



Supporting Information

for

A novel and robust heterogeneous Cu catalyst using modified lignosulfonate as support for the synthesis of nitrogen-containing heterocycles

Bingbing Lai, Meng Ye, Ping Liu, Minghao Li, Rongxian Bai and Yanlong Gu

Beilstein J. Org. Chem. **2020**, *16*, 2888–2902. [doi:10.3762/bjoc.16.238](https://doi.org/10.3762/bjoc.16.238)

Characterization data, copies of NMR spectra and the preparation of the referential catalysts

1. General remarks

Sodium lignosulfonate, o-anisaldehyde, propionaldehyde and 1,3-diaminopropane were purchased from Aladdin Industrial Corporation. 2-Formylbenzenesulfonic acid sodium salt, 4-(trifluoromethyl)benzaldehyde, 1-(4-propylphenyl)ethan-1-one and 3,4-dimethoxyaniline were purchased from Adamas Reagent, Ltd. Copper(II) trifluoromethanesulfonate, benzaldehyde, formaldehyde, acetophenone, 1-aminonaphthalene, butylamine and morpholine were purchased from Sinopharm Chemical Reagent Co., Ltd. 4-Aminoindole, 4'-*n*-amylacetophenone, 6-acetyl-1,4-benzodioxane and 3,4-methylenedioxyacetophenone were purchased from Bide Pharmatech Ltd. *p*-Tolualdehyde, 4'-*n*-amylacetophenone, 4-fluoroacetophenone, 5-acetyl-2,3-dihydrobenzo(*b*)furan and 4-bromoaniline were purchased from Accela Chem Bio Co., Ltd. Dimethyl acetylenedicarboxylate, 4-bromobenzaldehyde, 2-naphthaldehyde, 2,3-dichlorobenzaldehyde, 3,4,5-trimethoxybenzaldehyde, 2-bromo-4,5-methylenedioxybenzaldehyde, phenylpropylaldehyde, 3,3-dimethylbutyraldehyde, cyclopropanecarboxaldehyde, dimethyl acetylenedicarboxylate, 4'-methylacetophenone, 4'-cyclohexylacetophenone, 4'-methylthioacetophenone, 4'-methoxyacetophenone, 4'-benzyloxyacetophenone, 4-acetylbiphenyl, 4'-chloroacetophenone, 4'-iodoacetophenone, 3'-methylacetophenone, 3,4-dimethoxyacetophenone, 3',4',5'-trimethoxyacetophenone, 2-acetylfluorene, *p*-anisidine and urea were purchased from Energy Chemical Co., Ltd. 2-Acetonaphthone, 2',5'-dimethylacetophenone, 2-acetylbenzofuran, benzylamine and furfurylamine were purchased from Alfa Aesar Chemical Company. *p*-Toluidine was purchased from Jinshan Chemical Co., Ltd. 4-*tert*-Butylaniline was purchased from Heowns Biochem Technologies Co., Ltd.

2. Supplementary experiment section

2.1 Preparation of the referential catalyst LS-FM-Cu

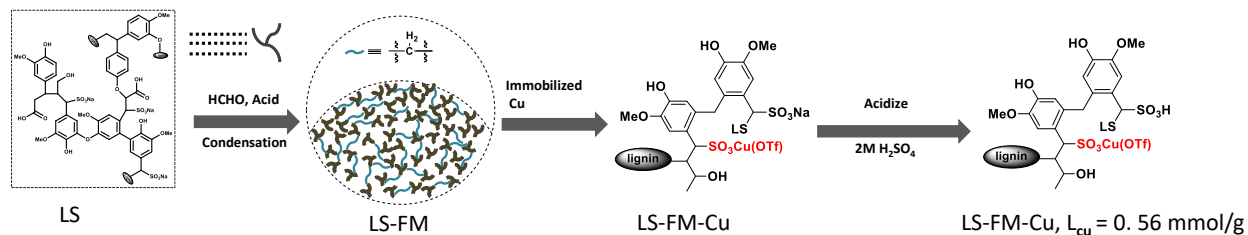


Fig. S1 Preparation of the referential catalyst LS-FM-Cu in this work.

2.2 Preparation of the referential catalyst Resin-Cu

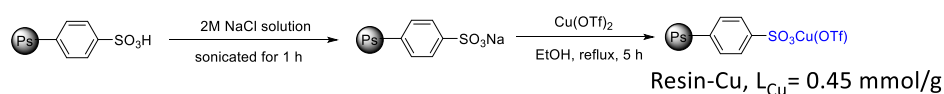


Fig. S2 Preparation of the referential catalyst Resin-Cu in this work.

2.3 Elemental analysis of the composites in this work

Table S1 Elemental analysis of the composite in this work.

Composite	Weight [mg]	Method	C [%]	H [%]	S [%]
LS	2.1080	2mg80s	30.84	3.658	2.626
LS-FAS	2.3860	2mg80s	53.79	4.851	6.650

2.4 Thermo gravimetric weight loss of the obtained referential catalyst Resin-Cu

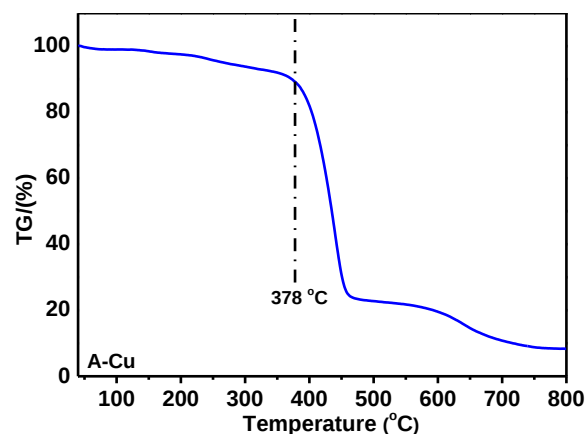


Fig. S3. Thermogravimetric weight loss of the obtained referential catalyst Resin-Cu.

2.5 Typical procedure for the synthesis of tricyclic indole alkaloids bearing 3,4-fused seven-membered rings (**4a** as an example)

In a V-type reaction flask which was equipped with magnetic stirring, 4-aminoindole (**1a**, 0.3 mmol, 39.6 mg), 4-methylbenzaldehyde (**2a**, 0.2 mmol, 24.0mg), diethyl acetylenedicarboxylate (**3a**, 0.3 mmol, 51.0 mg) and the catalyst LS-FAS-Cu (20 mol %, 43.5 mg) were added to 1.0 mL EtOH and the temperature of the mixture was allowed to increase to 60 °C. The reaction process was monitored by PTLC, after its completion the solution was centrifuged. The organic phase was further purified by preparative TLC using a mixture of ethyl acetate and petroleum ether as eluent (EA/PE 1:5 v/v), thus the product **4a** (69.2 mg, 86%) was obtained.

2.6 Typical procedure for the synthesis of 2-arylpyridine derivatives (**7a** as an example) [1]

In a 10 mL V-type reaction flask which was equipped with magnetic stirring, acetophenone **5a** (0.2 mmol, 24.0 mg), 1,3-diaminopropane (**6a**, 0.6 mmol, 44.5 mg), LS-FAS-Cu (20 mol %, 43.5 mg) and TsOH·H₂O (0.12 mmol, 22.8 mg) were added into 1.0 mL EtOH solution. The mixture was stirred for 24 hours at 100 °C under oxygen atmosphere. The reaction process was monitored by PTLC, after its completion the solution was centrifuged. The organic phase was further purified by preparative TLC using a mixture of ethyl acetate and petroleum ether as eluent (EA/PE 1:3 v/v), thus the product **7a** (23.3 mg, 75%) was obtained. In the substrate scope extending section, the catalyst was changed to LSA-FAS-Cu [Cu (40 mol %), -SO₃H (0.5 equiv)] without the presence of TsOH.H₂O.

2.7 Typical procedure for the synthesis of aminonaphthalenes derivatives (**10a** as an example) [2]

In a 10 mL V-type reaction flask which was equipped with magnetic stirring, 1-(2-(phenylethynyl)phenyl)ethan-1-one (**8a**, 0.2 mmol, 44.1 mg), *p*-toluidine (**9a**, 0.24 mmol, 25.7 mg) and catalyst LS-FAS-Cu (10 mol %, 21.7 mg) were added to 1.0 mL DCE solvent. The mixture solution was stirred for 12 hours at 100 °C under N₂ atmosphere. The reaction process was monitored by PTLC, after its completion the solution was centrifuged. The organic phase was further purified by preparative TLC using a mixture of ethyl acetate and petroleum ether as eluent (EA/PE 1:3 v/v), thus the product **10a** (50.1 mg, 81%) was obtained.

2.8 Typical procedure for the synthesis of 3-phenylisoquinolines derivatives **13a** [3]

In a 10 mL V-type reaction flask which was equipped with magnetic stirring, 2-(phenylethynyl)benzaldehyde (**11a**, 0.2 mmol, 41.2 mg), urea (**12a**, 0.4 mmol, 24.0 mg) and the catalyst LS-FAS-Cu (10 mol %, 21.7 mg) were added to 1.0 mL Toluene solvent. The mixture solution was stirred for 12 hours at 120 °C under N₂ atmosphere. The reaction process was monitored by PTLC, after its completion the solution was centrifuged. The organic phase was further purified by preparative TLC using a mixture of ethyl acetate and petroleum ether as eluent (EA/PE 1:3 v/v), thus the product **13a** (34.9 mg, 85%) was obtained.

3. Spectroscopic data for the compounds

Diethyl 4-(*p*-tolyl)-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (4a**)** Yellow solid, mp: 167–169 °C, ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 9.16 (d, *J* = 8.8 Hz, 1H), 7.65 (dd, *J* = 8.4, 7.0 Hz, 3H), 7.53 (d, *J* = 9.0 Hz, 1H), 7.37 (s, 1H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.23–7.16 (m, 1H), 4.53 (q, *J* = 7.1 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.08 ppm (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 168.5, 167.4, 155.6, 144.5, 139.8, 138.7, 137.8, 135.6, 129.0, 128.8, 124.0, 123.6, 121.3, 118.5, 117.2, 115.5, 103.7, 62.4, 61.8, 21.4, 14.1, 13.7 ppm. IR: ν = 3369, 2980, 1728, 1550, 1248, 1027, 747, 501 cm⁻¹; HRMS (TOF, ESI): *m/z* calcd for C₂₄H₂₂N₂O₄, [M + H]⁺ 402.1579, found 402.1601.

Diethyl 4-phenyl-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (4b**)** Yellow solid, mp: 150–152 °C, ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 9.04 (s, 1H), 7.76–7.72 (m, 2H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.59 (d, *J* = 9.0 Hz, 1H), 7.46 (q, *J* = 5.7 Hz, 3H), 7.39 (s, 1H), 7.25 (dd, *J* = 5.2, 2.5 Hz, 1H), 4.53 (q, *J* = 7.1 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.02 ppm (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 168.3, 167.3, 155.7, 144.5, 140.7, 140.0, 135.7, 128.9, 128.7, 128.2, 124.1, 123.6, 121.4, 118.7, 118.6, 117.4, 115.5, 103.9, 103.8, 62.4, 61.8, 14.1, 13.6 ppm. IR: ν = 3380, 2980, 1717, 1549, 1246, 1213, 1017, 737, 696, 597, 499 cm⁻¹; HRMS (TOF, ESI): *m/z* calcd for C₂₃H₂₀N₂O₄, [M + H]⁺ 388.1423, found 388.1426.

Diethyl 4-(4-bromophenyl)-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (4c**)** Yellow solid, mp: 172–174 °C, ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 8.96 (d, *J* = 11.2 Hz, 1H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.66–7.58 (m, 5H), 7.39 (d, *J* = 1.9 Hz, 1H), 7.33–7.27 (m, 1H), 4.54 (q, *J* = 7.1 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.10 ppm (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 168.04, 167.15, 154.42, 144.47, 140.18, 139.62, 135.68, 131.39, 130.55, 124.07, 123.65, 123.22, 121.07, 118.70, 117.51, 115.68, 103.87, 62.44, 61.91, 14.11, 13.67 ppm. IR: ν = 3372, 2971, 1735, 1707, 1254, 1215, 1007, 746, 582, 446 cm⁻¹; HRMS (TOF, ESI): *m/z* calcd for C₂₃H₁₉BrN₂O₄, [M + H]⁺ 466.0528, found 466.0540.

Diethyl 4-(4-(trifluoromethyl)phenyl)-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (4d**)** Yellow solid, mp: 126–128 °C, ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 9.11 (s, 1H), 7.84 (d, *J* = 7.9 Hz, 2H), 7.71 (dd, *J* = 16.0, 8.5 Hz, 3H), 7.62 (d, *J* = 9.0 Hz, 1H), 7.37 (s, 1H), 7.26 (d, *J* = 2.9 Hz, 1H), 4.55 (q, *J* = 7.1 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.04 ppm (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 167.8, 167.2, 154.3, 144.5, 144.3, 140.4, 135.8, 130.8, 130.5, 129.3, 125.6, 125.2, 125.1, 124.1, 123.8, 122.9, 121.0, 118.6, 117.7, 116.0, 103.8, 62.5, 62.0, 14.1, 13.5 ppm.

IR: ν = 3368, 2981, 1739, 1708, 1550, 1324, 1260, 748, 586, 449 cm^{-1} ; HRMS (TOF, ESI): m/z calcd for $\text{C}_{24}\text{H}_{19}\text{F}_3\text{N}_2\text{O}_4$, $[\text{M} + \text{H}]^+$ 456.1296, found 456.1305.

Diethyl 4-(2-methoxyphenyl)-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (4e) Yellow solid, mp: 125–127 °C, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 9.19 (s, 1H), 7.73 (dd, J = 7.4, 1.4 Hz, 1H), 7.61 (d, J = 9.0 Hz, 1H), 7.56 (d, J = 9.0 Hz, 1H), 7.42–7.31 (m, 2H), 7.21–7.17 (m, 1H), 7.13 (t, J = 7.4 Hz, 1H), 6.87 (d, J = 8.2 Hz, 1H), 4.52 (q, J = 7.1 Hz, 2H), 4.15–4.07 (m, 2H), 3.66 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H), 1.04 ppm (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 167.9, 167.3, 156.7, 154.0, 144.8, 140.4, 135.7, 131.3, 130.3, 130.1, 124.0, 123.6, 121.7, 121.0, 118.7, 118.6, 117.5, 115.4, 110.1, 103.8, 62.2, 61.2, 55.1, 14.1, 13.6 ppm. IR: ν = 3372, 2979, 1728, 1550, 1247, 1027, 751, 489 cm^{-1} ; HRMS (TOF, ESI): m/z calcd for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_4$, $[\text{M} + \text{H}]^+$ 418.1528, found 418.1550.

Diethyl 4-(naphthalen-2-yl)-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (4f) Yellow solid, mp: 199–201 °C, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 8.95 (s, 1H), 8.21 (s, 1H), 7.98–7.86 (m, 4H), 7.72 (d, J = 9.0 Hz, 1H), 7.64 (d, J = 9.0 Hz, 1H), 7.56–7.48 (m, 2H), 7.45 (s, 1H), 7.30 (s, 1H), 4.56 (q, J = 7.2 Hz, 2H), 4.12 (q, J = 7.1 Hz, 2H), 1.45 (t, J = 7.1 Hz, 3H), 0.93 ppm (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 168.4, 167.3, 155.5, 144.5, 140.1, 138.0, 135.7, 133.4, 133.2, 128.5, 128.5, 127.9, 127.7, 126.6, 126.5, 126.3, 124.1, 123.6, 121.6, 118.7, 117.4, 115.5, 104.0, 62.4, 61.8, 14.1, 13.6 ppm. IR: ν = 3381, 2980, 1727, 1550, 1243, 1021, 750, 479 cm^{-1} ; HRMS (TOF, ESI): m/z calcd for $\text{C}_{27}\text{H}_{22}\text{N}_2\text{O}_4$, $[\text{M} + \text{H}]^+$ 438.1579, found 438.1568.

Diethyl 4-(2,3-dichlorophenyl)-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (4g) Yellow solid, mp: 172–174 °C, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 9.18 (s, 1H), 7.67 (s, 2H), 7.52 (d, J = 7.9 Hz, 1H), 7.42 (d, J = 7.2 Hz, 1H), 7.33 (d, J = 7.8 Hz, 1H), 7.28 (dd, J = 9.3, 6.8 Hz, 2H), 4.56 (q, J = 7.1 Hz, 2H), 4.12 (dd, J = 13.7, 6.8 Hz, 2H), 1.45 (t, J = 7.1 Hz, 3H), 1.00 ppm (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 167.6, 166.2, 154.2, 144.7, 142.5, 141.7, 135.9, 132.8, 131.5, 130.1, 129.1, 127.2, 124.0, 123.9, 120.1, 118.9, 118.2, 116.0, 104.0, 62.4, 61.7, 29.7, 14.1, 13.4 ppm. IR: ν = 3379, 2981, 1724, 1549, 1412, 1246, 1031, 744, 515 cm^{-1} ; HRMS (TOF, ESI): m/z calcd for $\text{C}_{23}\text{H}_{18}\text{Cl}_2\text{N}_2\text{O}_4$, $[\text{M} + \text{H}]^+$ 456.0643, found 456.0626.

Diethyl 4-(3,4,5-trimethoxyphenyl)-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (4h) Yellow solid, mp: 200–202 °C, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 8.89 (s, 1H), 7.74 (d, J = 9.0 Hz, 1H), 7.68 (d, J = 9.0 Hz, 1H), 7.46 (s, 1H), 7.36 (d, J = 2.4 Hz, 1H), 6.99 (s, 2H), 4.54 (q, J = 7.1 Hz, 2H), 4.18 (q, J = 7.1 Hz, 2H), 3.91 (d, J = 4.5 Hz, 9H), 1.45 (t, J = 7.2 Hz, 3H), 1.09 ppm (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 168.5, 167.1, 155.3, 153.2, 144.3, 139.8, 136.2, 135.7, 124.1, 123.5, 121.7, 118.8, 117.5, 115.4, 106.2, 104.0, 62.4, 61.9, 61.0, 56.2, 14.1, 13.7 ppm. IR: ν = 3351, 2979, 1730, 1587, 1416, 1240, 1126, 1022, 873, 746, 531, 455 cm^{-1} ; HRMS (TOF, ESI): m/z calcd for $\text{C}_{26}\text{H}_{26}\text{N}_2\text{O}_7$, $[\text{M} + \text{H}]^+$ 478.1740, found 478.1749.

Diethyl 4-(6-bromobenzo[*d*][1,3]dioxol-5-yl)-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (4i) Yellow solid, mp: 160–162 °C, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 9.85 (s, 1H), 7.66 (q, J = 9.0 Hz, 2H), 7.35 (s, 1H), 7.28 (s, 1H), 7.04 (s, 1H), 7.00 (s, 1H), 6.00 (s, 2H), 4.55 (q, J = 7.0 Hz, 2H), 4.18 (q, J = 7.0 Hz, 2H), 1.45 (t, J = 7.1 Hz, 3H), 1.12 ppm (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 167.6, 166.5, 155.6, 148.4, 147.1, 144.5, 141.2, 136.1, 135.3, 124.0, 123.8, 120.6, 118.5, 118.0, 116.2, 113.4, 112.3, 110.9, 103.6, 101.9, 62.3, 61.7, 14.1, 13.7 ppm. IR: ν = 3377, 2979, 2900, 1726, 1549, 1479, 1238, 1037, 932, 876, 745, 444 cm^{-1} ; HRMS (TOF, ESI): m/z calcd for $\text{C}_{24}\text{H}_{19}\text{BrN}_2\text{O}_6$, $[\text{M} + \text{H}]^+$ 510.0426, found 510.0409.

Diethyl 4-phenethyl-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (4j) Yellow solid, mp: 172–174 °C, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 8.86 (s, 1H), 7.68 (d, J = 9.0 Hz, 1H), 7.61 (d, J

= 9.0 Hz, 1H), 7.42 (s, 1H), 7.37–7.27 (m, 5H), 7.21 (d, J = 6.8 Hz, 1H), 4.51 (q, J = 7.1 Hz, 2H), 4.40 (dd, J = 14.3, 7.1 Hz, 2H), 3.52 (dd, J = 9.8, 6.6 Hz, 2H), 3.25 (dd, J = 9.7, 6.6 Hz, 2H), 1.42 (dt, J = 21.2, 7.1 Hz, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 167.6, 167.5, 157.7, 144.6, 142.2, 139.8, 135.6, 128.6, 128.4, 125.9, 123.8, 123.3, 121.0, 119.0, 117.2, 114.8, 103.8, 62.1, 61.9, 39.0, 35.6, 14.2, 14.1 ppm. IR: ν = 3369, 2982, 1721, 1555, 1242, 1019, 742, 508 cm^{-1} ; HRMS (TOF, ESI): m/z calcd for $\text{C}_{25}\text{H}_{24}\text{N}_2\text{O}_4$, $[\text{M} + \text{H}]^+$ 416.1736, found 416.1763.

Diethyl 4-methyl-6H-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (4k) Yellow solid, mp: 164–166 °C, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 9.18 (s, 1H), 7.62 (d, J = 4.9 Hz, 2H), 7.39 (s, 1H), 7.32 (s, 1H), 4.52 (q, J = 7.1 Hz, 2H), 4.43 (q, J = 7.1 Hz, 2H), 2.95 (s, 3H), 1.43 ppm (q, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 167.6, 167.5, 155.4, 144.6, 140.2, 135.7, 123.5, 120.6, 118.9, 117.1, 114.8, 103.5, 62.1, 61.8, 25.1, 14.1 ppm. IR: ν = 3381, 2983, 1727, 1559, 1246, 1204, 1039, 742, 516 cm^{-1} ; HRMS (TOF, ESI): m/z calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4$, $[\text{M} + \text{H}]^+$ 326.1266, found 326.1258.

Diethyl 4-butyl-6H-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (4l) Yellow oil, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 9.05 (s, 1H), 7.65 (d, J = 9.0 Hz, 1H), 7.56 (d, J = 9.0 Hz, 1H), 7.38 (s, 1H), 7.29 (s, 1H), 4.50 (q, J = 7.1 Hz, 2H), 4.42 (q, J = 7.1 Hz, 2H), 3.24–3.13 (m, 2H), 1.90 (dd, J = 15.3, 7.6 Hz, 2H), 1.42 (q, J = 7.2 Hz, 6H), 1.04 ppm (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 167.9, 167.6, 158.7, 144.6, 139.7, 135.6, 123.7, 123.3, 121.1, 118.9, 117.0, 114.7, 103.7, 62.2, 61.8, 39.3, 23.2, 14.2, 14.2, 14.1 ppm. IR: ν = 2924, 2961, 2865, 2730, 1725, 1630, 1595, 1414, 1378, 1310, 1124, 736, 553 cm^{-1} . HRMS (TOF, ESI): m/z calcd for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_4$, $[\text{M} + \text{H}]^+$ 354.1580, found 354.1581.

Diethyl 4-neopentyl-6H-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (4m) Yellow solid, mp: 110–112 °C, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 9.16 (s, 1H), 7.67 (d, J = 9.0 Hz, 1H), 7.60 (d, J = 9.0 Hz, 1H), 7.37 (s, 1H), 7.31 (s, 1H), 4.49 (q, J = 7.1 Hz, 2H), 4.39 (q, J = 7.1 Hz, 2H), 3.24 (s, 2H), 1.42 (dt, J = 11.4, 7.2 Hz, 6H), 1.02 (s, 9H) ppm. ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 168.3, 167.6, 156.7, 144.1, 139.1, 135.4, 123.9, 123.2, 122.4, 118.7, 116.7, 114.8, 103.6, 62.1, 61.7, 47.9, 33.1, 29.9, 14.2, 14.1 ppm. IR: ν = 3375, 2958, 1716, 1552, 1247, 1206, 1019, 747, 588, 521 cm^{-1} ; HRMS (TOF, ESI): m/z calcd for $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_4$, $[\text{M} + \text{H}]^+$ 382.1892, found 382.1923.

Diethyl 4-cyclopropyl-6H-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (4n) Yellow solid, mp: 130–132 °C, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 8.79 (s, 1H), 7.63 (d, J = 9.0 Hz, 1H), 7.50 (d, J = 9.0 Hz, 1H), 7.26 (dd, J = 8.8, 2.4 Hz, 2H), 4.47 (dq, J = 24.1, 7.1 Hz, 4H), 2.60 (td, J = 8.1, 4.1 Hz, 1H), 1.42 (dd, J = 13.3, 7.0 Hz, 8H), 1.12–1.02 ppm (m, 2H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 168.0, 167.6, 158.6, 144.7, 138.9, 135.5, 123.6, 123.1, 121.4, 119.0, 116.6, 114.2, 103.5, 62.1, 61.9, 15.4, 14.2, 11.0 ppm. IR: ν = 3381, 2983, 1726, 1556, 1418, 1248, 1181, 1023, 865, 744, 667, 533 cm^{-1} ; HRMS (TOF, ESI): m/z calcd for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_4$, $[\text{M} + \text{H}]^+$ 352.1423, found 352.1432.

Dimethyl 4-(*p*-tolyl)-6H-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (4o) Yellow oil, ^1H NMR (400 MHz, $\text{DMSO}-d_6$, 25 °C): δ = 11.97 (s, 1H), 7.86 (d, J = 9.0 Hz, 1H), 7.60 (dd, J = 14.8, 8.4 Hz, 4H), 7.34 (d, J = 7.7 Hz, 2H), 7.20 (s, 1H), 4.00 (s, 3H), 3.70 (s, 3H), 2.39 ppm (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 168.4, 167.4, 154.5, 144.3, 139.7, 138.9, 137.4, 136.2, 129.5, 128.9, 125.6, 123.8, 120.6, 117.9, 117.2, 116.5, 102.7, 53.7, 53.2, 21.3 ppm. IR (KBr) ν = 3383, 2924, 1735, 1351, 1252, 1141, 1028, 749, 497 cm^{-1} ; HRMS (ESI, TOF) m/z : calcd for $\text{C}_{22}\text{H}_{19}\text{N}_2\text{O}_4^+$, $[\text{M} + \text{H}]^+$ 375.1339, found 375.1339.

2-Phenylpyridine (7a) Yellow oil, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 8.70 (d, J = 4.7 Hz, 1H), 7.99 (d, J = 7.5 Hz, 2H), 7.78–7.68 (m, 2H), 7.48 (t, J = 7.4 Hz, 2H), 7.41 (t, J = 7.2 Hz, 1H), 7.25–7.18 ppm (m, 1H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 157.5, 149.7, 139.4, 136.8, 129.0, 128.8, 126.9, 122.1, 120.6 ppm.

2-(*p*-Tolyl)pyridine (7b) Yellow oil, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 8.68 (d, J = 8.0 Hz, 1H), 7.89

(d, J = 8.0 Hz, 2H), 7.74–7.72 (m, 2H), 7.28 (t, J = 8.0 Hz, 2H), 7.22–7.19 (m, 1H), 2.41 ppm (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 157.5, 149.6, 139.0, 136.7, 136.6, 129.5, 126.8, 121.8, 120.3, 21.3 ppm.

2-(4-Propylphenyl)pyridine (7c) Yellow oil, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 8.67 (d, J = 4.6 Hz, 1H), 7.91 (d, J = 8.1 Hz, 2H), 7.76–7.66 (m, 2H), 7.28 (d, J = 8.1 Hz, 2H), 7.19 (dd, J = 8.9, 4.4 Hz, 1H), 2.64 (t, J = 7.6 Hz, 2H), 1.68 (dd, J = 15.0, 7.5 Hz, 2H), 0.96 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 157.6, 149.6, 143.7, 136.9, 136.7, 128.9, 126.8, 121.8, 120.3, 37.8, 24.5, 13.8 ppm.

2-(4-Pentylphenyl)pyridine (7d) Yellow oil, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 8.67 (d, J = 4.6 Hz, 1H), 7.90 (d, J = 8.1 Hz, 2H), 7.73–7.71 (m, 2H), 7.29 (d, J = 12.0 Hz, 2H), 7.20–7.18 (m, 1H), 2.66 (t, J = 4.0 Hz, 2H), 1.67–1.63 (m, 2H), 1.35–1.33 (m, 4H), 0.90 ppm (t, J = 4.0 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 157.6, 149.6, 144.0, 136.8, 136.7, 128.9, 126.8, 121.8, 120.3, 35.7, 31.5, 31.1, 22.6, 14.1 ppm.

2-(4-(*tert*-Butyl)phenyl)pyridine (7e) Yellow oil, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 8.69 (d, J = 4.1 Hz, 1H), 7.93 (d, J = 8.1 Hz, 2H), 7.74 (d, J = 7.0 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 7.22 (t, J = 5.0 Hz, 1H), 1.36 ppm (s, 9H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 157.4, 152.3, 149.4, 136.9, 136.3, 126.7, 125.8, 121.9, 120.4, 34.7, 31.3 ppm.

2-(4-Cyclohexylphenyl)pyridine (7f) Yellow oil, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 8.68 (d, J = 4.0 Hz, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.73–7.71 (m, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.21–7.18 (m, 1H), 2.58–2.53 (m, 1H), 1.92–1.84 (m, 4H), 1.48–1.39 (m, 4H), 1.29–1.25 ppm (m, 2H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 157.6, 149.6, 149.1, 137.0, 136.7, 127.3, 126.9, 121.8, 120.3, 44.4, 34.4, 26.9, 26.2 ppm.

2-(4-(Methylthio)phenyl)pyridine (7g) Yellow oil, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 8.67 (d, J = 4.4 Hz, 1H), 7.93 (d, J = 8.5 Hz, 2H), 7.77–7.65 (m, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.24–7.17 (m, 1H), 2.53 ppm (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 156.8, 149.7, 139.9, 136.8, 136.0, 128.8, 127.2, 126.4, 122.0, 120.1, 15.6 ppm.

2-(4-Methoxyphenyl)pyridine (7h) Yellow oil, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 8.65 (d, J = 4.4 Hz, 1H), 7.95 (d, J = 8.6 Hz, 2H), 7.75–7.60 (m, 2H), 7.22–7.13 (m, 1H), 7.00 (d, J = 8.6 Hz, 2H), 3.86 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 160.5, 157.1, 149.5, 136.7, 132.0, 128.2, 121.4, 119.8, 114.1, 55.4 ppm.

2-(4-(Benzyloxy)phenyl)pyridine (7i) Yellow oil, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 8.65 (d, J = 4.2 Hz, 1H), 7.95 (d, J = 8.6 Hz, 2H), 7.69 (dt, J = 15.8, 7.8 Hz, 2H), 7.46 (d, J = 7.2 Hz, 2H), 7.40 (t, J = 7.3 Hz, 2H), 7.36–7.30 (m, 1H), 7.20–7.13 (m, 1H), 7.07 (d, J = 8.6 Hz, 2H), 5.13 ppm (s, 2H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 159.7, 157.1, 149.6, 136.8, 136.7, 132.3, 128.6, 128.2, 128.0, 127.5, 121.5, 119.8, 115.1, 70.1 ppm.

2-([1,1'-Biphenyl]-4-yl)pyridine (7j) Yellow oil, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 8.72 (d, J = 4.0 Hz, 1H), 8.09 (d, J = 8.0 Hz, 2H), 7.77–7.75 (m, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.46 (t, J = 8.0 Hz, 2H), 7.38–7.35 (m, 1H), 7.25–7.22 ppm (m, 1H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 157.1, 149.8, 141.7, 140.6, 138.3, 136.8, 128.9, 127.6, 127.5, 127.3, 127.1, 122.2, 120.5 ppm.

2-(4-Fluorophenyl)pyridine (7k) Yellow oil, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 8.70 (d, J = 3.0 Hz, 1H), 8.05–7.94 (m, 2H), 7.80 (d, J = 7.2 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.27 (s, 1H), 7.18 ppm (t, J = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 156.4, 149.8, 138.9, 137.9, 136.9, 128.7, 122.5, 120.3, 95.3 ppm.

2-(4-Chlorophenyl)pyridine (7l) Yellow oil, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 8.70 (d, J = 3.0 Hz, 1H), 8.05–7.95 (m, 2H), 7.80 (d, J = 7.2 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.26–7.25 (m, 1H), 7.18 ppm (t, J = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 156.4, 149.8, 138.9, 137.9, 136.9, 128.7, 122.5, 120.3, 95.3 ppm.

2-(4-Iodophenyl)pyridine (7m) Yellow oil, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 8.69 (d, J = 4.3 Hz, 1H), 7.81 (d, J = 8.5 Hz, 2H), 7.77–7.67 (m, 4H), 7.25 ppm (d, J = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 156.4, 149.8, 138.9, 137.9, 136.9, 128.7, 122.5, 120.3, 95.3 ppm.

2-(*m*-Tolyl)pyridine (7n) Yellow oil, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 8.69 (d, J = 4.4 Hz, 1H), 7.84 (s, 1H), 7.74 (dd, J = 8.1, 6.9 Hz, 3H), 7.37 (t, J = 7.6 Hz, 1H), 7.29–7.18 (m, 2H), 2.44 ppm (s, 3H). ^{13}C NMR (100

MHz, CDCl₃, 25 °C) δ = 157.7, 149.6, 139.4, 138.4, 136.7, 129.7, 128.7, 127.7, 124.1, 122.0, 120.7, 21.5 ppm.

2-(Naphthalen-2-yl)pyridine (7o) Yellow oil, ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 8.75 (d, J = 4.0 Hz, 1H), 8.48 (s, 1H), 8.14 (d, J = 8.5 Hz, 1H), 7.94 (d, J = 7.7 Hz, 2H), 7.87 (d, J = 8.0 Hz, 2H), 7.78 (dd, J = 10.9, 4.4 Hz, 1H), 7.50 (dd, J = 6.0, 3.3 Hz, 2H), 7.25 ppm (t, J = 5.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 157.4, 149.8, 136.8, 136.7, 133.6, 133.5, 128.7, 128.5, 127.7, 126.5, 126.4, 126.3, 124.6, 122.2, 120.8 ppm.

2-(3,5-Dimethylphenyl)pyridine (7p) Yellow oil, ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 8.69 (d, J = 4.4 Hz, 1H), 7.73 (td, J = 7.7, 1.5 Hz, 1H), 7.39 (d, J = 7.8 Hz, 1H), 7.26–7.20 (m, 2H), 7.17 (d, J = 7.7 Hz, 1H), 7.11 (d, J = 7.8 Hz, 1H), 2.36 (s, 3H), 2.32 ppm (s, 3H). ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 160.1, 149.2, 140.2, 136.0, 135.3, 132.5, 130.7, 130.3, 129.0, 124.1, 121.5, 20.9, 19.8 ppm.

2-(3,5-Dimethoxyphenyl)pyridine (7q) Yellow oil, ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 8.67 (d, J = 4.0 Hz, 1H), 7.73–7.67 (m, 3H), 7.51 (d, J = 8.0 Hz, 1H), 7.21–7.17 (m, 1H), 6.96 (d, J = 8.0 Hz, 1H), 4.00 (s, 3H), 3.94 ppm (s, 3H). ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 157.1, 150.0, 149.5, 149.3, 136.7, 132.3, 121.6, 120.0, 119.4, 111.1, 109.9, 56.0 ppm.

2-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)pyridine (7r) Yellow oil, ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 8.64 (d, J = 8.0 Hz, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.54–7.49 (m, 2H), 7.19–7.16 (m, 1H), 6.95 ppm (d, J = 8.0 Hz, 1H), 4.30 ppm (s, 4H). ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 156.8, 149.5, 144.6, 143.8, 136.7, 133.0, 121.6, 120.1, 119.9, 117.5, 115.9, 64.6, 64.4 ppm.

2-(Benzo[*d*][1,3]dioxol-5-yl)pyridine (7s) Yellow oil, ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 8.64 (d, J = 4.2 Hz, 1H), 7.71 (td, J = 7.8, 1.7 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.53–7.47 (m, 2H), 7.18 (dd, J = 6.4, 5.0 Hz, 1H), 6.90 (d, J = 8.1 Hz, 1H), 6.02 ppm (s, 2H). ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 156.9, 149.5, 148.5, 148.3, 136.8, 133.9, 121.7, 120.9, 120.0, 108.5, 107.4, 101.3 ppm.

2-(3,4,5-Trimethoxyphenyl)pyridine (7t) Yellow oil, ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 8.67 (d, J = 4.0 Hz, 1H), 7.75 (t, J = 8.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.24–7.22 (m, 3H), 3.97 (s, 6H), 3.91 ppm (s, 3H). ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 157.1, 153.5, 149.5, 139.1, 136.8, 135.0, 122.0, 120.4, 104.2, 61.0, 56.3 ppm.

2-(Benzofuran-2-yl)pyridine (7u) Yellow oil, ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 8.69 (d, J = 4.6 Hz, 1H), 7.91 (d, J = 7.9 Hz, 1H), 7.80 (dd, J = 7.7, 1.5 Hz, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.57 (d, J = 8.2 Hz, 1H), 7.44 (s, 1H), 7.37–7.31 (m, 1H), 7.26 ppm (dd, J = 8.7, 6.1 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 155.3, 155.0, 149.8, 149.2, 136.9, 128.8, 128.3, 125.2, 123.9, 123.3, 123.2, 122.9, 121.7, 119.9, 113.1, 112.5, 111.5, 104.9, 100.0 ppm.

2-(2,3-Dihydrobenzofuran-2-yl)pyridine (7v) Yellow oil, ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 8.63 (d, J = 4.1 Hz, 1H), 7.89 (s, 1H), 7.76–7.67 (m, 2H), 7.64 (d, J = 8.0 Hz, 1H), 7.19–7.12 (m, 1H), 6.86 (d, J = 8.3 Hz, 1H), 4.63 (t, J = 8.7 Hz, 2H), 3.27 ppm (t, J = 8.7 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 161.1, 157.5, 149.5, 136.7, 132.2, 127.8, 127.2, 123.8, 121.3, 119.9, 109.4, 71.7, 29.6 ppm.

2-(9H-Fluoren-2-yl)pyridine (7w) Yellow oil, ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 8.71 (d, J = 4.3 Hz, 1H), 8.22 (s, 1H), 8.00 (d, J = 7.9 Hz, 1H), 7.85 (dd, J = 16.0, 7.7 Hz, 2H), 7.77 (dt, J = 7.1, 4.7 Hz, 2H), 7.56 (d, J = 7.3 Hz, 1H), 7.39 (t, J = 7.3 Hz, 1H), 7.32 (t, J = 7.3 Hz, 1H), 7.22 (dd, J = 8.4, 3.3 Hz, 1H), 3.98 (s, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 157.7, 149.7, 143.9, 143.9, 142.6, 141.3, 138.0, 136.8, 127.0, 126.9, 125.8, 125.1, 123.6, 121.9, 120.6, 120.2, 120.1, 37.0 ppm.

3-Phenyl-*N*-(*p*-tolyl)naphthalen-1-amine (10a) White solid, ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.99 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.70 (s, 1H), 7.65 (d, J = 7.6 Hz, 2H), 7.57 (s, 1H), 7.53–7.39 (m, 4H), 7.34 (t, J = 7.3 Hz, 1H), 7.10 (d, J = 8.1 Hz, 2H), 7.01 (d, J = 8.2 Hz, 2H), 2.31 ppm (s, 3H). ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 154.8, 142.7, 141.2, 138.5, 137.1, 135.2, 129.4, 129.0, 127.9, 127.3, 126.9, 125.3, 125.0, 122.8, 122.4, 117.3, 115.1, 108.7, 21.3 ppm.

***N*-(4-Methoxyphenyl)-3-phenylnaphthalen-1-amine (10b)** Light yellow oil, ^1H NMR (400 MHz, DMSO- d_6 , 25 °C): δ = 8.28 (d, J = 8.1 Hz, 1H), 8.12 (s, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 6.9 Hz, 3H), 7.54–7.42 (m, 4H), 7.34 (dd, J = 15.1, 7.7 Hz, 2H), 7.21 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 3.74 ppm (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6 , 25 °C) δ = 154.8, 142.7, 141.2, 138.5, 137.1, 135.2, 129.4, 129.0, 127.9, 127.3, 126.9, 125.3, 125.0, 122.8, 122.4, 117.3, 115.1, 108.7, 55.7 ppm.

***N*-(4-(*tert*-Butyl)phenyl)-3-phenylnaphthalen-1-amine (10c)** White solid, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 7.99 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 7.9 Hz, 1H), 7.70 (s, 1H), 7.68–7.61 (m, 3H), 7.52–7.40 (m, 4H), 7.35 (d, J = 7.4 Hz, 1H), 7.30 (d, J = 8.5 Hz, 2H), 7.03 (d, J = 8.5 Hz, 2H), 1.32 ppm (s, 9H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 143.9, 141.6, 141.3, 139.8, 139.0, 135.0, 128.9, 128.8, 127.5, 127.4, 126.6, 126.3, 125.6, 121.4, 120.1, 117.8, 113.8, 34.2, 31.6, 29.8 ppm.

***N*-(4-Bromophenyl)-3-phenylnaphthalen-1-amine (10d)** Light yellow solid, ^1H NMR (400 MHz, DMSO- d_6 , 25 °C): δ = 8.49 (s, 1H), 8.13 (d, J = 8.2 Hz, 1H), 8.00 (d, J = 7.9 Hz, 1H), 7.88 (s, 1H), 7.74 (d, J = 7.4 Hz, 2H), 7.62 (s, 1H), 7.58–7.46 (m, 4H), 7.42–7.34 (m, 3H), 7.06 ppm (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, DMSO- d_6 , 25 °C) δ = 145.0, 140.6, 139.8, 138.3, 135.3, 132.3, 129.5, 129.2, 128.1, 127.4, 127.2, 126.9, 125.9, 123.1, 120.3, 119.1, 114.4, 110.7 ppm.

***N*-(3,4-Dimethoxyphenyl)-3-phenylnaphthalen-1-amine (10e)** Yellow oil, ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS) δ = 8.00 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.68–7.61 (m, 3H), 7.54–7.39 (m, 5H), 7.34 (t, J = 7.3 Hz, 1H), 6.83 (d, J = 8.5 Hz, 1H), 6.79 (d, J = 2.2 Hz, 1H), 6.68 (dd, J = 8.5, 2.3 Hz, 1H), 3.88 (s, 3H), 3.82 ppm (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 149.8, 141.3, 141.1, 139.0, 137.3, 134.9, 129.0, 128.8, 127.4, 127.3, 126.5, 125.5, 125.3, 121.0, 119.1, 112.4, 112.1, 111.7, 105.3, 56.3, 55.9 ppm.

***N*-(Naphthalen-1-yl)-3-phenylnaphthalen-1-amine (10f)** Light yellow oil, ^1H NMR (400 MHz, DMSO- d_6 , 25 °C): δ = 8.47 (s, 1H), 8.22 (d, J = 8.3 Hz, 2H), 8.01 (d, J = 8.1 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.82 (s, 1H), 7.60–7.45 (m, 8H), 7.41 (dd, J = 15.0, 7.4 Hz, 3H), 7.36–7.32 (m, 1H), 7.11 (s, 1H), 6.97 ppm (d, J = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6 , 25 °C) δ = 142.5, 141.4, 140.8, 138.4, 135.2, 134.8, 129.4, 129.2, 128.7, 127.9, 127.4, 127.1, 127.0, 126.8, 126.6, 126.2, 125.7, 125.7, 123.5, 123.4, 122.3, 119.3, 116.4, 114.1 ppm.

***N*-((3-Phenylnaphthalen-1-yl)methyl)aniline (10g)** Yellow oil, ^1H NMR (400 MHz, DMSO- d_6 , 25 °C): δ = 8.28 (d, J = 7.9 Hz, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.59 (d, J = 7.5 Hz, 2H), 7.45 (dq, J = 15.1, 7.5 Hz, 6H), 7.34 (dd, J = 15.7, 8.3 Hz, 4H), 7.22 (d, J = 7.2 Hz, 1H), 7.11 (t, J = 5.6 Hz, 1H), 6.65 (s, 1H), 4.62 ppm (d, J = 5.5 Hz, 2H). ^{13}C NMR (100 MHz, DMSO- d_6 , 25 °C) δ = 144.6, 141.6, 140.6, 138.7, 134.9, 129.3, 129.0, 128.8, 127.7, 127.5, 127.2, 127.1, 126.6, 124.7, 123.0, 122.0, 113.9, 103.3, 46.9 ppm.

***N*-Butyl-3-phenylnaphthalen-1-amine (10h)** Light yellow solid, ^1H NMR (400 MHz, DMSO- d_6 , 25 °C): δ = 8.20 (d, J = 8.3 Hz, 1H), 7.83 (d, J = 7.9 Hz, 1H), 7.76 (d, J = 7.5 Hz, 2H), 7.51–7.43 (m, 3H), 7.42–7.33 (m, 3H), 6.73 (s, 1H), 6.19 (t, J = 4.8 Hz, 1H), 3.30 (dd, J = 12.4, 6.6 Hz, 2H), 1.78–1.66 (m, 2H), 1.47 (dd, J = 14.8, 7.4 Hz, 2H), 0.96 ppm (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, DMSO- d_6 , 25 °C) δ = 145.2, 141.9, 139.0, 134.9, 129.3, 128.9, 127.7, 127.4, 126.5, 124.5, 122.9, 122.1, 113.6, 102.2, 43.4, 30.8, 20.6, 14.4 ppm.

***N*-(Furan-3-ylmethyl)-3-phenylnaphthalen-1-amine (10i)** Yellow oil, ^1H NMR (400 MHz, DMSO- d_6 , 25 °C): δ = 8.22 (d, J = 8.2 Hz, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.73 (d, J = 7.5 Hz, 2H), 7.59 (s, 1H), 7.52–7.34 (m, 7H), 6.90 (d, J = 7.0 Hz, 2H), 6.40 (d, J = 2.1 Hz, 2H), 4.60 ppm (d, J = 5.5 Hz, 2H). ^{13}C NMR (100 MHz, DMSO- d_6 , 25 °C) δ = 153.7, 144.4, 142.4, 141.7, 138.7, 134.8, 129.3, 129.0, 127.8, 127.3, 126.6, 124.8, 123.0, 122.0, 114.3, 110.9, 107.5, 103.2 ppm.

4-(3-Phenylnaphthalen-1-yl)morpholine (10j) Yellow oil, ^1H NMR (400 MHz, DMSO- d_6 , 25 $^\circ\text{C}$): δ = 8.18–8.12 (m, 1H), 8.00–7.95 (m, 1H), 7.91 (s, 1H), 7.81 (d, J = 7.5 Hz, 2H), 7.52 (dd, J = 12.4, 5.4 Hz, 4H), 7.44–7.36 (m, 2H), 3.92–3.84 (m, 4H), 3.11 ppm (s, 4H). ^{13}C NMR (100 MHz, DMSO- d_6 , 25 $^\circ\text{C}$) δ = 150.3, 140.8, 138.2, 135.1, 129.4, 129.3, 128.0, 127.7, 127.5, 126.8, 126.1, 123.7, 121.3, 114.4, 67.1, 53.6 ppm.

8-Chloro-3-phenyl-*N*-(*p*-tolyl)naphthalen-1-amine (10k) Yellow oil, ^1H NMR (400 MHz, DMSO- d_6 , 25 $^\circ\text{C}$): δ = 8.34 (s, 1H), 8.29 (s, 1H), 7.97 (d, J = 8.8 Hz, 1H), 7.73 (s, 1H), 7.65 (d, J = 7.6 Hz, 2H), 7.56–7.50 (m, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 7.16 – 7.08 (m, 4H), 2.25 ppm (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6 , 25 $^\circ\text{C}$) δ = 141.6, 141.0, 140.7, 139.0, 133.7, 131.2, 130.3, 130.2, 130.2, 129.4, 128.1, 127.4, 127.3, 126.2, 122.0, 119.4, 118.0, 111.4, 20.8 ppm.

6-Fluoro-3-phenyl-*N*-(*p*-tolyl)naphthalen-1-amine (10l) Light yellow solid, ^1H NMR (400 MHz, DMSO- d_6 , 25 $^\circ\text{C}$): δ = 8.35–8.27 (m, 2H), 7.72–7.67 (m, 2H), 7.65 (d, J = 7.6 Hz, 2H), 7.46 (dd, J = 13.0, 5.0 Hz, 3H), 7.40–7.34 (m, 2H), 7.12 (t, J = 5.1 Hz, 4H), 2.25 ppm (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6 , 25 $^\circ\text{C}$) δ = 162.3, 159.8, 141.9, 141.7, 140.8, 139.8, 136.5, 136.4, 130.2, 130.1, 129.4, 128.1, 127.3, 126.2, 126.1, 122.8, 119.6, 117.6, 115.2, 115.0, 111.9, 111.7, 110.1, 20.8 ppm.

3-(4-Fluorophenyl)-*N*-(*p*-tolyl)naphthalen-1-amine (10m) Yellow oil, ^1H NMR (400 MHz, DMSO- d_6 , 25 $^\circ\text{C}$): δ = 8.35–8.27 (m, 2H), 7.72–7.67 (m, 2H), 7.65 (d, J = 7.6 Hz, 2H), 7.46 (dd, J = 13.0, 5.0 Hz, 3H), 7.40–7.34 (m, 2H), 7.12 (t, J = 5.1 Hz, 4H), 2.25 ppm (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6 , 25 $^\circ\text{C}$) δ = 162.3, 159.8, 141.9, 141.7, 140.8, 139.8, 136.5, 136.4, 130.2, 130.1, 129.4, 128.1, 127.3, 126.2, 126.1, 122.8, 119.6, 117.6, 115.2, 115.0, 111.9, 111.7, 110.1, 20.8 ppm.

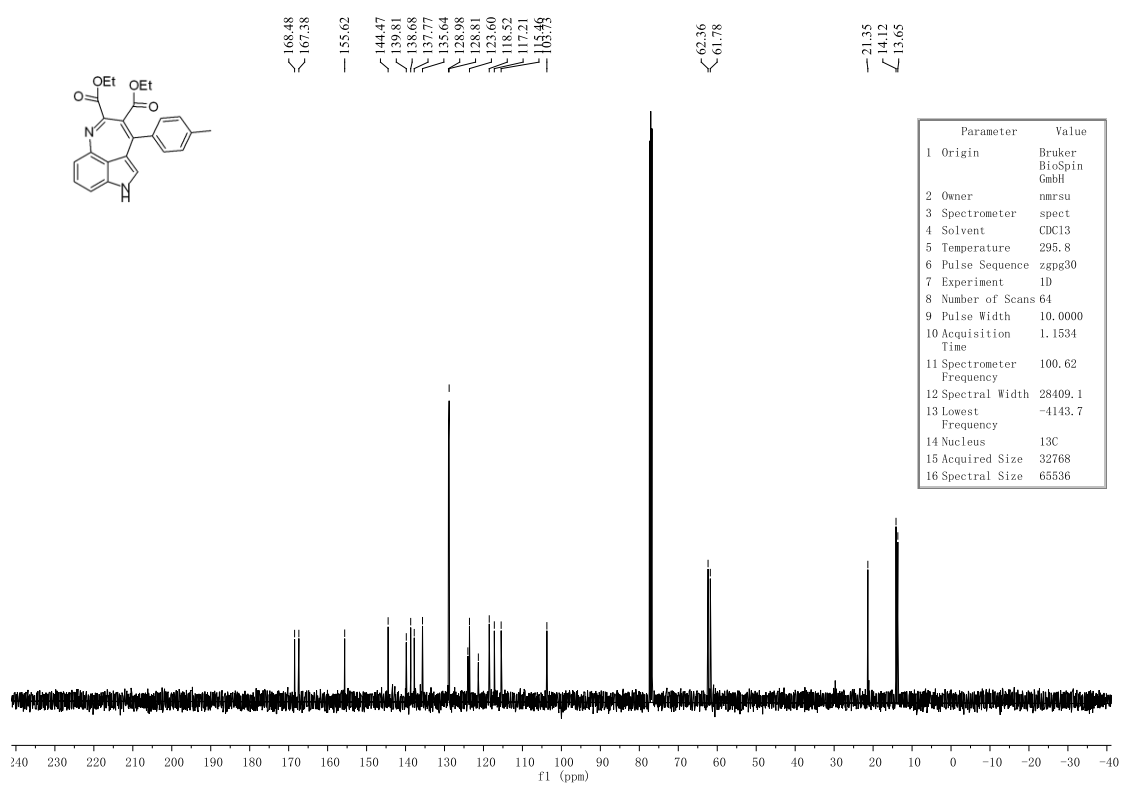
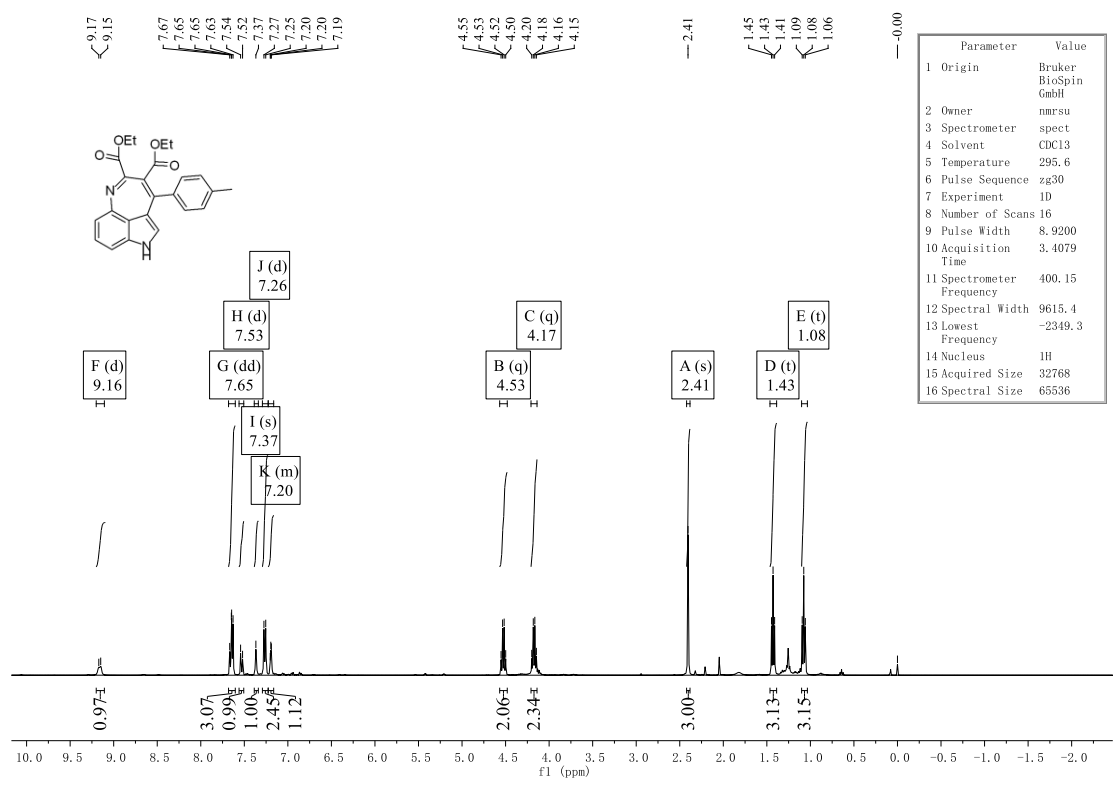
3-Heptyl-*N*-(*p*-tolyl)naphthalen-1-amine (10n) Yellow oil, ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS): δ = 7.94 (d, J = 8.3 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.45 (t, J = 7.4 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.30 (s, 1H), 7.17 (s, 1H), 7.08 (d, J = 8.1 Hz, 2H), 6.93 (d, J = 8.2 Hz, 2H), 2.67 (t, J = 7.7 Hz, 2H), 2.31 (s, 3H), 1.64 (dd, J = 14.7, 7.2 Hz, 2H), 1.39 – 1.22 (m, 8H), 0.88 ppm (t, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 142.1, 141.0, 139.2, 134.9, 130.2, 129.9, 128.1, 126.1, 125.7, 124.7, 121.4, 120.8, 118.2, 116.0, 36.3, 31.8, 31.3, 29.7, 29.1, 22.7, 20.7, 14.1 ppm.

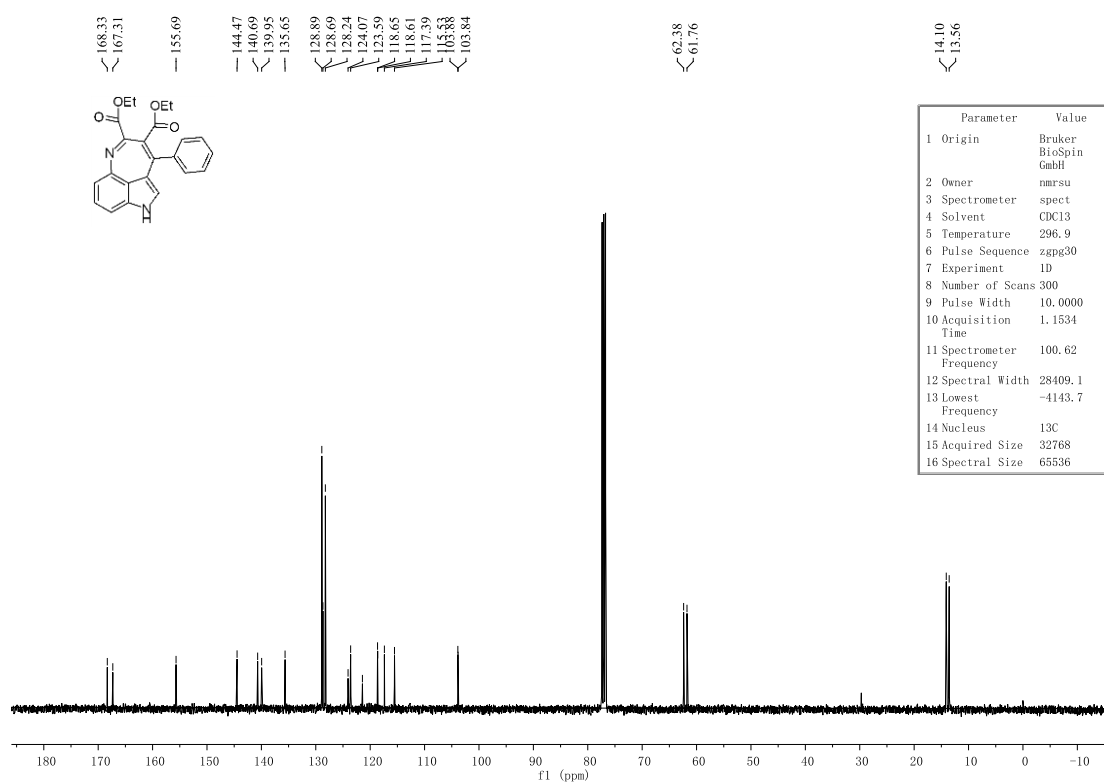
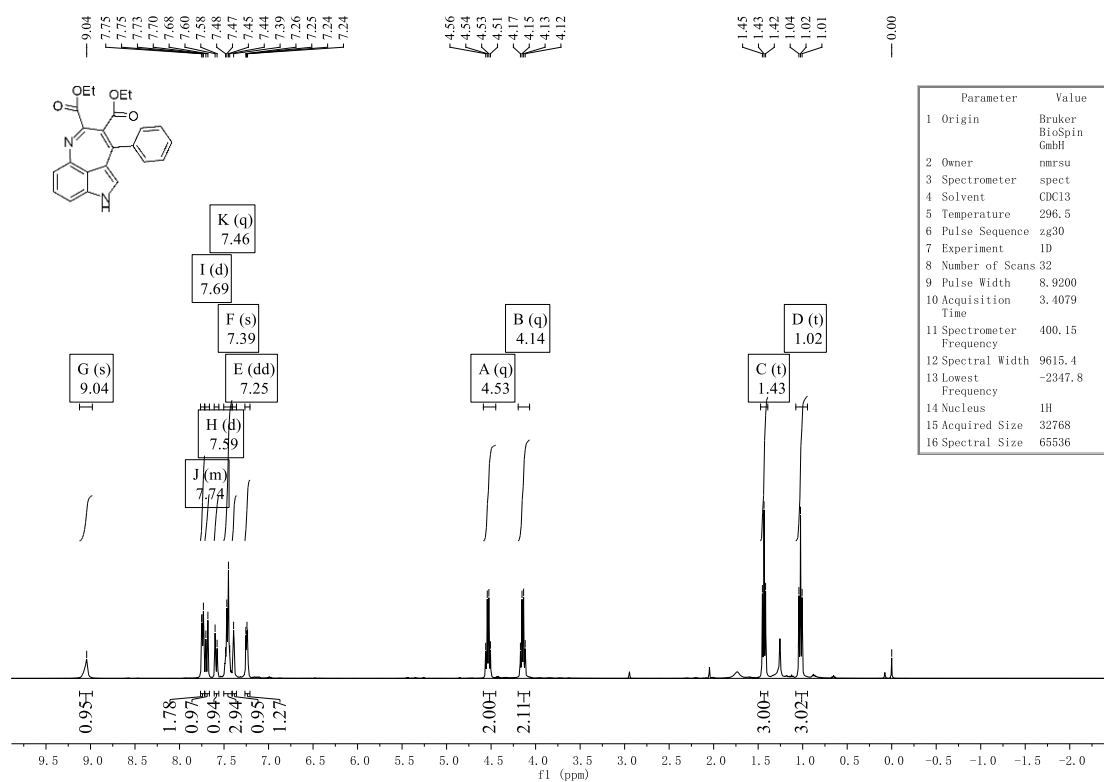
3-(Cyclohex-1-en-1-yl)-*N*-(*p*-tolyl)naphthalen-1-amine (10o) Yellow oil, ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS): δ = 7.93 (d, J = 8.3 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.49–7.35 (m, 4H), 7.08 (d, J = 8.1 Hz, 2H), 6.94 (d, J = 8.3 Hz, 2H), 6.19 (s, 1H), 2.49 (d, J = 1.6 Hz, 2H), 2.31 (s, 3H), 2.25 – 2.17 (m, 2H), 1.80 (dd, J = 7.6, 3.9 Hz, 2H), 1.72 – 1.63 ppm (m, 2H). ^{13}C NMR (100 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 141.1, 139.2, 138.0, 135.3, 133.8, 129.0, 128.9, 127.7, 125.4, 125.2, 124.4, 124.0, 120.4, 116.9, 116.9, 111.7, 28.7, 26.3, 25.0, 22.1, 21.2, 19.6 ppm.

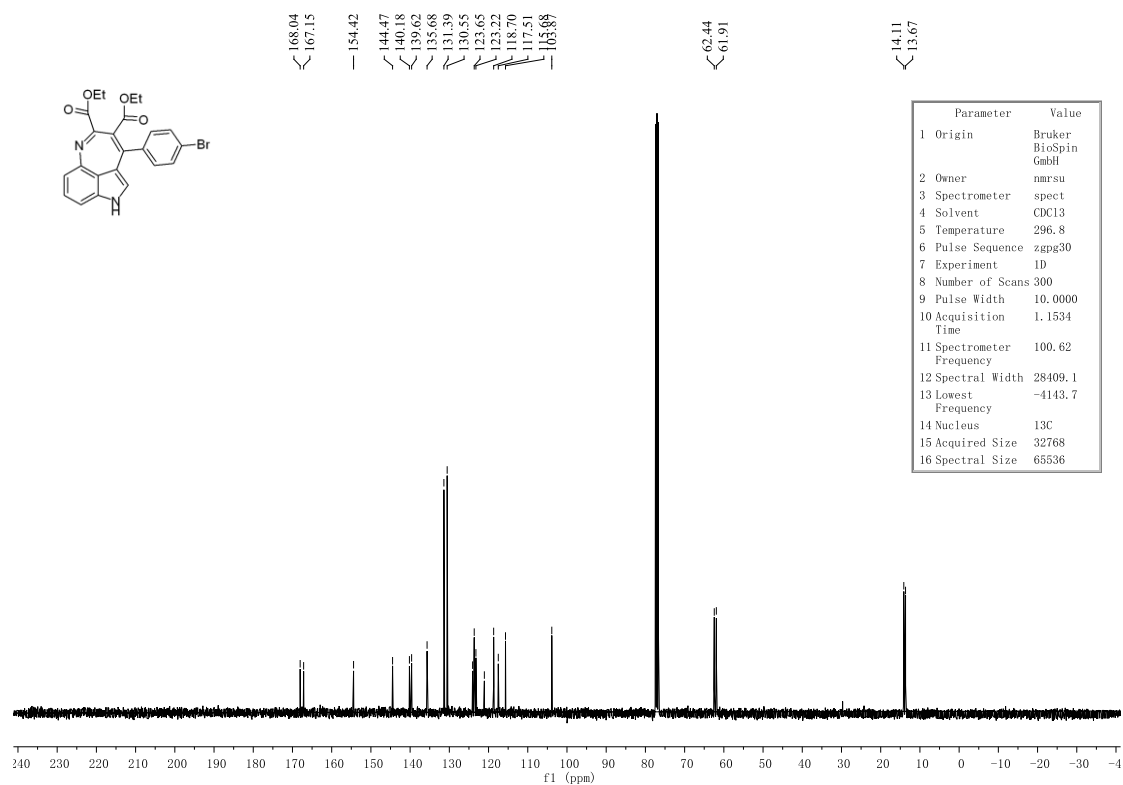
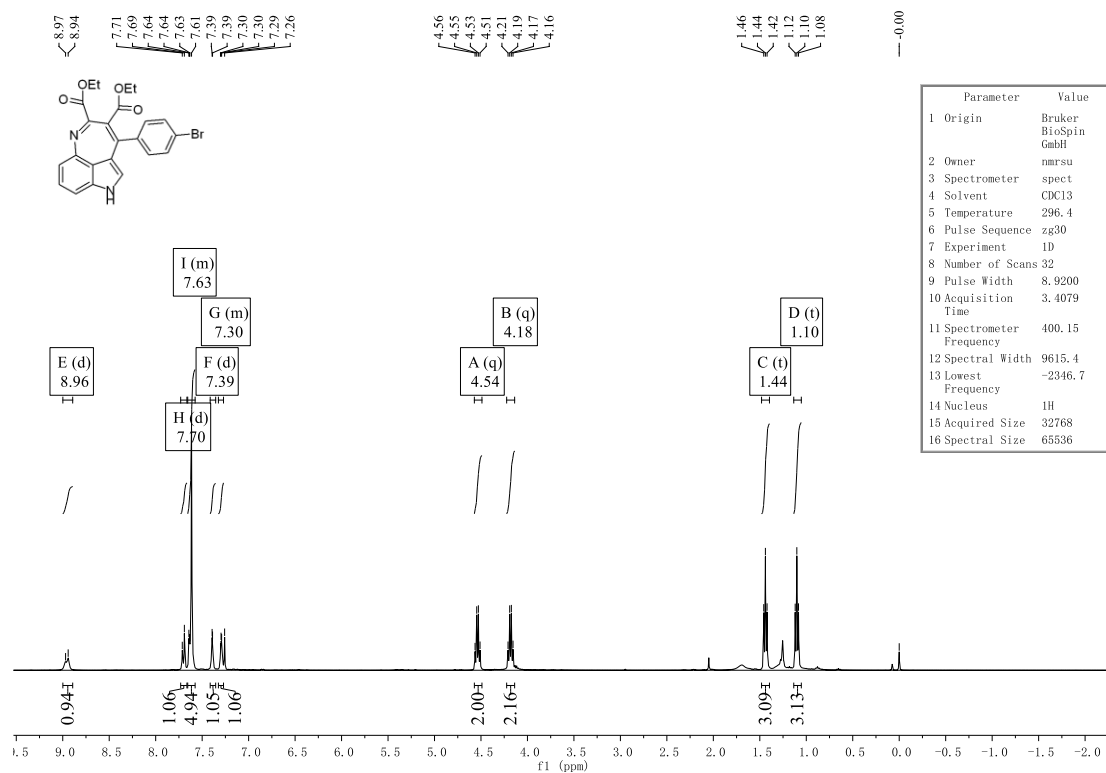
3-Phenylisoquinoline (13a) White solid, mp: 94–96 $^\circ\text{C}$ ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS): δ = 9.34 (s, 1H), 8.12 (d, J = 7.3 Hz, 2H), 8.06 (s, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.86 (d, J = 8.2 Hz, 1H), 7.68 (dd, J = 11.1, 4.0 Hz, 1H), 7.57 (dd, J = 11.1, 4.0 Hz, 1H), 7.51 (t, J = 7.5 Hz, 2H), 7.42 ppm (t, J = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 152.5, 151.4, 139.7, 136.7, 130.6, 128.9, 128.6, 127.9, 127.6, 127.14, 127.11, 127.0, 116.6 ppm.

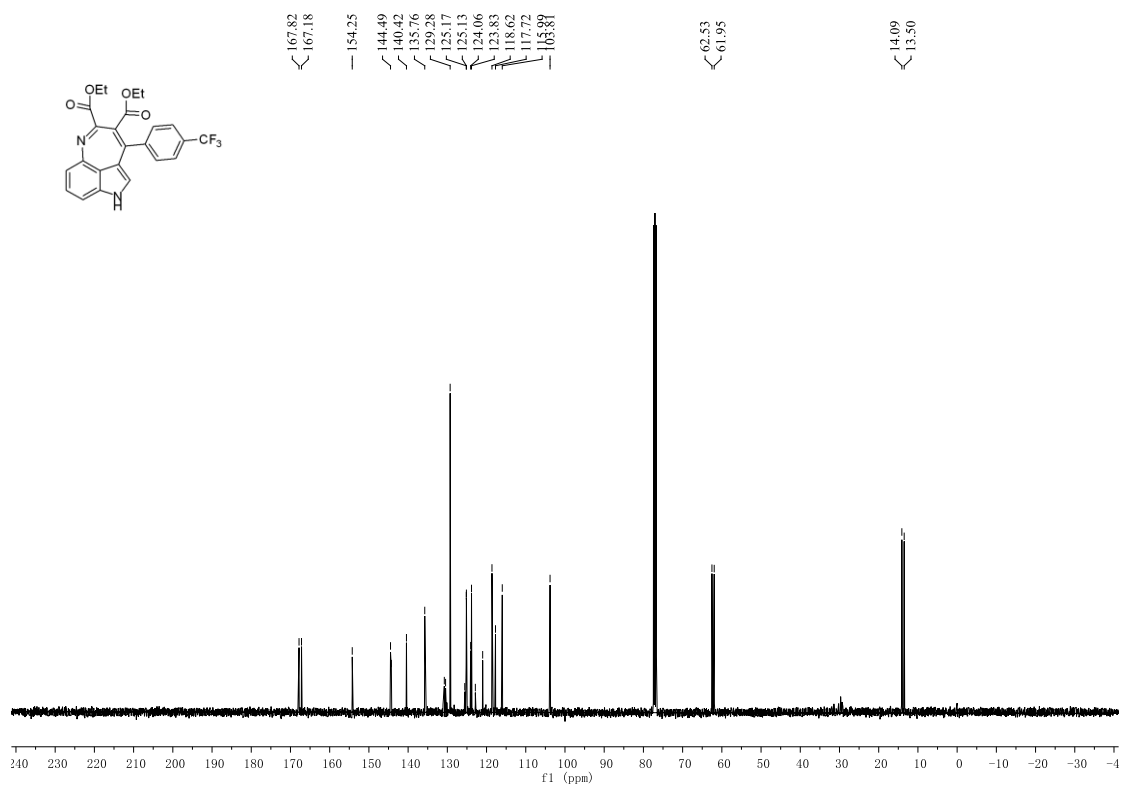
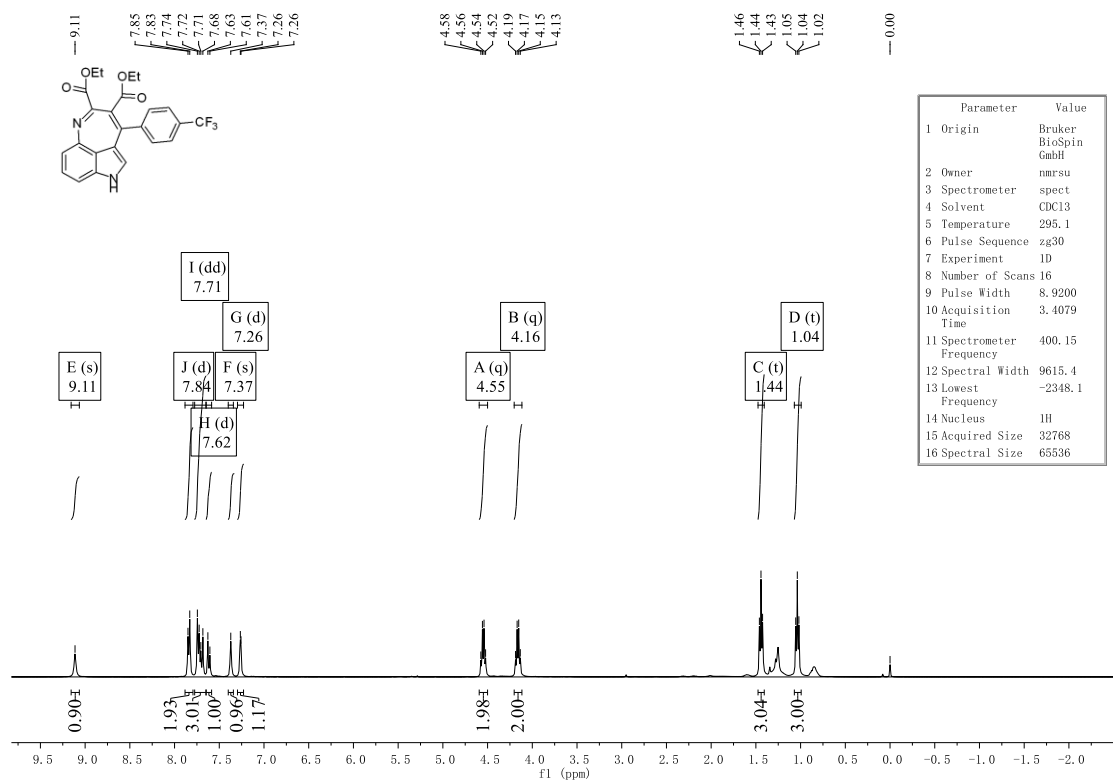
References

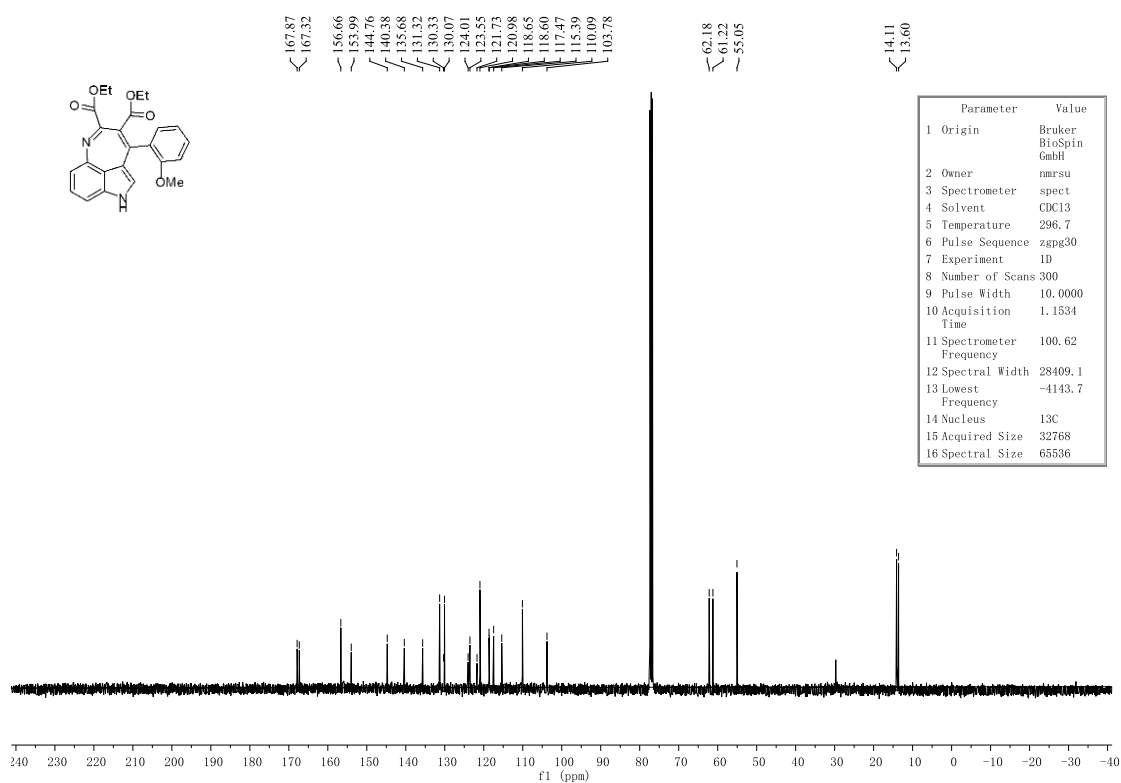
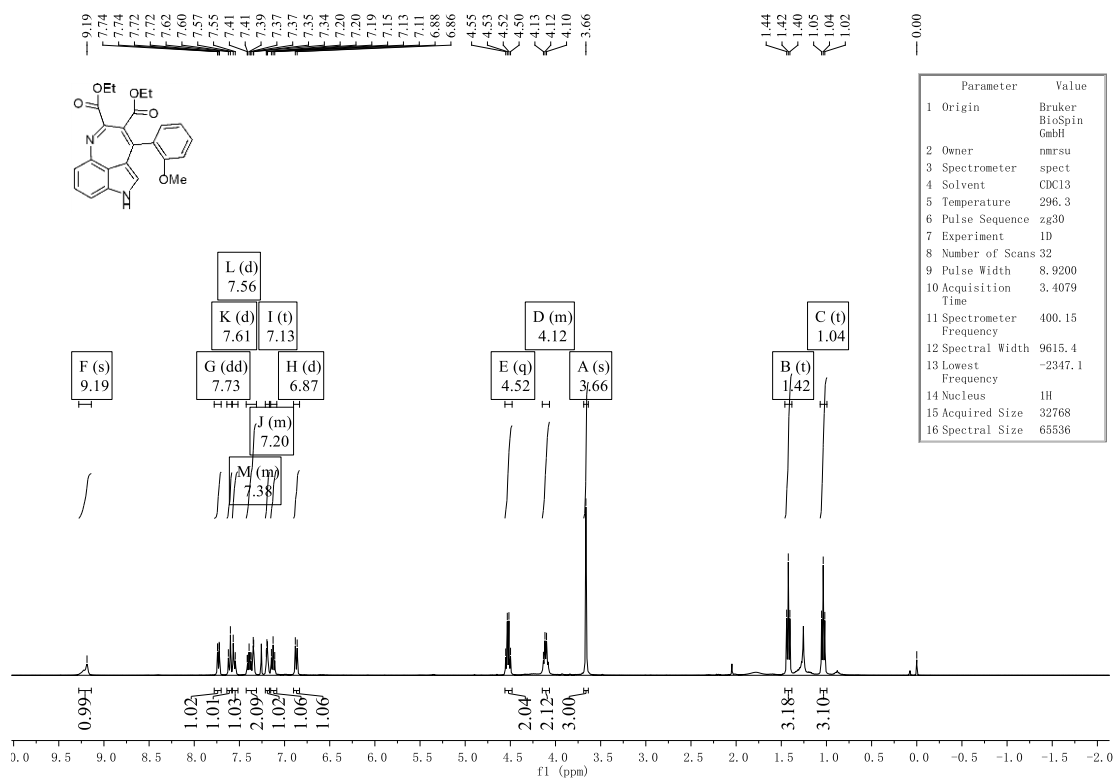
- [1] Xi, L.; Zhang, R.; Liang, S.; Chen, S.; Yu, X. *Org. Lett.* **2014**, *16*, 5269–5271.
- [2] Guo, B.; Hua, R. *Tetrahedron* **2016**, *72*, 4608–4615.
- [3] Ju, J.; Hua, R. *Curr. Org. Synth.* **2013**, *10*, 328–332.

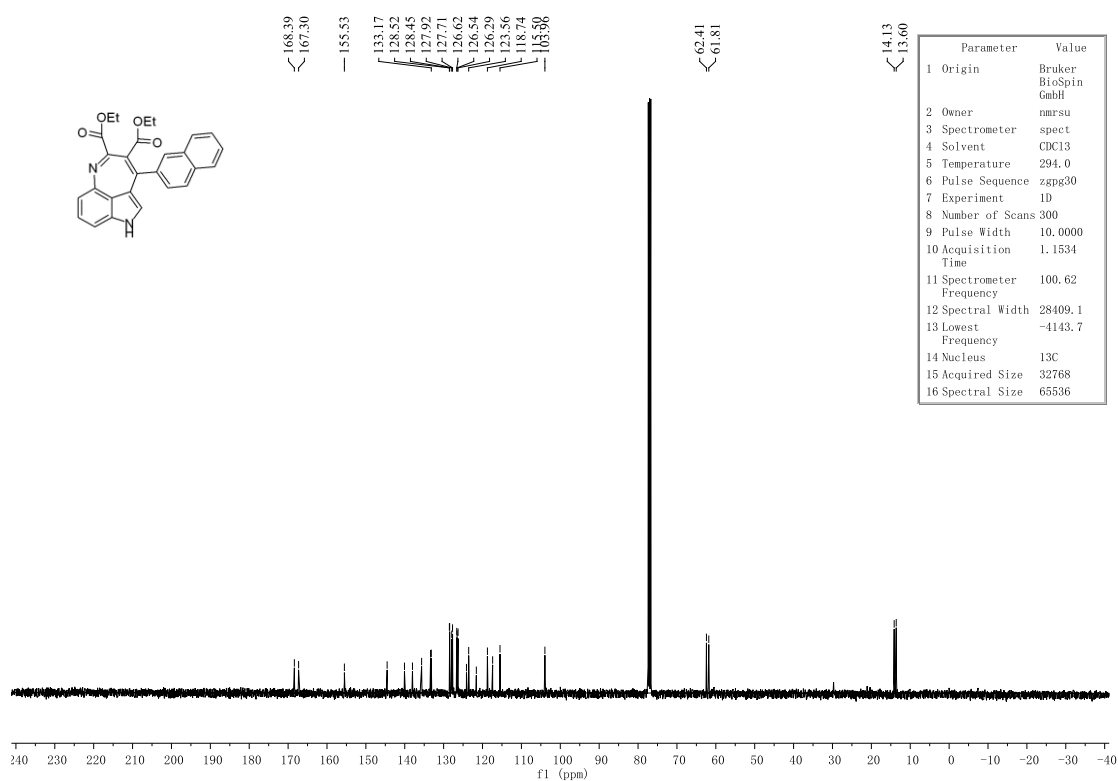
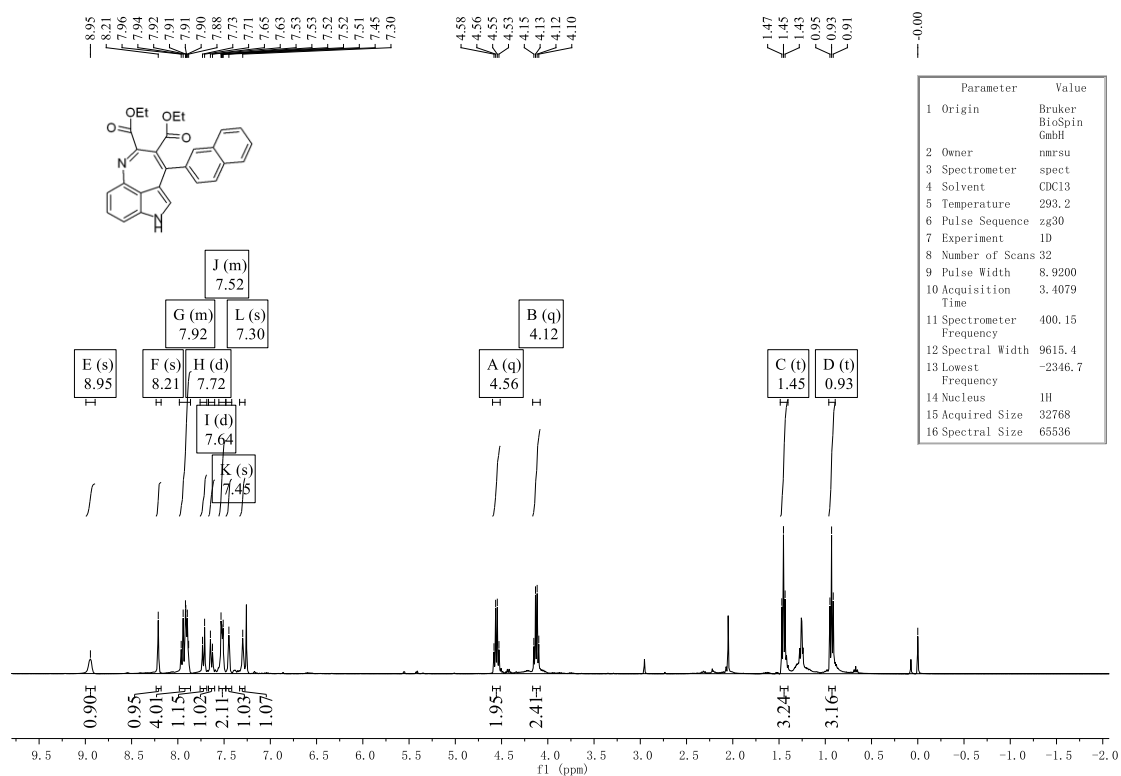


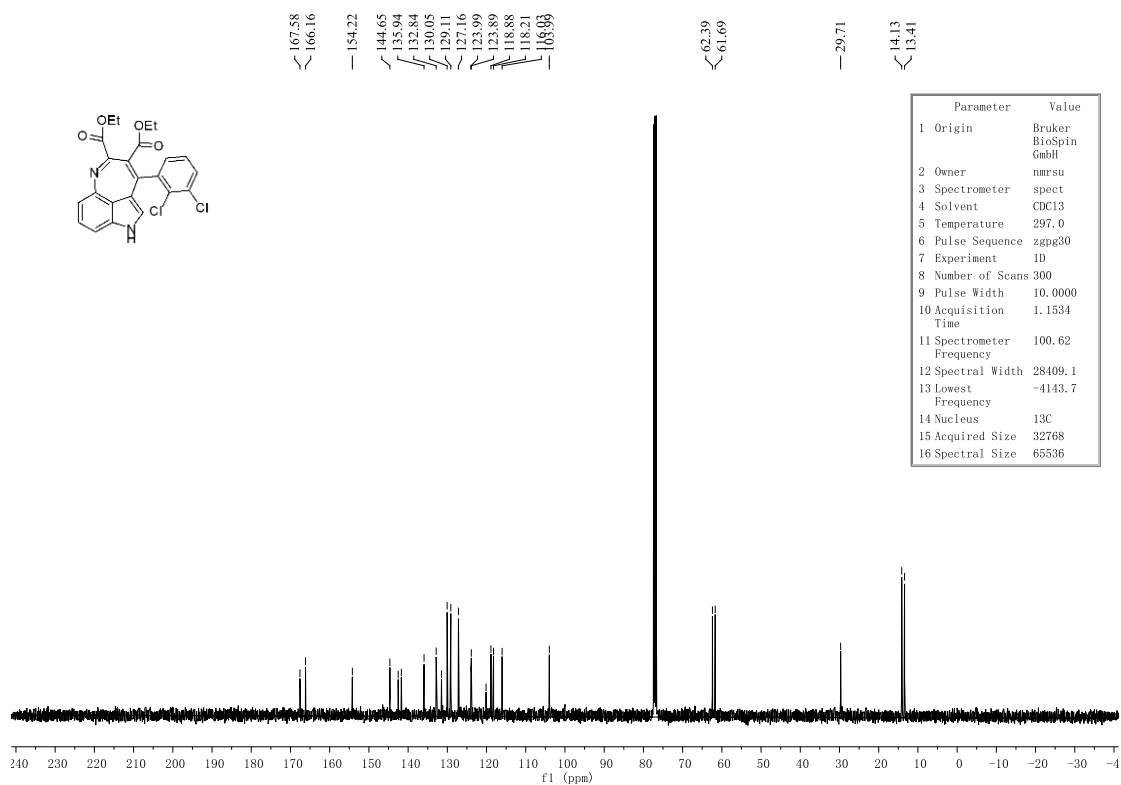
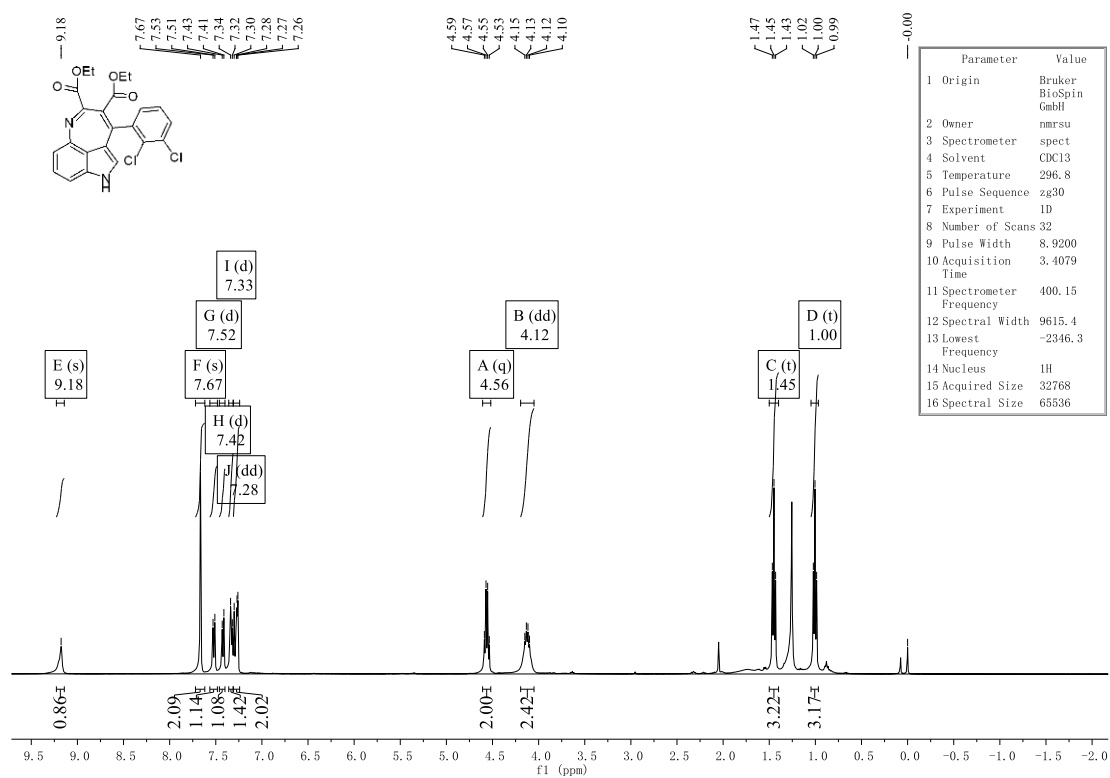


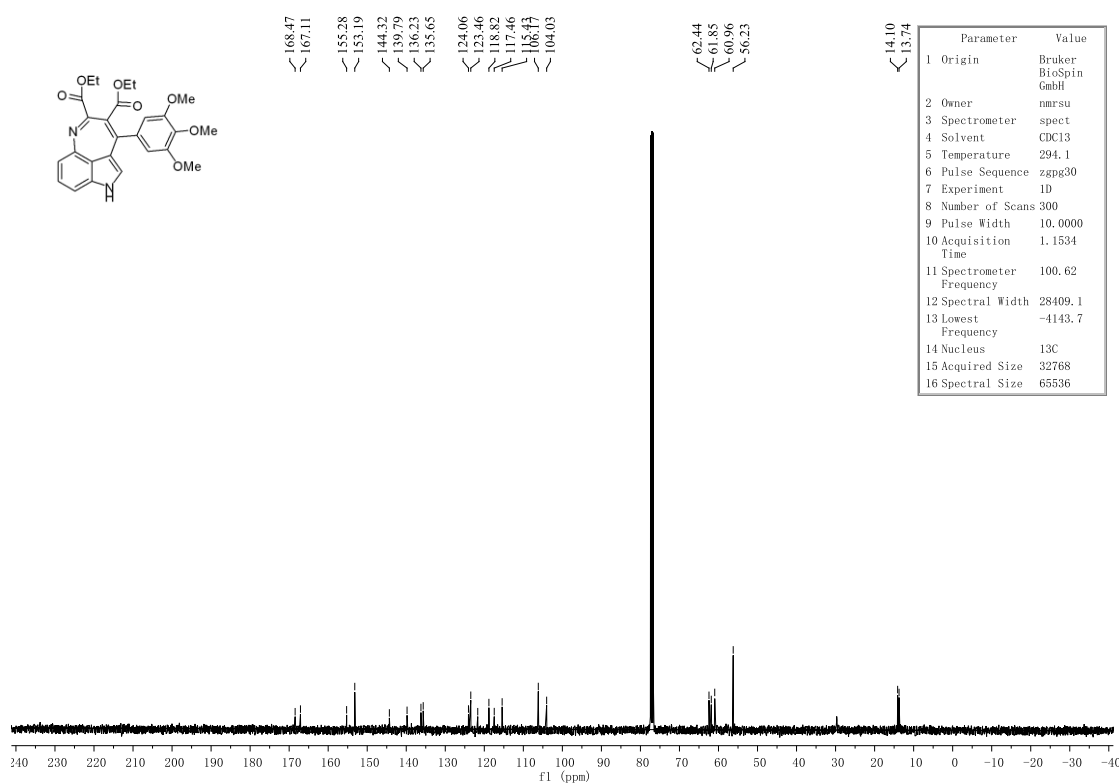
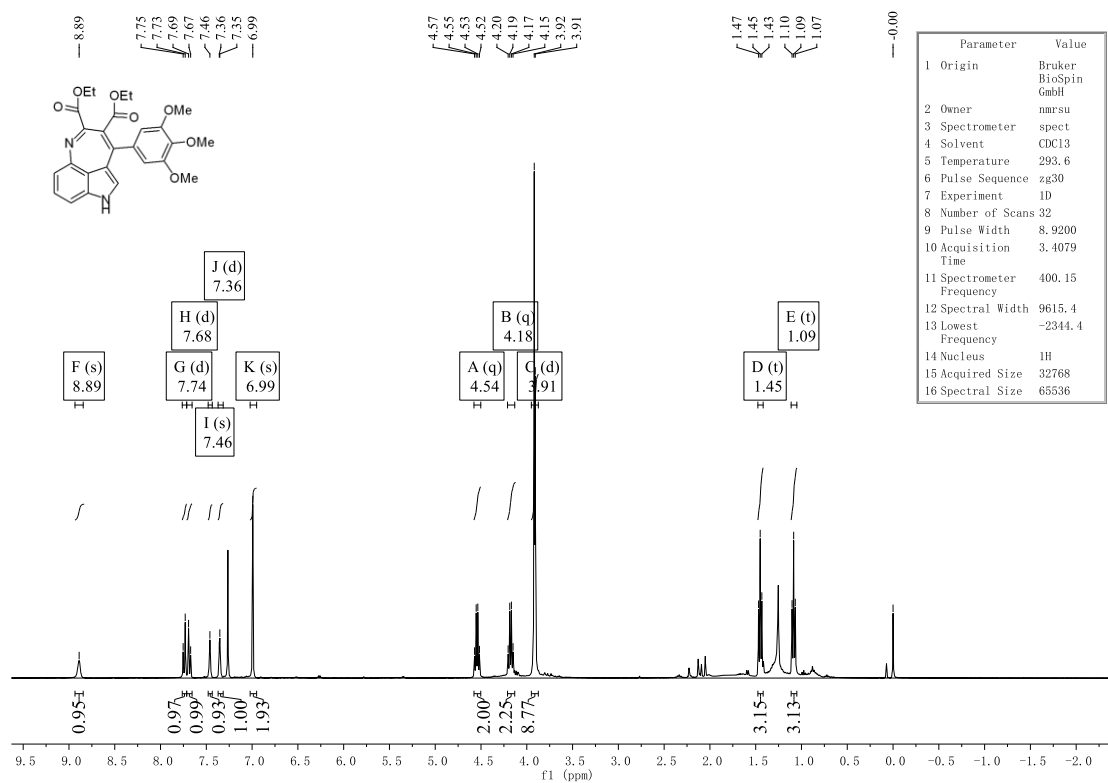


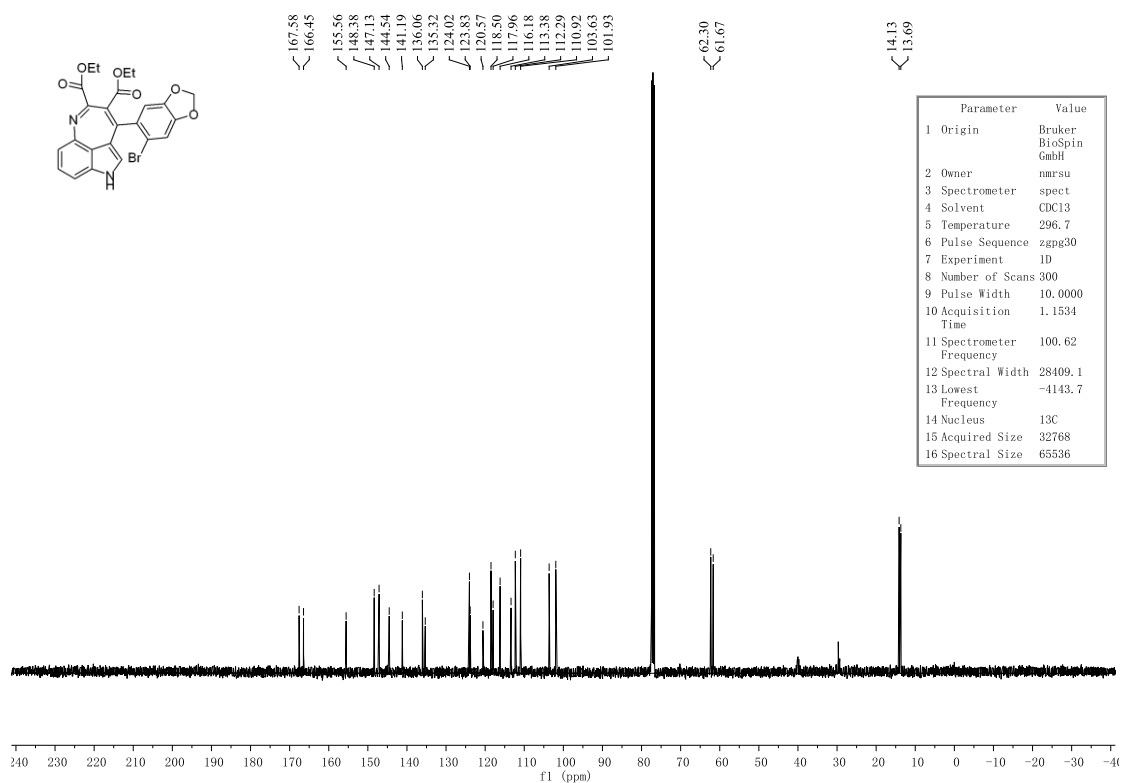
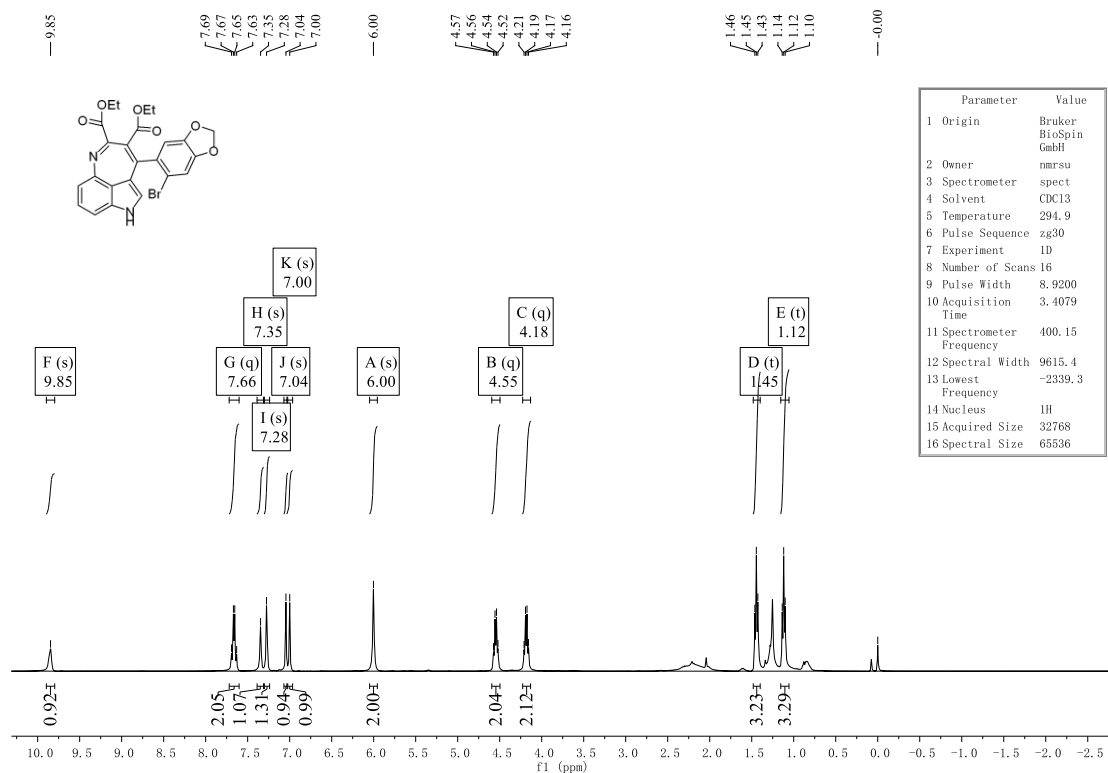


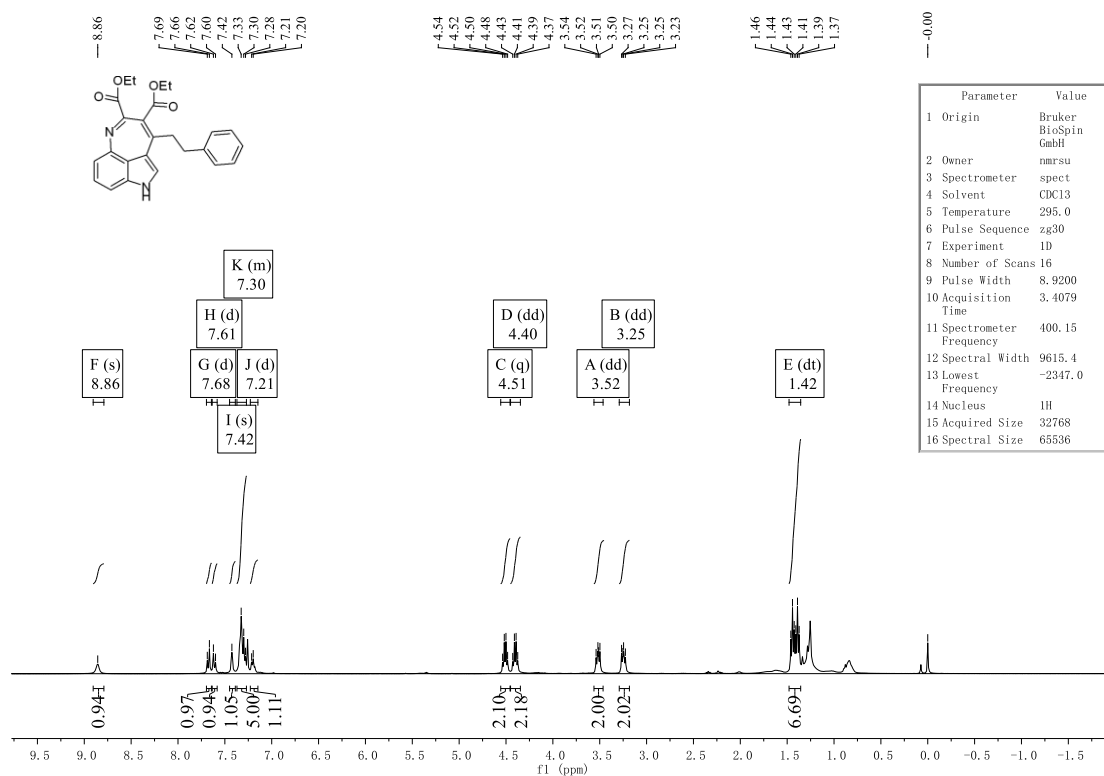




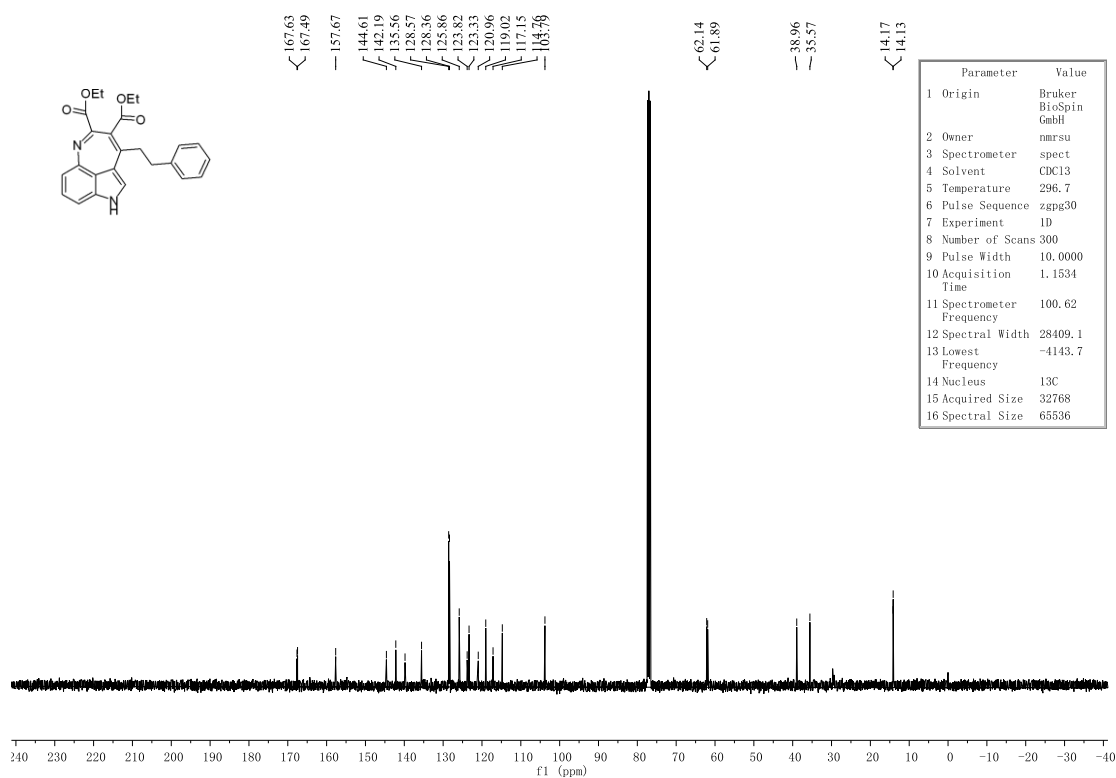




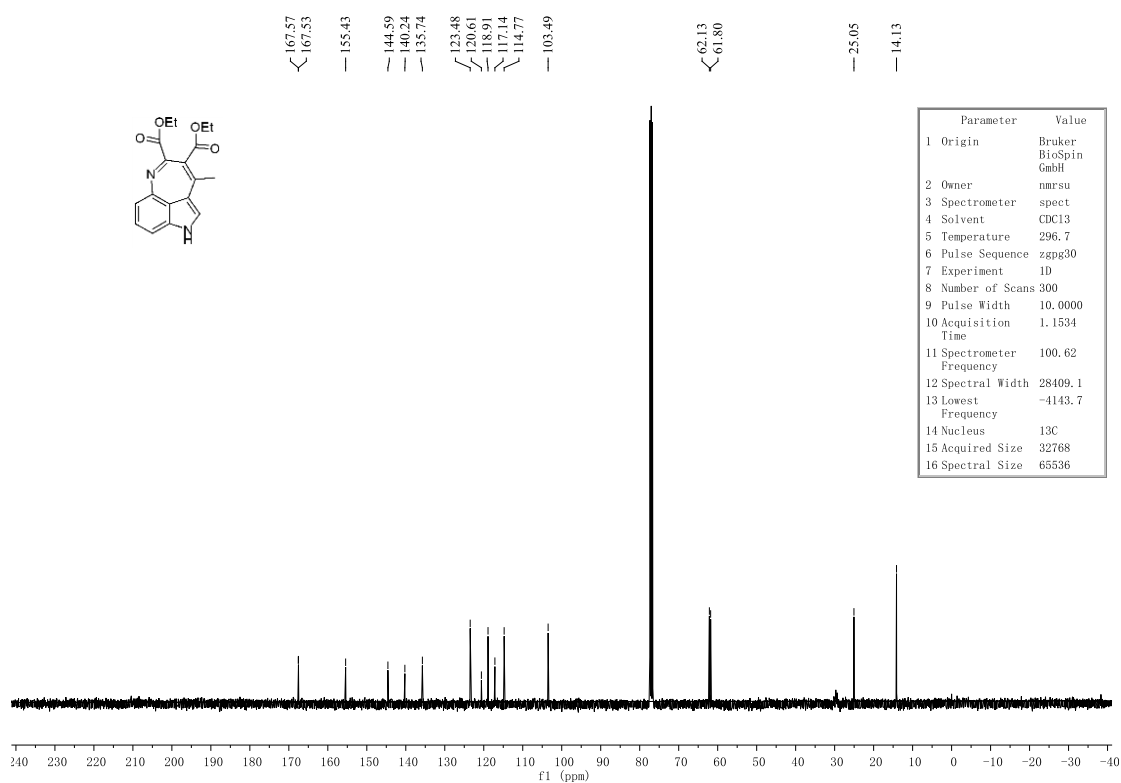
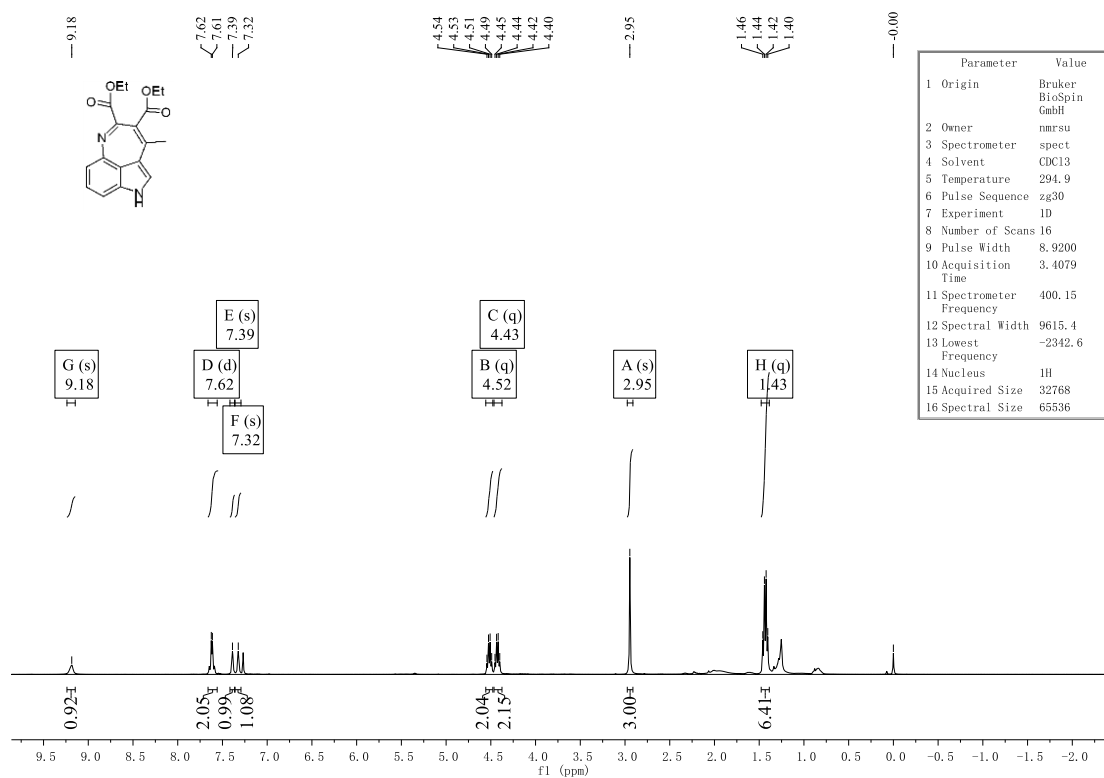


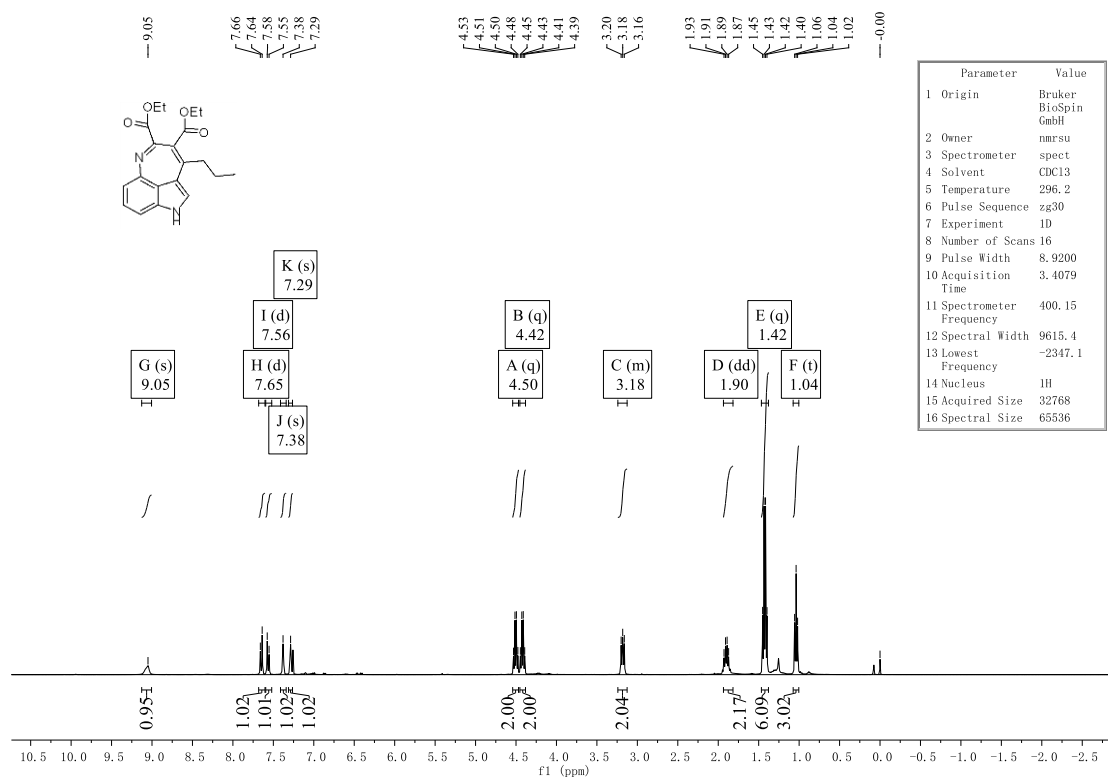


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Owner	nmsu
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	295.0
6 Pulse Sequence	zg30
7 Experiment	1D
8 Number of Scans	16
9 Pulse Width	8.9200
10 Acquisition Time	3.4079
11 Spectrometer Frequency	400.15
12 Spectral Width	9615.4
13 Lowest Frequency	-2347.0
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536

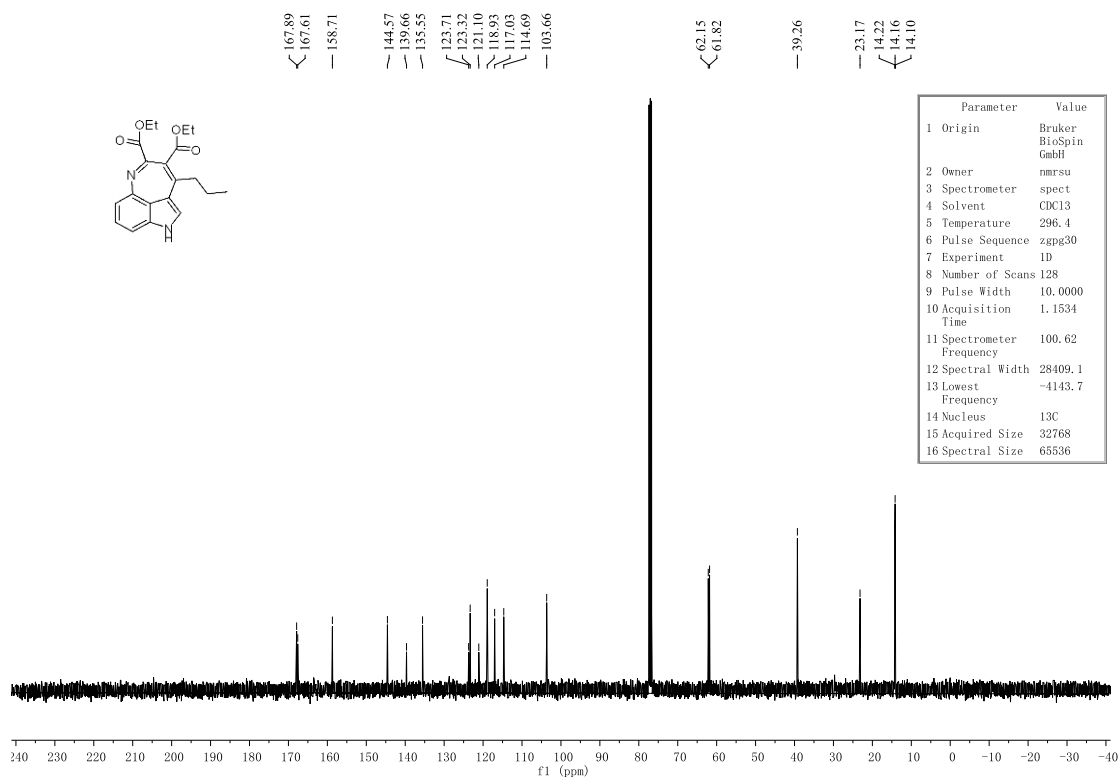


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Owner	nmsu
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	296.7
6 Pulse Sequence	zgpg30
7 Experiment	1D
8 Number of Scans	300
9 Pulse Width	10.0000
10 Acquisition Time	1.1534
11 Spectrometer Frequency	100.62
12 Spectral Width	28409.1
13 Lowest Frequency	-4143.7
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536

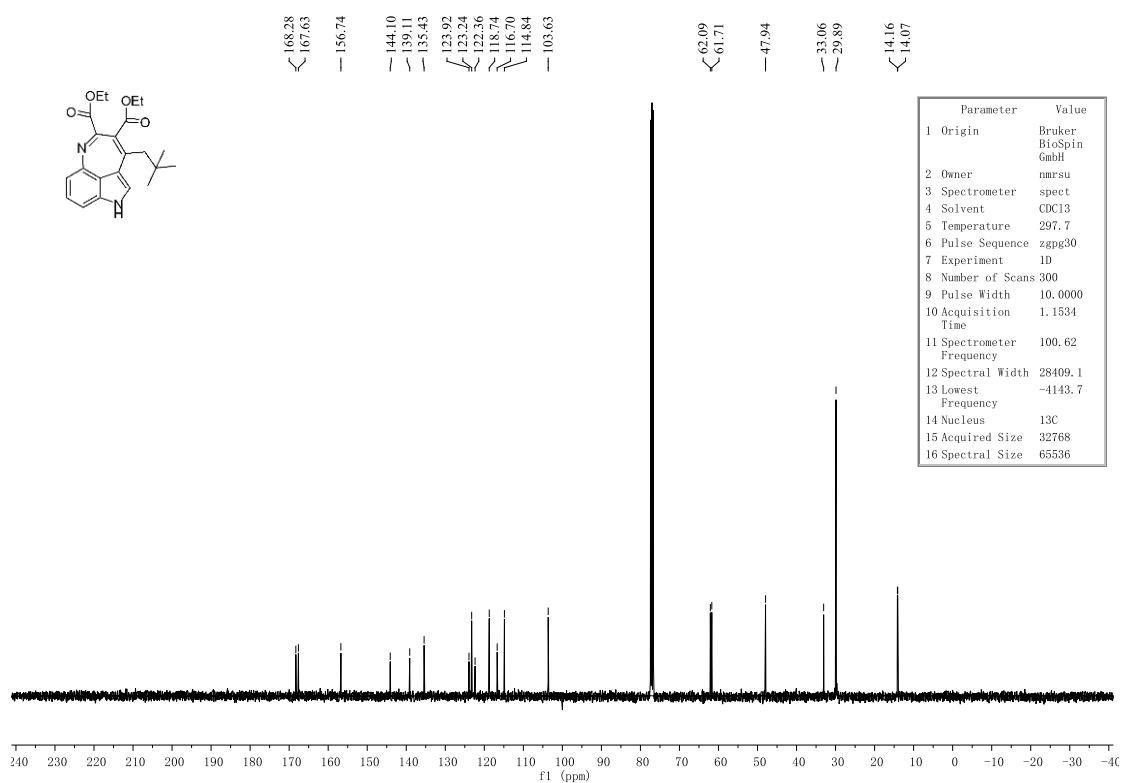
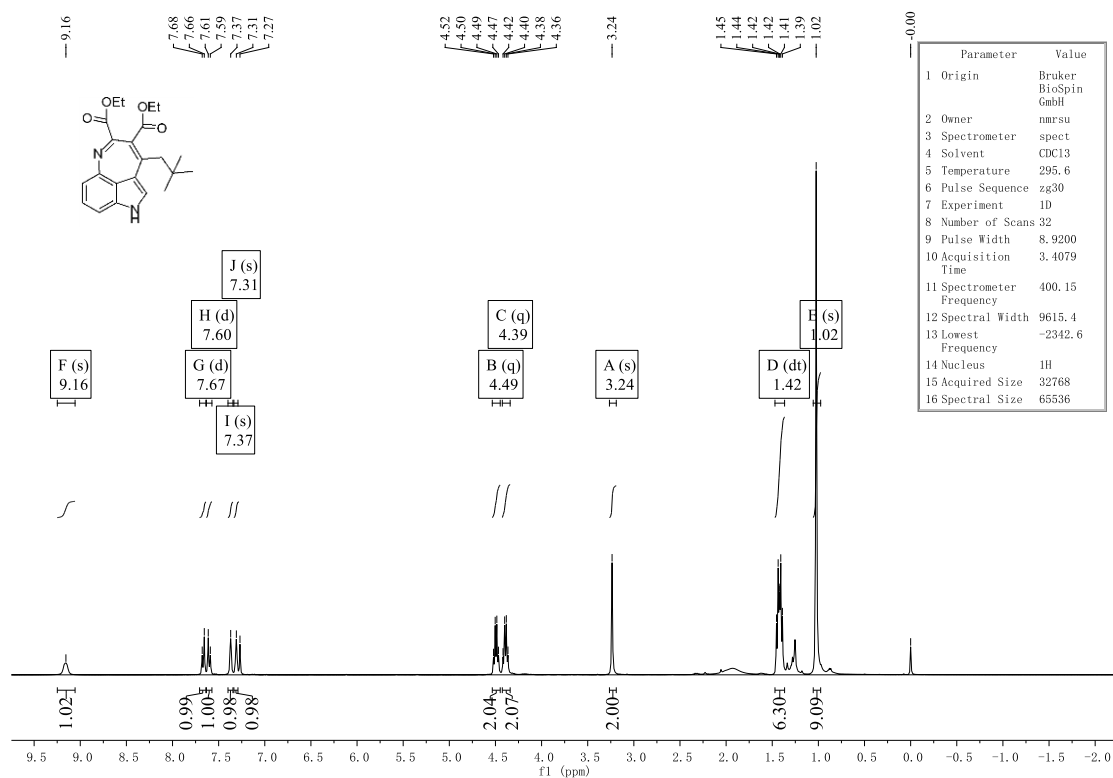


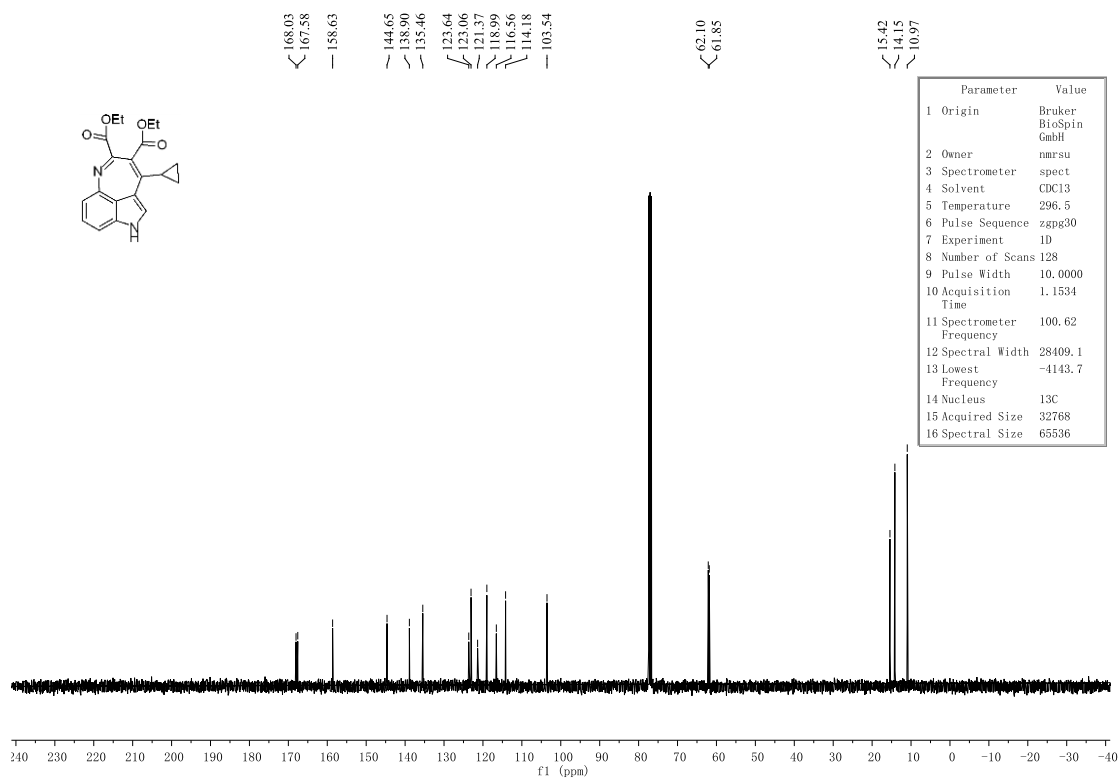
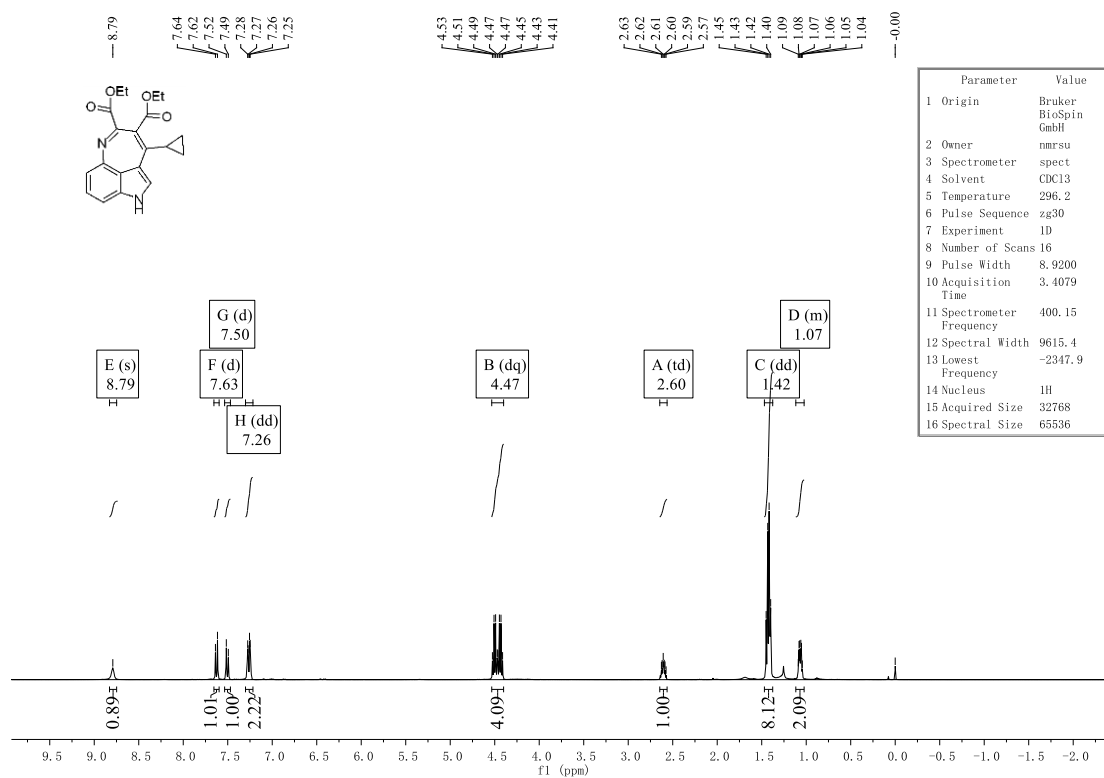


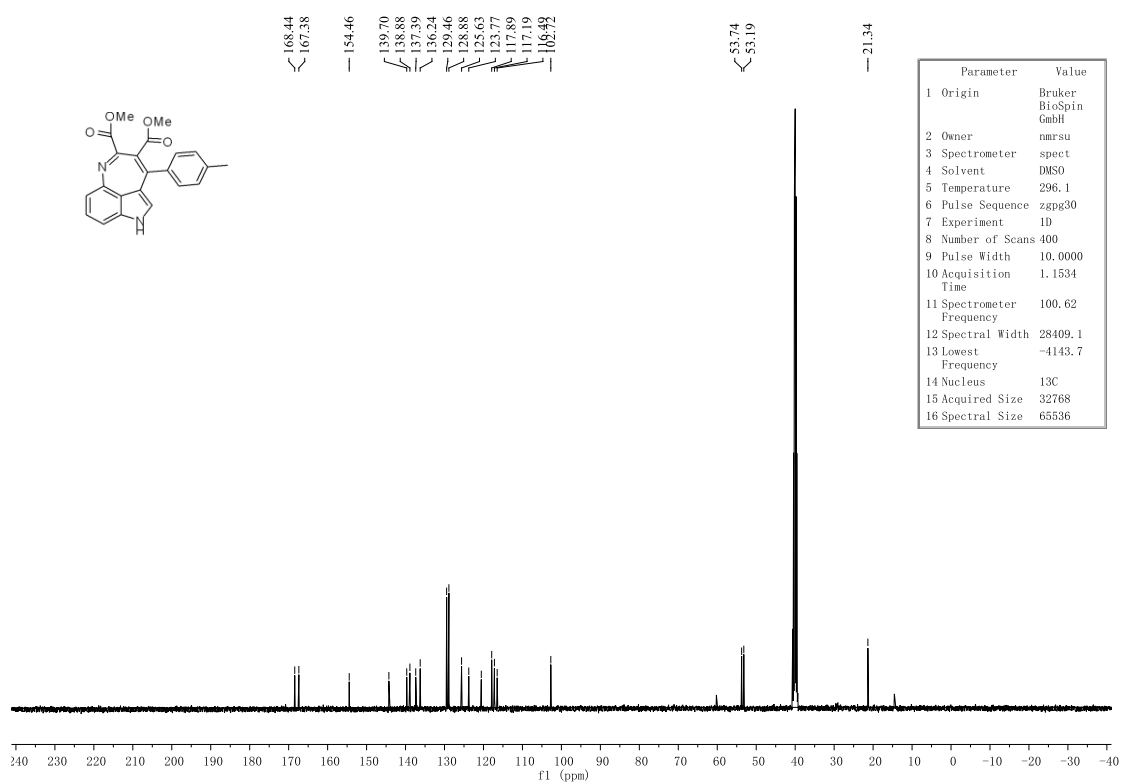
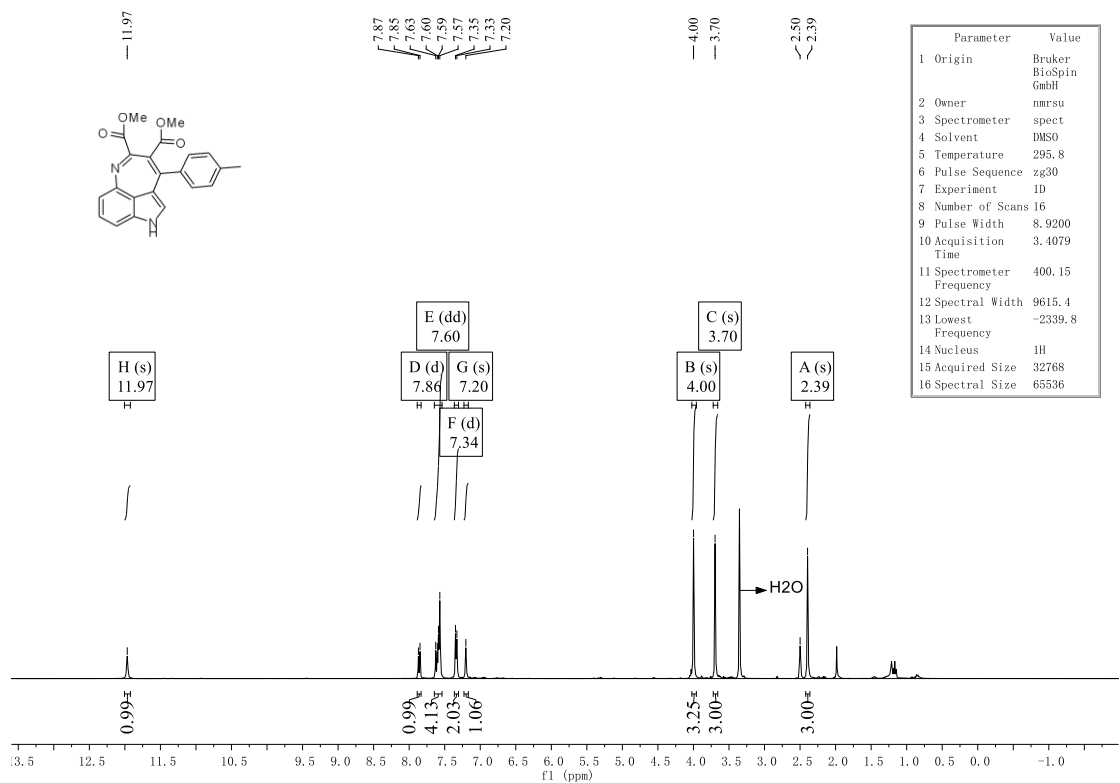
Parameter	Value
1 Origin	Brucker BioSpin GmbH
2 Owner	nmsu
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	296.2
6 Pulse Sequence	zg30
7 Experiment	1D
8 Number of Scans	16
9 Pulse Width	8.9200
10 Acquisition Time	3.4079
11 Spectrometer Frequency	400.15
12 Spectral Width	9615.4
13 Lowest Frequency	-2347.1
14 Nucleus	¹ H
15 Acquired Size	32768
16 Spectral Size	65536

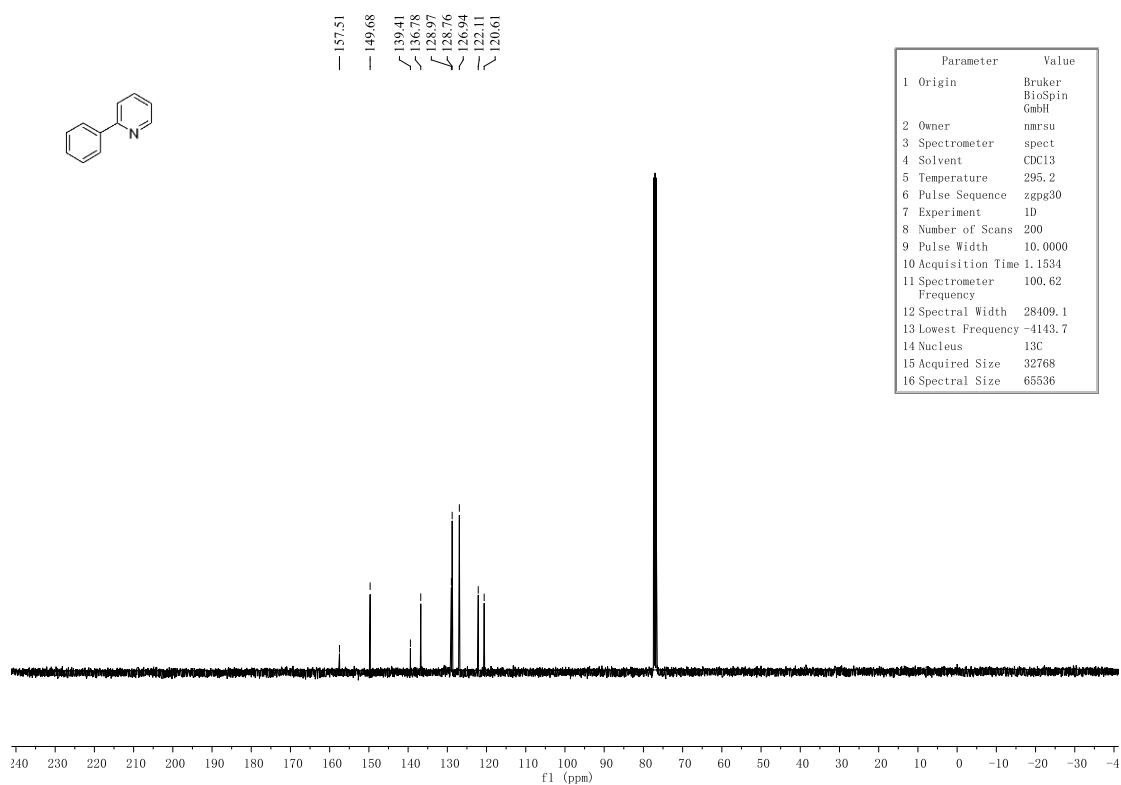
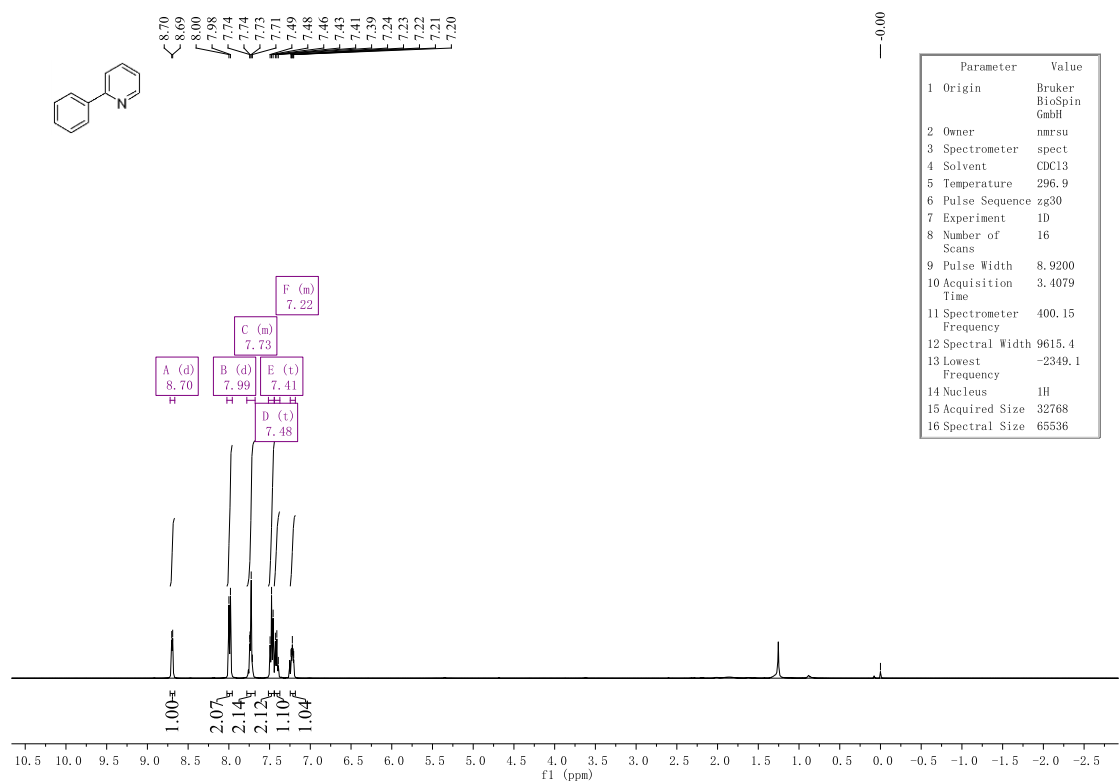


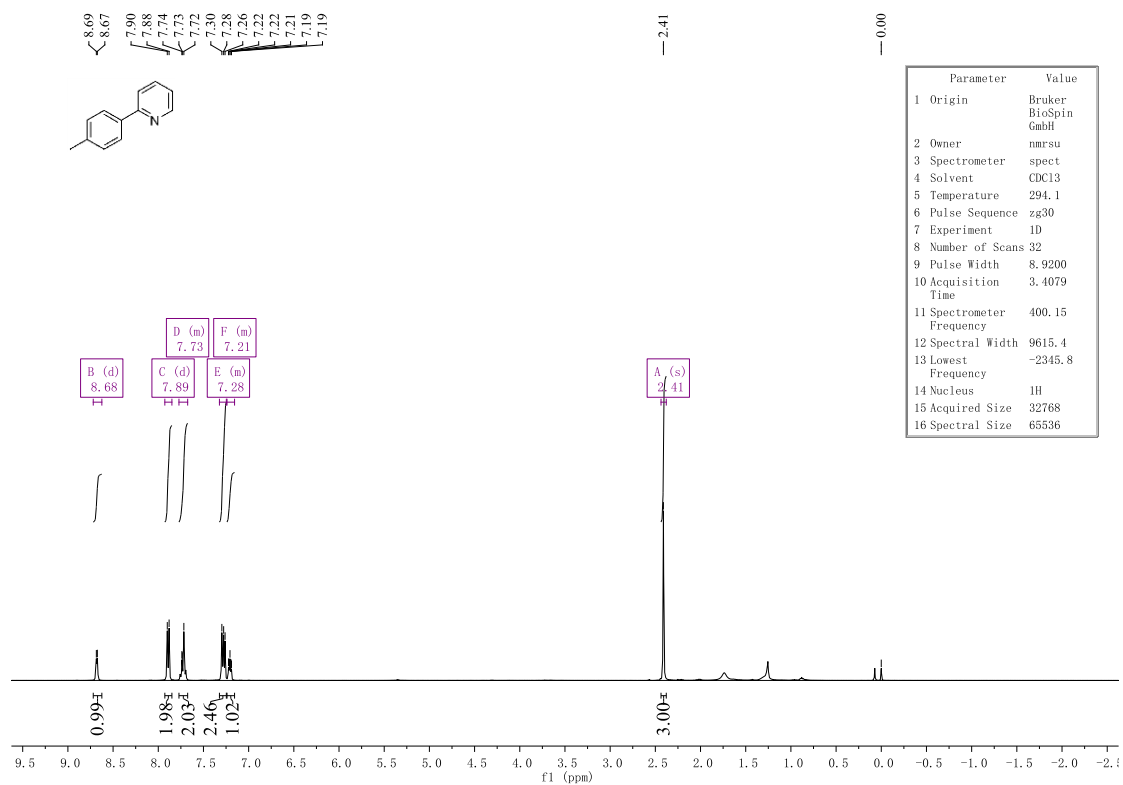
Parameter	Value
1 Origin	Brucker BioSpin GmbH
2 Owner	nmsu
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	296.4
6 Pulse Sequence	zgpg30
7 Experiment	1D
8 Number of Scans	128
9 Pulse Width	10.0000
10 Acquisition Time	1.1534
11 Spectrometer Frequency	100.62
12 Spectral Width	28409.1
13 Lowest Frequency	-4143.7
14 Nucleus	¹³ C
15 Acquired Size	32768
16 Spectral Size	65536



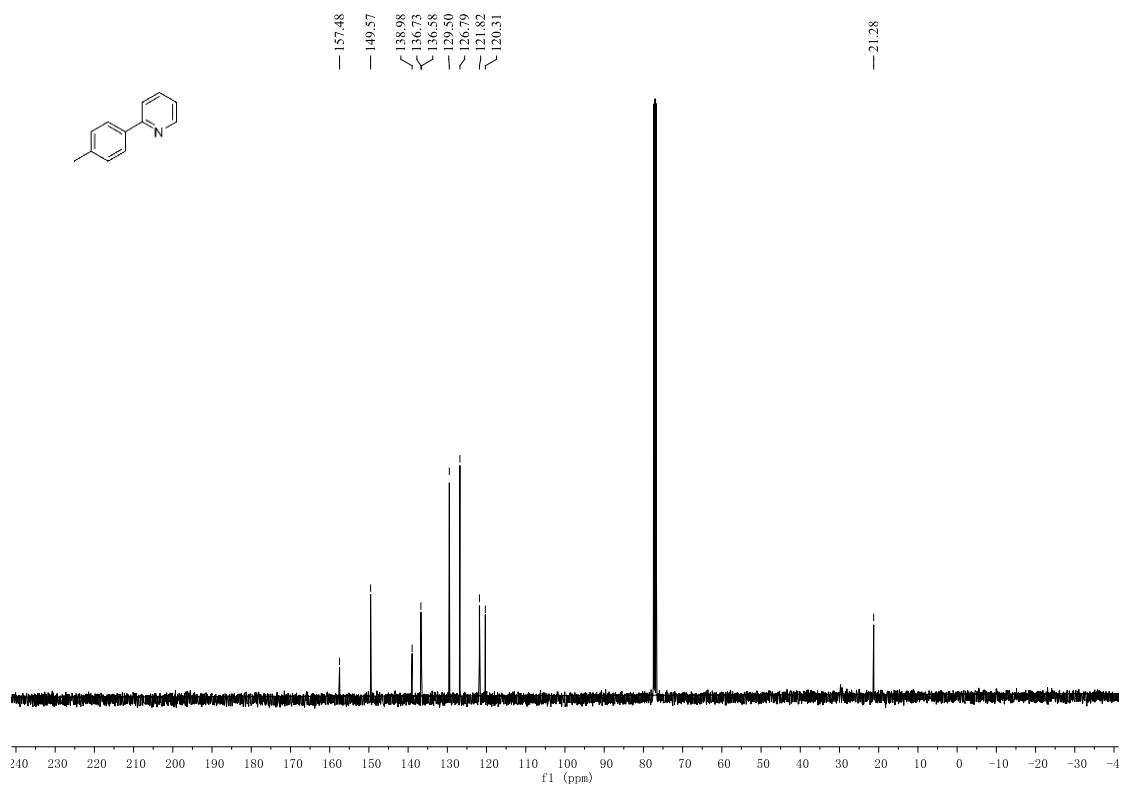


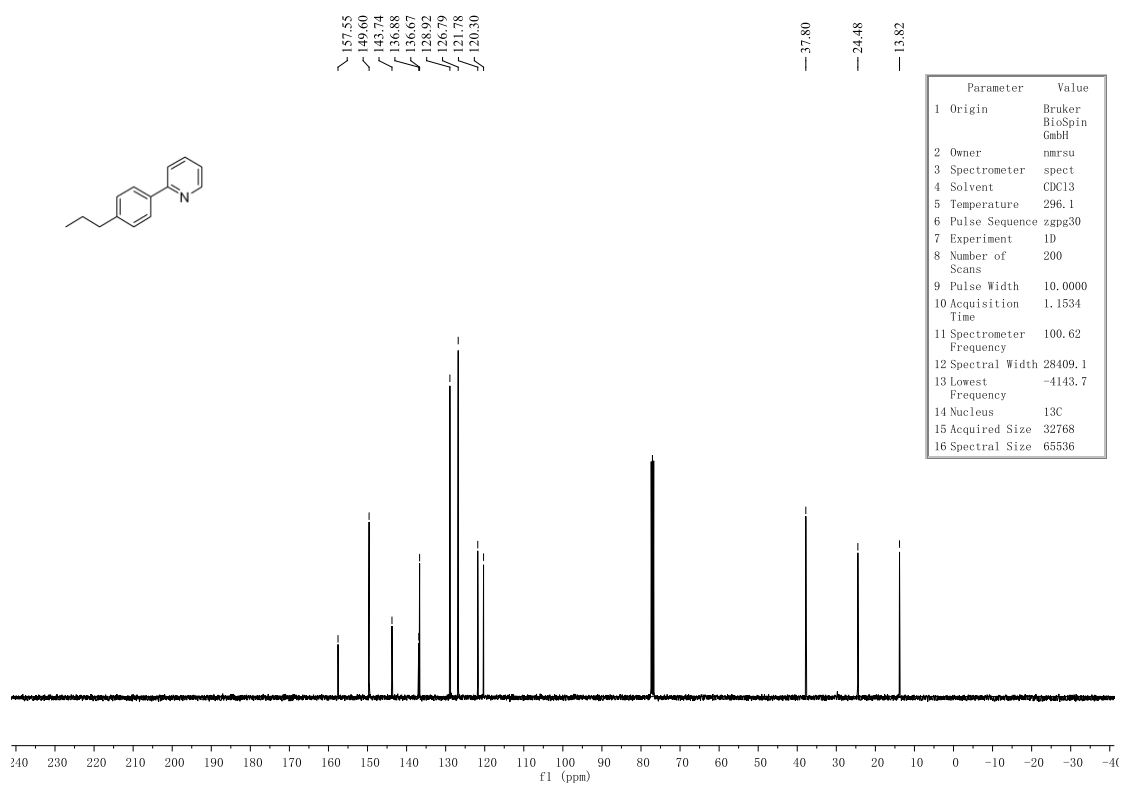
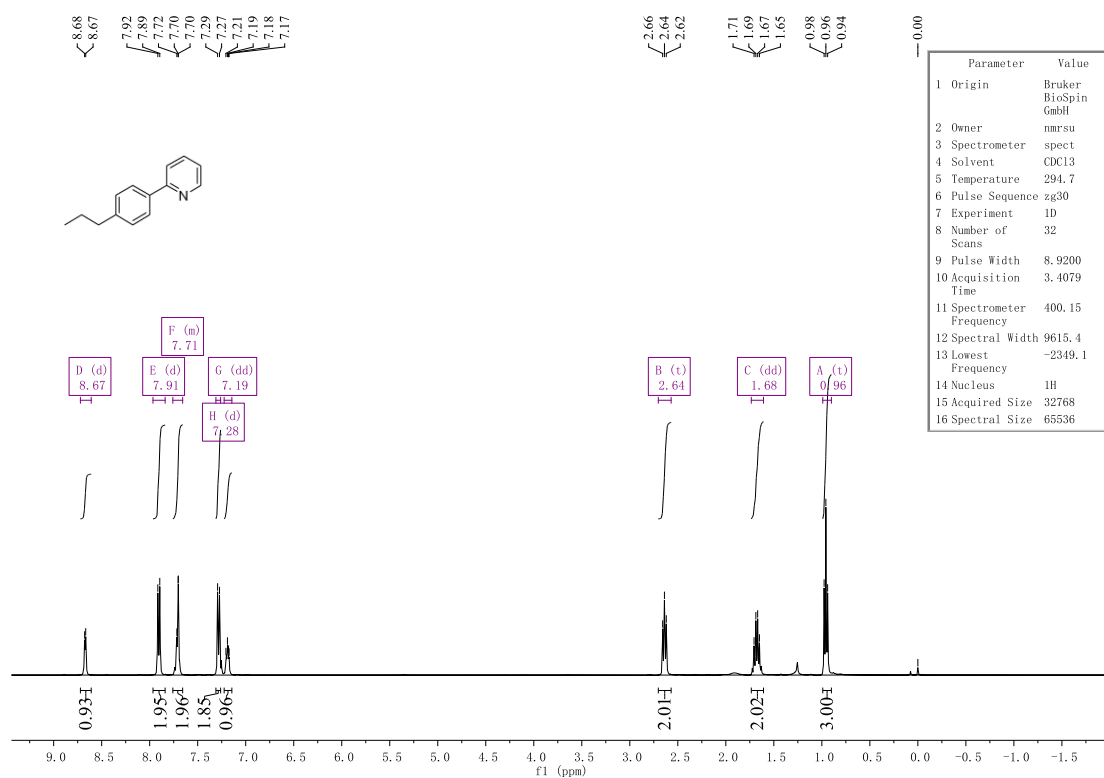


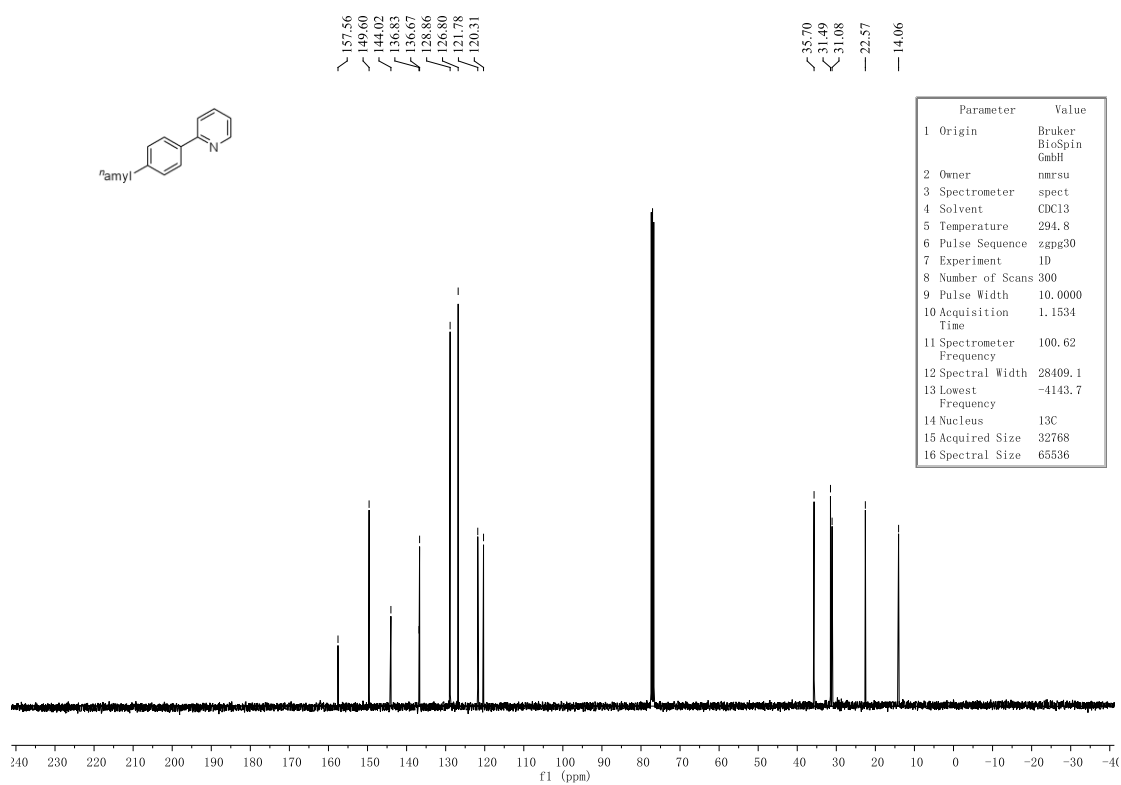
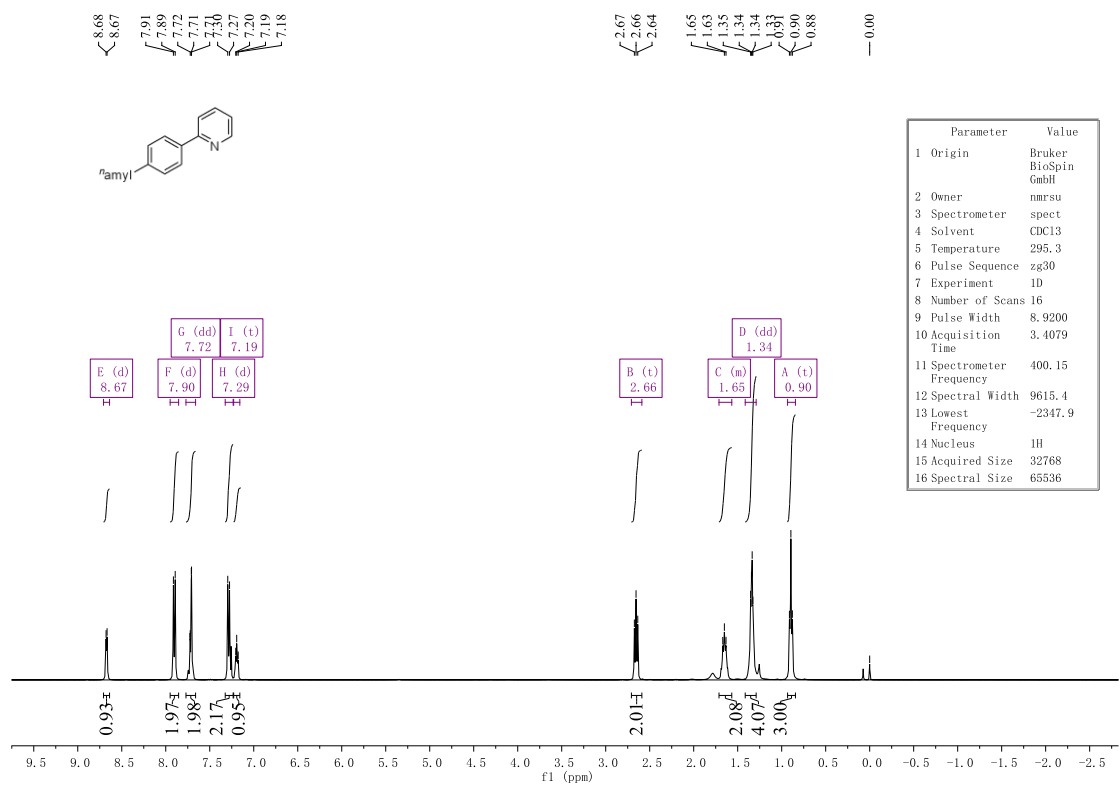


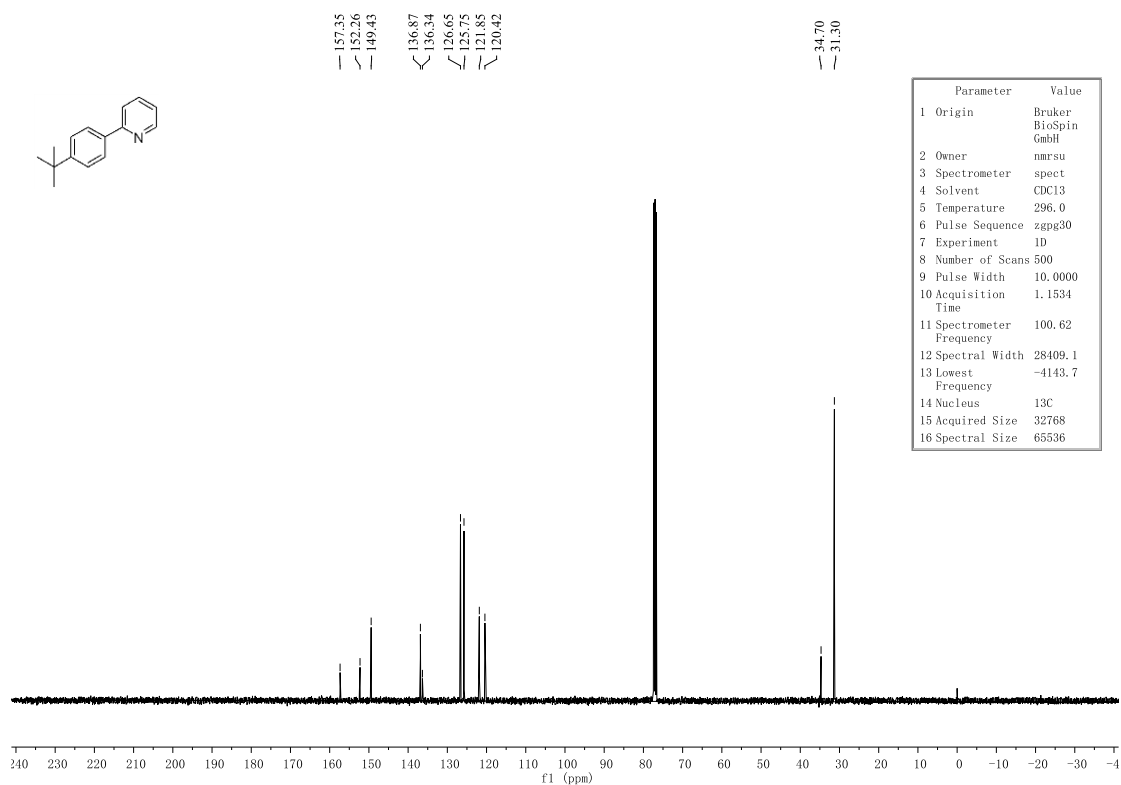
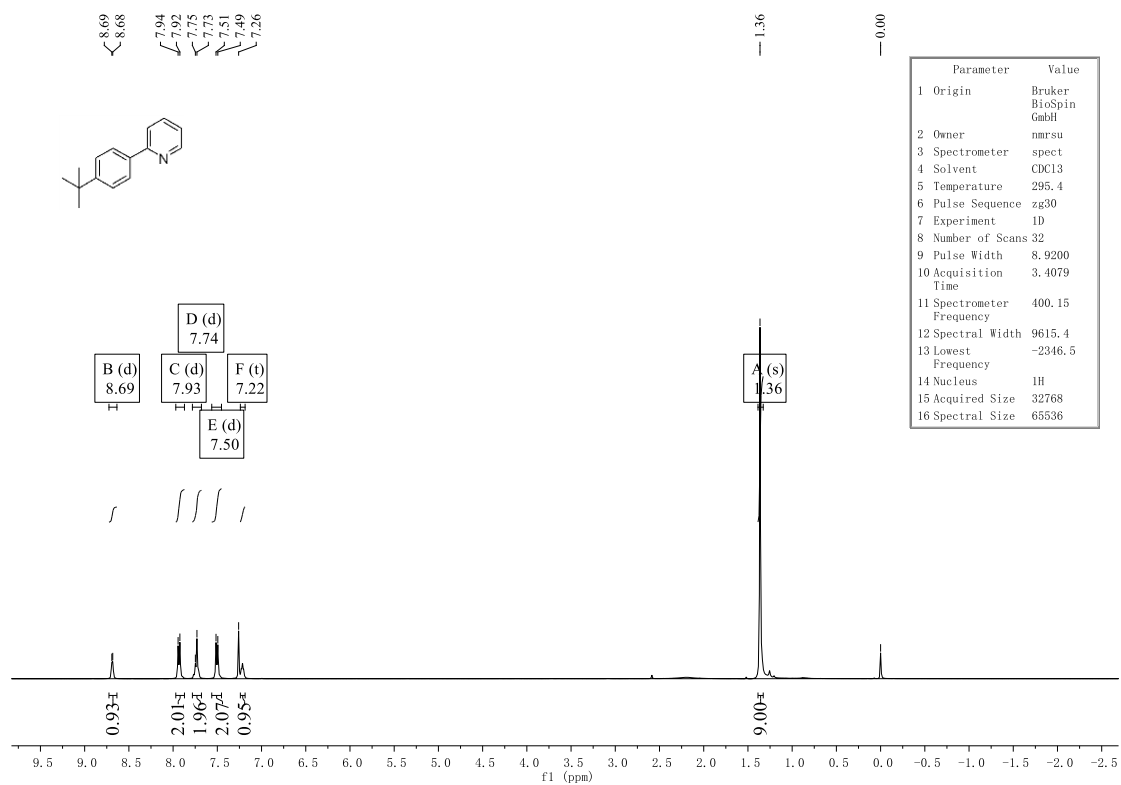


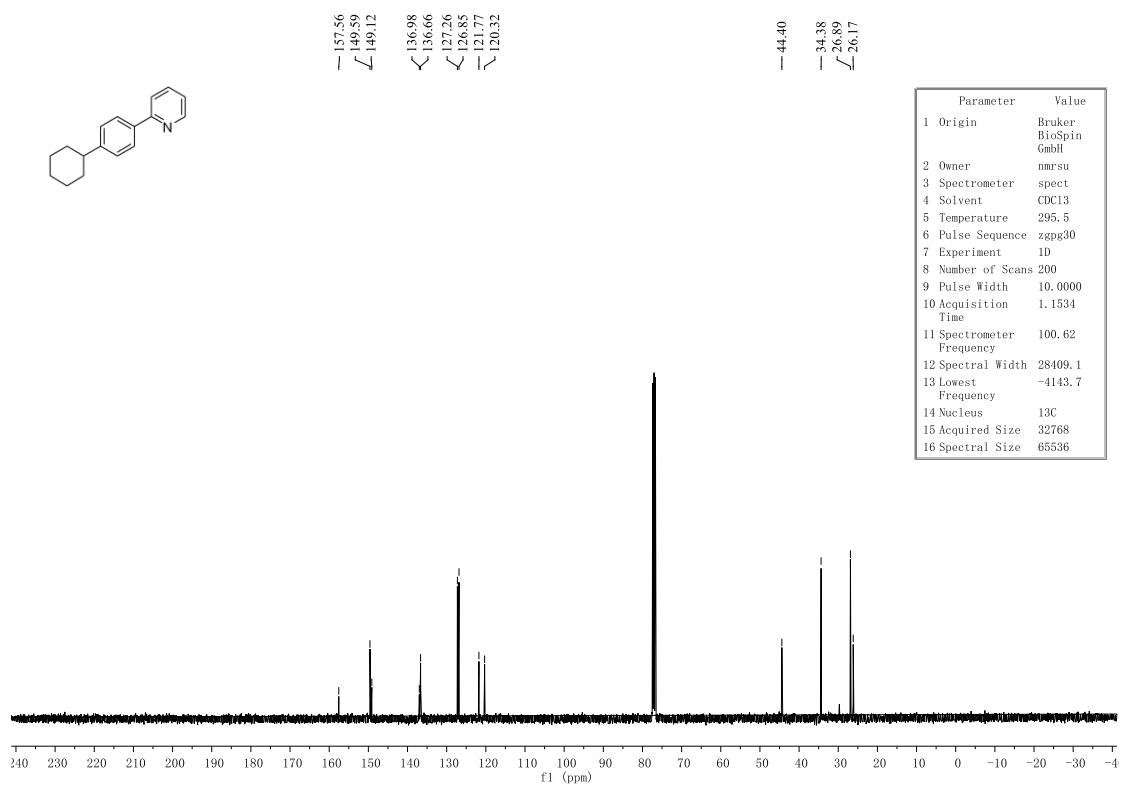
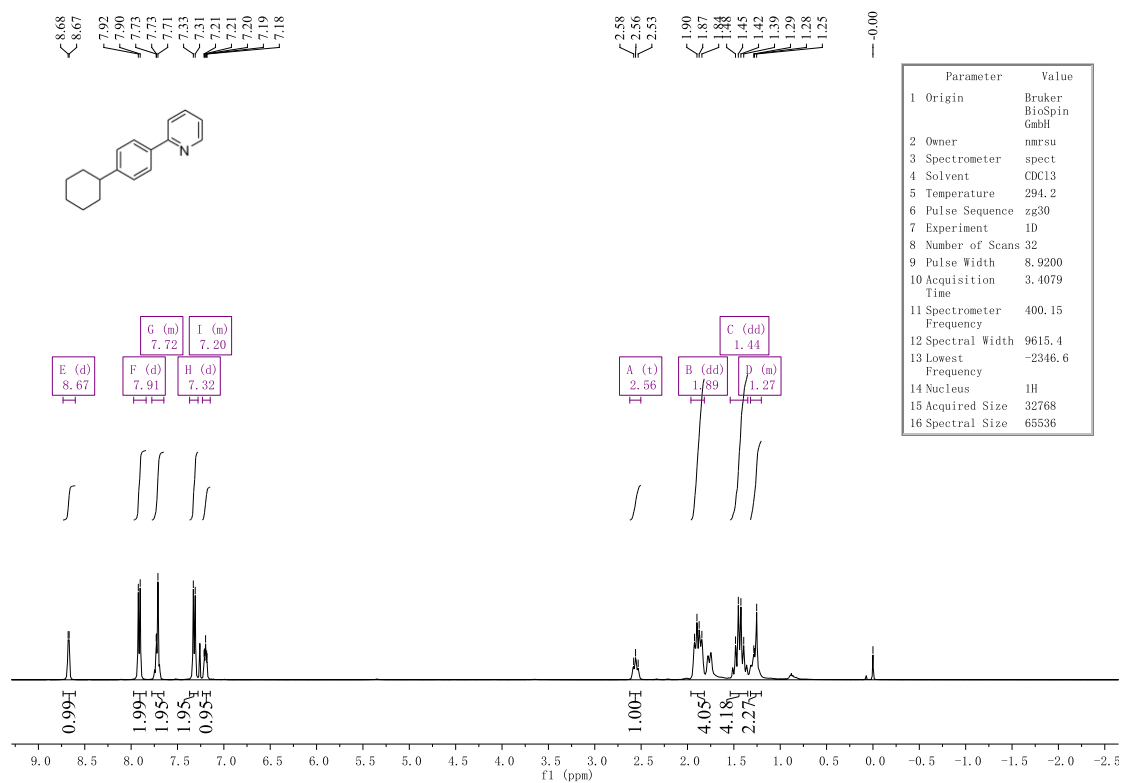
Parameter	Value
1 Origin	Broker BioSpin GmbH
2 Owner	nmsu
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	294.1
6 Pulse Sequence	zg30
7 Experiment	1D
8 Number of Scans	32
9 Pulse Width	8.9200
10 Acquisition Time	3.4079
11 Spectrometer Frequency	400.15
12 Spectral Width	9615.4
13 Lowest Frequency	-2345.8
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536

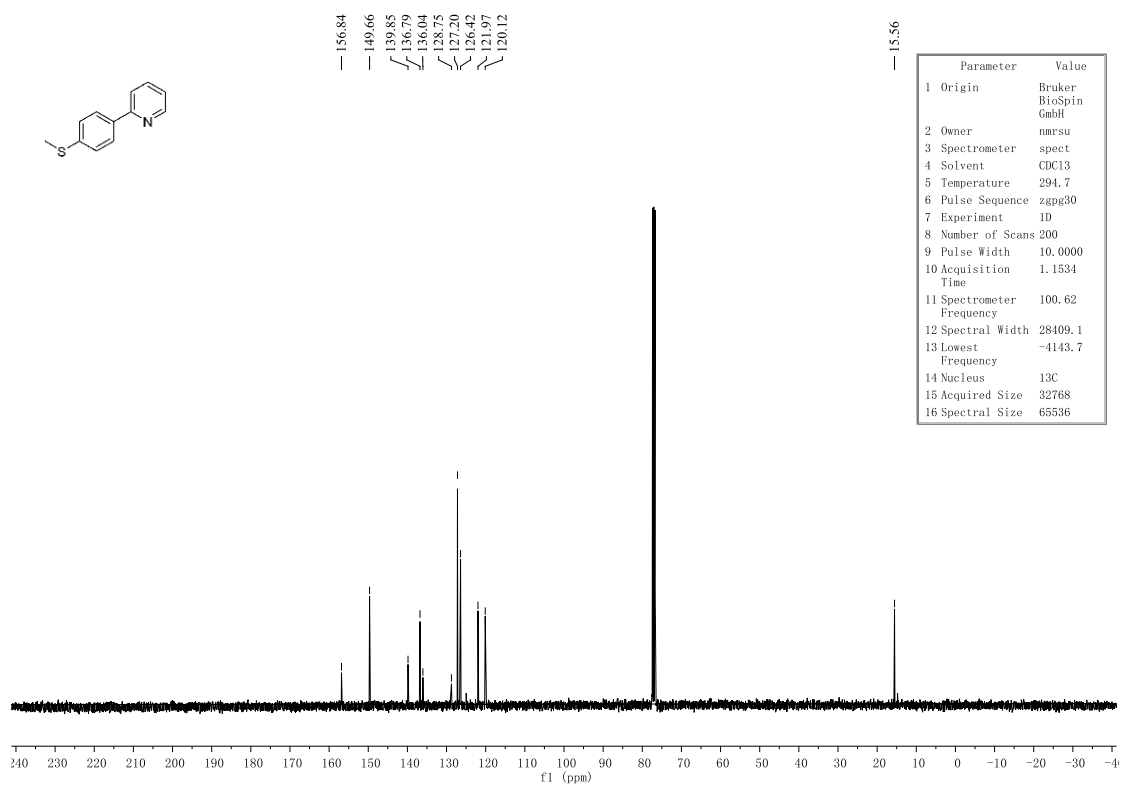
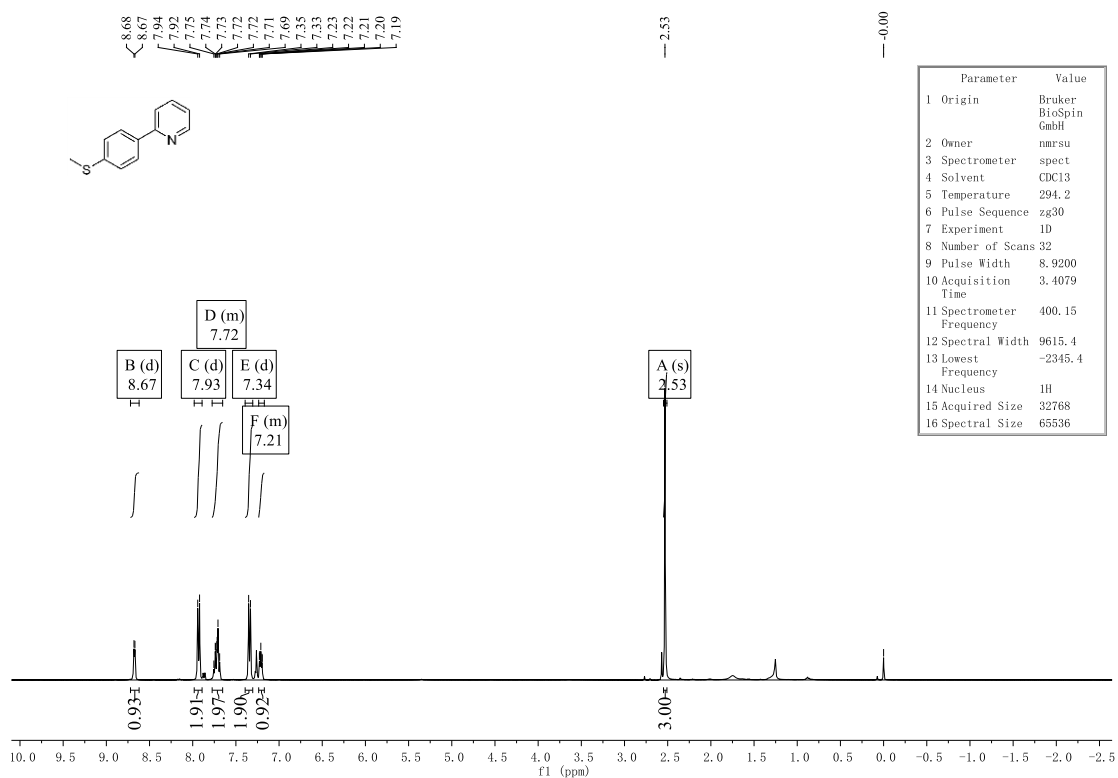


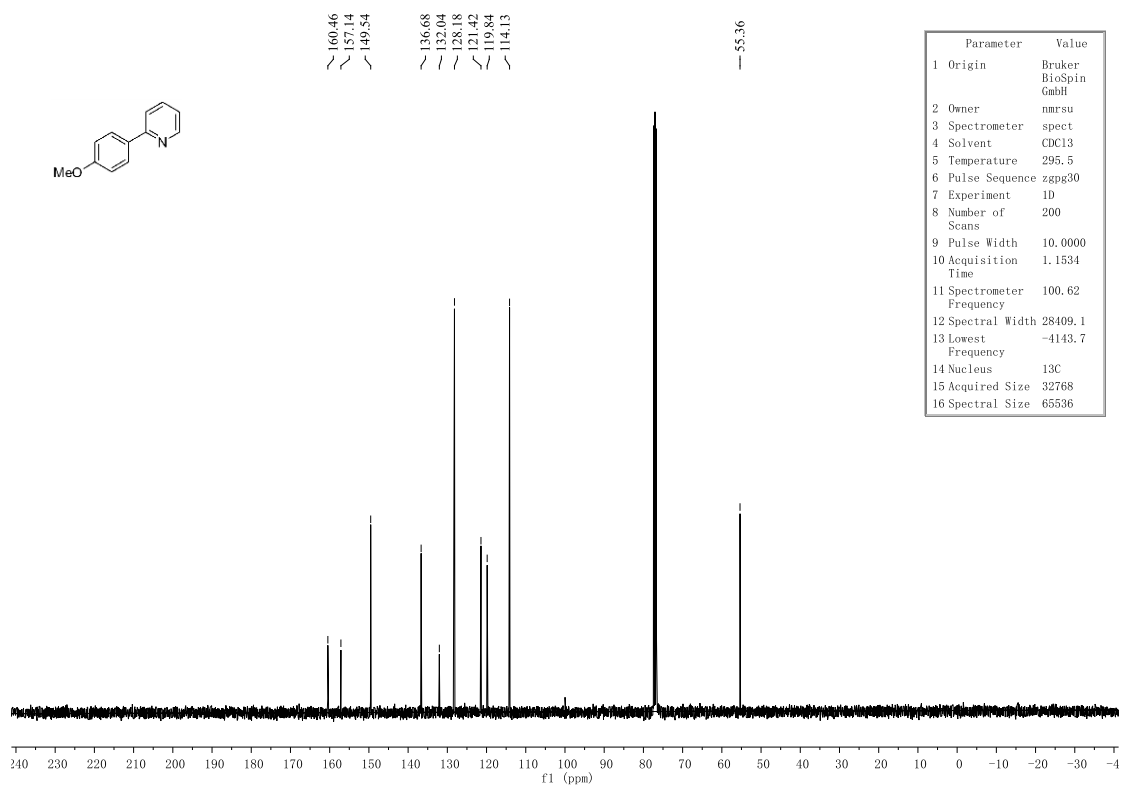
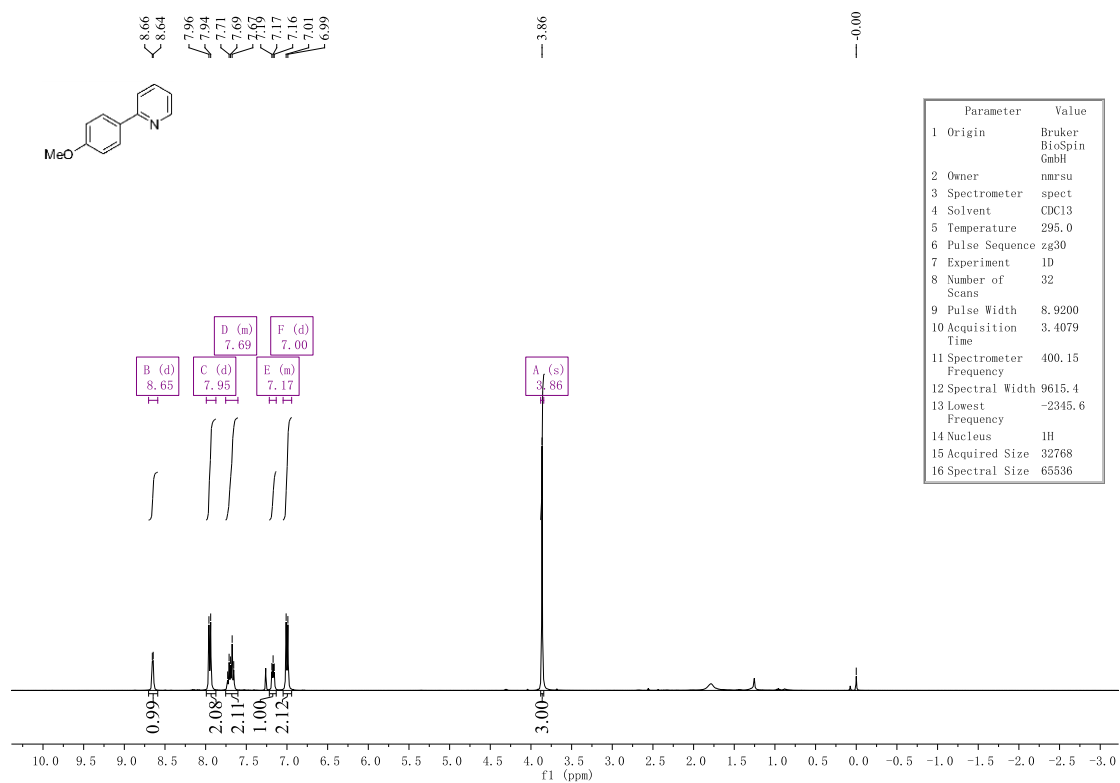


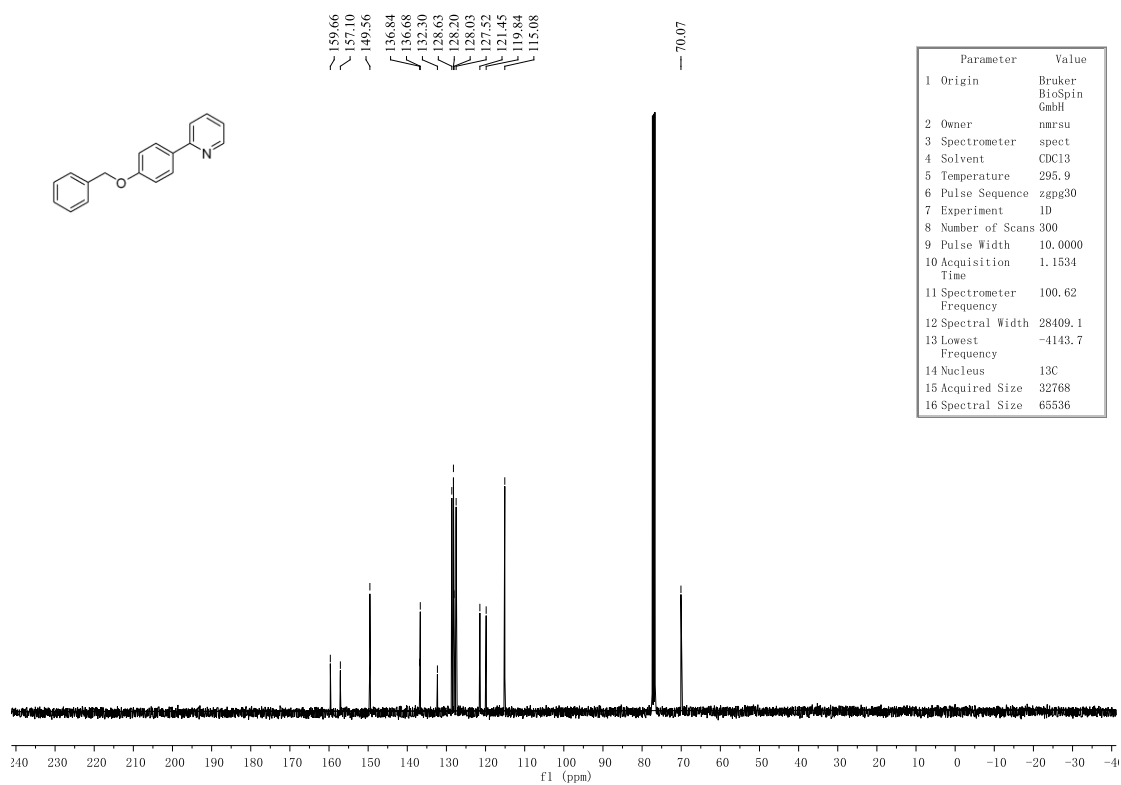
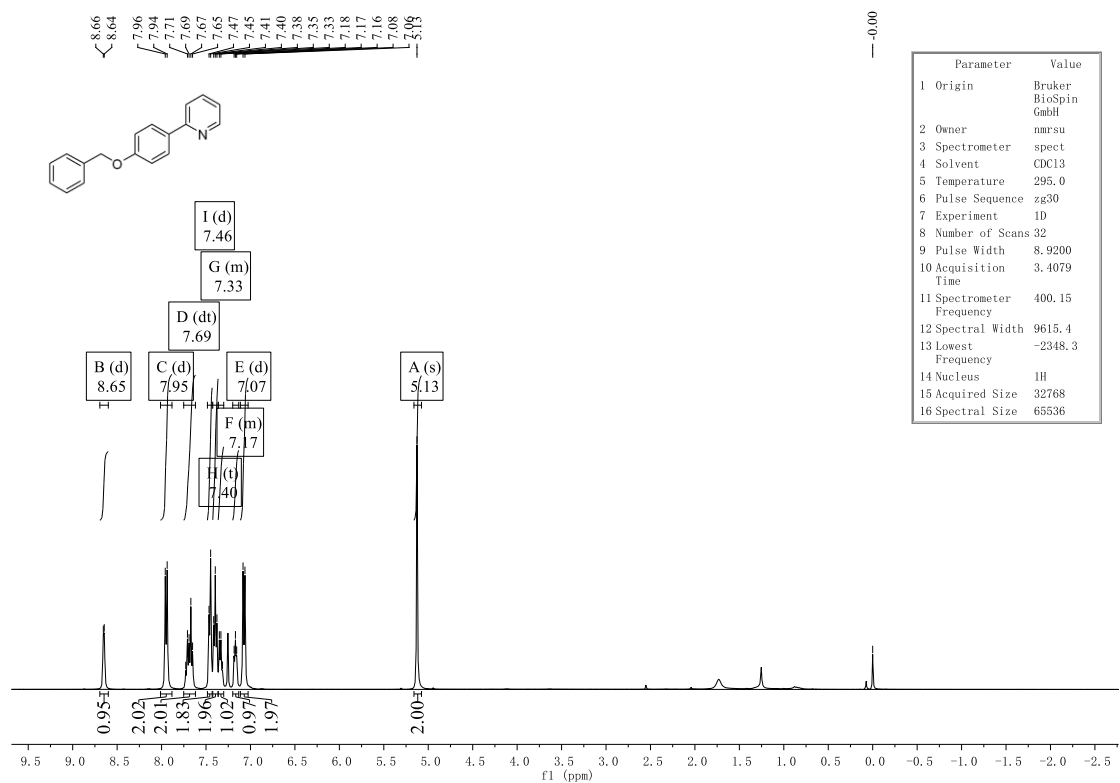


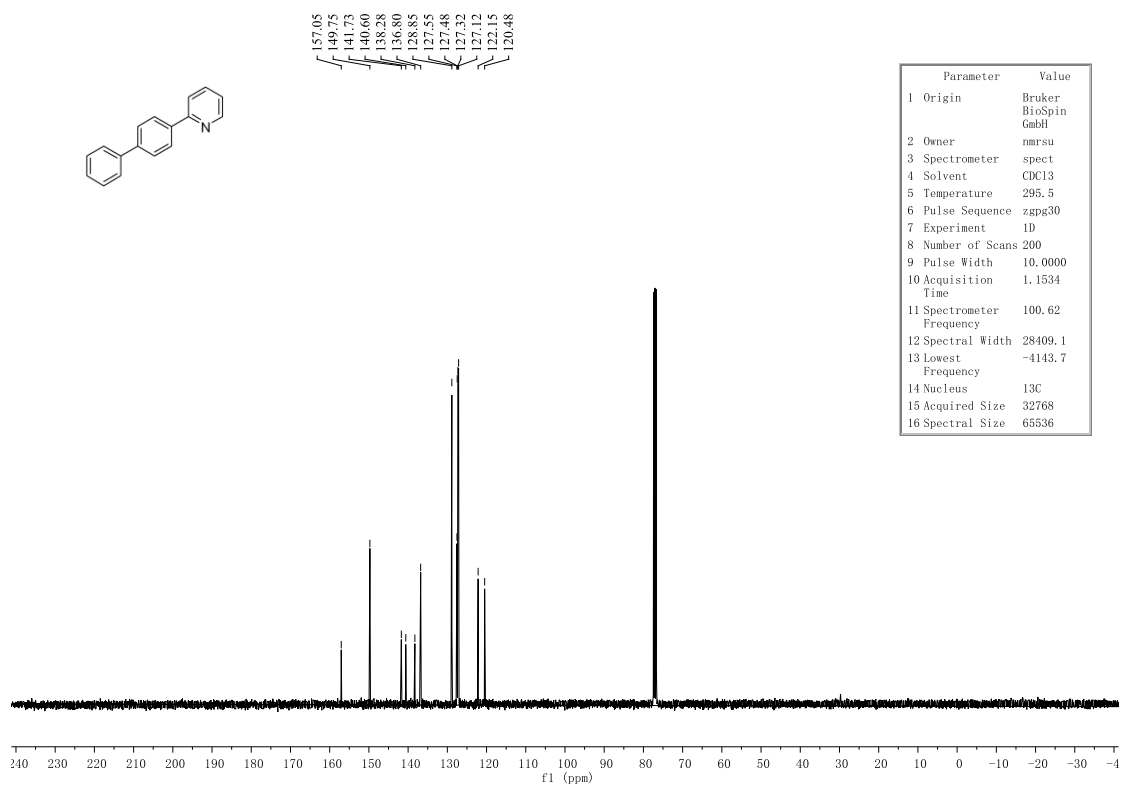
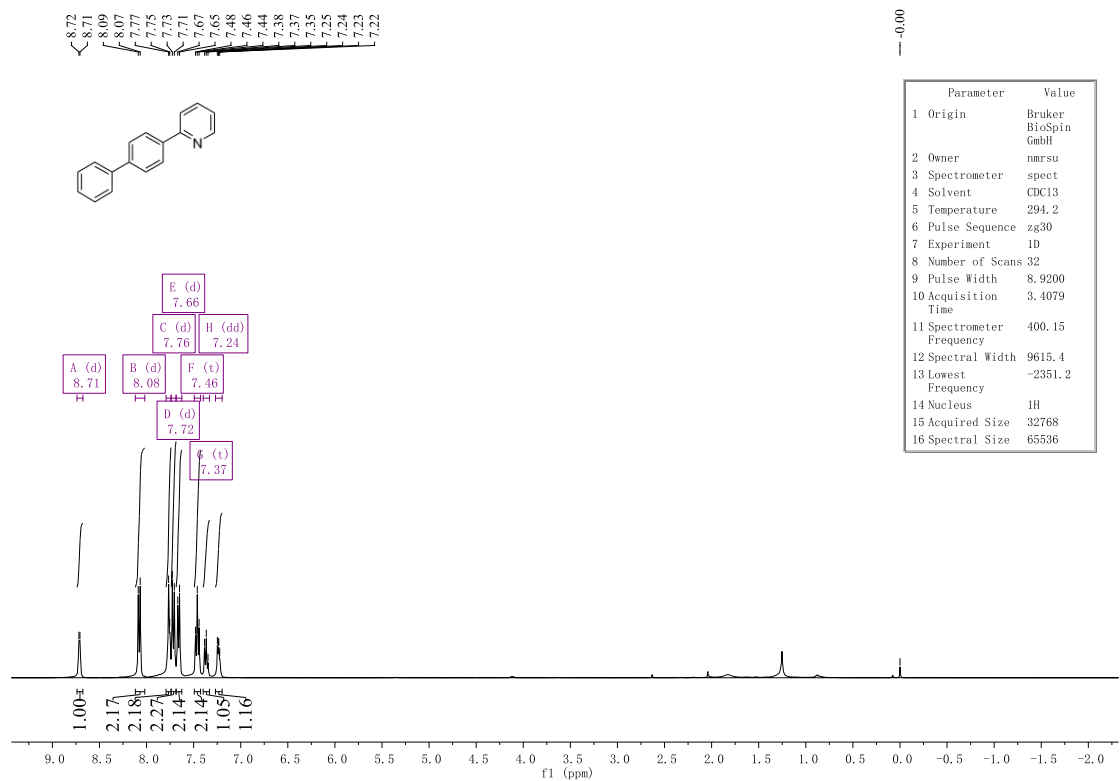


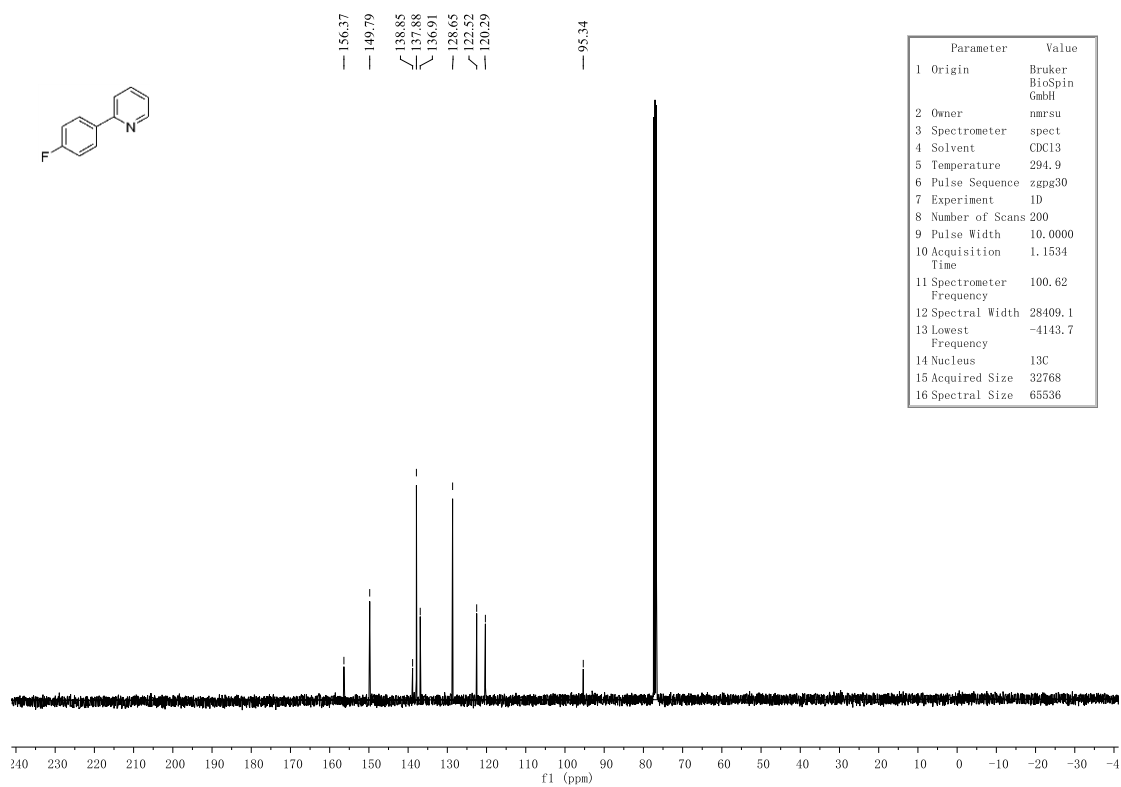
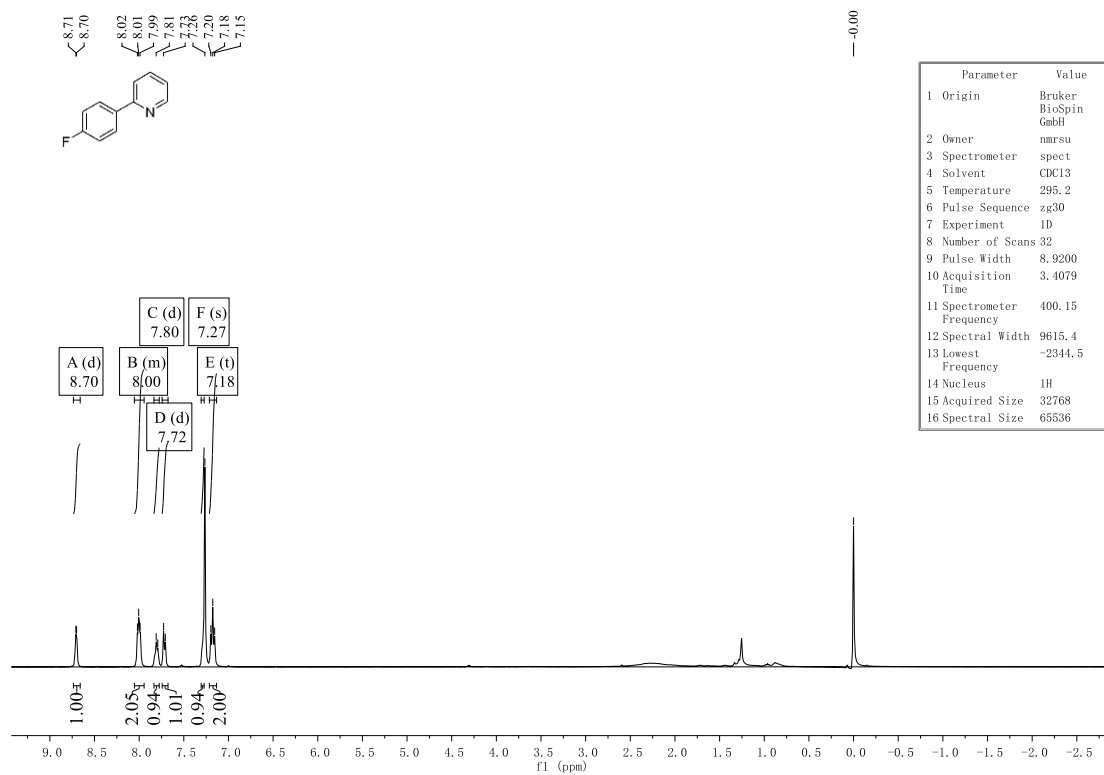


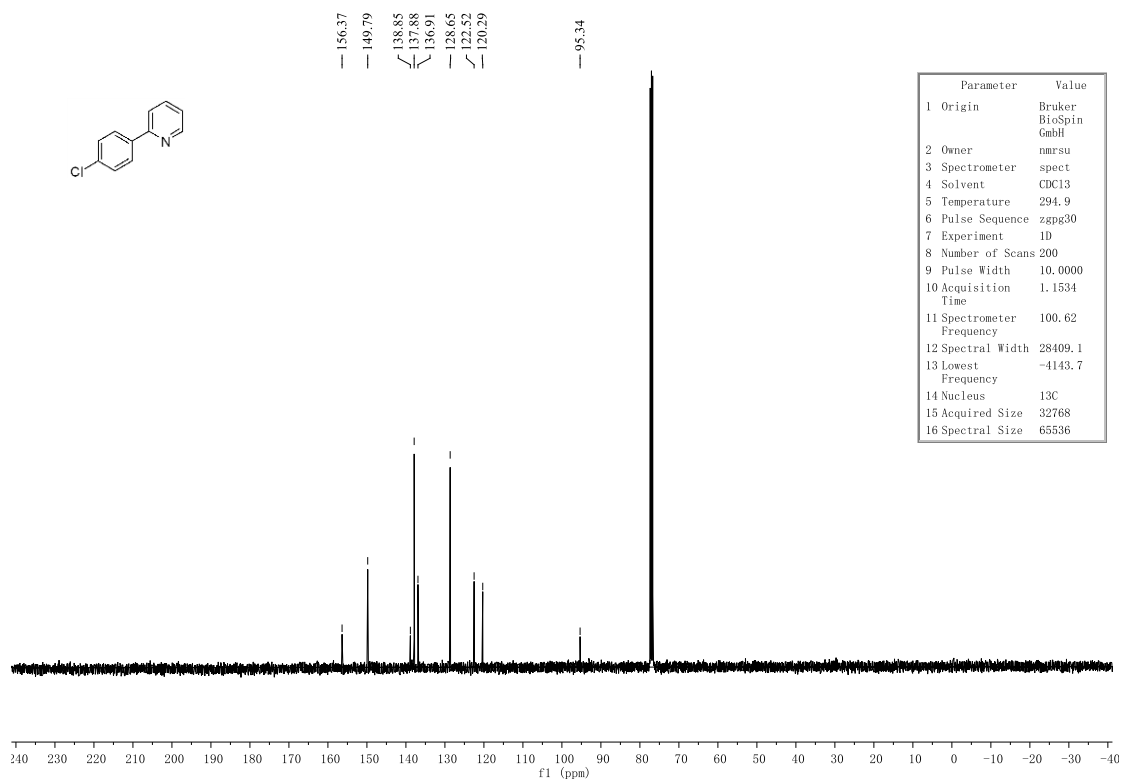
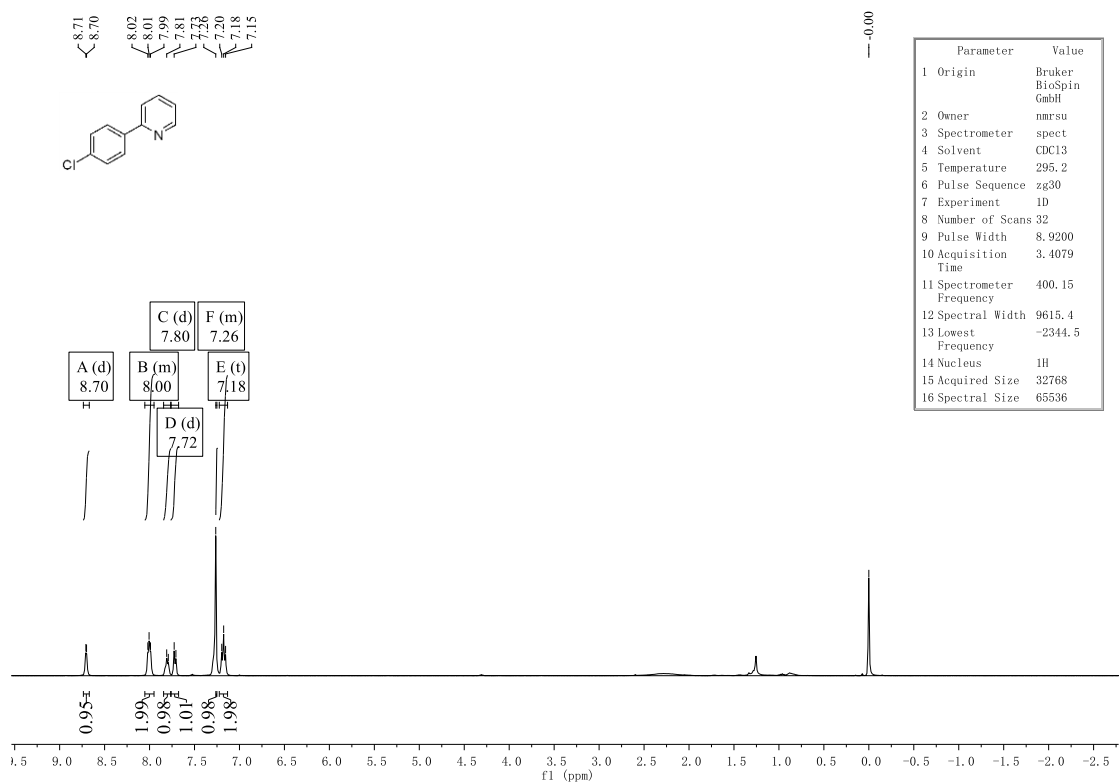


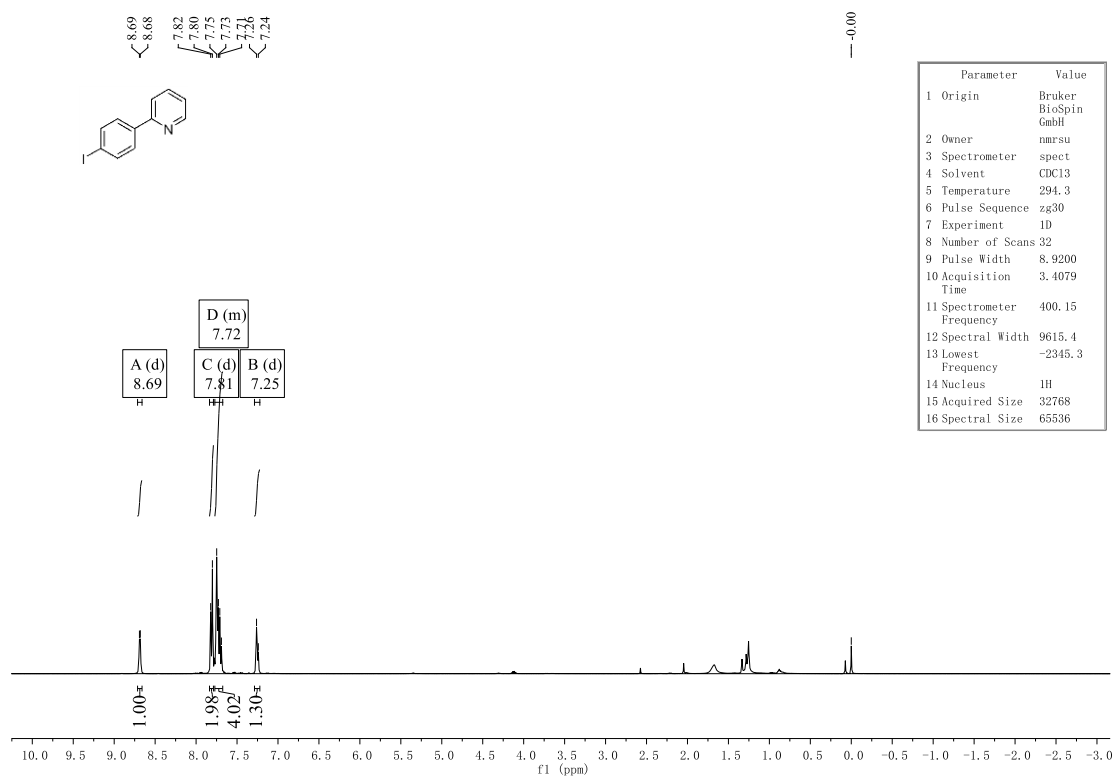




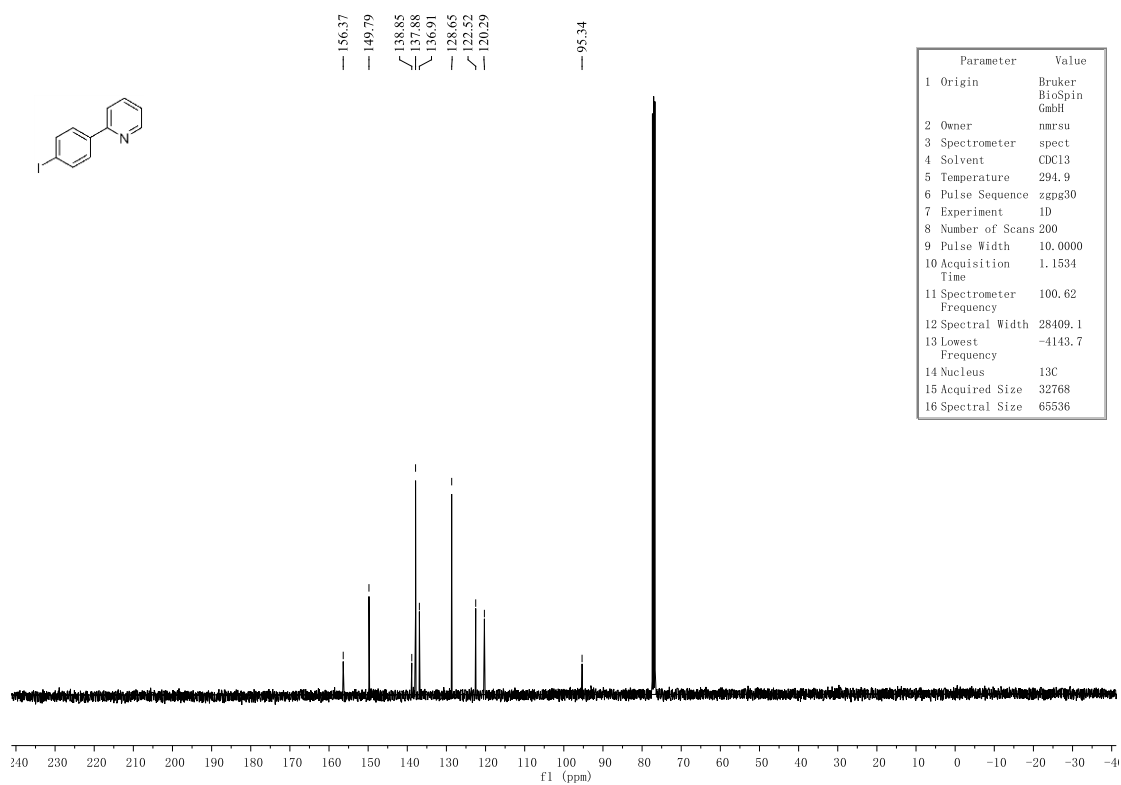








Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Owner	nmsu
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	294.3
6 Pulse Sequence	zg30
7 Experiment	1D
8 Number of Scans	32
9 Pulse Width	8.9200
10 Acquisition Time	3.4079
11 Spectrometer Frequency	400.15
12 Spectral Width	9615.4
13 Lowest Frequency	-2345.3
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Owner	nmsu
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	294.9
6 Pulse Sequence	zgpg30
7 Experiment	1D
8 Number of Scans	200
9 Pulse Width	10.0000
10 Acquisition Time	1.1534
11 Spectrometer Frequency	100.62
12 Spectral Width	28409.1
13 Lowest Frequency	-4143.7
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536

