Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Ruthenium-Catalyzed Enantioselective Hydrogenation of Quinoxalinones and Quinazolinones

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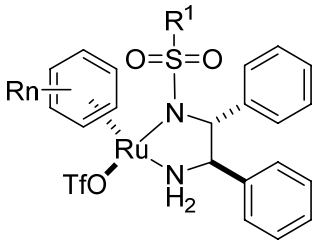
1. General information

Unless otherwise noted, all experiments were carried out under an atmosphere of nitrogen using standard Schlenk techniques or in a nitrogen-filled glovebox. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Model Avance DMX 300 Spectrometer (^{1}H 300 MHz and ^{13}C 75 MHz, respectively), Bruker Model Avance DMX 400 Spectrometer (^{1}H 400 MHz and ^{13}C 100 MHz, respectively), Bruker Model Avance DMX 500 Spectrometer (^{1}H 500 MHz and ^{13}C 125 MHz, respectively) and Bruker Model Avance DMX 600 Spectrometer (^{1}H 600 MHz and ^{13}C 150 MHz, respectively). Chemical shifts (δ) were given in ppm and were referenced to residual solvent or TMS peaks. Optical rotations were measured with Rudolph Autopl VI polarimeter. High resolution ESI mass spectra (P-ESI HRMS) were obtained on Thermo Fisher Q Exactive Mass Spectrometer. HPLC analyses were performed on a Varian Prostar 210 liquid chromatography. All organic solvents were dried using standard, published methods and were distilled before use. All other chemicals were used as received from Aldrich or Acros without further purification. The catalysts[1] and substrates[2] were synthesized according to the modified literature methods.

2. Optimization of conditions for asymmetric hydrogenation reactions

For this study, we chose the chiral diamines DPEN and CYDN as the ligand skeletons and prepared a series of Ru-complexes bearing chloride as anion according to the previous method.[1] Then, the anion Cl^- was exchanged to the weakly coordinating counteranions, giving the corresponding cationic ruthenium catalysts in quantitative yields, which did not require further purification. Their structures are shown in Scheme S1.



(*R*,*R*)-**C1**-**C5**

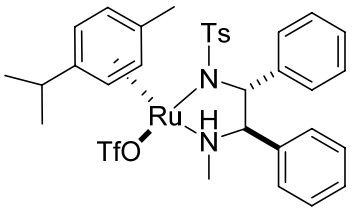
(*R*,*R*)-**C1**: R^1 = 4-$CH_3C_6H_4$; η^6-arene = *p*-cymene

(*R*,*R*)-**C2**: R^1 = CH_3; η^6-arene = *p*-cymene

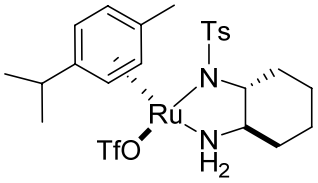
(*R*,*R*)-**C3**: R^1 = 4-$CF_3C_6H_4$; η^6-arene = *p*-cymene

(*R*,*R*)-**C4**: R^1 = 4-$CH_3C_6H_4$; η^6-arene = benzene

(*R*,*R*)-**C5**: R^1 = 4-$CH_3C_6H_4$; η^6-arene = hexamethylbenzene



(*R*,*R*)-**C6**

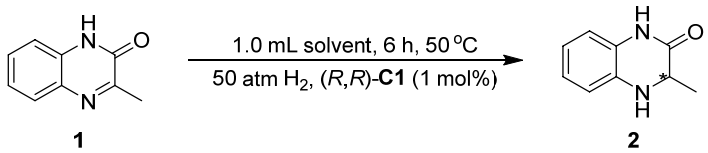


(*R*,*R*)-**C7**

Scheme S1. Chiral ruthenium diamine catalysts used in this study

Optimization of conditions for asymmetric hydrogenation reactions are shown in Table S1-S3.

Table S1. Optimization of reaction condition: solvents[a]

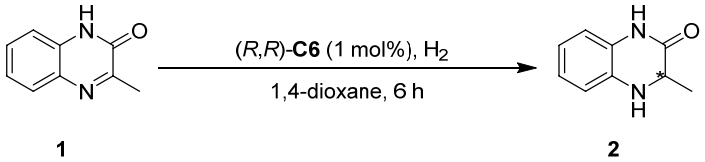


1 **2**

Entry	Solvent	Conv. (%)[b]	*ee* (%)[c]
1	MeOH	97	17
2	EtOH	>99	25
3	isopropanol	>99	28
4	CF_3CH_2OH	79	25
5	HFIP	18	29
6	dichloromethane	95	61
8	ethyl acetate	>99	71
9	toluene	>99	63
10	tetrahydrofuran	97	84
11	**1,4-dioxane**	**96**	**84**

[a]Reaction conditions: **1a** (0.1 mmol) in 1.0 mL solvent, (*R*,*R*)-C**1** (1.0 mol%), H_2 (50 atm), stirred at 50 °C for 6 h. [b]The conversions were determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [c]The enantiomeric excesses (*ee*) were determined by HPLC with a chiral OD-H column. HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol.

Table S2. Optimization of other reaction conditions[a]

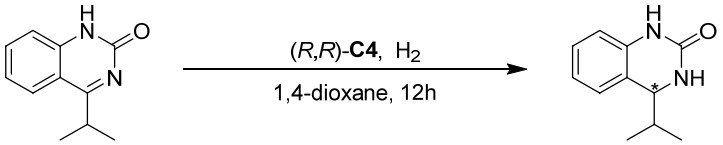


1 2

Entry	T (^{o}C)	H_2 (atm)	Conv. (%)[b]	*ee* (%)[c]
1	25	50	>99	98
2	50	50	>99	98
3	80	50	>99	98
4	25	80	>99	98
5	25	10	40	98

[a]Reaction conditions: **1a** (0.1 mmol) in 1.0 mL 1,4-dioxane, (*R,R*)-**C6** (1.0 mol%), stirred for 6 h. [b]The conversions were determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [c]The enantiomeric excesses (*ee*) were determined by HPLC with a chiral OD-H column.

Table S3. Optimization of other reaction conditions[a]



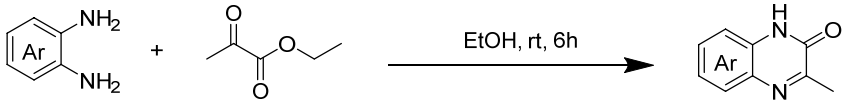
3 **4**

Entry	T (°C)	H_2 (atm)	Conv. (%)[b]	*ee* (%)[c]
1	25	50	>99	86
2	50	50	>99	87
3	80	50	>99	86
4	25	20	>99	86
5	25	70	>99	86
6[d]	25	50	>99	87
7[e]	25	50	<5	-

[a]Reaction conditions: **3b** (0.1 mmol) in 1.0 mL solvent, (*R*,*R*)-**C4** (10 mol%), H_2, stirred for 12 h. [b]The conversions were determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [c]The enantiomeric excesses (*ee*) were determined by HPLC with a chiral IC-H column. [d](*R*,*R*)-**C4** (5 mol%), [e](*R*,*R*)-**C4** (1 mol%).

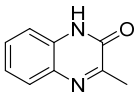
3. General procedure for the synthesis of substrates

3.1 Synthesis of substrate quinoxalin-2(1*H*)-ones (1)

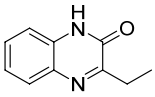


1a

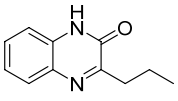
General procedure: In a 250 mL flask, 1,2-diaminobenzene (0.540 g, 5.0 mmol) was dissolved in ethyl alcohol (100 mL). Then, ethyl pyruvate (1.277 g, 11.0 mmol) was added, and the reaction mixture was stirred at room temperature until the reaction was completed. Then, the mixture was filtered and recrystallized from ethyl alcohol to afford 3-methylquinoxalin-2(*1H*)-one (**1a**) as white solid. The analytical data of the products are summarized below.



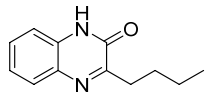
3-methylquinoxalin-2(1*H*)-one (1a): Known compound (Xia, Q.-H.; Hu, W.; Li, C.; Wu, J.-F.; Yang, L.; Han, X.-M.; Shen, Y.-M.; Li, Z.-Y.; Li, X. *Eur. J. Med. Chem.* **2016**, *124*, 311-325). White solid, 0.736 g, isolated yield 92%. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 12.29 (bs, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.28-7.24 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 159.2, 154.9, 131.9, 131.6, 129.3, 127.9, 123.0, 115.2, 20.5. HRMS-ESI exact mass calcd. for $C_9H_7N_2O^-$ ([M-H]$^-$) requires m/z 159.05639, found m/z 159.05539.



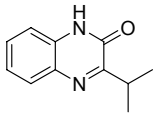
3-ethylquinoxalin-2(1*H*)-one (1b): Known compound (Blocher, R.; Ramirez, A. R.; Castro-Escarpulli, G.; Curiel-Quesada, E.; Reyes-Arellano, A. *Molecules* **2018**, *23*, 3075). Pale yellow solid, 0.783 g, isolated yield 90%. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 12.28 (bs, 1H), 7.70 (d, J = 7.5 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.28-7.24 (m, 2H), 2.79 (q, J = 7.3 Hz, 2H), 1.21 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 162.5, 154.6, 131.7, 131.6, 129.3, 128.0, 123.0, 115.2, 26.0, 10.5. HRMS-ESI exact mass calcd. for $C_{10}H_9N_2O^-$ ([M-H]$^-$) requires m/z 173.07204, found m/z 173.07117.



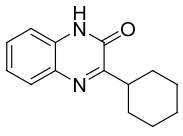
3-propylquinoxalin-2(1*H*)-one (1c): Known compound (see: Gobec, S. and Urleb, U. *Sci. Synth.* **2004**, *16*, 845-911). White solid, 0.828 g, isolated yield 88%. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 12.28 (bs, 1H), 7.70 (d, J = 7.5 Hz, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.28-7.24 (m, 2H), 2.75 (t, J = 7.5 Hz, 2H), 1.75-1.69 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 161.7, 154.6, 131.7, 131.6, 129.3, 128.1, 123.0, 115.2, 34.7, 19.4, 13.9. HRMS-ESI exact mass calcd. for $C_{11}H_{13}N_2O^+$ ([M-H]$^+$) requires m/z 189.10224, found m/z 189.10223.



3-butylquinoxalin-2(1*H*)-one (1d): Known compound (see: Kalinin, A. A.; Mamedov, V. A. *Russian J. Org. Chem.* **2009**, *45*, 1098-1101). White solid, 0.960 g, isolated yield 95%. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 12.29 (bs, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.28-7.24 (m, 2H), 2.77 (t, J = 7.8 Hz, 2H), 1.70-1.64 (m, 2H), 1.41-1.34 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 161.9, 154.6, 131.7, 131.7, 129.3, 128.0, 123.0, 115.2, 32.4, 28.2, 22.1, 13.8. HRMS-ESI exact mass calcd. for $C_{12}H_{13}N_2O^-$ ([M-H]$^-$) requires m/z 201.10334, found m/z 201.10263.

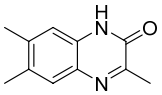


3-isopropylquinoxalin-2(1*H*)-one (1e): Known compound (see: Briguglio, I.; Piras, S.; Corona, P.; Pirisi, M. A.; Burrai, L.; Boatto, G.; Gavini, E.; Rassu, G. *J. Heterocycl. Chem.* **2016**, *53*, 1721-1737). White solid, 0.818 g, isolated yield 87%. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 12.30 (bs, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.47-7.44 (m, 1H), 7.28-7.24 (m, 2H), 3.48-3.43 (m, 1H), 1.21 (d, J = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 165.5, 154.2, 131.7, 131.5, 129.4, 128.2, 123.0, 115.2, 29.9, 20.0. HRMS-ESI exact mass calcd. for $C_{11}H_{11}N_2O^-$ ([M-H]$^-$) requires m/z 187.08769, found m/z 187.08681.

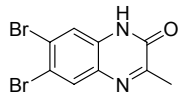


3-cyclohexylquinoxalin-2(1*H*)-one (1f): Known compound (see: Lian, F.; Xu, K.; Meng, W.; Zhang, H.; Tan, Z.; Zeng, C. *Chem. Commun.* **2019**, *55*, 14685-14688). White solid, 1.061 g, isolated yield 93%. ^{1}H NMR (400 MHz,

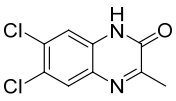
DMSO-d_6): δ (ppm) 12.30 (bs, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.27-7.23 (m, 2H), 3.17 (t, J = 11.0 Hz, 1H), 1.88-1.69 (m, 5H), 1.49-1.18 (m, 5H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 164.8, 154.2, 131.7, 131.5, 129.3, 128.2, 123.0, 115.1, 39.4, 30.0, 25.8, 25.8. HRMS-ESI exact mass calcd. for $C_{14}H_{15}N_2O^-$ ([M-H]$^-$) requires m/z 227.11899, found m/z 227.11838.



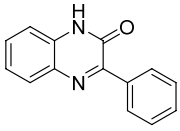
3,6,7-trimethylquinoxalin-2(1*H*)-one (1h): Known compound (see: unez-Rico, J. L.; Vidal-Ferran, A. *Org. Lett.* **2013**, *15*, 2066-2069). Pale yellow solid, 0.865 g, isolated yield 92%. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 12.15 (bs, 1H), 7.45 (s, 1H), 7.02 (s, 1H), 2.36 (s, 3H), 2.28-2.26 (m, 6H); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 157.7, 155.0, 138.6, 131.5, 130.2, 129.9, 127.8, 115.3, 20.4, 19.7, 18.9. HRMS-ESI exact mass calcd. for $C_{11}H_{13}N_2O^+$ ([M-H]$^+$) requires m/z 189.10224, found m/z 189.10223.



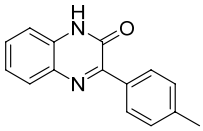
6,7-dibromo-3-methylquinoxalin-2(1*H*)-one (1i): (New compound). White solid, m.p. 290-292 ^{o}C, 1.279 g, isolated yield 81%. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 12.38 (bs, 1H), 8.00 (s, 1H), 7.54 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 161.4, 154.4, 132.3, 131.8, 131.7, 123.9, 119.3, 116.5, 20.6. HRMS-ESI exact mass calcd. for $C_9H_5Br_2N_2O^-$ ([M-H]$^-$) requires m/z 314.87741, found m/z 314.87659.



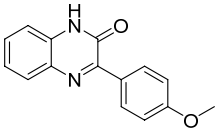
6,7-dichloro-3-methylquinoxalin-2(1*H*)-one (1j): Known compound (see: Mondieig, D.; Negrier, P.; Massip, S.; Leger, J. M.; Jarmoumi, C.; Lakhrissi, B. *J. Phy. Org. Chem.* **2011**, *24*, 1193-1200). White solid, 0.946 g, isolated yield 83%. ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 12.42 (bs, 1H), 7.93 (s, 1H), 7.40 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 161.4, 154.5, 131.9, 131.2, 131.1, 128.9, 124.7, 116.2, 20.6. HRMS-ESI exact mass calcd. for $C_9H_5Cl_2N_2O^-$ ([M-H]$^-$) requires m/z 226.97844, found m/z 226.97760.



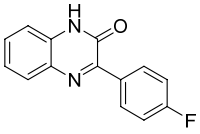
3-phenylquinoxalin-2(1*H*)-one (1k): Known compound (see: Rueping, M.; Tato, F.; Schoepke, F. R. *Chem. Eur. J.* **2010**, *16*, 2688-2691). Yellow solid, 0.966 g, isolated yield 87%. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 12.57 (bs, 1H), 8.31-8.29 (m, 2H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.56-7.47 (m, 4H), 7.35-7.31 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 154.6, 154.1, 135.6, 132.1, 132.0, 130.3, 130.2, 129.2, 128.8, 127.9, 123.4, 115.1. HRMS-ESI exact mass calcd. for $C_{14}H_9N_2O^-$ ([M-H]$^-$) requires m/z 221.07204, found m/z 221.07145.



3-(*p*-tolyl)quinoxalin-2(1*H*)-one (1l): Known compound (see: unez-Rico, J. L.; Vidal-Ferran, A. *Org. Lett.* **2013**, *15*, 2066-2069). Yellow solid, 0.992 g, isolated yield 84%. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 12.53 (bs, 1H), 8.26 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.33-7.28 (m, 4H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 154.6, 153.8, 140.1, 132.9, 132.0, 131.9, 130.1, 129.2, 128.6, 128.5, 123.3, 115.0, 21.1. HRMS-ESI exact mass calcd. for $C_{15}H_{11}N_2O^-$ ([M-H]$^-$) requires m/z 235.08659, found m/z 235.08684.

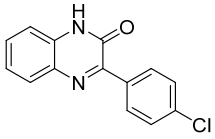


3-(4-methoxyphenyl)quinoxalin-2(1*H*)-one (1m): Known compound (see: Rueping, M.; Tato, F.; Schoepke, F. R. *Chem. Eur. J.* **2010**, *16*, 2688-2691). Yellow solid, 1.122 g, isolated yield 89%. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 12.50 (bs, 1H), 8.40 (d, J = 9.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 1H), 7.52-7.49 (m, 1H), 7.33-7.29 (m, 2H), 7.05 (d, J = 8.5 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 161.0, 154.7, 153.1, 132.1, 131.8, 131.0, 129.7, 128.5, 128.1, 123.3, 115.0, 113.3, 55.3. HRMS-ESI exact mass calcd. for $C_{15}H_{11}N_2O^-$ ([M-H]$^-$) requires m/z 251.08260, found m/z 251.08179.

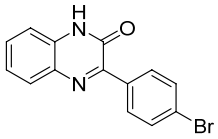


3-(4-fluorophenyl)quinoxalin-2(1*H*)-one (1n): Known compound (see: Yuan, J. W.; Liu, S. N.; Qu, L. B. *Adv. Synth. Catal.* **2017**, *359*, 4197-4207). Yellow solid, 0.890 g, isolated yield 74%. ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 12.61 (bs, 1H), 8.42 (dd, *J* = 6.0 Hz, *J* = 8.7 Hz, 2H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.55 (t,

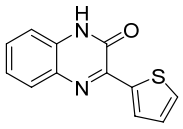
J = 7.5 Hz, 1H), 7.36-7.30 (m, 4H), ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 163.3 (d, $J_{C\text{-}F}$ = 246.3 Hz), 154.6, 152.8, 132.1 (d, $J_{C\text{-}F}$ = 2.5 Hz), 132.0, 131.9, 131.7 (d, $J_{C\text{-}F}$ = 8.7 Hz), 130.3, 128.7, 123.4, 115.1, 114.8 (d, $J_{C\text{-}F}$ = 21.2 Hz). HRMS-ESI exact mass calcd. for $C_{14}H_{10}FN_2O^+$ $[M+H]^+$) requires m/z 241.07717, found m/z 241.07640.



3-(4-chlorophenyl)quinoxalin-2(1*H*)-one (1o): Known compound (see: Nagaraj, M.; Sathiyamoorthy, S.; Boominathan, M.; Muthusubramanian, S.; Bhuvanesh, N. *J. Heterocycl. Chem.* **2013**, *50*, 1146-1151). Yellow solid, 1.191 g, isolated yield 93%. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 12.62 (bs, 1H), 8.37 (d, J = 8.5 Hz, 2H), 7.83 (d, J = 8.0 Hz, 1H), 7.56-7.53 (m, 3H), 7.34-7.31 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 154.5, 152.7, 135.1, 134.4, 132.1, 131.9, 131.0, 130.5, 128.8, 128.0, 123.5, 115.1. HRMS-ESI exact mass calcd. for $C_{14}H_8ClN_2O^-$ ($[M-H]^-$) requires m/z 255.03306, found m/z 255.03224.

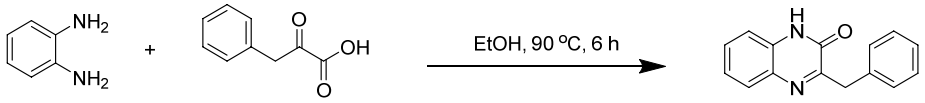


3-(4-bromophenyl)quinoxalin-2(1*H*)-one (1p): Known compound (see: Nagaraj, M.; Sathiyamoorthy, S.; Boominathan, M.; Muthusubramanian, S.; Bhuvanesh, N. *J. Heterocycl. Chem.* **2013**, *50*, 1146-1151). Yellow solid, 1.365 g, isolated yield 91%. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 12.63 (bs, 1H), 8.31 (d, J = 9.0 Hz, 2H), 7.84 (d, J = 8.5 Hz, 1H), 7.70 (d, J = 9.0 Hz, 2H), 7.56 (t, J = 7.8 Hz, 1H), 7.35-7.32 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 155.0, 153.3, 135.2, 132.6, 132.4, 131.7, 131.4, 131.1, 129.3, 124.5, 124.0, 115.6. HRMS-ESI exact mass calcd. for $C_{14}H_8BrN_2O^-$ ($[M-H]^-$) requires m/z 298.98255, found m/z 298.98181.



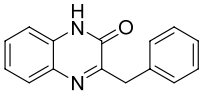
3-(thiophen-2-yl)quinoxalin-2(1*H*)-one (1q): Known compound (see: Xue, Z.-Y.; Jiang, Y.; Peng, X.-Z.; Yuan, W.-C.; Zhang, X.-M. *Adv. Synth. Catal.* **2010**, *352*, 2132-2136). Yellow solid, 0.775 g, isolated yield 68%. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 12.71 (bs, 1H), 8.41-8.40 (m, 1H), 7.83 (d, J = 5.0 Hz, 1H), 7.72 (d, J = 7.5 Hz, 1H), 7.51 (t, J = 7.8 Hz, 1H), 7.35-7.30 (m, 2H) , 7.23 (t, J = 4.3 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 153.5, 148.9, 139.0, 132.1, 131.9, 131.5, 131.4,

129.8, 128.2, 128.1, 123.7, 115.3. HRMS-ESI exact mass calcd. for $C_{12}H_7N_2OS^-$ ([M-H]$^-$) requires m/z 227.02846, found m/z 227.02803.

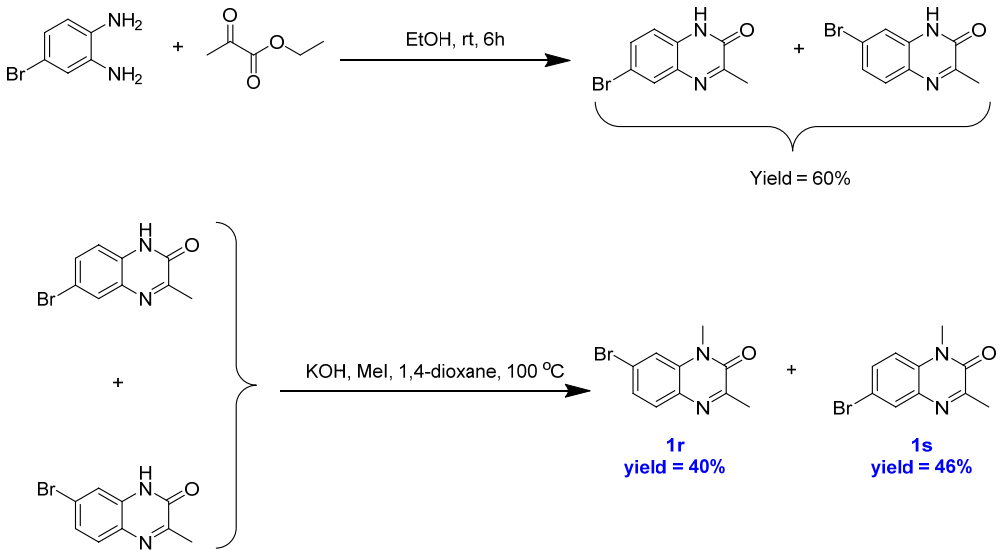


1g

General procedure: In a 250 mL flask, 1,2-diaminobenzene (0.540 g, 5.0 mmol) was dissolved in ethyl alcohol (100 mL). Then, 3-phenylpiruvic acid (1.806 g, 11.0 mmol) was added, and the reaction mixture was stirred at 90 ^oC for 6h. The reaction mixture was cooled to room temperature, the crude product was recrystallized by ethyl alcohol to afford benzylquinoxalin-2(1*H*)-one (**1g**) as pale yellow solid. The analytical data of the products are summarized below.

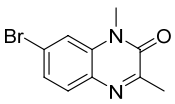


3-benzylquinoxalin-2(1*H*)-one (1g): Known compound (see: Piras, S.; Loriga, M.; Carta, A.; Paglietti, G.; Costi, M. P.; Ferrari, S. *J. Heterocycl. Chem.* **2006**, *43*, 541-548). Pale yellow solid, 1.003 g, isolated yield 85%. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 12.38 (bs, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.48-7.44 (m, 1H), 7.34-7.17 (m, 7H), 4.12 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 160.3, 154.5, 137.4, 132.0, 131.6, 129.7, 129.1, 128.3, 128.2, 126.3, 123.1, 115.3, 39.0. HRMS-ESI exact mass calcd. for $C_{15}H_{11}N_2O^-$ ([M-H]$^-$) requires m/z 235.08769, found m/z 235.08710.



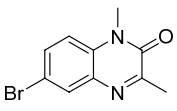
General procedure: In a 250 mL flask, 4-bromo-1,2-benzenediamine (0.540 g, 5.000 mmol) was dissolved in ethyl alcohol (100 mL). Then, ethyl pyruvate (1.277 g, 11.0 mmol) was added, and the reaction mixture was stirred at room temperature until the reaction was completed which was monitored by TLC. Then, the mixture was filtered to afford 7-bromo-3-methylquinoxalin-2(1*H*)-one and 6-bromo-3-methylquinoxalin-2(1*H*)-one (0.717 g, 3.0 mmol).

In a 250 mL flask, 7-bromo-3-methylquinoxalin-2(1*H*)-one and 6-bromo-3-methylquinoxalin-2(1*H*)-one (0.717 g, 3.0 mmol) were dissolved in 1,4-dioxane (100 mL). Potassium hydroxide (0.336 mg, 6.0 mmol) were added and the reaction mixture was stirred at 100 ^{o}C for 5 min . The reaction mixture was cooled to room temperature and iodomethane (0.511 g, 3.6 mmol) was added slowly and the reaction mixture was stirred at 100 ^{o}C until the reaction was completed which was monitored by TLC. Then, the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to yield the desired 7-bromo-1,3-dimethylquinoxalin-2(1*H*)-one (**1q**) and 6-bromo-1,3-dimethylquinoxalin-2(1*H*) -one (**1r**) as white solid. The analytical data of the products are summarized below.



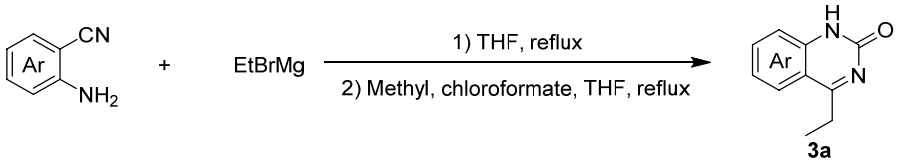
7-bromo-1,3-dimethylquinoxalin-2(1*H*)-one (1r): Known compound (see: Zhao, Z.-B.; Li, X.; Chen, M.-W.; Zhao Z. K.; Zhou, Y.-G. *Chem. Commun.*

2020, *56*, 7309-7312). White solid, 0.152 g, isolated yield 40%. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.63 (d, *J* = 8.5 Hz, 1H), 7.43-7.41 (m, 2H), 3.65 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 158.9, 154.9, 134.4, 131.5, 130.8, 127.0, 123.7, 116.8, 29.3, 21.7. HRMS-ESI exact mass calcd. for $C_{10}H_{10}BrN_2O^+$ ($[M+H]^+$) requires m/z 252.99710, found m/z 252.99701.

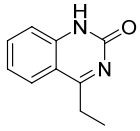


6-bromo-1,3-dimethylquinoxalin-2(1*H*)-one (1s): Known compound (see: Zhao, Z.-B.; Li, X.; Chen, M.-W.; Zhao Z. K.; Zhou, Y.-G. *Chem. Commun.* **2020**, *56*, 7309-7312). White solid, 0.175 g, isolated yield 46%. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.95 (s, 1H), 7.61-7.59 (m, 1H), 7.16 (d, *J* = 9.0 Hz, 1H), 3.67 (s, 3H), 2.59 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 160.0, 155.0, 133.6, 132.5, 132.5, 132.0, 116.3, 115.2, 29.3, 21.8. HRMS-ESI exact mass calcd. for $C_{10}H_{10}BrN_2O^-$ ($[M+H]^+$) requires m/z 252.99710, found m/z 252.99699.

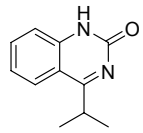
3.2 Synthesis of substrate quinazolin-2(1*H*)-ones (3)



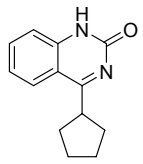
General procedure: In a 250 mL flask, 2-aminobenzonitrile (0.118 g, 1.0 mmol) was dissolved in dry tetrahydrofuran (100 mL). Then, a solution of ethylmagnesium bromide (0.7 mL, 2.0 mmol) was added slowly. After refluxing for 2 h, methyl chloroformate (0.142 g, 1.5 mol) was added dropwise at room temperation, and the resulting mixture was refluxed until completed which was monitored by TLC. The mixture was cooled to room temperature and poured into a hydrochloric acid solution (2 M). The mixture was neutralized with 10% sodium bicarbonate aqueous solution and extracted with dichloromethane (30 mL × 3). The combined organic layer was dried over anhydrous sodium sulfate, concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (eluent: ethyl acetate /petroleum ether) to yield the desired ethylquinazolin-2(1*H*)-one (**3a**) as yellow solid



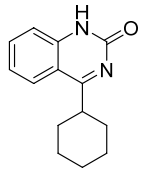
4-ethylquinazolin-2(1*H*)-one (3a): Known compound (see: Bergman, J.; Brynolf, A.; Elman, B.; Vuorinen, E. *Tetrahedron* **1986**, *42*, 3697-3706). Yellow solid, 0.117 g, isolated yield 67%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 12.51 (bs, 1H), 7.93-7.91 (m, 1H), 7.70-7.66 (m, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.30-7.26 (m, 1H), 3.18 (q, *J* = 7.3 Hz, 2H), 1.41 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 181.0, 158.4, 142.4, 135.3, 126.2, 123.3, 116.7, 116.0, 28.9, 11.5. HRMS-ESI exact mass calcd. for $C_{10}H_{11}N_2O^+$ ($[M+H]^+$) requires m/z 175.08659, found m/z 175.08510.



4-isopropylquinazolin-2(1*H*)-one (3b): Known compound (see: Bergman, J.; Brynolf, A.; Elman, B.; Vuorinen, E. *Tetrahedron* **1986**, *42*, 3697-3706). White solid, 0.122 g, isolated yield 65%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 12.80 (bs, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.72-7.67 (m, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 3.79-3.72 (m, 1H), 1.39 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 184.7, 158.7, 142.8, 135.3, 126.0, 123.4, 117.1, 115.5, 32.3, 21.4. HRMS-ESI exact mass calcd. for $C_{11}H_{13}N_2O^+$ ($[M+H]^+$) requires m/z 189.10224, found m/z 189.10063.

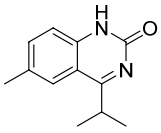


4-cyclopentylquinazolin-2(1*H*)-one (3c): (New compound). Pale yellow solid, m.p. 199-201 ^{o}C, 0.124 g, isolated yield 58%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 12.97 (bs, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.29-7.24 (m, 1H), 3.90-3.79 (m, 1H), 2.23-2.07 (m, 4H), 1.97-1.85 (m, 2H), 1.80-1.73 (m, 2H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ (ppm) 183.3, 158.8, 142.3, 134.9, 126.1, 123.1, 117.0, 116.2, 43.5, 32.3, 26.4. HRMS-ESI exact mass calcd. for $C_{13}H_{15}N_2O^+$ ($[M+H]^+$) requires m/z 215.11789, found m/z 215.11811.

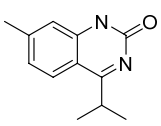


4-cyclohexylquinazolin-2(1*H*)-one (3d): Known compound (see: Milton, L. H.; Ann, H. US 3305553, **1967**). White solid, 0.162 g, isolated yield 71%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 12.92 (s, 1H), 7.97-7.29 (m, 4H), 3.43-3.37 (m, 1H), 1.93-1.38 (m, 10H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 183.7, 158.6, 142.6, 135.0, 125.8, 123.1, 116.9, 115.3, 42.4, 31.7, 26.6, 26.3. HRMS-ESI exact mass calcd.

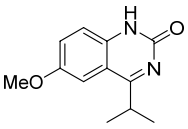
for $C_{14}H_{17}N_2O^+$ ([M+H]$^+$) requires m/z 229.13354, found m/z 229.13296.



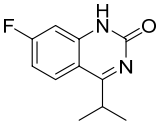
4-isopropyl-6-methylquinazolin-2(1*H*)-one (3e): (New compound). Pale yellow solid, m.p. 188-190 ^oC, 0.131 g, isolated yield 65%. ^1H NMR (400 MHz, CD_2Cl_2): δ (ppm) 12.92 (bs, 1H), 7.74 (s, 1H), 7.53 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 3.79-3.69 (m, 1H), 2.45 (s, 3H), 1.38 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 184.2, 158.8, 140.9, 136.8, 133.1, 125.3, 116.9, 115.4, 32.2, 21.4, 21.3. HRMS-ESI exact mass calcd. for $C_{12}H_{15}N_2O^+$ ([M+H]$^+$) requires m/z 203.11789, found m/z 203.11914.



7-isopropyl-6-methylquinazolin-2(1*H*)-one (3f): (New compound). Pale yellow solid, m.p. 186-188 ^oC, 0.126 g, isolated yield 63%. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 13.32 (bs, 1H), 7.80 (d, *J* = 8.4, 1H), 7.42 (s, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 3.73-3.66 (m, 1H), 2.44 (s, 3H), 1.40 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 184.1, 159.3, 146.7, 142.8, 125.3, 124.9, 116.8, 113.4, 31.9, 21.9, 21.3. HRMS-ESI exact mass calcd. for $C_{12}H_{13}N_2O^-$ ([M-H]$^-$) requires m/z 201.10334, found m/z 201.10278.

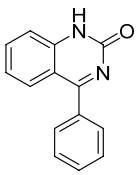


6-methoxy-4-isopropylquinazolin-2(1*H*)-one (3g): (New compound). Pale yellow solid, m.p. 198-200 ^oC, 0.122 g, isolated yield 56%. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 13.36 (bs, 1H), 7.56 (d, *J* = 8.8, 1H), 7.34-7.28 (m, 2H), 3.87 (s, 3H), 3.71-3.64 (m, 1H), 1.43 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 183.5, 158.8, 155.5, 137.5, 125.0, 118.6, 115.6, 106.4, 56.0, 32., 21.2. HRMS-ESI exact mass calcd. for $C_{12}H_{13}N_2O_2^-$ ([M-H]$^-$) requires m/z 217.09825, found m/z 217.09796.



7-fluoro-4-isopropylquinazolin-2(1*H*)-one (3h): (New compound). Pale yellow solid, m.p. 206-208 ^oC, 0.128 g, isolated yield 62%. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 13.35 (bs, 1H), 7.97 (dd, *J* = 5.6, *J* = 9.2, 1H), 7.31-7.28 (m, 1H), 7.03-6.98 (m, 1H), 3.73-3.66 (m, 1H), 1.43 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz,

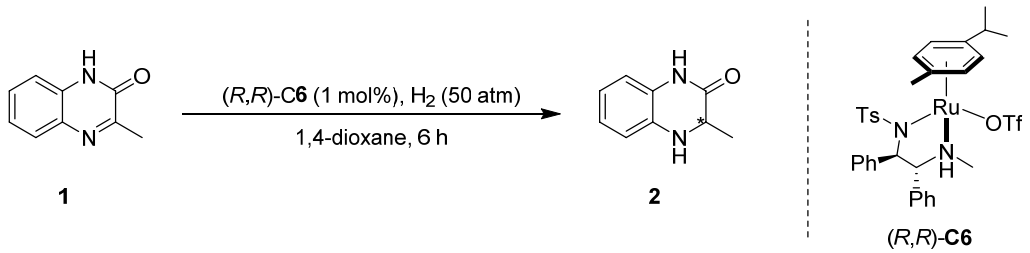
$CDCl_3$): δ (ppm) 184.1, 166.7 (d, $J_{C\text{-}F}$ = 256.0 Hz), 159.1, 144.6 (d, $J_{C\text{-}F}$ = 13.0 Hz), 128.5 (d, $J_{C\text{-}F}$ = 11.0 Hz), 112.3 (d, $J_{C\text{-}F}$ = 24.0 Hz), 112.3 (d, $J_{C\text{-}F}$ = 2.0 Hz), 103.1 (d, $J_{C\text{-}F}$ = 25.0 Hz),. HRMS-ESI exact mass calcd. for $C_{11}H_{10}FN_2O^-$ ([M-H]$^-$) requires m/z 205.07826, found m/z 205.07782.



4-phenylquinazolin-2(1*H*)-one (3i): Known compound (see: Bergman, J.; Brynolf, A.; Elman, B.; Vuorinen, E. *Tetrahedron* **1986**, *42*, 3697-3706). White solid, 0.140 g, isolated yield 63%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 12.83 (bs, 1H), 7.86-7.71 (m, 4H), 7.60-7.58 (m, 4H), 7.25 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 177.0, 158.3, 143.8, 137.1, 135.7, 131.1, 130.0, 129.2, 128.8, 123.4, 116.9, 115.8. HRMS-ESI exact mass calcd. for $C_{14}H_{11}N_2O^+$ ([M+H]$^+$) requires m/z 223.08659, found m/z 223.08466.

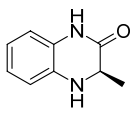
4. General procedure for asymmetric hydrogenation

4.1 Asymmetric hydrogenation of substrate quinoxalin-2(1*H*)-ones (1)



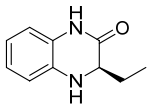
General procedure: A 15 mL glass-lined stainless-steel reactor equipped with a magnetic stirrer bar was charged with substrate **1** (0.2 mmol), Ru-catalyst (*R,R*)-**C6** (0.002 mmol) in 2.0 mL of solvent under N_2 atmosphere in a glove box. The autoclave was closed, and the final pressure of the hydrogen gas was adjusted to 50 atm after purging the autoclave with hydrogen gas several times. The reaction mixture was stirred at 25 ^{o}C for 6 h. Then the hydrogen gas was carefully released and the conversion was determined by ^{1}H NMR

spectroscopy. The reaction mixture was filtered through a short pad of silica eluted with ethyl acetate and petroleum ether to give the chiral product 3,4-dihydroquinoxalin-2(1*H*)-one (**2**). The enantiomeric excess of the product was determined by HPLC with a chiral column.



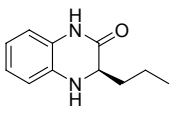
(*R*)-3-methyl-3,4-dihydroquinoxalin-2(1*H*)-one (2a): Known compound (see: Li, D.; Ollevier, T. *Eur. J. Org. Chem.* **2019**, *6*, 1273-1280). White solid, m.p. 114-116 ^{o}C, 31.8 mg, isolated yield 98%, 98% *ee*. $[\alpha]_D^{20}$ = -77.6 (*c* = 1.0, $CDCl_3$, 98% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.20 (bs, 1H), 6.90-6.66 (m, 4H), 4.02 (q, *J* = 6.2 Hz, 1H), 3.88 (s, 1H), 1.46 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 169.9, 133.6, 125.8, 123.9, 119.7, 115.7, 114.2, 52.0, 18.0. HRMS-ESI exact mass calcd. for $C_9H_{11}N_2O^+$ ($[M+H]^+$) requires m/z 163.08659, found m/z 163.08650.

The enantiomeric excess was determined by HPLC on the Chiralcel OD-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 ^{o}C, UV detection at λ = 254 nm), t_{R1} = 17.9 min (minor), t_{R2} = 19.1 min (major).



(*R*)-3-ethyl-3,4-dihydroquinoxalin-2(1*H*)-one (2b): Known compound (see: Pan, Y.; Chen, C.; Xu, X.; Zhao, H.; Han, J.; Li, H.; Xu, L.; Fan, Q.; Xiao, J. *Green Chem.* **2018**, *20*, 403-411). Pale yellow oil, 34.2 mg, isolated yield 97%, 98% *ee*. $[\alpha]_D^{20}$ = -54.0 (*c* = 1.0, $CDCl_3$, 98% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.68 (bs, 1H), 6.91-6.84 (m, 1H), 6.77-6.67 (m, 3H), 3.96 (s, 1H), 3.87 (q, *J* = 5.1 Hz, 1H), 1.95-1.72 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.1, 133.2, 125.4, 124.0, 119.4, 115.5, 114.2, 57.7, 25.2, 9.8. HRMS-ESI exact mass calcd. for $C_{10}H_{11}N_2O^+$ ($[M\_H]^+$) requires m/z 175.08659, found m/z 175.08659.

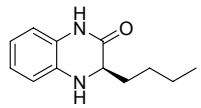
The enantiomeric excess was determined by HPLC on the Chiralcel OD-H column (*n*-hexane : isopropanol = 80 : 20, flowing rate = 1.0 mL/min, 25 ^{o}C, UV detection at λ = 220 nm), t_{R1} = 8.0 min (minor), t_{R2} = 9.4 min (major).



(*R*)-3-propyl-3,4-dihydroquinoxalin-2(1*H*)-one (2c): Known compound (see: Kamila, S.; Biehl, E. R. *Heterocycles* **2006**, *68*, 1931-1939). colourless oil,

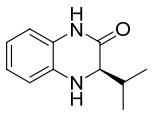
34.2 mg, isolated yield 90%, 97% *ee*. $[\alpha]_D^{20}$ = -36.0 (*c* = 1.0, $CDCl_3$, 97% *ee*); ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 9.19 (s, 1H), 6.88 (t, *J* = 7.3 Hz, 4H), 6.78-6.73 (m, 2H), 6.67 (t, *J* = 8.0 Hz, 1H), 3.97-3.91 (m, 2H), 1.85-1.70 (m, 2H), 1.55-1.41 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 169.6, 133.1, 125.5, 123.9, 119.4, 115.6, 114.2, 56.3, 34.1, 18.7, 13.9. HRMS-ESI exact mass calcd. for $C_{11}H_{15}N_2O^+$ ($[M+H]^+$) requires m/z 191.11789, found m/z 191.11806.

The enantiomeric excess was determined by HPLC on the Chiralcel OD-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 °C, UV detection at λ = 230 nm), t_{R1} = 14.8 min (minor), t_{R2} = 19.2 min (major).



(*R*)-3-butyl-3,4-dihydroquinoxalin-2(1*H*)-one (2d): Known compound (see: Kamila, S.; Biehl, E. R. *Heterocycles* **2006**, *68*, 1931-1939). Pale yellow oil, 37.2 mg, isolated yield 91%, 97% *ee*. $[\alpha]_D^{20}$ = -22.8 (*c* = 1.0, $CDCl_3$, 97% *ee*); ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.80 (bs, 1H), 6.91-6.86 (m, 1H), 6.75-6.66 (m, 3H), 3.95-3.89 (m, 2H), 1.89-1.68 (m, 2H), 1.53-1.26 (m, 4H), 0.91 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 169.3, 133.2, 125.5, 123.9, 119.4, 115.5, 114.2, 56.6, 31.7, 27.6, 22.6, 14.1. HRMS-ESI exact mass calcd. for $C_{12}H_{15}N_2O^+$ ($[M-H]^+$) requires m/z 203.11789, found m/z 203.11794.

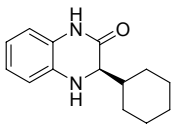
The enantiomeric excess was determined by HPLC on the Chiralcel OJ-H column (*n*-hexane : isopropanol = 80 : 20, flowing rate = 1.0 mL/min, 25 °C, UV detection at λ = 230 nm), t_{R1} = 6.6 min (major), t_{R2} = 7.5 min (minor).



(*R*)-3-isopropyl-3,4-dihydroquinoxalin-2(1*H*)-one (2e): Known compound (see: Li, D.; Ollevier, T. *Eur. J. Org. Chem.* **2019**, *6*, 1273-1280). Pale yellow viscous solid, 34.2 mg, isolated yield 90%, 94% *ee*. $[\alpha]_D^{20}$ = -69.2 (*c* = 1.0, $CDCl_3$, 94% *ee*); ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.66 (bs, 1H), 6.90-6.84 (m, 1H), 6.71-6.64 (m, 3H), 4.00 (s, 1H), 3.78-3.76 (m, 1H), 2.30-2.19 (m, 1H), 1.04 (d, *J* = 6.9 Hz, 3H), 0.98 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 168.3, 133.4, 124.9, 124.0, 119.0, 115.3, 113.6, 62.0, 30.9, 19.1, 17.6. HRMS-ESI exact mass calcd. for

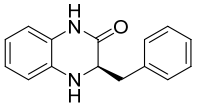
$C_{11}H_{15}N_2O^+$ ([M+H]$^+$) requires m/z 191.11789, found m/z 191.11781.

The enantiomeric excess was determined by HPLC on the Chiralcel OD-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 ^oC, UV detection at λ = 230 nm), t_{R1} = 11.5 min (minor), t_{R2} = 16.0 min (major).



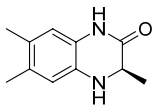
(*R*)-3-cyclohexyl-3,4-dihydroquinoxalin-2(1*H*)-one (2f): Known compound (see: Zhang, L.; Qiu, R.; Xue, X.; Pan, Y.; Xu, C.; Li, H.; Xu, L. *Adv. Synth. Catal.* **2015**, *357*, 3529-3537). White solid, m.p. 61-63 ^oC, 45.1 mg, isolated yield 98%, 94% *ee*. $[\alpha]_D^{20}$ = -28.4 (*c* = 1.0, $CDCl_3$, 94% *ee*); ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.14 (bs, 1H), 6.89-6.84 (m, 1H), 6.75-6.62 (m, 3H), 4.06 (s, 1H), 3.76 (d, *J* = 5.4 Hz, 1H), 1.86-1.63 (m, 6H), 1.28-1.09 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 168.4, 133.4, 125.0, 124.0, 118.8, 115.5, 113.5, 61.6, 40.7, 29.6, 27.9, 26.0, 25.7. HRMS-ESI exact mass calcd. for $C_{14}H_{19}N_2O^+$ ([M+H]$^+$) requires m/z 231.14919, found m/z 231.114919.

The enantiomeric excess was determined by HPLC on the Chiralcel OJ-H column (*n*-hexane : isopropanol = 80 : 20, flowing rate = 1.0 mL/min, 25 ^oC, UV detection at λ = 230 nm), t_{R1} = 6.3 min (major), t_{R2} = 7.6 min (minor).



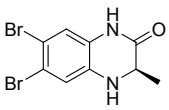
(*R*)-3-benzyl-3,4-dihydroquinoxalin-2(1*H*)-one (2g): Known compound (see: Li, D.; Ollevier, T. *Eur. J. Org. Chem.* **2019**, *6*, 1273-1280). White viscous solid, 46.2 mg, isolated yield 97%, 94% *ee*. $[\alpha]_D^{20}$ = 82.0 (*c* = 1.0, $CDCl_3$, 94% *ee*); ^1H NMR (300 MHz, DMSO-d_6): δ (ppm) 10.24 (s, 1H), 7.29-7.16 (m, 5H), 6.77-6.54 (m, 4H), 5.82 (s, 1H), 4.01 (t, *J* = 5.1 Hz, 1H), 2.97-2.82 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 166.9, 137.5, 133.5, 129.6, 128.1, 126.2, 125.7, 122.8, 117.6, 114.6, 113.6, 56.9, 37.4. HRMS-ESI exact mass calcd. for $C_{15}H_{15}N_2O^+$ ([M+H]$^+$) requires m/z 239.11798, found m/z 239.11783.

The enantiomeric excess was determined by HPLC on the Chiralcel OD-H column (*n*-hexane : isopropanol = 85 : 15, flowing rate = 1.0 mL/min, 25 ^oC, UV detection at λ = 240 nm), t_{R1} = 12.2 min (minor), t_{R2} = 13.6 min (major).



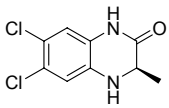
(*R*)-3,6,7-trimethyl-3,4-dihydroquinoxalin-2(1*H*)-one (2h): Known compound (see: Pan, Y.; Chen, C.; Xu, X.; Zhao, H.; Han, J.; Li, H.; Xu, L.; Fan, Q.; Xiao, J. *Green Chem.* **2018**, *20*, 403-411). Yellow solid, m.p. 180-182 ^{o}C, 33.8 mg, isolated yield 89%, 97% *ee*. $[\alpha]_D^{20}$ = -115.2 (*c* = 1.0, $CDCl_3$, 97% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.27 (bs, 1H), 6.52 (s, 1H), 6.49 (s, 1H), 3.95 (q, *J* = 6.7 Hz, 1H), 3.66 (s, 1H), 2.15 (s, 6H), 1.44 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 169.6, 131.9, 131.3, 127.9, 123.6, 116.7, 115.8, 52.4, 19.4, 19.0, 17.9. HRMS-ESI exact mass calcd. for $C_{11}H_{15}N_2O^+$ ($[M+H]^+$) requires m/z 191.11789, found m/z 191.11809.

The enantiomeric excess was determined by HPLC on the Chiralcel OD-H column (*n*-hexane : isopropanol = 80 : 20, flowing rate = 1.0 mL/min, 25 ^{o}C, UV detection at λ = 230 nm), t_{R1} = 9.4 min (minor), t_{R2} = 11.9 min (major).



(*R*)-6,7-dibromo-3-methyl-3,4-dihydroquinoxalin-2(1*H*)-one (2i): New compound. White solid, m.p. 162-164 ^{o}C, 61.0 mg, isolated yield 96%, 97% *ee*. $[\alpha]_D^{20}$ = -31.2 (*c* = 1.0, $CDCl_3$, 97% *ee*); ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 10.39 (s, 1H), 6.98 (s, H), 6.97 (s, 1H), 6.43 (s, 1H), 3.89-3.82 (m, 1H), 1.24 (d, *J* = 6.6 Hz, 3H) ; ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 167.9, 135.4, 127.2, 118.3, 116.9, 115.8, 109.6, 50.4, 17.7. HRMS-ESI exact mass calcd. for $C_9H_7Br_2N_2O^-$ ($[M-H]^-$) requires m/z 316.89306, found m/z 316.89236.

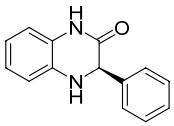
The enantiomeric excess was determined by HPLC on the Chiralcel OJ-H column (*n*-hexane : isopropanol = 80 : 20, flowing rate = 1.0 mL/min, 25 ^{o}C, UV detection at λ = 230 nm), t_{R1} = 15.5 min (minor), t_{R2} = 18.2 min (major).



(*R*)-6,7-dichloro-3-methyl-3,4-dihydroquinoxalin-2(1*H*)-one (2j): Known compound (see: Krchnak, V.; Smith, J.; Vagner, J. *Collect. Czech. Chem. Commun.* **2001**, *66*, 1078-1106). White solid, m.p. 190-192 ^{o}C, 42.8 mg, isolated yield 93%, 98% *ee*. $[\alpha]_D^{20}$ = -52.8 (*c* = 1.0, $CDCl_3$, 98% *ee*); ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 10.40 (bs, 1H), 6.85 (s, 1H), 6.82 (s, 1H), 6.42 (s, 1H), 3.85 (q, *J* = 6.4 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 167.9, 134.8,

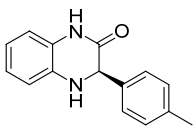
126.5, 123.8, 118.3, 115.3, 113.8, 50.4, 17.7. HRMS-ESI exact mass calcd. for $C_9H_7Cl_2N_2O^-$ ($[M-H]^-$) requires m/z 228.99409, found m/z 228.99327.

The enantiomeric excess was determined by HPLC on the Chiralcel OJ-H column (*n*-hexane : isopropanol = 80 : 20, flowing rate = 1.0 mL/min, 25 ^oC, UV detection at λ = 230 nm), t_{R1} = 10.9 min (minor), t_{R2} = 12.1 min (major).



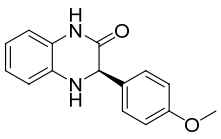
(*R*)-3-phenyl-3,4-dihydroquinoxalin-2(1*H*)-one (2k): Known compound (see: Li, D.; Ollevier, T. *Eur. J. Org. Chem.* **2019**, *6*, 1273-1280). White solid, m.p. 150-152 ^oC, 41.7 mg, isolated yield 93%, 97% *ee*. $[\alpha]_D^{20}$ = -110.0 (*c* = 1.0, $CDCl_3$, 97% *ee*); ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.91 (bs, 1H), 7.42-7.41 (m, 2H), 7.35-7.29 (m, 3H), 6.93-6.90 (m, 1H), 6.77-6.69 (m, 3H), 5.07 (s, 1H), 4.30 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 167.3, 139.2, 133.0, 128.9, 128.6, 127.3, 124.9, 124.2, 119.5, 115.8, 113.8, 60.8. HRMS-ESI exact mass calcd. for $C_{14}H_{13}N_2O^+$ ($[M+H]^+$) requires m/z 225.10224, found m/z 225.10225.

The enantiomeric excess was determined by HPLC on the Chiralcel OD-H column (*n*-hexane : isopropanol = 80 : 20, flowing rate = 1.0 mL/min, 25 ^oC, UV detection at λ = 210 nm), t_{R1} = 15.8 min (minor), t_{R2} = 27.1 min (major).



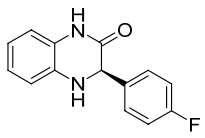
(*R*)-3-(*p*-tolyl)-3,4-dihydroquinoxalin-2(1*H*)-one (2l): Known compound (see: unez-Rico, J. L.; Vidal-Ferran, A. *Org. Lett.* **2013**, *15*, 2066-2069). Yellow solid, m.p. 143-145 ^oC, 45.2 mg, isolated yield 95%, 97% *ee*. $[\alpha]_D^{20}$ = -128.8 (*c* = 1.0, $CDCl_3$, 97% *ee*); ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.44 (bs, 1H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.88-6.83 (m, 1H), 6.69-6.61 (m, 3H), 4.97 (s, 1H), 4.27 (s, 1H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 167.8, 138.3, 136.3, 133.1, 129.6, 127.2, 124.9, 124.0, 119.3, 115.9, 113.7, 60.4, 21.2. HRMS-ESI exact mass calcd. for $C_{15}H_{15}N_2O^+$ ($[M+H]^+$) requires m/z 239.11789, found m/z 239.11784.

The enantiomeric excess was determined by HPLC on the Chiralcel OD-H column (*n*-hexane : isopropanol = 80 : 20, flowing rate = 1.0 mL/min, 25 ^oC, UV detection at λ = 230 nm), t_{R1} = 19.8 min (minor), t_{R2} = 22.4 min (major).



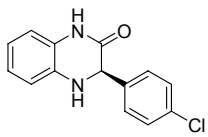
(*R*)-3-(4-methoxyphenyl)-3,4-dihydroquinoxalin-2(1*H*)-one (2m): Known compound (see: Rueping, M.; Tato, F.; Schoepke, F. R. *Chem. Eur. J.* **2010**, *16*, 2688-2691). White solid, m.p. 124-126 ^{o}C, 46.8 mg, isolated yield 92%, 96% *ee*. $[\alpha]_D^{20}$ = -124.0 (*c* = 1.0, $CDCl_3$, 96% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.78 (bs, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 6.93-6.84 (m, 3H), 6.77-6.67 (m, 3H), 5.01 (s, 1H), 4.25 (s, 1H), 3.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 167.6, 159.8, 133.2, 131.3, 128.6, 125.0, 124.2, 119.5, 115.7, 114.4, 113.9, 60.3, 55.4. HRMS-ESI exact mass calcd. for $C_{15}H_{14}N_2O_2^+$ ($[M+H]^+$) requires m/z 255.11280, found m/z 255.11299.

The enantiomeric excess was determined by HPLC on the Chiralcel OJ-H column (*n*-hexane : isopropanol = 80 : 20, flowing rate = 1.0 mL/min, 25 ^{o}C, UV detection at λ = 230 nm), t_{R1} = 28.5 min (major), t_{R2} = 35.6 min (minor).



(*R*)-3-(4-fluorophenyl)-3,4-dihydroquinoxalin-2(1*H*)-one (2n): Known compound (see: Ogino, E.; Nakamura, A.; Kuwano, S.; Arai, T. *Org. Lett.* **2021**, *23*, 1980-1985). White solid, m.p. 174-176 ^{o}C, 45.5mg, isolated yield 94%, 96% *ee*. $[\alpha]_D^{20}$ = -132.0 (*c* = 1.0, $CDCl_3$, 96% *ee*); ^{1}H NMR (400 MHz, $CDCl_3$/Methanol-d_4 = 10:1): δ (ppm) 7.35-7.31 (m, 2H), 6.96 (t, *J* = 8.6 Hz, 2H), 6.89-6.85 (m, 1H), 6.72-6.66 (m, 3H), 4.97 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$/Methanol-d_4 = 10:1): δ (ppm) 167.2, 162.8 (d, $J_{C\text{-}F}$ = 245.0 Hz), 134.9 (d, $J_{C\text{-}F}$ = 3.0 Hz), 133.0, 129.0 (d, $J_{C\text{-}F}$ = 8.0 Hz), 124.8, 124.2, 119.5, 115.6 (d, $J_{C\text{-}F}$ = 22.0 Hz), 115.6, 113.8, 59.9. ESI exact mass calcd. for $C_{14}H_{11}FN_2O^+$ ($[M+H]^+$) requires m/z 243.09282, found m/z 243.09214.

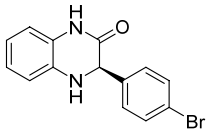
The enantiomeric excess was determined by HPLC on the Chiralcel OJ-H column (*n*-hexane : isopropanol = 80 : 20, flowing rate = 1.0 mL/min, 25 ^{o}C, UV detection at λ = 254 nm), t_{R1} = 15.3 min (major), t_{R2} = 26.8 min (minor).



(*R*)-3-(4-chlorophenyl)-3,4-dihydroquinoxalin-2(1*H*)-one (2o): Known compound (see: Kristoffersen, T.; Elumalai, V.; Starck, E.; Cousin, E.; Wagner, L. J.; Hansen, S. R.; Hansen, J. H. *Eur. J. Org. Chem.* **2020**, *45*, 7069-7078). Yellow solid, m.p. 70-72 ^{o}C, 49.0 mg, isolated yield 95%, 96% *ee*. $[\alpha]_D^{20}$ =

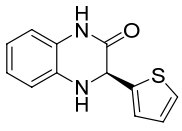
-104.8 (*c* = 1.0, $CDCl_3$, 96% *ee*); ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 10.46 (s, 1H), 7.42-7.34 (m, 4H), 6.82-6.58 (m, 5H), 4.96 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 165.7, 139.1, 133.7, 132.4, 128.9, 128.3, 125.3, 123.1, 117.9, 114.9, 113.5, 58.8. HRMS-ESI exact mass calcd. for $C_{14}H_{10}ClN_2O^-$ ([M-H]$^-$) requires m/z 257.04871, found m/z 257.04797.

The enantiomeric excess was determined by HPLC on the Chiralcel OJ-H column (*n*-hexane : isopropanol = 80 : 20, flowing rate = 1.0 mL/min, 25 ^{o}C, UV detection at λ = 230 nm), t_{R1} = 16.2 min (major), t_{R2} = 19.1 min (minor).



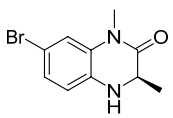
(*R*)-3-(4-bromophenyl)-3,4-dihydroquinoxalin-2(1*H*)-one (2p): Known compound (see: Kristoffersen, T.; Elumalai, V.; Starck, E.; Cousin, E.; Wagner, L. J.; Hansen, S. R.; Hansen, J. H. *Eur. J. Org. Chem.* **2020**, *45*, 7069-7078). White solid, m.p. 176-178 ^{o}C, 56.8 mg, isolated yield 94%, 92% *ee*. $[\alpha]_D^{20}$ = -106.4 (*c* = 1.0, $CDCl_3$, 92% *ee*); ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 10.46 (bs, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.82-6.58 (m, 5H), 4.94 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 165.5, 139.5, 133.6, 131.2, 129.2, 125.3, 123.1, 120.8, 117.9, 114.9, 113.4, 58.7. HRMS-ESI exact mass calcd. for $C_{14}H_{10}BrN_2O^-$ ([M-H]$^-$) requires m/z 300.99820, found m/z 300.99759.

The enantiomeric excess was determined by HPLC on the Chiralcel OD-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 ^{o}C, UV detection at λ = 230 nm), t_{R1} = 48.7 min (minor), t_{R2} = 60.6 min (major).



(*S*)-3-(thiophen-2-yl)-3,4-dihydroquinoxalin-2(1*H*)-one (2q): Known compound (see: Petasis, N.A.; Patel, D. A. *Tetrahedron. Lett.* **2000**, *41*, 9607-9611). White solid, m.p. 182-184 ^{o}C, 43.2 mg, isolated yield 94%, 97% *ee*. $[\alpha]_D^{20}$ = -46.3 (*c* = 1.0, $CDCl_3$, 97% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.77 (bs, 1H), 7.22 (dd, *J* = 5.1 Hz, *J* = 1.2 Hz, 2H), 7.06 (d, *J* = 3.6 Hz, 1H), 6.97-6.91 (m, 2H), 6.83-6.73 (m, 3H), 5.33 (s, 1H), 4.40 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 166.4, 141.4, 132.2, 127.0, 126.0, 125.9, 125.0, 124.4, 120.2, 115.9, 114.6, 56.9. HRMS-ESI exact mass calcd. for $C_{12}H_9N_2OS^-$ ([M-H]$^-$) requires m/z 229.04411, found m/z 229.04369.

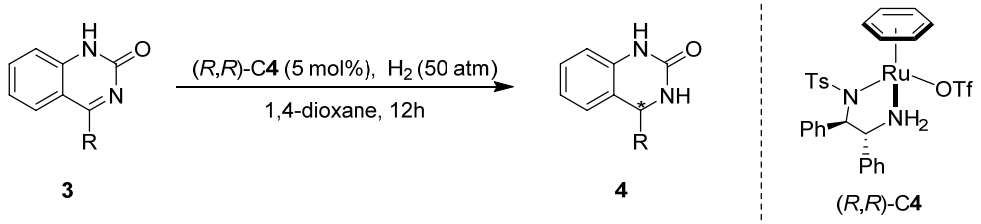
The enantiomeric excess was determined by HPLC on the Chiralcel OD-H column (*n*-hexane : isopropanol = 80 : 20, flowing rate = 1.0 mL/min, 25 ^{o}C, UV detection at λ = 254 nm), t_{R1} = 16.3 min (minor), t_{R2} = 23.2 min (major).



(*R*)-7-bromo-1,3-dimethyl-3,4-dihydroquinoxalin-2(1*H*)-one (2r): New compound. White solid, m.p. 124-126 ^{o}C, 47.2 mg, isolated yield 93%, 97% *ee*. $[\alpha]_D^{20}$ = -50.4 (*c* = 1.0, $CDCl_3$, 97% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.02-6.99 (m, 2H), 6.57 (d, *J* = 8.7 Hz, 1H), 3.97-3.91 (m, 2H), 3.33 (s, 3H), 1.42 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 168.1, 134.1, 130.6, 126.0, 117.7, 115.5, 111.5, 52.2, 29.3, 18.0. HRMS-ESI exact mass calcd. for $C_{10}H_{10}BrN_2O^+$ ($[M-H]^+$) requires m/z 252.99820, found m/z 252.99759.

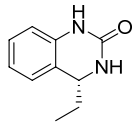
The enantiomeric excess was determined by HPLC on the Chiralcel OD-H column (*n*-hexane : isopropanol = 80 : 20, flowing rate = 1.0 mL/min, 25 ^{o}C, UV detection at λ = 220 nm), t_{R1} = 7.7 min (major), t_{R2} = 14.5 min (minor).

5.2 Asymmetric hydrogenation of substrate quinazolin-2(1*H*)-one (3)



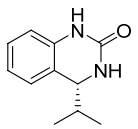
General procedure: A 15 mL glass-lined stainless-steel reactor equipped with a magnetic stirrer bar was charged with substrate **3** (0.1 mmol), Ru-catalyst (*R,R*)-**C4** (0.005 mmol) in 1.0 mL of solvent under N_2 atmosphere in a glove box. The autoclave was closed, and the final pressure of the hydrogen gas was adjusted to 50 atm after purging the autoclave with hydrogen gas several times. The reaction mixture was stirred at 25 ^{o}C for 12 h. Then the hydrogen gas was carefully released and the conversion was determined by ^{1}H NMR spectroscopy. The reaction mixture was filtered through a short pad of silica eluted with ethyl

acetate and petroleum ether to give the chiral product 3,4-dihydroquinazolin-2(1*H*)-one (**4**). The enantiomeric excess of the product was determined by HPLC with a chiral column.



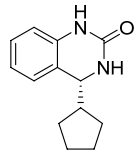
(*R*)-4-ethyl-3,4-dihydroquinazolin-2(1*H*)-one (4a): (New compound). White solid, m.p. 188-190 ^{o}C, 16.2 mg, isolated yield 92%, 41% *ee*. $[\alpha]_D^{20}$ = -5.6 (*c* = 1.0, $CHCl_3$, 41% *ee*); ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.02 (s, 1H), 7.11-7.04 (m, 2H), 6.95 (s, 1H), 6.85 (t, *J* = 7.2 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 4.32 (s, 1H), 1.61-1.57 (m, 2H), 0.78 (t, *J* =7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 154.0, 137.7, 127.5, 126.0, 121.3, 120.8, 113.6, 54.0, 31.1, 8.5. HRMS-ESI exact mass calcd. for $C_{10}H_{13}N_2O^+$ ($[M+H]^+$) requires m/z 177.10224, found m/z 177.10132.

The enantiomeric excess was determined by HPLC on the connection of Chiralcel IC-H column and Chiralcel IA-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 30 ^{o}C, UV detection at λ = 254 nm), t_{R1} = 15.3 min (minor), t_{R2} = 16.5 min (major).



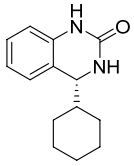
(*R*)-4-isopropyl-3,4-dihydroquinazolin-2(1*H*)-one (4b): Known compound (see: Feng, G.-S.; Zhao, Z.-B.; Shi, L.; Zhou, Y.-G. *Org. Chem. Front.* **2019**, *6*, 2250-2253). White solid, 17.9 mg, isolated yield 94%, 87% *ee*. $[\alpha]_D^{20}$ = -29.0 (*c* = 1.0, MeOH, 87% *ee*); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.84 (s, 1H), 7.18-7.14 (m, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.97-6.93 (m, 1H), 6.72 (d, *J* = 7.6 Hz, 1H), 5.50 (s, 1H), 4.37-4.35 (m, 1H), 1.99-1.94 (m, 1H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 155.4, 136.8, 128.2, 126.7, 122.1, 120.4, 114.3, 60.2, 36.8, 18.6, 16.1. HRMS-ESI exact mass calcd. for $C_{11}H_{15}N_2O^+$ ($[M+H]^+$) requires m/z 191.11789, found m/z 191.11661.

The enantiomeric excess was determined by HPLC on the Chiralcel IC-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 30 ^{o}C, UV detection at λ = 254 nm), t_{R1} = 13.4 min (minor), t_{R2} = 14.4 min (major).



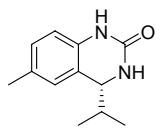
(*R*)-4-cyclopentyl-3,4-dihydroquinazolin-2(1*H*)-one (4c): (New compound). White solid, m.p. 230-232 ^{o}C, 19.4 mg, isolated yield 90%, 79% *ee*. $[\alpha]_D^{20}$ = -30.0 (*c* = 1.0, MeOH, 79% *ee*); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.55 (s, 1H), 7.13 (t, *J* =7.6 Hz, 1H), 7.05 (d, *J* =7.6 Hz, 1H), 6.93 (t, *J* = 7.2 Hz, 1H),6.76 (d, *J* = 8.0 Hz, 1H), 6.0 (s, 1H), 4.35-4.33 (m, 1H), 2.24-2.16 (m, 1H), 1.77-1.26 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.2, 136.6, 128.1, 126.5, 122.0, 121.6, 114.5, 58.1, 48.6, 29.1, 27.9, 25.2, 25.0. HRMS-ESI exact mass calcd. for $C_{13}H_{17}N_2O^+$ ($[M+H]^+$) requires m/z 217.13354, found m/z 217.13232.

The enantiomeric excess was determined by HPLC on the Chiralcel IA-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 30 ^{o}C, UV detection at λ = 254 nm), t_{R1} = 15.9 min (minor), t_{R2} = 17.7 min (major).



(*R*)-4-cyclohexyl-3,4-dihydroquinazolin-2(1*H*)-one (4d): Known compound (see: Feng, G.-S.; Zhao, Z.-B.; Shi, L.; Zhou, Y.-G. *Org. Chem. Front.* **2019**, *6*, 2250-2253). White solid, 21.4 mg, isolated yield 93%, 88% *ee*. $[\alpha]_D^{20}$ = -19.0 (*c* = 1.0, MeOH, 88% *ee*); ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.98 (s, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.03-6.99 (m, 2H), 6.84 (t, *J* = 6.6 Hz, 1H), 6.76 (d, *J* = 7.2 Hz, 1H), 4.10 (s, 1H), 1.65-1.41 (m, 6H), 1.11-0.93 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 154.3, 138.1, 127.5, 126.7, 120.5, 120.4, 113.4, 58.1, 46.4, 28.2, 26.7, 25.9, 25.7, 25.6. HRMS-ESI exact mass calcd. for $C_{14}H_{19}N_2O^+$ ($[M+H]^+$) requires m/z 231.14919, found m/z 231.14942.

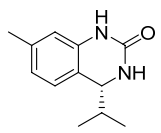
The enantiomeric excess was determined by HPLC on the Chiralcel OJ-H column (*n*-hexane : isopropanol = 80 : 20, flowing rate = 1.0 mL/min, 30 ^{o}C, UV detection at λ = 254 nm), t_{R1} = 4.2 min (minor), t_{R2} = 4.9 min (major).



(*R*)-4-isopropyl-6-methyl-3,4-dihydroquinazolin-2(1*H*)-one (4e): (New compound). White solid, m.p. 232-234 ^{o}C, 18.6 mg, isolated yield 91%, 87% *ee*. $[\alpha]_D^{20}$ = -61.6 (*c* = 1.0, MeOH, 87% *ee*); ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 8.86 (s, 1H), 6.92-6.85 (m, 3H), 6.65 (d, *J* = 7.8 Hz, 1H), 4.11(s, 1H), 2.20 (s, 3H), 1.80-1.74 (m, 1H), 0.84 (d, *J* =6.6 Hz, 3H), 0.73 (d, *J* =6.6 Hz, 3H); ^{13}C NMR (75 MHz,

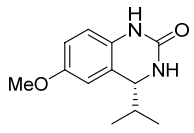
$CDCl_3$): δ (ppm) 154.3, 135.6, 129.2, 128.0, 127.0, 120.3, 113.3, 58.5, 36.5, 20.4, 18.3, 16.4. HRMS-ESI exact mass calcd. for $C_{12}H_{17}N_2O^+$ ($[M+H]^+$) requires m/z 205.13354, found m/z 205.13509.

The enantiomeric excess was determined by HPLC on the Chiralcel OJ-H column (*n*-hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 ^oC, UV detection at λ = 254 nm), t_{R1} = 8.0 min (major), t_{R2} = 9.6 min (minor).



(*R*)-4-isopropyl-7-methyl-3,4-dihydroquinazolin-2(1*H*)-one (4f): (New compound). White solid, m.p. 225-227 ^oC, 18.8 mg, isolated yield 92%, 89% *ee*. $[\alpha]_D^{20}$ = -33.0 (*c* = 1.0, MeOH, 89% *ee*); ^{1}HNMR (300 MHz, $CDCl_3$/Methanol-d_4 = 10:1): δ (ppm) 6.85 (d, *J* = 7.8 Hz, 1H), 6.72 (d, *J* = 7.5 Hz, 1H), 6.50 (s, 1H), 4.25 (d, *J* = 3.6 Hz, 1H), 2.23 (s, 3H), 1.89-1.83 (m, 1H), 0.90 (d, *J* = 6.9 Hz, 3H), 0.78 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$/Methanol-d_4 = 10:1): δ (ppm) 155.9, 138.2, 136.4, 126.5, 123.0, 117.4, 114.7, 59.7, 36.8, 21.1, 18.4, 16.1. HRMS-ESI exact mass calcd. for $C_{12}H_{17}N_2O^+$ ($[M+H]^+$) requires m/z 205.13354, found m/z 205.13322.

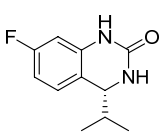
The enantiomeric excess was determined by HPLC on the Chiralcel AD-H column (*n*-hexane : isopropanol = 80 : 20, flowing rate = 1.0 mL/min, 25 ^oC, UV detection at λ = 254 nm), t_{R1} = 7.7 min (minor), t_{R2} = 30.2 min (major).



(*R*)-4-isopropyl-5-methoxy-3,4-dihydroquinazolin-2(1*H*)-one (4g): (New compound). White solid, m.p. 220-222 ^oC, 20.7mg, isolated yield 94%, 90% *ee*. $[\alpha]_D^{20}$ = -36.0 (*c* = 1.0, MeOH, 90% *ee*); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.84 (s, 1H), 6.74-6.71 (m, 1H), 6.66 (d, *J* = 8.4 Hz, 1H), 6.58 (d, *J* = 2.4 Hz, 1H), 5.46 (s, 1H), 4.32 (t, *J* = 3.2 Hz, 1H), 3.76 (s, 3H), 2.00-1.93 (m, 1H), 0.99 (d, *J* = 7.2 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 155.6, 155.0, 130.5, 121.6, 115.1, 113.5, 112.5, 60.3, 55.8, 36.8, 18.7, 16.1. HRMS-ESI exact mass calcd. for $C_{12}H_{17}N_2O_2^+$ ($[M+H]^+$) requires m/z 221.12845, found m/z 221.12801.

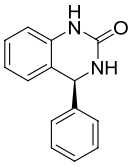
The enantiomeric excess was determined by HPLC on the Chiralcel AD-H column (*n*-hexane : isopropanol = 80 : 20, flowing rate = 1.0 mL/min, 25 ^oC, UV detection at λ = 254

nm), t_{R1} = 26.2 min (minor), t_{R2} = 33.1 min (major).



(*R*)-7-fluoro-4-isopropyl-3,4-dihydroquinazolin-2(1*H*)-one (4h): (New compound). White solid, m.p. 225-227 ^{o}C, 18.9mg, isolated yield 91%, 86% *ee*. $[\alpha]_D^{20}$ = -28.0 (*c* = 1.0, MeOH, 86% *ee*); ^{1}H NMR (500 MHz, $CDCl_3$/Methanol-d_4 = 10:1): δ (ppm) 6.94-6.91 (m, 1H), 6.45 (d, *J* = 9.5 Hz, 1H), 4.26 (d, *J* = 3.0 Hz, 1H), 1.88-1.85 (m, 1H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.80 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$/Methanol-d_4 = 10:1): δ (ppm). 162.5(d, $J_{C\text{-}F}$ = 243.8 Hz), 155.4, 138.2 (d, $J_{C\text{-}F}$ = 11.3 Hz), 128.0 (d, $J_{C\text{-}F}$ = 10.0 Hz), 116.0 (d, $J_{C\text{-}F}$ = 3.8 Hz), 108.9 (d, $J_{C\text{-}F}$ = 22.5 Hz), 101.5 (d, $J_{C\text{-}F}$ = 25.0 Hz), 59.4, 36.9, 18.2, 16.0. HRMS-ESI exact mass calcd. for $C_{11}H_{14}FN_2O^+$ ($[M+H]^+$) requires m/z 209.10847, found m/z 209.10803.

The enantiomeric excess was determined by HPLC on the Chiralcel AD-H column (*n*-hexane : isopropanol = 80 : 20, flowing rate = 1.0 mL/min, 25 ^{o}C, UV detection at λ = 254 nm), t_{R1} = 7.9 min (minor), t_{R2} = 20.7 min (major).

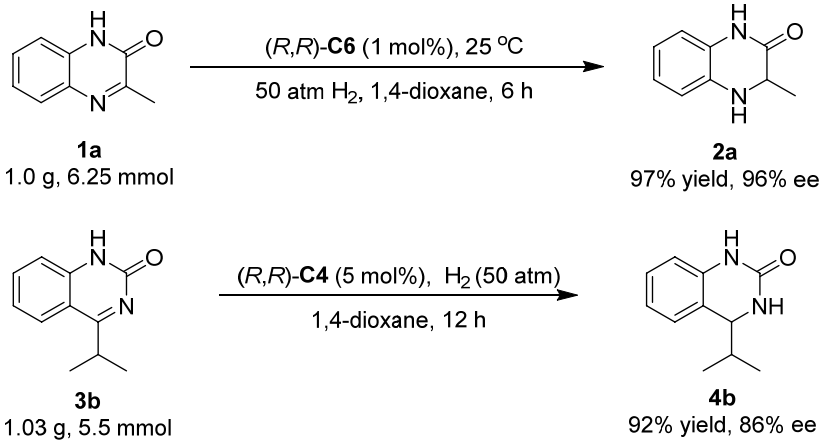


(*S*)-4-phenyl-3,4-dihydroquinazolin-2(1*H*)-one (4i): Known compound (see: Feng, G.-S.; Zhao, Z.-B.; Shi, L.; Zhou, Y.-G. *Org. Chem. Front.* **2019**, *6*, 2250-2253). White solid, 20.3 mg, isolated yield 91%, 9% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.88 (bs, 1H), 7.36-7.29 (m, 5H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.82-6.77 (m, 2H), 5.64 (s, 1H), 5.45 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 154.4, 142.8, 135.9, 129.2, 128.6, 128.5, 127.4, 127.2, 122.6, 121.4, 114.6, 58.9. HRMS-ESI exact mass calcd. for $C_{14}H_{13}N_2O^+$ ($[M+H]^+$) requires m/z 225.10224, found m/z 225.10200.

The enantiomeric excess was determined by HPLC on the Chiralcel OJ-H column (*n*-hexane : isopropanol = 80 : 20, flowing rate = 1.0 mL/min, 30 ^{o}C, UV detection at λ = 254 nm), t_{R1} =7.8 min (major), t_{R2} =12.3 min (minor).

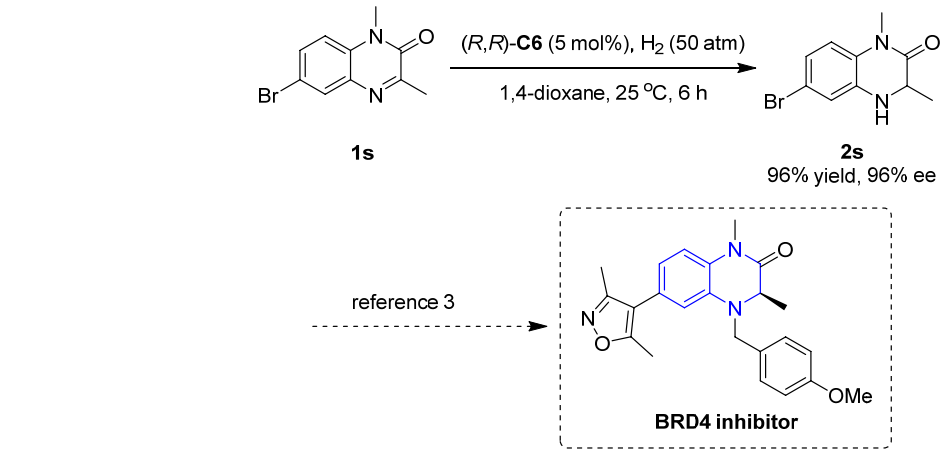
5. Scale-up syntheses and synthetic applications

5.1 Scale-up synthesis

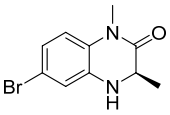


Scheme S3. Scale-up synthesis

General procedure: A 100 mL glass-lined stainless-steel reactor equipped with a magnetic stirrer bar was charged with substrate **1a** (6.25 mmol), Ru-catalyst (*R,R*)-**C6** (0.0625 mmol) in 62.5 mL of 1,4-dioxane under N_2 atmosphere in a glove box. The autoclave was closed, and the final pressure of the hydrogen gas was adjusted to 50 atm after purging the autoclave with hydrogen gas several times. The reaction mixture was stirred at 25 ^{o}C for 6 h. Then the hydrogen gas was carefully released and the conversion was determined by ^{1}H NMR spectroscopy. The reaction mixture was filtered through a short pad of silica eluted with ethyl acetate and petroleum ether to give the chiral product (*S,S*)-**2a**. The enantiomeric excess of the product was determined by HPLC with a chiral column.



Scheme S4. Synthesis of a key intermediate of a bioactive BRD4 inhibitor



(*R*)-6-bromo-1,3-dimethyl-3,4-dihydroquinoxalin-2(1H)-one (2s): Known compound (see: Zhao, Z.-B.; Li, X.; Chen, M.-W.; Zhao Z. K.; Zhou, Y.-G. *Chem. Commun.* **2020**, *56*, 7309-7312). White solid, m.p. 110-112 °C, 48.3 mg, isolated yield 95%, 96% *ee*. $[\alpha]_D^{20}$ = -76.8 (*c* = 1.0, $CDCl_3$, 96% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.97-6.93 (m, 1H), 6.82 (d, *J* = 2.1 Hz, 1H), 6.75 (d, *J* = 8.7 Hz, 1H), 3.99-3.93 (m, 2H), 3.33 (s, 3H), 1.42 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 167.9, 136.3, 128.4, 122.4, 116.9, 116.1, 116.1, 52.2, 29.3, 18.2. HRMS-ESI exact mass calcd. for $C_{10}H_{10}BrN_2O^-$ ([M-H]$^-$) requires m/z 253.09715, found m/z 253.09695.

The enantiomeric excess was determined by HPLC on the Chiralcel OD-H column (*n*-hexane : isopropanol = 80 : 20, flowing rate = 1.0 mL/min, 25 °C, UV detection at λ = 220 nm), t_{R1} = 7.4 min (major), t_{R2} = 17.5 min (minor).

6. References

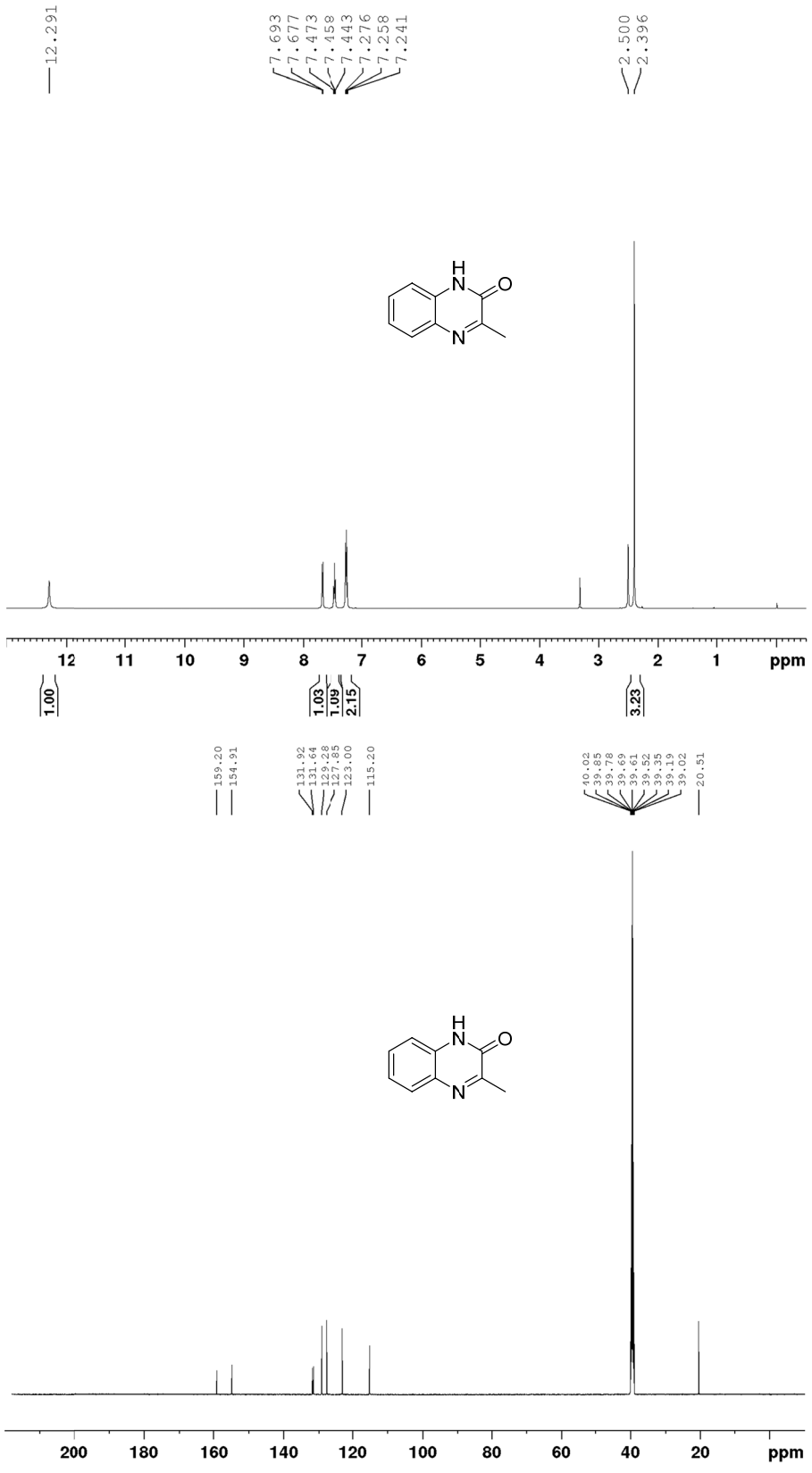
1. (a) Ohkuma, T.; Utsumi, N.; Tsutsumi, K.; Murata, K.; Sandoval, C.; Noyori, R. *J. Am. Chem. Soc*. **2006**, *128*, 8724. (b) Wang, T. L.; Zhuo, L.-G.; Li, Z.; Chen, F.; Ding, Z.; He, Y.-M.; Fan, Q.-H.; Xiang, J.-F.; Yu, Z.-X.; Chan, A. S. C. *J. Am. Chem. Soc*. **2011**, *133*, 9878.

2. (a) Rueping, M.; Tato, F.; Schoepke, F. R. *Chem. Eur. J.* **2010**, *16*, 2688-2691. (b) Shi, F.; Tan, W.; Zhang, H.-H.; Li, M.; Ye, Q.; Ma, G.-H.; Tu, S.-J.; Li, G. *Adv. Synth. Catal.* **2013**, *355*, 3715-3726. (c) Núñez-Rico, J. L.; Vidal-Ferran, A. *Org. Lett.* **2013**, *15*, 2066-2069. (d) Zhao, Z.-B.; Li, X.; Chen, M.-W.; Zhao Z. K.; Zhou, Y.-G. *Chem. Commun.* **2020**, *56*, 7309-7312. (e) Bergman, J.; Brynolf, A.; Elman, B.; Vuorinen, E. *Tetrahedron.* **1986**, *42*, 3697-3706.

3. Yang, Y.; Zhao, L.; Xu, B.; Yang, L.; Zhang, J.; Zhang, H.; Zhou, J. *Bioorg. Chem.* **2016**, *68*, 236-244.

7. Copy of NMR spectra for all substrates and products

Figure S1. ^{1}H NMR and ^{13}C NMR spectra of **1a** ($CDCl_3$)

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Current Data Parameters
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EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20210118
Time                   19.46
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PULPROG                 zg30
TD                     65536
SOLVENT                 DMSO
NS                        16
DS                         2
SWH                10000.000 Hz
FIDRES             0.152588 Hz
AQ                 3.2767999 sec
RG                     49.27
DW                    50.000 usec
DE                     6.50 usec
TE                    298.2 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      10.59 usec
PL1                    120.00 dB
PL1W          0 W
SFO1             500.1330885 MHz

F2 - Processing parameters
SI                         65536
SF                500.1300041 MHz
WDW                           EM
SSB           0
LB                      0.30 Hz
GB            0
PC                      1.00
```

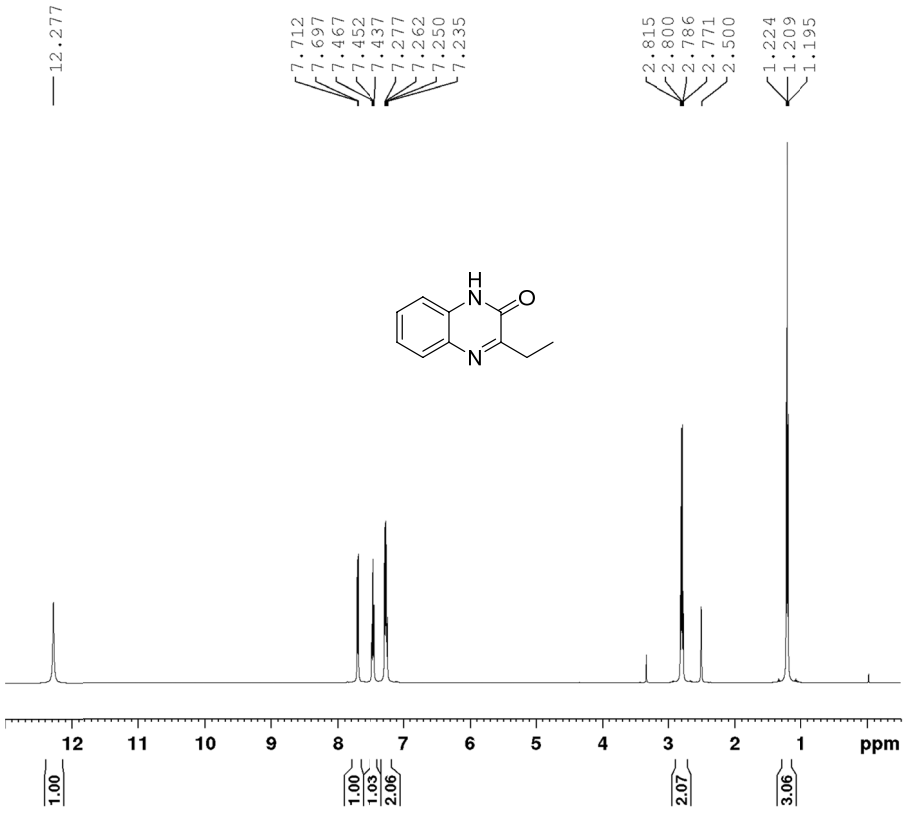
```
Current Data Parameters
NAME                  new-kwt
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_               20210118
Time                   19.50
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG                zgpg30
TD                     65536
SOLVENT                 DMSO
NS                       1024
DS                          4
SWH                29761.904 Hz
FIDRES             0.454131 Hz
AQ                 1.1010048 sec
RG                     192.89
DW                    16.800 usec
DE                     18.00 usec
TE                    298.2 K
D1                 2.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                      9.80 usec
PL1                    120.00 dB
PL1W          0 W
SFO1             125.7703637 MHz

F2 - Processing parameters
SI                         32768
SF                125.7578480 MHz
WDW                           EM
SSB           0
LB                      1.00 Hz
GB            0
PC                      1.40
```

Figure S2. ^{1}H NMR and ^{13}C NMR spectra of **1b**

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Current Data Parameters
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EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
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Time                   20.46
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG                 zg30
TD                     65536
SOLVENT                 DMSO
NS                        16
DS                         2
SWH                10000.000 Hz
FIDRES             0.152588 Hz
AQ                 3.2767999 sec
RG                     31.72
DW                    50.000 usec
DE                     6.50 usec
TE                     298.2 K
D1                1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                     10.59 usec
PL1                    120.00 dB
PL1W          0 W
SFO1           500.1330885 MHz

F2 - Processing parameters
SI                     65536
SF               500.1300041 MHz
WDW                       EM
SSB           0
LB                      0.30 Hz
GB            0
PC                      1.00
```

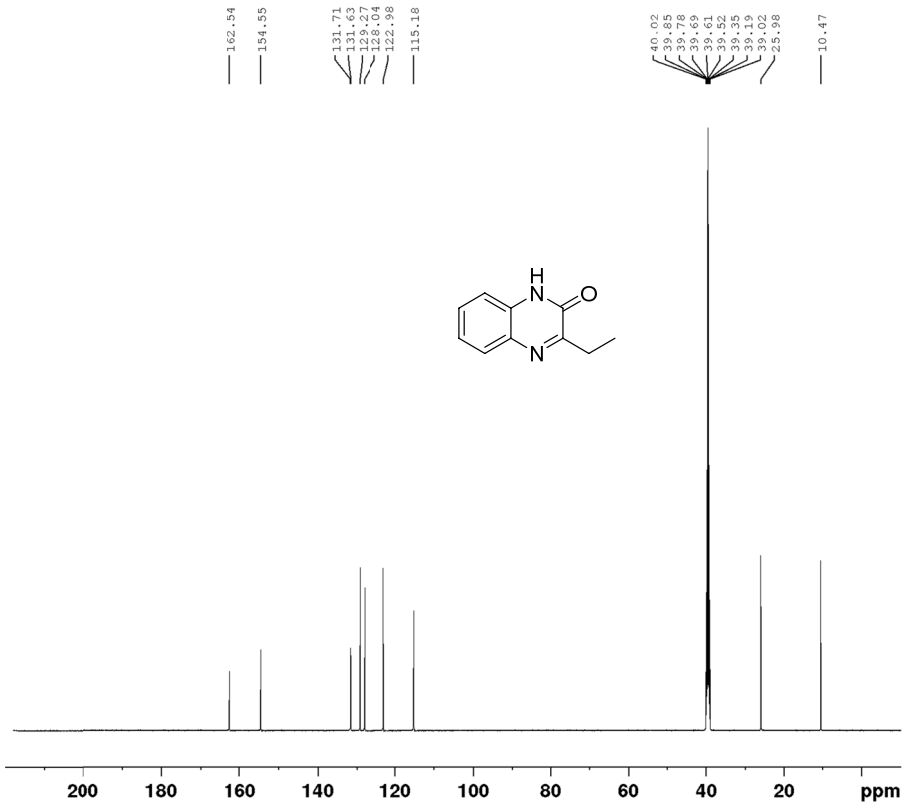


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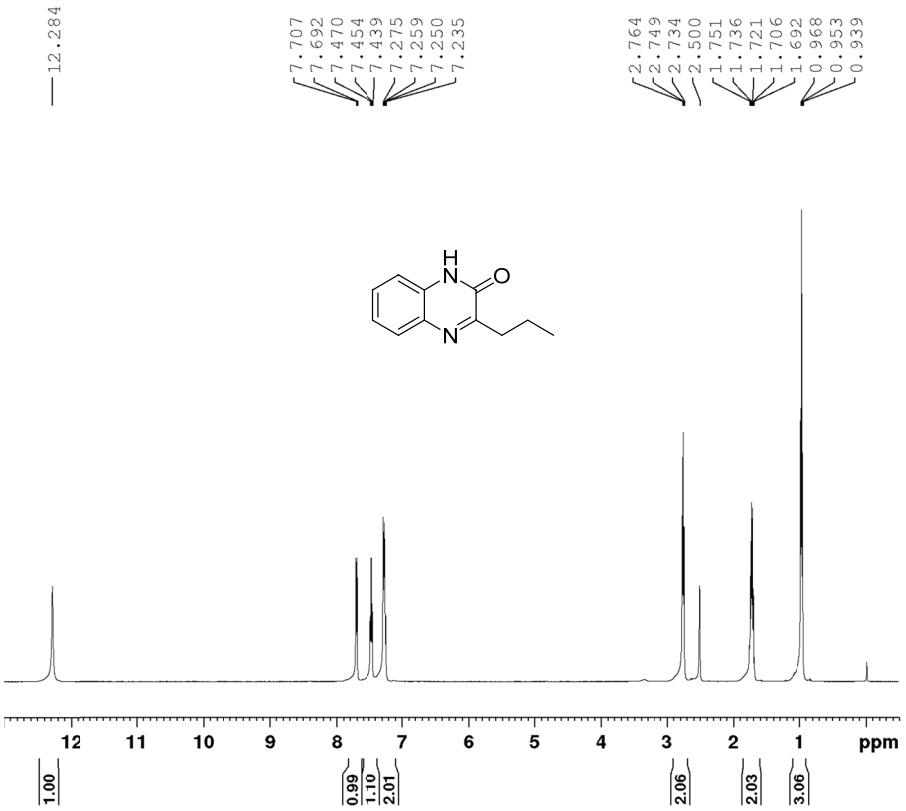
Current Data Parameters
NAME                  new-kwt
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_               20210118
Time                   20.52
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG               zgpg30
TD                     65536
SOLVENT                 DMSO
NS                       1024
DS                          4
SWH                29761.904 Hz
FIDRES             0.454131 Hz
AQ                 1.1010048 sec
RG                     192.89
DW                    16.800 usec
DE                     18.00 usec
TE                     298.2 K
D1                2.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                      9.80 usec
PL1                    120.00 dB
PL1W          0 W
SFO1           125.7703637 MHz

F2 - Processing parameters
SI                     32768
SF               125.7578473 MHz
WDW                       EM
SSB           0
LB                      1.00 Hz
GB            0
PC                      1.40
```

Figure S3. ^{1}H NMR and ^{13}C NMR spectra of **1c**

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Current Data Parameters
NAME                 new-kwt
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20210209
Time                   6.01
INSTRUM               spect
PROBHD    5 mm CPPEBO BB
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       16
DS                        2
SWH               10000.000 Hz
FIDRES             0.152588 Hz
AQ                3.2767999 sec
RG                     31.72
DW                    50.000 usec
DE                     6.50 usec
TE                    298.2 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     10.59 usec
PL1                   120.00 dB
PL1W       0 W
SFO1           500.1330885 MHz

F2 - Processing parameters
SI                        65536
SF              500.1300036 MHz
WDW                        EM
SSB        0
LB                      0.30 Hz
GB         0
PC                      1.00
```

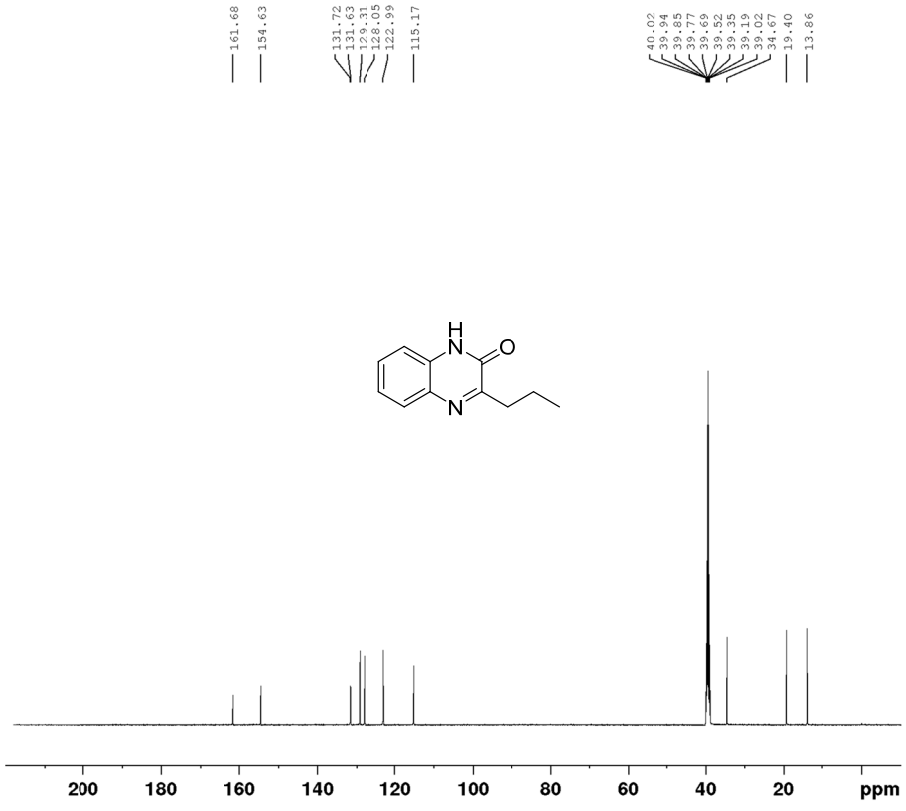


```
Current Data Parameters
NAME                 new-kwt
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20210209
Time                   6.56
INSTRUM               spect
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PULPROG             zgpg30
TD                    65536
SOLVENT                DMSO
NS                      1024
DS                         4
SWH               29761.904 Hz
FIDRES             0.454131 Hz
AQ                1.1010048 sec
RG                    192.89
DW                    16.800 usec
DE                     18.00 usec
TE                    298.2 K
D1              2.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      13C
P1                      9.80 usec
PL1                   120.00 dB
PL1W       0 W
SFO1           125.7703637 MHz

F2 - Processing parameters
SI                        32768
SF              125.7578476 MHz
WDW                        EM
SSB        0
LB                      1.00 Hz
GB         0
PC                      1.40
```
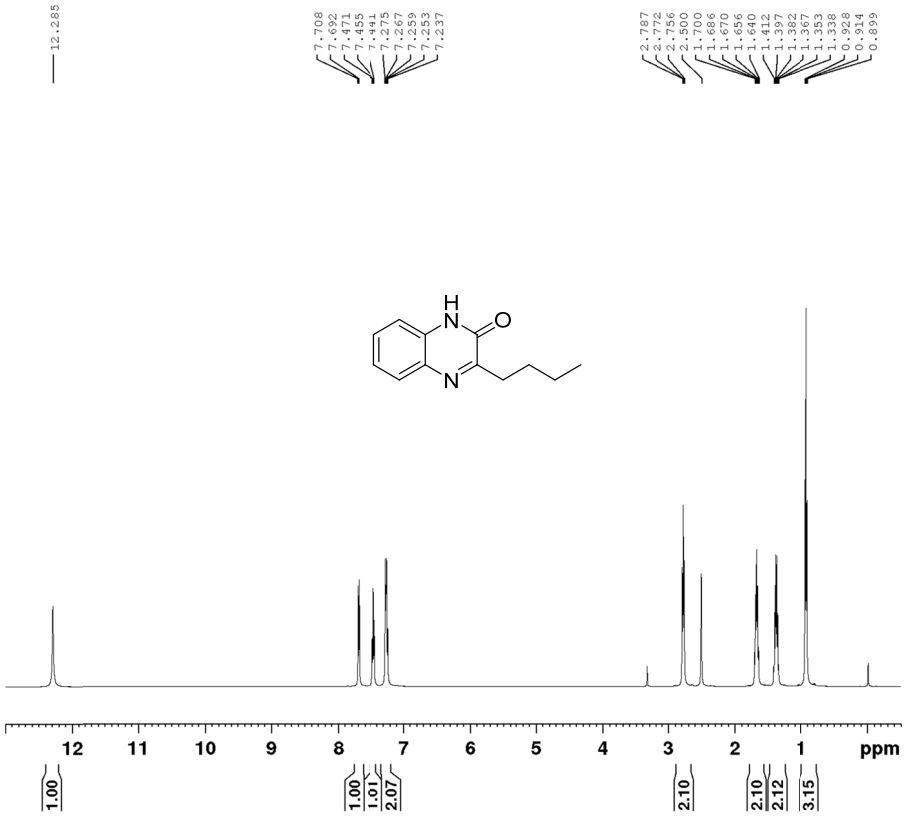

Figure S4. ^{1}H NMR and ^{13}C NMR spectra of **1d**




```
Current Data Parameters
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EXPNO                       3
PROCNO                      1

F2 - Acquisition Parameters
Date_               20210209
Time                    5.02
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG                 zg30
TD                     65536
SOLVENT                 DMSO
NS                        16
DS                         2
SWH                10000.000 Hz
FIDRES             0.152588 Hz
AQ                 3.2767999 sec
RG                     49.27
DW                    50.000 usec
DE                     6.50 usec
TE                     298.2 K
D1                1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                     10.59 usec
PL1                    120.00 dB
PL1W       0 W
SFO1            500.1330885 MHz

F2 - Processing parameters
SI                         65536
SF                500.1300027 MHz
WDW                         EM
SSB        0
LB                      0.30 Hz
GB         0
PC                      1.00
```

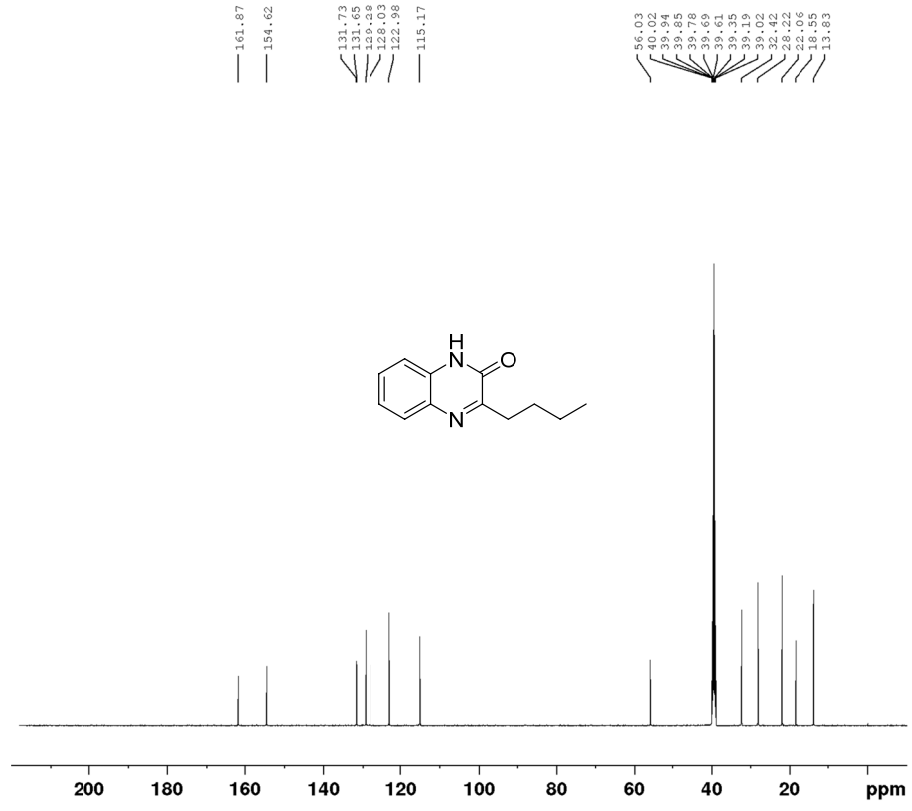


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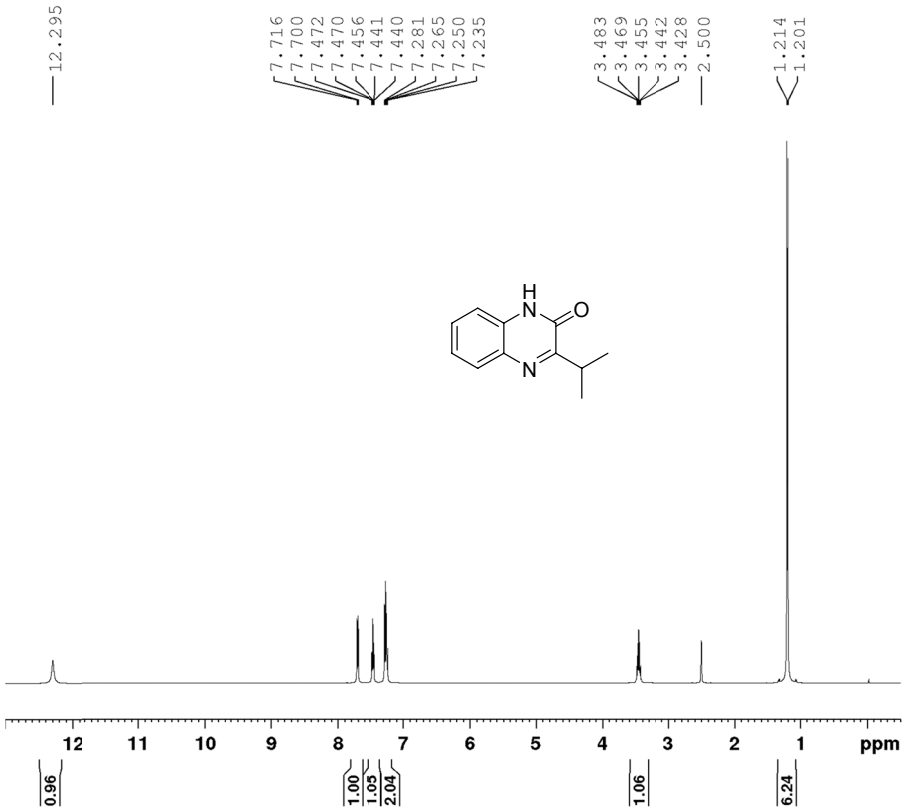
Current Data Parameters
NAME                  new-kwt
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_               20210119
Time                    0.37
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG             zgpg30
TD                     65536
SOLVENT                 DMSO
NS                       1024
DS                          4
SWH                29761.904 Hz
FIDRES             0.454131 Hz
AQ                 1.1010048 sec
RG                     192.89
DW                    16.800 usec
DE                     18.00 usec
TE                     298.2 K
D1                2.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       13C
P1                      9.80 usec
PL1                    120.00 dB
PL1W       0 W
SFO1            125.7703637 MHz

F2 - Processing parameters
SI                         32768
SF                125.7578464 MHz
WDW                         EM
SSB        0
LB                      1.00 Hz
GB         0
PC                      1.40
```

Figure S5. ^{1}H NMR and ^{13}C NMR spectra of **1e**

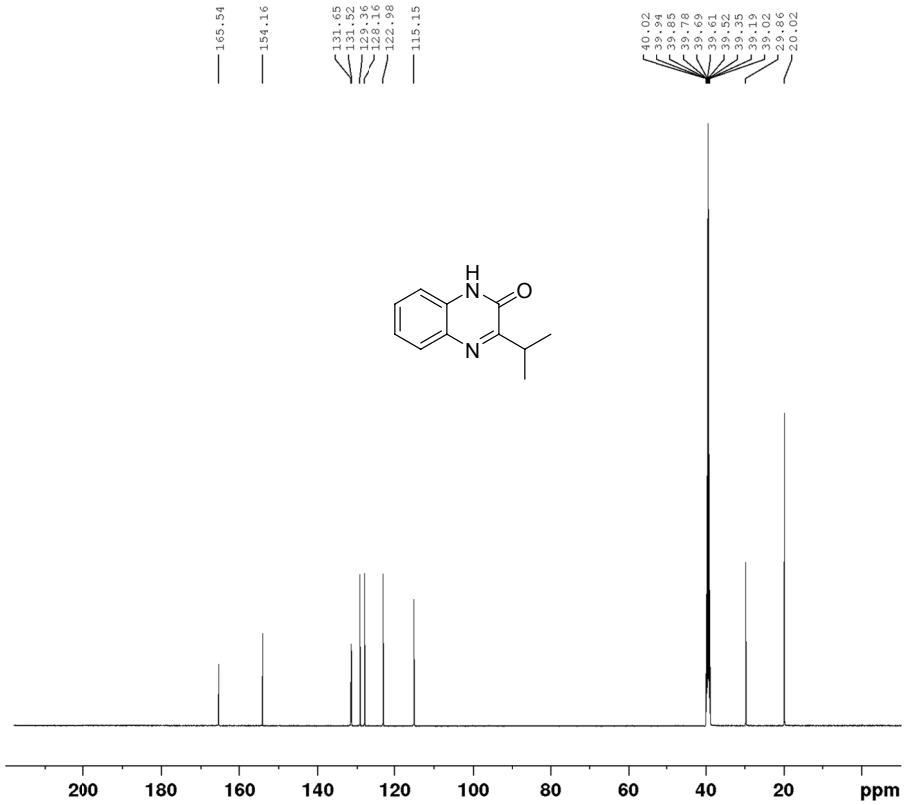



```
Current Data Parameters
NAME                  new-kwt
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20210118
Time                   21.45
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       16
DS                        2
SWH               10000.000 Hz
FIDRES                0.152588 Hz
AQ                 3.2767999 sec
RG                     31.72
DW                    50.000 usec
DE                     6.50 usec
TE                     298.2 K
D1                1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      10.59 usec
PL1                    120.00 dB
PL1W          0 W
SFO1             500.1330885 MHz

F2 - Processing parameters
SI                         65536
SF                500.1300041 MHz
WDW                        EM
SSB           0
LB                      0.30 Hz
GB            0
PC                      1.00
```

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Current Data Parameters
NAME                  new-kwt
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
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Time                   22.40
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG              zgpg30
TD                    65536
SOLVENT                DMSO
NS                      1024
DS                         4
SWH               29761.904 Hz
FIDRES                0.454131 Hz
AQ                 1.1010048 sec
RG                     192.89
DW                    16.800 usec
DE                     18.00 usec
TE                     298.2 K
D1                2.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       13C
P1                      9.80 usec
PL1                    120.00 dB
PL1W          0 W
SFO1             125.7703637 MHz

F2 - Processing parameters
SI                         32768
SF                125.7578476 MHz
WDW                        EM
SSB           0
LB                      1.00 Hz
GB            0
PC                      1.40
```
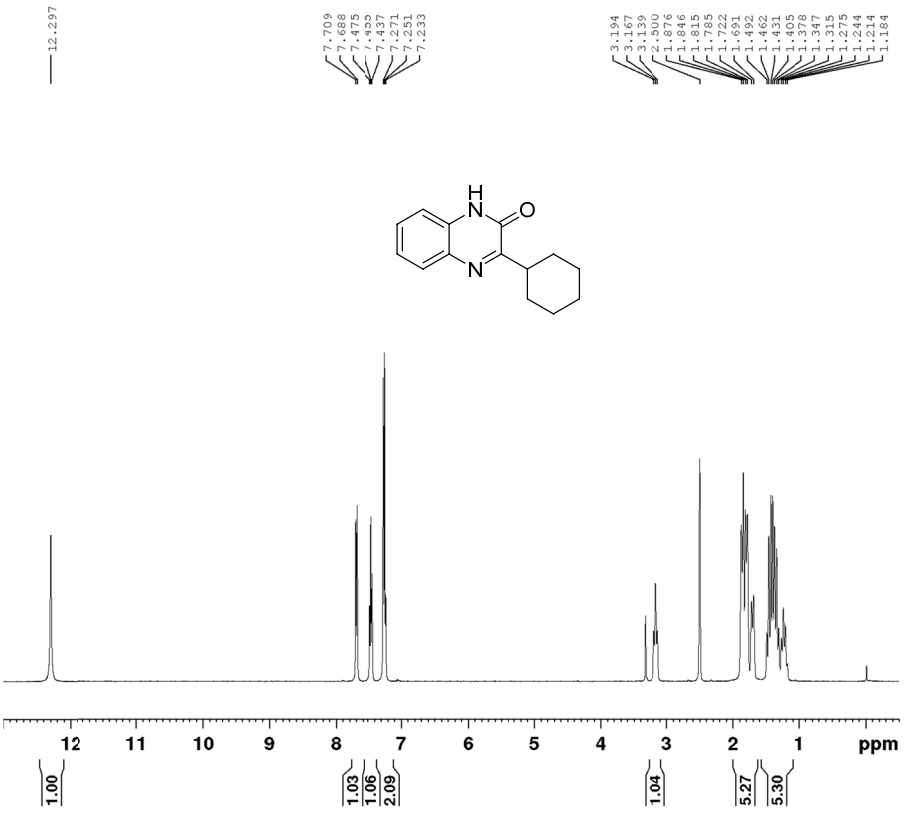

Figure S6. ^{1}H NMR and ^{13}C NMR spectra of **1f**




```
Current Data Parameters
NAME                 new-kwt
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
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Time                    9.56
INSTRUM                spect
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PULPROG                zg30
TD                    32768
SOLVENT                DMSO
NS                        16
DS                         0
SWH                8012.820 Hz
FIDRES                0.244532 Hz
AQ                 2.0447233 sec
RG                      206.33
DW                     62.400 usec
DE                      6.50 usec
TE                     298.0 K
D1                 2.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                       1H
P1                      14.30 usec
PL1                    120.00 dB
PL1W       0 W
SFO1              400.2424716 MHz

F2 - Processing parameters
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SF                400.2400033 MHz
WDW                        EM
SSB        0
LB                      0.30 Hz
GB         0
PC                      1.00
```

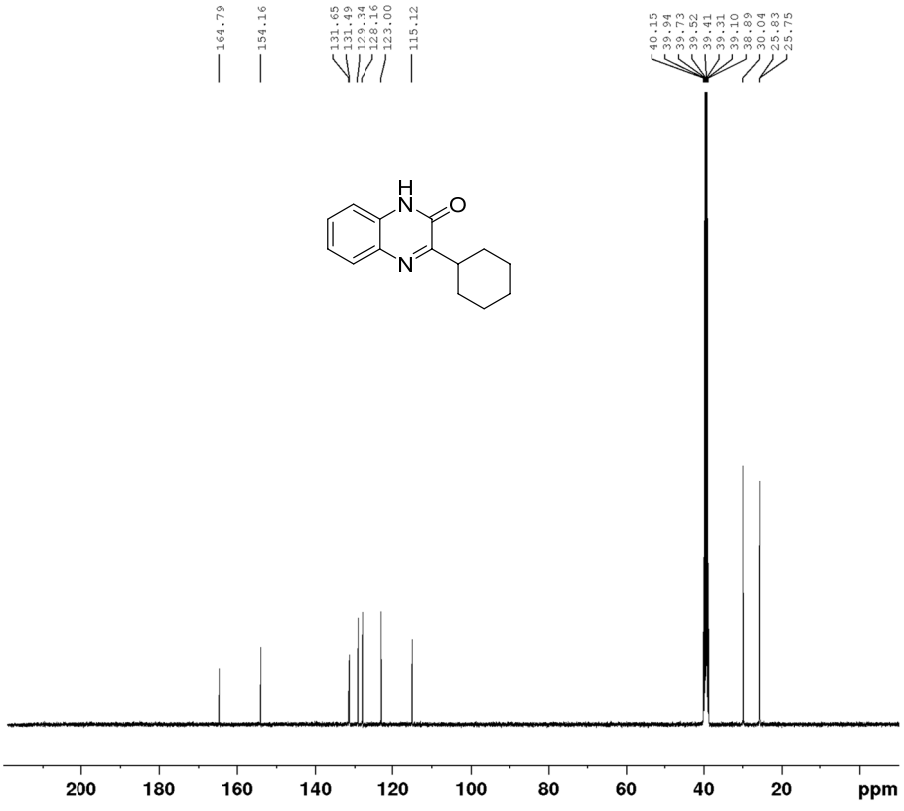


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Current Data Parameters
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EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_               20210119
Time                   11.16
INSTRUM                spect
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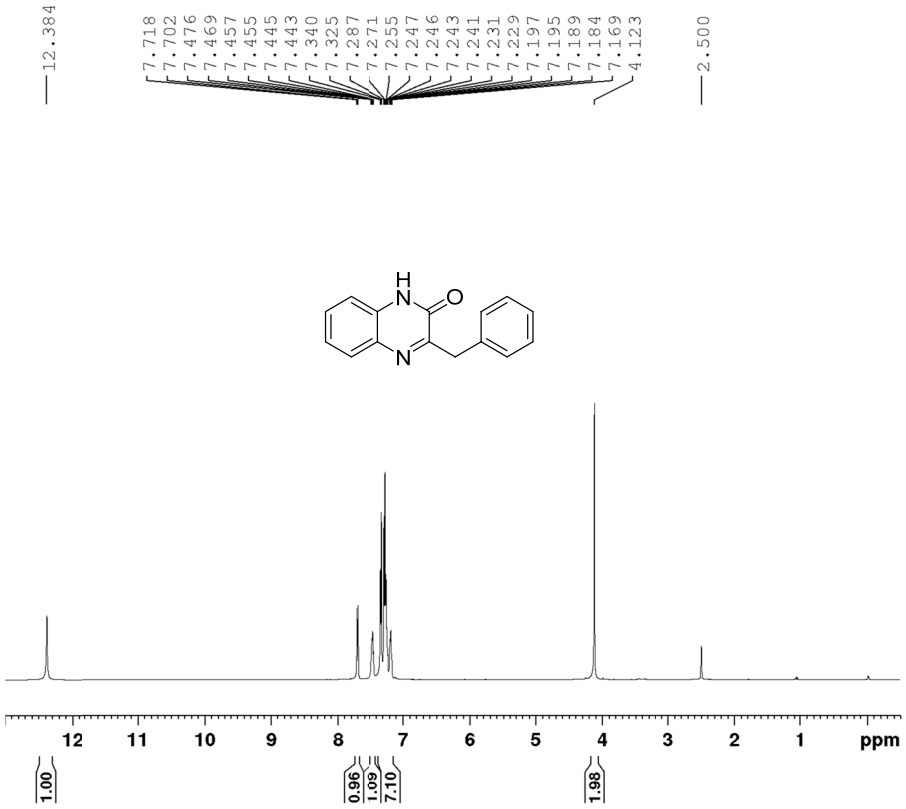
PULPROG              zgpg30
TD                    65536
SOLVENT                DMSO
NS                      2048
DS                         4
SWH               24038.461 Hz
FIDRES                0.366798 Hz
AQ                 1.3631488 sec
RG                      206.33
DW                     20.800 usec
DE                      6.50 usec
TE                     298.1 K
D1                 2.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      13C
P1                      10.00 usec
PL1                    120.00 dB
PL1W       0 W
SFO1              100.6504916 MHz

F2 - Processing parameters
SI                         32768
SF                100.6404760 MHz
WDW                        EM
SSB        0
LB                      1.00 Hz
GB         0
PC                      1.40
```

Figure S7. ^{1}H NMR and ^{13}C NMR spectra of **1g**

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Current Data Parameters
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EXPNO                   1
PROCNO                  1

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PULPROG             zg30
TD                 65536
SOLVENT             DMSO
NS                    16
DS                     2
SWH            10000.000 Hz
FIDRES          0.152588 Hz
AQ             3.2767999 sec
RG                 31.72
DW                50.000 usec
DE                 6.50 usec
TE                298.2 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.59 usec
PL1               120.00 dB
PL1W      0 W
SFO1         500.1330885 MHz

F2 - Processing parameters
SI                 65536
SF           500.1300045 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```
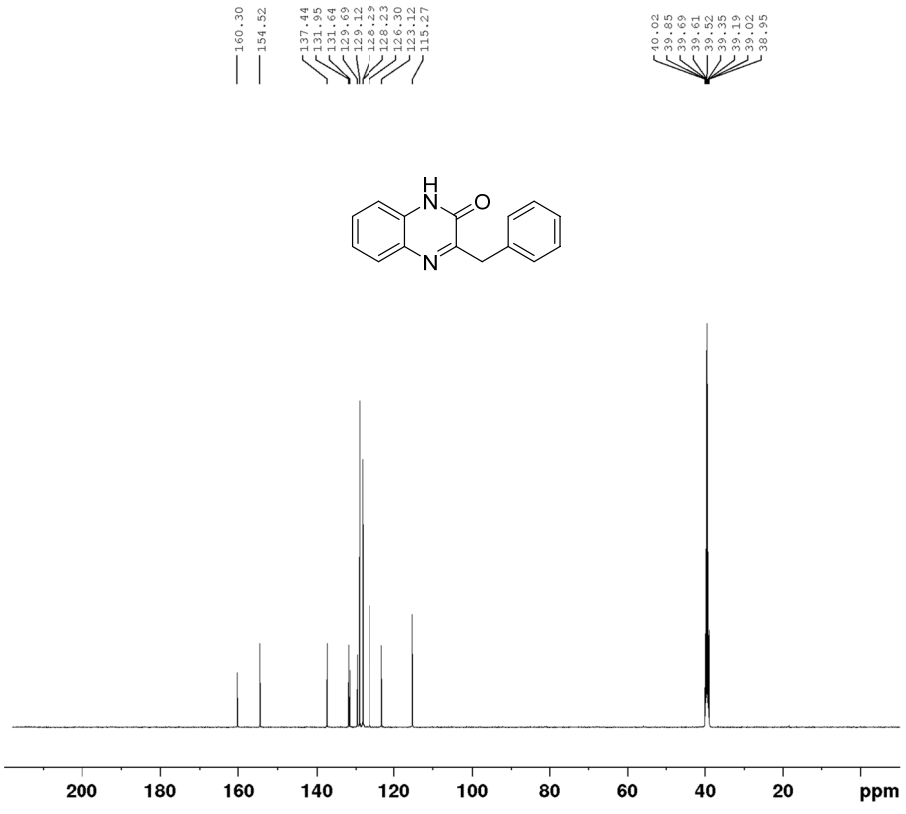




```
Current Data Parameters
NAME              new-kwt
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210119
Time                1.36
INSTRUM            spect
PROBHD    5 mm CPPBBO BB
PULPROG           zgpg30
TD                 65536
SOLVENT             DMSO
NS                  1024
DS                     4
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ             1.1010048 sec
RG                192.89
DW                16.800 usec
DE                18.00 usec
TE                298.2 K
D1             2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.80 usec
PL1               120.00 dB
PL1W      0 W
SFO1         125.7703637 MHz

F2 - Processing parameters
SI                 32768
SF           125.7578480 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

Figure S8. ^{1}H NMR and ^{13}C NMR spectra of **1h**

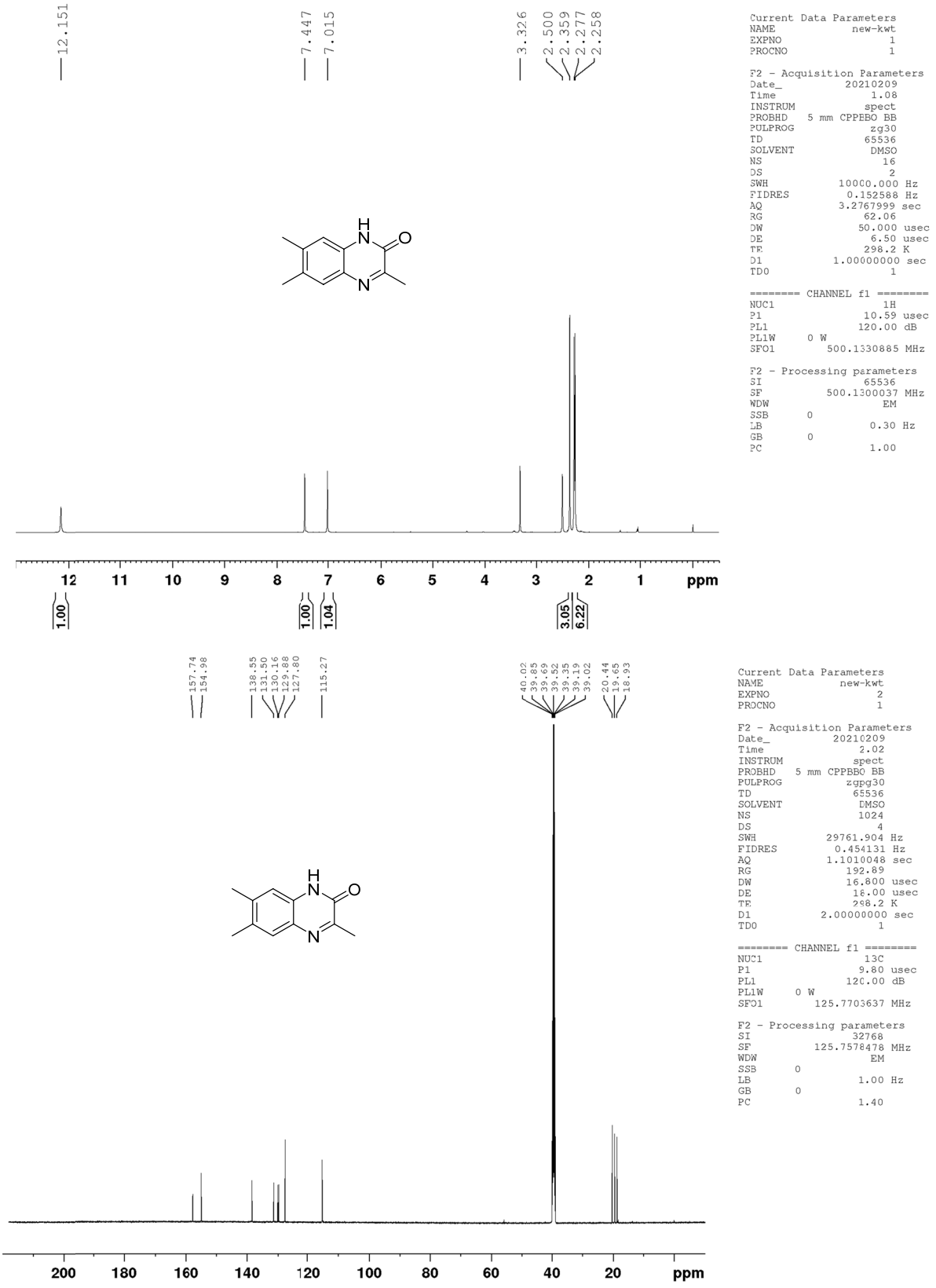
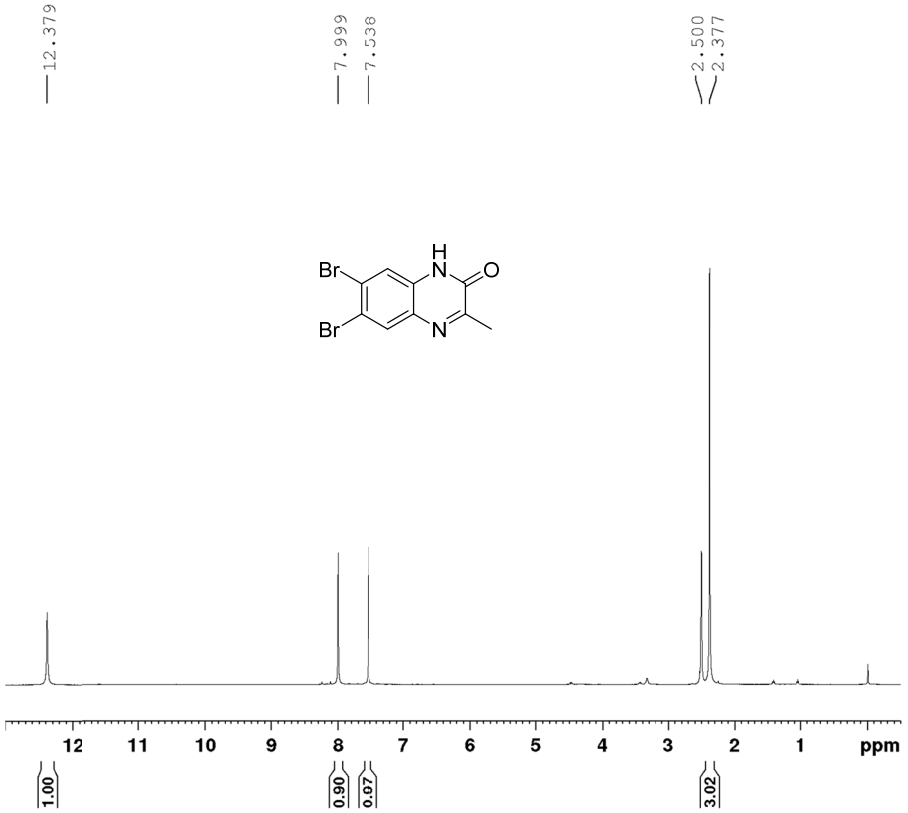
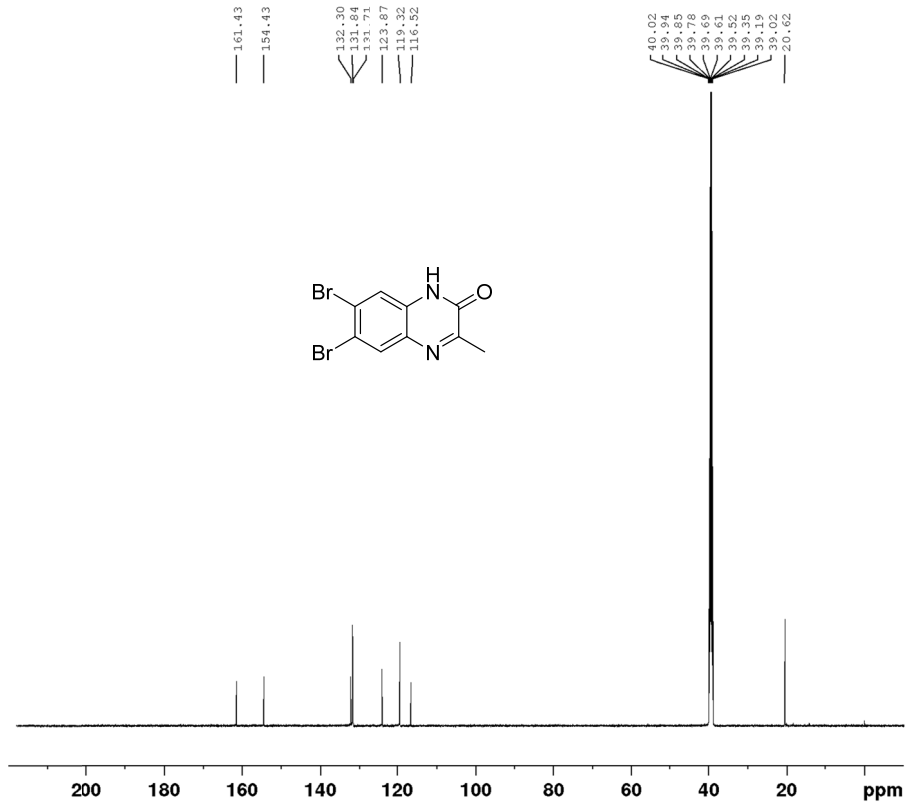


Figure S9. ^{1}H NMR and ^{13}C NMR spectra of **1i**

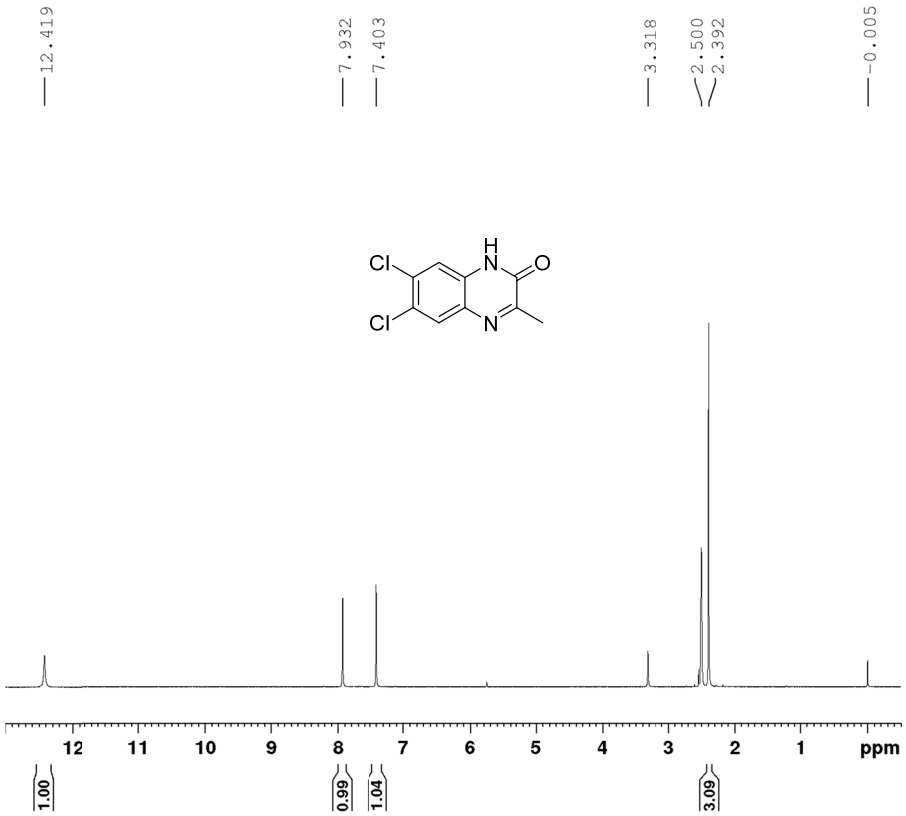



```
Current Data Parameters
NAME                 new-kwt
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20210209
Time                   0.08
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       16
DS                        2
SWH              10000.000 Hz
FIDRES               0.152588 Hz
AQ                3.2767999 sec
RG                     62.06
DW                   50.000 usec
DE                    6.50 usec
TE                    298.2 K
D1               1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     10.59 usec
PL1                   120.00 dB
PL1W      0 W
SFO1           500.1330885 MHz

F2 - Processing parameters
SI                     65536
SF               500.1300032 MHz
WDW                       EM
SSB       0
LB                     0.30 Hz
GB        0
PC                     1.00
```

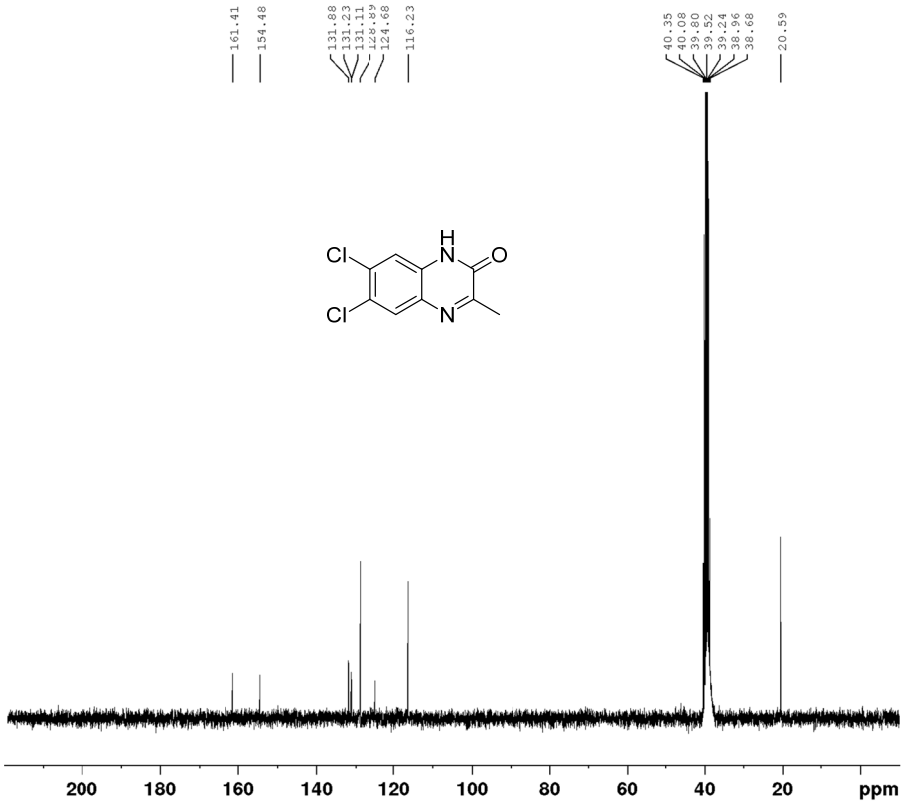



```
Current Data Parameters
NAME                 new-kwt
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20210209
Time                   0.11
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG             zgpg30
TD                    65536
SOLVENT                DMSO
NS                     1024
DS                        4
SWH              29761.904 Hz
FIDRES               0.454131 Hz
AQ                1.1010048 sec
RG                    192.89
DW                   16.800 usec
DE                    18.00 usec
TE                    298.2 K
D1               2.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      13C
P1                     9.80 usec
PL1                   120.00 dB
PL1W      0 W
SFO1           125.7703637 MHz

F2 - Processing parameters
SI                     32768
SF               125.7578483 MHz
WDW                       EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     1.40
```

Figure S10. ^{1}H NMR and ^{13}C NMR spectra of **1j**

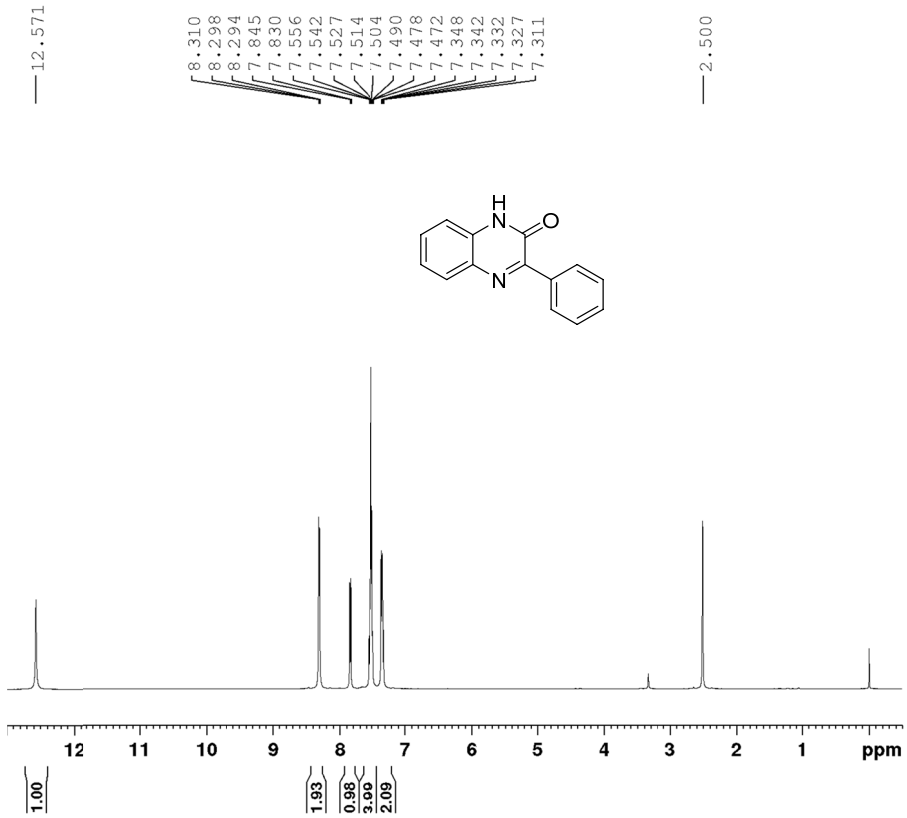



```
Current Data Parameters
NAME                 new-kwt
EXPNO                     18
PROCNO                     1

F2 - Acquisition Parameters
Date_              20210502
Time                  20.10
INSTRUM                spect
PROBHD    5 mm DUL 13C-1
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       16
DS                        2
SWH                6009.615 Hz
FIDRES            0.091699 Hz
AQ                5.4525952 sec
RG                   209.09
DW                  83.200 usec
DE                   6.50 usec
TE                  298.2 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                     8.00 usec
PL1                  120.00 dB
PL1W       0 W
SFO1           300.1318534 MHz

F2 - Processing parameters
SI                    65536
SF             300.1300024 MHz
WDW                      EM
SSB        0
LB                    0.30 Hz
GB         0
PC                    1.00
```

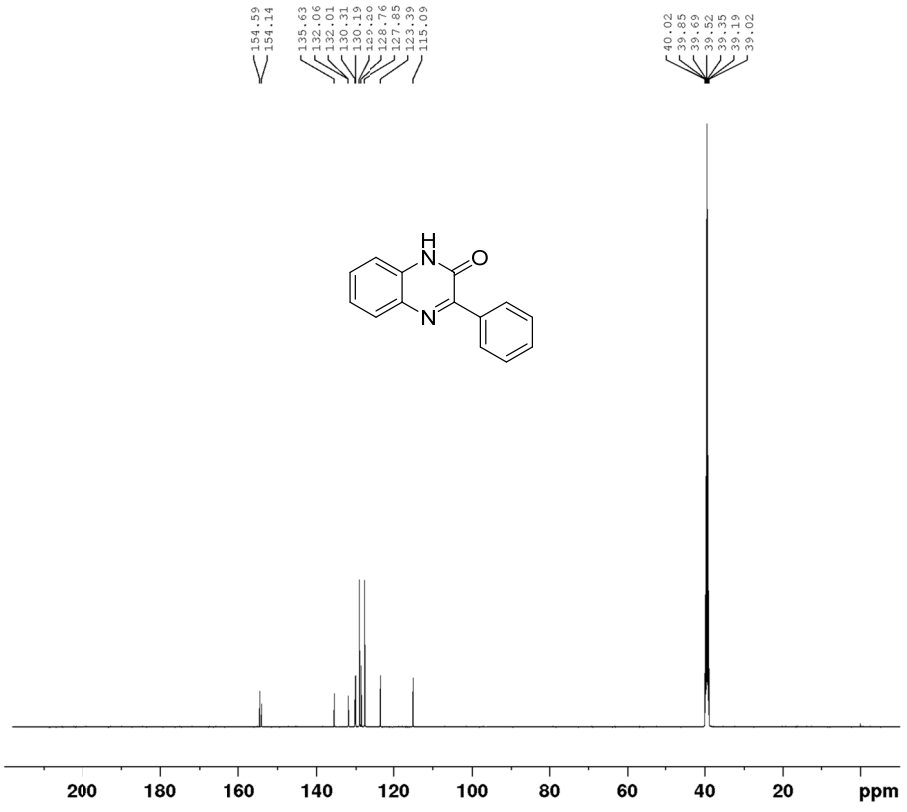



```
Current Data Parameters
NAME                 new-kwt
EXPNO                     19
PROCNO                     1

F2 - Acquisition Parameters
Date_              20210502
Time                  20.14
INSTRUM                spect
PROBHD    5 mm DUL 13C-1
PULPROG              zgpg30
TD                    65536
SOLVENT                DMSO
NS                      978
DS                        4
SWH               18028.846 Hz
FIDRES            0.275098 Hz
AQ                1.8175317 sec
RG                   209.09
DW                  27.733 usec
DE                   6.50 usec
TE                  298.3 K
D1              2.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     13C
P1                    11.00 usec
PL1                  120.00 dB
PL1W       0 W
SFO1            75.4752949 MHz

F2 - Processing parameters
SI                    32768
SF             75.4677846 MHz
WDW                      EM
SSB        0
LB                    1.00 Hz
GB         0
PC                    1.40
```

Figure S11. ^{1}H NMR and ^{13}C NMR spectra of **1k**

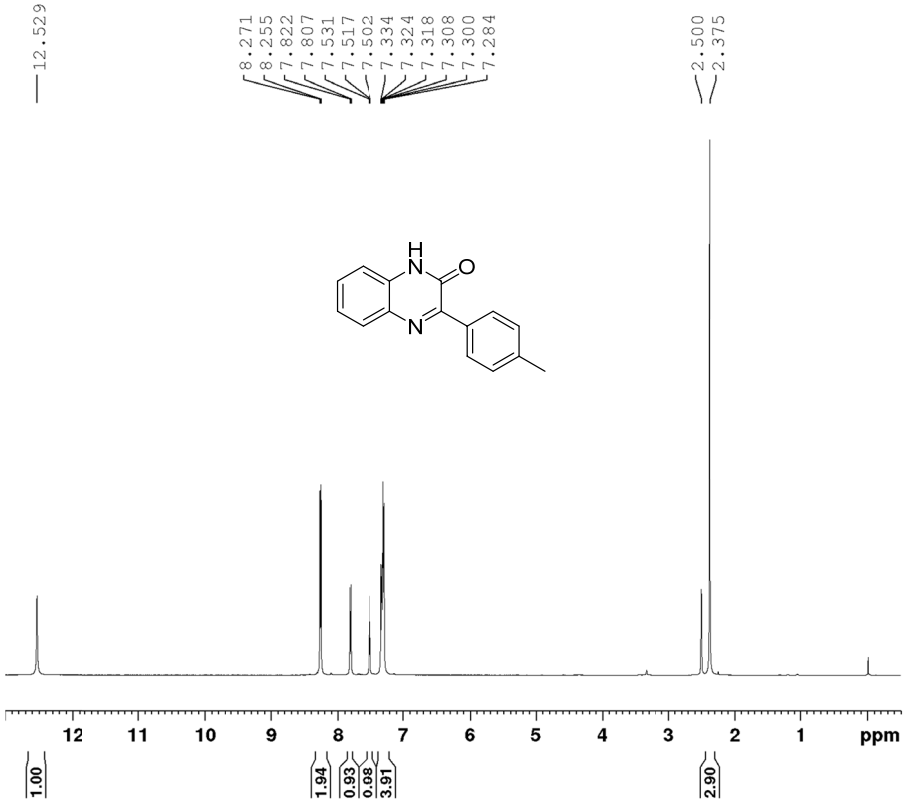



```
Current Data Parameters
NAME            new-kwt
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20210119
Time               1.41
INSTRUM           spect
PROBHD   5 mm CPPBBO BB
PULPROG            zg30
TD                65536
SOLVENT            DMSO
NS                   16
DS                    2
SWH           10000.000 Hz
FIDRES        0.152588 Hz
AQ            3.2767999 sec
RG                62.06
DW               50.000 usec
DE                6.50 usec
TE               298.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.59 usec
PL1              120.00 dB
PL1W     0 W
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                65536
SF          500.1300041 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

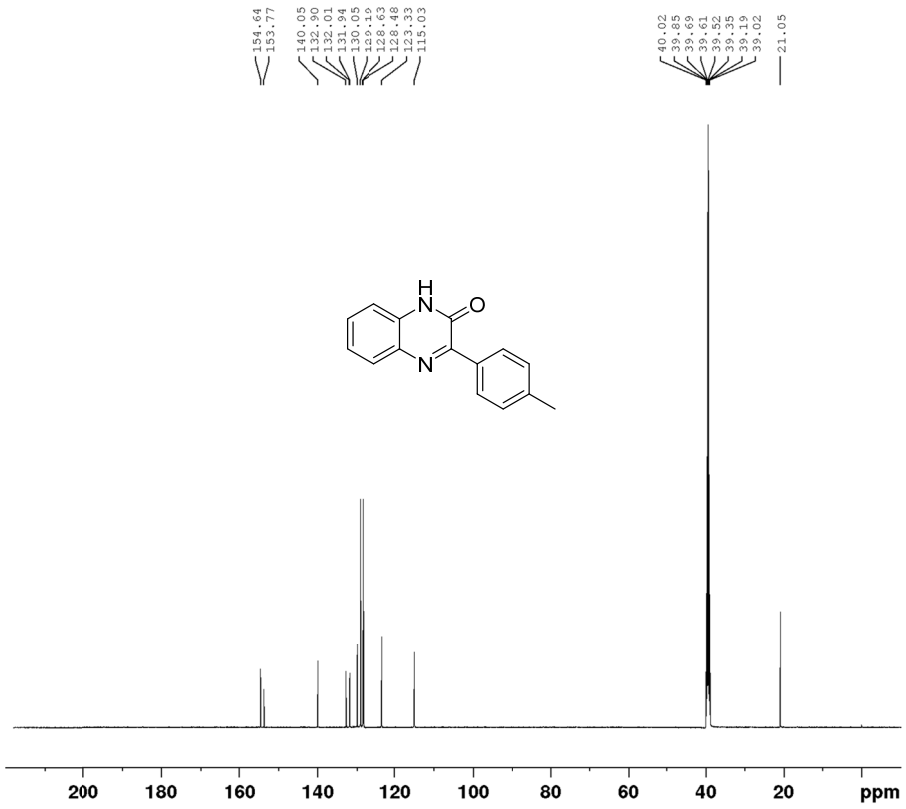



```
Current Data Parameters
NAME            new-kwt
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20210119
Time               2.35
INSTRUM           spect
PROBHD   5 mm CPPBBO BB
PULPROG          zgpg30
TD                65536
SOLVENT            DMSO
NS                 1024
DS                    4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010048 sec
RG                192.89
DW               16.800 usec
DE                18.00 usec
TE               298.2 K
D1           2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                9.80 usec
PL1              120.00 dB
PL1W     0 W
SFO1        125.7703637 MHz

F2 - Processing parameters
SI                32768
SF          125.7578486 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

Figure S12. ^{1}H NMR and ^{13}C NMR spectra of **1l**

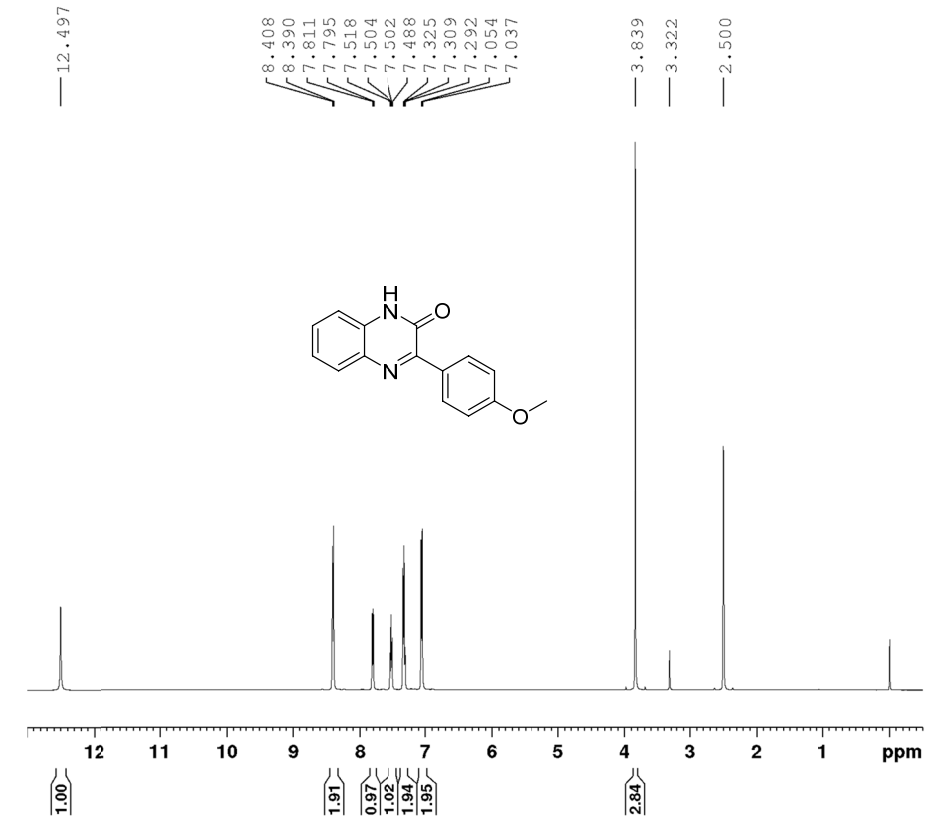



```
Current Data Parameters
NAME                 new-kwt
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_               20210209
Time                    4.04
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                        16
DS                         2
SWH               10000.000 Hz
FIDRES                0.152588 Hz
AQ                3.2767999 sec
RG                     49.27
DW                    50.000 usec
DE                     6.50 usec
TE                     298.2 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     10.59 usec
PL1                   120.00 dB
PL1W      0 W
SFO1             500.1330885 MHz

F2 - Processing parameters
SI                        65536
SF               500.1300036 MHz
WDW                       EM
SSB       0
LB                     0.30 Hz
GB        0
PC                     1.00
```

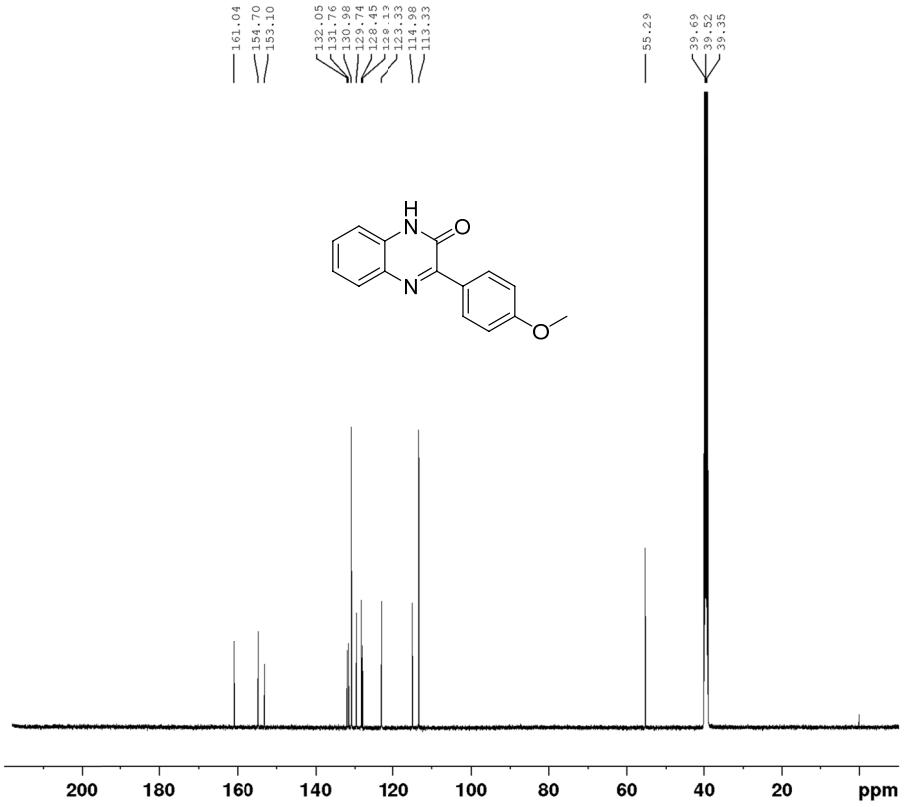



```
Current Data Parameters
NAME                 new-kwt
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_               20210209
Time                    4.58
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG              zgpg30
TD                    65536
SOLVENT                DMSO
NS                     1024
DS                         4
SWH               29761.904 Hz
FIDRES                0.454131 Hz
AQ                1.1010048 sec
RG                     192.89
DW                    16.800 usec
DE                     18.00 usec
TE                     298.2 K
D1                2.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      13C
P1                     9.80 usec
PL1                   120.00 dB
PL1W      0 W
SFO1             125.7703637 MHz

F2 - Processing parameters
SI                        32768
SF               125.7578482 MHz
WDW                       EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     1.40
```

Figure S13. ^{1}H NMR and ^{13}C NMR spectra of **1m**

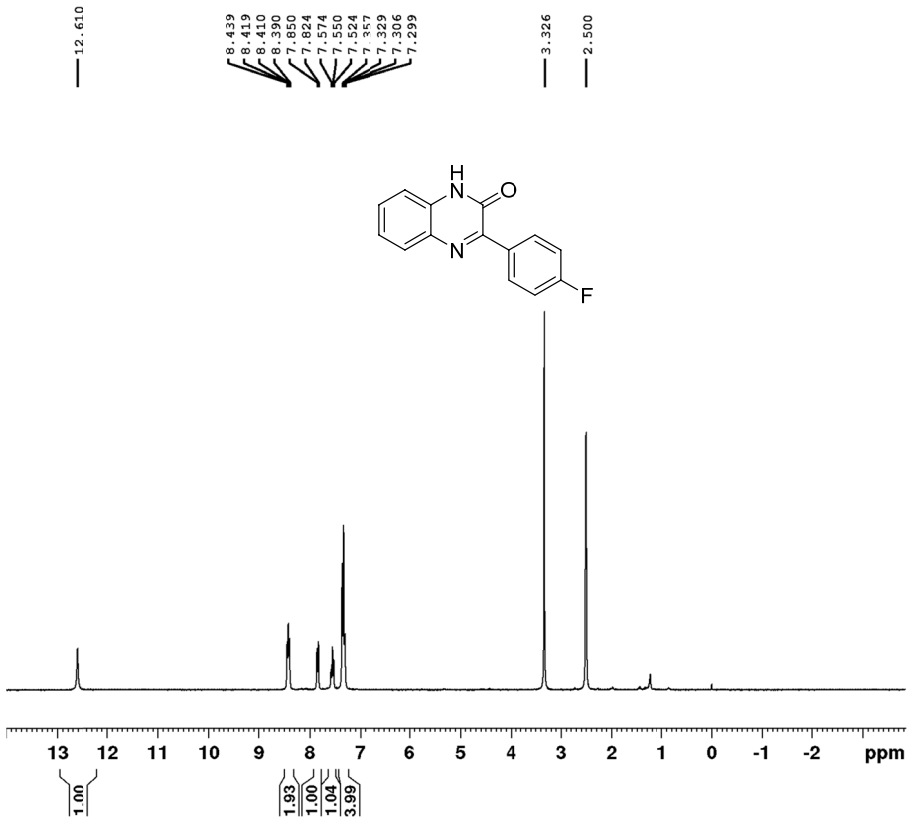



```
Current Data Parameters
NAME                  new-kwt
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20210209
Time                  12.00
INSTRUM               spect
PROBHD     5 mm CPPBBO BB
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       16
DS                        2
SWH              10000.000 Hz
FIDRES               0.152588 Hz
AQ                3.2767999 sec
RG                     82.06
DW                   50.000 usec
DE                    6.50 usec
TE                   298.2 K
D1               1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      10.59 usec
PL1                    120.00 dB
PL1W        0 W
SFO1            500.1330885 MHz

F2 - Processing parameters
SI                        65536
SF              500.1300039 MHz
WDW                       EM
SSB         0
LB                     0.30 Hz
GB          0
PC                     1.00
```

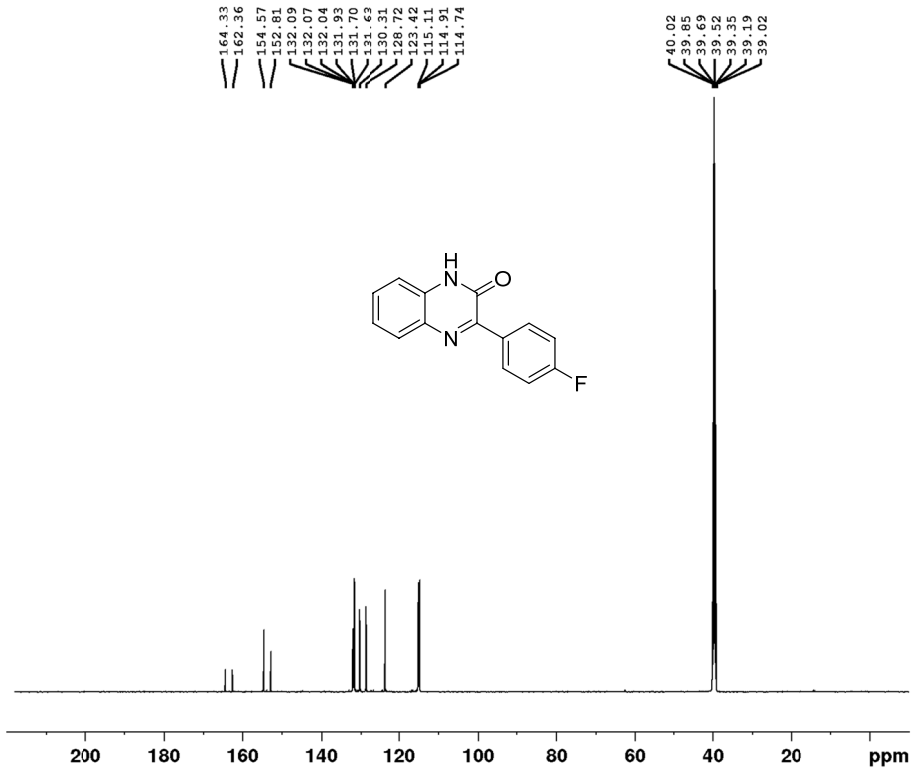



```
Current Data Parameters
NAME                  new-kwt
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_              20210209
Time                  12.55
INSTRUM               spect
PROBHD     5 mm CPPBBO BB
PULPROG             zgpg30
TD                    65536
SOLVENT                DMSO
NS                     1024
DS                        4
SWH              29761.904 Hz
FIDRES               0.454131 Hz
AQ                1.1010048 sec
RG                    192.89
DW                   16.800 usec
DE                    18.00 usec
TE                   298.2 K
D1               2.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                      9.80 usec
PL1                    120.00 dB
PL1W        0 W
SFO1            125.7703637 MHz

F2 - Processing parameters
SI                        32768
SF              125.7578482 MHz
WDW                       EM
SSB         0
LB                     1.00 Hz
GB          0
PC                     1.40
```

Figure S14. ^{1}H NMR and ^{13}C NMR spectra of **1n**

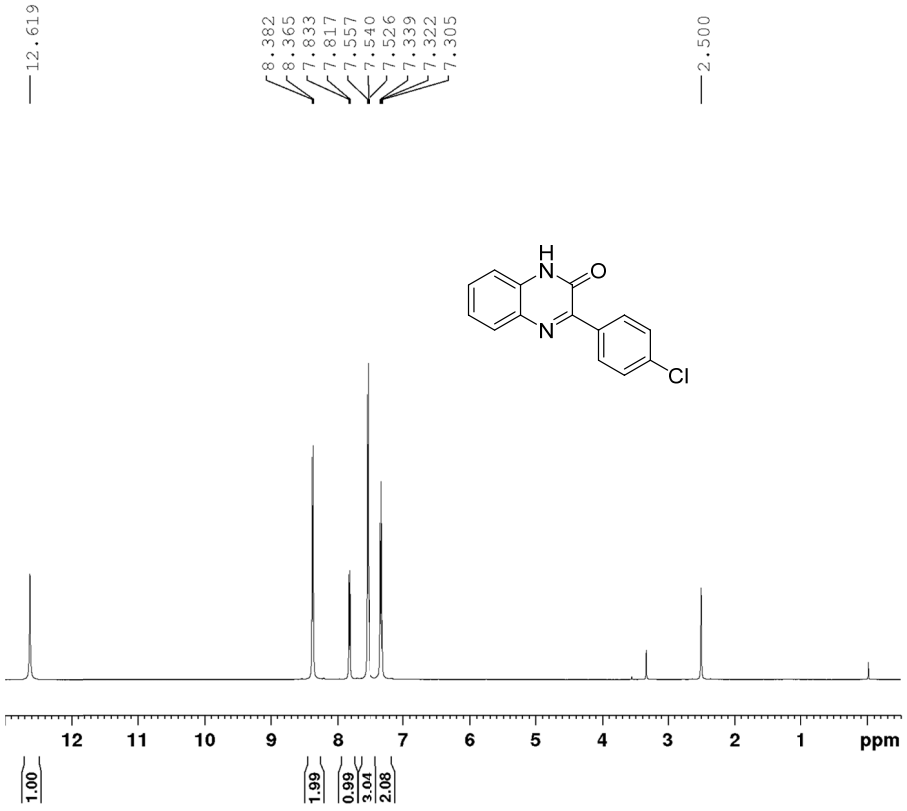



```
Current Data Parameters
NAME          zhangshuxin
EXPNO                 830
PROCNO                  1

F2 - Acquisition Parameters
Date_           20211019
Time               9.19 h
INSTRUM             spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT             DMSO
NS                    16
DS                     2
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ              5.4525952 sec
RG                 209.09
DW                 83.200 usec
DE                  6.50 usec
TE                 297.3 K
D1             1.00000000 sec
TD0                    1
SFO1          300.1318534 MHz
NUC1                  1H
P1                  8.00 usec
PLW1         18.00000000 W

F2 - Processing parameters
SI                 65536
SF            300.1300024 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

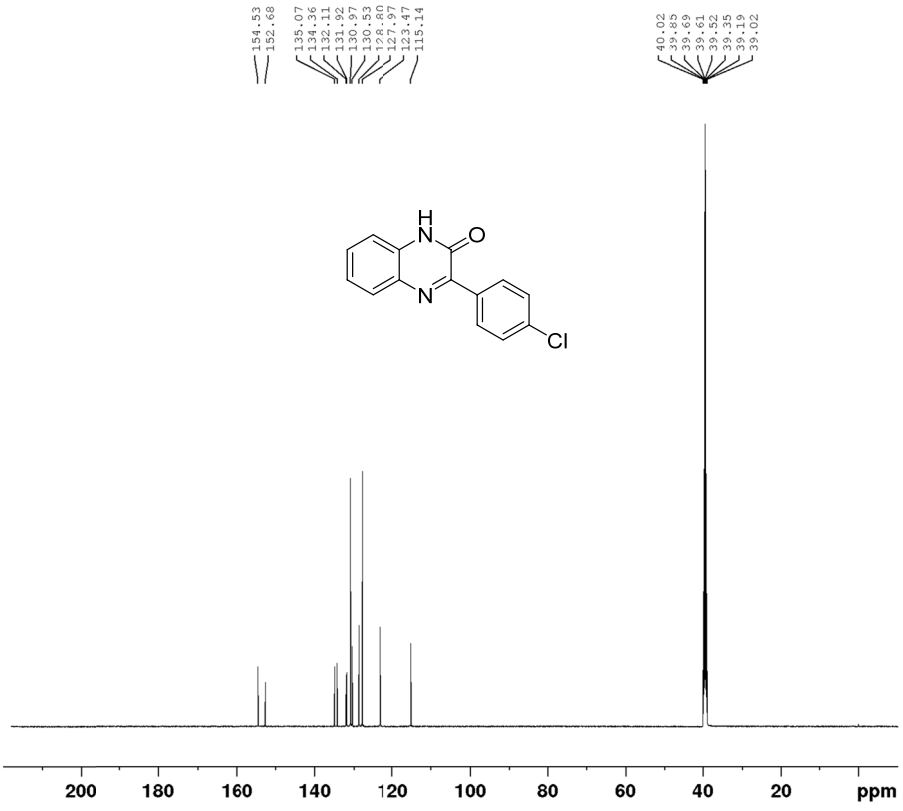



```
Current Data Parameters
NAME          500MHz-2021
EXPNO                  27
PROCNO                  1

F2 - Acquisition Parameters
Date_           20211018
Time               4.57 h
INSTRUM             spect
PROBHD   5 mm CPPBBO BB
PULPROG            zgpg30
TD                 65536
SOLVENT             DMSO
NS                  5000
DS                     4
SWH            29761.904 Hz
FIDRES          0.908261 Hz
AQ              1.1010048 sec
RG                 192.89
DW                 16.800 usec
DE                 18.00 usec
TE                 298.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                    1
SFO1          125.7703637 MHz
NUC1                  13C
P1                  9.80 usec
PLW1         57.00000000 W
SFO2          500.1320005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2         20.00000000 W
PLW12         0.35778001 W
PLW13         0.22898000 W

F2 - Processing parameters
SI                 32768
SF            125.7578470 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Figure S15. ^{1}H NMR and ^{13}C NMR spectra of **1o**

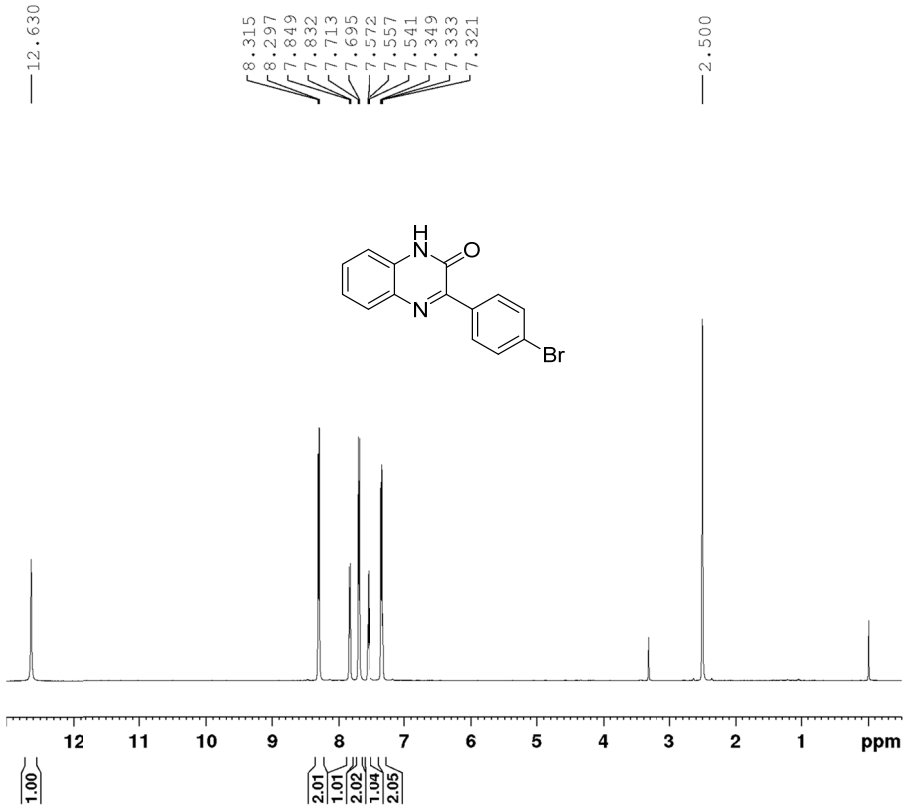



```
Current Data Parameters
NAME                  new-kwt
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20210209
Time                    2.06
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG                 zg30
TD                     65536
SOLVENT                 DMSO
NS                        16
DS                         2
SWH               10000.000 Hz
FIDRES             0.152588 Hz
AQ                3.2767999 sec
RG                     55.37
DW                  50.000 usec
DE                   6.50 usec
TE                   298.2 K
D1                1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      10.59 usec
PL1                    120.00 dB
PL1W       0 W
SFO1           500.1330885 MHz

F2 - Processing parameters
SI                         65536
SF              500.1300037 MHz
WDW                        EM
SSB        0
LB                      0.30 Hz
GB         0
PC                      1.00
```

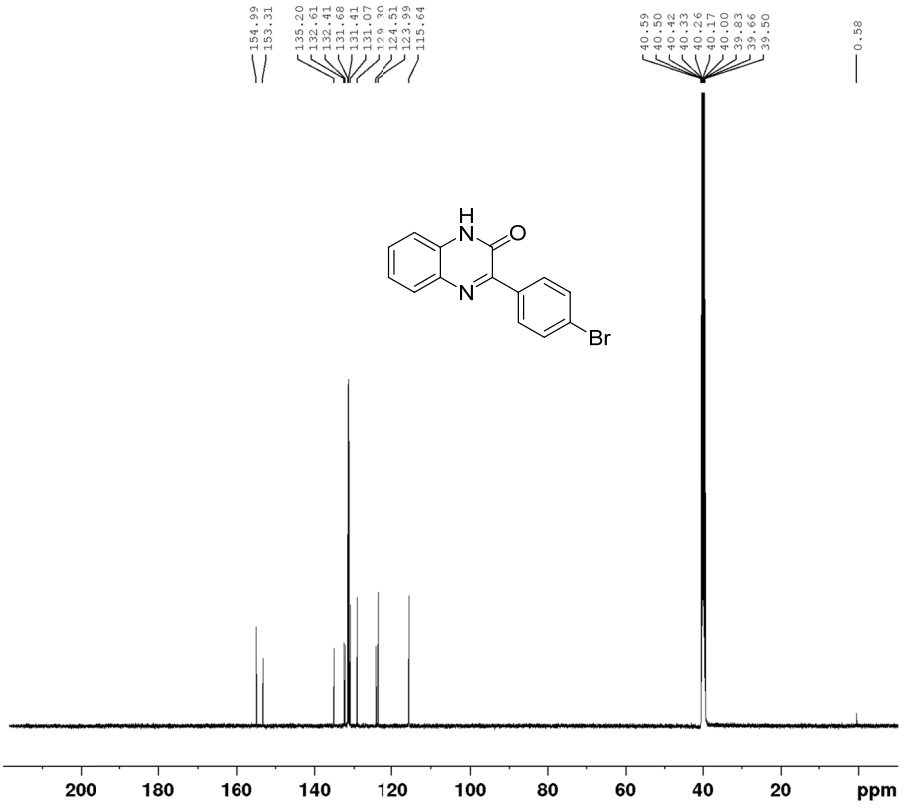



```
Current Data Parameters
NAME                  new-kwt
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_              20210209
Time                    3.01
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG              zgpg30
TD                     65536
SOLVENT                 DMSO
NS                      1024
DS                         4
SWH               29761.904 Hz
FIDRES             0.454131 Hz
AQ                1.1010048 sec
RG                    192.89
DW                  16.800 usec
DE                   18.00 usec
TE                   298.2 K
D1                2.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                      9.80 usec
PL1                    120.00 dB
PL1W       0 W
SFO1           125.7703637 MHz

F2 - Processing parameters
SI                         32768
SF              125.7573482 MHz
WDW                        EM
SSB        0
LB                      1.00 Hz
GB         0
PC                      1.40
```

Figure S16. ^{1}H NMR and ^{13}C NMR spectra of **1p**

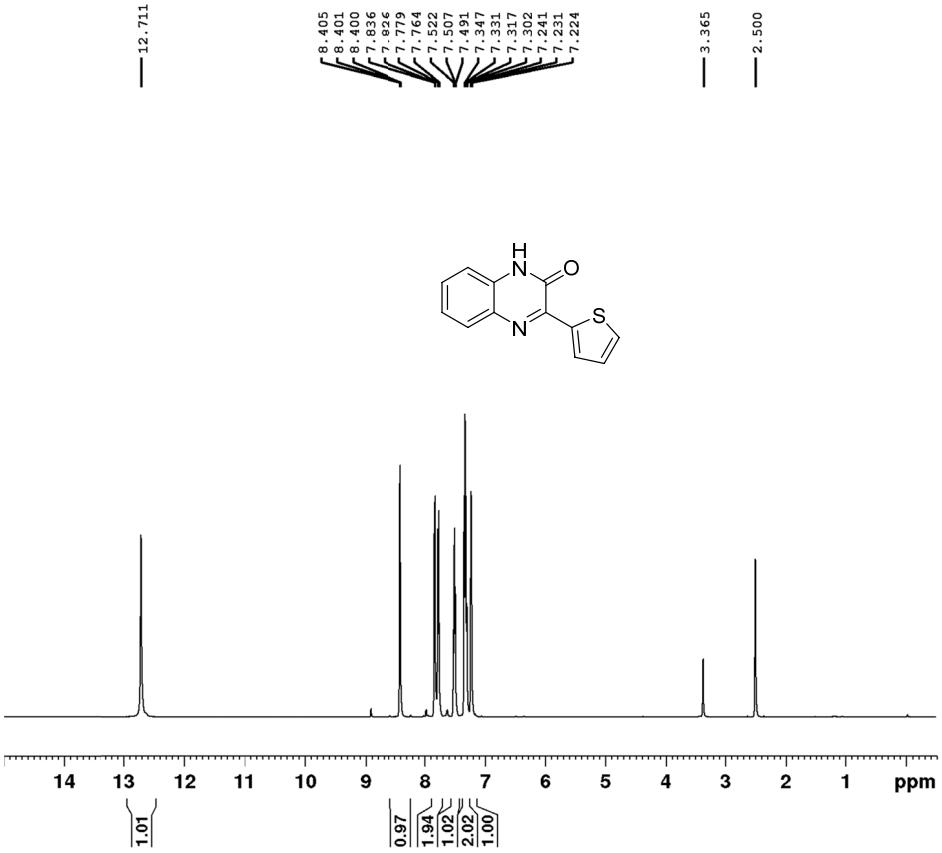



```
Current Data Parameters
NAME              new-kwt
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210209
Time                3.05
INSTRUM            spect
PROBHD    5 mm CPPBBO BB
PULPROG             zg30
TD                 65536
SOLVENT             DMSO
NS                    16
DS                     2
SWH            10000.000 Hz
FIDRES          0.152588 Hz
AQ             3.2767999 sec
RG                 62.06
DW                50.000 usec
DE                 6.50 usec
TE                298.2 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.59 usec
PL1               120.00 dB
PL1W      0 W
SFO1         500.1330885 MHz

F2 - Processing parameters
SI                 65536
SF           500.1300041 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

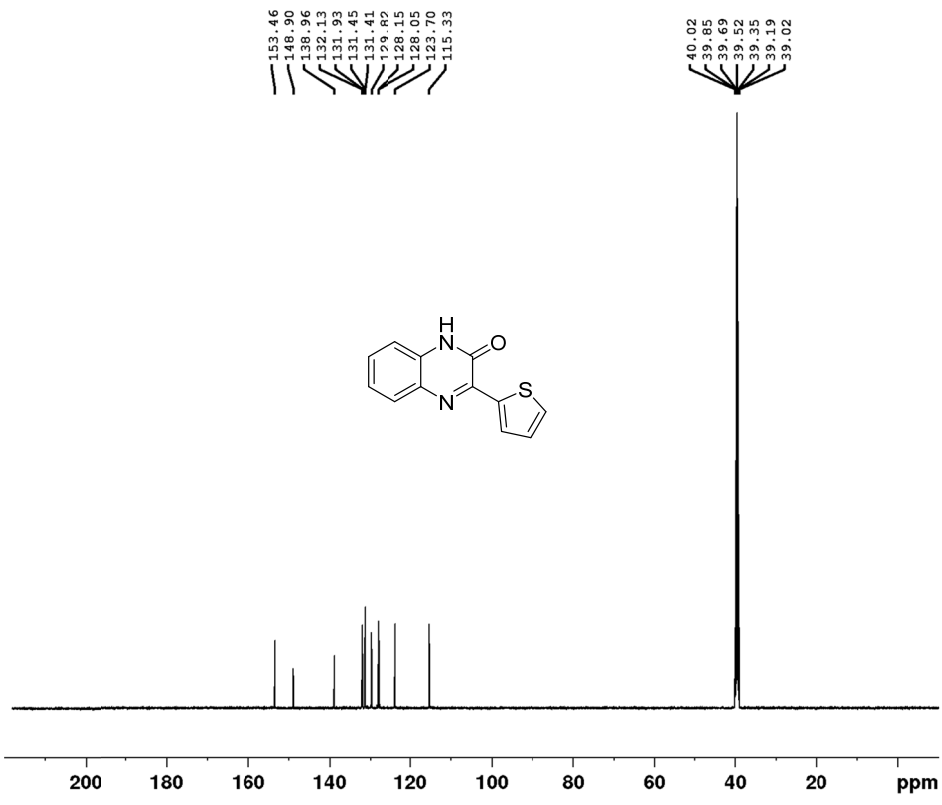



```
Current Data Parameters
NAME              new-kwt
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210209
Time                4.00
INSTRUM            spect
PROBHD    5 mm CPPBBO BB
PULPROG          zgpg30
TD                 65536
SOLVENT             DMSO
NS                  1024
DS                     4
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ             1.1010048 sec
RG                 192.89
DW                16.800 usec
DE                10.00 usec
TF                298.2 K
D1             2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                  9.80 usec
PL1               120.00 dB
PL1W      0 W
SFO1         125.7703637 MHz

F2 - Processing parameters
SI                 32768
SF           125.7577885 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

Figure S17. ^{1}H NMR and ^{13}C NMR spectra of **1q**

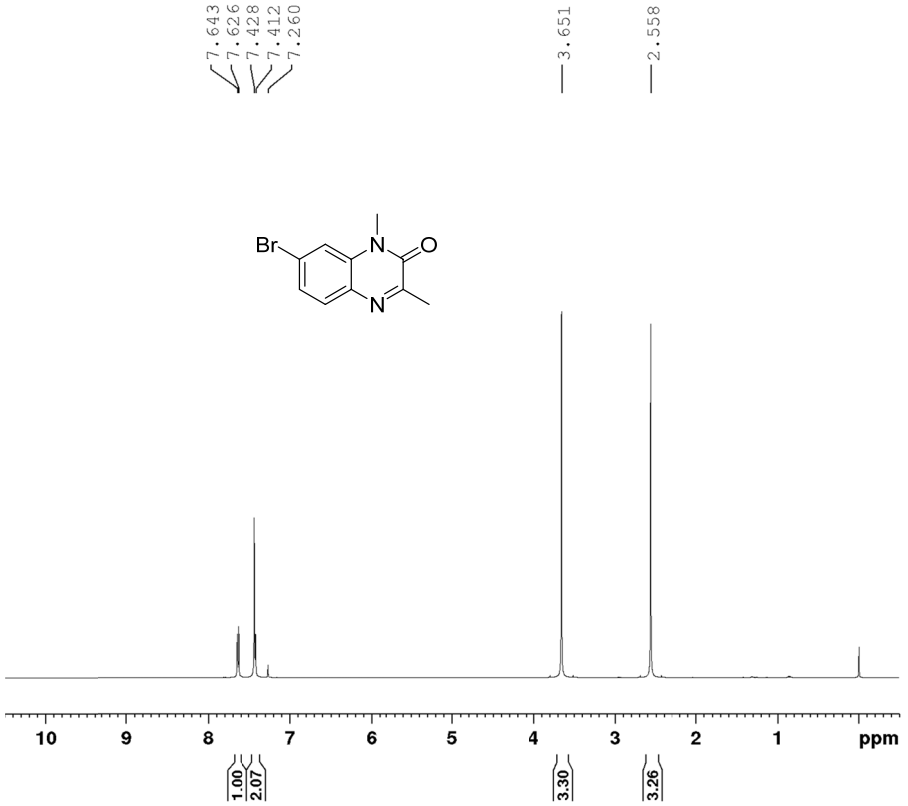



```
Current Data Parameters
NAME          500MHz-2021
EXPNO                  28
PROCNO                  1

F2 - Acquisition Parameters
Date_           20211123
Time               23.18 h
INSTRUM             spect
PROBHD   5 mm CPPBBO BB
PULPROG             zg30
TD                 65536
SOLVENT              DMSO
NS                     16
DS                      2
SWH            10000.000 Hz
FIDRES             0.305176 Hz
AQ                 3.2767999 sec
RG                    62.06
DW                 50.000 usec
DE                  6.50 usec
TE                     0 K
D1              1.00000000 sec
TD0                     1
SFO1           500.1330885 MHz
NUC1                   1H
P1                 10.59 usec
PLW1           20.00000000 W

F2 - Processing parameters
SI                 65536
SF            500.1300008 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

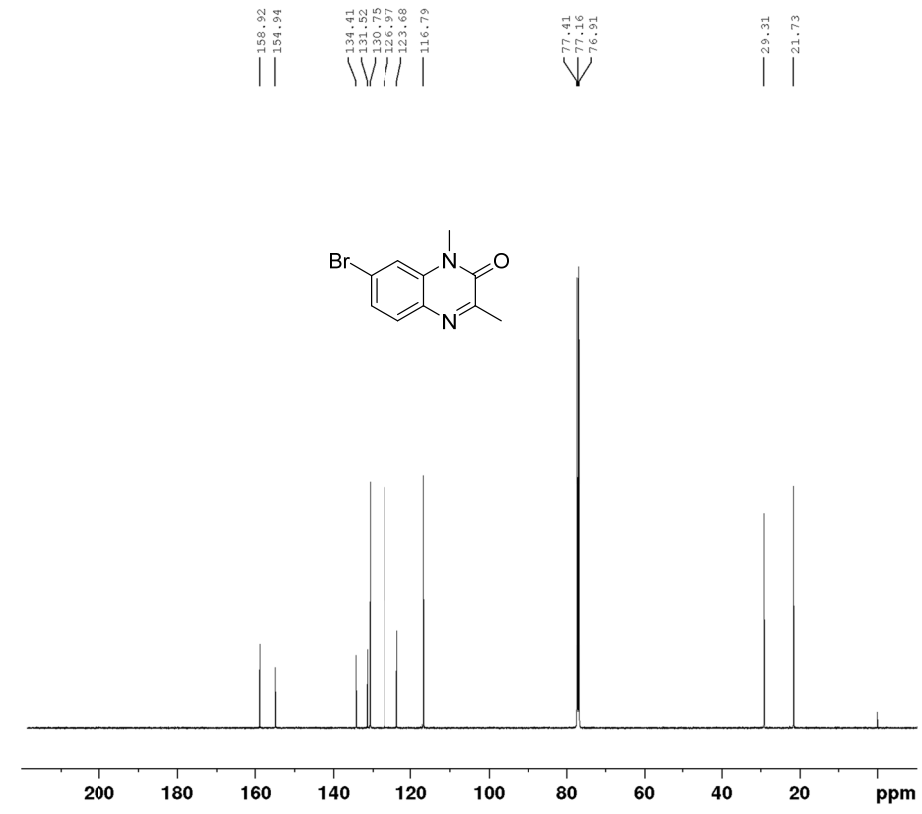



```
Current Data Parameters
NAME          500MHz-2021
EXPNO                  29
PROCNO                  1

F2 - Acquisition Parameters
Date_           20211123
Time               23.23 h
INSTRUM             spect
PROBHD   5 mm CPPBBO BB
PULPROG           zgpg30
TD                 65536
SOLVENT              DMSO
NS                    167
DS                      4
SWH            29761.904 Hz
FIDRES             0.908261 Hz
AQ                 1.1010048 sec
RG                   192.89
DW                 16.800 usec
DE                  18.00 usec
TE                     0 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                     1
SFO1           125.7703637 MHz
NUC1                   13C
P1                  9.80 usec
PLW1           57.00000000 W
SFO2           500.1320005 MHz
NUC2                   1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2           20.00000000 W
PLW12           0.35778001 W
PLW13           0.22898000 W

F2 - Processing parameters
SI                 32768
SF            125.7578422 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Figure S18. ^{1}H NMR and ^{13}C NMR spectra of **1r**

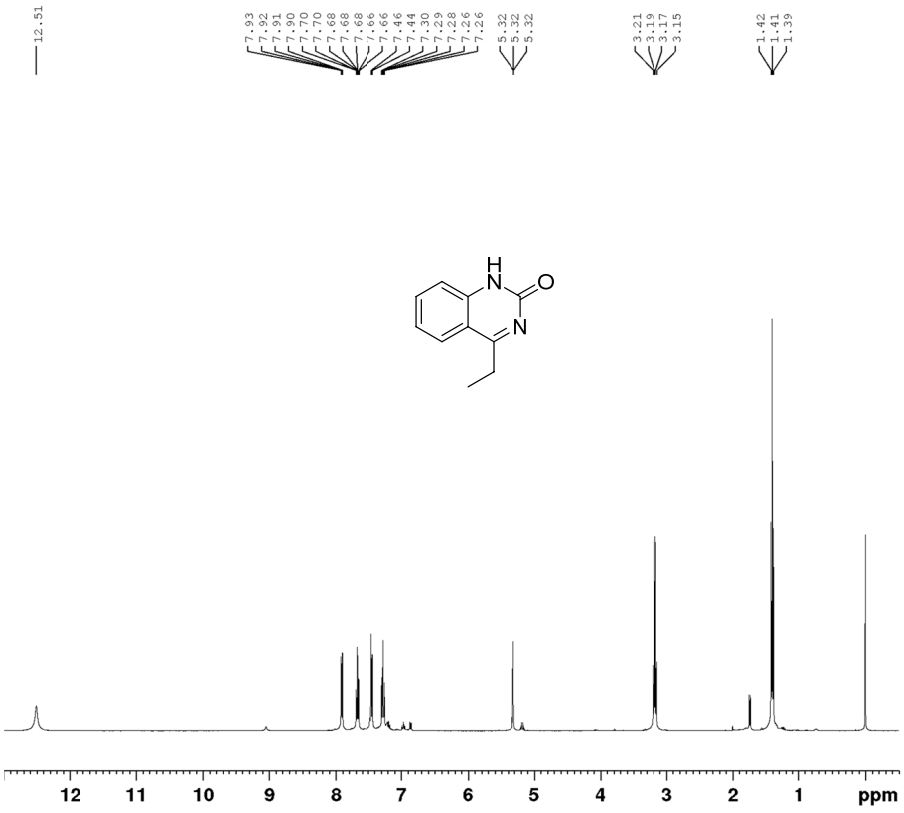



```
Current Data Parameters
NAME                 new-kwt
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20210209
Time                 13.58
INSTRUM              spect
PROBHD    5 mm CPPBBO BB
PULPROG              zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH              10000.000 Hz
FIDRES           0.152588 Hz
AQ               3.2767999 sec
RG                   49.27
DW                 50.000 usec
DE                  6.50 usec
TE                  298.2 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   10.59 usec
PL1                 120.00 dB
PL1W       0 W
SFO1          500.1330885 MHz

F2 - Processing parameters
SI                   65536
SF            500.1300123 MHz
WDW                     EM
SSB        0
LB                   0.30 Hz
GB         0
PC                   1.00
```

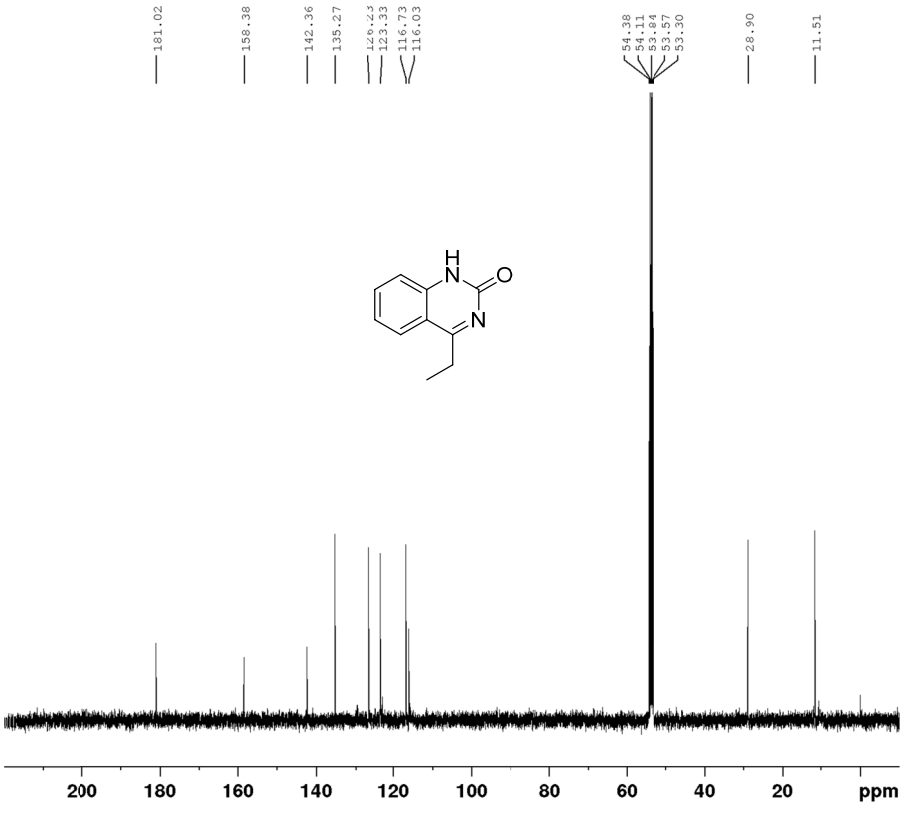



```
Current Data Parameters
NAME                 new-kwt
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20210209
Time                 14.52
INSTRUM              spect
PROBHD    5 mm CPPBBO BB
PULPROG              zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH              29761.904 Hz
FIDRES           0.454131 Hz
AQ               1.1010048 sec
RG                   192.89
DW                 16.800 usec
DE                  18.00 usec
TE                  298.2 K
D1              2.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.80 usec
PL1                 120.00 dB
PL1W       0 W
SFO1          125.7703637 MHz

F2 - Processing parameters
SI                   32768
SF            125.7577737 MHz
WDW                     EM
SSB        0
LB                   1.00 Hz
GB         0
PC                   1.40
```

Figure S19. ^{1}H NMR and ^{13}C NMR spectra of **3a**

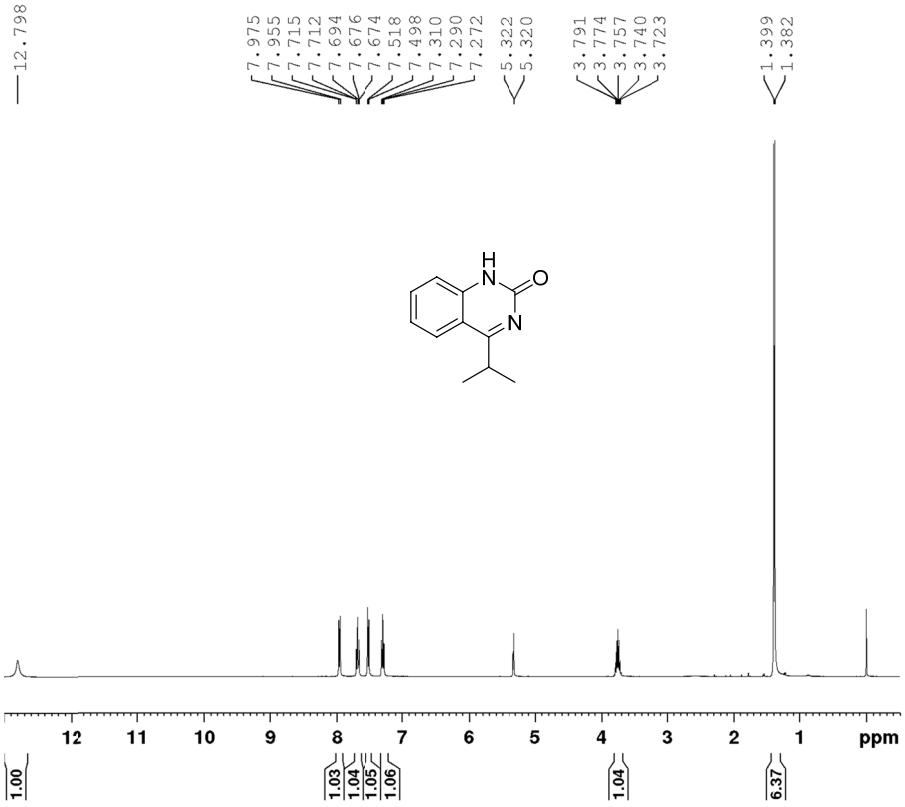



```
Current Data Parameters
NAME                 new-kzt
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_               20210404
Time                   17.06
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT              CD2Cl2
NS                        16
DS                         2
SWH                8012.820 Hz
FIDRES                0.122266 Hz
AQ                 4.0894465 sec
RG                    120.86
DW                   62.400 usec
DE                    6.50 usec
TE                   299.3 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             400.1324710 MHz
NUC1                       1H
P1                    10.00 usec
PLW1              13.26099968 W

F2 - Processing parameters
SI                        65536
SF               400.1300154 MHz
WDW                        EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```

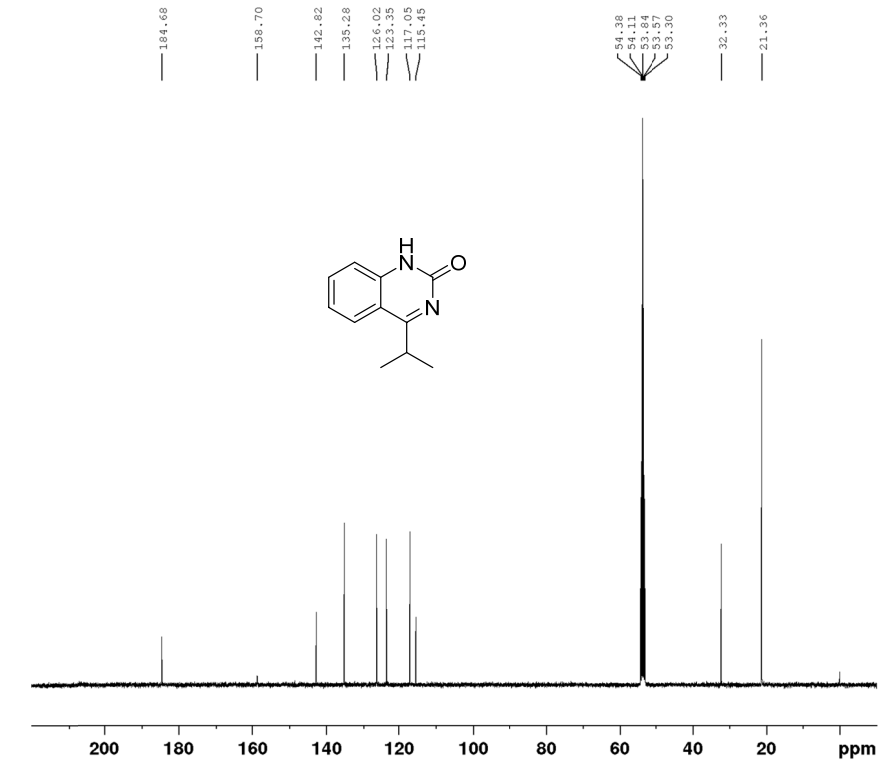



```
Current Data Parameters
NAME                 new-kzt
EXPNO                     20
PROCNO                     1

F2 - Acquisition Parameters
Date_               20210404
Time                   18.44
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG              zgpg30
TD                    65536
SOLVENT              CD2Cl2
NS                       300
DS                         4
SWH               24038.461 Hz
FIDRES                0.366798 Hz
AQ                 1.3631488 sec
RG                    199.89
DW                   20.800 usec
DE                    6.50 usec
TE                   300.1 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             100.6228293 MHz
NUC1                      13C
P1                    10.00 usec
PLW1              56.93000031 W

======== CHANNEL f2 ========
SFO2             400.1316005 MHz
NUC2                       1H
CPDPRG[2               waltz16
PCPD2                 90.00 usec
PLW2              13.26099968 W
PLW12              0.16372000 W
PLW13              0.13260999 W

F2 - Processing parameters
SI                        32768
SF               100.6127259 MHz
WDW                        EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```

Figure S20. ^{1}H NMR and ^{13}C NMR spectra of **3b**

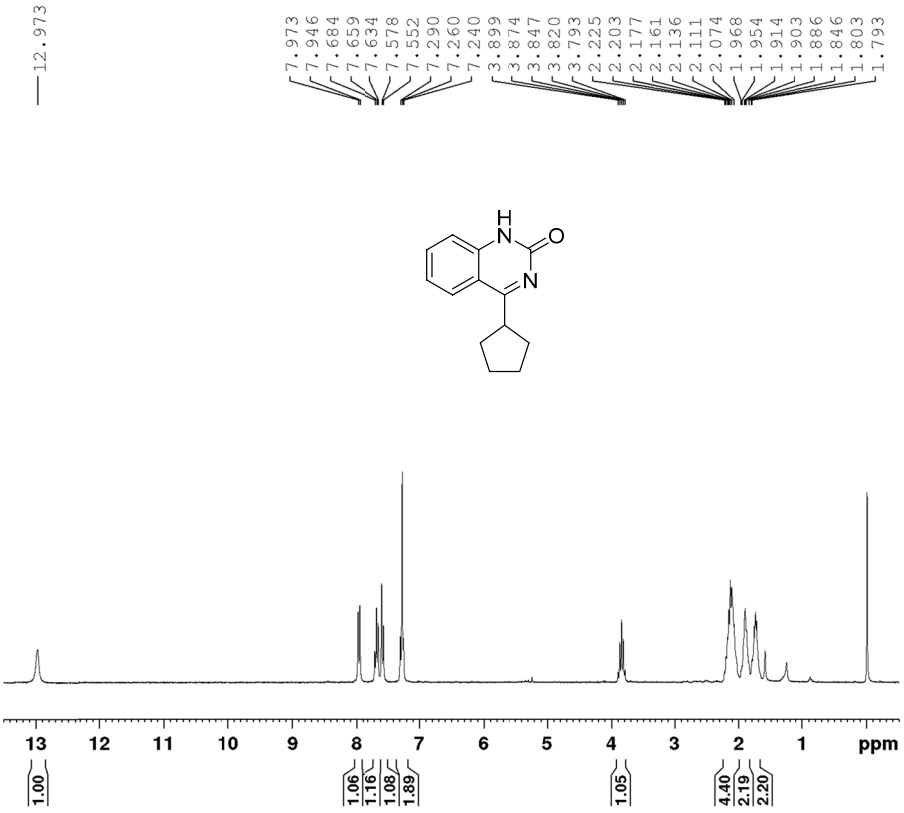



```
Current Data Parameters
NAME                  new-kzt
EXPNO                      20
PROCNO                      1

F2 - Acquisition Parameters
Date_               20210405
Time                   23.43
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                 zg30
TD                     65536
SOLVENT             CD2Cl2
NS                         16
DS                          2
SWH                 8012.820 Hz
FIDRES              0.122266 Hz
AQ                  4.0894465 sec
RG                      89.48
DW                     62.400 usec
DE                      6.50 usec
TE                     299.7 K
D1                  1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1              400.1324710 MHz
NUC1                       1H
P1                      10.00 usec
PLW1             13.26099968 W

F2 - Processing parameters
SI                         65536
SF                400.1300153 MHz
WDW                           no
SSB          0
LB           0 Hz
GB           0
PC                        1.00
```

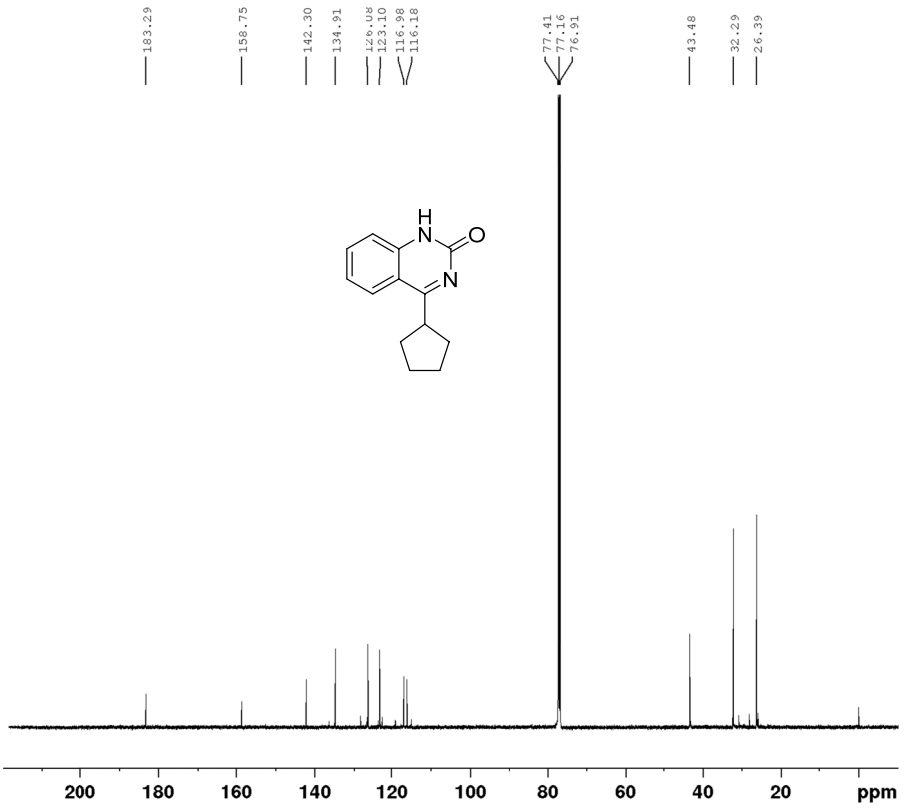



```
Current Data Parameters
NAME                  new-kzt
EXPNO                      21
PROCNO                      1

F2 - Acquisition Parameters
Date_               20210406
Time                    0.43
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG              zgpg30
TD                     65536
SOLVENT             CD2Cl2
NS                       1024
DS                          4
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631488 sec
RG                     199.89
DW                     20.800 usec
DE                      6.50 usec
TE                     300.2 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1              100.6228293 MHz
NUC1                       13C
P1                      10.00 usec
PLW1             56.93000031 W

======== CHANNEL f2 ========
SFO2              400.1316005 MHz
NUC2                       1H
CPDPRG[2              waltz16
PCPD2                   90.00 usec
PLW2             13.26099968 W
PLW12             0.16372000 W
PLW13             0.13260999 W

F2 - Processing parameters
SI                         32768
SF                100.6127264 MHz
WDW                           EM
SSB          0
LB                      1.00 Hz
GB           0
PC                        1.40
```

Figure S21. ^{1}H NMR and ^{13}C NMR spectra of **3c**

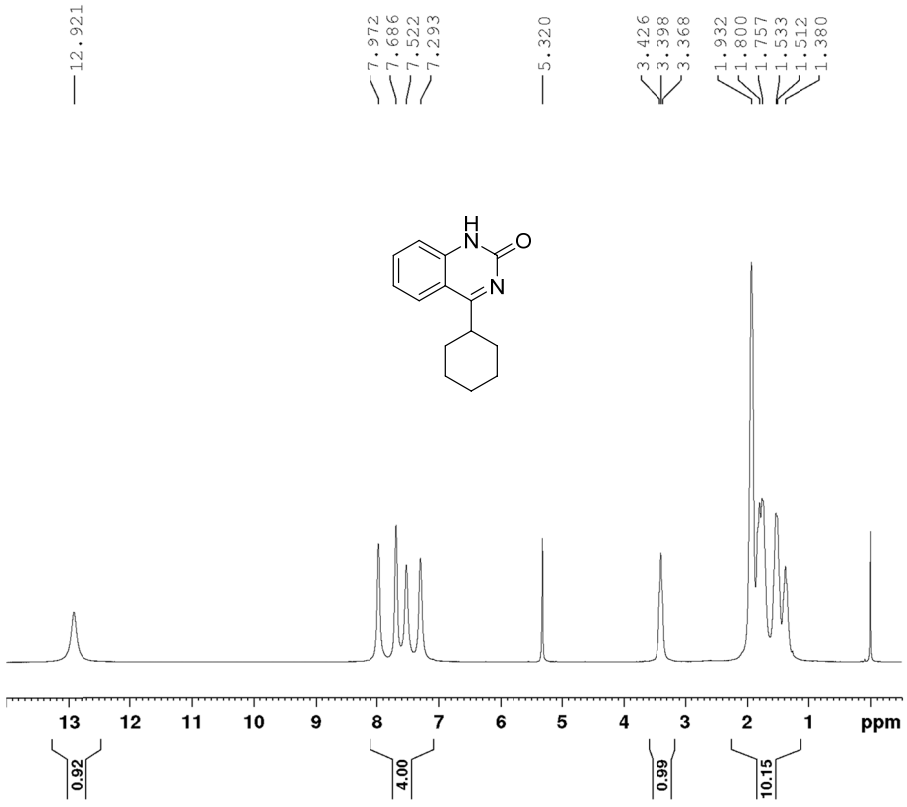



```
Current Data Parameters
NAME                  new-kzt
EXPNO                       3
PROCNO                      1

F2 - Acquisition Parameters
Date_               20210315
Time                   11.18
INSTRUM                spect
PROBHD    5 mm DUL 13C-1
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                6009.615 Hz
FIDRES            0.091699 Hz
AQ                5.4525952 sec
RG                     209.09
DW                   83.200 usec
DE                    6.50 usec
TE                    298.3 K
D1                1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                       8.00 usec
PL1                    120.00 dB
PL1W          0 W
SFO1             300.1318534 MHz

F2 - Processing parameters
SI                         65536
SF               300.1300073 MHz
WDW                        EM
SSB           0
LB                      0.30 Hz
GB            0
PC                      1.00
```

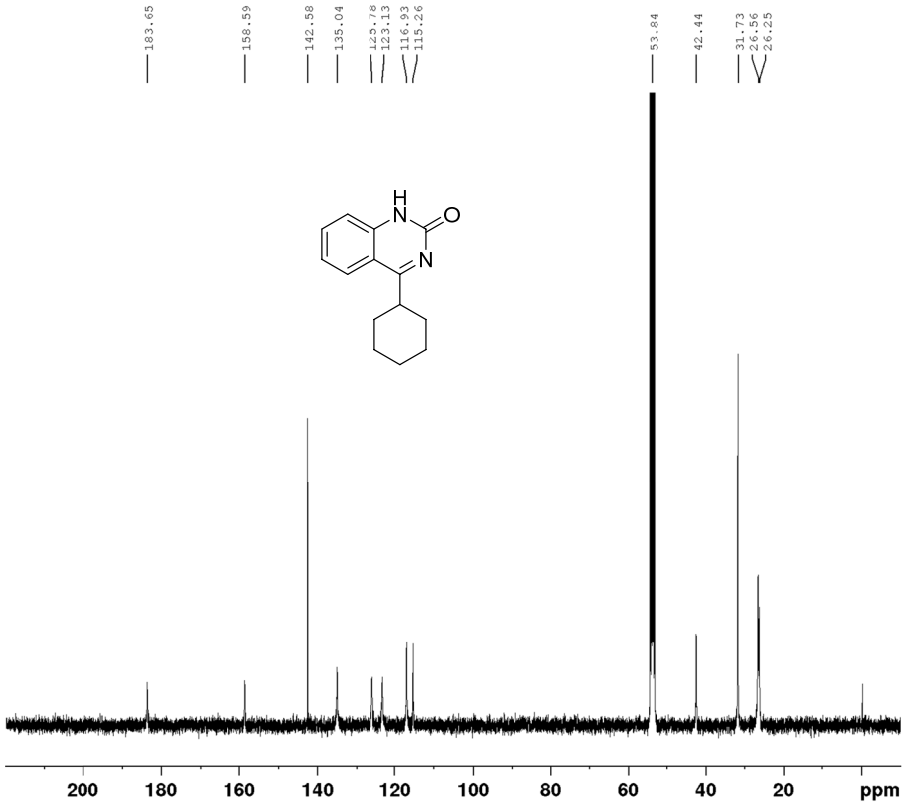



```
Current Data Parameters
NAME                  new-kzt
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_               20210315
Time                   14.42
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG             zgpg30
TD                     65536
SOLVENT                CDCl3
NS                      1024
DS                         4
SWH               29761.904 Hz
FIDRES            0.454131 Hz
AQ                1.1010048 sec
RG                     192.89
DW                   16.800 usec
DE                   18.00 usec
TE                    298.2 K
D1                2.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                       9.80 usec
PL1                    120.00 dB
PL1W          0 W
SFO1             125.7703637 MHz

F2 - Processing parameters
SI                         32768
SF               125.7577735 MHz
WDW                        EM
SSB           0
LB                      1.00 Hz
GB            0
PC                      1.40
```

Figure S22. ^{1}H NMR and ^{13}C NMR spectra of **3d**

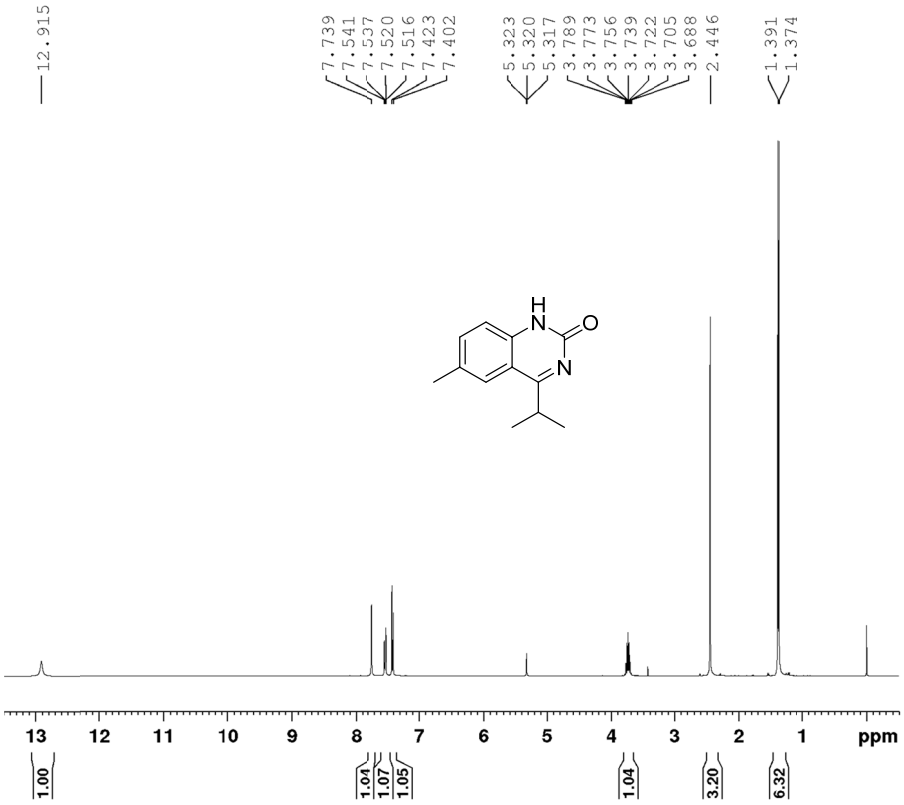



```
Current Data Parameters
NAME            new-kzt
EXPNO                30
PROCNO                1

F2 - Acquisition Parameters
Date_          20210405
Time              22.39
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CD2Cl2
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ             4.0894465 sec
RG                48.22
DW               62.400 usec
DE                6.50 usec
TE               299.7 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                 1H
P1                10.00 usec
PLW1         13.26099968 W

F2 - Processing parameters
SI                65536
SF           400.1300153 MHz
WDW                  EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```

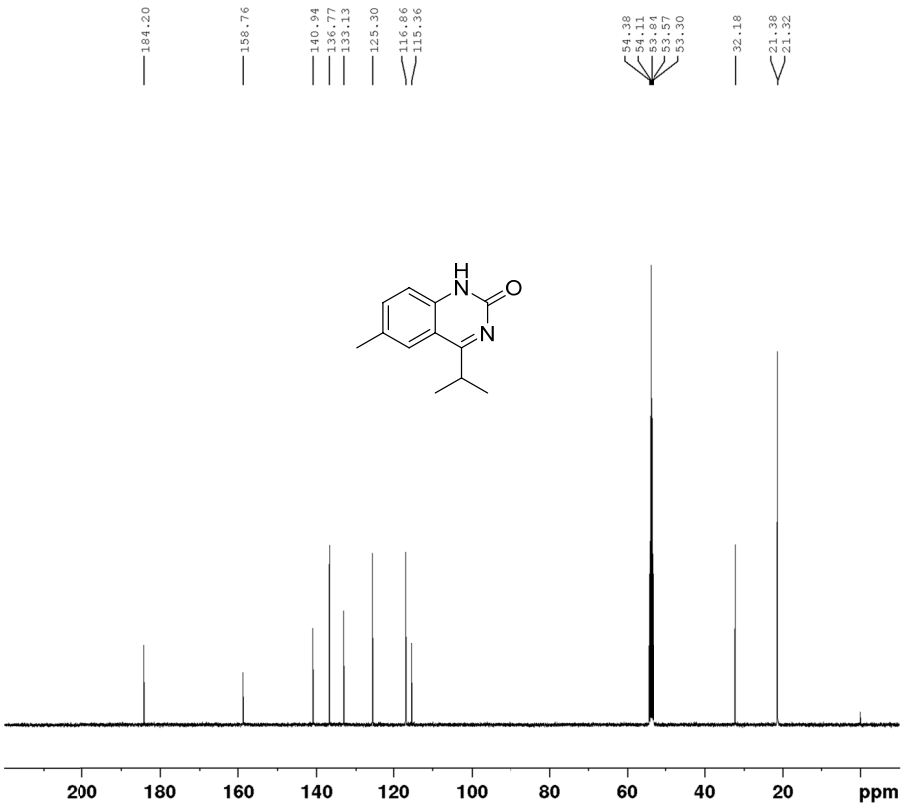



```
Current Data Parameters
NAME            new-kzt
EXPNO                31
PROCNO                1

F2 - Acquisition Parameters
Date_          20210405
Time              23.39
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CD2Cl2
NS                 1024
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                199.89
DW               20.800 usec
DE                6.50 usec
TE               300.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1                 13C
P1                10.00 usec
PLW1         56.93000031 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2             90.00 usec
PLW2         13.26099968 W
PLW12         0.16372000 W
PLW13         0.13260999 W

F2 - Processing parameters
SI                32768
SF           100.6127543 MHz
WDW                  EM
SSB      0
LB                1.00 Hz
GB       0
PC                1.40
```

Figure S23. ^{1}H NMR and ^{13}C NMR spectra of **3e**

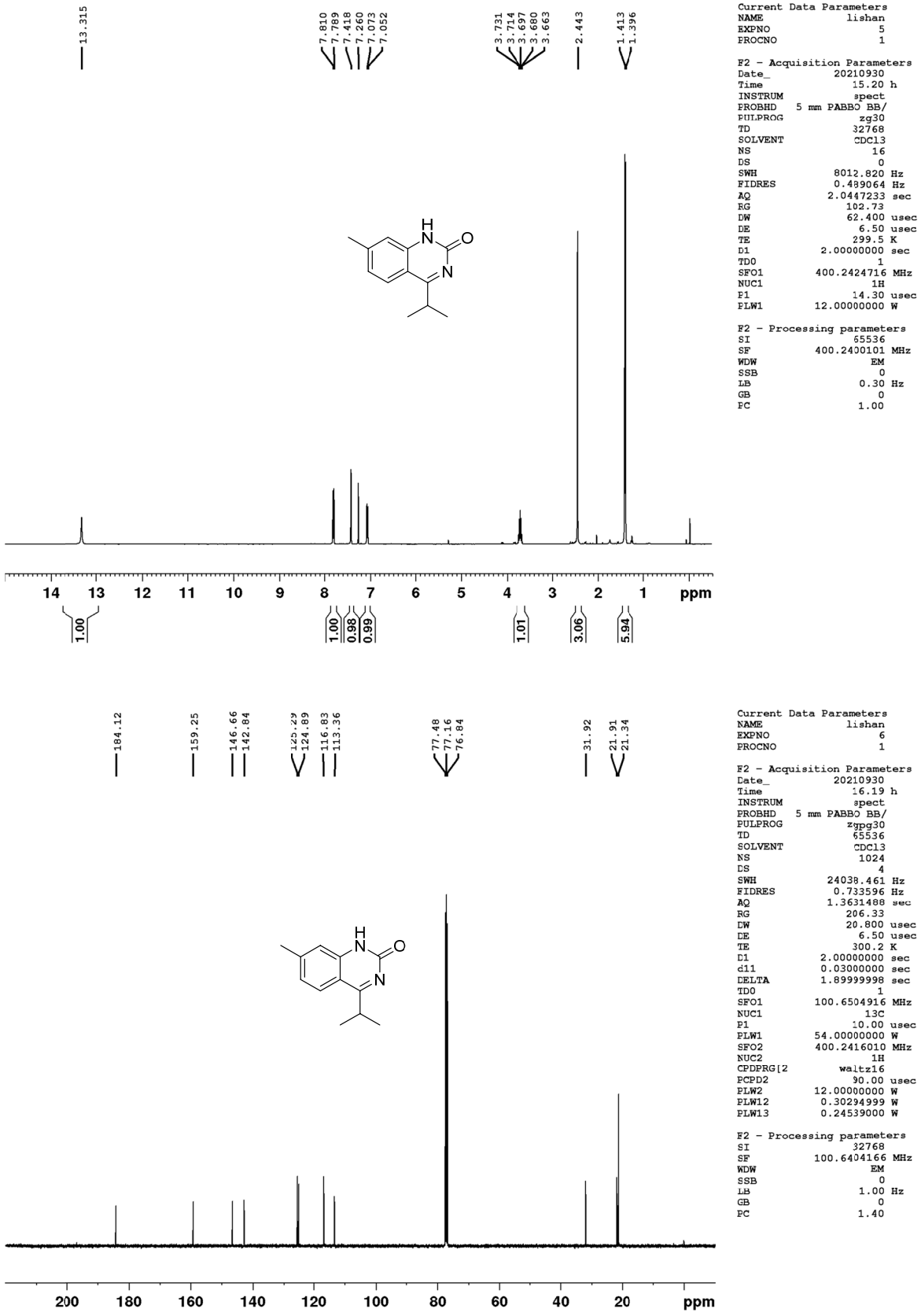



```
Current Data Parameters
NAME                  new-kzt
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_               20210406
Time                    6.10
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                 zg30
TD                     65536
SOLVENT             CD2Cl2
NS                         16
DS                          2
SWH                 8012.820 Hz
FIDRES              0.122266 Hz
AQ                  4.0894465 sec
RG                      60.55
DW                     62.400 usec
DE                      6.50 usec
TE                     299.4 K
D1                1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1              400.1324710 MHz
NUC1                      1H
P1                     10.00 usec
PLW1              13.26099968 W

F2 - Processing parameters
SI                         65536
SF                400.1300154 MHz
WDW                          EM
SSB          0
LB                      0.30 Hz
GB           0
PC                      1.00
```




```
Current Data Parameters
NAME                  new-kzt
EXPNO                      11
PROCNO                      1

F2 - Acquisition Parameters
Date_               20210406
Time                    7.10
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                zgpg30
TD                     65536
SOLVENT             CD2Cl2
NS                       1024
DS                          4
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631488 sec
RG                     199.89
DW                     20.800 usec
DE                      6.50 usec
TE                     300.0 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1              100.6228293 MHz
NUC1                      13C
P1                     10.00 usec
PLW1              56.93000031 W

======== CHANNEL f2 ========
SFO2              400.1316005 MHz
NUC2                      1H
CPDPRG[2             waltz16
PCPD2                  90.00 usec
PLW2              13.26099968 W
PLW12              0.16372000 W
PLW13              0.13260999 W

F2 - Processing parameters
SI                         32768
SF                100.6127272 MHz
WDW                          EM
SSB          0
LB                      1.00 Hz
GB           0
PC                      1.40
```

Figure S24. ^{1}H NMR and ^{13}C NMR spectra of **3f**



Current Data Parameters
NAME lishan
EXPNO 5
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210930
Time 15.20 h
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8012.820 Hz
FIDRES 0.489064 Hz
AQ 2.0447233 sec
RG 102.73
DW 62.400 usec
DE 6.50 usec
TE 299.5 K
D1 2.00000000 sec
TD0 1
SFO1 400.2424716 MHz
NUC1 1H
P1 14.30 usec
PLW1 12.00000000 W

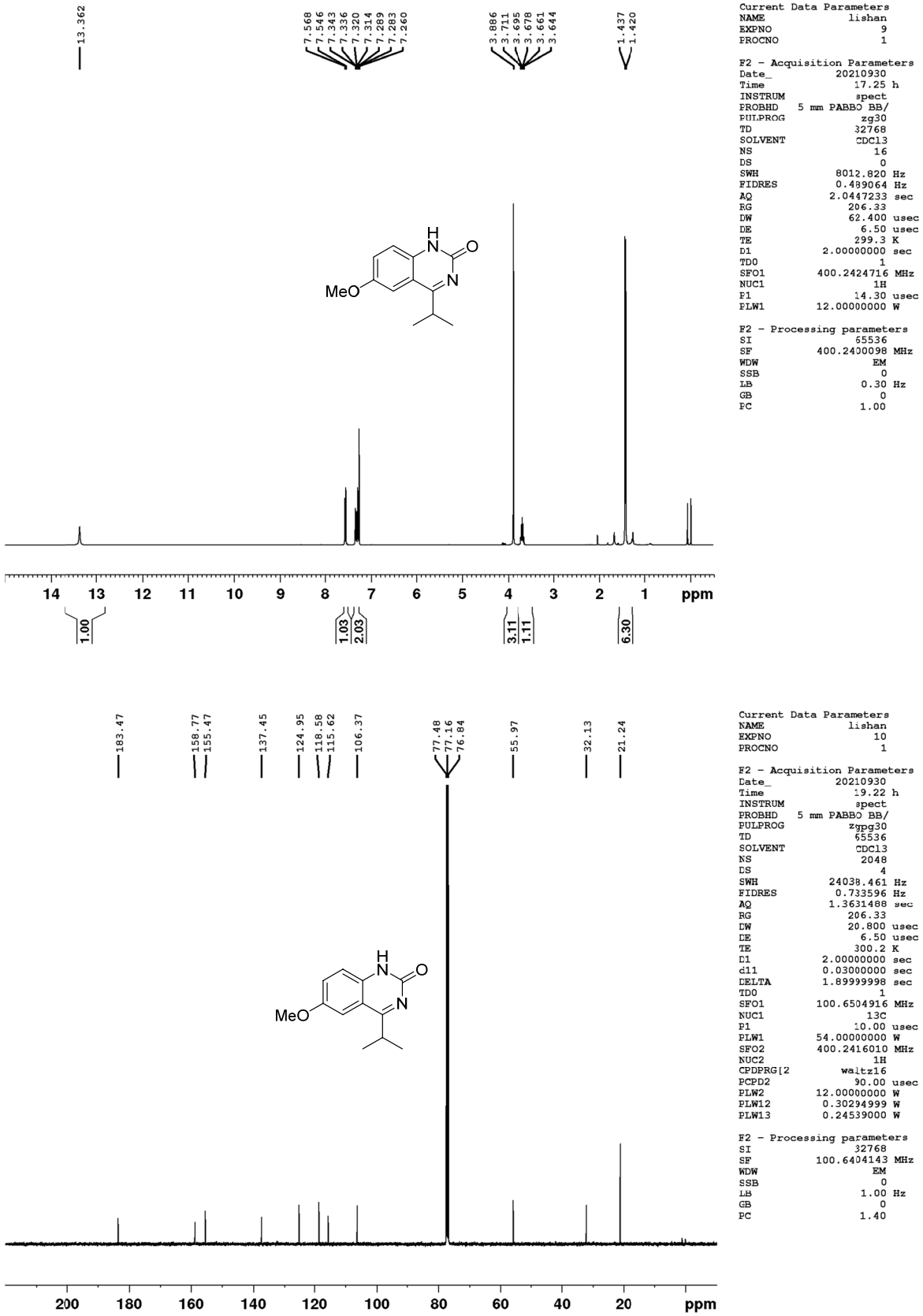
F2 - Processing parameters
SI 65536
SF 400.2400101 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Current Data Parameters
NAME lishan
EXPNO 6
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210930
Time 16.19 h
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 1.3631488 sec
RG 206.33
DW 20.800 usec
DE 6.50 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 100.6504916 MHz
NUC1 13C
P1 10.00 usec
PLW1 54.00000000 W
SFO2 400.2416010 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 12.00000000 W
PLW12 0.30294999 W
PLW13 0.24539000 W

F2 - Processing parameters
SI 32768
SF 100.6404166 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

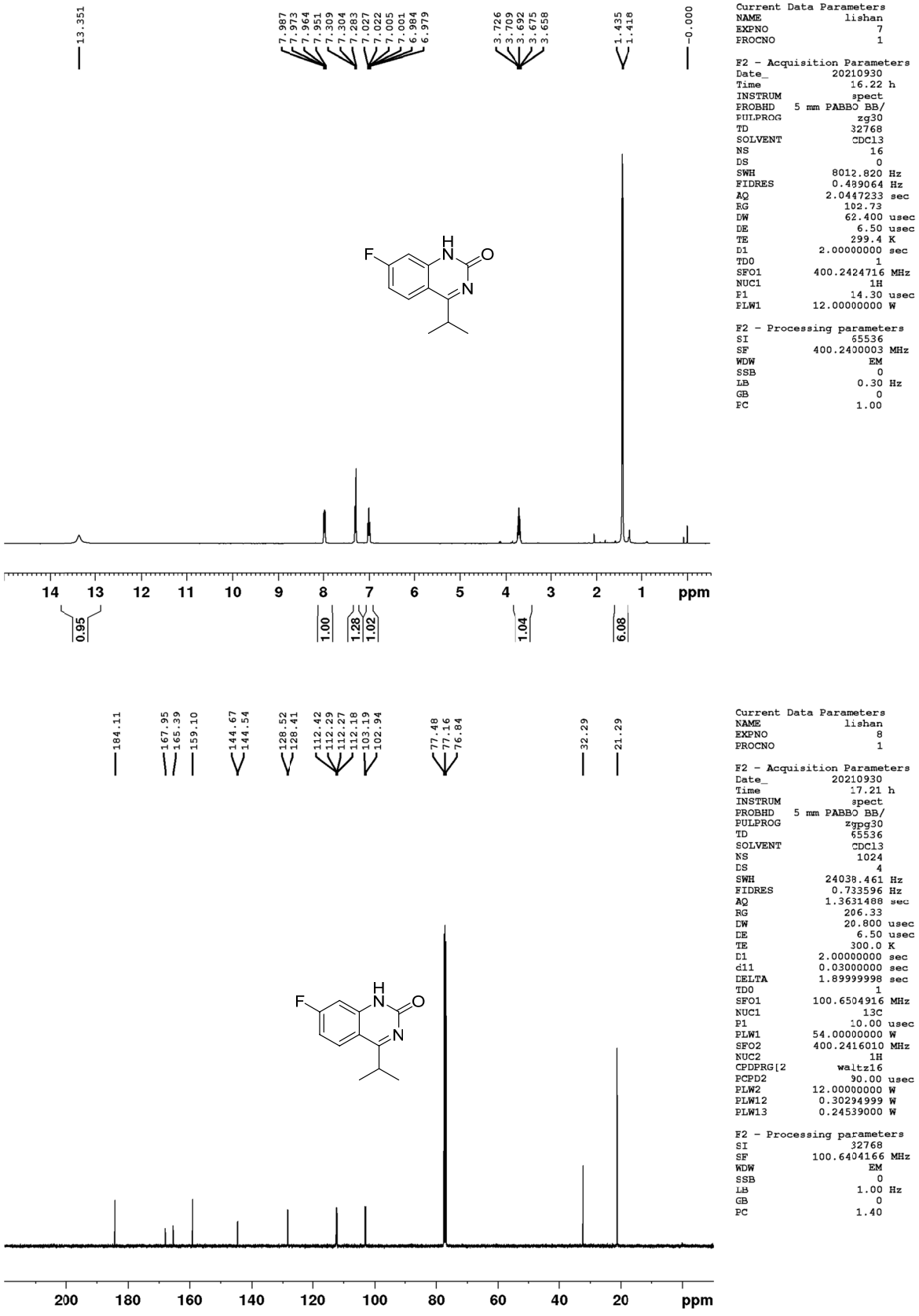
Figure S25. ^{1}H NMR and ^{13}C NMR spectra of **3g**




```
Current Data Parameters
NAME                  lishan
EXPNO                      9
PROCNO                     1

F2 - Acquisition Parameters
Date_              20210930
Time                 17.25 h
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        0
SWH                8012.820 Hz
FIDRES             0.489064 Hz
AQ                 2.0447233 sec
RG                    206.33
DW                    62.400 usec
DE                     6.50 usec
TE                    299.3 K
D1                 2.00000000 sec
TD0                        1
SFO1              400.2424716 MHz
NUC1                      1H
P1                     14.30 usec
PLW1              12.00000000 W

F2 - Processing parameters
SI                        65536
SF                400.2400098 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

```
Current Data Parameters
NAME                  lishan
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20210930
Time                 19.22 h
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     2048
DS                        4
SWH               24038.461 Hz
FIDRES             0.733596 Hz
AQ                 1.3631488 sec
RG                    206.33
DW                    20.800 usec
DE                     6.50 usec
TE                    300.2 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                        1
SFO1              100.6504916 MHz
NUC1                      13C
P1                     10.00 usec
PLW1              54.00000000 W
SFO2              400.2416010 MHz
NUC2                      1H
CPDPRG[2               waltz16
PCPD2                  90.00 usec
PLW2              12.00000000 W
PLW12              0.30294999 W
PLW13              0.24539000 W

F2 - Processing parameters
SI                        32768
SF                100.6404143 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```

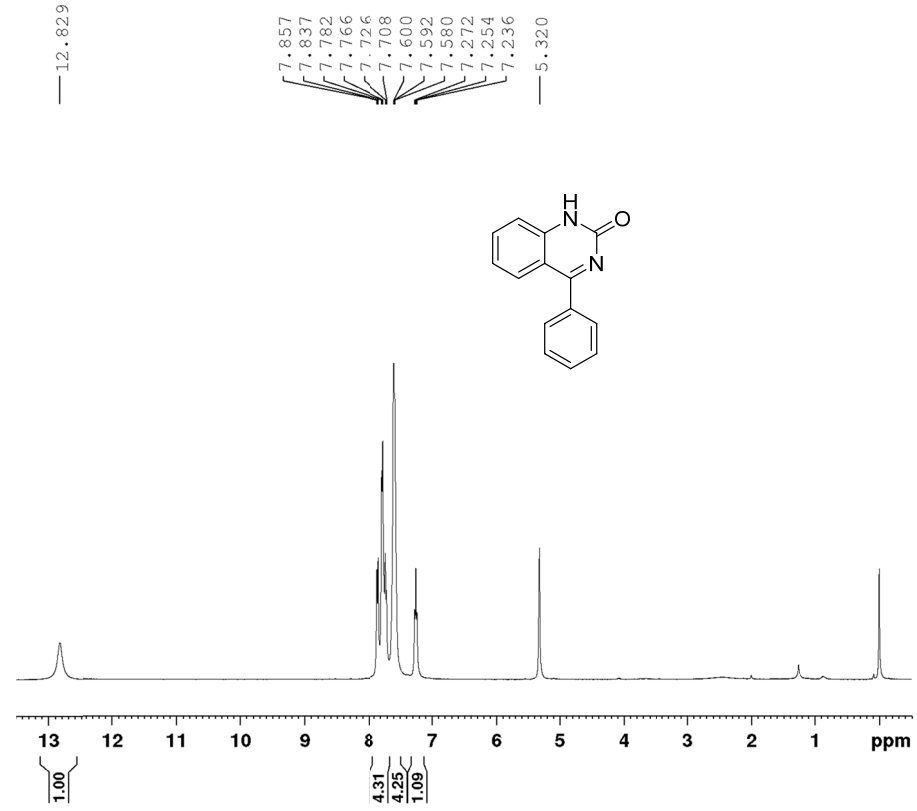
Figure S26. ^{1}H NMR and ^{13}C NMR spectra of **3h**



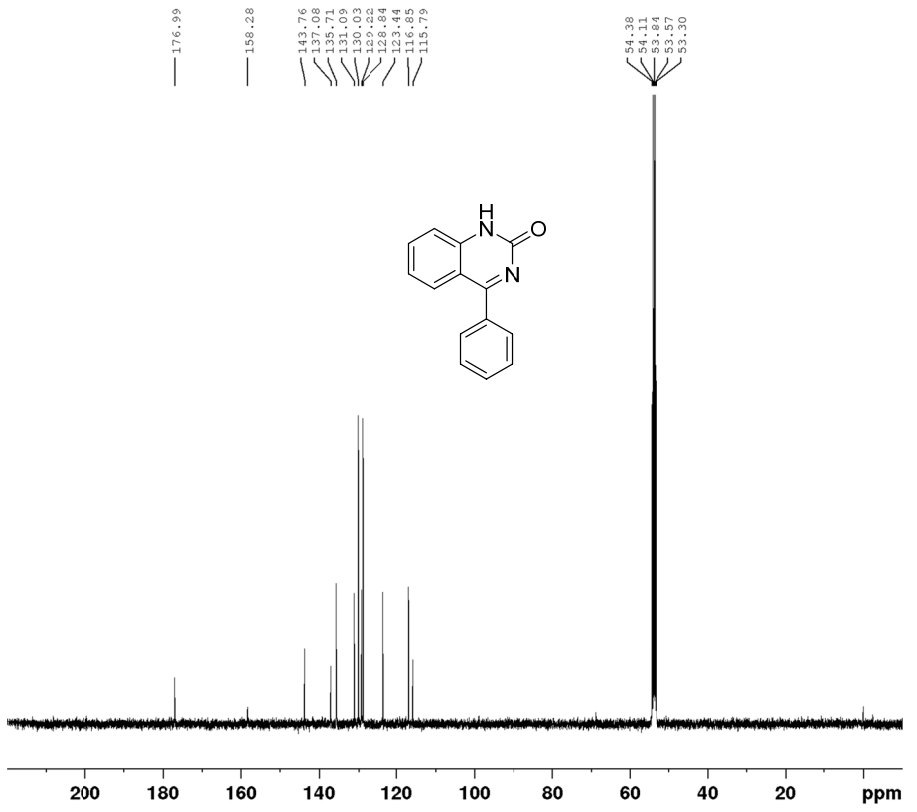

```
Current Data Parameters
NAME                  lishan
EXPNO                      7
PROCNO                     1

F2 - Acquisition Parameters
Date_              20210930
Time                 16.22 h
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        0
SWH                8012.820 Hz
FIDRES             0.489064 Hz
AQ                 2.0447233 sec
RG                    102.73
DW                    62.400 usec
DE                     6.50 usec
TE                    299.4 K
D1                 2.00000000 sec
TD0                       1
SFO1           400.2424716 MHz
NUC1                     1H
P1                    14.30 usec
PLW1           12.00000000 W

F2 - Processing parameters
SI                    65536
SF             400.2400003 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

```
Current Data Parameters
NAME                  lishan
EXPNO                      8
PROCNO                     1

F2 - Acquisition Parameters
Date_              20210930
Time                 17.21 h
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH               24038.461 Hz
FIDRES             0.733596 Hz
AQ                 1.3631488 sec
RG                    206.33
DW                    20.800 usec
DE                     6.50 usec
TE                    300.0 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                       1
SFO1           100.6504916 MHz
NUC1                     13C
P1                    10.00 usec
PLW1           54.00000000 W
SFO2           400.2416010 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                 90.00 usec
PLW2           12.00000000 W
PLW12           0.30294999 W
PLW13           0.24539000 W

F2 - Processing parameters
SI                    32768
SF             100.6404166 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

Figure S27. ^{1}H NMR and ^{13}C NMR spectra of **3i**

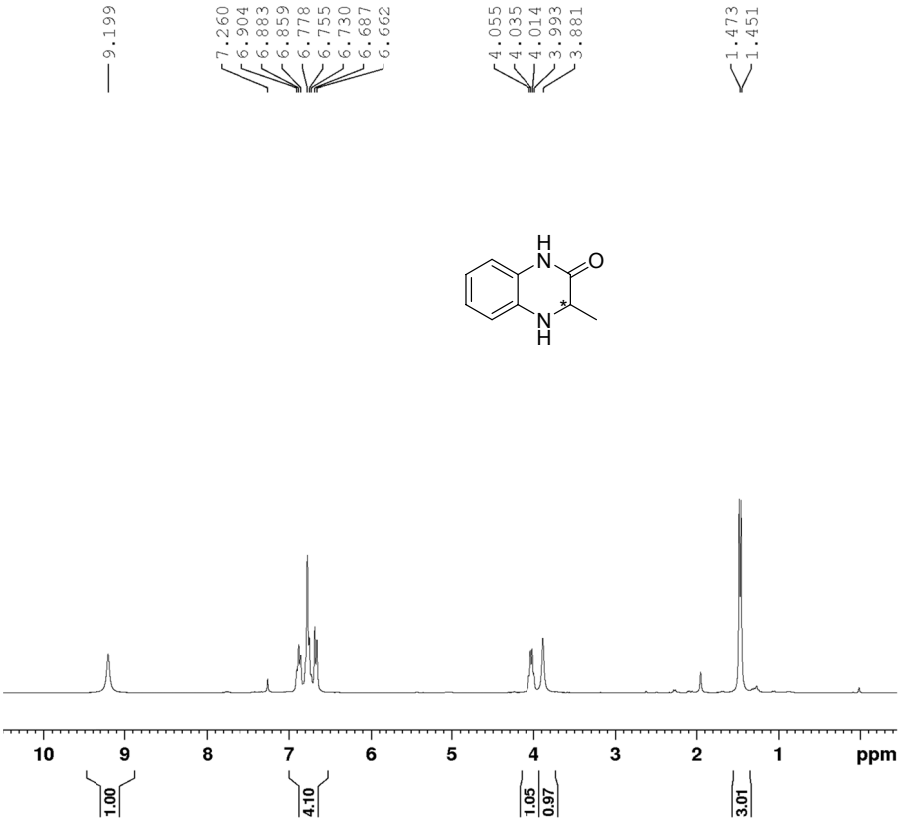



```
Current Data Parameters
NAME                  new-kzt
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_               20210406
Time                    7.15
INSTRUM                spect
PROBHD   5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT              CD2Cl2
NS                        16
DS                         2
SWH                 8012.820 Hz
FIDRES              0.122266 Hz
AQ                  4.0894465 sec
RG                      112.4
DW                     62.400 usec
DE                      6.50 usec
TE                     299.5 K
D1                  1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1             400.1324710 MHz
NUC1                       1H
P1                      10.00 usec
PLW1             13.26099968 W

F2 - Processing parameters
SI                        65536
SF               400.1300157 MHz
WDW                        EM
SSB          0
LB                      0.30 Hz
GB           0
PC                      1.00
```

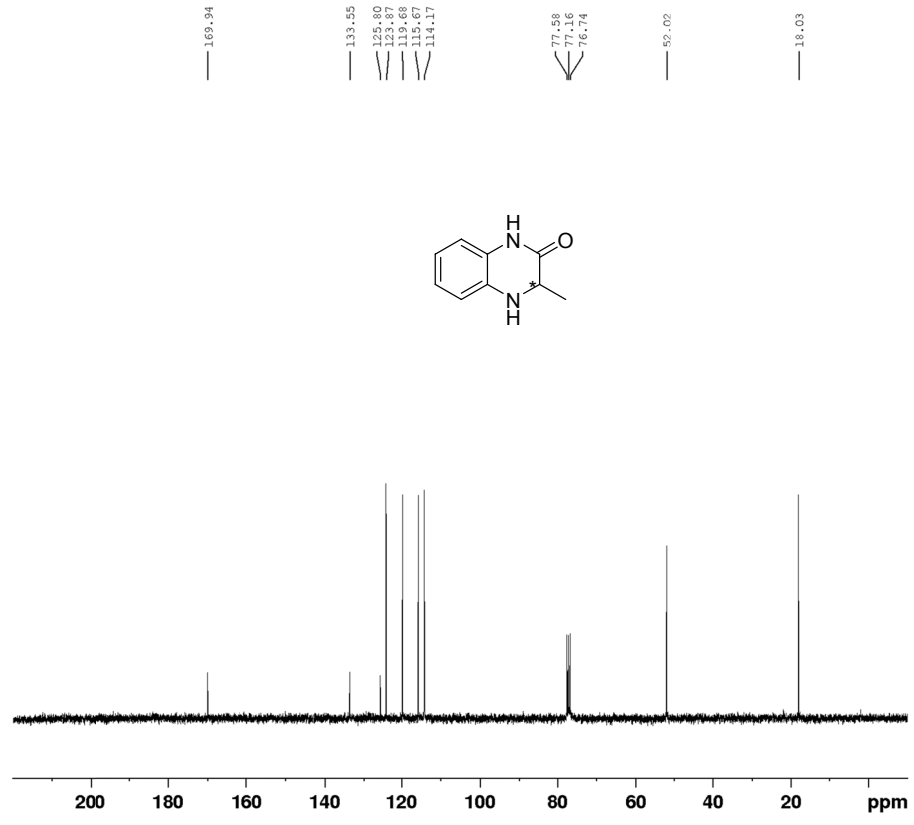



```
Current Data Parameters
NAME                  new-kzt
EXPNO                      11
PROCNO                      1

F2 - Acquisition Parameters
Date_               20210406
Time                    8.15
INSTRUM                spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                    65536
SOLVENT              CD2Cl2
NS                      1024
DS                         4
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631488 sec
RG                      199.89
DW                     20.800 usec
DE                      6.50 usec
TE                     300.0 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1             100.6228293 MHz
NUC1                       13C
P1                      10.00 usec
PLW1             56.93000031 W

======== CHANNEL f2 ========
SFO2             400.13[illegible]16005 MHz
NUC2                       1H
CPDPRG[2             waltz16
PCPD2                   90.00 usec
PLW2             13.26099968 W
PLW12             0.16372000 W
PLW13             0.13260999 W

F2 - Processing parameters
SI                        32768
SF               100.6127266 MHz
WDW                        EM
SSB          0
LB                      1.00 Hz
GB           0
PC                      1.40
```

Figure S28. ^{1}H NMR and ^{13}C NMR spectra of **2a**

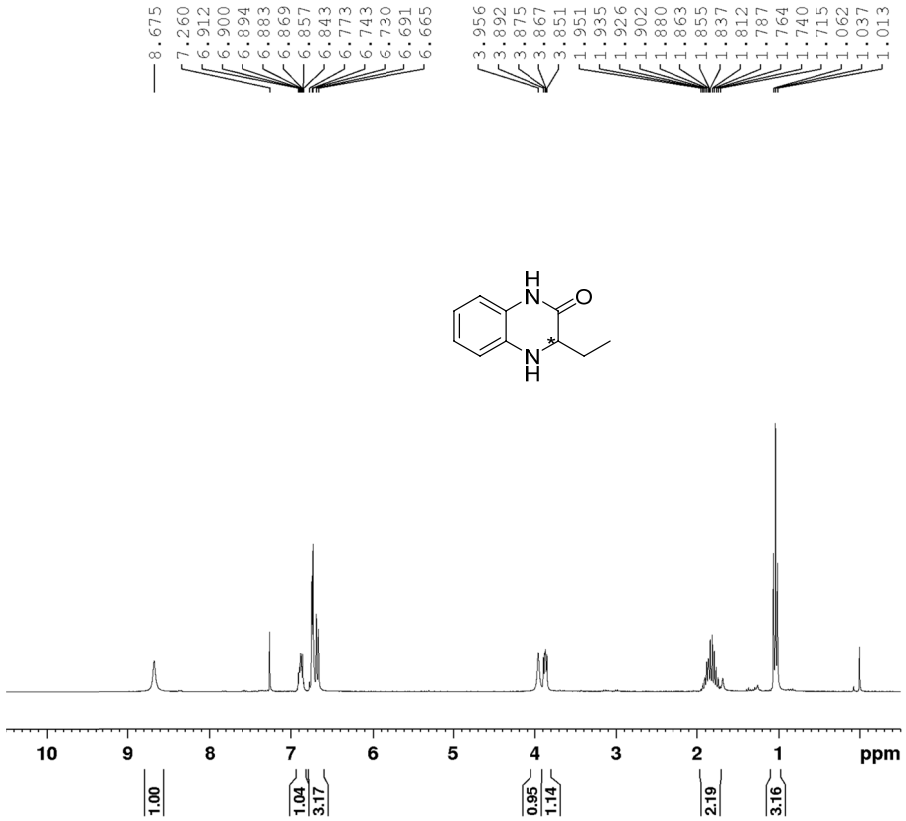



```
Current Data Parameters
NAME          lichenghao
EXPNO                 31
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time              18.58
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG           zg30
TD               65536
SOLVENT          CDC13
NS                  16
DS                   2
SWH            6009.615 Hz
FIDRES        0.091699 Hz
AQ            5.4525952 sec
RG               166.41
DW               83.200 usec
DE                6.50 usec
TE               298.3 K
D1            1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1                8.00 usec
PL1              120.00 dB
PL1W                0 W
SFO1       300.1318534 MHz

F2 - Processing parameters
SI                65536
SF          300.1300072 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```

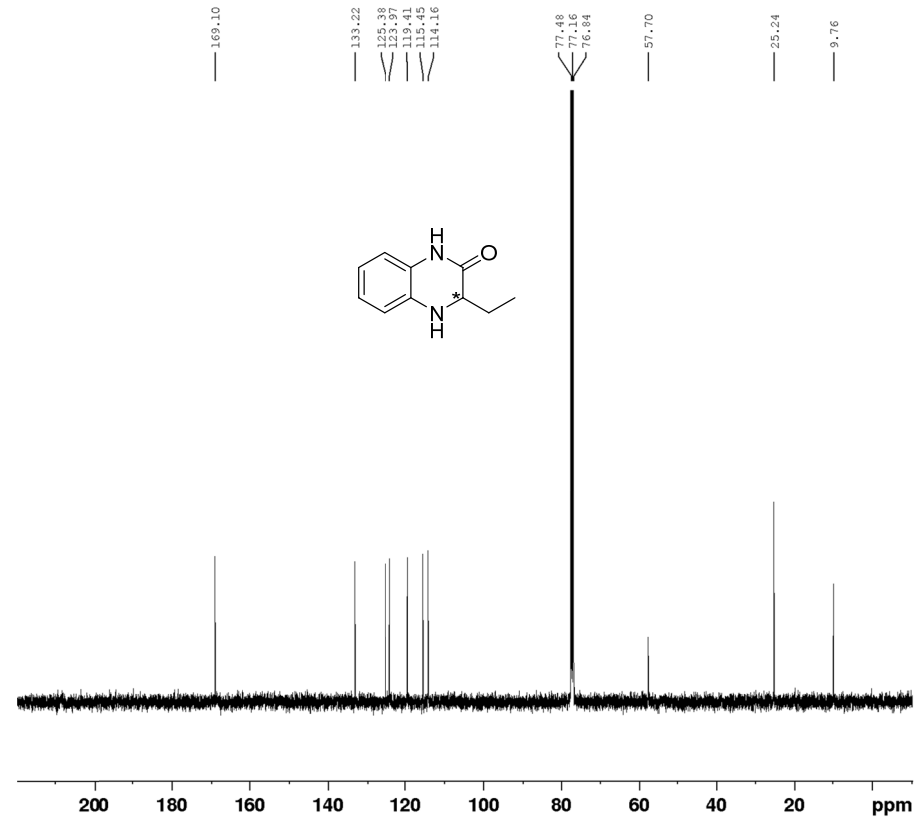



```
Current Data Parameters
NAME          lichenghao
EXPNO                 32
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time              19.08
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG         zgpg30
TD               65536
SOLVENT          CDC13
NS                  83
DS                   4
SWH           18028.846 Hz
FIDRES        0.275098 Hz
AQ            1.8175317 sec
RG               209.09
DW               27.733 usec
DE                6.50 usec
TE               298.2 K
D1            2.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                13C
P1               11.00 usec
PL1              120.00 dB
PL1W                0 W
SFO1          75.4752949 MHz

F2 - Processing parameters
SI                32768
SF          75.4677421 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

Figure S29 ^{1}H NMR and ^{13}C NMR spectra of **2b**

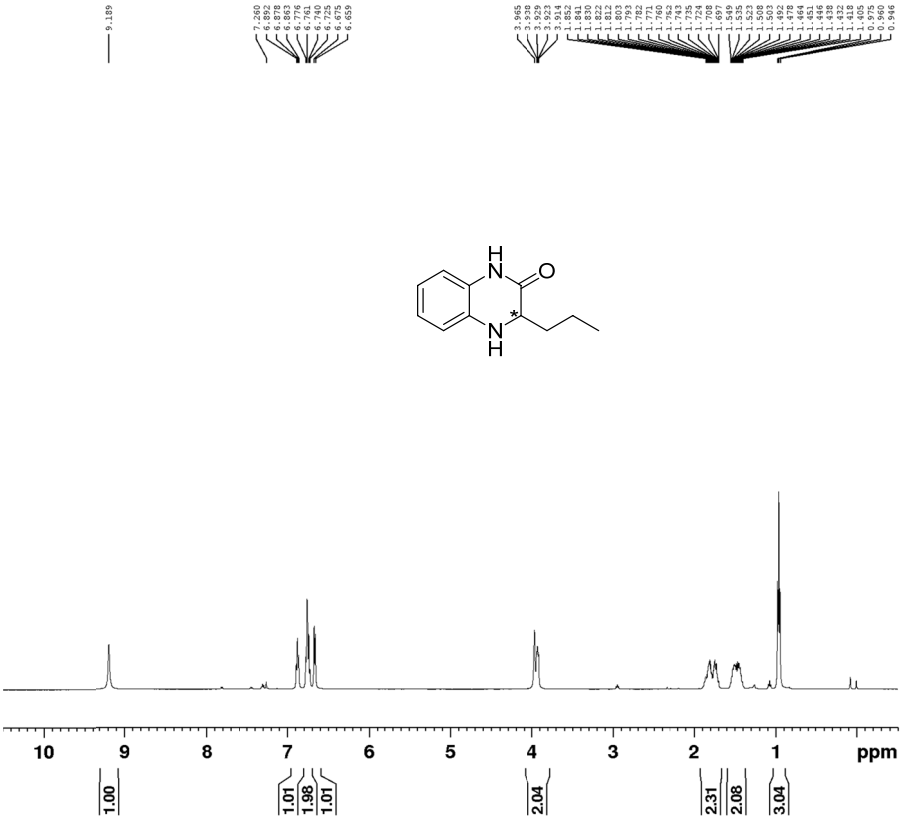



```
Current Data Parameters
NAME          KWT-Et-qh
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20210427
Time              22.04
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6009.615 Hz
FIDRES        0.091699 Hz
AQ            5.4525952 sec
RG               209.09
DW               83.200 usec
DE                6.50 usec
TE                298.4 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.00 usec
PL1              120.00 dB
PL1W                0 W
SFO1       300.1318534 MHz

F2 - Processing parameters
SI                65536
SF          300.1300072 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

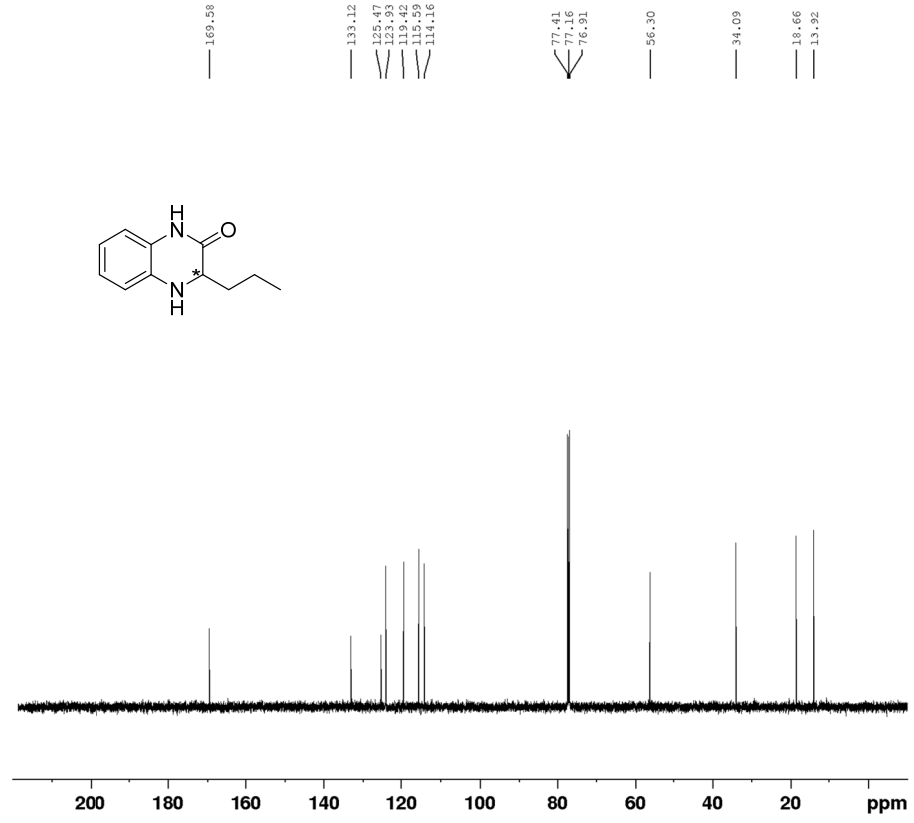



```
Current Data Parameters
NAME         KWT-Et-qh-C
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20210428
Time              1.14
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631488 sec
RG               206.33
DW               20.800 usec
DE                6.50 usec
TE                298.9 K
D1           2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                10.00 usec
PL1              120.00 dB
PL1W                0 W
SFO1       100.6504916 MHz

F2 - Processing parameters
SI                32768
SF          100.6404153 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

Figure S30. ^{1}H NMR and ^{13}C NMR spectra of **2c**

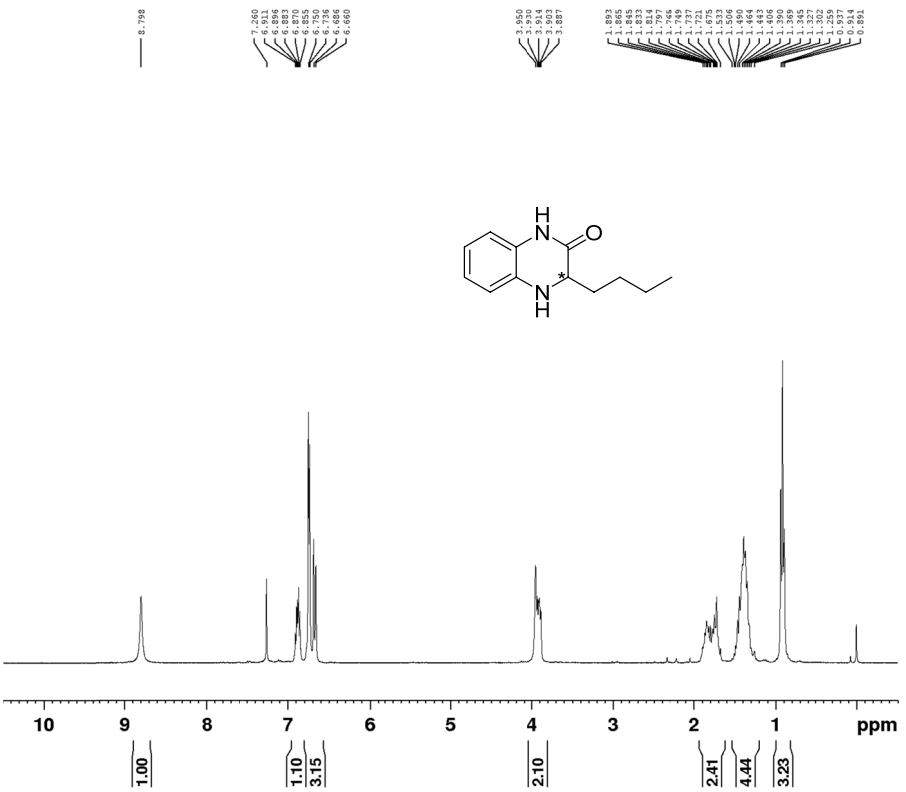



```
Current Data Parameters
NAME          KWY-npr-qh
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time              13.24
INSTRUM           spect
PROBHD   5 mm CPPBBO BB
PULPROG            zg30
TD                65536
SOLVENT           CDC13
NS                   16
DS                    2
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ             3.2767999 sec
RG                31.72
DW                50.000 usec
DE                 6.50 usec
TE                298.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.59 usec
PL1              120.00 dB
PL1W                   0 W
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                 65536
SF          500.1300121 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```

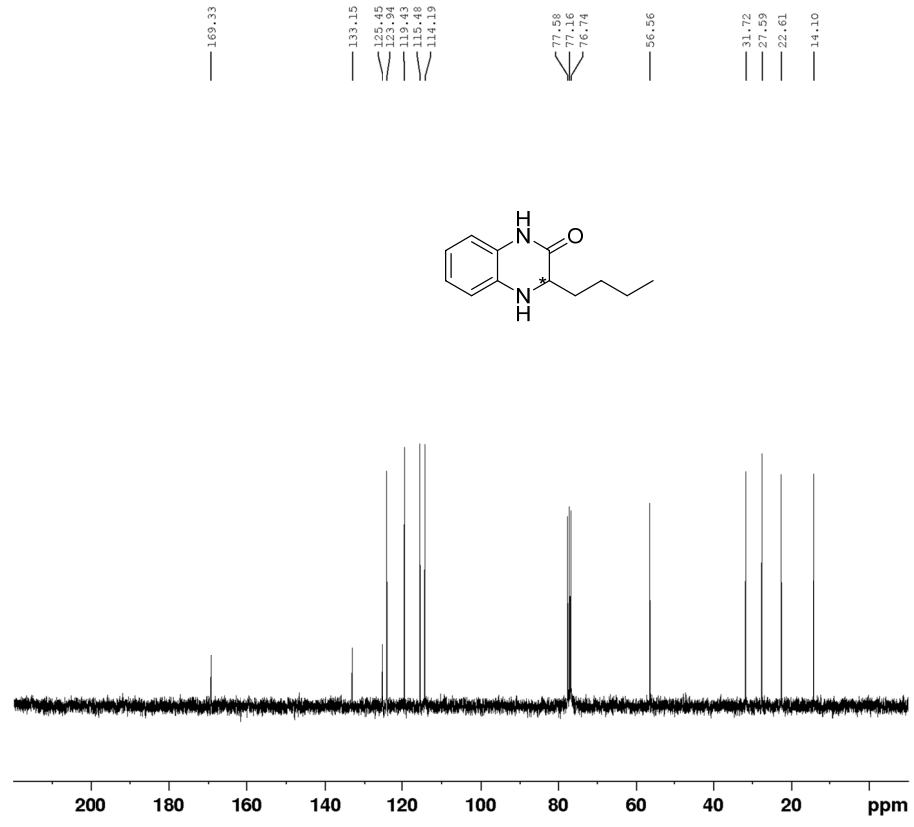



```
Current Data Parameters
NAME          KWY-npr-qh
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time              14.10
INSTRUM           spect
PROBHD   5 mm CPPBBO BB
PULPROG          zgpg30
TD                65536
SOLVENT           CDC13
NS                    6
DS                    4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ             1.1010048 sec
RG                192.89
DW                16.800 usec
DE                 18.00 usec
TE                298.2 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 9.80 usec
PL1              120.00 dB
PL1W                   0 W
SFO1        125.7703637 MHz

F2 - Processing parameters
SI                 32768
SF          125.7577746 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.40
```

Figure S31. ^{1}H NMR and ^{13}C NMR spectra of **2d**

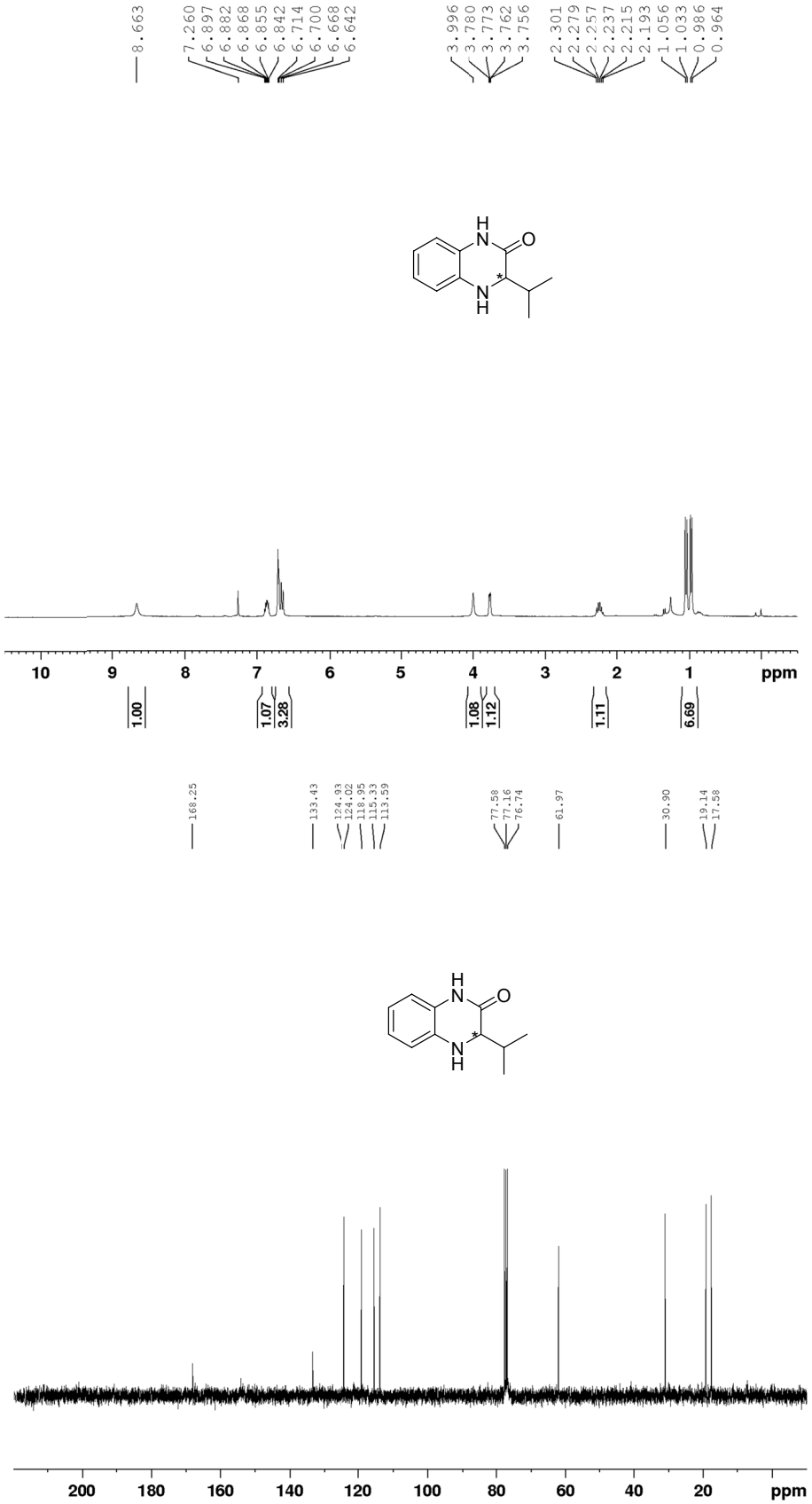



```
Current Data Parameters
NAME          KWT-NBU-QH
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time              14.50
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG            zg30
TD                65536
SOLVENT           CDC13
NS                   16
DS                    2
SWH            6009.615 Hz
FIDRES          0.091699 Hz
AQ             5.4525952 sec
RG                209.09
DW                83.200 usec
DE                 6.50 usec
TE                298.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.00 usec
PL1               120.00 dB
PL1W                   0 W
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 65536
SF           300.1300071 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```




```
Current Data Parameters
NAME          KWT-NBU-QH
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time              14.52
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDC13
NS                  120
DS                    4
SWH           18028.846 Hz
FIDRES          0.275098 Hz
AQ             1.8175317 sec
RG                209.09
DW                27.733 usec
DE                 6.50 usec
TE                298.3 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                11.00 usec
PL1               120.00 dB
PL1W                   0 W
SFO1         75.4752949 MHz

F2 - Processing parameters
SI                 32768
SF           75.4677394 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

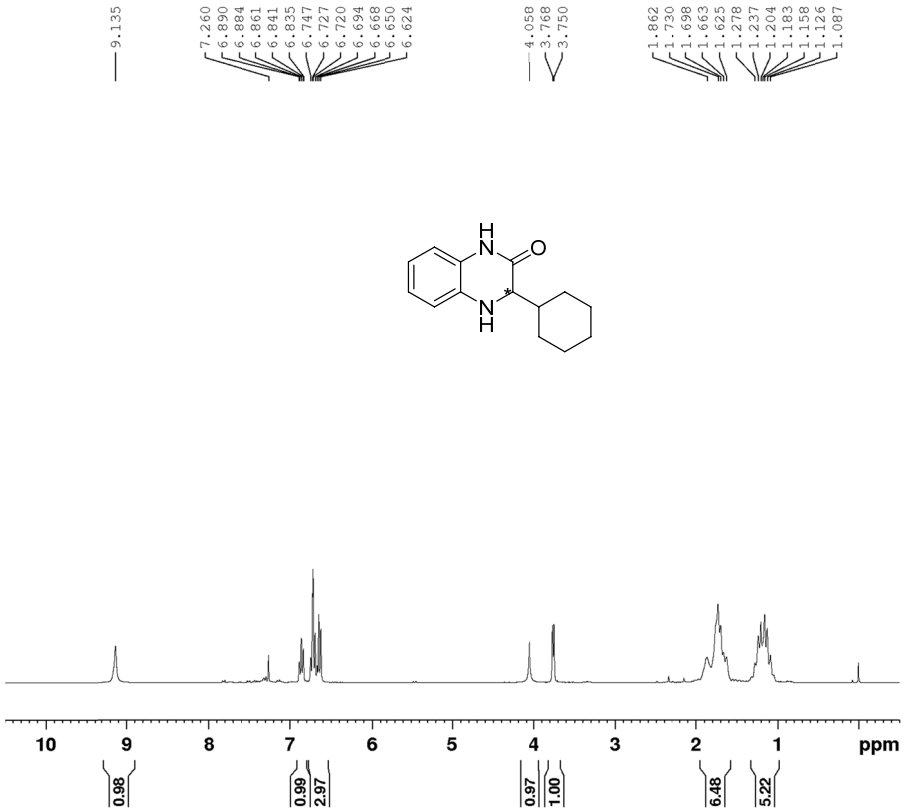
Figure S32. ^{1}H NMR and ^{13}C NMR spectra of **2e**



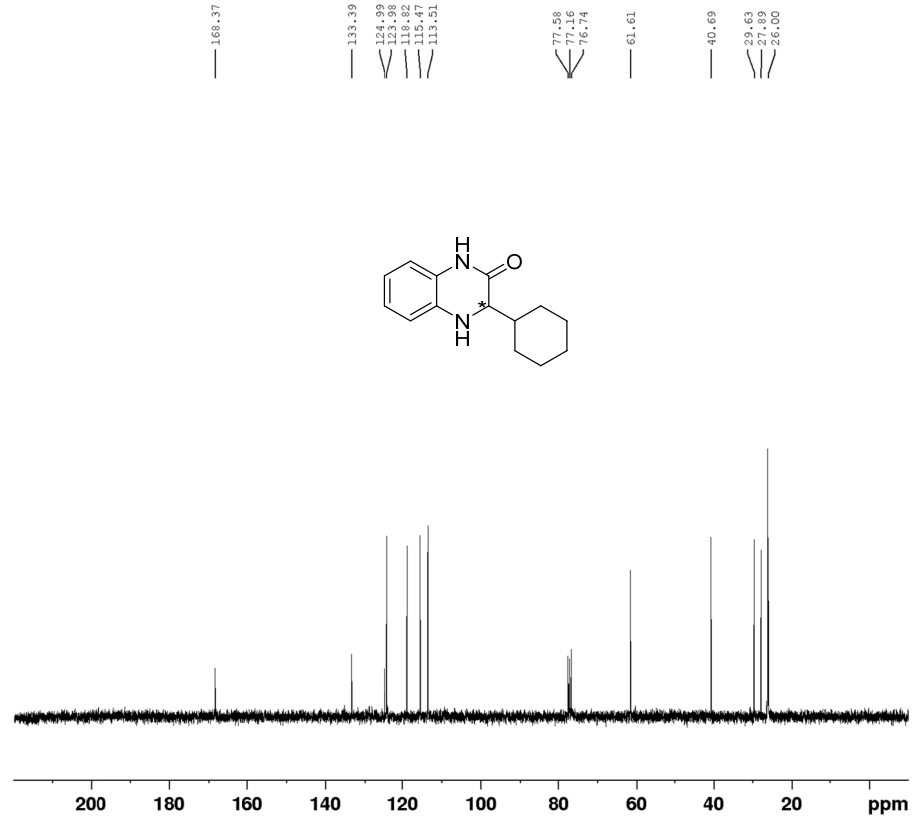

```
Current Data Parameters
NAME          KWT-ipr-qh
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210502
Time               12.18
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 55536
SOLVENT            CDC13
NS                    16
DS                     2
SWH             6009.615 Hz
FIDRES          0.091699 Hz
AQ              5.4525952 sec
RG                 209.09
DW                 83.200 usec
DE                  6.50 usec
TE                 298.2 K
D1              1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.00 usec
PL1               120.00 dB
PL1W                   0 W
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 55536
SF           300.1300073 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

```
Current Data Parameters
NAME        KWT-ipr-qh-C
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210502
Time               13.16
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDC13
NS                   128
DS                     4
SWH            18028.846 Hz
FIDRES          0.275098 Hz
AQ              1.8175317 sec
RG                 209.09
DW                 27.733 usec
DE                  6.50 usec
TE                 298.2 K
D1              2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                11.00 usec
PL1               120.00 dB
PL1W                   0 W
SFO1         75.4752949 MHz

F2 - Processing parameters
SI                 32768
SF           75.4677388 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Figure S33. ^{1}H NMR and ^{13}C NMR spectra of **2f**

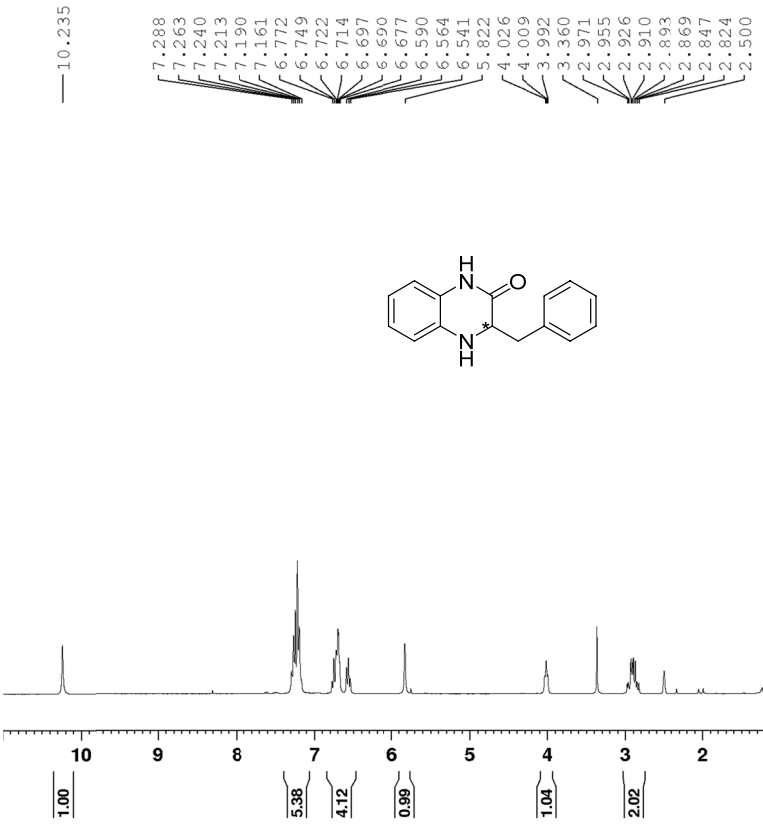



```
Current Data Parameters
NAME           KET-Cy-qh
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time              16.32
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG            zg30
TD                65536
SOLVENT           CDC13
NS                   16
DS                    2
SWH            6009.615 Hz
FIDRES        0.091699 Hz
AQ            5.4525952 sec
RG               142.81
DW               83.200 usec
DE                6.50 usec
TE               298.3 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.00 usec
PL1               120.00 dB
PL1W                   0 W
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                 65536
SF          300.1300072 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```

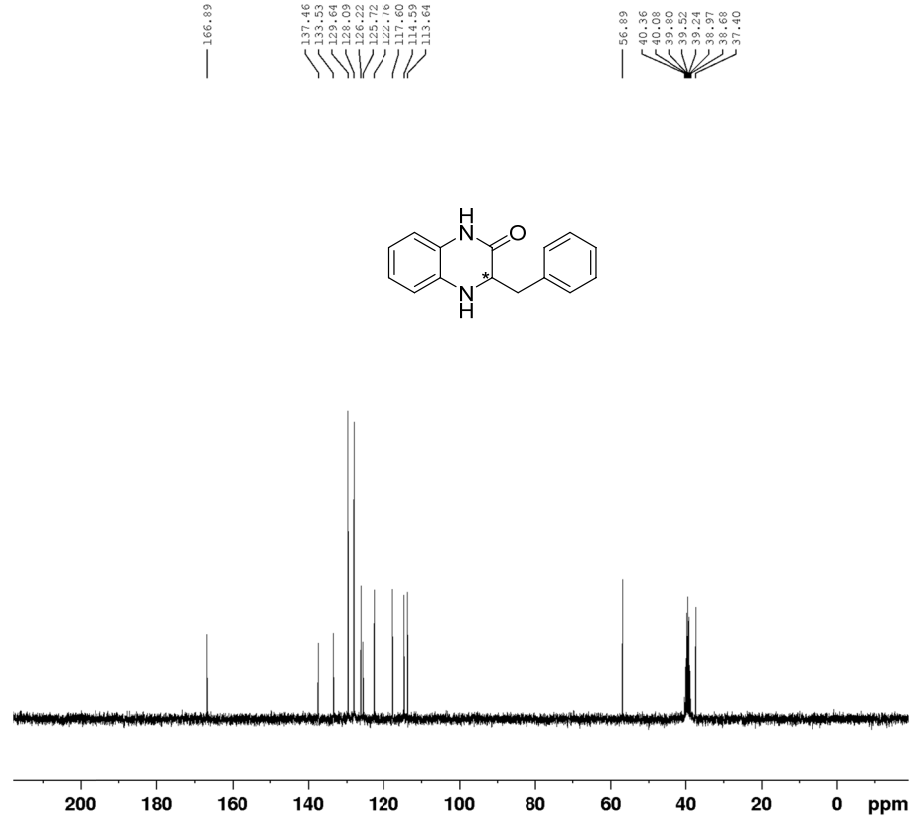



```
Current Data Parameters
NAME           KET-Cy-qh
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time              16.36
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDC13
NS                   48
DS                    4
SWH           18028.846 Hz
FIDRES        0.275098 Hz
AQ            1.8175317 sec
RG               209.09
DW               27.733 usec
DE                6.50 usec
TE               298.4 K
D1           2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                11.00 usec
PL1               120.00 dB
PL1W                   0 W
SFO1         75.4752949 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677400 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.40
```

Figure S34. ^{1}H NMR and ^{13}C NMR spectra of **2g**

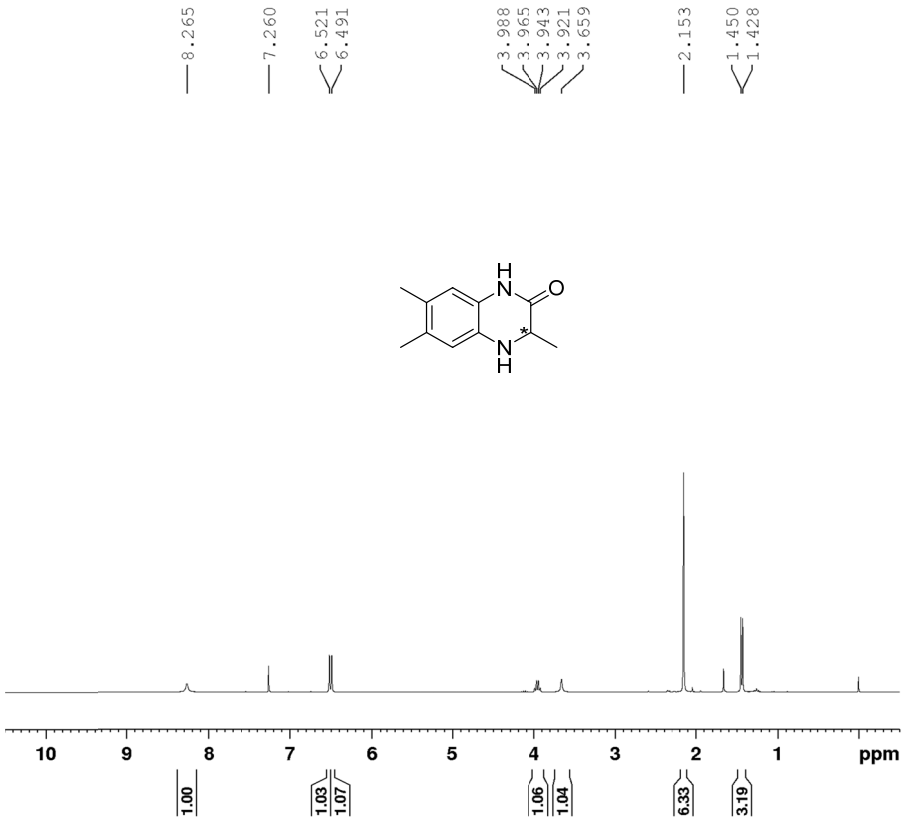



```
Current Data Parameters
NAME          lichanghao
EXPNO                 41
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time              20.59
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG           zg30
TD               65536
SOLVENT           DMSO
NS                   16
DS                    2
SWH            6009.615 Hz
FIDRES        0.091699 Hz
AQ            5.4525952 sec
RG               142.81
DW               83.200 usec
DE                6.50 usec
TE               298.3 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.00 usec
PL1               120.00 dB
PL1W                   0 W
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 65536
SF           300.1300025 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

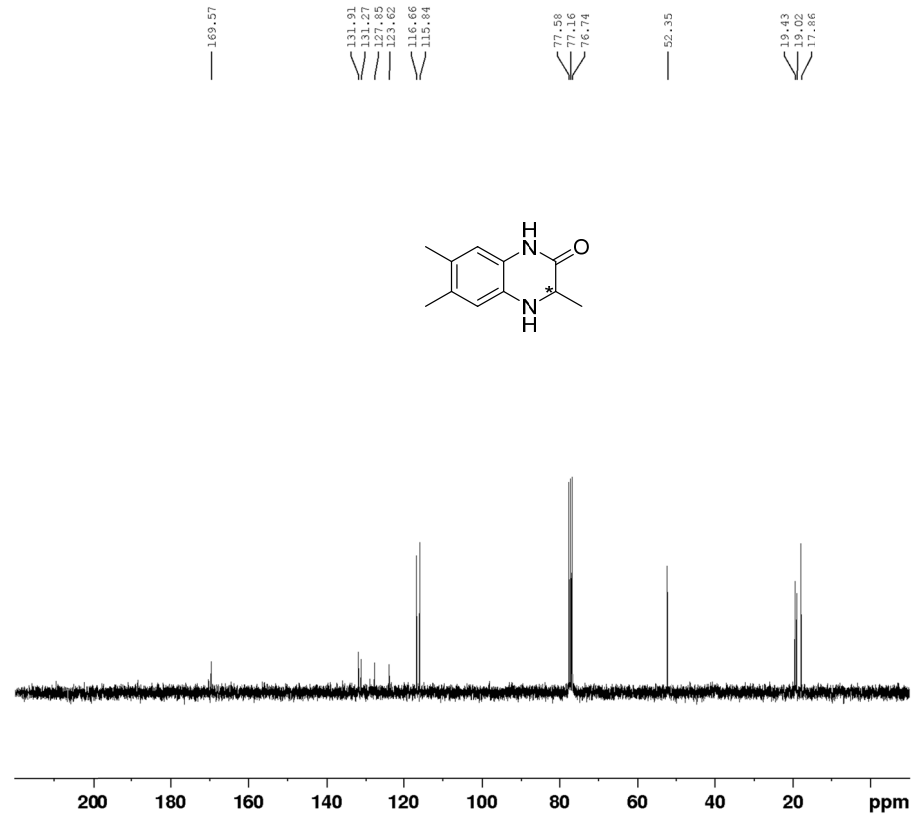



```
Current Data Parameters
NAME          lichanghao
EXPNO                 42
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time              21.02
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG         zgpg30
TD               65536
SOLVENT           DMSO
NS                   27
DS                    4
SWH           18028.846 Hz
FIDRES        0.275098 Hz
AQ            1.8175317 sec
RG               209.09
DW               27.733 usec
DE                6.50 usec
TE               298.3 K
D1           2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                11.00 usec
PL1              120.00 dB
PL1W                   0 W
SFO1         75.4752949 MHz

F2 - Processing parameters
SI                 32768
SF           75.4577841 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Figure S35. ^{1}H NMR and ^{13}C NMR spectra of **2h**

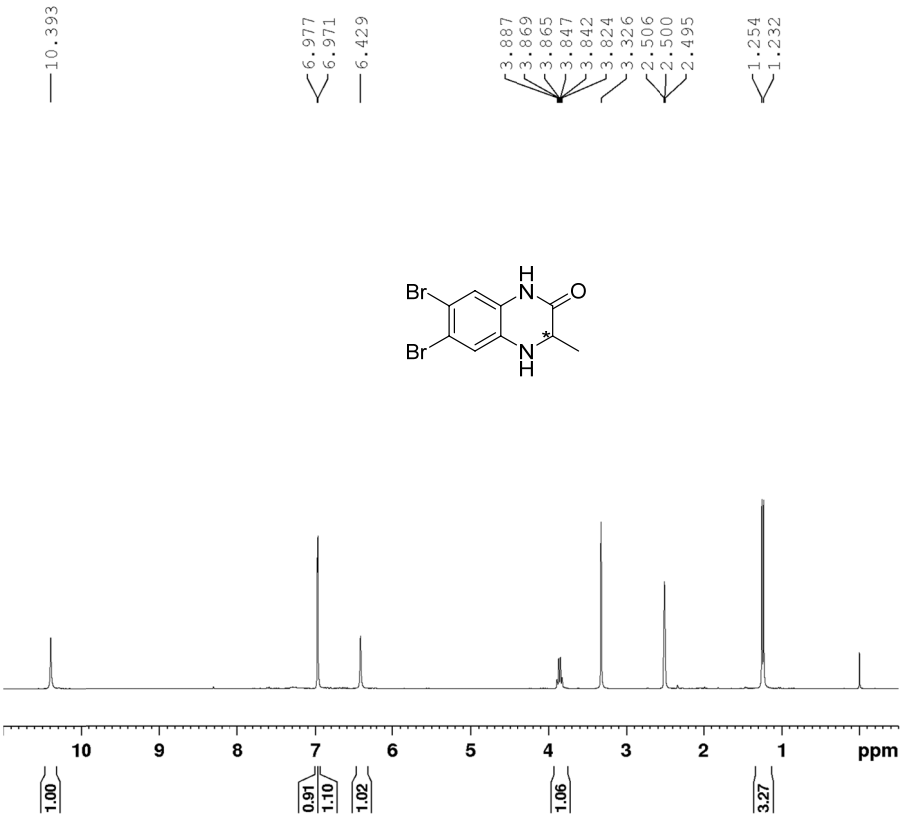



```
Current Data Parameters
NAME          KWT-3Me-qh
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time              16.18
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6009.615 Hz
FIDRES        0.091699 Hz
AQ            5.4525952 sec
RG               209.09
DW               83.200 usec
DE                6.50 usec
TE               298.3 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.00 usec
PL1              120.00 dB
PL1W                   0 W
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 65536
SF           300.1300072 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```

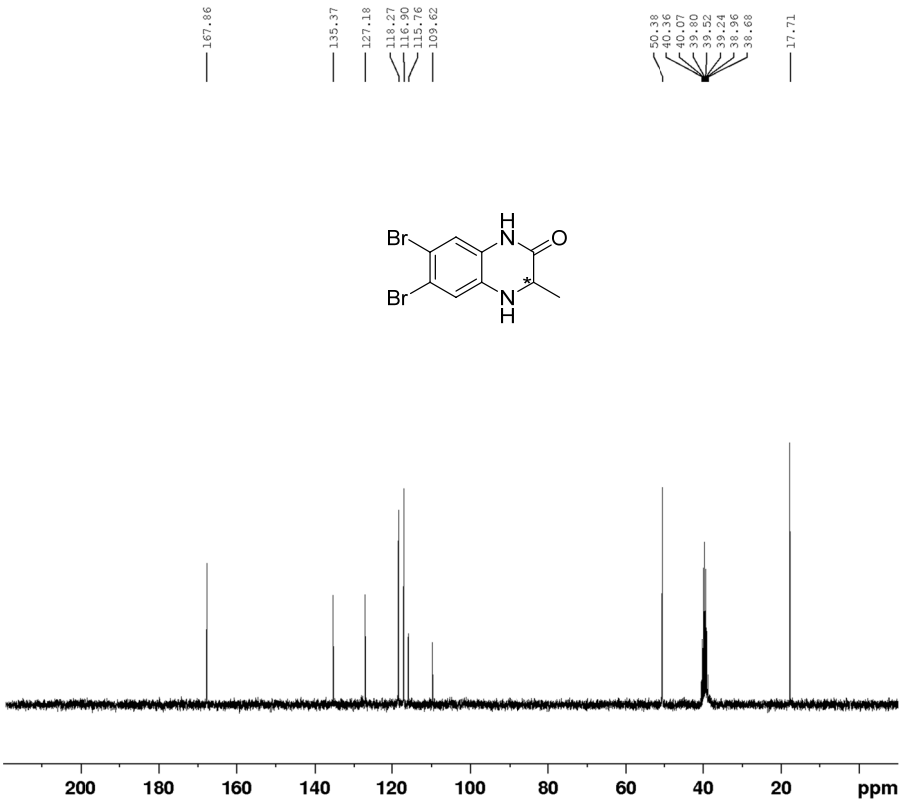



```
Current Data Parameters
NAME          KWT-3Me-qh
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time              16.21
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  149
DS                    4
SWH           18028.846 Hz
FIDRES        0.275098 Hz
AQ            1.8175317 sec
RG               209.09
DW               27.733 usec
DE                6.50 usec
TE               298.3 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                11.00 usec
PL1              120.00 dB
PL1W                   0 W
SFO1         75.4752949 MHz

F2 - Processing parameters
SI                 32768
SF           75.4677388 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.40
```

Figure S36. ^{1}H NMR and ^{13}C NMR spectra of **2i**

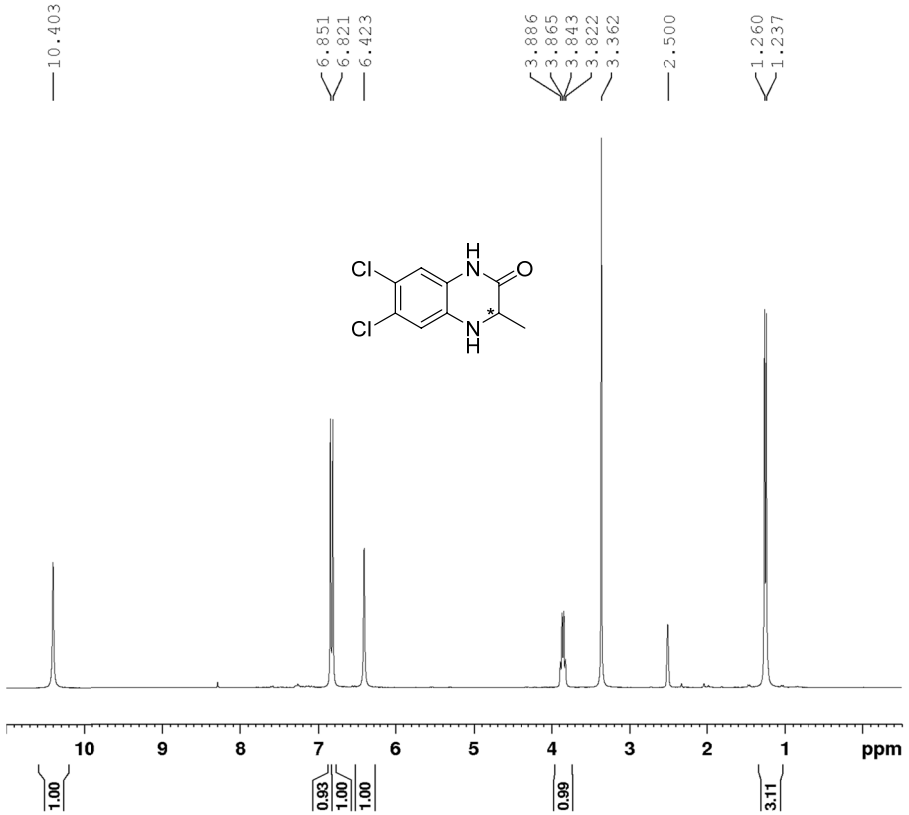



```
Current Data Parameters
NAME          lichenghao
EXPNO                 53
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time               23.29
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT             DMSO
NS                    16
DS                     2
SWH            6009.615 Hz
FIDRES        0.091699 Hz
AQ            5.4525952 sec
RG               209.09
DW               33.200 usec
DE                6.50 usec
TE                298.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.00 usec
PL1              120.00 dB
PL1W                0 W
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                 65536
SF          300.1300025 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

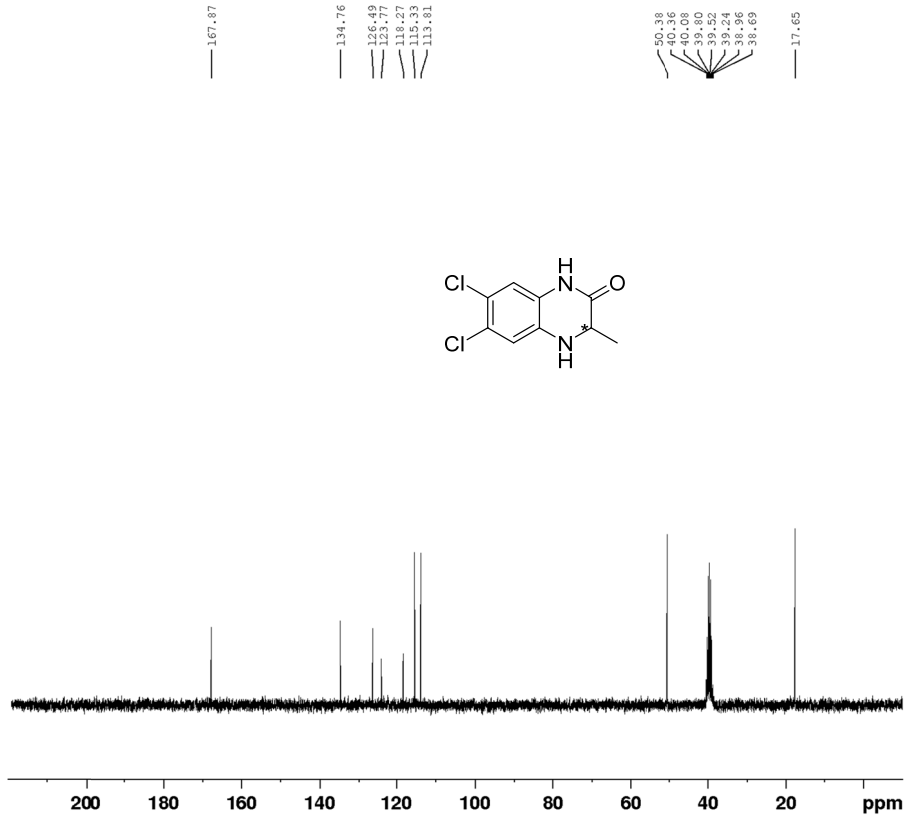



```
Current Data Parameters
NAME          lichenghao
EXPNO                 44
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time               22.32
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT             DMSO
NS                    41
DS                     4
SWH           18028.846 Hz
FIDRES        0.275098 Hz
AQ            1.8175317 sec
RG               209.09
DW               27.733 usec
DE                6.50 usec
TE                298.3 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                11.00 usec
PL1              120.00 dB
PL1W                0 W
SFO1         75.4752949 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677820 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Figure S37. ^{1}H NMR and ^{13}C NMR spectra of **2j**

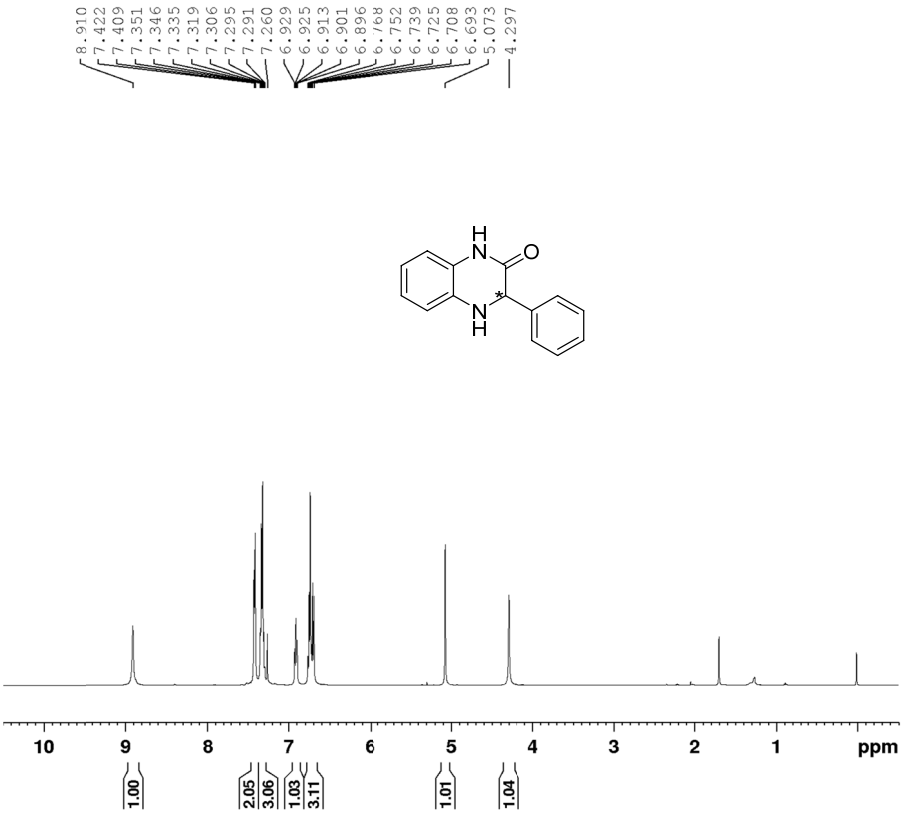



```
Current Data Parameters
NAME          lichenghao
EXPNO                 35
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time              20.00
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG            zg30
TD                65536
SOLVENT            DMSO
NS                   16
DS                    2
SWH            6009.615 Hz
FIDRES        0.091699 Hz
AQ            5.4525952 sec
RG               209.09
DW               83.200 usec
DE                6.50 usec
TE               298.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.00 usec
PL1              120.00 dB
PL1W                   0 W
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                 65536
SF          300.1300025 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

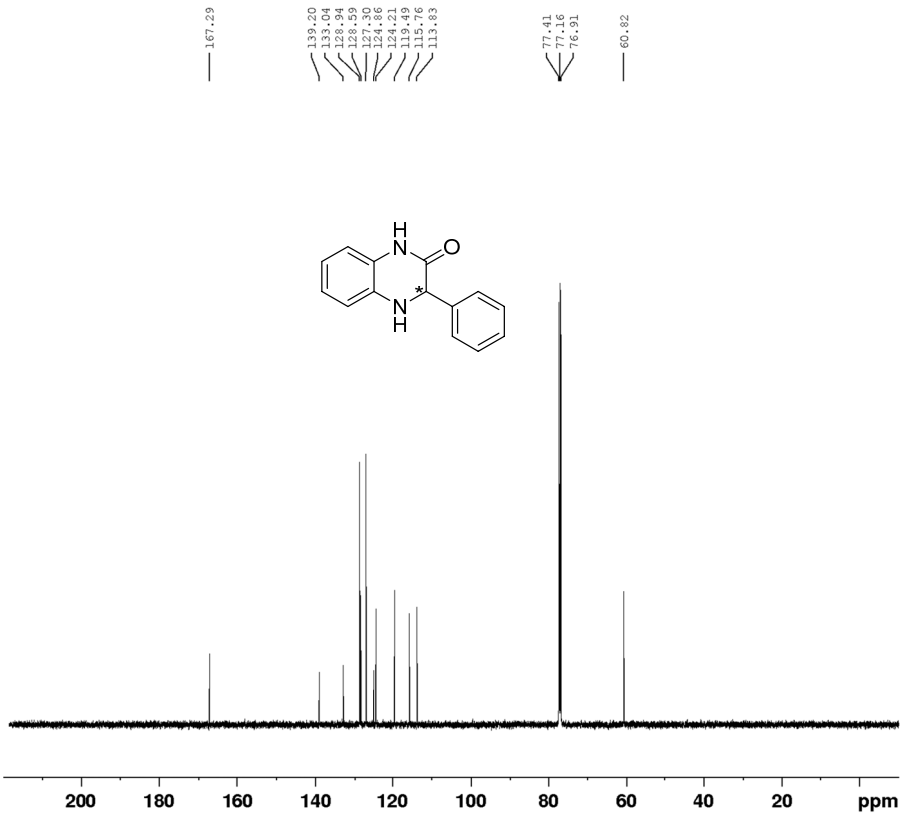



```
Current Data Parameters
NAME          lichenghao
EXPNO                 36
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time              20.03
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT            DMSO
NS                   32
DS                    4
SWH           18028.846 Hz
FIDRES        0.275098 Hz
AQ            1.8175317 sec
RG               209.09
DW               27.733 usec
DE                6.50 usec
TE               298.3 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                11.00 usec
PL1              120.00 dB
PL1W                   0 W
SFO1        75.4752949 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677823 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Figure S38. ^{1}H NMR and ^{13}C NMR spectra of **2k**

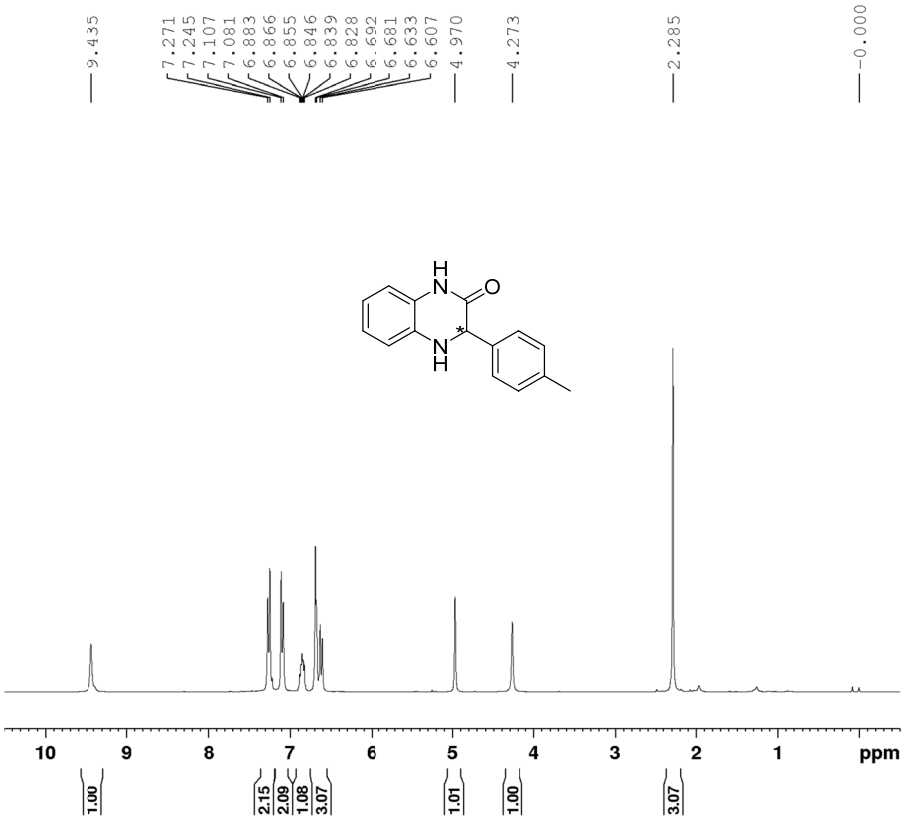



```
Current Data Parameters
NAME           KWT-ph-qh
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time               13.51
INSTRUM            spect
PROBHD   5 mm CPPBBO BB
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2767999 sec
RG                 31.72
DW                50.000 usec
DE                 6.50 usec
TE                298.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.59 usec
PL1               120.00 dB
PL1W                   0 W
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                 65536
SF          500.1300119 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

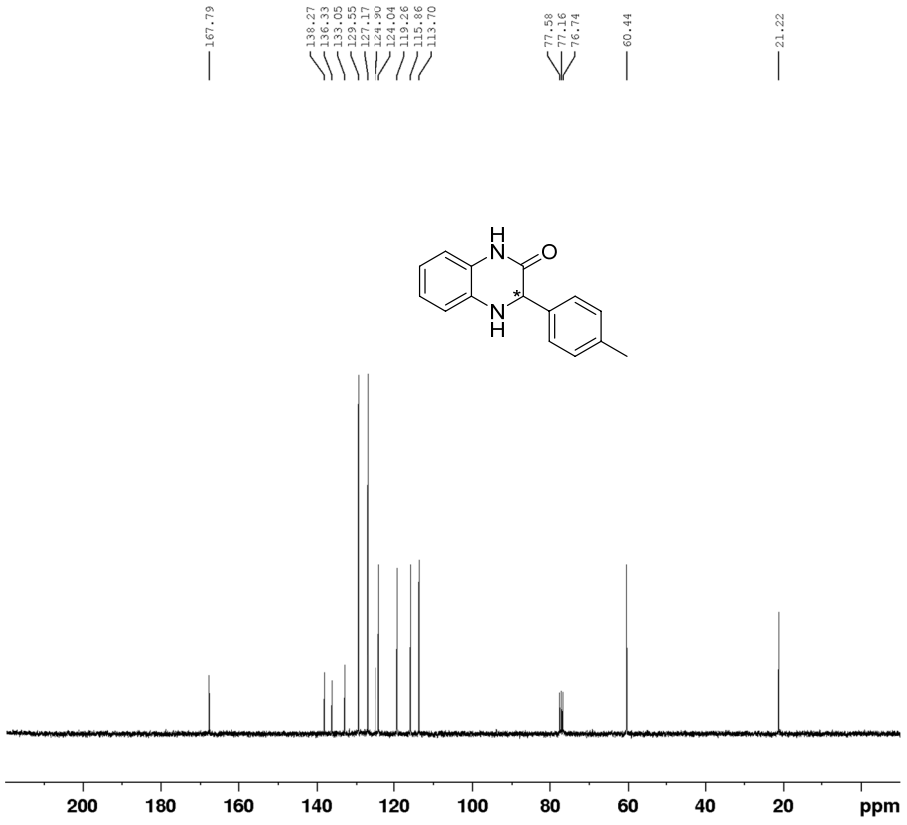



```
Current Data Parameters
NAME           KWT-Ph-qh
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time               13.53
INSTRUM            spect
PROBHD   5 mm CPPBBO BB
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    34
DS                     4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG                192.89
DW                16.800 usec
DE                 18.00 usec
TE                298.2 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 9.80 usec
PL1               120.00 dB
PL1W                   0 W
SFO1        125.7703637 MHz

F2 - Processing parameters
SI                 32768
SF          125.7577743 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Figure S39. ^{1}H NMR and ^{13}C NMR spectra of **2l**

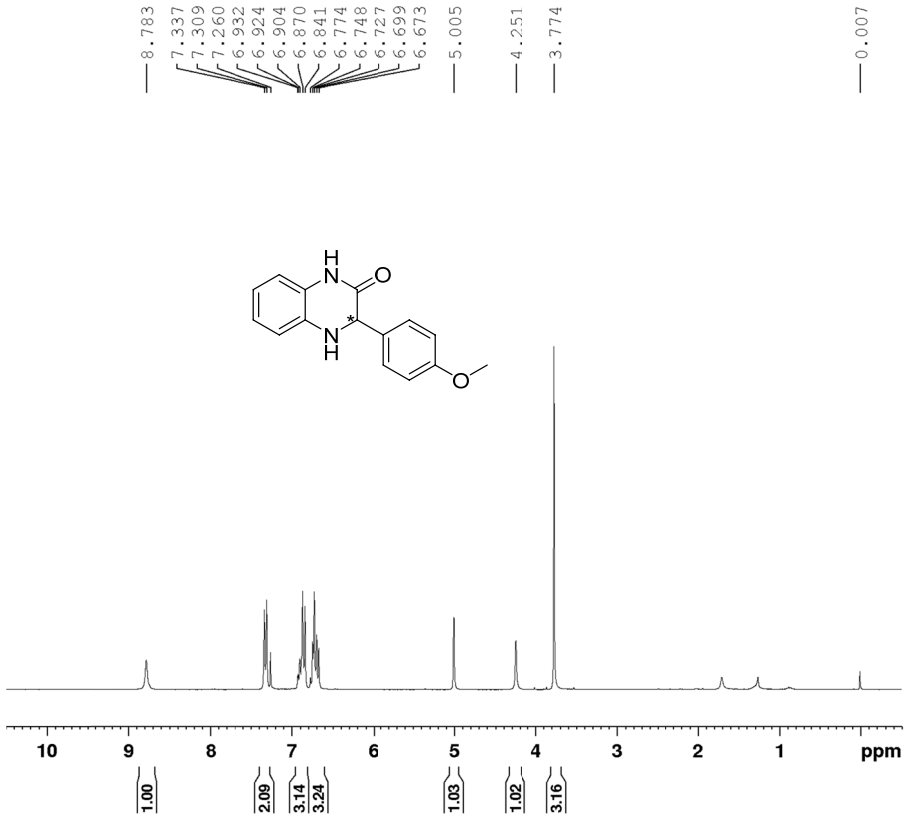



```
Current Data Parameters
NAME        KWT-4MePh-qh
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time               15.13
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6009.615 Hz
FIDRES          0.091699 Hz
AQ              5.4525952 sec
RG                103.37
DW                83.200 usec
DE                 6.50 usec
TE                298.3 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.00 usec
PL1              120.00 dB
PL1W                0 W
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                 65536
SF           300.1300196 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

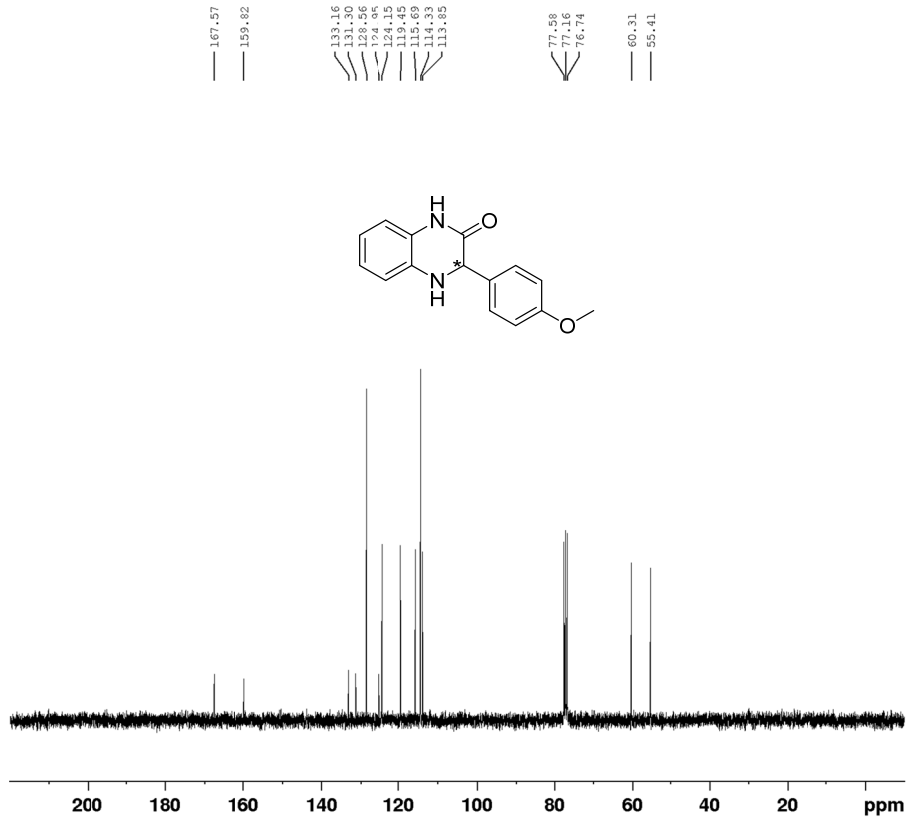



```
Current Data Parameters
NAME        KWT-4MePh-qh
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time               15.18
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     4
SWH            18028.846 Hz
FIDRES          0.275098 Hz
AQ              1.8175317 sec
RG                209.09
DW                27.733 usec
DE                 6.50 usec
TE                298.3 K
D1             2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                11.00 usec
PL1              120.00 dB
PL1W                0 W
SFO1         75.4752949 MHz

F2 - Processing parameters
SI                 32768
SF           75.4677458 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Figure S40. ^{1}H NMR and ^{13}C NMR spectra of **2m**

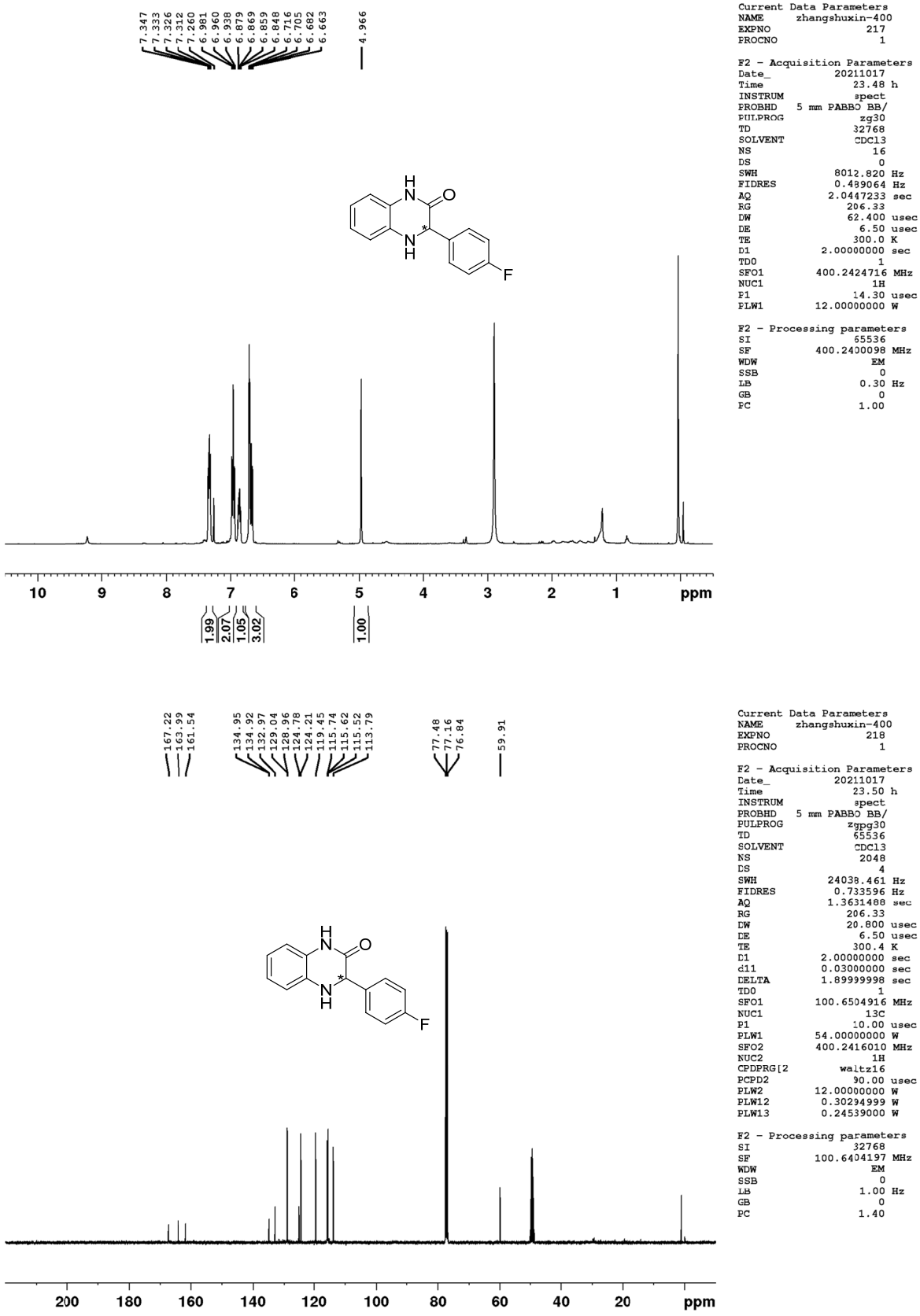



```
Current Data Parameters
NAME          lichenghao
EXPNO                 29
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time               18.36
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6009.615 Hz
FIDRES          0.091699 Hz
AQ              5.4525952 sec
RG                 209.09
DW                 83.200 usec
DE                  6.50 usec
TE                 298.2 K
D1              1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.00 usec
PL1               120.00 dB
PL1W                   0 W
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 65536
SF            300.1300072 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```




```
Current Data Parameters
NAME          lichenghao
EXPNO                 30
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time               18.44
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    93
DS                     4
SWH            18028.846 Hz
FIDRES          0.275098 Hz
AQ              1.8175317 sec
RG                 209.09
DW                 27.733 usec
DE                  6.50 usec
TE                 298.3 K
D1              2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 11.00 usec
PL1               120.00 dB
PL1W                   0 W
SFO1         75.4752949 MHz

F2 - Processing parameters
SI                 32768
SF            75.4577400 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

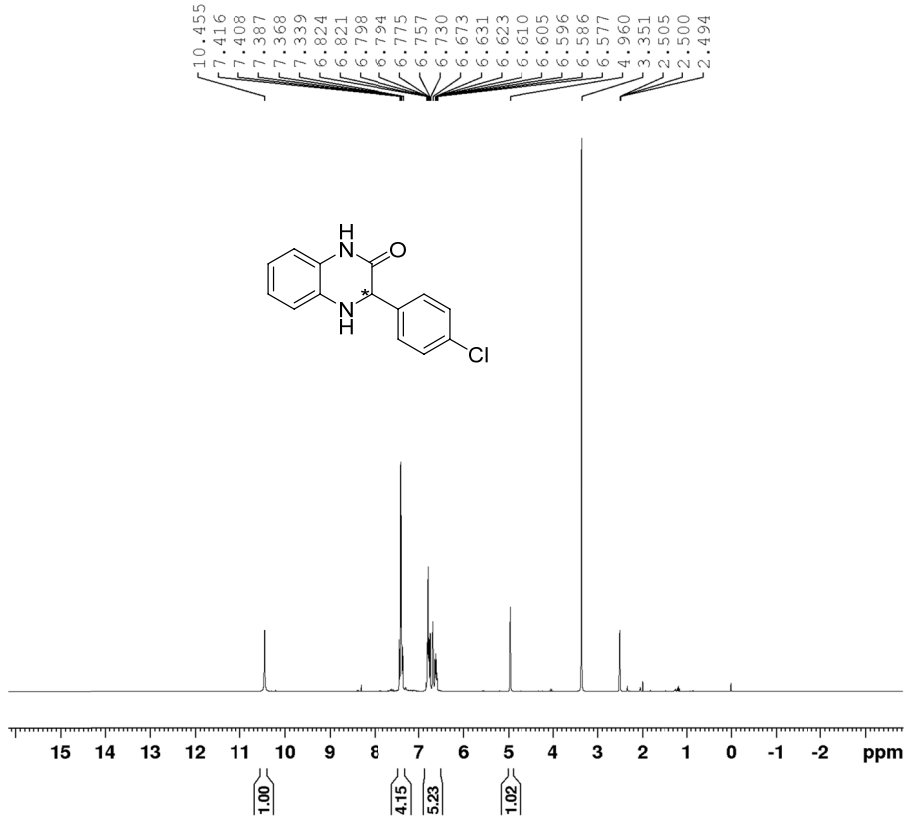
Figure S41. ^{1}H NMR and ^{13}C NMR spectra of **2n**



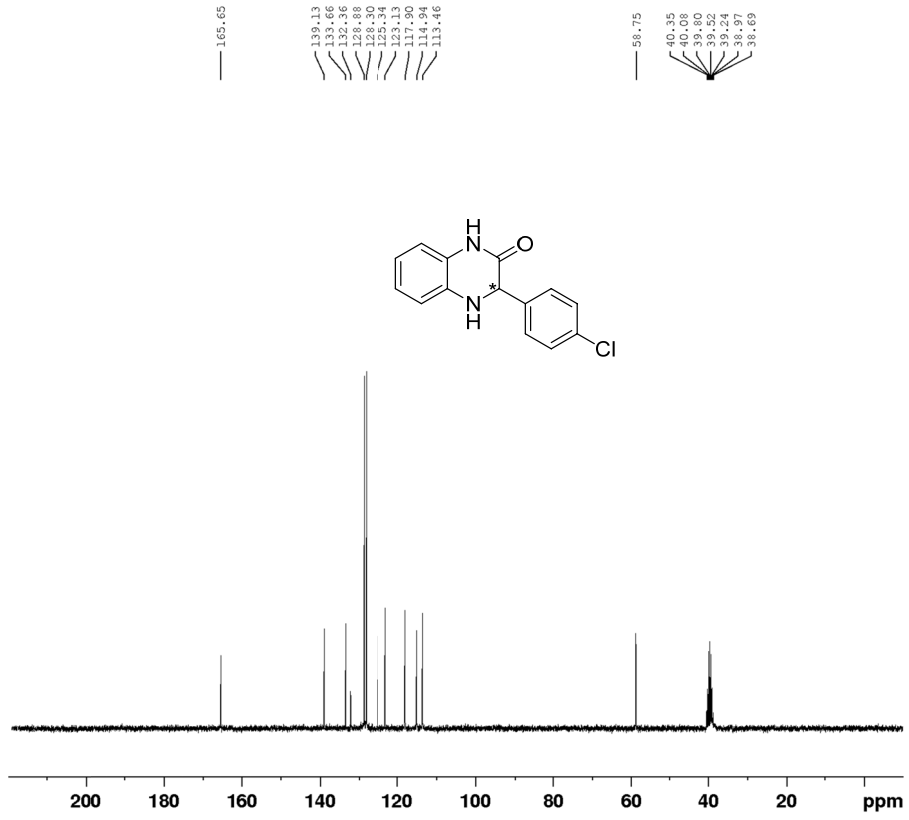

```
Current Data Parameters
NAME      zhangshuxin-400
EXPNO                 217
PROCNO                  1

F2 - Acquisition Parameters
Date_           20211017
Time              23.48 h
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 32768
SOLVENT             CDCl3
NS                     16
DS                      0
SWH             8012.820 Hz
FIDRES          0.489064 Hz
AQ              2.0447233 sec
RG                 206.33
DW                 62.400 usec
DE                  6.50 usec
TE                 300.0 K
D1              2.00000000 sec
TD0                     1
SFO1          400.2424716 MHz
NUC1                   1H
P1                  14.30 usec
PLW1         12.00000000 W

F2 - Processing parameters
SI                  65536
SF            400.2400098 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

```
Current Data Parameters
NAME      zhangshuxin-400
EXPNO                 218
PROCNO                  1

F2 - Acquisition Parameters
Date_           20211017
Time              23.50 h
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT             CDCl3
NS                   2048
DS                      4
SWH            24038.461 Hz
FIDRES          0.733596 Hz
AQ              1.3631488 sec
RG                 206.33
DW                 20.800 usec
DE                  6.50 usec
TE                 300.4 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                     1
SFO1          100.6504916 MHz
NUC1                   13C
P1                  10.00 usec
PLW1         54.00000000 W
SFO2          400.2416010 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               90.00 usec
PLW2         12.00000000 W
PLW12         0.30294999 W
PLW13         0.24539000 W

F2 - Processing parameters
SI                  32768
SF            100.6404197 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

Figure S42. ^{1}H NMR and ^{13}C NMR spectra of **2o**

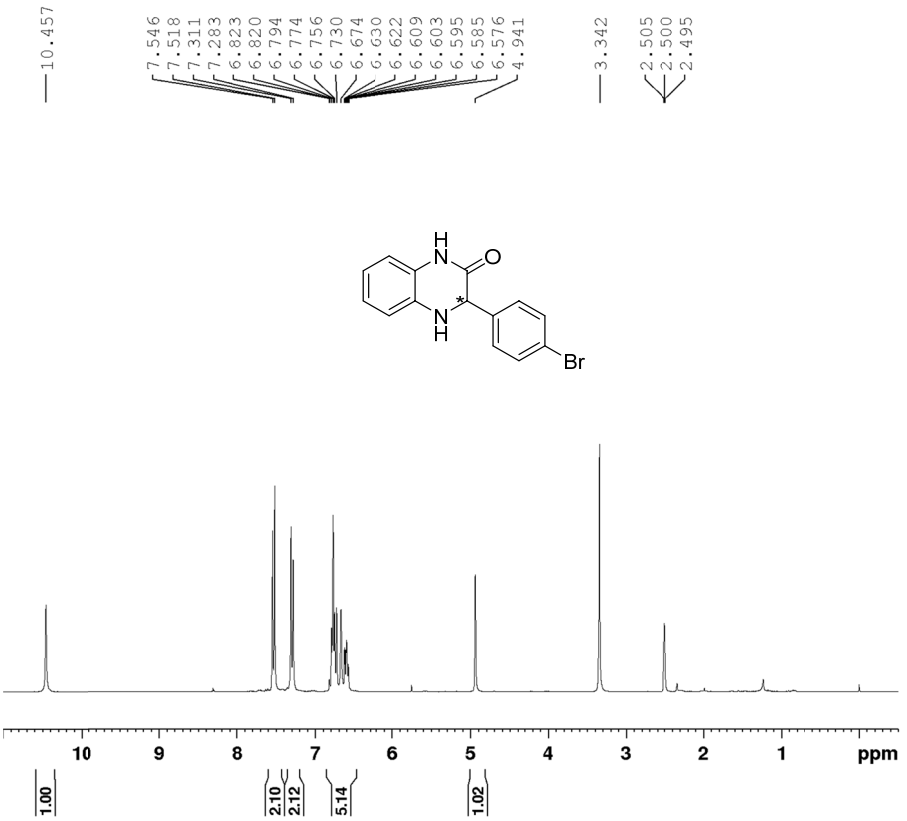



```
Current Data Parameters
NAME          lichenghao
EXPNO                 49
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time              23.07
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG           zg30
TD                65536
SOLVENT            DMSO
NS                   16
DS                    2
SWH            6009.615 Hz
FIDRES         0.091699 Hz
AQ             5.4525952 sec
RG                209.09
DW               83.200 usec
DE                6.50 usec
TE               298.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.00 usec
PL1              120.00 dB
PL1W                0 W
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                65536
SF          300.1300024 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

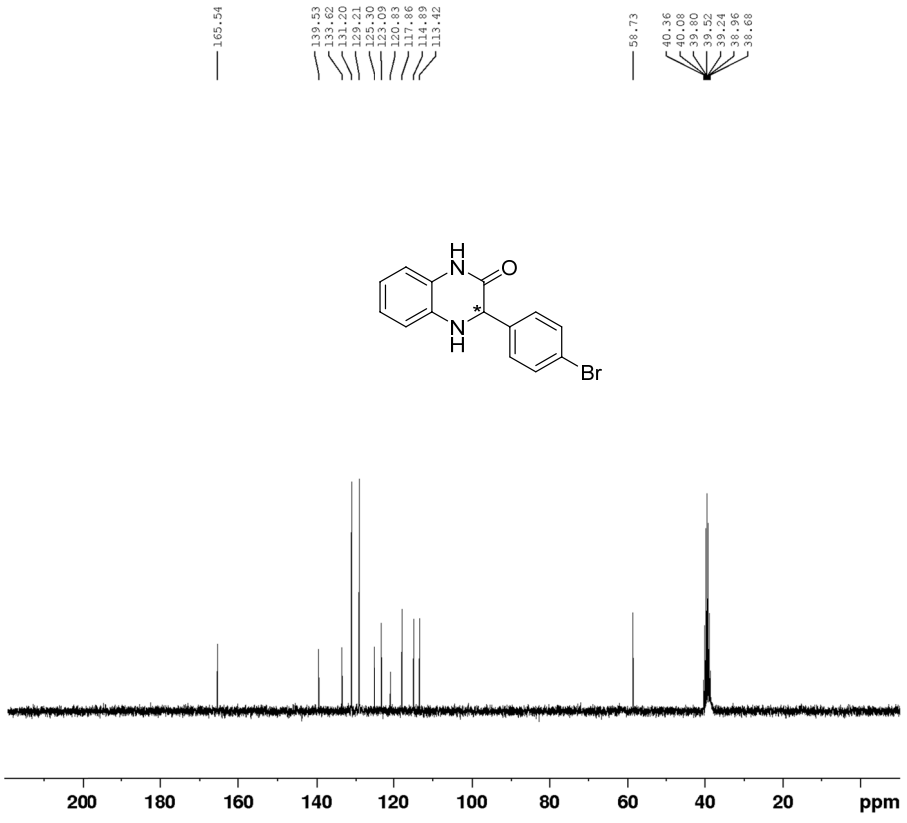



```
Current Data Parameters
NAME          lichenghao
EXPNO                 47
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time              22.27
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT            DMSO
NS                   43
DS                    4
SWH           18028.846 Hz
FIDRES         0.275098 Hz
AQ             1.8175317 sec
RG                209.09
DW               27.733 usec
DE                6.50 usec
TE               298.3 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                11.00 usec
PL1              120.00 dB
PL1W                0 W
SFO1         75.4752949 MHz

F2 - Processing parameters
SI                32768
SF          75.4577817 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

Figure S43. ^{1}H NMR and ^{13}C NMR spectra of **2p**




```
Current Data Parameters
NAME          lichenghao
EXPNO                 51
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time               23.15
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG            zg30
TD                65536
SOLVENT            DMSO
NS                    16
DS                     2
SWH            6009.615 Hz
FIDRES        0.091699 Hz
AQ            5.4525952 sec
RG               209.09
DW               83.200 usec
DE                6.50 usec
TE               298.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.00 usec
PL1              120.00 dB
PL1W                   0 W
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 65536
SF           300.1300015 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```




```
Current Data Parameters
NAME          lichenghao
EXPNO                 52
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time               23.17
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT            DMSO
NS                    68
DS                     4
SWH           18028.846 Hz
FIDRES        0.275098 Hz
AQ            1.8175317 sec
RG               209.09
DW               27.733 usec
DE                6.50 usec
TE               298.3 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                11.00 usec
PL1              120.00 dB
PL1W                   0 W
SFO1         75.4752949 MHz

F2 - Processing parameters
SI                 32768
SF           75.4677830 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Figure S44. ^{1}H NMR and ^{13}C NMR spectra of **2q**

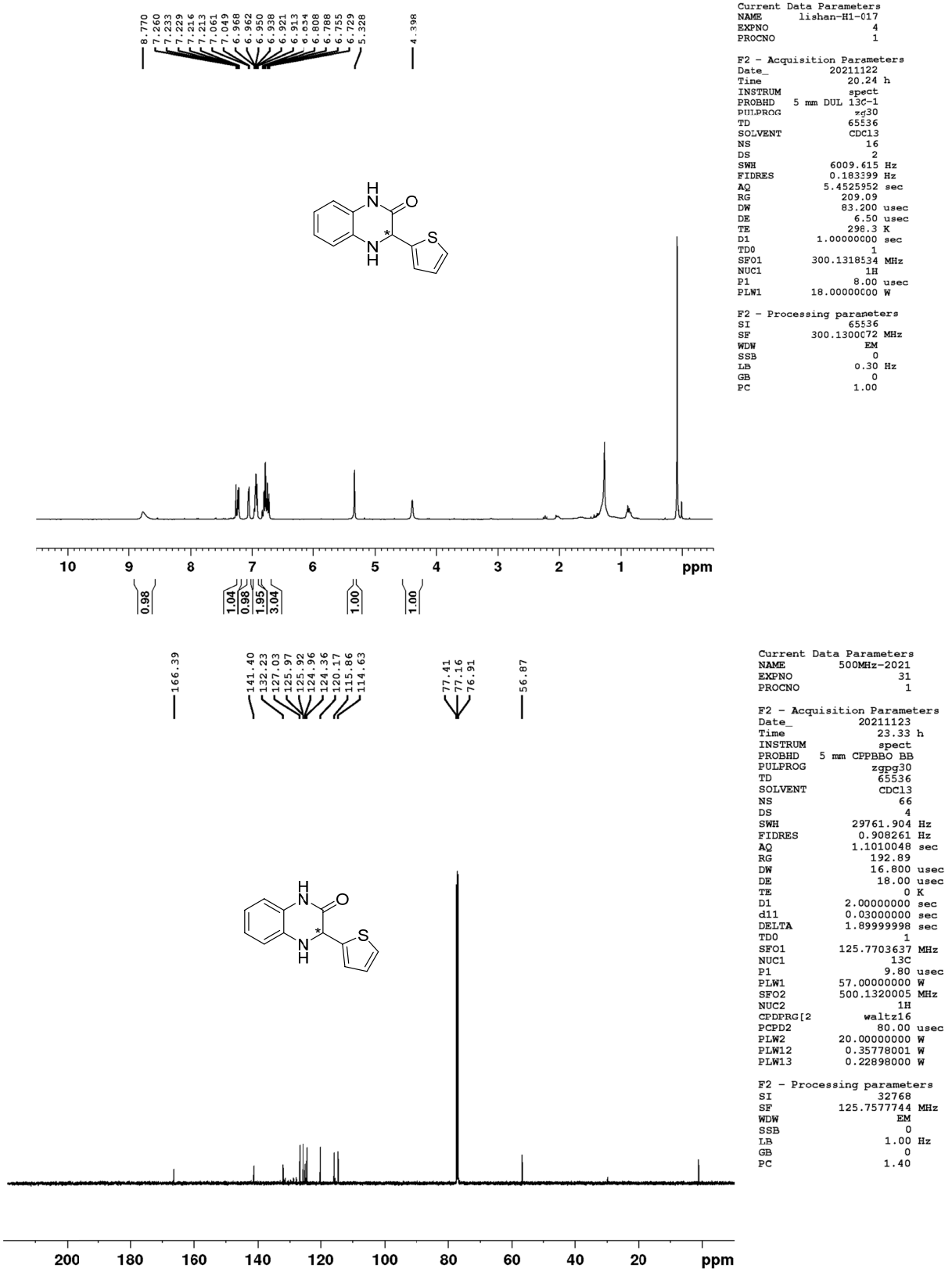
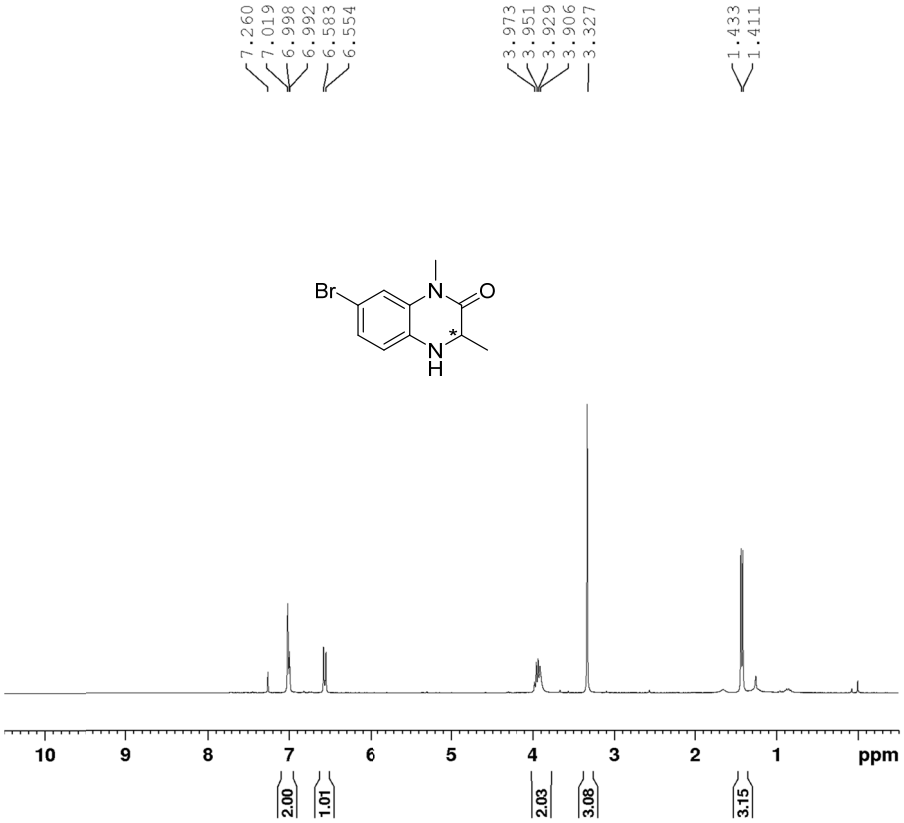
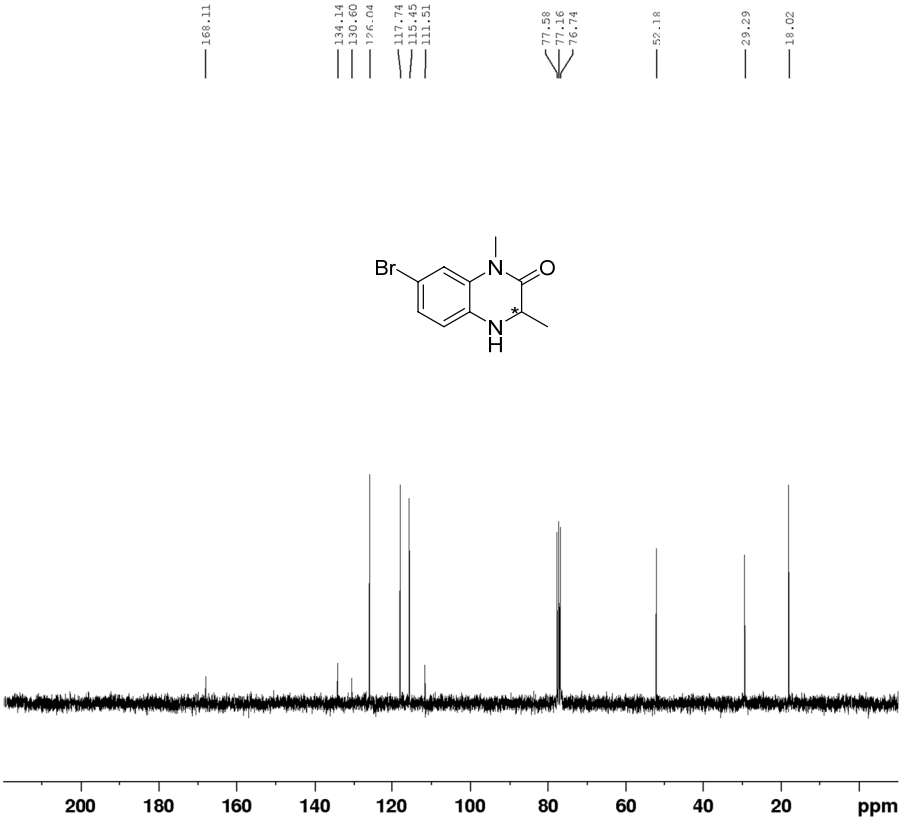


Figure S45. ^{1}H NMR and ^{13}C NMR spectra of **2r**

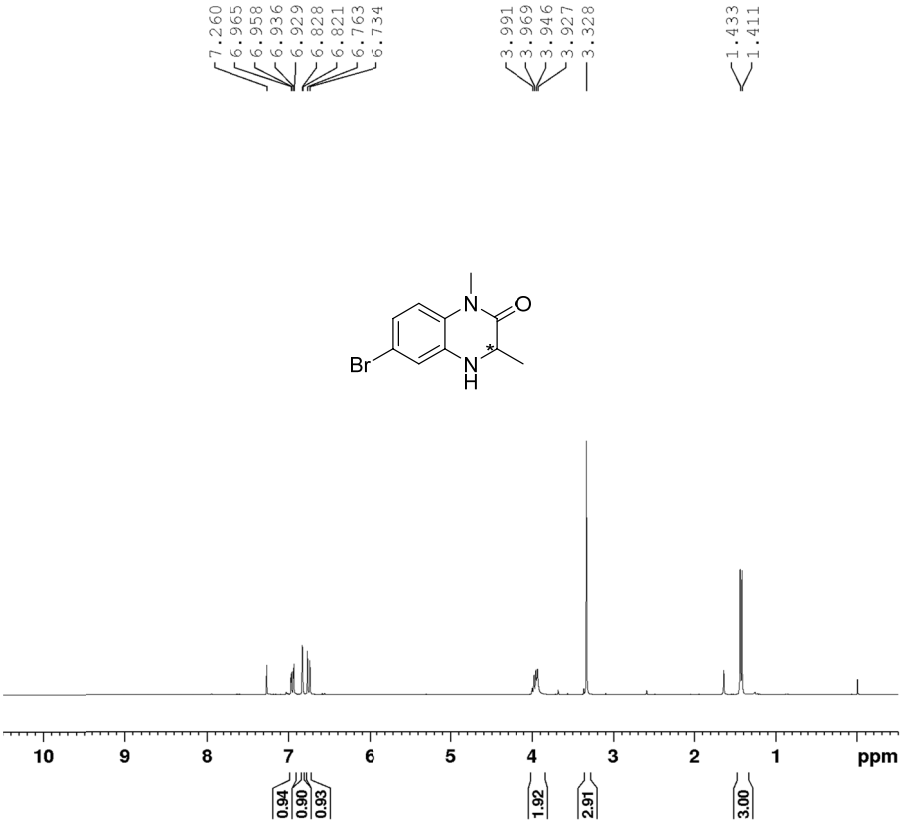



```
Current Data Parameters
NAME          lichenghao
EXPNO                 21
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210502
Time              22.41
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG           zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6009.615 Hz
FIDRES         0.091699 Hz
AQ             5.4525952 sec
RG               209.09
DW               83.200 usec
DE                6.50 usec
TE               298.2 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.00 usec
PL1              120.00 dB
PL1W                   0 W
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 65536
SF           300.1300070 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

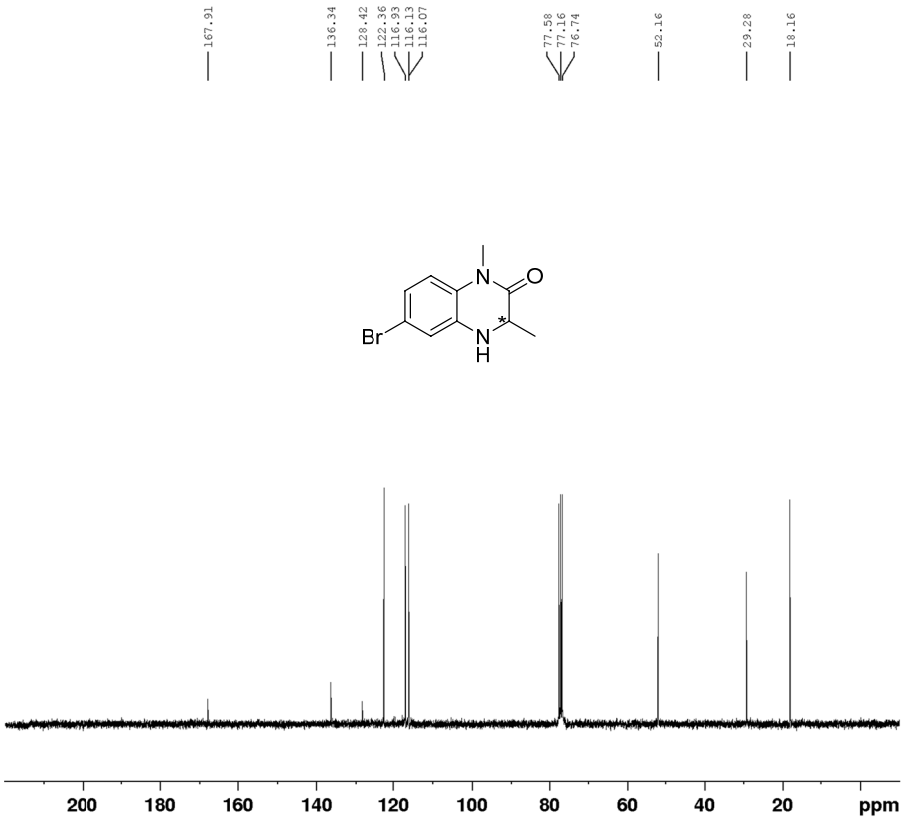



```
Current Data Parameters
NAME          lichenghao
EXPNO                 23
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210502
Time              22.58
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                   78
DS                    4
SWH           18028.846 Hz
FIDRES         0.275098 Hz
AQ             1.8175317 sec
RG               209.09
DW               27.733 usec
DE                6.50 usec
TE               298.2 K
D1             2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                11.00 usec
PL1              120.00 dB
PL1W                   0 W
SFO1          75.4752949 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677398 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Figure S46. ^{1}H NMR and ^{13}C NMR spectra of **2s**

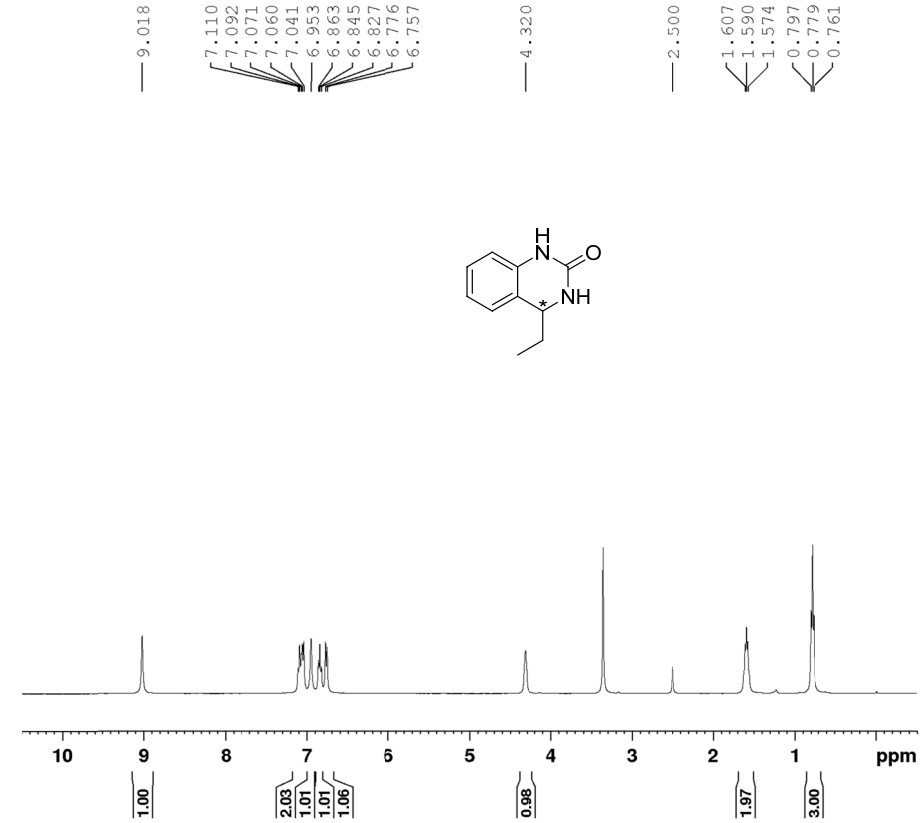



```
Current Data Parameters
NAME      KWT-6-Br-Me-qh
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time              17.10
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6009.615 Hz
FIDRES         0.091699 Hz
AQ             5.4525952 sec
RG                209.09
DW               83.200 usec
DE                6.50 usec
TE               298.3 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.00 usec
PL1              120.00 dB
PL1W                   0 W
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 65536
SF           300.1300072 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

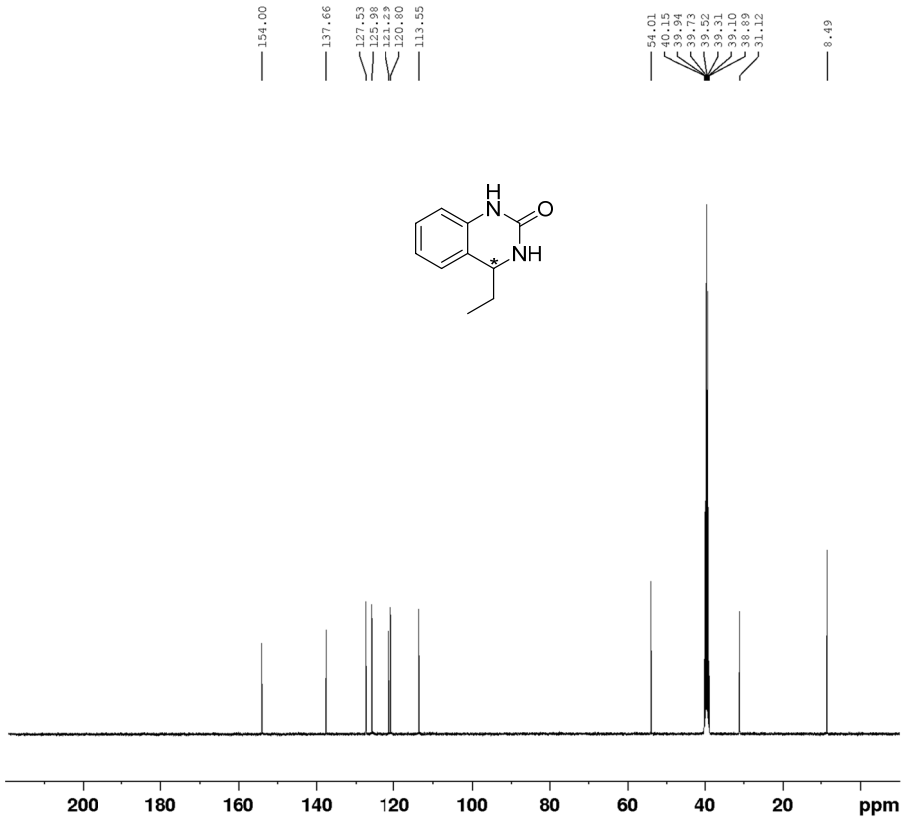



```
Current Data Parameters
NAME      KWT-6-Br-Me-qh
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time              17.12
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  512
DS                    4
SWH           18028.846 Hz
FIDRES         0.275098 Hz
AQ             1.8175317 sec
RG                209.09
DW               27.733 usec
DE                6.50 usec
TE               298.4 K
D1             2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                11.00 usec
PL1              120.00 dB
PL1W                   0 W
SFO1         75.4752949 MHz

F2 - Processing parameters
SI                 32768
SF           75.4577392 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Figure S47. ^{1}H NMR and ^{13}C NMR spectra of **4a**




```
Current Data Parameters
NAME      20210411-KZT-ET-QH
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_           20210411
Time              15.19
INSTRUM           spect
PROBHD    5 mm PABBO BB/
PULPROG             zg30
TD                65536
SOLVENT            DMSO
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES        0.122266 Hz
AQ            4.0894465 sec
RG                60.55
DW              62.400 usec
DE               6.50 usec
TE              298.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        400.1324710 MHz
NUC1                1H
P1                10.00 usec
PLW1        13.26099968 W

F2 - Processing parameters
SI                65536
SF          400.1300032 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```




```
Current Data Parameters
NAME      20210411-KZT-ET-QH
EXPNO                   20
PROCNO                   1

F2 - Acquisition Parameters
Date_           20210411
Time              16.25
INSTRUM           spect
PROBHD    5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT            DMSO
NS                 1024
DS                    4
SWH           24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631488 sec
RG                199.89
DW              20.800 usec
DE               6.50 usec
TE              298.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6228293 MHz
NUC1                13C
P1                10.00 usec
PLW1        56.93000031 W

======== CHANNEL f2 ========
SFO2        400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2        13.26099968 W
PLW12        0.16372000 W
PLW13        0.13260999 W

F2 - Processing parameters
SI                32768
SF          100.6128139 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

Figure S48. ^{1}H NMR and ^{13}C NMR spectra of **4b**

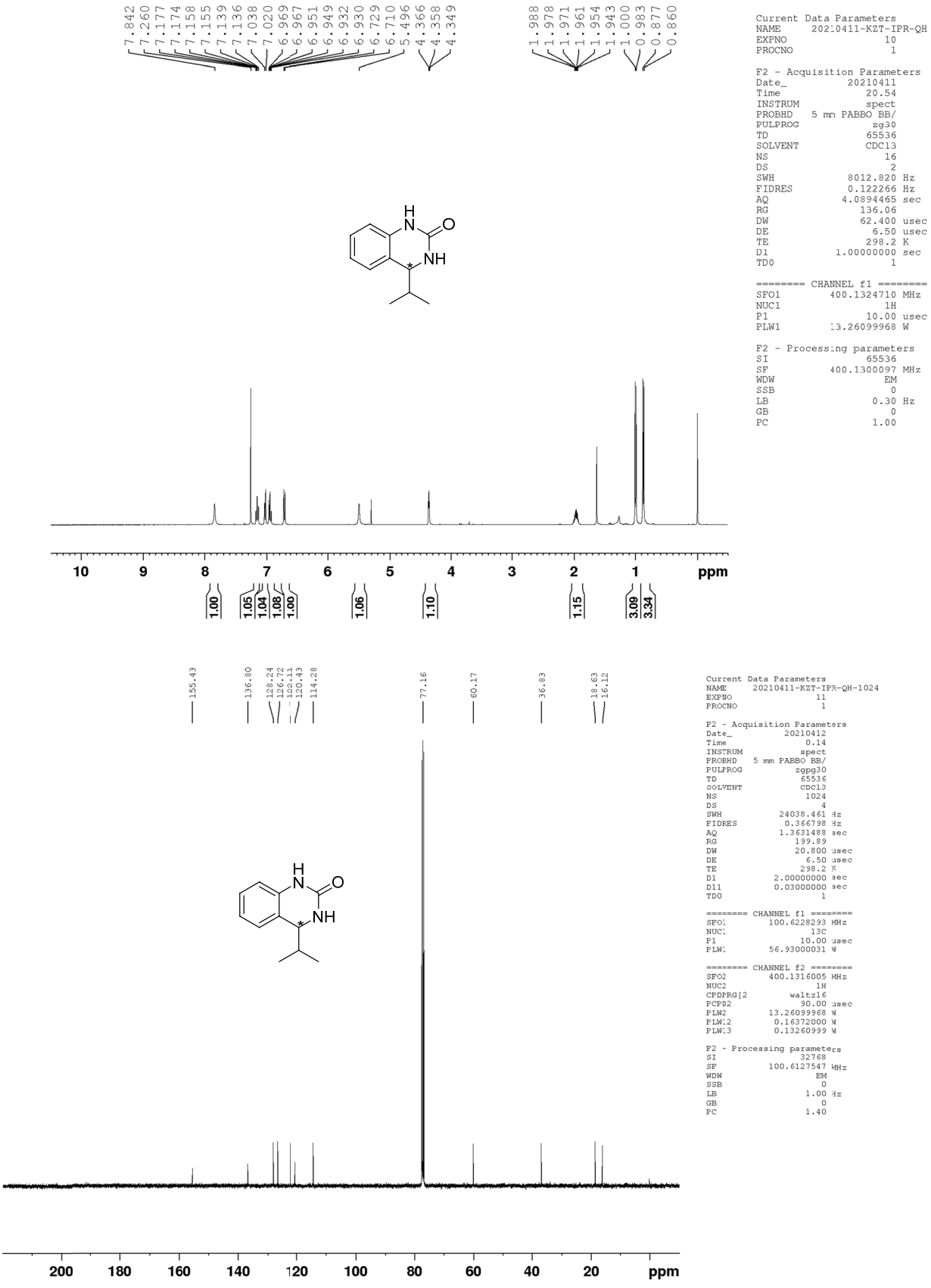
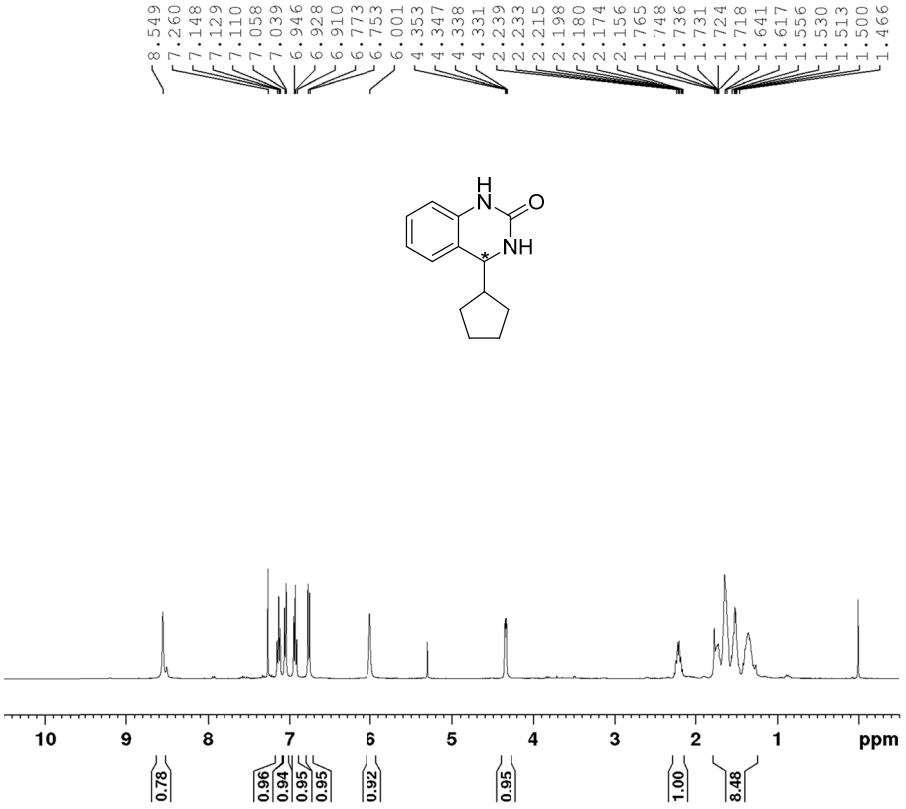
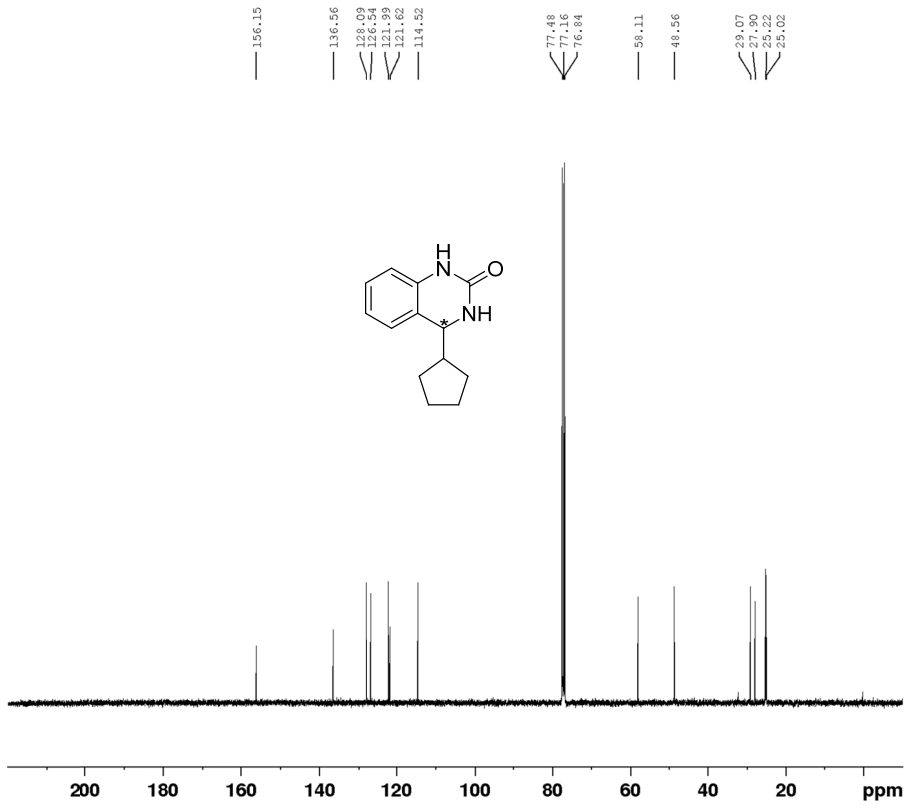


Figure S49. ^{1}H NMR and ^{13}C NMR spectra of **4c**




```
Current Data Parameters
NAME                 new-kzt
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_               20210411
Time                   20.59
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES                0.122266 Hz
AQ                 4.0894465 sec
RG                     89.48
DW                    62.400 usec
DE                     6.50 usec
TE                    298.2 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1              400.1324710 MHz
NUC1                      1H
P1                     10.00 usec
PLW1              13.26099968 W

F2 - Processing parameters
SI                        65536
SF                400.1300096 MHz
WDW                        EM
SSB             0
LB                      0.30 Hz
GB              0
PC                      1.00
```




```
Current Data Parameters
NAME      20210411-KZT-YWJ-QH-60(
EXPNO                     12
PROCNO                     1

F2 - Acquisition Parameters
Date_               20210412
Time                   0.52
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       600
DS                         4
SWH               24038.461 Hz
FIDRES                0.366798 Hz
AQ                 1.3631488 sec
RG                     199.89
DW                    20.800 usec
DE                     6.50 usec
TE                    298.2 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1              100.6228293 MHz
NUC1                      13C
P1                     10.00 usec
PLW1              56.93000031 W

======== CHANNEL f2 ========
SFO2              400.1316005 MHz
NUC2                      1H
CPDPRG[2              waltz16
PCPD2                  90.00 usec
PLW2              13.26099968 W
PLW12              0.16372000 W
PLW13              0.13260999 W

F2 - Processing parameters
SI                        32768
SF                100.6127560 MHz
WDW                        EM
SSB                         0
LB                      1.00 Hz
GB                          0
PC                      1.40
```

Figure S50. ^{1}H NMR and ^{13}C NMR spectra of **4d**

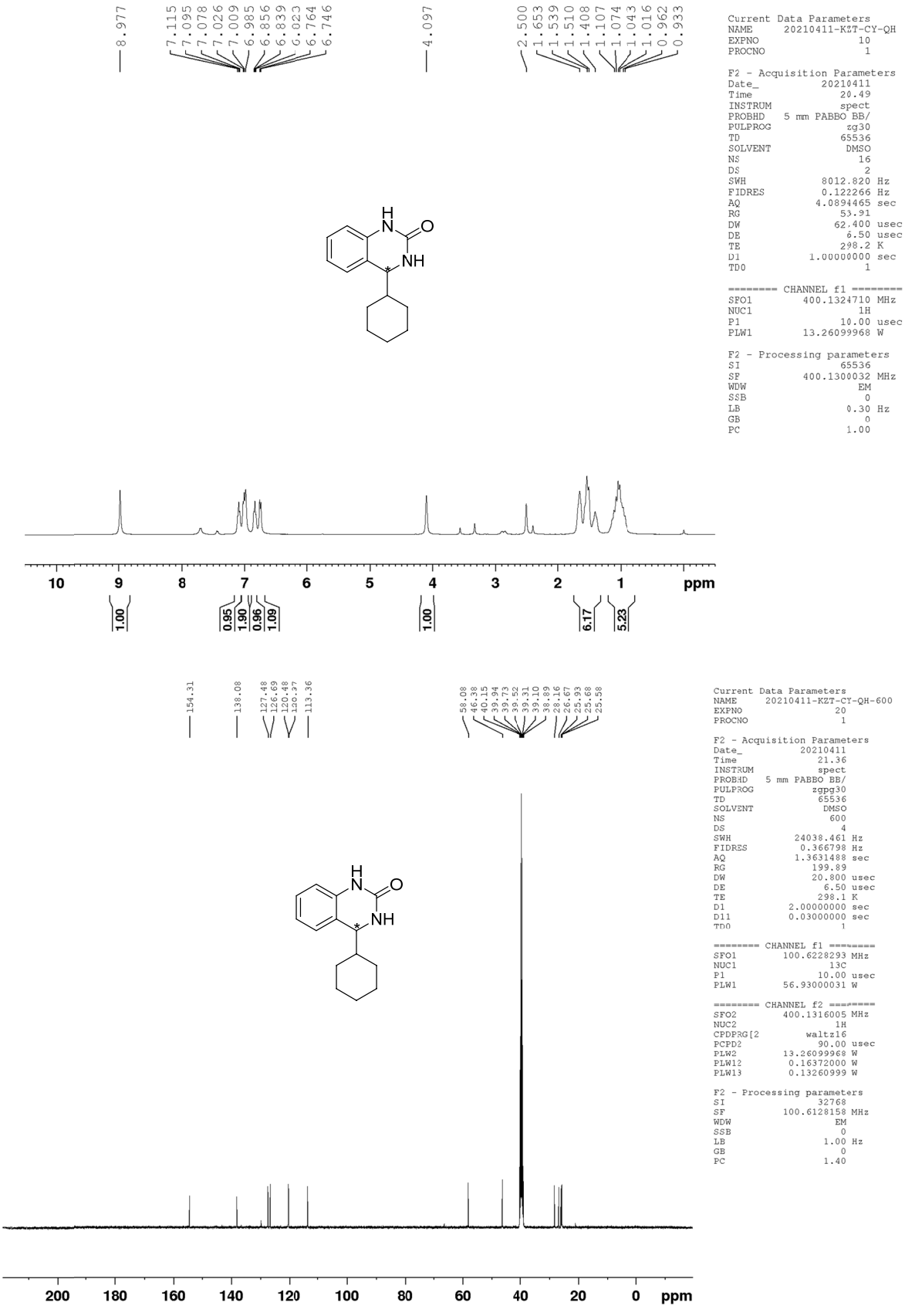
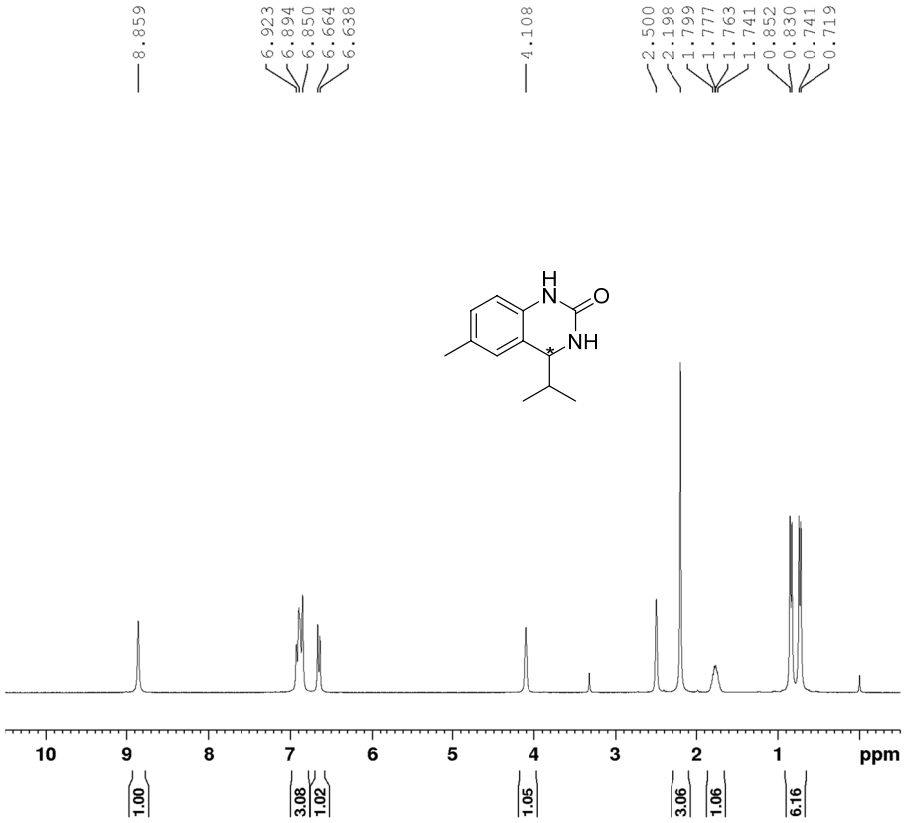
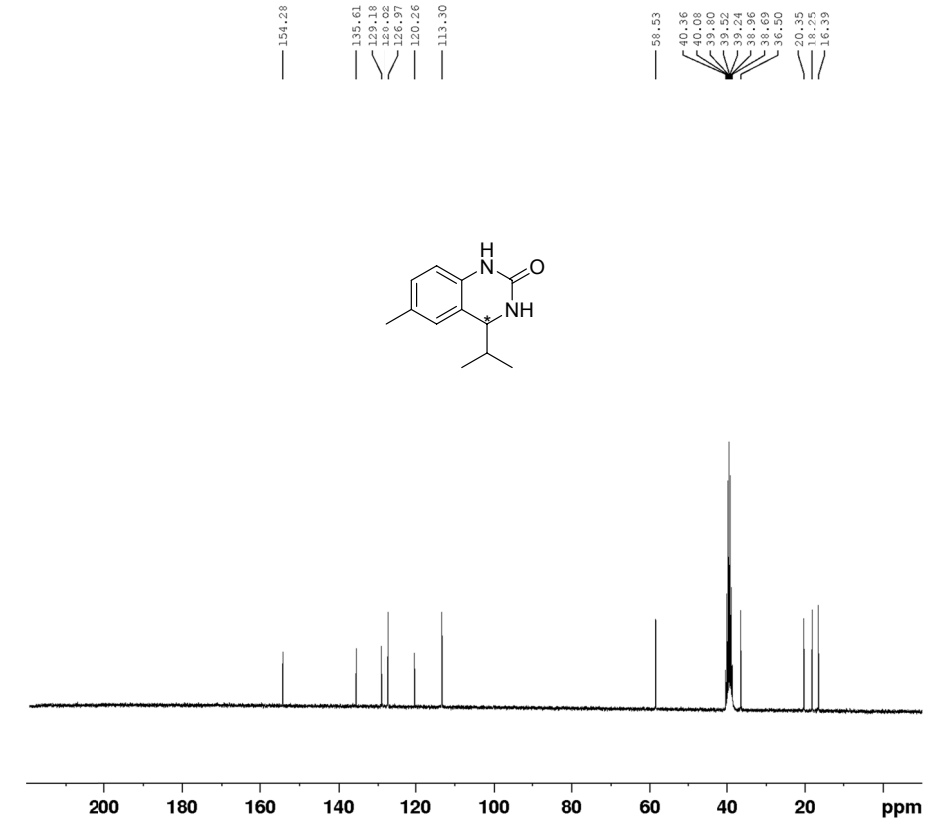


Figure S51. ^{1}H NMR and ^{13}C NMR spectra of **4e**

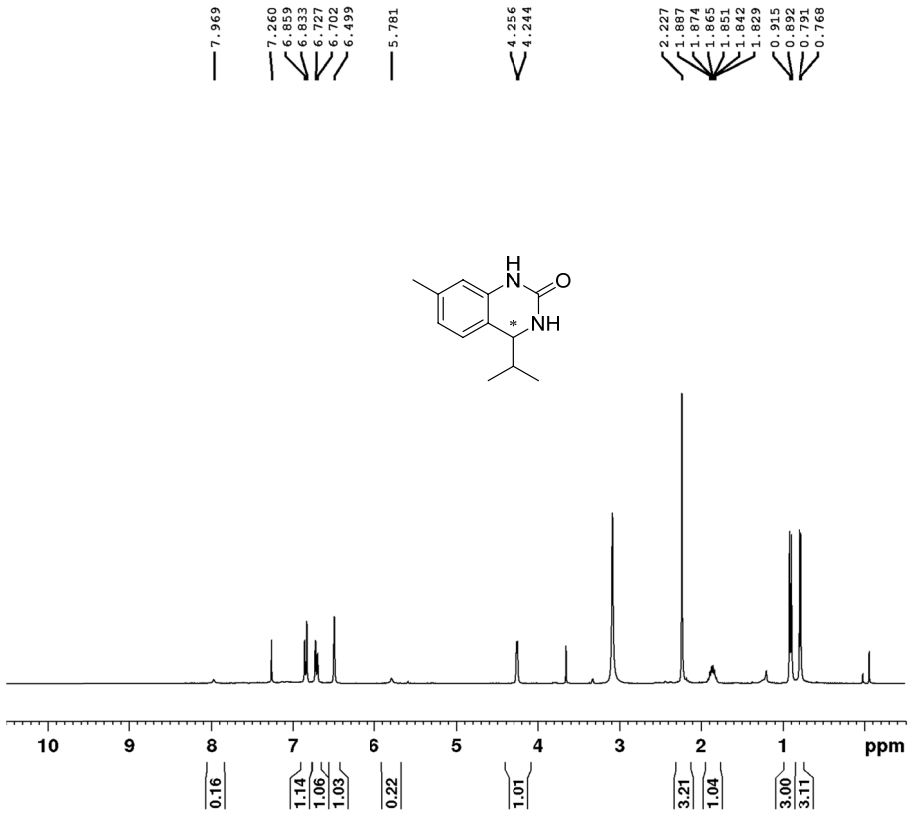



```
Current Data Parameters
NAME      KZT-Me-IPR-Qh
EXPNO                4
PROCNO               1

F2 - Acquisition Parameters
Date_          20210411
Time             22.43
INSTRUM          spect
PROBHD   5 mm DUL 13C-1
PULPROG          zg30
TD              65536
SOLVENT          DMSO
NS                 16
DS                  2
SWH          6009.615 Hz
FIDRES       0.091699 Hz
AQ           5.4525952 sec
RG              209.09
DW              83.200 usec
DE               6.50 usec
TE              298.2 K
D1           1.00000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1                1H
P1               8.00 usec
PL1             120.00 dB
PL1W               0 W
SFO1       300.1318534 MHz

F2 - Processing parameters
SI              65536
SF         300.1300024 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00
```

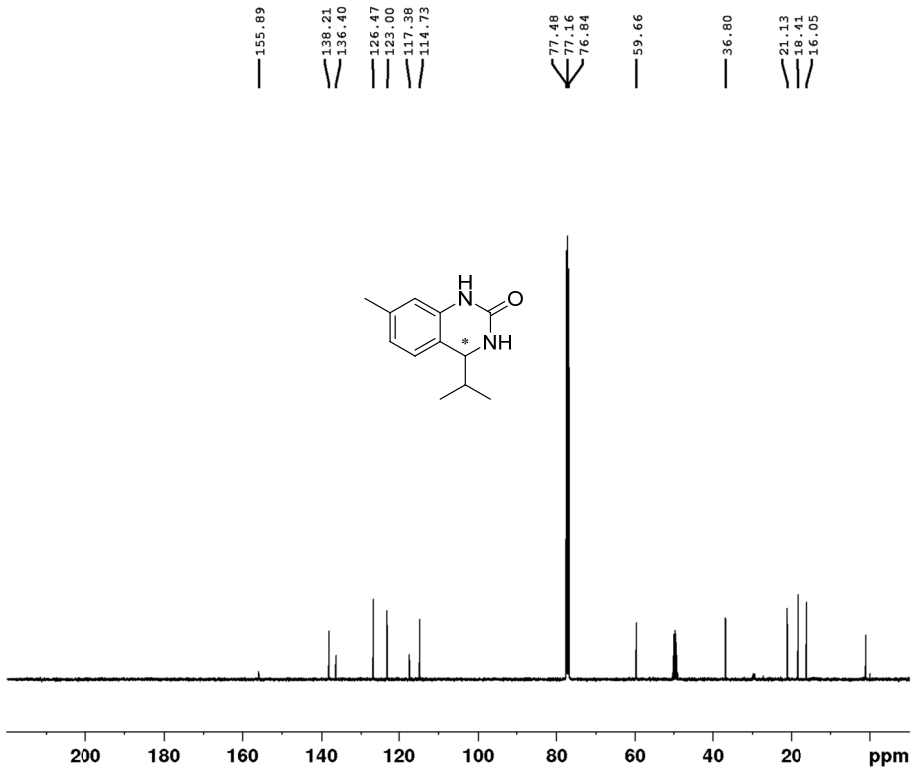



```
Current Data Parameters
NAME      KZT-Me-IPR-Qh
EXPNO                5
PROCNO               1

F2 - Acquisition Parameters
Date_          20210411
Time             23.49
INSTRUM          spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD              65536
SOLVENT          DMSO
NS                1024
DS                   4
SWH          18028.846 Hz
FIDRES        0.275098 Hz
AQ           1.8175317 sec
RG              209.09
DW              27.733 usec
DE               6.50 usec
TE              298.3 K
D1           2.00000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               13C
P1              11.00 usec
PL1             120.00 dB
PL1W               0 W
SFO1       75.4752949 MHz

F2 - Processing parameters
SI              32768
SF         75.4677843 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```

Figure S52. ^{1}H NMR and ^{13}C NMR spectra of **4f**

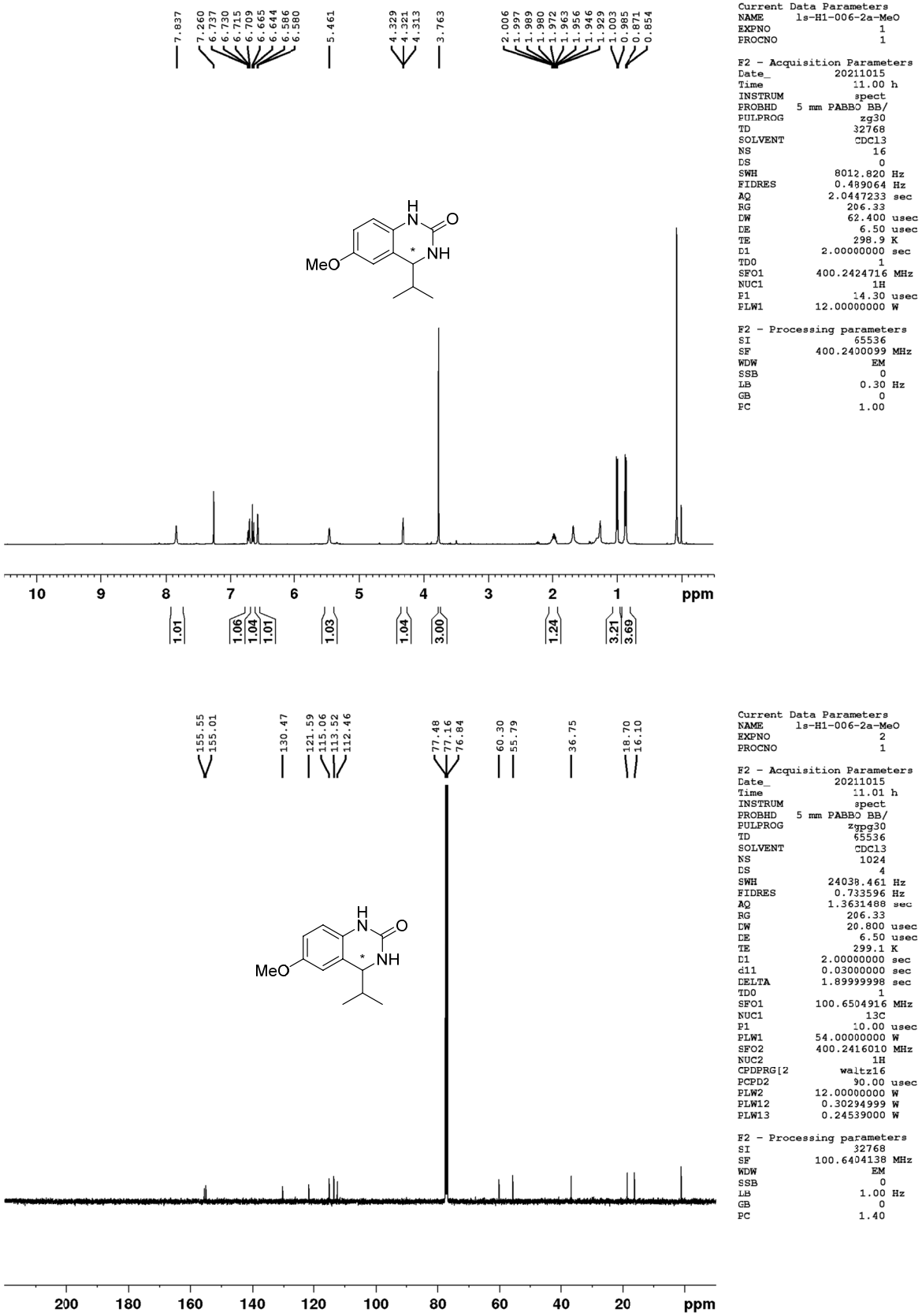



```
Current Data Parameters
NAME       lishan-H1-002
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211014
Time              17.17 h
INSTRUM             spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ              5.4525952 sec
RG                 209.09
DW                 83.200 usec
DE                  6.50 usec
TE                 298.3 K
D1             1.00000000 sec
TD0                    1
SFO1          300.1318534 MHz
NUC1                  1H
P1                  8.00 usec
PLW1         18.00000000 W

F2 - Processing parameters
SI                 65536
SF            300.1300070 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```




```
Current Data Parameters
NAME       lishan-H1-004a-Pd-C
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211015
Time              15.07 h
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  2048
DS                     4
SWH            24038.461 Hz
FIDRES          0.733596 Hz
AQ              1.3631488 sec
RG                 206.33
DW                 20.800 usec
DE                  6.50 usec
TE                 299.9 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                    1
SFO1          100.6504916 MHz
NUC1                  13C
P1                 10.00 usec
PLW1         54.00000000 W
SFO2          400.2416010 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              90.00 usec
PLW2         12.00000000 W
PLW12         0.30294999 W
PLW13         0.24539000 W

F2 - Processing parameters
SI                 32768
SF            100.6404173 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Figure S53. ^{1}H NMR and ^{13}C NMR spectra of **4g**




```
Current Data Parameters
NAME      ls-H1-006-2a-MeO
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20211015
Time                11.00 h
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       0
SWH               8012.820 Hz
FIDRES            0.489064 Hz
AQ                2.0447233 sec
RG                   206.33
DW                  62.400 usec
DE                   6.50 usec
TE                  298.9 K
D1                2.00000000 sec
TD0                      1
SFO1           400.2424716 MHz
NUC1                    1H
P1                   14.30 usec
PLW1          12.00000000 W

F2 - Processing parameters
SI                    65536
SF             400.2400099 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

```
Current Data Parameters
NAME      ls-H1-006-2a-MeO
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20211015
Time                11.01 h
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH              24038.461 Hz
FIDRES            0.733596 Hz
AQ                1.3631488 sec
RG                   206.33
DW                  20.800 usec
DE                   6.50 usec
TE                  299.1 K
D1                2.00000000 sec
d11               0.03000000 sec
DELTA             1.89999998 sec
TD0                      1
SFO1           100.6504916 MHz
NUC1                    13C
P1                   10.00 usec
PLW1          54.00000000 W
SFO2           400.2416010 MHz
NUC2                    1H
CPDPRG[2            waltz16
PCPD2                90.00 usec
PLW2          12.00000000 W
PLW12          0.30294999 W
PLW13          0.24539000 W

F2 - Processing parameters
SI                   32768
SF             100.6404138 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

Figure S54. ^{1}H NMR and ^{13}C NMR spectra of **4h**

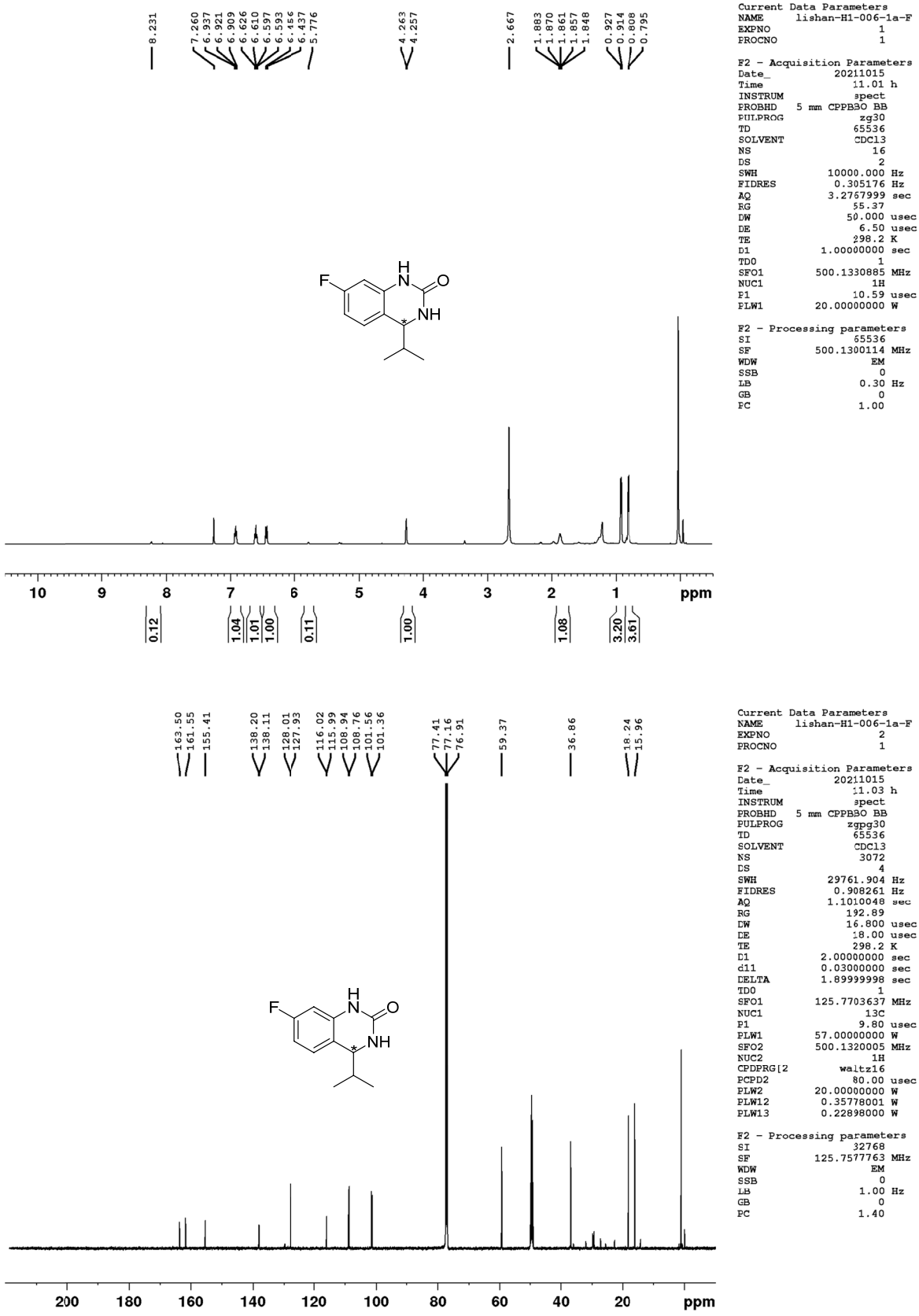
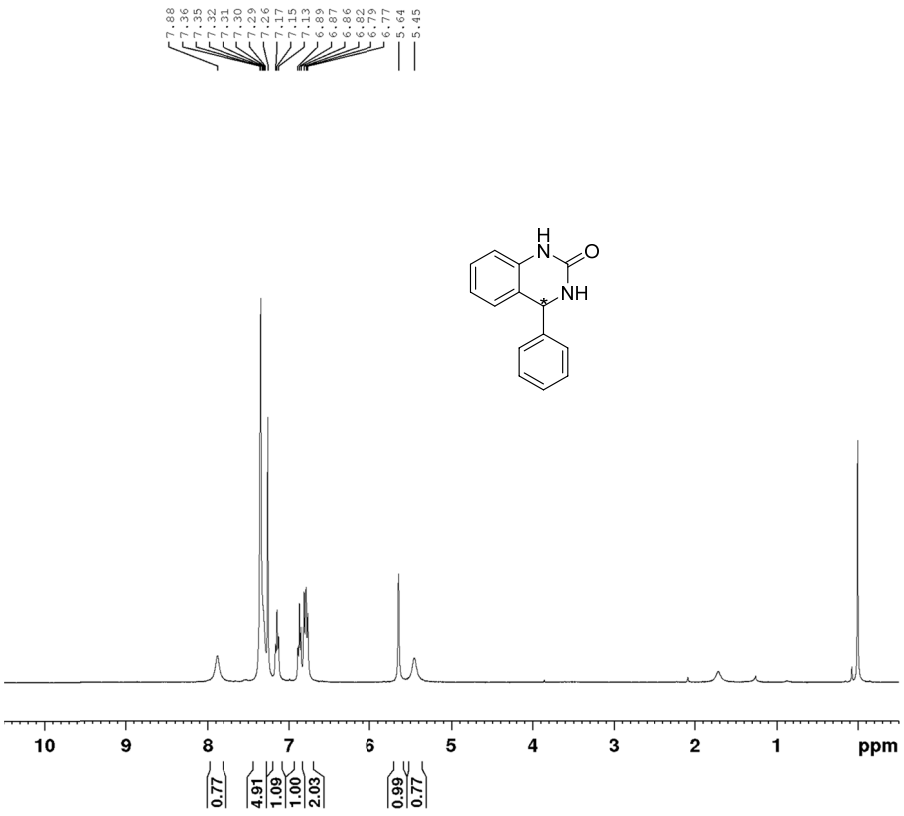
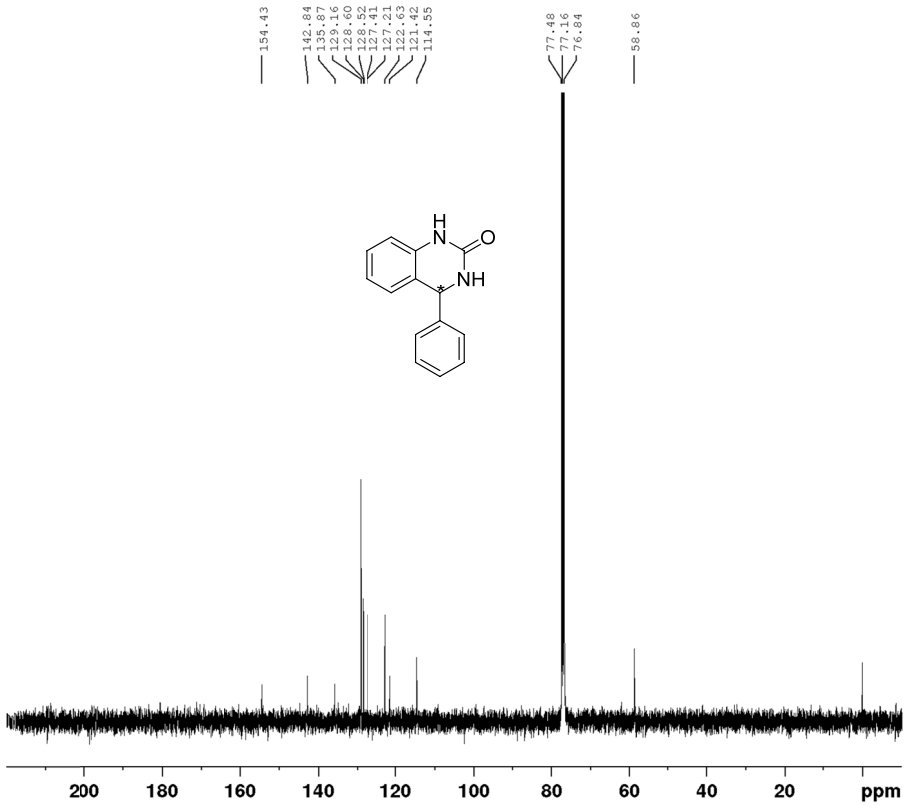


Figure S55. ^{1}H NMR and ^{13}C NMR spectra of **4i**



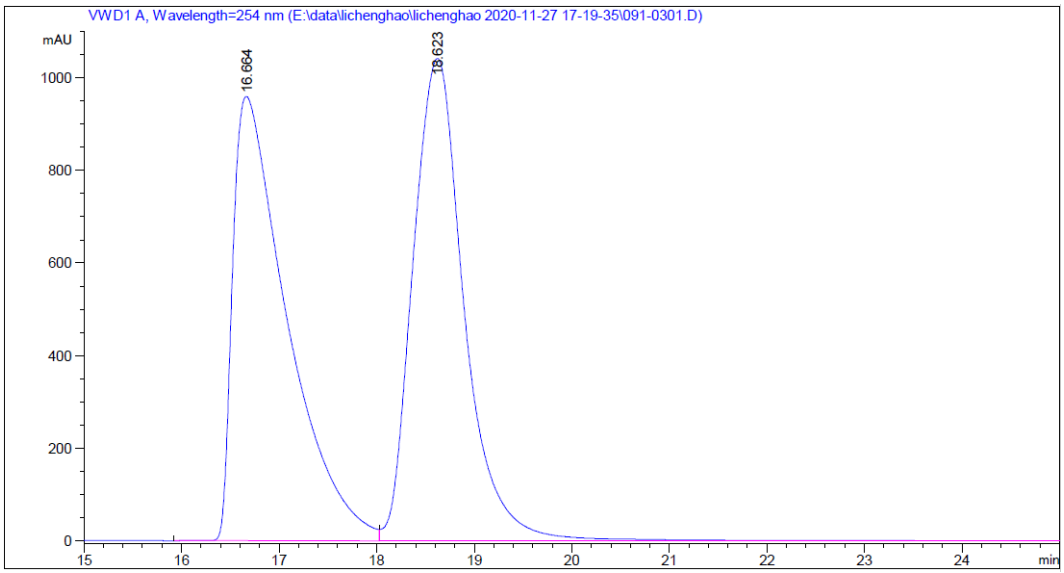

```
Current Data Parameters
NAME                  new-kzt
EXPNO                      20
PROCNO                      1

F2 - Acquisition Parameters
Date_               20210405
Time                   14.49
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.122266 Hz
AQ                 4.0894465 sec
RG                    158.77
DW                   62.400 usec
DE                    6.50 usec
TE                   299.2 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                     1H
P1                    10.00 usec
PLW1          13.26099968 W

F2 - Processing parameters
SI                    65536
SF            400.1300098 MHz
WDW                      EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```



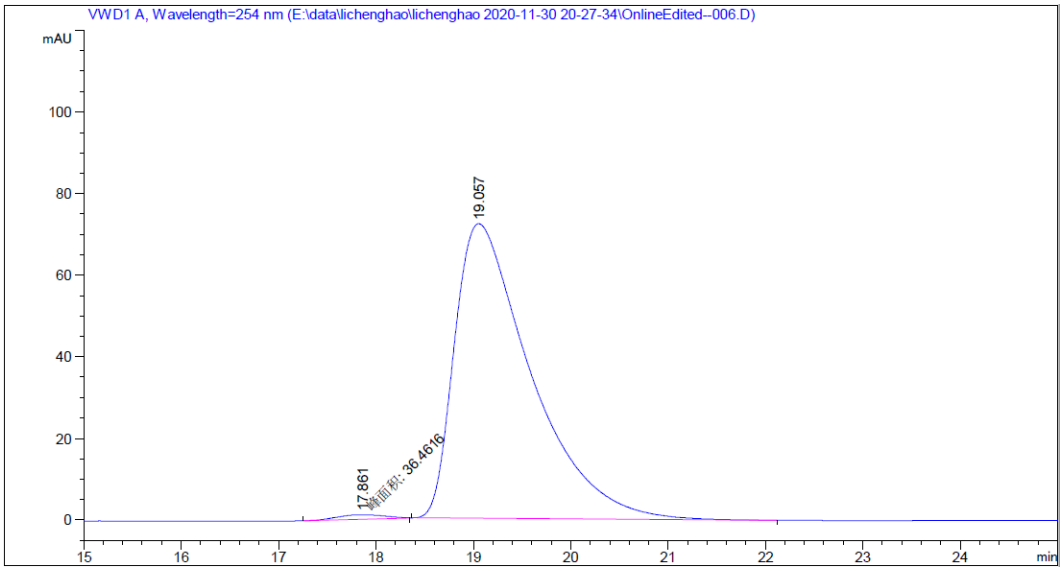

```
Current Data Parameters
NAME                  new-kzt
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_               20210405
Time                   22.34
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                    199.89
DW                   20.800 usec
DE                    6.50 usec
TE                   300.2 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1          100.6228293 MHz
NUC1                     13C
P1                    10.00 usec
PLW1          56.93000031 W

======== CHANNEL f2 ========
SFO2          400.1316005 MHz
NUC2                     1H
CPDPRG[2           waltz16
PCPD2                 90.00 usec
PLW2          13.26099968 W
PLW12          0.16372000 W
PLW13          0.13260999 W

F2 - Processing parameters
SI                    32768
SF            100.6127540 MHz
WDW                      EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

8. Copy of HPLC spectra

Figure S56. Copy of HPLC spectra of **2a**

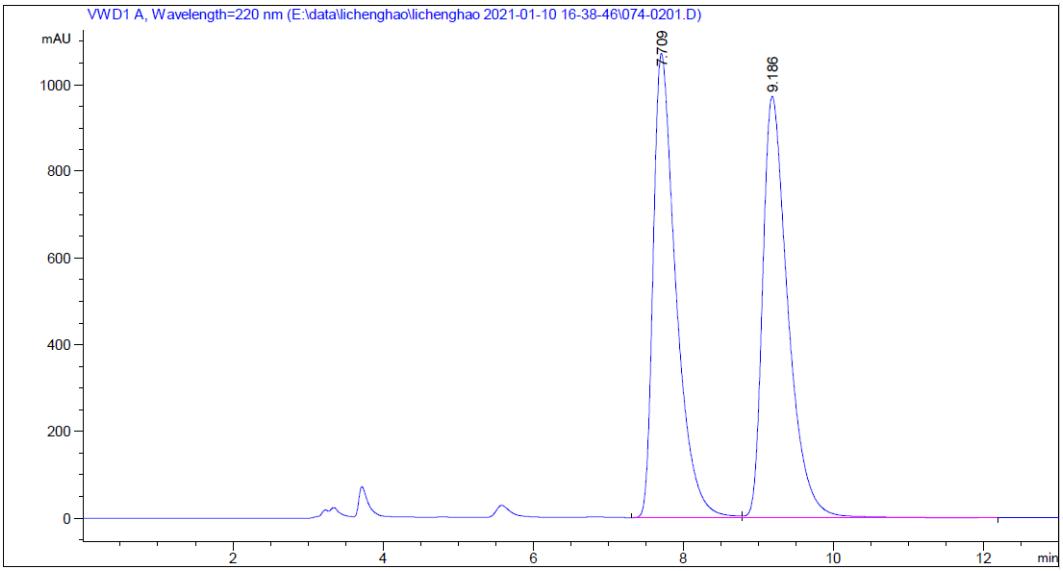


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.664	BV	0.5657	3.70550e4	959.17773	49.3659
2	18.623	VB	0.5709	3.80069e4	1041.13806	50.6341
总量：				7.50619e4	2000.31580	

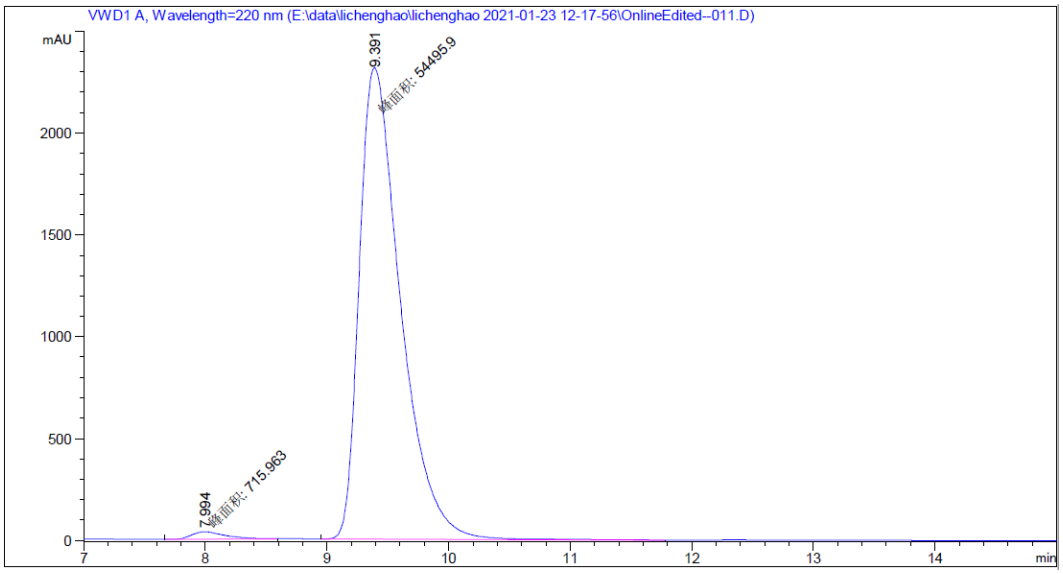


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.861	MM	0.5632	36.46165	1.07902	0.9182
2	19.057	BB	0.8105	3934.53931	72.23414	99.0818
总量：				3971.00095	73.31316	

Figure S57. Copy of HPLC spectra of **2b**

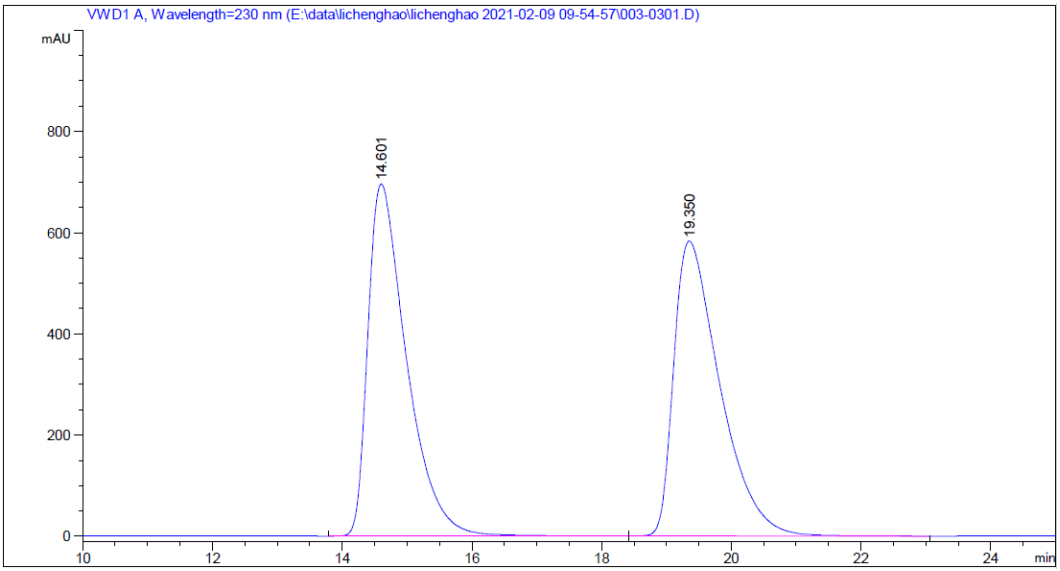


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.709	BV	0.3128	2.24610e4	1070.52710	49.7725
2	9.186	VB	0.3510	2.26663e4	972.14868	50.2275
总量：				4.51273e4	2042.67578	

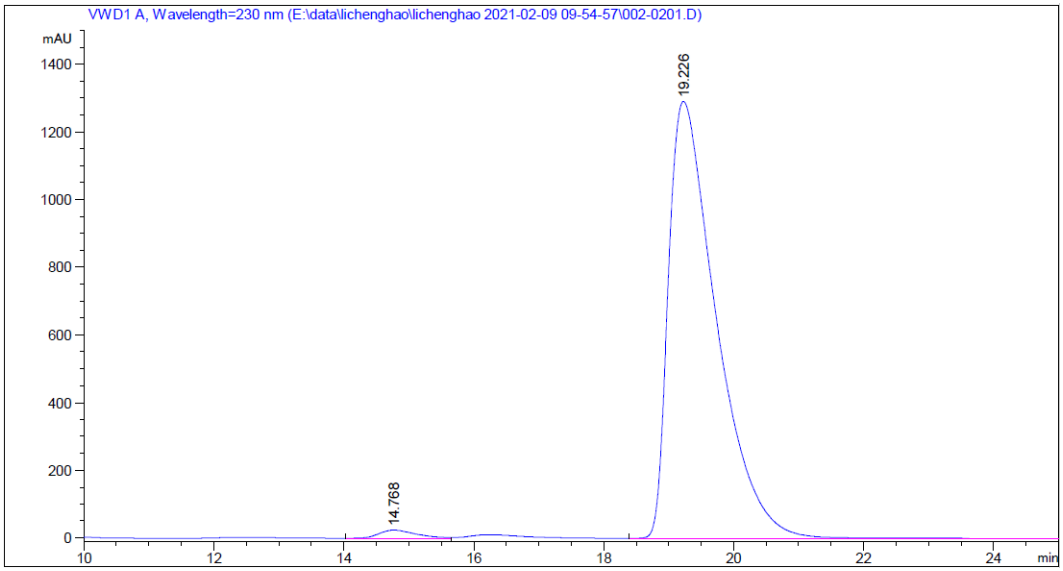


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.994	MM	0.3240	715.96295	36.82597	1.2968
2	9.391	MM	0.3923	5.44959e4	2315.45776	98.7032
总量：				5.52119e4	2352.28373	

Figure S58. Copy of HPLC spectra of **2c**

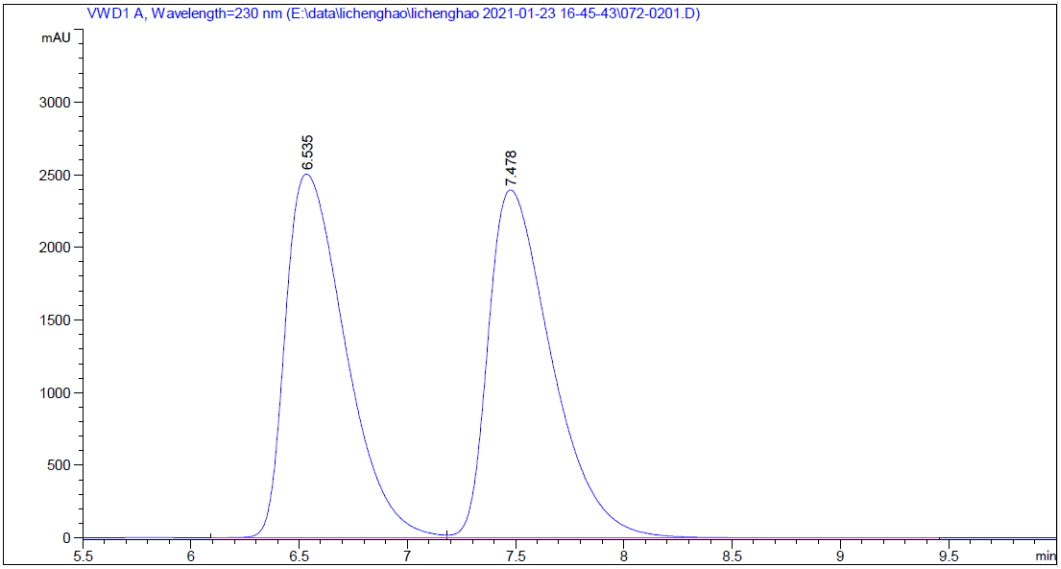


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	14.601	BB	0.6184	2.87642e4	695.66376	50.0060
2	19.350	BB	0.7444	2.87573e4	583.12433	49.9940
总量：				5.75216e4	1278.78809	

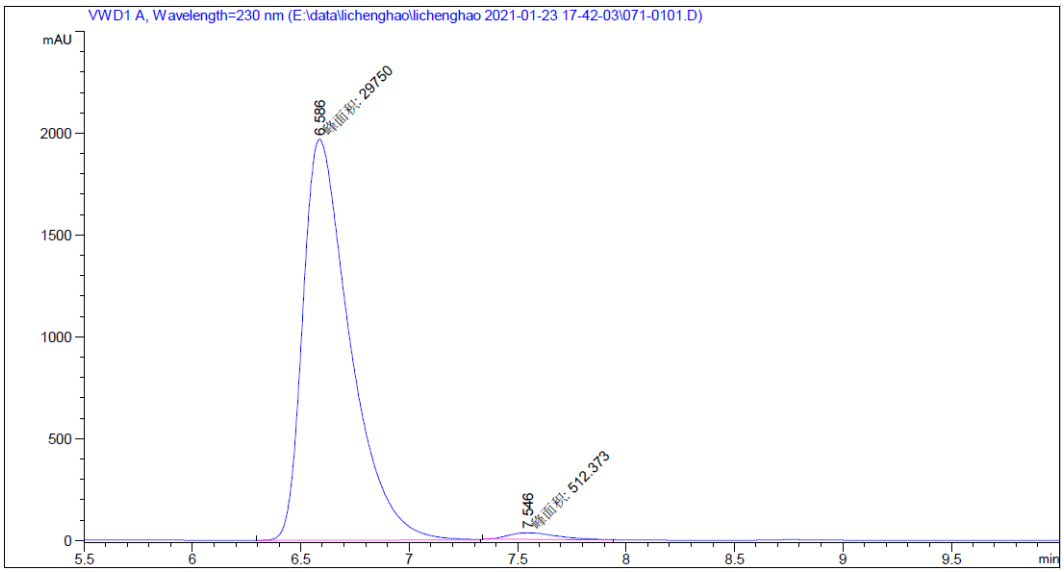


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	14.768	BV	0.6019	956.61603	24.05832	1.4341
2	19.226	BBA	0.7590	6.57505e4	1291.30261	98.5659
总量：				6.67071e4	1315.36094	

Figure S59. Copy of HPLC spectra of **2d**

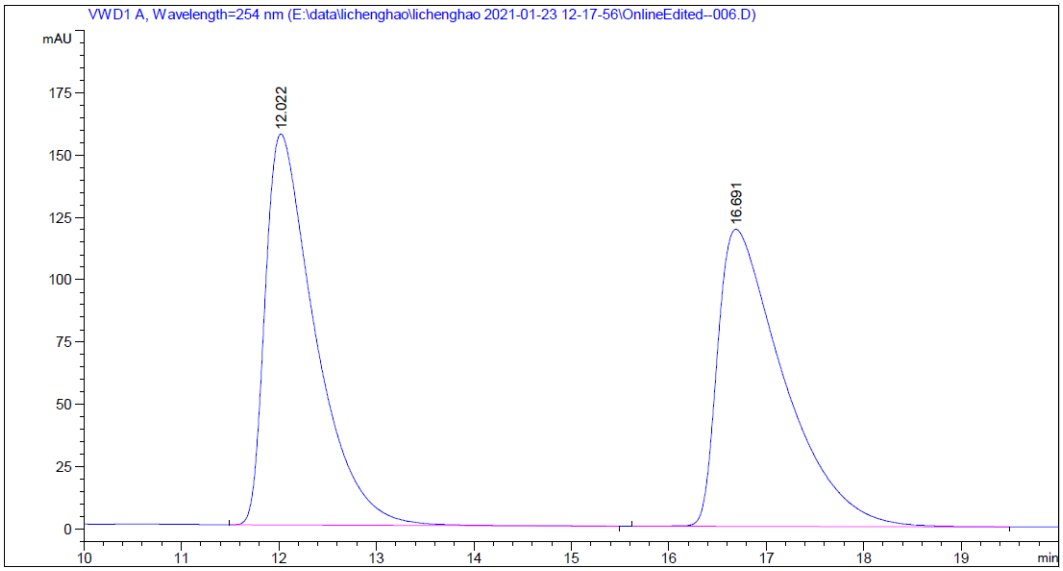


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.535	BV	0.2983	4.78979e4	2502.41284	49.6181
2	7.478	VB	0.3100	4.86353e4	2394.54688	50.3819
总量：				9.65333e4	4896.95972	

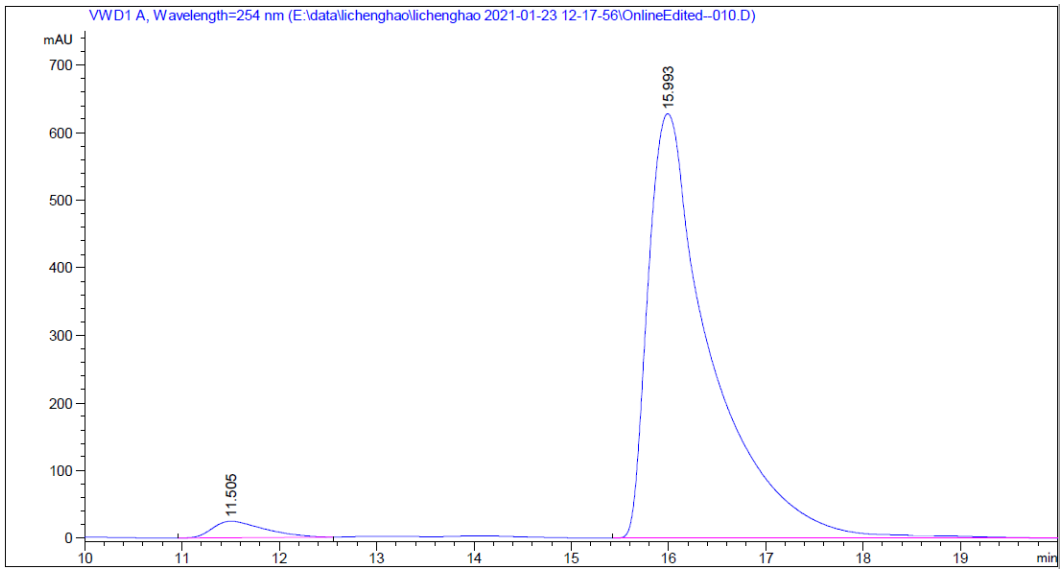


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.586	MM	0.2515	2.97500e4	1971.41284	98.3069
2	7.546	MM	0.2574	512.37317	33.17017	1.6931
总量：				3.02624e4	2004.58301	

Figure S60. Copy of HPLC spectra of **2e**

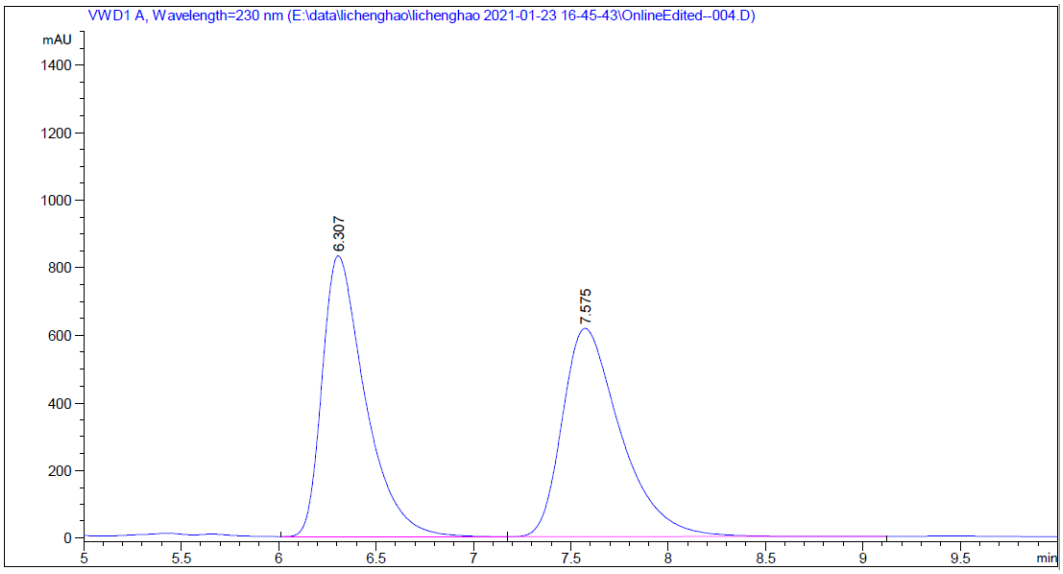


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.022	BB	0.5273	5570.41895	156.86319	49.9314
2	16.691	BB	0.6956	5585.72998	119.22216	50.0686
总量：				1.11561e4	276.08535	

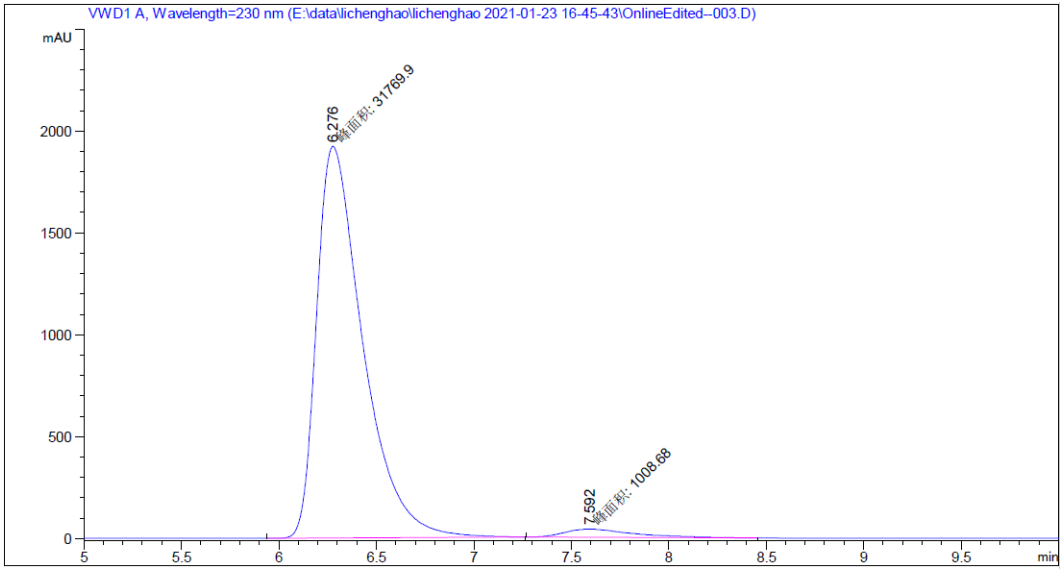


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.505	BB	0.5529	899.69263	24.36135	3.0961
2	15.993	BBA	0.6397	2.81591e4	628.45605	96.9039
总量：				2.90588e4	652.81741	

Figure S61. Copy of HPLC spectra of **2f**

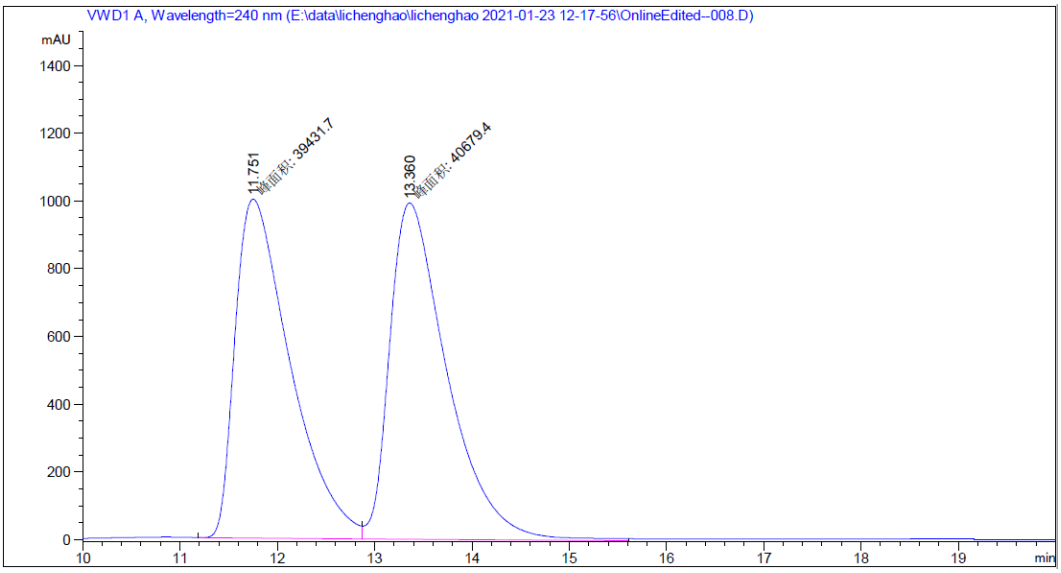


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.307	BB	0.2300	1.27568e4	831.37976	49.8210
2	7.575	BB	0.3141	1.28484e4	616.63257	50.1790
总量：				2.56052e4	1448.01233	

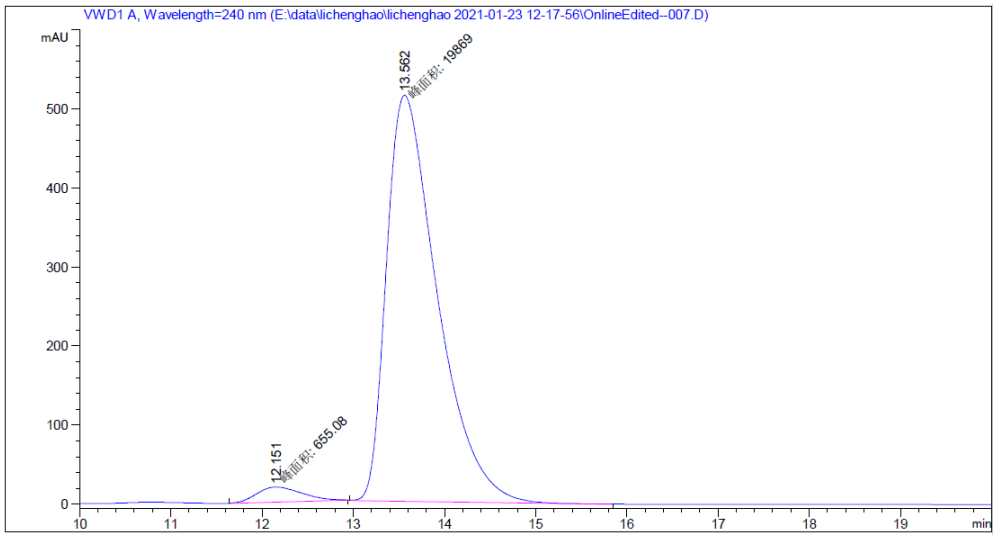


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.276	MM	0.2753	3.17699e4	1923.47571	96.9227
2	7.592	MM	0.4132	1008.68262	40.68394	3.0773
总量：				3.27785e4	1964.15965	

Figure S62. Copy of HPLC spectra of **2g**

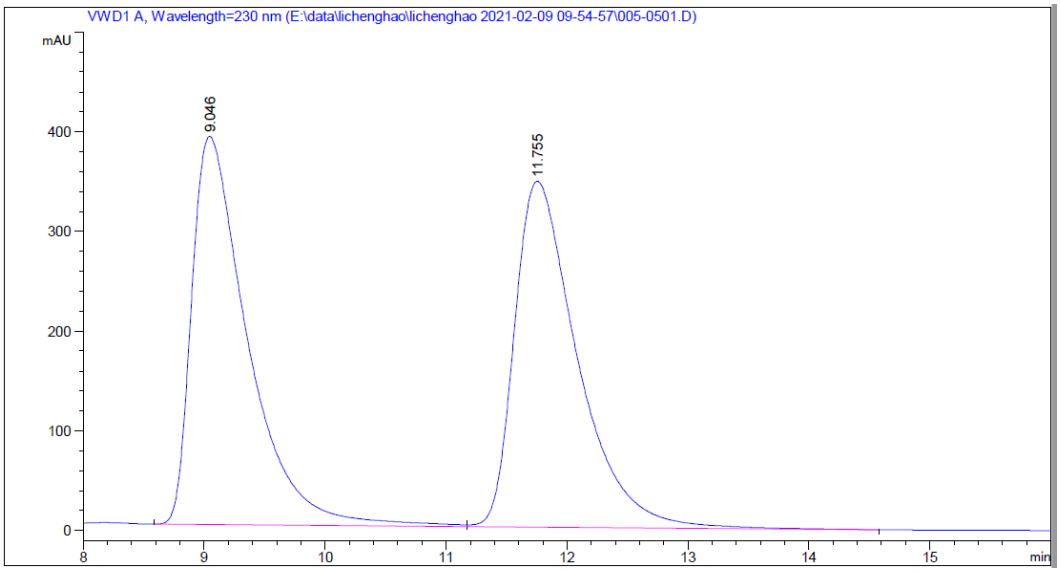


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.751	MF	0.6567	3.94317e4	1000.70264	49.2213
2	13.360	FM	0.6831	4.06794e4	992.52240	50.7787
总量 :				8.01110e4	1993.22504	

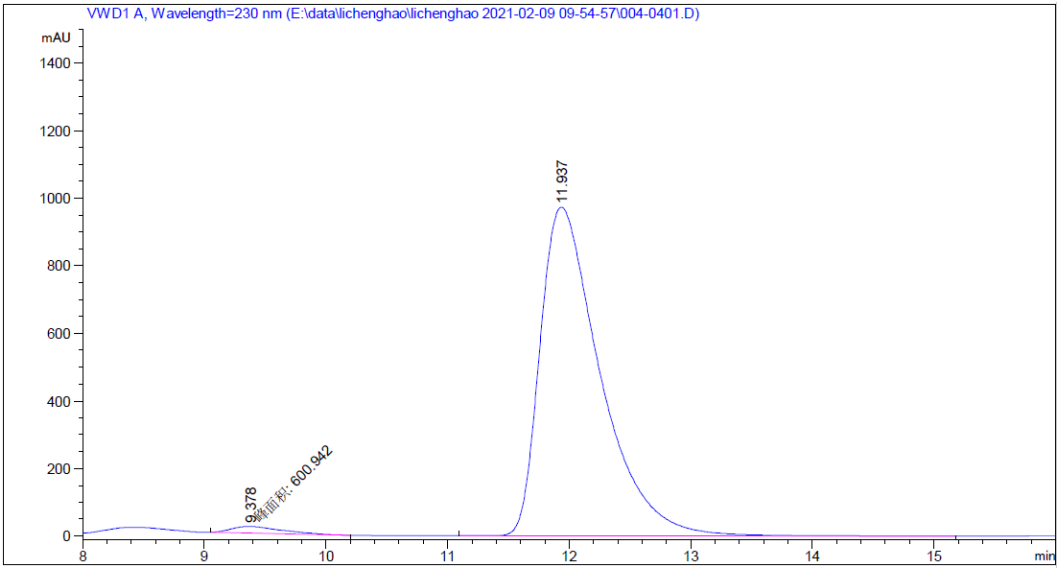


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.151	MM	0.5730	655.07996	19.05336	3.1918
2	13.562	MM	0.6449	1.98690e4	513.45728	96.8082
总量 :				2.05241e4	532.51063	

Figure S63. Copy of HPLC spectra of **2h**

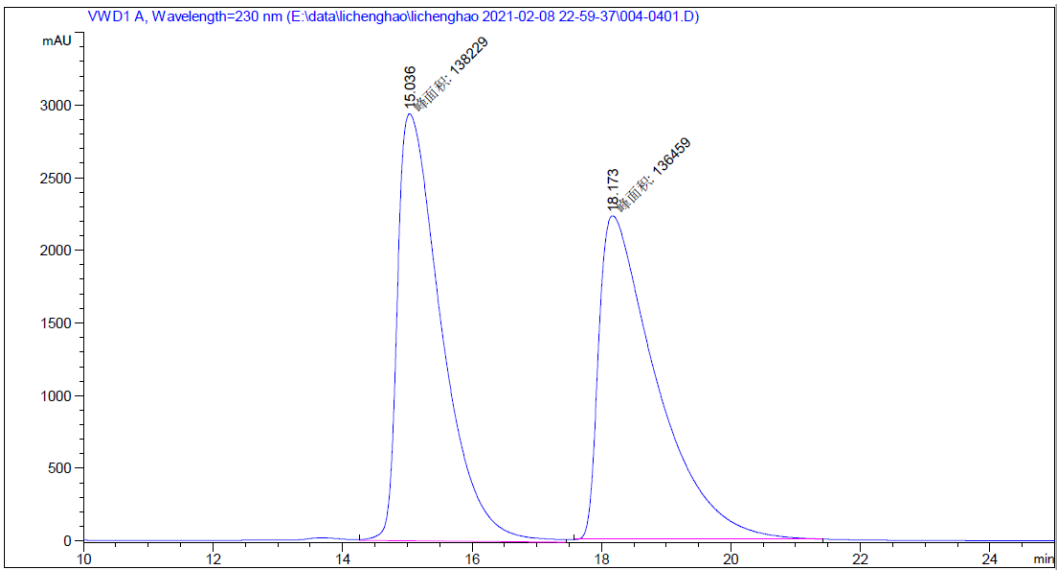


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.046	BV	0.4759	1.25135e4	389.44415	49.9214
2	11.755	VB	0.5431	1.25529e4	346.99478	50.0786
总量：				2.50663e4	736.43893	

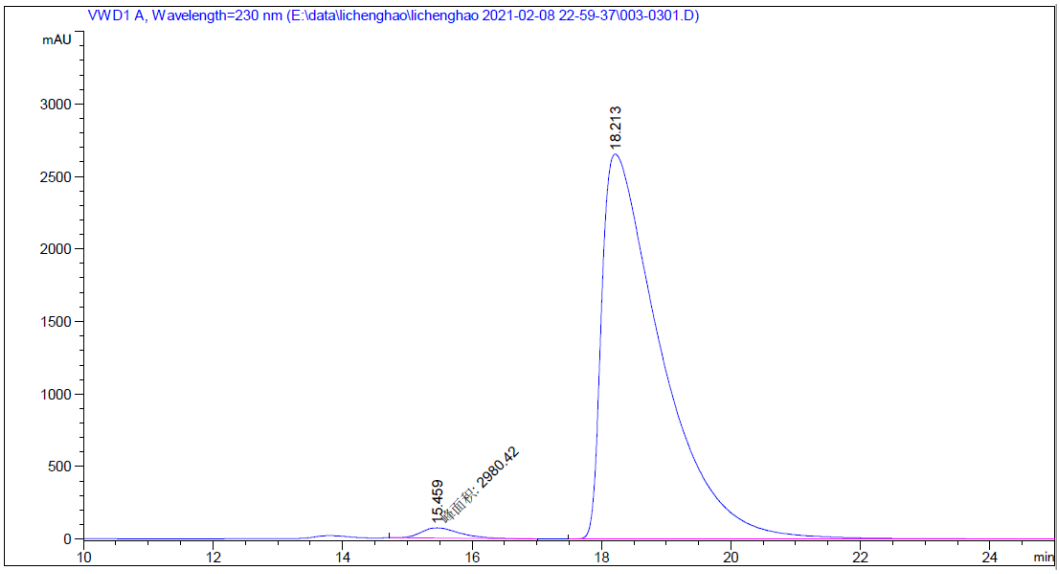


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.378	MM	0.4917	600.94196	20.36783	1.7631
2	11.937	BB	0.5173	3.34829e4	973.38226	98.2369
总量：				3.40838e4	993.75009	

Figure S64. Copy of HPLC spectra of **2i**

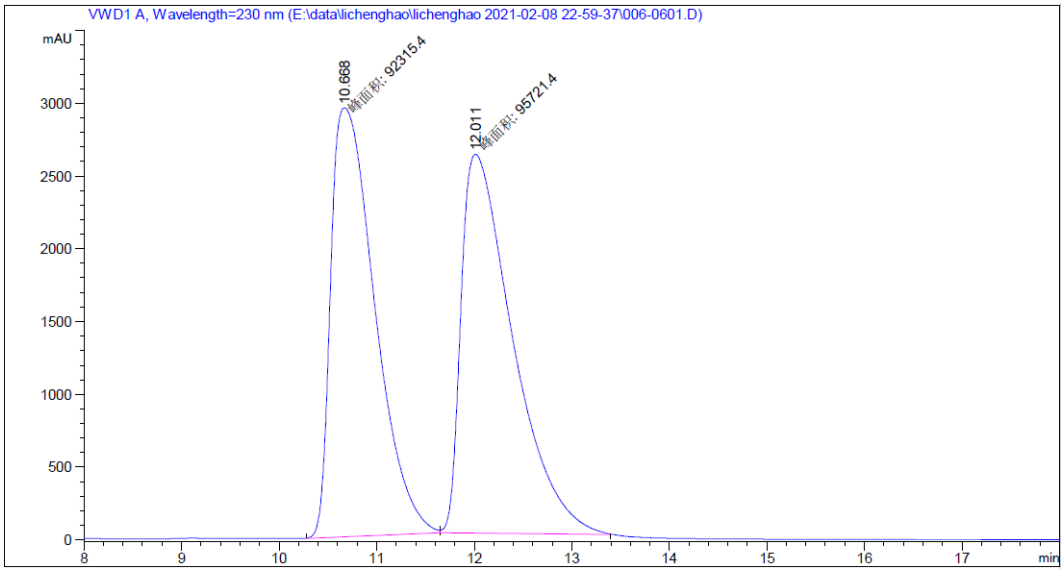


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.036	MM	0.7842	1.38229e5	2937.87061	50.3221
2	18.173	MM	1.0239	1.36459e5	2221.29224	49.6779
总量 :				2.74688e5	5159.16284	

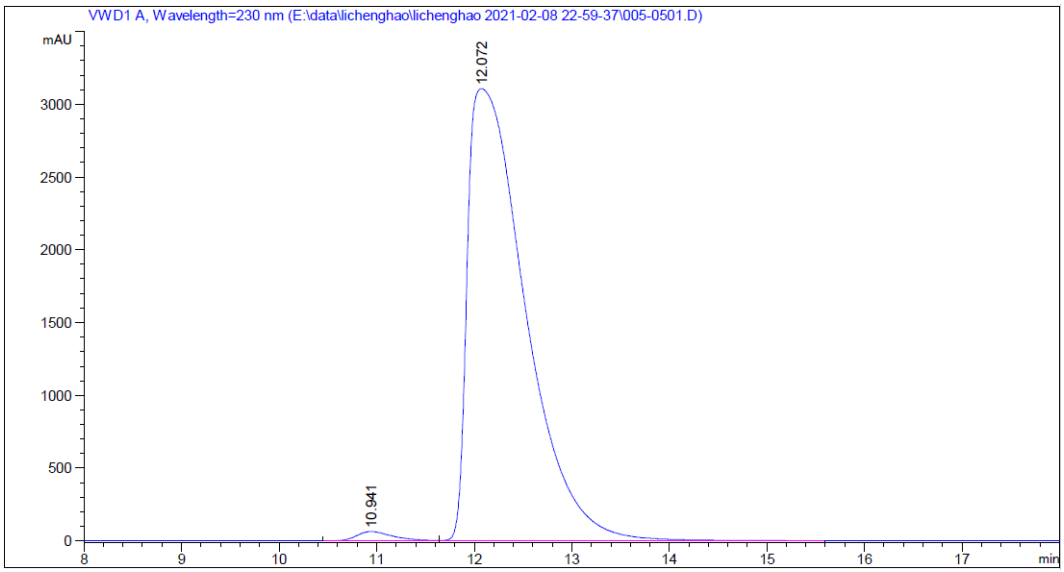


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.459	MM	0.6927	2980.42456	71.70898	1.7345
2	18.213	BB	0.9238	1.68853e5	2651.99976	98.2655
总量 :				1.71834e5	2723.70874	

Figure S65. Copy of HPLC spectra of **2j**

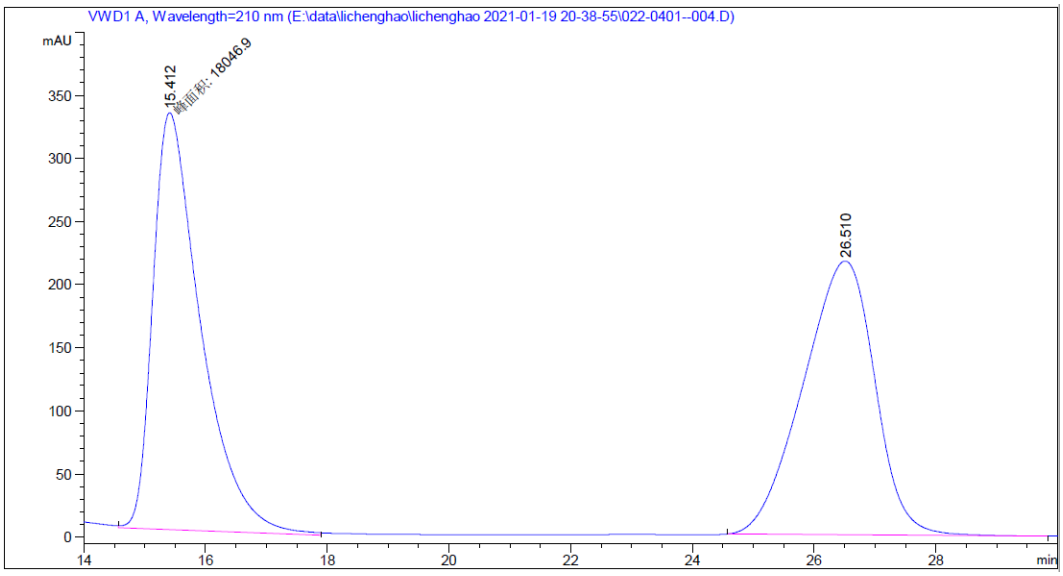


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.668	MM	0.5221	9.23154e4	2946.71924	49.0943
2	12.011	MM	0.6130	9.57214e4	2602.74683	50.9057
总量：				1.88037e5	5549.46606	

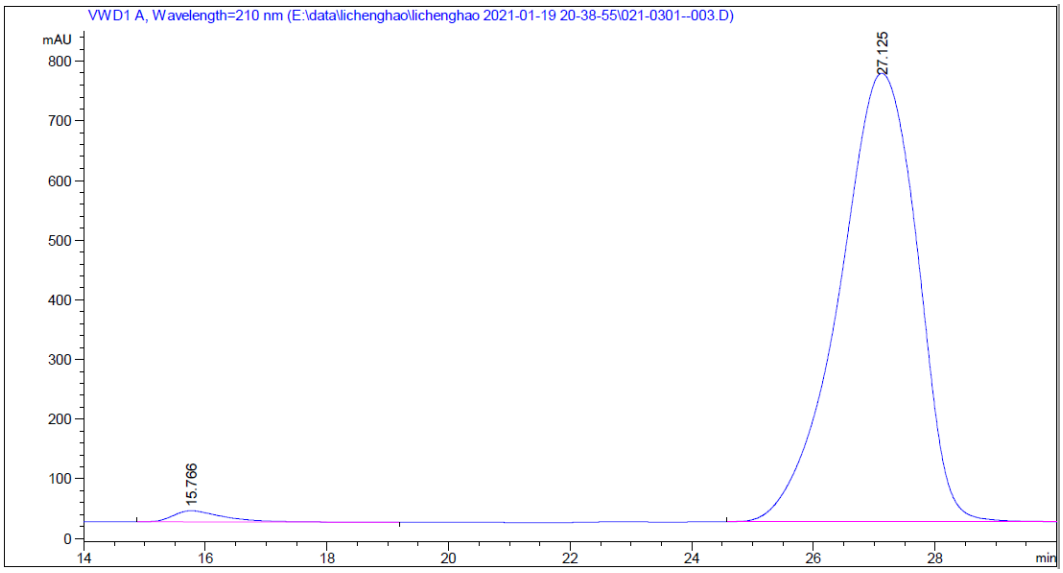


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.941	BV	0.3809	1613.04980	63.38098	1.2479
2	12.072	VB	0.6266	1.27651e5	3105.09277	98.7521
总量：				1.29264e5	3168.47375	

Figure S66. Copy of HPLC spectra of **2k**

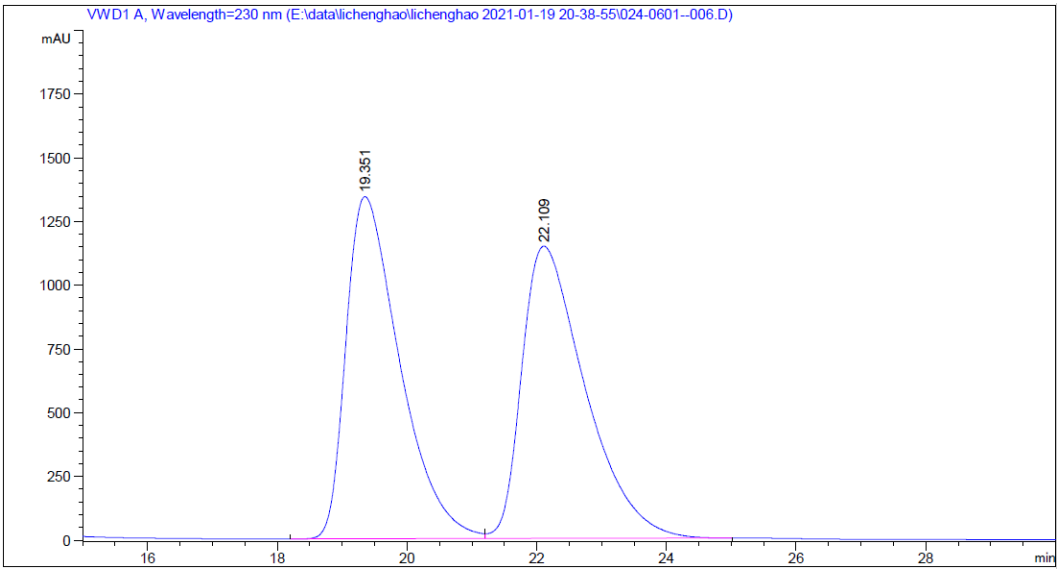


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.412	MM	0.9099	1.80469e4	330.55215	50.3990
2	26.510	BB	1.2169	1.77612e4	217.01056	49.6010
总量 :				3.58082e4	547.56271	

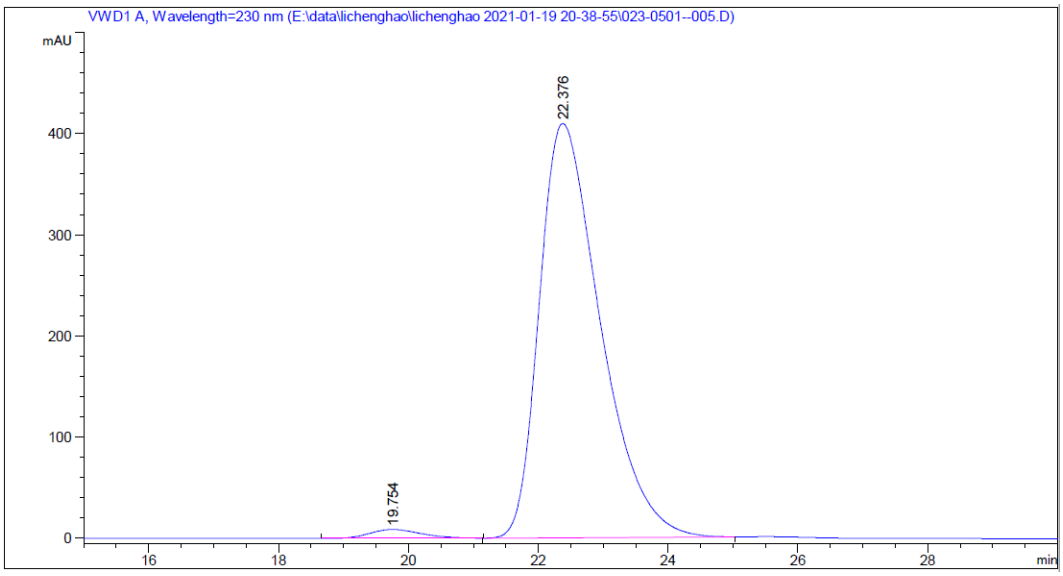


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.766	BB	0.8515	1098.01587	18.74114	1.6127
2	27.125	BB	1.4039	6.69890e4	752.26044	98.3873
总量 :				6.80870e4	771.00158	

Figure S67. Copy of HPLC spectra of **2l**

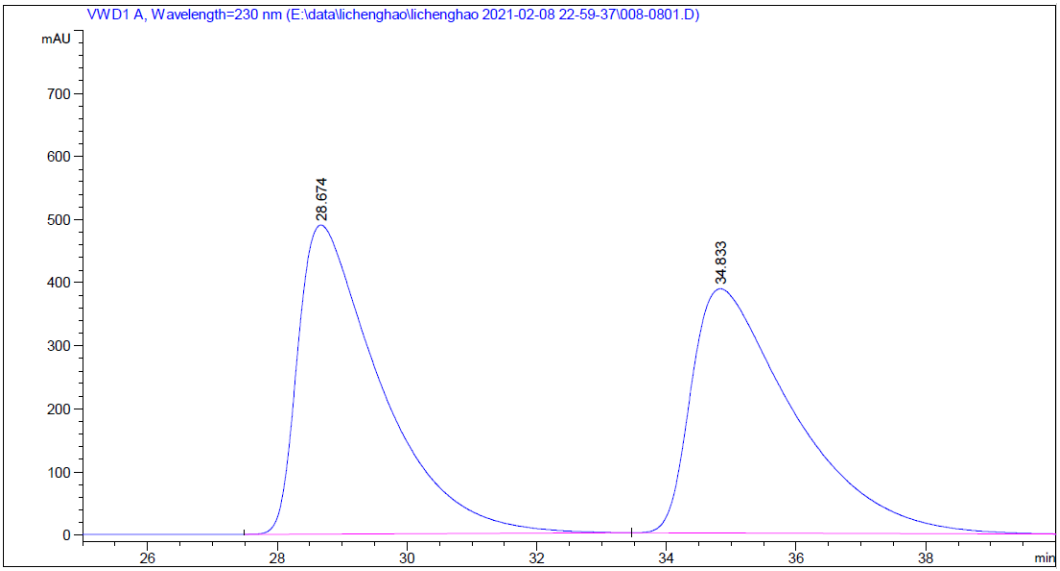


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	19.351	BV	0.8755	7.72724e4	1342.56787	49.8178
2	22.109	VB	1.0277	7.78378e4	1147.04639	50.1822
总量 :				1.55110e5	2489.61426	

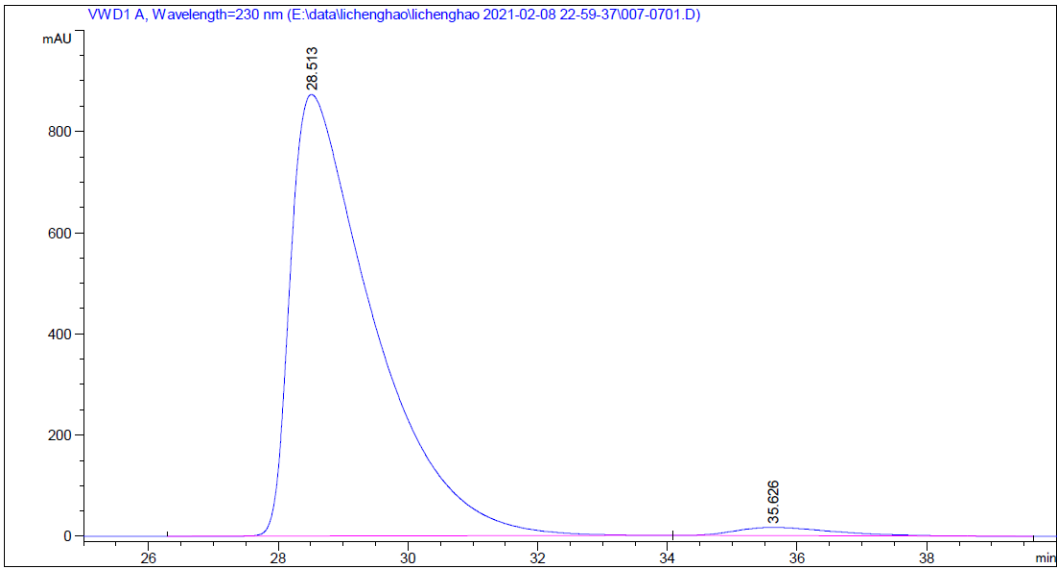


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	19.754	BB	0.8310	474.83063	8.72411	1.7481
2	22.376	BB	0.9947	2.66886e4	409.33804	98.2519
总量 :				2.71634e4	418.06216	

Figure S68. Copy of HPLC spectra of **2m**

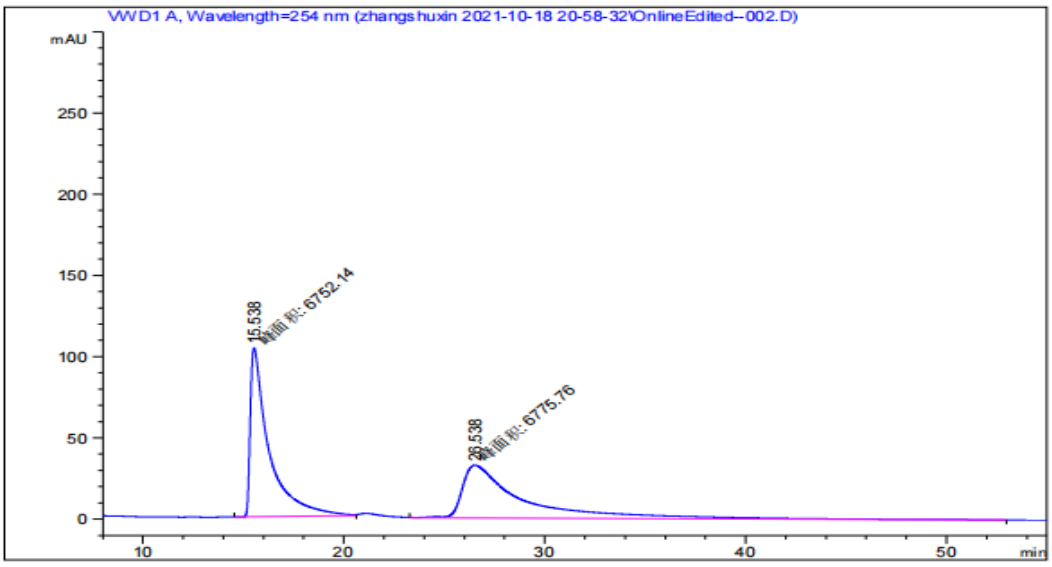


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	28.674	BB	1.2903	4.31724e4	489.82043	50.4465
2	34.833	BBA	1.6079	4.24082e4	387.18066	49.5535
总量：				8.55806e4	877.00110	

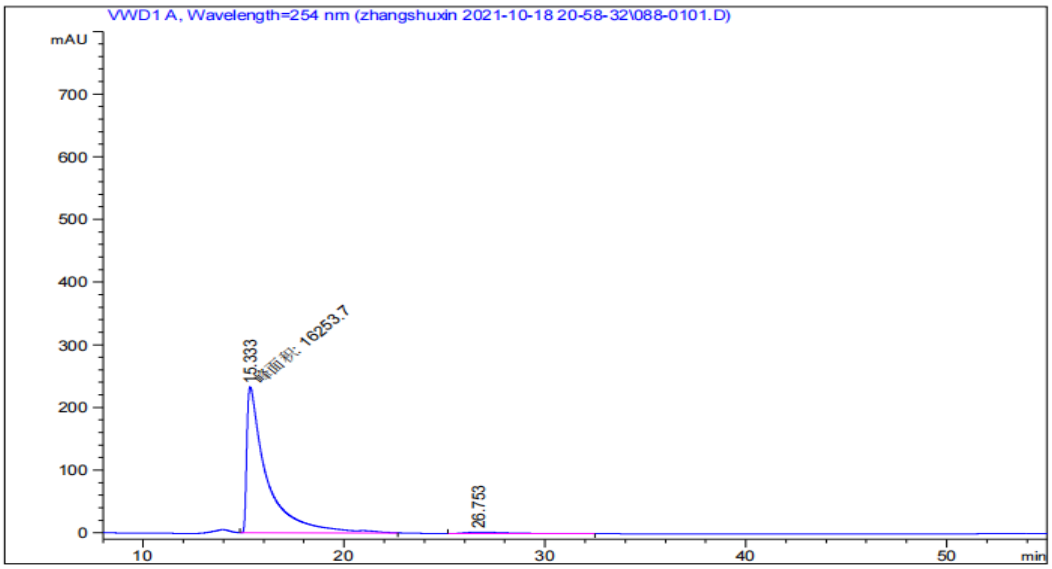


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	28.513	BB	1.2949	7.73398e4	872.73737	97.7836
2	35.626	BBA	1.5515	1753.00134	16.51332	2.2164
总量：				7.90928e4	889.25069	

Figure S69. Copy of HPLC spectra of **2n**

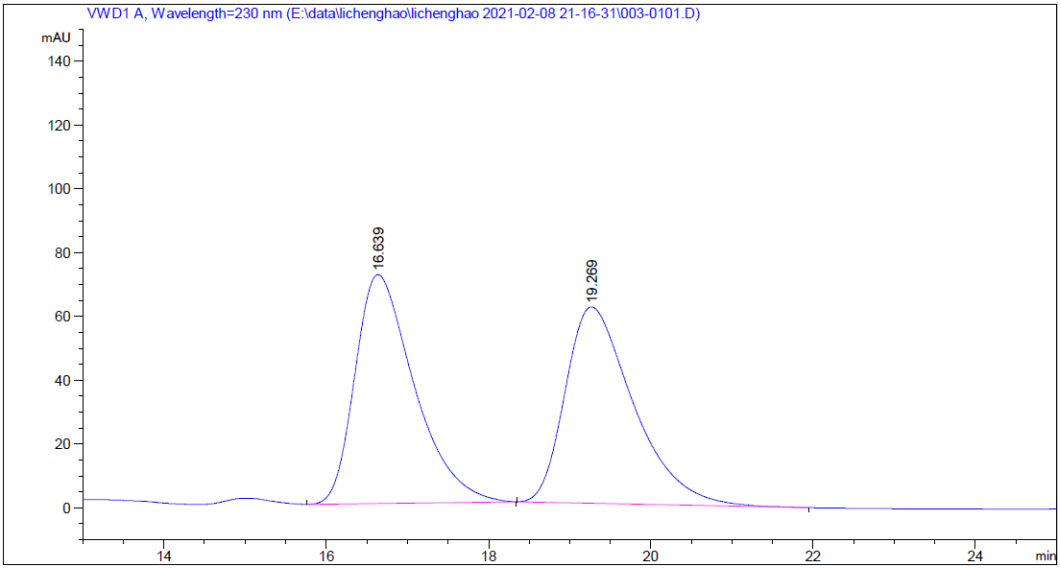


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.538	MM	1.0839	6752.13721	103.82909	49.9127
2	26.538	MM	3.4808	6775.76123	32.44366	50.0873
总量：				1.35279e4	136.27275	

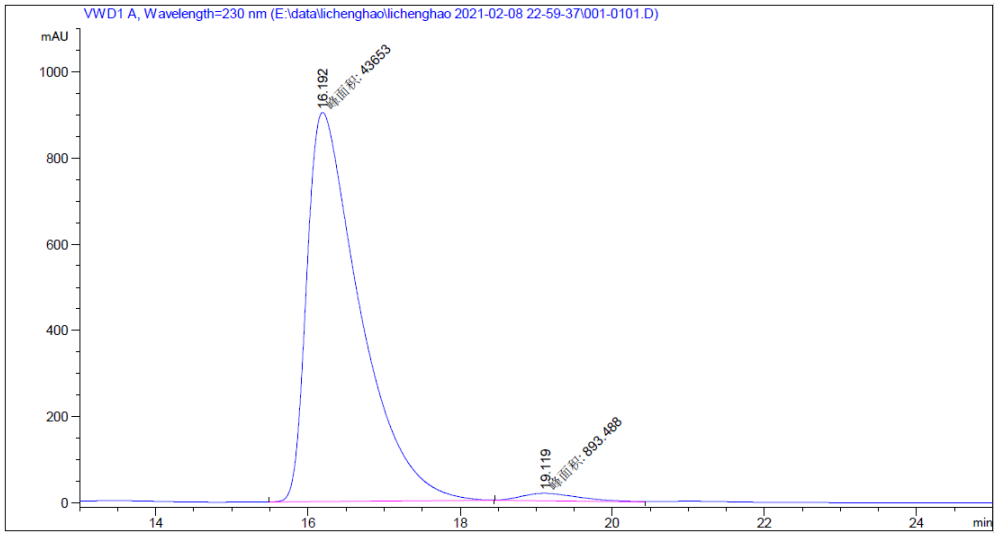


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.333	MM	1.1643	1.62537e4	232.66092	97.8706
2	26.753	BB	1.6851	353.63116	2.46596	2.1294
总量：				1.66073e4	235.12688	

Figure S70. Copy of HPLC spectra of **2o**

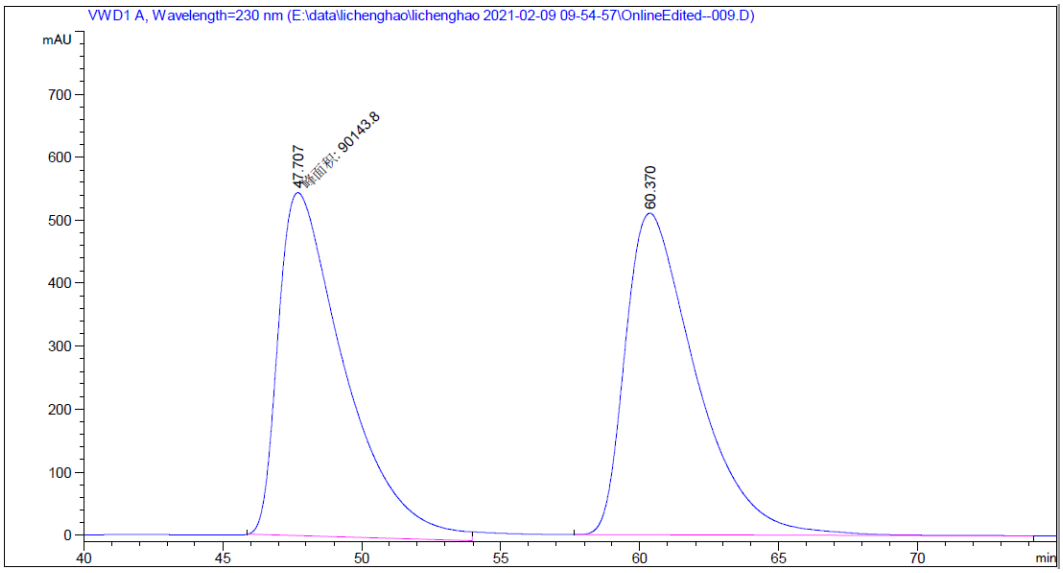


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.639	BB	0.7678	3633.31470	71.74956	50.2501
2	19.269	BB	0.8852	3597.14575	61.61126	49.7499

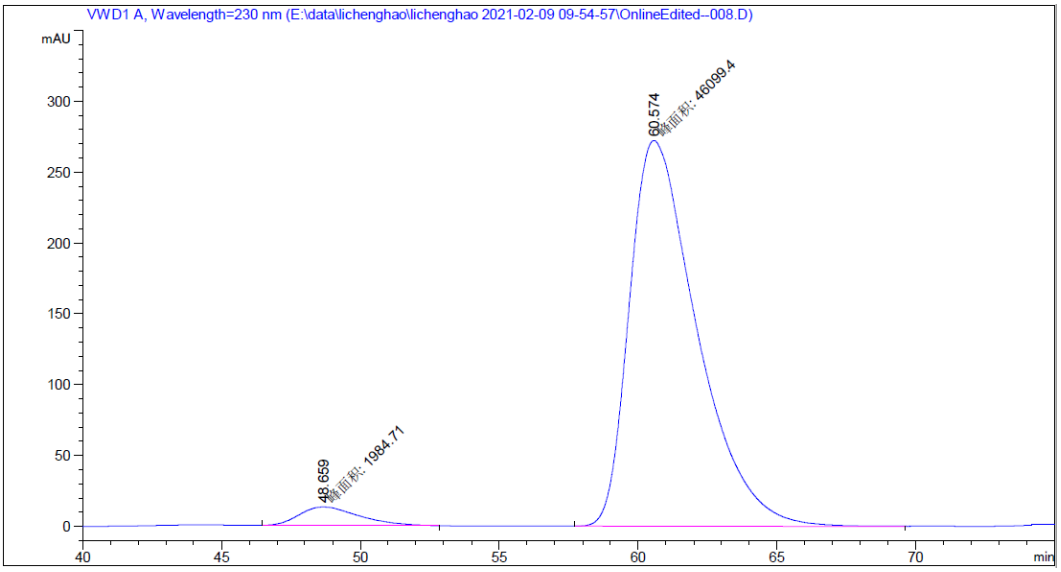


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.192	MM	0.8057	4.36530e4	902.95105	97.9943
2	19.119	MM	0.8744	893.48846	17.03008	2.0057
总量 :				4.45465e4	919.98113	

Figure S71. Copy of HPLC spectra of **2p**

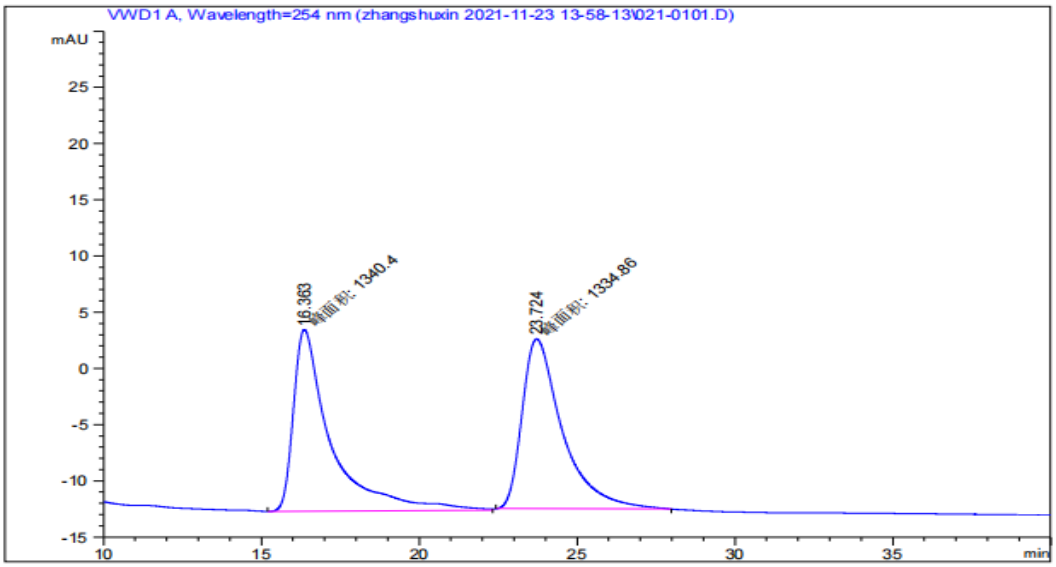


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	47.707	MM	2.7590	9.01438e4	544.54565	50.0476
2	60.370	BB	2.4921	8.99722e4	511.00781	49.9524
总量：				1.80116e5	1055.55347	

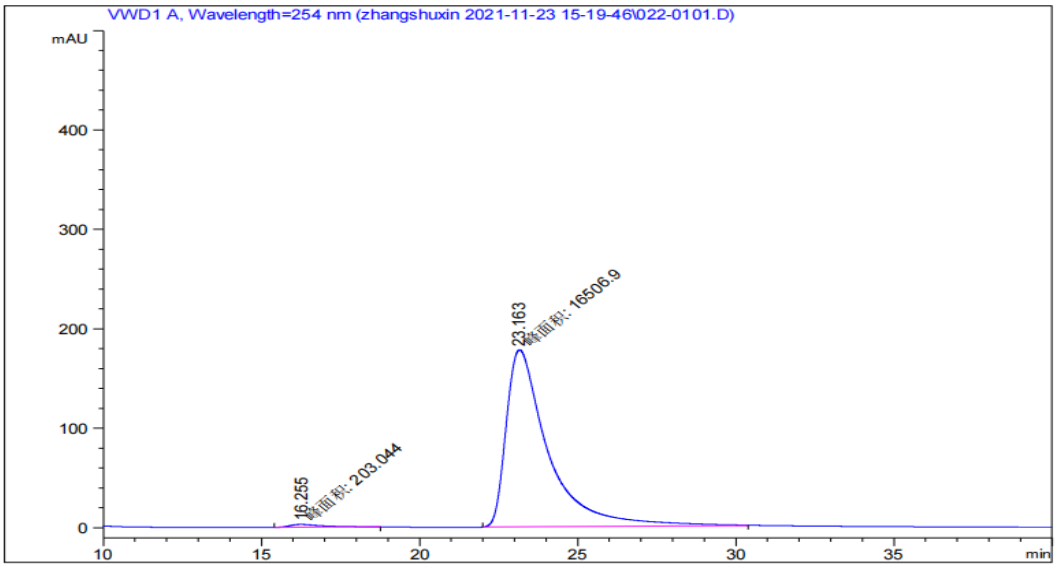


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	48.659	MM	2.5096	1984.71082	13.18088	4.1276
2	60.574	MM	2.8209	4.60994e4	272.36975	95.8724
总量：				4.80841e4	285.55063	

Figure S72. Copy of HPLC spectra of **2q**

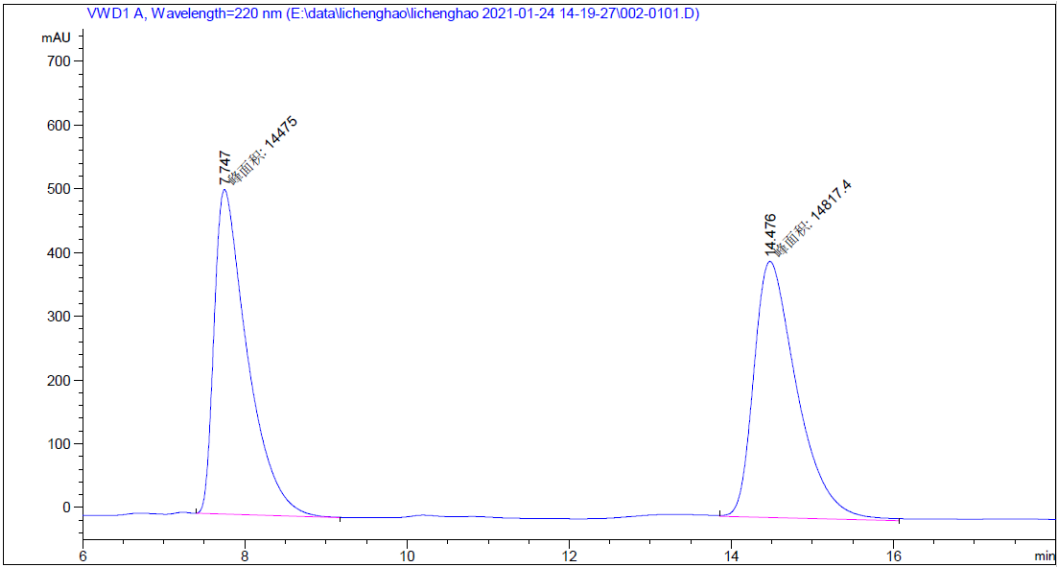


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.363	MM	1.3820	1340.39758	16.16502	50.1035
2	23.724	MM	1.4746	1334.86047	15.08761	49.8965
总量：				2675.25806	31.25263	

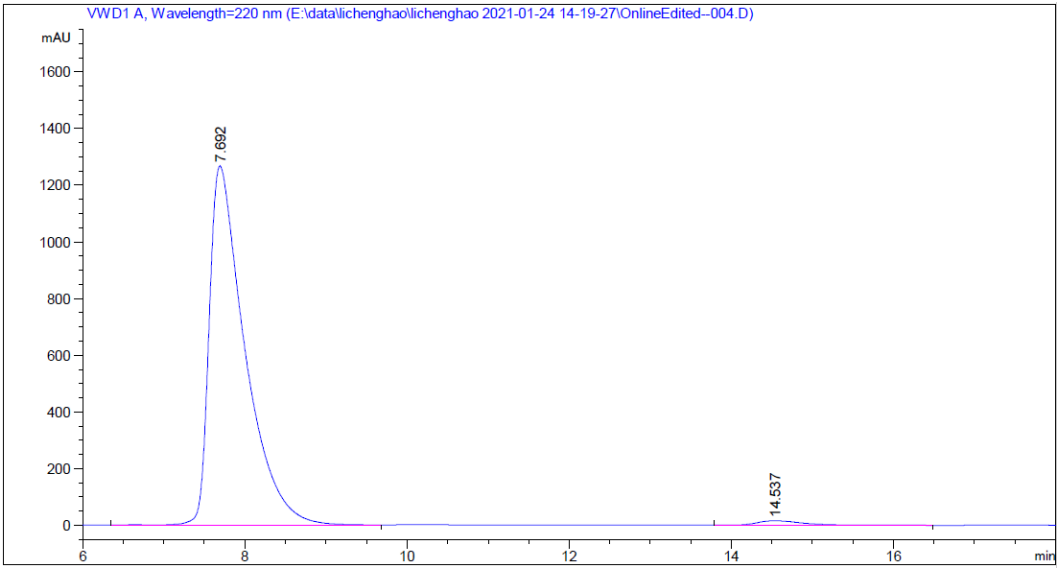


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.255	MM	1.1742	203.04422	2.88195	1.2151
2	23.163	MM	1.5445	1.65069e4	178.12419	98.7849

Figure S73. Copy of HPLC spectra of **2r**

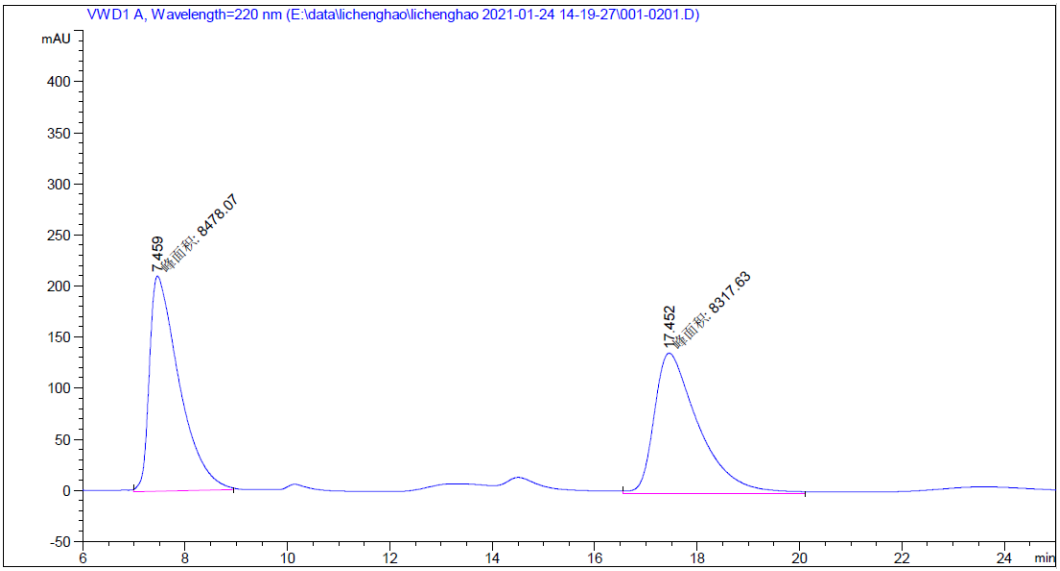


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.747	MM	0.4739	1.44750e4	509.12399	49.4155
2	14.476	MM	0.6151	1.48174e4	401.51736	50.5845
总量：				2.92924e4	910.64136	

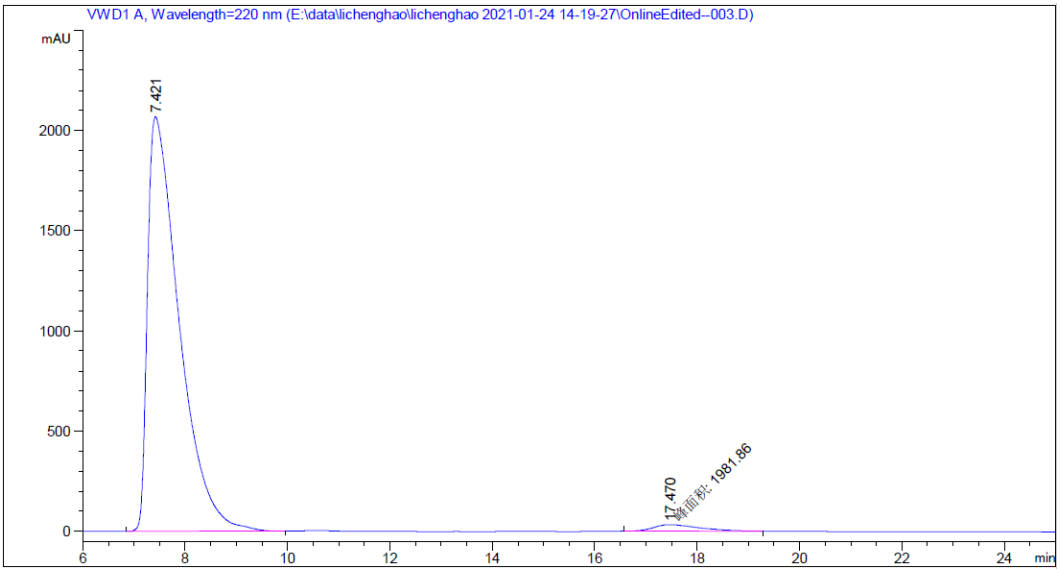


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.692	VB R	0.4447	3.87396e4	1267.04321	98.4327
2	14.537	BB	0.5716	616.83783	16.29574	1.5673
总量：				3.93565e4	1283.33895	

Figure S74. Copy of HPLC spectra of **2s**

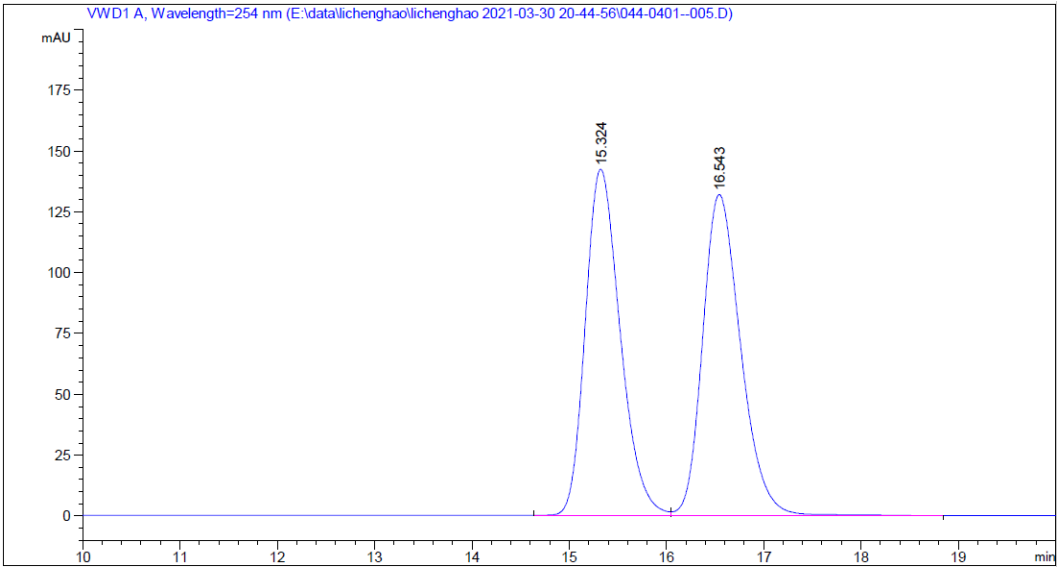


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.459	MM	0.6711	8478.07031	210.56204	50.4776
2	17.452	MM	1.0084	8317.62793	137.47853	49.5224
总量：				1.67957e4	348.04057	

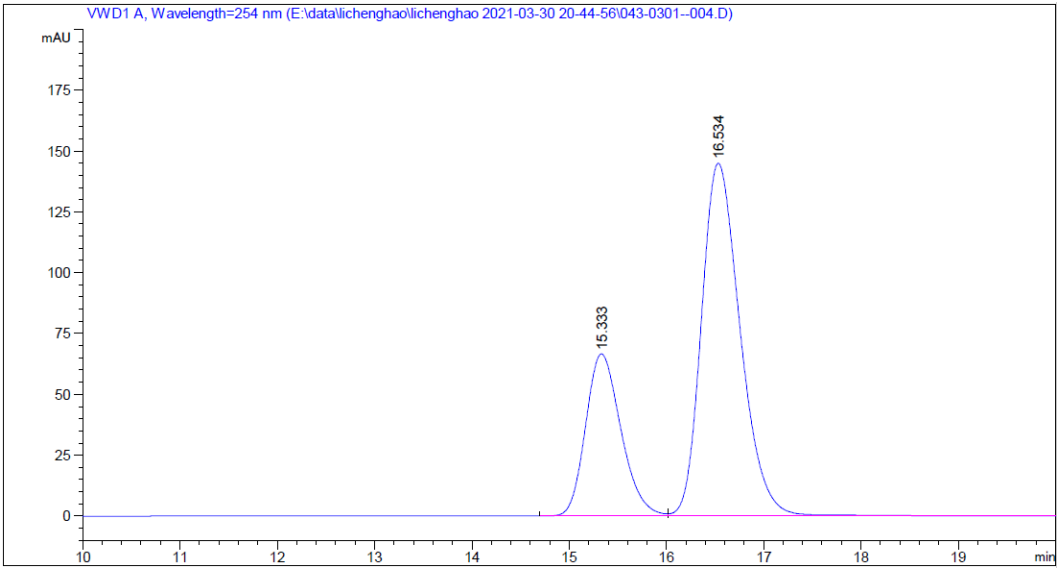


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.421	BB	0.6482	8.85527e4	2069.71875	97.8109
2	17.470	MM	1.0188	1981.86365	32.42062	2.1891
总量：				9.05346e4	2102.13937	

Figure S75. Copy of HPLC spectra of **4a**

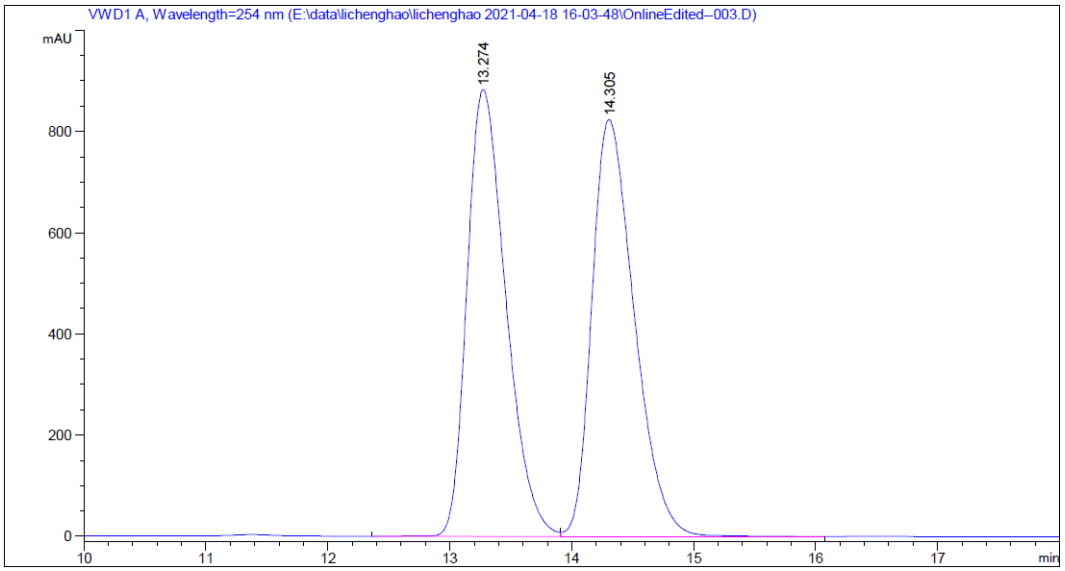


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.324	BV	0.3837	3531.19019	142.21953	49.7363
2	16.543	VB	0.4178	3568.62793	131.84190	50.2637
总量：				7099.81812	274.06143	

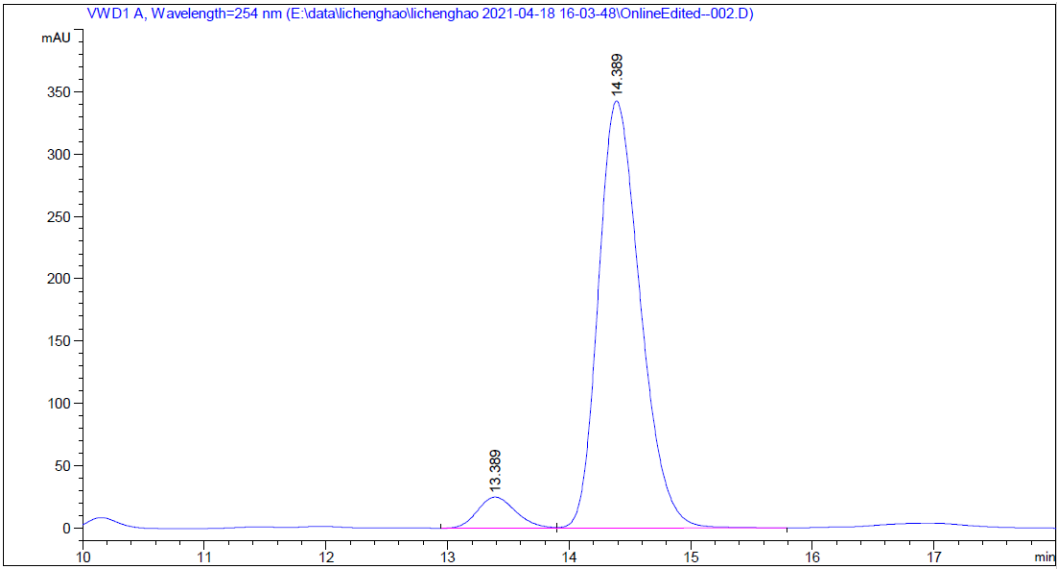


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.333	BV	0.3896	1676.02954	66.59358	29.4559
2	16.534	VBA	0.4270	4013.92847	144.99921	70.5441
总量：				5689.95801	211.59279	

Figure S76. Copy of HPLC spectra of **4b**

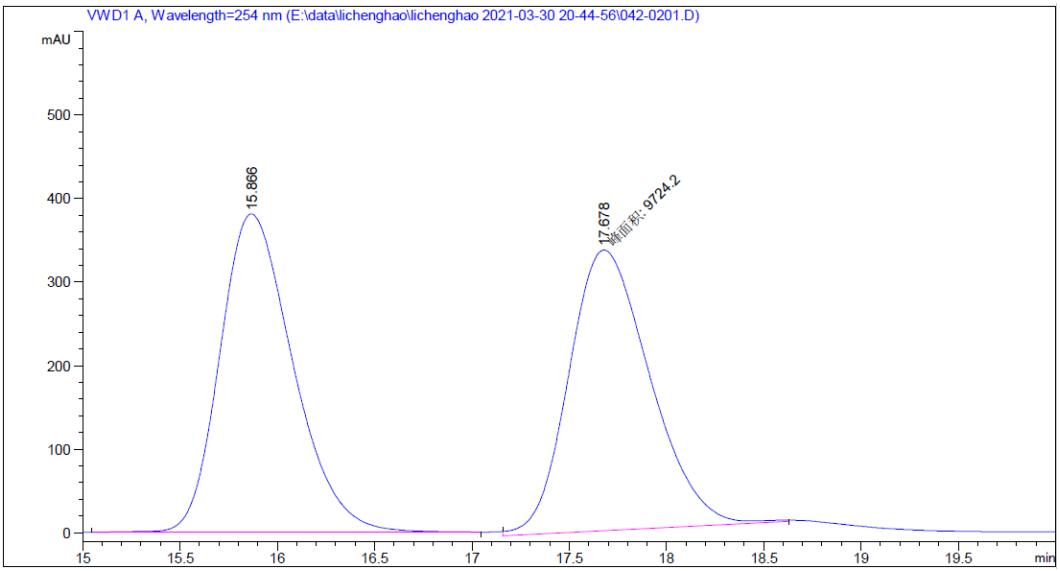


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.274	VV R	0.3420	1.95312e4	883.24719	49.5563
2	14.305	VB	0.3735	1.98810e4	824.10339	50.4437
总量：				3.94121e4	1707.35059	

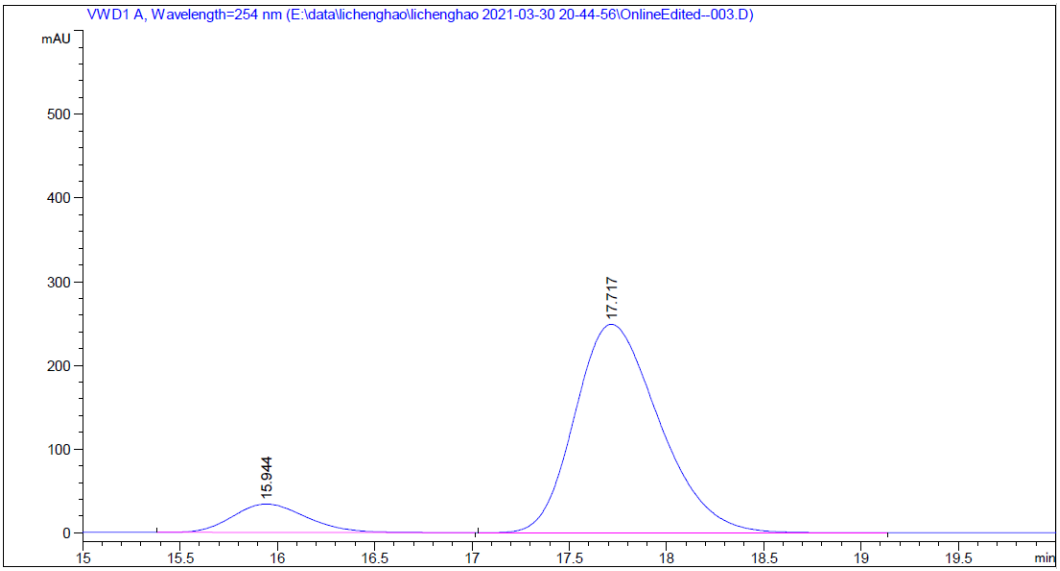


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.389	BV	0.3404	545.08173	24.89834	6.2406
2	14.389	VB	0.3709	8189.32959	342.58258	93.7594
总量：				8734.41132	367.48092	

Figure S77. Copy of HPLC spectra of **4c**

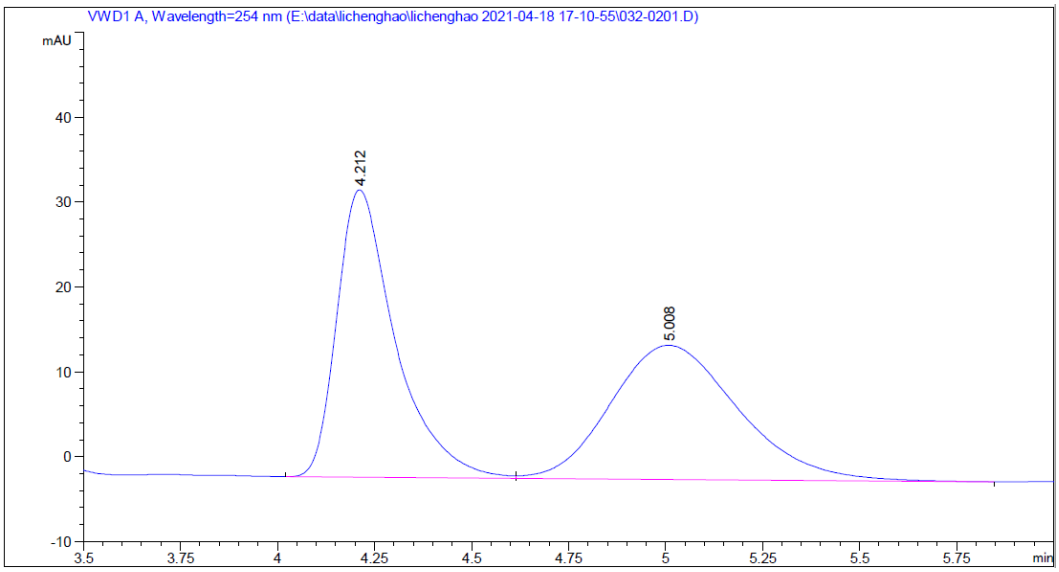


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.866	BB	0.4032	9924.75000	380.65872	50.5103
2	17.678	MM	0.4831	9724.20410	335.44534	49.4897
总量：				1.96490e4	716.10406	

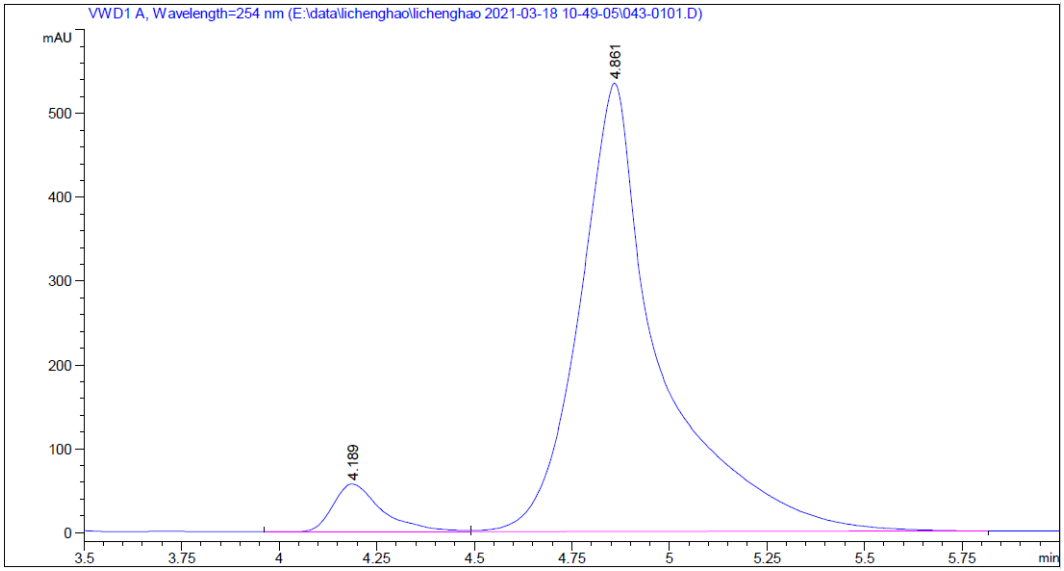


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.944	BB	0.4128	907.71216	34.07307	10.7943
2	17.717	BB	0.4676	7501.45605	248.93977	89.2057
总量：				8409.16821	283.01284	

Figure S78. Copy of HPLC spectra of **4d**

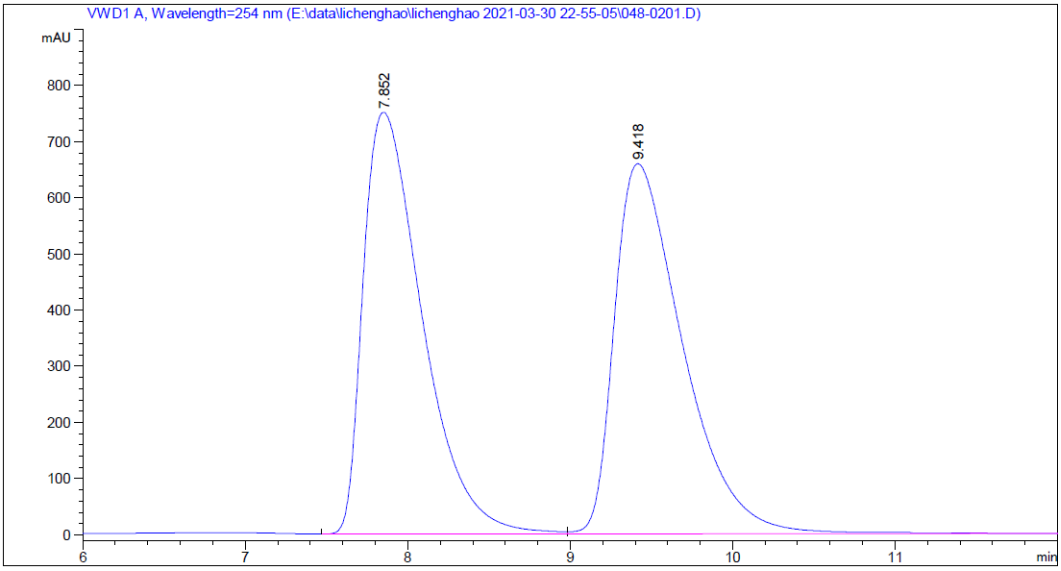


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	4.212	BV	0.1571	354.45859	33.87715	49.5439
2	5.008	VB	0.3535	360.98492	15.80097	50.4561
总量：				715.44351	49.67812	

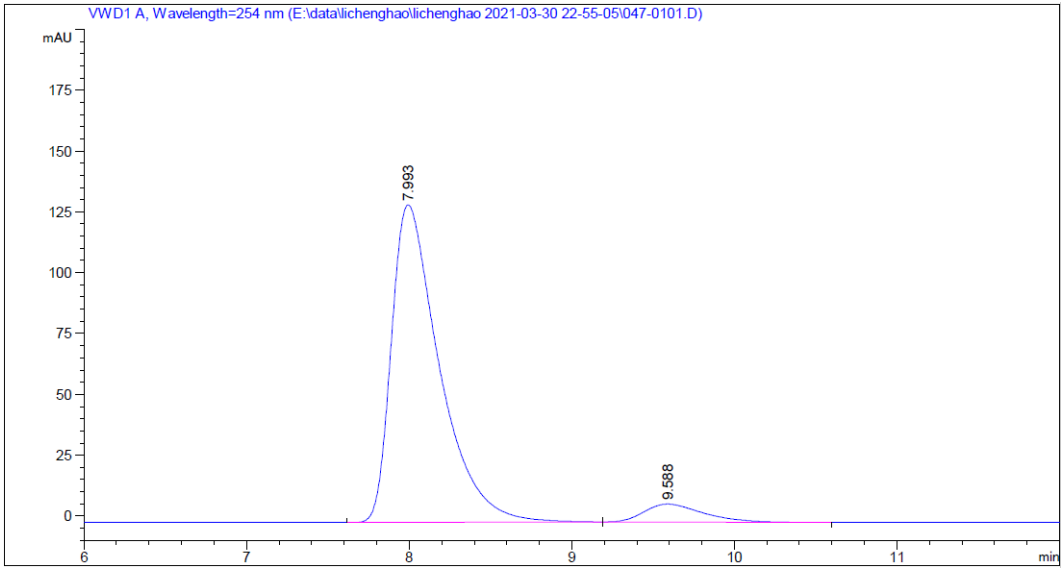


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	4.189	BV	0.1298	496.66385	56.92661	6.0831
2	4.861	VB	0.1965	7667.97656	534.12988	93.9169
总量：				8164.64041	591.05649	

Figure S79. Copy of HPLC spectra of **4e**

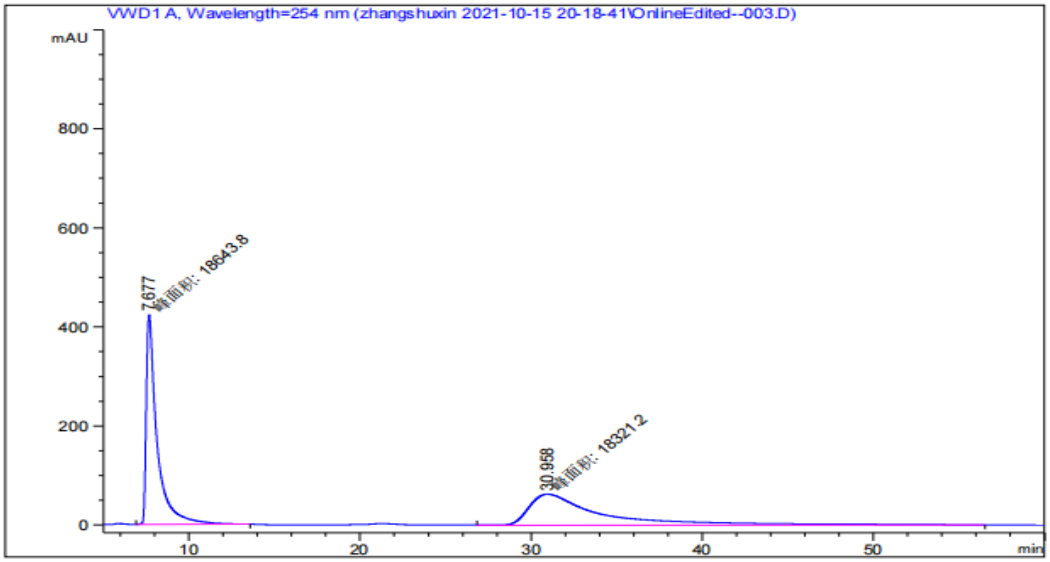


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.852	BV	0.3895	1.89609e4	751.26050	49.5380
2	9.418	VB	0.4448	1.93145e4	659.29108	50.4620
总量 :				3.82754e4	1410.55157	

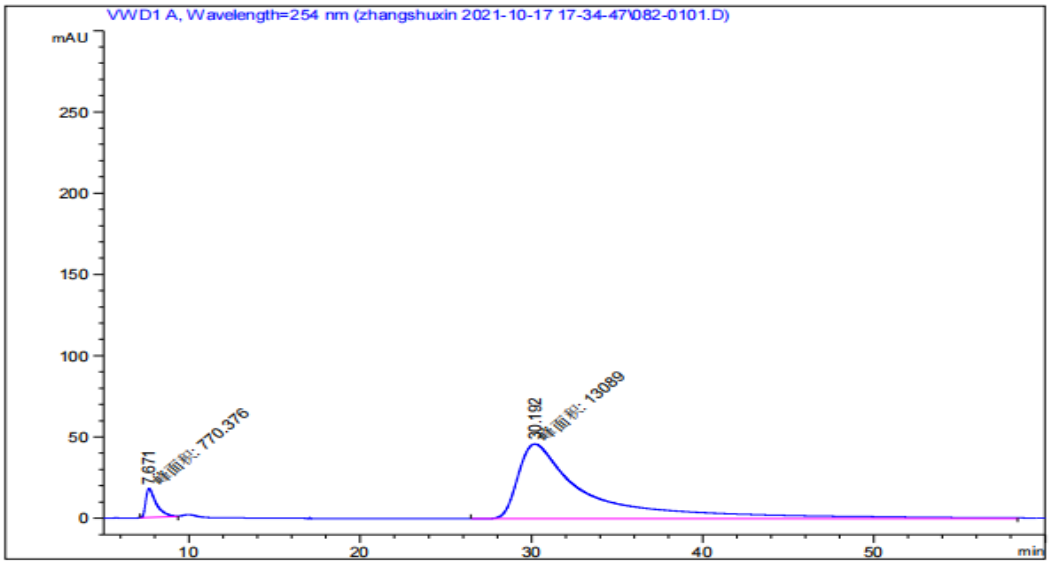


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.993	BB	0.3048	2673.29053	130.58397	93.4889
2	9.588	BB	0.3836	186.18167	7.37292	6.5111
总量 :				2859.47220	137.95688	

Figure S80. Copy of HPLC spectra of **4f**

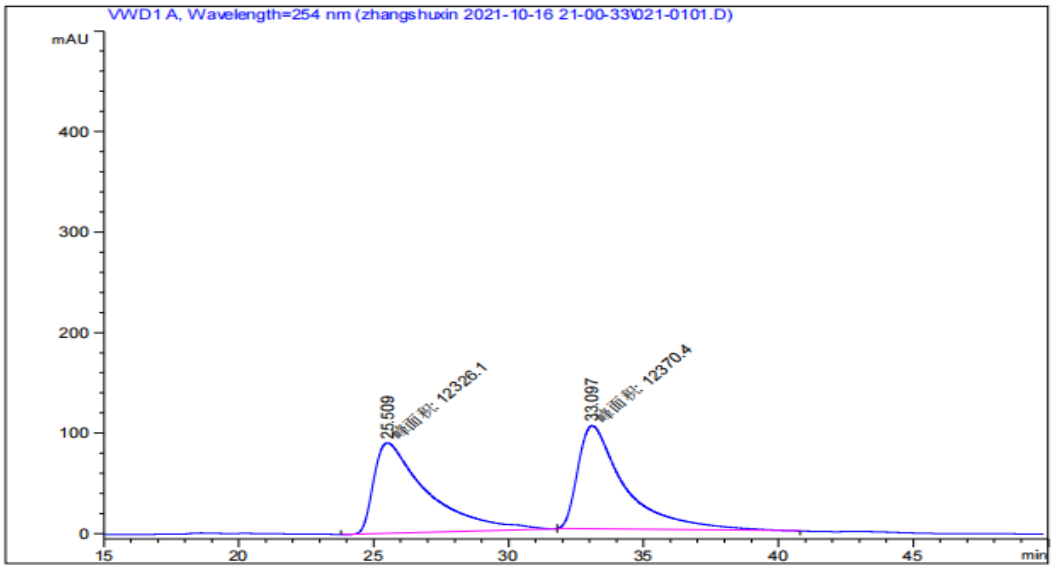


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.677	MM	0.7351	1.86438e4	422.72028	50.4364
2	30.958	MM	4.8984	1.83212e4	62.33804	49.5636
总量：				3.69651e4	485.05831	

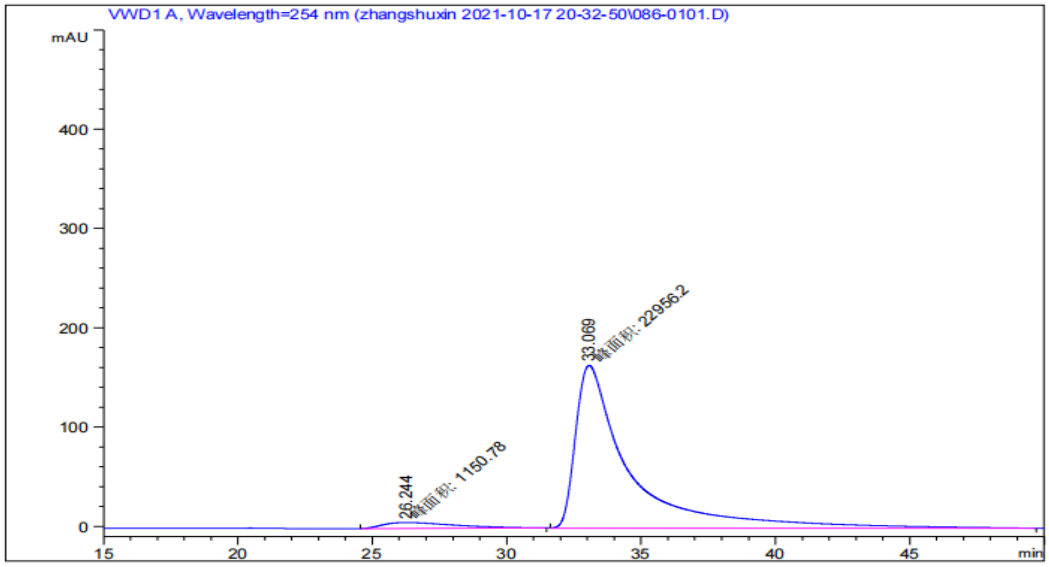


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.671	MM	0.7237	770.37561	17.74267	5.5585
2	30.192	MM	4.7499	1.30890e4	45.92723	94.4415

Figure S81. Copy of HPLC spectra of **4g**

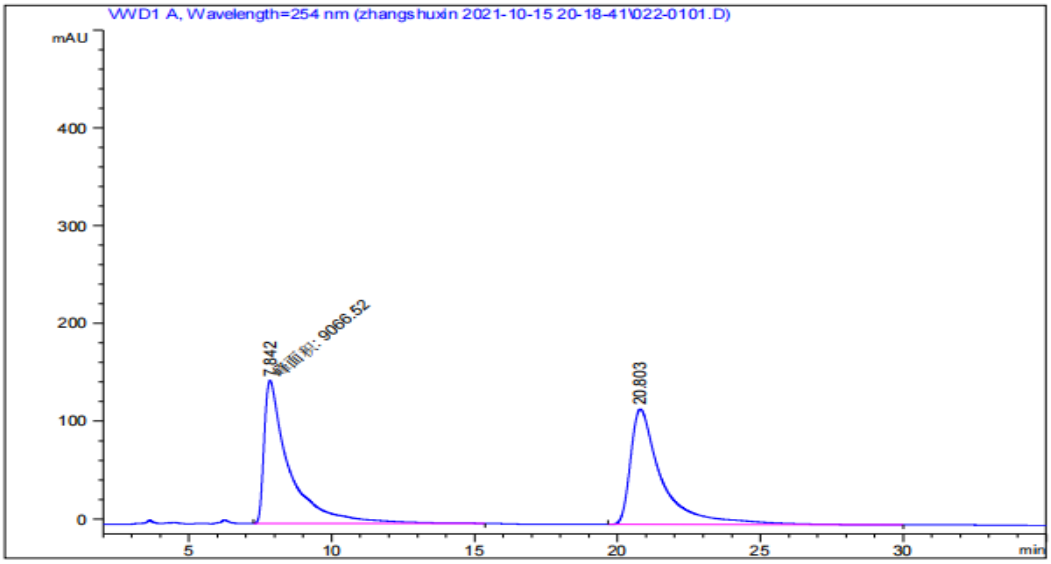


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	25.509	MM	2.2859	1.23261e4	89.86923	49.9103
2	33.097	MM	2.0124	1.23704e4	102.45327	50.0897
总量：				2.46965e4	192.32250	

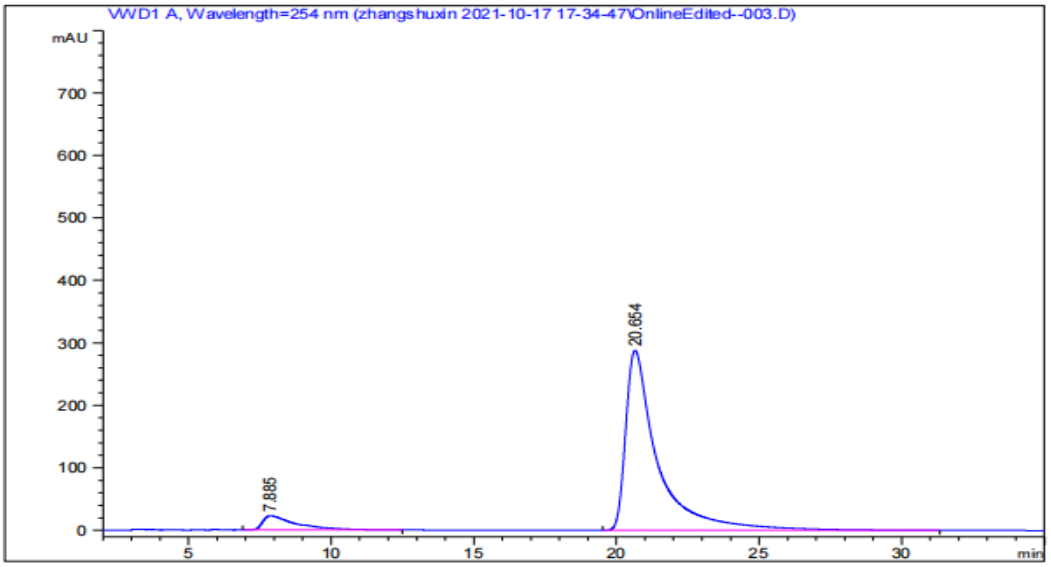


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	26.244	MM	3.1600	1150.78040	6.06959	4.7736
2	33.069	MM	2.3370	2.29562e4	163.71204	95.2264

Figure S82. Copy of HPLC spectra of **4h**

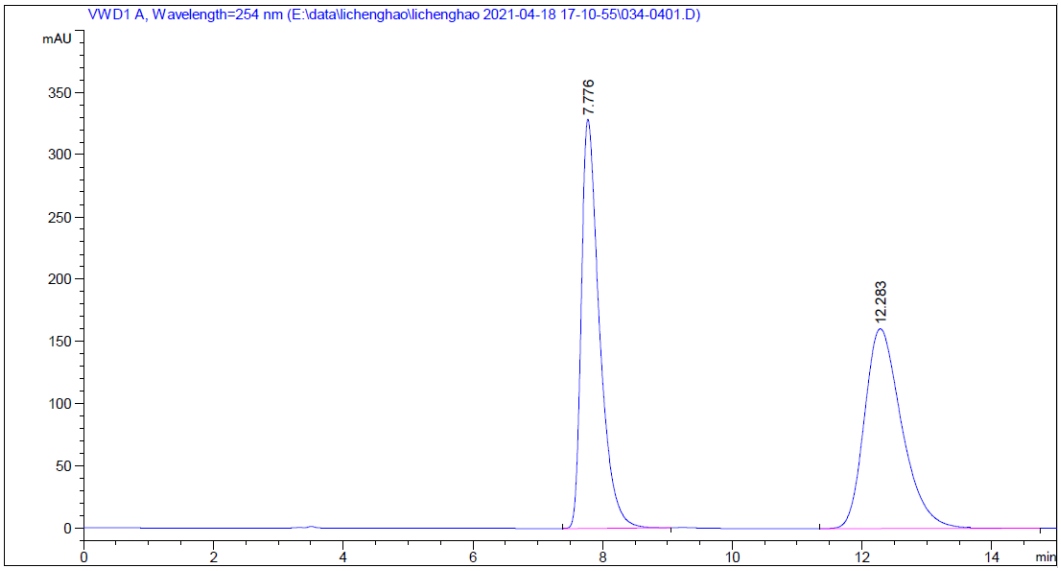


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.842	MM	1.0341	9066.51563	146.12718	50.0503
2	20.803	BB	1.0952	9048.27832	117.91988	49.9497

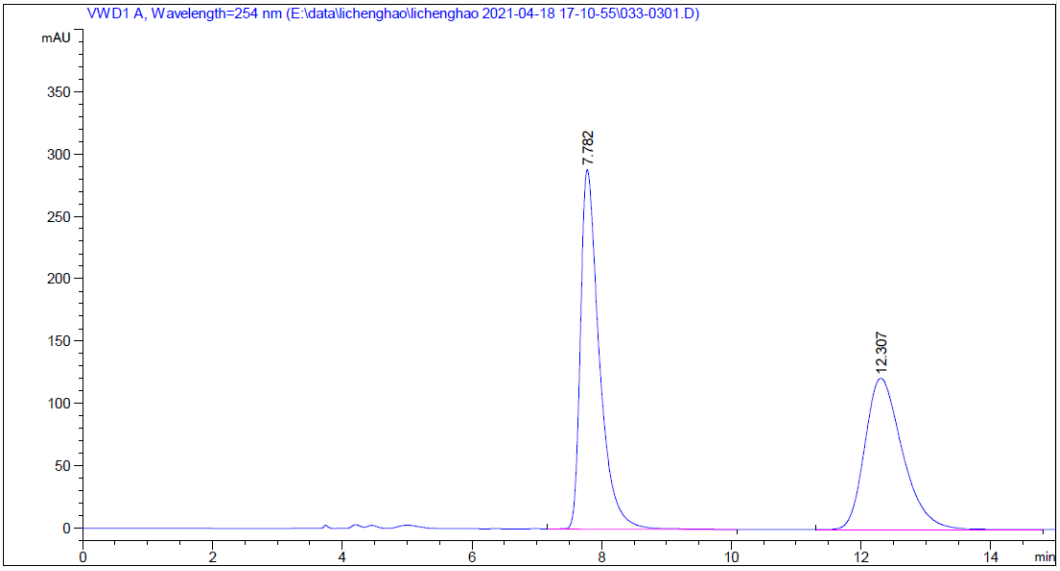


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.885	BB	1.1402	1850.11279	22.64442	7.6067
2	20.654	BB	1.1053	2.24720e4	287.99750	92.3933
总量：				2.43221e4	310.64191	

Figure S83. Copy of HPLC spectra of **4i**



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.776	BB	0.2893	6379.14795	328.89249	49.8845
2	12.283	BB	0.6096	6408.68457	160.57660	50.1155
总量：				1.27878e4	489.46909	



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.782	BB	0.2984	5795.67773	288.47263	54.2645
2	12.307	BB	0.6154	4884.74316	121.41721	45.7355
总量：				1.06804e4	409.88984	