*Electronic supplementary information*

# 2-Azidoazirines suitable for click chemistry: synthesis of 1-(azirin-2-yl)-1,2,3-triazoles

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# 1. General information

**Chemicals** were purchased from commercial suppliers (Alfa Aesar, Macklin, Merk) and used without further purification. All solvents were distilled and dried prior to use. Dichloromethane (DCM) and 1,2-dichloroethane (DCE) were washed with concentrated $H_2SO_4$, water, then distilled from $P_2O_5$ and stored over anhydrous $K_2CO_3$. MeCN was distilled from $P_2O_5$ and redistilled from $K_2CO_3$. 1,4-Dioxane was distilled over Na under argon atmosphere.

Sodium azide is a toxic chemical (LD50 oral = 27 mg/kg for rats) and can be easily absorbed through the skin. Sodium azide is relatively safe at room temperature especially in solutions, unless acidified to form $HN_3$, which is volatile and highly toxic.

Organic azides are potentially explosive compounds. All synthesized azides 1, in terms of the ratio of C, O and N atoms, satisfy the well-known equation used to assess the explosiveness of organic azides:

$$\frac{N_C + N_O}{N_N} \geqslant 3$$

, where $N_N$ - all nitrogen atoms in the organic azide, not just those in the azido group.

**Melting points (mp)** were measured in open glass capillaries on a Stuart® SMP30 melting point apparatus and are uncorrected.

**Nuclear magnetic resonance (NMR)** spectra were recorded with a Bruker AVANCE 400 (400.1 MHz for $^1$H and 100.6 MHz for $^{13}$C) at 298K. Spectra were internally referenced to residual deuterated solvent: $CHCl_3$ (7.28 ppm for $^1$H and 77.00 ppm for $^{13}$C), $CD_2HCN$ (1.94 ppm for $^1$H and 1.39 ppm for $^{13}$C), DMSO-$d_5$ (2.50 ppm for $^1$H and 39.50 ppm for $^{13}$C), $C_6D_5H$ (7.16 ppm for $^1$H and 128.00 ppm for $^{13}$C), $CDHCl_2$ (5.32 ppm for $^1$H). Chemical shifts are given in ppm and coupling constants are given in Hz.

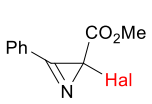
**High-resolution mass-spectra (HRMS)** with **electrospray ionization (ESI)** were measured on a Bruker MaXis HRMS-ESI-QTOF mass spectrometer.

**X-ray crystallography** was carried out on Agilent Technologies "Xcalibur" diffractometer. Crystallographic data for the structures **2a, 2l**, **3a** (CCDC 2347550, 2346171, 2346167, correspondingly) have been deposited with the Cambridge Crystallographic Data Centre.

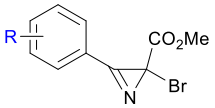
For **column chromatography** Macherey-Nagel silica gel 60 M (0.04–0.063 mm) was used as stationary phase. **Thin-layer chromatography** (TLC) was conducted on aluminum sheets precoated with SiO2 ALUGRAM SIL G/UV254.

**Starting compounds 1a$^{F}$**,**1a$^{Cl}$**, **1c**,**f**,**p**,**s**,[1] **1a**,**b**,**h**,**k**,[2] **1d**,**e**,**n**,[3] **1g**,[4] **1i**,**r**,[5] **1j**,[6] **1l**,**o**,[7] **1m**,[8] **1q**,[9] **1t**[10] were prepared by the reported procedures.

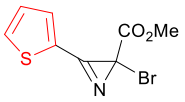
## 2. Structures of azirines 1a–q



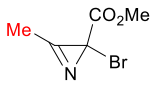
**1a**, Hal = Br
**1a**$^{F}$, Hal = F
**1a**$^{Cl}$, Hal = Cl



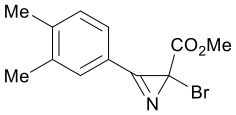
**1b**, R = 4-Me
**1c**, R = 2,4-$Me_2$
**1d**, R = 2,5-$Me_2$
**1e**, R = 4-Br
**1f**, R = 2-Br
**1g**, R = 2-I
**1h**, R = 4-Cl
**1i**, R = 4-F
**1j**, R = 4-$CF_3$
**1k**, R = 4-OMe
**1l**, R = 3-OMe



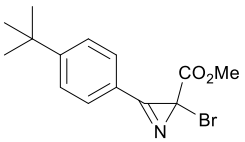
**1m**



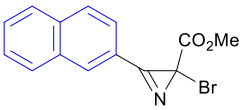
**1n**



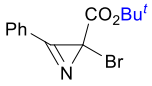
**1o**



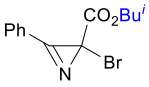
**1p**



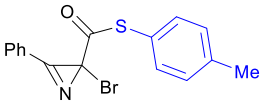
**1q**



**1r**

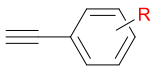


**1s**

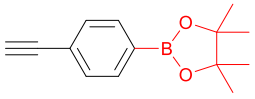


**1t**

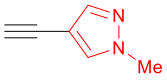
## 3. Structures of acetylenes 4a–t



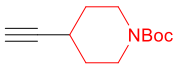
**4a**, R = H
**4b**, R = 3-Me
**4c**, R = 4-*t*-Bu
**4d**, R = 4-Br
**4e**, R = 4-Cl
**4f**, R = 2-F
**4g**, R = 4-OMe
**4h**, R = 4-OBn
**4i**, R = 2-$NO_2$



**4j**

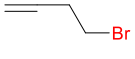


**4k**

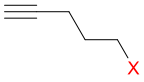


**4l**

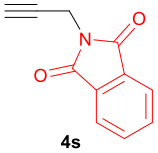
**4m**, R = *t*-Bu
**4n**, R = $CH_2OMe$
**4o**, R = $CH_2OPh$



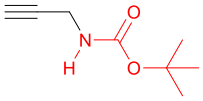
**4p**



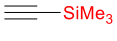
**4q**, X = Cl
**4r**, X = CN



**4s**



**4t**



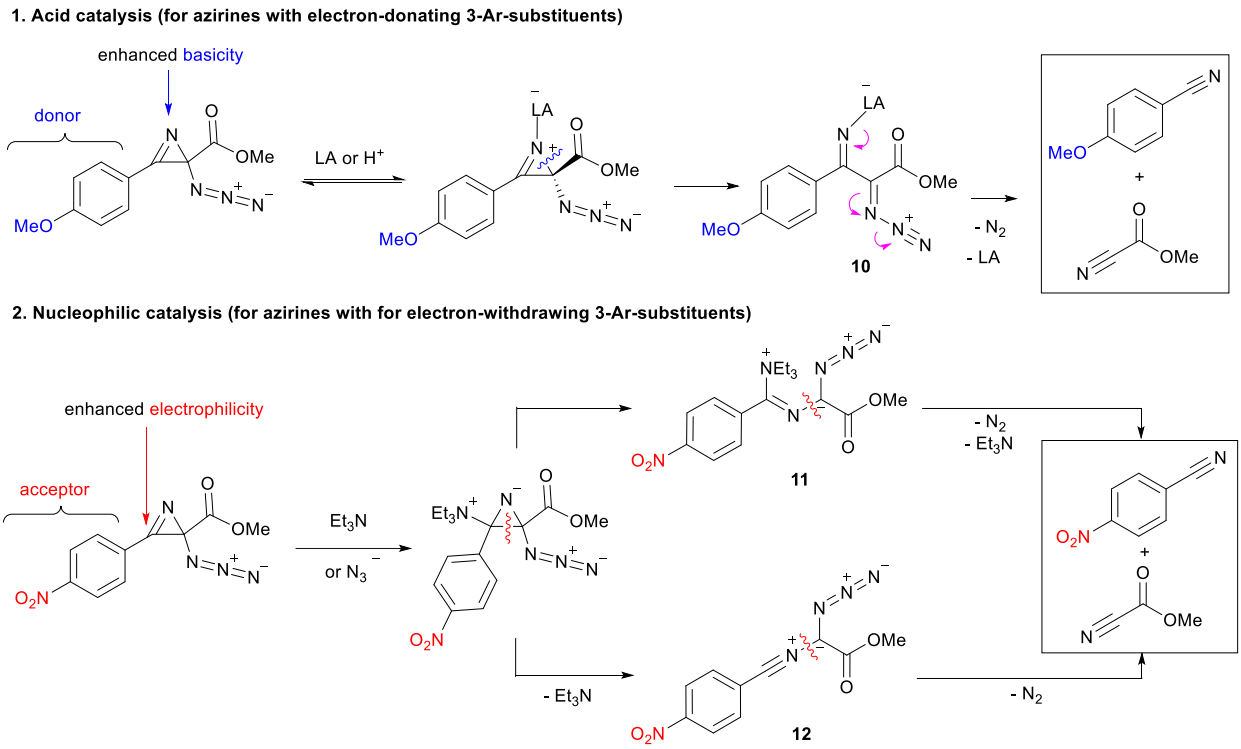
**4u**

## 4. Plausible mechanisms for the destruction of azidoazirines 3

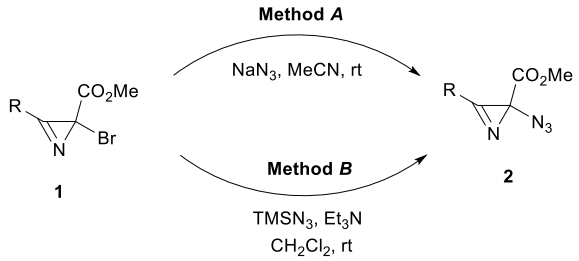
The "structure–stability" relationship for alkyl 3-aryl-2-azido-2*H*-azirine-2-carboxylates is quite complex, possibly because their decomposition can occur through several mechanisms. Scheme S1 shows a possible mechanism for the destruction of azirine **2k** (reaction 1). This reaction is most likely acid catalyzed and begins with the coordination of the nitrogen of the azirine ring with an acidic reagent, which can be traces of protic or Lewis acids in the solvent or starting reagents. This causes a weakening of the N–C2 bond of the azirine ring, which breaks to form intermediate **10**. Obviously, this compound is extremely unstable and should easily undergo cleavage of the central C–C bond to form methyl cyanoformate and *p*-anisonitrile.

Due to enhanced electrophilicity the C3-atom of methyl 2-azido-3-(4-nitrophenyl)-2*H*-azirine-2-carboxylate the nucleophilic catalysis of its decomposition is most possible (Scheme S1, reaction 2). Following addition of a nucleophile, the azirine ring opens via either betaine **11** or nitrile ylide **12**. Both of these intermediates readily decompose into two nitriles.

**Scheme S1.** Plausible mechanisms for the decomposition of 2-azidoazirines **2**



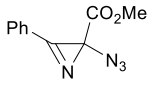

## 5. Synthesis of 2-azidoazirines 2a–o




*Method A:* Azirine **1** (0.5 mmol) was added to a suspension of sodium azide (65 mg, 1 mmol) in MeCN (8 mL). The reaction mixture was stirred at room temperature for 20 min (unless otherwise temperature and time specified). Ice (3 g) and water (15 mL) was added to the reaction mixture, the product was extracted with $Et_2O$ (3×15 mL). The combined organic layer was washed with cold brine (10 mL) and dried over anhydrous $Na_2SO_4$. The solvent was removed under reduced pressure at room temperature. The product was crystalized by addition of pentane/$Et_2O$ (50:1) mixture.

*Method B:* Trimethylsilyl azide (38 mg, 0.33 mmol) was added to a solution of azirine **1** (0.3 mmol) and triethylamine (30 mg, 0.3 mmol) in dichloromethane (2 mL) and stirred under argon atmosphere at room temperature for 24 h. The solvent was removed under reduced pressure at room temperature. The residue was purified by column chromatography on silica gel (EtOAc/hexane) and recrystallized from $Et_2O$/hexane mixture to give azidoazirines **2c**,**l**,**m**.

**Methyl 2-azido-3-phenyl-2*H*-azirine-2-carboxylate (2a)**




Compound **2a** (103 mg, 95%) was obtained as a colorless solid according to method *A* from azirine **1a**.

**3 mmol-scale synthesis.** Compound **2a** (545 mg, 84%) was obtained as a colorless solid according to method *A* from chloroazirine **1a**$^{Cl}$ (629 mg, 3 mmol), $NaN_3$ (390 mg, 6 mmol) in MeCN (24 mL); reaction time 4 h.

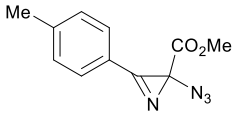
**Mp** 45 °C ($Et_2O$/pentane, dec.).

**$^1$H NMR** (400 MHz, $C_6D_6$) δ 7.44–7.37 (m, 2H), 6.95–6.89 (m, 1H), 6.86–6.79 (m, 2H), 3.17 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $C_6D_6$) δ 168.7, 162.5, 134.1, 130.4, 129.5, 121.1, 53.4, 52.7.

**HRMS (ESI-TOF)**: *m/z* $[M + Na]^+$ calcd for $C_{10}H_8N_4O_2^+$ 239.0539, found 239.0542.

**Methyl 2-azido-3-(4-methylphenyl)-2*H*-azirine-2-carboxylate (2b)**




Compound **2b** (77 mg, 67%) was obtained as a colorless solid, according to method *A* from azirine **1b**.

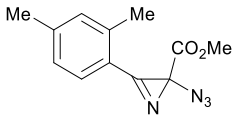
**Mp** 58 °C ($Et_2O$/pentane, dec.).

**$^1$H NMR** (400 MHz, $C_6D_6$) δ 7.42 (d, *J* = 7.9 Hz, 2H), 6.74 (d, *J* = 7.9 Hz, 2H), 3.23 (s, 3H), 1.88 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $C_6D_6$) δ 168.9, 162.1, 145.6, 130.5, 130.4, 118.2, 53.3, 52.7, 21.5.

**HRMS (ESI-TOF)**: *m/z* $[M + Na]^+$ calcd for $C_{11}H_{10}N_4O_2^+$ 253.0696, found 253.0697.

**Methyl 2-azido-3-(2,4-dimethylphenyl)-2*H*-azirine-2-carboxylate (2c)**




Compound **2c** (58 mg, 79%) was obtained as a colorless solid according to method *B* from azirine **1c** (85 mg, 0.3 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

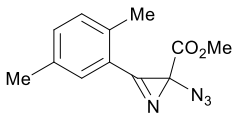
**Mp** 44 °C ($Et_2O$/hexane, dec.).

**$^1$H NMR** (400 MHz, $C_6D_6$) δ 7.33 (d, *J* = 7.8 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 1H), 6.57 (s, 1H), 3.21 (s, 3H), 2.40 (s, 3H), 1.88 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $C_6D_6$) δ 169.1, 161.1, 145.2, 142.0, 132.2, 127.5, 117.2, 53.4, 52.6, 52.0, 21.4, 19.5.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{12}H_{12}N_4NaO_2^+$ $[M+Na]^+$ 267.0852; found 267.0855.

**Methyl 2-azido-3-(2,5-dimethylphenyl)-2*H*-azirine-2-carboxylate (2d)**




Compound **2d** (108 mg, 88%) was obtained as a colorless solid, according to method *A* from azirine **1d**.

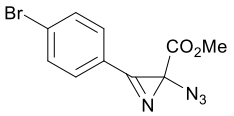
**Mp** 48 °C ($Et_2O$/pentane, dec.).

**$^1$H NMR** (400 MHz, $CD_3CN$) δ 7.61 (s, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 3.75 (s, 3H), 2.59 (s, 3H), 2.38 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CD_3CN$) δ 169.7, 162.5, 140.0, 138.1, 136.7, 133.5, 132.5, 119.9, 54.2, 52.3, 20.7, 19.5.

**HRMS (ESI-TOF)**: *m/z* $[M + Na]^+$ calcd for $C_{12}H_{12}N_4O_2^+$ 267.0852, found 267.0850.

**Methyl 2-azido-3-(4-bromophenyl)-2*H*-azirine-2-carboxylate (2e)**




The compound **2e** (130 mg, 88%) was obtained as a colorless solid, according to method *A* from azirine **1e**.

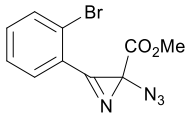
**Mp** 47 °C ($Et_2O$/pentane, dec.).

**$^1$H NMR** (400 MHz, $CD_3CN$) δ 7.94–7.77 (m, 4H), 3.75 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CD_3CN$) δ 169.2, 163.2, 134.3, 133.0, 130.7, 120.6, 54.2, 53.8.

**HRMS (ESI-TOF)**: *m/z* $[M + Na]^+$ calcd for $C_{10}H_7{}^{79}BrN_4O_2^+$ 316.9645, found 316.9655.

**Methyl 2-azido-3-(2-bromophenyl)-2*H*-azirine-2-carboxylate (2f)**




Compound **2f** (53 mg, 60%) was obtained as a colorless solid according to method *B* from azirine **1f** using EtOAc/hexane (1:4) as eluent for chromatography.

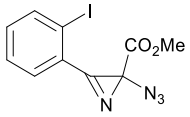
**Mp** 53 °C ($Et_2O$/hexane, dec.).

**$^1$H NMR** (400 MHz, $C_6D_6$) δ 7.45–7.41 (m, 1H), 7.03–6.99 (m, 1H), 6.59–6.54 (m, 1H), 6.52–6.47 (m, 1H), 3.20 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $C_6D_6$) δ 168.5, 163.2, 135.1, 133.9, 132.7, 127.1, 125.8, 121.9, 54.2, 52.8.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{10}H_7{}^{79}BrN_4NaO_2^+$ $[M+Na]^+$ 316.9645; found 316.9650.

**Methyl 2-azido-3-(2-iodophenyl)-2*H*-azirine-2-carboxylate (2g)**




Compound **2g** (64 mg, 62%) was obtained as a colorless solid according to method *B* from azirine **1g** using EtOAc/hexane (1:4) as eluent for chromatography.

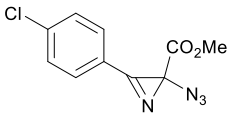
**Mp** 56–57 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $C_6D_6$) δ 7.49–7.40 (m, 1H), 7.38–7.30 (m, 1H), 6.67–6.59 (m, 1H), 6.41–6.34 (m, 1H), 3.23 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $C_6D_6$) δ 168.6, 165.4, 140.6, 134.9, 133.0, 128.6, 125.2, 99.3, 54.6, 52.8.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{10}H_7IN_4NaO_2^+$ $[M+Na]^+$ 364.9506; found 364.9517.

**Methyl 2-azido-3-(4-chlorophenyl)-2*H*-azirine-2-carboxylate (2h)**




Compound **2h** (103 mg, 82%) was obtained as a colorless solid, according to method *A* from azirine **1h**.

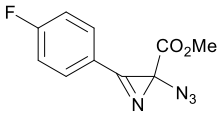
**Mp** 55 °C ($Et_2O$/pentane, dec.).

**$^1$H NMR** (400 MHz, $CD_3CN$) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 3.75 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CD_3CN$) δ 169.3, 163.0, 142.0, 133.0, 131.3, 120.2, 54.2, 53.9.

**HRMS (ESI-TOF)**: *m/z* $[M + Na]^+$ calcd for $C_{10}H_7ClN_4O_2^+$ 273.0150, found 273.0142.

**Methyl 2-azido-3-(4-fluorophenyl)-2*H*-azirine-2-carboxylate (2i)**




Compound **2i** (103 mg, 88%) was obtained as a colorless solid, according to method *A* from azirine **1i**.

**1 mmol-scale synthesis.** Compound **2i** (185 mg, 79%) was obtained as a colorless solid according to method *A* from azirine **1i** (272 mg, 1 mmol), $NaN_3$ (130 mg, 2 mmol) in MeCN (16 mL); reaction time 20 min. The product was recrystallized from pentane/$Et_2O$ (50:1) mixture.

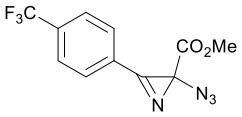
**Mp** 47 °C ($Et_2O$/pentane, dec.).

**$^1$H NMR** (400 MHz, $CD_3CN$) δ 8.05–8.02 (m, 2H), 7.41 (t, *J* = 8.8 Hz, 2H), 3.75 (s, 3H

**$^{13}$C{$^1$H} NMR** (100 MHz, $CD_3CN$) δ 169.4, 167.7 (d, *J* = 255.9 Hz), 162.7, 134.5 (d, *J* = 10.0 Hz), 118.4 (d, *J* = 22.9 Hz), 118.1 (d, *J* = 3.1 Hz), 54.2, 53.9.

**HRMS (ESI-TOF)**: *m/z* $[M + Na]^+$ calcd for $C_{10}H_7FN_4O_2^+$ 257.0445, found 257.0451.

**Methyl 2-azido-3-[4-(trifluoromethyl)phenyl]-2*H*-azirine-2-carboxylate (2j)**




Compound **2j** (95 mg, 67%) was obtained as a colorless solid, according to method *A* from azirine **1j**.

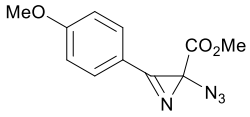
**Mp** 56 °C ($Et_2O$/pentane, dec.).

**$^1$H NMR** (400 MHz, $CD_3CN$) δ 8.16 (d, *J* = 8.3 Hz, 2H), 7.97 (d, *J* = 8.3 Hz, 1H), 3.76 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CD_3CN$) δ 169.1, 163.8, 136.3 (q, *J* = 32.5 Hz), 132.2, 127.8 (q, *J* = 3.9 Hz), 125.2, 124.7 (q, *J* = 272.1 Hz), 54.3, 54.0.

**HRMS (ESI-TOF)**: *m/z* $[M + Na]^+$ calcd for $C_{11}H_7F_3N_4O_2^+$ 307.0413, found 307.0417.

**Methyl 2-azido-3-(4-methoxyphenyl)-2*H*-azirine-2-carboxylate (2k)**




Compound **2k** (30 mg, 24%) was obtained as a colorless solid, according to method *A* from azirine **1k**.

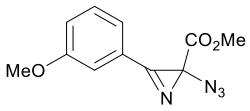
**Mp** 40 °C ($Et_2O$/pentane, dec.).

**$^1$H NMR** (400 MHz, $C_6D_6$) δ 7.48 (d, *J* = 8.7 Hz, 2H), 6.42 (t, *J* = 7.1 Hz, 1H), 3.23 (s, 3H), 3.03 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $C_6D_6$) δ 167.5, 164.9, 163.9, 133.1, 115.3, 112.2, 55.0, 53.4, 45.5.

**HRMS (ESI-TOF)**: *m/z* $[M + Na]^+$ calcd for $C_{11}H_{10}N_4NaO_3^+$ 269.0645, found 269.0643.

**Methyl 2-azido-3-(3-methoxyphenyl)-2*H*-azirine-2-carboxylate (2l)**

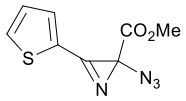



Compound **2l** (113 mg, 92%) was obtained as a colorless solid, according to method *A* from azirine **1l**.

**Mp** 48 °C ($Et_2O$/pentane, dec.).

**$^1$H NMR** (400 MHz, $CD_3CN$) δ 7.63–7.47 (m, 3H), 7.35–7.27 (m, 1H), 3.88 (s, 3H), 3.75 (s, 3H).
**$^{13}$C{$^1$H} NMR** (100 MHz, $CD_3CN$) δ 169.4, 163.6, 161.6, 132.1, 123.9, 122.6, 115.6, 56.6, 54.2, 54.0.
**HRMS (ESI-TOF)**: *m/z* $[M + Na]^+$ calcd for $C_{11}H_{10}N_4O_3^+$ 269.0645, found 269.0638.

**Methyl 2-azido-3-(thiophen-2-yl)-2H-azirine-2-carboxylate (2m)**



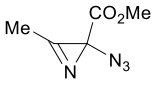

Compound **2m** (24 mg, 72%) was obtained as a brownish oil according to method *A* (reaction temperature 0 °C, rection time 3 h) from azirine **1m** (39 mg, 0.15 mmol).

**$^1$H NMR** (400 MHz, $CD_3CN$) δ 8.17 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.92 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.38 (dd, *J* = 5.0, 3.8 Hz, 2H), 3.75 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CD_3CN$) δ 169.1, 156.9, 139.2, 138.4, 130.5, 122.7, 54.2, 54.1.

**HRMS (ESI-TOF)**: *m/z* $[M + Na]^+$ calcd for $C_8H_6N_4NaO_2S^+$ 245.0104, found 245.0099.

**Methyl 2-azido-3-methyl-2*H*-azirine-2-carboxylate (2n)**

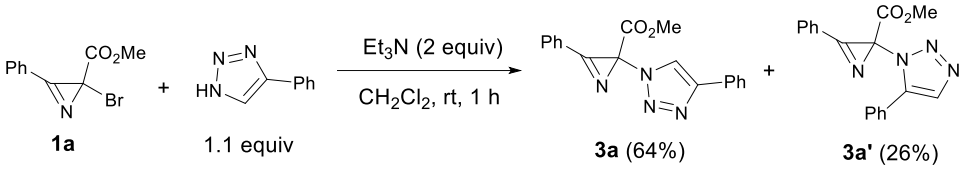


Compound **2n** (16 mg, 70%) was obtained as a colorless solid according to method *A* (reaction temperature 0 °C, rection time 3 h) from azirine **1n** (23 mg, 0.15 mmol). Due to the fact that this compound is significantly less thermally stable than azides **2a**–**m**, it turned out to be impossible to measure its exact mass as well as to carry out elemental analysis.

**$^1$H NMR** (400 MHz, $CD_3CN$) δ 3.73 (s, 3H), 2.53 (s, 3H).

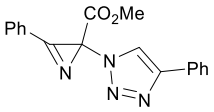
**$^{13}$C{$^1$H} NMR** (100 MHz, $CD_3CN$) δ 169.7, 165.6, 53.9, 52.4, 11.8.

## 6. Synthesis of triazoles 3a and 3a'




4-Phenyl-1*H*-1,2,3-triazole (80 mg, 0.55 mmol) was added to a solution of azirine **1a** (127 mg, 0.5 mmol) and triethylamine (101 mg, 1.0 mmol) in dichloromethane (6 mL) and stirred at room temperature for 1 h. Then the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane) and to give triazolylazirines **3a** and **3a'**.

**Methyl 3-phenyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate** (**3a)**



Compound **3a** (102 mg, 64%) was obtained as colorless solid using EtOAc/hexane (1:4) as eluent for chromatography.

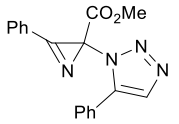
**mp** 120–122 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.26–8.15 (m, 2H), 7.94–7.84 (m, 2H), 7.79–7.72 (m, 1H), 7.71–7.63 (m, 2H), 7.50–7.41 (m, 2H), 7.41–7.32 (m, 1H), 3.84 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.5, 158.9, 148.2, 135.1, 131.6, 130.2, 129.6, 128.8, 128.3, 125.9, 120.9, 120.1, 53.7, 50.3.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{18}H_{16}N_4O_2^+$ $[M+H]^+$ 319.1190; found 319.1191.

**Methyl 3-phenyl-2-(5-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3a')**



Compound **3a'** (41 mg, 26%) was obtained as colorless solid using EtOAc/hexane (1:4) as eluent for chromatography.

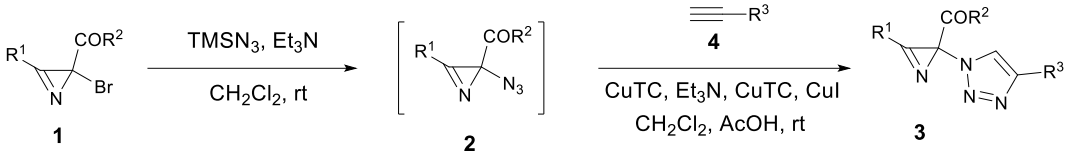
**Mp** 102–103 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.26–8.19 (m, 2H), 7.96 (s, 1H), 7.85–7.79 (m, 2H), 7.79–7.73 (m, 1H), 7.72–7.65 (m, 2H), 7.48–7.41 (m, 2H), 7.40–7.34 (m, 1H), 3.84 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.4, 158.3, 149.0, 134.9, 132.6, 131.5, 129.7, 129.5, 128.84, 128.80, 126.2, 120.3, 53.59, 53.56.

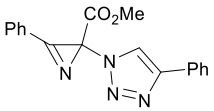
**HRMS (ESI-TOF)**: *m/z* calcd for $C_{18}H_{16}N_4O_2^+$ $[M+H]^+$ 319.1190; found 319.1191.

## 7. Synthesis of triazoles 3a–3zk




*General procedure:* Trimethylsilyl azide (38 mg, 0.33 mmol) was added to a solution of azirine **1** (0.3 mmol) and triethylamine (30 mg, 0.3 mmol) in dichloromethane (2 mL) and stirred under argon atmosphere at room temperature for 4 h. Triethylamine (30 mg, 0.3 mmol), alkyne **4** (0.45–0.6 mmol), copper(I) thiophene-2-carboxylate (17 mg, 0.09 mmol), copper(I) iodide (3.4 mg, 0.018 mmol, 6 mol %), and acetic acid (3.6 mg, 0.06 mmol) the following components were sequentially added, and the reaction mixture was stirred overnight at room temperature under argon atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel to give triazole **3**.

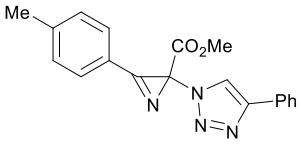
**Methyl 3-phenyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3a)**



Compound **3a** (53 mg, 55%) was obtained as a colorless solid according to the general procedure from azirine **1a** (76 mg, 0.3 mmol) and phenylacetylene (**4a**) (46 mg, 0.45 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

Compound **3a** (102 mg, 64%) was obtained as colorless solid using EtOAc/hexane (1:4) as eluent for chromatography.

**Methyl 3-(4-methylphenyl)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3b)**




Compound **3b** (54 mg, 54%) was obtained as a colorless solid according to the general procedure from azirine **1b** (80 mg, 0.3 mmol) and phenylacetylene (**4a**) (46 mg, 0.45 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

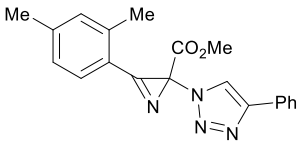
**Mp** 132–134 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.15–8.04 (m, 2H), 7.94–7.81 (m, 2H), 7.51–7.41 (m, 4H), 7.40–7.32 (m, 1H), 3.82 (s, 3H), 2.51 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.7, 158.4, 148.1, 146.5, 131.6, 130.3, 130.2, 128.8, 128.3, 125.8, 120.8, 117.2, 53.6, 50.1, 22.1.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{19}H_{16}N_4NaO_2^+$ $[M+Na]^+$ 355.1165; found 355.1153.

**Methyl 3-(2,4-dimethylphenyl)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3c)**




Compound **3c** (75 mg, 72%) was obtained as a colorless solid according to the general procedure from azirine **1c** (85 mg, 0.3 mmol) and phenylacetylene (**4a**) (46 mg, 0.45 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

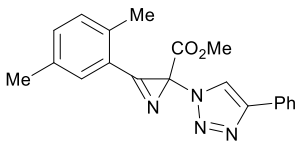
**Mp** 92–94 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.07–7.98 (m, 1H), 7.93–7.84 (m, 2H), 7.49–7.41 (m, 2H), 7.40–7.32 (m, 1H), 7.32–7.24 (m, 2H), 3.83 (s, 3H), 2.75 (s, 3H), 2.47 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 168.0, 157.4, 147.9, 146.2, 142.8, 133.9, 132.0, 130.3, 128.8, 128.3, 127.6, 125.8, 120.8, 116.1, 53.6, 48.5, 21.9, 20.0.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{20}H_{19}N_4O_2^+$ $[M+H]^+$ 347.1503; found 347.1503.

**Methyl 3-(2,5-dimethylphenyl)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3d)**




Compound **3d** (82 mg, 79%) was obtained as a colorless solid according to the general procedure from azirine **1d** (85 mg, 0.3 mmol) and phenylacetylene (**4a**) (46 mg, 0.45 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

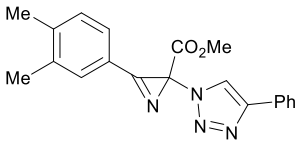
**Mp** 113–115 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.00–7.92 (m, 1H), 7.92–7.81 (m, 2H), 7.50–7.40 (m, 3H), 7.40–7.30 (m, 2H), 3.84 (s, 3H), 2.74 (s, 3H), 2.45 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 168.0, 157.9, 148.0, 139.9, 136.6, 135.7, 134.1, 131.1, 130.3, 128.8, 128.3, 125.8, 120.8, 118.6, 53.7, 48.6, 20.7, 19.6.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{20}H_{18}N_4NaO_2^+$ $[M+Na]^+$ 369.1322; found 369.1328.

**Methyl 3-(3,4-dimethylphenyl)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3e)**




Compound **3e** (37 mg, 36%) was obtained as a colorless solid according to the general procedure from azirine **1o** (85 mg, 0.3 mmol) and phenylacetylene (**4a**) (46 mg, 0.45 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

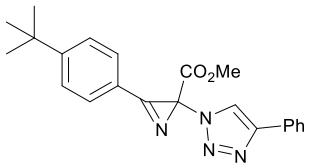
**Mp** 134–136 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.97–7.92 (m, 2H), 7.90–7.85 (m, 2H), 7.47–7.41 (m, 3H), 7.38–7.33 (m, 1H), 3.82 (s, 3H), 2.42 (s, 3H), 2.40 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.8, 158.4, 148.0, 145.3, 138.3, 132.5, 130.8, 130.3, 129.2, 128.8, 128.3, 125.8, 120.8, 117.4, 53.6, 50.2, 20.4, 19.6.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{20}H_{19}N_4O_2^+$ $[M+H]^+$ 347.1503; found 347.1503.

**Methyl 3-[4-(*tert*-butyl)phenyl]-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3f)**




Compound **3f** (50 mg, 45%) was obtained as a colorless solid according to the general procedure from azirine **1p** (93 mg, 0.3 mmol) and phenylacetylene (**4a**) (46 mg, 0.45 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

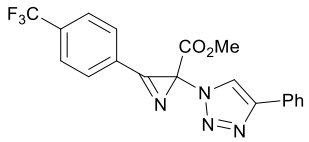
**Mp** 151–153 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.20–8.06 (m, 2H), 7.93–7.83 (m, 2H), 7.72–7.65 (m, 2H), 7.49–7.41 (m, 2H), 7.40–7.32 (m, 1H), 3.83 (s, 3H), 1.41 (s, 9H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.8, 159.4, 158.3, 148.1, 131.6, 130.3, 128.8, 128.3, 126.7, 125.9, 120.8, 117.2, 53.6, 50.1, 35.6, 31.0.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{22}H_{22}N_4NaO_2^+$ $[M+Na]^+$ 397.1635; found 397.1650.

**Methyl 2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-3-(4-(trifluoromethyl)phenyl)-2*H*-azirine-2-carboxylate (3g)**




Compound **3g** (35 mg, 30%) was obtained as a colorless solid according to the general procedure from azirine **1j** (97 mg, 0.3 mmol) and phenylacetylene (**4a**) (46 mg, 0.45 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

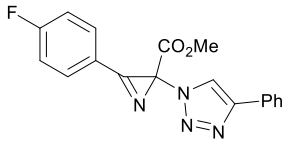
**Mp** 156–158 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.35 (s, 2H), 7.99–7.93 (m, 2H), 7.92–7.81 (m, 2H), 7.51–7.43 (m, 2H), 7.42–7.33 (m, 1H), 3.85 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.0, 158.8, 148.5, 136.3 (q, $J$ = 33.1 Hz), 131.9, 130.0, 128.9, 128.5, 126.6 (q, $J$ = 3.6 Hz), 125.9, 123.7, 123.2 (q, $J$ = 273.2 Hz), 121.0, 53.9, 50.5.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{19}H_{13}F_3N_4NaO_2^+$ $[M+Na]^+$ 409.0883; found 409.0882.

**Methyl 3-(4-fluorophenyl)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3h)**




Compound **3h** (60 mg, 60%) was obtained as a colorless solid according to the general procedure from azirine **1i** (82 mg, 0.3 mmol) and phenylacetylene (**4a**) (46 mg, 0.45 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

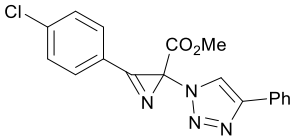
**Mp** 144–146 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.29–8.19 (m, 2H), 7.93–7.83 (m, 2H), 7.50–7.42 (m, 2H), 7.41–7.32 (m, 3H), 3.84 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.4, 166.8 (d, *J* = 165.5 Hz), 157.9, 148.3, 134.3 (d, *J* = 9.9 Hz), 130.1, 128.8, 128.4, 125.9, 120.9, 117.2 (d, *J* = 22.4 Hz), 116.6 (d, *J* = 3.1 Hz), 53.8, 50.3.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{18}H_{13}FN_4NaO_2^+$ $[M+Na]^+$ 359.0915; found 359.0917.

**Methyl 3-(4-chlorophenyl)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3i)**




Compound **3i** (48 mg, 45%) was obtained as a colorless solid according to the general procedure from azirine **1h** (86 mg, 0.3 mmol) and phenylacetylene (**4a**) (46 mg, 0.45 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

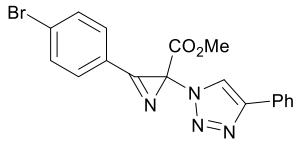
**Mp** 175–177 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.23–8.10 (m, 2H), 7.94–7.83 (m, 2H), 7.71–7.62 (m, 2H), 7.49–7.42 (m, 2H), 7.41–7.33 (m, 1H), 3.84 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.3, 158.3, 148.3, 141.8, 132.7, 130.1 (2C), 128.9, 128.4, 125.9, 120.9, 118.7, 53.8, 50.3.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{18}H_{13}{}^{35}ClN_4NaO_2^+$ $[M+Na]^+$ 375.0619; found 375.0620.

**Methyl 3-(4-bromophenyl)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3j)**




Compound **3j** (58 mg, 49%) was obtained as a colorless solid according to the general procedure from azirine **1e** (100 mg, 0.3 mmol) and phenylacetylene (**4a**) (46 mg, 0.45 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

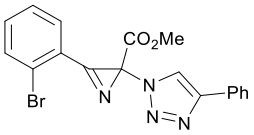
**Mp** 181–182 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.11–8.04 (m, 2H), 7.90–7.85 (m, 2H), 7.85–7.79 (m, 2H), 7.48–7.42 (m, 2H), 7.40–7.34 (m, 1H), 3.83 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.2, 158.5, 148.3 133.1, 132.7, 130.6, 130.1, 128.8, 128.4, 125.9, 120.9, 119.1, 53.8, 50.3.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{18}H_{13}{}^{79}BrN_4NaO_2^+$ $[M+Na]^+$ 419.0114; found 419.0118.

**Methyl 3-(2-bromophenyl)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3k)**




Compound **3k** (95 mg, 80%) was obtained as a colorless solid according to the general procedure from azirine **1f** (100 mg, 0.3 mmol) and phenylacetylene (**4a**) (46 mg, 0.45 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

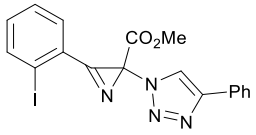
**Mp** 64–67 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.30–8.16 (m, 1H), 7.94–7.80 (m, 3H), 7.65–7.56 (m, 2H), 7.48–7.41 (m, 2H), 7.40–7.32 (m, 1H), 3.86 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.3, 158.5, 148.1, 135.8, 135.1, 134.3, 130.2, 128.8, 128.3, 128.2, 126.4, 125.9, 121.2, 121.1, 53.8, 50.1.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{18}H_{13}{}^{79}BrN_4NaO_2^+$ $[M+Na]^+$ 419.0114; found 419.0124.

**Methyl 3-(2-iodophenyl)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3l)**




Compound **3l** (92 mg, 69%) was obtained as a colorless solid according to the general procedure from azirine **1g** (114 mg, 0.3 mmol) and phenylacetylene (**4a**) (46 mg, 0.45 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

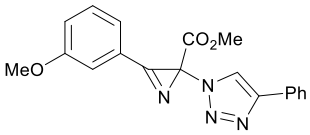
**Mp** 67–68 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.21–8.18 (m, 1H), 8.14–8.11 (m, 1H), 7.90–7.86 (m, 2H), 7.68–7.62 (m, 1H), 7.47–7.41 (m, 3H), 7.40–7.34 (m, 1H), 3.86 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.3, 160.3, 148.1, 141.1, 135.62, 135.58, 130.2, 128.8 (2C), 128.3, 125.9, 124.4, 121.1, 99.2, 53.8, 50.8.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{18}H_{14}IN_4O_2^+$ $[M+H]^+$ 445.0156; found 445.0169.

**Methyl 3-(3-methoxyphenyl)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3m)**




Compound **3m** (52 mg, 50%) was obtained as a colorless solid according to the general procedure from azirine **1l** (85 mg, 0.3 mmol) and phenylacetylene (**4a**) (46 mg, 0.45 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

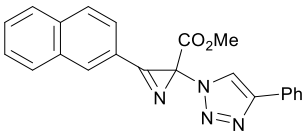
**Mp** 101–103 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.94–7.84 (m, 2H), 7.84–7.77 (m, 1H), 7.74–7.65 (m, 1H), 7.60–7.53 (m, 1H), 7.49–7.42 (m, 2H), 7.40–7.33 (m, 1H), 7.32–7.26 (m, 1H), 3.93 (s, 3H), 3.84 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.5, 160.2, 159.0, 148.2, 130.7, 130.2, 128.8, 128.3, 125.9, 124.2, 122.1, 121.1, 120.8, 115.1, 55.7, 53.7, 50.5.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{19}H_{17}N_4O_3^+$ $[M+H]^+$ 349.1295; found 349.1299.

**Methyl 3-(naphthalen-2-yl)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3n)**




Compound **3n** (65 mg, 59%) was obtained according as a colorless solid to the general procedure from azirine **1q** (91 mg, 0.3 mmol) and phenylacetylene (**4a**) (46 mg, 0.45 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

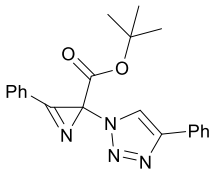
**Mp** 127–129 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.34 (s, 1H), 8.21–8.14 (m, 1H), 8.11–8.05 (m, 2H), 8.00–7.94 (m, 1H), 7.94–7.86 (m, 2H), 7.76–7.63 (m, 2H), 7.49–7.42 (m, 2H), 7.41–7.34 (m, 1H), 3.85 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.7, 159.0, 148.2, 136.3, 134.9, 132.7, 130.2, 129.8, 129.7, 129.6, 128.8, 128.3, 128.1, 127.6, 125.9, 125.1, 120.9, 117.2, 53.7, 50.5.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{22}H_{16}N_4NaO_2^+$ $[M+Na]^+$ 391.1165; found 391.1160.

***tert*-Butyl 3-phenyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3o)**




Compound **3o** (43 mg, 40%) was obtained as a colorless solid according to the general procedure from azirine **1r** (89 mg, 0.3 mmol) and phenylacetylene (**4a**) (46 mg, 0.45 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

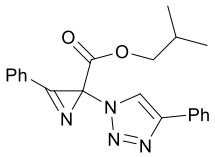
**Mp** 149–151 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.26–8.13 (m, 2H), 7.97–7.80 (m, 2H), 7.78–7.72 (m, 1H), 7.70–7.63 (m, 2H), 7.49–7.41 (m, 2H), 7.41–7.31 (m, 1H), 1.47 (s, 9H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 165.9, 159.3, 148.0, 134.8, 131.4, 130.4, 129.5, 128.8, 128.3, 125.8, 121.0, 120.5, 84.4, 51.0, 27.8.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{21}H_{21}N_4O_2^+$ $[M+H]^+$ 361.1659; found 361.1661.

**Isobutyl 3-phenyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3p)**



Compound **3p** (60 mg, 56%) was obtained as a colorless solid according to the general procedure from azirine **1s** (89 mg, 0.3 mmol) and phenylacetylene (**4a**) (46 mg, 0.45 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

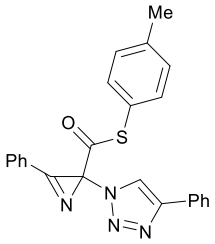
**Mp** 94–96 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.27–8.15 (m, 2H), 7.93–7.84 (m, 2H), 7.79–7.71 (m, 1H), 7.70–7.63 (m, 2H), 7.49–7.42 (m, 2H), 7.41–7.32 (m, 1H), 4.08–3.98 (m, 2H), 2.01–1.84 (m, 1H), 0.86 (d, *J* = 2.5 Hz, 3H), 0.84 (d, *J* = 2.5 Hz, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.0, 159.0, 148.1, 135.0, 131.5, 130.3, 129.5, 128.8, 128.3, 125.8, 120.9, 120.2, 72.8, 50.4, 27.5, 18.71, 18.68.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{21}H_{20}N_4NaO_2^+$ $[M+Na]^+$ 383.1478; found 383.1476.

***S*-(4-Methylphenyl) 3-phenyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carbothioate (3q)**



Compound **3q** (12 mg, 10%) was obtained as a colorless solid according to the general procedure from azirine **1t** (104 mg, 0.3 mmol) and phenylacetylene (**4a**) (46 mg, 0.45 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

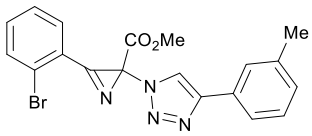
**Mp** 88–91 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.36–8.22 (m, 3H), 7.89–7.84 (m, 2H), 7.83–7.78 (m, 1H), 7.75–7.69 (m, 2H), 7.47–7.41 (m, 2H), 7.38–7.34 (m, 1H), 7.32–7.27 (m, 2H), 7.27–7.22 (m, 2H), 2.39 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 193.0, 158.6, 148.2, 140.6, 135.4, 134.6, 131.9, 130.3, 130.1, 129.7, 128.8, 128.4, 125.9, 122.3, 121.2, 119.8, 56.8, 21.3.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{24}H_{18}N_4NaOS^+$ $[M+Na]^+$ 433.1094; found 433.1086.

**Methyl 3-(2-bromophenyl)-2-[4-(3-methylphenyl)]-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3r)**




Compound **3r** (89 mg, 72%) was obtained as a colorless solid according to the general procedure from azirine **1f** (100 mg, 0.3 mmol) and alkyne **4b** (70 mg, 0.6 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

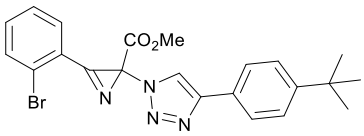
**Mp** 66–68 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.30–8.17 (m, 1H), 7.89–7.80 (m, 1H), 7.76–7.69 (m, 1H), 7.69–7.65 (m, 1H), 7.65–7.54 (m, 2H), 7.38–7.30 (m, 1H), 7.24–7.11 (m, 1H), 3.86 (s, 3H), 2.42 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.3, 158.5, 148.2, 138.5, 135.8, 135.1, 134.3, 130.0, 129.1, 128.7, 128.2, 126.5, 126.4, 123.0, 121.2, 121.0, 53.8, 50.1, 21.4.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{19}H_{15}{}^{79}BrN_4NaO_2^+$ $[M+Na]^+$ 433.0271; found 433.0270.

**Methyl 3-(2-bromophenyl)-2-(4-(4-(*tert*-butyl)phenyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3s)**




Compound **3s** (92 mg, 68%) was obtained as a colorless solid according to the general procedure from azirine **1f** (100 mg, 0.3 mmol) and alkyne **4c** (95 mg, 0.6 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

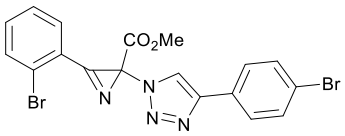
**Mp** 80–82 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.29–8.14 (m, 1H), 7.91–7.83 (m, 1H), 7.83–7.74 (m, 2H), 7.67–7.55 (m, 2H), 7.52–7.43 (m, 2H), 3.86 (s, 3H), 1.37 (s, 9H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.3, 158.5, 151.5, 148.1, 135.8, 135.1, 134.3, 128.2, 127.4, 126.4, 125.7, 125.6, 121.2, 120.8, 53.8, 50.1, 34.6, 31.2.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{22}H_{22}{}^{79}BrN_4O_2^+$ $[M+H]^+$ 453.0921; found 453.0920.

**Methyl 3-(2-bromophenyl)-2-(4-(4-bromophenyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3t)**




Compound **3t** (107 mg, 75%) was obtained as a colorless solid according to the general procedure from azirine **1f** (100 mg, 0.3 mmol) and alkyne **4d** (109 mg, 0.6 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

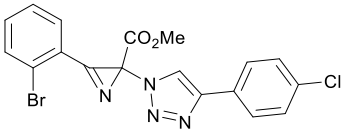
**Mp** 155–157 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.29–8.16 (m, 1H), 7.92–7.81 (m, 1H), 7.79–7.70 (m, 2H), 7.67–7.59 (m, 2H), 7.59–7.54 (m, 2H), 3.86 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.2, 158.5, 147.0, 135.9, 135.0, 134.4, 132.0, 129.2, 128.2, 127.4, 126.5, 122.3, 121.2, 121.1, 53.8, 50.2.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{18}H_{12}{}^{79}Br_2N_4NaO_2^+$ $[M+Na]^+$ 496.9219; found 496.9219.

**Methyl 3-(2-bromophenyl)-2-(4-(4-chlorophenyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3u)**




Compound **3u** (95 mg, 73%) was obtained as a colorless solid according to the general procedure from azirine **1f** (100 mg, 0.3 mmol) and alkyne **4e** (82 mg, 0.6 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

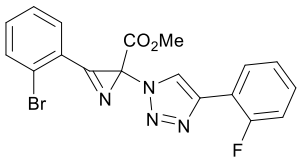
**Mp** 190–193 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.36–8.27 (m, 2H), 8.25–8.18 (m, 1H), 8.12–7.99 (m, 2H), 7.90–7.82 (m, 1H), 7.69–7.57 (m, 2H), 3.87 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.1, 158.4, 147.5, 145.9, 136.4, 136.0, 134.9, 134.4, 128.3, 126.5, 126.3, 124.3, 122.9, 120.9, 53.9, 50.4.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{18}H_{11}{}^{79}BrClN_4O_2^-$ $[M–H]^-$: 428.9759; found 428.9714.

**Methyl 3-(2-bromophenyl)-2-(4-(2-fluorophenyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3v)**




Compound **3v** (81 mg, 65%) was obtained as a colorless solid according to the general procedure from azirine **1f** (100 mg, 0.3 mmol) and alkyne **4f** (72 mg, 0.6 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

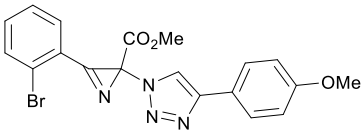
**Mp** 110–111 °C (EtOAc/hexane).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 3.5 Hz, 1H), 8.34–8.19 (m, 2H), 7.88–7.80 (m, 1H), 7.66–7.57 (m, 2H), 7.37–7.30 (m, 1H), 7.30–7.22 (m, 1H), 7.21–7.14 (m, 1H), 3.87 (s, 3H).

**$^{13}$C{$^{1}$H} NMR** (100 MHz, $CDCl_3$) δ 167.2, 159.3 (d, *J* = 248.1 Hz), 158.5, 141.5 (d, *J* = 2.4 Hz), 135.8, 135.0, 134.3, 129.5 (d, *J* = 8.4 Hz), 128.2, 127.9 (d, *J* = 3.6 Hz), 126.4, 124.5 (d, *J* = 3.6 Hz), 124.2 (d, *J* = 13.1 Hz), 121.1, 118.2 (d, *J* = 13.0 Hz), 115.7 (d, *J* = 21.6 Hz), 53.8, 50.2.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{18}H_{13}{}^{79}BrFN_4O_2^+$ $[M+H]^+$ 415.0200; found 415.0205.

**Methyl 3-(2-bromophenyl)-2-(4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3w)**




Compound **3w** (101 mg, 79%) was obtained as a colorless solid according to the general procedure from azirine **1f** (100 mg, 0.3 mmol) and alkyne **4g** (79 mg, 0.6 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

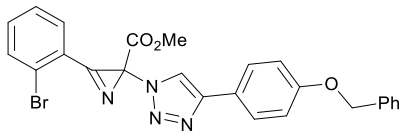
**mp** 55–57 °C (EtOAc/hexane).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.33–8.15 (m, 2H), 7.93–7.73 (m, 3H), 7.65–7.56 (m, 2H), 7.03–6.94 (m, 2H), 3.86 (s, 6H).

**$^{13}$C{$^{1}$H} NMR** (100 MHz, $CDCl_3$) δ 167.4, 159.8, 158.6, 148.0, 135.8, 135.1, 134.3, 128.2, 127.2, 126.4, 122.9, 121.2, 120.1, 114.3, 55.3, 53.8, 50.1.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{19}H_{16}{}^{79}BrN_4O_3^+$ $[M+H]^+$ 427.0400; found 427.0408.

**Methyl 2-{4-[4-(benzyloxy)phenyl]-1*H*-1,2,3-triazol-1-yl}-3-(2-bromophenyl)-2*H*-azirine-2-carboxylate (3x)**




Compound **3x** (86 mg, 57%) was obtained as a colorless solid according to the general procedure from azirine **1f** (100 mg, 0.3 mmol) and alkyne **4h** (95 mg, 0.6 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

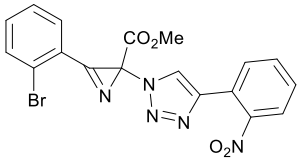
**Mp** 113–114 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.29–8.19 (m, 2H), 7.88–7.77 (m, 3H), 7.65–7.56 (m, 2H), 7.50–7.44 (m, 2H), 7.44–7.38 (m, 2H), 7.38–7.32 (m, 1H), 7.09–7.03 (m, 2H), 5.13 (s, 2H), 3.86 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.3, 159.0, 158.5, 147.9, 136.8, 135.7, 135.1, 134.3, 128.6, 128.2, 128.0, 127.5, 127.2, 126.4, 123.2, 121.21, 120.18, 115.2, 70.0, 53.8, 50.1.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{25}H_{19}{}^{79}BrN_4NaO_3^+$ $[M+Na]^+$ 525.0533; found 525.0540.

**Methyl 3-(2-bromophenyl)-2-(4-(2-nitrophenyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3y)**




Compound **3y** (60 mg, 45%) was obtained as a brown solid according to the general procedure from azirine **1f** (100 mg, 0.3 mmol) and alkyne **4i** (88 mg, 0.6 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

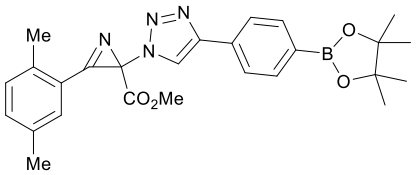
**Mp** 59–61 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.24–8.19 (m, 1H), 8.03–7.97 (m, 1H), 7.88–7.83 (m, 2H), 7.69–7.61 (m, 3H), 7.56–7.50 (m, 1H), 3.87 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.0, 158.4, 148.4, 142.5, 135.9, 135.0, 134.4, 132.5, 131.1, 129.2, 128.2, 126.5, 124.7, 124.2, 124.1, 121.0, 53.9, 50.4.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{18}H_{13}{}^{79}BrN_5O_4^+$ $[M+H]^+$ 442.0145; found 442.0151.

**Methyl 3-(2,5-dimethylphenyl)-2-{4-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-1*H*-1,2,3-triazol-1-yl}-2*H*-azirine-2-carboxylate (3z)**




Compound **3z** (198 mg, 70%) was obtained as a brown solid according to the general procedure (with double amounts of all reagents) from azirine **1d** (169 mg, 0.6 mmol) and alkyne **4j** (88 mg, 0.6 mmol) in dichloromethane (5 mL) using EtOAc/hexane (1:4) as eluent for chromatography.

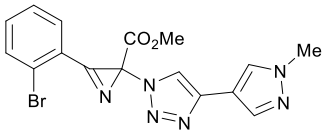
**Mp** 131–132 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $C_6D_6$) δ 8.23–8.14 (m, 2H), 8.04–7.98 (m, 1H), 7.98–7.90 (m, 2H), 7.90–7.82 (m, 1H), 6.89–6.81 (m, 1H), 6.81–6.74 (m, 1H), 3.21 (s, 3H), 2.54 (s, 3H), 1.88 (s, 3H), 1.13 (s, 12H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $C_6D_6$) δ 168.1, 158.7, 148.3, 139.9, 136.9, 135.9, 135.5, 134.2, 133.8, 131.2, 125.6, 121.8, 119.4, 83.7, 53.0, 49.3, 24.9, 20.3, 19.5.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{26}H_{29}BN_4NaO_4^+$ $[M+Na]^+$ 495.2174; found 495.2202.

**Methyl 3-(2-bromophenyl)-2-(4-(1-methyl-1*H*- pyrazol-4-yl)-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3za)**




Compound **3za** (85 mg, 71%) was obtained as a colorless solid according to the general procedure from azirine **1f** (100 mg, 0.3 mmol) and alkyne **4k** (64 mg, 0.6 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

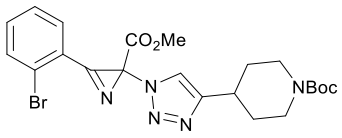
**Mp** 145–147 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.31–8.16 (m, 1H), 8.13 (s, 1H), 7.91–7.81 (m, 1H), 7.81–7.70 (m, 2H), 7.65–7.52 (m, 2H), 3.94 (s, 3H), 3.83 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.3, 158.5, 141.1, 137.1, 135.8, 135.0, 134.3, 128.1, 127.8, 126.3, 121.1, 120.0, 112.7, 53.7, 50.0, 39.0.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{16}H_{14}{}^{79}BrN_6O_2^+$ $[M+H]^+$ 401.0356; found 401.0357.

**_tert_-Butyl 4-(1-(3-(2-bromophenyl)-2-(methoxycarbonyl)-2*H*-azirin-2-yl)-1*H*-1,2,3-triazol-4-yl)piperidine-1-carboxylate (3zb)**




Compound **3zb** (120 mg, 79%) was obtained as a colorless solid according to the general procedure from azirine **1f** (100 mg, 0.3 mmol) and alkyne **4l** (95 mg, 0.6 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

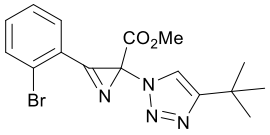
**Mp** 152–153 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.23–8.14 (m, 1H), 7.89–7.79 (m, 2H), 7.64–7.54 (m, 2H), 4.24–4.07 (m, 2H), 3.82 (s, 3H), 3.00–2.84 (m, 3H), 2.10–2.00 (m, 2H), 1.70–1.59 (m, 2H), 1.47 (s, 9H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.4, 158.5, 154.8, 152.0, 135.7, 135.1, 134.3, 128.1, 126.3, 121.2, 121.0, 79.4, 53.7, 49.9, 43.7, 33.5, 31.5, 28.4.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{22}H_{26}{}^{79}BrN_5NaO_4^+$ $[M+Na]^+$ 526.1060; found 526.1063.

**Methyl 3-(2-bromophenyl)-2-(4-(*tert*-butyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3zc)**



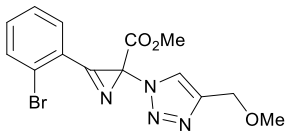

Compound **3zc** (65 mg, 57%) was obtained as a colorless oil according to the general procedure from azirine **1f** (100 mg, 0.3 mmol) and alkyne **4m** (49 mg, 0.6 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.26–8.13 (m, 1H), 7.89–7.75 (m, 2H), 7.61–7.52 (m, 2H), 3.82 (s, 3H), 1.37 (s, 9H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.5, 158.5, 158.0, 135.6, 135.2, 134.2, 128.0, 126.3, 121.3, 119.8, 53.6, 49.7, 30.8, 30.1.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{16}H_{18}{}^{79}BrN_4O_2^+$ $[M+H]^+$ 377.0608; found 377.0607.

**Methyl 3-(2-bromophenyl)-2-(4-(methoxymethyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3zd)**




Compound **3zd** (101 mg, 92%) was obtained as a colorless solid according to the general procedure from azirine **1f** (100 mg, 0.3 mmol) and alkyne **4n** (42 mg, 0.6 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

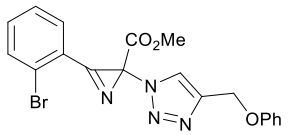
**Mp** 85–87 °C (EtOAc/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.23–8.16 (m, 1H), 8.11 (s, 1H), 7.88–7.80 (m, 1H), 7.64–7.56 (m, 2H), 4.62 (AB-q, *J* = 4.1 Hz, 2H), 3.83 (s, 3H), 3.43 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.2, 158.5, 145.4, 135.8, 135.0, 134.3, 128.2, 126.4, 124.0, 121.1, 65.8, 58.3, 53.7, 50.1.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{14}H_{13}{}^{79}BrN_4NaO_3^+$ $[M+Na]^+$ 387.0063; found 387.0060.

**Methyl 3-(2-bromophenyl)-2-(4-(phenoxymethyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3ze)**




Compound **3ze** (104 mg, 81%) was obtained as a colorless solid according to the general procedure from azirine **1f** (100 mg, 0.3 mmol) and alkyne **4o** (79 mg, 0.6 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

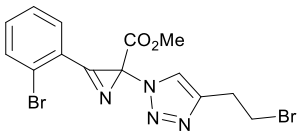
**Mp** 78–80 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.37–8.07 (m, 2H), 7.92–7.77 (m, 1H), 7.66–7.55 (m, 2H), 7.36–7.28 (m, 2H), 7.09–6.94 (m, 3H), 5.31–5.21 (m, 2H), 3.84 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.2, 158.5, 158.2, 144.6, 135.8, 135.0, 134.3, 129.5, 128.2, 126.4, 124.4, 121.3, 121.1, 114.8, 61.8, 53.8, 50.2.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{19}H_{16}{}^{79}BrN_4O_3^+$ $[M+H]^+$ 427.0400; found 427.0401.

**Methyl 2-(4-(2-bromoethyl)-1*H*-1,2,3-triazol-1-yl)-3-(2-bromophenyl)-2*H*-azirine-2-carboxylate (3zf)**




Compound **3zf** (108 mg, 84%) was obtained as a colorless solid according to the general procedure from azirine **1f** (100 mg, 0.3 mmol) and alkyne **4p** (80 mg, 0.6 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

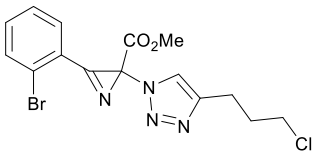
**Mp** 142–144 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.27–8.11 (m, 1H), 8.04 (s, 1H), 7.88–7.79 (m, 1H), 7.64–7.56 (m, 2H), 3.84 (s, 3H), 3.72–3.62 (m, 2H), 3.41–3.27 (m, 2H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.3, 158.5, 145.1, 135.8, 135.0, 134.3, 128.2, 126.4, 123.2, 121.2, 53.8, 50.0, 30.9, 29.4.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{14}H_{13}{}^{79}Br_2N_4O_2^+$ $[M+H]^+$ 426.9400; found 426.9404.

**Methyl 3-(2-bromophenyl)-2-(4-(3-chloropropyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3zg)**




Compound **3zg** (91 mg, 76%) was obtained as a colorless solid according to the general procedure from azirine **1f** (100 mg, 0.3 mmol) and alkyne **4q** (62 mg, 0.6 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

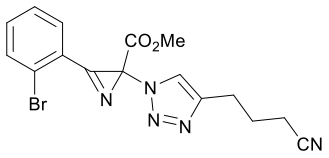
**Mp** 93–95 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.27–8.12 (m, 1H), 7.91 (s, 1H), 7.87–7.76 (m, 1H), 7.64–7.55 (m, 2H), 3.83 (s, 3H), 3.65–3.55 (m, 2H), 2.94 (t, $J$ = 7.3 Hz, 2H), 2.19 (p, $J$ = 6.8 Hz, 2H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.4, 158.5, 146.7, 135.7, 135.1, 134.3, 128.2, 126.3, 122.6, 121.2, 53.7, 49.9, 44.1, 31.7, 22.6.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{15}H_{14}{}^{79}BrClN_4NaO_2^+$ $[M+Na]^+$ 418.9881; found 418.9880.

**Methyl 3-(2-bromophenyl)-2-(4-(3-cyanopropyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3zh)**




Compound **3zh** (92 mg, 79%) was obtained as a colorless solid according to the general procedure from azirine **1f** (100 mg, 0.3 mmol) and alkyne **4r** (56 mg, 0.6 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

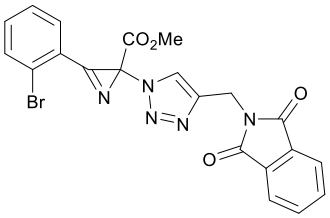
**Mp** 85–86 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.23–8.14 (m, 1H), 8.06 (s, 1H), 7.88–7.80 (m, 1H), 7.65–7.55 (m, 2H), 3.83 (s, 3H), 2.92 (t, *J* = 7.3 Hz, 2H), 2.45 (t, *J* = 7.4 Hz, 2H), 2.11 (p, *J* = 6.9 Hz, 2H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.3, 158.5, 145.9, 135.8, 135.0, 134.3, 128.2, 126.4, 122.8, 121.1, 119.2, 53.7, 50.0, 24.7, 24.2, 16.5.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{16}H_{15}{}^{79}BrN_5O_2^+$ $[M+H]^+$ 388.0404; found 388.0409.

**Methyl 3-(2-bromophenyl)-2-{4-[(1,3-dioxoisoindolin-2-yl)methyl]-1*H*-1,2,3-triazol-1-yl}-2*H*-azirine-2-carboxylate (3zi)**




Compound **3zi** (115 mg, 80%) was obtained as a colorless solid according to the general procedure from azirine **1f** (100 mg, 0.3 mmol) and alkyne **4s** (111 mg, 0.6 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

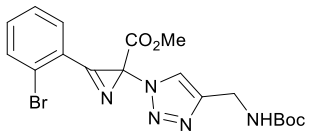
**Mp** 165–167 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.16–8.09 (m, 1H), 7.88–7.83 (m, 2H), 7.82–7.77 (m, 1H), 7.74–7.68 (m, 2H), 7.61–7.52 (m, 2H), 5.04 (AB-q, *J* = 7.5 Hz, 2H), 3.81 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.5, 167.1, 158.4, 143.0, 135.8, 135.0, 134.2, 134.0, 132.0, 128.1, 126.3, 124.3, 123.4, 121.0, 53.7, 50.0, 32.9.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{21}H_{14}{}^{79}BrN_5NaO_4^+$ $[M+Na]^+$ 502.0121; found 502.0122.

**Methyl 3-(2-bromophenyl)-2-(4-{[(*tert*-butoxycarbonyl)amino]methyl}-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate (3zj)**




Compound **3zj** (107 mg, 79%) was obtained as a colorless solid according to the general procedure from azirine **1f** (100 mg, 0.3 mmol) and alkyne **4t** (93 mg, 0.6 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

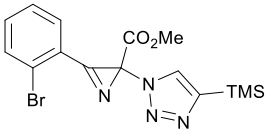
**Mp** 61–63 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.20–8.13 (m, 1H), 8.06 (s, 1H), 7.86–7.79 (m, 1H), 7.63–7.55 (m, 2H), 5.12 (s, 1H), 4.49–4.38 (m, 2H), 3.82 (s, 3H), 1.45 (s, 9H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.1, 158.5, 155.7, 145.7, 135.8, 134.9, 134.3, 128.2, 126.3, 123.4, 121.1, 79.7, 53.7, 50.1, 36.1, 28.3.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{18}H_{21}{}^{79}BrN_5O_4^+$ $[M+H]^+$ 450.0771; found 450.0778.

**Methyl 3-(2-bromophenyl)-2-[4-(trimethylsilyl)-1*H*-1,2,3-triazol-1-yl]-2*H*-azirine-2-carboxylate (3zk)**




Compound **3zk** (63 mg, 53%) was obtained as a colorless solid according to the general procedure from azirine **1f** (100 mg, 0.3 mmol) and alkyne **4u** (60 mg, 0.6 mmol) using EtOAc/hexane (1:4) as eluent for chromatography.

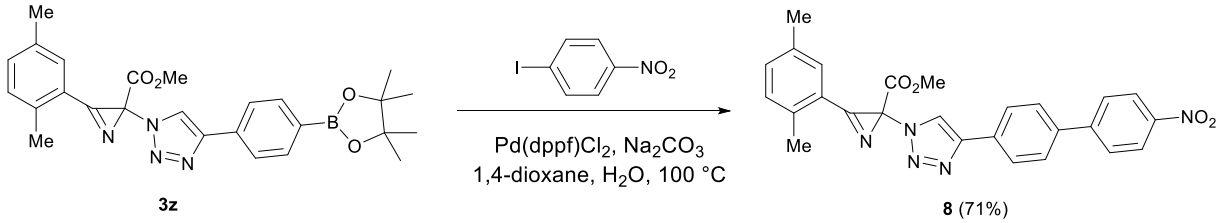
**Mp** 111–112 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.26–8.18 (m, 1H), 8.09 (s, 1H), 7.88–7.81 (m, 1H), 7.64–7.55 (m, 2H), 3.84 (s, 3H), 0.35 (s, 9H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.6, 158.8, 147.2, 135.6, 135.2, 134.2, 130.2, 128.1, 126.4, 121.3, 53.7, 49.4, -1.3.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{15}H_{17}{}^{81}BrN_4NaO_2Si^+$ $[M+Na]^+$ 417.0176; found 417.0217.

## 8. Synthesis of triazole 8




The mixture of triazole **3z** (144 mg, 0.305 mmol), 1-iodo-4-nitrobenzene (91 mg, 0.366 mmol), [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (22 mg, 0.031 mmol), sodium carbonate (97 mg, 0.915 mmol), 1,4-dioxane (8 mL) and water (1.5 mL) was stirred for 1 h at 100 °C under argon atmosphere in a screw-cap tube. The mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (eluent EtOAc/hexane, 1:4) as to give methyl 3-(2,5-dimethylphenyl)-2-(4-(4'-nitro-[1,1'-biphenyl]-4-yl)-1*H*-1,2,3-triazol-1-yl)-2*H*-azirine-2-carboxylate **8** (101 mg, 71%) as an orange solid.

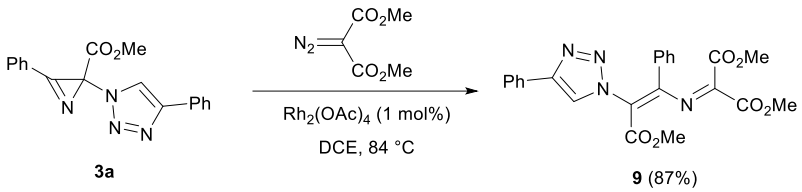
**Mp** 206–207 °C ($Et_2O$/hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.35–8.29 (m, 2H), 8.08–7.97 (m, 2H), 7.97–7.90 (m, 1H), 7.81–7.77 (m, 2H), 7.75–7.69 (m, 2H), 7.47–7.41 (m, 1H), 7.38–7.32 (m, 1H), 3.86 (s, 3H), 2.74 (s, 3H), 2.46 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 167.9, 157.9, 147.1, 146.9, 139.9, 138.4, 136.7, 135.8, 134.0, 131.1 (2C), 130.9, 127.8, 127.6, 126.5, 124.1, 121.3, 118.5, 53.7, 48.7, 20.7, 19.6.

**HRMS (ESI-TOF)**: *m/z* calcd for $C_{26}H_{21}N_5NaO_4^+$ $[M+Na]^+$ 490.1486; found 490.1467.

## 9. Synthesis of 2-azabuta-1,3-diene 9




To a solution of azirine **3a** (32 mg, 0.1 mmol) and dimethyl diazomalonate (24 mg, 0.15 mmol) in anhydrous 1,2-dichloroethane (1.5 mL) at reflux under argon $Rh_2(OAc)_4$ (2 mol %) was added. The stirred mixture was heated under reflux until nitrogen evolution stopped (15 min). The resulting mixture was evaporated under reduced pressure, and the residue purified by column chromatography on silica gel (eluent EtOAc/hexane, 1:4) to give (*E*)-dimethyl 2-[(3-methoxy-3-oxo-1-phenyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)prop-1-en-1-yl]imino)malonate **9** (39 mg, 87%) as a yellow oil.

**$^1$H NMR** (400 MHz, $CDCl_3$) 7.78–7.72 (m, 2H), 7.54 (s, 1H), 7.42–7.36 (m, 2H), 7.34–7.27 (m, 4H), 7.25–7.20 (m, 2H), 3.98 (s, 6H), 3.71 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ 163.0, 159.6, 159.5, 149.2, 147.1, 132.2, 130.8, 130.1, 128.7, 128.6, 128.1, 127.9, 125.7, 122.8, 106.3, 53.6, 52.6.

**HRMS (ESI-TOF):** *m/z* calcd for $C_{23}H_{21}N_4O_6^+$ $[M+H]^+$ 449.1456; found 449.1461.

## 10. X-ray data

### Compound 2a (CCDC 2347550)

Single crystals of **2a** were obtained by slow recrystallization from dichloromethane/pentane mixture at room temperature. Suitable crystals were selected and fixed on micro-amounts and the diffraction data were collected on diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2[11] the structure was solved with the ShelXT[12] structure solution program using Intrinsic Phasing and refined with the ShelXL[13] refinement package using Least Squares minimization.

**Figure S1.** X-Ray crystal structure of compound **2a** with 50% ellipsoid probability (CCDC 2347550)

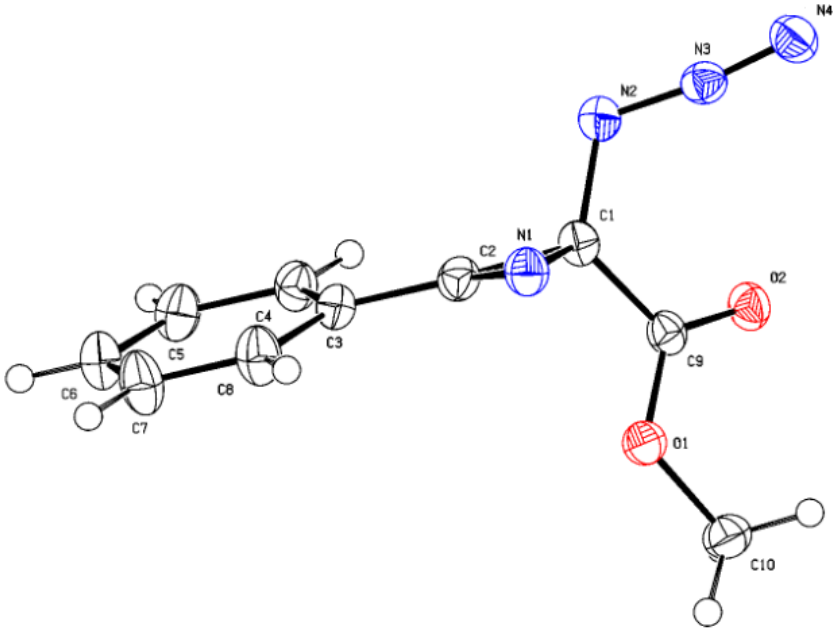



**Table 1.** Crystal data and structure refinement for **2a**.

| | |
|---|---|
| Empirical formula | $C_{10}H_8N_4O_2$ |
| Formula weight | 216.20 |
| Temperature/K | 99.8(7) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 5.9685(3) |
| b/Å | 9.2906(4) |
| c/Å | 9.6913(4) |
| α/° | 101.346(4) |
| β/° | 99.374(4) |
| γ/° | 99.632(4) |
| Volume/Å$^3$ | 508.69(4) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.412 |
| μ/mm$^{-1}$ | 0.867 |

| | |
|---|---|
| F(000) | 224.0 |
| Crystal size/mm$^3$ | 0.16 × 0.1 × 0.06 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 9.504 to 134.98 |
| Index ranges | $-7 \leq h \leq 7$, $-11 \leq k \leq 11$, $-11 \leq l \leq 11$ |
| Reflections collected | 7082 |
| Independent reflections | 1838 [$R_{int}$ = 0.0517, $R_{sigma}$ = 0.0404] |
| Data/restraints/parameters | 1838/0/146 |
| Goodness-of-fit on $F^2$ | 1.060 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0381, $wR_2$ = 0.1001 |
| Final R indexes [all data] | $R_1$ = 0.0444, $wR_2$ = 0.1048 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.21/-0.21 |

**Compound 2f (CCDC 2346171)**

Single crystals of **2f** were grown by slow evaporation of its solution in $Et_2O$/hexane mixture. A suitable crystal was selected and intensity data were collected on a XtaLAB Synergy, Single source at home/near, HyPix diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2,[11] the structure was solved with the ShelXT[12] structure solution program using Intrinsic Phasing and refined with the olex2.refine[13] refinement package using Gauss-Newton minimisation.

**Figure S2.** X-Ray crystal structure of compound **2f** with 50% ellipsoid probability (CCDC 2346171)

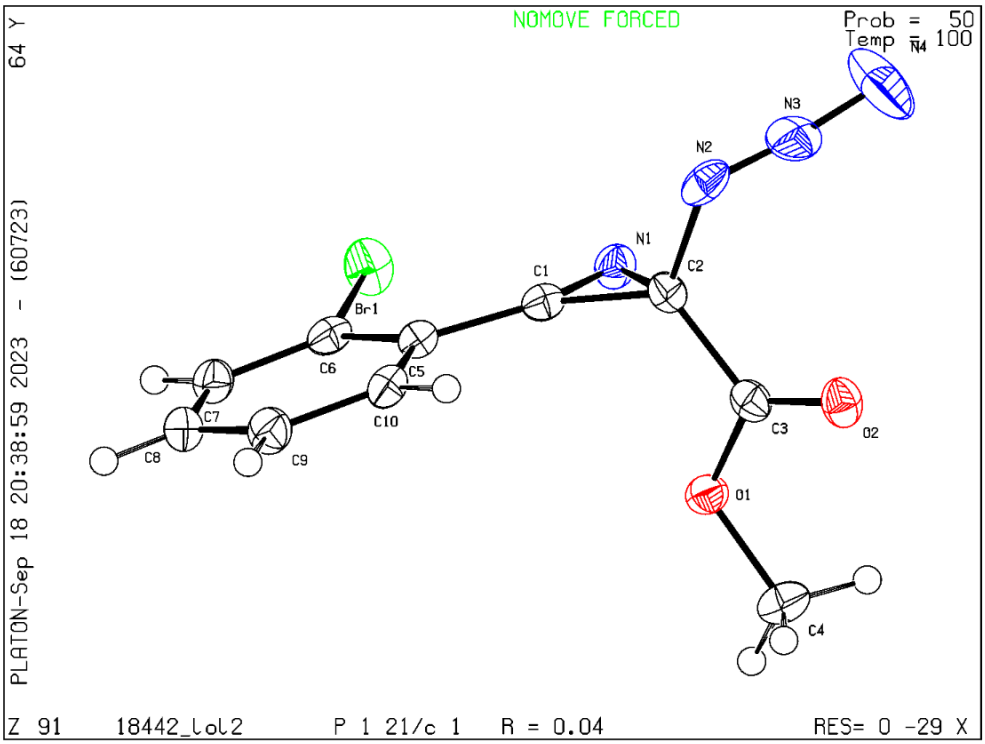


**Table S1.** Crystal data and structure refinement for **2f**.

| | |
|---|---|
| Empirical formula | $C_{12}H_9BrN_2O_2$ |
| Formula weight | 293.12 |
| Temperature/K | 99.9(3) |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 8.1274(4) |
| b/Å | 19.4244(7) |
| c/Å | 7.4857(3) |
| α/° | 90 |
| β/° | 110.223(5) |
| γ/° | 90 |
| Volume/Å$^3$ | 1108.92(9) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.756 |
| μ/mm$^{-1}$ | 4.992 |
| F(000) | 584.0 |
| Crystal size/mm$^3$ | 0.07 × 0.05 × 0.03 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 9.106 to 129.968 |
| Index ranges | $-8 \leq h \leq 9$, $-22 \leq k \leq 22$, $-8 \leq l \leq 8$ |
| Reflections collected | 5008 |
| Independent reflections | 1882 [$R_{int}$ = 0.0328, $R_{sigma}$ = 0.0400] |
| Data/restraints/parameters | 1882/0/155 |
| Goodness-of-fit on $F^2$ | 1.078 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0363, $wR_2$ = 0.0903 |
| Final R indexes [all data] | $R_1$ = 0.0422, $wR_2$ = 0.0932 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.92/-0.72 |

**Compound 3a (CCDC 2346167)**

Single crystals of **3a** were grown by slow evaporation of its solution in $Et_2O$/hexane mixture. A suitable crystal was selected and intensity data were collected on a XtaLAB Synergy, Single source at home/near, HyPix diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2[11], the structure was solved with the ShelXT[12] structure solution program using Intrinsic Phasing and refined with the olex2.refine[13] refinement package using Gauss-Newton minimisation.

**Figure S3.** X-Ray crystal structure of compound **3a** with 50% ellipsoid probability (CCDC 2346167)

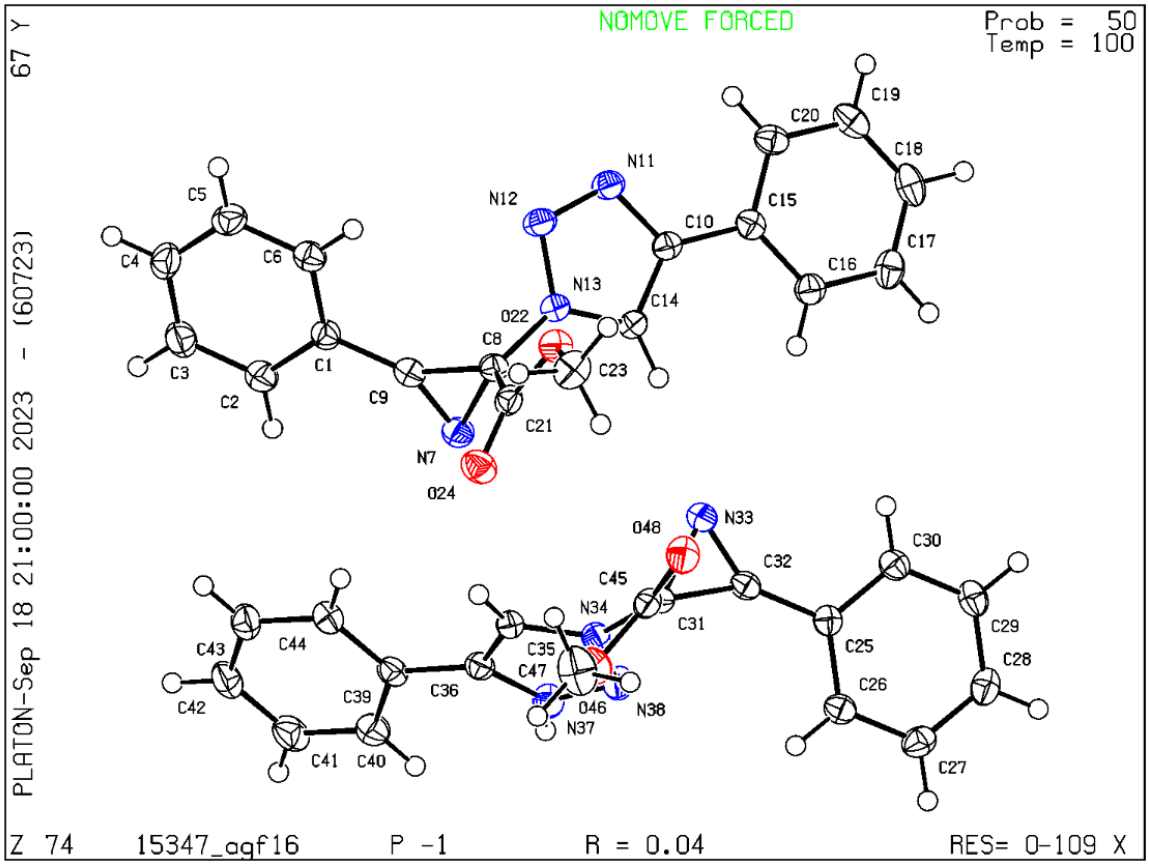


**Table S3.** Crystal data and structure refinement for **3a**.

| | |
|---|---|
| Empirical formula | $C_{36}H_{29}N_8O_4$ |
| Formula weight | 637.67 |
| Temperature/K | 100.01(13) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 7.88082(11) |
| b/Å | 12.52489(13) |
| c/Å | 16.01630(14) |
| α/° | 97.1059(8) |
| β/° | 91.7213(10) |
| γ/° | 94.7055(10) |
| Volume/Å$^3$ | 1562.19(3) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.356 |
| μ/mm$^{-1}$ | 0.750 |
| F(000) | 666.0 |
| Crystal size/mm$^3$ | 0.1 × 0.08 × 0.06 |
| Radiation | CuKα (λ = 1.54184) |
| 2Θ range for data collection/° | 5.566 to 154.876 |
| Index ranges | $-9 \leq h \leq 9$, $-15 \leq k \leq 15$, $-20 \leq l \leq 19$ |
| Reflections collected | 34701 |
| Independent reflections | 6491 [$R_{int}$ = 0.0398, $R_{sigma}$ = 0.0262] |
| Data/restraints/parameters | 6491/0/436 |
| Goodness-of-fit on F$^2$ | 1.051 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0360, $wR_2$ = 0.0955 |
| Final R indexes [all data] | $R_1$ = 0.0405, $wR_2$ = 0.0987 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.24/-0.67 |

**Responses to the Platon checks**

[PLAT230_ALERT_2_B Hirshfeld Test Diff for N2 --N3 . 8.5 s.u.],
[PLAT230_ALERT_2_B Hirshfeld Test Diff for N2 --C2 . 8.0 s.u.] (for **2f**)
**(Comment)**The anomalous data for Hirshfeld test is an artefact in the structure. It does not affect the correctness of the proposed structure (the azide group is attached to the C2 atom), which is confirmed by other characterization methods.
[PLAT196 No TEMP record and _measurement_temperature .NE. 293 Degree] (for **3a**)
**(Comment)** The temperature in the experiment was 100 K. The absence of this information in the .res file does not affect the correctness of the proposed structure, which is confirmed by other characterization methods.

## 11. Computation details

All calculations were performed by using the Gaussian 09 suite of quantum chemical programs.[14] Geometry optimizations and energy calculations for compounds **1a**, **2a**, **5**, *cis*-**6**, *trans*-**6**, **7**, $TMSN_3$, TMSBr, azide-anion, $Et_3N$, and transition states TS1–TS8, were performed at the DFT wB97XD/cc-pVTZ level using PCM model for dichloromethane. Stationary points on the respective potential-energy surfaces were characterized at the same level of theory by evaluating the corresponding Hessian indices. Careful verification of the unique imaginary frequencies for transition states was carried out to check whether the frequency indeed pertains to the desired reaction coordinate.

**Figure S1**. Energy profiles (Gibbs free energies, kcal/mol) for transformations of bromoazirine **1a** to azidoazirine **2a** (scenarios A, B) and passible pathways for azide anion formation

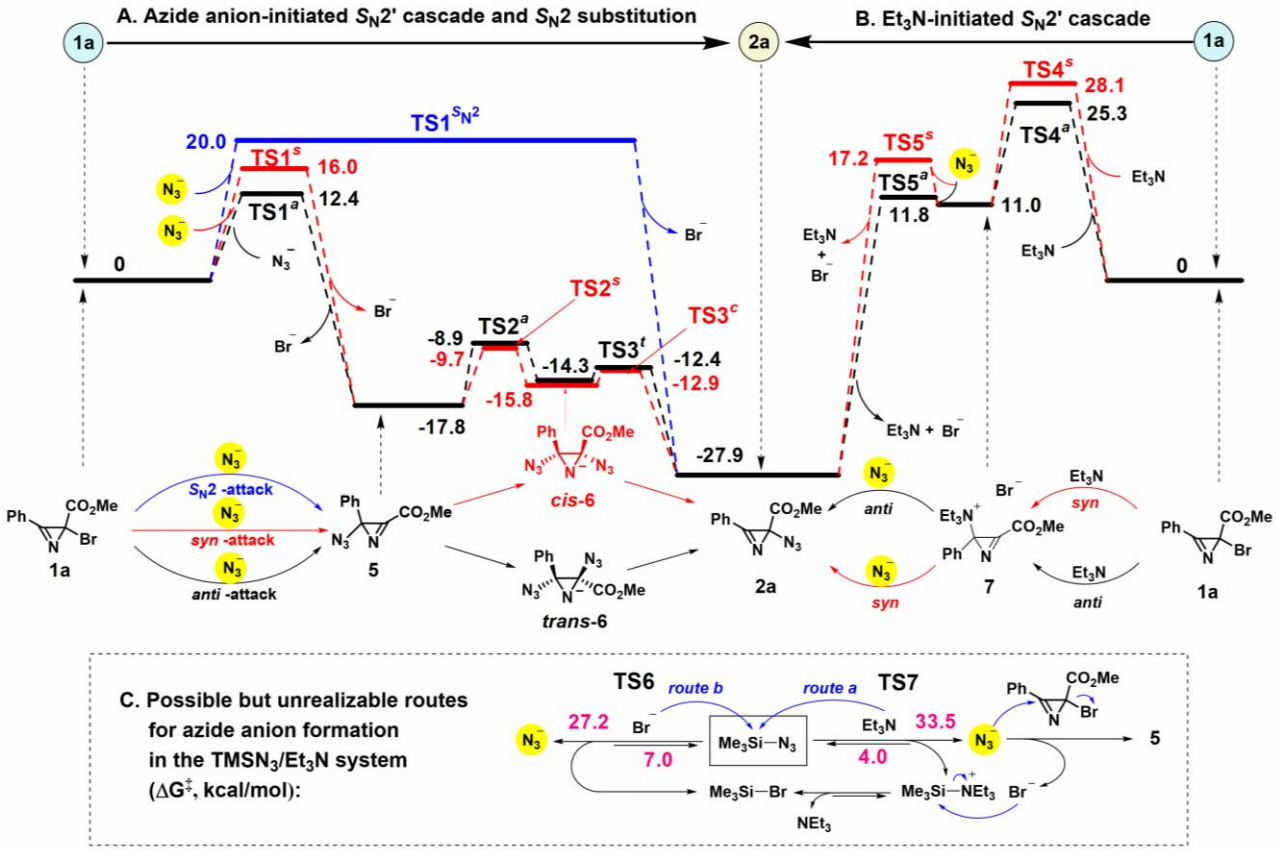
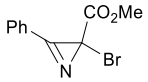
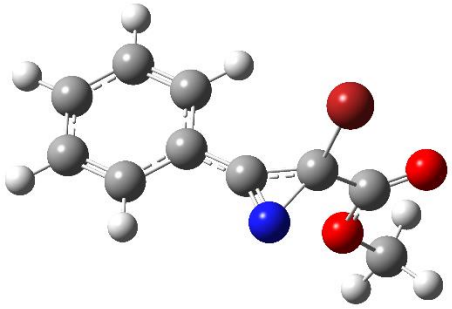


**Table S3.** Energies (au) and cartesian coordinates of stationary points for compounds **1a**, **2a**, **5**, *cis*-**6**, *trans*-**6**, **7**, $TMSN_3$, TMSBr, azide-anion, $Et_3N$, and transition states TS1–TS8.

### Compound **1a**

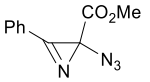



Zero-point correction = 0.161372
Thermal correction to Energy = 0.174340
Thermal correction to Enthalpy = 0.175284
Thermal correction to Gibbs Free Energy = 0.118948
$E_0$ = -3165.136381, E = -3165.123413,
H = -3165.122469, G = -3165.178804.
Imaginary frequency = 0.

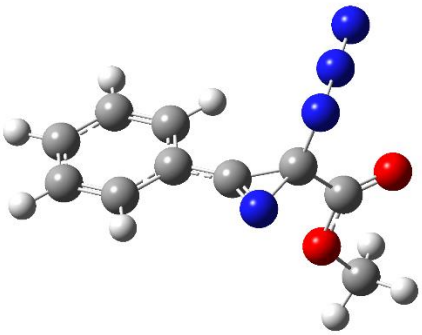


| | | | |
|---|---|---|---|
| N | -2.00037797 | -0.17049737 | 2.30806124 |
| C | -1.25416897 | -0.18945437 | 1.29769524 |
| C | -2.65022997 | -0.26038237 | 0.96718124 |
| C | 0.11278703 | -0.18027337 | 0.85168724 |
| Br | -3.43179097 | -1.95438037 | 0.47131124 |
| C | -3.42530097 | 0.92657663 | 0.46056924 |
| C | 0.38758803 | -0.24354337 | -0.51169776 |
| C | 1.70258703 | -0.23121837 | -0.94329576 |
| C | 2.73236403 | -0.15329637 | -0.01648376 |
| C | 2.45675103 | -0.08940137 | 1.34448624 |
| C | 1.14711003 | -0.10429637 | 1.78430024 |
| O | -4.44421097 | 0.86804363 | -0.17118876 |
| O | -2.80958297 | 2.04963163 | 0.80863524 |
| C | -3.44235897 | 3.26808563 | 0.40325924 |
| H | -0.42651597 | -0.30395637 | -1.22096876 |
| H | 1.92388003 | -0.28322637 | -1.99963676 |
| H | 3.75897403 | -0.14236437 | -0.35608276 |
| H | 3.26448503 | -0.02954837 | 2.05981824 |
| H | 0.91754403 | -0.05457137 | 2.83960724 |
| H | -2.78377897 | 4.06228363 | 0.73688624 |
| H | -3.55545097 | 3.29396963 | -0.67831476 |
| H | -4.41847597 | 3.35969763 | 0.87472024 |

### Compound **2a**

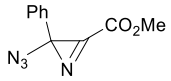



Zero-point correction = 0.175023
Thermal correction to Energy = 0.189136
Thermal correction to Enthalpy = 0.190080
Thermal correction to Gibbs Free Energy = 0.131691
$E_0$ = -755.046837, E = -755.032724,
H = -755.031780, G = -755.090169.
Imaginary frequency = 0.

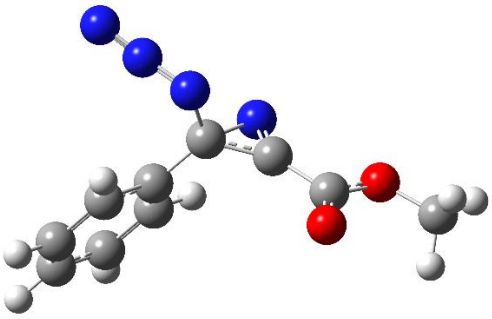


| | | | |
|---|---|---|---|
| N | 1.02727486 | -0.22959462 | 1.71092651 |
| C | 0.35202186 | 0.08113838 | 0.70198851 |
| C | 1.75916186 | 0.39406838 | 0.56398751 |
| C | -0.97515214 | 0.11025438 | 0.14371551 |
| C | 2.68744686 | -0.46800962 | -0.24368649 |
| C | -1.16598314 | 0.62068338 | -1.13733249 |
| C | -2.43864014 | 0.64747338 | -1.68047549 |
| C | -3.51251214 | 0.16424638 | -0.94660249 |
| C | -3.32173514 | -0.34720762 | 0.33178051 |
| C | -2.05460114 | -0.37457862 | 0.88237051 |
| O | 3.70178286 | -0.05803562 | -0.74642149 |
| O | 2.23458686 | -1.70850262 | -0.34677849 |
| C | 3.04051986 | -2.61270662 | -1.11027449 |
| H | -0.31949614 | 0.99257438 | -1.69847649 |
| H | -2.59373314 | 1.04547438 | -2.67300049 |
| H | -4.50571314 | 0.18510538 | -1.37354749 |
| H | -4.16355614 | -0.72276662 | 0.89588751 |
| H | -1.89132814 | -0.77033562 | 1.87516851 |
| H | 2.50876986 | -3.55760962 | -1.10151149 |
| H | 3.15553186 | -2.24734762 | -2.12842149 |
| H | 4.01966186 | -2.72383062 | -0.64948849 |
| N | 2.23502486 | 1.73374938 | 0.82422751 |
| N | 2.45221086 | 2.42502538 | -0.16686449 |
| N | 2.68333586 | 3.14979338 | -0.98861449 |

## Compound **5**

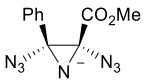



Zero-point correction = 0.174839
Thermal correction to Energy = 0.189019
Thermal correction to Enthalpy = 0.189963
Thermal correction to Gibbs Free Energy = 0.131190
$E_0$ = -755.030553, E = -755.016373,
H = -755.015429, G = -755.074202.
Imaginary frequency = 0.

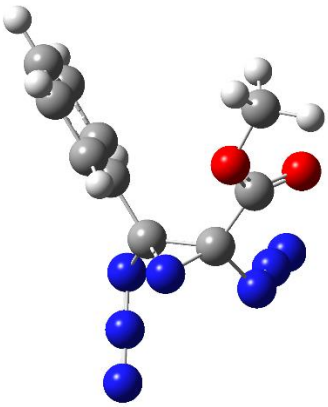


| | | | |
|---|---|---|---|
| N | -0.16620773 | 0.39359510 | 1.17946913 |
| C | 0.75395627 | 0.47143110 | -0.03850287 |
| C | -0.61892573 | 0.07238610 | 0.05948913 |
| C | 1.87190127 | -0.51723390 | -0.13729787 |
| C | -1.86274373 | -0.43196290 | -0.58300487 |
| C | 2.78389727 | -0.44706690 | -1.18621387 |
| C | 3.81045727 | -1.37300090 | -1.28183487 |
| C | 3.93914627 | -2.37328990 | -0.33005587 |
| C | 3.03325127 | -2.44531390 | 0.71756913 |
| C | 2.00284227 | -1.52403590 | 0.81302913 |
| O | -1.93425773 | -0.65124390 | -1.76037587 |
| O | -2.81696773 | -0.59150490 | 0.31081313 |
| C | -4.07399673 | -1.07469990 | -0.18931187 |
| H | 2.68858027 | 0.32594810 | -1.93662487 |
| H | 4.51232427 | -1.31143990 | -2.10200887 |
| H | 4.74041527 | -3.09539490 | -0.40464487 |
| H | 3.12750827 | -3.22040990 | 1.46555513 |
| H | 1.29786027 | -1.58598490 | 1.63083413 |
| H | -4.72480473 | -1.13985090 | 0.67478213 |
| H | -4.47463273 | -0.37650490 | -0.92066987 |
| H | -3.94112473 | -2.05224990 | -0.64694687 |
| N | 2.92070027 | 2.93236210 | 0.15873413 |
| N | 2.01634827 | 2.34448510 | -0.13662087 |
| N | 0.99093327 | 1.80159210 | -0.55124487 |

## Compound *cis*-**6**

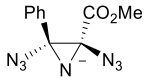



Zero-point correction = 0.186912
Thermal correction to Energy = 0.203959
Thermal correction to Enthalpy = 0.204903
Thermal correction to Gibbs Free Energy = 0.139508
$E_0$ = -919.342970, E = -919.325923,
H = -919.324979, G = -919.390373.
Imaginary frequency = 0.

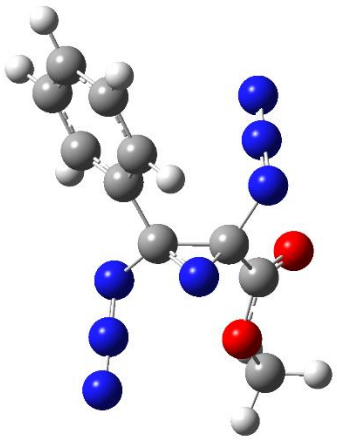


| | | | |
|---|---|---|---|
| N | 0.59400608 | -0.76053824 | -1.10828252 |
| C | 0.21084108 | -0.17960824 | 0.07907548 |
| C | 0.92464508 | -1.48908424 | 0.04630048 |
| C | -1.21586392 | 0.01092976 | 0.51170248 |
| C | 0.24851808 | -2.77068724 | 0.45267148 |
| C | -1.54385692 | 0.49370276 | 1.77609148 |
| C | -2.87000492 | 0.63443676 | 2.15463948 |
| C | -3.88804392 | 0.30343076 | 1.27047848 |
| C | -3.56804792 | -0.17433324 | 0.00807848 |
| C | -2.24034392 | -0.32424924 | -0.36428952 |
| O | 0.61558408 | -3.47705124 | 1.36493948 |
| O | -0.82943792 | -3.03700624 | -0.28079252 |
| C | -1.60310592 | -4.16137524 | 0.12691348 |
| H | -0.75469992 | 0.76518976 | 2.46373248 |
| H | -3.10899992 | 1.00765676 | 3.14192848 |
| H | -4.92311392 | 0.41895076 | 1.56376748 |
| H | -4.35390192 | -0.43497924 | -0.68887452 |
| H | -1.97185392 | -0.71899624 | -1.33383852 |
| H | -2.43018992 | -4.21834724 | -0.57379852 |
| H | -1.01169992 | -5.07466724 | 0.08715548 |
| H | -1.97794992 | -4.02058724 | 1.13967148 |
| N | 2.73816208 | 1.75259976 | -0.71147052 |
| N | 1.90346608 | 1.38313076 | -0.04906052 |
| N | 1.01263608 | 1.00134076 | 0.67627748 |
| N | 2.36250308 | -1.53661924 | 0.47171548 |
| N | 2.55983808 | -1.42997824 | 1.66925148 |
| N | 2.84062608 | -1.32584824 | 2.75491748 |

## Compound *trans*-**6**

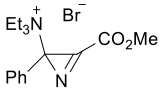



Zero-point correction = 0.187644
Thermal correction to Energy = 0.204369
Thermal correction to Enthalpy = 0.205314
Thermal correction to Gibbs Free Energy = 0.142025
$E_0$ = -919.342239, E = -919.325513,
H = -919.324569, G = -919.387857.
Imaginary frequency = 0.

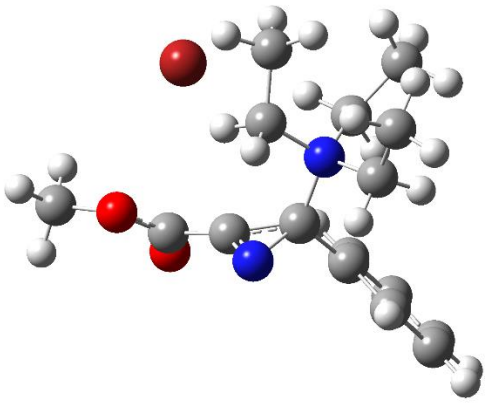


| | | | |
|---|---|---|---|
| N | 0.57442700 | -0.47762500 | 1.57697300 |
| C | -0.00382300 | -0.64516900 | 0.33387500 |
| C | 0.75674200 | 0.59003100 | 0.68449000 |
| C | -1.48921400 | -0.58477600 | 0.08407000 |
| C | 2.06585600 | 0.92964700 | 0.02005400 |
| C | -2.33148700 | -0.26470000 | 1.14269500 |
| C | -3.70009500 | -0.15460000 | 0.95219300 |
| C | -4.24782300 | -0.35981700 | -0.30583500 |
| C | -3.41475000 | -0.68209700 | -1.36829100 |
| C | -2.04675500 | -0.79620300 | -1.17439000 |
| O | 2.28559200 | 1.96264500 | -0.57132000 |
| O | 2.96716100 | -0.04190100 | 0.13970700 |
| C | 4.20773500 | 0.16573300 | -0.52895100 |
| H | -1.88244100 | -0.09884200 | 2.11222700 |
| H | -4.34112900 | 0.09489100 | 1.78776800 |
| H | -5.31485600 | -0.26758400 | -0.45855400 |
| H | -3.83304100 | -0.84379200 | -2.35313400 |
| H | -1.40427200 | -1.05425500 | -2.00436000 |
| H | 4.78858200 | -0.73433300 | -0.35438700 |
| H | 4.04938400 | 0.31267100 | -1.59607400 |
| H | 4.72215400 | 1.03424700 | -0.12080300 |
| N | 2.10937500 | -3.16045200 | 0.22741000 |
| N | 1.37492300 | -2.41269600 | -0.18767100 |
| N | 0.59939900 | -1.62295100 | -0.67897800 |
| N | 0.01379300 | 1.86386600 | 0.96371600 |
| N | -0.48179500 | 2.40847200 | -0.00534900 |
| N | -0.98794200 | 2.97320700 | -0.83885000 |

## Compound **7**




Zero-point correction = 0.376739
Thermal correction to Energy = 0.398916
Thermal correction to Enthalpy = 0.399860
Thermal correction to Gibbs Free Energy = 0.324987
$E_0$ = -3457.362555, E = -3457.340378,
H = -3457.339433, G = -3457.414306.
Imaginary frequency = 0.

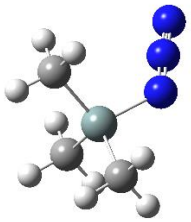


| | | | |
|---|---|---|---|
| N | -3.32192658 | 1.86359071 | -0.94843896 |
| C | -3.62475358 | 2.27086271 | 0.44972304 |
| C | -2.52457958 | 1.49799571 | -0.05274296 |
| C | -4.79046358 | 1.60765871 | 1.11902904 |
| C | -1.38590758 | 0.56359071 | 0.17482104 |
| C | -4.58872158 | 0.89387171 | 2.29659404 |
| C | -5.64333758 | 0.22683571 | 2.89808104 |
| C | -6.90273258 | 0.25630571 | 2.31907704 |
| C | -7.10151558 | 0.93843471 | 1.12800304 |
| C | -6.04869458 | 1.60780071 | 0.52605604 |
| O | -1.49072858 | -0.34529029 | 0.94813104 |
| O | -0.36809458 | 0.86276071 | -0.59404496 |
| C | 0.82275342 | 0.07901871 | -0.39671596 |
| H | -3.60242958 | 0.85469071 | 2.73958404 |
| H | -5.47792658 | -0.31797529 | 3.81673404 |
| H | -7.72702558 | -0.26290829 | 2.78806104 |
| H | -8.07616458 | 0.94461971 | 0.66066704 |
| H | -6.20704458 | 2.11241871 | -0.41651996 |
| H | 1.53771042 | 0.45468271 | -1.11914096 |
| H | 1.18194142 | 0.23203871 | 0.61862004 |
| H | 0.61120842 | -0.97241029 | -0.57412796 |
| N | -3.41103558 | 3.77513971 | 0.73828004 |
| C | -3.30928658 | 3.92775271 | 2.24809104 |
| C | -4.63257558 | 4.45753271 | 0.14487104 |
| C | -2.12596958 | 4.20982871 | 0.05729104 |
| C | -4.54743058 | 5.93419571 | -0.18195996 |
| C | -3.63908258 | 5.28059271 | 2.84692004 |
| C | -1.47462458 | 5.49687571 | 0.52040004 |

| | | | |
|---|---|---|---|
| H | -2.29953758 | 3.60281571 | 2.50001604 |
| H | -4.00773658 | 3.21151871 | 2.66238304 |
| H | -4.83518558 | 3.92073171 | -0.77810996 |
| H | -5.44658658 | 4.26143171 | 0.83738804 |
| H | -2.33748758 | 4.22563571 | -1.00905596 |
| H | -1.40348058 | 3.42019071 | 0.25465904 |
| H | -5.52310558 | 6.21244071 | -0.57851496 |
| H | -4.34846358 | 6.56300771 | 0.67905104 |
| H | -3.81353758 | 6.14087071 | -0.95671796 |
| H | -3.49036158 | 5.17536271 | 3.92080904 |
| H | -4.68055358 | 5.55453571 | 2.69167404 |
| H | -2.99980358 | 6.08695671 | 2.50511504 |
| H | -0.61437858 | 5.64253671 | -0.13198196 |
| H | -1.08990658 | 5.39913171 | 1.53253804 |
| H | -2.10115058 | 6.37810471 | 0.44307004 |
| Br | 0.24891942 | 2.65450371 | 2.51958004 |

## $Me_3SiN_3$

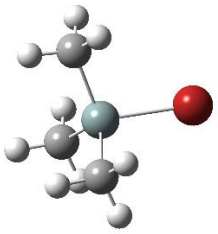
Zero-point correction = 0.124690
Thermal correction to Energy = 0.135109
Thermal correction to Enthalpy = 0.136053
Thermal correction to Gibbs Free Energy = 0.088301
$E_0$ = -573.393983, E = -573.383564,
H = -573.382620, G = -573.430372.
Imaginary frequency = 0.



| | | | |
|---|---|---|---|
| C | 2.44333201 | -0.10917906 | -0.78820868 |
| Si | 1.12939101 | -0.07827306 | 0.53149932 |
| C | 1.18407001 | -1.59743306 | 1.61865932 |
| C | 1.19453901 | 1.48287694 | 1.55695132 |
| N | -0.40558099 | -0.09167706 | -0.37929668 |
| N | -1.50025899 | -0.08387506 | 0.13592832 |
| N | -2.55082899 | -0.07767406 | 0.53931732 |
| H | 2.34646001 | 0.74673494 | -1.45660568 |
| H | 2.37726901 | -1.02073806 | -1.38273268 |
| H | 3.43273001 | -0.07247806 | -0.32973868 |
| H | 0.37530001 | -1.58813406 | 2.35075532 |
| H | 1.10011301 | -2.50808906 | 1.02495632 |
| H | 2.12909301 | -1.63274006 | 2.16375632 |
| H | 0.38477101 | 1.50828794 | 2.28743132 |
| H | 1.11857201 | 2.36973094 | 0.92728732 |
| H | 2.13923201 | 1.53213094 | 2.10151732 |

## $Me_3SiBr$

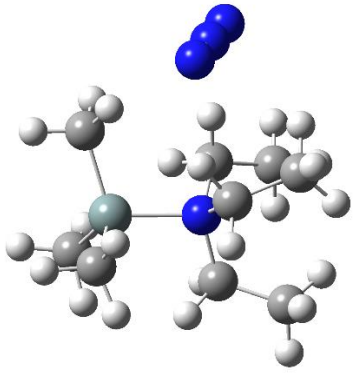
Zero-point correction = 0.112014
Thermal correction to Energy = 0.121004
Thermal correction to Enthalpy = 0.121948
Thermal correction to Gibbs Free Energy = 0.077861
$E_0$ = -2983.497030, E = -2983.488040,
H = -2983.487096, G = -2983.531183.
Imaginary frequency = 0.



| | | | |
|---|---|---|---|
| C | -0.76589172 | -1.25477373 | 1.42544561 |
| Si | -0.23390772 | -0.13457273 | 0.03159761 |
| C | -0.76697172 | 1.63226727 | 0.30377061 |
| C | -0.76637272 | -0.78307073 | -1.63465439 |
| H | -0.38585872 | -2.26584773 | 1.27956361 |
| H | -1.85617472 | -1.30011073 | 1.46366161 |
| H | -0.40439972 | -0.88390573 | 2.38443761 |
| H | -1.85746072 | 1.68783827 | 0.31112061 |
| H | -0.39830972 | 2.00932627 | 1.25756161 |
| H | -0.39614272 | 2.27842727 | -0.49170239 |
| H | -1.85673472 | -0.81079073 | -1.68591139 |
| H | -0.38995072 | -1.79290473 | -1.79752739 |
| H | -0.40123172 | -0.14342773 | -2.43801439 |
| Br | 2.04494128 | -0.13480873 | 0.03144961 |

## Salt $Me_3SiNEt_3^+ N_3^-$

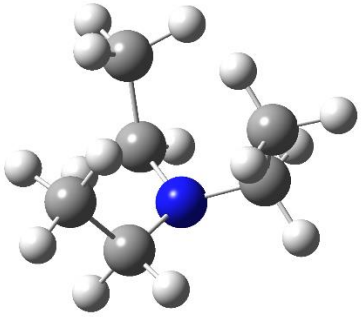
Zero-point correction = 0.338462
Thermal correction to Energy = 0.358038
Thermal correction to Enthalpy = 0.358982
Thermal correction to Gibbs Free Energy = 0.292722
$E_0$ = -865.590460, E = -865.570884,
H = -865.569940, G = -865.636200.
Imaginary frequency = 0.



| | | | |
|---|---|---|---|
| C | 1.75712070 | -2.02813629 | 1.87702672 |
| Si | 1.38748570 | -1.45782329 | 0.14306072 |
| C | -0.15788430 | -2.23986629 | -0.52200128 |
| C | 2.85267470 | -1.69913429 | -0.98421228 |
| N | -2.91138730 | -0.86935229 | 1.21941772 |
| N | -2.87813730 | -0.32170629 | 0.18613272 |
| N | -2.82494430 | 0.22522971 | -0.84682128 |
| H | 2.03915970 | -3.08103329 | 1.80928772 |
| H | 0.88322670 | -1.96130629 | 2.52283672 |
| H | 2.58481270 | -1.49727529 | 2.34531672 |
| H | -0.38913830 | -1.92014829 | -1.53605828 |
| H | 0.01900370 | -3.31772729 | -0.54097528 |
| H | -1.02423730 | -2.05325929 | 0.11474572 |
| H | 2.96865470 | -2.77450429 | -1.13283228 |
| H | 3.77787670 | -1.32304929 | -0.55030528 |
| H | 2.71686970 | -1.24689929 | -1.96569328 |
| N | 1.08358970 | 0.43621871 | 0.23497672 |
| C | 2.43207270 | 1.06744971 | 0.47278672 |
| C | 0.12813070 | 0.63954071 | 1.38981772 |
| C | 0.47908870 | 0.81564671 | -1.09826828 |
| C | -0.71158330 | 1.90332471 | 1.40177372 |
| C | 2.47366070 | 2.45532771 | 1.08683872 |
| C | 0.59818470 | 2.26068471 | -1.54564928 |
| H | 2.94630870 | 1.06010071 | -0.48553828 |
| H | 2.98016670 | 0.39820871 | 1.13471572 |
| H | -0.56699430 | -0.20039129 | 1.38406572 |
| H | 0.72728070 | 0.56493571 | 2.29503872 |
| H | -0.57046530 | 0.52001671 | -1.05745928 |
| H | 0.96941970 | 0.19534571 | -1.84754028 |
| H | -1.31952130 | 1.86269971 | 2.30474572 |
| H | -0.12714730 | 2.81818571 | 1.43178972 |

## $Et_3N$

Zero-point correction = 0.207134
Thermal correction to Energy = 0.216210
Thermal correction to Enthalpy = 0.217154
Thermal correction to Gibbs Free Energy = 0.174339
$E_0$ = -292.220308, E = -292.211232,
H = -292.210288, G = -292.253104.
Imaginary frequency = 0.



| | | | |
|---|---|---|---|
| N | -0.14375414 | -0.12837132 | -0.82673428 |
| C | -1.36370914 | 0.61753668 | -0.61440228 |
| C | 1.11211986 | 0.55452568 | -0.61040328 |
| C | -0.18074114 | -1.55781832 | -0.61484228 |
| C | 1.75086986 | 0.43973968 | 0.77763772 |
| C | -1.59535614 | 1.21772468 | 0.77647772 |
| C | -0.59834314 | -2.05867932 | 0.77194472 |
| H | -2.19526314 | -0.04749632 | -0.86001928 |
| H | -1.40401614 | 1.43499168 | -1.34318328 |
| H | 1.83817086 | 0.18795068 | -1.34491328 |
| H | 0.95035686 | 1.60972368 | -0.84316228 |
| H | 0.81317886 | -1.94611232 | -0.84990328 |
| H | -0.86310314 | -2.00244432 | -1.34803528 |
| H | 2.66678086 | 1.03185168 | 0.81598072 |
| H | 1.08073986 | 0.79142668 | 1.56116672 |
| H | 2.01779886 | -0.59420832 | 0.99869572 |
| H | -2.57129414 | 1.70497968 | 0.81391072 |
| H | -0.84229614 | 1.97195368 | 1.00790872 |
| H | -1.56226814 | 0.45717868 | 1.55564172 |
| H | -0.52369014 | -3.14679732 | 0.81339172 |
| H | -1.63384414 | -1.79131032 | 0.98550272 |
| H | 0.02789686 | -1.64148032 | 1.55973472 |

## Azide anion

Zero-point correction = 0.011169
Thermal correction to Energy = 0.013768
Thermal correction to Enthalpy = 0.014712
Thermal correction to Gibbs Free Energy = -0.009995
$E_0$ = -164.298199, E = -164.295601,
H = -164.294657, G = -164.319364.
Imaginary frequency = 0.

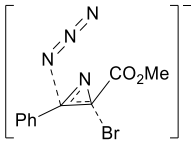
| | | | |
|---|---|---|---|
| H | -1.39628530 | 1.93043971 | 0.55651972 |
| H | 3.52354370 | 2.73143771 | 1.17668772 |
| H | 2.04694470 | 2.47103971 | 2.08699072 |
| H | 1.98004670 | 3.20854771 | 0.48107572 |
| H | 0.08988070 | 2.33450771 | -2.50624228 |
| H | 1.63164470 | 2.56486071 | -1.70163028 |
| H | 0.11935170 | 2.95936771 | -0.86683728 |

| | | | |
|---|---|---|---|
| N | 0.00000000 | 0.00000000 | 1.17093300 |
| N | 0.00000000 | 0.00000000 | -0.00000400 |
| N | 0.00000000 | 0.00000000 | -1.17092900 |

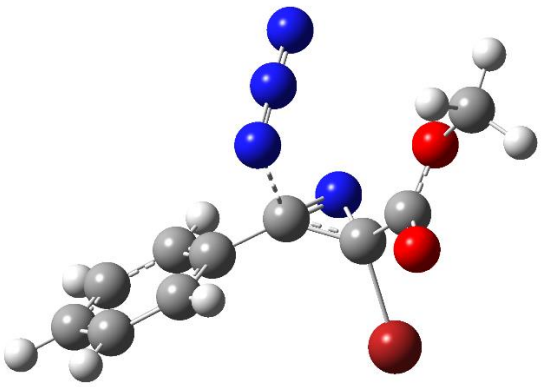
## Bromide anion

Zero-point correction = 0.000000
Thermal correction to Energy = 0.001416
Thermal correction to Enthalpy = 0.002360
Thermal correction to Gibbs Free Energy = -0.016176
$E_0$ = -2574.436217, E = -2574.434801,
H = -2574.433857, G = -2574.452393.
Imaginary frequency = 0.

## TS1$^a$

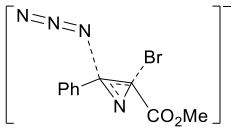



Zero-point correction = 0.172929
Thermal correction to Energy = 0.188894
Thermal correction to Enthalpy = 0.189838
Thermal correction to Gibbs Free Energy = 0.126288
$E_0$ = -3329.431839, E = -3329.415874,
H = -3329.414930, G = -3329.478480.
Imaginary frequency = 1.

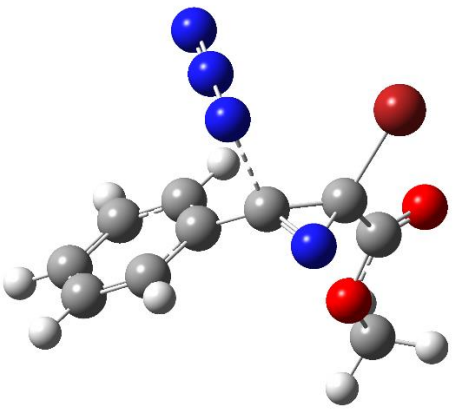


| | | | |
|---|---|---|---|
| N | 0.16478258 | -0.40793837 | -1.04569217 |
| C | -0.51941942 | -0.25118837 | 0.06341883 |
| C | 0.60278858 | -1.14149137 | 0.09346283 |
| C | -1.95147742 | -0.28871737 | 0.38553083 |
| Br | 0.27593458 | -3.11786137 | 0.09710383 |
| C | 1.86276958 | -0.86129737 | 0.87242883 |

## TS1$^s$



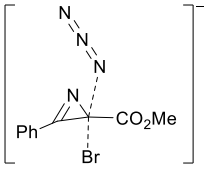

Zero-point correction = 0.173334
Thermal correction to Energy = 0.189076
Thermal correction to Enthalpy = 0.190020
Thermal correction to Gibbs Free Energy = 0.127702
$E_0$ = -3329.427094, E = -3329.411352,
H = -3329.410408, G = -3329.472727.
Imaginary frequency = 1.



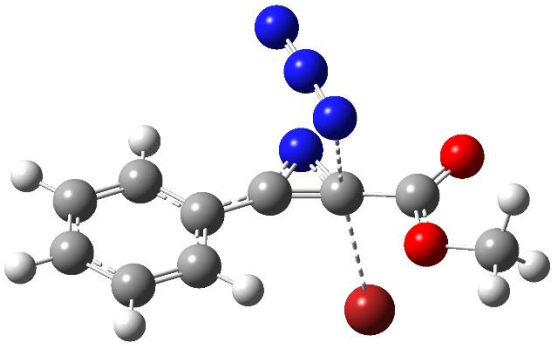
| | | | |
|---|---|---|---|
| N | 0.65511954 | 0.63950951 | 2.75854253 |
| C | 1.33686654 | 0.14389151 | 1.77052053 |
| C | 0.06719554 | 0.76871751 | 1.45535353 |
| C | 2.73611654 | 0.24637951 | 1.34351253 |
| Br | -1.53628146 | -0.30347249 | 0.99477953 |
| C | -0.01737046 | 2.11478851 | 0.78580653 |
| C | 3.05094654 | 0.40336951 | -0.00104747 |
| C | 4.37690154 | 0.53050351 | -0.39108547 |

| | | | |
|---|---|---|---|
| C | -2.37944242 | -0.52436937 | 1.68767583 |
| C | -3.73205342 | -0.59852637 | 1.96841983 |
| C | -4.66513742 | -0.42993037 | 0.95244483 |
| C | -4.23956942 | -0.19492337 | -0.34639017 |
| C | -2.88361542 | -0.13105437 | -0.63162317 |
| O | 2.11275758 | -1.32357037 | 1.95608383 |
| O | 2.65422358 | -0.02506637 | 0.21576483 |
| C | 3.80745658 | 0.43056863 | 0.92174283 |
| H | -1.64453442 | -0.64092437 | 2.47223283 |
| H | -4.06227842 | -0.78590537 | 2.98119683 |
| H | -5.72248442 | -0.48731937 | 1.17329183 |
| H | -4.96421042 | -0.06861937 | -1.13937717 |
| H | -2.53904242 | 0.03229363 | -1.64379617 |
| H | 4.31745158 | 1.10866963 | 0.24583083 |
| H | 3.50924158 | 0.95394163 | 1.82868483 |
| H | 4.45415658 | -0.40531937 | 1.18257483 |
| N | 0.87820058 | 2.74390063 | -0.52892517 |
| N | 0.43501658 | 2.08125763 | 0.29507983 |
| N | -0.02548442 | 1.34852663 | 1.11185083 |
| C | 5.38675854 | 0.50016651 | 0.55702653 |
| C | 5.07123554 | 0.34521651 | 1.90226253 |
| C | 3.75106154 | 0.22103851 | 2.29568853 |
| O | -0.81030546 | 2.44138851 | -0.05870147 |
| O | 0.95275054 | 2.91180051 | 1.23260153 |
| C | 1.04632554 | 4.19105951 | 0.60710653 |
| H | 2.25993154 | 0.43017951 | -0.73730447 |
| H | 4.61693354 | 0.65553651 | -1.43810047 |
| H | 6.41971654 | 0.60121951 | 0.25246753 |
| H | 5.85756654 | 0.32579651 | 2.64460953 |
| H | 3.49740954 | 0.10369451 | 3.34043353 |
| H | 1.89150054 | 4.68506851 | 1.07477553 |
| H | 1.21735254 | 4.07778751 | -0.46195547 |
| H | 0.13415754 | 4.76240451 | 0.76833453 |
| N | 1.50560954 | -2.51977549 | -0.59144647 |
| N | 1.35368754 | -2.18936549 | 0.49979253 |
| N | 1.20584154 | -1.84008449 | 1.6256805 |

## TS1$^{S_N2}$

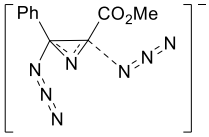



Zero-point correction = 0.172826
Thermal correction to Energy = 0.189643
Thermal correction to Enthalpy = 0.190587
Thermal correction to Gibbs Free Energy = 0.124745
$E_0$ = -3329.418216, E = -3329.401399,
H = -3329.400455, G = -3329.466297.
Imaginary frequency = 1.

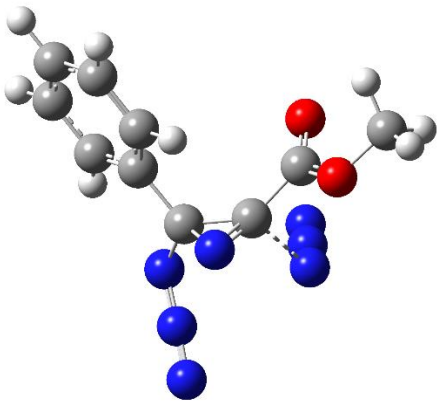


| | | | |
|---|---|---|---|
| N | 0.74931533 | -0.14168243 | -1.09432647 |
| C | 0.10144533 | -0.48633743 | 0.00589953 |
| C | 1.42675133 | -0.21833043 | 0.07327553 |
| C | -1.18055867 | -0.83249243 | 0.50176953 |
| Br | 2.57154133 | -2.68534143 | 0.08889953 |
| C | 2.68459533 | 0.33434457 | 0.65320953 |
| C | -2.26904267 | -0.86527843 | -0.37283947 |
| C | -3.51792767 | -1.18348343 | 0.12191753 |

## TS2$^{S}$



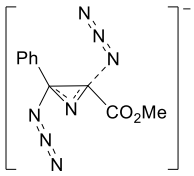

Zero-point correction = 0.186361
Thermal correction to Energy = 0.203355
Thermal correction to Enthalpy = 0.204299
Thermal correction to Gibbs Free Energy = 0.139604
$E_0$ = -919.333776, E = -919.316781,
H = -919.315837, G = -919.380532.
Imaginary frequency = 1.



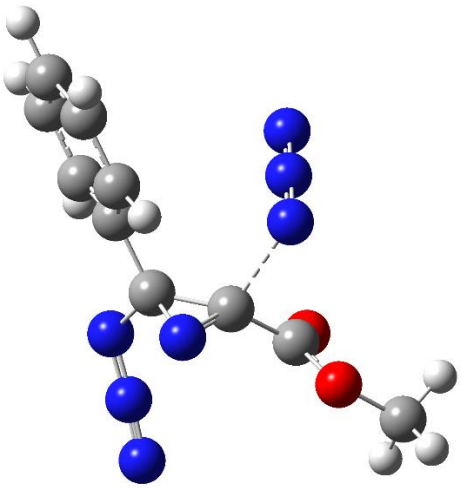
| | | | |
|---|---|---|---|
| N | 0.17751444 | -0.15992328 | -1.57022282 |
| C | 0.90525544 | -0.65710628 | -0.40033082 |
| C | -0.27743456 | 0.18056472 | -0.40294182 |
| C | 2.26182644 | -0.11057228 | -0.08840182 |
| C | -0.71453156 | 1.48342372 | 0.16560718 |
| C | 3.14857144 | -0.77748928 | 0.75240418 |
| C | 4.39184744 | -0.23431328 | 1.03891318 |
| C | 4.77222344 | 0.98009172 | 0.48769318 |

| | | | |
|---|---|---|---|
| C | -3.67319867 | -1.46549743 | 1.47397053 |
| C | -2.58818867 | -1.43327443 | 2.34255453 |
| C | -1.33496967 | -1.11358843 | 1.86043453 |
| O | 3.49164633 | 0.89714057 | -0.03293747 |
| O | 2.75142833 | 0.12138957 | 1.94909253 |
| C | 3.92122333 | 0.62816757 | 2.59650053 |
| H | -2.12241167 | -0.63846643 | -1.41916247 |
| H | -4.37121467 | -1.21030943 | -0.54002847 |
| H | -4.65390267 | -1.71143643 | 1.85766953 |
| H | -2.72649967 | -1.65153943 | 3.39133253 |
| H | -0.47546467 | -1.07333643 | 2.51424053 |
| H | 3.99611533 | 1.70352457 | 2.44886053 |
| H | 3.79578133 | 0.39644357 | 3.64810753 |
| H | 4.80928533 | 0.13956857 | 2.20014253 |
| N | 0.59755833 | 2.07335457 | 1.09700353 |
| N | 0.08609233 | 2.35701657 | 0.07631153 |
| N | -0.41241767 | 2.57505157 | -0.94994147 |
| C | 3.89498244 | 1.64918772 | -0.35318182 |
| C | 2.65059644 | 1.10960672 | -0.63605382 |
| O | -0.42494356 | 1.87053672 | 1.26960618 |
| O | -1.43097556 | 2.17485572 | -0.71477182 |
| C | -1.92732756 | 3.43673772 | -0.26607982 |
| H | 2.86241944 | -1.72612828 | 1.18246218 |
| H | 5.06680244 | -0.76720228 | 1.69552618 |
| H | 5.74327444 | 1.40172872 | 0.70936718 |
| H | 4.17986344 | 2.59509672 | -0.79424882 |
| H | 1.97360844 | 1.63170972 | -1.29835482 |
| H | -2.44098056 | 3.87059272 | -1.11746582 |
| H | -2.61969556 | 3.29808172 | 0.56251918 |
| H | -1.10862356 | 4.08018172 | 0.05037618 |
| N | -0.55412556 | -3.44098628 | -1.36607382 |
| N | 0.09023544 | -2.75277528 | -0.75450482 |
| N | 0.81296944 | -2.08310928 | -0.04100682 |
| N | -1.85402056 | -0.73265028 | 0.29439218 |
| N | -1.67828856 | -1.00139828 | 1.44560018 |
| N | -1.51784656 | -1.26242928 | 2.54885518 |

TS2[a]

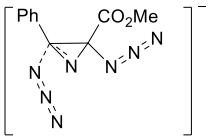



Zero-point correction = 0.186253
Thermal correction to Energy = 0.203248
Thermal correction to Enthalpy = 0.204192
Thermal correction to Gibbs Free Energy = 0.139776
$E_0$ = -919.332923, E = -919.315929,
H = -919.314984, G = -919.379400.
Imaginary frequency = 1.

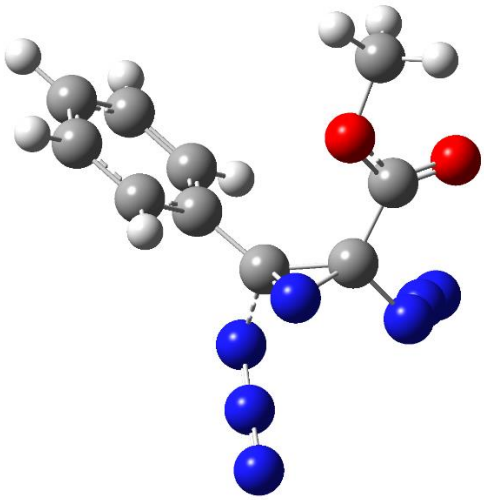


| | | | |
|---|---|---|---|
| N | -0.07738713 | 1.12429157 | 1.58725345 |
| C | 0.68599387 | 1.34335757 | 0.35999945 |
| C | -0.38602313 | 0.38939557 | 0.55814345 |
| C | 2.13203087 | 0.96989057 | 0.26759445 |
| C | -1.68593913 | 0.06077557 | -0.08667355 |

TS3[c]




Zero-point correction = 0.186986
Thermal correction to Energy = 0.203641
Thermal correction to Enthalpy = 0.204585
Thermal correction to Gibbs Free Energy = 0.140871
$E_0$ = -919.339605, E = -919.322950,
H = -919.322005, G = -919.385720.
Imaginary frequency = 1.

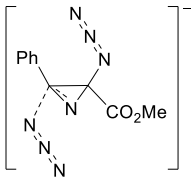


| | | | |
|---|---|---|---|
| N | 0.08244237 | -0.14948411 | -1.60094444 |
| C | 0.60780137 | -0.45189011 | -0.44553344 |
| C | -0.49046063 | 0.51986289 | -0.44604944 |
| C | 2.00977037 | -0.46406311 | 0.01883356 |
| C | -0.22962963 | 1.97654989 | -0.20393044 |
| C | 2.31924437 | -0.37107911 | 1.37053656 |

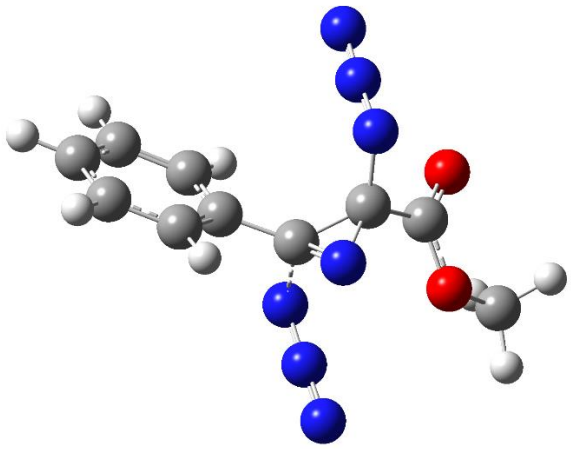
| | | | |
|---|---|---|---|
| C | 2.88928187 | 1.27981957 | -0.85731655 |
| C | 4.22610087 | 0.91939957 | -0.92612455 |
| C | 4.82364887 | 0.24620057 | 0.12920945 |
| C | 4.07271887 | -0.06581243 | 1.25338845 |
| C | 2.73587987 | 0.29446457 | 1.32090245 |
| O | -1.87868913 | 0.11790157 | -1.27602655 |
| O | -2.60576013 | -0.26112043 | 0.81472845 |
| C | -3.89492313 | -0.60045843 | 0.30143645 |
| H | 2.42920287 | 1.80318157 | -1.68348655 |
| H | 4.80103087 | 1.16342057 | -1.80962555 |
| H | 5.86733087 | -0.03339043 | 0.07482245 |
| H | 4.52967587 | -0.58812343 | 2.08346545 |
| H | 2.14237287 | 0.04925957 | 2.19054645 |
| H | -4.49326313 | -0.87143843 | 1.16490845 |
| H | -4.33522113 | 0.25270057 | -0.21146155 |
| H | -3.82269913 | -1.43930643 | -0.38824755 |
| N | -1.64119513 | 3.62547857 | -0.16423655 |
| N | -0.64870513 | 3.10121757 | -0.24442355 |
| N | 0.45034087 | 2.59958657 | -0.38403655 |
| N | 0.16998487 | -1.46917543 | 0.53658445 |
| N | 0.66267687 | -1.71787043 | -0.52325655 |
| N | 1.13688287 | -1.96291443 | -1.53630155 |

| | | | |
|---|---|---|---|
| C | 3.64173337 | -0.34247311 | 1.78125356 |
| C | 4.66422337 | -0.41792911 | 0.84418156 |
| C | 4.35732837 | -0.51344611 | -0.50522644 |
| C | 3.03310037 | -0.52829511 | -0.91739044 |
| O | -0.92302963 | 2.68515389 | 0.48747156 |
| O | 0.88369137 | 2.39503889 | -0.80114044 |
| C | 1.26773937 | 3.74235289 | -0.53599844 |
| H | 1.51843437 | -0.32989411 | 2.09659456 |
| H | 3.87573937 | -0.26236311 | 2.83436656 |
| H | 5.69690037 | -0.39873311 | 1.16592856 |
| H | 5.14944737 | -0.56826011 | -1.23993644 |
| H | 2.78457737 | -0.58040811 | -1.96879344 |
| H | 2.20413437 | 3.89154189 | -1.06360444 |
| H | 0.51324537 | 4.43713889 | -0.90066144 |
| H | 1.40982337 | 3.89542389 | 0.53244556 |
| N | -1.24483763 | -3.07728511 | -1.27736644 |
| N | -0.63341563 | -2.60470011 | -0.43350744 |
| N | 0.01472137 | -2.05297511 | 0.40039156 |
| N | -1.85028663 | 0.14211989 | -0.04597444 |
| N | -2.03378763 | 0.05696289 | 1.15803256 |
| N | -2.30653163 | -0.05108311 | 2.24252756 |

## TS3$^t$

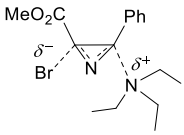



Zero-point correction = 0.186581
Thermal correction to Energy = 0.203573
Thermal correction to Enthalpy = 0.204517
Thermal correction to Gibbs Free Energy = 0.139235
$E_0$ = -919.337626, E = -919.320635,
H = -919.319691, G = -919.384973.
Imaginary frequency = 1.

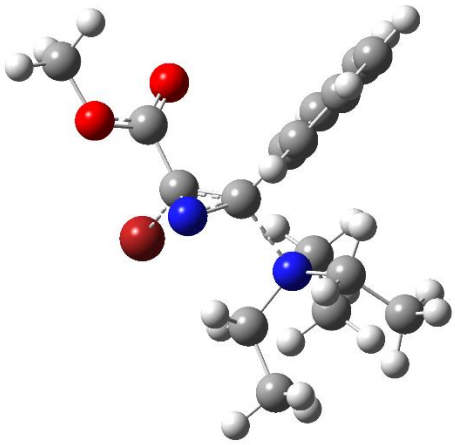


| | | | |
|---|---|---|---|
| N | 0.63723701 | -0.32989461 | 1.62031069 |
| C | 0.01229901 | -0.24370661 | 0.47637769 |
| C | 0.99538201 | 0.78896339 | 0.77051669 |
| C | -1.42634199 | -0.20702761 | 0.14354269 |

## TS4$^s$




Zero-point correction = 0.372284
Thermal correction to Energy = 0.394538
Thermal correction to Enthalpy = 0.395482
Thermal correction to Gibbs Free Energy = 0.320394
$E_0$ = -3457.335277, E = -3457.313024,
H = -3457.312080, G = -3457.387168.
Imaginary frequency = 1.

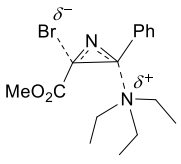


| | | | |
|---|---|---|---|
| N | -0.43283744 | 0.38987751 | -1.18812308 |
| C | -1.07754044 | 0.84630651 | -0.09892508 |
| C | 0.13397356 | 0.08181951 | 0.03725492 |
| C | -1.31436944 | 2.26424451 | 0.25903592 |

| | | | |
|---|---|---|---|
| C | 2.31404201 | 0.88595339 | 0.05546169 |
| C | -1.87202399 | 0.32477439 | -1.06177031 |
| C | -3.22790899 | 0.40354839 | -1.32849431 |
| C | -4.14933399 | -0.06095861 | -0.39783631 |
| C | -3.70735199 | -0.59462061 | 0.80341169 |
| C | -2.34916799 | -0.65923561 | 1.07765669 |
| O | 2.62549801 | 1.83004639 | -0.63347131 |
| O | 3.09392701 | -0.16247061 | 0.26760969 |
| C | 4.30735501 | -0.20956561 | -0.47868631 |
| H | -1.14799199 | 0.67091839 | -1.78688531 |
| H | -3.56972499 | 0.82742839 | -2.26312631 |
| H | -5.20883999 | 0.00091039 | -0.60693531 |
| H | -4.42156099 | -0.95200061 | 1.53303869 |
| H | -1.99324199 | -1.05036661 | 2.02114169 |
| H | 4.75090301 | -1.17502461 | -0.25806231 |
| H | 4.10229001 | -0.12267161 | -1.54411631 |
| H | 4.97700701 | 0.59303539 | -0.17389131 |
| N | 1.66104601 | -3.15406361 | 0.15477669 |
| N | 1.14923401 | -2.29628161 | -0.40574131 |
| N | 0.61423401 | -1.37901461 | -0.94519431 |
| N | 0.54161201 | 2.11081439 | 1.23846269 |
| N | 0.17713501 | 2.89082139 | 0.37080369 |
| N | -0.18803999 | 3.68664539 | -0.33356831 |

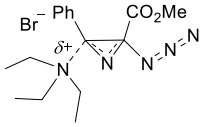
| | | | |
|---|---|---|---|
| Br | 0.29307556 | -1.85716549 | 0.79506992 |
| C | 1.46236156 | 0.65143751 | 0.47069392 |
| C | -1.30302644 | 2.68148351 | 1.58460792 |
| C | -1.48844744 | 4.02015751 | 1.89299092 |
| C | -1.67415144 | 4.94878951 | 0.88016092 |
| C | -1.65806444 | 4.53888951 | -0.44672308 |
| C | -1.47287444 | 3.20268951 | -0.75589908 |
| O | 1.66577056 | 1.15283751 | 1.54601692 |
| O | 2.35938256 | 0.55224351 | -0.49931808 |
| C | 3.65710956 | 1.08313851 | -0.21561408 |
| H | -1.12945944 | 1.96209351 | 2.37177592 |
| H | -1.47616144 | 4.33908351 | 2.92610692 |
| H | -1.81810444 | 5.99309651 | 1.12098292 |
| H | -1.78503544 | 5.26342951 | -1.23927408 |
| H | -1.44695644 | 2.87507451 | -1.78657408 |
| H | 4.25078356 | 0.89300451 | -1.10313408 |
| H | 3.59189056 | 2.15225051 | -0.02367908 |
| H | 4.09148956 | 0.58426351 | 0.64832692 |
| N | -2.77886044 | -0.04645749 | 0.22942592 |
| C | -3.81008144 | 0.91221951 | -0.24422708 |
| C | -2.83955544 | -0.28781149 | 1.69684192 |
| C | -2.70770444 | -1.26767649 | -0.60439408 |
| C | -3.74147544 | -1.41551549 | 2.17503792 |
| C | -5.25245044 | 0.70972351 | 0.20335792 |
| C | -3.99599644 | -1.87149149 | -1.14105508 |
| H | -3.73932044 | 0.93115651 | -1.33128708 |
| H | -3.51588044 | 1.89515851 | 0.10597392 |
| H | -1.82565444 | -0.49759249 | 2.02755892 |
| H | -3.13980244 | 0.65308651 | 2.15443792 |
| H | -2.17633244 | -2.01502149 | -0.02788308 |
| H | -2.05730244 | -1.00996449 | -1.44336008 |
| H | -3.66947744 | -1.46366549 | 3.26121792 |
| H | -4.78596344 | -1.26764549 | 1.91421692 |
| H | -3.41830644 | -2.37938949 | 1.78534192 |
| H | -5.84913544 | 1.48553351 | -0.27621308 |
| H | -5.35912044 | 0.84308951 | 1.27855292 |
| H | -5.67376844 | -0.25134049 | -0.07147708 |
| H | -3.71618044 | -2.74634949 | -1.72775708 |
| H | -4.53534944 | -1.19742549 | -1.80355708 |
| H | -4.66936744 | -2.20483849 | -0.35436808 |

TS4[a]

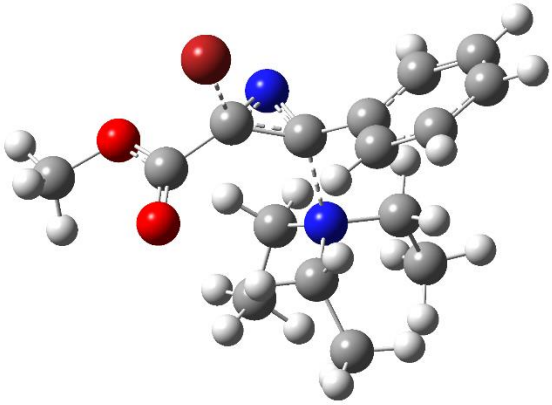



Zero-point correction = 0.372458
Thermal correction to Energy = 0.394725
Thermal correction to Enthalpy = 0.395669
Thermal correction to Gibbs Free Energy = 0.320692
$E_0$ = -3457.339853, E = -3457.317586,
H = -3457.316642, G = -3457.391619.
Imaginary frequency = 1.

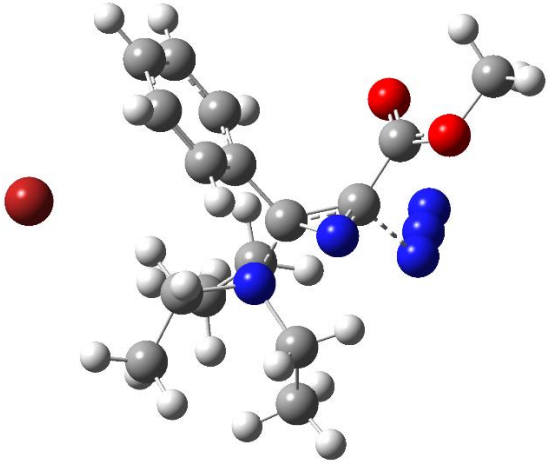
TS5[s]




Zero-point correction = 0.388606
Thermal correction to Energy = 0.413656
Thermal correction to Enthalpy = 0.414600
Thermal correction to Gibbs Free Energy = 0.332438
$E_0$ = -3621.667755, E = -3621.642705,
H = -3621.641761, G = -3621.723922.
Imaginary frequency = 1.



| | | | |
|---|---|---|---|
| N | -0.40556944 | 1.02657237 | -2.18928691 |
| C | 0.39453656 | 0.94302037 | -1.10514491 |
| C | -0.99280844 | 1.26738337 | -0.97213791 |
| C | 1.60707056 | 1.73523037 | -0.80417191 |
| Br | -1.48680544 | 3.28178137 | -0.51373891 |
| C | -2.17164744 | 0.56770537 | -0.35015691 |
| C | 1.84083056 | 2.23619137 | 0.47209209 |
| C | 2.95928756 | 3.01540437 | 0.72320809 |
| C | 3.84586556 | 3.30662937 | -0.30185591 |
| C | 3.59912156 | 2.83832137 | -1.58548491 |
| C | 2.47943356 | 2.06525637 | -1.83737691 |
| O | -2.23247744 | 0.21337537 | 0.79944009 |
| O | -3.13400844 | 0.39112037 | -1.24281991 |
| C | -4.32754244 | -0.23778463 | -0.76483591 |
| H | 1.12840956 | 2.04778037 | 1.26273109 |
| H | 3.12887956 | 3.40685437 | 1.71655709 |
| H | 4.71940556 | 3.91328437 | -0.10593891 |
| H | 4.27560756 | 3.08600237 | -2.39174791 |
| H | 2.26840856 | 1.72354137 | -2.84164291 |
| H | -5.00990944 | -0.25160363 | -1.60741291 |
| H | -4.11197244 | -1.25173263 | -0.43310791 |
| H | -4.75065144 | 0.33212437 | 0.05959409 |
| N | 0.85941756 | -0.88370663 | -0.68281491 |
| C | 0.79163556 | -0.96576663 | 0.79889809 |
| C | 2.22552356 | -1.06208663 | -1.23794891 |
| C | -0.13503244 | -1.70448963 | -1.40968191 |
| C | 2.71460256 | -2.48329163 | -1.48197291 |
| C | 1.53348156 | -2.09282763 | 1.50352009 |
| C | -0.46291444 | -3.08130363 | -0.85443491 |
| H | -0.26153044 | -0.97078063 | 1.06308609 |
| H | 1.20207456 | -0.03229763 | 1.17150009 |
| H | 2.23731456 | -0.53949463 | -2.19289991 |
| H | 2.91071756 | -0.53581163 | -0.57689591 |
| H | 0.21441356 | -1.78226463 | -2.43701091 |
| H | -1.05881244 | -1.13854963 | -1.47275291 |
| H | 3.72687756 | -2.41468163 | -1.87919791 |
| H | 2.74837656 | -3.08894363 | -0.58144491 |
| H | 2.11017656 | -2.99932863 | -2.22563191 |
| H | 1.34432956 | -1.98428663 | 2.57123709 |
| H | 2.60992456 | -2.02115563 | 1.35803209 |
| H | 1.20340756 | -3.08400363 | 1.20634409 |
| H | -1.20755844 | -3.52960463 | -1.51134791 |

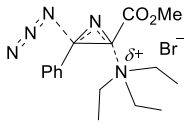


| | | | |
|---|---|---|---|
| N | 1.46095511 | 0.48827305 | 1.58055968 |
| C | 0.37663611 | 0.47418605 | 0.62741968 |
| C | 1.78707811 | 0.45827105 | 0.31935268 |
| C | -0.41845489 | 1.74371005 | 0.46610868 |
| C | 2.70106411 | 1.31006405 | -0.49019532 |
| C | -0.70670689 | 2.28319205 | -0.78162532 |
| C | -1.39091389 | 3.48606705 | -0.88676332 |
| C | -1.78435589 | 4.16683605 | 0.25238868 |
| C | -1.47136989 | 3.65116605 | 1.50304868 |
| C | -0.78546689 | 2.45501405 | 1.60599368 |
| O | 2.46871111 | 1.65428105 | -1.62134532 |
| O | 3.78324911 | 1.64114605 | 0.19988968 |
| C | 4.74832911 | 2.43803705 | -0.49219132 |
| H | -0.37184789 | 1.78800705 | -1.68148732 |
| H | -1.60908789 | 3.89149405 | -1.86486432 |
| H | -2.31912789 | 5.10283005 | 0.16804168 |
| H | -1.75711989 | 4.18523105 | 2.39896768 |
| H | -0.51770689 | 2.06768105 | 2.58009068 |
| H | 5.54991611 | 2.60825905 | 0.21831768 |
| H | 5.12009611 | 1.90806405 | -1.36697532 |
| H | 4.30731611 | 3.38350905 | -0.80141332 |
| N | -0.50012789 | -0.84812495 | 0.53118368 |
| C | -0.63221389 | -1.15455295 | -0.94579632 |
| C | -1.83219289 | -0.52327795 | 1.17796668 |
| C | 0.19621911 | -1.93781595 | 1.31623768 |
| C | -2.70864089 | -1.67544495 | 1.63154368 |
| C | -1.81790089 | -1.97363495 | -1.41556432 |
| C | -0.08731089 | -3.37258195 | 0.91580368 |
| H | 0.30204911 | -1.62103995 | -1.23359132 |
| H | -0.68081789 | -0.19002995 | -1.43665832 |
| H | -1.58580389 | 0.06996305 | 2.05347268 |
| H | -2.38223189 | 0.10872405 | 0.48409268 |
| H | -0.05606489 | -1.76019595 | 2.35791268 |
| H | 1.25651811 | -1.76733795 | 1.20357268 |
| H | -3.61001589 | -1.21992795 | 2.04001068 |
| H | -3.01701889 | -2.33676095 | 0.82928568 |
| H | -2.25081089 | -2.26179995 | 2.42513468 |
| H | -1.69978489 | -2.08561595 | -2.49321432 |
| H | -2.76103189 | -1.45723995 | -1.24614232 |
| H | -1.85906789 | -2.96943895 | -0.98562332 |

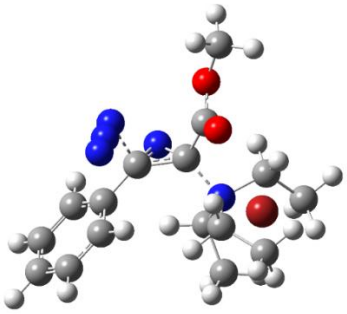
| | | | |
|---|---|---|---|
| H | -0.90016044 | -3.02057963 | 0.14070409 |
| H | 0.39612956 | -3.74628363 | -0.82115491 |

| | | | |
|---|---|---|---|
| H | 0.50900411 | -4.00007495 | 1.57750068 |
| H | 0.23971711 | -3.58024695 | -0.10101632 |
| H | -1.12559389 | -3.67009895 | 1.02343768 |
| N | 2.61190811 | -1.17276795 | -0.36257032 |
| N | 2.62251311 | -1.27526095 | -1.55446232 |
| N | 2.63663411 | -1.38802795 | -2.69191632 |
| Br | -4.78216189 | 0.72771205 | -1.08084032 |

## TS5[a]

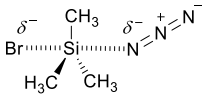



Zero-point correction = 0.387153
Thermal correction to Energy = 0.412536
Thermal correction to Enthalpy = 0.413480
Thermal correction to Gibbs Free Energy = 0.329323
$E_0$ = -3621.674576, E = -3621.649193,
H = -3621.648248, G = -3621.732406.
Imaginary frequency = 1.

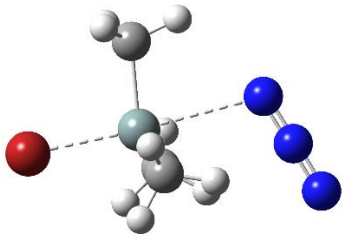


| | | | |
|---|---|---|---|
| N | 0.19885982 | -0.02285135 | -0.42164846 |
| C | -0.68915412 | -0.49162142 | 0.43632556 |
| C | 0.26503373 | 0.49315654 | 0.89676999 |
| C | -1.09748868 | -1.87990273 | 0.73151310 |
| C | -0.22480893 | 1.91041478 | 1.18798366 |
| C | -1.51905972 | -2.28380101 | 1.99462854 |
| C | -1.87624853 | -3.60592444 | 2.21764093 |
| C | -1.82167163 | -4.52703149 | 1.18361750 |
| C | -1.40585089 | -4.12556628 | -0.07952316 |
| C | -1.04210278 | -2.80981438 | -0.30360795 |
| O | -0.58837274 | 2.31181165 | 2.26860003 |
| O | -0.22010665 | 2.65025560 | 0.09437133 |
| C | -0.80100005 | 3.95007552 | 0.21287620 |
| H | -1.57037264 | -1.56998903 | 2.80352874 |
| H | -2.19601627 | -3.91378022 | 3.20367651 |
| H | -2.09909058 | -5.55737784 | 1.35996778 |
| H | -1.35873812 | -4.84099374 | -0.88908439 |
| H | -0.70307961 | -2.49110582 | -1.27985176 |
| H | -0.74979711 | 4.38522651 | -0.77915927 |
| H | -1.83601674 | 3.86496987 | 0.53838625 |
| H | -0.24426524 | 4.55618816 | 0.92505745 |
| N | 1.51139074 | 0.13400055 | 1.77930753 |
| C | 0.99300228 | -0.11368983 | 3.18399430 |
| C | 2.42505789 | 1.33992434 | 1.65848251 |

## TS6



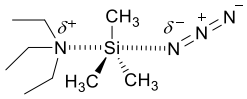

Zero-point correction = 0.125119
Thermal correction to Energy = 0.137111
Thermal correction to Enthalpy = 0.138056
Thermal correction to Gibbs Free Energy = 0.085335
$E_0$ = -3147.799584, E = -3147.787592,
H = -3147.786647, G = -3147.839368.
Imaginary frequency = 1.



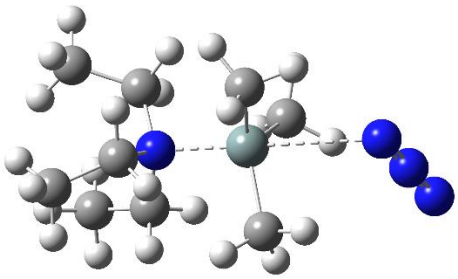
| | | | |
|---|---|---|---|
| C | -0.88438694 | 1.75838197 | 0.05805587 |
| Si | -0.71588194 | -0.10364803 | -0.02249913 |
| C | -0.24440694 | -1.02270803 | 1.53904987 |
| C | -0.19041594 | -0.89897003 | -1.63598013 |
| N | 1.90754606 | 0.60063997 | -0.04992213 |
| N | 2.53691706 | -0.39116603 | -0.03398313 |
| N | 3.13422906 | -1.38909803 | -0.01608513 |
| H | -1.38895594 | 2.12061797 | -0.83873013 |
| H | 0.09173306 | 2.22743397 | 0.13552887 |
| H | -1.49295894 | 2.03657097 | 0.91917787 |
| H | 0.83016406 | -1.18456103 | 1.60094687 |
| H | -0.56594494 | -0.45621403 | 2.41409387 |
| H | -0.74436294 | -1.99087003 | 1.56365487 |
| H | 0.77300406 | -1.39427403 | -1.51632613 |
| H | -0.08889994 | -0.13636603 | -2.40863413 |
| H | -0.92189594 | -1.63376003 | -1.96840313 |
| Br | -3.05624294 | -0.60639603 | -0.04611913 |

| | | | |
|---|---|---|---|
| C | 2.16994912 | -1.09762050 | 1.19364477 |
| C | 3.89449086 | 1.16699433 | 1.98577483 |
| C | 1.93386257 | 0.14884508 | 4.34231564 |
| C | 3.05436397 | -1.91362190 | 2.11639895 |
| H | 0.65283987 | -1.14496614 | 3.18712700 |
| H | 0.12512736 | 0.52583014 | 3.29310301 |
| H | 2.34141375 | 1.64428354 | 0.61678102 |
| H | 1.98625240 | 2.11807479 | 2.27753037 |
| H | 2.72915818 | -0.76806849 | 0.32161004 |
| H | 1.36773017 | -1.73315741 | 0.84079717 |
| H | 4.35426588 | 2.14486178 | 1.84395327 |
| H | 4.07671359 | 0.86394220 | 3.01184285 |
| H | 4.38564238 | 0.47620181 | 1.30286187 |
| H | 1.37553487 | -0.07254313 | 5.25134038 |
| H | 2.23244969 | 1.19383650 | 4.39546261 |
| H | 2.82158078 | -0.47603463 | 4.33737957 |
| H | 3.44200181 | -2.73150174 | 1.51083667 |
| H | 2.49956017 | -2.35318982 | 2.94308418 |
| H | 3.90732404 | -1.36824923 | 2.50609418 |
| Br | 5.43775653 | -0.99082880 | -0.99005276 |
| N | -3.65068503 | 0.20164931 | 2.21754206 |
| N | -3.00849709 | 0.27770288 | 1.27484741 |
| N | -2.34348356 | 0.35539242 | 0.28349015 |

TS7




Zero-point correction = 0.338075
Thermal correction to Energy = 0.357137
Thermal correction to Enthalpy = 0.358081
Thermal correction to Gibbs Free Energy = 0.292288
$E_0$ = -865.584089, E = -865.565027,
H = -865.564083, G = -865.629876.
Imaginary frequency = 1.



| | | | |
|---|---|---|---|
| C | 0.47483079 | -2.15812825 | 0.20182010 |
| Si | 0.42206179 | -0.31600225 | -0.09407490 |
| C | 0.89811679 | 0.24730275 | -1.80992090 |
| C | 0.99599079 | 0.77296375 | 1.30964110 |
| N | 3.28839279 | -0.85896025 | -0.08986190 |
| N | 3.77394879 | 0.21018675 | -0.10005990 |
| N | 4.22679079 | 1.28295275 | -0.10281690 |
| H | 1.47058879 | -2.39144125 | 0.57004510 |
| H | 0.32071479 | -2.70332625 | -0.72896690 |
| H | -0.25857421 | -2.50515025 | 0.92840410 |

| | | | |
|---|---|---|---|
| H | 1.07498679 | 1.32201775 | -1.83306790 |
| H | 1.83031179 | -0.25462025 | -2.06123790 |
| H | 0.15965079 | 0.00432175 | -2.57250690 |
| H | 1.96305779 | 1.20700075 | 1.05560010 |
| H | 1.11484279 | 0.18224875 | 2.21756310 |
| H | 0.31888079 | 1.59681175 | 1.52959510 |
| N | -1.54097621 | 0.02623275 | -0.09337890 |
| C | -1.99047221 | -0.09105225 | 1.33874710 |
| C | -2.14732221 | -1.02967225 | -0.97847590 |
| C | -1.71455521 | 1.41671575 | -0.64426590 |
| C | -3.49680921 | -0.74910425 | -1.61705190 |
| C | -3.44892221 | -0.41824625 | 1.61026710 |
| C | -2.98528621 | 2.17436975 | -0.30092990 |
| H | -1.72291321 | 0.84209875 | 1.82602610 |
| H | -1.38251321 | -0.86897325 | 1.79711210 |
| H | -1.43365921 | -1.21675625 | -1.77819290 |
| H | -2.19507821 | -1.93915625 | -0.38523090 |
| H | -1.60396521 | 1.33638875 | -1.72243590 |
| H | -0.86997021 | 2.00333675 | -0.28683690 |
| H | -3.76445221 | -1.63116525 | -2.19769490 |
| H | -4.28812021 | -0.57627325 | -0.89420690 |
| H | -3.45759521 | 0.09146675 | -2.30689890 |
| H | -3.57082321 | -0.46596925 | 2.69166310 |
| H | -3.73247321 | -1.38947725 | 1.21063310 |
| H | -4.13626121 | 0.33278275 | 1.23206410 |
| H | -2.91729321 | 3.14704075 | -0.78647190 |
| H | -3.08140021 | 2.35294475 | 0.76797410 |
| H | -3.88683321 | 1.68707875 | -0.65919490 |

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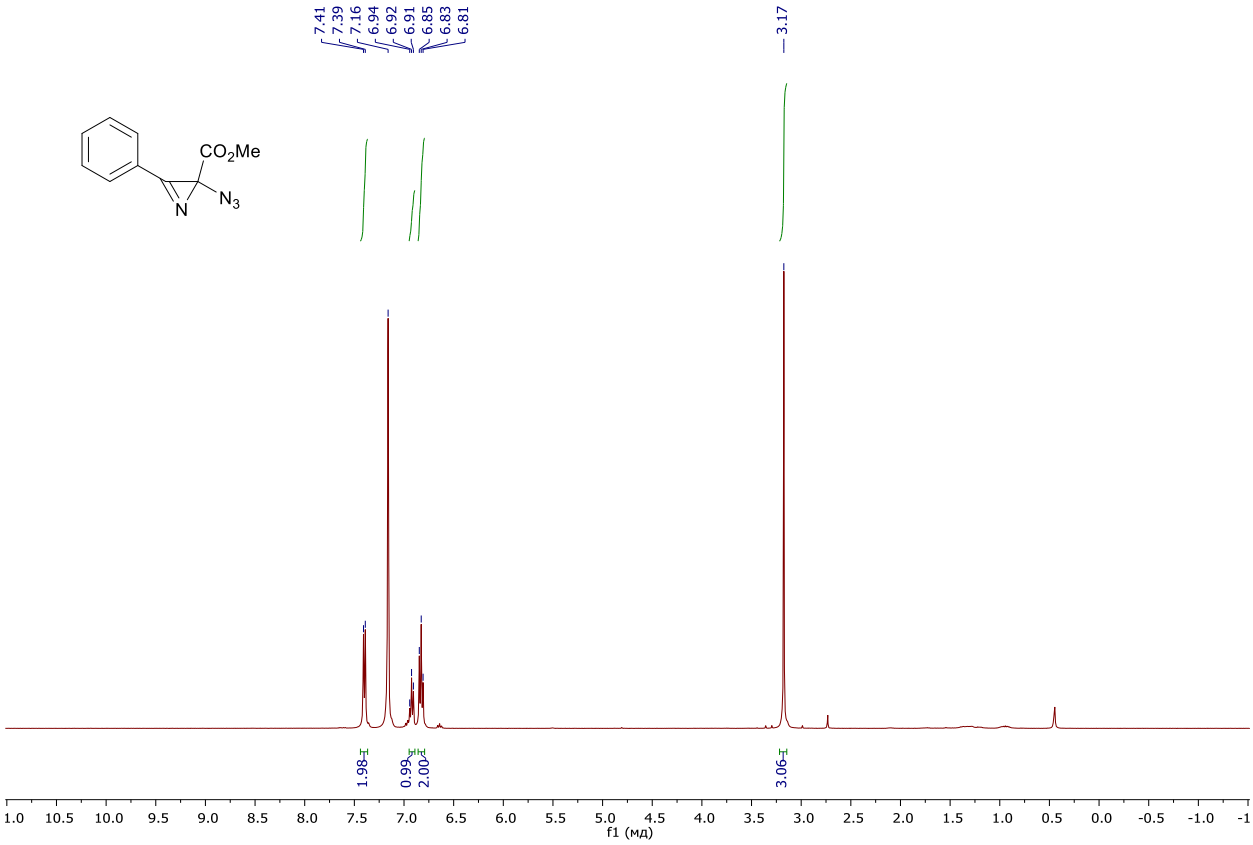
[13] G.M. Sheldrick, *Acta Cryst.*, **2015**, C71, 3–8.

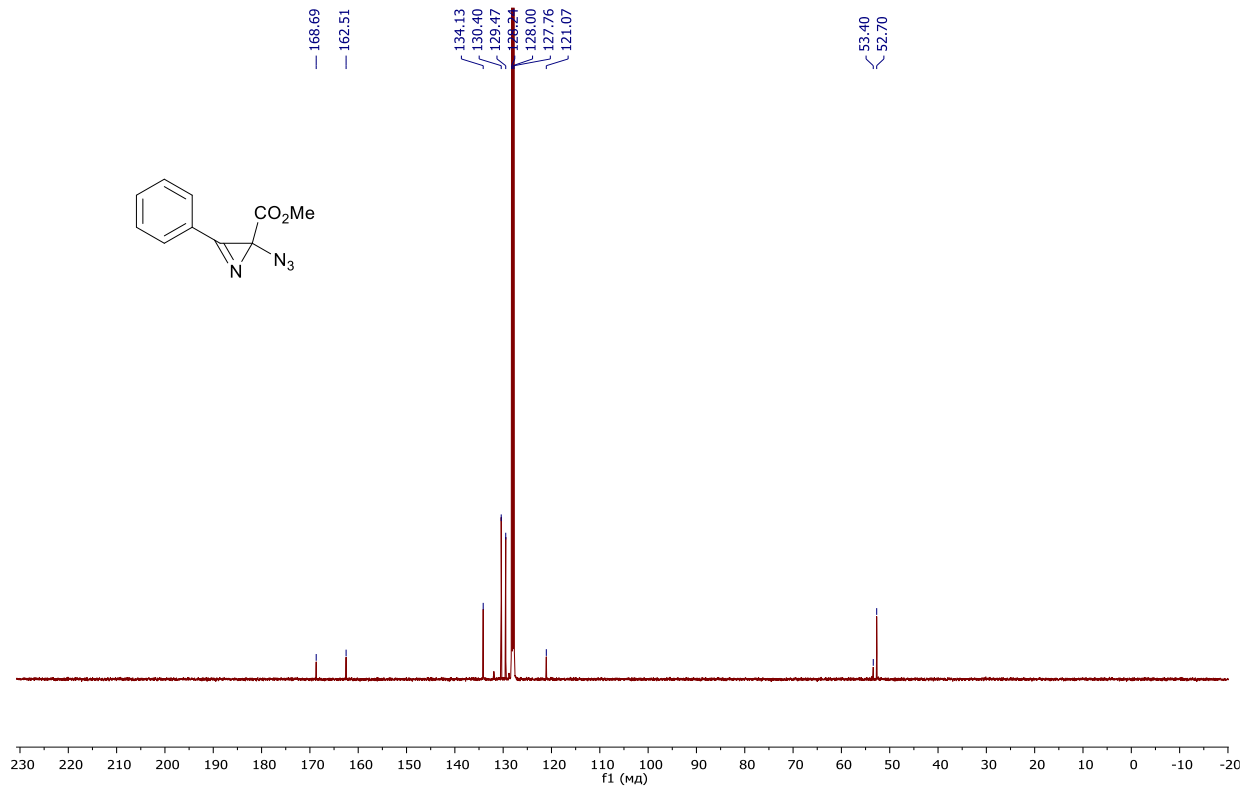
[14] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision D.01 Gaussian, Inc., Wallingford CT, 2013.

## 13. NMR spectra of new compounds

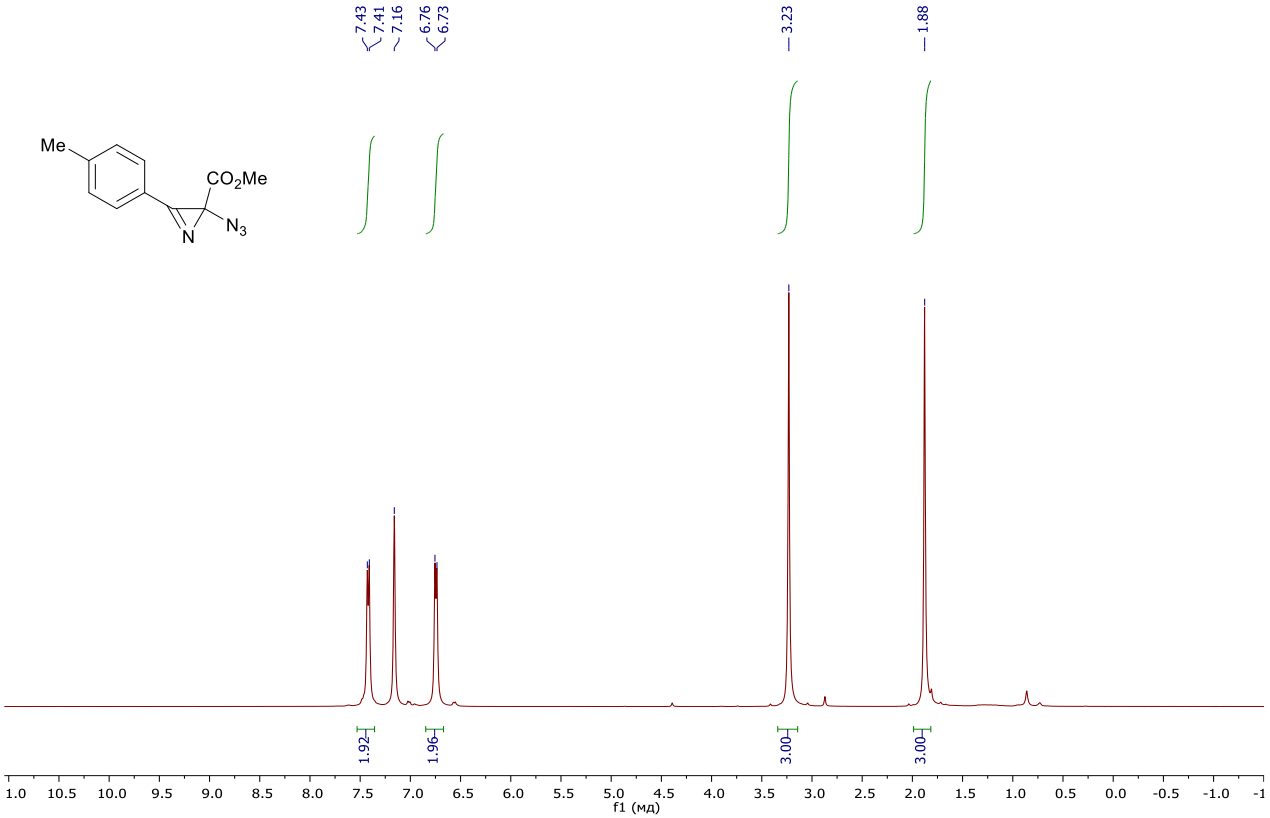
$^{1}$H NMR (400 MHz, $C_6D_6$) spectra of compound **2a**



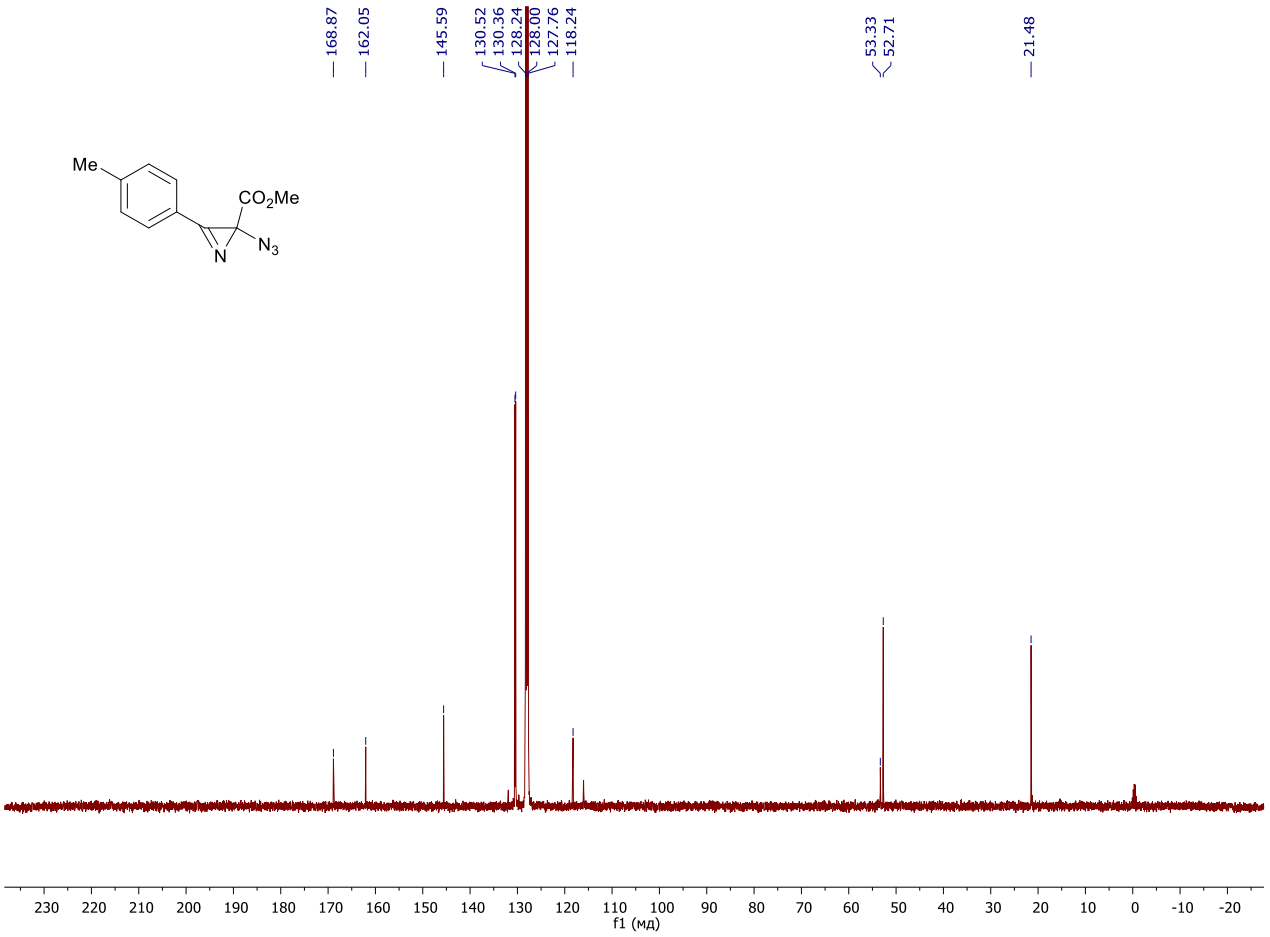

$^{13}$C{$^{1}$H} NMR (100 MHz, $C_6D_6$) spectrum of compound **2a**



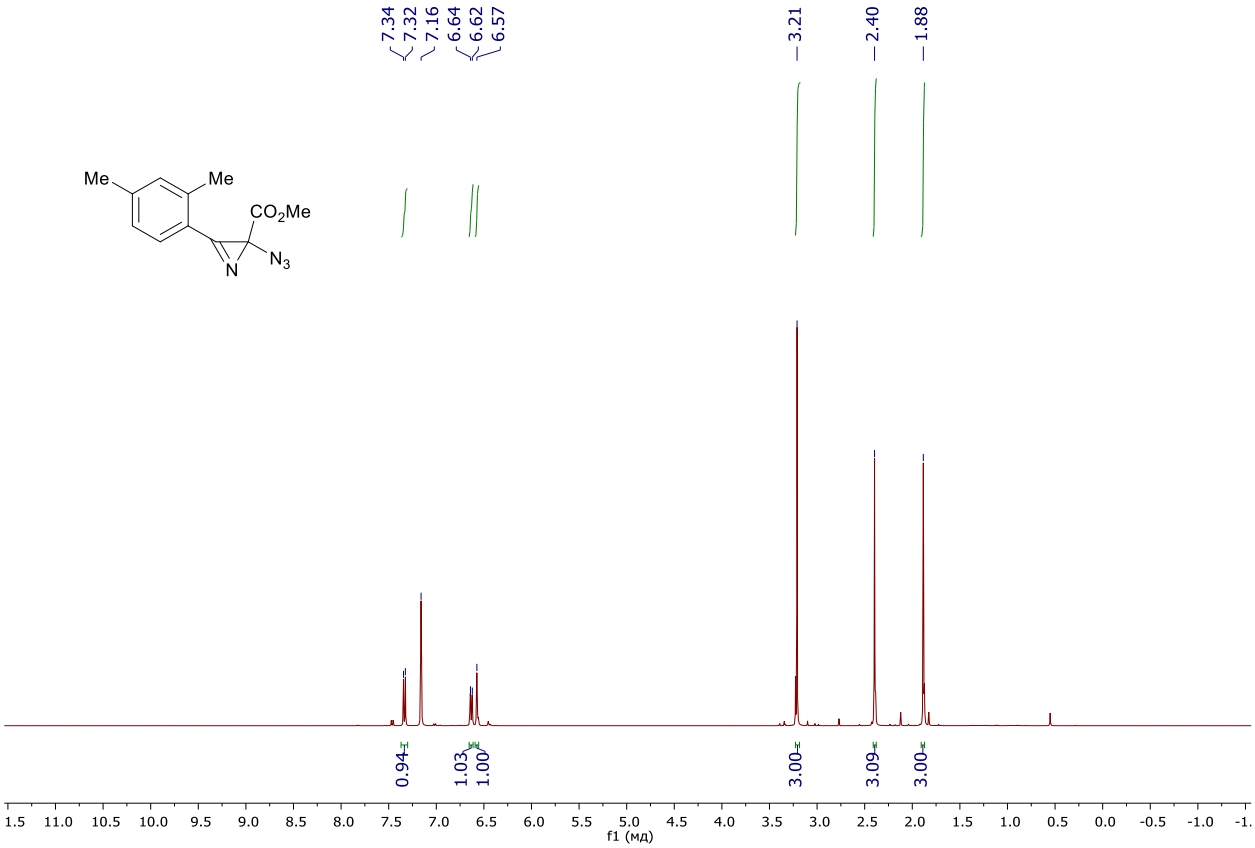
$^{1}$H NMR (400 MHz, $C_6D_6$) spectrum of compound **2b**



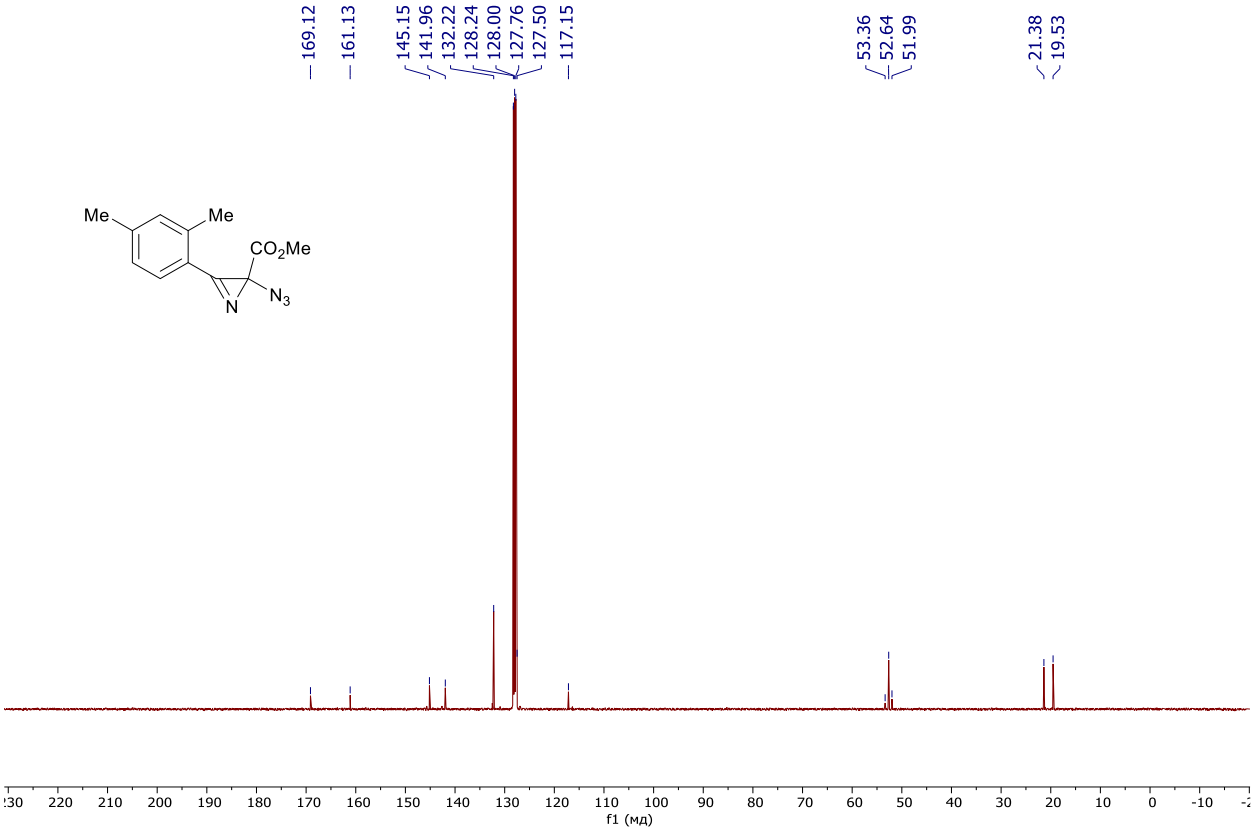

$^{13}$C{$^{1}$H} NMR (100 MHz, $C_6D_6$) spectrum of compound **2b**



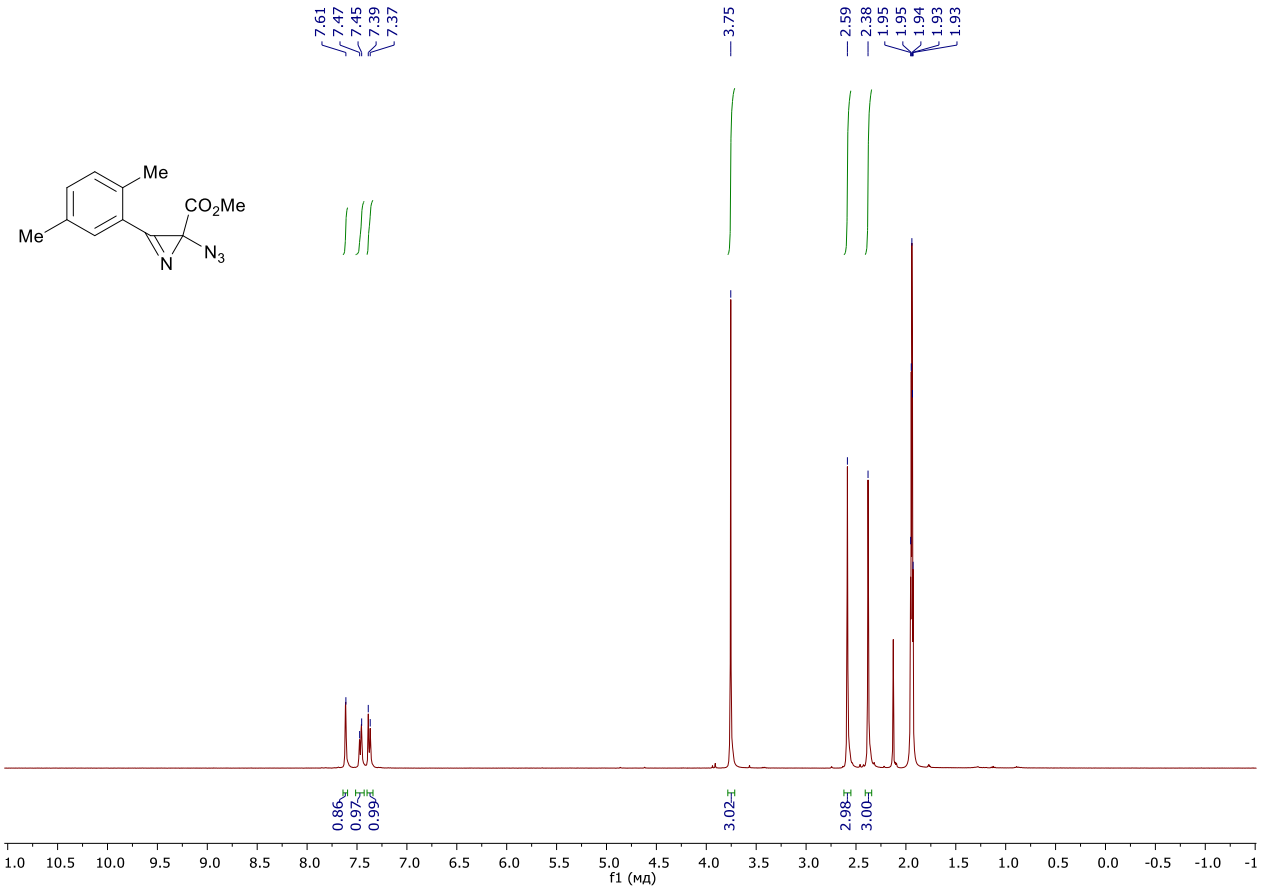
$^{1}$H NMR (400 MHz, $C_6D_6$) spectrum of compound **2c**



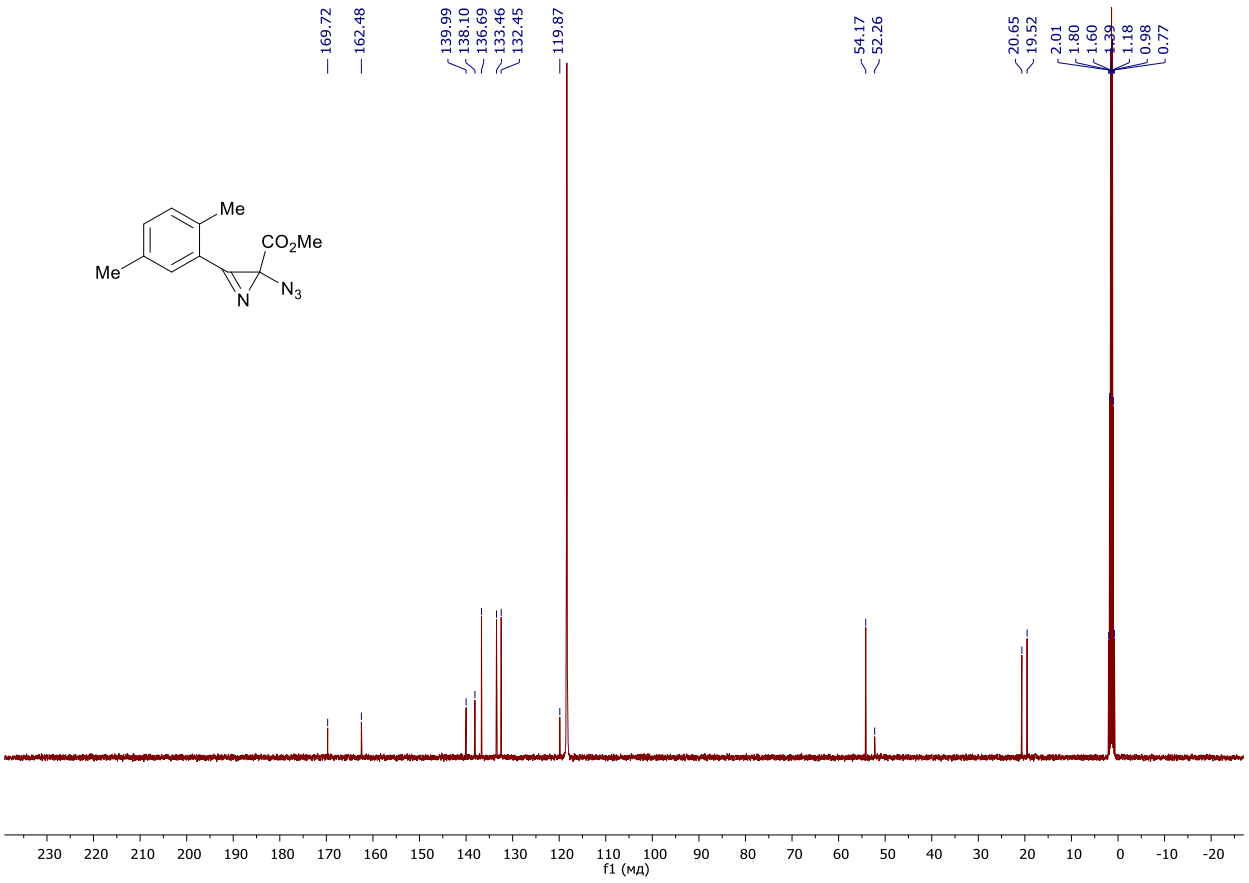

$^{13}$C{$^{1}$H} NMR (100 MHz, $C_6D_6$) spectrum of compound **2c**



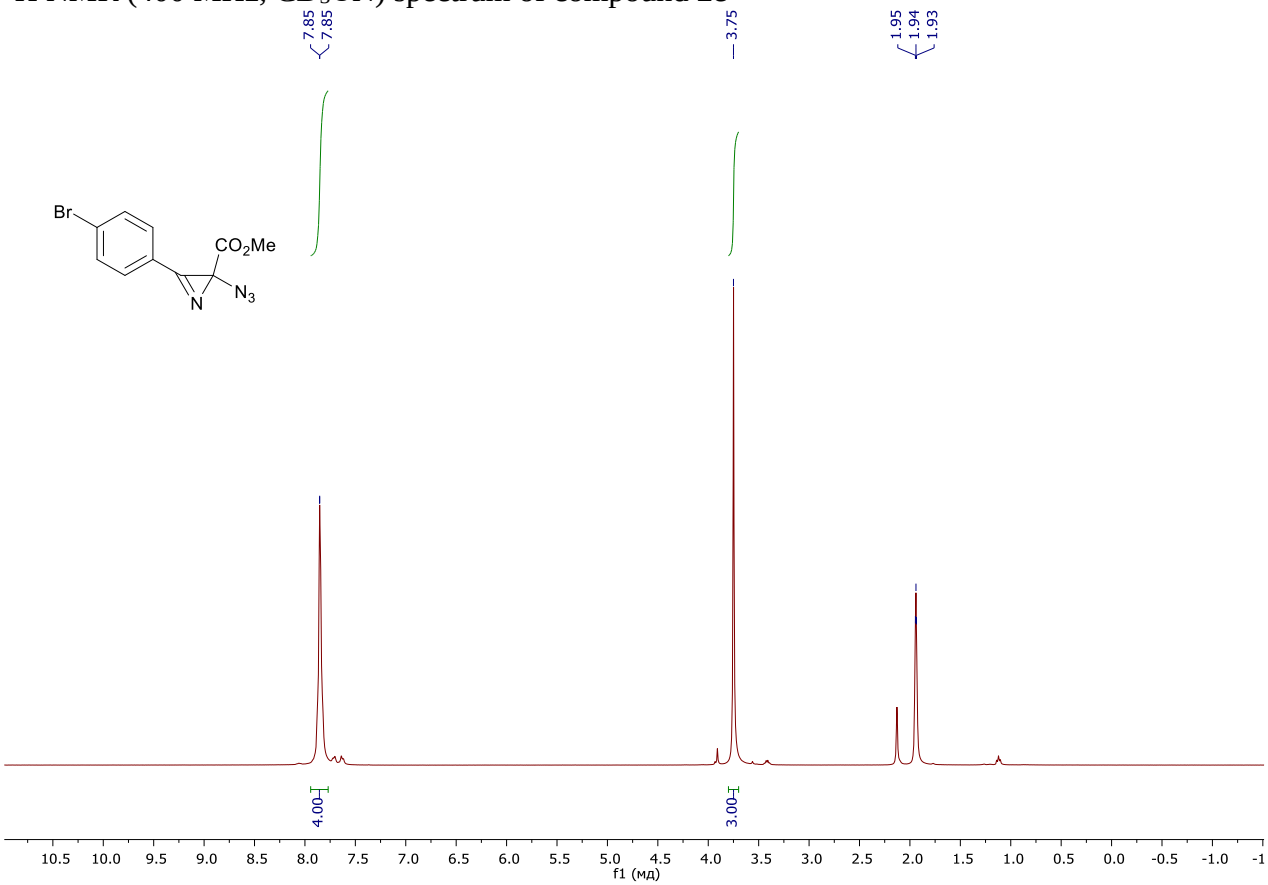
$^{1}$H NMR (400 MHz, $CD_3CN$) spectrum of compound **2d**



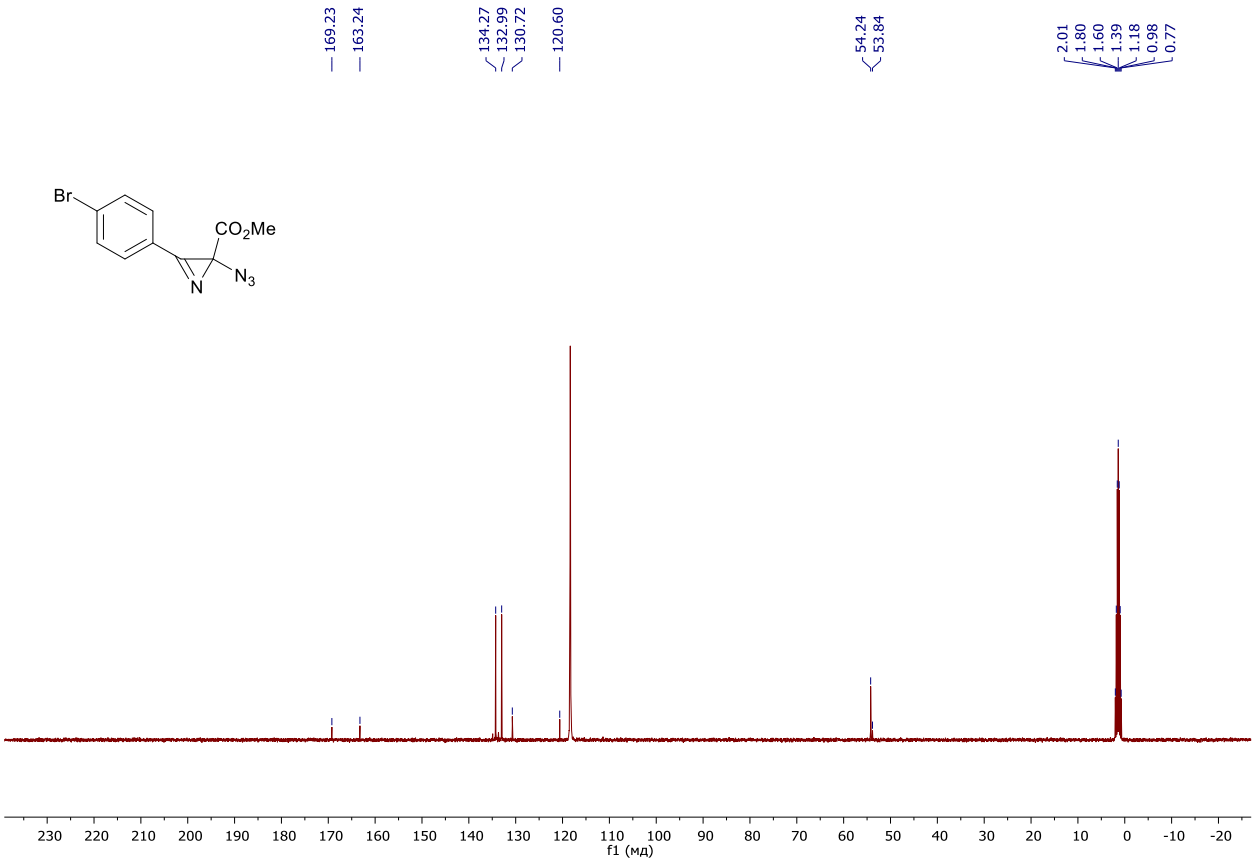

$^{13}$C{$^{1}$H} NMR (100 MHz, $CD_3CN$) spectrum of compound **2d**



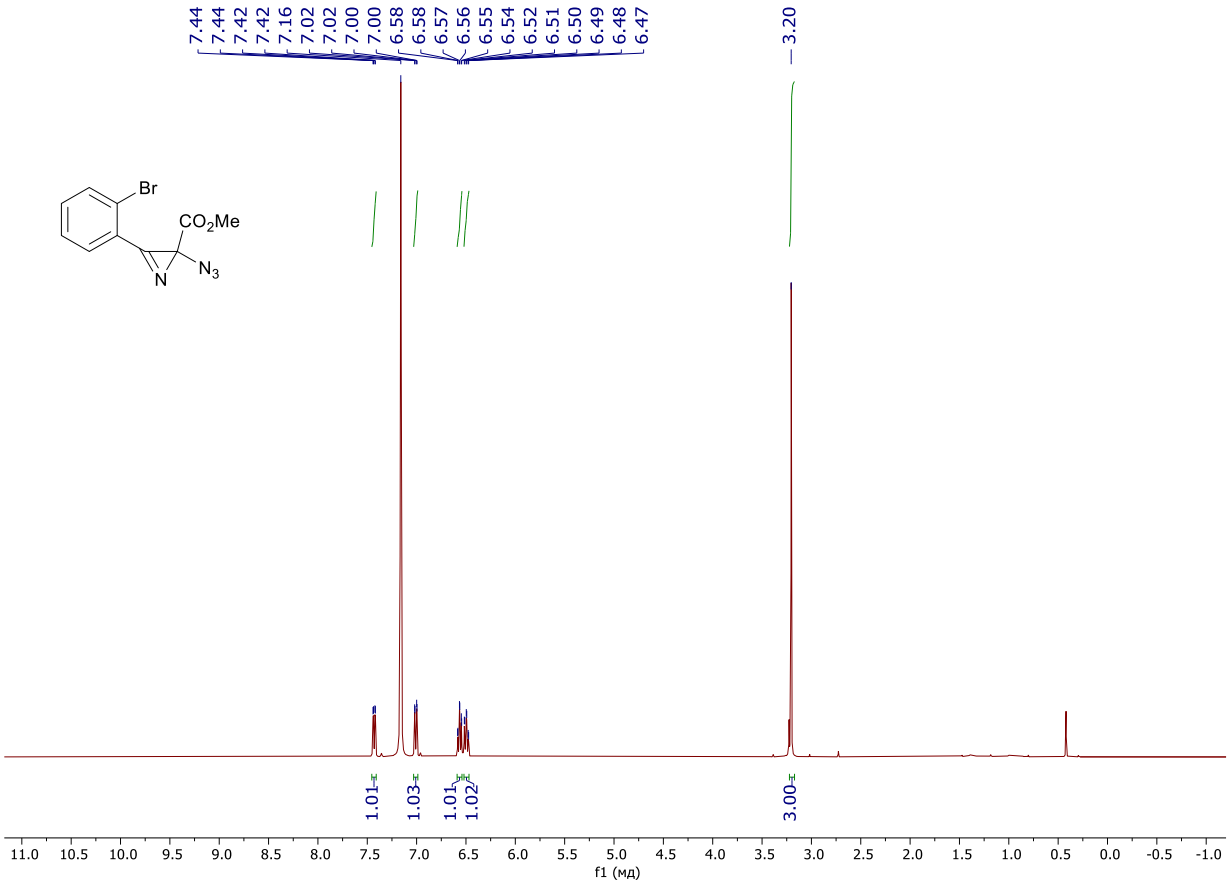
$^{1}$H NMR (400 MHz, $CD_3CN$) spectrum of compound **2e**



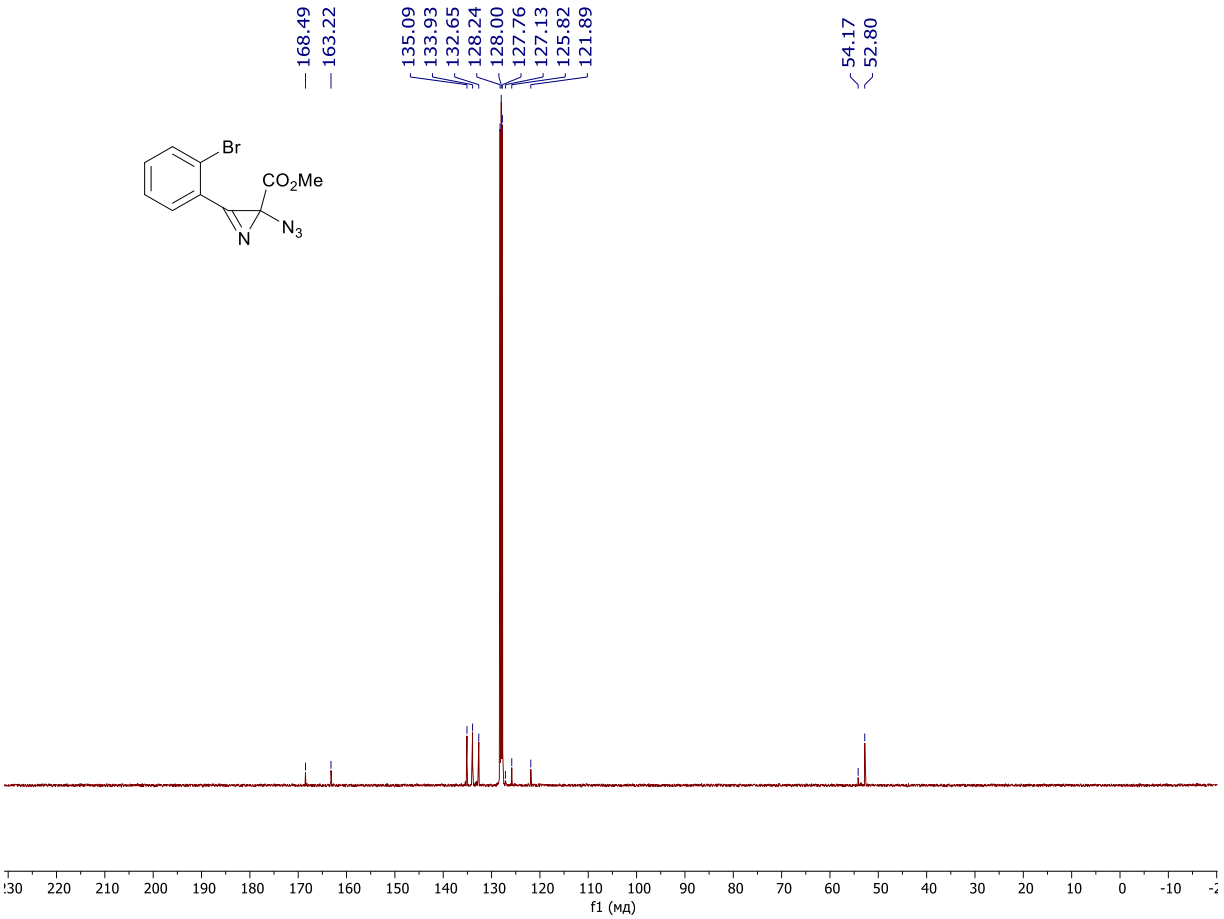

$^{13}$C{$^{1}$H} NMR (100 MHz, $CD_3CN$) spectrum of compound **2e**



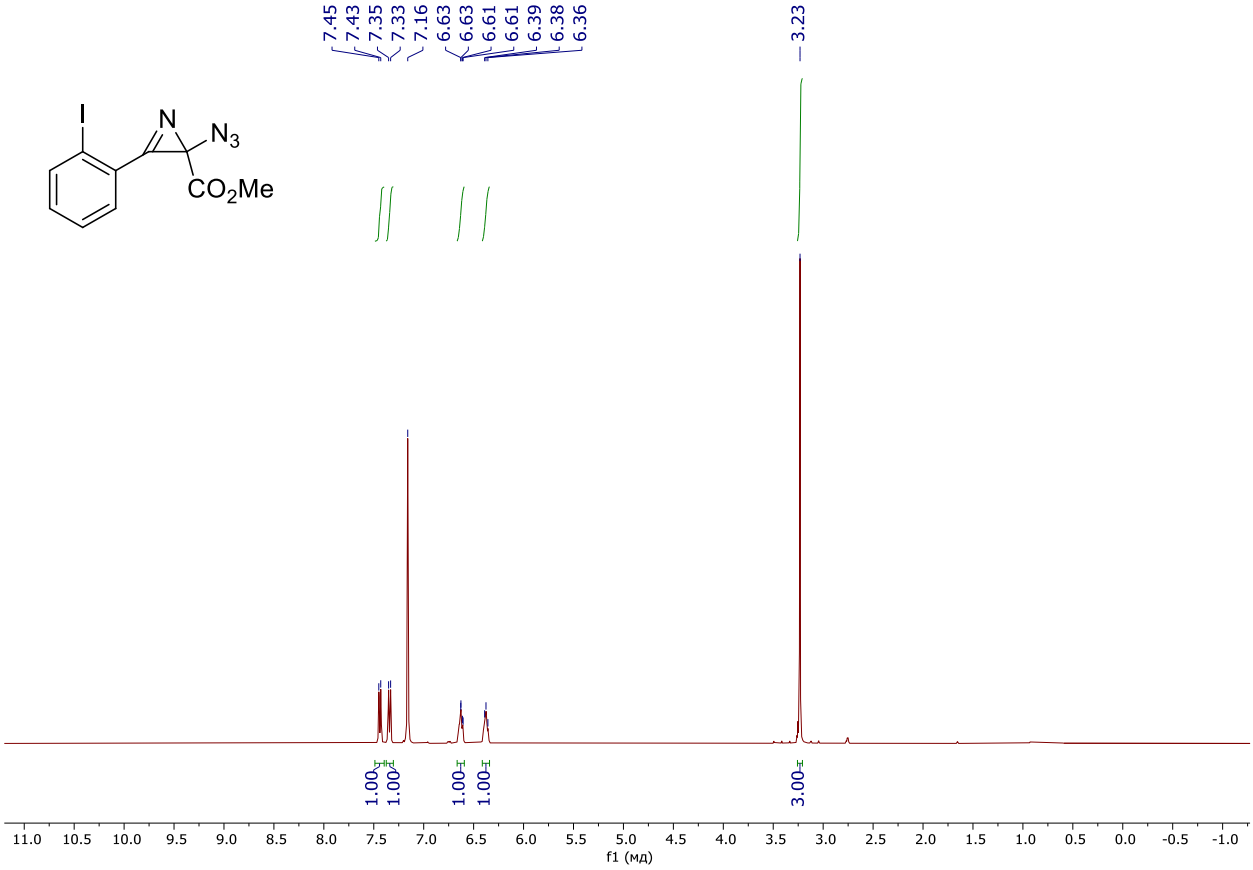
$^{1}$H NMR (400 MHz, $C_6D_6$) spectrum of compound **2f**



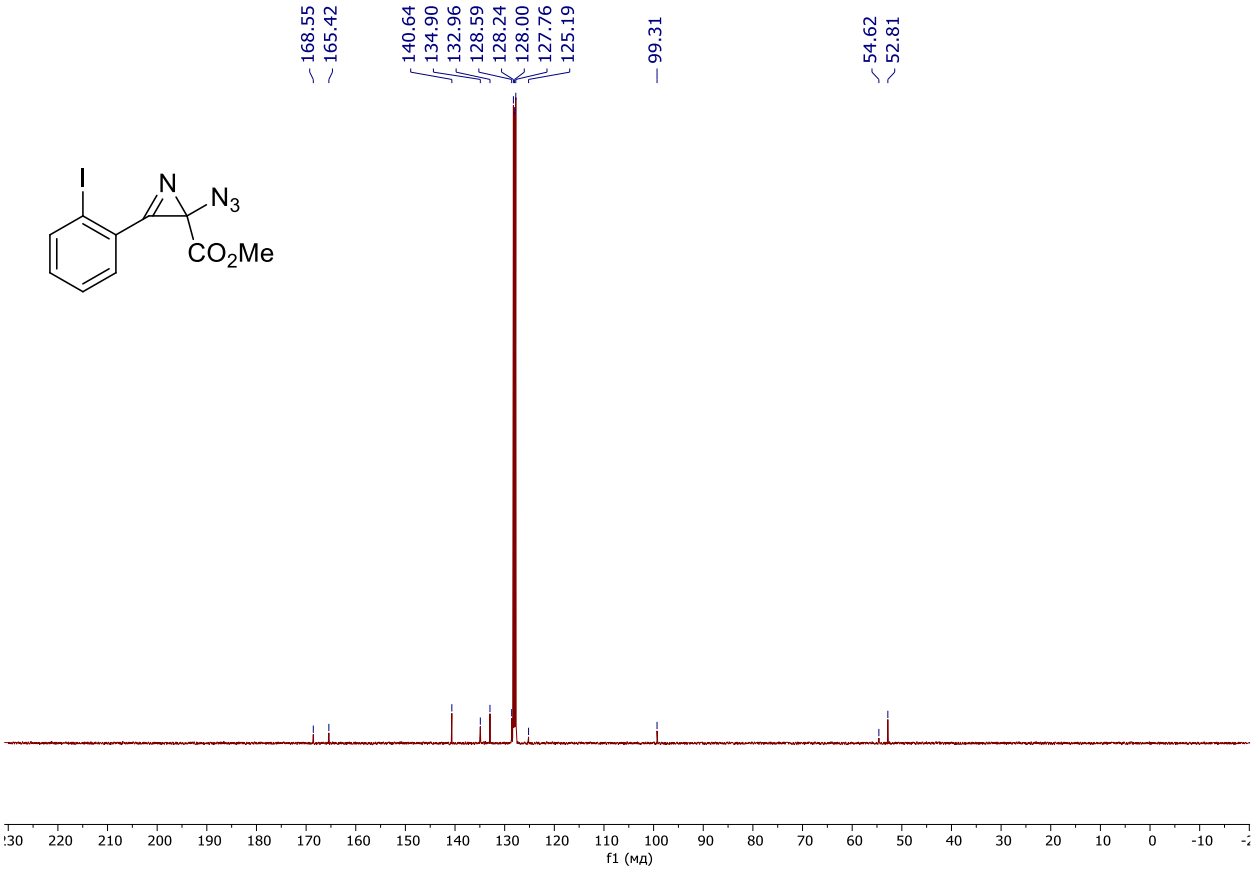

$^{13}$C{$^{1}$H} NMR (100 MHz, $C_6D_6$) spectrum of compound **2f**



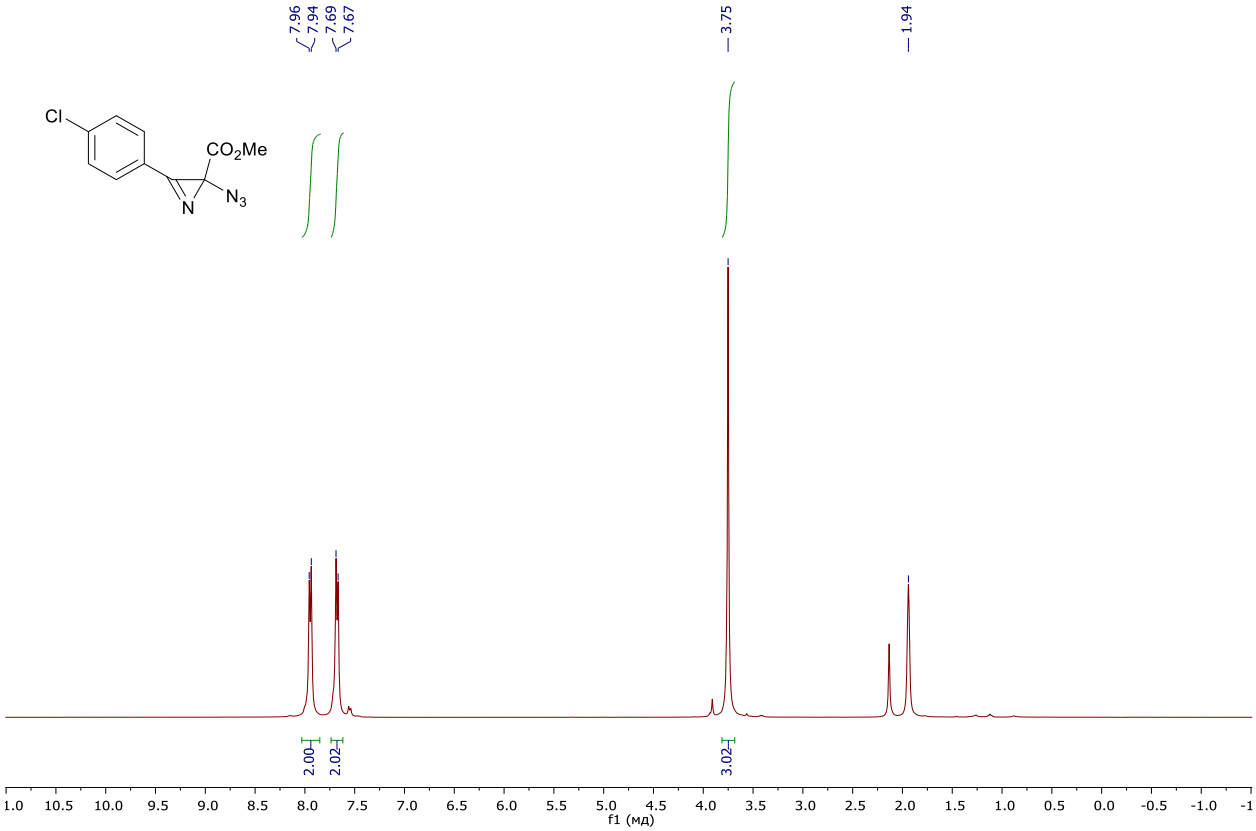
$^{1}$H NMR (400 MHz, $C_6D_6$) spectrum of compound **2g**



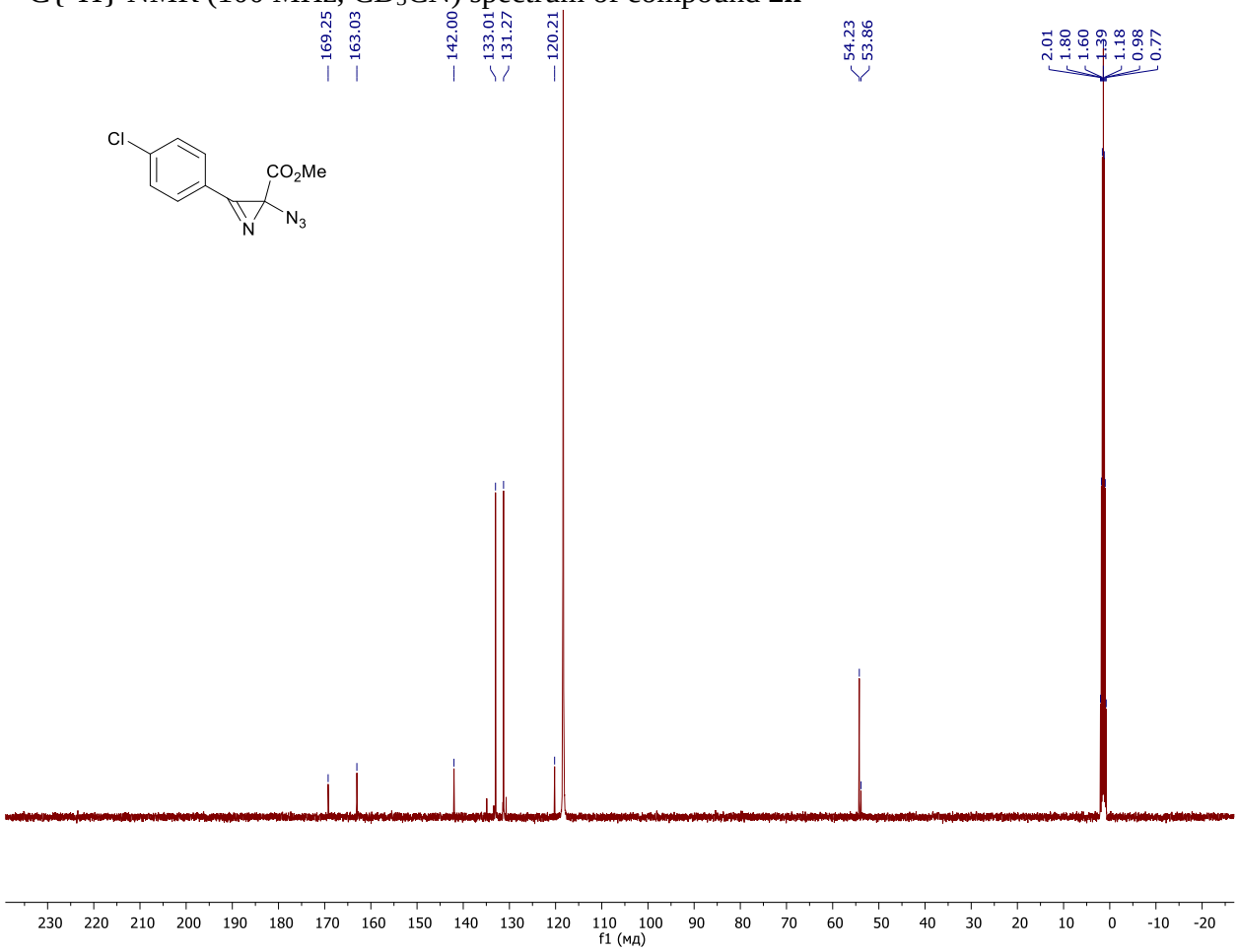

$^{13}$C{$^{1}$H} NMR (100 MHz, $C_6D_6$) spectrum of compound **2g**



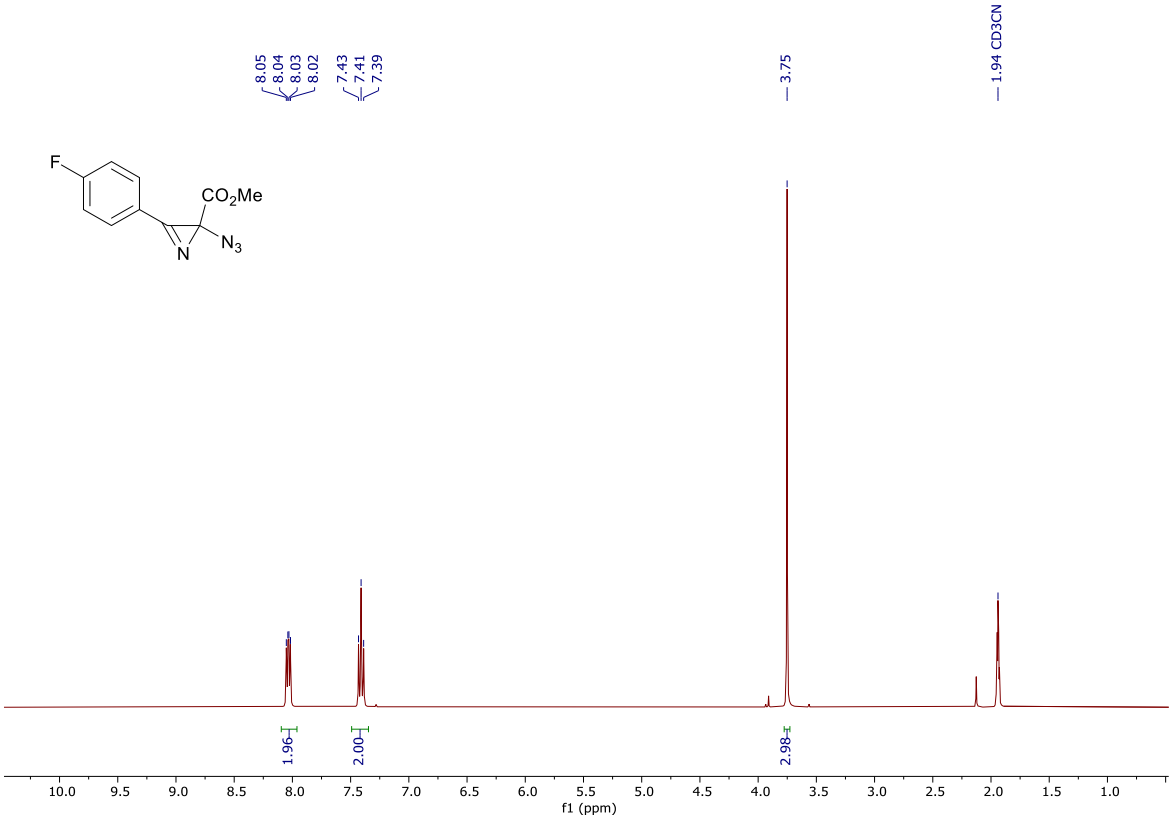
$^{1}$H NMR (400 MHz, $CD_3CN$) spectrum of compound **2h**



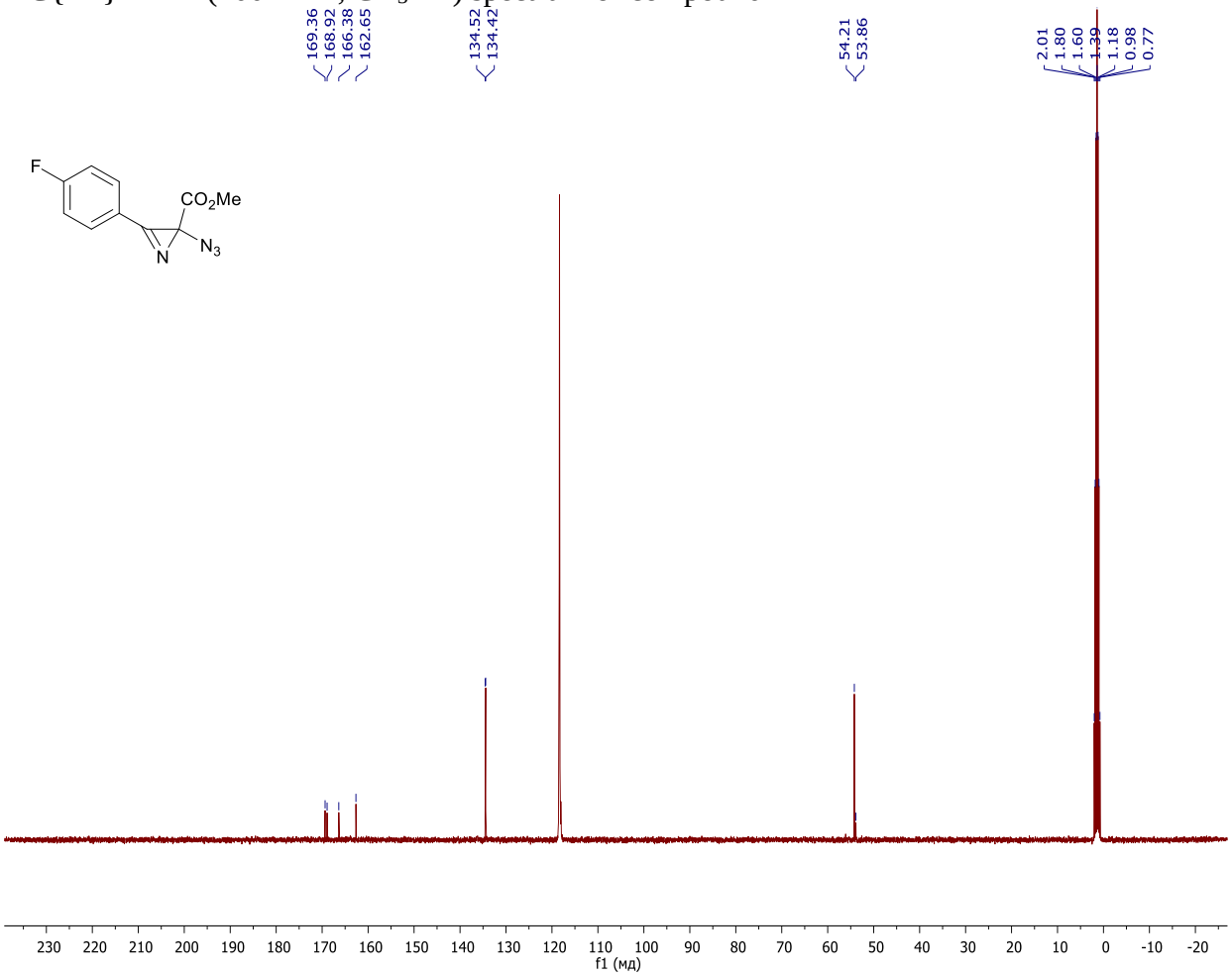

$^{13}$C{$^{1}$H} NMR (100 MHz, $CD_3CN$) spectrum of compound **2h**



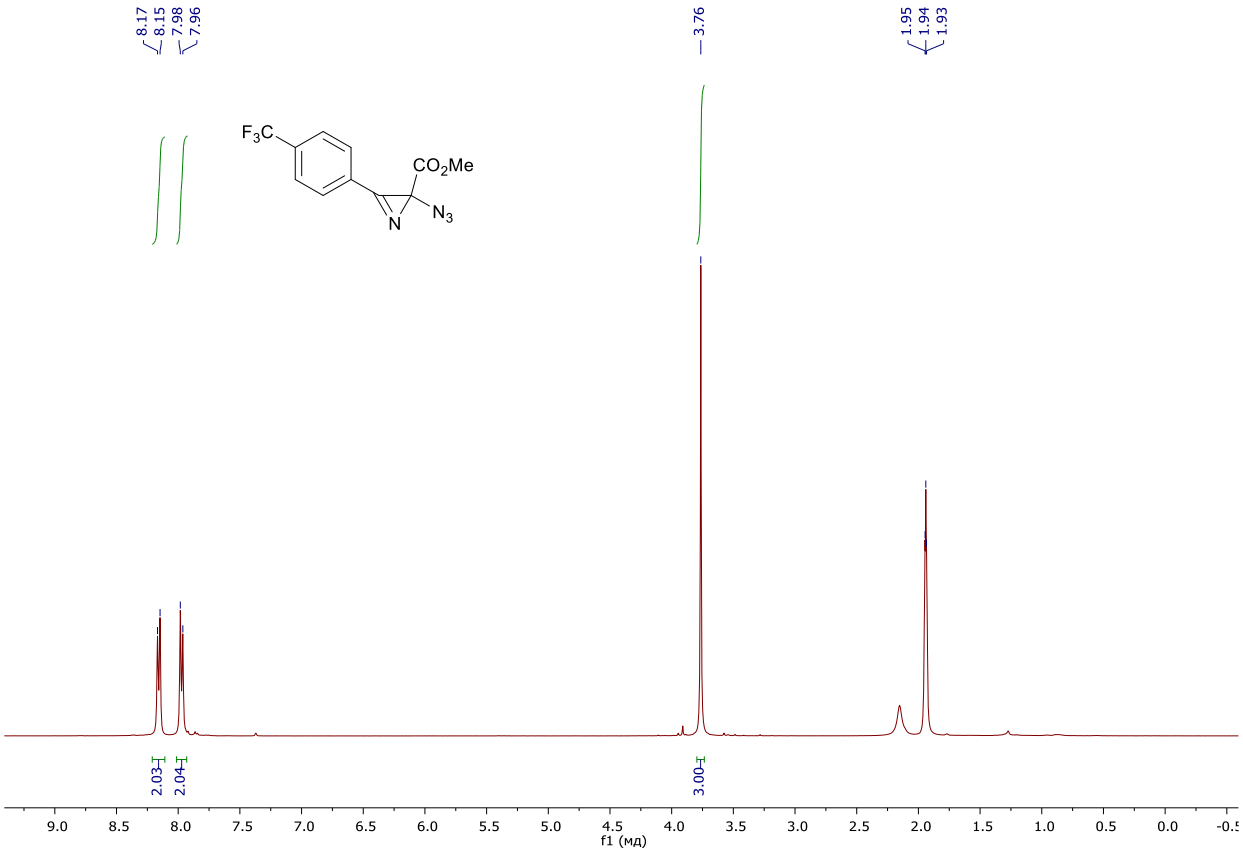
$^{1}$H NMR (400 MHz, $CD_3CN$) spectrum of compound **2i**



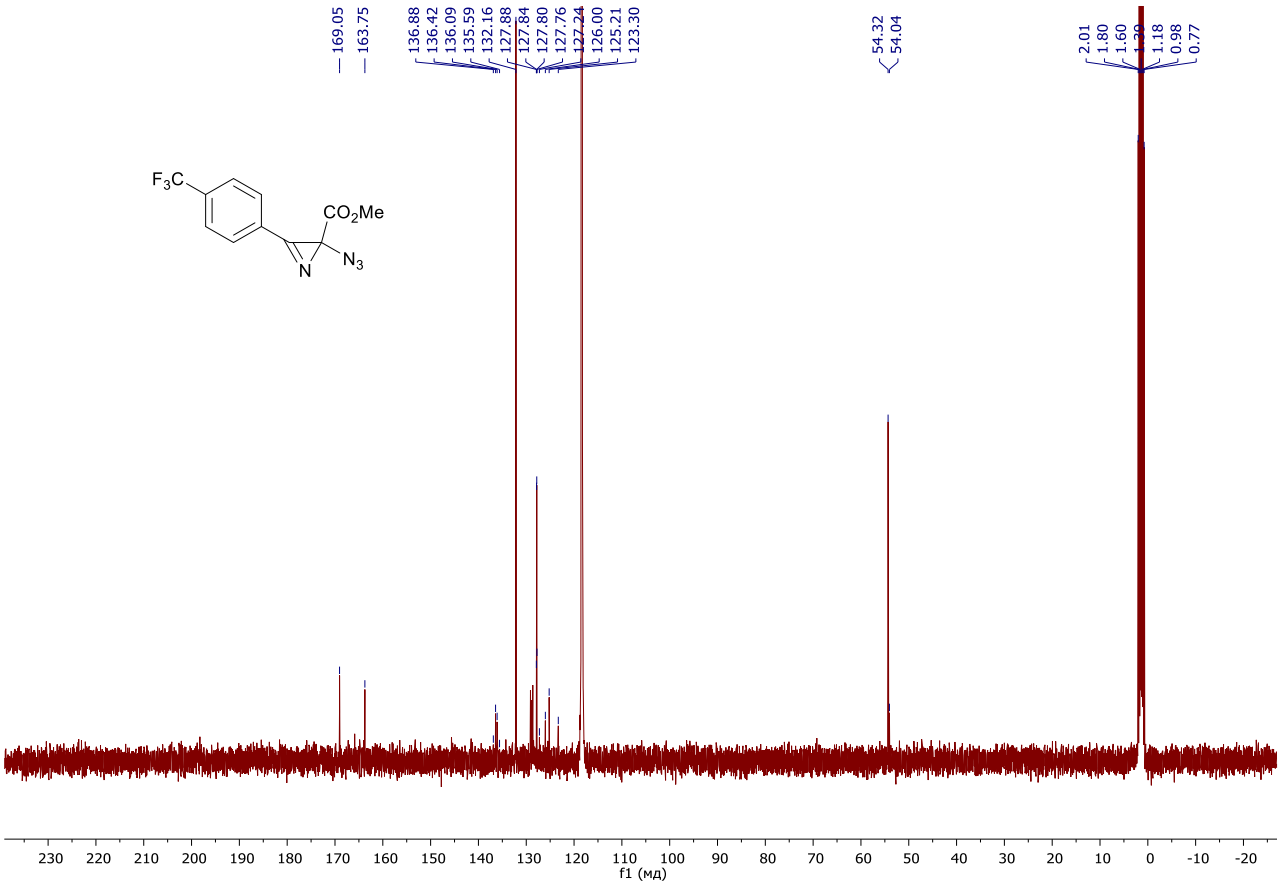

$^{13}$C{$^{1}$H} NMR (100 MHz, $CD_3CN$) spectrum of compound **2i**



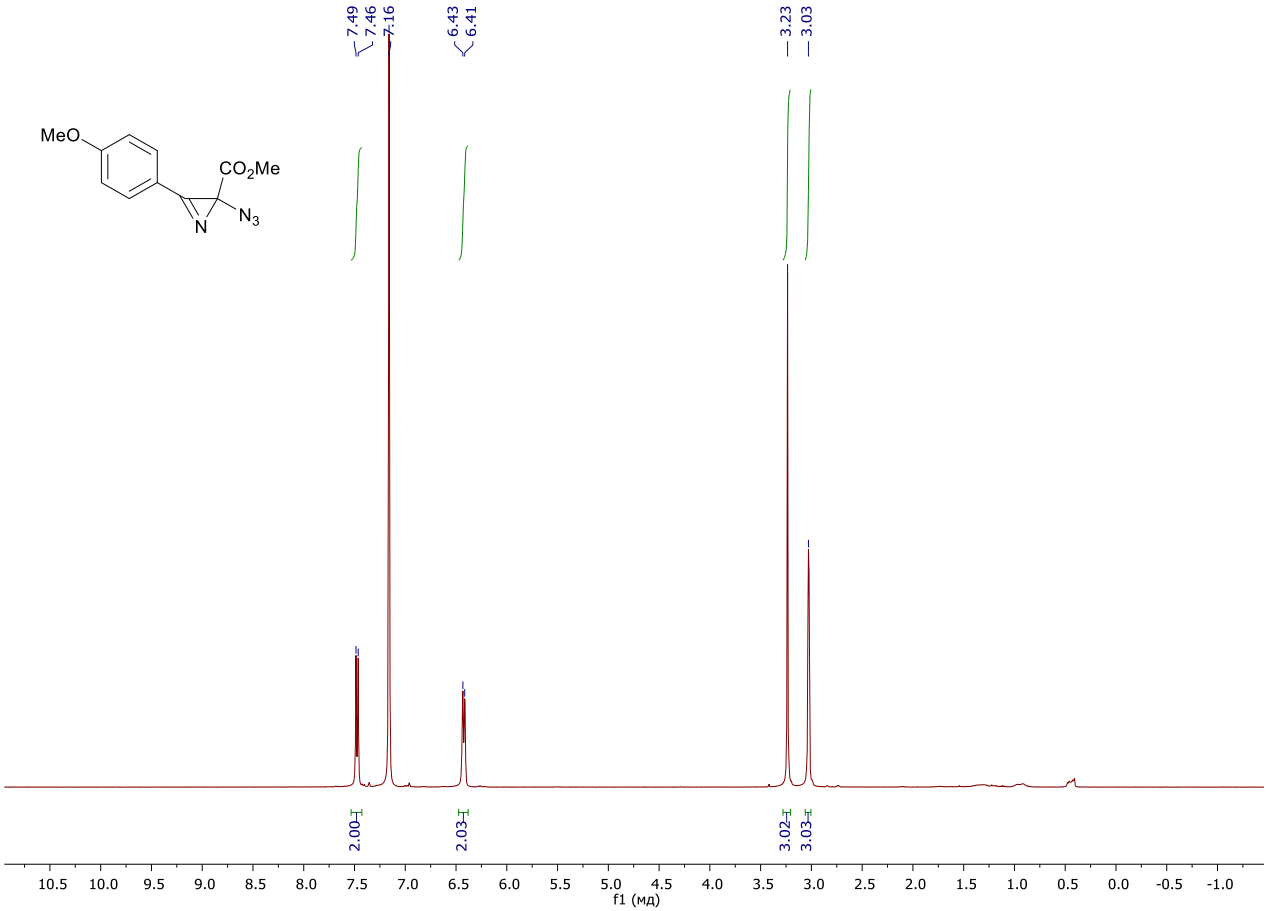
$^{1}$H NMR (400 MHz, $CD_3CN$) spectrum of compound **2j**



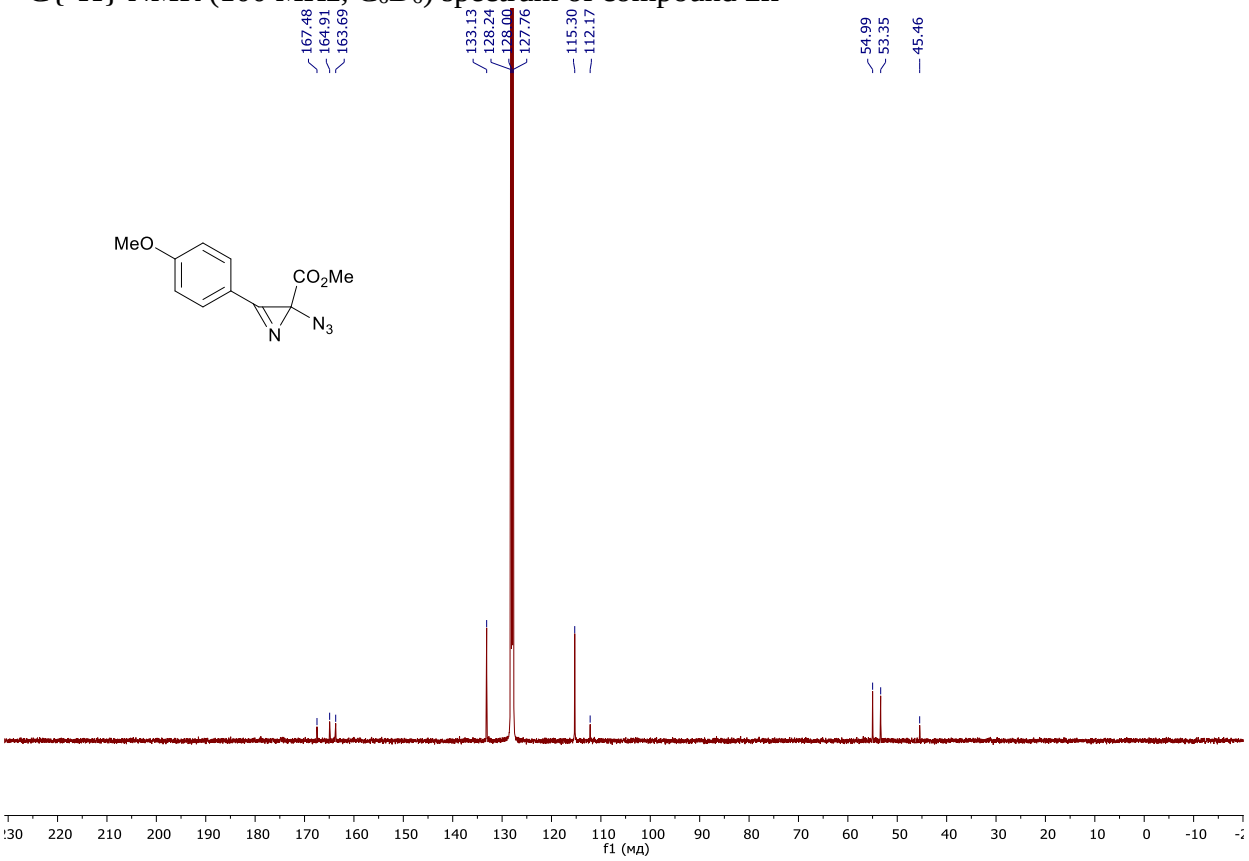

$^{13}$C{$^{1}$H} NMR (100 MHz, $CD_3CN$) spectrum of compound **2j**



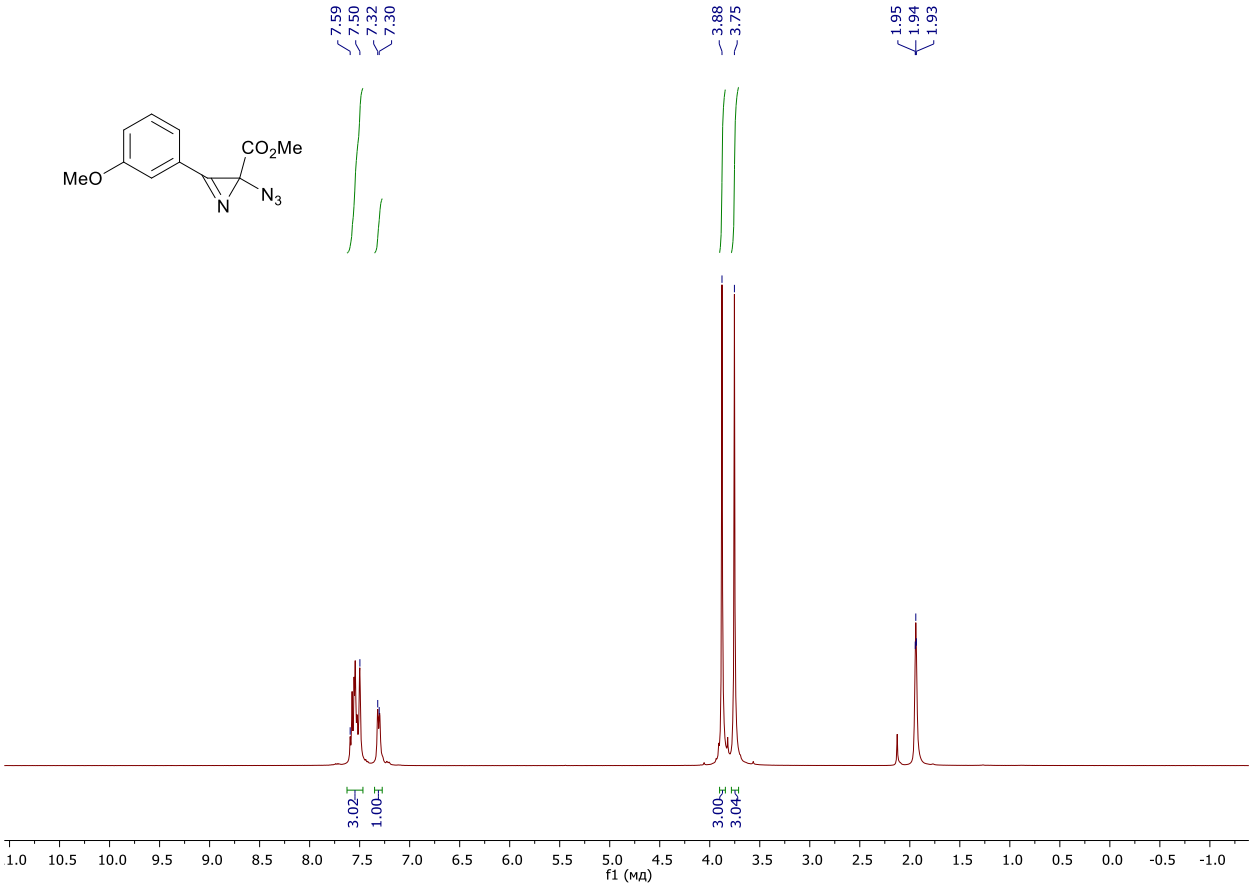
$^{1}$H NMR (400 MHz, $C_6D_6$) spectrum of compound **2k**



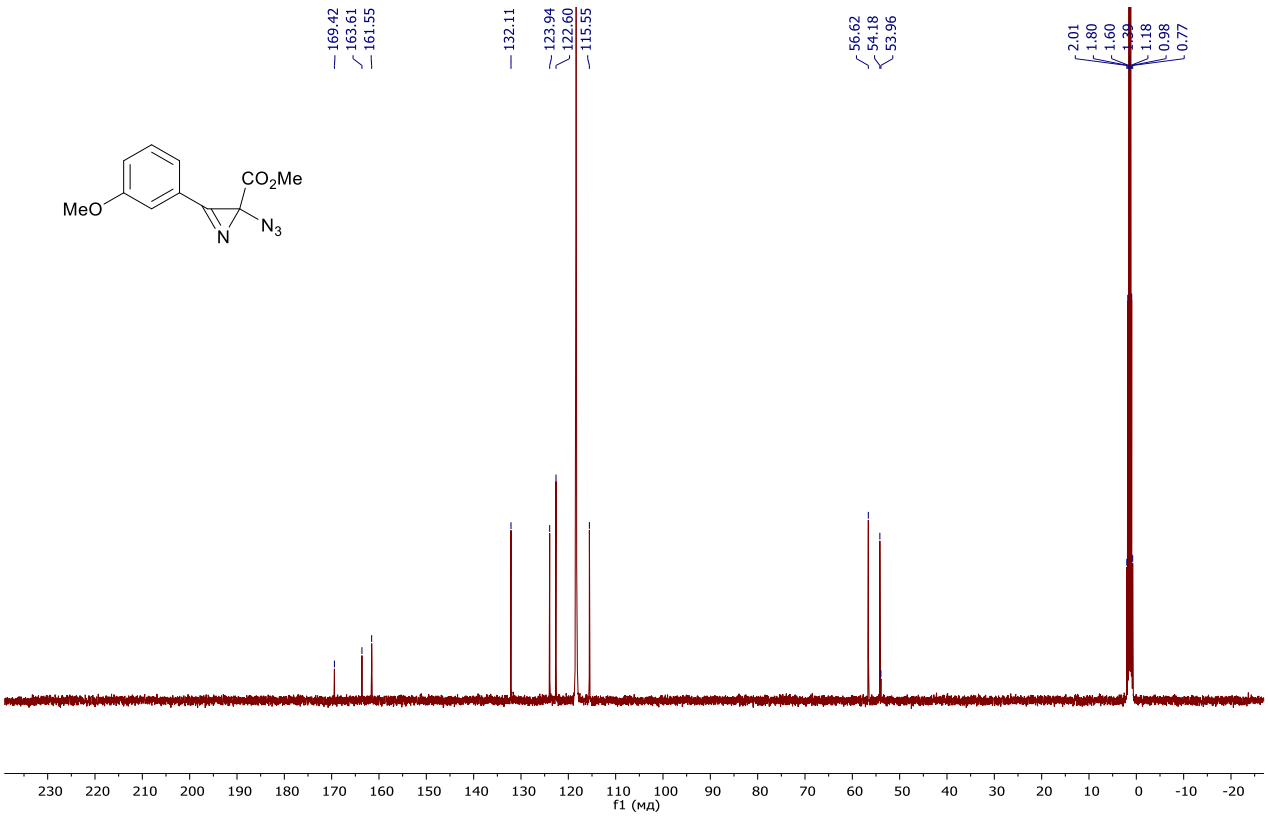

$^{13}$C{$^{1}$H} NMR (100 MHz, $C_6D_6$) spectrum of compound **2k**



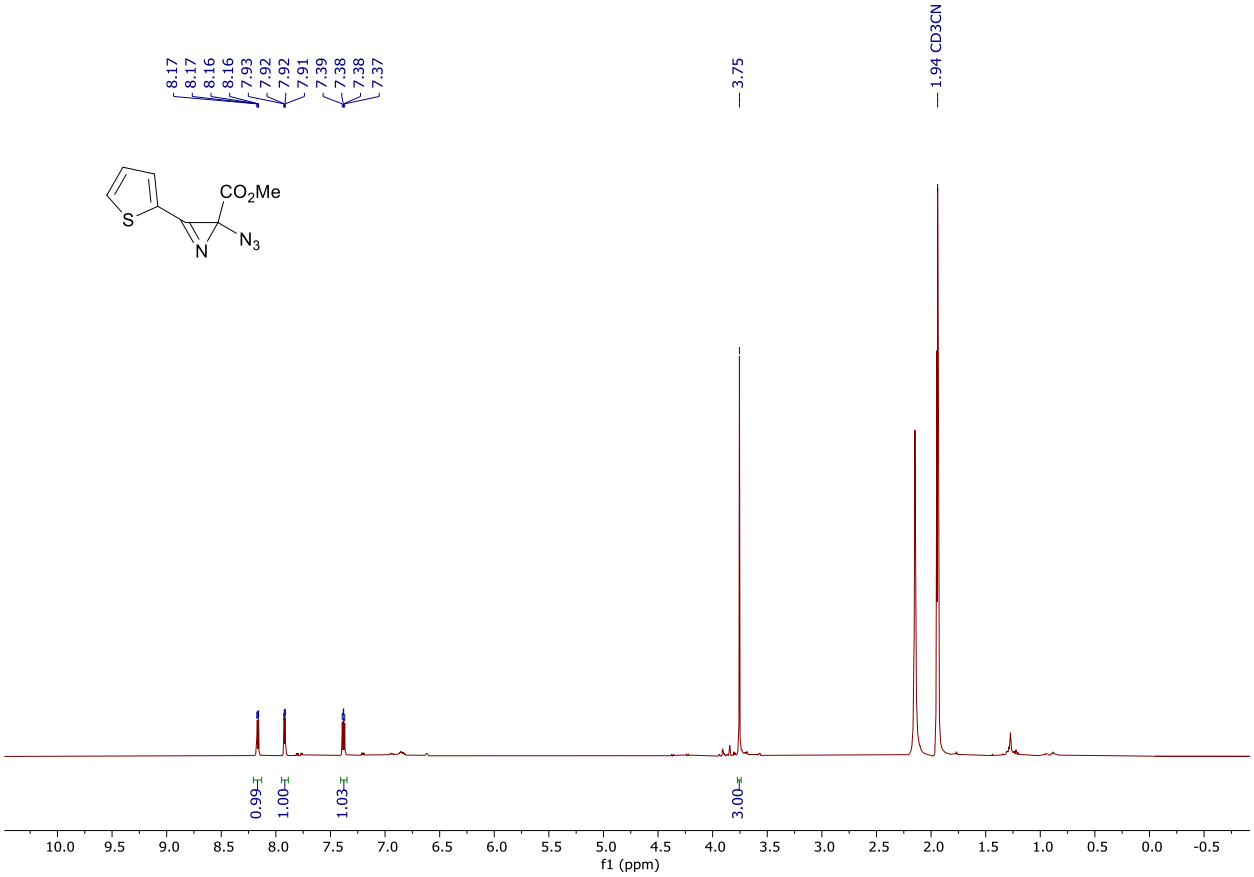
$^{1}$H NMR (400 MHz, $CD_3CN$) spectrum of compound **2l**



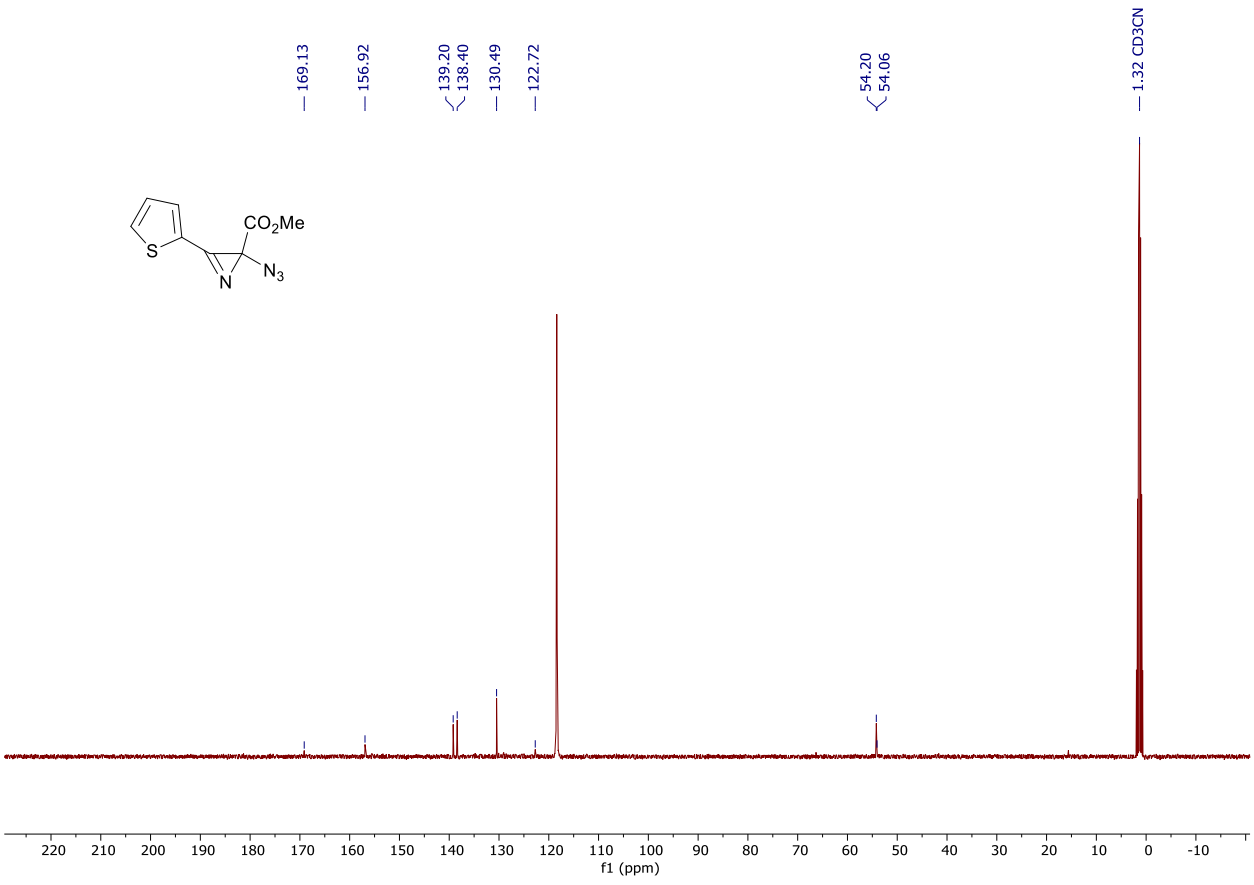

$^{13}$C{$^{1}$H} NMR (100 MHz, $CD_3CN$) spectrum of compound **2l**



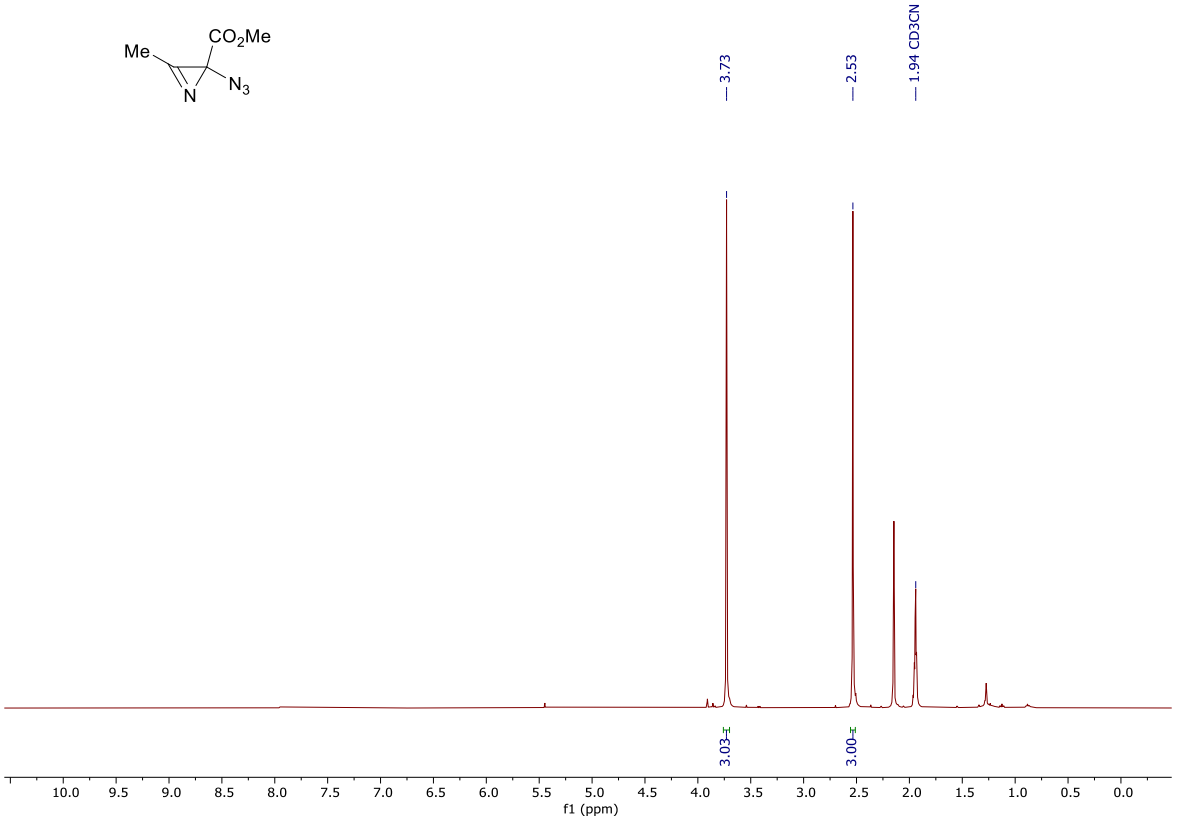
$^{1}$H NMR (400 MHz, $CD_3CN$) spectrum of compound **2m**



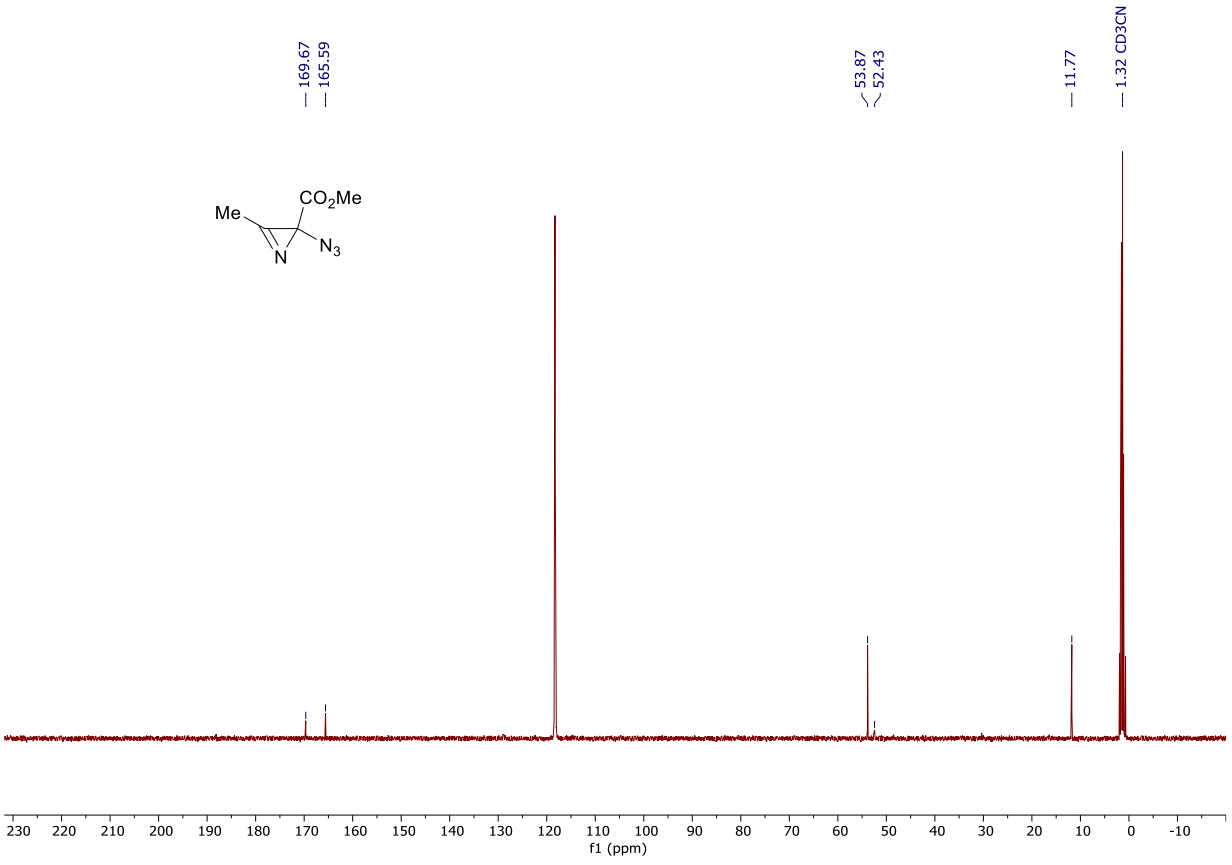

$^{13}$C{$^{1}$H} NMR (100 MHz, $CD_3CN$) spectrum of compound **2m**



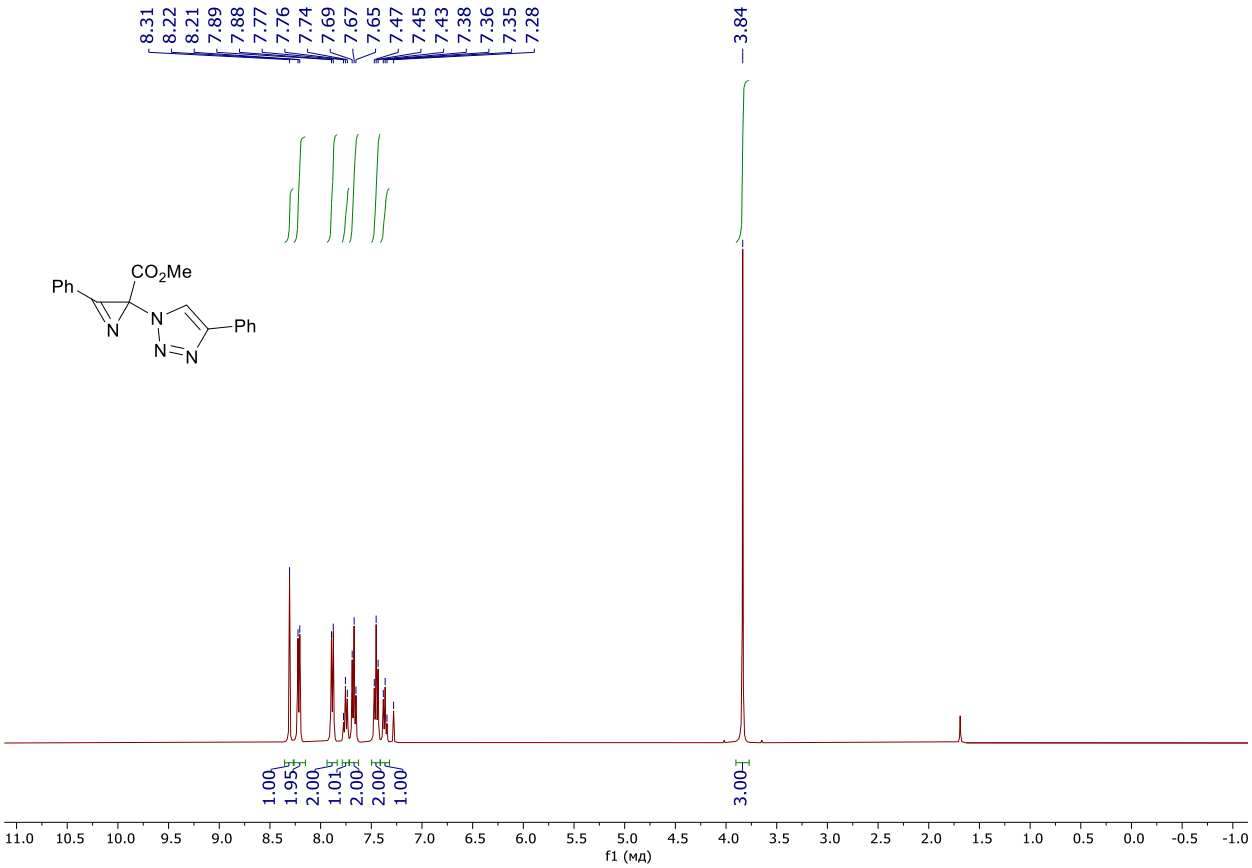
$^{1}$H NMR (400 MHz, $CD_3CN$) spectrum of compound **2n**



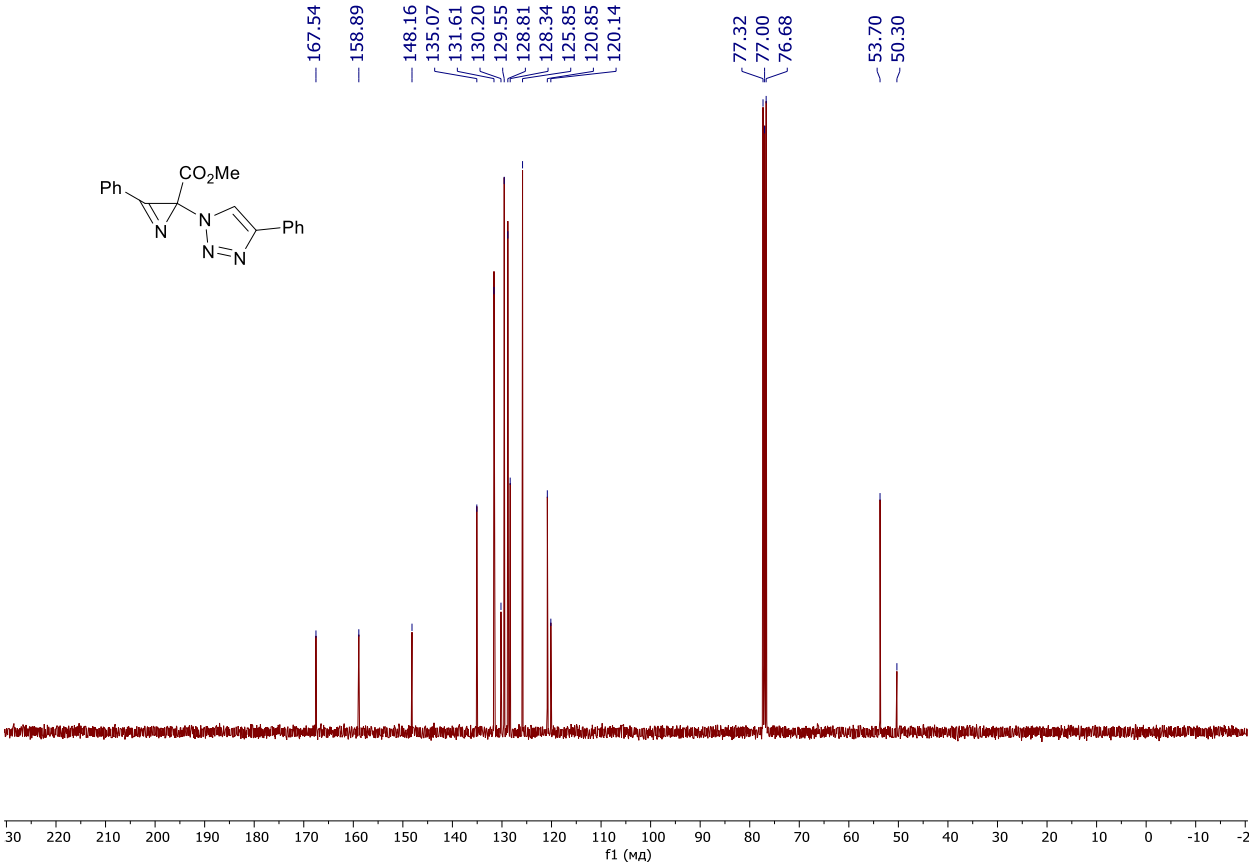

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CD_3CN$) spectrum of compound **2n**



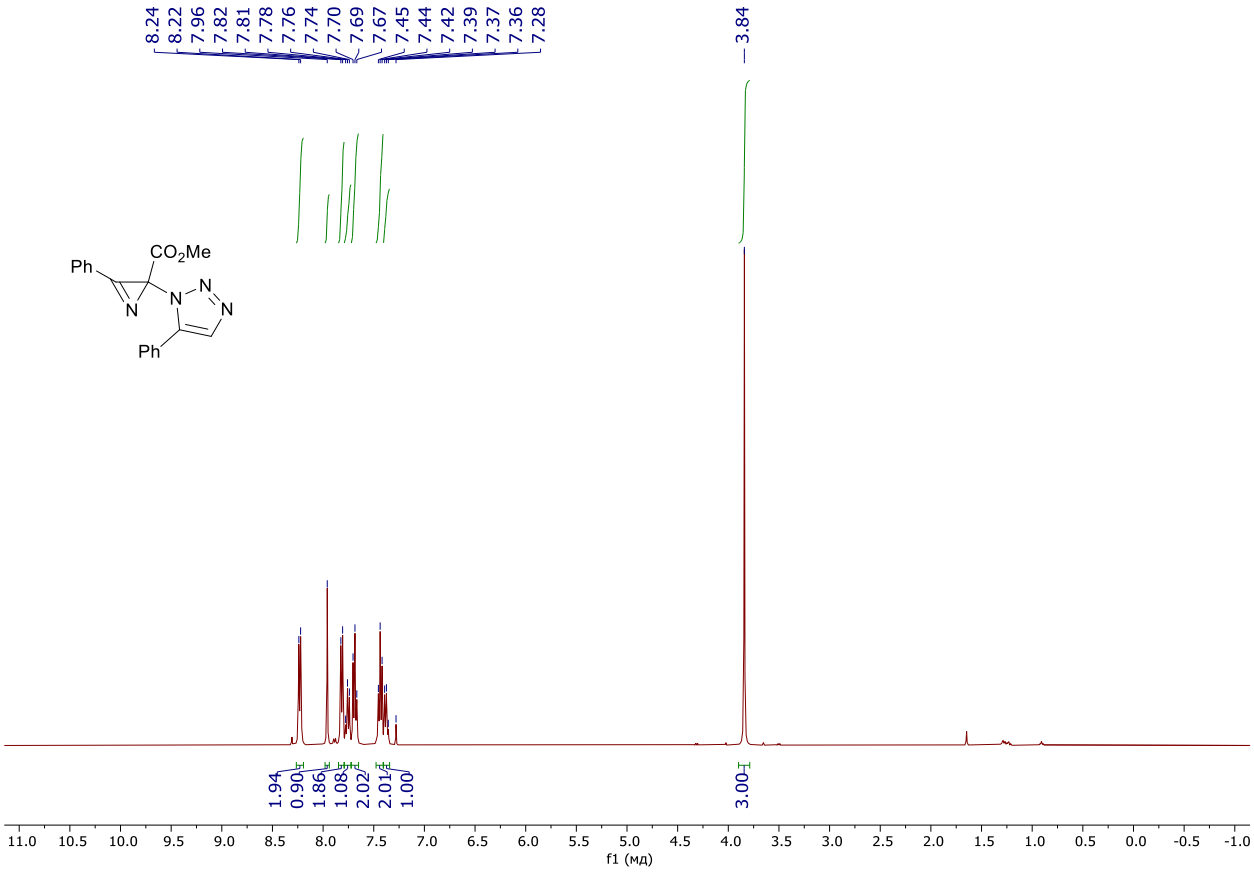
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3a**



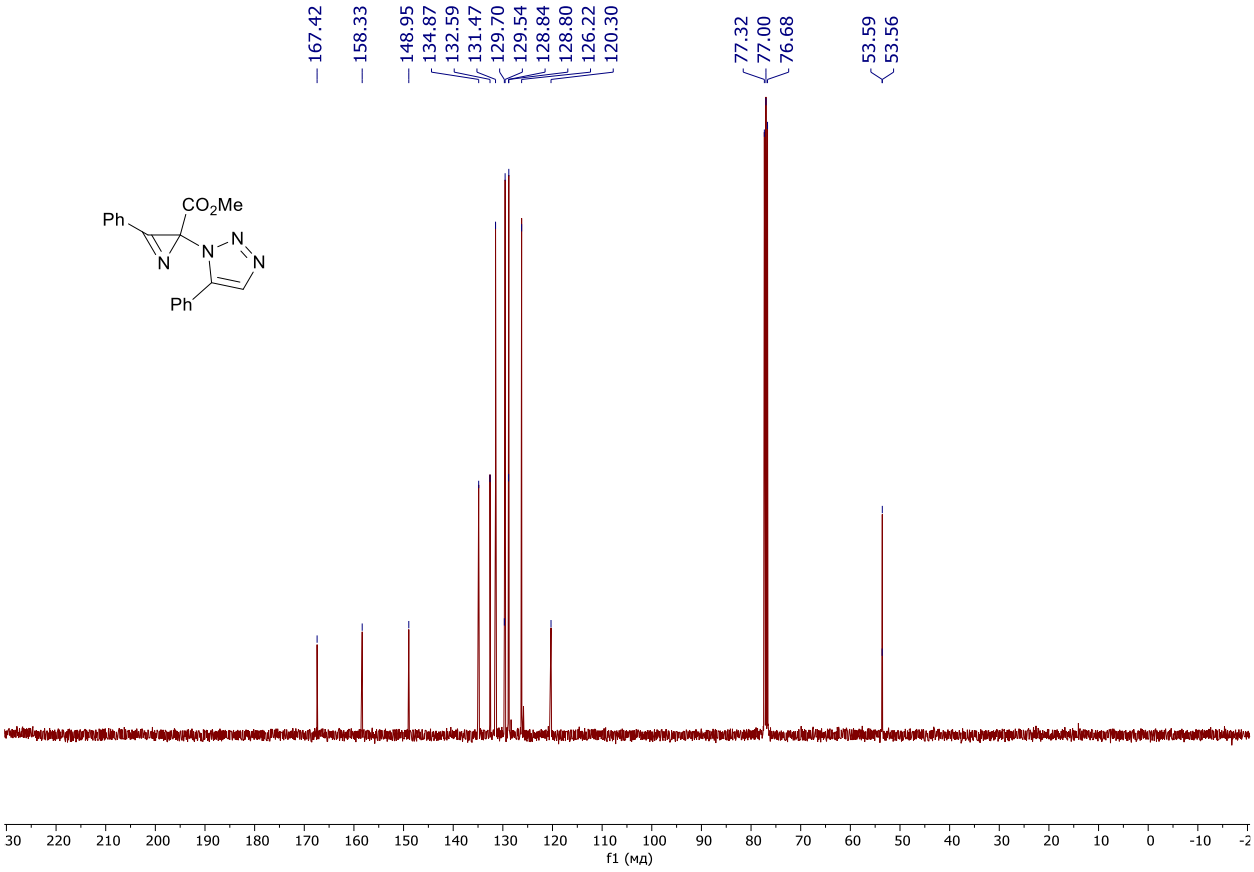

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3a**



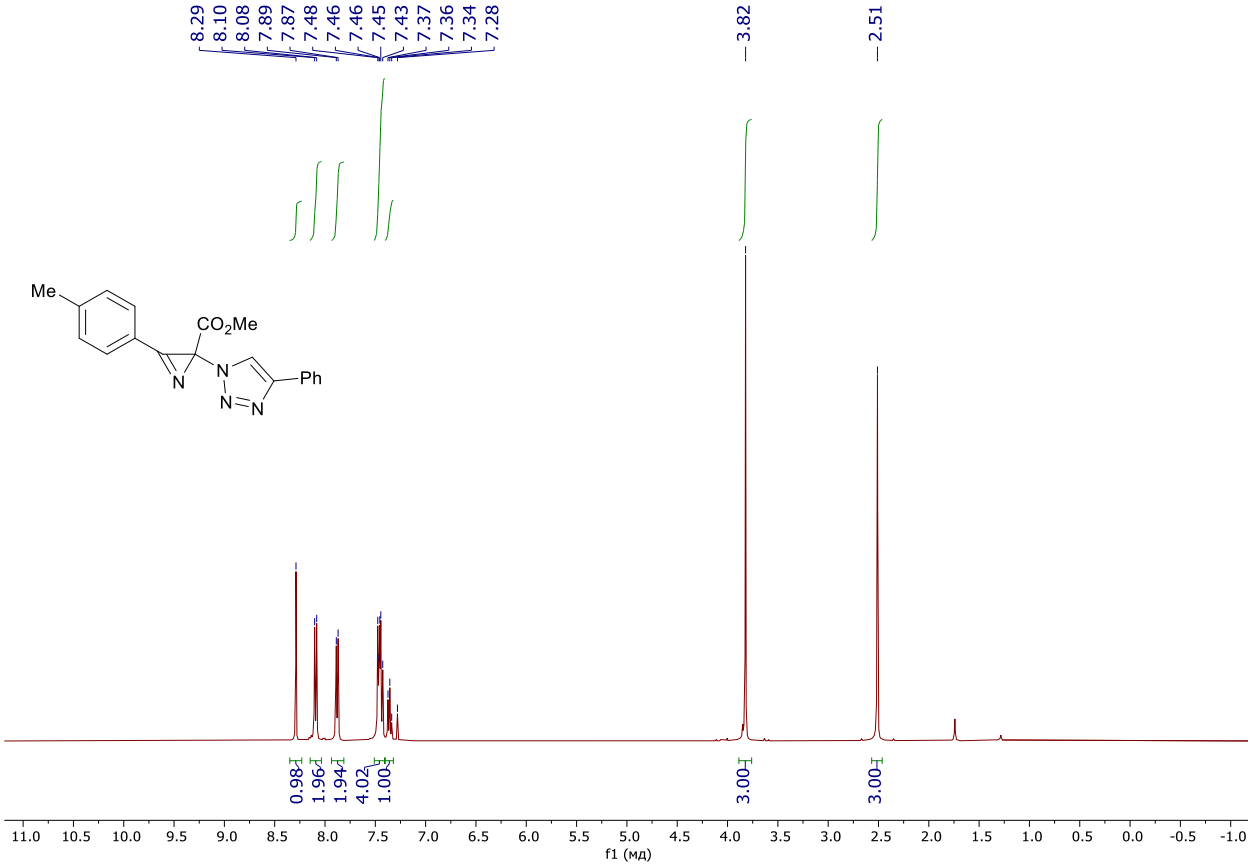
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3a'**



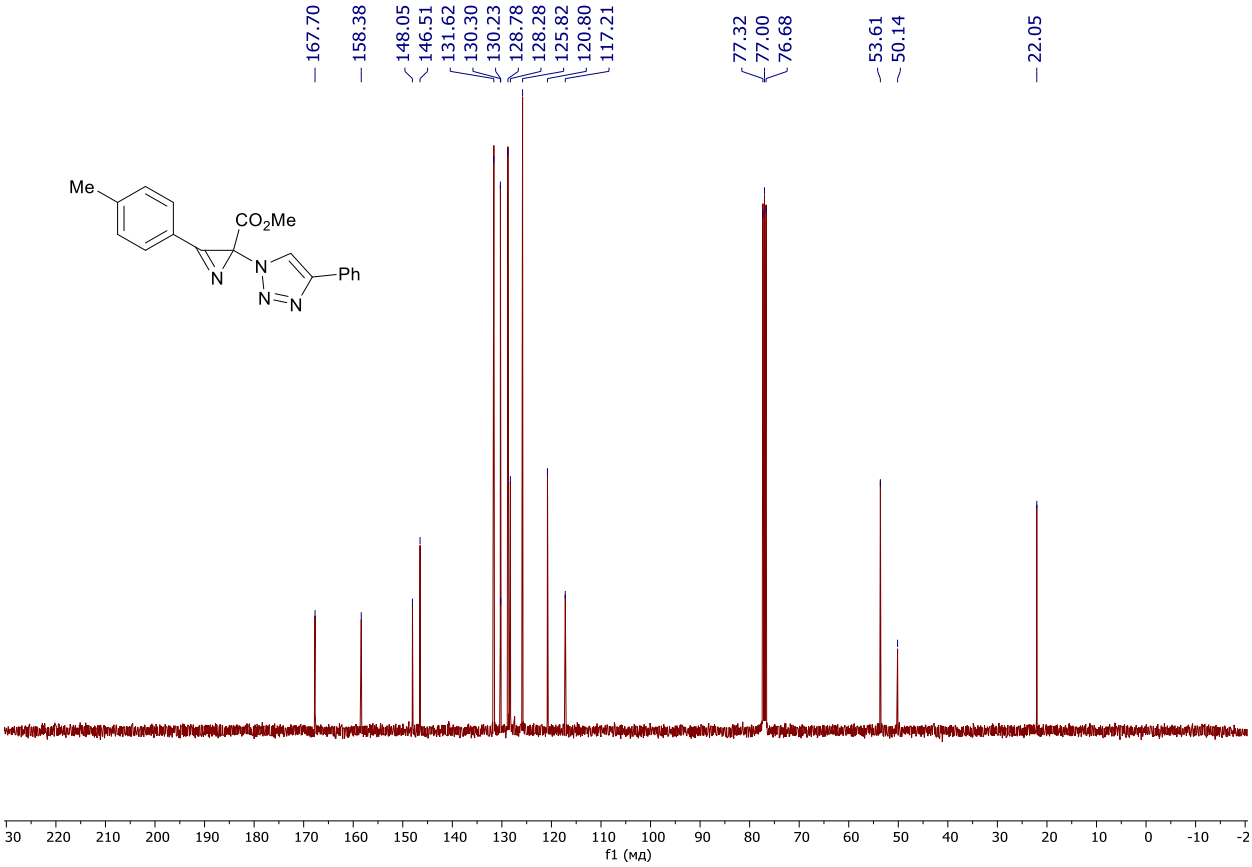

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3a'**



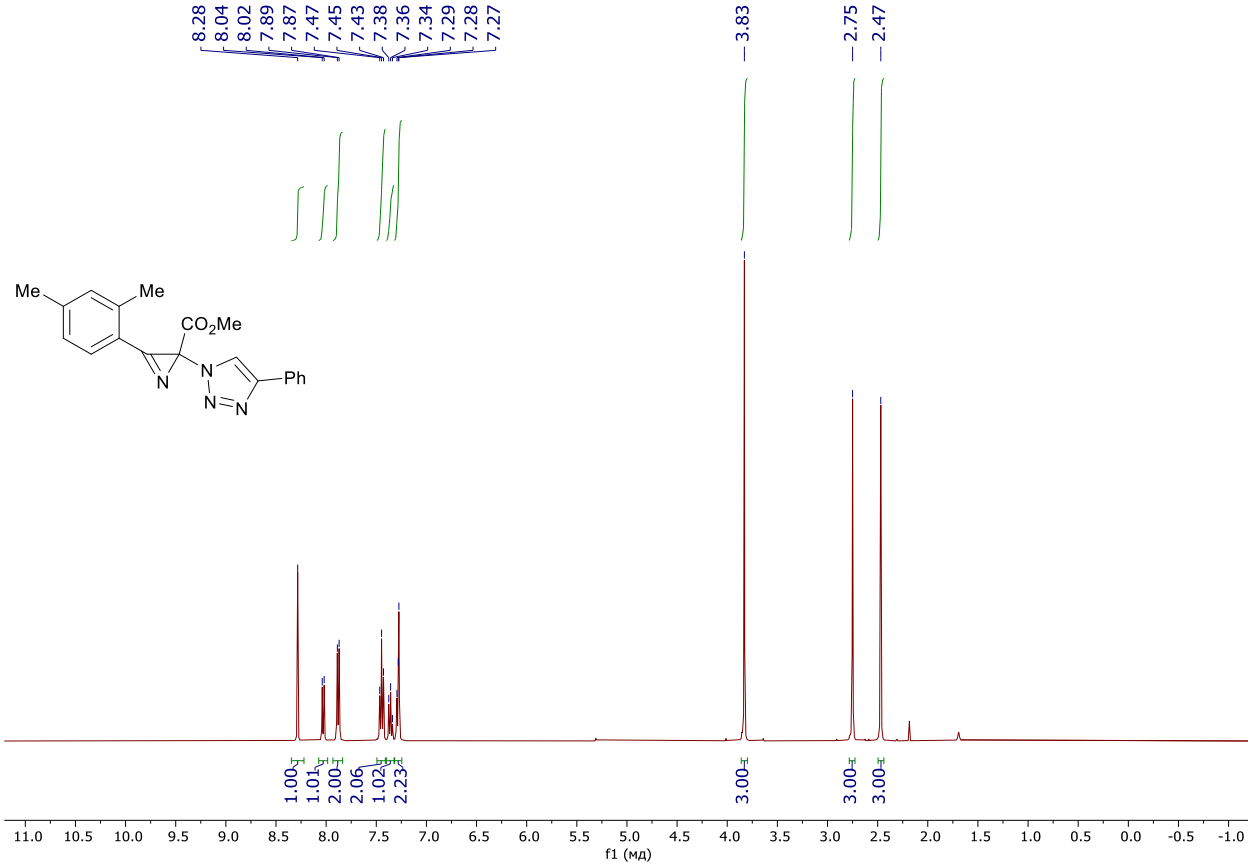
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3b**



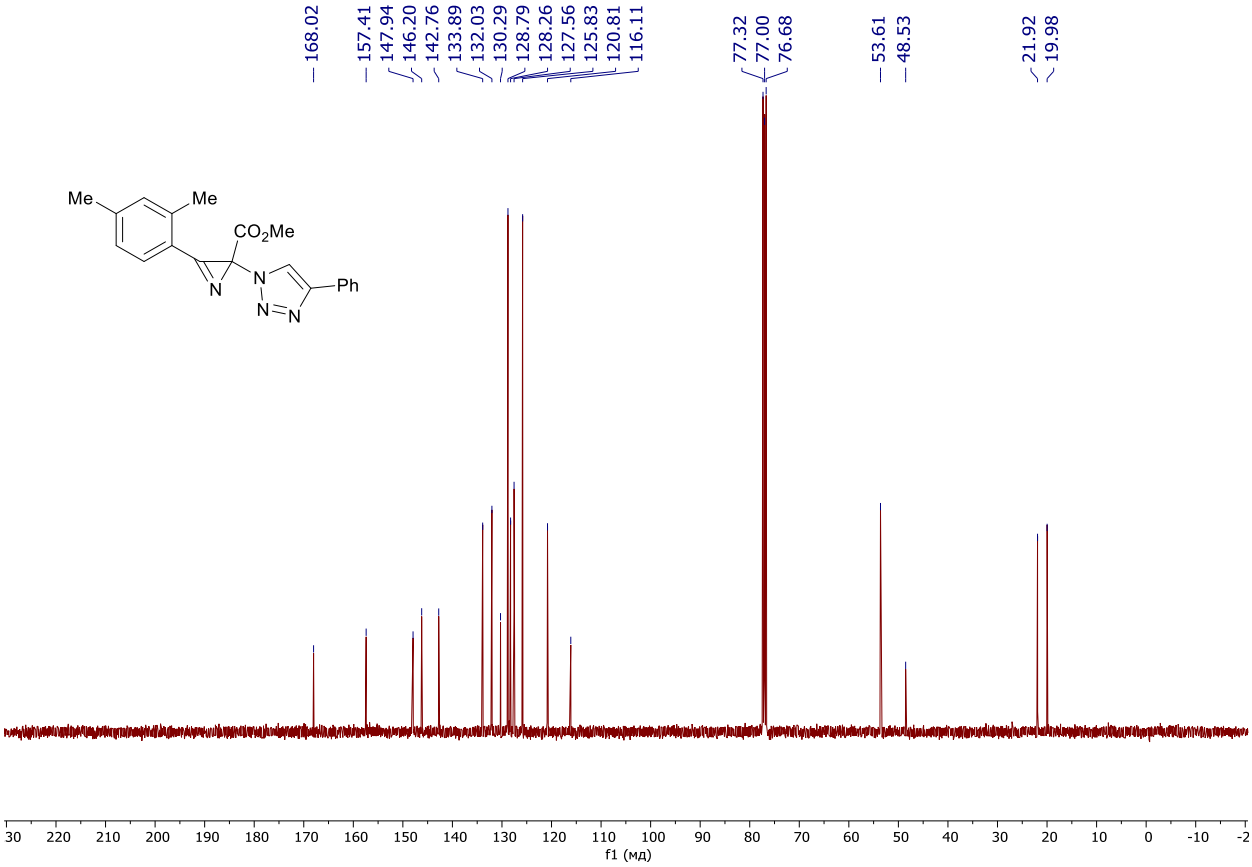

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3b**



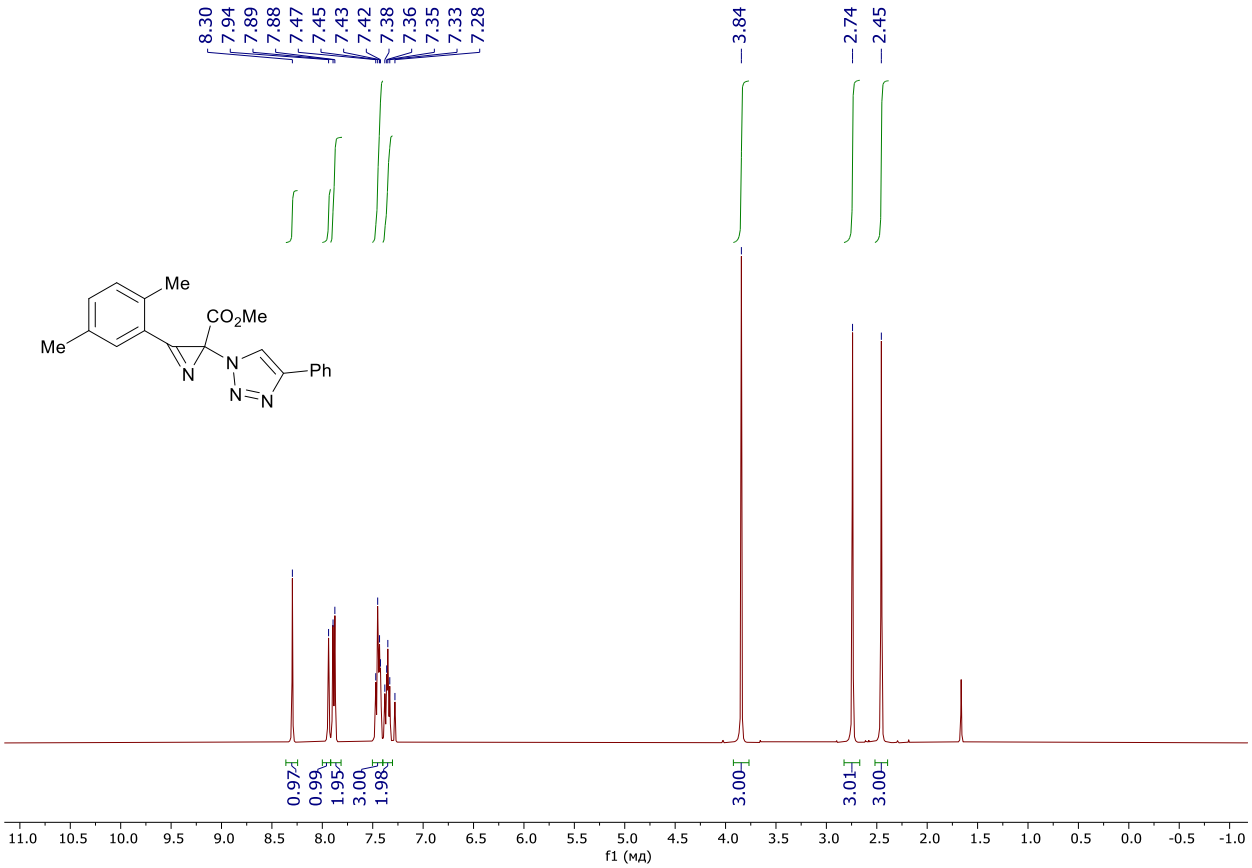
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3c**



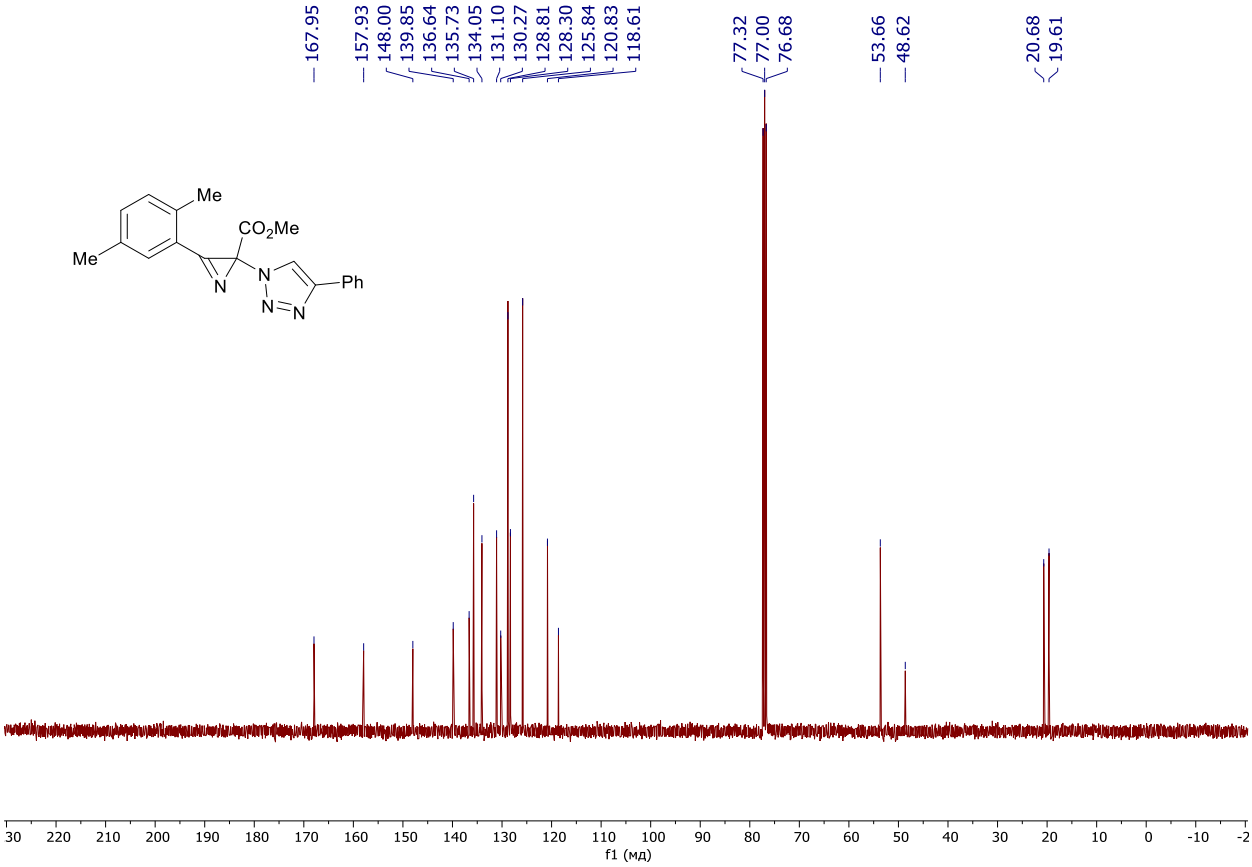

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3c**



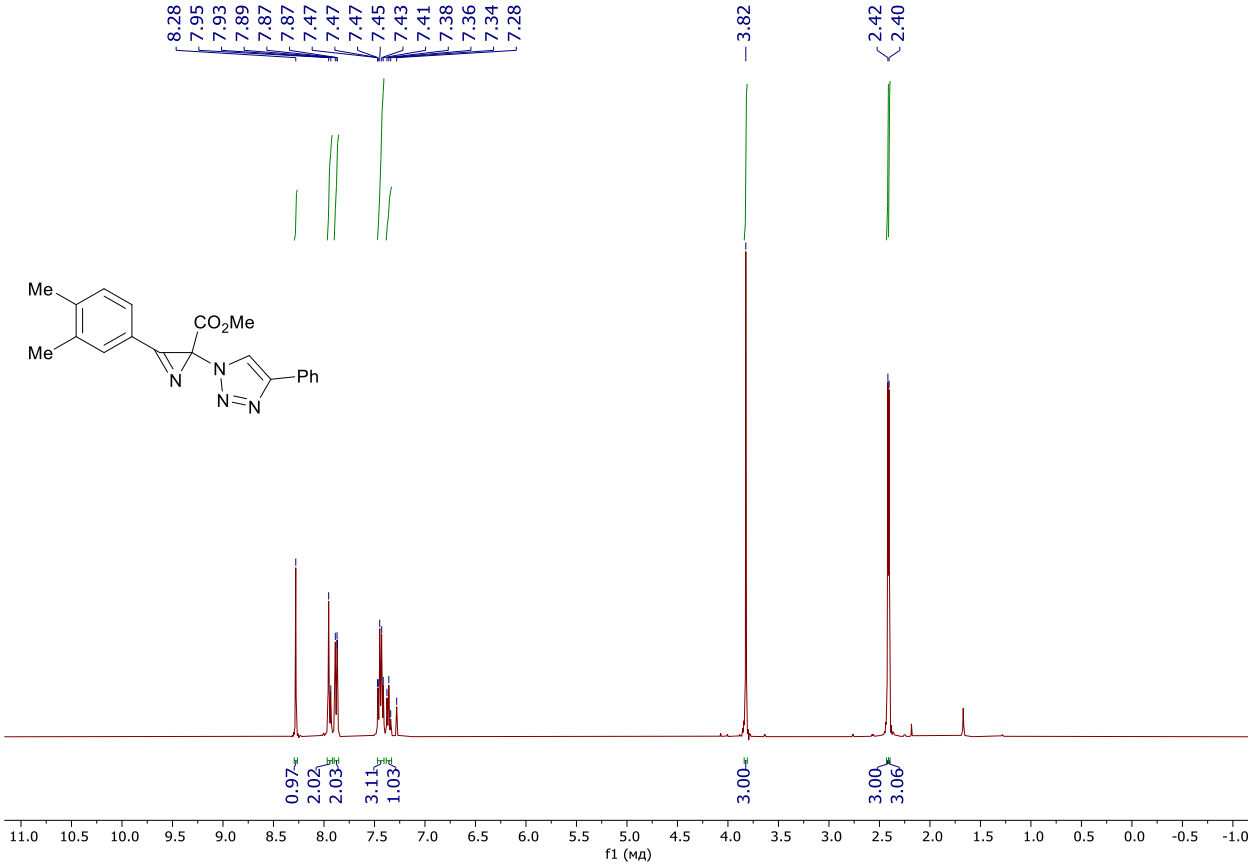
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3d**



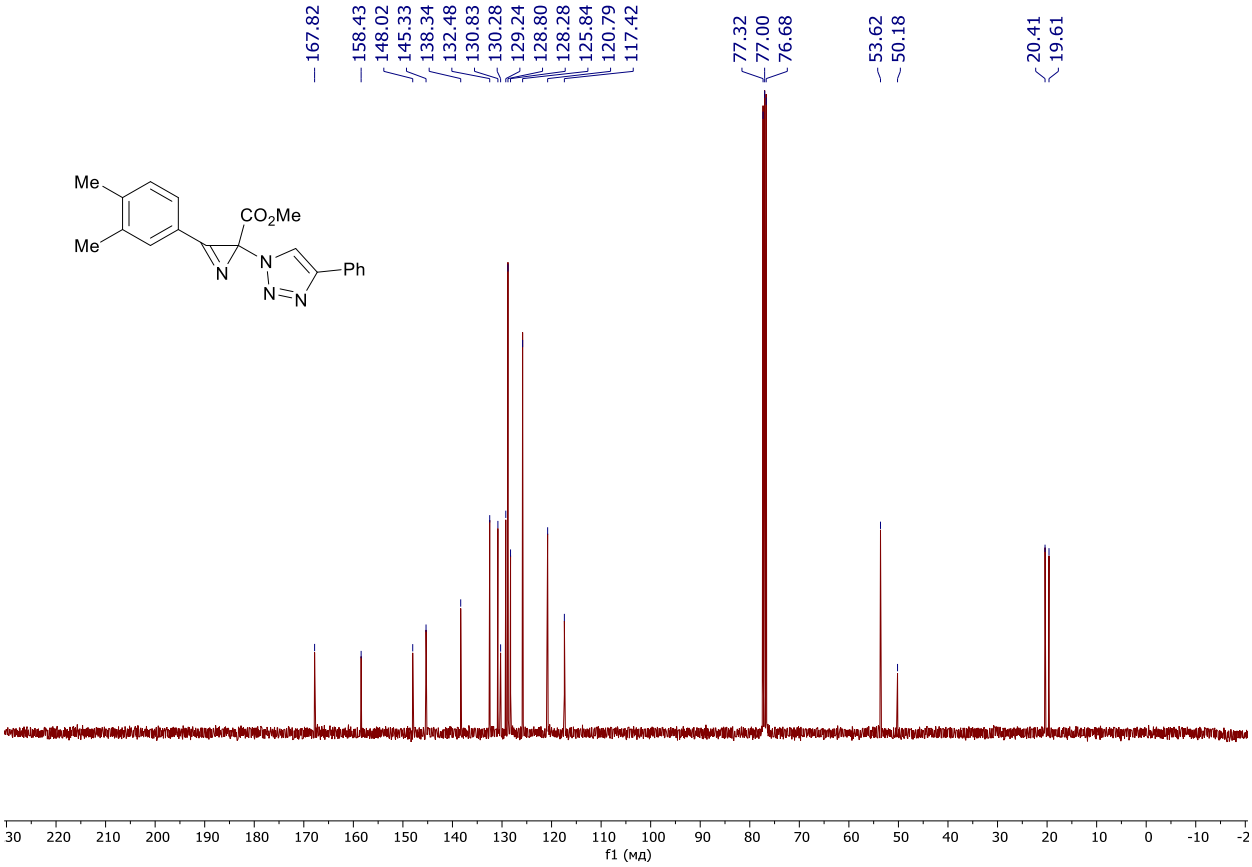

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3d**



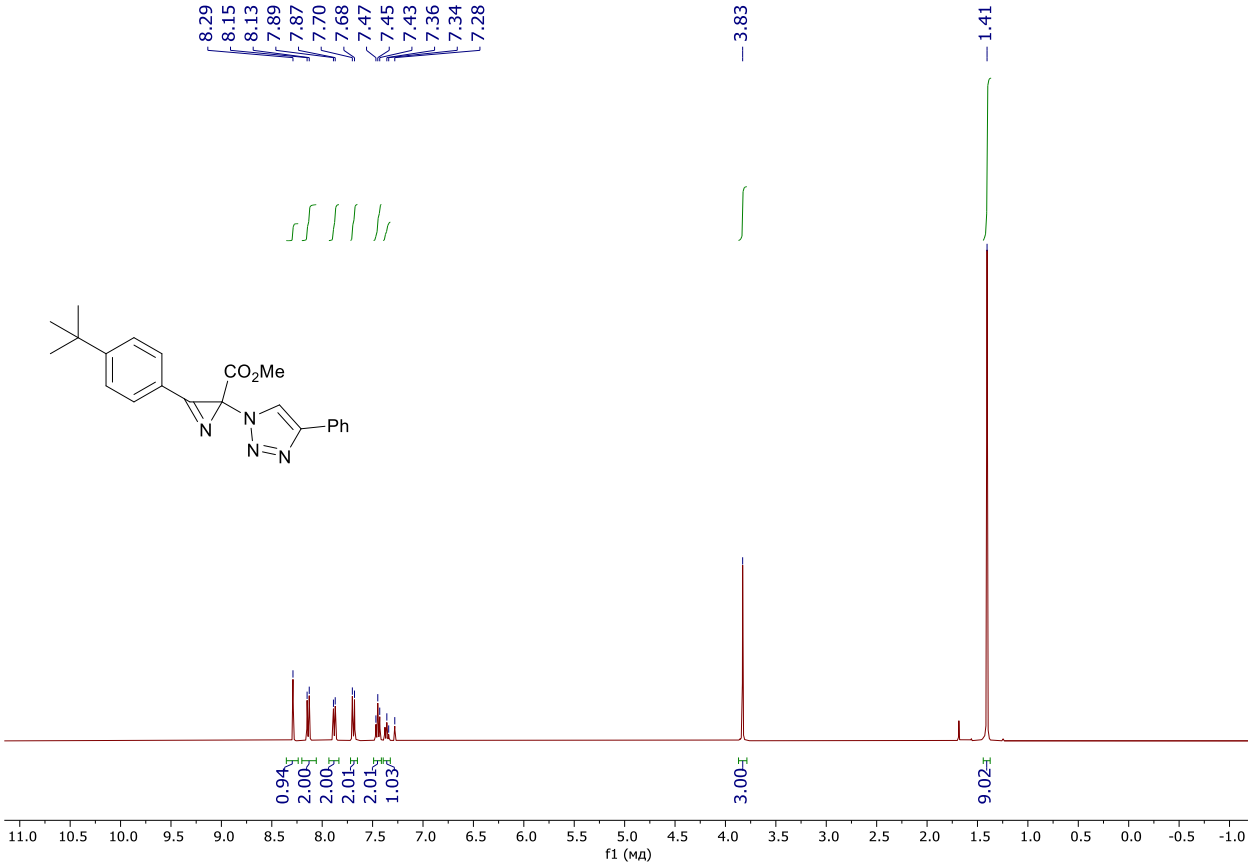
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3e**



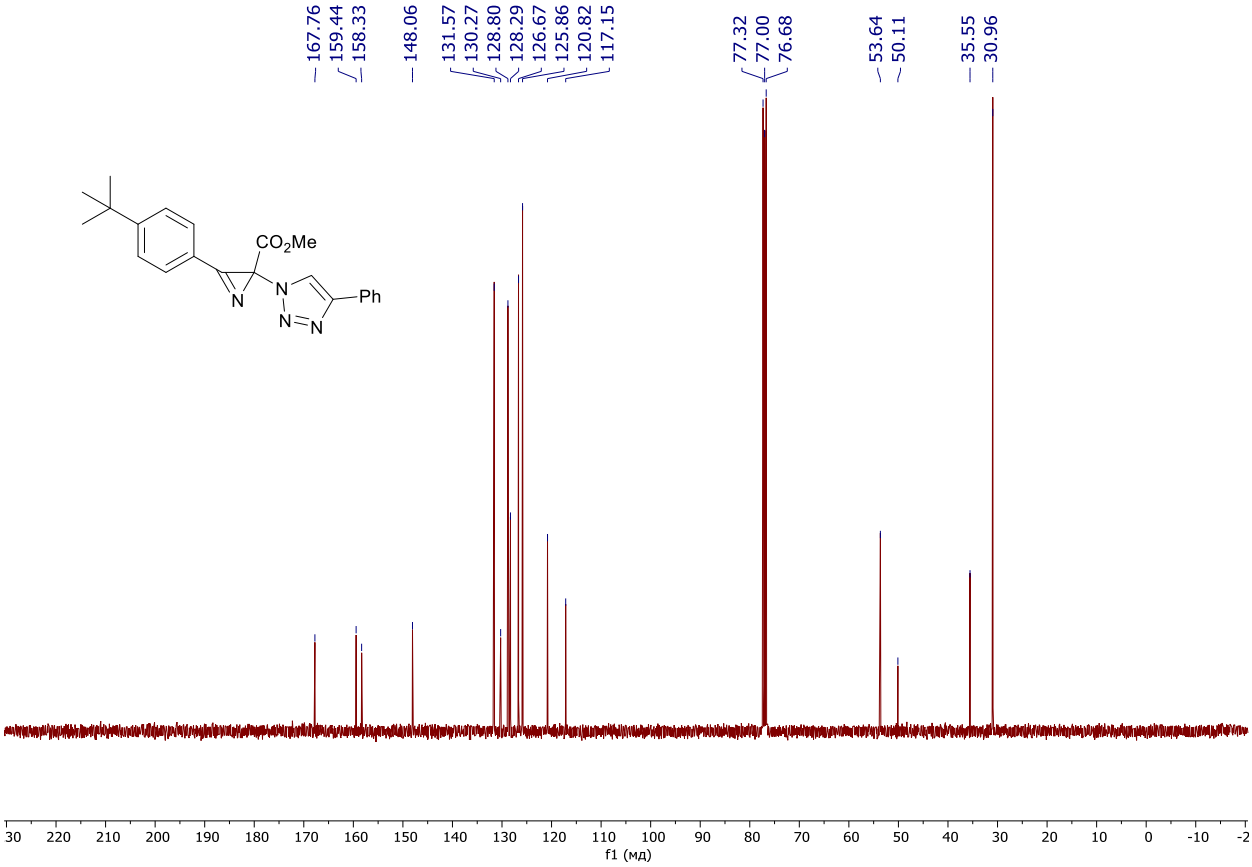

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3e**



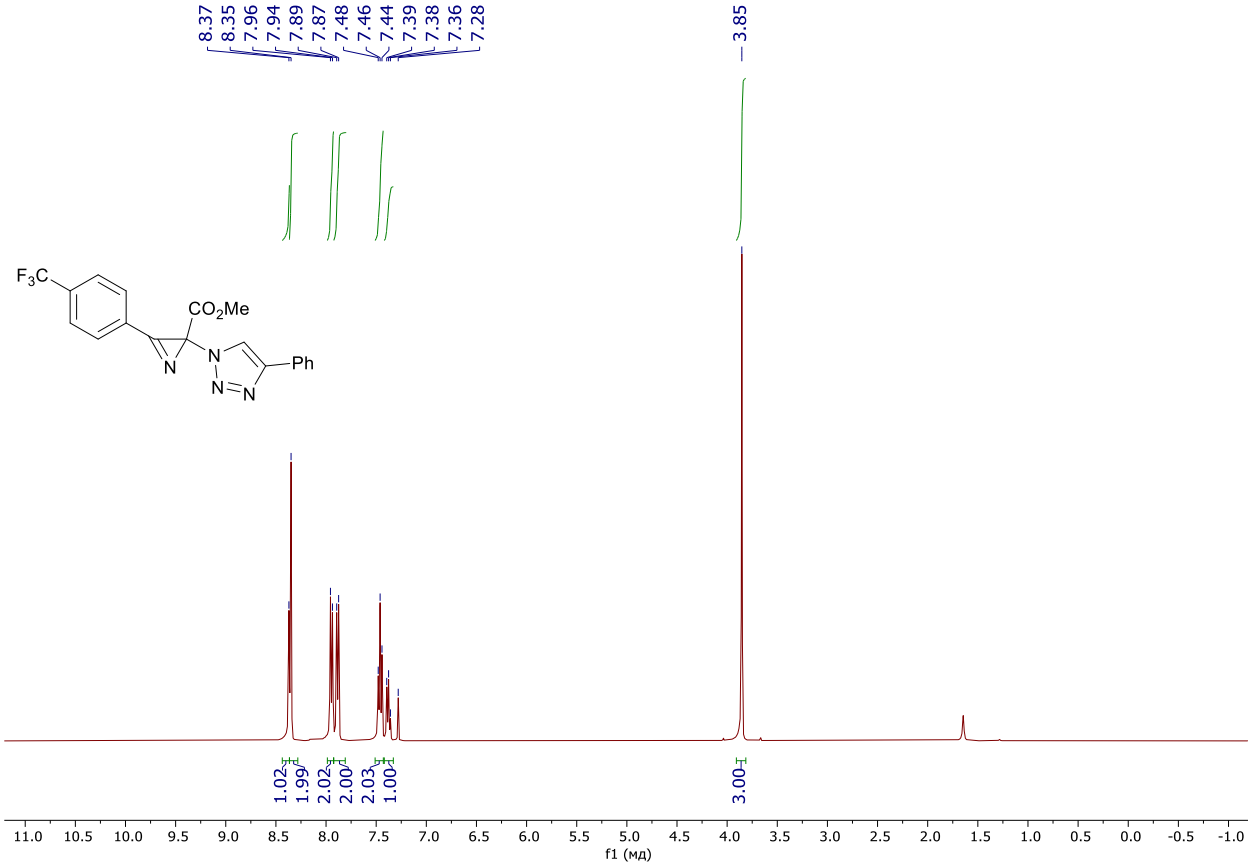
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3f**



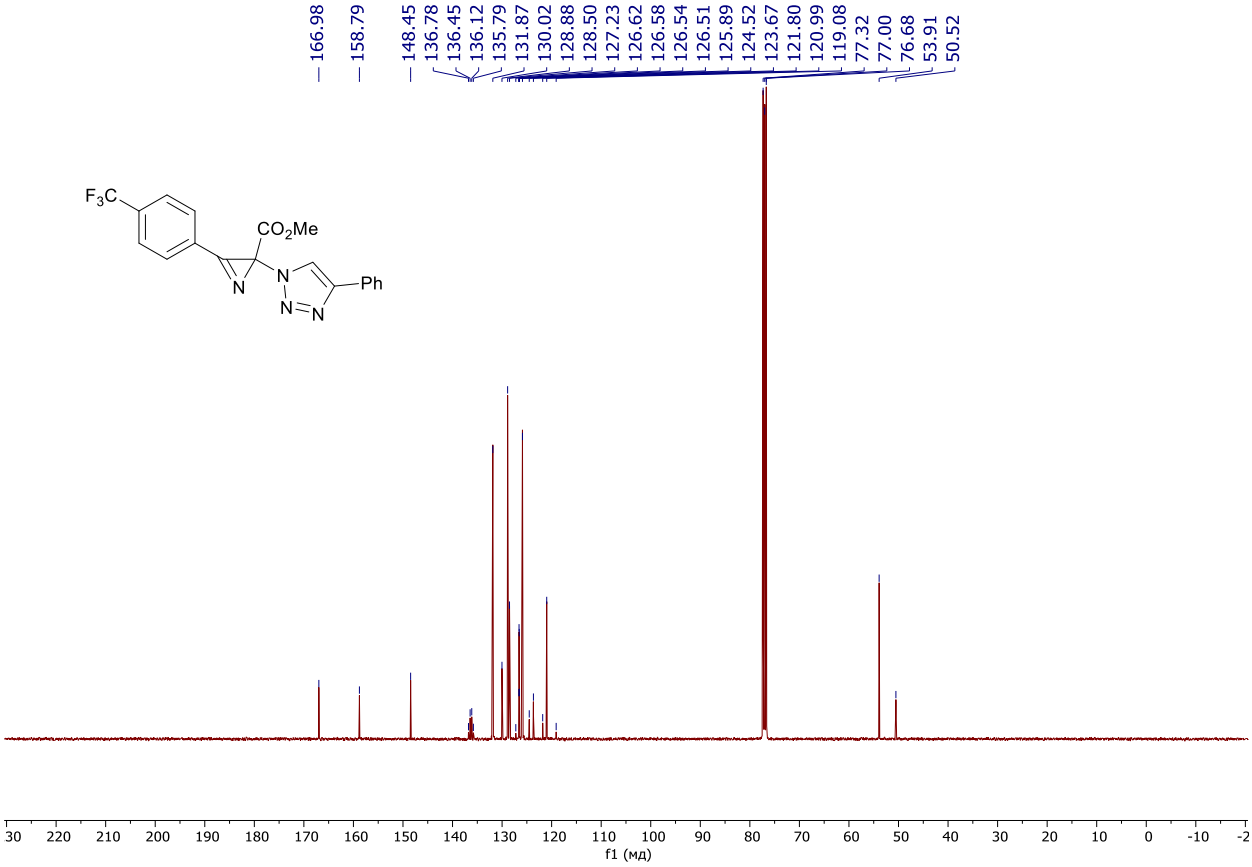

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3f**



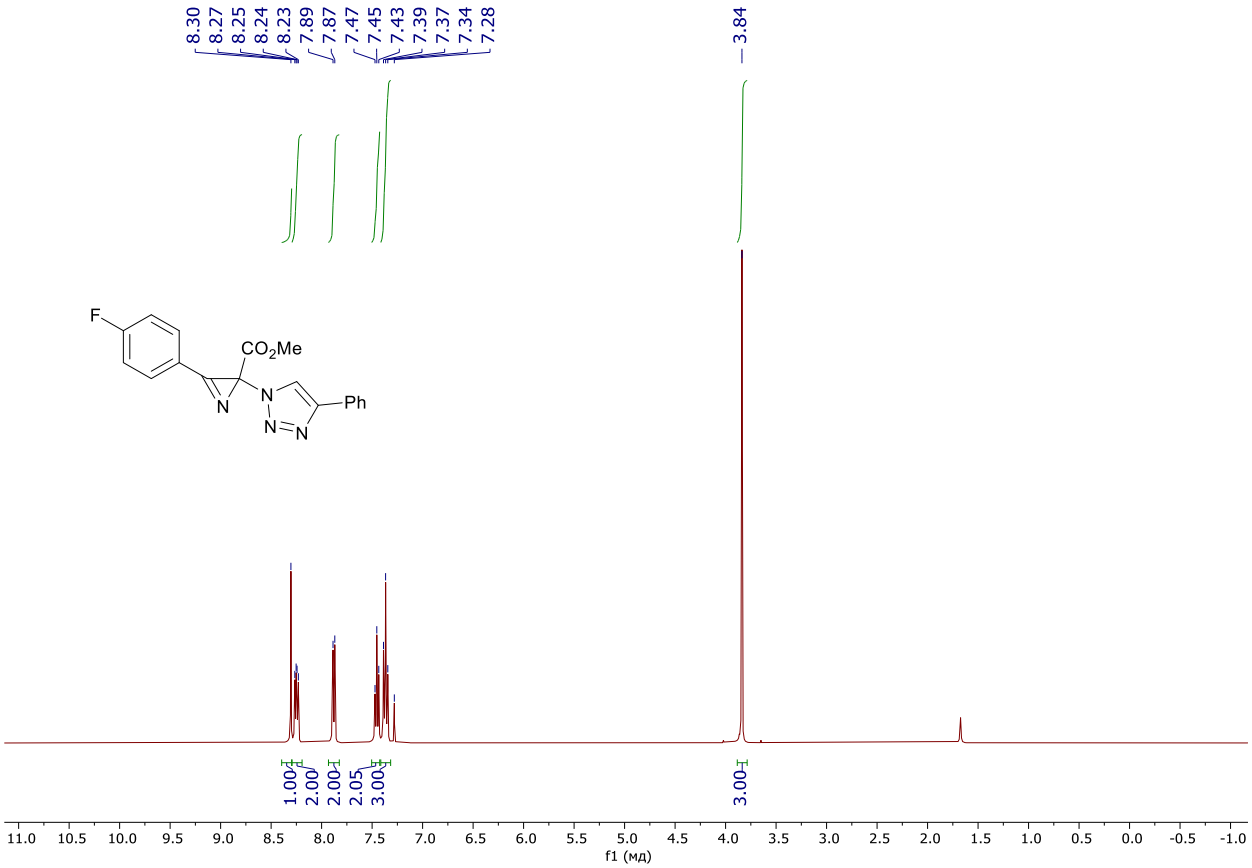
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3g**



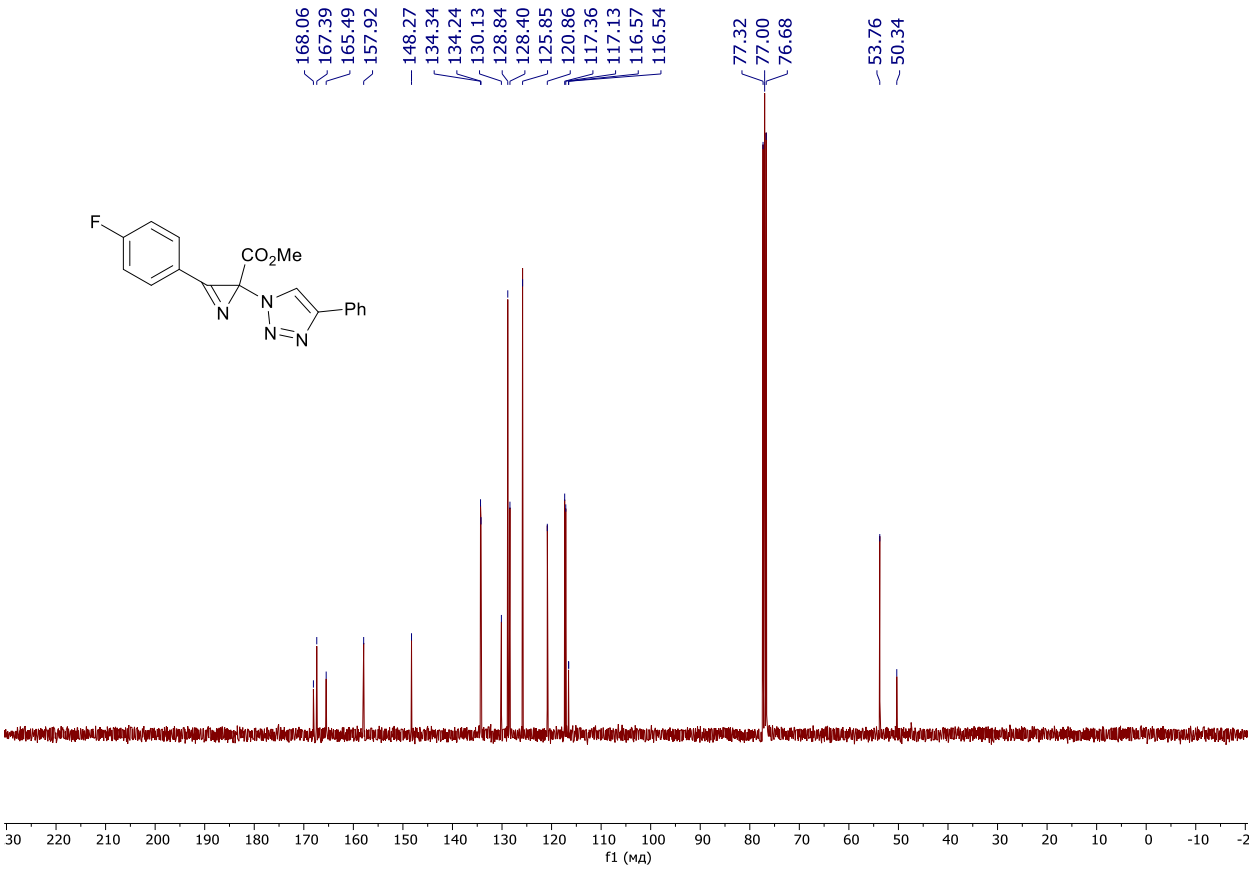

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3g**



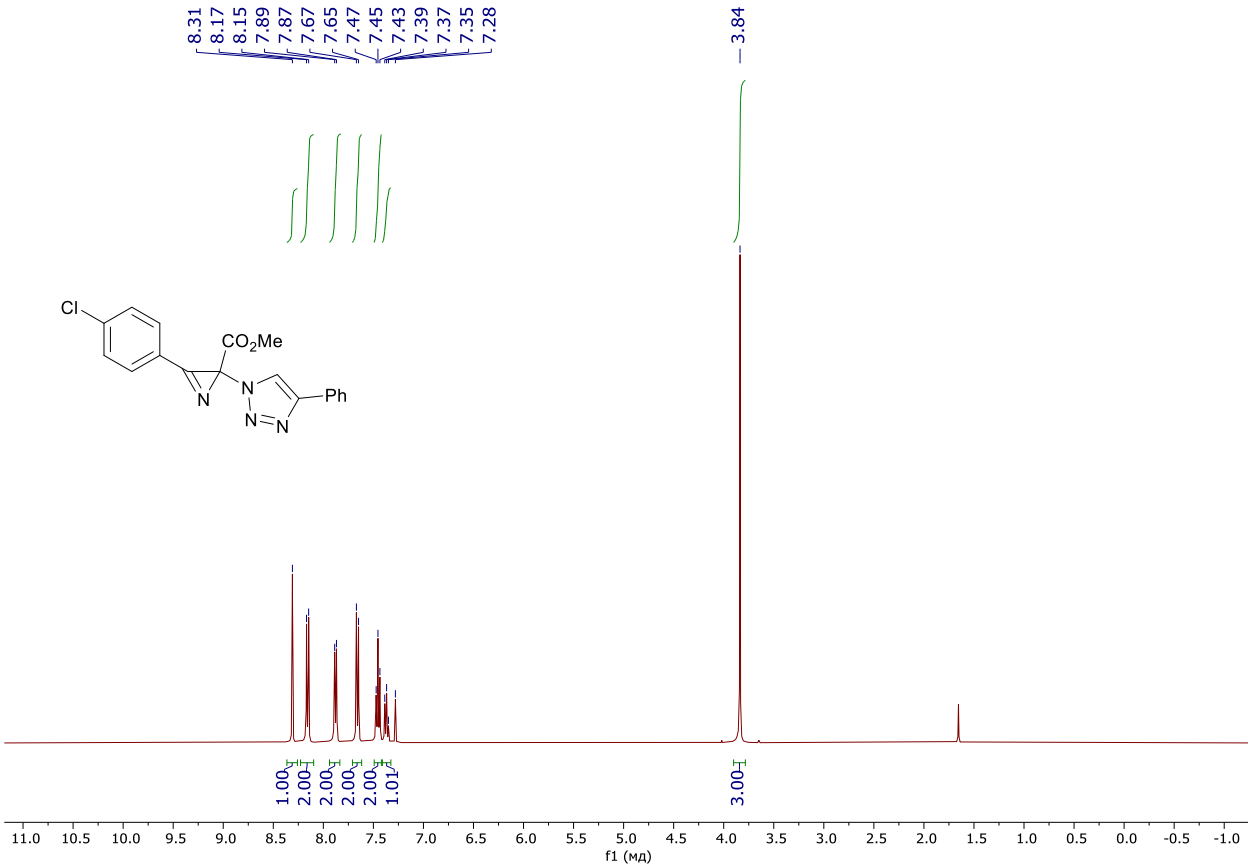
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3h**



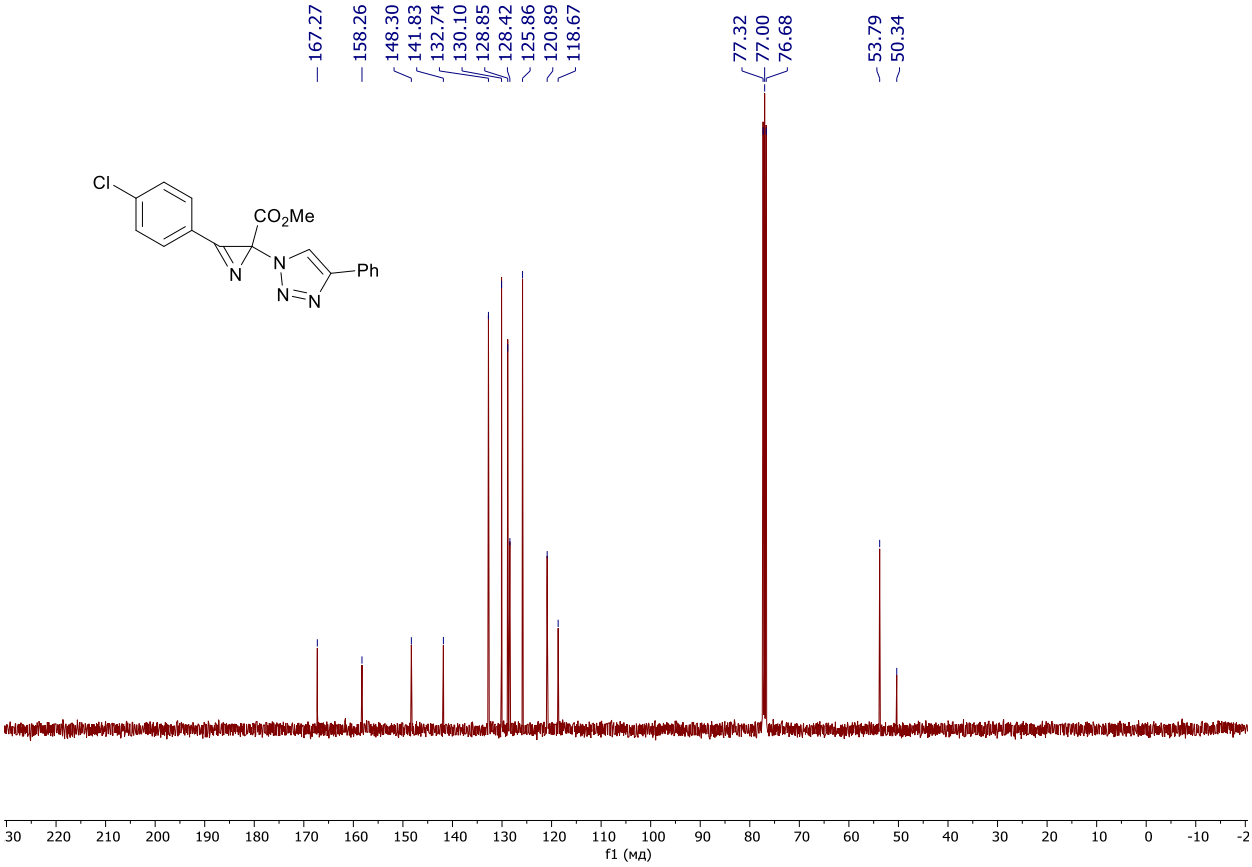

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3h**



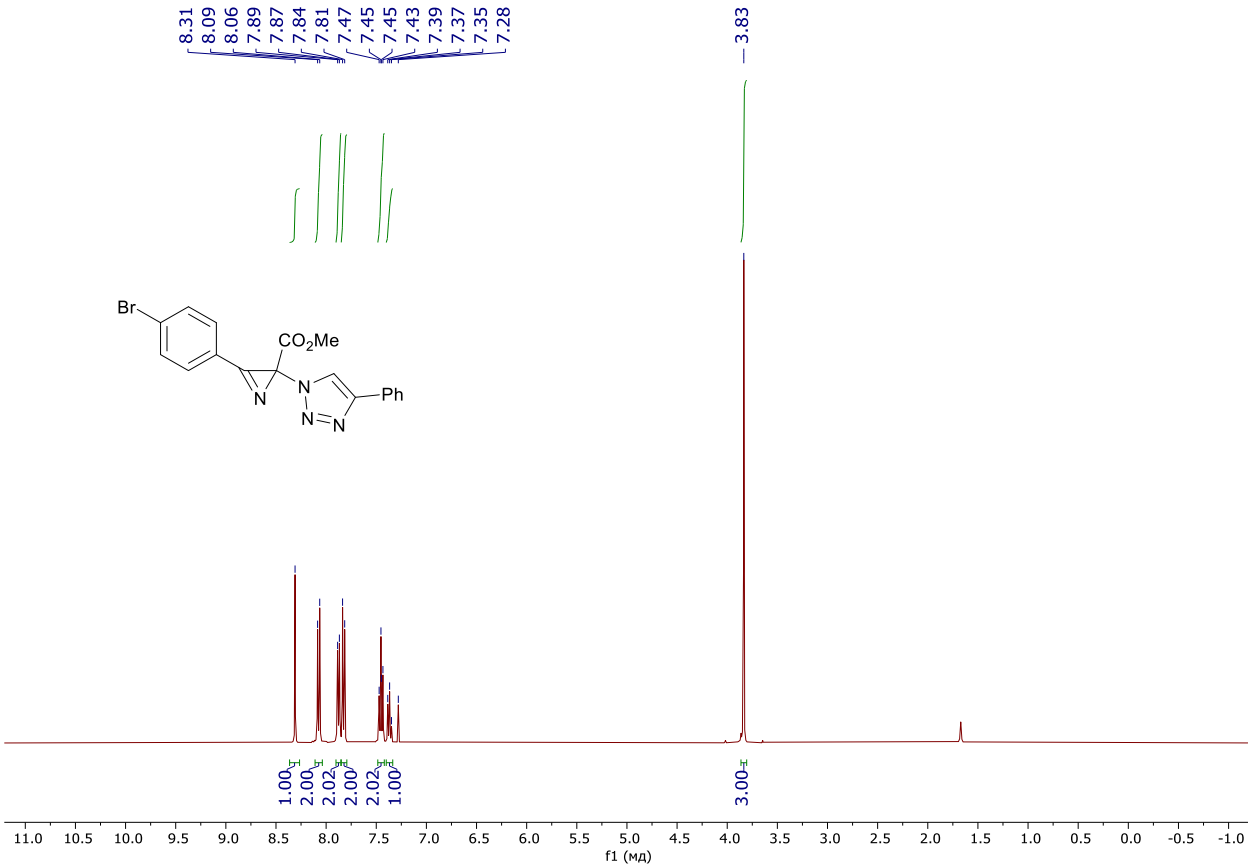
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3i**



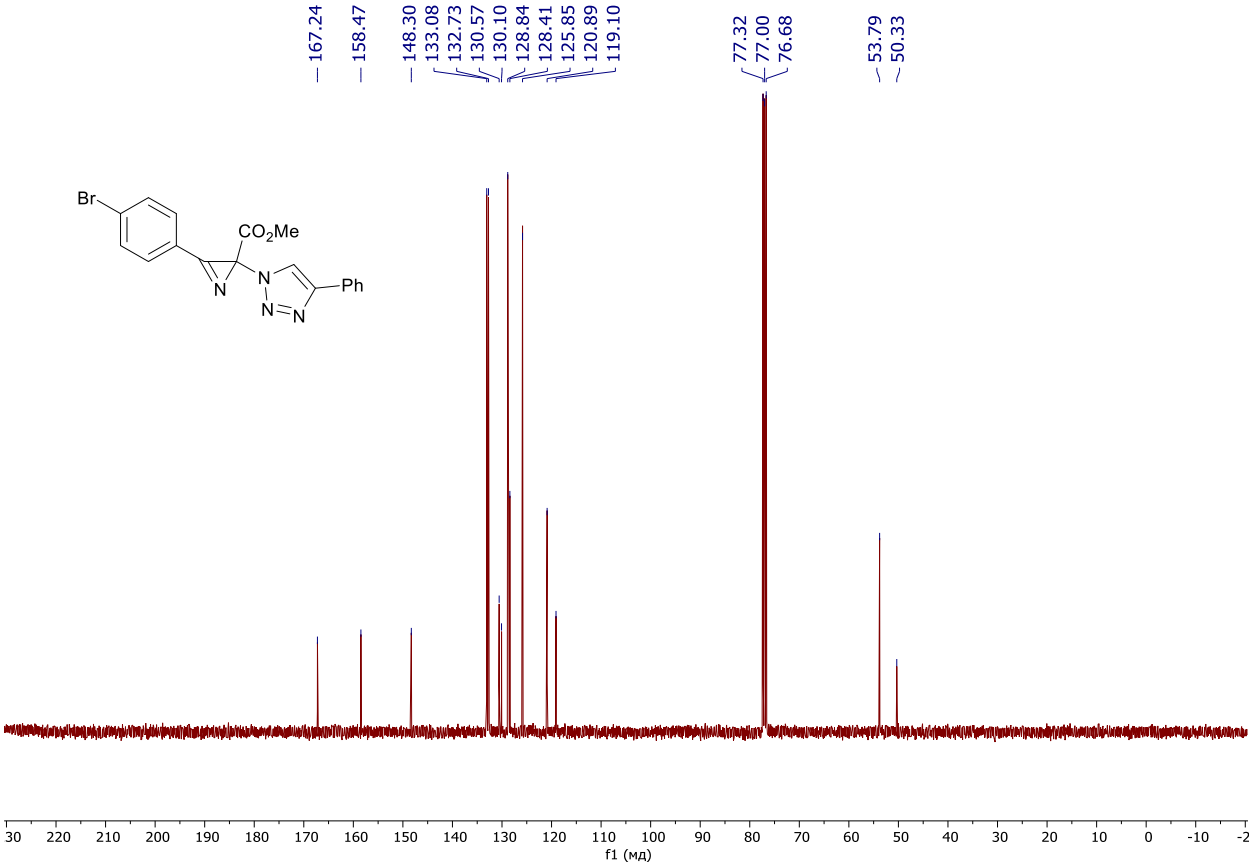

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3i**



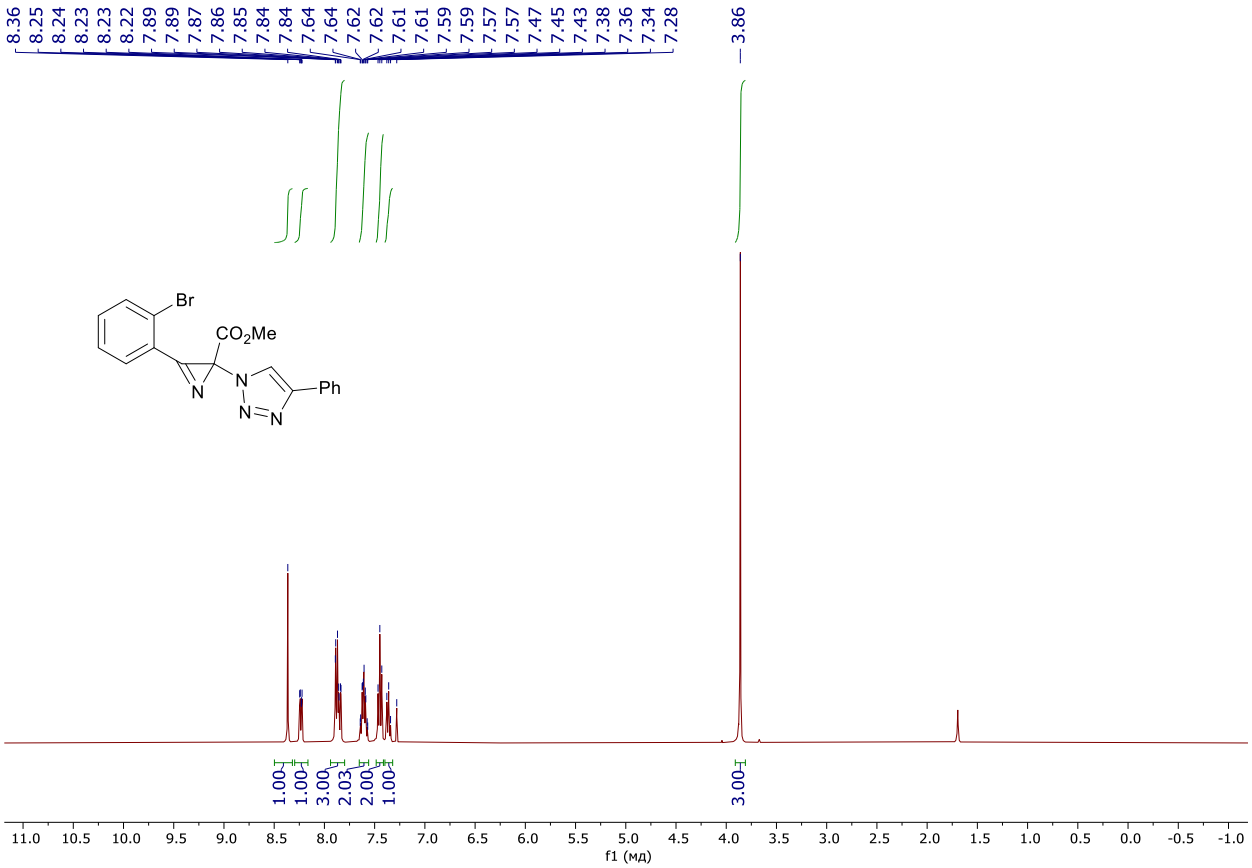
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3j**



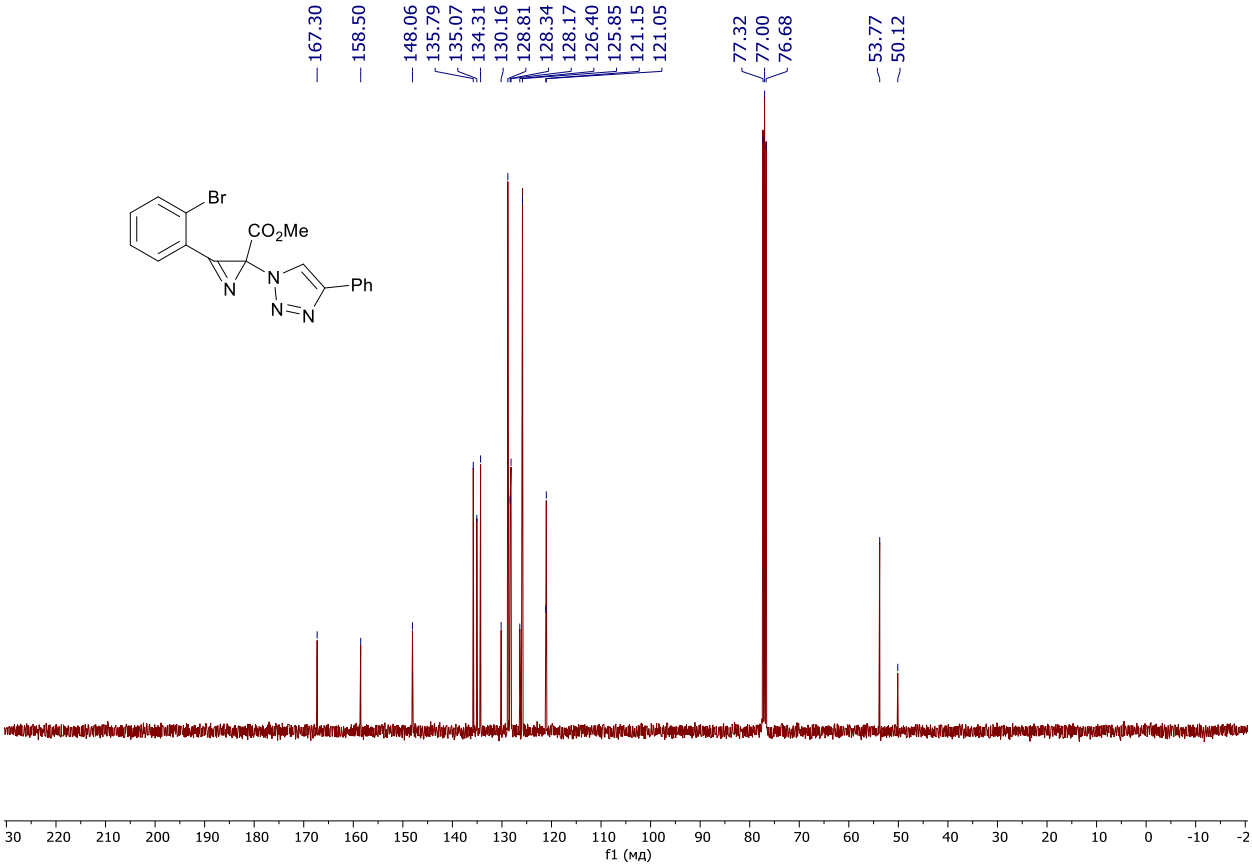

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3j**



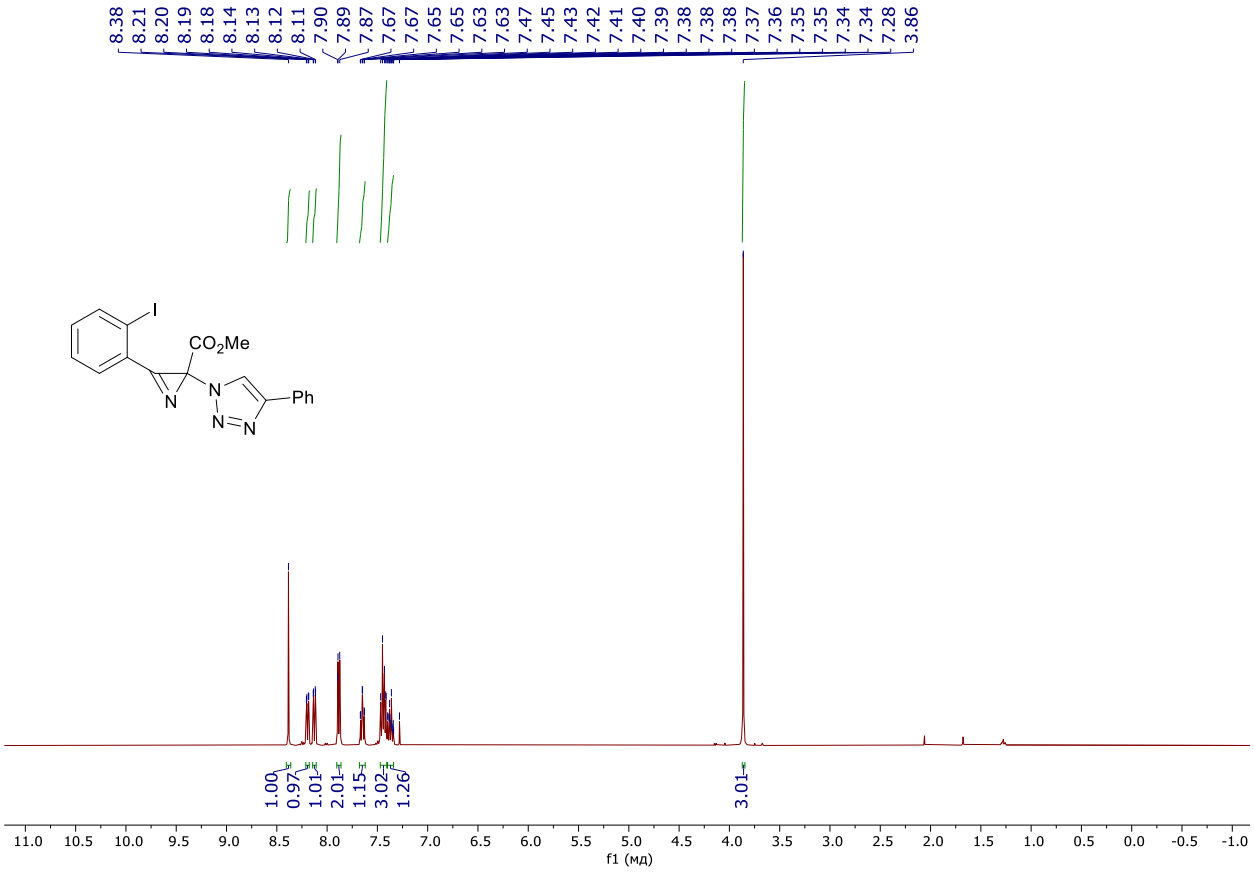
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3k**



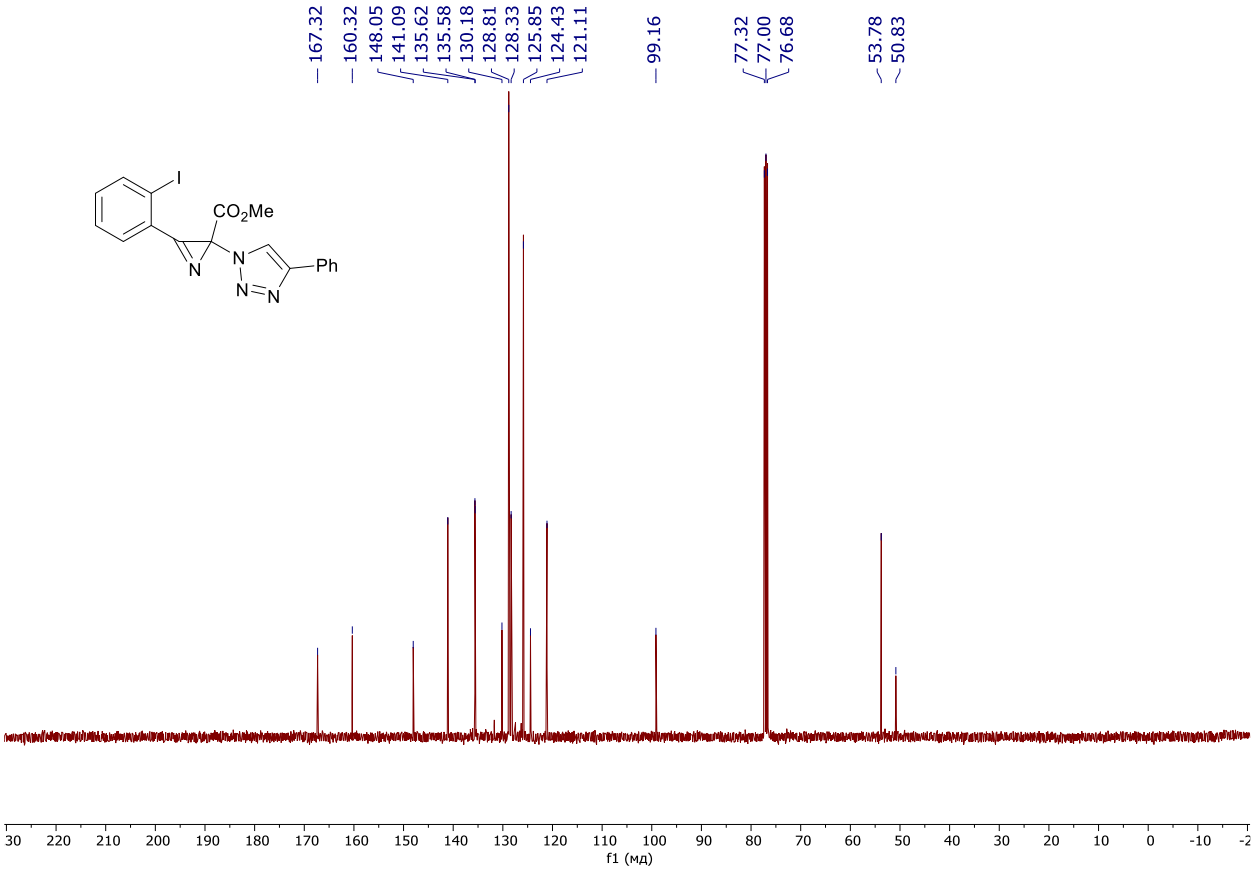

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3k**



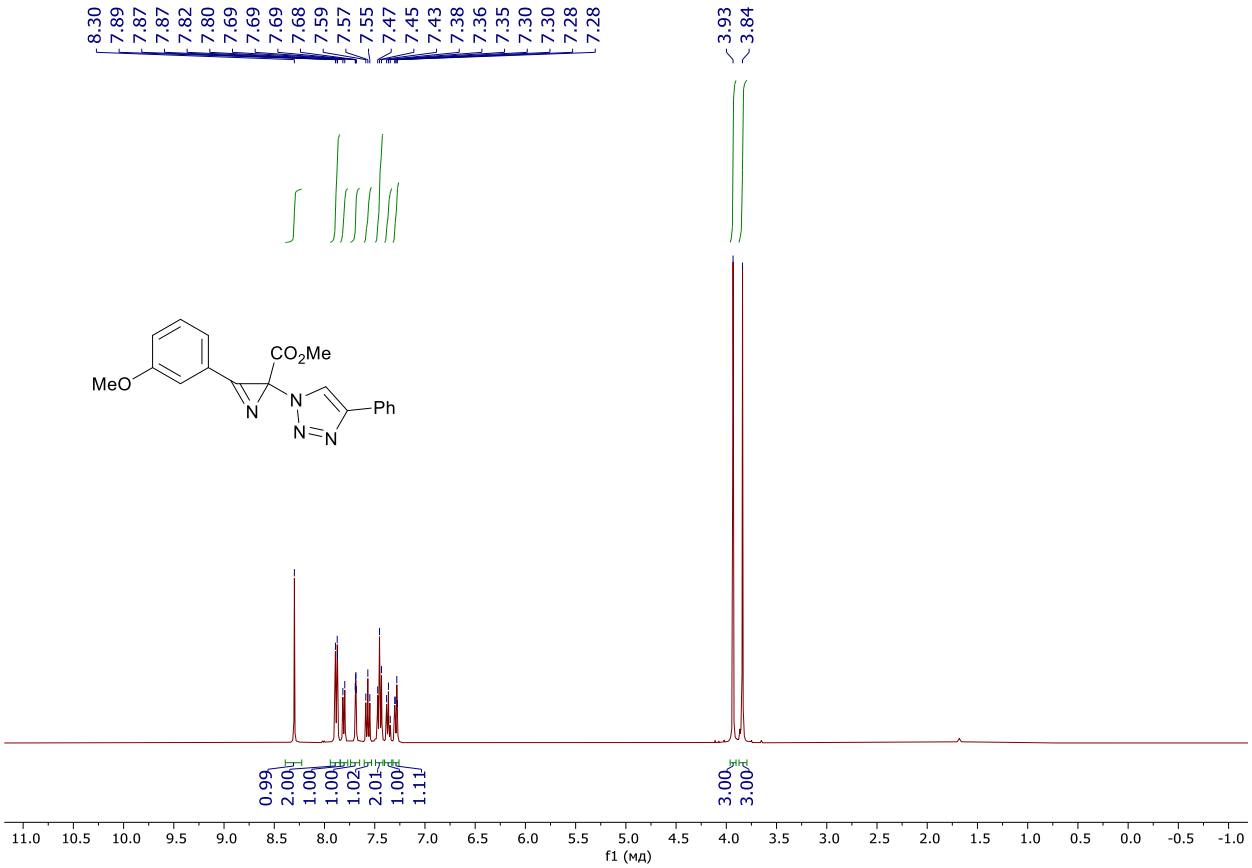
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3l**



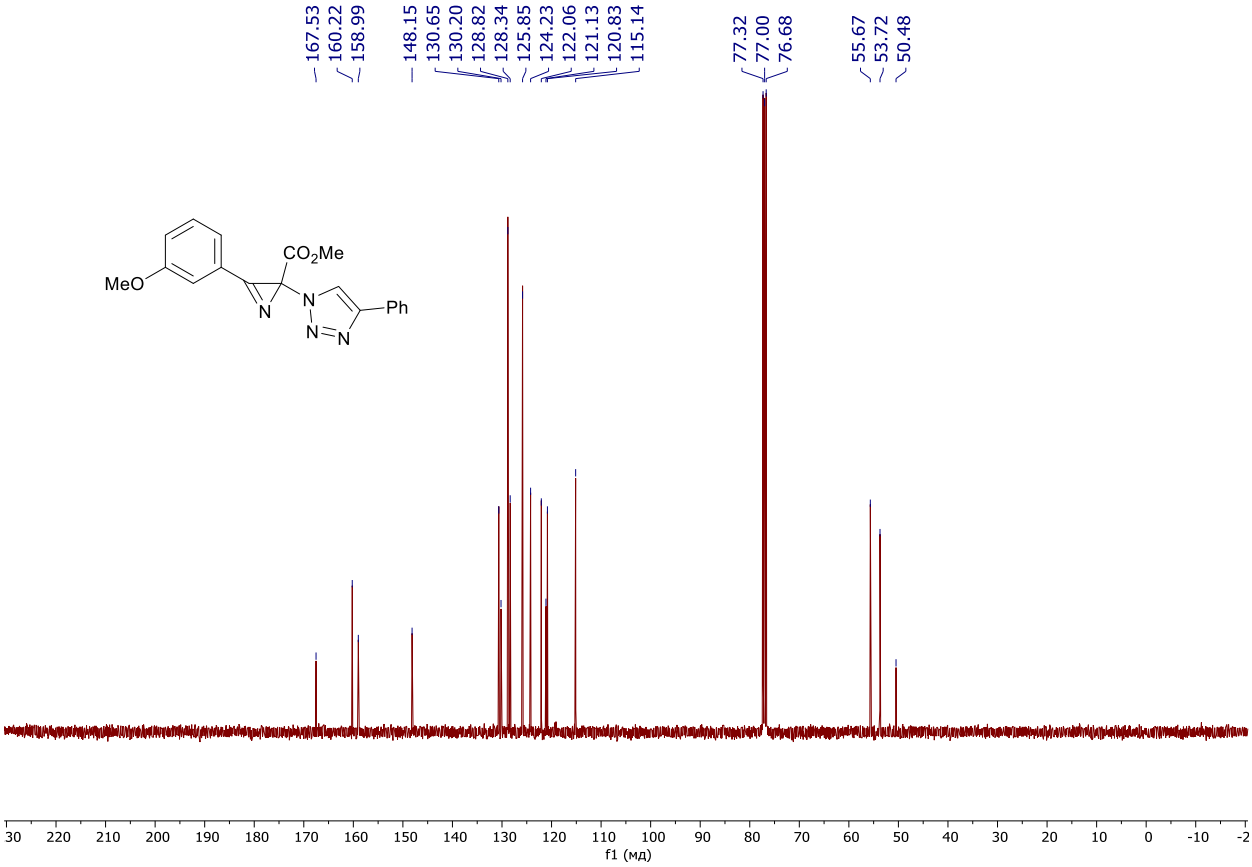

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3l**



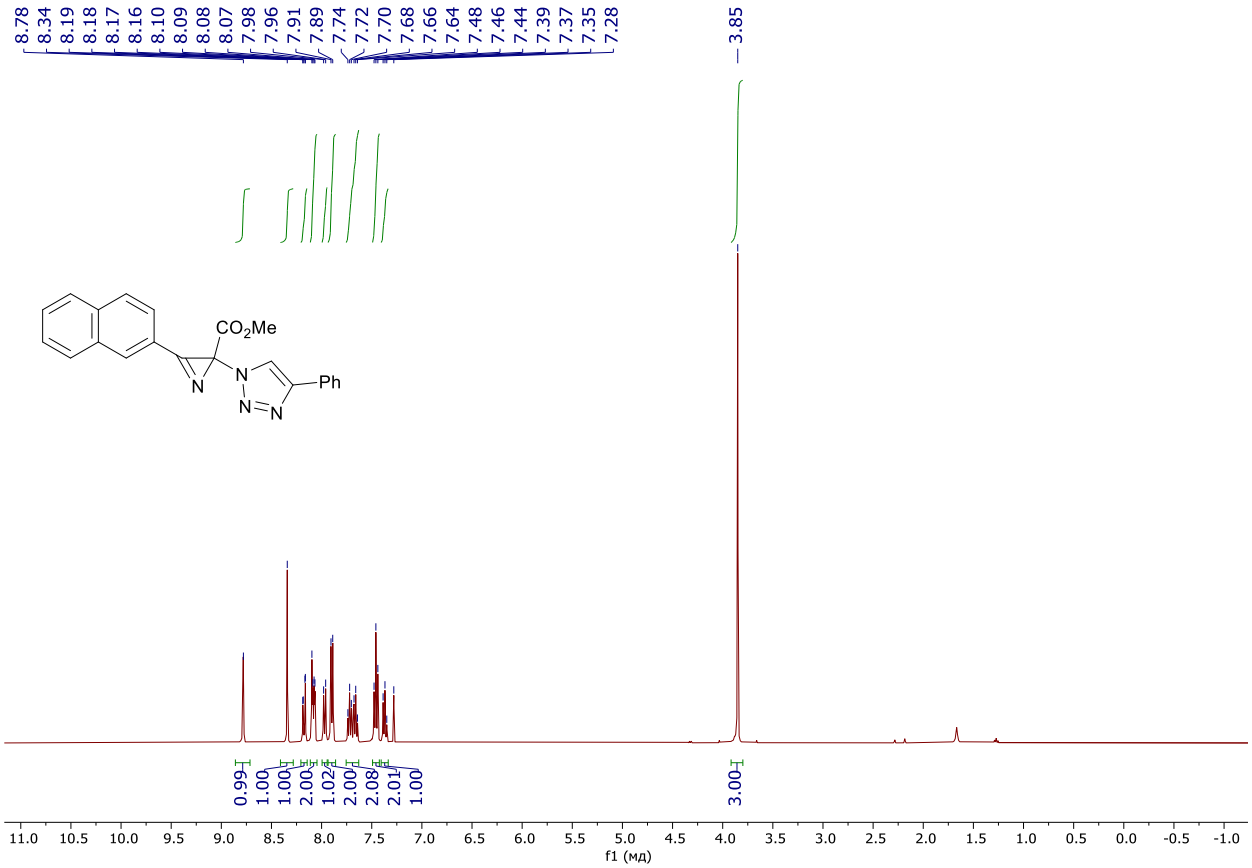
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3m**



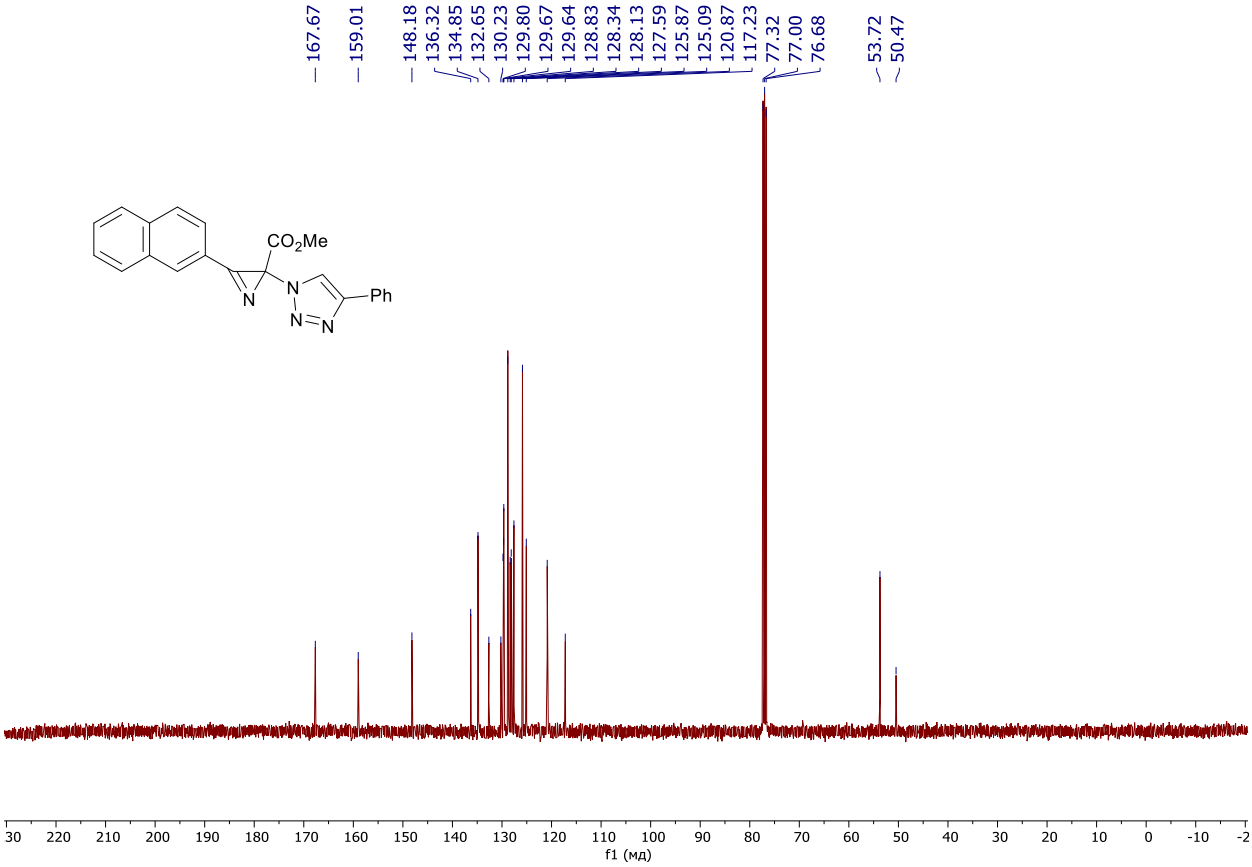

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3m**



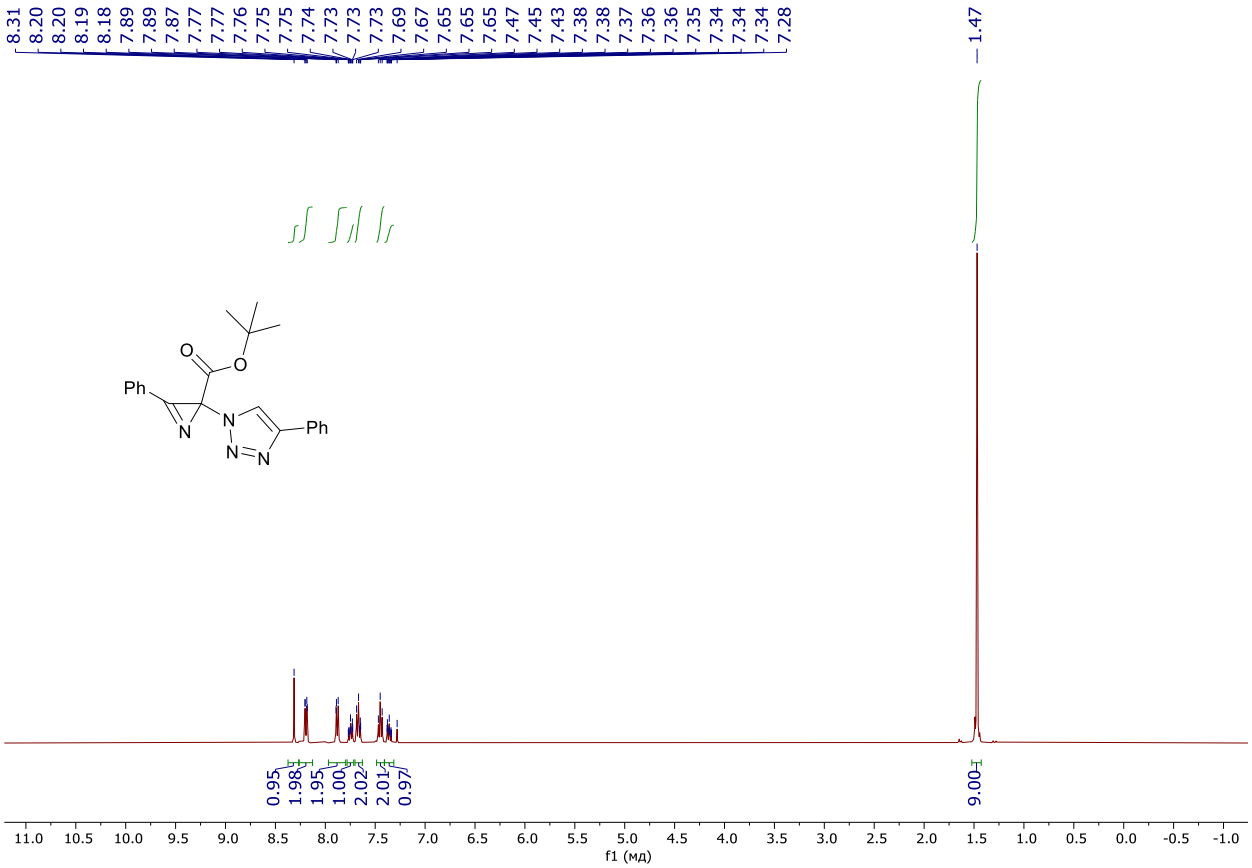
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3n**



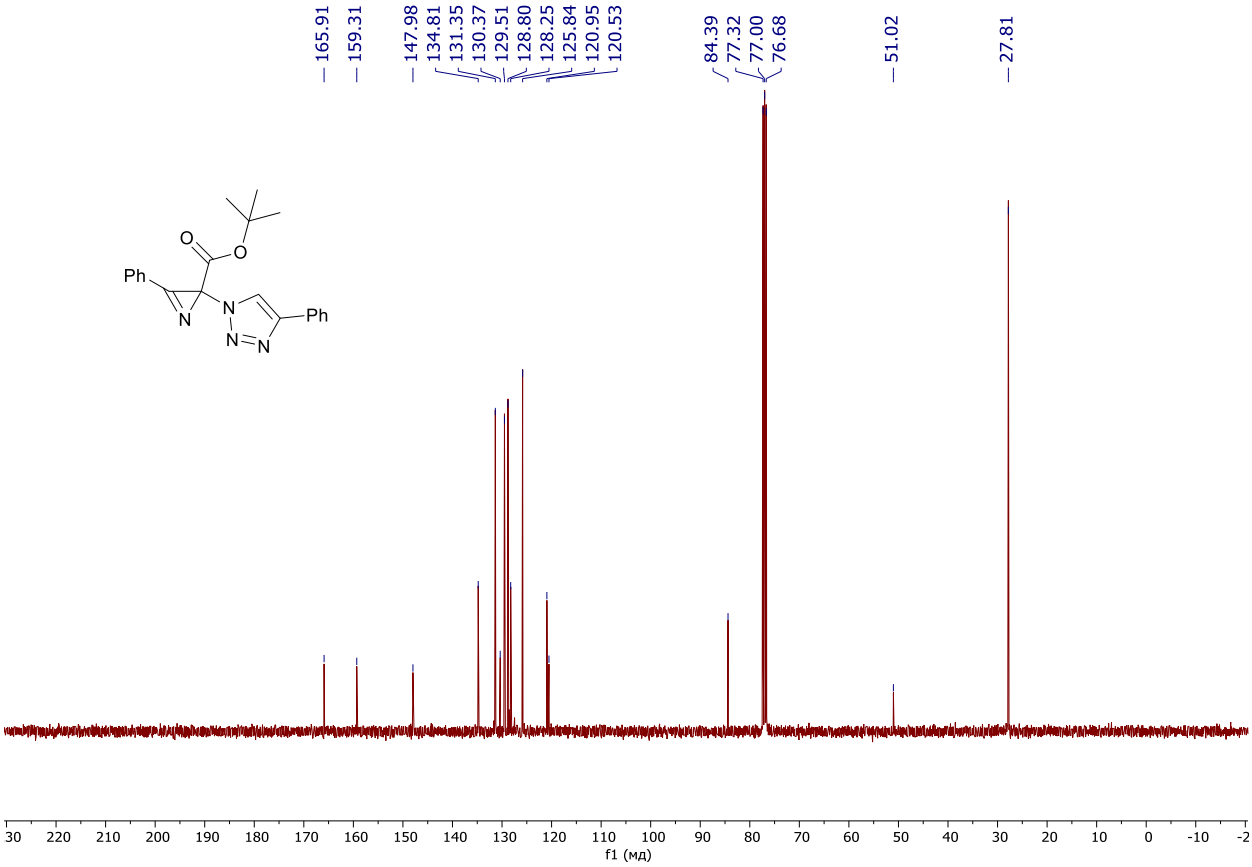

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3n**



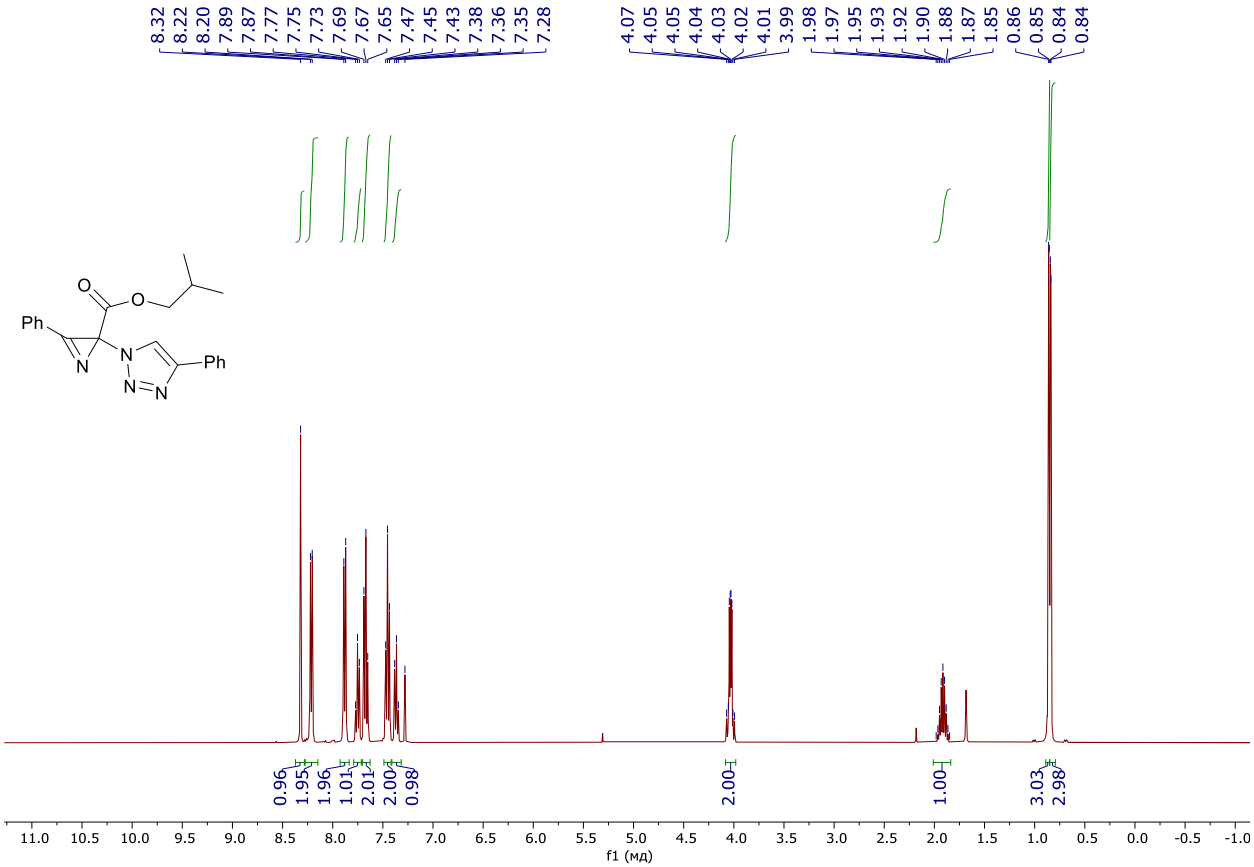
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3o**



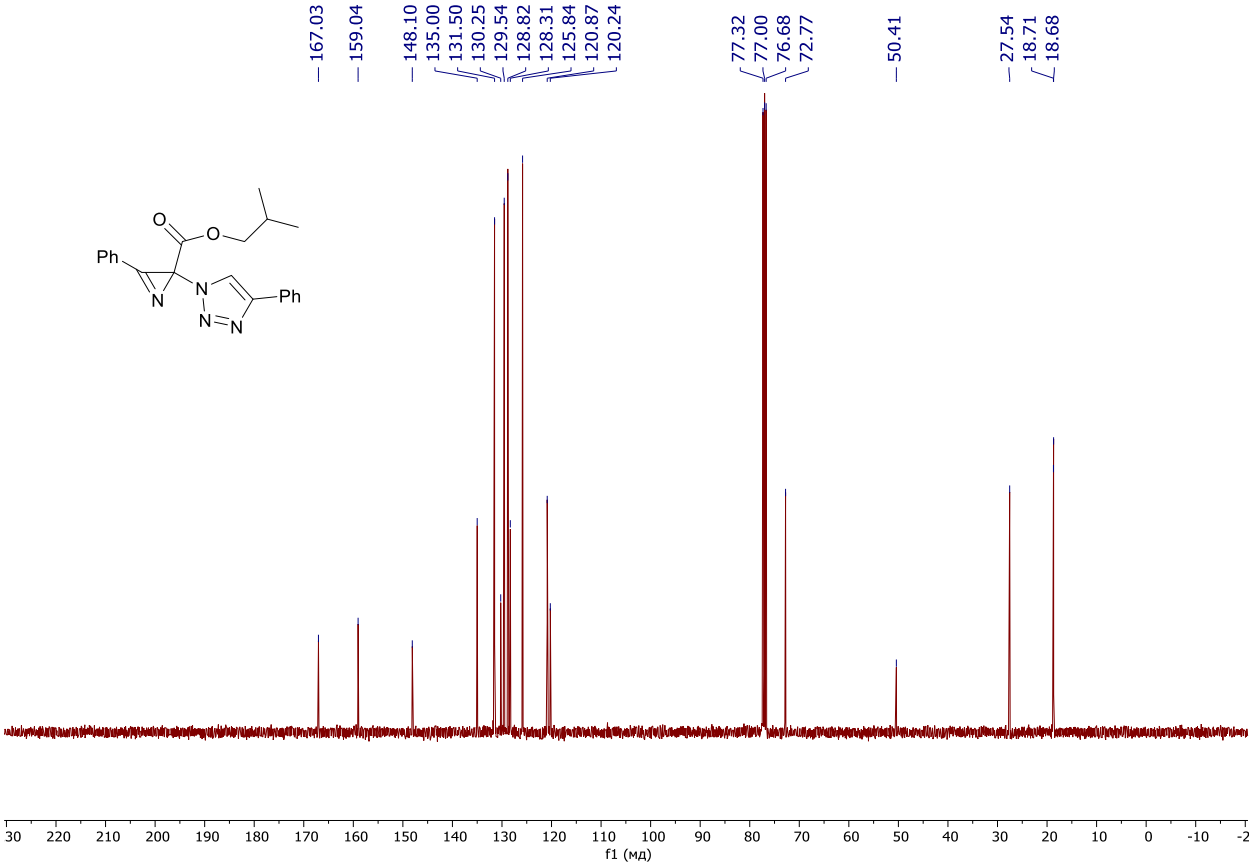

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3o**



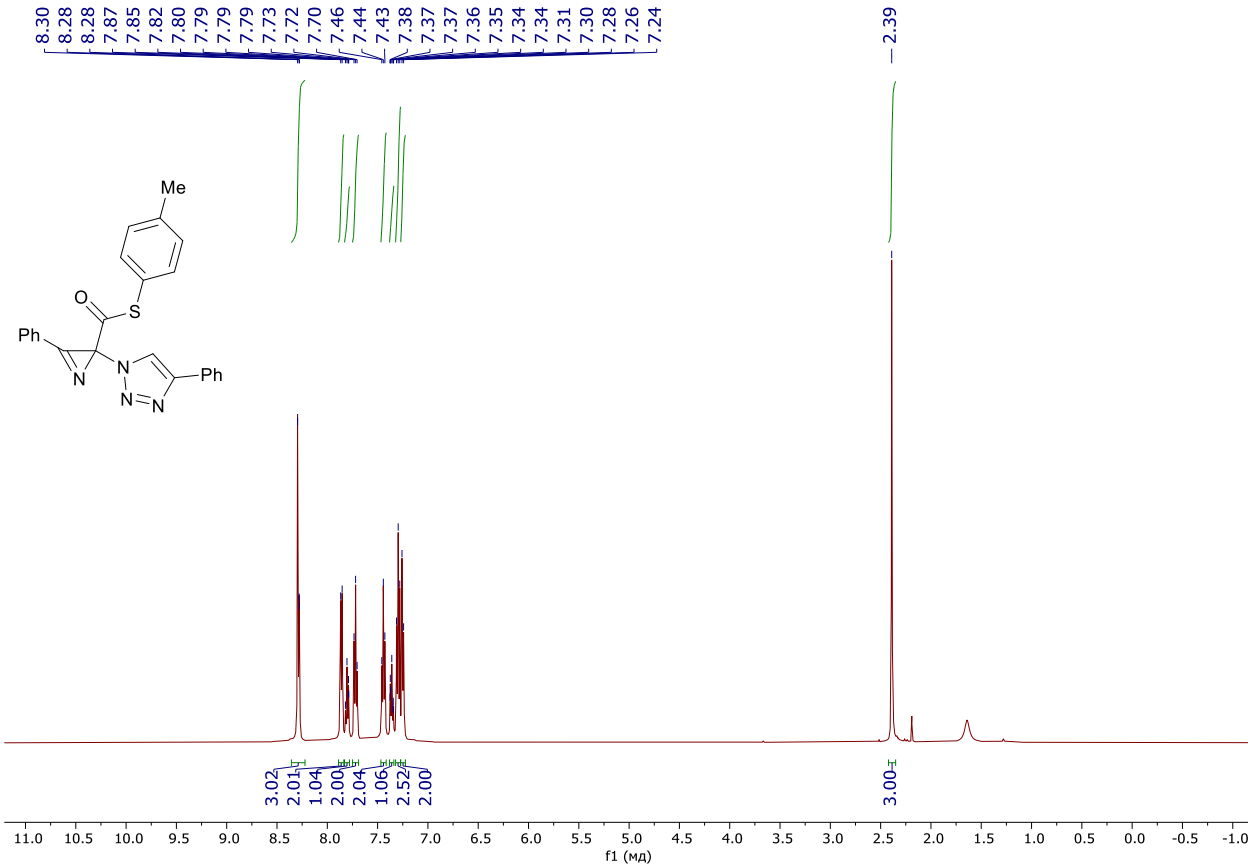
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3p**



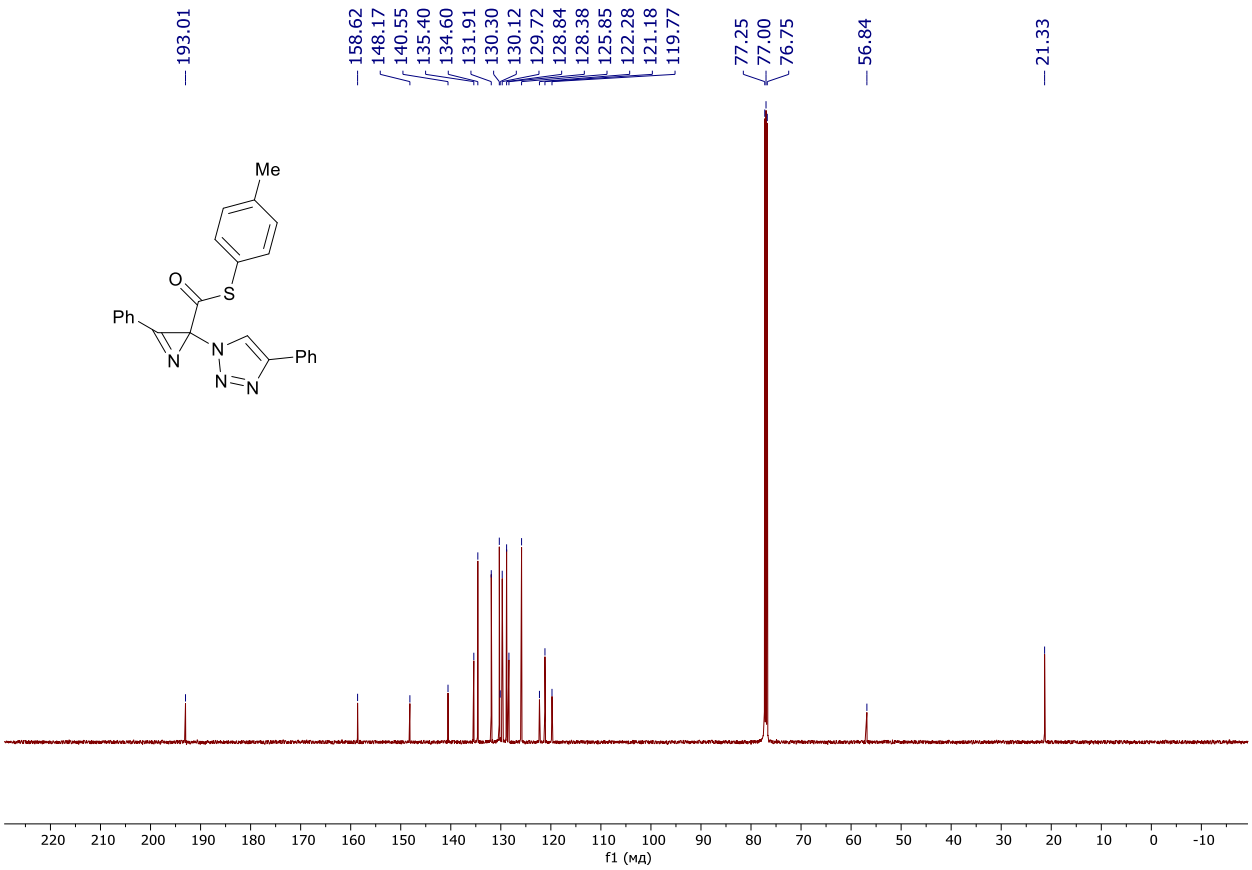

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3p**



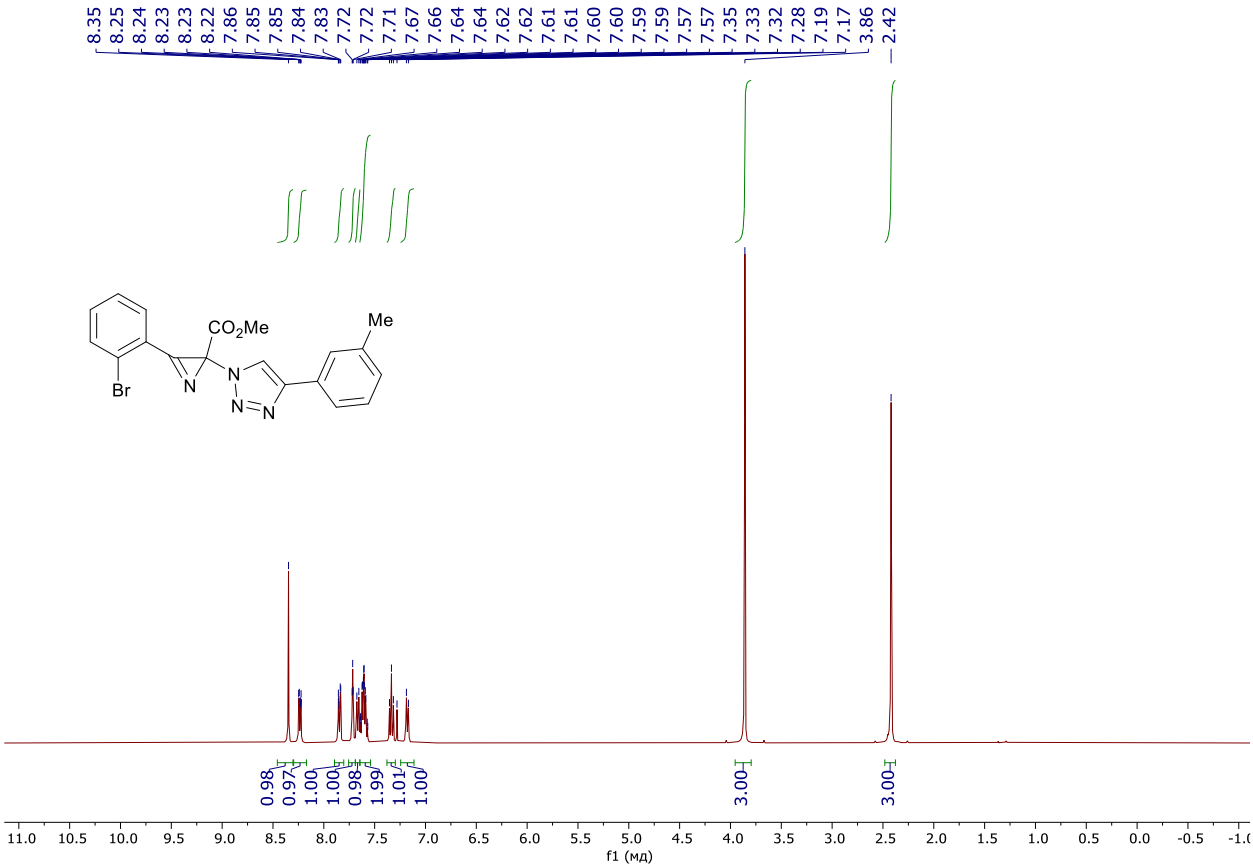
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3q**



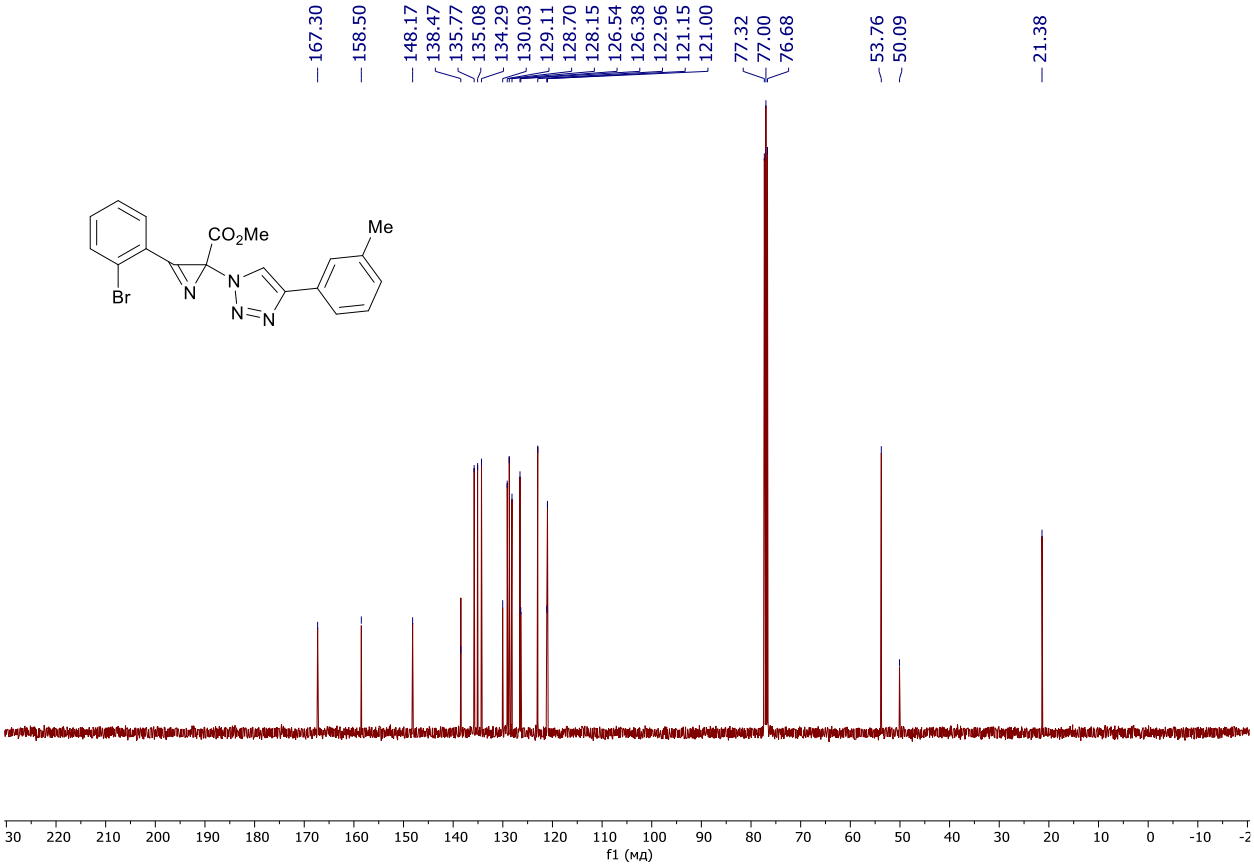

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3q**



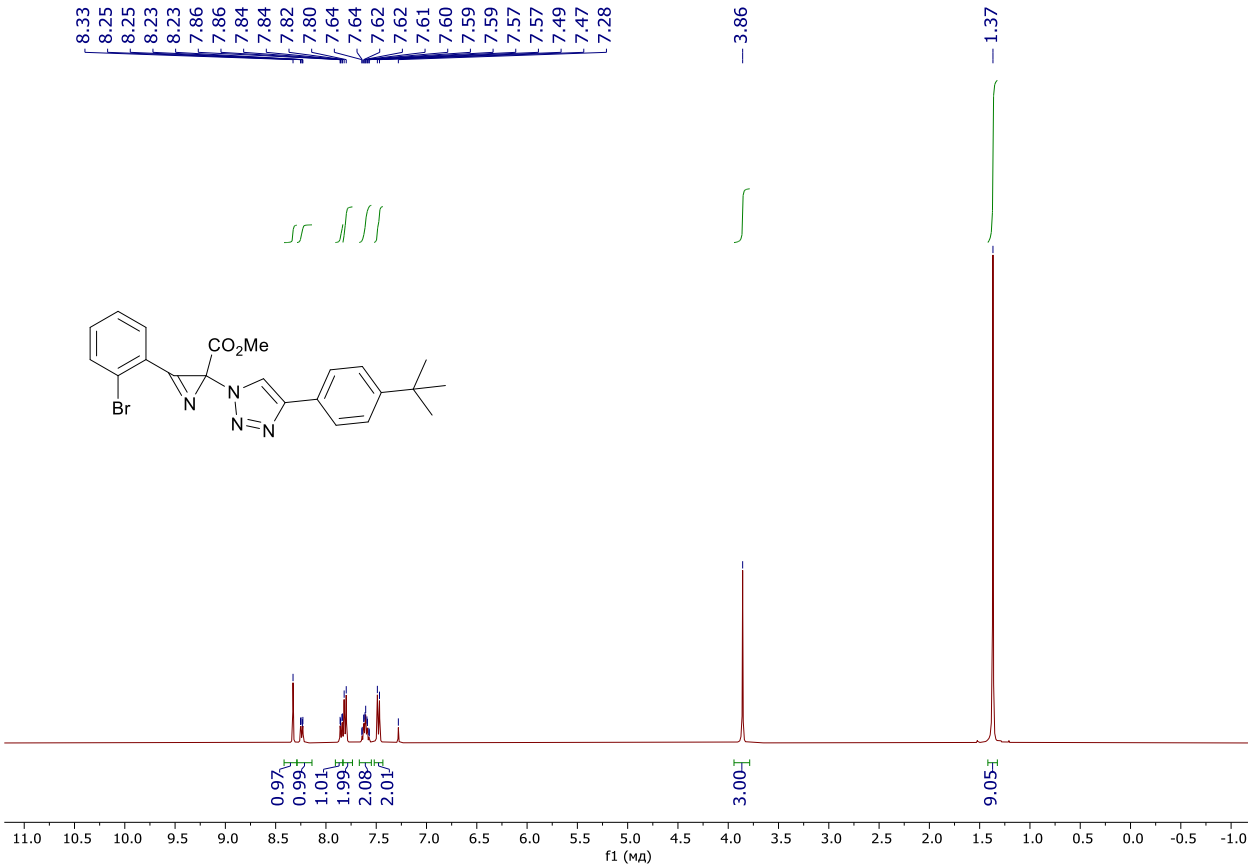
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3r**



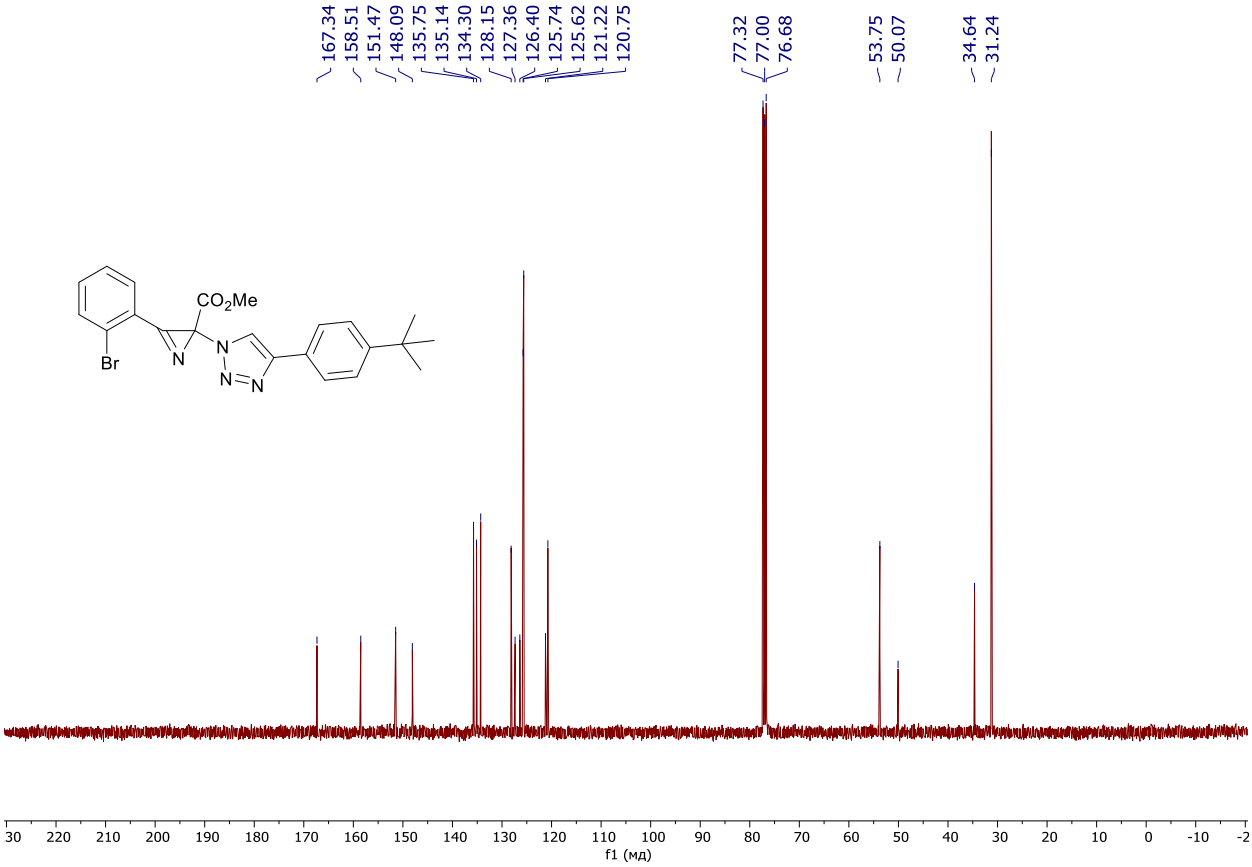

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3r**



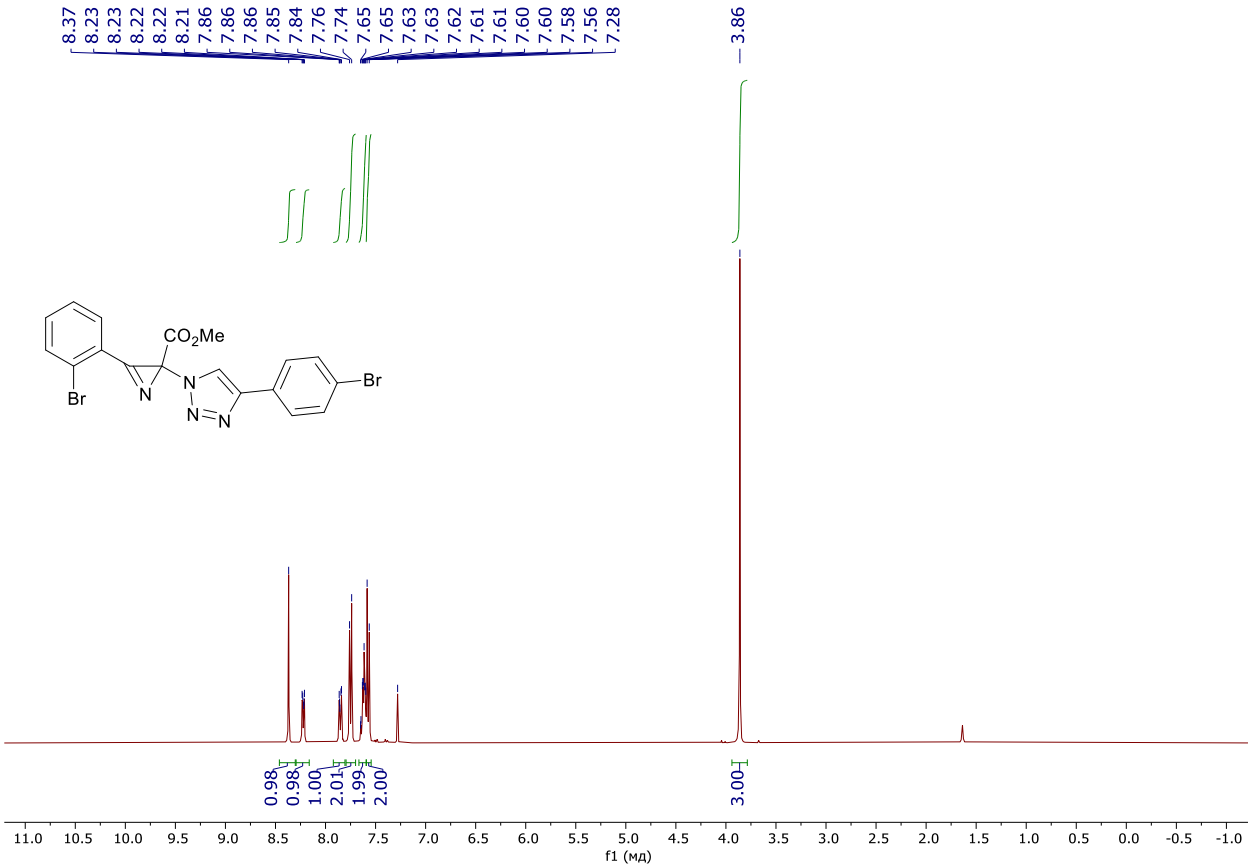
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3s**



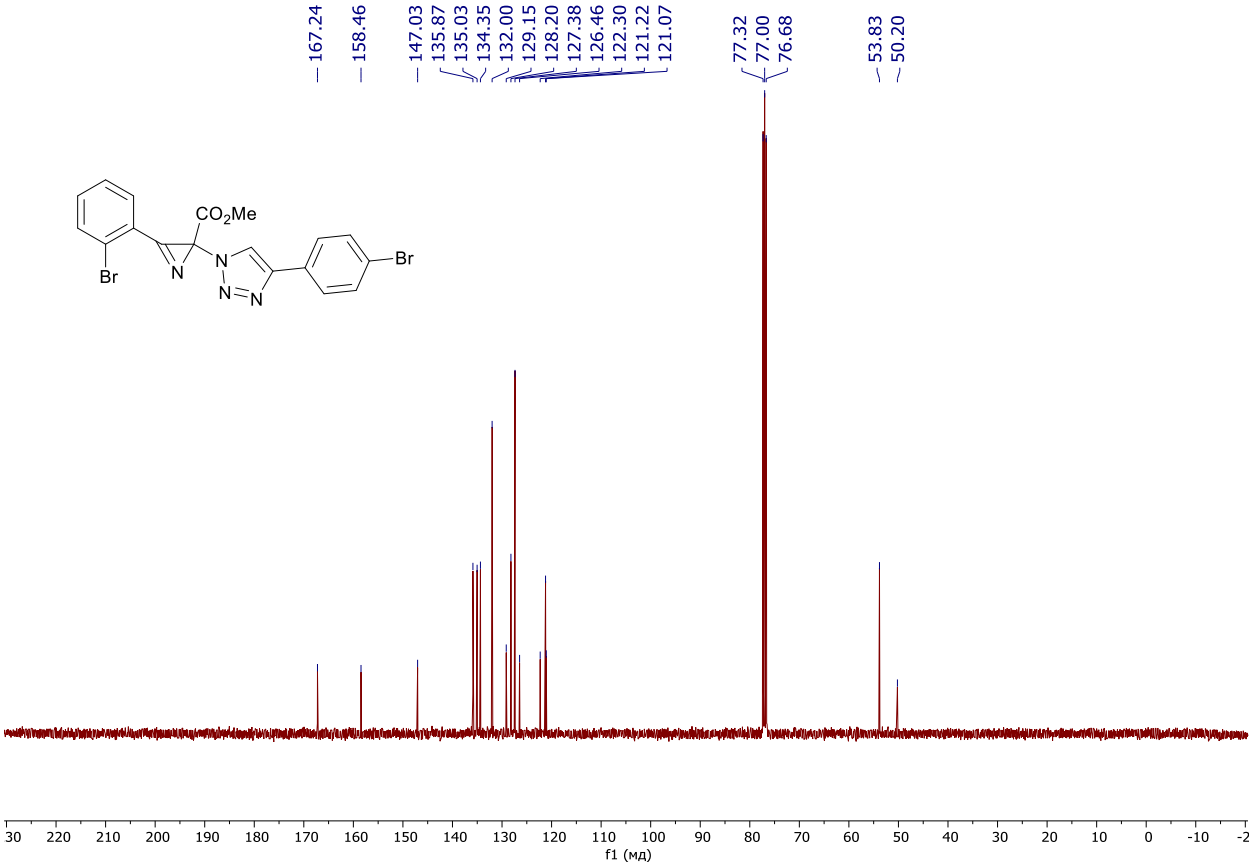

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3s**



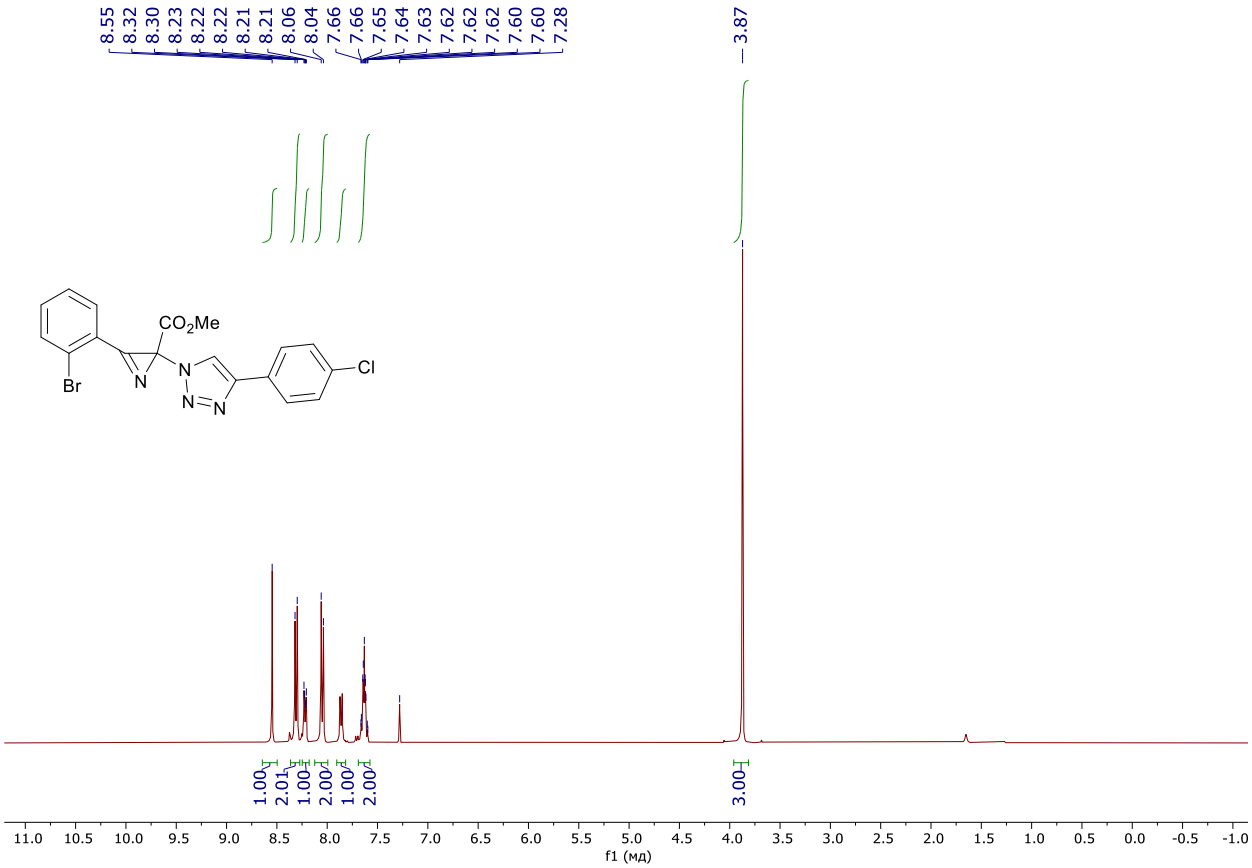
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3t**



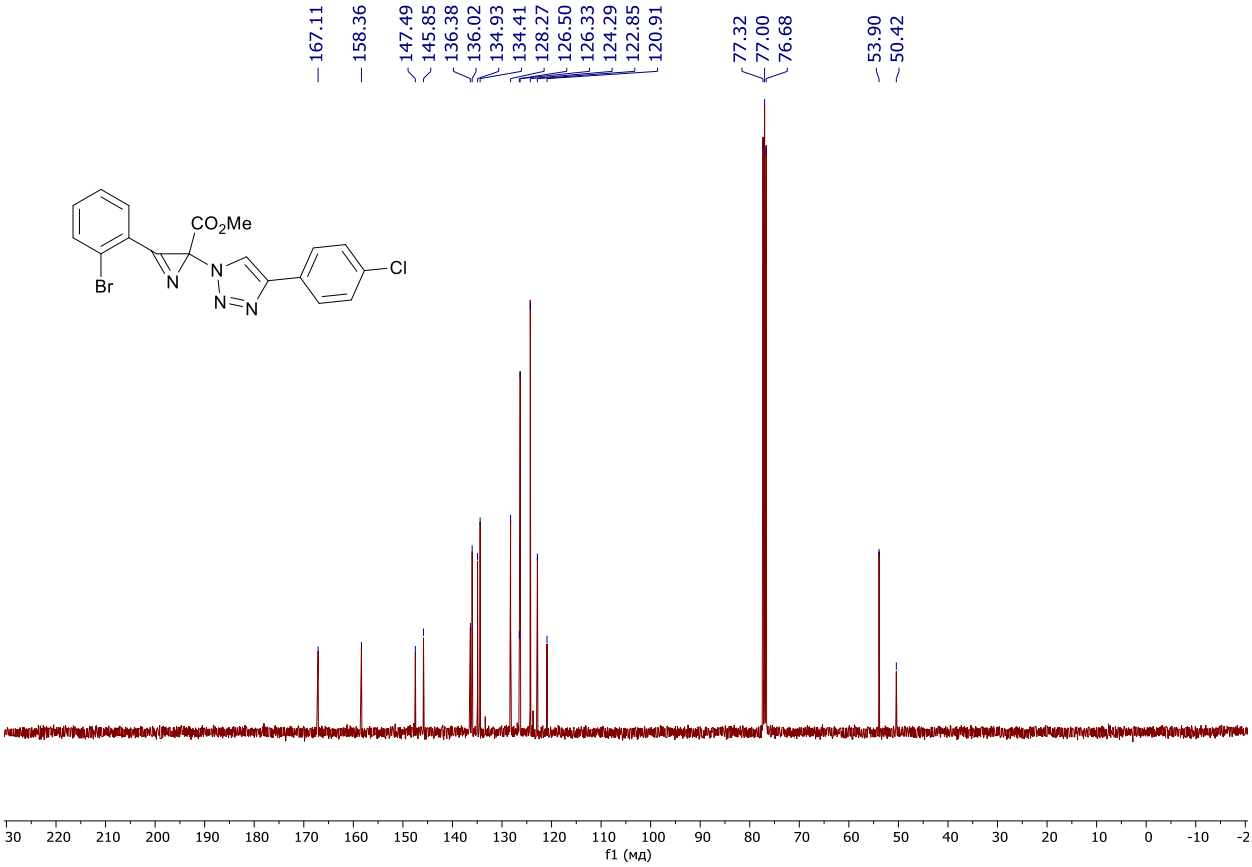

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3t**



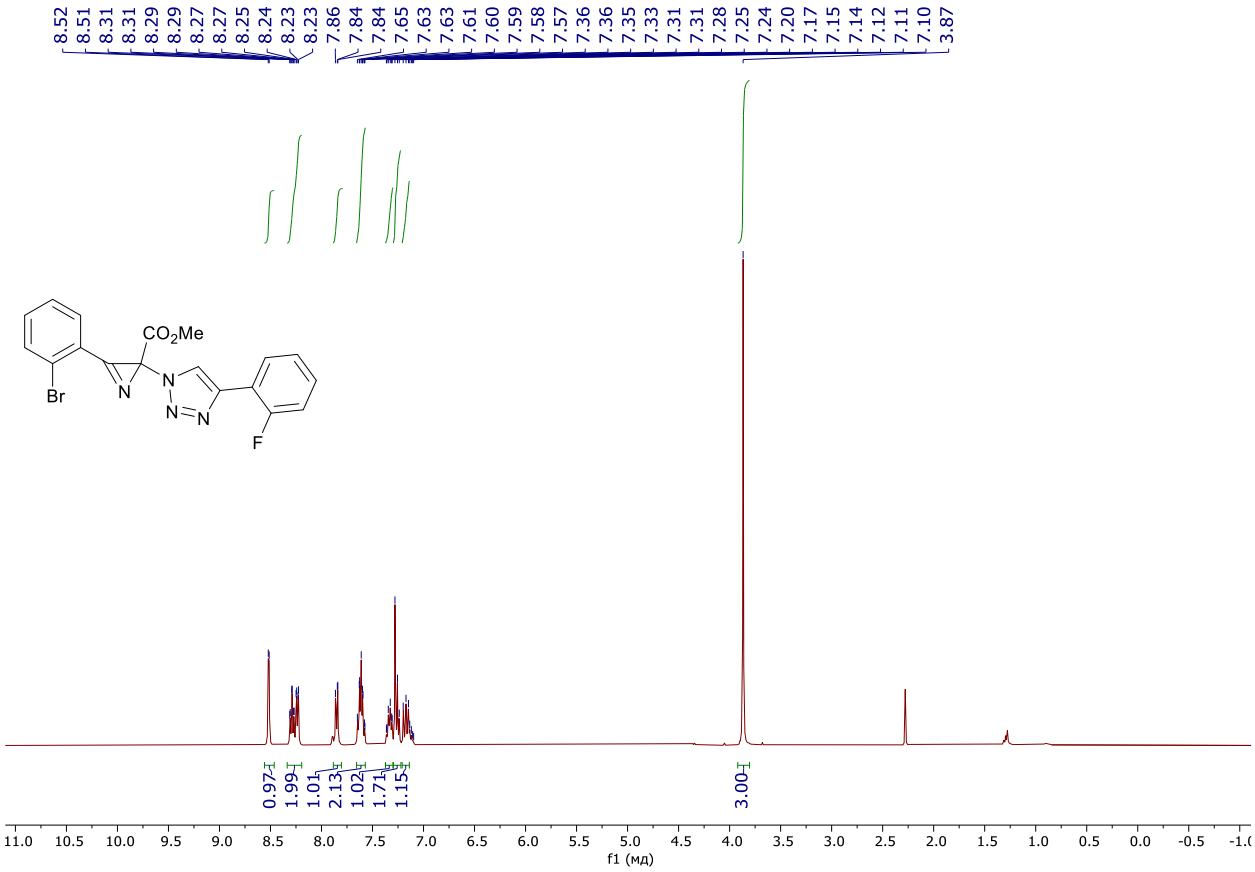
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3u**



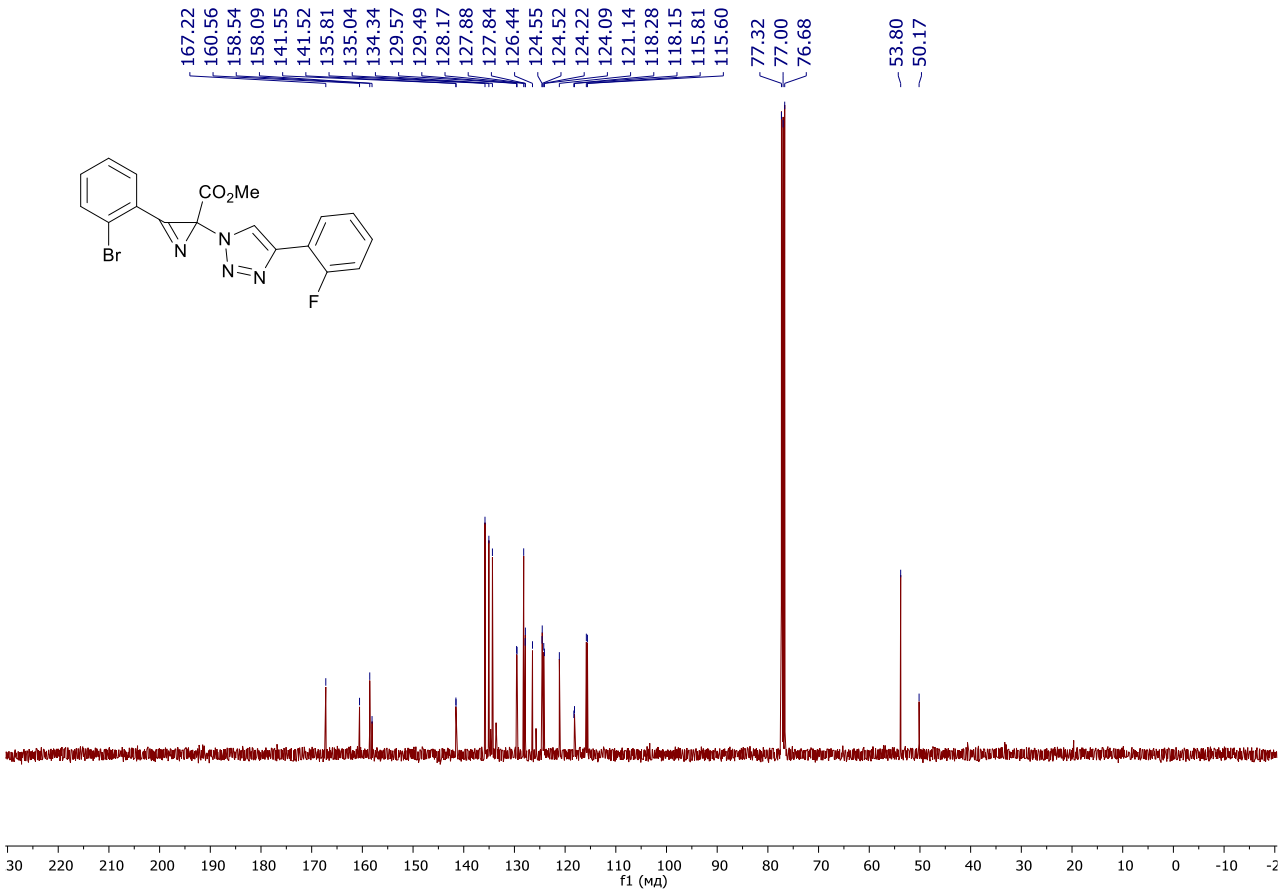

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3u**



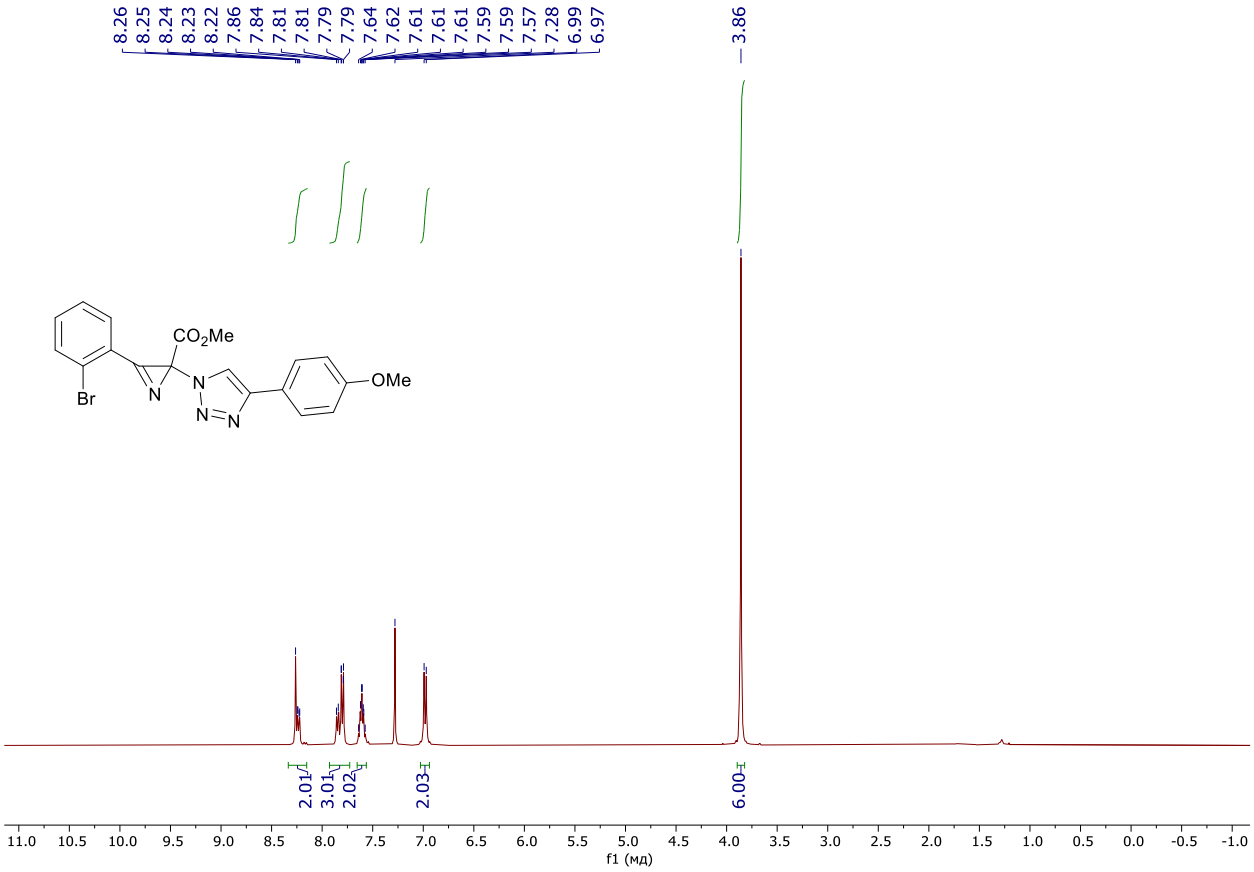
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3v**



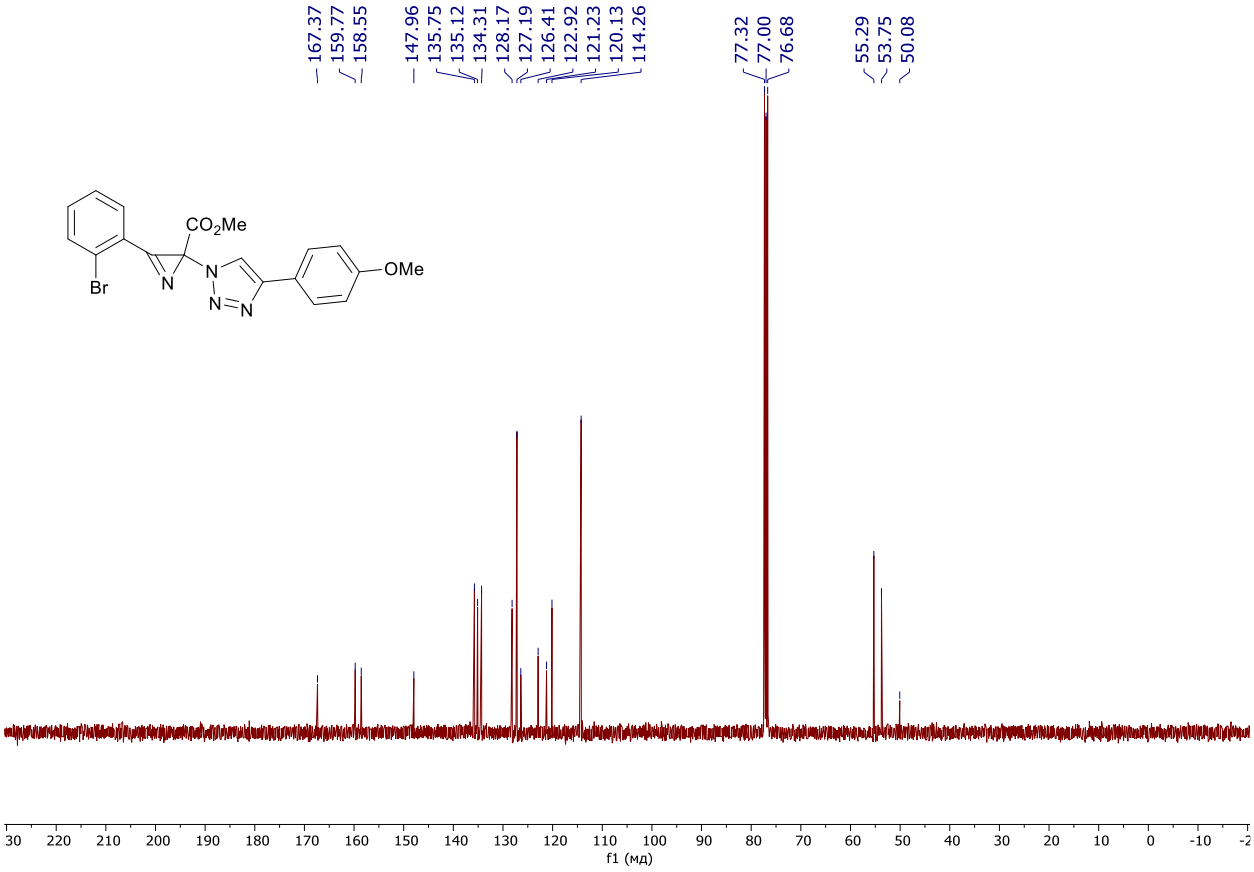

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3v**



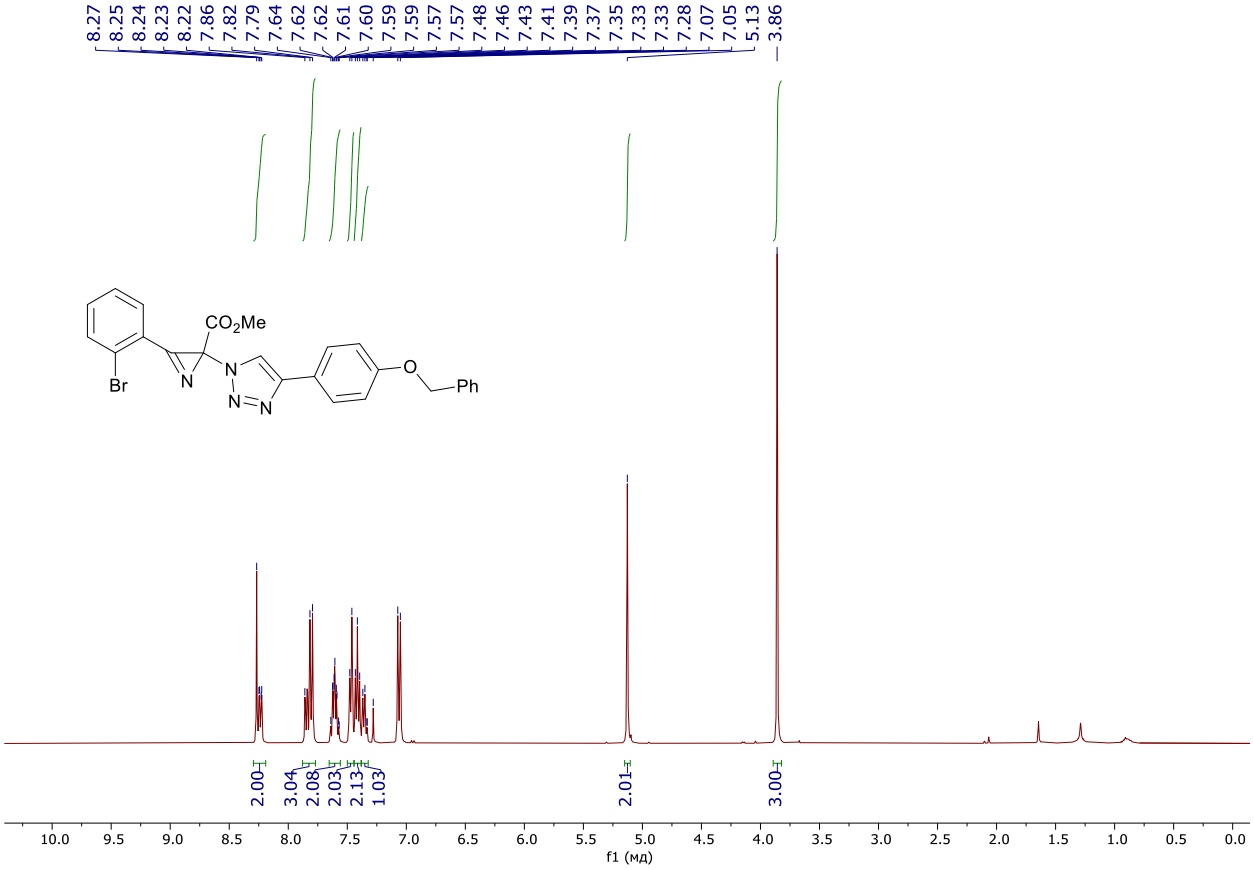
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3w**



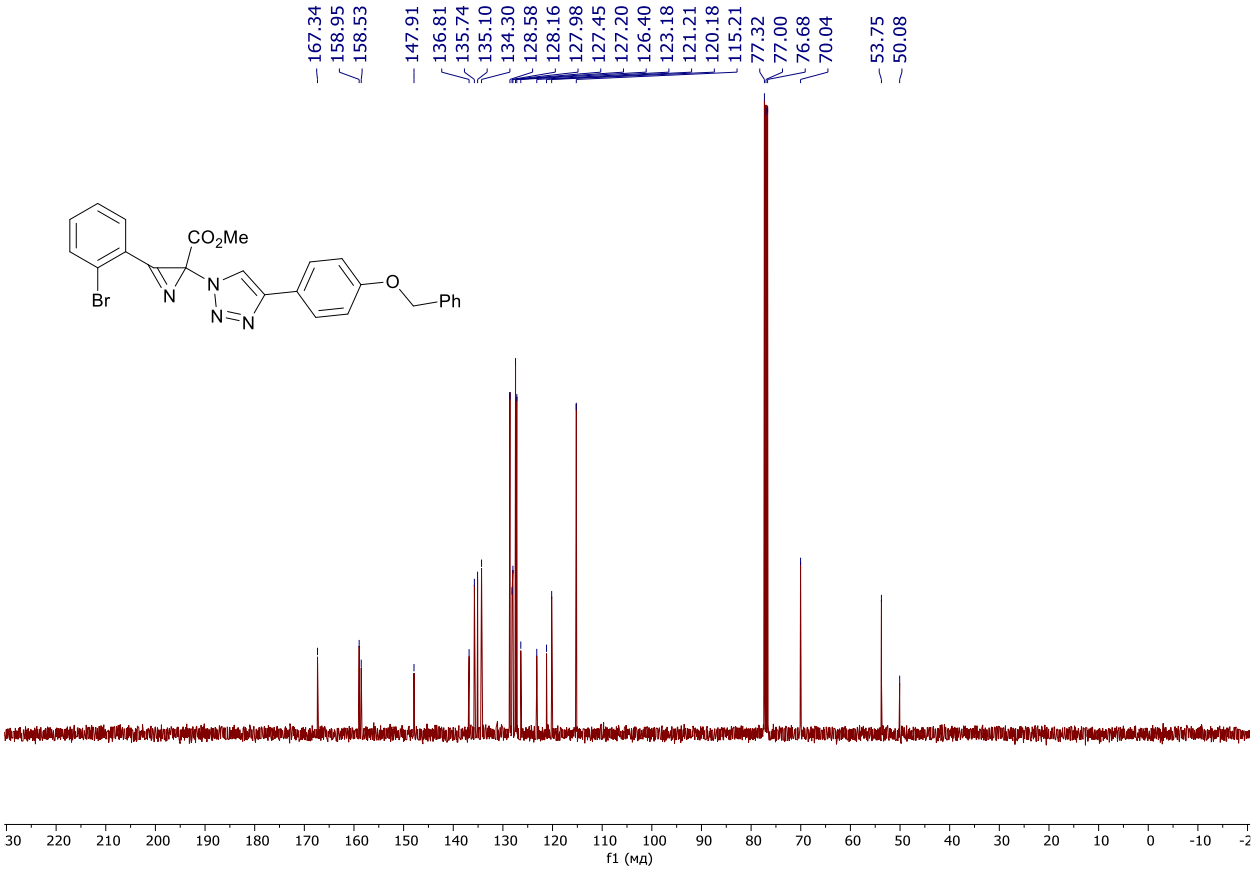

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3w**



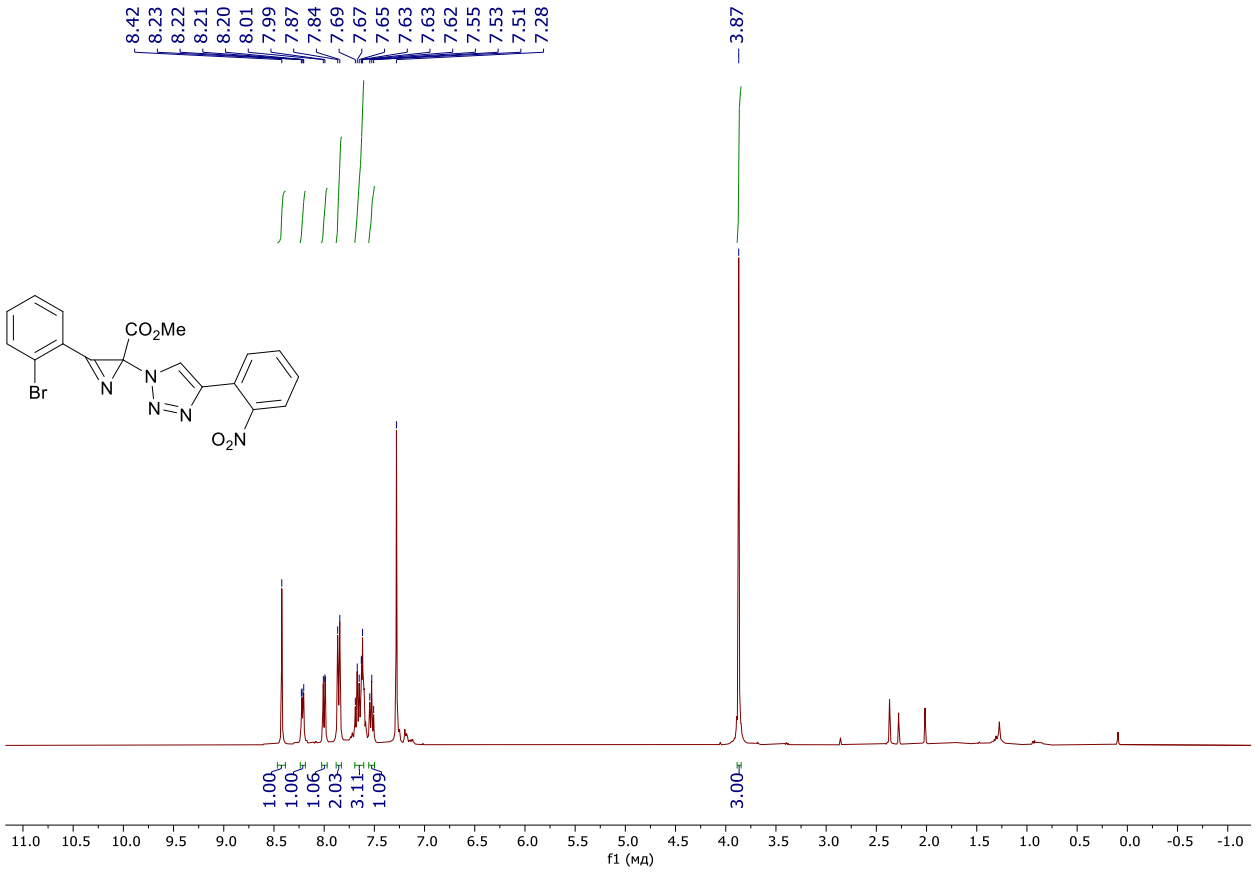
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3x**



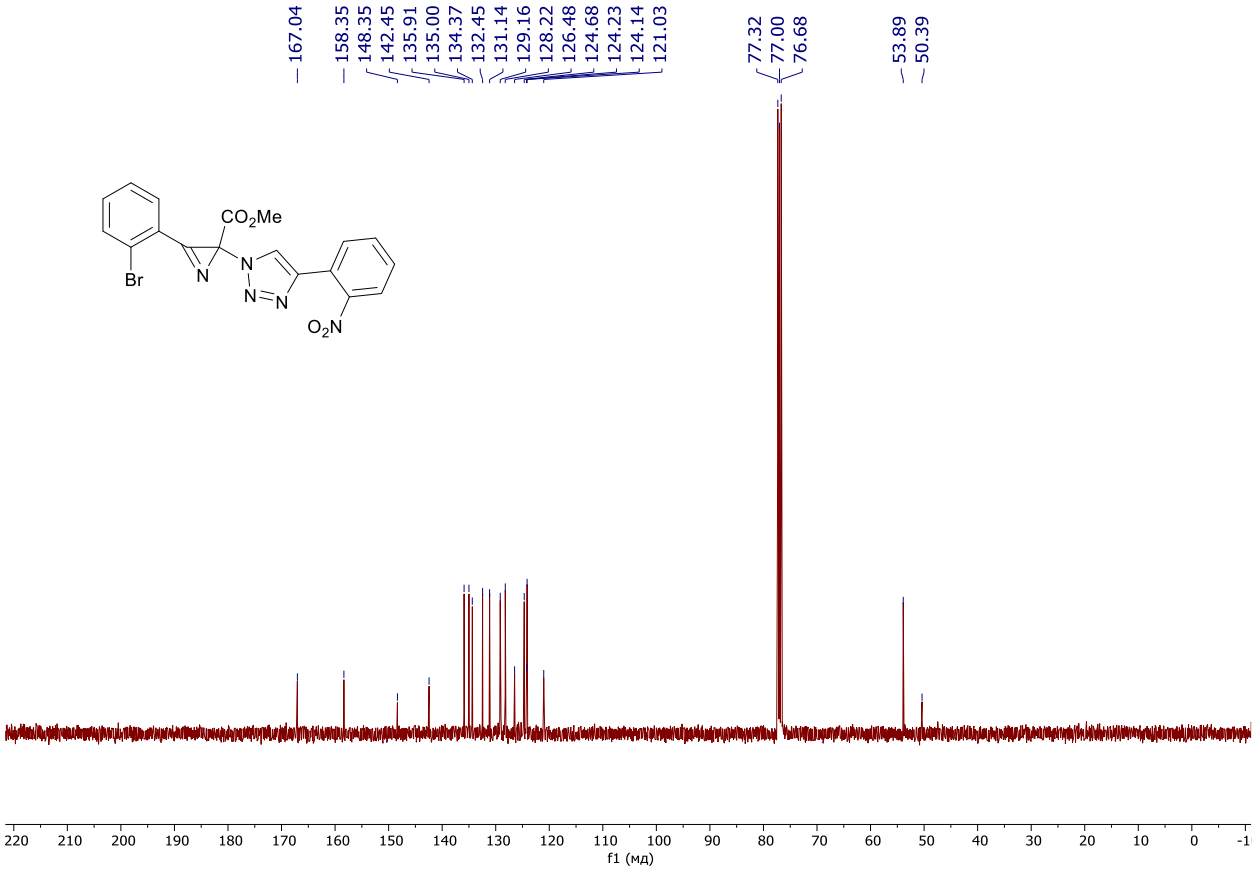

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3x**



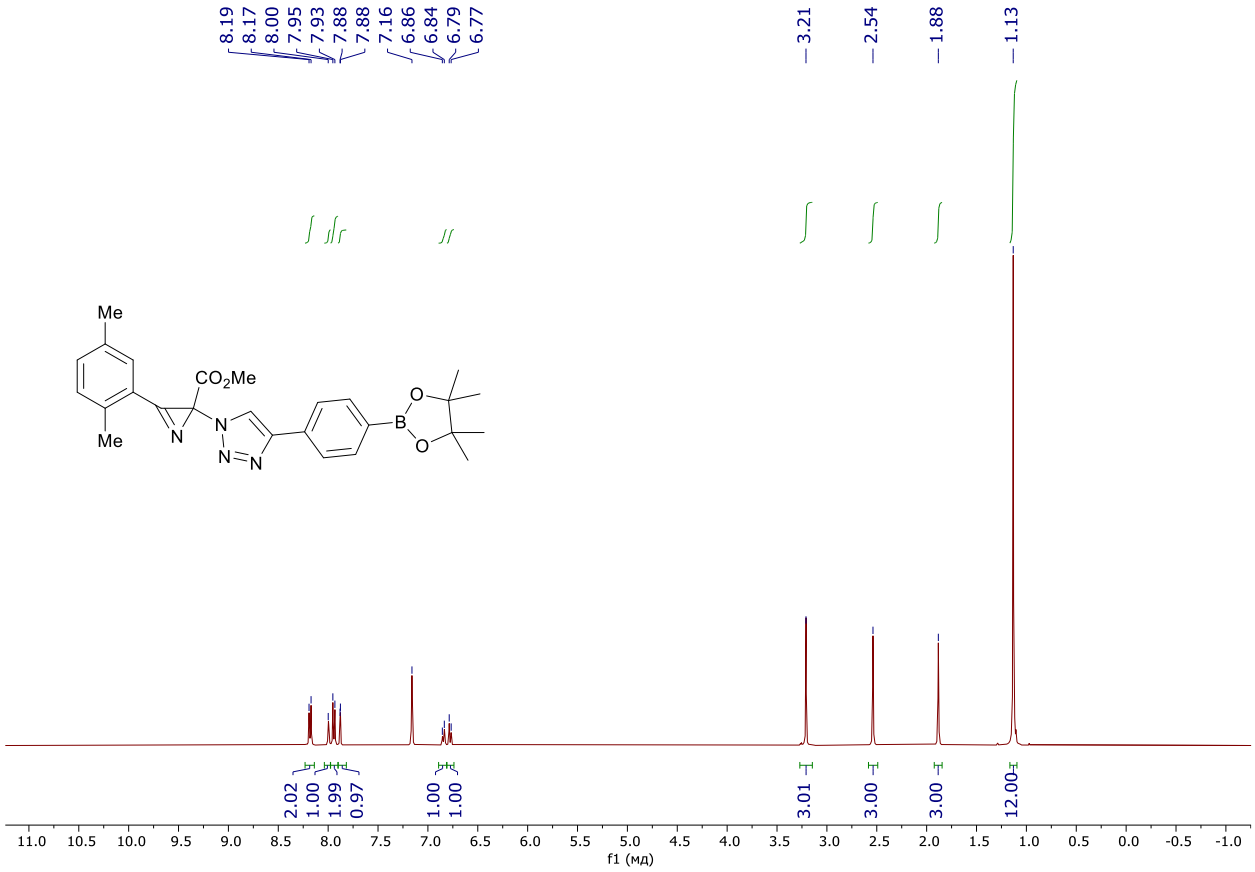
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3y**



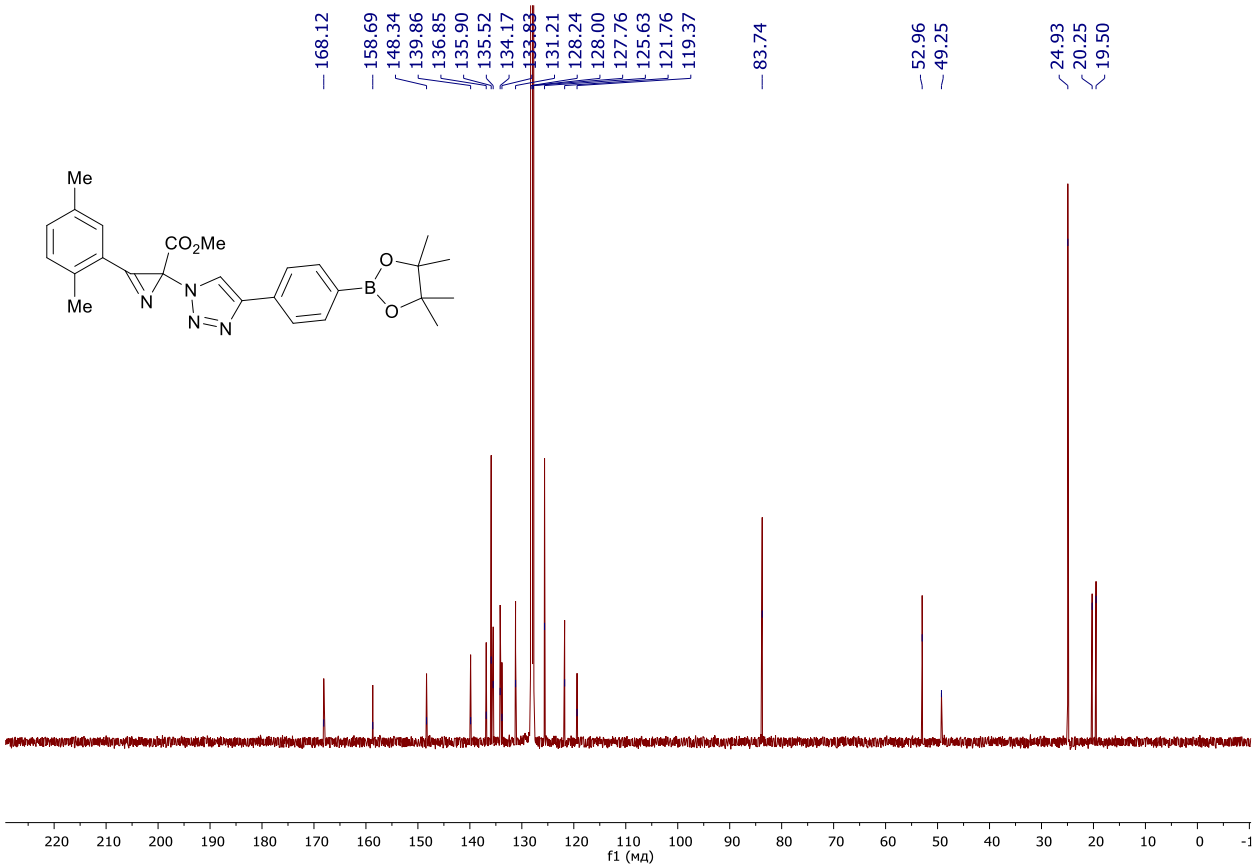

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3y**



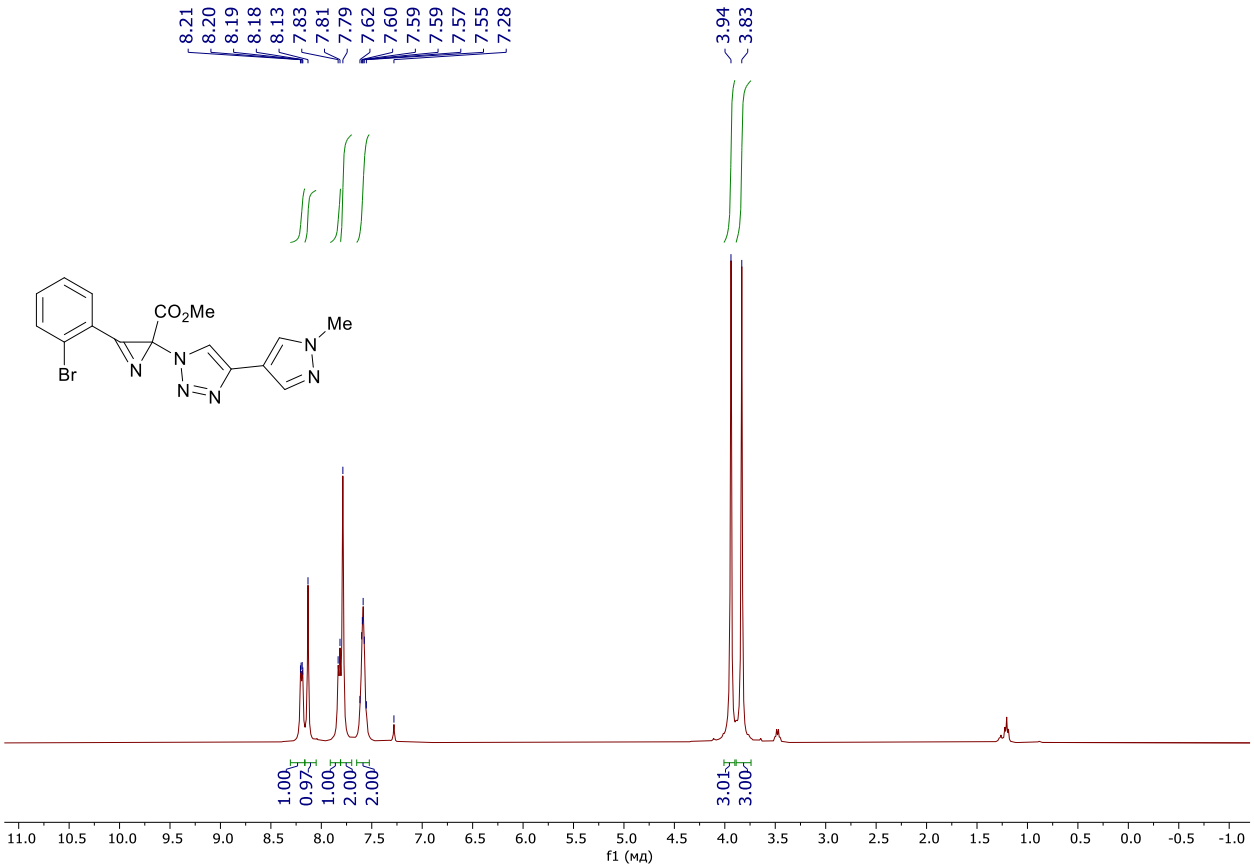
$^{1}$H NMR (400 MHz, $C_6D_6$) spectrum of compound **3z**



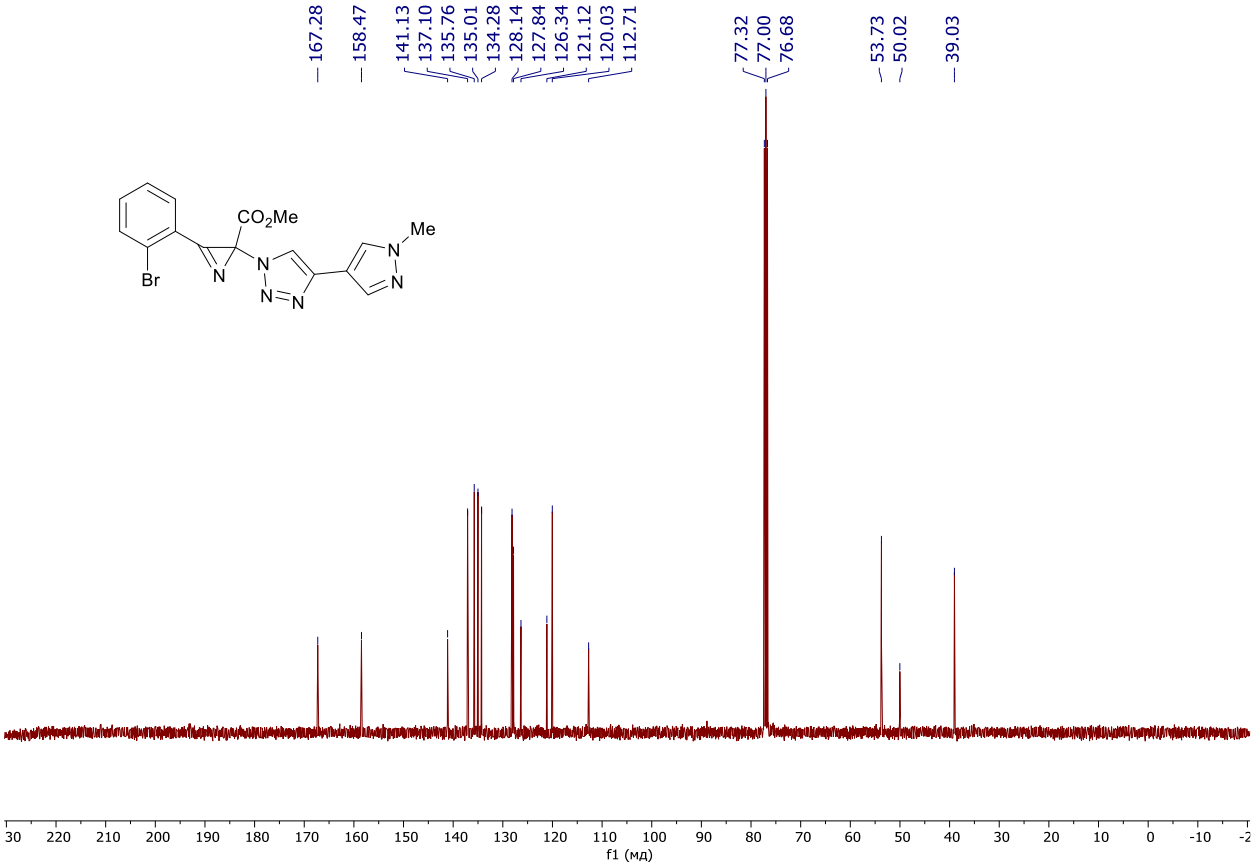

$^{13}$C{$^{1}$H} NMR (100 MHz, $C_6D_6$) spectrum of compound **3z**



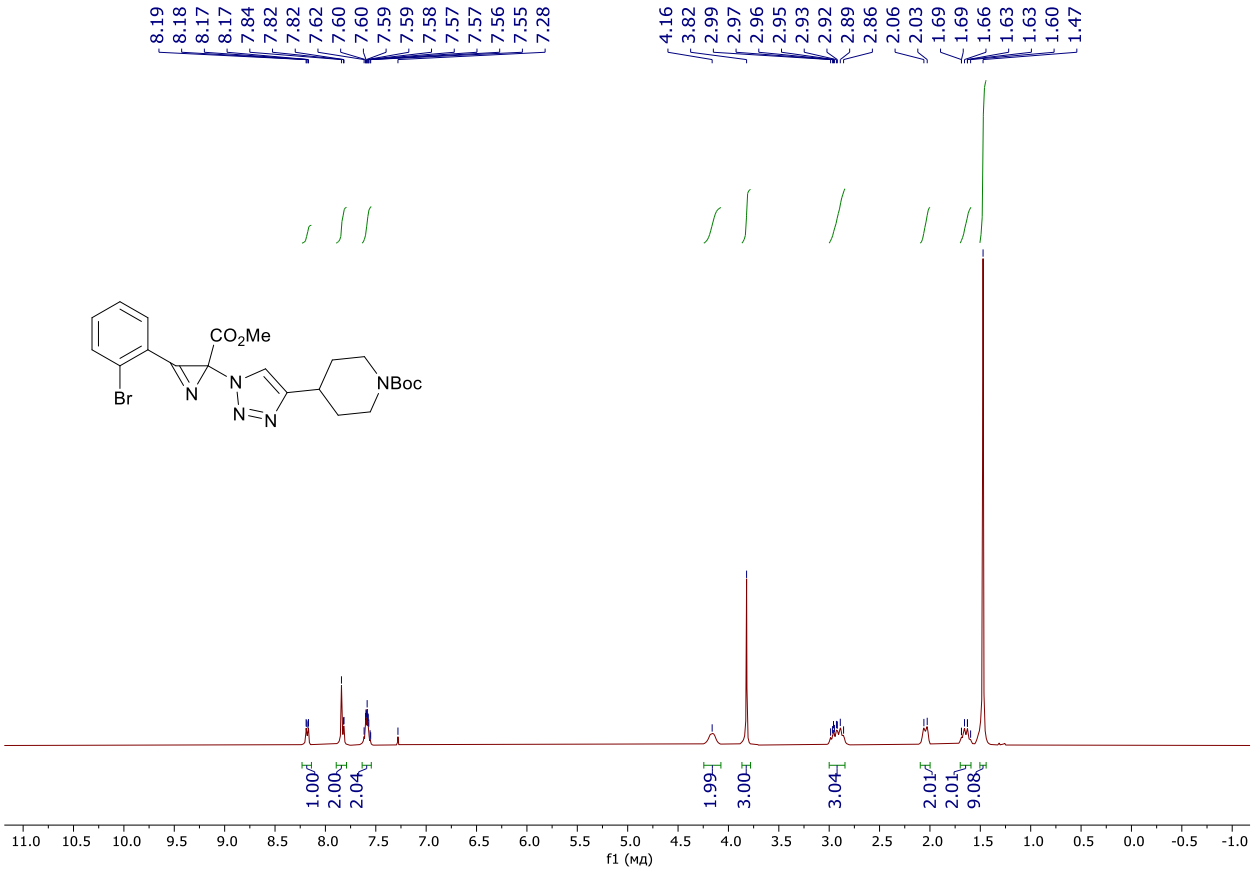
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3za**



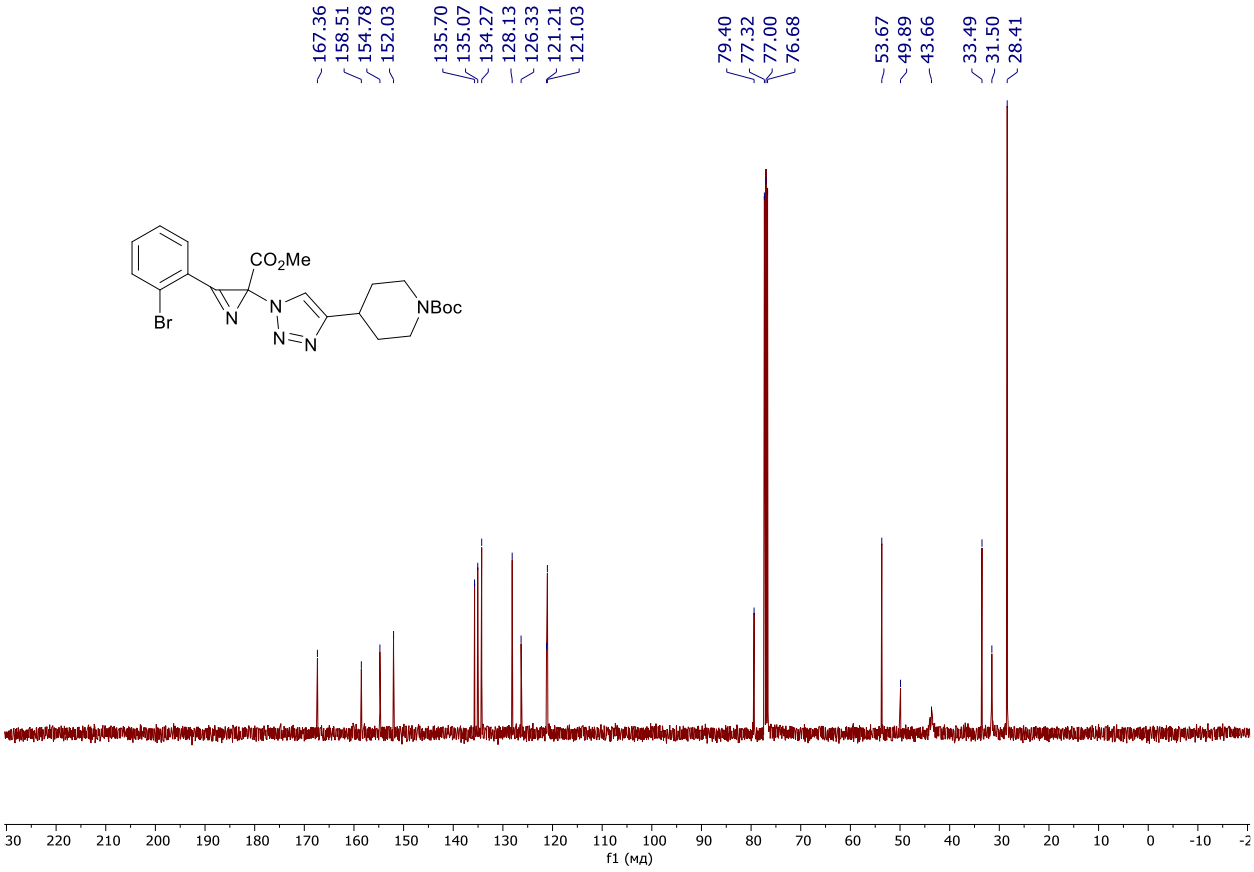

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3za**



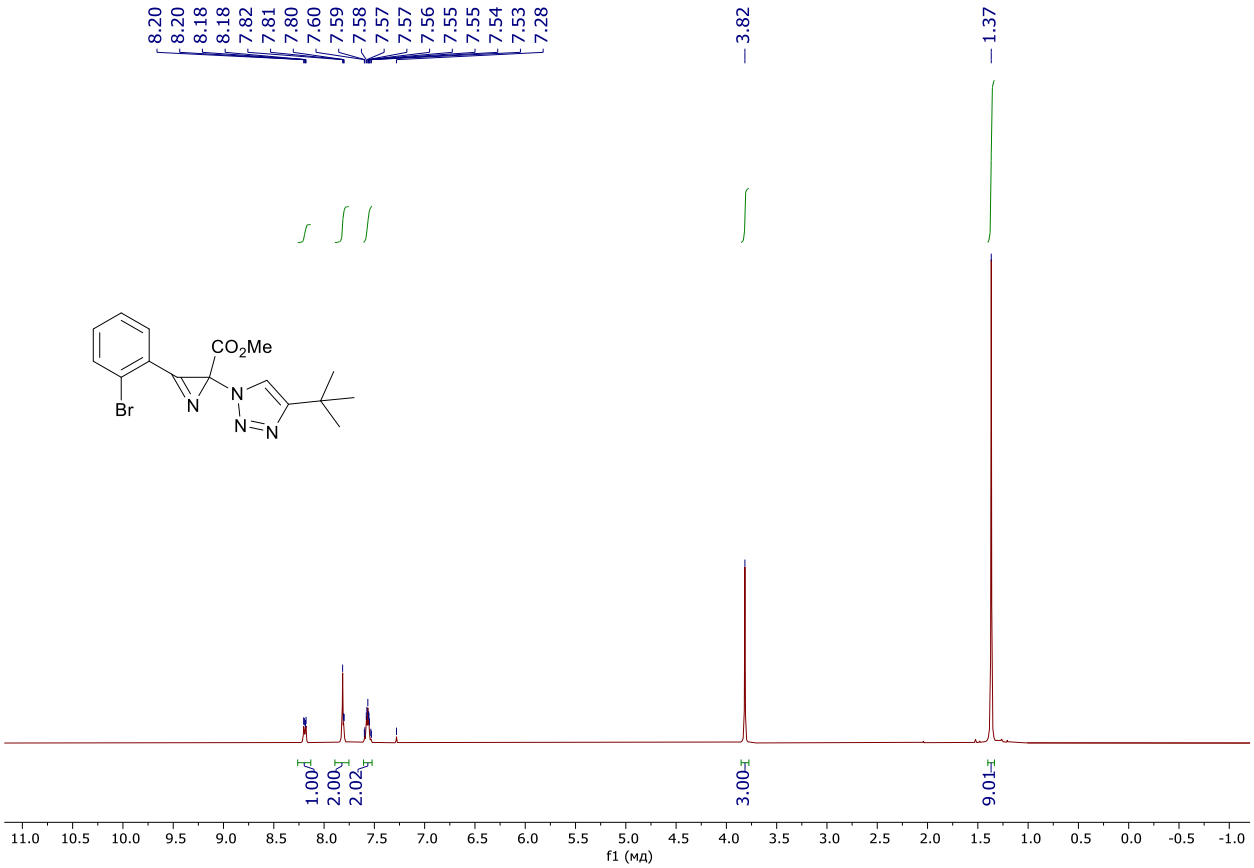
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3zb**



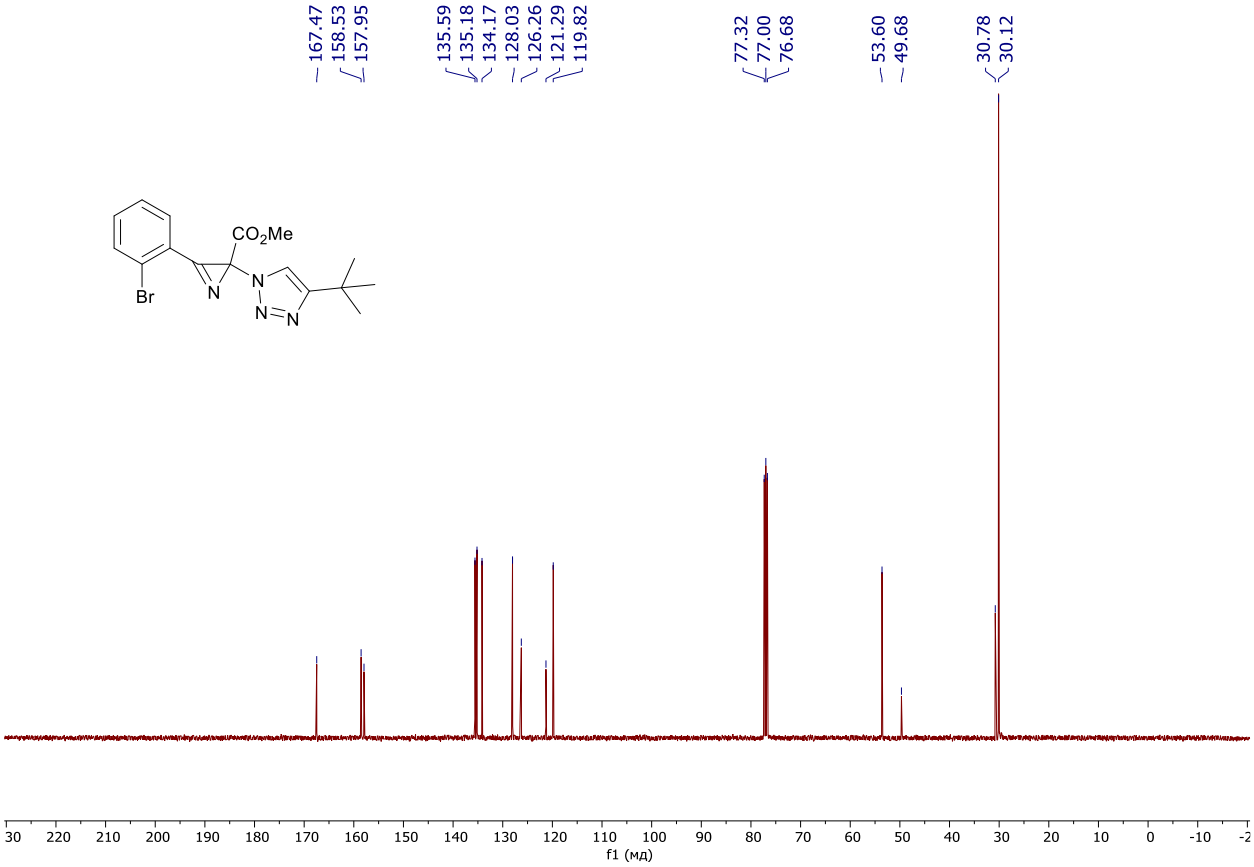

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3zb**



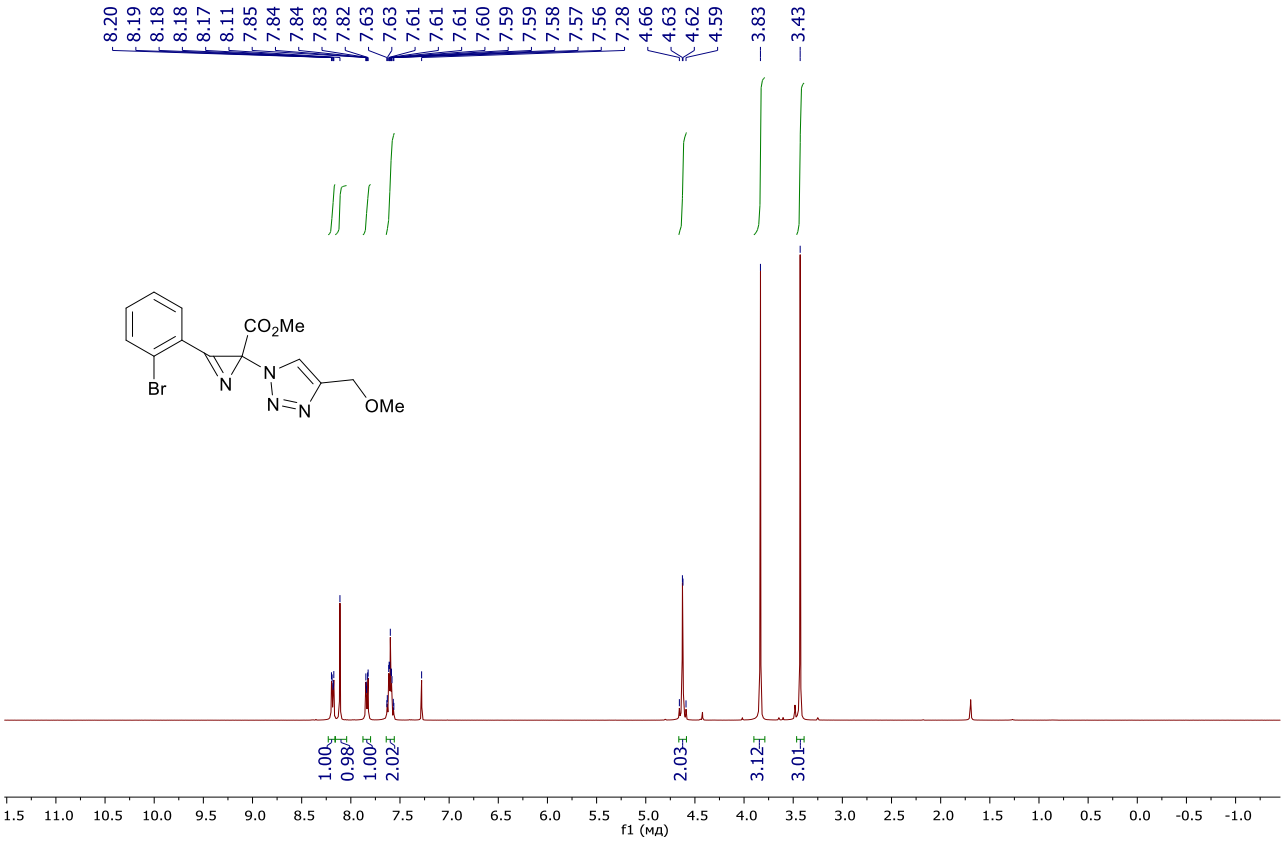
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3zc**



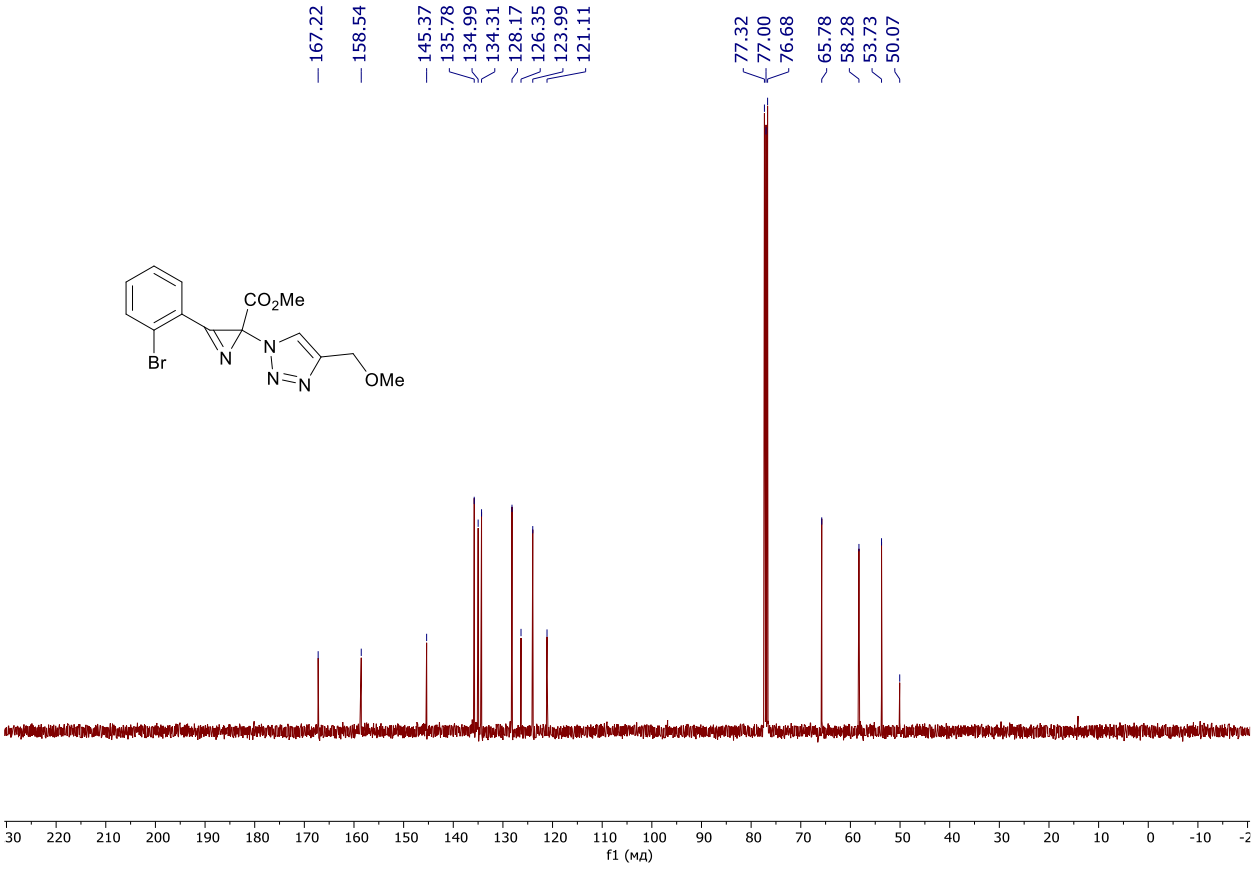

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3zc**



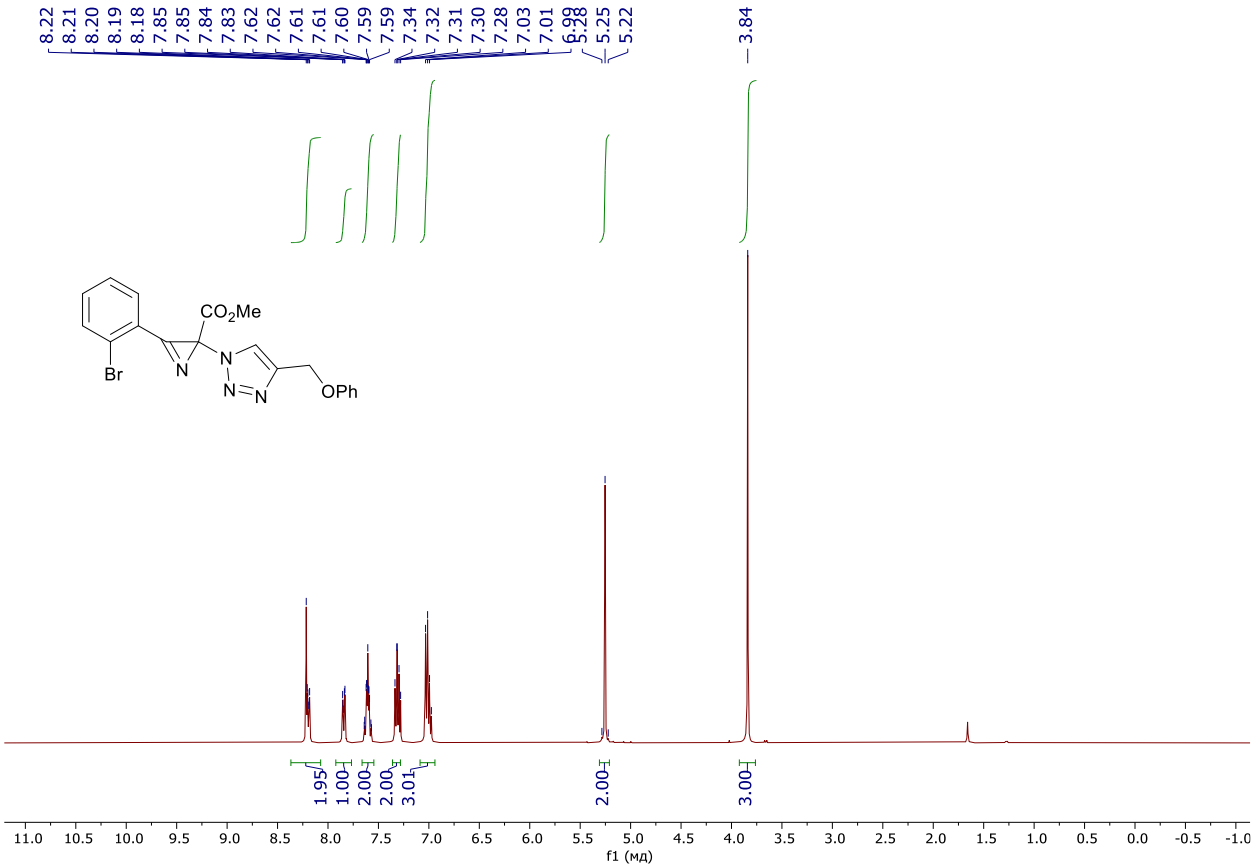
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3zd**



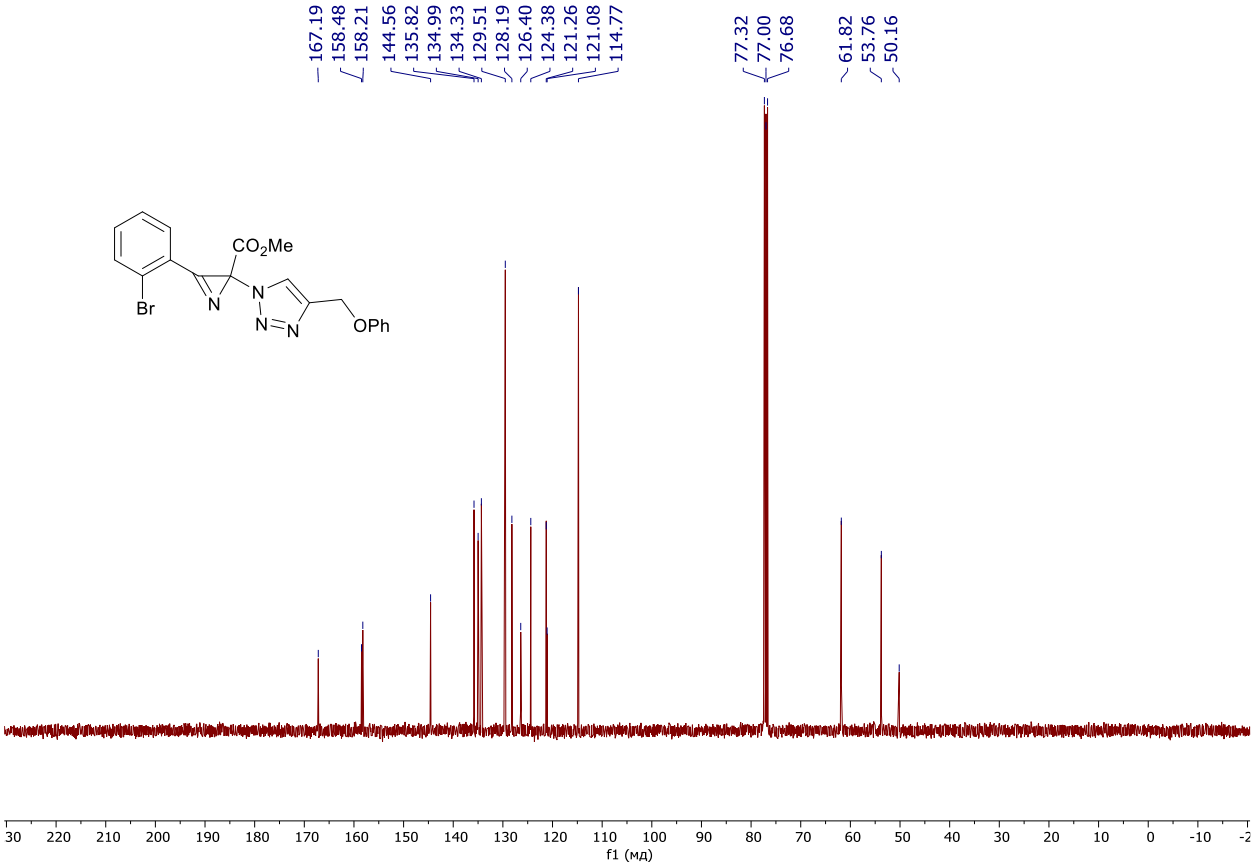

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3zd**



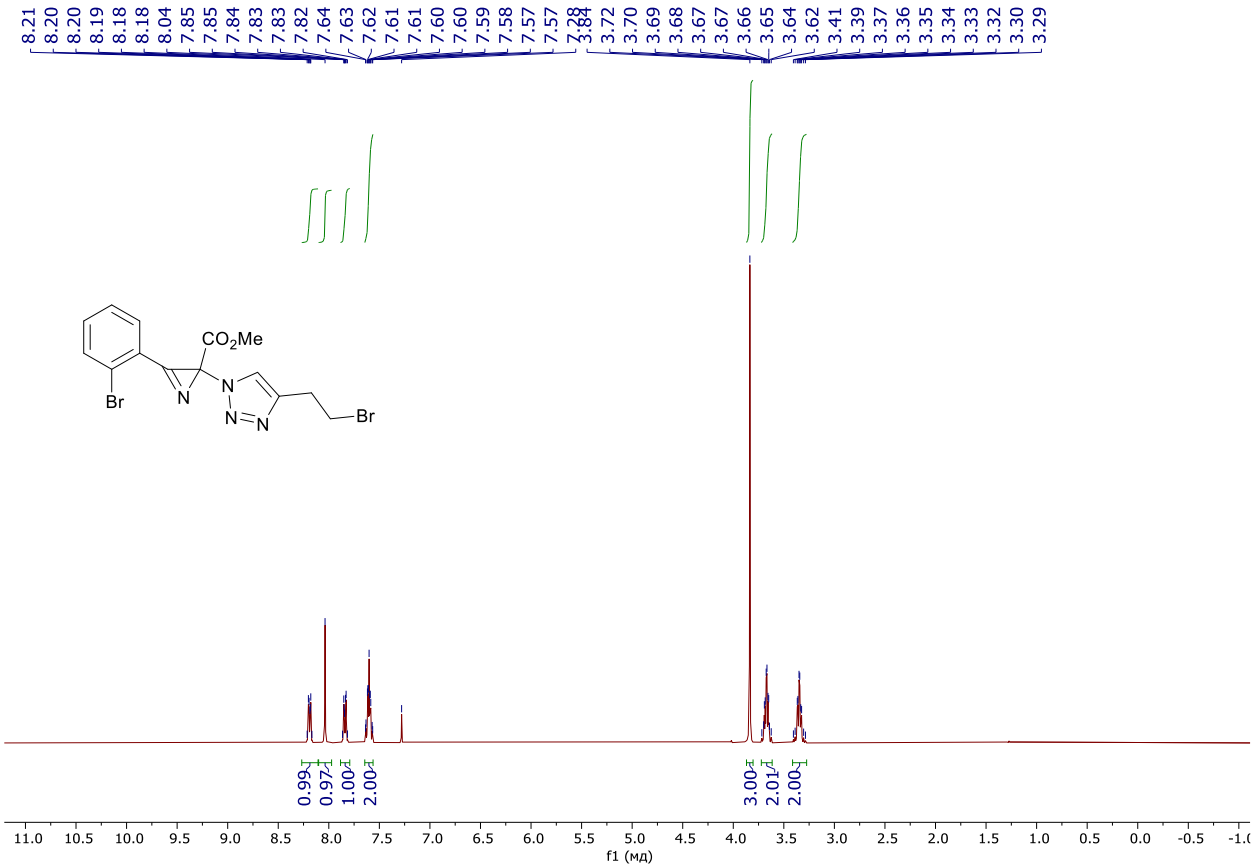
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ze**



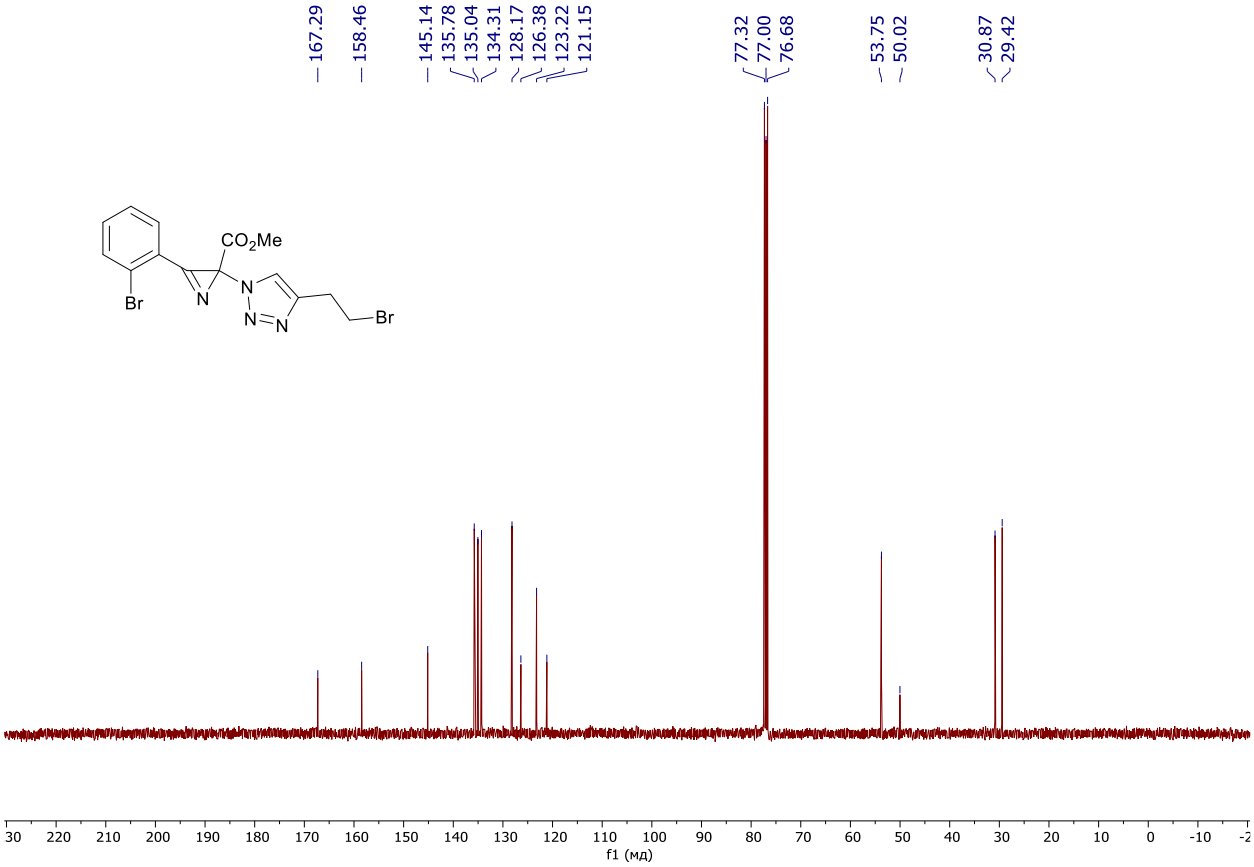

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3ze**



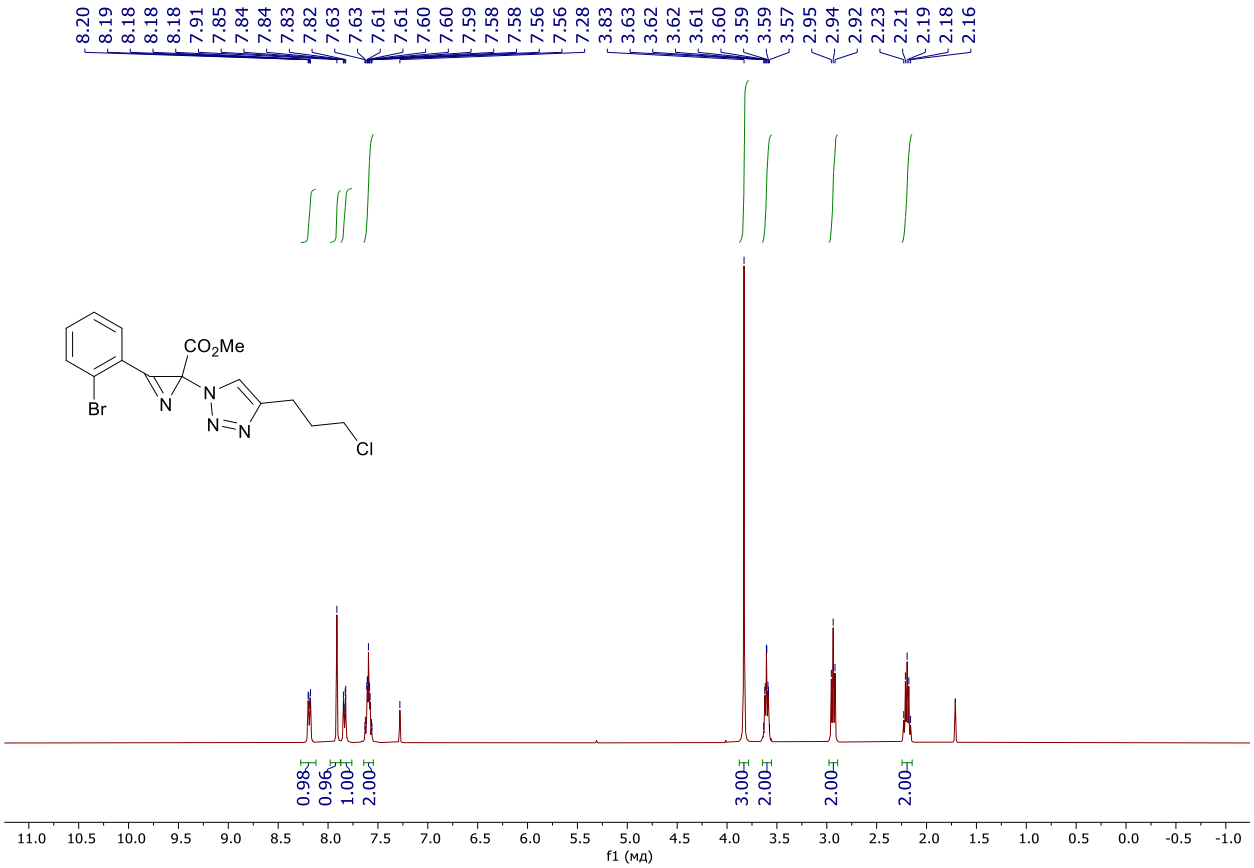
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3zf**



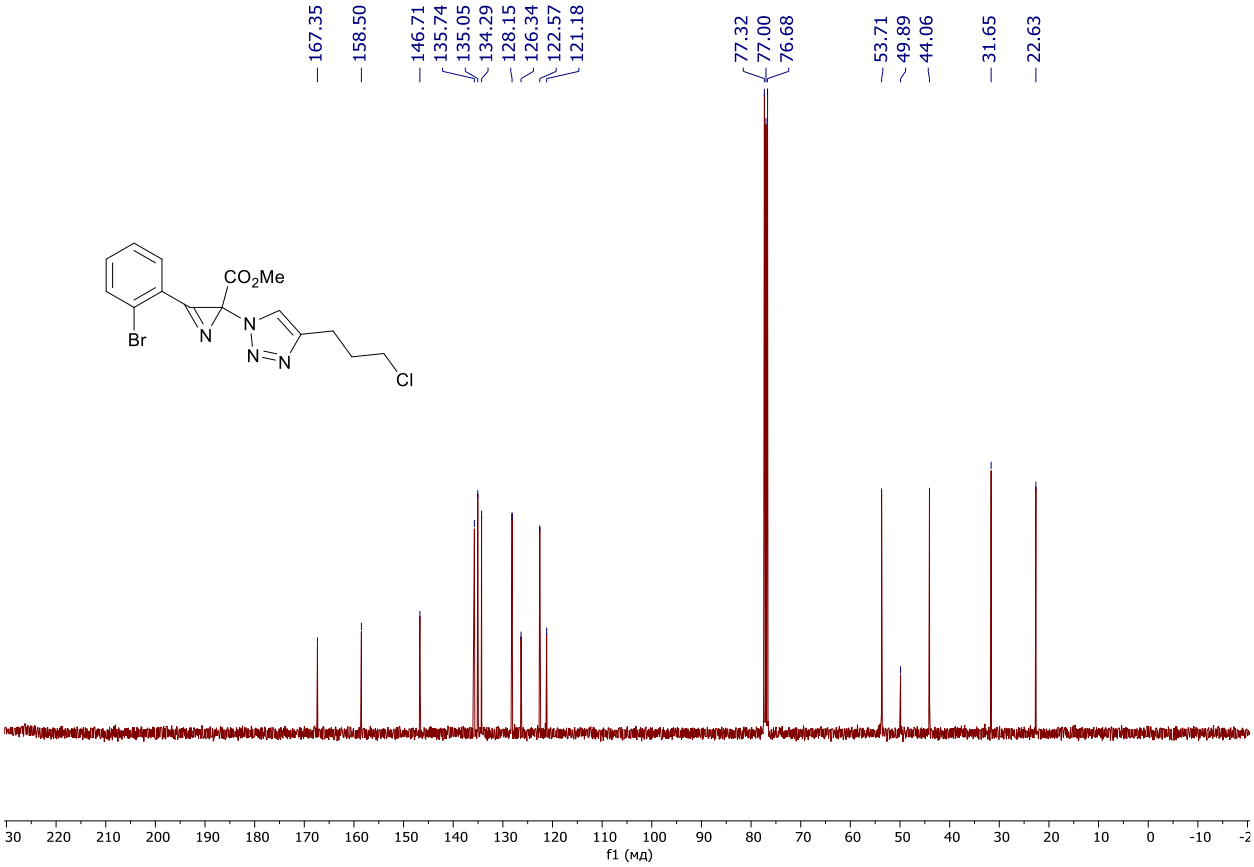

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3zf**



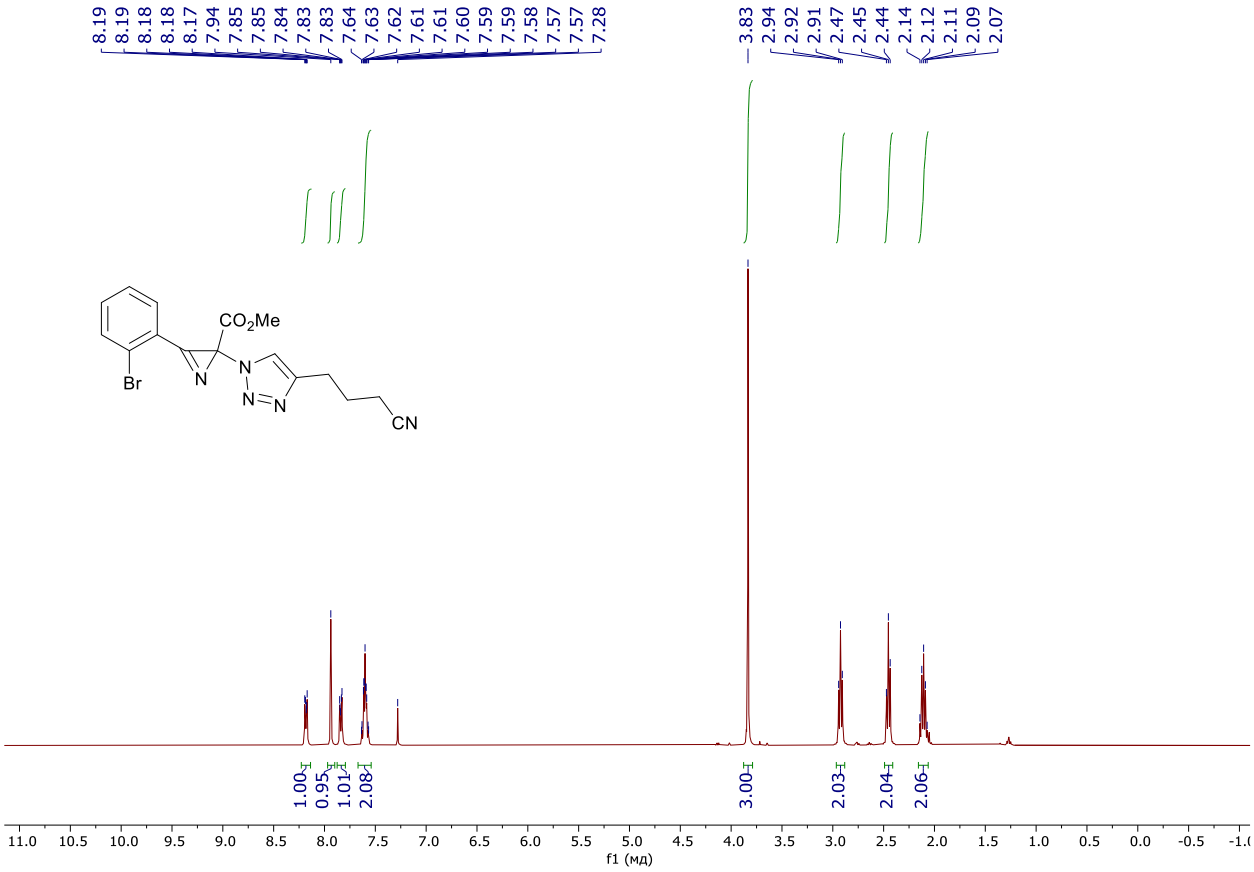
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3zg**



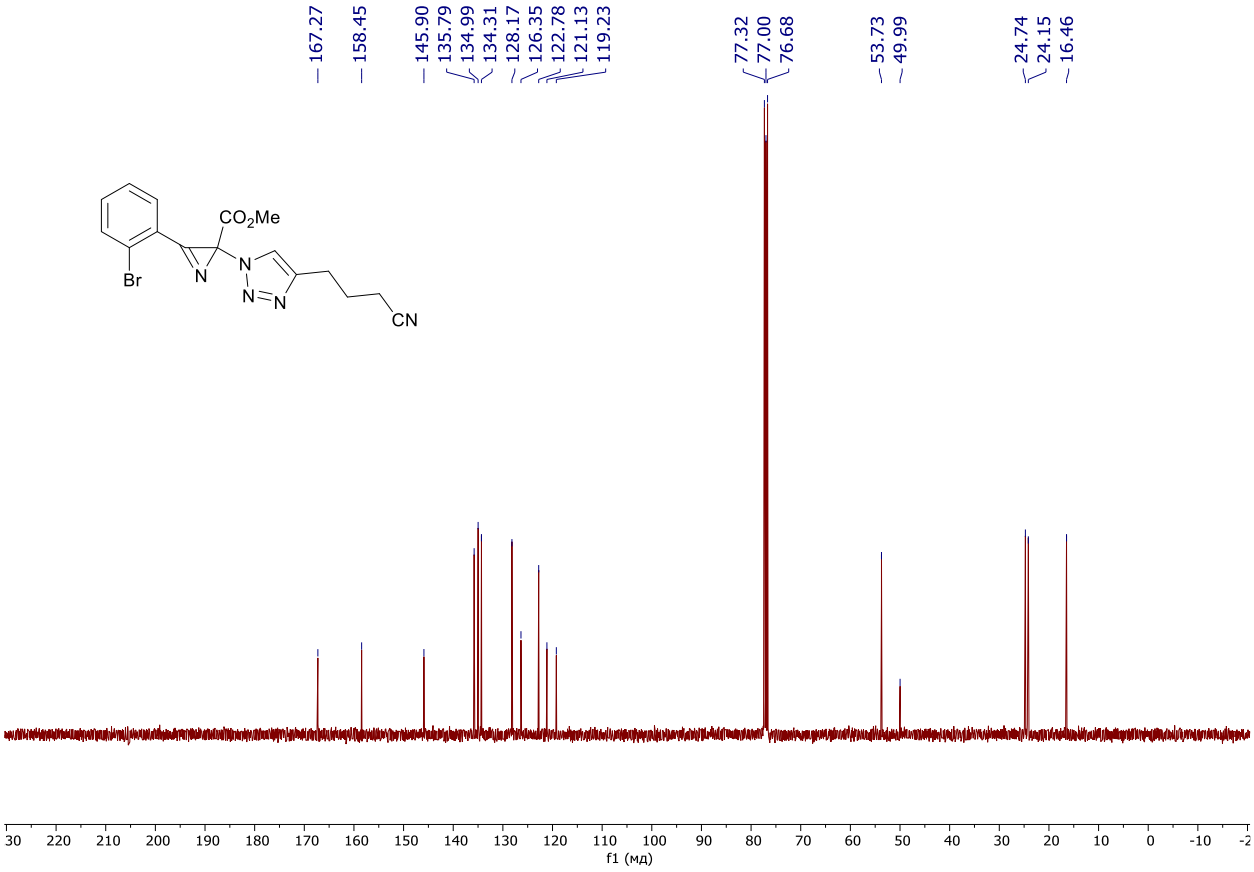

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3zg**



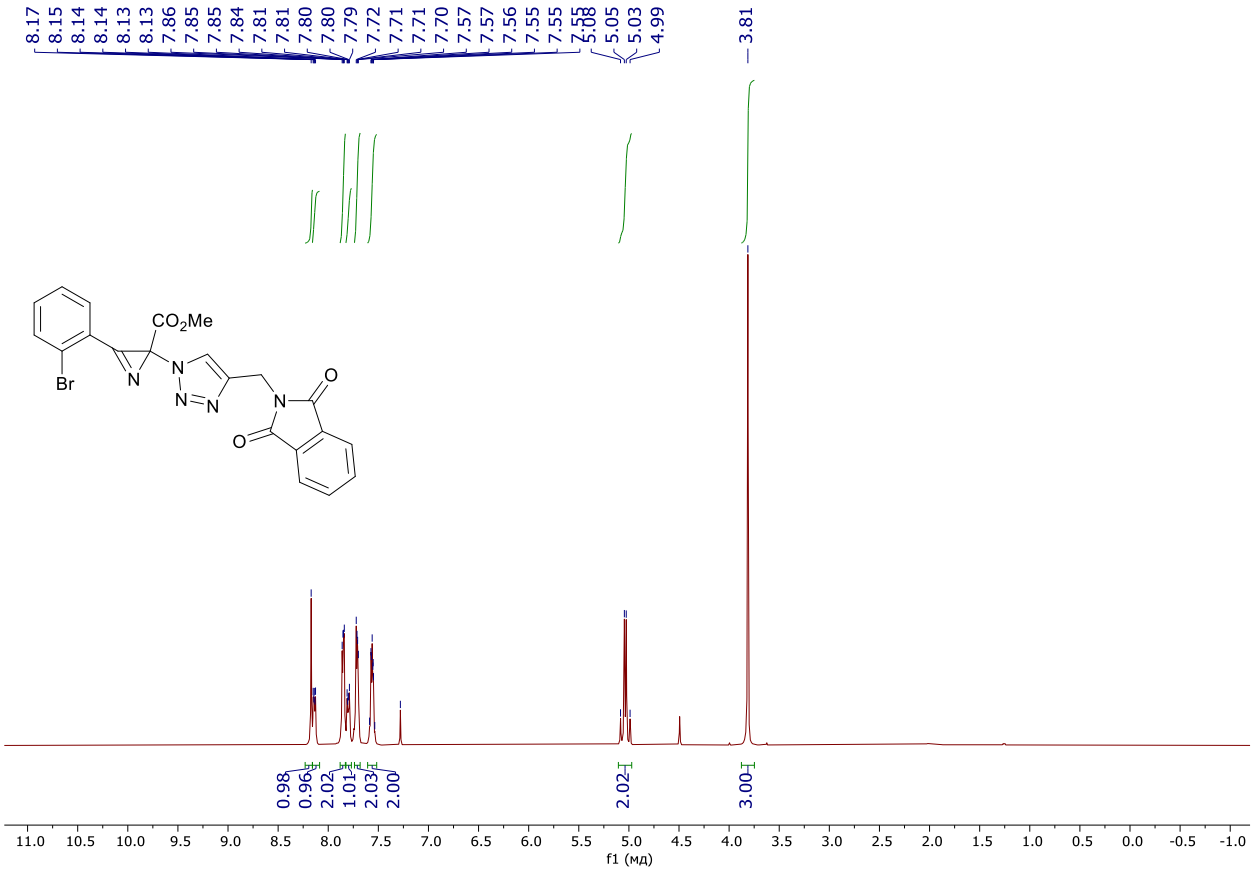
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3zh**



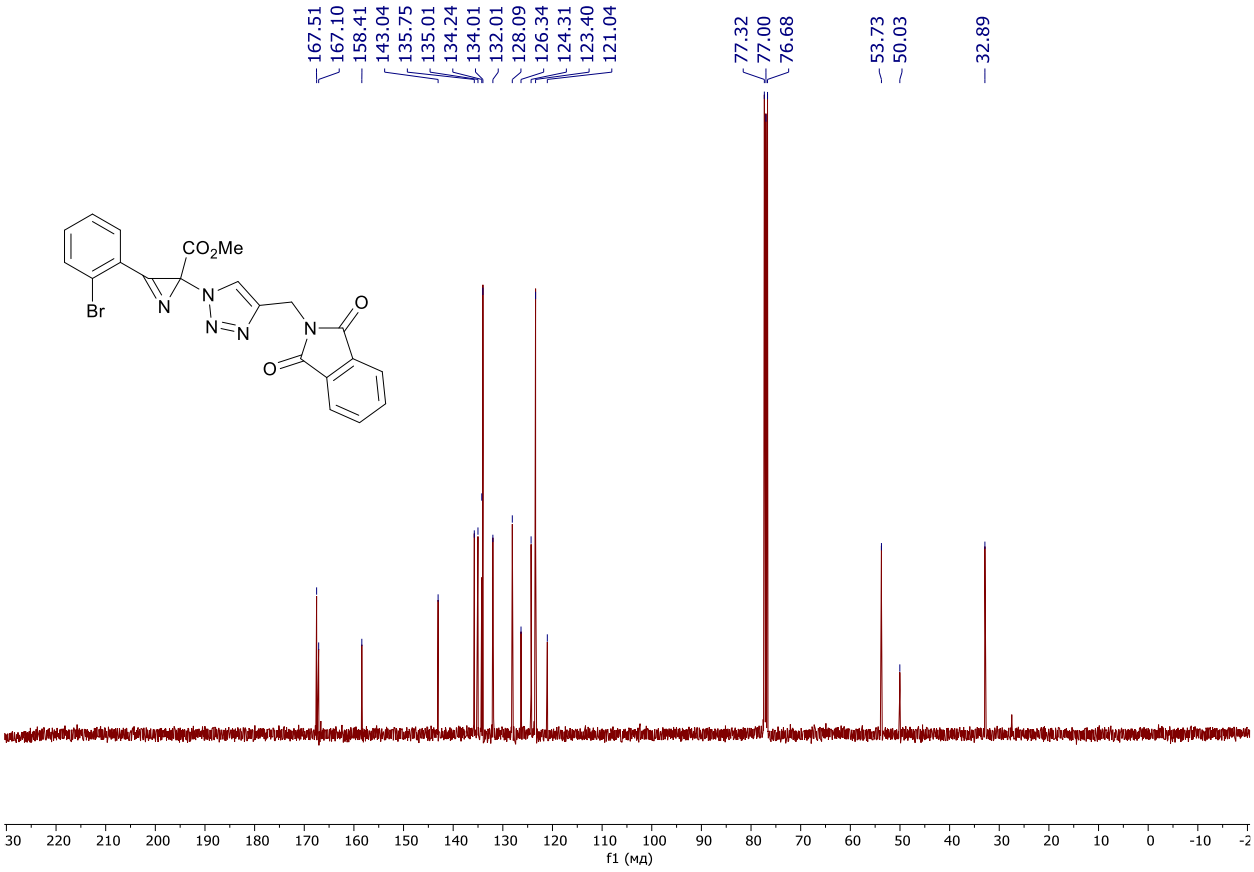

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3zh**



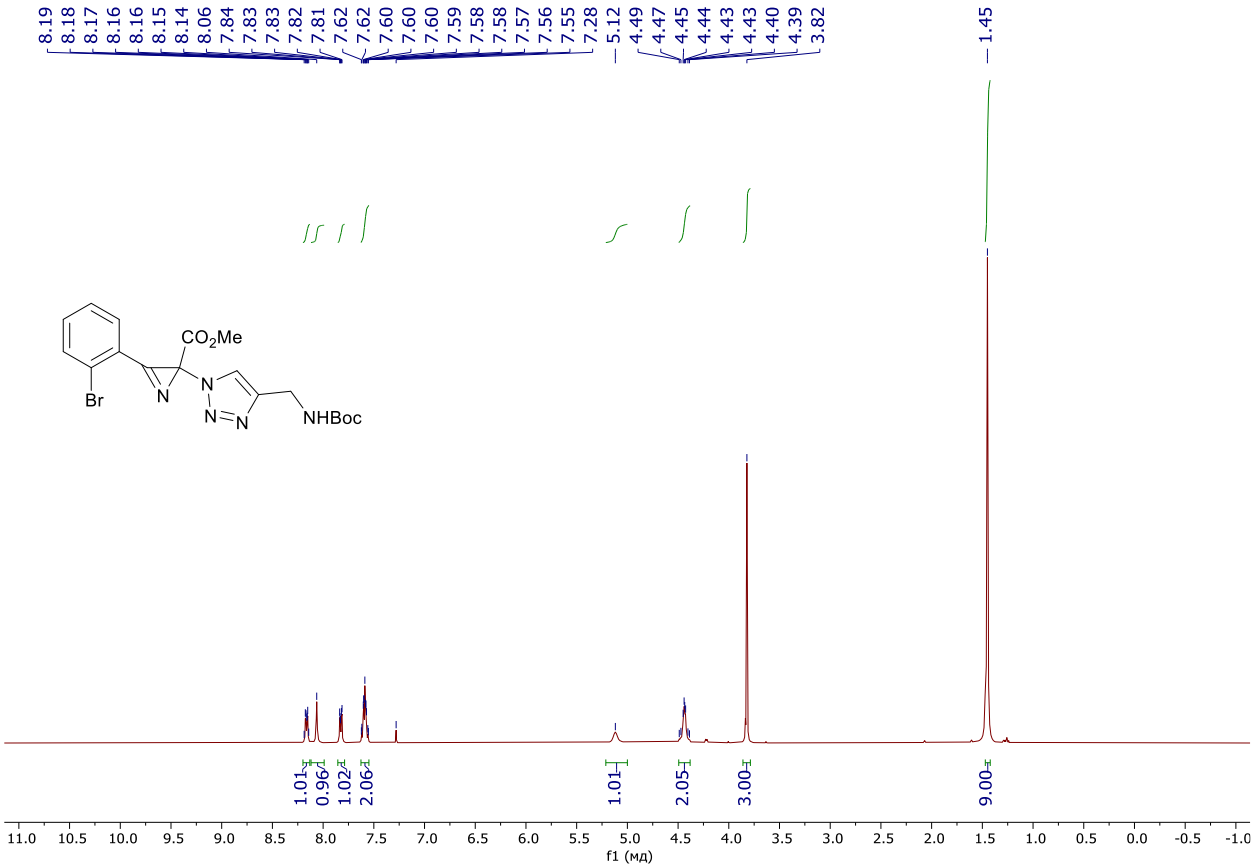
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3zi**



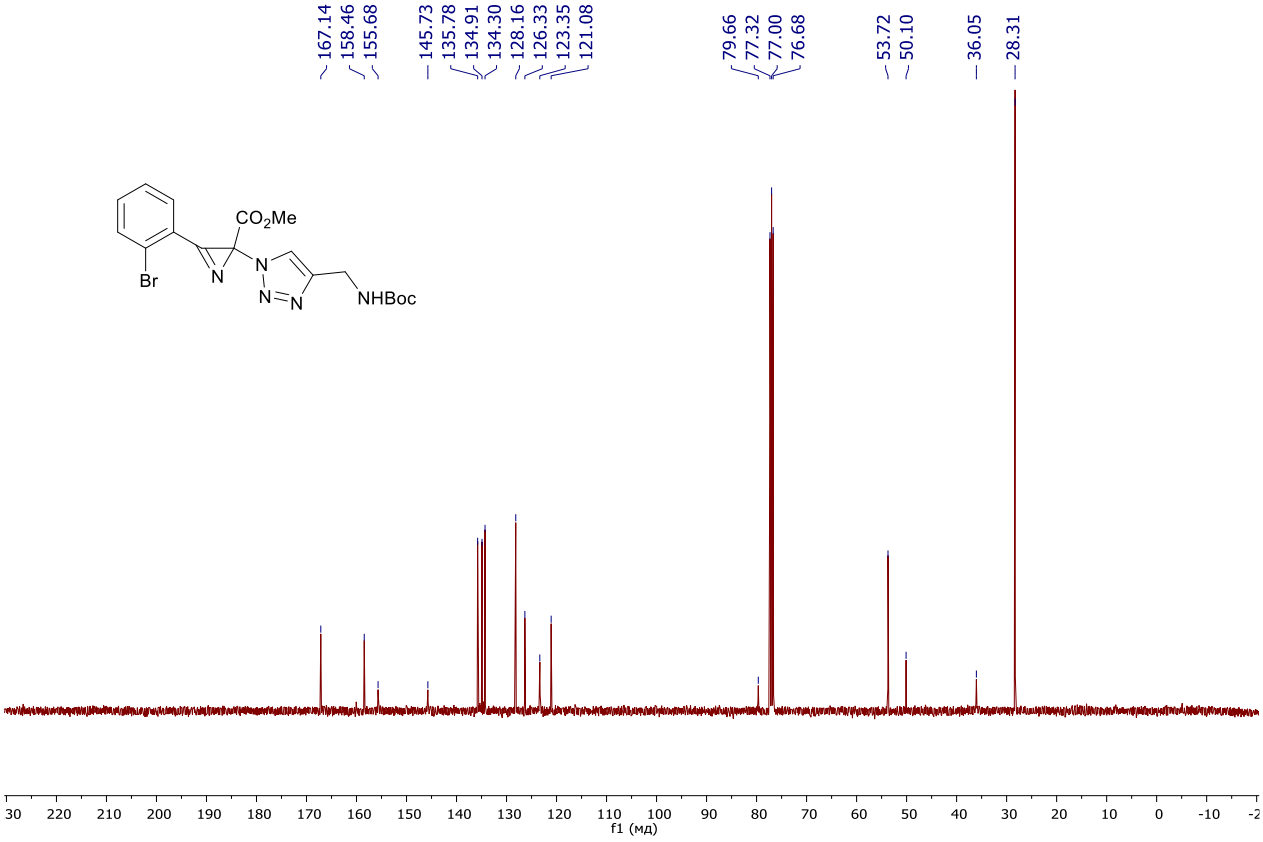

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3zi**



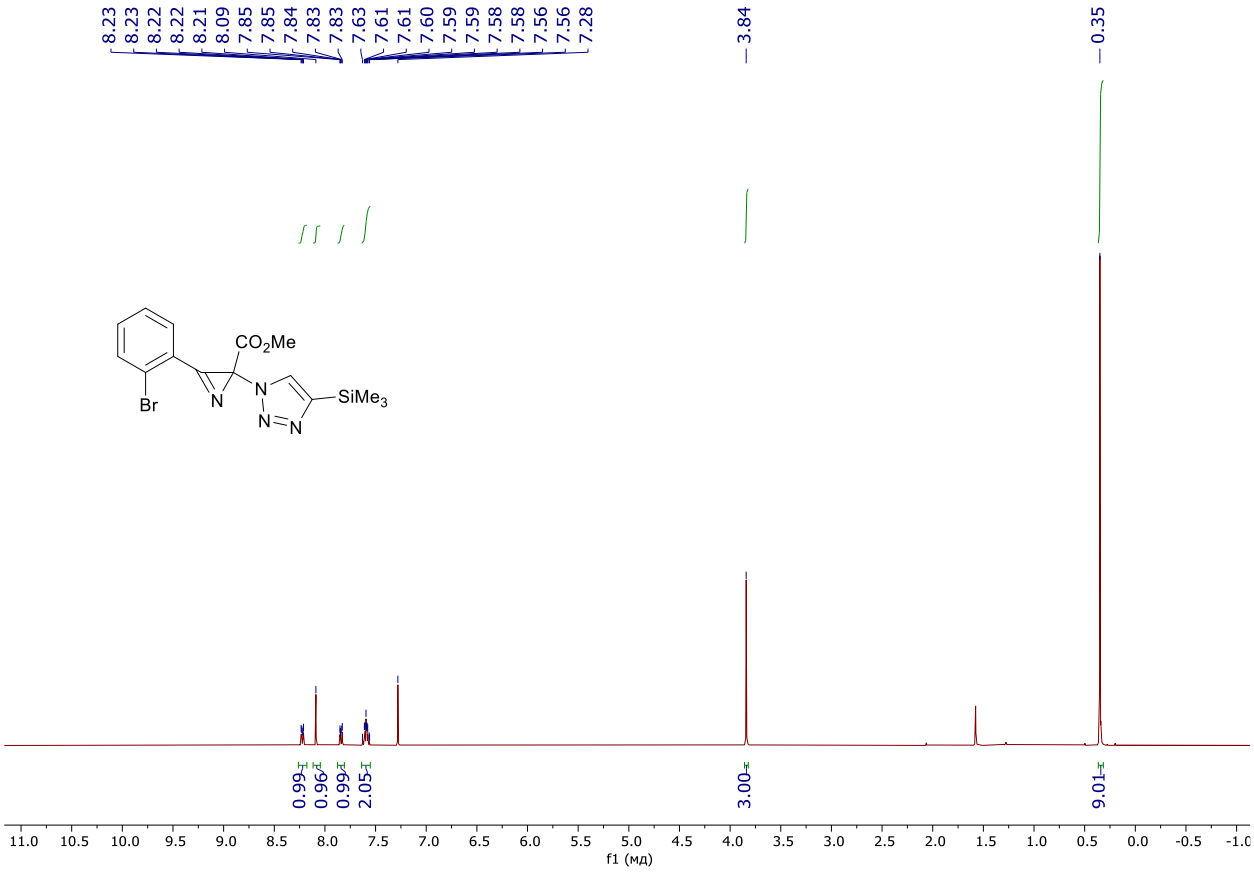
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3zj**



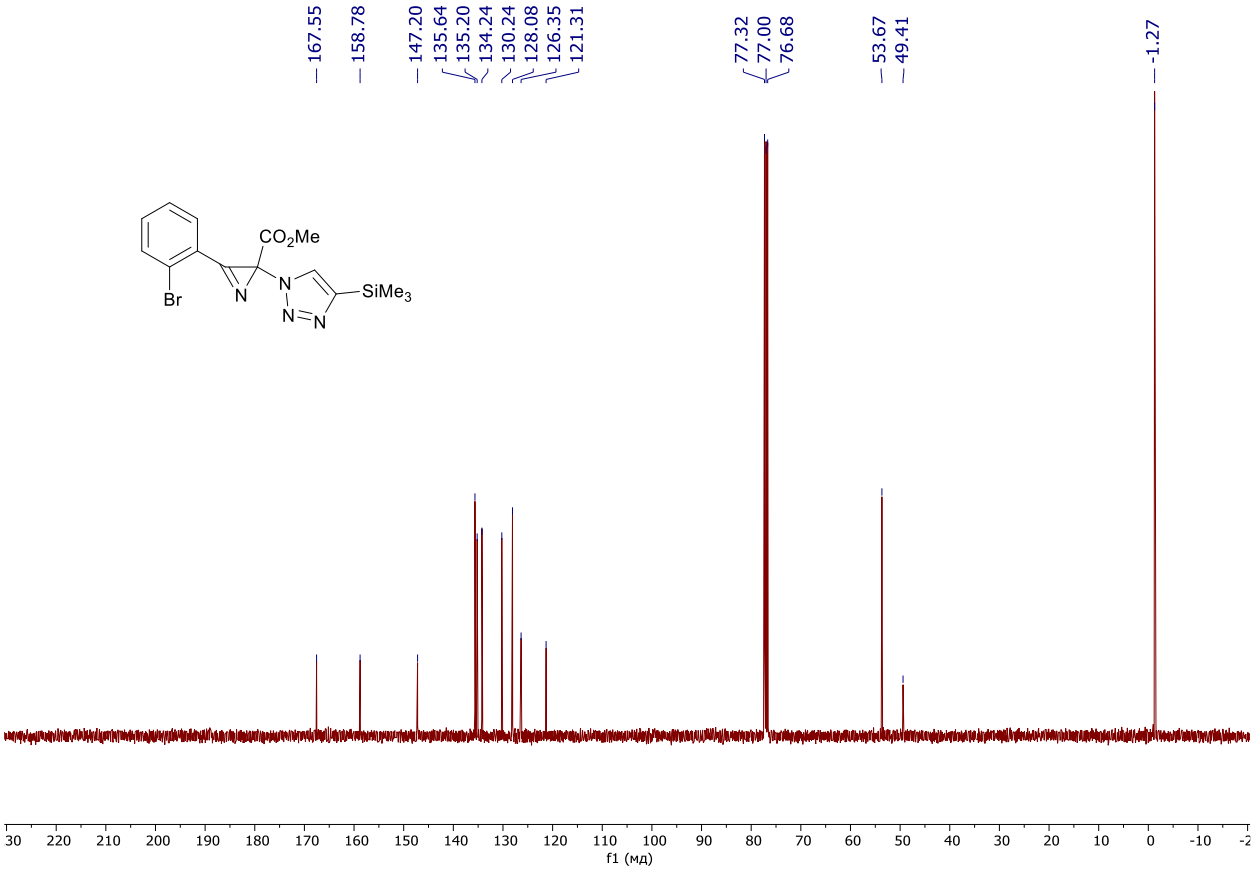

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3zj**



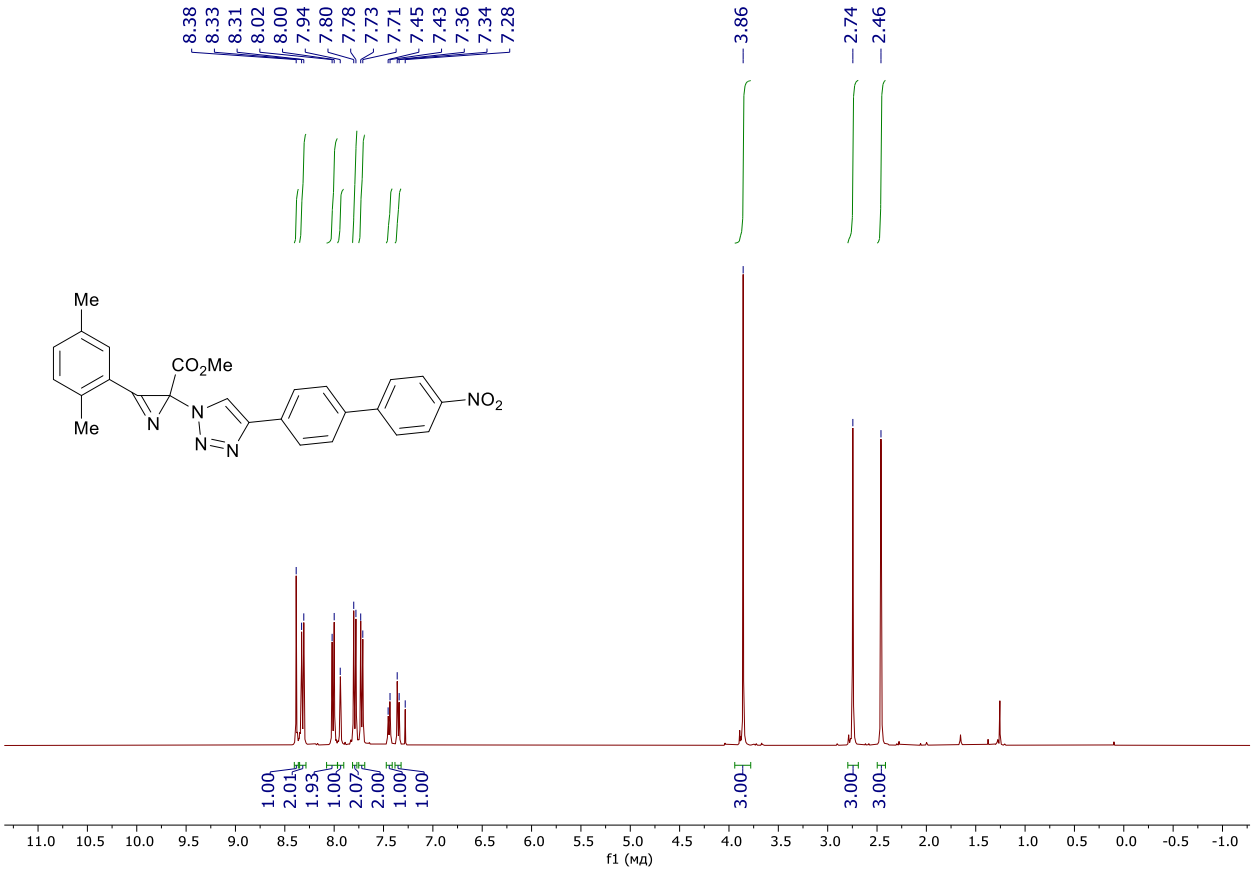
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **3zk**



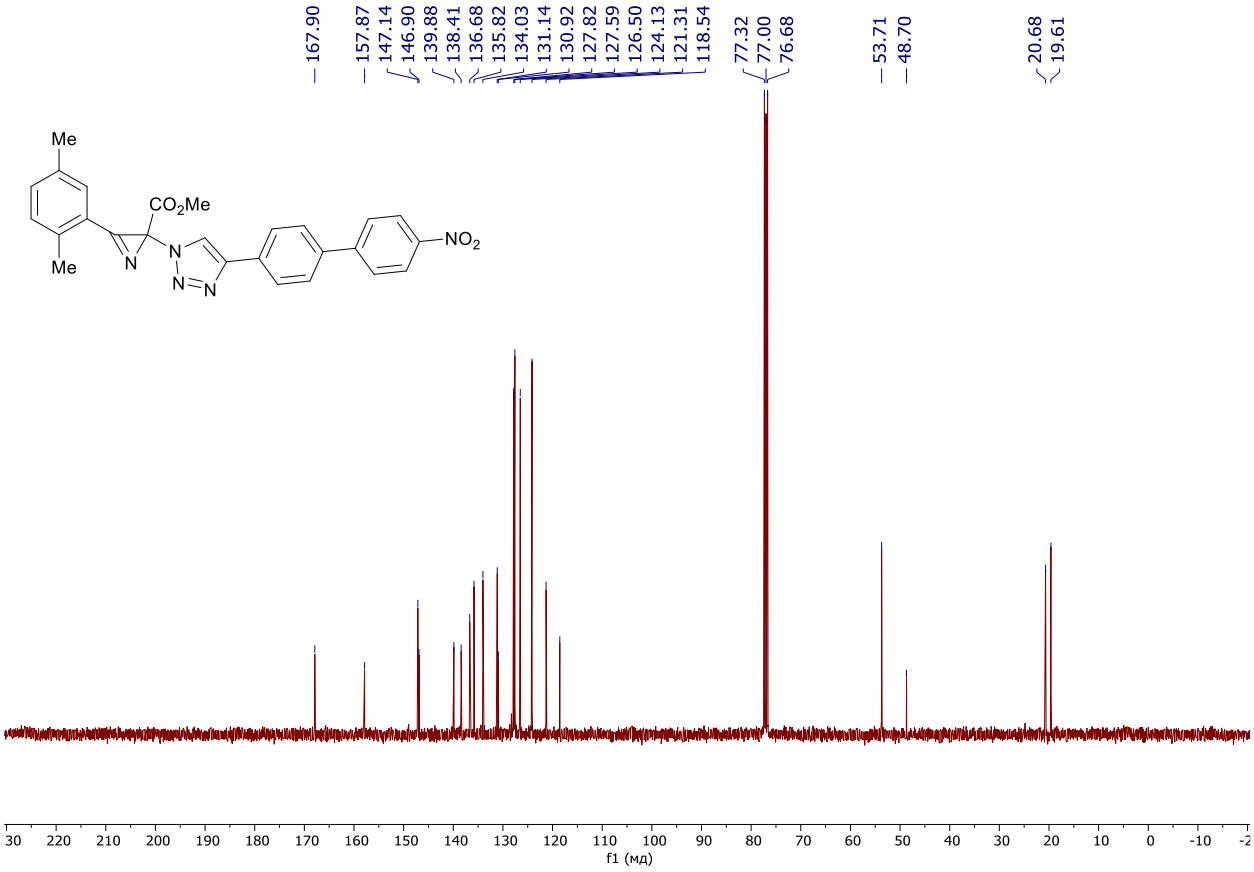

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3zk**



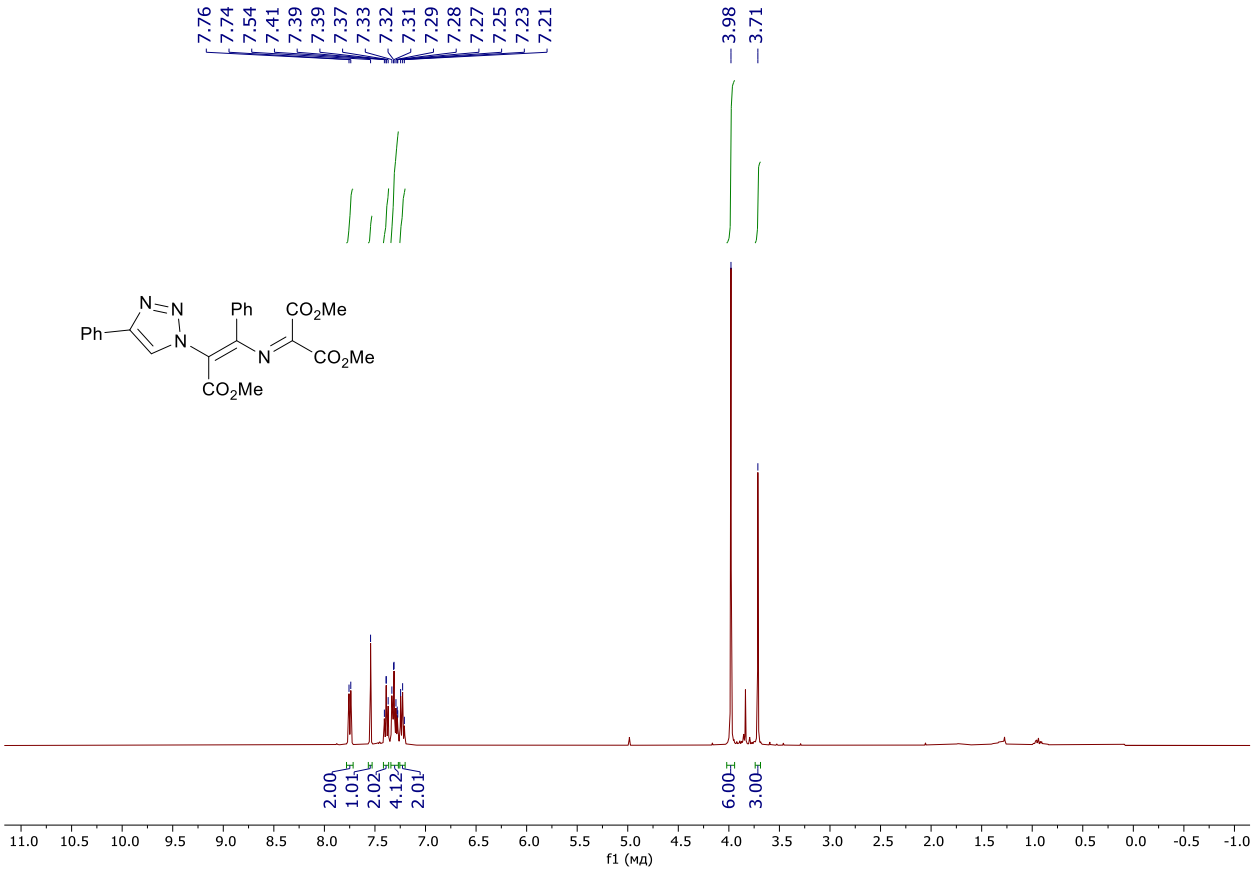
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **8**



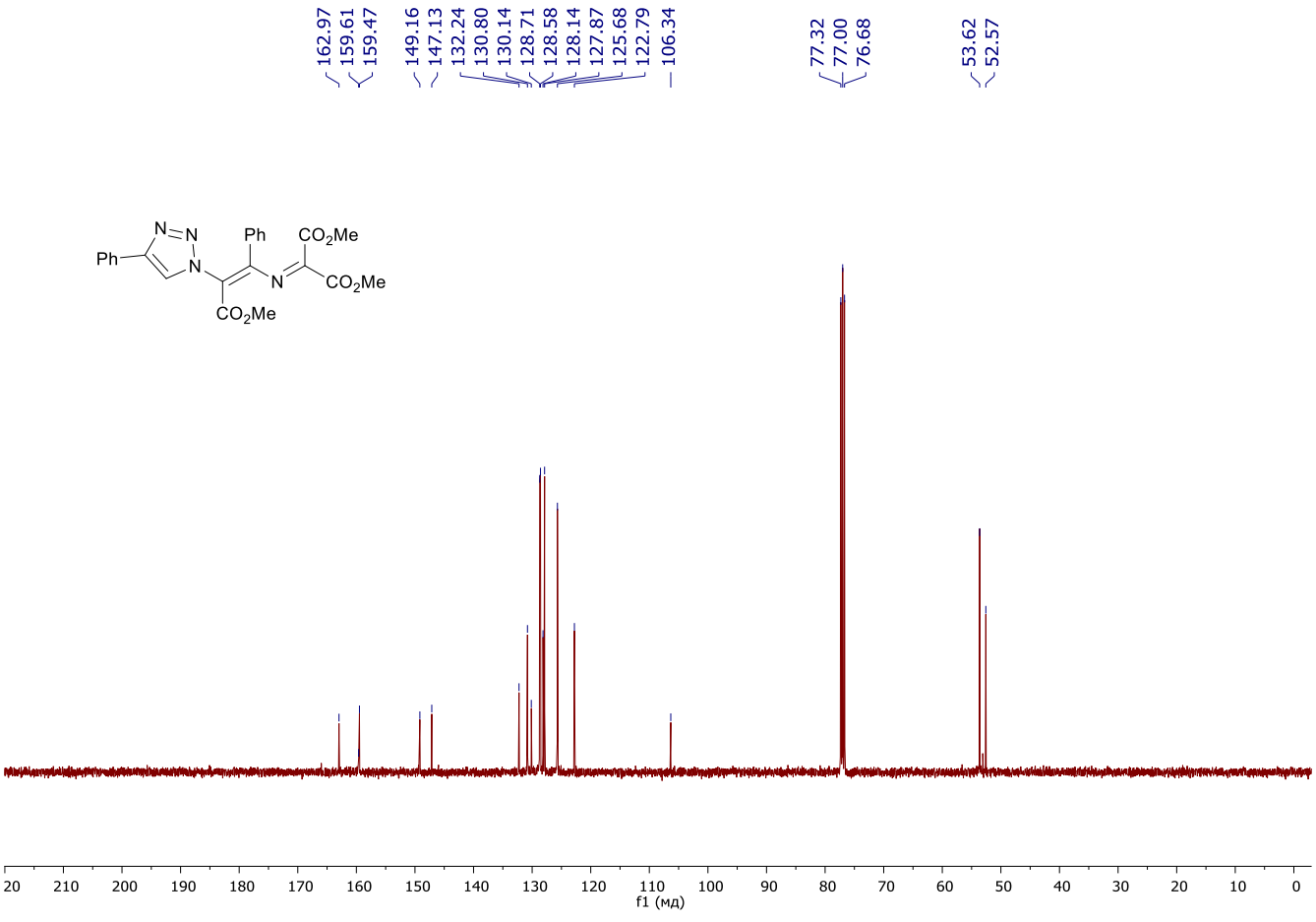

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **8**



$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **9**




$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of compound **9**



# 14. Study of the formation of 2a (method *B*) using $^{1}$H NMR