Supplementary Information for

Rhodium(I)-catalysed "ene-type" cycloisomerization of *N*-[2-(2-alkyn-1-yl)phenyl]carbodiimides leading to 3-(*cis*-alken-1-yl)-2-aminoquinolines

Takashi Otani,*[ab] Misato Onishi,[a] Takafumi Seino,[a] Naoki Furukawa[a] and Takao Saito*[a]

[a] *Department of Chemistry, Faculty of Science, Tokyo University of Science, Kagurazaka, Shinjuku, Tokyo 162-8601, Japan.*
[b] *Research Center for Chirality, Research Institute for Science & Technology, Tokyo University of Science, Kagurazaka, Shinjuku, Tokyo 162-8601, Japan.*

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Contents

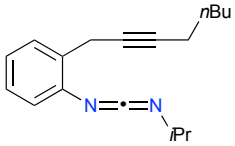
1. General

All melting points were determined on a Yanaco melting point apparatus and are uncorrected. Infrared spectra were recorded on a Horiba FT-710 model spectrophotometer. ^{1}H- and ^{13}C-NMR spectral data were obtained with a Bruker Avance-600, a JEOL JNM-LA 500, or a JEOL JNM-LA 300 instrument and chemical shifts are reported as values based on the internal standard (tetramethylsilane (TMS), δ ^{1}H = 0) and solvent ($CDCl_3$ δ ^{13}C = 77.0). HRMS analysis were performed on a Bruker Daltonics microTOF.

2. Synthesis and characterization data of carbodiimide-ynes 1,3,5 and 7

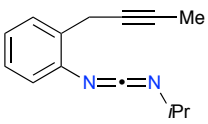
Carbodiimide-ynes **1**,**3**,**5** and **7** were prepared according to the reported procedure,[S1] and physical properties and spectral data of **1b–h,j,k** and **3a** have been reported in ref S1.

2-(2-Octyn-1-yl)-*N*-(isopropylcarbonimidoyl)benzenamine (1a).



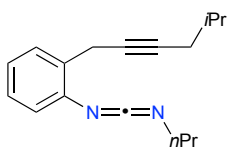
Yellow oil. IR (neat/cm^{-1}): 2931, 2129, 1219, 764. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 0.90 (t, J = 6.8 Hz, 3H), 1.33 (d, J = 6.4 Hz, 6H), 1.35–1.45 (m, 4H), 1.54 (tt, J = 6.9, 6.8 Hz, 2H), 2.22 (tt, J = 6.9, 6.8 Hz, 2H), 3.60 (s, 2H), 3.79 (q, J = 6.4 Hz, 1H), 7.05–7.23 (m, 3H), 7.53 (d, J = 7.5 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 14.0 (CH_3), 18.8 (CH_2), 21.2 (CH_2), 22.2 (CH_2), 24.8 (CH_2×2), 28.7 (CH_2), 31.1 (CH_2), 50.0 (CH), 77.1 (C), 82.8 (C), 123.3 (CH), 124.6 (CH), 127.4 (CH), 129.0 (CH), 131.3 (C), 135.7 (C), 138.4 (C). HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{18}H_{24}N_2Na$, 291.1837; found, 291.1832.

2-(2-Butyn-1-yl)-*N*-(isopropylcarbonimidoyl)benzenamine (1i).



Yellow oil. IR (neat/cm^{-1}): 2969, 2121, 1496, 756, 609. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.32 (d, J = 6.4 Hz, 3H), 1.34 (d, J = 6.4 Hz, 3H), 1.85 (t, J = 2.6 Hz, 3H), 3.57 (d, J = 2.5 Hz, 2H), 3.79 (q, J = 6.4 Hz, 1H), 7.06–7.21 (m, 3H), 7.49 (d, J = 7.5 Hz, 1H). ^{13}C-NMR (76 MHz, $CDCl_3$, δ): 3.6 (CH_3), 21.2 (CH_2), 24.8 (CH_3×2), 50.0 (CH), 76.4 (C), 77.8 (C), 123.4 (CH), 124.7 (CH), 127.4 (CH), 129.1 (CH), 131.2 (C), 135.7 (C), 138.4 (C). HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{14}H_{16}N_2Na$, 235.1211; found, 235.1203.

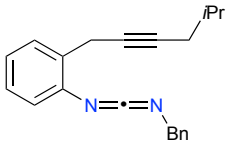
2-(5-Methylhex-2-yn-1-yl)-*N*-(propylcarbonimidoyl)benzenamine (1l).



Yellow oil. IR (neat/cm^{-1}): 2962, 2145, 910, 733. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 0.99 (d, J = 6.6 Hz, 6H), 1.01 (t, J = 7.4 Hz, 3H), 1.70 (qt, J = 7.5, 6.9 Hz, 2H), 1.82 (qt, J = 6.7, 6.6 Hz, 1H), 2.12 (d, J = 6.5 Hz, 2H), 3.38 (t, J = 6.8 Hz, 2H), 3.61 (s, 2H), 7.09 (dd, J = 7.1, 6.9 Hz, 1H), 7.13 (d, J = 6.9 Hz, 1H), 7.18 (dd, J = 7.9, 6.9 Hz, 1H), 7.53 (d, J = 7.4 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 11.5 (CH_3), 21.3 (CH_2), 22.0 (CH_3×2), 24.7 (CH_2), 28.1 (CH_2), 28.3 (CH), 48.6 (CH_2), 78.0 (C), 81.7 (C), 123.6 (CH), 124.6 (CH), 127.4 (CH), 129.0 (CH), 131.3 (C), 135.3 (C), 138.3 (C). HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{17}H_{22}N_2Na$, 277.1681; found, 277.1675.

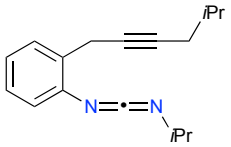
2-(5-Methylhex-2-yn-1-yl)-*N*-(phenylmethylcarbonimidoyl)benzenamine (1m).

Yellow oil. IR (neat/cm^{-1}): 3016, 2962, 2138, 1219, 756, 447. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 0.99 (d, J =



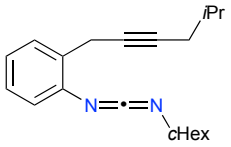
6.7 Hz, 6H), 1.81 (qt, *J* = 6.8, 6.5 Hz, 1H), 2.11 (d, *J* = 6.6 Hz, 2H), 3.55 (s, 2H), 4.57 (s, 2H), 6.97 (d, *J* = 7.6 Hz, 1H), 7.09 (dd, *J* = 7.5, 7.3 Hz, 1H), 7.13 (dd, *J* = 7.7, 7.4 Hz, 1H), 7.28–7.34 (m, 1H), 7.37 (d, *J* = 4.4 Hz, 4H), 7.51 (d, *J* = 7.3 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 21.3 (CH), 22.0 (CH_3×2), 28.1 (CH_2), 28.3 (CH), 50.5 (CH_2), 77.9 (C), 81.8 (C), 123.9 (CH), 124.9 (CH), 127.4 (CH×2), 127.4 (CH×2), 128.8 (CH×2), 129.0 (CH), 131.42 (C), 136.5 (C), 137.6 (C), 137.9 (C). HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{21}H_{22}N_2Na$, 325.1681; found, 325.1675.

2-(5-Methylhex-2-yn-1-yl)-*N*-(isopropylcarbonimidoyl)benzenamine (1n).



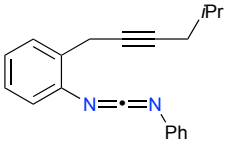
Yellow oil. IR (neat/cm^{-1}): 2969, 2129, 910, 733. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 0.99 (d, *J* = 6.6 Hz, 6H), 1.33 (d, *J* = 6.5 Hz, 6H), 1.82 (q, *J* = 6.6 Hz, 1H), 2.12 (d, *J* = 6.5 Hz, 2H), 3.61 (s, 2H), 3.79 (qt, *J* = 6.5, 6.3 Hz, 1H), 7.10 (dd, *J* = 7.6, 7.3 Hz, 1H), 7.14 (s, 1H), 7.18 (dd, *J* = 7.5, 7.1 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 21.3 (CH), 22.0 (CH_3×2), 24.8 (CH_3×2), 28.1 (CH_2), 28.3 (CH), 50.1 (CH), 78.0 (C), 81.7 (C), 123.3 (CH), 124.7 (CH), 127.4 (CH), 129.0 (CH), 131.3 (C), 135.69 (C), 138.4 (C). HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{17}H_{22}N_2Na$, 277.1681; found, 277.1675.

2-(5-Methylhex-2-yn-1-yl)-*N*-(cyclohexylcarbonimidoyl)benzenamine (1o).



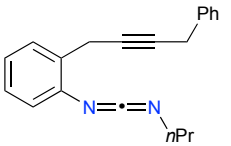
Yellow oil. IR (neat/cm^{-1}): 2931, 2260, 2129, 733. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 0.99 (d, *J* = 6.6 Hz, 6H), 1.20–1.30 (m, 1H), 1.30–1.38 (m, 2H), 1.42–1.51 (m, 2H), 1.52–1.59 (m, 1H), 1.76 (td, *J* = 9.2, 8.2 Hz, 2H), 1.81 (dq, *J* = 6.7, 6.5 Hz, 1H), 1.99 (td, *J* = 9.2, 8.2 Hz, 2H), 2.11 (d, *J* = 6.6 Hz, 2H), 3.46 (t, *J* = 9.5 Hz, 1H), 3.61 (s, 2H), 7.08 (dd, *J* = 7.9, 7.3 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.16 (dd, *J* = 7.7, 7.1 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 21.2 (CH_2×2), 22.0 (CH_3×2), 24.3 (CH_2), 25.3 (CH_2), 28.1 (CH_2×2), 28.2 (CH), 34.9 (CH_2), 56.5 (CH), 78.0 (C), 81.6 (C), 123.3 (CH), 124.5 (CH), 127.3 (CH), 128.9 (CH), 131.2 (C), 135.4 (C), 138.5 (C). HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{20}H_{26}N_2Na$, 317.1994; found, 317.1988.

2-(5-Methylhex-2-yn-1-yl)-*N*-(phenylcarbonimidoyl)benzenamine (1p).



Yellow oil. IR (neat/cm^{-1}): 3278, 2962, 2145, 1589, 1211, 756. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 0.99 (d, *J* = 6.7 Hz, 6H), 1.82 (qt, *J* = 6.7, 6.6 Hz, 1H), 2.11 (d, *J* = 6.6 Hz, 2H), 3.69 (s, 2H), 7.14–7.22 (m, 6H), 7.32 (dd, *J* = 7.4, 6.4 Hz, 1H), 7.33 (dd, *J* = 7.0, 6.4 Hz, 1H), 7.56 (d, *J* = 7.1 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 21.7 (CH_2), 22.1 (CH_3×2), 28.1 (CH_2), 28.2 (CH), 77.6 (C), 82.0 (C), 124.1 (CH×2), 124.6 (CH), 125.4 (CH), 125.7 (CH), 127.6 (CH), 129.3 (CH), 129.5 (CH×2), 131.9 (C), 134.3 (C), 136.1 (C), 138.6 (C). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{21}N_2$, 289.1705; found, 289.1699.

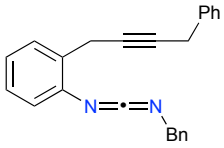
2-(4-Phenylbut-2-yn-1-yl)-*N*-(propylcarbonimidoyl)benzenamine (1q).



Colorless oil. IR (neat/cm^{-1}): 2962, 2137, 1705, 756. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 1.01 (t, *J* = 7.3 Hz, 3H), 1.72 (tq, *J* = 7.0, 7.1 Hz, 2H), 3.37 (t, *J* = 6.8 Hz, 2H), 3.67 (d, *J* = 2.4 Hz, 4H), 7.09 (dd, *J* = 7.3, 7.4 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.16–7.23 (m, 2H), 7.31 (dd, *J* = 7.5, 7.7 Hz, 2H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.53 (d, *J* = 7.7 Hz, 1H).

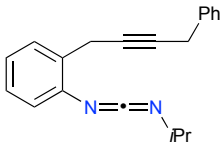
^{13}C-NMR (125 MHz, $CDCl_3$, δ): 11.4 (CH_3), 21.4 (CH_2), 24.7 (CH_2), 25.3 (CH_2), 48.6 (CH_2), 79.8 (C), 80.0 (C), 123.7 (CH), 124.6 (CH), 126.4 (CH), 127.5 (CH), 127.9 (CH×2), 128.4 (CH×2), 129.1 (CH), 131.0 (C), 132.0 (C), 137.3 (C), 138.5 (C). HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{20}H_{20}N_2Na$, 311.1524; found, 311.1519.

2-(4-Phenylbut-2-yn-1-yl)-*N*-(phenylmethylcarbonimidoyl)benzenamine (1r).



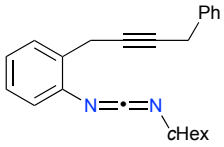
Yellow oil. IR (neat/cm^{-1}): 3031, 2144, 1496, 910, 702. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 3.61 (s, 2H), 3.64 (s, 2H), 4.51 (s, 2H), 6.98 (d, *J* = 7.6 Hz, 1H), 7.04–7.25 (m, 3H), 7.26–7.41 (m, 9H), 7.51 (d, *J* = 7.3 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 21.3 (CH_2), 25.2 (CH_2), 50.4 (CH_2), 79.6 (C), 80.0 (C), 123.9 (CH), 124.9 (CH), 126.4 (CH), 127.3 (CH×2), 127.5 (CH), 127.7 (CH), 127.8 (CH×2), 128.4 (CH×2), 128.7 (CH×2), 129.0 (CH), 131.0 (C), 136.3 (C), 137.2 (C), 137.6 (C), 137.8 (C). HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{24}H_{20}N_2Na$, 359.1524; found, 359.1519.

2-(4-Phenylbut-2-yn-1-yl)-*N*-(isopropylcarbonimidoyl)benzenamine (1s).



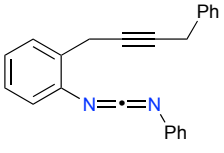
Yellow oil. IR (neat/cm^{-1}): 3016, 2129, 1218, 756. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.32 (d, *J* = 1.7 Hz, 3H), 1.32 (d, *J* = 1.7 Hz, 3H), 3.65 (s, 2H), 3.67 (s, 2H), 3.77 (q, *J* = 6.4 Hz, 1H), 7.03–7.25 (m, 4H), 7.29 (dd, *J* = 7.9, 6.9 Hz, 2H), 7.36 (d, *J* = 7.7 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 21.3 (CH_2), 24.8 (CH_3×2), 25.2 (CH_2), 50.0 (CH), 79.7 (C), 79.9 (C), 123.4 (CH), 124.7 (CH), 126.4 (CH), 127.5 (CH), 127.8 (CH×2), 128.4 (CH×2), 129.1 (CH), 130.9 (C), 135.6 (C), 137.3 (C), 138.5 (C). HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{20}H_{20}N_2Na$, 311.1524; found, 311.1514.

2-(4-Phenylbut-2-yn-1-yl)-*N*-(cyclohexylcarbonimidoyl)benzenamine (1t).



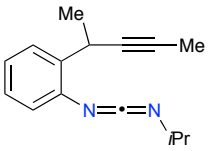
Yellow oil. IR (neat/cm^{-1}): 2931, 2129, 1496, 910, 733. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 1.19–1.29 (m, 1H), 1.33 (tt, *J* = 10.9, 10.5 Hz, 2H), 1.47 (tt, *J* = 11.4, 10.8 Hz, 2H), 1.52–1.59 (m, 1H), 1.65–1.82 (m, 2H), 1.99 (dt, *J* = 12.4, 9.0 Hz, 2H), 3.46 (t, *J* = 9.8 Hz, 1H), 3.65 (s, 2H), 3.68 (s, 2H), 7.08 (dd, *J* = 7.4, 7.2 Hz, 1H), 7.12–7.19 (m, 2H), 7.22 (dd, *J* = 7.7, 6.6 Hz, 1H), 7.31 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.37 (d, *J* = 7.3 Hz, 2H), 7.54 (dd, *J* = 6.6, 6.0 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 21.3 (CH_2), 24.3 (CH_2), 25.2 (CH_2×2), 25.3 (CH_2), 34.9 (CH_2×2), 56.5 (CH), 79.8 (C), 79.9 (C), 123.4 (CH), 124.5 (CH), 126.4 (CH), 127.5 (CH), 127.8 (CH×2), 128.4 (CH×2), 129.0 (CH), 130.9 (C), 135.4 (C), 137.3 (C), 138.6 (C). HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{23}H_{24}N_2Na$, 351.1837; found, 351.1832.

2-(4-Phenylbut-2-yn-1-yl)-*N*-(propylcarbonimidoyl)benzenamine (1u).



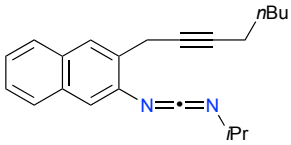
Yellow oil. IR (neat/cm^{-1}): 3062, 2144, 1489, 910, 733, 463. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 3.64 (s, 2H), 3.74 (s, 2H), 7.16 (dd, *J* = 9.4, 7.9 Hz, 4H), 7.22 (dd, *J* = 9.3, 4.2 Hz, 3H), 7.31 (dd, *J* = 7.8, 7.6 Hz, 4H), 7.37 (d, *J* = 7.4 Hz, 2H), 7.56 (d, *J* = 7.3 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 21.7 (CH_2), 25.2 (CH_2), 79.3 (C), 80.3 (C), 124.2 (CH×2), 124.7 (CH), 125.4 (CH), 125.7 (CH), 126.4 (CH), 127.7 (CH), 127.8 (CH×2), 128.4 (CH×2), 129.3 (CH), 129.4 (CH×2), 131.5 (C), 134.3 (C), 136.2 (C), 137.2 (C), 138.5 (C). HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{23}H_{18}N_2Na$, 345.1368; found, 345.1363.

2-(1-Methylbut-2-yn-1-yl)-*N*-(isopropylcarbonimidoyl)benzenamine (3).



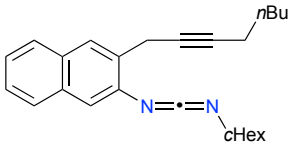
Yellow oil. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 1.34 (d, J = 6.4 Hz, 6H), 1.39 (d, J = 7.1 Hz, 3H), 1.85 (tt, J = 2.4 Hz, 3H), 3.79 (q, J = 6.4 Hz, 1H), 4.18 (q, J = 2.5 Hz, 1H), 7.08–7.19 (m, 3H), 7.57 (d, J = 7.3 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 3.6 (CH_3), 23.5 (CH_3), 24.9 (CH_3×2), 27.1 (CH), 50.1 (CH), 76.9 (C), 82.2 (C), 123.6 (CH), 124.9 (CH), 127.4 (CH), 127.8 (CH), 136.0 (C), 137.5 (C), 140.6 (C). HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_{18}N_2Na$, 249.1368; found, 249.1370.

3-(2-Octyn-1-yl)-*N*-(isopropylcarbonimidoyl)-2-naphthalenamine (7a).



Yellow oil. IR (neat/cm^{-1}): 2931, 2129, 1219, 764, 455. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 0.92 (t, J = 7.3 Hz, 3H), 1.35 (tq, J = 7.5, 7.3 Hz, 2H), 1.38 (d, J = 6.5 Hz, 6H), 1.44 (tt, J = 6.5, 7.2 Hz, 2H), 1.59 (tt, J = 7.2, 7.4 Hz, 2H), 2.29 (t, J = 7.1 Hz, 2H), 3.73 (s, 2H), 3.86 (q, J = 6.5 Hz, 1H), 7.39 (dd, J = 6.9, 7.6 Hz, 2H), 7.54 (s, 1H), 7.70 (d, J = 7.9 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.98 (s, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 14.0 (CH_3), 18.9 (CH_2), 21.8 (CH_2), 22.3 (CH_2), 24.9 (CH_3×2), 28.8 (CH_2), 31.2 (CH_2), 50.2 (CH), 77.0 (C), 83.6 (C), 120.3 (CH), 125.0 (CH), 125.9 (CH), 126.3 (CH), 127.5 (CH), 127.6 (CH), 130.98 (C), 131.11 (C), 133.0 (C) 135.2 (C), 137.3 (C). HRMS-ESI calcd for $[M+Na]^+$: $C_{22}H_{26}N_2Na$: 341.1994, found: 341.1995.

3-(2-Octyn-1-yl)-*N*-(cyclohexylcarbonimidoyl)-2-naphthalenamine (7b).



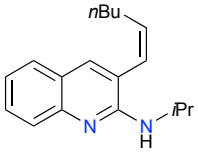
Yellow oil. IR (neat/cm^{-1}): 2931, 2129, 1219, 764, 486. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 0.92 (t, J = 7.4 Hz, 3H), 1.25–1.47 (m, 7H), 1.49–1.63 (m, 5H), 1.74–1.83 (m, 2H), 1.99–2.09 (m, 2H), 2.28 (t, J = 7.2 Hz, 2H), 3.54 (t, J = 9.6 Hz, 1H), 3.73 (s, 2H), 7.39 (dd, J = 6.6, 8.7 Hz, 2H), 7.54 (s, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.98 (s, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 14.0 (CH_3), 18.9 (CH_2×2), 21.8 (CH_2), 22.3 (CH_2), 24.4 (CH_2), 25.3 (CH_2), 28.8 (CH_2×2), 31.2 (CH_2), 35.0 (CH_2), 56.7 (CH), 77.1 (C), 83.6 (C), 120.3 (CH), 125.9 (CH), 125.8 (CH), 126.3 (CH), 127.5 (CH), 127.6 (CH), 131.0 (C), 131.1 (C), 133.0 (C), 135.0 (C), 135.5 (C). HRMS-ESI calcd for $[M+Na]^+$: $C_{25}H_{30}N_2Na$: 381.2307, found: 381.2303.

3. Synthesis and characterization data of *cis*-alkenylquinolines *cis*-2, 4 and *cis*-8

$Rh(dppp)_2Cl$, $Rh(dppe)_2Cl$, and $Rh(dppb)_2Cl$ were prepared according to the literature method.[S2]

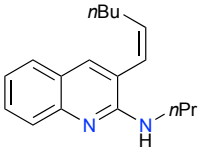
Typical procedure for the catalytic cycloisomerization using $Rh(dppp)_2Cl$

(*Z*)-3-(Hex-1-en-1-yl)-*N*-isopropylquinolin-2-amine (*cis*-2a) (Table 1, Entry 5). A pale yellow suspension of $Rh(dppp)_2Cl$ (59.3 mg, 0.062 mmol, 12 mol%) in *p*-xylene (5 mL) was heated at 130 °C, to which *p*-xylene (1 mL) solution of carbodiimide-yne **1a** (137.6 mg, 0.51 mmol) was added. The mixture was stirred for 1 h at 130 °C, cooled to room temperature, and condensed under reduced pressure. The residue was purified by a silica gel column



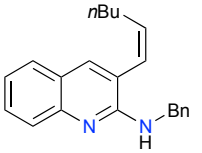
chromatography using ethyl acetate/*n*-hexane (1/40, v/v) as an eluent to afford *cis*-**2a** (88.1 mg, 64%) as a yellow oil. IR (neat/cm^{-1}): 1219, 756, 463. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 0.84 (t, *J* = 7.2 Hz, 3H), 1.28 (d, *J* = 6.2 Hz, 6H), 1.31–1.42 (m, 4H), 2.13 (dd, *J* = 7.5, 7.3 Hz, 2H), 4.42–4.58 (m, 2H), 5.93 (dt, *J* = 11.2, 7.4 Hz, 1H), 6.21 (d, *J* = 11.2 Hz, 1H), 7.17 (dd, *J* = 7.9, 6.9 Hz, 1H), 7.43–7.57 (m, 3H), 7.69 (d, *J* = 8.3 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 14.0 (CH_3), 22.3 (CH_2), 23.1 (CH×2), 28.4 (CH_2), 31.7 (CH_2), 42.3 (CH), 121.0 (C), 121.7 (CH), 123.1 (C), 123.4 (CH), 126.1 (CH), 127.2 (CH), 128.9 (CH), 135.3 (CH), 137.7 (CH), 147.6 (C), 154.3 (C). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{18}H_{25}N_2$, 269.2018; found, 269.2010.

(*Z*)-3-(Hex-1-en-1-yl)-*N*-propylquinolin-2-amine (*cis*-2b).



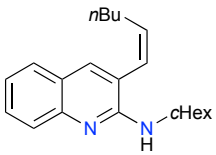
Yellow oil. IR (neat/cm^{-1}): 2923, 1519, 756, 416. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 0.85 (t, *J* = 7.3 Hz, 3H), 1.02 (t, *J* = 7.5 Hz, 3H), 1.29 (tq, *J* = 7.5, 7.3 Hz, 2H), 1.38 (tt, *J* = 8.0, 7.0 Hz, 2H), 1.69 (tq, *J* = 7.5, 7.3 Hz, 2H), 2.14 (ddt, *J* = 7.5, 6.0, 1.6 Hz, 2H), 3.58 (dt, *J* = 6.1, 6.0 Hz, 2H), 4.63–4.82 (br s, 1H), 5.96 (dt, *J* = 11.3, 7.4 Hz, 1H), 6.23 (dd, *J* = 11.2, 1.1 Hz, 1H), 7.19 (ddd, *J* = 7.7, 7.7, 1.2 Hz, 1H), 7.49 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.54 (s, 1H), 7.55 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.74 (br d, *J* = 7.8 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 11.6 (CH_3), 13.9 (CH_3), 22.3 (CH_2), 22.9 (CH_2), 28.3 (CH_2), 31.7 (CH_2), 43.3 (CH_2), 121.0 (C), 121.9 (CH), 123.1 (C), 123.1 (CH), 125.9 (CH), 127.2 (CH), 129.0 (CH), 135.5 (CH), 138.0 (CH), 147.5 (C), 154.9 (C). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{18}H_{25}N_2$, 269.2018; found, 269.2012.

(*Z*)-*N*-Benzyl-3-(hex-1-en-1-yl)quinolin-2-amine (*cis*-2c).



Yellow oil. IR (neat/cm^{-1}): 1219, 756, 424. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 0.84 (t, *J* = 7.2 Hz, 3H), 1.20–1.38 (m, 4H), 2.14 (dt, *J* = 7.3, 6.0 Hz, 2H), 4.82 (d, *J* = 5.3 Hz, 2H), 4.96 (br s, 1H), 5.91 (dt, *J* = 11.2, 7.4 Hz, 1H), 6.23 (dd, *J* = 11.2, 1.3 Hz, 1H), 7.17–7.37 (m, 4H), 7.41 (dd, *J* = 6.5, 1.7 Hz, 2H), 7.51 (ddd, *J* = 6.9, 5.4, 1.6 Hz, 1H), 7.58 (dd, *J* = 5.1, 1.3 Hz, 2H), 7.73 (dd, *J* = 7.3, 6.7 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 13.9 (CH_3), 22.3 (CH_2), 28.3 (CH_2), 31.6 (CH_2), 45.6 (CH_2), 120.9 (C), 122.0 (CH), 123.0 (CH), 123.4 (C), 126.2 (CH), 127.15 (CH), 127.18 (CH), 128.0 (CH×2), 128.5 (CH×2), 128.9 (CH), 135.5 (CH), 138.0 (CH), 139.8 (C), 147.3 (C), 154.6 (C). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{22}H_{25}N_2$, 317.2018; found, 317.2012.

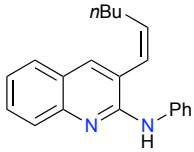
(*Z*)-*N*-Cyclohexyl-3-(hex-1-en-1-yl)quinolin-2-amine (*cis*-2d).



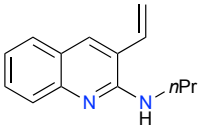
Yellow oil. IR (neat/cm^{-1}): 1219, 764, 432. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 0.85 (t, *J* = 7.3 Hz, 3H), 1.12–1.57 (m, 12H), 2.06–2.19 (m, 4H), 4.12–4.27 (m, 1H), 4.60 (br s, 1H), 5.93 (dt, *J* = 11.3, 7.4 Hz, 1H), 6.21 (dd, *J* = 11.2, 1.2 Hz, 1H), 7.16 (ddd, *J* = 7.1, 6.8, 1.1 Hz, 1H), 7.43–7.56 (m, 3H), 7.68 (dd, *J* = 8.4, 0.6 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 13.9 (CH_3), 22.3 (CH_2), 25.0 (CH_2), 26.0 (CH_2), 28.3 (CH_2), 31.0 (CH_2), 33.4 (CH_2), 49.0 (CH_2), 53.4 (CH), 121.0 (C), 121.6 (CH), 121.7 (CH), 123.0 (C), 123.4 (CH), 126.0 (CH), 127.1 (CH), 128.7 (CH), 135.3 (CH), 137.7 (CH), 147.5 (C), 154.2 (C). HRMS-ESI (*m/z*) : $[M+H]^+$ calcd for $C_{21}H_{29}N_2$, 309.2331; found, 309.2324.

(*Z*)-3-(Hex-1-en-1-yl)-*N*-phenylquinolin-2-amine (*cis*-2f).

Yellow oil. IR (neat/cm^{-1}): 1219, 756, 417. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 0.83 (t, J = 7.2 Hz, 3H), 1.28 (qt, J = 7.2, 5.9 Hz, 2H), 1.40 (tt, J = 7.1, 5.9 Hz, 2H), 2.16 (dt, J = 7.3, 5.9 Hz, 2H), 6.07 (dt, J = 11.2, 7.4 Hz, 1H), 6.39 (dd, J = 11.2, 1.2 Hz, 1H), 6.79 (br s, 1H), 7.03 (ddd, J = 7.3, 7.3, 1.1 Hz, 1H), 7.28 (ddd, J = 7.1, 7.1, 1.1 Hz, 1H), 7.36 (ddd, J = 7.6, 7.6, 1.8 Hz, *m*-Ph, 2H), 7.56 (ddd, J = 7.3, 7.3, 1.4 Hz, 1H), 7.61 (dd, J = 8.1, 1.3 Hz, 1H), 7.68 (s, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.88 (dd, J = 8.4, 1.1 Hz, *o*-Ph, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 13.9 (CH_3), 22.3 (CH_2), 28.4 (CH_2), 31.5 (CH_2), 119.1 (CH×2), 121.5 (C), 122.0 (CH), 122.9 (CH), 123.1 (CH), 123.8 (C), 126.9 (CH), 127.1 (CH), 128.8 (CH×2), 129.1 (CH), 136.1 (CH), 139.0 (CH), 140.4 (C), 146.6 (C), 151.6 (C). HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{21}H_{22}N_2Na$, 325.1681; found, 325.1681.

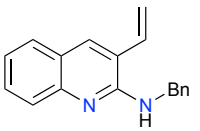


_N_-Propyl-3-vinylquinolin-2-amine (2g).



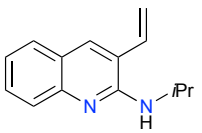
Yellow oil. IR (neat/cm^{-1}): 3456, 2962, 1519, 1219, 764. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.06 (t, J = 7.4 Hz, 3H), 1.74 (tq, J = 7.4, 7.3 Hz, 2H), 3.60 (td, J = 7.3, 7.0 Hz, 2H), 4.65–4.78 (br s, 1H), 5.51 (dd, J = 10.9, 1.4 Hz, 1H), 5.78 (dd, J = 17.4, 1.4 Hz, 1H), 6.74 (dd, J = 17.4, 10.9 Hz, 1H), 7.22 (dd, J = 7.9, 6.9 Hz, 1H), 7.52 (dd, J = 8.4, 6.9 Hz, 1H), 7.60 (d, J = 7.9 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.78 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 11.7 (CH_3), 22.9 (CH_2), 43.4 (CH_2), 119.3 (CH_2), 122.1 (CH), 122.5 (C), 123.4 (C), 126.1 (CH), 127.4 (CH), 129.2 (CH), 132.0 (CH), 133.8 (CH), 147.8 (C), 154.5 (C). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{14}H_{17}N_2$, 213.1392; found, 213.1386.

_N_-Benzyl-3-vinylquinolin-2-amine (2h).



Yellow oil. IR (neat/cm^{-1}): 3055, 2962, 2145, 741. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 4.86 (d, J = 5.3 Hz, 2H), 4.93–5.02 (br s, 1H), 5.48 (dd, J = 10.9, 1.3 Hz, 1H), 5.79 (dd, J = 17.3, 1.3 Hz, 1H), 6.74 (dd, J = 17.3, 11.1 Hz, 1H), 7.25 (dd, J = 8.0, 7.0 Hz, 1H), 7.32 (dd, J = 7.4, 7.3 Hz, 1H), 7.38 (dd, J = 7.8, 7.3 Hz, 2H), 7.46 (d, J = 7.6 Hz, 2H), 7.54 (dd, J = 8.4, 7.1 Hz, 1H), 7.63 (d, J = 7.9 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.83 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 45.8 (CH_2), 119.5 (CH_2), 121.0 (C), 122.4 (CH), 123.7 (C), 126.3 (CH), 127.3 (CH), 127.4 (CH), 128.2 (CH×2), 128.6 (CH×2), 129.3 (CH), 131.7 (CH), 134.0 (CH), 139.7 (C), 147.6 (C), 154.1 (C). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{18}H_{17}N_2$, 261.1392; found, 261.1386.

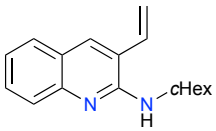
_N_-Isopropyl-3-vinylquinolin-2-amine (2i).



Yellow oil. IR (neat/cm^{-1}): 3440, 2969, 1612, 1519, 756. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.29 (d, J = 6.2 Hz, 6H), 4.42–4.61 (m, 2H), 5.45 (dd, J = 10.9, 1.5 Hz, 1H), 5.73 (dd, J = 17.2, 1.5 Hz, 1H), 6.68 (dd, J = 17.2, 10.9 Hz, 1H), 7.17 (dd, J = 7.9, 7.0 Hz, 1H), 7.48 (dd, J = 8.4, 6.9 Hz, 1H), 7.55 (d, J = 7.9 Hz, 1H), 7.68 (d, J = 8.3 Hz, 1H), 7.73 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 23.0 (CH_3×2). 42.4 (CH), 119.1 (CH_2), 121.9 (CH), 122.4 (C), 123.3 (C), 126.1 (CH), 127.3 (CH), 129.1 (CH), 131.9 (CH), 133.6 (CH), 147.8 (C), 153.7 (C). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{14}H_{17}N_2$, 213.1392; found, 213.1388.

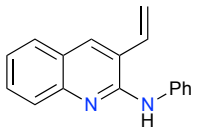
_N_-Cyclohexyl-3-vinylquinolin-2-amine (2j).

Yellow oil. IR (neat/cm^{-1}): 1219, 756, 432. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.15–1.35 (m, 4H), 1.49 (tt, J = 8.2, 3.5 Hz, 2H), 1.62–1.82 (m, 4H), 4.22 (td, J = 7.9, 3.9 Hz, 1H), 4.55 (br s, 1H), 5.47 (dd, J = 10.9, 1.4



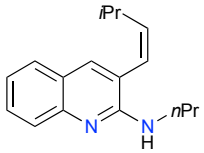
Hz, 1H), 5.74 (dd, *J* = 17.2, 1.5 Hz, 1H), 6.69 (dd, *J* = 17.2, 10.9 Hz, 1H), 7.16 (dd, *J* = 8.0, 6.8 Hz, 1H), 7.43–7.60 (m, 2H), 7.67 (dd, *J* = 8.5, 7.9 Hz, 1H), 7.74 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 25.0 (CH_2×2), 26.0 (CH_2), 33.4 (CH_2×2), 49.2 (CH), 119.1 (CH_2), 121.9 (CH), 122.4 (C), 123.3 (C), 126.1 (CH), 127.3 (CH), 129.1 (CH), 132.1 (CH), 133.8 (CH), 147.9 (C), 153.7 (C). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{17}H_{21}N_2$, 253.1705; found, 253.1696.

***N*-Phenyl-3-vinylquinolin-2-amine (2k).**



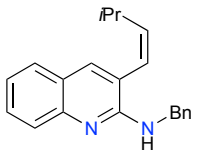
Yellow oil. IR (neat/cm^{-1}): 3440, 3016, 1527, 1219, 756. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 5.63 (dd, *J* = 10.9, 0.9 Hz, 1H), 5.86 (dd, *J* = 17.4, 0.9 Hz, 1H), 6.73 (br s, 1H), 6.89 (dd, *J* = 17.2, 10.9 Hz, 1H), 7.08 (dd, *J* = 7.5, 7.3 Hz, 1H), 7.32 (dd, *J* = 7.8, 7.0 Hz, 1H), 7.39 (dd, *J* = 8.1, 7.6 Hz, 2H), 7.59 (dd, *J* = 8.3, 6.9 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.83–7.87 (m, 3H), 7.92 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 119.4 (CH×2), 120.6 (CH_2), 122.3 (CH), 123.3 (C), 123.4 (CH), 124.3 (C), 127.0 (CH), 127.3 (CH), 128.9 (CH×2), 129.5 (CH), 131.8 (CH), 134.9 (CH), 140.4 (C), 146.9 (C), 151.1 (C). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{17}H_{15}N_2$, 247.1235; found, 247.1230.

(*Z*)-3-(3-Methylbut-1-en-1-yl)-*N*-propylquinolin-2-amine (*cis*-2l).



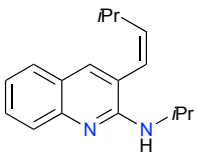
Yellow oil. IR (neat/cm^{-1}): 3440, 2962, 1519, 1219, 764. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 0.99 (d, *J* = 6.6 Hz, 6H), 1.01 (t, *J* = 7.4 Hz, 3H) 1.69 (qt, *J* = 7.3, 7.2 Hz, 2H), 2.59 (dq, *J* = 10.3, 6.6 Hz, 1H), 3.56 (td, *J* = 7.0, 5.6 Hz, 2H), 4.71 (br s, 1H), 5.76 (dd, *J* = 11.1, 10.4 Hz, 1H), 6.11 (d, *J* = 11.3 Hz, 1H), 7.18 (dd, *J* = 7.9, 6.9 Hz, 1H), 7.49 (dd, *J* = 8.4, 6.9 Hz, 1H), 7.52 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 11.6 (CH_3), 22.8 (CH_2), 23.0 (CH_3×2), 27.6 (CH), 43.1 (CH_2), 120.9 (CH), 121.2 (C), 121.7 (CH), 123.1 (C), 126.0 (CH), 127.2 (CH), 128.8 (CH), 135.0 (CH), 145.0 (CH), 147.4 (C), 155.0 (C). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{17}H_{23}N_2$, 255.1861; found, 255.1856.

(*Z*)-*N*-Benzyl-3-(3-methylbut-1-en-1-yl)quinolin-2-amine (*cis*-2m).



Yellow oil. IR (neat/cm^{-1}): 3440, 2962, 1265, 910, 741. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 0.96 (d, *J* = 6.7 Hz, 6H), 2.59 (dq, *J* = 10.9, 6.7 Hz, 1H), 4.82 (d, *J* = 5.4 Hz, 2H), 4.95 (br s, 1H), 5.71 (dd, *J* = 10.8, 10.6 Hz, 1H), 6.10 (d, *J* = 11.2 Hz, 1H), 7.20 (dd, *J* = 7.9, 7.0 Hz, 1H), 7.27 (d, *J* = 6.9 Hz, 1H), 7.32 (dd, *J* = 7.5, 6.9 Hz, 2H), 7.39 (d, *J* = 7.3 Hz, 2H), 7.50 (dd, *J* = 7.4, 7.0 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.59 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 22.9 (CH_3×2), 27.6 (CH), 45.5 (CH_2), 120.7 (CH), 121.1 (C), 122.0 (CH), 123.3 (C), 126.1 (CH), 127.2 (CH), 127.2 (CH), 128.0 (CH×2), 128.5 (CH×2), 128.9 (CH), 135.3 (CH), 139.7 (C), 145.1 (CH), 147.3 (C), 154.6 (C). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{21}H_{23}N_2$, 303.1861; found, 303.1856.

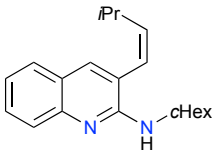
(*Z*)-*N*-Isopropyl-3-(3-methylbut-1-en-1-yl)quinolin-2-amine (*cis*-2n).



Yellow oil. IR (neat/cm^{-1}): 3425, 2962, 1612, 1512, 748. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 0.99 (d, *J* = 6.6 Hz, 6H), 1.28 (d, *J* = 6.2 Hz, 6H), 2.57 (dq, *J* = 10.3, 6.6 Hz, 1H), 4.51 (dq, *J* = 7.7, 6.1 Hz, 1H), 4.53–4.63 (br s, 1H), 5.76 (dd, *J* = 11.1, 10.3 Hz, 1H), 6.09 (d, *J* = 11.2 Hz, 1H), 7.17 (dd, *J* = 8.0, 6.9 Hz, 1H), 7.48 (dd, *J* = 7.1, 6.9 Hz, 1H), 7.51 (s, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 22.9 (CH_3×2), 23.1

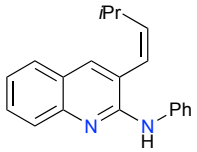
(CH_3×2), 27.7 (CH), 42.2 (CH), 121.0 (CH), 121.2 (C), 121.7 (CH), 123.0 (C), 126.1 (CH), 127.1 (CH), 128.8 (CH), 135.0 (CH), 144.9 (CH), 147.5 (C), 154.2 (C). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{17}H_{23}N_2$, 255.1861; found, 255.1856.

(*Z*)-*N*-Cyclohexyl-3-(3-methylbut-1-en-1-yl)quinolin-2-amine (*cis*-2o).



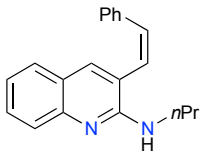
Yellow oil. IR (neat/cm^{-1}): 3425, 2931, 1612, 1512, 748. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 0.99 (d, *J* = 6.6 Hz, 6H), 1.10–1.33 (m, 3H), 1.38–1.59 (m, 2H), 1.60–1.80 (m, 3H), 2.05–2.21 (m, 2H), 2.57 (dq, *J* = 10.2, 6.6 Hz, 1H), 4.19 (dt, *J* = 6.6, 3.8 Hz, 1H), 4.57–4.71 (br s, 1H), 5.75 (dd, *J* = 10.9, 10.4 Hz, 1H), 6.09 (d, *J* = 11.2 Hz, 1H), 7.16 (dd, *J* = 7.9, 7.0 Hz, 1H), 7.48 (dd, *J* = 8.1, 7.0 Hz, 1H), 7.51 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 22.9 (CH_3×2), 25.0 (CH_2×2), 26.0 (CH_2), 27.7 (CH_2), 33.4 (CH_2×2), 49.0 (CH), 121.1 (CH), 121.3 (C), 121.6 (CH), 123.0 (C), 126.0 (CH), 127.1 (CH), 128.7 (CH), 135.0 (CH), 144.9 (CH), 147.5 (C), 154.1 (C). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{27}N_2$, 295.2174; found, 295.2169.

(*Z*)-3-(3-Methylbut-1-en-1-yl)-*N*-phenylquinolin-2-amine (*cis*-2p).



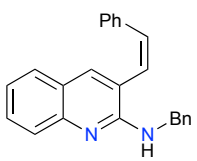
Yellow oil. IR (neat/cm^{-1}): 3409, 2962, 1527, 756. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 1.00 (d, *J* = 6.6 Hz, 6H), 2.58 (dq, *J* = 10.3, 6.1 Hz, 1H), 5.89 (dd, *J* = 10.8, 10.6 Hz, 1H), 6.26 (d, *J* = 11.1 Hz, 1H), 6.83 (br s, 1H), 7.03 (dd, *J* = 7.4, 6.8 Hz, 1H), 7.27 (dd, *J* = 7.6, 7.4 Hz, 1H), 7.35 (dd, *J* = 8.5, 7.3 Hz, 2H), 7.55 (dd, *J* = 8.2, 7.1 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.67 (s, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 22.8 (CH_3×2), 27.8 (CH), 119.0 (CH×2), 120.6 (CH), 121.8 (C), 122.0 (CH), 123.1 (CH), 123.8 (C), 126.9 (CH), 127.1 (CH), 128.9 (CH×2), 129.1 (CH), 135.8 (CH), 140.4 (C), 146.1 (CH), 146.6 (C), 151.6 (C). HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{20}H_{20}N_2Na$, 311.1524; found, 311.1519.

(*Z*)-*N*-Propyl-3-styrylquinolin-2-amine (*cis*-2q).



Yellow oil. IR (neat/cm^{-1}): 3440, 3016, 1612, 1519. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 0.87 (t, *J* = 7.3 Hz, 3H), 1.50 (tq, *J* = 7.3, 7.4 Hz, 2H), 3.47 (dt, *J* = 5.9, 6.8 Hz, 2H), 4.80 (br s, 1H), 6.49 (d, *J* = 12.2 Hz, 1H), 6.80 (d, *J* = 12.1 Hz, 1H), 7.12–7.24 (m, 6H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.49 (ddd, *J* = 7.1, 6.5, 6.4 Hz, 1H), 7.64 (s, 1H), 7.71 (d, *J* = 8.3 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 11.5 (CH_3), 22.7 (CH_2), 43.1 (CH_2), 121.3 (C), 121.8 (CH), 123.1 (C), 124.4 (CH), 126.0 (CH), 127.3 (CH), 128.0 (CH), 128.4 (CH×2), 128.7 (CH×2), 129.1 (CH), 134.2 (CH), 135.5 (CH), 135.8 (C), 147.6 (C), 154.1 (C). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{21}N_2$, 289.1705; found, 289.1704.

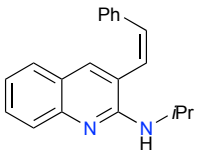
(*Z*)-*N*-Benzyl-3-styrylquinolin-2-amine (*cis*-2r).



Yellow oil. IR (neat/cm^{-1}): 1219, 756, 417. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 4.72 (d, *J* = 5.3 Hz , 2H), 5.06 (br s, 1H), 6.50 (d, *J* = 12.2 Hz, 1H), 6.77 (d, *J* = 12.1 Hz, 1H), 7.14–7.20 (m, 8H), 7.22–7.28 (m, 3H), 7.48–7.55 (m, 2H), 7.70 (s, 1H), 7.74 (d, *J* = 8.3 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 45.6 (CH_2), 121.2 (C), 122.1 (CH), 123.3 (C), 124.1 (CH), 126.1 (CH), 127.0 (CH), 127.3 (CH), 127.9 (CH×2), 128.0 (CH), 128.4 (CH×4), 128.7 (CH×2), 129.2 (CH),

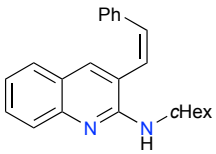
134.4 (CH), 135.8 (CH), 135.8 (C), 139.5 (C), 147.4 (C), 153.7 (C). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{21}N_2$, 345.1368; found, 345.1363.

(*Z*)-*N*-Isopropyl-3-styrylquinolin-2-amine (*cis*-2s).



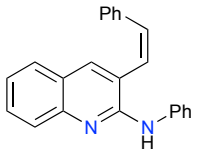
Yellow oil. IR (neat/cm^{-1}): 1219, 756, 440. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 1.07 (d, *J* = 6.5 Hz, 3H), 1.08 (d, *J* = 6.6 Hz, 3H), 4.39 (q, *J* = 6.5 Hz, 1H), 4.62 (br s, 1H), 6.48 (d, *J* = 12.1 Hz, 1H), 6.78 (d, *J* = 12.1 Hz, 1H), 7.11–7.21 (m, 6H), 7.53 (dd, *J* = 7.8, 6.8 Hz, 1H), 7.57 (dd, *J* = 7.7, 6.9 Hz, 1H), 7.63 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 22.7 (CH_3×2), 42.1 (CH), 121.2 (C), 121.6 (CH), 122.9 (C), 124.7 (CH), 126.1 (CH), 127.2 (CH), 127.9 (CH), 128.4 (CH×2), 128.6 (CH×2), 129.0 (CH), 134.0 (CH), 135.5 (CH), 136.0 (C), 147.7 (C), 153.1 (C). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{21}N_2$, 289.1705; found, 289.1700.

(*Z*)-*N*-Cyclohexyl-3-styrylquinolin-2-amine (*cis*-2t).



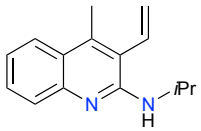
Yellow oil. IR (neat/cm^{-1}): 1219, 756, 455. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 0.88–1.04 (m, 2H), 1.06–1.21 (m, 1H), 1.30–1.48 (m, 2H), 1.52–1.69 (m, 3H), 1.86–1.99 (m, 2H), 4.12 (td, *J* = 3.7, 7.7 Hz , 1H), 4.71 (br s, 1H), 6.47 (d, *J* = 12.1 Hz, 1H), 6.77 (d, *J* = 12.1 Hz, 1H), 7.09–7.22 (m, 6H), 7.40–7.51 (m, 2H), 7.61 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 24.8 (CH_2×2), 25.8 (CH_2), 33.0 (CH_2×2), 48.8 (CH), 121.3 (C), 121.6 (CH), 122.9 (C), 124.6 (CH), 126.0 (CH), 127.2 (CH), 127.9 (CH), 128.4 (CH×2), 128.6 (CH×2), 129.0 (CH), 134.0 (CH), 135.5 (CH), 135.9 (C), 147.6 (C), 153.1 (C). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{23}H_{25}N_2$, 329.2018; found, 329.2021.

(*Z*)-*N*-Phenyl-3-styrylquinolin-2-amine (*cis*-2u).



Brown solid. IR (neat/cm^{-1}): 1589, 748, 548. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 6.64 (d, *J* = 12.2 Hz, 1H), 6.87 (br s, 1H), 6.94 (d, *J* = 12.4 Hz, 1H), 6.99 (dd, *J* = 7.3, 7.1 Hz, 1H), 7.15–7.19 (m, 3H), 7.23–7.32 (m, 5H), 7.54–7.60 (m, 2H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.80 (s, 1H), 7.84 (d, *J* = 8.5 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 119.3 (CH×2), 121.9 (C), 122.2 (CH), 123.2 (CH), 123.8 (C), 124.0 (CH), 126.9 (CH), 127.2 (CH), 128.3 (CH), 128.6 (CH×2), 128.7 (CH×2), 128.8 (CH×2), 129.4 (CH), 135.1 (CH), 135.4 (C), 136.4 (CH), 140.2 (C), 146.8 (C), 150.8 (C). HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{23}H_{18}N_2Na$, 345.1368; found, 345.1363.

***N*-Isopropyl-4-methyl-3-vinylquinolin-2-amine (4).**

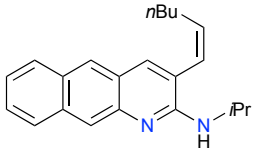


Yellow oil. IR (neat/cm^{-1}): 3433, 2969, 1512, 756. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.26 (d, *J* = 6.5 Hz, 6H), 2.50 (s, 3H), 4.46 (dq, *J* = 7.0, 6.5 Hz, 1H), 4.62–4.81 (br s, 1H), 5.47 (dd, *J* = 17.9, 2.0 Hz, 1H), 5.74 (dd, *J* = 11.3, 2.0 Hz, 1H), 6.61 (dd, *J* = 17.9, 11.3 Hz, 1H), 7.19 (dd, *J* = 8.1, 6.9 Hz, 1H), 7.48 (dd, *J* = 8.3, 7.0 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 15.1 (CH), 23.1 (CH_3×2), 42.2 (CH) 121.2 (C), 121.5 (CH), 122.9 (CH_2), 123.2 (C), 123.8 (CH), 126.7 (CH), 128.6 (CH), 132.5 (CH), 139.9 (C), 147.0 (C), 153.5 (C). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{15}H_{19}N_2$, 227.1548; found, 227.1546.

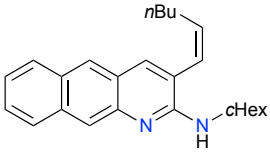
(*Z*)-3-(Hex-1-en-1-yl)-*N*-isopropylbenzo[*g*]quinolin-2-amine (*cis*-8a).

Yellow oil. IR (neat/cm^{-1}): 3425, 2962, 1504, 756, 455. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 0.84 (t, *J* = 7.3 Hz,

3H), 1.27 (tq, *J* = 7.2, 6.9 Hz, 2H), 1.30 (d, *J* = 6.3 Hz, 6H), 1.38 (tt, *J* = 7.4, 6.9 Hz, 2H), 2.16 (dt, *J* = 7.5, 7.1 Hz, 2H), 4.57 (q, *J* = 6.5 Hz, 1H), 4.67–4.75 (br s, 1H), 5.95 (dt, *J* = 11.3, 7.5 Hz, 1H), 6.23 (d, *J* = 11.2 Hz, 1H), 7.31 (dd, *J* = 8.0, 6.9 Hz, 1H), 7.39 (dd, *J* = 8.1, 6.9 Hz, 1H), 7.64 (s, 1H), 7.86 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 8.05 (s, 1H), 8.16 (s, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 13.9 (CH_3), 22.3 (CH_2), 23.0 (CH_3×2), 28.3 (CH_2), 31.6 (CH_2), 42.2 (CH), 121.7 (CH), 122.8 (C), 123.2 (CH), 123.5 (C), 123.6 (CH), 125.5 (CH), 125.9 (CH), 127.5 (CH), 127.9 (CH), 129.2 (C), 134.3 (C), 135.1 (CH), 138.1 (CH), 144.6 (C), 154.0 (C). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{22}H_{27}N_2$, 319.2174; found, 319.2169.



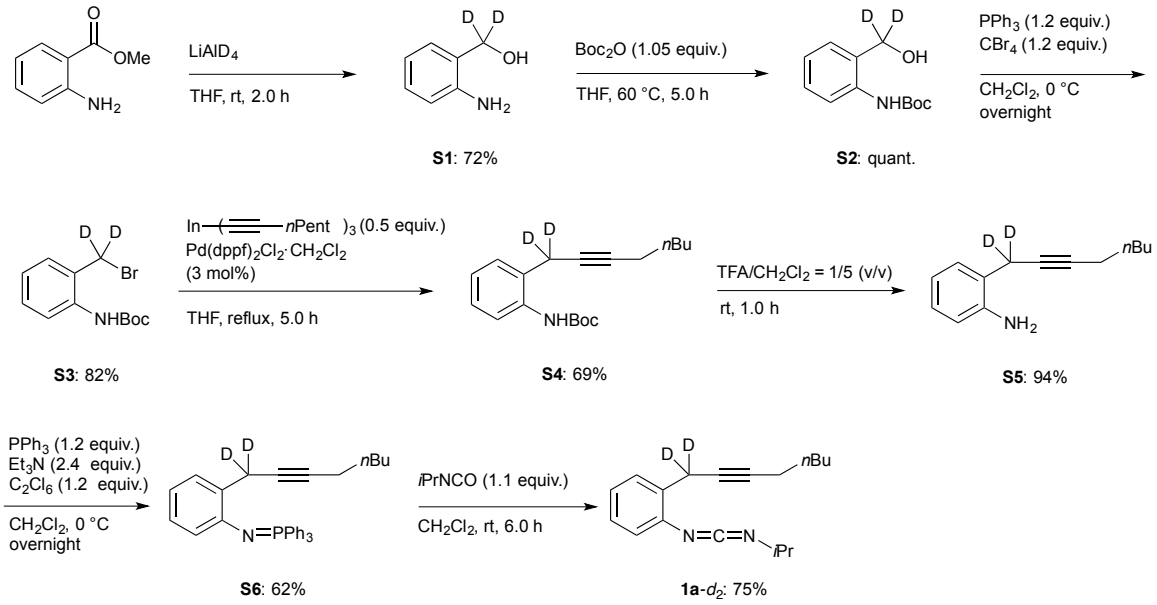
(*Z*)-*N*-Cyclohexyl-3-(hex-1-en-1-yl)benzo[*g*]quinolin-2-amine (*cis*-8b).



Yellow oil. IR (neat/cm^{-1}): 3425, 2931, 1504, 764. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 0.85 (t, *J* = 7.3 Hz, 3H), 1.18–1.32 (m, 5H), 1.34–1.41 (m, 2H), 1.45–1.56 (m, 2H), 1.63–1.70 (m, 1H), 1.72–1.81 (m, 2H), 2.16 (tt, *J* = 7.6, 7.3 Hz, 4H), 4.16–4.32 (m, 1H), 4.79 (br s, 1H), 5.96 (dt, *J* = 11.3, 7.1 Hz, 1H), 6.24 (d, *J* = 11.2 Hz, 1H), 7.31 (dd, *J* = 8.1, 7.0 Hz, 1H), 7.38 (dd, *J* = 8.2, 6.9 Hz, 1H), 7.64 (s, 1H), 7.86 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 8.06 (s, 1H), 8.15 (s, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 13.9 (CH_3), 22.3 (CH_2), 25.0 (CH_2×2), 26.0 (CH_2), 28.4 (CH_2), 31.6 (CH_2), 33.4 (CH_2×2), 49.0 (CH), 121.6 (CH), 122.9 (C), 123.2 (CH), 123.6 (CH), 125.5 (CH), 125.9 (CH), 127.5 (CH), 127.9 (CH), 129.2 (C), 134.3 (C), 135.2 (CH), 137.4 (C), 138.2 (CH), 144.6 (C), 154.0 (C). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{31}N_2$, 359.2487; found, 359.2482.

4. Synthesis and characterization data of 1a-d_2 and cis-2a-d_2

Carbodiimide-yne **1a-d_2** was prepared according to the following route (Scheme S1).



Scheme S1

***tert*-Butyl (2-(hydroxymethyl-d_2)phenyl)carbamate (S2).**

To a stirred THF (100 mL) solution of $LiAlD_4$ (1.00 g, 23.9 mmol) at 0 °C was added slowly THF (20 mL) solution of methyl anthanilate (3.00 mL, 22.7 mmol). After being stirred for 2 h at room temperature, the resulting mixture was quenched by addition of Na_2SO_4•$10H_2O$ (5 g), filtered through a pad of Celite, and the filtrate was evaporated. The residue was purified by a silica gel column chromatography using ethyl acetate/*n*-hexane (1/2, v/v) as an eluent to afford crude 2-aminobenzenemethan-d_2-ol (**S1**), (2.05 g, 16.4 mmol, 72%, if pure).

A mixture of 2-amino-benzenemethan-d_2-ol (**S1**) (2.02 g, 16.1 mmol, if pure), and di-*tert*-butyl dicarbonate (3.90 mL, 16.9 mmol), and THF (50 mL) was heated at 60 °C for 5 h. The mixture was quenched with H_2O (10 mL), extracted with ethyl acetate (10 mL×3), washed brine (10 mL), dried over anhydrous Na_2SO_4, and evaporated. The residue was purified by a silica gel column chromatography (ethyl acetate/*n*-hexane = 1/4, v/v) to yield *tert*-butyl (2-(hydroxymethyl-d_2)phenyl)carbamate (**S2**) (4.38 g, 16.4 mmol, quant) as a yellow oil: IR (neat/cm^{-1}): 3363, 2978, 1705, 1527, 1165. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 1.51 (s, 9H), 2.58 (br s, 1H), 7.00 (dd, *J* = 7.6, 7.5 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 7.28 (dd, *J* = 7.8, 7.6 Hz, 1H), 7.64 (br s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 28.3 (CH_3×3), 63.3 (quintet, *J* = 22.0 Hz, C), 80.4 (C), 121.2 (CH), 123.2 (CH), 128.9 (CH), 129.0 (CH), 129.1 (C), 137.8 (C), 153.6 (C). HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{15}D_2NO_3Na$, 248.1226; found, 248.1224.

***N*-(2-(Oct-2-yn-1-yl-1,1-d_2)phenyl)-1,1,1-triphenyl-λ^5-phosphanimine (S6).**

To a stirred solution of **S2** (388 mg, 1.72 mmol), carbon tetrabromide (653 mg, 2.06 mmol), in dichloromethane (15 mL) at 0 °C was slowly added a dichloromethane (5 mL) solution of triphenylphosphine (542 mg, 2.1 mmol). After being stirred for 2 h, the mixture was condensed under reduced pressure. The residue was purified by a silica gel column chromatography using ethyl acetate/*n*-hexane (1/15, v/v) as an eluent to yield benzyl bromide **S3** (337 mg, 1.17 mmol, 82%, if pure).

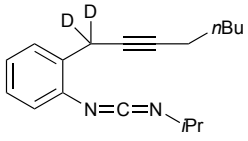
To a mixture of **S3** (337 mg, 1.17 mmol, if pure), $Pd(dppf)_2Cl_2$•CH_2Cl_2 (28.6 mg, 0.0351 mmol, 3 mol%), and THF (10 mL) was added THF (16 mL) solution of In(C≡C*n*Pent)$_3$ (0.584 mmol, prepared from *n*PentC≡CLi and indium(III) trichloride).[S3] After being stirred for 3 h, the mixture was quenched by addition of methanol (5 mL), extracted with chloroform (5 mL×3), washed with brine (5 mL), dried over anhydrous sodium sulfate, and evaporated. The residue was purified by a silica gel column chromatography using ethyl acetate/*n*-hexane (1/10, v/v) as an eluent to yield **S4** (246 mg, 0.81 mmol, 69%, if pure).

Trifluoroacetic acid (1 mL) was added to a dichloromethane (5 mL) solution of **S4** (181 mg, 0.60 mmol, if pure). After being stirred for 1 h, the reaction mixture was quenched by addition of saturated aqueous sodium hydrogen carbonate, extracted with chloroform (5 mL×3), washed with brine (5 mL), dried over anhydrous sodium sulfate, and evaporated. The residue was purified by a silica gel column chromatography (ethyl acetate/*n*-hexane = 1/4, v/v) to yield aniline **S5** (113 mg, 0.56 mmol, 94%, if pure).

To a dichloromethane (5 mL) solution of **S5** (113 mg, 0.56 mmol, if pure), triphenylphosphine (173 mg, 0.67 mmol), and hexachloroethane (191 mg, 0.67 mmol) was added triethylamine (0.18 mL, 1.34 mmol), and the mixture was stirred overnight at room temperature. The resulting salt was removed by filtration, and

the filtrate was evaporated. The residue was purified by a silica gel column chromatography using ethyl acetate/*n*-hexane (1/20, v/v) as an eluent to yield *N*-(2-(oct-2-yn-1-yl-1,1-d_2)phenyl)-1,1,1-triphenyl-λ^5-phosphanimine (**S6**) (159 mg, 0.34 mmol, 62%) as a brown oil. IR (neat/cm^{-1}): 3055, 2931, 1589, 1342, 1111. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 0.92 (t, *J* = 7.7 Hz, 3H), 1.29–1.46 (m, 4H), 1.57 (tt, *J* = 7.7, 7.7 Hz, 2H), 2.26 (t, *J* = 7.7 Hz, 2H), 6.48 (d, *J* = 8.8 Hz, 1H), 6.73 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.83 (dd, *J* = 8.8, 7.5 Hz, 1H), 7.44–7.47 (m, 6H), 7.52–7.56 (m, 4H), 7.78–7.82 (m, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$, *δ*): 13.9 (CH_3), 18.9 (CH_2), 22.2 (CH_2), 28.9 (CH_2), 31.1 (CH_2), 79.3 (C), 82.0 (C), 117.2 (CH), 120.3 (CH, d, *J* = 9.0 Hz), 126.4 (CH), 128.0 (CH, d, *J* = 1.7 Hz), 128.5 (CH×6, d, *J* = 11.6 Hz), 131.5 (CH×3, d, *J* = 2.9 Hz), 131.6 (C×3, d, *J* = 99.4 Hz), 131.7 (C), 132.5 (CH×6, d, *J* = 9.6 Hz), 148.5 (C). (The signal of benzylic carbon is missing.)

***N*-Isopropyl-*N*-(2-(oct-2-yn-1-yl-1,1-d_2)phenyl)methanediimine (1a-d_2).**



The aza-Wittig reaction of **S6** with isopropyl isocyanate according to the reported method[S2] afforded **1a-d_2**. Pale yellow oil. IR (neat/cm^{-1}): 2931, 2129, 1172, 756. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 0.90 (t, *J* = 7.8 Hz, 3H), 1.28–1.42 (m, 10H), 1.54 (tt, *J* = 7.8, 7.0 Hz, 2H), 2.22 (t, *J* = 7.0 Hz, 2H), 3.79 (septet, *J* = 6.4 Hz, 1H), 7.08–7.20 (m, 3H), 7.52 (dd, *J* = 7.5, 1.5 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 14.0 (CH_3), 18.9 (CH_2), 22.2 (CH_2), 24.8 (CH_3×2), 28.8 (CH_2), 31.1 (CH_2), 50.1 (CH), 77.2 (C), 82.8 (C), 123.4 (CH), 124.7 (CH), 127.4 (CH), 129.1 (CH), 131.3 (C), 135.7 (C), 138.5 (C). (The signal of benzylic carbon is missing.) HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{18}H_{22}D_2N_2Na$, 293.1957; found, 293.1949.

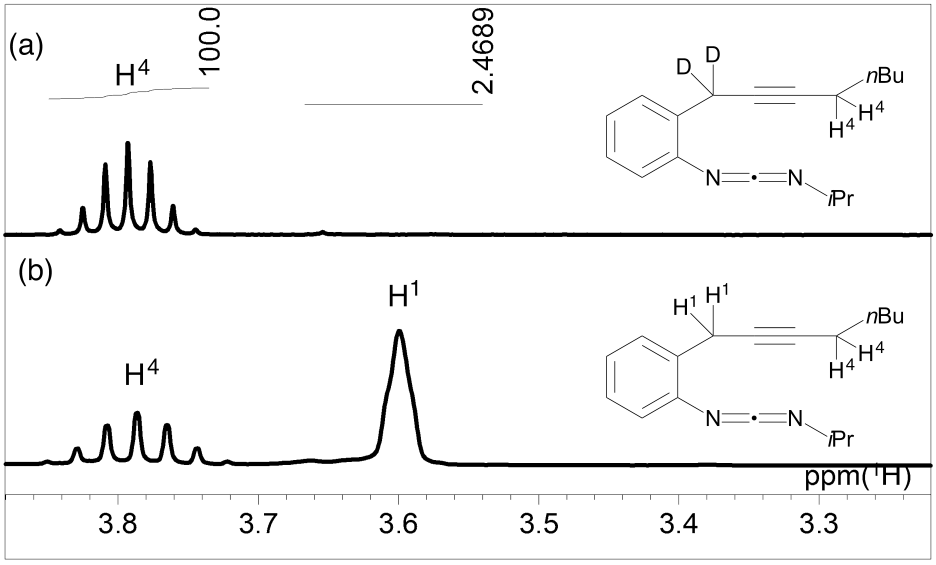


Fig. S1 Enlarged NMR spectra of (a) **1a-d_2** (400 MHz), and (b) **1a** (300 MHz) in $CDCl_3$.

(*Z*)-3-(Hex-1-en-1-yl-1-*d*)-*N*-isopropylquinolin-4-d_2-amine (*cis*-2a-d_2).

From **1a-d_2** (24 mg, 0.088 mmol) and $Rh(dppp)_2Cl$ (8.5 mg, 0.0089 mmol, 10 mol%), *cis*-**2a-d_2** (14 mg, 0.053 mmol, 60%, *Z*:*E* = >95:5, D:H = 92:8) was obtained as pale yellow oil. IR (neat/cm^{-1}): 2931, 1219, 756, 463. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 0.85 (t, *J* = 7.2 Hz, 3H), 1.26–1.42 (m, 10H), 2.14 (dt, *J* = 7.4, 7.2

Hz, 2H), 4.45–4.55 (m, 2H), 5.94 (t, J = 7.4 Hz, 1H), 7.17 (dd, J = 8.0, 7.3 Hz, 1H), 7.48 (ddd, J = 8.1, 7.3, 1.3 Hz, 1H), 7.54 (dd, J = 8.0, 1.3 Hz, 1H), 7.68 (d, J = 8.1 Hz, 1H). HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{18}H_{22}D_2N_2Na$, 293.1957; found, 293.1949.

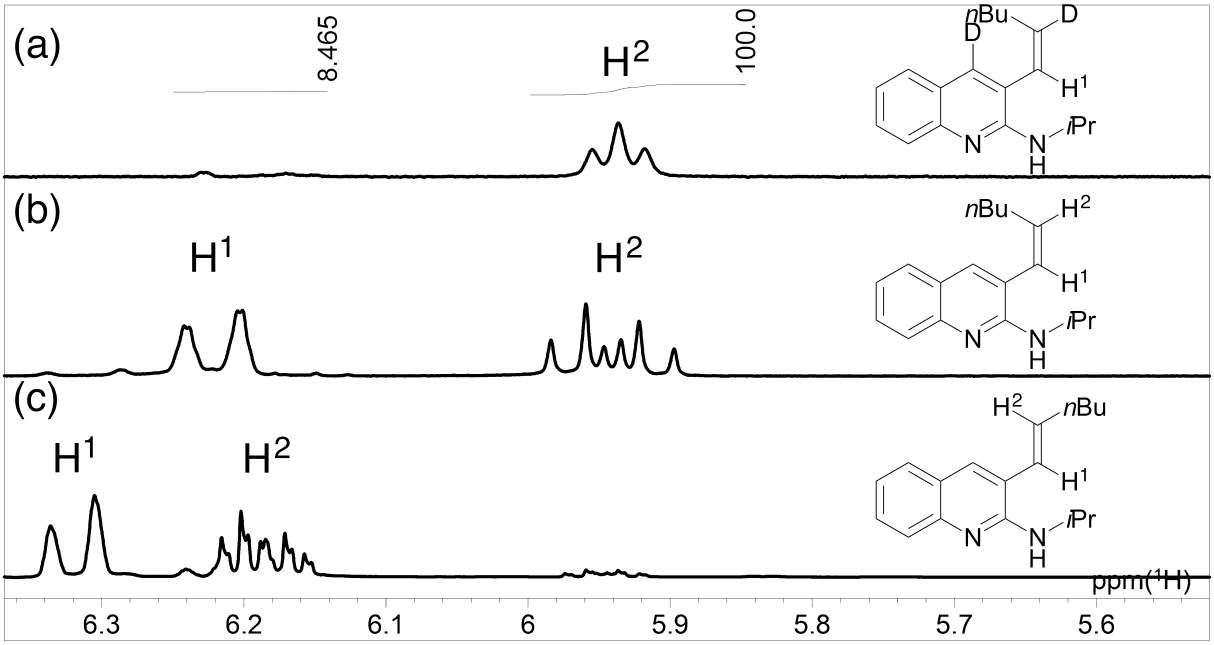
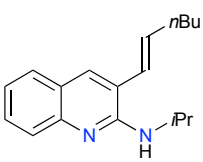


Fig. S2 Enlarged NMR spectra of (a) *cis*-**2a-*d*$_2$** (400 MHz), (b) *cis*-**1a** (400 MHz), and (c) *trans*-**1a** (500 MHz) in $CDCl_3$.

5. One pot synthesis of *trans*-alkenylquinolin-2-amine *trans*-2

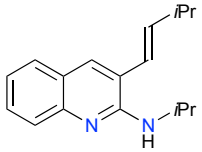
(*E*)-3-(Hex-1-en-1-yl)-*N*-isopropylquinolin-2-amine (*trans*-2a).



A pale yellow suspension of $[Rh(dppp)_2]Cl$ (47.6 mg, 0.049 mmol, 12 mol%) in *p*-xylene (5 mL) was heated at 130 °C, to which *p*-xylene (1 mL) solution of carbodiimide-yne **1a** (110.7 mg, 0.41 mmol) was added. The mixture was stirred for 1 h at 130 °C, cooled to room temperature, and condensed under reduced pressure. To the residue was added iodine (314 mg, 1.2 mmol) and dichloromethane (5 mL), and the mixture was stirred for 3 days. The mixture was quenched by aqueous sodium sulfite, extracted with dichloromethane, washed with brine, dried over anhydrous magnesium sulfate, and evaporated. The residue was purified by a silica gel column chromatography using *n*-hexane to ethyl acetate/*n*-hexane (1/30, v/v) as an eluent to afford *trans*-**2a** (56.3 mg, 51%) as a yellow oil. IR (neat/cm^{-1}): 3440, 2962, 1512, 756, 424. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 0.95 (t, J = 7.3 Hz, 3H), 1.29 (d, J = 6.1 Hz, 6H), 1.40 (tt, J = 7.4, 7.1 Hz, 2H), 1.49 (tt, J = 7.0, 6.4 Hz, 2H), 2.26 (dt, J = 6.9, 6.9 Hz, 2H), 4.44–4.55 (m, 2H), 6.15 (dt, J = 15.6, 6.9 Hz, 1H), 6.30 (d, J = 15.6 Hz, 1H), 7.16 (dd, J = 8.0, 7.9 Hz, 1H), 7.45 (dd, J = 8.0, 7.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.67 (s, 1H), 7.68 (d, J = 8.0 H, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 13.9 (CH_3), 22.3 (CH_2), 23.1 (CH_3×2), 31.3 (CH_2), 33.0 (CH_2), 42.4 (CH), 121.8 (CH), 122.5 (C), 123.5 (C), 124.1 (CH), 126.0 (CH), 127.1 (CH), 128.6 (CH), 133.2 (CH),

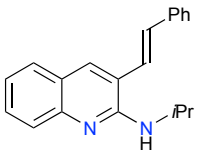
136.8 (CH), 147.5 (C), 153.9 (C). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{18}H_{25}N_2$, 269.2018; found, 269.2012.

(*E*)-*N*-Isopropyl-3-(3-methylbut-1-en-1-yl)quinolin-2-amine (*trans*-2n).



Yellow oil. IR (neat/cm^{-1}): 3440, 2962, 1512, 764, 471. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 1.13 (d, *J* = 6.7 Hz, 6H), 1.30 (d, *J* = 6.3 Hz, 6H), 2.52 (dq, *J* = 6.9, 6.7 Hz, 1H), 4.48–4.35 (m, 2H), 6.13 (dd, *J* = 15.6, 6.9 Hz, 1H), 6.25 (d, *J* = 15.6 Hz, 1H), 7.15 (dd, *J* = 7.9, 6.9 Hz, 1H), 7.46 (dd, *J* = 7.2, 6.9 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.666 (s, 1H), 7.672 (d, *J* = 7.6 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 22.4 (CH_3×2), 23.1 (CH_3×2), 31.9 (CH), 42.4 (CH), 121.2 (CH), 121.8 (CH), 122.5 (C), 123.5 (C), 126.1 (CH), 127.1 (CH), 128.6 (CH), 133.2 (CH), 143.6 (CH), 147.5 (C), 154.0 (C). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{17}H_{23}N_2$, 255.1861; found, 255.1856.

(*E*)-*N*-Isopropyl-3-styrylquinolin-2-amine (*trans*-2s).



Yellow oil. IR (neat/cm^{-1}): 3440, 2969, 1512, 910. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 1.30 (d, *J* = 6.1 Hz, 6H), 4.54 (br s, 2H), 6.99 (d, *J* = 15.8 Hz, 1H), 7.05 (d, *J* = 15.8 Hz, 1H), 7.17 (dd, *J* = 6.9, 6.8 Hz, 1H), 7.29 (dd, *J* = 7.4, 7.1 Hz, 1H), 7.37 (dd, *J* = 7.6, 6.9 Hz, 2H), 7.43–7.59 (m, 4H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.82 (s, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 23.0 (CH_3×2), 42.5 (CH), 121.98 (CH), 122.02 (C), 122.8 (CH), 123.4 (C), 126.1 (CH), 126.7 (CH×2), 127.3 (CH), 128.2 (CH), 128.7 (CH×2), 129.0 (CH), 133.4 (CH), 133.6 (CH), 136.8 (C), 147.8 (C), 153.9 (C). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{21}N_2$, 289.1705; found, 289.1705.

6. References

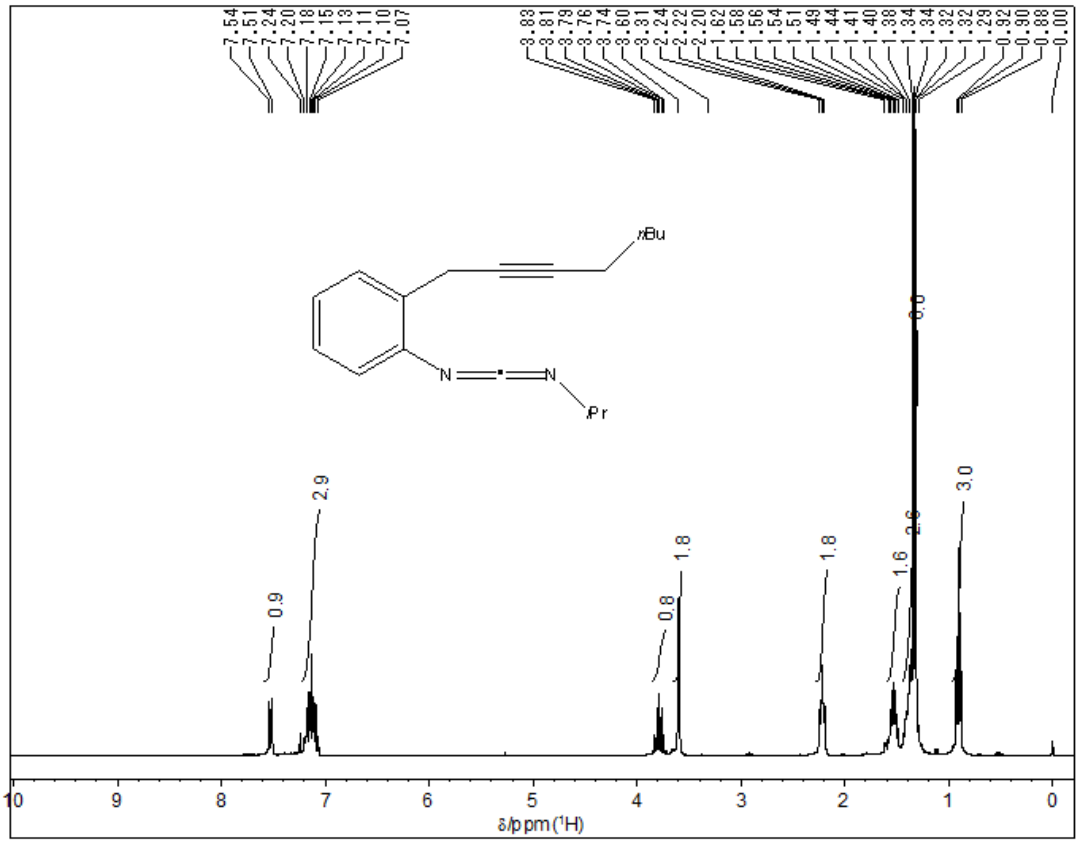
S1 T. Saito, N. Furukawa and T. Otani, *Org. Biomol. Chem.*, 2010, **8**, 1126–1132.

S2 (*a*) G. La Monica, C. Monti and S. Cenini, *J. Mol. Catal.*, 1983, **18**, 93–98. (*b*) D. P. Fairlie and B. Bosnich, *Organometallics*, 1988, **7**, 936–945.

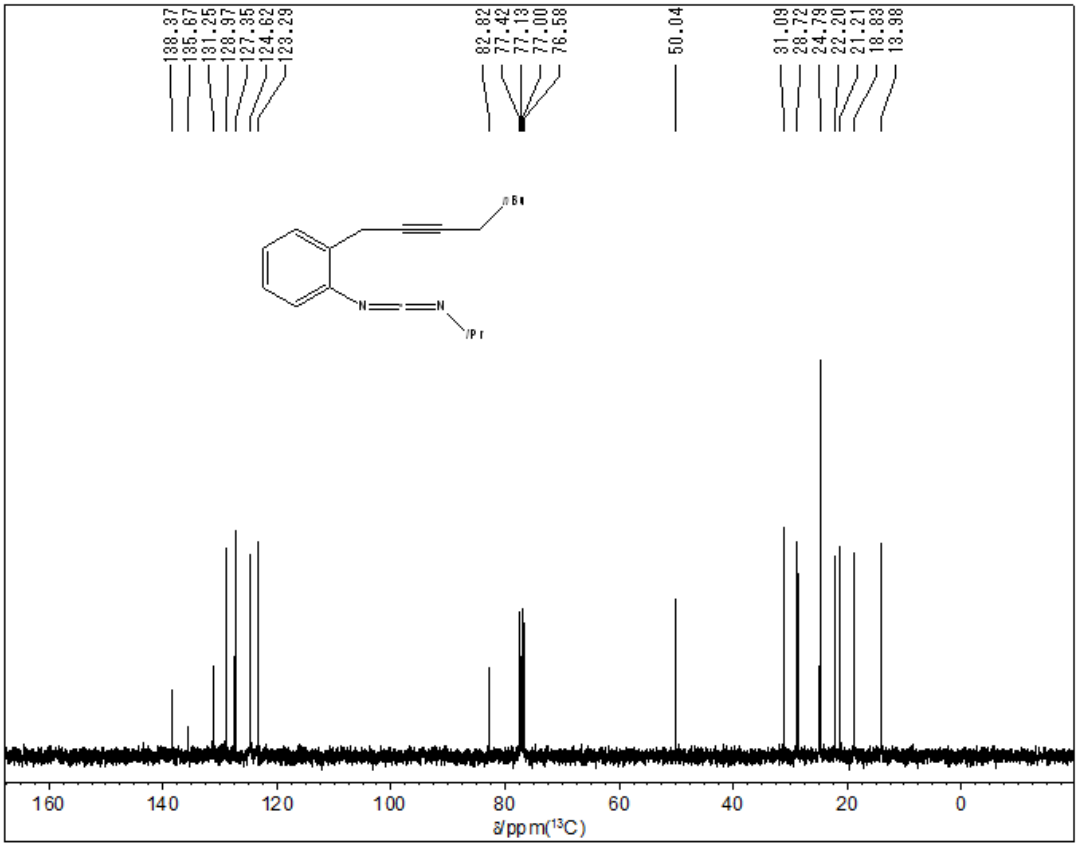
S3 I. Pérez, J. P. Sestelo and L. A. Sarandeses, *J. Am. Chem. Soc.*, 2001, **123**, 4155–4160.

7. ^{1}H and ^{13}C NMR spectra of new compounds

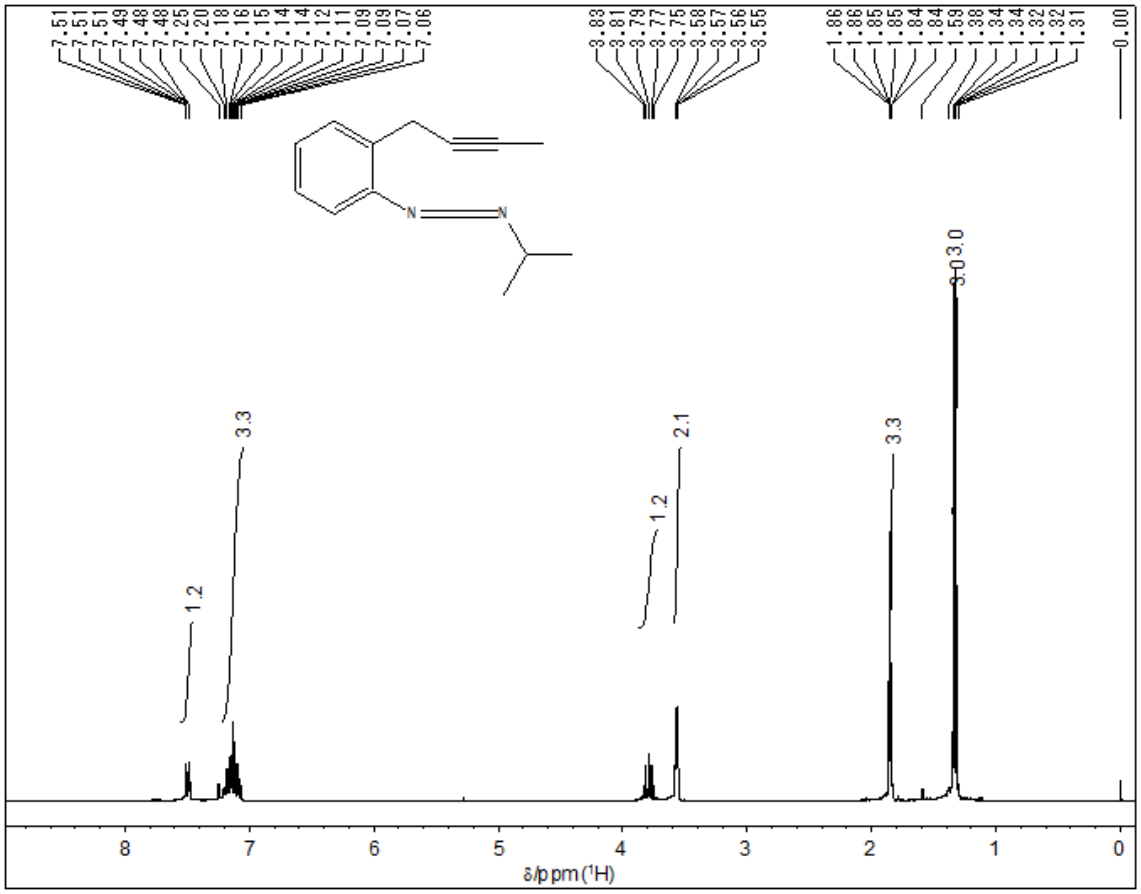
- ^{1}H-NMR spectrum of **1a**



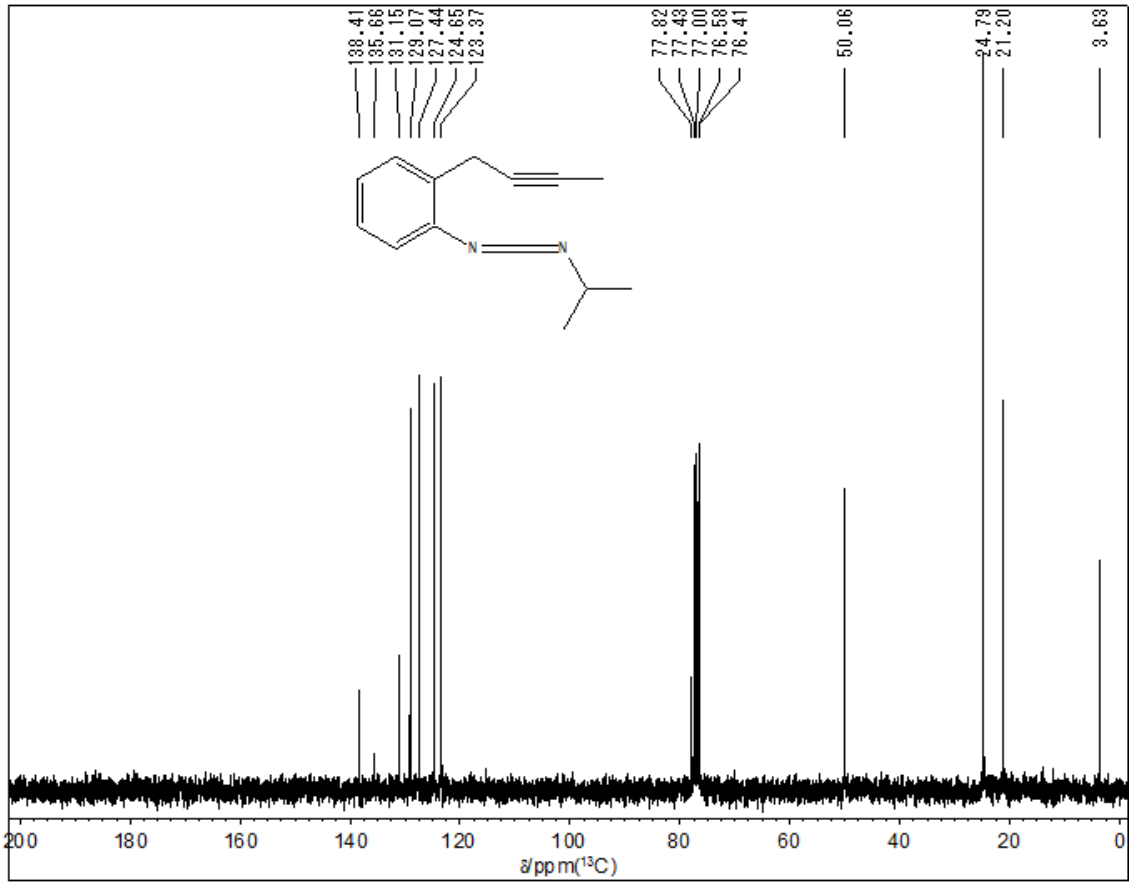
- ^{13}C-NMR spectrum of **1a**



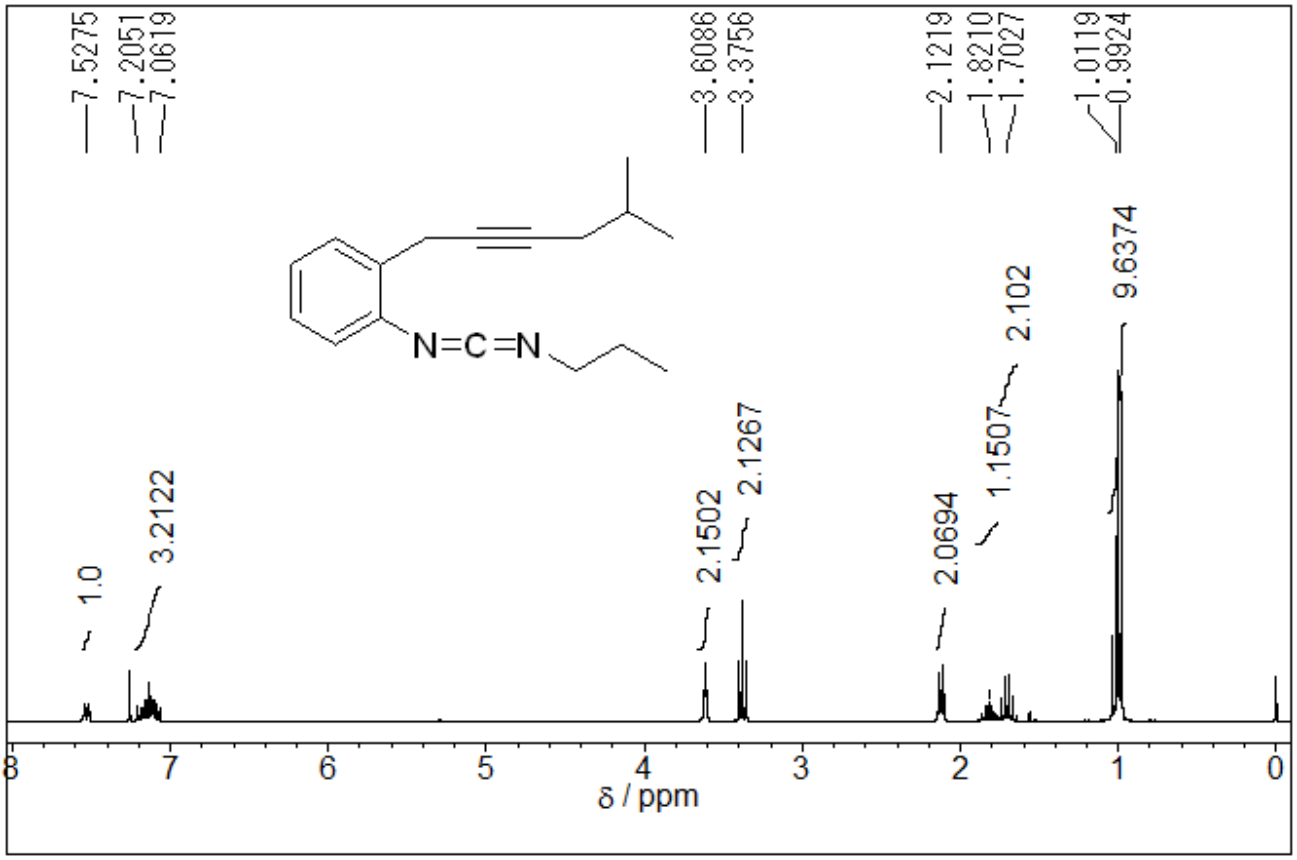
• ^{1}H-NMR spectrum of **1i**



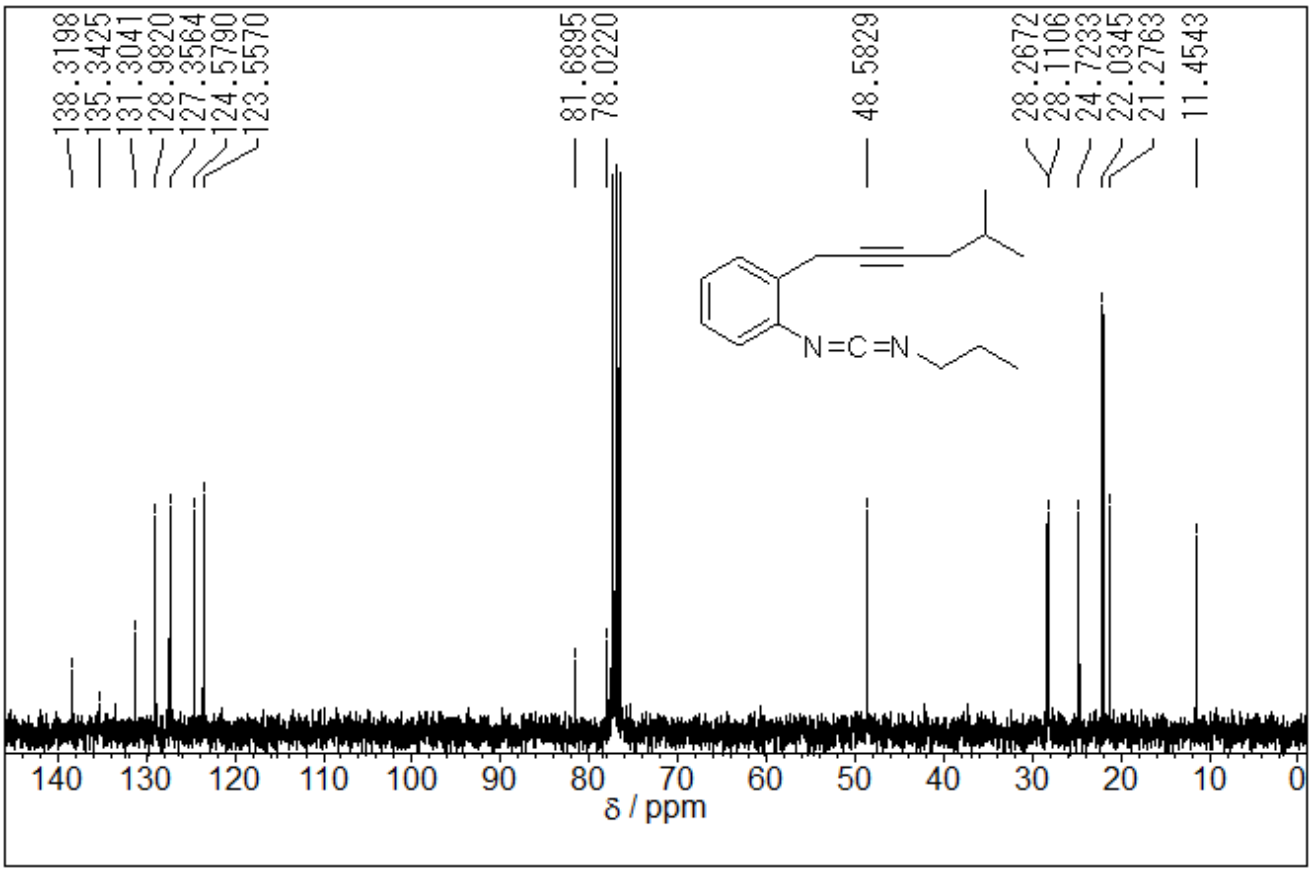
• ^{13}C-NMR spectrum of **1i**



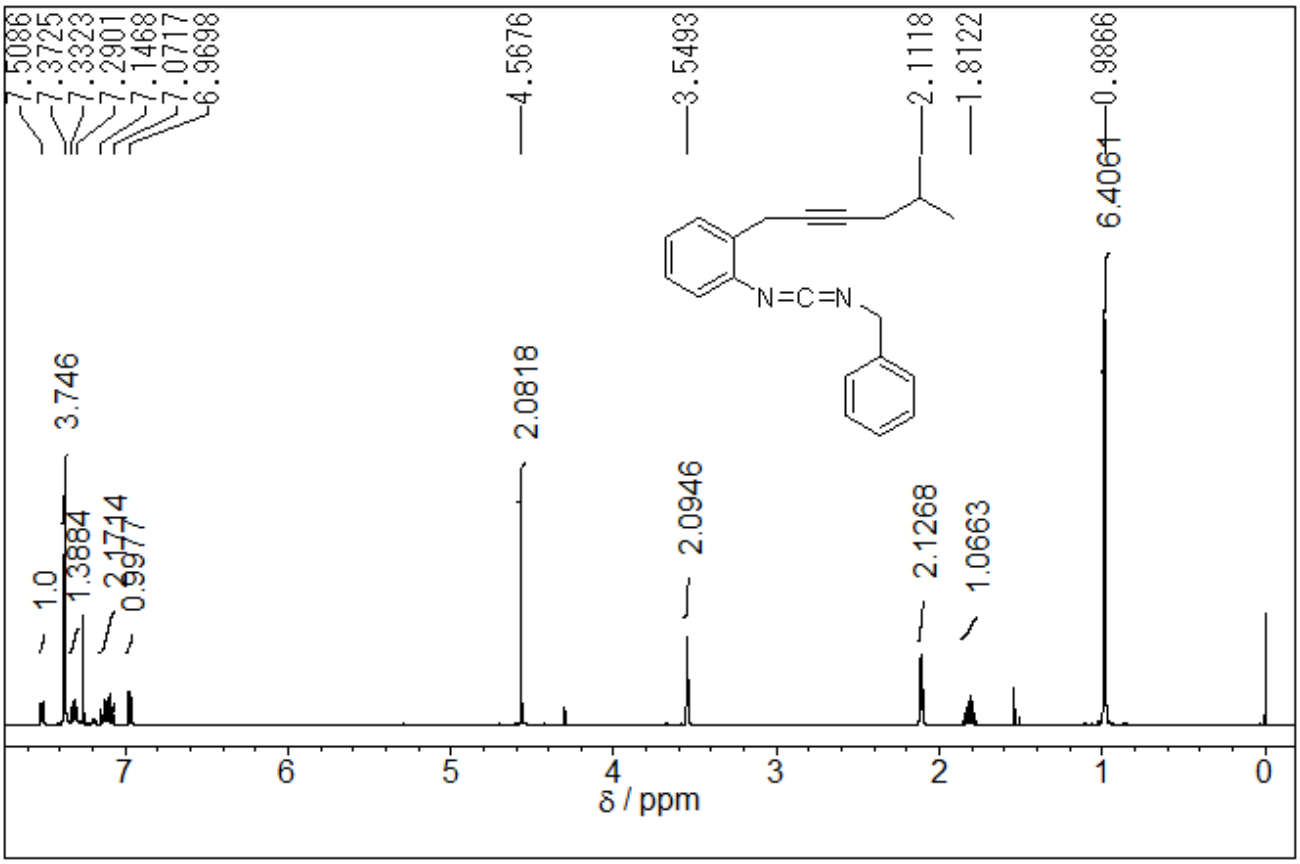
• ^{1}H-NMR spectrum of **1l**



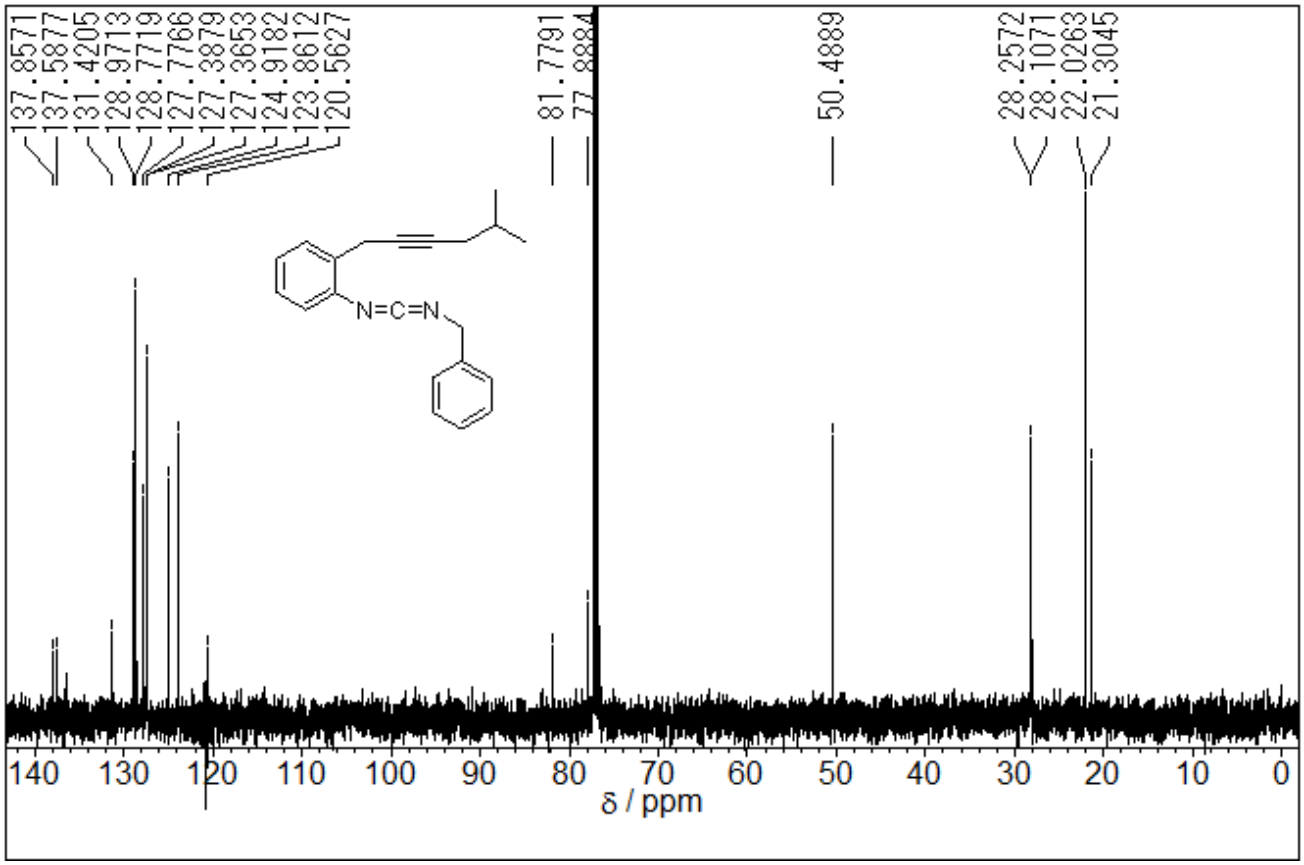
• ^{13}C-NMR spectrum of **1l**



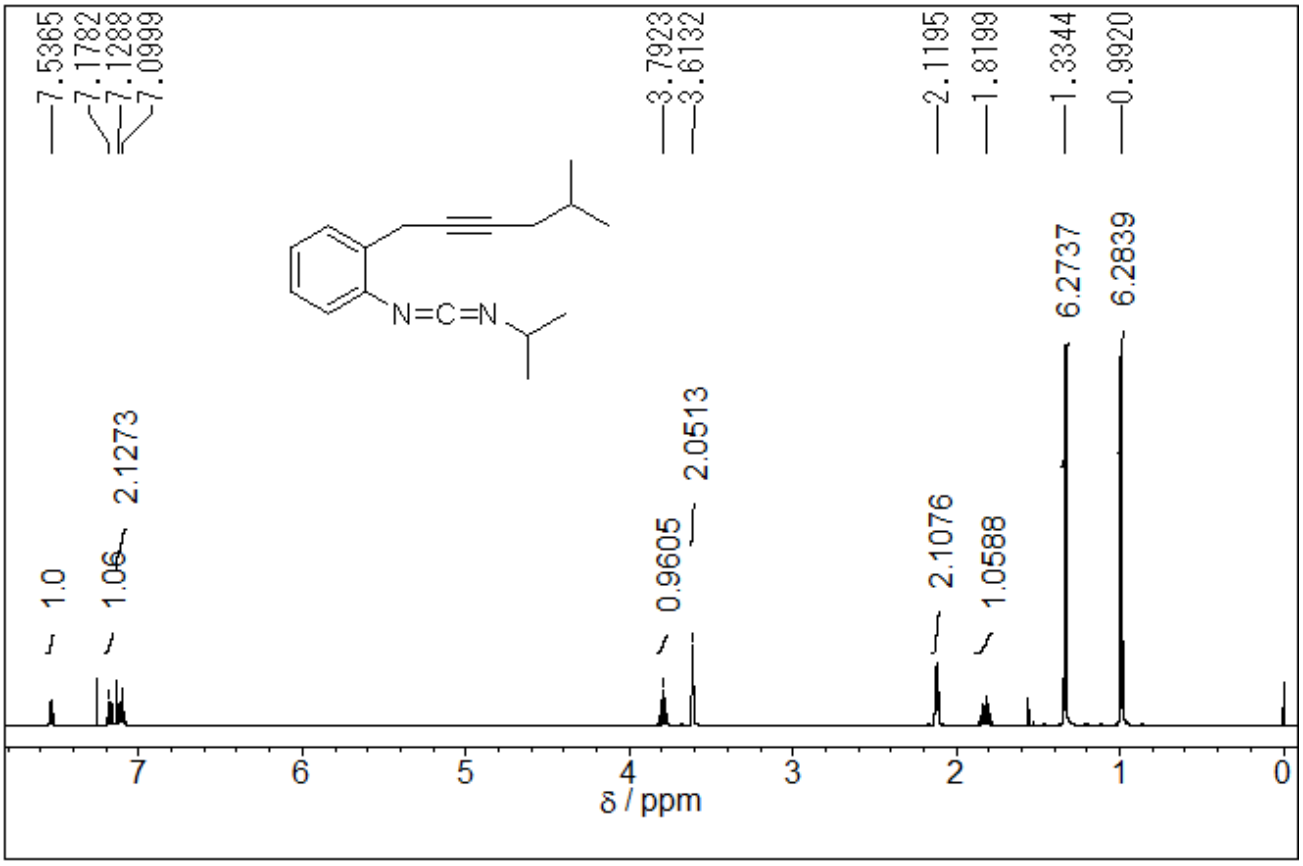
• ^{1}H-NMR spectrum of **1m**



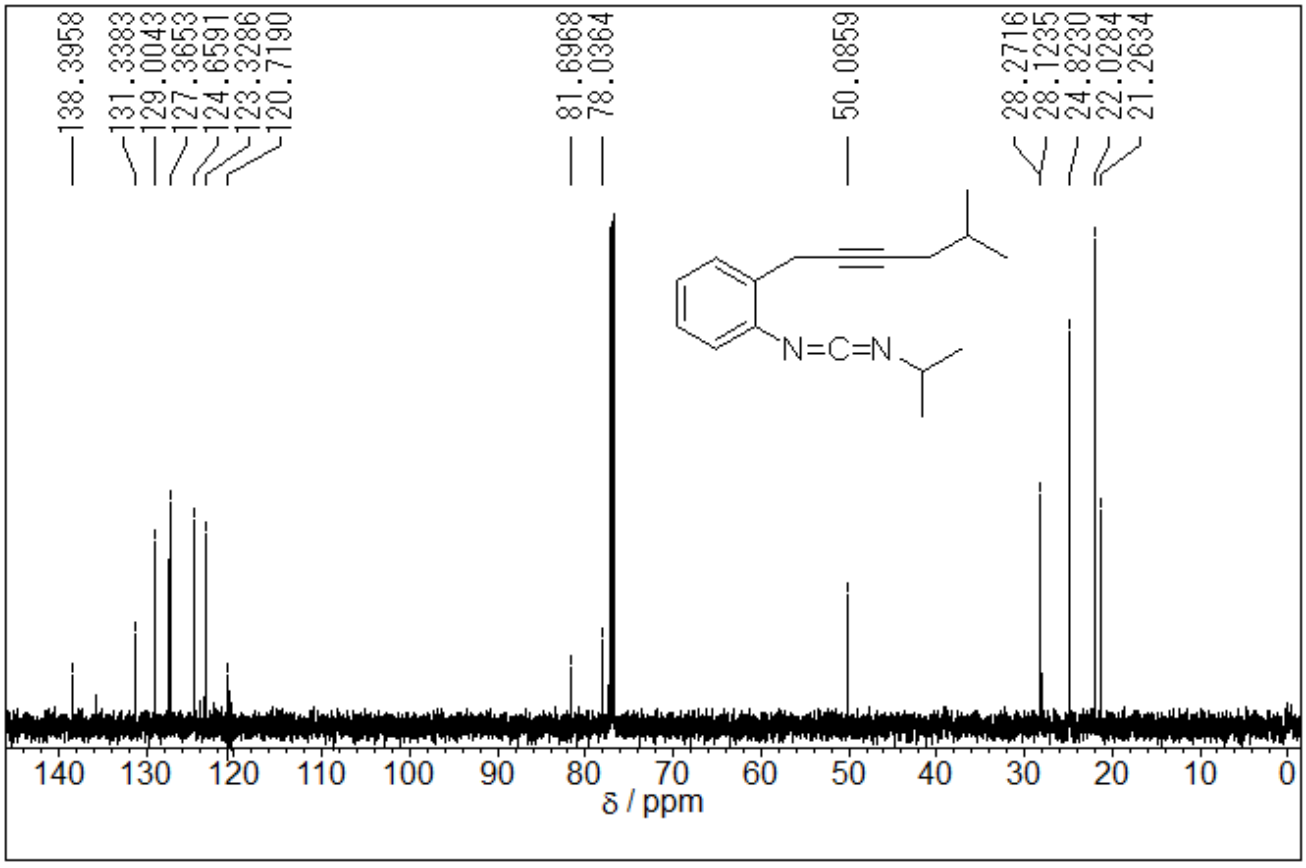
• ^{13}C-NMR spectrum of **1m**



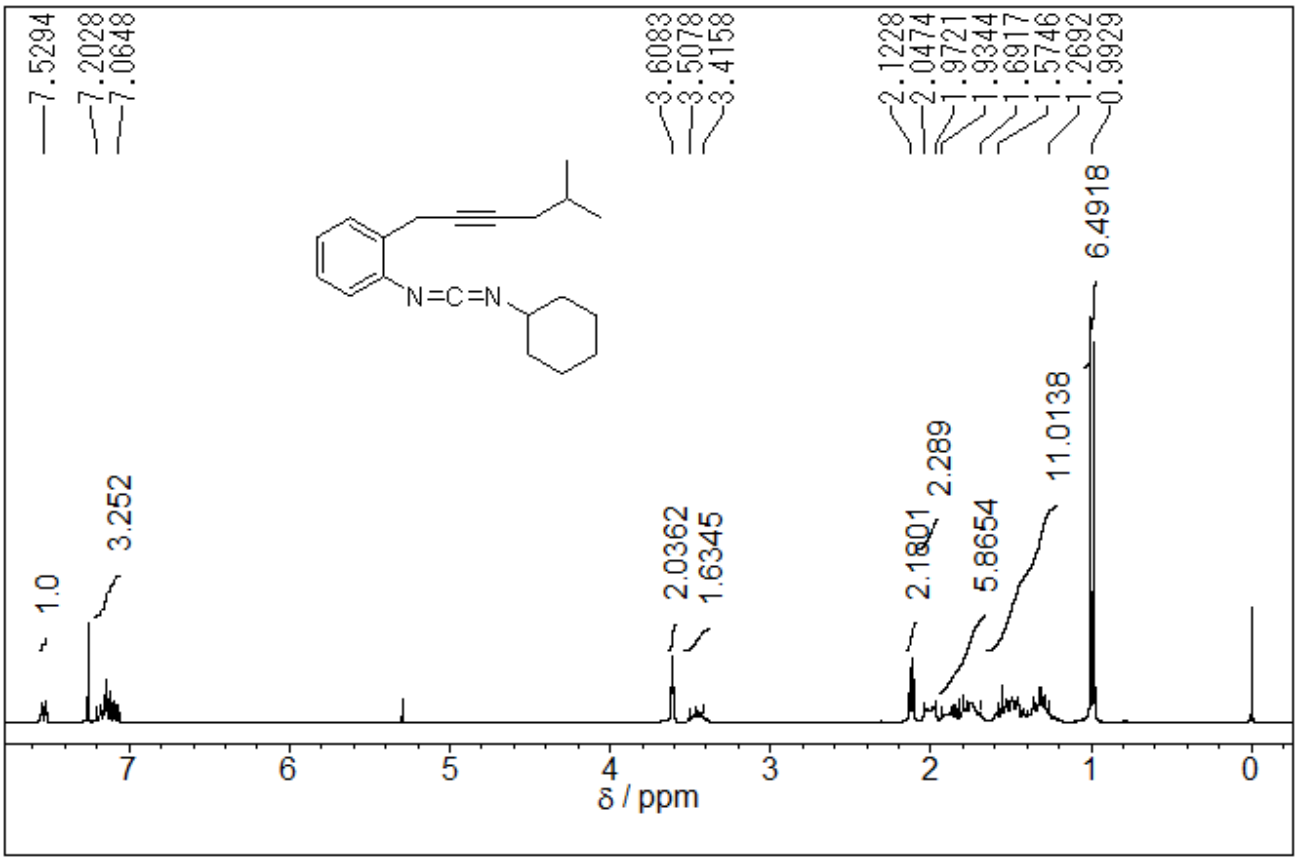
• ^{1}H-NMR spectrum of **1n**



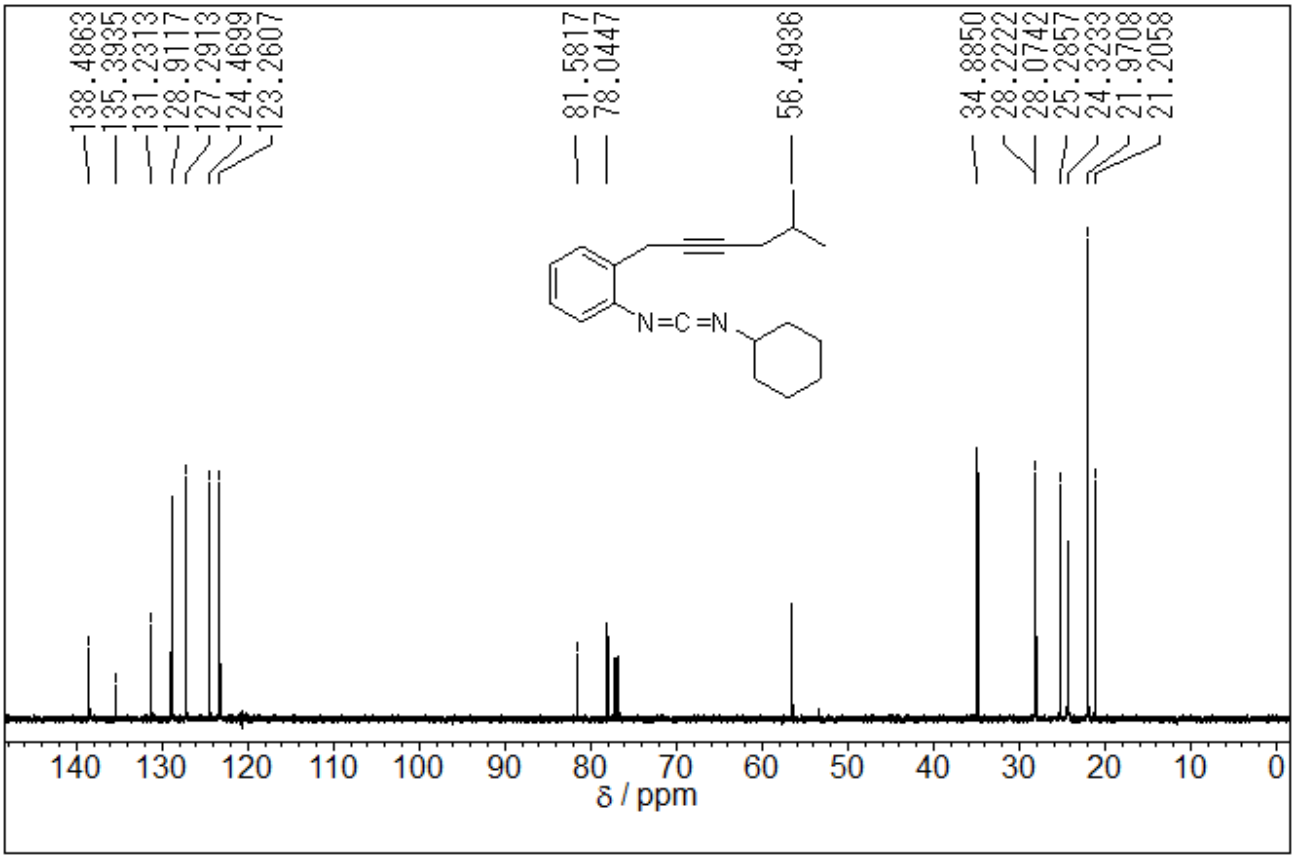
• ^{13}C-NMR spectrum of **1n**



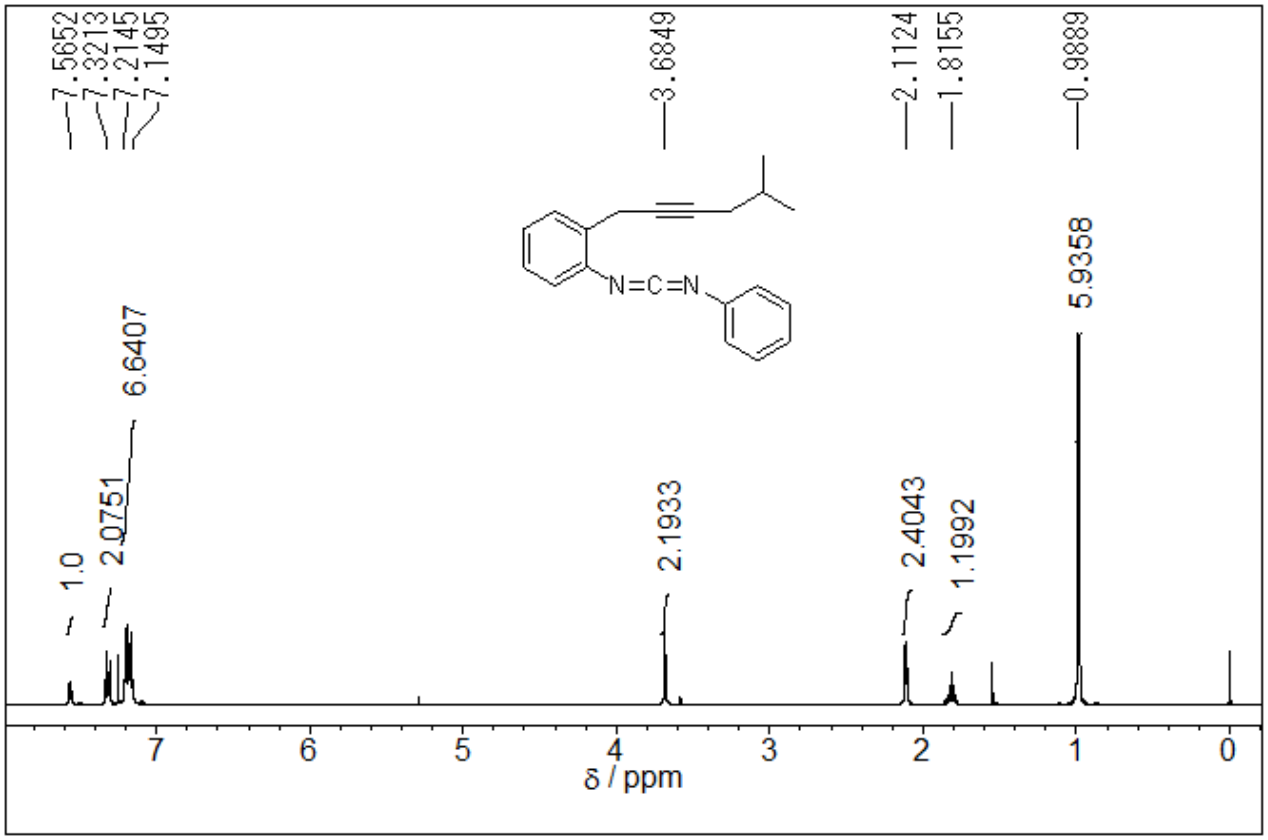
• ^{1}H-NMR spectrum of **1o**



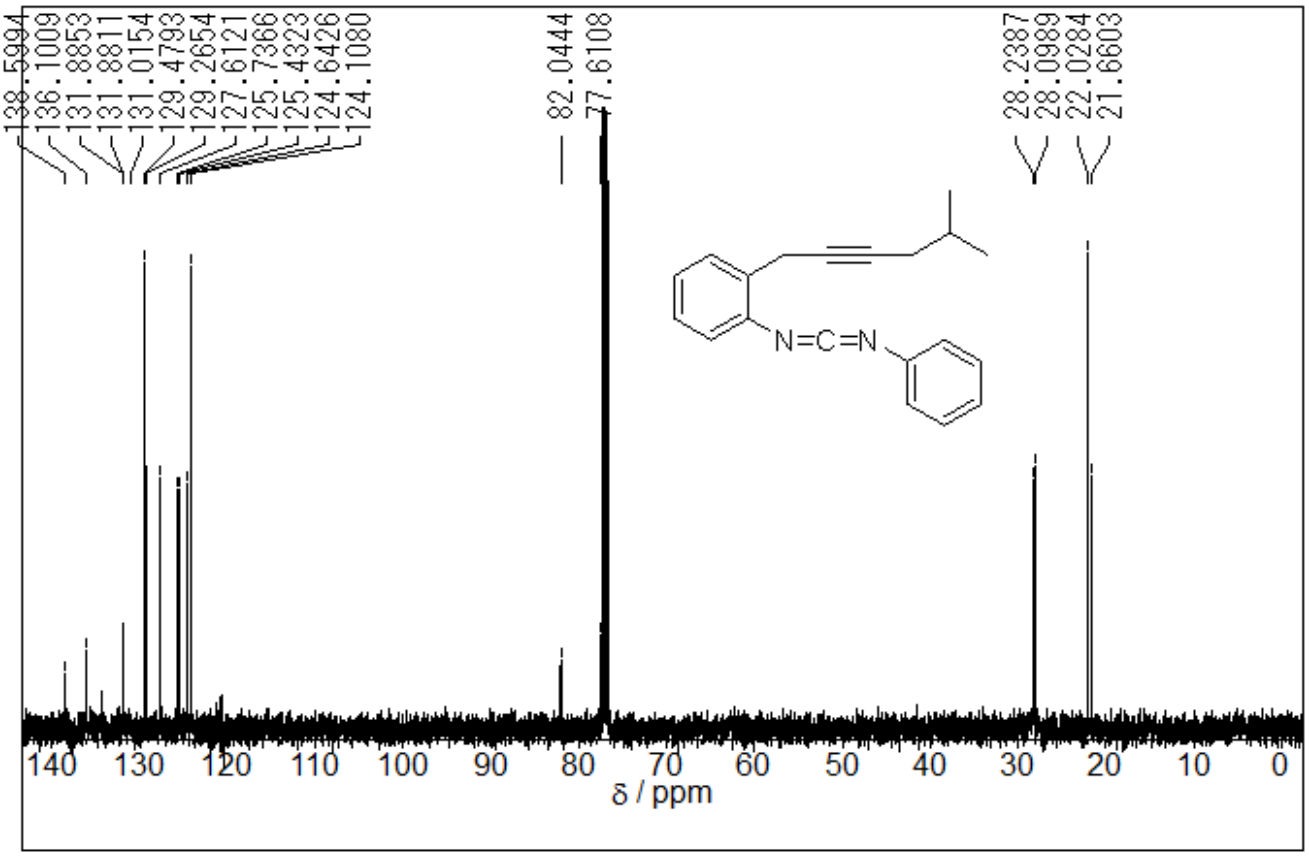
• ^{13}C-NMR spectrum of **1o**



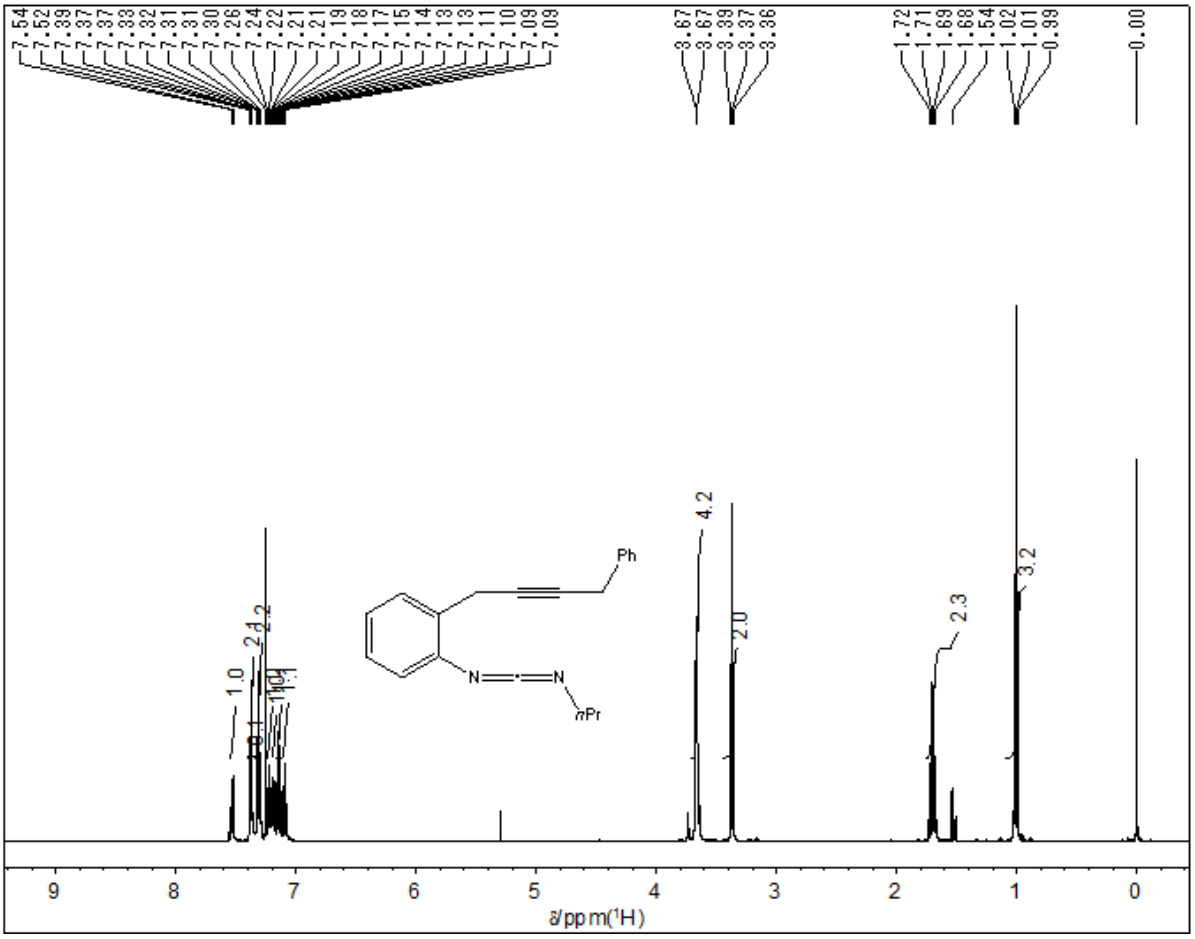
• ^{1}H-NMR spectrum of **1p**



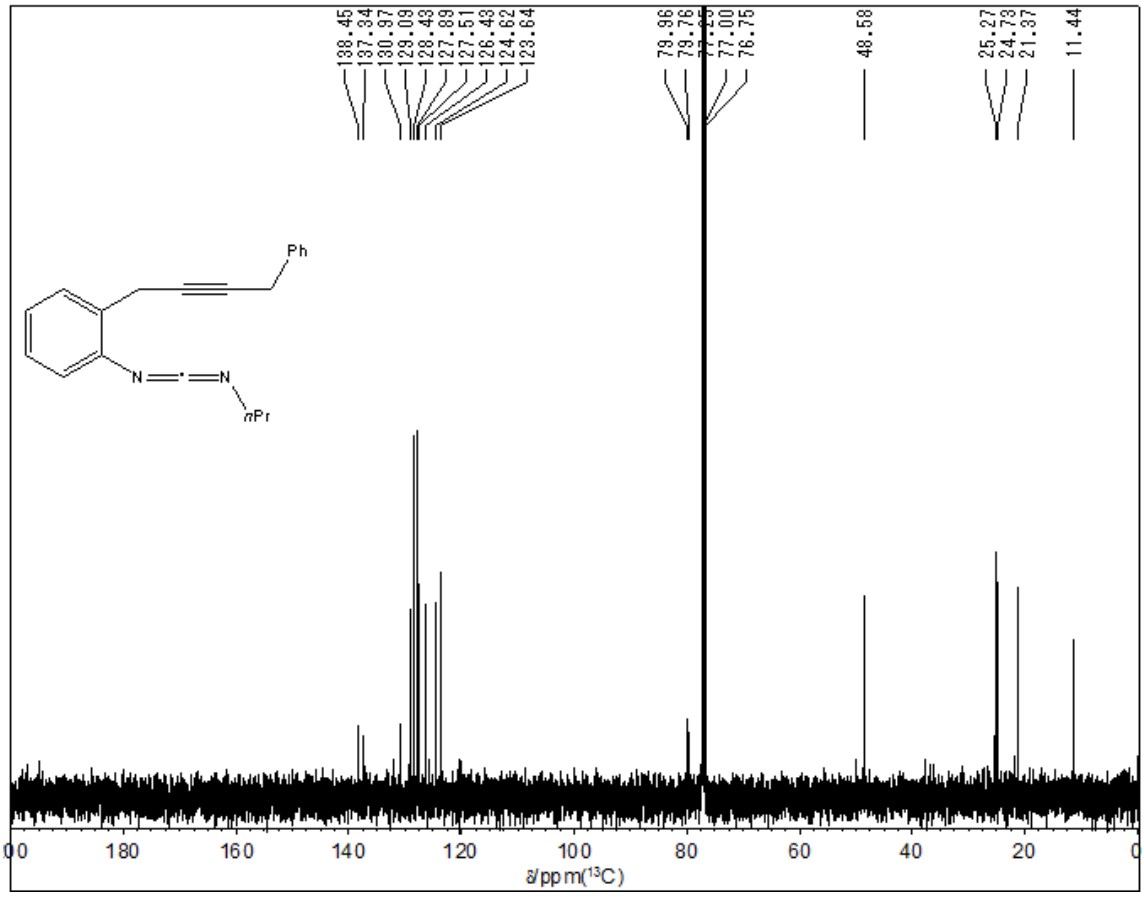
• ^{13}C-NMR spectrum of **1p**



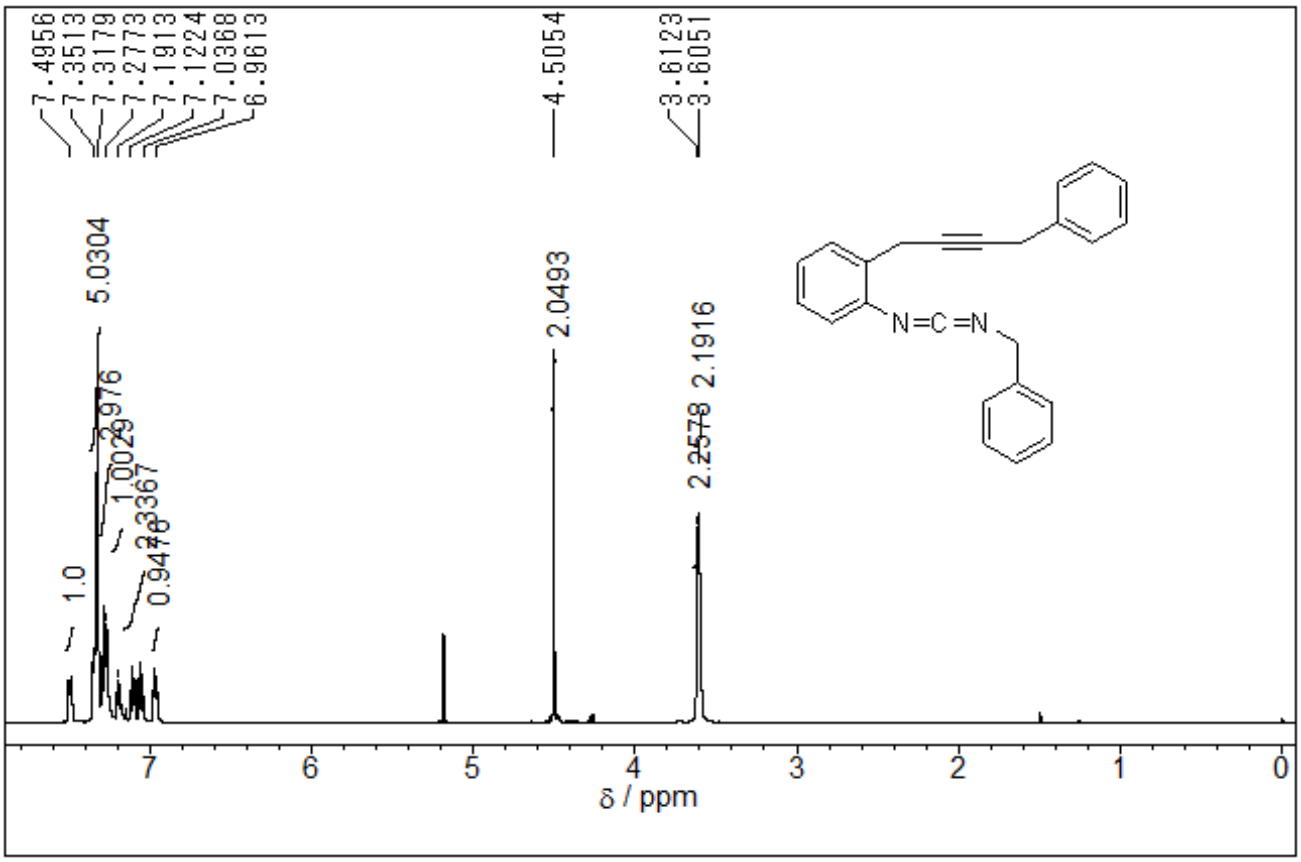
• ^{1}H-NMR spectrum of **1q**



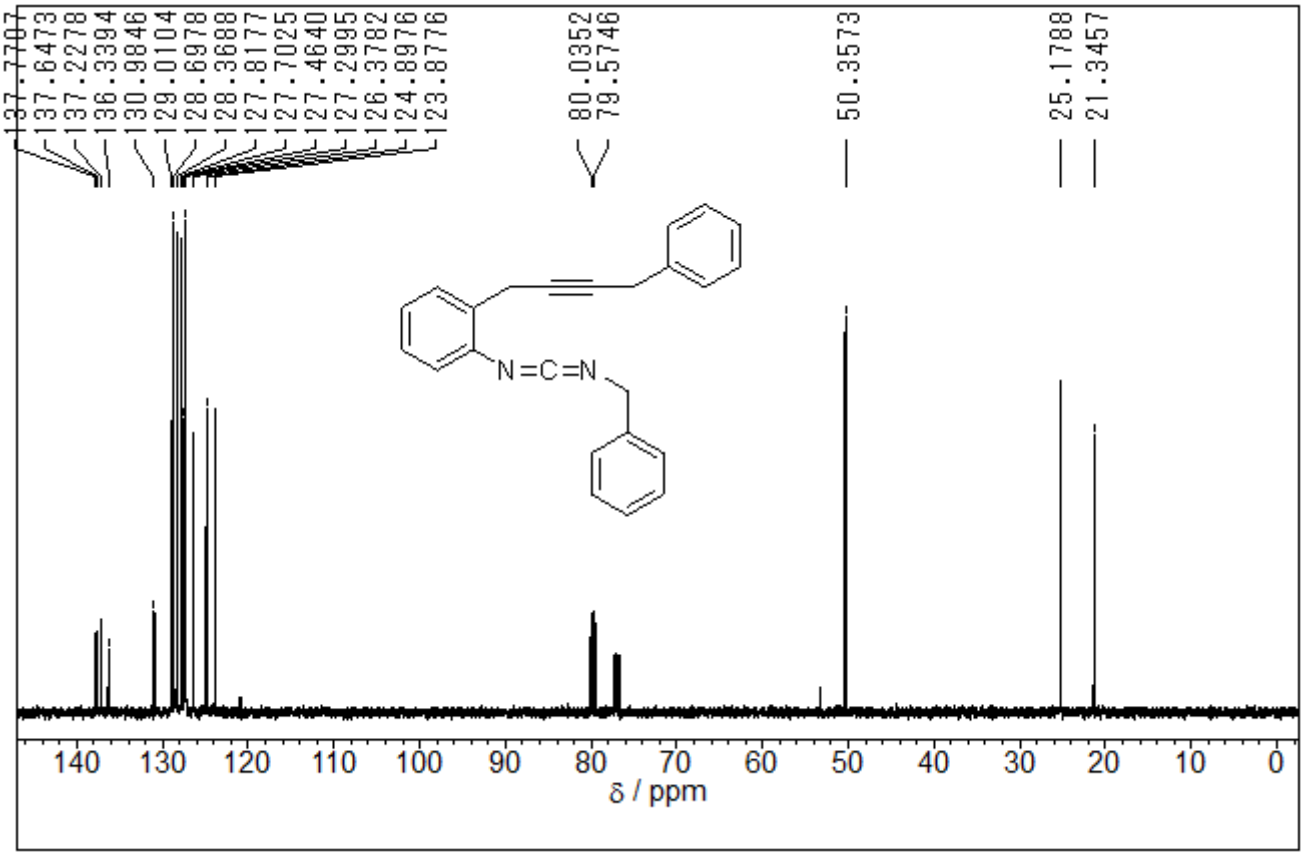
• ^{13}C-NMR spectrum of **1q**



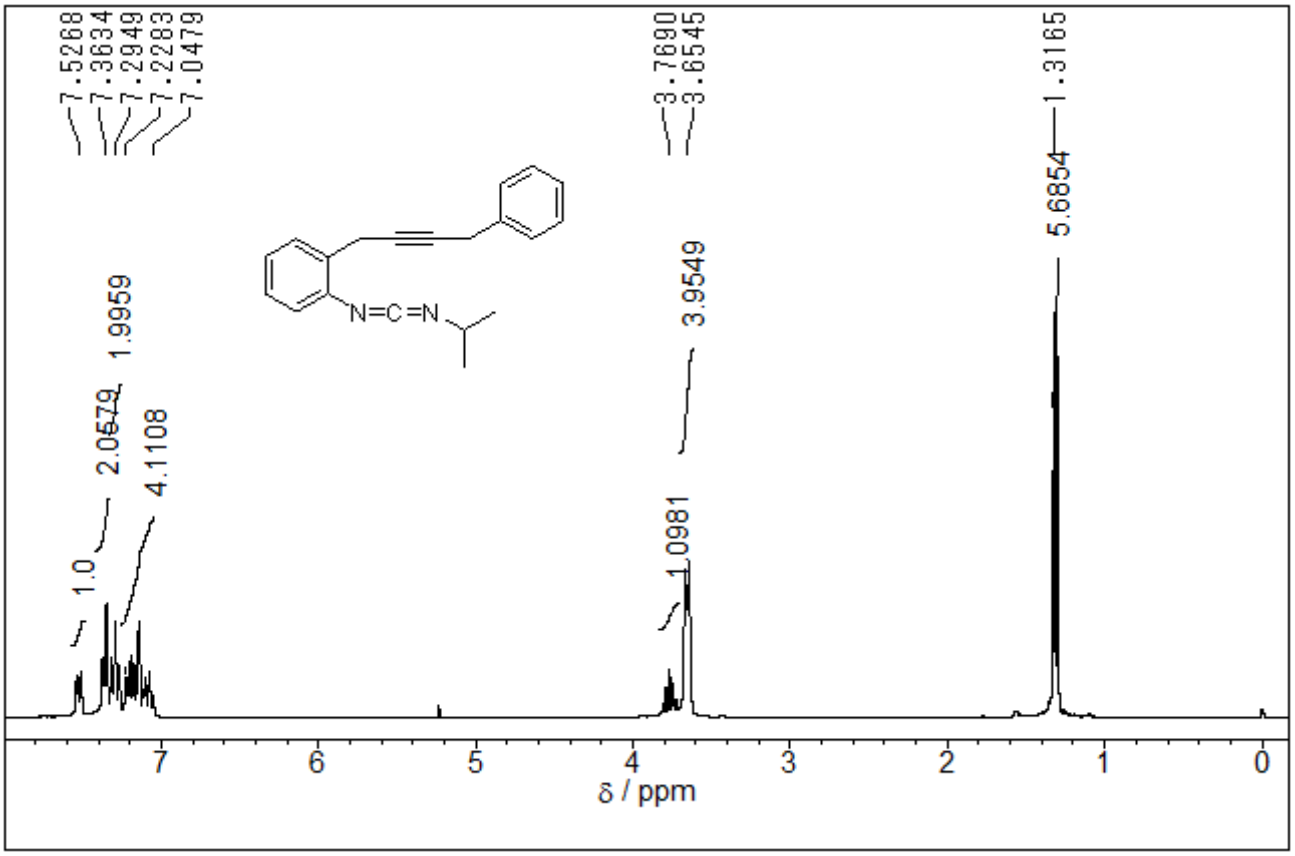
• ^{1}H-NMR spectrum of **1r**



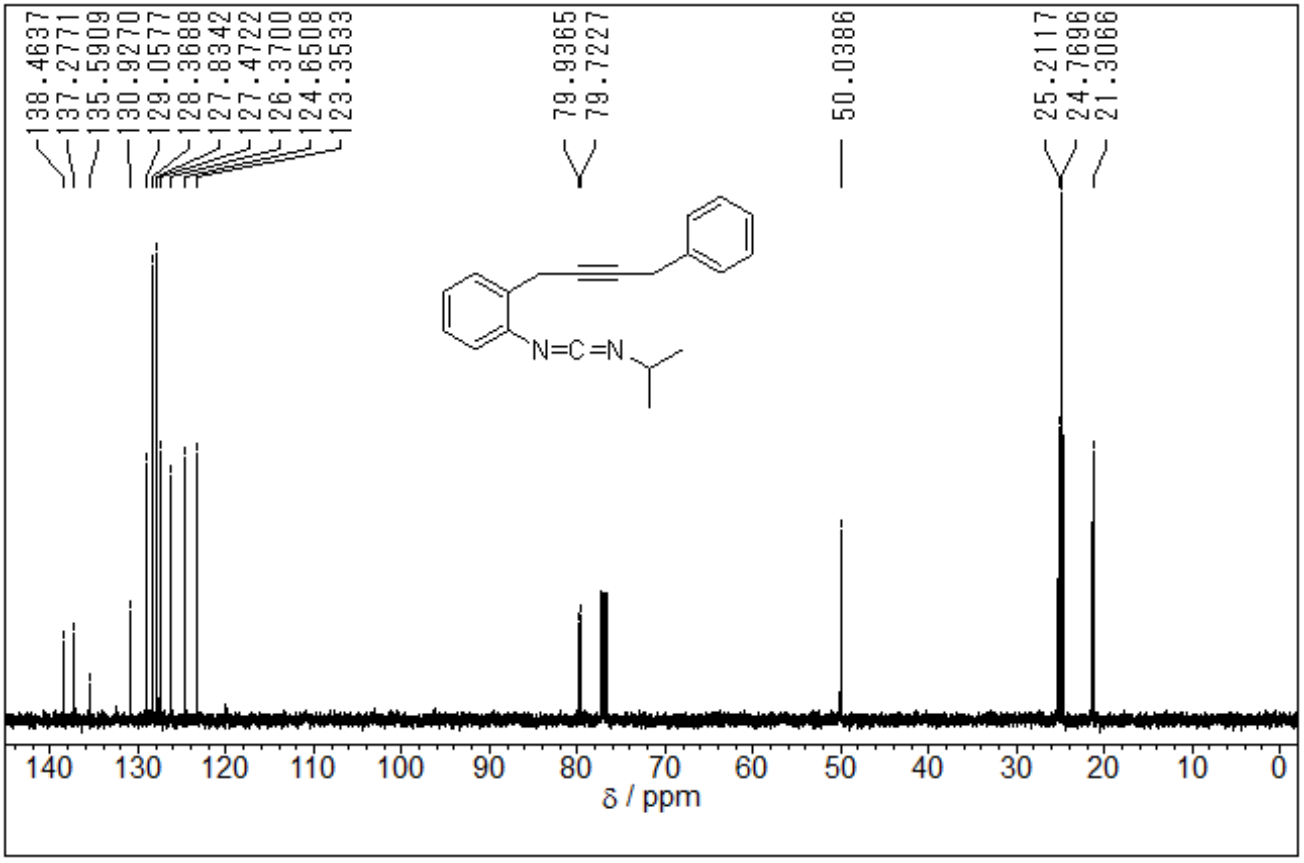
• ^{13}C-NMR spectrum of **1r**



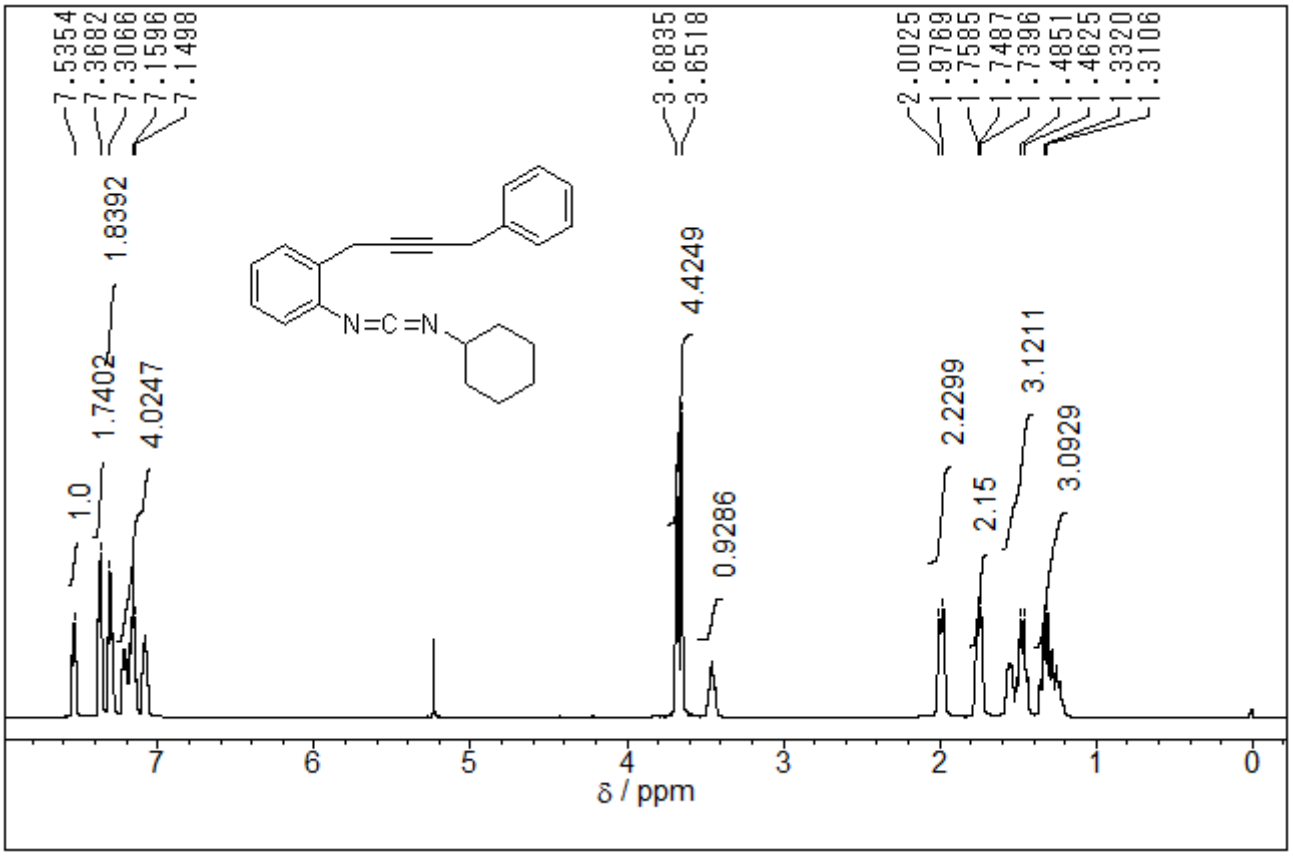
• [1]H-NMR spectrum of **1s**



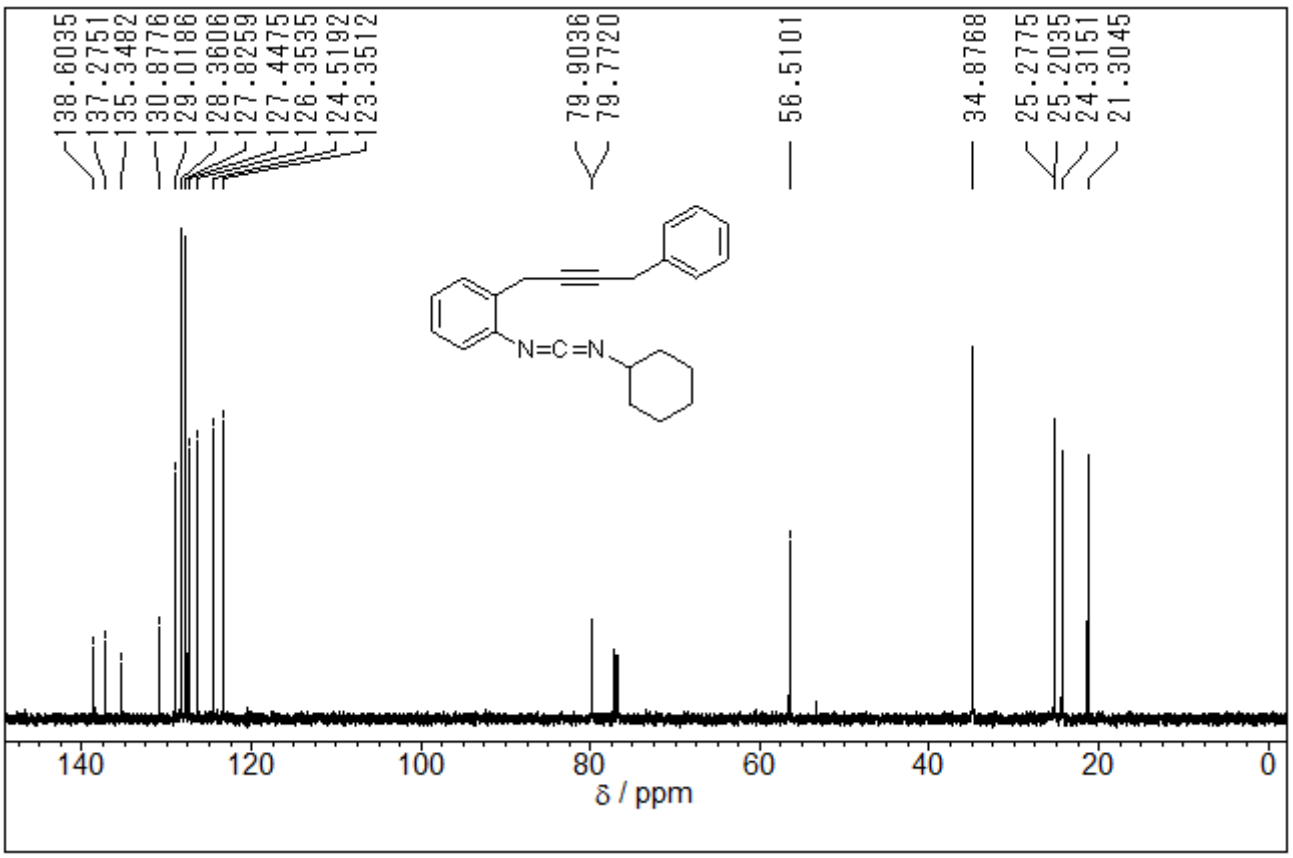
• [13]C-NMR spectrum of **1s**



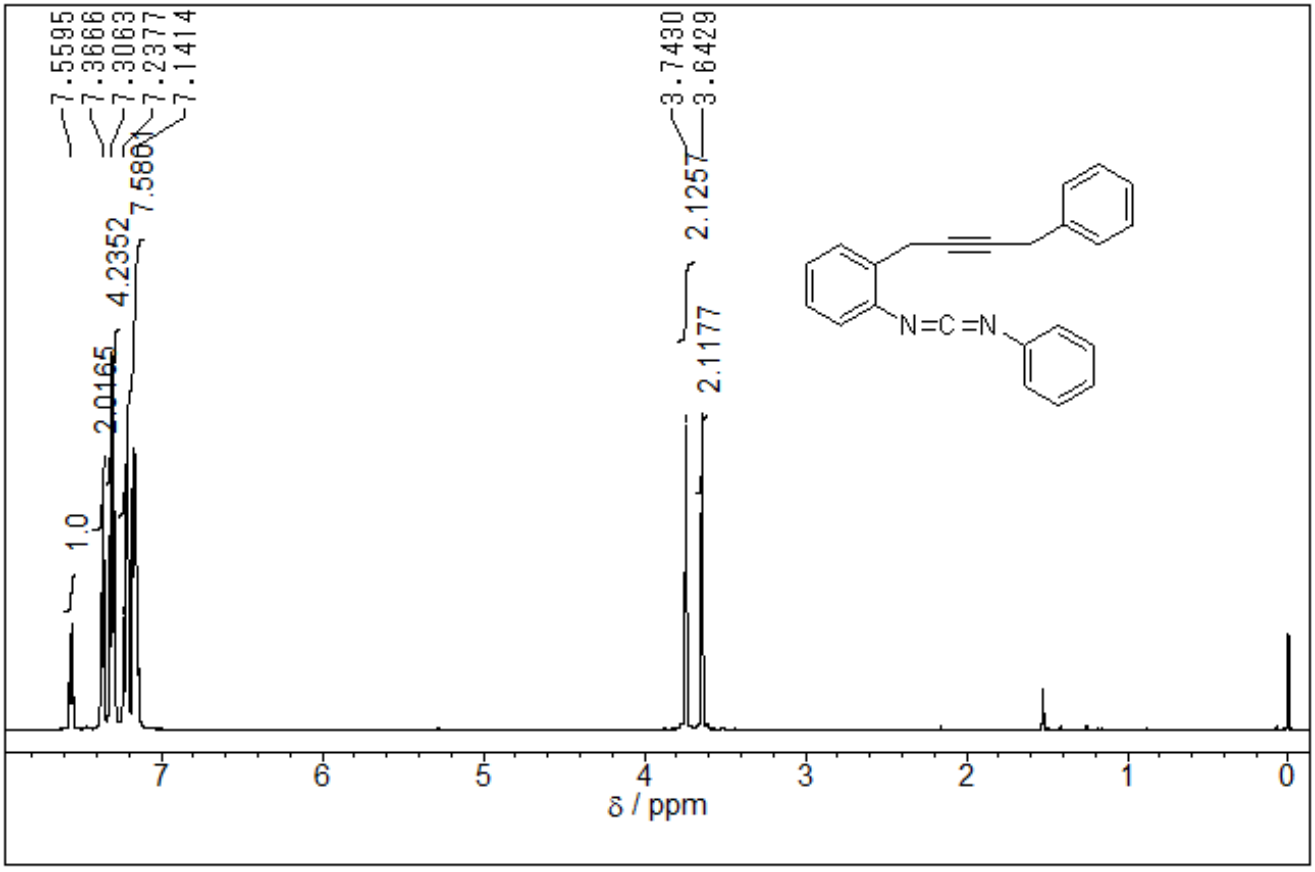
• ^{1}H-NMR spectrum of **1t**



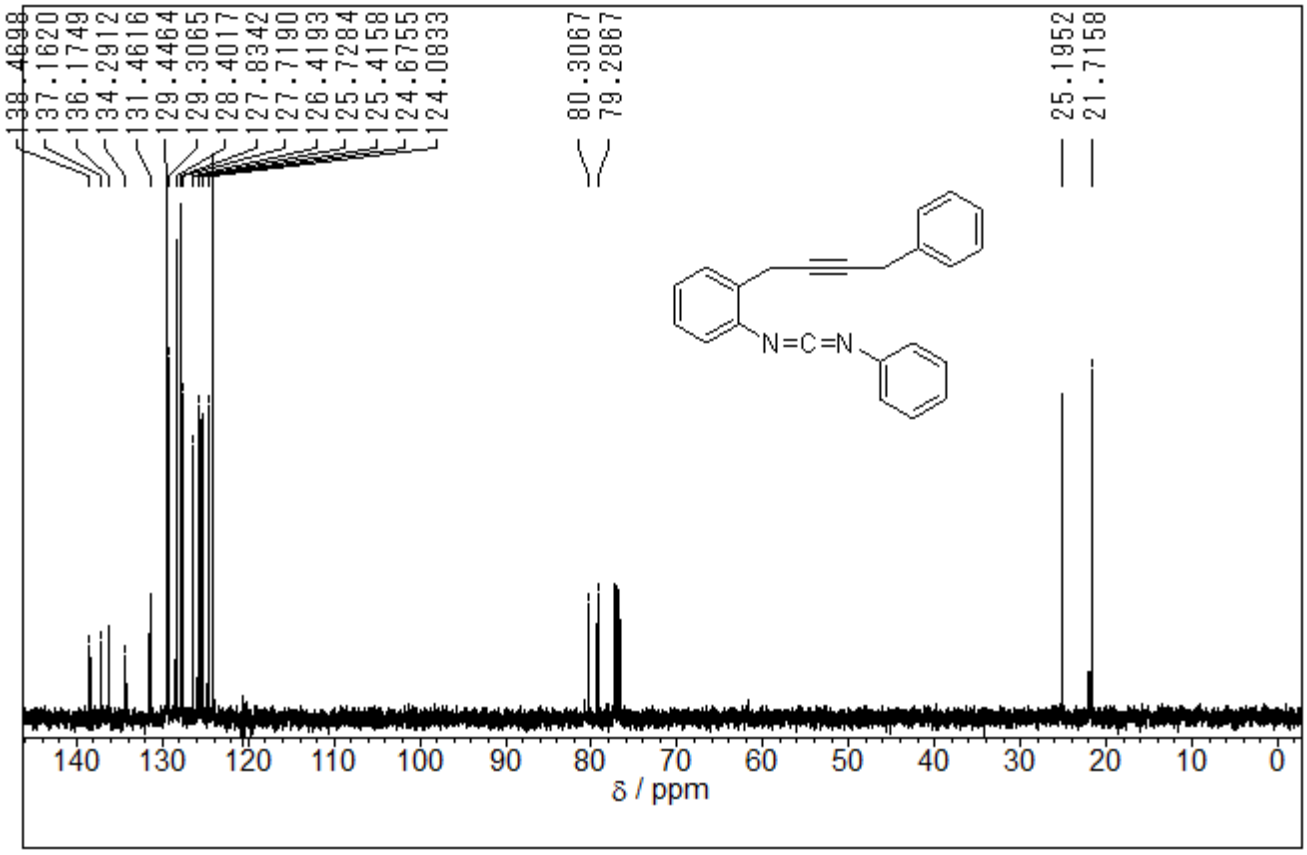
• ^{13}C-NMR spectrum of **1t**



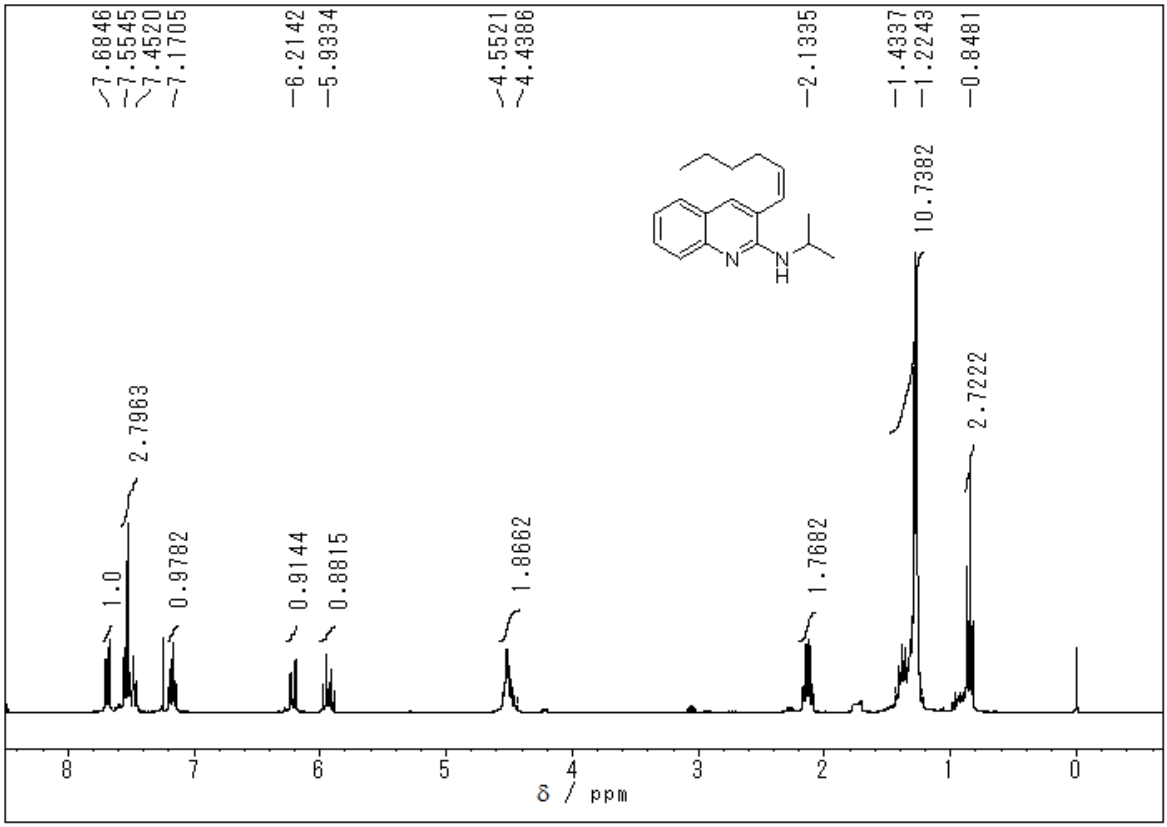
• ^{1}H-NMR spectrum of **1u**



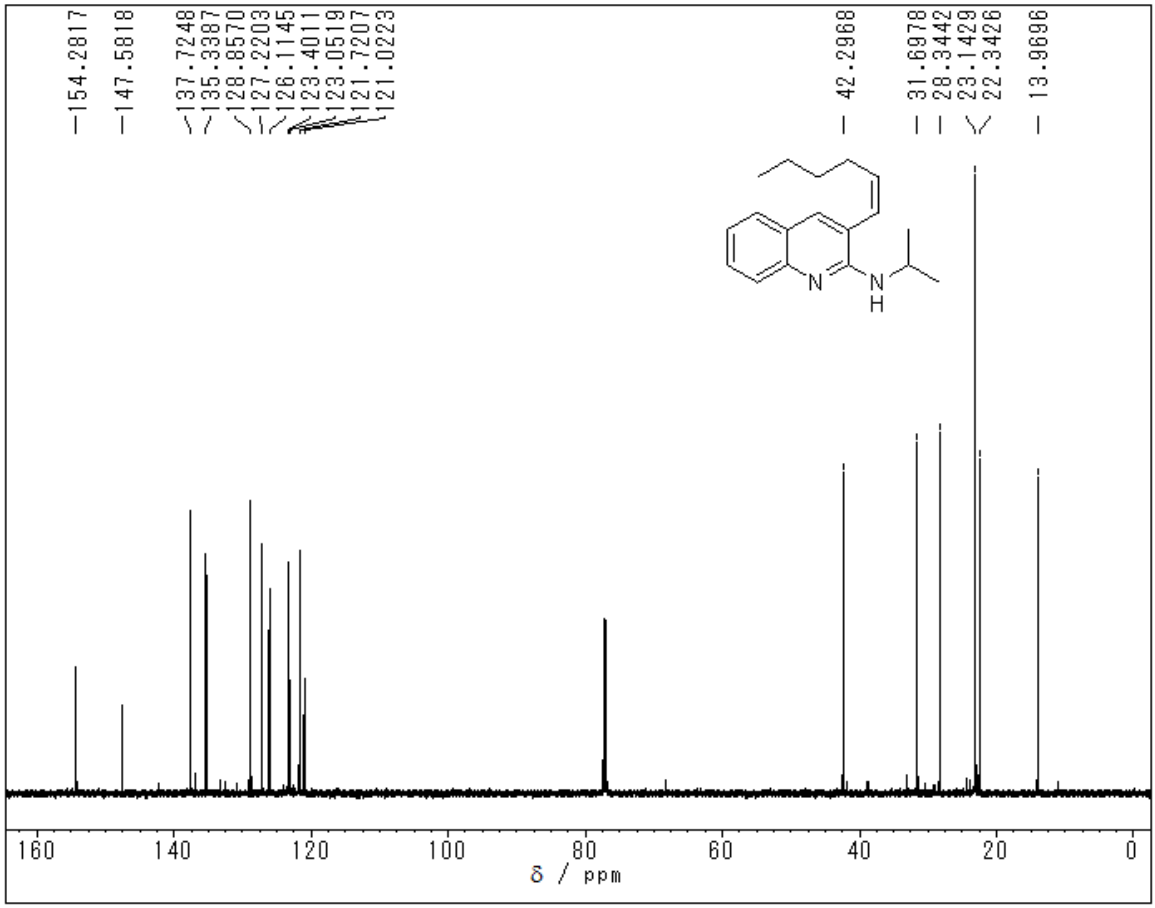
• ^{13}C-NMR spectrum of **1u**



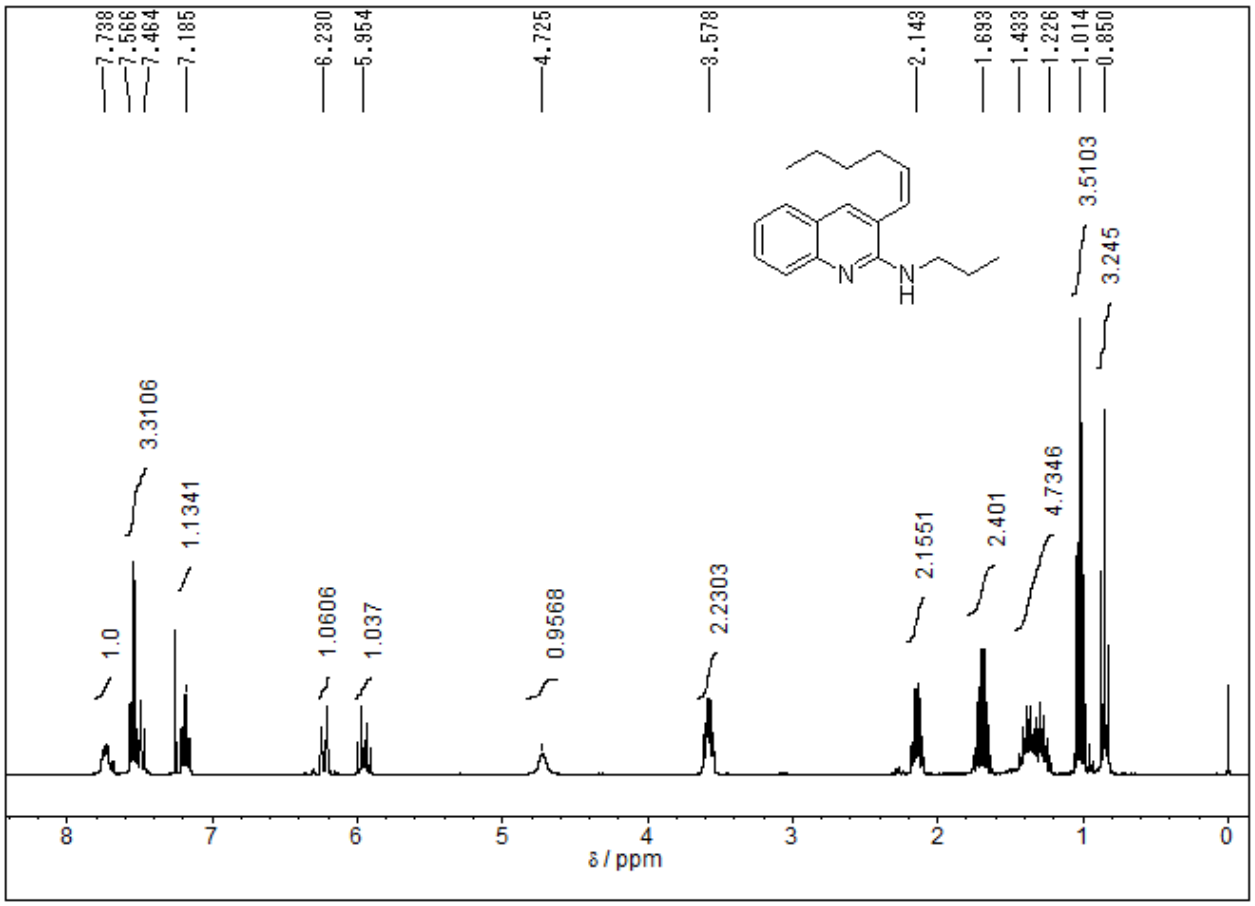
• ^{1}H-NMR spectrum of ***cis*-2a**



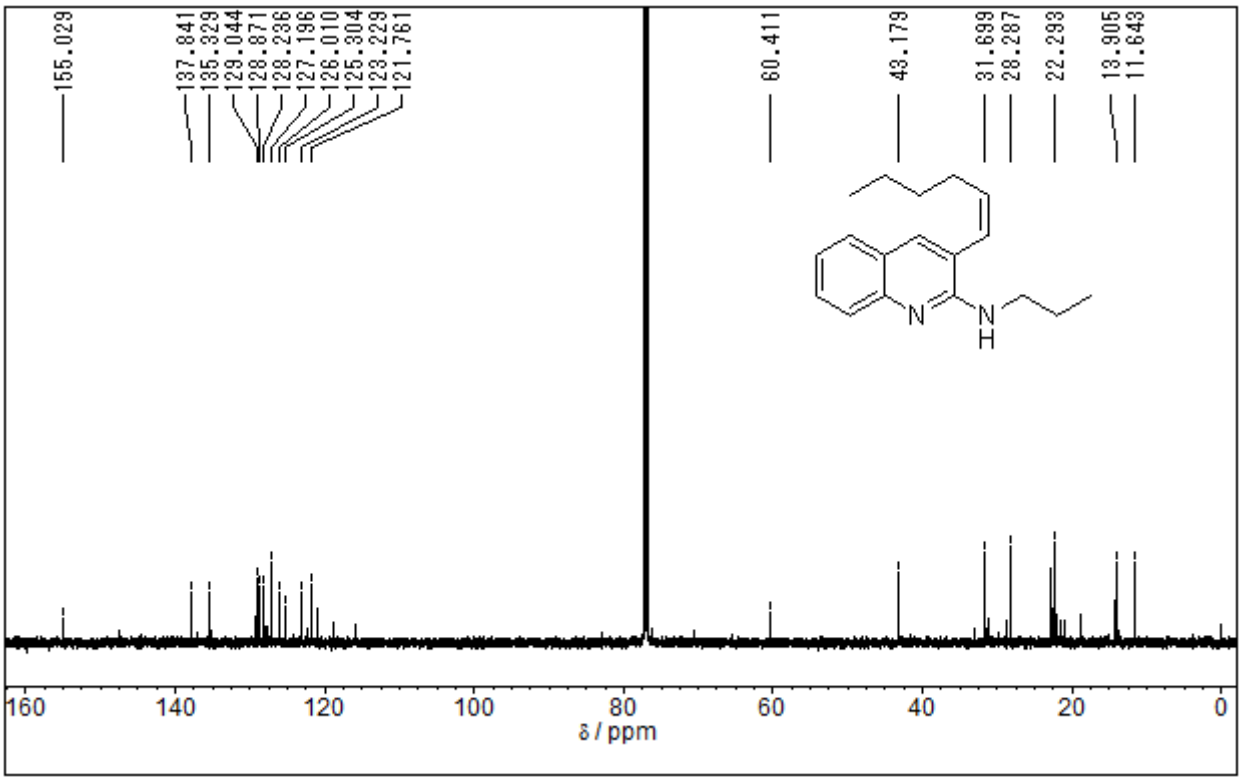
• ^{13}C-NMR spectrum of ***cis*-2a**



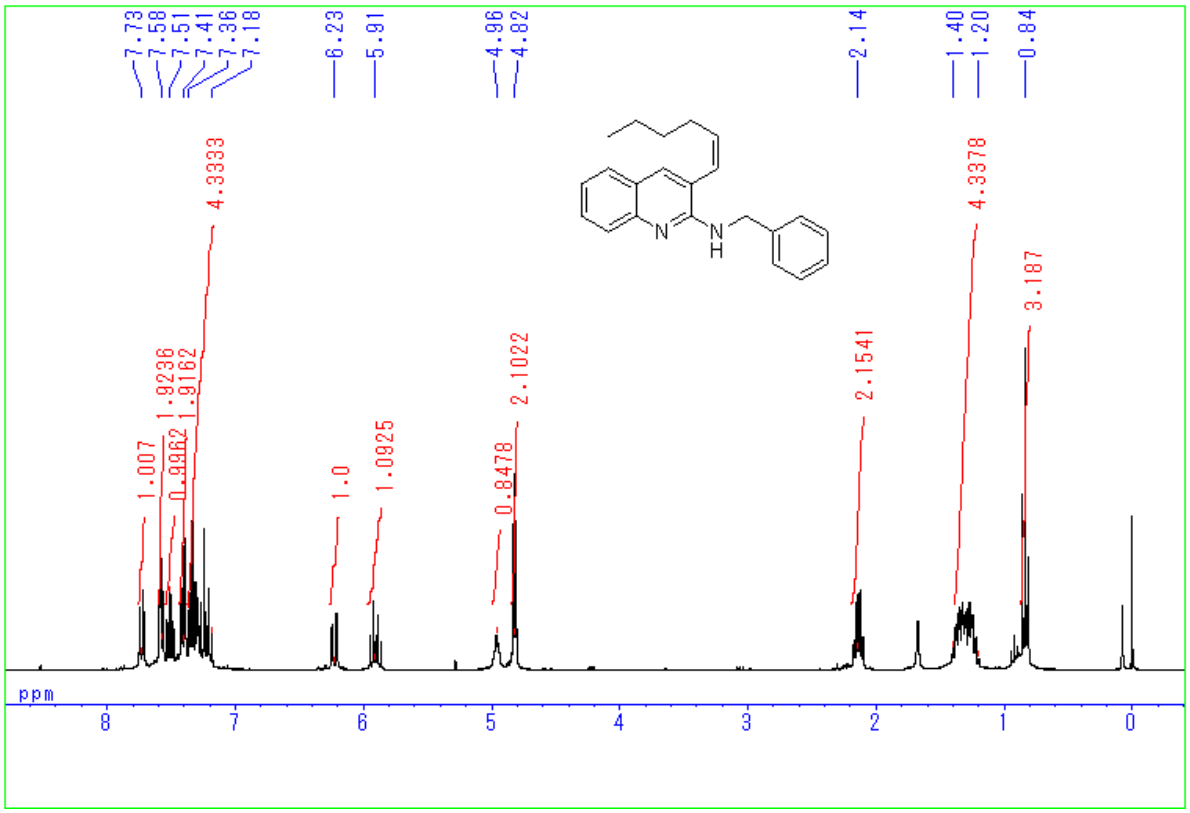
• ^{1}H-NMR spectrum of ***cis*-2b**



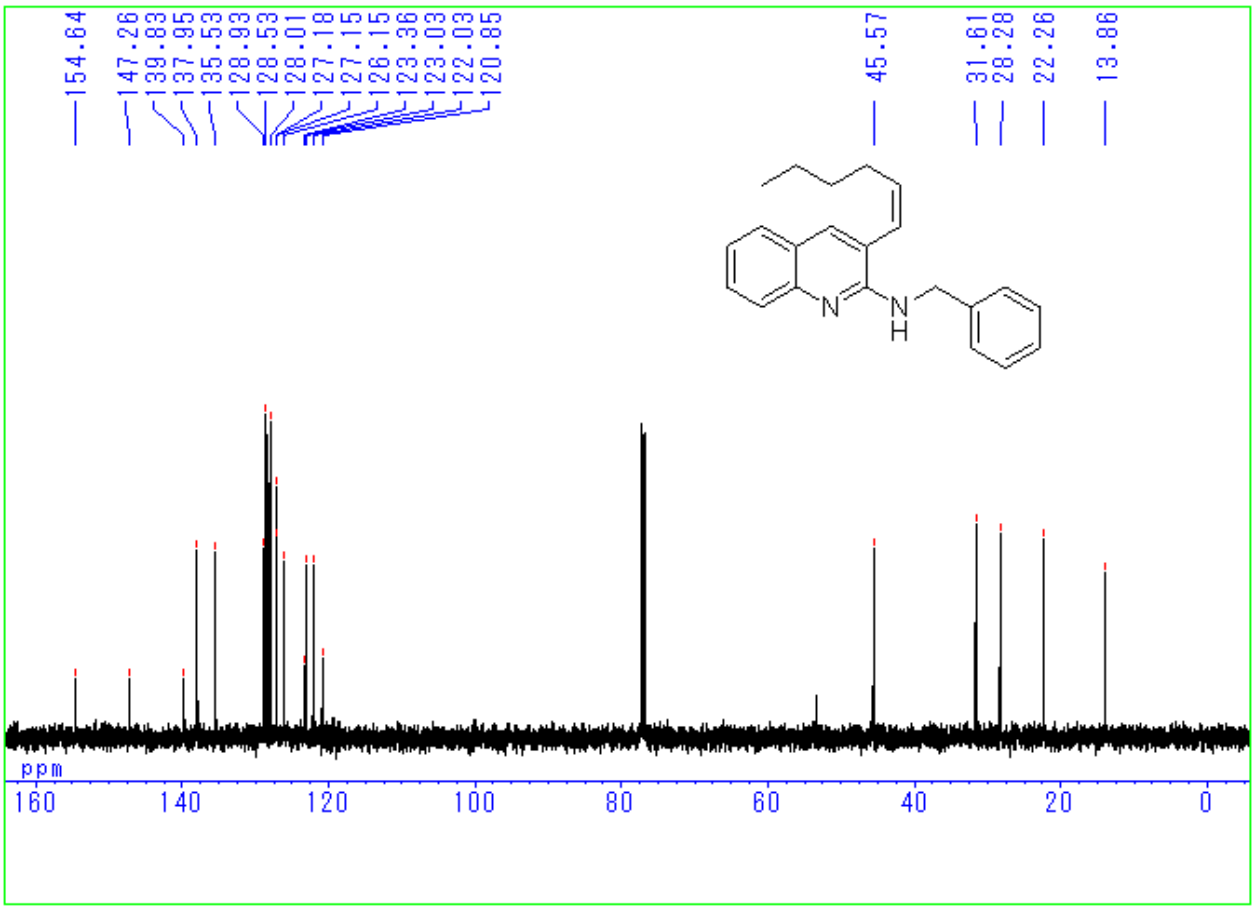
• ^{13}C-NMR spectrum of ***cis*-2b**



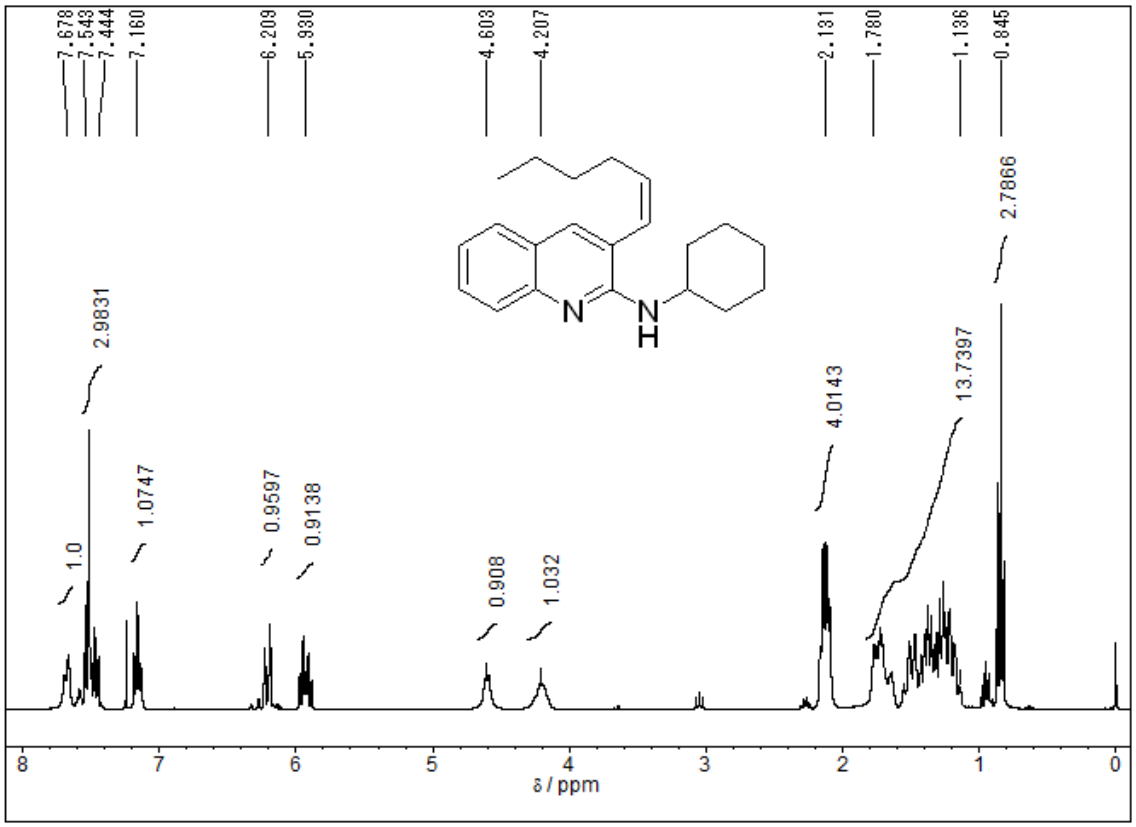
• ^{1}H-NMR spectrum of ***cis*-2c**



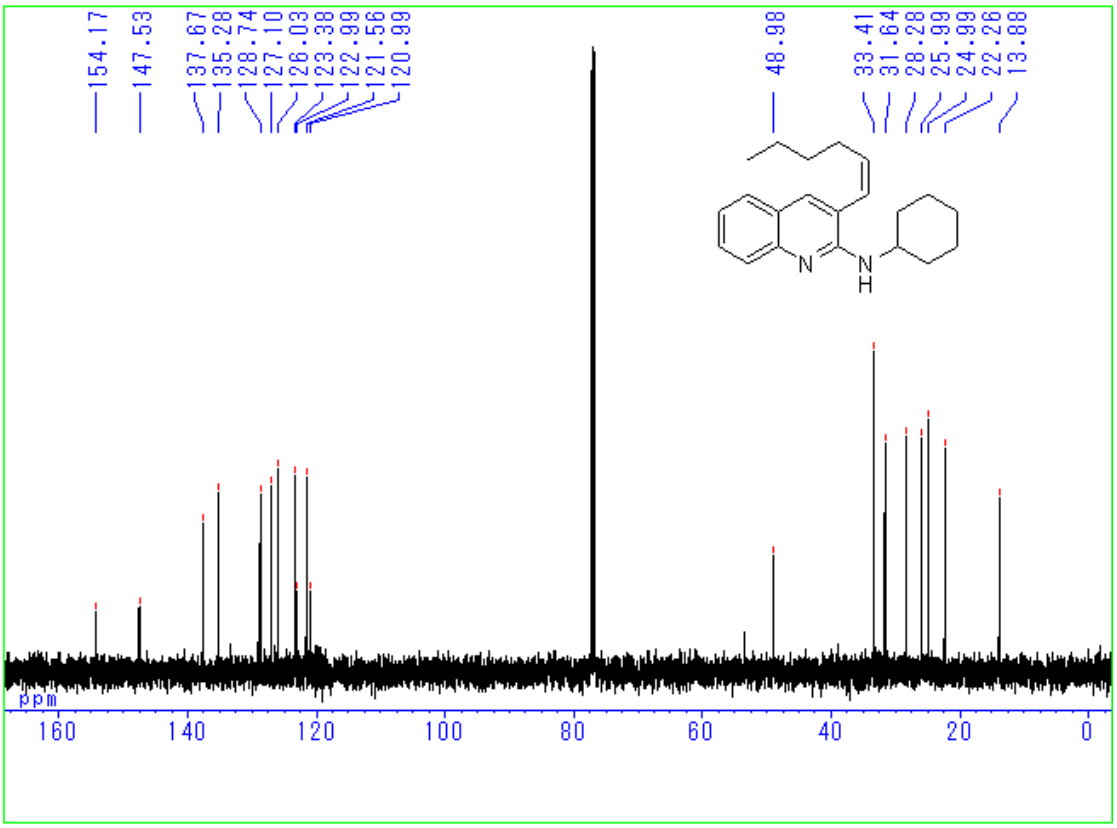
• ^{13}C-NMR spectrum of ***cis*-2c**



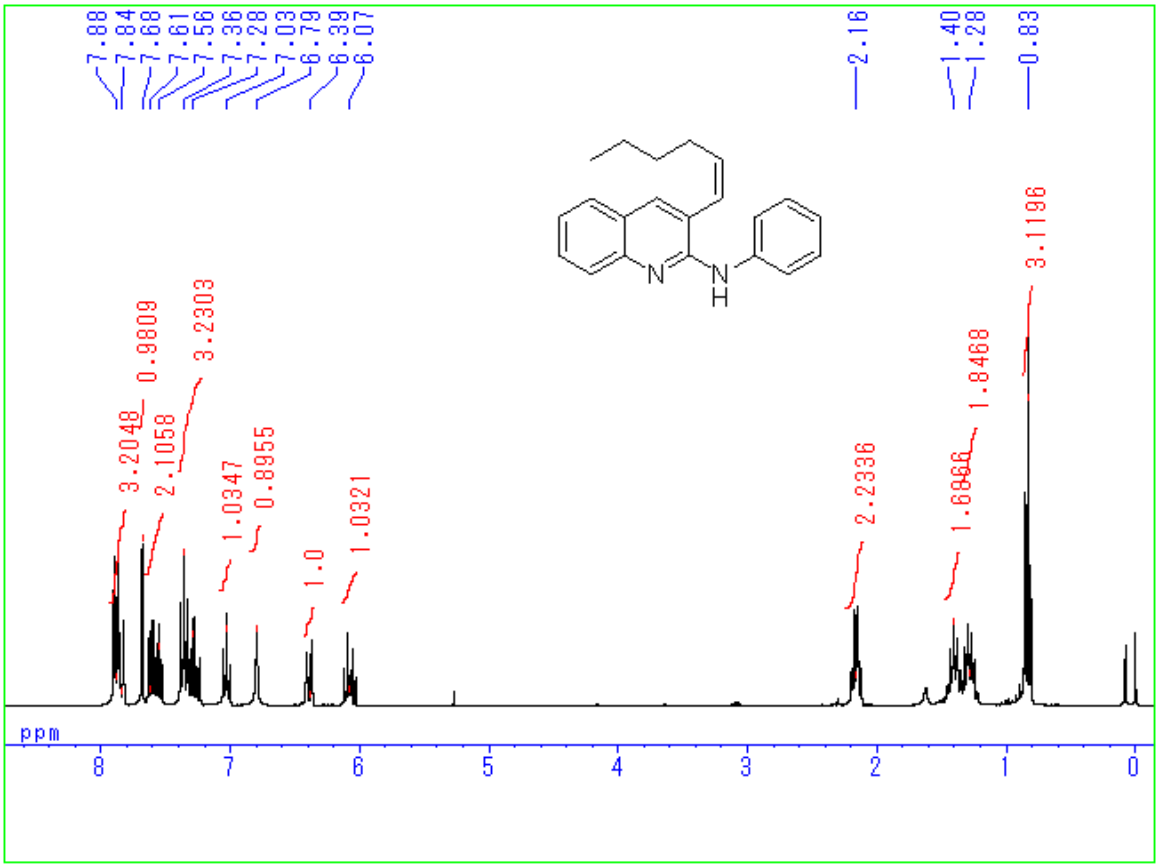
• ^{1}H-NMR spectrum of ***cis*-2d**



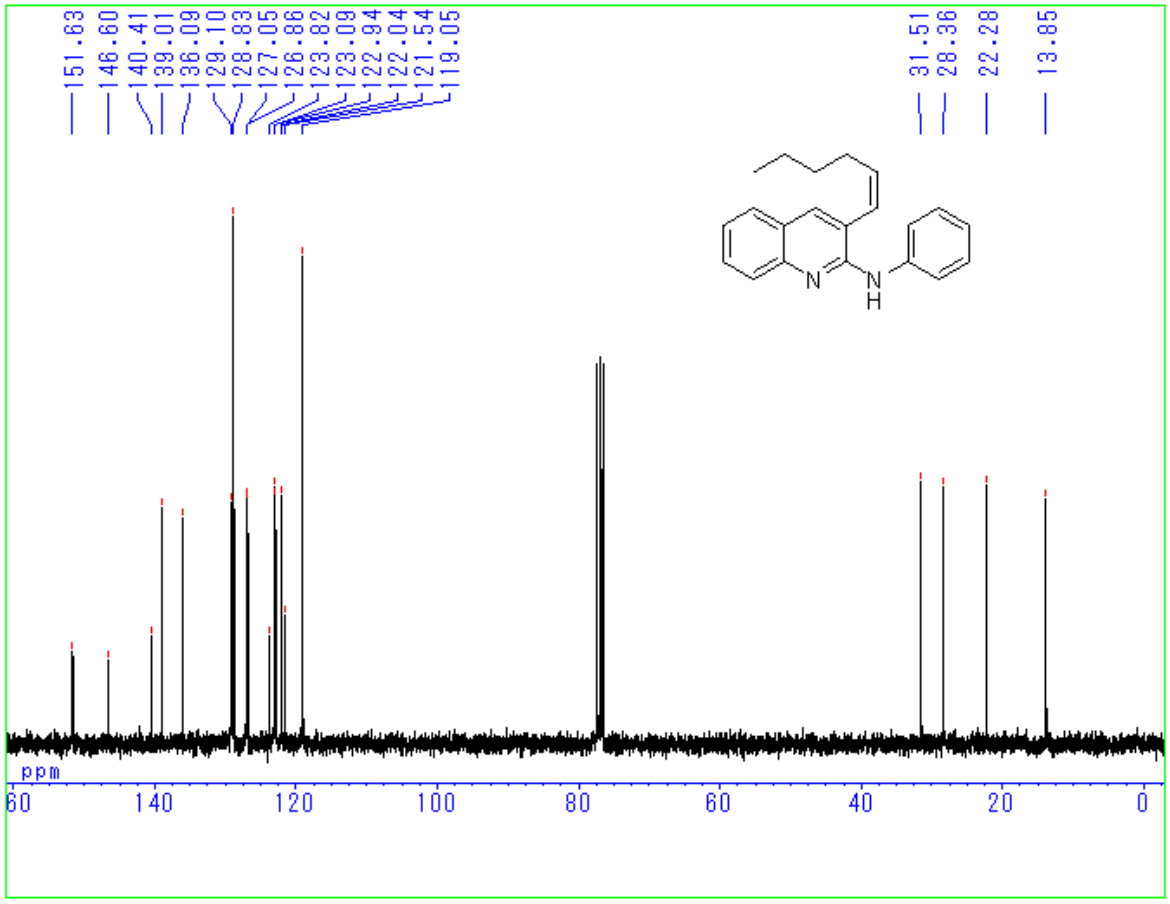
• ^{13}C-NMR spectrum of ***cis*-2d**



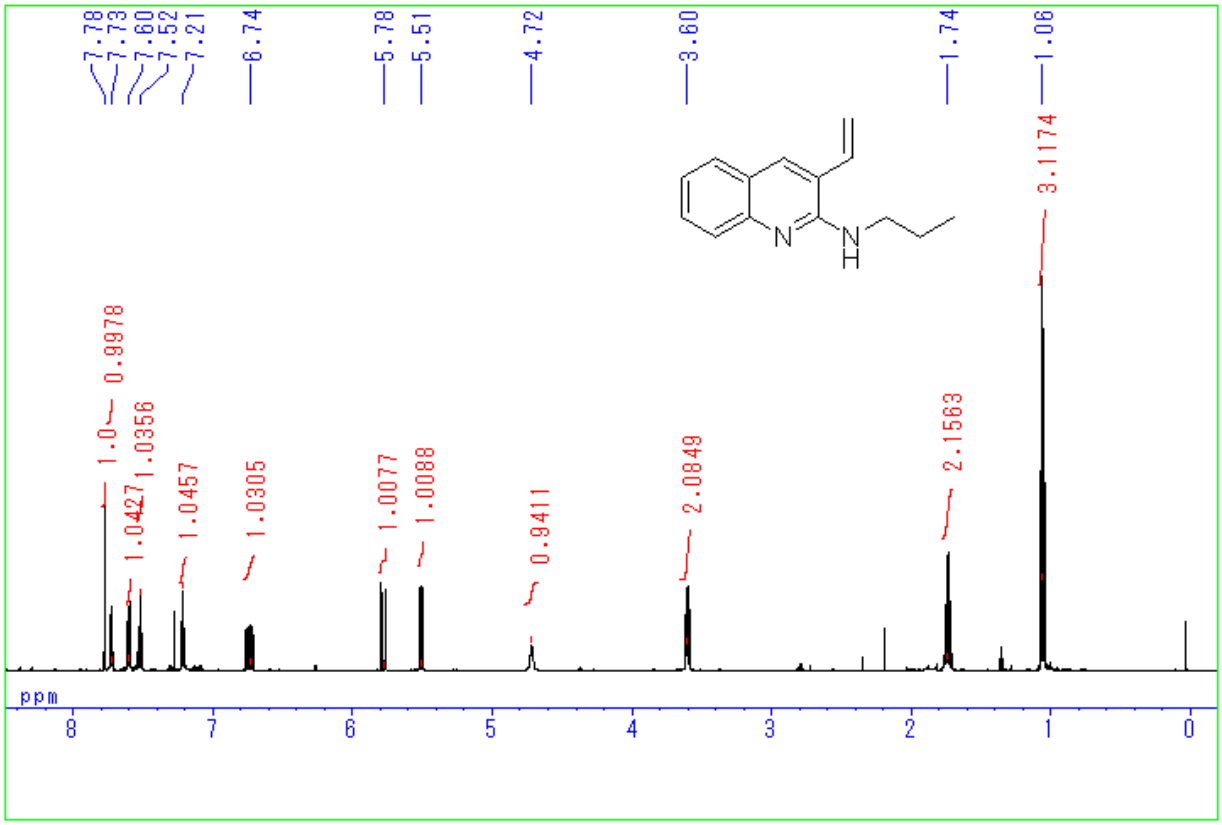
• ^{1}H-NMR spectrum of ***cis*-2f**



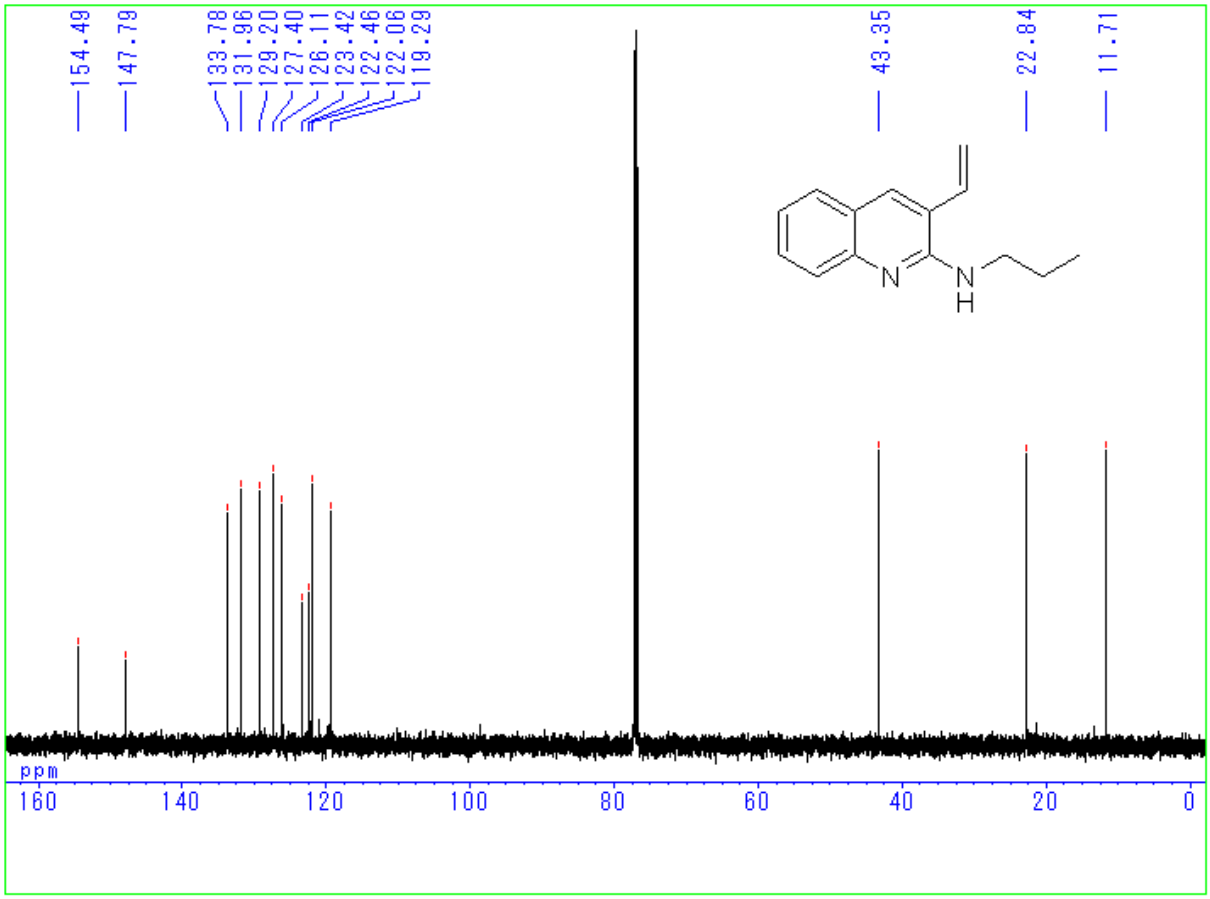
• ^{13}C-NMR spectrum of ***cis*-2f**



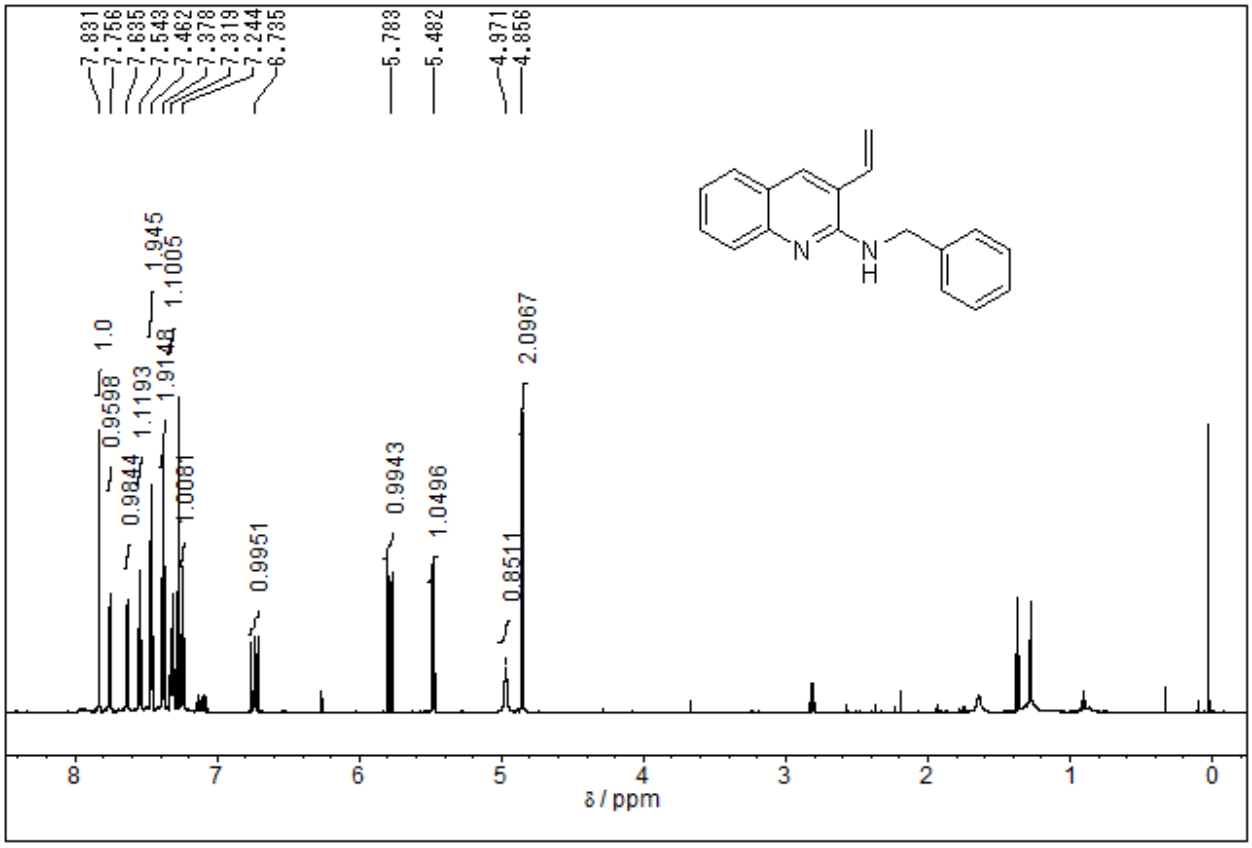
• ^{1}H-NMR spectrum of **2g**



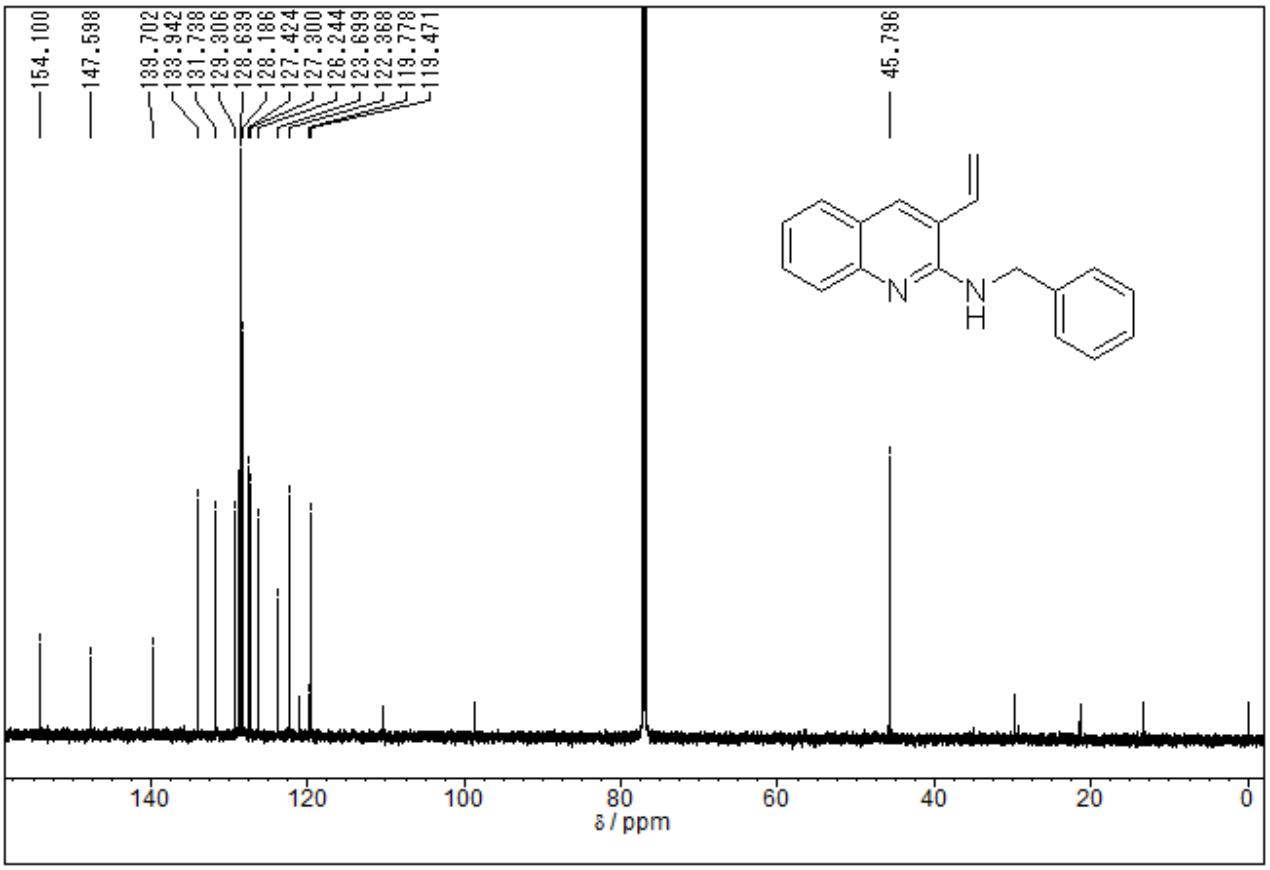
• ^{13}C-NMR spectrum of **2g**



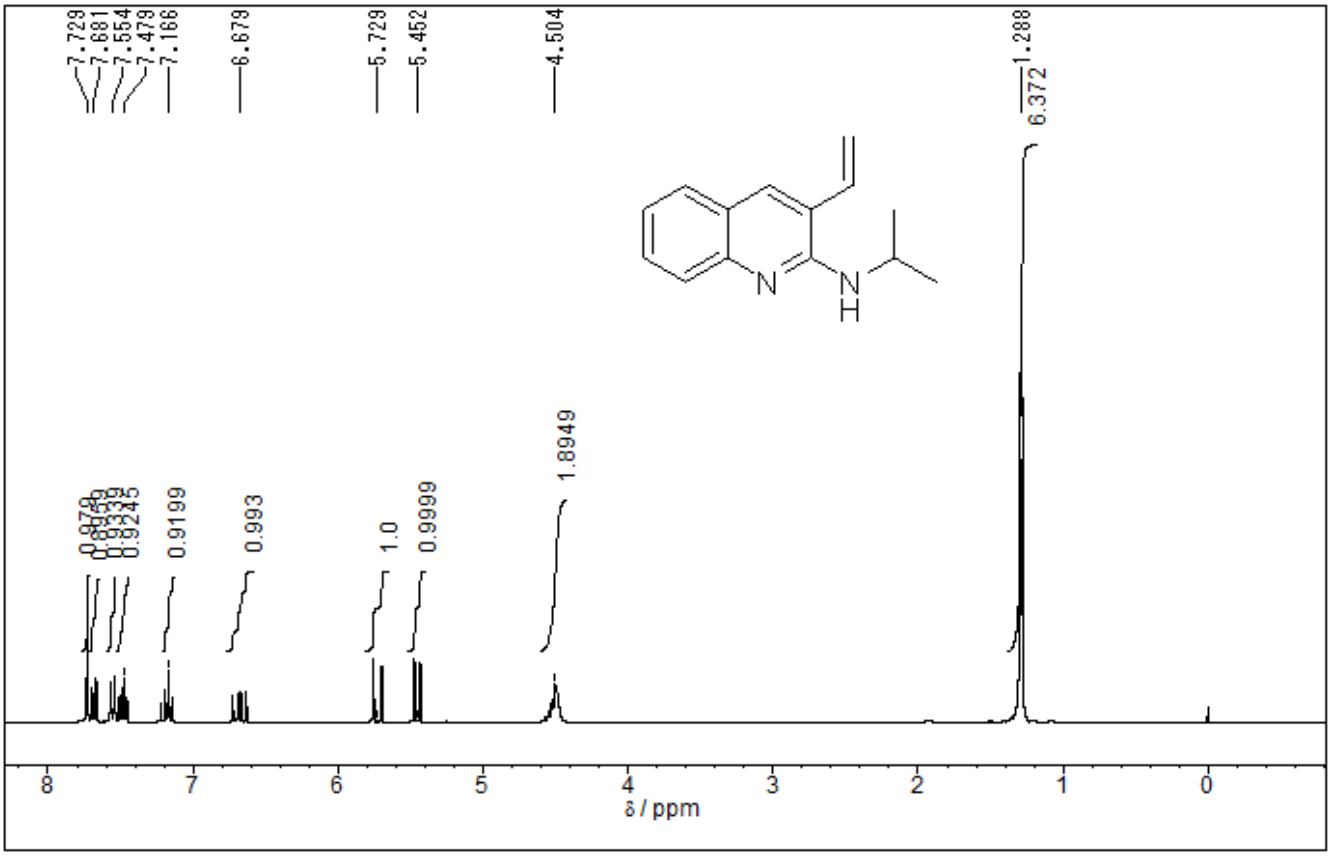
• ^{1}H-NMR spectrum of **2h**



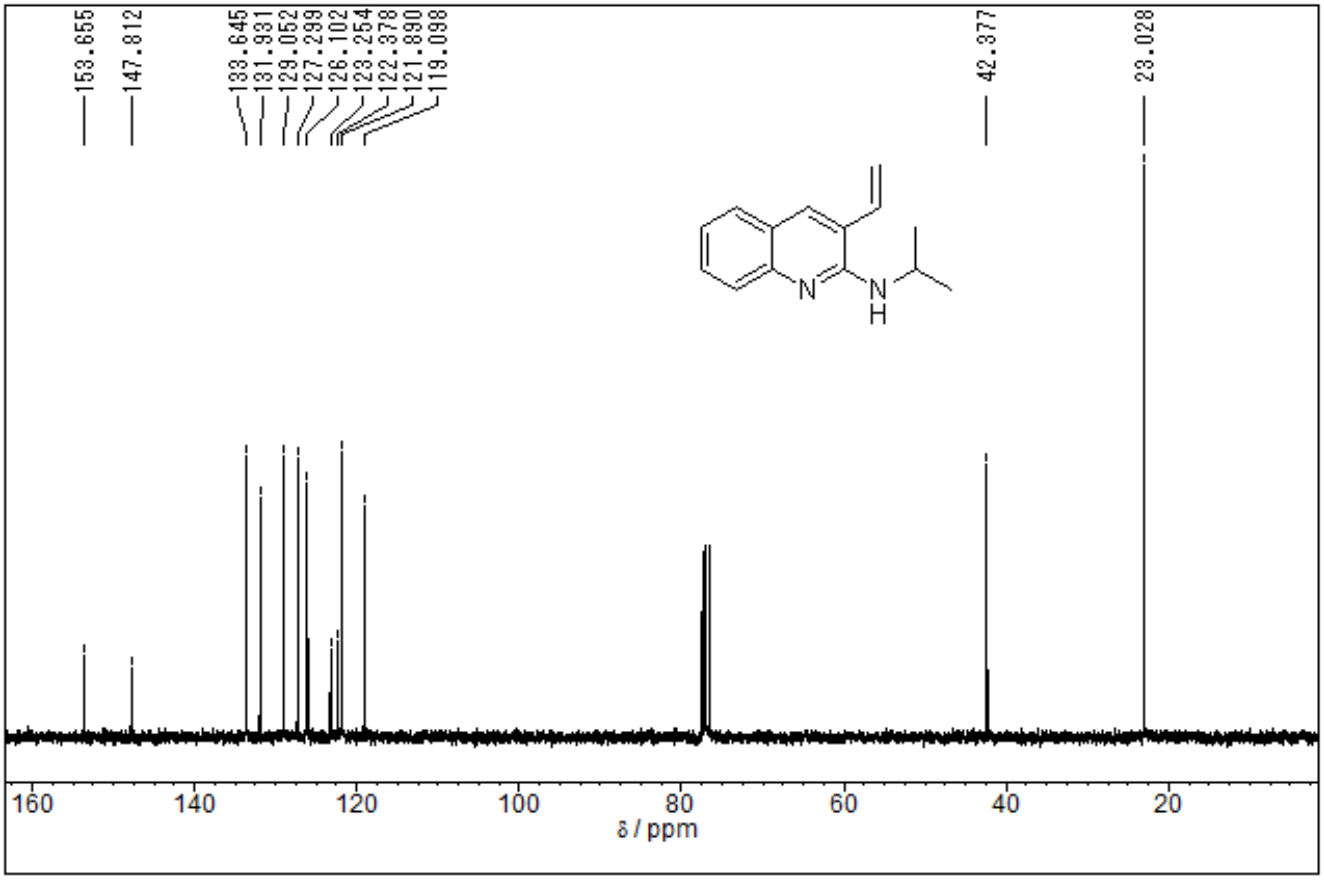
• ^{13}C-NMR spectrum of **2h**



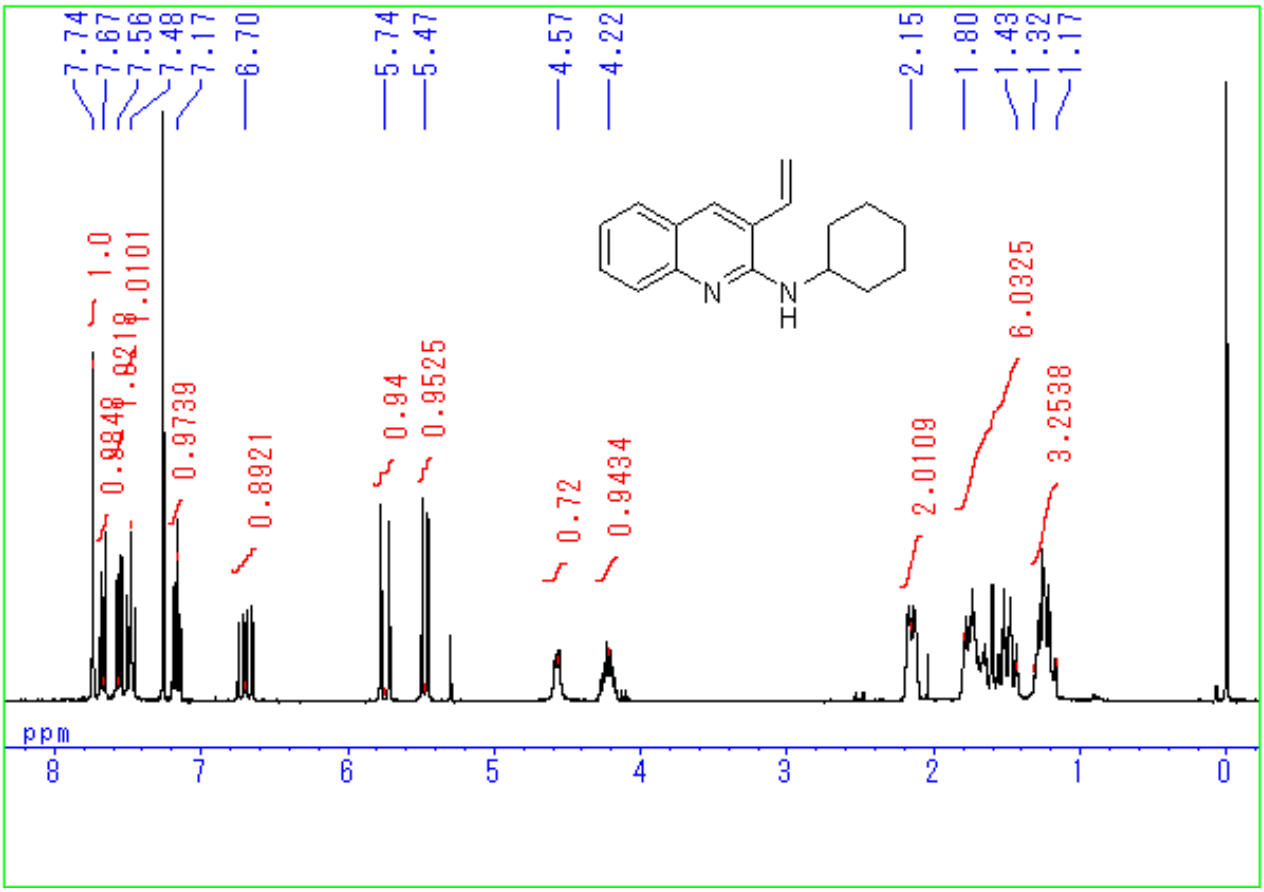
• ^{1}H-NMR spectrum of **2i**



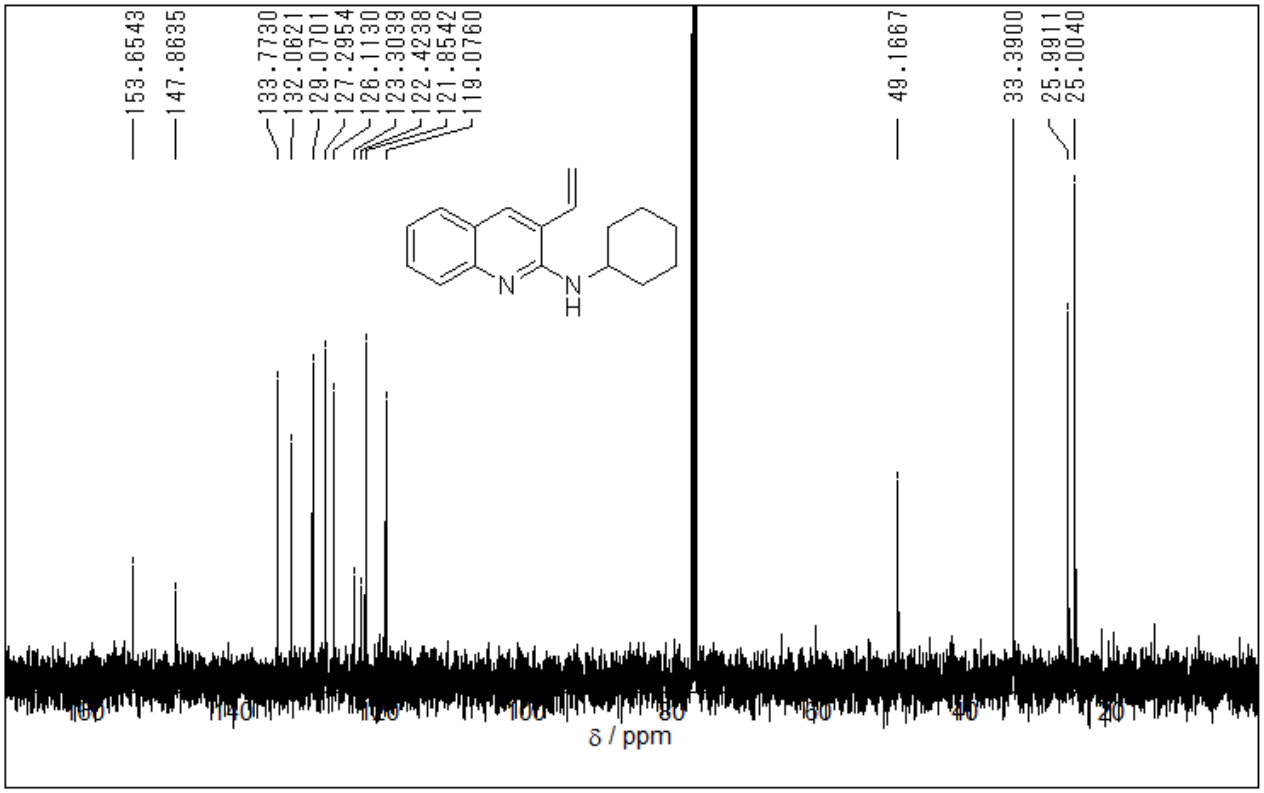
• ^{13}C-NMR spectrum of **2i**



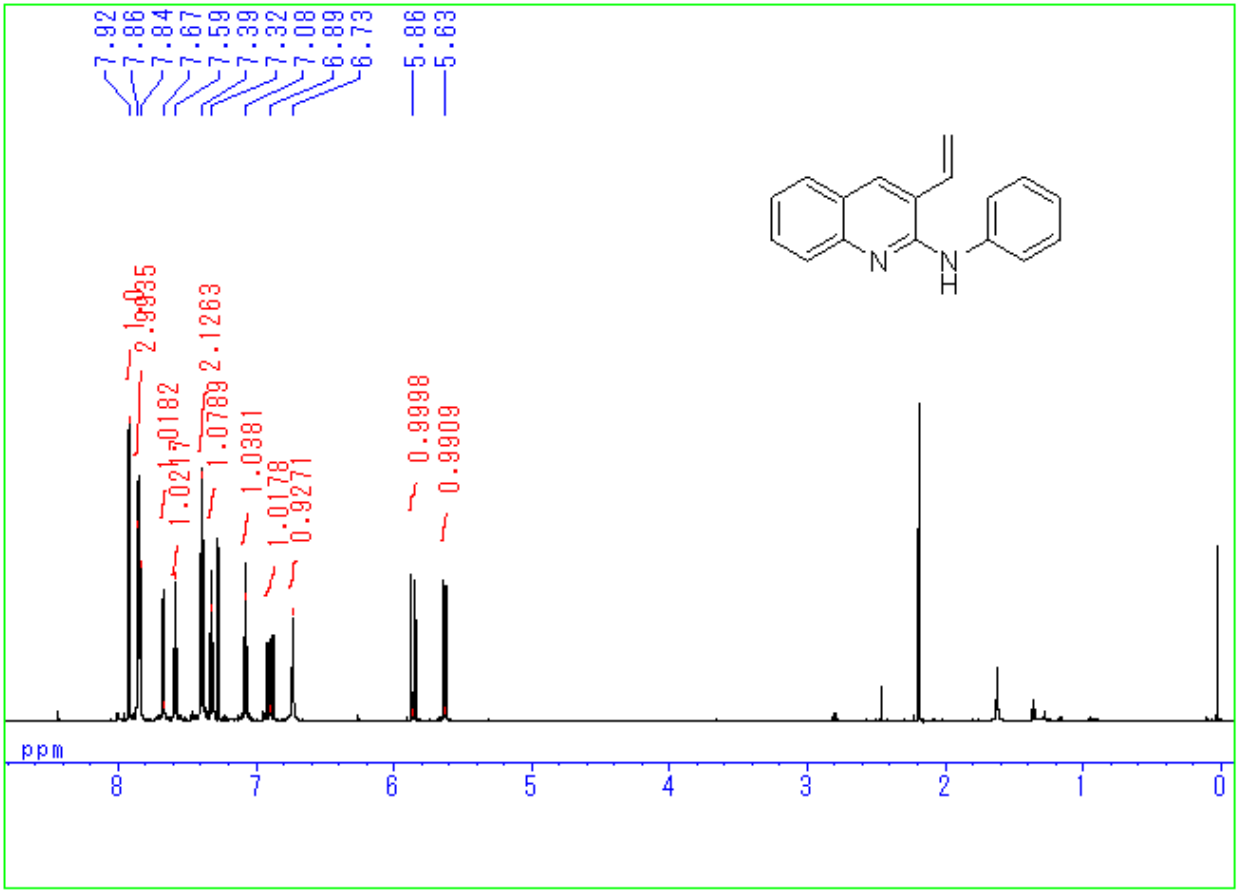
• ^{1}H-NMR spectrum of **2j**



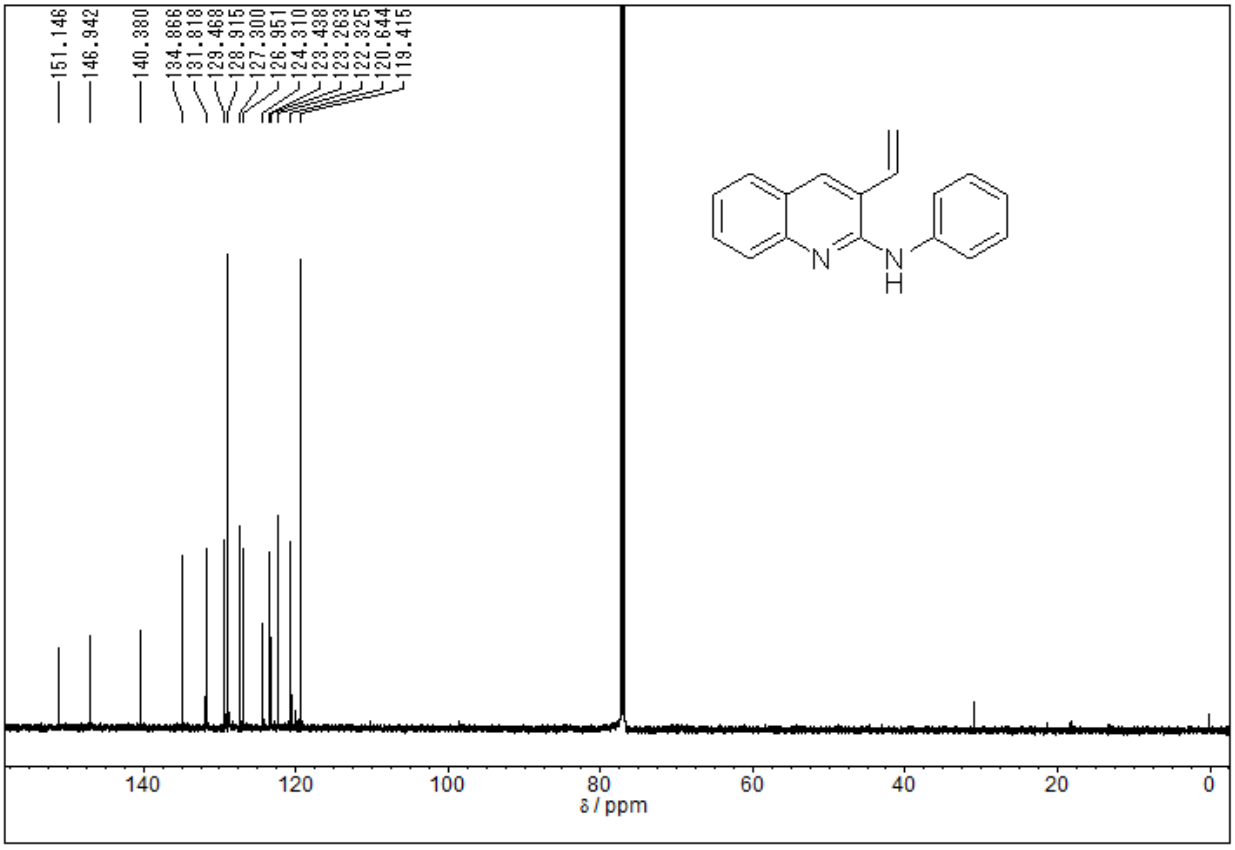
• ^{13}C-NMR spectrum of **2j**



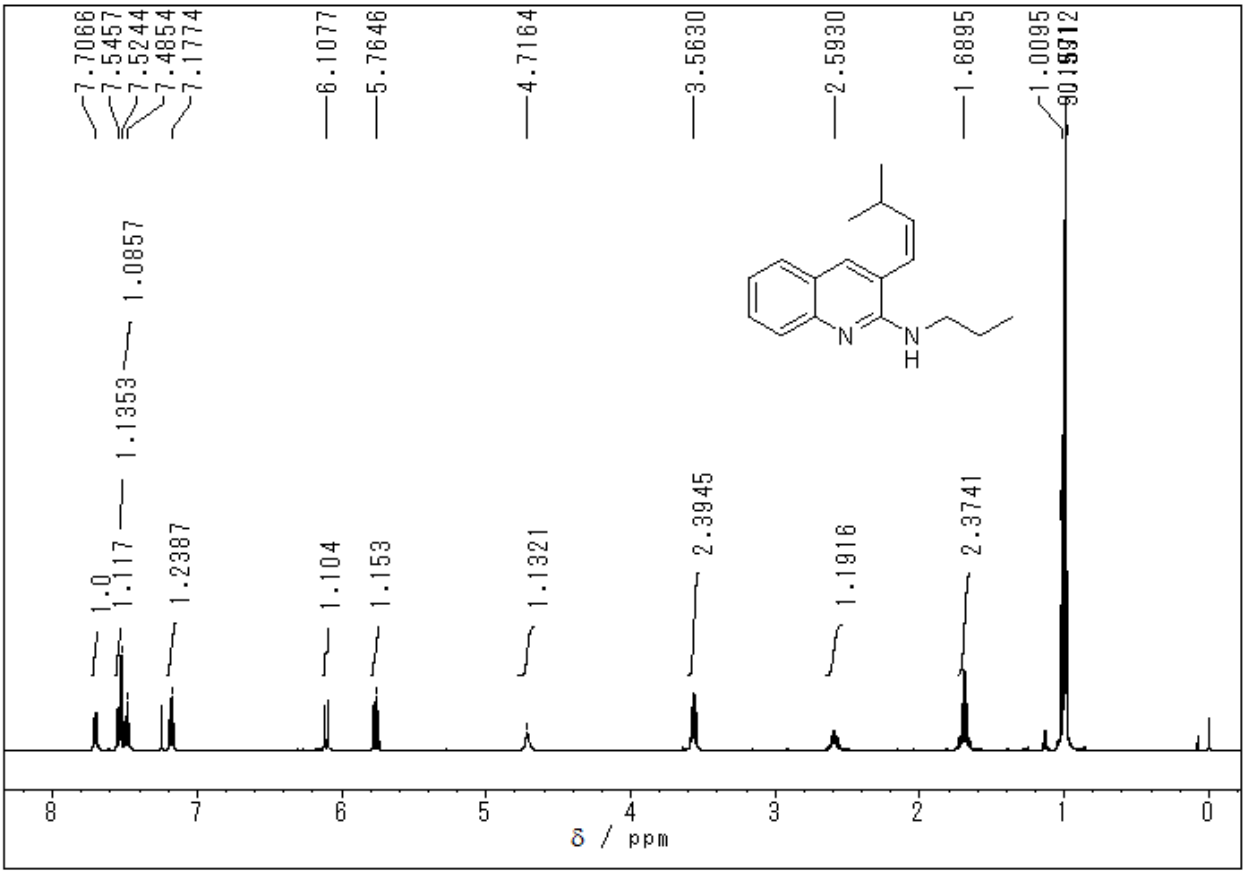
• ^{1}H-NMR spectrum of **2k**



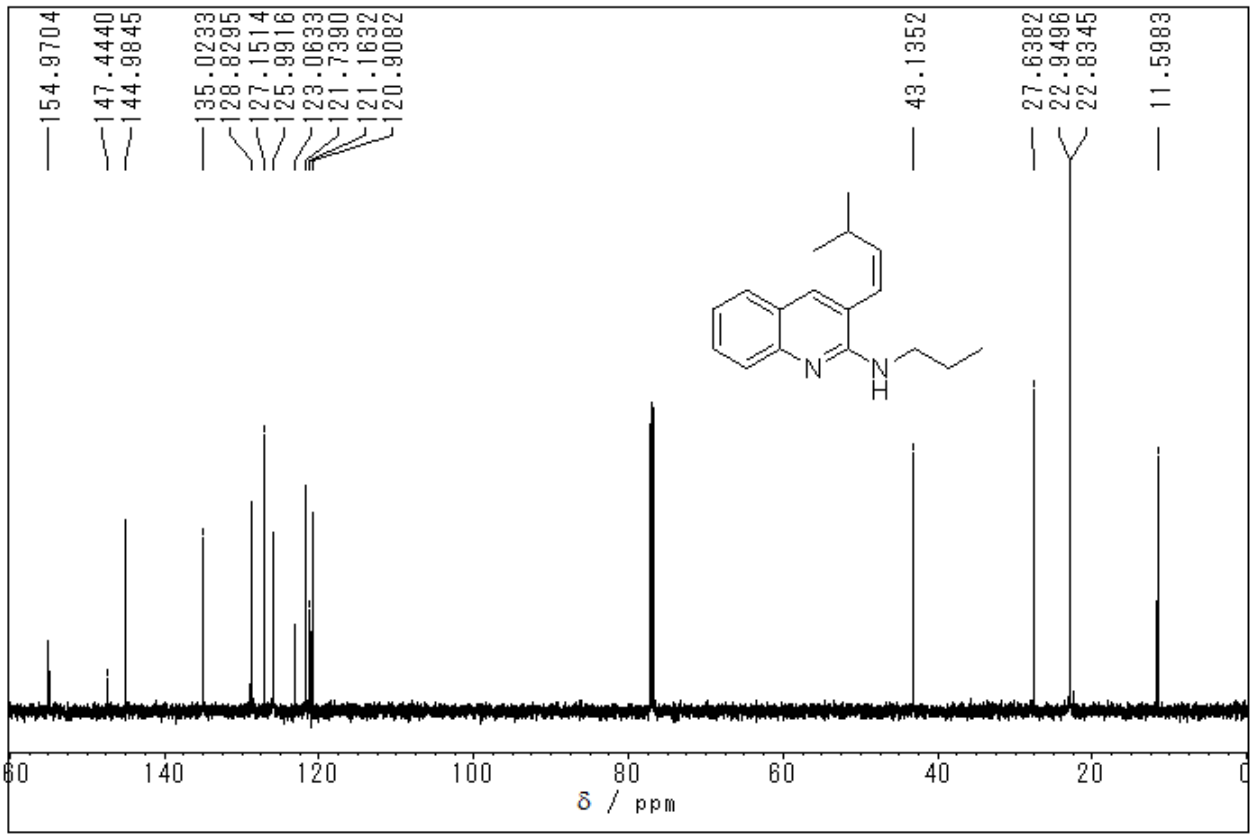
• ^{13}C-NMR spectrum of **2k**



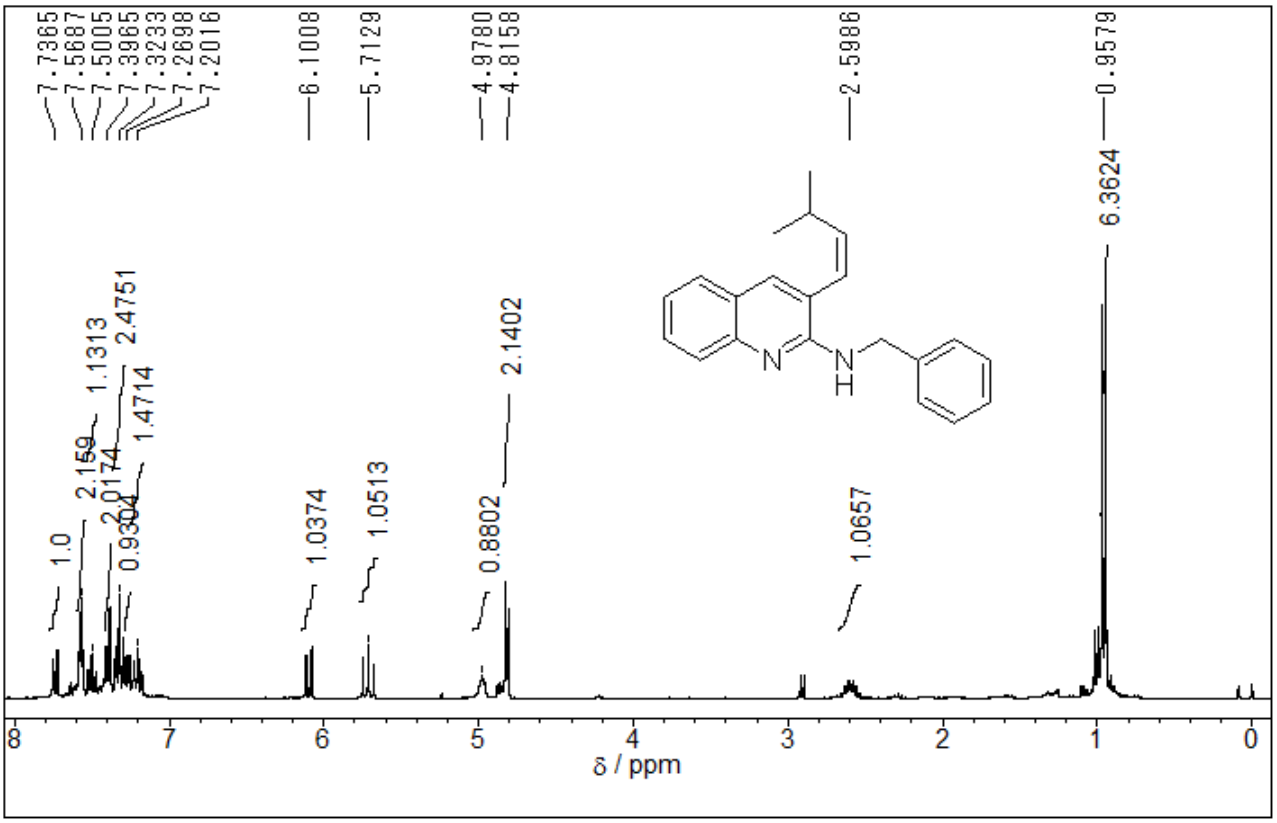
• ^{1}H-NMR spectrum of ***cis*-2l**



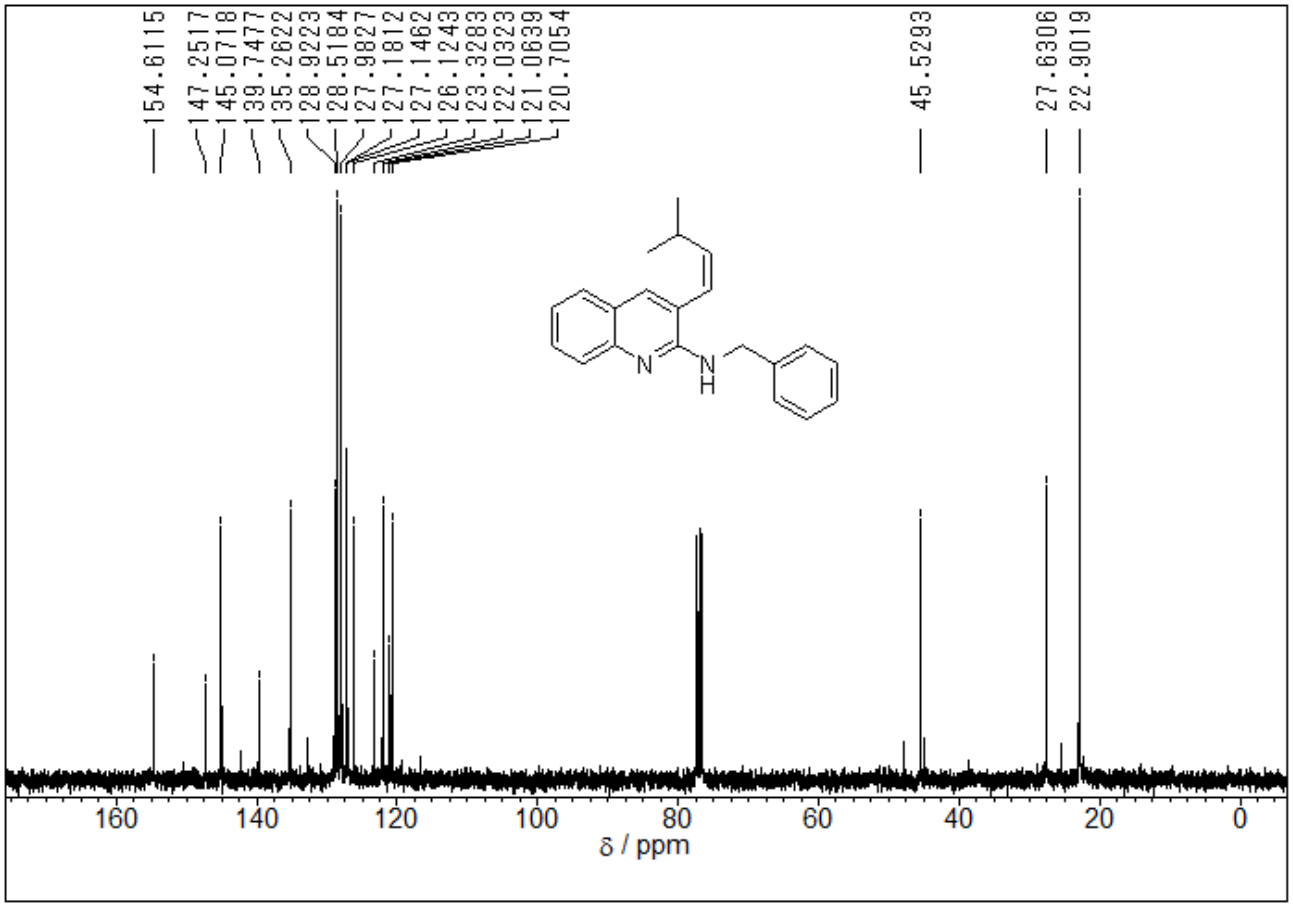
• ^{13}C-NMR spectrum of ***cis*-2l**



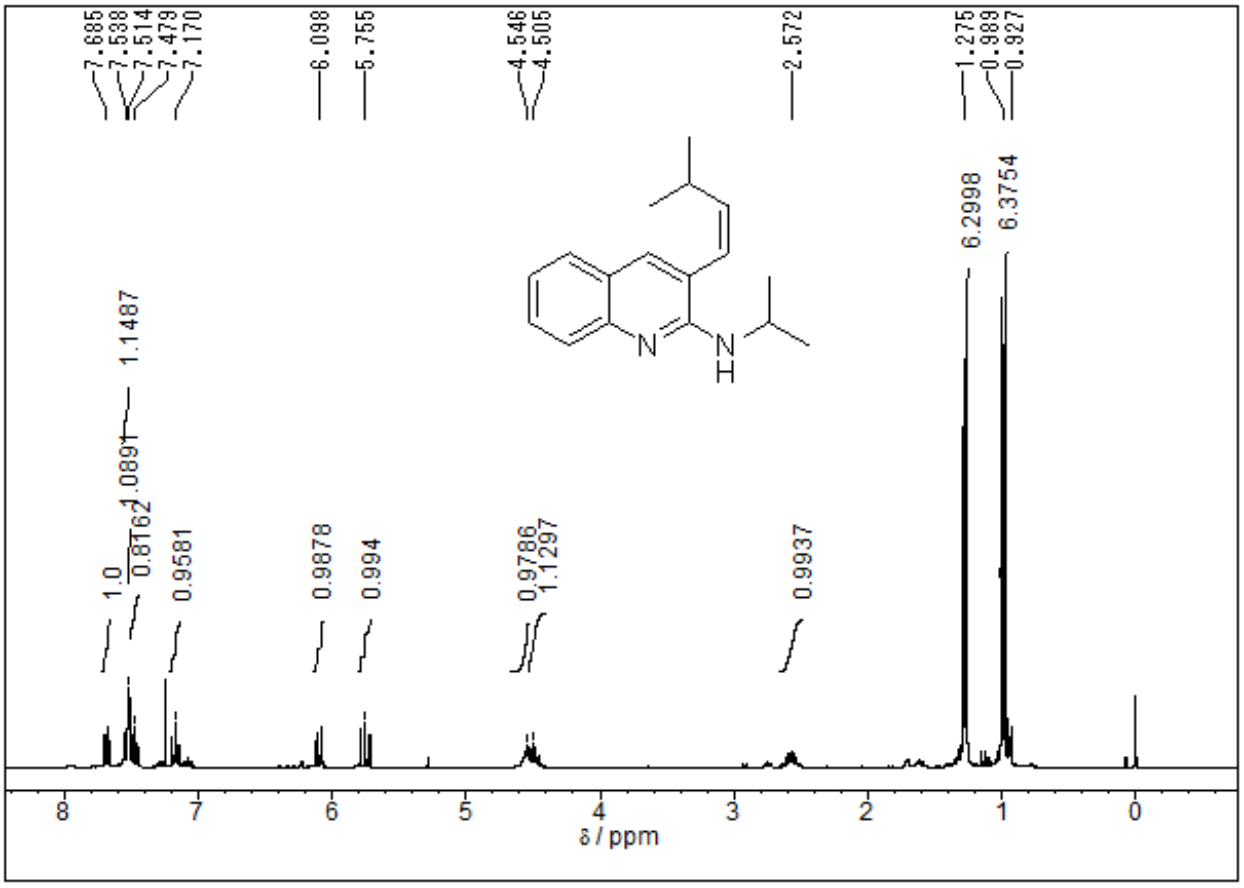
• ^{1}H-NMR spectrum of ***cis*-2m**



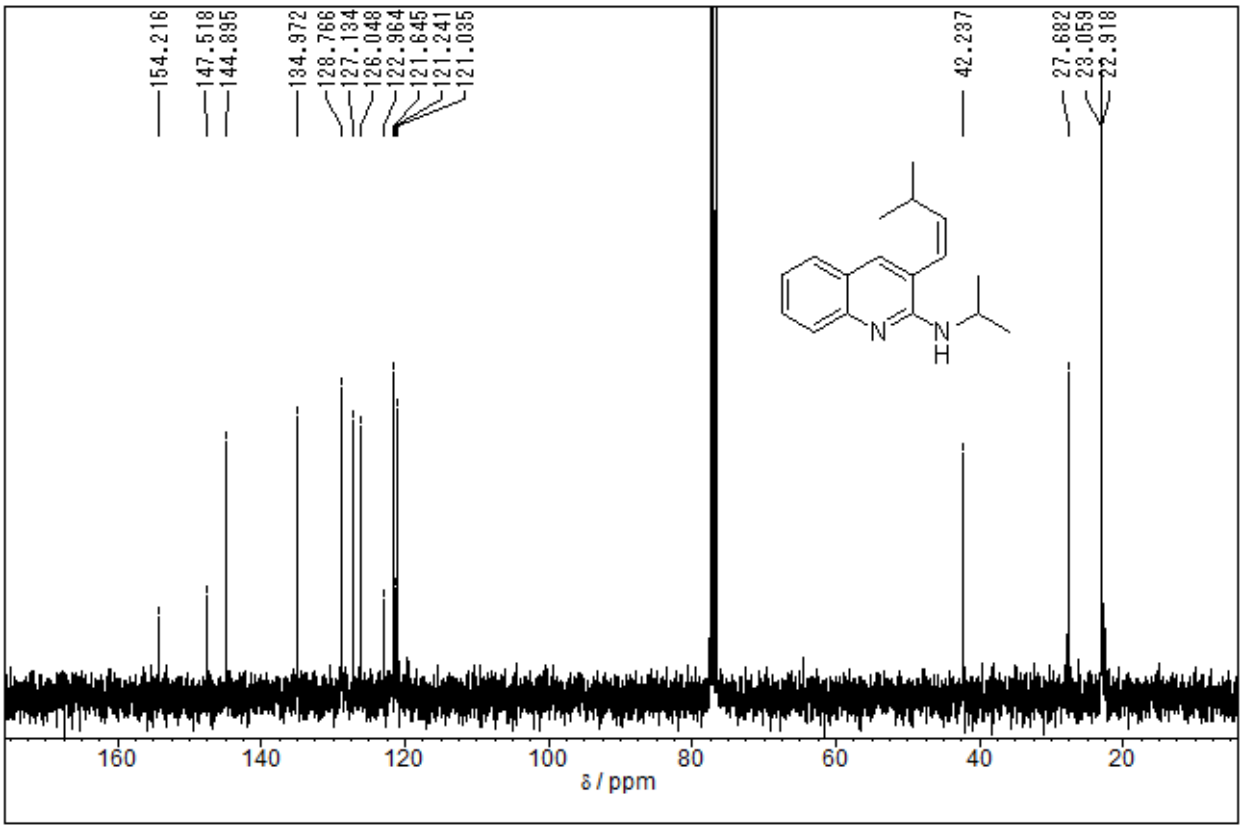
• ^{13}C-NMR spectrum of ***cis*-2m**



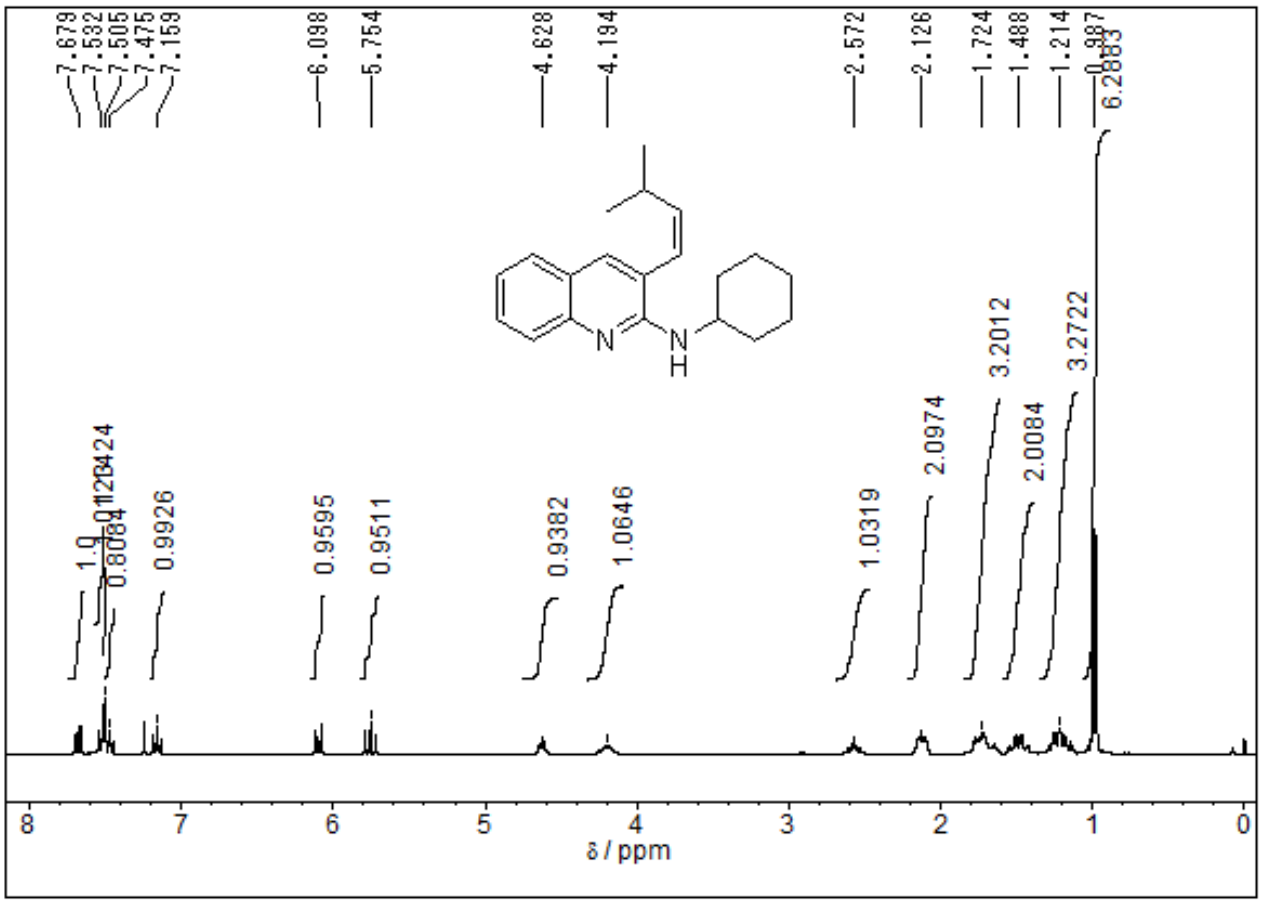
• ^{1}H-NMR spectrum of ***cis*-2n**



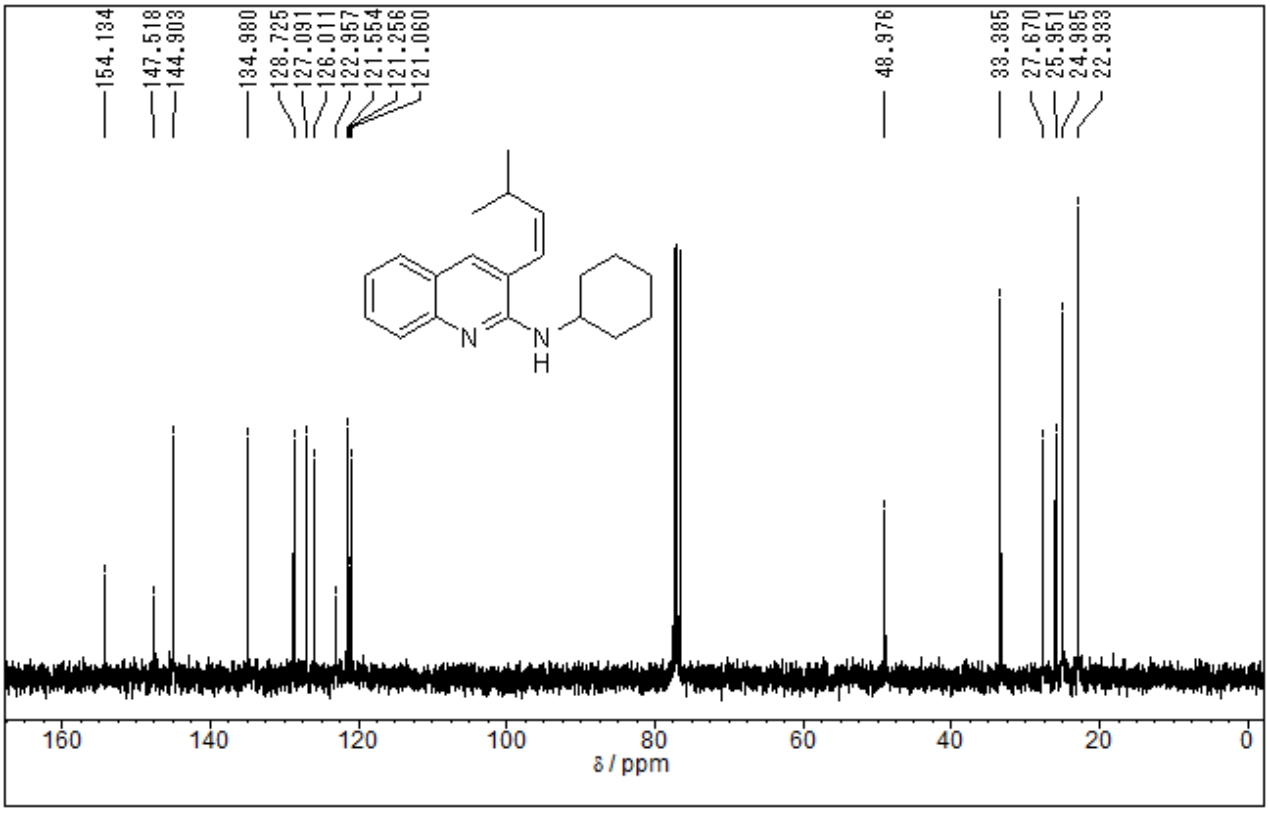
• ^{13}C-NMR spectrum of



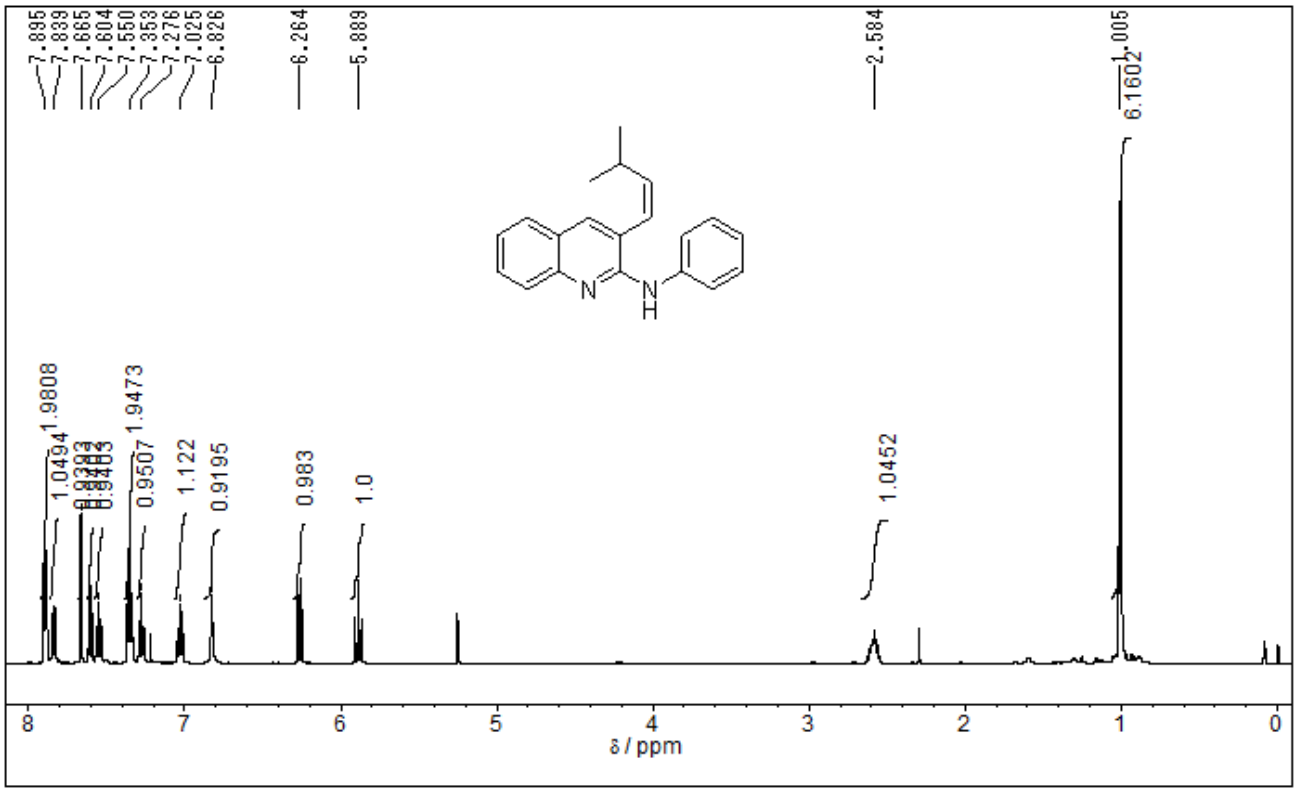
• ^{1}H-NMR spectrum of ***cis*-2n**



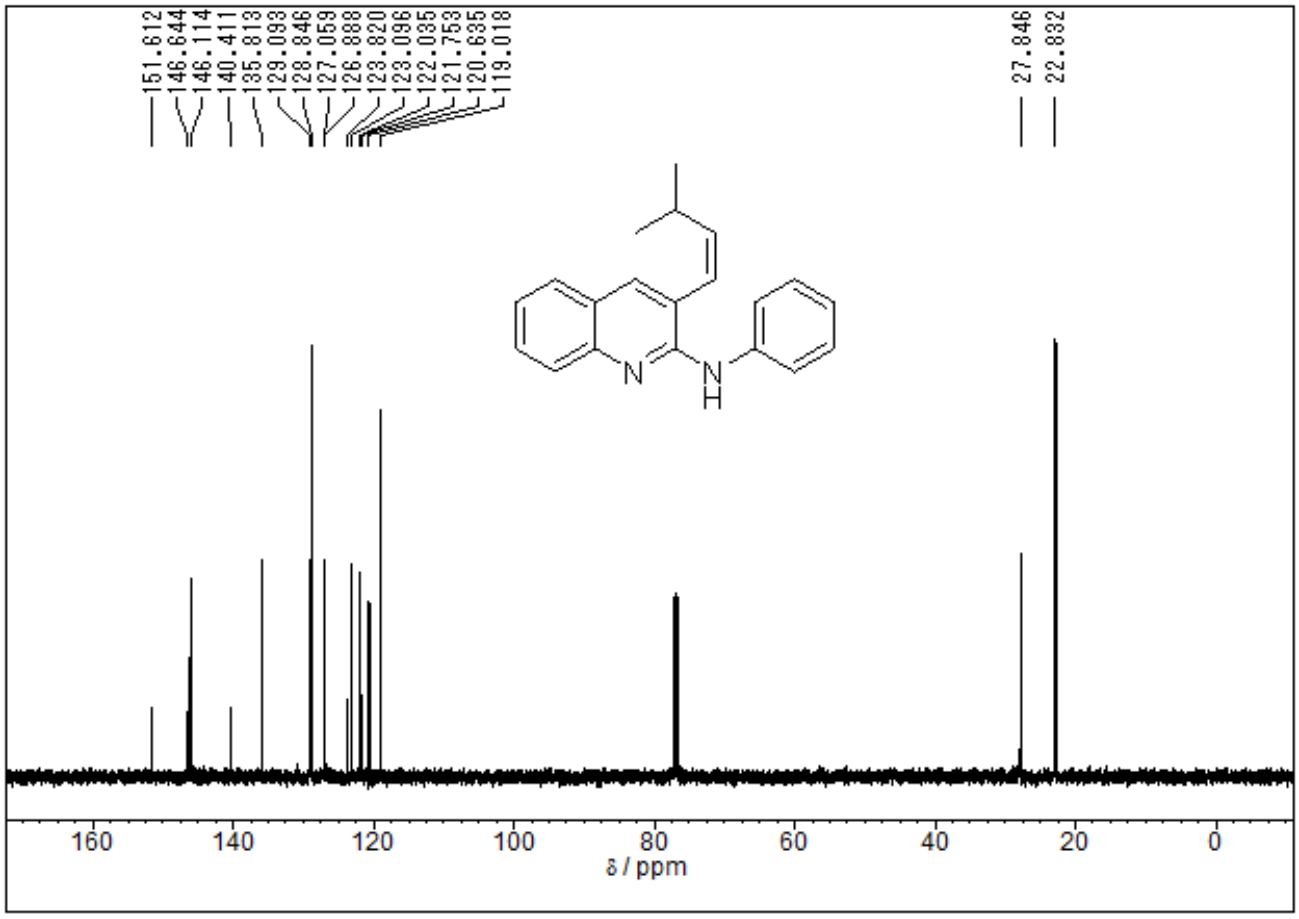
• ^{13}C-NMR spectrum of



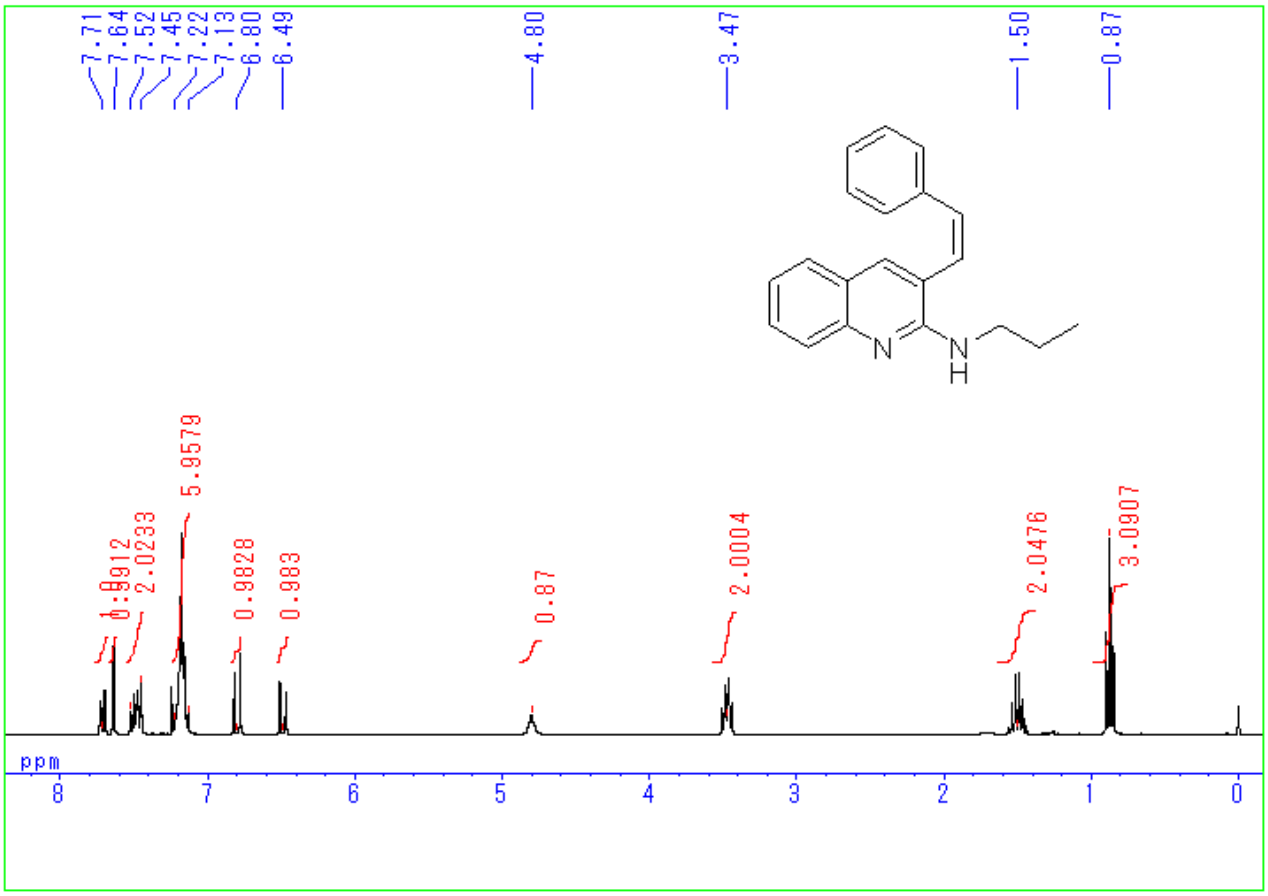
• ^{1}H-NMR spectrum of ***cis*-2p**



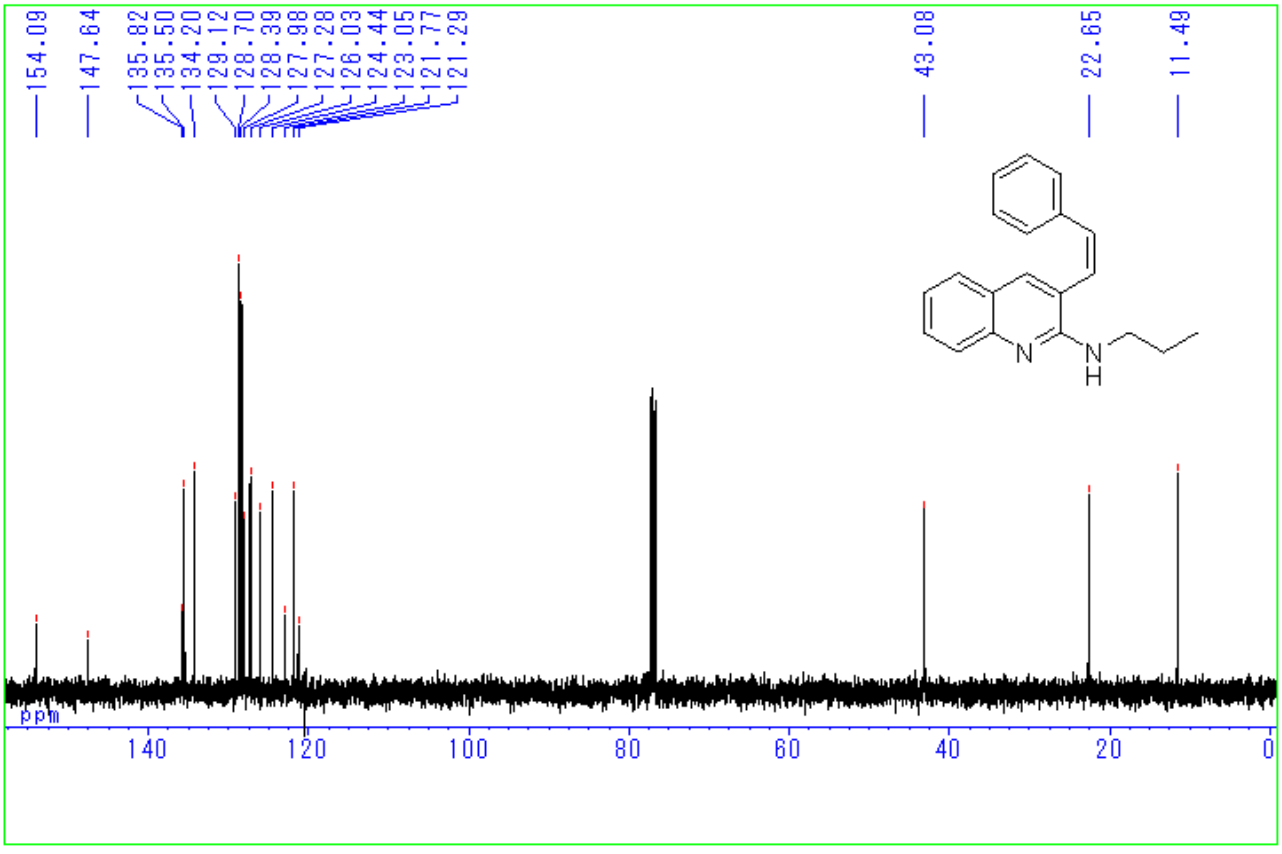
• ^{13}C-NMR spectrum of ***cis*-2p**



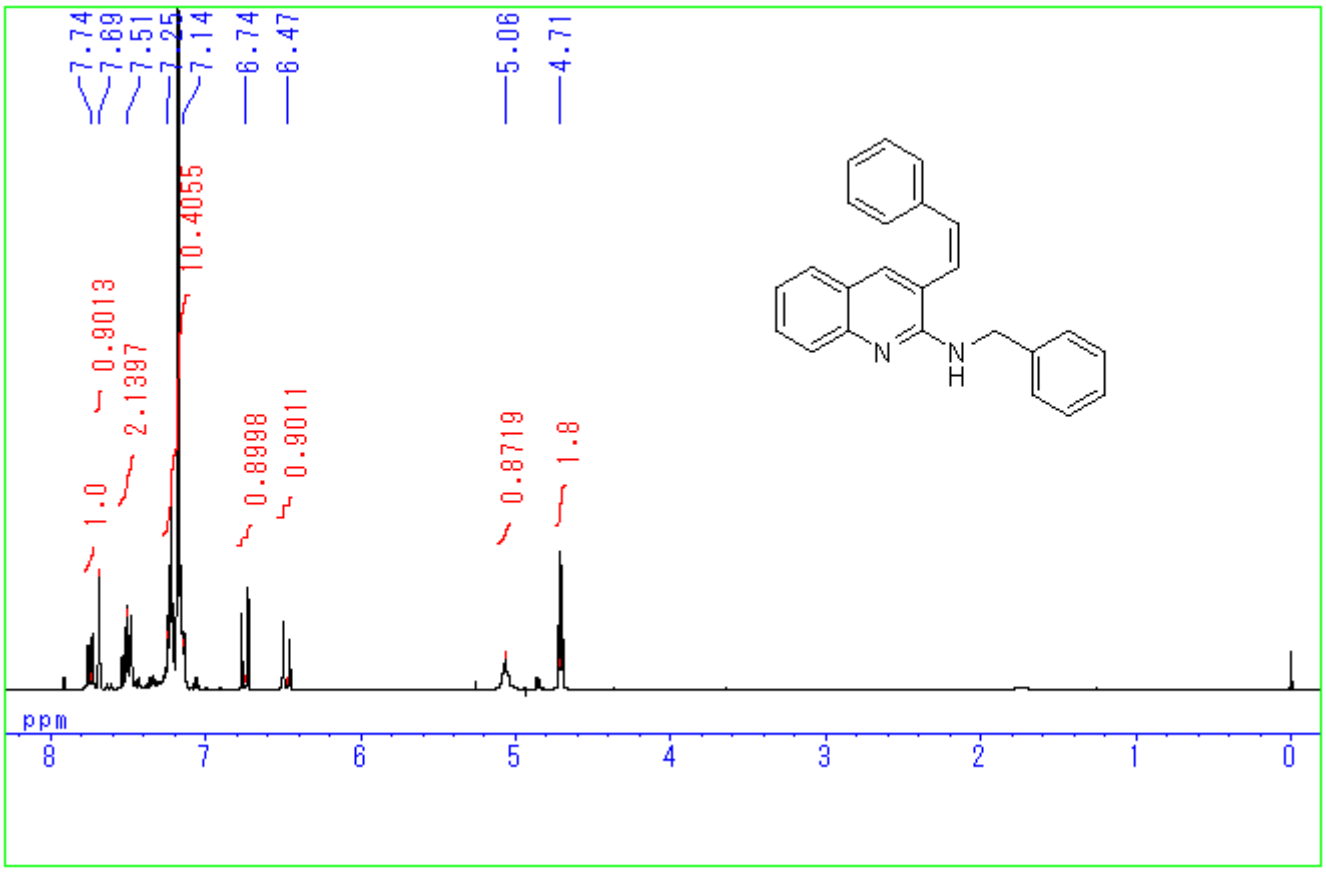
• ^{1}H-NMR spectrum of ***cis*-2q**



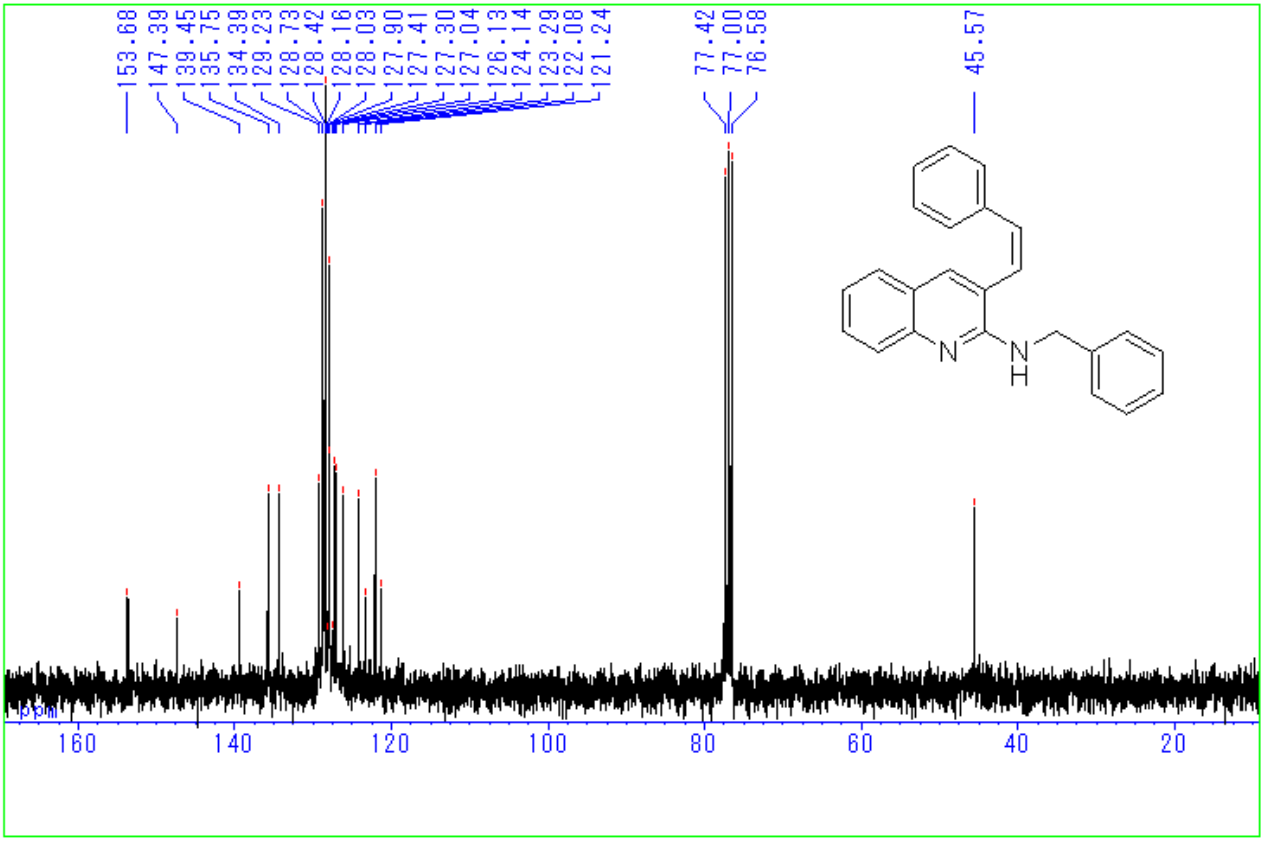
• ^{13}C-NMR spectrum of ***cis*-2q**



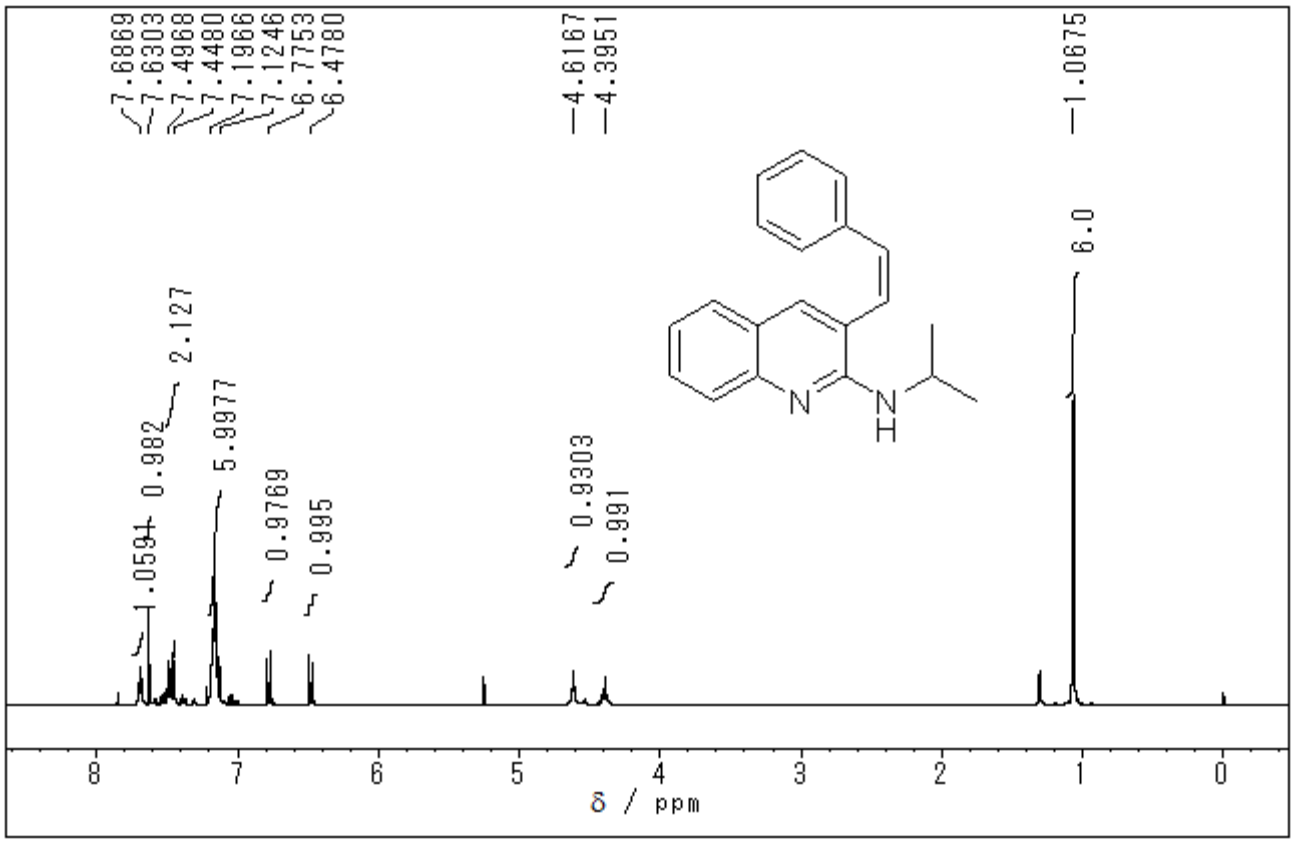
• ^{1}H-NMR spectrum of ***cis*-2r**



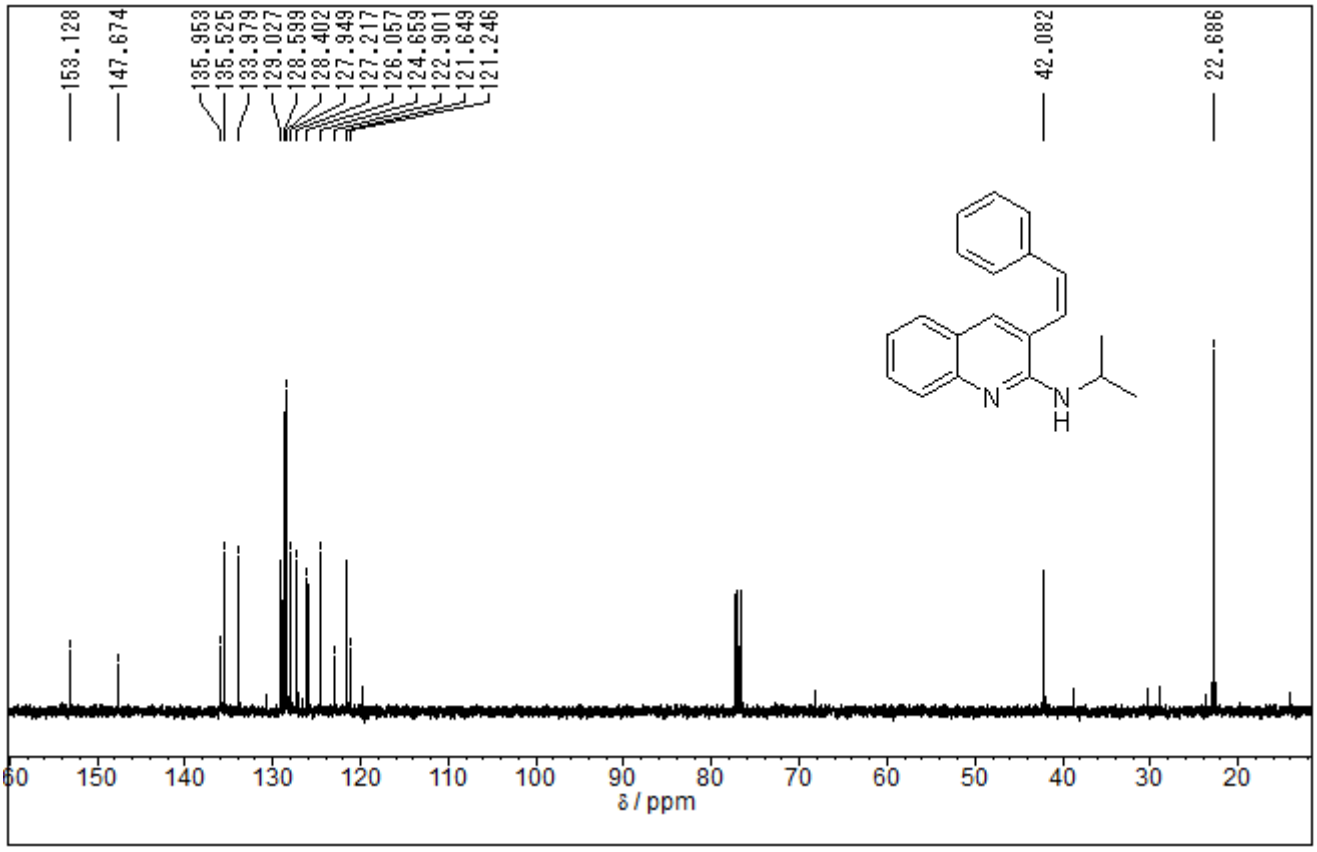
• ^{13}C-NMR spectrum of ***cis*-2r**



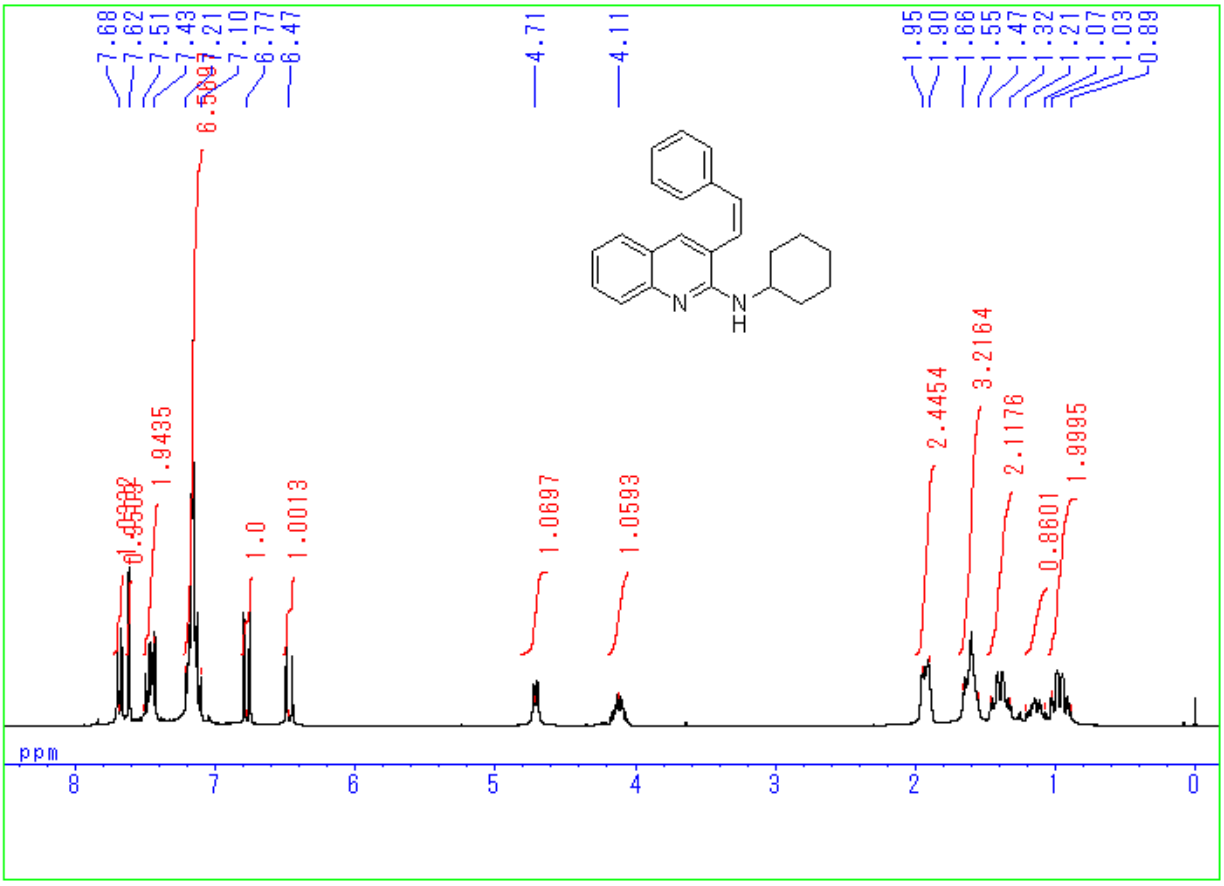
• ^{1}H-NMR spectrum of ***cis*-2s**



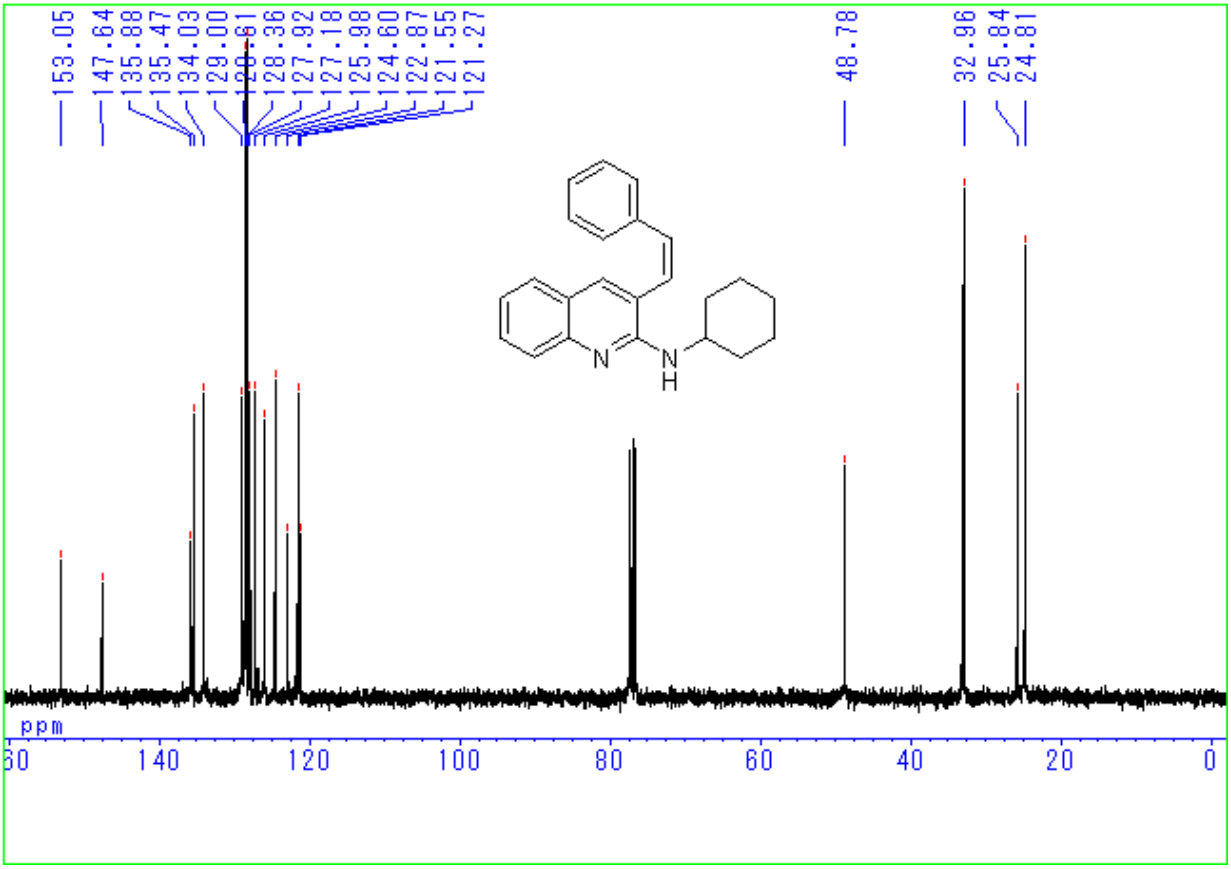
• ^{13}C-NMR spectrum of ***cis*-2s**



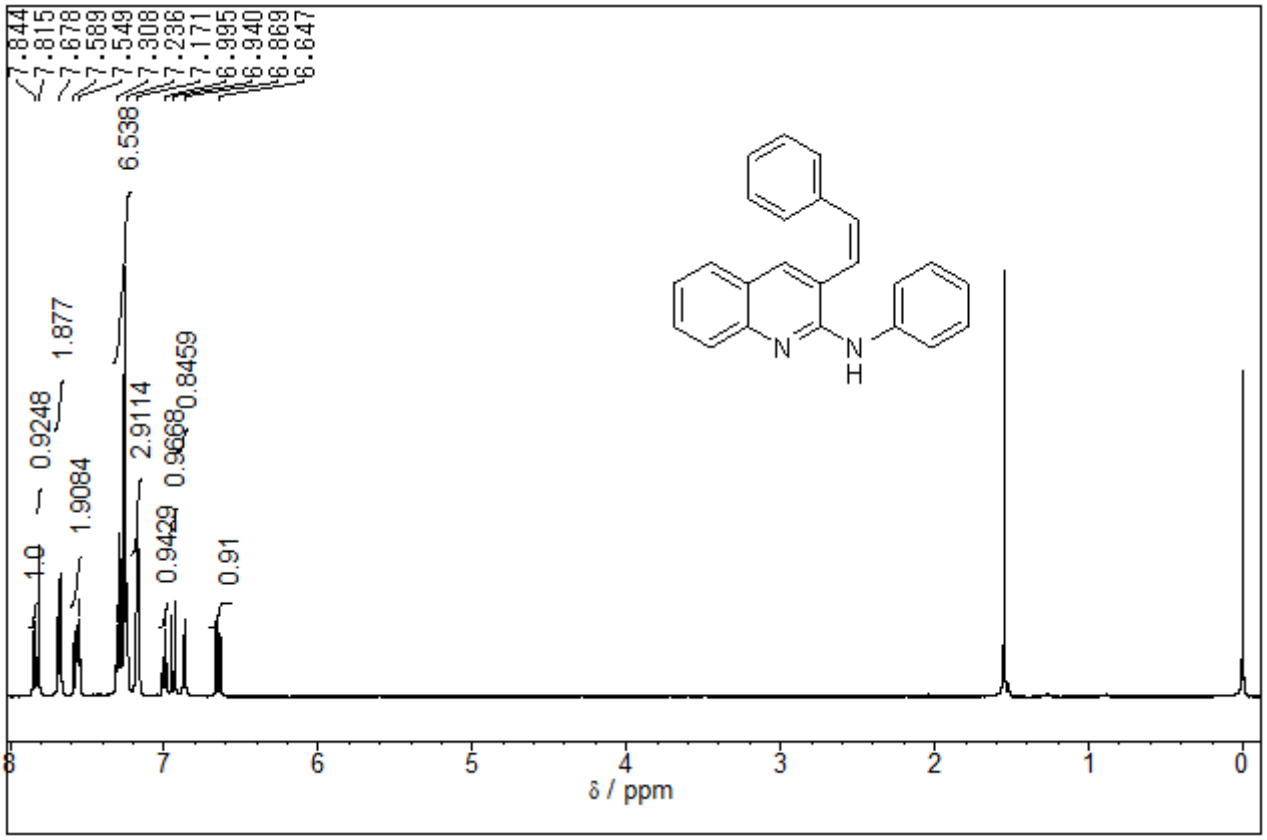
• ^{1}H-NMR spectrum of ***cis*-2t**



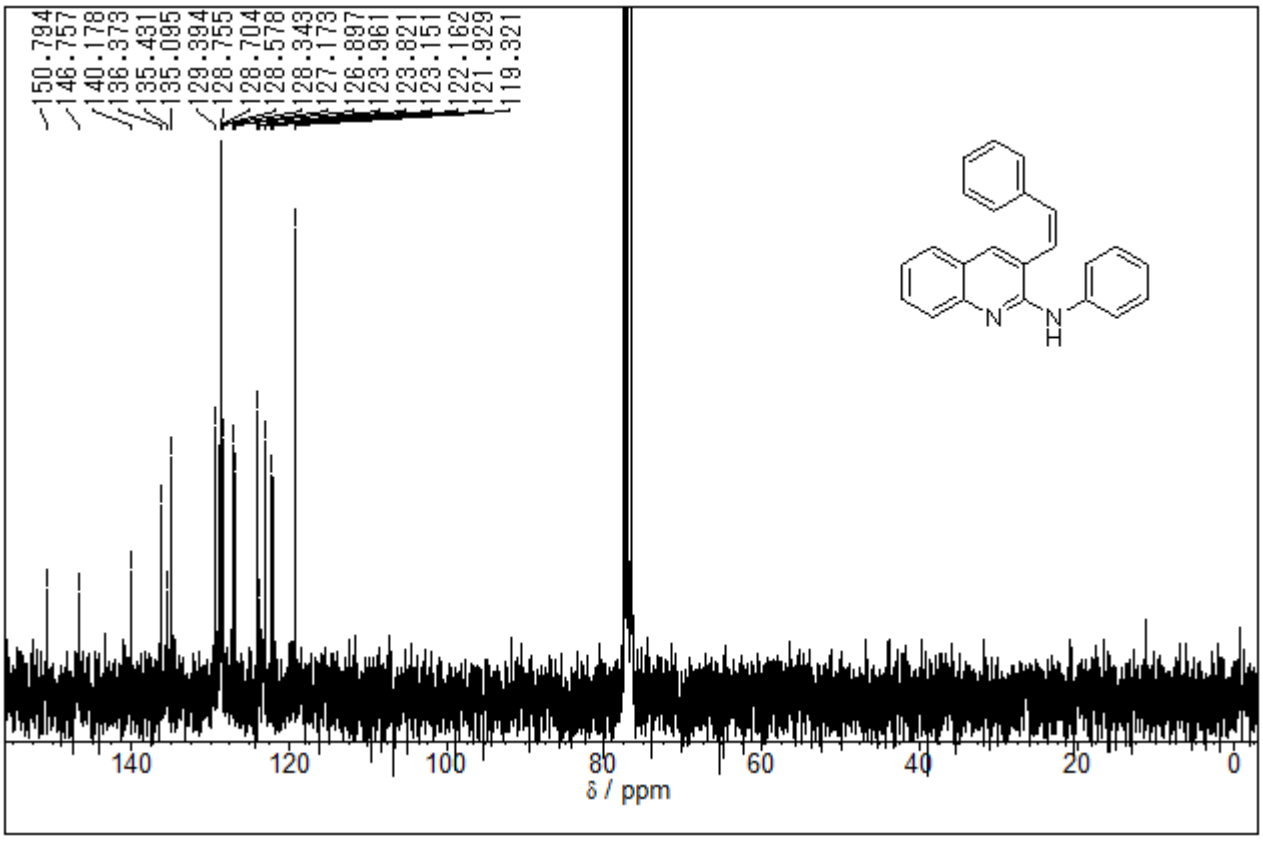
• ^{13}C-NMR spectrum of ***cis*-2t**



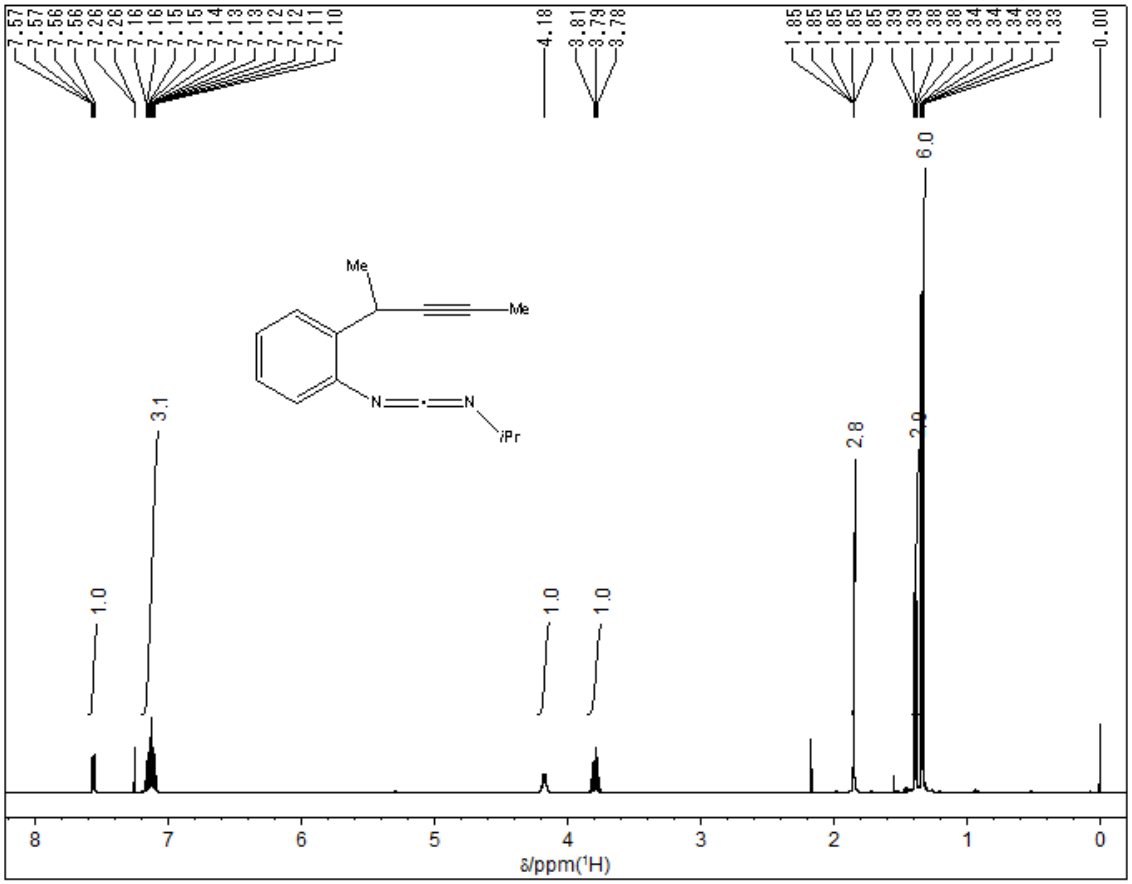
• ^{1}H-NMR spectrum of ***cis*-2u**



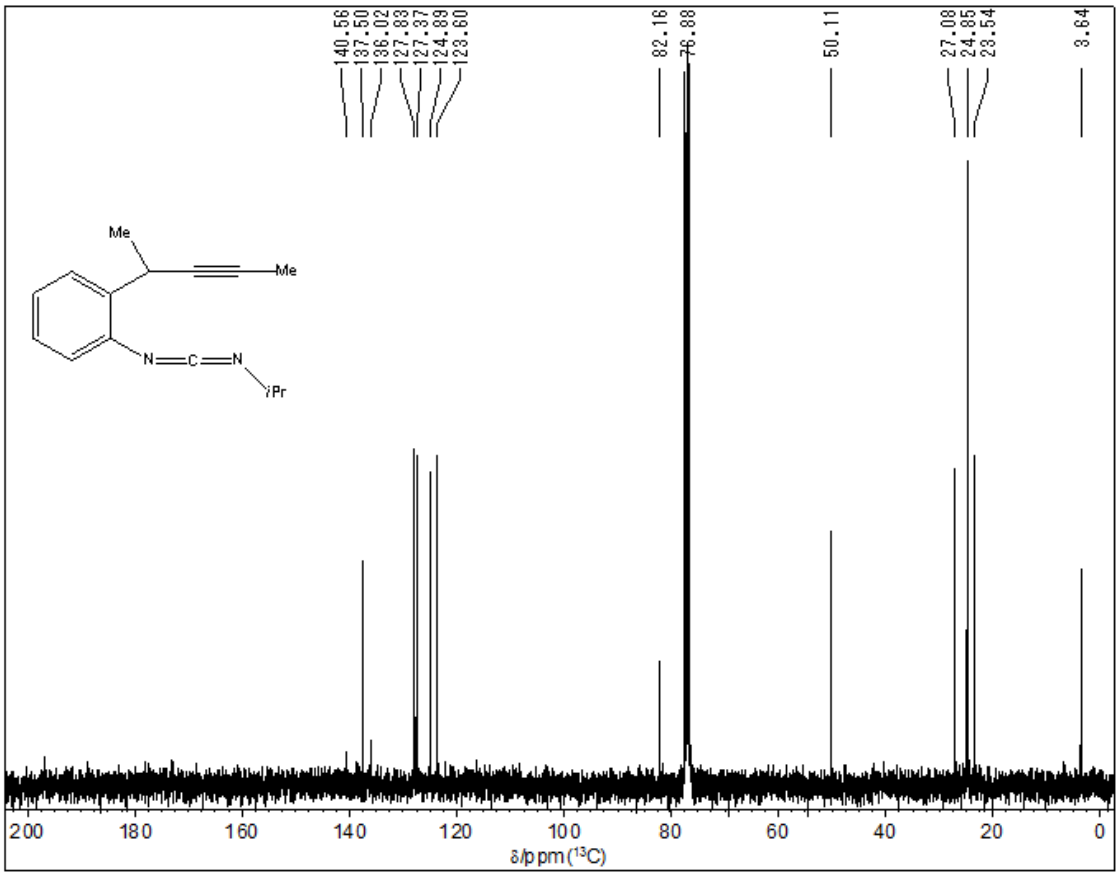
• ^{13}C-NMR spectrum of ***cis*-2u**



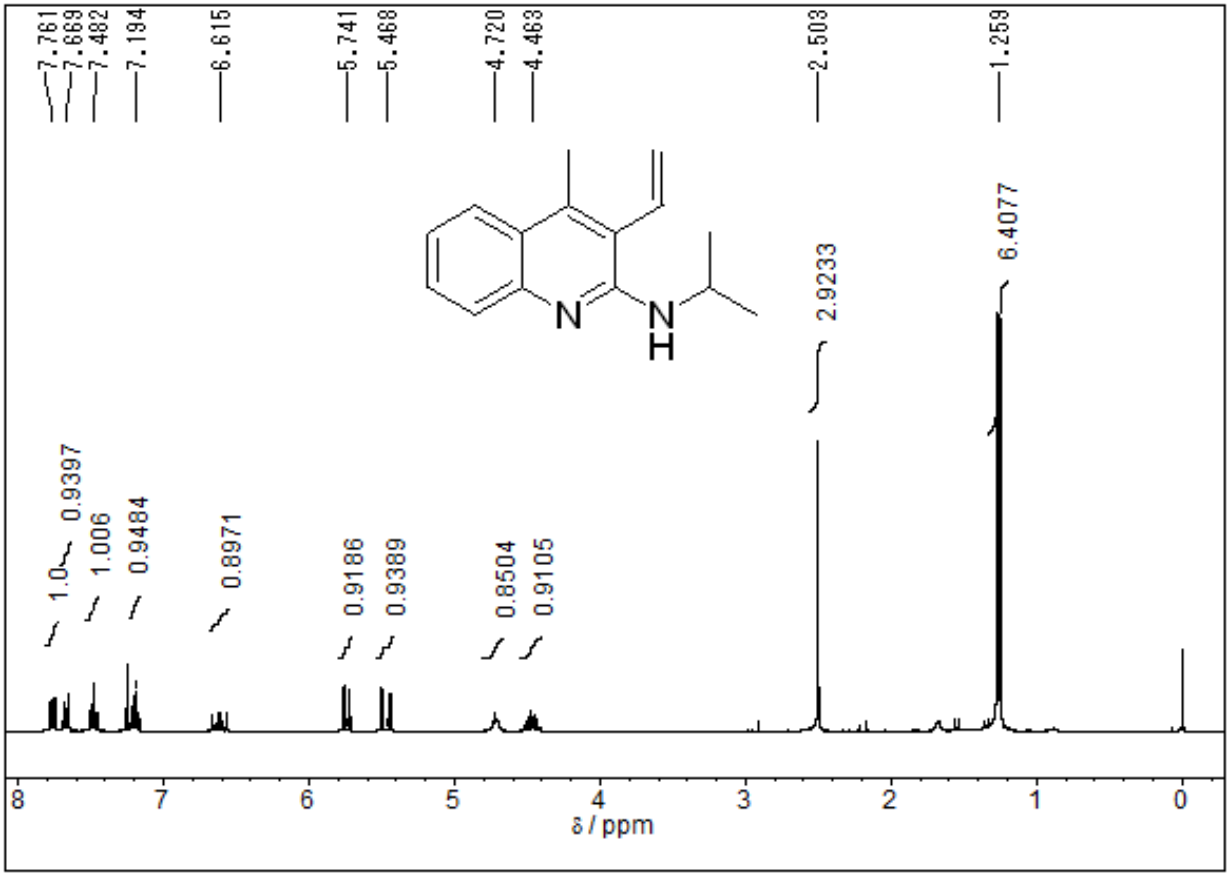
• ^{1}H-NMR spectrum of **3**



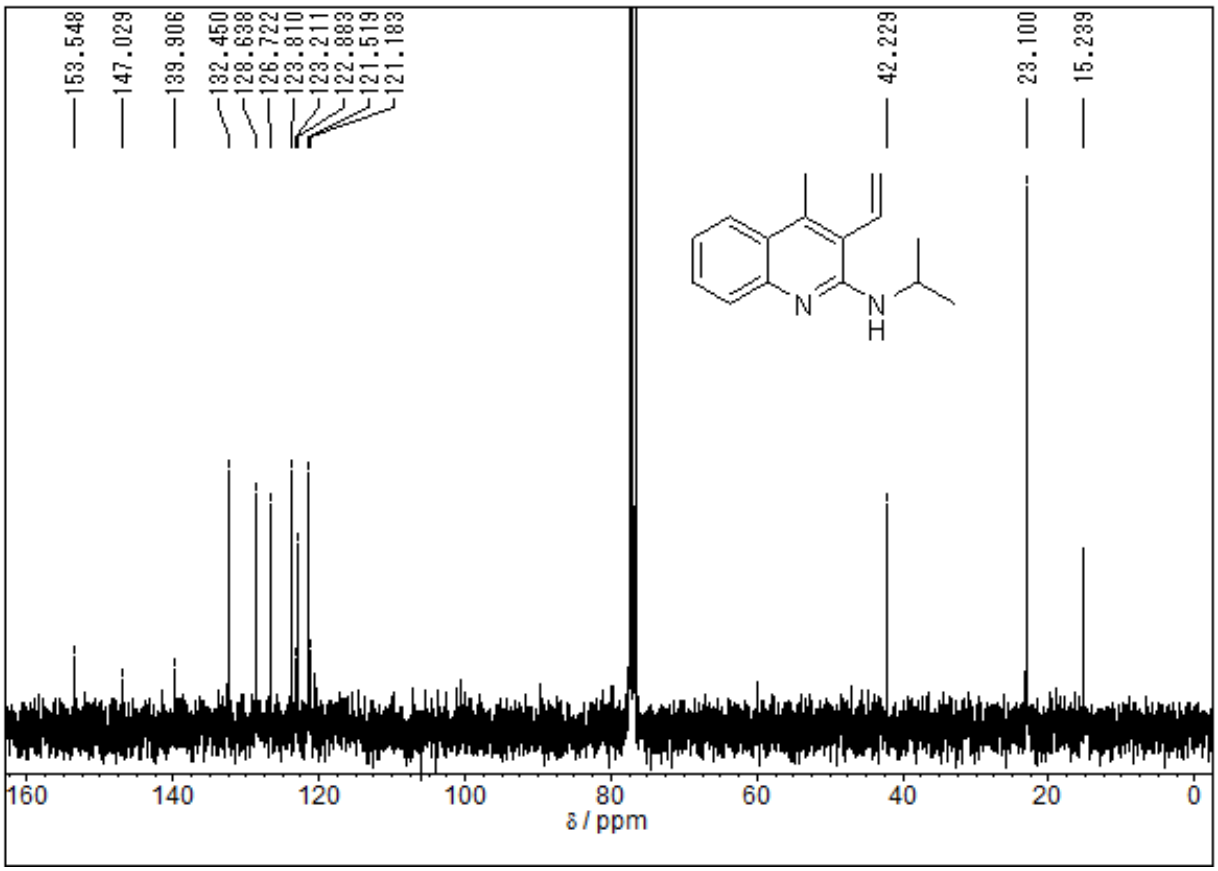
• ^{13}C-NMR spectrum of **3**



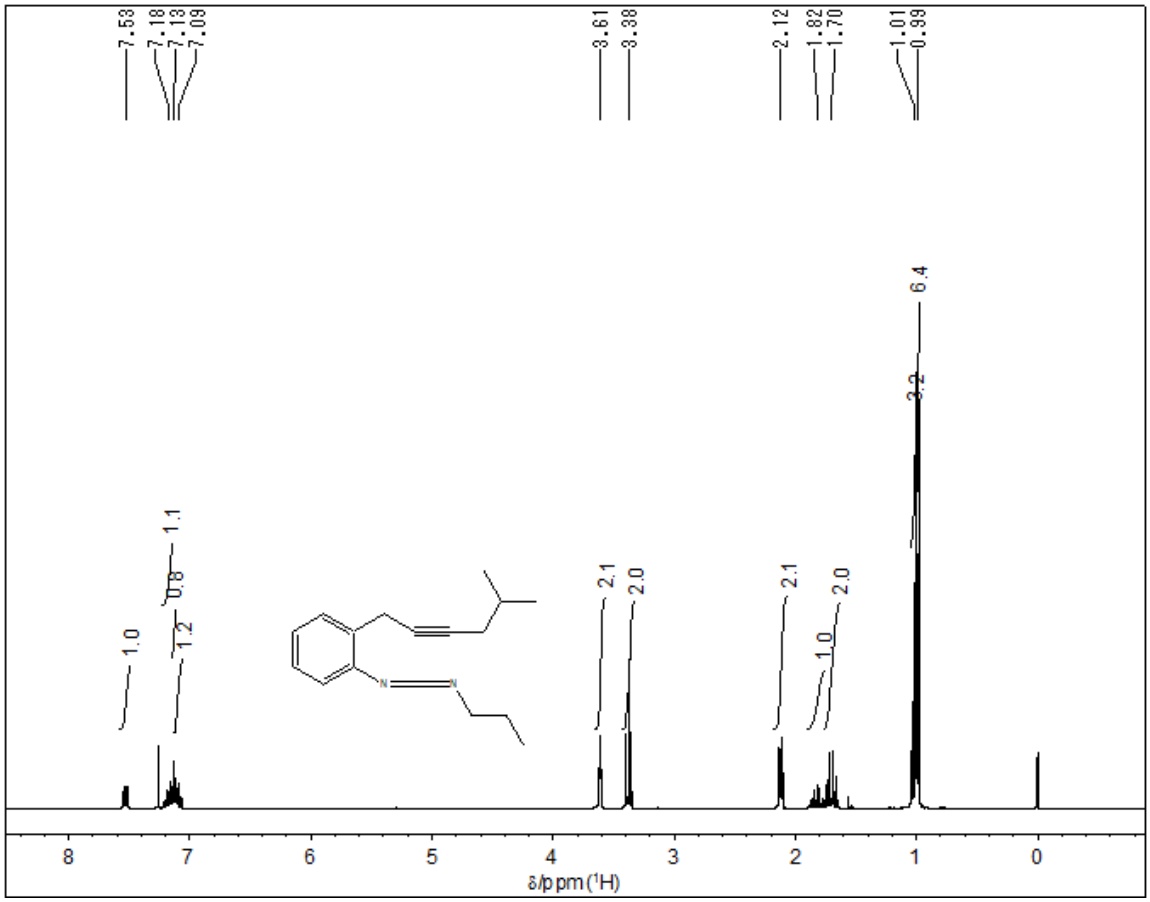
• ^{1}H-NMR spectrum of **4**



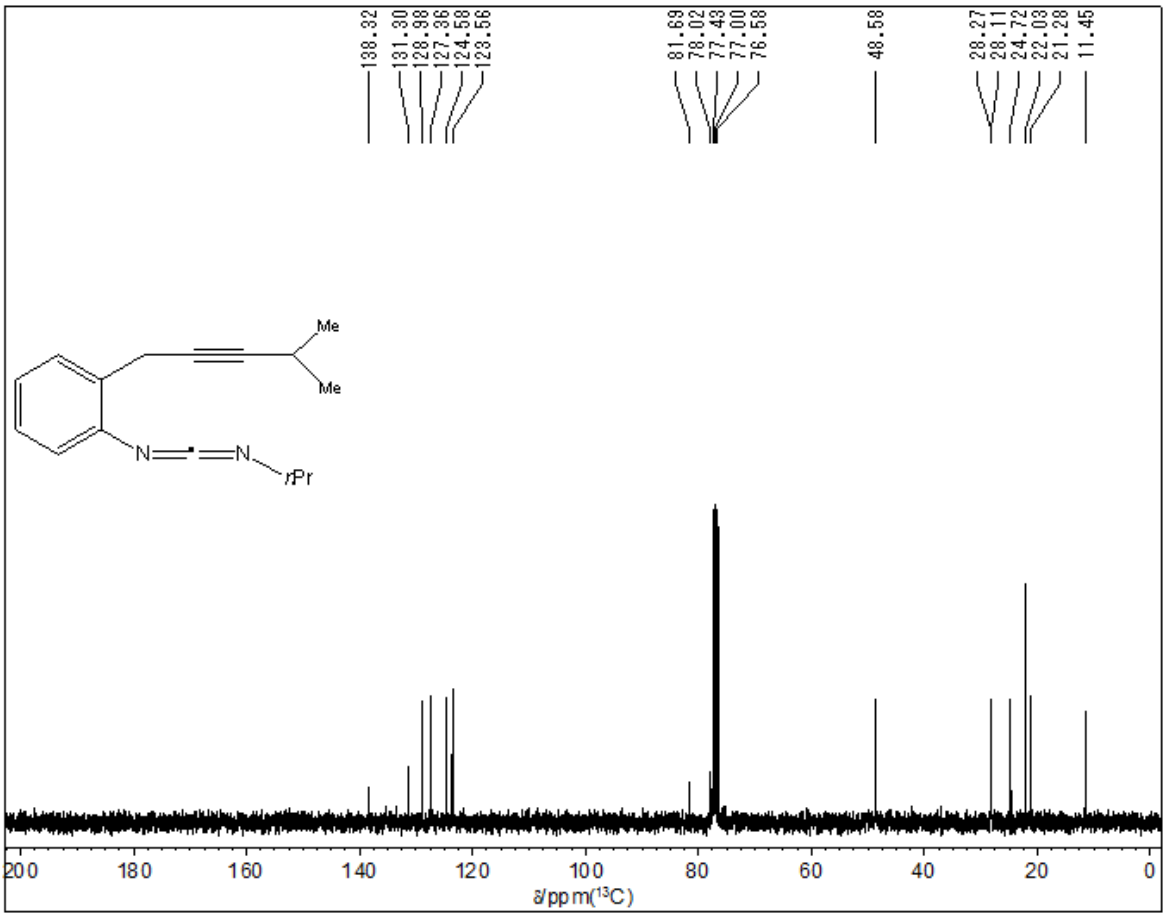
• ^{13}C-NMR spectrum of **4**



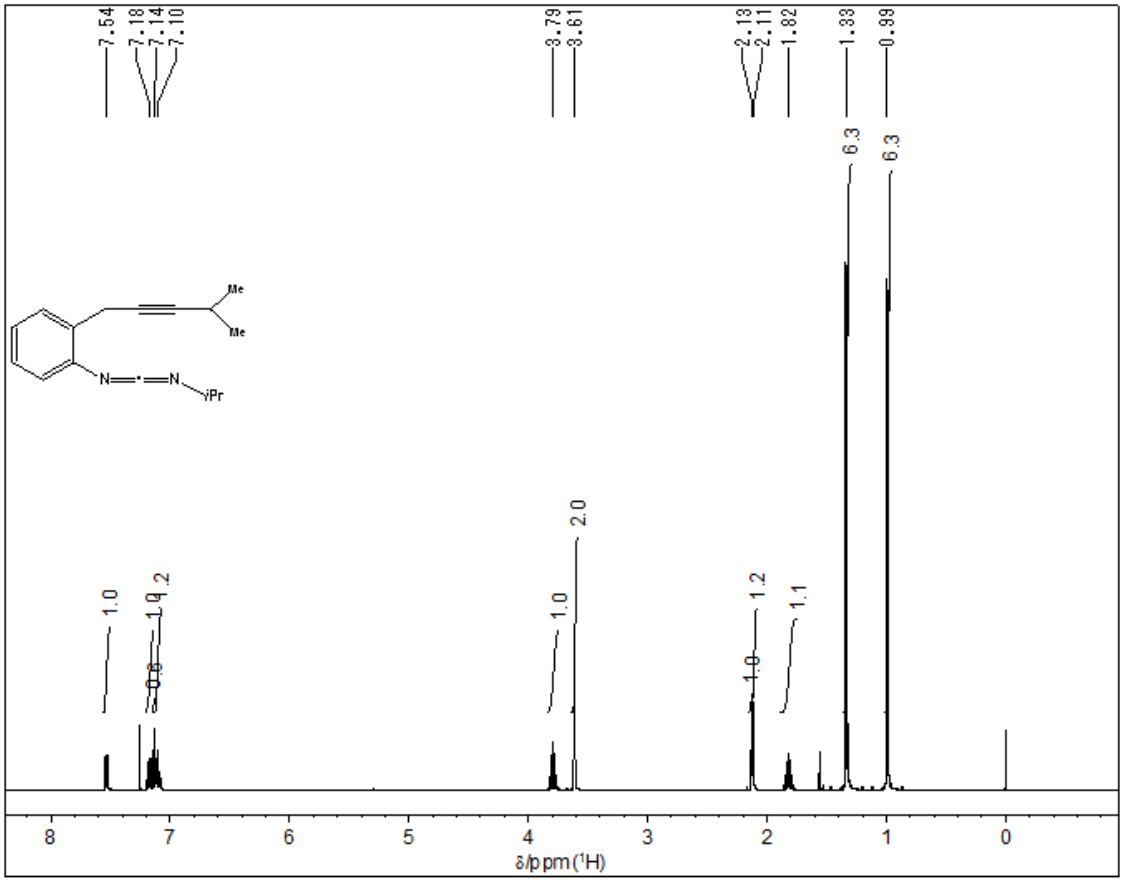
• ^{1}H-NMR spectrum of **5a**



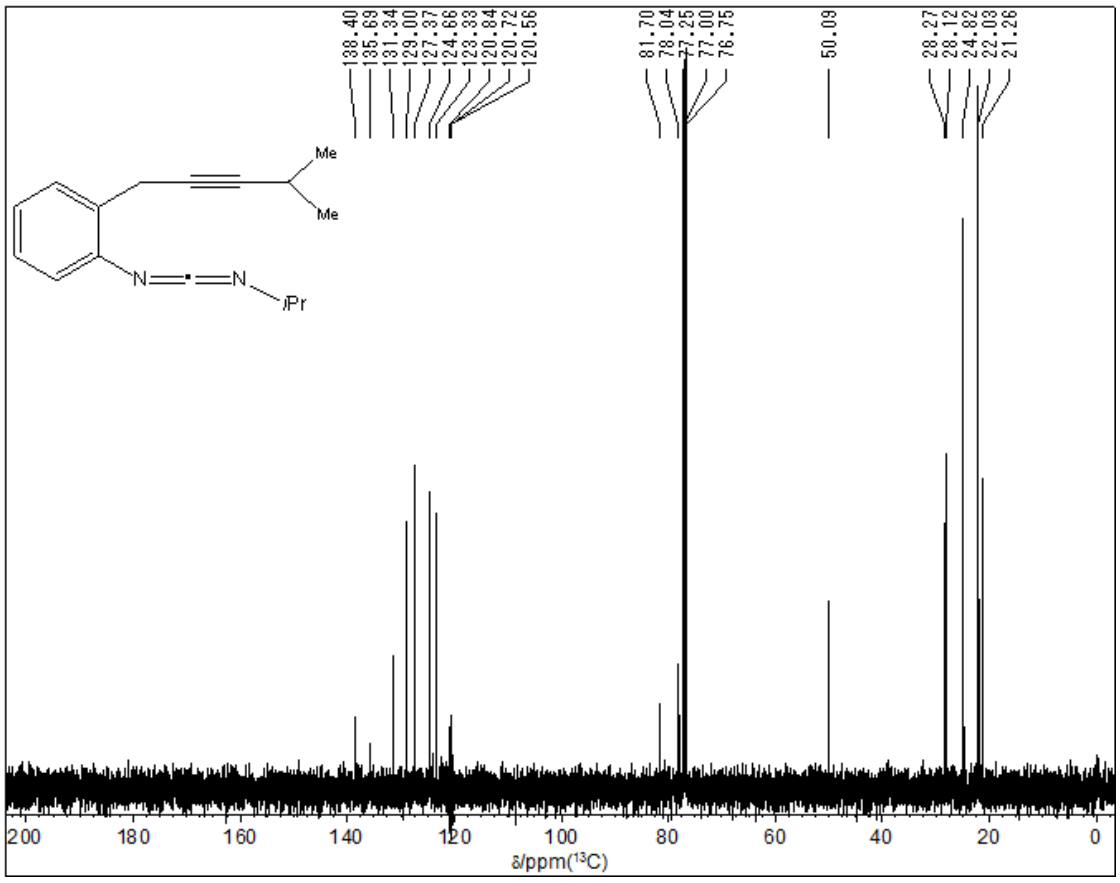
• ^{13}C-NMR spectrum of **5a**



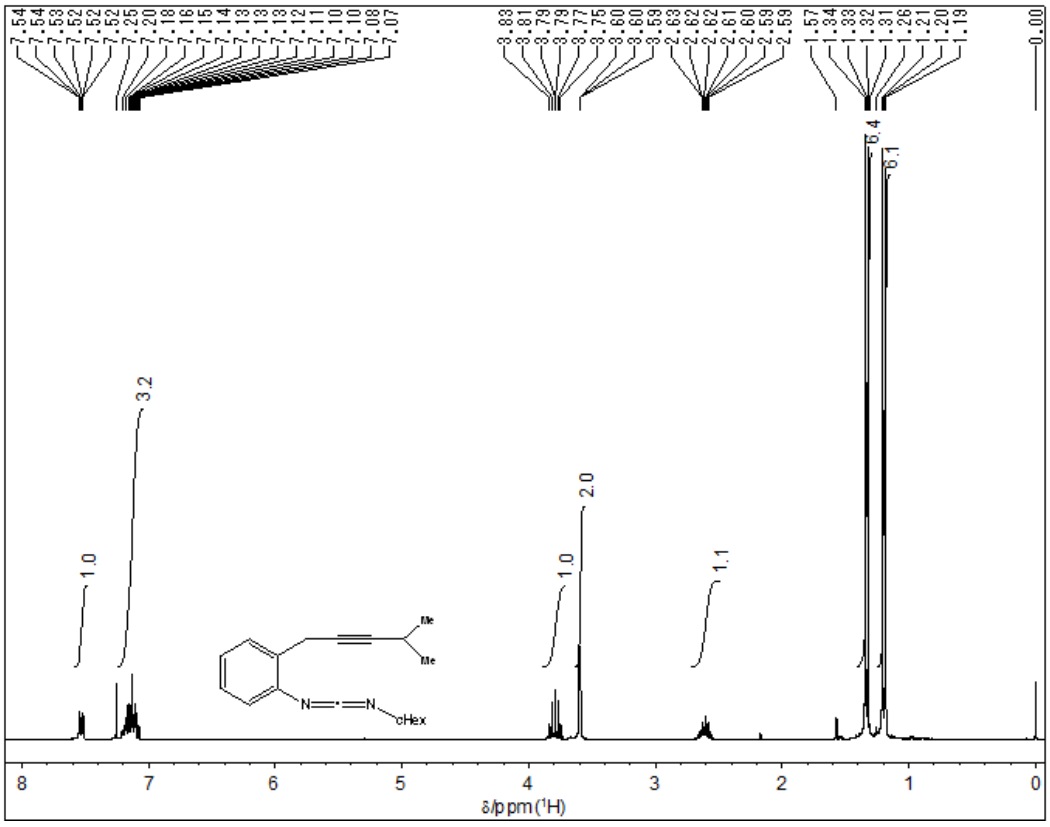
• ^{1}H-NMR spectrum of **5b**



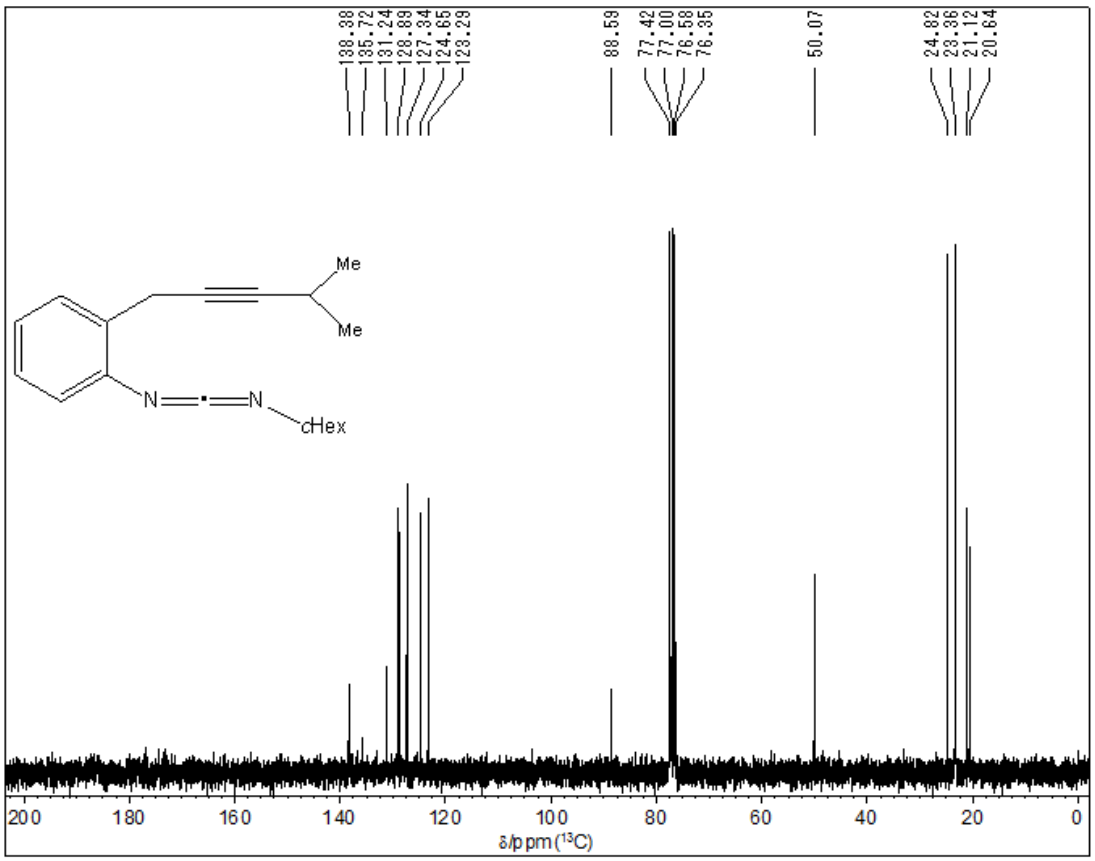
• ^{13}C-NMR spectrum of **5b**



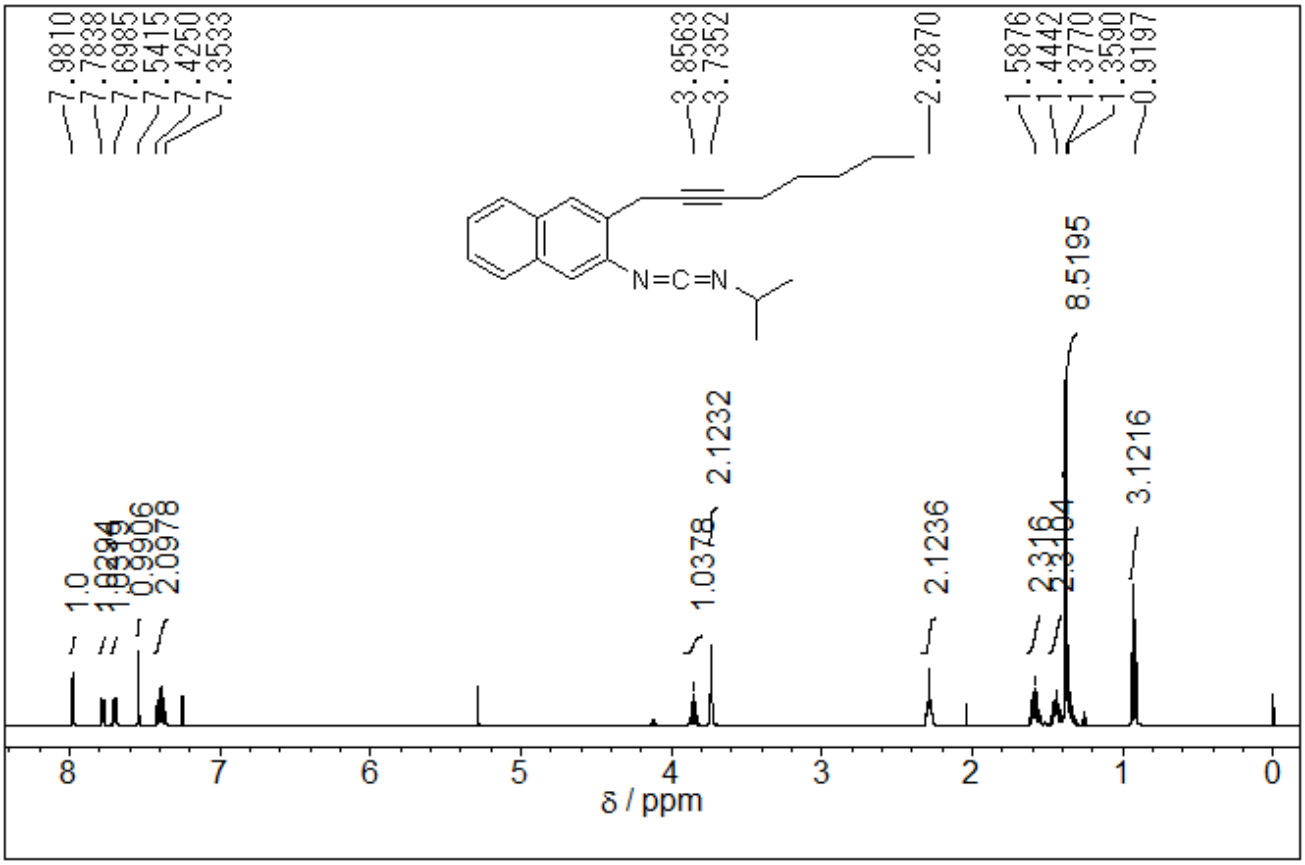
• ^{1}H-NMR spectrum of **5c**



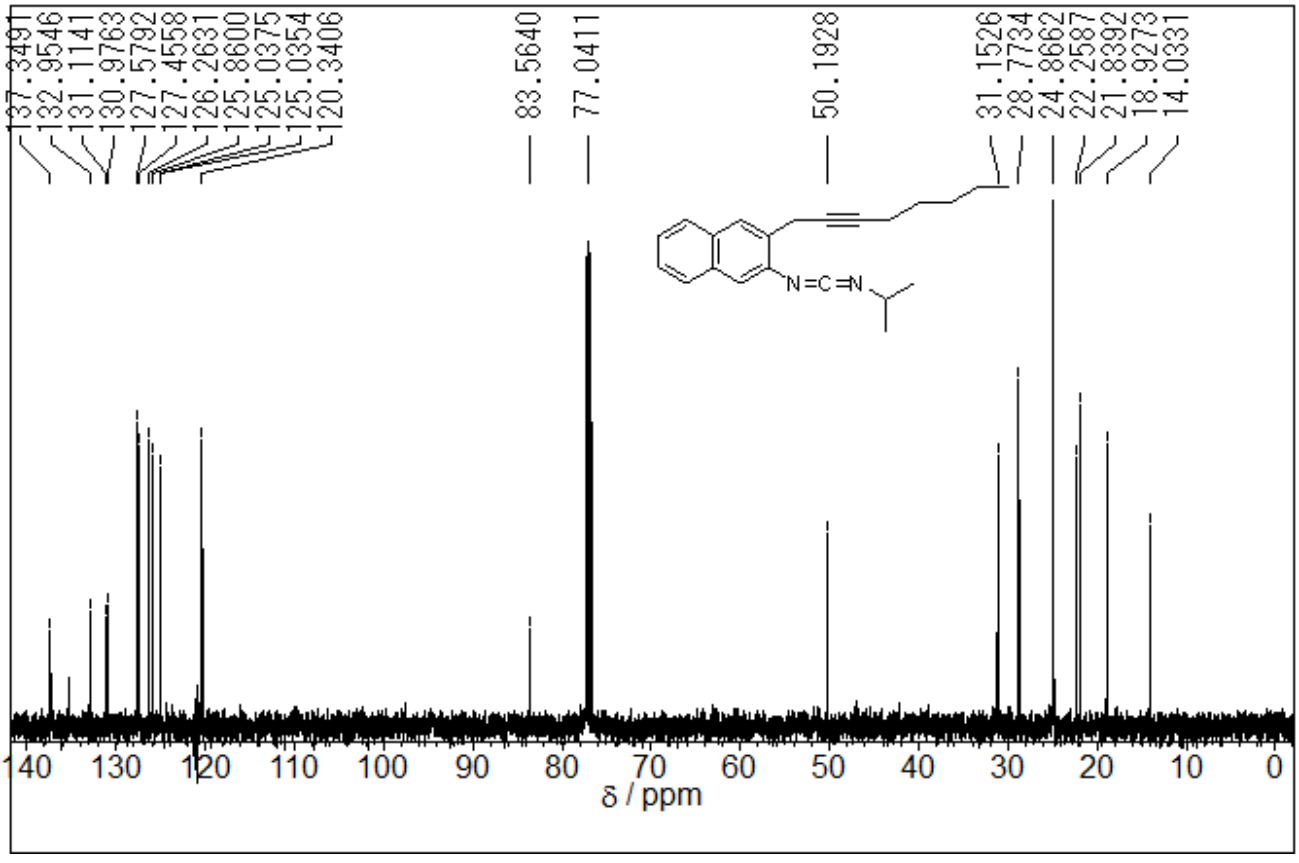
• ^{13}C-NMR spectrum of **5c**



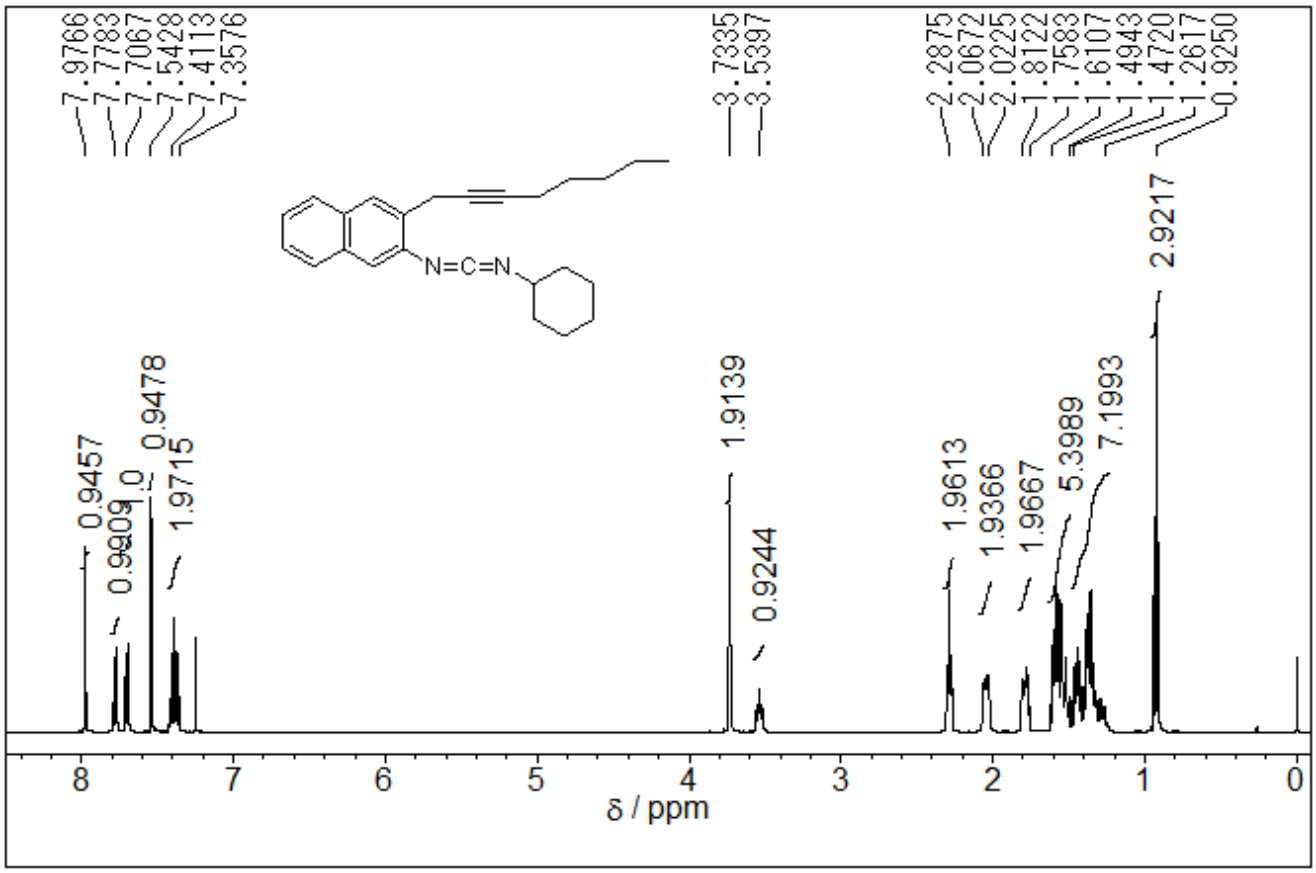
• ^{1}H-NMR spectrum of **7a**



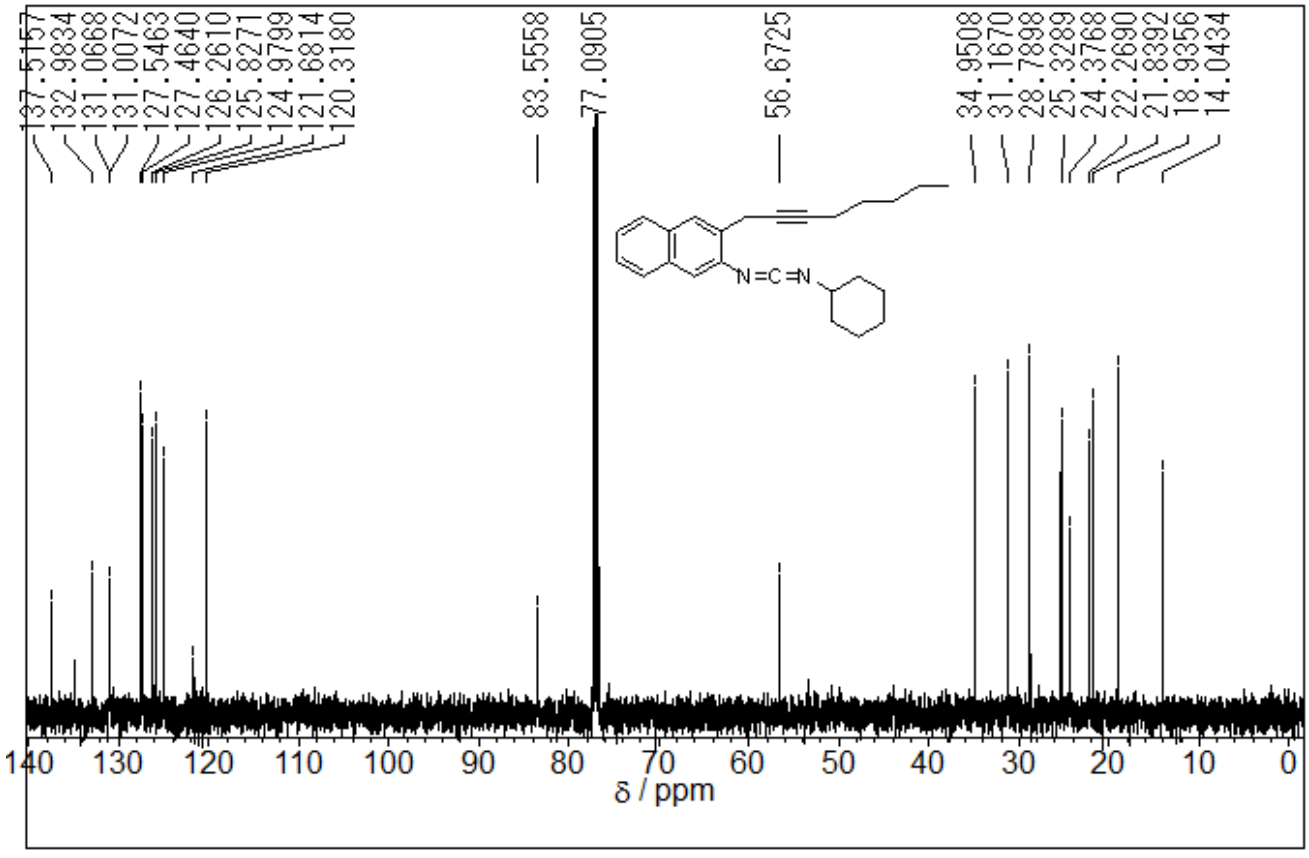
• ^{13}C-NMR spectrum of **7a**



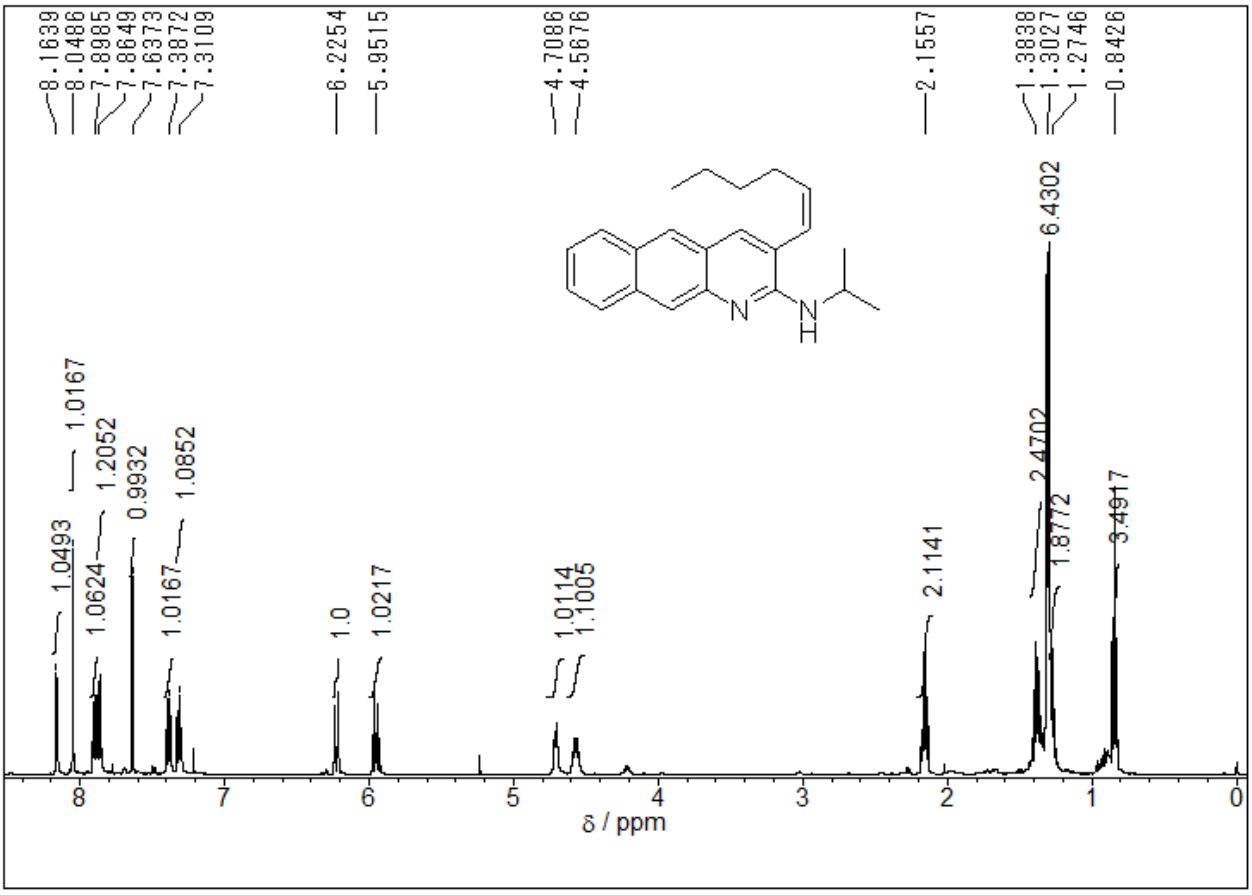
• ^{1}H-NMR spectrum of **7b**



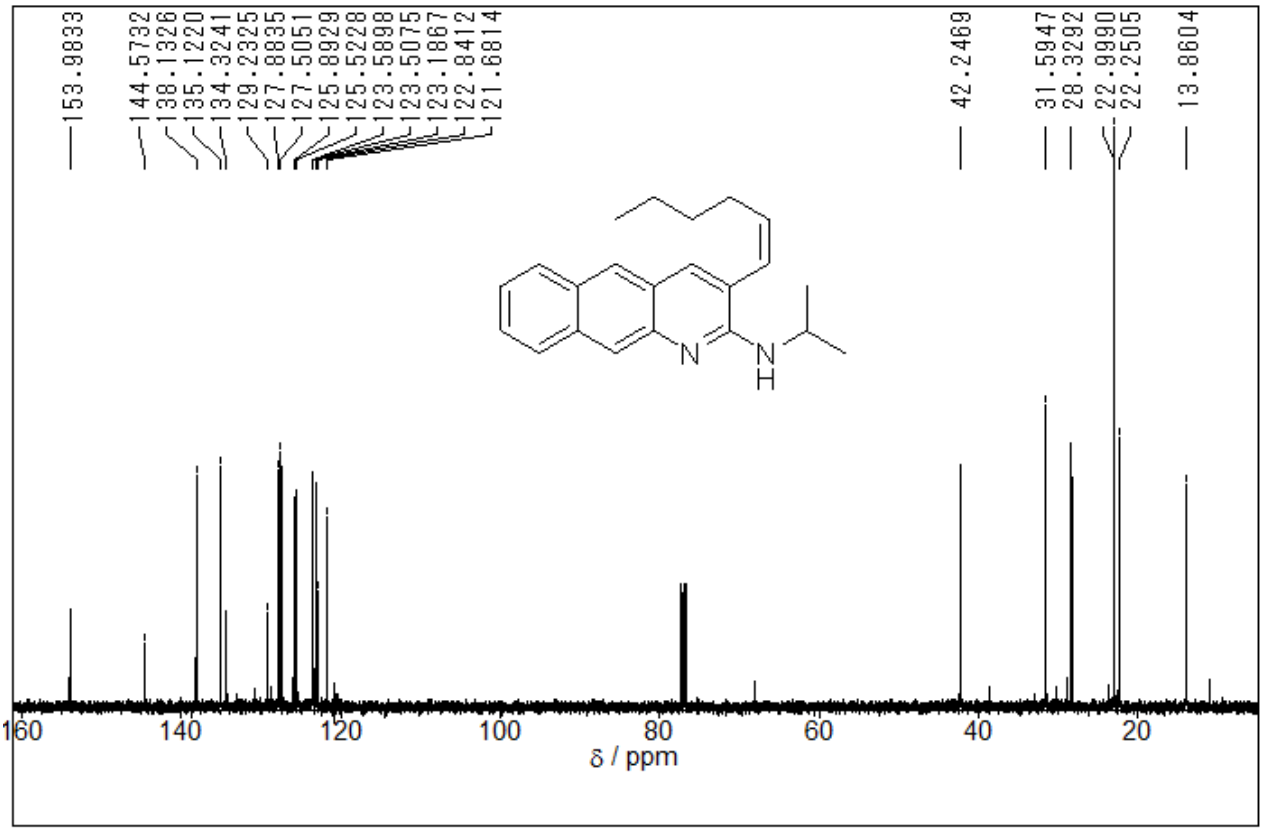
• ^{13}C-NMR spectrum of **7b**



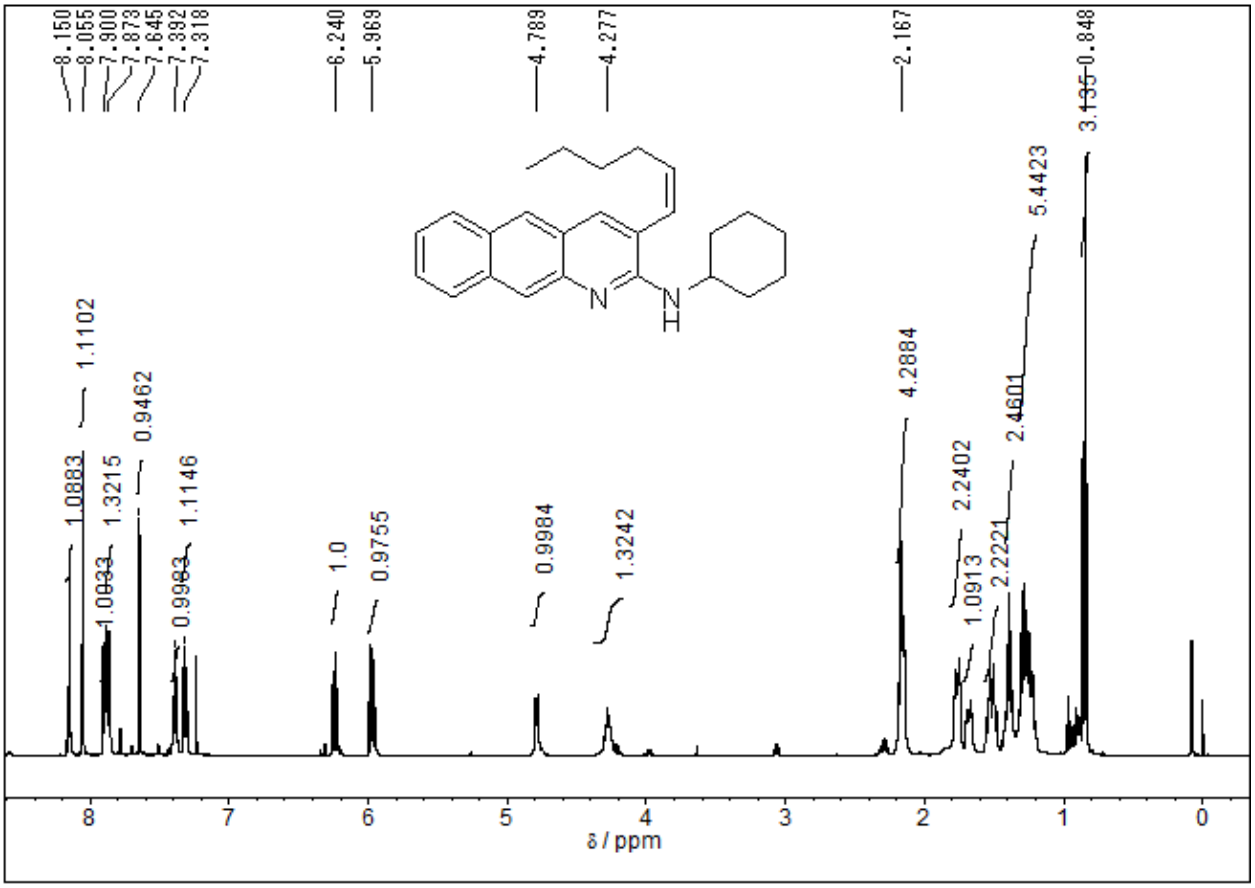
• ^{1}H-NMR spectrum of ***cis*-8a**



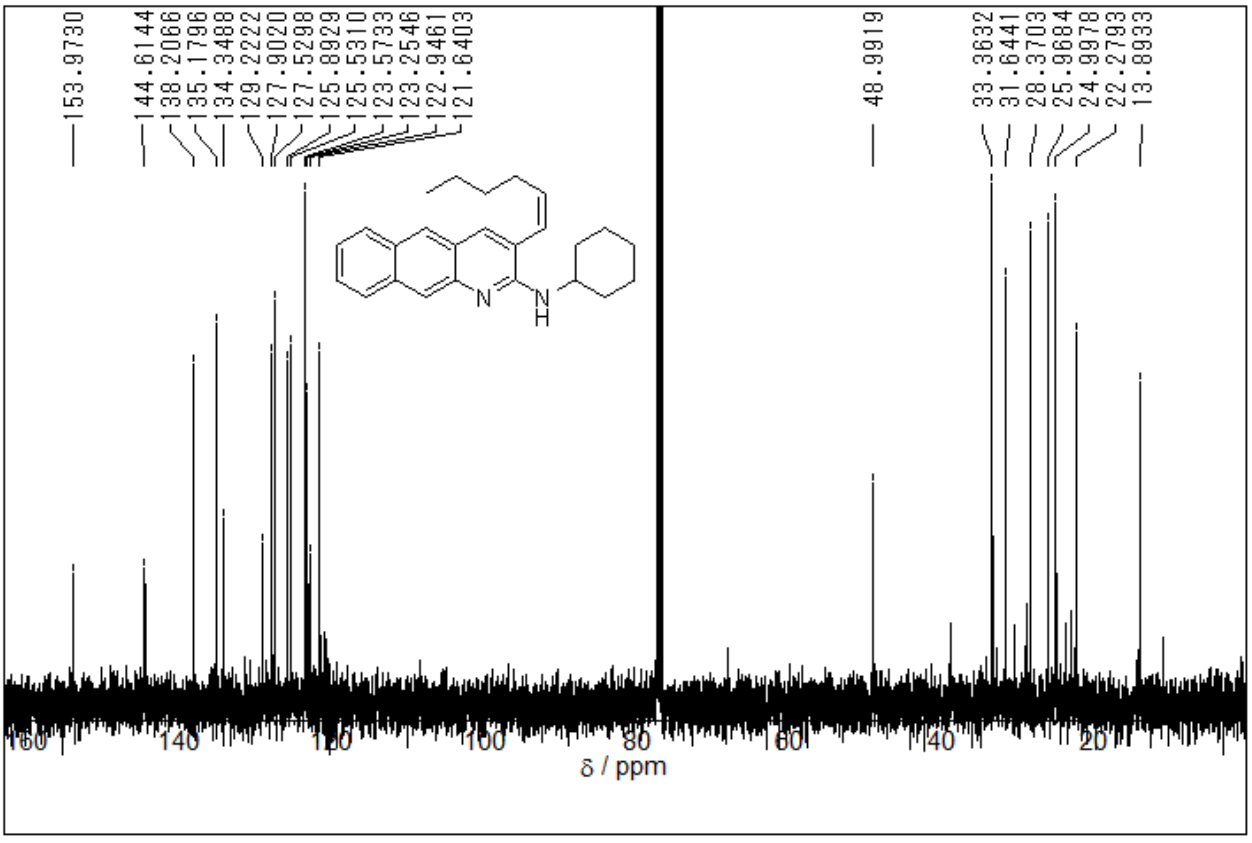
• ^{13}C-NMR spectrum of ***cis*-8a**



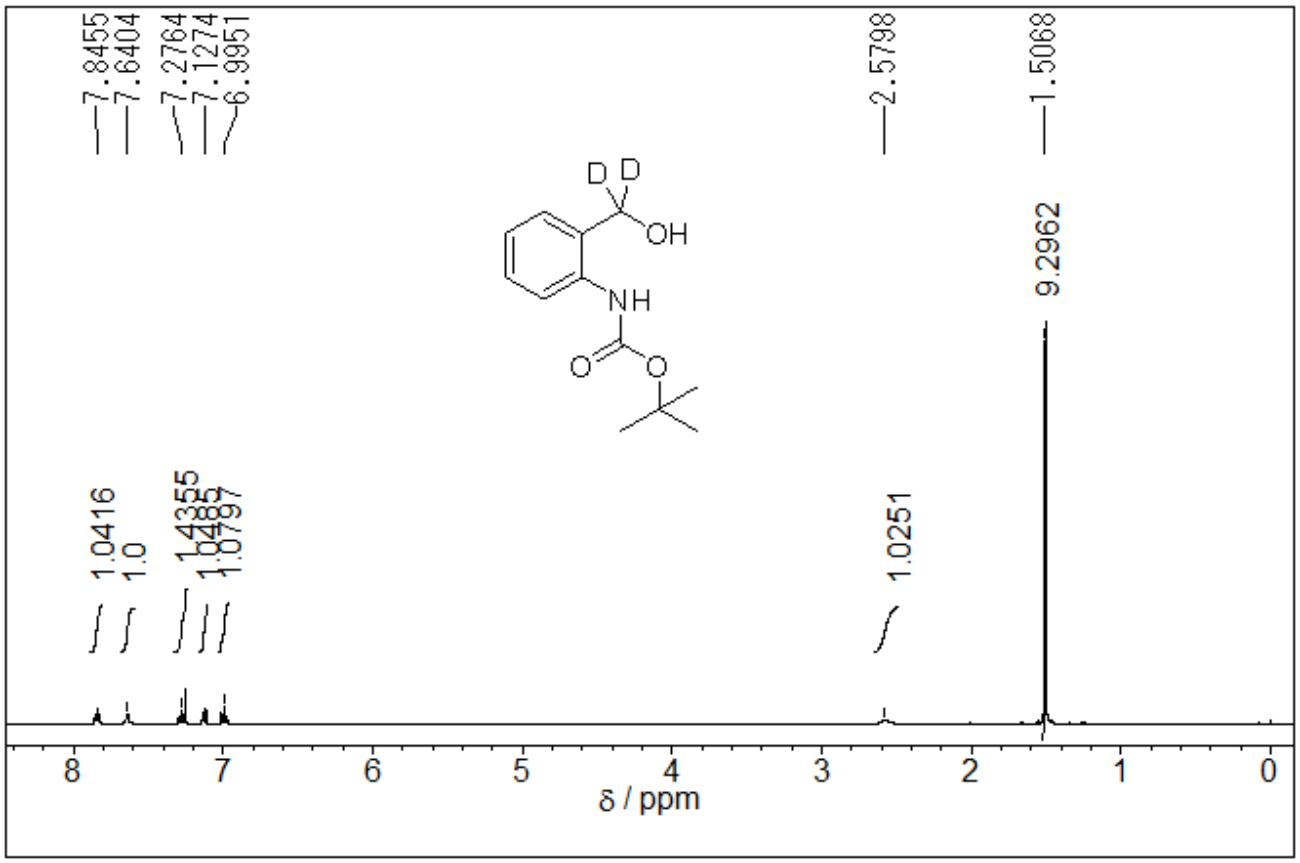
• ^{1}H-NMR spectrum of ***cis*-8b**



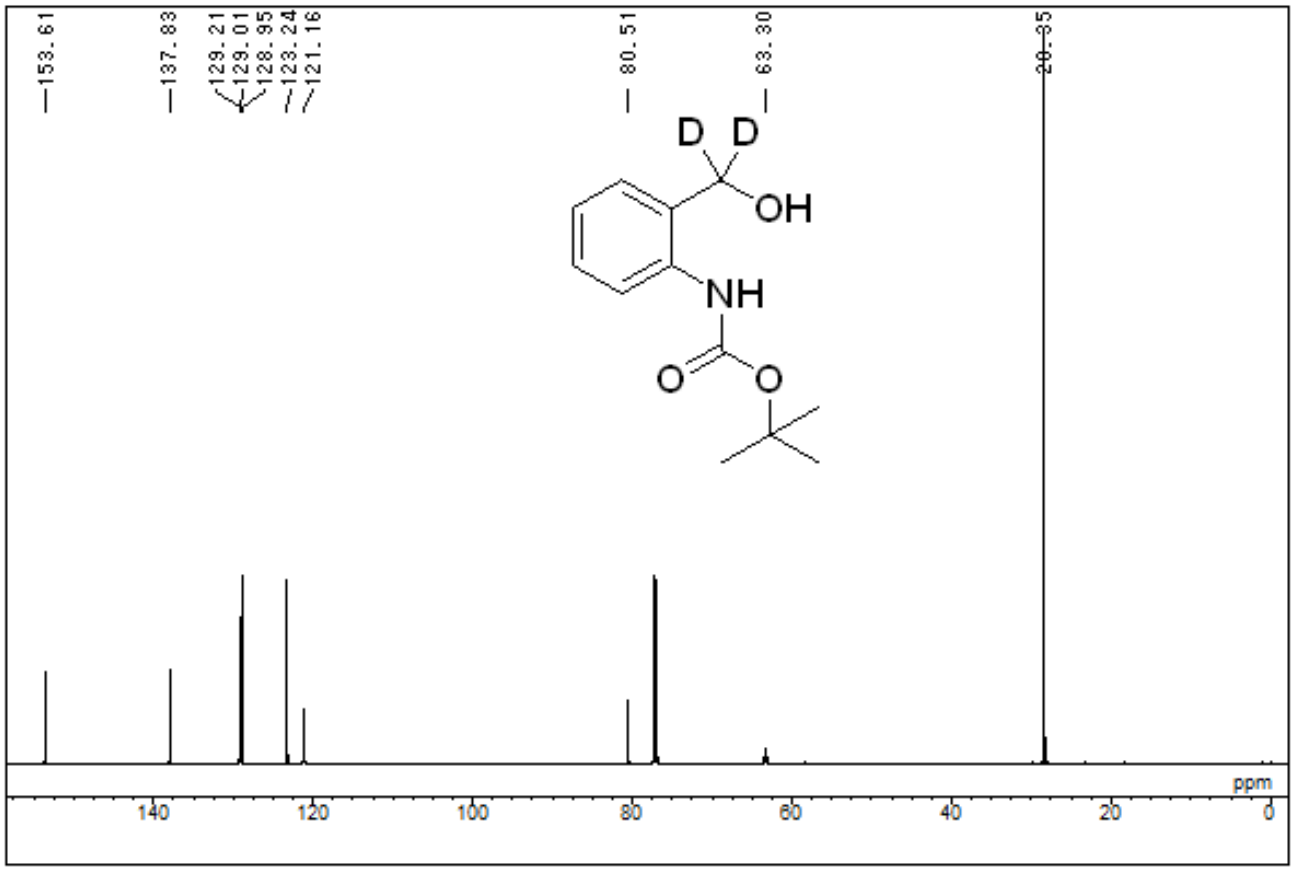
• ^{13}C-NMR spectrum of ***cis*-8b**



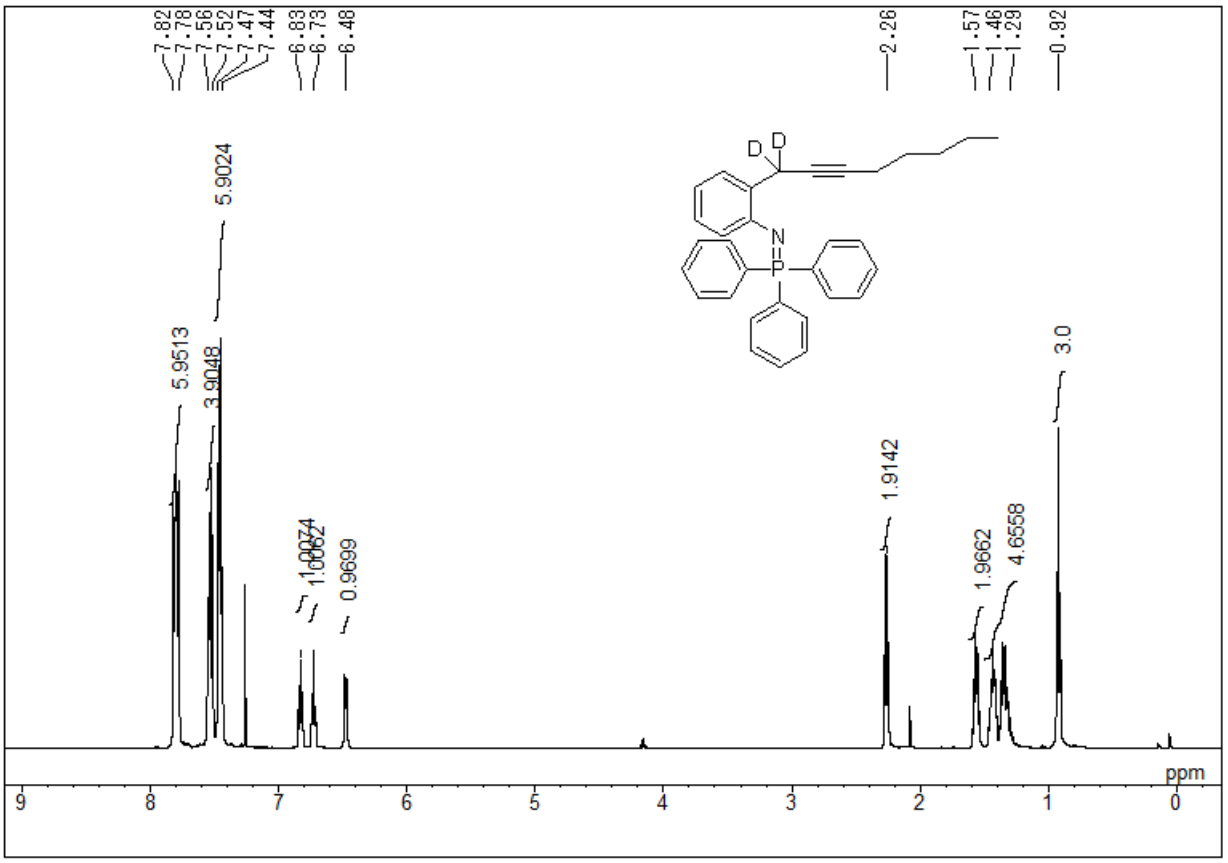
• ^{1}H-NMR spectrum of **S2**



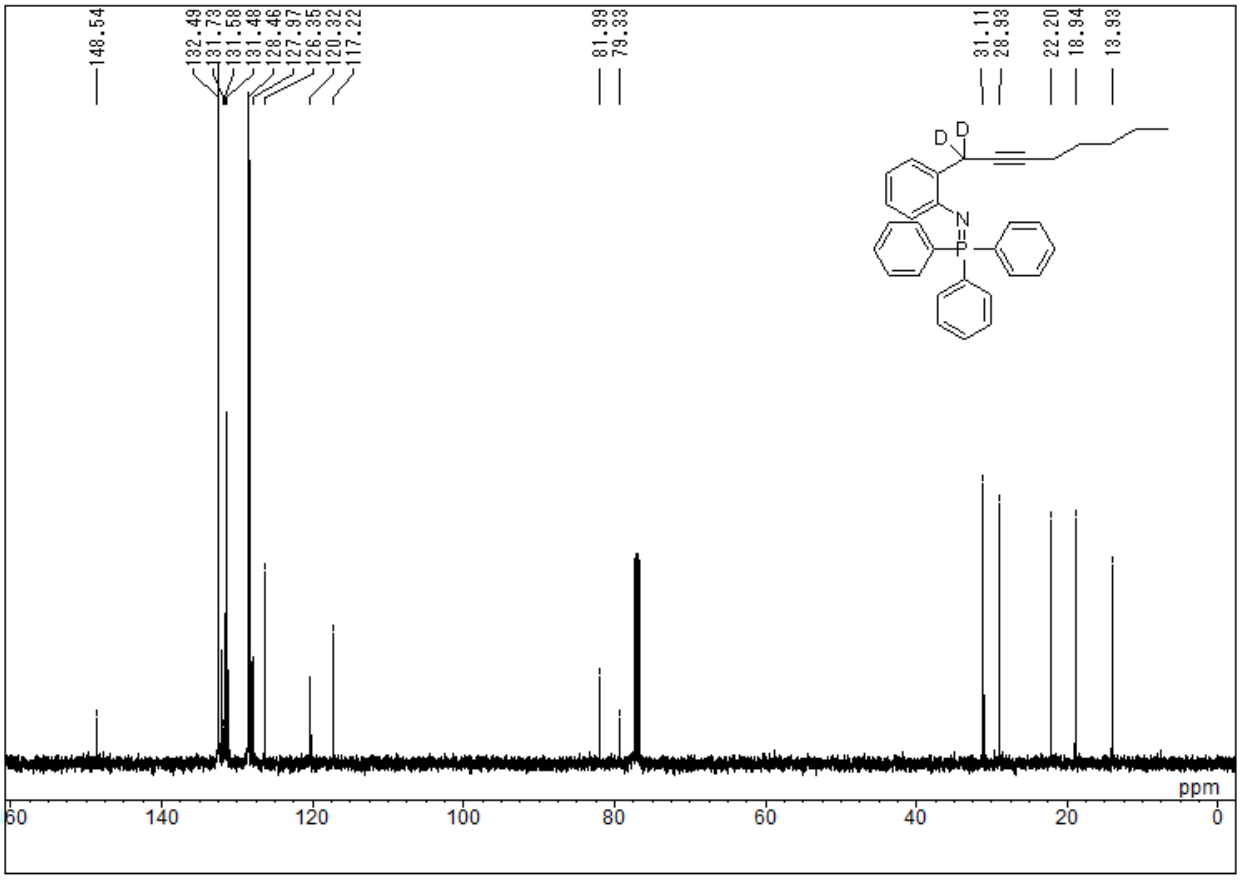
• ^{13}C-NMR spectrum of of **S2**



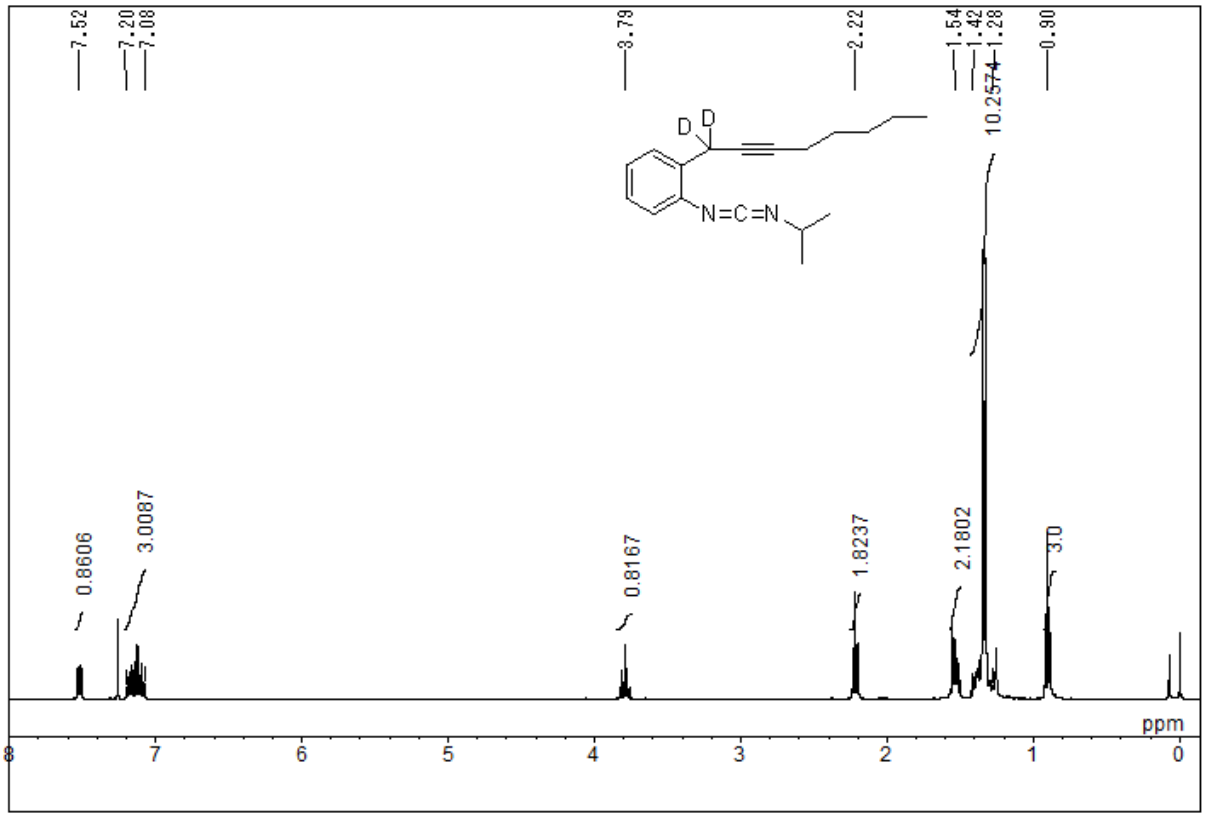
• ^{1}H-NMR spectrum of **S6**



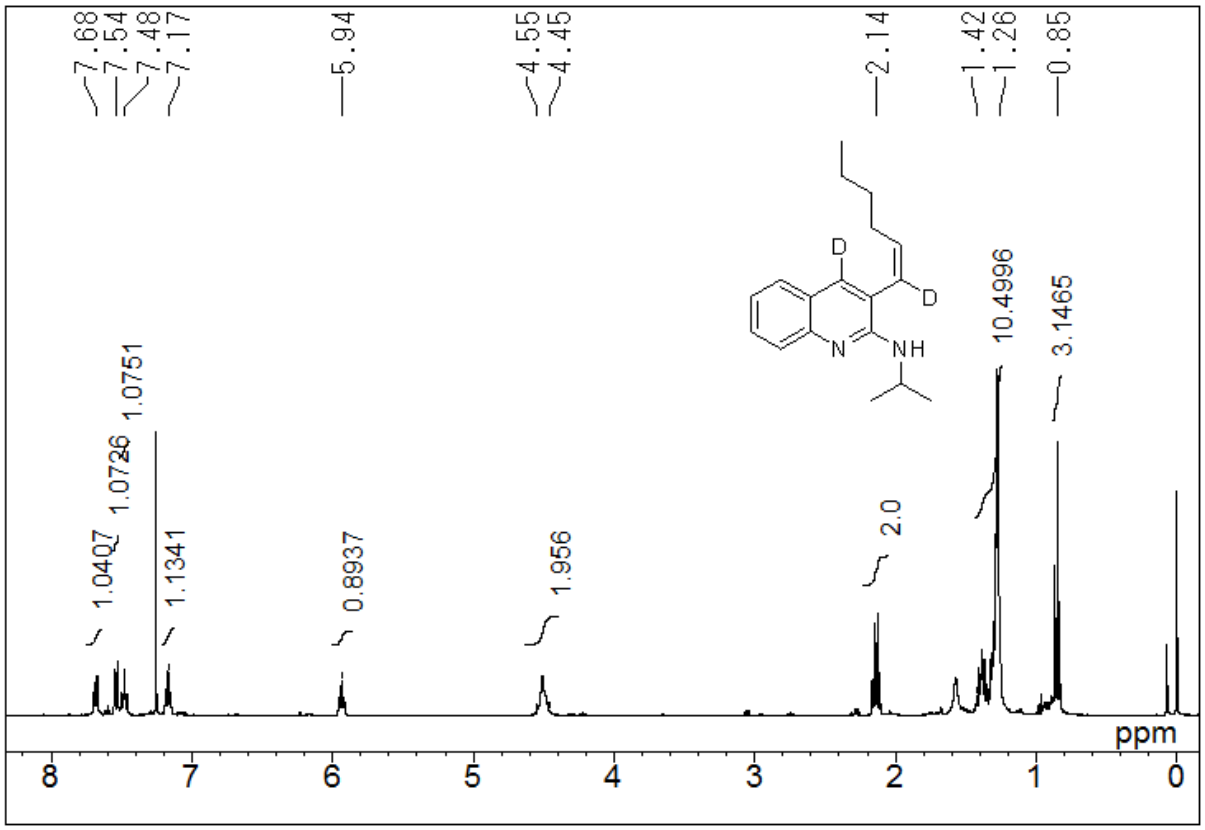
• ^{13}C-NMR spectrum of **S6**



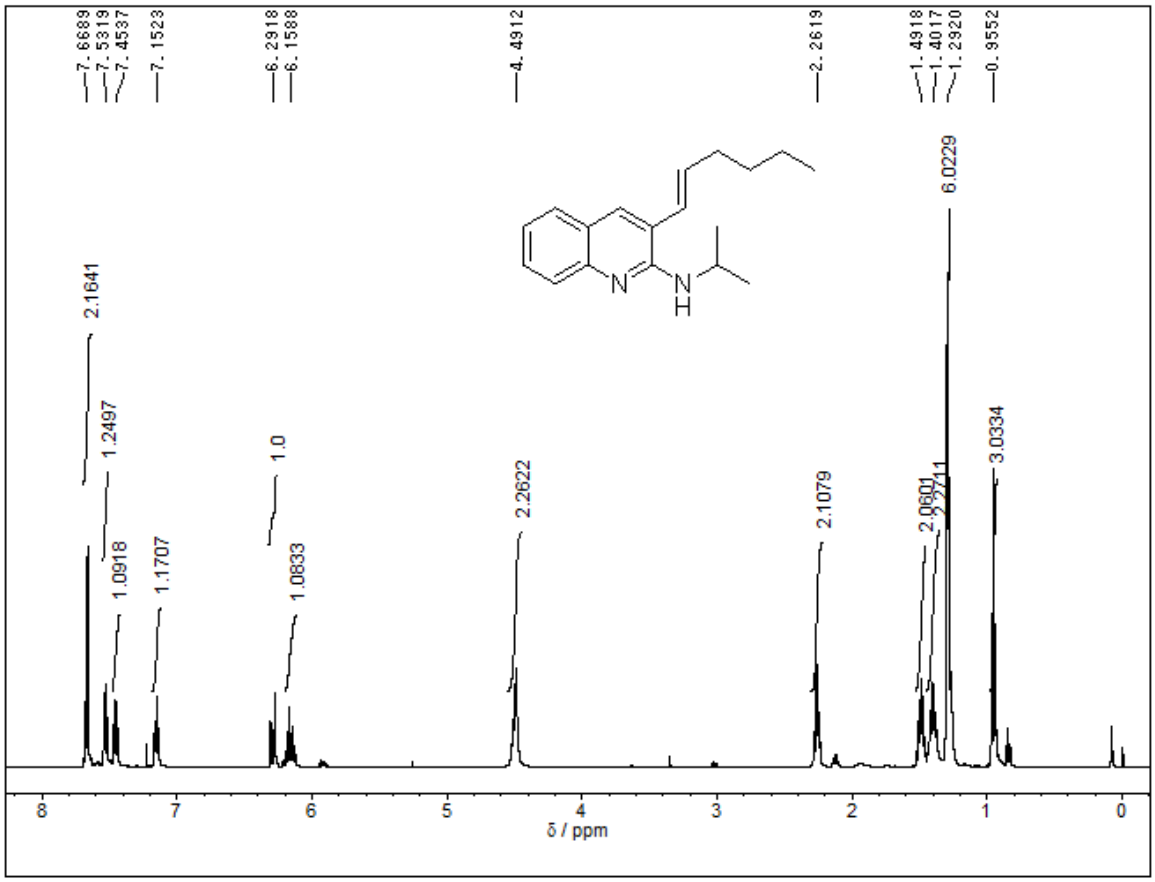
• ^{1}H-NMR spectrum of **1a-d_2**



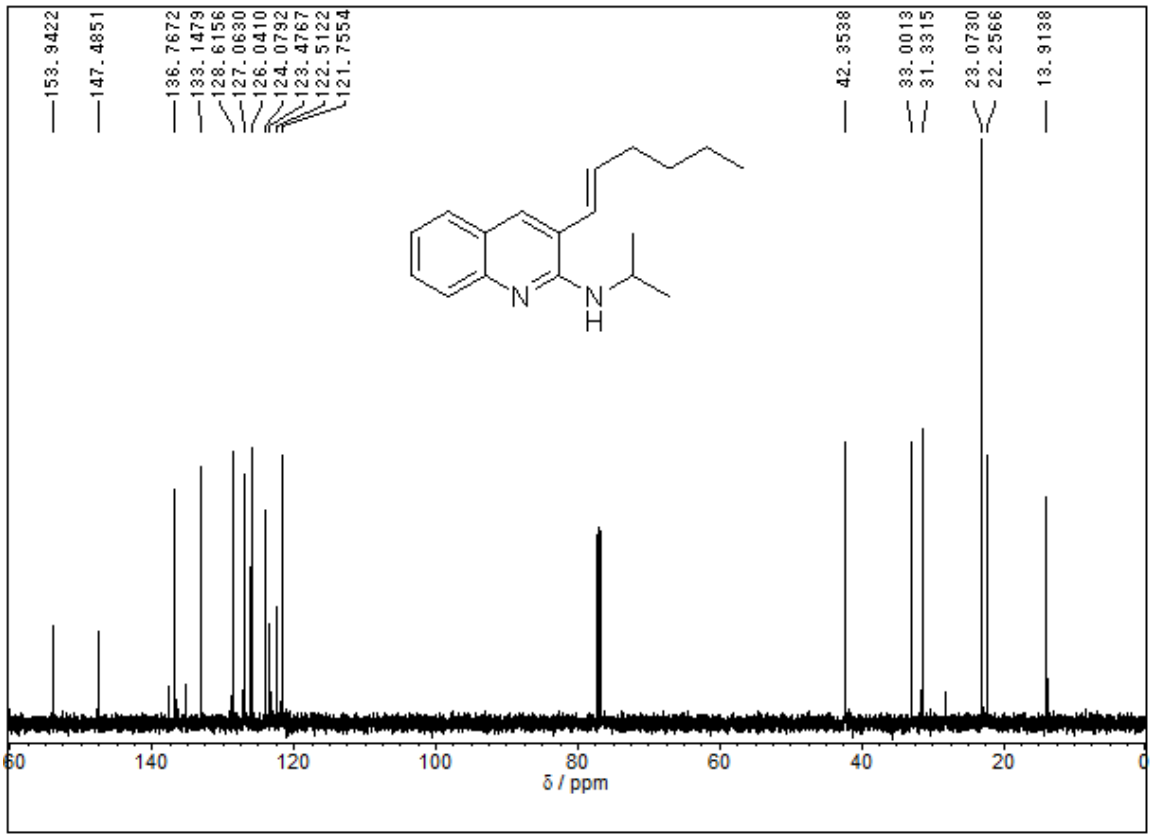
• ^{1}H-NMR spectrum of ***cis*-2a-d_2**



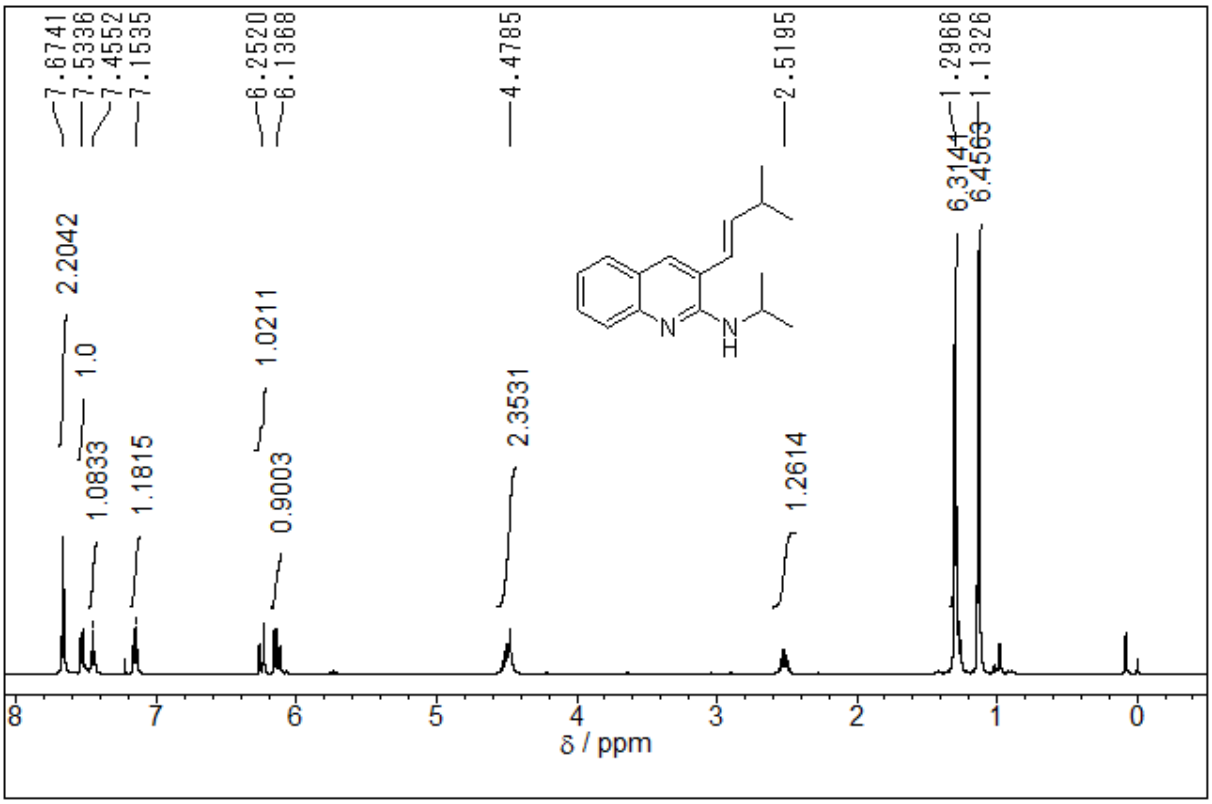
• ^{1}H-NMR spectrum of ***trans*-2a**



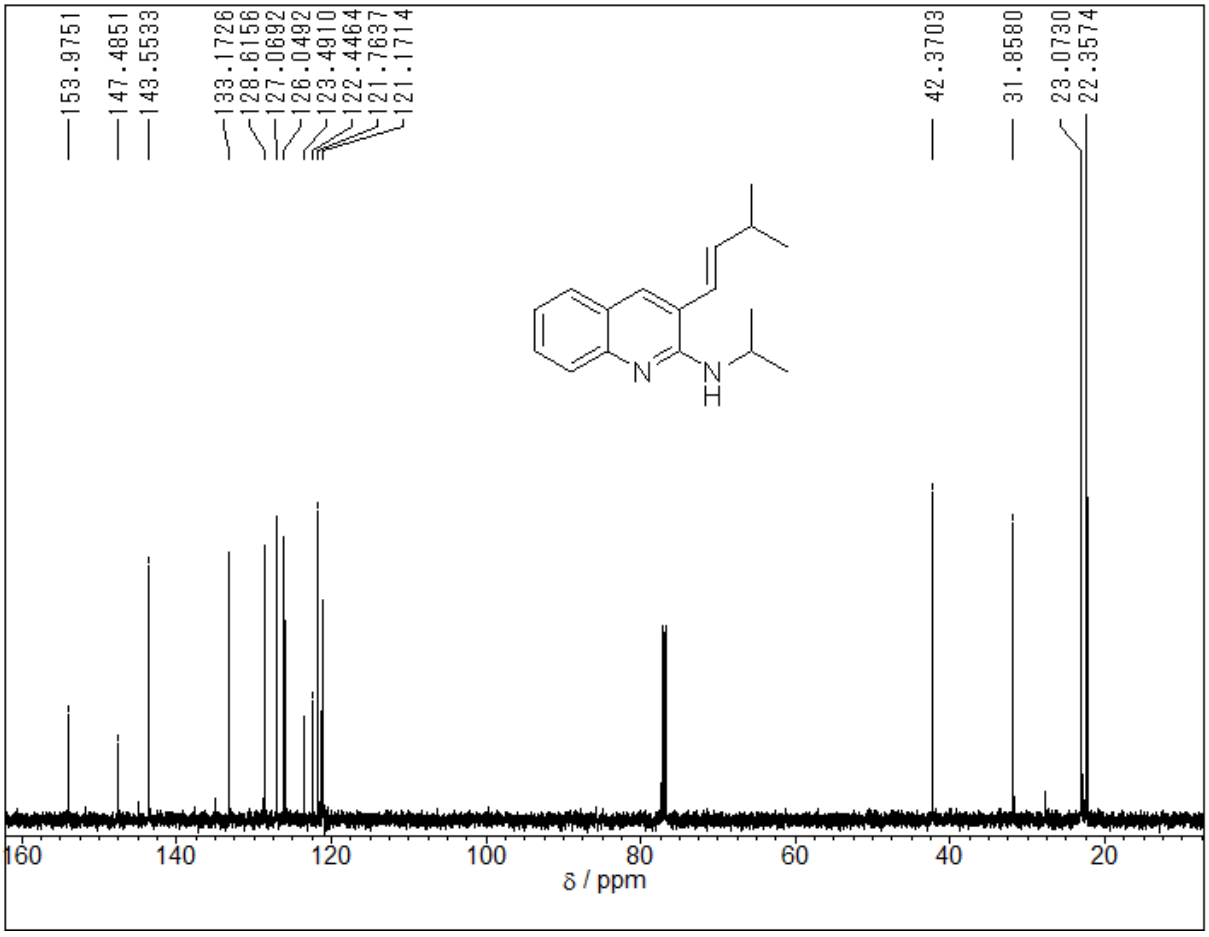
• ^{13}C-NMR spectrum of ***trans*-2a**



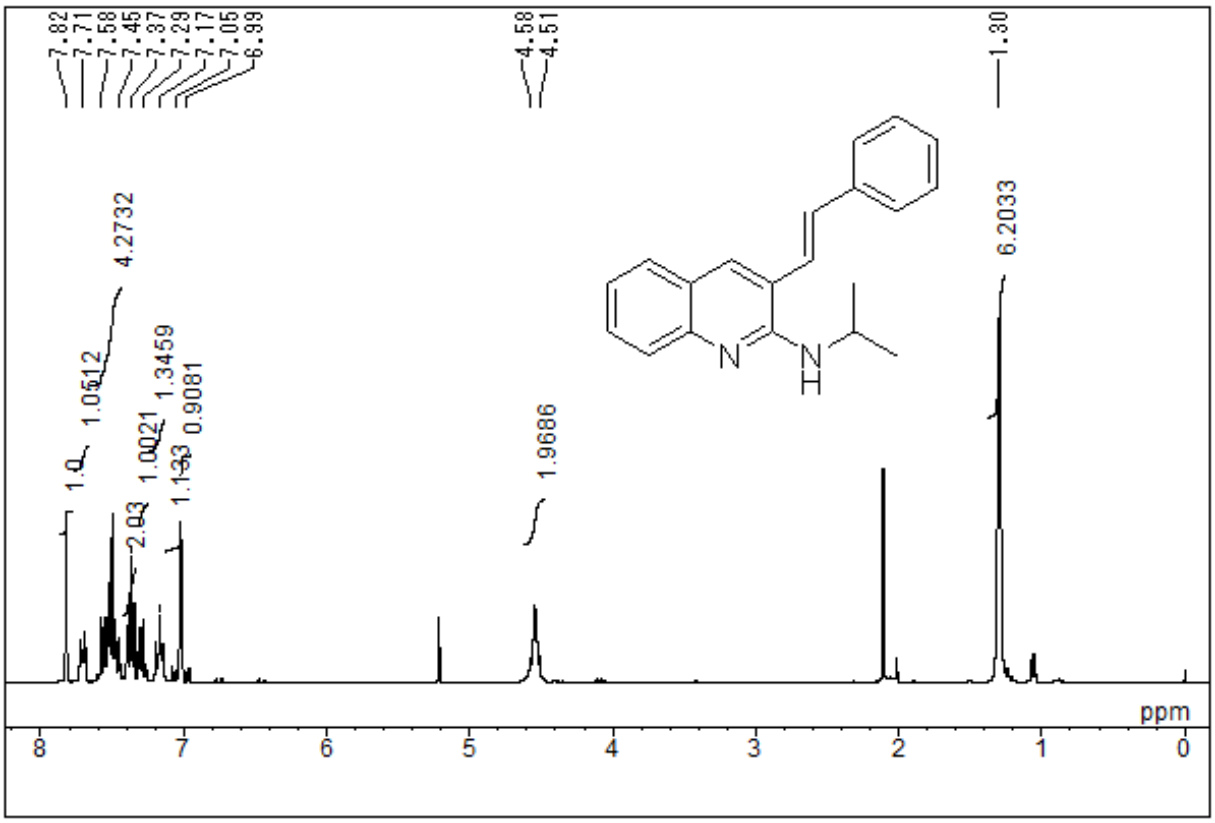
• ^{1}H-NMR spectrum of ***trans*-2n**



• ^{13}C-NMR spectrum of ***trans*-2n**



• ^{1}H-NMR spectrum of ***trans*-2s**



• ^{13}C-NMR spectrum of ***trans*-2s**