Supporting Information for:

A highly efficient heterogeneous copper-catalyzed three-component coupling of tetrahydroisoquinolines, aldehydes and 1-alkynes

Hong Zhao,[a,b] Wen He,[a] Li Wei,[a] and Mingzhong Cai[a]*

[a] *Key Laboratory of Functional Small Organic Molecule, Ministry of Education and College of Chemistry & Chemical Engineering, Jiangxi Normal University, Nanchang 330022, P. R. China*

[b] *School of Chemistry and Chemical Engineering, Guangdong Pharmaceutical University, Guangzhou 510006, P. R. China*

mzcai@jxnu.edu.cn

The Spectral Data of C1-alkynylated THIQs 4a-4t:

2-Benzyl-1-(oct-1-ynyl)-1,2,3,4-tetrahydroisoquinoline (4a). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 6.8 Hz, 2H), 7.33 (t, J = 7.4 Hz, 2H), 7.28–7.09 (m, 5H), 4.54 (s, 1H), 3.88 (d, J = 13.0 Hz, 1H), 3.80 (d, J = 13.0 Hz, 1H), 3.05-2.88 (m, 2H), 2.81-2.64 (m, 2H), 2.23 (td, J = 6.8, 2.0 Hz, 2H), 1.56–1.49 (m, 2H), 1.48-1.41 (m, 2H), 1.35-1.25 (m, 4H), 0.89 (t, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6, 136.4, 133.9, 129.3, 128.9, 128.3, 127.7, 127.1, 126.7, 125.7, 87.2, 77.9, 59.5, 54.1, 45.6, 31.4, 29.1, 29.0, 28.6, 22.6, 18.9, 14.1. MS (EI, 70 eV) *m/z*: 331 $[M]^+$. Anal. Calcd for $C_{24}H_{29}N$: C, 86.96; H, 8.82; N, 4.22. Found: C, 86.69; H, 8.71; N, 4.34.

2-(4-Methylbenzyl)-1-(oct-1-ynyl)-1,2,3,4-tetrahydroisoquinoline (4b). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 8.0 Hz, 2H), 7.19-7.05 (m, 6H), 4.54 (s, 1H), 3.84 (d, J = 13.0 Hz, 1H), 3.76 (d, J = 13.0 Hz, 1H), 2.98-2.90 (m, 2H), 2.78-2.67 (m, 2H), 2.34 (s, 3H), 2.22 (td, J = 6.8, 2.0 Hz, 2H), 1.54–1.47 (m, 2H), 1.46-

1.39 (m, 2H), 1.33-1.24 (m, 4H), 0.89 (t, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.7, 136.3, 135.3, 133.8, 129.3, 129.0, 128.9, 127.7, 126.7, 125.7, 87.3, 77.9, 59.1, 54.1, 45.5, 31.4, 29.7, 29.0, 28.6, 22.6, 21.2, 18.9, 14.1. MS (EI, 70 eV) *m/z*: 345 $[M]^+$. Anal. Calcd for $C_{25}H_{31}N$: C, 86.90; H, 9.04; N, 4.05. Found: C, 86.64; H, 9.16; N, 3.79.

2-(4-Methoxybenzyl)-1-(oct-1-ynyl)-1,2,3,4-tetrahydroisoquinoline (4c). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 8.4 Hz, 2H), 7.20-7.04 (m, 4H), 6.86 (d, J = 8.4 Hz, 2H), 4.52 (s, 1H), 3.81 (d, J = 13.0 Hz, 1H), 3.80 (s, 3H), 3.75 (d, J = 13.0 Hz, 1H), 2.97-2.91 (m, 2H), 2.76-2.65 (m, 2H), 2.23 (td, J = 7.0, 2.0 Hz, 2H), 1.53–1.46 (m, 2H), 1.45-1.38 (m, 2H), 1.32-1.23 (m, 4H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3, 135.8, 133.3, 130.4, 130.0, 128.4, 127.2, 126.2, 125.2, 113.2, 86.8, 77.4, 58.3, 54.8, 53.4, 45.0, 30.9, 28.5, 28.1, 22.1, 18.4, 13.6. MS (EI, 70 eV) *m/z*: 361 $[M]^+$. Anal. Calcd for $C_{25}H_{31}NO$: C, 83.06; H, 8.64; N, 3.87. Found: C, 82.79; H, 8.41; N, 3.71.

2-(4-Bromobenzyl)-1-(oct-1-ynyl)-1,2,3,4-tetrahydroisoquinoline (4d). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.23-7.07 (m, 4H), 4.51 (s, 1H), 3.82 (d, J = 13.4 Hz, 1H), 3.74 (d, J = 13.4 Hz, 1H), 2.99-2.92 (m, 2H), 2.77-2.66 (m, 2H), 2.22 (td, J = 6.8, 2.0 Hz, 2H), 1.58–1.49 (m, 2H), 1.47-1.40 (m, 2H), 1.33-1.24 (m, 4H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 136.2, 133.7, 131.4, 130.9, 128.9, 127.7, 126.8, 125.8, 120.9, 87.4, 77.7, 58.8, 54.1, 45.6, 31.4, 29.1, 29.0, 28.6, 22.6, 18.9, 14.1. MS (EI, 70 eV) *m/z*: 410 $[M]^+$. Anal. Calcd for $C_{24}H_{28}NBr$: C, 70.22; H, 6.88; N, 3.41. Found: C, 69.96; H, 6.58; N, 3.50.

2-(4-Chlorobenzyl)-1-(oct-1-ynyl)-1,2,3,4-tetrahydroisoquinoline (4e). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.20-7.06 (m, 4H), 4.51 (s, 1H), 3.84 (d, J = 13.2 Hz, 1H), 3.76 (d, J = 13.2 Hz, 1H), 2.98-2.91 (m, 2H), 2.78-2.67 (m, 2H), 2.22 (td, J = 6.8, 2.0 Hz, 2H), 1.59-1.50 (m, 2H), 1.48-1.41 (m, 2H), 1.32-1.23 (m, 4H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100

MHz, $CDCl_3$): δ 136.8, 136.0, 133.6, 132.9, 130.6, 128.9, 128.4, 127.7, 126.8, 125.8, 86.6, 77.5, 58.7, 54.0, 45.6, 31.3, 29.0, 28.9, 28.6, 22.6, 18.9, 14.0. MS (EI, 70 eV) *m/z*: 365 $[M]^+$. Anal. Calcd for $C_{24}H_{28}NCl$: C, 78.76; H, 7.71; N, 3.83. Found: C, 78.88; H, 7.52; N, 3.67.

1-(Oct-1-ynyl)-2-(4-trifluoromethylbenzyl)-1,2,3,4-tetrahydroisoquinoline (4f). Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.61-7.54 (m, 4H), 7.21-7.07 (m, 4H), 4.53 (s, 1H), 3.93 (d, J = 13.6 Hz, 1H), 3.85 (d, J = 13.6 Hz, 1H), 3.04-2.93 (m, 2H), 2.82-2.66 (m, 2H), 2.23 (td, J = 6.8, 1.6 Hz, 2H), 1.58-1.49 (m, 2H), 1.46-1.38 (m, 2H), 1.33-1.24 (m, 4H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.9, 136.1, 133.6, 129.4 (q, $^2J_{C\text{-}F}$ = 32.0 Hz), 129.3, 128.9, 127.7, 126.8, 125.8, 125.2 (q, $^3J_{C\text{-}F}$ = 4.0 Hz), 124.3 (q, $^1J_{C\text{-}F}$ = 271.0 Hz), 87.4, 77.6, 59.0, 54.2, 45.7, 31.3, 29.0, 28.9, 28.6, 22.6, 18.8, 14.0. MS (EI, 70 eV) *m/z*: 399 $[M]^+$. Anal. Calcd for $C_{25}H_{28}NF_3$: C, 75.16; H, 7.06; N, 3.50. Found: C, 74.87; H, 7.23; N, 3.62.

2-(2-Methylbenzyl)-1-(oct-1-ynyl)-1,2,3,4-tetrahydroisoquinoline (4g). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.43-7.37 (m, 1H), 7.21-7.06 (m, 7H), 4.54 (s, 1H), 3.85 (d, J = 13.2 Hz, 1H), 3.76 (d, J = 13.2 Hz, 1H), 3.01-2.92 (m, 2H), 2.76-2.68 (m, 2H), 2.39 (s, 3H), 2.23 (td, J = 6.8, 1.6 Hz, 2H), 1.55–1.48 (m, 2H), 1.46-1.38 (m, 2H), 1.34-1.25 (m, 4H), 0.88 (t, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 136.5, 134.0, 130.3, 129.9, 128.9, 127.7, 127.1, 126.7, 126.6, 125.7, 125.5, 87.2, 78.1, 57.3, 54.2, 45.4, 31.4, 29.2, 29.0, 28.6, 22.6, 19.3, 18.9, 14.1. MS (EI, 70 eV) *m/z*: 345 $[M]^+$. Anal. Calcd for $C_{25}H_{31}N$: C, 86.90; H, 9.04; N, 4.05. Found: C, 86.71; H, 8.79; N, 3.82.

2-(2-Bromobenzyl)-1-(oct-1-ynyl)-1,2,3,4-tetrahydroisoquinoline (4h). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.59-7.53 (m, 2H), 7.28-7.20 (m, 2H), 7.17-7.07 (m, 4H), 4.64 (s, 1H), 3.96 (d, J = 14.4 Hz, 1H), 3.92 (d, J = 14.4 Hz, 1H), 3.12-2.93 (m, 2H), 2.77-2.67 (m, 2H), 2.23 (td, J = 6.8, 1.6 Hz, 2H), 1.57–1.49 (m, 2H), 1.48-1.39 (m, 2H), 1.35-1.26 (m, 4H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1, 136.4, 133.9, 132.8, 130.6, 128.9, 128.4, 127.7, 127.2, 126.7, 125.7,

124.8, 87.1, 78.1, 58.8, 54.5, 45.6, 31.4, 29.2, 29.0, 28.6, 22.6, 18.9, 14.1. MS (EI, 70 eV) *m/z*: 410 $[M]^+$. Anal. Calcd for $C_{24}H_{28}NBr$: C, 70.22; H, 6.88; N, 3.41. Found: C, 69.93; H, 6.64; N, 3.29.

2-(Naphthalen-1-ylmethyl)-1-(oct-1-ynyl)-1,2,3,4-tetrahydroisoquinoline (4i). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 8.40-8.37 (m, 1H), 7.84-7.81 (m, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 6.8 Hz, 1H), 7.46-7.40 (m, 3H), 7.21-7.18 (m, 1H), 7.14-7.04 (m, 3H), 4.59 (s, 1H), 4.40 (d, J = 13.2 Hz, 1H), 4.12 (d, J = 13.2 Hz, 1H), 3.07-3.01 (m, 1H), 2.98-2.87 (m, 1H), 2.79-2.68 (m, 2H), 2.28 (td, J = 6.8, 1.6 Hz, 2H), 1.60–1.53 (m, 2H), 1.48-1.40 (m, 2H), 1.34-1.25 (m, 4H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.0, 133.8, 133.6, 133.4, 132.3, 128.3, 127.8, 127.5, 127.2, 127.1, 126.1, 125.3, 125.2, 125.1, 124.7, 124.5, 86.8, 77.8, 57.2, 54.1, 45.2, 30.9, 28.7, 28.6, 28.2, 22.1, 18.5, 13.6. MS (EI, 70 eV) *m/z*: 381 $[M]^+$. Anal. Calcd for $C_{28}H_{31}N$: C, 88.14; H, 8.19; N, 3.67. Found: C, 87.89; H, 8.26; N, 3.48.

1-(Oct-1-ynyl)-2-(thiophen-2-ylmethyl)-1,2,3,4-tetrahydroisoquinoline(4j). Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.24-7.20 (m, 2H), 7.15-7.11 (m, 2H), 7.10-7.05 (m, 1H), 7.02 (d, J = 2.7 Hz, 1H), 6.96 (dd, J = 4.8, 3.6 Hz, 1H), 4.64 (s, 1H), 4.07 (d, J = 13.8 Hz, 1H), 4.02 (d, J = 13.8 Hz, 1H), 3.03-2.91 (m, 2H), 2.84-2.71 (m, 2H), 2.22 (td, J = 7.0, 2.0 Hz, 2H), 1.61-1.49 (m, 2H), 1.46-1.36 (m, 2H), 1.34-1.25 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.5, 135.5, 133.3, 128.4, 127.2, 126.2, 126.0, 125.7, 125.3, 124.6, 86.9, 77.2, 53.5, 53.4, 45.0, 30.8, 28.6, 28.4, 28.1, 22.1, 18.4, 13.6. MS (EI, 70 eV) *m/z*: 337 $[M]^+$. Anal. Calcd for $C_{22}H_{27}NS$: C, 78.29; H, 8.06; N, 4.15. Found: C, 78.02; H, 7.82; N, 3.89.

2-(Cyclopropylmethyl)-1-(oct-1-ynyl)-1,2,3,4-tetrahydroisoquinoline (4k). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.27-7.23 (m, 1H), 7.16-7.11 (m, 2H), 7.10-7.06 (m, 1H), 4.83 (s, 1H), 3.04-2.93 (m, 2H), 2.88-2.73 (m, 2H), 2.67 (dd, J = 12.5, 6.0 Hz, 1H), 2.49 (dd, J = 12.5, 7.1 Hz, 1H), 2.18 (td, J = 7.0, 2.0 Hz, 2H), 1.54–1.44 (m, 2H), 1.43-1.35 (m, 2H), 1.34-1.23 (m, 4H), 1.00-0.90 (m, 1H), 0.88 (t, J = 6.8 Hz, 3H), 0.59-0.48 (m, 2H), 0.40-0.32 (m, 1H), 0.20-0.13 (m, 1H). ^{13}C NMR

(100 MHz, $CDCl_3$): δ 136.3, 133.7, 128.9, 127.7, 126.7, 125.7, 87.2, 77.8, 59.9, 54.0, 46.0, 31.3, 28.9, 28.8, 28.5, 22.6, 18.8, 14.0, 8.7, 4.1, 3.3. MS (EI, 70 eV) *m/z*: 295 $[M]^+$. Anal. Calcd for $C_{21}H_{29}N$: C, 85.37; H, 9.89; N, 4.74. Found: C, 85.18; H, 9.67; N, 4.50.

2-Benzyl-1-(hex-1-ynyl)-1,2,3,4-tetrahydroisoquinoline (4l).[1] Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.28-7.09 (m, 5H), 4.54 (s, 1H), 3.88 (d, J = 13.2 Hz, 1H), 3.79 (d, J = 13.2 Hz, 1H), 2.98-2.93 (m, 2H), 2.77-2.70 (m, 2H), 2.24 (t, J = 6.8 Hz, 2H), 1.53-1.42 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 136.4, 133.9, 129.3, 128.9, 128.3, 127.7, 127.1, 126.7, 125.7, 87.2, 77.9, 59.4, 54.2, 45.6, 31.1, 29.0, 22.0, 18.6, 13.6. MS (EI, 70 eV) *m/z*: 303 $[M]^+$.

2-Benzyl-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline (4m).[1] Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.48-7.43 (m, 4H), 7.35-7.28 (m, 7H), 7.25-7.12 (m, 3H), 4.79 (s, 1H), 3.94 (d, J = 13.2 Hz, 1H), 3.91 (d, J = 13.2 Hz, 1H), 3.11-2.99 (m, 2H), 2.85-2.77 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 135.5, 134.1, 131.8, 129.3, 129.0, 128.3, 128.2, 128.0, 127.8, 127.2, 126.9, 125.8, 123.3, 87.6, 86.9, 59.6, 54.4, 45.8, 29.0. MS (EI, 70 eV) *m/z*: 323 $[M]^+$.

2-Benzyl-1-(5-phenylpent-1-ynyl)-1,2,3,4-tetrahydroisoquinoline (4n).[1] Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 7.2 Hz, 2H), 7.34-7.24 (m, 4H), 7.22-7.12 (m, 8H), 4.58 (s, 1H), 3.91 (d, J = 13.2 Hz, 1H), 3.84 (d, J = 13.2 Hz, 1H), 3.08-2.92 (m, 2H), 2.83-2.71 (m, 4H), 2.26-2.24 (m, 2H), 1.88-1.81 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 138.4, 136.2, 133.8, 129.3, 129.0, 128.6, 128.4, 128.3, 127.7, 127.2, 126.8, 126.0, 125.8, 86.9, 78.5, 59.5, 54.2, 45.6, 34.9, 30.7, 29.0, 18.4. MS (EI, 70 eV) *m/z*: 365 $[M]^+$.

2-Benzyl-1-(5-cyanopent-1-ynyl)-1,2,3,4-tetrahydroisoquinoline (4o).[1] Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, J = 7.2 Hz, 2H), 7.35-7.26 (m, 3H), 7.15-7.08 (m, 4H), 4.56 (s, 1H), 3.86 (d, J = 13.2 Hz, 1H), 3.77 (d, J = 13.2 Hz, 1H), 3.05-

2.91 (m, 2H), 2.82-2.72 (m, 2H), 2.48-2.42 (m, 4H), 1.90-1.83 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 135.8, 133.9, 129.1, 129.0, 128.4, 127.5, 127.2, 126.9, 125.8, 119.2, 84.1, 80.2, 59.5, 54.0, 45.6, 28.9, 24.8, 18.0, 16.2. MS (EI, 70 eV) *m/z*: 314 $[M]^+$.

2-Benzyl-1-(5-chloropent-1-ynyl)-1,2,3,4-tetrahydroisoquinoline (4p).[1] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 6.8 Hz, 2H), 7.36-7.25 (m, 3H), 7.17-7.07 (m, 4H), 4.56 (s, 1H), 3.87 (d, J = 13.6 Hz, 1H), 3.79 (d, J = 12.8 Hz, 1H), 3.65 (t, J = 6.0 Hz, 2H), 3.06-2.92 (m, 2H), 2.86-2.73 (m, 2H), 2.46-2.40 (m, 2H), 2.05-1.91 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 136.0, 133.8, 129.2, 128.9, 128.3, 127.6, 127.2, 126.8, 125.8, 85.0, 79.1, 59.4, 54.1, 45.6, 43.7, 31.6, 30.6, 16.4. MS (EI, 70 eV) *m/z*: 323 $[M]^+$.

1-(3-Acetoxyprop-1-ynyl)-2-benzyl-1,2,3,4-tetrahydroisoquinoline (4q). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 7.6 Hz, 2H), 7.35-7.26 (m, 4H), 7.16-7.06 (m, 3H), 4.73 (s, 2H), 4.62 (s, 1H), 3.86 (d, J = 13.2 Hz, 1H), 3.80 (d, J = 13.2 Hz, 1H), 3.02-2.93 (m, 2H), 2.85-2.73 (m, 2H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 138.1, 134.9, 134.1, 129.2, 129.0, 128.3, 127.7, 127.2, 127.1, 125.8, 84.8, 80.7, 59.4, 53.9, 52.5, 45.6, 28.9, 20.8. MS (EI, 70 eV) *m/z*: 319 $[M]^+$. Anal. Calcd for $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63; N, 4.38. Found: C, 78.72; H, 6.45; N, 4.21.

2-Benzyl-1-(trimethylsilylethynyl)-1,2,3,4-tetrahydroisoquinoline (4r).[1] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 7.2 Hz, 2H), 7.35-7.27 (m, 3H), 7.17-7.06 (m, 4H), 4.55 (s, 1H), 3.89 (d, J = 13.2 Hz, 1H), 3.81 (d, J = 13.2 Hz, 1H), 3.02-2.95 (m, 2H), 2.83-2.73 (m, 2H), 0.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1, 134.2, 133.8, 129.1, 128.7, 128.1, 127.6, 127.0, 126.6, 125.5, 103.4, 88.4, 59.2, 54.3, 45.5, 28.8, 0.0. MS (EI, 70 eV) *m/z*: 319 $[M]^+$.

2-(4-Bromobenzyl)-1-(hex-1-ynyl)-1,2,3,4-tetrahydroisoquinoline (4s). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 7.6 Hz, 2H), 7.46 (d, J = 7.6 Hz, 2H), 7.21-7.05 (m, 4H), 4.50 (s, 1H), 3.82 (d, J = 13.2 Hz, 1H), 3.73 (d, J = 13.6 Hz, 1H),

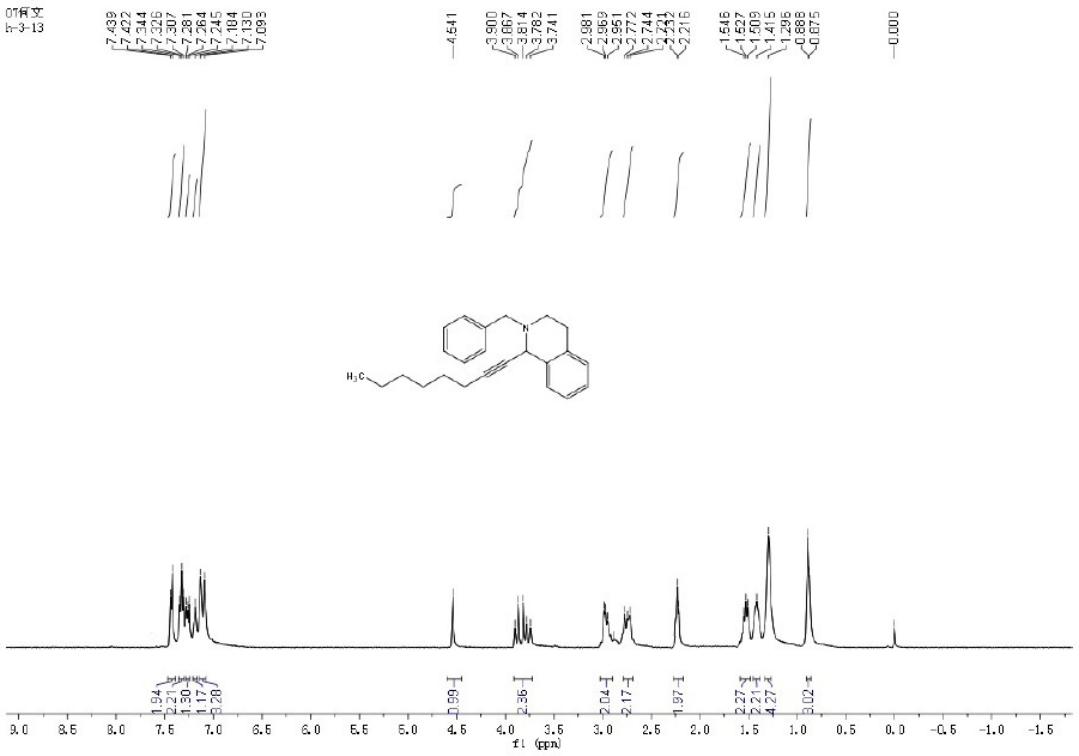
3.01-2.92 (m, 2H), 2.77-2.68 (m, 2H), 2.22 (t, J = 6.8 Hz, 2H), 1.53-1.38 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 136.1, 133.7, 131.4, 130.9, 128.9, 127.7, 126.8, 125.8, 120.9, 87.3, 77.6, 58.8, 54.0, 45.6, 31.1, 29.0, 22.0, 18.6, 13.6. MS (EI, 70 eV) *m/z*: 382 $[M]^+$. Anal. Calcd for $C_{22}H_{24}NBr$: C, 69.10; H, 6.33; N, 3.66. Found: C, 68.84; H, 6.12; N, 3.79.

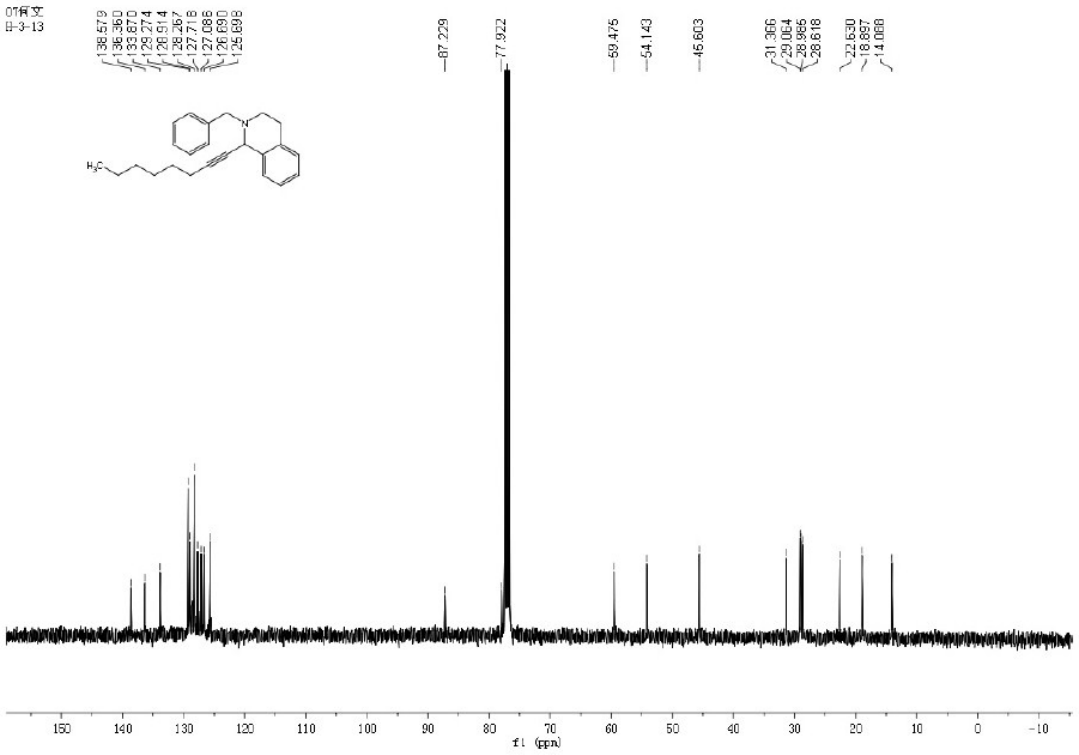
2-(4-Bromobenzyl)-1-(4-tolylethynyl)-1,2,3,4-tetrahydroisoquinoline (4t). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 8.0 Hz, 2H), 7.37-7.31 (m, 4H), 7.27-7.06 (m, 6H), 4.75 (s, 1H), 3.89 (d, J = 14.4 Hz, 1H), 3.84 (d, J = 13.2 Hz, 1H), 3.09-2.97 (m, 2H), 2.87-2.75 (m, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 135.4, 133.9, 131.7, 131.5, 131.0, 130.2, 129.0, 127.8, 127.0, 125.9, 121.0, 120.1, 87.1, 86.5, 58.9, 54.4, 45.8, 29.1, 21.5. MS (EI, 70 eV) *m/z*: 416 $[M]^+$. Anal. Calcd for $C_{25}H_{22}NBr$: C, 72.10; H, 5.32; N, 3.36. Found: C, 71.87; H, 5.11; N, 3.45.

References

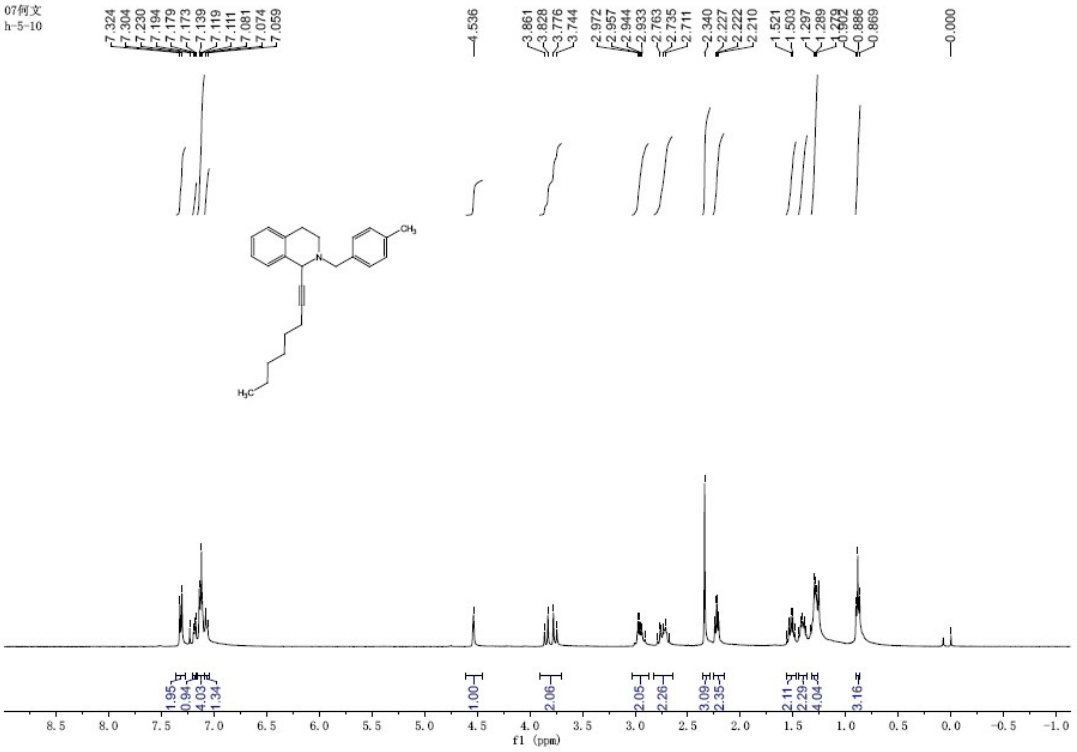
1 Q.-H Zheng, W. Meng, G.-J. Jiang and Z.-X. Yu, *Org. Lett.*, 2013, **15**, 5928–5931.

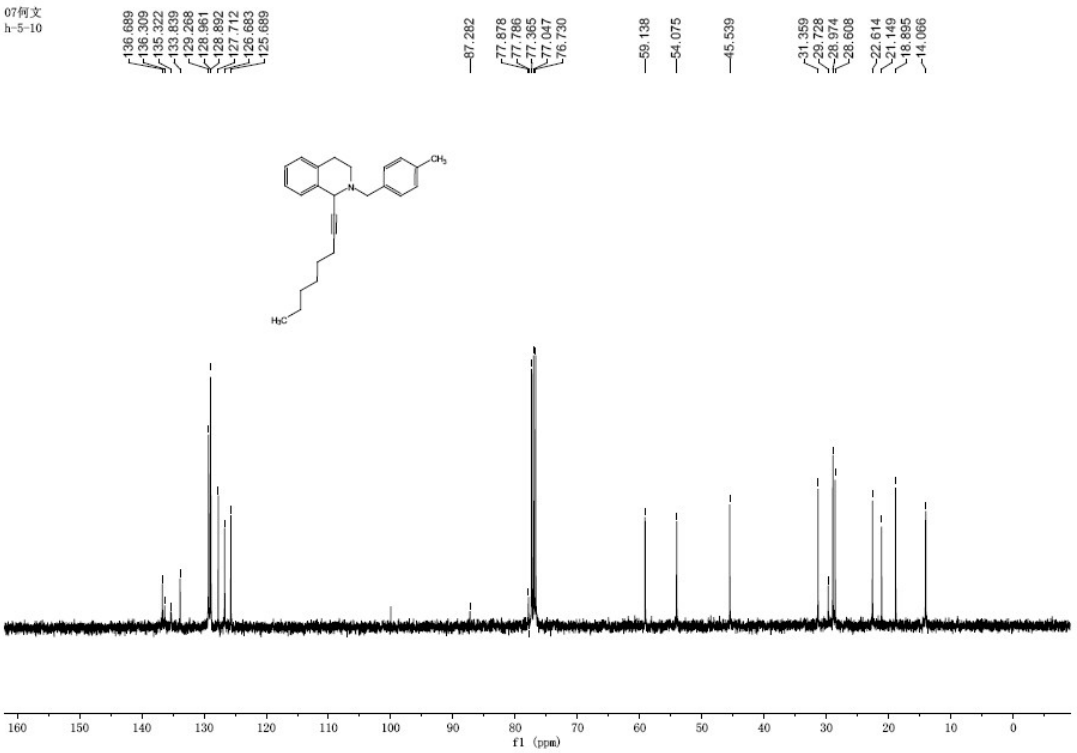
Copies of ^{1}H NMR and ^{13}C NMR Spectra of Compounds 4a-t



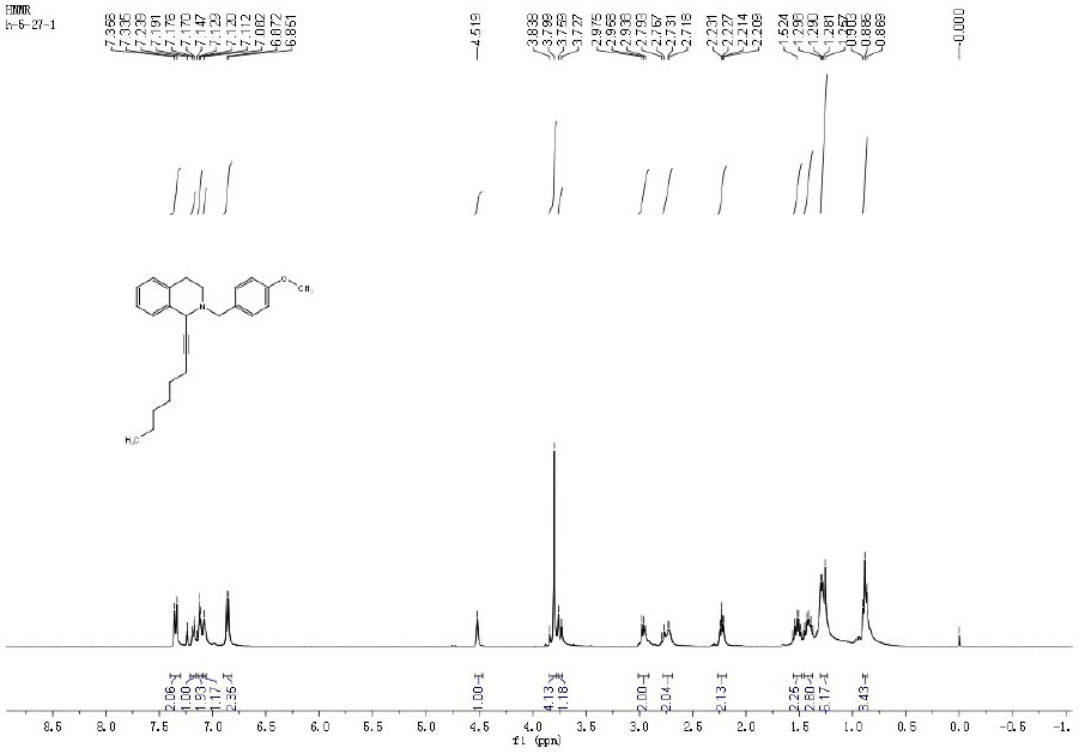


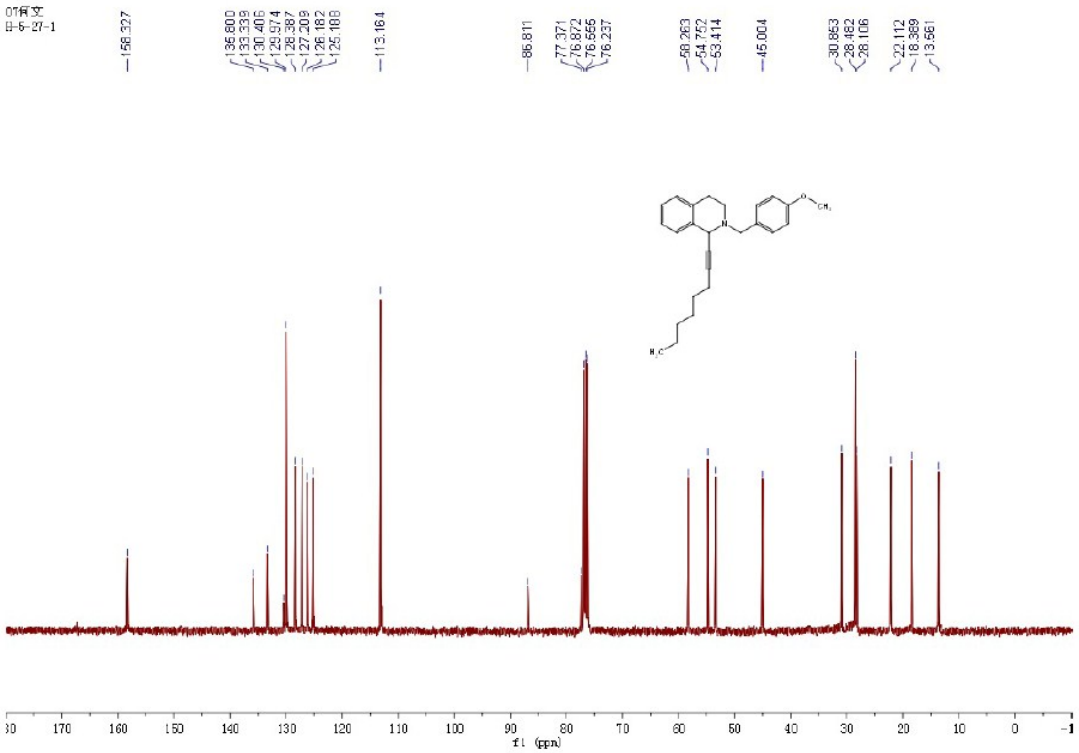
^{1}H NMR and ^{13}C NMR spectra of **4a**



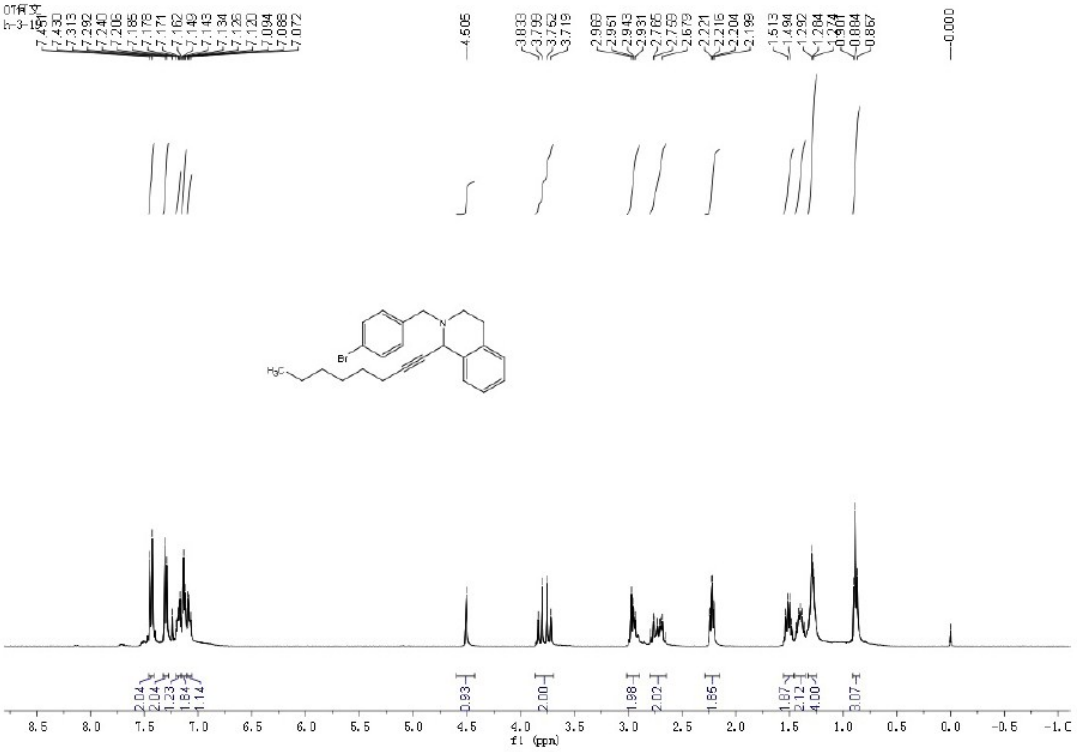


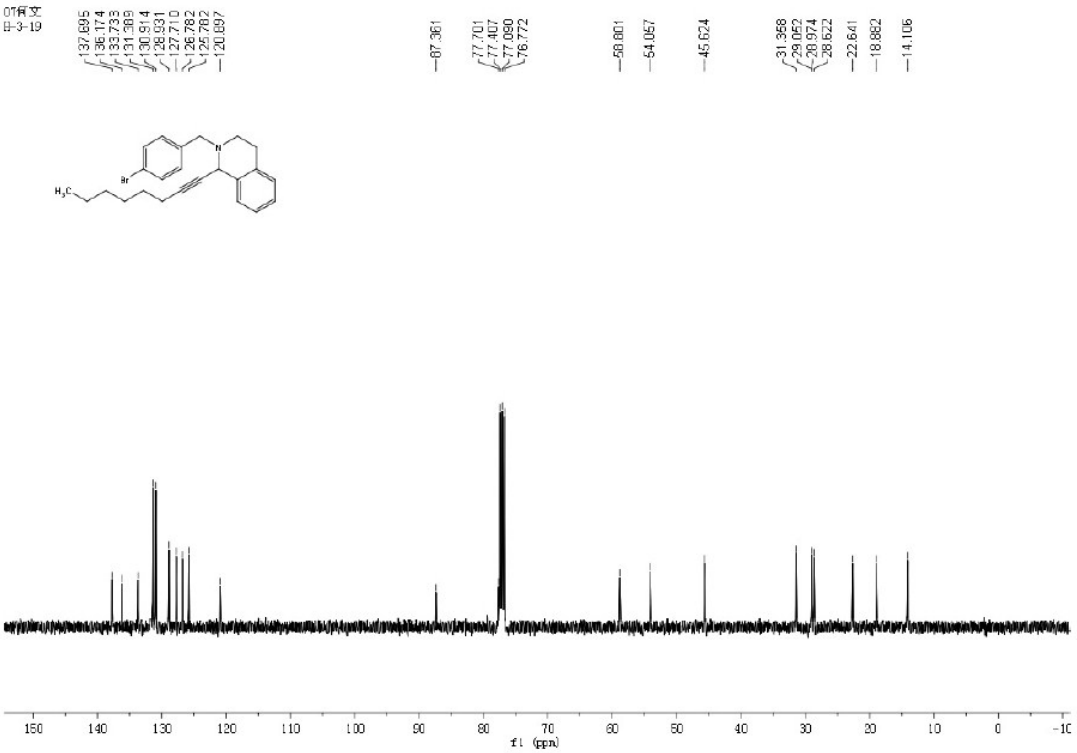
^{1}H NMR and ^{13}C NMR spectra of **4b**



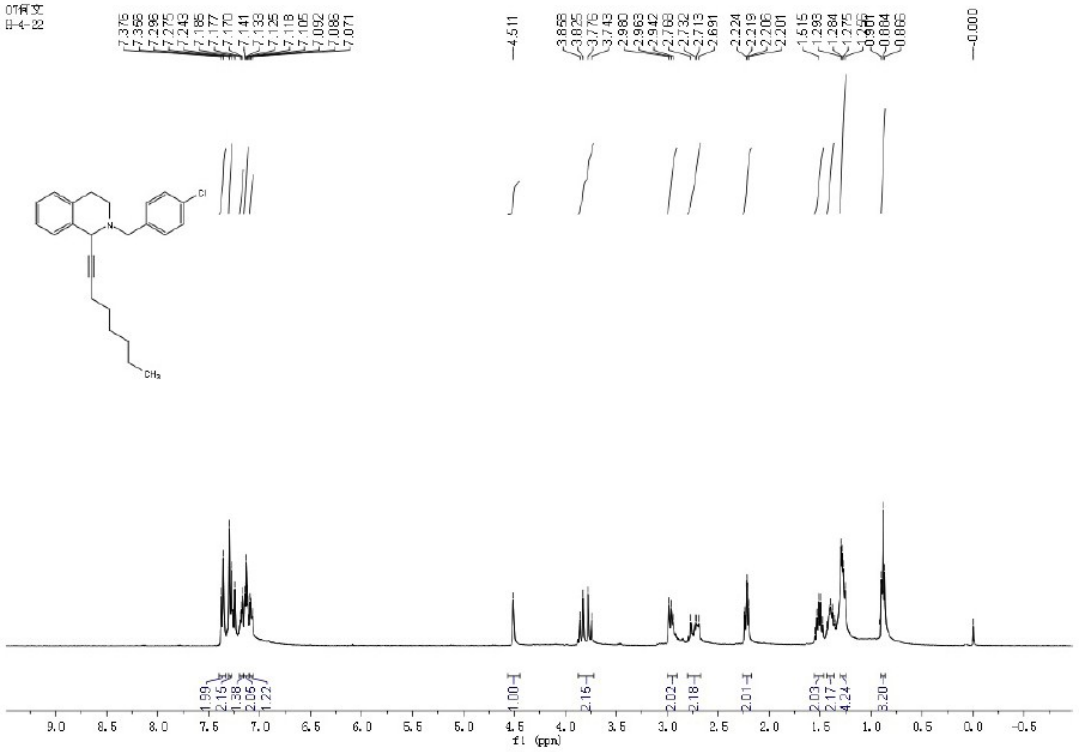


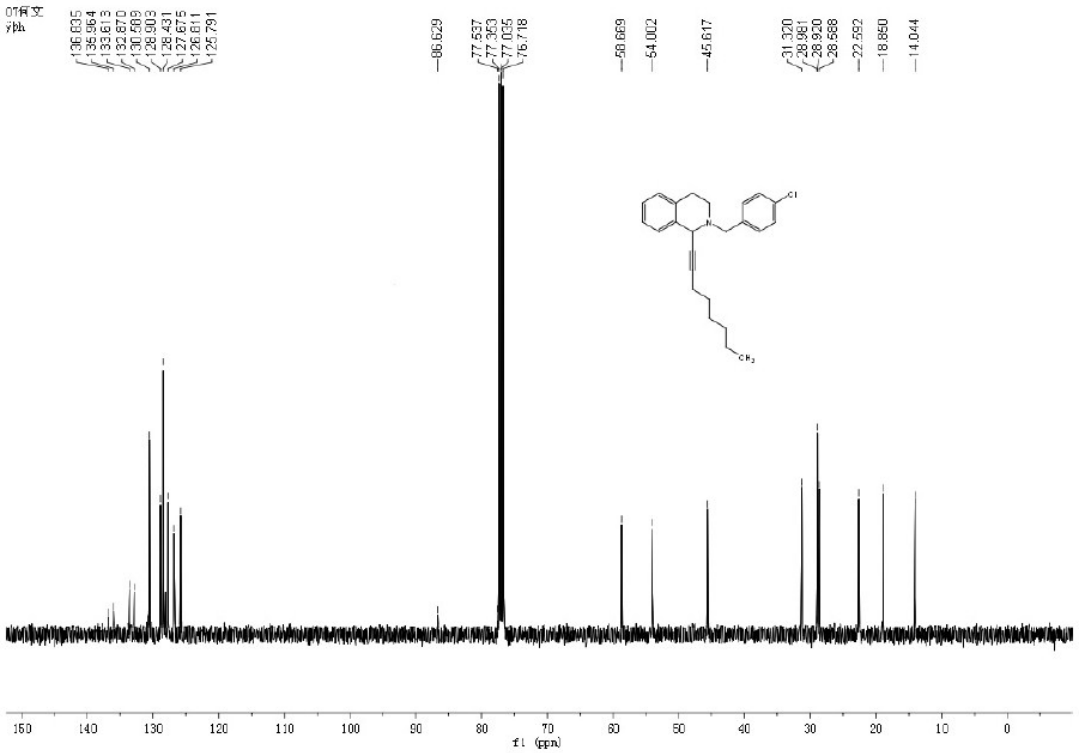
^{1}H NMR and ^{13}C NMR spectra of **4c**



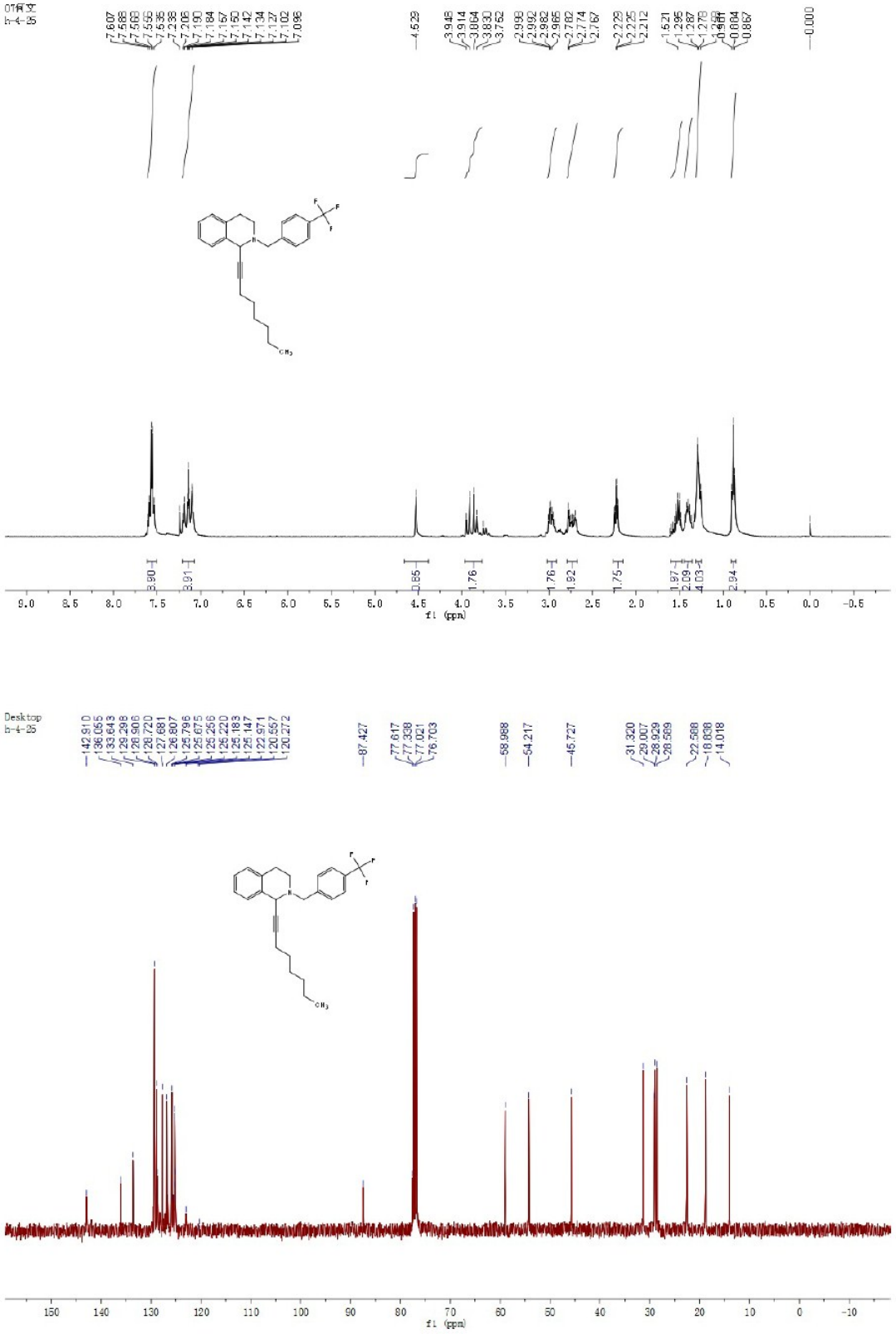


^{1}H NMR and ^{13}C NMR spectra of **4d**

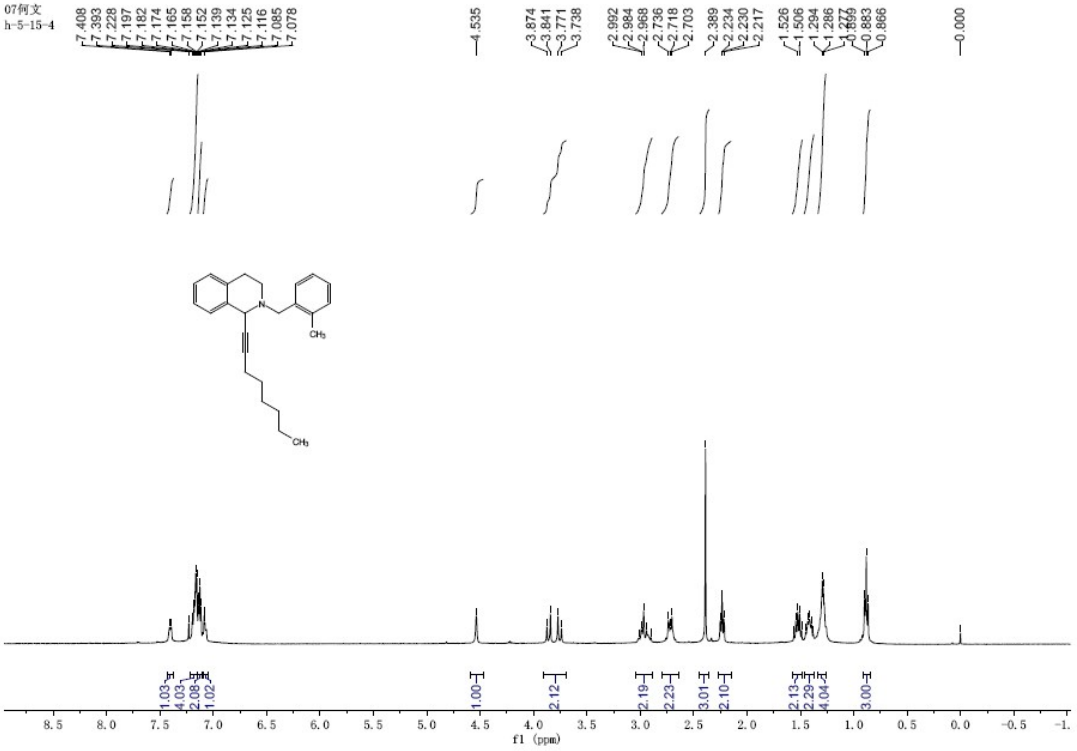


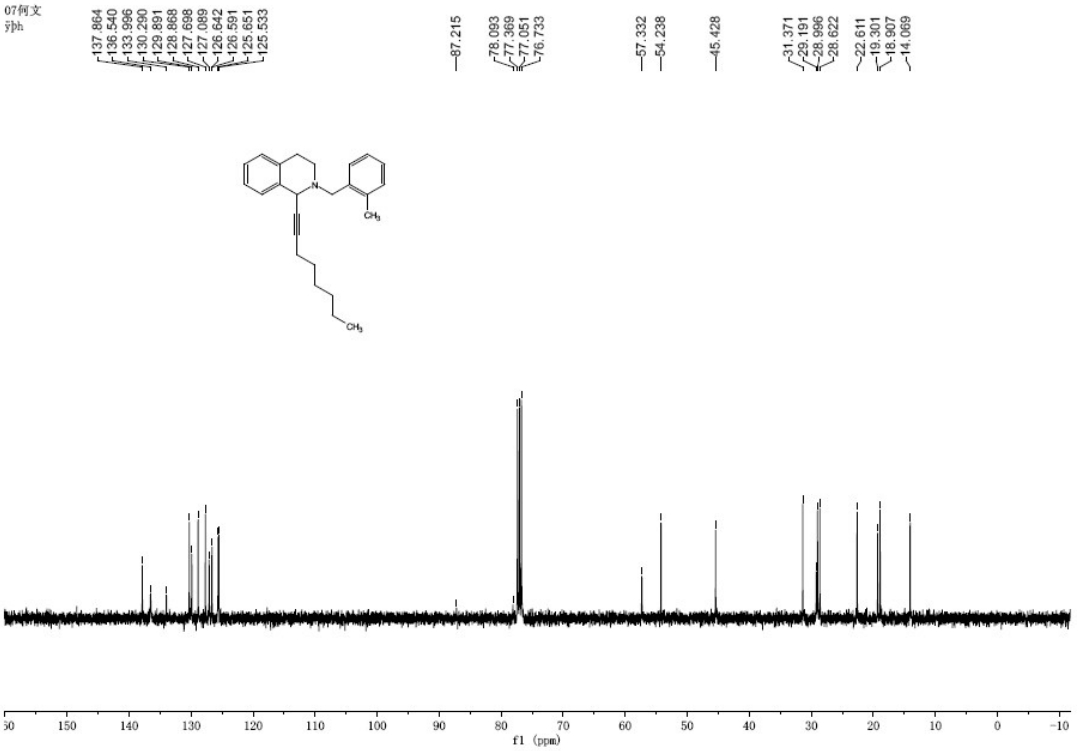


^{1}H NMR and ^{13}C NMR spectra of **4e**

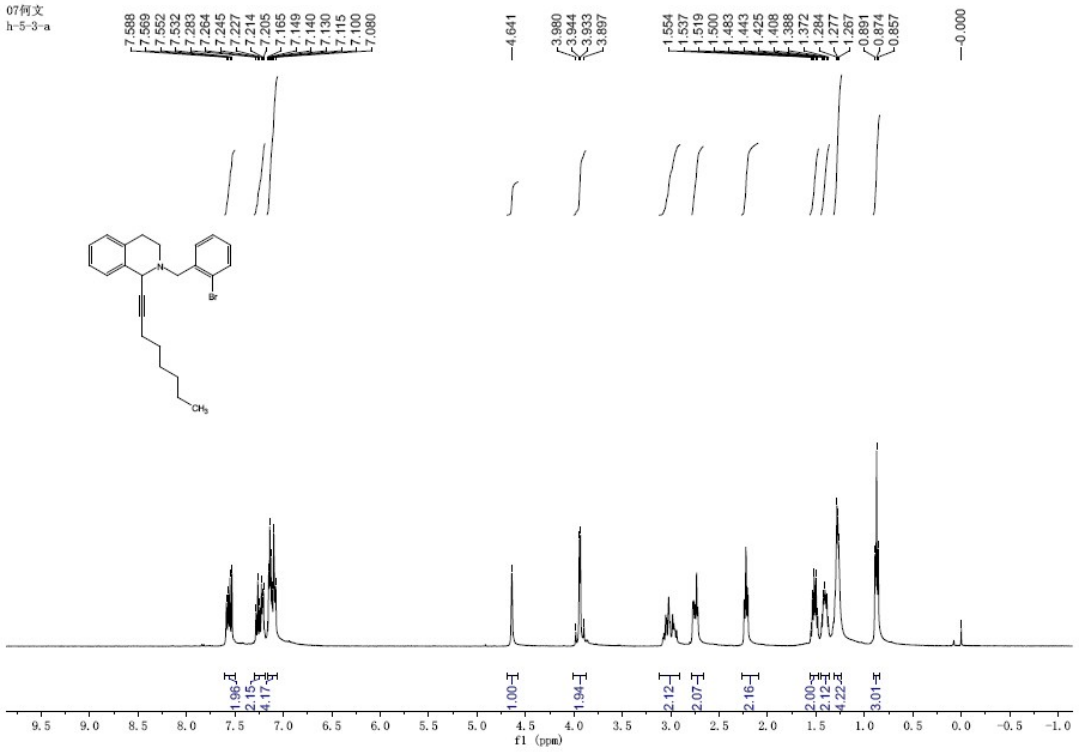


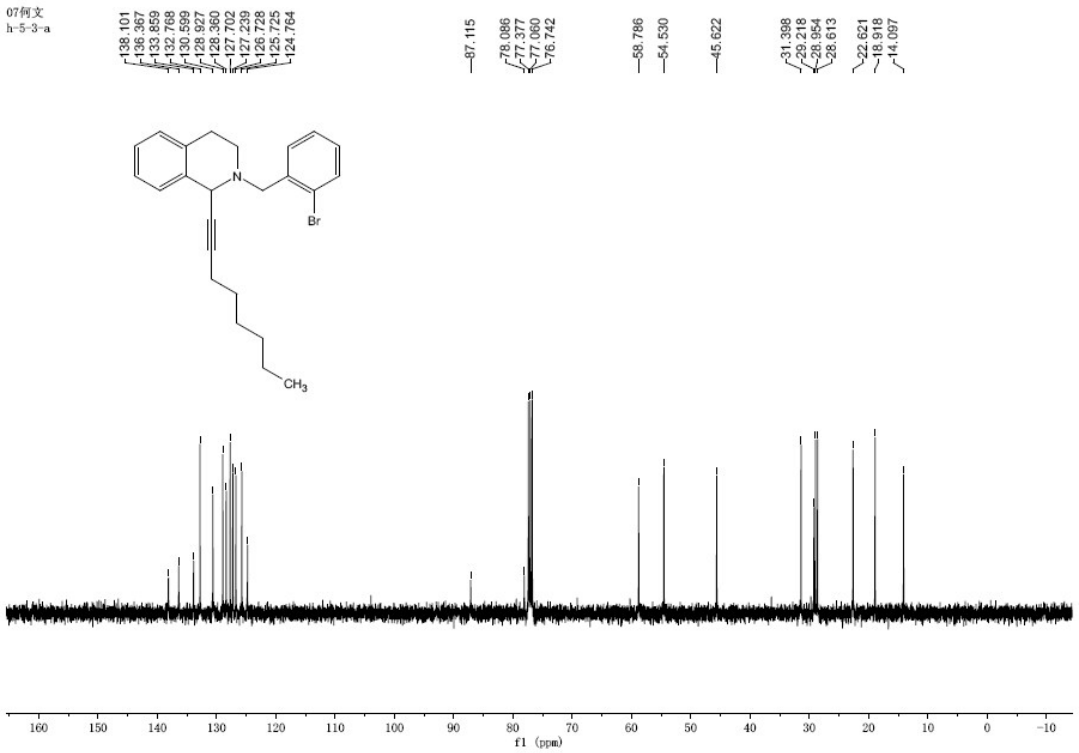
^{1}H NMR and ^{13}C NMR spectra of **4f**



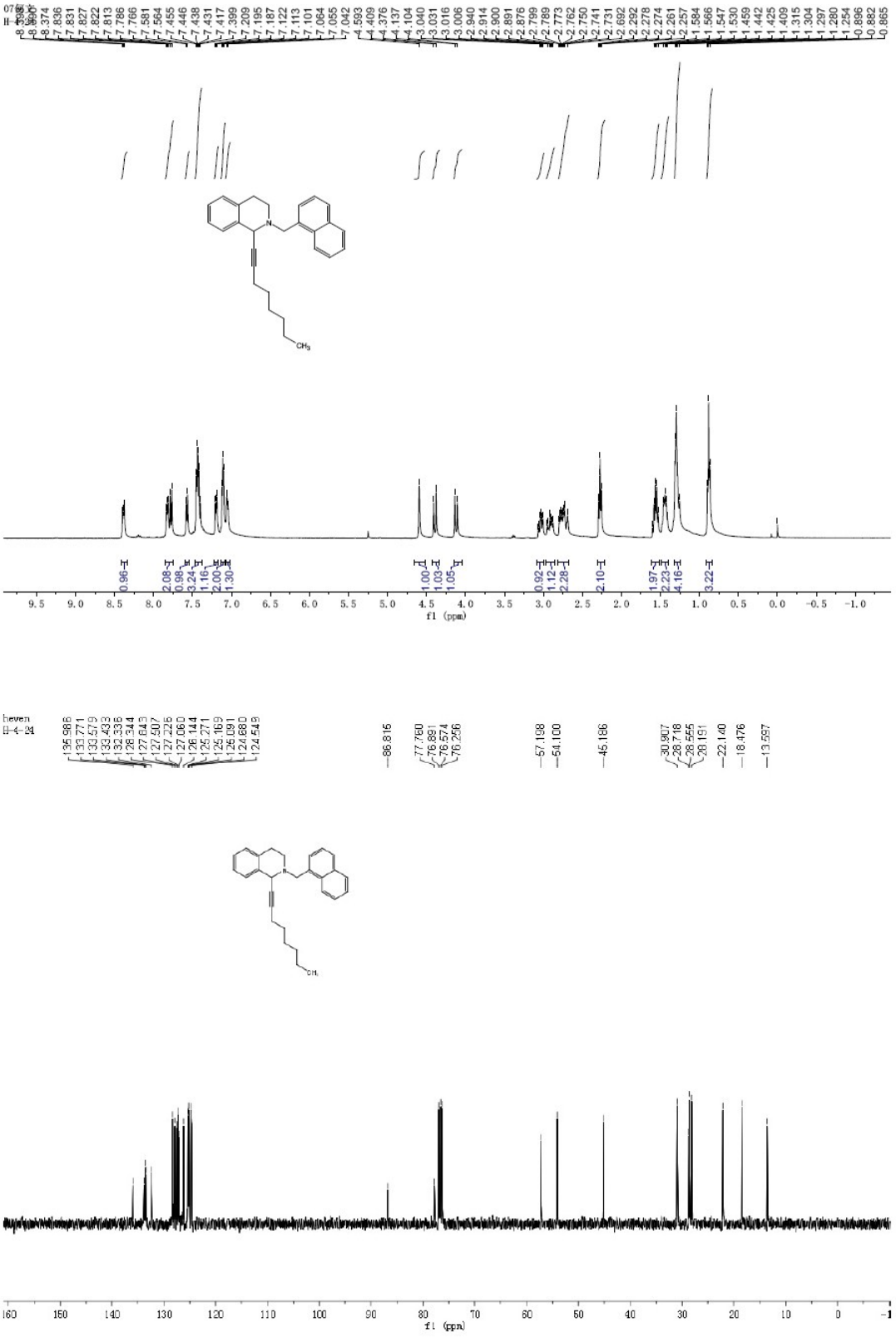


^{1}H NMR and ^{13}C NMR spectra of **4g**

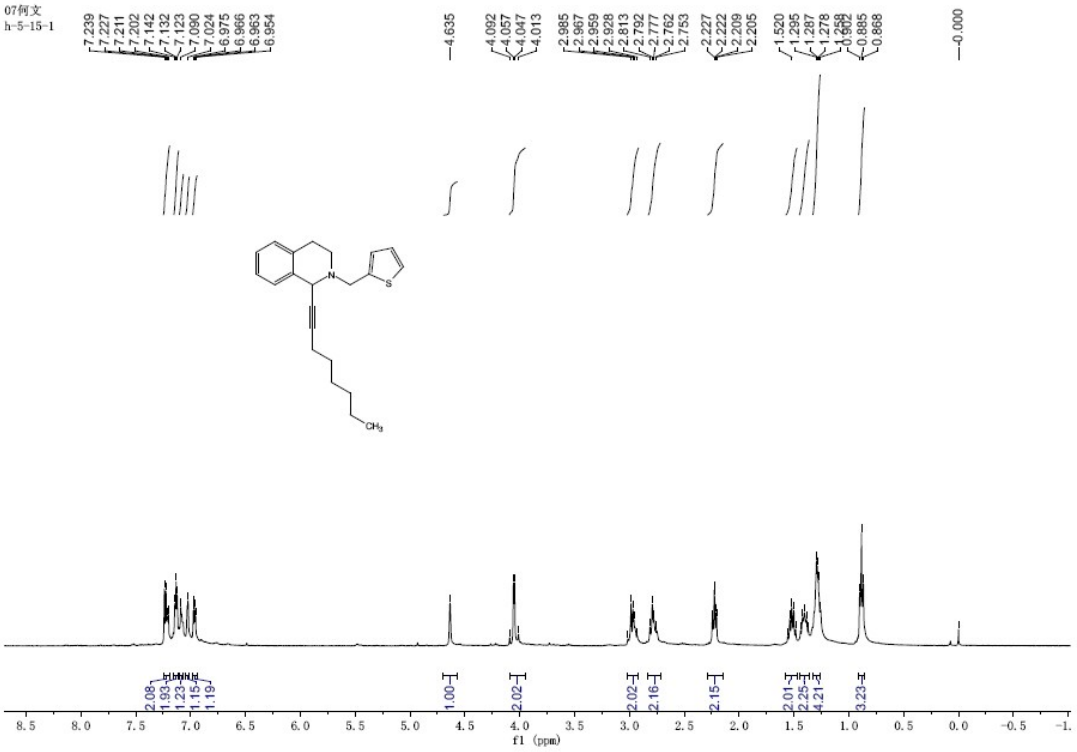


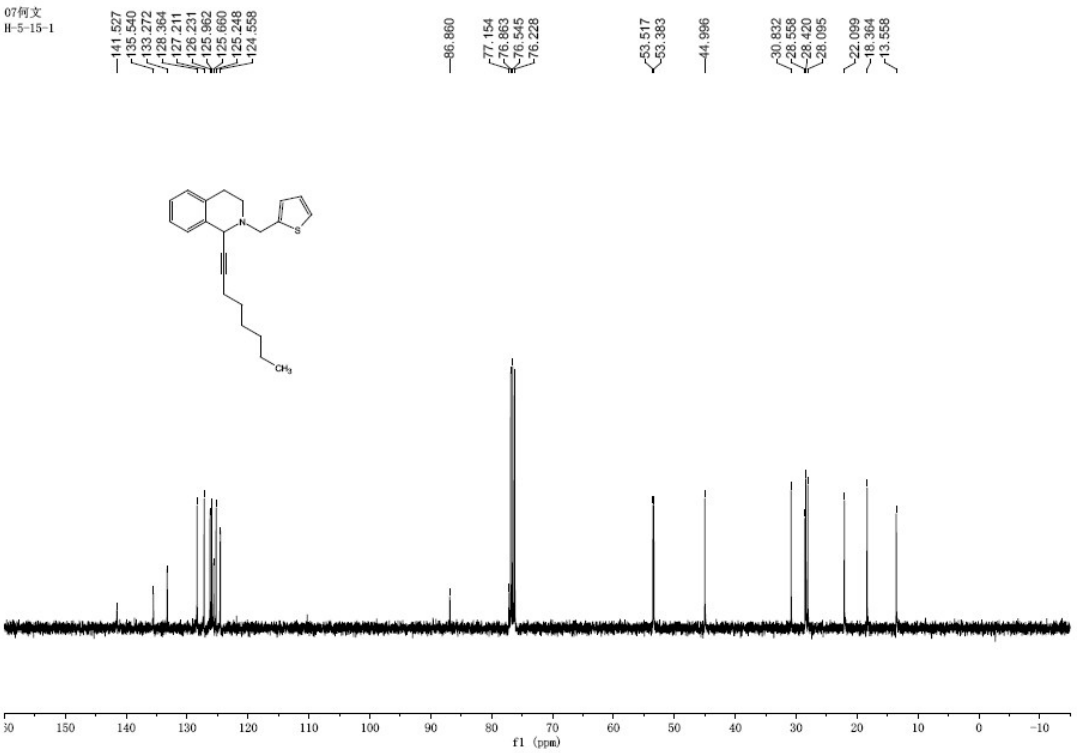


^{1}H NMR and ^{13}C NMR spectra of **4h**

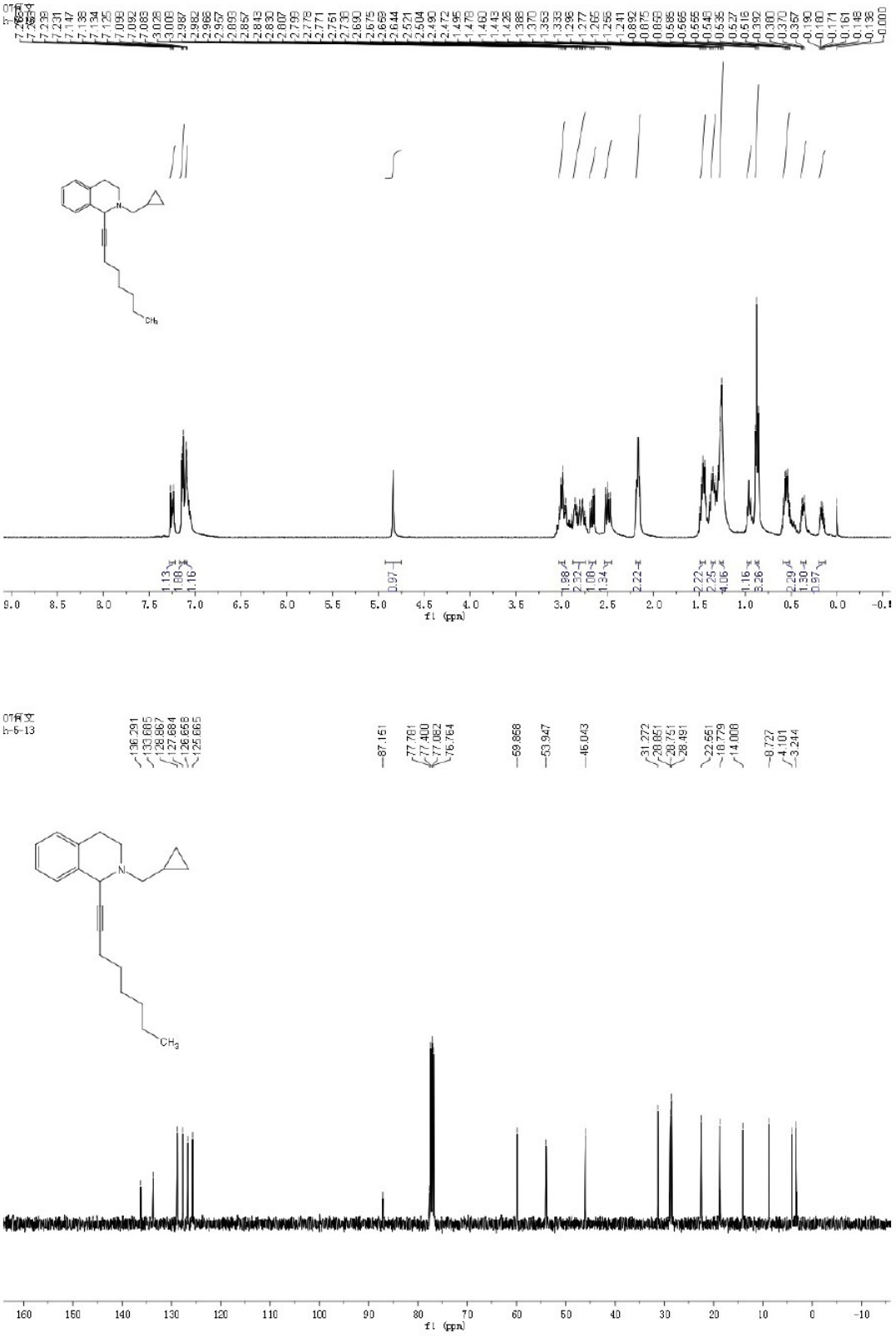


^{1}H NMR and ^{13}C NMR spectra of **4i**

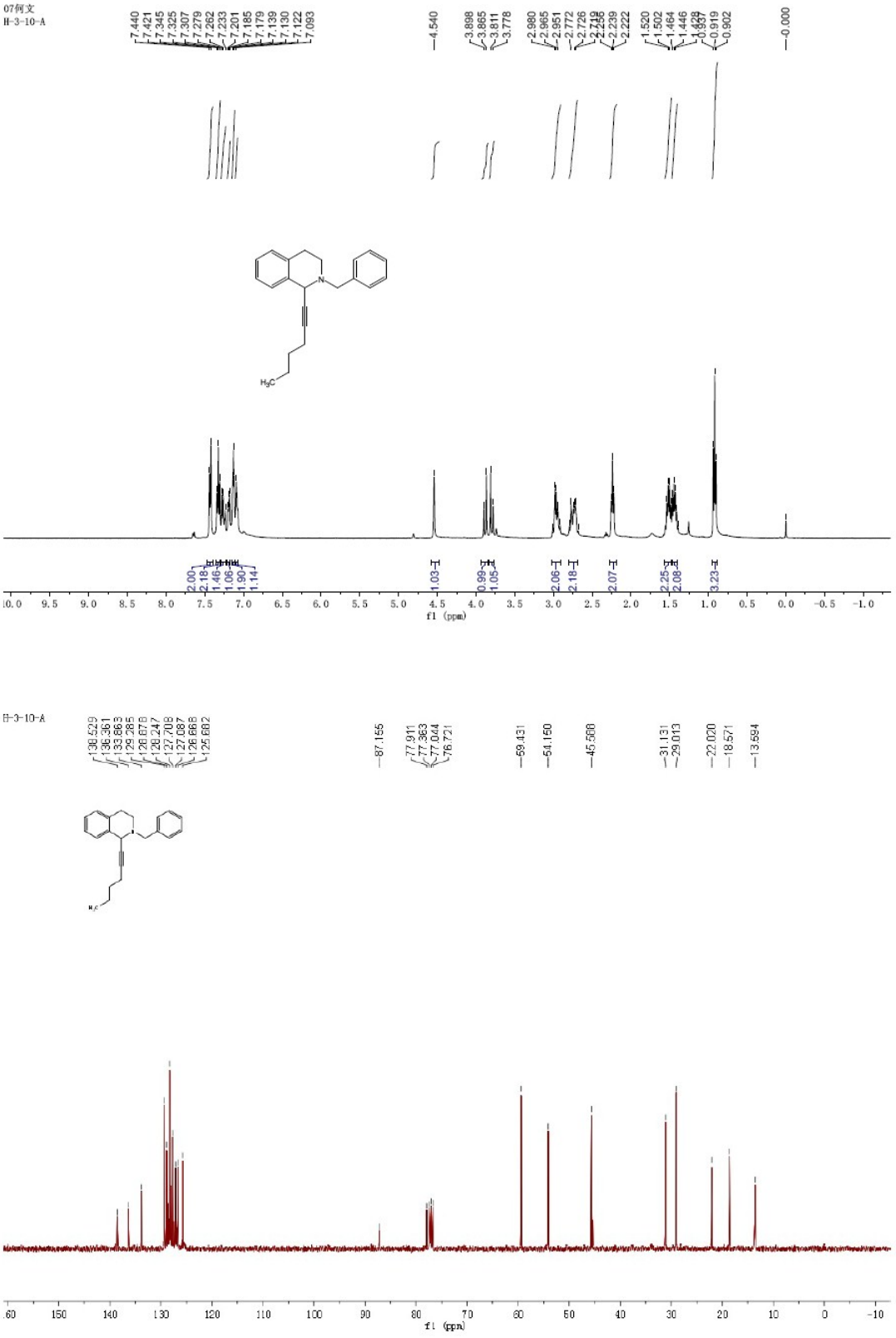




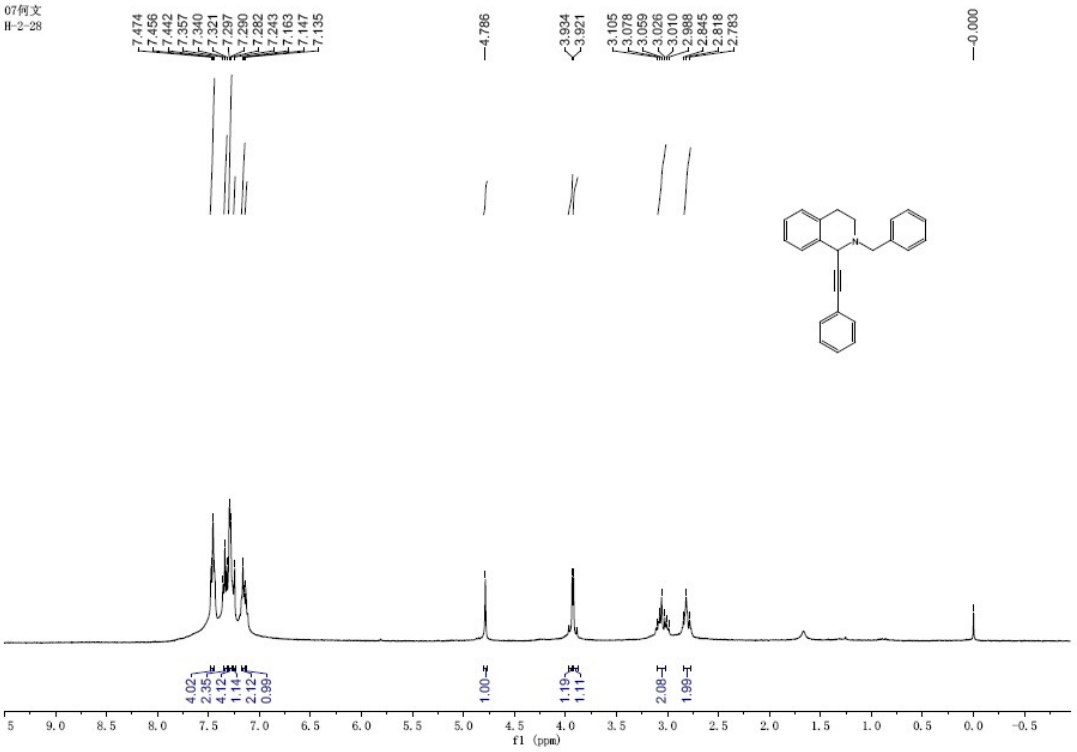
^{1}H NMR and ^{13}C NMR spectra of **4j**

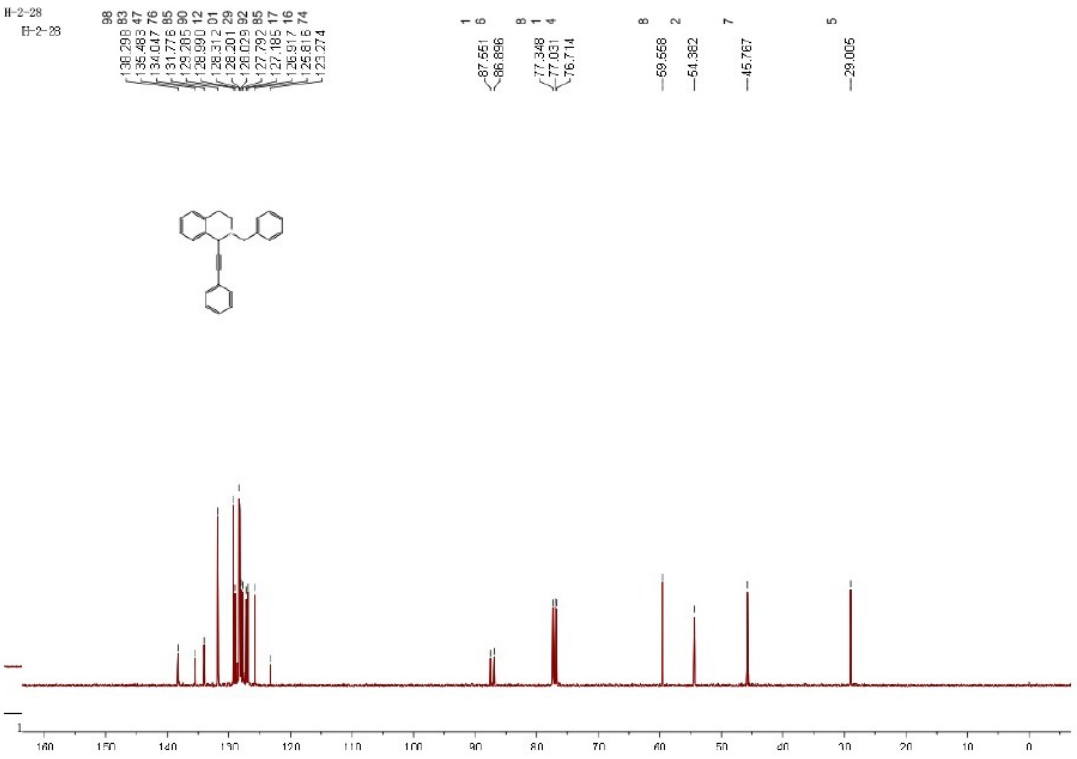


^{1}H NMR and ^{13}C NMR spectra of **4k**

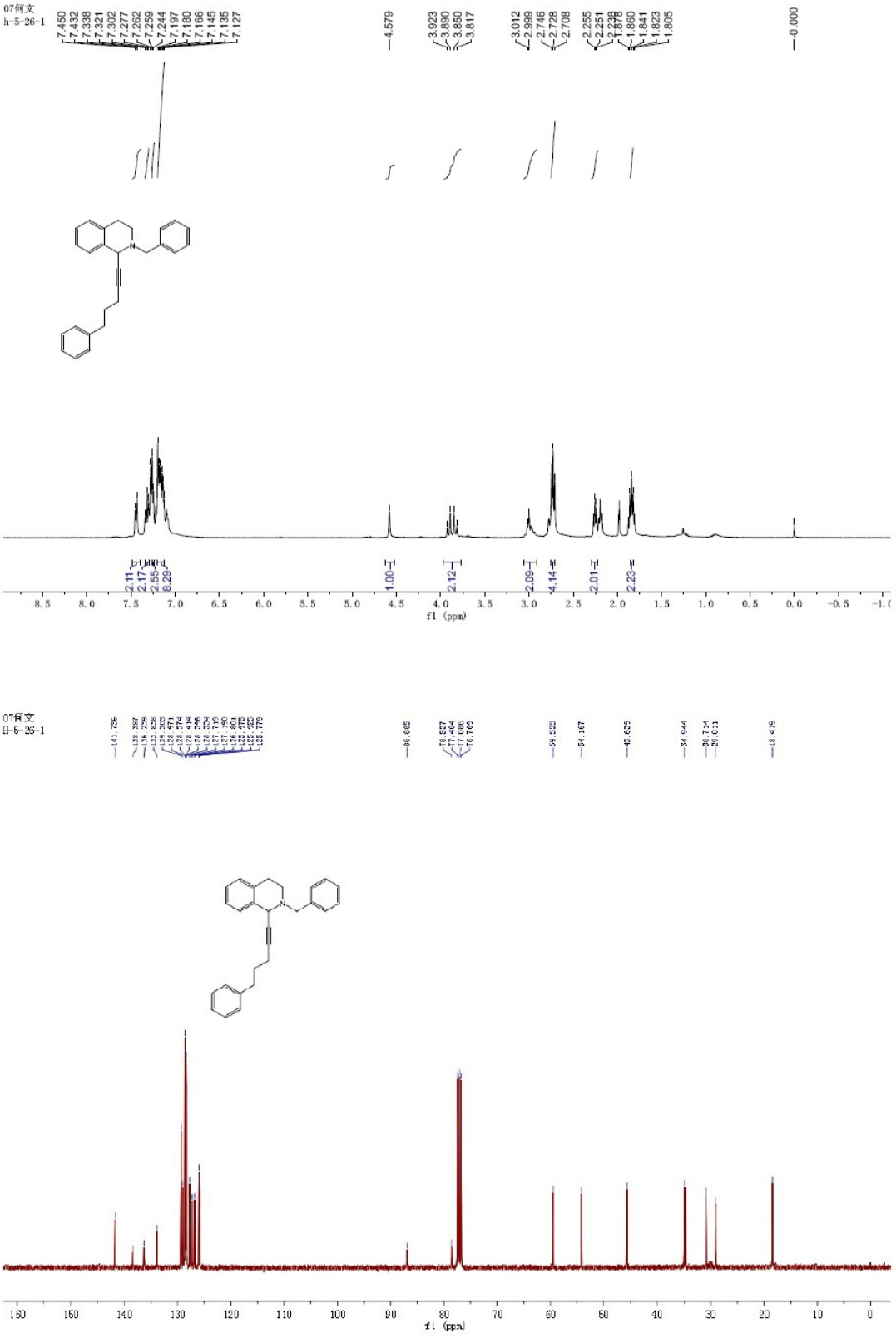


^{1}H NMR and ^{13}C NMR spectra of **4l**

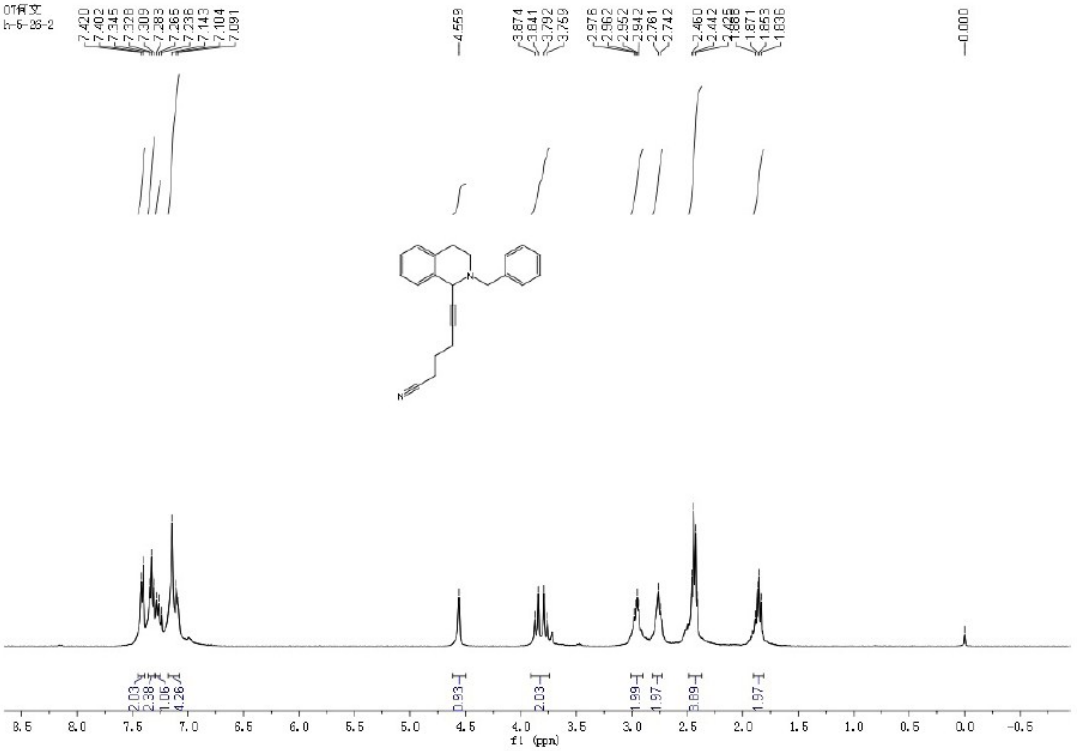


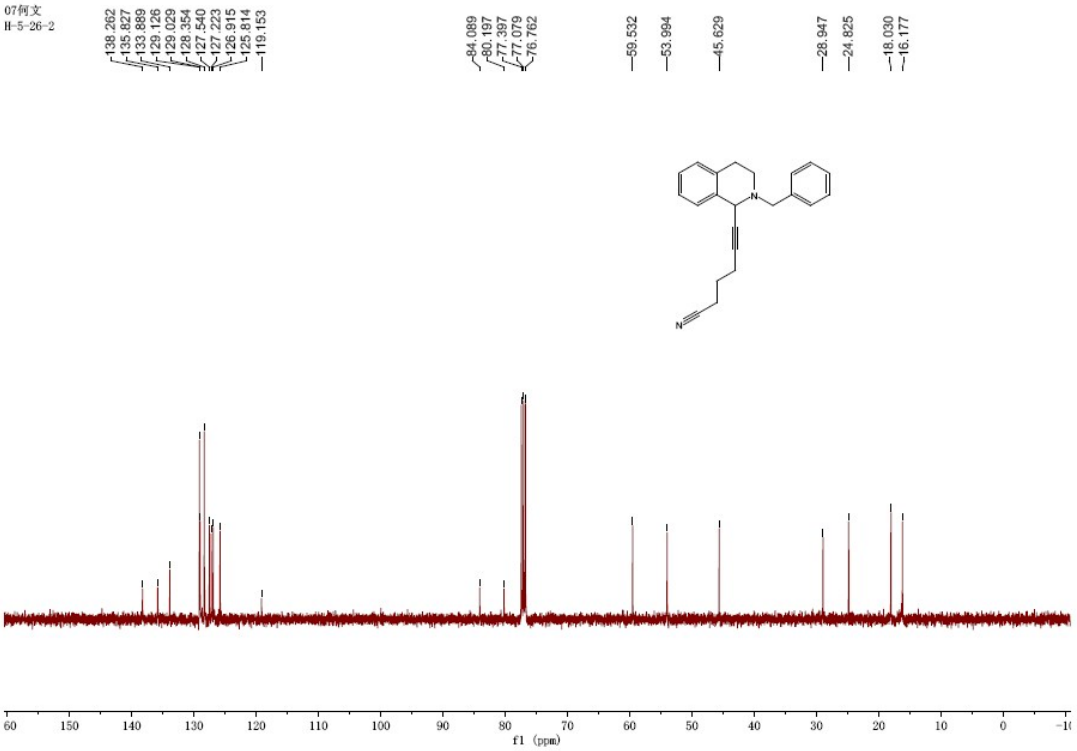


^{1}H NMR and ^{13}C NMR spectra of **4m**

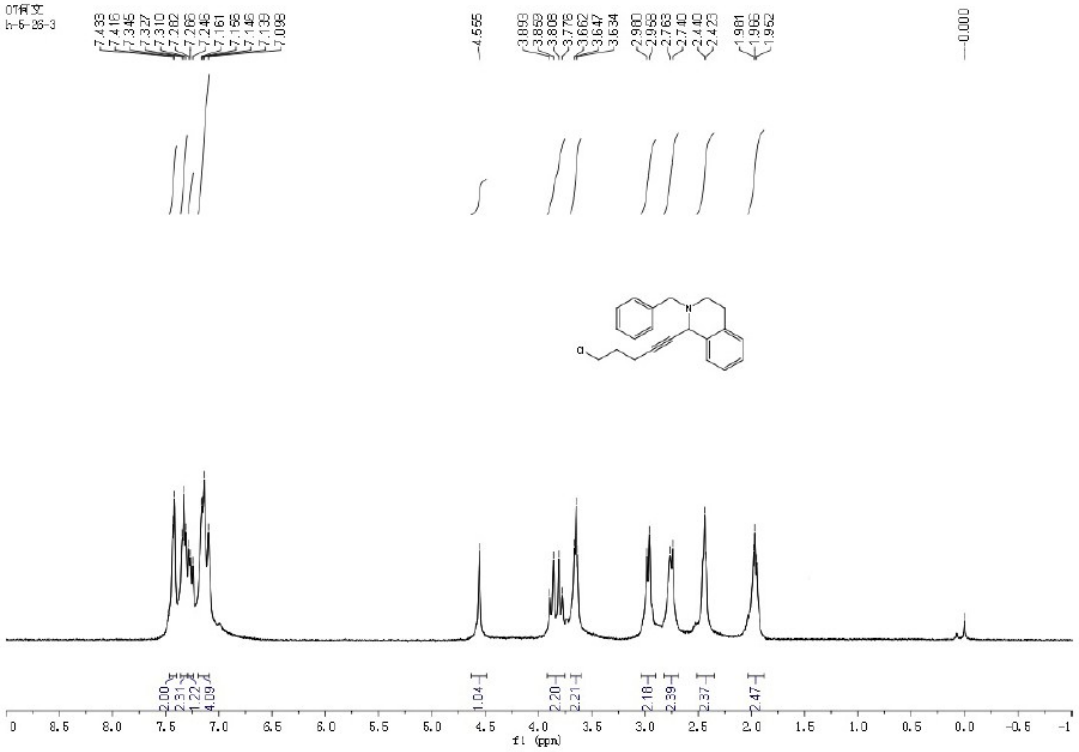


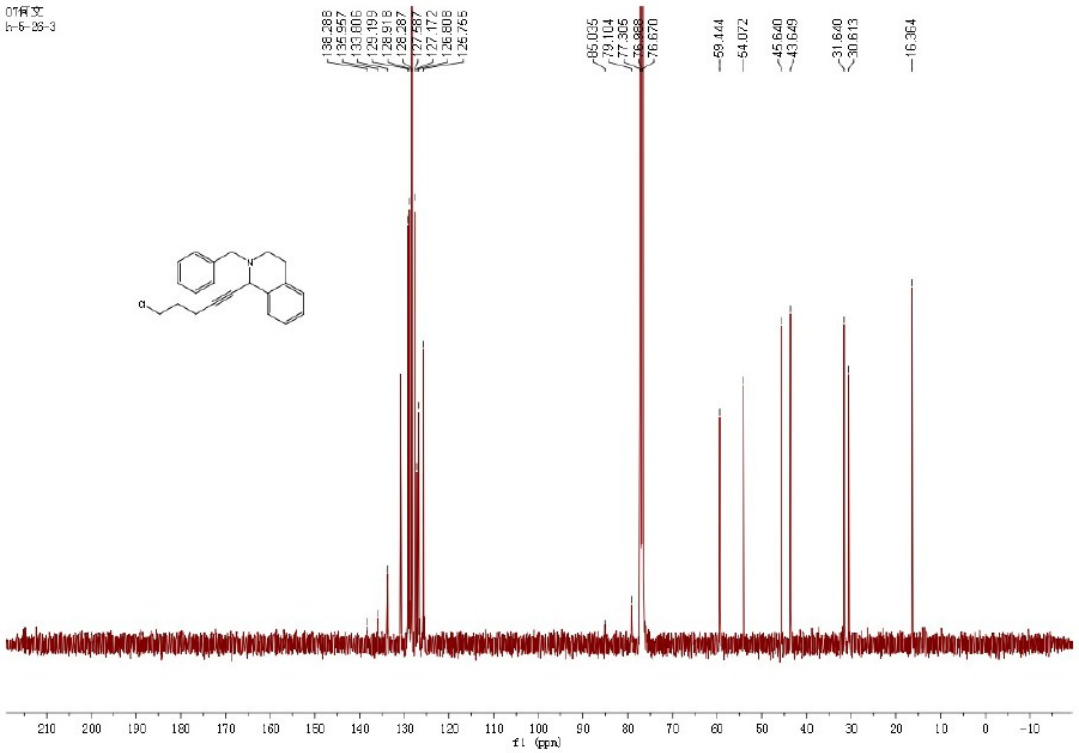
^{1}H NMR and ^{13}C NMR spectra of **4n**



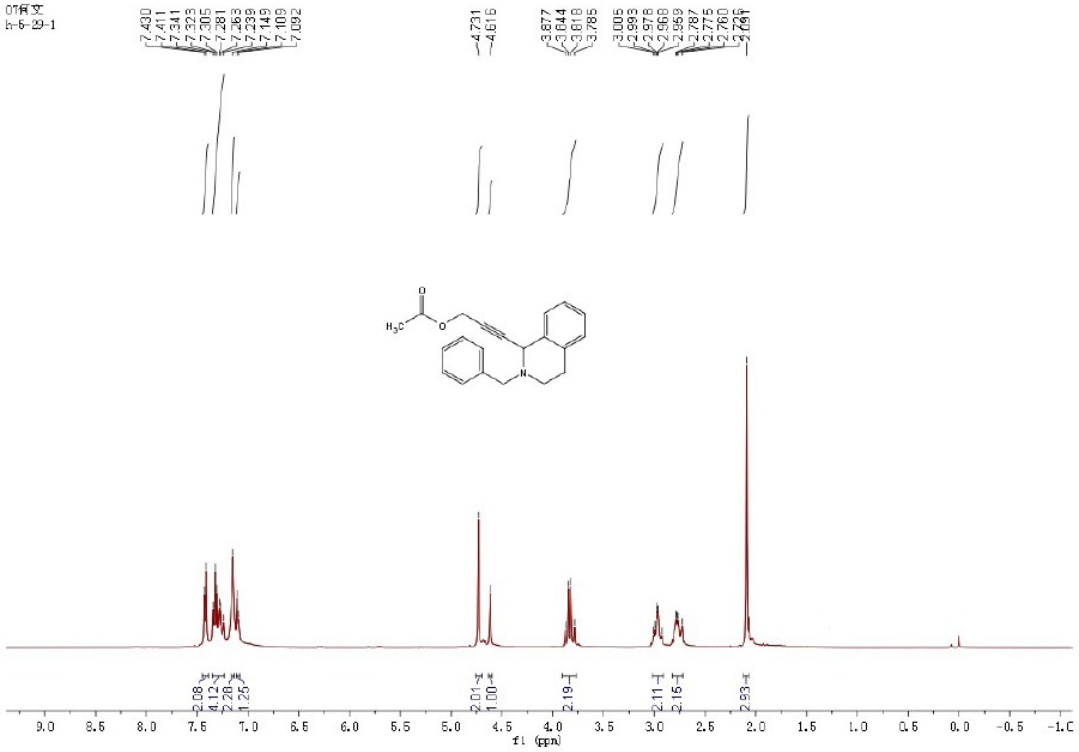


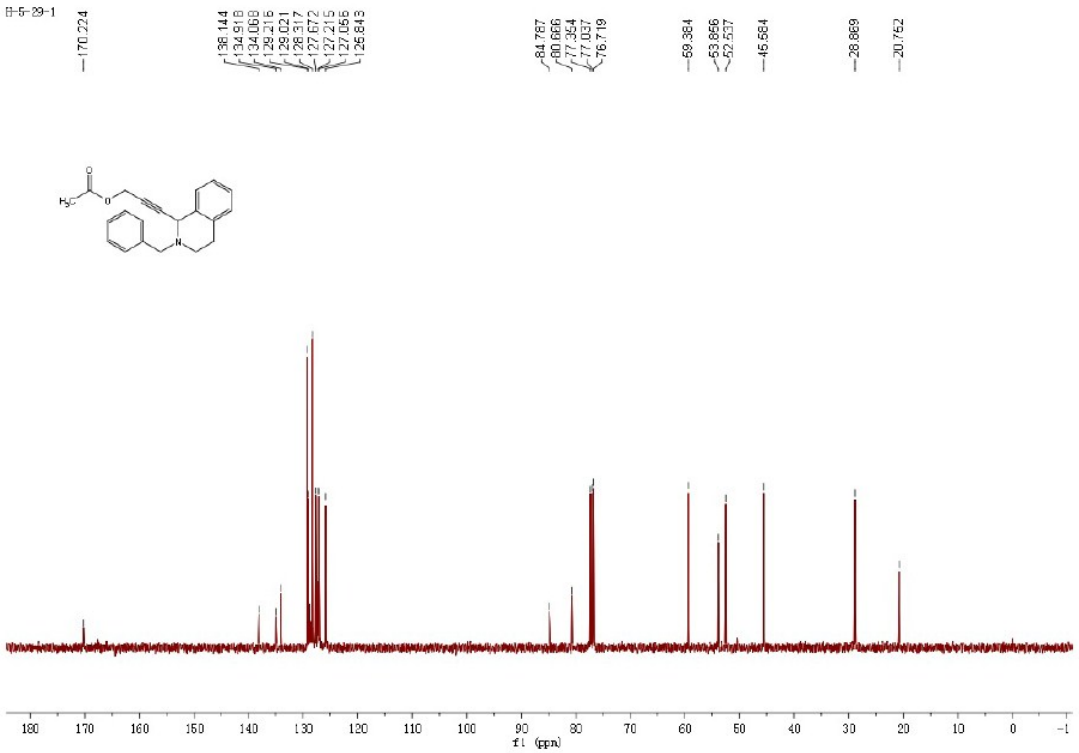
^{1}H NMR and ^{13}C NMR spectra of **4o**



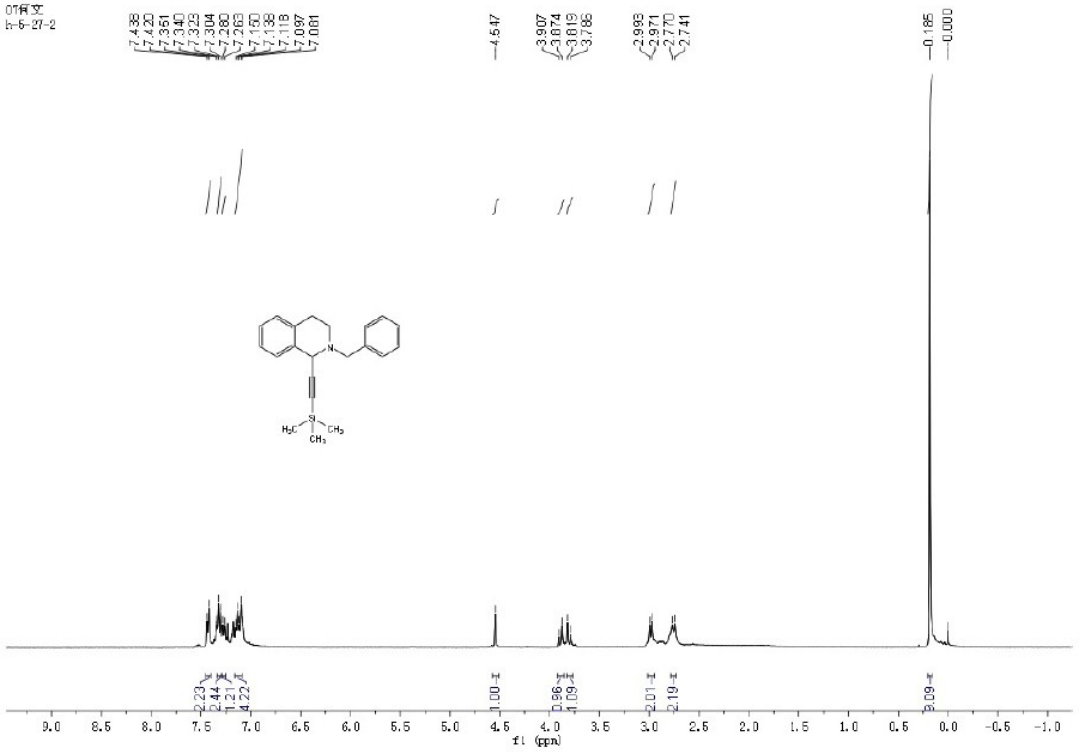


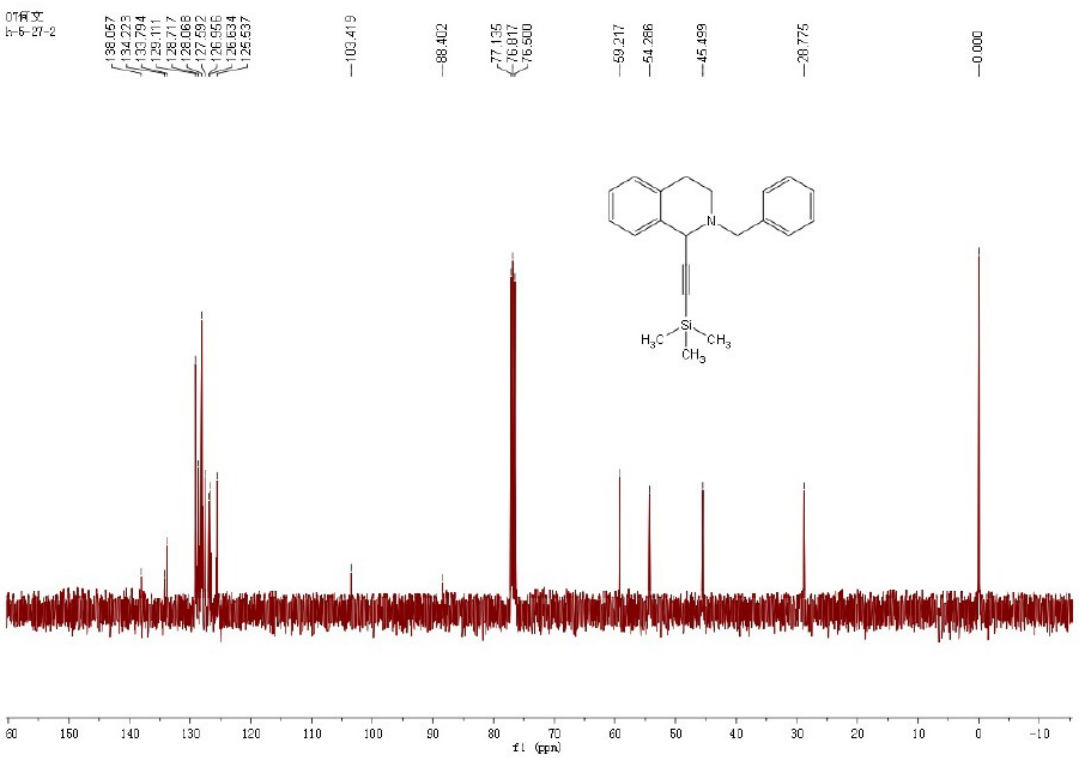
^{1}H NMR and ^{13}C NMR spectra of **4p**



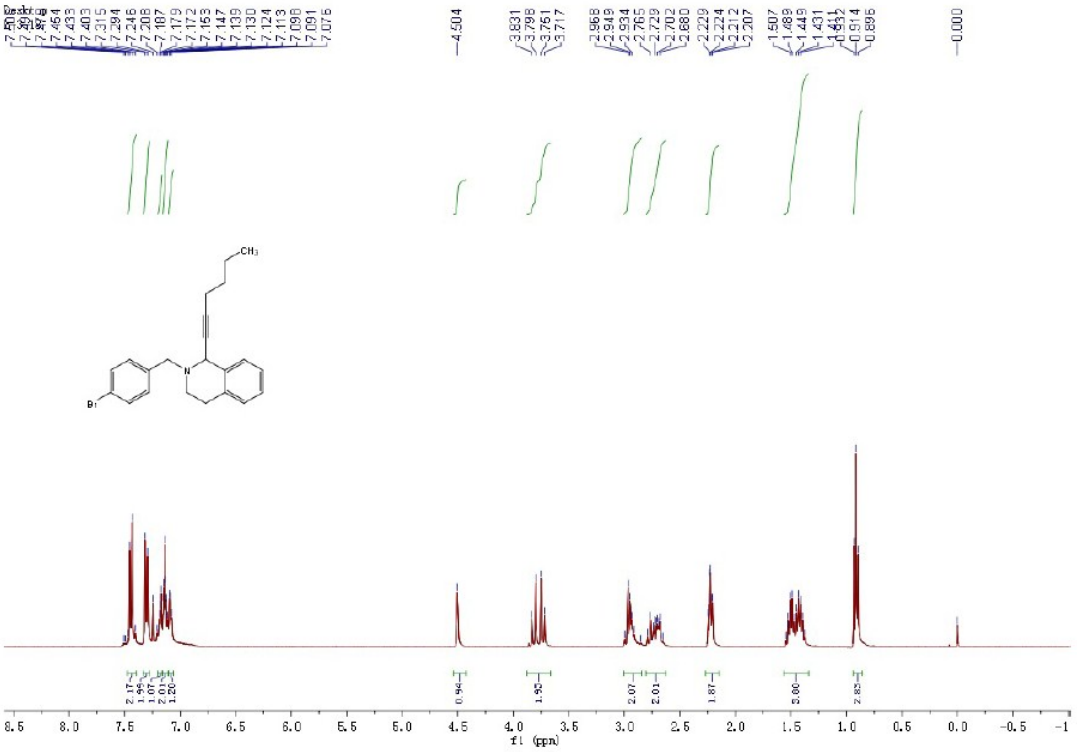


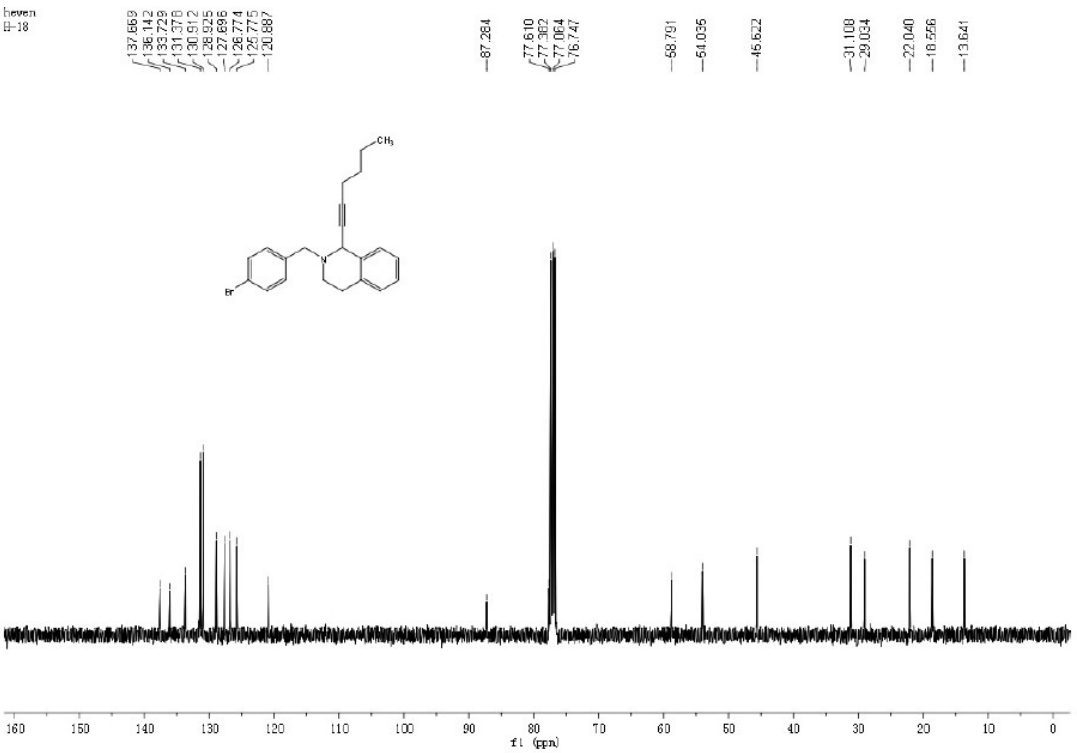
^{1}H NMR and ^{13}C NMR spectra of **4q**



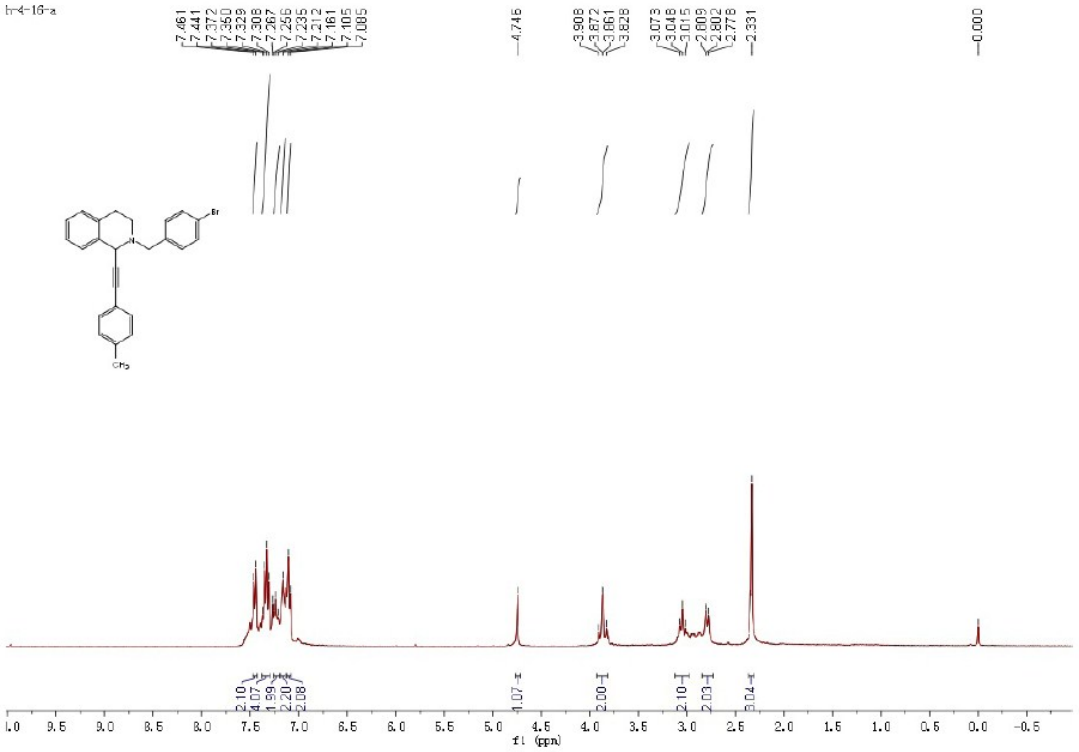


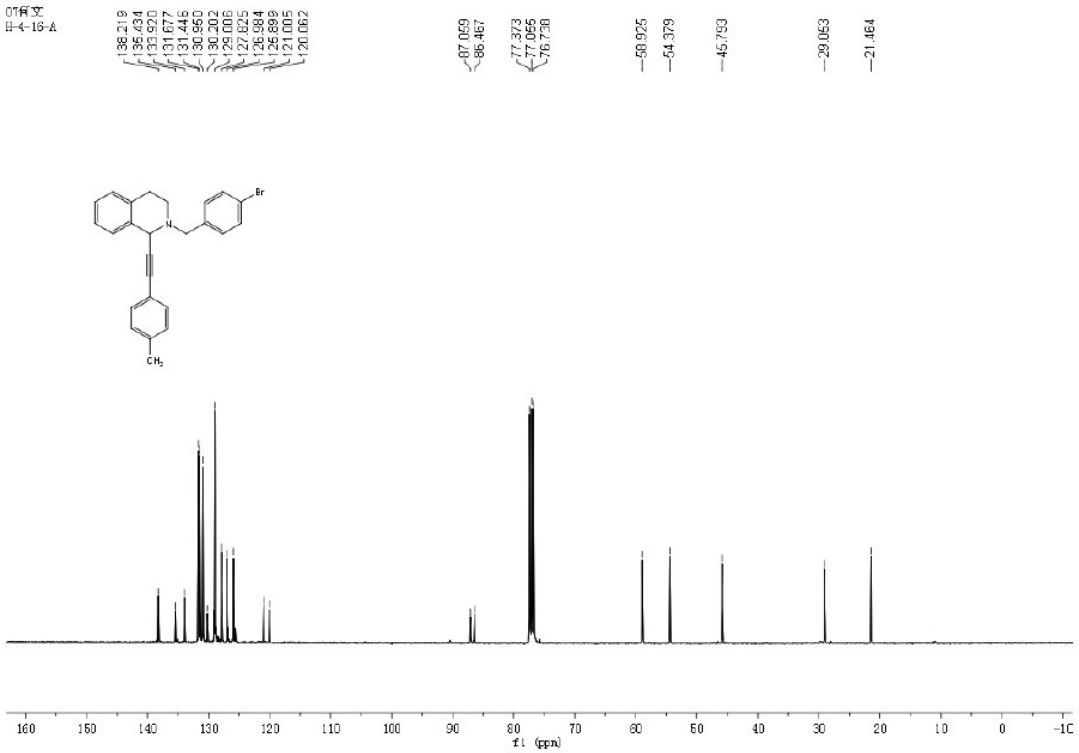
^{1}H NMR and ^{13}C NMR spectra of **4r**





^{1}H NMR and ^{13}C NMR spectra of **4s**





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