Supplementary Information

Visible Light Photoredox Alkylazidation of Alkenes with Sodium Azide and Heteroarenium Salts: Entry to Azido-Containing 1,4-Dihydropyridines

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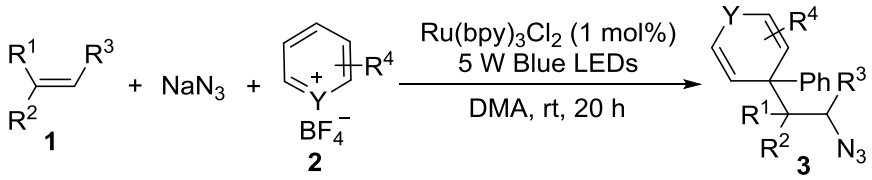
(A) General Information

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 or 500 MHz advance spectrometer at room temperature in $CDCl_3$ with tetramethylsilane as internal standard. High-resolution mass spectra (HRMS) was recorded on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Melting Point were recorded on Hanon MP100 Apparatus. All products were identified by ^{1}H ^{13}C NMR, and HRMS. Unless otherwise noted, all reactions were carried out using standard Schlenk techniques, and all starting materials and solvents were commercially available and were used without further purification. Column chromatography was performed on silica gel (300-400 mesh) using petroleum ether (PE)/ethyl acetate (EA). **1l**,[1] **1p**,[1] **2a-2f**,[2] **2g**[3] and **2h**[3] were prepared according to the literatures.

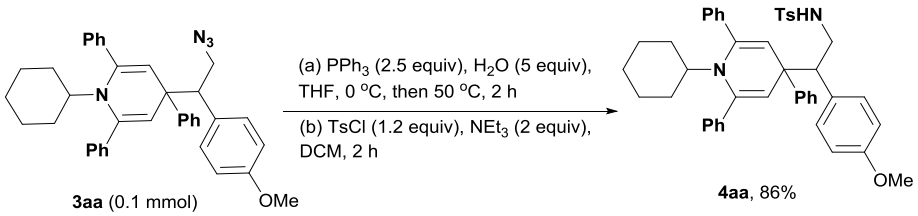
(a) General Procedure for Alkylazidation of Alkenes with Sodium Azide and Heteroarenium Salts:



To a Schlenk tube were added alkenes **1** (0.2 mmol), sodium azide (2 equiv), pyridinium salts **2** (2 equiv), $Ru(bpy)_3Cl_2$ (1 mol%), and $MeCONMe_2$ (1.5 mL). Then the tube is evacuated briefly under high vacuum and charged with argon using standard Schlenk techniques. The reaction mixture was then stirred and irradiated by 5W blue LEDs at room temperature for 20 h. The reaction was quenched with water and extracted with ethyl acetate. The organic layer was washed with saturated NaCl solution, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (petroleum

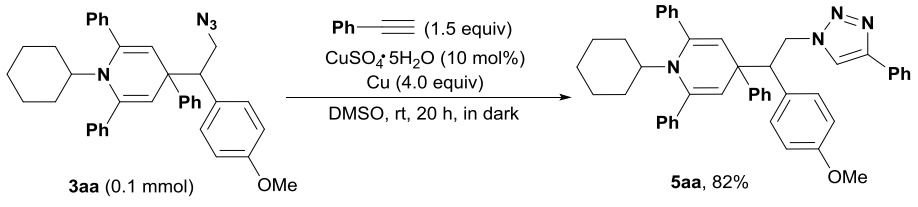
ether/ethyl acetate) to afford the desired products **3**.

(b) Synthetic Utilizations of the Product 3aa:



A mixture of 4-(2-azido-1-(4-methoxyphenyl)ethyl)-1-cyclohexyl-2,4,6-triphenyl-1,4-dihydropyridine **3aa** (0.1 mmol), H_2O (5 equiv), and THF (1 mL) was placed in a Schlenk tube under air at 0 ^oC, followed by the addition of PPh_3 (2.5 equiv). After 10 min, the reaction mixture was moved to an oil bath at 50 ^oC for 2 h. The reaction was then quenched with water and extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the corresponding amine.

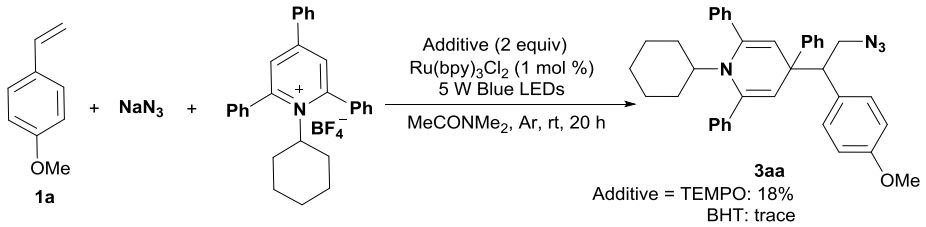
To a Schlenk tube were added amine, TsCl (1.2 equiv), NEt_3 (2 equiv), and DCM (1.5 mL). The reaction mixture was then stirred at room temperature for 2 h. The reaction was quenched with water and extracted with DCM. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the desired products **4aa** in 86% total yield.



The reaction of 4-(2-azido-1-(4-methoxyphenyl)ethyl)-1-cyclohexyl-2,4,6-triphenyl-1,4-dihydropyridine **3aa** (0.1 mmol), ethynybenzene (1.5 equiv), $CuSO_4$ •$5H_2O$ (10 mol%) and Cu powder (4 equiv) was performed in a Schlenk tube (25 mL)

under air, followed by the addition of DMSO (2.0 mL). The reaction worked at rt for 20 h in dark place. Then, water was added and the reaction mixture was extracted with EtOAc. After evaporation, the crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the desired products **5aa** in 82% yield.

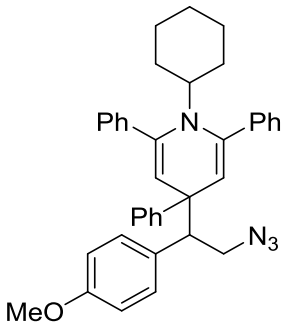
(c) Control Experiments:



To a Schlenk tube were added alkenes **1** (0.2 mmol), sodium azide (2 equiv), pyridinium salts **2** (2 equiv), $Ru(bpy)_3Cl_2$ (1 mol%), TEMPO or BHT (2 equiv), and $MeCONMe_2$ (1.5 mL). Then the tube was evacuated briefly under high vacuum and charged with argon using standard Schlenk techniques. The reaction mixture was then stirred and irradiated by 5W blue LEDs at room temperature for 20 h: (1) When additive was BHT, the target product 3aa was hardly detected by TLC analysis and GC-MS; (2) when additive was TEMPO, The reaction was quenched with water and extracted with ethyl acetate. The organic layer was washed with saturated NaCl solution, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the desired products **3aa** in 18% yield.

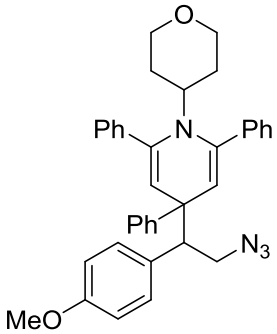
(B) Analytical Data

4-(2-azido-1-(4-methoxyphenyl)ethyl)-1-cyclohexyl-2,4,6-triphenyl-1,4-dihydropyridine (3aa):



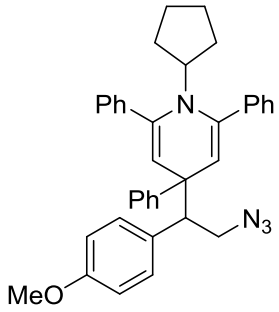
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59-7.53 (m, 4H), 7.39-7.34 (m, 6H), 7.23-7.20 (m, 4H), 7.10-7.09 (m, 1H), 6.74 (d, *J* = 8.0 Hz, 2H), 6.65 (d, *J* = 8.0 Hz, 2H), 5.41 (s, 1H), 5.37 (s, 1H), 3.81 (dd, *J* = 13.2, 3.2 Hz, 1H), 3.70 (s, 3H), 3.56 (t, *J* = 12.0 Hz, 1H), 3.20 (dd, *J* = 11.2, 3.2 Hz, 1H), 2.78 (t, *J* = 10.0 Hz, 1H), 1.22-1.12 (m, 5H), 0.87-0.83 (m, 1H), 0.68-0.55 (m, 3H), 0.51-0.45 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.2, 149.7, 146.0, 145.5, 140.4, 140.2, 130.6, 129.6, 128.1, 128.0 (2C), 127.9 (2C), 127.8, 126.7, 125.5, 115.4, 113.0, 111.5, 62.8, 56.4, 55.0, 53.1, 46.6, 33.1, 32.9, 26.5, 25.2; HRMS *m/z* (ESI) calcd for $C_{38}H_{39}N_4O$ $[M+H]^+$ 567.3118, found 567.3120.

4-(2-azido-1-(4-methoxyphenyl)ethyl)-2,4,6-triphenyl-1-(tetrahydro-2*H*-pyran-4-yl)-1,4-dihydropyridine (3ab):



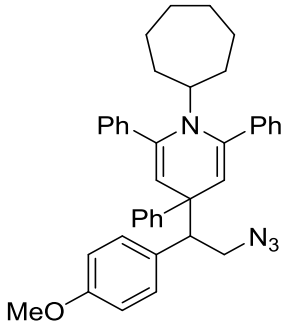
White solid, mp 78.2-80.5 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52-7.47 (m, 4H), 7.32-7.28 (m, 6H), 7.13-7.08 (m, 4H), 7.01 (t, *J* = 6.2 Hz, 1H), 6.66-6.56 (m, 4H), 5.47 (s, 1H), 5.42 (s, 1H), 3.71 (d, *J* = 11.6 Hz, 1H), 3.63 (s, 3H), 3.49 (t, *J* = 12.2 Hz, 1H), 3.35 (d, *J* = 10.8 Hz, 2H), 3.12 (d, *J* = 10.4 Hz, 1H), 2.92 (s, 1H), 2.63 (t, *J* = 10.2 Hz, 2H), 0.98-0.93 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3, 149.6, 145.6, 145.1, 139.9, 139.7, 130.5, 129.4, 128.3, 128.2, 127.9, 127.8 (2C), 126.8, 125.7, 116.7, 113.0, 112.8, 67.8, 59.8, 56.3, 55.0, 52.9, 46.5, 33.1, 33.0; HRMS *m/z* (ESI) calcd for $C_{37}H_{37}N_4O_2$ $[M+H]^+$ 569.2911, found 569.2924.

4-(2-azido-1-(4-methoxyphenyl)ethyl)-1-cyclopentyl-2,4,6-triphenyl-1,4-dihydropyridine (3ac):



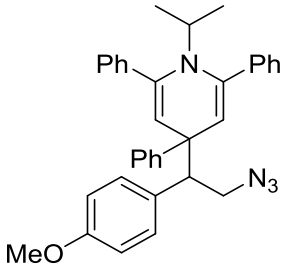
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (t, *J* = 7.6 Hz, 4H), 7.31-7.24 (m, 6H), 7.15-7.11 (s, 4H), 7.02-7.01 (m, 1H), 6.69 (d, *J* = 8.0 Hz, 2H), 6.59 (d, *J* = 7.6 Hz, 2H), 5.38 (s, 1H), 5.37 (s, 1H), 3.78 (dd, *J* = 12.4, 2.4 Hz, 1H), 3.65 (s, 3H), 3.51 (t, *J* = 12.2 Hz, 1H), 3.36-3.25 (m, 1H), 3.17 (dd, *J* = 11.2, 2.4 Hz, 1H), 0.98-0.82 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.2, 149.4, 146.2, 145.5, 139.9, 139.7, 130.6, 129.7, 128.1, 128.0, 127.9, 127.6, 127.0, 125.6, 115.6, 113.0, 111.5, 63.3, 55.9, 55.0, 53.1, 46.7, 31.0, 30.8, 22.5; HRMS *m/z* (ESI) calcd for $C_{37}H_{37}N_4O$ $[M+H]^+$ 553.2962, found 553.2969.

4-(2-azido-1-(4-methoxyphenyl)ethyl)-1-cycloheptyl-2,4,6-triphenyl-1,4-dihydropyridine (3ad):



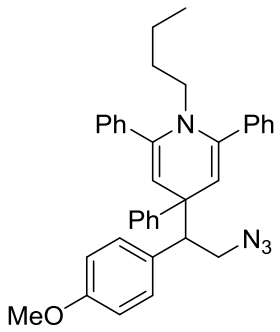
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47-7.41 (m, 4H), 7.32-7.27 (m, 6H), 7.17-7.15 (m, 4H), 7.05-7.03 (m, 1H), 6.72 (d, *J* = 7.6 Hz, 2H), 6.60 (d, *J* = 7.6 Hz, 2H), 5.22 (s, 1H), 5.16 (s, 1H), 3.75-3.71 (m, 1H), 3.66 (s, 3H), 3.51 (t, *J* = 12.2 Hz, 1H), 3.16 (d, *J* = 11.2 Hz, 1H), 2.86 (t, *J* = 10.4 Hz, 1H), 1.31-1.22 (m, 2H), 1.02-0.73 (m, 8H), 0.67-0.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.2, 149.8, 145.8, 145.6, 140.2, 140.1, 130.7, 129.8, 128.5, 128.4, 128.0, 127.9 (2C), 126.6, 125.5, 113.9, 113.0, 110.9, 64.3, 56.3, 55.0, 53.0, 46.7, 34.8, 34.5, 27.0 (2C), 25.4 (2C); HRMS *m/z* (ESI) calcd for $C_{39}H_{41}N_4O$ $[M+H]^+$ 581.3275, found 581.3281.

4-(2-azido-1-(4-methoxyphenyl)ethyl)-1-isopropyl-2,4,6-triphenyl-1,4-dihydropyridine (3ae):



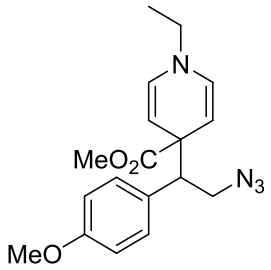
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.59 (d, *J* = 7.0 Hz, 2H), 7.56 (d, *J* = 7.0 Hz, 2H), 7.40-7.33 (m, 6H), 7.24-7.19 (m, 4H), 7.12-7.09 (m, 1H), 6.74 (d, *J* = 8.5 Hz, 2H), 6.65 (d, *J* = 8.5 Hz, 2H), 5.44 (d, *J* = 1.5 Hz, 1H), 5.39 (d, *J* = 1.5 Hz, 1H), 3.85-3.81 (m, 1H), 3.72 (s, 3H), 3.58 (t, *J* = 12.5 Hz, 1H), 3.29-3.24 (m, 1H), 3.20 (dd, *J* = 11.5, 4.0 Hz, 1H), 0.51 (d, *J* = 7.0 Hz, 3H), 0.49 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.2, 149.9, 146.0, 145.3, 140.3, 140.1, 130.6, 129.6, 128.2, 128.1 (2C), 128.0 (3C), 127.8, 126.7, 125.5, 115.7, 113.0, 111.5, 56.4, 55.0, 53.7, 53.1, 46.5, 22.4, 22.2; HRMS *m/z* (ESI) calcd for $C_{35}H_{35}N_4O$ $[M+H]^+$ 527.2805, found 527.2813.

4-(2-azido-1-(4-methoxyphenyl)ethyl)-1-butyl-2,4,6-triphenyl-1,4-dihydropyridine (3af):



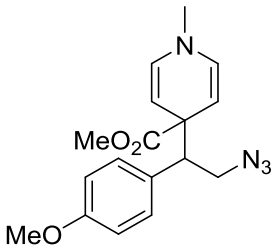
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 (d, *J* = 7.2 Hz, 2H), 7.36 (d, *J* = 7.2 Hz, 2H), 7.32-7.21 (m, 6H), 7.16-7.12 (m, 4H), 7.01-6.97 (m, 1H), 6.76 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 8.0 Hz, 2H), 5.12 (s, 1H), 5.06 (s, 1H), 3.77-3.74 (m, 1H), 3.62 (s, 3H), 3.54 (t, *J* = 12.2 Hz, 1H), 3.22 (d, *J* = 11.2 Hz, 1H), 2.81 (t, *J* = 7.0 Hz, 2H), 0.60-0.43 (m, 4H), 0.18 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.2, 149.8, 144.0 (2C), 138.0, 137.9, 130.7, 129.9, 128.2 (2C), 128.0 (2C), 127.9, 126.5, 125.5, 113.0, 110.6, 108.0, 56.1, 55.0, 53.1, 47.5, 46.7, 30.7, 19.3, 13.3; HRMS *m/z* (ESI) calcd for $C_{36}H_{37}N_4O$ $[M+H]^+$ 541.2962, found 541.2971.

methyl 4-(2-azido-1-(4-methoxyphenyl)ethyl)-1-ethyl-1,4-dihydropyridine-4-carboxylate (3ag):



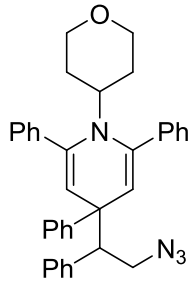
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.08 (d, *J* = 7.6 Hz, 2H), 6.82 (d, *J* = 7.6 Hz, 2H), 6.03 (t, *J* = 9.0 Hz, 2H), 4.60 (d, *J* = 8.0 Hz, 1H), 4.52 (d, *J* = 8.0 Hz, 1H), 3.80-3.78 (m, 4H), 3.58-3.52 (m, 4H), 3.13-3.05 (m, 3H), 1.09 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.4, 158.7, 130.8, 130.4, 129.9, 129.3, 113.5, 98.2, 95.1, 55.1, 54.0, 52.5, 51.7, 50.4, 47.9, 15.2; HRMS *m/z* (ESI) calcd for $C_{18}H_{23}N_4O_3$ $[M+H]^+$ 343.1765, found 343.1778.

methyl 4-(2-azido-1-(4-methoxyphenyl)ethyl)-1-methyl-1,4-dihydropyridine-4-carboxylate (3ah):



Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.08 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 7.6 Hz, 2H), 5.99 (d, *J* = 7.2 Hz, 2H), 4.59 (d, *J* = 7.6 Hz, 1H), 4.52 (d, *J* = 7.6 Hz, 1H), 3.83-3.78 (m, 4H), 3.58-3.52 (m, 4H), 3.07 (dd, *J* = 11.2, 4.0 Hz, 1H), 2.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.3, 158.7, 132.0, 131.7, 129.9, 129.3, 113.5, 98.3, 95.0, 55.1, 53.8, 52.7, 51.8, 50.1, 40.2; HRMS *m/z* (ESI) calcd for $C_{17}H_{21}N_4O_3$ $[M+H]^+$ 329.1608, found 329.1613.

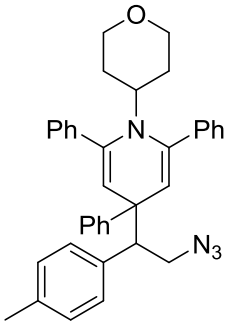
4-(2-azido-1-phenylethyl)-2,4,6-triphenyl-1-(tetrahydro-2*H*-pyran-4-yl)-1,4-dihydropyridine (3bb):



White solid, mp 70.9-72.8 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53-7.47 (m, 4H), 7.33-7.30 (m, 6H), 7.14-7.02 (m, 8H), 6.76 (d, *J* = 6.4 Hz, 2H), 5.48 (s, 1H), 5.45 (s, 1H), 3.74 (d, *J* = 12.4 Hz, 1H), 3.56 (t, *J* = 12.0 Hz, 1H), 3.36 (d, *J* = 10.8 Hz, 2H), 3.17 (d, *J* = 10.4 Hz, 1H), 3.00-2.90 (m, 1H), 2.64 (t, *J* = 10.4 Hz, 2H),

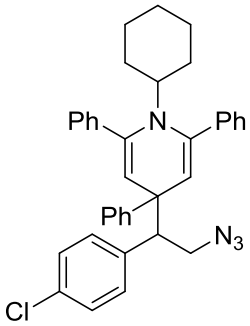
0.99-0.93 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.5, 145.7, 145.2, 139.9, 139.7, 137.6, 129.7, 128.3 (2C), 127.9 (2C), 127.8, 127.6, 126.7 (2C), 125.7, 116.7, 112.7, 67.9, 59.8, 57.2, 52.9, 46.6, 33.1, 33.0; HRMS *m/z* (ESI) calcd for $C_{36}H_{35}N_4O$ $[M+H]^+$ 539.2805, found 539.2811.

4-(2-azido-1-(*p*-tolyl)ethyl)-2,4,6-triphenyl-1-(tetrahydro-2*H*-pyran-4-yl)-1,4-dihydropyridine (3cb):



White solid, mp 74.5-76.1 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53-7.48 (m, 4H), 7.34-7.29 (m, 6H), 7.15-7.09 (m, 4H), 7.02 (t, *J* = 6.2 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 2H), 6.64 (d, *J* = 7.6 Hz, 2H), 5.47 (s, 1H), 5.44 (s, 1H), 3.73 (dd, *J* = 12.4, 2.8 Hz, 1H), 3.53 (t, *J* = 12.0 Hz, 1H), 3.36 (d, *J* = 10.8, 2H), 3.14 (dd, *J* = 10.8, 2.7, 1H), 2.95-2.90 (m, 1H), 2.64 (t, *J* = 10.6 Hz, 2H), 2.17 (s, 3H), 1.02-0.92 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.6, 145.6, 145.1, 140.0, 139.7, 136.2, 134.3, 129.5, 128.4, 128.3, 128.2 (2C), 127.9 (2C), 127.8, 126.8, 125.7, 116.7, 112.9, 67.9, 59.8, 56.7, 53.0, 46.5, 33.1, 33.0, 21.0; HRMS *m/z* (ESI) calcd for $C_{37}H_{37}N_4O$ $[M+H]^+$ 553.2962, found 553.2973.

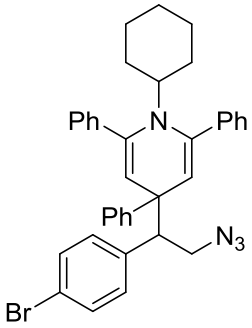
4-(2-azido-1-(4-chlorophenyl)ethyl)-1-cyclohexyl-2,4,6-triphenyl-1,4-dihydropyridine (3da):



White solid, mp 81.8-83.1 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58-7.52 (m, 4H), 7.39-7.36 (m, 6H), 7.25-7.18 (m, 4H), 7.13-7.07 (m, 3H), 6.76 (d, *J* = 7.6 Hz, 2H), 5.38 (s, 1H), 5.28 (s, 1H), 3.82 (dd, *J* = 12.8, 3.2 Hz, 1H), 3.57 (t, *J* = 12.2 Hz, 1H), 3.23 (dd, *J* = 11.6, 2.8 Hz, 1H), 2.78 (t, *J* = 8.6 Hz, 1H), 1.26-1.13 (m, 5H), 0.71-0.45 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.3, 146.8, 146.6, 140.1, 139.6, 139.2, 135.2, 132.8, 132.3, 130.8, 128.6, 128.2, 128.1, 128.0 (2C),

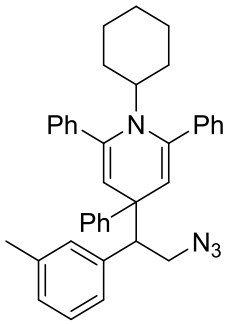
127.8, 127.3, 126.5, 125.8, 114.1, 110.4, 62.9, 58.5, 52.3, 48.1, 33.0, 32.8, 26.4, 25.1; HRMS *m/z* (ESI) calcd for $C_{37}H_{36}ClN_4$ $[M+H]^+$ 571.2623, found 571.2630.

4-(2-azido-1-(4-bromophenyl)ethyl)-1-cyclohexyl-2,4,6-triphenyl-1,4-dihydropyridine (3ea):



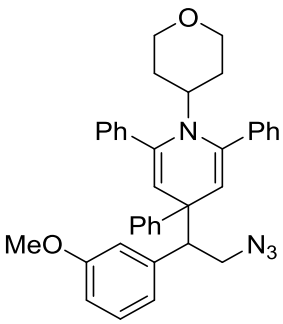
White solid, mp 89.1-90.9 ^oC (uncorrected); ^1H NMR (400 MHz, $CDCl_3$) δ: 7.50-7.44 (m, 4H), 7.32-7.29 (m, 6H), 7.17-7.11 (m, 6H), 7.05 (t, *J* = 6.8 Hz, 1H), 6.63 (d, *J* = 7.6 Hz, 2H), 5.31 (s, 1H), 5.19 (s, 1H), 3.75 (d, *J* = 12.8 Hz, 1H), 3.49 (t, *J* = 12.2 Hz, 1H), 3.14 (d, *J* = 10.8 Hz, 1H), 2.70 (t, *J* = 9.0 Hz, 1H), 1.19-1.06 (m, 5H), 0.63-0.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.3, 146.3, 145.8, 140.2, 140.0, 136.9, 131.3, 130.7, 128.1 (2C), 128.0 (2C), 126.6, 125.8, 120.8, 114.6, 110.8, 62.9, 56.7, 52.7, 46.5, 33.1, 33.0, 26.5, 25.2; HRMS *m/z* (ESI) calcd for $C_{37}H_{36}{}^{79}BrN_4$ $[M+H]^+$ 615.2118, found 615.2123.

4-(2-azido-1-(*m*-tolyl)ethyl)-1-cyclohexyl-2,4,6-triphenyl-1,4-dihydropyridine (3ga):



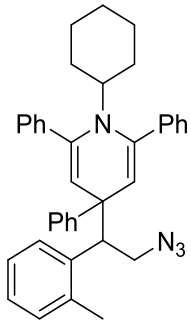
Light yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.59-7.52 (m, 4H), 7.40-7.35 (m, 6H), 7.20 (t, *J* = 8.0 Hz, 4H), 7.10 (t, *J* = 5.6 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 6.55 (s, 1H), 5.40 (s, 1H), 5.36 (s, 1H), 3.81 (d, *J* = 12.4 Hz, 1H), 3.62 (t, *J* = 12.2 Hz, 1H), 3.21 (d, *J* = 11.2 Hz, 1H), 2.77 (t, *J* = 9.6 Hz, 1H), 2.15 (s, 3H), 1.26-1.13 (m, 5H), 0.68-0.46 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.6, 145.9, 145.5, 140.5, 140.3, 137.5, 136.9, 131.0, 128.1, 128.0 (3C), 127.9, 127.7, 127.4, 127.3, 126.7, 126.4, 125.6, 115.2, 111.6, 62.8, 57.2, 52.9, 46.6, 33.1, 32.9, 26.5, 25.2, 21.3; HRMS *m/z* (ESI) calcd for $C_{38}H_{39}N_4$ $[M+H]^+$ 551.3169, found 551.3176.

4-(2-azido-1-(3-methoxyphenyl)ethyl)-2,4,6-triphenyl-1-(tetrahydro-2*H*-pyran-4-yl)-1,4-dihydropyridine (3hb):



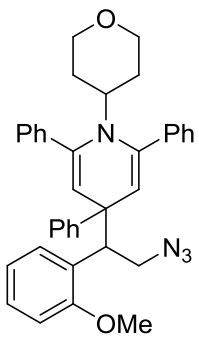
White solid, mp 58.6-60.1 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.60 (d, *J* = 6.5 Hz, 2H), 7.56 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.42-7.35 (m, 6H), 7.23-7.18 (m, 4H), 7.11-7.05 (m, 2H), 6.69 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 6.21 (s, 1H), 5.56 (d, *J* = 2.0 Hz, 1H), 5.53 (d, *J* = 2.0 Hz, 1H), 3.82 (dd, *J* = 13.0, 4.0 Hz, 1H), 3.62 (t, *J* = 12.0 Hz, 1H), 3.52 (s, 3H), 3.43 (d, *J* = 11.5 Hz, 2H), 3.20 (dd, *J* = 11.5, 4.0 Hz, 1H), 3.04-2.98 (m, 1H), 2.75-2.69 (m, 2H), 1.10-0.99 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.8, 149.6, 145.7, 145.2, 139.9, 139.7, 139.0, 128.5, 128.3 (2C), 127.9 (2C), 126.8, 125.8, 121.5, 116.7, 115.5, 112.8, 112.6, 67.9, 59.8, 57.3, 54.9, 52.9, 46.5, 33.1, 33.0; HRMS *m/z* (ESI) calcd for $C_{37}H_{37}N_4O_2$ $[M+H]^+$ 569.2911, found 569.2921.

4-(2-azido-1-(*o*-tolyl)ethyl)-1-cyclohexyl-2,4,6-triphenyl-1,4-dihydropyridine (3ia):



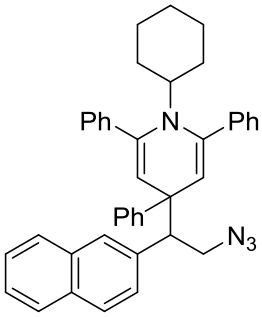
Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, *J* = 7.2 Hz, 2H), 7.49 (d, *J* = 6.8 Hz, 2H), 7.43-7.33 (m, 6H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.18-7.15 (m, 5H), 7.09 (t, *J* = 6.8 Hz, 2H), 6.96 (d, *J* = 7.2 Hz, 1H), 5.57 (s, 1H), 5.42 (s, 1H), 3.79 (d, *J* = 11.2 Hz, 1H), 3.62-3.52 (m, 2H), 2.74 (s, 1H), 1.82 (s, 3H), 1.26-1.06 (m, 5H), 0.66-0.44 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.6, 145.9, 145.3, 140.4 (2C), 139.0, 137.0, 130.4, 128.1, 128.0 (2C), 127.9, 127.7, 127.5, 127.0, 126.6, 125.6, 125.3, 114.9, 112.7, 62.8, 54.1, 51.2, 46.6, 33.1, 32.8, 26.5, 25.2, 20.0; HRMS *m/z* (ESI) calcd for $C_{38}H_{39}N_4$ $[M+H]^+$ 551.3169, found 551.3173.

4-(2-azido-1-(2-methoxyphenyl)ethyl)-2,4,6-triphenyl-1-(tetrahydro-2*H*-pyran-4-yl)-1,4-dihydropyridine (3jb):



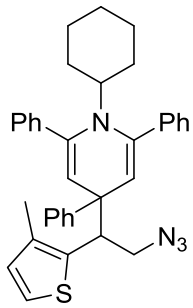
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.62 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.49 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.43-7.30 (m, 6H), 7.24-7.12 (m, 6H), 7.05 (t, *J* = 7.0 Hz, 1H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 5.64 (s, 1H), 5.56 (d, *J* = 2.0 Hz, 1H), 3.98 (s, 1H), 3.70-3.61 (m, 2H), 3.42 (dd, *J* = 10.0, 2.5 Hz, 2H), 3.36 (s, 3H), 3.00-2.93 (m, 1H), 2.71 (td, *J* = 12.0, 2.0 Hz, 2H), 1.02-0.86 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.1, 149.7, 145.5, 144.7, 140.1 (2C), 128.3, 128.2, 128.1, 128.0, 127.8 (2C), 127.3, 126.9, 125.4, 119.8, 116.4, 114.6, 110.4, 67.9 (2C), 59.8, 54.9, 52.7, 46.9, 33.0, 32.9; HRMS *m/z* (ESI) calcd for $C_{37}H_{37}N_4O_2$ $[M+H]^+$ 569.2911, found 569.2916.

4-(2-azido-1-(naphthalen-2-yl)ethyl)-1-cyclohexyl-2,4,6-triphenyl-1,4-dihydropyridine (3ka):



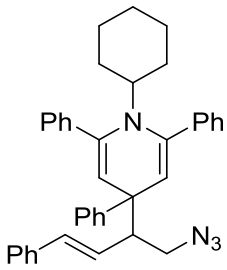
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (t, *J* = 6.2 Hz, 1H), 7.63-7.50 (m, 6H), 7.39-7.33 (m, 9H), 7.20-7.16 (m, 4H), 7.10 (d, *J* = 6.4 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 5.47 (s, 1H), 5.43 (s, 1H), 3.92 (dd, *J* = 12.8, 3.2 Hz, 1H), 3.75 (t, *J* = 12.2 Hz, 1H), 3.43 (dd, *J* = 11.2, 2.8 Hz, 1H), 2.76 (t, *J* = 10.4 Hz, 1H), 1.26-1.01 (m, 5H), 0.68-0.42 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.5, 146.1, 145.6, 140.4, 140.2, 135.4, 132.9, 132.3, 128.7, 128.5, 128.2, 128.1 (2C), 128.0 (2C), 127.8, 127.4, 127.1 (2C), 126.8 (2C), 125.7, 125.6, 125.4, 115.0, 111.4, 62.8, 57.2, 52.9, 46.8, 33.1, 32.9, 26.5, 25.2; HRMS *m/z* (ESI) calcd for $C_{41}H_{39}N_4$ $[M+H]^+$ 587.3169, found 587.3176.

4-(2-azido-1-(3-methylthiophen-2-yl)ethyl)-1-cyclohexyl-2,4,6-triphenyl-1,4-dihydropyridine (3lb):



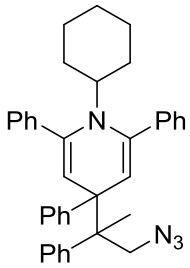
White solid, mp 53.6-54.7 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.65 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.59 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.44-7.34 (m, 6H), 7.25 (d, *J* = 7.0 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 2H), 7.08 (t, *J* = 6.5 Hz, 2H), 6.60 (d, *J* = 5.0 Hz, 1H), 5.86 (d, *J* = 1.5 Hz, 1H), 5.58 (d, *J* = 1.5 Hz, 1H), 3.71 (dd, *J* = 12.5, 3.5 Hz, 1H), 3.54 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.45-3.40 (m, 3H), 3.06-3.00 (m, 1H), 2.73 (td, *J* = 11.5, 2.5 Hz, 2H), 1.63 (s, 3H), 1.08-0.93 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 149.6, 145.9, 145.6, 139.7 (2C), 137.2, 135.0, 129.5, 128.4, 128.3 (2C), 127.9 (2C), 127.7, 126.7, 125.8, 122.7, 116.5, 113.3, 67.9, 59.8, 55.9, 51.1, 46.8, 33.2, 33.0, 13.7; HRMS *m/z* (ESI) calcd for $C_{36}H_{37}N_4S$ $[M+H]^+$ 557.2733, found 557.2736.

(*E*)-4-(1-azido-4-phenylbut-3-en-2-yl)-1-cyclohexyl-2,4,6-triphenyl-1,4-dihydropyridine (3pa):



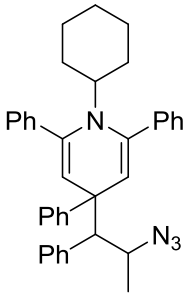
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61-7.57 (m, 4H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.39-7.31 (m, 8H), 7.24-7.16 (m, 6H), 6.20 (d, *J* = 15.6 Hz, 1H), 5.96-5.90 (m, 1H), 5.33 (s, 1H), 5.27 (s, 1H), 3.62 (d, *J* = 12.4 Hz, 1H), 3.19 (t, *J* = 11.6 Hz, 1H), 2.83 (t, *J* = 9.6 Hz, 2H), 1.28-1.15 (m, 5H), 0.79-0.48 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.5, 146.3, 145.8, 140.3, 140.1, 137.3, 133.6, 128.3, 128.2, 128.1, 128.0 (2C), 127.4, 127.1, 126.6, 126.3, 125.7, 114.9, 111.9, 62.9, 54.6, 53.2, 46.4, 33.2 (2C), 26.5, 25.2; HRMS *m/z* (ESI) calcd for $C_{39}H_{39}N_4$ $[M+H]^+$ 563.3169, found 563.3175.

4-(1-azido-2-phenylpropan-2-yl)-1-cyclohexyl-2,4,6-triphenyl-1,4-dihydropyridine (3qa):



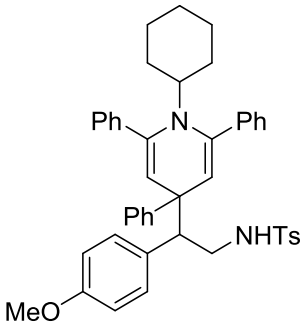
Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.59 (d, *J* = 7.0 Hz, 2H), 7.52 (d, *J* = 6.5 Hz, 2H), 7.41-7.35 (m, 6H), 7.23-7.10 (m, 6H), 6.90 (d, *J* = 7.0 Hz, 2H), 6.77 (d, *J* = 7.0 Hz, 2H), 5.57 (d, *J* = 5.5 Hz, 2H), 4.09 (d, *J* = 12.5 Hz, 1H), 3.66 (d, *J* = 12.5 Hz, 1H), 2.72 (t, *J* = 11.0 Hz, 1H), 1.48 (s, 3H), 1.15-1.00 (m, 5H), 0.54-0.41 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 148.2, 145.7, 145.4, 140.5, 140.4, 140.2, 129.5, 129.2, 128.2, 128.1, 128.0 (2C), 127.9, 126.9, 126.5, 126.3, 125.6, 113.1, 112.9, 62.7, 59.2, 49.6, 48.7, 33.1, 33.0, 26.5, 25.2, 20.8; HRMS *m/z* (ESI) calcd for $C_{38}H_{39}N_4$ $[M+H]^+$ 551.3169, found 551.3181.

4-(2-azido-1-phenylpropyl)-1-cyclohexyl-2,4,6-triphenyl-1,4-dihydropyridine (3ra):



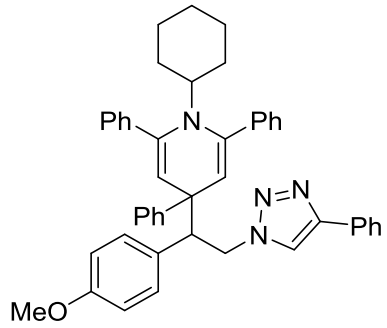
Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, *J* = 7.2 Hz, 2H), 7.52 (d, *J* = 6.4 Hz, 2H), 7.41-7.29 (m, 8H), 7.25-7.21 (m, 2H), 7.10-7.07 (m, 6H), 5.69 (s, 1H), 5.49 (s, 1H), 4.15-4.14 (m, 1H), 2.92 (s, 1H), 2.76-2.73 (m, 1H), 1.26-1.14 (m, 5H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.67-0.44 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.0, 145.5, 144.6, 140.9, 140.8, 137.6, 131.3, 128.5, 128.1, 128.0, 127.8 (3C), 127.6, 127.3, 126.8, 126.3, 125.3, 115.6, 114.3, 63.0, 62.7, 59.0, 47.5, 33.1, 32.9, 26.6, 25.3, 20.3; HRMS *m/z* (ESI) calcd for $C_{38}H_{39}N_4$ $[M+H]^+$ 551.3169, found 551.3177.

***N*-(2-(1-cyclohexyl-2,4,6-triphenyl-1,4-dihydropyridin-4-yl)-2-(4-methoxyphenyl)ethyl)-4-methylbenzenesulfonamide (4aa):**



White solid, mp 120.6-122.8 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52-7.47 (m, 6H), 7.38-7.32 (m, 6H), 7.15 (t, *J* = 8.0 Hz, 4H), 7.05 (t, *J* = 7.8 Hz, 3H), 6.58-6.50 (m, 4H), 5.18 (s, 1H), 5.16 (s, 1H), 4.08 (d, *J* = 8.4 Hz, 1H), 3.70 (s, 3H), 3.51 (t, *J* = 10.4 Hz, 1H), 3.16 (t, *J* = 12.4 Hz, 1H), 2.91 (d, *J* = 11.2 Hz, 1H), 2.74 (s, 1H), 2.41 (s, 3H), 1.23-1.12 (m, 5H), 0.66-0.43 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3, 149.5, 145.8, 145.4, 143.1, 140.4, 140.1, 136.6, 130.7, 129.5, 128.5, 128.1, 128.0, 127.9 (2C), 127.8, 127.7, 127.2, 126.6, 125.4, 114.8, 113.2, 111.0, 62.7, 56.2, 55.0, 46.4, 44.5, 33.0, 32.9, 26.4, 25.1, 21.5; HRMS *m/z* (ESI) calcd for $C_{45}H_{47}N_2O_3S$ $[M+H]^+$ 695.3302, found 695.3308.

1-cyclohexyl-4-(1-(4-methoxyphenyl)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)ethyl)-2,4,6-triphenyl-1,4-dihydropyridine (5aa):



White solid, mp 156.8-158.3 ^{o}C (uncorrected);; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60-7.55 (m, 6H), 7.38-7.35 (m, 6H), 7.26-7.19 (m, 7H), 7.09 (t, *J* = 6.2 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 2H), 6.55 (d, *J* = 7.6 Hz, 2H), 5.55 (s, 1H), 5.50 (s, 1H), 4.96 (d, *J* = 12.8 Hz, 1H), 4.59 (t, *J* = 12.8 Hz, 1H), 3.66-3.62 (m, 4H), 2.83 (t, *J* = 9.6 Hz, 1H), 1.26-1.13 (m, 5H), 0.72-0.46 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.2, 149.2, 146.7, 146.5, 145.9, 140.3, 139.9, 130.6, 130.4, 128.5 (2C), 128.0, 127.9, 127.8, 127.6, 126.6, 125.6, 125.4, 119.8, 115.0, 113.0, 111.0, 62.9, 57.3, 54.8, 52.4, 46.9, 33.0, 32.9, 26.4, 25.1; HRMS *m/z* (ESI) calcd for $C_{46}H_{45}N_4O$ $[M+H]^+$ 669.3588, found 669.3595.

(C) Reference

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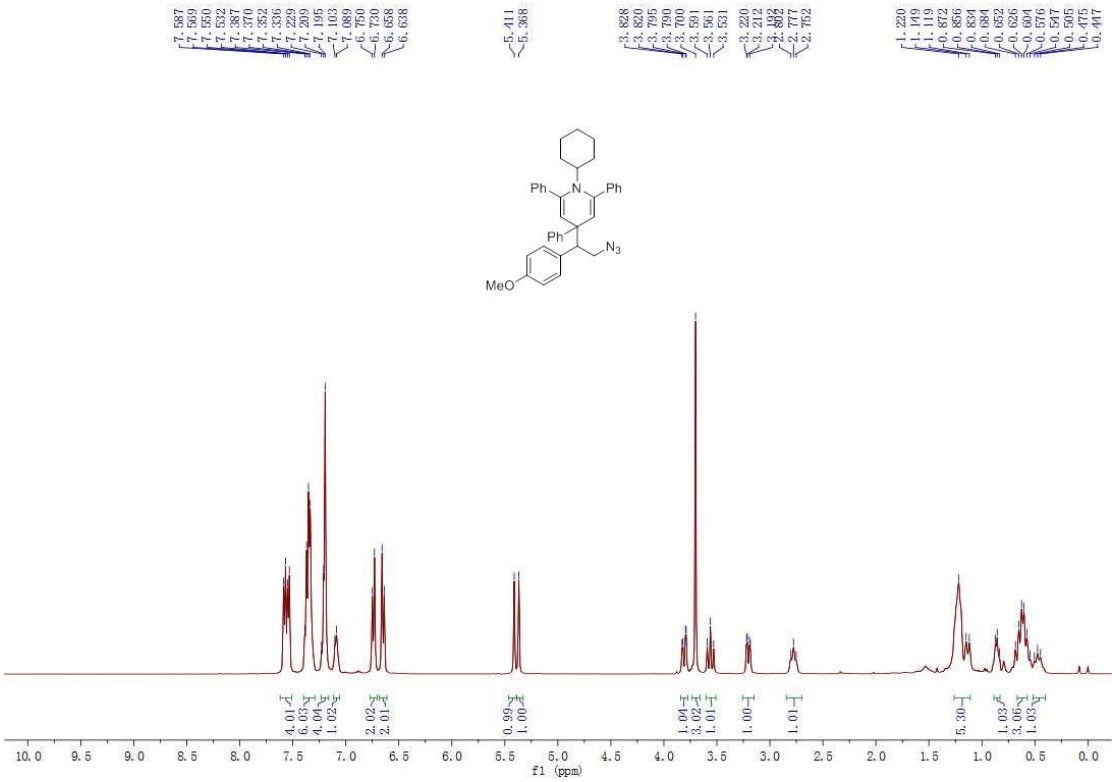
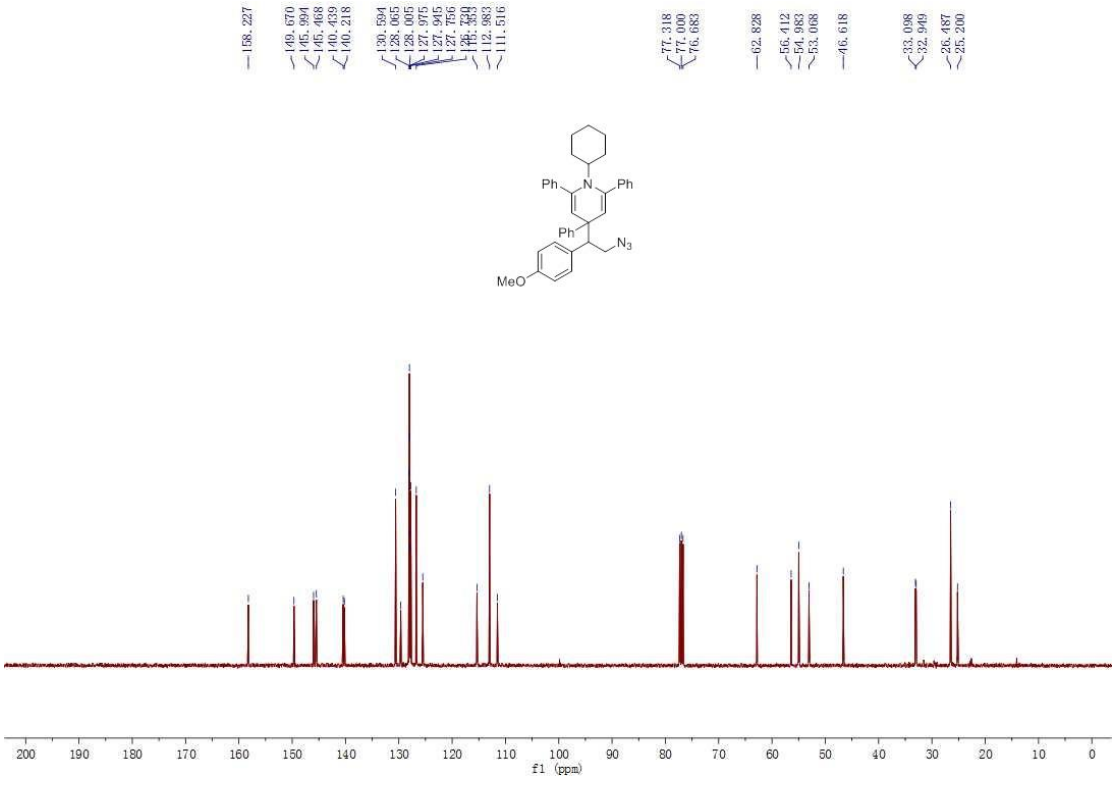
(2) F. J. R. Klauck, M. J. James and F. Glorius, *Angew. Chem. Int. Ed.*, **2017**, **56**, 12336.

(3) C. S. Sevov, R. E. M. Brooner, E. Chénard, R. S. Assary, J. S. Moore, J. Rodríguez-López and M. S. Sanford, *J. Am. Chem. Soc.*, 2015, **137**, 14465.

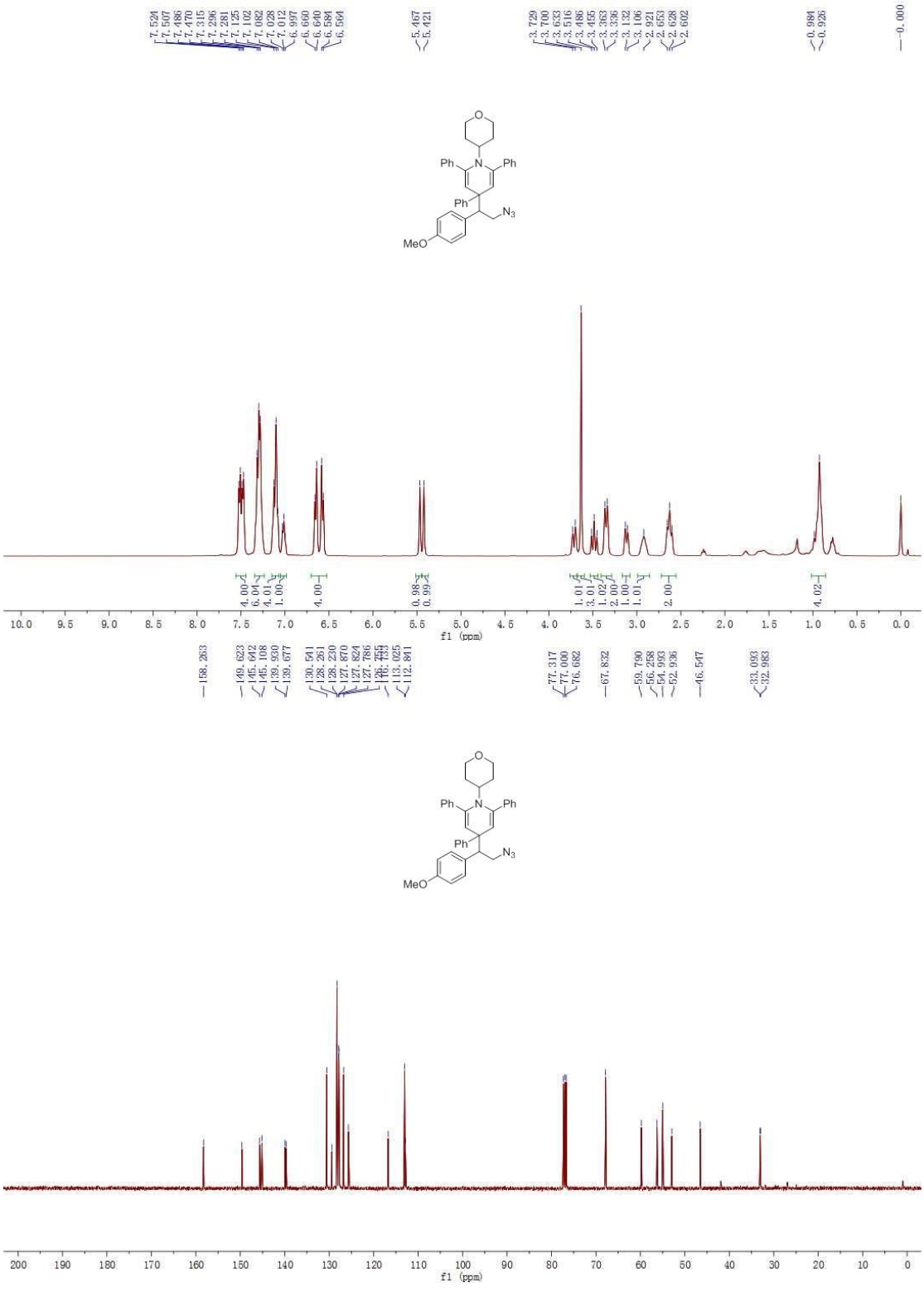
(D) Spectra

4-(2-azido-1-(4-methoxyphenyl)ethyl)-1-cyclohexyl-2,4,6-triphenyl-1,4-dihydropyridine (3aa)

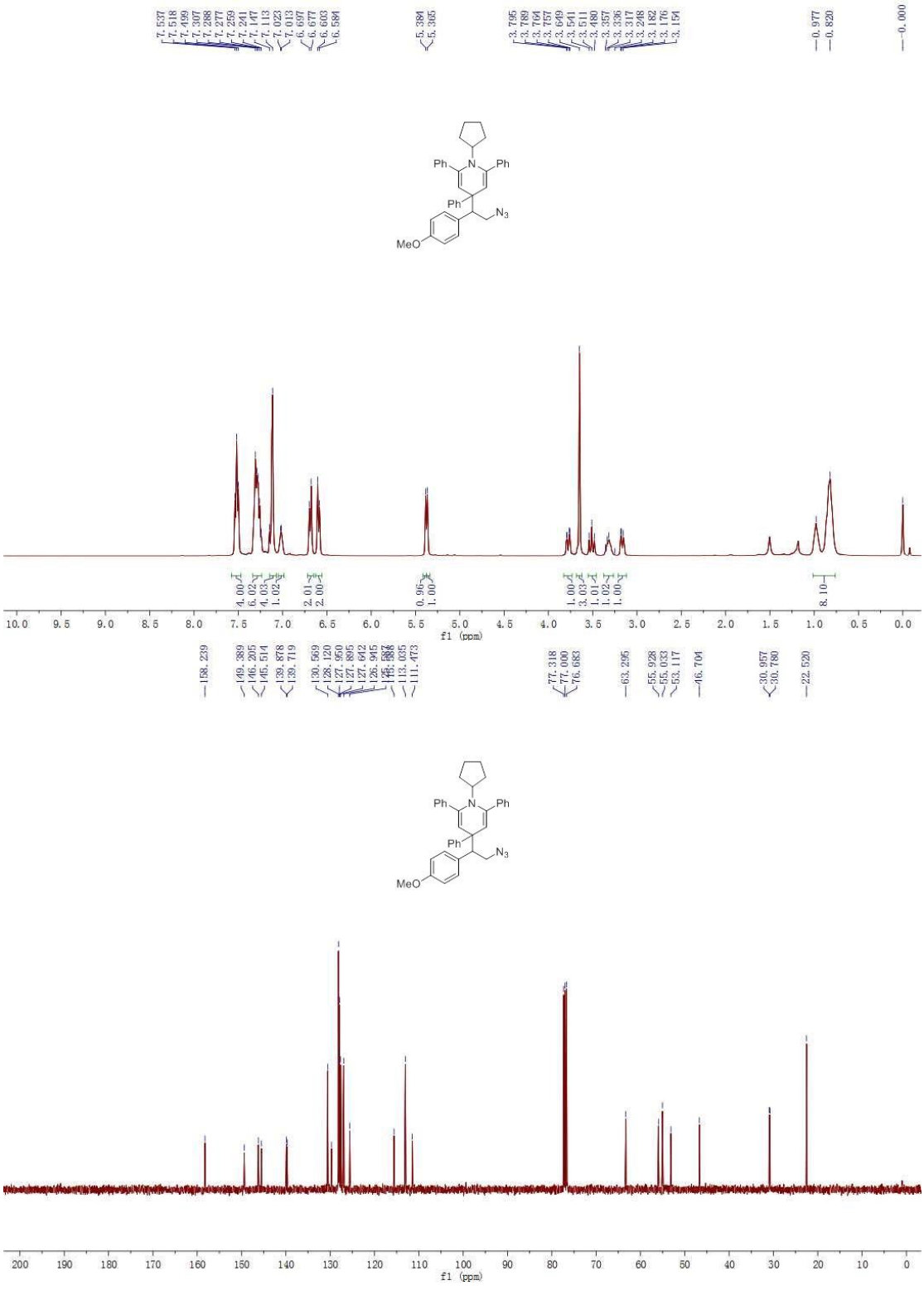




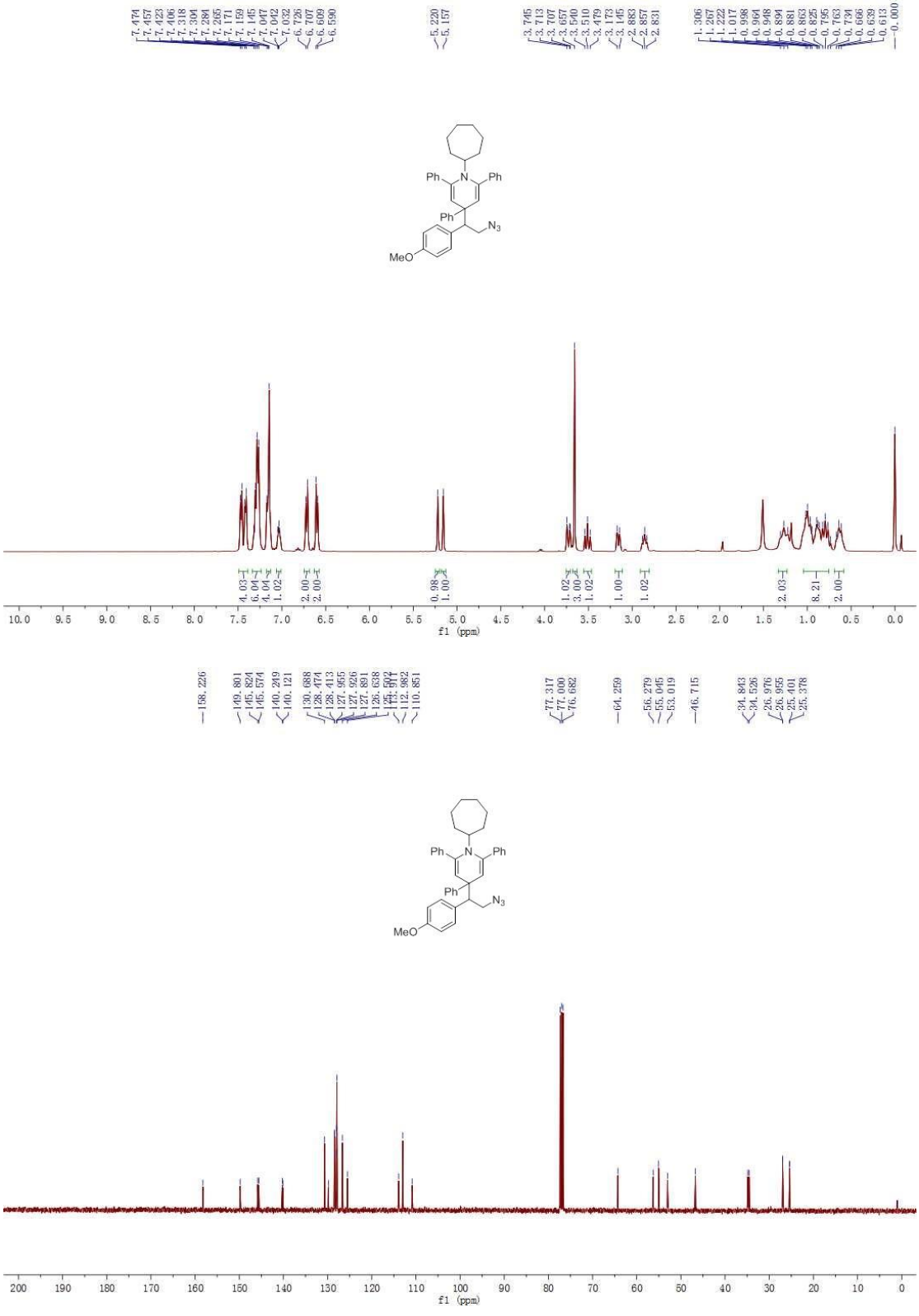
4-(2-azido-1-(4-methoxyphenyl)ethyl)-2,4,6-triphenyl-1-(tetrahydro-2H-pyran-4-yl)-1,4-dihydropyridine (3ab)



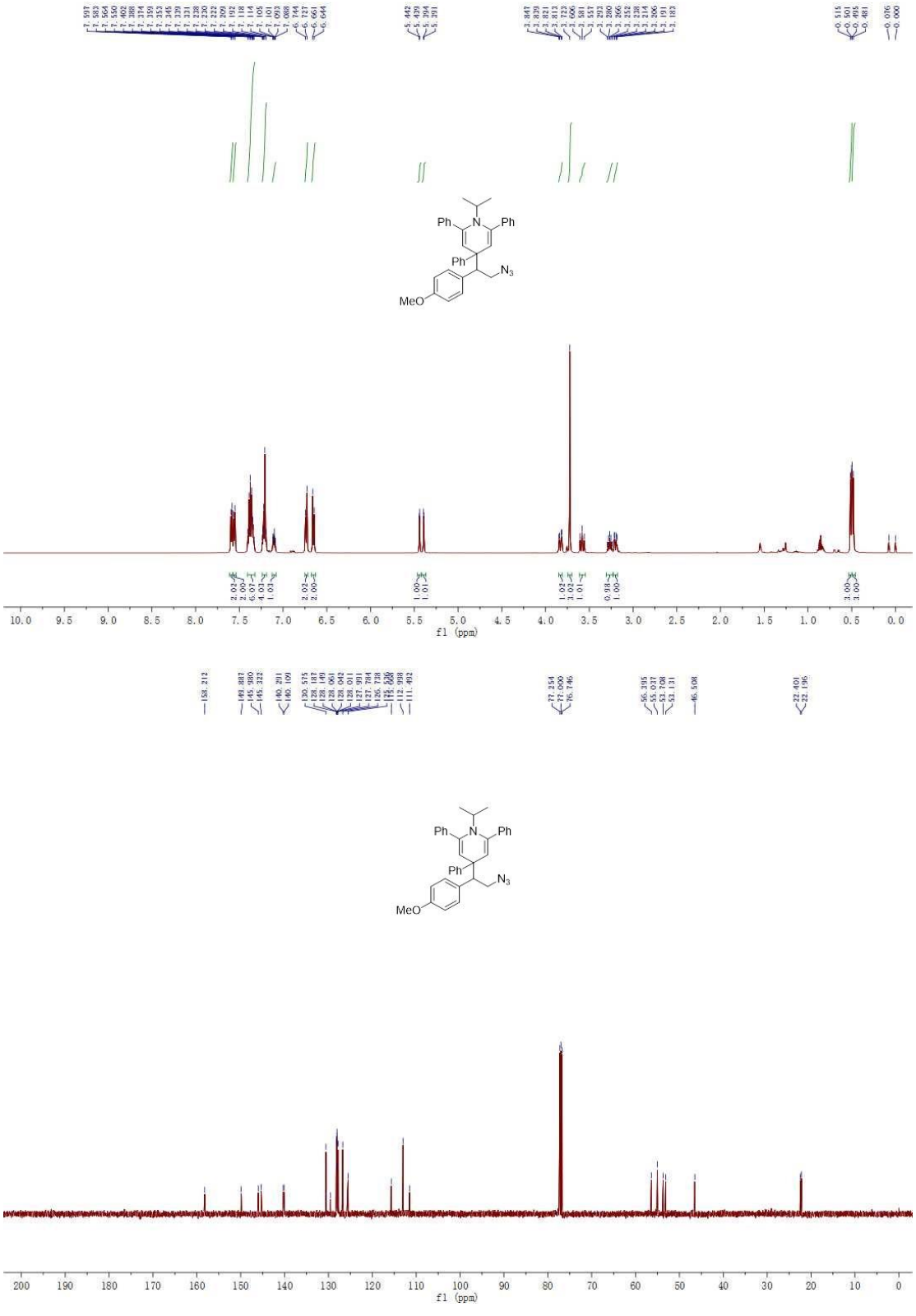
4-(2-azido-1-(4-methoxyphenyl)ethyl)-1-cyclopentyl-2,4,6-triphenyl-1,4-dihydropyridine (3ac)



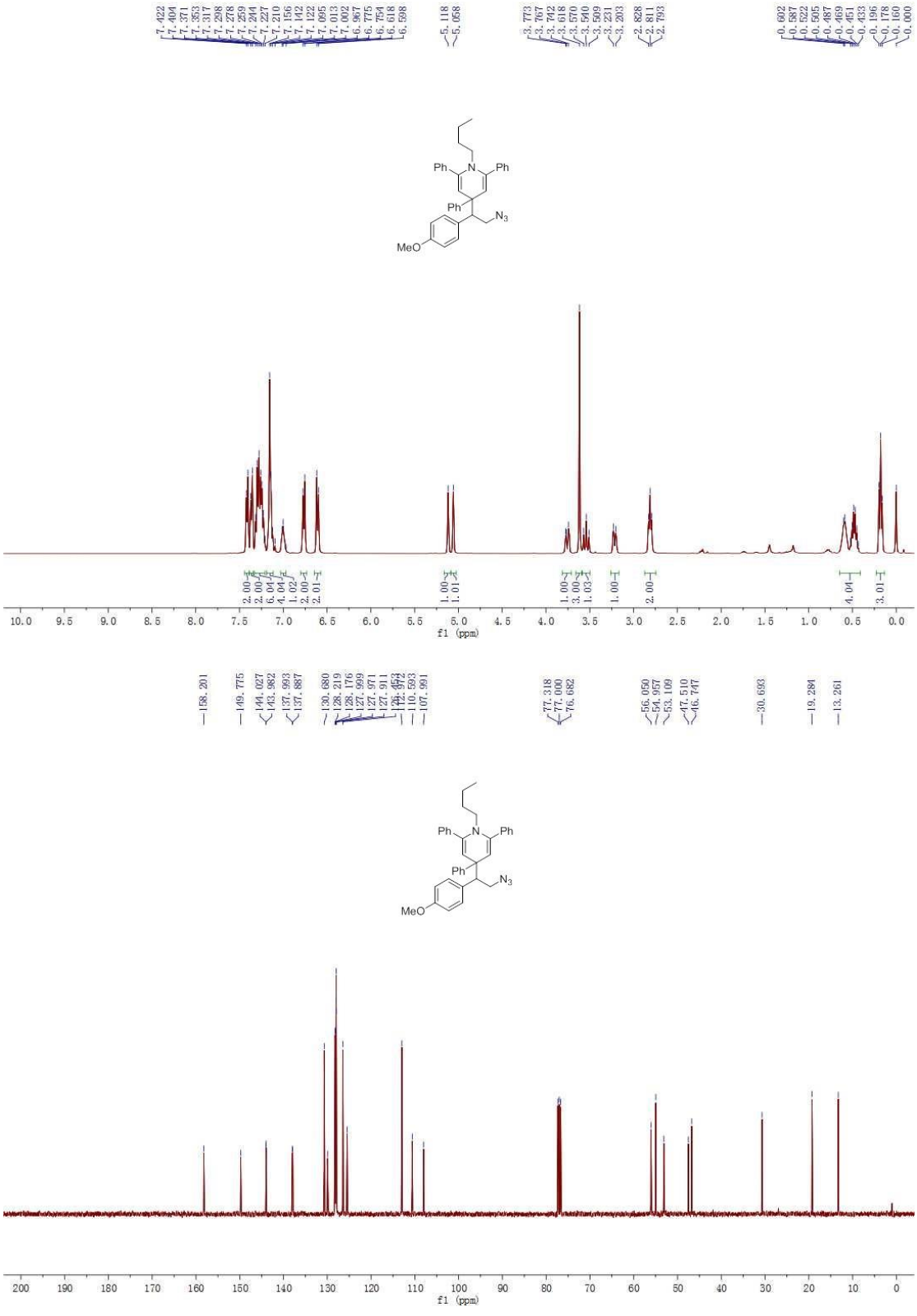
4-(2-azido-1-(4-methoxyphenyl)ethyl)-1-cycloheptyl-2,4,6-triphenyl-1,4-dihydropyridine (3ad)



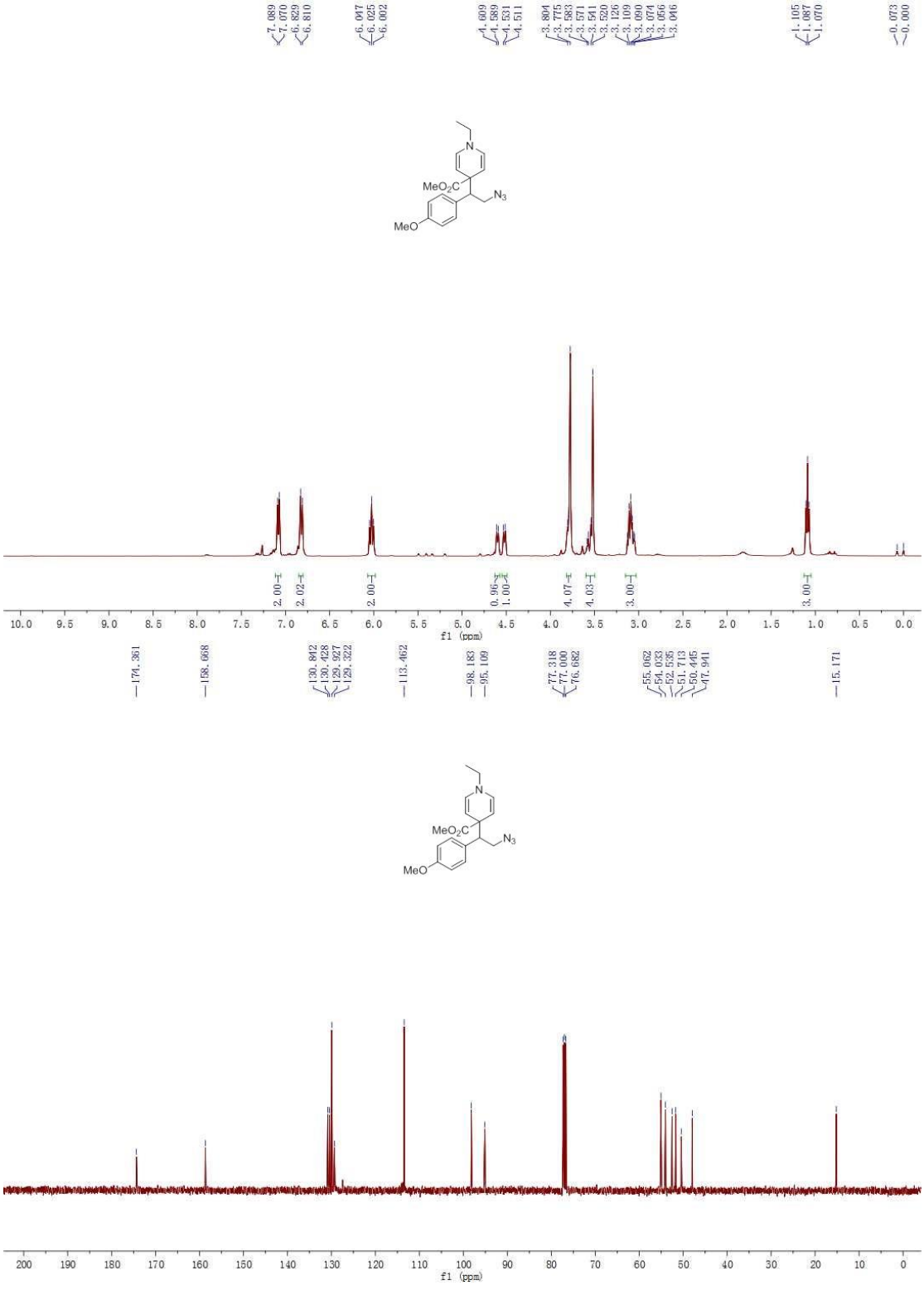
4-(2-azido-1-(4-methoxyphenyl)ethyl)-1-isopropyl-2,4,6-triphenyl-1,4-dihydropyridine (3ae)



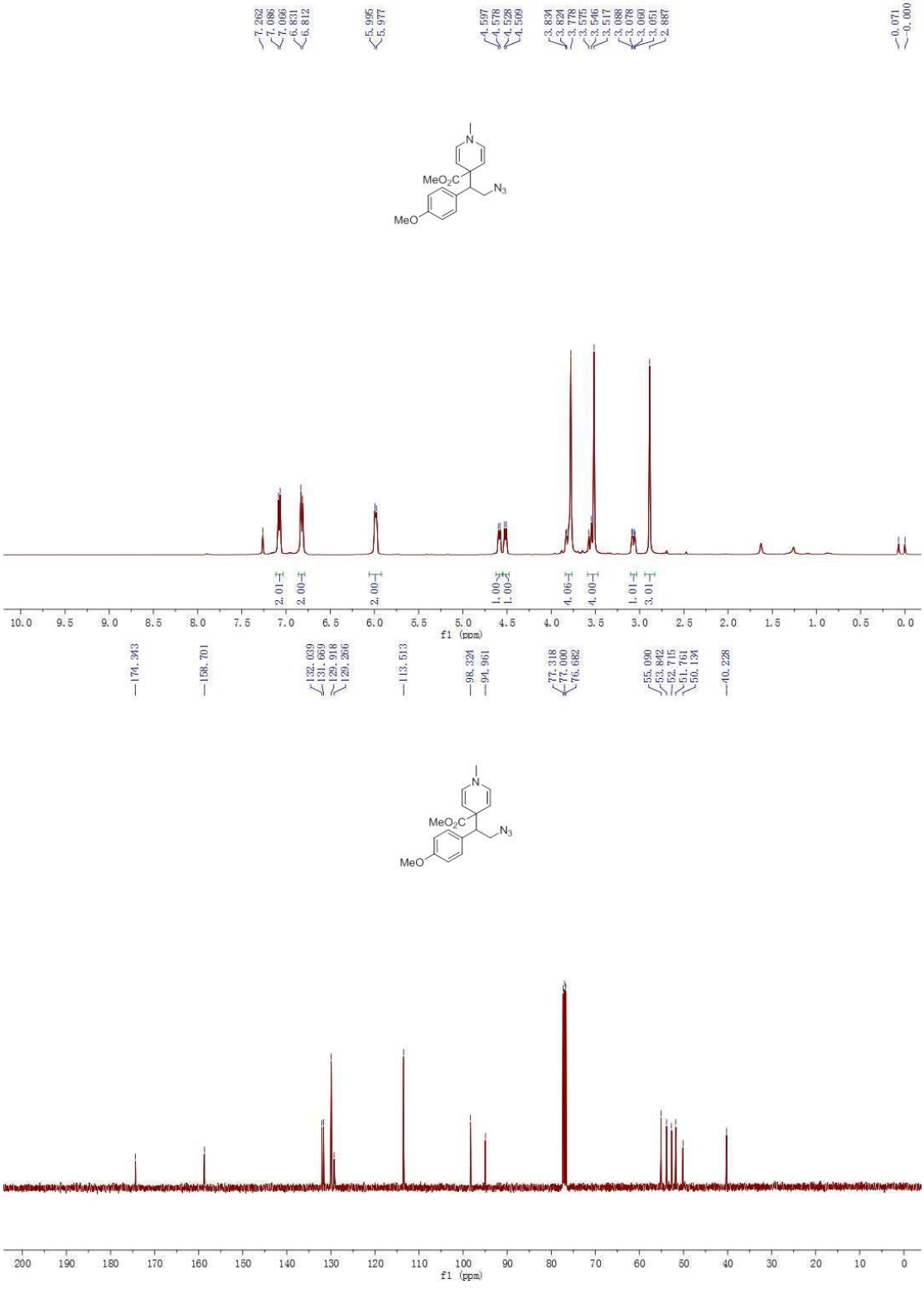
4-(2-azido-1-(4-methoxyphenyl)ethyl)-1-butyl-2,4,6-triphenyl-1,4-dihydropyridine (3af)



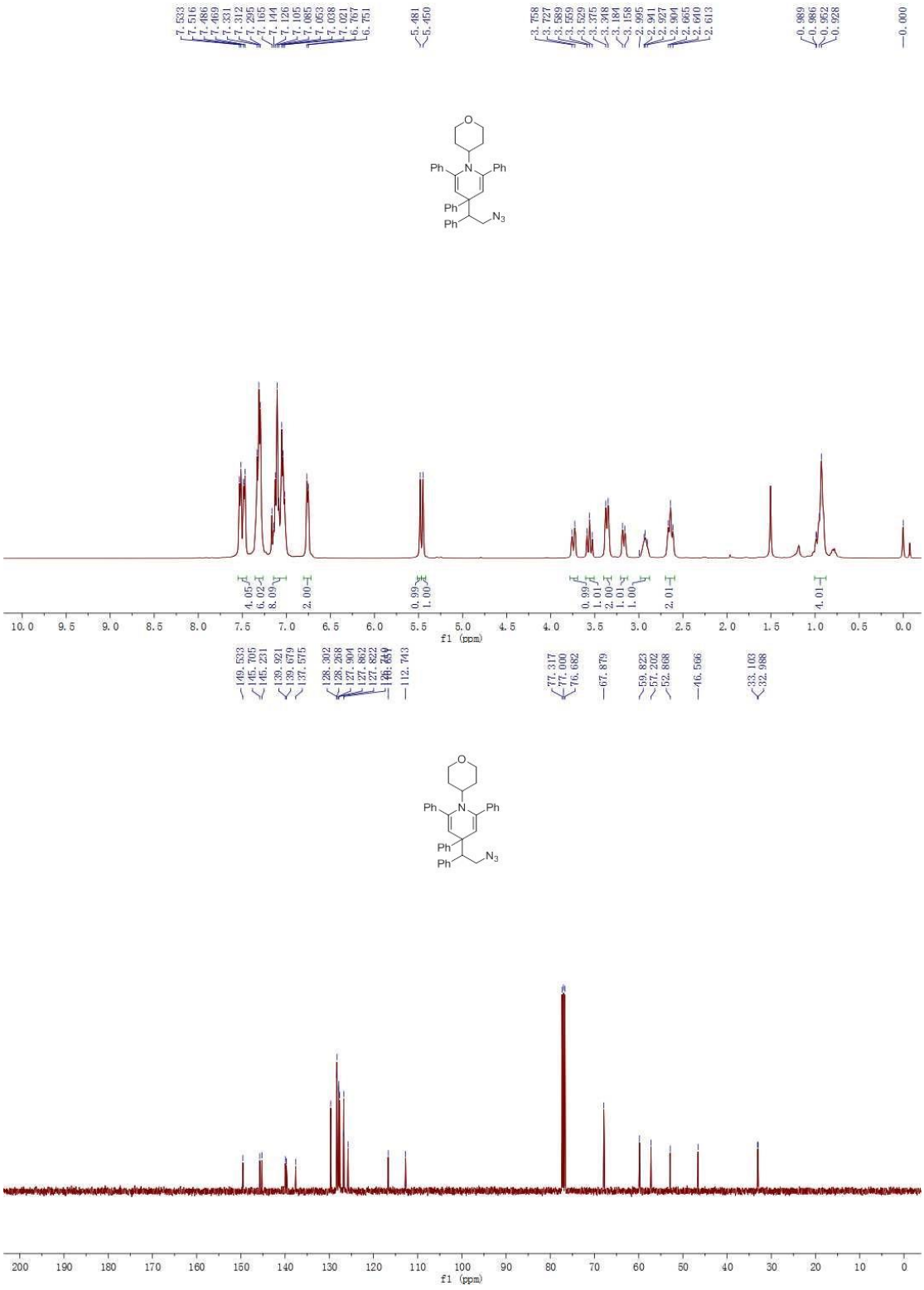
methyl 4-(2-azido-1-(4-methoxyphenyl)ethyl)-1-ethyl-1,4-dihydropyridine-4-carboxylate (3ag)



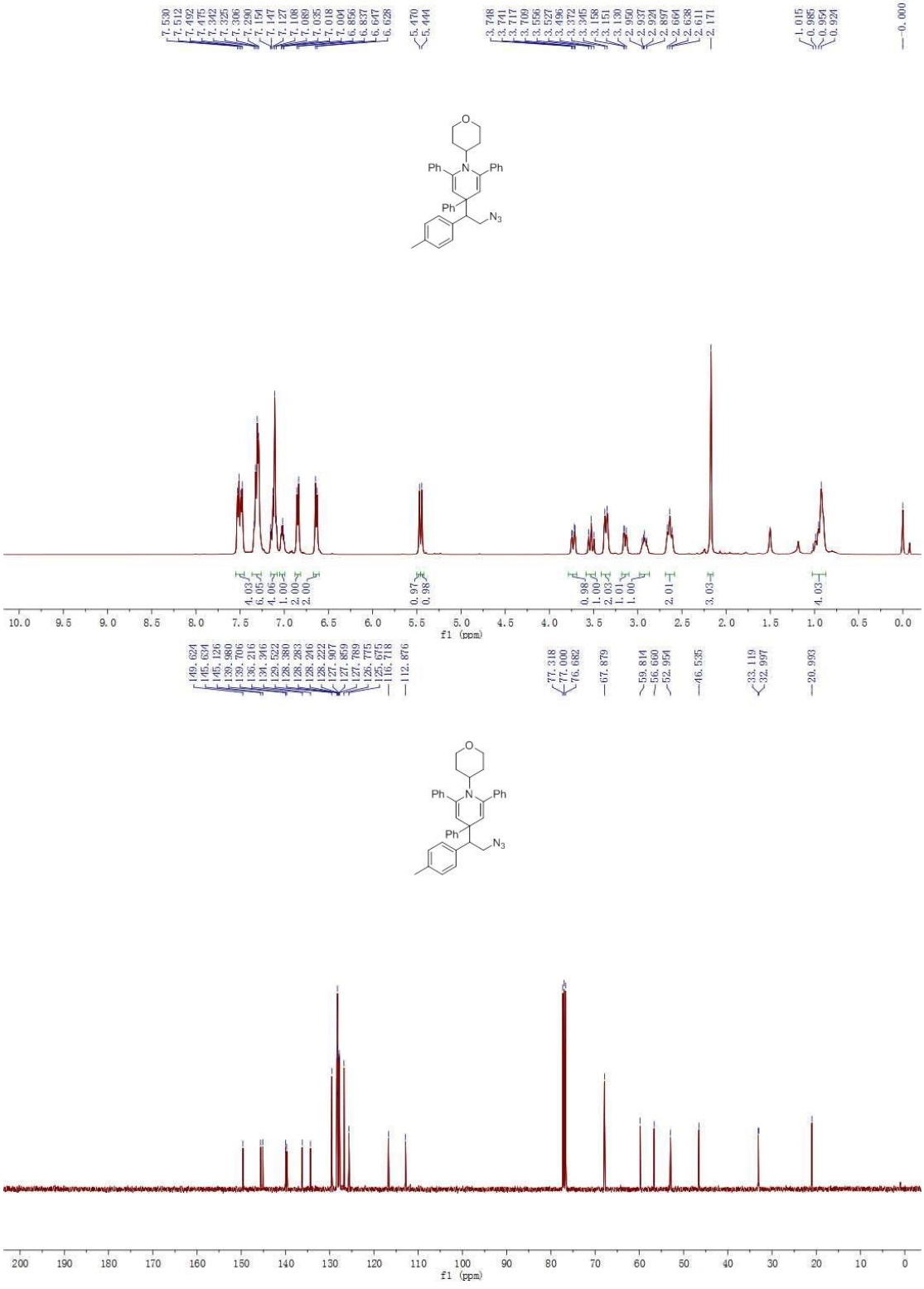
methyl 4-(2-azido-1-(4-methoxyphenyl)ethyl)-1-methyl-1,4-dihydropyridine-4-carboxylate (3ah)



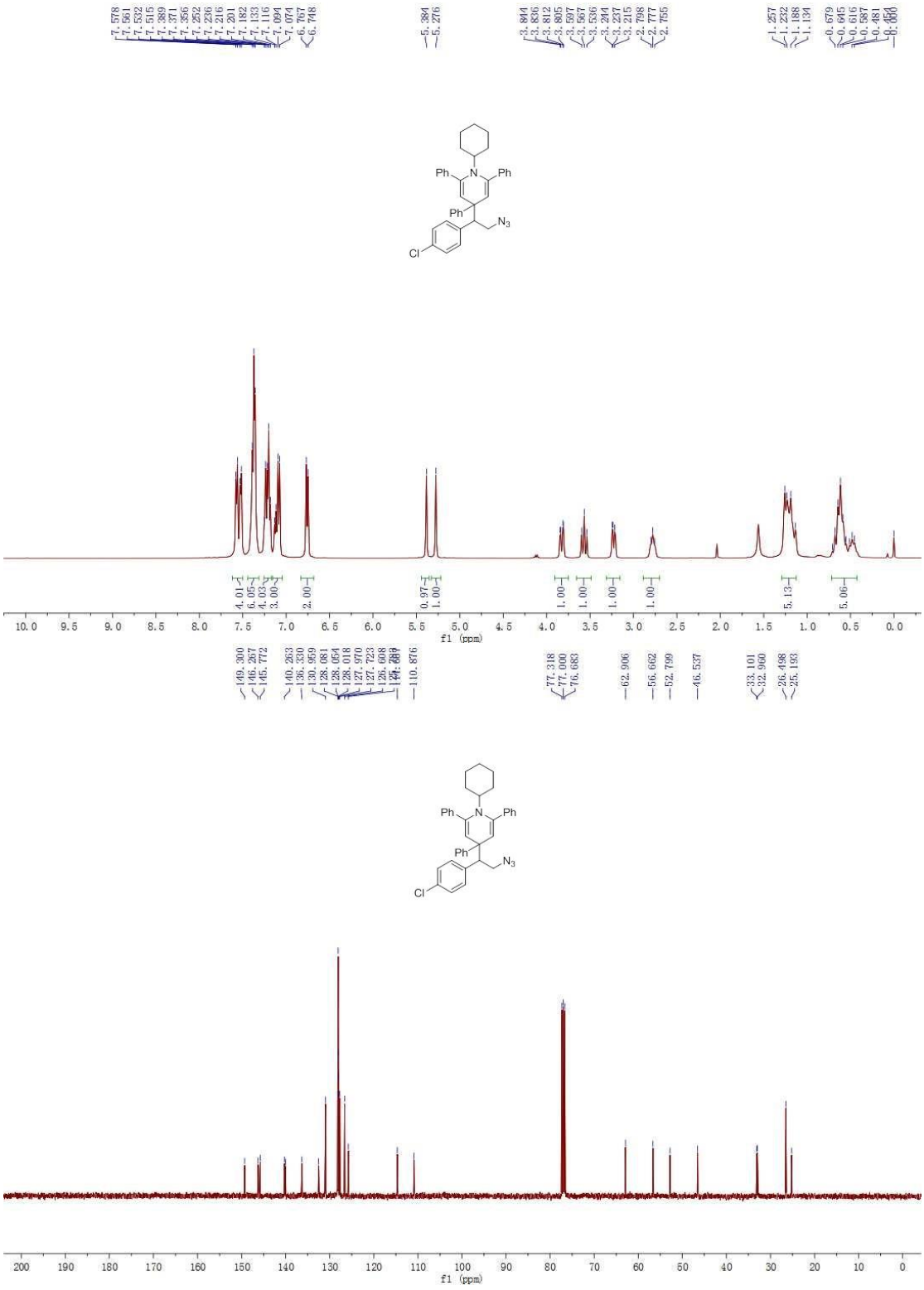
4-(2-azido-1-phenylethyl)-2,4,6-triphenyl-1-(tetrahydro-2*H*-pyran-4-yl)-1,4-dihydropyridine (3bb)



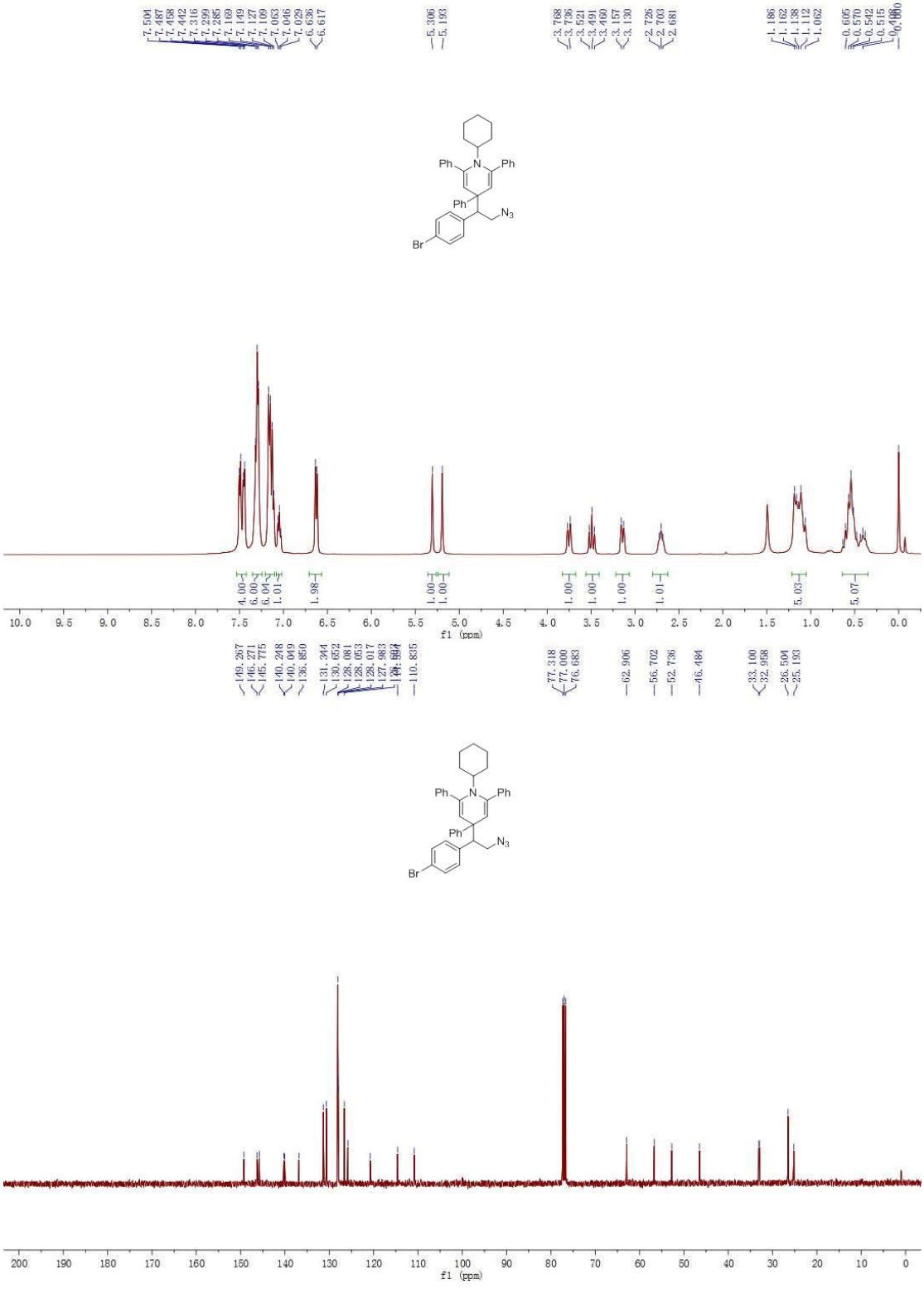
4-(2-azido-1-(*p*-tolyl)ethyl)-2,4,6-triphenyl-1-(tetrahydro-2*H*-pyran-4-yl)-1,4-dihydropyridine (3cb)



4-(2-azido-1-(4-chlorophenyl)ethyl)-1-cyclohexyl-2,4,6-triphenyl-1,4-dihydropyridine (3da)

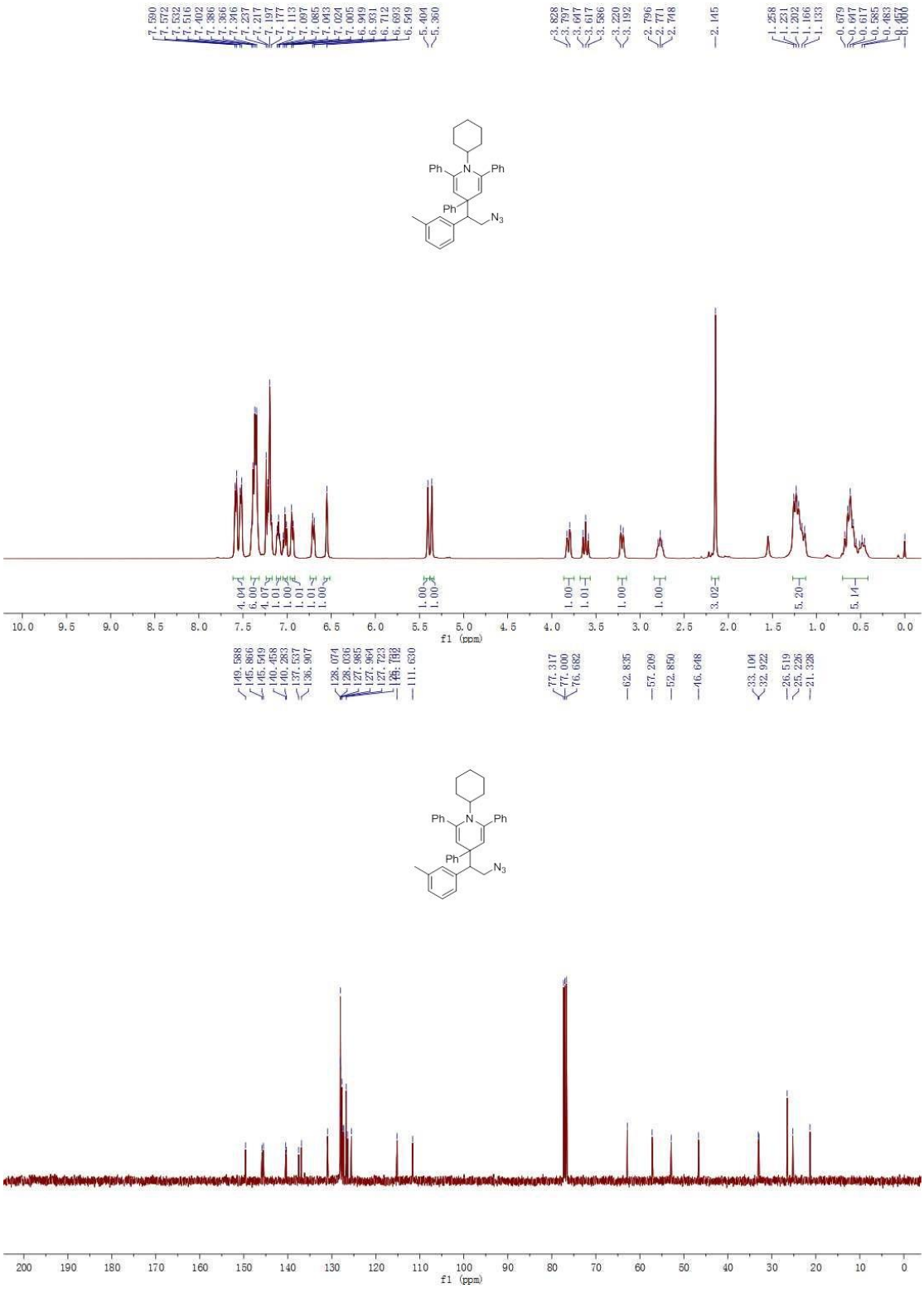


4-(2-azido-1-(4-bromophenyl)ethyl)-1-cyclohexyl-2,4,6-triphenyl-1,4-dihydropyridine (3ea)

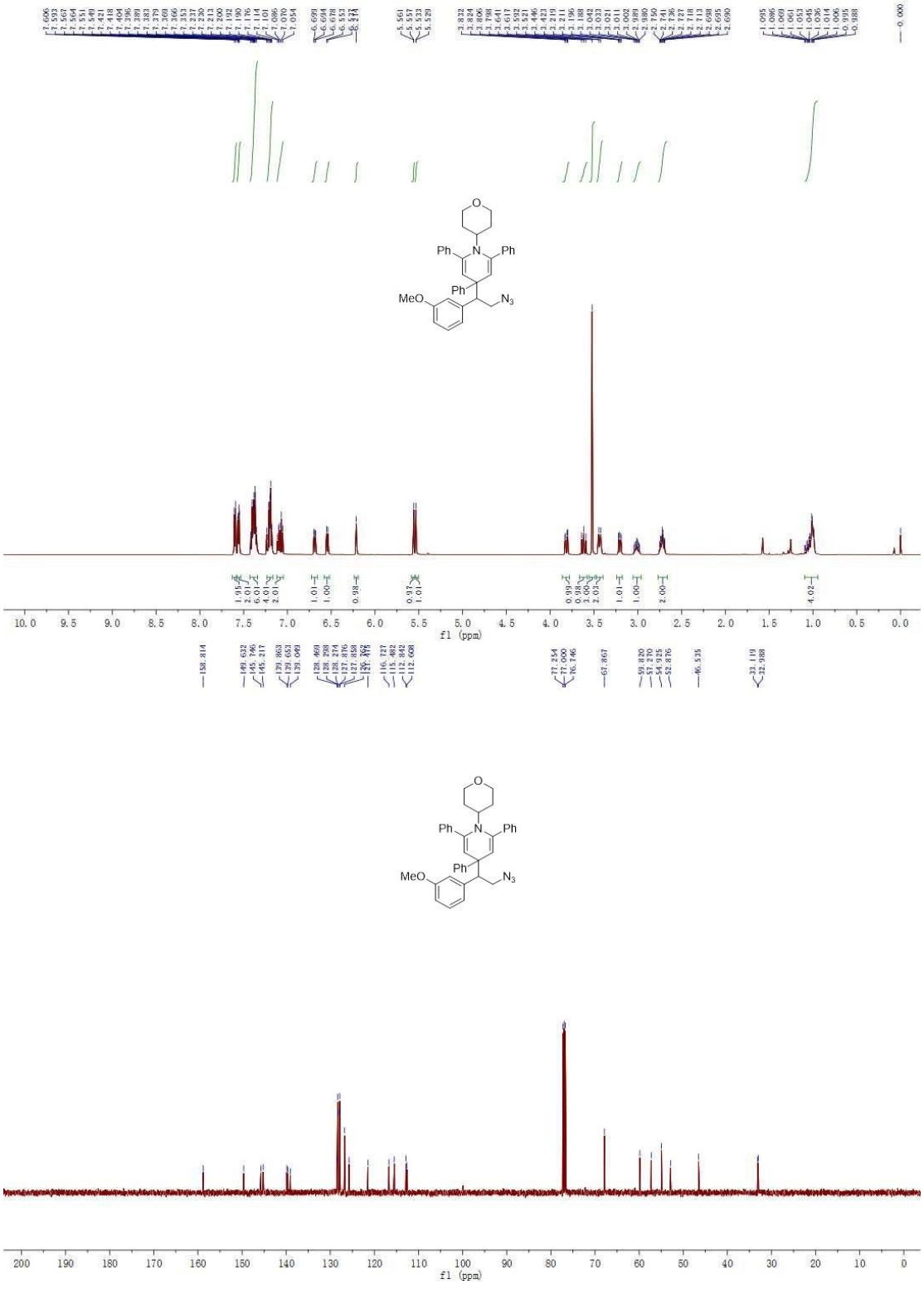


4-(2-azido-1-(*m*-tolyl)ethyl)-1-cyclohexyl-2,4,6-triphenyl-1,4-dihydropyridine

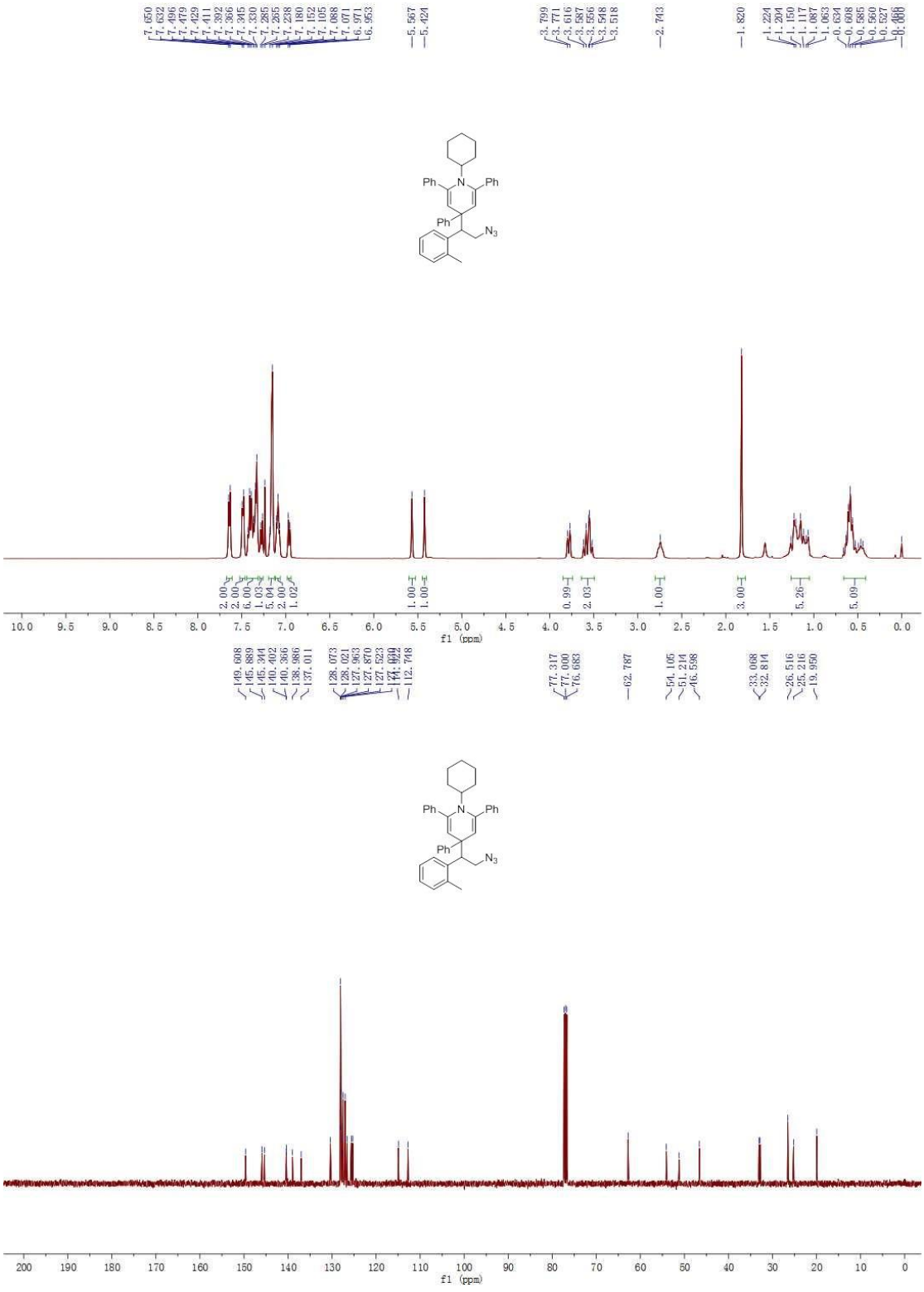
(3ga)



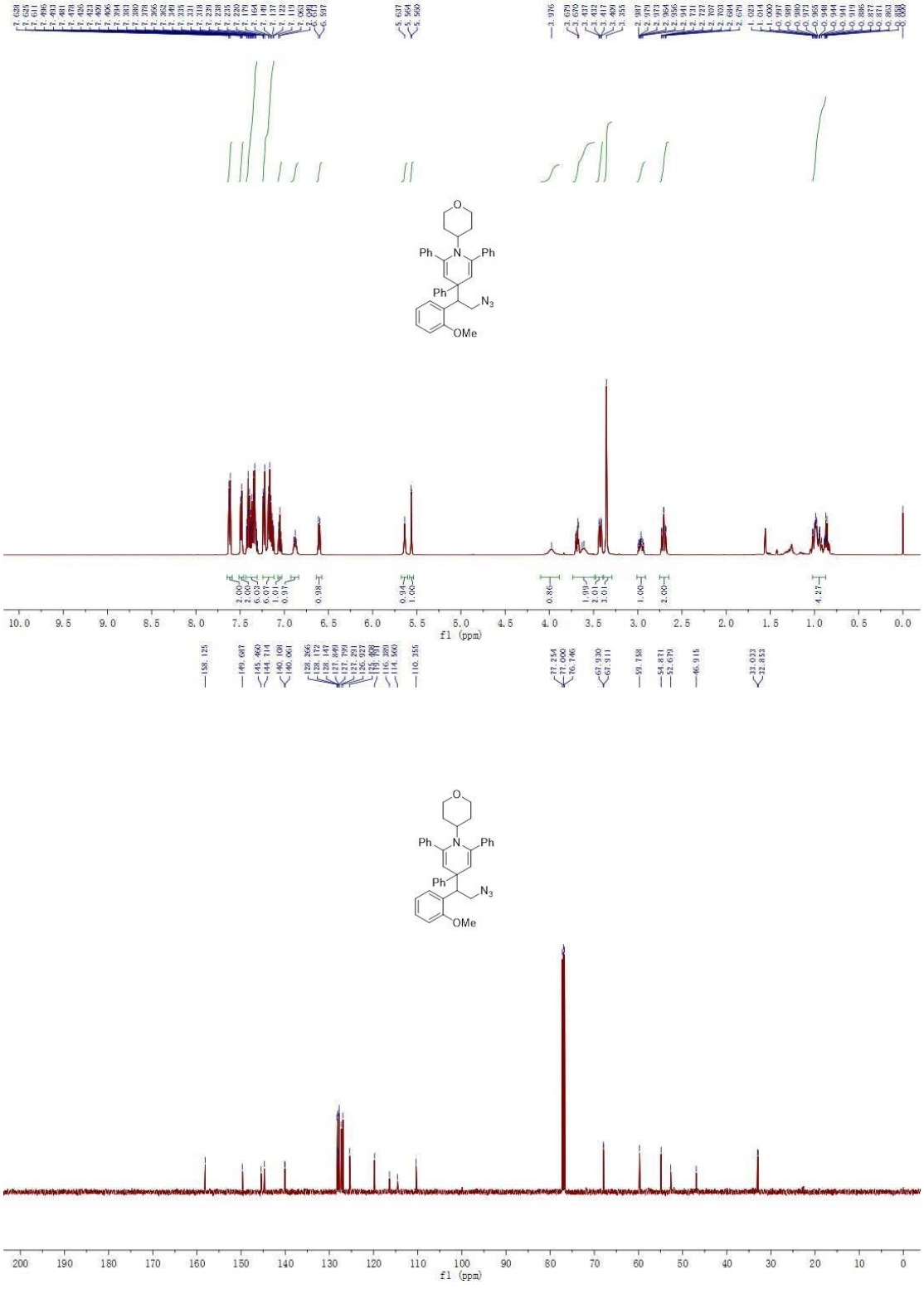
4-(2-azido-1-(3-methoxyphenyl)ethyl)-2,4,6-triphenyl-1-(tetrahydro-2*H*-pyran-4-yl)-1,4-dihydropyridine (3hb)



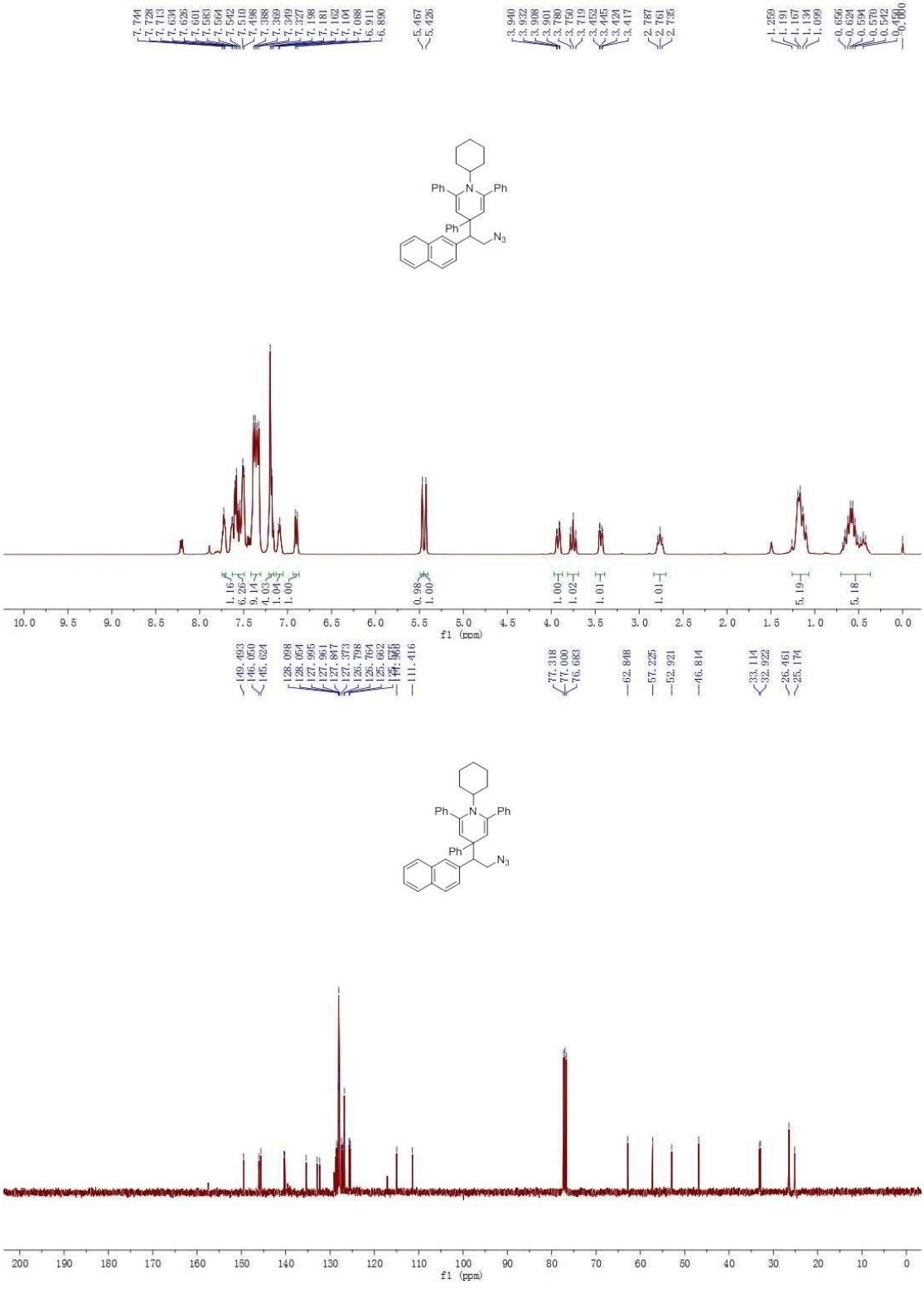
4-(2-azido-1-(*o*-tolyl)ethyl)-1-cyclohexyl-2,4,6-triphenyl-1,4-dihydropyridine (3ia)



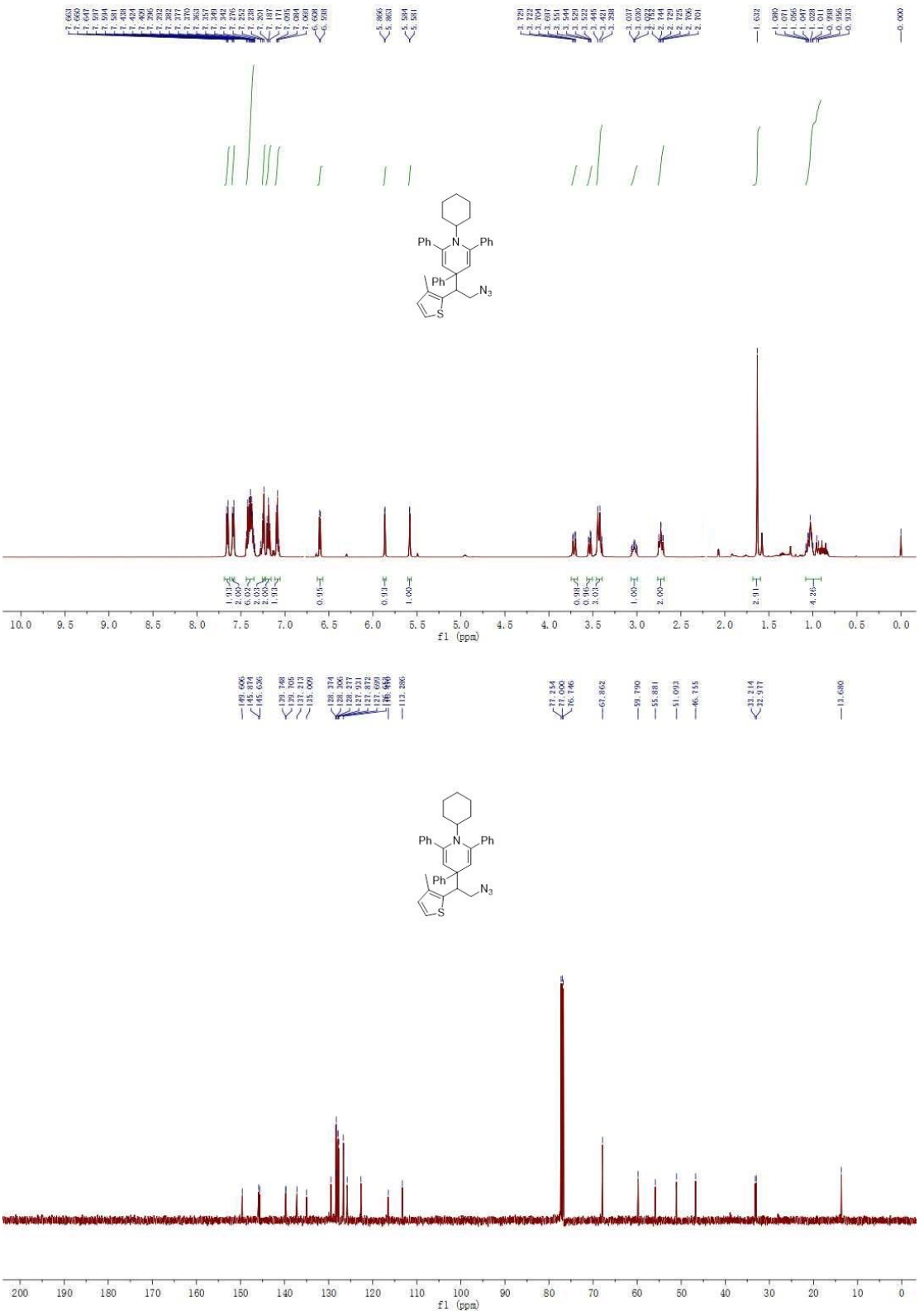
4-(2-azido-1-(2-methoxyphenyl)ethyl)-2,4,6-triphenyl-1-(tetrahydro-2*H*-pyran-4-yl)-1,4-dihydropyridine (3jb)



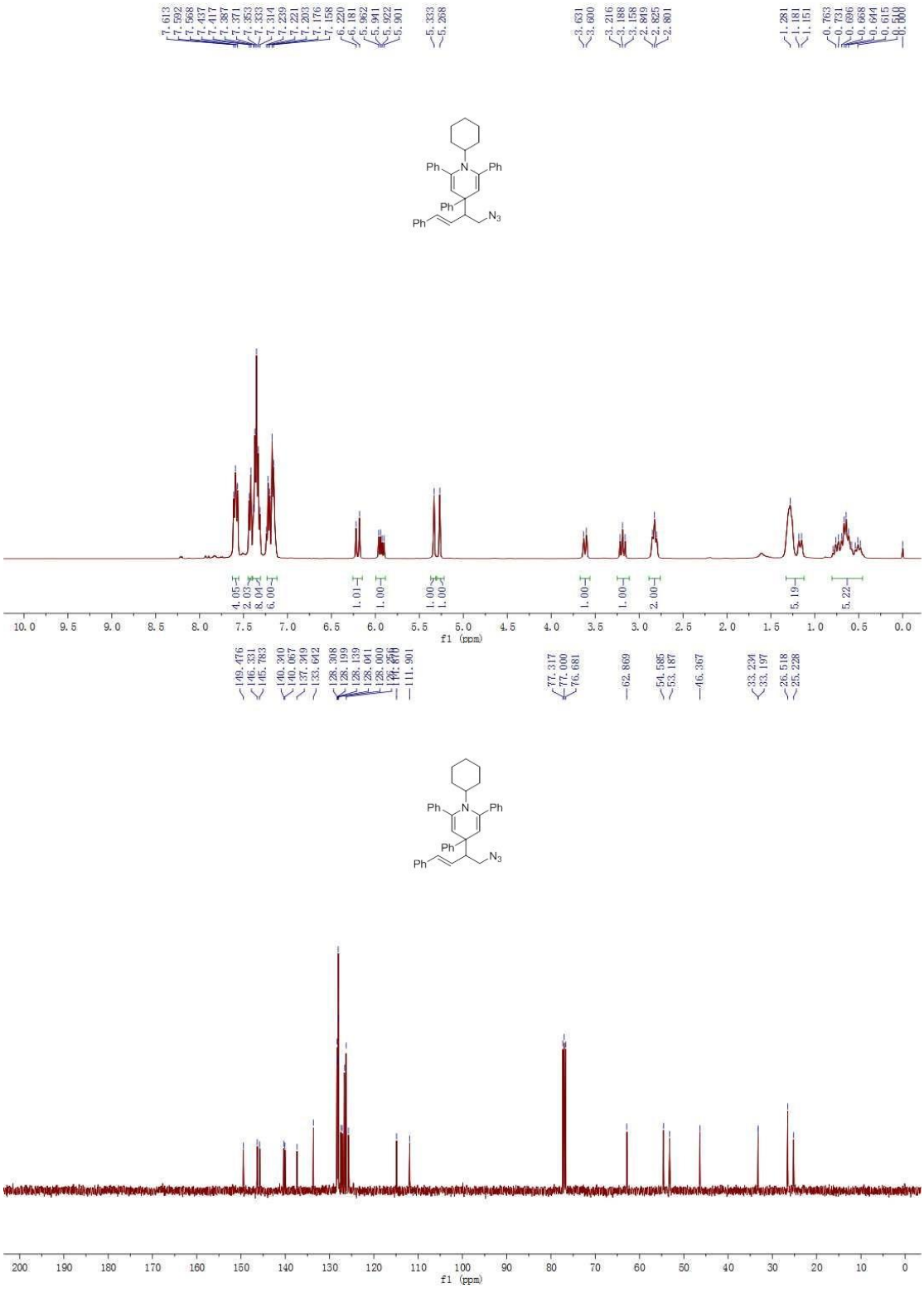
4-(2-azido-1-(naphthalen-2-yl)ethyl)-1-cyclohexyl-2,4,6-triphenyl-1,4-dihydropyridine (3ka)



4-(2-azido-1-(3-methylthiophen-2-yl)ethyl)-1-cyclohexyl-2,4,6-triphenyl-1,4-dihydropyridine (3lb)

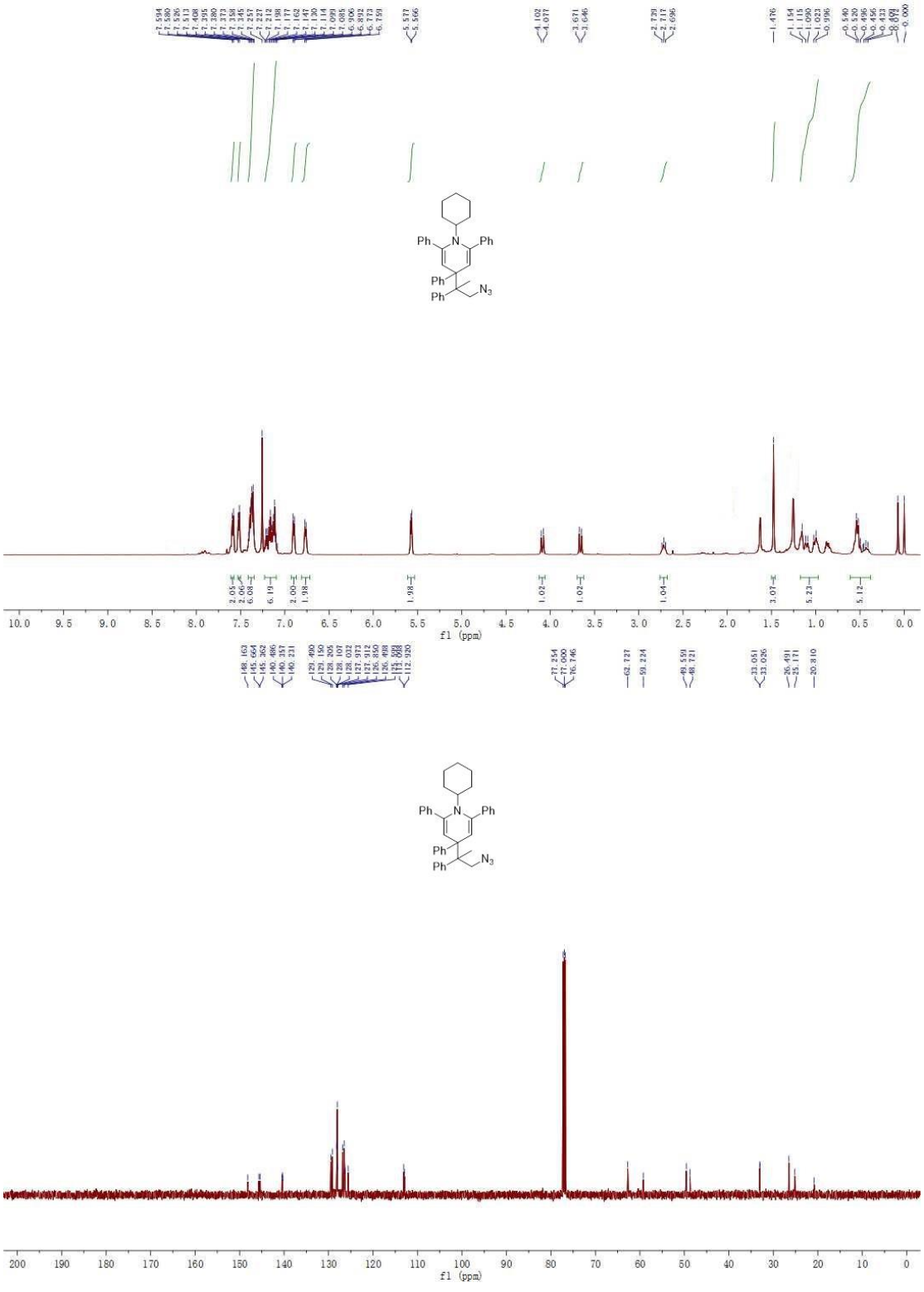


(*E*)-4-(1-azido-4-phenylbut-3-en-2-yl)-1-cyclohexyl-2,4,6-triphenyl-1,4-dihydropyridine (3pa)



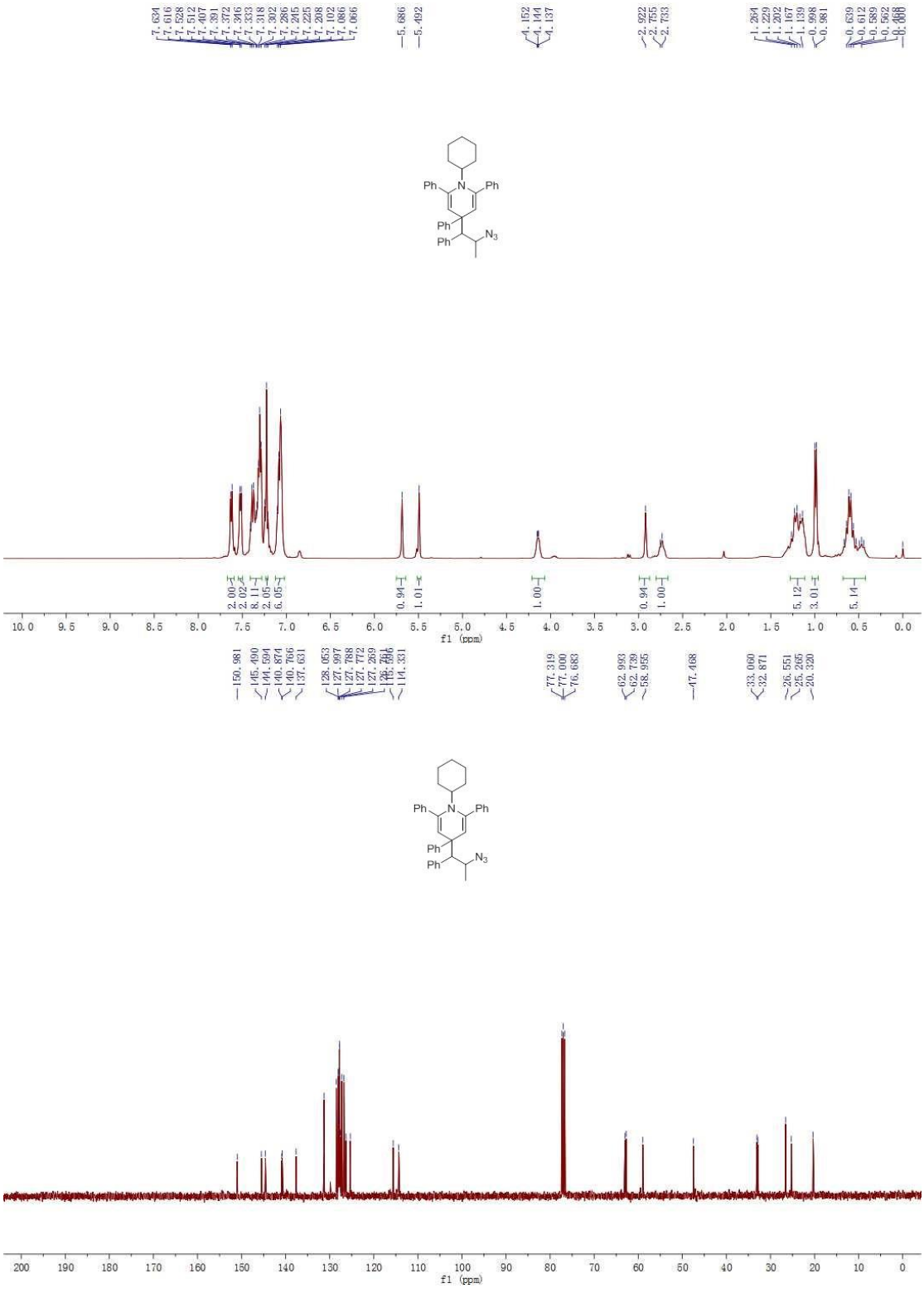
4-(1-azido-2-phenylpropan-2-yl)-1-cyclohexyl-2,4,6-triphenyl-1,4-

dihydropyridine (3qa)

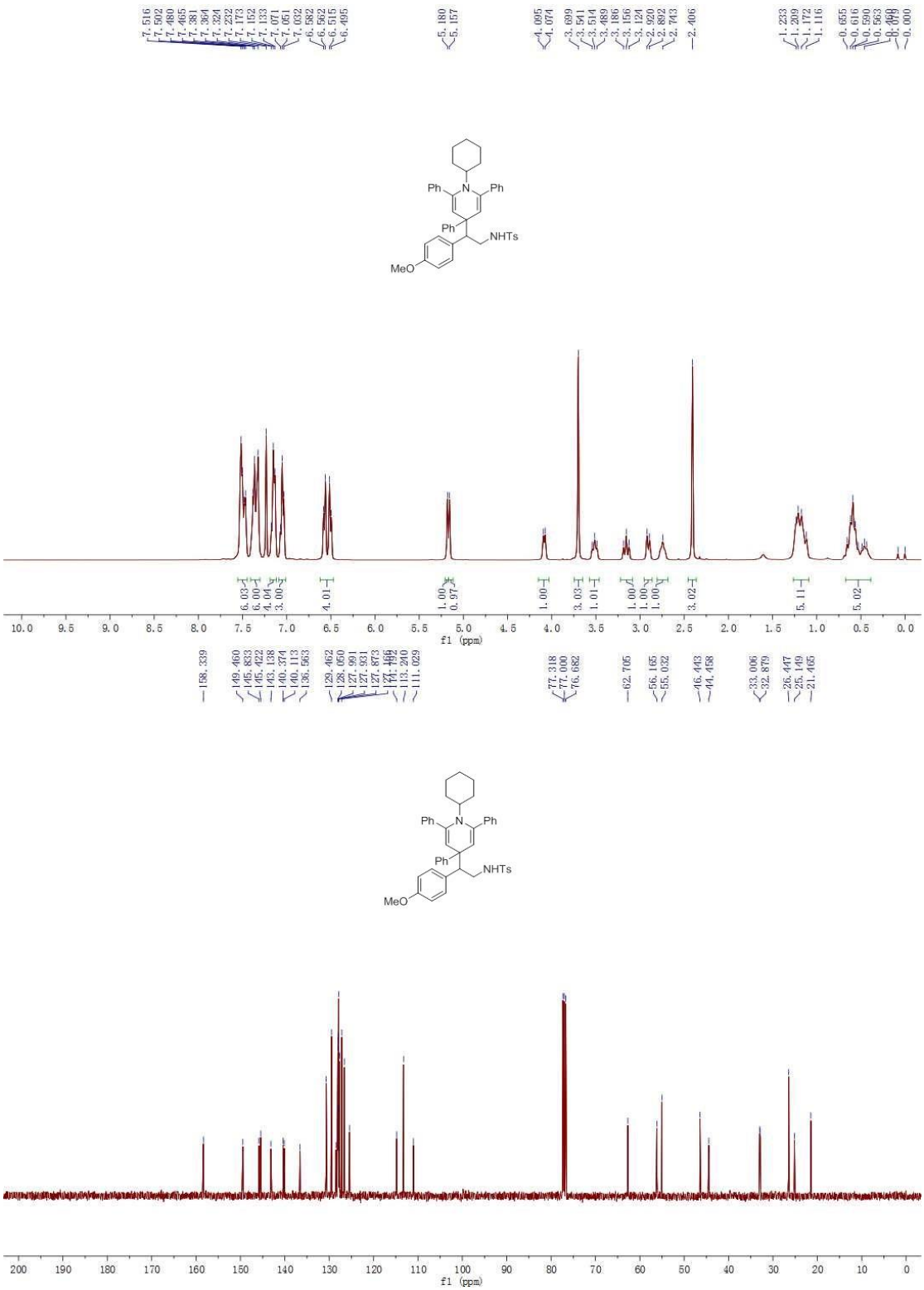


4-(2-azido-1-phenylpropyl)-1-cyclohexyl-2,4,6-triphenyl-1,4-dihydropyridine

(3ra)



_N_-(2-(1-cyclohexyl-2,4,6-triphenyl-1,4-dihydropyridin-4-yl)-2-(4-methoxyphenyl)ethyl)-4-methylbenzenesulfonamide (4aa)



1-cyclohexyl-4-(1-(4-methoxyphenyl)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)ethyl)-2,4,6-triphenyl-1,4-dihydropyridine (5aa)