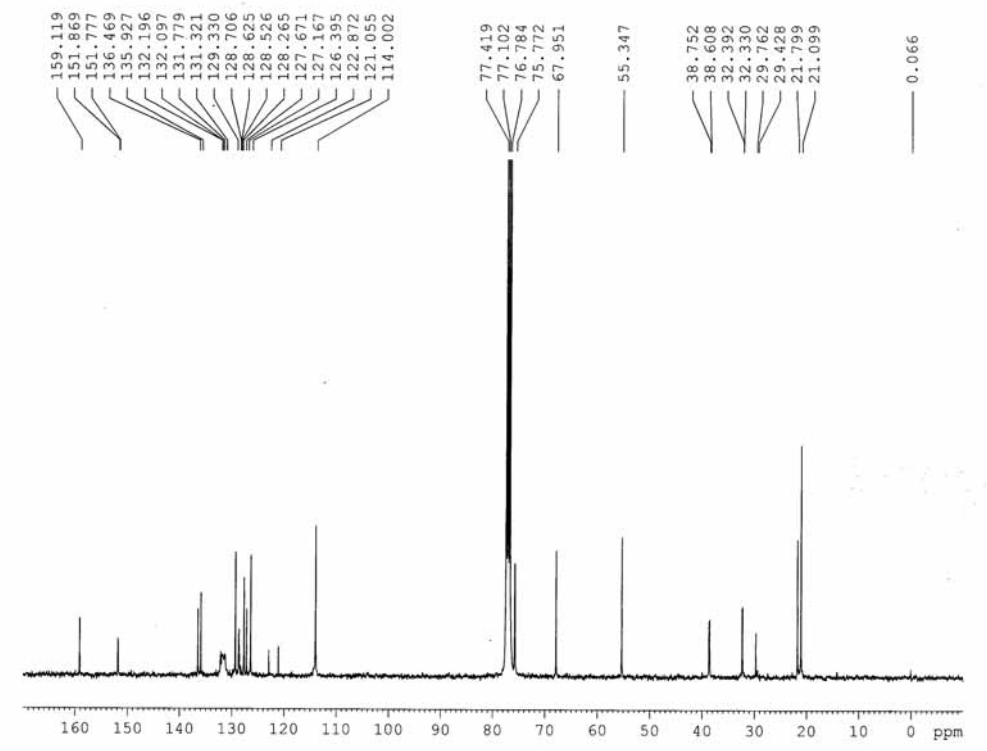



**Figure S19b**. $^{13}$C NMR spectrum of compound **(*Z*)-19**

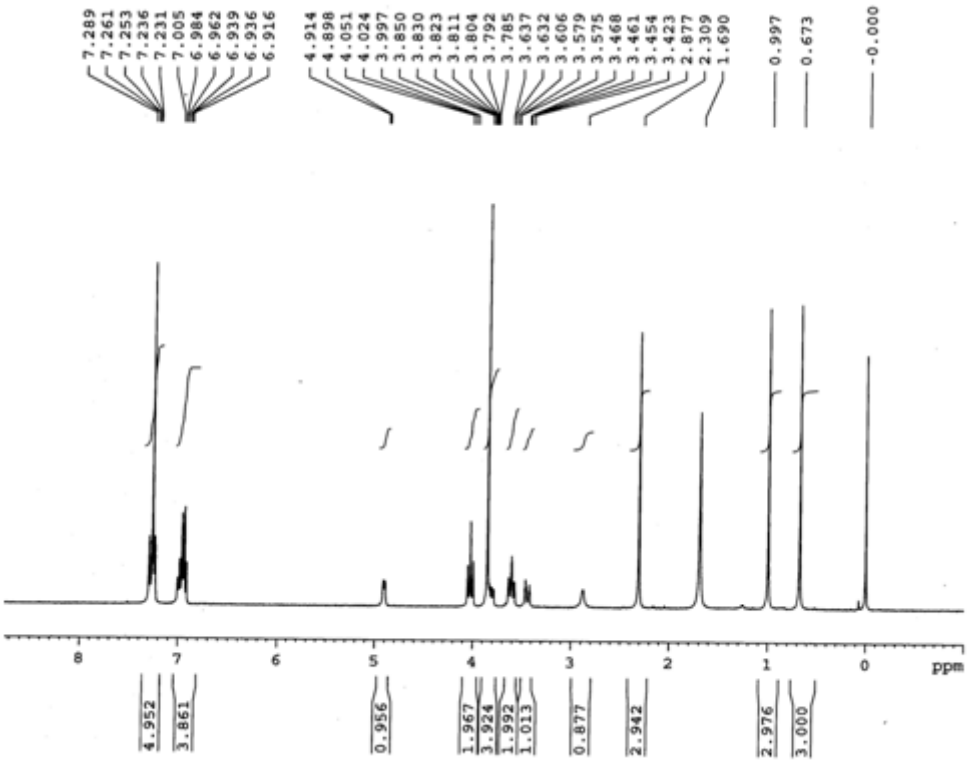



**Figure S20a**. $^{1}$H NMR spectrum of compound **(*E*)-19**

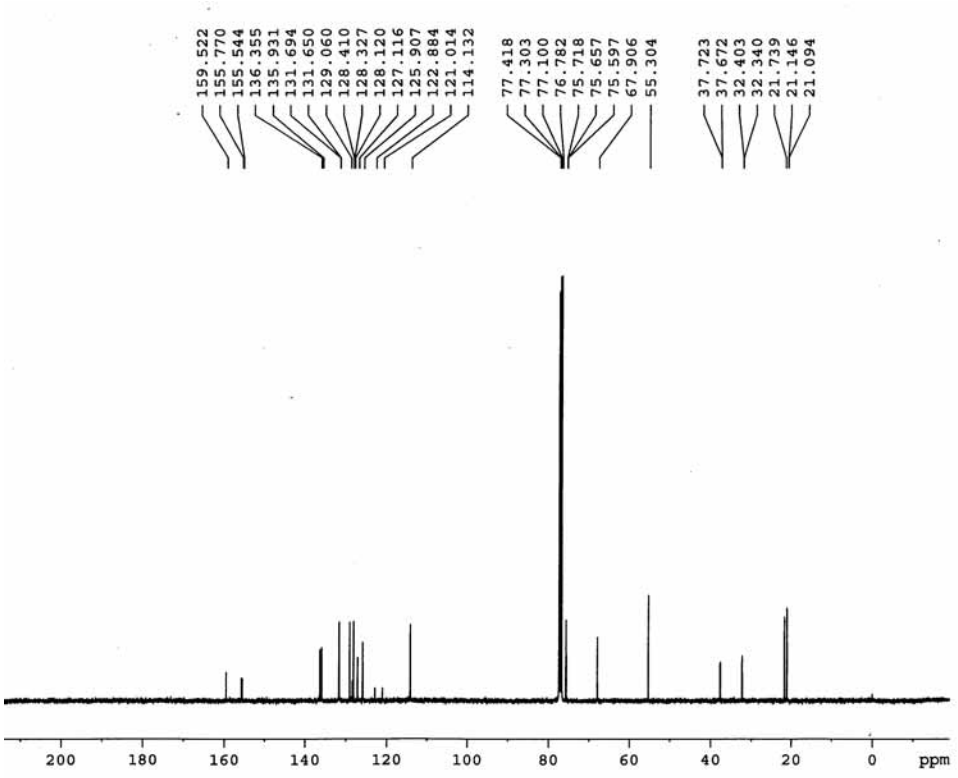



**Figure S20b**. $^{13}$C NMR spectrum of compound **(*E*)-19**

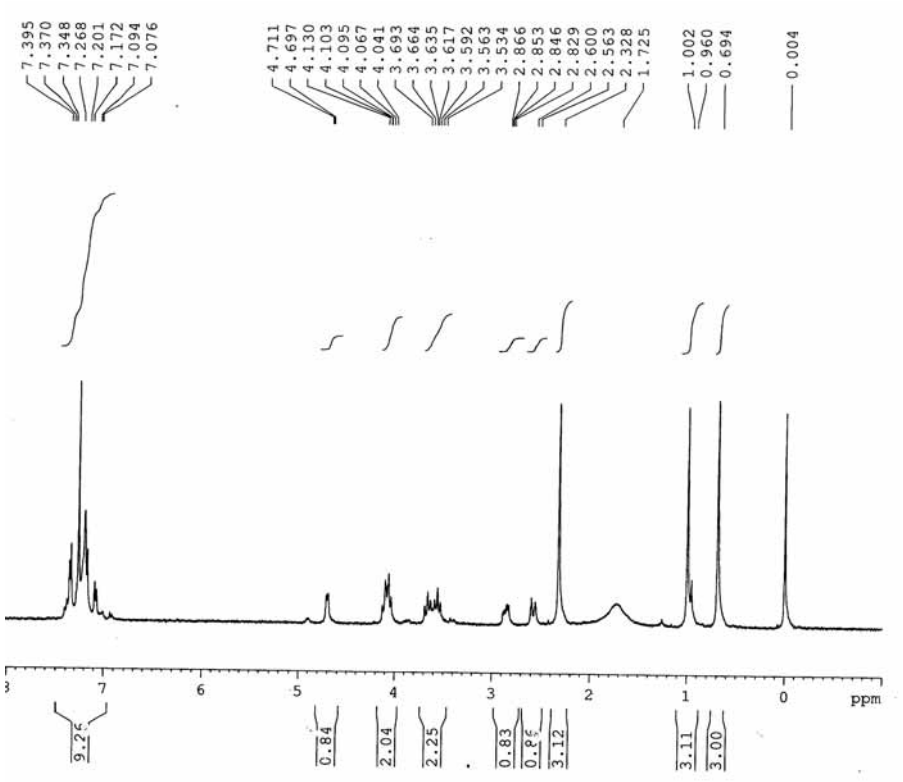



**Figure S21a**. $^{1}$H NMR spectrum of compound **(*Z*)-20**

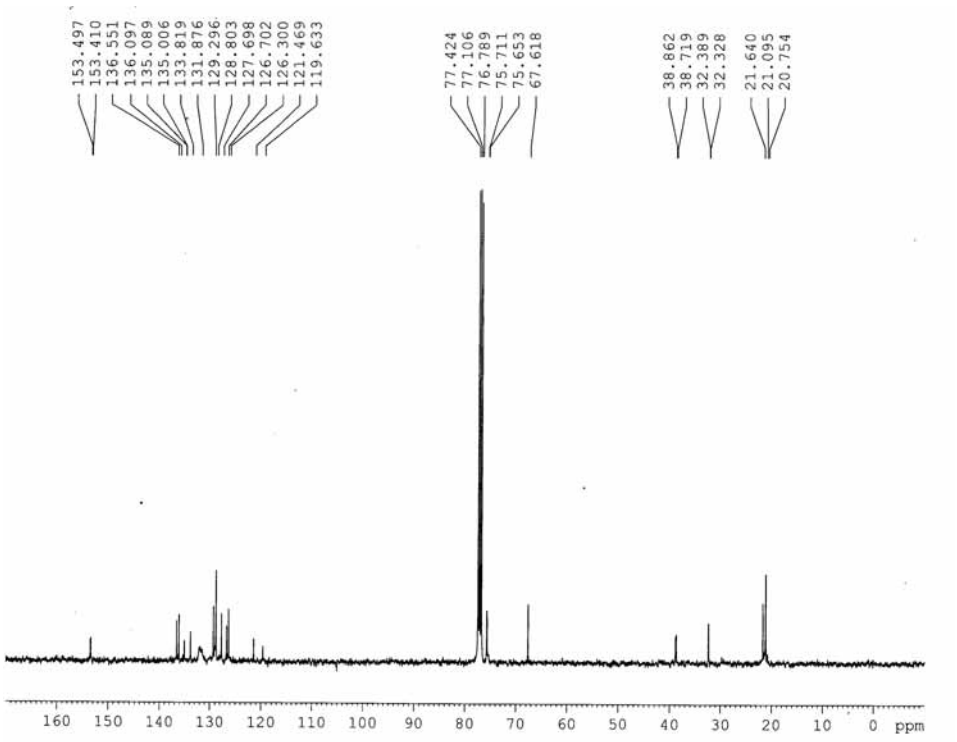



**Figure S21b**. $^{13}$C NMR spectrum of compound **(*Z*)-20**

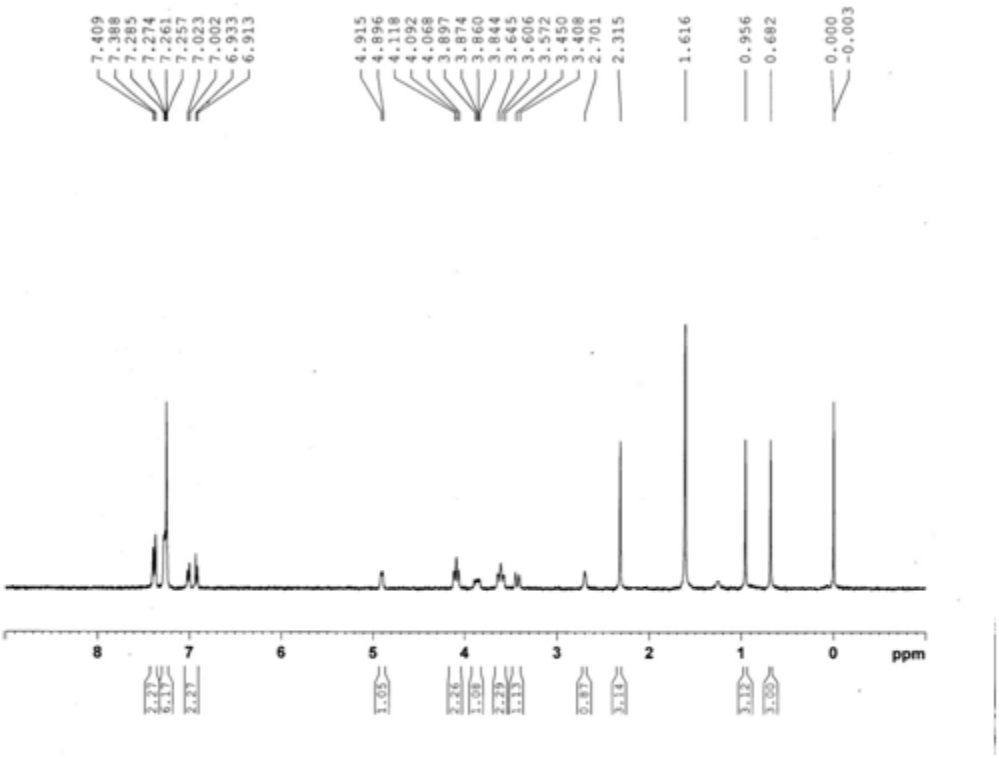



**Figure S22a**. $^{1}$H NMR spectrum of compound **(*E*)-20**

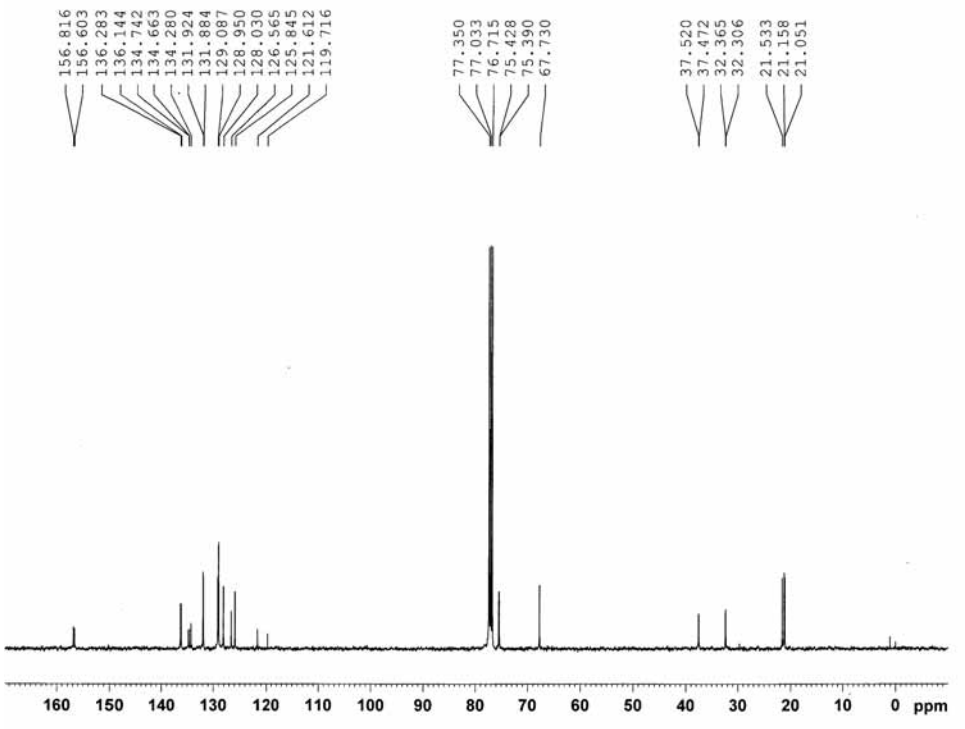



**Figure S22b**. $^{13}$C NMR spectrum of compound **(*E*)-20**

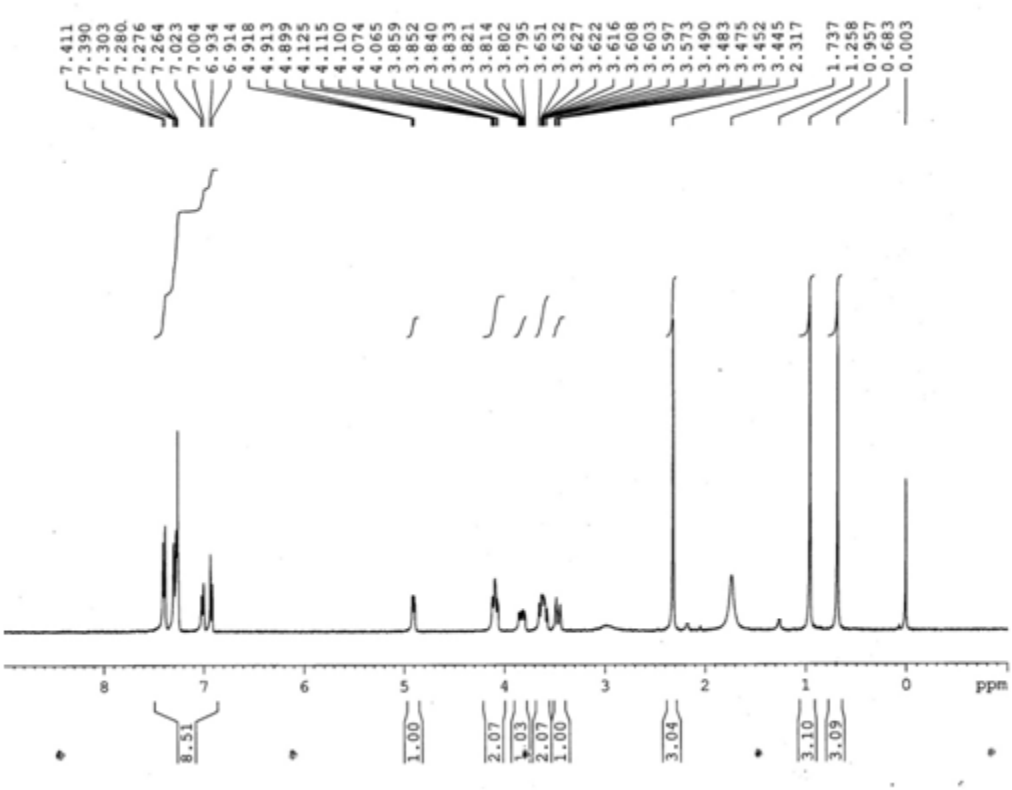



**Figure S23a**. [1]H NMR spectrum of compound **(*E*)-21**

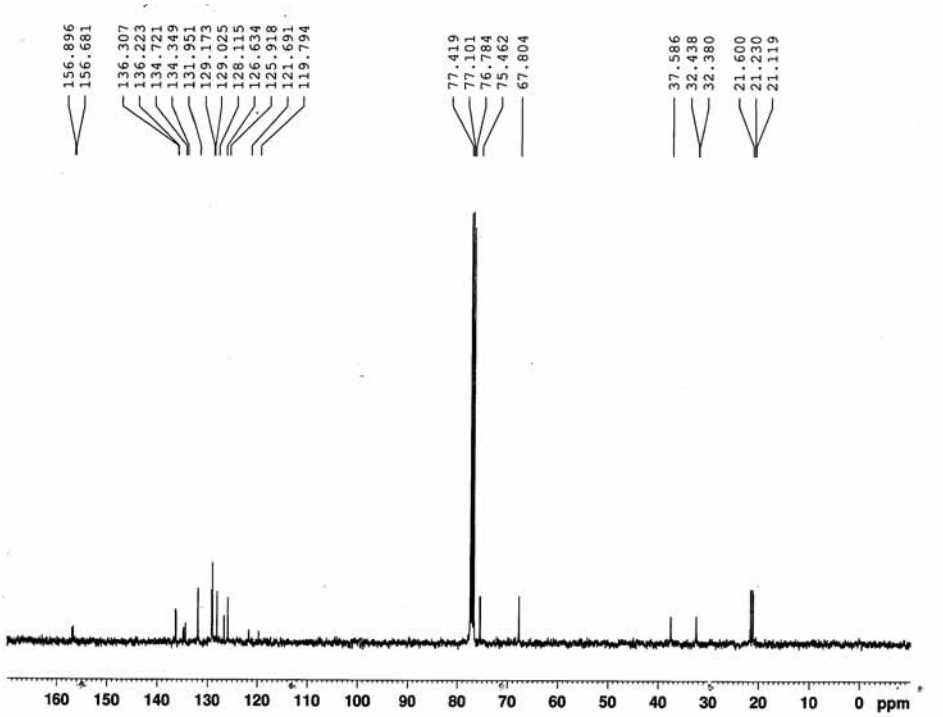



**Figure S23b**. [13]C NMR spectrum of compound **(*E*)-21**

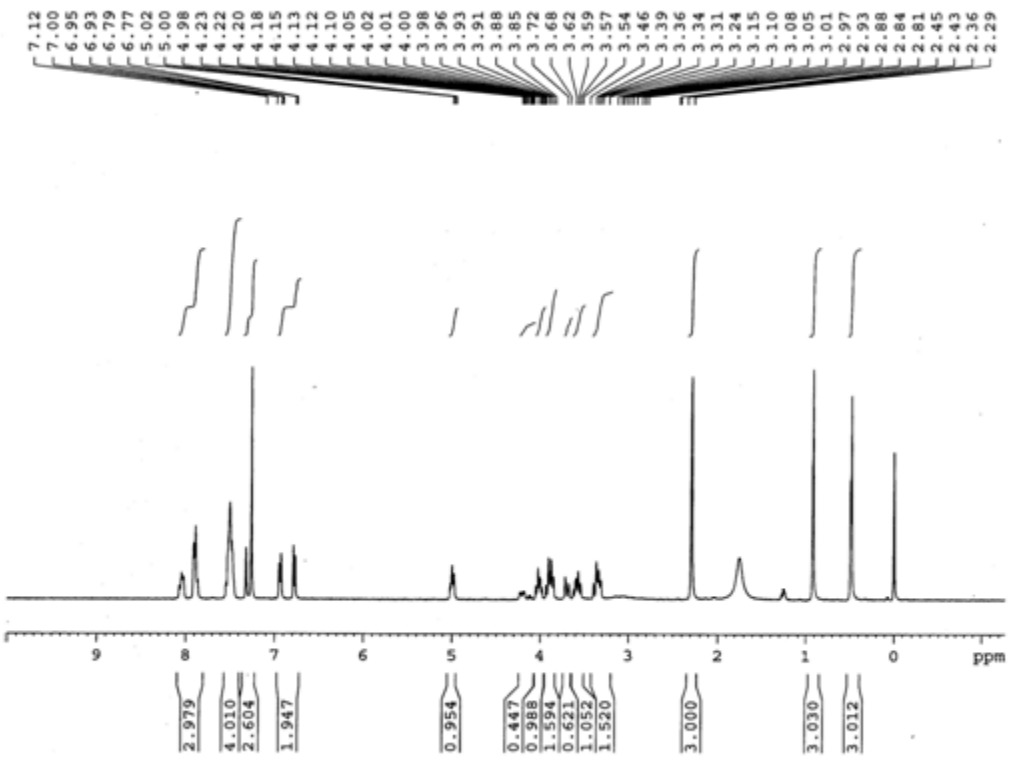



**Figure S24a**. $^{1}$H NMR spectrum of compound **22**

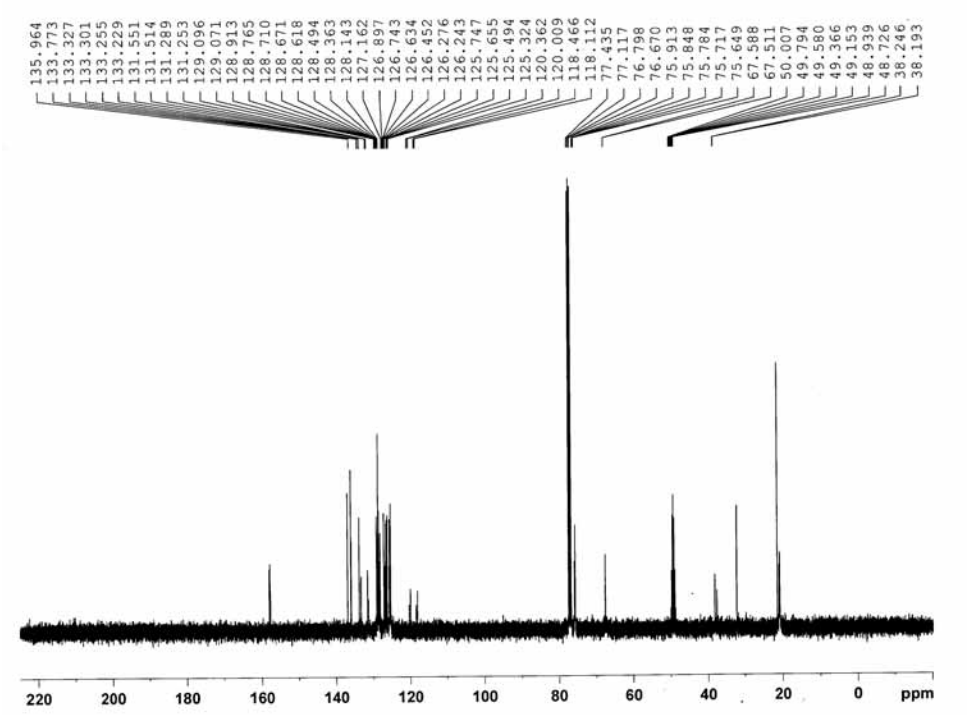



**Figure S24b**. $^{13}$C NMR spectrum of compound 2**2**

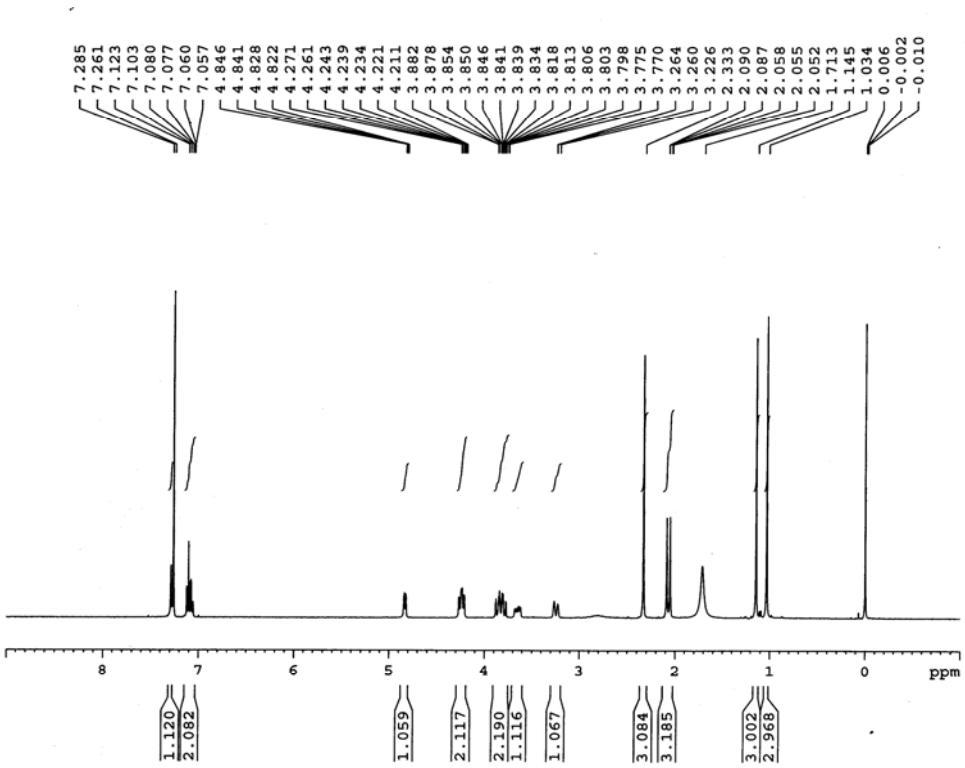



**Figure S25a**. $^{1}$H NMR spectrum of compound **(*E*)-23**

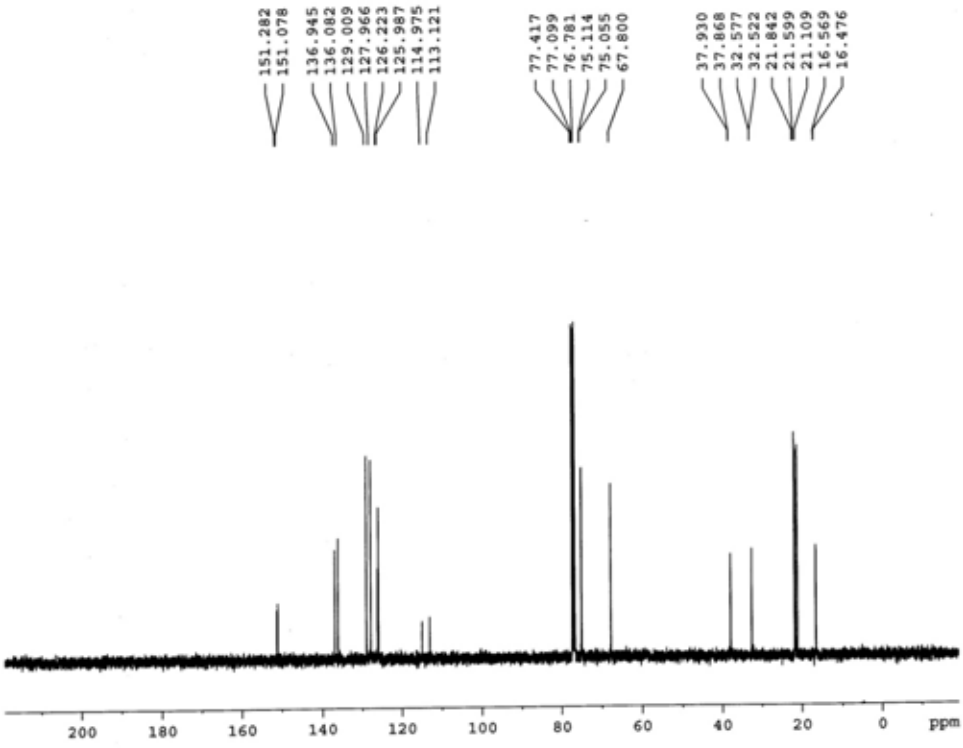



**Figure S25b**. $^{13}$C NMR spectrum of compound **(*E*)-23**

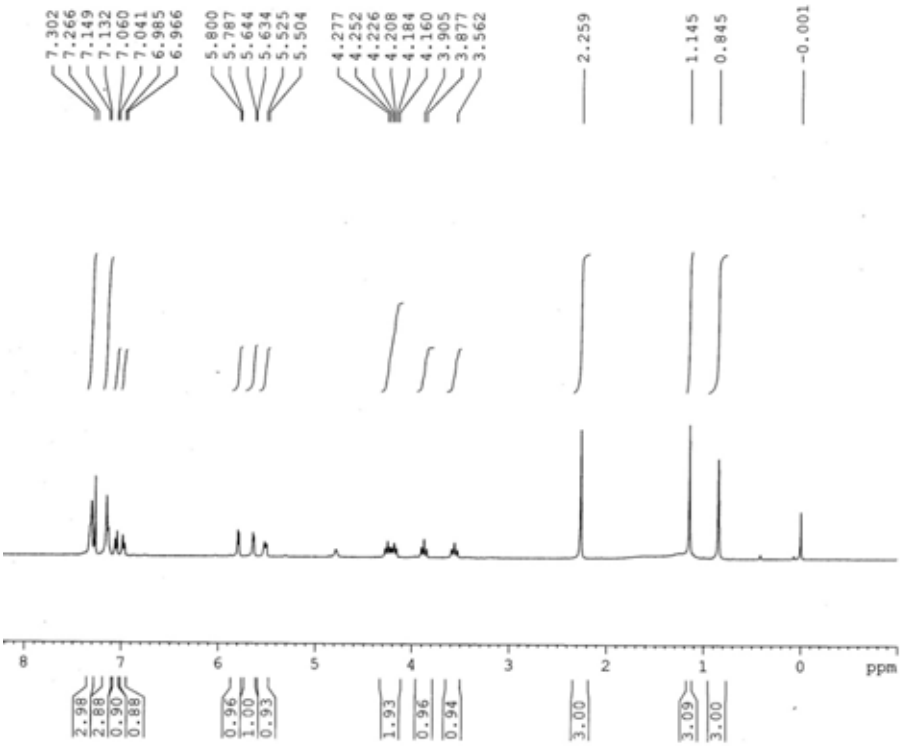



**Figure S26a**. $^{1}$H NMR spectrum of compound **24**

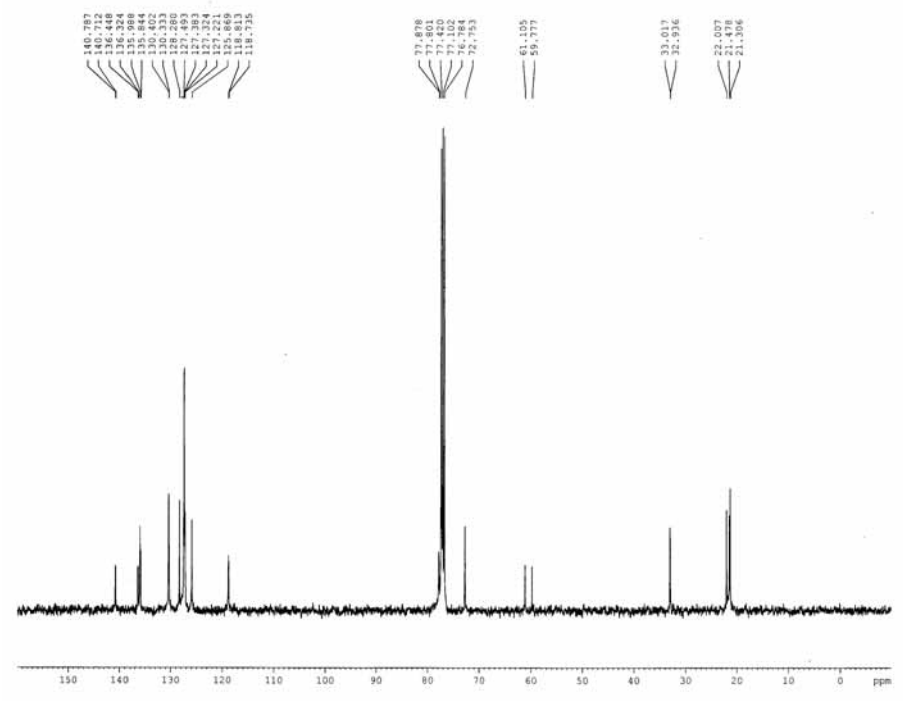



**Figure S26b**. $^{13}$C NMR spectrum of compound **24**

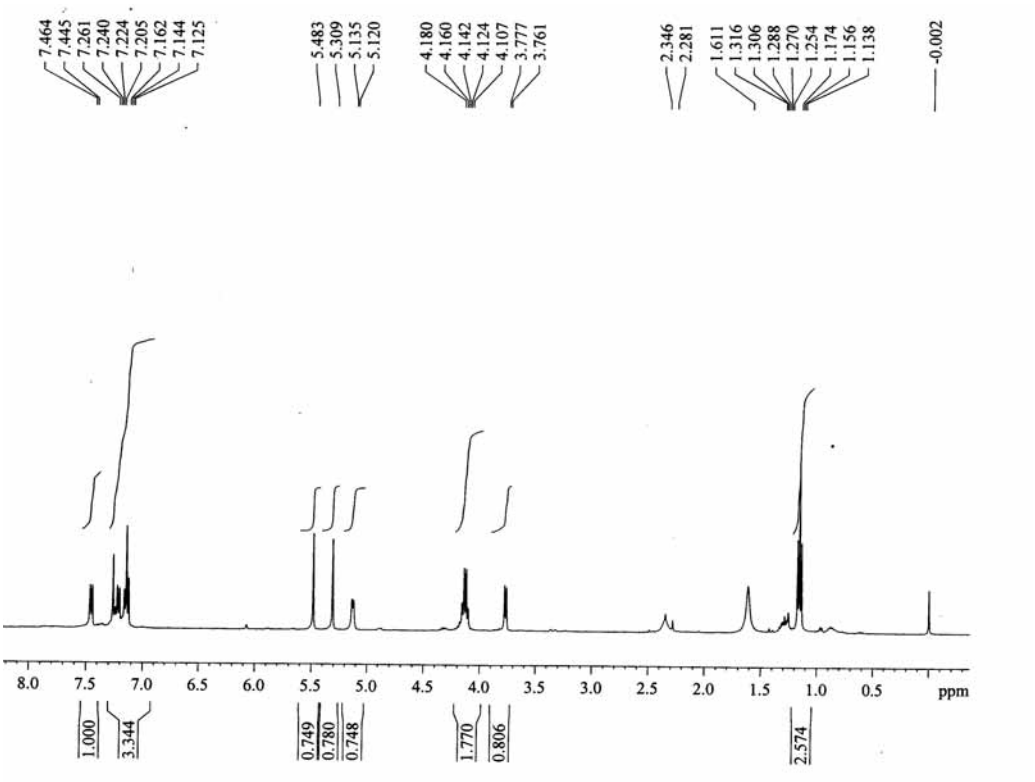



**Figure S27a**. $^{1}$H NMR spectrum of compound **25**

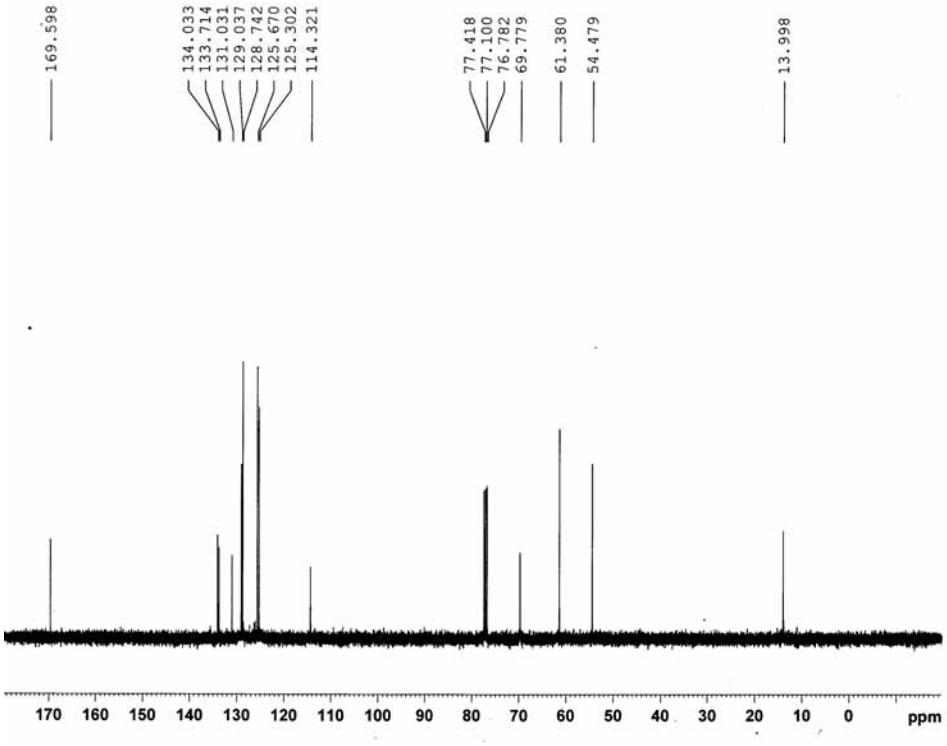



**Figure S27b**. $^{13}$C NMR spectrum of compound **25**

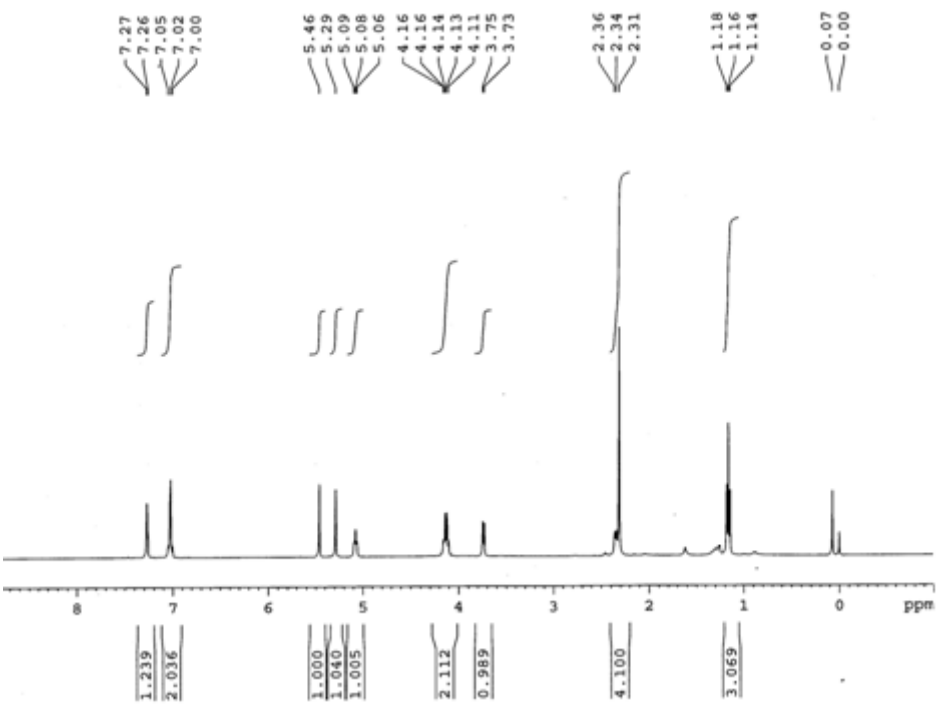



**Figure S28a**. $^{1}$H NMR spectrum of compound **26**

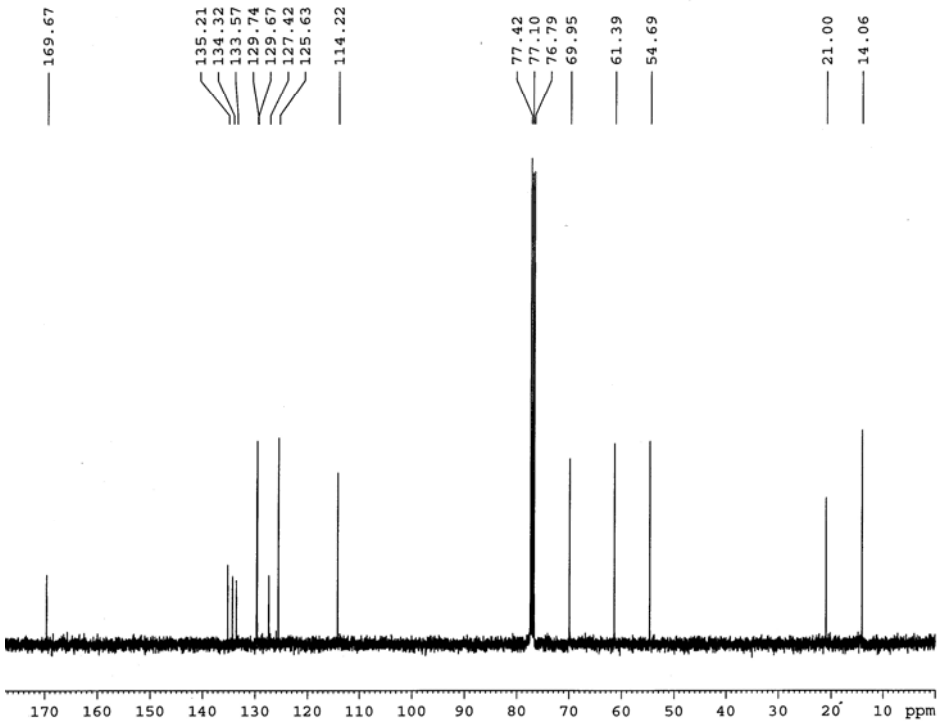



**Figure S28b**. $^{13}$C NMR spectrum of compound **26**

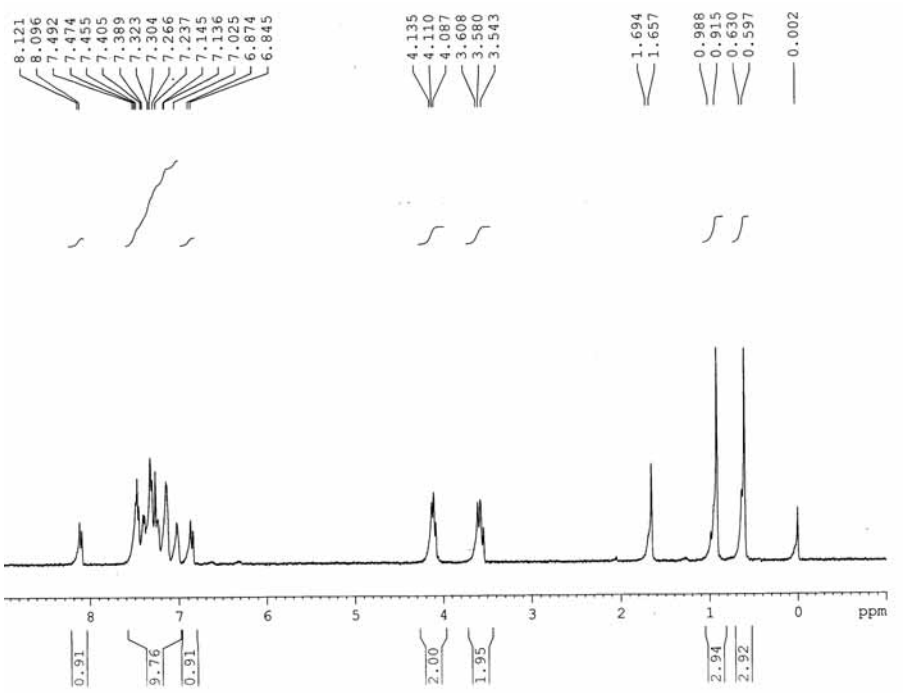



**Figure S29a**. $^{1}$H NMR spectrum of compound **27**

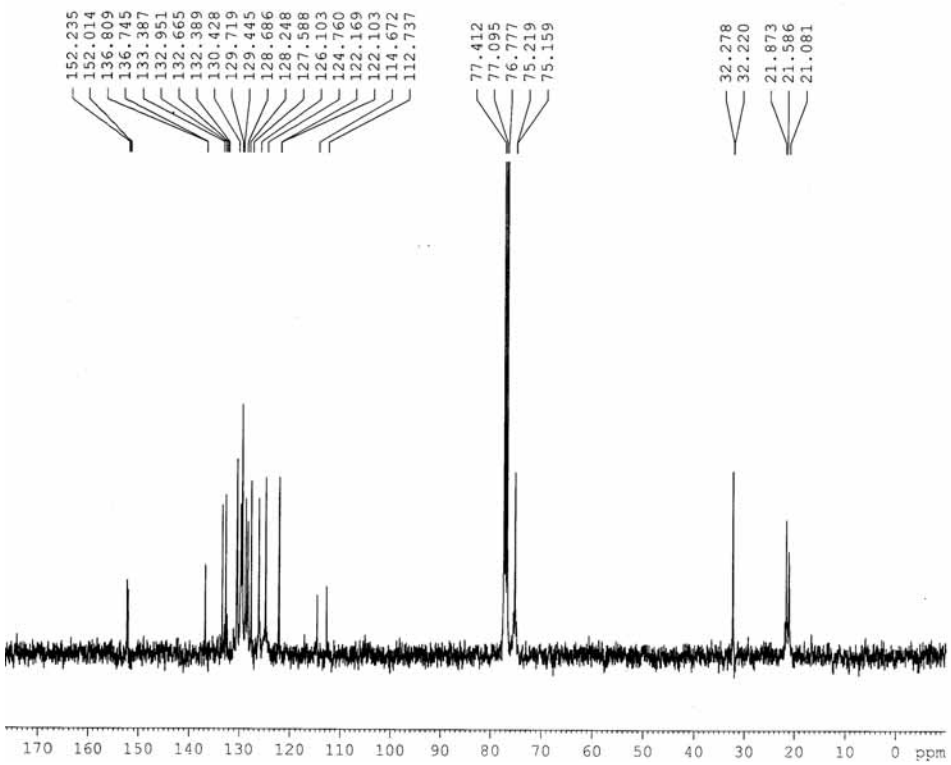



**Figure S29b**. $^{13}$C NMR spectrum of compound **27**

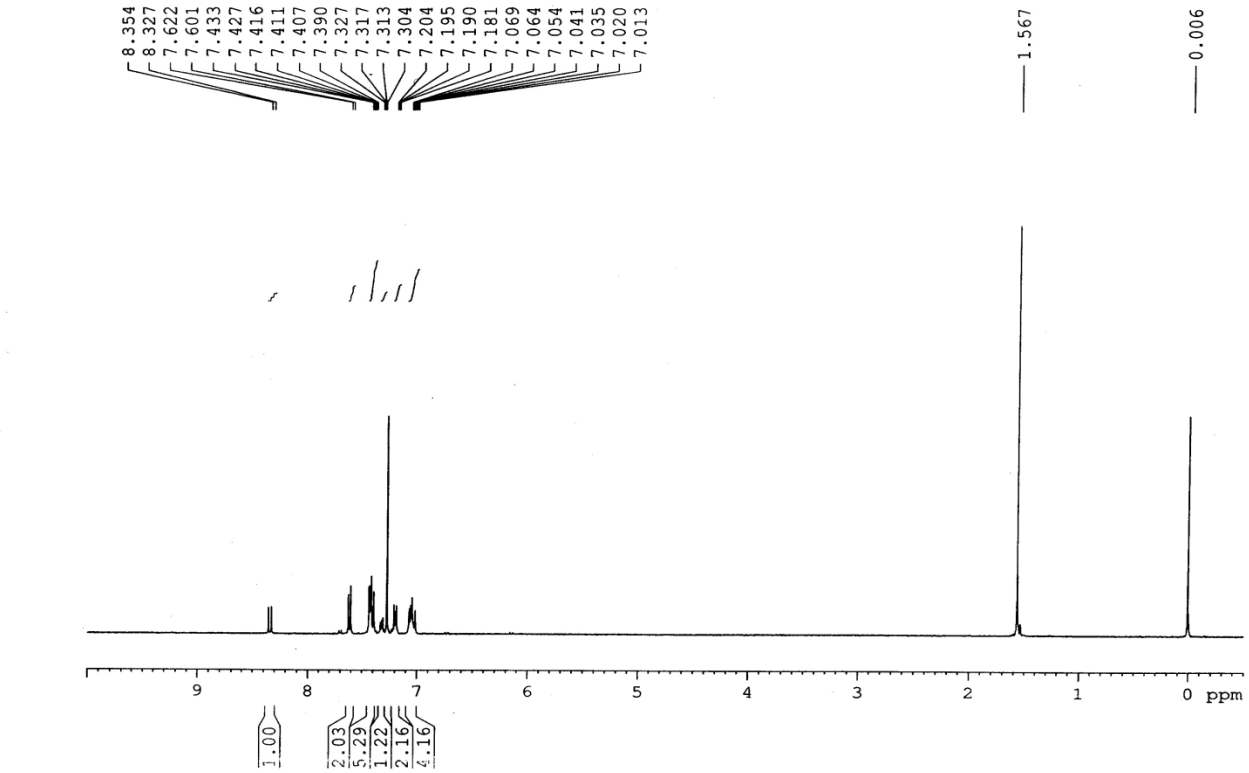



**Figure S30a**. $^{1}$H NMR spectrum of compound **28**

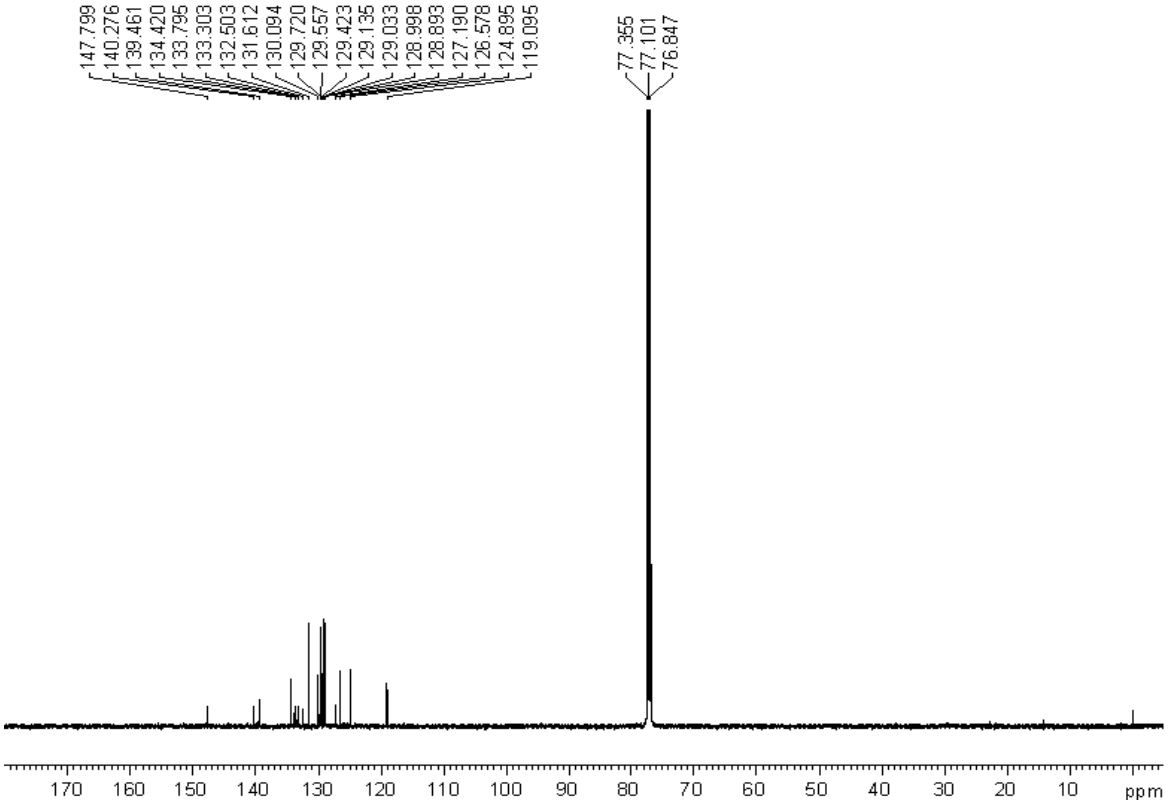



**Figure S30b**. $^{13}$C NMR spectrum of compound **28**

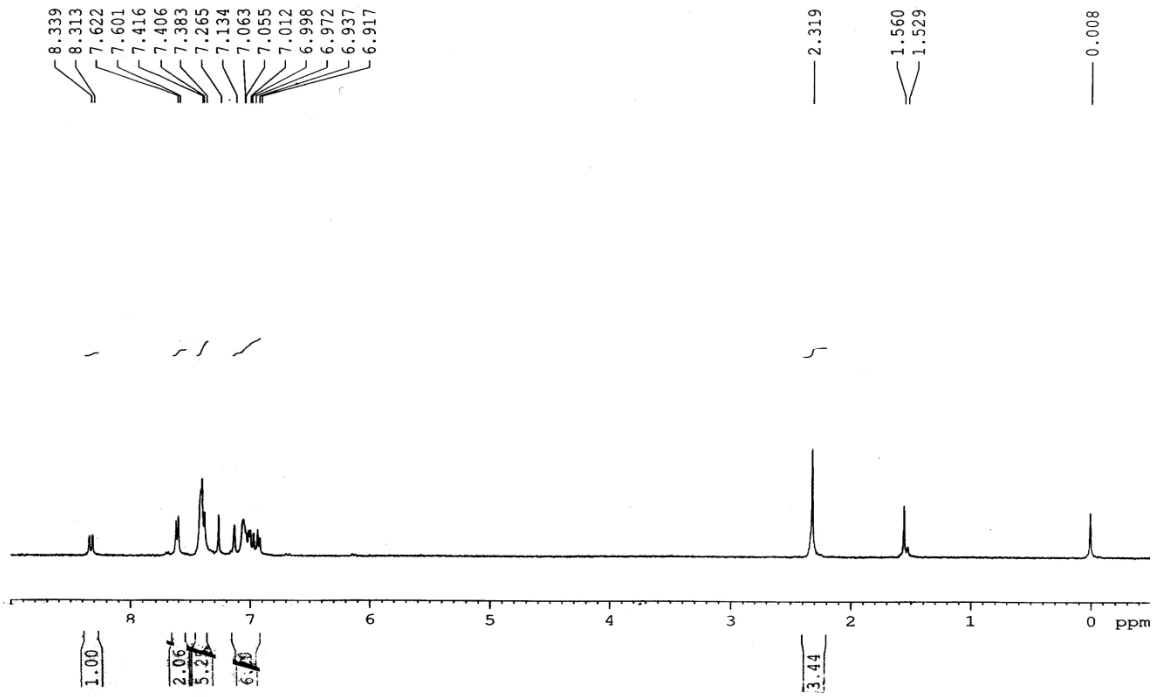



**Figure S31a**. $^{1}$H NMR spectrum of compound **29**

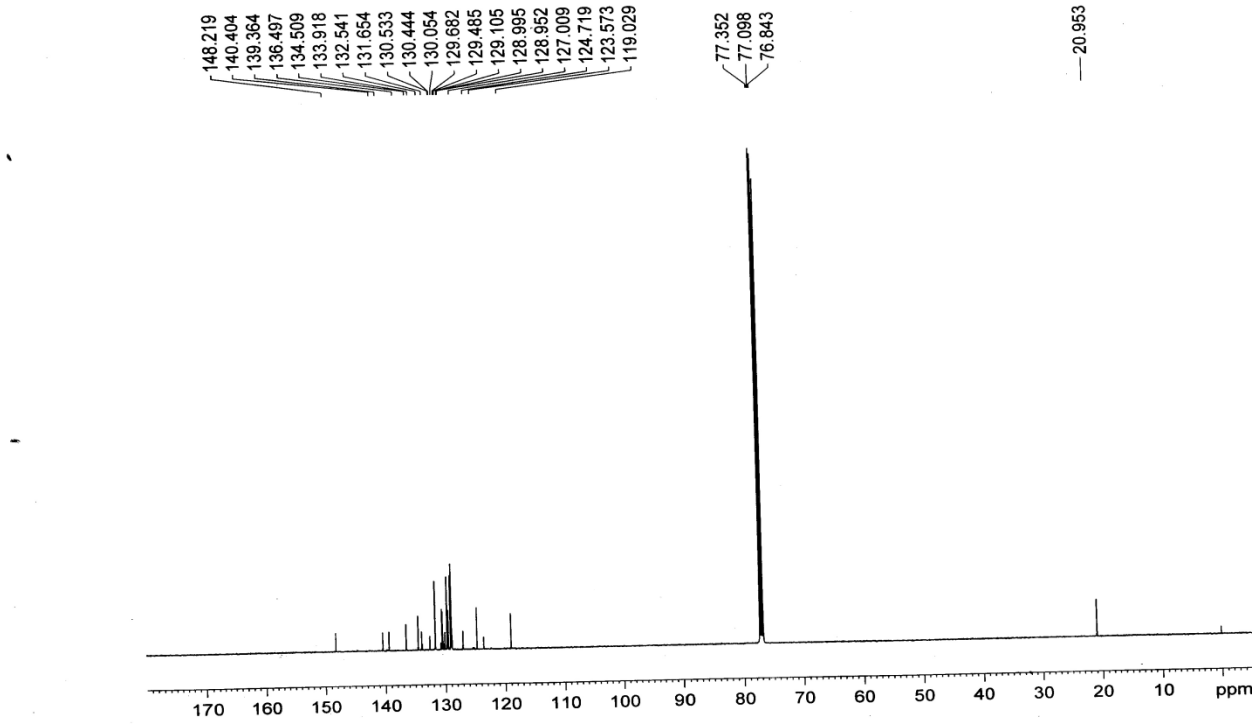



**Figure S31b**. $^{13}$C NMR spectrum of compound **29**

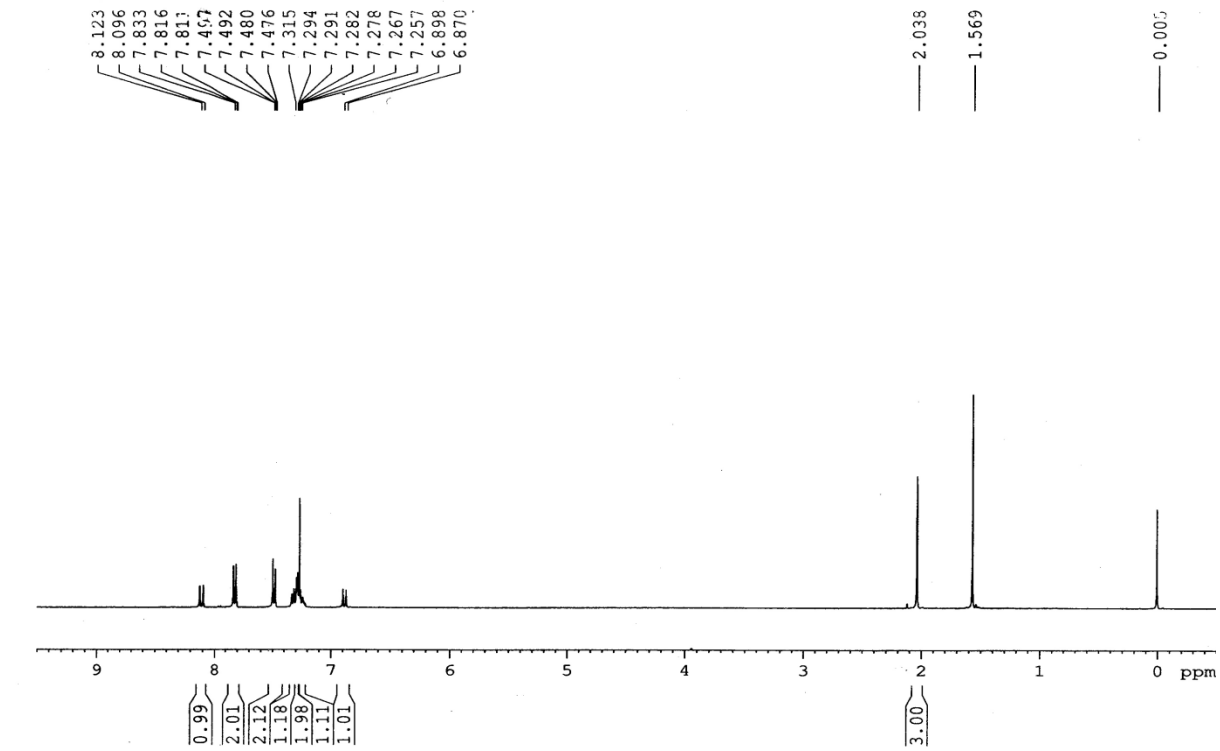



**Figure S32a**. $^{1}$H NMR spectrum of compound **30**

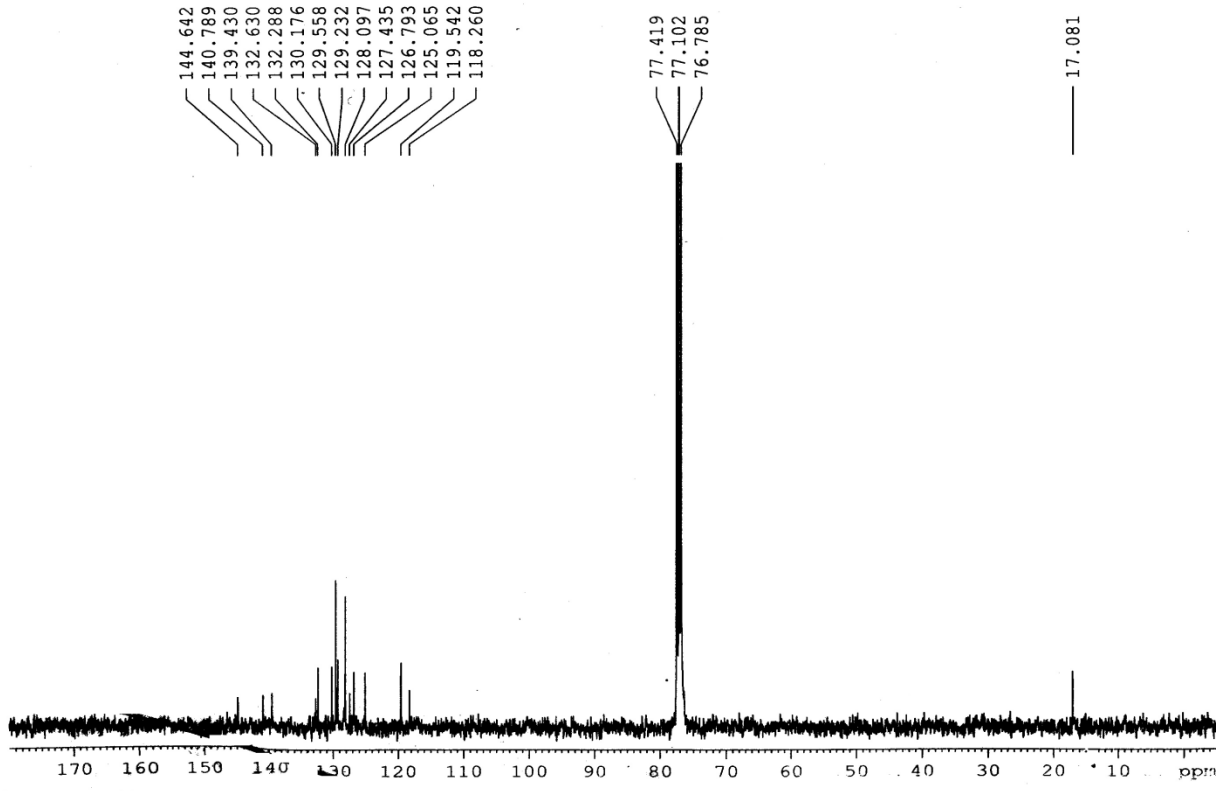



**Figure S32b**. $^{13}$C NMR spectrum of compound **30**

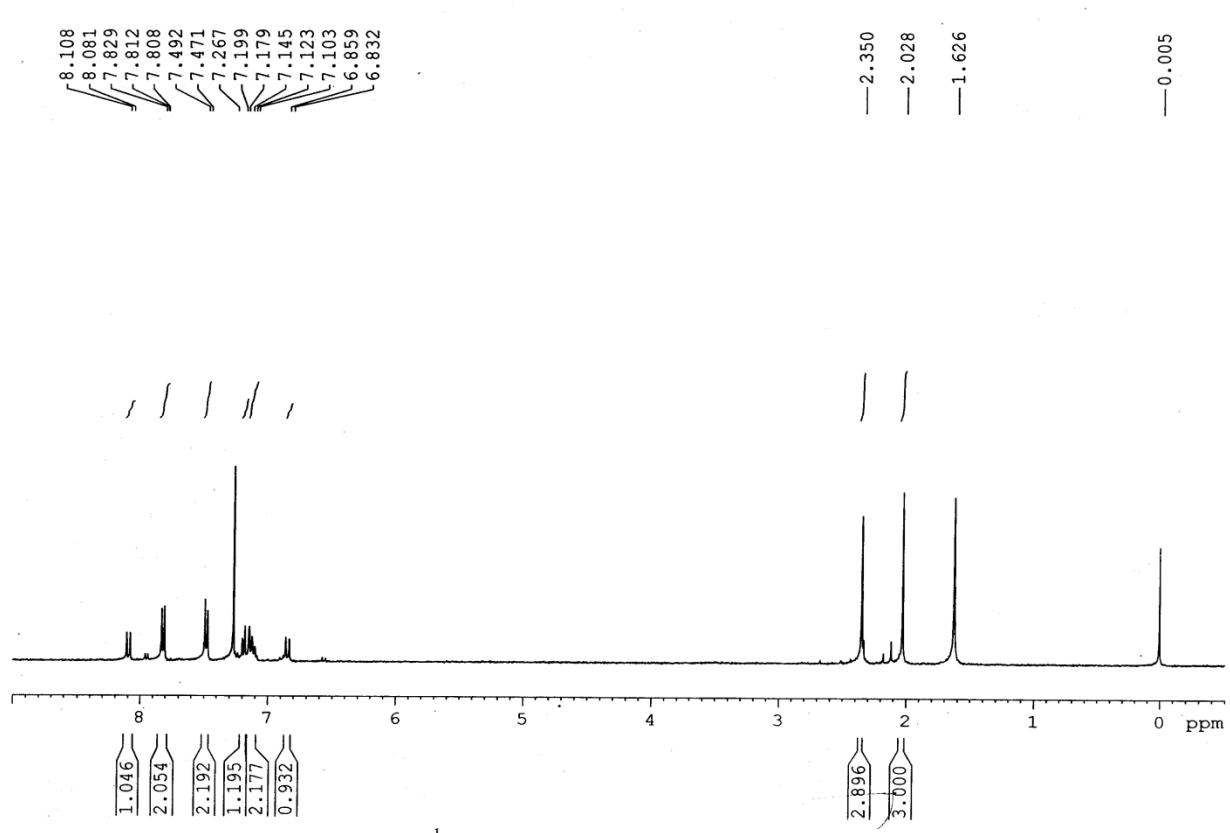



**Figure S33a**. $^{1}$H NMR spectrum of compound **31**

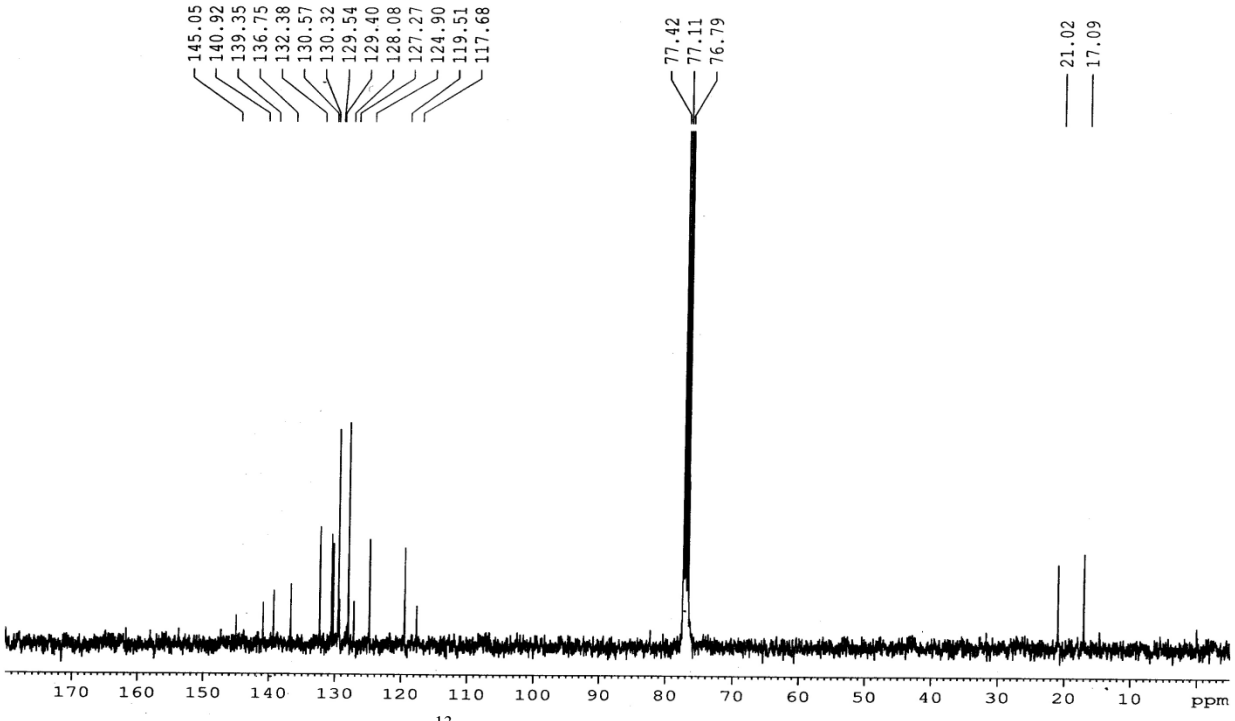



**Figure S33b**. $^{13}$C NMR spectrum of compound **31**

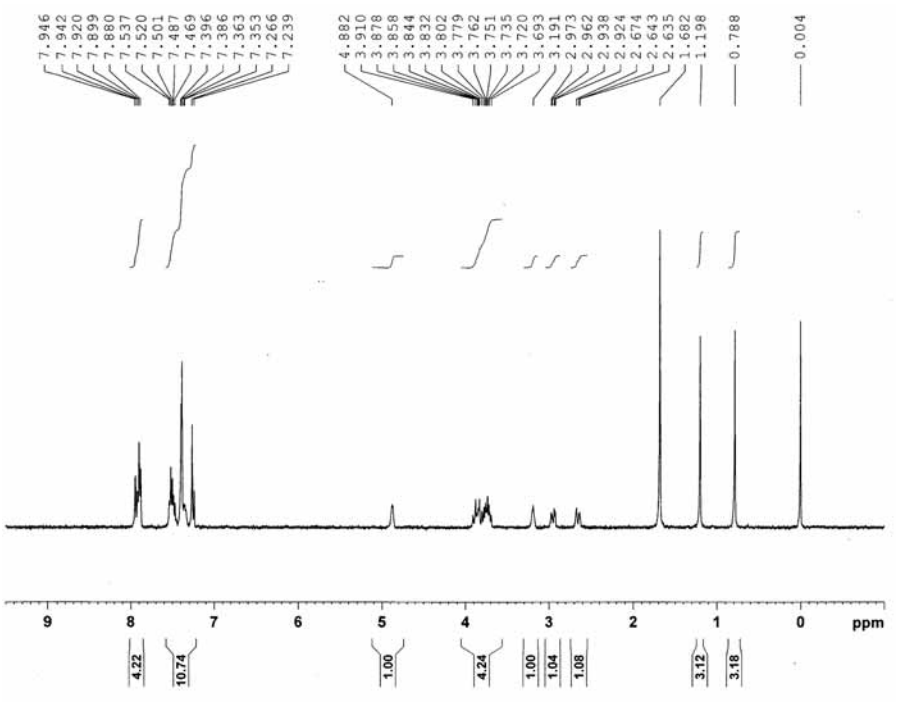



**Figure S34a**. $^{1}$H NMR spectrum of compound **(*E*)-32**

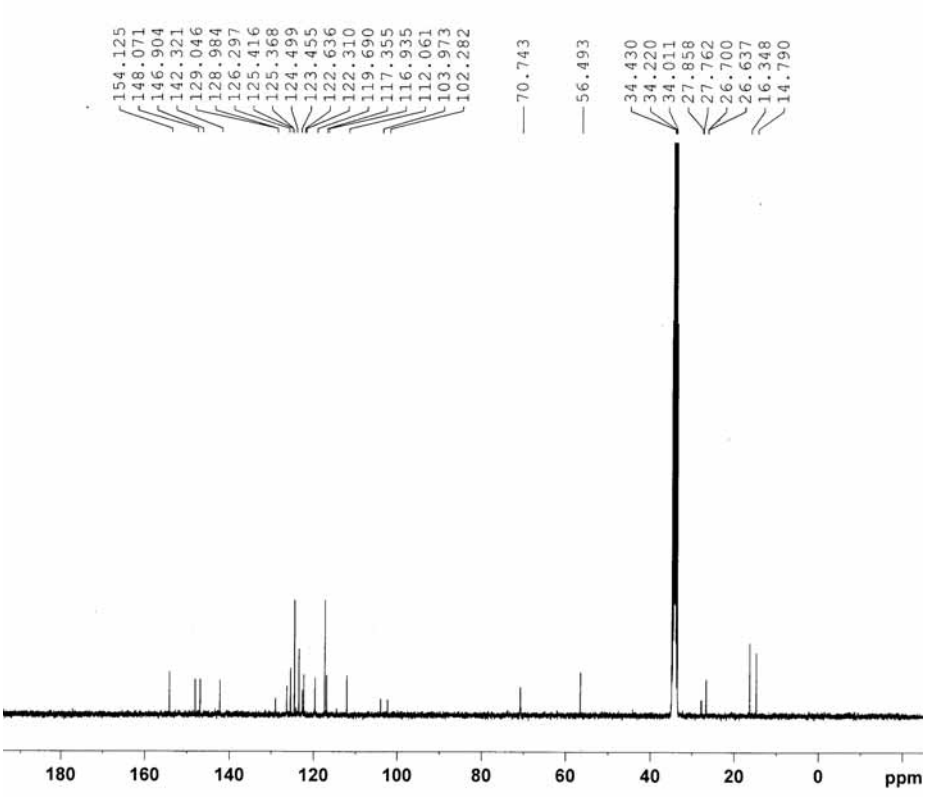



**Figure S34b**. $^{13}$C NMR spectrum of compound **(*E*)-32**

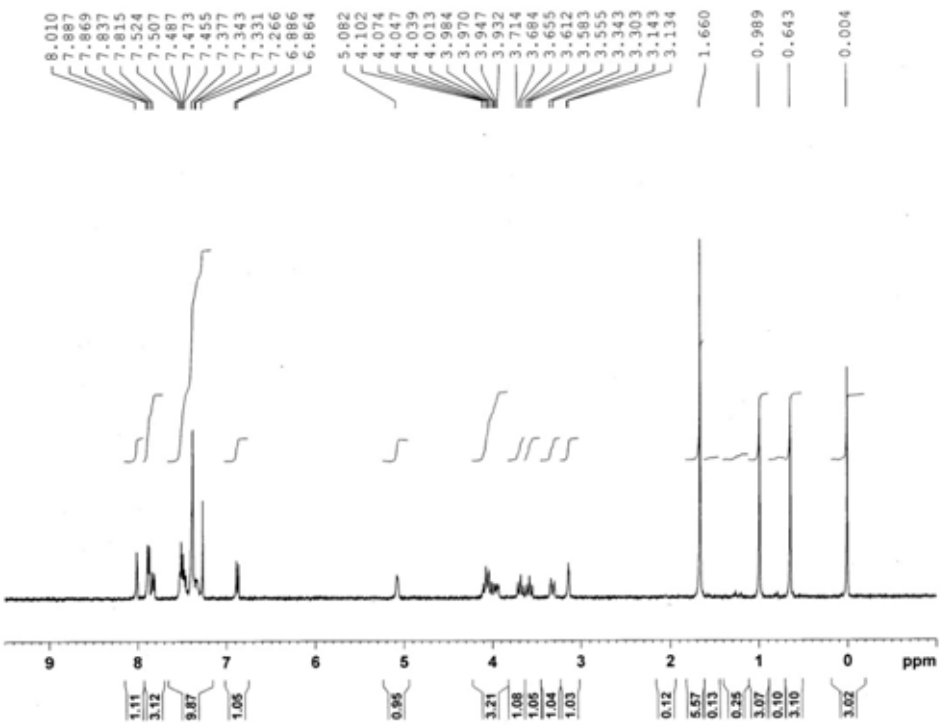



**Figure S35a**. $^{1}$H NMR spectrum of compound **(*Z*)-32**

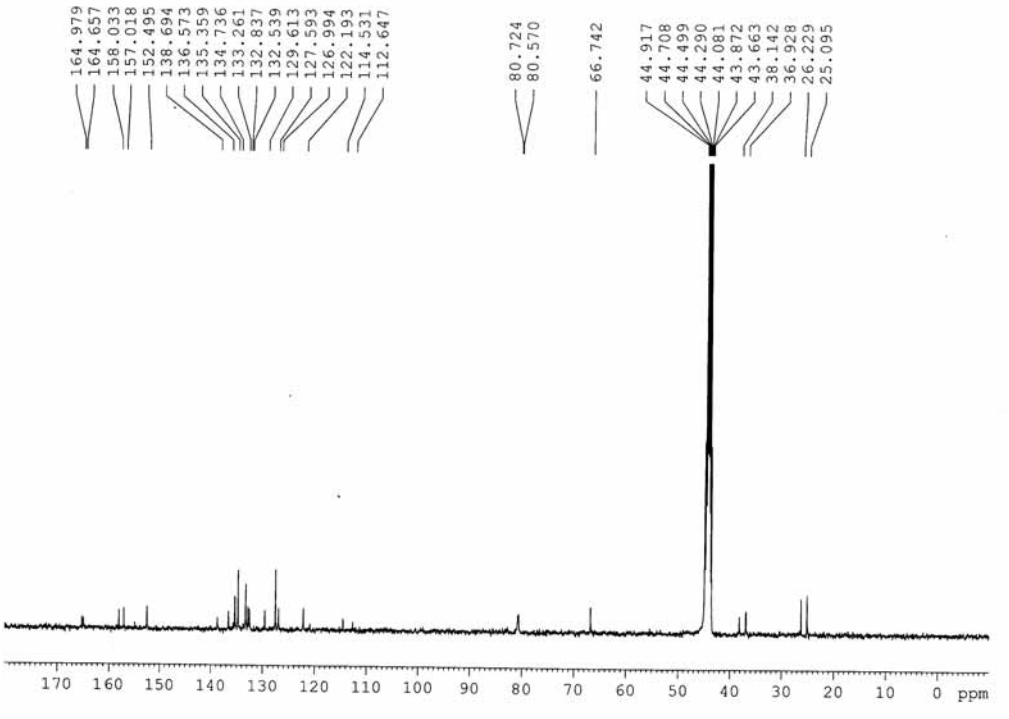



**Figure S35b**. $^{13}$C NMR spectrum of compound **(*Z*)-32**

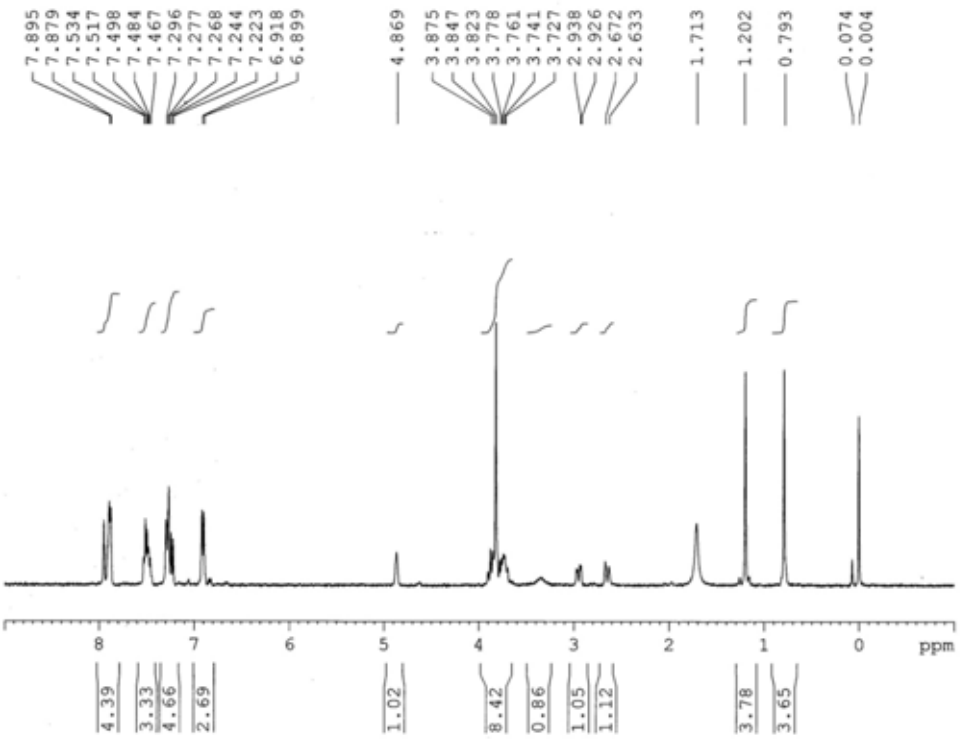



**Figure S36a**. $^{1}$H NMR spectrum of compound **(*E*)-33**

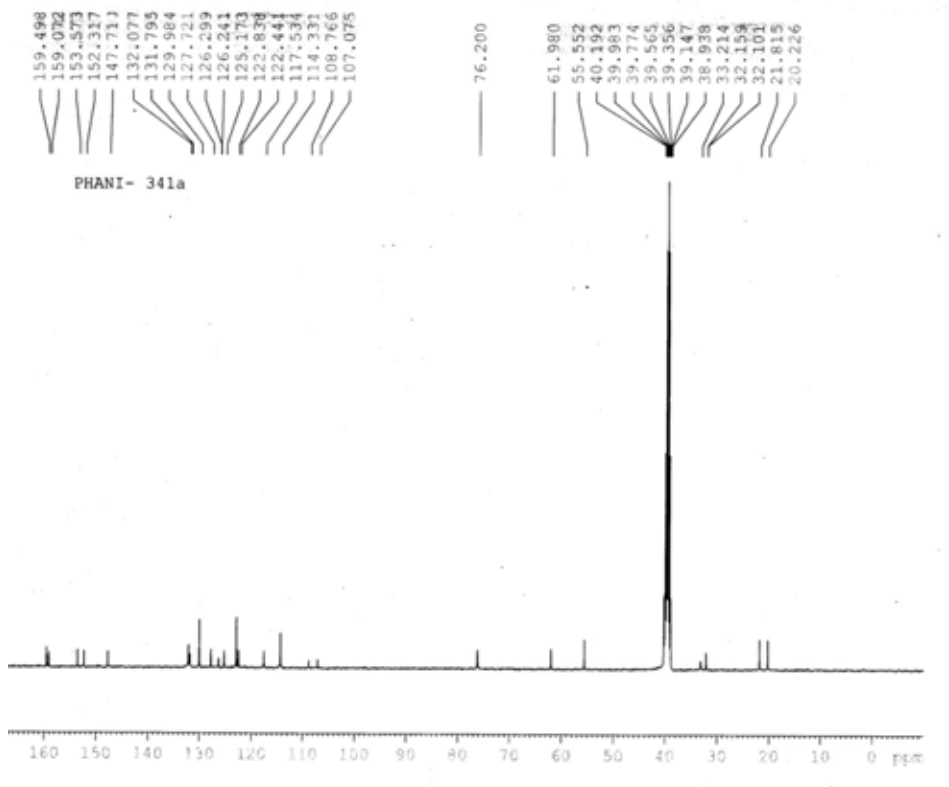



**Figure S36b**. $^{13}$C NMR spectrum of compound **(*E*)-33**

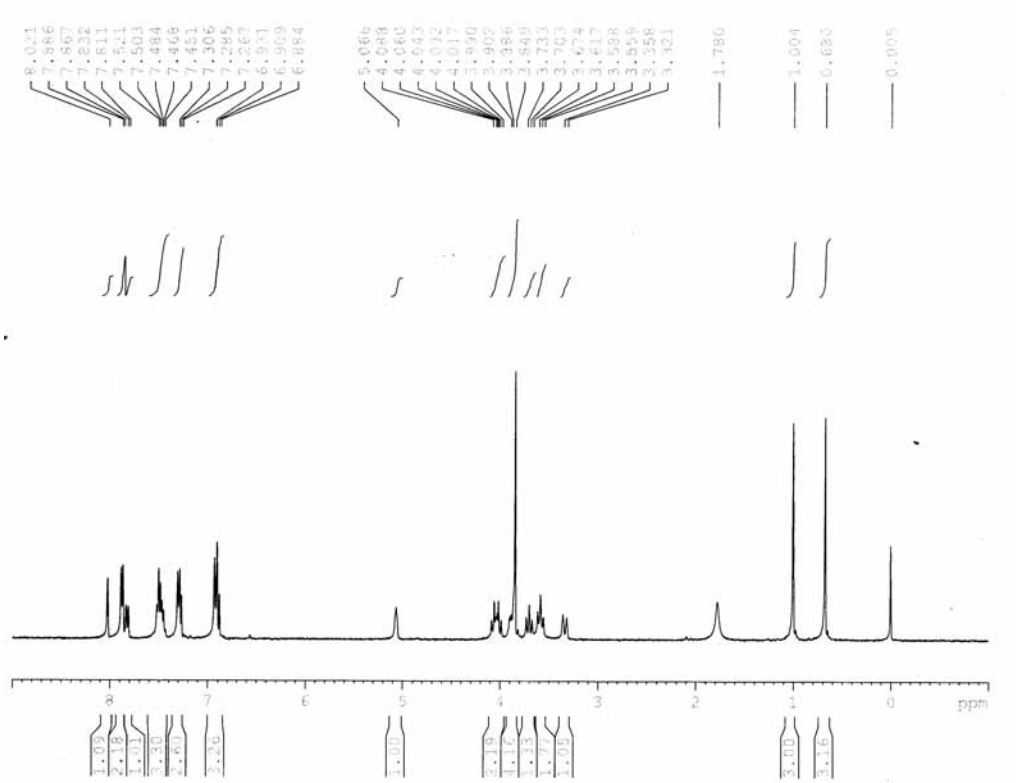


**Figure S37a**. $^{1}$H NMR spectrum of compound **(*Z*)-33**

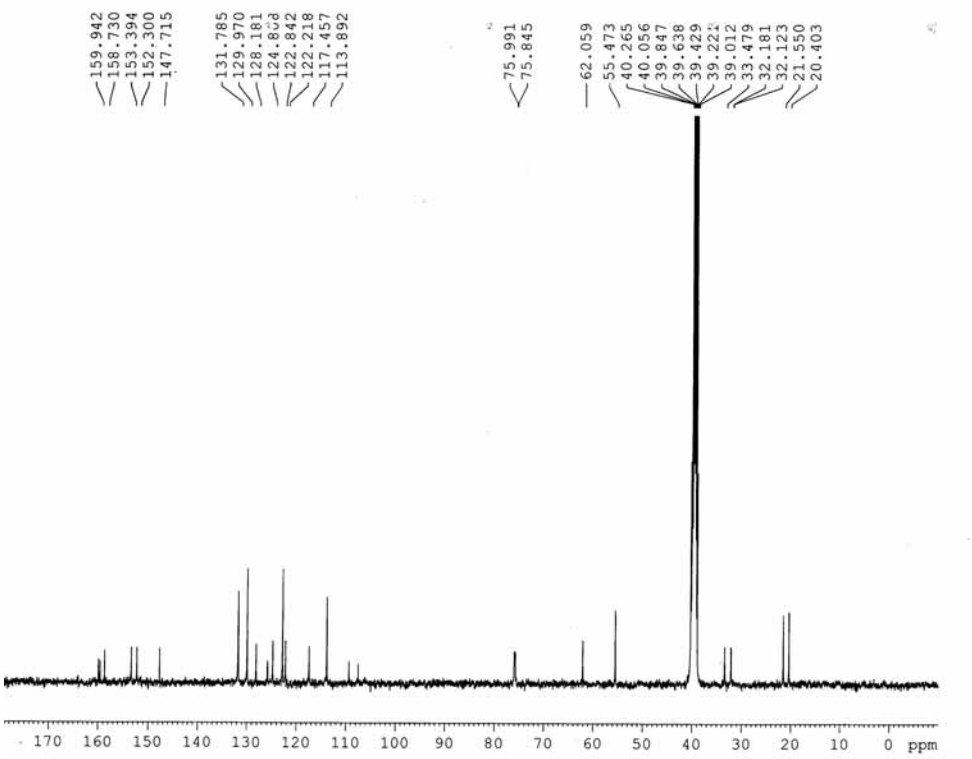


**Figure S37b**. $^{13}$C NMR spectrum of compound **(*Z*)-33**

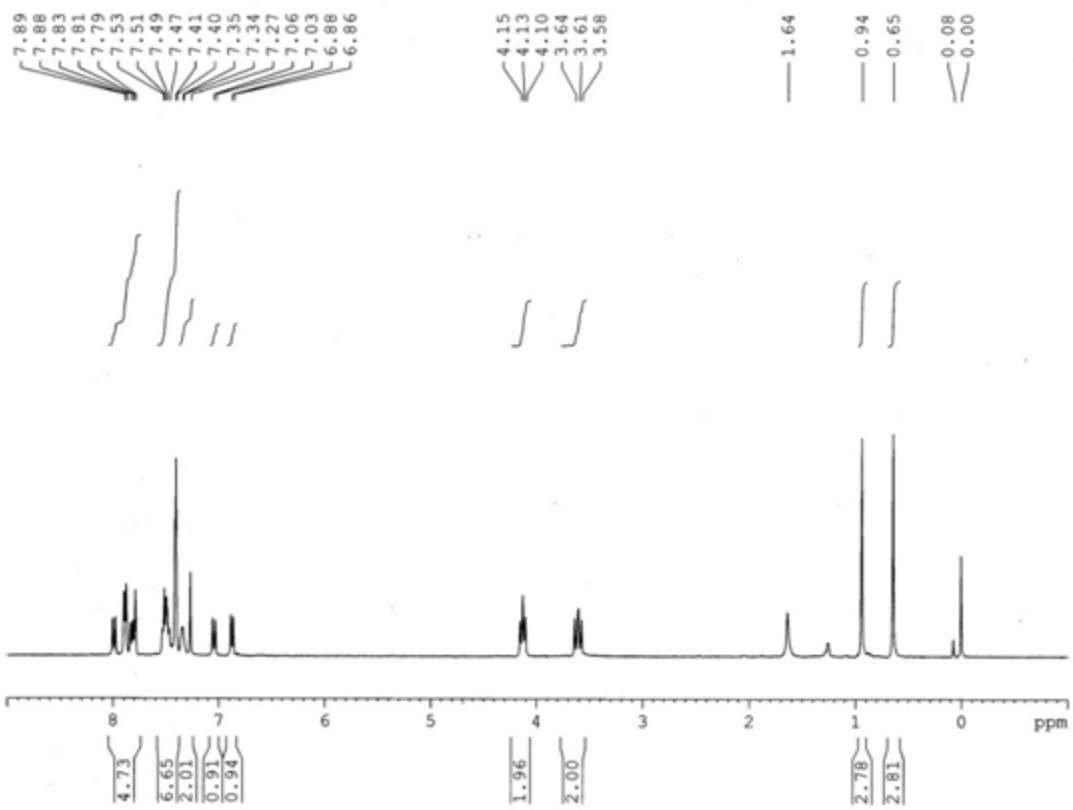



**Figure S38a**. $^{1}$H NMR spectrum of compound **(*E*)-34**

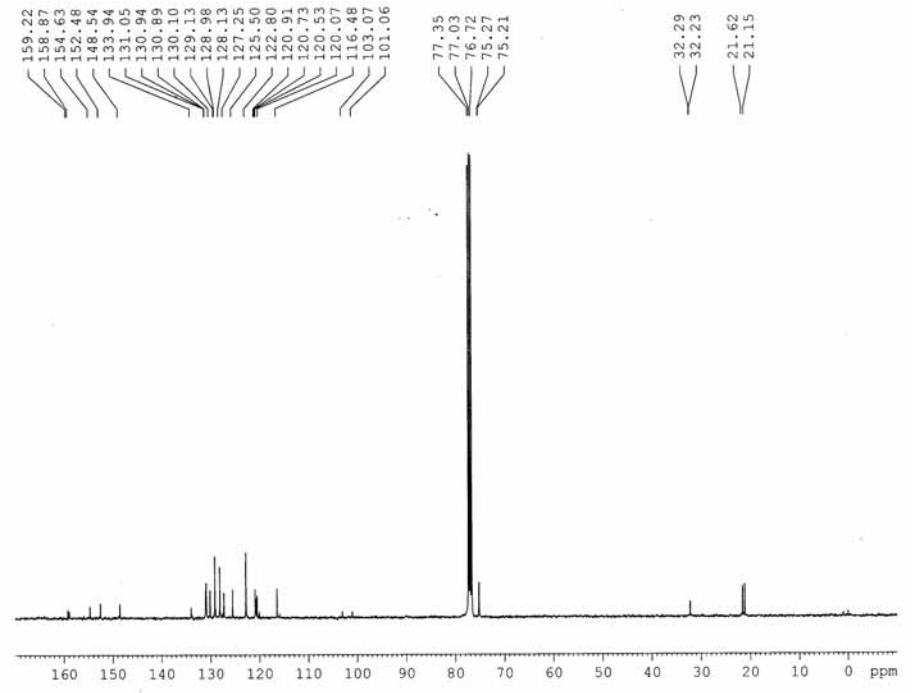



**Figure S38b**. $^{13}$C NMR spectrum of compound **(*E*)-34**

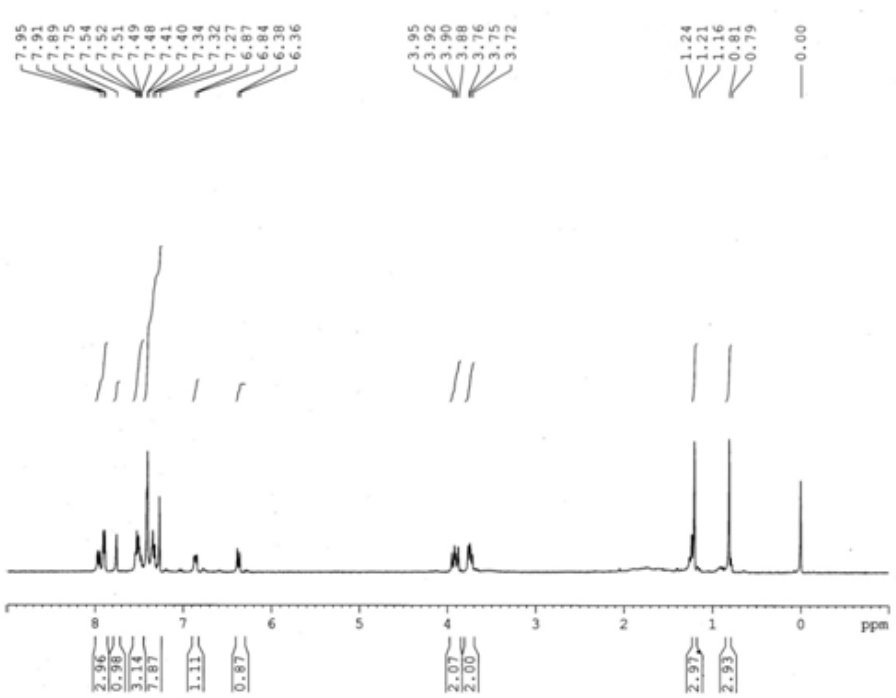



**Figure S39a**. $^{1}$H NMR spectrum of compound **(*Z*)-34**

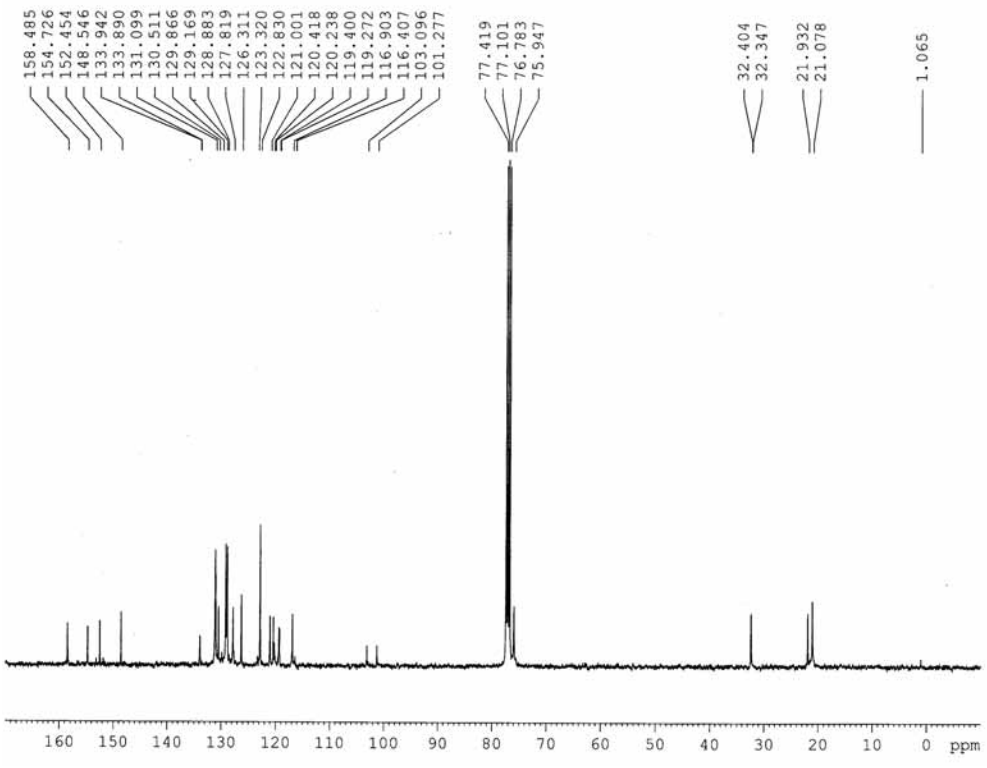



**Figure S39b**. $^{13}$C NMR spectrum of compound **(*Z*)-34**

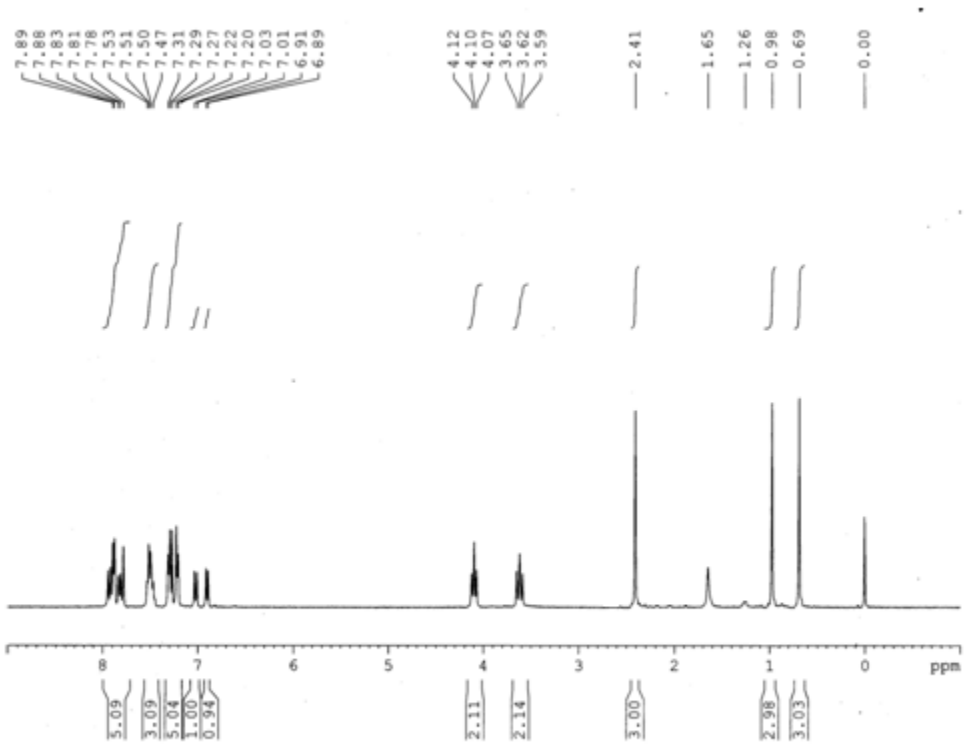



**Figure S40a**. $^{1}$H NMR spectrum of compound **(*E*)-35**

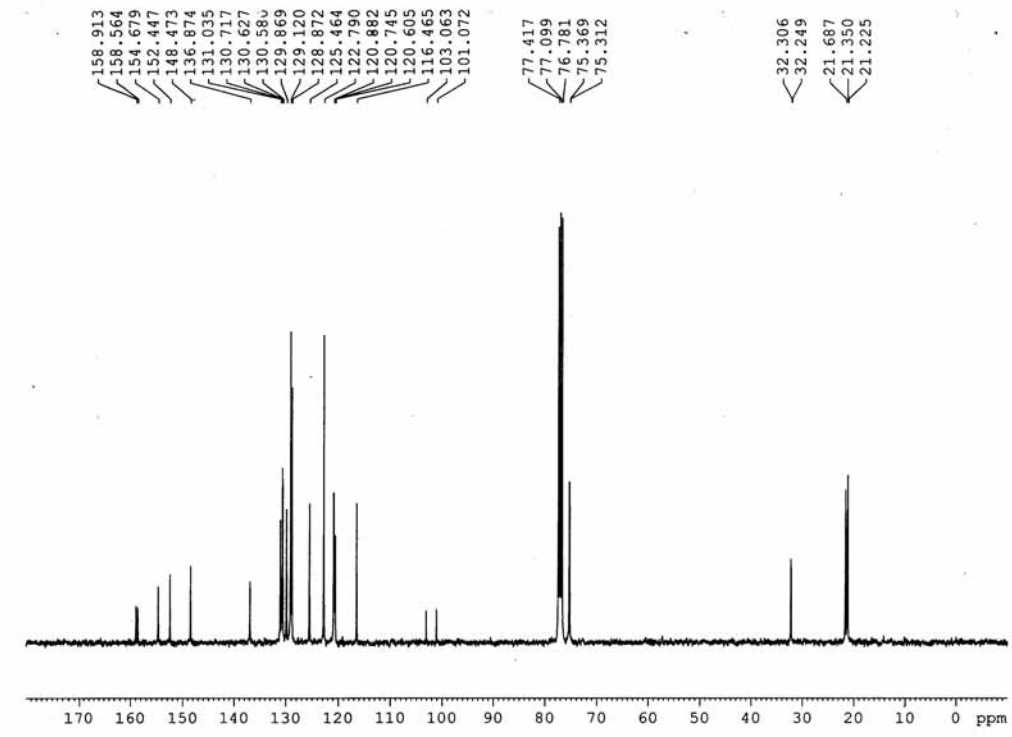



**Figure S40b**. $^{13}$C NMR spectrum of compound **(*E*)-35**

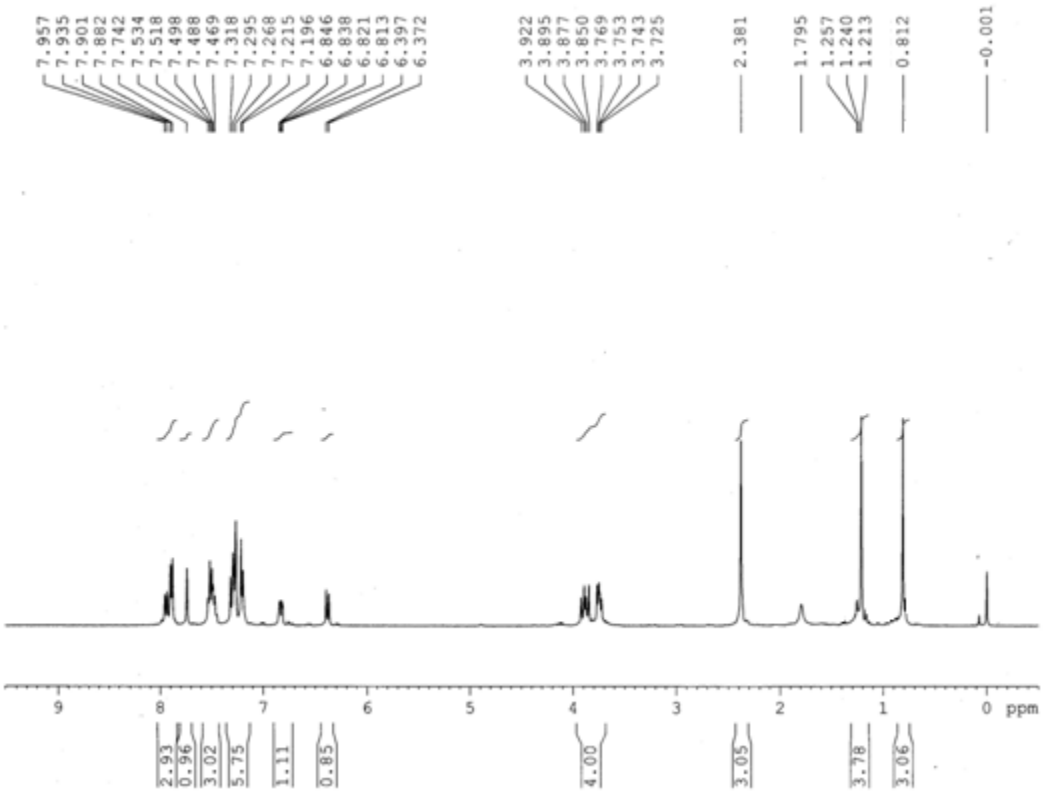



**Figure S41a**. $^{1}$H NMR spectrum of compound **(*Z*)-35**

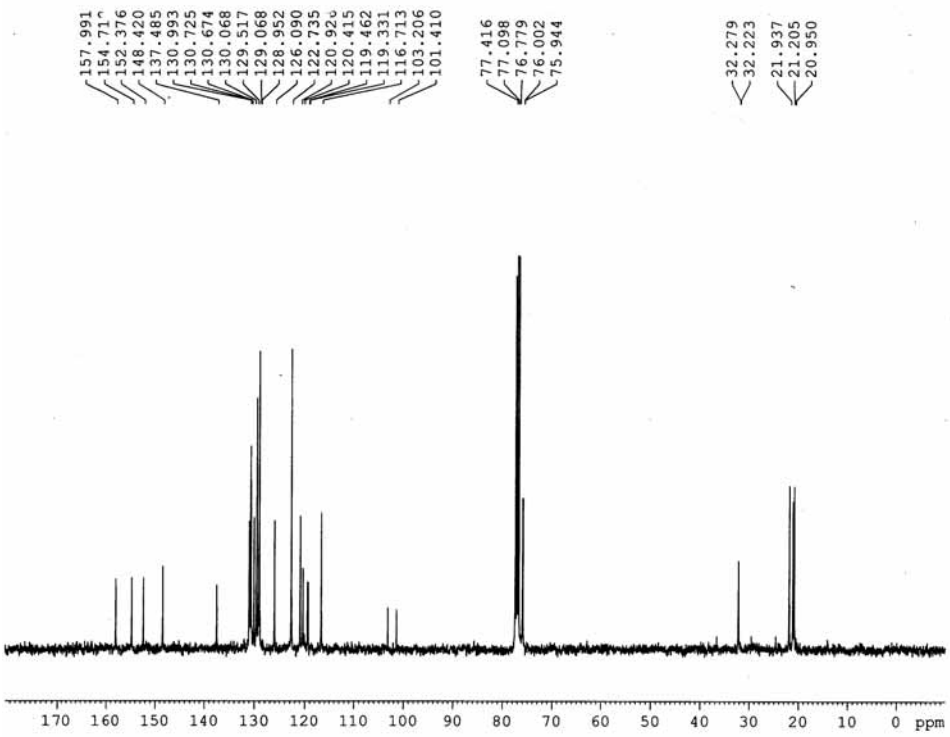



**Figure S41b**. $^{13}$C NMR spectrum of compound **(*Z*)-35**

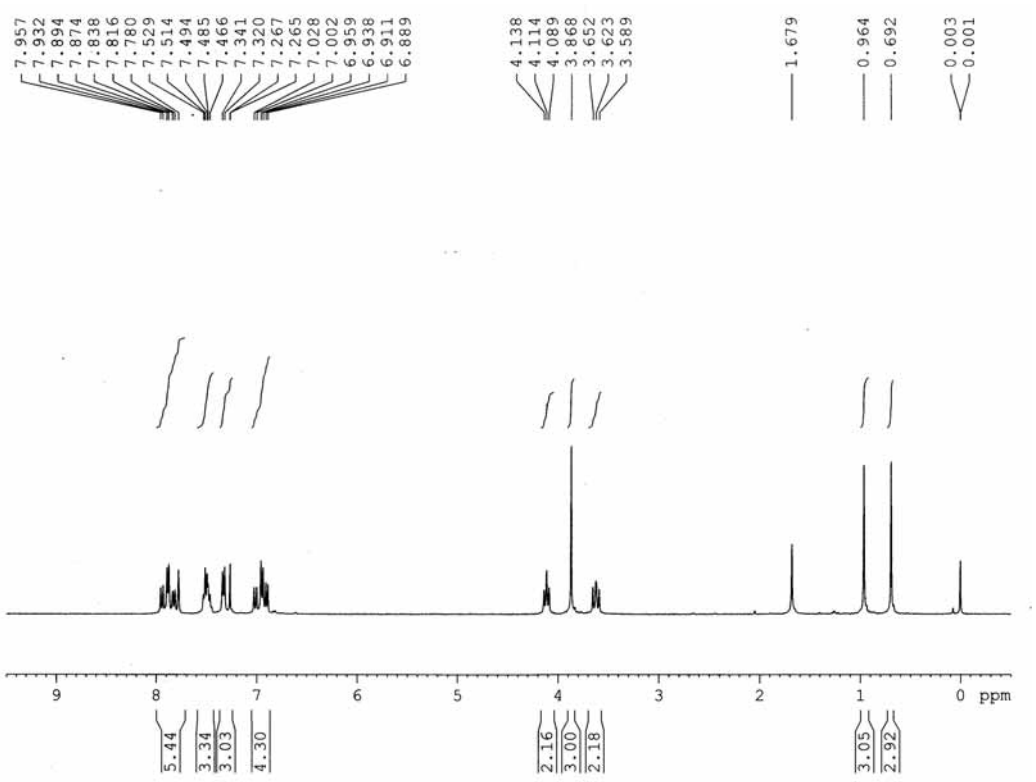



**Figure S42a**. $^{1}$H NMR spectrum of compound **(*E*)-36**

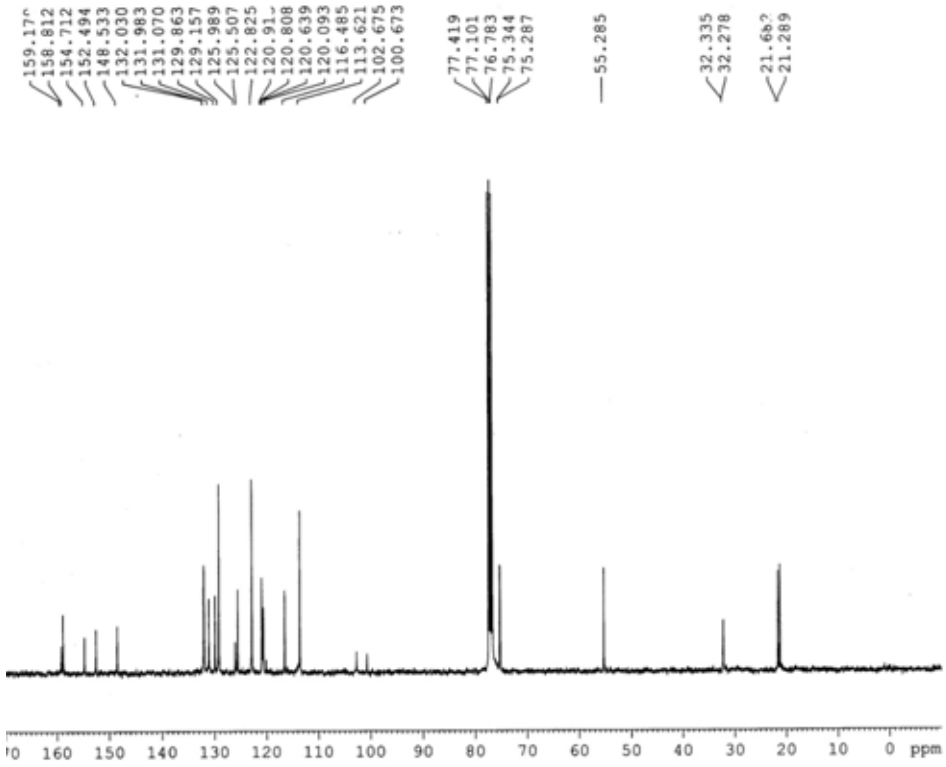



**Figure S42b**. $^{13}$C NMR spectrum of compound **(*E*)-36**

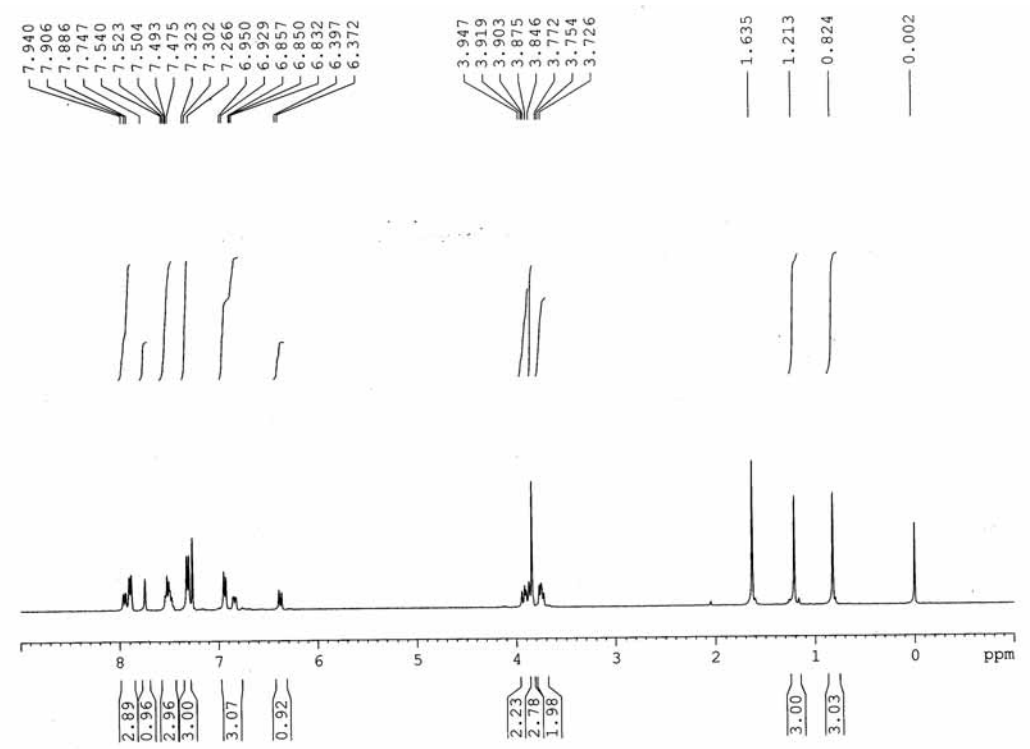



**Figure S43a**. $^{1}$H NMR spectrum of compound **(*Z*)-36**

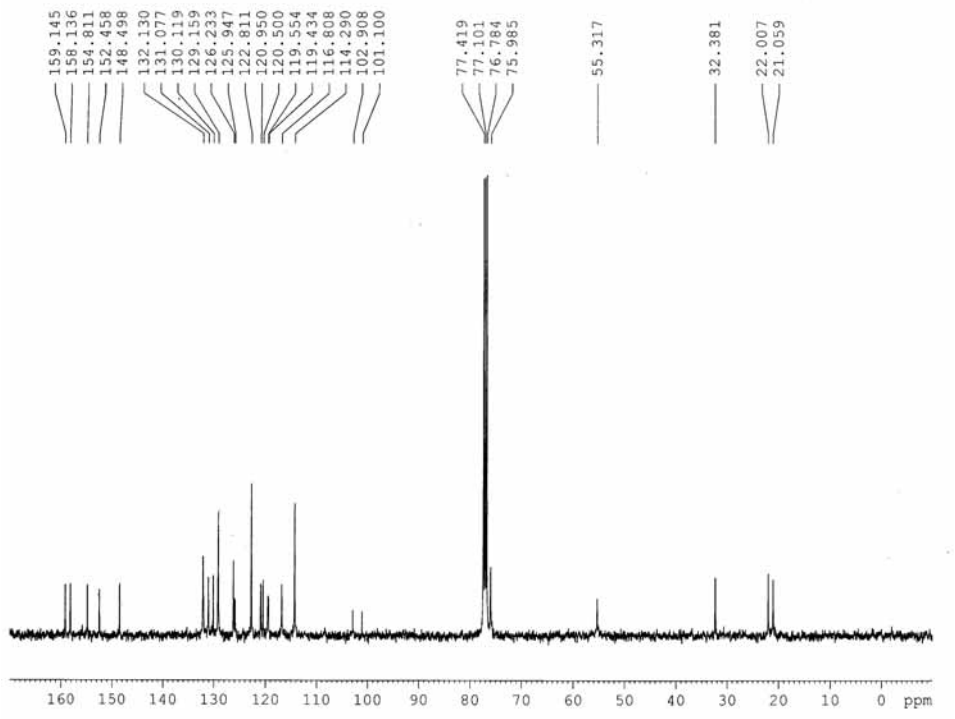



**Figure S43b**. $^{13}$C NMR spectrum of compound **(*Z*)-36**

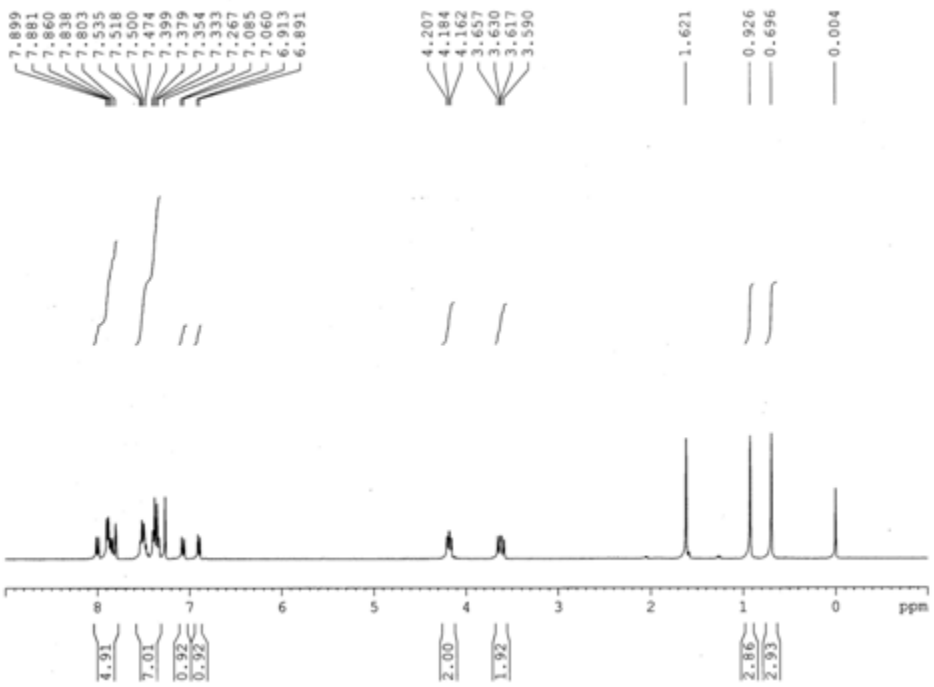



**Figure S44a**. [1]H NMR spectrum of compound **(*E*)-37**

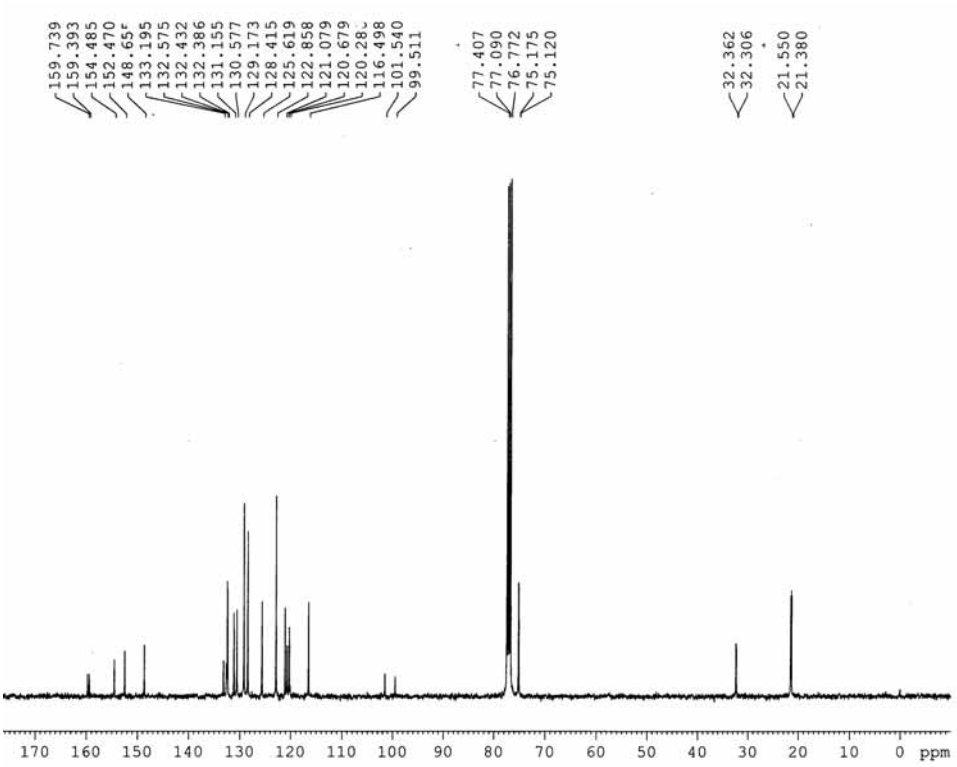



**Figure S44b**. [13]C NMR spectrum of compound **(*E*)-37**

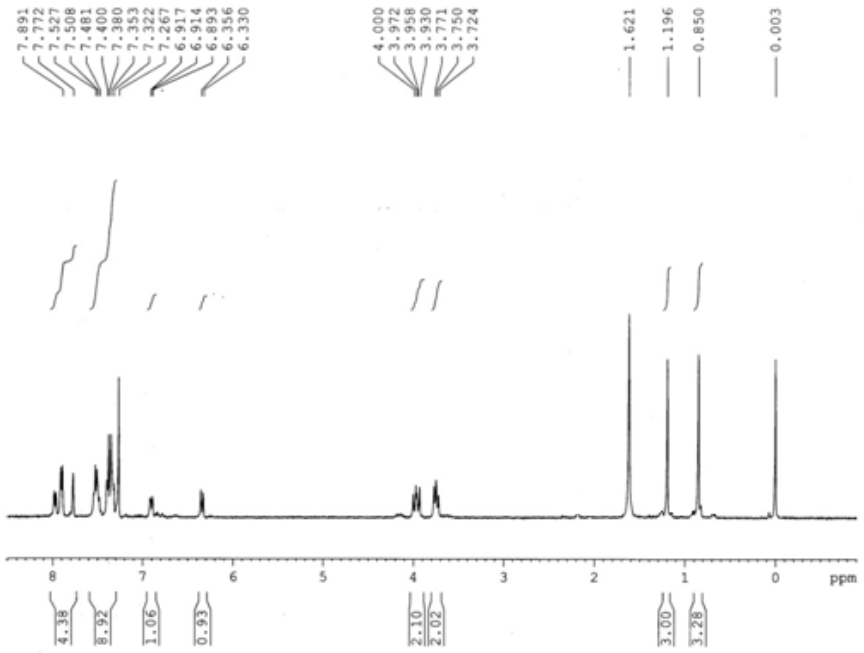



**Figure S45a**. $^{1}$H NMR spectrum of compound **(*Z*)-37**

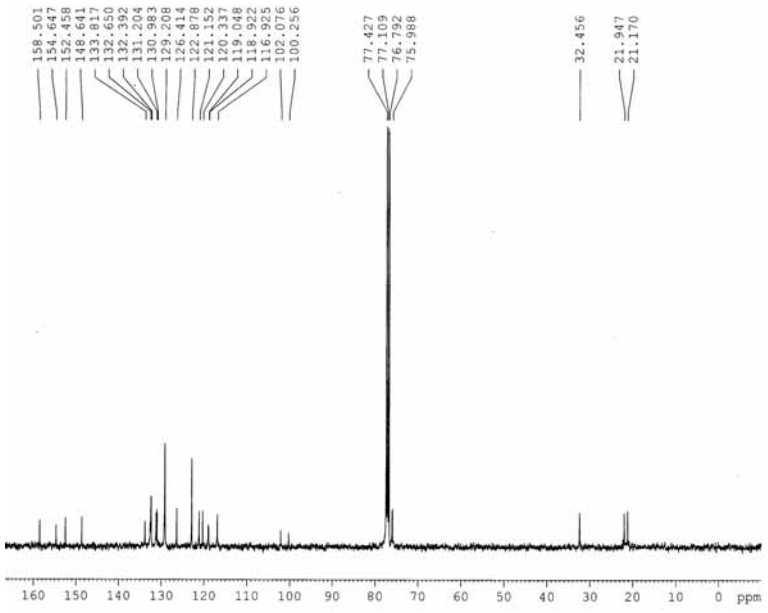



**Figure S45b**. $^{13}$C NMR spectrum of compound **(*Z*)-37**

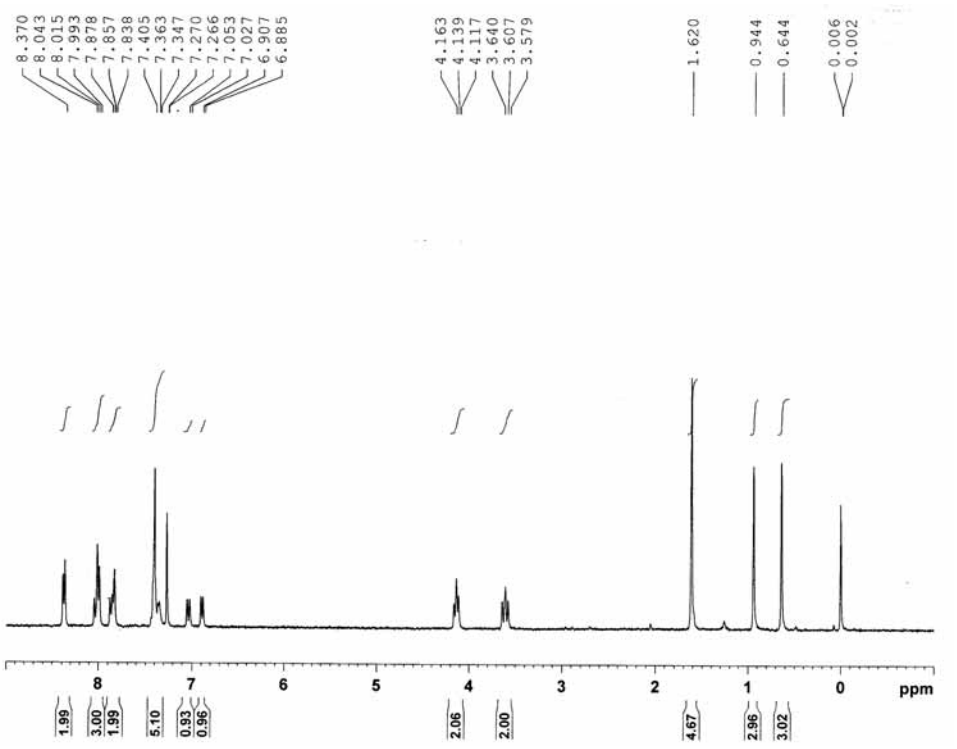



**Figure S46a**. $^{1}$H NMR spectrum of compound **(*E*)-38**

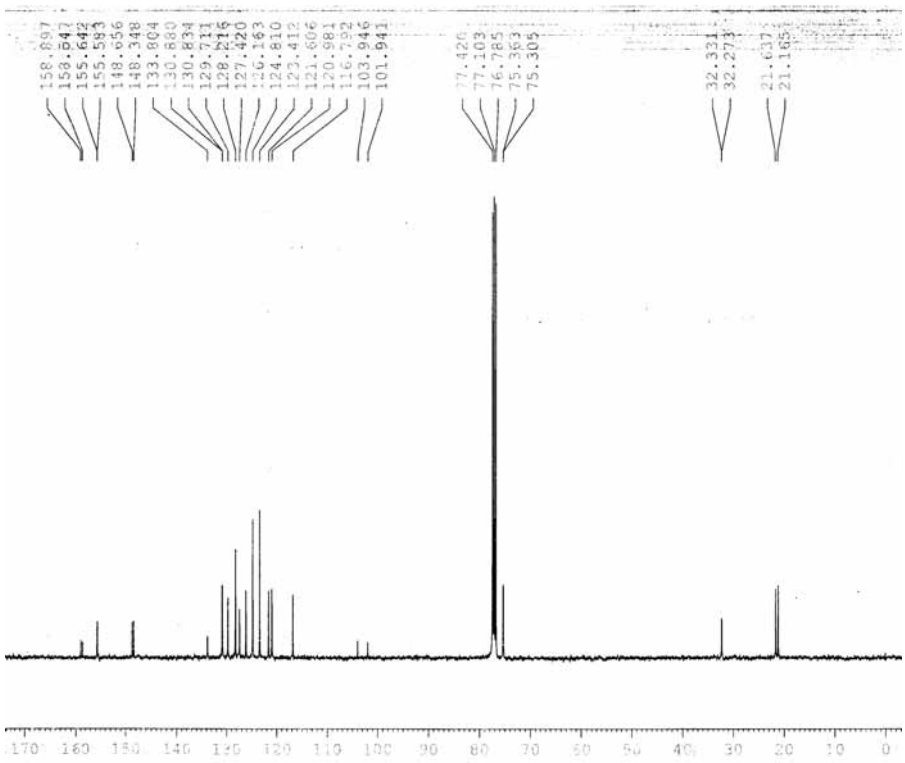



**Figure S46b**. $^{13}$C NMR spectrum of compound **(*E*)-38**

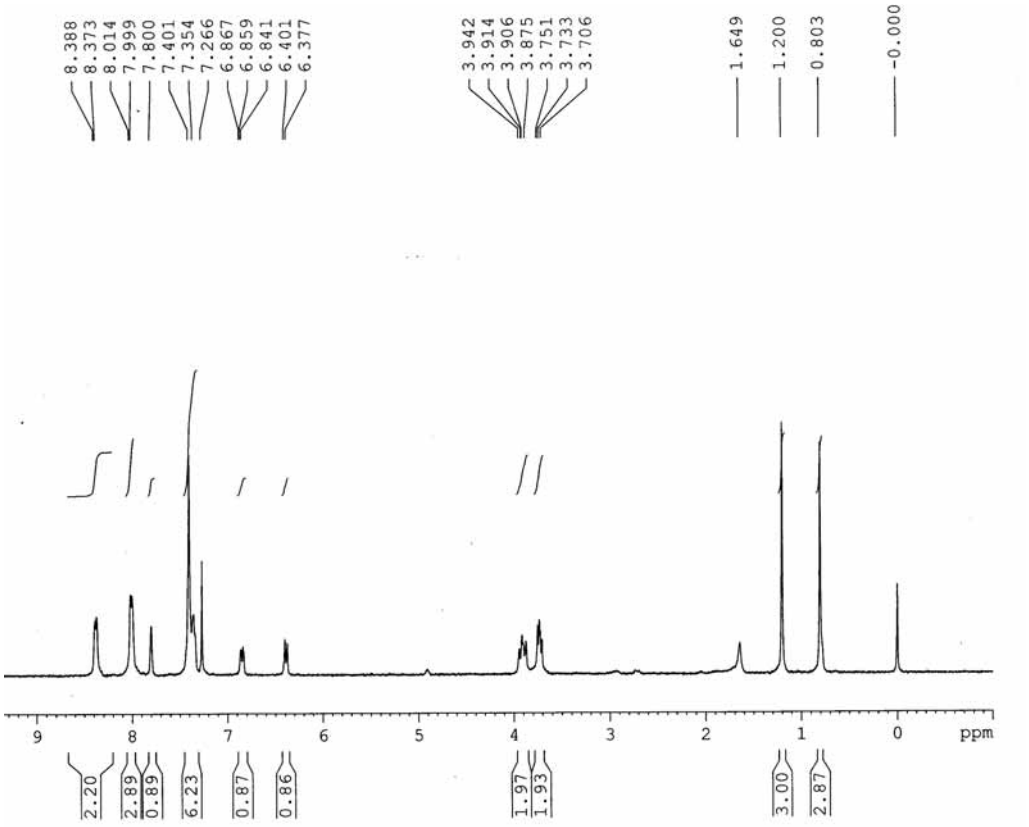



**Figure S47a**. $^{1}$H NMR spectrum of compound **(*Z*)-38**

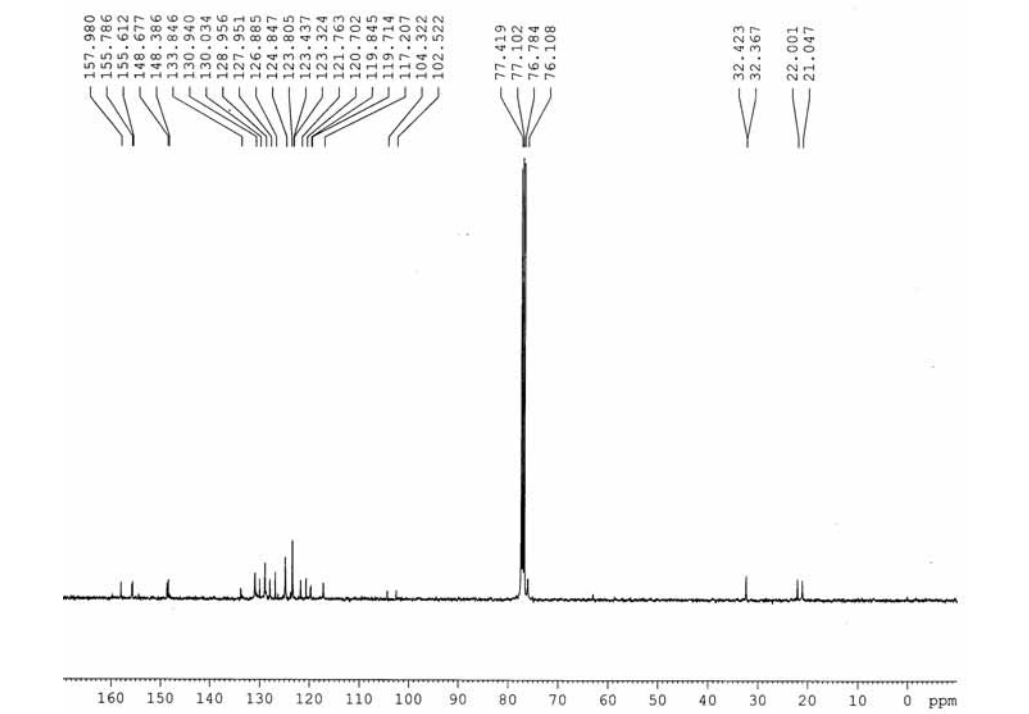



**Figure S47b**. $^{13}$C NMR spectrum of compound **(*Z*)-38**

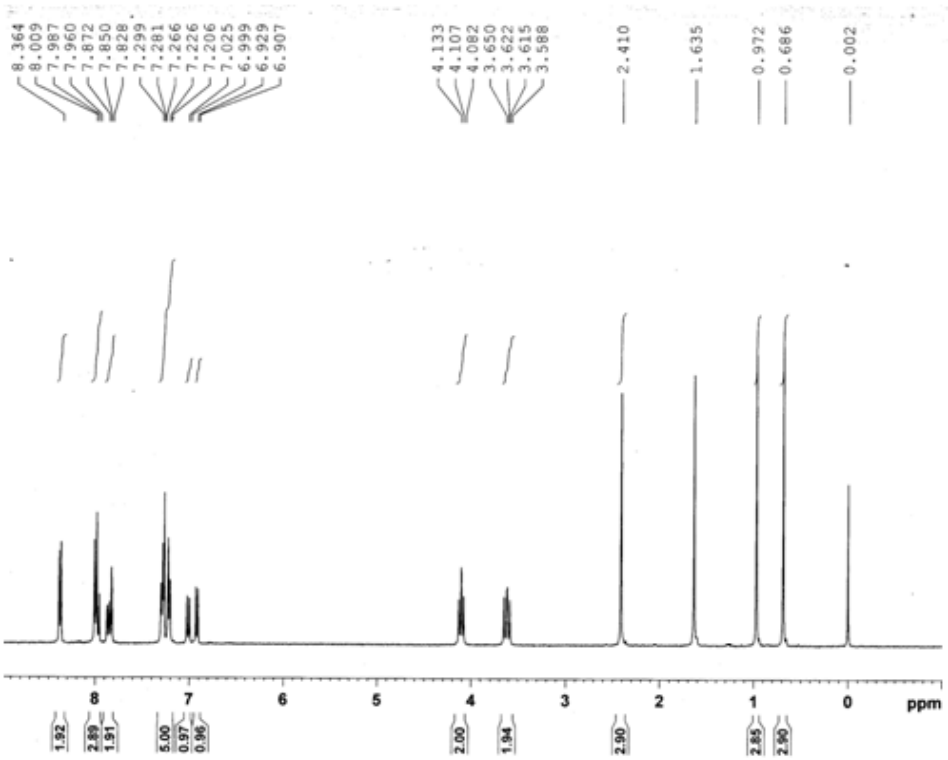



**Figure S48a**. $^{1}$H NMR spectrum of compound **(*E*)-39**

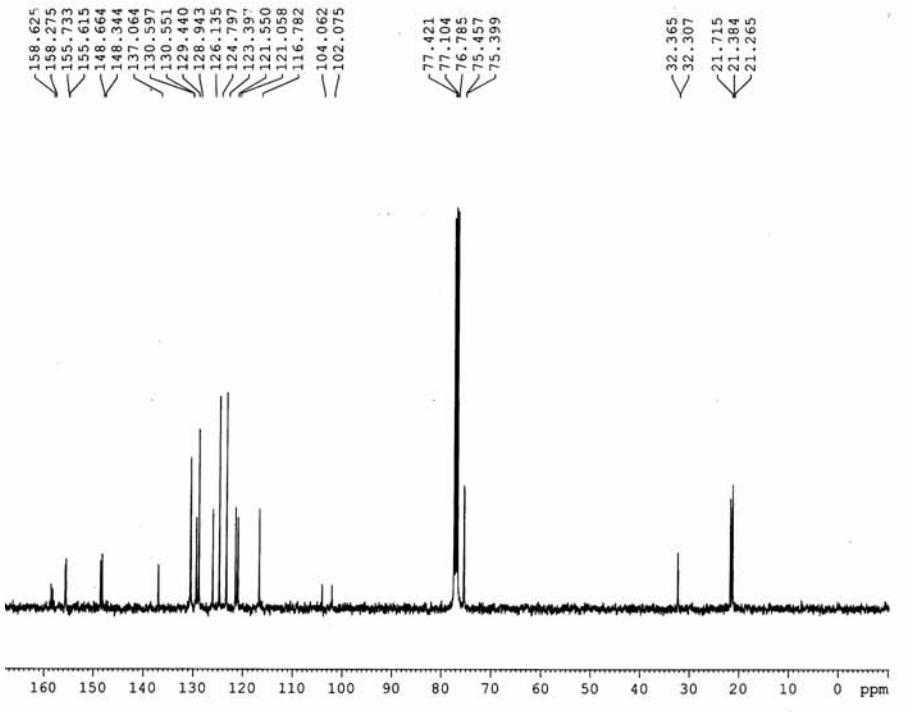



**Figure S48b**. $^{13}$C NMR spectrum of compound **(*E*)-39**

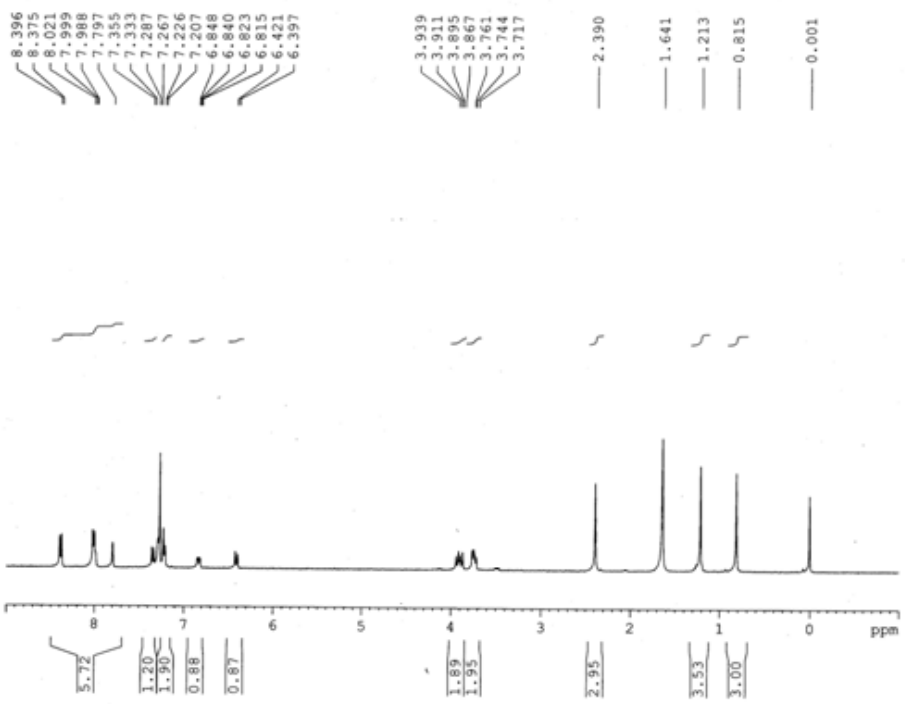



**Figure S49a**. $^{1}$H NMR spectrum of compound **(*Z*)-39**

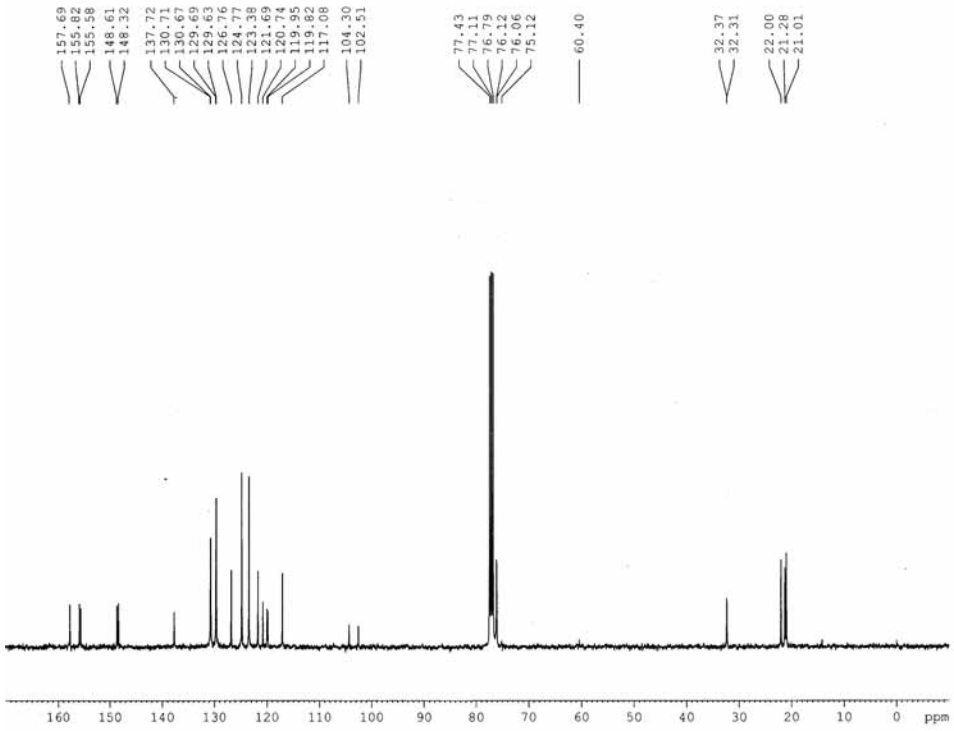



**Figure S49b**. $^{13}$C NMR spectrum of compound **(*Z*)-39**

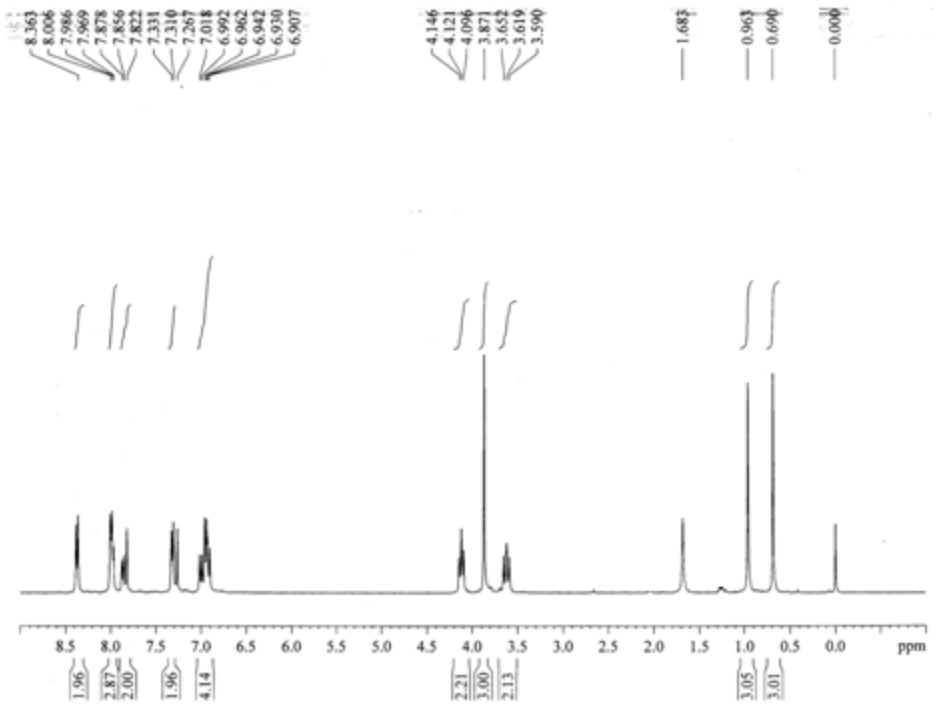



**Figure S50a**. $^{1}$H NMR spectrum of compound **(*E*)-40**

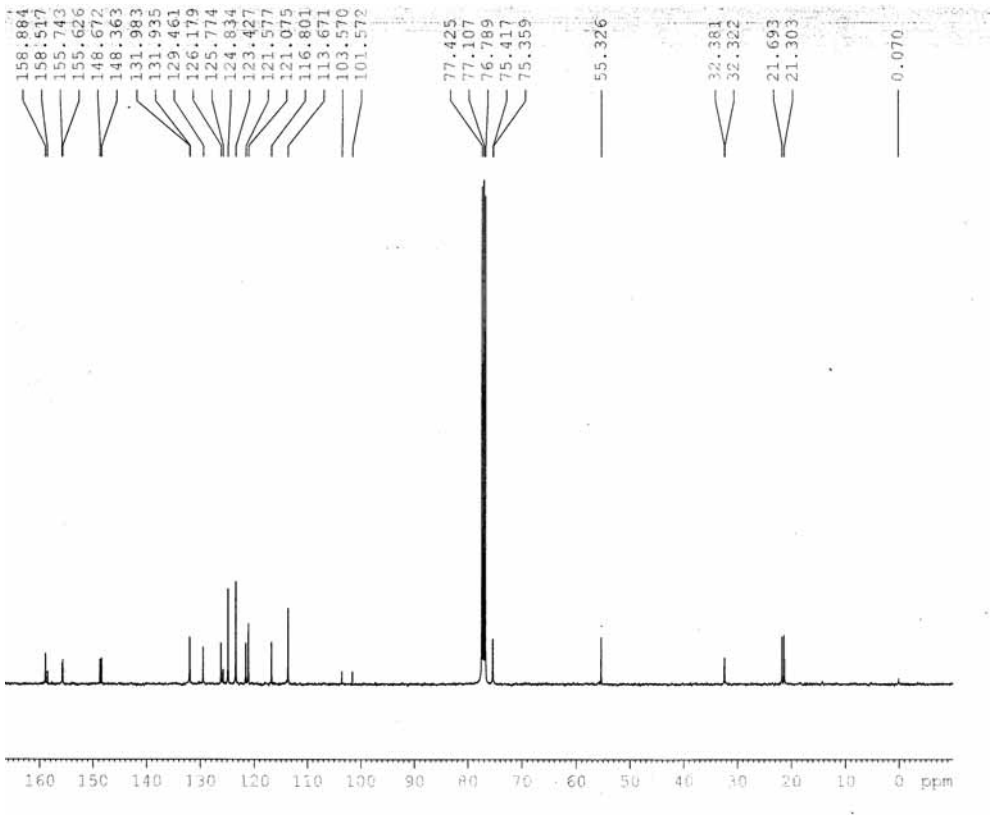



**Figure S50b**. $^{13}$C NMR spectrum of compound **(*E*)-40**

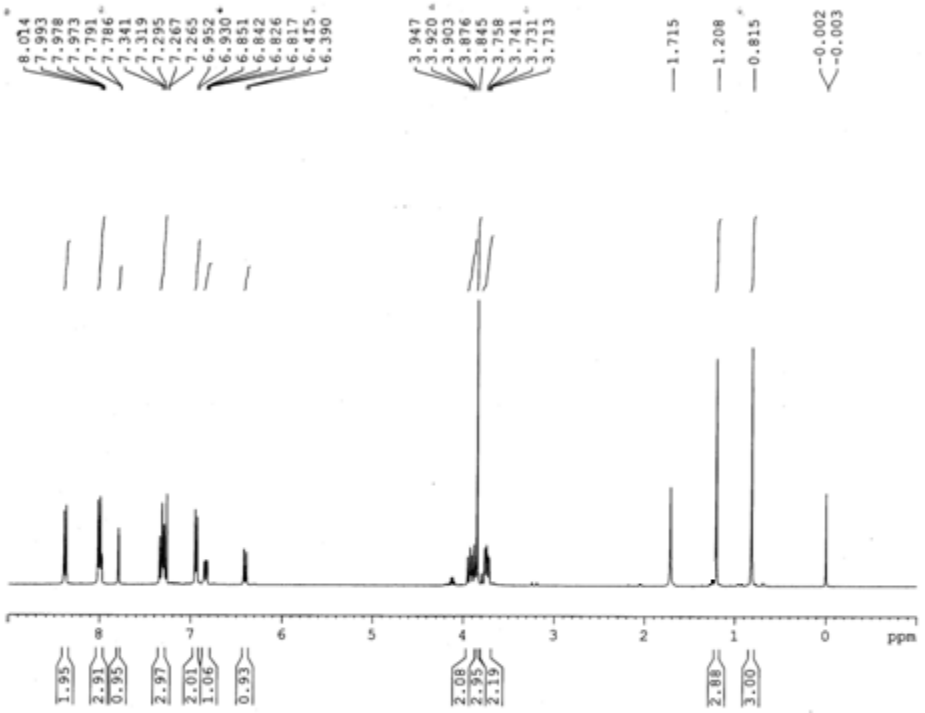



**Figure S51a**. $^{1}$H NMR spectrum of compound **(*Z*)-40**

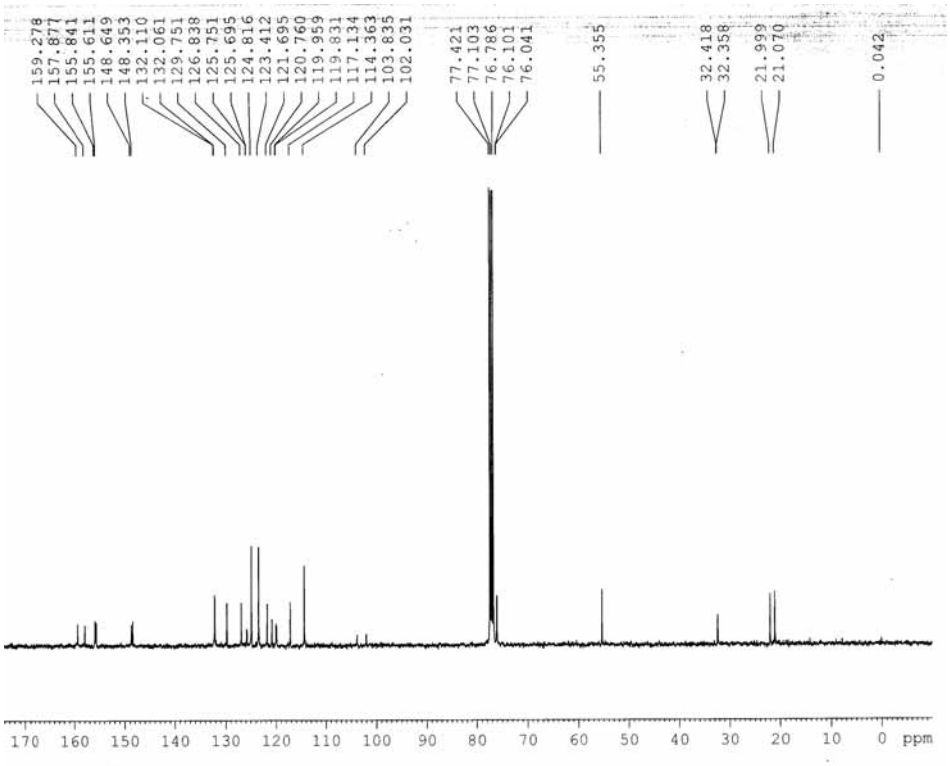



**Figure S51b**. $^{13}$C NMR spectrum of compound **(*Z*)-40**

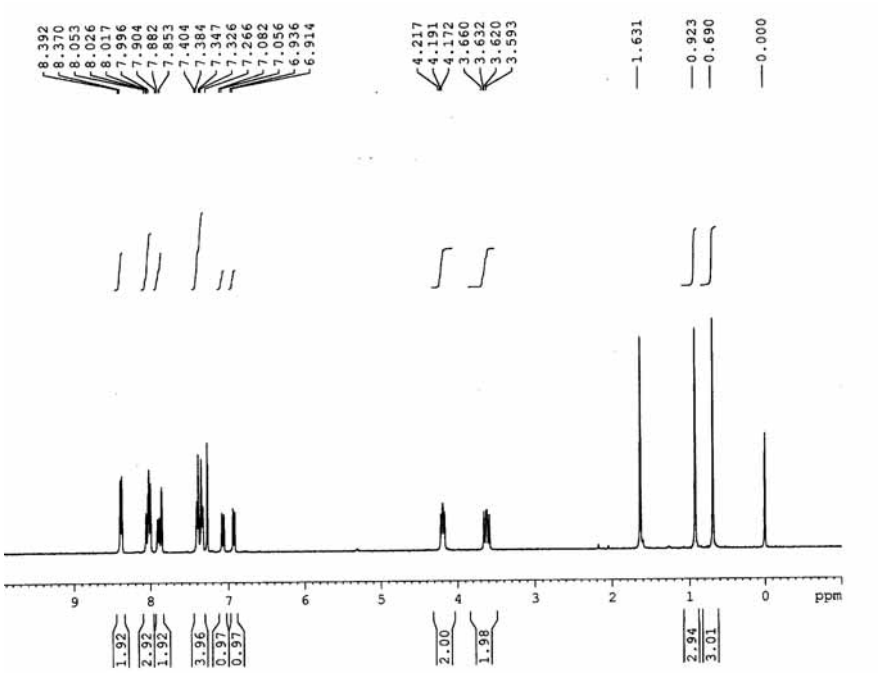



**Figure S52a**. $^{1}$H NMR spectrum of compound **(*E*)-41**

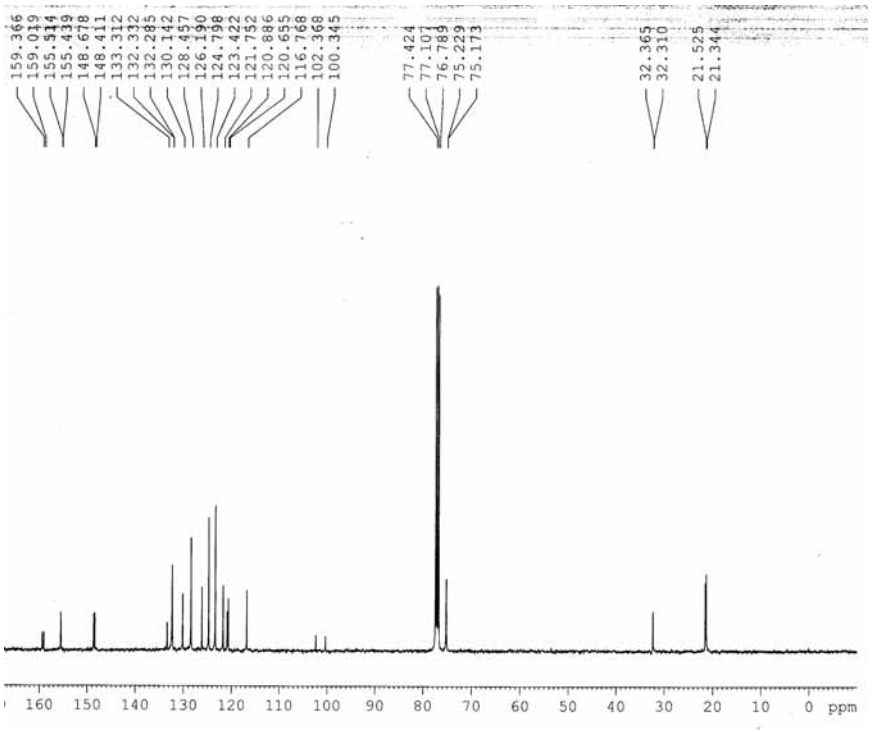



**Figure S52b**. $^{13}$C NMR spectrum of compound **(*E*)-41**

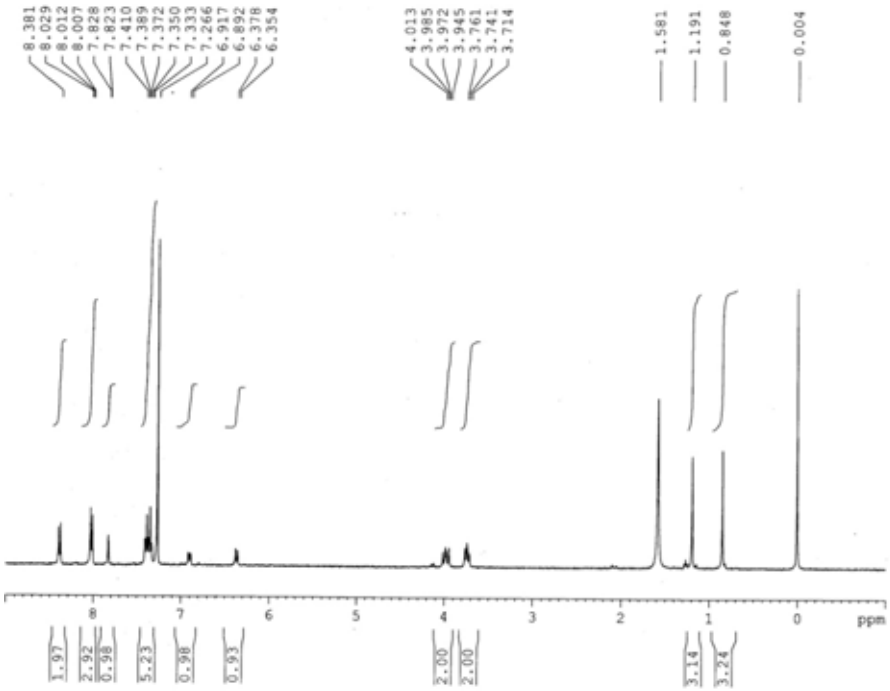



**Figure S53a**. $^{1}$H NMR spectrum of compound **(*Z*)-41**

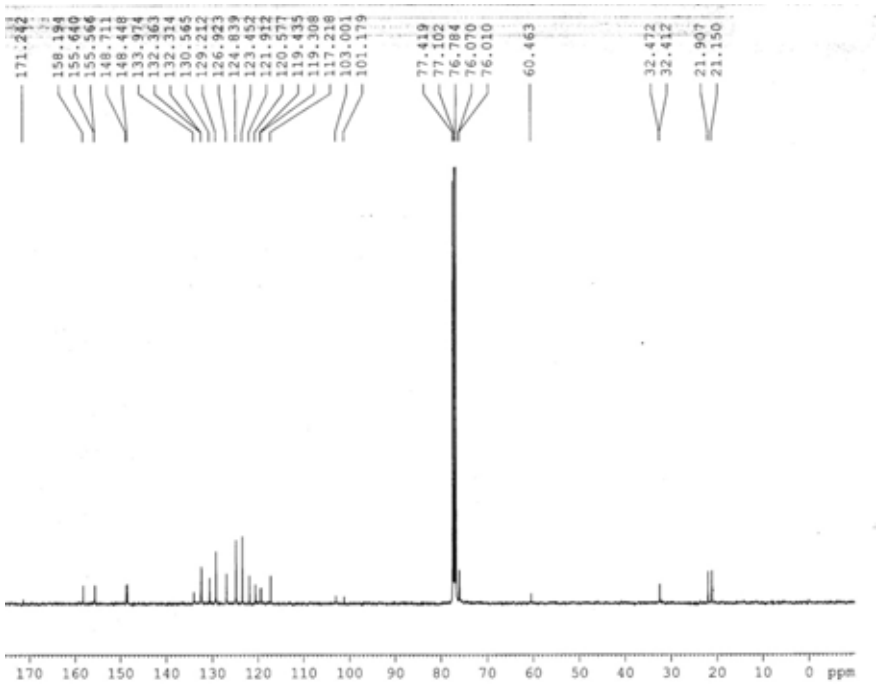



**Figure S53b**. $^{13}$C NMR spectrum of compound **(*Z*)-41**

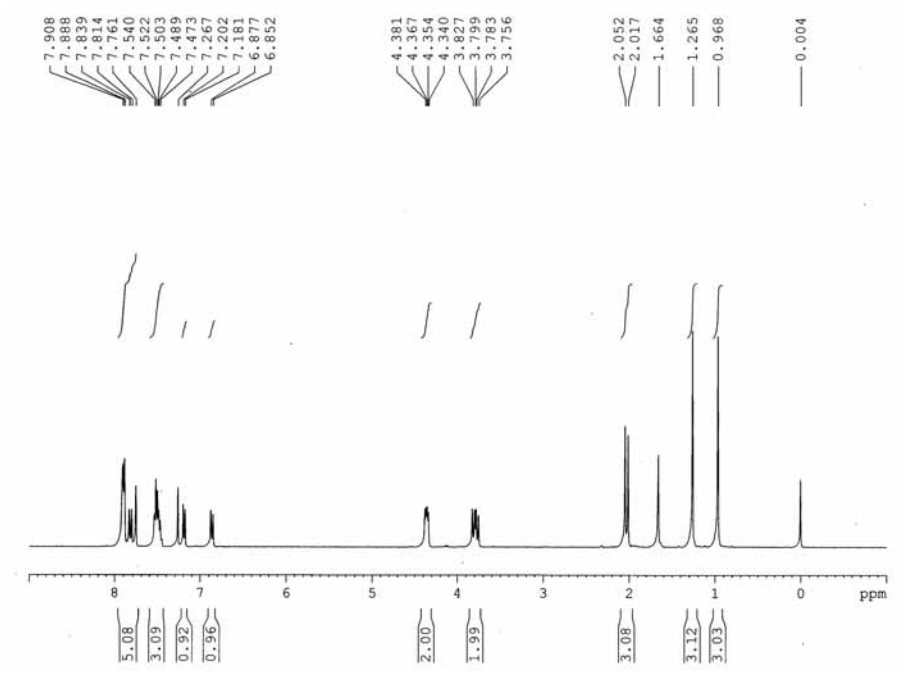



**Figure S54a**. $^{1}$H NMR spectrum of compound **(*E*)-42**

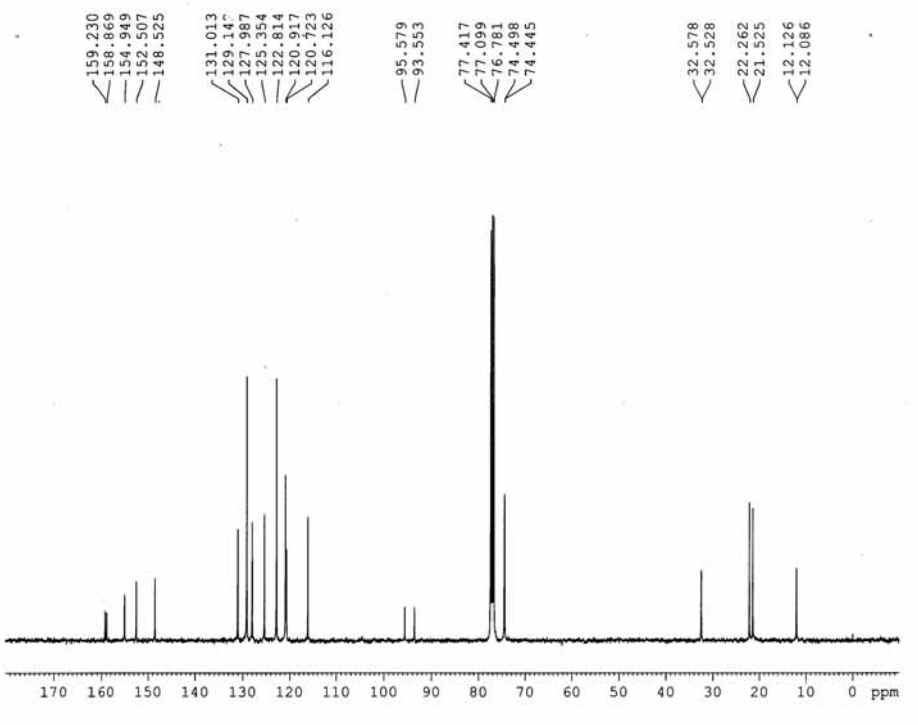



**Figure S54b**. $^{13}$C NMR spectrum of compound **(*E*)-42**

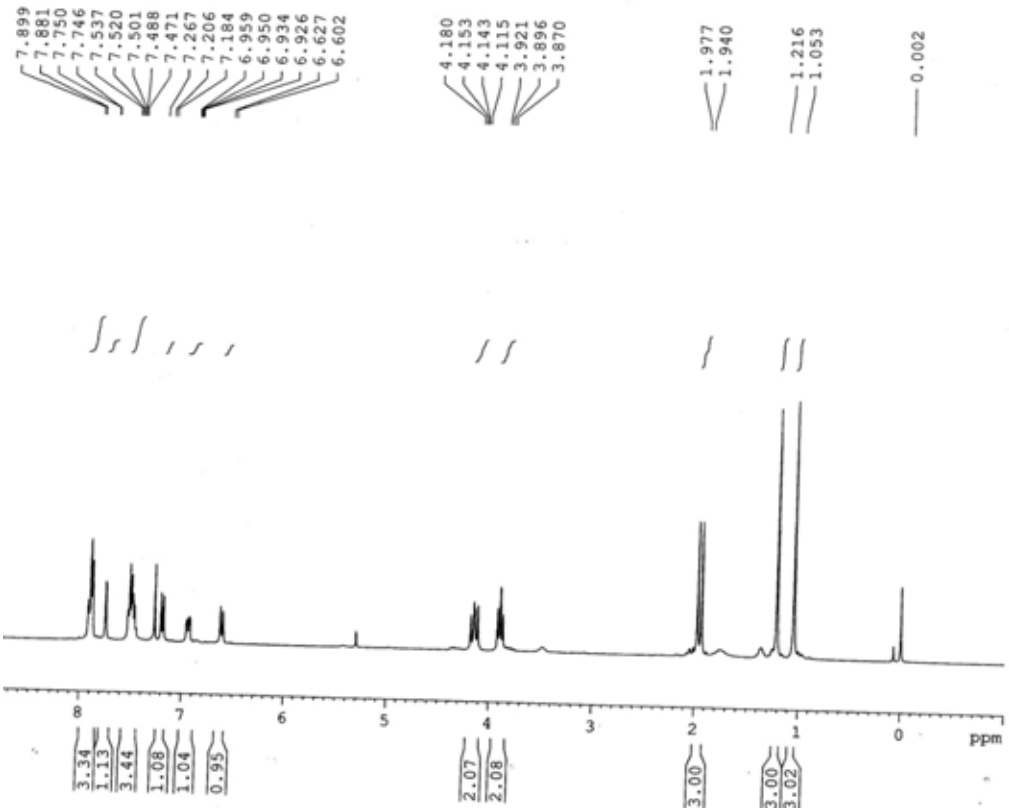



**Figure S55a**. $^{1}$H NMR spectrum of compound **(*Z*)-42**

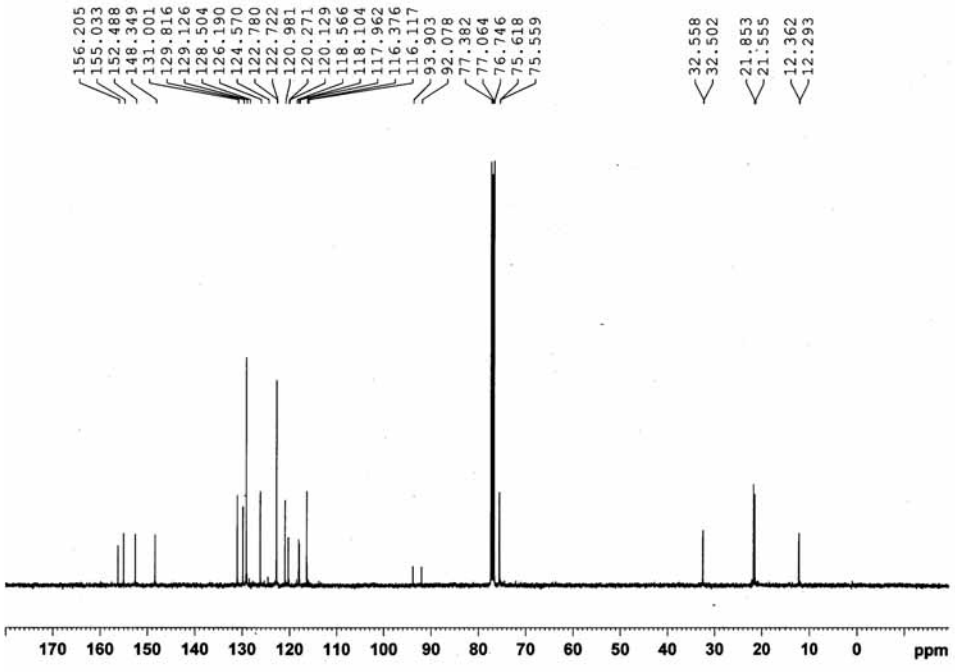



**Figure S55b**. $^{13}$C NMR spectrum of compound **(*Z*)-42**

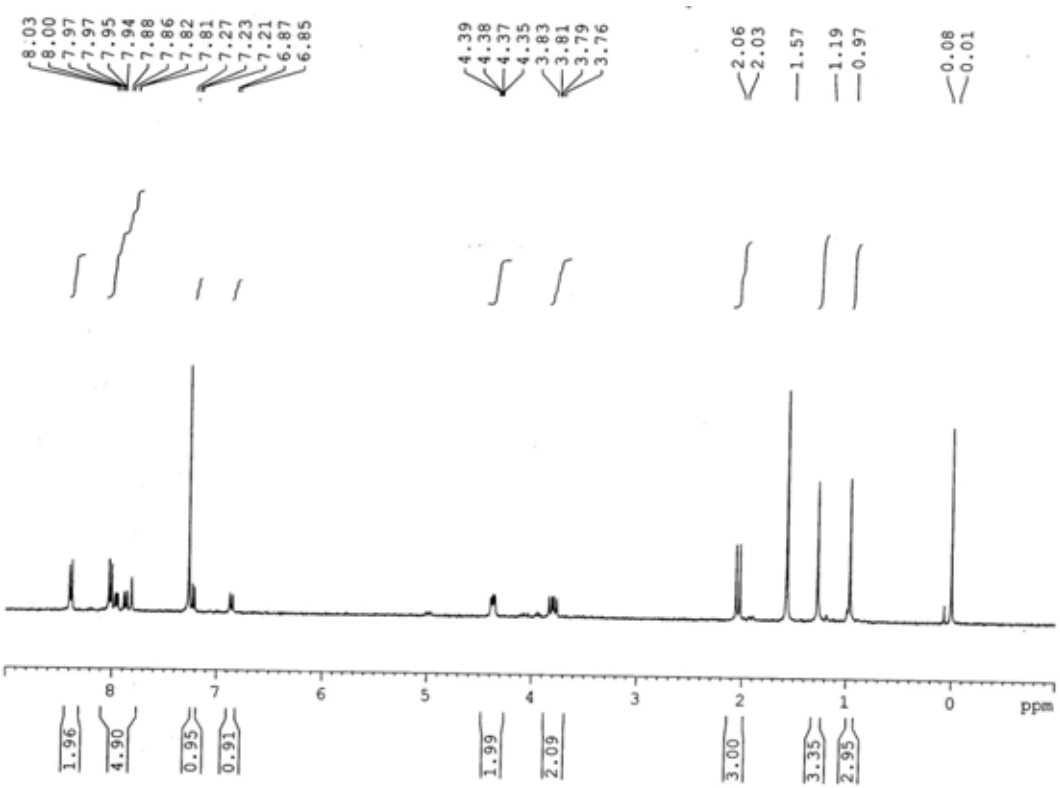



**Figure S56a**. $^{1}$H NMR spectrum of compound **(*E*)-43**

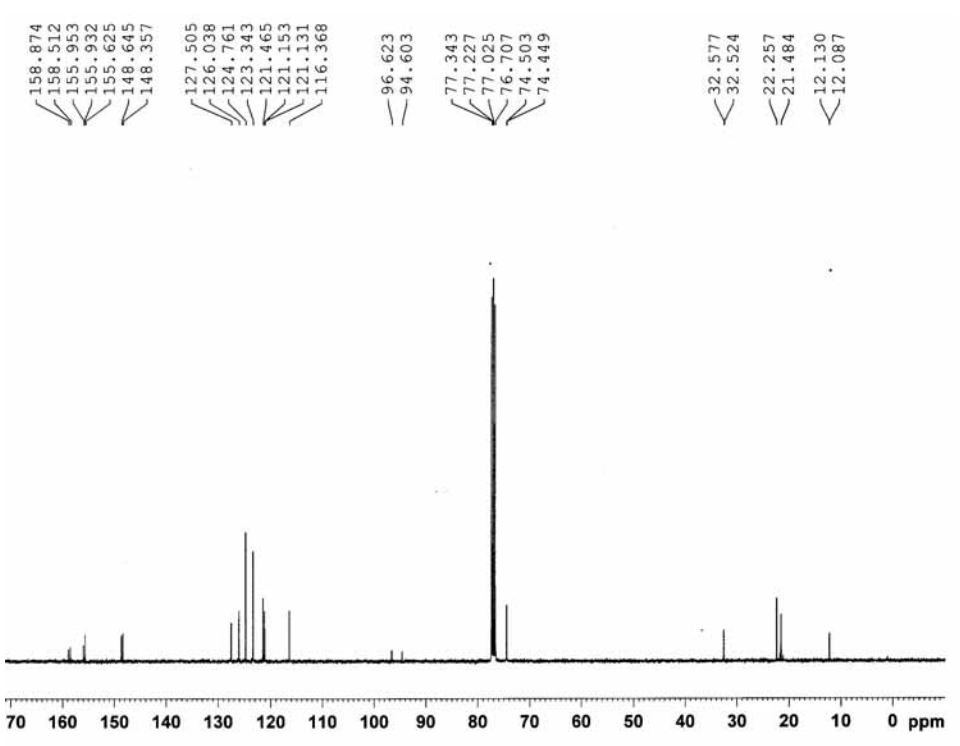



**Figure S56b**. $^{13}$C NMR spectrum of compound **(*E*)-43**

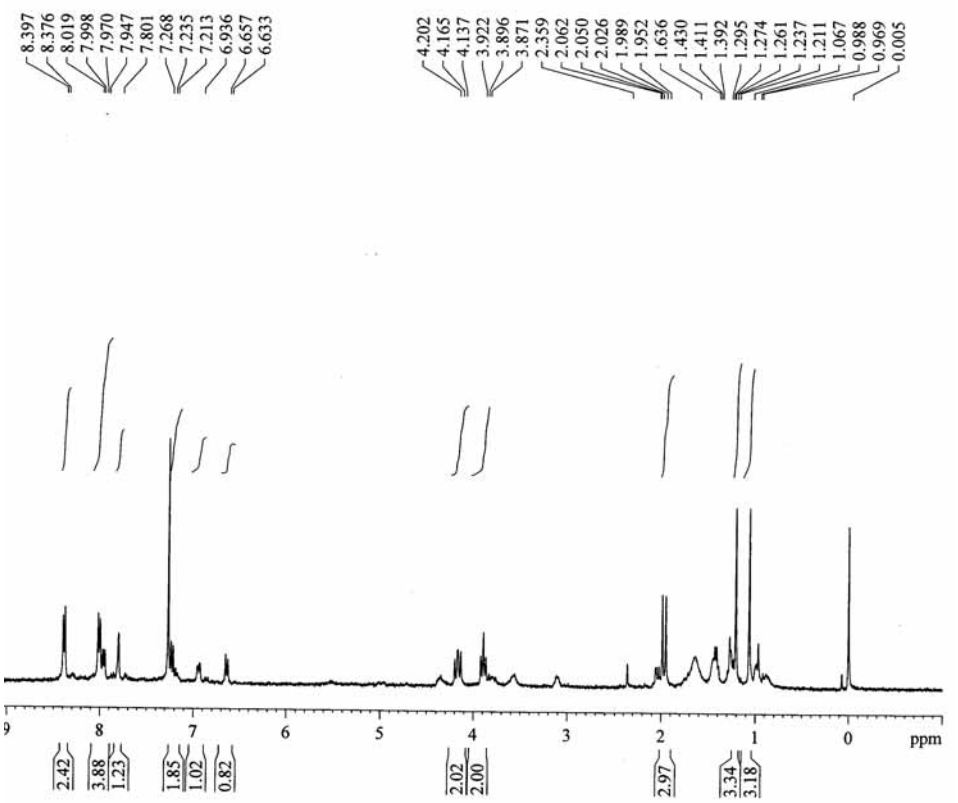



**Figure S57a**. $^{1}$H NMR spectrum of compound **(*Z*)-43**

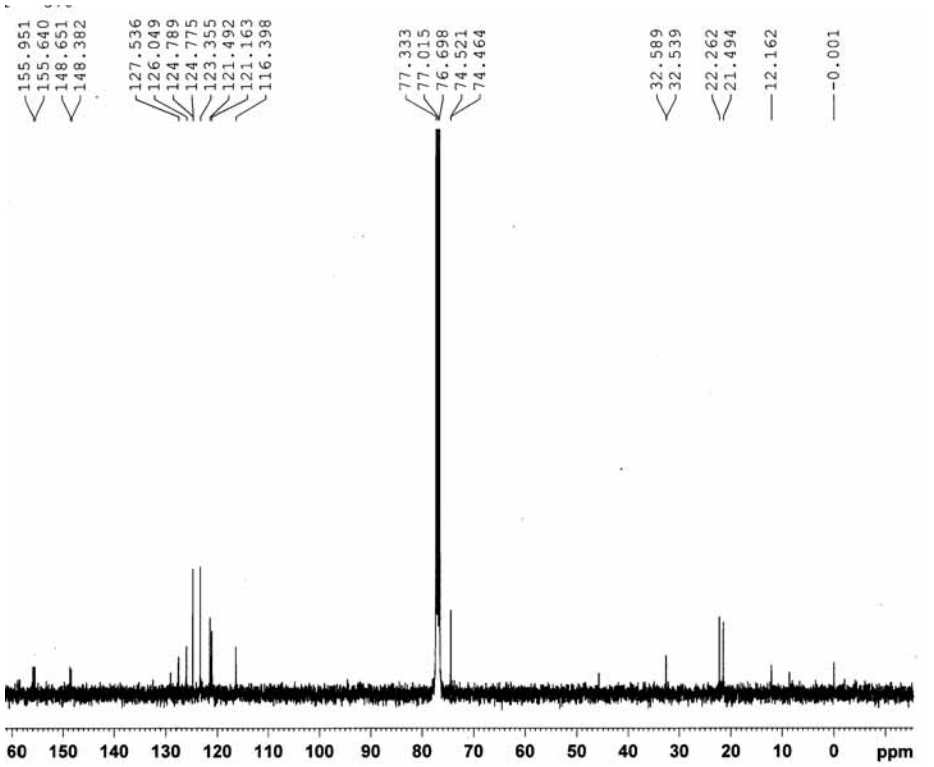



**Figure S57b**. $^{13}$C NMR spectrum of compound **(*Z*)-43**

## Reference

(1) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: Oxford, UK, **1986**.