Supporting Information

Vinylogous Reactivity of Enoldiazoacetates with Donor-Acceptor Substituted Hydrazones. Synthesis of Substituted Pyrazole Derivatives

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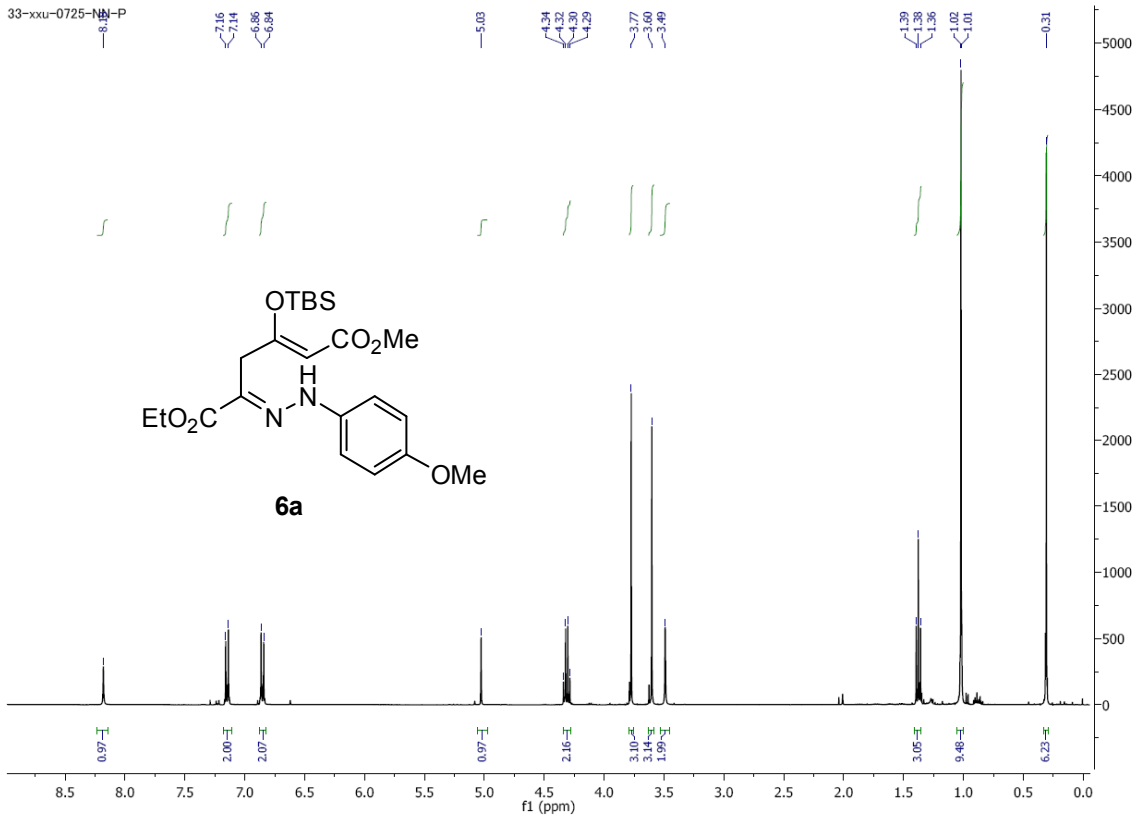
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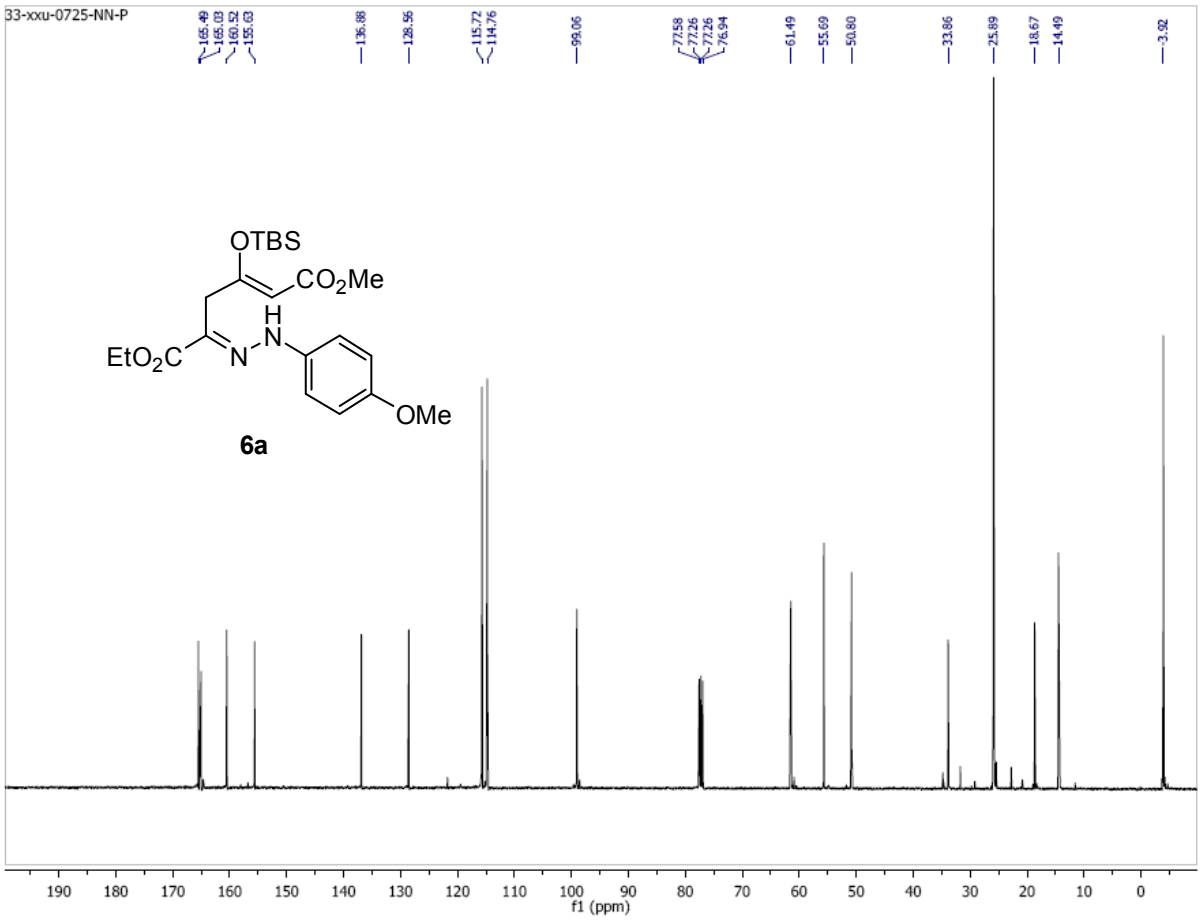
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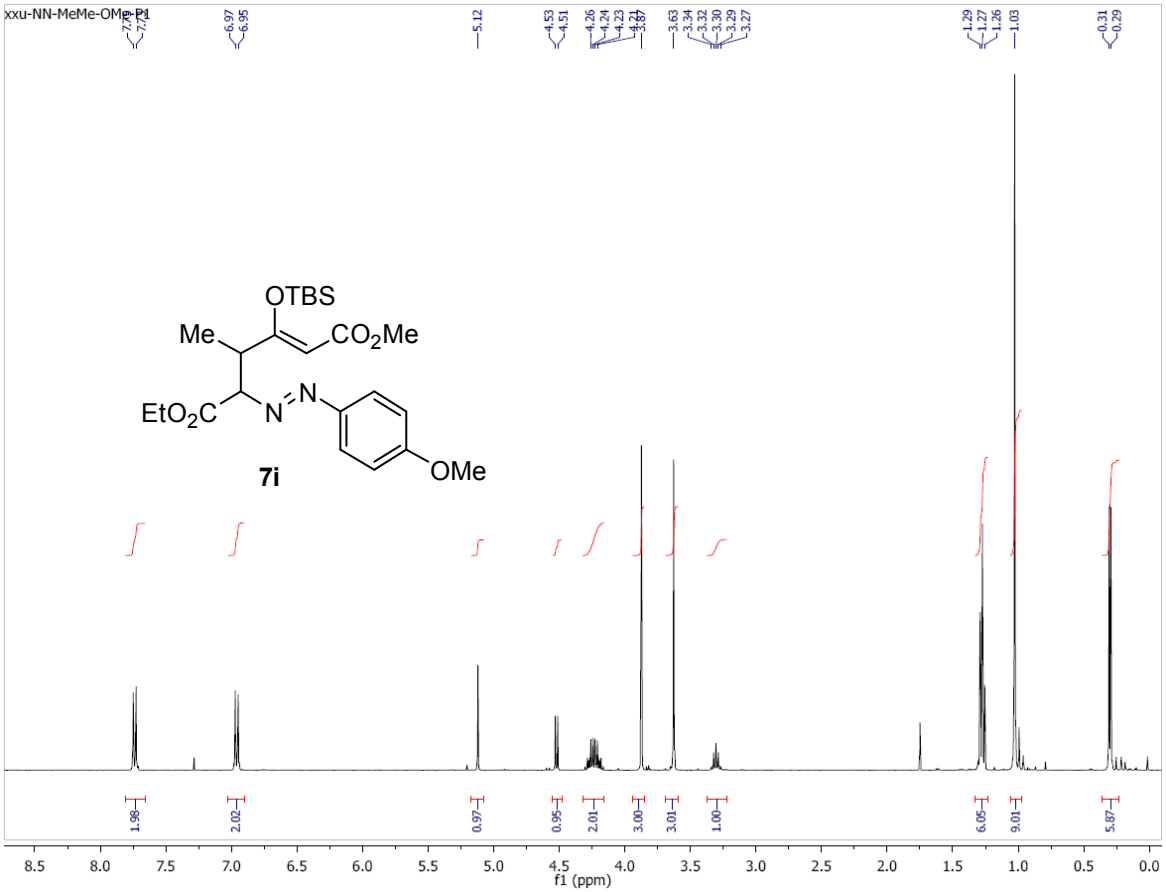
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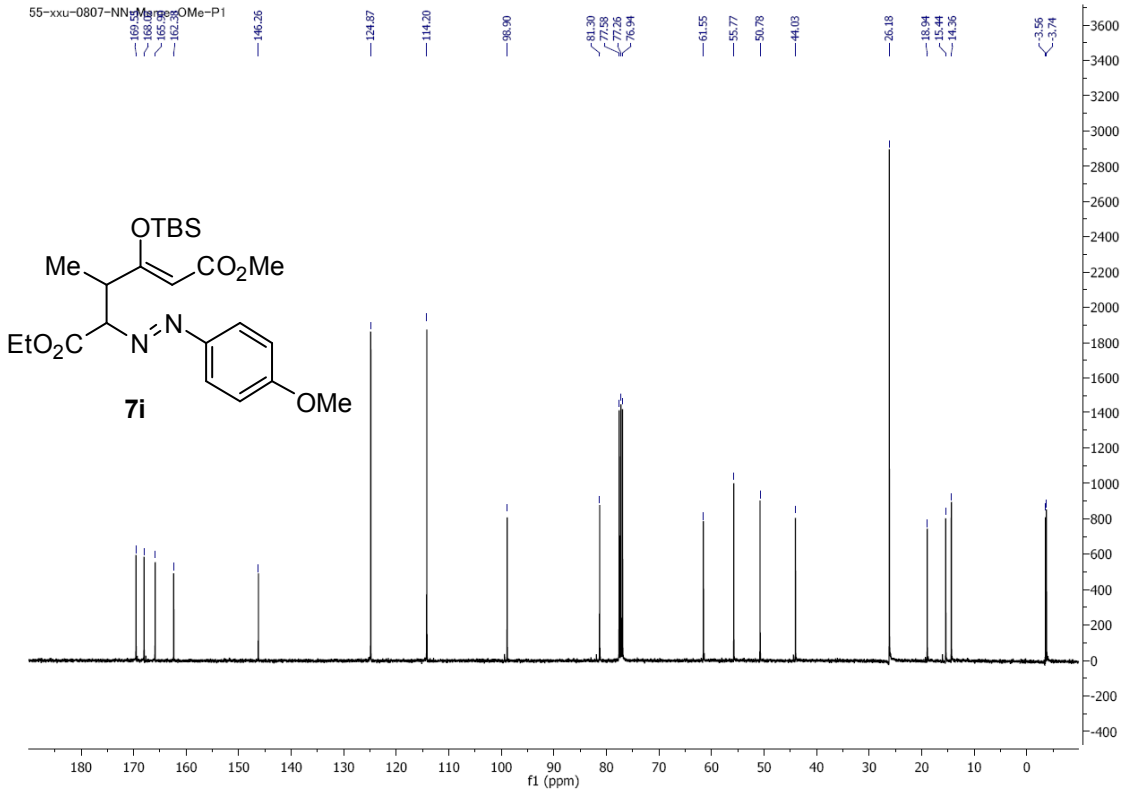
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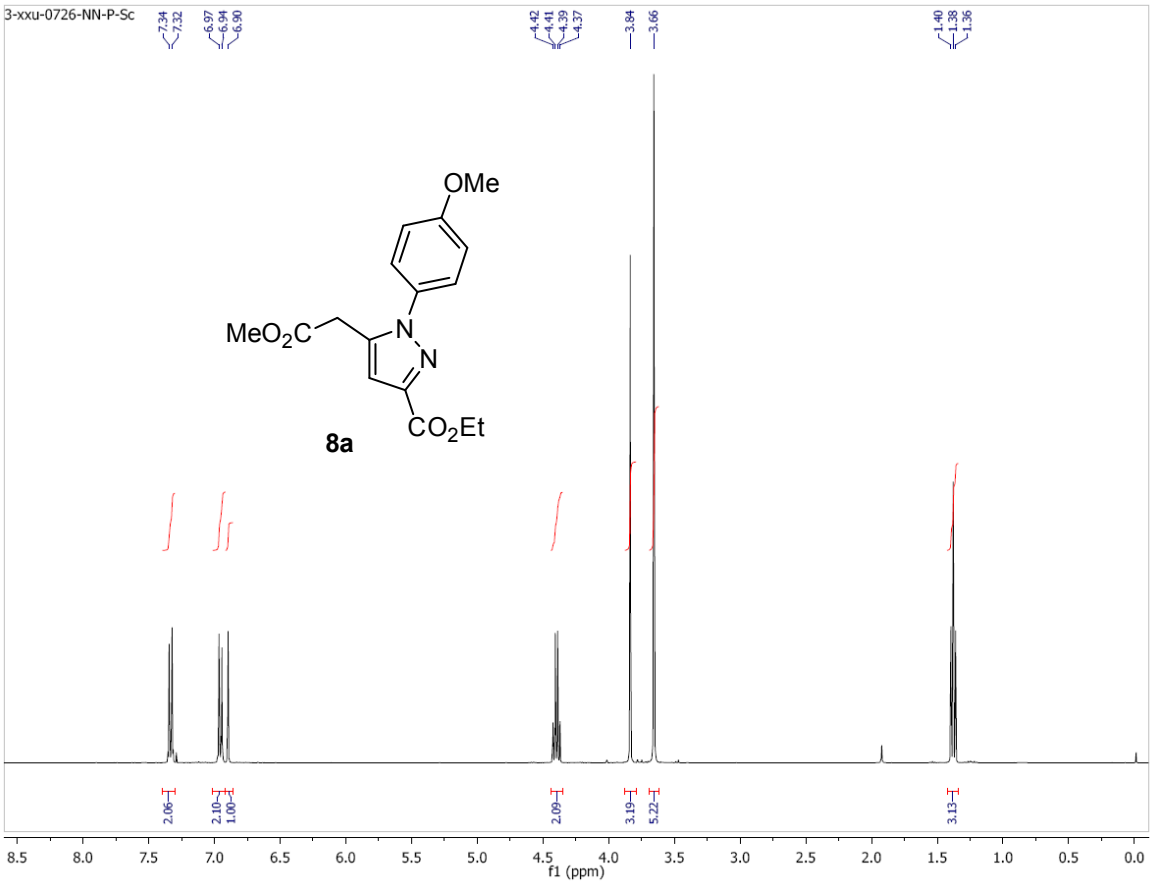
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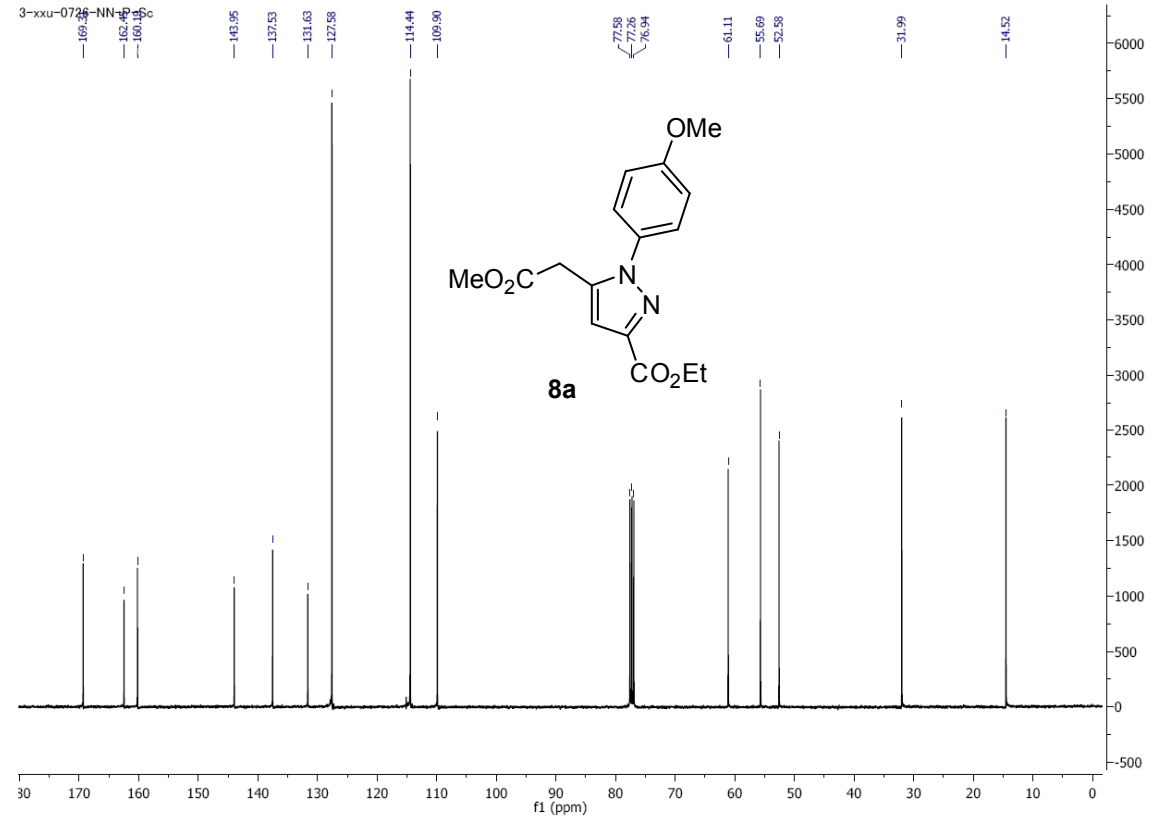
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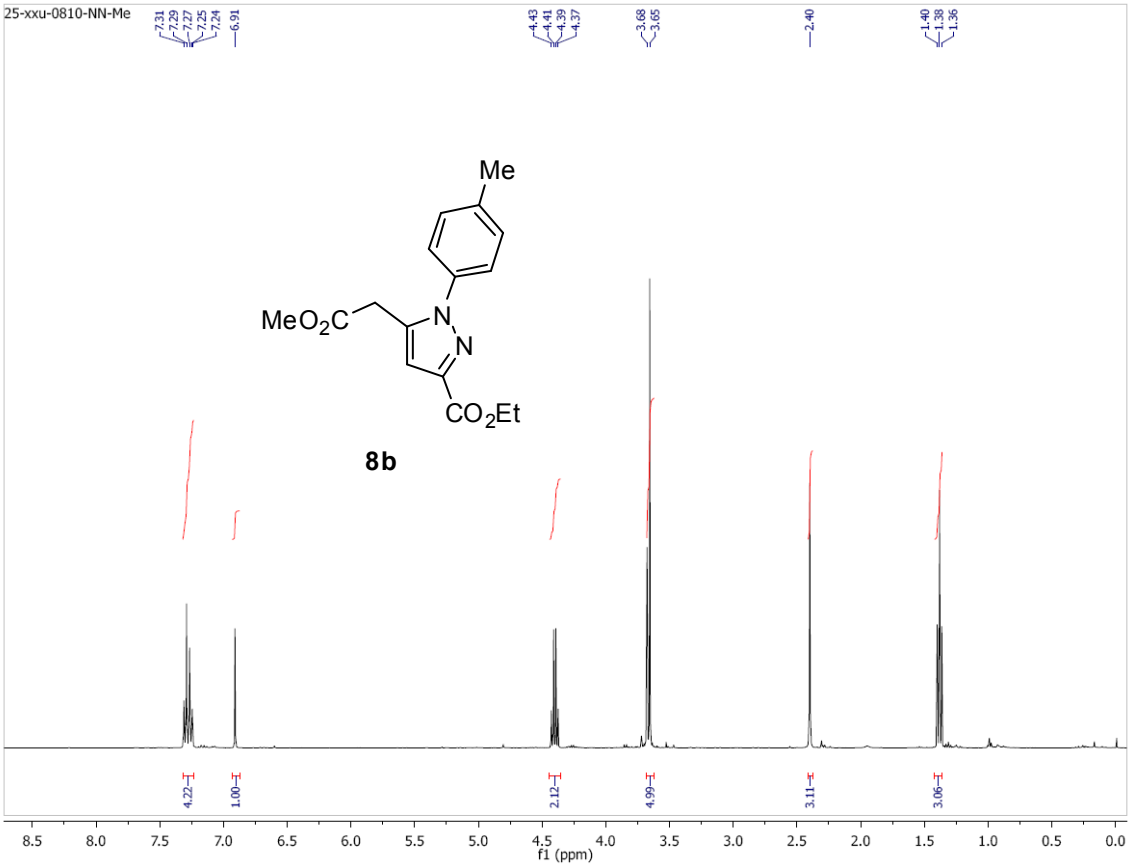
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N
CO2Et
8b
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7.0
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6.0
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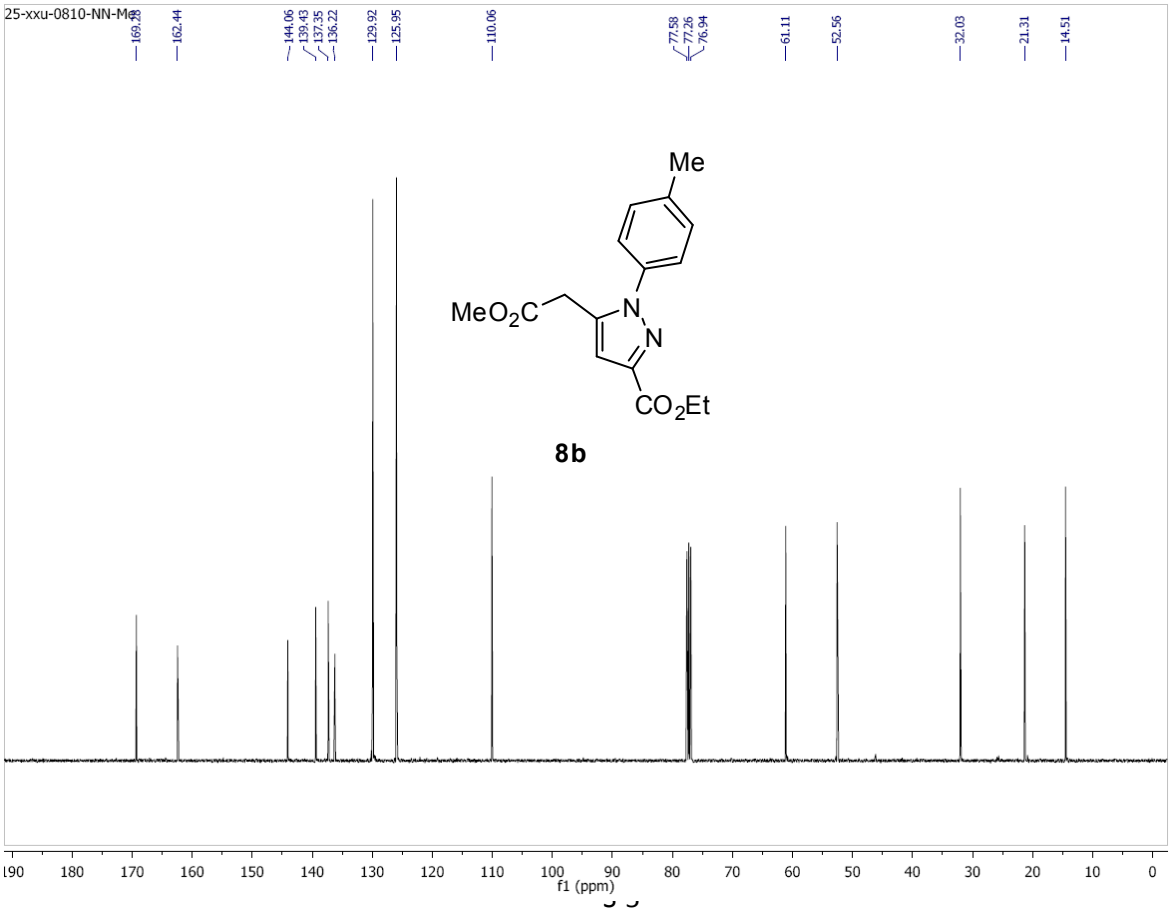
f1 (ppm)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77.26
76.94
61.11
52.56
32.03
21.31
14.51
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N
N
CO2Et
8b
190
180
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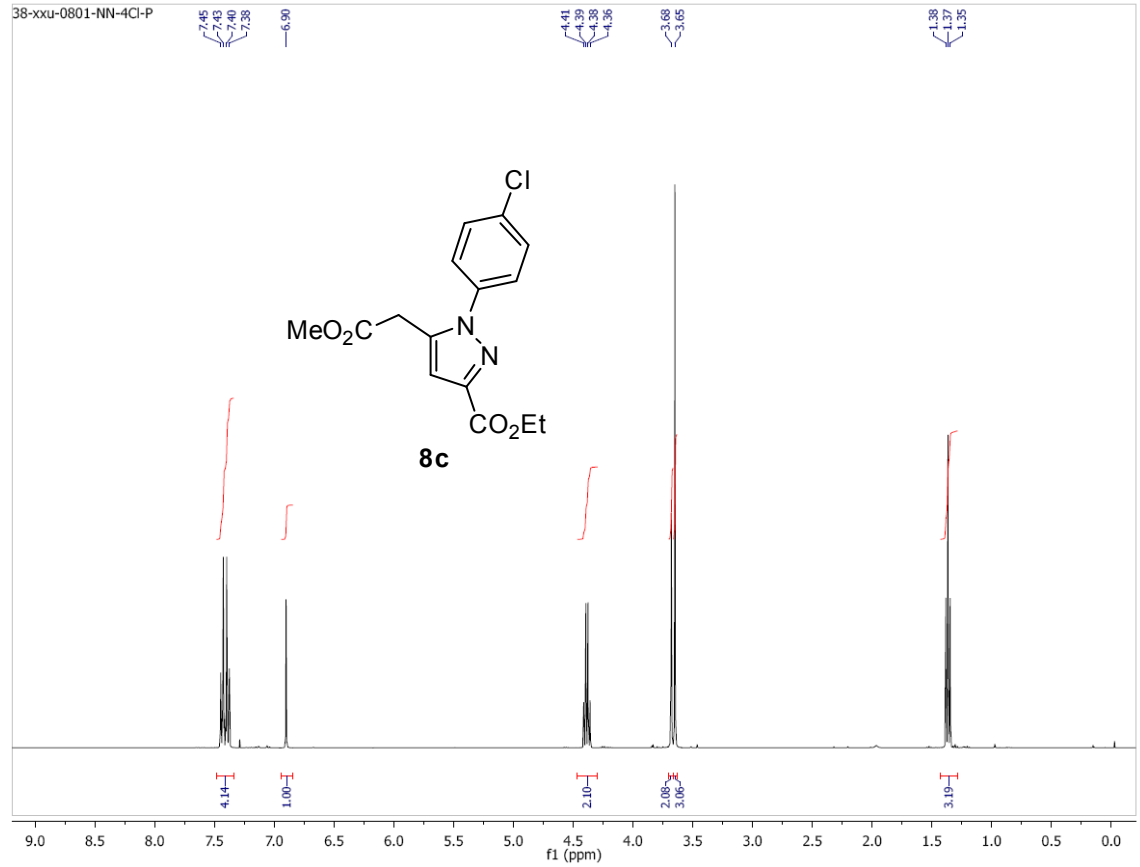
f1 (ppm)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1.38
1.37
1.35
Cl
MeO2C
N
N
CO2Et
8c
4.14
1.00
2.10
2.08
3.06
3.19
9.0
8.5
8.0
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7.0
6.5
6.0
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2.0
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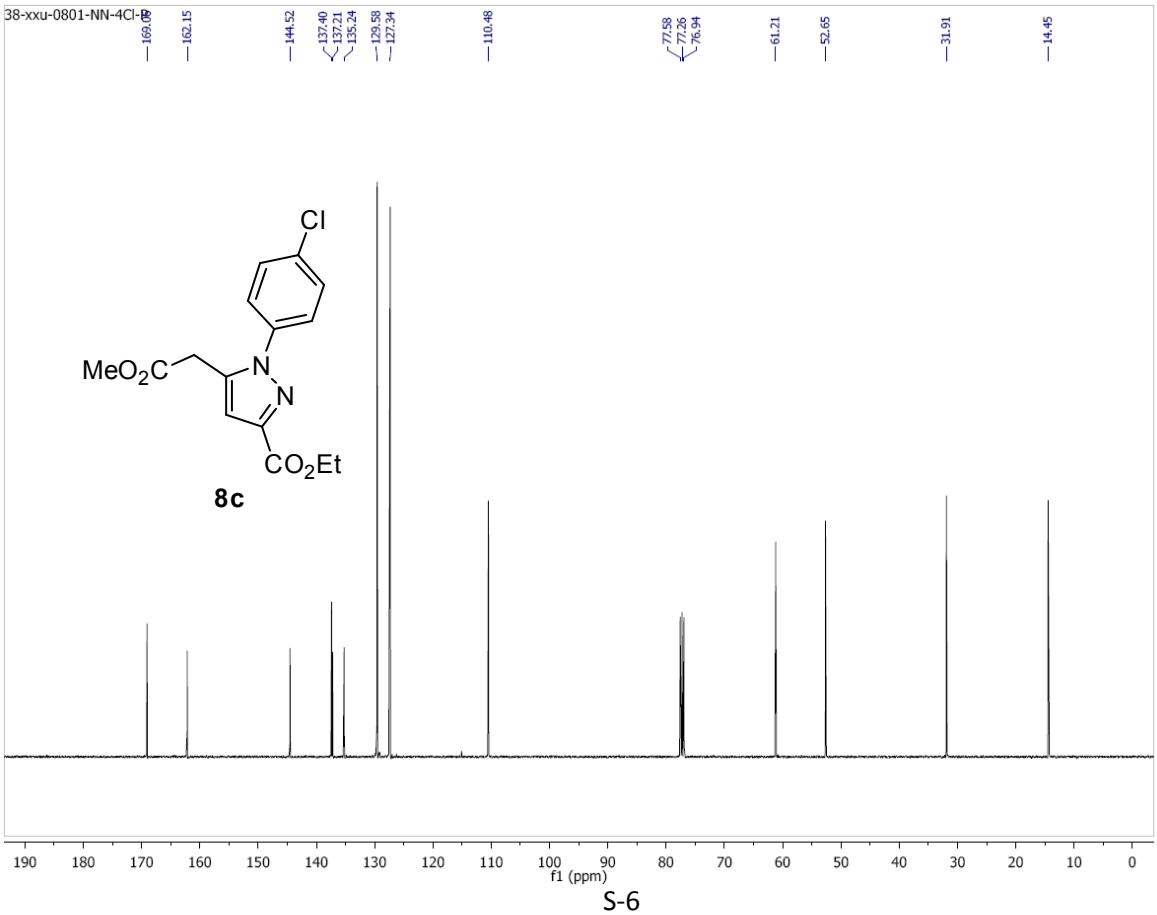
f1 (ppm)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77.26
76.94
61.21
52.65
31.91
14.45
Cl
MeO2C
N
N
CO2Et
8c
190
180
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130
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80
70
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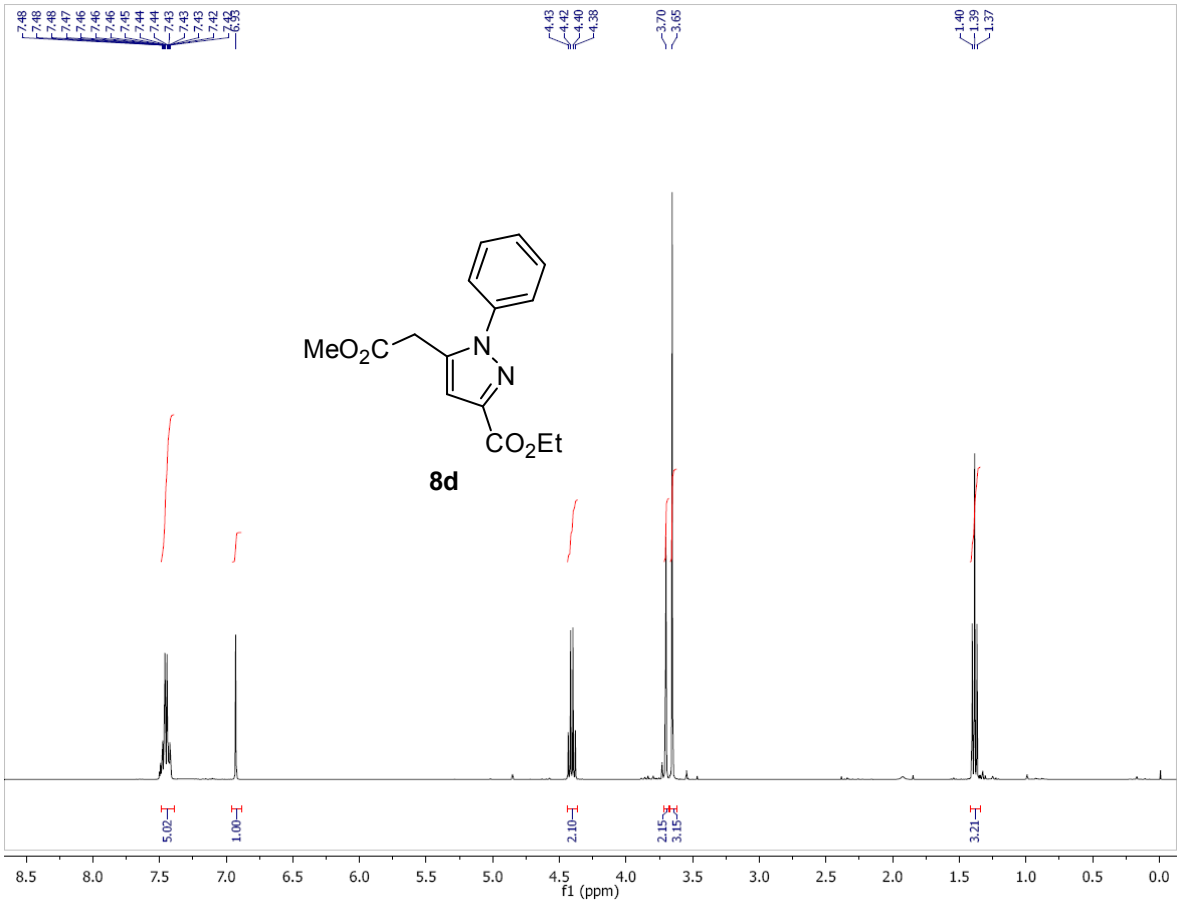
f1 (ppm)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CO2Et
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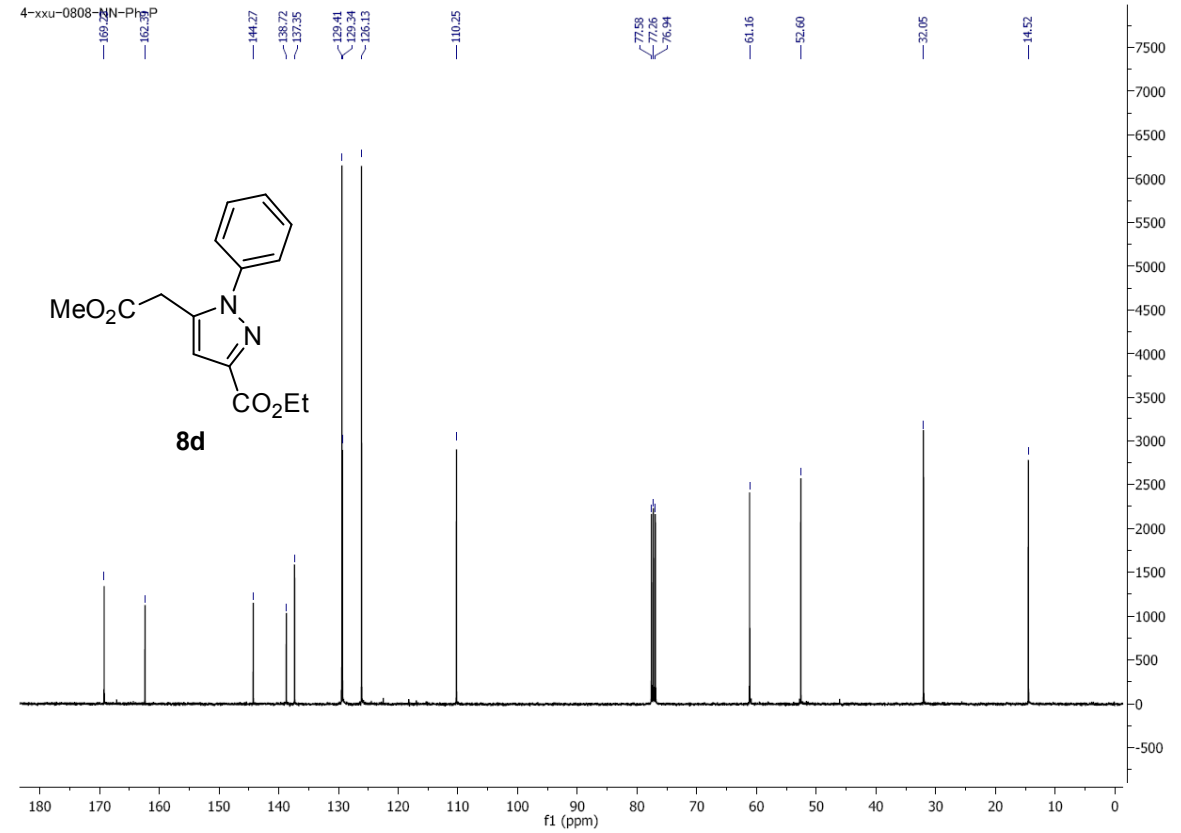
f1 (ppm)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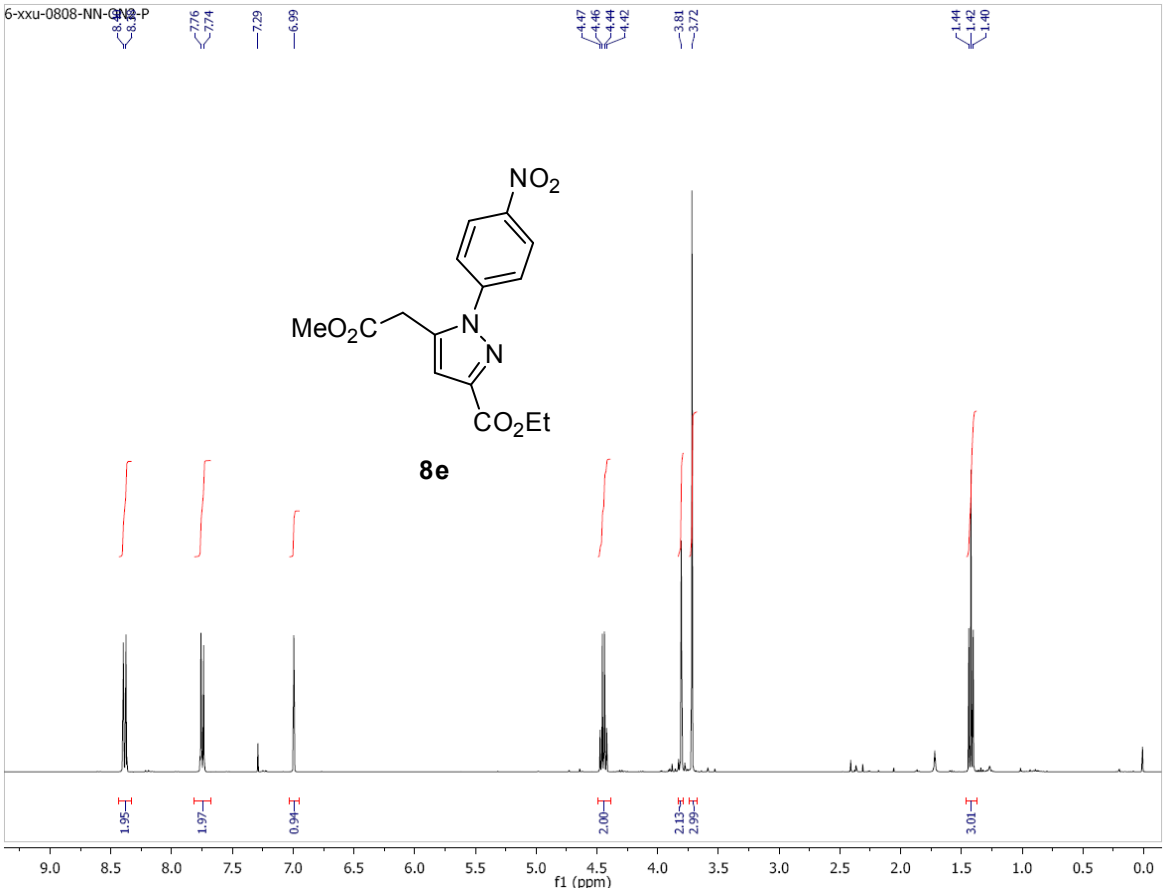
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1.42
1.40
NO2
MeO2C
N
N
CO2Et
8e
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1.97
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2.13
2.99
3.01
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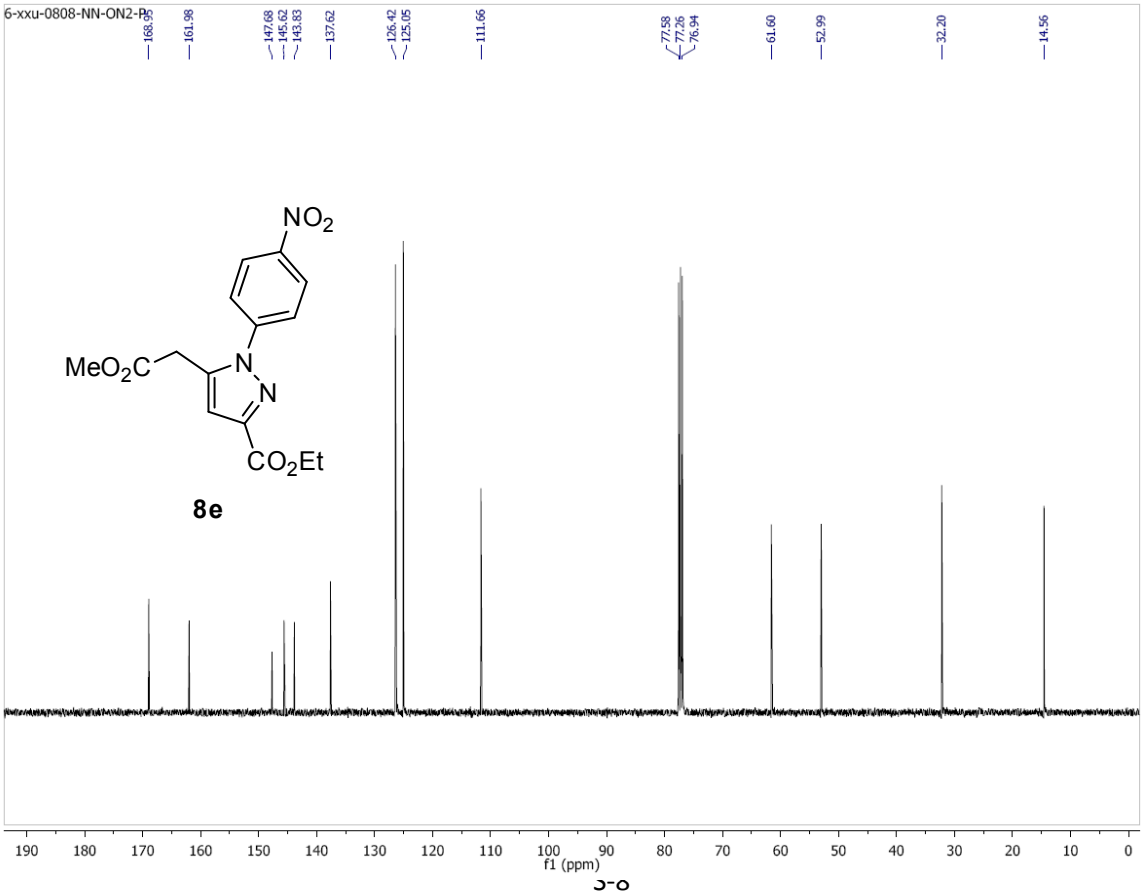
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77.26
76.94
61.60
52.99
32.20
14.56
NO2
MeO2C
N
N
CO2Et
8e
190
180
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130
120
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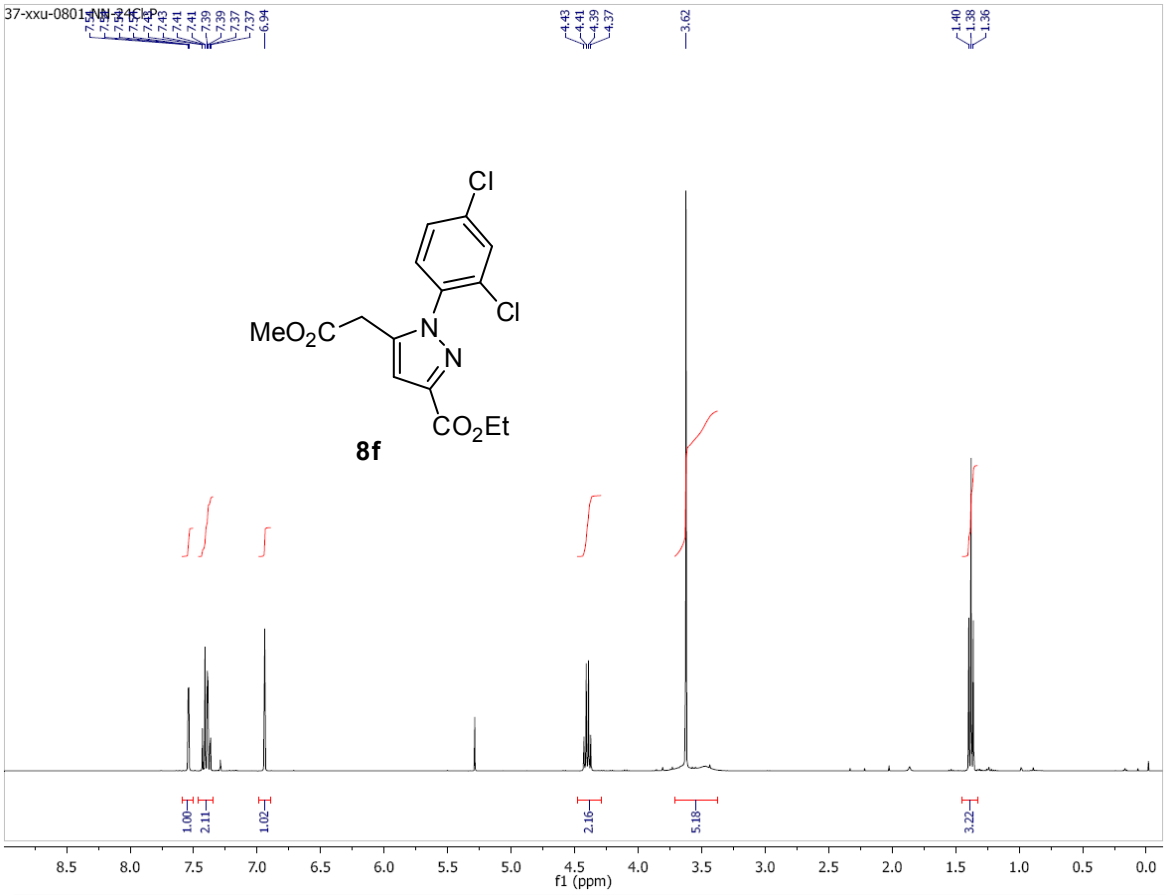
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4.41
4.39
4.37
3.62
1.40
1.38
1.36
Cl
Cl
MeO2C
N
N
CO2Et
8f
1.00
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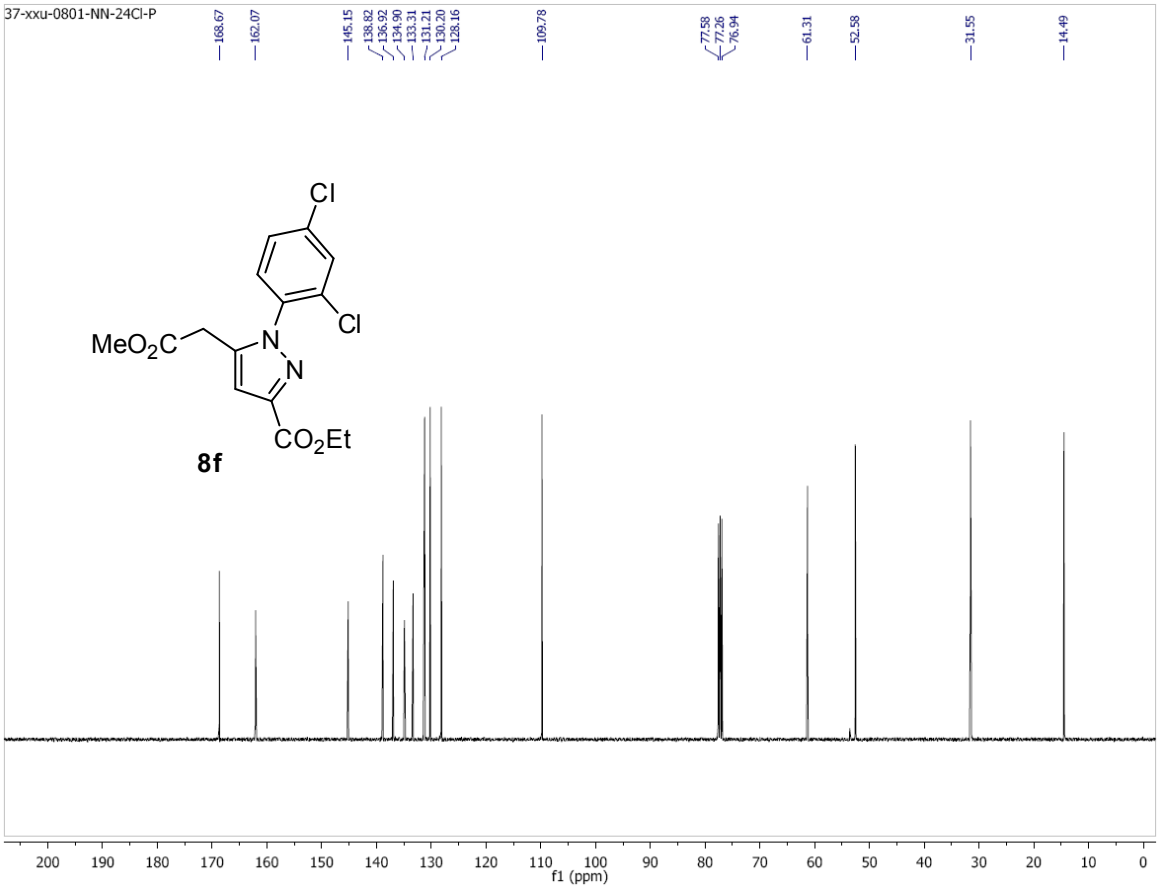
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77.26
76.94
61.31
52.58
31.55
14.49
Cl
Cl
MeO2C
N
N
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8f
200
190
180
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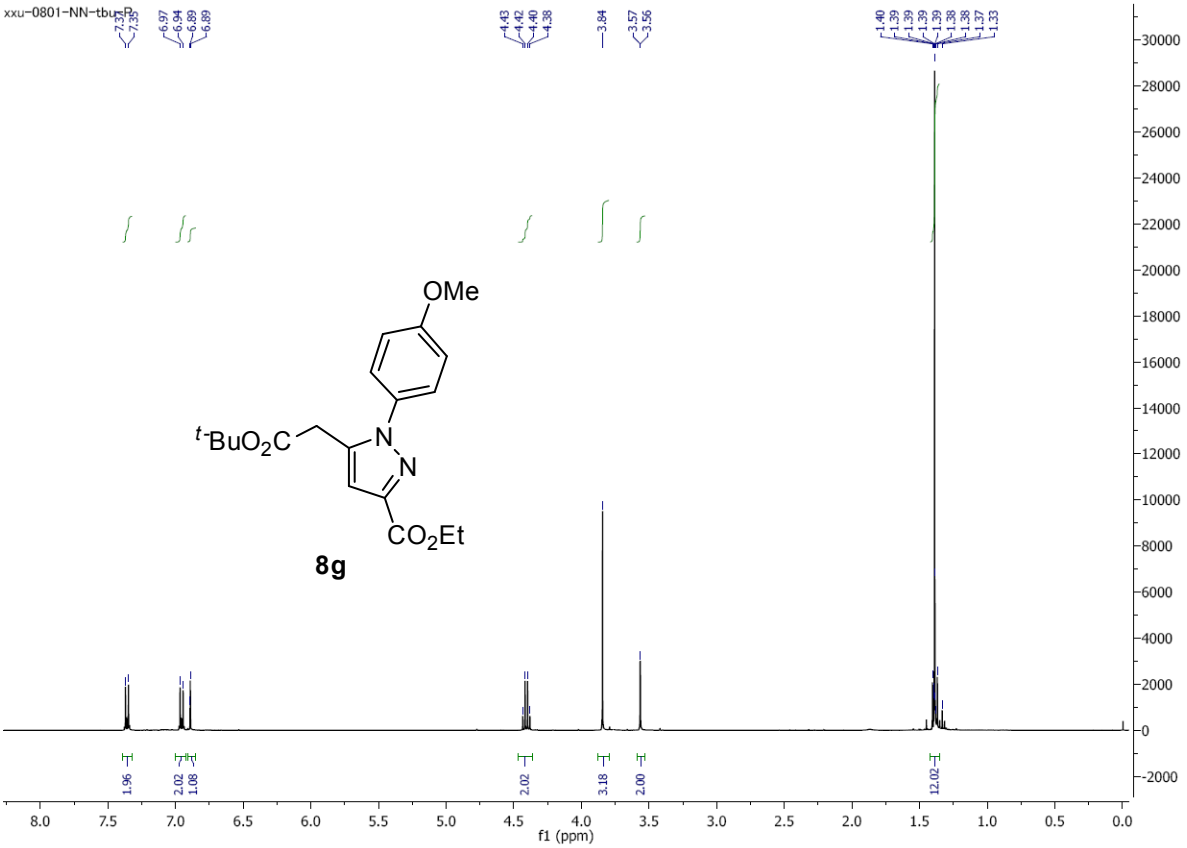
f1 (ppm)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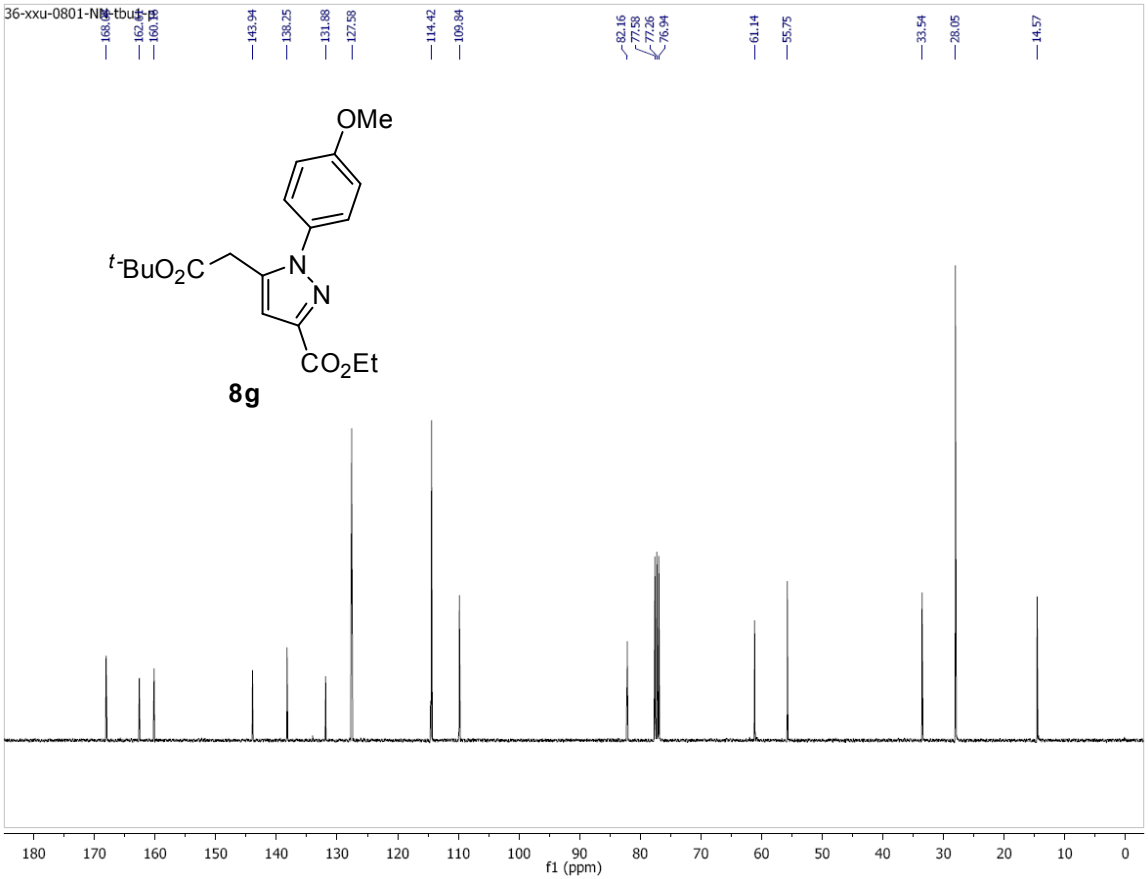
t-BuO$_2$C
N
N
CO$_2$Et
8g
f1 (ppm)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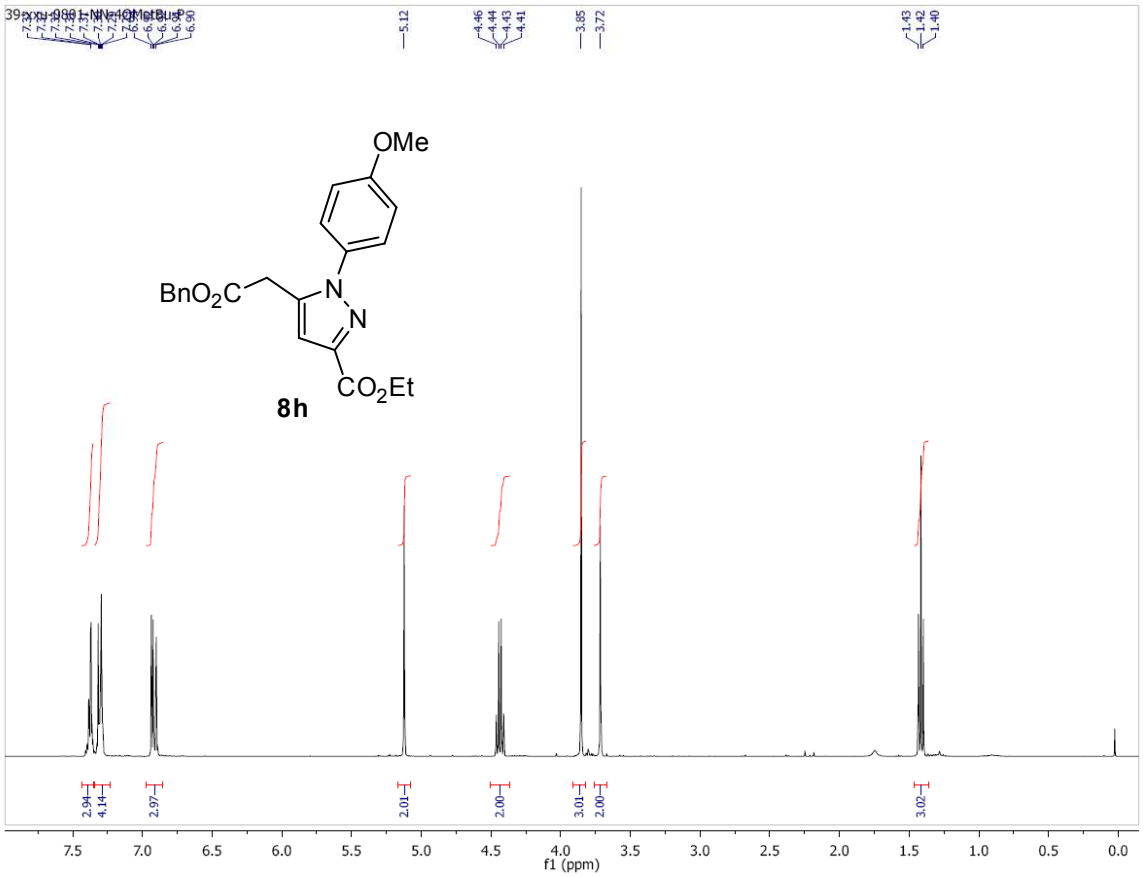
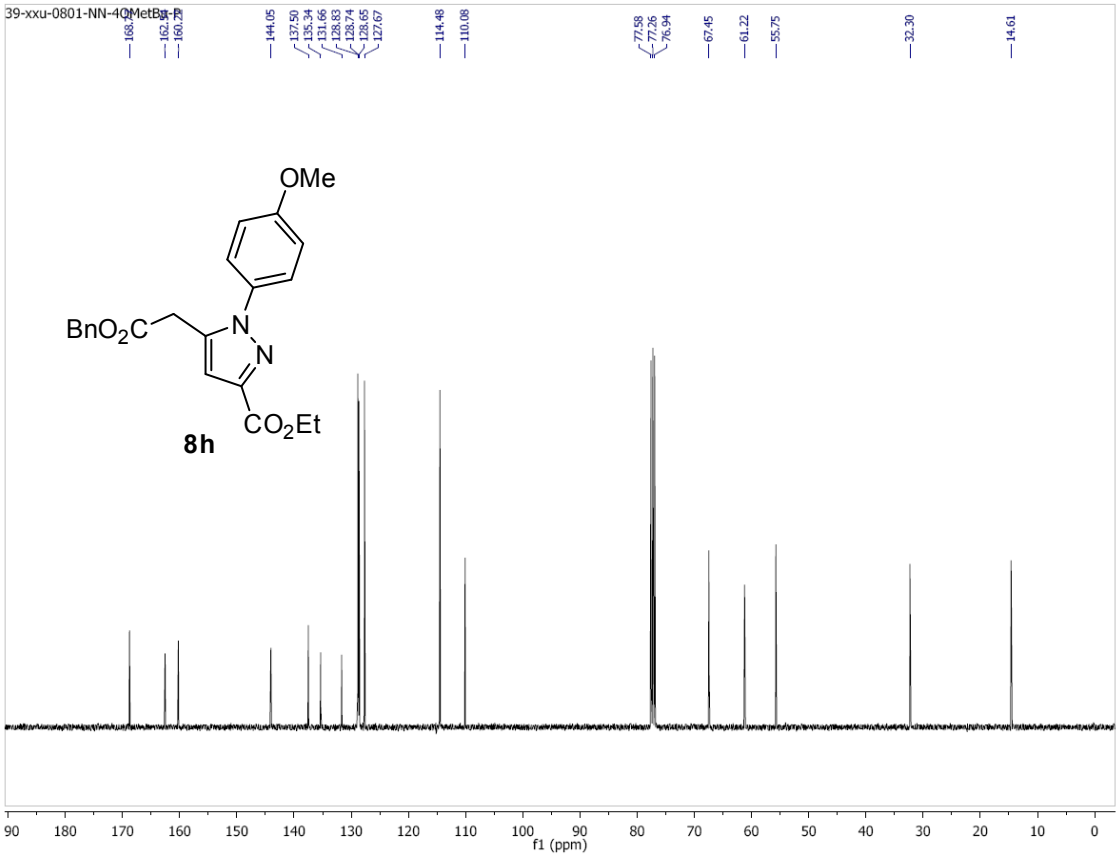
CO$_2$Et
8g
f1 (ppm)


OMe
BnO2C
N
N
CO2Et
8h
f1 (ppm)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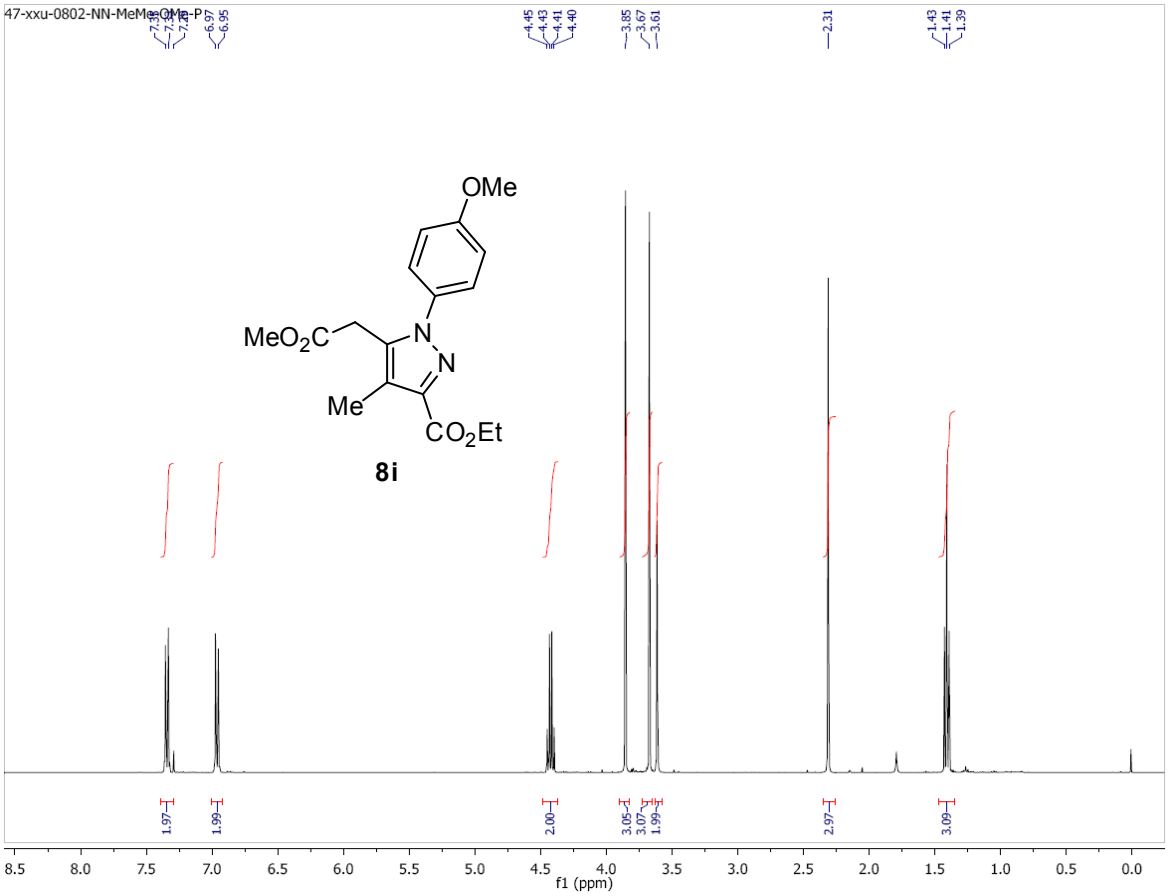
N
CO2Et
8h
f1 (ppm)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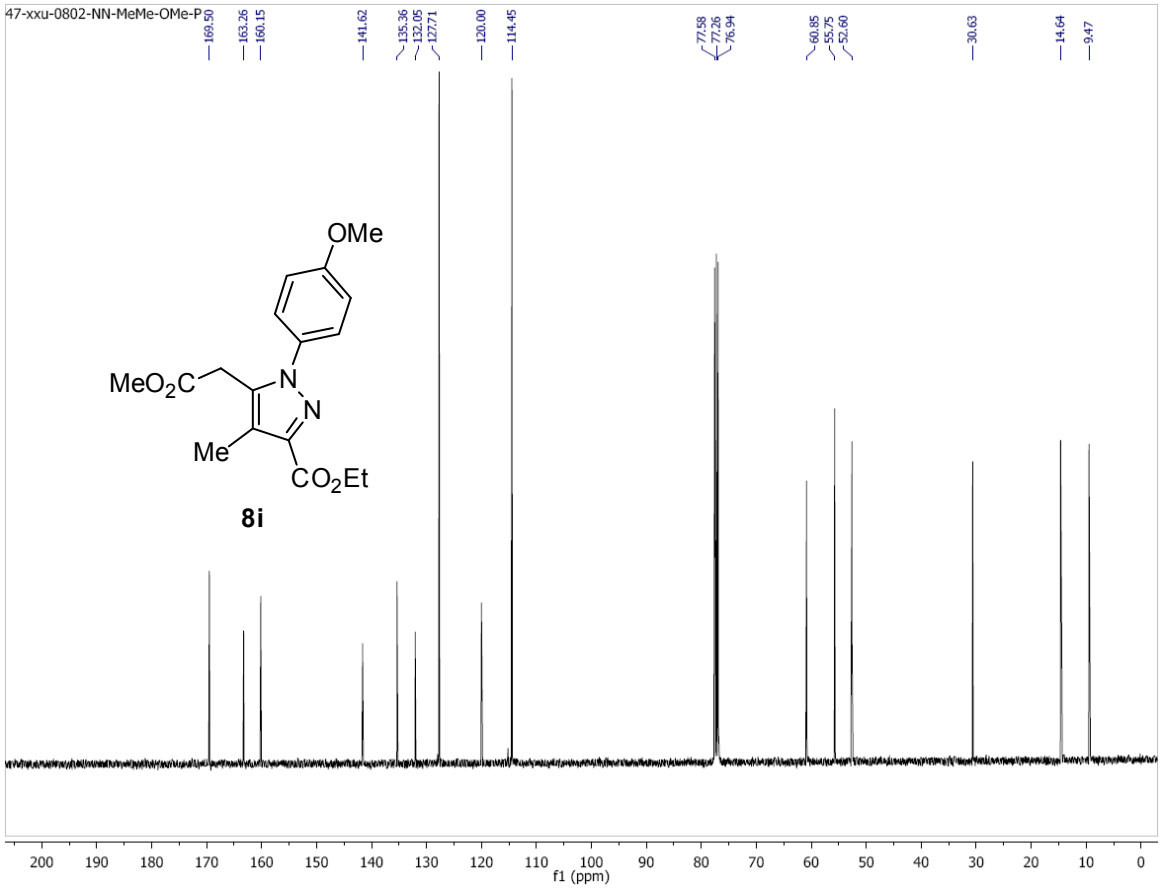
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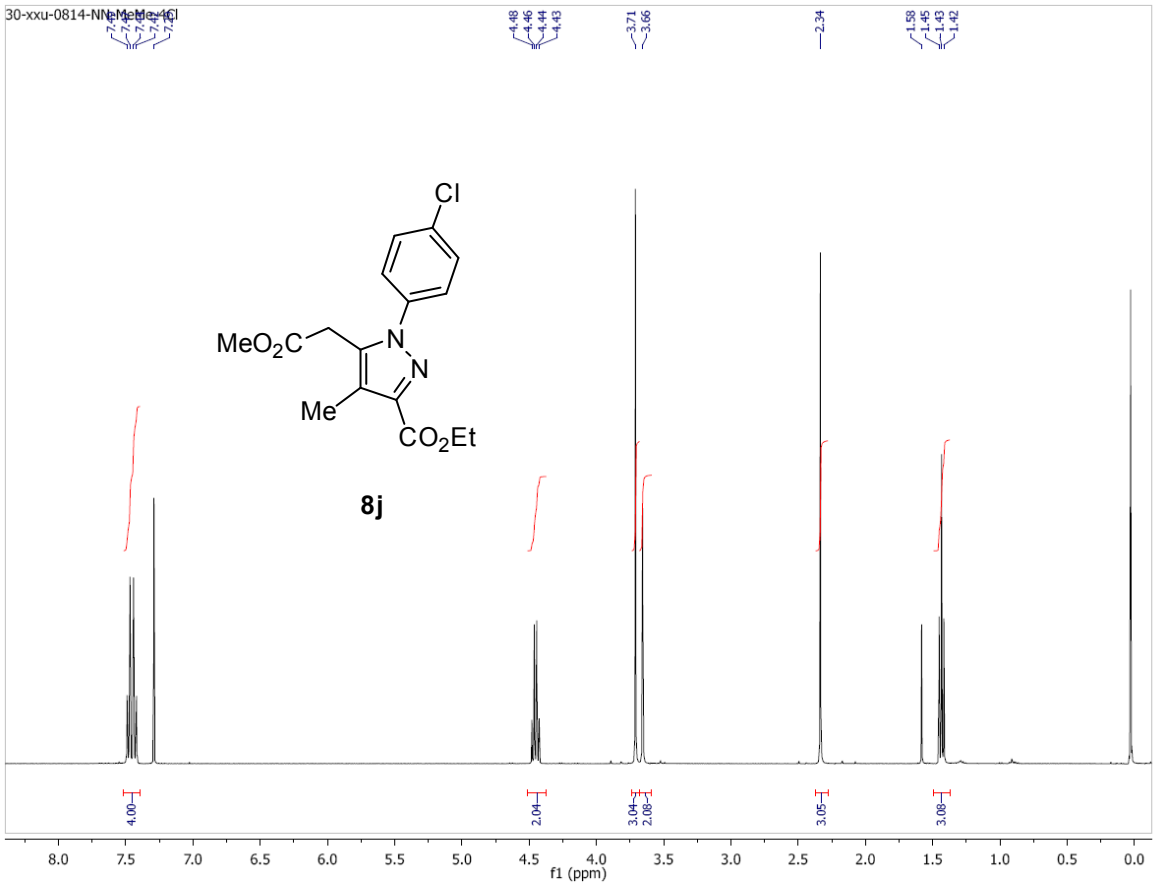
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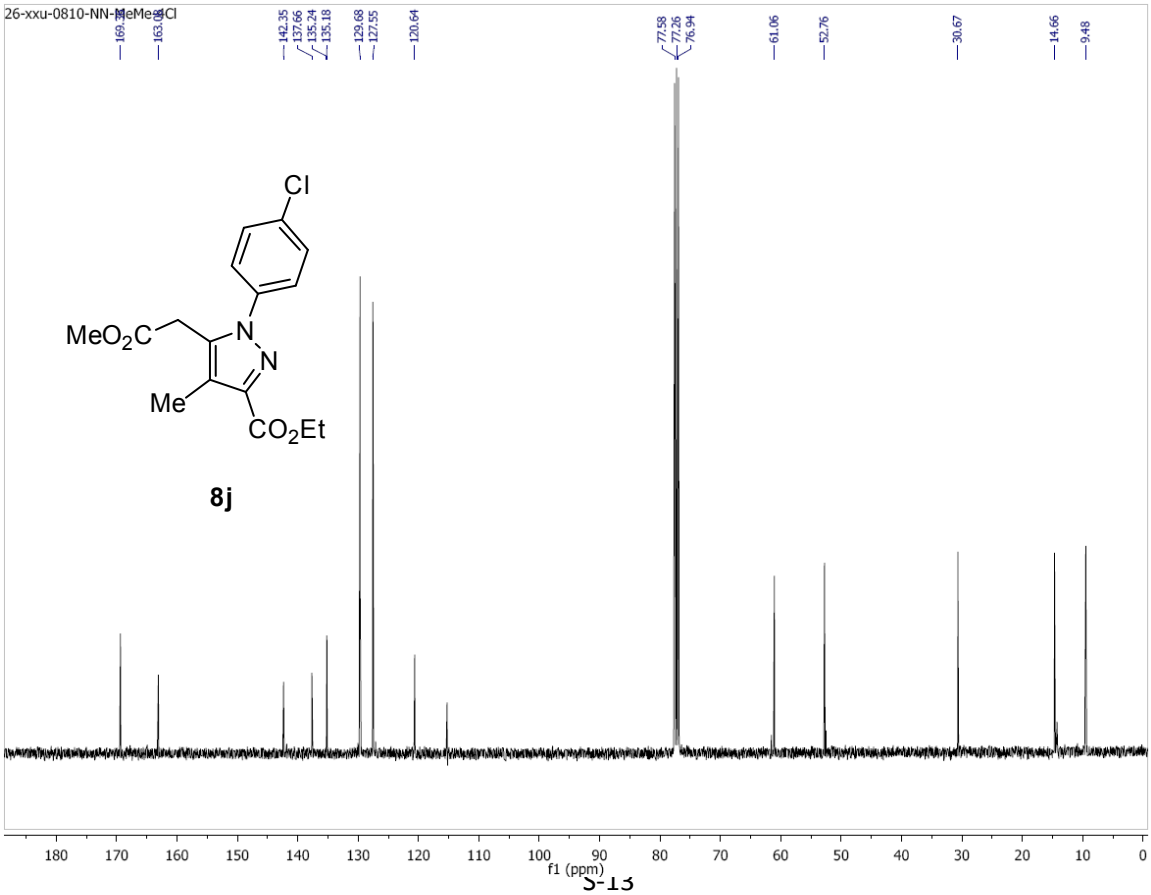
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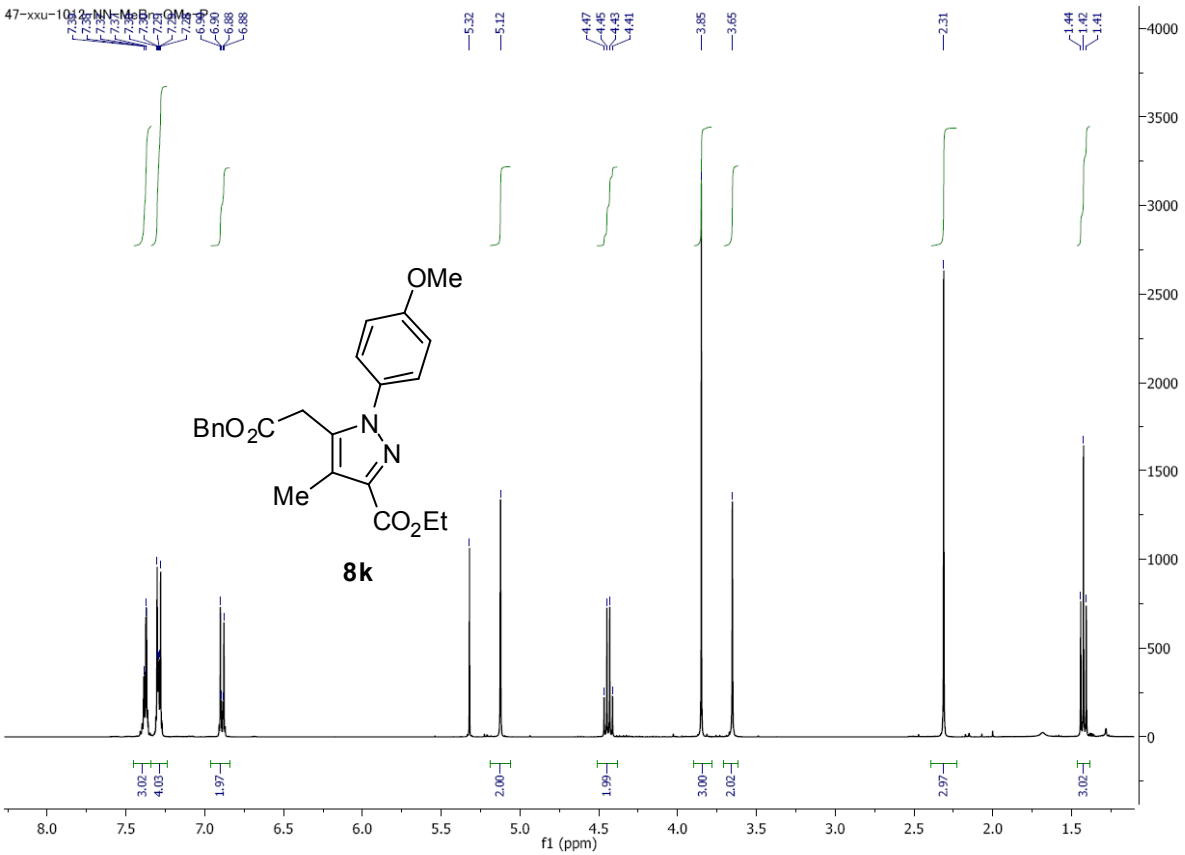
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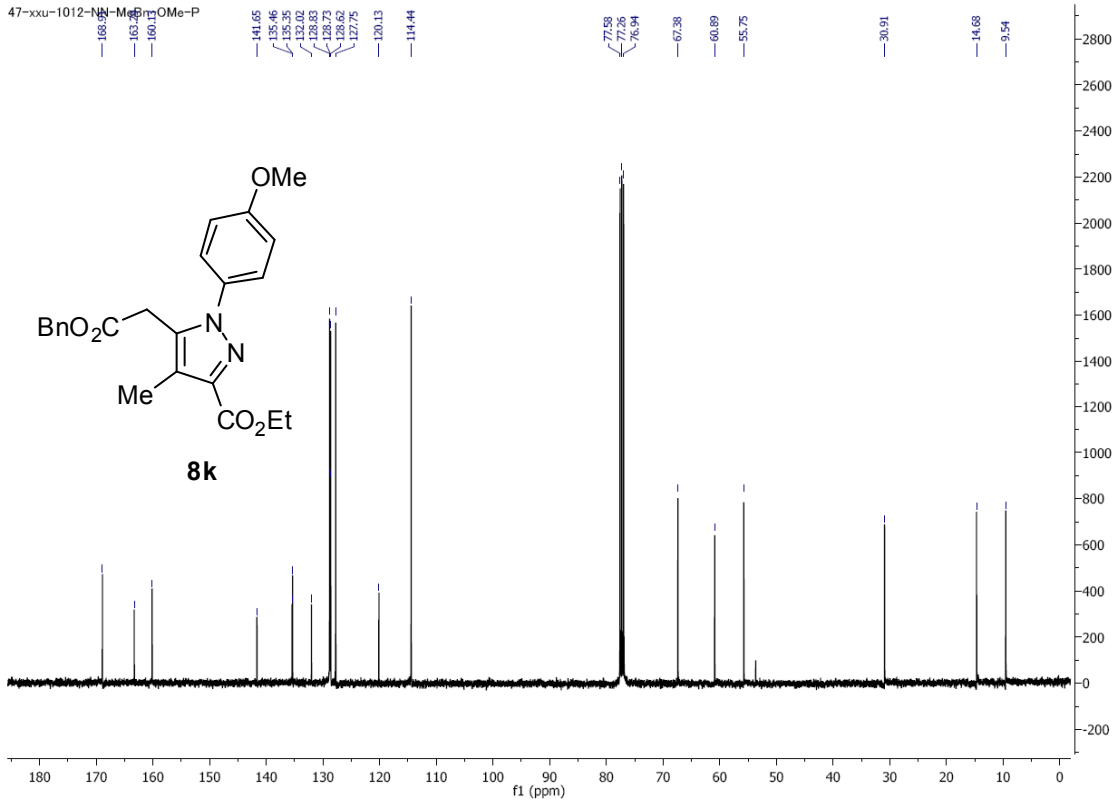
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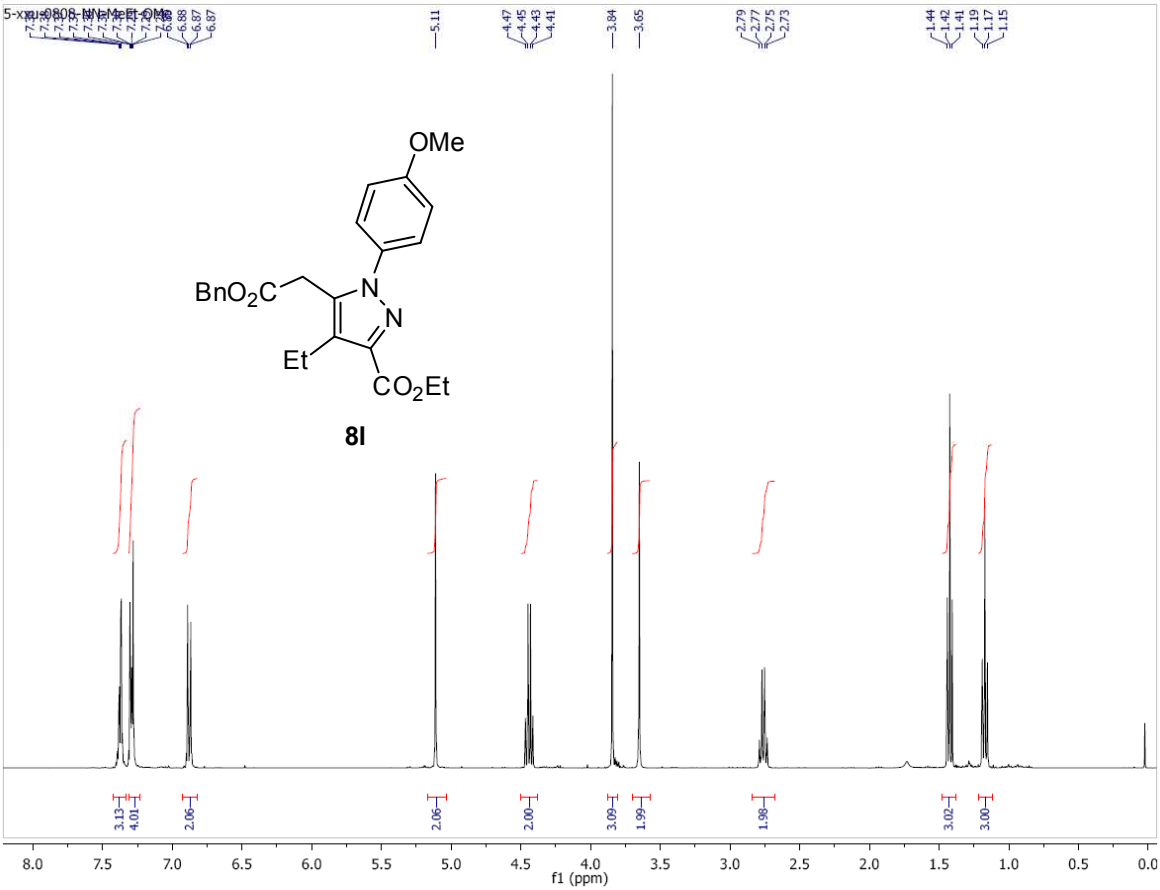
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Et
CO2Et
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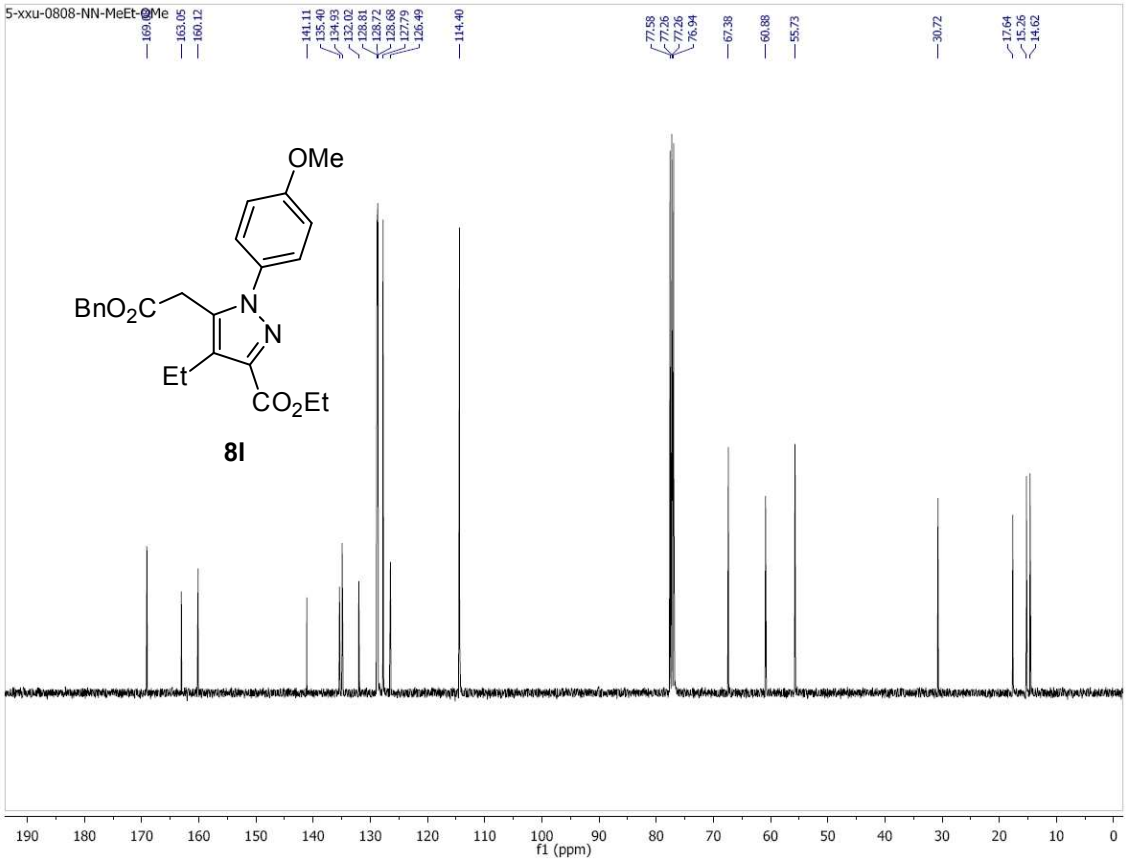
f1 (ppm)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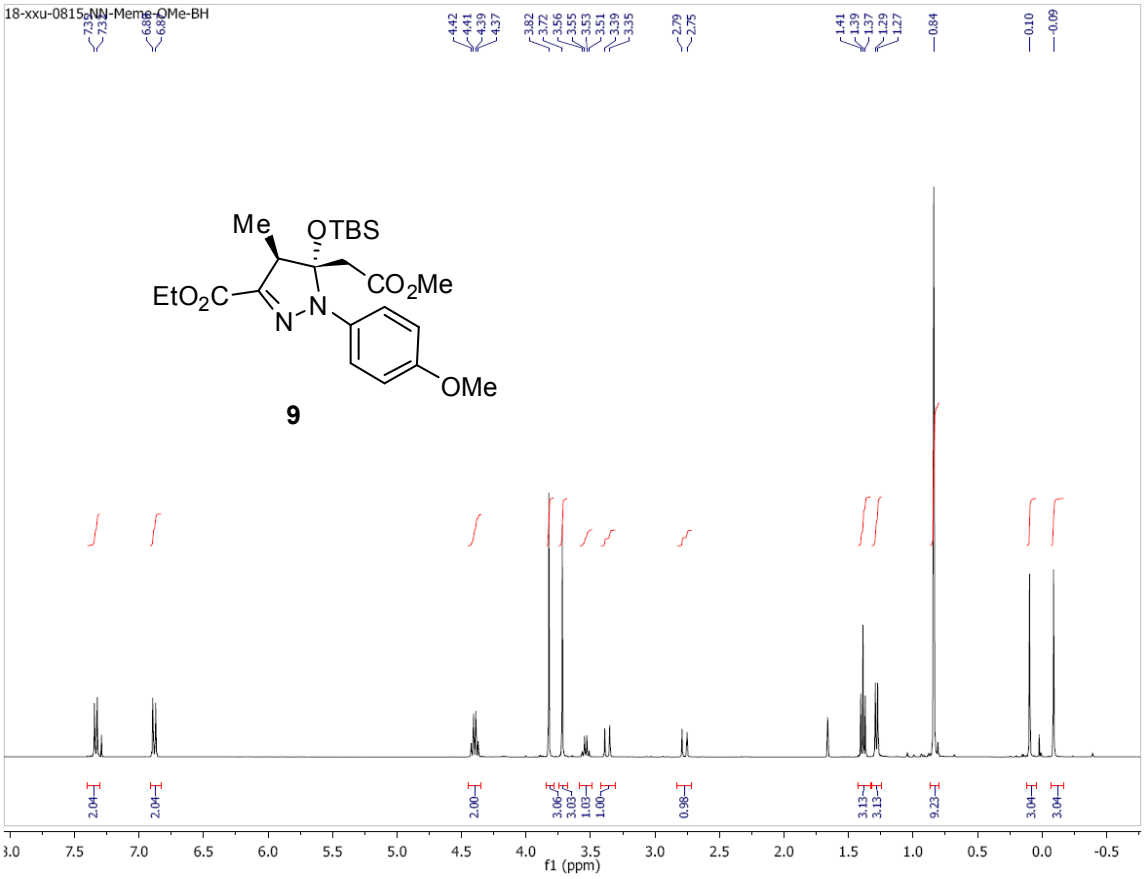
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OMe
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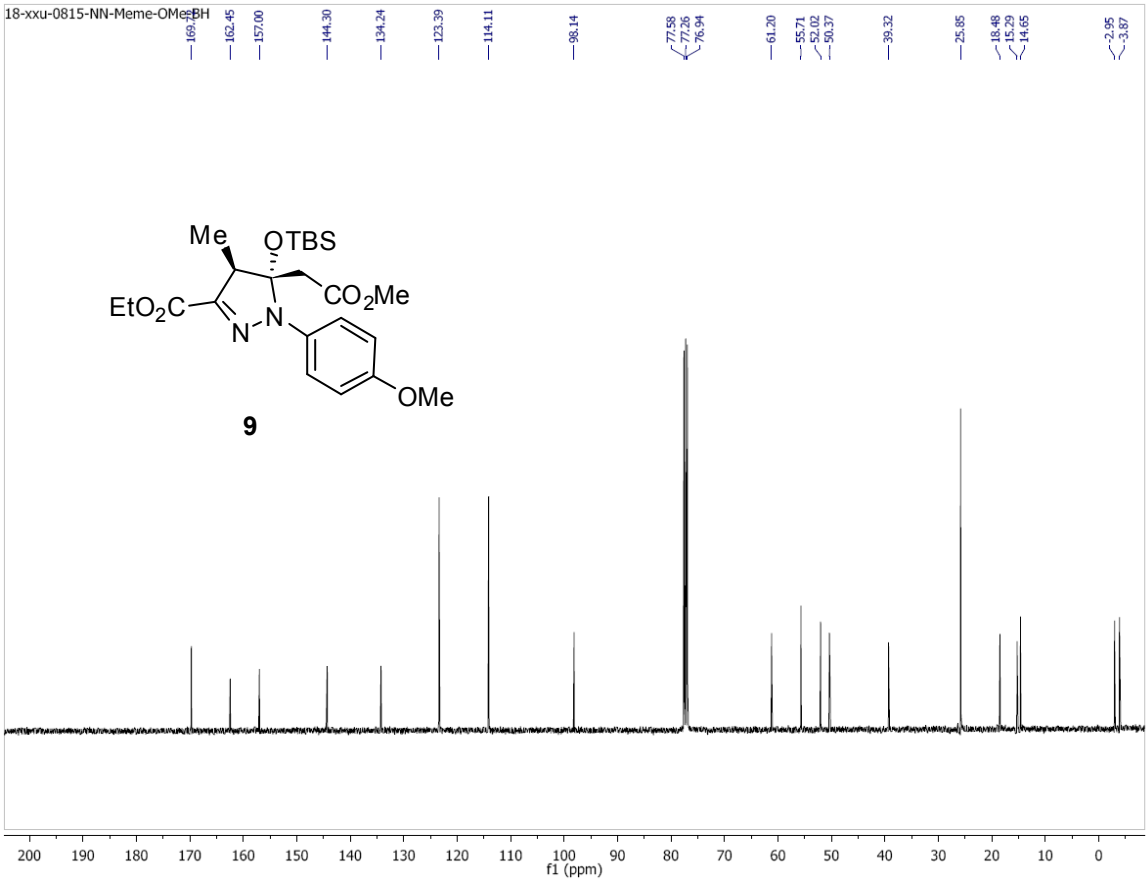
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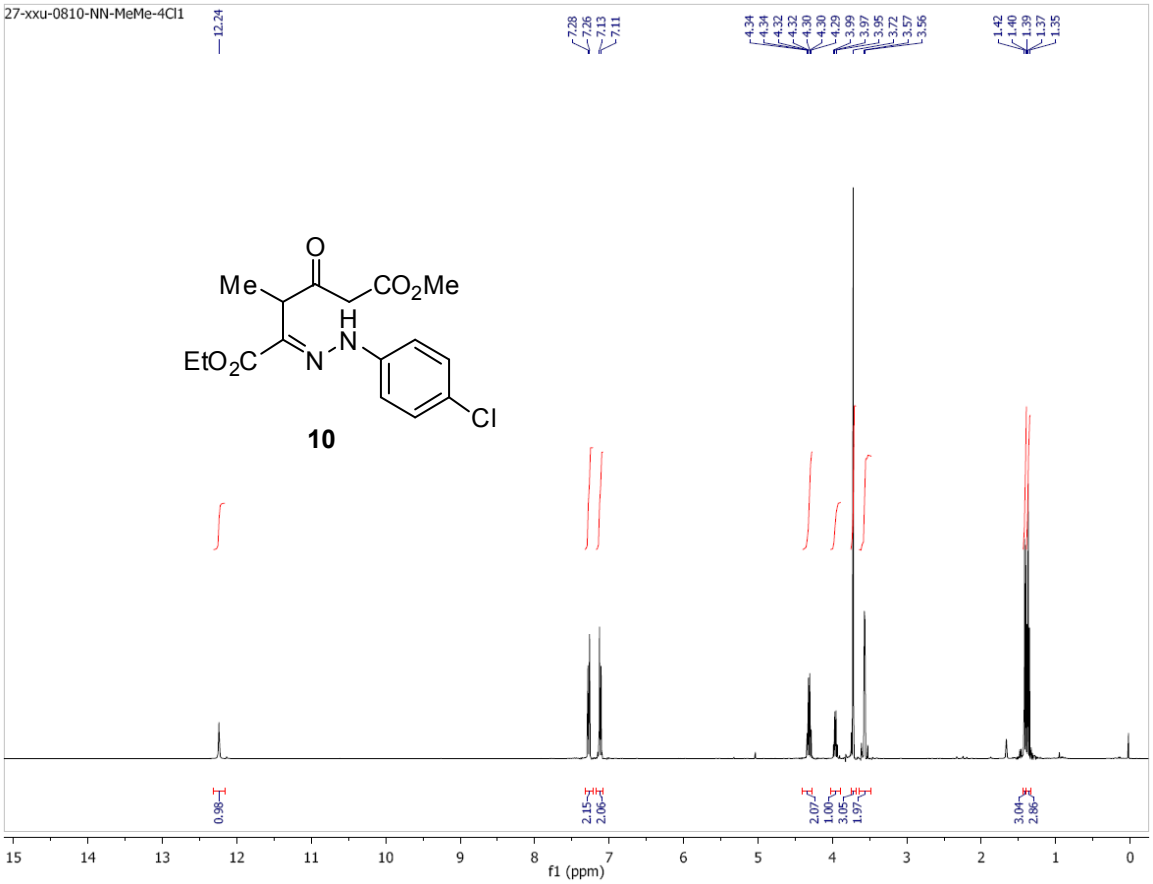
CO2Me
N
N
OMe
9
f1 (ppm)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4.32
4.32
4.30
4.30
4.29
3.99
3.97
3.95
3.72
3.57
3.56
1.42
1.40
1.39
1.37
1.35
Me
CO2Me
EtO2C
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1.00
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1.97
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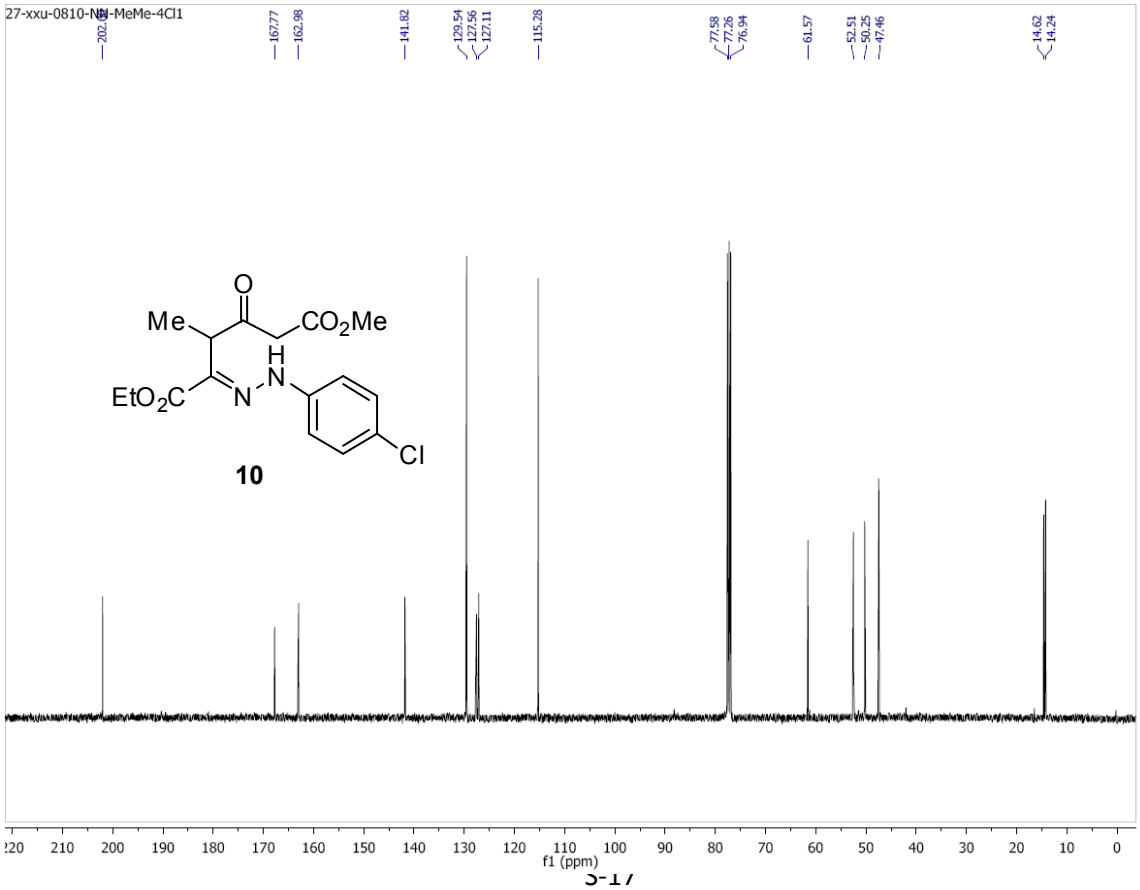
2.86
f1 (ppm)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141.82
129.54
127.56
127.11
115.28
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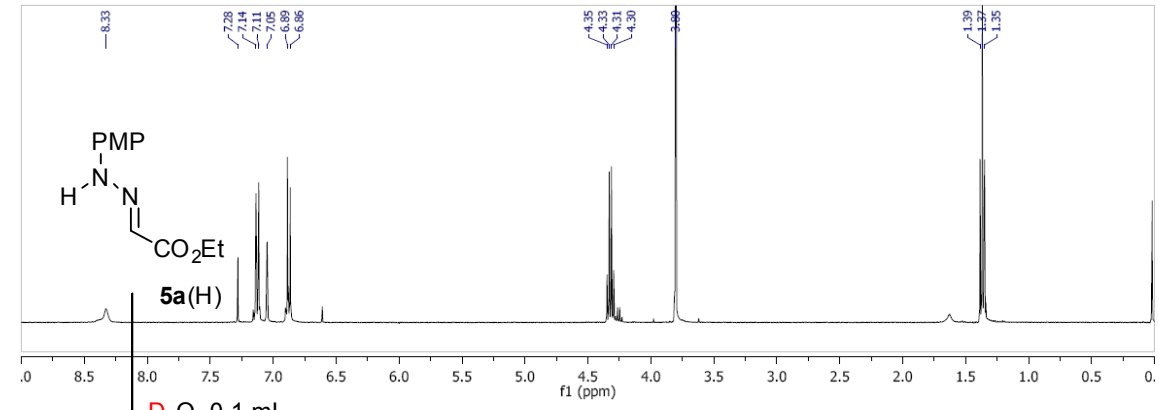
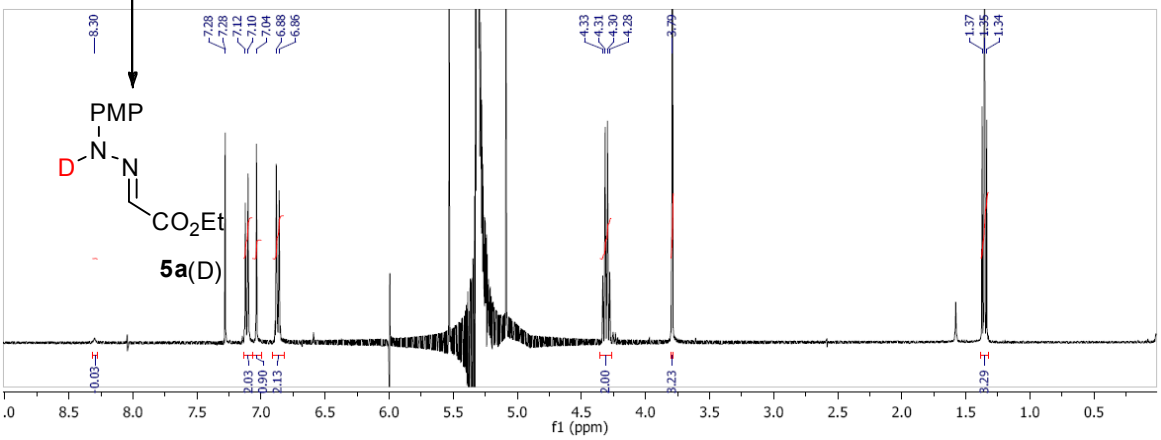
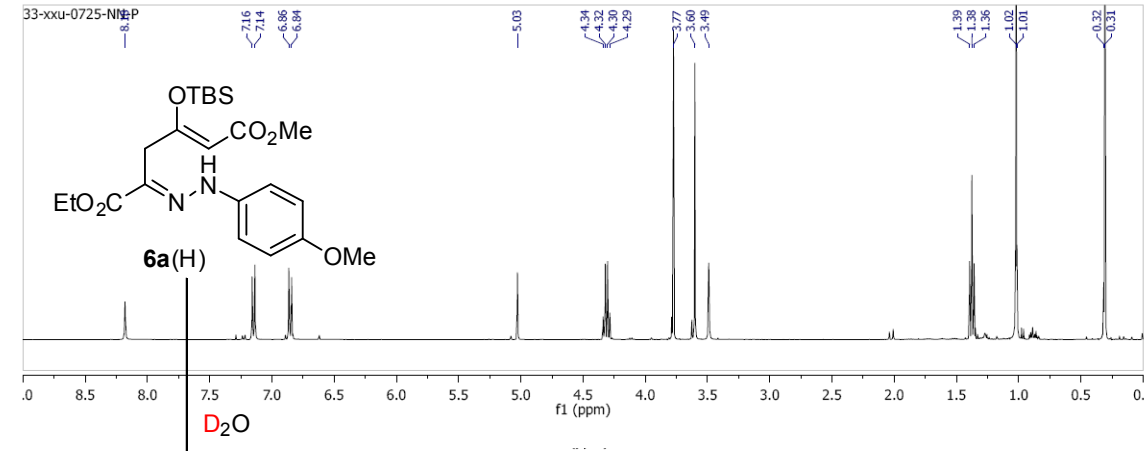
77.26
76.94
61.57
52.51
50.25
47.46
14.62
14.24
Me
CO2Me
EtO2C
H
N
N
Cl
O
10
f1 (ppm)

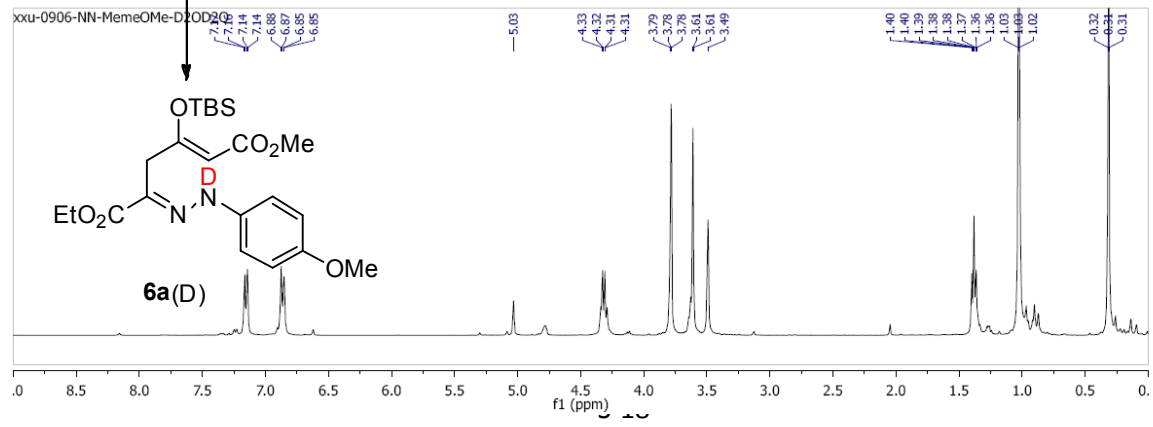


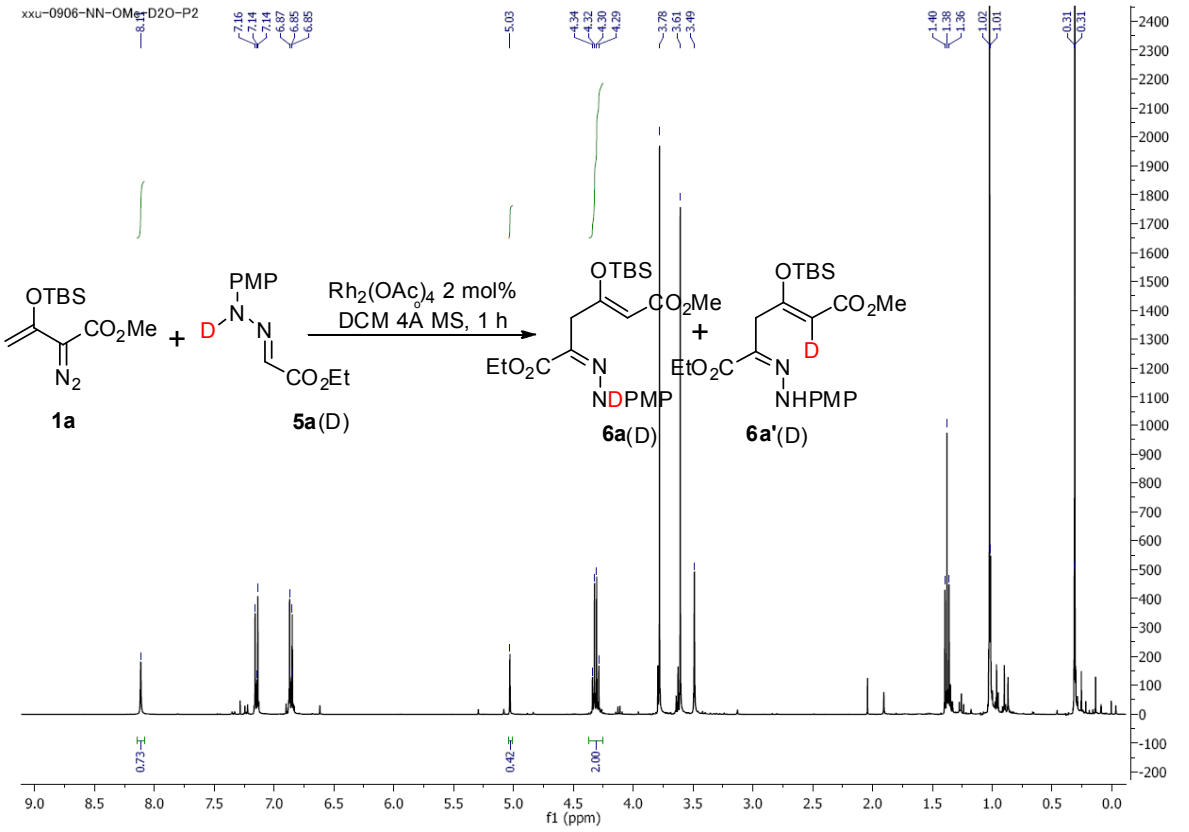
D_2O, 0.1 mL
DCM, 0.5 h





D_2O

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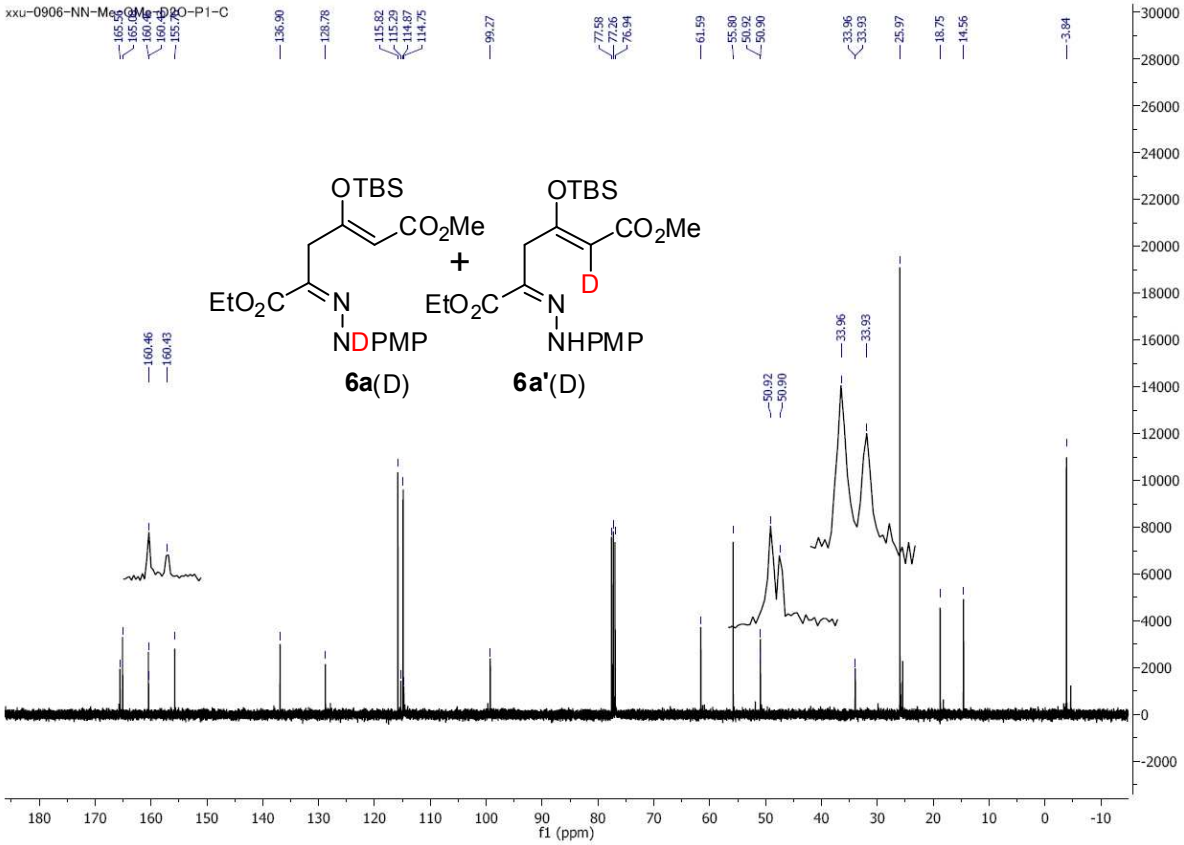
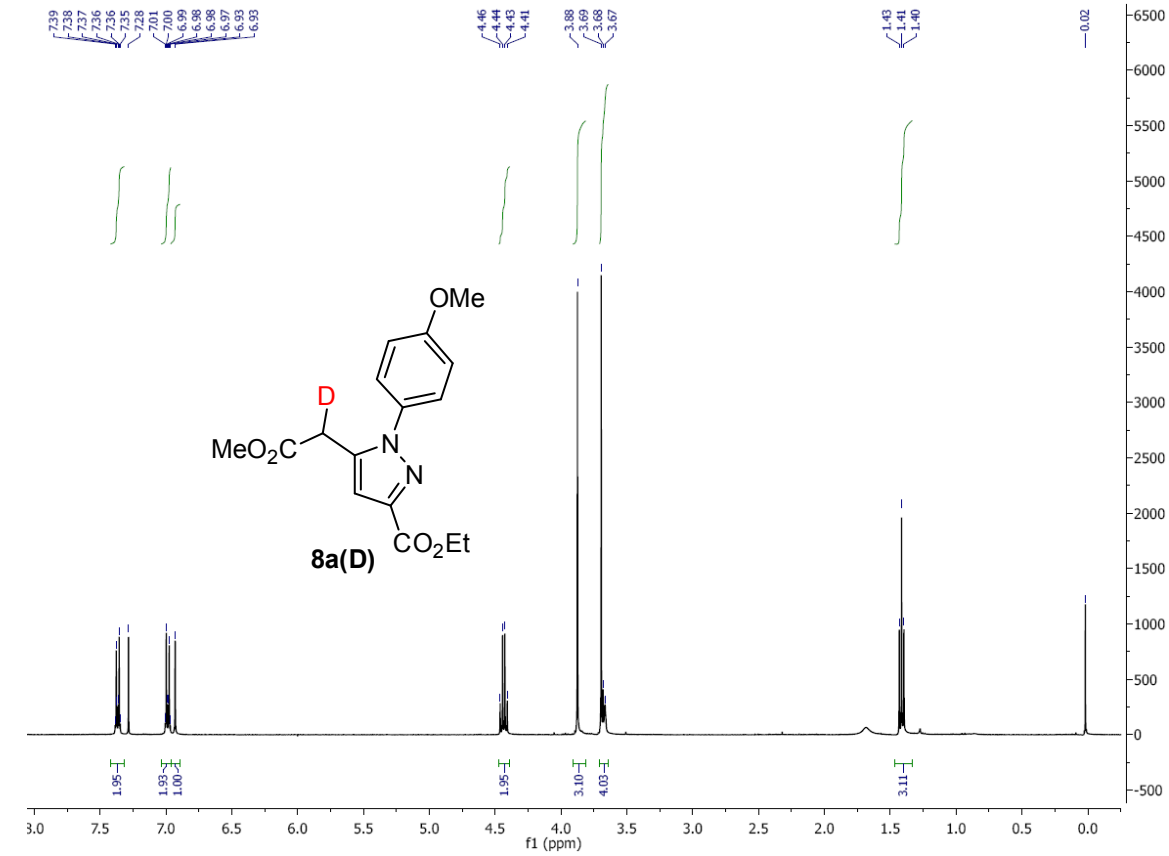
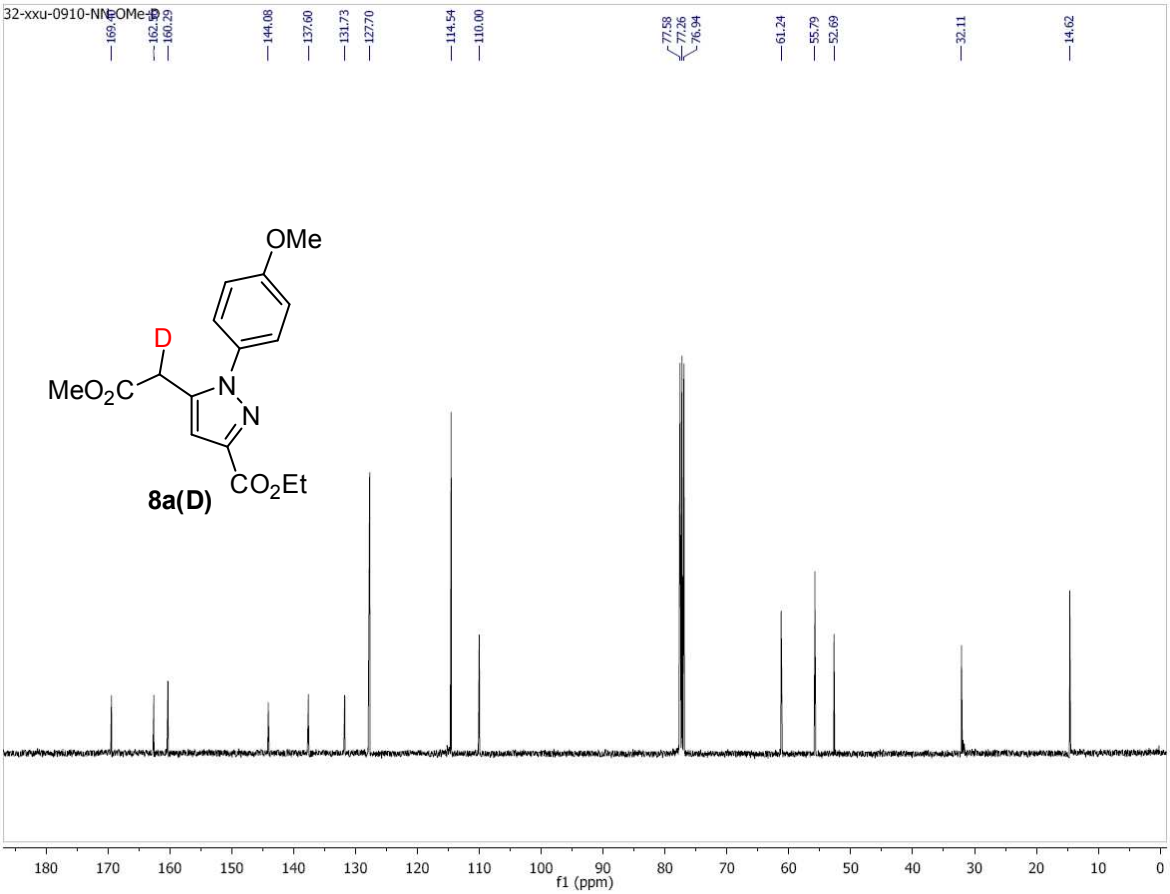
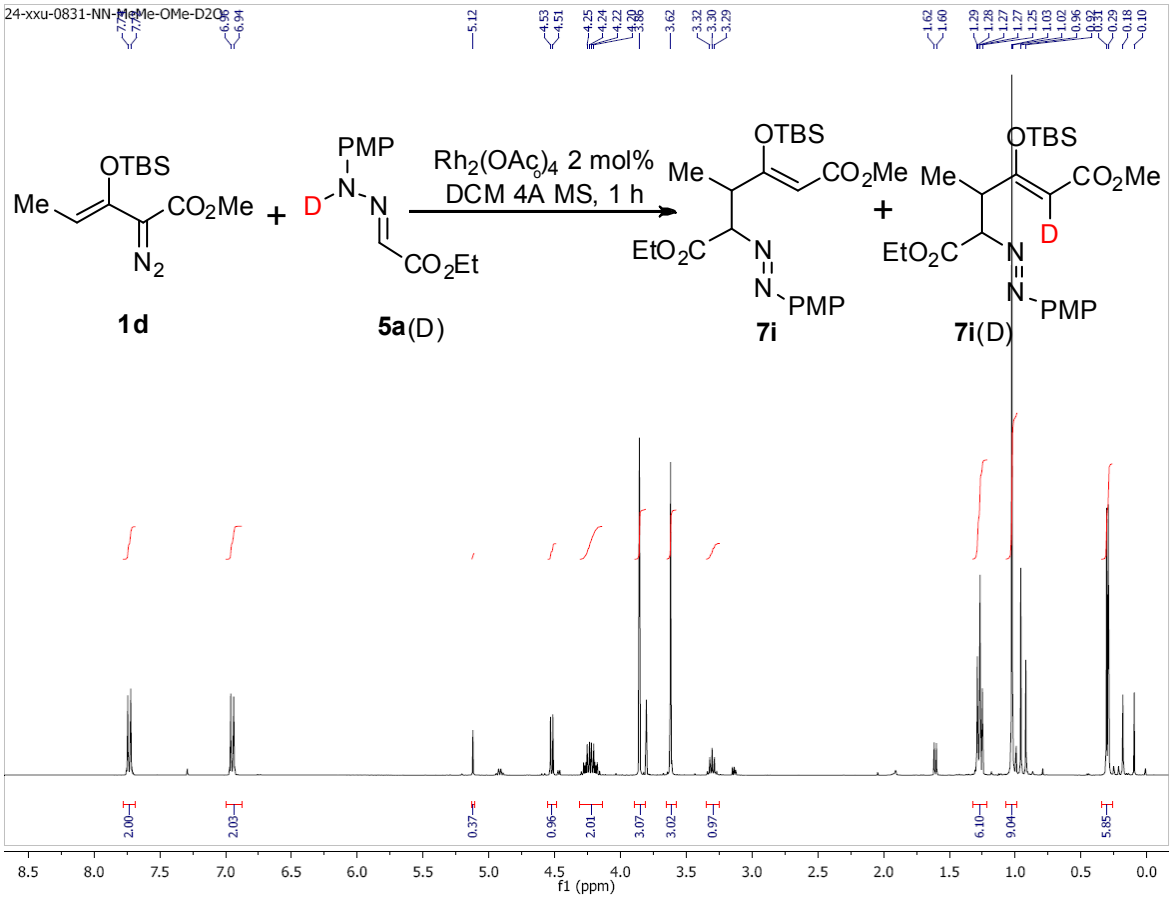
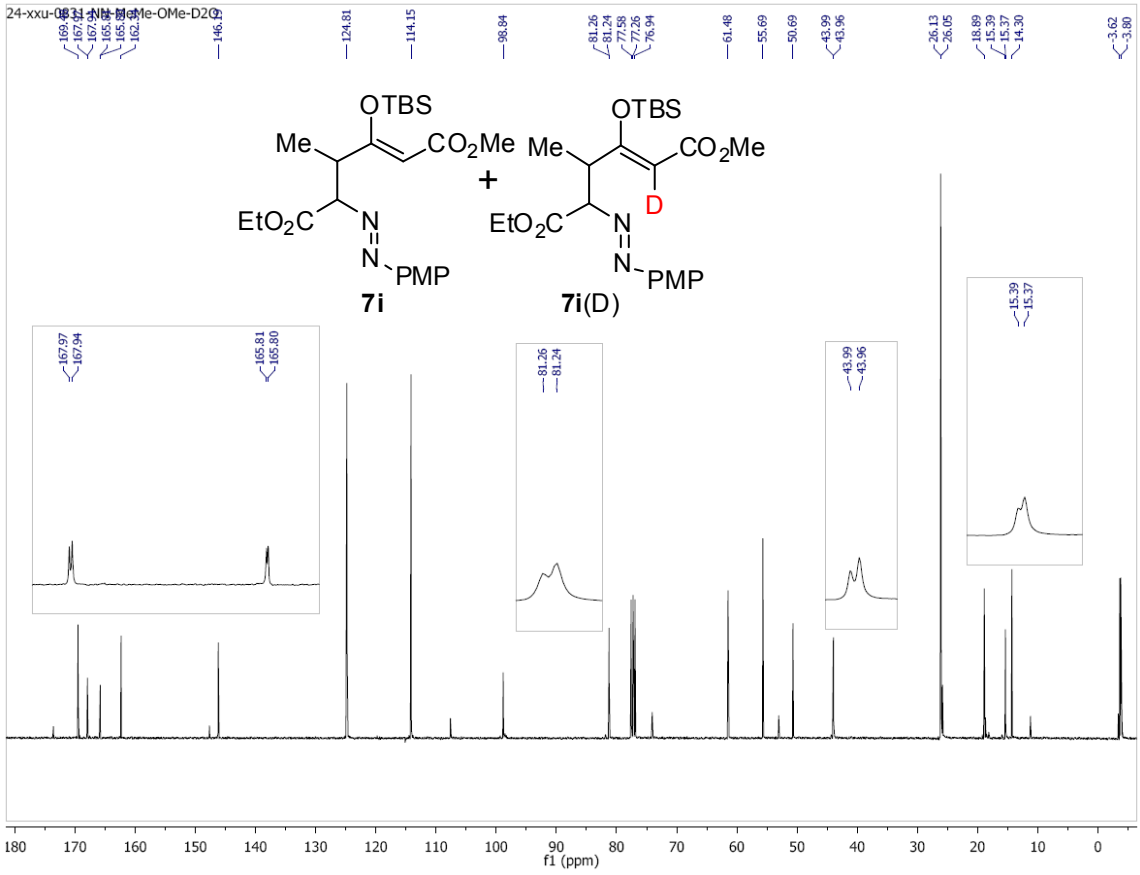
1a
PMP
N
N
D
CO2Et
5a(D)
Rh2(OAc)4 2 mol%
DCM 4A MS, 1 h
OTBS
CO2Me
EtO2C
N
NDPMP
6a(D)
OTBS
CO2Me
D
EtO2C
N
NHPMP
6a'(D)
f1 (ppm)

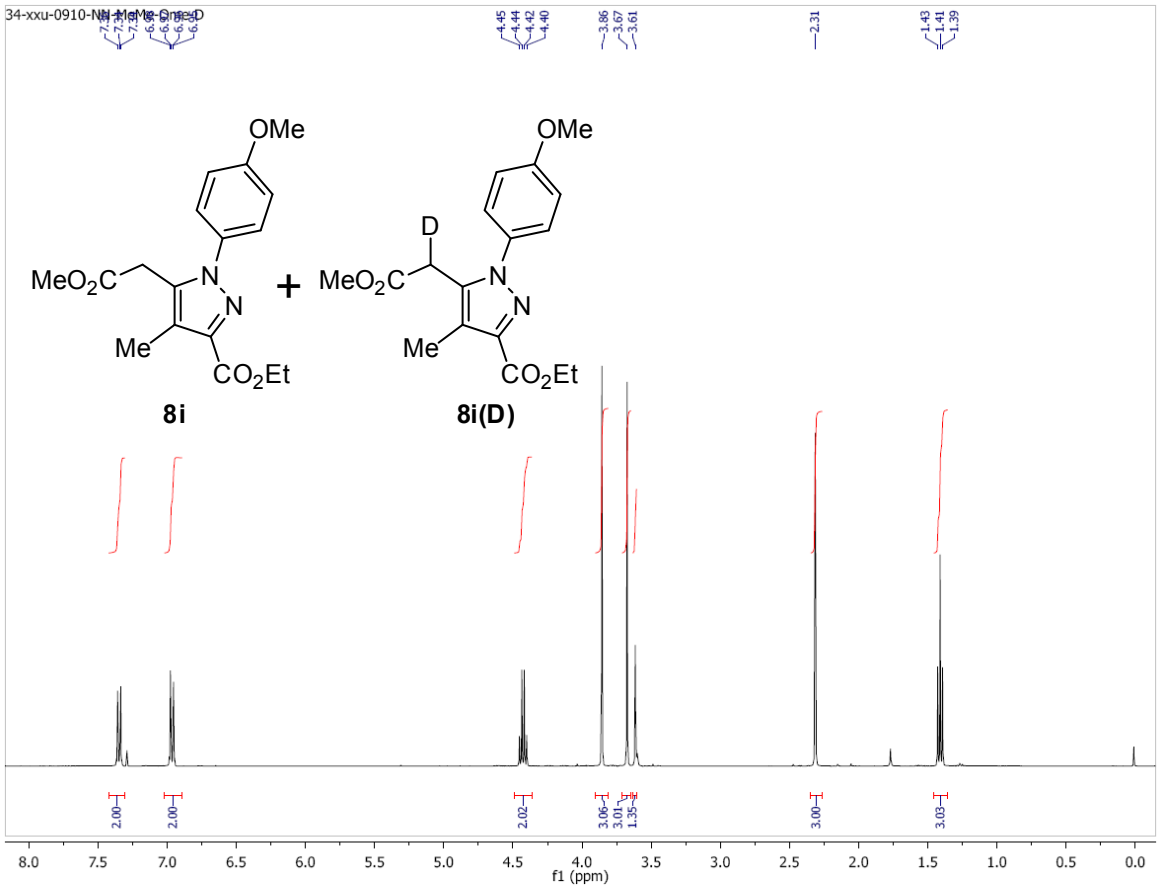

xxu-0906-NN-Me-OMe-D2O-P1-C
OTBS
CO2Me
EtO2C
N
NDPMP
6a(D)
OTBS
CO2Me
D
EtO2C
N
NHPMP
6a'(D)
f1 (ppm)

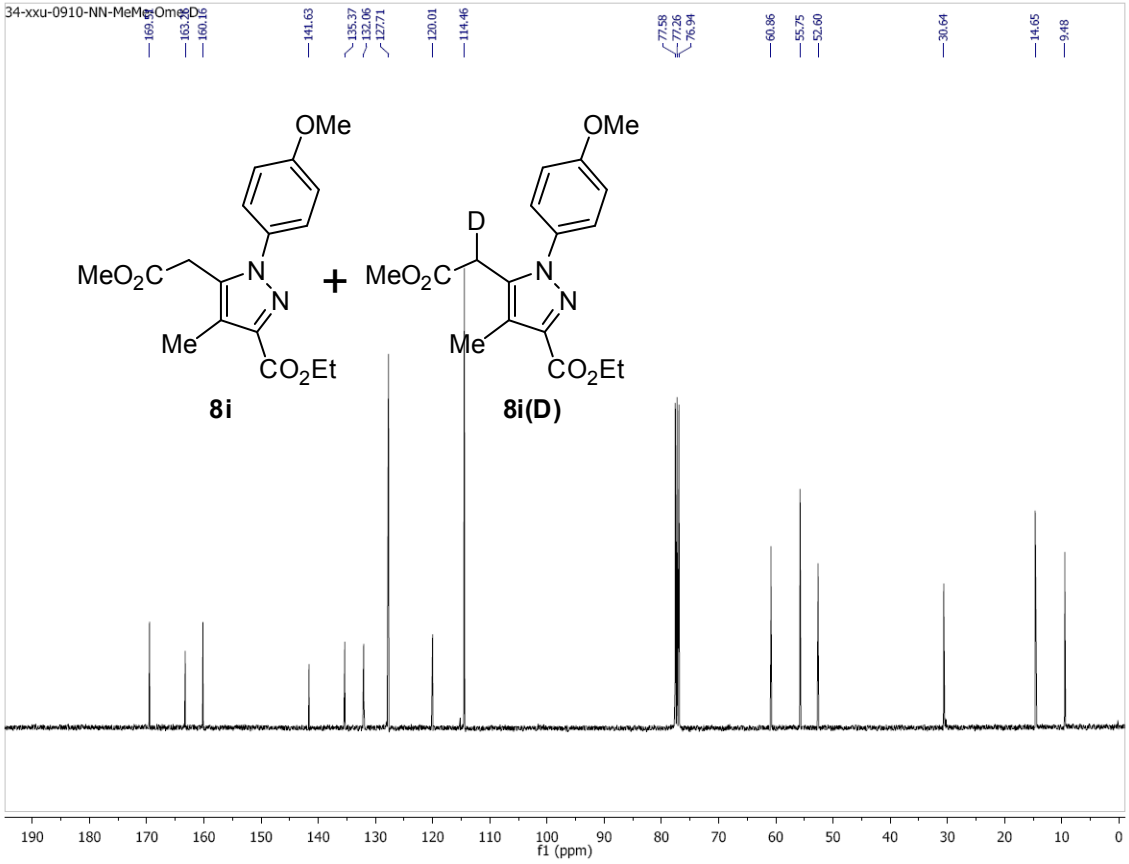

OMe
D
MeO2C
N
N
CO2Et
8a(D)
f1 (ppm)

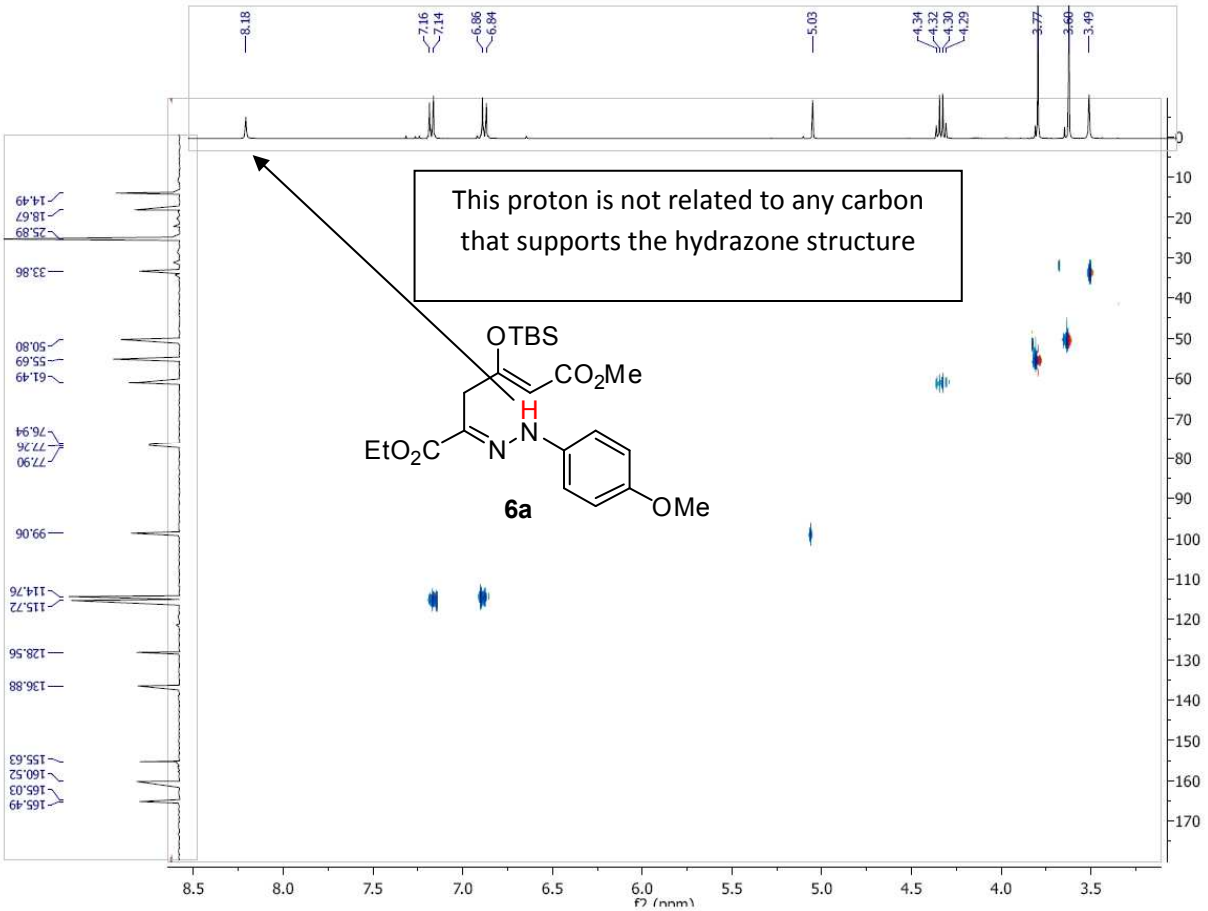

OMe
D
MeO2C
N
N
CO2Et
8a(D)
f1 (ppm)

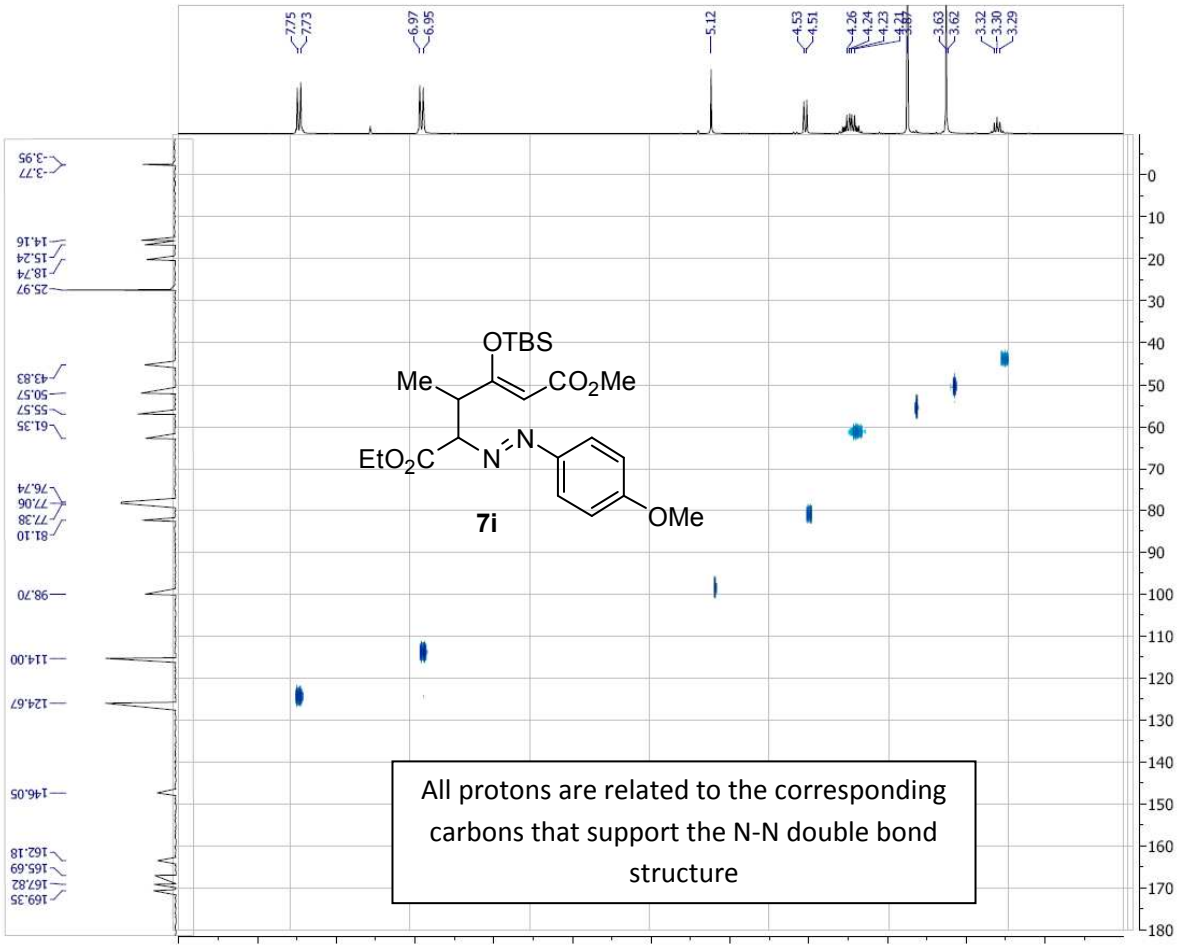

24-xxu-0831-NN-MeMe-OMe-D2O
OTBS
Me
CO2Me
N2
1d
PMP
D
N
N
CO2Et
5a(D)
Rh2(OAc)4 2 mol%
DCM 4A MS, 1 h
EtO2C
PMP
7i
7i(D)
f1 (ppm)

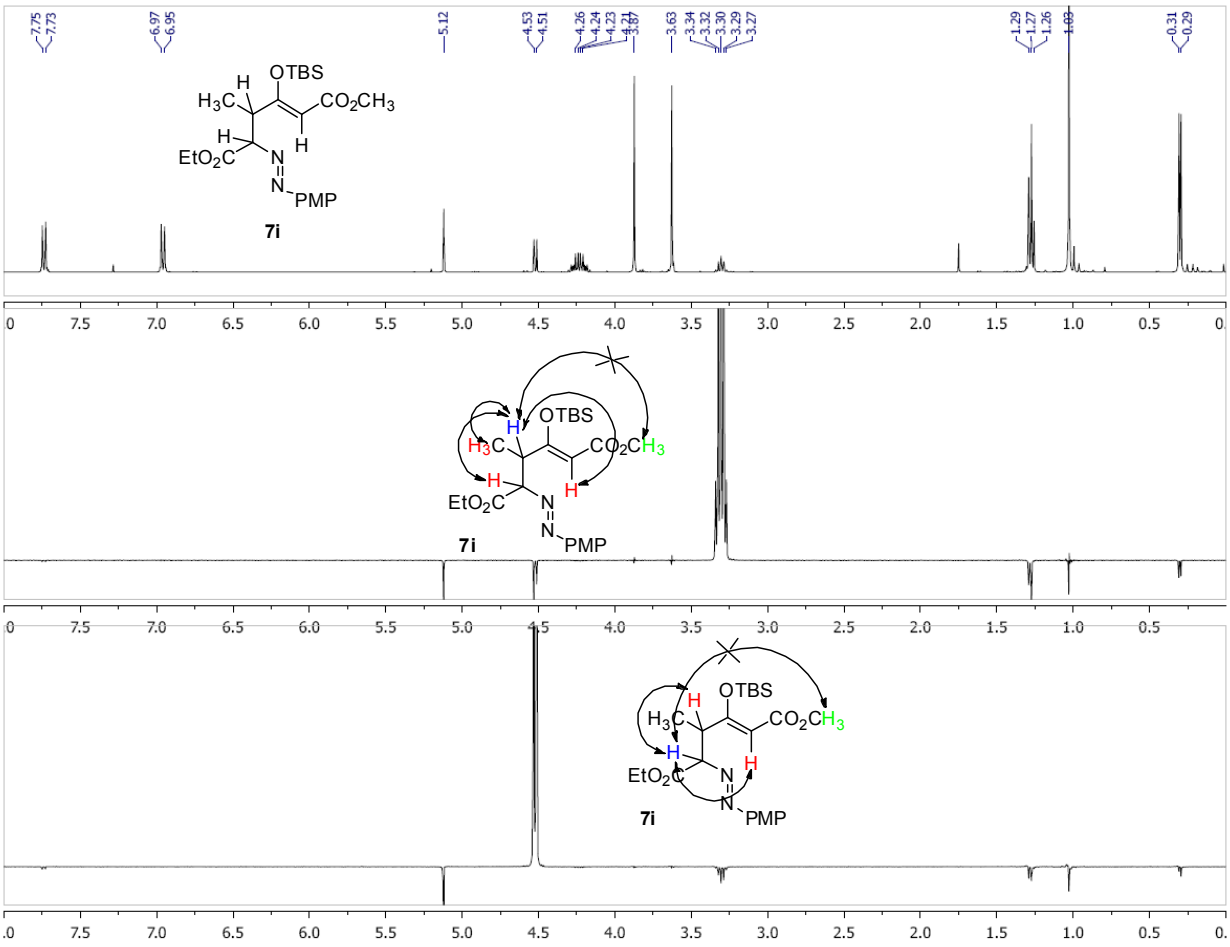

24-xxu-0831-NN-MeMe-OMe-D2O
OTBS
Me
CO2Me
EtO2C
N
PMP
7i
7i(D)
D
f1 (ppm)

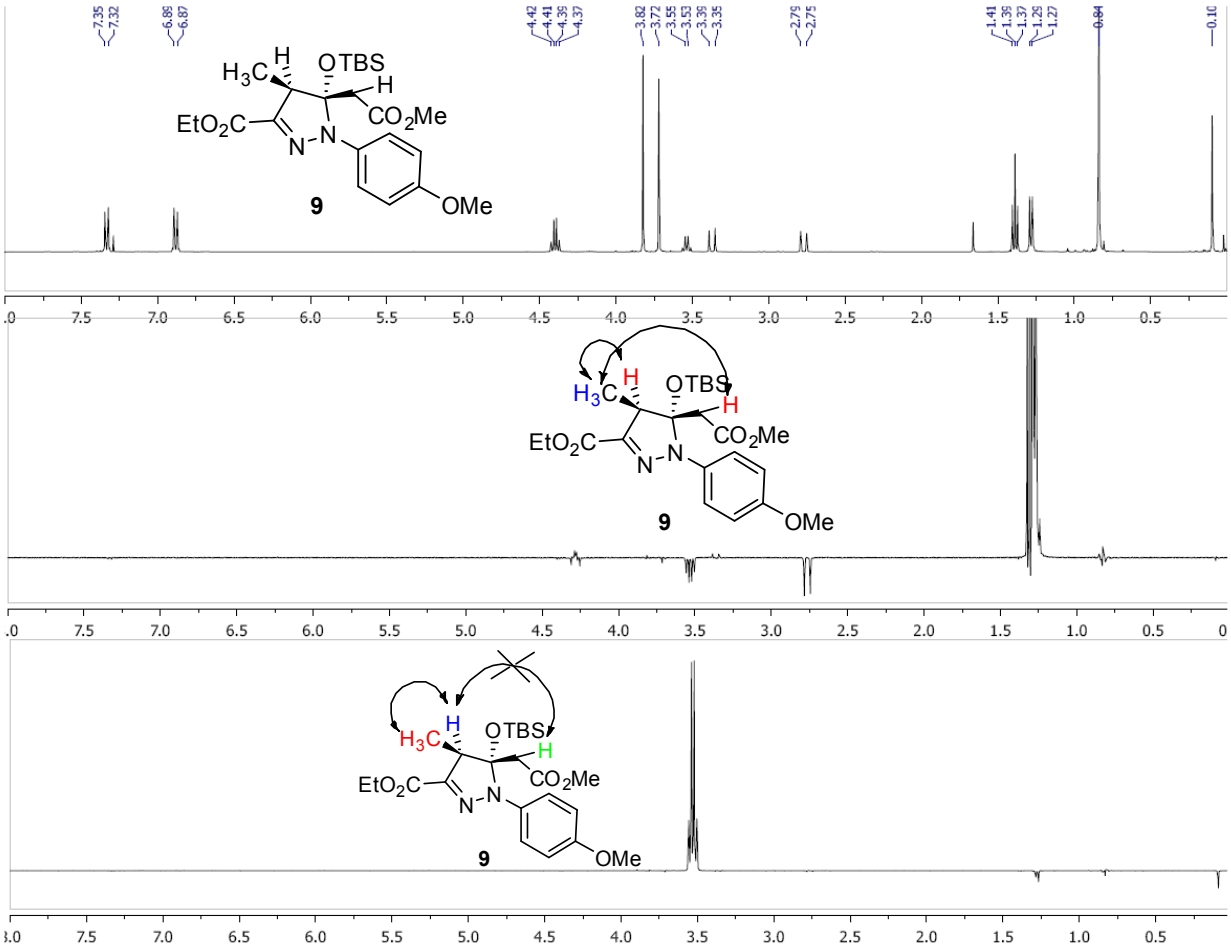

OMe
MeO2C
N
N
Me
CO2Et
8i
OMe
D
MeO2C
N
N
Me
CO2Et
8i(D)
f1 (ppm)

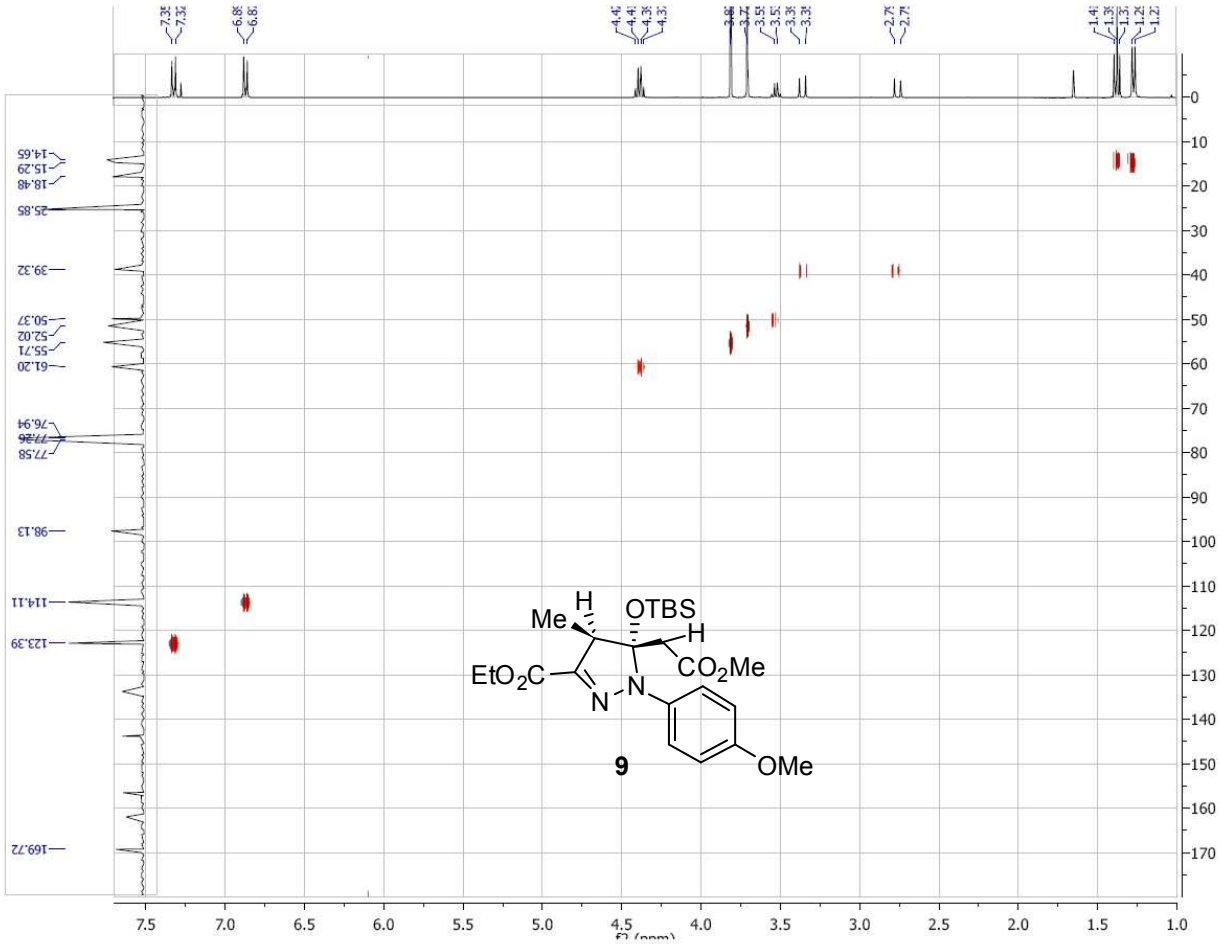

OMe
MeO2C
N
N
Me
CO2Et
8i
OMe
D
MeO2C
N
N
Me
CO2Et
8i(D)
f1 (ppm)


This proton is not related to any carbon that supports the hydrazone structure
OTBS
CO2Me
H
N
N
EtO2C
OMe
6a
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
f2 (ppm)

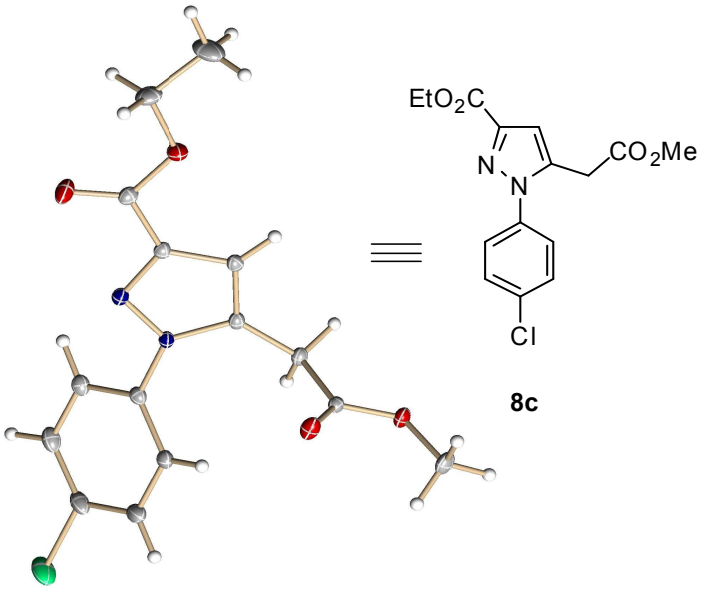

7.75
7.73
6.97
6.95
5.12
4.53
4.51
4.26
4.24
4.23
4.21
3.63
3.62
3.32
3.30
3.29
OTBS
Me
CO2Me
EtO2C
N
N
OMe
7i
All protons are related to the corresponding carbons that support the N-N double bond structure


7.75
7.73
6.97
6.95
5.12
4.53
4.51
4.26
4.24
4.23
4.21
4.07
3.63
3.34
3.32
3.30
3.29
3.27
1.29
1.27
1.26
1.03
0.31
0.29
OTBS
H
H3C
CO2CH3
H
EtO2C
N
N
PMP
7i
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


7.35
7.32
6.88
6.87
4.42
4.41
4.39
4.37
3.82
3.72
3.55
3.53
3.36
3.35
2.79
2.75
1.41
1.39
1.37
1.25
1.27
0.84
0.10
H3C
H
OTBS
H
EtO2C
CO2Me
N
N
9
OMe
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


Me
H
OTBS
H
EtO2C
CO2Me
N
N
OMe
9

Crystallographic data for compound 8c (UM2325)



A colorless prism-like specimen of $C_{15}H_{15}ClN_2O_4$, approximate dimensions 0.30 mm × 0.49 mm × 0.51 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker APEX-II CCD system equipped with a graphite monochromator and a MoKα sealed tube (λ = 0.71073 Å). Data collection temperature was 150 K.

The total exposure time was 10.63 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 25171 reflections to a maximum θ angle of 30.00° (0.71 Å resolution), of which 4552 were independent (average redundancy 5.530, completeness = 99.8%, R_{int} = 1.68%, R_{sig} = 1.60%) and 3819 (83.90%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.8557(8) Å, b = 7.3889(5) Å, c = 19.8046(14) Å, β = 100.4064(10)°, V = 1562.43(19) Å^3, are based upon the refinement of the XYZ-centroids of 9912 reflections above 20 σ(I) with 5.513° < 2θ < 60.98°. Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8690 and 0.9240.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P2(1)/n, with Z = 4 for the formula unit, $C_{15}H_{15}ClN_2O_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 238 variables converged at R_1 = 3.78%, for the observed data and wR_2 = 7.61% for all data. The goodness-of-fit was 1.000. The largest peak in the final difference electron density synthesis was 0.439 e$^-$/Å^3 and the largest hole was -0.489 e$^-$/Å^3 with an RMS deviation of 0.042 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.372 g/cm^3 and F(000), 672 e$^-$