Supplementary Information for

Copper-catalysed bromoalkynylation of arynes

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General Remarks:

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on a JEOL EX-270 (^{1}H, 270 MHz; ^{13}C, 67.8 MHz) spectrometer or a JEOL Lambda-400 (^{1}H, 400 MHz; ^{13}C, 99.5 MHz) spectrometer using residual chloroform (^{1}H) or $CDCl_3$ (^{13}C) as an internal standard. High-resolution mass spectra were obtained with a JEOL JMS-SX102A spectrometer. The preparative recycling gel permeation chromatography was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and -2002L columns (chloroform as an eluent). Unless otherwise noted, commercially available reagents were used without purification. 18-Crown-6 was recrystallized from distilled MeCN. KF (spray-dried) was vacuum dried at 100 °C for 12 h. 1,2-Dimethoxyethane (DME) was distilled from sodium/benzophenone ketyl. MeCN was distilled from phosphorus pentoxide.

Preparation of aryne precursors:

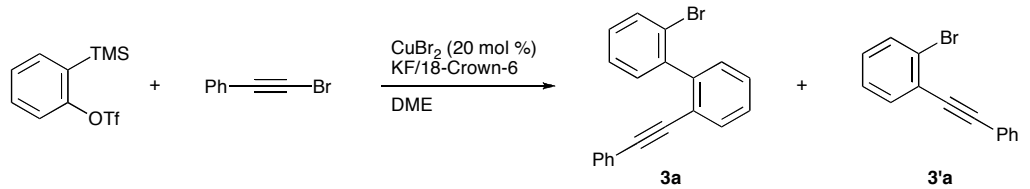
2-(Trimethylsilyl)phenyl triflate (**1a**),[1] 4,5-dimethyl-2-(trimethylsilyl)phenyl triflate (**1b**),[2] 6-(trimethylsilyl)-5-indanyl triflate (**1c**)[3] and 3-(trimethylsilyl)-5,6,7,8-tetrahydro-2-naphthyl triflate (**1d**)[4] were prepared according to literature procedures.

Copper-catalysed reaction of arynes with organic bromides. *A General Procedure:*

A Schlenk tube equipped with a magnetic stirring bar was charged with KF (0.45 mmol), 18-crown-6 (0.45 mmol) and cupric bromide (0.015 mmol). To this mixture were added DME (5 mL), an organic bromide (bromoalkyne **2**, propagyl bromide **7** or allyl bromide **9)** (0.075 mmol) and an aryne precursor **1** (0.225 mmol), and the resulting mixture was stirred at 25 °C for the period as specified in Table 1, Scheme 1 or Scheme 3. The

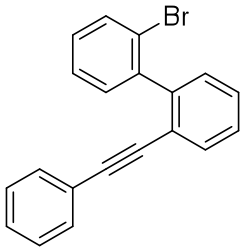
mixture was diluted with ethyl acetate, filtered through a Celite plug and washed three times with brine. The organic layer was dried over $MgSO_4$ before evaporation of the solvent. Gel permeation chromatography (chloroform as an eluent) gave the corresponding product.

Effect of temperatures on the formation of 3a and 3'a.



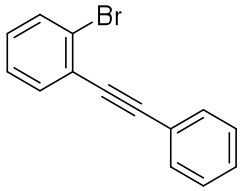
Temperature (°C)	Time (h)	Yield (%)	**3a:3'a**
25	17	61	85:15
0	71	trace	N/A
21	22	55	82:18
30	22	61	64:36
80	21	60	<1:99

2'-Bromo-2-(phenylethynyl)biphenyl (3a)



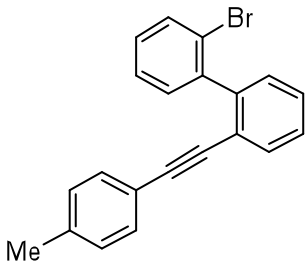
Isolated in 52% yield as a pale yellow solid; ^{1}H NMR ($CDCl_3$) δ 7.12–7.21 (m, 2 H), 7.21–7.44 (m, 9 H), 7.61–7.67 (m, 2 H), 7.71 (d, J = 7.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 88.4, 92.8, 122.9, 123.2, 123.6, 123.8, 126.8, 127.7, 127.9, 128.08, 128.15, 129.0, 129.6, 131.4, 131.5, 131.7, 132.5, 141.7, 143.7; HRMS Calcd for $C_{20}H_{13}Br$: M^+, 332.0201. Found: *m/z* 332.0198.

2-Bromodiphenylacetylene (3'a)[5]



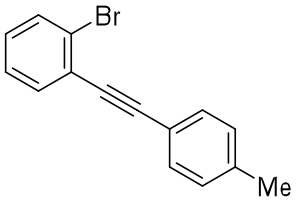
Isolated in 9% yield as a pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 7.18 (td, *J* = 7.6, 1.9 Hz, 1 H), 7.24–7.39 (m, 4 H), 7.53–7.65 (m, 4 H).

2'-Bromo-2-[(4-methylphenyl)ethynyl]biphenyl (3b)



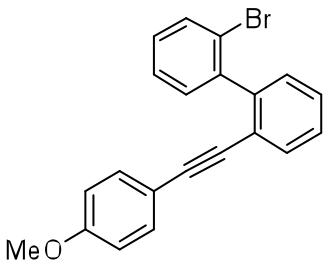
Isolated in 58% yield as a pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 2.31 (s, 3 H), 7.01–7.10 (m, 4 H), 7.23–7.29 (m, 1 H), 7.31–7.42 (m, 5 H), 7.59–7.64 (m, 1 H), 7.70 (d, *J* = 7.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.5, 87.7, 93.0, 120.1, 123.1, 123.6, 126.8, 127.70, 127.72, 128.92, 128.95, 129.5, 131.2, 131.5, 131.6, 132.5, 138.2, 141.7, 143.6; HRMS Calcd for $C_{21}H_{15}Br$: M^+, 346.0357. Found: *m/z* 346.0351.

4-[(2-bromophenyl)ethynyl]toluene (3'b)[6]



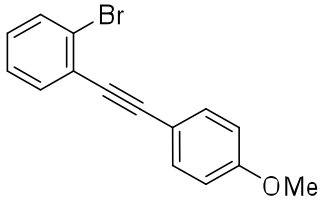
Isolated in 23% yield as a colorless oil; ^{1}H NMR ($CDCl_3$) δ 2.38 (s, 3 H), 7.12–7.21 (m, 3 H), 7.28 (ddd, *J* = 7.6, 7.6, 1.3 Hz, 1 H), 7.47 (d, *J* = 8.2 Hz, 2 H), 7.54 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.61 (dd, *J* = 7.9, 1.3 Hz, 1 H).

2'-Bromo-2-[(4-methoxyphenyl)ethynyl]biphenyl (3c)



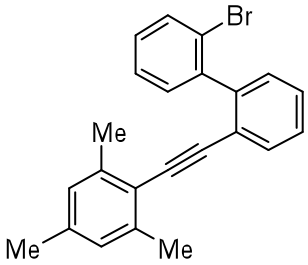
Isolated in 47% yield as a pale brown oil; ^{1}H NMR ($CDCl_3$) δ 3.78 (s, 3 H), 6.77 (dt, *J* = 8.9, 2.4 Hz, 2 H), 7.10 (dt, *J* = 8.9, 2.4 Hz, 2 H), 7.23–7.43 (m, 6 H), 7.58–7.64 (m, 1 H), 7.70 (d, *J* = 7.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 55.2, 87.1, 92.9, 113.8, 115.4, 123.2, 123.6, 126.8, 127.5, 127.7, 128.9, 129.5, 131.45, 131.55, 132.5, 132.8, 141.8, 143.4, 159.5; HRMS Calcd for $C_{21}H_{15}BrO$: M^+, 362.0306. Found: *m/z* 362.0304.

4-[(2-bromophenyl)ethynyl]anisole (3'c)



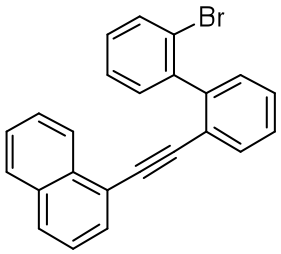
Isolated in 16% yield as a pale yellow solid; ^{1}H NMR ($CDCl_3$) δ 3.84 (s, 3 H), 6.89 (d, *J* = 8.9, Hz, 2 H), 7.15 (dt, *J* = 7.6, 2.0 Hz, 2 H), 7.23–7.38 (m, 2 H), 7.48–7.57 (m, 1 H), 7.00 (dd, *J* = 7.9, 1.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 55.3, 86.8, 94.0, 114.0, 115.0, 125.4, 125.7, 127.0, 129.0, 132.4, 133.0, 133.2, 159.9; HRMS Calcd for $C_{15}H_{11}BrO$: M^+, 285.9993. Found: *m/z* 258.9993.

2'-Bromo-2-(mesitylethynyl)biphenyl (3d)



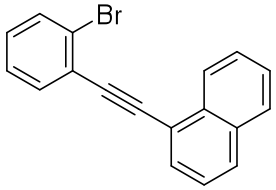
Isolated in 51% yield as a pale brown solid; ^{1}H NMR ($CDCl_3$) δ 2.10 (s, 6 H), 2.23 (s, 3 H), 6.77 (s, 2 H), 7.22 (ddd, *J* = 8.2, 6.5, 2.7 Hz, 1 H), 7.25–7.29 (m, 1 H), 7.32–7.42 (m, 4 H), 7.63–7.68 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.5, 21.3, 90.6, 95.8, 119.9, 123.6, 123.7, 127.1, 127.4, 127.6, 127.7, 128.9, 129.6, 131.2, 132.0, 132.6, 137.7, 140.2, 142.1, 143.1; HRMS Calcd for $C_{23}H_{19}Br$: M^+, 374.0670. Found: *m/z* 374.0672.

2'-Bromo-2-[(1-naphthyl)ethynyl]biphenyl (3e)



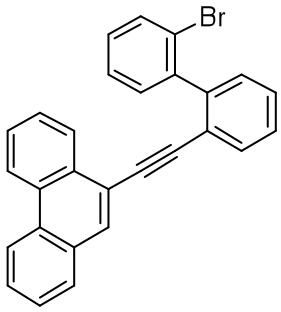
Isolated in 59% yield as a pale yellow solid; ^{1}H NMR ($CDCl_3$) δ 7.27–7.51 (m, 10 H), 7.55 (dd, *J* = 7.3, 1.0 Hz, 1 H), 7.71–7.82 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 91.0, 93.1, 120.9, 123.1, 123.7, 125.1, 126.2, 126.5, 127.2, 127.8, 128.00, 128.03, 128.6, 129.1, 129.6, 130.2, 131.4, 132.1, 132.7, 133.0, 133.1, 142.1, 143.6; HRMS Calcd for $C_{24}H_{15}Br$: M^+, 382.0357. Found: *m*/*z* 382.0355.

1-[(2-Bromophenyl)ethynyl]naphthalene (3'e)



Isolated in 17% yield as a pale brown oil; ^{1}H NMR ($CDCl_3$) δ 7.22 (td, *J* = 7.7, 1.9 Hz, 1 H), 7.34 (t, *J* = 7.7 Hz, 1 H), 7.48 (t, *J* = 7.7 Hz, 1 H), 7.55 (t, *J* = 7.7 Hz, 1 H), 7.62 (t, *J* = 6.8 Hz, 1 H), 7.65–7.70 (m, 2 H), 7.82 (d, *J* = 6.8 Hz, 1 H), 7.87 (d, *J* = 7.7 Hz, 2 H), 8.59 (d, *J* = 8.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 92.1, 92.7, 120.6, 125.2, 125.5, 125.6, 126.4, 126.5, 127.1, 128.2, 129.2, 129.4, 130.7, 132.5, 133.2, 133.3, 133.4, 134.7; HRMS Calcd for $C_{18}H_{11}Br$: M^+, 306.0044. Found: *m*/*z* 306.0044.

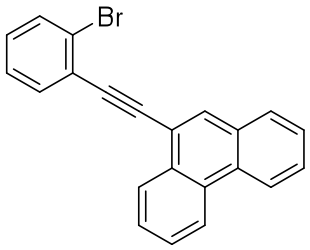
2'-Bromo-2-[(9-phenanthrenyl)ethynyl]biphenyl (3f)



Isolated in 59% yield as a pale yellow solid; ^{1}H NMR ($CDCl_3$) δ 7.35–7.53 (m, 7 H), 7.54–7.67 (m, 4 H), 7.76–7.84 (m, 3 H), 7.87 (s, 1 H), 8.61 (dd, *J* = 7.7, 3.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 91.2, 92.8, 119.7, 122.50, 122.55, 123.1, 123.8, 126.81, 126.83, 126.9, 127.2,

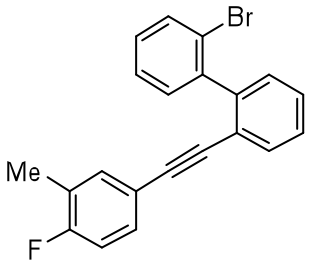
127.3, 127.9, 128.1, 128.5, 129.1, 129.6, 129.9, 130.2, 130.9, 131.2, 131.5, 131.7, 132.1, 132.8, 142.1, 143.7; HRMS Calcd for $C_{28}H_{17}Br$: M^+, 432.0514. Found: *m/z* 432.0507.

9-[(2-Bromophenyl)ethynyl]phenanthrene (3'f)



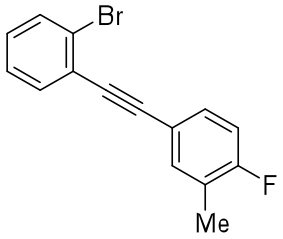
Isolated in 8% yield as a pale yellow solid; ^{1}H NMR ($CDCl_3$) δ 7.21–7.28 (m, 1 H), 7.36 (t, *J* = 7.7, Hz, 1 H), 7.62 (t, *J* = 7.9 Hz, 1 H), 7.65–7.75 (m, 5 H), 7.90 (d, *J* = 7.7 Hz, 1 H), 8.15 (s, 1 H), 8.66–8.75 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 92.33, 92.34, 119.4, 122.66, 122.74, 125.57, 125.59, 127.0, 127.14, 127.16, 127.18, 127.2, 127.6, 128.7, 129.5, 130.1, 130.5, 131.1, 131.2, 132.3, 132.6, 133.5; HRMS Calcd for $C_{22}H_{13}Br$: M^+, 356.0200. Found: *m/z* 356.0202.

2'-Bromo-2-[(4-fluoro-3-methylphenyl)ethynyl]biphenyl (3g)



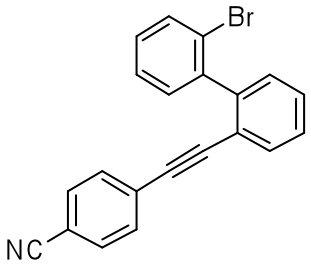
Isolated in 45% yield as a pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 2.19 (d, *J* = 2.0 Hz, 3 H), 6.82–7.02 (m, 3 H), 7.23–7.44 (m, 6 H), 7.59–7.63 (m, 1 H), 7.71 (d, *J* = 7.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.3 ($J_{C\text{-}F}$ = 4.1 Hz), 87.7 ($J_{C\text{-}F}$ = 1.7 Hz), 92.1, 115.1 ($J_{C\text{-}F}$ = 22.9 Hz), 118.9 ($J_{C\text{-}F}$ = 3.9 Hz), 122.9, 123.6. 124.0 ($J_{C\text{-}F}$ = 18.5 Hz), 126.8, 127.8, 127.9 129.0, 129.6, 130.5 ($J_{C\text{-}F}$ = 8.4 Hz), 131.5, 131.6, 132.5, 134.5 ($J_{C\text{-}F}$ = 5.6 Hz), 141.7, 143.6, 161.1 ($J_{C\text{-}F}$ = 248.1 Hz); HRMS Calcd for $C_{21}H_{14}BrF$: M^+, 364.0263. Found: *m/z* 364.0259.

5-[(2-bromophenyl)ethynyl]-2-fluorotoluene (3'g)



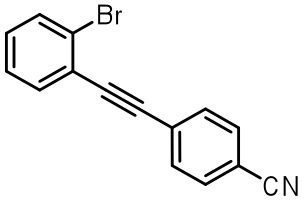
Isolated in 21% yield as a colorless oil; ^{1}H NMR ($CDCl_3$) δ 2.28 (d, J = 2.0 Hz, 3 H), 6.99 (t, J = 8.6 Hz, 1 H), 7.17 (td, J = 7.9, 1.6 Hz, 1 H), 7.29 (td, J = 7.6, 1.3 Hz, 1 H), 7.34–7.45 (m, 2 H), 7.53 (dd, J = 7.6, 2.0 Hz, 1 H), 7.61 (dd, J = 7.6, 2.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.4 ($J_{C\text{-}F}$ = 3.4 Hz), 87.3, 93.1 ($J_{C\text{-}F}$ = 1.1 Hz), 115.3 ($J_{C\text{-}F}$ = 22.5 Hz), 118.7 ($J_{C\text{-}F}$ = 3.6 Hz), 125.32, 125.35 ($J_{C\text{-}F}$ = 25.7 Hz), 125.43, 127.0, 129.3, 130.9 ($J_{C\text{-}F}$ = 8.4 Hz), 132.4, 133.1, 134.8 ($J_{C\text{-}F}$ = 5.6 Hz), 161.4 ($J_{C\text{-}F}$ = 248.6 Hz); HRMS Calcd for $C_{15}H_{10}BrF$: M^+, 287.9950. Found: *m/z* 287.9946.

2'-Bromo-2-[(4-cyanophenyl)ethynyl]biphenyl (3h)



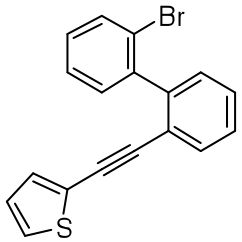
Isolated in 43% yield as a white solid; ^{1}H NMR ($CDCl_3$) δ 7.18–7.56 (m, 10 H), 7.62–7.67 (m, 1 H), 7.71 (dd, J = 7.9, 0.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 91.0, 92.8, 111.2, 118.5, 121.9, 123.5, 126.9, 127.9, 128.1, 128.9, 129.2, 129.7, 131.4, 131.8, 131.9, 132.5, 141.4, 144.1; HRMS Calcd for $C_{21}H_{12}BrN$: M^+, 357.0153. Found: *m/z* 357.0150.

4-[(2-bromophenyl)ethynyl]benzonitrile (3'h)



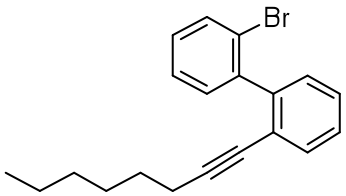
Isolated in 20% yield as a white solid; ^{1}H NMR ($CDCl_3$) δ 7.23 (td, J = 7.6, 2.0 Hz, 1 H), 7.32 (td, J = 7.6, 1.3 Hz, 1 H), 7.57 (dd, J = 7.9, 1.6 Hz, 1 H), 7.62–7.68 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 77.9, 91.9, 111.8, 118.5, 124.4, 125.8, 126.6, 127.2, 127.8, 130.3, 132.07, 132.15, 132.6, 133.4; HRMS Calcd for $C_{15}H_8BrN$: M^+, 280.9840. Found: *m/z* 280.9845.

2'-Bromo-2-[(2-thienyl)ethynyl]biphenyl (3i)



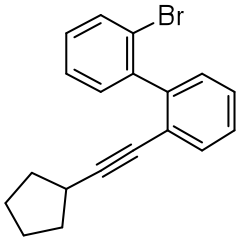
Isolated in 33% yield as a yellow solid; ^{1}H NMR ($CDCl_3$) δ 6.91 (dd, *J* = 5.8, 3.9 Hz, 1 H), 6.97 (d, *J* = 3.9 Hz, 1 H), 7.16–7.48 (m, 7 H), 7.57–7.64 (m, 1 H), 7.70 (d, *J* = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 86.1, 92.2, 122.6, 123.2, 123.5, 126.88, 126.93, 127.2, 127.7, 128.0, 129.1, 129.7, 131.3, 131.5, 131.6, 132.6, 141.4, 143.4; HRMS Calcd for $C_{18}H_{11}BrS$: M^+, 337.9765. Found: *m/z* 337.9762.

2'-Bromo-2-(oct-1-ynyl)biphenyl (3j)



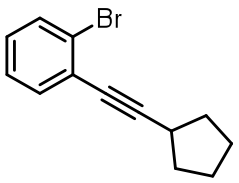
Isolated in 46% yield as a pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, *J* = 6.8 Hz, 3 H), 1.27–1.34 (m, 8 H), 2.19 (t, *J* = 6.8 Hz, 2 H), 7.17–7.27 (m, 2 H), 7.27–7.37 (m, 4 H), 7.46–7.52 (m, 1 H), 7.64 (d, *J* = 7.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 19.3, 22.5, 28.2, 28.3, 31.4, 79.3, 94.1, 123.5, 123.6, 126.7, 127.1, 127.6, 128.7, 129.4, 131.3, 131.8, 132.4, 142.0, 143.5; HRMS Calcd for $C_{20}H_{21}Br$: M^+, 340.0827. Found: *m/z* 340.0820.

2'-Bromo-2-(cyclopentylethynyl)biphenyl (3k)



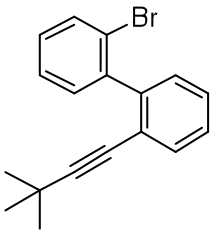
Isolated in 49% yield as a colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.20–1.61 (m, 6 H), 1.63–1.80 (m, 2 H), 2.63 (quint, *J* = 6.8 Hz, 1 H), 7.18–7.37 (m, 6 H), 7.44–7.50 (m, 1 H), 7.65 (d, *J* = 6.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 24.7, 30.6, 33.4, 78.8, 98.5, 123.6, 123.8, 126.7, 127.1, 127.6, 128.7, 129.2, 131.3, 131.5, 132.3, 142.1, 143.7; HRMS Calcd for $C_{19}H_{17}Br$: M^+, 324.0513. Found: *m/z* 324.0509.

1-Bromo-2-(cyclopentylethynyl)benzene (3'k)



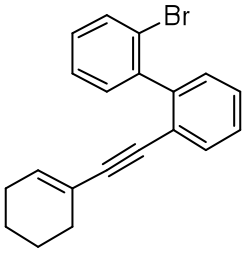
Isolated in 11% yield as a pale yellow solid; ^{1}H NMR ($CDCl_3$) δ 1.52–1.70 (m, 2 H), 1.71–1.89 (m, 4 H), 1.92–2.06 (m, 2 H), 2.89 (quint, *J* = 7.7 Hz, 1 H), 7.10 (td, *J* = 7.7, 1.9 Hz, 1 H), 7.21 (td, *J* = 7.7, 1.9 Hz, 1 H), 7.41 (dd, *J* = 7.7, 1.9 Hz, 1 H), 7.54 (d, *J* = 7.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 25.0, 30.9, 33.8, 78.9, 99.9, 125.6, 126.8, 128.5, 132.2, 133.1; HRMS Calcd for $C_{13}H_{13}Br$: M^+, 248.0201. Found: *m/z* 248.0207.

2'-Bromo-2-(*tert*-butylethynyl)biphenyl (3l)



Isolated in 41% yield as a pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.04 (s, 9 H), 7.16–7.38 (m, 6 H), 7.44–7.50 (m, 1 H), 7.64 (dd, *J* = 7.7, 1.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 27.8, 30.5, 77.8, 102.3, 123.6, 123.7, 126.7, 127.1, 127.5, 128.6, 129.1, 131.2, 131.3, 132.3, 142.2, 143.9; HRMS Calcd for $C_{18}H_{17}Br$: M^+, 312.0514. Found: *m/z* 312.0519.

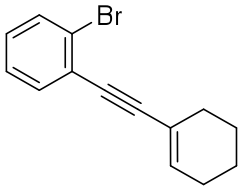
2'-Bromo-2-[(cyclohex-1-enyl)ethynyl]biphenyl (3m)



Isolated in 39% yield as a brown oil; ^{1}H NMR ($CDCl_3$) δ 1.48–1.60 (m, 4 H), 1.83–1.95 (m, 2 H), 1.99–2.07 (m, 2 H), 5.85–5.91 (m, 1 H), 7.19–7.38 (m, 6 H), 7.48–7.54 (m, 1 H), 7.66 (d, *J* = 7.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.4, 22.2, 25.7, 28.6, 85.8, 94.8, 120.7, 123.4, 123.5, 126.7, 127.3, 127.6, 128.8, 129.4, 131.4, 131.5, 132.4, 134.9, 141.8, 143.4; HRMS

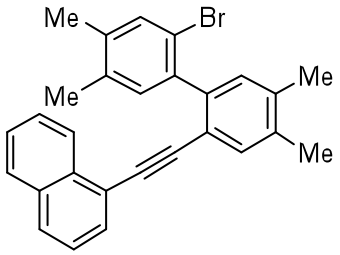
Calcd for $C_{20}H_{17}Br$: M^+, 336.0513. Found: *m/z* .336.0514

1-Bromo-2-[(cyclohex-1-enyl)ethynyl]benzene (3'm)



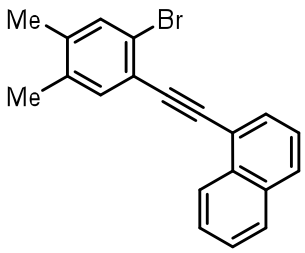
Isolated in 16% yield as a pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.55–1.75 (m, 4 H), 2.12–2.21 (m, 2 H), 2.23–2.31 (m, 2 H), 6.29 (sept, *J* = 2.0, 1 H), 7.11 (td, *J* = 7.9, 1.6 Hz, 1 H), 7.23 (td, *J* = 7.6, 1.3 Hz, 1 H), 7.44 (dd, *J* = 7.8, 1.6 Hz, 1 H), 7.56 (dd, *J* = 8.2, 1.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.5, 22.2, 25.8, 29.0, 95.9, 100.5, 120.6, 125.4, 125.8, 126.9, 128.8, 132.3, 133.0, 136.0; HRMS Calcd for $C_{14}H_{13}Br$: M^+, 260.0200. Found: *m/z* 260.0203.

2'-Bromo-4,5,4',5'-tetramethyl-2-[(1-naphthyl)ethynyl]biphenyl (3n)



Isolated in 70% yield as a white solid; ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 3 H), 2.34 (s, 3 H), 2.35 (s, 3 H), 2.37 (s, 3 H), 7.10 (s, 1 H), 7.23 (d, *J* = 10.1 Hz, 2 H), 7.37 (t, *J* = 8.0 Hz, 1 H), 7.44 (t, *J* = 7.2 Hz, 1 H), 7.47–7.54 (m, 3 H), 7.56 (d, *J* = 7.0 Hz, 1 H), 7.74 (d, *J* = 7.5 Hz, 1 H), 7.76 (d, *J* = 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 19.3, 19.41, 19.43, 19.9, 89.7, 93.8, 120.4, 121.4, 125.2, 126.08, 126.12, 126.4, 127.9, 128.2, 129.9, 131.0, 132.6, 133.0, 133.06, 133.15, 133.3, 135.6, 136.1, 137.0, 137.6, 139.3, 141.3; HRMS Calcd for $C_{26}H_{23}Br$: M^+, 438.0983. Found: *m/z* 438.0976.

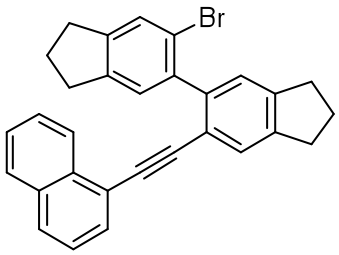
2-Bromo-4,5-dimethyl-1-[(1-naphthyl)ethynyl]benzene (3'n)



Isolated in 16% yield as a white solid; ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 3 H), 2.28 (s, 3 H), 7.42–7.66 (m, 5 H), 7.80 (d, *J* = 6.9 Hz, 1 H), 7.83–7.91 (m, 2 H), 8.60 (d, *J* = 8.2 Hz, 1 H);

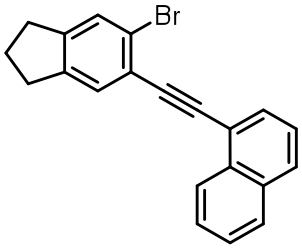
^{13}C NMR ($CDCl_3$) δ 19.1, 19.6, 91.0, 93.0, 120.8, 122.2, 122.6, 125.2, 126.4, 126.5, 126.8, 128.2, 128.9, 130.5, 133.17, 133.22, 133.3, 134.2, 135.8, 139.1; HRMS Calcd for $C_{20}H_{15}Br$: M^+, 334.0357. Found: *m/z* 334.0364.

2'-Bromo-4,5,4',5'-bistrimethylene-2-[(1-naphthyl)ethynyl]biphenyl (3o)



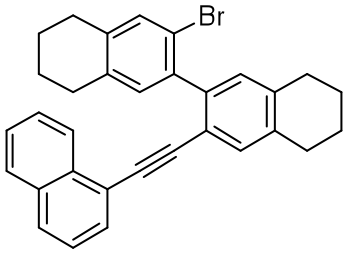
Isolated in 36% yield as a white solid; ^{1}H NMR ($CDCl_3$) δ 2.05–2.27 (m, 4 H), 2.89 (t, *J* = 7.7 Hz, 2 H), 2.92–3.11 (m, 6 H), 7.18 (s, 1 H), 7.20–7.31 (m, 2 H), 7.37 (t, *J* = 7.7 Hz, 1 H), 7.44 (t, *J* = 7.7 Hz, 1 H), 7.49 (d, *J* = 8.7 Hz, 1 H), 7.55 (d, *J* = 6.8 Hz, 1 H), 7.60 (s, 2 H), 7.73 (d, *J* = 8.7 Hz, 1 H), 7.77 (d, *J* = 8.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 25.3, 25.7, 32.4, 32.5, 32.7, 33.0, 89.6, 94.3, 120.8, 121.1, 121.5, 125.2, 125.8, 126.06, 126.10, 126.4, 127.3, 127.7, 127.9, 128.2, 128.3, 129.95, 130.05, 133.1, 139.9, 142.4, 143.5, 143.7, 144.8, 145.5; HRMS Calcd for $C_{30}H_{23}Br$: M^+, 462.0983. Found: *m/z* 462.0980.

2-Bromo-4,5-trimethylene-1-[(1-naphthyl)ethynyl]benzene (3'o)



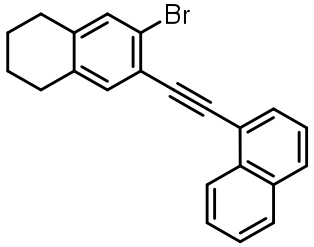
Isolated in 19% yield as a white solid; ^{1}H NMR ($CDCl_3$) δ 2.12 (quint, *J* = 7.6 Hz, 2 H), 2.92 (td, *J* = 11.5, 7.6 Hz, 4 H), 7.42–7.65 (m, 5 H), 7.80 (dd, *J* = 7.2, 1.3 Hz, 1 H), 7.82–7.91 (m, 2 H), 8.60 (d, *J* = 8.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 25.5, 32.5, 32.8, 90.9, 93.4, 116.7, 119.2, 122.7, 124.7, 125.2, 126.4, 126.6, 126.8, 128.2, 128.4, 128.8, 129.0, 130.5, 133.2, 143.6, 146.9; HRMS Calcd for $C_{21}H_{15}Br$: M^+, 346.0357. Found: *m/z* 346.0355.

2'-Bromo-4,5,4',5'-bistetramethylene-2-[(1-naphthyl)ethynyl]biphenyl (3p)



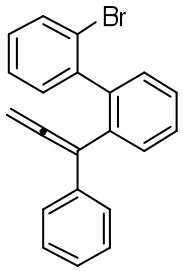
Isolated in 41% yield as a pale yellow solid; ^{1}H NMR ($CDCl_3$) δ 1.73–1.96 (m, 8 H), 2.64–2.98 (m, 8 H), 7.03 (s, 1 H), 7.14 (s, 1 H), 7.27–7.50 (m, 5 H), 7.55 (t, *J* = 7.9 Hz, 2 H), 7.63 (t, *J* = 8.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.90, 22.97, 22.99, 23.03, 28.78, 28.97, 29.00, 29.4, 89.5, 94.0, 120.0, 120.2, 121.4, 125.2, 126.1, 126.2, 126.4, 127.9, 128.2, 129.9, 130.4, 132.1, 132.5, 132.7, 133.0, 133.1, 136.2, 136.6, 137.6, 138.2, 139.0, 140.8; HRMS Calcd for $C_{32}H_{27}Br$: M^+, 490.1296. Found: *m/z* 490.1299.

2-Bromo-4,5-tetramethylene-1-[(1-naphthyl)ethynyl]benzene (3'p)



Isolated in 13% yield as a pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.74–1.88 (m, 4 H), 2.69–2.84 (m, 4 H), 7.36 (s, 1 H), 7.39 (s, 1 H), 7.46 (t, *J* = 7.7 Hz, 1 H), 7.50–7.63 (m, 2 H), 7.79 (d, *J* = 6.8 Hz, 1 H), 7.81–7.88 (m, 2 H), 8.59 (d, *J* = 7.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.7, 22.8, 28.7, 29.2, 90.7, 93.1, 120.9, 121.8, 122.2, 125.2, 126.4, 126.5, 126.8, 128.2, 128.8, 130.5, 132.69, 132.71, 133.2, 133.3, 133.8, 139.7; HRMS Calcd for $C_{22}H_{17}Br$: M^+, 360.0514. Found: *m/z* 360.0510.

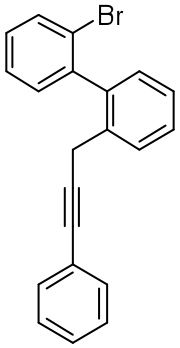
2'-Bromo-2-(1-phenylpropa-1,2-dienyl)biphenyl (8a)



Isolated in 41% yield as a brown oil; ^{1}H NMR ($CDCl_3$) δ 4.75 (d, *J* = 12.6 Hz, 1 H), 4.82 (d, *J* = 12.6 Hz, 1 H), 7.02–7.08 (m, 1 H), 7.10–7.24 (m, 7 H), 7.29–7.34 (m, 1 H), 7.36–7.45 (m, 3 H), 7.51 (d, *J* = 8.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 107.1, 123.7, 126.6, 127.2, 127.4, 127.9, 128.0, 128.3, 130.3, 131.0, 131.6, 132.4, 135.2, 136.9, 140.9, 141.9; HRMS Calcd for

$C_{21}H_{15}Br$: M^+, 346.0357. Found: *m/z* 346.0353

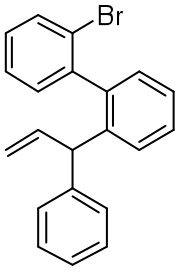
2'-Bromo-2-(3-phenylprop-2-ynyl)biphenyl (8b)



Isolated in 13% yield as a pale brown oil; ^{1}H NMR ($CDCl_3$) δ 3.50 (d, *J* = 18.4 Hz, 1 H), 3.66 (d, *J* = 19.3 Hz, 1 H), 7.16 (d, *J* = 7.7 Hz, 1 H), 7.21–7.47 (m, 10 H), 7.67 (d, *J* = 6.8 Hz, 1 H), 7.72 (d, *J* = 7.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.9, 82.8, 87.4, 123.7, 126.6, 127.3, 127.7, 128.2, 128.36, 128.43, 129.1, 129.5, 131.1, 132.6, 134.6, 140.4, 141.6; HRMS Calcd for $C_{21}H_{15}Br$: M^+-H, 345.0279. Found: *m/z* 345.0269

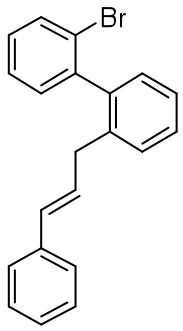
2'-Bromo-2-(1-phenyl-2-propen-1-yl)biphenyl (10a)

(A mixture of two diastereomers, ratio = 53.5:46.5)



Isolated in 15% yield as a pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 4.48 (d, *J* = 6.8 Hz), 4.52 (d, *J* = 6.8 Hz), 4.65 (d, *J* = 16.4 Hz), 4.77 (d, *J* = 16.4 Hz), 5.13 (d, *J* = 9.6 Hz), 6.08 (ddd, *J* = 16.4, 9.7, 6.8 Hz, *major*), 6.22 (ddd, *J* = 17.4, 10.6, 6.8 Hz, *minor*), 6.73 (dd, *J* = 7.7, 1.9 Hz), 6.81 (d, *J* = 6.8 Hz), 6.95–7.43 (m), 7.60 (d, *J* = 7.7 Hz), 7.62 (d, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 50.9, 51.3, 116.58, 116.65, 123.7, 123.9, 125.9, 126.0, 126.18, 126.25, 126.67, 126.75, 128.00, 128.06, 128.11, 128.4, 128.6, 128.77, 128.83, 128.96, 128.98, 129.8, 130.0, 131.56, 131.65, 132.3, 132.58, 132.62, 140.4, 140.5, 140.92, 140.99, 141.03, 141.1, 141.7, 141.8, 142.8; HRMS Calcd for $C_{21}H_{17}Br$: M^+, 348.0514. Found: *m/z* 348.0515

2'-Bromo-2-(3-phenyl-(*E*)-2-propen-1-yl)biphenyl (10b)

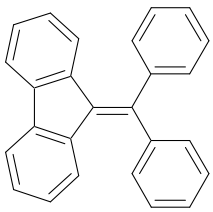


Isolated in 34% yield as a pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 3.23 (dd, *J* = 16.4, 6.8 Hz, 1 H), 3.35 (dd, *J* = 15.5, 5.8 Hz, 1 H), 6.02–6.21 (m, 2 H), 6.95–7.40 (m, 12 H), 7.62 (d, *J* = 7.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 36.9, 123.9, 126.0, 126.9, 127.0, 128.1, 128.4, 128.7, 128.5, 129.3, 129.7, 131.0, 131.2, 132.5, 137.5, 137.9, 140.9, 142.0; HRMS Calcd for $C_{21}H_{17}Br$: M^+, 348.0514. Found: *m/z* 348.0513

Synthesis of dibenzofulvene derivatives. ***A General Procedure:***

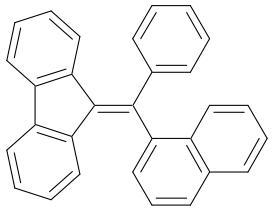
A Schlenk tube equipped with a magnetic stirring bar was charged with ethanol (0.5 mL), aryl boronic acid **11** (0.075 mmol) and Cs_2CO_3 (0.095 mol). To this mixture was added an ethanol solution (1.0 ml) of $Pd(PPh_3)_4$ (0.0075 mmol) and **3** (0.05 mmol), and the resulting mixture was stirred at 70 °C for the period as specified in Scheme 4. The mixture was diluted with ether at 0 °C, filtered through a Celite plug and washed three times with brine. The organic layer was dried over $MgSO_4$ before evaporation of the solvent. Gel permeation chromatography (chloroform as an eluent) gave the corresponding product.

Diphenyldibenzofulvene (12a)



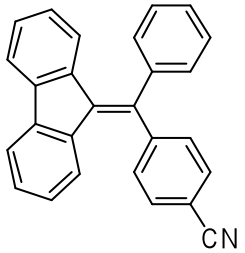
Isolated in 81% yield as a white solid; ^{1}H NMR ($CDCl_3$) δ 6.64 (d, *J* = 7.9 Hz, 2 H), 6.94 (t, *J* = 7.4 Hz, 2 H), 7.25 (t, *J* = 7.6 Hz, 2 H), 7.34–7.51 (m, 10 H), 7.71 (d, *J* = 7.6 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 119.2, 124.8, 126.4, 127.6, 128.2, 128.8, 129.6, 134.1, 138.6, 140.4, 142.9, 145.5; HRMS Calcd for $C_{26}H_{18}$: M^+, 330.1408. Found: *m/z* 330.1409.

(1-Naphthyl)phenyldibenzofulvene (12b)



Isolated in 89% yield as a yellow solid; ^{1}H NMR ($CDCl_3$) δ 6.02 (d, *J* = 7.7 Hz, 1 H), 6.69 (t, *J* = 7.7 Hz, 1 H), 6.83 (d, *J* = 7.7 Hz, 1 H), 7.00 (t, *J* = 7.7 Hz, 1 H), 7.15 (t, *J* = 6.8 Hz, 1 H), 7.31 (t, *J* = 7.7 Hz, 1 H), 7.33–7.43 (m, 4 H), 7.44–7.61 (m, 5 H), 7.67 (d, *J* = 7.7 Hz, 1 H), 7.72 (d, *J* = 7.7 Hz, 1 H), 7.91 (d, *J* = 7.7 Hz, 1 H), 7.92 (d, *J* = 7.7 Hz, 1 H), 8.11 (d, *J* = 8.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 119.1, 119.3, 124.9, 125.1, 125.7, 126.0, 126.1, 126.46, 126.57, 126.61, 126.7, 127.6, 127.9, 128.1, 128.3, 128.4, 128.7, 128.8, 128.9, 129.2, 131.0, 134.0, 135.8, 138.1, 138.3, 140.3, 140.6, 140.8, 142.6, 142.7; HRMS Calcd for $C_{30}H_{20}$: M^+, 380.1565. Found: *m/z* 380.1558.

(4-Cyanophenyl)phenyldibenzofulvene (12c)



Isolated in 52% yield as a pale brown solid; ^{1}H NMR ($CDCl_3$) δ 6.57 (d, *J* = 7.7 Hz, 1 H), 6.58 (d, *J* = 7.7 Hz, 1 H), 6.92 (d, *J* = 7.7 Hz, 1 H), 6.96 (d, *J* = 6.8 Hz, 1 H), 7.23–7.31 (m, 2 H), 7.32–7.37 (m, 2 H), 7.42–7.47 (m, 3 H), 7.52 (d, *J* = 7.7 Hz, 2 H), 7.66–7.74 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 111.8, 118.7, 119.4, 119.6, 124.7, 125.0, 126.6, 126.7, 128.3, 128.4, 128.7, 129.1, 129.7, 130.7, 132.6, 135.5, 137.8, 138.2, 140.6, 140.9, 141.8, 142.4, 147.6; HRMS Calcd for $C_{27}H_{17}N$: M^+, 355.1361. Found: *m/z* 355.1359.

References

1 Y. Himeshima, T. Sonoda and H. Kobayashi, *Chem. Lett.*, 1983, 1211–1214.

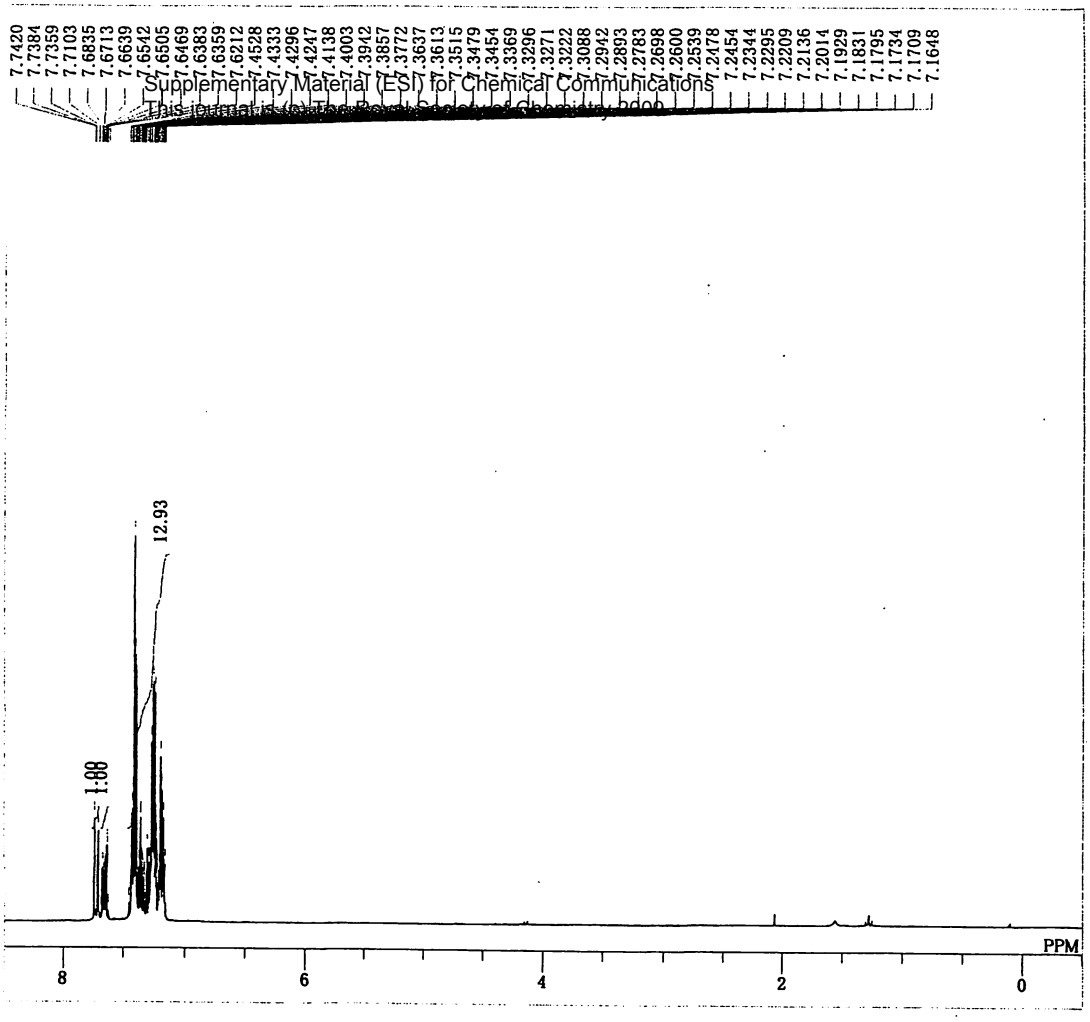
2 H. Yoshida, S. Sugiura and A. Kunai, *Org. Lett.*, 2002, **4**, 2767–2769.

3 D. Peña, A. Cobas, D. Pérez and E. Guitián, *Synthesis,* 2002, 1454–1458

4 H. Yoshida, T. Terayama, J. Ohshita and A. Kunai, *Chem. Commun.*, 2004, 1980–1981.

5 Z. U. Levi and T. D. Tilley, *J. Am. Chem. Soc.*, 2009, **131**, 2796–2797.

6 I. Nakamura, T. Sato, M. Terada, and Y. Yamamoto, *Org. Lett.*, 2007, **9**, 4081–4083.



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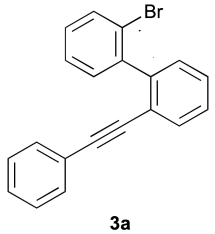
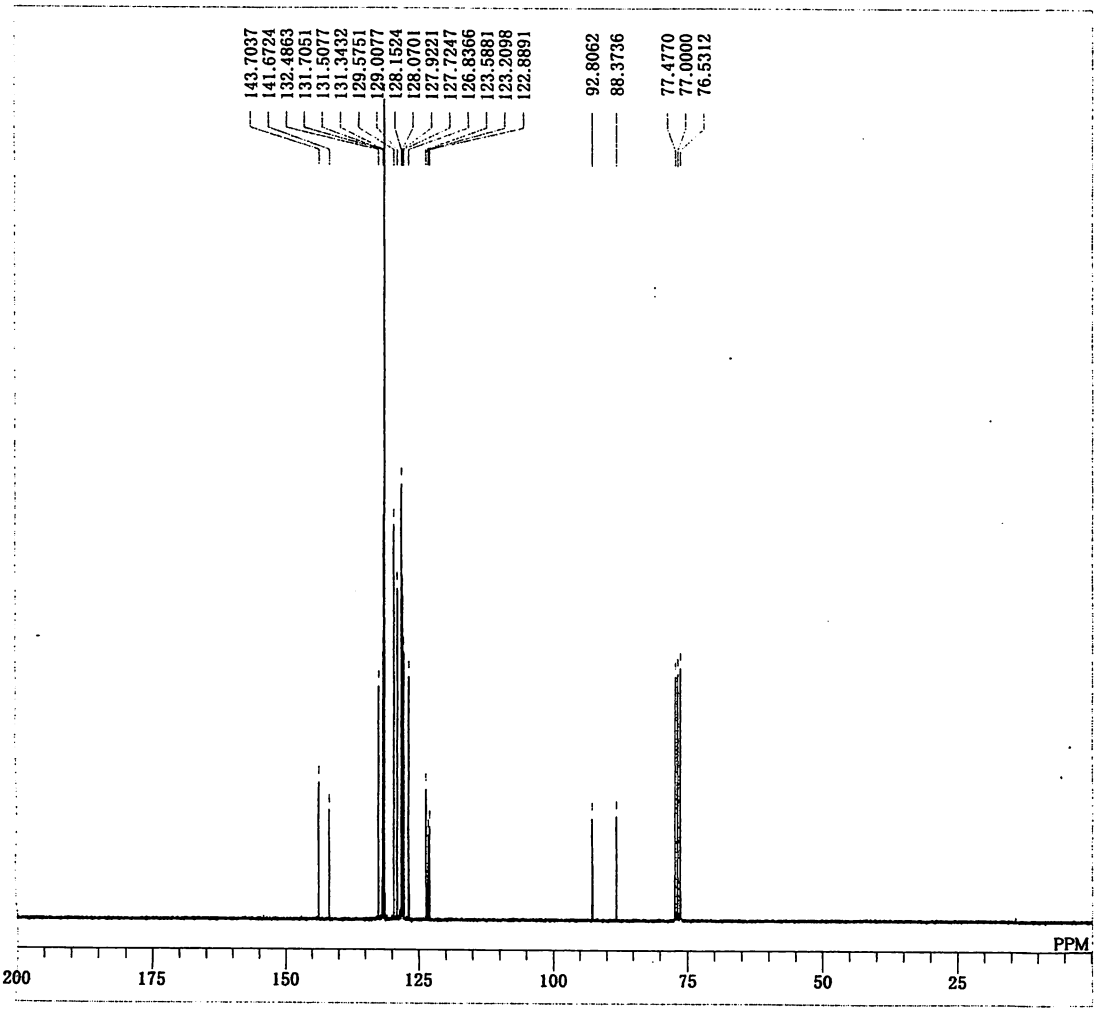
OBFIN 5800.00 Hz
POINT 16384
FREQU 5401.76 Hz
SCANS 16
ACQTM 3.0331 sec
PD 3.9670 sec
PW1 5.40 usec
IRNUC 1H
CTEMP 18.2 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 17



3a



DFILE _DEFAULT.ALS
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DATIM Tue Mar 18 08:39:03 2
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EXMOD BCM
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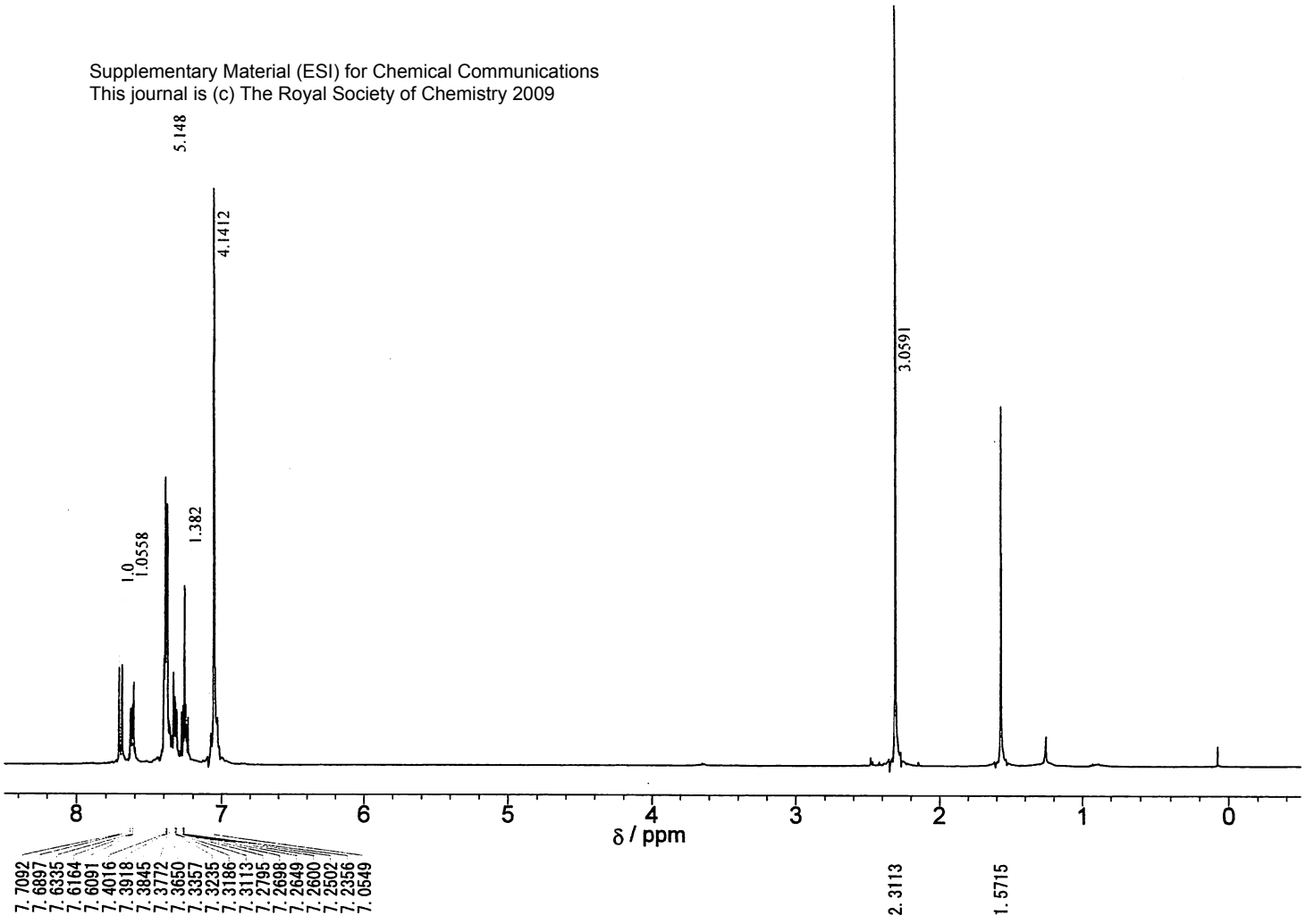
OBSET 135.00 KHz
OBFIN 5200.00 Hz
POINT 32768
FREQU 18306.64 Hz
SCANS 11432
ACQTM 1.7900 sec
PD 1.2100 sec
PW1 3.50 usec
IRNUC 1H
CTEMP 19.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 27


5.148
4.1412
3.0591
1.382
1.0
1.0558
δ / ppm
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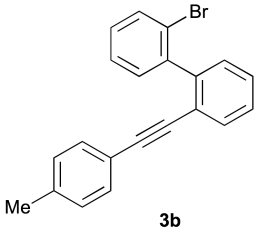
7.6897
7.6335
7.6164
7.6091
7.4016
7.3918
7.3845
7.3772
7.3650
7.3357
7.3235
7.3186
7.3113
7.2795
7.2698
7.2649
7.2600
7.2502
7.2356
7.0549
2.3113
1.5715


Br
Me

3b

δ / ppm
143.5969
141.7344
138.2154
132.4796
131.5977
131.5318
131.2434
129.5457
128.9523
128.9194
127.7162
127.6997
126.8096
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123.0929
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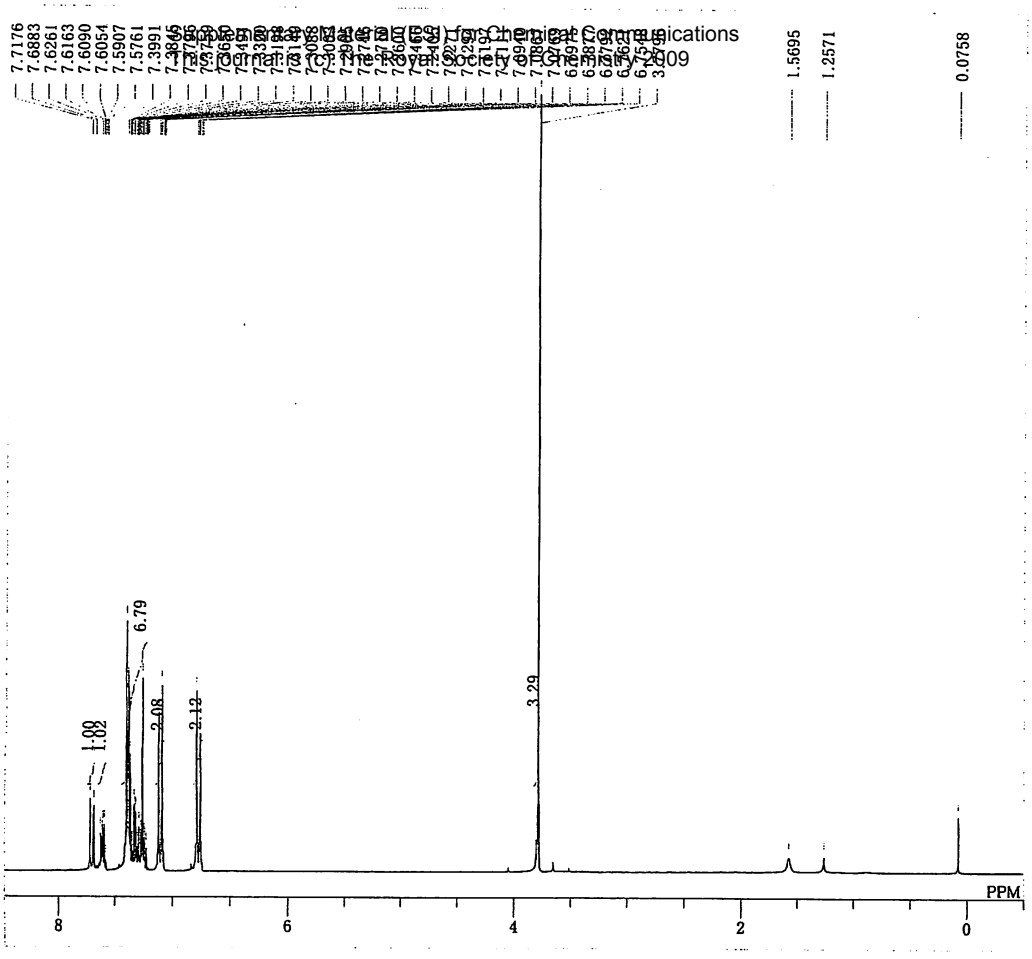
87.7300
77.3214
77.0000
76.6786
21.4628



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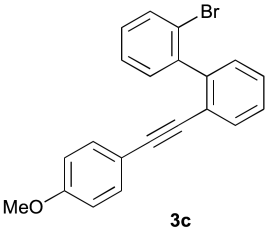
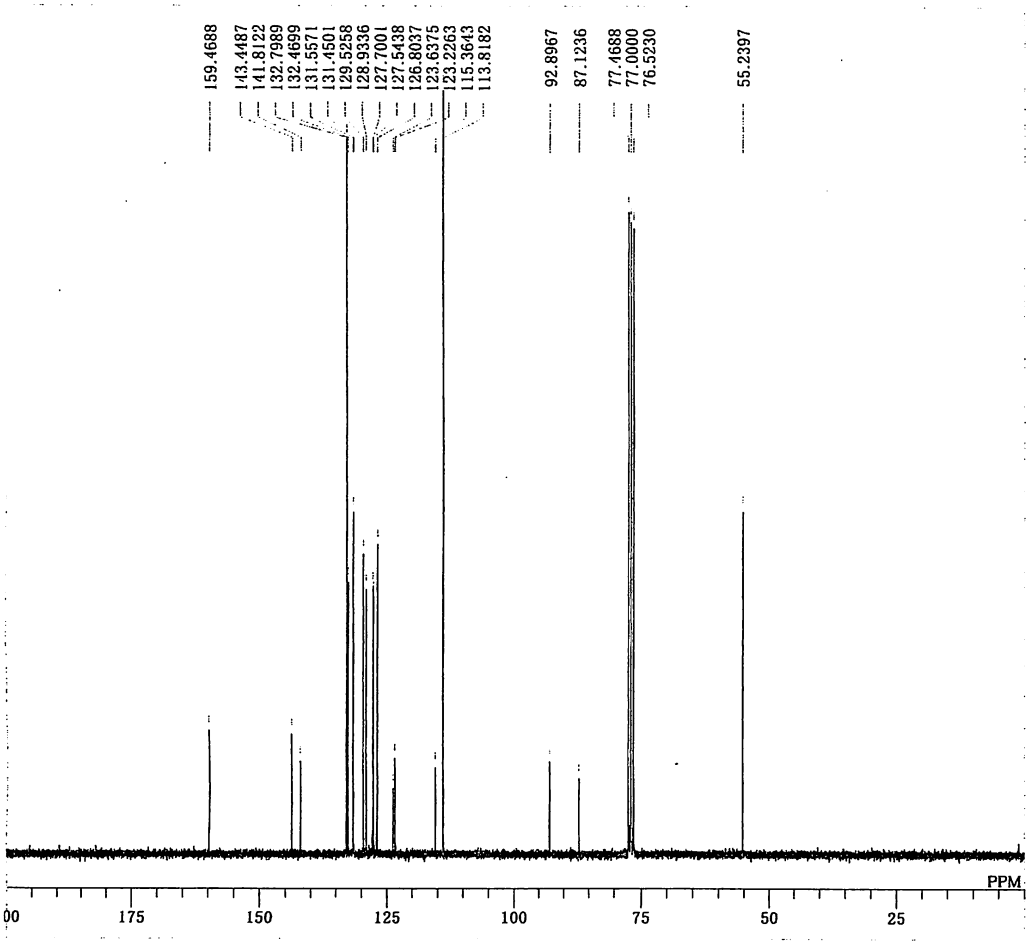
OBFIN	5800.00 Hz
POINT	16384
FREQU	5401.76 Hz
SCANS	16
ACQTM	3.0331 sec
PD	3.9670 sec
PW1	5.40 usec
IRNUC	1H
CTEMP	17.9 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	21



3c



DFILE	_DEFAULT.ALS
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EXMOD	BCM
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OBSET	135.00 KHz
OBFIN	5200.00 Hz
POINT	32768
FREQU	18306.64 Hz
SCANS	11799
ACQTM	1.7900 sec
PD	1.2100 sec
PW1	3.50 usec
IRNUC	1H
CTEMP	20.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
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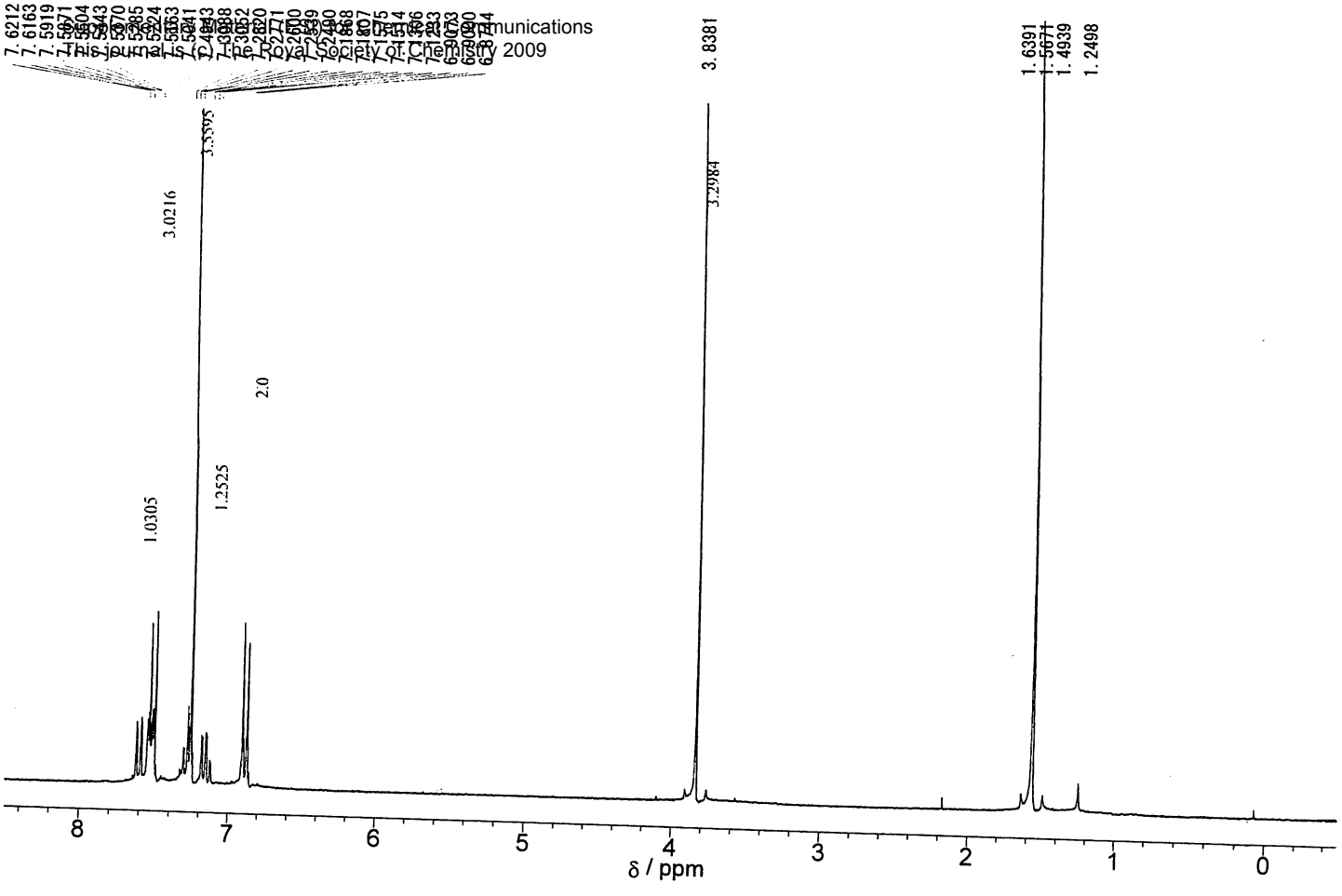
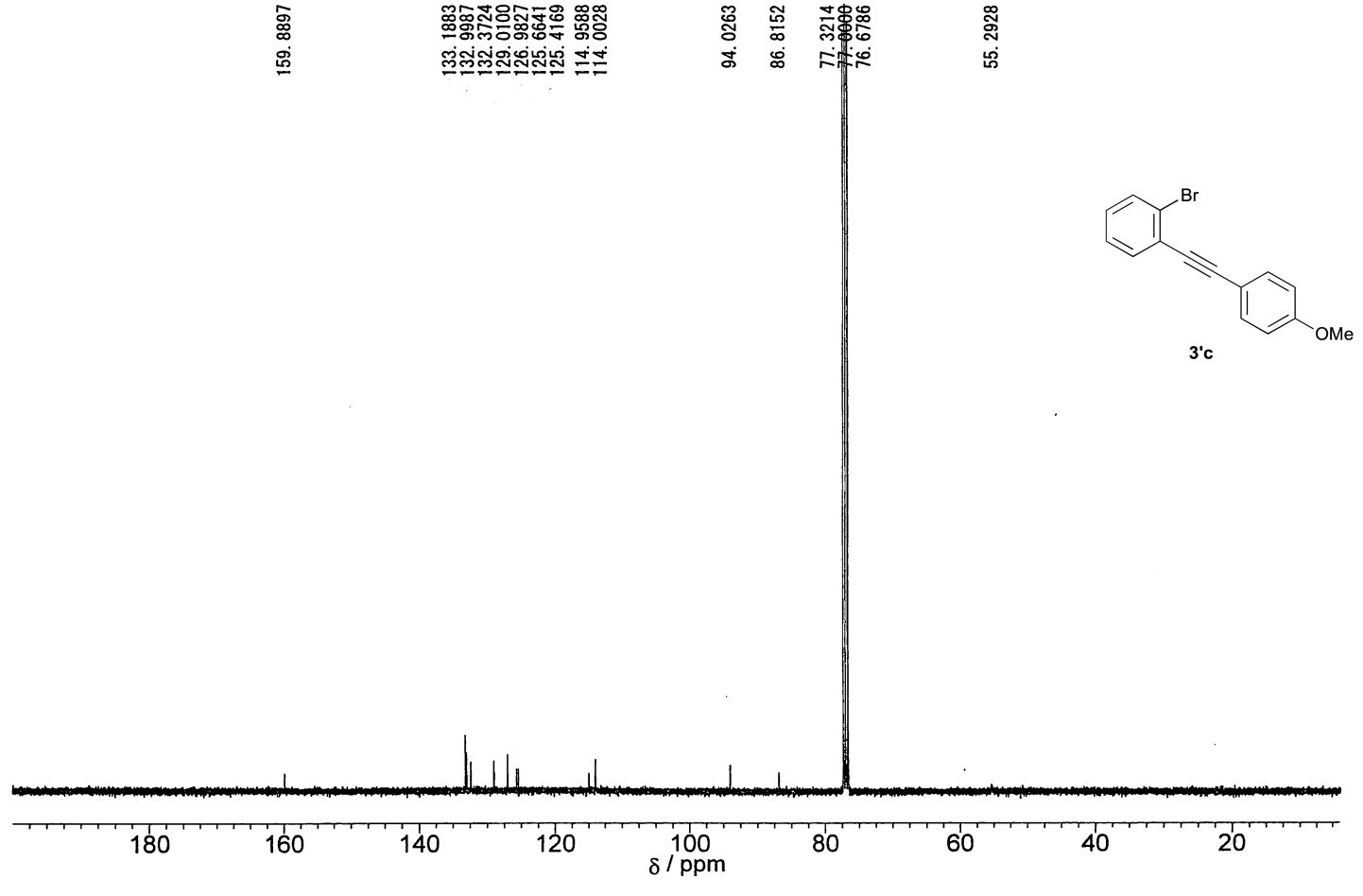
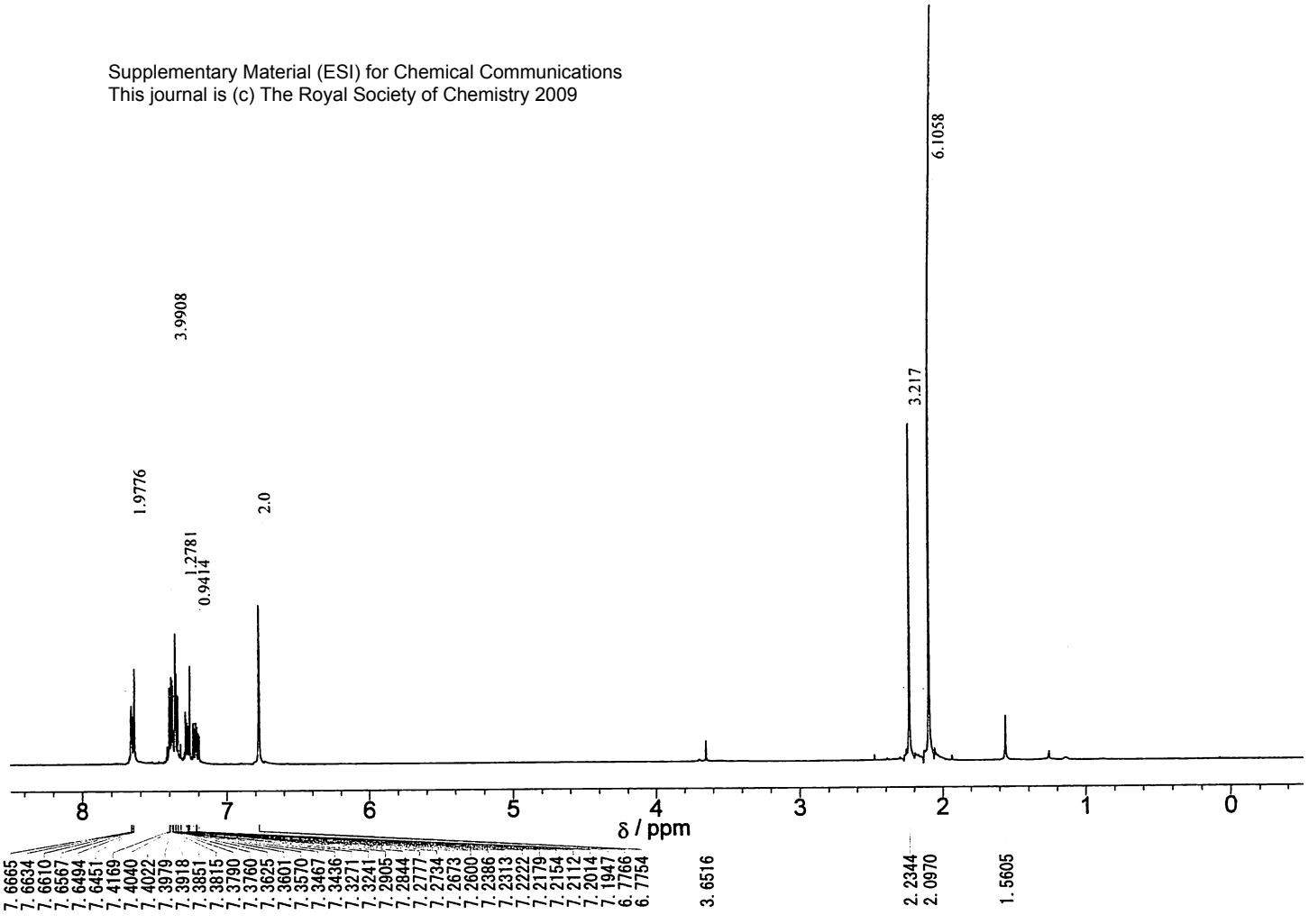
RGAIN	27





3'c


6.1058
3.9908
3.217
1.9776
2.0
1.2781
0.9414
δ / ppm
7.6665
7.6634
7.6610
7.6567
7.6494
7.6451
7.4169
7.4040
7.4022
7.3979
7.3918
7.3851
7.3815
7.3790
7.3760
7.3625
7.3601
7.3570
7.3467
7.3436
7.3271
7.3241
7.2905
7.2844
7.2777
7.2734
7.2673
7.2600
7.2386
7.2313
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7.2179
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7.2014
7.1947
6.7766
6.7754
3.6516
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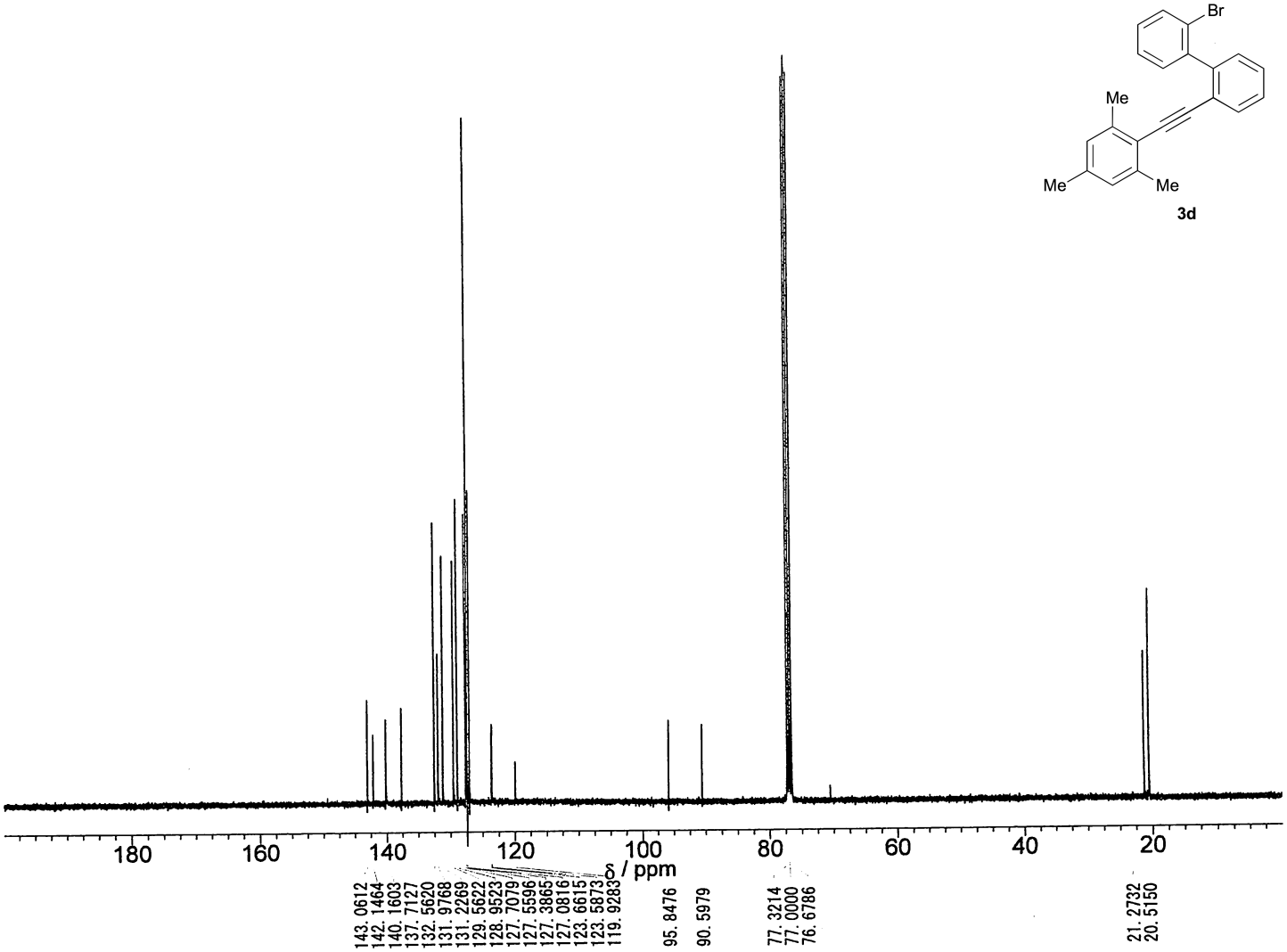
2.0970
1.5605


Br
Me
Me
Me
3d
δ / ppm
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142.1464
140.1603
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132.5620
131.9768
131.2269
129.5622
128.9523
127.7079
127.5596
127.3865
127.0816
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119.9283
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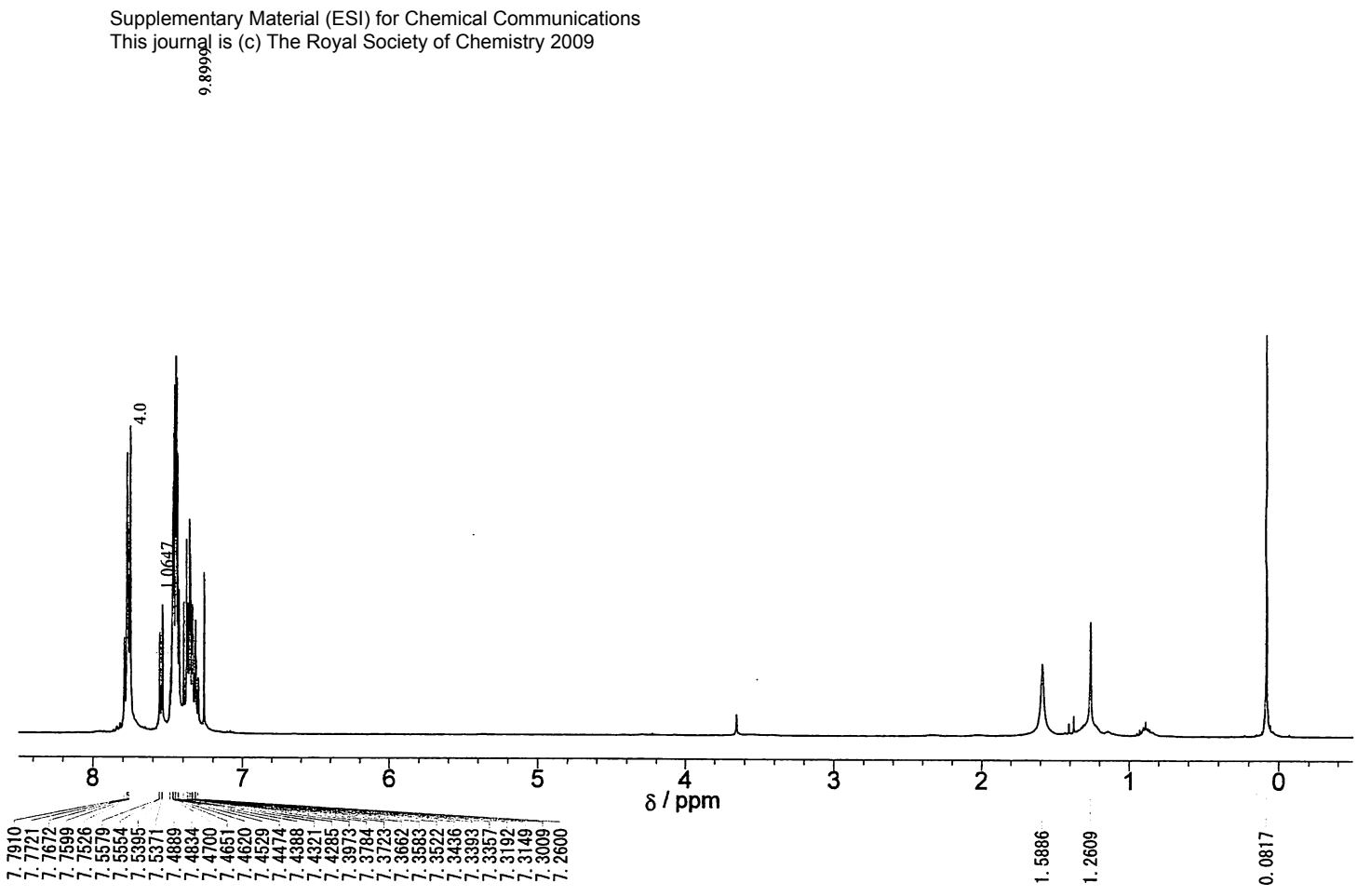
77.0000
76.6786
21.2732
20.5150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4.0
1.0647
δ / ppm
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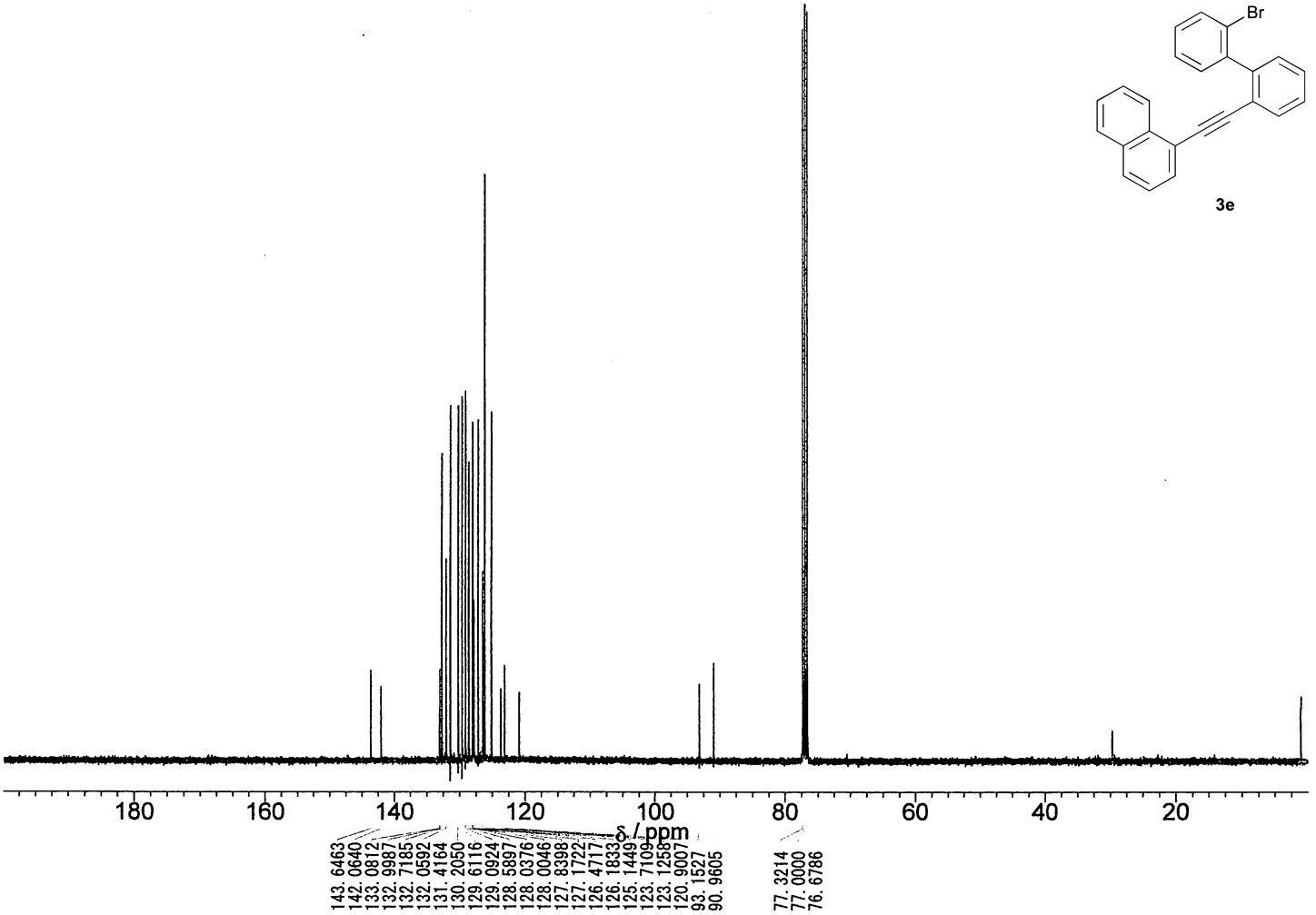
7.7721
7.7672
7.7599
7.7526
7.5579
7.5554
7.5395
7.5371
7.4889
7.4834
7.4700
7.4651
7.4620
7.4529
7.4474
7.4388
7.4321
7.4285
7.3973
7.3784
7.3723
7.3662
7.3583
7.3522
7.3436
7.3393
7.3357
7.3192
7.3149
7.3009
7.2600
1.5886
1.2609
0.0817


Br
δ / ppm
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132.9987
132.7185
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131.4164
130.2050
129.6116
129.0924
128.5897
128.0376
128.0046
127.8398
127.1722
126.4717
126.1833
125.1449
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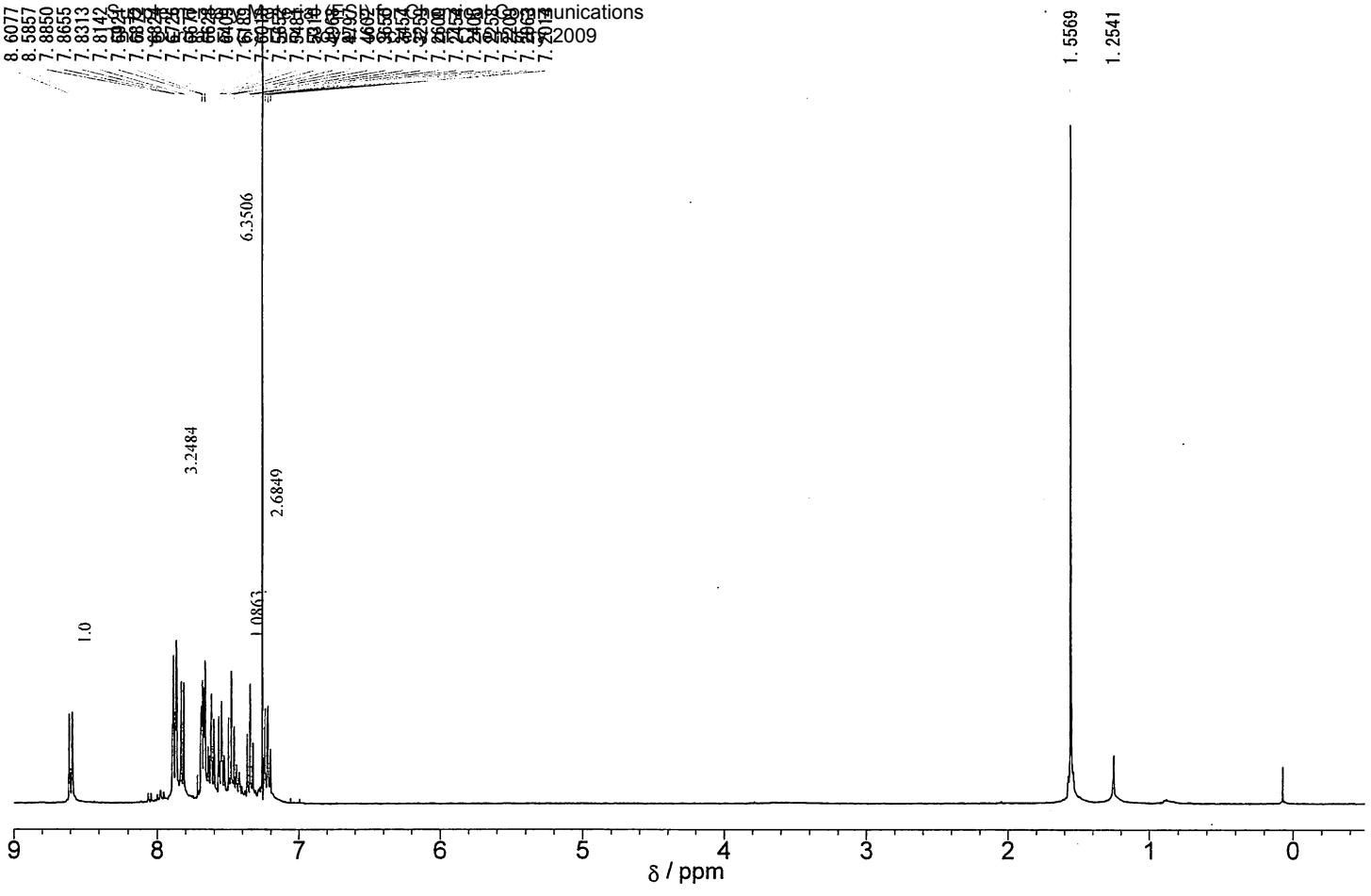
123.1258
120.9007
93.1527
90.9605
77.3214
77.0000
76.6786

3e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7.8850
7.8655
7.8313
7.8142
1.5569
1.2541
6.3506
3.2484
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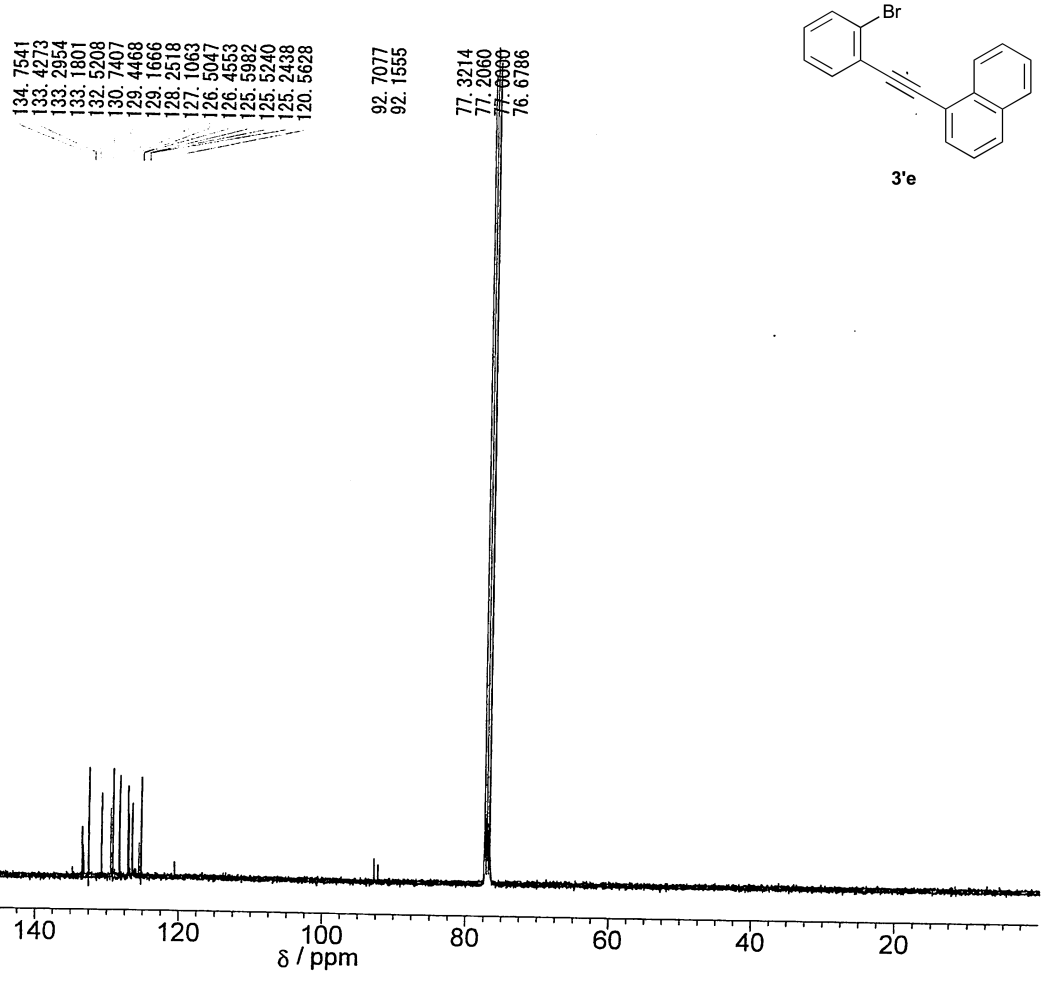
1.0863
1.0
9
8
7
6
5
4
3
2
1
0
δ / ppm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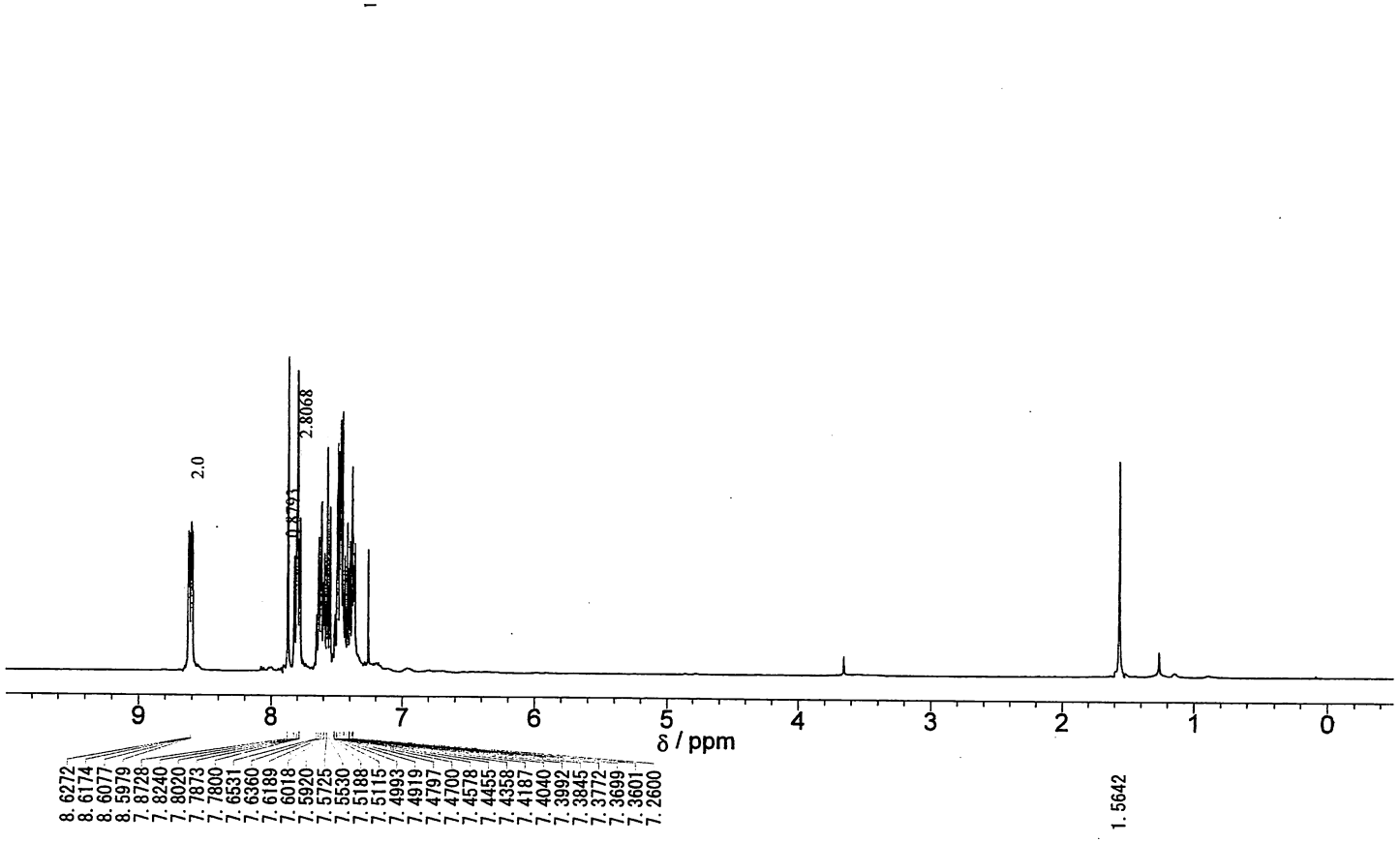
128.2518
127.1063
126.5047
126.4553
125.5982
125.5240
125.2438
120.5628
92.7077
92.1555
77.3214
77.2060
77.0000
76.6786
Br
3'e
180
160
140
120
100
80
60
40
20
δ / ppm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2.0
0.8791
2.8068
δ / ppm
8.6272
8.6174
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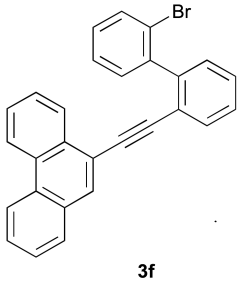
8.5979
8.8728
7.8240
7.8020
7.7873
7.7800
7.6531
7.6360
7.6189
7.6018
7.5920
7.5725
7.5530
7.5188
7.5115
7.4993
7.4919
7.4797
7.4700
7.4578
7.4455
7.4358
7.4187
7.4040
7.3992
7.3845
7.3772
7.3699
7.3601
7.2600
1.5642


Br

3f

δ / ppm
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132.7598
132.1169
131.7214
131.4824
131.1774
130.9467
130.1967
129.8918
129.6446
129.1419
128.5073
128.1117
127.8810
127.3453
127.2134
126.9003
126.8344
126.8096
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92.7983
91.1666
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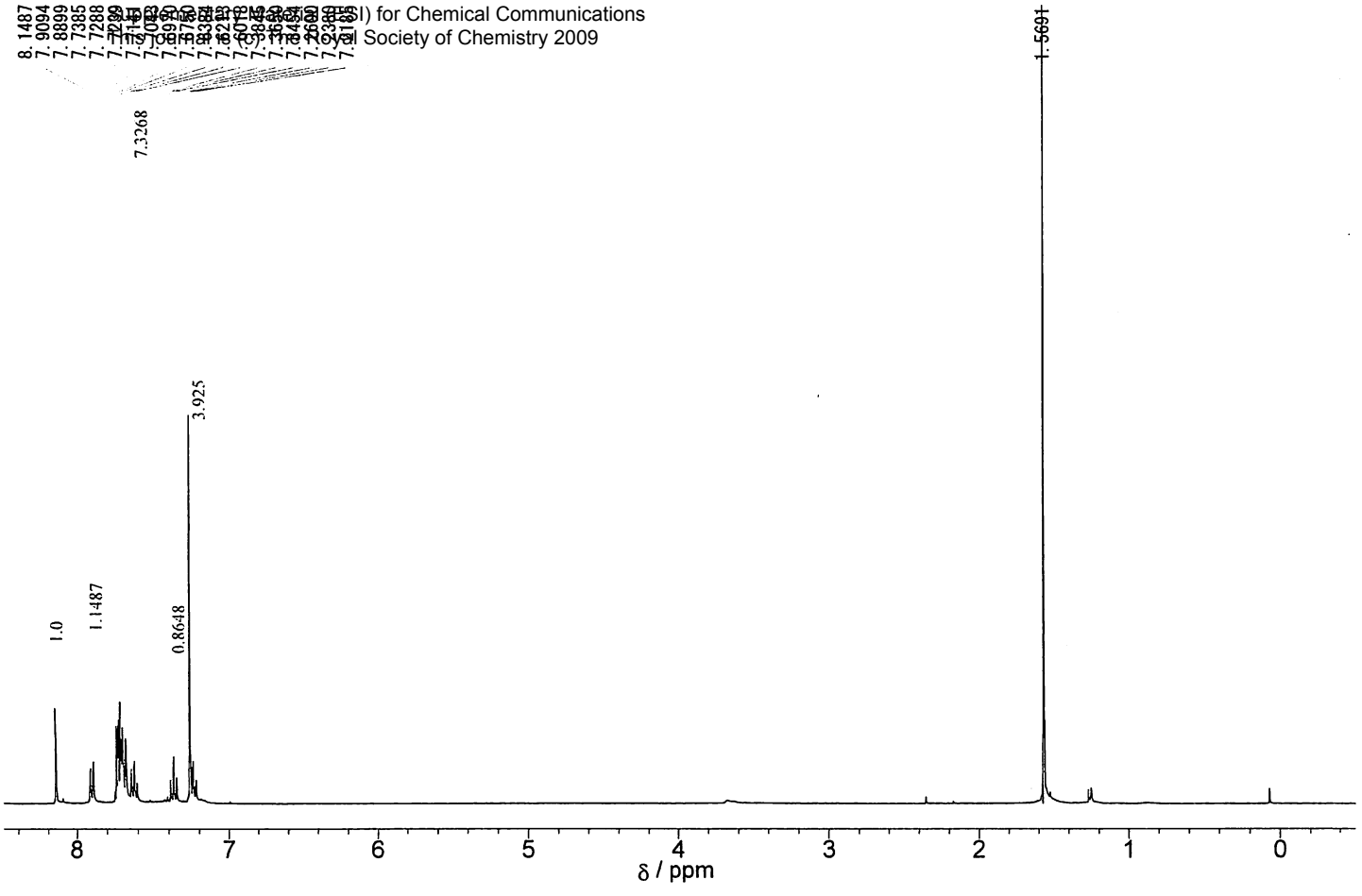
77.0000
76.6786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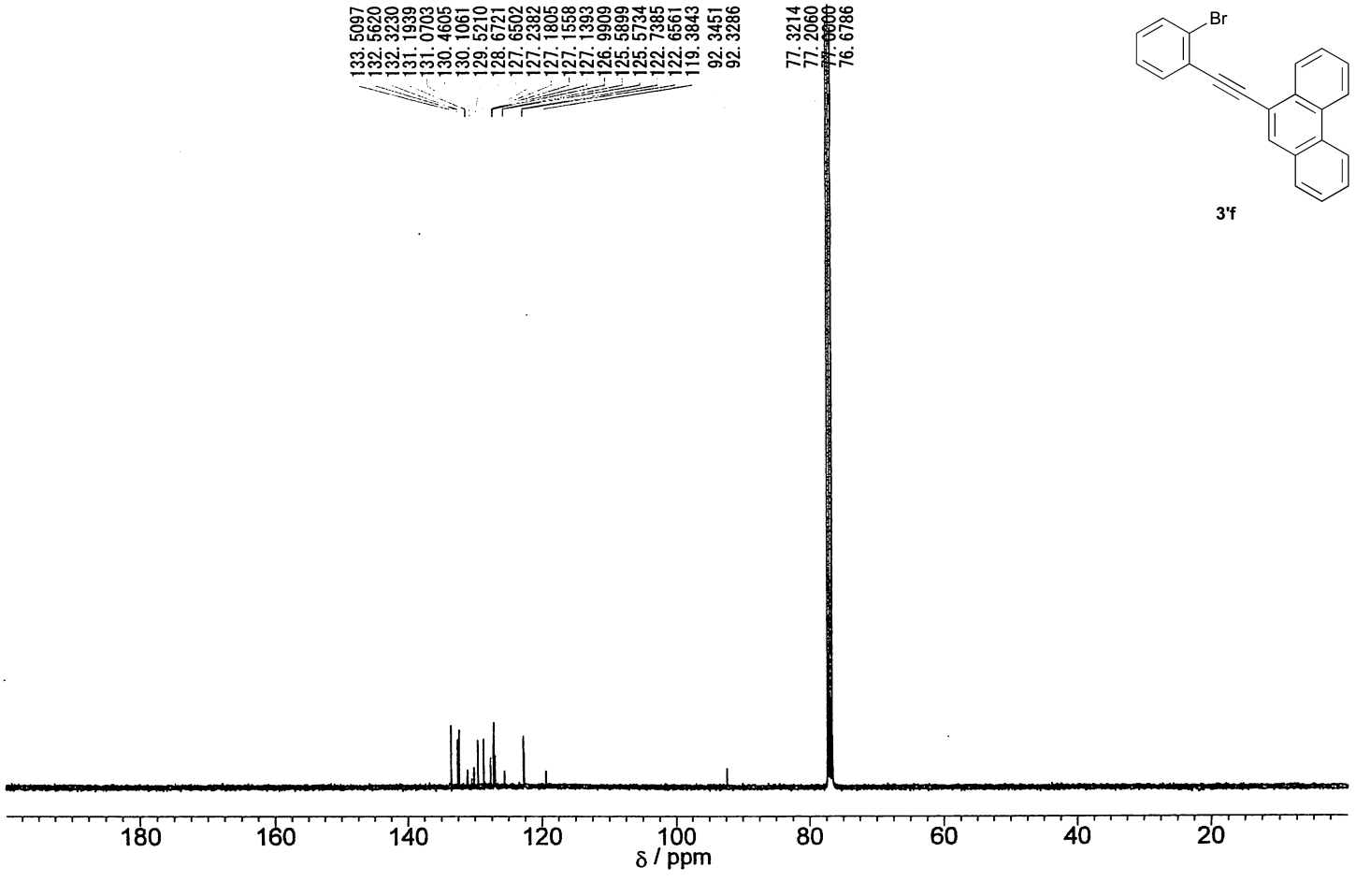
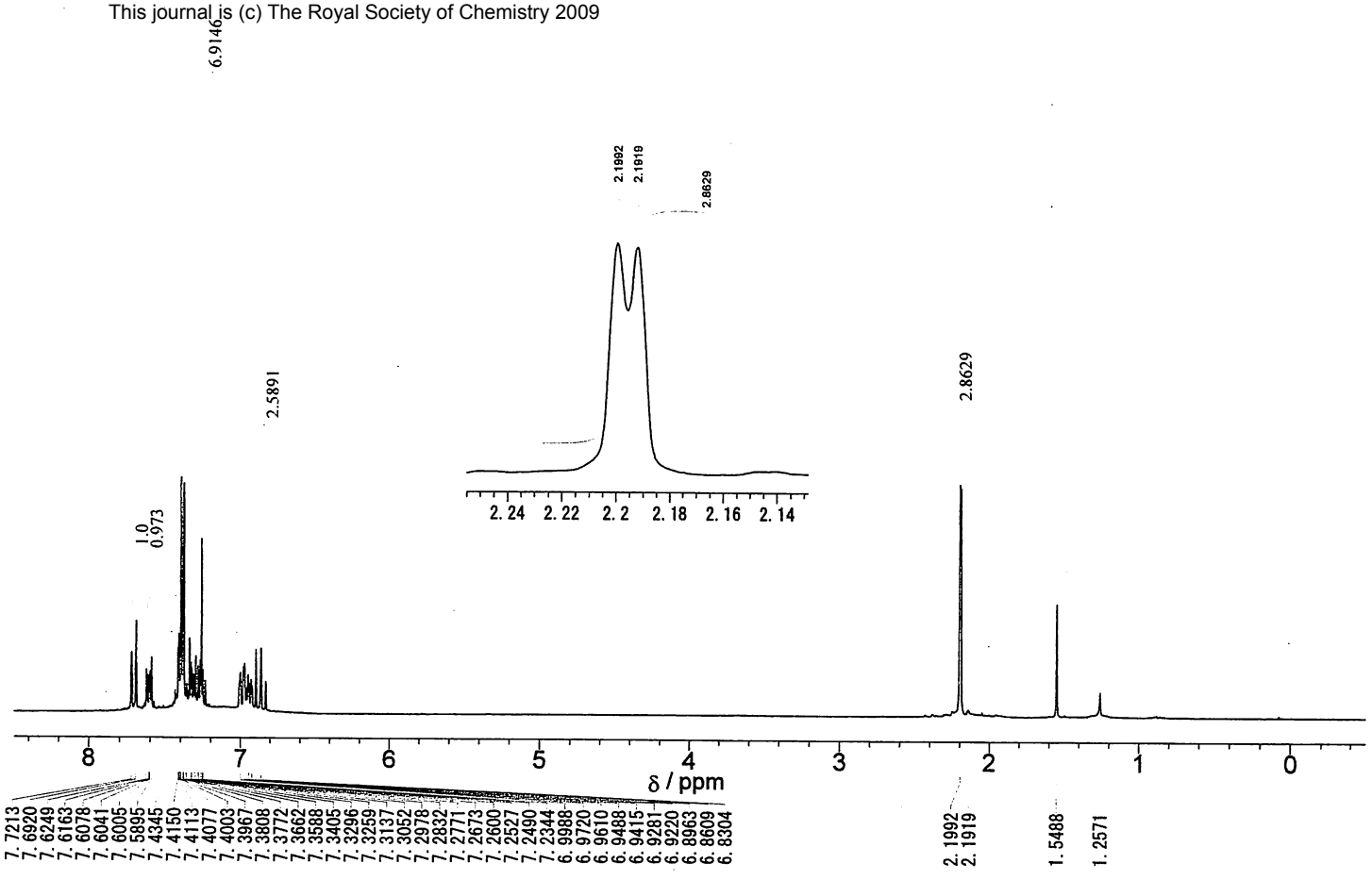
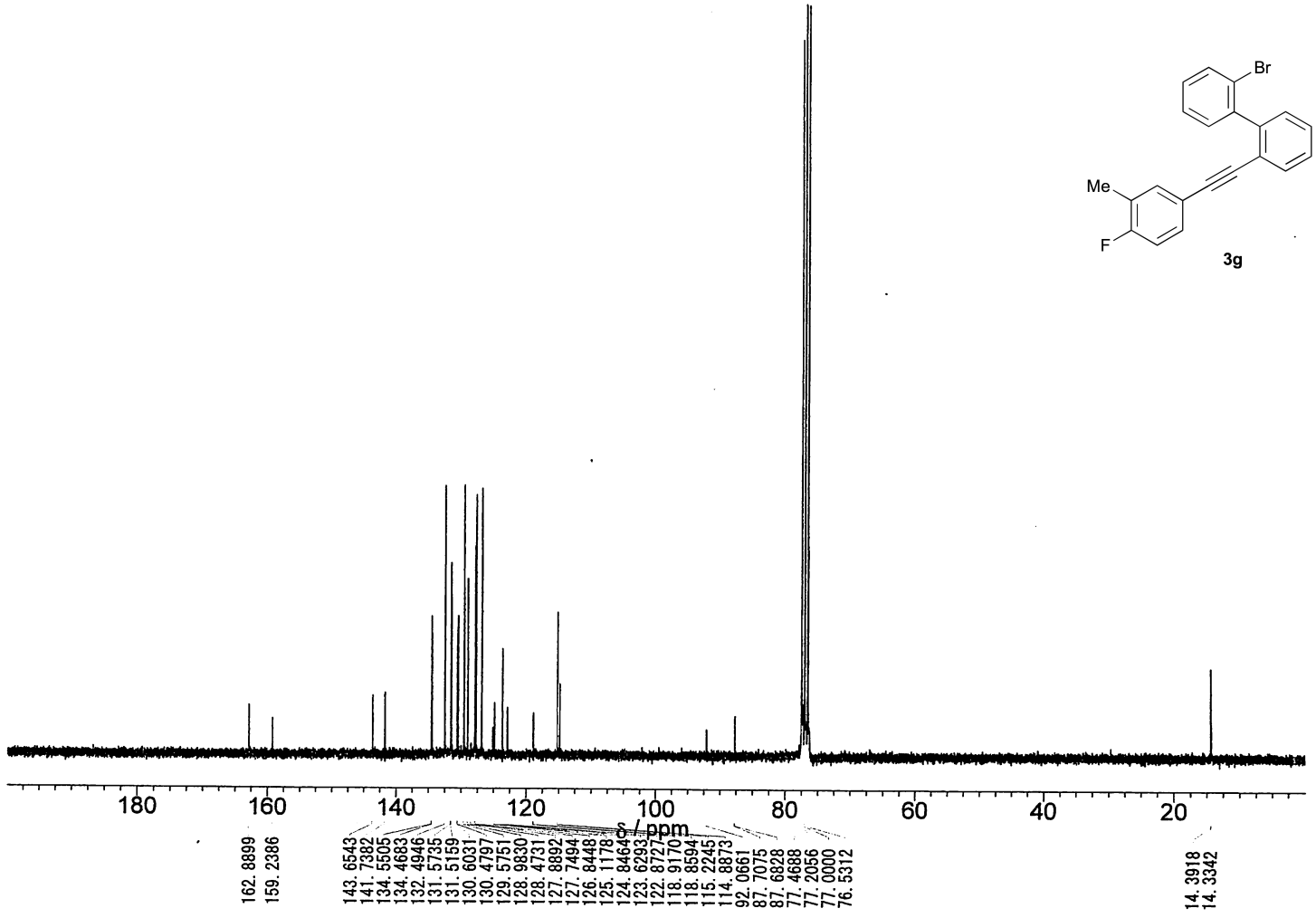
7.7288
7.3268
1.5691
3.925
1.0
1.1487
0.8648
δ / ppm

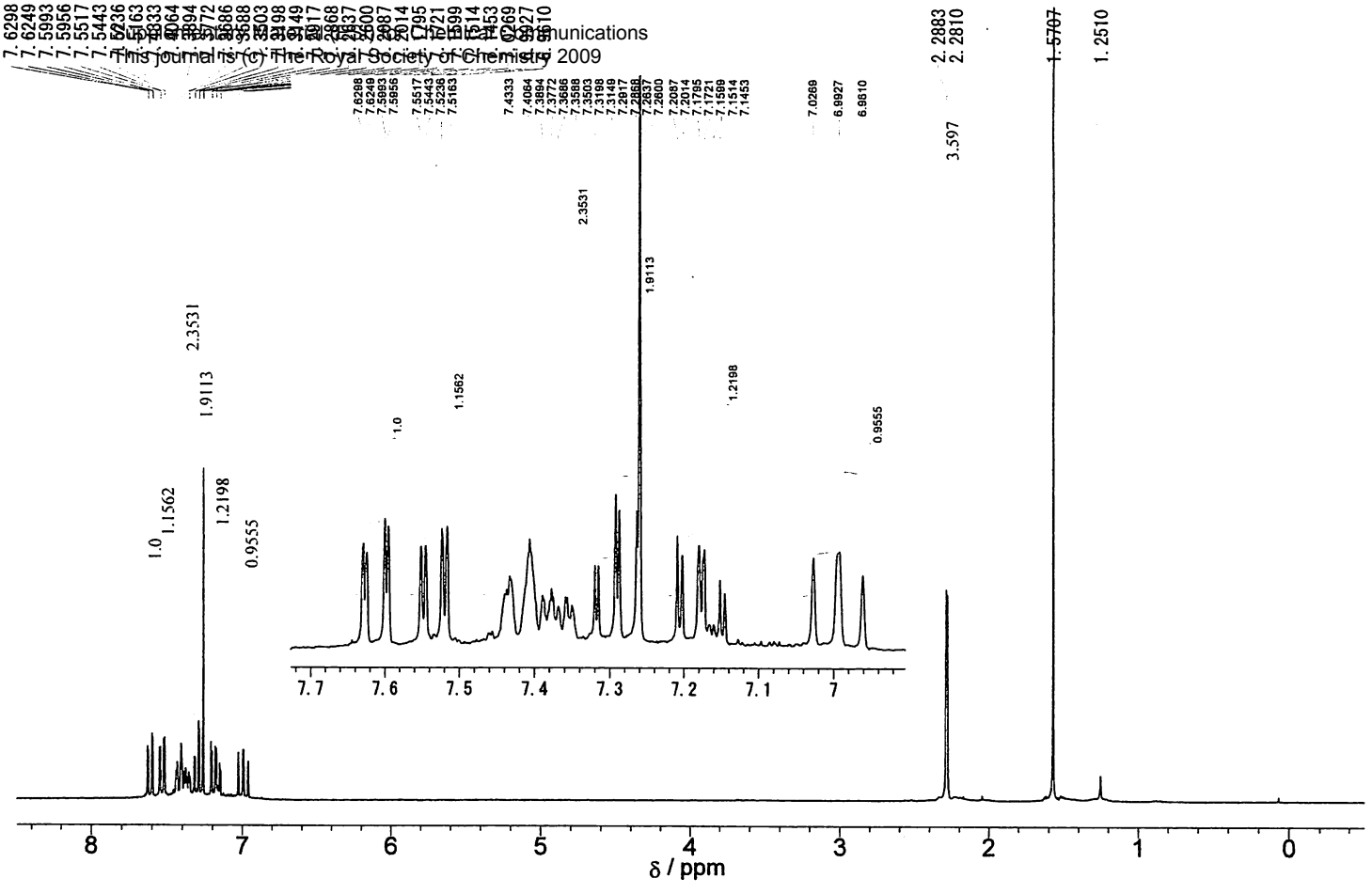

133.5097
132.5620
132.3230
131.1939
131.0703
130.4605
130.1061
129.5210
128.6721
127.6502
127.2382
127.1805
127.1558
127.1393
126.9909
125.5899
125.5734
122.7385
122.6561
119.3843
92.3451
92.3286
77.3214
77.2060
76.6786
δ / ppm

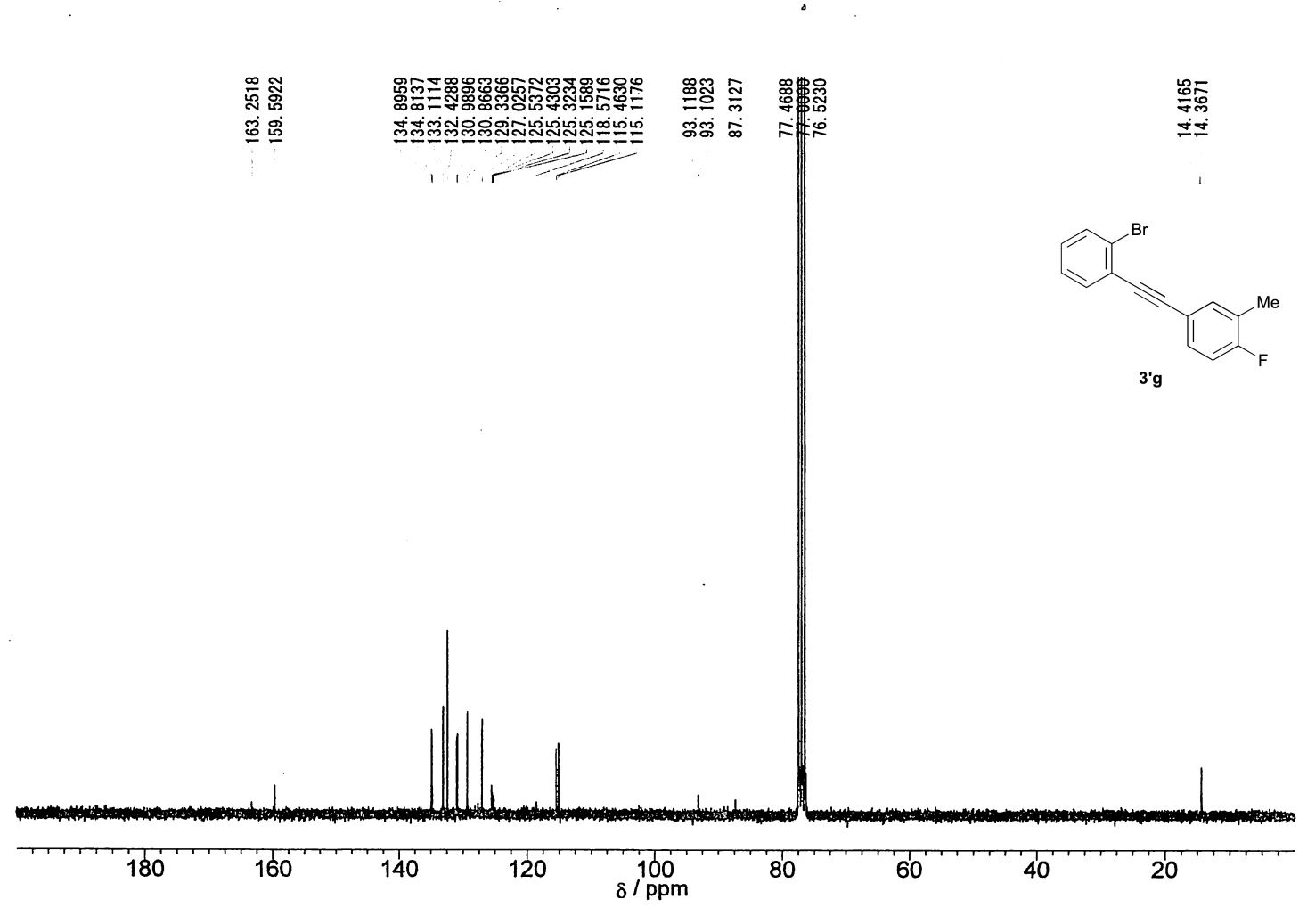
Br

3'f

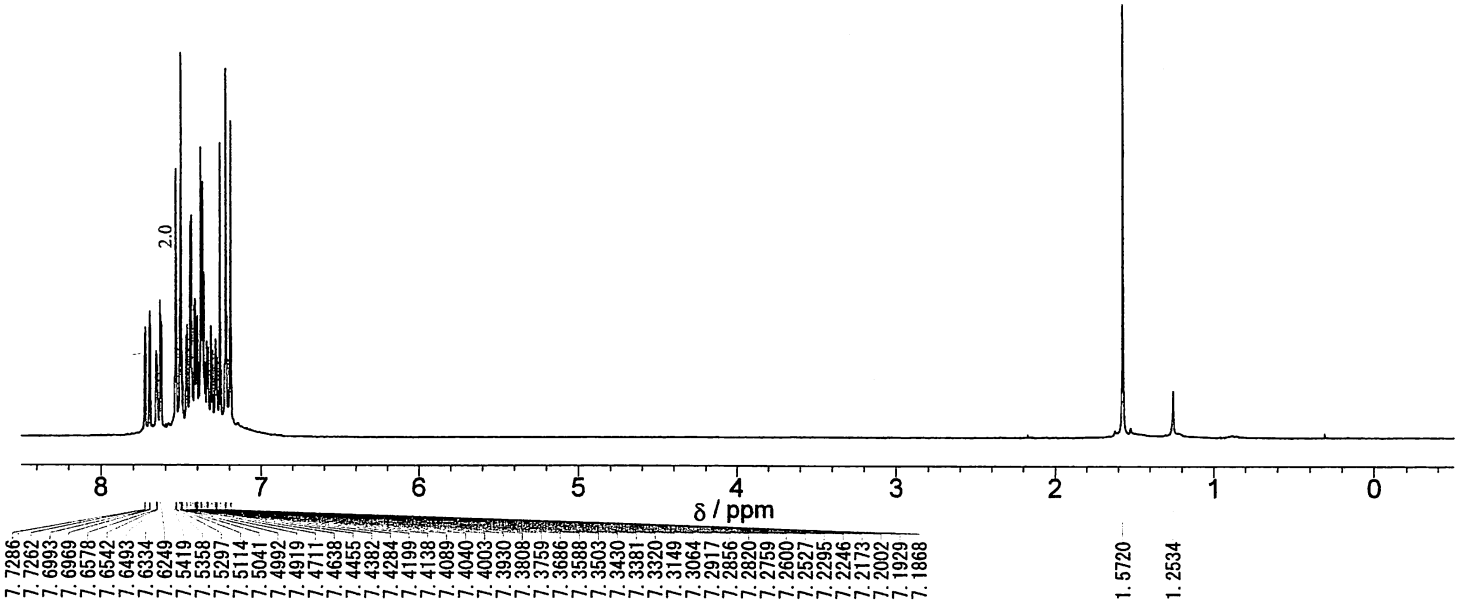

6.9146
2.1992
2.1919
2.8629
2.5891
2.8629
1.0
0.973
2.24 2.22 2.2 2.18 2.16 2.14
8 7 6 5 4 3 2 1 0
δ / ppm
7.7213 7.6920 7.6249 7.6163 7.6078 7.6041 7.6005 7.5895 7.4345 7.4150 7.4113 7.4077 7.4003 7.3967 7.3808 7.3772 7.3662 7.3588 7.3405 7.3296 7.3259 7.3137 7.3052 7.2978 7.2832 7.2771 7.2673 7.2600 7.2527 7.2490 7.2344 6.9988 6.9720 6.9610 6.9488 6.9415 6.9281 6.9220 6.8963 6.8609 6.8304
2.1992 2.1919
1.5488
1.2571


Br
Me
F
3g
180 160 140 120 100 80 60 40 20
δ / ppm
162.8899 159.2386 143.6543 141.7382 134.5505 134.4683 132.4946 131.5735 131.5159 130.6031 130.4797 129.5751 128.9830 128.4731 127.8892 127.7494 126.8448 125.1178 124.8464 123.6293 122.8727 118.9170 118.8594 115.2245 114.8873 92.0661 87.7075 87.6828 77.4688 77.2056 77.0000 76.5312
14.3918 14.3342





3'g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2.0
δ / ppm
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7.7262
7.6993
7.6969
7.6578
7.6542
7.6493
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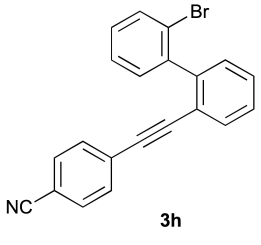
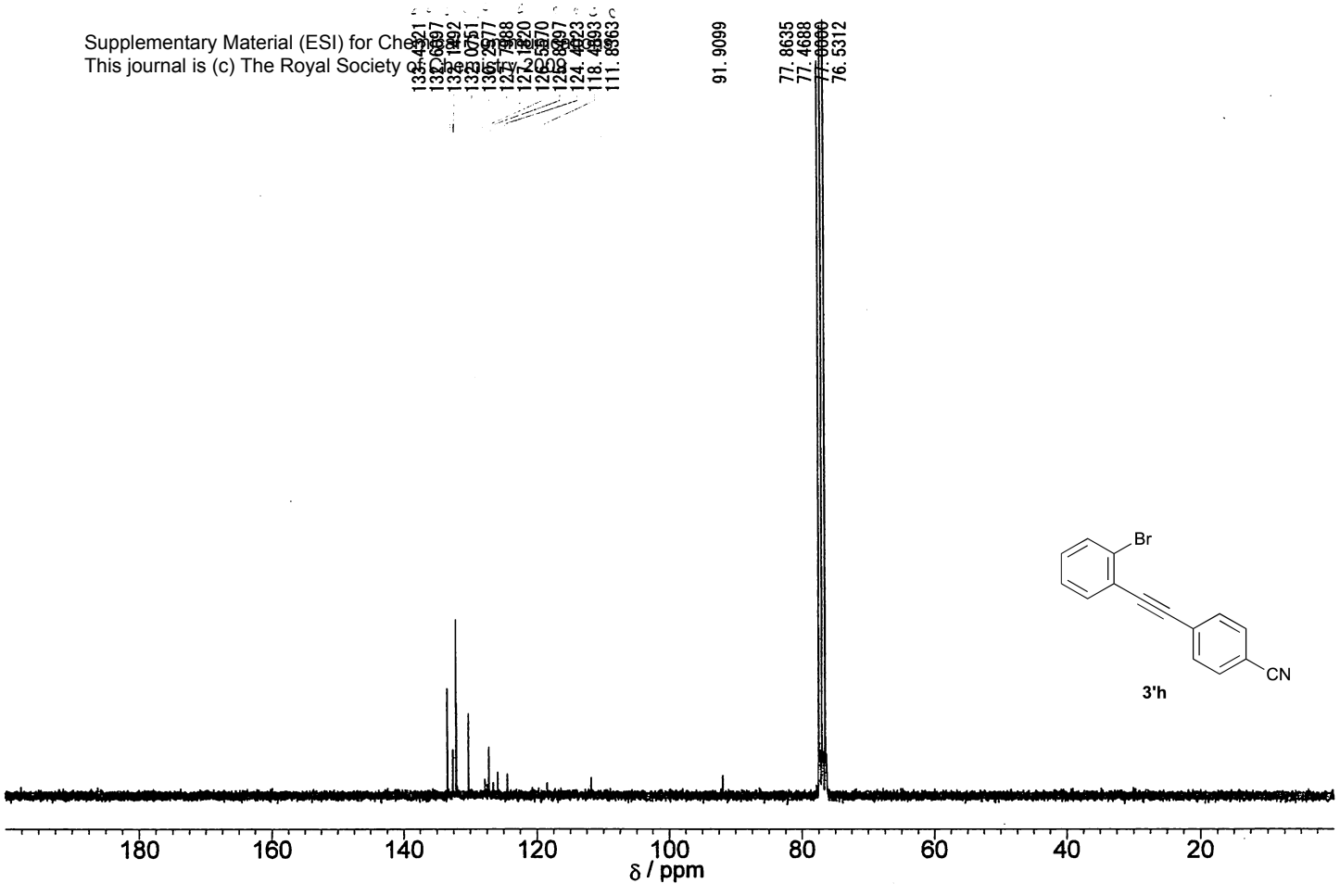
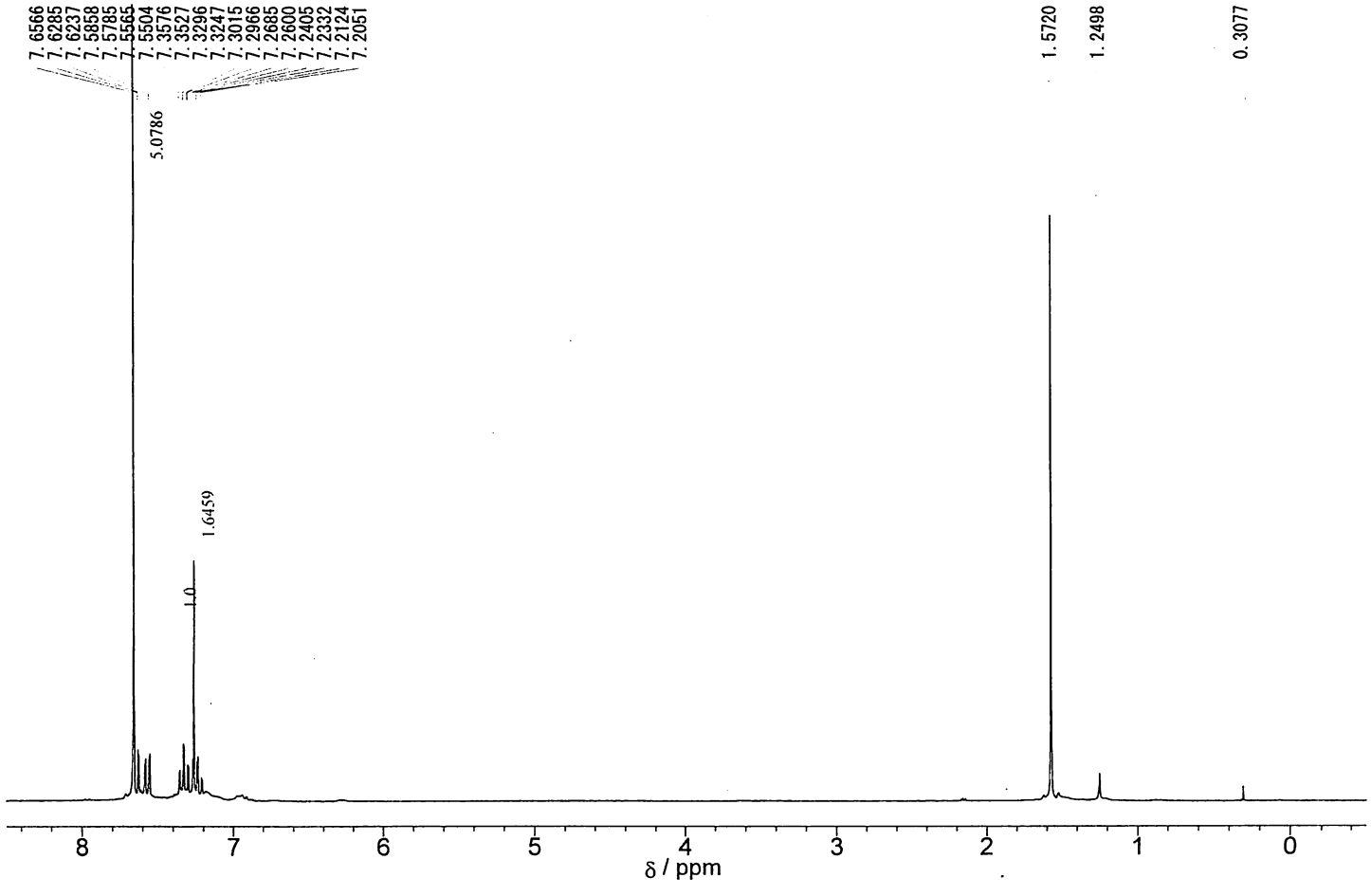
7.6249
7.5419
7.5358
7.5297
7.5114
7.5041
7.4992
7.4919
7.4711
7.4638
7.4455
7.4382
7.4284
7.4199
7.4138
7.4089
7.4040
7.4003
7.3930
7.3808
7.3759
7.3686
7.3588
7.3503
7.3430
7.3381
7.3320
7.3149
7.3064
7.2917
7.2856
7.2820
7.2759
7.2600
7.2527
7.2295
7.2246
7.2173
7.2002
7.1929
7.1868
1.5720
1.2534

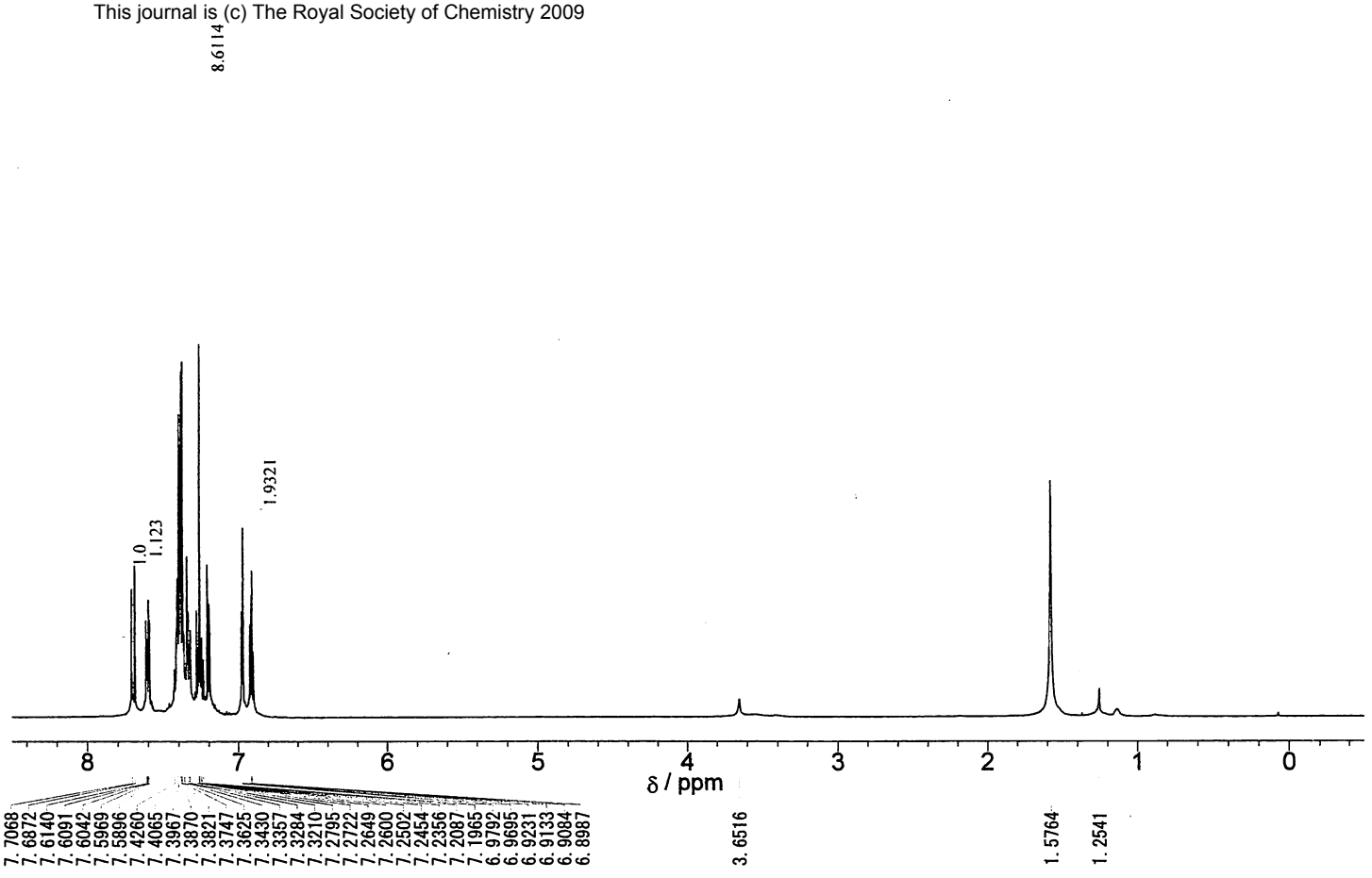

Br
NC

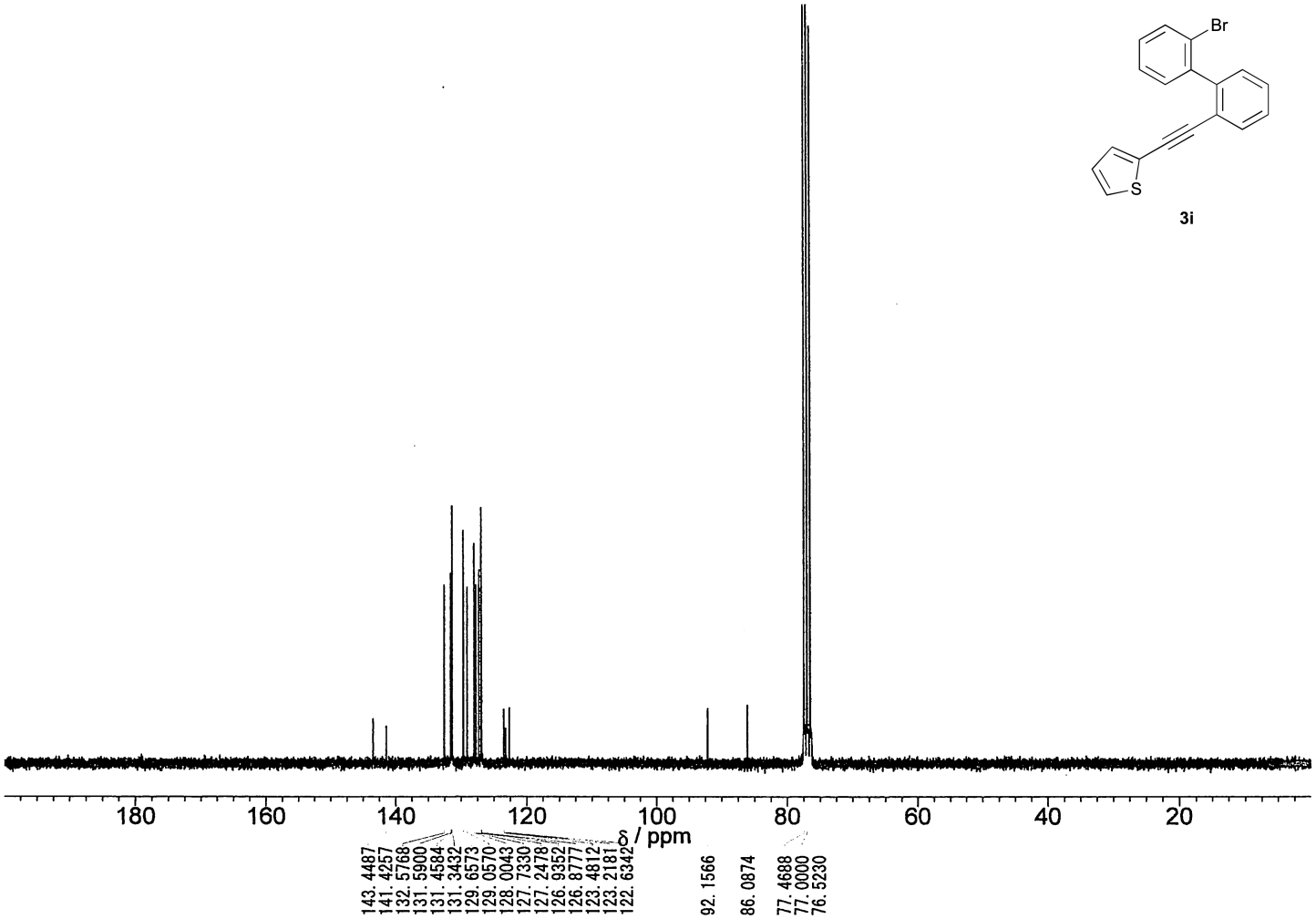
3h

δ / ppm
144.1478
141.4010
132.5439
131.8860
131.7626
131.4173
129.7067
129.2297
128.8925
128.1359
127.8892
126.9270
123.5223
121.9022
118.5305
111.2030
92.8391
91.0381
77.4688
77.0000
76.5312

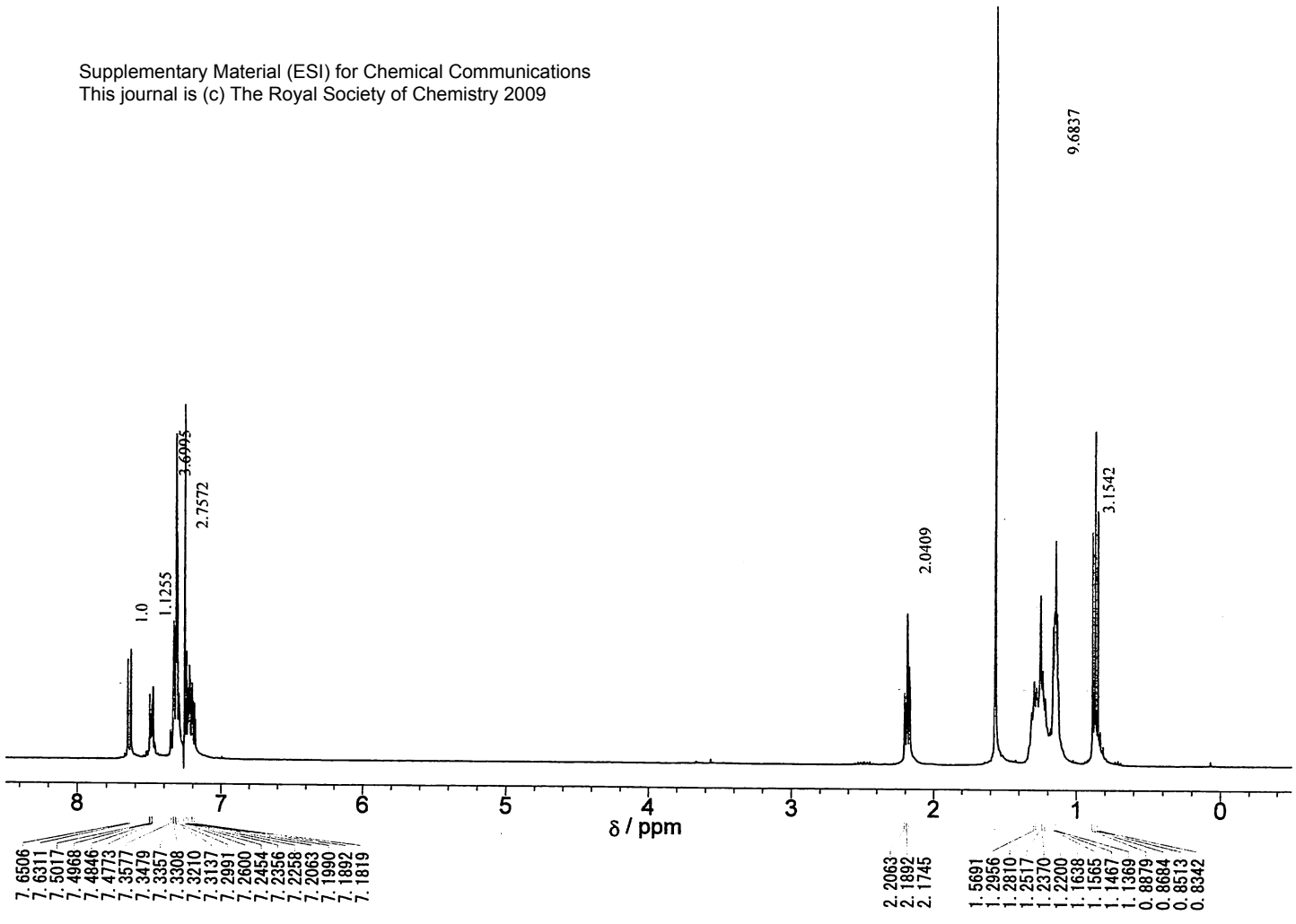

91.9099
77.8635
77.4688
76.5312
Br
CN
3'h
180
160
140
120
100
80
60
40
20
δ / ppm

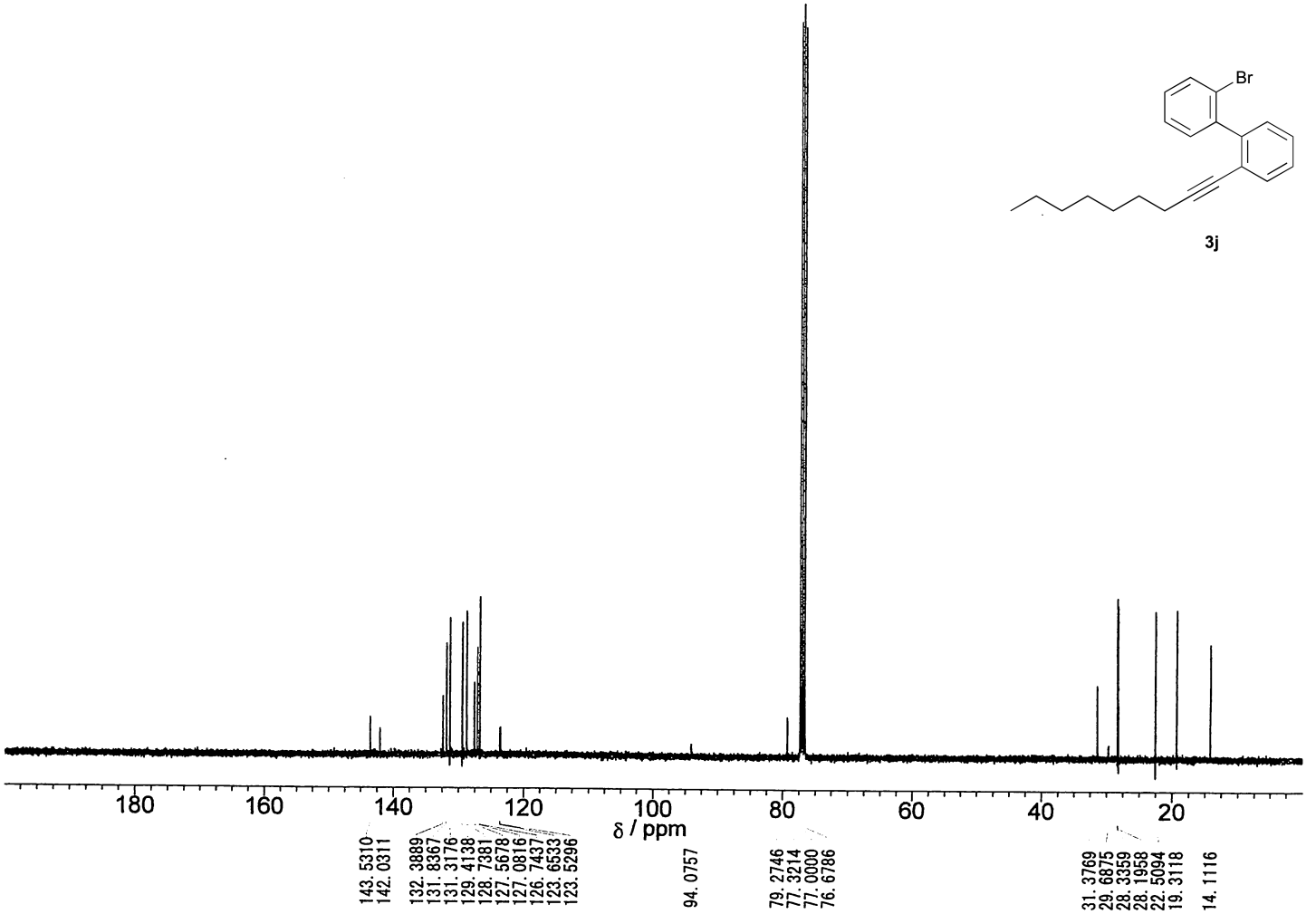

7.6566
7.6285
7.6237
7.5858
7.5785
7.5565
7.5504
7.3576
7.3527
7.3296
7.3247
7.3015
7.2966
7.2685
7.2600
7.2405
7.2332
7.2124
7.2051
1.5720
1.2498
0.3077
5.0786
1.6459
1.0
8
7
6
5
4
3
2
1
0
δ / ppm


8.6114
1.0
1.123
1.9321
δ / ppm
7.7068
7.6872
7.6140
7.6091
7.6042
7.5969
7.5896
7.4260
7.4065
7.3967
7.3870
7.3821
7.3747
7.3625
7.3430
7.3357
7.3284
7.3210
7.2795
7.2722
7.2649
7.2600
7.2502
7.2454
7.2356
7.2087
7.1965
6.9792
6.9695
6.9231
6.9133
6.9084
6.8987
3.6516
1.5764
1.2541


Br
S
δ / ppm
143.4487
141.4257
132.5768
131.5900
131.4584
131.3432
129.6573
129.0570
128.0043
127.7330
127.2478
126.9352
126.8777
123.4812
123.2181
122.6342
92.1566
86.0874
77.4688
77.0000
76.5230

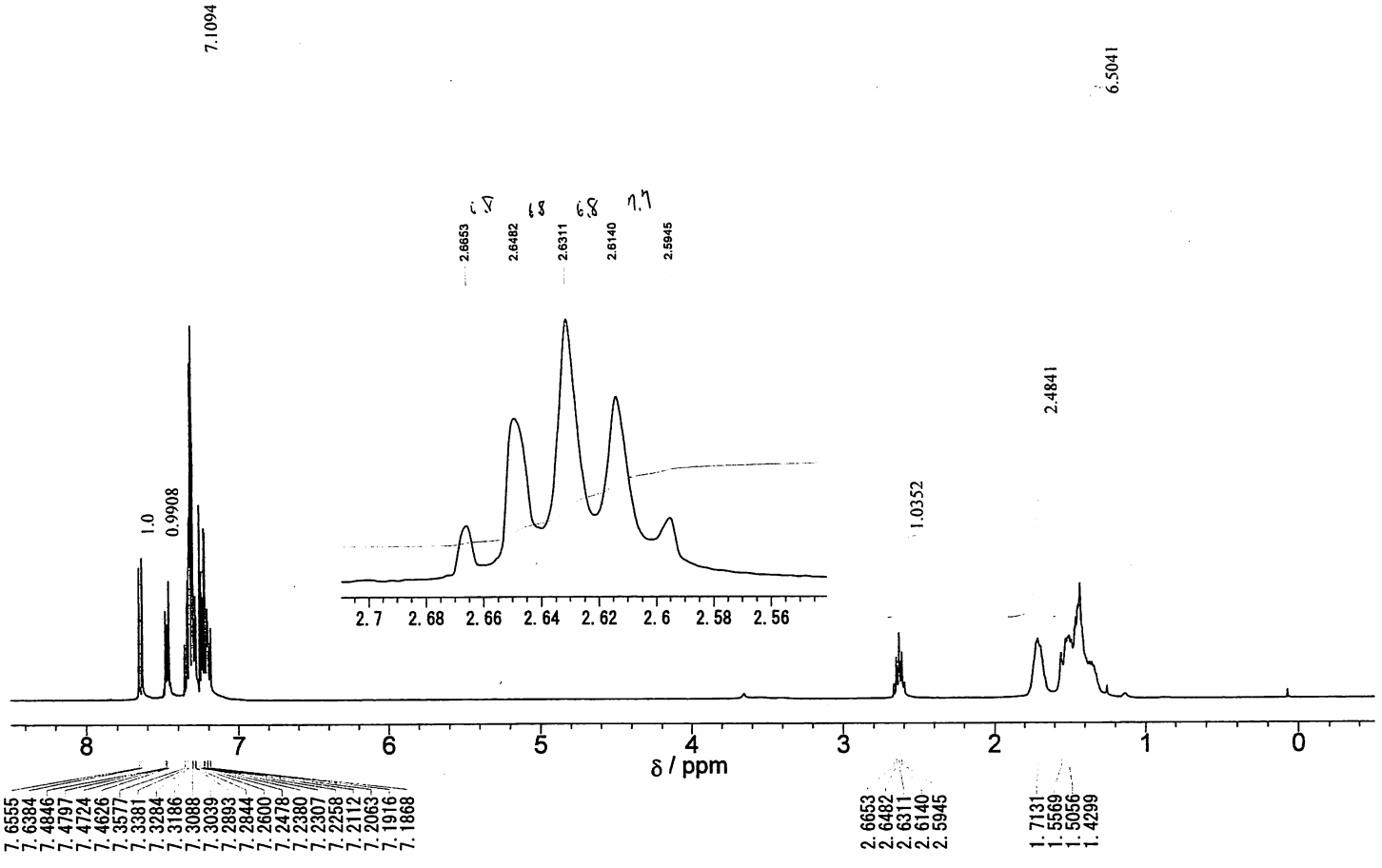
3i

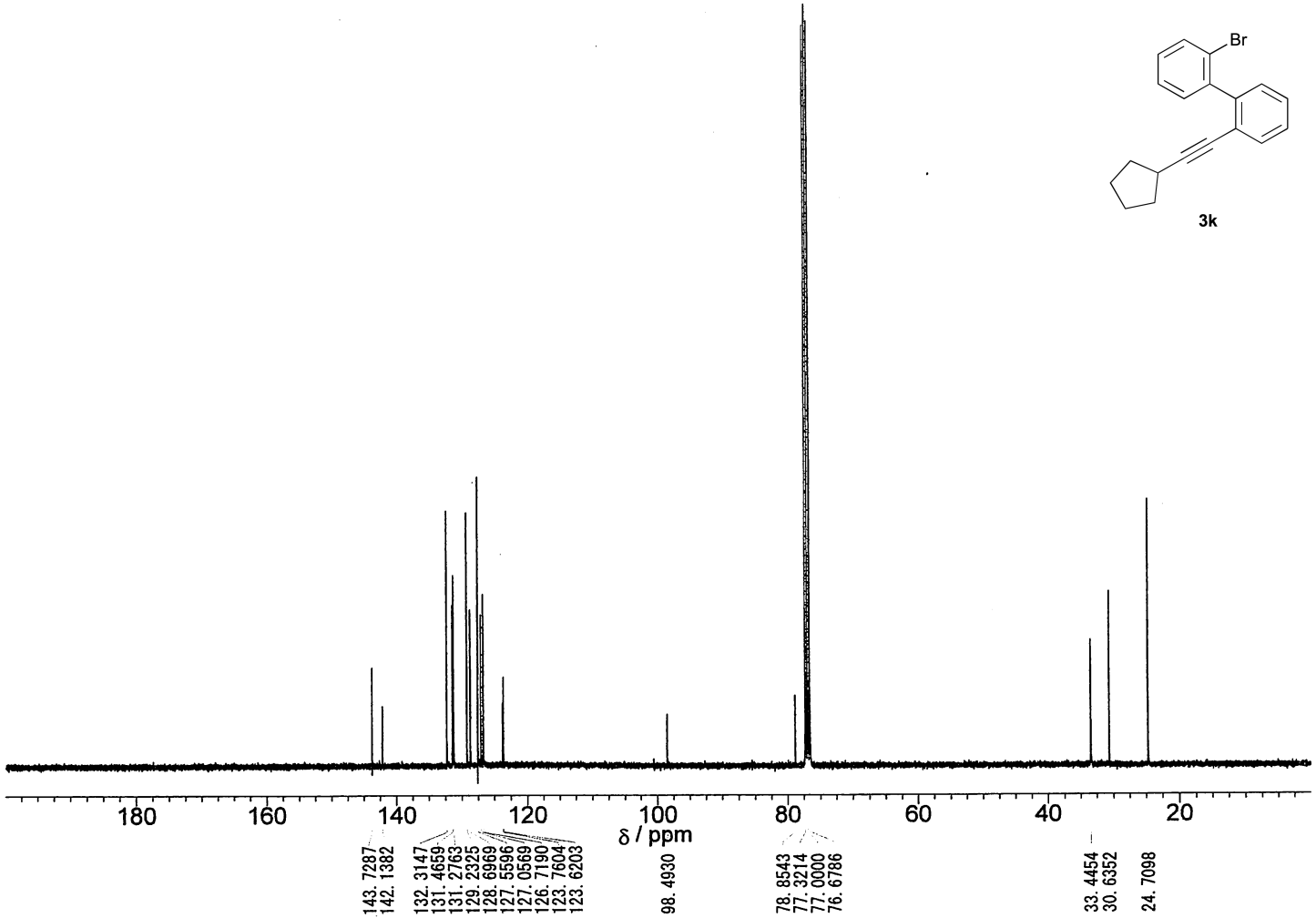

9.6837
3.6995
2.7572
1.1255
1.0
2.0409
3.1542
δ / ppm
7.6506
7.6311
7.5017
7.4968
7.4846
7.4773
7.3577
7.3479
7.3357
7.3308
7.3210
7.3137
7.2991
7.2600
7.2454
7.2356
7.2258
7.2063
7.1990
7.1892
7.1819
2.2063
2.1892
2.1745
1.5691
1.2956
1.2810
1.2517
1.2370
1.2200
1.1638
1.1565
1.1467
1.1369
0.8879
0.8684
0.8513
0.8342

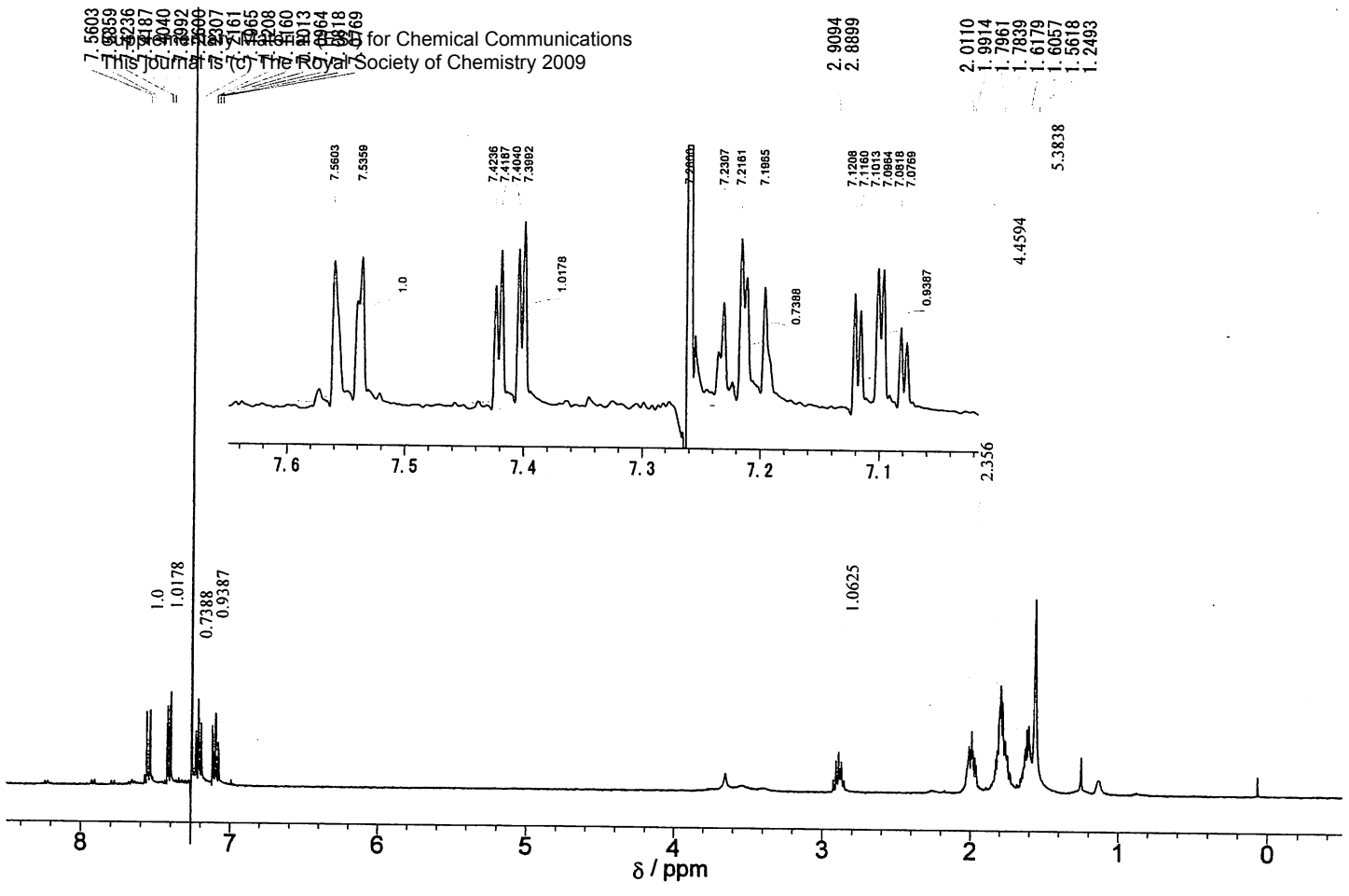

δ / ppm
143.5310
142.0311
132.3889
131.8367
131.3176
129.4138
128.7381
127.5678
127.0816
126.7437
123.6533
123.5296
94.0757
79.2746
77.3214
77.0000
76.6786
31.3769
29.6875
28.3359
28.1958
22.5094
19.3118
14.1116

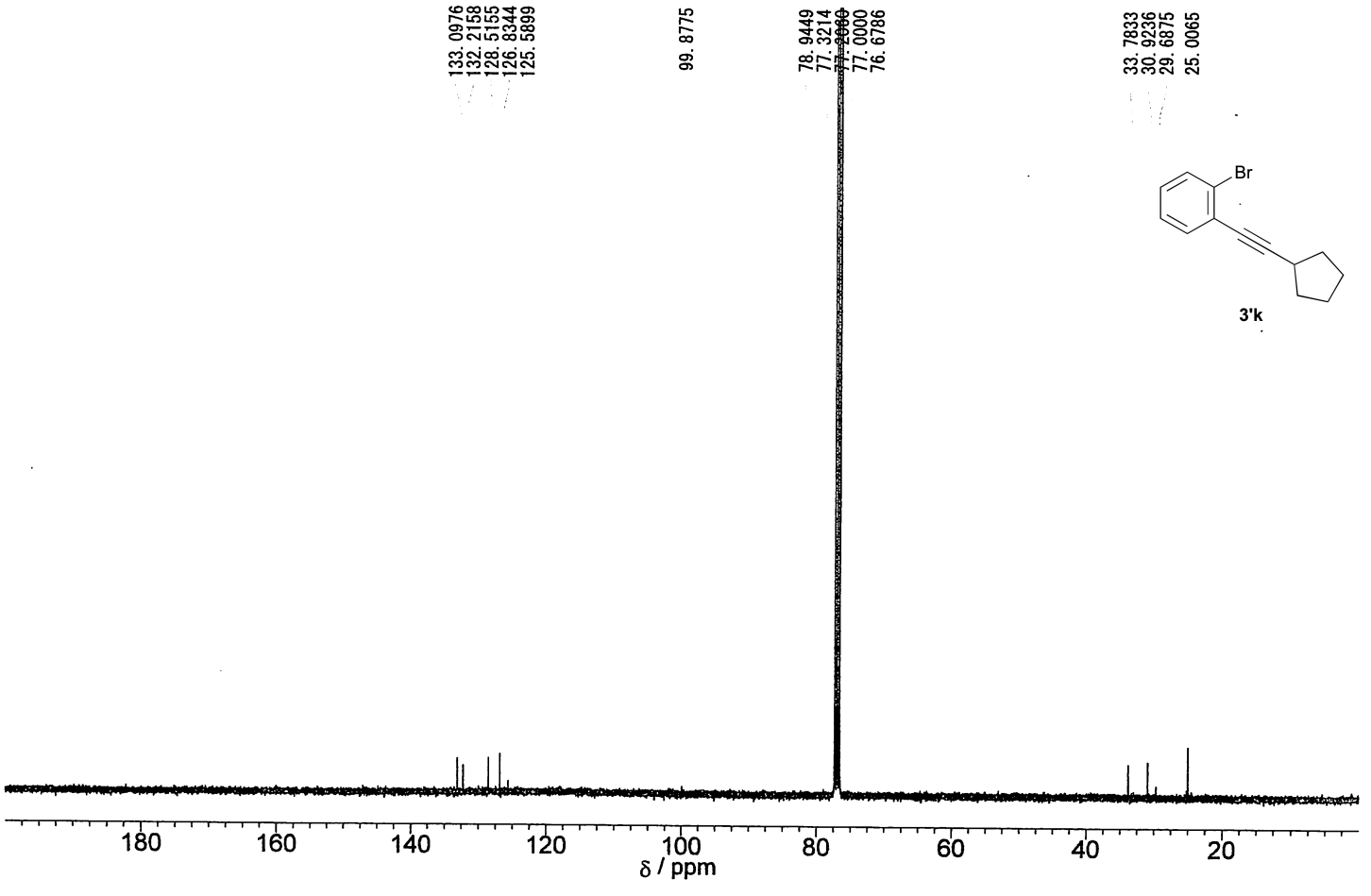
Br

3j

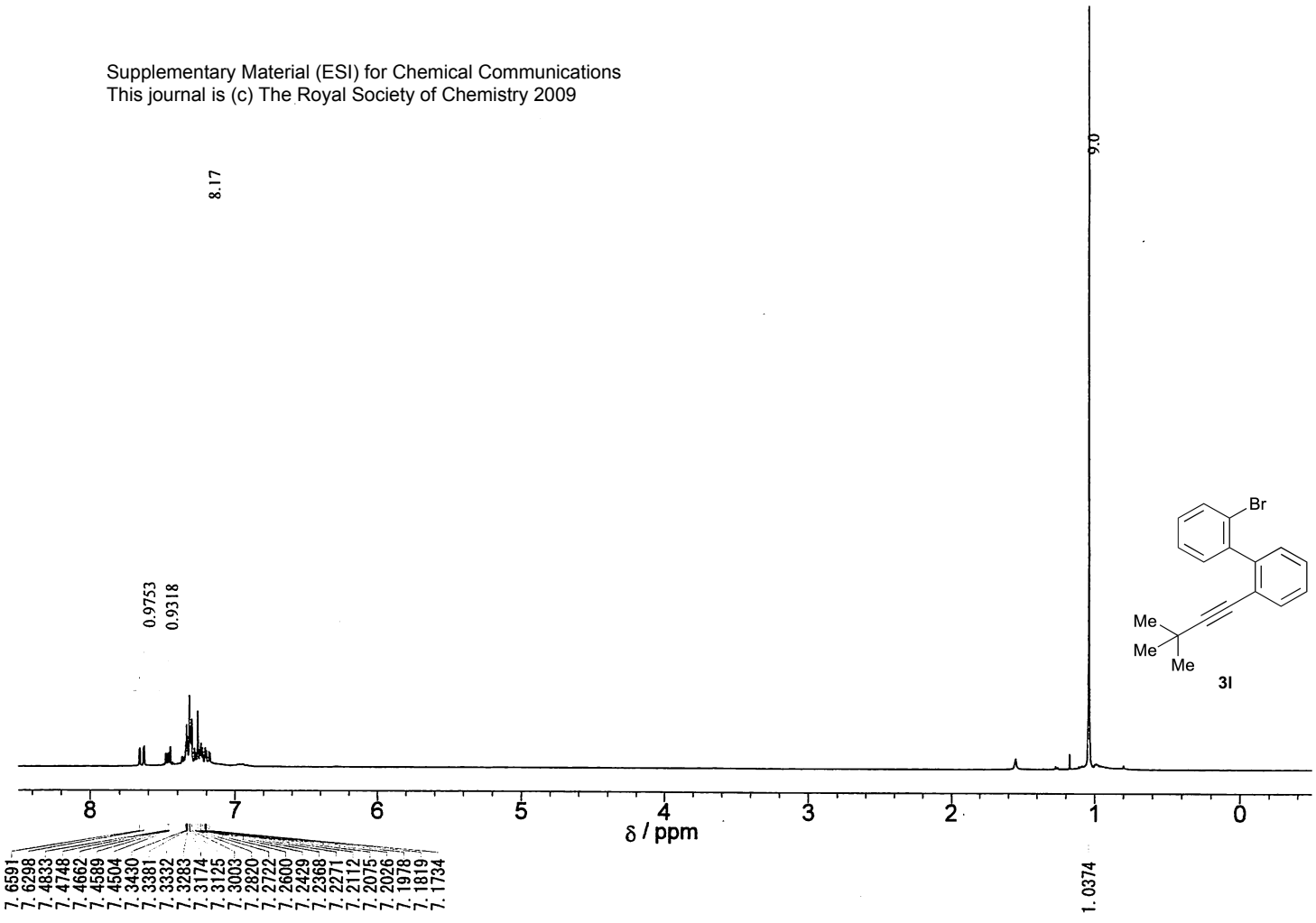

7.1094
6.5041
2.6653
2.6482
2.6311
2.6140
2.5945
2.4841
1.0352
1.0
0.9908
2.7 2.68 2.66 2.64 2.62 2.6 2.58 2.56
8 7 6 5 4 3 2 1 0
δ / ppm
7.6555
7.6384
7.4846
7.4797
7.4724
7.4626
7.3577
7.3381
7.3284
7.3186
7.3088
7.3039
7.2893
7.2844
7.2600
7.2478
7.2380
7.2307
7.2258
7.2112
7.2063
7.1916
7.1868
2.6653
2.6482
2.6311
2.6140
2.5945
1.7131
1.5569
1.5056
1.4299

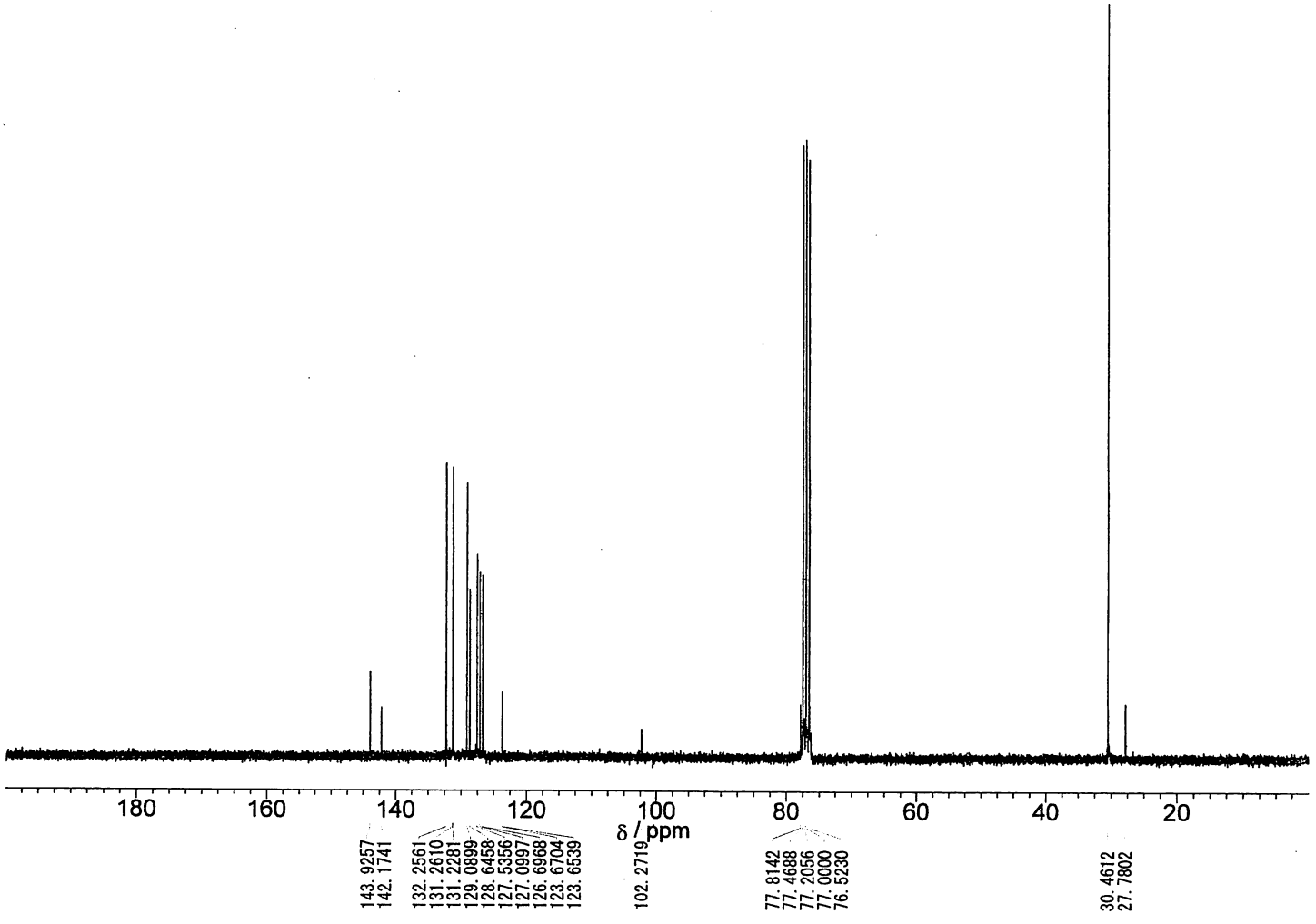

Br
3k
180 160 140 120 100 80 60 40 20
δ / ppm
143.7287
142.1382
132.3147
131.4659
131.2763
129.2325
128.6969
127.5596
127.0569
126.7190
123.7604
123.6203
98.4930
78.8543
77.3214
77.0000
76.6786
33.4454
30.6352
24.7098

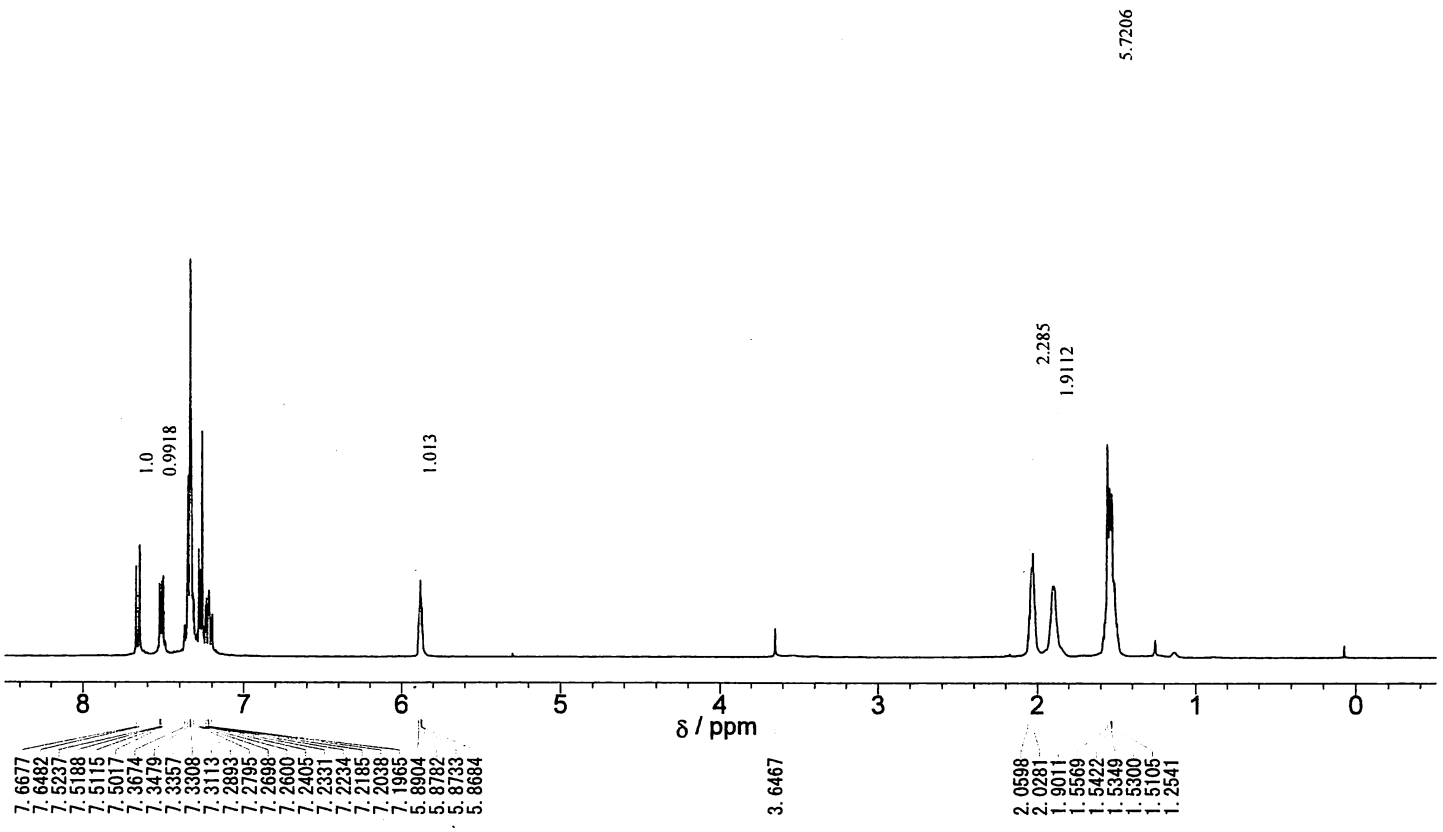


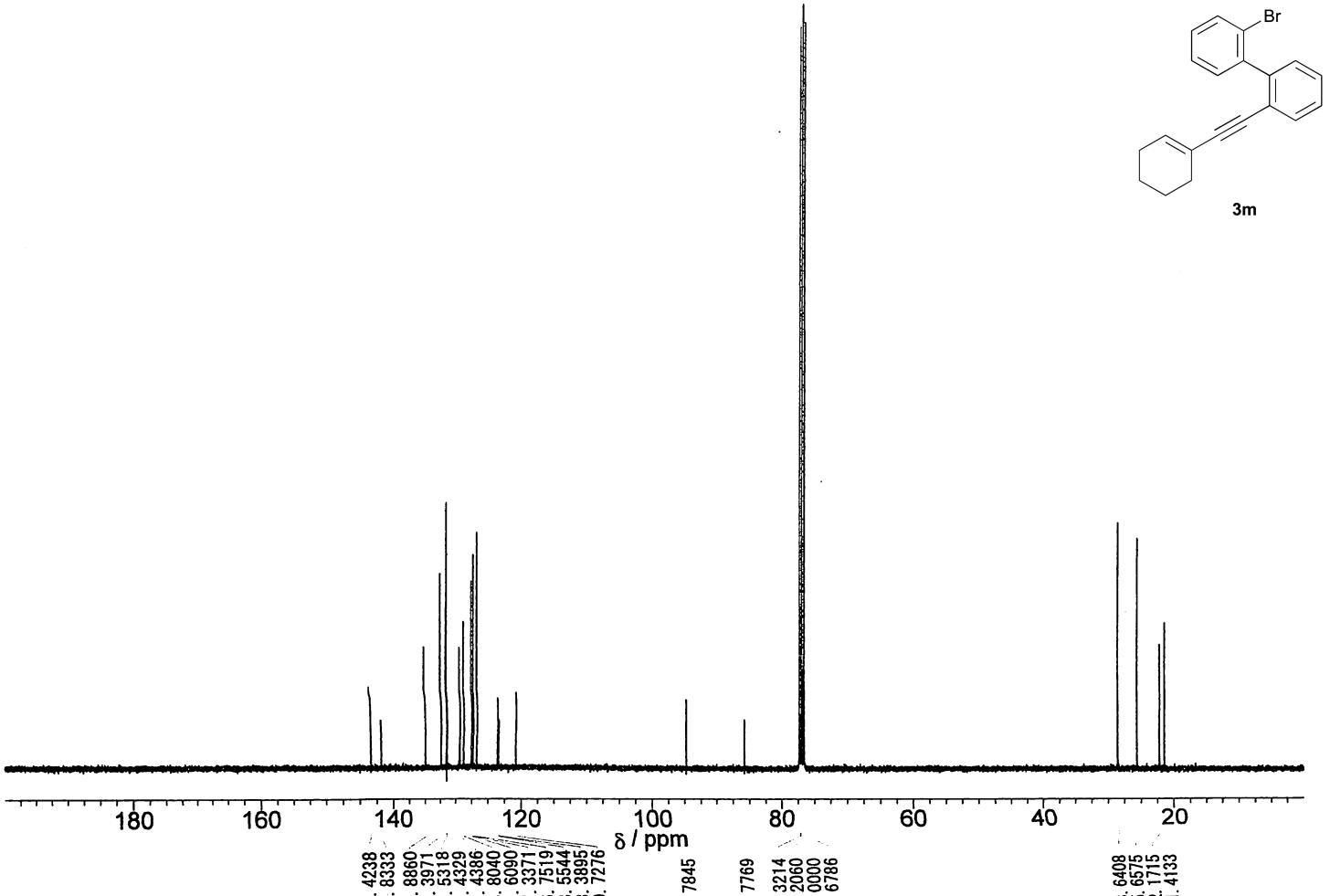


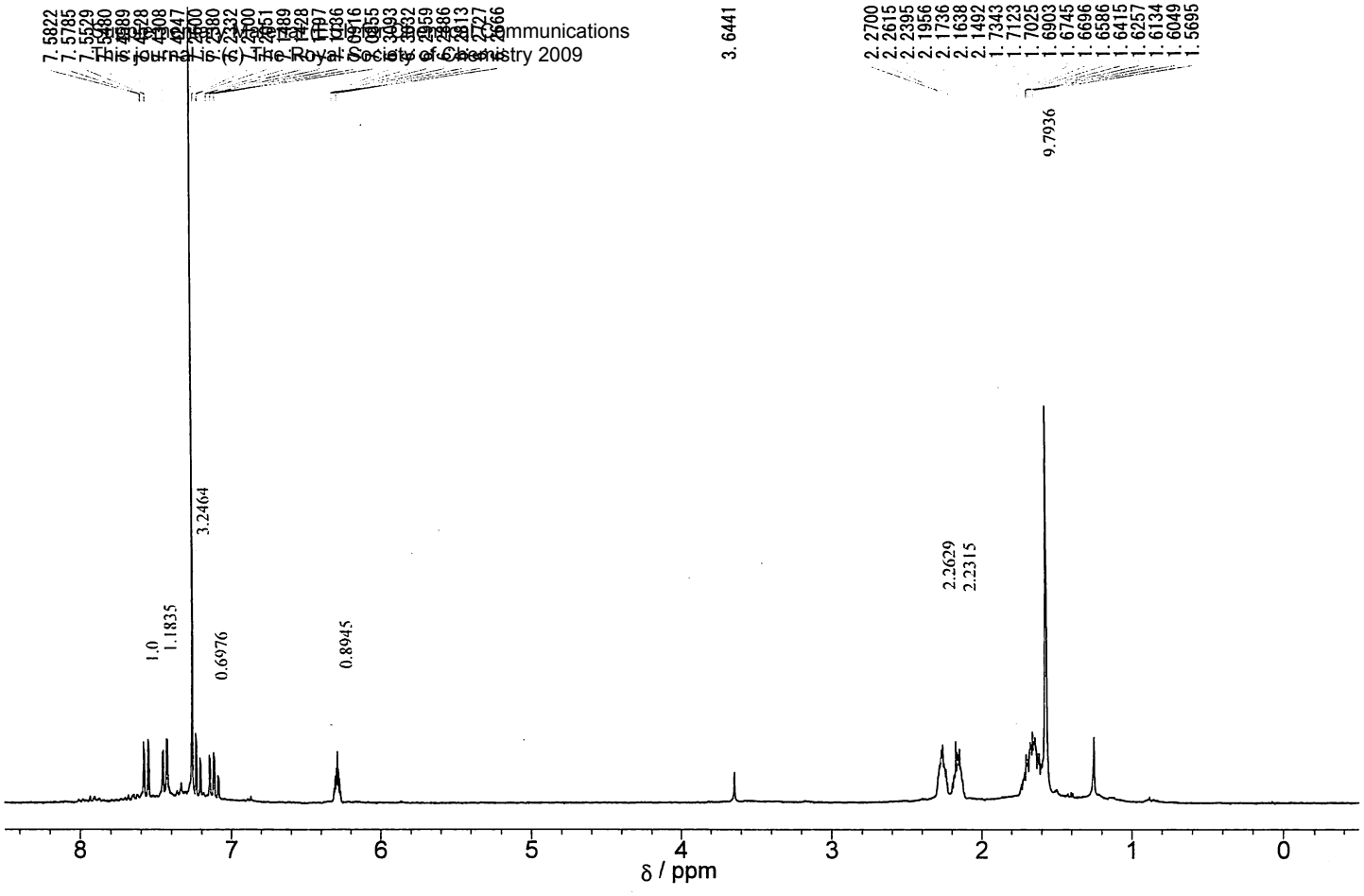
3'k

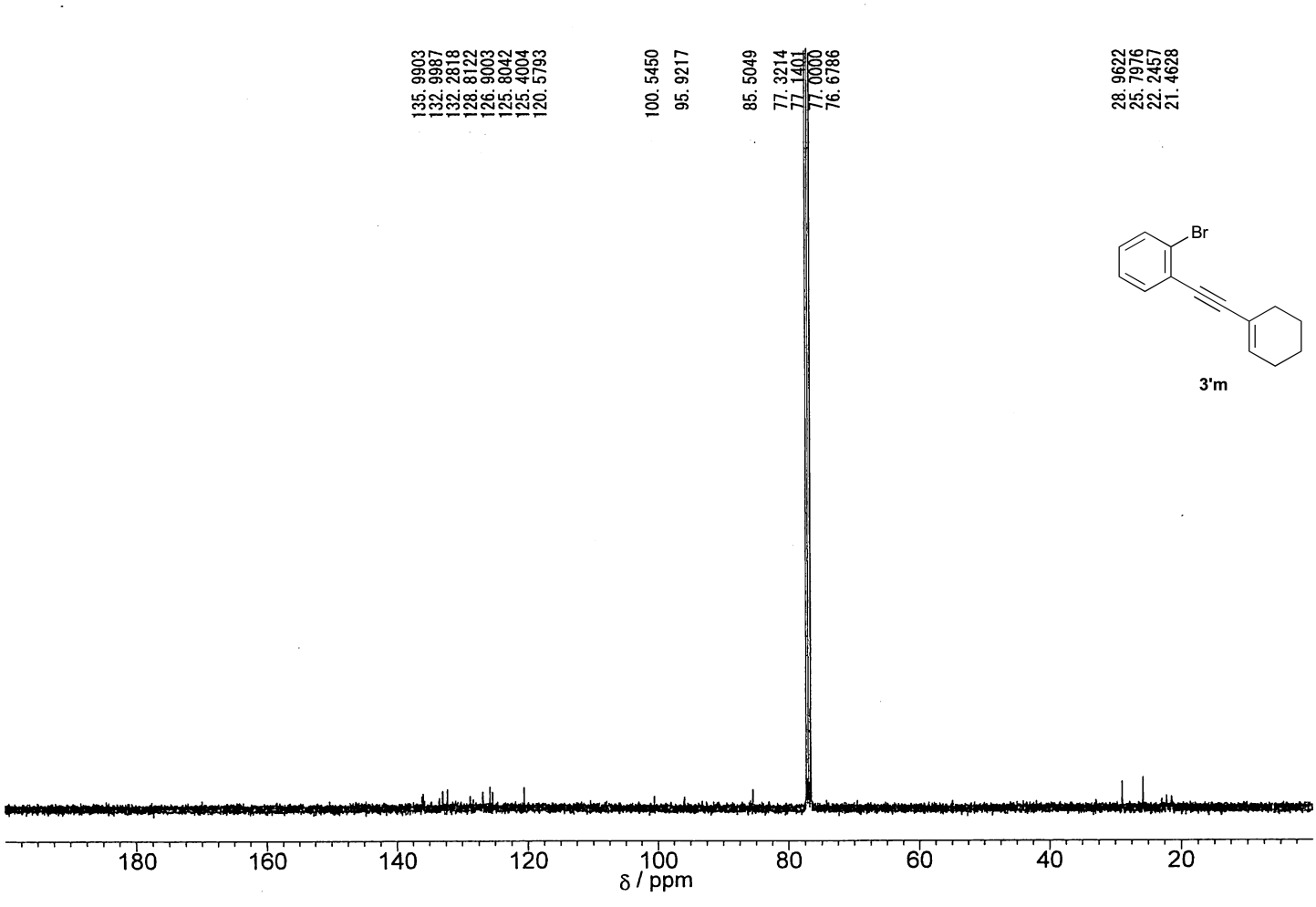

8.17
9.0
0.9753
0.9318
Br
Me
Me
Me
3l
δ / ppm
7.6591
7.6298
7.4833
7.4748
7.4662
7.4589
7.4504
7.3430
7.3381
7.3332
7.3283
7.3174
7.3125
7.3003
7.2820
7.2722
7.2600
7.2429
7.2368
7.2271
7.2112
7.2075
7.2026
7.1978
7.1819
7.1734
1.0374


δ / ppm
143.9257
142.1741
132.2561
131.2610
131.2281
129.0899
128.6458
127.5356
127.0997
126.6968
123.6704
123.6539
102.2719
77.8142
77.4688
77.2056
77.0000
76.5230
30.4612
27.7802

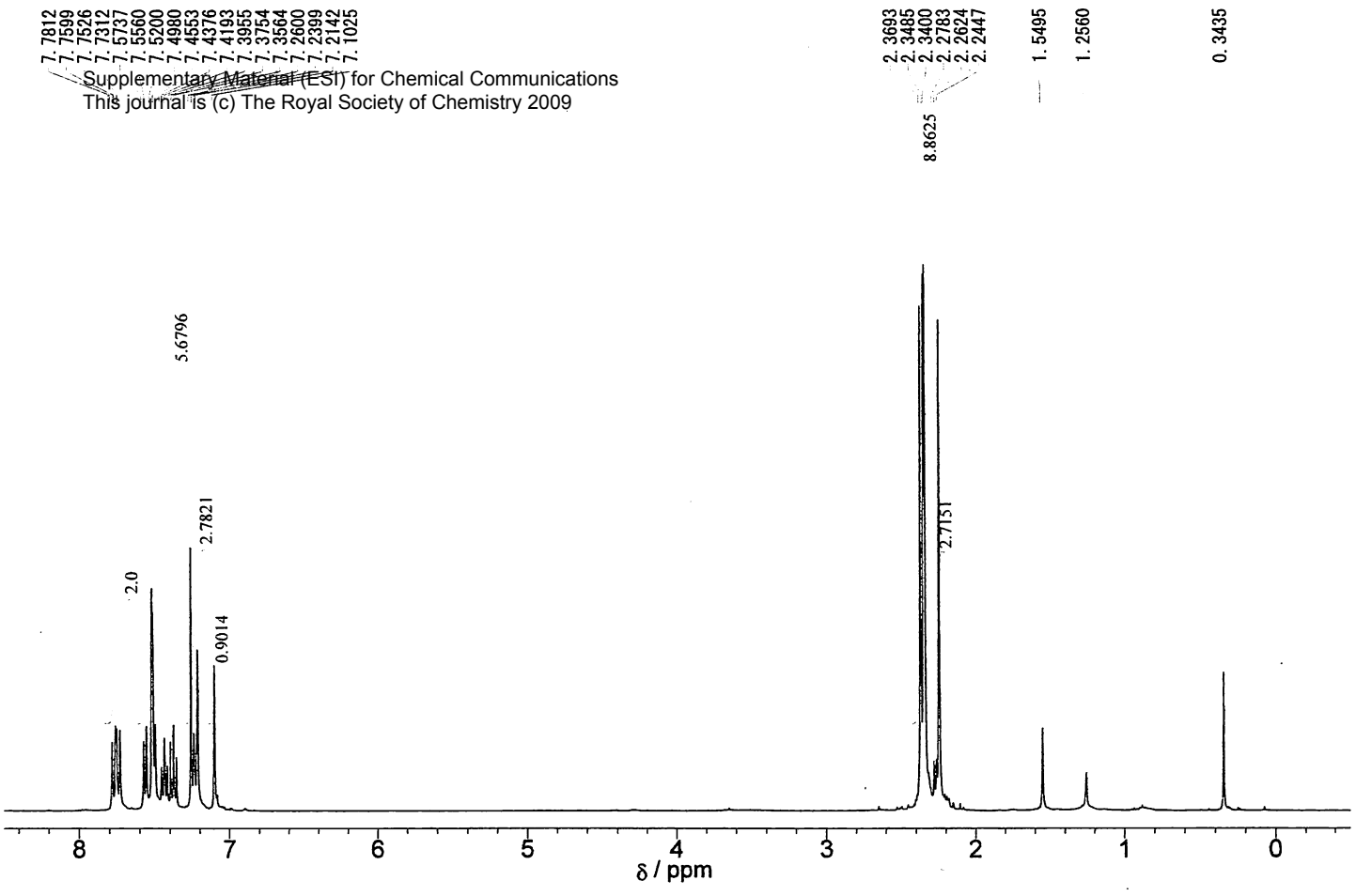

6.6982
5.7206
2.285
1.9112
1.0
0.9918
1.013
δ / ppm
7.6677
7.6482
7.5237
7.5188
7.5115
7.5017
7.3674
7.3479
7.3357
7.3308
7.3113
7.2893
7.2795
7.2698
7.2600
7.2405
7.2331
7.2234
7.2185
7.2038
7.1965
5.8904
5.8782
5.8733
5.8684
3.6467
2.0598
2.0281
1.9011
1.5569
1.5422
1.5349
1.5300
1.5105
1.2541

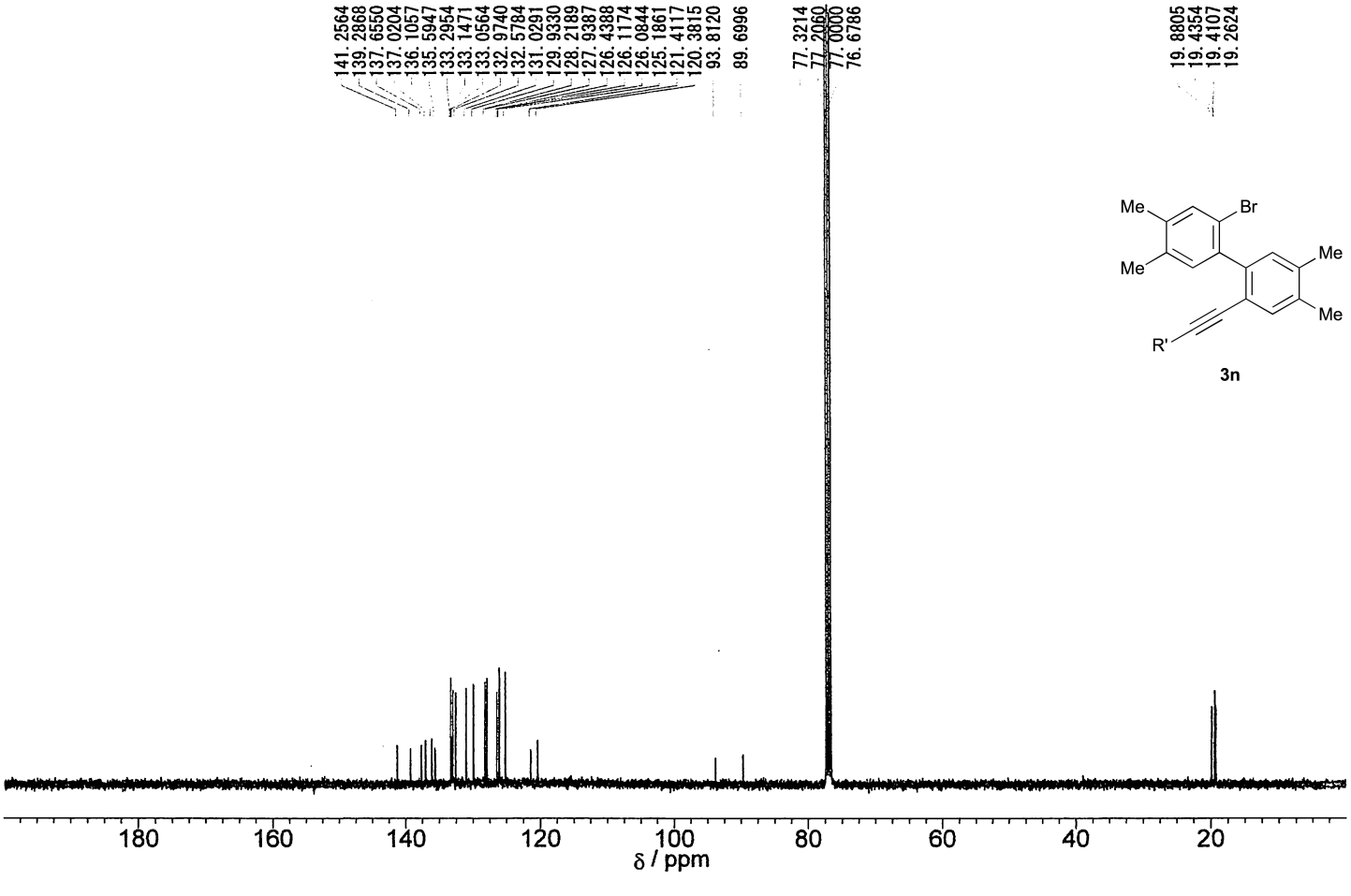

Br
3m
δ / ppm
143.4238
141.8333
134.8860
132.3971
131.5318
131.4329
129.4386
128.8040
127.6090
127.3371
126.7519
123.5544
123.3895
120.7276
94.7845
85.7769
77.3214
77.2060
77.0000
76.6786
28.6408
25.6575
22.1715
21.4133



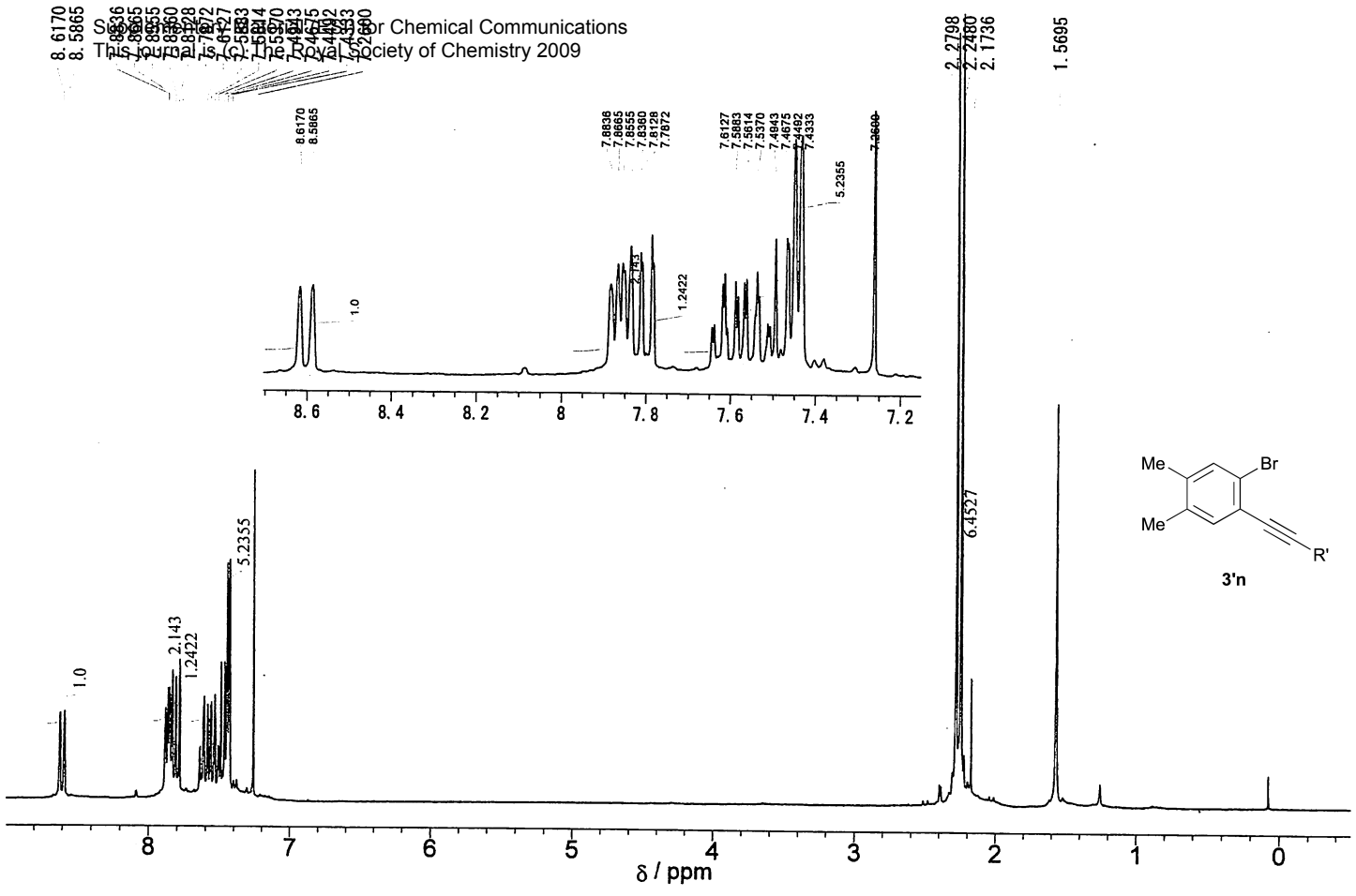


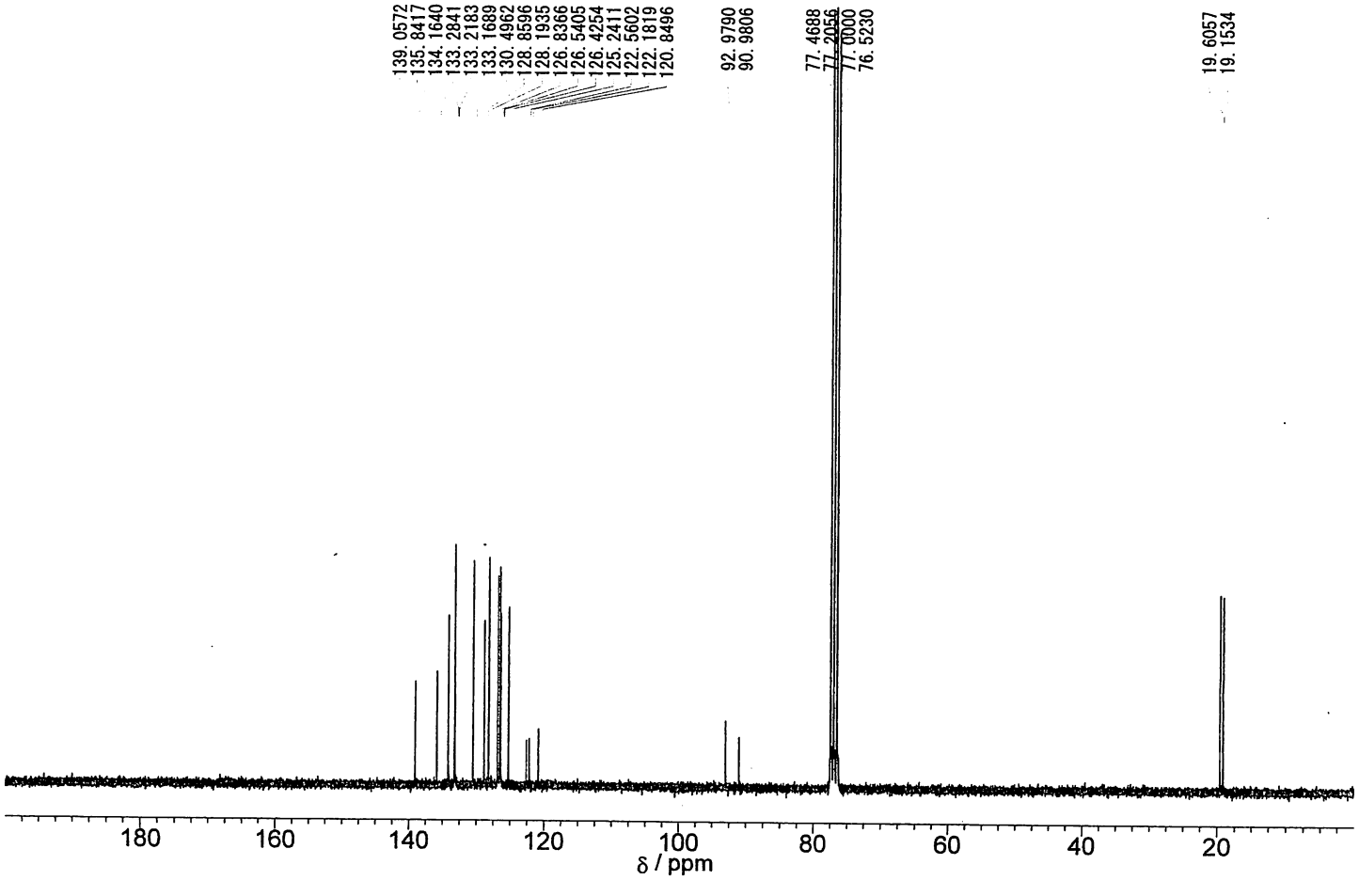
3'm

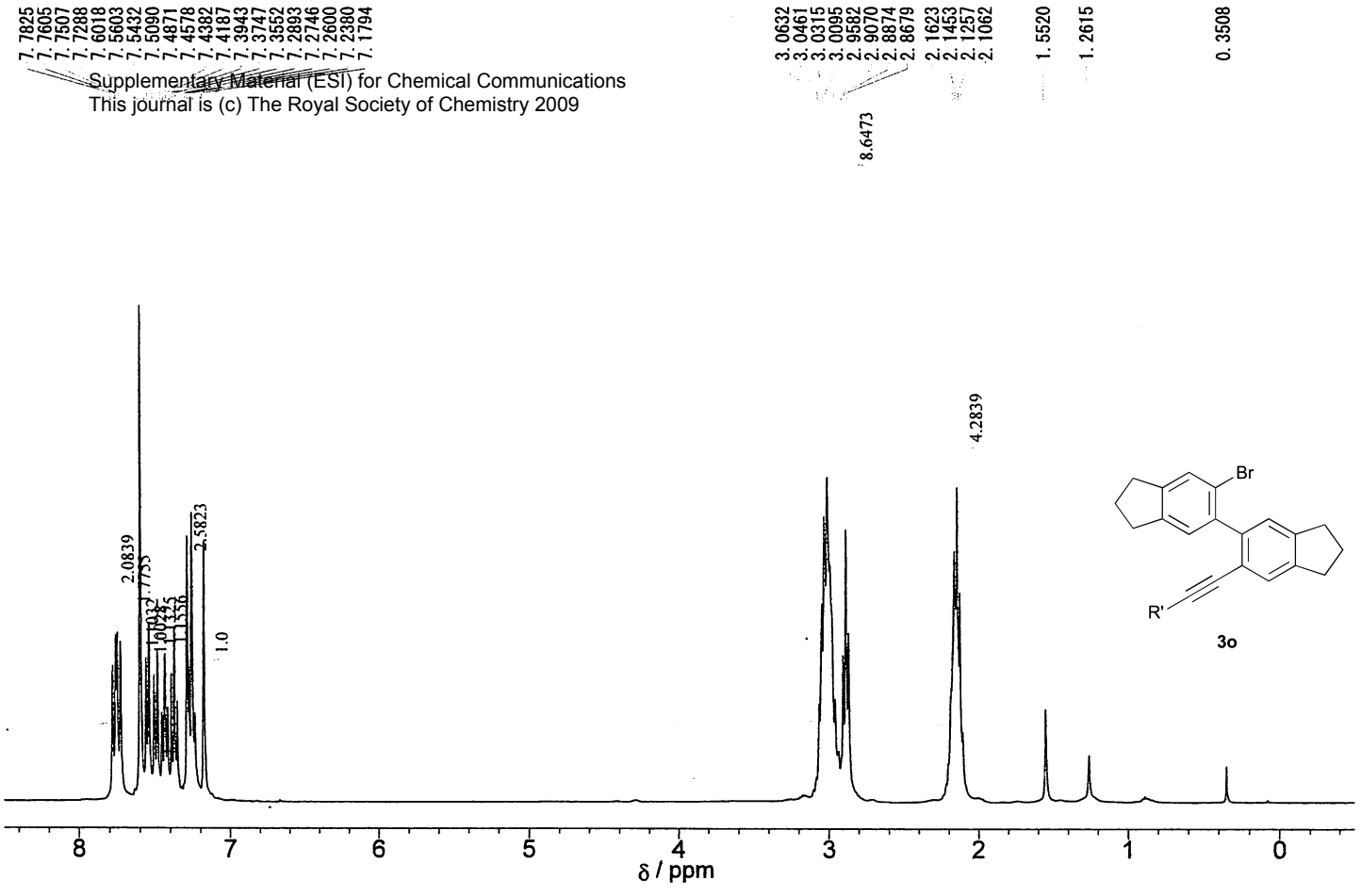

7.7812
7.7599
7.7526
7.7312
7.5737
7.5560
7.5200
7.4980
7.4553
7.4376
7.4193
7.3955
7.3754
7.3564
7.2600
7.2399
7.2142
7.1025
2.3693
2.3485
2.3400
2.2783
2.2624
2.2447
1.5495
1.2560
0.3435
8.8625
5.6796
2.7821
2.0
0.9014
2.7151
δ / ppm

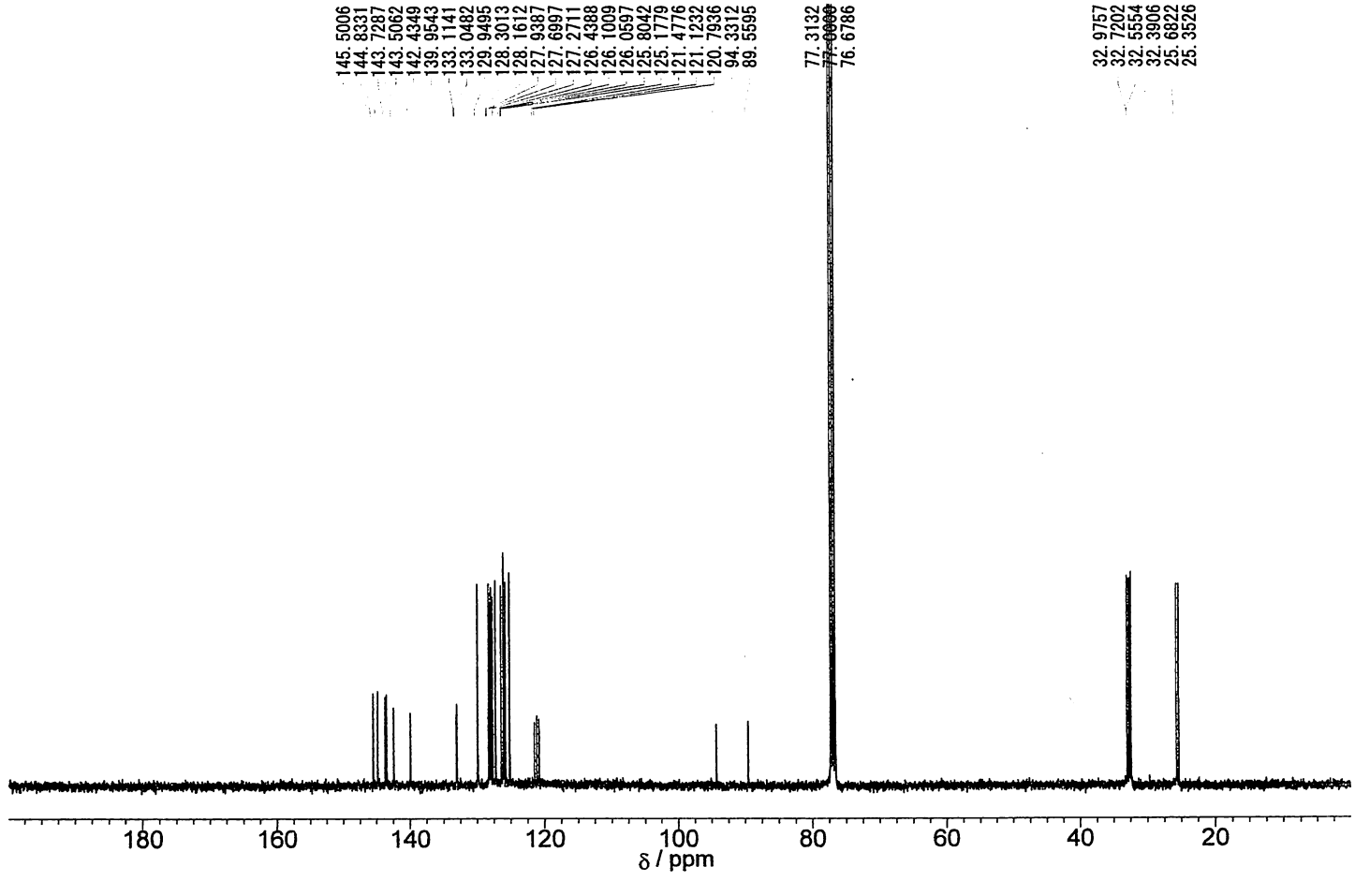

141.2564
139.2868
137.6550
137.0204
136.1057
135.5947
133.2954
133.1471
133.0564
132.9740
132.5784
131.0291
129.9330
128.2189
127.9387
126.4388
126.1174
126.0844
125.1861
121.4117
120.3815
93.8120
89.6996
77.3214
77.2060
77.0000
76.6786
19.8805
19.4354
19.4107
19.2624
Me
Br
Me
Me
Me
R'
δ / ppm

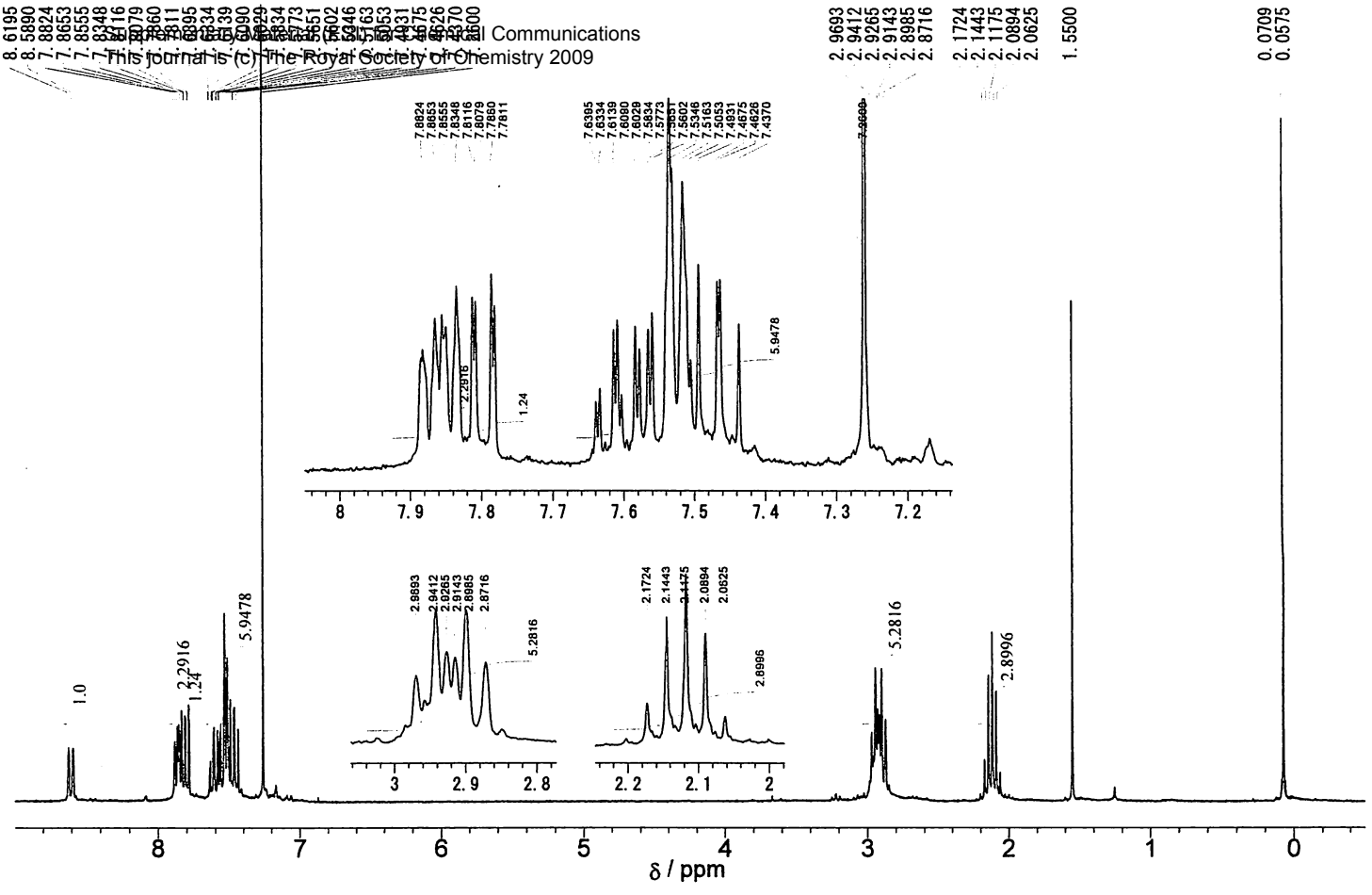
3n

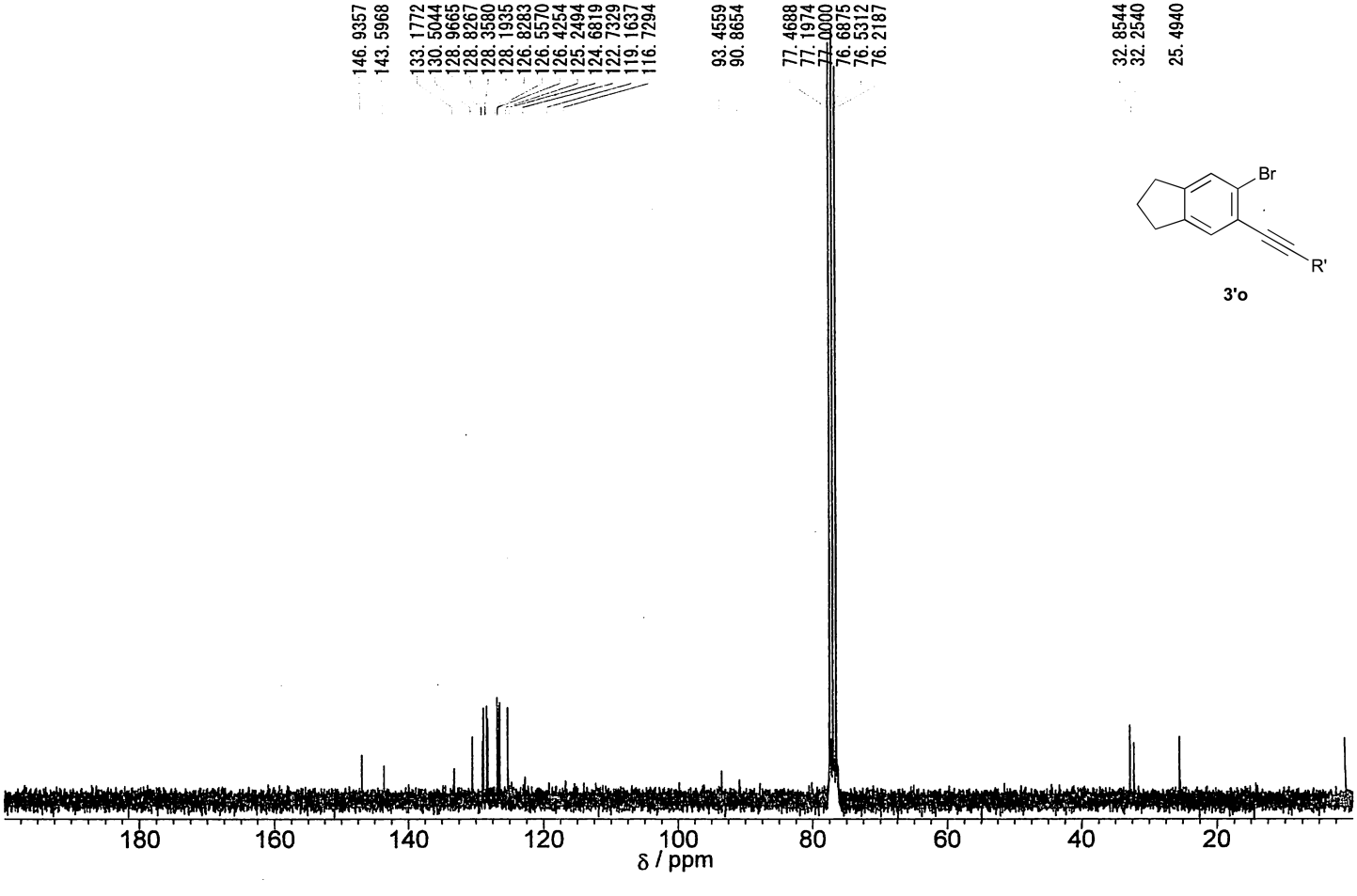




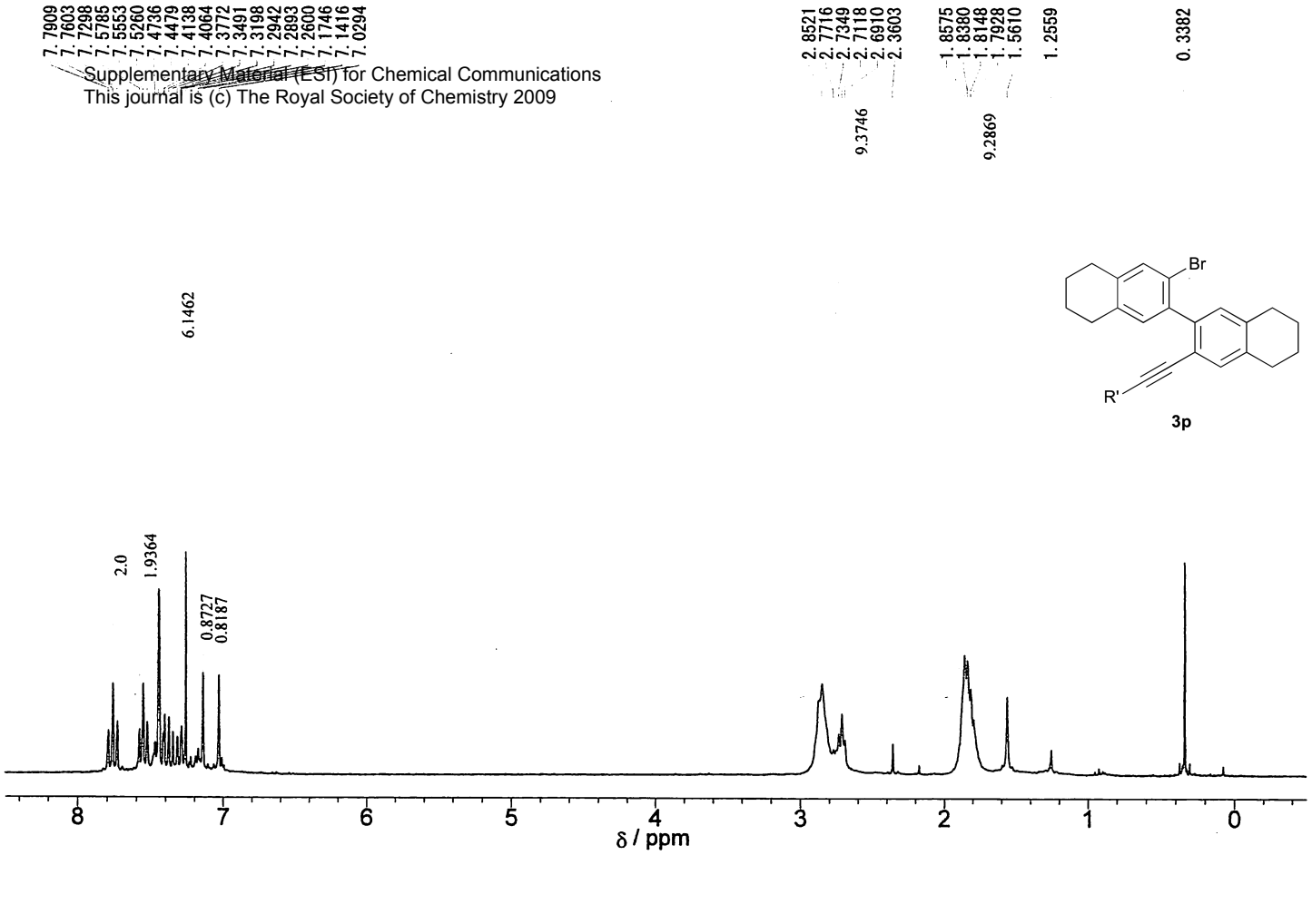

7.7825
7.7605
7.7507
7.7288
7.6018
7.5603
7.5432
7.5090
7.4871
7.4578
7.4382
7.4187
7.3943
7.3747
7.3552
7.2893
7.2746
7.2600
7.2380
7.1794
3.0632
3.0461
3.0315
3.0095
2.9582
2.9070
2.8874
2.8679
2.1623
2.1453
2.1257
2.1062
1.5520
1.2615
0.3508
8.6473
4.2839
2.0839
2.5823
1.0
Br
R'
3o
δ / ppm

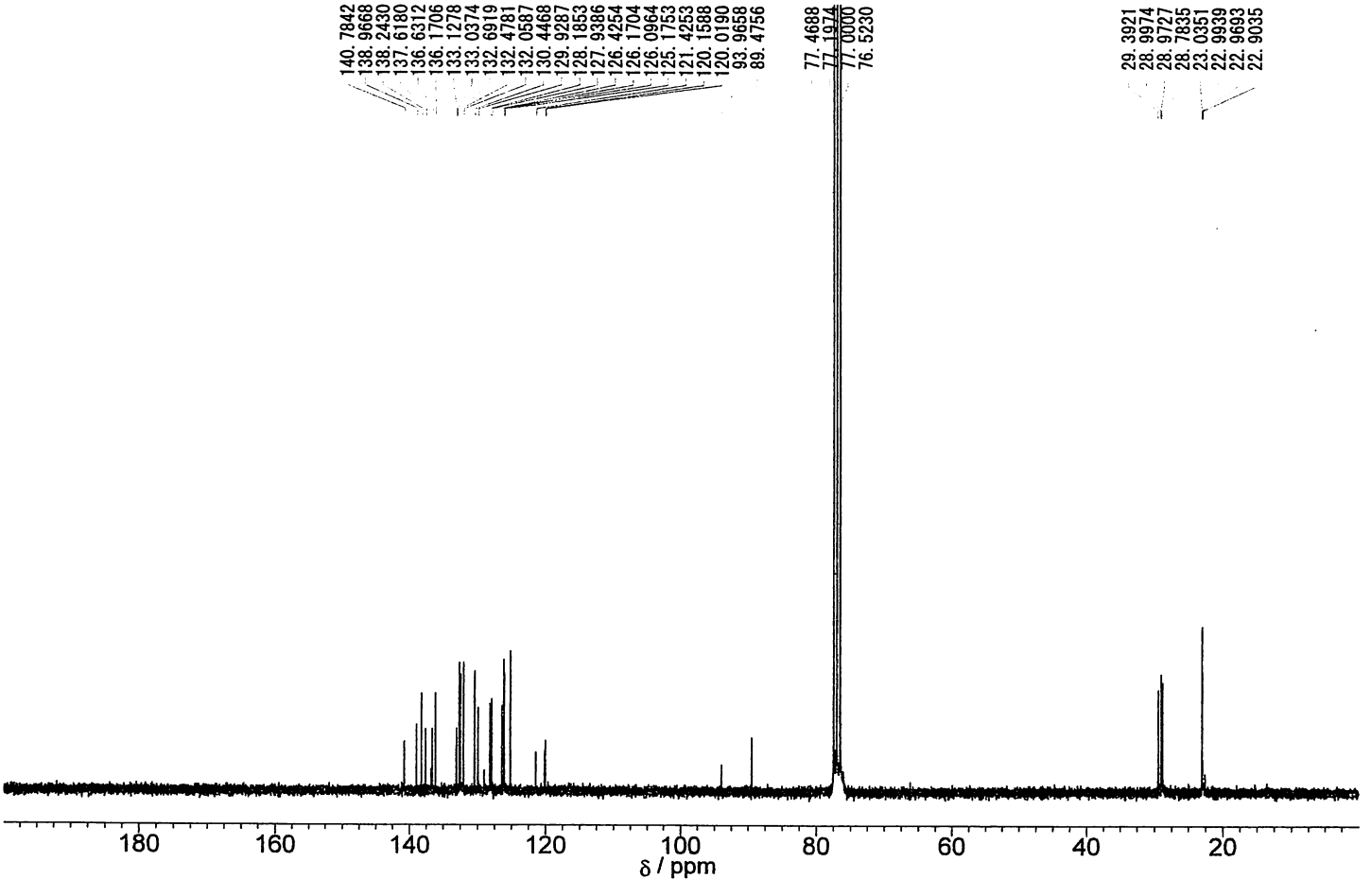

145.5006
144.8331
143.7287
143.5062
142.4349
139.9543
133.1141
133.0482
129.9495
128.3013
128.1612
127.9387
127.6997
127.2711
126.4388
126.1009
126.0597
125.8042
125.1779
121.4776
121.1232
120.7936
94.3312
89.5595
77.3132
77.0000
76.6786
32.9757
32.7202
32.5554
32.3906
25.6822
25.3526
δ / ppm





3'o


7.7909
7.7603
7.7298
7.5785
7.5553
7.5260
7.4736
7.4479
7.4138
7.4064
7.3772
7.3491
7.3198
7.2942
7.2893
7.2600
7.1746
7.1416
7.0294
2.8521
2.7716
2.7349
2.7118
2.6910
2.3603
1.8575
1.8380
1.8148
1.7928
1.5610
1.2559
0.3382
9.3746
9.2869
6.1462
Br
R'
3p
2.0
1.9364
0.8727
0.8187
δ / ppm


140.7842
138.9668
138.2430
137.6180
136.6312
136.1706
133.1278
133.0374
132.6919
132.4781
132.0587
130.4468
129.9287
128.1853
127.9386
126.4254
126.1704
126.0964
125.1753
121.4253
120.1588
120.0190
93.9658
89.4756
77.4688
77.1974
77.0000
76.5230
29.3921
28.9974
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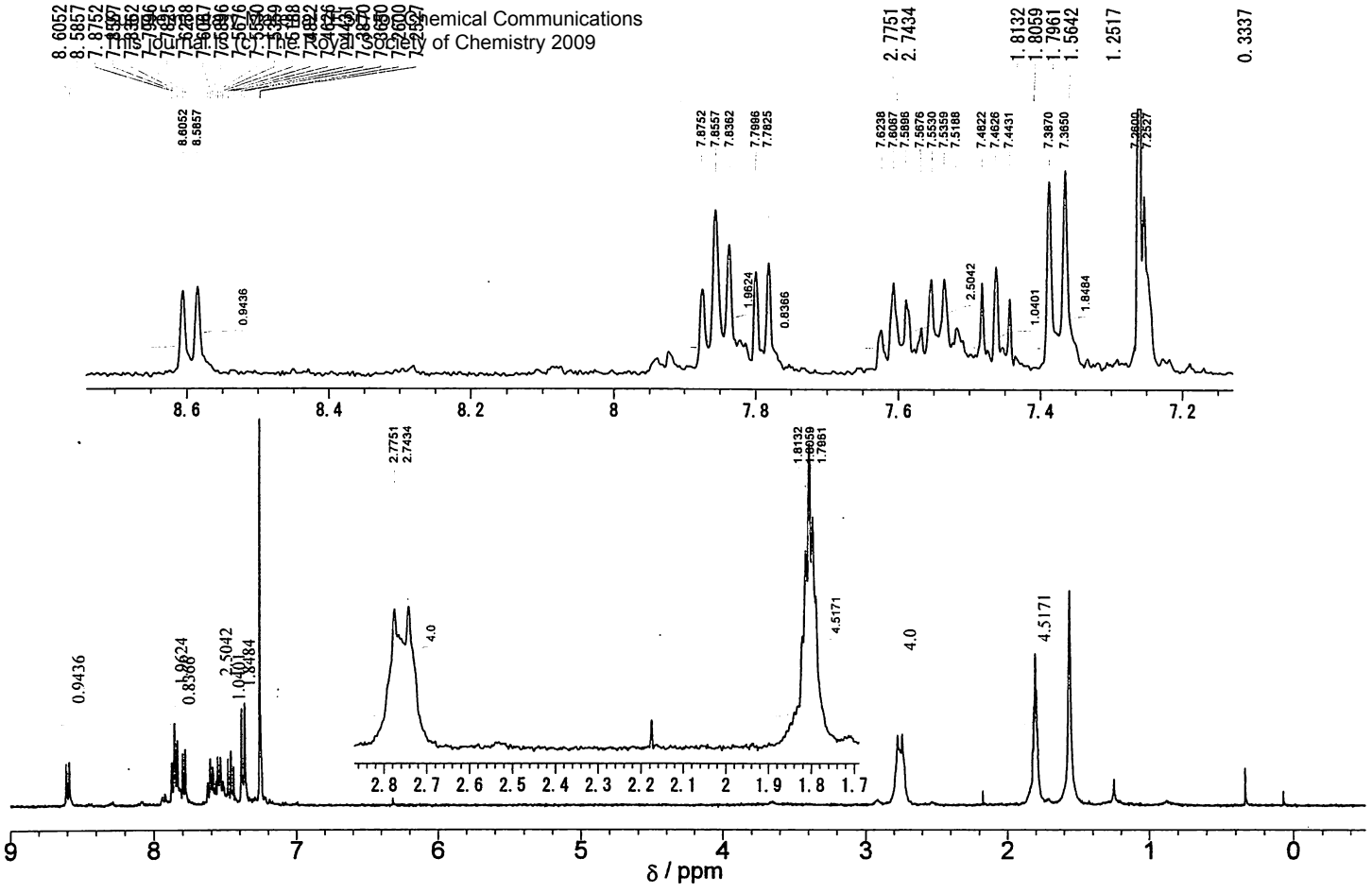
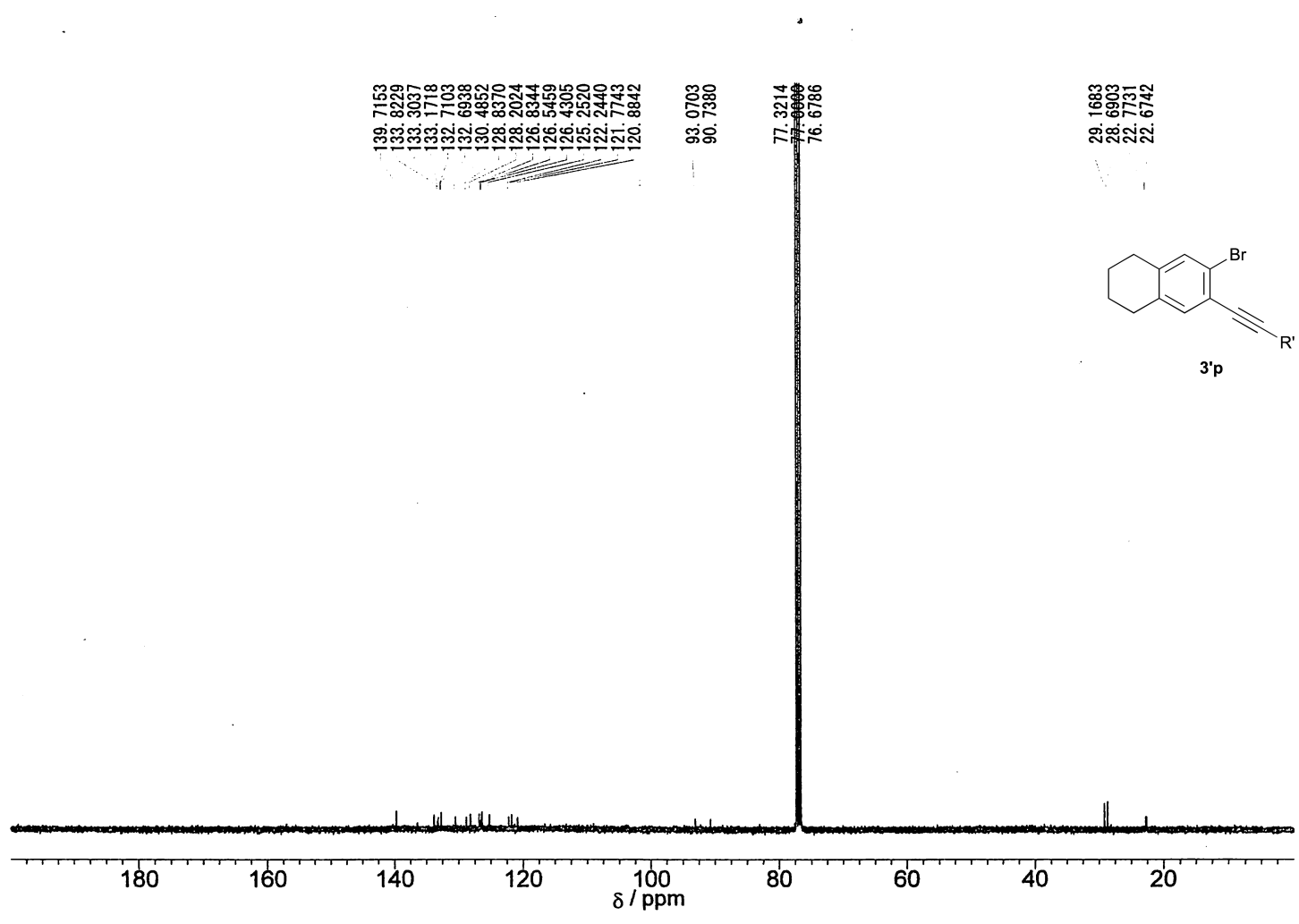
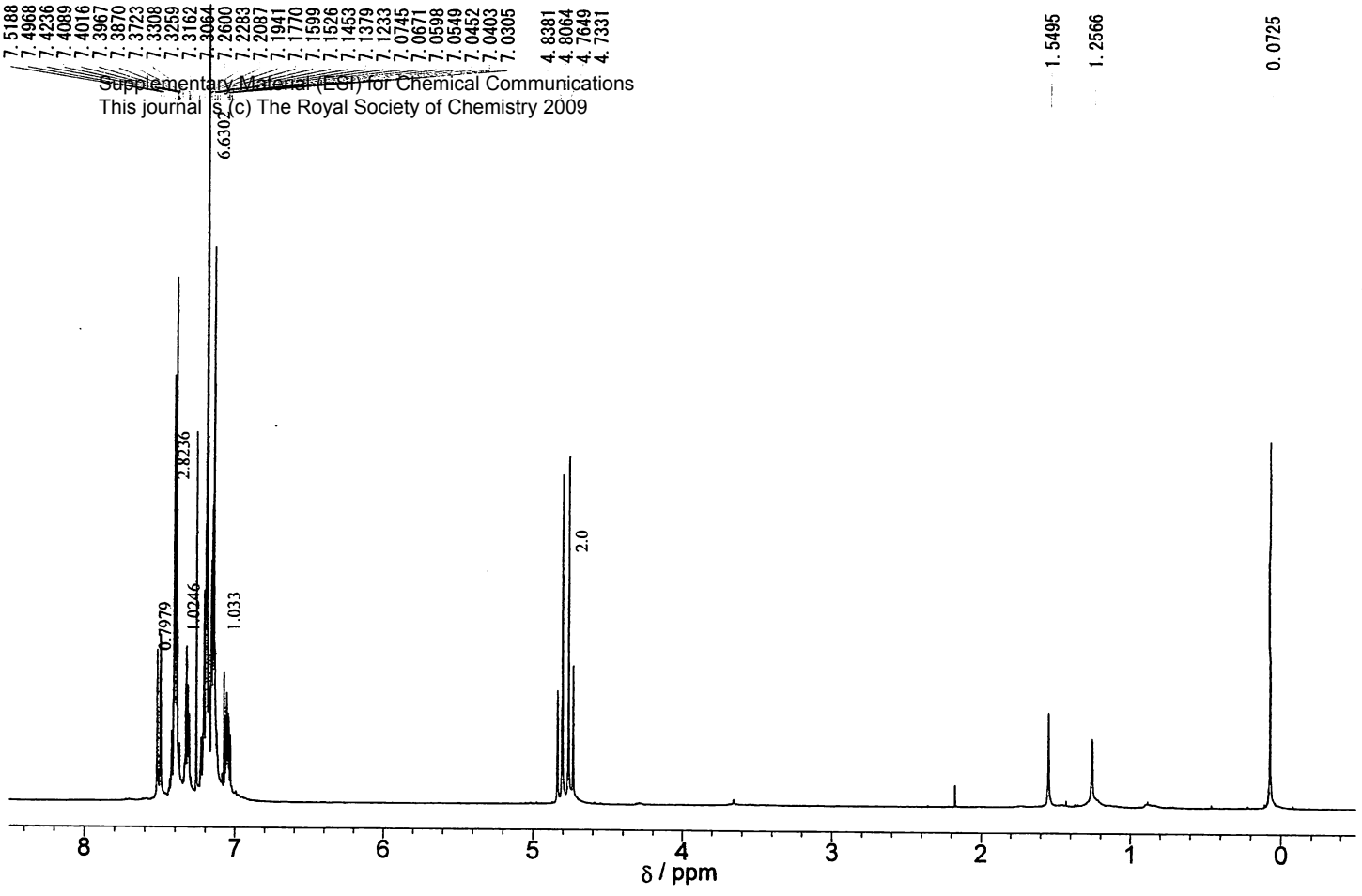
23.0351
22.9939
22.9693
22.9035
δ / ppm





3'p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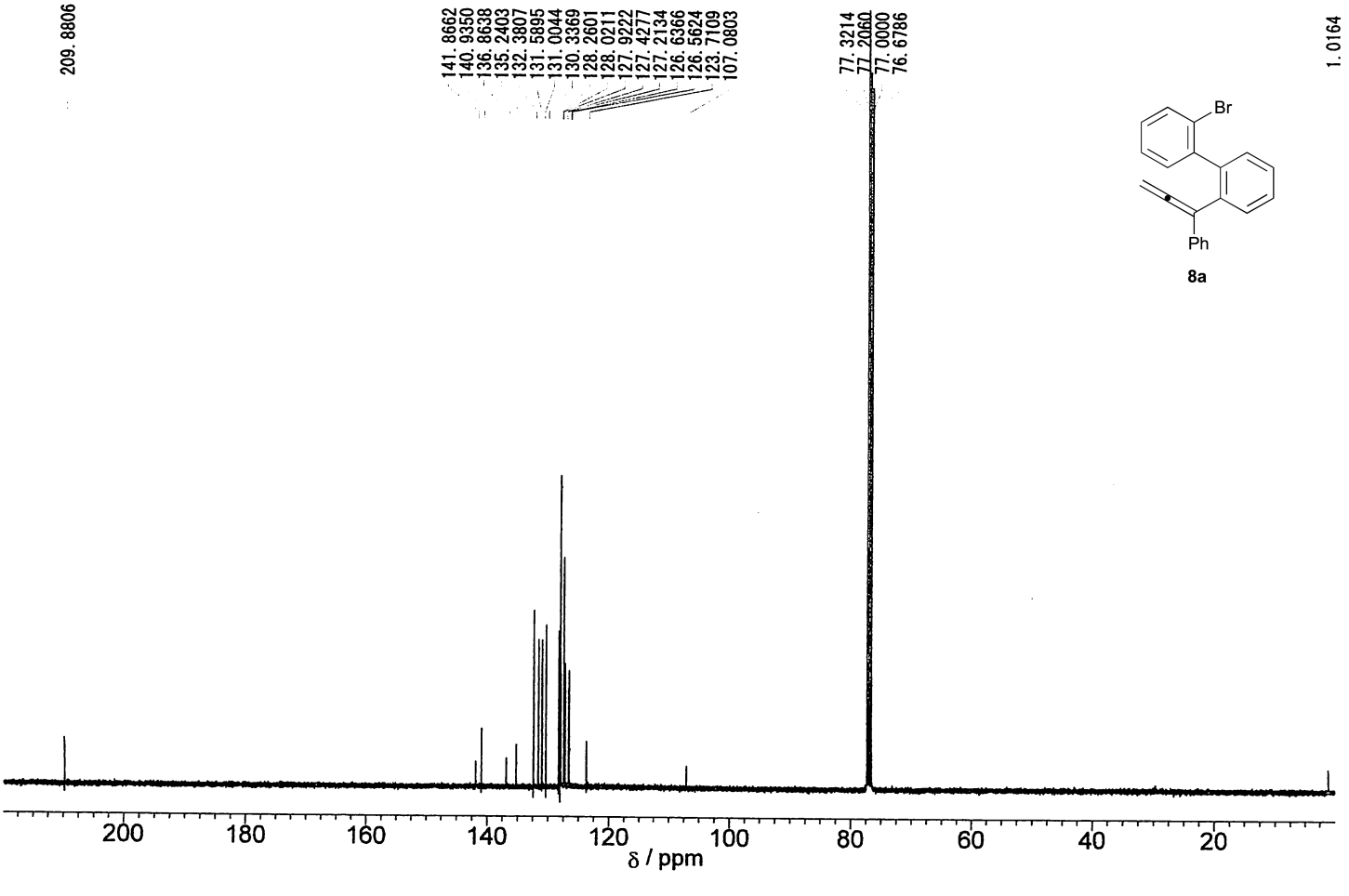
7.4968
7.4236
7.4089
7.4016
7.3967
7.3870
7.3723
7.3308
7.3259
7.3162
7.3064
7.2600
7.2283
7.2087
7.1941
7.1770
7.1599
7.1526
7.1453
7.1379
7.1233
7.0745
7.0671
7.0598
7.0549
7.0452
7.0403
7.0305
4.8381
4.8064
4.7649
4.7331
1.5495
1.2566
0.0725
6.6302
2.8236
2.0
1.033
1.0246
0.7979
δ / ppm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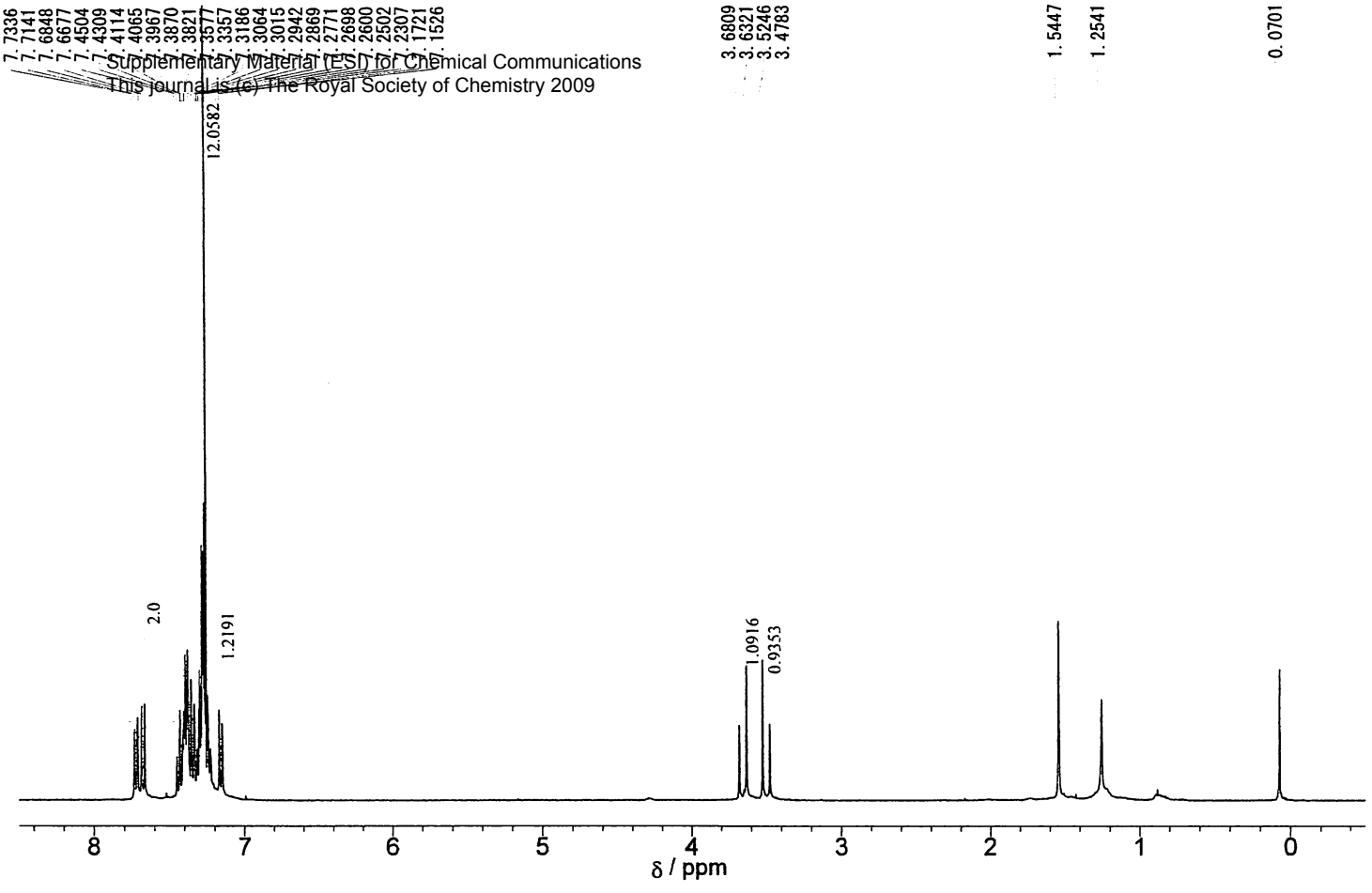
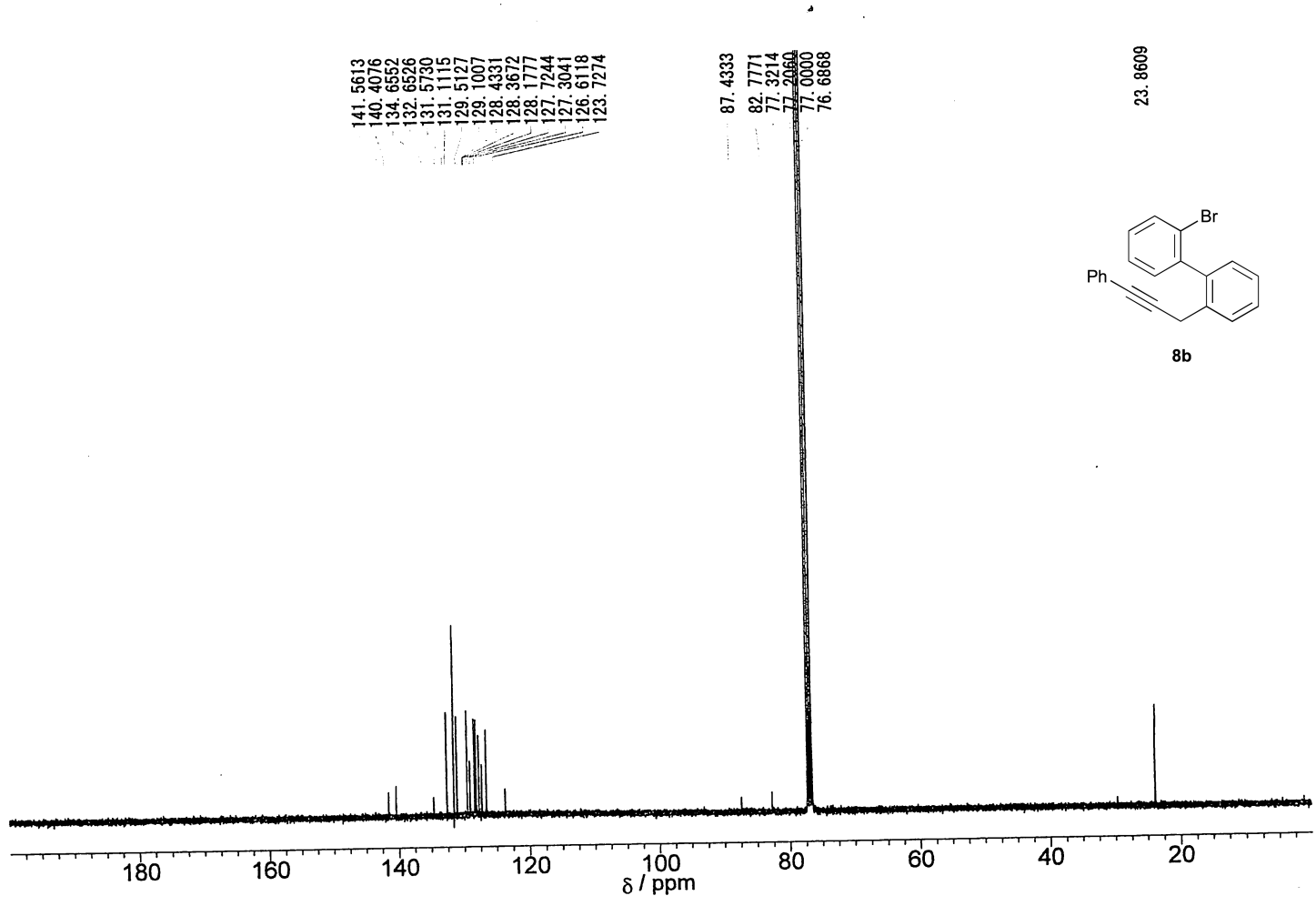
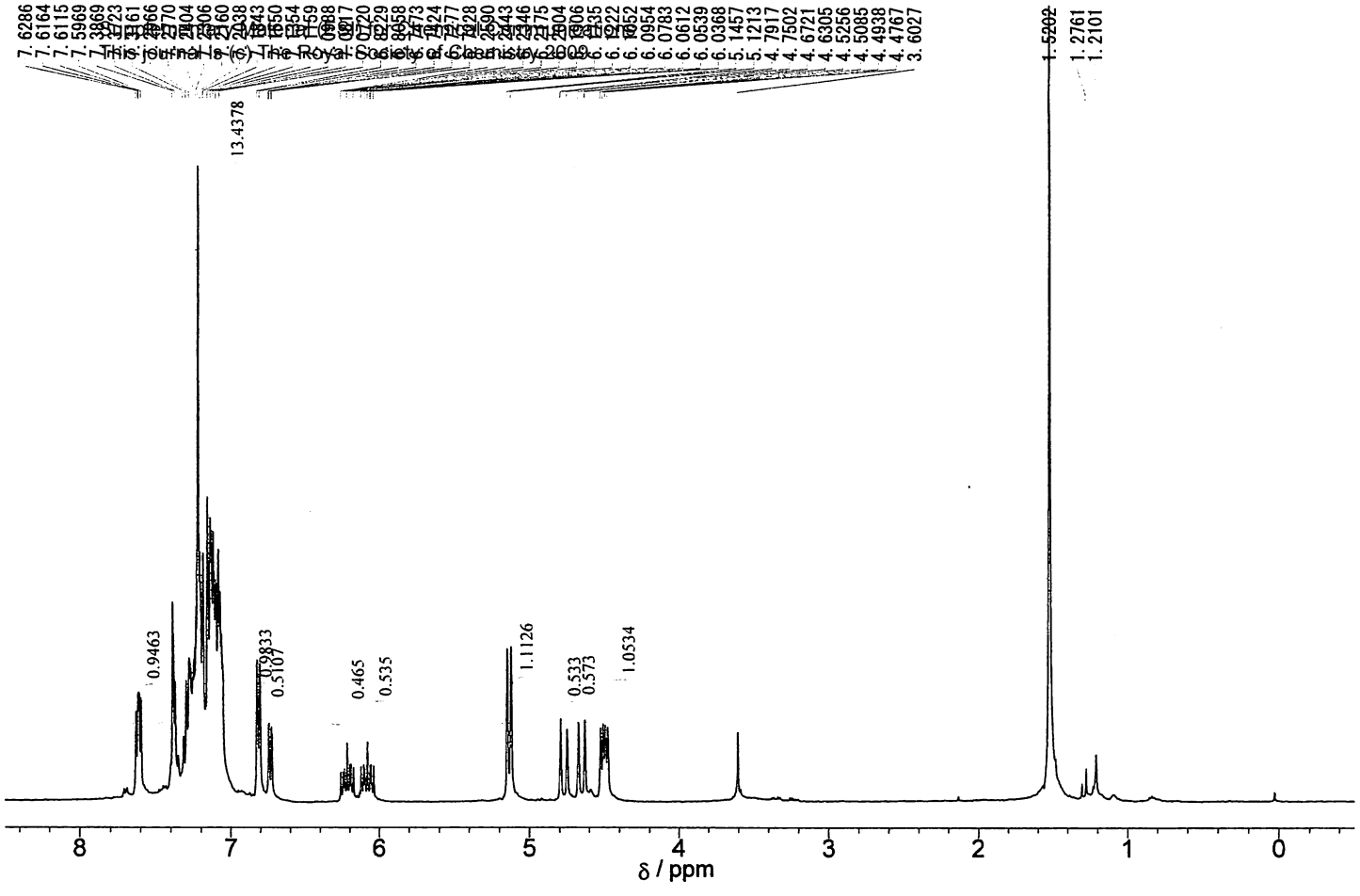
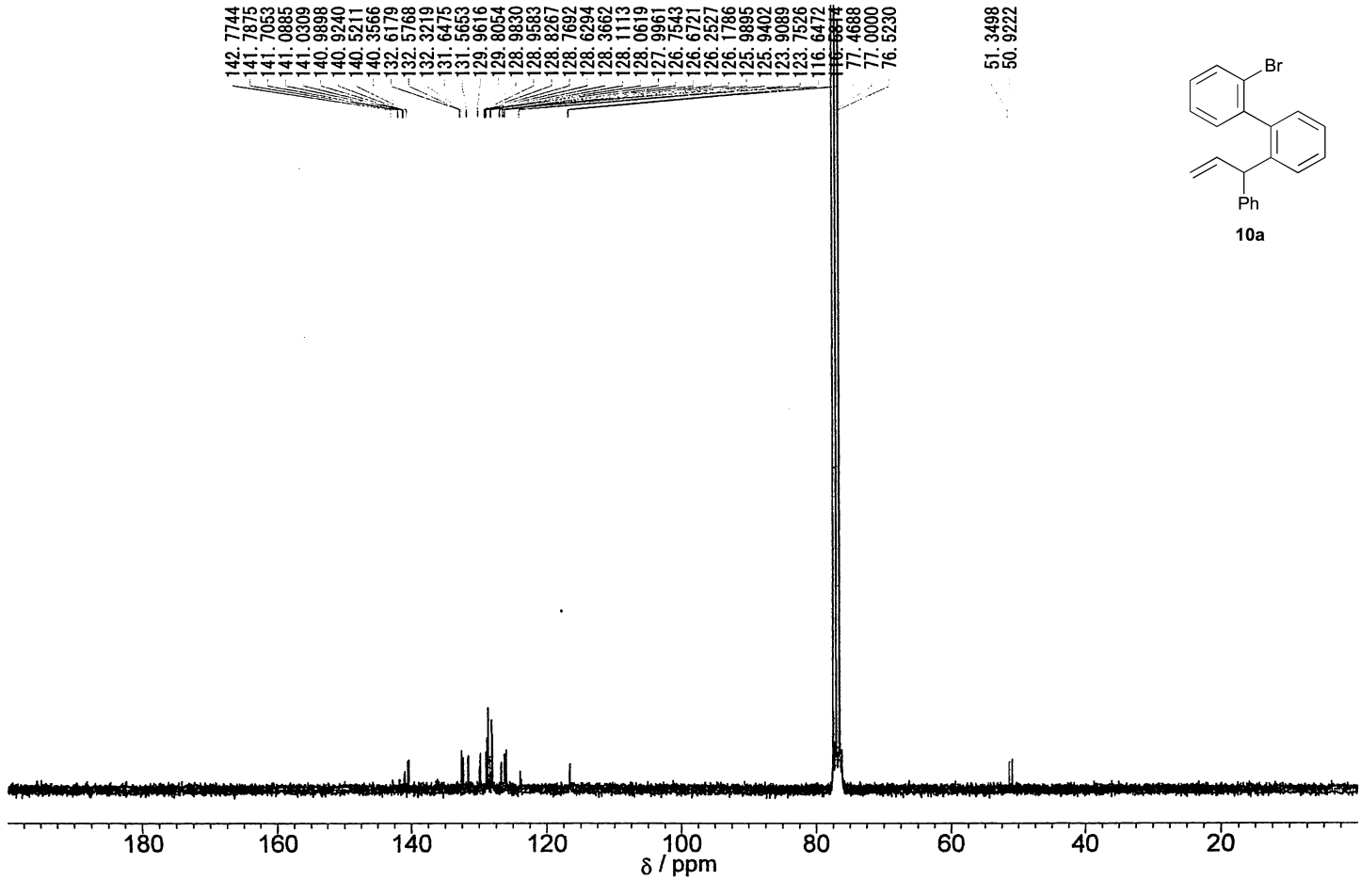
141.8662
140.9350
136.8638
135.2403
132.3807
131.5895
131.0044
130.3369
128.2601
128.0211
127.9222
127.4277
127.2134
126.6366
126.5624
123.7109
107.0803
77.3214
77.2060
77.0000
76.6786
1.0164
Br
Ph
8a
δ / ppm



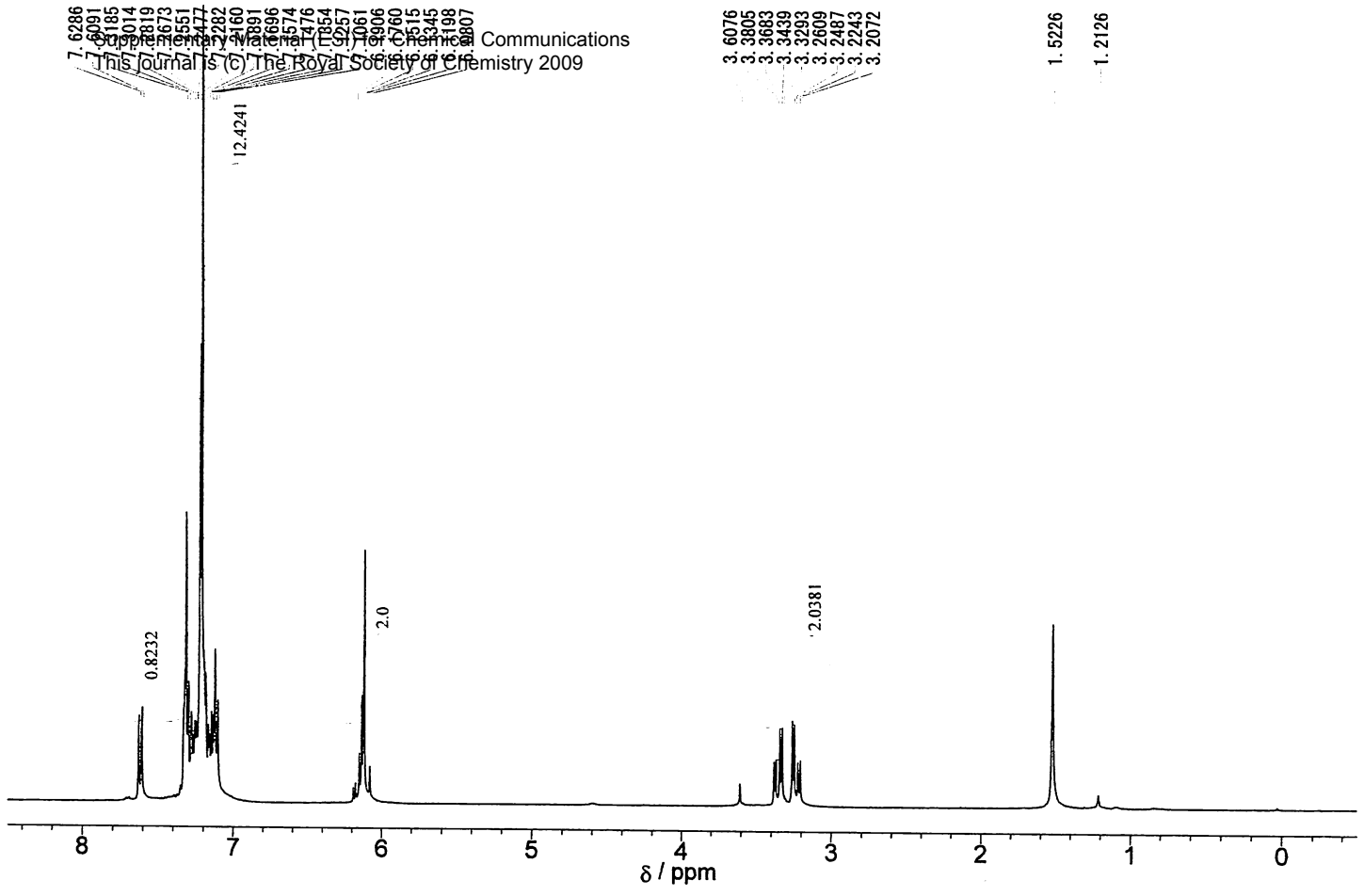


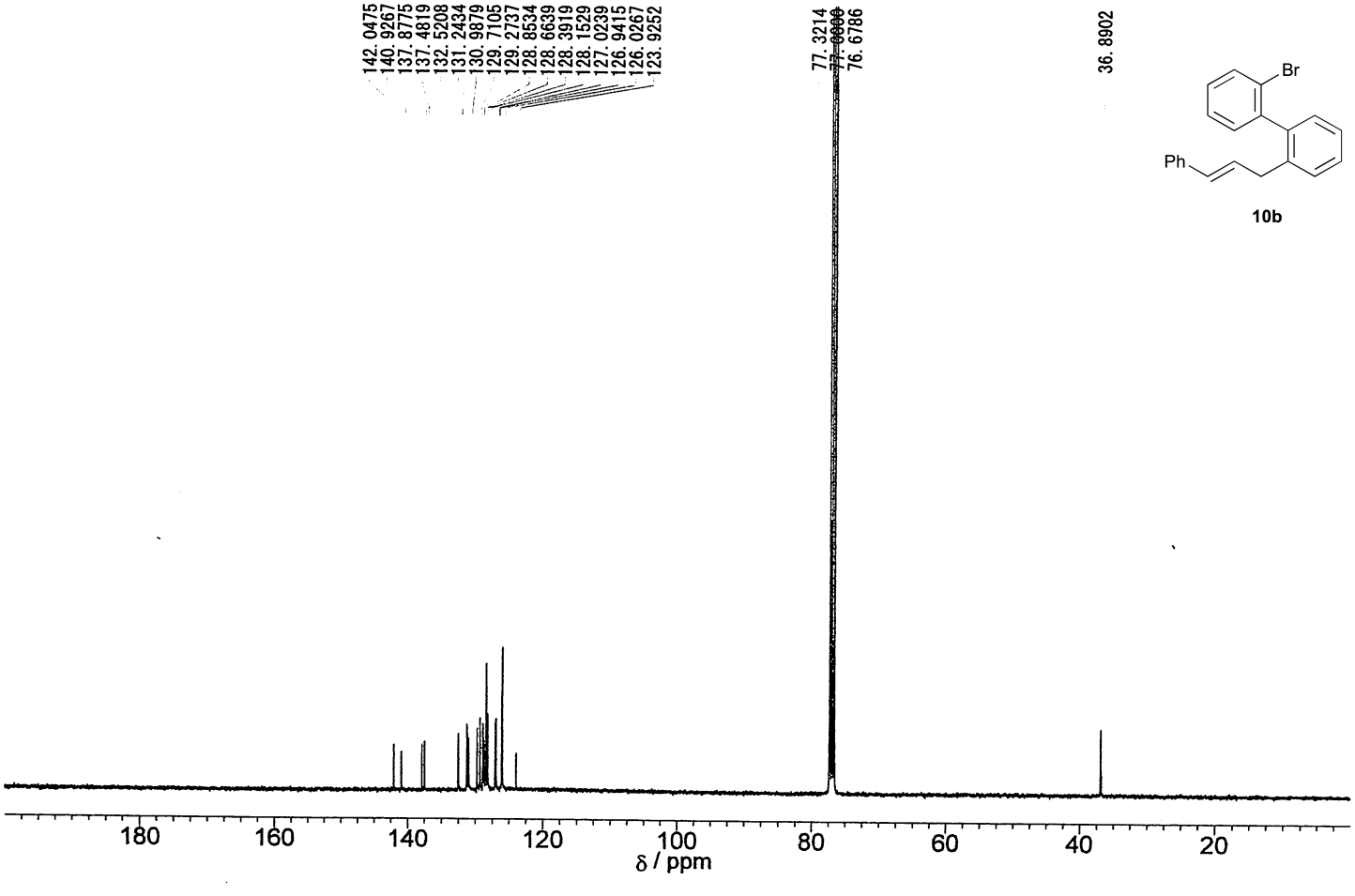
8b



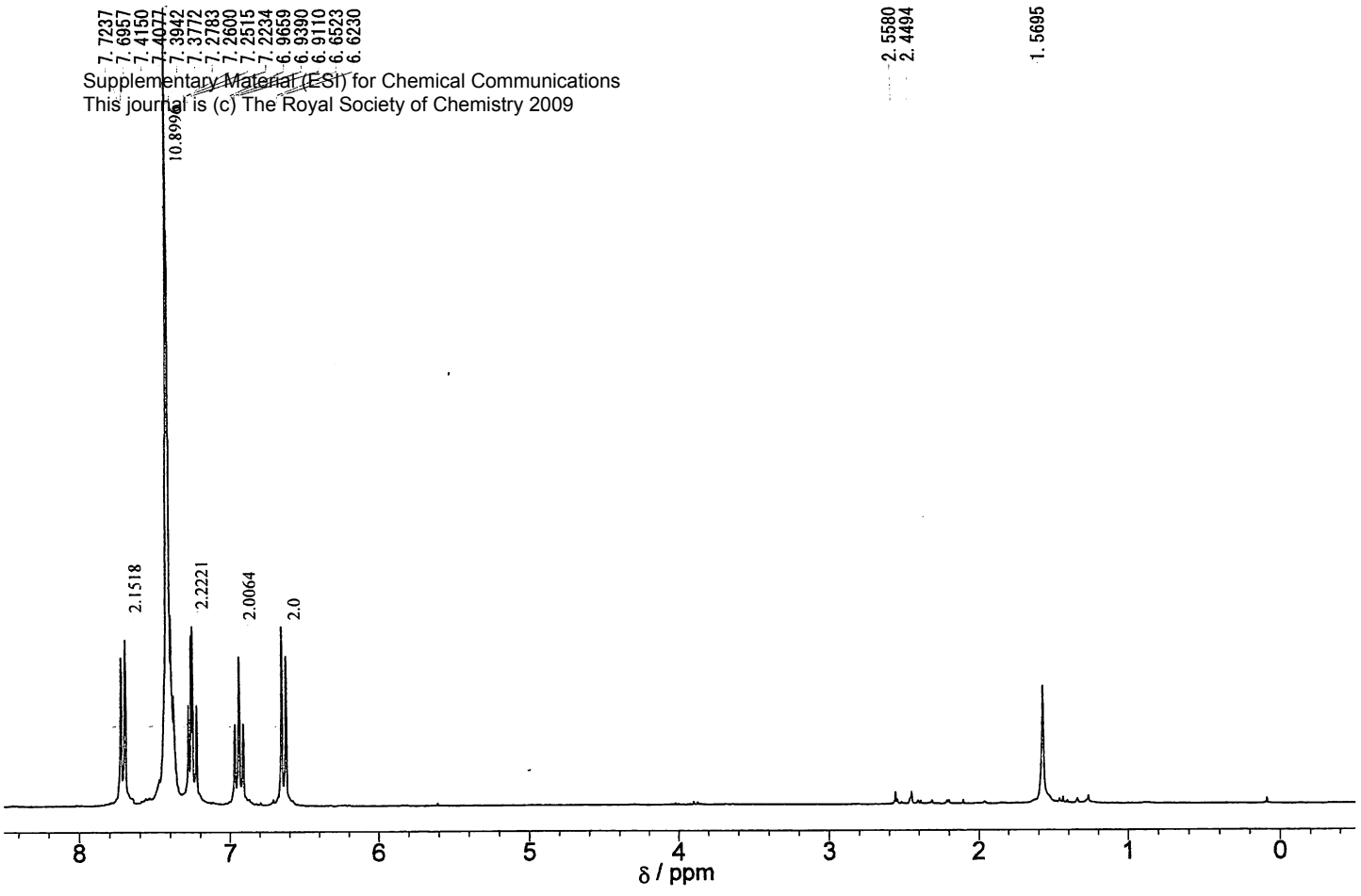


10a





10b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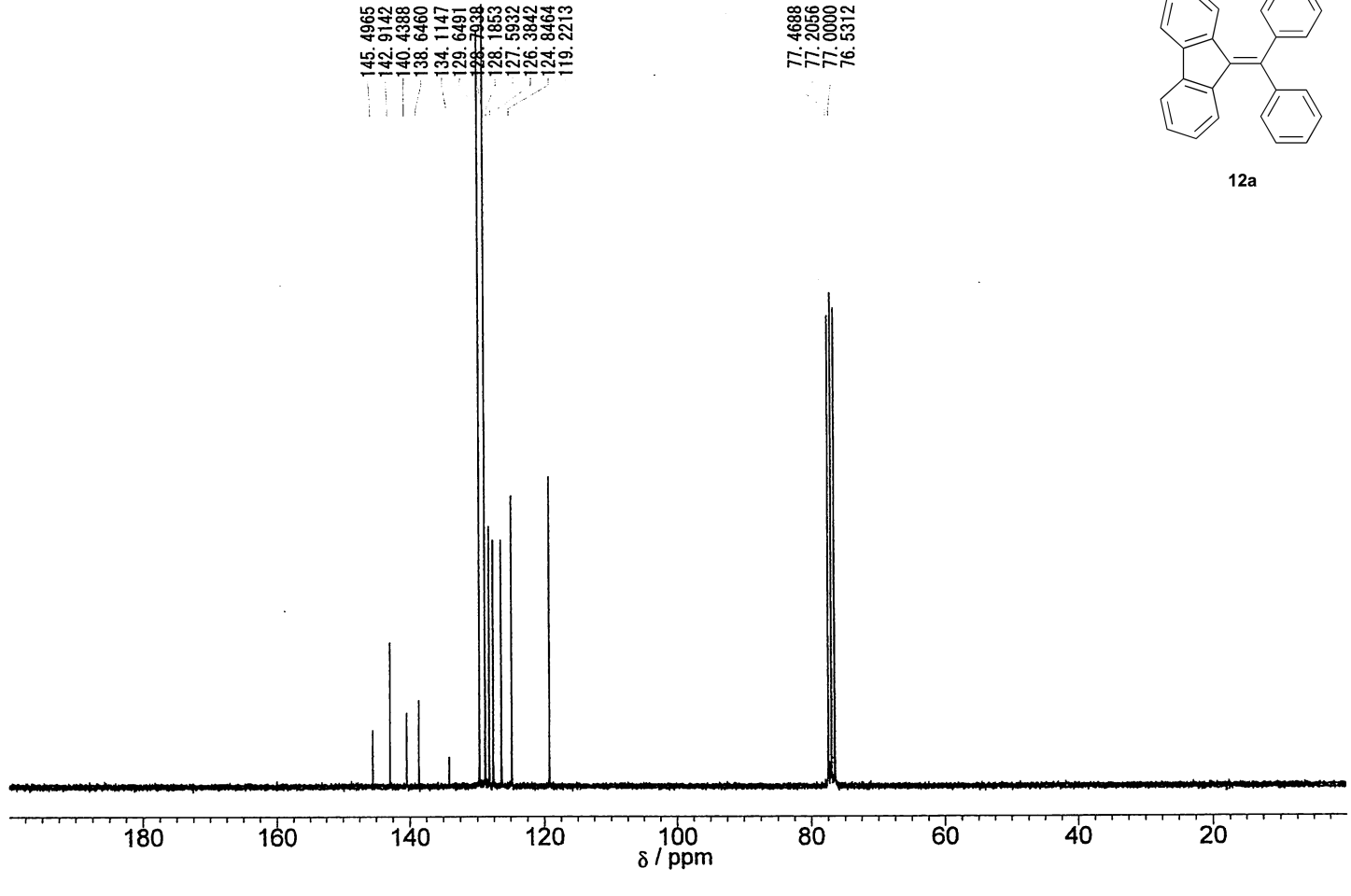
7.6957
7.4150
7.4077
10.8996
7.3942
7.3772
7.2783
7.2600
7.2515
7.2234
6.9659
6.9390
6.9110
6.6523
6.6230
2.5580
2.4494
1.5695
2.1518
2.2221
2.0064
2.0
8
7
6
5
4
3
2
1
0
δ / ppm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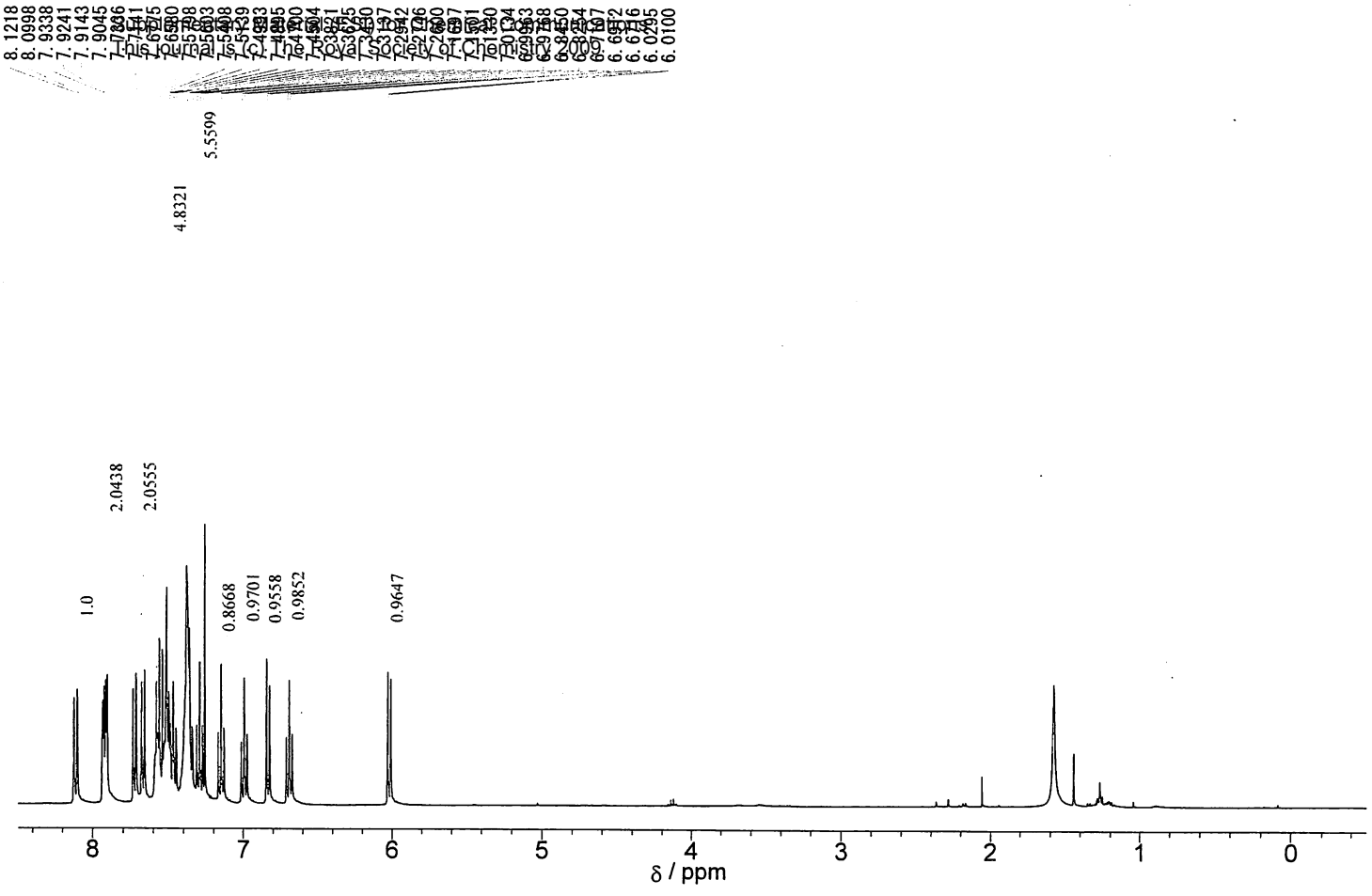
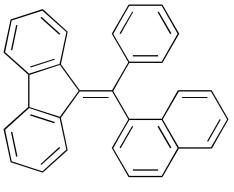
142.9142
140.4388
138.6460
134.1147
129.6491
128.7938
128.1853
127.5932
126.3842
124.8464
119.2213
77.4688
77.2056
77.0000
76.5312
180
160
140
120
100
80
60
40
20
δ / ppm

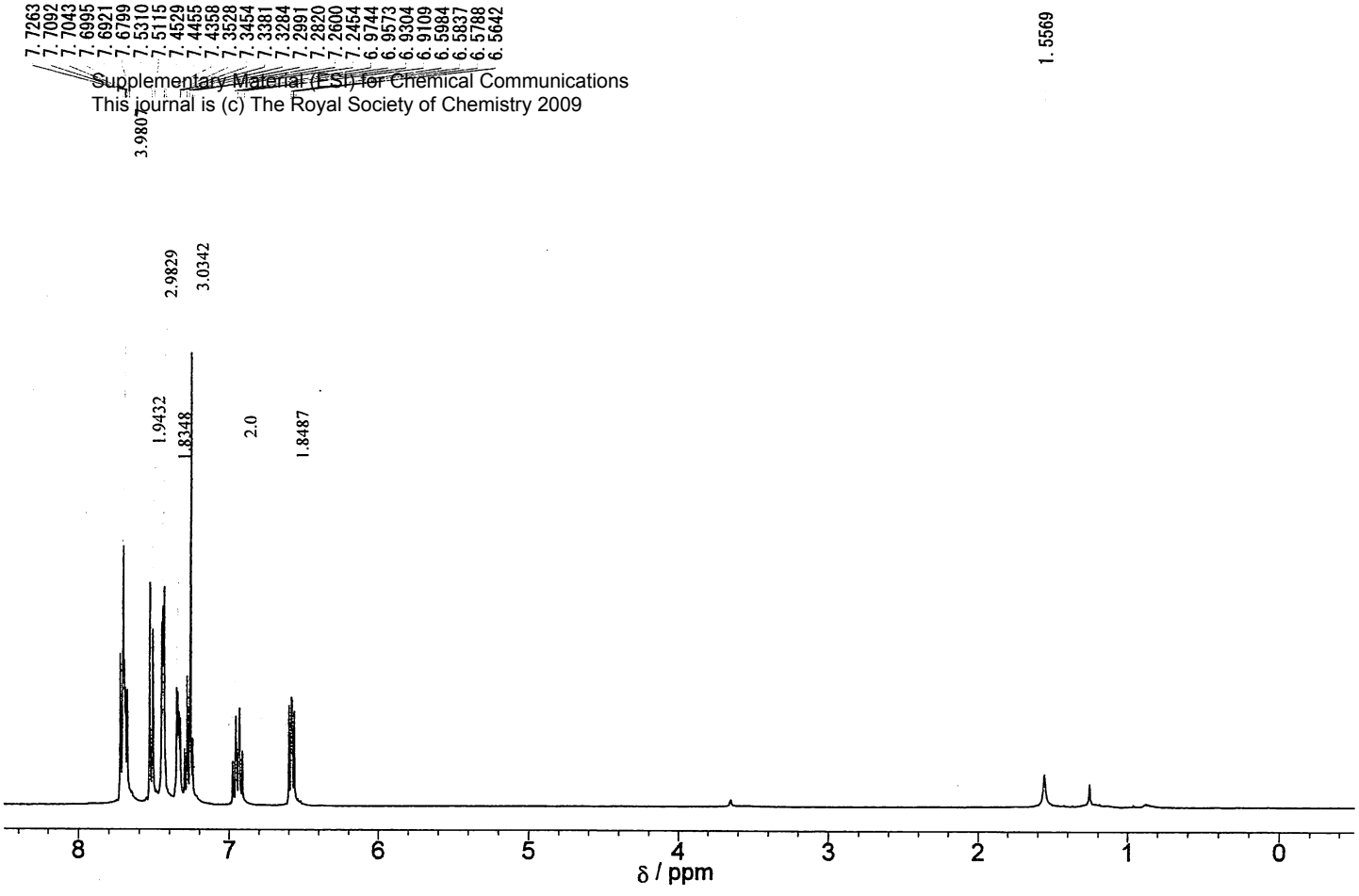
12a


8.1218
8.0998
7.9338
7.9241
7.9143
7.9045
5.5599
4.8321
2.0438
2.0555
1.0
0.8668
0.9701
0.9558
0.9852
0.9647
8
7
6
5
4
3
2
1
0
δ / ppm



12b

142.6656
142.6079
140.7867
140.5724
140.3499
138.2978
138.1330
135.8172
133.9877
130.9961
129.1913
128.9111
128.8040
128.7463
128.3590
128.2930
128.1035
127.8892
127.6090
126.7107
126.6118
126.5706
126.4635
126.1339
126.0267
125.7383
125.1449
124.9554
119.3102
119.0876
180
160
140
120
100
80
60
40
20
δ / ppm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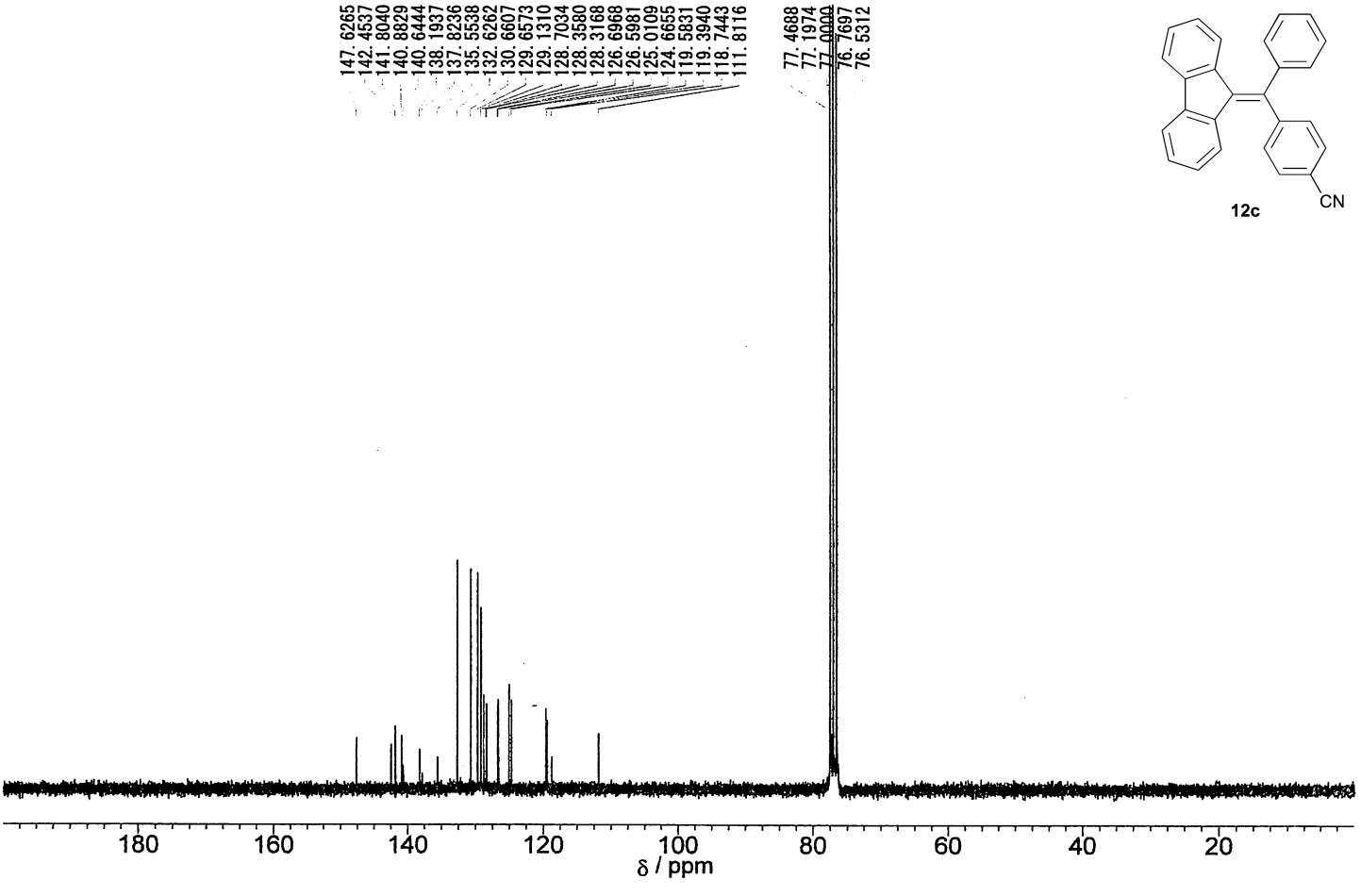
7.7092
7.7043
7.6995
7.6921
7.6799
7.5310
7.5115
7.4529
7.4455
7.4358
7.3528
7.3454
7.3381
7.3284
7.2991
7.2820
7.2600
7.2454
6.9744
6.9573
6.9304
6.9109
6.5984
6.5837
6.5788
6.5642
1.5569
3.9807
2.9829
3.0342
1.9432
1.8348
2.0
1.8487
δ / ppm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140.8829
140.6444
138.1937
137.8236
135.5538
132.6262
130.6607
129.6573
129.1310
128.7034
128.3580
128.3168
126.6968
126.5981
125.0109
124.6655
119.5831
119.3940
118.7443
111.8116
77.4688
77.1974
77.0000
76.7697
76.5312
δ / ppm

CN

12c