*Supplementary Materials*

# New antineoplastic naphthohydroquinones attached to labdane and rearranged diterpene skeletons

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**Figure S18**: $^{1}H$ and $^{13}C$ NMR spectra for compound **16a**.

**Figure S19**: $^{1}H$ and $^{13}C$ NMR spectra for compounds **16a-c**.

**Figure S20**: $^{1}H$ and $^{13}C$ NMR spectra for compound **17**.

**Figure S21**: $^{1}H$ and $^{13}C$ NMR spectra for compound **18a**.

**Figure S22**: $^{1}H$ and $^{13}C$ NMR spectra for compounds **18b** and **18c**.

**Figure S23**: $^{1}H$ and $^{13}C$ NMR spectra for compound **18c**.

**Figure S24**: $^{1}H$ and $^{13}C$ NMR spectra for compounds **19**.

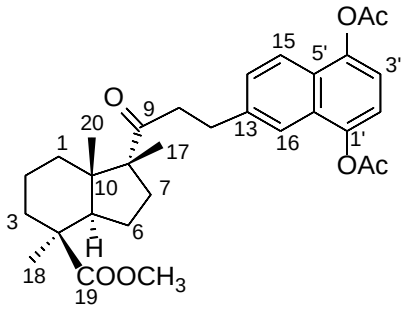
**Figure S25**: HMQC and HMBC experiments for compound **19**.

**Figure S26**: IR, $^{1}H$ and $^{13}C$ NMR spectra for compounds **20**.

**Figure S27**: $^{1}H$ and $^{13}C$ NMR spectra for compounds **21a**.

**Figure S28**: 1H and 13C NMR spectra for compounds **21c**.

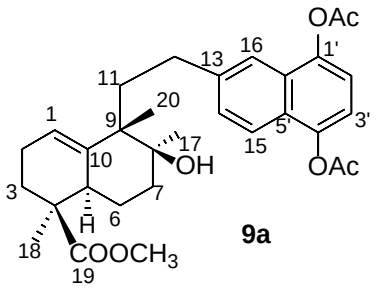
**Table S1**. Correlations and assignments for compound **8** (δ in ppm).




| δ $^{13}$C | TYPE* | HMQC, δ $^{1}$H (*J* in Hz) | HMBC, δ $^{1}$H (H number) | Assigned |
|---|---|---|---|---|
| 35.1 | $CH_2$ | 1.55 *m*, 0.65 *m* | 0.65 (20) | 1 |
| 36.8 | $CH_2$ | 2.06 *m*, 0.65 *m* | 1.15 (18) | 3 |
| 44.0 | C | -- | 1.15 (18) | 4 |
| 52.9 | CH | 1.65 *m* | 0.65 (20), 1.15 (18) | 5 |
| 23.1 | $CH_2$ | 2.10 *m*, 1.88 *m* | 1.65 (5) | 6 |
| 33.2 | $CH_2$ | 1.32 *m* | 1.17 (17) | 7 |
| 60.6 | C | -- | 1.17 (17), 0.65 (20) | 8 |
| 216.1 | C | -- | 1.17 (17), 2.97 (12b) 2.79 (11) | 9 |
| 47.0 | C | -- | 0.65 (20), 1.17 (17) | 10 |
| 43.2 | $CH_2$ | 2.79 *m* | -- | 11 |
| 30.4 | $CH_2$ | 3.09 *m*, 2.97 *m* | 7.63 (16) | 12 |
| 140.5 | C | -- | 7.77 (15) | 13 |
| 128.4 | CH | 7.38 *d* (8.6 Hz) | 7.63 (16) | 14 |
| 121.8 | CH | 7.77 *d* (8.6 Hz) | -- | 15 |
| 120.4 | CH | 7.63 *s* | 7.38 (14) | 16 |
| 20.1 | $CH_3$ | 1.17 *s* | -- | 17 |
| 28.3 | $CH_3$ | 1.15 *s* | -- | 18 |
| 178.1 | C | -- | 3.63 ($COO\underline{CH_3}$)<br>1.15 (18) | 19 |
| 14.8 | $CH_3$ | 0.65 *s* | -- | 20 |
| 143.9 | C | -- | 7.63 (16), 7.17 (2') | 1' |
| 116.9 | CH | 7.21 *d* (8.2 Hz) | -- | 2' |
| 117.8 | CH | 7.17 *d* (8.2 Hz) | -- | 3' |
| 144.3 | C | -- | 7.77 (15), 7.21 (2') | 4' |
| 126.2 | C | -- | 7.63 (16), 7.17 (3'), 7.38 (14) | 5' |
| 127.7 | C | -- | 7.21 (2'), 7.77 (15) | 6' |
| 169.3 169.2 | C | -- | 2.48, 2.44 [OAc ($2xCH_3$)] | OAc (2xCO) |
| 21.0 | $CH_3$ | 2.44 *s*, 2.48 *s* | -- | OAc ($2xCH_3$) |
| 51.1 | $CH_3$ | 3.63 *s* | -- | $COO\underline{CH_3}$ |

* Carbon type according to DEPT experiment

**Table S2**. Correlations and assignments for compound **9a** (δ in ppm).

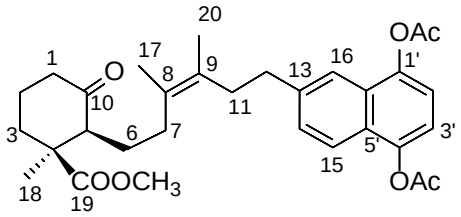



**9a**

| δ $^{13}$C | TYPE* | HMQC, δ $^{1}$H (*J* in Hz) | HMBC, δ $^{1}$H (H number) | Assigned |
|---|---|---|---|---|
| 120.5 | CH | 5.52 m | -- | 1 |
| 22.3 | $CH_2$, $CH_3$ | 1.37 s | -- | 2, 18 |
| 24.7 | $CH_2$ | -- | 1.37 (18) | 3 |
| 44.4 | C | -- | 1.37 (18) | 4 |
| 41.4 | CH | 2.15 m | 1.37 (18) | 5 |
| 37.3 | $CH_2$ | 1.55 m | 1.13 (17) | 7 |
| 75.9 | C | -- | 1.13 (17) | 8 |
| 48.5 | C | -- | 1.15 (20) | 9 |
| 140.9 | C | -- | 1.15 (20) | 10 |
| 35.7 | $CH_2$ | 2.11 m | 1.15 (20) | 11 |
| 30.9 | $CH_2$ | 2.46 m | 7.59 (16), 7,39 (14) | 12 |
| 142.3 | C | -- | 7.78 (15) | 13 |
| 128.5 | CH | .39 *dd* (8.8, 1.6 Hz | 7.59 (16) | 14 |
| 121.7 | CH | 7.78 *d* (8.8 Hz) | -- | 15 |
| 119.8 | CH | 7.59 *bs* | 7.39 (14) | 16 |
| 24.0 | $CH_3$ | 1.13 *s* | -- | 17 or 20 |
| 117.7 | C | -- | 3.70 ($COO\underline{CH_3}$) | 19 |
| 16.8 | $CH_3$ | 1.15 *s* | 1.37 (18) | 20 or 17 |
| 143.8 | C | -- | | 1’ |
| 116.7 | CH | 7.16 *d* (8.4 Hz) | 7.59 (16), 7.21 (3’) | 2’ |
| 117.7 | CH | 7.21 *d* (8.4 Hz) | -- | 3’ |
| 144.3 | C | -- | -- | 4’ |
| 125.2 | C | -- | 7.78 (15), 7.16 (2’) | 5’ |
| 127.8 | C | -- | 7.59 16, 7.21 (3’), 7.39 (14) | 6’ |
| 169.4 | C | -- | 2.48, 2.44 [OAc ($2xCH_3$)] | OAc (2xCO) |
| 21.0 | $CH_3$ | 2.45 *s*, 2.46 *s* | -- | OAc ($2xCH_3$) |
| 51.5 | $CH_3$ | 3.70 *s* | -- | $COO\underline{CH_3}$ |

* Carbon type according to DEPT experiment

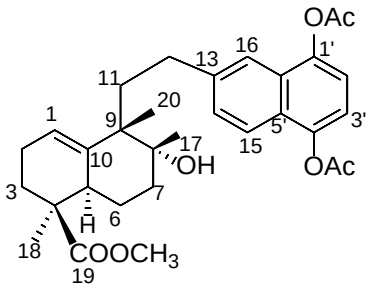
**Table S3.** Correlations and assignments for compound **10** (δ in ppm).




| δ $^{13}$C | TYPE* | HMQC, δ $^{1}$H (*J* in Hz) | HMBC, δ $^{1}$H (H number) | Assigned |
|---|---|---|---|---|
| 18.3 | $CH_3$ | 1.68 s | - | 17 |
| 18.5 | $CH_3$ | 1.70 s | - | 20 |
| 21.0 | $CH_3$ | 2.44 s; 2.48 s | - | OAc (Me) |
| 24.2 | $CH_3$ | 1.28 s | - | 18 |
| 33.3 | $CH_2$ | - | 1.68 (17) | 7 |
| 33.8 | $CH_2$ | - | 1.28 (18) | 3 |
| 35.4 | $CH_2$ | 2.79 m | 7.42 (14), 7.63 (16) | 12 |
| 36.2 | $CH_2$ | - | 1.70 (20), 2.79 (12) | 11 |
| 50.4 | C | - | 1.28 (18) | 4 |
| 51.7 | $CH_3$ | 3.61 s | - | OMe |
| 58.0 | CH | - | 1.28 (18) | 5 |
| 116.6 | CH | 7.20 d | - | 3´ |
| 117.6 | CH | 7.16 d | - | 2´ |
| 119.9 | CH | 7.63 bs | 7.42 (14), 2.79 (12) | 16 |
| 121.5 | CH | 7.78 d | - | 15 |
| 126.1 | C | - | 7.20 (3´), 7.63 (16), 7.42 (14) | 5´ |
| 127.8 | C | - | 1.70 (20) | 8 |
| 127.8 | C | - | 7.16 (2´), 7.78 (15) | 6´ |
| 127.9 | C | - | 1.68 (17), 2.79 (12) | 9 |
| 128.5 | CH | 7.42 dd | 7.63 (16), 2.79 (12) | 14 |
| 141.5 | C | - | 7.78 (15), 2.79 (12) | 13 |
| 144.0 | C | - | 7.20 (3´), 7.63 (16) | 1´ |
| 144.3 | C | - | 7.16 (2´), 7.78 (15) | 4´ |
| 169.2;169.4 | C | - | 2.44;2.48 (OAc-Me) | OAc (CO) |
| 175.5 | C | - | 1.28 (18), 3.61 (OMe) | 19 |

* Carbon type according to DEPT experiment

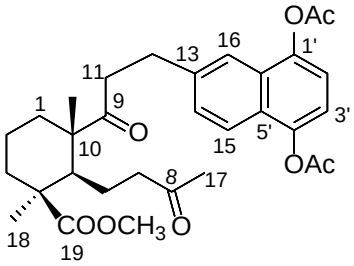
**Table S4.** Correlations and assignments for compound **11** (δ in ppm).




| δ $^{13}$C | TYPE* | HMQC, δ $^{1}$H (*J* in Hz) | HMBC, δ $^{1}$H (H number) | Assigned |
|---|---|---|---|---|
| 122.4 | CH | 5.61 m | 2.25 (5) | 1 |
| 24.3 | $CH_2$ | -- | 1.40 (18) | 3 |
| 44.4 | C | -- | 1.40 (18) | 4 |
| 41.4 | CH | 2.25 m | 1.40 (18) | 5 |
| 27.4 | $CH_2$ | 1.39 m | -- | 6 or 2 |
| 35.4 | $CH_2$ | 1.71 m, 1.52 m | 1.11 (17) | 7 |
| 75.0 | C | -- | 1.11 (17), 1.19 (20) | 8 |
| 49.0 | C | -- | 1.11 (17), 1.19 (20) | 9 |
| 140.8 | C | -- | 1.64 (11b), 1.19 (20) | 10 |
| 38.0 | $CH_2$ | 2.09 m, 1.64 m | 1.19 (20) | 11 |
| 31.4 | $CH_2$ | 2.64 m, 2.43 m | 7.59 (16), 7.39 (14) | 12 |
| 141.8 | C | -- | 6.62 (12a), 2.43 (12b), 7.80 (15) | 13 |
| 128.2 | CH | 7.39 *dd* (8.6, 1.6 Hz) | 6.62 (12a), 2.43 (12b), 7.59 (16) | 14 |
| 121.9 | CH | 7.80 *d* (8.6 Hz) | -- | 15 |
| 119.8 | CH | 7.59 *bs* | 6.62 (12a), 2.43 (12b), 7.39 (14) | 16 |
| 17.2 | $CH_3$ | 1.11 *s* | -- | 17 |
| 22.4 | CH, $CH_3$ | 1.40 *s* | -- | 2 or 6, 18 |
| 177.5 | C | -- | 1.40 (18), 3.72 (COO$\underline{CH_3}$) | 19 |
| 22.7 | $CH_3$ | 1.19 *s* | -- | 20 |
| 143.9 | C | -- | 7.59 (16), 7.18 (3') | 1´ |
| 116.8 | CH | 7.23 *d* (8.2 Hz) | -- | 2´ |
| 117.8 | CH | 7.21 *d* (8.2 Hz) | -- | 3´ |
| 144.3 | C | -- | 7.80 (15), 7.23 (2') | 4´ |
| 126.1 | C | -- | 7.59 (16), 7.39 (14), 7.18 (3') | 5´ |
| 127.8 | C | -- | 7.23 (2'), 7.80 (15) | 6´ |
| 169.3 | C | -- | 2.47, 2.45 [OAc (2x$CH_3$)] | OAc (2x CO) |
| 20.9 | $CH_3$ | 2.47 *s*, 2.45 *s* | -- | OAc (2x$CH_3$) |
| 51.5 | $CH_3$ | 3.72 *s* | -- | $OCH_3$ |

* Carbon type according to DEPT experiment

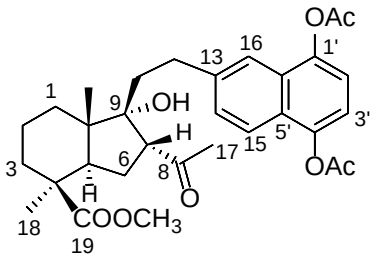
**Table S5.** Correlations and assignments for compound **14** (δ in ppm).




| δ $^{13}$C | TYPE* | HMQC, δ $^{1}$H (*J* in Hz) | HMBC, δ $^{1}$H (H number) | Assigned |
|---|---|---|---|---|
| 18.8 | $CH_2$,$CH_3$ | 56 m, 1.11 m, 1.0( | -- | 2, 20 |
| 34.5 | $CH_2$ | 8 m, 1.61 m, 1.25 | 1.12 (18), 1.00 (20) | 1, 3 |
| 48.0 | CH | 1.99 m | 1.12 (18), 1.00 (20) | 5 |
| 23.3 | $CH_2$ | -- | 2.47 (7b) | 6 |
| 46.1 | C, $CH_2$ | 2.51 m, 2.47 m | 1.99 (5), 1.12 (18) | 4,7 |
| 208.5 | C | -- | 2.04 (17), 2.47 (7b) | 8 |
| 214.7 | C | -- | 1.00 (20); 3.03, 2.89 (11/12) | 9 |
| 52.6 | C | 3.03 m, 2.89 m | 1.00 (20) | 10 |
| 39.9 | $CH_2$ | 3.03 m, 2.89 m | 3.03 (12a) | 11 |
| 30.5 | $CH_2$ | -- | 7.63 (16), 7.39 (14), 2.89 (11b) | 12 |
| 140.5 | C | .39 *dd* (8.8, 1.3 H: | 7.78 (15); 3.03, 2.89 (11/12) | 13 |
| 128.3 | CH | 7.78 *d* (8.8 Hz) | 7.63 (16), 3.03 (12a) | 14 |
| 122.0 | CH | 7.63 *bs* | -- | 15 |
| 120.4 | CH | 2.04 *s* | 7.39 (14), 3.03 (12a | 16 |
| 29.8 | $CH_3$ | 1.12 *s* | -- | 17 |
| 27.0 | $CH_3$ | | -- | 18 |
| 177.7 | C | | 3.64 (COO$\underline{CH_3}$), 1.12 (18) | 19 |
| 144.0 | C | | 7.63 (16) | 1´ |
| 117.1 | CH | 7.21 *d* (8.3 Hz) | -- | 2´ |
| 118.0 | CH | 7.16 *d* (8.3 Hz) | -- | 3´ |
| 144.4 | C | -- | 7.78 (15) | 4´ |
| 126.3 | C | | 7.63 (16), 7.39 (14), 7.16 (3') | 5´ |
| 127.8 | C | | 7.78 (15); 7.21 (2') | 6´ |
| 169.5 | C | | 2.47, 2.44 [OAc (2x $CH_3$)] | OAc (2xCO) |
| 21.1 | $CH_3$ | 2.47 *s*, 2.44 *s* | | OAc (2x$CH_3$) |
| 51.6 | $CH_3$ | 3.64 *s* | | $OCH_3$ |

* Carbon type according to DEPT experiment

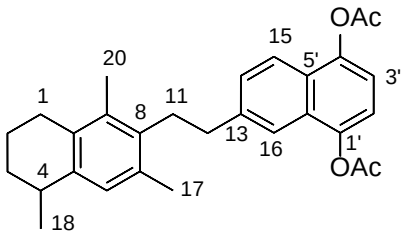
**Table S6.** Correlations and assignments for compound **15** (δ in ppm).




| δ $^{13}$C | TYPE* | HMQC, δ $^{1}$H (*J* in Hz) | HMBC, δ $^{1}$H (H number) | Assigned |
|---|---|---|---|---|
| 30.4 | $CH_2$ | 1.37 *m*, 1.37 *m* | 0.70 (20) | 1 |
| 19.9 | $CH_2$ | 1.57 *m*, 184 *m* | 1.37 (1b) | 2 |
| 37.2 | $CH_2$ | 1,01 *m*, 2.21 *m* | 1.20 (18), 1.37 (1b) | 3 |
| 43.9 | C | -- | 1.20 (18), 1.57 (2b), 2,32 (5) | 4 |
| 51.8 | CH | 2.32 *dd* (8.7, 11.9 Hz) | 0.70 (20), 1.20 (18), 1.37 (1b) | 5 |
| 27.9 | $CH_2$ | 1.81 *m*, 2.76 *m* | 2.32 (5), 2.96 (7) | 6 |
| 53.2 | CH | 2.96 *m* | 2.22 (17), 5.34 (OH) | 7 |
| 216.1 | C | -- | 1.81 (6b), 2.22 (17), 2.96 (7) | 8 |
| 84.3 | C | -- | 0.70 (20), 5.34 (OH) | 9 |
| 49.2 | C | -- | 7 (1b), 2.32 (5), 0.70 (20), 5.34 (C | 10 |
| 38.8 | $CH_2$ | 1.87 *m* | -- | 11 |
| 31.3 | $CH_2$ | 2.66 *m*, 2,92 *m* | 1.87 (11), 7.36 (14), 7.60 (16) | 12 |
| 141.6 | C | -- | 2.92 (12a), 2.66 (12b), 7.76 (15) | 13 |
| 128.3 | CH | 7.36 *dd* (8.6, 1.4 Hz) | 7.60 (16) | 14 |
| 121.7 | CH | 7.78 *d* (8.6 Hz) | 7.36 (14) | 15 |
| 119.9 | CH | 7.60 *bs* | 7.36 (14) | 16 |
| 31.5 | $CH_3$ | 2.22 *s* | -- | 17 |
| 28.2 | $CH_3$ | 1.20 *s* | 1.01 (3b), 1.37 (1b), | 18 |
| 177.8 | C | -- | .20 (18), 3.68 ($COOCH_3$), 2.32 (5 | 19 |
| 14.9 | $CH_3$ | 0.70 *s* | 1.37 (1b), 2.32 (5) | 20 |
| 143.9 | C | -- | 7.20 (2') 7.76 (15) | 1´ |
| 116.7 | CH | 7.20 *d* (8.3 Hz) | 7.15 (3') | 2´ |
| 117.7 | CH | 7.15 *d* (8.3 Hz) | 7.20 (2') | 3´ |
| 144.3 | C | -- | 7.20 (2') 7.76 (15) | 4´ |
| 126.1 | C | -- | 7.15 (3'), 7.36 (14), 7.60 (16) | 5´ |
| 127.8 | C | -- | 7.20 (2') 7.76 (15) | 6´ |
| 169.3,169.2 | C | -- | 2.44, 2.47 [OAc (2x$CH_3$)] | OAc (2xCO) |
| 20.9,21.0 | $CH_3$ | 2.47 *s*, 2.44 *s* | | OAc (2x$CH_3$) |
| 51.3 | $CH_3$ | 3.68 *s* | | $OCH_3$ |

* Carbon type according to DEPT experiment

**Table S7.** Correlations and assignments for compound **19** (δ in ppm).




| δ $^{13}$C | TYPE* | HMQC, δ $^{1}$H (*J* in Hz) | HMBC, δ $^{1}$H (H number) | Assigned |
|---|---|---|---|---|
| 27.8 | $CH_2$ | 2.62 *m* | -- | 1 |
| 20.4 | $CH_2$ | 2.62 *m* | -- | 2 |
| 30.7 | $CH_2$ | 1.91 *m* | 1.30 (18) | 3 |
| 32.7 | CH | -- | 6.94 (6), 1.30 (18) | 4 |
| 139.9 | C | -- | 1.30 (18) | 5 |
| 127.9 | CH | 6.94 *bs* | 2.35 (17) | 6 |
| 132.9 | C | -- | 2.35 (17) | 7 |
| 135.2 | C | -- | 6.94 (6), 2.35 (17) | 8 |
| 134.2 | C | -- | 2.23 (20) | 9 |
| 133.2 | C | -- | 6.94 (6), 2.23 (20) | 10 |
| 31.9 | $CH_2$ | 2.89-3.01 *m* | 2.89-3.01 (12) | 11 |
| 36.0 | $CH_2$ | 2.89-3.01 *m* | 2.89-3.01 (11), 7.65 (16, 7.47 (14) | 12 |
| 141.3 | C | -- | 2.89-3.01 (11,12) 7.82 (15) | 13 |
| 128.3 | CH | 7.47 *d* (8.6 Hz) | 7.65 (16) | 14 |
| 121.8 | CH | 7.82 *d* (8.6 Hz) | -- | 15 |
| 119.7 | CH | 7.65 *bs* | 7.47 (14) | 16 |
| 20.0 | $CH_3$ | 2.35 *s* | 6.94 (6) | 17 |
| 23.0 | $CH_3$ | 1.30 *d* (7.0 Hz) | -- | 18 |
| 15.0 | $CH_3$ | 2.23 *s* | -- | 20 |
| 143.9 | C | -- | 7.65 (16), 7.19 (3') | 1´ |
| 116.8 | CH | 7.22 *d* (8.2 Hz) | -- | 2´ |
| 117.7 | CH | 7.17 *d* (8.2 Hz) | -- | 3´ |
| 144.3 | C | -- | 7.82 (15), 7.22 (2') | 4´ |
| 126.2 | C | -- | 7.65 (16), 7.47 (14), 7.19 (3') | 5´ |
| 127.9 | C | -- | 7.22 (2'), 7.82 (15) | 6´ |
| 169.3 | C | -- | 2.47, 2.47 [(OAc (2x $CH_3$)] | OAc (2xCO) |
| 20.9 | $CH_3$ | 2.46 *s*, 2.47 *s* | -- | OAc (2x $CH_3$) |

* Carbon type according to DEPT experiment

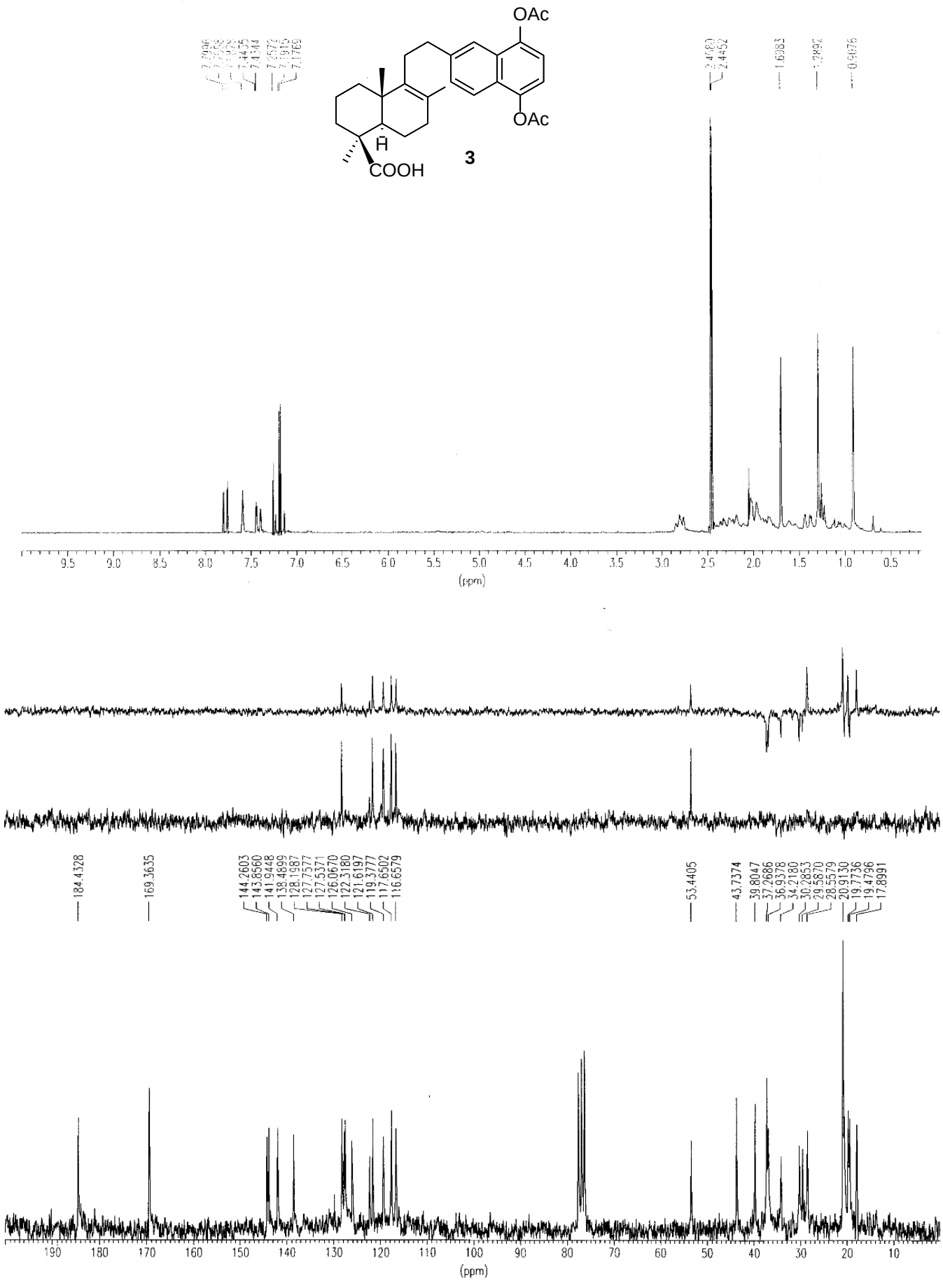



**Figure S1**: $^{1}H$ and $^{13}C$ NMR spectra for compound **3**.

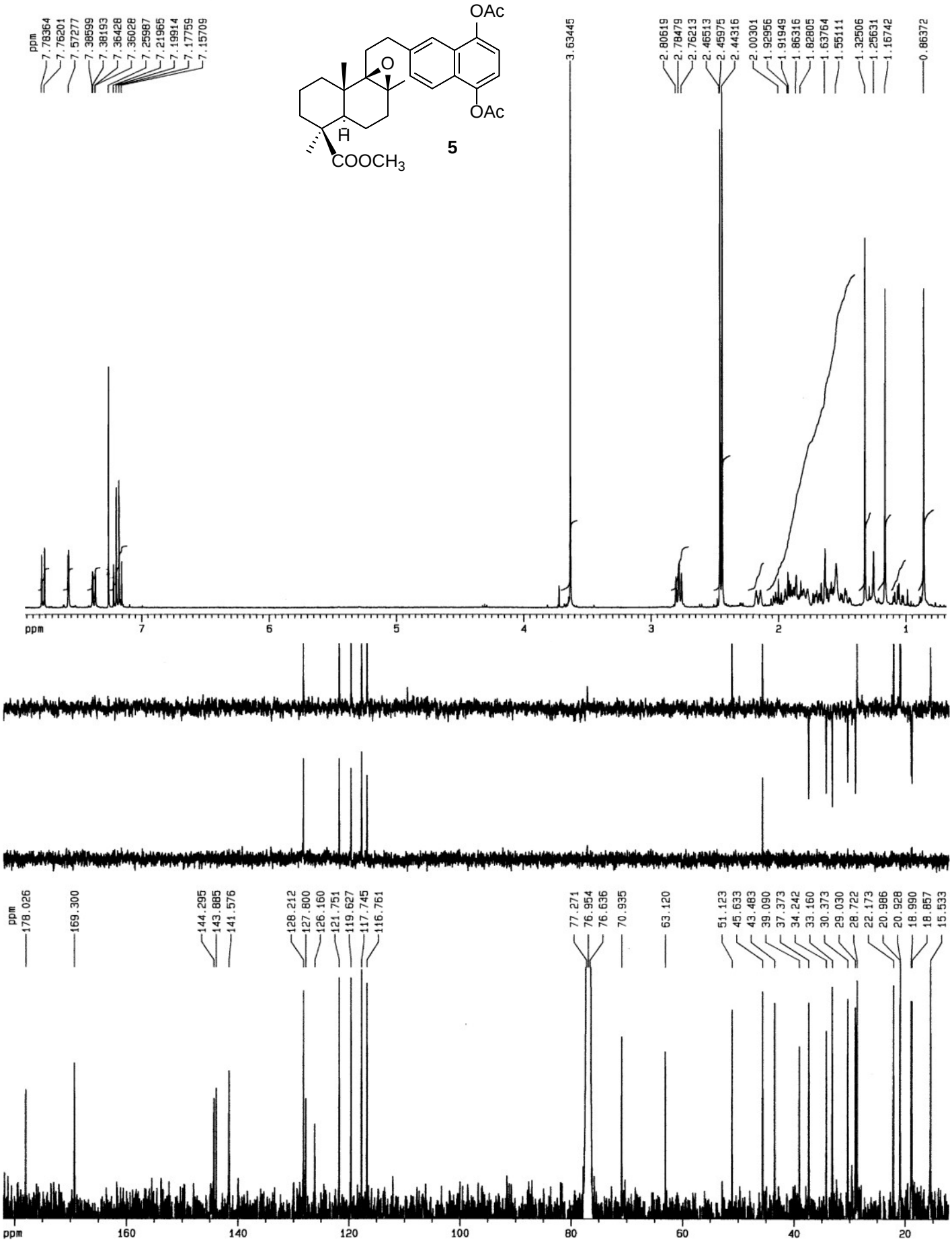



**Figure S2**: $^{1}H$ and $^{13}C$ NMR spectra for compound **5.**

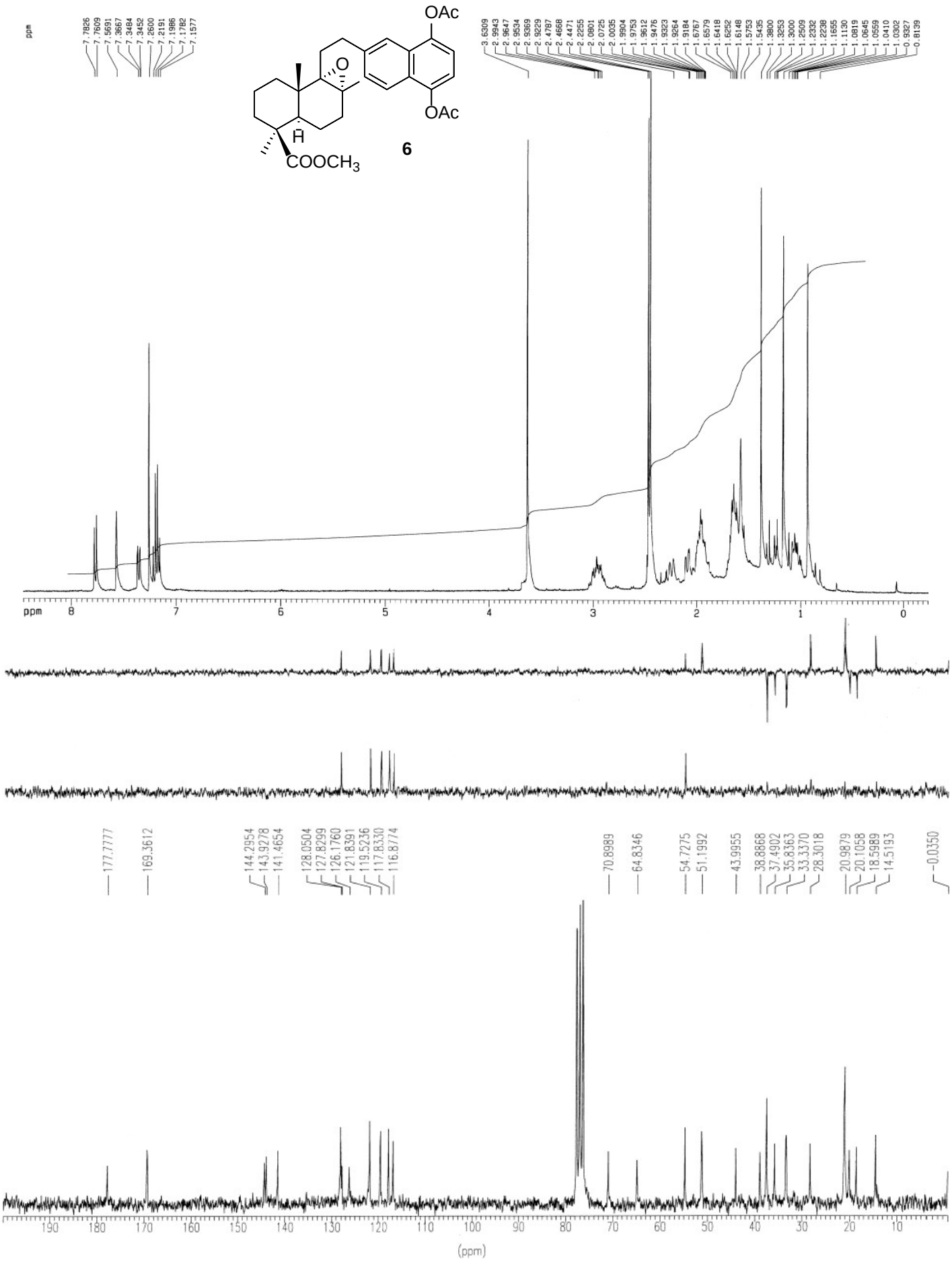



**Figure S3**: $^{1}H$ and $^{13}C$ NMR spectra for compound **6.**

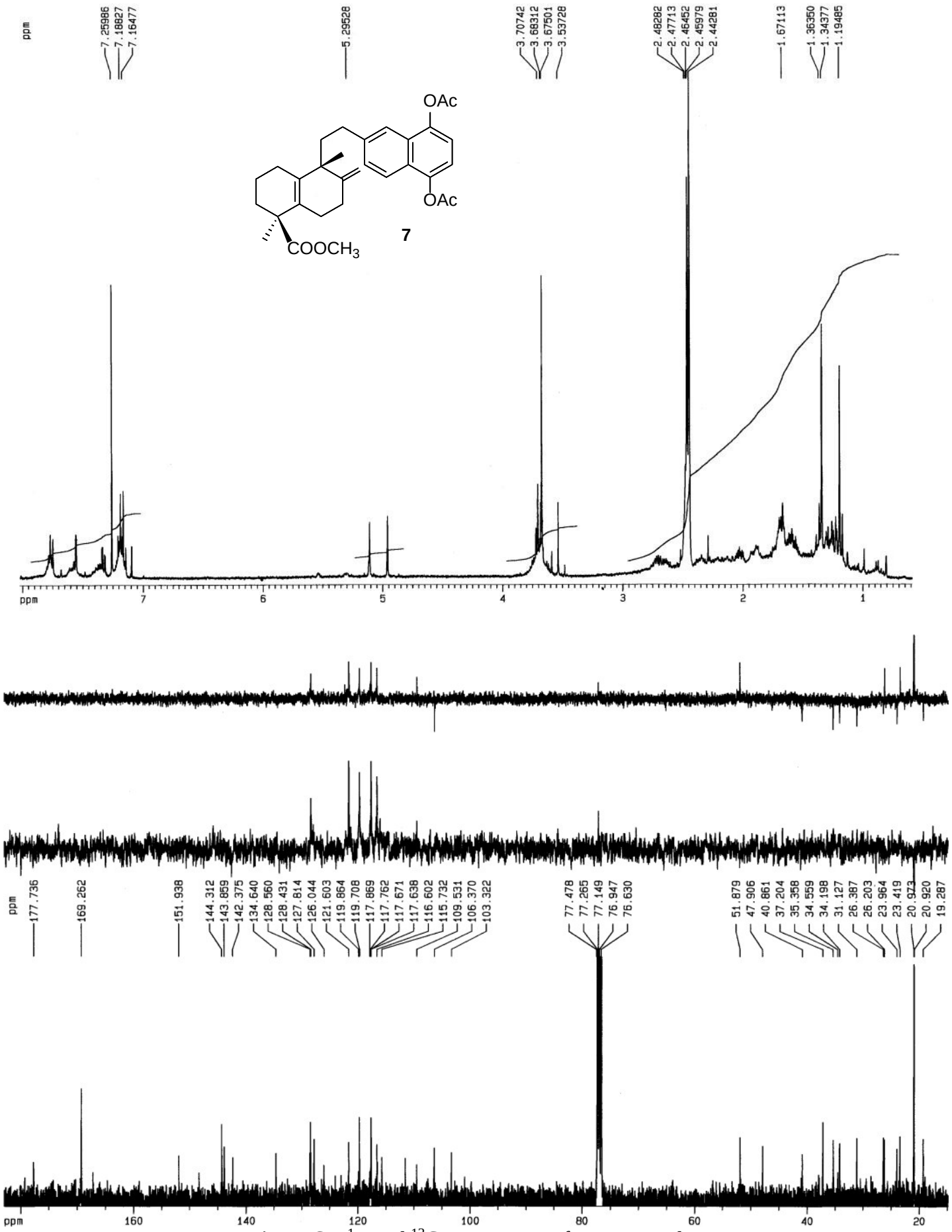



**Figure S4**: $^{1}H$ and $^{13}C$ NMR spectra for compound **7.**

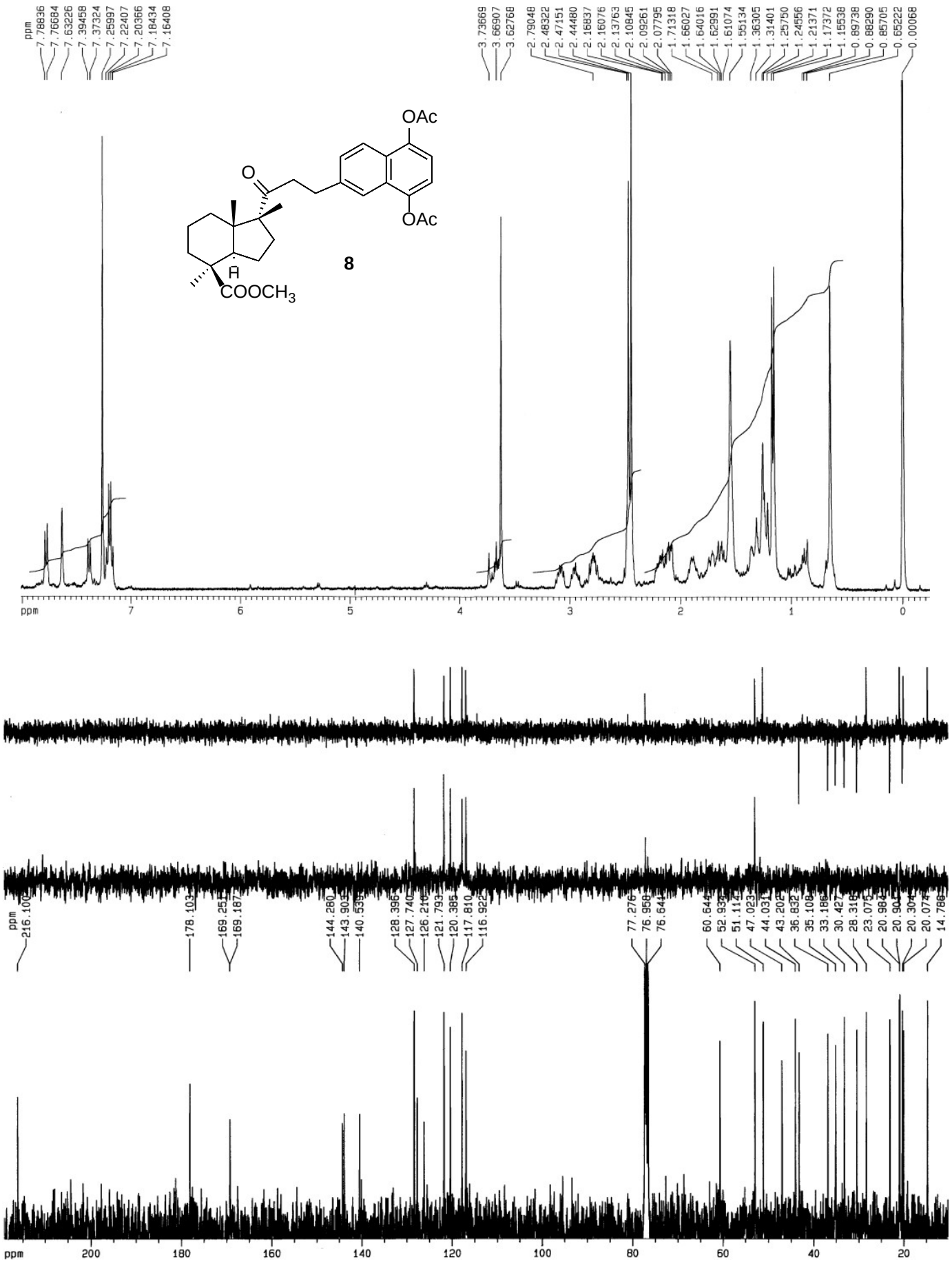



**Figure S5**:[1]H and [13]C NMR spectra for compound **8**.

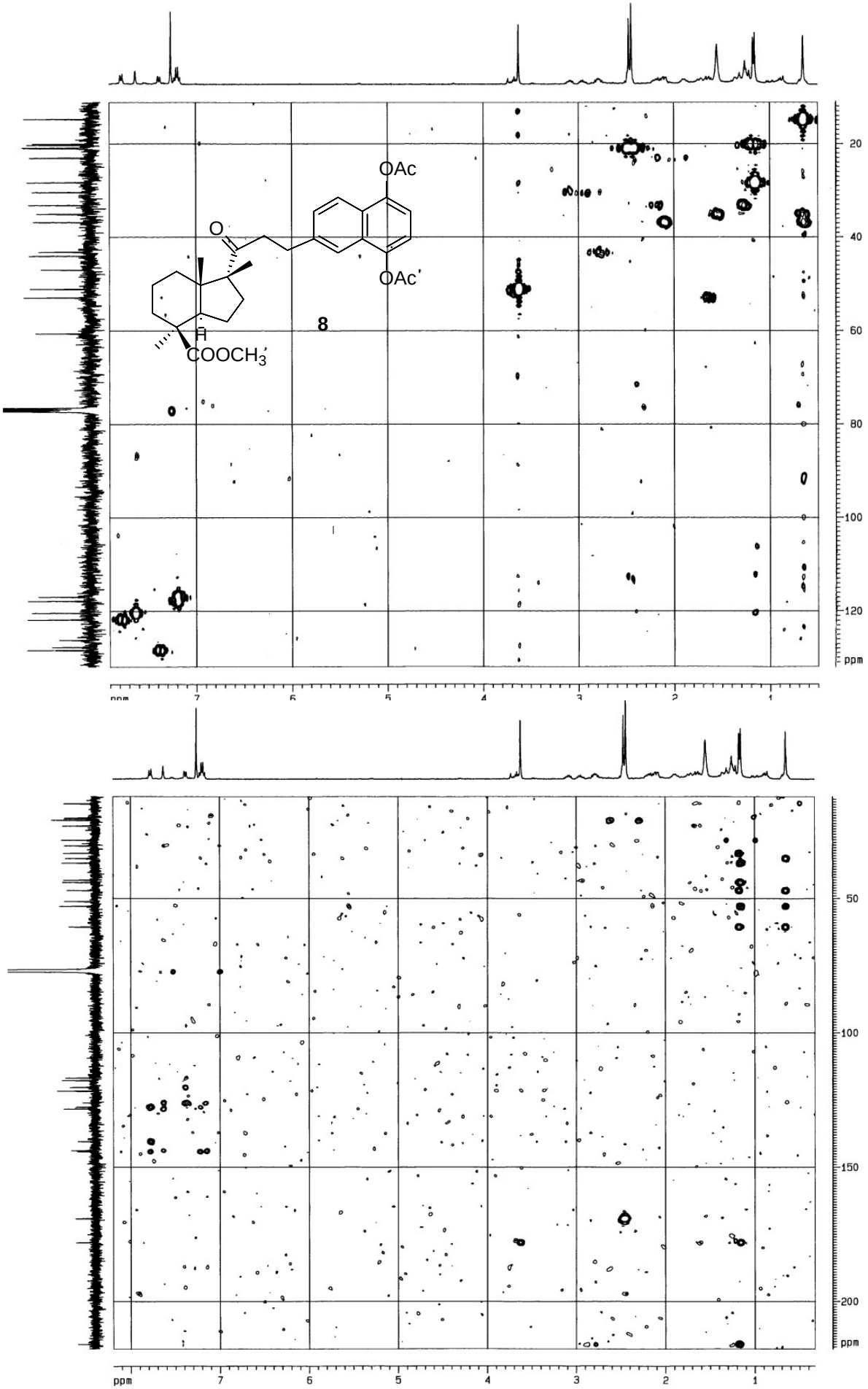



**Figure S6**: HMQC and HMBC experiments for compound **8**.

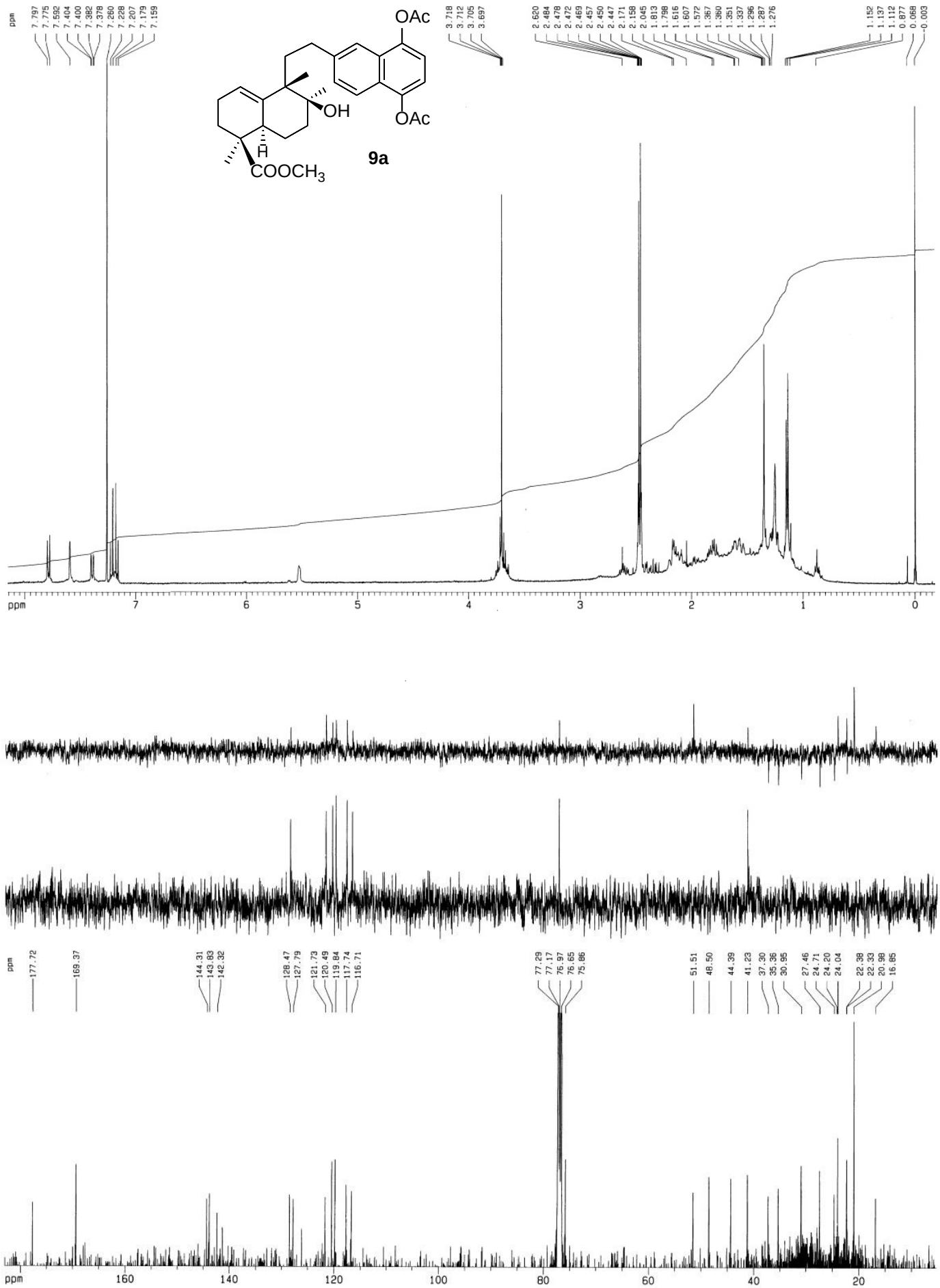



**Figure S7**: IR, $^{1}H$ and $^{13}C$ NMR spectra for compound **9a**.

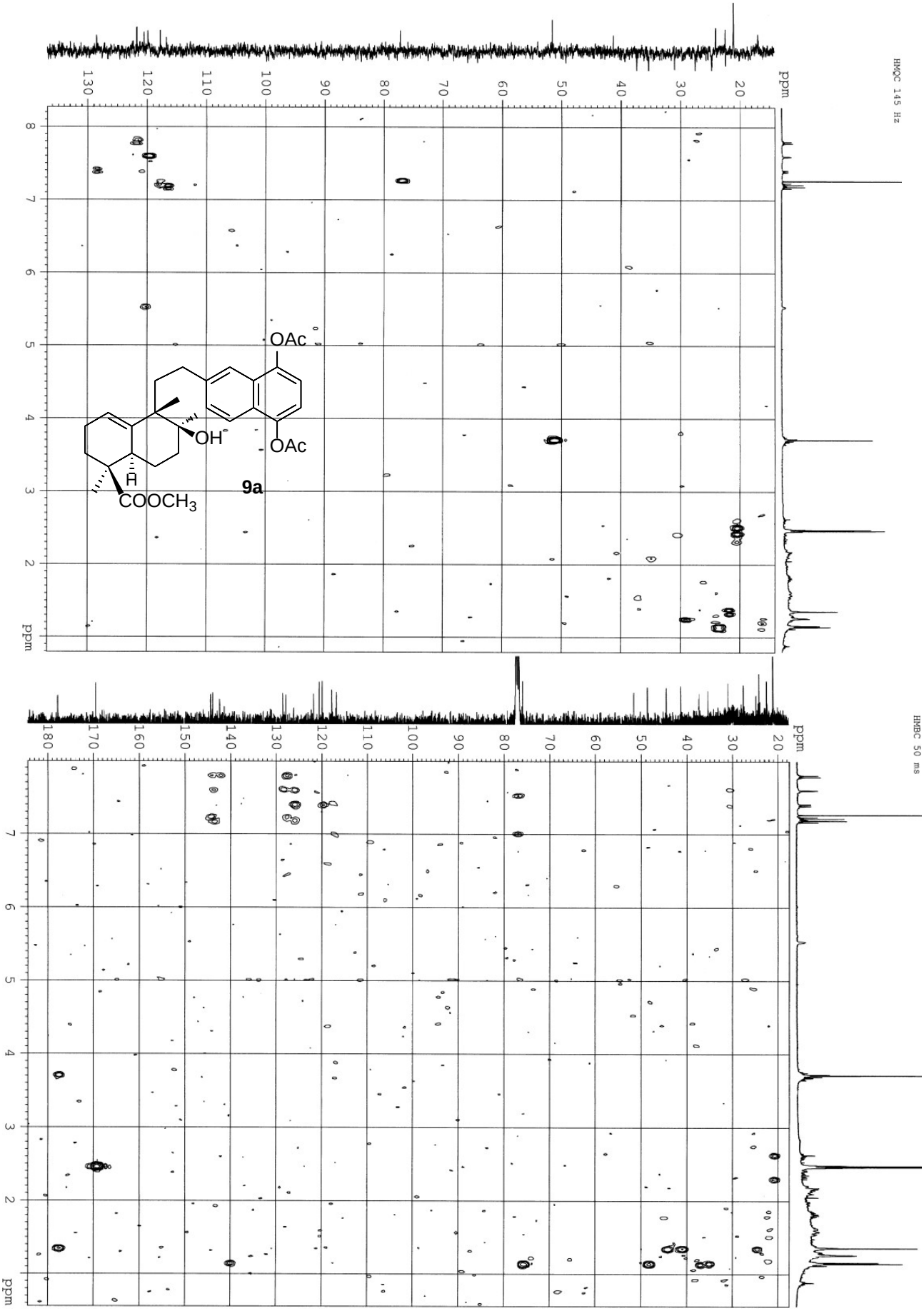



**Figure S8**: HMQC and HMBC experiments for compound **9a**.

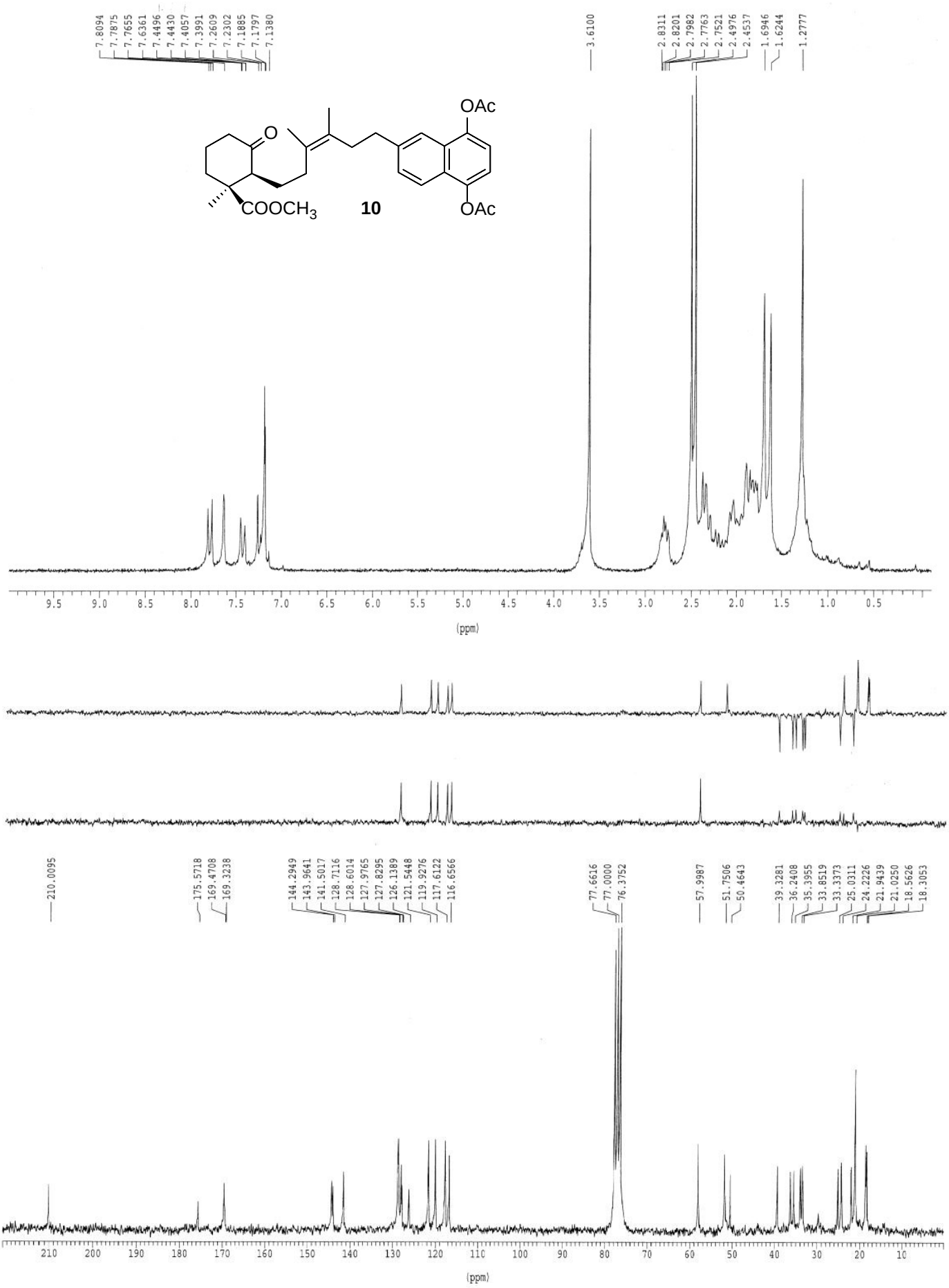



**Figure S9**: $^{1}H$ and $^{13}C$ NMR spectra for compound **10**.

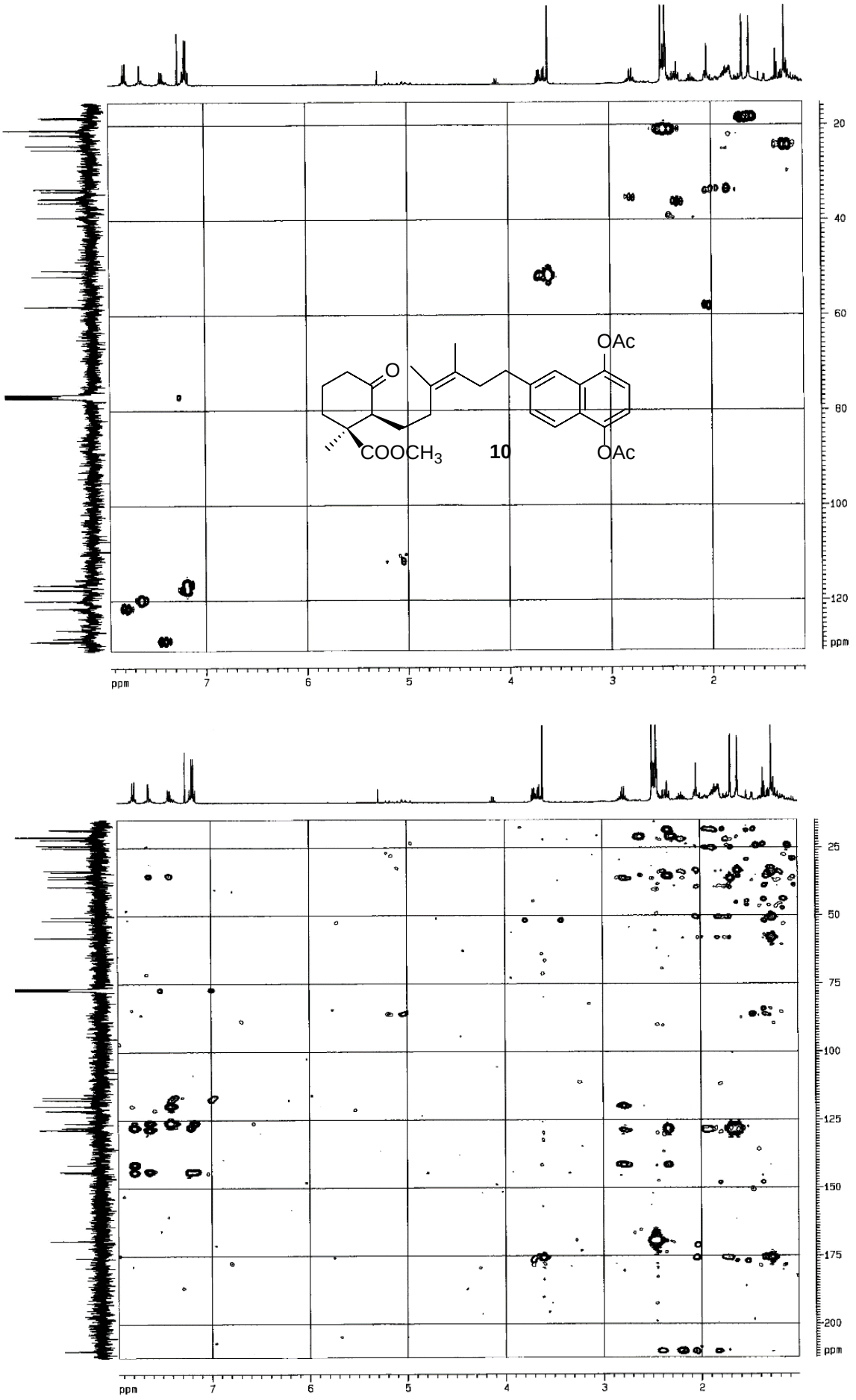



**Figure S10**: HMQC and HMBC experiments for compound **10**

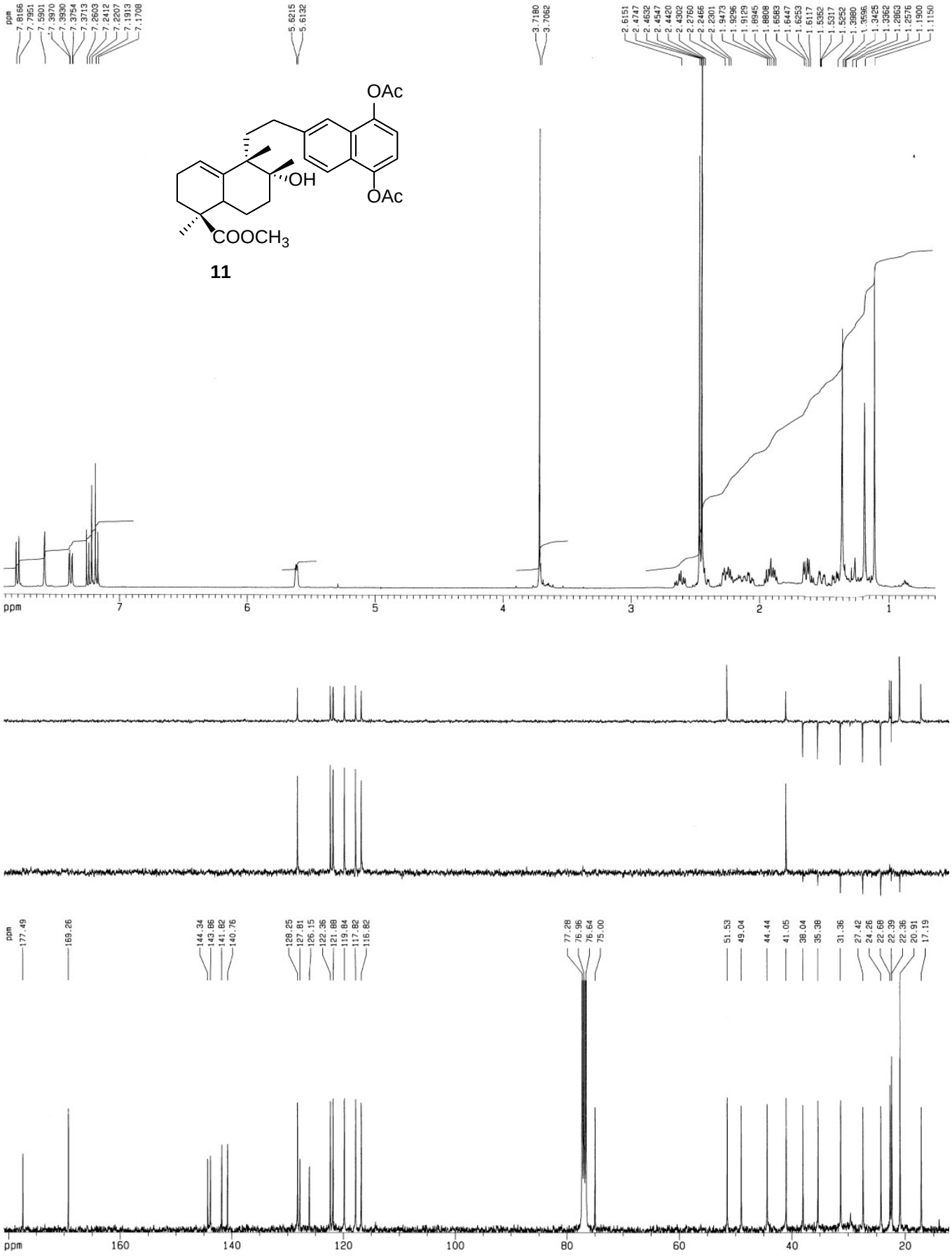



**Figure S11**: $^{1}H$ and $^{13}C$ NMR spectra for compound **11**.

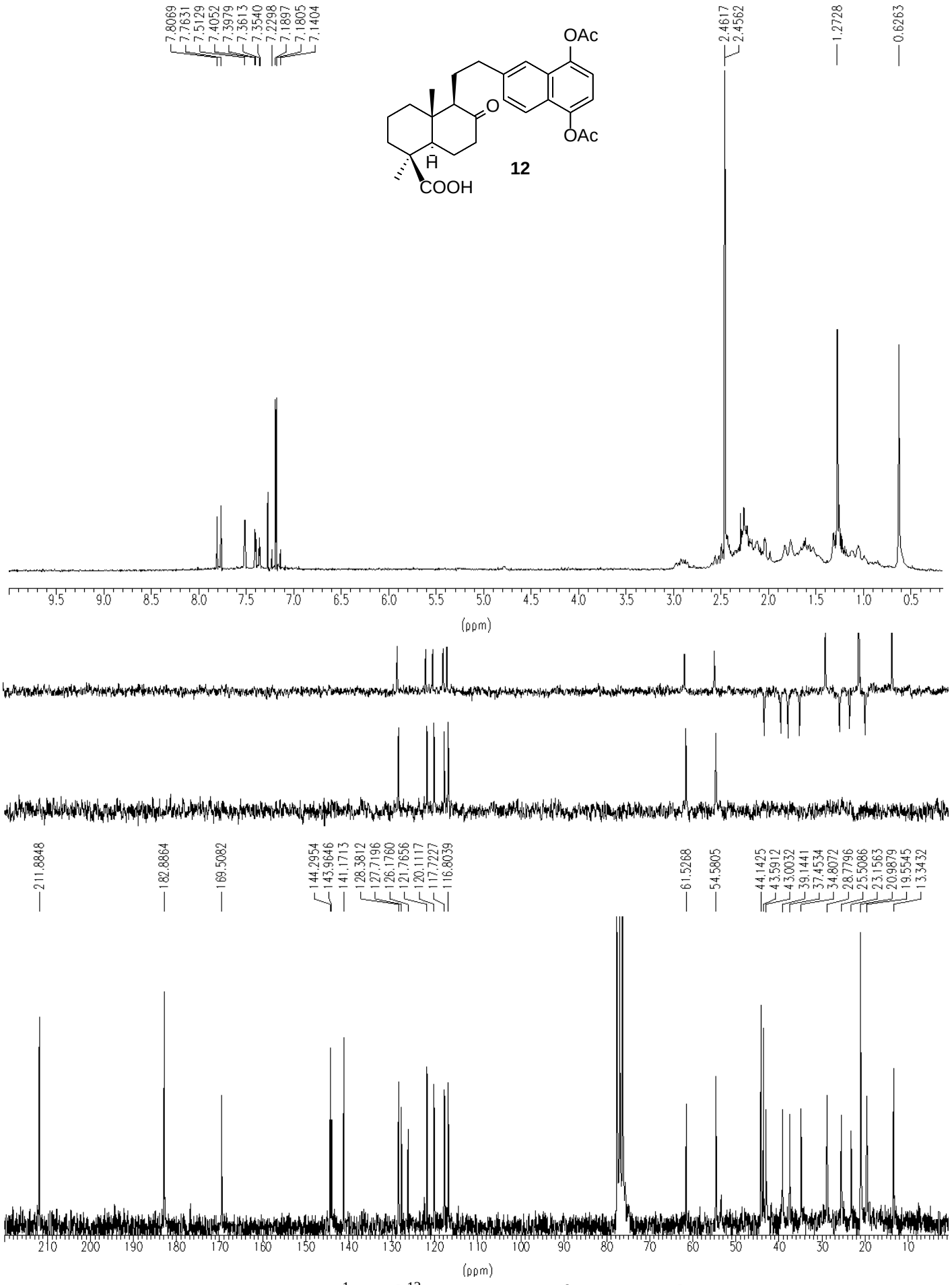
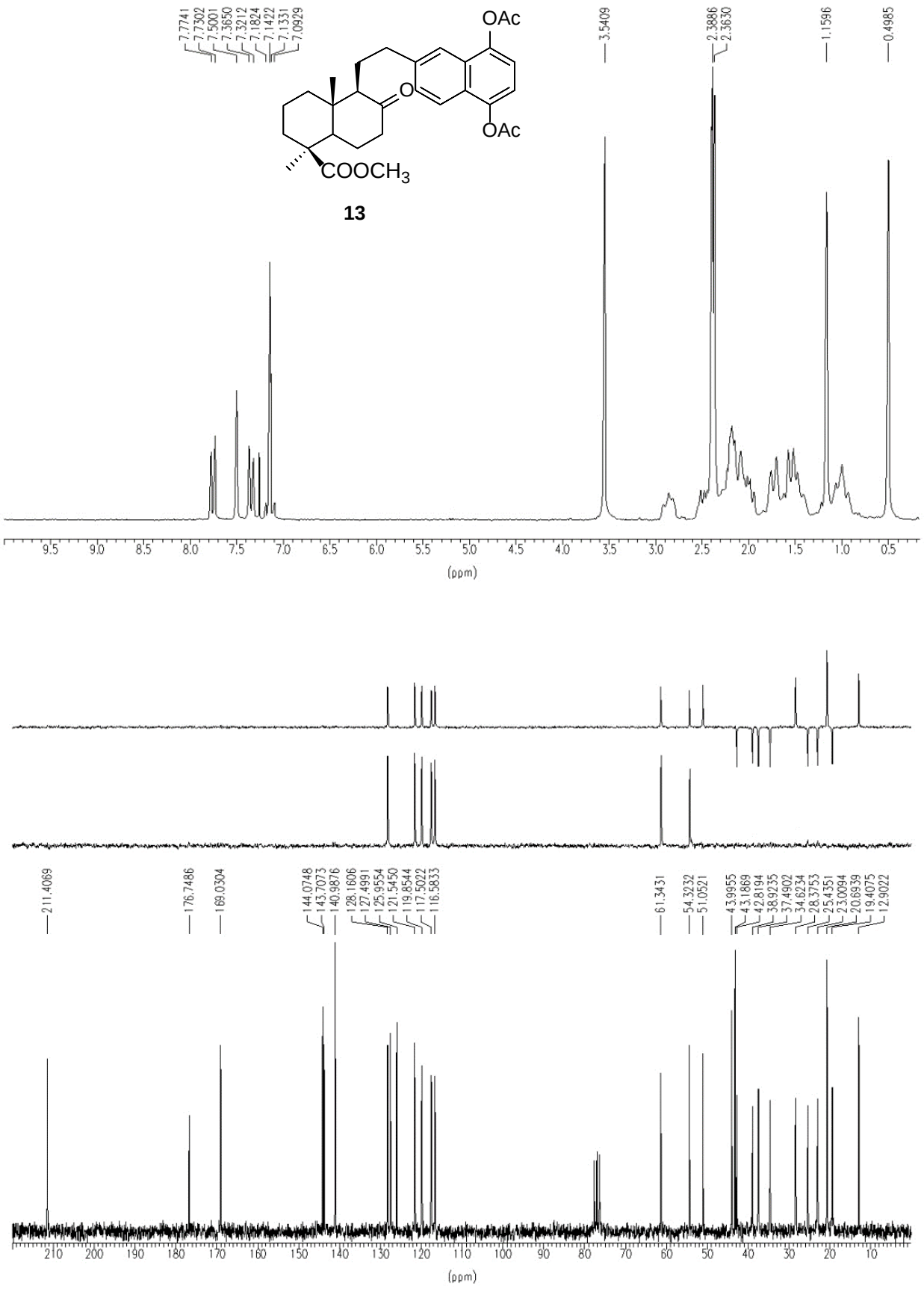
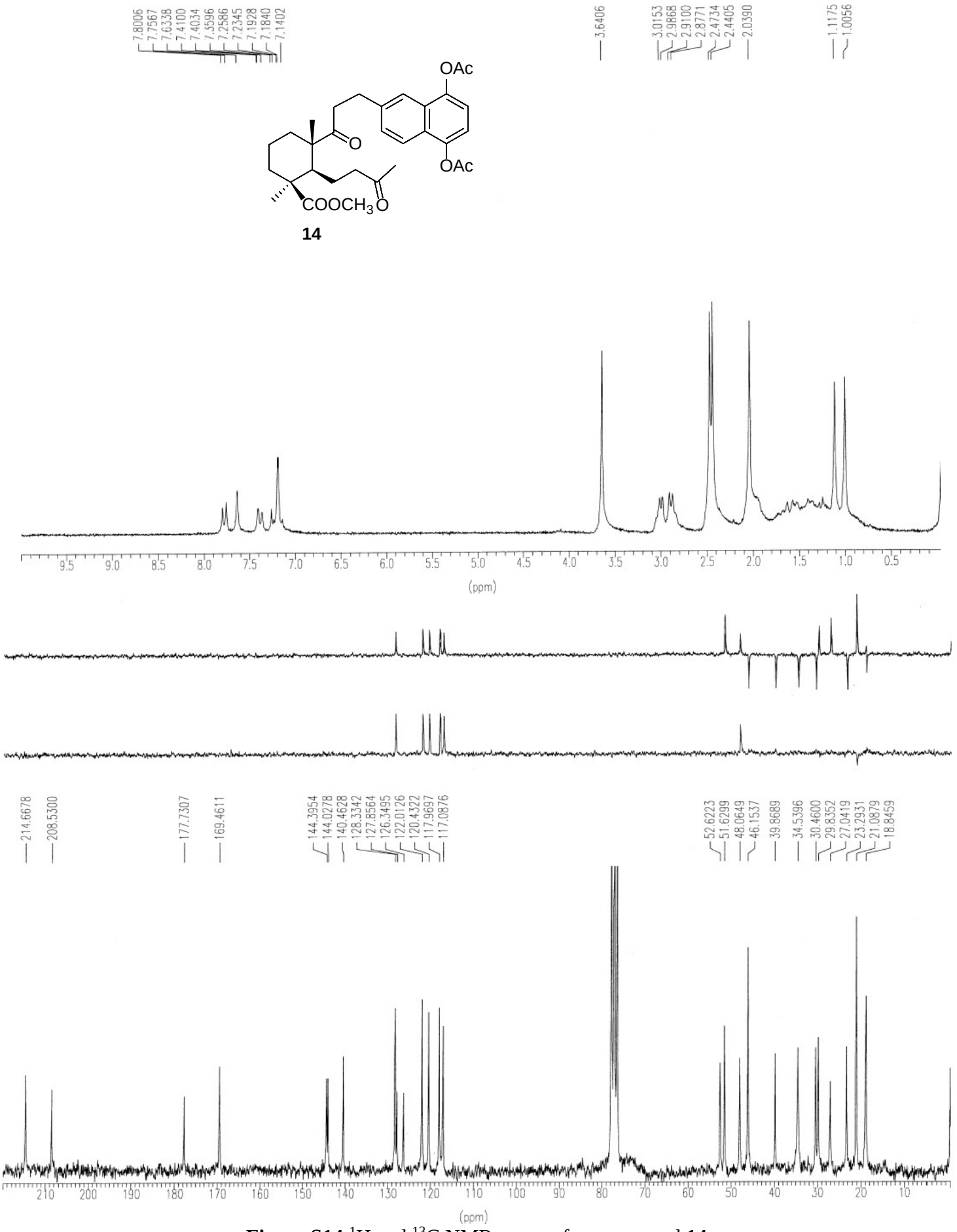



**Figure S12**:[1]H and [13]C NMR spectra for compound **12**.




**13**

**Figure S13**: $^{1}H$ and $^{13}C$ NMR spectra for compound **13**.




**14**

**Figure S14**:[1]H and [13]C NMR spectra for compound **14**.

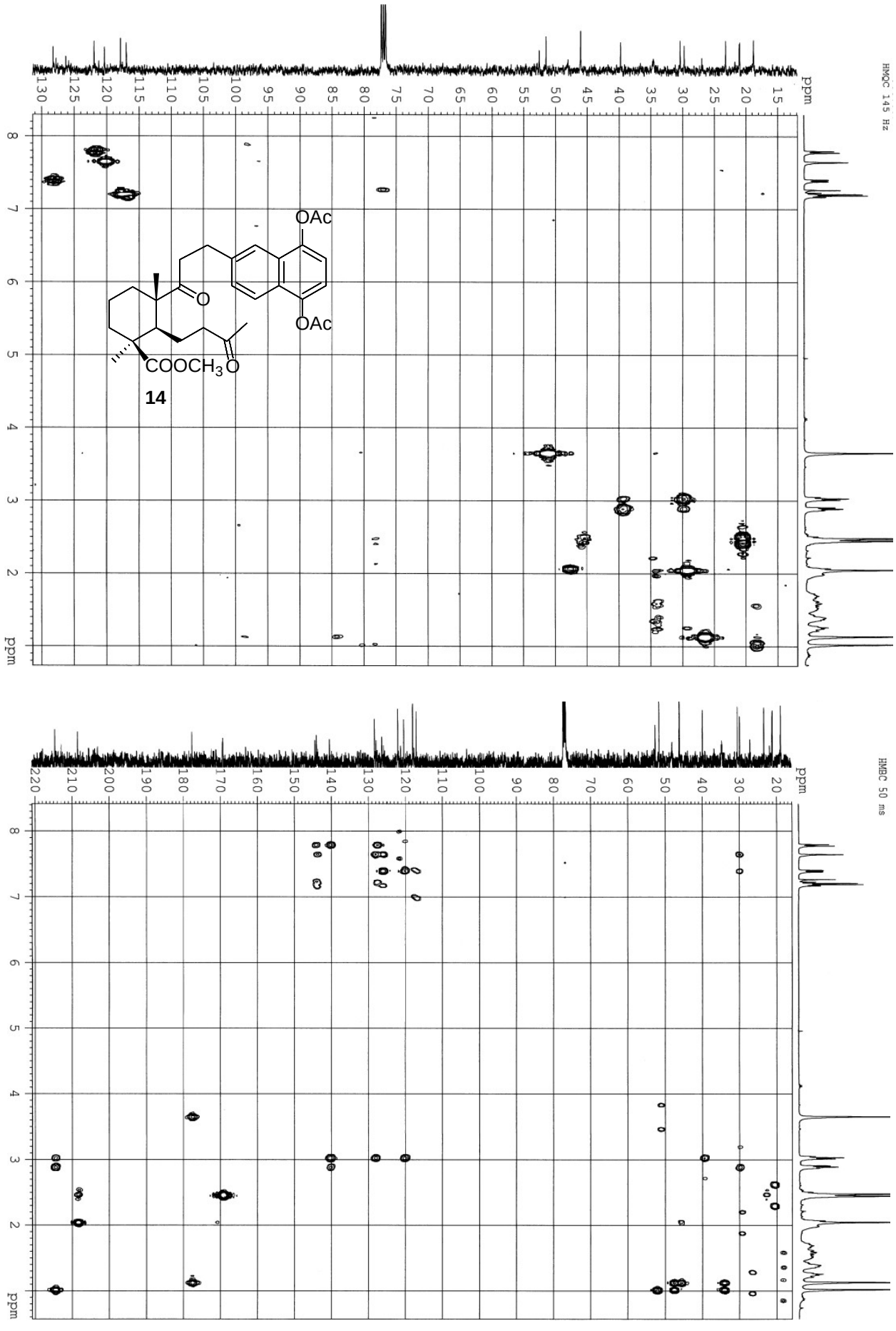



**Figure S15**: HMQC and HMBC experiments for compound **14.**

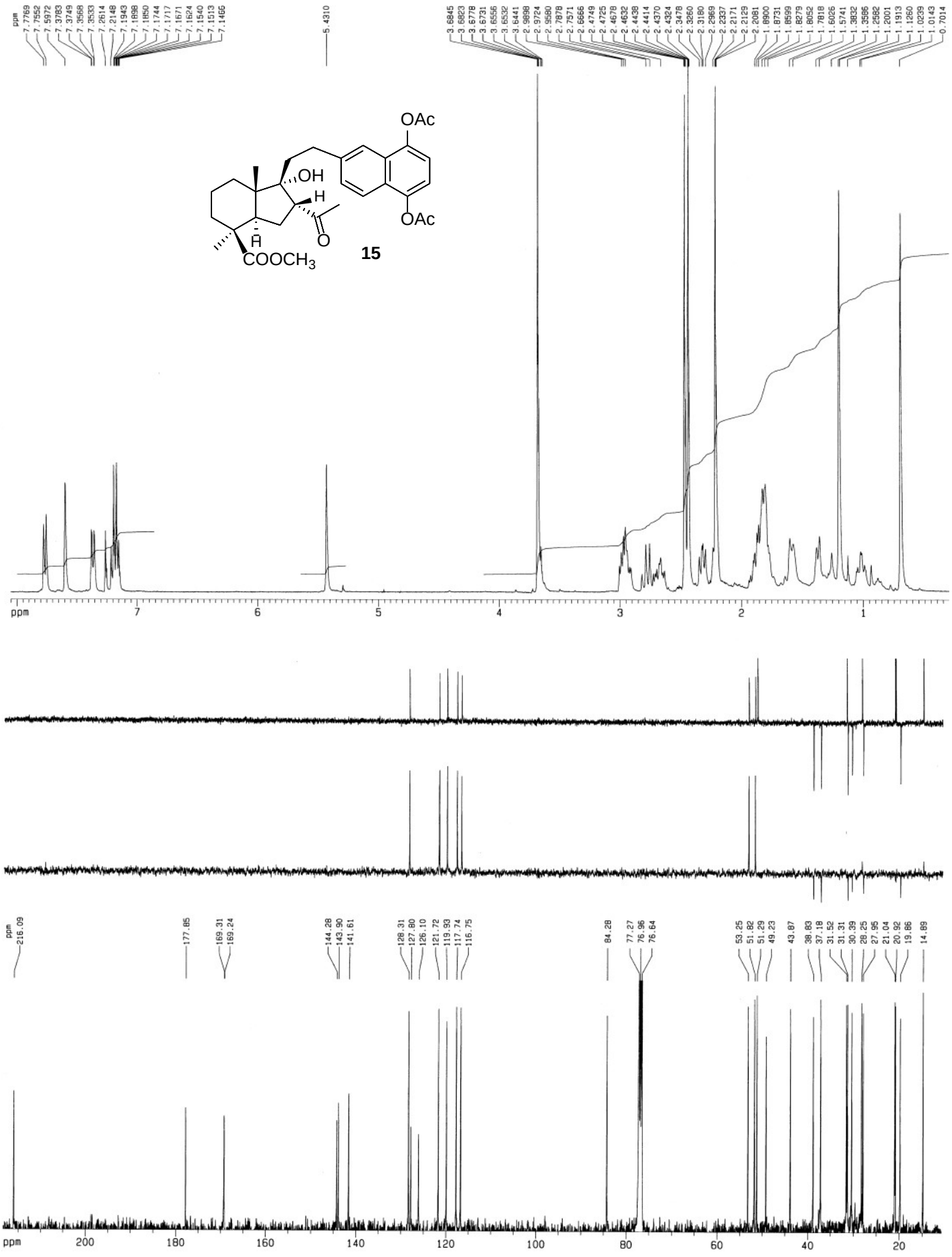



**Figure S16**: $^{1}H$ and $^{13}C$ NMR spectra for compound **15**.

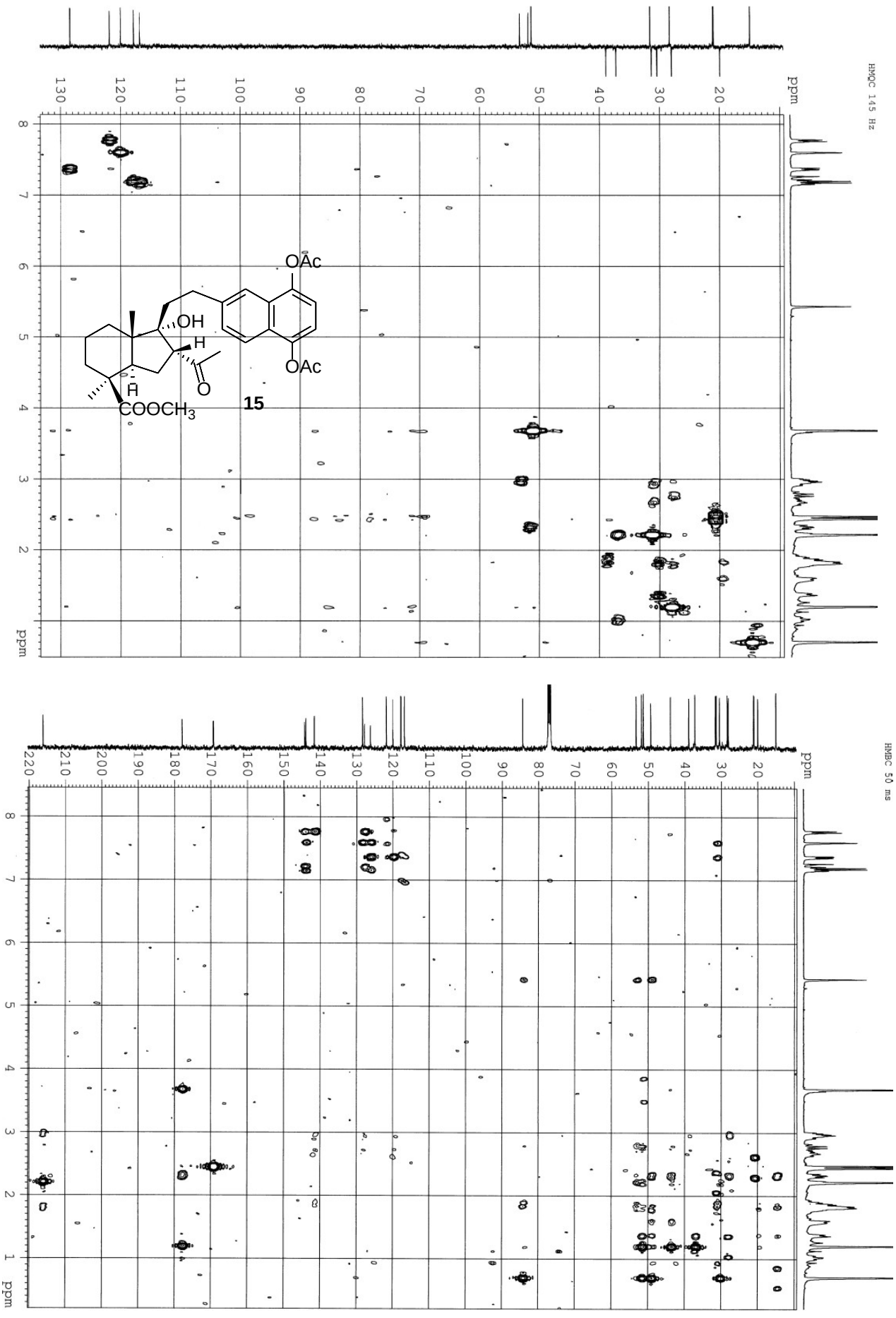



**Figure S17**: HMQC and HMBC experiments for compound **15.**


**Figure S18**: $^{1}H$ and $^{13}C$ NMR spectra for compound **16a**.

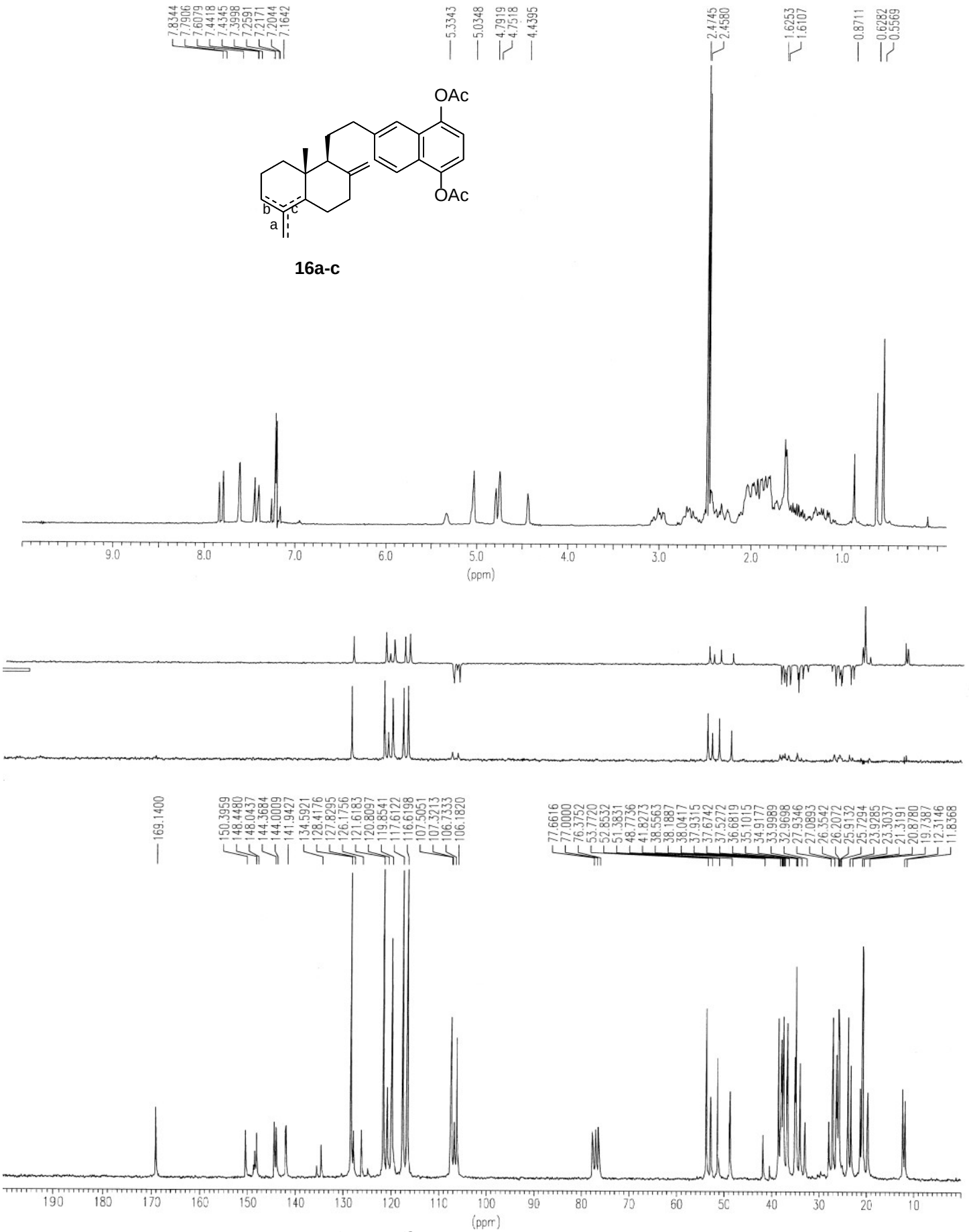



**Figure S19**: $^{1}H$ and $^{13}C$ NMR spectra for compounds **16a-c**.

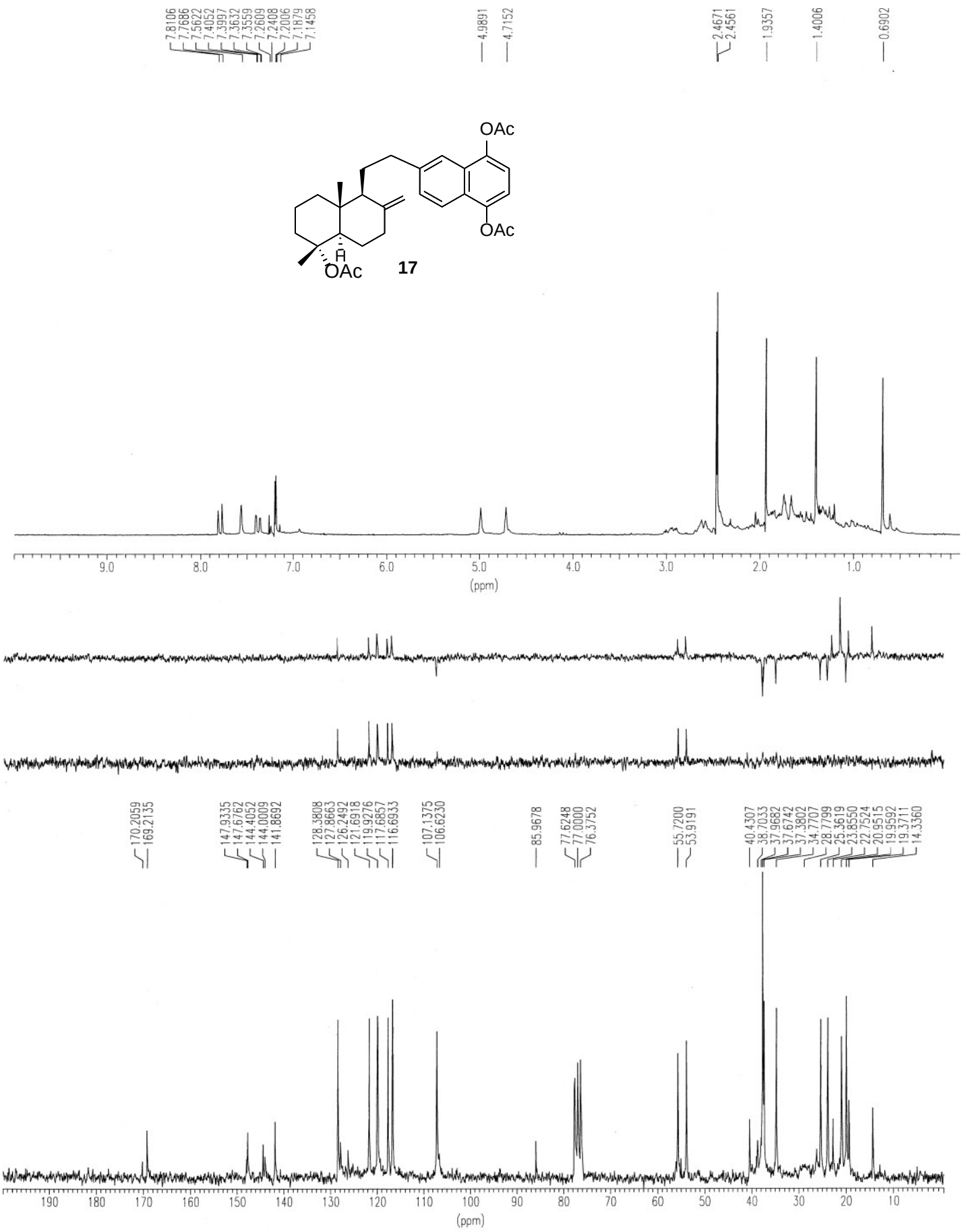



**Figure S20**: $^{1}H$ and $^{13}C$ NMR spectra for compound **17**.

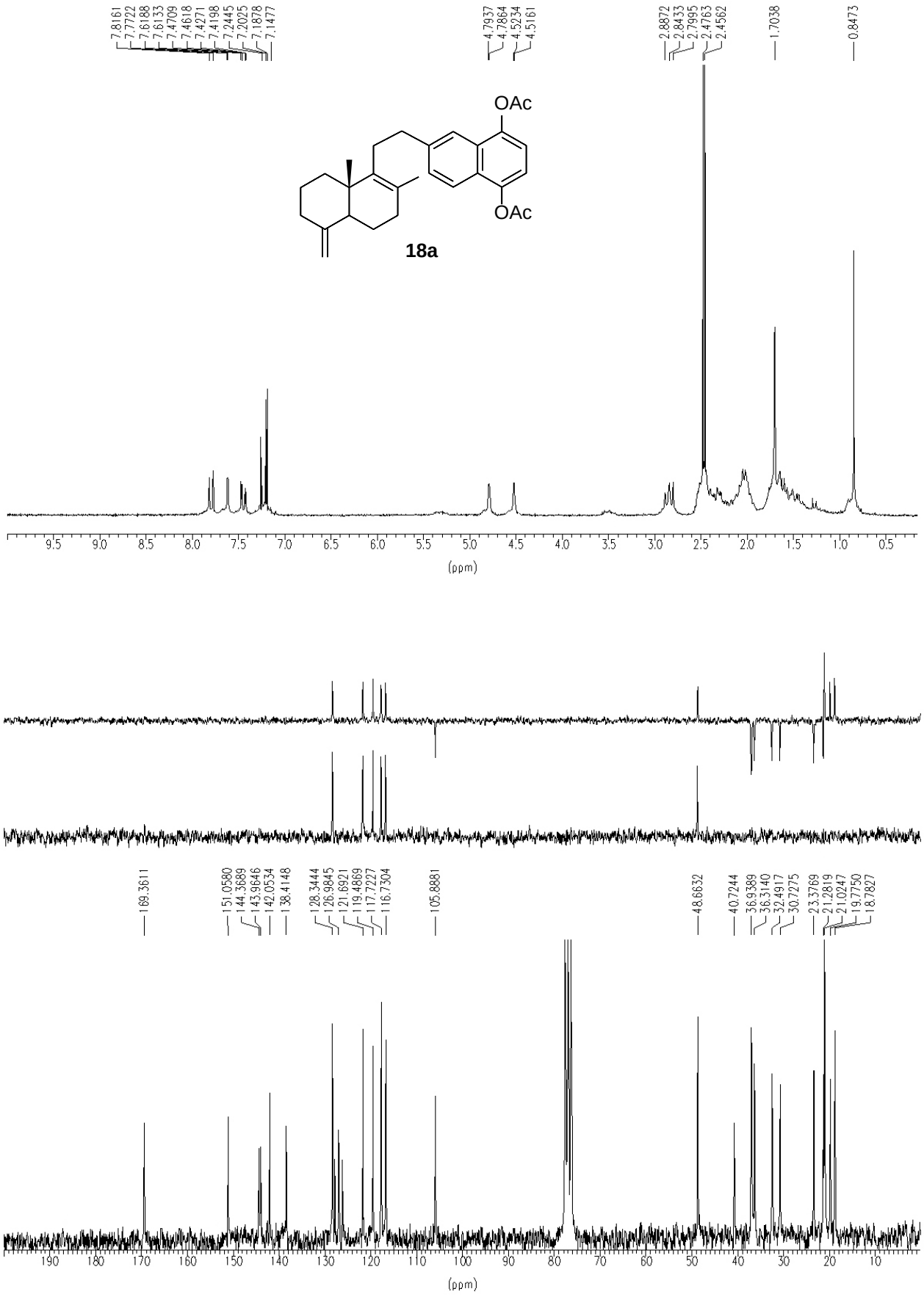



**Figure S21**: $^{1}H$ and $^{13}C$ NMR spectra for compound **18a**.

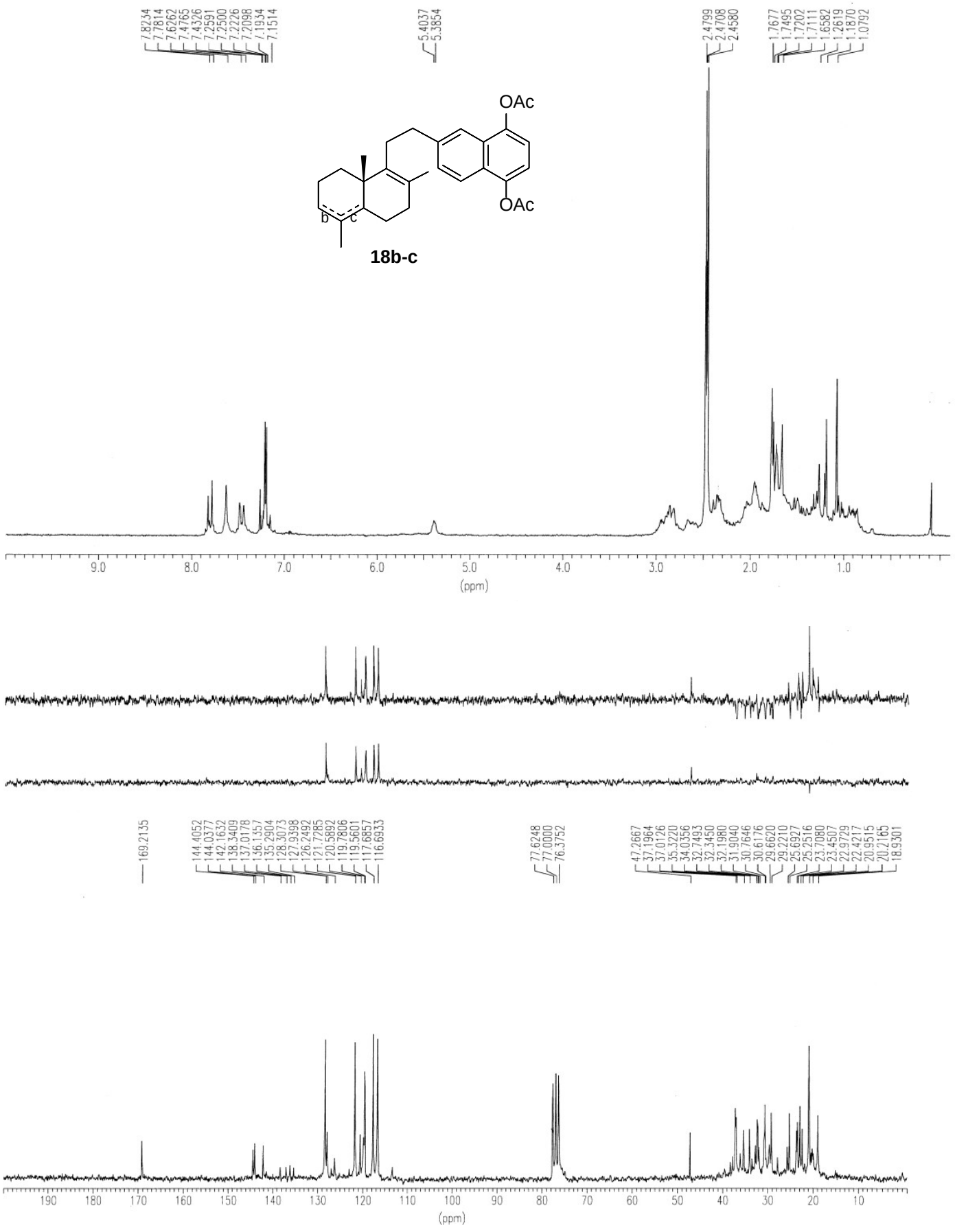



**Figure S22**: $^{1}H$ and $^{13}C$ NMR spectra for compounds **18b** and **18c**.

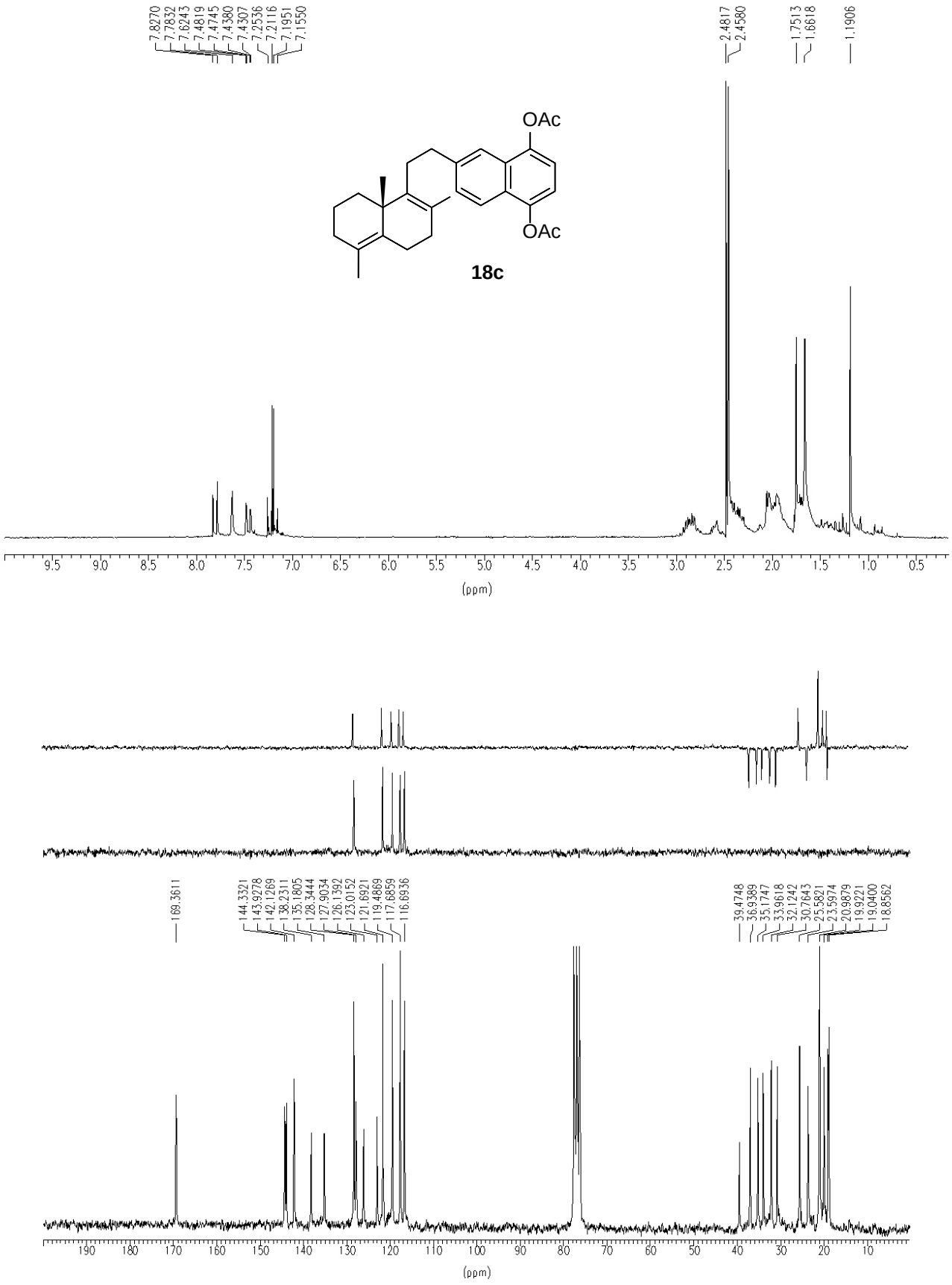



**Figure S23**: $^{1}H$ and $^{13}C$ NMR spectra for compound **18c**.

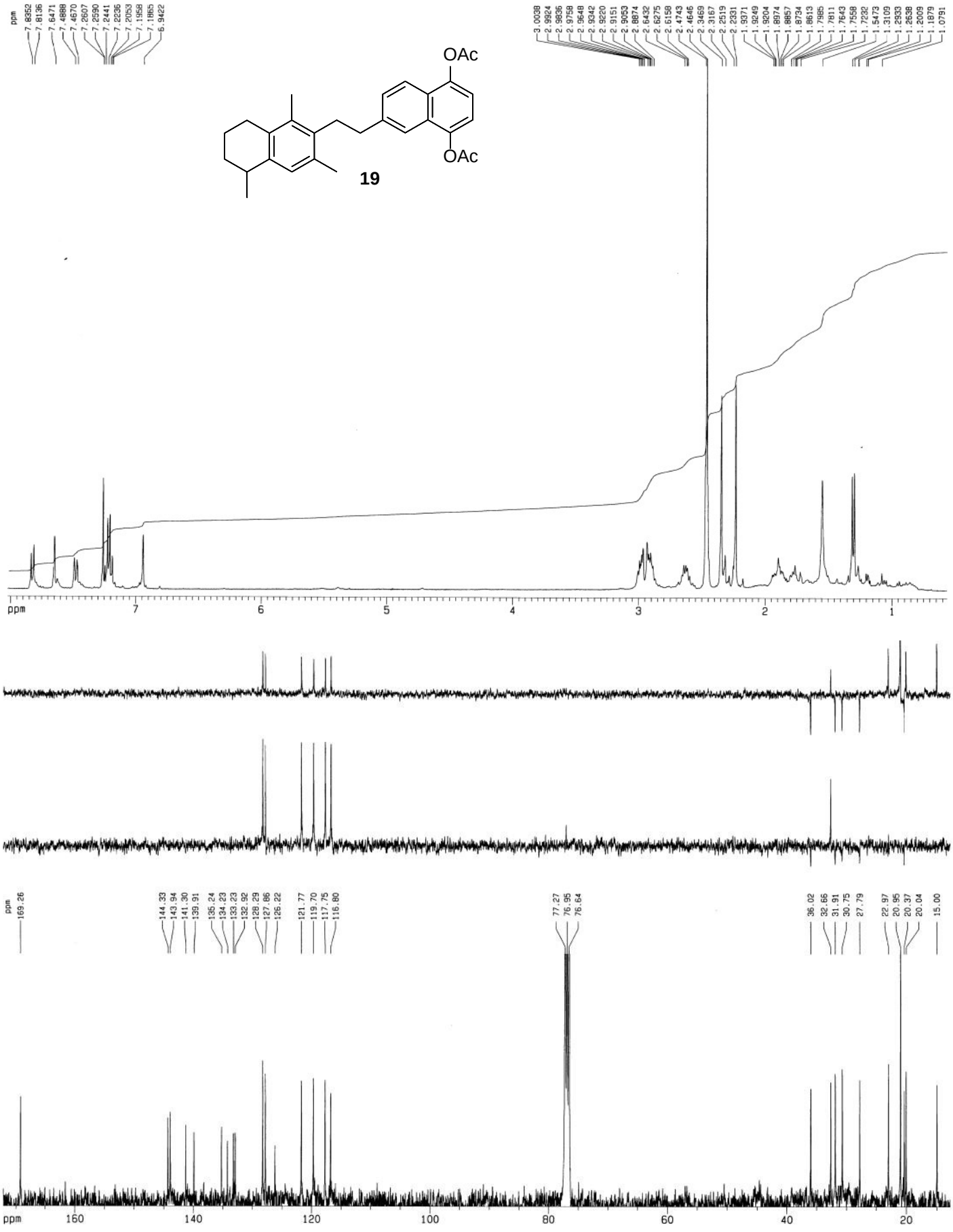



**Figure S24**: $^{1}H$ and $^{13}C$ NMR spectra for compounds **19**.

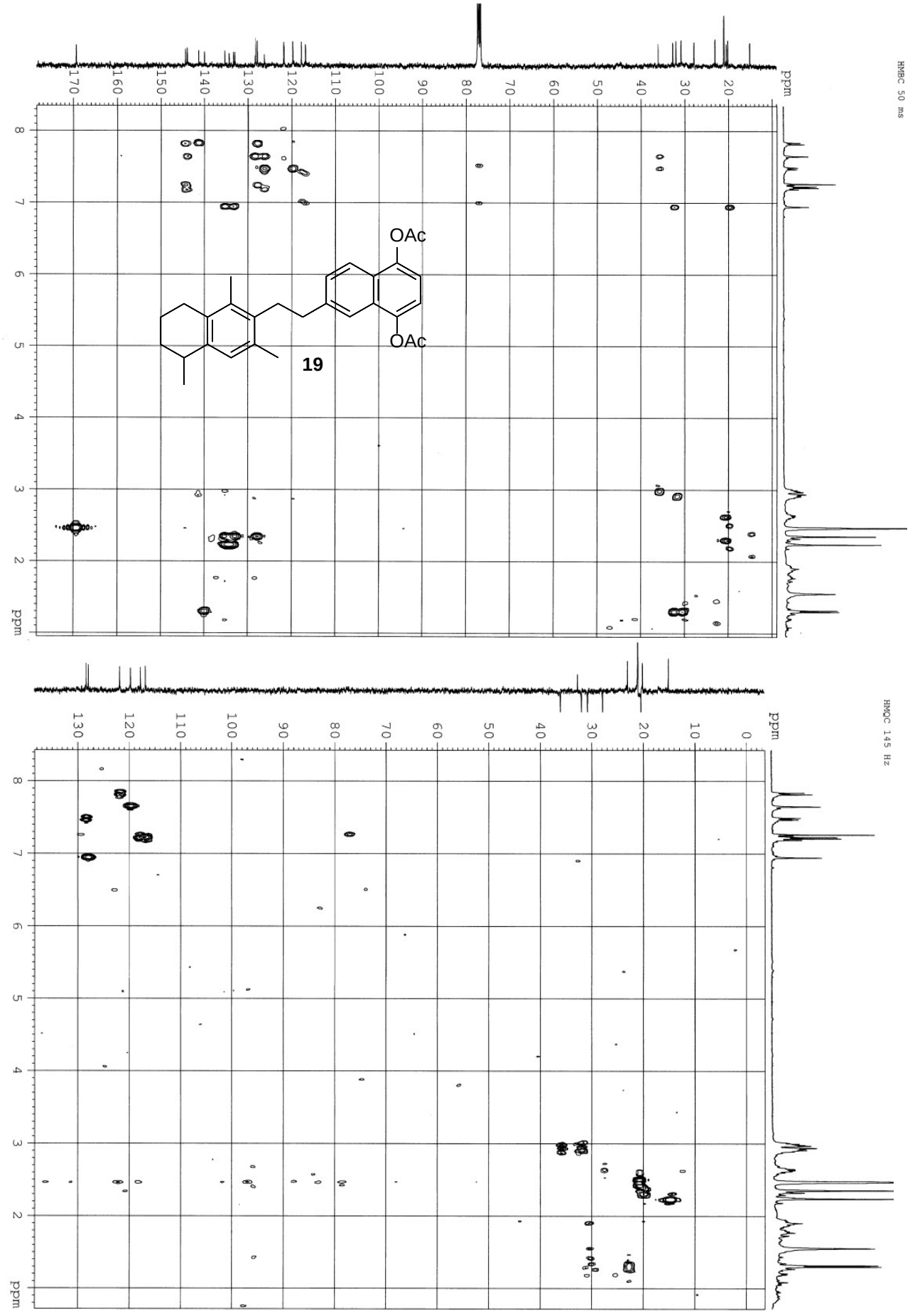



**Figure S25**: HMQC and HMBC experiments for compound **19**.

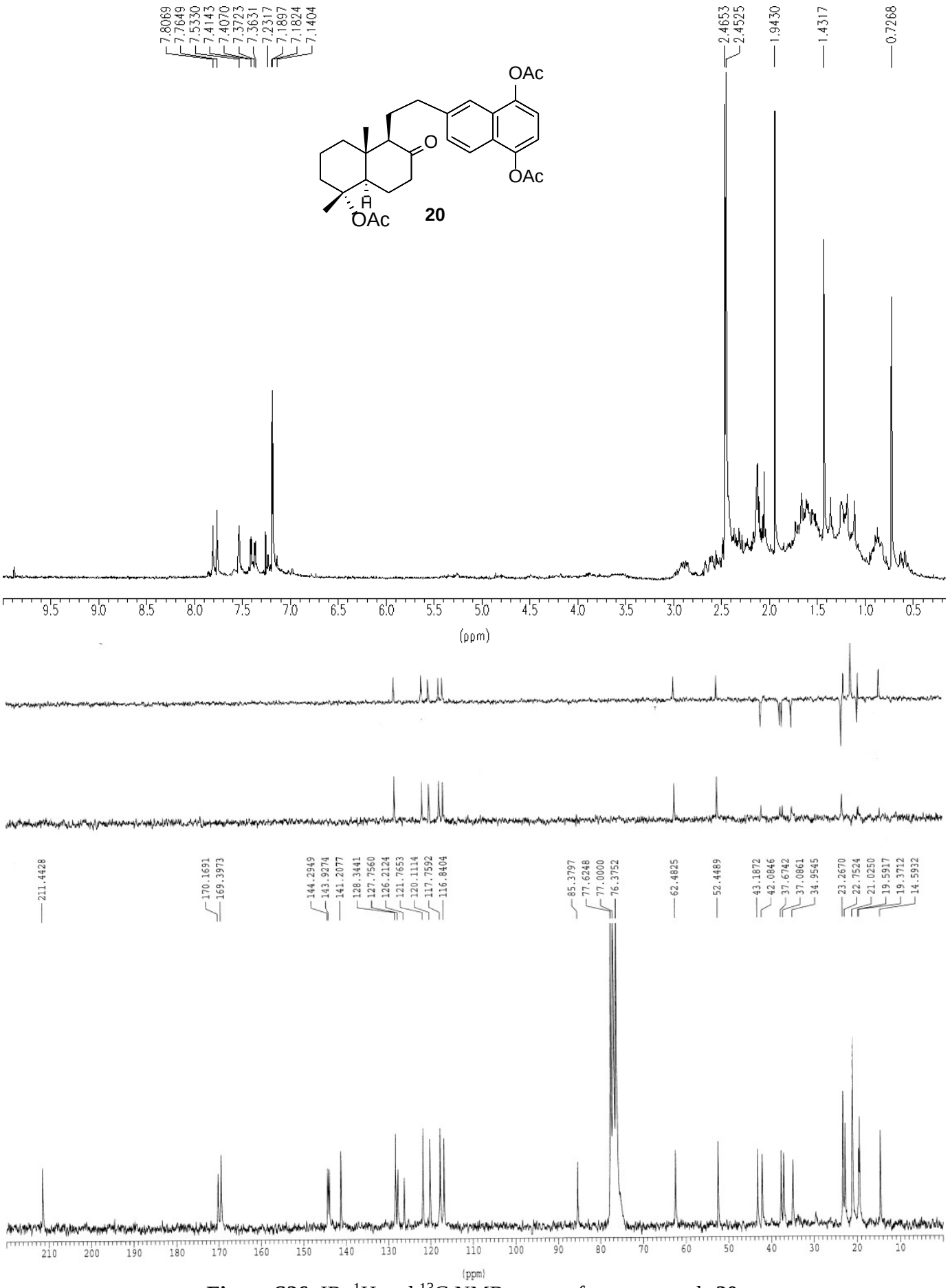
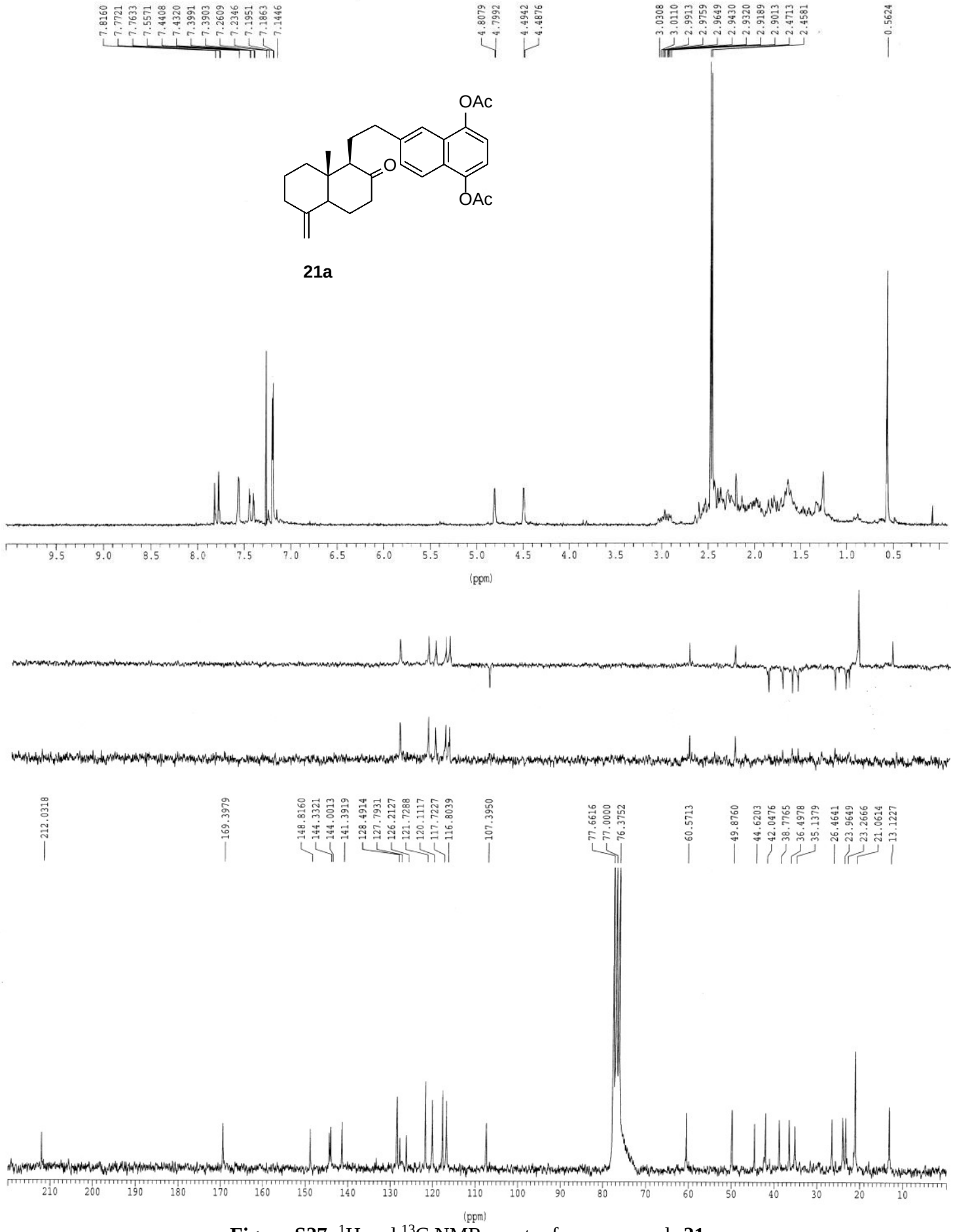



**Figure S26**: IR, $^{1}H$ and $^{13}C$ NMR spectra for compounds **20**.




**21a**

**Figure S27**: $^{1}H$ and $^{13}C$ NMR spectra for compounds **21a**.

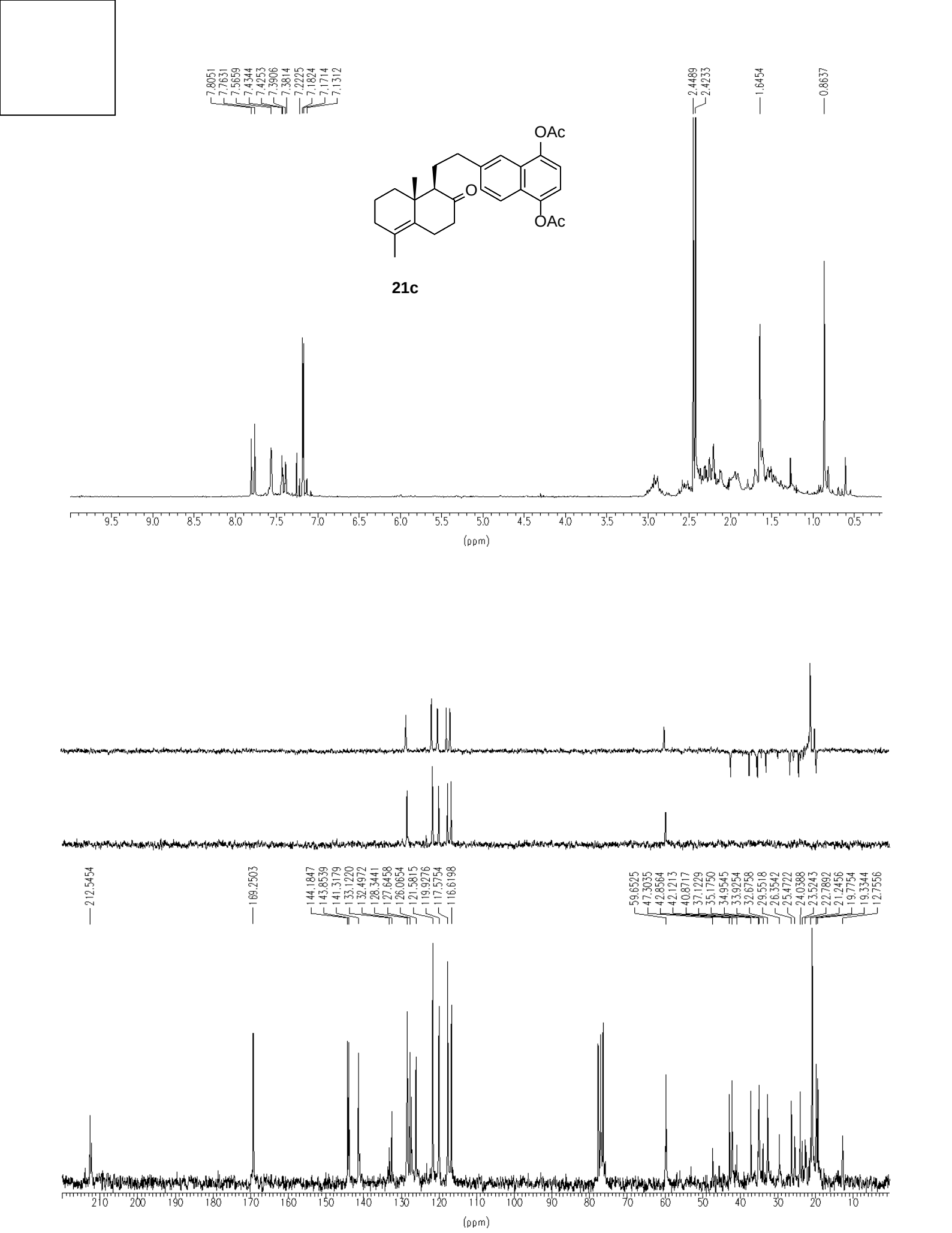



**Figure S28**: 1H and 13C NMR spectra for compounds **21c**.